Investigations into Higher Dendralenes

A thesis submitted for the degree of

Doctor of Philosophy

of The Australian National University

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Declaration

This thesis is a report of the scientific investigations undertaken by myself during the period of December 2010 to February 2016 in the Research School of Chemistry of the Australian National University, under the supervision of Professor Michael S. Sherburn. Except where specific acknowledgements of others are made, all of the material contained within is my own work. The material presented has not been submitted for any other degree and is less than 100,000 words in length.

Mehmet Fatih Saglam
February 2016

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Publications and Presentations

This thesis is submitted in publication format.

The following list details the publications and presentation that have resulted the author's research during his candidature for the Degree of Doctor of Philosophy:

Publications;

Sherburn, M. S.; Green, N. J.; **Saglam, M. F.** Synthesis of Dendralenes, *Cross Conjugation: Dendralene, Radialene and Fulvene Chemistry,* 1st Edn.*,* Wiley-VCH Verlag GmbH & Co. KGaA. **2016**, *Book Chapter*, in press.

Saglam, M. F.; Fallon, T.; Paddon-Row, M. N.; Sherburn, M. S. Discovery and Computational Rationalization of Diminishing Alternation in [*n*]Dendralenes, *J. Am. Chem. Soc.* **2016**, *138*, 1022.

Saglam, M. F.; Alborzi, A. R.; Payne, A. D.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. Synthesis and Diels–Alder Reactivity of Substituted [4]Dendralenes, *J. Org. Chem.* **DOI:** 10.1021/acs.joc.5b02583.

Presentations;

Saglam, M. F.; Fallon, T.; Sherburn, M. S. *The Last Branch of the Dendralene Story.* Oral Presentation: Royal Australian Chemical Institute, 35th Annual One-Day Symposium, The Australian National University, 2014, Canberra, Australian Capital Territory, Australia.

Saglam, M. F.; Fallon, T.; Sherburn, M. S. *Higher Dendralenes.* Poster Presentation: Royal Australian Chemical Institute, 34th Annual One-Day Symposium, The Australian National University, 2013, Canberra, Australian Capital Territory, Australia.

Green, N. J.; **Saglam, M. F.**; Sherburn, M. S. *Taming [4]Dendralenes.* Poster Presentation: Royal Australian Chemical Institute, 34th Annual One-Day Symposium, The Australian National University, 2013, Canberra, Australian Capital Territory, Australia.

Saglam, M. F.; Fallon, T.; Sherburn, M. S. *The Higher Dendralenes Revealed! Syntheses, Chemical and Physical Properties.* Poster Presentation: 23rd International Symposium: Synthesis in Organic Chemistry, University of Oxford, 2013, Oxford, England, United Kingdom.

Saglam, M. F.; Fallon, T.; Sherburn, M. S. *Higher Dendralenes.* Poster Presentation: 19th IUPAC International Conference on Organic Synthesis, 2012, Melbourne, Victoria, Australia.

Saglam, M. F.; Alborzi, A. R.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *Synthesis and Diels–Alder Reactions of Substituted [4]Dendralenes.* Poster Presentation: Royal Australian Chemical Institute, 32nd Annual One-Day Symposium, The University of New South Wales, 2011, Sydney, New South Wales, Australia.

Saglam, M. F.; Alborzi, A. R.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *Synthesis and Diels–Alder Reactions of Substituted [4]Dendralenes.* Poster Presentation. 22nd Southern Highlands Conference on Heterocyclic Chemistry, 2011, Moss Vale, New South Wales, Australia.

Abbreviations

%	percentage
°C	degree/s Celsius
δ	chemical shift
μ	micro
ν	absorption maxima (IR)
Ac	acetyl
aq.	aqueous
APT	attached proton test
Ar	aryl or argon
ATR	attenuated total reflectance
BHT	2,6-di-*tert*-butyl-4-methylphenol
BINOL	1,1'-bi-2-naphthol
Bn	benzyl
bp	boiling point
br	broad
brsm	based on recovered starting material
Bu	butyl
ca.	*circa* (approximately)
calc	calculated
cm^{-1}	wave number
COSY	correlated spectroscopy
d	doublet/s
DA	Diels–Alder
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DEPT	distortionless enhancement by polarisation transfer
DFT	density functional theory
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,2-bis(diphenylphosphino)ferrocene
dppp	1,2-bis(diphenylphosphino)propane
dr	diastereomeric ratio
dt	doublet of triplets
EI	electron impact
equiv	molar equivalent(s)
er	enantiomeric ratio
Et	ethyl

Et_3N	triethylamine
Et_2O	diethyl ether
EtOAc	ethyl acetate
eV	electron Volts
FMO	frontier molecular orbital
g	gram
G	Gibbs free energy
GC	gas chromatography
h	hour/s
H	enthalpy
hexane	*n*-hexane
HMBC	heteronuclear multiple bond coherence
HSQC	heteronuclear single quantum coherence
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
Hz	Hertz
i-Pr	isopropyl
IR	infrared
J	coupling constant
K	Kelvin
kJ	kilojoules
L	litre
LDA	lithium diisopropylamide
lit.	literature
LRMS	low resolution mass spectrometry
LUMO	lowest unoccupied molecular orbital
m	multiplet or milli
M	molar
M^+	molecular ion
Me	methyl
MeCN	acetonitrile
MeOH	methanol
mg	milligram
MHz	megaHertz
min	minute
mL	millilitre
mm Hg	millimetres of mercury
mmol	millimole
MO	molecular orbital
mol	mole

mp	melting point
MS	mass spectroscopy
m/z	mass to charge ratio
n-BuLi	*n*-butyl lithium
NBS	*N*-bromosuccinimide
nm	nanometre
NMM	*N*-methylmaleimide
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
OAc	acetoxy
OMs	mesylate
PCM	polarizable continuum model
Ph	phenyl
pin	pinacol
ppm	parts per million
q	quartet
R_f	retention factor
rt	room temperature
s	singlet
SiO_2	silicon dioxide
SPhos	2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl
t	time
t_R	retention time
t-Bu	*tert*-butyl
TD	time dependent
temp	temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TMP	2,2,6,6-tetramethylpiperidine
TS	transition state
UV	ultraviolet
Vis	visible
vol.	volume
w/w	weight per weight
XantPhos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
XPhos	2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl

Abstract

As synthetic organic chemists, one of our most important desires is to synthesize complex target molecules efficiently in the shortest time and lowest step count, with cheap starting materials. One of the classes of fundamental hydrocarbons, dendralenes, acyclic cross-conjugated alkenes, have great potential to build up complex polycyclic carbon frameworks rapidly due to having the ability to participate in diene-transmissive Diels–Alder sequences. These π-bond rich hydrocarbons are therefore attracting a growing interest. The goals of the research presented in this thesis are not only to investigate possible synthetic applications of dendralenes but also to understand in a broad sense how fundamental aspects of structure impacts upon chemical stability and reactivity.

A detailed literature survey can achieve two goals: it forms the basis of a future research program and can also improve current knowledge. Chapter One of this thesis is a review of the synthesis of dendralenes, organized on the basis of which key carbon-carbon bond is formed during their synthesis. Categorization of previously reported syntheses, including interpretations of these publications in terms of synthetic strategies and tactics are presented accordingly.

The work detailed in Chapter Two describes the first syntheses of the parent (unsubstituted) higher dendralenes, specifically [9]dendralene to [12]dendralene, and an investigation into the spectroscopic properties and chemical reactivity of the first ten members of this family ([3]dendralene to [12]dendralene). These studies reveal the first documented case of diminishing alternation in behavior in a series of related chemical structures. This dampening oscillatory effect in both spectroscopic measurements and chemical reactivity is traced to conformational preferences, through a comprehensive series of computational studies performed by a collaborator.

Previous studies showed that the Diels–Alder reaction between parent [4]dendralene and an excess quantity of the electron deficient dienophile *N*-methylmaleimide (NMM) at room temperature produces five different products. Two of these products contain a hydrophenanthrene carbon skeleton, which is the backbone of many different medicinal drugs. It was postulated that substituents on the [4]dendralene framework might influence the outcome of this very powerful reaction, thereby promoting its application in efficient synthesis. The work presented in Chapter Three describes the first synthesis of the five possible mono-substituted [4]dendralenes, which required the development of new methods in conjugated alkene synthesis. The reactivity of these hydrocarbons towards the dienophile *N*-methylmaleimide was performed, in order to document the influence of the role of substituent on the selectivity of the Diels–Alder sequence. Conclusions are made, on the basis of these findings, regarding the application of dendralenes in the synthesis of biologically active natural products and their analogues.

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The author has embargoed chapter 4 for a period of 3 years from 12 December 2019 to 12 December 2022.

Chapter One

Synthesis of Dendralenes

Synthesis of Dendralenes

Context

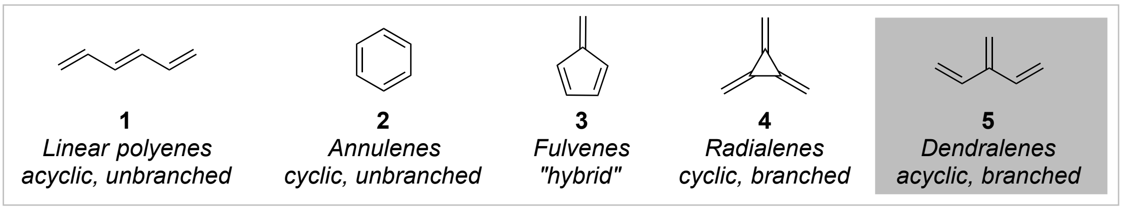
The following review brings together and summarizes recent publications describing the synthesis of dendralenes. The review is a thorough survey of papers published between 2011 and April 2015 but also includes a summary of the best previous methods reported in the literature. In this review, strategies towards the synthesis of dendralenes are categorized on the basis of which specific carbon-carbon bond of a dendralene is formed, with approaches and literature examples being discussed in detail.

This review is about to be published as the first chapter in the book “Cross Conjugation: Dendralene, Radialene and Fulvene Chemistry”, *Wiley-VCH*. The book is currently at the proof correction stage.

The review was researched, drafted and edited in collaboration with my supervisor, Professor Michael S. Sherburn and postdoctoral fellow Dr Nicholas J. Green. I wrote the first draft of this review, under advice and following discussions with the other two co-authors.

1.1 Introduction

The synthesis and study of conjugated polyenes has been at the heart of the chemical sciences ever since an appreciation of their structure began to develop. Of the five classes of conjugated alkenes that arise from the different possible modes of connectivity (***Figure 1.1***), some have received significantly more attention than others. The linear and cyclic classes featuring vicinal connections between alkene units – the linear polyenes **1** and annulenes **2** – are common structural motifs in naturally occurring compounds and contrived structures of industrial, commercial, and academic importance, and have hence been extensively synthesized and studied. Oligoalkenes with geminal connections between alkenes – cyclic radialenes **4** and acyclic dendralenes **5** – are yet to receive such attention, nor are "hybrid" structures featuring both geminal and vicinal connections, the fulvenes **3**. There is, however, undoubtedly a growing interest in the subject of this chapter: the synthesis of dendralenes.



1 *Linear polyenes* *acyclic, unbranched*

2 *Annulenes* *cyclic, unbranched*

3 *Fulvenes* *"hybrid"*

4 *Radialenes* *cyclic, branched*

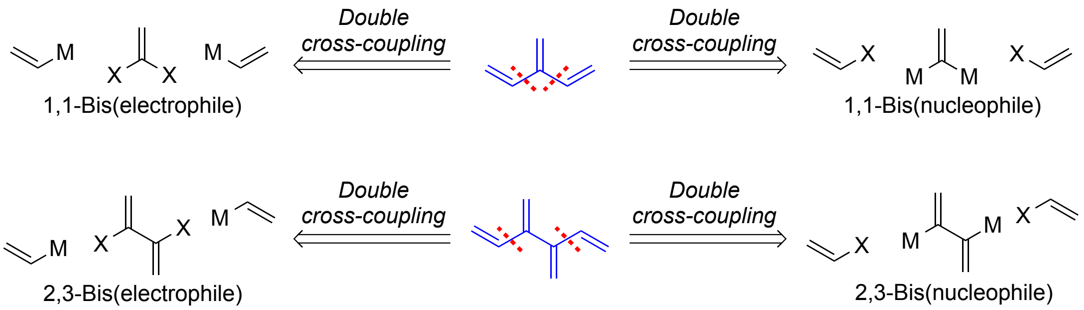
5 *Dendralenes* *acyclic, branched*

Figure 1.1: *Fundamental conjugated hydrocarbons.*

Dendralenes have been the subject of two comprehensive reviews [1–2]. The first covers research in the area until 1984; the second from the period between 1984 and 2011. Whilst it would be impossible to summarize the evolution of dendralene synthesis without some repetition of the key strategies found in each of these reviews, we seek to present the subject differently herein, by summarizing the best methods from both reviews, and placing emphasis on the significant work that has appeared between 2011 and the present. We also present the synthetic strategies in a new way, based upon which carbon–carbon bonds of the dendralene are formed in the approach. Newly formed bonds are highlighted in bold, and should not be confused with wedged bonds, used to indicate stereochemistry. A broad measure of the synthetic power of a strategy is the number of bonds formed in the process, and we have therefore first highlighted strategies that form more than one bond per step [3]. This has allowed us insight into the strengths, weaknesses, and gaps present amongst current approaches. Our review covers examples in the literature up until April 2015, and we exclusively deal with the synthesis of the parent and substituted dendralenes, directing readers to other reviews or chapters of this book dealing with their closely related, cross-conjugated relatives (fulvenes [4], radialenes [5–6], quinomethanes [7], etc.). We have not included related compounds that may be generated by substituting a carbon atom in the dendralene backbone with a similar unsaturated moiety, such as an alkyne or aromatic ring. We have also limited our survey to exclude cross-conjugated polymers, which have been reviewed elsewhere [8].

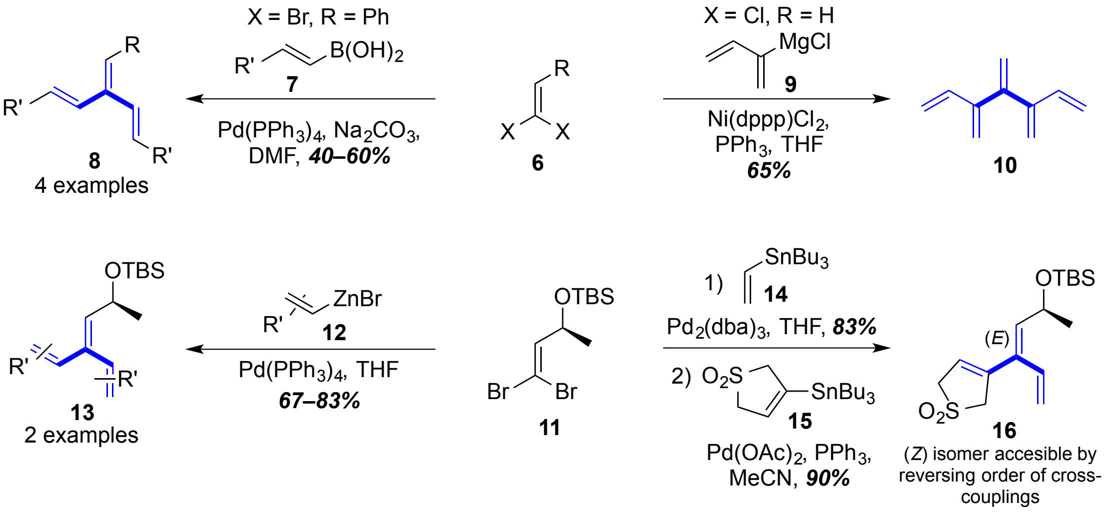
1.2 Multi-Bond Forming Processes

1.2.1 Double Alkenylation Reactions



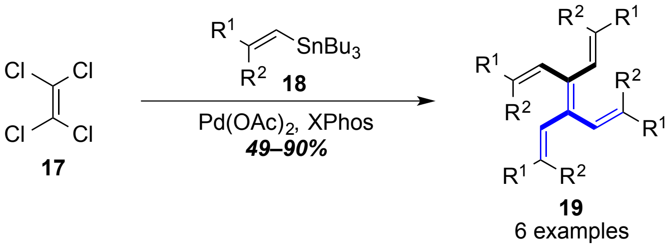
Scheme 1.1: *Double alkenylation approaches to [3]- and [4]dendralene, via* sp^2*–*sp^2 *cross-coupling.*

The double alkenylation approach (***Scheme 1.1***) has only been exploited relatively recently, most probably because of the rise to prominence of cross-coupling methodologies in recent times. The first double cross-couplings between 1,1-dihaloalkenes and metalloalkenes were isolated examples appearing in 1998 [9] and 2000 [10]. In 2002, Oh and Lim reported a series of double Suzuki–Miyaura reactions between a 1,1-dibromoalkene **6** and alkenyl boronic acids **7** (***Scheme 1.2***) [11]. In 2007 and 2008, the Sherburn research group reported syntheses of substituted [3]dendralenes [12] and the state-of-the-art synthesis of [5]dendralene [13] respectively, transforming a 1,1-dihaloalkene *via* double Negishi or Kumada–Tamao–Corriu cross-couplings to incorporate one alkenyl substituent (**9** or **12**) twice, and also, in the former case, the related stepwise, stereoselective Stille couplings to form unsymmetrically substituted, chiral [3]dendralenes **16** (***Scheme 1.2***). An application of this stepwise approach *en route* to the natural product triptolide [14] highlighted that when using two different metalloalkene cross-coupling partners, complete control of the stereochemistry of the resulting alkene is sometimes unattainable. Thus, most successful applications of this method incorporate two identical alkenes, so no issues of stereochemistry arise. A recent example is the synthesis by Ichikawa and co-workers of a single tetra-fluoro[3]dendralene *via* double Negishi cross-coupling of 2,2-difluorovinylzinc bromide to a dibromoolefin [15].



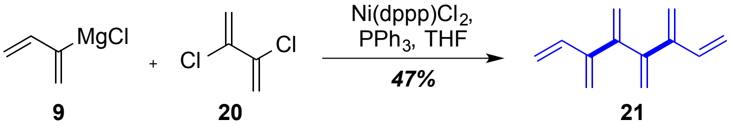
Scheme 1.2: *Examples of double cross-coupling approaches to dendralenes by Oh and Lim* [11] *and Sherburn and co-workers* [12–13].

Recently, a new benchmark in alkenyl cross-coupling syntheses was set by the Sherburn group, using an extension of this double cross-coupling strategy. Tetravinylethylene (TVE) and substituted analogues **19**, previously only accessible by longer, lower-yielding, sequences [16–18], were generated *via* a four-fold Stille cross-coupling of alkenyl stannanes **18** and tetrachloroethylene (**17**), a cheap and readily available starting material produced annually on a kiloton scale (***Scheme 1.3***) [19–21]. TVEs possess an interesting carbon framework composed of two [3]dendralene subunits sharing the same central, tetrasubstituted alkene. The bold, one-step approach was used to generate six different symmetrically substituted TVEs, is unique in its use of a tetrachloroalkene, and cannot be surpassed in terms of step economy [22].



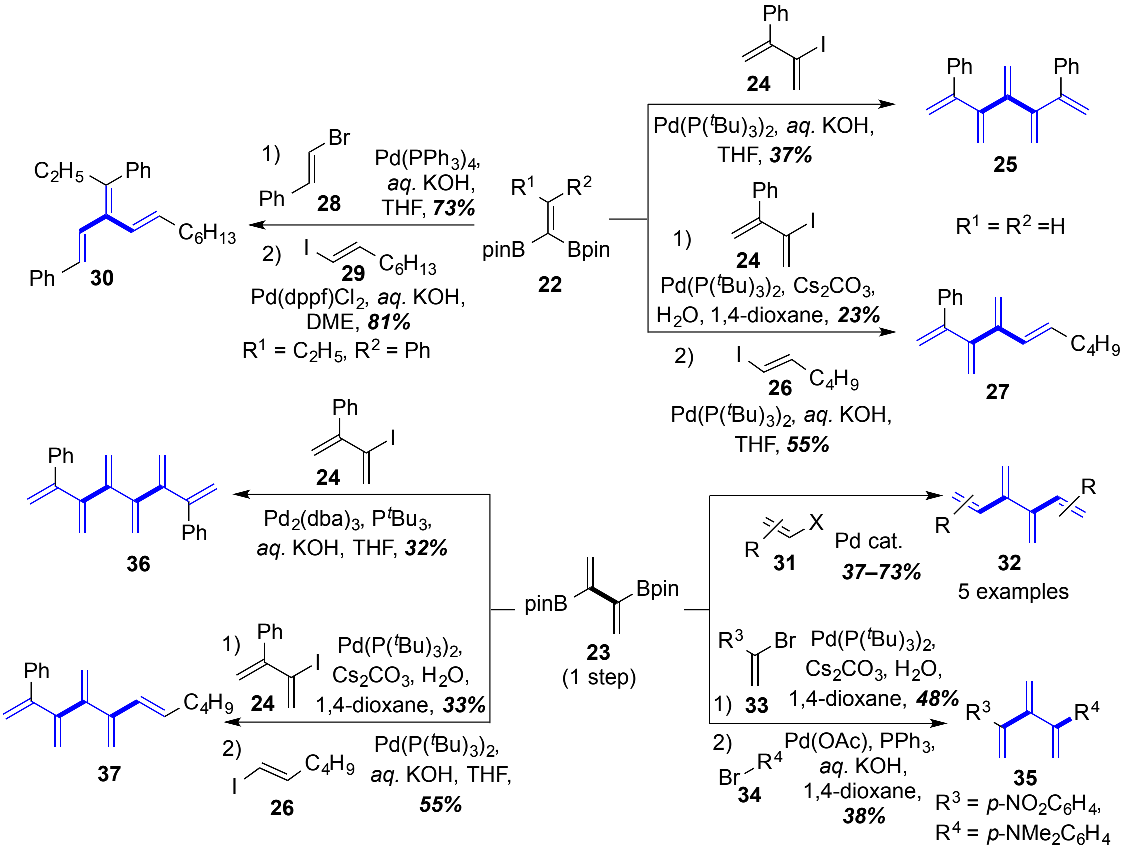
Scheme 1.3: *Synthesis of TVEs via four-fold* sp^2–sp^2 *cross-coupling reactions* [20–21].

Higher dendralenes are accessible by double cross-coupling by including branched alkenes into the electrophile unit. For example, in their state-of-the-art synthesis of the parent dendralenes [23], the Sherburn and co-workers prepared [6]dendralene (**21**) by the reaction between 2,3-dichloro-1,3-butadiene (**20**), and the Grignard reagent (**9**) prepared from chloroprene, another readily available unsaturated halide produced annually on a megaton scale (***Scheme 1.4***) [24]. The scope of this reaction in the synthesis of substituted higher dendralenes remains unexplored.



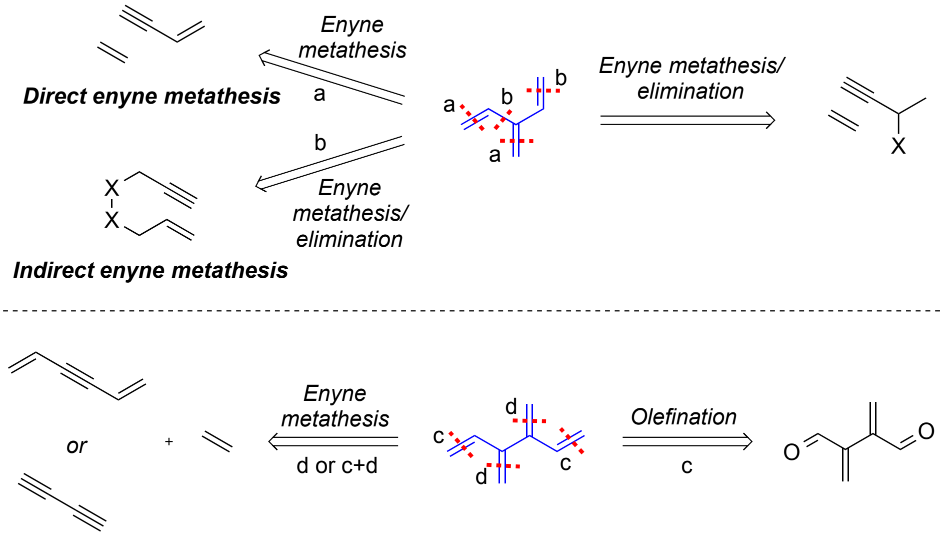
Scheme 1.4: *Synthesis of [6]dendralene via a double* sp^2*–*sp^2 *cross-coupling reaction* [23].

The same double cross-couplings are feasible by swapping the reactivity of components, i.e. using a double nucleophilic ethylene or 1,3-butadiene and two alkenyl electrophiles. So far, apart from an isolated example by the Sherburn group using 2,3-bis(trimethylstannyl)-1,3-butadiene [10], the Shimizu group is presently the only one to explore this avenue of dendralene synthesis, and have published a series of papers detailing the use of 1,1-bis(pinacolatoboryl)ethylene (**22**) and 2,3-bis(pinacolatoboryl)-1,3-butadiene (**23**) as nucleophilic components in Suzuki–Miyaura cross-coupling reactions (***Scheme 1.5***) [25 – 27]. A double cross-coupling reaction leads to symmetrically substituted [4]-, [5]- and [6]dendralenes (**32**, **25**, **36**), and a two-step process leads to unsymmetrically substituted [3]-, [4]- and [5]dendralenes (**30**, **35**, **27**, **37**). Whilst the yields for many of these reactions remain quite low, the potential scope is broad. The two strategies are complementary, and many interesting substituted dendralene frameworks are within rapid, step-economic reach from some very readily available starting materials.



Scheme 1.5: *Syntheses of dendralenes utilizing a double nucleophilic cross-coupling building block, from the Shimizu group* [25–27].

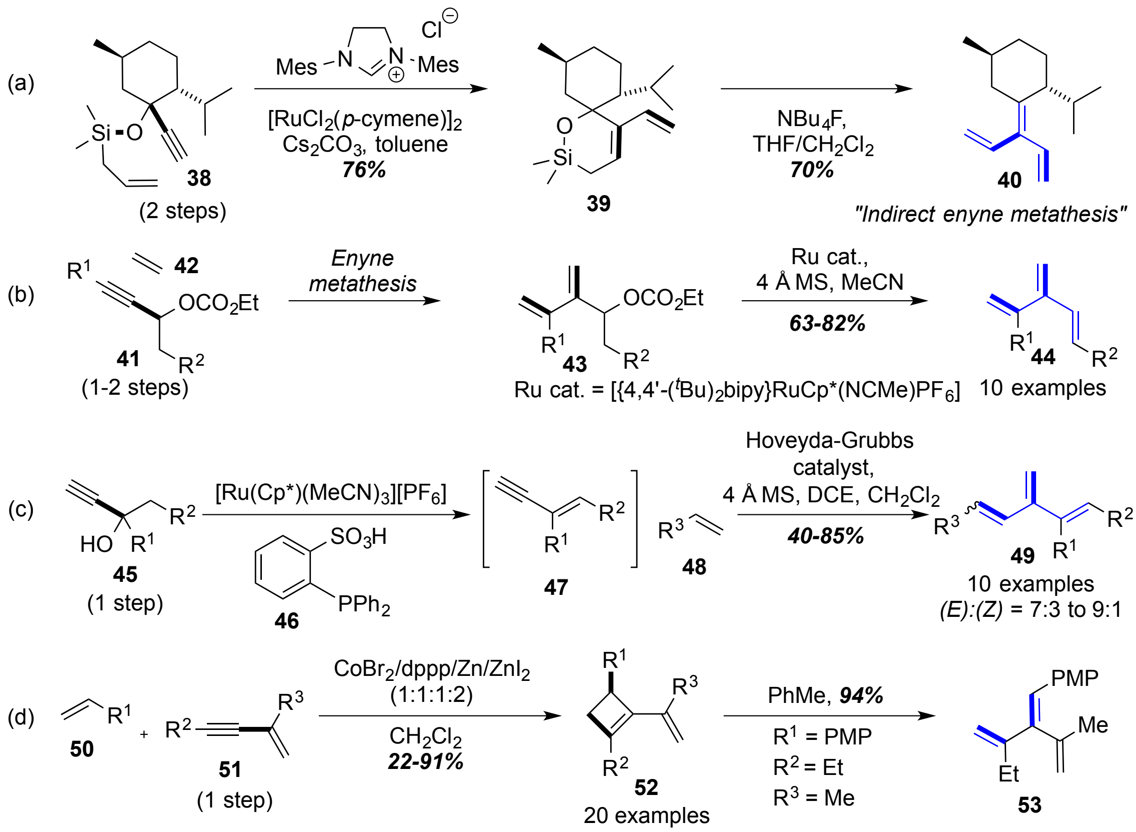
1.2.2 Double Alkenation Reactions



Scheme 1.6: *Possibilities for the synthesis of dendralenes via reactions forming two or more alkene groups.*

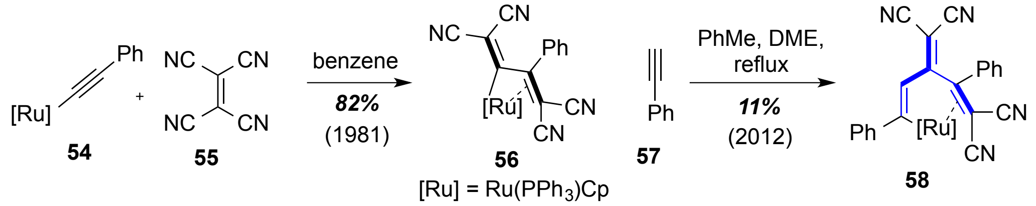
Various approaches that synthesize butadienes by the installation of methylene groups on two adjacent carbon atoms can be classified as the same overall transformation as the enyne metathesis reaction (***Scheme 1.6***). Unsurprisingly, metal-catalyzed enyne metathesis has proved versatile in this regard, as have [2+2] cycloaddition/4π electrocyclic ring-opening sequences (referred to herein as uncatalyzed enyne metathesis reactions), but other complementary examples of multi-bond forming processes that effect the same bond formations have also been developed.

In 2003, Bruneau and co-workers reported the first use of enyne metathesis to synthesize masked dendralenes **39** (***Scheme 1.7 (a)***) [28]. This worked paved the way for a series of related syntheses of dendralenes with a variety of substitution patterns [29 – 30], including a remarkable synthesis of a [4]dendralene *via* a double intramolecular enyne metathesis/double elimination sequence by Park and Lee [29]; however, because the products are masked dendralenes, the carbon-carbon bond disconnections for this strategy are different to a direct metathesis approach, in which the newly formed butadiene unit stays intact (***Scheme 1.6***). It was Bruneau again who first developed this route, using metathesis between ethylene (**42**) and propargylic carbonates **41** to synthesize 1,3-butadiene **43**, revealing the third alkene *via* subsequent elimination (***Scheme 1.7 (b)***) [31]. The same group has now published metathesis reactions that directly furnish intact [3]dendralenes **49** by conducting the elimination first, and then performing metathesis on an alkyne **47** already bearing the third alkene (***Scheme 1.7 (c)***) [32]. The related, intramolecular ring-closing enyne metathesis had been reported by Chang and co-workers [33]. A promising, if isolated, example of a related metal-catalyzed synthesis of a [3]dendralene **53** was reported by the Ogoshi group in 2014 (***Scheme 1.7 (d)***) [34]. A cobalt catalyst was used to generate a variety of alkenyl cyclobutenes **52** from the reaction of an alkene **50** and alkyne **51**. One of the cyclobutenes **52** was converted by thermal electrocyclic ring-opening to a substituted [3]dendralene **53**. If this ring-opening proves general, the methodology provides a modern, step-efficient incarnation of older methods that unmasked dendralenes from alkenyl cyclobutenes, derived from lengthy sequences [1]. A couple of isolated examples of dendralene synthesis *via* Ru(II)-catalyzed double carbene addition to alkynes have also been reported, albeit with only moderate (*E*)/(*Z*) selectivity [35]; and a coupling of an organozirconium reagent and vinyl bromide, equivalent to an enyne metathesis, has also been used to prepare a [3]dendralene [36].



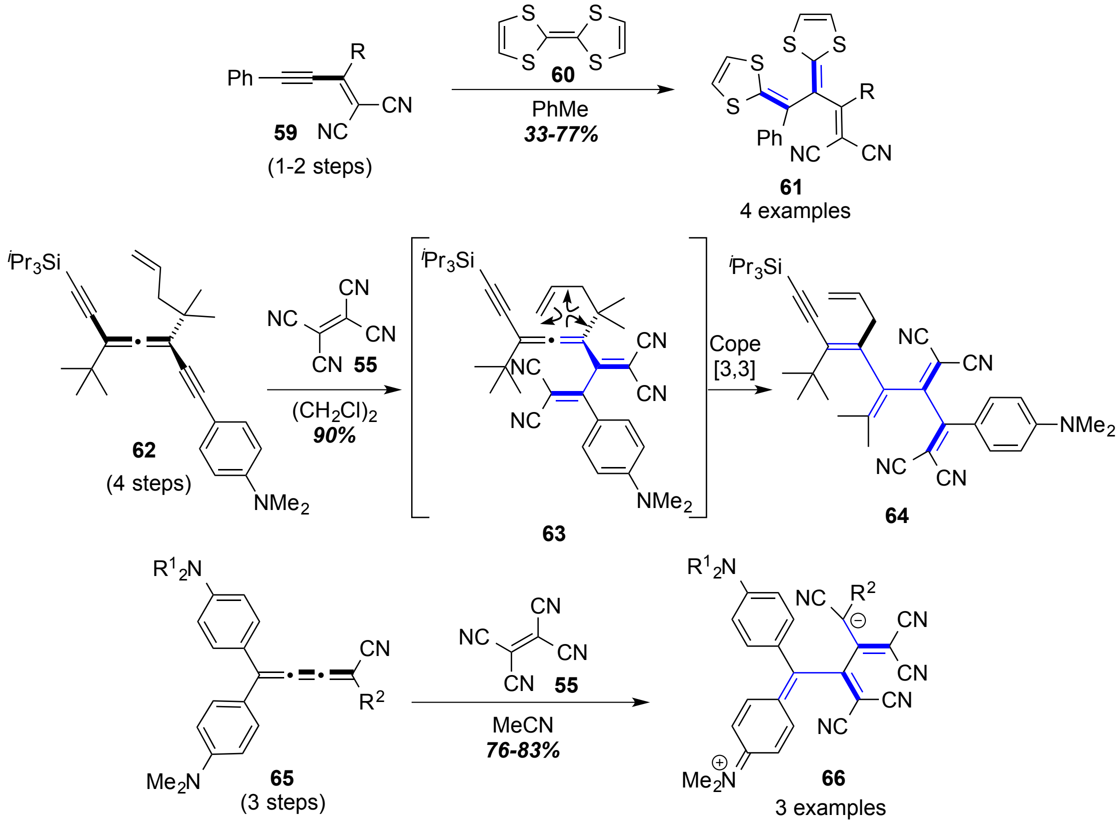
Scheme 1.7: *Representative examples of substituted [3]dendralene syntheses involving enyne metathesis or an equivalent transformation* [28, 31–32, 34].

In the 1970s and 1980s, it was discovered that electron deficient alkenes, such as tetracyanoethylene (TCNE, **55**) reacted with metallated alkynes **54** to furnish a metallated hexasubstituted 1,3-diene unit **56**, an overall transformation akin to enyne metathesis (***Scheme 1.8***) [37–38]. In a recent (2012) addition to this work, the Bruce group reported the synthesis of a ruthenated [3]dendralene **58** *via* insertion of phenylacetylene (**57**) into **56** (***Scheme 1.8***) [39]. The metallated dendralene synthesis is low-yielding and as yet an isolated example, but presents an interesting avenue for future investigations.



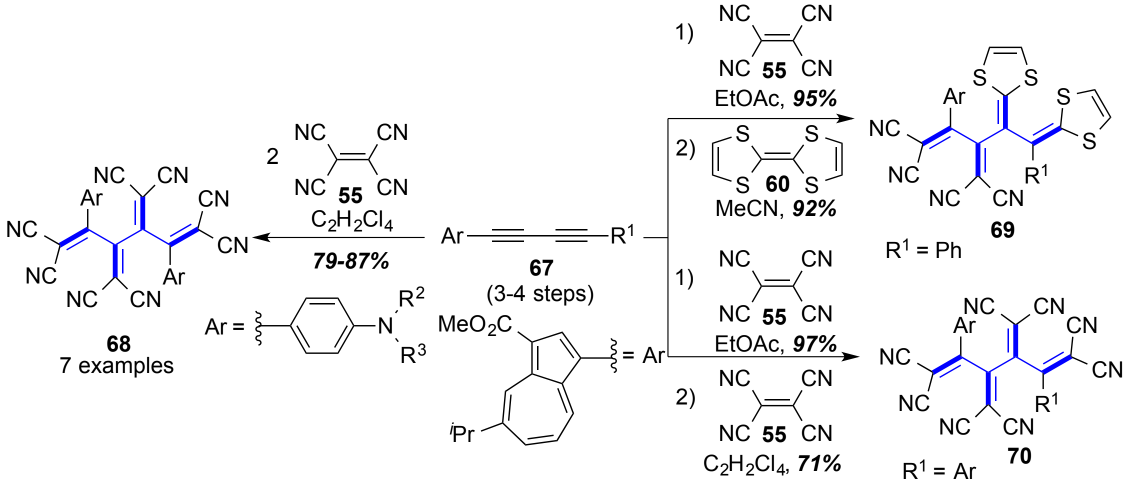
Scheme 1.8: *Synthesis of a ruthenated [3]dendralene* [38–39].

Uncatalyzed metathesis has also been performed on systems without metal components. Hopf was the first to show that highly electron rich olefins such as tetrathiafulvalene (TTF, **60**) undergo a sequence of [2+2] cycloaddition and 4π electrocyclic ring-opening with electron-deficient alkynes **59** to generate a new butadiene unit, which may be part of a dendralene (e.g., **61**) if a neighboring alkene is already in place (***Scheme 1.9***) [40]. The group of Diederich has made extensive use of the cycloaddition/4π electrocyclic ring-opening pathway to generate butadienes, some of which appear in dendralene frameworks [41–43]. Examples from recent papers demonstrate the versatility of this approach. TCNE (**55**) undergoes the cycloaddition/ring-opening process with alkyne **62** [44]. A pre-existing alkene in the alkyne starting material (akin to Hopf's strategy) allows the generation of the [3]dendralene framework in **63**. Finally, the presence of the requisite functionality for a Cope rearrangement allows further downstream functionalization, and the *in situ* generation of [4]dendralene **64**. A similar strategy from the same group has also led to interesting zwitterionic dendralene structures **66** derived from the cycloaddition/4π electrocyclic ring-opening sequence between cumulenes **65** and TCNE (**55**) [45].



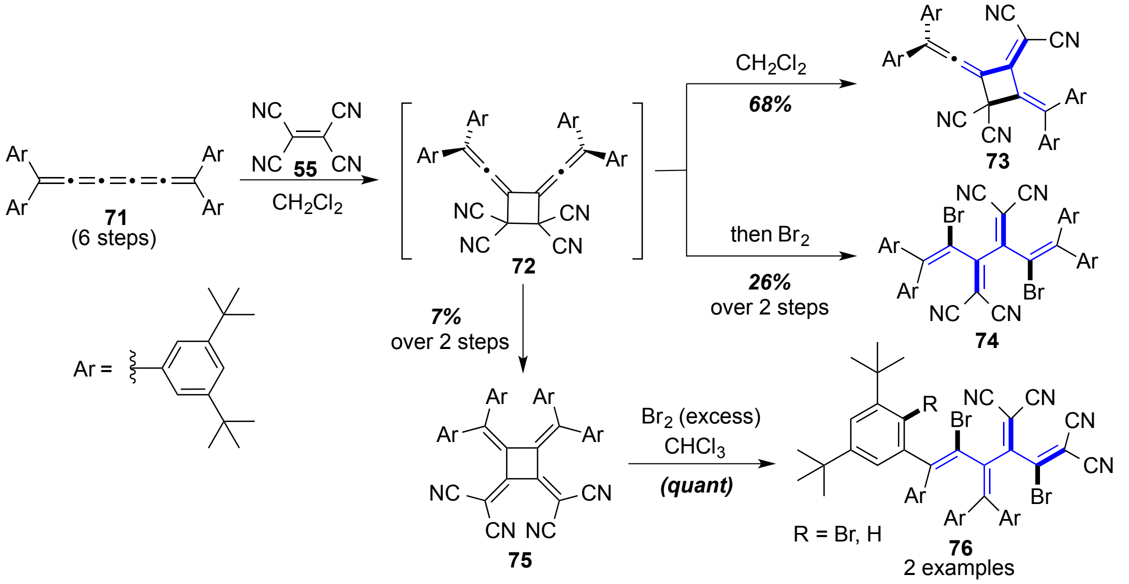
Scheme 1.9: *Representative dendralene syntheses featuring uncatalyzed metathesis reactions* [40, 44–45].

Uncatalyzed metathesis can also be performed on substrates that contain two reactive alkyne sites, for the rapid synthesis of highly substituted [4]dendralenes. Diederich and co-workers recently reported double [2+2] cycloaddition/retro-4π-electrocyclization cascades to yield a number of fully substituted [4]dendralenes **68** featuring push-pull chromophores (***Scheme 1.10***) [46–47]. Using a similar double alkyne substrate **67**, Diederich has also used different alkenes to incorporate varied functional groups into the product dendralene, a strategy recently also adopted by Morita and co-workers [48], who in 2012 reported stepwise or one-pot reactions to incorporate both TCNE (**55**) and TTF (**60**) into the structure of [4]dendralenes **69**, *via* double uncatalyzed metathesis.



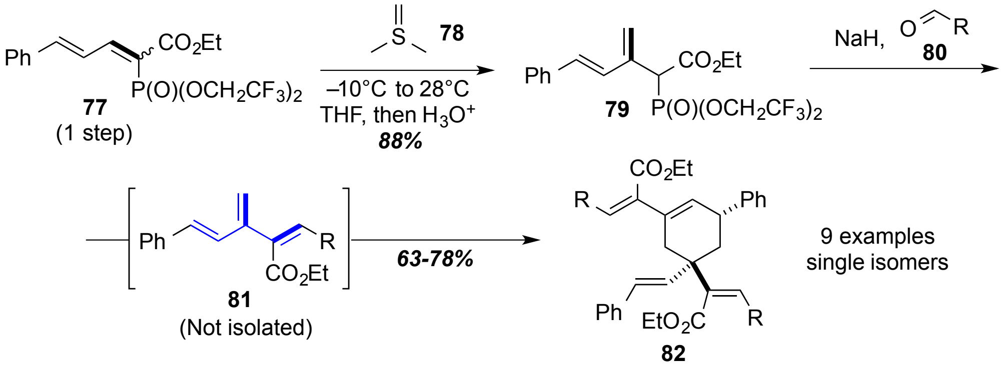
Scheme 1.10: *Stepwise or double [2+2]cycloaddition/retro-4π-electrocyclization cascades to synthesize [4]dendralenes* [46, 48].

Further varied examples of the [2+2] cycloaddition/ring-opening sequence, this time promoted by the addition of bromine, were reported by the group of Tykwinski (***Scheme 1.11***) [49]. By using a [5]cumulene **71** as starting material, the group generated unsaturated cyclobutanes **72** which formed highly substituted [4]dendralenes **74** when a ring-opening was triggered by bromination, or underwent thermal, radical isomerization to yield cyclic [3]dendralene **73**, or [4]radialene **75**. [4]Radialene **75** could itself undergo bromination and ring-opening to furnish [4]dendralene **76**.



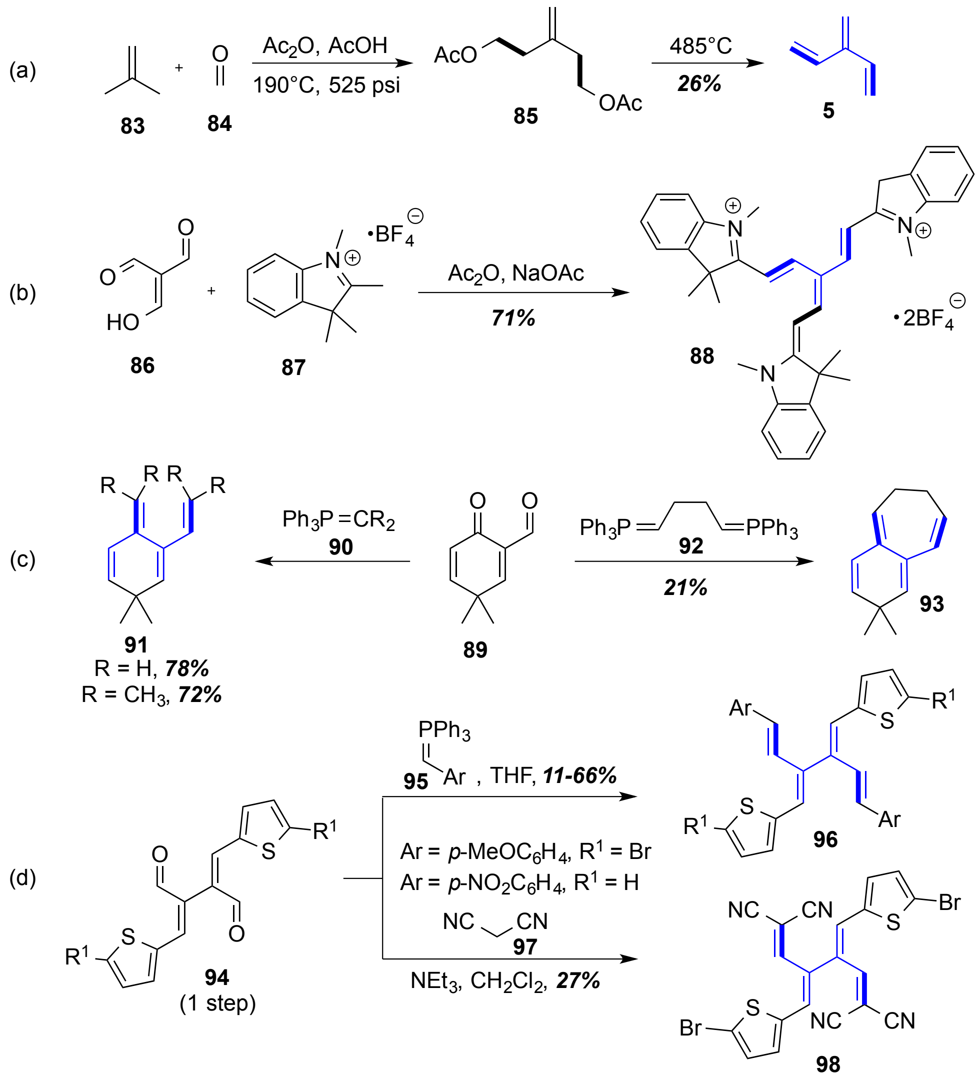
Scheme 1.11: *Cycloaddition/ring-opening sequences by Tykwinski and co-workers to synthesize various dendralenes* [49].

A new, complementary approach to enyne metathesis has also emerged in the work of Singh and Ghosh (***Scheme 1.12***) [50–51]. A stepwise methylenation (using dimethyl sulfonium methylide ylid **78**) and Stille–Gennari olefination sequence was used to furnish a variety of 1,2,5-trisubstituted [3]dendralenes **81**, which rapidly underwent Diels–Alder (DA) dimerization to yield the isolated DA dimer products **82**. The sequence can be performed in one pot, *via* the intermediacy of the ylid adduct of **77** and **78**, but was highest yielding when proceeding after quenching this intermediate with water and isolating dienyl phosphonate **79**.



Scheme 1.12: *The methylenation/olefination sequence of Singh and Ghosh that forms [3]dendralene prior to in situ dimerization* [50–51].

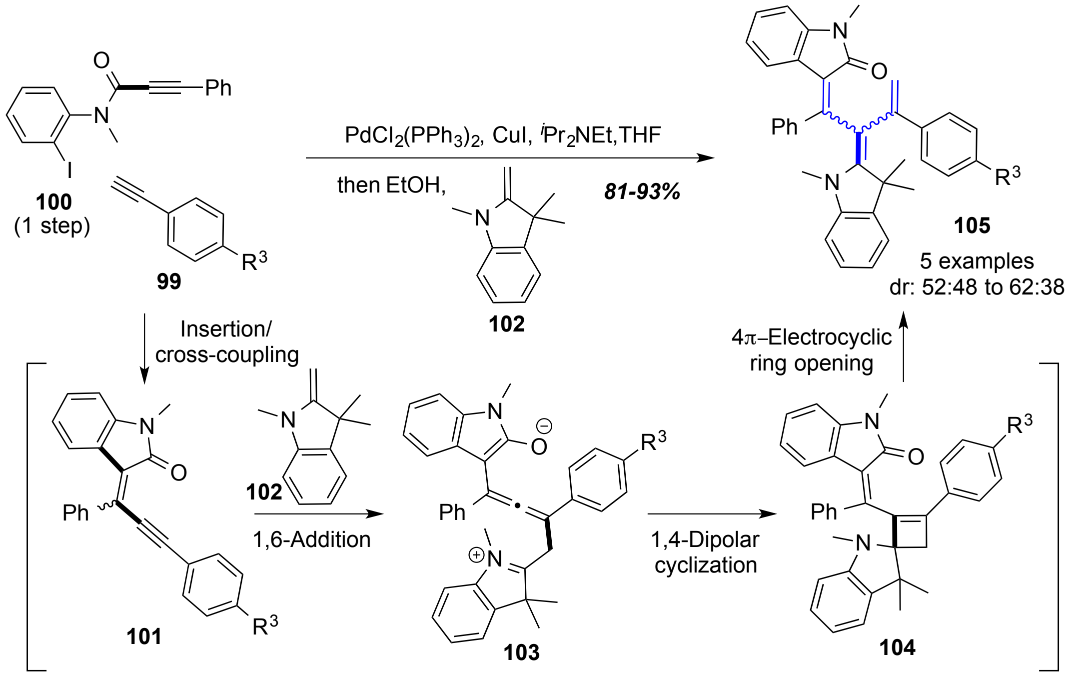
Olefination-type reactions (including addition/elimination sequences) are a reliable method of generating alkenes, and have therefore seen many applications in dendralene synthesis. Their use in multi-bond forming approaches to dendralenes has also been documented. The landmark first synthesis of [3]dendralene (**5**) by Blomquist in 1955 employed a double Alder–ene reaction between 2-methylpropene (**83**) and two molecules of formaldehyde (**84**), followed by acetylation and elimination to furnish the target hydrocarbon **5** (***Scheme 1.13 (a)***) [52]. Double addition/elimination strategies have also been employed on 1,1-dicarbonylalkenes and 2,3-dicarbonylbutadienes to form [3]- and [4]dendralenes, respectively [53–58]. Another notable and very early example of this approach was used by Reichardt and Mormann to synthesize tri-substituted [3]dendralene **88**, *via* a triple condensation reaction (***Scheme 1.13 (b)***) [59]. This strategy has found application in a number of related examples [60–63]. Cassens and Lüttke used double Wittig olefinations to form cyclic and bicyclic [4]dendralene structures from 1,3-diketones **89** (***Scheme 1.13 (c)***) [1, 64]. Bryce and co-workers also used the double olefination approach to install the terminal alkenes of a [3]dendralene [65]. Talpur and co-workers [66] have recently used the same double Wittig reaction, and also a double Knoevenagel condensation, to form functionalized [4]dendralenes **96** and **98** (***Scheme 1.13 (d)***).



Scheme 1.13: *Representative examples of double alkenation syntheses of dendralenes, featuring double addition/elimination sequences or double olefination reactions* [1, 52, 59, 64, 66].

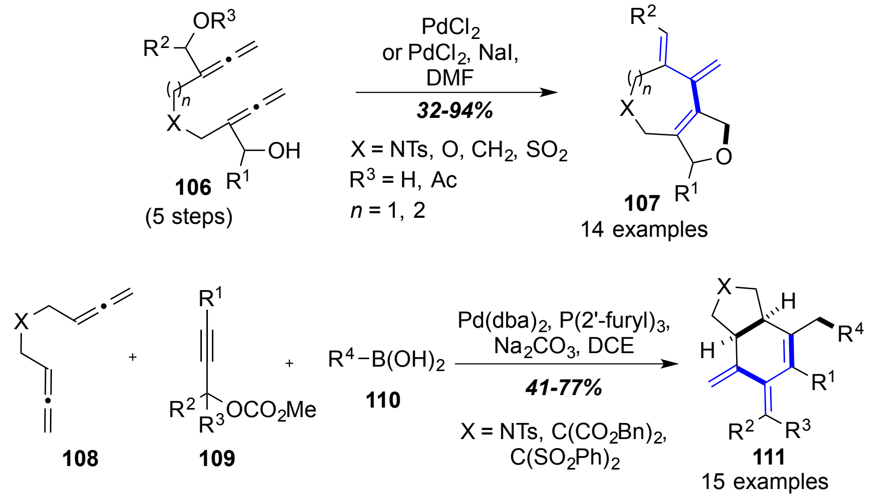
1.2.3 Other Multi-Bond Forming Processes

The Müller group has reported a rapid approach to highly substituted [3]dendralenes *via* a remarkable, consecutive one-pot palladium(0)-catalyzed sequence (***Scheme 1.14***) [67]. Pd(0)-mediated 5-*exo*-*dig* cyclization followed by Sonogashira cross-coupling between alkyne **99** and the alkenyl palladium(II) species generated from cyclization yielded intermediate **101**, which underwent 1,6-addition from Fischer's base **102**, followed by Mannich type 1,4-dipolar cyclization to form cyclobutene intermediate **104.** Ultimately a 4π electrocyclic ring-opening furnished [3]dendralenes **105** as the product of this complex mechanism. The methyl substituent on the nitrogen of anilide **100** was found to be crucial to enforce the mechanistic pathway that generates dendralenes, as opposed to other structures. Whilst five examples were catalogued, only the substituent on one aryl group was varied, and the dendralenes were formed as mixtures of (*E*) and (*Z*) isomers about the central alkene. Evidently, increased scope and selectivity is worth pursuing in this impressive sequence.



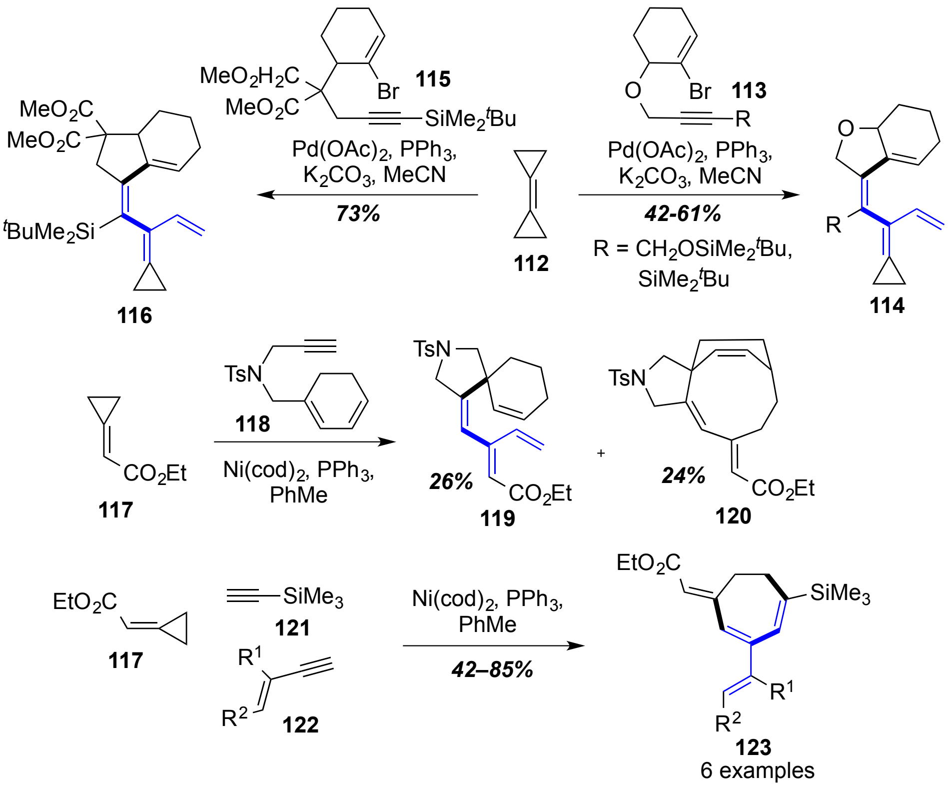
Scheme 1.14: *The Pd–catalyzed cascade synthesis of substituted [3]dendralenes by Müller and co-workers* [67].

The Ma group has reported some very elegant multi-bond forming processes to synthesize dendralenes, including both palladium(II)- and rhodium(I)-catalyzed cycloisomerizations of di-allenes **106** to form cyclic dendralenes **107** (***Scheme 1.15***) [68–70], and also the remarkable palladium(0)-catalyzed three component reaction of di-allenes **108**, propargylic carbonates **109** and boronic acids **110** to form bicyclic [3]dendralenes **111** (***Scheme 1.15***) [71]. Similar, intermolecular transformations to those used to form dendralenes **107** had been reported earlier by Alcaide, to synthesize dihydrofuran-containing dendralenes [72–73].



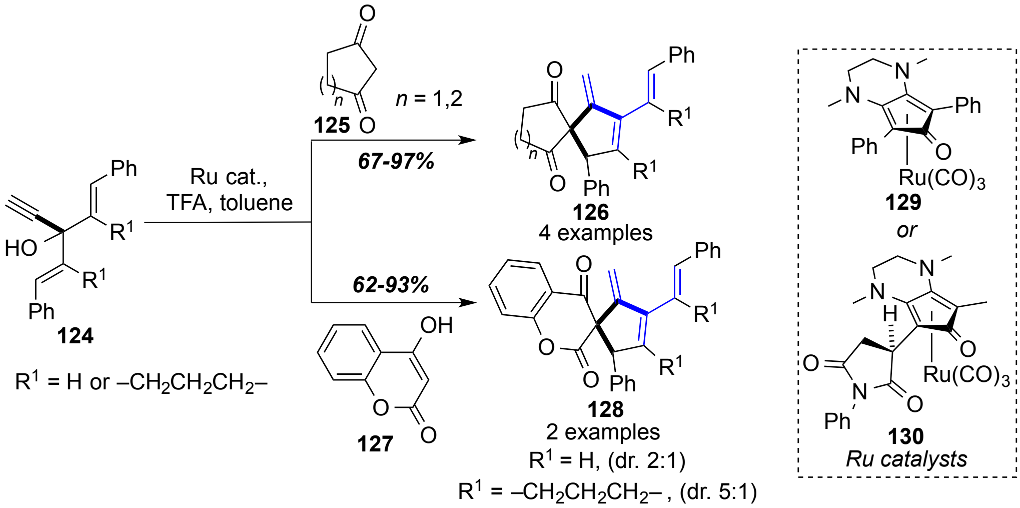
Scheme 1.15: *Multi-bond forming syntheses of [3]dendralenes from the Ma group* [69–71].

Alkynes are also versatile starting materials to couple with alkenes or allenes in transition-metal catalyzed processes to form dendralenes. In 2014, building on earlier work from Schelper and de Meijere [74], Demircan reported [75] the synthesis of 3-cyclopropylidene-containing dendralenes using Pd(0)-catalyzed cascade reactions of alkynes and 1,1'-bi(cyclopropylidene) (**112**) (***Scheme 1.16***). In 2013 Saito and co-workers [76] had reported a related, isolated synthesis of [3]dendralene **119** employing a Ni(0) catalyst, building on their earlier, more general work employing alkynes **121**, ene-ynes **122** and ethyl cyclopropylideneacetate (**117**) in Ni(0)-catalyzed three component cycloaddition reactions (***Scheme 1.16***) [77].



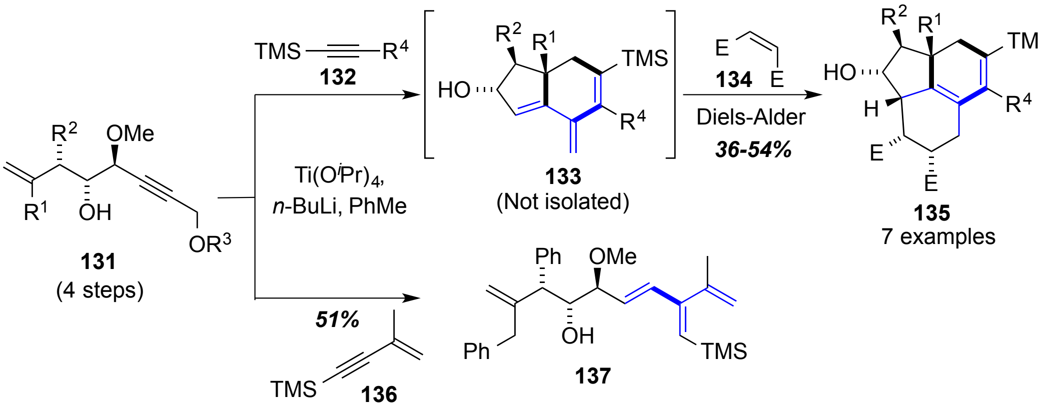
Scheme 1.16: *Transition-metal catalyzed reactions of alkynes and cyclopropylidenes to form [3]dendralenes* [75–77].

Haak and co-workers in 2015 [78] and 2012 [79] reported monocyclic and bicyclic [3]dendralenes which were generated *via* ruthenium-catalyzed cascade transformations. The complex mechanism involves ruthenium(0)-mediated dehydration of the alkyne **124**, addition of the nucleophile to an alkenyl ruthenium allenylidene and cyclization at a ruthenated alkyne to furnish unusual spirocyclic [3]dendralenes **126** and **128** (***Scheme 1.17***).



Scheme 1.17: *Ru(0) catalyzed synthesis of cyclic [3]dendralenes by Haak and co-workers* [78–79].

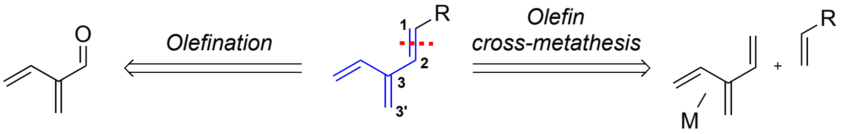
In a very nice titanium-mediated annulation cascade, Cheng and Micalizio (2014) synthesized functionalized, bicyclic [3]dendralenes **133** *in situ* as intermediates that were trapped *via* a subsequent DA reaction (***Scheme 1.18***) [80]. The report includes one example of a DA dimerization product, seven examples of intermolecular metallocycle-mediated annulation followed by intermolecular [4+2] cycloaddition reaction to afford **135**, and one example of an isolated, acyclic substituted [3]dendralene **137**.



Scheme 1.18: *Ti(IV)-mediated cascade syntheses of [3]dendralenes by Cheng and Micalizio* [80].

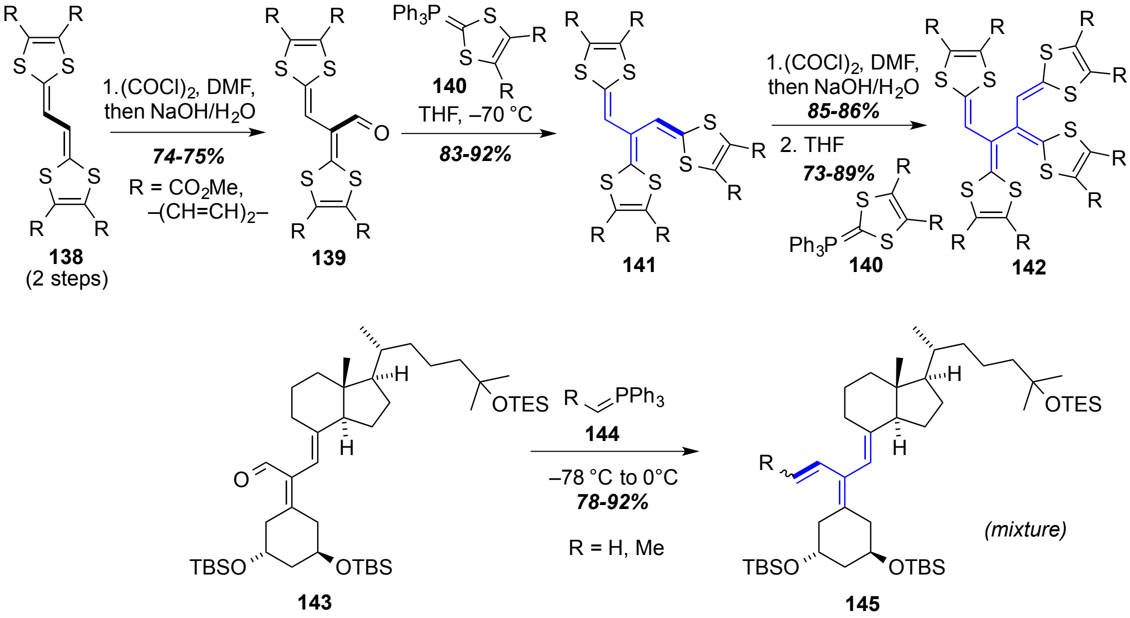
1.3 Solo-Bond Forming Reactions

1.3.1 C1–C2 Alkenation Reactions



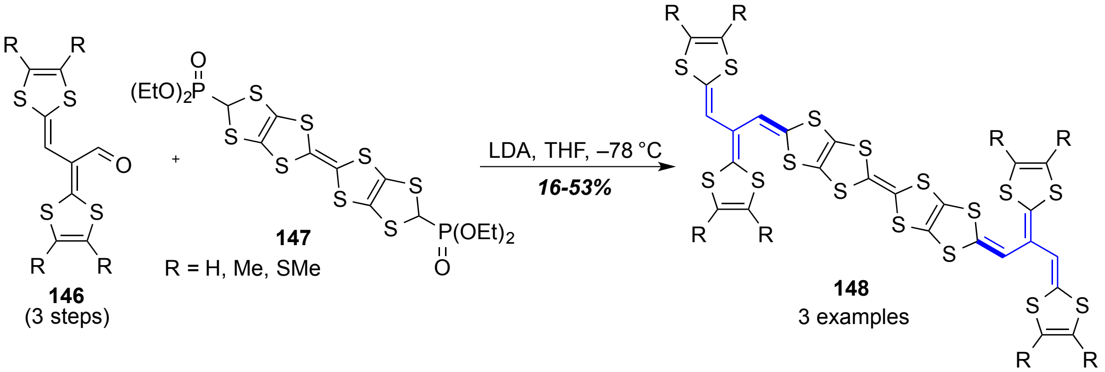
Scheme 1.19: *Single alkene (C1–C2) bond disconnections of [3]dendralenes.*

The most obvious method to install the C1–C2 alkene of a dendralene is an olefination reaction (***Scheme 1.19***), but it has seen very little use, because of the propensity of 2-carbonyl-1,3-butadiene derivatives to undergo rapid DA dimerization [81]. In fact, the only successful uses of 2-carbonyl-1,3-butadienes in such processes feature substrates stabilized by 1,1-disubstitution and a 4*Z* substituent. Such an example is the iterative formylation/olefination sequence reported by Yoshida and co-workers (***Scheme 1.20***) [82]. A selective, single electrophilic formylation followed by a Wittig reaction gave hexa-substituted [3]dendralenes **141**, which could be further homologated to octa-substituted [4]dendralenes **142** using the same sequence. Related examples have also been reported [83–84]. A similar iterative formylation/Horner–Wadsworth–Emmons (HWE) sequence was used by Bryce *et. al.* to synthesize [3]- and [4]dendralenes containing dithiole and ferrocene functionalities [65]. DeLuca and co-workers recently (2013) reported the synthesis of two [3]dendralenes **145** using a Wittig reaction, however, the stereoselectivities of the reactions were not reported (***Scheme 1.20***) [85].



Scheme 1.20: *Syntheses of dendralenes using Wittig reactions* [82, 85].

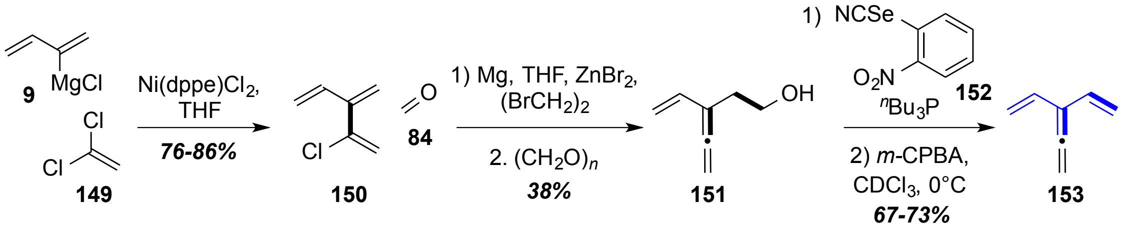
In 2012, Misaki and co-workers prepared three examples of compounds containing two hexa-substituted [3]dendralene subunits **148** using a double HWE reaction (***Scheme 1.21***) [86]. The starting materials were synthesized using Yoshida's method *via* a single electrophilic formylation to give the cross-conjugated diene aldehyde **146**.



Scheme 1.21: *Syntheses of dendralenes using double HWE reactions, by Misaki and co-workers* [86].

Recently, Sherburn and co-workers (2012) attempted to use Wittig olefination to synthesize 1-substituted [3]dendralenes, only to determine that [3]dendralenes featuring a 1*E*-conjugating substituent underwent rapid DA dimerization, and could not be isolated [87]. The Wittig reaction furnished only an isolated example of a 1*Z*-phenyl substituted [3]dendralene in low yield (20%), along with a mixture of three DA dimerization products. This led to the development of a cross-metathesis approach involving tricarbonyl-iron complexed dendralenes, which is discussed in Section 1.4.

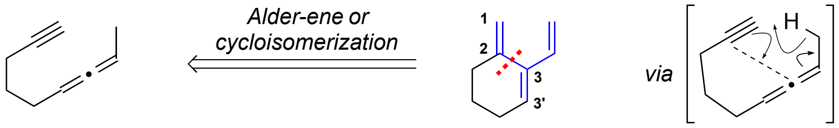
1,1-Divinylallene (**153**) is a dendralene prone to decomposition, but could be isolated and characterized through a cautious approach [88]. The extreme sensitivity of this compound to dimerization and decomposition dictated that a mild elimination method be used to reveal the last alkene, after the C3–C3′ bond was established *via* by Kumada–Tamao–Corriu cross-coupling (***Scheme 1.22***). The isolation of this compound (with a half life of 43 h at 0.02M) *via* this method suggests that similar strategies could be used to obtain and characterize highly reactive dendralenes.



Scheme 1.22: *Synthesis of 1,1-divinylallene, by Sherburn and co-workers, using a mild elimination method* [88].

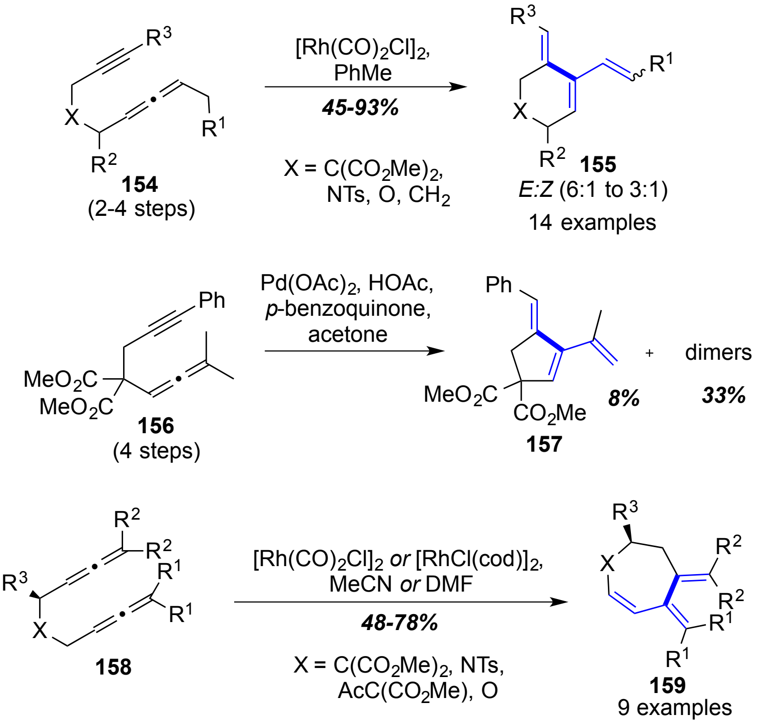
Finally, we note the absence of general cross-metathesis routes to functionalize pre-existing dendralene frameworks. This is no doubt due to the reduced reactivity of conjugated alkenes in cross-metathesis reactions [87, 89]. A solution to this problem is addressed below, in Section 1.4.

1.3.2 C2–C3 Alkenylation Reactions



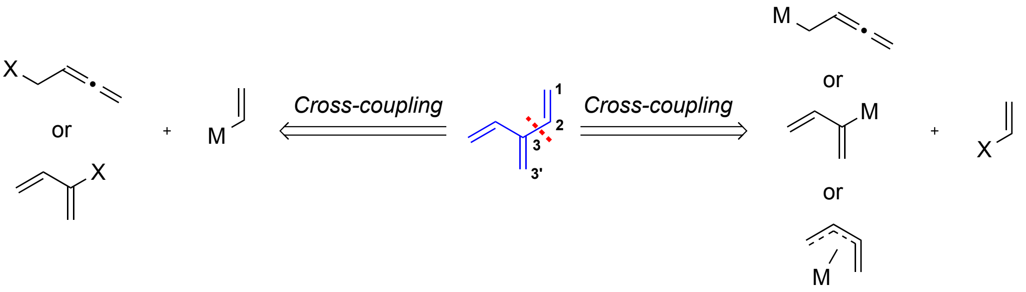
Scheme 1.23: *Formation of dendralene via Alder-ene or metal catalyzed cycloisomerization reaction.*

Reactions that incorporate a new alkene onto an existing carbon framework, forming the C2–C3 bond, are very common. From the 1970s onwards, a few examples of thermal rearrangements, Alder-ene reactions [90–93], and isomerizations were published that generally require harsh conditions and show limited scope. Hullio and Mastoi also reported an isolated example of a substituted [3]dendralene, prepared by pyridine-catalyzed addition of dimethylacetylene dicarboxylate to *trans*-cinnamyl aldehyde [94]. Developments in transition metal catalysis have allowed much milder transformations with significantly enhanced scope. Foremost among these are the transition metal-catalyzed cycloisomerizations, which are formal Alder-ene reactions, that provide robust access to a wide variety of cyclic dendralenes, most especially 2,3′-cyclodendralenes [95–105]. For example, Brummond and co-workers reported the rhodium(I)-catalyzed synthesis of 14 different cyclic [3]dendralenes **155** featuring a variety of different functional groups and heterocycles (***Scheme 1.24***) [99]. In many cases, mixtures of alkene isomers are observed. Iridium(I) [105], platinum(II) [106–107], cobalt/rhodium nanoparticles [108], palladium(II) [69], rhodium(I) [70, 109] and gold(I) catalysts [107, 110–111] have also been used to perform these and related cycloisomerizations, with the mechanism, scope and limitations varying among catalysts. Recently, Deng and Bäckvall [112] reported another palladium(II)-catalyzed example, but only formed dendralenes **157** as the unwanted by-products of acetoxylation reactions (***Scheme 1.24***). Aside from developments in the metal-catalyzed formal Alder-ene reaction, Malacria *et al.* and Mukai and co-workers have revisited the thermal variant, with some promising results [107, 113–114]. A related reaction, the intermolecular ruthenium(II)-catalyzed coupling of cyclic allenes and alkynes, has also been used to synthesize a variety of 2,4-cyclo-[3]dendralenes [115]. Di-allenes are also useful substrates for similar transition-metal catalyzed processes [68]. Lu and Ma reported Rh(I)-catalyzed cycloisomerizations of 1,5-diallenes **158**, to provide seven-membered heterocycle-containing [3]dendralenes **159** (***Scheme 1.24***) [70]. Where chiral, enantioenriched substrates were used, no significant racemization was observed under the reaction conditions.



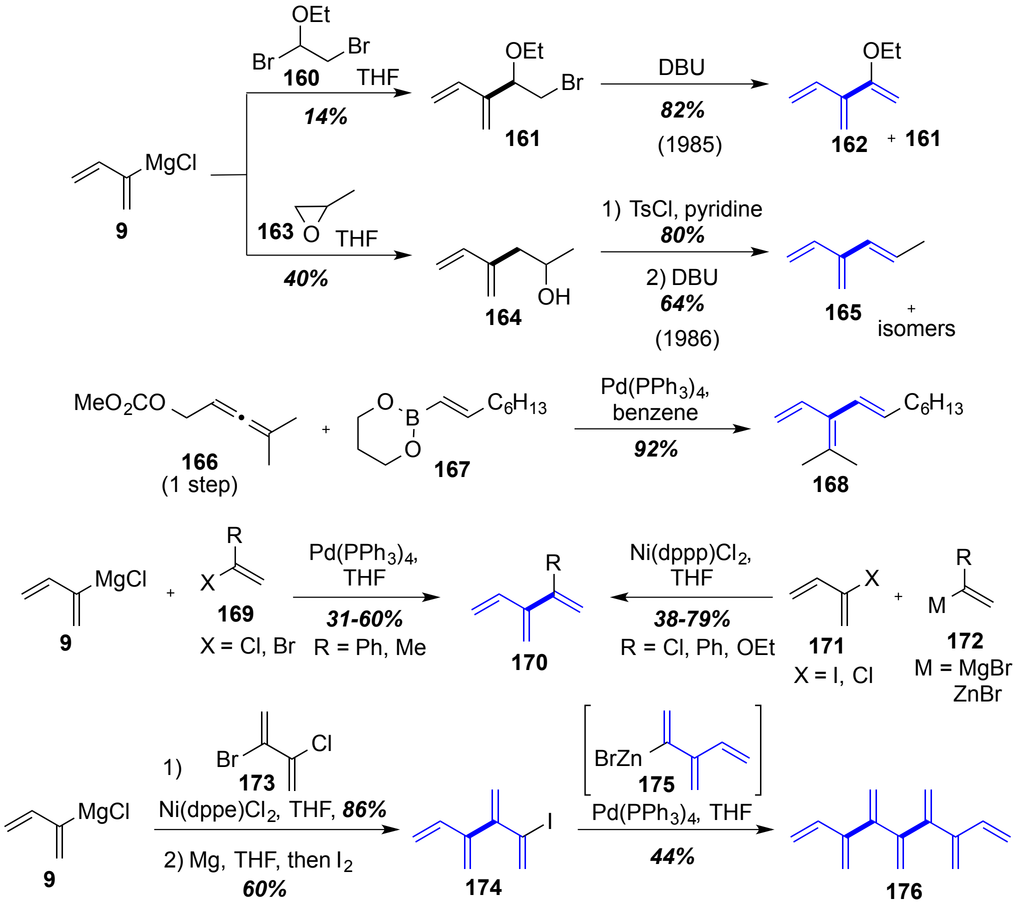
Scheme 1.24: *Representative examples of transition metal catalyzed cycloisomerization reactions forming the C2–C3 bond of cyclic [3]dendralenes* [70, 99, 112].

The first syntheses of dendralenes by C2–C3 bond formation (***Scheme 1.25***) were reported by Tsuge and co-workers in 1985 and 1986, and proceed *via* substitution at either a bromide **160** or an epoxide **163**, followed by elimination (***Scheme 1.26***) [116–117]. Similar addition/elimination sequences to carbonyl groups or epoxides [118], and substitution reactions [119], followed. Such methods have been superseded by cross-coupling techniques that take place between a 2-functionalized 1,3-butadiene and an alkene (each can be either electrophilic or nucleophilic); or a 4-functionalized 1,2-butadiene and alkene, and occur with allylic transposition (***Scheme 1.25***). No doubt due to the ready availability of alkenyl halides and allenes, and the variety of increasingly mild and selective reaction variants, cross-coupling has provided access to a large number of diversely substituted dendralenes over the last twenty years, some of which have even been part of natural product syntheses [14, 120–121].



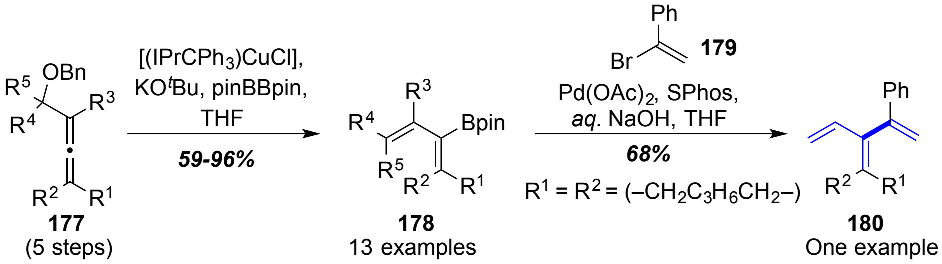
Scheme 1.25: *Alkenylation approaches to [3]dendralene via cross-coupling C2–C3 bond formation.*

The first reports of cross-coupling routes to dendralenes were isolated examples in 1994 by Suzuki *et. al.* (***Scheme 1.26***, **166** + **167**→**168**) [122] and 1998 by Allain *et. al.* [123]. This early work paved the way for a more general approach featuring Kumada–Tamao–Corriu, Stille and Negishi reactions to synthesize mono-substituted [3]dendralenes **170** and the parent dendralenes, developed by the Sherburn group (***Scheme 1.26***) [124]. Aside from cross-couplings with readily available alkenyl and butadienyl units, including the use of 3-sulfolene building blocks as 'masked butadienes' to synthesize higher dendralenes [10, 125], the group also reported bond formations between higher dendralene cross-coupling partners, such as the Negishi cross-coupling of 2-iodo[4]dendralene (**174**) and the organozinc derivative of 2-chloro[3]dendralene (**175**) (***Scheme 1.26***) [23]. Double cross-coupling reactions that furnish the C2–C3 bond in addition to another bond, have already been discussed (Section 1.2.1).



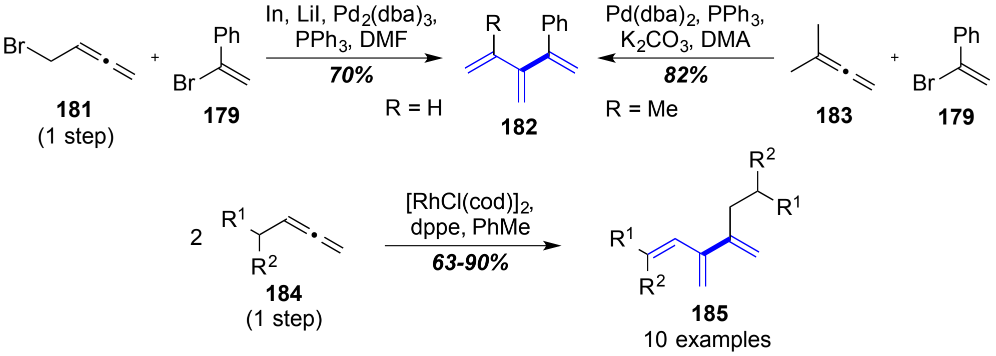
Scheme 1.26: *Representative syntheses of dendralenes via C2–C3 bond formation, featuring either classical approaches, or transition-metal catalyzed sp^2–sp^2 cross-coupling* [23, 116–117, 122, 124].

Recently, Tsuji and co-workers reported an isolated synthesis of a [3]dendralene **180** *via* a Suzuki–Miyaura cross-coupling reaction (***Scheme 1.27***) [126]. A variety of different 2-boryl-1,3-butadienes **178** were synthesized. Whilst only one was coupled with an alkenyl halide **179**, these butadien-2-yl coupling partners **178** in principle offer a variety of building blocks to add to those already available for simple cross-coupling routes to dendralenes. 1,3-Butadien-2-yl cross-coupling partners have also been used in other Stille and Negishi cross-couplings [127–130].



Scheme 1.27: *Recent [3]dendralene synthesis by Tsuji and co-workers using a metalated butadiene* [126].

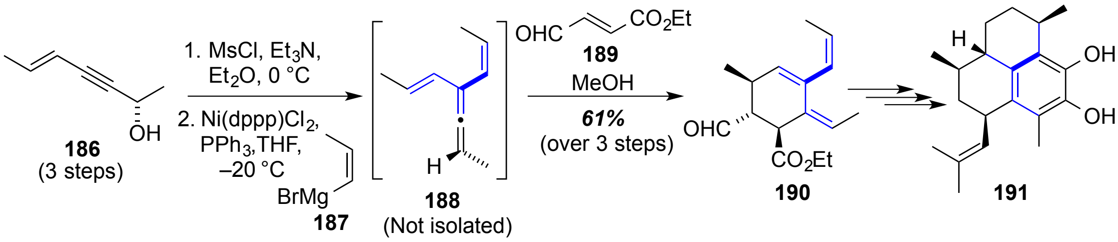
Despite being a less obvious starting material than a 1,3-butadiene-2-yl coupling partner, 1,2-butadien-4-yl precursors (such as **166** in Suzuki's pioneering example in ***Scheme 1.26***) have seen the most use in dendralene synthesis [122, 131–136]. A couple of more recent examples include the palladium-catalyzed cross-coupling reaction of alkenyl bromides **179** with, for example, the organoindium derived from allenyl bromide **181**, or 1,1-dimethyl allene (**183**) (*via* a Mizoroki-Heck reaction) (***Scheme 1.28***) [132, 135]. Palladium(0) catalyzed dimerizations or homocouplings can also furnish the C2–C3 bond [137–141], as can nickel(0)- [142–143] and rhodium(I)-catalyzed ones [144].



Scheme 1.28: *Cross-coupling syntheses of [3]dendrelenes using allene starting materials* [132, 135, 144].

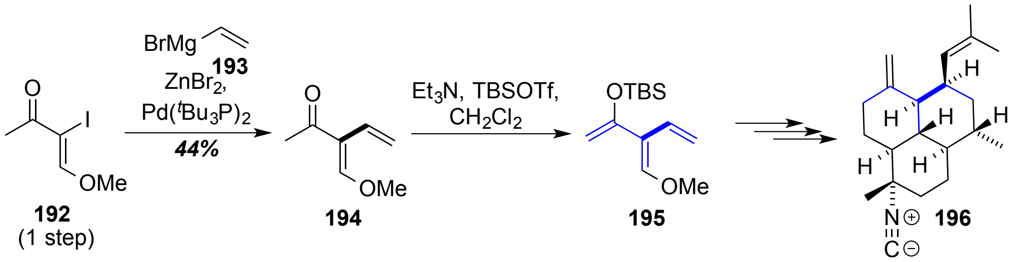
Two final examples of cross-coupling to furnish [3]dendralenes *via* C2–C3 bond formation are part of very short and efficient total syntheses, and highlight the versatility and attractiveness of the approach. As an extension of their work on 1,1-divinylallene (**153**) (***Scheme 1.22***), Sherburn *et. al.* (2015) synthesized allenic [3]dendralene **188** *via* Kumada–Tamao–Corriu cross-coupling of a metallated alkene **187** and a chiral, propargyl mesylate [121]. A subsequent DA reaction produced cyclic

[3]dendralene **190** *en route* to a pseudopterosin aglycone **191** (***Scheme 1.29***). Allenic [3]dendralenes are prone to decomposition [136], so the subsequent DA reaction was carried out *in situ.*



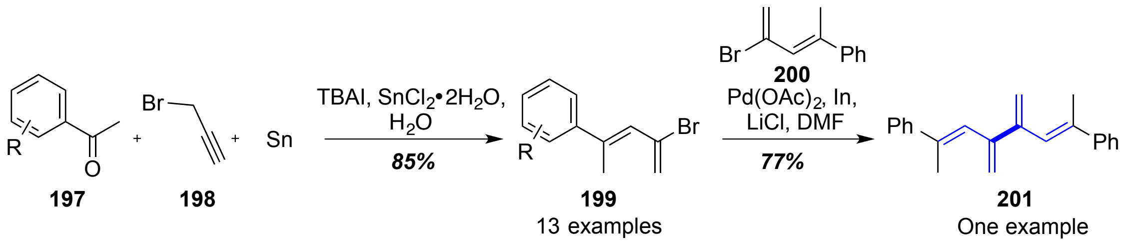
Scheme 1.29: *Chiral [3]dendralene synthesis via sp^2–sp cross-coupling as part of a total synthesis by Sherburn and co-workers (2015)* [121].

In another total synthesis involving a [3]dendralene, Pronin and Shenvi (2012) synthesized a 'Danishefsky dendralene' **195** using a Negishi cross-coupling reaction with a functionalized alkenyl iodide **192** followed by silyl enol ether formation to generate the dendralene (***Scheme 1.30***) [120]. A subsequent series of transformations, including two DA reactions, led to the total synthesis of amphilectene natural product **196**.



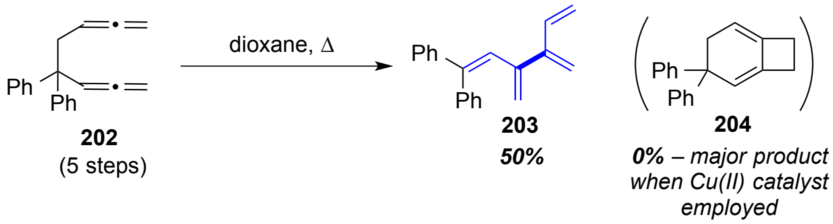
Scheme 1.30: *[3]Dendralene synthesis via sp^2–sp^2 cross coupling as part of a total synthesis by Pronin and Shenvi (2012)* [120].

[4]Dendralenes have also been assembled by solo sp^2–sp^2 bond-forming reactions. The most prominently targeted C–C bond has been the central one. This approach is maximally convergent, and especially well-suited to symmetrical targets. Li and co-workers (2014) recently synthesized a symmetrical, 1,1,6,6-tetrasubstituted [4]dendralene **201** by a palladium(0) catalyzed homocoupling reaction (***Scheme 1.31***) [145]. Whilst only an isolated example of a [4]dendralene **201** was synthesized in this study, in principle, many different butadienyl halide coupling partners **199** could be employed in this way. Other palladium-catalyzed homocouplings of functionalized 1,3-butadienes [146], and thermal oxidative homocoupling of highly electron-rich butadienes [147] have also been reported. In fact, the first practical synthesis of the parent [4]dendralene was an oxidative homocoupling of the chloroprene Grignard reagent [148].



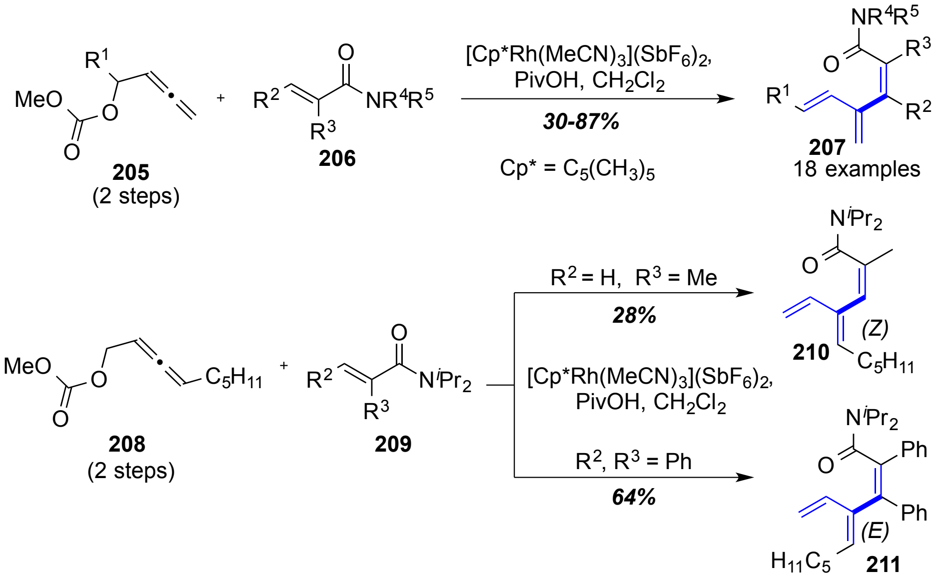
Scheme 1.31: *Synthesis of 2-bromo-1,3-butadienes and subsequent homocoupling to form a [4]dendralene, by Li and co-workers (2014)* [145].

Isomerizations and rearrangements featured heavily in early approaches to [4]dendralene and derivatives [17, 149 – 155]. An interesting, recent case of unsymmetrical [4]dendralene formation was reported by Mukai and co-workers in 2012 (***Scheme 1.32***) [156]. Cu(II)-promoted intramolecular [2+2] cycloaddition of 1,4-diallenes **202** yielded bicyclooactadienes **204**, however, under uncatalyzed thermal conditions the authors noted that the formal [3,3]-sigmatropic rearrangement product, [4]dendralene **203**, was formed in 50% yield. If optimized, this presents a nice method to form unsymmetrical [4]dendralenes, but relies on a lengthy synthesis of starting materials.



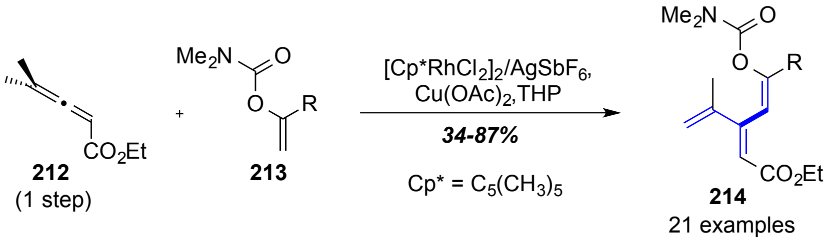
Scheme 1.32: *Thermal isomerization synthesis of an unsymmetrical [4]dendralene by Mukai and co-workers* [156].

C–H activation is an important and rapidly developing area of dendralene synthesis. In very recent years, several C2–C3 bond forming approaches to dendralenes involving C–H activation have been reported. In 2013, Glorius and co-workers developed a Rh(III)–catalyzed, Heck–type alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates **205** and acrylamides **206** (***Scheme 1.33***) [157]. This new reaction performs well for the synthesis of highly substituted [3]dendralenes.



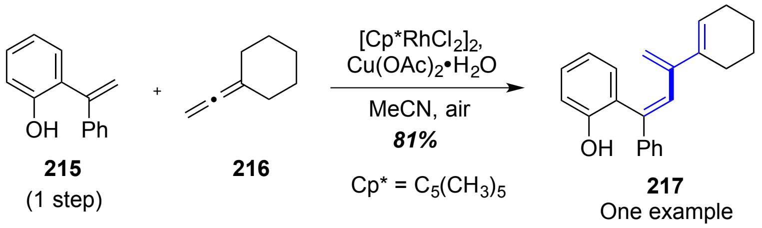
Scheme 1.33: *Rh(III)-catalyzed Heck-type C–H activation of carbonates by Glorius and co-workers (2013)* [157].

A similar transformation was subsequently reported in 2014 by Fu and co-workers, who used allene and carbamate precursors to generate [3]dendralenes *via* rhodium(III) catalysis (***Scheme 1.34***) [158]. A variety of different carbamates **213** successfully underwent Rh(III)-catalyzed C–H activation and coupling to generate cyclic and acyclic substituted [3]dendralenes **214**. While the general route works quite well between the tri-substituted allene and acyclic carbamates, the reaction is not high-yielding if the enol ester is cyclic or the allene is mono- or tetra-substituted.



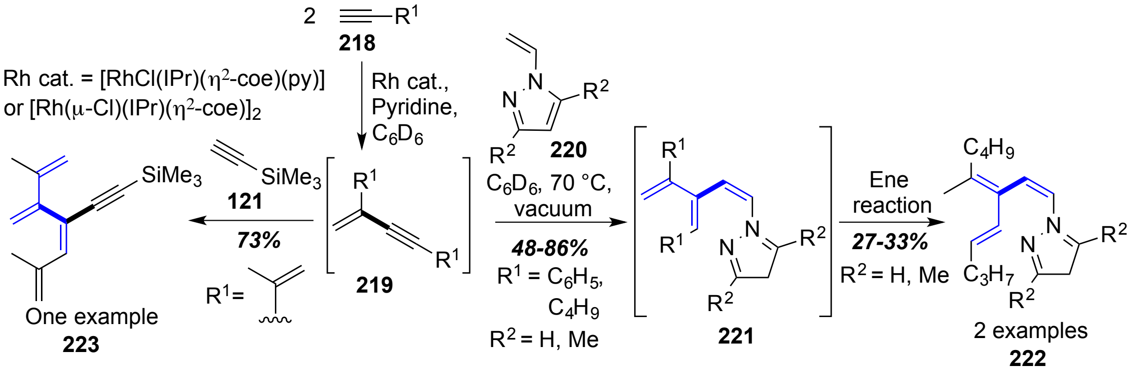
Scheme 1.34: *Rh(III) catalyzed C–H activations of carbamates by Fu and co-workers (2014)* [158].

Another C–H activation method that has potential in the synthesis of dendralenes was reported by Gulías and co-workers in 2015 (***Scheme 1.35***) [159]. A stable dendralene intermediate **217** was prepared from substituted phenol **215** and allene **216**, as an intermediate in the Rh(III)-catalyzed synthesis of 2*H*-chromenes. In principle, this method could be adapted to target substituted dendralenes.



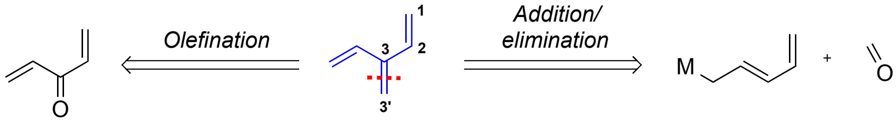
Scheme 1.35: *Rh(III)-catalyzed allene alkenylation by Gulías and co-workers (2015)* [159].

A final recent contribution to C–H activation-based methods is the work by Oro and co-workers, who reported the Rh(I)-catalyzed hydrovinylation of alkynes **218** with *N*-vinylpyrazoles **220** to form pyrazole-containing [3]dendralenes **221** (***Scheme 1.36***) [160–161]. Some of these dendralenes could also be subjected to thermal Alder-ene reactions to alter the substitution pattern on the dendralene products.



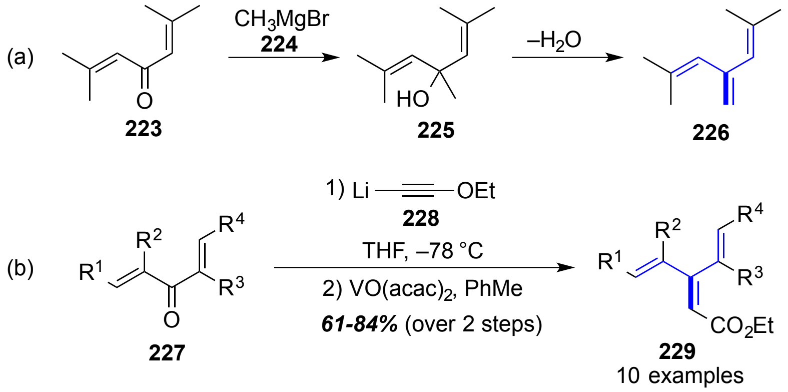
Scheme 1.36: *Rh(I)-catalyzed hydrovinylation of alkynes by Oro and co-workers (2014), and a subsequent ene reaction, to synthesize [3]dendralenes* [160–161].

1.3.3 C3–C3′ Alkenation Reactions



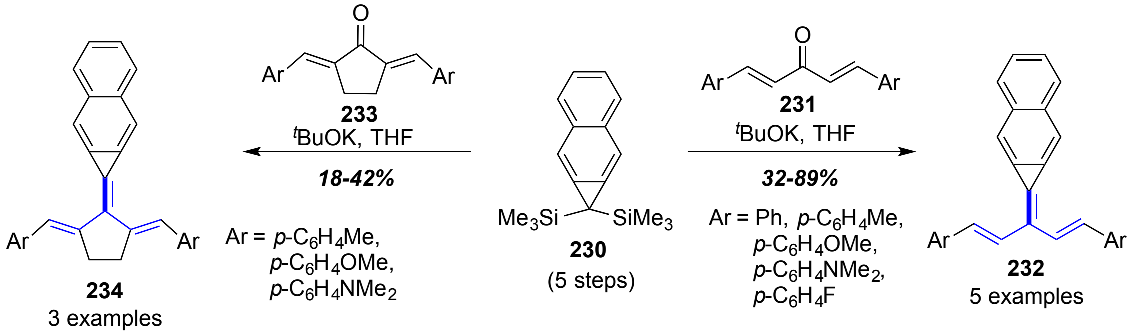
Scheme 1.37: *Single alkenation (C3–C3′) bond disconnections of [3]dendralene.*

The first example of a dendralene synthesis *via* C3–C3′ bond formation (***Scheme 1.37***) dates back to 1904, when Fellenberg reported an addition/elimination sequence between methyl magnesium bromide (**224**) and phorone (**223**) (***Scheme 1.38 (a)***) [162]. Since then, a number of variations leading to different substituents have been reported. In fact, early syntheses of dendralenes prominently feature the C3–C3′ bond disconnection, utilizing classical reactions such as Wittig reactions [163–173], Horner–Wadsworth–Emmons olefination [174–176], ketene additions/decarboxylation sequences [177–181], and Grignard addition/dehydration sequences [162, 182–183] to transform readily available 1,4-dien-3-ones into dendralenes. Recently, West and co-workers made several cyclic and acyclic derivatives of substituted [3]dendralenes **229** through catalytic Meyer-Schuster rearrangements of propargyl alcohols derived from alkyne **228** addition to dienones **227** (***Scheme 1.38 (b)***) [184–185]. It was found for these highly substituted dendralenes, that if the dienone **227** was not symmetrical, mixtures of (*E*) and (*Z*) alkene isomers were formed. Despite this limitation, a very noteworthy feature of the work is the use of a less substituted dienone **227** starting material – prior to this, only highly substituted variants had been employed.



Scheme 1.38: *(a) Addition/elimination sequence by von Fellenberg (1904)* [162] *and (b) Meyer-Schuster rearrangement by West and co-workers (2011)* [184–185].

Other variants of olefination have also been applied to dendralene synthesis [186–188]. In 2004, Dixon and Halton prepared a variety of cyclic [3]dendralenes using Peterson-type olefination reactions (***Scheme 1.39***) [189]. These examples feature symmetrical dienone starting materials, so the stereoselectivity of the Peterson olefination approach to dendralenes is yet to be tested.

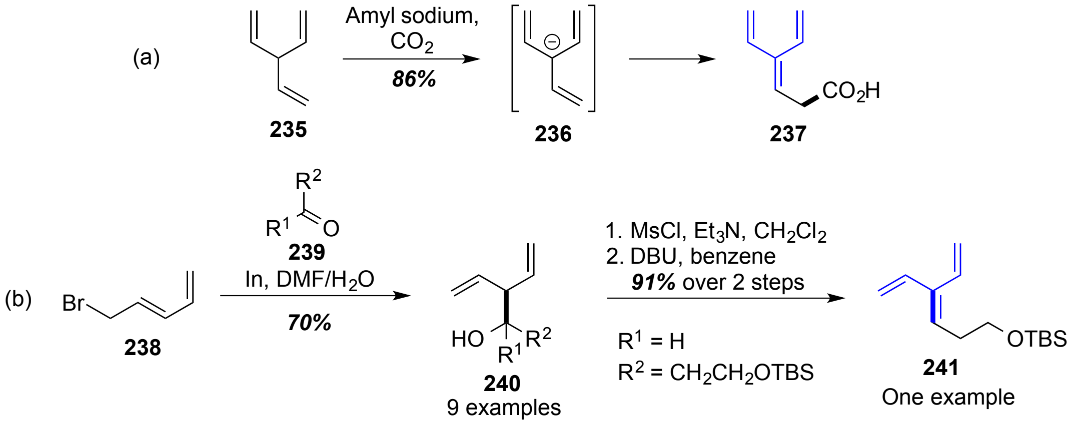


Scheme 1.39: *Peterson-type olefination approach to [3]dendralenes by Dixon and Halton (2004)* [189].

Another way to circumvent the stereoselectivity issues that may arise from olefination or addition/elimination sequences to 1,4-dien-3-ones is to switch the polarity of components, and olefinate a carbonyl compound with a symmetrical nucleophilic pentadienyl anion equivalent. A seminal contribution was reported by Paul and

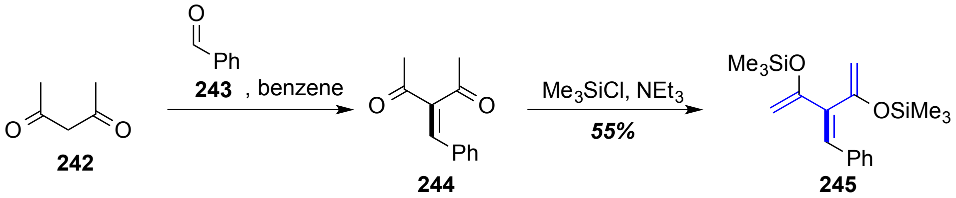
Tchelitcheff in 1951, who combined trivinylmethane (**235**) and carbon dioxide to form a [3]dendralene **237** (***Scheme 1.40 (a)***) [190]. In this instance, the anion of trivinyl methane **236** is indeed a pentadienyl anion, but bond formation occurs with allylic transposition through a vinyl unit.

Fallis and co-workers [191–192] have synthesized substituted [3]dendralenes using a similar approach, by reacting indium metal with bromodiene **238**, and using the resulting indium pentadienyl species in addition/elimination sequences with a number of functionalized aldehydes or ketones **239** (***Scheme 1.40 (b)***). This strategy builds on work by the Miginiacs in 1964 [193], and has also seen subsequent use [12, 194–196].



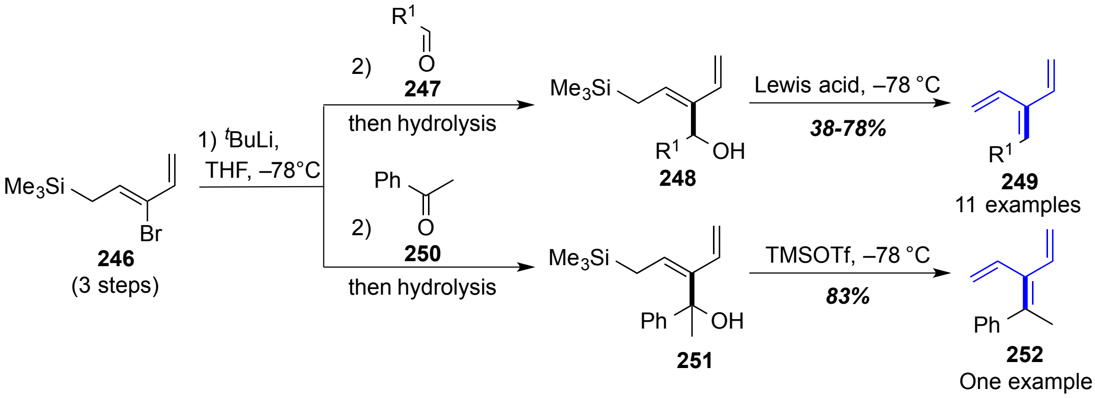
Scheme 1.40: *[3]Dendralene synthesis using (a) a trivinyl methide anion* [190] *and (b) an indium pentadienyl nucleophile* [191–192].

A separate approach to this bond formation is the Knoevenagel condensation of a 1,3-diketone with a carbonyl compound, followed by conversion of the carbonyl groups to alkenes. For example, in 1983 Tsuge and co-workers reported condensation between diketone **242** and benzaldehyde (**243**), followed by double silyl enol ether formation to generate a [3]dendralene **245** (***Scheme 1.41***) [197–199]. The ready availability of the carbonyl compounds involved suggests that this method could be useful for other substituted dendralenes. Silyl enol ether formation to generate a [3]dendralene was subsequently used to great effect in total synthesis by Pronin and Shenvi (***Scheme 1.30***, [120]). The Knoevenagel condensation can also be performed with different electrophiles, followed by chlorinative dehydration to reveal a dihalodendralene [200–201], or hydride reduction/elimination to reveal a terminally unsubstituted [3]dendralene [202].



Scheme 1.41: *A Knoevenagel condensation/silyl enol ether formation approach to a [3]dendralene* [197].

Recently, a Peterson-type olefination variant of this strategy was explored by Parrain and co-workers (2013) [203]. By incorporating a trimethylsilyl group in the pentadienyl anion equivalent **246**, alcohols **248** that readily undergo Lewis-acid catalyzed γ-elimination were formed as addition products of aldehydes **247** (***Scheme 1.42***). The one step, facile elimination is an improvement on the mesylation/elimination approach of Fallis. Interestingly, whilst alcohols of the type **248** and **251** bearing different, substituted alkenyl substituents have been prepared [204], the corresponding elimination reactions (now with the possibility of forming mixtures of (*E*) and (*Z*) isomers), do not appear to have been reported. This presents an avenue worthy of further investigation.

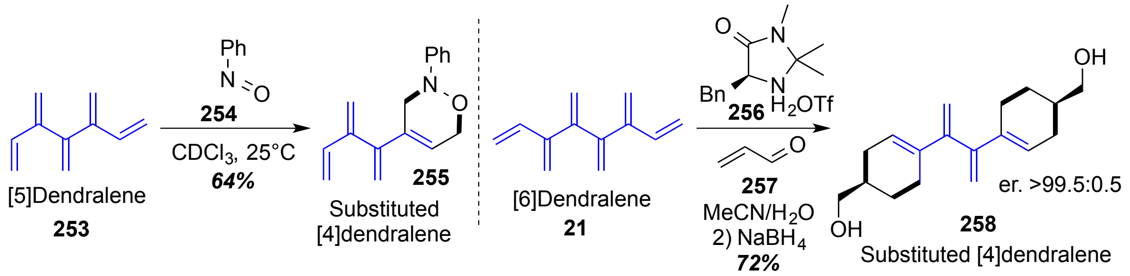


Scheme 1.42: *Syntheses of dendralenes via Peterson-type olefination by Parrain and co-workers* [203].

1.4 Dendralenes from Dendralenes

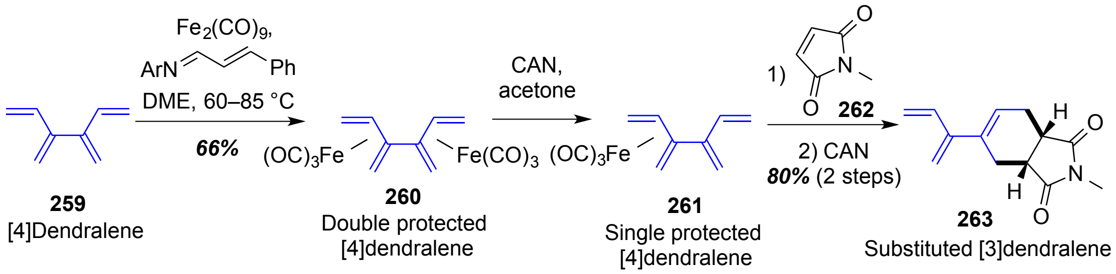
Aside from the synthesis of dendralenes from non-dendralenic materials, there also exist a variety of transformations that can be applied to a pre-existing dendralene framework to add further functionality. Most of these examples form part of exploratory studies to test the reactivity of dendralenes; nevertheless, they show potential for the synthesis of a variety of functionalized dendralenes. Broadly, these can be divided into transformations that reduce the length of the [*n*]dendralene framework (e.g., *n*→ *n*–1), ones that functionalize and preserve an existing [*n*]dendralene framework (i.e., $n \rightarrow n$), or ones that add extra branched alkenes to form a higher [*n*]dendralene (e.g., $n \rightarrow n+1$).

In the first category, the Sherburn group, first to synthesize the parent family of dendralenes, have documented a number of transformations that result in the conversion of a higher dendralene into a lower one. [5]Dendralene (**253**) and higher [*n*]dendralenes undergo DA reactions to furnish [*n*–1]dendralenes. Aside from reactions with *N*-methylmaleimide (NMM) (**262**) [20–21, 23, 89, 148] and SO_2 [10], these include hetero-DA reactions to form heterocycle-containing dendralenes **255** [205], and enantioselective DA reactions to form chiral, enantioenriched dendralenes **258** [206] (***Scheme 1.43***).



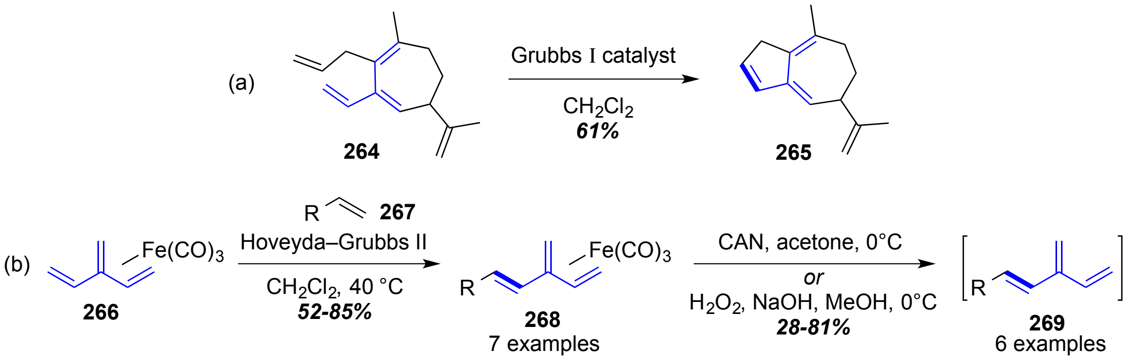
Scheme 1.43: *Hetero-DA and enantioselective DA reactions of dendralenes from the Sherburn group* [205–206].

Singly complexed tricarbonyliron-[4]dendralene **261** (prepared from [4]dendralene (**259**)) [89, 207] can be reacted with NMM (**262**) to undergo a single DA reaction at a terminal diene site to produce, after decomplexation, a reactive [3]dendralene **263** (***Scheme 1.44***), which cannot be isolated by reacting uncomplexed [4]dendralene (**259**) and dienophiles (see chapter 12). Complexation and reaction, therefore, provides a viable avenue towards dendralenes not isolable from other reaction conditions.



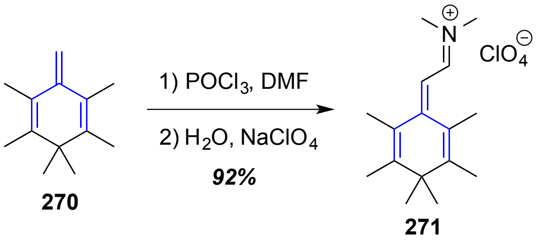
Scheme 1.44: *Tricarbonyl iron-complexed dendralenes enabling the synthesis of a formal terminal single DA-adduct of [4]dendralene* [89].

Dendralenes may also be functionalized at one of the alkene positions without destroying the alkene. An interesting case is the ring closing metathesis (RCM) reaction of cyclic dendralene **264**, using Grubbs I catalyst, to form a bicyclic dendralene **265**, maintaining the [3]dendralene framework (***Scheme 1.45 (a)***) [118]. In contrast to the ‘naked’ parent dendralene, tricarbonyliron-complexed [3]dendralene (**266**) undergoes smooth cross- and homo-metathesis reactions to furnish a variety of highly reactive, 1*E*-substituted [3]dendralenes **269** (***Scheme 1.45 (b)***) [87, 89].



Scheme 1.45: *Examples of (a) RCM* [118] *and (b) cross-metathesis using dendralene precursors* [87, 89].

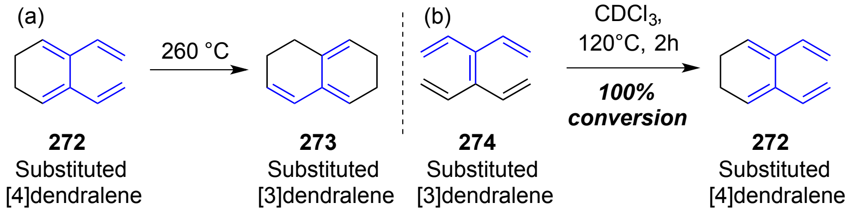
Instances where a dendralenic alkene participates as a nucleophile in an addition or substitution, and the alkene is regenerated by elimination, appear surprisingly rare. One such example is the preparation of the Vilsmeier salt **271** of cyclic [3]dendralene **270** (***Scheme 1.46***) [208]. Formylation of very electron-rich dendralenes has also been reported, such as part of the iterative formylation/olefination sequence to build higher dendralenes reported by Yoshida *et. al.* (***Scheme 1.20***) [82].



Scheme 1.46: *Synthesis of the Vilsmeier salt of a cyclic [3]dendralene* [208].

Halo-dendralenes are valuable substrates for dendralene to dendralene transformations that preserve or extend the dendralene framework. They are intermediates in the synthesis of [7]- and [8]dendralene (***Scheme 1.26***) [23], as are their nucleophilic relatives, pinacolatoboryldendralenes, in the synthesis of substituted [4]-, [5]-, and [6]dendralenes [25, 27]. (Pseudo)halo-dendralenes have also been used in Stille [209] and Sonagashira cross-couplings [176, 210]. Dendralene dimers can be obtained *via* homocoupling of halo-dendralenes [211]. Dendralene frameworks can also be extended by uncatalyzed metathesis reactions on alkyne-containing dendralenes, and olefination reactions on carbonyl-containing ones [1, 211–214], each of which have been discussed.

Rearrangements and isomerizations can lead to either an extension or reduction of an existing dendralene framework. For example, the Cope rearrangement shown in ***Scheme 1.9*** converted a [3]dendralene **63** to a [4]dendralene **64**, whilst changing the path of the dendralene backbone. In contrast, rearrangement and electrocyclic ring closure of [4]dendralene **272** leads to bicyclic [3]dendralene **273** (***Scheme 1.47 (a)***) [215]. **272** is itself the product of thermally or photochemically promoted electrocyclic ring closure of tetravinylethylene (**274**) (a [3]dendralene), (***Scheme 1.47 (b)***) [20]. The intramolecular Alder-ene reaction of a [3]dendralene reported by Oro and co-workers in ***Scheme 1.36*** provides an example of an isomerization that neither reduces or extends the dendralene framework, but does alter the connectivity [160–161].

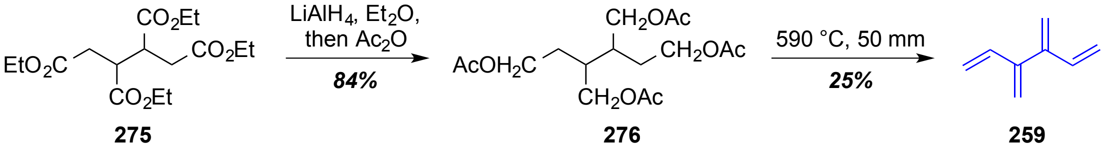


Scheme 1.47: *Isomerization reactions that either reduce* [215] *or extend the dendralene framework* [20].

Elimination reactions to reveal masked dendralenes featured prominently in early attempts to synthesize cross-conjugated compounds [1]. Cheletropic extrusion of sulfur dioxide was used to convert lower dendralenes to [5]-, [6]- and [8]dendralene [10], and to make substituted chiral [4]dendralenes [12].

1.5 Functional Group Interconversion Reactions

Our review has focused on syntheses of dendralenes that construct the carbon framework *via* carbon–carbon bond formation. Whilst almost all strategies ultimately rely on carbon–carbon bond formation, some are better considered as distinct isomerization or functional group interconversion strategies that unmask a hidden dendralene. For example, one of the earliest syntheses of [3]dendralene (**5**) [216], and the very first synthesis of [4]dendralene (**259**) (***Scheme 1.48***) [217], proceed from commercially available starting materials without any carbon–carbon bond formations. Therefore, whilst we have made note in each section on strategies that, whilst ultimately relying on an elimination or isomerization, have included an earlier key carbon–carbon bond-forming reaction, there are a number of somewhat esoteric strategies that we have not mentioned in this review. These approaches, which typically feature long sequences of steps to form synthetic intermediates primed for a key thermal elimination and/or isomerization, and are therefore limited in their preparative utility, are more prevalent in the early literature, and are very well-summarized by Hopf's earliest review [1], with more recent variations being covered by the 2012 review of Hopf and Sherburn [2].



Scheme 1.48: *The first synthesis of [4]dendralene, by Bailey and Nielsen, has no C–C bond forming events* [217].

1.6 Concluding Remarks

By categorizing syntheses of dendralenes based on the carbon–carbon bonds formed in their approach, it is clear that over the past few decades there has been a massive shift away from lengthy and scope-limited isomerization and elimination-based strategies to unmask dendralenes, towards direct formation of functionalized dendralene frameworks *via* carbon–carbon bond-forming reactions. A plethora of techniques to directly and rapidly access dendralenes with a wide variety of substitution levels and functionality now exist. Some of these reactions, the most notable example being C–H activation, have only very recently enjoyed intense research focus. Given the number of short and practical preparative methods that now exist for the preparation of dendralenic structures, selective 'dendralene to dendralene' functionalization reactions are also likely to see significant growth in the near future. It is therefore likely that the current trend of rapid expansion in synthetic means to dendralenes will continue strongly, driven by research in these areas, and in other reactions that are yet to be realized.

1.7 References

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Chapter Two

Discovery and Computational Rationalization of Diminishing Alternation in [n]Dendralenes

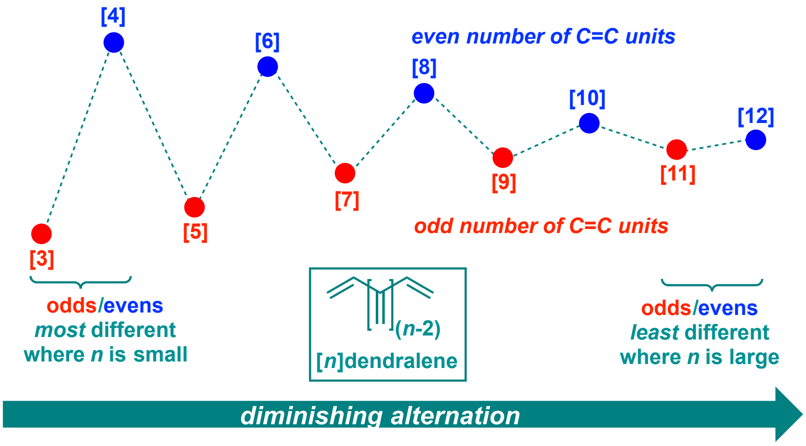
Discovery and Computational Rationalization of Diminishing Alternation in [n]Dendralenes

Context

Dendralenes are simple acyclic starting materials that can rapidly generate complex polycyclic carbon frameworks. Until recently, interest in these acyclic cross-conjugated hydrocarbons has been low, due to an incorrect assumption of their instability. This myth was broken with the first synthesis of [5]dendralene, [6]dendralene and [8]dendralene in 2000. Interest in these fundamental hydrocarbons has since grown. Nevertheless, none of the higher members of the dendralene family (i.e. higher than [8]dendralene) has been reported to date. The work presented in this chapter describes the first synthesis of the higher dendralenes, namely [9]dendralene to [12]dendralene. In addition, investigations into the chemical reactivity and spectroscopic properties of the complete family of hydrocarbons from [3]dendralene through [12]dendralene have been investigated. A comprehensive series of computational studies has also been performed by a collaborator.

The manuscript was published in the *Journal of American Chemical Society* on 31 December, 2015. Reprinted (adapted) with permission (Saglam, M. F.; Fallon, T.; Paddon-Row, M. N.; Sherburn, M. S. *J. Am. Chem. Soc.* **2016**, *138*, 1022.). Copyright (2016) American Chemical Society. The other authors are Dr Thomas Fallon, Professor Michael N. Paddon-Row, and my supervisor Professor Michael S. Sherburn. This paper has been highlighted in Chemical & Engineering News (by Ritter, S. K. "*Chemists Welcome More Dendralenes To The Family" C&EN* **2016**, *94,* 28.) and in a "Spotlight" in the *Journal of American Chemical Society* (by Herman, C. "*New Study Sheds Light On A Family Of Branched Molecules" J. Am. Chem. Soc.* **2016**, *138*, 703.). The project was conceived, designed, evolved, and drafted in collaboration with Professor Sherburn. The computational studies of the paper were carried out and drafted by Professor Paddon-Row. Dr Thomas Fallon investigated the synthesis of dichloro[4]dendralene and 2,3-dibromo-1,3-butadiene as well as developing modified reaction conditions to prepare 1,1-di(pinacolylboronyl)ethylene and 2,3-di(pinacolylboronyl)-1,3-butadiene. Samples of [3]dendralene, [4]dendralene, and [6]dendralene were provided by Mr Joshua Boyle, Mr Nicholas Green, and Mr Erik Lindeboom, respectively, and are acknowledged in the manuscript. All other reactions that appear in the paper were conducted by myself.

TOC Graphic



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Discovery and Computational Rationalization of Diminishing Alternation in [*n*]Dendralenes

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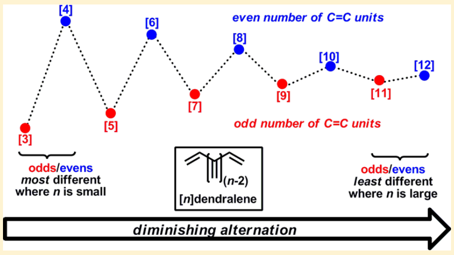
Ⓢ *Supporting Information*

ABSTRACT: The [*n*]dendralenes are a family of acyclic hydrocarbons which, by virtue of their ability to rapidly generate structural complexity, have attracted significant recent synthetic attention. [3]Dendralene through [8]dendralene have been previously prepared but no higher member of the family has been reported to date. Here, we describe the first chemical syntheses of the "higher" dendralenes, [9]dendralene through [12]dendralene. We also report a detailed investigation into the spectroscopic properties and chemical reactivity of the complete family of fundamental hydrocarbons, [3]dendralene to [12]dendralene. These studies reveal the first case of diminishing alternation in behavior in a series of related structures. We also report a comprehensive series of computational studies, which trace this dampening oscillatory effect in both spectroscopic measurements and chemical reactivity to conformational preferences.



INTRODUCTION

The dendralenes are one of the four fundamental classes of oligo-olefinic hydrocarbon structures comprising exclusively sp^2-hybridized carbons (Figure 1).[1,2] The dendralenes are acyclic, branched chain systems; the remaining three families are the "polyenes" (acyclic and unbranched), the radialenes (cyclic and branched) and the annulenes (cyclic and unbranched).[3] Until the turn of the century, the dendralenes had received the least attention, most likely due to the erroneous assumption that they were too unstable to be handled in the laboratory using standard equipment and methods. Indeed, only the triene[4−8] and tetraene[1a,7−11] were reported prior to 2000.

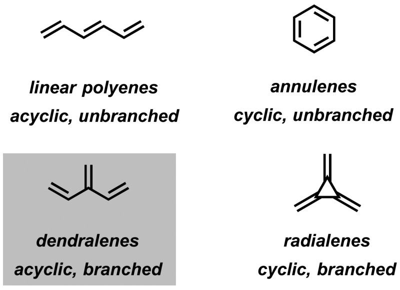


Figure 1. Four fundamental classes of conjugated oligo-alkenes and the family under scrutiny (shaded).

The radialenes[12] are also relatively poorly investigated, with only the triene,[13] tetraene,[14] pentaene,[15] and hexaene[16] reported in the literature. In contrast, the unbranched systems have received significant attention, which is unsurprising when the number of natural products containing linear polyenic[17] and annulenic systems[18] is considered. Regarding our understanding of how structure relates to reactivity and stability, the alternating behavior of the planarized annulenes, predicted by Hückel's rule,[19] is an essential chemistry concept.[3,20] Thus, the "1,2-ethenologous" series of annulenes, namely 1,3-cyclobutadiene (antiaromatic) → benzene (aromatic) → 1,3,5,7-cyclooctatetraene (antiaromatic) and so forth represents an alternating progression of less and more stable compounds. The physical and chemical properties of the annulenes are dominated by this parity-dependent behavior. Alternations in melting points in families of compounds of even- and odd-length chains has also been reported, a property traced to the packing of molecules in crystal lattices.[21] In these systems, alternation in behavior does not extend to any other physical or chemical property. In 2009, we reported parity dependent behavior in the [*n*]dendralenes (*n* = 3−8) (**1**−**6**), whereupon we noted that the odd members of the family (**1**, **3** and **5**) are less stable than the even parity members (**2**, **4** and **6**).[8] Furthermore, in the UV−visible spectra, we observed a linear correlation for the even parity dendralenes in a plot of the extinction coefficient versus the number of C=C units, whereas the odd members showed no such correlation. In addition, the odd parity dendralenes were shown to react as dienes, undergoing relatively clean and site-selective monocycloadditions on exposure to 1 mol equiv of the electron poor

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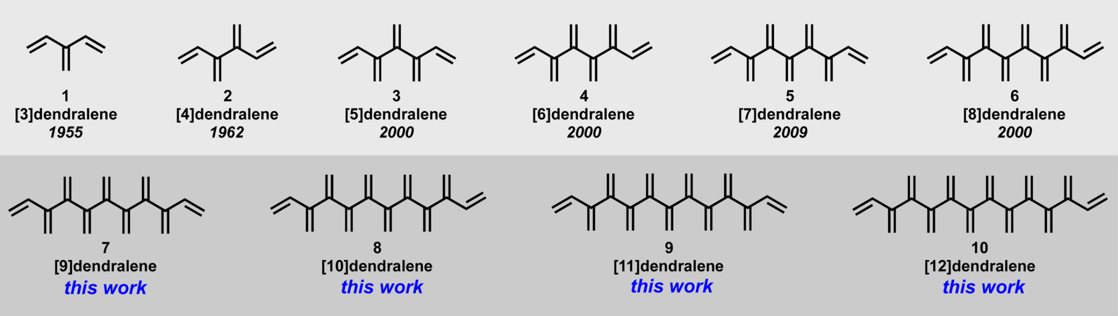


Figure 2. First ten members of the [*n*]dendralene family of cross conjugated hydrocarbons and the year first reported.

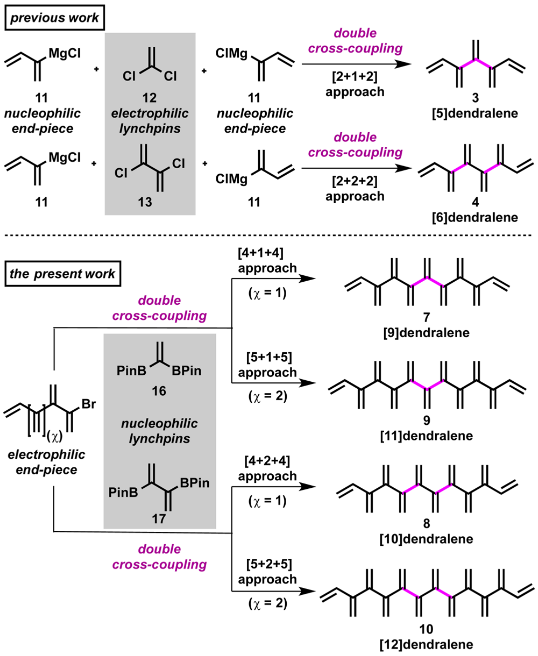
dienophile *N*-methylmaleimide (NMM), whereas, in contrast, the even parity dendralenes were shown to undergo unselective Diels−Alder reactions. Herein we report the first syntheses of the "higher" dendralenes, [9]−[12]dendralene (Figure 2). We also disclose a thorough investigation into the spectroscopic behavior and chemical reactivity of the first ten dendralenes ([3]−[12]dendralene inclusive), which unequivocally establish a diminishing, parity-dependent alternation in this fundamental hydrocarbon family.

■ RESULTS AND DISCUSSION

Synthesis. The early syntheses of [3]dendralene and [4]dendralene (Figure 2) involved classical pyrolytic elimination reactions of tri- and tetra-acyloxy (di-, tri-, and tetra-) derivatives of branched saturated hydrocarbons.[5,9] No member of the family higher than the tetra-ene was reported prior to our contributions in this area. Due to the prevailing attitude at the time, specifically, that these compounds were likely to be unstable, our first synthesis of the family of [*n*]dendralenes (*n* = 3, 4, 5, 6, and 8) involved first the preparation of 3-sulfolene derivatives of the hydrocarbons.[7] The dendralenes were conveniently generated, a few mg at a time, by cheletropic elimination of SO_2 from these stable precursors. Our most recent contribution in this area involved the preparation of the complete family of the six "lowest" [*n*]dendralenes (*n* = 3, 4, 5, 6, 7, and 8) by direct cross-couplings.[8] The first three members of the family were prepared by one-step synthesis from commercially available precursors, whereas the synthesis of [6]-, [7]-, and [8]dendralene (**4**−**6**) mandates multistep syntheses.[8] Until now, none of the "higher" dendralenes ([9]−[12]dendralene) (**7**−**10**) have been reported, most likely due to the significant synthetic challenge that these structures represent, along with the lack of availability of suitable coupling partners. A synthetic plan for the higher [*n*]dendralenes, which draws upon the most synthetically powerful feature of our previous [5]- and [6]dendralene (**3**−**4**) synthesis, is depicted in Scheme 1. We propose that higher [*n*]dendralenes are best prepared by employing a 2-fold cross-coupling process, between a bifunctional central unit (the "lynchpin") and two identical monofunctional end-pieces. To prepare odd parity [*n*]dendralenes, the lynchpin should contain an odd number of C=C units; an even number of C=C bonds in the lynchpin will furnish even [*n*]dendralenes.[22]

Our earlier approaches to [5]- and [6]dendralene (**3**−**4**) took advantage of this strategy, employing 2-fold cross-couplings between the chloroprene Grignard reagent (**11**), as a monofunctional nucleophilic end-piece, and the readily accessible lynchpin double electrophiles, 1,1-dichloroethylene (**12**) and 2,3-dichloro-1,3-butadiene (**13**), respectively (Scheme 1).[8] [6]Dendralene (**4**) represents the limit of this approach for 1,3-butadiene coupling partners: either a dendralenic lynchpin or dendralenic end-piece are needed to prepare [7]dendralene (**5**) and higher.

Scheme 1. Proposal for a Lynchpin-Based, Double Cross-Coupling Approach to the [*n*]Dendralenes

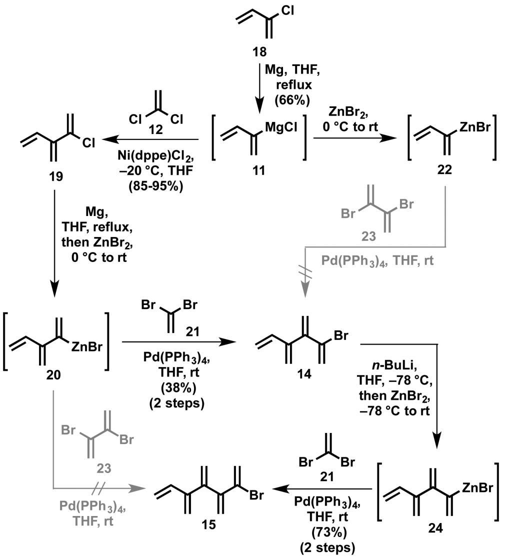


Ultimately, we elected to pursue an approach involving the union of [4]- and [5]dendralenic end-pieces with the known ethylenic and 1,3-butadiene lynchpins. Both double electrophilic lynchpins[23,24] and double nucleophilic lynchpins[25,26] were already known, and their success in double cross-coupling reactions were proven.[7,8,26−29] The synthetic problem was thus reduced to (a) the preparation of the dendralenic end-pieces, namely 2-halo[4]dendralene and 2-halo[5]dendralene, and (b) the successful deployment of these partners in double cross-coupling reactions.

The highest 2-halo[*n*]dendralene reported thus far is 2-chloro[4]dendralene.[8] Frustratingly, this compound is unreactive as an electrophilic coupling partner in Kumada–Tamao–Corriu and Negishi cross-coupling reactions.[8] In the hope of higher reactivity, we therefore targeted 2-bromo[4]-dendralene (**14**) and its higher "ethenologue", 2-bromo[5]-dendralene (**15**).

In order to prepare 2-bromo[4]dendralene (**14**) and 2-bromo[5]dendralene (**15**) we envisioned a single sp^2–sp^2 cross-coupling involving the 1,1-dibromoethylene (**21**)[23] and 2,3-dibromo-1,3-butadiene (**23**) lynchpins. During the course of these investigations it became evident that, whereas 1,1-dibromoethylene (**21**) participated in single cross-coupling reactions, 2,3-dibromo-1,3-butadiene (**23**) did not (Scheme 2).

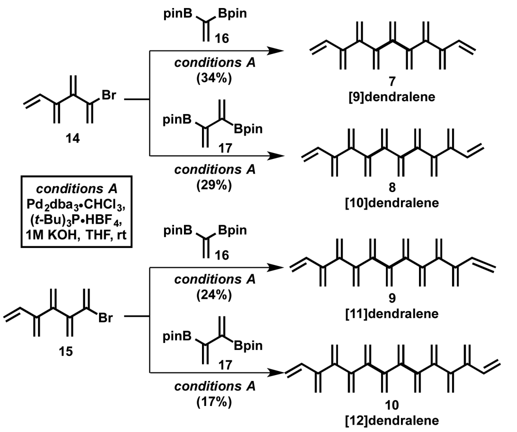
Scheme 2. Iterative Syntheses of 2-Bromo[4]dendralene (14) and 2-Bromo[5]dendralene (15)



(We presume that the product of oxidative insertion of $L_nPd(0)$ into the C—Br bond undergoes facile elimination of $L_nPd(II)Br_2$. Our suspicions are fuelled by the lack of reports of successful cross-coupling reactions involving 2,3-dibromo-1,3-butadiene (**23**) in the literature.) Thus, an iterative Negishi cross-coupling sequence with 1,1-dibromoethylene (**21**) was employed to convert the organozinc species derived from 2-chloro[3]dendralene (**19**)[4] into 2-bromo[4]dendralene (**14**) (38% yield), and thence into 2-bromo[5]dendralene (**15**) (73% yield) (Scheme 2). The discrepancy in yield between these two steps is related to the method of preparation of the organozinc species: the latter case employed an efficient low temperature Li/Br exchange followed by transmetalation with $ZnBr_2$, whereas the former mandated the generation of the Grignard reagent in refluxing THF, which led to significant decomposition.

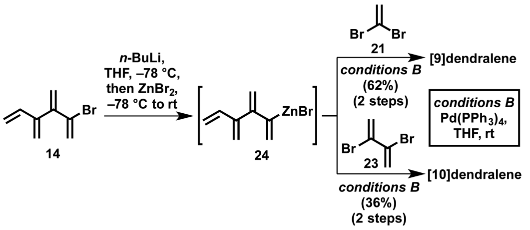
With the requisite end-pieces in hand, the synthesis of the higher dendralenes could now be attempted. Many different sets of conditions[30] were screened for the final 2-fold cross-coupling sequence, in which attempts were made to unite nucleophilic and electrophilic end-pieces with electrophilic and nucleophilic lynchpins, respectively (Scheme 3). Double cross-coupling reactions between electrophilic lynchpins and nucleophilic end-groups were found to be particularly challenging transformations. Problematic side reactions include lynchpin eliminations[31] and difficulties encountered in the generation of the nucleophilic component. Gratifyingly, the two nucleophilic lynchpins introduced by Hiyama and Shimizu[25,26] successfully participated in Suzuki–Miyaura reactions, performed under Fu conditions, to deliver the desired higher dendralene in all four cases (Scheme 3).

Scheme 3. Syntheses of [9]–[12]Dendralenes



[9]Dendralene (**7**) was synthesized in higher yield through a 2-fold Negishi cross-coupling reaction between the organozinc species **24** derived from 2-bromo[4]dendralene (**14**) and 1,1-dibromoethylene (**21**) (Scheme 4). [10]Dendralene (**8**) was also prepared through Negishi cross-coupling, in comparable yield to the Suzuki–Miyaura method. Interestingly, this protocol was not successful for the preparation of [11]- and [12]dendralene (**9**–**10**), with difficulties being encountered during the generation of the organometallic derivative of 2-bromo[5]dendralene.

Scheme 4. Second Generation Syntheses of [9]- and [10]Dendralenes



Spectroscopic Studies. As mentioned earlier, one of the most striking features of our previous investigations into the dendralene family was the first observation of their parity-dependent alternation in behavior, which was manifested in (a) their UV–visible spectra; (b) their reactivity toward the dienophile *N*-methylmaleimide (NMM), and (c) their stability. With the present study giving access to an extended series of compounds, namely the first ten [*n*]dendralenes (**1**–**10**), we were keen to find out if parity-dependent behavior would be seen throughout the family.

The increasing conjugation witnessed in the parent all-*E*-linear polyenes (Figure 1) with increased chain length is evidenced by longer wavelengths (λ_{max} increases by ca. 25 nm for each additional —HC=CH— unit) and increasing molar extinction coefficients for their UV–visible absorption maxima.[32] In contrast (Figure 3 (a)), the collection of nine compounds [4]dendralene to [12]dendralene (**2**–**10**) show a single UV–visible absorption maximum at λ_{max} = 215–216 nm (hexane), very close to that of 1,3-butadiene (217 nm, hexane).[33] The wavelength of the absorption exhibited by the dendralenes clearly shows that conjugation in these structures is restricted to 1,3-butadiene.

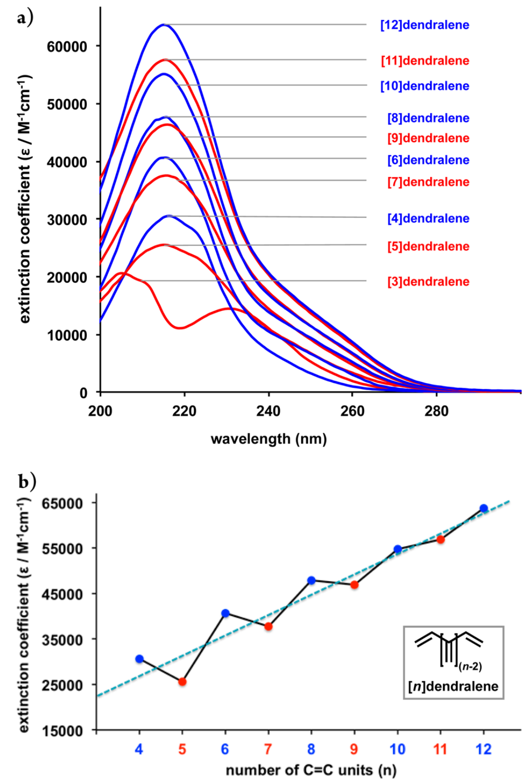


Figure 3. (a) UV–visible spectra of the [*n*]dendralene family, and (b) UV extinction coefficients (*ε*) of absorption maxima plotted as a function of the number of C=C bonds. λ_{max} = 215–216 nm in all cases except [3]dendralene, which exhibits two maxima at 205 and 231 nm (hexane, 25 °C).

When the molar extinction coefficients are plotted against the number of C=C bonds present in the structure, a clear pattern of diminishing alternation emerges (Figure 3 (b)). Intriguingly, the inclusion of more C=C units does not give rise to gradually increasing extinction coefficient and instead, an alternating up–down pattern is seen for even and odd parity family members and notably, one whose magnitude decreases with increasing chain length. Within each of the two subfamilies of even and odd parity dendralenes, the incorporation of two C=C units (and hence progression to the next subfamily member) always results in an increase in extinction coefficient, and one of generally diminishing magnitude with progression to higher family members.[34] Thus, the difference between extinction coefficients of the λ_{max} = 215–216 nm absorption for [5]- and [6]dendralene (**3**–**4**) is relatively large ($\Delta\varepsilon$ = 15100), whereas the difference is relatively small ($\Delta\varepsilon$ = 6000) between [11]- and [12]dendralene (**9**–**10**). By extrapolating these experimental observations, at a rough approximation, the limit of measurable (by UV–visible spectroscopy) alternation should occur at [13]- or [14]dendralene and we predict a gradually increasing extinction coefficient for consecutive members of the dendralene family beyond this point.

To summarize the new findings from the UV–visible spectra of the dendralene family in the present study: first, all [*n*]dendralenes higher than the triene show a single absorption maximum at around the same wavelength as 1,3-butadiene. More accurate molar extinction coefficient values for [5]-dendralene (**3**) and [7]dendralene (**5**) have been obtained,[34] along with values for the previously unprepared [9]–[12]-dendralenes (**7**–**10**). These data confirm that the even parity dendralenes exhibit gradually increasing molar extinction coefficients and that this property extends to the higher members of the family. Importantly—and new to the present study—the odd dendralenes have also been shown to exhibit gradually increasing molar extinction coefficients with increasing chain lengths. When viewed together, the magnitudes of the UV–visible absorption maxima for the dendralene family exhibit an even/odd zigzag alternation, with a diminishing difference upon progression to higher members of the series (Figure 3b).

We initially assumed that the difference in behavior between even and odd parity dendralenes would be manifested only in UV–visible spectra. This assumption proved to be false: the diminishing alternation pattern is clearly visible in ^{1}H and ^{13}C NMR spectra of the dendralene family. ^{1}H NMR spectra of the first 11 members of the [*n*]dendralene family in $CDCl_3$ at 800 MHz are reproduced in Figure 4.

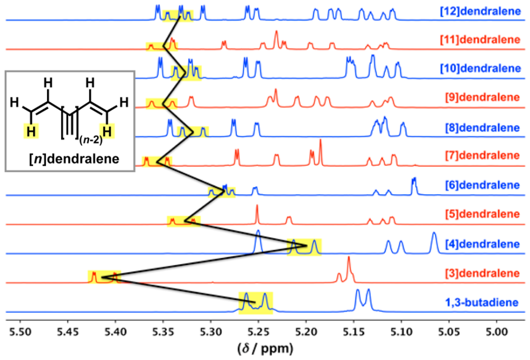


Figure 4. ^{1}H NMR spectra of the [*n*]dendralene family, exhibiting diminishing alternation in chemical shift of the *Z*-C1*H* resonance (800 MHz, $CDCl_3$, 25 °C).

The diminishing alternation is observable in all three proton resonances associated with the terminal monosubstituted olefin on the branched chain, but it is most pronounced in the resonance of the proton residing on the terminal carbon cis- to the longest carbon chain (*Z*-C1*H*; *δ* 5.20–5.41 ppm: this resonance is highlighted in yellow in Figure 4). Thus, the *Z*-C1*H* chemical shift difference is largest ($\Delta\delta$ = 0.21 ppm) between [3]dendralene (**1**) (*δ* 5.41 ppm) and [4]dendralene

(**2**) (δ 5.20 ppm), and smallest ($\Delta\delta$ = 0.02 ppm) between [11]dendralene (**9**) (δ 5.35 ppm) and [12]dendralene (**10**) (δ 5.33 ppm), with the variance diminishing with progression up the series.

^{13}C NMR spectra of the first 11 members of the [*n*]dendralene family in CDCl$_3$ at 200 MHz are reproduced in Figure 5. The diminishing alternation is observable in both ^{13}C resonances associated with the terminal monosubstituted olefin of the branched chain, but it is most pronounced in the C2 methine resonance (δ 138.0−135.9 ppm: this resonance is highlighted in yellow in Figure 5). Again, the chemical shift difference is largest ($\Delta\delta$ = 1.7 ppm) between [3]dendralene (1) (δ 135.9 ppm) and [4]dendralene (2) (δ 137.6 ppm) and smallest ($\Delta\delta$ = 0.1 ppm) between [11]dendralene (9) (δ 137.7 ppm) and [12]dendralene (10) (δ 137.8 ppm), with the variance diminishing with progression up the series.

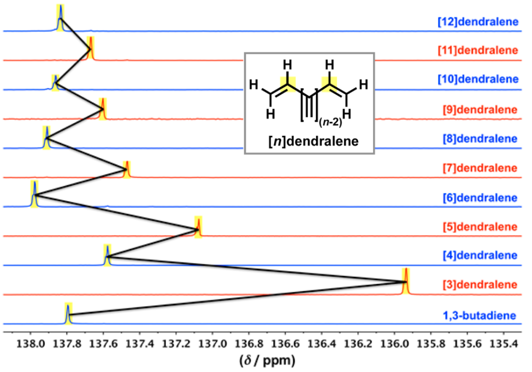


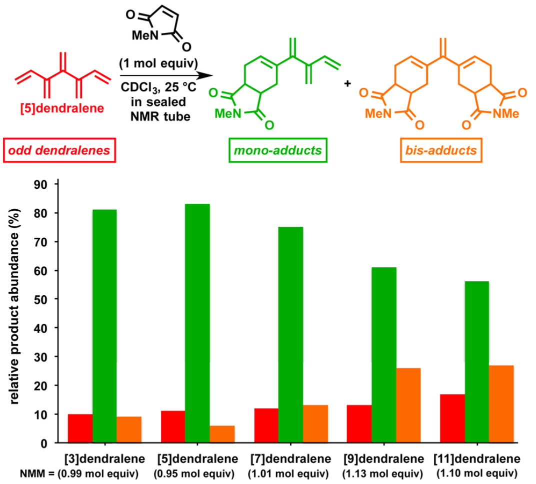
Figure 5. ^{13}C NMR spectra of the [*n*]dendralene family, exhibiting diminishing alternation in chemical shift of the C2 methine resonance (200 MHz, CDCl$_3$, 25 °C).

Diels−Alder Reactions. In our earlier investigation[8] on [3]−[8]dendralenes (**1**−**6**), it was demonstrated that parity-dependent behavior was also manifested in the chemical reactivity of the hydrocarbons. Whereas all dendralenes were shown to react as dienes in Diels−Alder cycloadditions with the electron-poor dienophile *N*-methylmaleimide (NMM) regioselectively at the terminal 1,3-butadiene residue, odd and even parity dendralenes reacted differently. Specifically, when exposed to 1 mol equiv of the dienophile, odd parity dendralenes underwent predominantly single cycloaddition, whereas even dendralenes gave mixtures of single and double adducts along with unreacted dendralene. It was also observed experimentally that odd parity dendralenes were significantly more reactive than even parity ones. Single cycloaddition occurs with odd parity dendralenes because the product of monoaddition to the terminal diene site with a dienophile generates an even dendralene, which is less reactive than the precursor but the converse is true for the even parity hydrocarbons. Would this divergent reactivity for even and odd systems hold for all dendralenes? With the higher dendralenes in hand, we set about answering this question and, at the same time, we re-examined the outcomes of reactions of the lower dendralenes to a higher level of precision.

The Diels−Alder reactions of [3]- to [12]dendralenes (**1**−**10**) toward the dienophile NMM (1.00 ± 0.10 mol equiv) were examined in ca. 0.3 M CDCl$_3$ solutions at 25 °C, with the progress of reactions being followed, and the product compositions being analyzed by 800 MHz ^{1}H NMR spectroscopy. Isolated yields were consistent with crude product compositions. All reactions were run until all NMM was consumed and in every case, mixtures of unreacted starting materials, monocycloadducts and bis-cycloadducts were generated. With the exception of [4]dendralene (**2**), the majority of the monoadduct fraction was the product of addition to the terminal 1,3-butadiene unit of the dendralene, and the major bis-cycloadducts were those resulting from additions to the two ends of the dendralene chain.[35]

The outcomes of reactions of the odd parity dendralenes are depicted in Chart 1. All reactions produce the monoadduct as the major product. As the odd parity dendralene subfamily is ascended, the selectivity for monoaddition generally deteriorates, and the amounts of unreacted starting dendralene and bis-adducts increases.

Chart 1. Diels−Alder Reactions of *Odd* Dendralenes (Diene) with 1 mol Equiv of NMM (Dienophile)



The outcomes of reactions of the even parity dendralenes with NMM are depicted in Chart 2. All reactions are less selective than those of the odd parity dendralenes. Nonetheless, as the even parity dendralene subfamily is ascended, there is a gradual improvement in the selectivity for the monoaddition product, with amounts of unreacted starting dendralene and bis-adducts decreasing.

When the selectivity for the monoadduct is graphed for the complete dendralene family, the diminishing alternation pattern is revealed once again (Chart 3). Thus, the gradually diminishing selectivity for the monoadduct in the odd parity subseries interweaves with the steadily improving selectivity in the even dendralenes, with a significant difference between the lower family members but a negligible difference in selectivity for the highest members.

Computational studies were conducted to explain these experimental findings. Our investigations commenced with a detailed analysis of the conformational preferences of the dendralenes.

Computational Studies. *Conformational Analysis.* The conformations and energies of the series of [*n*]dendralenes (*n* =

Chart 2. Diels–Alder Reactions of *Even* Dendralenes (Diene) with 1 mol Equiv of NMM (Dienophile)

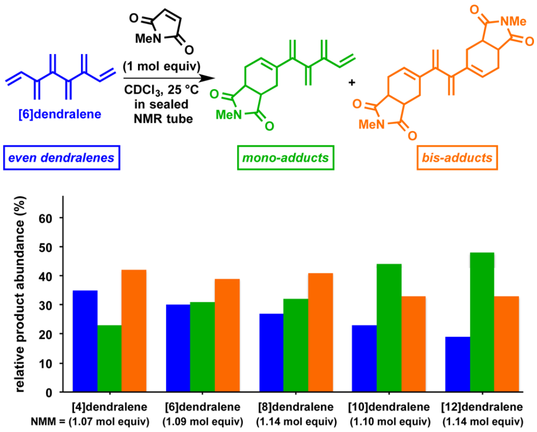
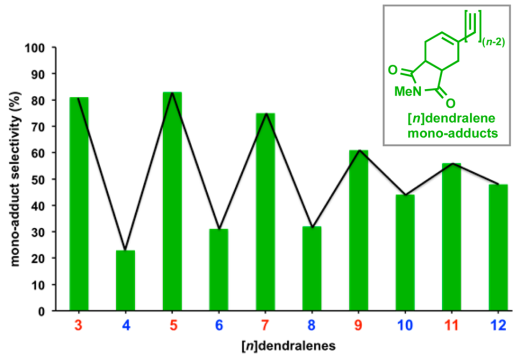


Chart 3. Selectivity for Mono-Cycloaddition in Diels–Alder Reactions of [*n*]Dendralenes (Diene) with 1 mol Equiv of NMM (Dienophile)



3–8) were obtained using the accurate composite ab initio MO G4(MP2) procedure.[36] We first confirmed the suitability of G4(MP2) to handle the task in hand by applying it to the conformational analysis of 1,3-butadiene. We calculated the rotational barrier to the conversion of the more stable C_{2h} anti conformer to the C_2 gauche conformer to be $\Delta H^{\ddagger}(0\ \mathrm{K}) = 23.9$ kJ/mol and the gauche–anti energy difference to be $\Delta H^{\ddagger}(0\ \mathrm{K}) = 12.4$ kJ/mol, favoring the anti conformer and these energies are in satisfactory agreement with the experimental[37] values of $\Delta H^{\ddagger}(0\ \mathrm{K}) = 24.8$ kJ/mol and $\Delta H^{\ddagger}(0\ \mathrm{K}) = 11.9$ kJ/mol, respectively.

The structures of [3]dendralene and [4]dendralene have been determined using gas phase electron diffraction[11,38] and their conformations have been studied computationally using a variety of methods.[11,38,39] Our G4(MP2) calculations on these two dendralenes are in general agreement with these earlier studies. [3]Dendralene has three stable conformations and they are shown in Figure 6, together with the transition structures for their interconversion and relative energies. The most stable conformation is anti-gauche, in which the two dihedral angles between the double bonds in the anti and gauche units are 174° and 41°, respectively. The gauche dihedral angle is 11° larger than that calculated for 1,3-butadiene, which probably reflects the presence of steric repulsion between the terminal vinyl groups in the anti–gauche conformer. The anti–anti conformer is only 3.7 kJ/mol above the anti–gauche structure and has C_2 symmetry. The *anti*-butadiene units are rather bent, the dihedral angle between the vinyl groups in each unit being 157°. This bending is probably due to steric congestion between the *Z*-C1*H* atoms of the terminal methylene groups, their separation being 2.22 Å. The C_2 symmetric gauche–gauche conformer is the least stable, lying 9.8 kJ/mol above the anti–gauche conformer. The dihedral angle between adjacent vinyl groups is 33°. The anti–gauche/anti–anti/gauche–gauche distribution at 25 °C is calculated to be 82:16:2, respectively. The rotational barriers for the conversion of the anti–gauche conformer into the anti–anti and gauche–gauche conformers are 7.7 and 20.0 kJ/mol, respectively. These barriers, particularly the former, are sufficiently small enough to permit rapid conformer interconversion on the NMR time scale, as we have confirmed experimentally for the whole series of dendralenes studied herein (see above).

The most stable conformation of [4]dendralene was shown by gas phase electron diffraction to comprise two *anti*-butadiene groups twisted 72° with respect to each other.[11] MP2/6-311G(d) calculations located five conformations of this molecule, the most stable being identical to that found experimentally.[11] The G4(MP2) calculations gave similar results and the two lowest energy conformations, of the five that were located, are shown in Figure 7. The most stable conformation has C_2 symmetry with the two *anti*-1,3-butadiene units making a 76° dihedral angle with respect to the two internal double bonds. The dihedral angle between the double bonds within each *anti*-butadiene group is 174°. The next most stable conformer is 10.3 kJ/mol higher in energy (Figure 7) than the global minimum energy conformer and consists of an *anti*-butadiene attached to a *gauche*-butadiene moiety in which the twist angle is 30°. The dihedral angle between the two internal double bonds in this conformer is 54°. A gaseous sample of [4]dendralene at 25 °C is calculated to contain ca. 97% of the *bis*-*anti*-butadiene conformer (cf. ca. 90% from MP2 calculations[11]).

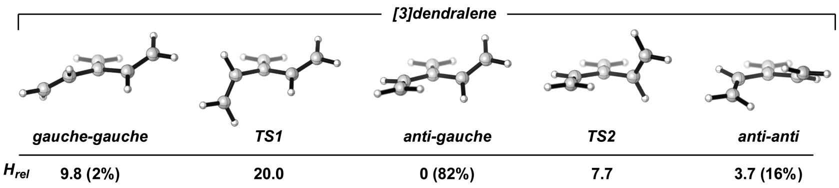


Figure 6. G4(MP2) optimized geometries of conformations and transition structures of [3]dendralene. H_{rel} (kJ/mol) refers to 0 K. Populations were derived from free energy data at 25 °C. Values in parentheses are the percentage population values.

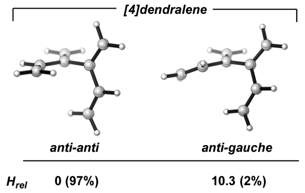


Figure 7. G4(MP2) optimized geometries of the two lowest energy conformations of [4]dendralene. H_{rel} (kJ/mol) refers to 0 K and percentage populations are for 25 °C (the residual 1% is spread over the remaining three higher energy conformations). Values in parentheses are the percentage population values.

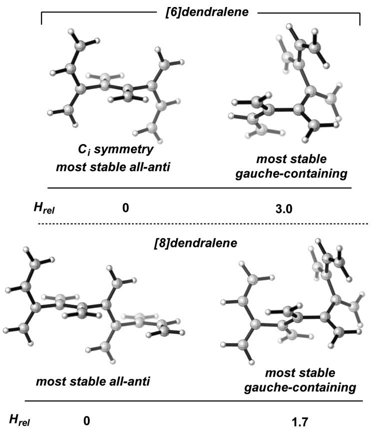


Figure 8. G4(MP2) optimized geometries of the global minimum energy structures (left) and lowest energy structures possessing a *gauche* butadiene unit (right) for [6]dendralene and [8]dendralene; H_{rel} (0 K) in kJ/mol.

These findings lead to a generalization concerning the preferred conformation of dendralenes, particularly those containing even numbers of double bonds, namely that it possesses the maximum possible number of *anti*-butadiene units. This prediction was confirmed for [6]dendralene and [8]dendralene; of the 16 and ten conformations located for the former and latter dendralene, respectively, the most stable conformer for each dendralene does possess the maximal *anti*-butadiene count (Figure 8). In fact, we found two such conformers of [6]dendralene which possessed three *anti*-butadiene moieties, one of C_i symmetry (Figure 8) and the other of C_2 symmetry (not shown). Similarly, there are three conformers of [8]dendralene which possess four *anti*-butadiene groups, two of C_2 symmetry and the other of C_1 symmetry. The most stable conformers of [6]dendralene and [8]dendralene, each of which possesses a single *gauche*-butadiene conformation within its structure, are also shown in Figure 8. In both conformers, the *gauche*-butadiene group is sandwiched between *anti*-butadienes. The energy difference between the all-*anti*-butadiene conformer and the most stable conformer with a *gauche*-butadiene unit decreases along the series [4]dendralene > [6]dendralene > [8]dendralene, that is 10.3, 3.0, and 1.7 kJ/mol, respectively. Consequently, this trend, together with the increase in the number of different *gauche* conformers with increasing dendralene chain length, the population of the all-*anti*-butadiene conformers decreases rapidly with increasing chain length. The number of different lowest energy conformers of the even-membered series of [*n*]dendralenes ($n = 4$, 6, 8) which lie within 3 kJ/mol of each other, and whose combined abundances add up to more than 80% of the mixture at 25 °C, increases along the series, from one ($n = 4$), to three ($n = 6$), to five ($n = 8$).

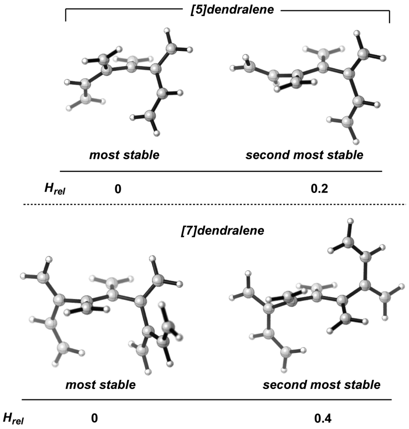


Figure 9. G4(MP2) optimized geometries of the two lowest energy conformers of [5]dendralene and [7]dendralene; H_{rel} (0 K) in kJ/mol.

The two lowest energy conformers of the odd-membered [5]dendralene and [7]dendralene may be described as the attachment of *anti*-butadiene groups to either an *anti*−*anti*- or *anti*−*gauche*-[3]dendralene unit (Figure 9), although this characterization becomes less definite in the case of [7]-dendralene. The terminal double bonds in these dendralenes may adopt either a gauche or an anti orientation with respect to its adjacent double bond. The percentage of those conformations bearing at least one terminal gauche vinyl group decreases with increasing chain length in the odd-membered series of [*n*]dendralenes.

Computed NMR Chemical Shifts. Using the method of Tantillo et al.,[40] the ^{1}H and ^{13}C chemical shifts (in chloroform) for the terminal methylene *Z*-C1*H* proton and C2 methine carbon, respectively, were calculated for various conformers of the series of [*n*]dendralenes, for $n = 3$−8. The chemical shifts for the three conformations of [3]dendralene and the major conformer of [4]dendralene are depicted in Figure 10.

Upon changing the conformation of the terminal butadienyl group from gauche to anti, the methylene *Z*-C1*H* and C2

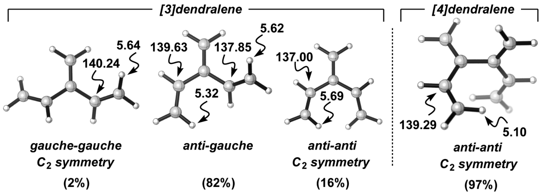


Figure 10. Calculated ^{1}H and ^{13}C chemical shifts (δ/ppm, in chloroform) for the terminal methylene *Z*-C1*H* proton and C2 methine carbon; percentage abundances at 25 °C. Values in parentheses are the percentage population values.

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methine ^{13}C nuclei experience upfield and downfield shifts of ca. 0.5 and 1.5 ppm, respectively (cf. *anti*−*gauche*-[3]-dendralene with [4]dendralene). Since the even-membered dendralenes favor all-*anti*-butadiene units and the odd-membered series are populated with *gauche*-butadiene groups, the average chemical shifts of the aforementioned nuclei should display oscillatory behavior with increasing dendralene length, although it should be progressively damped as the even- and odd-membered dendralenes acquire increasing populations of, respectively, terminal *gauche*- and *anti*-butadiene groups with increasing dendralene length. This damped oscillatory behavior is observed both experimentally and computationally (Figures 4 and 5, Table 1). The computational values in Table 1 were derived from calculating the average of the chemical shifts of interest associated with both terminal vinyl groups of each conformer and then taking the conformer-weighted average of these chemical shifts. The qualitative agreement between experimental and calculated trends in chemical shifts along the dendralene series is acceptable and confirms the origin of the oscillatory behavior to conformational effects rather than to parity-dependent electronic effects.

Table 1. Calculated weighted average chemical shifts for the terminal methylene *Z*-C1*H* and C2 methine ^{13}C nuclei of [*n*]dendralenes

dendralene	^{1}H	^{13}C
[3]dendralene	5.51	138.74
[4]dendralene	5.10	139.29
[5]dendralene	5.37	138.84
[6]dendralene	5.27	139.19
[7]dendralene	5.38	139.21
[8]dendralene	5.29	139.53

Calculations of Excited States. Time-dependent (TD) theory, using the ωB97X functional,[41] was employed to calculate the lowest energy (π, p*) transitions in selected dendralenes and the results for all conformations of [3]-dendralene and for the major conformer of [4]dendralene, which dominates the equilibrium mixture of conformers (97%), are presented in Table 2.

The calculated electronic transitions corresponding to 235 and 202 nm for the major anti−gauche conformer of [3]dendralene (82%) are in reasonable agreement with the experimental λ_{max} values of 231 and 205 nm. The anti−anti conformer of [3]dendralene, which makes up 16% of the equilibrium mixture of conformers at 25 °C, is predicted to have excitation energies very similar to those of the anti−gauche conformer, although the shorter wavelength transition exhibits a 10 nm bathochromic shift, relative to the latter conformer. The longer wavelength transition in the gauche−gauche conformer displays a 11 nm bathochromic shift, relative to the other two conformers, but this has no importance to the current investigation owing to its negligible 2% abundance in the mixture. The two lowest electronic transitions of each conformer of [3]dendralene are well-separated in energy and they give rise to distinct Franck−Condon bands, as we have observed experimentally (Figure 3a). This distinct separation between the bands probably reflects the fairly strong degree of conjugative coupling between adjacent double bonds. For example, the 41° dihedral angle between the two double bonds in the *gauche*-butadienyl group in the major anti−gauche conformer suggests a coupling strength within this group that is about 50% of that within the *anti*-butadienyl group.

Table 2. TD-ωB97X/6-311+G(22d,p)[a] Vertical Excitations, Expressed in Wavelengths (nm), and Experimental Values

molecule	conformer	calcd. λ [f][b]	exptl. λ_{max}[c]
[3]dendralene	anti−gauche	235 [0.41]	231
		202 [0.53]	205
	anti−anti	235 [0.64]	
		212 [0.15]	
	gauche−gauche	246 [0.12]	
		206 [0.58]	
[4]dendralene	bis−anti	224 [0.31]	216
		222 [0.40]	
		213 [0.21]	
		212 [0.37]	

[a] Heptane solvent using the PCM method. [b] Oscillator strength. [c] Values for equilibrium mixture of conformers.

The situation becomes more complex for the higher members of the [*n*]dendralenes. Our TD calculations on the predominant conformer of [4]dendralene predict four transitions lying within the range 212−224 nm and all having oscillator strengths greater than 0.2. This tight bunching of the excitation wavelengths may be attributed to the large value of the dihedral angle of 76° between the adjacent double bonds from the two *anti*-butadienyl groups, a value which implies a coupling strength between the two *anti*-butadienyl groups of only ca. 6% of that between two double bonds within the *anti*-butadienyl group. Thus, these four close lying transitions, once Franck−Condon factors and solvent effects are taken into account, may well give rise to a broad featureless absorption band that is observed experimentally. As the dendralene chain length increases, the number of electronic transitions per conformer increases, as does the number of conformers in the dendralene mixture. For example, our TD calculations on [8]dendralene predict a total number of 39 transitions lying within 206−237 nm for the four conformers which constitute ca. 80% of the mixture. The most intense transitions occur in the 210−220 nm range, which is consistent with the experimental observation that the maximum absorption occurs at 216 nm and that the band is very broad.

In summary, our TD calculations on [*n*]dendralenes qualitatively reproduce the main features of the experimentally observed UV−visible absorption spectra of the dendralenes, namely that the relatively strong electronic coupling between adjacent double bonds in [3]dendralene leads to two distinct absorption bands, whereas weaker coupling between contiguous *anti*-butadienyl groups in the higher homologues produces broad featureless bands for $n > 3$.

Diels−Alder Reactions. Experimentally, [3]dendralene was found to be substantially more reactive than [4]dendralene toward Diels−Alder dimerization and its Diels−Alder reaction with *N*-methylmaleimide (NMM). G4(MP2) calculations on these reactions traced the origin of this reactivity difference to the difference in populations of the reactive conformation in the two dendralenes:[42] The major conformer of [3]dendralene possesses a gauche butadiene moiety which is predisposed to participate in a Diels−Alder reaction. In contrast, the major conformer of [4]dendralene (97%) possesses two *anti*-butadienyl groups; consequently, a distortion energy penalty must be paid by [4]dendralene to convert an *anti*-butadiene group into its reactive gauche conformation. We may generalize this argument to state that the Diels–Alder reactivity of [n]dendralenes is parity-dependent. That is, those dendralenes with odd values of n (which necessarily possess at least one *gauche*-butadienyl group) should be more reactive than their neighbors with even values of n.

This generalization was tested by calculating the six lowest energy endo transition states (TSs) for the NMM Diels–Alder additions to [5]dendralene and [6]dendralene. The G4(MP2) activation energy for the lowest energy pathway for each of these reactions are given in Table 3, together with those reported[42] for [3]dendralene and [4]dendralene.

Table 3. G4(MP2) Activation Enthalpies and Free Energies for the Diels–Alder Reaction between *N*-Methylmaleimide (NMM) and [*n*]Dendralenes

dendralene	$\Delta H^{\ddagger}$ (0 K)[a]	$\Delta G^{\ddagger}$ (298 K)[a]
[3]dendralene	34.9[b]	93.5[b]
[4]dendralene	46.6[b]	105.0[b]
[5]dendralene	32.2	87.1
[6]dendralene	41.9	104.2

[a] kJ/mol. [b] Ref 42.

The data in Table 3 clearly reveal the parity-dependent, oscillatory behavior of the activation energies, those for odd parity dendralenes lying well below the even parity ones. The energy required to convert the most stable conformer of [4]dendralene and [6]dendralene is about 13 and 8 kJ/mol, respectively and is consistent with the aforementioned explanation of the origin of the parity effect.[42]

Finally, we investigated, using G4(MP2) and B3LYP/6-31G(d) model chemistries, the regioselectivities of the Diels–Alder reactions of [n]dendralenes for n = 4–6. Experimentally, *terminal* addition of NMM is preferred over *internal* addition. First, we investigated endo/exo selectivity in the Diels–Alder reactions involving [4]dendralene and [5]dendralene. It was found that endo addition was favored over exo addition by more than 12 kJ/mol. Consequently, attention was paid only to endo modes of addition. The lowest energy B3LYP/6-31G(d) TS for each site of addition of NMM to the dendralenes are shown in Figure 11, together with the B3LYP and G4(MP2) relative enthalpies (0 K).

These TSs show a relatively small degree of bond length asynchronicity, with the TSs for *internal* addition to [5]- and [6]dendralene displaying the largest values of Δr = 0.32 and 0.33 Å, respectively. Whereas B3LYP correctly predicts *terminal* selectivity for all three dendralenes, the G4(MP2) method incorrectly predicts preferred *internal* addition by NMM on [4]dendralene. Moreover, the B3LYP method predicts much stronger *terminal* preferences than does G4(MP2), which is more in keeping with the strong preference observed experimentally. Thus, on the basis of the free energies of all TS conformations for each position of addition at 25 °C, the *terminal*/*internal* ratio is only 60:40 for G4(MP2), but 86:14 for B3LYP. The ratios are comparable for [6]dendralene, being 86:14 (G4(MP2)) and 94:6 (B3LYP).

The preferred *terminal* site selection by NMM may be understood in terms of steric interactions between spectator groups at positions 2 and 3 of the reactive butadiene component of the dendralene. In the *terminal* mode of addition, only position 2 bears a non-hydrogen substituent, whereas both 2 and 3 positions are substituted when *internal* addition takes place. The steric argument is also consistent with the prediction that, of the two different modes of *internal* addition by NMM on [6]dendralene, addition to the central diene moiety, which bears two 2′-butadienyl groups at positions 2 and 3, is strongly disfavored, compared to addition at the other *internal* diene, which has a vinyl and 2′-[3]dendralenyl substituents at positions 2 and 3.

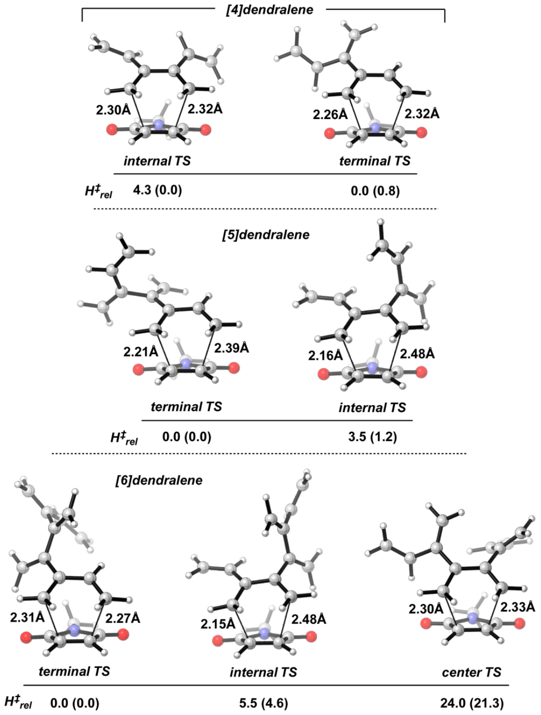

Figure 11. B3LYP/6-31G(d) lowest energy endo transition structures (TSs) for the different modes of addition of *N*-methylmaleimide (NMM) to [4]-, [5]- and [6]dendralenes. $H^{\ddagger}_{\mathrm{rel}}$ (0 K) in kJ/mol. Values in parentheses are the G4(MP2) values.

■ CONCLUSIONS

The simplest cross-conjugated triene, [3]dendralene, and cross-conjugated tetraene, [4]dendralene, exhibit very different physical and chemical behaviors. This odd versus even parity difference continues through the family but gradually fades with increasing numbers of C=C units until the difference becomes negligible in compounds with more than ten C=C bonds. This dampening oscillation has been recorded experimentally in extinction coefficients of UV–visible spectra, and in chemical shifts in both ^{1}H and ^{13}C NMR spectra. The same effect has also been measured experimentally in the Diels–Alder reactions of the series of [n]dendralenes with the dienophile *N*-methylmaleimide.

The diminishing alternation trend observed on ascending the family of [n]dendralenes has been traced to conformational effects. The conformational preferences of the dendralenes contrast most strongly between [3]dendralene and [4]dendralene, the former exhibiting a preferred conformation with a *gauche*-butadiene moiety, with the latter displaying two *anti*-butadienes at an angle of 72° to one another. With increasing chain length, for odd [n]dendralenes, the percentage of conformations bearing at least one terminal *gauche* vinyl group decreases, whereas for even [*n*]dendralenes, the percentage of conformations bearing at least one terminal *gauche* vinyl group increases. It is these conformational preferences which determine the physical and chemical properties of the branched acyclic polyenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11889.

Synthetic and computational work (PDF)

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Notes

The authors declare no competing financial interest.

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(35) By ^{1}H NMR spectroscopic analysis, the product ratio of the monoadducts is ca. 85:15 (*terminal/internal* monoadduct). This ratio is reversed in [4]dendralene. A similar analysis of the bis-adducts shows a ca. 75% preference for the *terminal/terminal* regioisomer. The *terminal/internal* regioisomer dominates with [4]dendralene (65% selectivity).

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Supporting Information for:

Discovery and Computational Rationalization of Diminishing Alternation in [*n*]Dendralenes

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1. General Methods

Reactions were performed under a positive pressure of dry argon in oven or flame dried glassware, unless otherwise specified. Anhydrous THF was dried over sodium wire and distilled from sodium benzophenone ketyl. Other anhydrous solvents were dried using a solvent purification system outlined in the procedure by Grubbs et al.[1] Commercially available chemicals were used as purchased or purified by standard procedures.[2] *n*-BuLi solution in hexane was titrated against menthol with 2,2'-bipyridine as an indicator in anhydrous THF.[3] Grignard reagents were titrated against salicylaldehyde phenylhydrazone according to procedure of Love and Jones.[4] Microwave reactions were performed using a CEM Discovery instrument.

Chromatography

Analytical TLC was performed with Merck silica gel plates, precoated with silica gel 60 F_{254} (0.2 mm) on aluminium sheets and visualized using UV fluorescence (λ_{max} = 254 nm). Flash column chromatography employed Merck Kieselgel 60 (230–400 mesh) silica gel and reversed phase flash column chromatography employed Davisil 633NC18E chemically modified C18 bonded porous silica gel. Analytical HPLC was performed using an Agilent 1100 instrument consisting of a G1311A quaternary pump, autosampler, column compartment and G1315A diode array detector. Preparative HPLC was performed on either of the following instruments: (1) Waters instrument consisting of a Waters 600 pump with a Waters 600 controller monitored by a Waters 2996 photodiode array detector with Empower 2 software used for instrument control and data processing; or (2) Agilent 1100 instrument consisting of a G1361A preparative binary pump system, autosampler, column compartment and G1315B diode array detector with Agilent Chem Station software used for instrument control and data processing.

NMR Spectroscopy

^{1}H and ^{13}C NMR spectra were recorded at 298 K using a Bruker Avance 800 MHz, Varian INOVA 500 MHz, Varian MR400 MHz or Varian Mercury 300 MHz NMR spectrometers. Residual chloroform ($CDCl_3$) (δ = 7.26 ppm) was used for ^{1}H NMR spectra and the central line of the chloroform ($CDCl_3$) triplet ($\delta = 77.10$ ppm) was used for ^{13}C NMR spectra as internal reference. Assignment of proton signals was assisted by COSY, HSQC or HMBC experiments where necessary and assignment of carbon signals was assisted by DEPT, APT, HSQC or HMBC experiments where necessary. The following abbreviations and combinations thereof are used to describe ^1H NMR spectra multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad.

Infrared Spectroscopy

IR spectra were recorded on either of the following two instruments: (1) Perkin-Elmer 1600 FTIR spectrometer as neat films on NaCl plates for oils or as KBr disks for solids; or (2) Bruker Alpha-Platinum single reflection diamond ATR spectrometer for both oils and solids.

Mass Spectroscopy

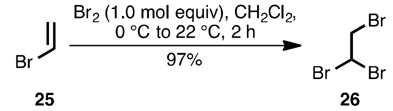
Both low resolution (LR) and high resolution (HR) mass spectra were recorded on a Waters AutoSpec Premier spectrometer magnetic sector instrument using electron impact (EI) ionization mode at 70 eV.

Ultraviolet-visible Spectroscopy

Ultraviolet-visible measurements were recorded on a Shimadzu UV-2450 spectrophotometer at 25 °C.

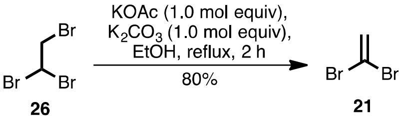
2. Synthetic Details

1,1,2-Tribromoethane (26)[5]



The title compound **26** was prepared following a modification of the procedure reported by Eicher-Lorka et al.[5] To a stirred solution of bromine (58 g, 0.36 mol, 1.0 mol equiv) in dry CH_2Cl_2 (0.10 L) was added an ice-cold solution of vinylbromide (**25**) (40 g, 0.37 mol, 1.0 mol equiv) in dry CH_2Cl_2 (80 mL) at 0 °C under a nitrogen filled balloon. The red reaction mixture was then allowed to warm to room temperature and stirred for 2 hours. The resulting yellow mixture was concentrated under reduced pressure (1 mbar, 25 °C) to give the title compound **26** as an orange oil (93 g, 0.35 mol, 97%), which was used without further purification. The data for this compound **26** was in agreement with that previously reported within the group.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.67 (t, J = 6.6 Hz, 1H), 4.10 (d, J = 6.7 Hz, 2H) ppm.

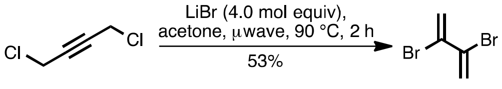
1,1-Dibromoethylene (21)[7]



The title compound **21** was prepared following a modification of the procedure reported by Jacobsen et al.[7] A 3-necked round bottomed flask equipped with a dropping funnel and a distillation unit connected to a separating funnel was charged with KOAc (19 g, 0.19 mol, 1.0 mol equiv) and K_2CO_3 (26 g, 0.19 mol, 1.0 mol equiv) in dry EtOH (0.14 L) at room temperature. The reaction mixture was heated to reflux until the EtOH began to distil. At this point, 1,1,2-tribromoethane (**26**) (50 g, 0.19 mol, 1.0 mol equiv) was added rapidly through the dropping funnel. The reaction mixture was heated to 130 °C and stirred vigorously until the distillation was complete and a solid cake remained. Degassed water (0.22 L) was added to the separating funnel under an argon atmosphere and two phases were separated. The bottom organic phase was collected and dried over

$CaCl_2$ under an argon atmosphere to give the title compound **21** (28 g, 0.15 mol, 80%) as a dense colorless oil which was used without further purification. Compound **21** was stored in a Young's tap Schlenk flask over a small amount of $CaCl_2$ with the exclusion of light at –80 °C. This compound was found to be extremely air sensitive and slowly decomposed after a few weeks at –80 °C. The data for this compound was in agreement with that previously reported within the group.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.27 (s, 2H) ppm.

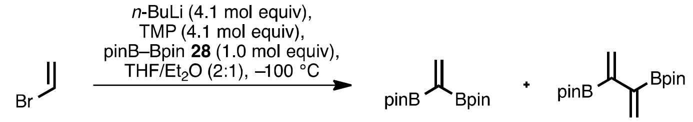
2,3-Dibromo-1,3-butadiene (23)[8]



27 **23**

A microwave reactor vial was charged with 1,4-dichloro-2-butyne (**27**) (0.40 g, 3.3 mmol, 1.0 mol equiv), LiBr (1.1 g, 13 mmol, 4.0 mol equiv) and acetone (5.0 mL). The reaction was then heated to 90 °C using microwave irradiation (50W) for 2 hours. The resulting mixture was diluted with acetone (25 mL) in the presence of 2 crystals of BHT and filtered through a plug of SiO_2 (15 g) into a flask containing K_2CO_3. The solution was concentrated under reduced pressure (30 mbar, 0 °C) and the system purged with nitrogen before removing the flask from the rotary evaporator. The resulting mixture was then diluted in pentane (25 mL) and filtered through a plug of SiO_2 (10 g) into a flask containing K_2CO_3. The solution was concentrated under reduced pressure (10 mbar, 0 °C) and the system purged with nitrogen before removing the flask from the rotary evaporator to give the title compound **23** (0.37 g, 1.7 mmol, 53%) as a yellow oil, which was used without further purification and stored over K_2CO_3 in the presence of a crystal of BHT at –80 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.43 (d, J = 1.6 Hz, 2H), 5.89 (d, J = 1.6 Hz, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 125.1 (2 × C), 124.7 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 2955, 2923, 1577, 1430, 1209, 900, 610 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 214 ($[M^{81}Br_2]^{+\bullet}$, 7%), 212 ($[M^{81}Br^{79}Br]^{+\bullet}$, 18), 210 ($[M^{79}Br_2]^{+\bullet}$, 7), 205 (100); **HRMS** (EI): calc for $C_4H_4{}^{79}Br_2$ $[M]^{+\bullet}$: 209.8680; found 209.8675, calc for $C_4H_4{}^{79}Br^{81}Br$ $[M]^{+\bullet}$: 211.8659; found 211.8711.

1,1-Bis(pinacolatoboryl)ethene (16)[9] and 2,3-bis(pinacolatoboryl)1,3-butadiene (17)[10,11]



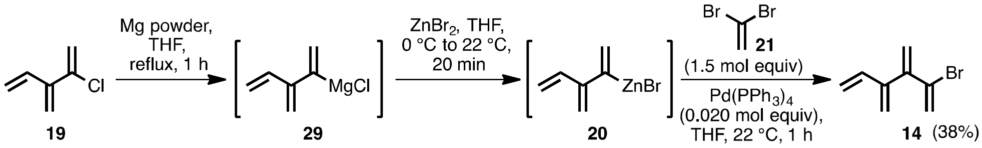
25 (3.9 mol equiv)

16 (18%)

17 (23%)

The title compounds **16** and **17** were prepared following a modification of the procedure reported by Shimizu et al.[10] A round bottomed flask was charged with 2,2,6,6-tetramethylpiperidine (TMP) (7.7 mL, 45 mmol, 4.1 mol equiv) and diluted with a 2:1 mixture of THF:Et_2O (25 mL) at 0 °C. To this was added *n*-BuLi (34 mL, 1.3 M solution in hexane, 45 mmol, 4.1 mol equiv) and the mixture was stirred for 5 minutes at 0 °C. Another 3-necked round bottomed flask was charged with a solution of vinyl bromide (**25**) (3.0 mL, 43 mmol, 3.9 mol equiv) in a 2:1 mixture of THF:Et_2O (21 mL) and cooled to –100 °C as determined by an internal temperature sensor. To this was slowly added the freshly prepared solution of LiTMP over approximately 30 minutes and the solution stirred for 5 minutes. A solution of bis(pinacolato)diboron (**28**) (2.8 g, 11 mmol, 1.0 mol equiv) in a 2:1 mixture of THF:Et_2O (20 mL) was then slowly added dropwise to the reaction mixture at –101 °C over approximately 20 minutes. The resulting solution was allowed to warm to room temperature, quenched with a saturated solution of aqueous NH_4Cl (50 mL) and diluted with Et_2O (0.10 L) and water (50 mL). The phases were separated and the aqueous phase was washed with Et_2O (50 mL). The organic phases were combined, washed with brine (0.10 L), dried over $MgSO_4$, and concentrated under reduced pressure (1 mbar, 25 °C). Purification by flash column chromatography (SiO_2, hexane:EtOAc; 90:10) gave **17** as a white solid (0.69 g, 2.2 mmol, 20%) and a mixture of **16** and **17** (0.90 g, ratio of 76:24, respectively). Further purification of the mixture by flash column chromatography (SiO_2, hexane:EtOAc; 95:5 to 75:25) gave **17** (98 mg, 0.32 mmol, 3%) and **16** (0.55 g, 2.0 mmol, 18%) as a white solid. The data for 2,3-bis(pinacolatoboryl)1,3-butadiene (**17**) was in agreement with that reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, J = 3.5 Hz, 2H), 5.84 (d, J = 3.5 Hz, 2H), 1.27 (s, 24H) ppm. The data for 1,1-bis(pinacolatoboryl)ethene **(16)** was in agreement with that reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 1.26 (s, 24H) ppm.

2-Bromo[4]dendralene (14)

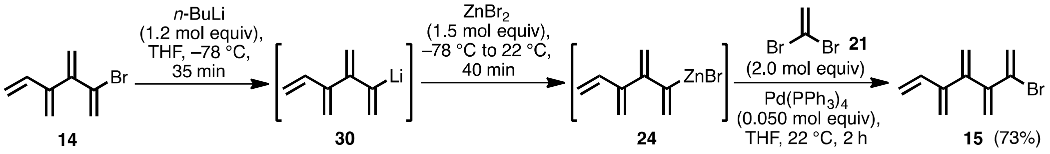


A 3-necked round bottomed flask equipped with a condenser and dropping funnel was charged with oven-dried magnesium powder (3.1 g, 0.13 mol, 2.9 mol equiv) and flushed with argon for 1 hour. To this was added THF (50 mL) followed by portionwise addition of 1,2-dibromoethane (1.5 mL) (WARNING exothermic). After the refluxing had subsided, a solution of $ZnBr_2$ (1.5 mL, 1.5 M solution in THF, 2.2 mmol, 0.050 mol equiv) was added and the reaction mixture was heated to reflux. A solution of 2-chloro[3]dendralene (**19**)[12] (5.0 g, 38% (w/w) solution in THF, 44 mmol, 1.0 mol equiv) and 1,2-dibromoethane (2.3 mL) in THF (40 mL) was added dropwise over approximately 40 minutes and the reaction mixture was stirred for a further 20 minutes at reflux. The resulting 2-[3]dendralenylmagnesium chloride (**29**)[12] was cannulated over 10 minutes into a solution of $ZnBr_2$ (21 mL, 1.5 M solution in THF, 32 mmol, 1.5 mol equiv) and THF (55 mL) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature and stirred for a further 20 minutes. $Pd(PPh_3)_4$ (0.49 g, 0.42 mmol, 0.020 mol equiv) was then added followed by addition of a solution of 1,1-dibromoethylene (**21**)[7] (2.6 mL, 32 mmol, 1.5 mol equiv) in THF (5 mL) in one portion and the mixture was stirred at 22 °C for 1 hour with the exclusion of light. The resulting slurry was poured into ice-cold water (0.10 L), diluted with ice-cold petroleum ether (30–40 °C) (0.10 L) and a solution of aqueous HCl (50 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 50 mL). The organic phases were combined, washed with brine (0.10 L), dried over $MgSO_4$ and a few crystals of BHT was added. The solution was then concentrated under reduced pressure (30 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave 2-

bromo[4]dendralene (**14**) as a colorless oil (3.0 g, 16 mmol, 38%). The compound was stored as a solution (35% (w/w) solution in THF) at –20 °C to prevent decomposition. **R*f*** 0.59 in petroleum ether (30–40 °C); **^{1}H NMR** (300 MHz, $CDCl_3$) *δ* 6.40 (ddt, *J* = 17.5, 10.8, 0.7 Hz, 1H), 5.86 (dt, *J* = 1.6, 0.6 Hz, 1H), 5.76 (dt, *J* = 1.2, 0.6 Hz, 1H), 5.69 (td, *J* = 1.5, 0.6 Hz, 1H), 5.28 (tt, *J* = 1.4, 0.7 Hz, 2H), 5.22 – 5.12 (m, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 146.1 (C), 145.0 (C), 137.0 (CH), 130.4 (C), 121.6 (CH_2), 120.9 (CH_2), 119.0 (CH_2), 117.2 (CH_2) ppm; **IR** (thin film): ν_{max} = 3091, 1825, 1578, 906, 890 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 186 ($[M^{81}Br]^{+\bullet}$, 3%), 185 (6), 184 ($[M^{79}Br]^{+\bullet}$, 3), 183 (6), 157 (7), 129 (12), 105 (100); **HRMS** (EI): calc for $C_8H_9{}^{81}Br$ $[M]^{+\bullet}$: 185.9867; found 185.9864; calc for $C_8H_9{}^{79}Br$ $[M]^{+\bullet}$: 183.9888; found 183.9891; **UV/Vis** (hexane) λ_{max} 219 nm (ε = 27,300 $M^{-1}cm^{-1}$).

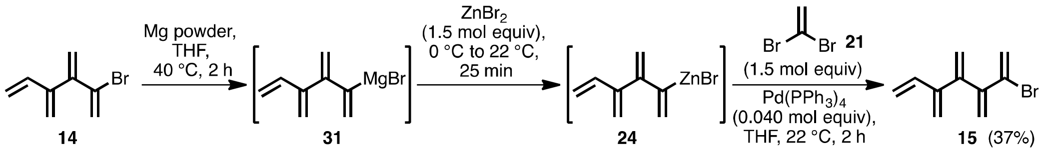
2-Bromo[5]dendralene (15)

Via lithium/halogen exchange reaction;



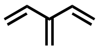
A 2-necked round bottomed flask was charged with 2-bromo[4]dendralene (**14**) (0.60 g, 1.3 M solution in THF, 3.2 mmol, 1.0 mol equiv) and THF (30 mL) and cooled to –78 °C. To this was added *n*-BuLi (2.6 mL, 1.5 M solution in hexane, 3.9 mmol, 1.2 mol equiv) dropwise over 15 minutes at which point the reaction mixture turned orange. The solution was stirred for 20 minutes at –78 °C and then a solution of $ZnBr_2$ (3.9 mL, 1.3 M solution in THF, 4.9 mmol, 1.5 mol equiv) was added dropwise over 15 minutes. The reaction mixture was stirred for 5 minutes at –78 °C and then warmed to ambient temperature and stirred for 20 minutes. $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol, 0.050 mol equiv) was then added followed by addition of 1,1-dibromoethylene (**21**)[7] (0.55 mL, 6.5 mmol, 2.0 mol equiv) in one portion. The mixture was stirred at an ambient temperature for 2 hours with the exclusion of light and then poured into ice-cold water (0.20 L), diluted with ice-cold petroleum ether (30–40 °C) (0.20 L) and a solution of aqueous HCl (10 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was washed with petroleum ether (30–40 °C) (2 × 0.10 L). The organic phases were combined, washed with brine (0.10 L), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave **15** as a colorless oil (0.50 g, 2.4 mmol, 73%). 2-Bromo[5]dendralene (**15**) was stored as a solution (26% (w/w) solution in THF) at –20 °C to prevent decomposition. **R_f** 0.62 (petroleum ether (30–40 °C)); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.43 (ddd, J = 17.4, 10.7, 0.9 Hz, 1H), 5.84 (d, J = 1.6 Hz, 1H), 5.69 (dd, J = 1.6, 0.7 Hz, 1H), 5.56 (d, J = 1.3 Hz, 1H), 5.39 (dd, J = 17.4, 1.4 Hz, 1H), 5.36 – 5.32 (m, 2H), 5.30 – 5.27 (m, 1H), 5.26 – 5.23 (m, 1H), 5.15 (ddd, J = 10.7, 1.5, 0.7 Hz, 1H), 5.12 – 5.09 (m, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.2 (C), 146.1 (C), 145.2 (C), 136.7 (CH), 130.0 (C), 120.8 (CH_2), 120.6 (CH_2), 118.3 (CH_2), 117.5 (CH_2), 116.9 (CH_2) ppm; **IR** (thin film): ν_{max} = 3091, 1831, 1579, 989, 904, 568 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 212 ([M^{81}Br]$^{+\bullet}$, 3%), 211 (3), 210 ([M^{79}Br]$^{+\bullet}$, 3), 209 (3), 195 (1), 131 (100); **HRMS** (EI): calc for $C_{10}H_{11}{}^{79}Br$ [M]$^{+\bullet}$: 210.0044; found 210.0047, calc for $C_{10}H_{10}{}^{79}Br$ [M]$^{+\bullet}$: 208.9966; found 208.9967, calc for $C_{10}H_{10}{}^{81}Br$ [M]$^{+\bullet}$: 210.9945; found 210.9943; **UV/Vis**: (hexane) λ_{max} 217 nm (ε = 24,200 M^{-1}cm^{-1}).

Via the Grignard reaction;



A 3-necked round bottomed flask equipped with a condenser and a dropping funnel was charged with oven-dried magnesium powder (0.31 g, 13 mmol, 2.7 mol equiv) and the system flushed with argon for 1 hour. To this was added THF (7 mL) followed by portionwise addition of 1,2-dibromoethane (0.14 mL) (WARNING exothermic) (In small scale reaction gently heating with a heat gun was required to initiate to reflux). After the refluxing had subsided, a solution of $ZnBr_2$ (0.16 mL, 1.5 M solution in THF, 0.24 mmol, 0.050 mol equiv) was added at room temperature and then the reaction mixture was heated to 40 °C. A solution of 2-bromo[4]dendralene (**14**) (0.87 g, 20% (w/w) solution in THF, 4.7 mmol, 1.0 mol equiv) and 1,2-dibromoethane (0.22 mL) in THF (13 mL) was added dropwise over approximately 10 minutes and the reaction mixture was stirred for a further 110 minutes at 40 °C. The resulting yellowy-green solution of 2-[4]dendralenylmagnesium chloride (**31**) in THF was then cannulated over 3 minutes into a solution of $ZnBr_2$ (4.8 mL, 1.5 M solution in THF, 6.9 mmol, 1.5 mol equiv) in THF (15 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for a further 20 minutes, then $Pd(PPh_3)_4$ (0.22 g, 0.18 mmol, 0.040 mol equiv) was added followed by addition of a solution of 1,1-dibromoethylene (**21**)[7] (0.60 mL, 6.9 mmol, 1.5 mol equiv) in THF (1.0 mL) in one portion. The reaction mixture was stirred at 22 °C for 2 hours with the exclusion of light and then poured into ice-cold water (50 mL), diluted with ice-cold petroleum ether (30–40 °C) (30 mL) and a solution of aqueous HCl (5.0 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was washed with petroleum ether (30–40 °C) (2 × 30 mL). The organic phases were combined, washed with brine (0.10 L), dried over $MgSO_4$ and a crystal of BHT was added. The solution was then concentrated under reduced pressure (30 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave **15** as a pale yellow oil (0.36 g, 1.7 mmol, 37%). 2-Bromo[5]dendralene (**15**) was stored as a solution (35%, (w/w) solution in THF) at –20 °C.

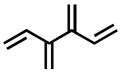
[3]Dendralene (1)[13]



1
[3]dendralene

[3]Dendralene (**1**)[13] was synthesised using the literature route.[14] The data for **1** was in agreement with that previously reported.[13] **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.46 (dd, J = 17.5, 10.9 Hz, 2H), 5.41 (dd, J = 17.5, 1.7 Hz, 2H), 5.17 (d, J = 10.5 Hz, 2H), 5.16 (br.s, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 144.7 (C), 135.9 (2 × CH), 115.7 (2 × CH_2), 115.6 (CH_2) ppm; **UV/Vis** (hexane) λ_{max} 205 nm (ε = 20,600 $M^{-1}cm^{-1}$), λ_{max} 231 nm (ε = 14,500 $M^{-1}cm^{-1}$).

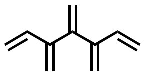
[4]Dendralene (2)[13]



2
[4]dendralene

[4]Dendralene (**2**)[13] was synthesised using the literature route.[15] The data for **2** was in agreement with that previously reported.[13] **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.44 (dd, J = 17.4, 10.5 Hz, 2H), 5.25 (d, J = 1.9 Hz, 2H), 5.20 (dd, J = 17.3, 1.6 Hz, 2H), 5.11 (dd, J = 10.9, 1.7 Hz, 2H), 5.07 5.06 (m, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 146.7 (2 × C), 137.6 (2 × CH), 117.7 (2 × CH_2), 116.6 (2 × CH_2) ppm; **UV/Vis** (hexane) λ_{max} 216 nm (ε = 30,500 $M^{-1}cm^{-1}$).

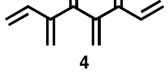
[5]Dendralene (3)[13]



3
[5]dendralene

[5]Dendralene (**3**)[13] was synthesised using the literature route.[16] The data for **3** was in agreement with that previously reported.[13] **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.44 (ddd, J = 17.3, 10.7, 0.8 Hz, 2H), 5.33 (dd, J = 17.4, 1.6 Hz, 2H), 5.25 (s, 2H), 5.23 – 5.20 (m, 2H), 5.14 – 5.11 (m, 2H), 5.11 (dd, J = 2.0, 0.9 Hz, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 147.2 (2 × C), 146.8 (C), 137.1 (2 × CH), 116.9 (2 × CH_2), 116.5 (2 × CH_2), 116.4 (CH_2) ppm; **UV/Vis** (hexane) λ_{max} 215 nm (ε = 25,500 $M^{-1}cm^{-1}$).

[6]Dendralene (4)[13]

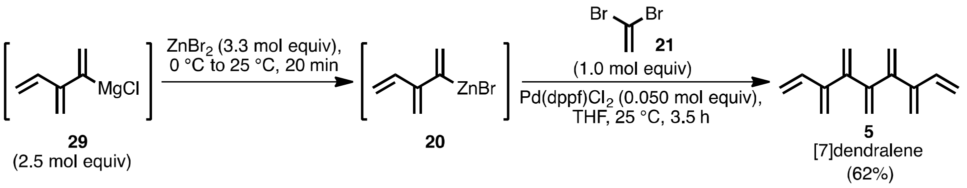


4
[6]dendralene

[6]Dendralene (**4**)[13] was synthesised using the route previously reported within the group.[17] The data for **4** was in agreement with that previously published.[13] **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.46 (dd, J = 17.3, 10.6 Hz, 2H), 5.29 (dd, J = 17.4, 1.6 Hz, 2H), 5.29 (s,

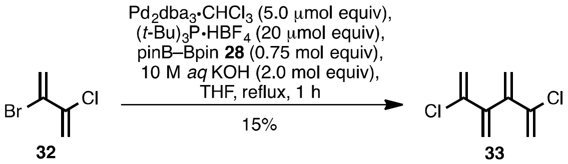
2H), 5.25 (d, *J* = 2.0 Hz, 2H), 5.12 (d, *J* = 10.7 Hz, 2H), 5.09 – 5.08 (m, 4H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 147.6 (2 × C), 146.7 (2 × C), 138.0 (2 × CH), 117.8 (2 × CH_2), 117.5 (2 × CH_2), 116.3 (2 × CH_2) ppm; **UV/Vis** (hexane) λ_{max} 216 nm (ε = 40,600 $M^{-1}cm^{-1}$).

[7]Dendralene (5)[15]



A 2-necked round bottomed flask was charged with a solution of $ZnBr_2$ (0.51 g, 2.3 mmol, 3.3 mol equiv) in THF (5.0 mL) and freshly prepared 2-[3]dendralenylmagnesium chloride (**29**)[12] (5.0 mL, 0.35 M solution in THF, 1.8 mmol, 2.5 mol equiv) was cannulated portionwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. Pd(dppf)Cl_2 (26 mg, 35 μmol, 0.050 mol equiv) was added followed by addition of a solution of 1,1-dibromoethylene (**21**)[7] (0.13 g, 0.70 mmol, 1.0 mol equiv) in THF (0.50 mL) *via* a syringe pump over 30 minutes. The reaction mixture was stirred for a further 3 hours at room temperature and then a solution of aqueous HCl (5.0 mL, 1.0 M) was added along with petroleum ether (30–40 °C) (30 mL). The phases were separated and the organic phase dried over $MgSO_4$ and concentrated under reduced pressure (40 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave [7]dendralene (**5**) (80 mg, 0.43 mmol, 62%) as a colorless oil and [6]dendralene (**4**) (5.0 mg, 0.030 mmol, 4%) as a colorless oil. The data for [7]dendralene (**5**)[15] and [6]dendralene (**4**)[13] were in agreement with that reported in the literature. [7]Dendralene (**5**): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.44 (ddd, *J* = 17.4, 10.6, 0.8 Hz, 2H), 5.36 (dd, *J* = 17.4, 1.6 Hz, 2H), 5.27 (d, *J* = 1.9 Hz, 2H), 5.23 (d, *J* = 2.0 Hz, 2H), 5.19 (d, *J* = 1.9 Hz, 2H), 5.18 (s, 2H), 5.13 (ddt, *J* = 10.7, 1.5, 0.7 Hz, 2H), 5.11 (dd, *J* = 2.0, 1.1 Hz, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 148.3 (C), 147.3 (2 × C), 147.2 (2 × C), 137.5 (2 × CH), 117.8 (CH_2), 117.3 (2 × CH_2), 117.0 (2 × CH_2), 116.4 (2 × CH_2) ppm; **UV/Vis** (hexane) λ_{max} 216 nm (ε = 37,600 $M^{-1}cm^{-1}$).

Dichloro[4]dendralene (33)



A 2-necked round bottomed flask was charged with Pd_2dba_3•$CHCl_3$ (16 mg, 15 μmol, 5.0 μmol equiv), (*t*-Bu)$_3$P•HBF_4 (18 mg, 60 μmol, 20 μmol equiv), and bis(pinacolato)diboron (**28**) (0.57 g, 2.3 mmol, 0.75 mol equiv). The reaction flask was evacuated and refilled with nitrogen three times. This was diluted with degassed THF (3.5 mL) and followed by addition of 2-bromo-3-chloro-1,3-butadiene (**32**)^{15} (0.50 g, 3.0 mmol, 1.0 mol equiv). The reaction mixture was heated up to 55 °C and a degassed solution of aqueous KOH (0.6 mL, 10 M, 6.0 mmol, 2.0 mol equiv) was added dropwise. The reaction mixture was then heated to reflux and stirred for 1 hour. The resulting mixture was diluted with water (10 mL) and extracted with Et_2O (10 mL). The organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 10 mL). The organic phases were combined, washed with brine (30 mL), dried over $MgSO_4$, filtered through a plug of celite (0.5 cm) on a sintered funnel, and washed with hexane (25 mL) into a flask containing a crystal of BHT and K_2CO_3. The solution was concentrated under reduced pressure (40 mbar, 20 °C). The resulting mixture was then diluted in petroleum ether (30–40 °C) (25 mL), filtered through a plug of celite (0.5 cm) on a sintered funnel into a flask containing a crystal of BHT and K_2CO_3 and concentrated under reduced pressure (40 mbar, 20 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave the title compound **33** as a yellow oil (40 mg, 0.23 mmol, 15%). The title compound **33**[i] was stored as a solution (10% (w/w) solution in THF) over K_2CO_3 in the presence of a crystals of BHT at –80 °C to prevent decomposition. **R*f*** 0.62 (petroleum ether (30–40 °C)); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86 – 5.83 (m, 2H), 5.48 – 5.45 (m, 2H), 5.45 – 5.42 (m, 2H), 5.36 – 5.33 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5 (2 × C), 138.5 (2 × C), 120.7 (2 × CH_2), 116.5 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 3107, 3031, 1845, 1782, 1579, 1225, 1075, 920, 886,

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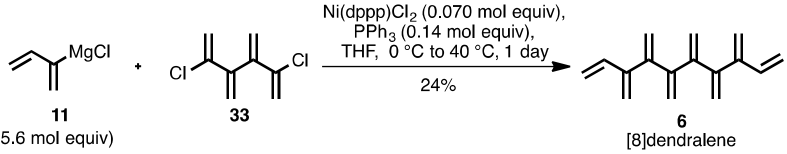
[i] Due to insufficient signal intensity, HRMS could not be obtained for the compound **33**.

716 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 176 ([M^{37}Cl]$^{+\bullet}$, 16%), 174 ([M^{35}Cl]$^{+\bullet}$, 19), 173 (30), 139 (76), 103 (100).

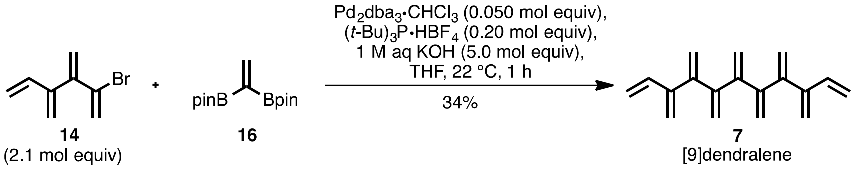
[8]Dendralene (6)[13]



A 2-necked round bottomed flask was charged with Ni(dppp)Cl$_2$ (23 mg, 43 µmol, 70 mmol equiv), triphenylphosphine (23 mg, 86 µmol, 0.14 mol equiv) in THF (2.0 mL) and 2-(1,3-butadienyl)magnesium chloride (**11**)[18] (5.0 mL, 0.7 M solution in THF, 3.5 mmol, 5.6 mol equiv) was added dropwise at 0 °C. Dichloro[4]dendralene (**33**) (0.11 g, 10% (w/w) solution in THF, 0.63 mmol, 1.00 mol equiv) was added dropwise at 0 °C and stirred for 5 minutes at 0 °C. The reaction mixture was then heated to 40 °C for 1 day. The mixture was then poured into a mixture of ice-cold water (30 mL) and ice-cold petroleum ether (30–40 °C) (15 mL) and stirred for 10 minutes before a solution of aqueous HCl (6.0 mL, 1.0 M) was added. The organic phase was separated, washed with a saturated solution of aqueous NaHCO$_3$ (15 mL) and brine (20 mL), dried over MgSO$_4$ and concentrated under reduced pressure (40 mbar, 0 °C). Purification by flash column chromatography (SiO$_2$, petroleum ether (30–40 °C)) gave **6** as a colorless oil (32 mg, 0.15 mmol, 24%). The data for **6** was in agreement with that reported in the literature.[13] **^{1}H NMR** (800 MHz, CDCl$_3$) δ 6.46 (ddd, J = 17.4, 10.6, 0.8 Hz, 2H), 5.34 (d, J = 1.9 Hz, 2H), 5.32 (dd, J = 17.3, 1.5 Hz, 2H), 5.28 (d, J = 1.9 Hz, 2H), 5.25 (d, J = 2.0 Hz, 2H), 5.13 – 5.09 (m, 8H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 147.8 (2 × C), 147.6 (2 × C), 147.2 (2 × C), 137.9 (2 × CH), 118.0 (2 × CH$_2$), 117.6 (2 × CH$_2$), 117.3 (2 × CH$_2$), 116.3 (2 × CH$_2$) ppm; **UV/Vis** (hexane) λ_{max} 216 nm (ε = 47,800 M^{-1}cm^{-1}).

[9]Dendralene (7)

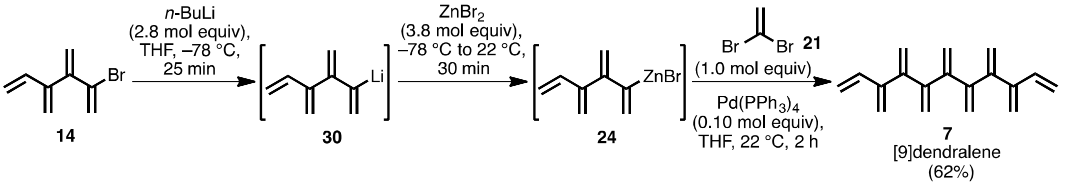
Via a double Suzuki–Miyaura cross-coupling reaction;



A 2-necked round bottomed flask was charged with Pd_2dba_3•$CHCl_3$ (65 mg, 63 μmol, 0.050 mol equiv), (*t*-Bu)$_3$P•HBF_4 (73 mg, 0.25 mmol, 0.20 mol equiv) and 1,1-bis(pinacolatoboryl)ethene (**16**)[9] (0.35 g, 1.3 mmol, 1.0 mol equiv) and the reaction flask then evacuated and refilled with argon three times. A degassed solution of 2-bromo[4]dendralene (**14**) (0.48 g, 1.3 M solution in THF, 2.6 mmol, 2.1 mol equiv) was added and the resulting solution was diluted with degassed THF (17 mL). A degassed solution of aqueous KOH (6.3 mL, 1.0 M, 6.3 mmol, 5.0 mol equiv) was then added *via* syringe pump over 30 minutes. The reaction mixture was stirred for a further 30 minutes at 22 °C with the exclusion of light. The resulting solution was poured into ice-cold water (70 mL), diluted with ice-cold petroleum ether (30–40 °C) (70 mL). The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 70 mL). The organic phases were combined, washed with brine (0.10 L), dried over $MgSO_4$ and concentrated under reduced pressure (30 mbar, 20 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave slightly impure [9]dendralene (**7**) as a colorless oil (0.10 g, 0.42 mmol, 34%) and [8]dendralene (**6**) (20 mg, 95 μmol, 7%) as a by-product. The impure [9]dendralene (**7**) was combined with similar material from multiple runs and further purified by reversed phase flash column chromatography (C18 SiO_2, MeCN:H_2O (80:20 to 85:15)). **R*f*** 0.44 (petroleum ether (30–40 °C)); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.45 (dd, J = 17.3, 10.6 Hz, 2H), 5.35 (dd, J = 17.5, 1.5 Hz, 2H), 5.32 (d, J = 1.9 Hz, 2H), 5.24 (d, J = 2.1 Hz, 2H), 5.23 (s, 2H), 5.21 (d, J = 2.0 Hz, 2H), 5.19 (d, J = 2.0 Hz, 2H), 5.18 (d, J = 1.9 Hz, 2H), 5.12 (d, J = 10.7 Hz, 2H), 5.11 (s, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 148.3 (2 × C), 147.8 (C), 147.4 (2 × C), 147.2 (2 × C), 137.6 (2 × CH), 118.0 (CH_2), 117.8 (2 × CH_2), 117.3 (2 × CH_2), 117.2 (2 × CH_2), 116.4 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 3090, 3007, 2973, 1580, 987, 900 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 236 ([M]$^{+\bullet}$, 20%), 235 (35), 221 (77), 193

(68), 179 (85), 165 (100); **HRMS** (EI): calc for $C_{18}H_{20}$ $[M]^{+\bullet}$: 236.1565; found 236.1568; **UV/Vis**: (hexane) λ_{max} 216 nm (ε = 46,400 $M^{-1}cm^{-1}$).

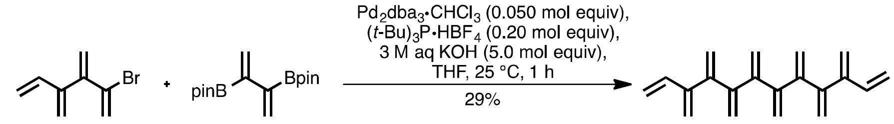
Via a double Negishi cross-coupling reaction;



A 2-necked round bottomed flask was charged with 2-bromo[4]dendralene (**14**) (0.11 g, 1.3 M solution in THF, 0.59 mmol, 2.5 mol equiv) in THF (4.0 mL) and *n*-BuLi (0.42 mL, 1.5 M solution in hexane, 0.65 mmol, 2.8 mol equiv) was added dropwise over approximately 3 minutes at –78 °C. The orange mixture was stirred for 20 minutes at –78 °C and then a solution of $ZnBr_2$ (0.71 mL, 1.3 M solution in THF, 0.89 mmol, 3.8 mol equiv) was added dropwise over approximately 4 minutes. The reaction mixture was stirred for 5 minutes at –78 °C, then allowed to warm to ambient temperature and stirred for 20 minutes. $Pd(PPh_3)_4$ (27 mg, 24 µmol, 0.10 mol equiv) was added followed by addition of 1,1-dibromoethylene (**21**)[7] (20 µL, 0.24 mmol, 1.0 mol equiv) in one portion and the mixture was stirred at 22 °C for 2 hours with the exclusion of light. The reaction mixture was poured into ice-cold water (30 mL), diluted with ice-cold petroleum ether (30–40 °C) (30 mL) and a solution of aqueous HCl (3.0 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 15 mL). The organic phases were combined, washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave [9]dendralene (**7**) as a colorless oil (35 mg, 0.15 mmol, 62%).

[10]Dendralene (8)

Via a double Suzuki–Miyaura cross-coupling reaction;

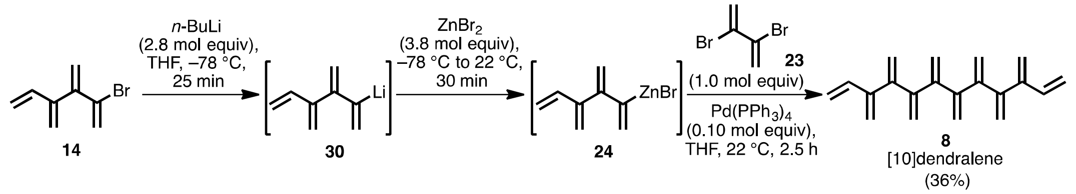


14 (2.1 mol equiv) + **23** → **8** [10]dendralene

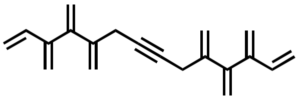
A 2-necked round bottomed flask was charged with $Pd_2dba_3•CHCl_3$ (0.14 mg, 0.14 mmol, 0.050 mol equiv), (t-Bu)$_3$P•HBF_4 (0.16 g, 0.56 mmol, 0.20 mol equiv), and 2,3-bis(pinacolatoboryl)1,3-butadiene (**23**)[11] (0.85 g, 2.8 mmol, 1.0 mol equiv) and the reaction flask was then evacuated and refilled with argon three times. A degassed solution of 2-bromo[4]dendralene (**14**) (1.1 g, 20% (w/w) solution in THF, 5.7 mmol, 2.1 mol equiv) was added and the resulting solution was diluted with degassed THF (37 mL). A degassed solution of aqueous KOH (4.6 mL, 3.0 M, 14 mmol, 5.0 mol equiv) was then added *via* syringe pump over 30 minutes. The reaction mixture was stirred for a further 30 minutes at 25 °C with the exclusion of light. The resulting solution was poured into ice-cold water (0.14 L) and diluted with ice-cold petroleum ether (30–40 °C) (70 mL). The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 70 mL). The organic phases were combined, washed with brine (0.15 L), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, at 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave slightly impure [10]dendralene (**8**) as a colorless oil (0.21 g, 0.80 mmol, 29%) and alkyne **34** as a by-product (45 mg, 0.17 mmol, 6%). The impure [10]dendralene (**8**) was combined with similar material from multiple runs and was further purified by reversed phase flash column chromatography (C18 SiO_2, MeCN:H_2O (80:20)). **R*f*** 0.41 (petroleum ether (30–40 °C)); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.46 (ddd, J = 17.3, 10.5, 0.8 Hz, 2H), 5.35 (d, J = 1.9 Hz, 2H), 5.33 (dd, J = 17.3, 1.5 Hz, 2H), 5.32 (d, J = 2.1 Hz, 2H), 5.26 (d, J = 1.9 Hz, 2H), 5.25 (d, J = 2.0 Hz, 2H), 5.17 – 5.14 (m, 4H), 5.14 – 5.10 (m, 6H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 148.1 (2 × C), 147.9 (2 × C), 147.6 (2 × C), 147.2 (2 × C), 137.9 (2 × CH), 117.9 (2 × CH_2), 117.8 (2 × CH_2), 117.5 (2 × CH_2), 117.4 (2 × CH_2), 116.3 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 3091, 3008, 2925, 2854, 1580, 987, 901 cm^{-1}; **LRMS** (70 eV, EI): m/z (%): 262 ([M]$^{+•}$, 33%), 261 (48), 247 (98), 233 (52), 205

(74), 191 (75), 165 (100); **HRMS** (EI): calc for $C_{20}H_{21}$ $[M]^{+\bullet}$: 261.1643; found 261.1642; UV/Vis (hexane) λ_{max} 215 nm ($\varepsilon = 55{,}100\ M^{-1}cm^{-1}$).

Via a double Negishi cross-coupling reaction;



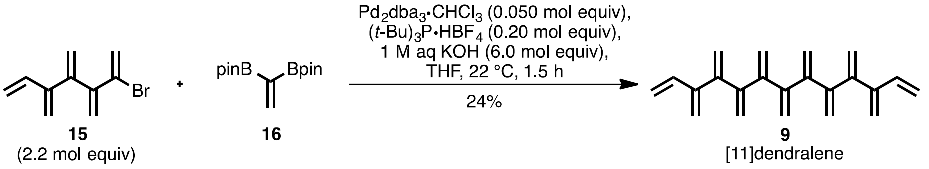
A 2-necked round bottomed flask was charged with 2-bromo[4]dendralene (**14**) (0.11 g, 1.3 M solution in THF, 0.59 mmol, 2.5 mol equiv) in THF (4.0 mL) and *n*-BuLi (0.44 mL, 1.5 M solution in hexane, 0.65 mmol, 2.8 mol equiv) was added dropwise over 3 minutes at –78 °C. The orange mixture was stirred for 20 minutes at –78 °C and then a solution of $ZnBr_2$ (0.71 mL, 1.3 M solution in THF, 0.89 mmol, 3.8 mol equiv) was added dropwise over 4 minutes. The reaction mixture was stirred for 5 minutes at –78 °C, then allowed to warm to ambient room temperature and stirred for 20 minutes. $Pd(PPh_3)_4$ (27 mg, 24 μmol, 0.10 mol equiv) was then added followed by addition of 2,3-dibromo-1,3-butadiene (**23**) (50 mg, 0.24 mmol, 1.0 mol equiv) in one portion and the mixture was stirred at 22 °C for 2.5 hours with the exclusion of light. The reaction mixture was poured into ice-cold water (30 mL), diluted with ice-cold petroleum ether (30–40 °C) (30 mL) and a solution of aqueous HCl (3.0 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 15 mL). The organic phases were combined, washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave [10]dendralene (**8**) as a colorless oil (23 mg, 0.86 mmol, 36%) and [8]dendralene (**6**) (5.0 mg, 0.24 mmol, 8%) as a by-product.



34

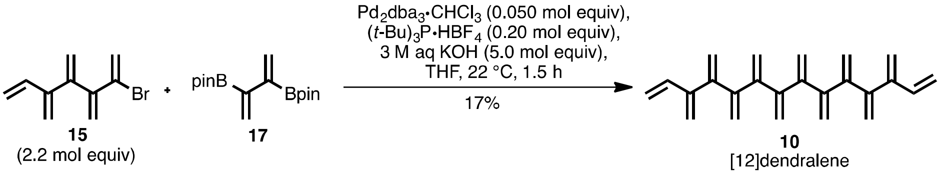
[10]Dendralene by-product **34:** **R$_f$** 0.19 (petroleum ether (30–40 °C)); **^{1}H NMR** (800 MHz, CDCl$_3$) δ 6.41 (dd, J = 17.4, 10.5 Hz, 2H), 5.41 (s, 2H), 5.32 (d, J = 1.4 Hz, 2H), 5.22 (d, J = 2.1 Hz, 2H), 5.20 (s, 2H), 5.17 (dd, J = 17.5, 1.4 Hz, 2H), 5.08 (d, J = 10.8 Hz, 2H), 5.07 – 5.05 (m, 4H), 3.20 (s, 4H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 148.1 (2 × C), 147.2 (2 × C), 141.6 (2 × C), 137.8 (2 × CH), 117.9 (2 × CH$_2$), 116.6 (2 × CH$_2$), 116.5 (2 × CH$_2$), 114.5 (2 × CH$_2$), 80.2 (2 × C), 23.9 (2 × CH$_2$) ppm; **IR** (thin film): ν_{max} = 3089, 3005, 2964, 2924, 2201, 898 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 262 ([M]$^{+\bullet}$, 2%), 261 (7), 247 (21), 131 (65), 105 (31), 91 (100); **HRMS** (EI): calc for C$_{20}$H$_{21}$ [M]$^{+\bullet}$: 261.1643; found 261.1640.

[11]Dendralene (9)



A 2-necked round bottomed flask was charged with Pd$_2$dba$_3$•CHCl$_3$ (35 mg, 33 µmol, 0.050 mol equiv), (t-Bu)$_3$P•HBF$_4$ (39 mg, 0.13 mmol, 0.20 mol equiv), and 1,1-bis(pinacolatoboryl)ethene (**16**)^9 (0.19 g, 0.67 mmol, 1.0 mol equiv) and the reaction flask was evacuated and refilled with argon three times. A degassed solution of 2-bromo[5]dendralene (**15**) (0.31 g, 20% (w/w) solution in THF, 1.5 mmol, 2.2 mol equiv) was added and the resulting solution was diluted with THF (6.9 mL). A degassed solution of aqueous KOH (4.0 mL, 1.0 M, 4.0 mmol, 6.0 mol equiv) was then added *via* syringe pump over 1 hour. After the addition was complete, the reaction mixture was stirred for a further 30 minutes at 22 °C with the exclusion of light. The resulting mixture was poured into ice-cold water (15 mL), diluted with ice-cold petroleum ether (30–40 °C) (15 mL), and a solution of aqueous HCl (3.0 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (30–40 °C) (2 × 15 mL). The organic phases were combined, washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, 15 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave [11]dendralene (**9**) as a colorless oil (46 mg, 0.16 mmol, 24%). **R_f** 0.39 (petroleum ether (30–40 °C)); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.46 (ddd, J = 17.3, 10.6, 0.8 Hz, 2H), 5.37 – 5.33 (m, 4H), 5.29 (d, J = 2.0 Hz, 2H), 5.25 (d, J = 2.0 Hz, 2H), 5.23 (d, J = 1.3 Hz, 4H), 5.22 (d, J = 2.0 Hz, 2H), 5.20 (dd, J = 2.0, 0.7 Hz, 2H), 5.17 (dd, J = 1.8, 0.7 Hz, 2H), 5.14 – 5.10 (m, 4H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 148.3 (C), 148.2 (2 × C), 147.9 (2 × C), 147.5 (2 × C), 147.3 (2 × C), 137.7 (2 × CH), 118.0 (2 × CH_2), 117.8 (2 × CH_2), 117.7 (CH_2), 117.3 (2 × CH_2), 117.2 (2 × CH_2), 116.3 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 3091, 3007, 2971, 2925, 2854, 1579, 988, 901 cm^{-1}; LRMS (70 eV, EI): *m/z* (%): 288 ($[M]^{+\bullet}$, 11%), 287 (29), 273 (56), 259 (37), 217 (58), 165 (100); **HRMS** (EI): calc for $C_{22}H_{24}$ $[M]^{+\bullet}$: 288.1878; found 288.1877; **UV/Vis** (hexane) λ_{max} 216 nm (ε = 57,600 M^{-1}cm^{-1}).

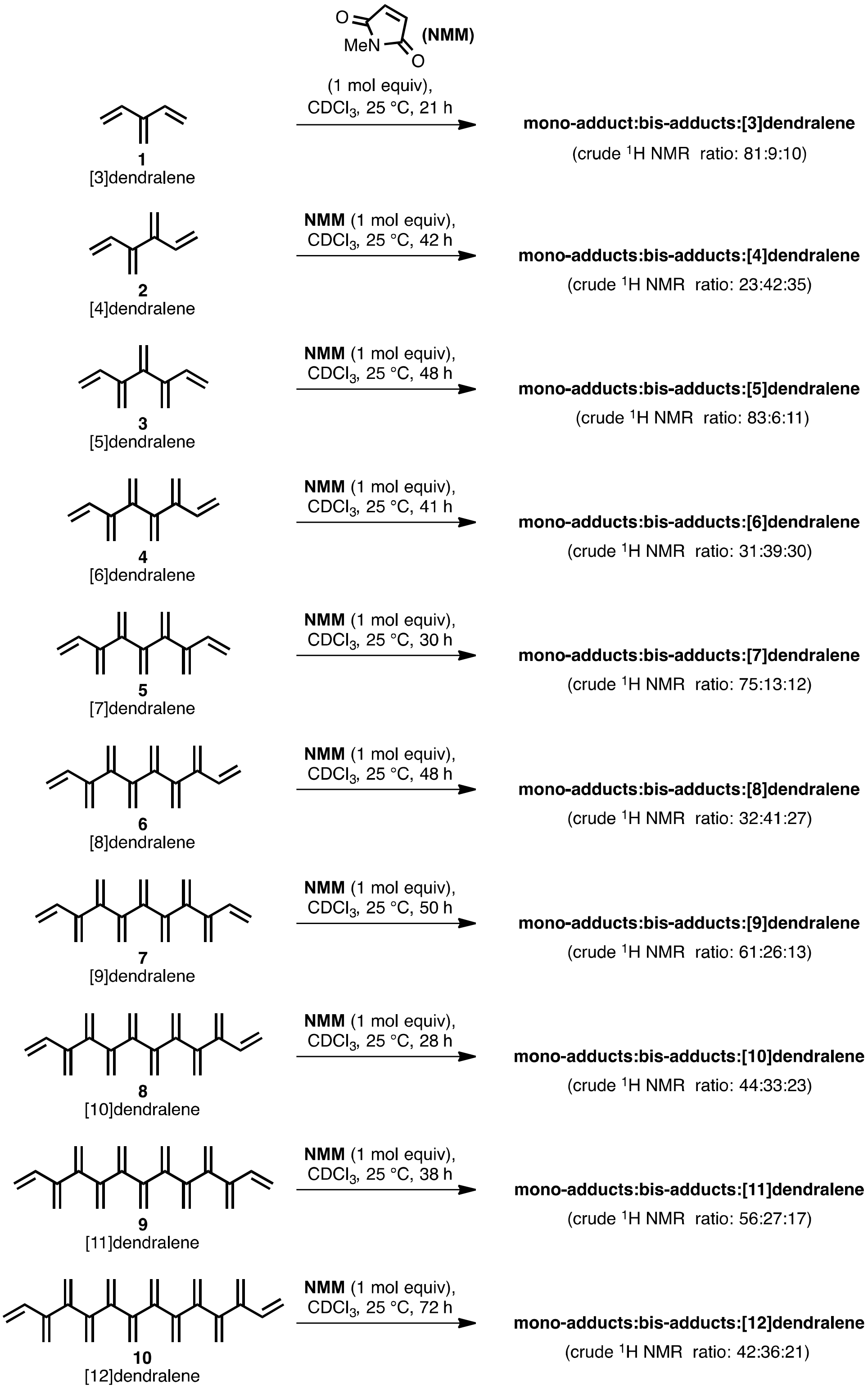
[12]Dendralene (10)



A 2-necked round bottomed flask was charged with Pd_2dba_3•$CHCl_3$ (39 mg, 38 µmol, 0.050 mol equiv), (t-Bu)$_3$P•HBF_4 (44 mg, 0.15 mmol, 0.20 mol equiv), and 2,3-bis(pinacolatoboryl)1,3-butadiene (**17**)[11] (0.23 g, 0.75 mmol, 1.0 mol equiv) and the reaction flask was evacuated and refilled with argon three times. A degassed solution of 2-bromo[5]dendralene (**15**) (0.35 g, 26% (w/w) solution in THF, 1.7 mmol, 2.2 mol equiv) was added and the resulting solution was diluted with degassed THF (4.0 mL). A degassed solution of aqueous KOH (1.3 mL, 3.0 M, 3.8 mmol, 5.0 mol equiv) was then added *via* syringe pump over 1 hour. The reaction solution was stirred for a further 30 minutes at 22 °C with the exclusion of light. The resulting reaction mixture was poured into ice-cold water (15 mL), diluted with ice-cold petroleum ether (30–40 °C) (15 mL) and a solution of aqueous HCl (5.0 mL, 1.0 M) was added. The organic phase was separated and the aqueous phase was then extracted with petroleum ether (30–40 °C) (2 × 15 mL). The organic phases were combined, washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 mbar, 15 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave [12]dendralene (**10**) as a colorless oil (39 mg, 0.12 mmol, 17%). **R_f** 0.34 (petroleum ether (30–40 °C)); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.46 (ddd, J = 17.3, 10.6, 0.7 Hz, 2H), 5.36 (d, J = 1.9 Hz, 2H), 5.33 (dd, J = 17.4, 1.5 Hz, 2H), 5.33 (d, J = 2.0 Hz, 2H), 5.31 (d, J = 1.9 Hz, 2H), 5.26 (d, J = 2.0 Hz, 2H), 5.25 (d, J = 2.0 Hz, 2H), 5.20 – 5.18 (m, 2H), 5.18 – 5.17 (m, 2H), 5.17 – 5.16 (m, 2H), 5.15 – 5.14 (m, 2H), 5.13 (m, 2H), 5.11 – 5.10 (m, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ 148.2 (2 × C), 148.1 (2 × C), 148.0 (2 × C), 147.6 (2 × C), 147.2 (2 × C), 137.8 (2 × CH), 117.9 (2 × CH_2), 117.9 (2 × CH_2), 117.8 (2 × CH_2), 117.4 (2 × CH_2), 117.4 (2 × CH_2), 116.3 (2 × CH_2) ppm; **IR** (thin film): ν_{max} = 3091, 3007, 2960, 2925, 2854, 1578, 987, 900 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 314 ($[M]^{+\bullet}$, 9%), 313 (20), 299 (52), 285 (30), 271 (40), 243 (41), 229 (46), 215 (45), 105 (33), 91 (78), 77 (72); **HRMS** (EI): calc for $C_{24}H_{26}$ $[M]^{+\bullet}$: 314.2035; found 314.2036; **UV/Vis** (hexane) λ_{max} 215 nm (ε = 63,600 $M^{-1}cm^{-1}$)

3. General Experimental Procedure for the Diels–Alder Reaction Between [*n*]Dendralene and 1 mol equiv of *N*-methylmaleimide (NMM)

A vial was charged with [*n*]dendralene (1.0 mol equiv), diluted with $CDCl_3$ and the solution transferred to a Young's tap NMR tube. The vial was then rinsed twice with $CDCl_3$ and these washings were added to the NMR tube. To this was added a solution of 1,4-dinitrobenzene (0.18 M solution in $CDCl_3$), *N*-methylmaleimide (NMM) (1 mol equiv, 0.38 M solution in $CDCl_3$) and diluted with $CDCl_3$ to give an overall concentration of 0.29 M with respect to [*n*]dendralene. The NMR tube was sealed and the reaction mixture left to stand at 25 °C. The reaction progression was monitored by ^{1}H NMR spectroscopy and the reaction was deemed complete when NMM could no longer be observed. The ratio of the corresponding products was calculated according to the ^{1}H NMR spectrum of the crude reaction mixture.



1 [3]dendralene — (1 mol equiv), $CDCl_3$, 25 °C, 21 h → **mono-adduct:bis-adducts:[3]dendralene** (crude ^1H NMR ratio: 81:9:10)

2 [4]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 42 h → **mono-adducts:bis-adducts:[4]dendralene** (crude ^1H NMR ratio: 23:42:35)

3 [5]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 48 h → **mono-adducts:bis-adducts:[5]dendralene** (crude ^1H NMR ratio: 83:6:11)

4 [6]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 41 h → **mono-adducts:bis-adducts:[6]dendralene** (crude ^1H NMR ratio: 31:39:30)

5 [7]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 30 h → **mono-adducts:bis-adducts:[7]dendralene** (crude ^1H NMR ratio: 75:13:12)

6 [8]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 48 h → **mono-adducts:bis-adducts:[8]dendralene** (crude ^1H NMR ratio: 32:41:27)

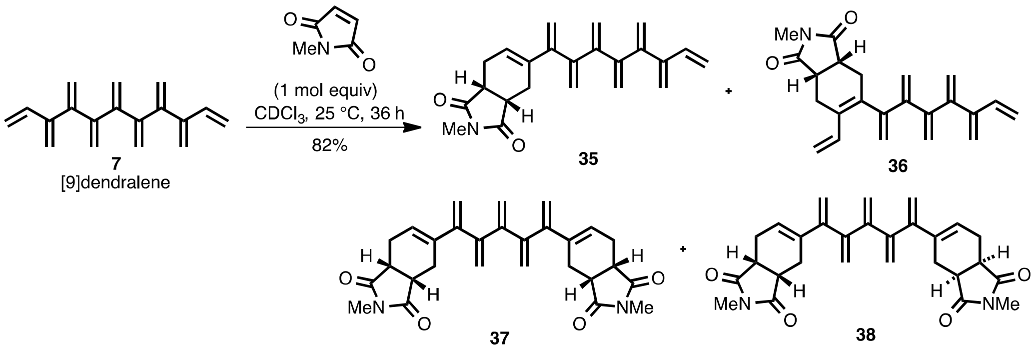
7 [9]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 50 h → **mono-adducts:bis-adducts:[9]dendralene** (crude ^1H NMR ratio: 61:26:13)

8 [10]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 28 h → **mono-adducts:bis-adducts:[10]dendralene** (crude ^1H NMR ratio: 44:33:23)

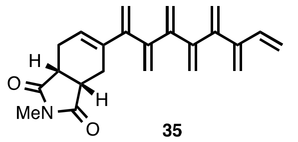
9 [11]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 38 h → **mono-adducts:bis-adducts:[11]dendralene** (crude ^1H NMR ratio: 56:27:17)

10 [12]dendralene — **NMM** (1 mol equiv), $CDCl_3$, 25 °C, 72 h → **mono-adducts:bis-adducts:[12]dendralene** (crude ^1H NMR ratio: 42:36:21)

Reaction between [9]dendralene (7) and 1 mol equiv of *N*-methylmaleimide.

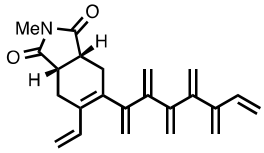


A Young's tap NMR tube was charged with [9]dendralene (**7**) (14 mg, 57 μmol, 1.0 mol equiv), NMM (6.3 mg, 57 μmol, 1.0 mol equiv), a solution of durene (0.40 mL, 96 mM solution in $CDCl_3$) and $CDCl_3$ (0.74 mL) and left at 25 °C for 36 hours. Purification by flash column chromatography (SiO_2, EtOAc:hexane (20:80 to 40:60)) gave a mixture of mono-adducts **35** and **36** (9.9 mg, 29 μmol, 69%) and a mixture of bis-adducts **37** and **38** (2.5 mg, 5.5 μmol, 13%). The experiment was repeated and the crude mixtures of the mono-adducts and bis-adducts were combined. The two mono-adducts **35** and **36** were separated by preparative HPLC (Agilent Prep-C18 Cartridge column, 5μm, 21.2 × 150 mm, eluting with $MeCN:H_2O$ (65:35), flow rate = 17 mL/minute) for characterization to give terminal mono-adduct **35** as a colorless oil (t_R = 19.3 minutes, 9.7 mg) and internal mono-adduct **36** as a colorless oil (t_R = 18.1 minutes, 2.6 mg). The two bis-adducts **37** and **38** were also separated by preparative HPLC (Agilent Prep-C18 Cartridge column, 5μm, 21.2 × 150 mm, eluting with $MeOH:H_2O$ (65:35), flow rate = 17 mL/minute) for characterization to give terminal-terminal bis-adduct **37** *or* **38** as a colorless oil (t_R = 31.5 minutes, 1.6 mg) and an impure fraction of the other diastereomer of the terminal-terminal bis-adduct **37** *or* **38** as a colorless oil (t_R = 30.0 minutes, 1.7 mg).



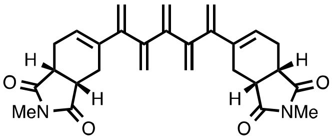
35

Mono-adduct **35**: $\mathbf{R_f}$ 0.57 (EtOAc:$CHCl_3$, 20:80); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.43 (dd, J = 17.3, 10.6 Hz, 1H), 5.92 (ddd, J = 6.6, 3.8, 2.2 Hz, 1H), 5.30 (d, J = 2.0 Hz, 1H), 5.27 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 5.24 (s, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 5.22 (d, *J* = 1.9 Hz, 1H), 5.10 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.07 (s, 1H), 5.05 (s, 1H), 5.04 (s, 1H), 5.03 (s, 1H), 5.01 (d, *J* = 1.9 Hz, 1H), 4.99 (s, 1H), 4.98 (s, 1H), 3.18 (ddd, *J* = 9.6, 7.1, 2.9 Hz, 1H), 3.07 (ddd, *J* = 9.3, 7.5, 2.6 Hz, 1H), 2.98 (dd, *J* = 15.0, 3.0 Hz, 1H), 2.90 (s, 3H), 2.69 (ddd, *J* = 15.7, 7.0, 2.7 Hz, 1H), 2.31 (ddt, *J* = 15.1, 7.2, 2.2 Hz, 1H), 2.29 – 2.23 (m, 1H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 180.0 (C), 179.7 (C), 148.3 (C), 147.9 (C), 147.7 (C), 147.7 (C), 147.5 (C), 147.1 (C), 137.9 (C), 137.9 (CH), 125.1 (CH), 118.0 (CH$_2$), 117.8 (CH$_2$), 117.7 (CH$_2$), 117.6 (CH$_2$), 117.2 (CH$_2$), 116.3 (CH$_2$), 114.1 (CH$_2$), 39.9 (CH), 38.9 (CH), 25.1 (CH$_2$), 25.0 (CH$_3$), 24.8 (CH$_2$) ppm; **IR** (thin film): ν_{max} = 3090, 2948, 2847, 1700, 902 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 347 ([M]$^{+\bullet}$, 100%), 332 (79), 319 (19), 261 (13), 235 (68), 221 (99); **HRMS** (EI): calc for C$_{23}$H$_{25}$NO$_2$ [M]$^{+\bullet}$: 347.1885; found 347.1885.

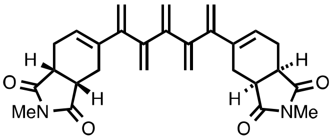


36

Mono-adduct **36**: **R**$_f$ 0.57 (EtOAc:CHCl$_3$, 20:80); **^{1}H NMR** (800 MHz, CDCl$_3$) δ 6.59 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.44 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.33 (d, *J* = 17.9 Hz, 1H), 5.32 (d, *J* = 1.8 Hz, 2H), 5.28 (d, *J* = 1.8 Hz, 1H), 5.27 – 5.24 (m, 2H), 5.12 – 5.08 (m, 4H), 5.07 – 5.05 (m, 1H), 5.03 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 1.8 Hz, 1H), 4.78 (s, 1H), 3.16 (ddd, *J* = 10.3, 6.8, 4.0 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.96 (dd, *J* = 15.4, 4.0 Hz, 1H), 2.95 (s, 3H), 2.62 (dd, *J* = 15.4, 3.7 Hz, 1H), 2.54 (dd, *J* = 15.4, 7.3 Hz, 1H), 2.37 (ddd, *J* = 15.1, 6.7, 1.5 Hz, 1H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 179.5 (C) 179.5 (C), 147.5 (C) 147.5 (C), 147.3 (C), 147.3 (C), 146.8 (C), 137.9 (CH), 137.3 (C), 134.2 (CH), 132.9 (C), 118.3 (CH$_2$), 118.0 (CH$_2$), 117.8 (CH$_2$), 117.7 (CH$_2$), 117.5 (CH$_2$), 116.3 (CH$_2$), 113.2 (CH$_2$), 39.8 (CH), 39.7 (CH), 30.3 (CH$_2$), 25.0 (CH$_3$), 23.2 (CH$_2$) ppm; **IR** (thin film): ν_{max} = 3091, 3055, 2925, 2853, 1700, 908 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 347 ([M]$^{+\bullet}$, 100%), 332 (50), 319 (38), 261 (10), 221 (72); **HRMS** (EI): calc for C$_{23}$H$_{25}$NO$_2$ [M]$^{+\bullet}$: 347.1885; found 347.1891.

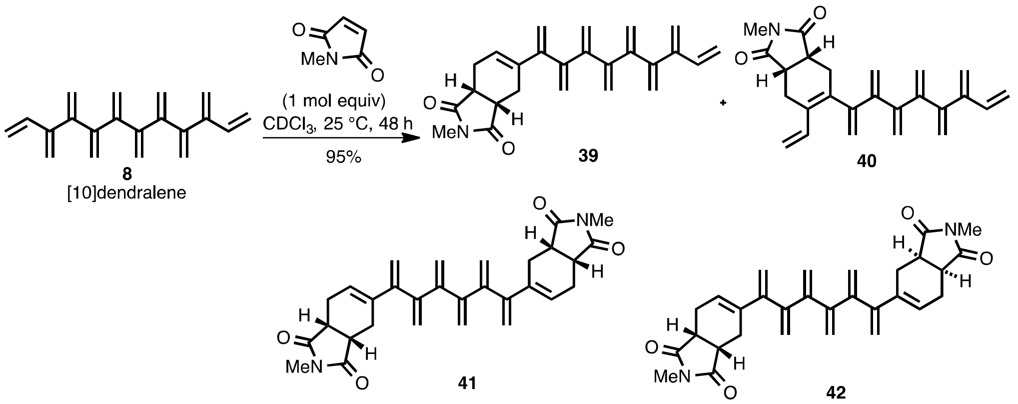

37

or

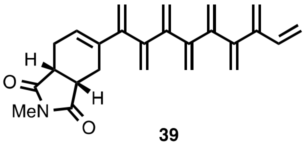

38

Bis-adduct **37** *or* **38**: **R_f** 0.32 (EtOAc:CHCl$_3$, 50:50); **^{1}H NMR** (800 MHz, CDCl$_3$) δ 5.86 (dt, J = 6.4, 3.0 Hz, 2H), 5.21 (s, 2H), 5.12 (s, 2H), 5.04 (s, 2H), 4.98 (s, 2H), 4.88 (s, 2H), 3.16 (td, J = 8.5, 7.6, 2.9 Hz, 2H), 3.07 (ddd, J = 9.6, 7.4, 2.6 Hz, 2H), 2.90 (s, 6H), 2.87 (dd, J = 15.1, 2.9 Hz, 2H), 2.68 (ddt, J = 15.9, 7.3, 1.8 Hz, 2H), 2.32 – 2.23 (m, 4H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 180.1 (2 × C), 179.7 (2 × C), 148.8 (2 × C), 147.8 (C), 147.7 (2 × C), 138.7 (2 × C), 125.0 (2 × CH), 118.0 (2 × CH$_2$), 117.4 (CH$_2$), 114.4 (2 × CH$_2$), 39.9 (2 × CH), 39.0 (2 × CH), 25.9 (2 × CH$_2$), 25.0 (2 × CH$_3$), 24.7 (2 × CH$_2$) ppm; **IR** (thin film): ν_{max} = 3092, 3055, 2924, 2850, 1698, 906 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 458 ([M]$^{+\bullet}$, 100%), 443 (18), 372 (4), 346 (34), 332 (35); **HRMS** (EI): calc for $C_{28}H_{30}N_2O_4$ [M]$^{+\bullet}$: 458.2206; found 458.2208.

Reaction between [10]dendralene (8) and 1 mol equiv of *N*-methylmaleimide.

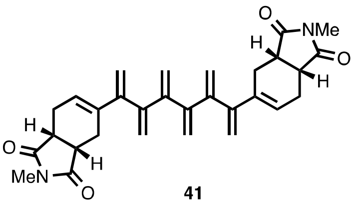


A Young's tap NMR tube was charged with [10]dendralene (**8**) (11 mg, 40 μmol, 1.0 mol equiv), NMM (4.4 mg, 40 μmol, 1.0 mol equiv), durene (0.40 mL, 96 mM solution in CDCl$_3$) and CDCl$_3$ (0.40 mL) and left at 25 °C for 48 hours. Purification by flash column chromatography (SiO$_2$, EtOAc:hexane (20:80 to 40:60)) gave a mixture of mono-adducts **39** and **40** (5.8 mg, 16 μmol, 57%) and a mixture of bis-adducts **41** and **42** (5.0 mg, 10 μmol, 38%). The experiment was repeated and the crude mixtures of the mono-adducts and bis-adducts were combined. The two mono-adducts **39** and **40** were separated by preparative HPLC (Agilent Prep-C18 Cartridge column, 5 μm, 21.2 × 150 mm, eluting with MeCN:H_2O (65:35), flow rate = 17 mL/minute) for characterization to give terminal mono-adduct **39** as a colorless oil (t_R = 29.2 minutes, 1.0 mg) and an impure fraction of suspected internal mono-adduct **40** (t_R = 27.6 minutes, <0.5 mg) as a colorless oil. The two bis-adducts **41** and **42** were separated by preparative HPLC (Agilent Prep-C18 Cartridge column, 5 μm, 21.2 × 150 mm, eluting with MeOH:H_2O (65:35), flow rate = 17 mL/minute) for characterization to give the terminal-terminal bis-adduct **41** *or* **42** as a colorless oil (t_R = 27.1 minutes, 7.4 mg) and an impure fraction of the other diastereomeric terminal-terminal bis-adduct **41** *or* **42** as a colorless oil (t_R = 23.4 minutes, 7.3 mg).



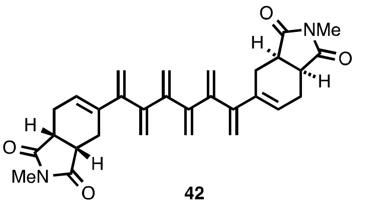
39

Mono-adduct **39**: **R*f*** 0.71 (EtOAc:$CHCl_3$, 30:70); **^{1}H NMR** (800 MHz, $CDCl_3$) *δ* 6.43 (ddd, *J* = 17.4, 10.6, 2.1 Hz, 1H), 5.94 – 5.89 (m, 1H), 5.34 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.29 (d, *J* = 2.0 Hz, 1H), 5.27 (d, *J* = 2.0 Hz, 1H), 5.24 (d, *J* = 1.9 Hz, 1H), 5.23 (s, 1H), 5.20 (s, 1H), 5.18 (d, *J* = 1.4 Hz, 1H), 5.18 – 5.16 (m, 2H), 5.12 (d, *J* = 10.9 Hz, 1H), 5.10 (d, *J* = 1.4.0 Hz, 1H), 5.09 (s, 1H), 5.05 (s, 2H), 5.03 (s, 1H), 4.99 (d, *J* = 2.0 Hz, 1H), 3.17 (ddd, *J* = 9.7, 7.2, 3.1 Hz, 1H), 3.07 (ddd, *J* = 9.3, 7.6, 2.7 Hz, 1H), 2.94 (dd, *J* = 15.3, 3.0 Hz, 1H), 2.90 (s, 3H), 2.68 (ddd, *J* = 15.7, 6.9, 2.8 Hz, 1H), 2.33 (ddt, *J* = 15.1, 7.1, 2.3 Hz, 1H), 2.29 – 2.24 (m, 1H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) *δ* 180.1 (C), 179.7 (C), 148.6 (C), 148.2 (C), 148.1 (C), 147.8 (C), 147.7 (C), 147.3 (C), 147.2 (C), 138.5 (C), 137.5 (CH), 125.1 (CH), 118.1 (CH_2), 117.9 (CH_2), 117.7 (CH_2), 117.5 (CH_2), 117.3 (CH_2), 117.1 (CH_2), 116.4 (CH_2), 114.2 (CH_2), 39.9 (CH), 39.0 (CH), 25.5 (CH_2), 25.0 (CH_3), 24.7 (CH_2) ppm; **IR** (thin film): ν_{max} = 3090, 2920, 2850, 1701, 903 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 373 ($[M]^{+\bullet}$, 78%), 359 (28), 358 (100); **HRMS** (EI): calc for $C_{25}H_{27}NO_2$ $[M]^{+\bullet}$: 373.2042; found 373.2040.



41

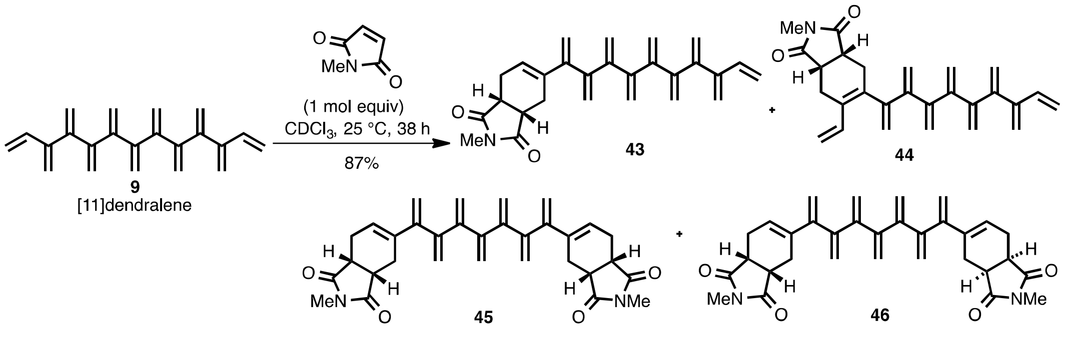
or



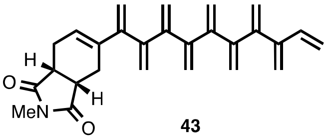
42

Bis-adduct **41** *or* **42**: $\mathbf{R}_f$ 0.32 (EtOAc:CHCl$_3$, 30:70); ^{1}H **NMR** (800 MHz, CDCl$_3$) δ 5.91 – 5.86 (m, 2H), 5.25 (s, 2H), 5.18 (d, J = 2.0 Hz, 2H), 5.00 (d, J = 1.2 Hz, 2H), 4.99 (d, J = 1.9 Hz, 2H), 4.95 (t, J = 1.6 Hz, 2H), 4.91 (t, J = 1.6 Hz, 2H), 3.18 (ddd, J = 9.0, 7.1, 2.9 Hz, 2H), 3.07 (ddd, J = 9.0, 7.5, 2.7 Hz, 2H), 2.97 (dd, J = 15.0, 3.0 Hz, 2H), 2.90 (s, 6H), 2.68 (ddd, J = 15.7, 7.0, 2.7 Hz, 2H), 2.30 (ddq, J = 14.1, 7.0, 2.4 Hz, 2H), 2.28 – 2.23 (m, 2H) ppm; ^{13}**C NMR** (200 MHz, CDCl$_3$) δ 180.1 (2 × C), 179.7 (2 × C), 148.1 (2 × C), 147.9 (2 × C), 147.5 (2 × C), 138.4 (2 × C), 125.1 (2 × CH), 117.6 (2 × CH$_2$), 117.6 (2 × CH$_2$), 114.1 (2 × CH$_2$), 39.9 (2 × CH), 38.9 (2 × CH), 25.1 (2 × CH$_3$), 25.0 (2 × CH$_2$), 24.8 (2 × CH$_2$) ppm; **IR** (thin film): $\nu_{\max}$ = 3090, 2949, 2848, 1698, 904 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 484 ([M]$^{+\bullet}$, 100%), 470 (11), 469 (31); **HRMS** (EI): calc for C$_{30}$H$_{32}$N$_2$O$_4$ [M]$^{+\bullet}$: 484.2362; found 484.2364.

Reaction between [11]dendralene (9) and 1 mol equiv of *N*-methylmaleimide.

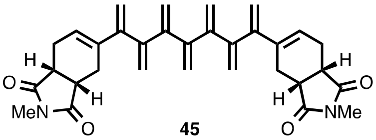


A Young's tap NMR tube was charged with [11]dendralene (**9**) (20 mg, 68 μmol, 1.0 mol equiv), NMM (0.16 mL, 0.38 M solution in CDCl$_3$, 68 μmol, 1.0 mol equiv), CDCl$_3$ (1.1 mL) and left at 25 °C for 38 hours. Purification by flash column chromatography (SiO$_2$, EtOAc:CHCl$_3$ (5:95)) gave a mixture of mono-adducts **43** and **44** (11 mg, 27 μmol, 48%) as a colorless oil and a mixture of diastereomeric bis-adducts **45** and **46** (11 mg, 22 μmol, 39%) as a colorless oil. Mono-adduct **43** was characterized as a mixture with the suspected internal mono-adduct **44** (^{1}H NMR ratio of **43**:**44**; 85:15) and the bis-adducts **45** and **46** characterized as a mixture of diastereomers.



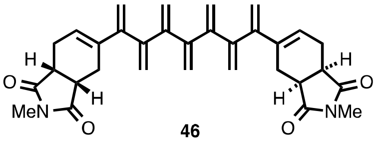
43

Mono-adduct **43**: **R*f*** 0.68 (EtOAc:CHCl$_3$, 20:80); **^{1}H NMR** (800 MHz, CDCl$_3$) δ 6.44 (dd, J = 17.4, 10.6 Hz, 1H), 5.94 – 5.90 (m, 1H), 5.32 – 5.28 (m, 4H), 5.25 (d, J = 2.0 Hz, 1H), 5.24 (s, 2H), 5.20 (d, J = 2.0 Hz, 1H), 5.13 – 5.09 (m, 4H), 5.08 (s, 2H), 5.04 (s, 1H), 5.02 (d, J = 1.9 Hz, 1H), 5.01 – 4.99 (m, 2H), 3.17 (dtd, J = 9.0, 6.6, 6.0, 3.0 Hz, 1H), 3.07 (ddd, J = 9.4, 7.5, 2.7 Hz, 1H), 2.98 (dd, J = 15.0, 3.0 Hz, 1H), 2.90 (s, 3H), 2.69 (ddd, J = 15.7, 7.0, 2.8 Hz, 1H), 2.32 (ddt, J = 15.0, 7.2, 2.3 Hz, 1H), 2.29 – 2.24 (m, 1H) ppm; **^{13}C NMR** (200 MHz, CDCl$_3$) δ 180.1 (C), 179.7 (C), 148.3 (C), 148.0 (C), 147.9 (C) (two coincident signals), 147.8 (C), 147.7 (C), 147.6 (C), 147.2 (C), 138.4 (C), 137.9 (CH), 125.1 (CH), 117.9 (CH$_2$), 117.8 (CH$_2$) (two coincident signals), 117.7 (CH$_2$), 117.6 (CH$_2$), 117.5 (CH$_2$), 117.3 (CH$_2$), 116.3 (CH$_2$), 114.1 (CH$_2$), 39.9 (CH), 38.9 (CH), 25.2 (CH$_2$), 25.0 (CH$_3$), 24.8 (CH$_2$) ppm; **IR** (thin film): ν_{max} = 3090, 2948, 2848, 1700, 903 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 399 ([M]$^{+\bullet}$, 94%), 384 (94), 370 (30), 356 (26), 273 (52), 91 (100); **HRMS** (EI): calc for C$_{27}$H$_{29}$NO$_2$ [M]$^{+\bullet}$: 399.2198; found 399.2198.



45

and



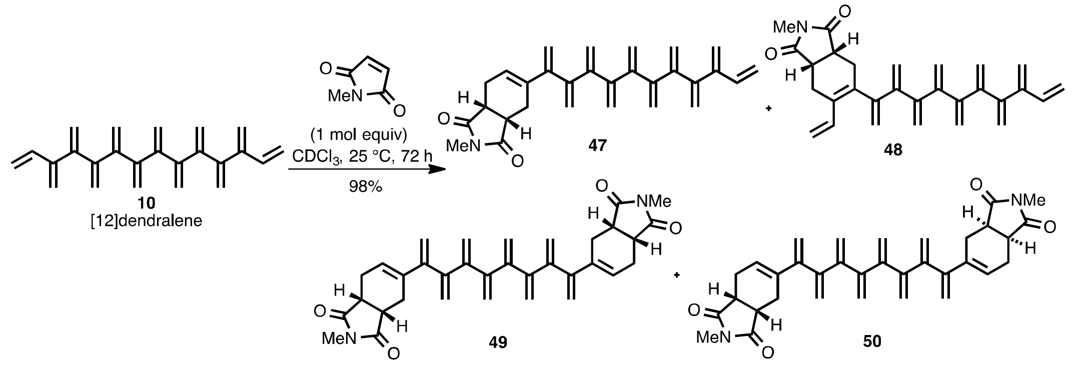
46

Bis-adducts[ii] **45** and **46**: **R*f*** 0.35 (EtOAc:CHCl$_3$, 50:50) **^{1}H NMR** (800 MHz, CDCl$_3$) δ 5.91 – 5.87 (m, 2H), 5.24 – 5.23 (m, 2H), 5.19 – 5.16 (m, 4H), 5.02 (d, J = 3.2 Hz, 4H), 4.99 – 4.97 (m, 2H), 4.97 – 4.95 (m, 2H), 3.16 (ddt, J = 10.5, 6.4, 3.2 Hz, 2H), 3.08 –

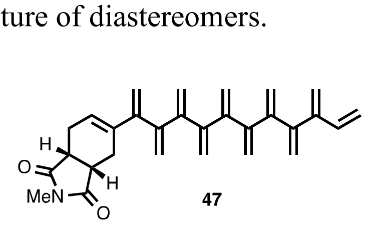
[ii] It is assumed that bis-adducts **45** and **46** are formed as a 1:1 mixture of diastereomers, however, this can not be clearly observed by ^{1}H NMR (see ^{1}H NMR spectrum on page S77), presumably due to the large distance between the two pairs of stereocenters. On the other hand, splitting of a few of the ^{13}C NMR signals was observed and all peaks observed are reported (see ^{13}C spectrum on page S78 for more details).

3.04 (m, 2H), 2.94 – 2.91 (m, 2H), 2.90 (s, 6H), 2.66 (ddd, *J* = 15.6, 7.0, 2.8 Hz, 2H), 2.32 (ddt, *J* = 15.0, 7.2, 2.2 Hz, 2H), 2.29 – 2.23 (m, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) δ ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.0 (C), 179.7 (C), 148.6 (C), 148.6 (C), 148.0 (C), 147.7 (C), 138.6 (C), 138.5 (C), 125.1 (CH), 118.0 (CH_2), 117.9 (CH_2), 117.5 (CH_2), 114.3 (CH_2), 39.9 (CH), 39.0 (CH), 39.0 (CH), 25.6 (CH_2), 25.0 (CH_3), 24.7 (CH_2) ppm; **LRMS** (70 eV, EI): *m/z* (%): 510 ($[M]^{+\bullet}$, 9%), 495 (3), 468 (3), 452 (3), 446 (94), 268 (23), 183 (100); **HRMS** (EI): calc for $C_{32}H_{34}N_2O_4$ $[M]^{+\bullet}$: 510.2519; found 510.2519.

Reaction between [12]dendralene (10) and 1 mol equiv of *N*-methylmaleimide.



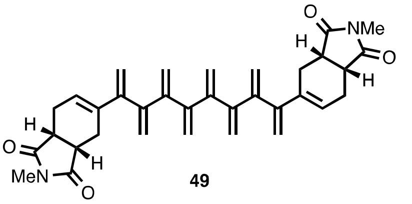
A Young's tap NMR tube was charged with [12]dendralene (**10**) (20 mg, 62 μmol, 1.0 mol equiv), NMM (0.15 mL, 0.38 M solution in $CDCl_3$, 62 μmol, 1.0 mol equiv), $CDCl_3$ (0.90 mL) and left at 25 °C for 72 hours. Purification by flash column chromatography (SiO_2, EtOAc:$CHCl_3$ (5:95)) gave a mixture of mono-adducts **47** and **48** (11 mg, 25 μmol, 52%) as a colorless oil and a mixture of diastereomeric bis-adducts **49** and **50** (12 mg, 22 μmol, 46%) as a colorless oil. Mono-adduct **47** was characterized as a mixture with the suspected internal mono-adduct **48** (^{1}H NMR ratio of **47**:**48**; 93:7) and the bis-adducts **49** and **50** characterized as a mixture of diastereomers.



47

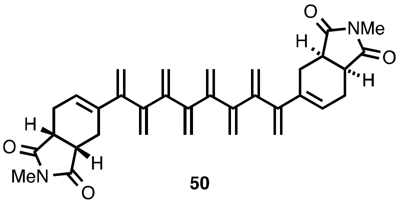
Mono-adduct **47**: **R*f*** 0.62 (EtOAc:CH_2Cl_2, 20:80); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.44 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.94 – 5.90 (m, 1H), 5.34 (dd, *J* = 17.4, 1.6 Hz, 1H), 5.32 –

5.28 (m, 3H), 5.25 – 5.19 (m, 5H), 5.18 – 5.09 (m, 7H), 5.06 – 5.04 (m, 2H), 5.02 (s, 1H), 5.00 (d, *J* = 2.0 Hz, 1H), 3.17 (ddd, *J* = 9.5, 7.0, 3.0 Hz, 1H), 3.07 (ddd, *J* = 9.3, 7.5, 2.8 Hz, 1H), 2.97 – 2.93 (m, 1H), 2.90 (s, 3H), 2.68 (ddd, *J* = 15.8, 6.9, 2.8 Hz, 1H), 2.33 (ddt, *J* = 15.1, 7.3, 2.4 Hz, 1H), 2.29 – 2.24 (m, 1H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) *δ* 180.1 (C), 179.7 (C), 148.5 (C), 148.3 (C) (two coincident signals), 148.0 (C), 147.9 (C), 147.8 (C) (two coincident signals), 147.4 (C), 147.3 (C), 138.5 (C), 137.6 (CH), 125.1 (CH), 118.0 (CH_2) (two coincident signals), 117.9 (CH_2), 117.8 (CH_2), 117.7 (CH_2), 117.6 (CH_2), 117.3 (CH_2), 117.2 (CH_2), 116.4 (CH_2), 114.2 (CH_2), 39.9 (CH), 38.9 (CH), 25.4 (CH_2), 25.0 (CH_3), 24.7 (CH_2) ppm; **IR** (thin film): ν_{max} = 3088, 2923, 1697, 902 cm^{-1}; **LRMS** (70 eV, EI): *m/z* (%): 425 ($[M]^{+\bullet}$, 80%), 410 (100), 397 (43), 396 (31), 313 (19); **HRMS** (EI): calc for $C_{29}H_{31}NO_2$ $[M]^{+\bullet}$: 425.2355; found 425.2347.



49

and



50

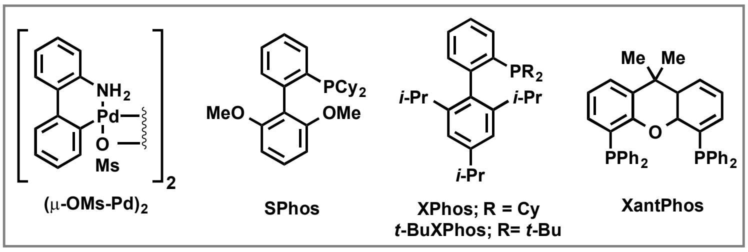
Bis-adducts[iii] **49** and **50**: **R*f*** 0.26 (EtOAc:CH_2Cl_2, 20:80); **^{1}H NMR** (800 MHz, $CDCl_3$) *δ* 5.94 – 5.89 (m, 2H), 5.28 (d, *J* = 2.6 Hz, 2H), 5.25 (d, *J* = 4.4 Hz, 2H), 5.19 (s, 1H), 5.18 (s, 1H), 5.03 (s, 4H), 5.01 (s, 2H), 4.99 (s, 2H), 4.96 (s, 2H), 3.20 – 3.15 (m, 2H), 3.08 (td, *J* = 8.2, 2.7 Hz, 2H), 2.98 (dt, *J* = 15.0, 3.1 Hz, 2H), 2.90 (s, 6H), 2.72 – 2.66 (m, 2H), 2.34 – 2.29 (m, 2H), 2.29 – 2.24 (m, 2H) ppm; **^{13}C NMR** (200 MHz, $CDCl_3$) *δ* 180.1 (C), 179.7 (C), 148.3 (C), 147.9 (C), 147.8 (C), 147.8 (C), 147.7 (C), 147.6 (C), 138.4 (C), 138.4 (C), 125.1 (CH), 125.1 (CH), 118.1 (CH_2), 118.0 (CH_2), 117.8 (CH_2), 117.7 (CH_2), 117.6 (CH_2), 114.1 (CH_2), 39.9 (CH), 39.0 (CH), 38.9 (CH), 25.2 (CH_2), 25.0 (CH_3), 24.8 (CH_2) ppm; **LRMS** (70 eV, EI): *m/z* (%): 536 ($[M]^{+\bullet}$, 34%), 521 (18), 451 (4), 424 (6), 410 (9), 372 (9), 294 (11), 268 (13), 183 (30), 165 (27), 84 (100); **HRMS** (EI): calc for $C_{34}H_{36}N_2O_4$ $[M]^{+\bullet}$: 536.2675; found 536.2686.

[iii] It is assumed that bis-adducts **49** and **50** are formed as a 1:1 mixture of diastereomers, however, this can not be clearly observed by ^{1}H NMR (see ^{1}H NMR spectrum on page S81), presumably due to the large distance between the two pairs of stereocenters. On the other hand, splitting of a few of the ^{13}C NMR signals was observed and all peaks observed are reported (see ^{13}C spectrum on page S82 for more details).

4. A Summary of Examined Conditions for the Syntheses of Higher Dendralenes

Various reaction conditions have been screened for the syntheses of higher dendralenes using different pre-catalysts/catalysts, ligands, bases in different solvents at various reaction temperatures as summarized below.

Pre-catalysts/Catalysts: $Pd_2dba_3•CHCl_3$, $Pd(OAc)_2$, $\{\mu\text{-}Pd(OMs)\}_2$, $Pd(dppf)Cl_2$.
Ligands: P(*t*-Bu)$_3$, SPhos, XPhos, *t*-BuXPhos, XantPhos, PPh_3.
Bases: KOH, KF, Cs_2CO_3, K_3PO_4, K_2CO_3, KOAc.
Solvents: THF, 1,4-dioxane, 1,2-dimethoxyethane, toluene.
Temperature: 25 °C, 40 °C, 60°C, 70 °C.



5. UV-visible Spectra Data of the [*n*]Dendralene Family

Dendralenes	**λ_{max} (nm)**	**ε ($M^{-1}cm^{-1}$)**
[3]dendralene	205 231	20600 14500
[4]dendralene	216	30500
[5]dendralene	215	25500
[6]dendralene	216	40600
[7]dendralene	216	37600
[8]dendralene	216	47800
[9]dendralene	216	46400
[10]dendralene	215	55100
[11]dendralene	216	57600
[12]dendralene	215	63600

Table S1. UV-visible spectra data of the [*n*]dendralene family (hexane, 25 °C).

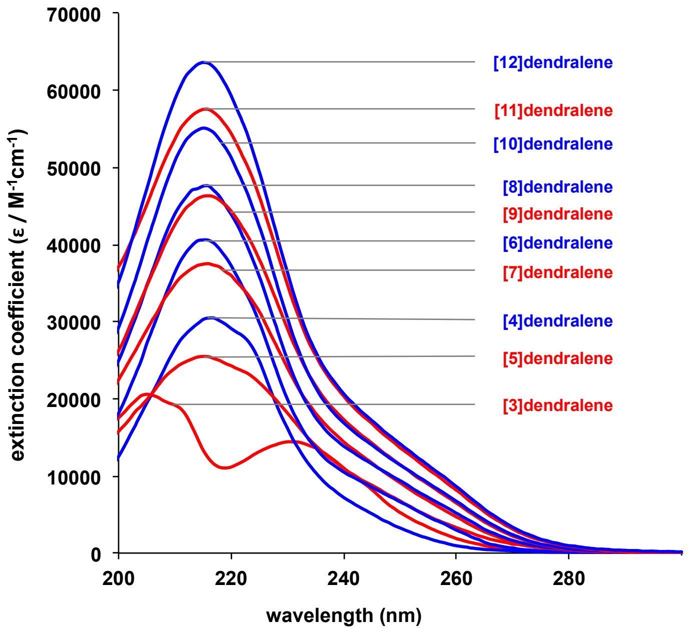


Figure S1. UV-visible spectra of the [*n*]dendralene family (hexane, 25 °C).

6. Diminishing Alternation of the [*n*]Dendralene Family in ^{1}H NMR Spectrum

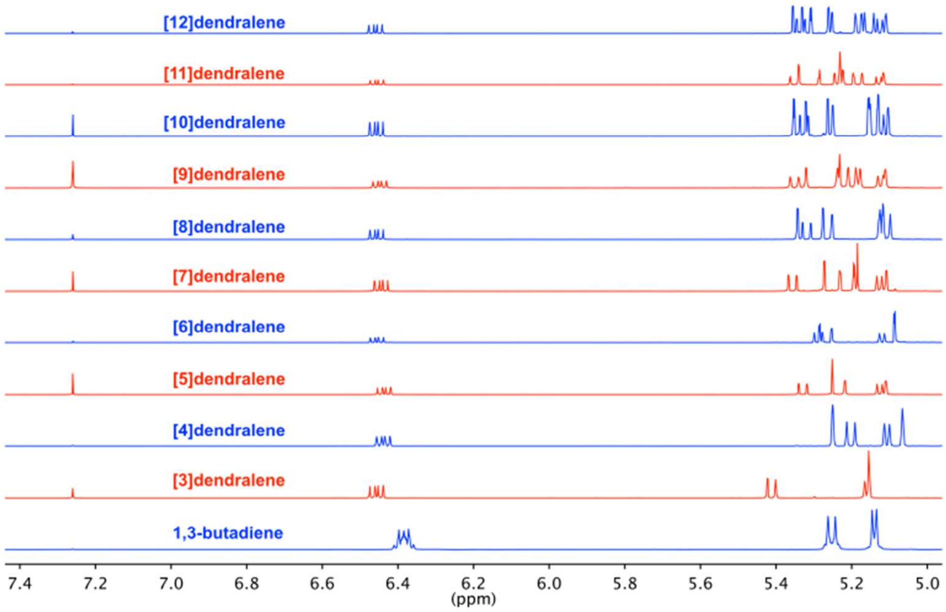


Figure S2. ^{1}H NMR spectra of the [*n*]dendralene family ($CDCl_3$, 25 °C).

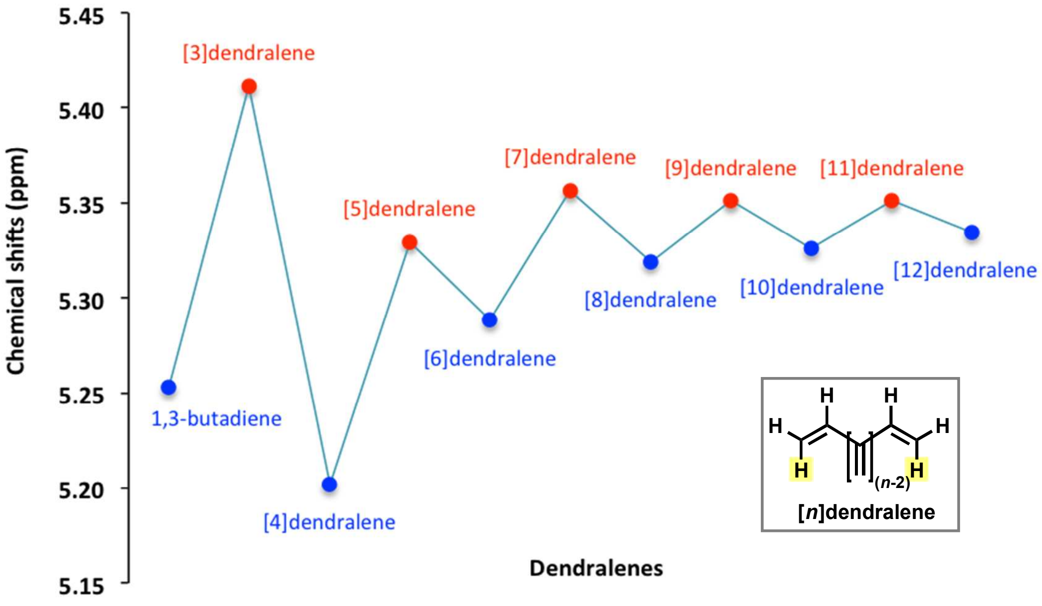


Figure S3. Diminishing alternation in ^{1}H chemical shift of terminal *Z*-C1*H* resonance in members of the [*n*]dendralene family ($CDCl_3$, 25 °C).

7. Diminishing Alternation of the [*n*]Dendralene Family in ^{13}C NMR Spectrum

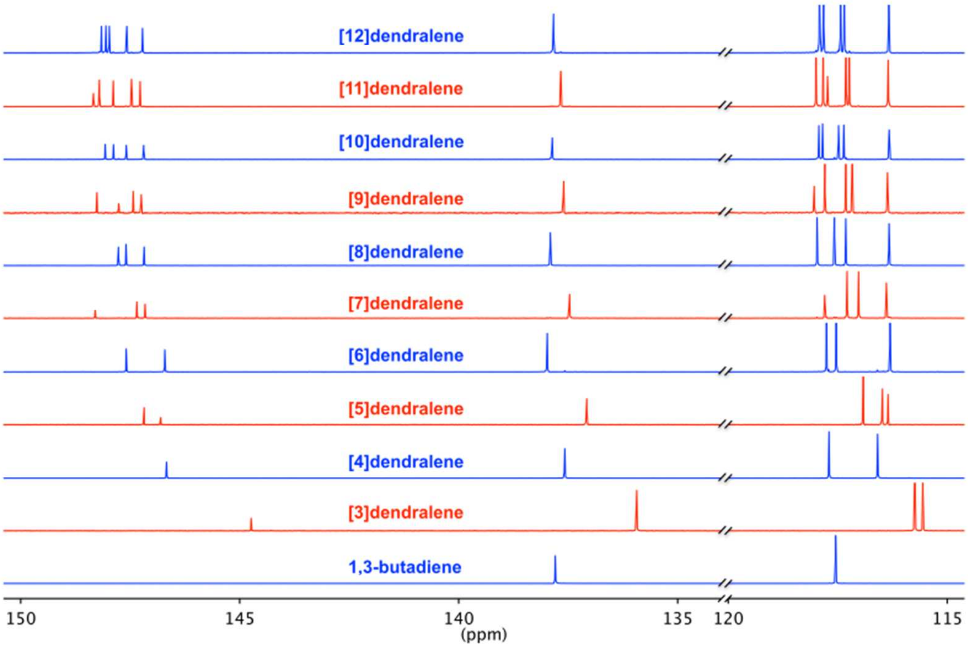


Figure S4. ^{13}C NMR spectra of the [*n*]dendralene family (CDCl$_3$, 25 °C).

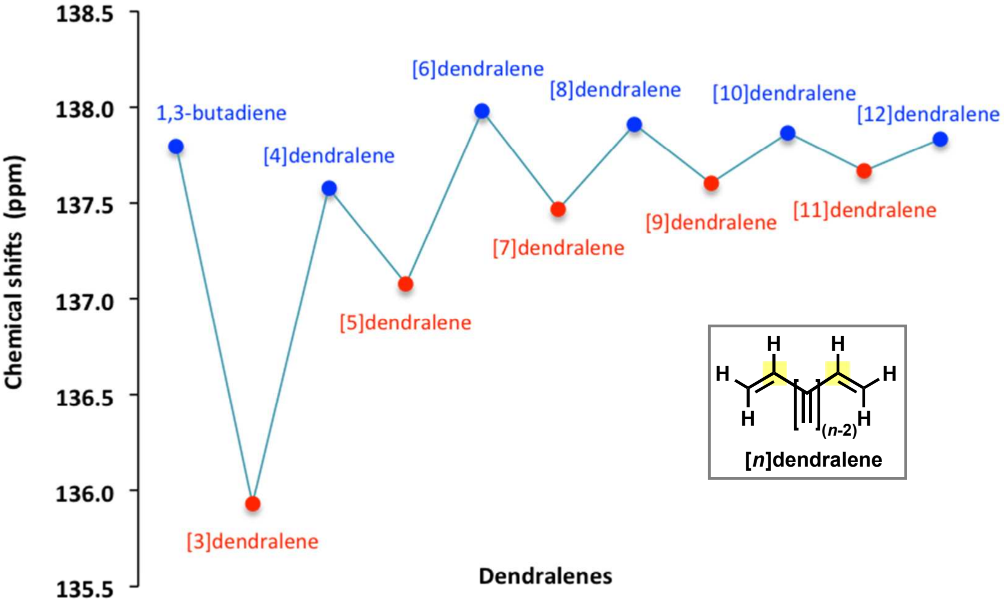
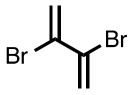
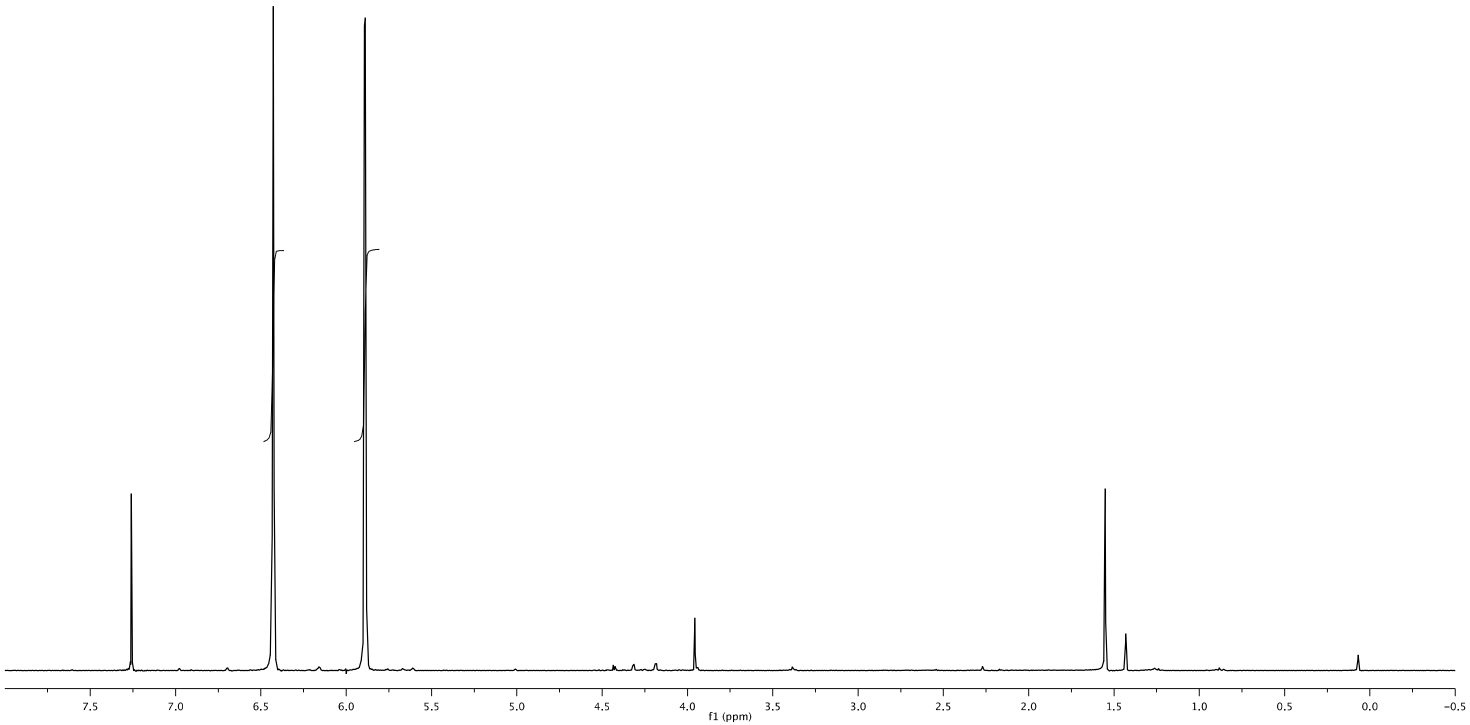


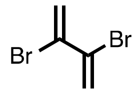
Figure S5. Diminishing alternation in ^{13}C chemical shift of in the C2 methine *C*H resonance in members of the [*n*]dendralene family (CDCl$_3$, 25 °C).

8) ^{1}H and ^{13}C NMR Spectra

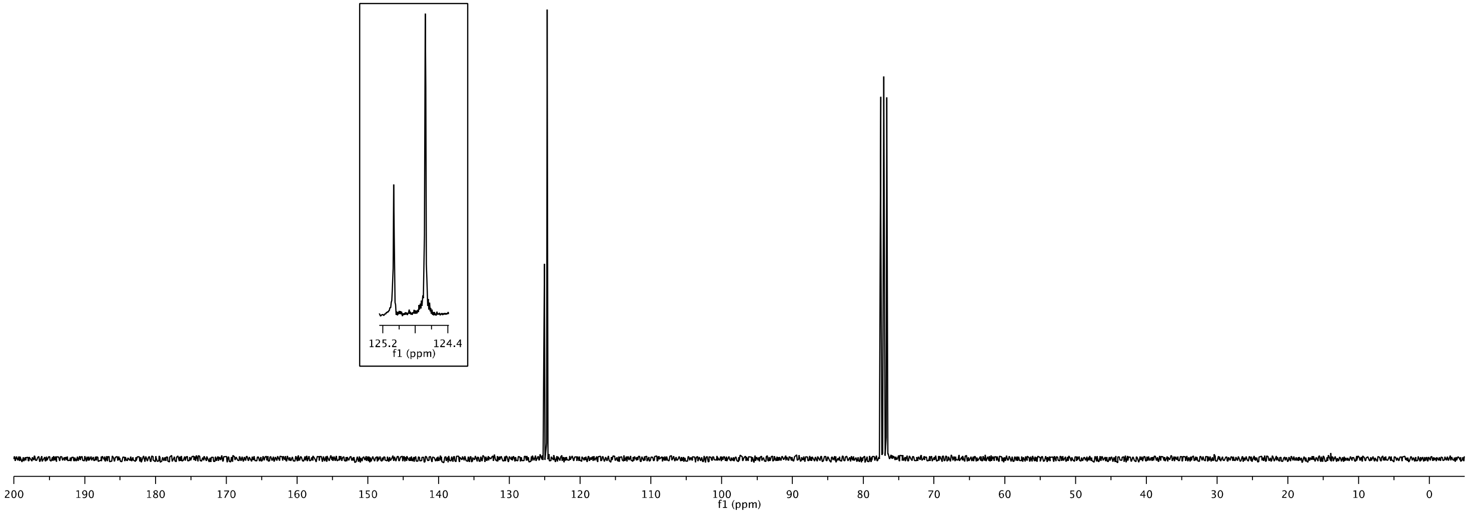


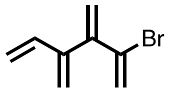
23
^{1}H NMR spectrum
300 MHz, in $CDCl_3$





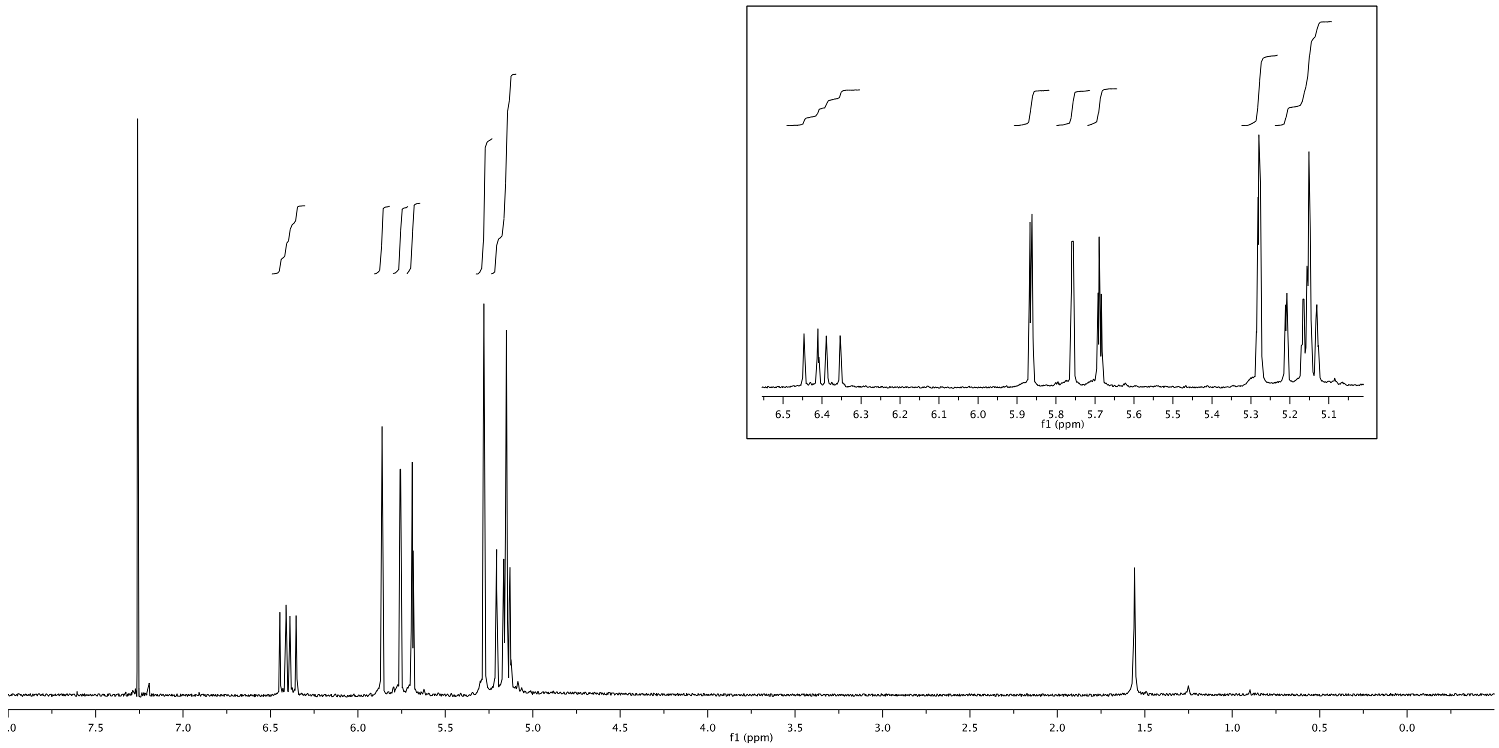
23
^{13}C NMR spectrum
75 MHz, in $CDCl_3$



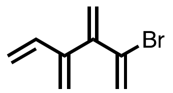


14

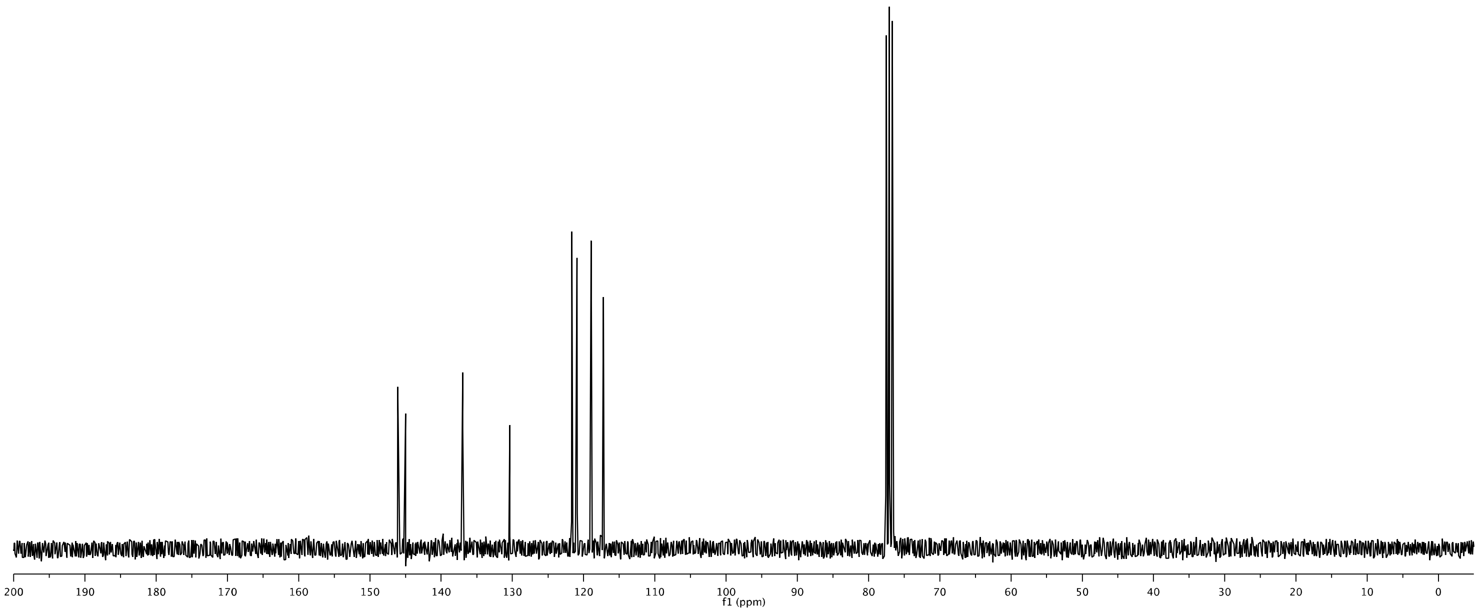
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

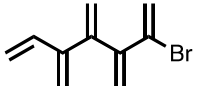


S37



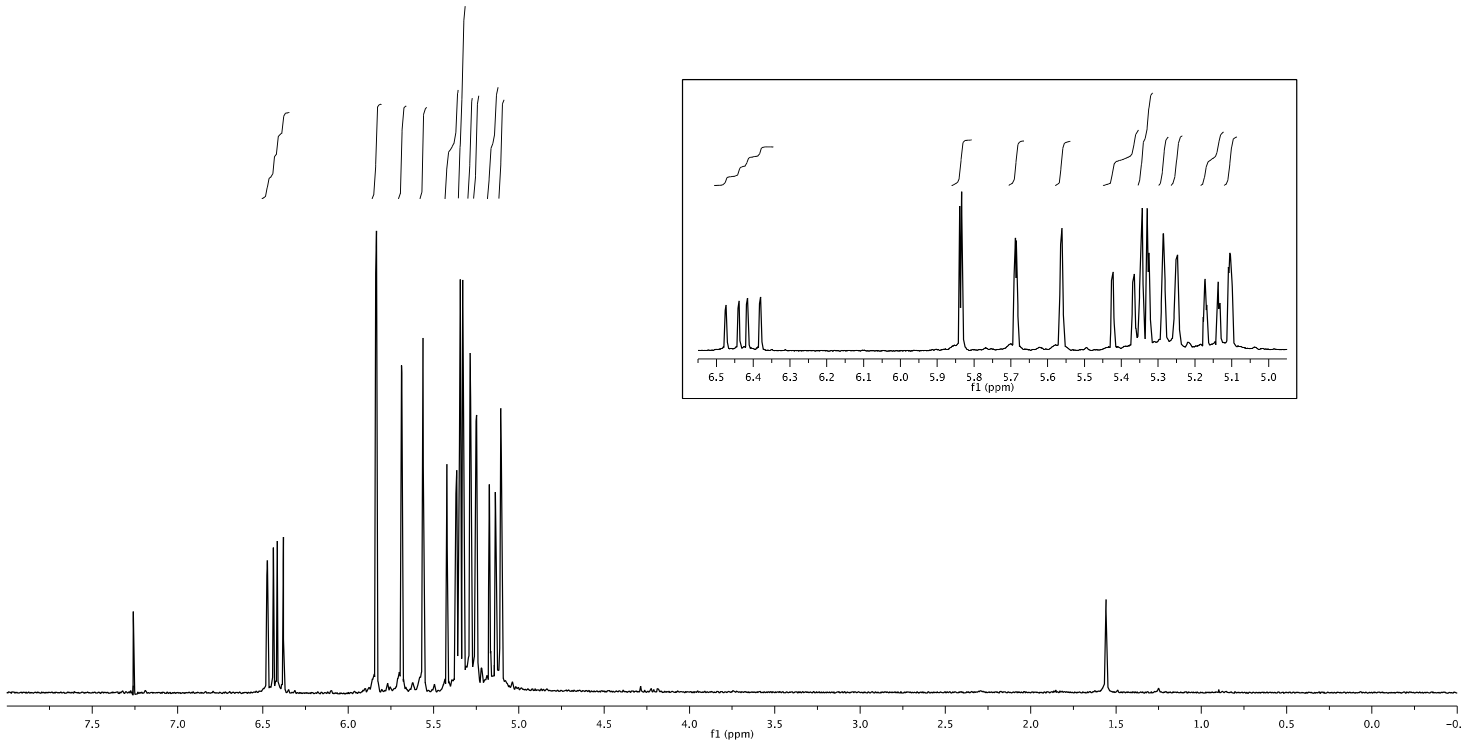
14
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

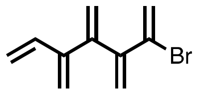




15

^{1}H NMR spectrum
300 MHz, in $CDCl_3$





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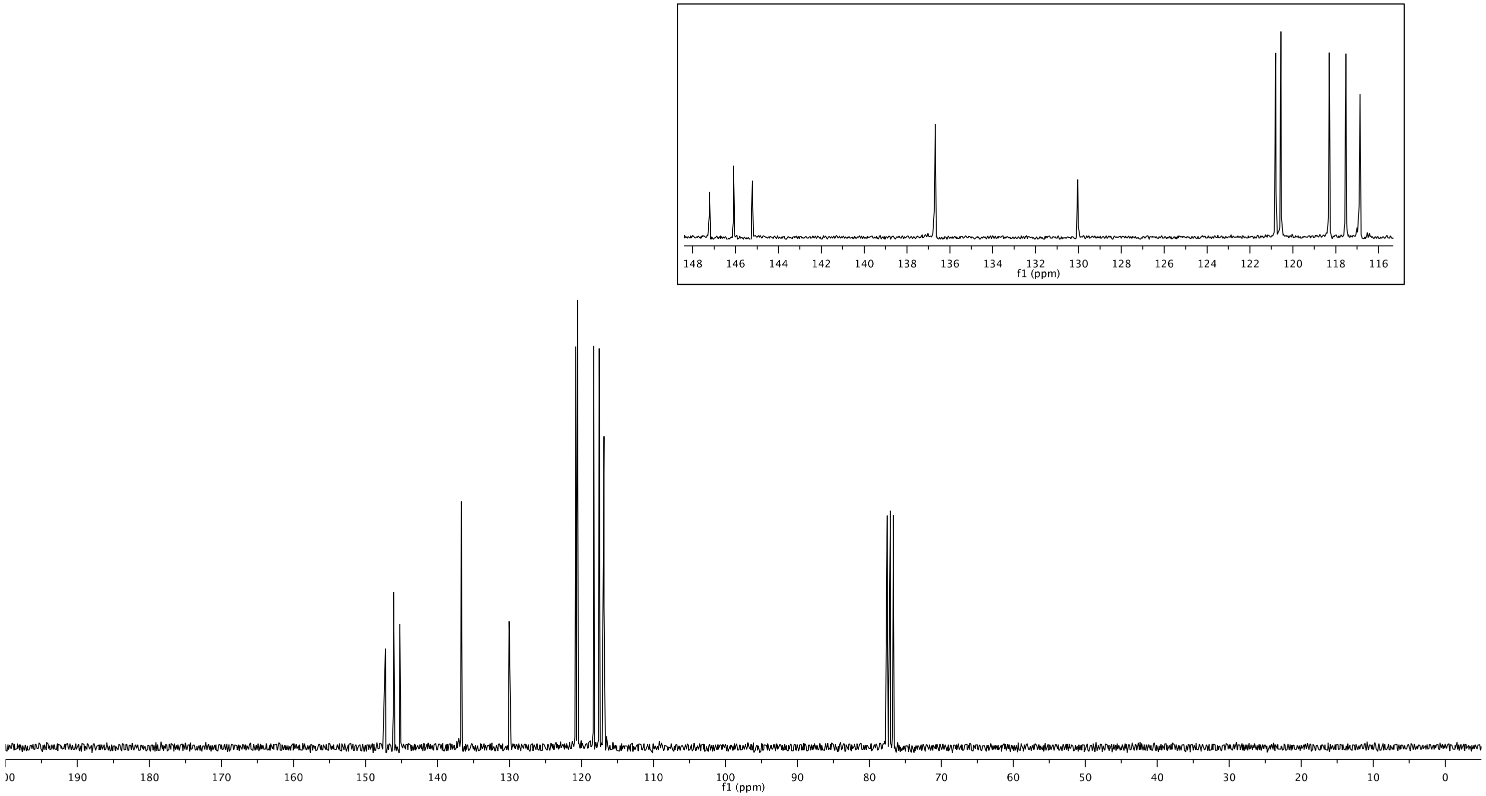
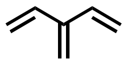
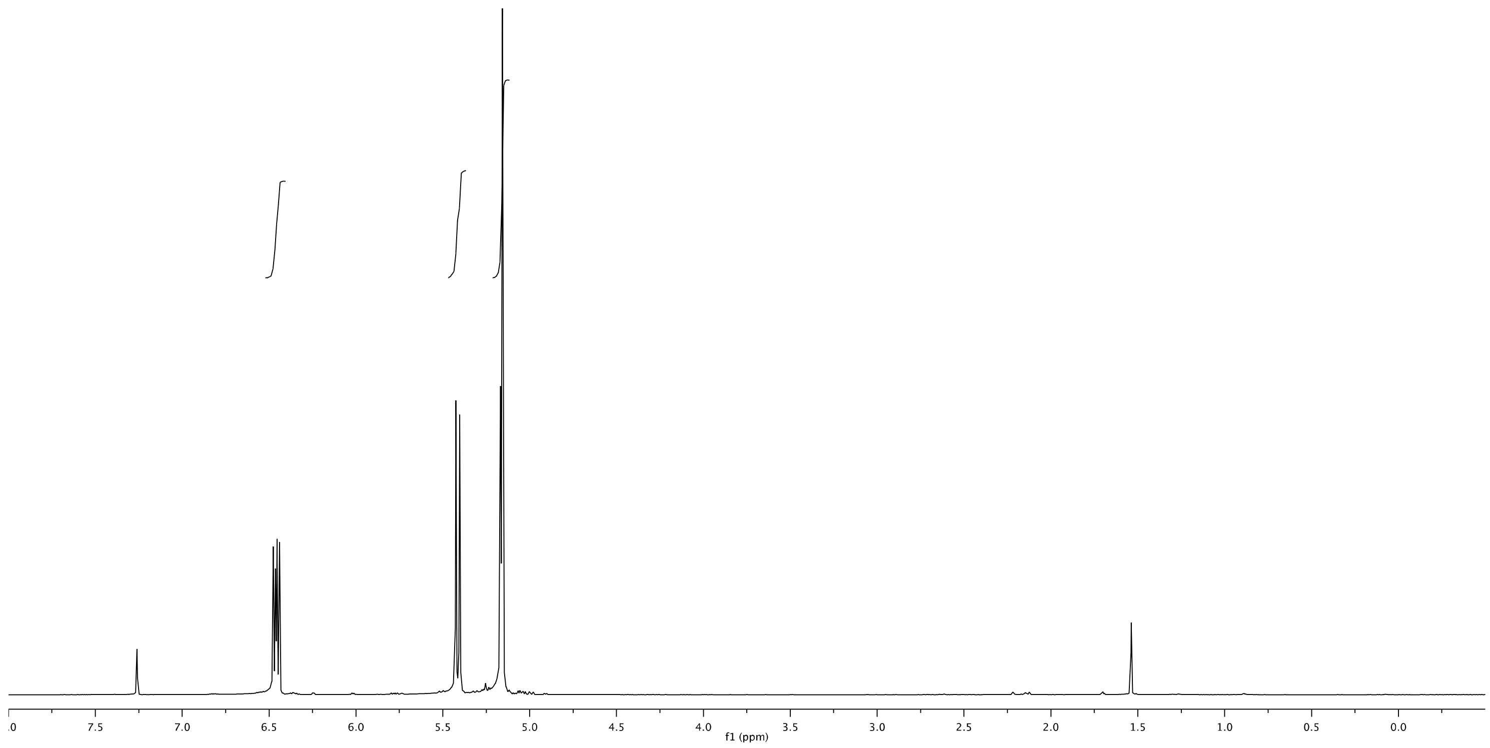
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

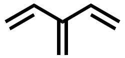




1

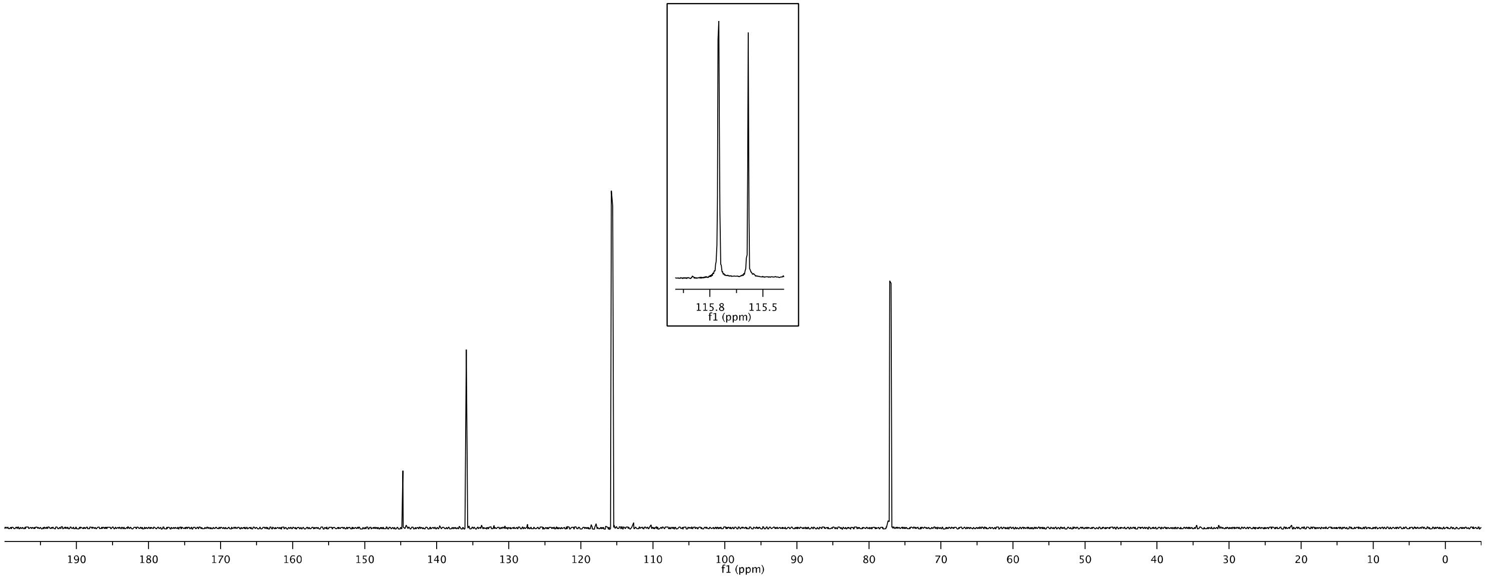
^{1}H NMR spectrum
800 MHz, in CDCl$_3$

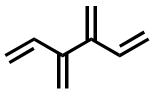




1

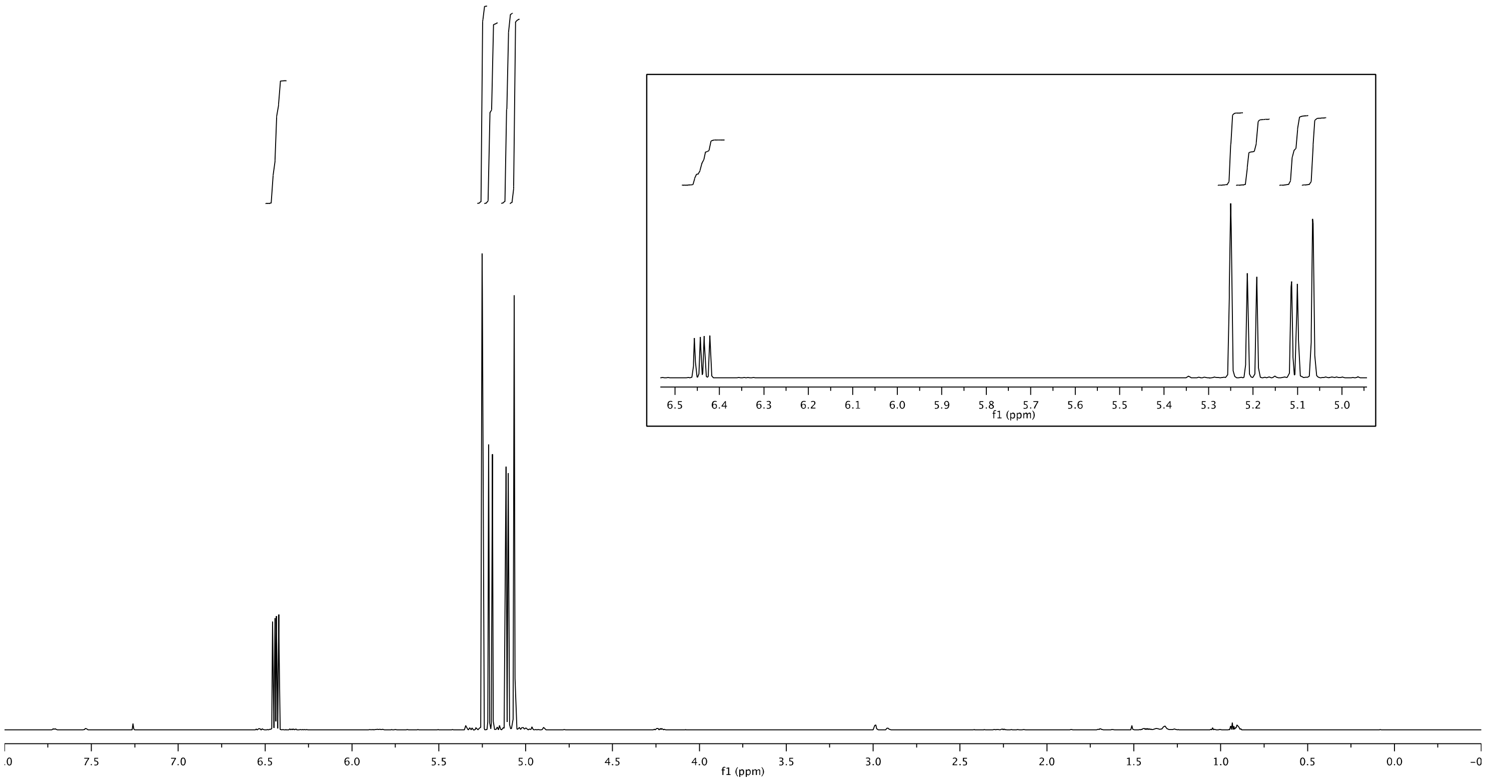
^{13}C NMR spectrum
200 MHz, in CDCl$_3$

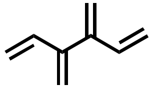




2

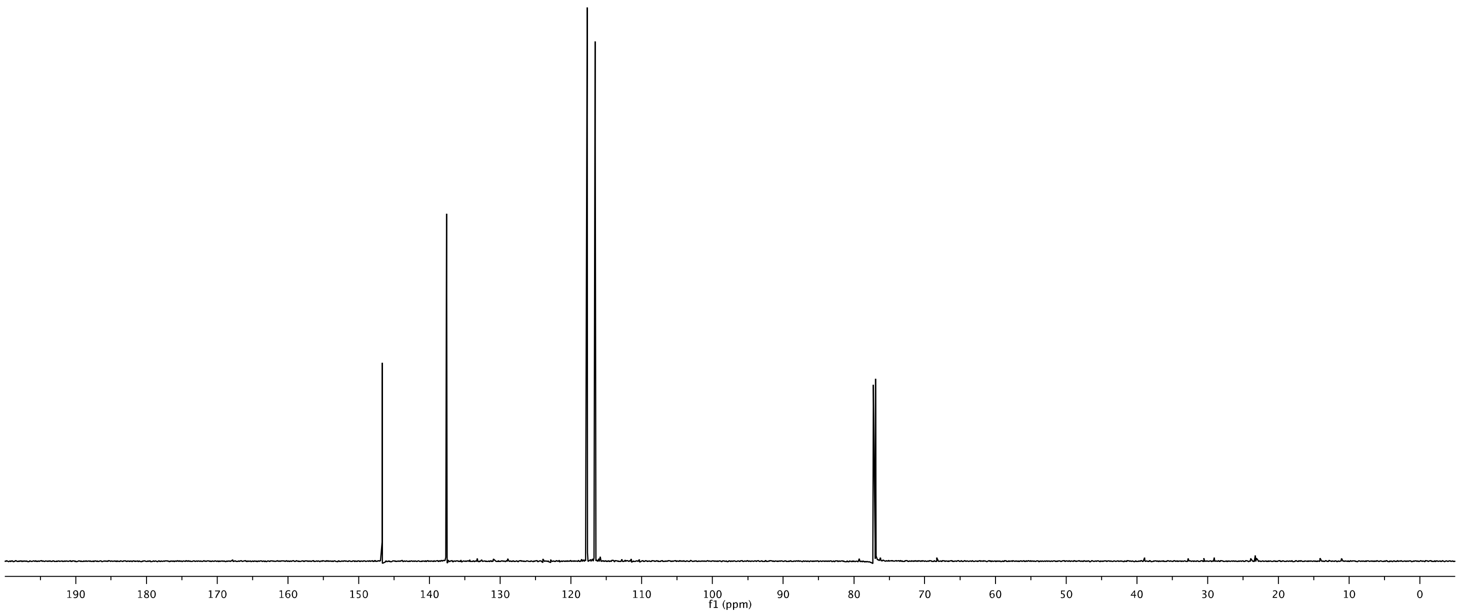
^{1}H NMR spectrum
800 MHz, in CDCl$_3$

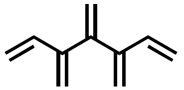




2

^{13}C NMR spectrum
200 MHz, in $CDCl_3$

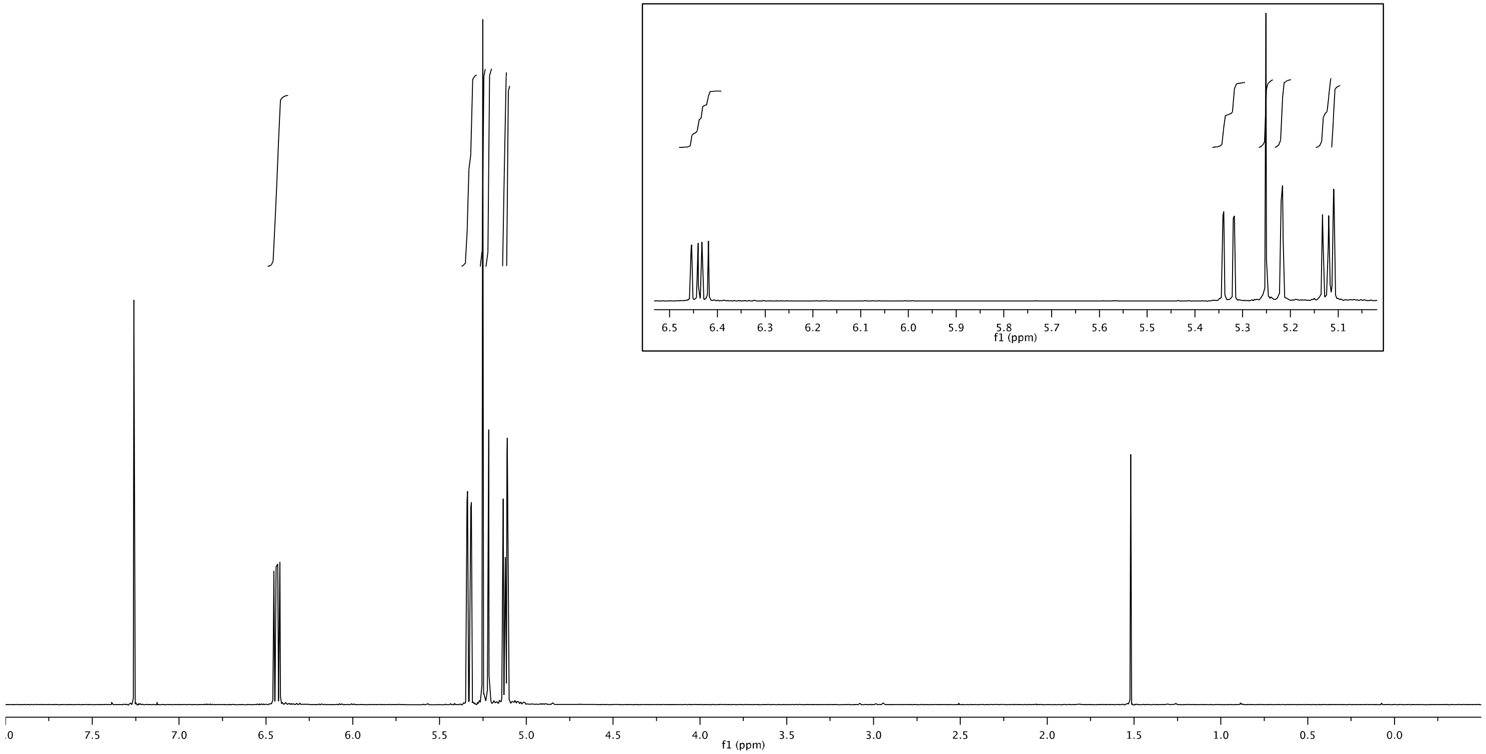


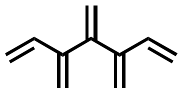


3

^{1}H NMR spectrum

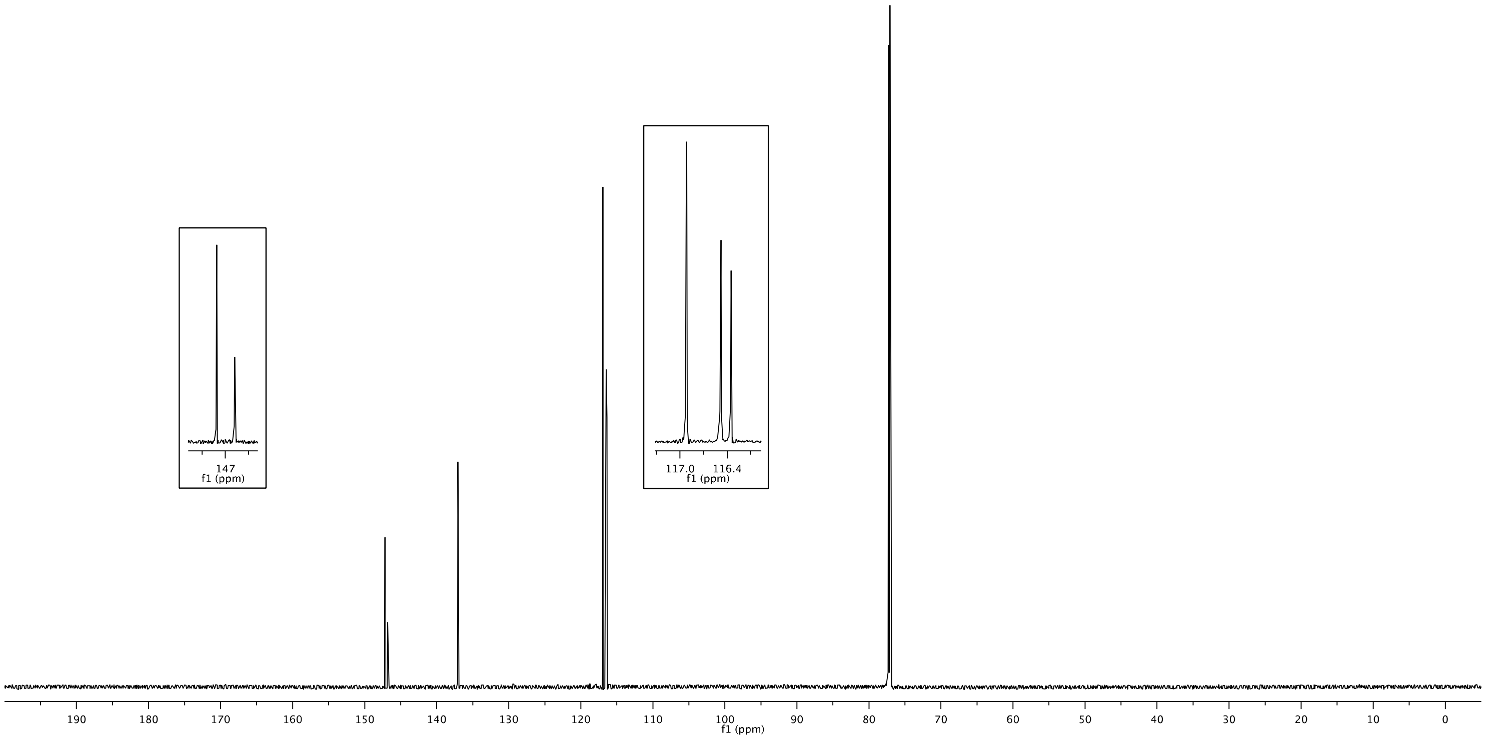
800 MHz, in $CDCl_3$

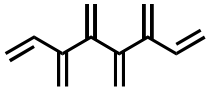




3

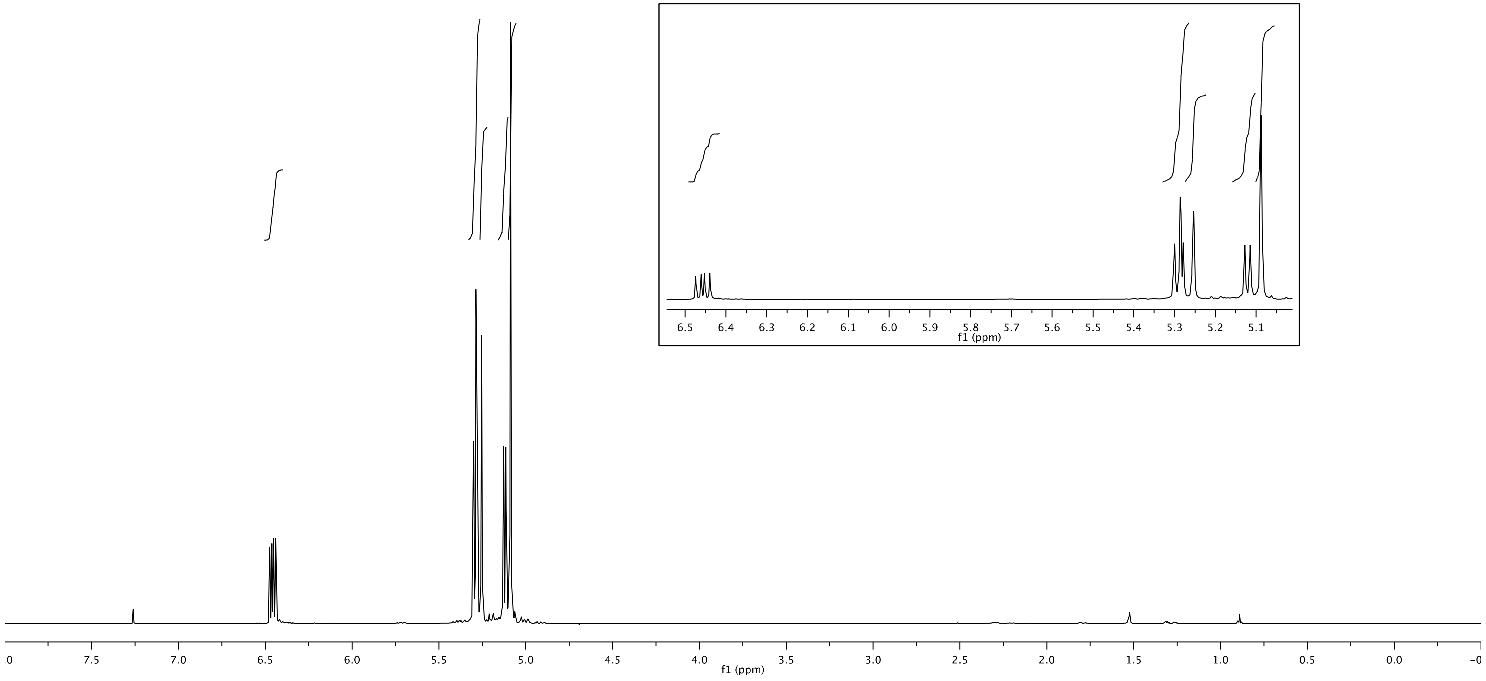
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

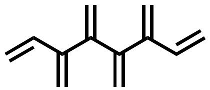




4

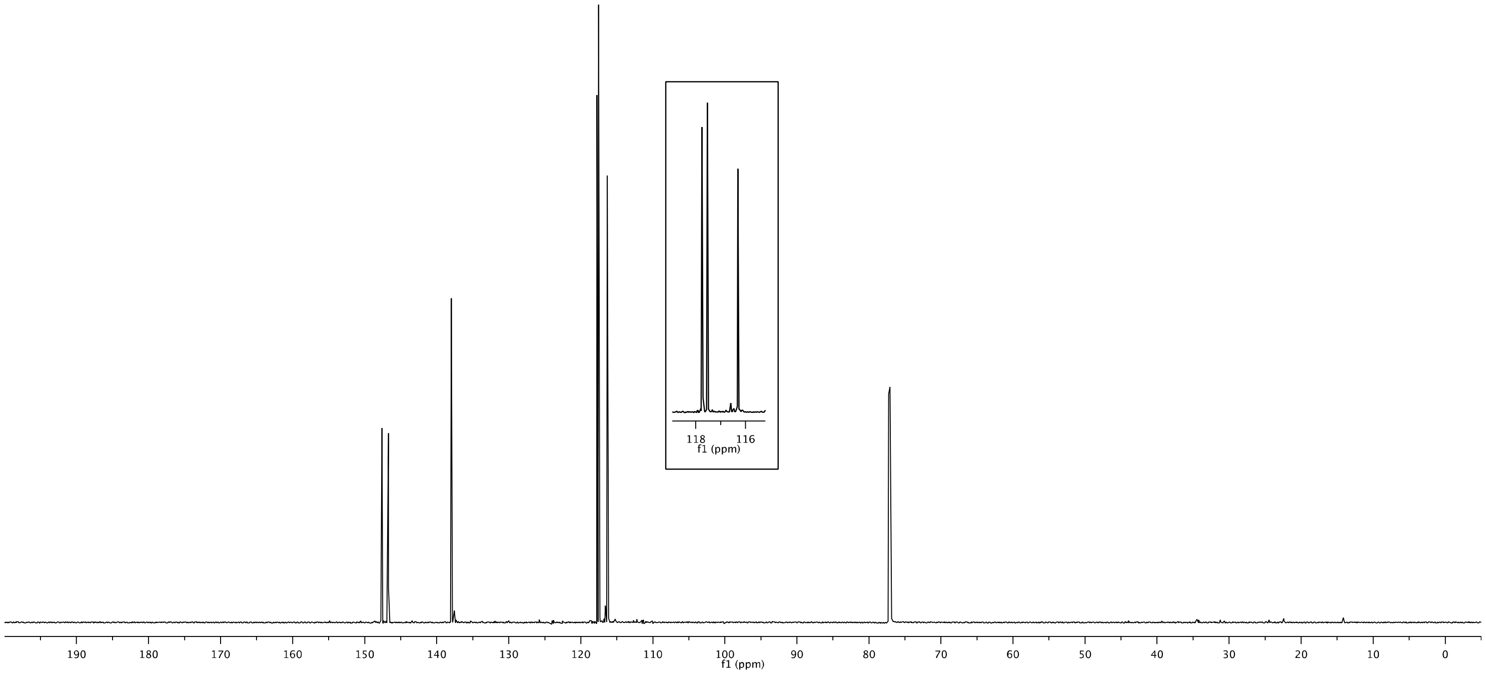
^1H NMR spectrum
800 MHz, in $CDCl_3$

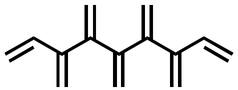




4

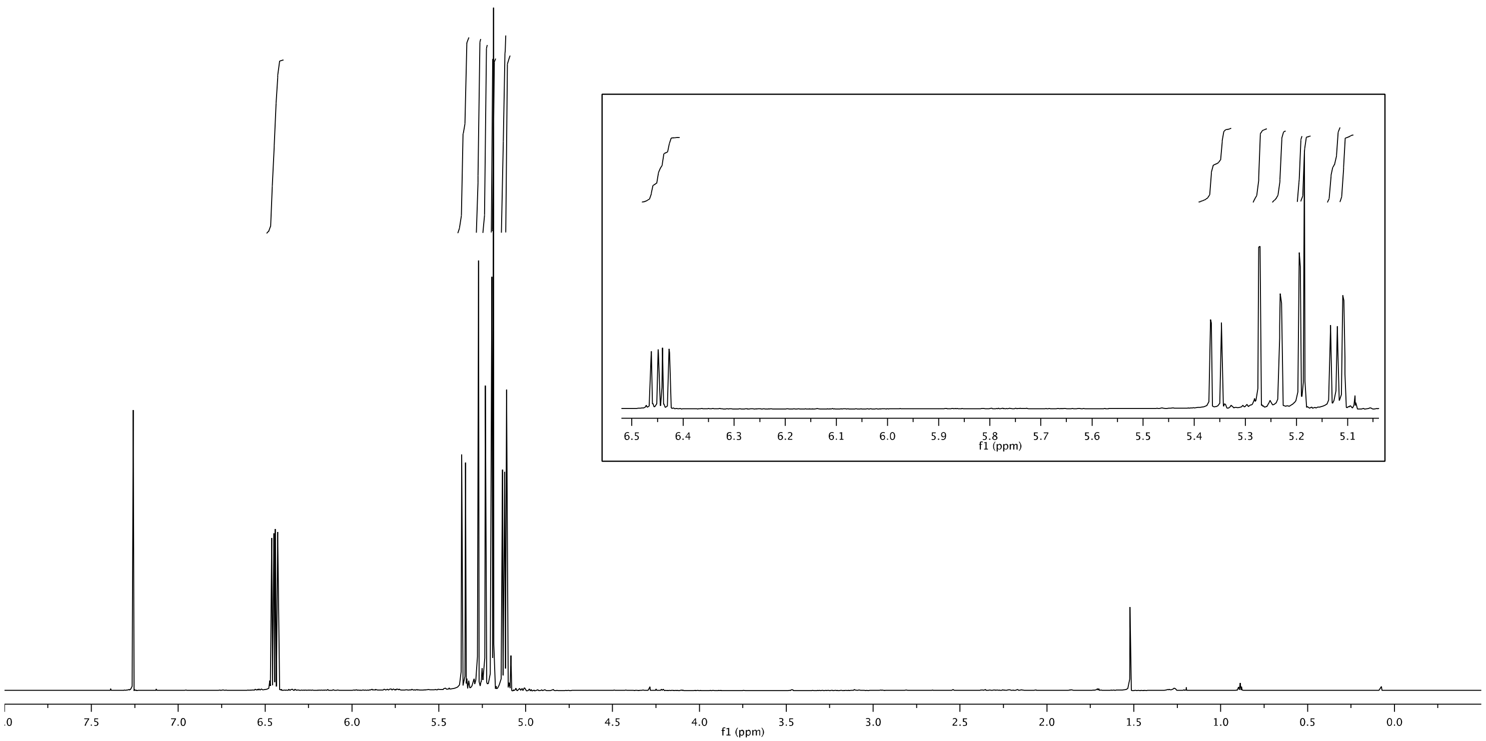
^{13}C NMR spectrum
200 MHz, in $CDCl_3$



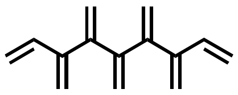


5

^{1}H NMR spectrum
800 MHz, in CDCl$_3$

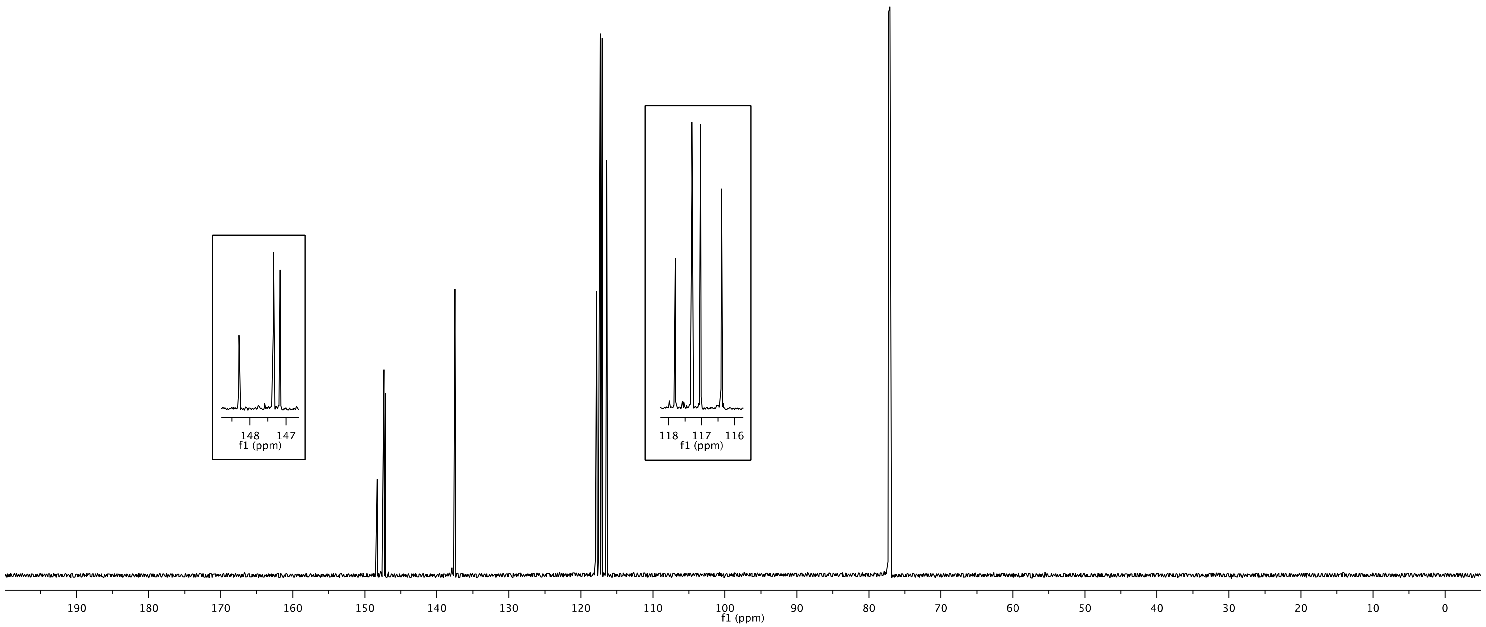


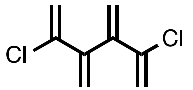
S49



5

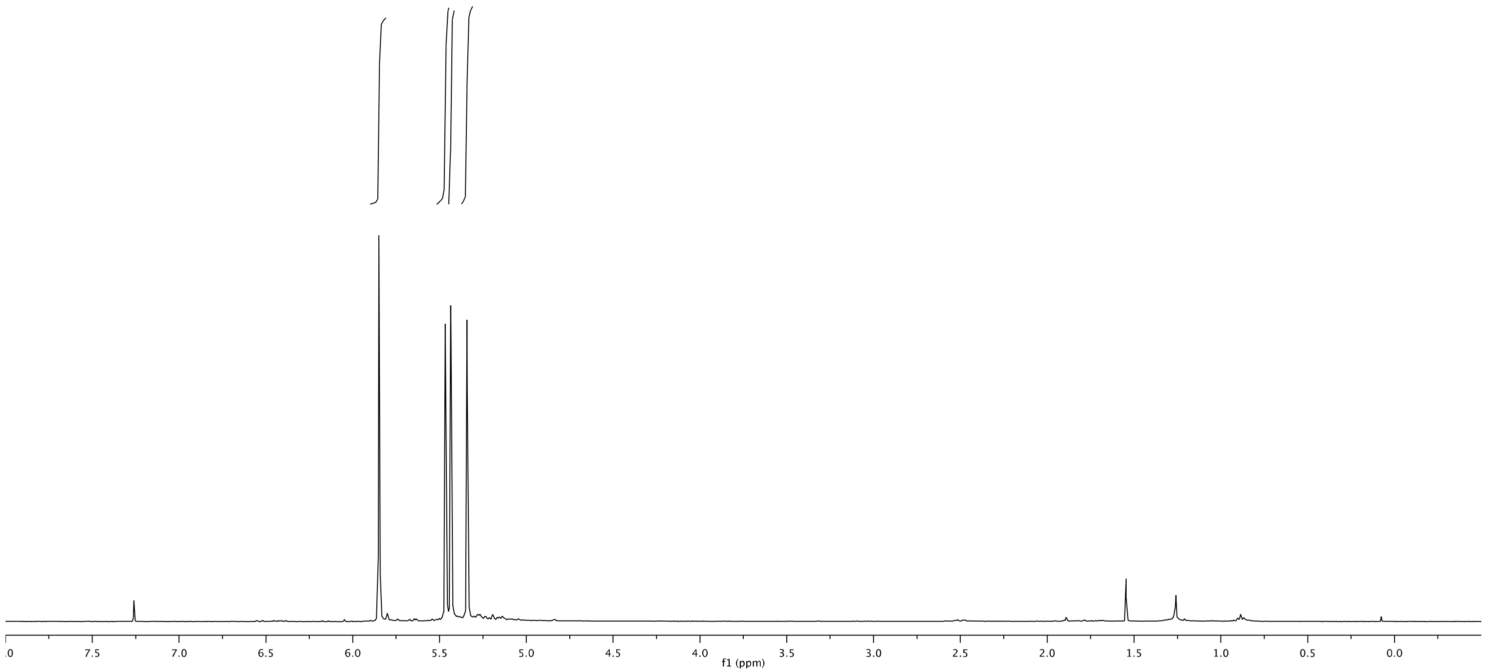
^{13}C NMR spectrum
200 MHz, in CDCl$_3$

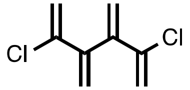




33

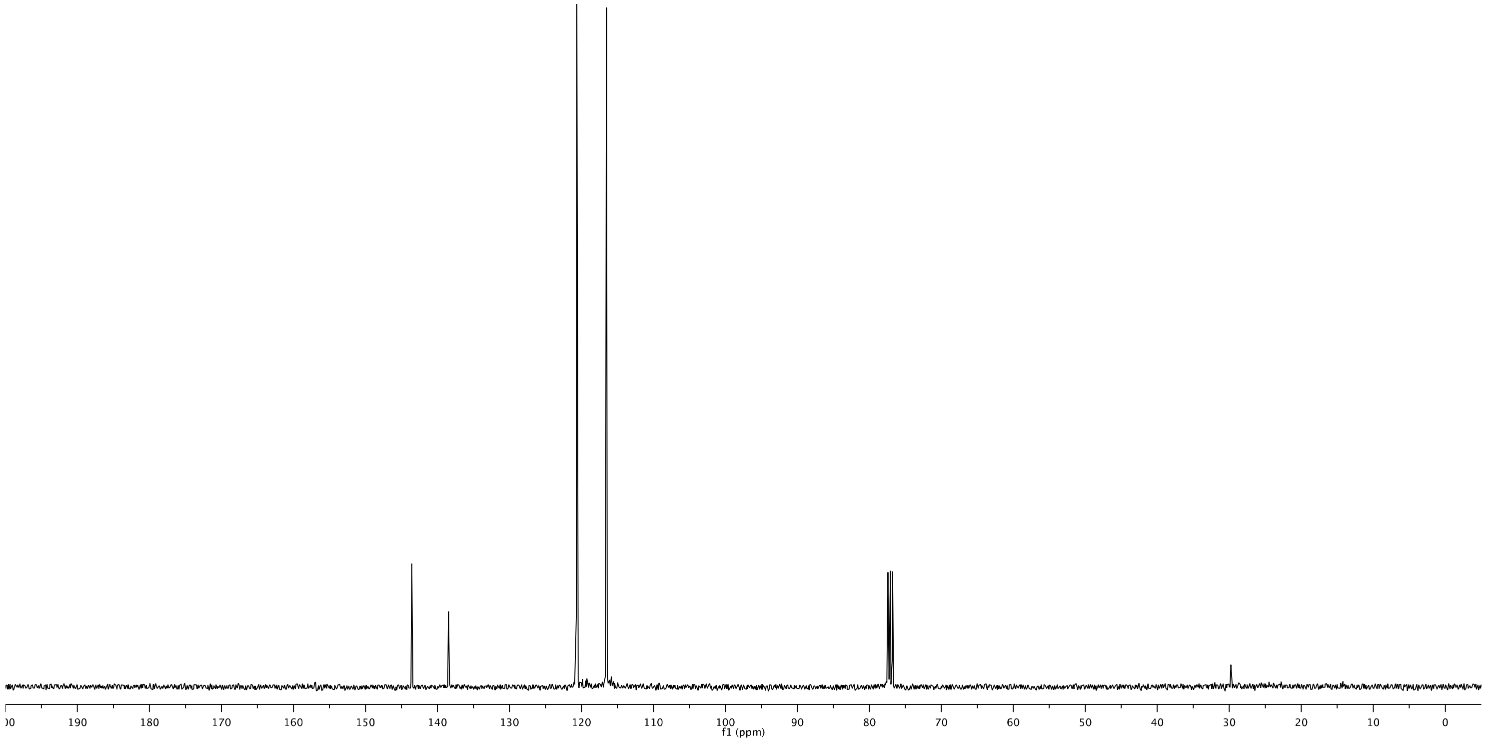
^1H NMR spectrum
400 MHz, in $CDCl_3$

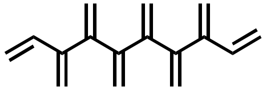




33

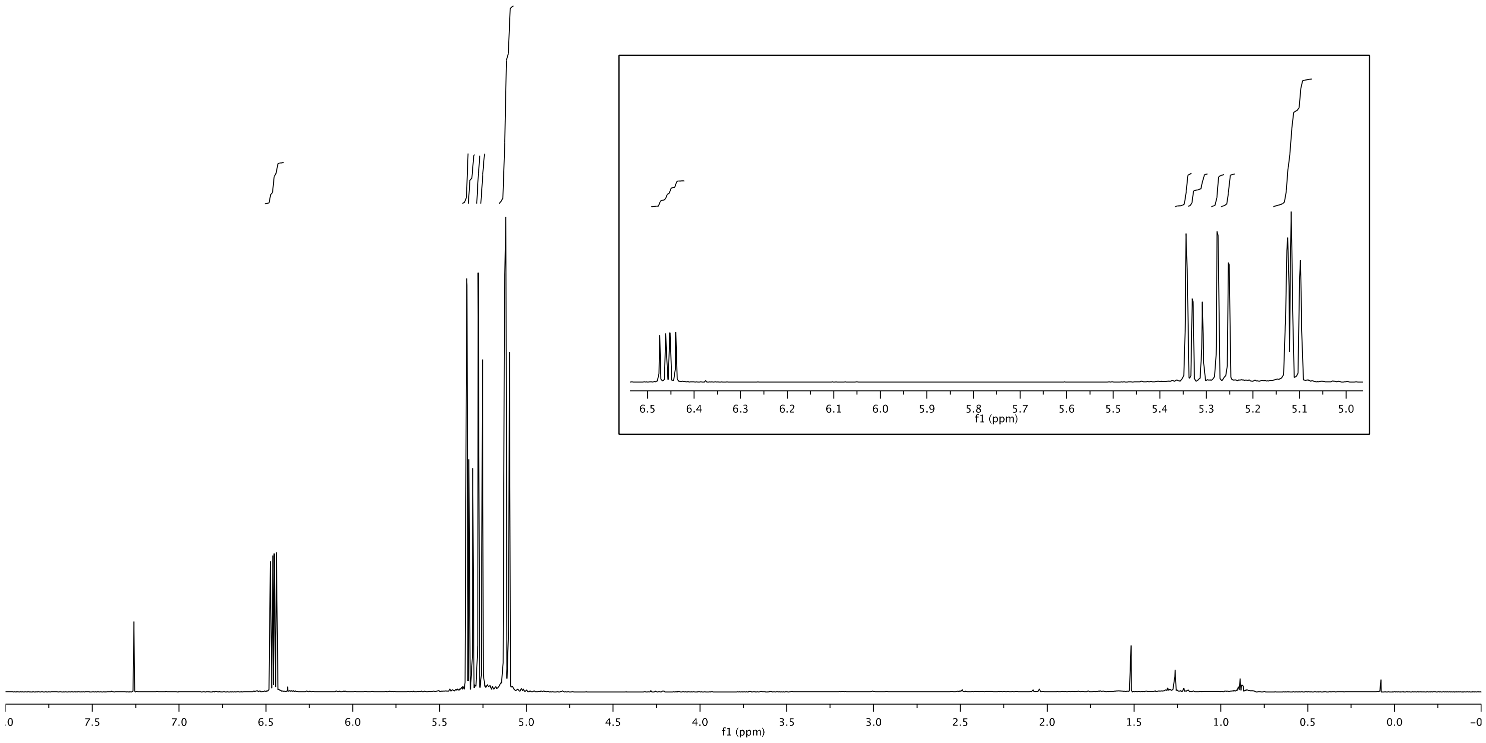
^{13}C NMR spectrum
100 MHz, in $CDCl_3$

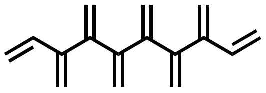




6

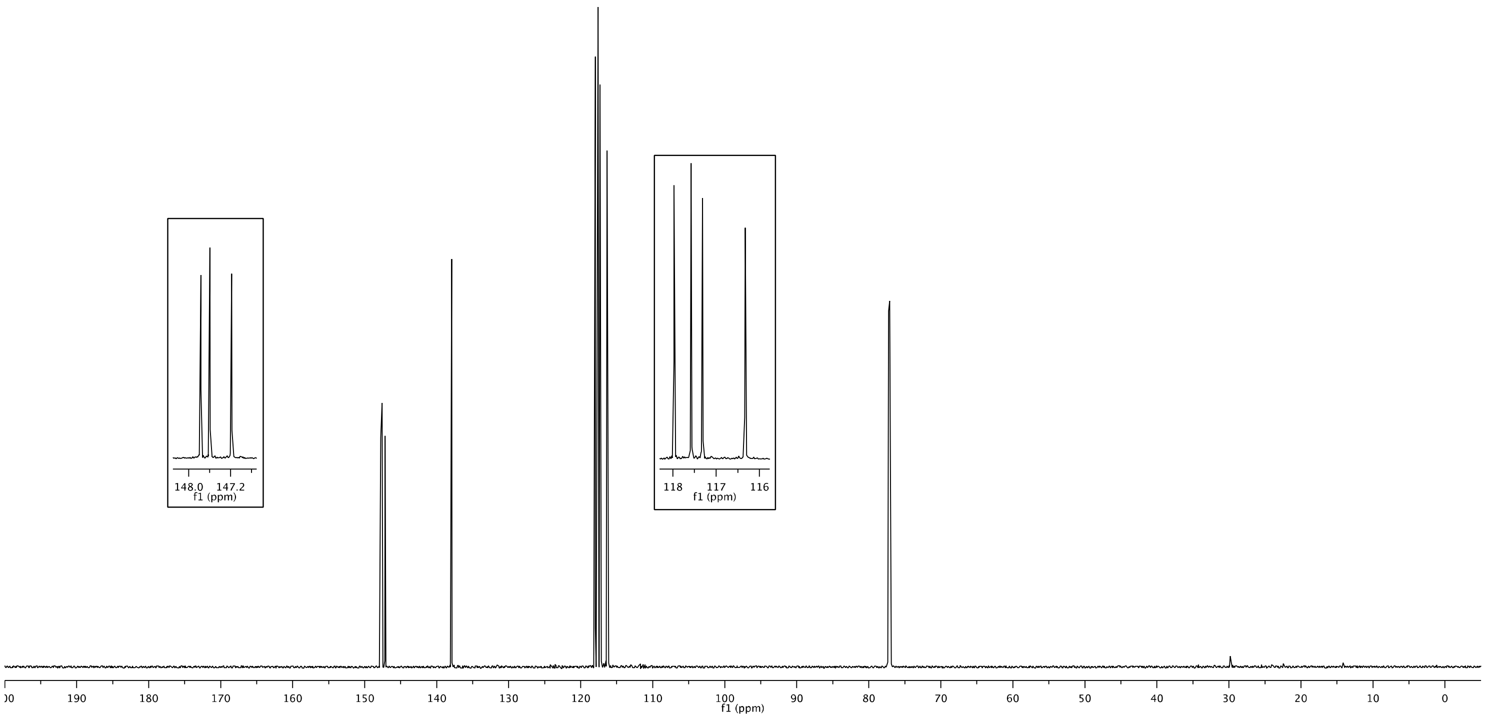
^{1}H NMR spectrum
800 MHz, in $CDCl_3$

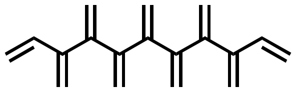




6

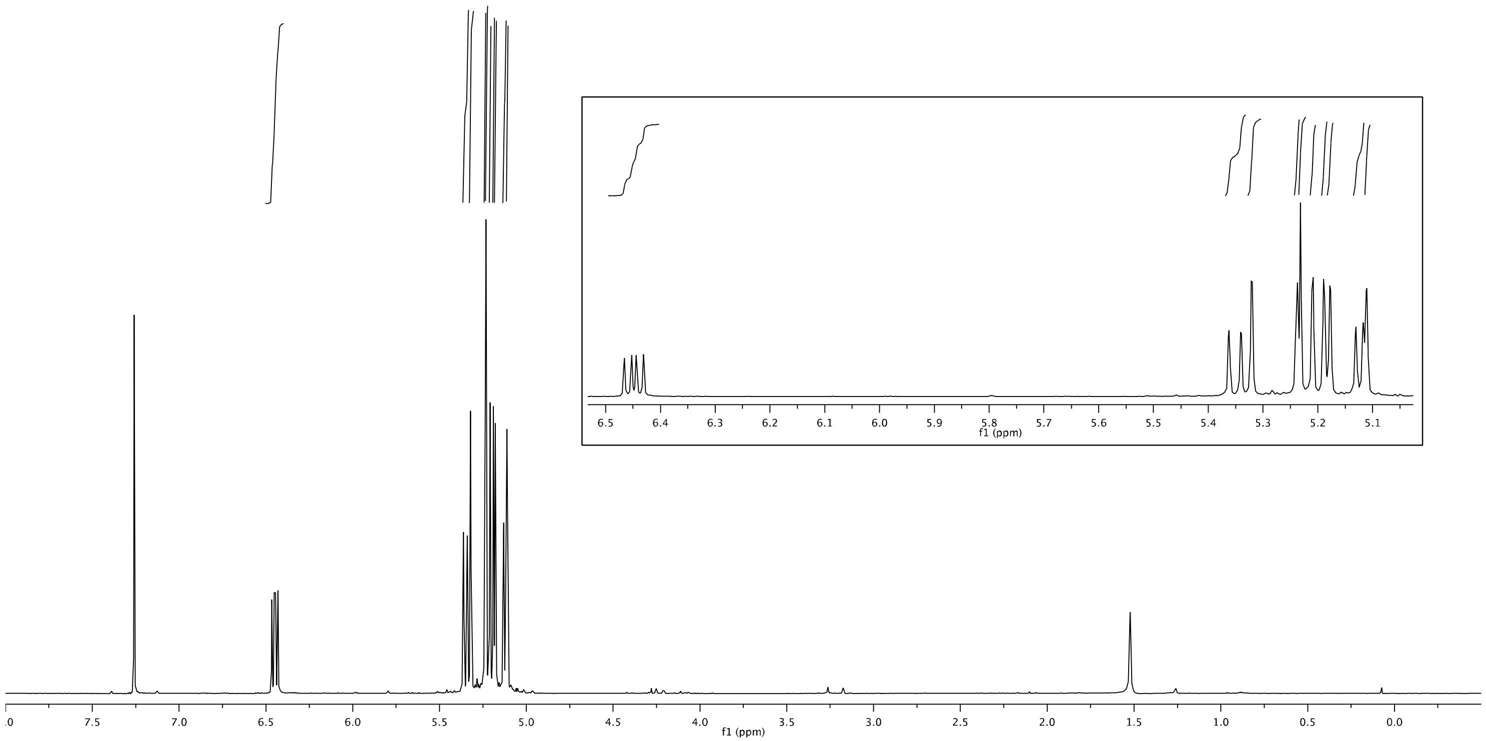
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

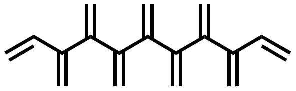




7

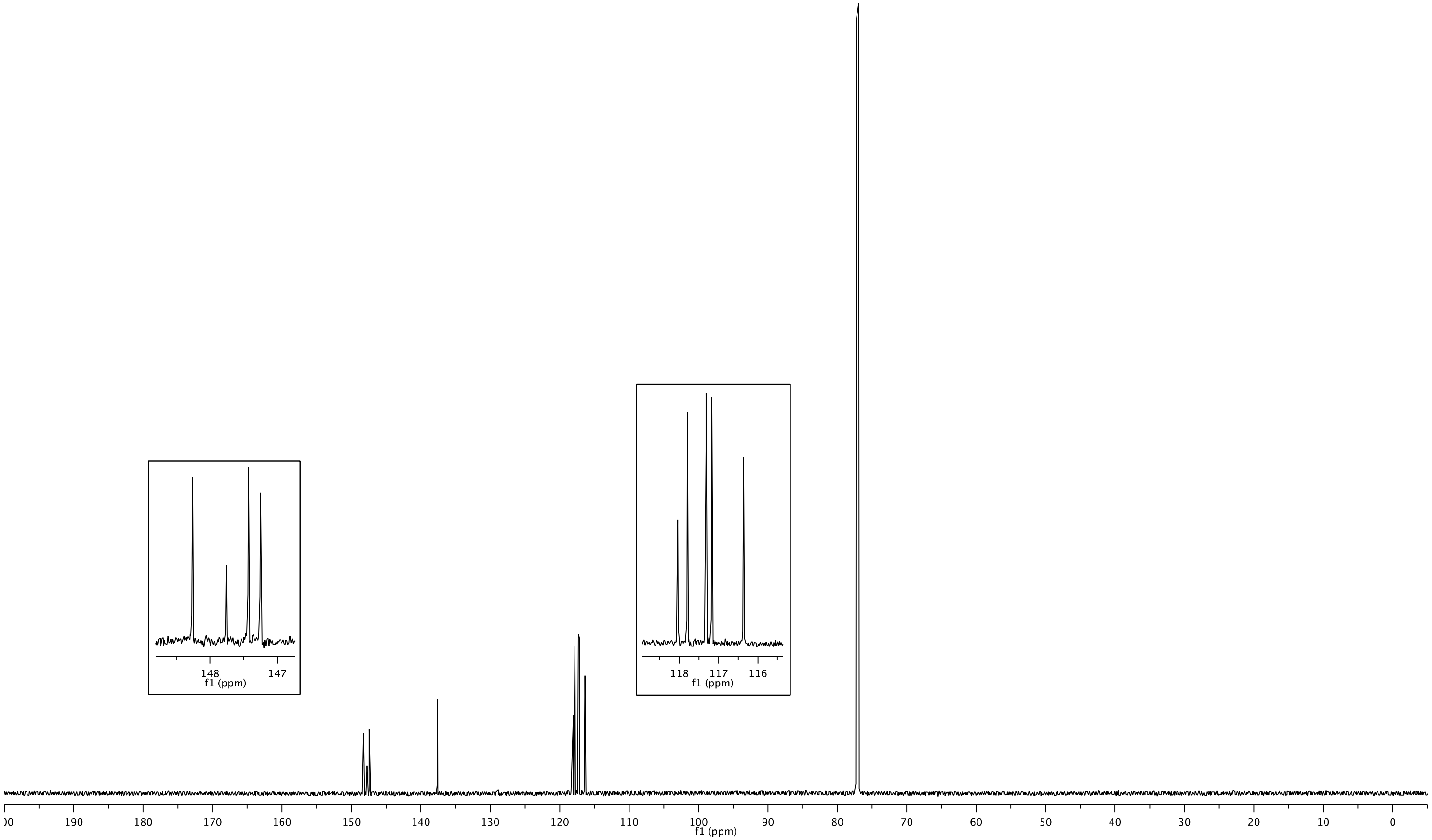
^{1}H NMR spectrum
800 MHz, in $CDCl_3$

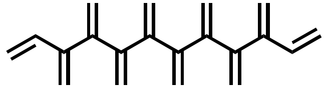




7

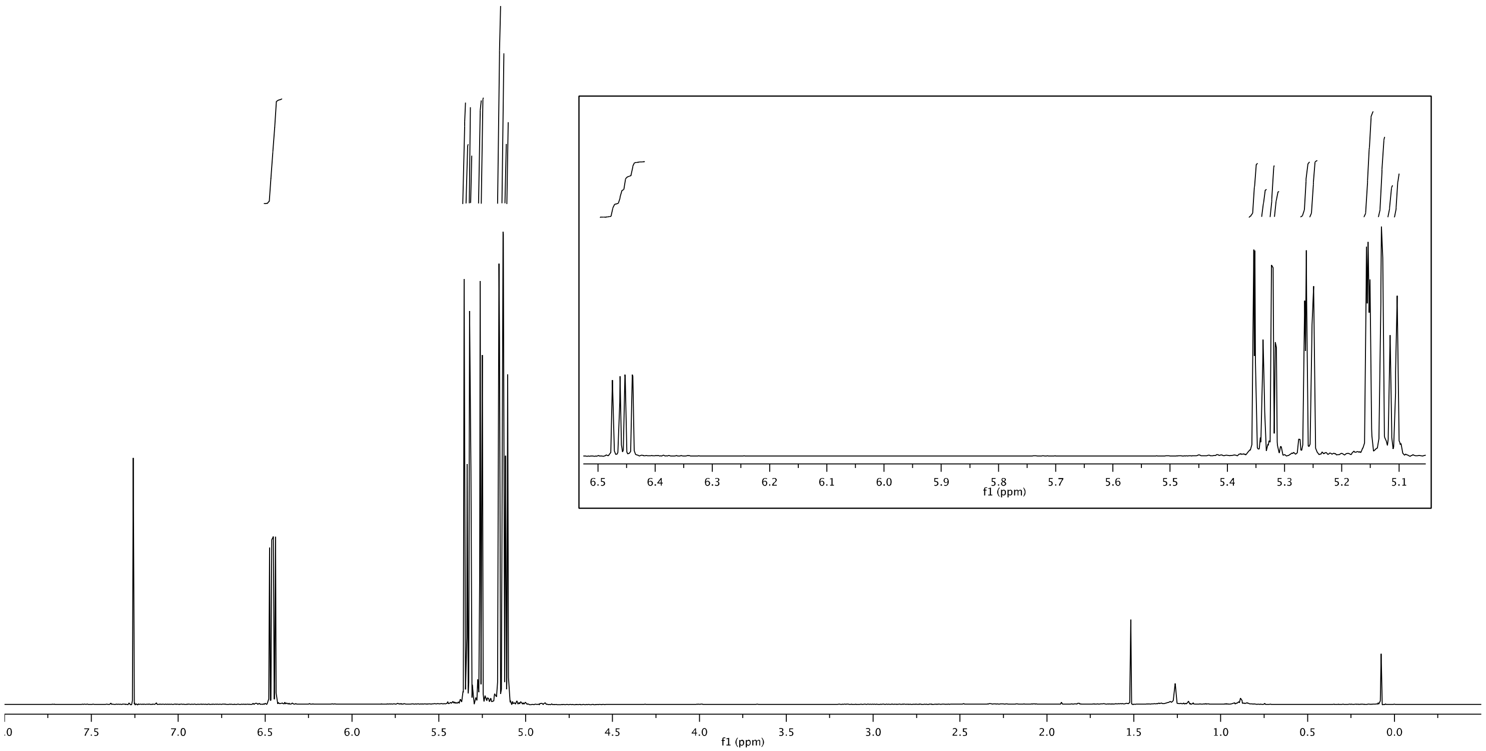
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

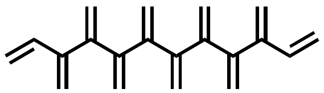




8

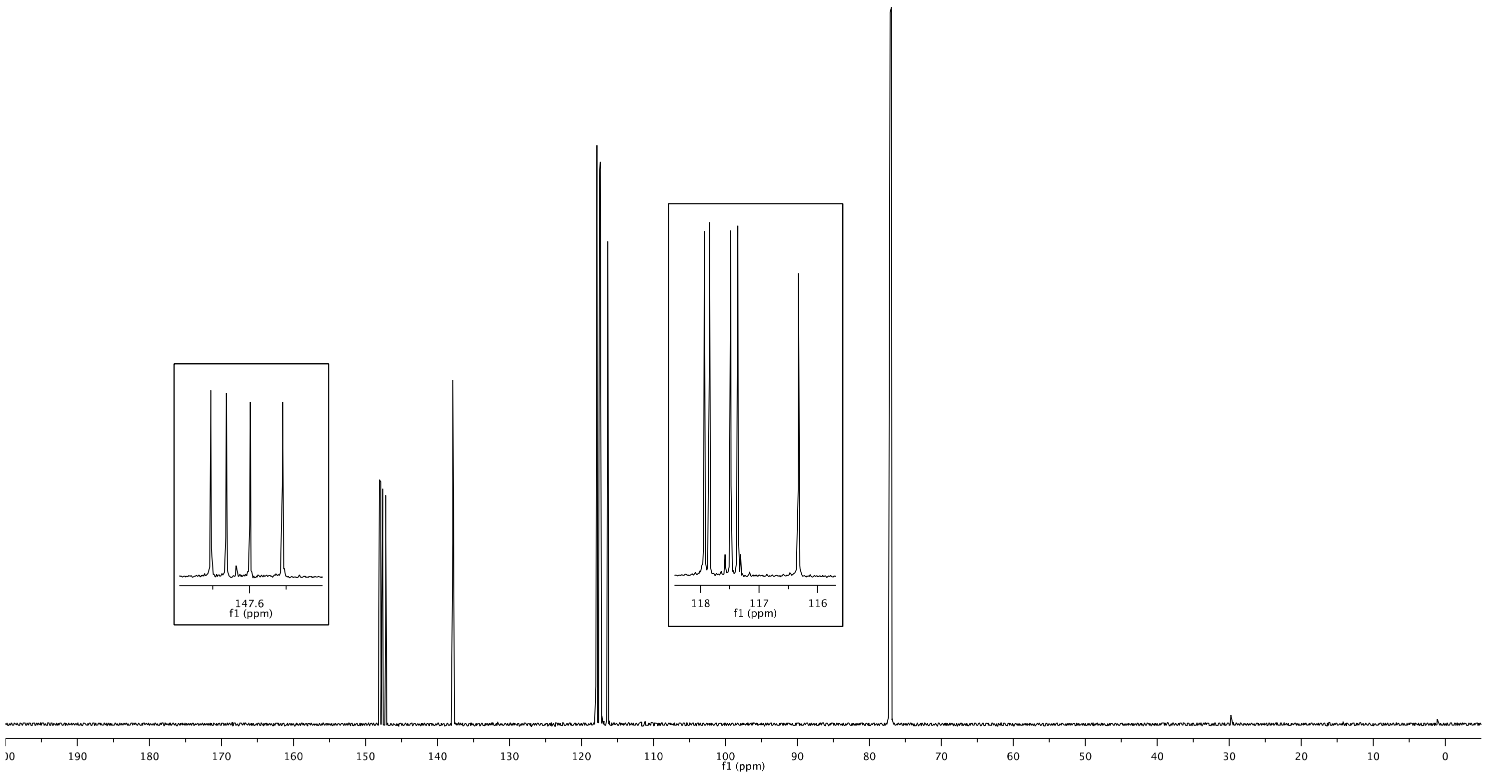
^{1}H NMR spectrum
800 MHz, in CDCl$_3$

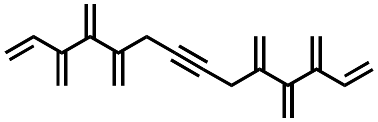




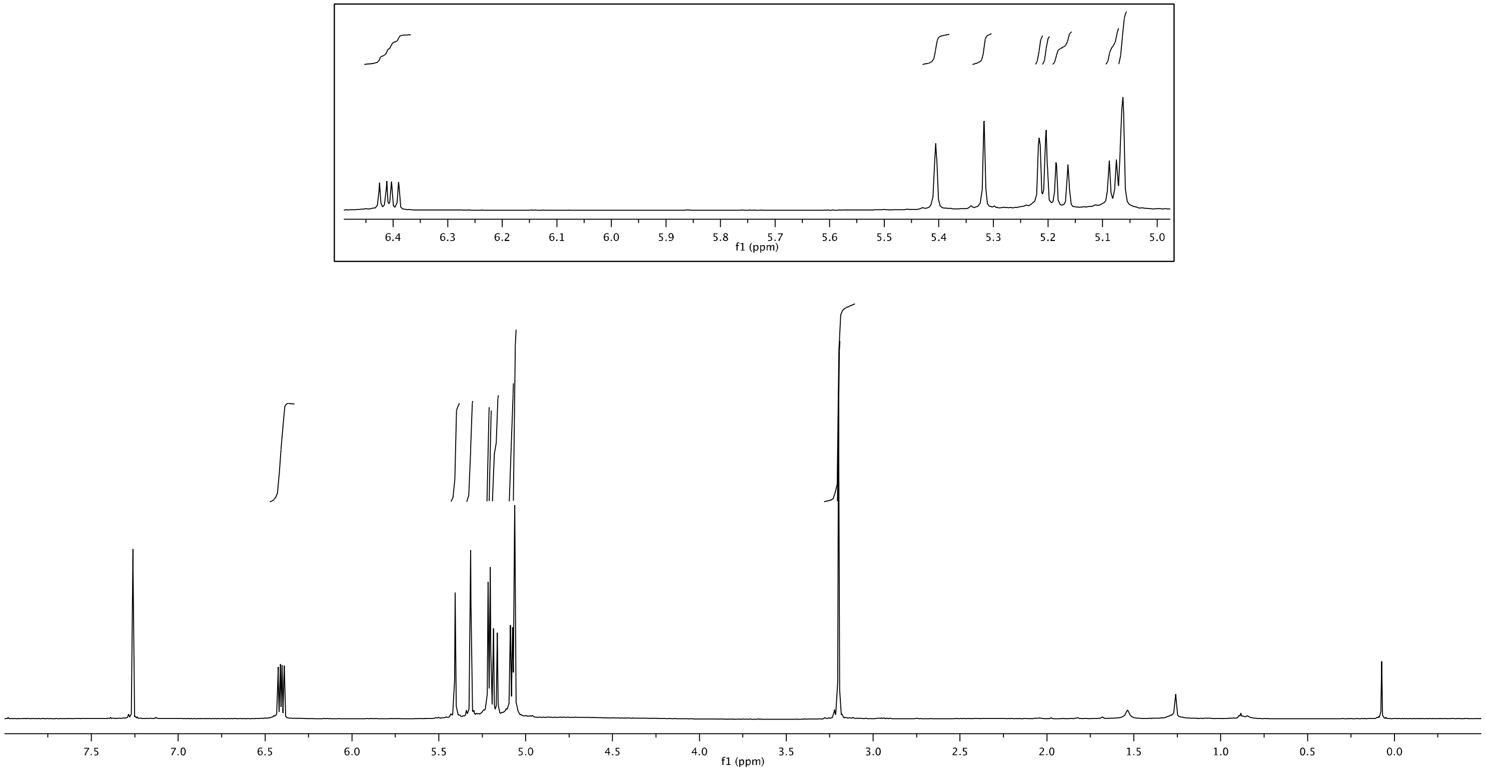
8

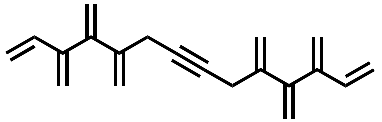
^{13}C NMR spectrum
200 MHz, in $CDCl_3$





34
^{1}H NMR spectrum
800 MHz, in CDCl$_3$

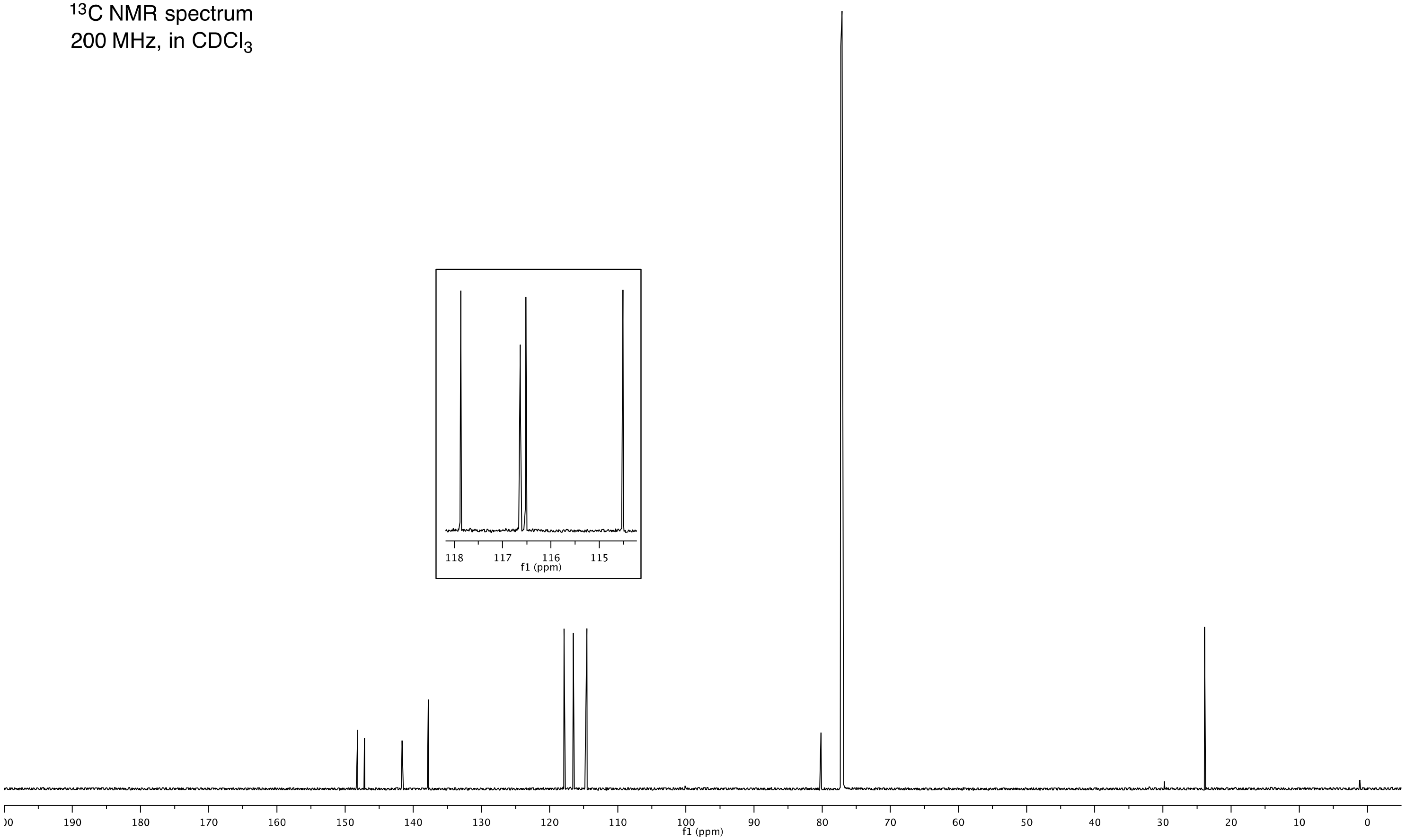


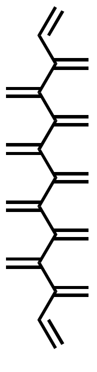


34

^{13}C NMR spectrum

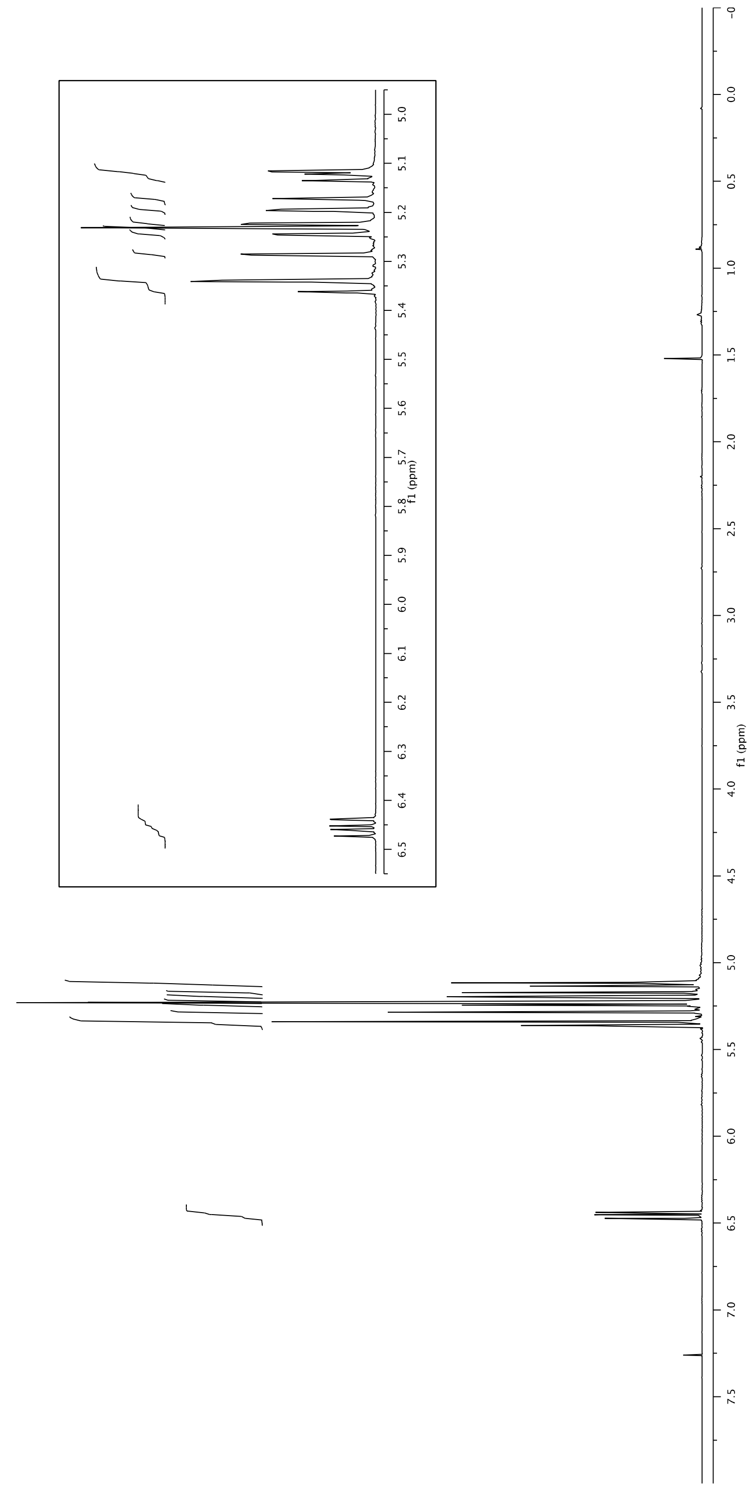
200 MHz, in $CDCl_3$

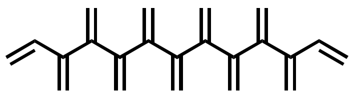




9

^{1}H NMR spectrum
800 MHz, in $CDCl_3$





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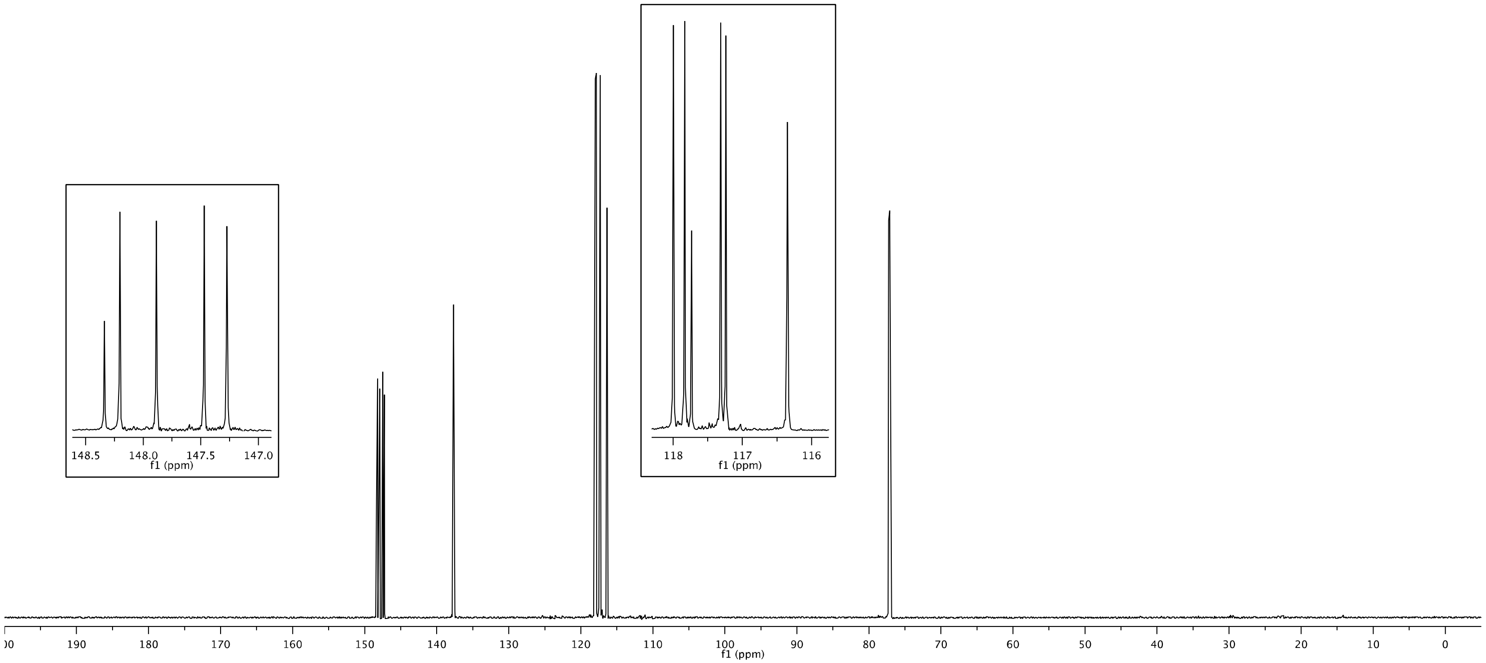
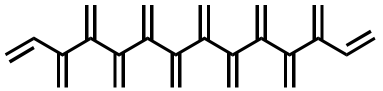
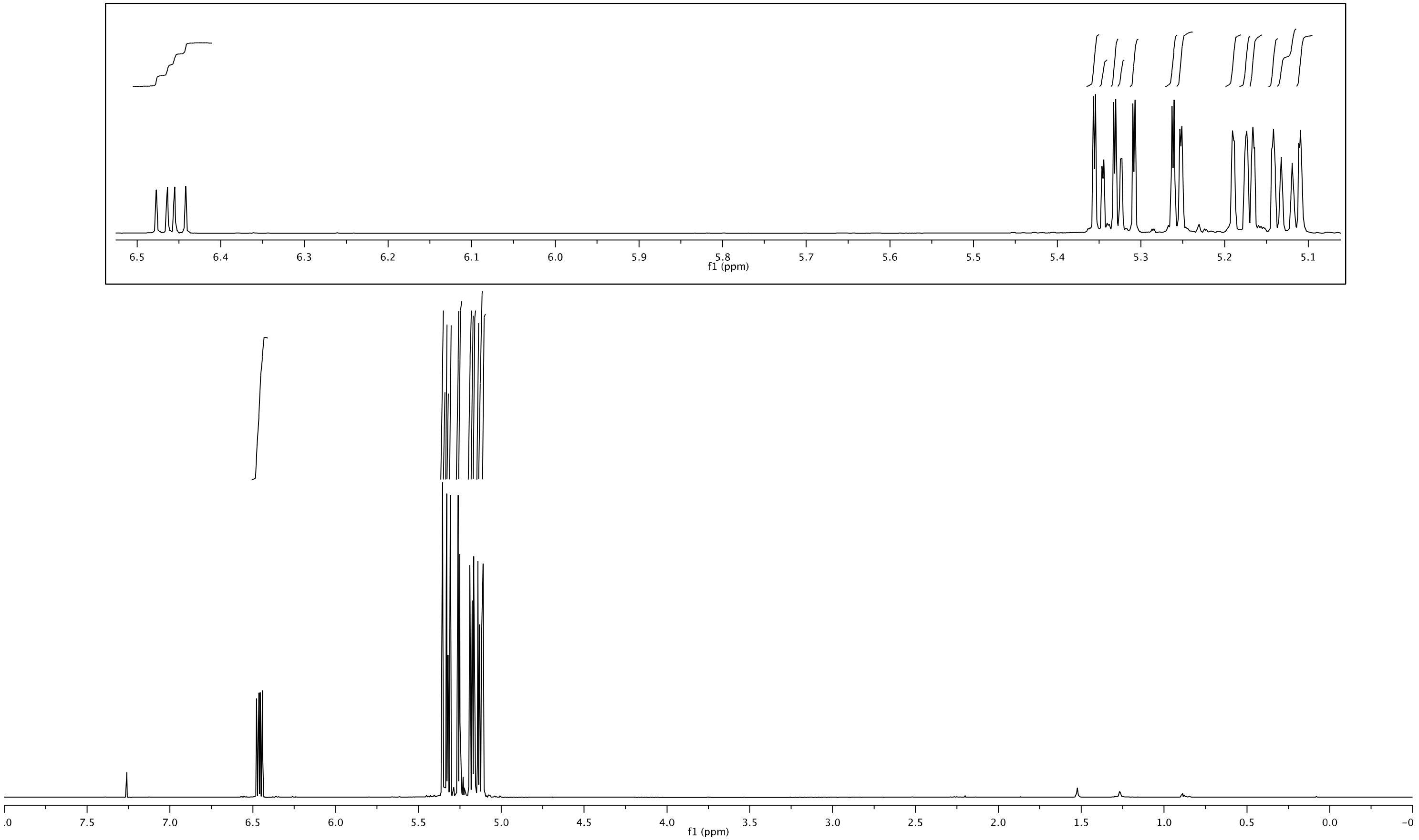
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

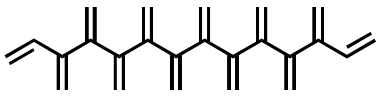




10

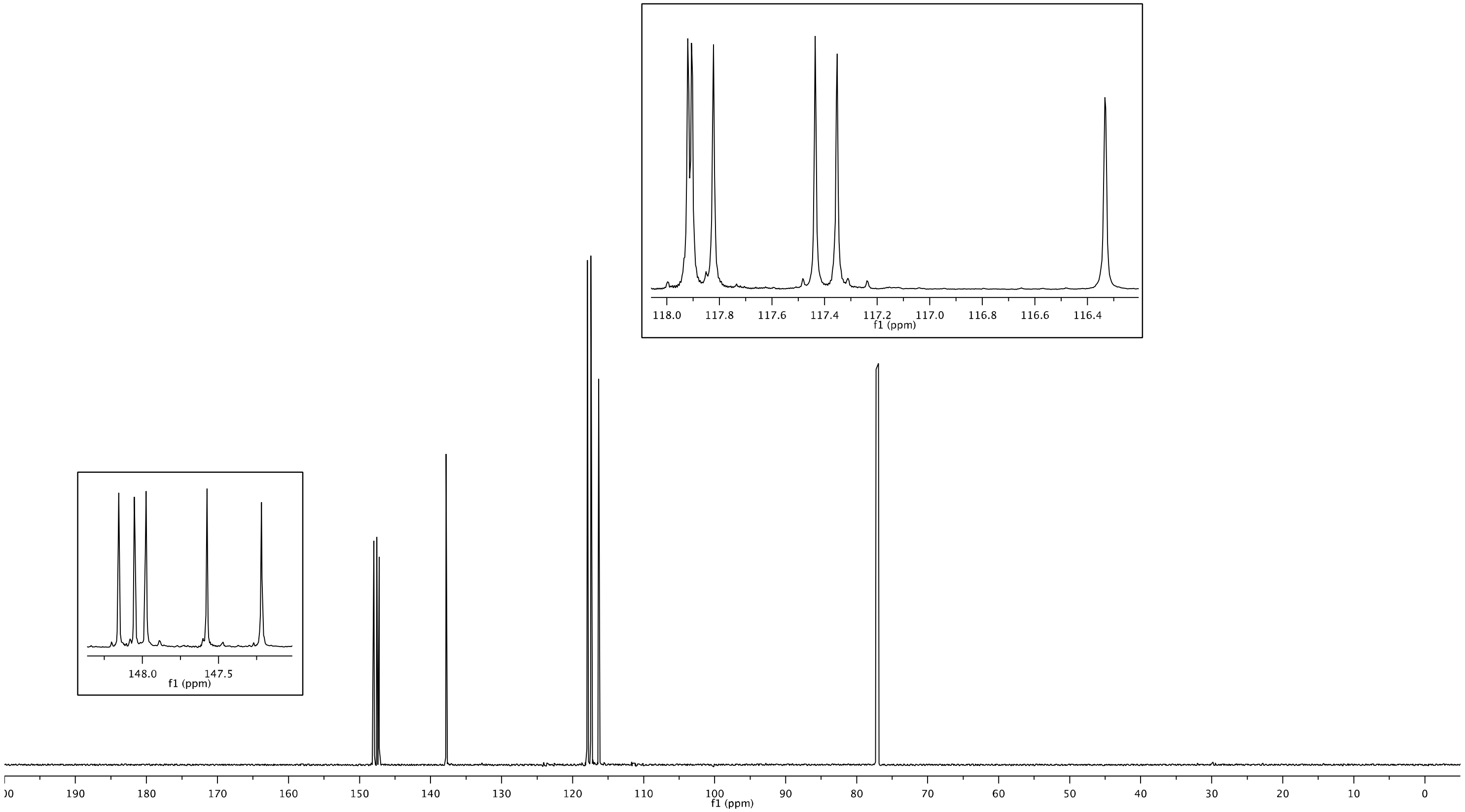
^{1}H NMR spectrum
800 MHz, in $CDCl_3$

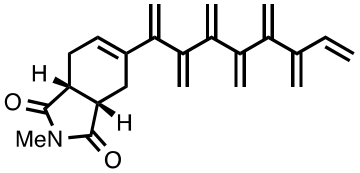




10

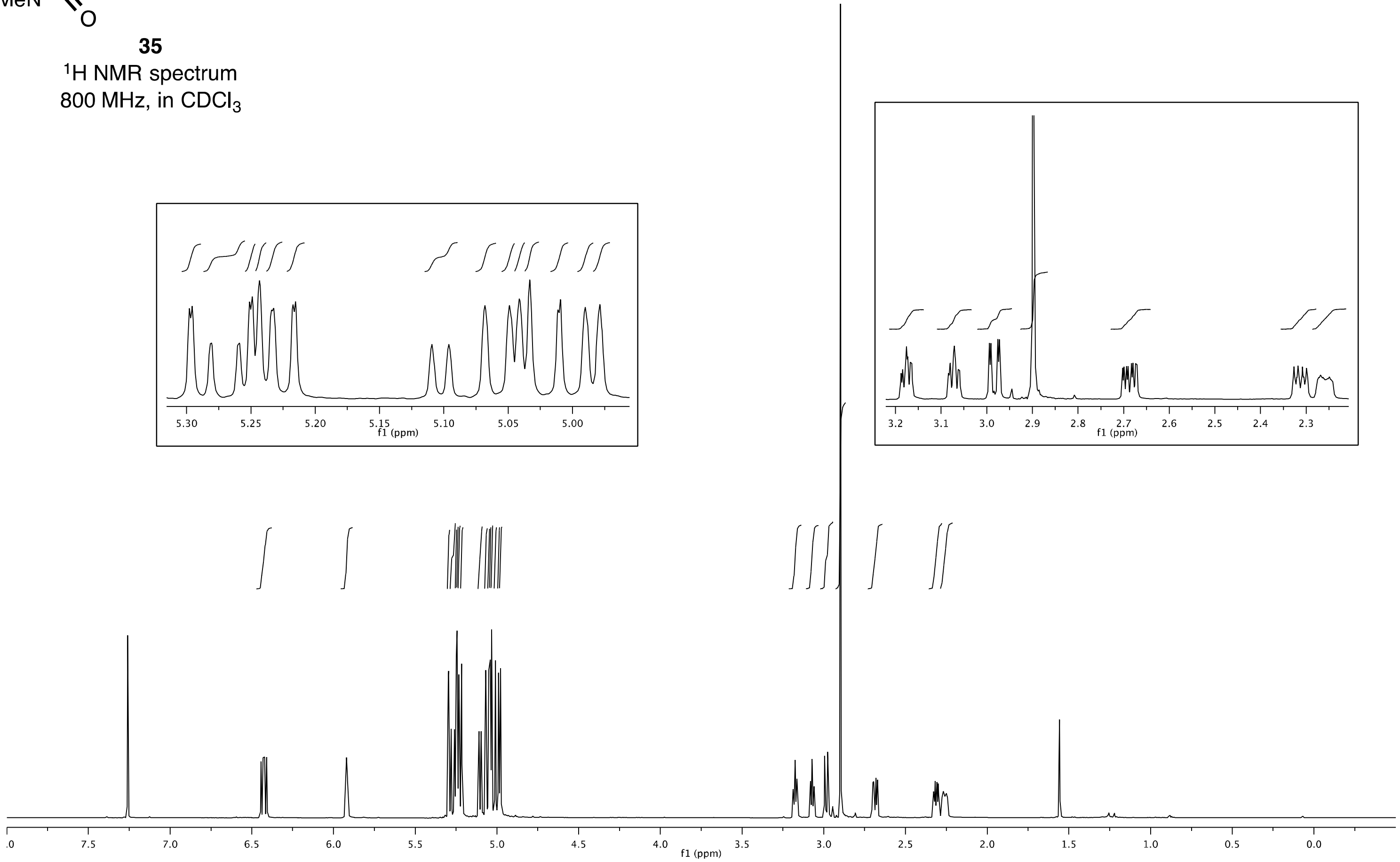
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

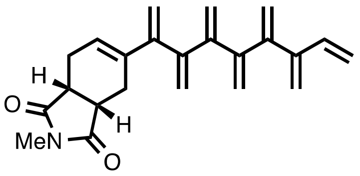




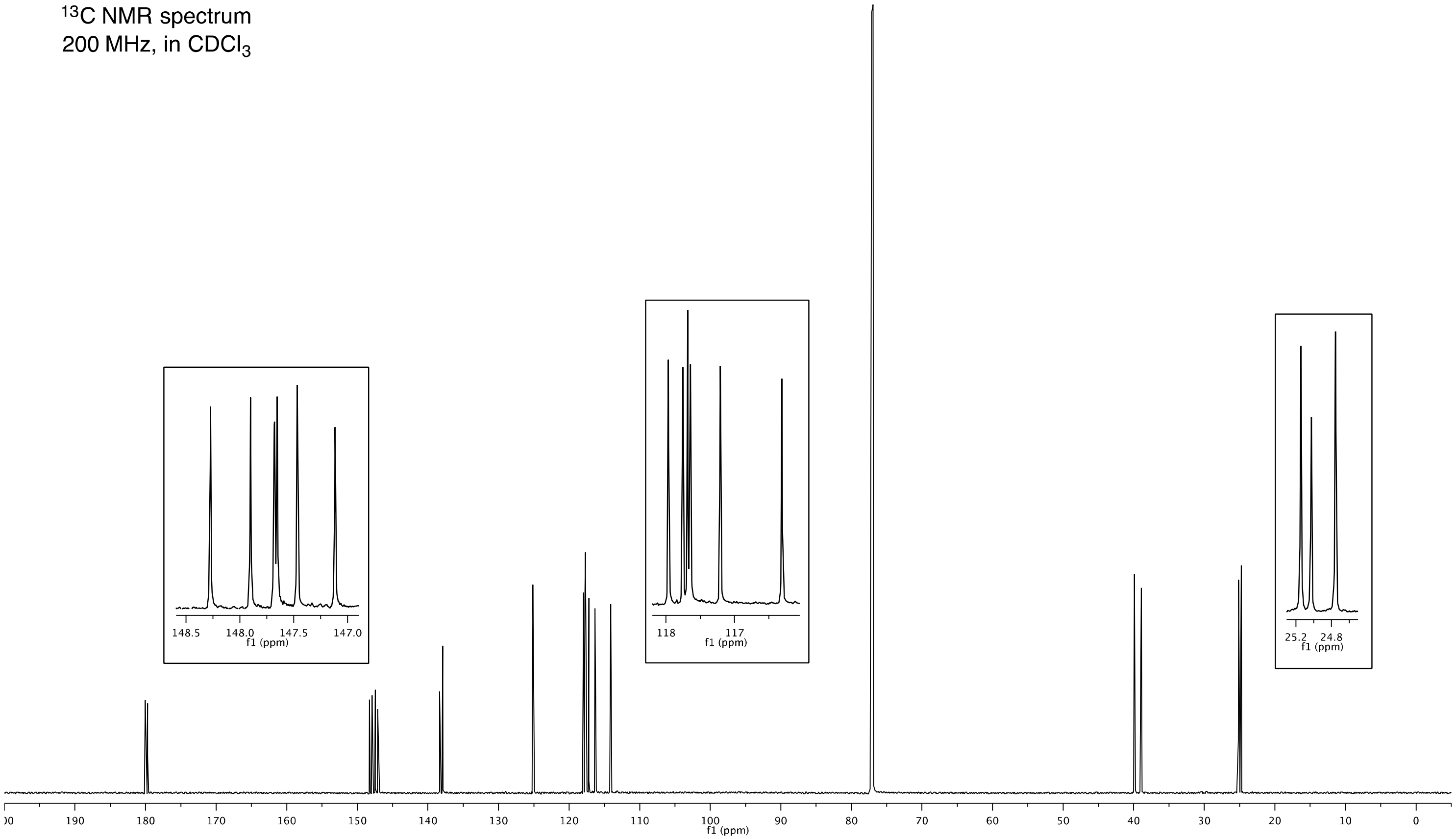
35

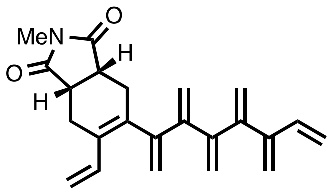
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





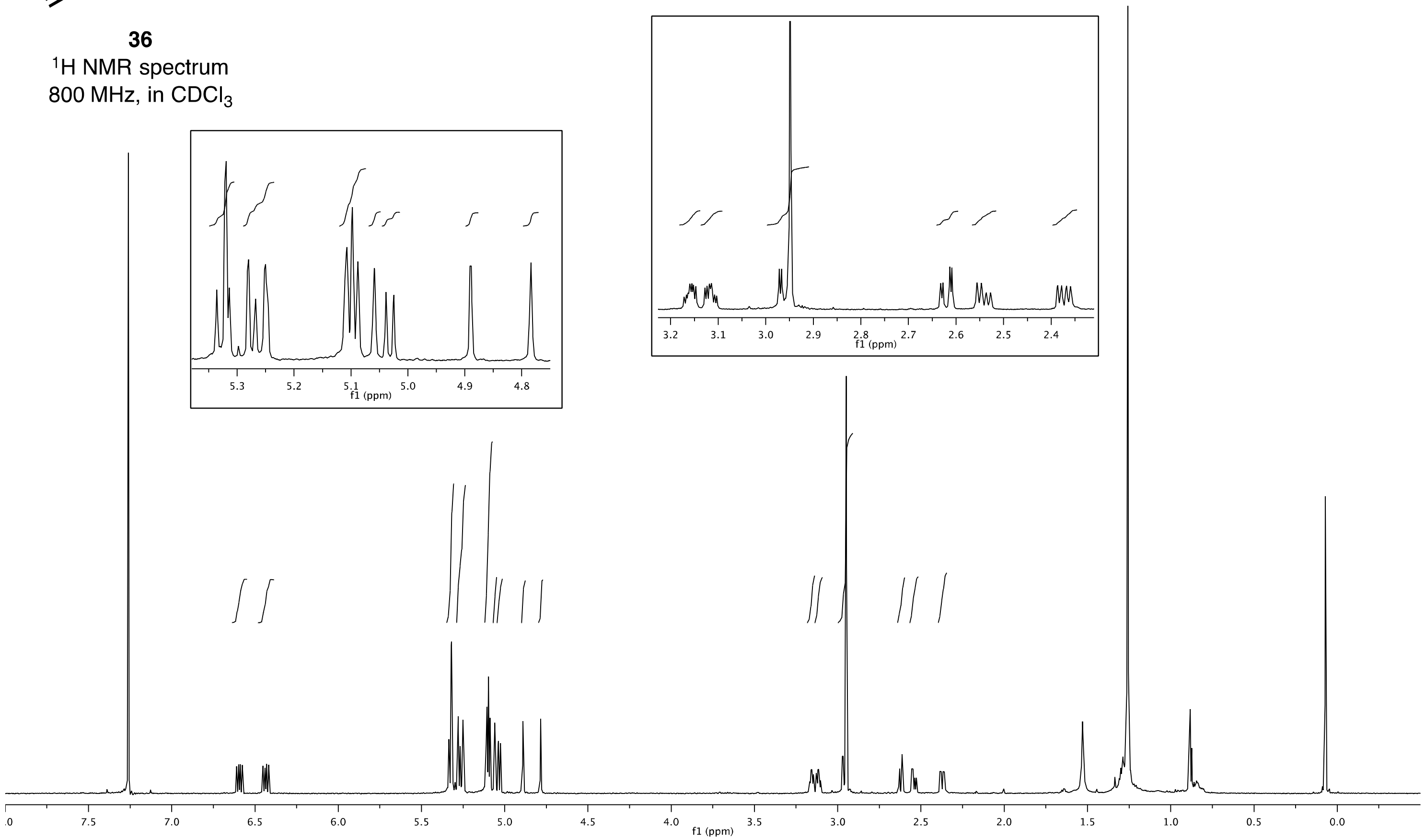
35
^{13}C NMR spectrum
200 MHz, in $CDCl_3$

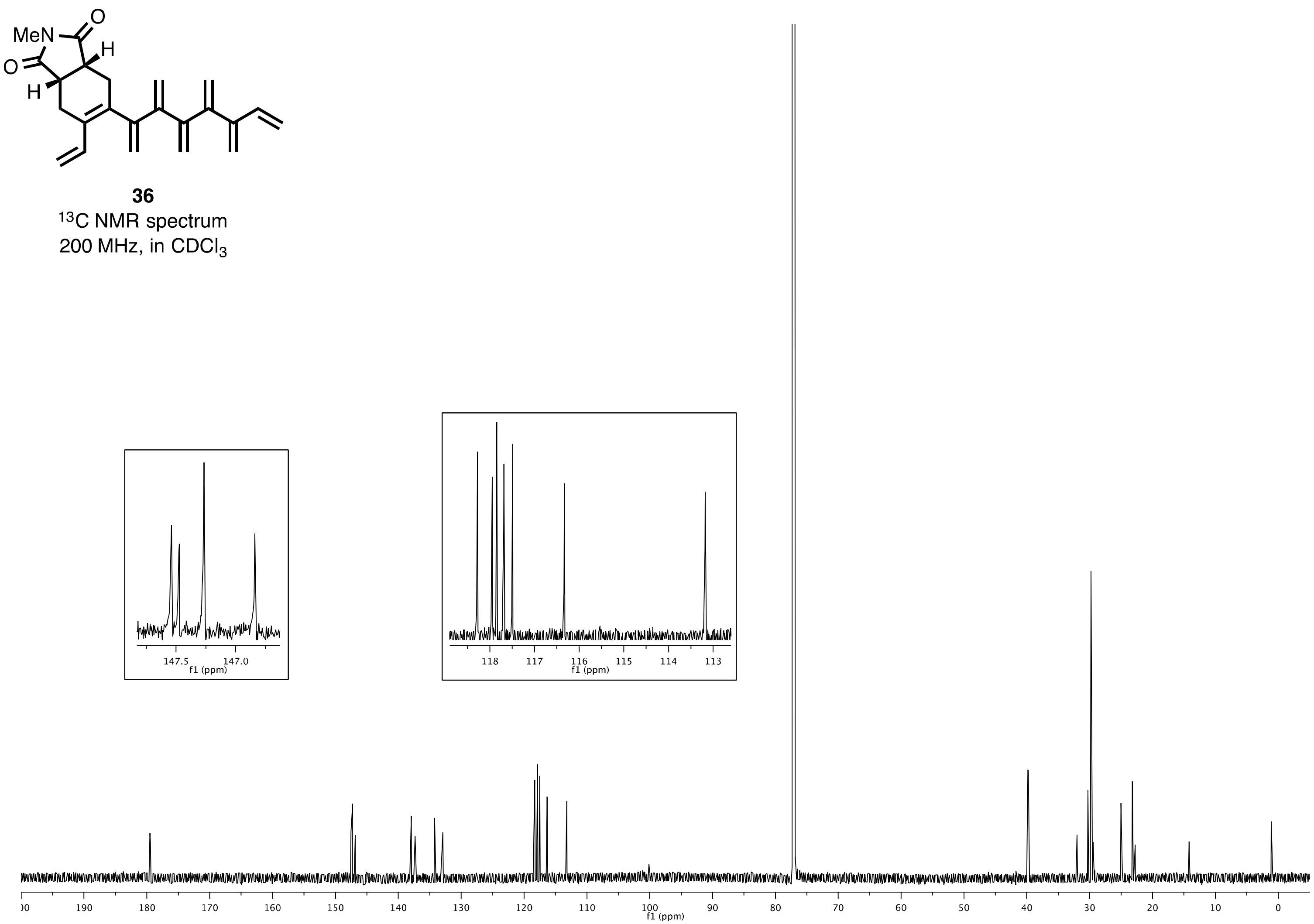




36

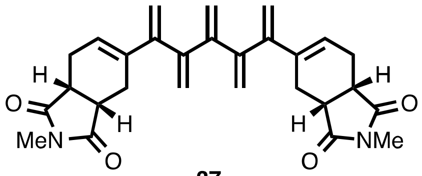
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





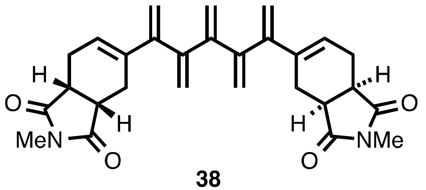
36

^{13}C NMR spectrum
200 MHz, in $CDCl_3$



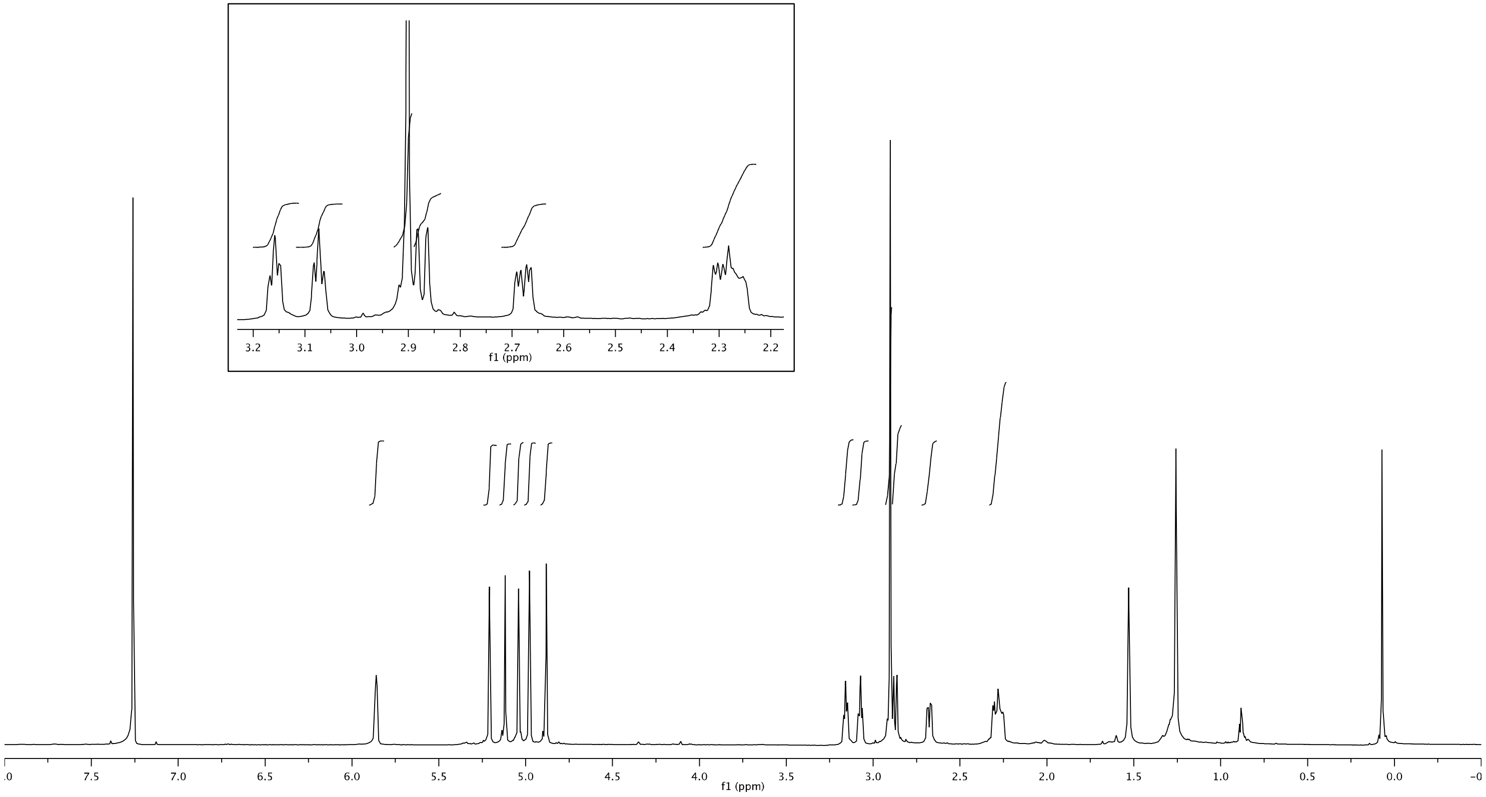
37

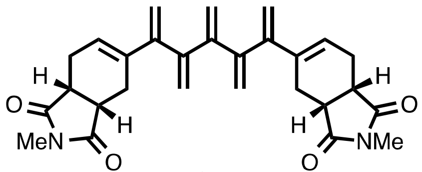
or



38

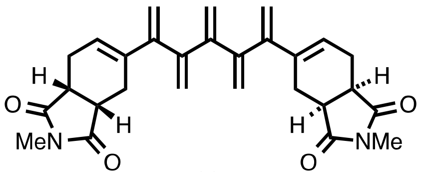
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





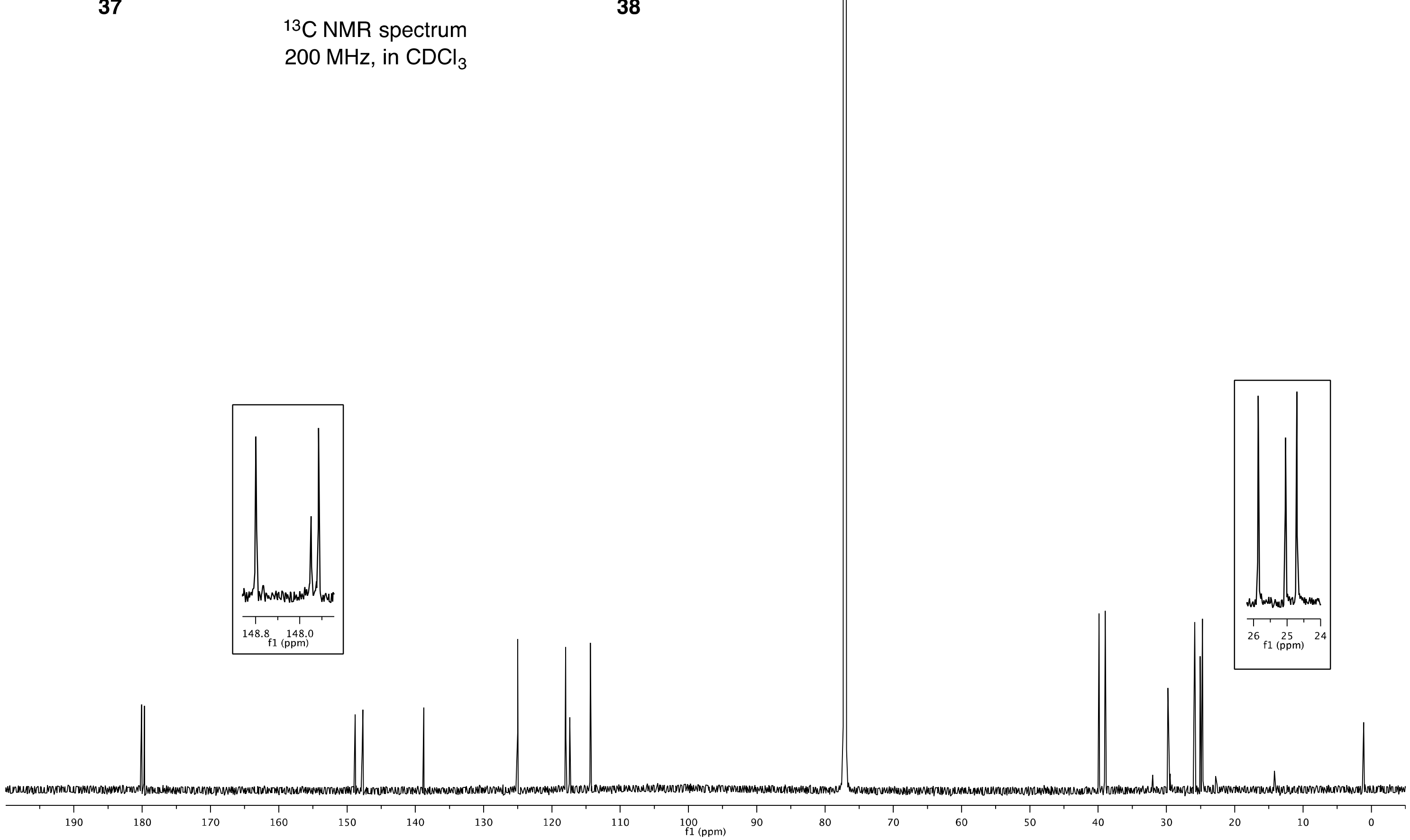
37

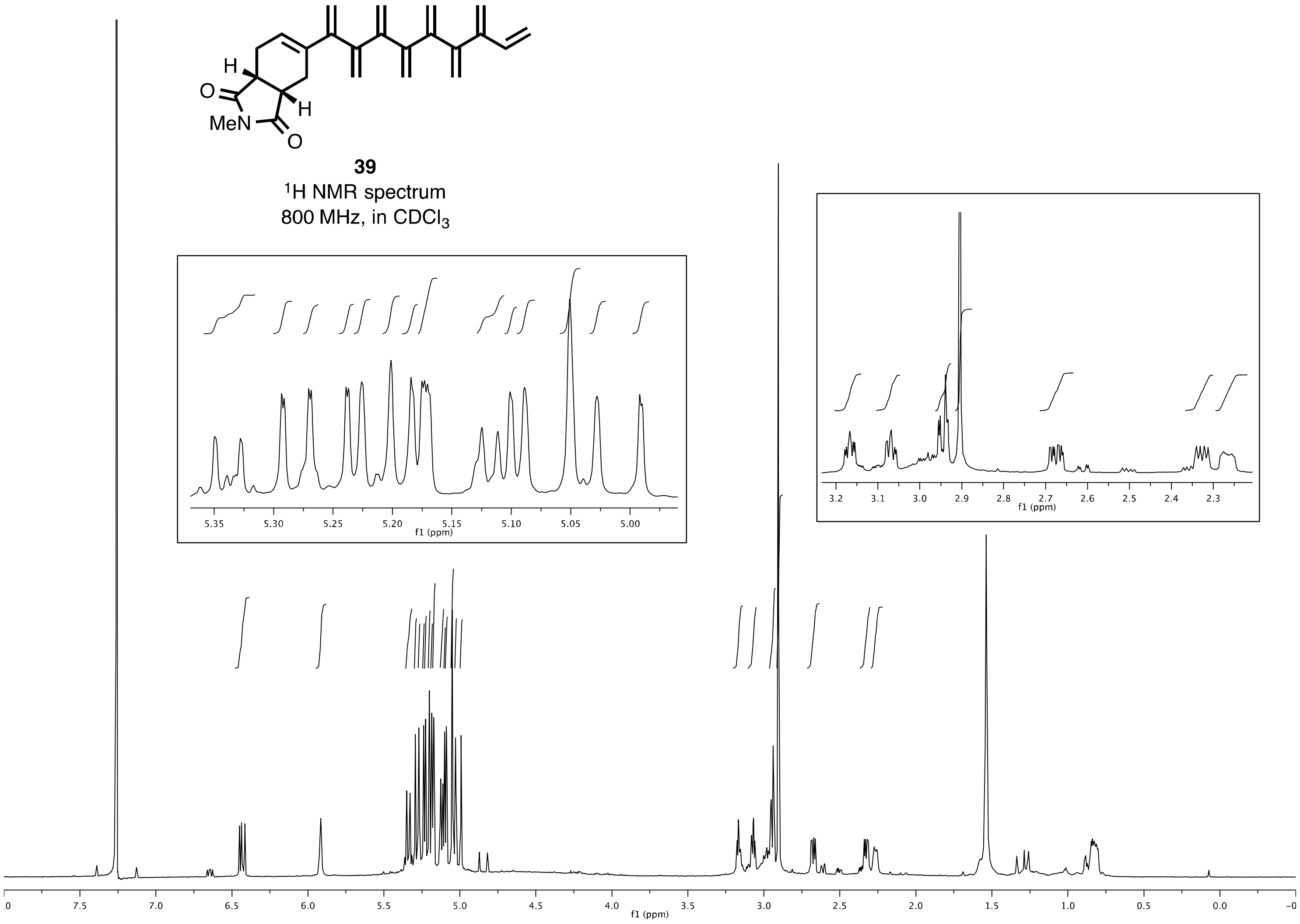
or



38

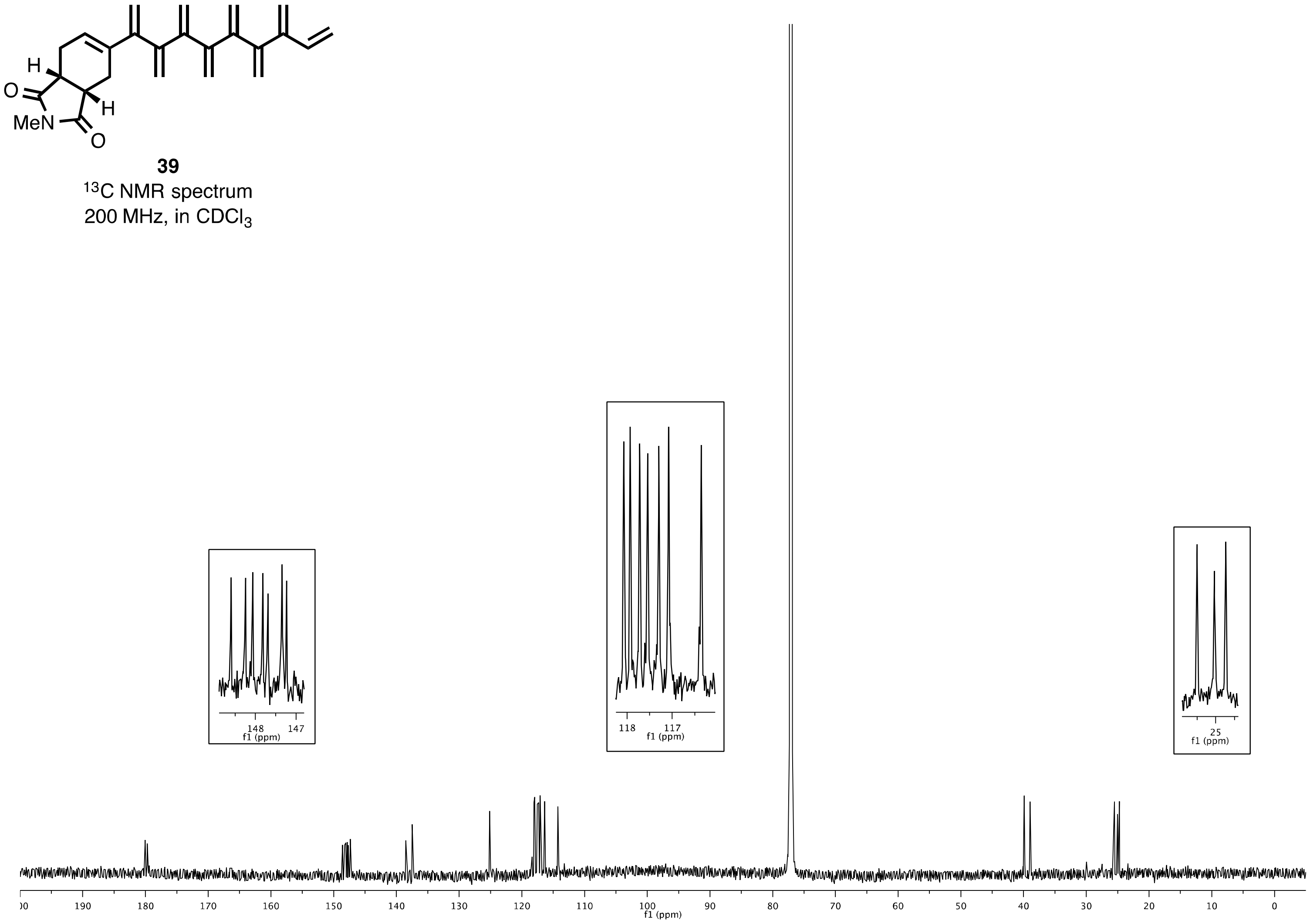
^{13}C NMR spectrum
200 MHz, in CDCl$_3$





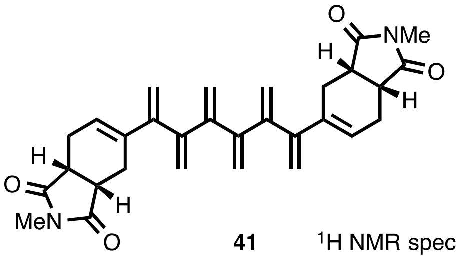
39

^{1}H NMR spectrum
800 MHz, in CDCl$_3$



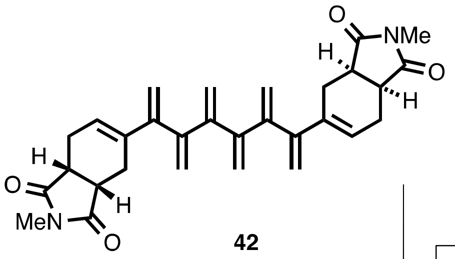
39

^{13}C NMR spectrum
200 MHz, in $CDCl_3$



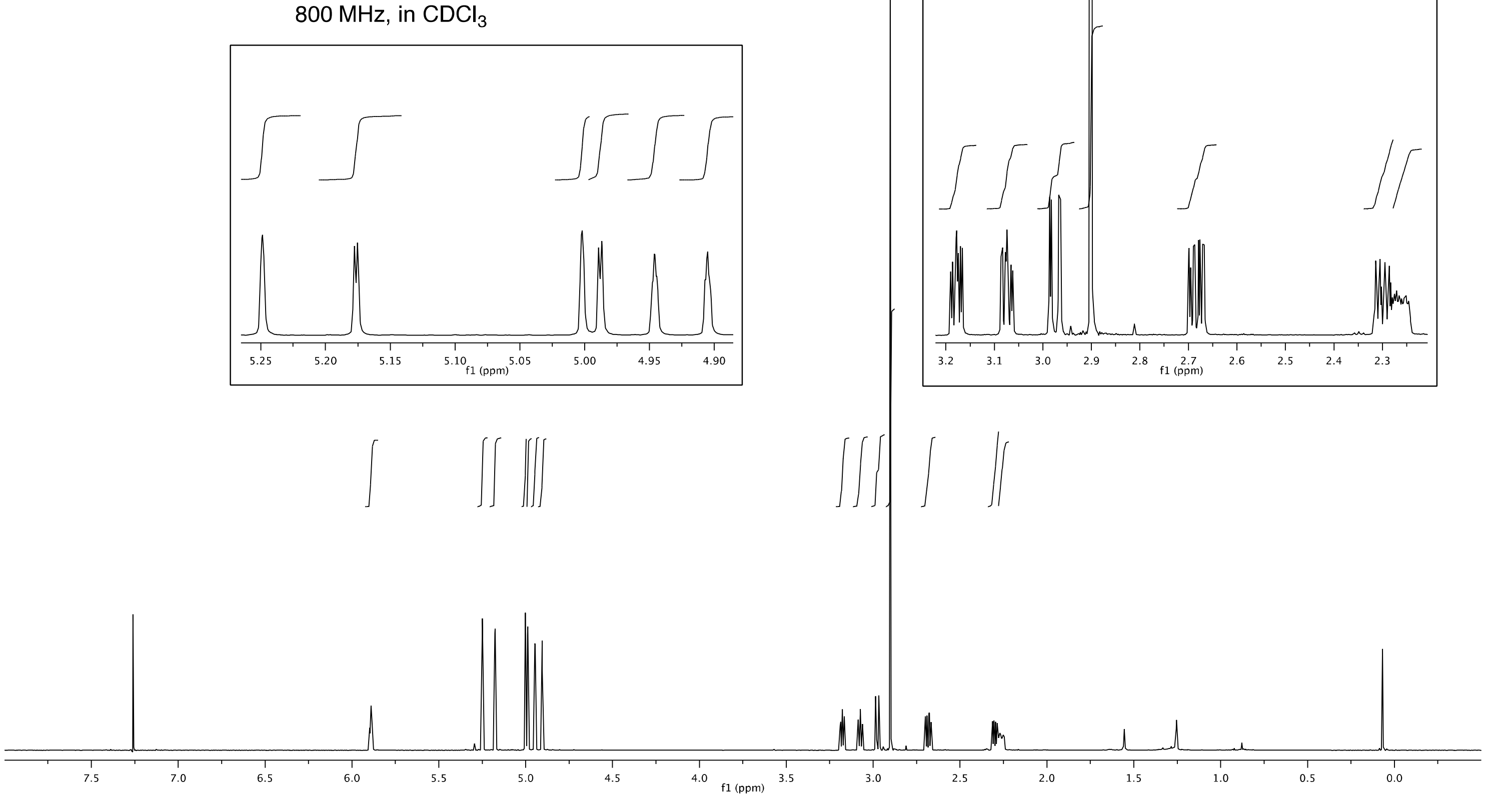
41

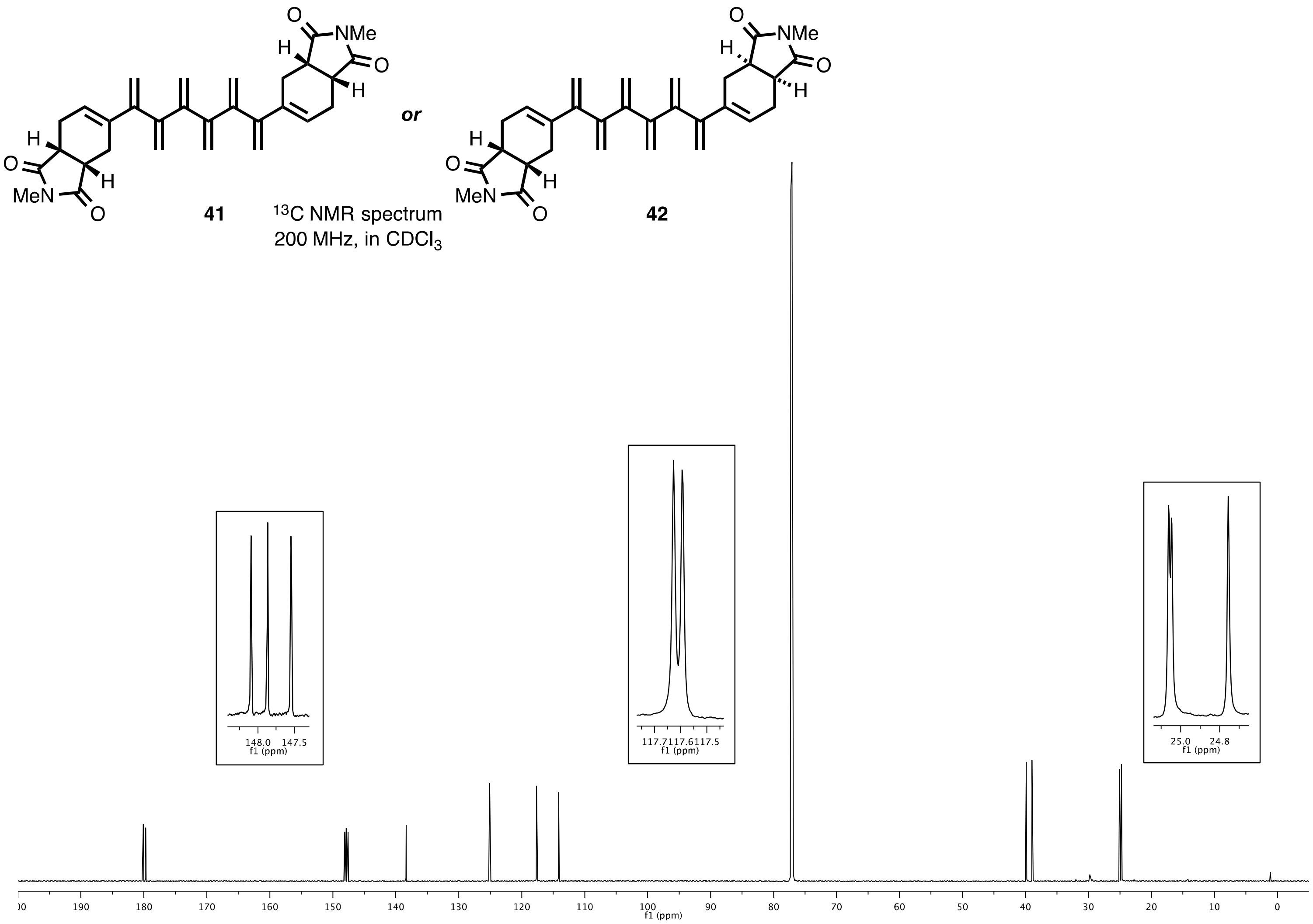
or



42

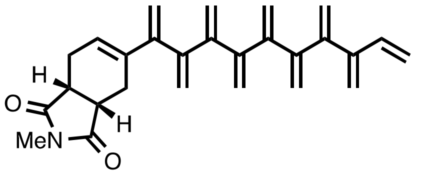
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





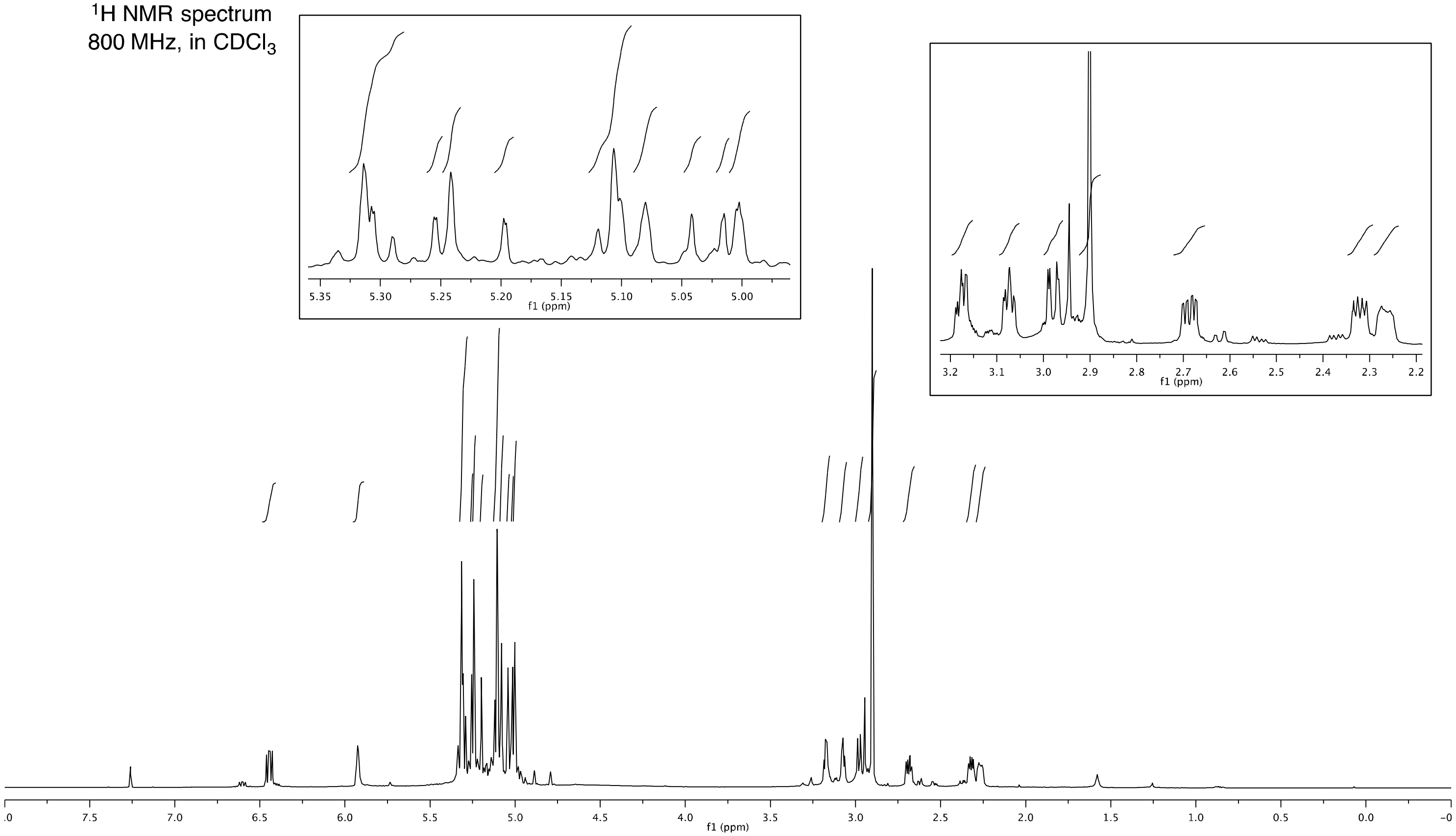
41 or **42**

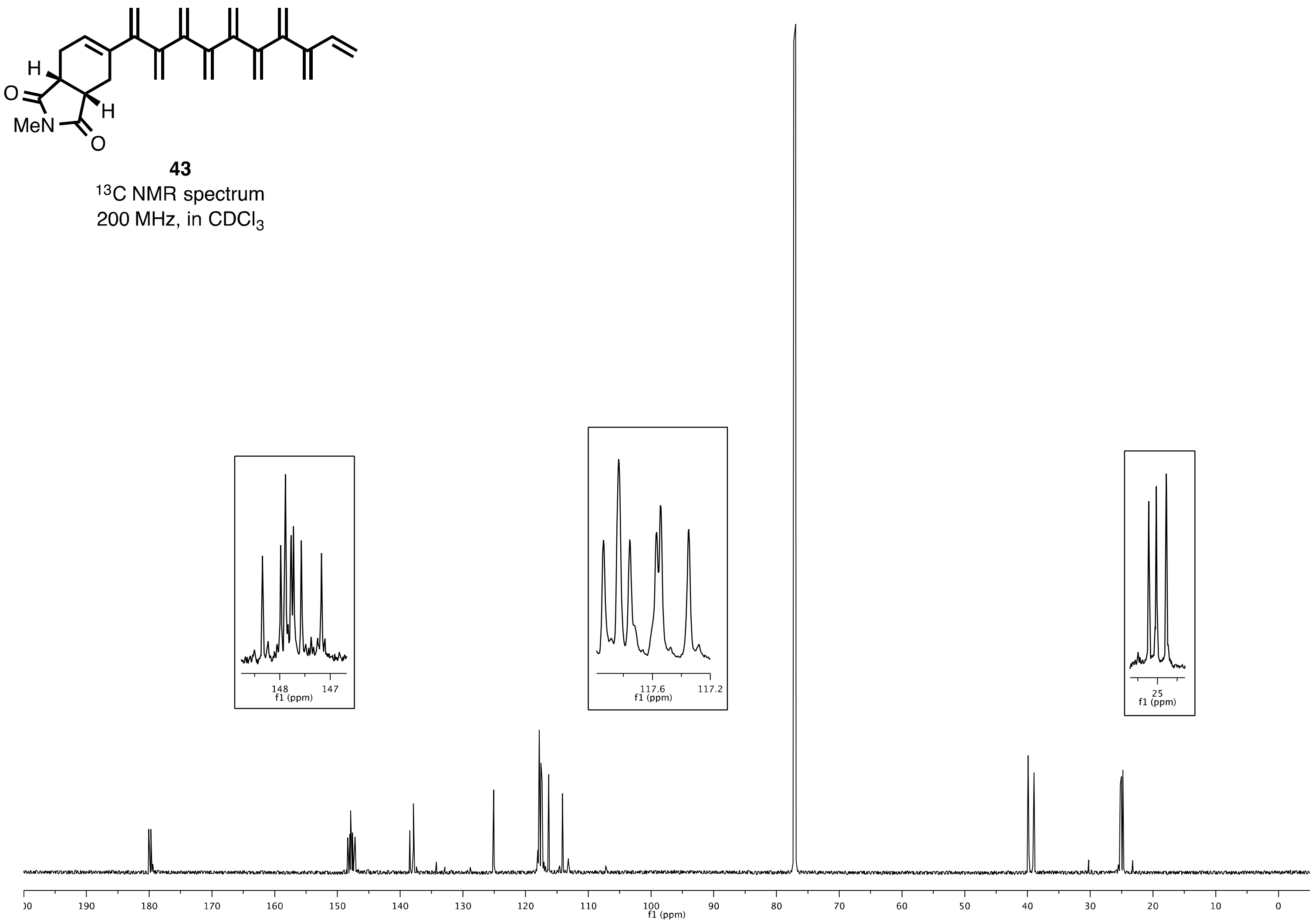
^{13}C NMR spectrum
200 MHz, in $CDCl_3$



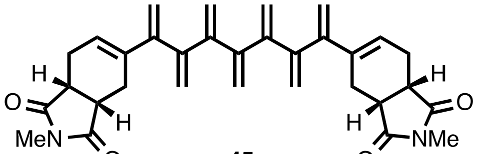
43

^{1}H NMR spectrum
800 MHz, in CDCl$_3$



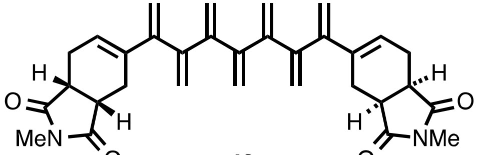


43
^{13}C NMR spectrum
200 MHz, in $CDCl_3$



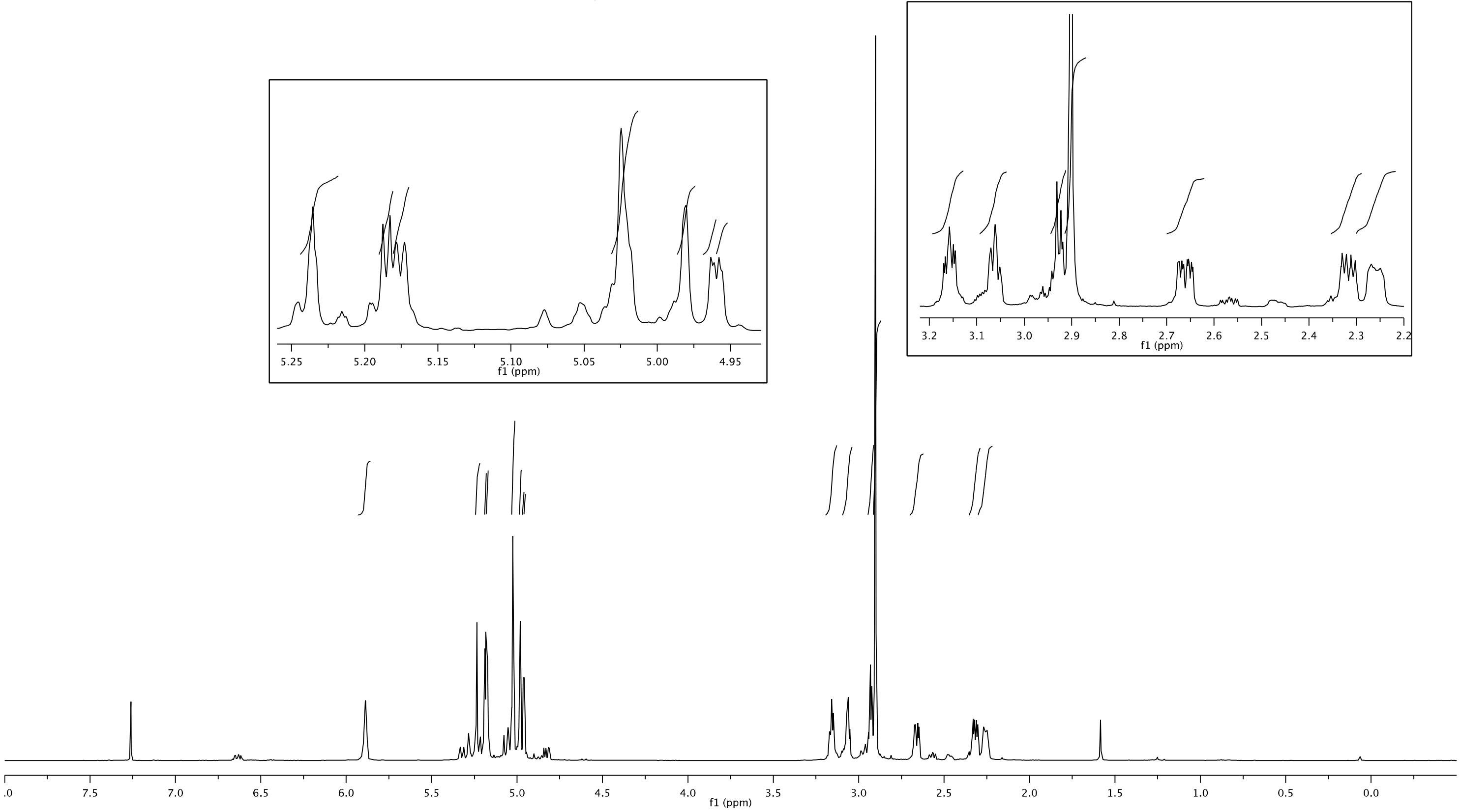
45

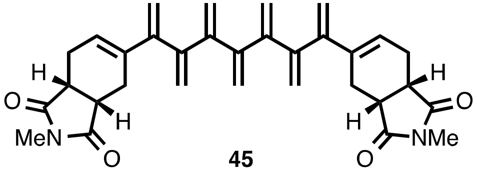
and



46

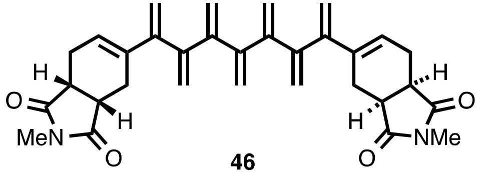
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





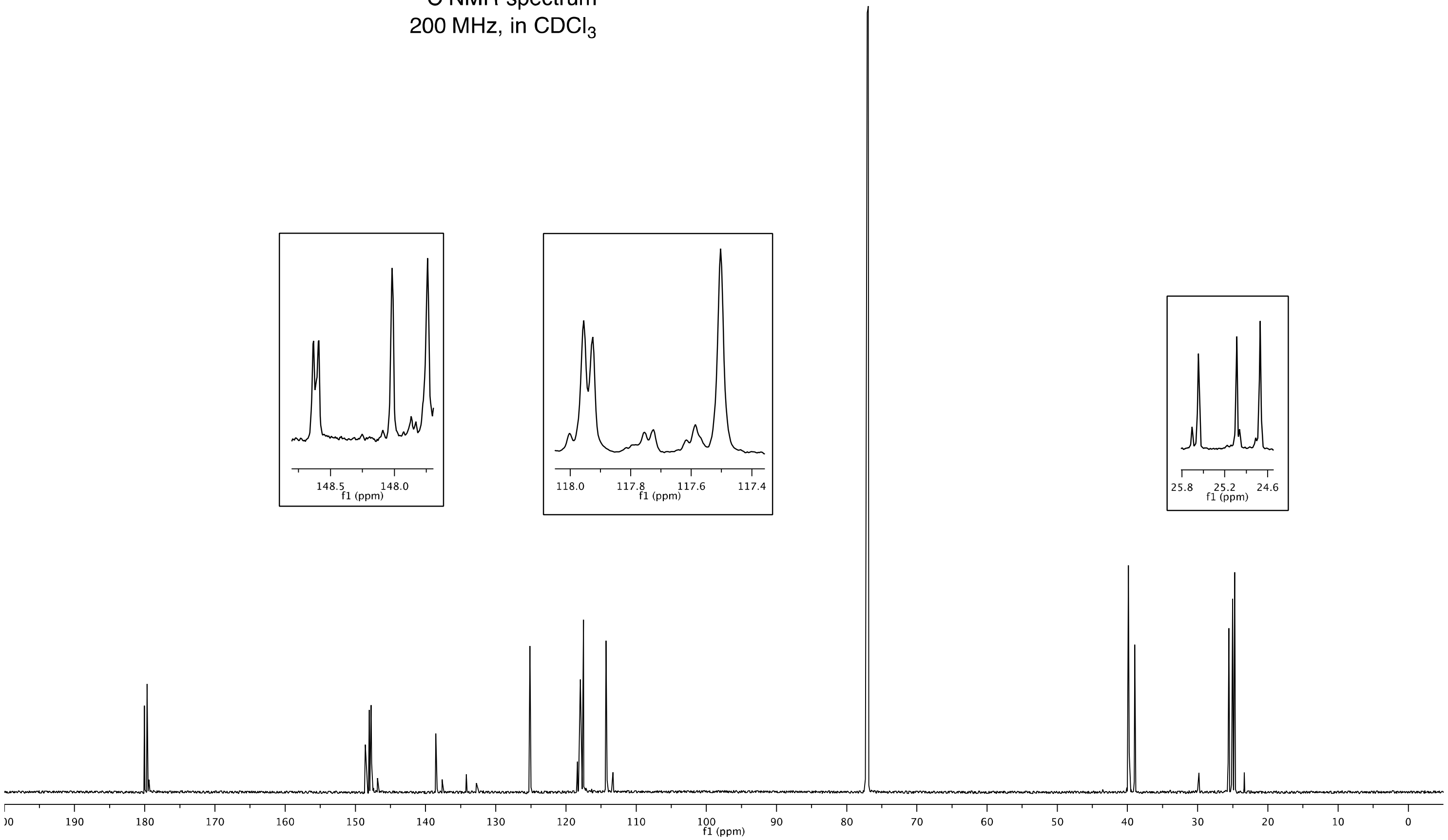
45

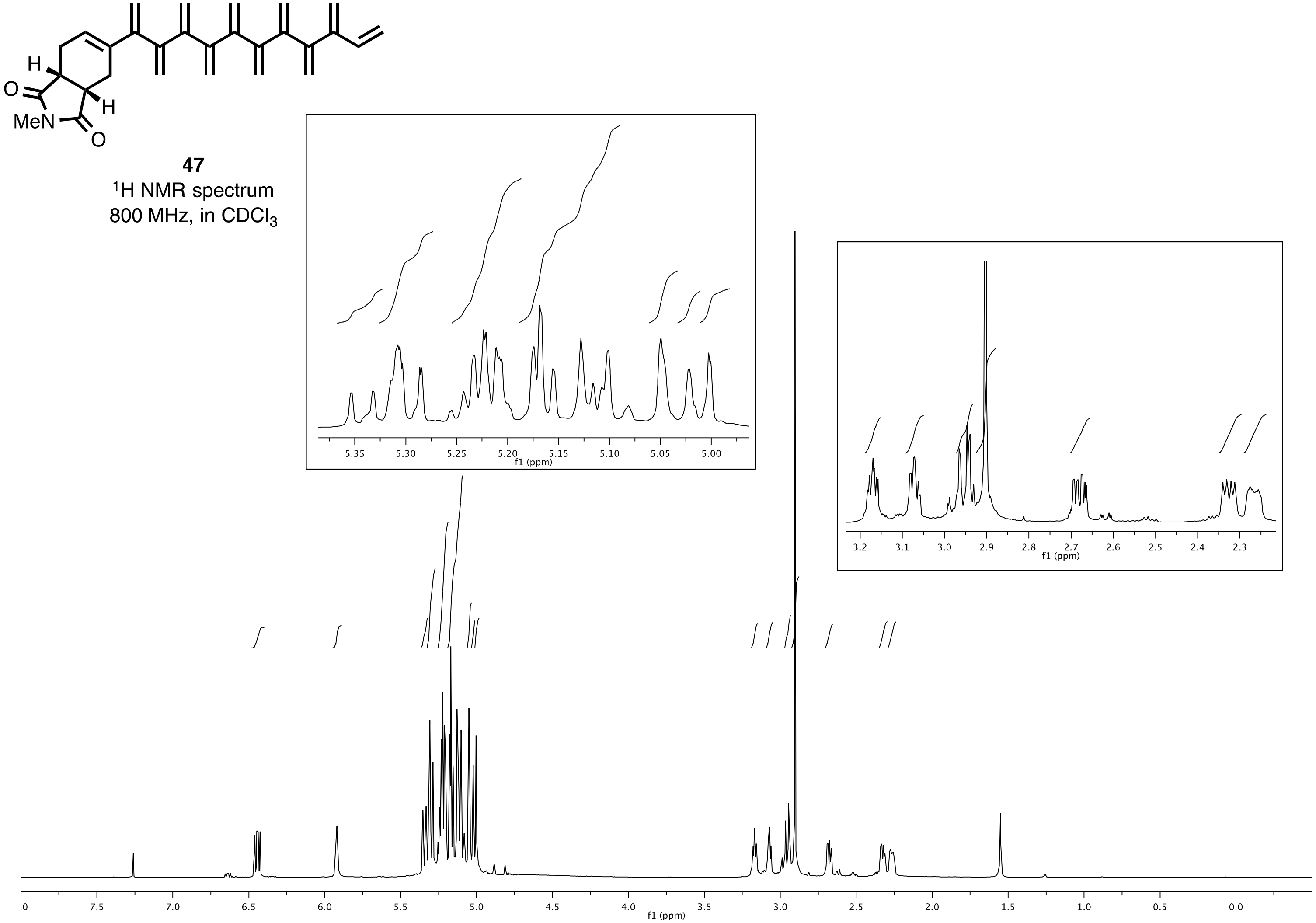
and



46

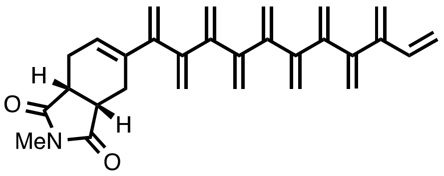
^{13}C NMR spectrum
200 MHz, in $CDCl_3$





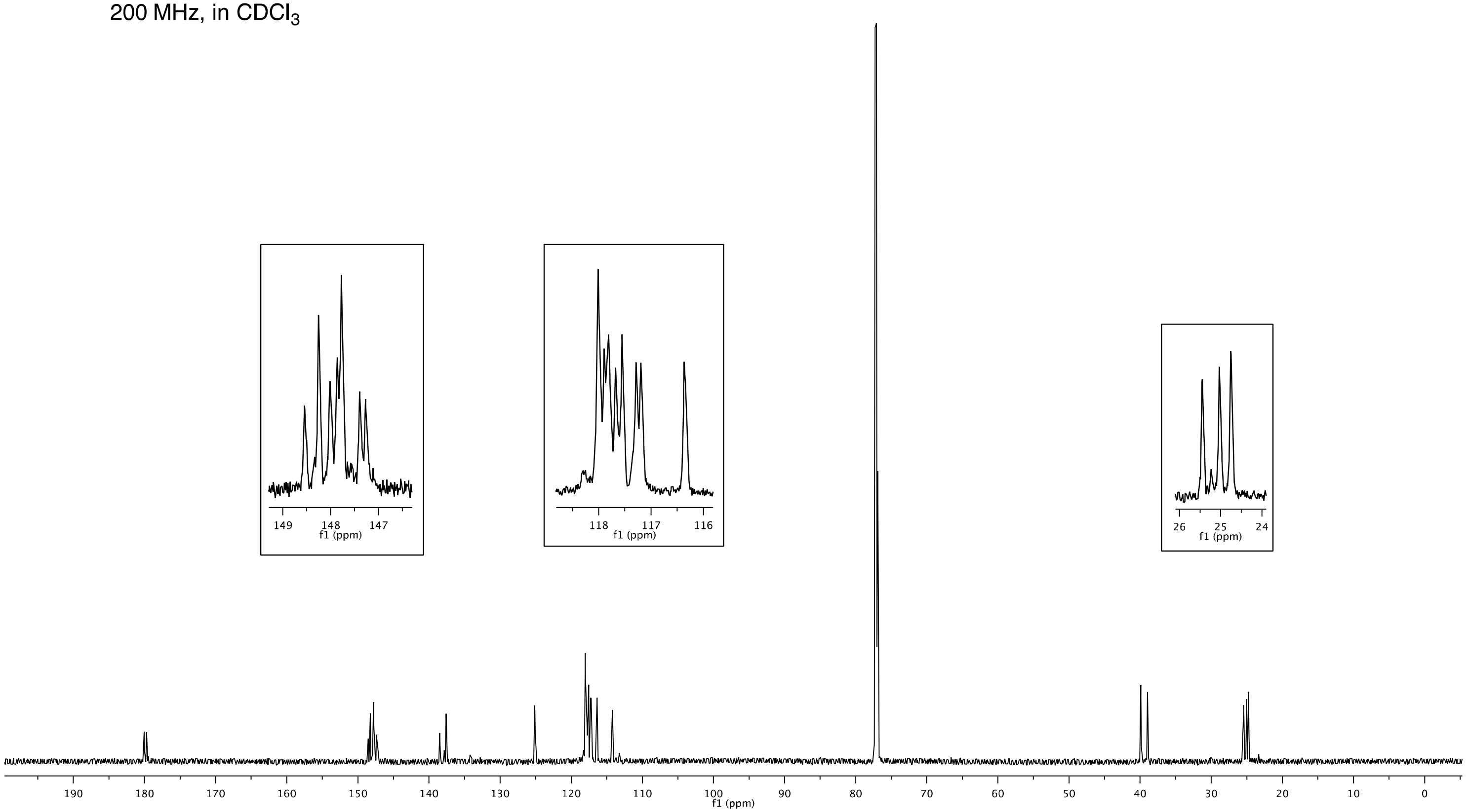
47

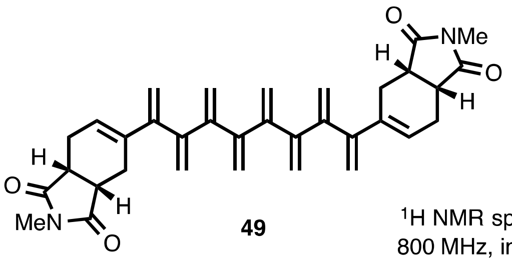
^{1}H NMR spectrum
800 MHz, in $CDCl_3$



47

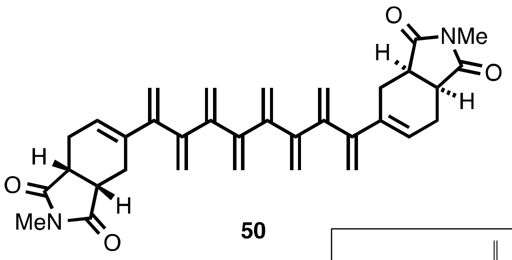
^{13}C NMR spectrum
200 MHz, in $CDCl_3$





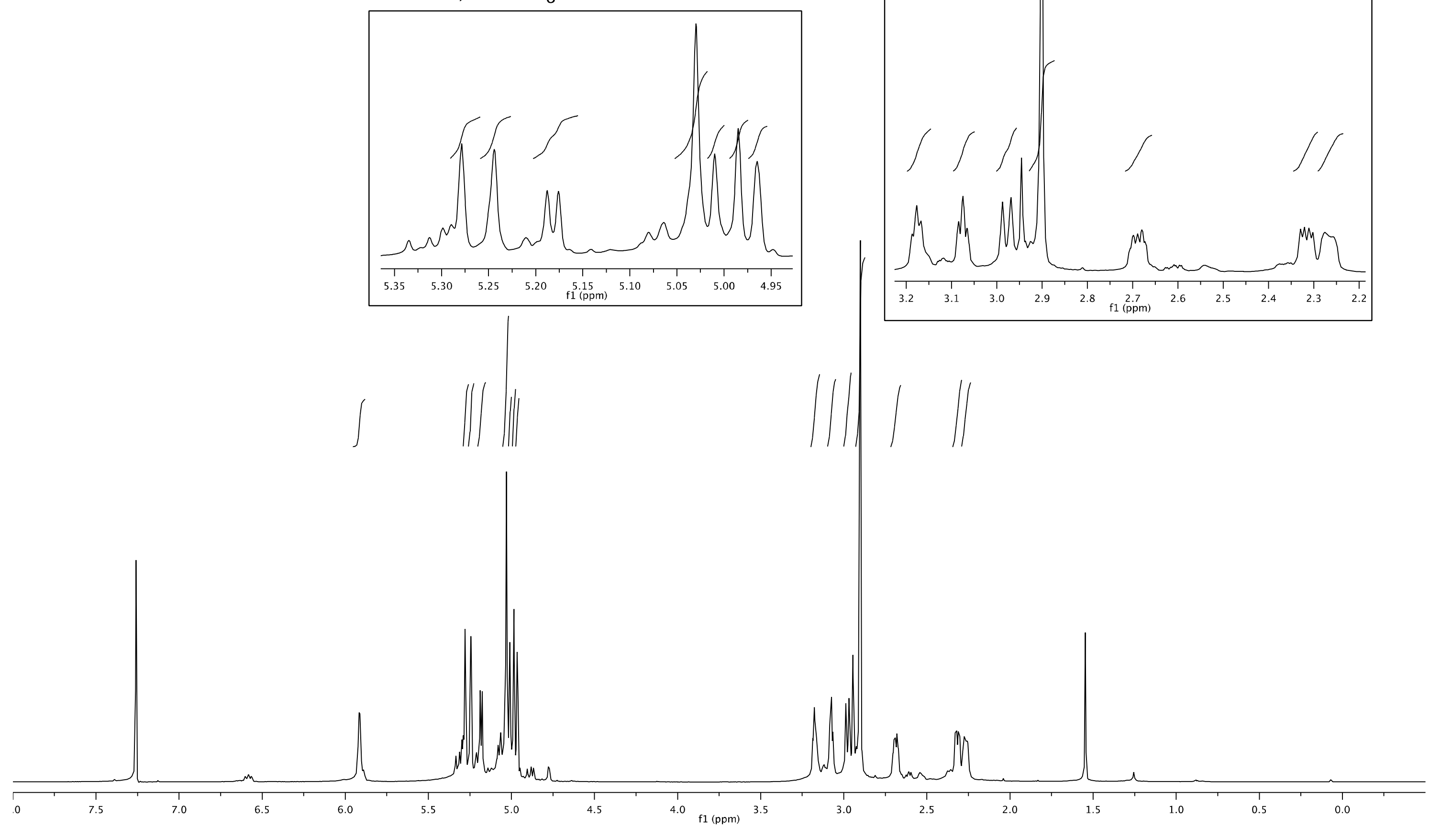
49

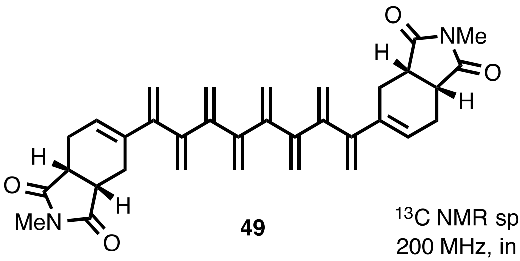
and



50

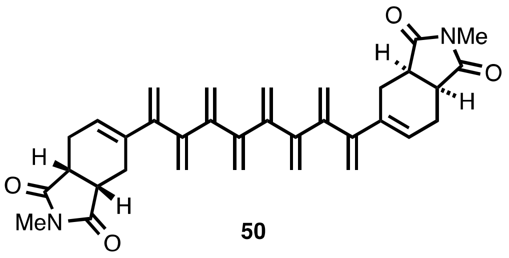
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





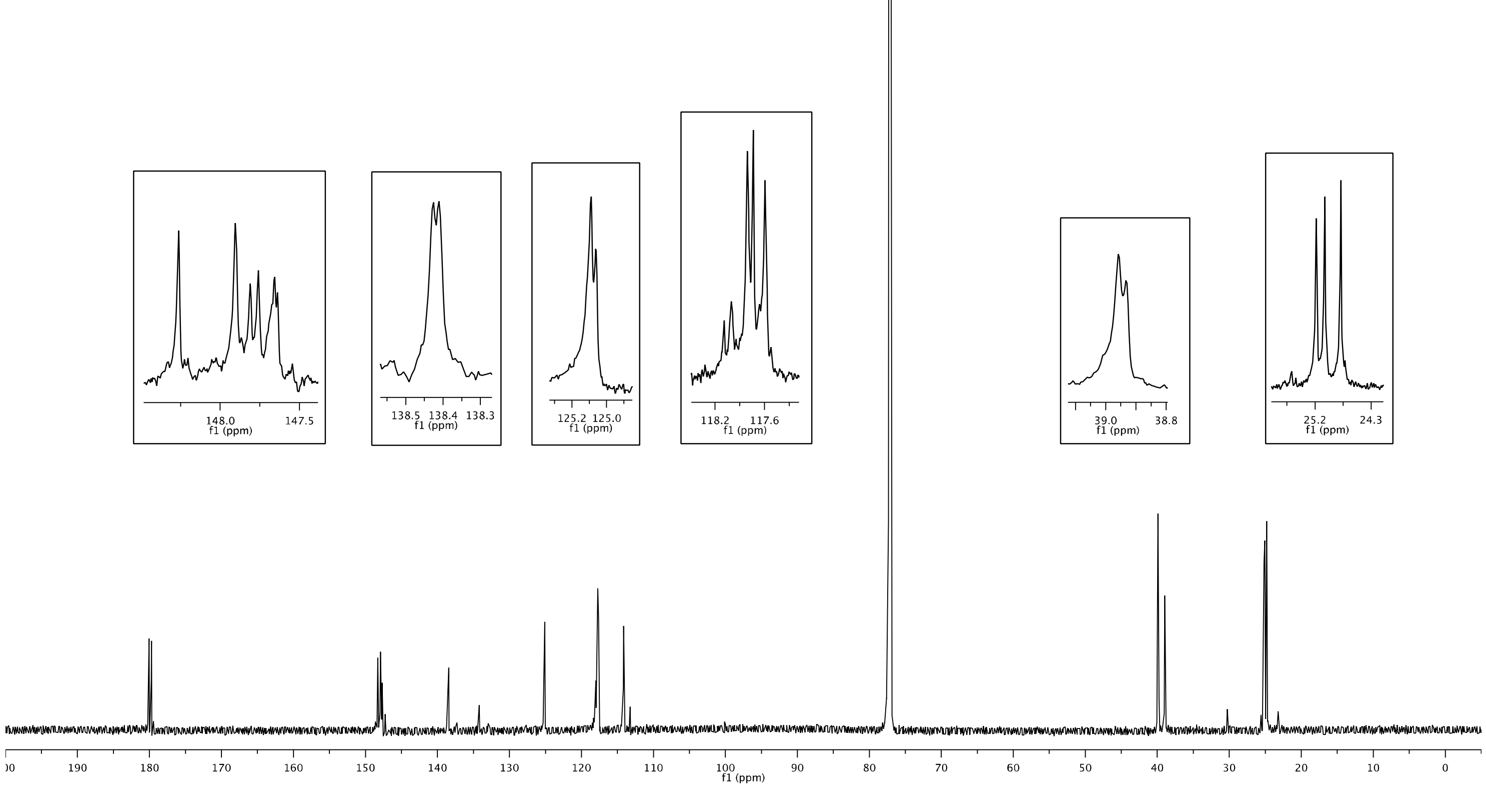
49

and



50

^{13}C NMR spectrum
200 MHz, in CDCl$_3$



9) Computational Studies

Computational methods

All calculations were carried out using the GAUSSIAN 09 software package.[19] All calculations were carried out using gas phase conditions at a temperature of 298.15 K and 1 atm pressure. All optimised molecular geometries and reaction energetics were calculated using the G4(MP2) method[20] and the B3LYP[21] functional[22] and the 6-31G(d) basis set as model chemistries. The NMR and TD-DFT calculations were carried out using the B3LYP/6-31G(d) optimised geometries. Entropies were corrected using the quasi harmonic approximation as described by Truhlar and co-workers.[22]

Cartesian coordinates and energies

The geometries of the conformations for each molecule are listed in descending order of higher conformer energy (0 K), i.e., most stable first.

[3]Dendralene
anti_gauche
G4(MP2)
Eel = -233.10734900 au; Energy(0K)) = -232.99048954 au
Enthalpy = -232.98288760 au; Gibbs energy = -233.02057394 au

C	2.064344	-0.900055	-0.114170
C	1.444203	0.280264	-0.040340
H	1.524572	-1.840601	-0.092625
H	3.142345	-0.963878	-0.210586
H	2.038959	1.190736	-0.087123
C	-0.002177	0.494294	0.091660
C	-0.504054	1.739422	0.031129
H	-1.560884	1.933924	0.170303
H	0.136114	2.596595	-0.151013
C	-0.873839	-0.676890	0.321399
C	-2.069189	-0.867262	-0.235687
H	-0.481713	-1.432391	0.999851
H	-2.671361	-1.738497	-0.001220
H	-2.483769	-0.164525	-0.951531

############################

anti_anti
G4(MP2)
Eel = -233.10607500 au; Energy(0K)) = -232.98906347 au
Enthalpy = -232.98148221 au; Gibbs energy = -233.01904610 au

C	-1.591937	-1.266599	0.202801
C	-1.282918	-0.022744	-0.170263
H	-0.880255	-1.928022	0.681081
H	-2.595878	-1.652278	0.062303
H	-2.069819	0.591700	-0.604698
C	-0.000024	0.681403	-0.000021
C	-0.000140	2.027684	0.000098
H	0.911117	2.596335	0.150370
H	-0.911490	2.596208	-0.150076
C	1.282977	-0.022552	0.170036
C	1.592044	-1.266504	-0.202681
H	2.069934	0.592127	0.604041
H	2.596072	-1.652005	-0.062321
H	0.880309	-1.928189	-0.680519

############################

ag_to_aa_barrier
G4(MP2)
Eel = -233.10387600 au; Energy(0K)) = -232.98757455 au
Enthalpy = -232.98060149 au; Gibbs energy = -233.01689034 au

C	-1.698389	-1.209217	0.062328
C	-1.360030	0.075178	-0.079106
H	-0.964896	-1.969480	0.305930
H	-2.724154	-1.536123	-0.066512
H	-2.132268	0.802165	-0.326191
C	-0.015761	0.641522	0.074163
C	0.188824	1.955393	-0.097639
H	1.171038	2.400624	0.014125
H	-0.626731	2.622935	-0.358493
C	1.110835	-0.255308	0.463337
C	1.744686	-1.081842	-0.363388
H	1.417922	-0.207595	1.507405
H	2.565990	-1.704248	-0.023211
H	1.472110	-1.162634	-1.411220

############################

gauche_gauche
G4(MP2)
Eel = -233.10324200 au; Energy(0K)) = -232.98677294 au
Enthalpy = -232.97901511 au; Gibbs energy = -233.01704123 au

C	2.463394	-0.267275	0.104740
C	1.225941	-0.617399	-0.247525
H	2.665000	0.652044	0.645556
H	3.317296	-0.893929	-0.128329
H	1.073631	-1.576144	-0.741818
C	0.000000	0.170305	0.000001
C	-0.000001	1.512353	0.000000
H	-0.889144	2.078104	0.253794
H	0.889139	2.078106	-0.253796
C	-1.225941	-0.617401	0.247525
C	-2.463393	-0.267275	-0.104741
H	-1.073630	-1.576145	0.741818
H	-3.317296	-0.893929	0.128328
H	-2.664999	0.652045	-0.645555

############################

ag_to_gg_barrier
G4(MP2)
Eel = -233.09883000 au; Energy(0K)) = -232.98285374 au
Enthalpy = -232.97575291 au; Gibbs energy = -233.01245780 au

C	2.308959	-0.616112	0.100535
C	1.000701	-0.717090	-0.139189
H	2.750691	0.297152	0.486573
H	2.981704	-1.448800	-0.073532
H	0.593603	-1.671964	-0.467119
C	0.005704	0.359606	0.041592
C	0.280895	1.647587	-0.191802
H	-0.459483	2.423700	-0.031409
H	1.250193	1.960141	-0.565564
C	-1.346508	-0.068101	0.508415
C	-2.282940	-0.599964	-0.271308
H	-1.545162	0.054353	1.572749
H	-3.244443	-0.908474	0.125751
H	-2.127967	-0.741662	-1.336911

############################

anti_gauche
B3LYP/6-31G(d)
Eel = -233.38782016 au; Energy(0K)) = -233.26872031 au
Enthalpy = -233.26118315 au; Gibbs energy = -233.29876833 au

C	2.071998	-0.899655	-0.116137
C	1.448321	0.283410	-0.037393
H	1.534268	-1.843501	-0.102549

H	3.152209	-0.959491	-0.209707
H	2.044661	1.194681	-0.077569
C	-0.002347	0.493325	0.092347
C	-0.508049	1.741365	0.029745
H	-1.566783	1.935149	0.168680
H	0.130642	2.601662	-0.153509
C	-0.874119	-0.681489	0.320444
C	-2.076060	-0.867578	-0.234376
H	-0.481161	-1.443127	0.993724
H	-2.678375	-1.740927	-0.000042
H	-2.493921	-0.160714	-0.946801

############################

anti_anti
B3LYP/6-31G(d)
Eel = -233.38684322 au; Energy(0K)) = -233.26752503 au
Enthalpy = -233.26003786 au; Gibbs energy = -233.29740951 au

C	-1.598788	-1.260886	0.207477
C	-1.284456	-0.016449	-0.174523
H	-0.890198	-1.920889	0.696164
H	-2.604447	-1.645652	0.063550
H	-2.069536	0.596572	-0.617244
C	0.003918	0.683603	-0.000083
C	0.010824	2.033826	0.000427
H	0.925957	2.599694	0.150905
H	-0.898472	2.609146	-0.149569
C	1.284917	-0.029879	0.173552
C	1.584655	-1.278335	-0.207068
H	2.077179	0.575149	0.614454
H	2.585973	-1.674567	-0.064125
H	0.867131	-1.930736	-0.692827

############################

gauche_gauche
B3LYP/6-31G(d)
Eel = -233.38360338 au; Energy(0K)) = -233.26495375 au
Enthalpy = -233.25725563 au; Gibbs energy = -233.29516962 au

C	2.408021	-0.268440	0.369366
C	1.252366	-0.617974	-0.205881
H	2.514379	0.654866	0.933249
H	3.286308	-0.904012	0.302982
H	1.192350	-1.584018	-0.709528
C	-0.000029	0.171494	-0.197720
C	0.000024	1.517590	-0.222706

H	-0.925551	2.084525	-0.246488
H	0.925672	2.084405	-0.246412
C	-1.252354	-0.618027	-0.205842
C	-2.408051	-0.268389	0.369313
H	-1.192343	-1.584238	-0.709141
H	-3.286272	-0.904068	0.303138
H	-2.514414	0.655016	0.933023

############################

[4]Dendralene

tct_4_Dendralene_G4MP2
G4(MP2)
Eel = -310.41543900 au; Energy(0K)) = -310.26606922 au
Enthalpy = -310.25620936 au; Gibbs energy = -310.29827227 au

C	-0.524750	1.796010	-1.377405
C	0.454449	1.608214	-0.489707
H	-1.378656	1.130501	-1.438759
H	-0.501977	2.628227	-2.071930
H	1.287137	2.309360	-0.462157
C	0.524750	0.534906	0.507656
C	1.506442	0.518495	1.420267
H	1.574998	-0.262263	2.168689
H	2.270104	1.290353	1.439294
C	-0.524750	-0.534906	0.507656
C	-1.506442	-0.518495	1.420267
H	-2.270104	-1.290353	1.439294
H	-1.574998	0.262263	2.168689
C	-0.454449	-1.608214	-0.489707
C	0.524750	-1.796010	-1.377405
H	-1.287137	-2.309360	-0.462157
H	0.501977	-2.628227	-2.071930
H	1.378656	-1.130501	-1.438759

############################

cct_4_Dendralene_G4MP2
G4(MP2)
Eel = -310.41157500 au; Energy(0K)) = -310.26215276 au
Enthalpy = -310.25235101 au; Gibbs energy = -310.29513125 au

C	-2.600596	0.635142	-0.302465
C	-1.373250	0.272721	-0.680494
H	-3.013019	0.349586	0.660196
H	-3.232742	1.239703	-0.943441
H	-0.990953	0.632290	-1.633972

C	-0.446347	-0.586020	0.086637
C	-0.876303	-1.545111	0.917615
H	-0.180790	-2.141006	1.496998
H	-1.932781	-1.760710	1.036262
C	1.016153	-0.390577	-0.151569
C	1.775574	-1.421194	-0.556511
H	2.840665	-1.301766	-0.730369
H	1.352841	-2.403539	-0.729739
C	1.623314	0.930846	0.044798
C	1.033529	2.010853	0.564042
H	2.668253	0.996489	-0.254203
H	1.577389	2.941824	0.680506
H	-0.001305	2.007170	0.885447

############################

ctc_4_Dendralene_G4MP2
G4(MP2)
Eel = -310.41089100 au; Energy(0K)) = -310.26123846 au
Enthalpy = -310.25154817 au; Gibbs energy = -310.29412013 au

C	0.669364	1.707646	0.059756
C	0.639920	0.376413	-0.115431
H	-0.230502	2.277861	0.258744
H	1.601887	2.258054	0.014493
C	-0.639925	-0.376466	-0.115280
C	-0.669380	-1.707636	0.060380
H	-1.601915	-2.258044	0.015355
H	0.230480	-2.277798	0.259545
C	-1.888534	0.384853	-0.334995
C	-3.031127	0.194993	0.324689
H	-1.840527	1.161091	-1.096604
H	-3.922040	0.767827	0.090459
H	-3.113402	-0.532783	1.125702
C	1.888519	-0.384978	-0.334930
C	3.031161	-0.194852	0.324595
H	1.840473	-1.161513	-1.096234
H	3.922059	-0.767770	0.090516
H	3.113498	0.533238	1.125317

############################

ctt_4_Dendralene_G4MP2
G4(MP2)
Eel = -310.41066800 au; Energy(0K)) = -310.26102547 au
Enthalpy = -310.25133274 au; Gibbs energy = -310.29380235 au

C	-0.404265	1.960840	-0.354540

C	-0.658358	0.656071	-0.152041
H	0.605410	2.332756	-0.483648
H	-1.206675	2.689484	-0.404484
C	0.473042	-0.316368	-0.102247
C	0.399775	-1.534209	-0.659010
H	1.232508	-2.225878	-0.597162
H	-0.480293	-1.866114	-1.195667
C	1.704972	0.145005	0.572440
C	2.950406	-0.097120	0.161314
H	1.549767	0.750852	1.463460
H	3.809484	0.253569	0.723034
H	3.153949	-0.644968	-0.753243
C	-2.052546	0.225897	0.035076
C	-2.495535	-0.942868	0.504588
H	-2.785027	0.994892	-0.205804
H	-3.557643	-1.122271	0.630600
H	-1.826421	-1.745816	0.789441

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ccc_4_Dendralene_G4MP2
G4(MP2)
Eel = -310.40734600 au; Energy(0K)) = -310.25817974 au
Enthalpy = -310.24827577 au; Gibbs energy = -310.29140860 au

C	-2.656510	-1.109156	0.001644
C	-1.563972	-0.582418	0.556109
H	-2.997050	-0.807304	-0.983744
H	-3.243305	-1.864568	0.512966
H	-1.234552	-0.954730	1.525580
C	-0.724635	0.479362	-0.038406
C	-1.251091	1.494007	-0.737053
H	-0.621736	2.237926	-1.211946
H	-2.324128	1.606522	-0.846780
C	0.747241	0.383375	0.196800
C	1.438041	1.434924	0.659288
H	2.500624	1.369345	0.866736
H	0.950904	2.381373	0.862257
C	1.371828	-0.927467	-0.073386
C	2.627726	-1.129682	-0.474188
H	0.713805	-1.787698	0.032732
H	3.009554	-2.129833	-0.646914
H	3.314115	-0.308696	-0.655740

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tct_4_Dendralene

B3LYP/6-31G(d)
Eel = -310.78637621 au; Energy(0K)) = -310.63416339 au
Enthalpy = -310.62440335 au; Gibbs energy = -310.66694197 au

C	-1.555086	-1.397769	1.016491
C	-1.672282	-0.494520	0.034627
H	-0.662813	-1.467590	1.631519
H	-2.356463	-2.097680	1.233784
H	-2.592964	-0.462865	-0.548406
C	-0.669031	0.513188	-0.340175
C	-0.953215	1.440377	-1.272103
H	-0.230221	2.195605	-1.563743
H	-1.920370	1.464637	-1.769355
C	0.669022	0.513198	0.340170
C	0.953186	1.440385	1.272106
H	1.920339	1.464655	1.769360
H	0.230178	2.195597	1.563752
C	1.672297	-0.494486	-0.034637
C	1.555111	-1.397756	-1.016484
H	2.592979	-0.462804	0.548393
H	2.356496	-2.097659	-1.233771
H	0.662831	-1.467607	-1.631497

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cct_4_Dendralene
B3LYP/6-31G(d)
Eel = -310.78350545 au; Energy(0K)) = -310.63116673 au
Enthalpy = -310.62148200 au; Gibbs energy = -310.66406618 au

C	-2.609935	0.636101	-0.290329
C	-1.377625	0.282895	-0.676111
H	-3.021612	0.335790	0.670040
H	-3.245266	1.248086	-0.924054
H	-0.997767	0.660052	-1.625204
C	-0.447702	-0.586114	0.081704
C	-0.882031	-1.558236	0.902823
H	-0.187943	-2.159765	1.481350
H	-1.940166	-1.777960	1.013757
C	1.018857	-0.391513	-0.148869
C	1.783607	-1.429582	-0.539340
H	2.852410	-1.314499	-0.703906
H	1.360913	-2.414284	-0.710134
C	1.629415	0.933681	0.038373
C	1.038181	2.020924	0.552119
H	2.675856	0.998841	-0.260088
H	1.584954	2.953119	0.661124
H	0.002019	2.021681	0.874889

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ctc_4_Dendralene
B3LYP/6-31G(d)
Eel = -310.78325777 au; Energy(0K)) = -310.63073084 au
Enthalpy = -310.62114161 au; Gibbs energy = -310.66353796 au

C	-0.678233	-1.708764	0.069326
C	-0.643251	-0.373937	-0.110662
H	0.219004	-2.283310	0.277341
H	-1.613424	-2.257376	0.018936
C	0.643224	0.374246	-0.110950
C	0.678656	1.708981	0.069352
H	1.614075	2.257178	0.019169
H	-0.218360	2.283728	0.277819
C	1.890877	-0.391758	-0.337459
C	3.042414	-0.196584	0.313962
H	1.838460	-1.174562	-1.094051
H	3.932427	-0.772033	0.074597
H	3.131696	0.536025	1.112106
C	-1.890971	0.391875	-0.337003
C	-3.042836	0.195969	0.313595
H	-1.837993	1.175754	-1.092467
H	-3.932745	0.771640	0.074382
H	-3.132419	-0.537218	1.111201

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ctt_4_Dendralene
B3LYP/6-31G(d)
Eel = -310.78320415 au; Energy(0K)) = -310.63064225 au
Enthalpy = -310.62106204 au; Gibbs energy = -310.66333667 au

C	-0.410183	1.969006	-0.345155
C	-0.661117	0.658219	-0.150054
H	0.599671	2.346360	-0.471509
H	-1.215341	2.697438	-0.392868
C	0.475096	-0.312588	-0.098798
C	0.401333	-1.536506	-0.653091
H	1.234764	-2.229674	-0.589185
H	-0.480066	-1.870892	-1.189582
C	1.712641	0.151687	0.569961
C	2.959239	-0.103232	0.155984
H	1.565592	0.768451	1.456547
H	3.822825	0.248357	0.713600
H	3.157969	-0.661214	-0.755535
C	-2.058686	0.222860	0.027201

C	-2.500791	-0.949856	0.500171
H	-2.795416	0.986544	-0.222779
H	-3.564949	-1.133172	0.617594
H	-1.830239	-1.749732	0.796404

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ccc_4_Dendralene
B3LYP/6-31G(d)
Eel = -310.77975772 au; Energy(0K)) = -310.62770448 au
Enthalpy = -310.61791112 au; Gibbs energy = -310.66086495 au

C	-2.665320	-1.112234	-0.004651
C	-1.567762	-0.591565	0.556196
H	-3.006011	-0.801073	-0.988929
H	-3.253987	-1.872246	0.501430
H	-1.238897	-0.975370	1.522943
C	-0.728281	0.477122	-0.033287
C	-1.263308	1.499169	-0.723522
H	-0.638246	2.247050	-1.201887
H	-2.338926	1.612419	-0.822970
C	0.748606	0.383609	0.191460
C	1.442763	1.444637	0.640410
H	2.509062	1.385163	0.839059
H	0.954145	2.392537	0.842335
C	1.378426	-0.929358	-0.073890
C	2.643381	-1.130491	-0.461027
H	0.721214	-1.792939	0.023102
H	3.027389	-2.132359	-0.629965
H	3.333226	-0.308510	-0.635258

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[5]Dendralene

tctt_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71944700 au; Energy(0K)) = -387.53700776 au
Enthalpy = -387.52518012 au; Gibbs energy = -387.57219987 au

C	0.593042	-0.217958	2.038257
C	0.924496	-0.255118	0.736618
H	-0.402771	-0.471969	2.380938
H	1.316108	0.071227	2.793583
C	-0.087193	-0.687351	-0.274625
C	0.215549	-1.512692	-1.283610
H	-0.543844	-1.829358	-1.989586
H	1.216680	-1.903084	-1.423217

C	-1.498702	-0.232520	-0.082530
C	-2.473078	-1.131002	0.131949
H	-3.506258	-0.821570	0.258043
H	-2.263690	-2.192521	0.188735
C	2.285629	0.136807	0.341163
C	2.748131	0.385324	-0.887217
H	2.962509	0.274909	1.183025
H	3.772730	0.706827	-1.038310
H	2.130528	0.287925	-1.771970
C	-1.818325	1.198739	-0.144881
C	-0.983624	2.184942	-0.479843
H	-2.853743	1.440941	0.088923
H	-1.320554	3.215090	-0.513625
H	0.056750	2.006561	-0.728218

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ctct_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71902100 au; Energy(0K)) = -387.53691896 au
Enthalpy = -387.52494129 au; Gibbs energy = -387.57242031 au

C	-0.079299	1.546891	-1.242851
C	0.127789	0.631718	-0.286324
H	-1.071376	1.762943	-1.623402
H	0.743654	2.114029	-1.662153
C	-0.986767	-0.155563	0.298802
C	-0.849950	-0.809990	1.462816
H	-1.658855	-1.408193	1.865510
H	0.068763	-0.766865	2.035030
C	-2.261195	-0.203135	-0.451046
C	-3.475690	-0.101100	0.088346
H	-2.171784	-0.326457	-1.529058
H	-4.372454	-0.179179	-0.517005
H	-3.615396	0.070470	1.150908
C	1.515644	0.410559	0.232825
C	2.105593	1.339754	0.999179
H	3.116787	1.204045	1.371282
H	1.596433	2.255925	1.274249
C	2.233833	-0.817567	-0.126893
C	1.815851	-1.755428	-0.979518
H	3.206453	-0.930978	0.349382
H	2.422545	-2.626660	-1.199246
H	0.860378	-1.685914	-1.487506

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tcct_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71865100 au; Energy(0K)) = -387.53615259 au
Enthalpy = -387.52433001 au; Gibbs energy = -387.57153093 au

C	-2.081844	1.233039	0.523377
C	-1.279752	0.216795	0.160344
H	-1.807254	1.919861	1.315053
H	-3.033064	1.402499	0.028637
C	0.000127	-0.022799	0.896963
C	0.000211	-0.056671	2.235859
H	0.921874	-0.166251	2.796375
H	-0.921375	0.024222	2.801339
C	1.279952	-0.224515	0.149047
C	2.082298	-1.257621	0.460137
H	3.033413	-1.401739	-0.042747
H	1.807959	-1.983695	1.216079
C	1.699229	0.712539	-0.901178
C	1.143985	1.886503	-1.210815
H	2.585310	0.396165	-1.449129
H	1.561010	2.505649	-1.997602
H	0.265547	2.267223	-0.705329
C	-1.699562	-0.666083	-0.935615
C	-1.144577	-1.823015	-1.304186
H	-2.585842	-0.322463	-1.466573
H	-1.561940	-2.401777	-2.120966
H	-0.266047	-2.228720	-0.818744

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ctct1_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71820300 au; Energy(0K)) = -387.53610885 au
Enthalpy = -387.52410588 au; Gibbs energy = -387.57153492 au

C	0.025301	-1.309729	-1.447505
C	-0.127129	-0.611174	-0.314288
H	0.995260	-1.466165	-1.904728
H	-0.830414	-1.732938	-1.961076
C	1.021330	-0.021521	0.415321
C	0.851938	0.761685	1.492778
H	1.705461	1.146940	2.038018
H	-0.131103	1.026861	1.861184
C	2.385140	-0.354508	-0.055021
C	3.383541	0.517682	-0.186889
H	2.563463	-1.399574	-0.301368
H	4.372846	0.202915	-0.501650
H	3.245773	1.576263	0.009492

C	-1.510734	-0.407161	0.232937
C	-2.070346	-1.330113	1.026923
H	-3.074991	-1.201284	1.418602
H	-1.545370	-2.235961	1.307344
C	-2.249864	0.805598	-0.133421
C	-1.834086	1.758608	-0.971219
H	-3.229208	0.899229	0.333552
H	-2.451287	2.622597	-1.190375
H	-0.870973	1.704914	-1.466692

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ccct_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71640200 au; Energy(0K)) = -387.53438775 au
Enthalpy = -387.52238410 au; Gibbs energy = -387.57002920 au

C	-2.000887	0.421692	-1.581301
C	-1.389034	0.057688	-0.442649
H	-1.686040	1.295175	-2.139308
H	-2.830157	-0.152489	-1.983304
C	-0.267611	0.885816	0.100587
C	-0.457661	2.185915	0.354650
H	0.357972	2.824345	0.676080
H	-1.434596	2.642748	0.244064
C	1.068633	0.248002	0.299717
C	1.807927	0.511538	1.387780
H	2.775512	0.046160	1.539085
H	1.453672	1.181180	2.162873
C	1.526785	-0.676969	-0.757623
C	2.791368	-0.843869	-1.145944
H	0.743636	-1.229872	-1.270212
H	3.052311	-1.550515	-1.926132
H	3.607547	-0.276542	-0.709807
C	-1.832289	-1.146009	0.271042
C	-1.409488	-1.568785	1.465253
H	-2.600922	-1.718423	-0.246031
H	-1.815479	-2.469209	1.912930
H	-0.649909	-1.042666	2.030690

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cctt_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71559400 au; Energy(0K)) = -387.53357975 au
Enthalpy = -387.52157610 au; Gibbs energy = -387.56922120 au

C	2.755196	-1.380939	-0.708719

C	1.621321	-0.688296	-0.822746
H	3.505635	-1.137676	0.036890
H	2.967061	-2.225976	-1.354411
H	0.882642	-1.012331	-1.553476
C	1.245035	0.502932	-0.032052
C	2.152663	1.347752	0.479343
H	1.855072	2.183787	1.101208
H	3.212999	1.225781	0.287137
C	-0.216309	0.749428	0.144892
C	-0.733517	1.965008	-0.076495
H	-1.784775	2.175500	0.080227
H	-0.107219	2.783288	-0.413127
C	-1.054405	-0.398400	0.605527
C	-0.597338	-1.205944	1.577842
H	-1.190570	-2.037370	1.944127
H	0.375089	-1.058612	2.032099
C	-2.369930	-0.673835	0.009676
C	-2.892045	-0.149717	-1.102028
H	-2.942896	-1.432698	0.540567
H	-3.865880	-0.465672	-1.459539
H	-2.371190	0.594047	-1.693143

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ctcc_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71543300 au; Energy(0K)) = -387.53335638 au
Enthalpy = -387.52138315 au; Gibbs energy = -387.56900058 au

C	-0.473479	2.014577	-0.412437
C	-0.088144	0.773184	-0.080048
H	-1.519649	2.278162	-0.520585
H	0.254229	2.800491	-0.576509
C	-1.077054	-0.316812	0.114534
C	-0.770242	-1.429758	0.800751
H	-1.488559	-2.234319	0.908545
H	0.198590	-1.567251	1.264394
C	-2.419957	-0.140980	-0.480272
C	-3.571542	-0.458311	0.111221
H	-2.440478	0.291647	-1.479055
H	-4.522042	-0.333685	-0.396437
H	-3.604549	-0.846186	1.124417
C	1.365366	0.470519	0.092703
C	2.119652	1.207454	0.920040
H	3.192324	1.062740	0.991116
H	1.680984	1.977637	1.543567
C	1.924155	-0.621778	-0.732392

C	2.987345	-1.369365	-0.431937
H	1.396103	-0.815040	-1.664238
H	3.353523	-2.128815	-1.113877
H	3.522929	-1.257758	0.505676

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cttc_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71465600 au; Energy(0K)) = -387.53226184 au
Enthalpy = -387.52046767 au; Gibbs energy = -387.56756683 au

C	1.414035	1.513991	0.670850
C	1.294435	0.315933	0.078053
H	0.571286	2.009273	1.136405
H	2.369166	2.025848	0.700623
C	0.000007	-0.419667	-0.000055
C	0.000008	-1.763819	-0.000106
H	-0.921741	-2.330355	-0.061800
H	0.921752	-2.330365	0.061554
C	-1.294440	0.315920	-0.078089
C	-1.414089	1.513952	-0.670925
H	-2.369225	2.025802	-0.700661
H	-0.571374	2.009221	-1.136555
C	-2.474019	-0.354790	0.511259
C	-3.694156	-0.387306	-0.025366
H	-2.296024	-0.870327	1.453436
H	-4.521721	-0.873280	0.480207
H	-3.905840	0.062434	-0.990181
C	2.474073	-0.354771	-0.511193
C	3.694154	-0.387296	0.025556
H	2.296173	-0.870292	-1.453396
H	4.521771	-0.873264	-0.479937
H	3.905737	0.062426	0.990402

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cccc_5_Dendralene_G4MP2
G4(MP2)
Eel = -387.71305800 au; Energy(0K)) = -387.53130901 au
Enthalpy = -387.51919013 au; Gibbs energy = -387.56711666 au

C	2.252184	0.698715	0.919942
C	1.275773	0.341548	0.072053
H	2.112235	1.503627	1.631945
H	3.213876	0.197455	0.920578
C	-0.000001	1.112640	0.000000
C	-0.000004	2.452380	0.000001

H	-0.926695	3.015117	0.008964
H	0.926685	3.015121	-0.008962
C	-1.275776	0.341546	-0.072055
C	-2.252181	0.698704	-0.919954
H	-3.213871	0.197442	-0.920592
H	-2.112229	1.503611	-1.631961
C	-1.411405	-0.799966	0.857114
C	-2.137096	-1.898857	0.646747
H	-0.844438	-0.716573	1.782369
H	-2.205848	-2.681457	1.394251
H	-2.676870	-2.061803	-0.280771
C	1.411397	-0.799974	-0.857104
C	2.137108	-1.898853	-0.646743
H	0.844408	-0.716600	-1.782348
H	2.205852	-2.681459	-1.394241
H	2.676905	-2.061784	0.280764

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tctt_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.18187204 au; Energy(0K)) = -387.99592604 au
Enthalpy = -387.98422427 au; Gibbs energy = -388.03103690 au

C	0.601374	-0.179430	2.048106
C	0.929036	-0.241427	0.742384
H	-0.394216	-0.428603	2.400284
H	1.326528	0.126518	2.797474
C	-0.087852	-0.693307	-0.259347
C	0.216193	-1.544153	-1.252606
H	-0.542276	-1.874867	-1.955783
H	1.218554	-1.940063	-1.381657
C	-1.502522	-0.233921	-0.080447
C	-2.480642	-1.132961	0.141634
H	-3.517253	-0.824279	0.256196
H	-2.270415	-2.194990	0.216696
C	2.291860	0.143479	0.333606
C	2.747561	0.369810	-0.906401
H	2.976357	0.297409	1.168061
H	3.773281	0.687814	-1.069158
H	2.124147	0.256925	-1.787290
C	-1.825184	1.199101	-0.164132
C	-0.984473	2.184323	-0.504142
H	-2.863872	1.446046	0.055983
H	-1.323373	3.215019	-0.553748
H	0.060434	2.003983	-0.738994

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ctct_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.18143106 au; Energy(0K)) = -387.99579572 au
Enthalpy = -387.98395407 au; Gibbs energy = -388.03120505 au

C	-0.078726	1.590698	-1.203461
C	0.130787	0.643358	-0.272781
H	-1.073513	1.825970	-1.570339
H	0.745782	2.165527	-1.613417
C	-0.988609	-0.156649	0.294660
C	-0.853885	-0.837324	1.448683
H	-1.664233	-1.445944	1.837010
H	0.064366	-0.807329	2.025794
C	-2.265344	-0.185832	-0.457110
C	-3.483022	-0.105871	0.089730
H	-2.179559	-0.274784	-1.540259
H	-4.381492	-0.170295	-0.517869
H	-3.622497	0.033812	1.158723
C	1.523132	0.403766	0.232603
C	2.130256	1.326610	1.001167
H	3.145675	1.182183	1.363583
H	1.630220	2.246224	1.288060
C	2.232185	-0.830301	-0.139474
C	1.800600	-1.761623	-0.999208
H	3.208211	-0.956653	0.329484
H	2.401749	-2.636586	-1.227919
H	0.841050	-1.683124	-1.501703

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tcct_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.18098522 au; Energy(0K)) = -387.99501448 au
Enthalpy = -387.98330874 au; Gibbs energy = -388.03032183 au

C	2.084838	-1.255416	0.489122
C	1.283309	-0.224272	0.152830
H	1.805342	-1.967289	1.259065
H	3.039982	-1.412861	-0.005931
C	0.000021	-0.004247	0.895261
C	0.000043	-0.010606	2.239055
H	-0.922786	0.080821	2.804266
H	0.922889	-0.107339	2.803347
C	-1.283262	0.222843	0.154983
C	-2.084758	1.250758	0.501071
H	-3.039895	1.412965	0.007547
H	-1.805220	1.955237	1.277771

C	-1.708710	-0.683139	-0.924260
C	-1.153331	-1.852455	-1.267991
H	-2.595879	-0.351421	-1.463837
H	-1.572727	-2.448490	-2.073498
H	-0.273043	-2.249265	-0.774574
C	1.708756	0.691938	-0.917743
C	1.153106	1.864259	-1.250638
H	2.596164	0.365563	-1.460173
H	1.572519	2.467969	-2.050397
H	0.272582	2.256129	-0.753724

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ctct1_5_Dendralene_B3LYP
b3lyp/6-31g(d)
Eel = -388.18032842 au; Energy(0K)) = -387.99473193 au
Enthalpy = -387.98284672 au; Gibbs energy = -388.03006661 au

C	0.025250	-1.324647	-1.438754
C	-0.126581	-0.611706	-0.309251
H	0.994770	-1.481607	-1.901088
H	-0.831939	-1.758443	-1.944429
C	1.026474	-0.008414	0.409482
C	0.858013	0.804458	1.470277
H	1.713253	1.197885	2.010160
H	-0.125604	1.086746	1.829328
C	2.392195	-0.357853	-0.051108
C	3.399999	0.509482	-0.188049
H	2.567576	-1.407875	-0.284666
H	4.390512	0.182762	-0.492803
H	3.268166	1.573336	-0.007192
C	-1.511833	-0.409931	0.241790
C	-2.063151	-1.330064	1.052105
H	-3.068646	-1.205395	1.448002
H	-1.528882	-2.229445	1.342407
C	-2.265445	0.794954	-0.135109
C	-1.859855	1.743679	-0.989521
H	-3.244726	0.888782	0.335063
H	-2.487179	2.600869	-1.215244
H	-0.897699	1.692632	-1.490704

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ccct_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.17910351 au; Energy(0K)) = -387.99351854 au
Enthalpy = -387.98166182 au; Gibbs energy = -388.02908007 au

C	-2.038384	0.438298	-1.554344
C	-1.400649	0.059026	-0.429767
H	-1.737077	1.321504	-2.107892
H	-2.875512	-0.132466	-1.949719
C	-0.271715	0.887331	0.104517
C	-0.462191	2.191905	0.360057
H	0.356891	2.834500	0.670031
H	-1.442812	2.647718	0.261663
C	1.071379	0.253242	0.293767
C	1.824744	0.533113	1.373416
H	2.797719	0.073471	1.519143
H	1.476137	1.209572	2.147628
C	1.525433	-0.681985	-0.760613
C	2.791511	-0.842320	-1.161368
H	0.742145	-1.250220	-1.258827
H	3.050068	-1.557737	-1.936825
H	3.608589	-0.260674	-0.741773
C	-1.826607	-1.161941	0.272426
C	-1.378681	-1.602726	1.455778
H	-2.601711	-1.732678	-0.239446
H	-1.772467	-2.514947	1.894547
H	-0.611015	-1.081700	2.018247

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cctt_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.17898770 au; Energy(0K)) = -387.99327144 au
Enthalpy = -387.98148260 au; Gibbs energy = -388.02863744 au

C	2.787747	-1.357138	-0.709760
C	1.639349	-0.680397	-0.824726
H	3.534020	-1.104478	0.039439
H	3.013739	-2.198176	-1.358831
H	0.906365	-1.016157	-1.557778
C	1.246354	0.505717	-0.028678
C	2.149643	1.360214	0.486321
H	1.846024	2.190080	1.116596
H	3.212140	1.251465	0.288754
C	-0.219331	0.740872	0.153161
C	-0.742429	1.962937	-0.046322
H	-1.795023	2.168792	0.119037
H	-0.119835	2.790169	-0.373374
C	-1.058518	-0.417296	0.593878
C	-0.594576	-1.255223	1.542700
H	-1.187461	-2.096714	1.891568
H	0.383591	-1.124620	1.993615

C	-2.384857	-0.673588	0.004448
C	-2.914133	-0.123210	-1.096469
H	-2.960918	-1.439029	0.524882
H	-3.895043	-0.426845	-1.450479
H	-2.393091	0.628182	-1.680745

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ctcc_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.17873147 au; Energy(0K)) = -387.99308884 au
Enthalpy = -387.98127697 au; Gibbs energy = -388.02862670 au

C	-0.473853	2.024598	-0.396046
C	-0.087336	0.775257	-0.076374
H	-1.521627	2.294565	-0.488801
H	0.255438	2.810474	-0.564374
C	-1.082333	-0.314713	0.114416
C	-0.778892	-1.433822	0.800491
H	-1.499308	-2.239480	0.902036
H	0.189383	-1.576039	1.267782
C	-2.426904	-0.133305	-0.481271
C	-3.581692	-0.461916	0.107801
H	-2.450381	0.312141	-1.475893
H	-4.532993	-0.333620	-0.401211
H	-3.615973	-0.860789	1.118472
C	1.369638	0.469505	0.083811
C	2.137405	1.223064	0.891140
H	3.212766	1.080490	0.949958
H	1.706868	2.003819	1.510221
C	1.922908	-0.641406	-0.725698
C	2.996021	-1.379399	-0.417589
H	1.385836	-0.860426	-1.648066
H	3.358862	-2.153487	-1.087547
H	3.541354	-1.244838	0.513332

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cttc_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.17866537 au; Energy(0K)) = -387.99275687 au
Enthalpy = -387.98108920 au; Gibbs energy = -388.02799640 au

C	-1.416205	1.514385	-0.673556
C	-1.297359	0.312740	-0.077970
H	-0.573011	2.008566	-1.143472
H	-2.371040	2.030356	-0.700612
C	-0.000062	-0.423915	0.000094

C	0.000023	-1.772221	0.000226
H	0.922344	-2.340421	0.067644
H	-0.922244	-2.340550	-0.066920
C	1.297346	0.312751	0.078105
C	1.416292	1.514382	0.673659
H	2.371166	2.030292	0.700604
H	0.573216	2.008567	1.143767
C	2.480725	-0.356893	-0.511700
C	3.705920	-0.377826	0.024947
H	2.306124	-0.881315	-1.451252
H	4.536436	-0.862468	-0.480861
H	3.917603	0.078951	0.988404
C	-2.480847	-0.356816	0.511616
C	-3.705873	-0.377841	-0.025402
H	-2.306511	-0.880966	1.451343
H	-4.536596	-0.862305	0.480214
H	-3.917253	0.078805	-0.988974

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cccc_5_Dendralene
b3lyp/6-31g(d)
Eel = -388.17655236 au; Energy(0K)) = -387.99124464 au
Enthalpy = -387.97928266 au; Gibbs energy = -388.02698250 au

C	2.261679	0.709224	0.914863
C	1.280524	0.340644	0.070126
H	2.120020	1.516616	1.626416
H	3.228581	0.214421	0.913320
C	-0.000120	1.109543	-0.000001
C	0.000058	2.454077	-0.000157
H	-0.927356	3.018734	0.016287
H	0.927662	3.018398	-0.016724
C	-1.280667	0.340620	-0.070005
C	-2.262011	0.709214	-0.914521
H	-3.228854	0.214291	-0.912911
H	-2.120589	1.516715	-1.626001
C	-1.420720	-0.810033	0.851805
C	-2.166266	-1.899899	0.636308
H	-0.843952	-0.744909	1.773961
H	-2.238456	-2.689523	1.378619
H	-2.717375	-2.047739	-0.289109
C	1.420767	-0.809857	-0.851848
C	2.166664	-1.899528	-0.636543
H	0.843885	-0.744763	-1.773931
H	2.239093	-2.689054	-1.378926
H	2.717891	-2.047222	0.288827

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[6]Dendralene

tctct_Ci_SYMMETRY_6_Dendralene
G4(MP2)
Eel = -465.02691700 au; Energy(0K)) = -464.81223620 au
Enthalpy = -464.79800042 au; Gibbs energy = -464.85001428 au

C	-0.625073	0.016768	-1.736791
C	-0.625481	0.004123	-0.397390
H	0.294353	0.023405	-2.309814
H	-1.554930	0.025919	-2.293831
C	0.625481	-0.004123	0.397390
C	0.625073	-0.016768	1.736791
H	1.554930	-0.025919	2.293831
H	-0.294353	-0.023405	2.309814
C	1.936176	-0.008555	-0.334549
C	2.617311	1.131437	-0.515163
H	3.572944	1.141331	-1.031008
H	2.244240	2.082387	-0.152759
C	2.475014	-1.281298	-0.826646
C	1.949566	-2.490955	-0.619527
H	3.398331	-1.194097	-1.397406
H	2.421500	-3.384395	-1.012504
H	1.038491	-2.628288	-0.047723
C	-1.936176	0.008555	0.334549
C	-2.617311	-1.131437	0.515163
H	-3.572944	-1.141331	1.031008
H	-2.244240	-2.082387	0.152759
C	-2.475014	1.281298	0.826646
C	-1.949566	2.490955	0.619527
H	-3.398331	1.194097	1.397406
H	-2.421500	3.384395	1.012504
H	-1.038491	2.628288	0.047723

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tctct_C2_SYMMETRY_6_Dendralene
G4(MP2)
Eel = -465.02676500 au; Energy(0K)) = -464.81191889 au
Enthalpy = -464.79776959 au; Gibbs energy = -464.84894270 au

C	-1.824994	-0.264686	-0.602144
C	-0.515907	-0.532868	-0.512123
H	-2.196497	0.750328	-0.675972
H	-2.557883	-1.063410	-0.607776

C	0.515907	0.532868	-0.512123
C	1.824994	0.264686	-0.602144
H	2.557883	1.063410	-0.607776
H	2.196497	-0.750328	-0.675972
C	0.060091	1.960398	-0.426686
C	-0.135333	2.679128	-1.541023
H	-0.459080	3.714721	-1.493786
H	0.024323	2.257338	-2.526618
C	-0.060091	-1.960398	-0.426686
C	0.135333	-2.679128	-1.541023
H	0.459080	-3.714721	-1.493786
H	-0.024323	-2.257338	-2.526618
C	0.153182	-2.563919	0.893195
C	-0.153182	-2.013143	2.070452
H	0.583311	-3.564209	0.871735
H	0.027101	-2.539751	3.000908
H	-0.603924	-1.029531	2.141490
C	-0.153182	2.563919	0.893195
C	0.153182	2.013143	2.070452
H	-0.583311	3.564209	0.871735
H	-0.027101	2.539751	3.000908
H	0.603924	1.029531	2.141490

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tccct_6_Dendralene
G4(MP2)
Eel = -465.02589500 au; Energy(0K)) = -464.81110935 au
Enthalpy = -464.79696081 au; Gibbs energy = -464.84906703 au

C	1.174271	-1.927143	-1.127995
C	1.298322	-0.783000	-0.438940
H	0.482915	-2.702218	-0.821129
H	1.756728	-2.107960	-2.026467
C	0.493743	-0.559912	0.803061
C	0.655108	-1.355614	1.866725
H	0.038547	-1.247591	2.752805
H	1.406019	-2.137684	1.873748
C	-0.493722	0.559716	0.803110
C	-0.655054	1.355346	1.866831
H	-1.405927	2.137453	1.873907
H	-0.038498	1.247235	2.752904
C	-1.298230	0.782988	-0.438904
C	-1.173975	1.927150	-1.127890
H	-1.756389	2.108121	-2.026358
H	-0.482493	2.702091	-0.820965
C	2.236018	0.250641	-0.891622

C	2.593323	1.347332	-0.218544
H	3.314020	2.045969	-0.628885
H	2.183869	1.584804	0.756347
H	2.688148	0.057920	-1.863120
C	-2.236104	-0.250460	-0.891666
C	-2.593689	-1.347092	-0.218639
H	-2.688144	-0.057617	-1.863182
H	-3.314512	-2.045561	-0.629045
H	-2.184358	-1.584674	0.756276

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tctcc_6_Dendralene
G4(MP2)
Eel = -465.02357600 au; Energy(0K)) = -464.80895271 au
Enthalpy = -464.79470514 au; Gibbs energy = -464.84696731 au

C	0.121833	-1.363834	-1.503529
C	-0.318148	-0.702552	-0.423208
H	1.173978	-1.574671	-1.654020
H	-0.569209	-1.707351	-2.264037
C	0.609588	-0.217421	0.628318
C	0.177830	0.152519	1.841593
H	0.873471	0.490929	2.600974
H	-0.871913	0.128723	2.107887
C	2.077790	-0.189633	0.327425
C	2.890540	-1.125356	0.839083
H	3.958153	-1.114166	0.640248
H	2.513657	-1.923361	1.468023
C	-1.784845	-0.453979	-0.260392
C	-2.648504	-1.477775	-0.234857
H	-3.720684	-1.314571	-0.209255
H	-2.303074	-2.504983	-0.246493
C	-2.225865	0.955716	-0.203311
C	-3.305930	1.415789	0.430067
H	-3.580350	2.464140	0.389872
H	-3.947856	0.765765	1.016506
H	-1.592909	1.661186	-0.738885
C	2.620248	0.882616	-0.514639
C	1.958041	1.959727	-0.942165
H	3.670985	0.768779	-0.776641
H	2.443182	2.714977	-1.550091
H	0.917087	2.129701	-0.690392

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tcctt_6_Dendralene

G4(MP2)
Eel = -465.02399200 au; Energy(0K)) = -464.80880829 au
Enthalpy = -464.79487041 au; Gibbs energy = -464.84637918 au

C	-2.598210	0.008221	1.271454
C	-1.683055	0.375375	0.359698
H	-2.872896	-1.029610	1.417148
H	-3.091799	0.742861	1.900010
C	-1.042526	-0.651259	-0.518893
C	-1.802222	-1.521122	-1.198049
H	-1.359325	-2.321325	-1.780463
H	-2.884132	-1.452054	-1.185809
C	0.448821	-0.716806	-0.606706
C	1.050409	-0.893816	-1.791761
H	2.124238	-1.011454	-1.873261
H	0.475290	-0.934045	-2.709919
C	1.228273	-0.664834	0.666942
C	0.789206	-1.338097	1.743851
H	1.348796	-1.337474	2.673409
H	-0.131597	-1.907750	1.727277
C	2.481595	0.097044	0.772080
C	2.985156	0.983014	-0.090145
H	3.023885	-0.082471	1.699301
H	3.912480	1.501427	0.127533
H	2.493481	1.231870	-1.022532
C	-1.338274	1.795106	0.218358
C	-0.625903	2.354582	-0.762600
H	-1.750167	2.436318	0.995798
H	-0.449192	3.424314	-0.782264
H	-0.198681	1.774940	-1.571593

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ttctt_6_Dendralene
G4(MP2)
Eel = -465.02375100 au; Energy(0K)) = -464.80857055 au
Enthalpy = -464.79461382 au; Gibbs energy = -464.84602662 au

C	-0.691039	-0.814975	1.893457
C	-1.328172	-0.302865	0.826982
H	0.254424	-0.416697	2.240709
H	-1.103879	-1.652616	2.445718
C	-0.738992	0.865729	0.105106
C	-1.479929	1.905130	-0.301373
H	-1.026223	2.743386	-0.817692
H	-2.547022	1.952012	-0.119245
C	0.738969	0.865820	-0.104806
C	1.479829	1.905115	0.302087

H	2.546916	1.952155	0.119970
H	1.026058	2.743135	0.818732
C	-2.594902	-0.912560	0.398059
C	-3.273881	-0.697570	-0.731568
H	-2.979346	-1.656520	1.094282
H	-4.185651	-1.245527	-0.942246
H	-2.948219	0.014152	-1.480499
C	1.328232	-0.302454	-0.827134
C	0.691203	-0.814104	-1.893892
H	1.104103	-1.651501	-2.446478
H	-0.254227	-0.415679	-2.241065
C	2.594927	-0.912332	-0.398363
C	3.273770	-0.697903	0.731452
H	2.979458	-1.655948	-1.094906
H	4.185520	-1.245959	0.941961
H	2.948004	0.013421	1.480714

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ctcct_6_Dendralene
G4(MP2)
Eel = -465.02326600 au; Energy(0K)) = -464.80828463 au
Enthalpy = -464.79426613 au; Gibbs energy = -464.84614774 au

C	0.818800	1.297802	1.616103
C	0.383425	0.756749	0.466935
H	1.866533	1.271861	1.893916
H	0.135427	1.784255	2.302323
C	1.328315	0.065055	-0.448616
C	1.099777	-0.021659	-1.768036
H	1.786801	-0.550430	-2.418717
H	0.228599	0.424869	-2.229777
C	2.546224	-0.521399	0.150995
C	3.770975	-0.454752	-0.371282
H	2.401625	-1.033484	1.100582
H	4.617299	-0.936806	0.106300
H	3.970703	0.089033	-1.289135
C	-1.057603	0.874881	0.084846
C	-1.676636	2.060753	0.155128
H	-2.736018	2.157240	-0.054831
H	-1.136930	2.961572	0.425230
C	-1.805953	-0.333543	-0.381430
C	-2.544098	-0.277671	-1.502957
H	-3.119908	-1.133668	-1.840409
H	-2.588197	0.617204	-2.112315
C	-1.772244	-1.585075	0.386346
C	-1.268398	-1.776276	1.608204

H	-2.248100	-2.425957	-0.115642
H	-1.325153	-2.749189	2.084201
H	-0.788194	-0.985707	2.170850

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tcttc_6_Dendralene
G4(MP2)
Eel = -465.02320800 au; Energy(0K)) = -464.80819907 au
Enthalpy = -464.79418776 au; Gibbs energy = -464.84593414 au

C	0.815986	-1.674975	1.195071
C	0.853105	-0.722627	0.254212
H	-0.115133	-2.120771	1.523417
H	1.728630	-2.033787	1.656932
C	-0.370169	-0.223404	-0.439428
C	-0.297620	0.150455	-1.727711
H	-1.167884	0.512924	-2.261676
H	0.636388	0.113630	-2.275060
C	-1.674651	-0.145103	0.277761
C	-1.770255	0.055471	1.601766
H	-2.738347	0.098211	2.087497
H	-0.896518	0.175243	2.229883
C	-2.895052	-0.274902	-0.549284
C	-3.997605	0.463729	-0.422300
H	-2.853730	-1.035358	-1.327139
H	-4.868908	0.290947	-1.044912
H	-4.064794	1.270382	0.300706
C	2.177775	-0.185040	-0.189595
C	3.080054	-1.000403	-0.757964
H	4.054724	-0.634191	-1.066276
H	2.868182	-2.048900	-0.930557
C	2.500420	1.231392	0.022224
C	1.756496	2.130651	0.669670
H	3.462387	1.539491	-0.384279
H	2.093938	3.154237	0.788632
H	0.790166	1.886473	1.096308

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ctctc_6_Dendralene
G4(MP2)
Eel = -465.02279000 au; Energy(0K)) = -464.80793698 au
Enthalpy = -464.79382094 au; Gibbs energy = -464.84588231 au

C	1.152809	1.753172	1.042395
C	0.715140	0.787679	0.221976
H	2.189123	1.811072	1.356438

H	0.481719	2.520228	1.411035
C	1.622011	-0.271507	-0.289368
C	1.309922	-1.003803	-1.369802
H	1.963591	-1.795656	-1.716238
H	0.398877	-0.832794	-1.930600
C	2.889690	-0.499310	0.438088
C	4.077183	-0.705686	-0.130926
H	2.820750	-0.485437	1.524562
H	4.963601	-0.900537	0.463198
H	4.205509	-0.680152	-1.208363
C	-0.715140	0.787679	-0.221976
C	-1.152809	1.753172	-1.042395
H	-2.189123	1.811072	-1.356438
H	-0.481719	2.520228	-1.411036
C	-1.622012	-0.271507	0.289368
C	-1.309922	-1.003803	1.369803
H	-1.963591	-1.795655	1.716239
H	-0.398877	-0.832794	1.930601
C	-2.889690	-0.499310	-0.438088
C	-4.077183	-0.705686	0.130926
H	-2.820750	-0.485437	-1.524562
H	-4.963601	-0.900537	-0.463198
H	-4.205509	-0.680152	1.208363

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cccct_6_Dendralene
G4(MP2)
Eel = -465.02170500 au; Energy(0K)) = -464.80715292 au
Enthalpy = -464.79290706 au; Gibbs energy = -464.84519189 au

C	1.925667	-1.077901	-1.282225
C	1.432226	-0.510905	-0.172425
H	1.412032	-1.897986	-1.769634
H	2.850971	-0.733842	-1.731582
C	0.222134	-1.070724	0.499829
C	0.129089	-2.380685	0.765075
H	-0.762993	-2.803406	1.214447
H	0.944426	-3.058327	0.538304
C	-0.855485	-0.119304	0.903159
C	-1.410022	-0.179260	2.120307
H	-2.221107	0.483084	2.401881
H	-1.064001	-0.890140	2.862755
C	-1.283216	0.931109	-0.072145
C	-1.216787	2.228711	0.264662
H	-1.535314	3.005675	-0.423540
H	-0.833546	2.546879	1.226417

C	2.069996	0.652436	0.478621
C	2.778812	1.602724	-0.132268
H	1.924641	0.719046	1.555388
H	3.242800	2.407942	0.426642
H	2.910856	1.617183	-1.209445
C	-1.791875	0.548204	-1.394492
C	-2.082316	-0.685399	-1.814930
H	-1.965622	1.385725	-2.068153
H	-2.475117	-0.856539	-2.811138
H	-1.937358	-1.559321	-1.191355

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ctctt_6_Dendralene
G4(MP2)
Eel = -465.02206700 au; Energy(0K)) = -464.80688798 au
Enthalpy = -464.79289625 au; Gibbs energy = -464.84455858 au

C	-1.182902	-0.073109	2.049882
C	-1.583871	-0.027410	0.767797
H	-0.308967	0.465621	2.394963
H	-1.725961	-0.656641	2.785764
C	-0.836377	0.810925	-0.217748
C	-1.454591	1.550692	-1.145258
H	-0.887647	2.176001	-1.825745
H	-2.533878	1.568052	-1.239286
C	0.654038	0.888372	-0.077551
C	1.203943	2.045118	0.323233
H	2.271827	2.162028	0.463889
H	0.584686	2.907781	0.538876
C	-2.759951	-0.816907	0.369631
C	-3.181264	-1.107867	-0.864243
H	-3.305853	-1.240904	1.211106
H	-4.048313	-1.740960	-1.017459
H	-2.681010	-0.741252	-1.752441
C	1.470721	-0.312154	-0.384427
C	0.919522	-1.469875	-0.782477
H	1.544170	-2.313550	-1.051751
H	-0.151180	-1.609710	-0.861493
C	2.944379	-0.191164	-0.296866
C	3.751259	-1.087050	0.269534
H	3.380929	0.700620	-0.742572
H	4.828600	-0.959585	0.268606
H	3.363167	-1.974933	0.758503

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ccctt_2nd_Conf_6_Dendralene
G4(MP2)
Eel = -465.02150400 au; Energy(0K)) = -464.80675777 au
Enthalpy = -464.79261784 au; Gibbs energy = -464.84454418 au

C	1.220299	-1.591318	-1.292533
C	0.564933	-0.979672	-0.296492
H	0.680114	-2.104221	-2.080132
H	2.302528	-1.606567	-1.339977
C	-0.926604	-1.038349	-0.231048
C	-1.570282	-2.208099	-0.343334
H	-2.653185	-2.255346	-0.372819
H	-1.027461	-3.144086	-0.411143
C	-1.668083	0.246254	-0.068568
C	-2.750617	0.334877	0.717884
H	-3.340352	1.243552	0.765308
H	-3.073102	-0.497643	1.332462
C	-1.169407	1.397750	-0.848465
C	-1.218602	2.674075	-0.465420
H	-0.710997	1.153905	-1.804960
H	-0.854228	3.470829	-1.104568
H	-1.612072	2.965037	0.503418
C	1.276126	-0.274156	0.811189
C	0.833651	-0.408690	2.073199
H	1.342806	0.073232	2.901263
H	-0.041021	-1.000995	2.312551
C	2.457914	0.564102	0.559968
C	2.914952	1.015829	-0.610202
H	2.977509	0.869352	1.466998
H	3.785201	1.661528	-0.652507
H	2.438578	0.775808	-1.552961

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ctccc_6_Dendralene
G4(MP2)
Eel = -465.02113800 au; Energy(0K)) = -464.80643439 au
Enthalpy = -464.79228311 au; Gibbs energy = -464.84448214 au

C	-0.969555	1.503442	-1.502038
C	-0.493847	0.880110	-0.413407
H	-2.002396	1.396304	-1.814609
H	-0.334549	2.145549	-2.101181
C	-1.353376	-0.016144	0.401249
C	-1.062641	-0.290224	1.682581
H	-1.678742	-0.967877	2.262180
H	-0.205711	0.146830	2.180050
C	-2.546244	-0.598658	-0.249922

C	-3.751020	-0.713126	0.308850
H	-2.400814	-0.946594	-1.271089
H	-4.576128	-1.182803	-0.215866
H	-3.955863	-0.336297	1.305897
C	0.927461	1.088762	0.001461
C	1.396230	2.322358	0.227833
H	2.443442	2.496892	0.449298
H	0.742406	3.186473	0.191980
C	1.808409	-0.112331	0.098507
C	2.734259	-0.227201	1.062120
H	3.433169	-1.056025	1.077023
H	2.816788	0.504592	1.857571
C	1.633978	-1.143609	-0.945423
C	1.790328	-2.456429	-0.772007
H	1.332783	-0.774966	-1.924071
H	1.671517	-3.153821	-1.594108
H	2.030207	-2.879948	0.198098

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cctcc_6_Dendralene
G4(MP2)
Eel = -465.02008700 au; Energy(0K)) = -464.80551791 au
Enthalpy = -464.79128151 au; Gibbs energy = -464.84372351 au

C	0.117934	1.825665	-0.634777
C	-0.417572	0.613500	-0.425291
H	1.177214	1.958983	-0.818556
H	-0.499560	2.716153	-0.622949
C	0.417585	-0.613665	-0.425113
C	-0.117885	-1.825891	-0.634339
H	0.499634	-2.716358	-0.622309
H	-1.177152	-1.959277	-0.818143
C	1.889402	-0.484072	-0.196644
C	2.762404	-1.009492	-1.067438
H	3.829668	-1.006108	-0.873638
H	2.428460	-1.461485	-1.994035
C	-1.889397	0.483991	-0.196808
C	-2.762380	1.009163	-1.067771
H	-3.829646	1.005861	-0.873978
H	-2.428419	1.460860	-1.994505
C	-2.317144	-0.185185	1.050178
C	-3.466839	-0.834628	1.239537
H	-3.718741	-1.267014	2.201546
H	-4.191186	-0.965636	0.441787
H	-1.606881	-0.130653	1.873176
C	2.317113	0.185515	1.050134

C	3.466778	0.835069	1.239296
H	1.606840	0.131226	1.873139
H	3.718649	1.267775	2.201170
H	4.191125	0.965859	0.441511

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ccccc_6_Dendralene
G4(MP2)
Eel = -465.01865900 au; Energy(0K)) = -464.80429544 au
Enthalpy = -464.79000332 au; Gibbs energy = -464.84244540 au

C	-2.235318	-0.562679	-1.203174
C	-1.539905	-0.057601	-0.173713
H	-2.113421	-0.178083	-2.208916
H	-2.940228	-1.375017	-1.065025
C	-0.661679	1.136670	-0.346027
C	-1.053385	2.189205	-1.077093
H	-0.395287	3.034941	-1.242046
H	-2.040312	2.228823	-1.524540
C	0.661679	1.136670	0.346027
C	1.053385	2.189205	1.077093
H	2.040312	2.228823	1.524540
H	0.395287	3.034941	1.242046
C	1.539905	-0.057601	0.173713
C	2.235318	-0.562679	1.203174
H	2.940228	-1.375017	1.065025
H	2.113421	-0.178083	2.208916
C	-1.628465	-0.620842	1.189467
C	-1.842978	-1.902106	1.490758
H	-1.487052	0.091777	1.999885
H	-1.923638	-2.234654	2.519848
H	-1.932578	-2.663668	0.722677
C	1.628465	-0.620843	-1.189467
C	1.842978	-1.902106	-1.490758
H	1.487051	0.091777	-1.999885
H	1.923638	-2.234654	-2.519848
H	1.932578	-2.663668	-0.722677

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ccccc_C2_SYMMETRY_6_Dendralene
G4(MP2)
Eel = -465.01862000 au; Energy(0K)) = -464.80423398 au
Enthalpy = -464.78994632 au; Gibbs energy = -464.84171763 au

C	0.946149	2.356096	-0.560191
C	0.000662	1.548691	-0.057490

H	1.958128	2.349094	-0.172788
H	0.731290	3.040206	-1.373679
C	0.268043	0.696882	1.138342
C	0.946149	1.170989	2.192530
H	1.182903	0.537214	3.039782
H	1.277065	2.202830	2.231968
C	-0.268043	-0.696882	1.138342
C	-0.946149	-1.170989	2.192530
H	-1.277065	-2.202830	2.231968
H	-1.182903	-0.537214	3.039782
C	-0.000662	-1.548691	-0.057490
C	-0.946149	-2.356096	-0.560191
H	-0.731290	-3.040206	-1.373679
H	-1.958128	-2.349094	-0.172788
C	-1.362200	1.481973	-0.624573
C	-1.682993	1.665124	-1.905989
H	-2.152788	1.245661	0.085171
H	-2.713706	1.627740	-2.241170
H	-0.928571	1.845819	-2.665047
C	1.362200	-1.481973	-0.624573
C	1.682993	-1.665124	-1.905989
H	2.152788	-1.245661	0.085171
H	2.713706	-1.627740	-2.241170
H	0.928571	-1.845819	-2.665047

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tccct_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57776233 au; Energy(0K)) = -465.35890743 au
Enthalpy = -465.34489502 au; Gibbs energy = -465.39678294 au

C	1.219902	-1.931936	-1.113741
C	1.317485	-0.773768	-0.435520
H	0.539961	-2.717594	-0.802122
H	1.810899	-2.113983	-2.008531
C	0.502226	-0.555658	0.803410
C	0.670866	-1.349798	1.873008
H	0.047358	-1.250230	2.757408
H	1.435121	-2.121167	1.886634
C	-0.502324	0.553187	0.804535
C	-0.671742	1.344459	1.876125
H	-1.435957	2.115838	1.891242
H	-0.048903	1.242508	2.760731
C	-1.316739	0.774636	-0.434413
C	-1.217388	1.933955	-1.110402

H	-1.807656	2.118382	-2.005190
H	-0.536683	2.718218	-0.796955
C	2.237379	0.275418	-0.899932
C	2.571169	1.390586	-0.236772
H	3.279431	2.099214	-0.656161
H	2.153968	1.633754	0.735339
H	2.697991	0.082430	-1.868903
C	-2.237637	-0.272561	-0.901317
C	-2.573099	-1.388604	-0.240495
H	-2.697463	-0.077158	-1.870177
H	-3.281930	-2.095623	-0.661630
H	-2.156733	-1.634095	0.731390

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tctcc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57661035 au; Energy(0K)) = -465.35791982 au
Enthalpy = -465.34381533 au; Gibbs energy = -465.39586130 au

C	0.133890	-1.381144	-1.481759
C	-0.316649	-0.696568	-0.414547
H	1.187794	-1.601987	-1.616722
H	-0.549947	-1.732388	-2.247648
C	0.609171	-0.196894	0.637176
C	0.170735	0.187639	1.848563
H	0.864469	0.538165	2.606547
H	-0.881062	0.167134	2.113587
C	2.082846	-0.175975	0.349415
C	2.895280	-1.081379	0.924439
H	3.967915	-1.075373	0.743352
H	2.511729	-1.849172	1.588900
C	-1.787172	-0.445609	-0.269199
C	-2.655865	-1.471651	-0.294500
H	-3.729847	-1.307608	-0.288094
H	-2.311698	-2.500591	-0.328985
C	-2.235357	0.962884	-0.168751
C	-3.338836	1.392717	0.454645
H	-3.618060	2.442366	0.448311
H	-3.993539	0.716054	0.998357
H	-1.591289	1.695846	-0.654409
C	2.639112	0.852864	-0.542670
C	1.977048	1.899121	-1.052218
H	3.698670	0.736876	-0.771737
H	2.474134	2.622345	-1.691738
H	0.925521	2.072309	-0.843286

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ttctt_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57726386 au; Energy(0K)) = -465.35789746 au
Enthalpy = -465.34409384 au; Gibbs energy = -465.39526620 au

C	-0.706523	-0.833048	1.888332
C	-1.343110	-0.306729	0.823281
H	0.248013	-0.450160	2.233533
H	-1.127946	-1.668652	2.440779
C	-0.741146	0.857903	0.100653
C	-1.477859	1.903415	-0.312912
H	-1.018030	2.739571	-0.830903
H	-2.547060	1.957094	-0.134819
C	0.741219	0.857998	-0.101142
C	1.477716	1.903709	0.312239
H	2.546935	1.957589	0.134321
H	1.017687	2.739877	0.830044
C	-2.624071	-0.899206	0.400302
C	-3.301206	-0.680190	-0.734927
H	-3.023187	-1.632602	1.101271
H	-4.223794	-1.215300	-0.940344
H	-2.963575	0.019696	-1.492138
C	1.343170	-0.307167	-0.823095
C	0.706378	-0.833873	-1.887862
H	1.127579	-1.669853	-2.439931
H	-0.248071	-0.451013	-2.233272
C	2.624116	-0.899421	-0.400014
C	3.301384	-0.679842	0.735045
H	3.023276	-1.633148	-1.100626
H	4.224087	-1.214671	0.940672
H	2.963677	0.020275	1.492014

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tcttc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57688455 au; Energy(0K)) = -465.35766875 au
Enthalpy = -465.34383258 au; Gibbs energy = -465.39528567 au

C	0.815827	-1.725414	1.130955
C	0.855838	-0.732237	0.226729
H	-0.117369	-2.187352	1.436121
H	1.727364	-2.100492	1.586018
C	-0.370110	-0.208727	-0.451037
C	-0.295863	0.212354	-1.728808
H	-1.165145	0.598487	-2.251174

H	0.639976	0.194159	-2.277289
C	-1.677942	-0.157722	0.268721
C	-1.772856	-0.008037	1.603975
H	-2.741619	0.013089	2.093347
H	-0.897606	0.089539	2.236770
C	-2.901826	-0.253647	-0.562464
C	-4.009332	0.477537	-0.395764
H	-2.863443	-0.977054	-1.376934
H	-4.883791	0.330230	-1.023537
H	-4.076136	1.251652	0.364477
C	2.184991	-0.176464	-0.189264
C	3.097547	-0.975975	-0.773873
H	4.077206	-0.600899	-1.061359
H	2.888657	-2.020573	-0.981231
C	2.505068	1.237082	0.065500
C	1.748692	2.118970	0.731050
H	3.471860	1.560579	-0.320627
H	2.083694	3.141047	0.881529
H	0.776144	1.861276	1.139566

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ctctc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57665804 au; Energy(0K)) = -465.35764152 au
Enthalpy = -465.34369039 au; Gibbs energy = -465.39547728 au

C	1.165050	1.774649	1.025317
C	0.718072	0.797325	0.216590
H	2.205986	1.837680	1.329037
H	0.496391	2.546521	1.393246
C	1.623728	-0.270778	-0.288700
C	1.307672	-1.008732	-1.369441
H	1.956709	-1.808528	-1.711316
H	0.396974	-0.834960	-1.933295
C	2.892987	-0.500370	0.440417
C	4.079506	-0.730387	-0.131935
H	2.830566	-0.468109	1.528358
H	4.966598	-0.926905	0.463892
H	4.205395	-0.722433	-1.211654
C	-0.717907	0.797466	-0.216765
C	-1.164711	1.774556	-1.025856
H	-2.205674	1.837663	-1.329471
H	-0.495930	2.546130	-1.394187
C	-1.623917	-0.270156	0.289064
C	-1.308132	-1.007431	1.370339
H	-1.957218	-1.807019	1.712599

H	-0.397463	-0.833358	1.934154
C	-2.892886	-0.500107	-0.440419
C	-4.079492	-0.730794	0.131476
H	-2.830087	-0.467426	-1.528320
H	-4.966298	-0.927501	-0.464710
H	-4.205773	-0.723190	1.211146

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tcctt_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57675142 au; Energy(0K)) = -465.35749829 au
Enthalpy = -465.34367891 au; Gibbs energy = -465.39503059 au

C	2.620133	-0.020296	-1.262715
C	1.697232	0.364814	-0.359998
H	2.884622	-1.063920	-1.398925
H	3.129687	0.703897	-1.893703
C	1.039575	-0.650996	0.523275
C	1.791039	-1.526981	1.212632
H	1.338614	-2.323124	1.796601
H	2.875304	-1.466972	1.207088
C	-0.455342	-0.705125	0.609273
C	-1.058244	-0.867530	1.800700
H	-2.133851	-0.981938	1.885384
H	-0.482078	-0.898190	2.720614
C	-1.238736	-0.663079	-0.665213
C	-0.797071	-1.339170	-1.744410
H	-1.358744	-1.344265	-2.674853
H	0.129030	-1.903406	-1.730146
C	-2.501731	0.089473	-0.771444
C	-3.004296	0.987609	0.085650
H	-3.053087	-0.105324	-1.691599
H	-3.938537	1.497042	-0.132266
H	-2.505115	1.255682	1.010650
C	1.363799	1.792211	-0.234651
C	0.649697	2.366946	0.742051
H	1.783641	2.425905	-1.015751
H	0.480870	3.439840	0.750380
H	0.213313	1.797525	1.555628

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ctcct_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57653163 au; Energy(0K)) = -465.35734859 au
Enthalpy = -465.34350061 au; Gibbs energy = -465.39509852 au

C	-0.819823	1.415152	-1.529732
C	-0.382221	0.791447	-0.418815
H	-1.870758	1.419717	-1.803402
H	-0.134867	1.941284	-2.187227
C	-1.331103	0.041471	0.450837
C	-1.100053	-0.134685	1.765291
H	-1.786187	-0.708094	2.380849
H	-0.225850	0.277887	2.256093
C	-2.554678	-0.500155	-0.184857
C	-3.778810	-0.477267	0.353584
H	-2.419334	-0.937883	-1.173860
H	-4.628710	-0.925107	-0.154040
H	-3.973564	-0.005201	1.313284
C	1.063909	0.876596	-0.037028
C	1.692231	2.064876	-0.045186
H	2.755819	2.143699	0.159603
H	1.155805	2.984888	-0.257958
C	1.811400	-0.360644	0.358220
C	2.563736	-0.365695	1.476729
H	3.142394	-1.239998	1.764417
H	2.615715	0.496573	2.133726
C	1.764140	-1.573141	-0.474955
C	1.249208	-1.693312	-1.705903
H	2.236470	-2.445639	-0.023492
H	1.294261	-2.641397	-2.234239
H	0.771187	-0.868593	-2.222872

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ctctt_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57541356 au; Energy(0K)) = -465.35604434 au
Enthalpy = -465.34221678 au; Gibbs energy = -465.39360717 au

C	-1.200179	-0.065048	2.056007
C	-1.594368	-0.024573	0.767531
H	-0.326711	0.475477	2.404785
H	-1.747172	-0.646421	2.793404
C	-0.837983	0.809483	-0.219337
C	-1.455749	1.548653	-1.154036
H	-0.887026	2.170151	-1.839268
H	-2.536680	1.567307	-1.249636
C	0.654687	0.888196	-0.076451
C	1.203157	2.052504	0.318714
H	2.271995	2.175191	0.461154
H	0.580474	2.916157	0.528738
C	-2.771944	-0.815561	0.364409

C	-3.180774	-1.114918	-0.876432
H	-3.330318	-1.233313	1.202369
H	-4.049699	-1.747196	-1.034386
H	-2.668786	-0.756392	-1.763328
C	1.477521	-0.314639	-0.375450
C	0.926484	-1.483153	-0.756256
H	1.553132	-2.328326	-1.022435
H	-0.145937	-1.629543	-0.823018
C	2.953725	-0.187228	-0.299043
C	3.769431	-1.084088	0.263501
H	3.387304	0.705828	-0.748653
H	4.848127	-0.953409	0.252760
H	3.387254	-1.973274	0.758572

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ctccc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57480600 au; Energy(0K)) = -465.35599373 au
Enthalpy = -465.34198867 au; Gibbs energy = -465.39395593 au

C	-0.985807	1.527334	-1.484239
C	-0.504590	0.882739	-0.404834
H	-2.021627	1.428240	-1.795593
H	-0.351919	2.180013	-2.076157
C	-1.363572	-0.032193	0.395163
C	-1.066535	-0.335492	1.672944
H	-1.679306	-1.029057	2.240122
H	-0.206130	0.090091	2.177976
C	-2.563437	-0.600299	-0.262018
C	-3.765798	-0.731220	0.308621
H	-2.430424	-0.923099	-1.294657
H	-4.596374	-1.190355	-0.220455
H	-3.961962	-0.378400	1.317990
C	0.919612	1.092226	0.009271
C	1.382376	2.331601	0.244352
H	2.431286	2.513193	0.460449
H	0.721507	3.192945	0.221276
C	1.814690	-0.103028	0.096028
C	2.749649	-0.209588	1.058132
H	3.462389	-1.028796	1.065895
H	2.825074	0.519532	1.859157
C	1.649075	-1.136360	-0.951249
C	1.842280	-2.449336	-0.783097
H	1.324289	-0.773997	-1.926203
H	1.729474	-3.147463	-1.607717
H	2.106064	-2.871145	0.183464

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cccct_5_Dendralene
b3lyp/6-31g(d)
Eel = -465.57470315 au; Energy(0K)) = -465.35596786 au
Enthalpy = -465.34190235 au; Gibbs energy = -465.39389843 au

C	-1.997919	-1.054836	1.239012
C	-1.454507	-0.482065	0.150061
H	-1.519522	-1.895110	1.731794
H	-2.929566	-0.694193	1.665483
C	-0.240280	-1.069479	-0.496615
C	-0.169226	-2.387529	-0.752846
H	0.725280	-2.833991	-1.177848
H	-1.005306	-3.047792	-0.542733
C	0.869372	-0.146948	-0.892089
C	1.439501	-0.238239	-2.105334
H	2.276544	0.395021	-2.384429
H	1.080699	-0.946924	-2.846365
C	1.317837	0.906820	0.074087
C	1.313126	2.202608	-0.292349
H	1.651288	2.982862	0.385455
H	0.960520	2.516951	-1.269004
C	-2.044935	0.712145	-0.496251
C	-2.750659	1.668095	0.118792
H	-1.868196	0.800282	-1.568094
H	-3.180600	2.497190	-0.435860
H	-2.911906	1.663278	1.193840
C	1.783608	0.533943	1.418727
C	2.018780	-0.704521	1.871673
H	1.975261	1.377958	2.081416
H	2.382915	-0.867806	2.881884
H	1.854401	-1.587693	1.263247

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ccctt_2nd_Conf_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57488204 au; Energy(0K)) = -465.35590277 au
Enthalpy = -465.34196807 au; Gibbs energy = -465.39359872 au

C	1.245138	-1.588527	-1.282321
C	0.581665	-0.971257	-0.288955
H	0.709849	-2.112409	-2.068439
H	2.329201	-1.597479	-1.328760
C	-0.911989	-1.048563	-0.225681
C	-1.538479	-2.233554	-0.331855

H	-2.621938	-2.299204	-0.368421
H	-0.980273	-3.163281	-0.387457
C	-1.680282	0.225032	-0.073508
C	-2.775436	0.291527	0.705491
H	-3.388484	1.187025	0.744107
H	-3.084171	-0.546636	1.322592
C	-1.200059	1.390052	-0.850352
C	-1.291313	2.668634	-0.467554
H	-0.720040	1.159971	-1.801149
H	-0.939742	3.475670	-1.103905
H	-1.705252	2.949869	0.497487
C	1.290110	-0.248952	0.813063
C	0.843568	-0.366225	2.079674
H	1.349520	0.129519	2.903905
H	-0.032880	-0.955769	2.326768
C	2.476508	0.586495	0.554180
C	2.931702	1.030732	-0.624620
H	3.001718	0.898391	1.457160
H	3.804890	1.674908	-0.673142
H	2.450802	0.787064	-1.566106

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cctcc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57416596 au; Energy(0K)) = -465.35543305 au
Enthalpy = -465.34137873 au; Gibbs energy = -465.39351649 au

C	-0.119658	-1.829864	-0.632627
C	0.418928	-0.614555	-0.419807
H	-1.179453	-1.962659	-0.822882
H	0.496138	-2.723456	-0.613876
C	-0.418960	0.615042	-0.419282
C	0.119404	1.830581	-0.631374
H	-0.496582	2.724034	-0.612218
H	1.179141	1.963704	-0.821692
C	-1.893485	0.488971	-0.188745
C	-2.766559	1.044565	-1.047885
H	-3.834897	1.048556	-0.850841
H	-2.431039	1.513241	-1.967673
C	1.893442	-0.488877	-0.189051
C	2.766488	-1.043944	-1.048584
H	3.834801	-1.048309	-0.851420
H	2.430958	-1.511716	-1.968823
C	2.330947	0.208210	1.042988
C	3.494886	0.846156	1.214087
H	3.754130	1.300550	2.165941

H	4.221885	0.945289	0.411762
H	1.620164	0.189547	1.868841
C	-2.330660	-0.209295	1.042736
C	-3.494754	-0.846957	1.213811
H	-1.619407	-0.191781	1.868173
H	-3.753674	-1.302307	2.165293
H	-4.222279	-0.944895	0.411810

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cttcc_6_Dendralene
b3lyp/6-31g(d)
Eel = -465.57421678 au; Energy(0K)) = -465.35521204 au
Enthalpy = -465.34130299 au; Gibbs energy = -465.39305631 au

C	-0.489492	2.201565	-0.037860
C	-0.661187	0.872645	-0.155616
H	0.490280	2.662023	-0.108877
H	-1.336147	2.858604	0.134869
C	0.478711	-0.064518	-0.392993
C	0.288630	-1.162750	-1.151281
H	1.091941	-1.867439	-1.341571
H	-0.677095	-1.389879	-1.589762
C	1.826140	0.205792	0.191958
C	1.996480	0.869554	1.351076
H	2.990987	1.061359	1.741799
H	1.157500	1.237237	1.931626
C	2.995411	-0.318861	-0.552857
C	4.067472	-0.898475	-0.001534
H	2.944444	-0.225181	-1.637710
H	4.905144	-1.231030	-0.608329
H	4.140049	-1.067953	1.069774
C	-2.039878	0.293121	-0.087559
C	-3.041982	0.820055	-0.814543
H	-4.065788	0.472811	-0.708508
H	-2.861012	1.614632	-1.531493
C	-2.245463	-0.840191	0.844530
C	-3.185818	-1.785991	0.737109
H	-1.550304	-0.888804	1.682201
H	-3.290399	-2.564319	1.487396
H	-3.873750	-1.823741	-0.103987

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ccccc_5_Dendralene
b3lyp/6-31g(d)
Eel = -465.57240492 au; Energy(0K)) = -465.35385847 au

Enthalpy = -465.33974749 au; Gibbs energy = -465.39191055 au

C	2.272252	-0.541596	1.185703
C	1.551277	-0.053691	0.159621
H	2.163671	-0.147555	2.191231
H	2.984177	-1.349484	1.044654
C	0.668211	1.139816	0.336631
C	1.069360	2.200442	1.059617
H	0.409887	3.045202	1.235012
H	2.065611	2.247367	1.489491
C	-0.667955	1.139943	-0.336771
C	-1.069037	2.200601	-1.059717
H	-2.065316	2.247592	-1.489521
H	-0.409516	3.045321	-1.235125
C	-1.551163	-0.053517	-0.159724
C	-2.272066	-0.541416	-1.185840
H	-2.984080	-1.349232	-1.044854
H	-2.163343	-0.147409	-2.191371
C	1.620365	-0.638204	-1.198805
C	1.850178	-1.925377	-1.482344
H	1.451925	0.057434	-2.020530
H	1.916239	-2.274226	-2.508938
H	1.965816	-2.673825	-0.702497
C	-1.620309	-0.637758	1.198802
C	-1.851036	-1.924676	1.482747
H	-1.451020	0.057917	2.020311
H	-1.916999	-2.273230	2.509445
H	-1.967521	-2.673269	0.703170

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[7]Dendraleene

C14
G4(MP2)
Eel = -542.33198700 au; Energy(0K)) = -542.08424645 au
Enthalpy = -542.06803490 au; Gibbs energy = -542.12418252 au

H	1.525953	-2.700819	1.045812
C	2.011968	-1.751901	0.848974
C	1.292339	-0.648122	0.616407
H	3.095516	-1.736105	0.865932
C	-0.202379	-0.704986	0.680622
C	1.930574	0.682773	0.377449
C	-0.798429	-1.023504	1.839200
C	-0.979888	-0.442612	-0.555930
H	-1.876026	-1.098418	1.924281
H	-0.212906	-1.218722	2.729833

C	-0.405947	-0.396627	-1.764864
C	-2.465523	-0.270749	-0.440011
H	0.660498	-0.529998	-1.903387
H	-0.998425	-0.217972	-2.654938
C	-3.288708	-1.288444	-0.730230
C	-3.008200	1.028282	-0.027338
H	-2.910767	-2.254058	-1.045417
H	-4.366933	-1.177968	-0.661354
C	1.450748	1.773898	0.999249
C	3.086735	0.830196	-0.518493
H	0.593585	1.723268	1.659633
H	1.913390	2.745934	0.863430
C	3.607183	-0.075115	-1.351629
H	3.527705	1.825779	-0.501534
H	3.216905	-1.082317	-1.435126
H	4.449327	0.176940	-1.986633
C	-2.312456	2.157552	0.124935
H	-4.084658	1.040949	0.137027
H	-1.242216	2.198243	-0.045070
H	-2.799045	3.081415	0.417470

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C34
G4(MP2)
Eel = -542.33178400 au; Energy(0K)) = -542.08409700 au
Enthalpy = -542.06787196 au; Gibbs energy = -542.12344988 au

H	-1.191735	0.364372	-2.191799
C	-0.919591	1.274627	-1.671366
C	-0.313163	1.258111	-0.476754
H	-1.157889	2.213376	-2.158001
C	0.000000	0.000000	0.261133
C	0.000000	2.559457	0.195169
C	0.000000	0.000000	1.603964
C	0.313163	-1.258111	-0.476754
H	0.203124	-0.901921	2.167768
H	-0.203124	0.901921	2.167768
C	0.919591	-1.274627	-1.671366
C	0.000000	-2.559457	0.195169
H	1.191735	-0.364372	-2.191799
H	1.157889	-2.213376	-2.158001
C	0.991810	-3.390805	0.550797
C	-1.397638	-2.937517	0.437438
H	2.032135	-3.135999	0.387100
H	0.783586	-4.348736	1.017876
C	-0.991810	3.390805	0.550797

C	1.397638	2.937517	0.437438
H	-2.032135	3.135999	0.387100
H	-0.783586	4.348736	1.017876
C	2.483543	2.271047	0.040021
H	1.523677	3.873336	0.979637
H	2.423166	1.334902	-0.503497
H	3.478840	2.644355	0.253801
C	-2.483543	-2.271047	0.040021
H	-1.523677	-3.873336	0.979637
H	-2.423166	-1.334902	-0.503497
H	-3.478840	-2.644355	0.253801

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C21
G4(MP2)
Eel = -542.33140500 au; Energy(0K)) = -542.08361767 au
Enthalpy = -542.06744567 au; Gibbs energy = -542.12367806 au

H	1.606189	-2.549033	1.643281
C	2.123071	-1.809059	1.042427
C	1.458551	-0.810412	0.447373
H	3.198615	-1.907148	0.944458
C	-0.016069	-0.664169	0.678930
C	2.200163	0.144961	-0.434955
C	-0.478379	-0.622813	1.938926
C	-0.947515	-0.653328	-0.477152
H	-1.538506	-0.573239	2.155228
H	0.201646	-0.638090	2.782519
C	-0.572218	-1.017627	-1.710497
C	-2.385485	-0.298231	-0.234085
H	0.442719	-1.312042	-1.943082
H	-1.286372	-1.024698	-2.526046
C	-3.315330	-1.264527	-0.203800
C	-2.775214	1.105345	-0.062114
H	-3.055491	-2.308254	-0.336218
H	-4.364423	-1.031835	-0.046393
C	2.993234	-0.320869	-1.414742
C	2.120863	1.594410	-0.214024
H	3.083946	-1.381378	-1.617908
H	3.570321	0.353233	-2.039900
C	1.575750	2.224849	0.830099
H	2.605034	2.189776	-0.986497
H	1.084813	1.696219	1.637306
H	1.606342	3.306608	0.902354
C	-1.985307	2.169941	-0.218658
H	-3.823618	1.255642	0.191441

H	-0.937003	2.078186	-0.478893
H	-2.370899	3.175223	-0.088015

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C5
G4(MP2)
Eel = -542.33102600 au; Energy(0K)) = -542.08341830 au
Enthalpy = -542.06712682 au; Gibbs energy = -542.12335183 au

H	0.981001	-2.536825	1.239426
C	1.681764	-1.759921	0.955119
C	1.255147	-0.526715	0.659235
H	2.733190	-2.021547	0.942342
C	-0.200913	-0.194017	0.776589
C	2.193748	0.581172	0.305236
C	-0.788758	-0.254588	1.981020
C	-0.945113	0.191109	-0.446309
H	-1.838243	-0.024334	2.119437
H	-0.221873	-0.534938	2.860931
C	-0.398234	0.143855	-1.667684
C	-2.374929	0.629551	-0.305241
H	0.625562	-0.169361	-1.834212
H	-0.972825	0.422280	-2.543937
C	-2.677126	1.930761	-0.199714
C	-3.436358	-0.382709	-0.307676
H	-1.909602	2.696149	-0.202330
H	-3.706625	2.264591	-0.109748
C	1.993409	1.812290	0.805801
C	3.343684	0.360822	-0.585130
H	1.150628	2.036438	1.448356
H	2.674679	2.626344	0.581945
C	3.602958	-0.699392	-1.355422
H	4.027639	1.207003	-0.630926
H	2.962824	-1.573064	-1.380378
H	4.475389	-0.714585	-1.999377
C	-3.271391	-1.695903	-0.484120
H	-4.440711	0.011085	-0.158507
H	-2.291839	-2.132152	-0.645926
H	-4.116527	-2.374965	-0.477321

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C16
G4(MP2)
Eel = -542.33087500 au; Energy(0K)) = -542.08340819 au
Enthalpy = -542.06706720 au; Gibbs energy = -542.12355514 au

H	-1.126035	-2.998510	-0.275084
C	-1.727871	-2.104063	-0.161986
C	-1.182083	-0.884930	-0.264619
H	-2.787851	-2.242521	0.021174
C	0.281757	-0.752026	-0.564463
C	-1.998277	0.347566	-0.117196
C	0.720268	-0.960975	-1.813236
C	1.202954	-0.433679	0.554897
H	1.771540	-0.896378	-2.067680
H	0.029229	-1.206938	-2.611224
C	0.808302	-0.462747	1.834094
C	2.632034	-0.109044	0.231389
H	-0.208188	-0.714343	2.112562
H	1.501286	-0.240982	2.637555
C	3.570579	-1.065077	0.278009
C	2.993134	1.268931	-0.118433
H	3.329190	-2.087956	0.542898
H	4.610047	-0.845144	0.053069
C	-1.586850	1.528105	-0.606895
C	-3.292105	0.229281	0.590014
H	-0.657186	1.622990	-1.154491
H	-2.178787	2.425631	-0.469926
C	-4.431165	0.811325	0.215100
H	-3.288325	-0.397041	1.480534
H	-4.498002	1.403351	-0.692065
H	-5.338735	0.708281	0.800258
C	2.193100	2.335310	-0.043266
H	4.024154	1.400528	-0.443455
H	1.165536	2.256666	0.293616
H	2.549460	3.324495	-0.308196

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C6
G4(MP2)
Eel = -542.33063100 au; Energy(0K)) = -542.08335340 au
Enthalpy = -542.06692816 au; Gibbs energy = -542.12353292 au

H	-0.279555	0.001375	-2.065754
C	0.694850	-0.347736	-1.745869
C	1.101083	-0.247751	-0.473796
H	1.337781	-0.778717	-2.504720
C	0.251940	0.346242	0.586542
C	2.471443	-0.737975	-0.103382
C	0.693273	0.529941	1.838590
C	-1.147902	0.757869	0.236542
H	0.051583	0.966661	2.595019

H	1.695245	0.249696	2.140455
C	-1.438743	2.057979	0.095273
C	-2.185840	-0.295195	0.095897
H	-0.673570	2.817969	0.204523
H	-2.445519	2.400643	-0.116139
C	-1.993483	-1.540337	0.559318
C	-3.447362	0.070954	-0.584919
H	-1.086963	-1.818554	1.083049
H	-2.744690	-2.309096	0.421219
C	2.676803	-2.033837	0.169818
C	3.587280	0.213651	-0.069523
H	1.870630	-2.757835	0.141140
H	3.664113	-2.405442	0.427684
C	3.532776	1.503606	-0.409573
H	4.536096	-0.209879	0.256552
H	2.613325	1.966799	-0.750072
H	4.412618	2.135341	-0.362669
C	-4.667795	-0.289078	-0.188190
H	-3.343753	0.689647	-1.474770
H	-4.825903	-0.864552	0.718356
H	-5.551360	-0.014050	-0.754227

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C15
G4(MP2)
Eel = -542.33035600 au; Energy(0K)) = -542.08268684 au
Enthalpy = -542.06645274 au; Gibbs energy = -542.12264633 au

H	0.854811	-2.617890	1.137664
C	1.645378	-1.929191	0.862542
C	1.408138	-0.838072	0.126203
H	2.647587	-2.163705	1.203217
C	0.046937	-0.500107	-0.404806
C	2.544132	0.042216	-0.286961
C	-0.070832	-0.188285	-1.705249
C	-1.140822	-0.522549	0.486623
H	-1.028085	0.036035	-2.156978
H	0.799302	-0.152153	-2.350072
C	-1.074450	-0.645379	1.819874
C	-2.499783	-0.364090	-0.139612
H	-0.134856	-0.755739	2.345801
H	-1.977789	-0.627610	2.419055
C	-3.232627	-1.445102	-0.439620
C	-3.029644	0.981321	-0.384950
H	-2.866776	-2.449941	-0.262822
H	-4.223594	-1.350538	-0.873552

C	3.546647	-0.455403	-1.028877
C	2.567164	1.449806	0.128150
H	3.553376	-1.489416	-1.352432
H	4.385406	0.164613	-1.330780
C	1.742024	2.034462	0.999888
H	3.367626	2.039495	-0.315602
H	0.936127	1.496053	1.486107
H	1.853489	3.081358	1.259669
C	-2.421602	2.135498	-0.100589
H	-4.020112	1.001417	-0.837277
H	-1.434732	2.170588	0.347440
H	-2.895744	3.086687	-0.315135

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C26
G4(MP2)
Eel = -542.32987400 au; Energy(0K)) = -542.08263464 au
Enthalpy = -542.06617657 au; Gibbs energy = -542.12281068 au

H	0.319348	-0.192884	-2.033268
C	-0.680439	-0.475518	-1.726253
C	-1.110655	-0.301366	-0.469508
H	-1.328976	-0.902873	-2.482371
C	-0.252452	0.278098	0.591510
C	-2.511977	-0.704130	-0.112548
C	-0.671047	0.409063	1.856743
C	1.133317	0.733048	0.223101
H	-0.024779	0.831698	2.617630
H	-1.660549	0.096303	2.167607
C	1.323050	2.005765	-0.150442
C	2.246819	-0.244828	0.290178
H	0.496996	2.707072	-0.184866
H	2.294732	2.383891	-0.445680
C	2.036984	-1.542086	0.566020
C	3.624084	0.256755	0.080792
H	1.042729	-1.940950	0.723085
H	2.867538	-2.232626	0.653299
C	-2.806678	-1.986113	0.144574
C	-3.562064	0.319897	-0.075691
H	-2.051267	-2.762782	0.113553
H	-3.818815	-2.292847	0.391327
C	-3.424276	1.601293	-0.423757
H	-4.535693	-0.038441	0.255216
H	-2.478180	2.000572	-0.772073
H	-4.260045	2.290290	-0.377381
C	4.550205	-0.340484	-0.667930

H	3.877806	1.183632	0.591831
H	4.334517	-1.245262	-1.227361
H	5.555422	0.058833	-0.751278

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C28
G4(MP2)
Eel = -542.32956600 au; Energy(0K)) = -542.08213689 au
Enthalpy = -542.06581026 au; Gibbs energy = -542.12240454 au

H	-0.475317	-0.797683	2.096573
C	0.540907	-0.520192	1.845523
C	0.980563	-0.497658	0.580156
H	1.196657	-0.252569	2.666115
C	0.117973	-0.885576	-0.562739
C	2.412940	-0.140447	0.309910
C	0.623048	-1.093829	-1.788125
C	-1.346913	-1.100963	-0.330680
H	-0.018062	-1.386176	-2.611343
H	1.679898	-0.978856	-1.996735
C	-1.889065	-2.303987	-0.556089
C	-2.191095	0.055895	0.091408
H	-1.275266	-3.153385	-0.834072
H	-2.958523	-2.465086	-0.475360
C	-3.179951	-0.093620	0.986112
C	-1.922559	1.351001	-0.566744
H	-3.337614	-1.034030	1.501544
H	-3.858184	0.719067	1.221151
C	3.383574	-1.024181	0.584888
C	2.750213	1.181698	-0.228614
H	3.161960	-2.004777	0.989520
H	4.428732	-0.784868	0.412091
C	1.908072	2.202404	-0.404196
H	3.802649	1.313979	-0.475382
H	0.853781	2.130439	-0.161487
H	2.256971	3.152325	-0.794490
C	-2.113373	2.555040	-0.023447
H	-1.523636	1.289652	-1.577136
H	-2.453762	2.674808	1.000168
H	-1.926292	3.463652	-0.585328

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C8
G4(MP2)
Eel = -542.32946300 au; Energy(0K)) = -542.08194869 au

Enthalpy = -542.06559733 au; Gibbs energy = -542.12202143 au

H	0.211785	-0.514124	2.146443
C	-0.810958	-0.322925	1.845012
C	-1.197992	-0.402017	0.565073
H	-1.518902	-0.066696	2.625037
C	-0.263340	-0.754204	-0.532251
C	-2.633390	-0.135511	0.214457
C	-0.679513	-0.971827	-1.786463
C	1.197049	-0.898088	-0.203483
H	0.023826	-1.232689	-2.569215
H	-1.724222	-0.900039	-2.063813
C	1.653143	-2.088077	0.211293
C	2.078215	0.286527	-0.344308
H	0.987114	-2.938817	0.300167
H	2.688134	-2.249914	0.487707
C	1.608754	1.476519	-0.753567
C	3.521948	0.117970	-0.061111
H	0.562189	1.632181	-0.982761
H	2.277651	2.317758	-0.891992
C	-3.529572	-1.132127	0.210642
C	-3.046635	1.234093	-0.110131
H	-3.251018	-2.150788	0.454782
H	-4.571730	-0.951281	-0.035522
C	-2.296075	2.333033	0.001187
H	-4.075715	1.328228	-0.453870
H	-1.273871	2.292882	0.360527
H	-2.690397	3.310732	-0.251949
C	4.264774	0.964051	0.650827
H	3.992966	-0.768063	-0.482360
H	3.835550	1.843070	1.121198
H	5.328195	0.803057	0.792565

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C14
b3lyp/6-31g(d)
Eel = -542.97544560 au; Energy(0K)) = -542.72291535 au
Enthalpy = -542.70688066 au; Gibbs energy = -542.76273647 au

H	-1.534274	-2.687181	-1.089087
C	-2.018913	-1.738023	-0.880753
C	-1.295842	-0.635901	-0.625690
H	-3.104122	-1.719490	-0.903849
C	0.201390	-0.696693	-0.686567
C	-1.938854	0.692060	-0.366672
C	0.799310	-1.013183	-1.849754
C	0.981965	-0.443099	0.554116

H	1.878111	-1.094422	-1.935251
H	0.213507	-1.199561	-2.744170
C	0.404753	-0.399115	1.766450
C	2.471294	-0.278677	0.442644
H	-0.664246	-0.526842	1.904354
H	0.997774	-0.225574	2.659167
C	3.290163	-1.303643	0.739766
C	3.027124	1.017822	0.026879
H	2.904649	-2.268016	1.055638
H	4.371342	-1.201116	0.676283
C	-1.457904	1.797559	-0.970353
C	-3.100961	0.822313	0.529758
H	-0.599014	1.759096	-1.632138
H	-1.921435	2.769017	-0.819404
C	-3.618770	-0.102273	1.350434
H	-3.549789	1.815825	0.528386
H	-3.222150	-1.109838	1.420541
H	-4.465434	0.136016	1.987648
C	2.337160	2.155214	-0.128540
H	4.105119	1.024855	-0.136613
H	1.265573	2.205293	0.040839
H	2.832899	3.075767	-0.422648

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C34
b3lyp/6-31g(d)
Eel = -542.97509214 au; Energy(0K)) = -542.72264101 au
Enthalpy = -542.70658777 au; Gibbs energy = -542.76188524 au

H	-1.200328	0.360028	-2.191182
C	-0.924677	1.273271	-1.674127
C	-0.313389	1.260598	-0.476898
H	-1.161920	2.211300	-2.166386
C	0.000000	0.000000	0.262977
C	0.000000	2.566943	0.190748
C	0.000000	0.000000	1.609697
C	0.313389	-1.260598	-0.476898
H	0.204997	-0.902563	2.175118
H	-0.204997	0.902563	2.175118
C	0.924677	-1.273271	-1.674127
C	0.000000	-2.566943	0.190748
H	1.200328	-0.360028	-2.191182
H	1.161920	-2.211300	-2.166386
C	0.995865	-3.404971	0.535775
C	-1.399225	-2.946668	0.442294
H	2.037414	-3.150063	0.368290

H	0.790513	-4.367965	0.997894
C	-0.995865	3.404971	0.535775
C	1.399225	2.946668	0.442294
H	-2.037414	3.150063	0.368290
H	-0.790513	4.367965	0.997894
C	2.489761	2.273863	0.053769
H	1.525511	3.885671	0.981562
H	2.431797	1.333698	-0.486488
H	3.485375	2.647799	0.273805
C	-2.489761	-2.273863	0.053769
H	-1.525511	-3.885671	0.981562
H	-2.431797	-1.333698	-0.486488
H	-3.485375	-2.647799	0.273805

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C16
b3lyp/6-31g(d)
Eel = -542.97464992 au; Energy(0K)) = -542.72242238 au
Enthalpy = -542.70624790 au; Gibbs energy = -542.76245596 au

H	-1.131855	-3.008543	-0.294672
C	-1.734227	-2.112496	-0.180959
C	-1.183959	-0.889626	-0.272504
H	-2.797515	-2.252282	-0.007521
C	0.284048	-0.758672	-0.564180
C	-2.002576	0.344817	-0.119286
C	0.730382	-0.978827	-1.812961
C	1.203546	-0.431345	0.558815
H	1.784462	-0.918289	-2.064069
H	0.042196	-1.230090	-2.614021
C	0.802693	-0.455539	1.840737
C	2.635844	-0.104456	0.240383
H	-0.215422	-0.709071	2.118483
H	1.492907	-0.227023	2.646920
C	3.580118	-1.059906	0.305860
C	2.998246	1.272344	-0.127192
H	3.339390	-2.081717	0.582410
H	4.622810	-0.841142	0.085892
C	-1.592369	1.528644	-0.613506
C	-3.295391	0.226579	0.594923
H	-0.666149	1.623166	-1.170297
H	-2.182419	2.428628	-0.471522
C	-4.435127	0.823981	0.230676
H	-3.294348	-0.410388	1.479675
H	-4.503225	1.426502	-0.671529
H	-5.341369	0.721311	0.821211

C	2.193115	2.341145	-0.066706
H	4.030859	1.404513	-0.451353
H	1.163317	2.265865	0.269325
H	2.550305	3.328708	-0.343524

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C5
b3lyp/6-31g(d)
Eel = -542.97443392 au; Energy(0K)) = -542.72204085 au
Enthalpy = -542.70592570 au; Gibbs energy = -542.76186456 au

H	0.987922	-2.558623	1.206648
C	1.688081	-1.774130	0.935333
C	1.258141	-0.534039	0.652824
H	2.741931	-2.033583	0.922986
C	-0.201387	-0.206639	0.773723
C	2.201306	0.578585	0.313766
C	-0.791845	-0.294769	1.979979
C	-0.948444	0.204118	-0.443608
H	-1.844235	-0.073230	2.123584
H	-0.223560	-0.590429	2.856050
C	-0.397204	0.186758	-1.668609
C	-2.382792	0.634113	-0.296639
H	0.630275	-0.117071	-1.841210
H	-0.972483	0.482830	-2.540621
C	-2.692036	1.936675	-0.173735
C	-3.444394	-0.383098	-0.311913
H	-1.926452	2.706413	-0.165550
H	-3.724193	2.267143	-0.079667
C	2.003422	1.806785	0.832683
C	3.353254	0.366774	-0.581525
H	1.160834	2.024431	1.480630
H	2.685464	2.625311	0.618755
C	3.605212	-0.687435	-1.369983
H	4.044486	1.209063	-0.616854
H	2.958538	-1.557904	-1.408092
H	4.478932	-0.698399	-2.015156
C	-3.273751	-1.697093	-0.508432
H	-4.452233	0.002899	-0.156341
H	-2.291858	-2.129321	-0.677741
H	-4.118749	-2.379173	-0.510605

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C6
b3lyp/6-31g(d)

Eel = -542.97403954 au; Energy(0K)) = -542.72201402 au
Enthalpy = -542.70575449 au; Gibbs energy = -542.76207626 au

H	-0.289920	-0.044696	-2.066446
C	0.687469	-0.386468	-1.741694
C	1.101165	-0.258495	-0.469954
H	1.327798	-0.835087	-2.494856
C	0.254477	0.361924	0.582355
C	2.475350	-0.743519	-0.096796
C	0.703917	0.575686	1.831454
C	-1.149910	0.766427	0.232507
H	0.064431	1.029085	2.582316
H	1.709655	0.305435	2.136067
C	-1.445072	2.068945	0.080511
C	-2.190527	-0.290585	0.103809
H	-0.679290	2.832333	0.177926
H	-2.455090	2.410072	-0.127200
C	-1.999940	-1.530906	0.592370
C	-3.451316	0.063965	-0.589764
H	-1.095794	-1.800238	1.128318
H	-2.749954	-2.304495	0.462159
C	2.682753	-2.040251	0.191858
C	3.595609	0.208843	-0.076685
H	1.875000	-2.765473	0.175020
H	3.671997	-2.411178	0.451012
C	3.540610	1.498273	-0.435032
H	4.547251	-0.209297	0.252573
H	2.620011	1.959766	-0.780033
H	4.423327	2.129679	-0.397924
C	-4.675599	-0.304040	-0.197445
H	-3.348152	0.678615	-1.484261
H	-4.837235	-0.874225	0.713869
H	-5.557945	-0.039085	-0.773509

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C21
b3lyp/6-31g(d)
Eel = -542.97443556 au; Energy(0K)) = -542.72183871 au
Enthalpy = -542.70585070 au; Gibbs energy = -542.76177834 au

H	1.605646	-2.535463	1.673844
C	2.125166	-1.799370	1.067381
C	1.460573	-0.804435	0.456041
H	3.203119	-1.897848	0.977246
C	-0.017130	-0.656885	0.683606
C	2.209951	0.139553	-0.436590
C	-0.482208	-0.610497	1.946870

C	-0.950304	-0.653505	-0.475687
H	-1.544038	-0.562836	2.163719
H	0.197798	-0.617799	2.792775
C	-0.570440	-1.024838	-1.710338
C	-2.392664	-0.302253	-0.238179
H	0.447282	-1.317473	-1.941141
H	-1.283371	-1.035697	-2.529074
C	-3.322939	-1.274522	-0.219208
C	-2.791197	1.101728	-0.059344
H	-3.058731	-2.318576	-0.354791
H	-4.376019	-1.047196	-0.068129
C	3.011915	-0.343271	-1.406596
C	2.131940	1.595437	-0.236872
H	3.100698	-1.408331	-1.595818
H	3.597639	0.320259	-2.038130
C	1.583510	2.240070	0.802304
H	2.618717	2.183144	-1.015324
H	1.089163	1.720716	1.615799
H	1.614979	3.324336	0.861513
C	-2.000982	2.172764	-0.206466
H	-3.842450	1.249484	0.189640
H	-0.949333	2.086240	-0.461928
H	-2.392244	3.177197	-0.071718

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C28
b3lyp/6-31g(d)
Eel = -542.97322635 au; Energy(0K)) = -542.72099545 au
Enthalpy = -542.70485789 au; Gibbs energy = -542.76115768 au

H	-0.477462	-0.788568	2.104578
C	0.540235	-0.510924	1.852168
C	0.983569	-0.494411	0.583371
H	1.194459	-0.235240	2.673482
C	0.120239	-0.892057	-0.560402
C	2.418514	-0.136386	0.314928
C	0.630619	-1.117153	-1.785328
C	-1.348692	-1.101440	-0.332848
H	-0.009733	-1.414401	-2.609638
H	1.690268	-1.010344	-1.992860
C	-1.895150	-2.306951	-0.562409
C	-2.196442	0.057057	0.088215
H	-1.281878	-3.160540	-0.835425
H	-2.967370	-2.465442	-0.489720
C	-3.192169	-0.096807	0.981106
C	-1.928188	1.358076	-0.564619

H	-3.349396	-1.039114	1.497005
H	-3.875474	0.714425	1.214204
C	3.393251	-1.015842	0.609808
C	2.758671	1.180671	-0.243778
H	3.171725	-1.992902	1.027540
H	4.441036	-0.777184	0.440552
C	1.913149	2.201657	-0.433540
H	3.812074	1.312302	-0.492698
H	0.857307	2.133384	-0.189125
H	2.263563	3.147362	-0.837333
C	-2.121312	2.561446	-0.010373
H	-1.529358	1.305368	-1.577073
H	-2.460588	2.673696	1.016276
H	-1.936944	3.475585	-0.567556

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C26
b3lyp/6-31g(d)
Eel = -542.97295828 au; Energy(0K)) = -542.72099404 au
Enthalpy = -542.70469112 au; Gibbs energy = -542.76104759 au

H	0.311261	-0.225653	-2.046640
C	-0.690387	-0.499970	-1.732083
C	-1.118763	-0.307984	-0.472580
H	-1.343663	-0.934320	-2.482475
C	-0.252541	0.282256	0.581155
C	-2.522600	-0.704826	-0.108804
C	-0.666527	0.423861	1.851317
C	1.134728	0.733098	0.203533
H	-0.014642	0.851770	2.606852
H	-1.656517	0.115821	2.171308
C	1.322399	2.002848	-0.195873
C	2.254831	-0.241265	0.289120
H	0.493156	2.702141	-0.244203
H	2.293875	2.379349	-0.500516
C	2.046488	-1.542066	0.570067
C	3.634685	0.264943	0.090689
H	1.050811	-1.946364	0.715944
H	2.879946	-2.229469	0.672913
C	-2.823070	-1.991259	0.142588
C	-3.572251	0.324163	-0.058189
H	-2.069775	-2.772046	0.103429
H	-3.836497	-2.297422	0.392763
C	-3.431170	1.611118	-0.400766
H	-4.547413	-0.030887	0.276135
H	-2.484697	2.011366	-0.752107

H	-4.266522	2.302672	-0.344751
C	4.576683	-0.343345	-0.636863
H	3.879804	1.202610	0.589262
H	4.372783	-1.258677	-1.186810
H	5.583063	0.059680	-0.710973

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C15
b3lyp/6-31g(d)
Eel = -542.97339213 au; Energy(0K)) = -542.72097910 au
Enthalpy = -542.70490672 au; Gibbs energy = -542.76081992 au

H	0.843702	-2.624642	1.123201
C	1.640024	-1.937512	0.853658
C	1.409306	-0.836579	0.121486
H	2.641080	-2.180502	1.197342
C	0.046713	-0.490119	-0.407607
C	2.555373	0.038420	-0.284966
C	-0.070368	-0.163074	-1.708470
C	-1.144161	-0.519866	0.485755
H	-1.027566	0.072018	-2.159080
H	0.801051	-0.123197	-2.354089
C	-1.073926	-0.644205	1.823067
C	-2.507613	-0.368454	-0.138200
H	-0.131781	-0.750380	2.348903
H	-1.977239	-0.632154	2.425352
C	-3.237217	-1.457148	-0.437837
C	-3.049353	0.976098	-0.383760
H	-2.863763	-2.461381	-0.262716
H	-4.231519	-1.370274	-0.870358
C	3.561624	-0.467691	-1.023865
C	2.588238	1.448986	0.131559
H	3.561593	-1.502355	-1.351341
H	4.410091	0.145140	-1.319731
C	1.757371	2.040398	0.999826
H	3.397023	2.035320	-0.304670
H	0.941583	1.507309	1.479140
H	1.875520	3.087950	1.261212
C	-2.445135	2.137258	-0.099334
H	-4.042137	0.992689	-0.834345
H	-1.455883	2.178783	0.346909
H	-2.927005	3.086602	-0.313597

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C8

b3lyp/6-31g(d)
Eel = -542.97302500 au; Energy(0K)) = -542.72076780 au
Enthalpy = -542.70457692 au; Gibbs energy = -542.76070551 au

H	0.188977	-0.530532	2.160511
C	-0.832706	-0.339634	1.849402
C	-1.209508	-0.409219	0.561319
H	-1.549914	-0.092094	2.626078
C	-0.260936	-0.746731	-0.533553
C	-2.645068	-0.141335	0.201704
C	-0.666139	-0.945269	-1.799110
C	1.199326	-0.893203	-0.194445
H	0.046618	-1.192757	-2.580011
H	-1.709361	-0.870587	-2.087762
C	1.650341	-2.085526	0.233101
C	2.089970	0.288561	-0.337533
H	0.979675	-2.934514	0.324067
H	2.684195	-2.250499	0.519136
C	1.622290	1.489509	-0.730296
C	3.538137	0.107842	-0.071959
H	0.572379	1.656824	-0.943564
H	2.296509	2.328061	-0.871592
C	-3.539526	-1.144834	0.169843
C	-3.064189	1.234540	-0.104455
H	-3.257932	-2.168280	0.397797
H	-4.582317	-0.965697	-0.082910
C	-2.316461	2.337776	0.031963
H	-4.091612	1.332881	-0.456028
H	-1.295708	2.297437	0.400319
H	-2.714803	3.318742	-0.209500
C	4.298909	0.953158	0.630107
H	3.999347	-0.783611	-0.496487
H	3.882570	1.837137	1.106702
H	5.364737	0.783685	0.756728

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[8]Dendralene

C6b_8_Dendralene
G4(MP2)
Eel = -619.63866200 au; Energy(0K)) = -619.35892783 au
Enthalpy = -619.34020324 au; Gibbs energy = -619.40132881 au

C	-1.399621	1.358617	1.222111
C	-1.688739	0.494891	0.239950
H	-0.418633	1.396183	1.680280
H	-2.148409	2.046664	1.597425

C	-0.691444	-0.462687	-0.295324
C	-0.984771	-1.324594	-1.277754
H	-0.240128	-2.017816	-1.652256
H	-1.966619	-1.361888	-1.734062
C	0.691444	-0.462687	0.295324
C	0.984771	-1.324594	1.277754
H	1.966619	-1.361888	1.734062
H	0.240129	-2.017816	1.652256
C	1.688739	0.494892	-0.239950
C	1.399621	1.358617	-1.222111
H	2.148409	2.046664	-1.597425
H	0.418633	1.396183	-1.680280
C	-3.073475	0.483425	-0.340083
C	-3.425093	1.372703	-1.279153
H	-4.427181	1.383250	-1.697555
H	-2.728060	2.113518	-1.653581
C	-4.046315	-0.497493	0.153958
C	-3.854135	-1.362101	1.152803
H	-5.008718	-0.480004	-0.355341
H	-4.634713	-2.048345	1.461227
H	-2.917078	-1.408132	1.696520
C	3.073476	0.483426	0.340083
C	3.425093	1.372703	1.279153
H	4.427181	1.383250	1.697555
H	2.728061	2.113519	1.653581
C	4.046315	-0.497493	-0.153958
C	3.854135	-1.362101	-1.152803
H	5.008718	-0.480004	0.355341
H	4.634712	-2.048345	-1.461227
H	2.917078	-1.408132	-1.696519

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C6c_8_Dendralene
G4(MP2)
Eel = -619.63907300 au; Energy(0K)) = -619.35882735 au
Enthalpy = -619.34033239 au; Gibbs energy = -619.40102396 au

C	1.266604	1.870108	1.013018
C	0.742009	1.023565	0.117307
H	2.332838	1.915264	1.199998
H	0.633789	2.545046	1.577943
C	1.585363	0.104303	-0.686761
C	1.114890	-0.557805	-1.752313
H	1.759647	-1.210993	-2.329328
H	0.086568	-0.459070	-2.078631
C	3.027793	-0.051595	-0.302911

C	3.975042	0.669480	-0.919147
H	5.023577	0.562979	-0.657008
H	3.731872	1.380676	-1.700040
C	-0.742085	1.023558	-0.117406
C	-1.266641	1.869846	-1.013382
H	-2.332868	1.914959	-1.200411
H	-0.633800	2.544608	-1.578486
C	-1.585476	0.104508	0.686862
C	-1.115093	-0.557252	1.752670
H	-1.759881	-1.210307	2.329800
H	-0.086824	-0.458339	2.079100
C	3.390755	-1.015454	0.741653
C	2.573092	-1.904145	1.311403
H	4.438267	-0.991829	1.038435
H	2.931512	-2.593208	2.067923
H	1.527419	-1.979215	1.034619
C	-3.027837	-0.051631	0.302858
C	-3.975251	0.669467	0.918814
H	-5.023738	0.562796	0.656550
H	-3.732270	1.380851	1.699594
C	-3.390538	-1.015743	-0.741562
C	-2.572660	-1.904383	-1.311083
H	-4.438024	-0.992345	-1.038457
H	-2.930883	-2.593638	-2.067521
H	-1.526993	-1.979201	-1.034203

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C6a_8_Dendralene
G4(MP2)
Eel = -619.63841100 au; Energy(0K)) = -619.35854542 au
Enthalpy = -619.33987861 au; Gibbs energy = -619.40082899 au

C	1.032957	1.463629	-0.856627
C	1.512136	0.456370	-0.114573
H	0.046735	1.425092	-1.303129
H	1.629952	2.348358	-1.046709
C	0.728531	-0.771997	0.157437
C	1.253125	-1.831584	0.787309
H	0.659177	-2.719531	0.971583
H	2.279498	-1.843779	1.133844
C	-0.705185	-0.821210	-0.291050
C	-1.008689	-1.370647	-1.474240
H	-2.031257	-1.447178	-1.823916
H	-0.232946	-1.764705	-2.120974
C	-1.744435	-0.288575	0.625016
C	-1.469537	0.086850	1.880927

H	-2.249089	0.463913	2.533070
H	-0.468542	0.020507	2.290152
C	2.899948	0.559140	0.450486
C	3.111982	1.176030	1.621049
H	4.111109	1.267678	2.036546
H	2.299634	1.608568	2.193800
C	4.023094	-0.003210	-0.307214
C	3.955886	-0.557744	-1.519948
H	4.988429	0.066436	0.192043
H	4.841825	-0.942288	-2.012497
H	3.019199	-0.638941	-2.060174
C	-3.155515	-0.195936	0.121325
C	-4.016134	-1.203188	0.325095
H	-5.041503	-1.148066	-0.028483
H	-3.724121	-2.105105	0.850551
C	-3.587048	1.017042	-0.581785
C	-2.888936	2.148767	-0.704534
H	-4.585550	0.961171	-1.012920
H	-3.294975	3.004684	-1.231871
H	-1.900664	2.260774	-0.272959

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C19
G4(MP2)
Eel = -619.63854000 au; Energy(0K)) = -619.35828812 au
Enthalpy = -619.33984853 au; Gibbs energy = -619.40072052 au

H	2.369491	-2.798136	0.652087
C	1.372529	-2.416989	0.846259
C	0.944356	-1.271216	0.301153
H	0.736214	-2.996735	1.505381
C	1.801621	-0.512052	-0.658009
C	-0.407517	-0.735312	0.669391
C	2.503469	-1.139057	-1.610536
C	1.868903	0.977723	-0.543561
H	3.168514	-0.592836	-2.269954
H	2.428687	-2.211631	-1.754547
C	1.510739	1.748229	-1.583693
C	2.365217	1.597626	0.690781
H	1.137697	1.318498	-2.505292
H	1.578568	2.830799	-1.531758
C	2.942958	0.970435	1.718262
H	2.266388	2.681331	0.723952
H	3.076781	-0.104666	1.737335
H	3.301447	1.522874	2.579766
C	-0.651776	-0.403498	1.945326

C	-1.461975	-0.659361	-0.371050
H	0.125376	-0.471707	2.696534
H	-1.623592	-0.048685	2.266686
C	-1.302887	-1.191150	-1.591108
C	-2.785787	-0.046485	-0.015910
H	-0.385163	-1.681446	-1.890642
H	-2.098536	-1.141971	-2.325495
C	-3.856222	-0.838019	0.150676
C	-2.924249	1.407697	0.119248
H	-3.787543	-1.915187	0.054732
H	-4.831316	-0.423631	0.389214
C	-1.982119	2.322204	-0.120011
H	-3.915081	1.737095	0.428871
H	-0.980810	2.050993	-0.434838
H	-2.190683	3.380402	-0.005342

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C28
G4(MP2)
Eel = -619.63786700 au; Energy(0K)) = -619.35804670 au
Enthalpy = -619.33942175 au; Gibbs energy = -619.40050858 au

H	-1.447347	0.217025	-2.234063
C	-0.567450	-0.302216	-1.873641
C	-0.367735	-0.531646	-0.568231
H	0.159770	-0.620019	-2.610662
C	-1.341620	-0.105250	0.464338
C	0.870505	-1.251557	-0.128868
C	-1.289448	-0.556550	1.724717
C	-2.440942	0.838132	0.065538
H	-2.023509	-0.245112	2.459492
H	-0.524208	-1.247327	2.056156
C	-2.215893	2.158305	0.016408
C	-3.763370	0.296904	-0.264021
H	-1.243722	2.578111	0.248259
H	-3.002703	2.853106	-0.261994
C	-4.122390	-0.989119	-0.236712
H	-4.497548	1.045445	-0.558848
H	-3.429358	-1.770053	0.055728
H	-5.127129	-1.297010	-0.503526
C	1.088802	-2.517900	-0.502755
C	1.853367	-0.502667	0.710007
H	0.351286	-3.068735	-1.075683
H	2.010997	-3.031544	-0.252190
C	2.488593	-1.080085	1.736370
C	2.105669	0.935667	0.380810

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H	2.277018	-2.102887	2.029896
H	3.233775	-0.541325	2.310791
C	1.798042	1.895371	1.267257
C	2.713473	1.289473	-0.906709
H	1.346292	1.660588	2.223239
H	1.989268	2.942381	1.050989
C	3.233766	0.440290	-1.796303
H	2.754221	2.358114	-1.111007
H	3.228960	-0.632202	-1.640270
H	3.683715	0.798535	-2.715533

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C14
G4(MP2)
Eel = -619.63772200 au; Energy(0K)) = -619.35750601 au
Enthalpy = -619.33904763 au; Gibbs energy = -619.39970495 au

H	-2.248063	1.189843	1.743102
C	-1.220592	1.465298	1.539015
C	-0.617064	1.135176	0.387173
H	-0.694291	2.021565	2.305375
C	-1.339701	0.381586	-0.667864
C	0.785037	1.600056	0.133798
C	-0.901143	0.314943	-1.932435
C	-2.652855	-0.255760	-0.319667
H	-1.465518	-0.221234	-2.686786
H	0.019987	0.787246	-2.249094
C	-3.796371	0.299762	-0.747726
C	-2.683986	-1.495097	0.464805
H	-3.801204	1.212146	-1.332402
H	-4.759358	-0.148748	-0.521936
C	-1.630413	-2.233755	0.818980
H	-3.682531	-1.826178	0.746411
H	-0.616432	-1.960295	0.552732
H	-1.756512	-3.149150	1.386842
C	1.082171	2.902295	0.238705
C	1.856209	0.612232	-0.203642
H	0.312476	3.640367	0.434779
H	2.101442	3.257669	0.134663
C	2.717362	0.861065	-1.200222
C	1.993710	-0.599640	0.658801
H	2.619345	1.749403	-1.813954
H	3.542081	0.194033	-1.420310
C	1.854198	-0.491126	1.991074
C	2.296907	-1.919084	0.082734
H	1.619813	0.452720	2.467301

H	1.977071	-1.351350	2.640784
C	2.234096	-2.288877	-1.198887
H	2.560777	-2.671476	0.824589
H	1.955657	-1.600676	-1.987760
H	2.449867	-3.310336	-1.492190

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C6d_8_Dendralene
G4(MP2)
Eel = -619.63716800 au; Energy(0K)) = -619.35699911 au
Enthalpy = -619.33848798 au; Gibbs energy = -619.39935769 au

C	0.978811	0.913892	-1.654050
C	0.688327	-0.037049	-0.755323
H	1.993426	1.255016	-1.820195
H	0.198965	1.375081	-2.249066
C	1.744367	-0.717047	0.032710
C	1.485398	-1.820104	0.750031
H	2.269304	-2.321470	1.305283
H	0.490097	-2.245073	0.801511
C	3.158194	-0.217739	-0.036338
C	4.097665	-0.986876	-0.608958
H	5.136603	-0.673361	-0.646375
H	3.854181	-1.943279	-1.056073
C	-0.741041	-0.487652	-0.623712
C	-1.274604	-1.215454	-1.614992
H	-2.304594	-1.550620	-1.588323
H	-0.682154	-1.500601	-2.476553
C	-1.544585	-0.093250	0.561930
C	-1.014104	0.413740	1.682383
H	-1.648037	0.697664	2.514558
H	0.052779	0.538053	1.813631
C	3.546986	1.069674	0.553217
C	2.761480	1.958891	1.164787
H	4.611894	1.284512	0.476291
H	3.172873	2.873011	1.578312
H	1.690987	1.824412	1.258960
C	-3.033460	-0.265785	0.484693
C	-3.634662	-1.280383	1.122091
H	-4.712739	-1.407353	1.088637
H	-3.069940	-2.007379	1.694056
C	-3.824950	0.711558	-0.271377
C	-3.364506	1.835531	-0.825220
H	-4.885410	0.476971	-0.349567
H	-4.024324	2.512834	-1.355646
H	-2.319804	2.119894	-0.760678

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C31
G4(MP2)
Eel = -619.63629100 au; Energy(0K)) = -619.35598915 au
Enthalpy = -619.33759515 au; Gibbs energy = -619.39830844 au

H	-1.582301	3.432845	0.649880
C	-0.620851	2.935057	0.711036
C	-0.475967	1.655627	0.340939
H	0.217874	3.511568	1.084880
C	-1.637017	0.920075	-0.250618
C	0.846804	0.975277	0.530947
C	-2.346772	1.476432	-1.245195
C	-2.028648	-0.403375	0.300558
H	-3.226199	0.992268	-1.654671
H	-2.067394	2.434747	-1.667515
C	-1.735774	-0.758658	1.561857
C	-2.775683	-1.316293	-0.592274
H	-1.214897	-0.093035	2.237931
H	-2.013407	-1.733878	1.945272
C	-3.821528	-2.060909	-0.233014
H	-2.427439	-1.352817	-1.622853
H	-4.235983	-2.017161	0.769157
H	-4.303544	-2.734889	-0.933058
C	1.444918	1.032000	1.731463
C	1.513371	0.318041	-0.621365
H	0.961516	1.513317	2.573439
H	2.424766	0.603088	1.901843
C	1.118398	0.502506	-1.888637
C	2.730585	-0.521520	-0.362060
H	0.268644	1.120689	-2.146187
H	1.647638	0.026464	-2.706245
C	3.945325	-0.045953	-0.674938
C	2.590982	-1.868790	0.201326
H	4.077054	0.943320	-1.097191
H	4.840812	-0.639183	-0.514667
C	1.447026	-2.514601	0.437314
H	3.535058	-2.368606	0.413345
H	0.479630	-2.067052	0.241549
H	1.447146	-3.521188	0.841051

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C1
G4(MP2)

Eel = -619.63611100 -619.63772200 -619.63854000 au; Energy(0K)) = -619.35554152 -619.35750601 -619.35828812 au
Enthalpy = -619.33722884 -619.33904763 -619.33984853 au; Gibbs energy = -619.39763383 -619.39970495 -619.40072052 au

H	-0.927760	-1.307449	-1.696824
C	-0.227275	-0.605685	-1.261033
C	-0.480730	-0.004142	-0.087585
H	0.684743	-0.415715	-1.812648
C	-1.743490	-0.319157	0.641811
C	0.496170	0.976615	0.467415
C	-1.833876	-0.325495	1.977973
C	-2.937412	-0.721084	-0.167822
H	-2.763112	-0.590677	2.468964
H	-0.993559	-0.072804	2.612801
C	-3.438389	-1.961604	-0.059737
C	-3.577549	0.254002	-1.059084
H	-2.983768	-2.702336	0.587254
H	-4.317238	-2.265252	-0.620617
C	-3.260979	1.544147	-1.188123
H	-4.405139	-0.145415	-1.643205
H	-2.447932	2.000683	-0.634899
H	-3.809452	2.189807	-1.864912
C	0.134898	2.012888	1.238786
C	1.934263	0.815037	0.088753
H	-0.895831	2.186104	1.523059
H	0.875844	2.714012	1.604653
C	2.583680	1.809225	-0.529586
C	2.614023	-0.452817	0.494964
H	2.069695	2.724222	-0.801279
H	3.639335	1.743960	-0.765200
C	2.377080	-0.975121	1.710215
C	3.547837	-1.147606	-0.402663
H	1.691067	-0.510798	2.408107
H	2.871339	-1.883689	2.037581
C	3.787797	-0.907969	-1.694487
H	4.067581	-1.980229	0.069128
H	3.302774	-0.107348	-2.239847
H	4.485135	-1.524483	-2.250908

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C24
G4(MP2)
Eel = -619.63567100 au; Energy(0K)) = -619.35539357 au
Enthalpy = -619.33695420 au; Gibbs energy = -619.39772188 au

H	-0.880183	2.167588	2.160000

C	-0.114684	1.585507	1.660033
C	-0.412701	0.847774	0.581468
H	0.887787	1.630596	2.067984
C	-1.811846	0.874064	0.046860
C	0.605387	0.059482	-0.173021
C	-2.329344	2.029890	-0.395146
C	-2.606517	-0.380629	0.046808
H	-3.351591	2.099811	-0.750023
H	-1.740894	2.939874	-0.400263
C	-2.260473	-1.436957	0.798504
C	-3.803766	-0.433619	-0.820471
H	-1.400271	-1.415707	1.456309
H	-2.831771	-2.357158	0.763974
C	-4.984696	-0.943322	-0.471069
H	-3.685326	-0.010249	-1.816533
H	-5.165200	-1.332441	0.525931
H	-5.813685	-0.982527	-1.169619
C	0.456392	-0.122754	-1.495108
C	1.788697	-0.524412	0.522171
H	-0.398303	0.276847	-2.026683
H	1.186216	-0.673260	-2.075436
C	1.768490	-0.922380	1.801193
C	3.034811	-0.739292	-0.281138
H	0.890582	-0.812966	2.425886
H	2.644836	-1.370973	2.254592
C	3.473411	-1.983507	-0.527085
C	3.792505	0.418049	-0.772301
H	2.932671	-2.855298	-0.178364
H	4.386999	-2.158082	-1.087541
C	3.539992	1.702658	-0.512722
H	4.653051	0.164784	-1.389472
H	2.699039	2.016834	0.095281
H	4.172099	2.489018	-0.909886

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C6c_8_Dendralene
b3lyp/6-31g(d)
Eel = -620.37278280 au; Energy(0K)) = -620.08720832 au
Enthalpy = -620.06887886 au; Gibbs energy = -620.12929018 au

C	1.270969	-1.878876	-1.013517
C	0.743457	-1.029498	-0.115776
H	2.338977	-1.925726	-1.200204
H	0.637824	-2.554884	-1.580029
C	1.589178	-0.107715	0.689765
C	1.117975	0.549955	1.763160

H	1.762690	1.205500	2.340663
H	0.090451	0.444513	2.095446
C	3.031978	0.057546	0.301780
C	3.987892	-0.657880	0.920789
H	5.037689	-0.546361	0.658182
H	3.749766	-1.369477	1.705297
C	-0.743430	-1.029419	0.116050
C	-1.271022	-1.878604	1.013925
H	-2.339039	-1.925363	1.200579
H	-0.637933	-2.554560	1.580562
C	-1.589063	-0.107755	-0.689727
C	-1.117756	0.549678	-1.763224
H	-1.762431	1.205086	-2.340929
H	-0.090214	0.444147	-2.095426
C	3.390332	1.021081	-0.749656
C	2.563839	1.906950	-1.321061
H	4.437897	1.003208	-1.051440
H	2.918795	2.595724	-2.082001
H	1.517012	1.979450	-1.041500
C	-3.031931	0.057538	-0.301996
C	-3.987740	-0.657781	-0.921296
H	-5.037594	-0.546235	-0.658924
H	-3.749473	-1.369317	-1.705817
C	-3.390520	1.020980	0.749443
C	-2.564119	1.906599	1.321368
H	-4.438211	1.003245	1.050802
H	-2.919287	2.595292	2.082282
H	-1.517155	1.978965	1.042295

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C6a_8_Dendralene
b3lyp/6-31g(d)
Eel = -620.37189308 au; Energy(0K)) = -620.08669444 au
Enthalpy = -620.06819682 au; Gibbs energy = -620.12885079 au

C	1.030950	1.446911	-0.893053
C	1.513023	0.452273	-0.128426
H	0.046057	1.396575	-1.345521
H	1.625808	2.332261	-1.096018
C	0.730257	-0.777201	0.161266
C	1.260545	-1.830813	0.805438
H	0.667286	-2.718157	1.004124
H	2.290071	-1.839040	1.148178
C	-0.707408	-0.835033	-0.280824
C	-1.015938	-1.408247	-1.456360
H	-2.040782	-1.492491	-1.802920

H	-0.240757	-1.814494	-2.099032
C	-1.746918	-0.282832	0.629322
C	-1.467842	0.112242	1.882883
H	-2.246290	0.503629	2.530660
H	-0.465774	0.047678	2.294409
C	2.899509	0.574314	0.442758
C	3.101917	1.220872	1.604021
H	4.098895	1.328748	2.025533
H	2.282140	1.661916	2.162851
C	4.034718	-0.000167	-0.294437
C	3.977960	-0.585937	-1.497717
H	4.998767	0.086716	0.207496
H	4.871695	-0.976851	-1.974811
H	3.044443	-0.687520	-2.043314
C	-3.160982	-0.190532	0.126566
C	-4.027224	-1.195901	0.344139
H	-5.055293	-1.143299	-0.007624
H	-3.736377	-2.093965	0.880366
C	-3.592834	1.016565	-0.593632
C	-2.888678	2.147713	-0.732758
H	-4.593404	0.960678	-1.023287
H	-3.295120	2.998376	-1.271796
H	-1.897692	2.263877	-0.304408

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C23
b3lyp/6-31g(d)
Eel = -620.37166015 au; Energy(0K)) = -620.08661953 au
Enthalpy = -620.06805724 au; Gibbs energy = -620.12890025 au

H	-1.974580	-1.371534	-1.731512
C	-0.990197	-1.330731	-1.276839
C	-0.693473	-0.464261	-0.293518
H	-0.244683	-2.024929	-1.652679
C	-1.692521	0.497025	0.242128
C	0.693472	-0.464261	0.293518
C	-1.399317	1.365819	1.224572
C	-3.081328	0.487219	-0.334566
H	-2.148310	2.055611	1.601035
H	-0.415724	1.405928	1.681104
C	-3.438546	1.388786	-1.266096
C	-4.055261	-0.502254	0.150802
H	-2.742207	2.135233	-1.635680
H	-4.443207	1.404099	-1.682926
C	-3.859120	-1.378612	1.144349
H	-5.020590	-0.483020	-0.355749

H	-2.920048	-1.429789	1.687456
H	-4.640336	-2.069540	1.446847
C	0.990197	-1.330731	1.276840
C	1.692521	0.497025	-0.242128
H	0.244682	-2.024928	1.652680
H	1.974580	-1.371533	1.731513
C	1.399317	1.365818	-1.224573
C	3.081328	0.487219	0.334566
H	0.415724	1.405926	-1.681105
H	2.148311	2.055610	-1.601036
C	3.438545	1.388785	1.266096
C	4.055261	-0.502254	-0.150802
H	2.742206	2.135232	1.635681
H	4.443206	1.404099	1.682927
C	3.859121	-1.378611	-1.144349
H	5.020590	-0.483019	0.355749
H	2.920049	-1.429789	-1.687457
H	4.640337	-2.069539	-1.446847

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C6b_8_Dendralene
b3lyp/6-31g(d)
Eel = -620.37166016 au; Energy(0K)) = -620.08661948 au
Enthalpy = -620.06805726 au; Gibbs energy = -620.12890017 au

C	1.399314	1.365799	-1.224577
C	1.692527	0.497027	-0.242119
H	0.415696	1.405950	-1.681052
H	2.148322	2.055544	-1.601094
C	0.693459	-0.464161	0.293658
C	0.990138	-1.330497	1.277111
H	0.244602	-2.024632	1.653022
H	1.974515	-1.371266	1.731800
C	-0.693470	-0.464211	-0.293423
C	-0.990154	-1.330716	-1.276728
H	-1.974520	-1.371513	-1.731438
H	-0.244624	-2.024921	-1.652522
C	-1.692539	0.497084	0.242145
C	-1.399399	1.365907	1.224585
H	-2.148422	2.055700	1.600983
H	-0.415829	1.406033	1.681167
C	3.081371	0.487172	0.334500
C	3.438673	1.388718	1.266017
H	4.443365	1.404011	1.682774
H	2.742376	2.135182	1.635646
C	4.055241	-0.502321	-0.150948

C	3.858995	-1.378705	-1.144452
H	5.020621	-0.483093	0.355507
H	4.640173	-2.069658	-1.446996
H	2.919879	-1.429881	-1.687483
C	-3.081323	0.487222	-0.334598
C	-3.438623	1.388797	-1.266087
H	-4.443287	1.404024	-1.682914
H	-2.742369	2.135344	-1.635633
C	-4.055178	-0.502359	0.150708
C	-3.859007	-1.378751	1.144222
H	-5.020500	-0.483215	-0.355864
H	-4.640199	-2.069747	1.446632
H	-2.919965	-1.429898	1.687384

############################

C18
b3lyp/6-31g(d)
Eel = -620.37105533 au; Energy(0K)) = -620.08534730 au
Enthalpy = -620.06712996 au; Gibbs energy = -620.12762153 au

H	1.643286	-0.060217	2.276668
C	0.667704	-0.411586	1.957360
C	0.414418	-0.738133	0.677342
H	-0.107406	-0.477510	2.713326
C	1.467078	-0.660529	-0.370184
C	-0.942962	-1.271061	0.316229
C	1.304426	-1.202383	-1.590157
C	2.791988	-0.038372	-0.025961
H	2.096379	-1.150939	-2.330785
H	0.387016	-1.700559	-1.883867
C	3.874970	-0.824546	0.118922
C	2.922765	1.419020	0.122148
H	3.813864	-1.903238	0.015590
H	4.852272	-0.404850	0.347245
C	1.968152	2.330352	-0.103482
H	3.913879	1.756245	0.427043
H	0.965289	2.053963	-0.414275
H	2.170478	3.390661	0.019132
C	-1.376921	-2.412708	0.876494
C	-1.803781	-0.521184	-0.652143
H	-0.740481	-2.991766	1.538927
H	-2.378626	-2.790845	0.691025
C	-2.506155	-1.164899	-1.599481
C	-1.879011	0.972142	-0.557406
H	-2.424999	-2.240159	-1.732969
H	-3.177625	-0.630105	-2.264592

C	-1.533580	1.731740	-1.615149
C	-2.368696	1.610645	0.674249
H	-1.162607	1.290427	-2.534195
H	-1.609673	2.816277	-1.581236
C	-2.935712	0.993337	1.719067
H	-2.276524	2.696609	0.692658
H	-3.063664	-0.083660	1.756659
H	-3.288968	1.558651	2.576550

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C19
b3lyp/6-31g(d)
Eel = -620.37105533 au; Energy(0K)) = -620.08534730 au
Enthalpy = -620.06712996 au; Gibbs energy = -620.12762153 au

H	2.378626	-2.790846	0.691022
C	1.376920	-2.412709	0.876491
C	0.942962	-1.271061	0.316227
H	0.740480	-2.991768	1.538924
C	1.803781	-0.521184	-0.652144
C	-0.414418	-0.738133	0.677341
C	2.506156	-1.164897	-1.599482
C	1.879011	0.972143	-0.557405
H	3.177625	-0.630103	-2.264593
H	2.424999	-2.240158	-1.732971
C	1.533580	1.731742	-1.615146
C	2.368697	1.610644	0.674250
H	1.162606	1.290430	-2.534193
H	1.609673	2.816279	-1.581232
C	2.935714	0.993334	1.719068
H	2.276525	2.696608	0.692661
H	3.063665	-0.083663	1.756659
H	3.288969	1.558648	2.576551
C	-0.667703	-0.411586	1.957359
C	-1.467078	-0.660529	-0.370184
H	0.107407	-0.477511	2.713325
H	-1.643285	-0.060217	2.276668
C	-1.304427	-1.202381	-1.590158
C	-2.791989	-0.038373	-0.025960
H	-0.387016	-1.700556	-1.883869
H	-2.096379	-1.150936	-2.330785
C	-3.874970	-0.824547	0.118925
C	-2.922767	1.419020	0.122148
H	-3.813863	-1.903239	0.015593
H	-4.852271	-0.404852	0.347249
C	-1.968154	2.330352	-0.103483

H	-3.913881	1.756244	0.427042
H	-0.965290	2.053964	-0.414275
H	-2.170481	3.390661	0.019131

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C28
b3lyp/6-31g(d)
Eel = -620.37067699 au; Energy(0K)) = -620.08521434 au
Enthalpy = -620.06689774 au; Gibbs energy = -620.12744166 au

H	1.348499	0.476644	2.335732
C	0.468747	-0.066795	2.007254
C	0.318618	-0.472050	0.733949
H	-0.301946	-0.259900	2.745948
C	1.356078	-0.229480	-0.304501
C	-0.919582	-1.224026	0.343898
C	1.385151	-0.940185	-1.445998
C	2.406735	0.816327	-0.053952
H	2.154993	-0.770438	-2.192544
H	0.649569	-1.706728	-1.664356
C	2.065582	2.114483	0.042825
C	3.817868	0.422003	0.080610
H	1.033676	2.440138	-0.041862
H	2.815620	2.884299	0.208950
C	4.312982	-0.822933	0.070725
H	4.505632	1.256698	0.219868
H	3.679996	-1.694700	-0.062288
H	5.376999	-1.000214	0.196935
C	-1.206436	-2.405913	0.913739
C	-1.826599	-0.608765	-0.675159
H	-0.522170	-2.872814	1.615976
H	-2.133136	-2.930701	0.697529
C	-2.410577	-1.344879	-1.633909
C	-2.064724	0.870307	-0.612567
H	-2.205279	-2.406838	-1.738706
H	-3.105619	-0.900908	-2.340366
C	-1.674199	1.661007	-1.629989
C	-2.745043	1.451924	0.554207
H	-1.161068	1.258401	-2.496812
H	-1.854183	2.733754	-1.613295
C	-3.338258	0.773803	1.545574
H	-2.776735	2.541489	0.569435
H	-3.347995	-0.311026	1.580132
H	-3.834913	1.293880	2.359487

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C6d_8_Dendralene
b3lyp/6-31g(d)
Eel = -620.37035055 au; Energy(0K)) = -620.08479780 au
Enthalpy = -620.06648405 au; Gibbs energy = -620.12702563 au

C	-0.985607	0.943737	1.646807
C	-0.690624	-0.021782	0.758716
H	-2.002314	1.286218	1.808401
H	-0.206105	1.417123	2.235728
C	-1.748583	-0.717377	-0.020700
C	-1.486738	-1.838412	-0.716905
H	-2.269776	-2.350665	-1.266698
H	-0.490359	-2.266337	-0.757580
C	-3.165622	-0.218454	0.035439
C	-4.111154	-0.987940	0.607787
H	-5.153201	-0.677429	0.635485
H	-3.869115	-1.941649	1.065534
C	0.742165	-0.471959	0.636534
C	1.279254	-1.175839	1.648788
H	2.311719	-1.509666	1.632298
H	0.686374	-1.441999	2.518184
C	1.548037	-0.105366	-0.561126
C	1.013374	0.376316	-1.695904
H	1.646404	0.642213	-2.536814
H	-0.055461	0.497012	-1.829114
C	-3.555652	1.067006	-0.566615
C	-2.765135	1.950787	-1.189032
H	-4.621041	1.286758	-0.492677
H	-3.176064	2.863040	-1.611587
H	-1.693424	1.812420	-1.283531
C	3.039584	-0.275942	-0.483951
C	3.640671	-1.304097	-1.108949
H	4.720551	-1.432117	-1.078731
H	3.072924	-2.041767	-1.667433
C	3.838036	0.713646	0.255538
C	3.378522	1.849903	0.795194
H	4.900331	0.481413	0.334440
H	4.043100	2.535047	1.313065
H	2.332286	2.135020	0.731304

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C13
b3lyp/6-31g(d)
Eel = -620.37032264 au; Energy(0K)) = -620.08462153 au
Enthalpy = -620.06640817 au; Gibbs energy = -620.12667359 au

H	-2.103118	3.260032	0.173956
C	-1.081129	2.903967	0.266679
C	-0.781781	1.598773	0.146971
H	-0.310565	3.643506	0.463400
C	-1.858268	0.614726	-0.197758
C	0.625013	1.134671	0.390265
C	-2.722734	0.878723	-1.193495
C	-2.003194	-0.607558	0.653267
H	-3.553372	0.217962	-1.418765
H	-2.620333	1.772386	-1.801889
C	-1.855136	-0.515797	1.990040
C	-2.324625	-1.920168	0.062633
H	-1.607984	0.421050	2.477410
H	-1.981400	-1.383380	2.632346
C	-2.259545	-2.276882	-1.227028
H	-2.603636	-2.679216	0.793897
H	-1.964387	-1.583987	-2.007943
H	-2.488957	-3.293505	-1.532840
C	1.238733	1.470424	1.539995
C	1.344052	0.379176	-0.670880
H	0.715407	2.024978	2.312113
H	2.270262	1.199037	1.738059
C	0.898653	0.320036	-1.938163
C	2.659234	-0.265051	-0.333405
H	-0.022821	0.798361	-2.250675
H	1.456657	-0.218799	-2.697670
C	3.802611	0.271597	-0.798507
C	2.698993	-1.491361	0.477515
H	3.804188	1.174587	-1.400742
H	4.768133	-0.182312	-0.585995
C	1.642859	-2.210888	0.876794
H	3.701188	-1.831538	0.739746
H	0.623501	-1.927974	0.635510
H	1.774818	-3.117516	1.460542

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C14
b3lyp/6-31g(d)
Eel = -620.37032264 au; Energy(0K)) = -620.08462153 au
Enthalpy = -620.06640817 au; Gibbs energy = -620.12667359 au

H	-2.270262	1.199037	1.738059
C	-1.238733	1.470424	1.539995
C	-0.625013	1.134671	0.390265
H	-0.715407	2.024978	2.312113
C	-1.344052	0.379176	-0.670880

C	0.781781	1.598773	0.146971
C	-0.898653	0.320036	-1.938163
C	-2.659234	-0.265051	-0.333405
H	-1.456657	-0.218799	-2.697670
H	0.022821	0.798361	-2.250675
C	-3.802611	0.271597	-0.798508
C	-2.698993	-1.491361	0.477515
H	-3.804188	1.174587	-1.400742
H	-4.768133	-0.182312	-0.585995
C	-1.642859	-2.210888	0.876794
H	-3.701189	-1.831538	0.739746
H	-0.623501	-1.927974	0.635511
H	-1.774818	-3.117516	1.460542
C	1.081129	2.903967	0.266679
C	1.858268	0.614726	-0.197758
H	0.310565	3.643506	0.463400
H	2.103118	3.260032	0.173956
C	2.722734	0.878723	-1.193495
C	2.003194	-0.607558	0.653267
H	2.620333	1.772386	-1.801889
H	3.553372	0.217962	-1.418765
C	1.855136	-0.515797	1.990040
C	2.324625	-1.920168	0.062633
H	1.607984	0.421050	2.477410
H	1.981400	-1.383380	2.632346
C	2.259545	-2.276882	-1.227028
H	2.603636	-2.679216	0.793897
H	1.964387	-1.583987	-2.007943
H	2.488957	-3.293505	-1.532840

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C1
b3lyp/6-31g(d)
Eel = -620.37054830 -620.37032264 -620.37032264 -620.37105533 -620.37105533 au;
Energy(0K)) = -620.08457674 -620.08462153 -620.08462153 -620.08534730 -620.08534730 au
Enthalpy = -620.06646021 -620.06640817 -620.06640817 -620.06712996 -620.06712996 au; Gibbs energy = -620.12653417 -620.12667359 -620.12667359 -620.12762153 -620.12762153 au

H	-0.926451	-1.234937	-1.761858
C	-0.225184	-0.559099	-1.284163
C	-0.486100	-0.015181	-0.080137
H	0.694332	-0.347756	-1.818758
C	-1.760722	-0.359901	0.621607
C	0.493037	0.930587	0.535603

C	-1.856548	-0.451248	1.958790
C	-2.958442	-0.696363	-0.216375
H	-2.792738	-0.732351	2.431134
H	-1.013617	-0.252398	2.612237
C	-3.483929	-1.935567	-0.175990
C	-3.578451	0.335866	-1.062085
H	-3.045055	-2.719400	0.432939
H	-4.366810	-2.195132	-0.755880
C	-3.237311	1.629307	-1.121133
H	-4.409956	-0.016324	-1.672858
H	-2.419143	2.042910	-0.539130
H	-3.771068	2.319092	-1.768302
C	0.128223	1.919637	1.372487
C	1.935027	0.799838	0.148325
H	-0.904837	2.076133	1.664404
H	0.868736	2.596708	1.786330
C	2.580961	1.843500	-0.398190
C	2.628275	-0.489240	0.463671
H	2.060961	2.773242	-0.608356
H	3.639415	1.802792	-0.634794
C	2.383095	-1.111547	1.633739
C	3.585569	-1.100512	-0.475069
H	1.680379	-0.713766	2.358328
H	2.884977	-2.039126	1.895652
C	3.825111	-0.763795	-1.749818
H	4.122935	-1.954324	-0.061828
H	3.322670	0.062306	-2.242184
H	4.539604	-1.325357	-2.344661

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C24
b3lyp/6-31g(d)
Eel = -620.37015304 au; Energy(0K)) = -620.08445240 au
Enthalpy = -620.06621977 au; Gibbs energy = -620.12664002 au

H	-0.872064	2.174068	2.167662
C	-0.108167	1.591956	1.661665
C	-0.412965	0.848941	0.582941
H	0.898194	1.639545	2.064429
C	-1.817201	0.877028	0.055320
C	0.606272	0.058382	-0.173620
C	-2.339443	2.040758	-0.373679
C	-2.614264	-0.380213	0.044569
H	-3.366195	2.116330	-0.719635
H	-1.749741	2.951972	-0.375842
C	-2.267191	-1.444960	0.791527

C	-3.813517	-0.427930	-0.824531
H	-1.406973	-1.427961	1.452383
H	-2.836435	-2.367943	0.747889
C	-4.992932	-0.956207	-0.480822
H	-3.702216	0.012891	-1.815442
H	-5.170394	-1.362846	0.511609
H	-5.822827	-0.991817	-1.181244
C	0.454837	-0.127258	-1.498883
C	1.793545	-0.524191	0.522694
H	-0.401196	0.272484	-2.031748
H	1.183902	-0.680727	-2.080554
C	1.769929	-0.924059	1.805772
C	3.044323	-0.739034	-0.277869
H	0.887732	-0.818275	2.428194
H	2.647362	-1.369163	2.264479
C	3.490846	-1.987489	-0.511825
C	3.800622	0.418286	-0.781534
H	2.951887	-2.860147	-0.157069
H	4.408340	-2.165214	-1.068387
C	3.541481	1.708132	-0.532488
H	4.663921	0.164727	-1.397067
H	2.697631	2.025337	0.072974
H	4.172018	2.493884	-0.938045

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C31
b3lyp/6-31g(d)
Eel = -620.36984761 au; Energy(0K)) = -620.08413520 au
Enthalpy = -620.06594151 au; Gibbs energy = -620.12631627 au

H	-1.592017	3.429505	0.683696
C	-0.627392	2.932801	0.733444
C	-0.480850	1.652104	0.351677
H	0.213145	3.511012	1.105599
C	-1.647252	0.921532	-0.242266
C	0.847422	0.974650	0.533517
C	-2.365917	1.494323	-1.226954
C	-2.037250	-0.412523	0.292801
H	-3.252543	1.019121	-1.636013
H	-2.086188	2.458028	-1.641147
C	-1.738206	-0.784902	1.552259
C	-2.789773	-1.316065	-0.609196
H	-1.214421	-0.127216	2.236637
H	-2.011410	-1.767505	1.924555
C	-3.830158	-2.075114	-0.248123
H	-2.454262	-1.335834	-1.645968

H	-4.235540	-2.049348	0.760238
H	-4.315791	-2.742277	-0.954898
C	1.454219	1.036295	1.734157
C	1.513034	0.318483	-0.624480
H	0.971297	1.513683	2.580842
H	2.439123	0.613290	1.900743
C	1.107692	0.502879	-1.893176
C	2.739432	-0.515018	-0.375230
H	0.251589	1.117281	-2.146055
H	1.632916	0.027419	-2.715840
C	3.950227	-0.036739	-0.716942
C	2.619146	-1.859548	0.208218
H	4.070621	0.950315	-1.152080
H	4.853471	-0.624403	-0.567775
C	1.479328	-2.509305	0.475717
H	3.569707	-2.355056	0.407865
H	0.503982	-2.068518	0.295148
H	1.494109	-3.512617	0.891906

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_N_-Methyl Maleimide

NMe_Maleimide_G4MP2
G4(MP2)
Eel = -398.33518200 au; Energy(0K)) = -398.24042441 au
Enthalpy = -398.23221040 au; Gibbs energy = -398.27191458 au

C	0.650994	-1.632048	0.000000
C	-0.681720	-1.618869	0.000002
C	1.146195	-0.213027	-0.000002
C	-1.150482	-0.191287	-0.000007
O	-2.284163	0.223246	0.000001
O	2.285548	0.185801	-0.000001
H	-1.379352	-2.443945	0.000006
N	0.006649	0.589761	-0.000001
C	0.023472	2.038745	0.000004
H	0.536381	2.418193	-0.887694
H	-1.013503	2.376853	-0.000026
H	0.536327	2.418191	0.887733
H	1.331762	-2.471083	0.000003

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NMe_Maleimide_B3LYP
b3lyp/6-31g(d)
Eel = -398.74426237 au; Energy(0K)) = -398.64761327 au

Enthalpy = -398.63946266 au; Gibbs energy = -398.67908594 au

C	0.648962	-1.635328	-0.000001
C	-0.687108	-1.619422	0.000003
C	1.146789	-0.216105	0.000000
C	-1.152765	-0.189625	-0.000001
O	-2.292689	0.227376	0.000000
O	2.294046	0.180470	0.000000
H	-1.386621	-2.445565	-0.000003
N	0.007507	0.591791	-0.000001
C	0.029639	2.043058	0.000000
H	0.544133	2.418626	-0.889298
H	-1.006320	2.385759	-0.000029
H	0.544081	2.418628	0.889329
H	1.328210	-2.478214	-0.000003

############################

N-Methyl Maleimide + [5]Dendralene Transition Structures

N_MMI_5_Dend_ttt_trien_G4MP2
G4(MP2)
Energy(0K) = -785.765165
Enthalpy(298K) = -785.746173; Gibbs free energy(298K) = -785.811118

C	-1.027972	2.611446	0.138010
C	-0.095847	1.810614	0.750323
C	0.758030	0.929543	0.043969
C	0.669133	0.887258	-1.345882
C	-1.370224	0.182631	-1.703582
C	-2.289180	0.993348	-1.044820
C	-1.279445	-1.106934	-0.943381
C	-2.774506	0.274992	0.162163
O	-3.619818	0.596411	0.965634
O	-0.678824	-2.120088	-1.224051
H	-0.897374	2.967982	-0.874558
H	-1.751730	3.156991	0.733125
H	-0.129777	1.729908	1.831981
H	1.246358	0.154900	-1.896740
H	0.404327	1.778014	-1.900223
H	-1.178730	0.186328	-2.767379
H	-2.872155	1.794166	-1.473912
C	1.558851	-0.097119	0.763447
C	1.294922	-0.497877	2.015402
H	1.932361	-1.221902	2.509038
H	0.448867	-0.128845	2.583871
C	2.713811	-0.714223	0.033815

C	2.641404	-1.985312	-0.388471
H	3.474362	-2.448086	-0.909979
H	1.745399	-2.578371	-0.253167
N	-2.052660	-0.931082	0.200861
C	-2.207719	-1.938282	1.228273
H	-3.003311	-1.605530	1.896265
H	-2.471118	-2.899064	0.778580
H	-1.276422	-2.062843	1.790250
C	3.917366	0.089033	-0.203141
C	4.143645	1.325225	0.248774
H	4.684170	-0.405666	-0.797137
H	5.070549	1.843122	0.029550
H	3.418376	1.859827	0.852354

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N_MMI_5_Dend_ct_Butdien_c_Vinyl_G4MP2
G4(MP2)
Energy(0K) = -785.764695
Enthalpy(298K) = -785.745450; Gibbs free energy(298K) = -785.811154

C	0.769355	-1.088442	1.770244
C	1.227647	-0.365907	0.693028
C	0.843488	1.003959	0.515462
C	0.034304	1.612813	1.476176
C	-1.837617	0.553618	1.434741
C	-1.654541	-0.821125	1.532247
C	-2.167674	0.868117	0.004500
C	-1.782068	-1.407231	0.178691
O	-1.746575	-2.567374	-0.174879
O	-2.515921	1.919318	-0.479776
H	0.451459	-0.616062	2.687261
H	0.980741	-2.149177	1.836978
H	-0.348200	2.609519	1.289965
H	0.145049	1.355351	2.521645
H	-2.229069	1.188786	2.217395
H	-1.755251	-1.435835	2.413148
C	1.102773	1.665481	-0.771117
C	0.994533	2.973564	-1.022503
H	1.409981	1.010654	-1.580547
H	1.179515	3.366068	-2.015848
H	0.727673	3.699309	-0.261949
C	2.031154	-1.084048	-0.351783
C	1.521027	-2.104077	-1.059228
H	2.139238	-2.636029	-1.776585
H	0.500664	-2.448445	-0.938448
N	-1.989757	-0.327435	-0.692670

C	-2.175790	-0.470751	-2.121915
H	-1.220238	-0.646044	-2.625697
H	-2.836225	-1.316953	-2.324571
H	-2.617936	0.454773	-2.493110
C	3.434407	-0.693070	-0.537750
C	4.114940	0.205853	0.178024
H	3.946335	-1.227215	-1.336504
H	5.158860	0.412243	-0.029256
H	3.660039	0.763010	0.989140

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N_MMI_5_Dend_cct_trien_G4MP2
G4(MP2)
Energy(0K) = -785.764186
Enthalpy(298K) = -785.745184; Gibbs free energy(298K) = -785.810341

C	-0.312318	-2.413330	-0.673701
C	0.547825	-1.341883	-0.638875
C	0.851988	-0.623915	0.543542
C	0.249399	-1.008892	1.735194
C	-1.941870	-0.795628	1.338646
C	-2.268561	-1.467973	0.166784
C	-1.933605	0.668470	1.036759
C	-2.439801	-0.462628	-0.918453
O	-2.787306	-0.619008	-2.066136
O	-1.798098	1.606011	1.792218
H	-0.438285	-3.066716	0.180075
H	-0.628776	-2.825148	-1.625327
H	0.860661	-0.902052	-1.580993
H	0.405242	-0.429670	2.637629
H	-0.003246	-2.047597	1.898491
H	-2.150245	-1.133479	2.343587
H	-2.736373	-2.437767	0.087513
C	1.641046	0.636546	0.432879
C	1.430042	1.703990	1.214631
H	2.049984	2.587543	1.114963
H	0.632454	1.741433	1.947208
C	2.702788	0.685982	-0.622092
C	2.633940	1.591081	-1.611123
H	3.406681	1.654330	-2.371310
H	1.809895	2.290602	-1.684827
N	-2.125505	0.777459	-0.338211
C	-2.144858	2.037650	-1.050311
H	-2.393487	1.821928	-2.090168
H	-2.892472	2.710244	-0.620819
H	-1.167245	2.524381	-0.990268

C	3.836044	-0.245243	-0.558834
C	4.117171	-1.086552	0.438844
H	4.507882	-0.200140	-1.414298
H	4.993524	-1.724010	0.404566
H	3.490201	-1.168168	1.319463

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N_MMI_5_Dend_ctt_trien_G4MP2
G4(MP2)
Energy(0K) = -785.762241
Enthalpy(298K) = -785.743178; Gibbs free energy(298K) = -785.809007

C	-0.781255	-2.246992	-1.227387
C	0.310986	-1.489270	-0.878047
C	0.666678	-1.204646	0.463728
C	-0.137086	-1.696108	1.485827
C	-2.137799	-0.792592	1.090737
C	-2.525149	-1.076706	-0.213729
C	-1.737293	0.647922	1.143973
C	-2.366065	0.157741	-1.028885
O	-2.667624	0.368937	-2.180824
O	-1.431568	1.318198	2.105911
H	-1.147597	-3.040810	-0.589259
H	-1.095784	-2.302007	-2.263418
H	0.818507	-0.930080	-1.657837
H	0.071433	-1.433713	2.516148
H	-0.663887	-2.631040	1.353082
H	-2.513543	-1.273048	1.982666
H	-3.205612	-1.852937	-0.530155
C	1.763970	-0.232099	0.732935
C	1.741652	0.614384	1.771706
H	2.571005	1.287188	1.955529
H	0.899348	0.680251	2.449597
C	2.940462	-0.268357	-0.195585
C	3.574641	-1.427280	-0.437945
H	4.435613	-1.469877	-1.097180
H	3.256718	-2.360099	0.012799
N	-1.793140	1.109527	-0.170696
C	-1.476026	2.464721	-0.571120
H	-2.239443	2.823569	-1.264566
H	-1.452357	3.083709	0.326938
H	-0.502439	2.513172	-1.069341
C	3.410092	0.956957	-0.855683
C	2.847699	2.168106	-0.822824
H	4.309393	0.818204	-1.453993
H	3.278116	2.995480	-1.375901

H	1.952997	2.373596	-0.247143

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X_MMI_5_Dend_ccc_trien_G4MP2
G4(MP2)
Energy(0K) = -785.756237
Enthalpy(298K) = -785.736813; Gibbs free energy(298K) = -785.804137

C	-0.494138	0.050810	-1.069650
C	-1.243925	1.085039	-0.520197
C	-0.580306	2.232191	-0.019563
C	0.780760	2.405496	-0.079087
C	1.470403	0.516233	1.138342
C	0.832418	-0.589892	0.589266
C	2.878981	0.536560	0.650665
C	1.836323	-1.318133	-0.255982
O	1.711343	-2.366349	-0.845473
O	3.780611	1.290939	0.936271
H	0.417026	0.278413	-1.606606
H	-0.971907	-0.876355	-1.363712
H	-1.157409	2.898537	0.615274
H	1.257748	3.224980	0.446353
H	1.374685	1.968774	-0.871577
H	1.205694	1.028813	2.049279
H	0.013835	-1.139142	1.028743
C	-2.707310	0.926824	-0.315472
C	-3.536285	1.976630	-0.397456
H	-4.602175	1.860777	-0.240761
H	-3.175569	2.972142	-0.633510
C	-3.251694	-0.437605	-0.040520
C	-4.182972	-0.979424	-0.836584
H	-4.642962	-1.933462	-0.602277
H	-4.512047	-0.476720	-1.738516
N	2.995206	-0.535445	-0.245429
C	4.215876	-0.876060	-0.946903
H	4.373700	-0.227142	-1.814429
H	5.068059	-0.764752	-0.272844
H	4.128591	-1.910408	-1.282660
C	-2.753070	-1.115062	1.175112
C	-2.613953	-2.432470	1.338623
H	-2.483832	-0.452568	1.996800
H	-2.280286	-2.852817	2.281062
H	-2.821863	-3.134508	0.537435

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X_MMI_5_Dend_ctca_trien_G4MP2
G4(MP2)
Energy(0K) = -785.755978
Enthalpy(298K) = -785.736689; Gibbs free energy(298K) = -785.803618

C	-0.035457	0.741694	0.878827
C	-1.048754	-0.073838	0.395798
C	-0.761646	-1.426729	0.093211
C	0.486245	-1.983357	0.246220
C	1.722131	-0.587561	-1.149997
C	1.418351	0.727199	-0.813911
C	3.059153	-0.917194	-0.575086
C	2.575203	1.280157	-0.037281
O	2.746840	2.406115	0.368350
O	3.710758	-1.930732	-0.680428
H	0.759788	0.318166	1.478019
H	-0.211763	1.797538	1.045420
H	-1.509994	-1.981187	-0.465403
H	0.699143	-2.974713	-0.137427
H	1.170590	-1.639702	1.010874
H	1.349313	-1.136762	-1.999664
H	0.796826	1.395975	-1.390011
C	-2.342432	0.513696	-0.059844
C	-2.372899	1.679898	-0.724797
H	-3.308320	2.131851	-1.032194
H	-1.468961	2.227050	-0.965510
C	-3.604103	-0.212162	0.246165
C	-3.694207	-1.089205	1.259217
H	-4.616748	-1.624703	1.451072
H	-2.858862	-1.293757	1.917507
N	3.462093	0.214328	0.147600
C	4.715609	0.312361	0.867009
H	4.659355	-0.187312	1.839553
H	5.509178	-0.157636	0.282148
H	4.930315	1.371111	1.019028
C	-4.776394	0.075638	-0.609259
C	-6.025564	0.236653	-0.172969
H	-4.570930	0.168138	-1.674179
H	-6.846260	0.413541	-0.859744
H	-6.269540	0.205555	0.884130

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N_MMI_5_Dend_ttt_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90517897 au; Energy(0K)) = -786.62013002 au
Enthalpy = -786.60133714 au; Gibbs energy = -786.66349338 au

C	-1.015523	2.626894	0.139238
C	-0.084936	1.819719	0.749929
C	0.766788	0.931036	0.039978
C	0.676351	0.885596	-1.350884
C	-1.384629	0.182340	-1.707516
C	-2.299008	0.996195	-1.044728
C	-1.296845	-1.109316	-0.949392
C	-2.780616	0.279665	0.165962
O	-3.622070	0.612140	0.979607
O	-0.694902	-2.128039	-1.236199
H	-0.888862	2.980362	-0.876728
H	-1.734794	3.177343	0.738180
H	-0.119157	1.737746	1.832974
H	1.250354	0.148540	-1.902006
H	0.412091	1.776222	-1.908770
H	-1.196126	0.188001	-2.773801
H	-2.880562	1.801826	-1.471974
C	1.564160	-0.101129	0.762393
C	1.288991	-0.505989	2.015301
H	1.923851	-1.231084	2.514187
H	0.436130	-0.139172	2.578457
C	2.726352	-0.719098	0.040260
C	2.660440	-1.998302	-0.372286
H	3.497214	-2.465009	-0.887801
H	1.764945	-2.594766	-0.235337
N	-2.067265	-0.933965	0.200082
C	-2.221119	-1.944636	1.227305
H	-3.002962	-1.604142	1.908296
H	-2.505059	-2.899963	0.776775
H	-1.281810	-2.080972	1.774058
C	3.931327	0.086685	-0.203613
C	4.154787	1.330446	0.241490
H	4.701947	-0.408757	-0.794414
H	5.082468	1.848542	0.017409
H	3.427825	1.869579	0.842035

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N_MMI_5_Dend_cct_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90473974 au; Energy(0K)) = -786.61965046 au
Enthalpy = -786.60084903 au; Gibbs energy = -786.66307448 au

C	-0.301965	-2.426869	-0.667754
C	0.556179	-1.351139	-0.635110
C	0.859412	-0.626073	0.549387
C	0.255353	-1.006154	1.743616

C	-1.955059	-0.794115	1.339695
C	-2.276397	-1.470604	0.167559
C	-1.951086	0.669831	1.034591
C	-2.443924	-0.467872	-0.922002
O	-2.783499	-0.633230	-2.078201
O	-1.818895	1.612840	1.794916
H	-0.430153	-3.078454	0.189231
H	-0.615626	-2.842305	-1.620558
H	0.865051	-0.910927	-1.580023
H	0.412323	-0.423152	2.645421
H	-0.001184	-2.044763	1.911442
H	-2.166690	-1.132070	2.346057
H	-2.743179	-2.443340	0.089857
C	1.646301	0.639220	0.432051
C	1.425175	1.713279	1.209454
H	2.043051	2.600382	1.110539
H	0.620634	1.751924	1.936848
C	2.714464	0.690873	-0.619940
C	2.647359	1.601225	-1.610194
H	3.423783	1.670331	-2.368632
H	1.820290	2.299709	-1.686114
N	-2.138602	0.777749	-0.343708
C	-2.157352	2.039346	-1.057762
H	-2.403073	1.822917	-2.098672
H	-2.908003	2.710117	-0.629202
H	-1.178394	2.524604	-0.995049
C	3.851079	-0.241797	-0.557681
C	4.132183	-1.085274	0.443949
H	4.525517	-0.198371	-1.412826
H	5.009972	-1.723652	0.408521
H	3.504704	-1.167321	1.326243

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N_MMI_5_Dend_ct_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.90353673 au; Energy(0K)) = -786.61880839 au
Enthalpy = -786.59974399 au; Gibbs energy = -786.66235686 au

C	0.780641	-1.093694	1.776005
C	1.239405	-0.369706	0.697516
C	0.854850	1.006117	0.519431
C	0.044769	1.616975	1.480632
C	-1.843259	0.560891	1.433946
C	-1.670238	-0.816130	1.534023
C	-2.173507	0.874721	0.002314
C	-1.802477	-1.404400	0.181406

O	-1.771321	-2.572788	-0.169158
O	-2.513031	1.935920	-0.483741
H	0.453861	-0.622252	2.692395
H	0.994491	-2.155404	1.844131
H	-0.334411	2.616719	1.295527
H	0.154373	1.358939	2.527793
H	-2.233969	1.198978	2.217354
H	-1.771701	-1.428805	2.418865
C	1.112862	1.667160	-0.770948
C	1.007920	2.980368	-1.019696
H	1.418657	1.013548	-1.583541
H	1.191414	3.373676	-2.014831
H	0.744229	3.707187	-0.256552
C	2.039578	-1.091210	-0.351404
C	1.520134	-2.114002	-1.056141
H	2.131380	-2.653437	-1.776422
H	0.496713	-2.452252	-0.929413
N	-2.007110	-0.324780	-0.695175
C	-2.194373	-0.472034	-2.126006
H	-1.241272	-0.681507	-2.622651
H	-2.883247	-1.296991	-2.325654
H	-2.605240	0.465539	-2.504140
C	3.446365	-0.705121	-0.547332
C	4.135224	0.195224	0.166711
H	3.954827	-1.240290	-1.349355
H	5.179960	0.398356	-0.048586
H	3.687140	0.755458	0.981771

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N_MMI_5_Dend_ctt_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90324281 au; Energy(0K)) = -786.61827212 au
Enthalpy = -786.59942785 au; Gibbs energy = -786.66149875 au

C	-0.784912	-2.319059	-1.098956
C	0.304123	-1.528501	-0.804282
C	0.661923	-1.152417	0.519038
C	-0.132720	-1.580295	1.577626
C	-2.181459	-0.736168	1.116423
C	-2.540551	-1.096747	-0.178637
C	-1.813833	0.713006	1.100101
C	-2.384729	0.096465	-1.057894
O	-2.658243	0.227427	-2.235677
O	-1.537244	1.446091	2.033569
H	-1.137178	-3.076593	-0.407886
H	-1.099533	-2.447014	-2.130190

H	0.802017	-1.013329	-1.621865
H	0.077539	-1.242719	2.587302
H	-0.656962	-2.525539	1.512407
H	-2.558166	-1.182975	2.027490
H	-3.213257	-1.895233	-0.461930
C	1.757631	-0.153783	0.717498
C	1.688879	0.808156	1.654896
H	2.515125	1.494249	1.809549
H	0.812449	0.947535	2.279099
C	2.979056	-0.310107	-0.139528
C	3.536105	-1.526041	-0.309440
H	4.430927	-1.656748	-0.912423
H	3.120274	-2.418637	0.146436
N	-1.853054	1.107958	-0.237890
C	-1.542453	2.449069	-0.693493
H	-1.822385	2.510505	-1.746399
H	-2.104180	3.185052	-0.111230
H	-0.473504	2.655815	-0.580933
C	3.593247	0.849965	-0.809194
C	3.107453	2.094426	-0.909085
H	4.539734	0.625792	-1.301526
H	3.647601	2.857062	-1.462270
H	2.168227	2.391114	-0.453985

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N_MMI_5_Dend_ccc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90124945 au; Energy(0K)) = -786.61644048 au
Enthalpy = -786.59753798 au; Gibbs energy = -786.66006923 au

C	-0.421087	2.513205	0.187798
C	0.472961	1.469569	0.283814
C	0.724182	0.553362	-0.774015
C	0.033426	0.696975	-1.972090
C	-2.148851	0.520144	-1.365019
C	-2.399203	1.389366	-0.308470
C	-2.076453	-0.865311	-0.809090
C	-2.454711	0.591664	0.950803
O	-2.712869	0.955387	2.082208
O	-1.976999	-1.926094	-1.400315
H	-0.622516	3.002930	-0.758341
H	-0.685943	3.083135	1.073157
H	0.857981	1.209873	1.267301
H	0.152097	-0.039258	-2.760419
H	-0.278947	1.678793	-2.305393
H	-2.441602	0.671287	-2.396035

H	-2.896192	2.348553	-0.366792
C	1.569851	-0.646423	-0.492160
C	1.309840	-1.860411	-1.007487
H	1.978489	-2.694132	-0.816536
H	0.427883	-2.061974	-1.607080
C	2.758507	-0.443543	0.399432
C	2.924855	-1.199727	1.498982
H	3.771379	-1.056987	2.164620
H	2.208817	-1.970704	1.765606
N	-2.154314	-0.730117	0.578063
C	-2.079530	-1.844947	1.502470
H	-2.301199	-1.459579	2.498992
H	-2.806848	-2.614422	1.227974
H	-1.078307	-2.286854	1.486141
C	3.718014	0.613085	0.004387
C	5.037390	0.588642	0.225182
H	3.296318	1.453563	-0.544715
H	5.676408	1.406646	-0.094700
H	5.526178	-0.248311	0.717419

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N_MMI_5_Dend_ttc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90147725 au; Energy(0K)) = -786.61643030 au
Enthalpy = -786.59767361 au; Gibbs energy = -786.65970163 au

C	-1.643660	-2.391106	-0.787530
C	-0.506801	-1.710005	-1.155892
C	0.462114	-1.237783	-0.229732
C	0.271389	-1.487871	1.127328
C	-1.638350	-0.446989	1.602629
C	-2.638543	-0.835123	0.718292
C	-1.209754	0.939953	1.226768
C	-2.850436	0.262217	-0.265542
O	-3.668060	0.347711	-1.162508
O	-0.430524	1.682439	1.793078
H	-1.683943	-2.989668	0.114461
H	-2.411094	-2.607658	-1.524635
H	-0.422600	-1.375053	-2.186606
H	0.939734	-1.045403	1.857616
H	-0.231678	-2.392158	1.450279
H	-1.542291	-0.774806	2.630021
H	-3.417190	-1.563987	0.897927
C	1.520513	-0.285112	-0.682890
C	1.293678	0.596394	-1.677735
H	2.078632	1.255654	-2.034309

H	0.329183	0.679520	-2.166624
C	2.863592	-0.321465	-0.029632
C	3.382297	-1.453140	0.483127
H	4.351914	-1.451748	0.971039
H	2.858960	-2.402332	0.428660
N	-1.902401	1.251244	0.054200
C	-1.774553	2.517122	-0.640286
H	-2.489103	2.512689	-1.465174
H	-1.993622	3.347916	0.037386
H	-0.756923	2.639313	-1.023855
C	3.619543	0.951654	0.018952
C	4.930651	1.078066	-0.213340
H	3.030100	1.837707	0.254221
H	5.429726	2.039248	-0.127305
H	5.545595	0.229981	-0.504164

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N_MMI_5_Dend_tcc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.90095743 au; Energy(0K)) = -786.61627070 au
Enthalpy = -786.59735575 au; Gibbs energy = -786.65993268 au

C	-1.274158	2.592355	0.362420
C	-0.302653	1.804141	0.933573
C	0.625346	1.039196	0.177781
C	0.575924	1.105990	-1.215172
C	-1.421529	0.304473	-1.697268
C	-2.406075	0.986796	-0.988046
C	-1.257770	-1.045046	-1.061240
C	-2.863234	0.124968	0.135328
O	-3.743564	0.321061	0.952027
O	-0.575450	-1.985552	-1.422329
H	-1.146388	3.038169	-0.616493
H	-2.045078	3.041061	0.981688
H	-0.353417	1.627838	2.004780
H	1.209103	0.452055	-1.805711
H	0.267972	2.021202	-1.707570
H	-1.210292	0.425196	-2.752462
H	-3.036789	1.784045	-1.357437
C	1.468685	0.000106	0.834029
C	1.150592	-0.572509	2.009213
H	1.819354	-1.288388	2.476086
H	0.226301	-0.353726	2.535320
C	2.728933	-0.410571	0.131571
C	2.870716	-1.667170	-0.322837
H	3.762028	-1.977089	-0.861806

H	2.079476	-2.400130	-0.205309
N	-2.068915	-1.035142	0.074394
C	-2.174172	-2.148337	0.996304
H	-2.982342	-1.921558	1.693692
H	-2.395943	-3.070526	0.451588
H	-1.234235	-2.282045	1.542352
C	3.761438	0.636829	-0.031492
C	5.083181	0.432933	-0.076811
H	3.388669	1.659690	-0.079409
H	5.776391	1.259611	-0.202540
H	5.518358	-0.558414	0.020766

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N_MMI_5_Dend_tc_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.90055604 au; Energy(0K)) = -786.61559322 au
Enthalpy = -786.59670879 au; Gibbs energy = -786.65902113 au

C	1.014984	-0.253052	1.888057
C	1.097487	0.633740	0.826673
C	0.013247	1.551904	0.580600
C	-1.055632	1.600683	1.471995
C	-1.984491	-0.446764	1.341658
C	-1.005153	-1.425252	1.460185
C	-2.359488	-0.339264	-0.102547
C	-0.695781	-1.936901	0.097259
O	0.047949	-2.842368	-0.241274
O	-3.247547	0.312217	-0.616628
H	0.435675	-0.029362	2.772587
H	1.784388	-1.007551	2.019960
H	-1.934412	2.183896	1.218096
H	-0.910137	1.415990	2.529879
H	-2.699610	-0.165627	2.104062
H	-0.785808	-2.025198	2.332730
C	-0.111084	2.251149	-0.714272
C	-0.780925	3.395012	-0.909492
H	0.390938	1.791625	-1.561774
H	-0.868230	3.830348	-1.900432
H	-1.254528	3.939577	-0.096836
C	2.274549	0.514717	-0.087774
C	2.859898	1.603929	-0.621464
H	3.713791	1.507816	-1.285094
H	2.512289	2.609485	-0.408752
N	-1.464068	-1.172262	-0.789785
C	-1.477700	-1.373036	-2.226513
H	-0.540002	-1.032127	-2.676652

H	-1.609000	-2.434180	-2.456121
H	-2.310570	-0.794733	-2.629801
C	2.823840	-0.842359	-0.327338
C	4.128885	-1.130966	-0.393273
H	2.098408	-1.647525	-0.436483
H	4.471117	-2.140616	-0.602500
H	4.895145	-0.376015	-0.233691

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N_MMI_5_Dend_cca_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.89990807 au; Energy(0K)) = -786.61530896 au
Enthalpy = -786.59622289 au; Gibbs energy = -786.65905464 au

C	-0.446350	-0.934653	-2.030623
C	-1.059095	-0.202747	-1.033554
C	-0.634533	1.143752	-0.757242
C	0.379808	1.714544	-1.527855
C	2.154535	0.486411	-1.141833
C	1.883613	-0.863934	-1.337969
C	2.209728	0.730949	0.337607
C	1.701259	-1.501501	-0.010976
O	1.511346	-2.672982	0.271598
O	2.527088	1.743168	0.931071
H	0.056486	-0.461538	-2.862519
H	-0.713297	-1.976209	-2.175884
H	0.787838	2.676886	-1.236219
H	0.472079	1.476529	-2.581371
H	2.738075	1.112621	-1.805334
H	2.119611	-1.458784	-2.209517
C	-1.081392	1.812223	0.478465
C	-1.054825	3.133931	0.699241
H	-1.468216	1.166016	1.261546
H	-1.374238	3.547677	1.650892
H	-0.725489	3.846974	-0.051783
C	-2.090995	-0.877539	-0.174602
C	-1.853828	-2.066467	0.408194
H	-2.642445	-2.592084	0.939417
H	-0.881317	-2.547525	0.366805
N	1.809268	-0.469940	0.934398
C	1.689988	-0.674529	2.365274
H	0.661634	-0.940318	2.629296
H	2.354058	-1.481346	2.688455
H	1.969425	0.259750	2.854849
C	-3.408418	-0.202700	-0.090639
C	-4.281904	-0.305650	0.918320

H	-3.661934	0.435642	-0.936901
H	-5.244197	0.196526	0.882826
H	-4.065952	-0.885268	1.812455

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X_MMI_5_Dend_ctca_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.89984076 au; Energy(0K)) = -786.61522016 au
Enthalpy = -786.59614774 au; Gibbs energy = -786.65910412 au

C	-0.033234	0.737145	0.899562
C	-1.052210	-0.074536	0.416056
C	-0.769926	-1.433553	0.110256
C	0.476221	-1.998607	0.263271
C	1.723427	-0.588075	-1.150678
C	1.419946	0.726802	-0.810158
C	3.063746	-0.918202	-0.583013
C	2.582867	1.281108	-0.041833
O	2.750327	2.412605	0.370885
O	3.712658	-1.941992	-0.686748
H	0.764003	0.308431	1.495218
H	-0.206325	1.794217	1.072698
H	-1.520685	-1.983755	-0.452137
H	0.682536	-2.992303	-0.122686
H	1.167519	-1.656409	1.024649
H	1.341066	-1.138527	-1.997721
H	0.792892	1.395526	-1.384020
C	-2.343818	0.521297	-0.044022
C	-2.365978	1.698580	-0.698514
H	-3.298786	2.159737	-1.006247
H	-1.457096	2.245521	-0.928868
C	-3.613178	-0.206395	0.241436
C	-3.716292	-1.091291	1.252207
H	-4.640959	-1.631818	1.428161
H	-2.889611	-1.297251	1.923811
N	3.476755	0.216407	0.134064
C	4.737018	0.312264	0.846395
H	4.699944	-0.237232	1.793158
H	5.538859	-0.105168	0.232058
H	4.924457	1.368564	1.046910
C	-4.776803	0.086396	-0.628289
C	-6.037157	0.230323	-0.204912
H	-4.559588	0.198317	-1.690475
H	-6.850465	0.410750	-0.902242
H	-6.296693	0.182102	0.849599

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X_MMI_5_Dend_ccc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.89961911 au; Energy(0K)) = -786.61519217 au
Enthalpy = -786.59602455 au; Gibbs energy = -786.65916963 au

C	-0.497095	0.056391	-1.079446
C	-1.249029	1.088634	-0.524642
C	-0.585355	2.240760	-0.020600
C	0.776695	2.420733	-0.083649
C	1.475291	0.510009	1.141756
C	0.838643	-0.595196	0.586216
C	2.885042	0.533993	0.656440
C	1.845650	-1.320666	-0.259181
O	1.715625	-2.368543	-0.862345
O	3.786684	1.299463	0.942420
H	0.415148	0.288106	-1.616010
H	-0.973698	-0.871798	-1.378231
H	-1.162981	2.902120	0.621567
H	1.251250	3.242541	0.443833
H	1.373077	1.984186	-0.876643
H	1.204029	1.022422	2.053150
H	0.018112	-1.146891	1.023554
C	-2.714282	0.927089	-0.311882
C	-3.545765	1.980903	-0.393595
H	-4.612350	1.867289	-0.228107
H	-3.186345	2.976804	-0.638084
C	-3.261266	-0.438191	-0.031373
C	-4.208838	-0.974085	-0.819959
H	-4.673825	-1.926507	-0.581391
H	-4.545238	-0.468032	-1.719468
N	3.008430	-0.539124	-0.240943
C	4.234161	-0.874303	-0.940710
H	4.449508	-0.145836	-1.729338
H	5.072777	-0.885483	-0.239137
H	4.100319	-1.863121	-1.382742
C	-2.751765	-1.128176	1.176253
C	-2.613913	-2.451916	1.323379
H	-2.473302	-0.475604	2.004616
H	-2.273784	-2.884262	2.260062
H	-2.829223	-3.145294	0.514340

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N_MMI_5_Dend_ctc_trien_B3LYP
b3lyp/6-31g(d)

Eel = -786.90019065 au; Energy(0K)) = -786.61502493 au
Enthalpy = -786.59622672 au; Gibbs energy = -786.65847692 au

C	-0.899900	2.454358	0.313316
C	0.177346	1.587462	0.369806
C	0.611060	0.813884	-0.737873
C	-0.087887	0.888239	-1.933261
C	-2.293704	0.346876	-1.302695
C	-2.615334	1.138933	-0.203343
C	-2.031350	-1.033670	-0.813863
C	-2.559935	0.275896	1.019501
O	-2.850185	0.556067	2.166455
O	-1.813347	-2.050567	-1.450457
H	-1.132262	2.989968	-0.601201
H	-1.259832	2.920733	1.225541
H	0.588007	1.337720	1.345233
H	0.159545	0.219689	-2.751831
H	-0.610046	1.794389	-2.212808
H	-2.603343	0.510454	-2.326142
H	-3.266322	2.003832	-0.216162
C	1.691655	-0.211646	-0.544134
C	1.457704	-1.506944	-0.827609
H	2.219933	-2.267010	-0.695756
H	0.495566	-1.851368	-1.191298
C	3.022460	0.255777	-0.060574
C	3.316590	1.556532	0.137283
H	4.317163	1.853903	0.433550
H	2.592608	2.350019	-0.006661
N	-2.097165	-0.972745	0.583478
C	-1.874349	-2.112787	1.452813
H	-2.202016	-1.831182	2.454873
H	-2.447825	-2.972507	1.095759
H	-0.813044	-2.380296	1.471830
C	4.083686	-0.761422	0.151418
C	4.883584	-0.813615	1.220349
H	4.215318	-1.500931	-0.637491
H	5.670908	-1.557970	1.301906
H	4.774301	-0.121468	2.051528

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N_MMI_5_Dend_cc_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.89937474 au; Energy(0K)) = -786.61480849 au
Enthalpy = -786.59572300 au; Gibbs energy = -786.65859040 au

C	0.691142	-0.847606	1.917533
C	1.141003	-0.068497	0.871493

C	0.573949	1.230515	0.633318
C	-0.409896	1.720152	1.493880
C	-2.098476	0.340875	1.284107
C	-1.692206	-0.979169	1.451613
C	-2.320598	0.567024	-0.182510
C	-1.588562	-1.610052	0.113047
O	-1.328299	-2.763514	-0.186664
O	-2.781579	1.543021	-0.741602
H	0.229486	-0.417462	2.795688
H	1.059261	-1.862081	2.031459
H	-0.925713	2.640447	1.239015
H	-0.378832	1.488467	2.552524
H	-2.667264	0.918666	2.002107
H	-1.789230	-1.585484	2.341555
C	0.844041	1.915968	-0.644021
C	0.695277	3.228534	-0.871004
H	1.199984	1.286584	-1.457009
H	0.887452	3.651566	-1.852319
H	0.384456	3.924196	-0.096207
C	2.150877	-0.649319	-0.079513
C	1.915034	-1.785351	-0.758112
H	2.657739	-2.187228	-1.441987
H	0.985184	-2.336952	-0.659320
N	-1.879160	-0.599796	-0.816876
C	-1.897167	-0.807303	-2.252405
H	-0.881708	-0.955353	-2.633126
H	-2.494955	-1.689810	-2.497179
H	-2.336392	0.082127	-2.707089
C	3.434854	0.086388	-0.170901
C	4.632640	-0.468030	-0.391435
H	3.381127	1.161273	-0.004375
H	5.530600	0.140042	-0.452632
H	4.760475	-1.541257	-0.507402

############################

N_MMI_5_Dend_tca_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.89875324 au; Energy(0K)) = -786.61431738 au
Enthalpy = -786.59521659 au; Gibbs energy = -786.65795184 au

C	0.695054	-0.150542	2.162979
C	1.114820	0.518731	1.031876
C	0.339132	1.606350	0.495713
C	-0.822857	2.008493	1.152694
C	-2.174459	0.255120	1.055352
C	-1.551762	-0.877705	1.562768

C	-2.212891	0.124762	-0.439223
C	-1.148915	-1.741379	0.425238
O	-0.650506	-2.854305	0.433816
O	-2.756136	0.846333	-1.252653
H	0.065148	0.322170	2.903398
H	1.228092	-1.031845	2.507507
H	-1.471420	2.739274	0.680781
H	-0.897225	1.954397	2.232556
H	-2.935800	0.837160	1.559225
H	-1.650022	-1.287155	2.558804
C	0.634315	2.131598	-0.850960
C	0.271377	3.338297	-1.306537
H	1.205135	1.480453	-1.507273
H	0.496624	3.642177	-2.324341
H	-0.250481	4.064576	-0.689037
C	2.331045	0.009131	0.309316
C	3.390098	0.818420	0.135452
H	4.308727	0.457004	-0.317538
H	3.373769	1.856132	0.454510
N	-1.480346	-1.030468	-0.738214
C	-1.250296	-1.531438	-2.080455
H	-0.177570	-1.640506	-2.264384
H	-1.730344	-2.506036	-2.211486
H	-1.679766	-0.809527	-2.776933
C	2.321029	-1.399732	-0.143373
C	2.985245	-1.870904	-1.206883
H	1.679647	-2.083574	0.408487
H	2.934298	-2.921909	-1.475816
H	3.591134	-1.230955	-1.843993

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N_MMI_5_Dend_tta_Butdien_c_Vinyl_B3LYP
b3lyp/6-31g(d)
Eel = -786.89908150 au; Energy(0K)) = -786.61424790 au
Enthalpy = -786.59519772 au; Gibbs energy = -786.65762256 au

C	1.230930	-0.539473	1.845220
C	1.460421	0.295170	0.777794
C	0.580150	1.411936	0.519450
C	-0.429770	1.718689	1.447944
C	-1.860920	0.253505	1.390718
C	-1.373707	-1.043912	1.563410
C	-2.253087	0.388940	-0.062684
C	-1.341820	-1.715608	0.256226
O	-1.037985	-2.862429	-0.034142
O	-2.830415	1.313509	-0.602134

H	0.611173	-0.254382	2.680784
H	1.841023	-1.424764	1.989329
H	-1.089954	2.551859	1.229847
H	-0.229067	1.577803	2.505149
H	-2.461432	0.771488	2.131078
H	-1.295846	-1.603465	2.484767
C	0.597820	2.067077	-0.795332
C	-0.012011	3.219319	-1.117386
H	1.161485	1.556154	-1.570502
H	0.024659	3.599100	-2.133751
H	-0.560032	3.822950	-0.400126
C	2.653363	0.039626	-0.099894
C	3.524950	1.047185	-0.309243
H	4.421602	0.899369	-0.905655
H	3.372542	2.037935	0.106489
N	-1.793758	-0.766163	-0.686155
C	-1.928313	-1.044837	-2.103119
H	-0.952253	-1.279641	-2.537302
H	-2.595729	-1.897025	-2.264185
H	-2.343618	-0.153282	-2.575475
C	2.951130	-1.280746	-0.678258
C	2.188623	-2.382469	-0.680944
H	3.921065	-1.325631	-1.174119
H	2.546103	-3.285954	-1.167486
H	1.205240	-2.444418	-0.228963

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X_MMI_5_Dend_tcc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.89835718 au; Energy(0K)) = -786.61399938 au
Enthalpy = -786.59471884 au; Gibbs energy = -786.65806626 au

C	0.445794	-0.447756	0.419209
C	1.128940	0.759979	0.293941
C	0.475924	1.967166	0.657440
C	-0.826336	2.019384	1.096514
C	-1.890936	0.996491	-0.784066
C	-1.197077	-0.183539	-1.038936
C	-3.165671	0.651421	-0.093699
C	-2.044650	-1.323081	-0.547145
O	-1.840359	-2.517322	-0.647687
O	-4.072329	1.380207	0.263047
H	-0.293531	-0.578902	1.201322
H	0.892894	-1.369977	0.061910
H	0.978039	2.901757	0.417801
H	-1.324530	2.974121	1.236611

H	-1.291114	1.185524	1.608392
H	-1.793651	1.932239	-1.314527
H	-0.516812	-0.346180	-1.864074
C	2.418123	0.799935	-0.454612
C	2.737934	1.808438	-1.285748
H	3.701876	1.837991	-1.783767
H	2.052331	2.623309	-1.498642
C	3.366757	-0.344864	-0.266790
C	3.813760	-1.039593	-1.327955
H	4.481747	-1.888326	-1.211970
H	3.504445	-0.787808	-2.337503
N	-3.149447	-0.741941	0.087015
C	-4.218509	-1.489297	0.722156
H	-4.241304	-1.303127	1.800870
H	-5.182583	-1.195511	0.298004
H	-4.033901	-2.548823	0.537002
C	3.765590	-0.657227	1.124354
C	4.939279	-1.177652	1.500629
H	3.038932	-0.396533	1.892233
H	5.155032	-1.380078	2.545659
H	5.726238	-1.408008	0.786945

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X_MMI_5_Dend_ctc_trien_B3LYP
b3lyp/6-31g(d)
Eel = -786.89686329 au; Energy(0K)) = -786.61227803 au
Enthalpy = -786.59313570 au; Gibbs energy = -786.65609454 au

C	-0.063120	1.025541	0.969061
C	-1.041237	0.045271	1.074734
C	-0.665992	-1.308033	1.260658
C	0.649823	-1.717977	1.336427
C	1.451053	-0.975282	-0.717324
C	1.069322	0.355131	-0.870304
C	2.901916	-1.003264	-0.360265
C	2.276993	1.209481	-0.630686
O	2.387388	2.416183	-0.731828
O	3.633616	-1.960389	-0.192339
H	0.878115	0.921390	1.497342
H	-0.334734	2.046329	0.718995
H	-1.441471	-2.064130	1.158248
H	0.897608	-2.775195	1.355118
H	1.419015	-1.068121	1.736846
H	1.000002	-1.832348	-1.196669
H	0.274616	0.718351	-1.506809
C	-2.477385	0.401768	0.817520

C	-3.115541	1.146259	1.739196
H	-4.160539	1.422135	1.643419
H	-2.604818	1.478980	2.637407
C	-3.155561	-0.058460	-0.424886
C	-2.553087	-0.853222	-1.331590
H	-3.058488	-1.124071	-2.252660
H	-1.552633	-1.245324	-1.188264
N	3.302453	0.335576	-0.240397
C	4.650032	0.752619	0.099001
H	4.870120	0.553277	1.152901
H	5.374440	0.211868	-0.516165
H	4.720127	1.824636	-0.093115
C	-4.532233	0.432436	-0.683664
C	-5.545441	-0.328184	-1.108565
H	-4.705310	1.494979	-0.515654
H	-6.523345	0.097149	-1.316482
H	-5.435177	-1.399798	-1.254210

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***N*-Methyl Maleimide + [6]Dendralene Transition Structures**

N_term_ctct
G4(MP2)
Eel = -863.34970200 au; Energy(0K)) = -863.03754727 au
Enthalpy = -863.01642557 au; Gibbs energy = -863.08309913 au

C	-1.494431	-1.983231	-1.538680
C	-0.309901	-1.430609	-1.100259
C	0.085636	-1.414431	0.258690
C	-0.758063	-1.976666	1.205691
C	-2.717087	-0.811386	0.948150
C	-3.044625	-0.803952	-0.403253
C	-2.178367	0.533852	1.296486
C	-2.694893	0.538626	-0.957967
O	-2.885511	0.981877	-2.066636
O	-1.880837	0.984319	2.381541
H	-1.933507	-2.837706	-1.039218
H	-1.807234	-1.838078	-2.566653
H	0.256296	-0.819070	-1.795113
H	-0.524894	-1.895326	2.260636
H	-1.403538	-2.801815	0.938796
H	-3.171449	-1.423751	1.713041
H	-3.813177	-1.396584	-0.877368
C	1.285269	-0.620058	0.668928
C	1.260382	0.176371	1.749467
H	2.145067	0.721966	2.054712

H	0.368597	0.316316	2.347639
C	2.536425	-0.769288	-0.125003
C	2.796587	-1.845818	-0.879708
H	3.729208	-1.927711	-1.425712
H	2.098209	-2.669045	-0.971674
N	-2.085917	1.236010	0.093656
C	-1.572962	2.586819	-0.013449
H	-1.850540	2.966117	-0.997834
H	-2.007403	3.213060	0.769468
H	-0.483898	2.598659	0.093917
C	3.575523	0.305039	-0.012872
C	4.738632	0.051314	0.606132
H	5.513307	0.808462	0.681833
H	4.945408	-0.914105	1.052581
C	3.334988	1.625645	-0.606550
C	2.297036	1.983897	-1.365743
H	4.117281	2.356769	-0.409083
H	2.222987	2.983189	-1.779700
H	1.490595	1.300273	-1.605459

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N_term_ttct1
G4(MP2)
Eel = -863.34888600 au; Energy(0K)) = -863.03668283 au
Enthalpy = -863.01558741 au; Gibbs energy = -863.08223745 au

C	-2.162766	-2.460309	-0.397262
C	-0.958126	-1.965141	-0.838271
C	0.026114	-1.416288	0.018847
C	-0.219052	-1.392042	1.386568
C	-2.083354	-0.159881	1.592254
C	-3.055099	-0.620901	0.713733
C	-1.524758	1.108819	1.033044
C	-3.117620	0.313434	-0.446545
O	-3.865421	0.309852	-1.396770
O	-0.736792	1.882555	1.529821
H	-2.272099	-2.891467	0.588961
H	-2.926494	-2.742902	-1.113301
H	-0.817449	-1.837902	-1.907060
H	0.462412	-0.879673	2.054039
H	-0.817068	-2.168417	1.845556
H	-2.057957	-0.329571	2.658891
H	-3.908041	-1.235961	0.957960
C	1.192410	-0.693646	-0.574381
C	1.053939	0.032725	-1.696615
H	1.902904	0.519626	-2.159718

H	0.094445	0.158680	-2.182128
C	2.534563	-0.840033	0.054608
C	2.846495	-1.858048	0.869006
H	3.842688	-1.946429	1.286175
H	2.131495	-2.627667	1.133390
N	-2.113315	1.267993	-0.220406
C	-1.843035	2.388693	-1.096692
H	-2.486151	2.282811	-1.971375
H	-2.060139	3.333267	-0.589879
H	-0.792169	2.392456	-1.398683
C	3.607726	0.140716	-0.313218
C	4.670983	-0.278241	-1.017654
H	5.475766	0.402226	-1.279085
H	4.763459	-1.304826	-1.351800
C	3.519743	1.541516	0.116739
C	2.576433	2.092691	0.883368
H	4.342350	2.163928	-0.232659
H	2.625250	3.142796	1.150476
H	1.720132	1.549430	1.263494

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N_butdien_vinyl_1
G4(MP2)
Eel = -863.34748100 au; Energy(0K)) = -863.03580087 au
Enthalpy = -863.01432073 au; Gibbs energy = -863.08159713 au

C	-0.086051	-0.619930	-2.099547
C	-0.614527	0.025866	-1.005567
C	-0.061315	1.271095	-0.559440
C	0.994875	1.841725	-1.272629
C	2.635112	0.476655	-1.099413
C	2.272176	-0.818288	-1.455037
C	2.741957	0.522846	0.397833
C	2.066424	-1.603667	-0.217975
O	1.798308	-2.778352	-0.074803
O	3.143391	1.419795	1.101554
H	0.460366	-0.093827	-2.867234
H	-0.443882	-1.606860	-2.367812
H	1.484165	2.722926	-0.874149
H	1.037027	1.745975	-2.350211
H	3.259367	1.132826	-1.690362
H	2.438079	-1.309818	-2.401021
C	-0.441812	1.802192	0.756360
C	-0.208181	3.039134	1.204733
H	-0.957383	1.107200	1.411967
H	-0.499961	3.332925	2.206505

H	0.268398	3.802983	0.599976
C	-1.690794	-0.663503	-0.218303
C	-1.475449	-1.860924	0.346418
H	-2.273853	-2.387445	0.857693
H	-0.515760	-2.361798	0.291188
N	2.270103	-0.711387	0.845819
C	2.177503	-1.089123	2.240816
H	1.136067	-1.257664	2.530314
H	2.739408	-2.009534	2.418130
H	2.595309	-0.272372	2.830803
C	-3.024043	-0.008719	-0.153555
C	-3.378376	0.969667	-1.002520
H	-4.344110	1.454466	-0.921880
H	-2.718366	1.313295	-1.789375
C	-3.962071	-0.472733	0.892237
C	-5.265699	-0.686746	0.716316
H	-3.525491	-0.653680	1.872933
H	-5.904121	-0.995107	1.537239
H	-5.737938	-0.569602	-0.253798

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N_term_ttct2
G4(MP2)
Eel = -863.34712800 au; Energy(0K)) = -863.03499693 au
Enthalpy = -863.01392554 au; Gibbs energy = -863.08044733 au

C	-2.193349	-2.442540	-0.593133
C	-1.003629	-1.876058	-0.980154
C	-0.046414	-1.365943	-0.069630
C	-0.303482	-1.467880	1.294192
C	-2.141742	-0.281018	1.577602
C	-3.132314	-0.692525	0.694347
C	-1.605434	1.027695	1.083436
C	-3.236285	0.312862	-0.397168
O	-4.011999	0.368974	-1.323152
O	-0.800890	1.768719	1.604178
H	-2.305408	-2.937305	0.362036
H	-2.944225	-2.690956	-1.334948
H	-0.859238	-1.663056	-2.034534
H	0.362368	-0.996589	2.006006
H	-0.871255	-2.305115	1.679242
H	-2.103597	-0.506034	2.633906
H	-3.963151	-1.346978	0.909997
C	1.076876	-0.516298	-0.564084
C	0.943418	0.244777	-1.663597
H	1.763417	0.848801	-2.031369

H	0.016584	0.292426	-2.221411
C	2.378437	-0.546456	0.167256
C	2.811138	-1.659192	0.776507
H	3.767879	-1.686234	1.284272
H	2.225832	-2.571141	0.781799
N	-2.232653	1.262984	-0.136475
C	-1.997232	2.438512	-0.947918
H	-2.723477	2.425193	-1.761767
H	-2.123182	3.344488	-0.349068
H	-0.981148	2.430639	-1.353255
C	3.206090	0.703805	0.197102
C	2.670182	1.851956	0.642959
H	3.268932	2.756054	0.699239
H	1.635697	1.926244	0.960121
C	4.605816	0.683351	-0.247253
C	5.259572	-0.317110	-0.843468
H	5.131755	1.623287	-0.085740
H	6.290831	-0.198795	-1.156869
H	4.793183	-1.274989	-1.042509

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N_bis_butdiene_2
G4(MP2)
Eel = -863.34137500 au; Energy(0K)) = -863.02944331 au
Enthalpy = -863.00816713 au; Gibbs energy = -863.07508965 au

C	-0.362749	-1.401934	-1.791132
C	-1.043703	-0.689061	-0.817471
C	-0.940660	0.740414	-0.793291
C	-0.168529	1.373482	-1.762099
C	1.938742	0.557075	-1.607628
C	1.875549	-0.827329	-1.536493
C	2.324196	1.072752	-0.258638
C	2.172618	-1.232444	-0.131218
O	2.258826	-2.345215	0.341478
O	2.587196	2.201211	0.082807
H	-0.133903	-0.966979	-2.752428
H	-0.394494	-2.484673	-1.771331
H	0.011228	2.438618	-1.680323
H	-0.081117	0.964158	-2.759105
H	2.185460	1.140480	-2.482419
H	2.057556	-1.526051	-2.338910
C	-1.568092	1.628100	0.241521
C	-2.290170	2.675486	-0.198811
H	-2.761501	3.363178	0.495750
H	-2.444768	2.863914	-1.254254

C	-1.792022	-1.493133	0.203631
C	-1.187262	-2.473120	0.893903
H	-1.752672	-3.083545	1.591095
H	-0.130302	-2.692910	0.794143
N	2.368066	-0.045915	0.582374
C	2.794259	0.009857	1.966384
H	2.251912	0.799318	2.488991
H	2.586316	-0.960173	2.419626
H	3.867185	0.217132	2.035958
C	-3.235009	-1.278391	0.369595
C	-4.036251	-0.557865	-0.417783
H	-3.669718	-1.813723	1.211621
H	-5.100718	-0.492485	-0.222333
H	-3.666528	-0.013795	-1.279014
C	-1.430224	1.455578	1.692559
C	-0.635212	0.617228	2.357568
H	-2.050578	2.140719	2.267482
H	-0.618083	0.613916	3.441996
H	0.007202	-0.093828	1.858978

############################

N_bis_butdiene_1
G4(MP2)
Eel = -863.34044700 au; Energy(0K)) = -863.02860615 au
Enthalpy = -863.00734282 au; Gibbs energy = -863.07438354 au

C	-0.751730	1.012570	-2.075991
C	0.266868	1.098189	-1.139845
C	1.214732	0.030329	-1.025818
C	1.038481	-1.115521	-1.790426
C	-1.032722	-1.899585	-1.252868
C	-1.935586	-0.873300	-1.491686
C	-0.914579	-2.071018	0.226876
C	-2.442641	-0.382883	-0.177238
O	-3.314782	0.419257	0.059388
O	-0.281804	-2.896605	0.849566
H	-0.617080	0.477055	-3.006027
H	-1.540650	1.754902	-2.072140
H	1.708639	-1.955826	-1.646454
H	0.566203	-1.072973	-2.760289
H	-0.819993	-2.735259	-1.902756
H	-2.533193	-0.736610	-2.380698
C	2.362904	0.045354	-0.072017
C	3.096942	1.152811	0.116557
H	3.931485	1.152508	0.808382
H	2.884997	2.079667	-0.400658

C	0.201630	2.249629	-0.179856
C	0.182284	3.500387	-0.663771
H	0.145620	4.360932	-0.005199
H	0.225411	3.695064	-1.729184
N	-1.714553	-1.079006	0.797500
C	-1.948820	-0.942587	2.221313
H	-2.987830	-1.185597	2.462896
H	-1.281133	-1.637977	2.731565
H	-1.747009	0.081855	2.540407
C	2.708184	-1.229902	0.596835
C	3.951499	-1.660562	0.816607
H	1.872053	-1.854631	0.904178
H	4.139304	-2.592017	1.339653
H	4.820579	-1.105048	0.477814
C	0.110893	1.972373	1.269410
C	-0.585071	2.703110	2.142654
H	0.636977	1.092056	1.622866
H	-0.597570	2.453780	3.198312
H	-1.171850	3.563581	1.838784

############################

N_term_ctct
b3lyp/6-31g(d)
Eel = -864.30088002 au; Energy(0K)) = -863.98242842 au
Enthalpy = -863.96153539 au; Gibbs energy = -864.02783385 au

C	-1.485582	-2.001689	-1.540354
C	-0.302496	-1.443371	-1.099581
C	0.092018	-1.421905	0.265176
C	-0.752681	-1.982389	1.214748
C	-2.729325	-0.809830	0.947229
C	-3.051028	-0.806682	-0.406581
C	-2.195582	0.538234	1.294823
C	-2.699157	0.535141	-0.964267
O	-2.881620	0.971822	-2.084587
O	-1.900331	0.990822	2.387319
H	-1.926376	-2.856010	-1.038430
H	-1.795616	-1.859557	-2.571258
H	0.260436	-0.826042	-1.794397
H	-0.519041	-1.898522	2.271099
H	-1.401138	-2.808045	0.950347
H	-3.187416	-1.422972	1.712131
H	-3.818657	-1.402939	-0.882331
C	1.289921	-0.618915	0.673804
C	1.258885	0.184819	1.753760
H	2.141122	0.736370	2.061162

H	0.362106	0.326272	2.347120
C	2.546287	-0.767347	-0.118170
C	2.811944	-1.853151	-0.865644
H	3.745139	-1.935566	-1.413895
H	2.116964	-2.682449	-0.949859
N	-2.100255	1.241526	0.089970
C	-1.585871	2.594137	-0.016636
H	-1.846195	2.967000	-1.008696
H	-2.036749	3.225101	0.754043
H	-0.498332	2.604179	0.110349
C	3.584234	0.312198	-0.013519
C	4.754096	0.061246	0.603372
H	5.530577	0.819603	0.674221
H	4.964404	-0.903728	1.053381
C	3.339965	1.635098	-0.609329
C	2.296874	1.988522	-1.371258
H	4.119214	2.371912	-0.413944
H	2.219674	2.988780	-1.786859
H	1.492258	1.300072	-1.611266

############################

N_term_ttct1
b3lyp/6-31g(d)
Eel = -864.30054668 au; Energy(0K)) = -863.98203255 au
Enthalpy = -863.96118129 au; Gibbs energy = -864.02743444 au

C	-2.156510	-2.478417	-0.395999
C	-0.951921	-1.977035	-0.836096
C	0.033196	-1.421152	0.024281
C	-0.212651	-1.393385	1.393448
C	-2.097037	-0.155125	1.595540
C	-3.065559	-0.622137	0.715165
C	-1.542926	1.115690	1.035140
C	-3.126885	0.307851	-0.449640
O	-3.874274	0.292339	-1.409039
O	-0.754490	1.896181	1.537152
H	-2.267645	-2.906876	0.593074
H	-2.917981	-2.766000	-1.114869
H	-0.811948	-1.848132	-1.906288
H	0.468645	-0.876453	2.060348
H	-0.811504	-2.169083	1.856228
H	-2.074548	-0.323799	2.664419
H	-3.917579	-1.242068	0.959462
C	1.198970	-0.693996	-0.571568
C	1.056303	0.033088	-1.697552
H	1.903794	0.522827	-2.164136

H	0.093457	0.159333	-2.180296
C	2.545769	-0.837775	0.056367
C	2.860615	-1.860901	0.870649
H	3.857794	-1.947815	1.290011
H	2.147048	-2.634934	1.133286
N	-2.128018	1.271136	-0.223404
C	-1.858128	2.393804	-1.100962
H	-2.487403	2.277645	-1.984957
H	-2.094948	3.337207	-0.599332
H	-0.802310	2.405764	-1.387001
C	3.620886	0.144543	-0.311324
C	4.692505	-0.279269	-1.008495
H	5.501199	0.399708	-1.269223
H	4.787688	-1.309016	-1.337855
C	3.531045	1.552072	0.108398
C	2.580503	2.107881	0.870370
H	4.354106	2.175883	-0.241426
H	2.626594	3.161612	1.130200
H	1.722745	1.563673	1.250934

############################

N_term_ttct2
b3lyp/6-31g(d)
Eel = -864.29966453 au; Energy(0K)) = -863.98122927 au
Enthalpy = -863.96038321 au; Gibbs energy = -864.02654980 au

C	-2.186481	-2.461953	-0.587473
C	-0.998523	-1.888116	-0.975944
C	-0.039472	-1.369262	-0.064045
C	-0.294932	-1.466124	1.302067
C	-2.150318	-0.272866	1.584233
C	-3.141377	-0.693577	0.704355
C	-1.621648	1.037050	1.082556
C	-3.250155	0.304252	-0.394410
O	-4.029856	0.345691	-1.327072
O	-0.813291	1.785883	1.602003
H	-2.298393	-2.952990	0.371582
H	-2.936199	-2.716460	-1.330730
H	-0.856818	-1.674738	-2.032150
H	0.372022	-0.990190	2.012305
H	-0.862275	-2.303243	1.692516
H	-2.110969	-0.493029	2.643540
H	-3.968868	-1.354037	0.924891
C	1.081193	-0.514593	-0.564464
C	0.939152	0.247796	-1.666945
H	1.756753	0.853871	-2.041394

H	0.006319	0.296203	-2.218127
C	2.389821	-0.542471	0.161183
C	2.827663	-1.660007	0.767828
H	3.786665	-1.686407	1.274916
H	2.244224	-2.575284	0.772262
N	-2.252337	1.265325	-0.139828
C	-2.022555	2.440591	-0.957164
H	-2.738436	2.412171	-1.780385
H	-2.170025	3.348602	-0.365031
H	-1.000493	2.441000	-1.348721
C	3.219017	0.709471	0.190764
C	2.678412	1.865385	0.623528
H	3.276779	2.771889	0.679144
H	1.639806	1.942684	0.931631
C	4.627533	0.686689	-0.238126
C	5.287463	-0.318529	-0.829410
H	5.156514	1.625435	-0.071474
H	6.324198	-0.200654	-1.130741
H	4.821985	-1.277122	-1.035896

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N_butdien_vinyl_1
b3lyp/6-31g(d)
Eel = -864.29837529 au; Energy(0K)) = -863.98032756 au
Enthalpy = -863.95911186 au; Gibbs energy = -864.02603846 au

C	-0.094330	-0.616095	-2.111571
C	-0.624360	0.028388	-1.015118
C	-0.070699	1.278245	-0.563797
C	0.987490	1.852604	-1.274416
C	2.642906	0.487253	-1.095022
C	2.290865	-0.810664	-1.455239
C	2.749011	0.528976	0.403667
C	2.089285	-1.601789	-0.220709
O	1.825700	-2.785387	-0.083998
O	3.143251	1.434990	1.111775
H	0.461221	-0.091119	-2.875898
H	-0.454201	-1.602758	-2.384315
H	1.473773	2.736454	-0.874180
H	1.031988	1.759335	-2.353785
H	3.267219	1.148162	-1.684278
H	2.459378	-1.297430	-2.405652
C	-0.451661	1.804526	0.757000
C	-0.221579	3.046527	1.205961
H	-0.965358	1.107807	1.414353
H	-0.512498	3.338068	2.210460

H	0.251245	3.814190	0.599917
C	-1.699052	-0.668166	-0.227071
C	-1.473955	-1.871042	0.332397
H	-2.267626	-2.409520	0.842105
H	-0.508393	-2.363525	0.273215
N	2.287256	-0.712093	0.849913
C	2.197330	-1.098902	2.244842
H	1.157884	-1.298824	2.523491
H	2.787188	-2.002518	2.422472
H	2.586665	-0.271991	2.840959
C	-3.038091	-0.019108	-0.152319
C	-3.403068	0.960971	-1.001528
H	-4.369833	1.445747	-0.912021
H	-2.750490	1.306498	-1.796177
C	-3.968930	-0.487847	0.901227
C	-5.279631	-0.693610	0.734860
H	-3.525722	-0.679946	1.878456
H	-5.912342	-1.004520	1.561559
H	-5.761689	-0.567885	-0.231269

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N_bis_butdiene_1
b3lyp/6-31g(d)
Eel = -864.29135748 au; Energy(0K)) = -863.97328441 au
Enthalpy = -863.95222476 au; Gibbs energy = -864.01897829 au

C	-0.736766	1.026557	-2.085151
C	0.283580	1.096873	-1.147221
C	1.221060	0.011958	-1.034247
C	1.027314	-1.134734	-1.796315
C	-1.066191	-1.898063	-1.246284
C	-1.956948	-0.861088	-1.490877
C	-0.952304	-2.064720	0.235373
C	-2.458155	-0.357229	-0.178884
O	-3.325379	0.462464	0.051087
O	-0.326141	-2.901359	0.863421
H	-0.611253	0.487907	-3.016751
H	-1.518822	1.778309	-2.079842
H	1.690247	-1.983338	-1.655997
H	0.548645	-1.089311	-2.764667
H	-0.865014	-2.741078	-1.893806
H	-2.551356	-0.720731	-2.383910
C	2.372342	0.014765	-0.079383
C	3.121062	1.118314	0.105229
H	3.955888	1.113312	0.799252
H	2.919397	2.046987	-0.416664

C	0.232581	2.247408	-0.180496
C	0.219525	3.502977	-0.664567
H	0.192658	4.364999	-0.004746
H	0.259210	3.699708	-1.731572
N	-1.738891	-1.057257	0.803131
C	-1.974930	-0.908368	2.227578
H	-3.009285	-1.169872	2.473298
H	-1.292839	-1.584006	2.746278
H	-1.790658	0.124937	2.529995
C	2.705964	-1.264241	0.593937
C	3.949726	-1.702183	0.822716
H	1.864637	-1.886245	0.897430
H	4.128533	-2.635213	1.349653
H	4.825847	-1.152033	0.487764
C	0.146443	1.971396	1.272430
C	-0.530255	2.719477	2.152544
H	0.656963	1.080184	1.625517
H	-0.538276	2.471009	3.210196
H	-1.104407	3.591847	1.852299

############################

N_bis_butdiene_2
b3lyp/6-31g(d)
Eel = -864.29014335 au; Energy(0K)) = -863.97190612 au
Enthalpy = -863.95085840 au; Gibbs energy = -864.01745901 au

C	-0.368936	-1.406891	-1.795856
C	-1.051207	-0.693322	-0.821405
C	-0.951225	0.742472	-0.797546
C	-0.179917	1.379015	-1.767344
C	1.944589	0.567290	-1.605954
C	1.890680	-0.818999	-1.540551
C	2.326610	1.079558	-0.253751
C	2.192527	-1.228838	-0.137529
O	2.290097	-2.350545	0.329439
O	2.583999	2.215682	0.091054
H	-0.135235	-0.971624	-2.757709
H	-0.400178	-2.491185	-1.777093
H	-0.002802	2.446171	-1.685504
H	-0.089943	0.970445	-2.766357
H	2.191190	1.155129	-2.480289
H	2.074518	-1.513544	-2.348908
C	-1.581857	1.628292	0.240485
C	-2.306709	2.678938	-0.199766
H	-2.780739	3.366803	0.495573
H	-2.461896	2.869508	-1.256600

C	-1.795134	-1.499086	0.205705
C	-1.181007	-2.478746	0.895997
H	-1.739392	-3.094323	1.597004
H	-0.121412	-2.692254	0.792460
N	2.375844	-0.042995	0.585779
C	2.809362	0.009840	1.969951
H	2.289402	0.819528	2.485327
H	2.574664	-0.949991	2.432864
H	3.888976	0.186035	2.033022
C	-3.241617	-1.290774	0.378762
C	-4.051186	-0.575241	-0.411953
H	-3.673246	-1.823798	1.225439
H	-5.116565	-0.513456	-0.210707
H	-3.687725	-0.031536	-1.278251
C	-1.447632	1.450617	1.694944
C	-0.633601	0.621143	2.356548
H	-2.082171	2.119897	2.275217
H	-0.619629	0.609636	3.442681
H	0.026069	-0.073173	1.853019

############################

wB97X first five excited singlet states for each conformer of [3]-[8]dendralenes. The conformers for each dendralene are ordered in decreasing energy, with the most stable conformer first.

[3]Dendralene conformers

ct_trans_3_Dendralene   6-311+G(2d,p) basis set

```
wB97X   State 1:  Singlet-A  5.263 eV   235.6 nm   f=0.4065 <S**2>=0.000
wB97X   State 2:  Singlet-A  6.153 eV   201.5 nm   f=0.5291 <S**2>=0.000
wB97X   State 3:  Singlet-A  6.390 eV   194.0 nm   f=0.0386 <S**2>=0.000
wB97X   State 4:  Singlet-A  6.741 eV   183.9 nm   f=0.0184 <S**2>=0.000
wB97X   State 5:  Singlet-A  7.205 eV   172.1 nm   f=0.0091 <S**2>=0.000
```

tt_3_Dendralene   6-311+G(2d,p) basis set

```
wB97X   State 1:  Singlet-A  5.280 eV   234.8 nm   f=0.6366 <S**2>=0.000
wB97X   State 2:  Singlet-A  5.851 eV   211.9 nm   f=0.1455 <S**2>=0.000
wB97X   State 3:  Singlet-A  6.374 eV   194.5 nm   f=0.0643 <S**2>=0.000
wB97X   State 4:  Singlet-A  6.665 eV   186.0 nm   f=0.0020 <S**2>=0.000
wB97X   State 5:  Singlet-A  7.108 eV   174.4 nm   f=0.0002 <S**2>=0.000
```

```
cc_3_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.039 eV    246.1 nm    f=0.1248 <S**2>=0.000
wB97X    State 2:  Singlet-B   6.026 eV    205.8 nm    f=0.5812 <S**2>=0.000
wB97X    State 3:  Singlet-B   6.451 eV    192.2 nm    f=0.1193 <S**2>=0.000
wB97X    State 4:  Singlet-B   6.783 eV    182.8 nm    f=0.0315 <S**2>=0.000
wB97X    State 5:  Singlet-A   7.267 eV    170.6 nm    f=0.0010 <S**2>=0.000
```

[4]Dendralene conformers

```
ttt_4_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-B   5.543 eV    223.7 nm    f=0.3176 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.574 eV    222.4 nm    f=0.4030 <S**2>=0.000
wB97X    State 3:  Singlet-B   5.810 eV    213.4 nm    f=0.2086 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.837 eV    212.4 nm    f=0.3692 <S**2>=0.000
wB97X    State 5:  Singlet-B   6.840 eV    181.2 nm    f=0.0050 <S**2>=0.000
```

```
cct_4_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.340 eV    232.2 nm    f=0.1037 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.613 eV    220.9 nm    f=0.7666 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.875 eV    211.1 nm    f=0.0239 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.994 eV    206.9 nm    f=0.1322 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.787 eV    182.7 nm    f=0.0053 <S**2>=0.000
```

```
ctc_4_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.179 eV    239.4 nm    f=0.4207 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.691 eV    217.9 nm    f=0.0059 <S**2>=0.000
wB97X    State 3:  Singlet-A   6.139 eV    202.0 nm    f=0.0008 <S**2>=0.000
wB97X    State 4:  Singlet-A   6.481 eV    191.3 nm    f=0.4348 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.721 eV    184.5 nm    f=0.3899 <S**2>=0.000
```

```
ctt_4_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.146 eV    240.9 nm    f=0.3999 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.539 eV    223.8 nm    f=0.1879 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.951 eV    208.3 nm    f=0.0179 <S**2>=0.000
wB97X    State 4:  Singlet-A   6.402 eV    193.7 nm    f=0.4253 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.640 eV    186.7 nm    f=0.0400 <S**2>=0.000
```

ccc_4_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.224 eV    237.3 nm    f=0.0886 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.612 eV    220.9 nm    f=0.3700 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.958 eV    208.1 nm    f=0.1300 <S**2>=0.000
wB97X    State 4:  Singlet-A   6.440 eV    192.5 nm    f=0.3556 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.777 eV    182.9 nm    f=0.0111 <S**2>=0.000
```

[5]Dendralene conformers

tctt_5_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.277 eV    235.0 nm    f=0.4205 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.504 eV    225.2 nm    f=0.2523 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.688 eV    218.0 nm    f=0.2072 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.901 eV    210.1 nm    f=0.2107 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.935 eV    208.9 nm    f=0.1673 <S**2>=0.000
```

ctct_5_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.235 eV    236.8 nm    f=0.2819 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.555 eV    223.2 nm    f=0.4045 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.696 eV    217.7 nm    f=0.0839 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.845 eV    212.1 nm    f=0.2321 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.188 eV    200.4 nm    f=0.3565 <S**2>=0.000
```

tcct_5_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.284 eV    234.7 nm    f=0.0035 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.499 eV    225.5 nm    f=0.7329 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.787 eV    214.2 nm    f=0.2495 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.825 eV    212.8 nm    f=0.0906 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.260 eV    198.1 nm    f=0.2343 <S**2>=0.000
```

ccct_5_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.158 eV    240.4 nm    f=0.0574 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.570 eV    222.6 nm    f=0.5520 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.815 eV    213.2 nm    f=0.2035 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.865 eV    211.4 nm    f=0.1186 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.177 eV    200.7 nm    f=0.3089 <S**2>=0.000
```

```
cctt_5_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.147 eV    240.9 nm    f=0.1647 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.365 eV    231.1 nm    f=0.4427 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.643 eV    219.7 nm    f=0.1812 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.813 eV    213.3 nm    f=0.0653 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.095 eV    203.4 nm    f=0.1211 <S**2>=0.000
```

```
ctcc_5_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.222 eV    237.4 nm    f=0.2264 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.348 eV    231.8 nm    f=0.3229 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.759 eV    215.3 nm    f=0.1832 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.872 eV    211.1 nm    f=0.0114 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.288 eV    197.2 nm    f=0.2908 <S**2>=0.000
```

```
cttc_5_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.136 eV    241.4 nm    f=0.4655 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.160 eV    240.3 nm    f=0.0923 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.827 eV    212.8 nm    f=0.0133 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.880 eV    210.9 nm    f=0.0054 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.495 eV    190.9 nm    f=0.1641 <S**2>=0.000
```

```
cccc_5_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-B   5.151 eV    240.7 nm    f=0.1450 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.182 eV    239.2 nm    f=0.0091 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.772 eV    214.8 nm    f=0.6190 <S**2>=0.000
wB97X    State 4:  Singlet-B   6.033 eV    205.5 nm    f=0.0272 <S**2>=0.000
wB97X    State 5:  Singlet-B   6.343 eV    195.5 nm    f=0.3627 <S**2>=0.000
```

[6]Dendralene conformers

```
tctct_C2_SYMMETRY_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-B   5.403 eV    229.5 nm    f=0.2012 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.522 eV    224.5 nm    f=0.4025 <S**2>=0.000
wB97X    State 3:  Singlet-B   5.558 eV    223.1 nm    f=0.1859 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.656 eV    219.2 nm    f=0.0122 <S**2>=0.000
wB97X    State 5:  Singlet-B   5.865 eV    211.4 nm    f=0.0784 <S**2>=0.000
```

```
tctct_Ci_SYMMETRY_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-AU  5.335 eV   232.4 nm   f=0.2156 <S**2>=0.000
wB97X   State 2:  Singlet-AU  5.448 eV   227.6 nm   f=0.3701 <S**2>=0.000
wB97X   State 3:  Singlet-AG  5.489 eV   225.9 nm   f=0.0000 <S**2>=0.000
wB97X   State 4:  Singlet-AG  5.773 eV   214.8 nm   f=0.0000 <S**2>=0.000
wB97X   State 5:  Singlet-AU  5.841 eV   212.3 nm   f=0.7887 <S**2>=0.000
```

```
tctct_C2_SYMMETRY_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-B   5.403 eV   229.5 nm   f=0.2012 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.522 eV   224.5 nm   f=0.4025 <S**2>=0.000
wB97X   State 3:  Singlet-B   5.558 eV   223.1 nm   f=0.1859 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.656 eV   219.2 nm   f=0.0122 <S**2>=0.000
wB97X   State 5:  Singlet-B   5.865 eV   211.4 nm   f=0.0784 <S**2>=0.000
```

```
tctct_Ci_SYMMETRY_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-AU  5.335 eV   232.4 nm   f=0.2156 <S**2>=0.000
wB97X   State 2:  Singlet-AU  5.448 eV   227.6 nm   f=0.3701 <S**2>=0.000
wB97X   State 3:  Singlet-AG  5.489 eV   225.9 nm   f=0.0000 <S**2>=0.000
wB97X   State 4:  Singlet-AG  5.773 eV   214.8 nm   f=0.0000 <S**2>=0.000
wB97X   State 5:  Singlet-AU  5.841 eV   212.3 nm   f=0.7887 <S**2>=0.000
```

```
tccct_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.481 eV   226.2 nm   f=0.1584 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.543 eV   223.7 nm   f=0.0427 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.758 eV   215.3 nm   f=1.0520 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.854 eV   211.8 nm   f=0.1544 <S**2>=0.000
wB97X   State 5:  Singlet-A   5.888 eV   210.6 nm   f=0.0417 <S**2>=0.000
```

```
tctcc_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.311 eV   233.4 nm   f=0.1086 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.511 eV   225.0 nm   f=0.3246 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.575 eV   222.4 nm   f=0.5783 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.673 eV   218.5 nm   f=0.0688 <S**2>=0.000
wB97X   State 5:  Singlet-A   5.832 eV   212.6 nm   f=0.1868 <S**2>=0.000
```

```
tcctt_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.131 eV   241.7 nm   f=0.1191 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.345 eV   232.0 nm   f=0.1542 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.420 eV   228.7 nm   f=0.3057 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.712 eV   217.1 nm   f=0.2094 <S**2>=0.000
wB97X   State 5:  Singlet-A   5.866 eV   211.3 nm   f=0.3291 <S**2>=0.000
```

```
ttctt_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.146 eV   240.9 nm   f=0.4161 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.240 eV   236.6 nm   f=0.0854 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.626 eV   220.4 nm   f=0.4938 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.715 eV   216.9 nm   f=0.0043 <S**2>=0.000
wB97X   State 5:  Singlet-A   6.003 eV   206.6 nm   f=0.1399 <S**2>=0.000
```

```
ctcct_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.122 eV   242.1 nm   f=0.1339 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.361 eV   231.3 nm   f=0.4105 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.582 eV   222.1 nm   f=0.1959 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.782 eV   214.4 nm   f=0.0773 <S**2>=0.000
wB97X   State 5:  Singlet-A   5.932 eV   209.0 nm   f=0.1867 <S**2>=0.000
```

```
tcttc_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.128 eV   241.8 nm   f=0.3281 <S**2>=0.000
wB97X   State 2:  Singlet-A   5.339 eV   232.2 nm   f=0.1100 <S**2>=0.000
wB97X   State 3:  Singlet-A   5.540 eV   223.8 nm   f=0.3830 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.739 eV   216.0 nm   f=0.0041 <S**2>=0.000
wB97X   State 5:  Singlet-A   5.834 eV   212.5 nm   f=0.2121 <S**2>=0.000
```

```
ctctc_6_Dendralene    6-311+G(2d,p) basis set
wB97X   State 1:  Singlet-A   5.144 eV   241.0 nm   f=0.1581 <S**2>=0.000
wB97X   State 2:  Singlet-B   5.296 eV   234.1 nm   f=0.4893 <S**2>=0.000
wB97X   State 3:  Singlet-B   5.621 eV   220.6 nm   f=0.0238 <S**2>=0.000
wB97X   State 4:  Singlet-A   5.831 eV   212.6 nm   f=0.0722 <S**2>=0.000
wB97X   State 5:  Singlet-A   6.167 eV   201.0 nm   f=0.3312 <S**2>=0.000
```

```
cccct_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.263 eV    235.6 nm    f=0.0261 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.449 eV    227.5 nm    f=0.0331 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.659 eV    219.1 nm    f=0.8039 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.908 eV    209.8 nm    f=0.1089 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.941 eV    208.7 nm    f=0.1120 <S**2>=0.000
```

```
ctctt_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.265 eV    235.5 nm    f=0.2779 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.400 eV    229.6 nm    f=0.5371 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.639 eV    219.9 nm    f=0.0162 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.785 eV    214.3 nm    f=0.0105 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.854 eV    211.8 nm    f=0.1798 <S**2>=0.000
```

```
ccctt_2nd_Conf_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.169 eV    239.9 nm    f=0.1216 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.300 eV    233.9 nm    f=0.3707 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.453 eV    227.4 nm    f=0.0608 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.698 eV    217.6 nm    f=0.1156 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.872 eV    211.2 nm    f=0.2397 <S**2>=0.000
```

```
ctccc_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.218 eV    237.6 nm    f=0.1678 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.335 eV    232.4 nm    f=0.3010 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.542 eV    223.7 nm    f=0.0709 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.922 eV    209.3 nm    f=0.0351 <S**2>=0.000
wB97X    State 5:  Singlet-A   6.083 eV    203.8 nm    f=0.4681 <S**2>=0.000
```

```
cctcc_6_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.274 eV    235.1 nm    f=0.0652 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.318 eV    233.1 nm    f=0.1943 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.550 eV    223.4 nm    f=0.6871 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.721 eV    216.7 nm    f=0.0563 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.928 eV    209.2 nm    f=0.0915 <S**2>=0.000
```

ccccc_6_Dendralene   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   4.899 eV    253.1 nm    f=0.0068 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.021 eV    246.9 nm    f=0.0066 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.465 eV    226.9 nm    f=0.4103 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.932 eV    209.0 nm    f=0.0016 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.972 eV    207.6 nm    f=0.7111 <S**2>=0.000
```

[7]Dendralene conformers

C14   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.270 eV    235.3 nm    f=0.3165 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.385 eV    230.3 nm    f=0.1770 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.592 eV    221.7 nm    f=0.4311 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.691 eV    217.9 nm    f=0.1585 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.826 eV    212.8 nm    f=0.1219 <S**2>=0.000
```

C34   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.205 eV    238.2 nm    f=0.3049 <S**2>=0.000
wB97X    State 2:  Singlet-B   5.370 eV    230.9 nm    f=0.0686 <S**2>=0.000
wB97X    State 3:  Singlet-B   5.537 eV    223.9 nm    f=0.4804 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.551 eV    223.3 nm    f=0.1166 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.712 eV    217.1 nm    f=0.0057 <S**2>=0.000
```

C16   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.194 eV    238.7 nm    f=0.2174 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.455 eV    227.3 nm    f=0.3368 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.576 eV    222.3 nm    f=0.3297 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.676 eV    218.4 nm    f=0.0544 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.764 eV    215.1 nm    f=0.1326 <S**2>=0.000
```

C5   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.237 eV    236.7 nm    f=0.1924 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.368 eV    230.9 nm    f=0.3990 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.474 eV    226.5 nm    f=0.2949 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.649 eV    219.5 nm    f=0.0430 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.772 eV    214.8 nm    f=0.0222 <S**2>=0.000
```

C6   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.203 eV    238.3 nm    f=0.2066 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.355 eV    231.6 nm    f=0.2369 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.468 eV    226.7 nm    f=0.2100 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.695 eV    217.7 nm    f=0.2097 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.769 eV    214.9 nm    f=0.0078 <S**2>=0.000
```

C21   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.293 eV    234.2 nm    f=0.0252 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.478 eV    226.3 nm    f=0.5541 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.542 eV    223.7 nm    f=0.3591 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.628 eV    220.3 nm    f=0.0965 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.739 eV    216.1 nm    f=0.1725 <S**2>=0.000
```

C28   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.200 eV    238.4 nm    f=0.0656 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.396 eV    229.8 nm    f=0.2398 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.542 eV    223.7 nm    f=0.3390 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.680 eV    218.3 nm    f=0.2762 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.791 eV    214.1 nm    f=0.2002 <S**2>=0.000
```

C26   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.194 eV    238.7 nm    f=0.2445 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.316 eV    233.2 nm    f=0.1889 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.454 eV    227.3 nm    f=0.1163 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.739 eV    216.0 nm    f=0.3860 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.777 eV    214.6 nm    f=0.0278 <S**2>=0.000
```

C15   6-311+G(2d,p) basis set

```
wB97X    State 1:  Singlet-A   5.154 eV    240.6 nm    f=0.2456 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.382 eV    230.4 nm    f=0.2706 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.499 eV    225.5 nm    f=0.2549 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.632 eV    220.2 nm    f=0.1493 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.736 eV    216.2 nm    f=0.1401 <S**2>=0.000
```

```
C8     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.263 eV    235.6 nm    f=0.1660 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.382 eV    230.4 nm    f=0.3246 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.501 eV    225.4 nm    f=0.2429 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.653 eV    219.3 nm    f=0.0130 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.749 eV    215.7 nm    f=0.1865 <S**2>=0.000
```

[8]Dendralene conformers

```
C6c_8_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.344 eV    232.0 nm    f=0.0326 <S**2>=0.000
wB97X    State 2:  Singlet-B   5.527 eV    224.3 nm    f=0.4245 <S**2>=0.000
wB97X    State 3:  Singlet-B   5.598 eV    221.5 nm    f=0.3291 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.603 eV    221.3 nm    f=0.2330 <S**2>=0.000
wB97X    State 5:  Singlet-B   5.698 eV    217.6 nm    f=0.0753 <S**2>=0.000
```

```
C6a_8_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.264 eV    235.5 nm    f=0.0709 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.387 eV    230.2 nm    f=0.3849 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.466 eV    226.8 nm    f=0.1661 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.539 eV    223.8 nm    f=0.1591 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.632 eV    220.2 nm    f=0.1103 <S**2>=0.000
```

```
C23     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-B   5.219 eV    237.6 nm    f=0.1886 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.311 eV    233.4 nm    f=0.1742 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.445 eV    227.7 nm    f=0.1574 <S**2>=0.000
wB97X    State 4:  Singlet-B   5.471 eV    226.6 nm    f=0.1069 <S**2>=0.000
wB97X    State 5:  Singlet-B   5.740 eV    216.0 nm    f=0.0352 <S**2>=0.000
```

```
C6b_8_Dendralene     6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-B   5.219 eV    237.6 nm    f=0.1883 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.311 eV    233.4 nm    f=0.1746 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.445 eV    227.7 nm    f=0.1565 <S**2>=0.000
wB97X    State 4:  Singlet-B   5.471 eV    226.6 nm    f=0.1065 <S**2>=0.000
wB97X    State 5:  Singlet-B   5.740 eV    216.0 nm    f=0.0363 <S**2>=0.000
```

```
C19    6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.298 eV    234.0 nm    f=0.1080 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.405 eV    229.4 nm    f=0.0995 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.507 eV    225.1 nm    f=0.2659 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.593 eV    221.7 nm    f=0.0880 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.699 eV    217.6 nm    f=0.6836 <S**2>=0.000
```

```
C28    6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.305 eV    233.7 nm    f=0.1702 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.422 eV    228.7 nm    f=0.1645 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.530 eV    224.2 nm    f=0.0526 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.656 eV    219.2 nm    f=0.4944 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.787 eV    214.2 nm    f=0.0700 <S**2>=0.000
```

```
C6d_8_Dendralene    6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.277 eV    234.9 nm    f=0.1090 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.431 eV    228.3 nm    f=0.2947 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.488 eV    225.9 nm    f=0.1189 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.524 eV    224.4 nm    f=0.2387 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.571 eV    222.6 nm    f=0.0826 <S**2>=0.000
```

```
C14    6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.126 eV    241.9 nm    f=0.0839 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.351 eV    231.7 nm    f=0.3231 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.421 eV    228.7 nm    f=0.0901 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.554 eV    223.2 nm    f=0.3603 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.607 eV    221.1 nm    f=0.0773 <S**2>=0.000
```

```
C1    6-311+G(2d,p) basis set
wB97X    State 1:  Singlet-A   5.155 eV    240.5 nm    f=0.1810 <S**2>=0.000
wB97X    State 2:  Singlet-A   5.202 eV    238.4 nm    f=0.2924 <S**2>=0.000
wB97X    State 3:  Singlet-A   5.379 eV    230.5 nm    f=0.2001 <S**2>=0.000
wB97X    State 4:  Singlet-A   5.546 eV    223.5 nm    f=0.3414 <S**2>=0.000
wB97X    State 5:  Singlet-A   5.664 eV    218.9 nm    f=0.1471 <S**2>=0.000
```

C24 6-311+G(2d,p) basis set

```
wB97X   State 1:  Singlet-A  5.115 eV   242.4 nm   f=0.1436 <S**2>=0.000
wB97X   State 2:  Singlet-A  5.266 eV   235.4 nm   f=0.4784 <S**2>=0.000
wB97X   State 3:  Singlet-A  5.350 eV   231.8 nm   f=0.0293 <S**2>=0.000
wB97X   State 4:  Singlet-A  5.547 eV   223.5 nm   f=0.3335 <S**2>=0.000
wB97X   State 5:  Singlet-A  5.682 eV   218.2 nm   f=0.0166 <S**2>=0.000
```

C31 6-311+G(2d,p) basis set

```
wB97X   State 1:  Singlet-A  5.103 eV   242.9 nm   f=0.1647 <S**2>=0.000
wB97X   State 2:  Singlet-A  5.357 eV   231.4 nm   f=0.3359 <S**2>=0.000
wB97X   State 3:  Singlet-A  5.515 eV   224.8 nm   f=0.2981 <S**2>=0.000
wB97X   State 4:  Singlet-A  5.584 eV   222.0 nm   f=0.1724 <S**2>=0.000
wB97X   State 5:  Singlet-A  5.621 eV   220.6 nm   f=0.1147 <S**2>=0.000
```

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Chapter Three

Synthesis and Diels–Alder Reactivity of Substituted [4]Dendralenes

Context

As outlined in Chapter Two, different [*n*]dendralenes show different reactivity in Diels–Alder reactions towards dienophiles. While the simplest *odd* dendralene, [3]dendralene, undergoes a clean Diels–Alder reaction at room temperature, the smallest *even* dendralene, [4]dendralene, produces a complex mixture. This lack of selectivity limits use of [4]dendralene in targeted synthetic applications. The aim of the study presented in this chapter is to synthesize all five possible mono-methylated [4]dendralenes and investigate the influence of the methyl substituent on domino Diels–Alder sequences, as an exploratory investigation towards synthetic applications of [4]dendralenes.

The manuscript was published in the *Journal of Organic Chemistry* on 12 January, 2016. Reprinted (adapted) with permission (Saglam, M. F.; Alborzi, A. R.; Payne, A. D.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *J. Org. Chem.* **2016**, acs.joc.5b02583.). Copyright (2016) American Chemical Society. This paper was selected as an **ACS Editor's Choice** article on January 29, 2016. The other authors are Dr Ali R. Alborzi, Dr Alan D. Payne, Anthony C. Willis, Professor Michael N. Paddon-Row, and my supervisor Professor Michael S. Sherburn. The project was conceived, designed, and evolved, in collaboration with Dr Alborzi, Dr Payne, and Professor Sherburn. The draft manuscript was prepared in collaboration with Professor Sherburn and myself. Anthony C. Willis solved and refined X-ray crystallographic data from samples provided by Dr Alborzi and myself. The synthetic experiments were carried out by Dr Alborzi, Dr Payne, and myself. Syntheses of 2-methyl-, 3′*E*- and 3′*Z*—methyl substituted [4]dendralenes and their Diels–Alder reactions were originally carried out by Dr Alborzi and Dr Payne. I repeated and optimized both the synthesis of 2-methyl[4]dendralene and its Diels–Alder reaction with NMM. In addition, I prepared the two "missing" dendralenes to complete the set of five, namely 1*E*- and 1*Z*-methyl[4]dendralenes, and performed their Diels–Alder reactions with NMM.

Specific experimental contribution by myself:

Synthesis of chloroprene (**62**)

Synthesis of buta-1,3-dien-2-ylmagnesium chloride (**15**)

Synthesis of 2-chloro[3]dendralene (**17**)

Synthesis of (3-methylenepenta-1,4-dien-2-yl)magnesium chloride (**63**)

Synthesis of 1*E*-methyl[4]dendralene (**10**)

Synthesis of (*Z*)-prop-1-en-1-ylmagnesium bromide (**20**)

Synthesis of 1*Z*-methyl[4]dendralene (**11**)

Synthesis of prop-1-en-2-ylmagnesium bromide (**21**)

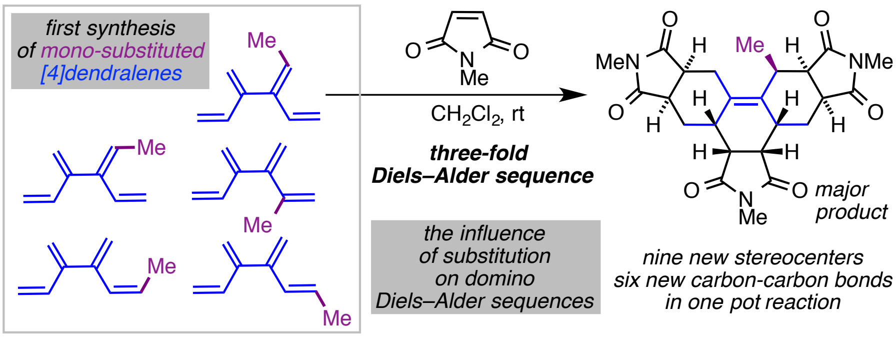
Synthesis of 2-methyl[4]dendralene (**12**)

Diels –Alder reaction between 1*E*-methyl[4]dendralene (**10**) and NMM

Diels –Alder reaction between 1*Z*-methyl[4]dendralene (**11**) and NMM

Diels –Alder reaction between parent [4]dendralene (**1**) and NMM in different solvents.

TOC Graphic



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Synthesis and Diels–Alder Reactivity of Substituted [4]Dendralenes

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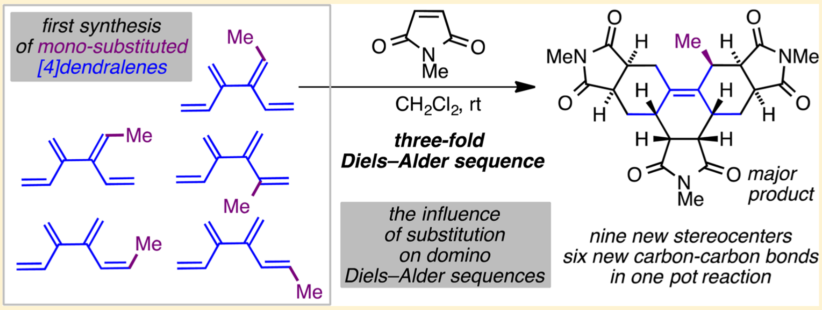
Supporting Information



ABSTRACT: The first synthesis of all five possible monomethylated [4]dendralenes has been achieved via two distinct synthetic strategies. The Diels–Alder chemistry of these new dendralenes (as multidienes) with an electron poor dienophile, *N*-methylmaleimide (NMM), has been studied. Thus, simply upon mixing the dendralene and an excess of dienophile at ambient temperature in a common solvent, sequences of cycloadditions result in the rapid generation of complex multicyclic products. Distinct product distributions are obtained with differently substituted dendralenes, demonstrating that dendralene substitution influences the pathway followed, when a matrix of mechanistic possibilities exists. Dendralene site selectivities are traced to electronic, steric and conformational effects, thereby allowing predictive tools for applications of substituted dendralenes in future synthetic endeavors.

INTRODUCTION

Dendralenes are acyclic, branched oligo-alkenes that have only recently become available through synthesis.[1] Dendralenes serve as multi-1,3-butadienes and possess the unique ability to participate in diene-transmissive Diels–Alder[2] reaction sequences.[3,4] Such processes rapidly generate complex polycyclic frameworks, and are beginning to feature in remarkably short step count total synthesis.[5] As depicted in Scheme 1, the first cycloaddition to the terminal site of a dendralene "transmits" olefinic character to a new site that is also conjugated to a pre-existing olefin on the dendralene framework. If this new 1,3-butadiene group can adopt an *s-cis* conformation, a second cycloaddition with either the same or a different dienophile can occur.

In principle, if successive cycloadditions occur at the 1,3-butadiene termini of the cross-conjugated chain, an [*n*]-dendralene can participate as diene in a maximum of ($n - 1$) diene-transmissive Diels–Alder cycloaddition reactions. [3]-Dendralenes, therefore, can undergo two cycloadditions, [4]dendralenes can undergo three cycloadditions, and so forth (Scheme 1).

Until now, studies into the Diels–Alder reactivity of *substituted* branched oligo-olefins have been limited to [3]-dendralene systems. With both the parent unsubstituted [3]dendralene and symmetrically multisubstituted systems (i.e., those carrying the same groups on both sides of the central C=C bond), the two 1,3-butadiene units are equivalent and there is no issue of site selection in the first cycloaddition event with a dienophile. With unsymmetrically substituted [3]dendralenes, different constitutional isomers can result from initial addition to the two dissimilar 1,3-butadiene sites. For target synthesis applications, it is imperative that the outcomes of these reactions can be predicted, and exploratory investigations have led to simple predictive guidelines (Figure 1).

With unsubstituted [4]dendralene (and its symmetrically multisubstituted analogues), diene-transmissive Diels–Alder sequences are more complex, since two different diene sites are available for both the first and second cycloaddition events (Scheme 2). With an excess of the electron poor dienophile *N*-methylmaleimide (NMM), for example, the parent [4]-dendralene (**1**) undergoes an initial Diels–Alder reaction favoring the terminal diene site, generating terminal mono-

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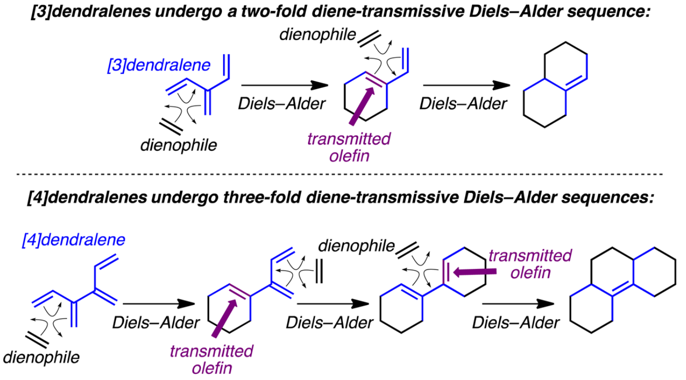
Scheme 1. Diene-Transmissive Diels–Alder Cycloaddition Sequences of [3]- and [4]Dendralene with the Prototypical Olefinic Dienophile



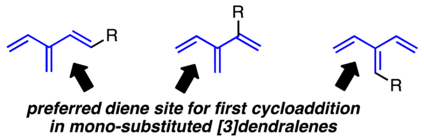


Figure 1. Site selection in dienophile additions to monosubstituted [3]dendralenes.

adduct **2**.[3] The minor monoadduct **3**, resulting from addition to the internal diene site, is inert toward further reaction at ambient temperature. Terminal monoadduct **2**, an unsymmetrically substituted [3]dendralene, is a more reactive diene than its progenitor [4]dendralene (**1**), hence is not isolated and undergoes a second cycloaddition. Of the two available diene sites in monoadduct **2**, a slight preference is seen for the semicyclic diene site, and two *endo*-mode bis-adducts **4** and **5** are generated, the former being the major product from the reaction. Diastereomeric bis-adducts **4** and **5** are the result of addition to the two distinct π-diastereofaces of the semicyclic diene of monoadduct **2**, with the former generated in high selectivity over the latter since it results from addition to the less sterically encumbered face. The transmitted 1,3-butadiene residue of **4** and **5** is unreactive toward further reaction with the dienophile under the reaction conditions since it cannot readily adopt the requisite *s-cis* conformation. Monocycloadduct **2** also undergoes Diels–Alder reaction to a substantial degree at the acyclic diene site, delivering two diastereomeric *terminal–terminal* bis-adducts **6** and **7**, both of which undergo a third—and final—cycloaddition at the newly transmitted 1,3-butadiene site to give two diastereomeric tris-adducts **8** and **9**. These two diastereomeric triple adducts are generated in a 1:1 ratio, which are the result of *endo*-stereoselective additions to the two *terminal–terminal* bis-adducts **6** and **7**, one of which is a *meso*-isomer (which has one unblocked π-diastereoface) and the other a chiral C_2 symmetric structure (with equivalent π-diastereofaces). We can deduce that the *terminal–terminal* bis-adducts **6** and **7** are formed in equal amounts, perhaps not too surprisingly when the substantial distance between the terminal diene site and *cis*-fused bicyclic ring section of monoadduct **2** are taken into account, in addition to the expected conformational freedom about the bond connecting the terminal diene of **2** with the bicycle.

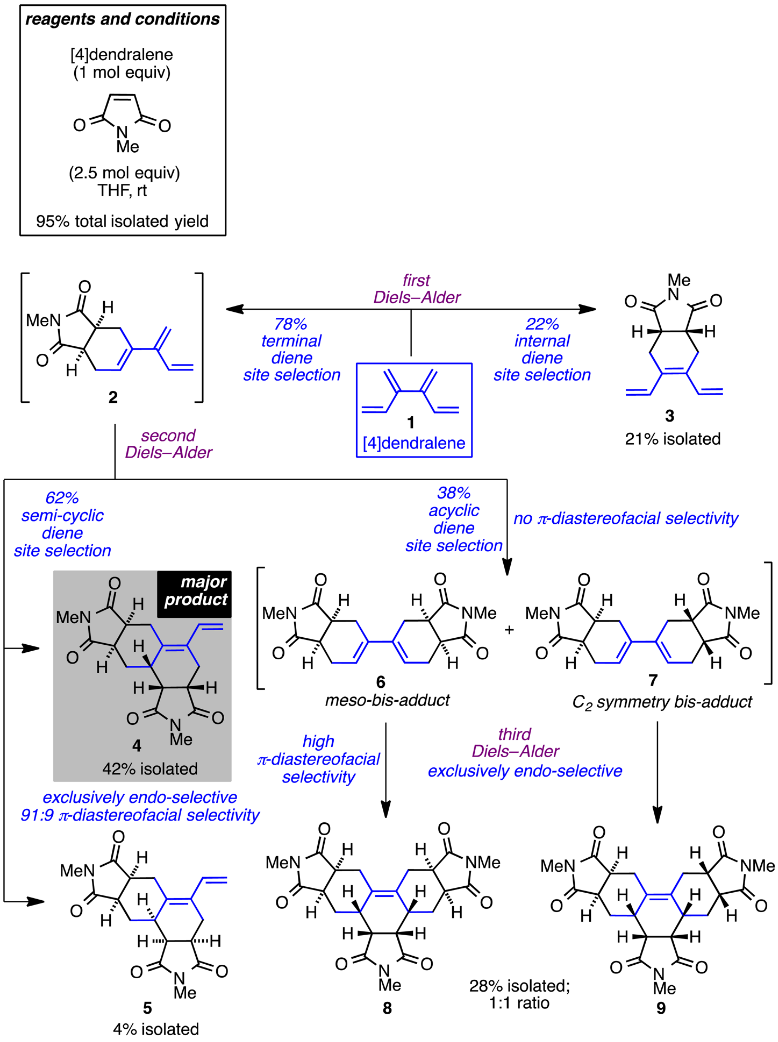
Evidently, target synthesis applications of diene-transmissive multifold cycloadditions involving [4]dendralene will require substituents to be present in the multicyclic products. Such groups would, most efficiently, be incorporated into the precursor [4]dendralene framework. In light of the experience gained with substituted [3]dendralenes (Figure 1), two points are clear: (a) unsymmetrically substituted [4]dendralenes have more multifold cycloaddition pathways available to them than does the parent system (Scheme 2), since unsymmetrical substitution removes degeneracy from the terminal diene sites; and (b) the presence of a substituent is likely to have a strong steering influence upon the site selectivity of the initial cycloaddition (and perhaps subsequent ones). Since there are no reports in the literature on the site selectivity of cycloadditions to any unsymmetrically substituted [4]-dendralene, we elected to study all five possible monosubstituted-[4]dendralenes, **10**–**14** (Figure 2). We chose the methyl group as substituent due to its small size and relatively mild electronic influence.

This project mandated the development of new approaches for polyene synthesis, since there are no general methods for syntheses of substituted [4]dendralenes in the literature.

■ RESULTS AND DISCUSSION

Dendralene Synthesis. Upon a thorough review of the literature, it became abundantly clear that, while several significant contributions have been made, no general synthetic methods are available for substituted [4]dendralene synthesis. Thus, *fully substituted* [4]dendralenes have been prepared by multifold [2 + 2] cycloaddition/ring opening sequences between tetracyanoethylene and conjugated oligo-alkynes by Diederich[6] and Shoji,[7] with a related process involving cumulenes recently described by Tykwinski.[8] Highly substituted 1,3-dithiole-containing [4]dendralenes have been prepared as electron donors by several groups,[9] in studies based upon a pioneering Wittig approach by Sugimoto and Yoshida,[10] and Talpur et al.[11] Several isolated reports of dimerizations affording C_2 symmetric multisubstituted [4]-dendralenes have also appeared.[12] The thermal [3,3]-sigmatropic rearrangement of 1,4-bisallenes, described by Mukai as an unwanted side reaction,[13] has the potential to be a more general route to [4]dendralenes, as does Lee's 2-fold intramolecular metathesis/elimination approach.[14] The electrocyclization of tetravinylethylene is a very effective way to

Scheme 2. Diene-Transmissive Diels–Alder Cycloaddition Sequences of [4]Dendralene (1) with the Dienophile *N*-Methylmaleimide (NMM)[3]



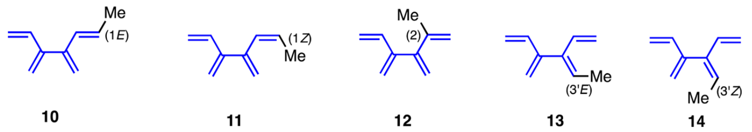
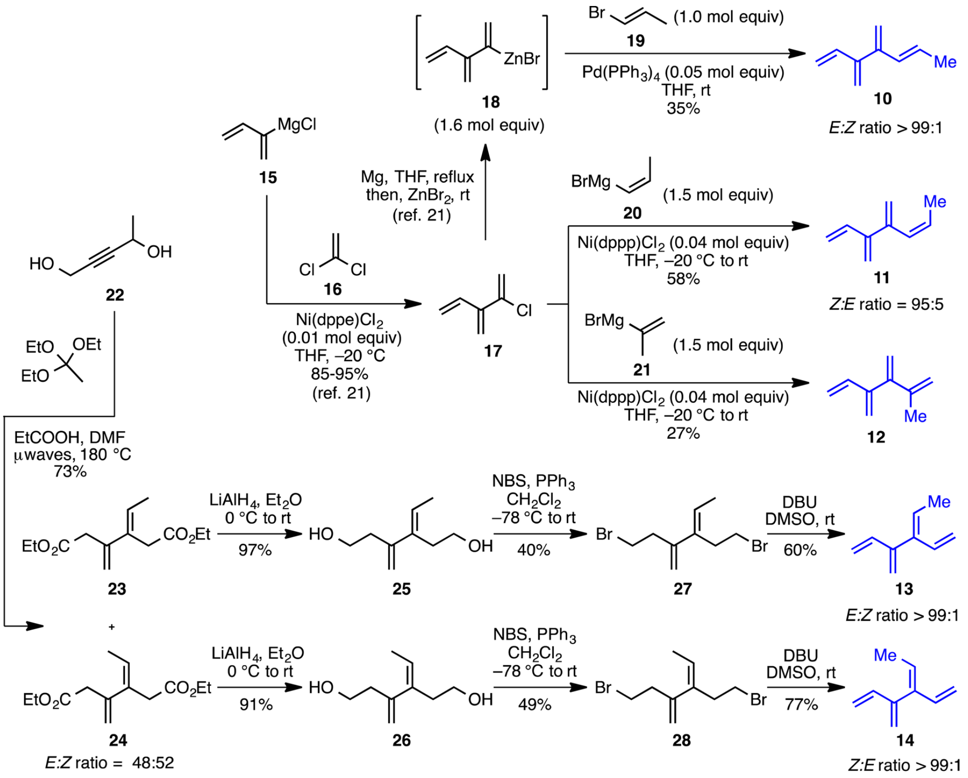


Figure 2. Five possible [4]dendralene structures carrying a methyl substituent.

prepare a specific subclass of cyclic [4]dendralenes,[15] but it lacks the ability to generate acyclic structures. Cross-couplings have been utilized by ourselves[16,17] and Shimizu and Hiyama[18] for a limited number of [4]dendralene substitution patterns. Herein we extend the cross-coupling methodology to a broader range of dendralene substitution patterns. We also introduce a complementary approach, involving a 2-fold Claisen rearrangement, to access dendralenes with substitution patterns that are presently inaccessible by cross-coupling reactions.

We considered several different routes for the preparation of these substituted [4]dendralenes. The unsubstituted hydrocarbon **1** is best prepared through a Kumada–Tamao–Corriu[19] type cross-coupling reaction between chloroprene and its corresponding Grignard reagent **15**. Had the requisite *substituted* 1,3-butadiene partners been readily accessible then we would have followed a similar pathway to the monomethylated [4]dendralenes. Disappointingly, this was not the case. In fact, there is a severe shortage of practical synthetic

Scheme 3. Syntheses of the Five Mono-Methyl-Substituted-[4]Dendralenes



routes to useful 1,3-butadiene coupling partners in the literature, which represents an opportunity for future synthetic invention. We ultimately elected to prepare the five targets through serviceable approaches based upon solid literature precedent. Two distinct pathways were ultimately adopted (Scheme 3): the three congeners substituted at the terminal C=C bond (**10**, **11** and **12**) were prepared by Kumada–Tamao–Corriu or Negishi[20] cross-coupling reactions between 2-chloro[3]dendralene (**17**)[21] (or its corresponding organozinc species **18**[21]) with the requisite (and known[22]) propenyl-coupling partner **19**, **20**[23] and **21**.[24] The two derivatives that are methyl-substituted at the internal C=C bond of [4]-dendralene, **13** and **14**, were accessed by double HBr elimination of dibromides **27** and **28**.[25] The dibromides were accessed from the corresponding diols **25** and **26** through 2-fold Appel reactions.[26] The diols, in turn, were the products of 2-fold reductions of the diesters **23** and **24**, which were the readily separated diastereomeric products of a 2-fold[27] Johnson–Claisen rearrangement[28] of pent-2-yne-1,4-diol (**22**).

In stark contrast to the parent [3]dendralene, which rapidly decomposes through Diels–Alder dimerization at ambient temperature,[16] the parent [4]dendralene **1** can be stored neat on the bench without decomposition over extended time periods.[3] The monomethylated [4]dendralenes **10**–**14** were also sufficiently stable to be handled neat at room temperature without appreciable decomposition over several minutes and were stored neat in a –20 °C freezer without significant decomposition over several months.

Diels–Alder Reactions. In order to allow a direct comparison between the cycloaddition behaviors of the methyl-substituted [4]dendralenes with the parent unsubstituted hydrocarbon **1**,[29] the new tetraenes were exposed to the same dienophile, *N*-methylmaleimide (NMM). (For the reaction between [4]dendralene (**1**) and NMM, see Scheme 2.) NMM has many positive attributes as a model dienophile, including commercial availability, adduct stability toward purification, adduct crystallinity to facilitate structure determination through single crystal X-ray analysis, and predictable *endo*-stereoselection in Diels–Alder reactions with substituted 1,3-butadienes. To emphasize this last point, all cycloadditions reported herein were found to proceed with the exclusive formation of the *endo*-cycloadduct.

When 1*E*-methyl[4]dendralene (**10**) was treated with an excess[30] (3 mol equiv) of NMM at room temperature, five different products were formed (Scheme 4): a single internal monoadduct **29** in 14% yield, two bis-adducts **32** and **33** in 7% and 48% yields, both as single diastereomers, and two diastereomeric tris-adducts **36** and **37** in a 1:1 ratio (20% yield).[31] Upon the basis of this product distribution we can determine that the first cycloaddition reaction proceeds with ca. 84:16 site selectivity in favor of the two, dissimilar, terminal diene sites (i.e., **30**+**31**:**29** = 84:16). It is not possible to resolve the site selectivity of the two different terminal diene sites from the first Diels–Alder event, since both monoadducts **30** and **31** can, in principle, give rise to the tris-adducts **36** and **37**, by way of diastereomeric bis-adducts **34** and **35**. Assuming a worst-case scenario, that is tris-adducts **36** and **37** result exclusively from

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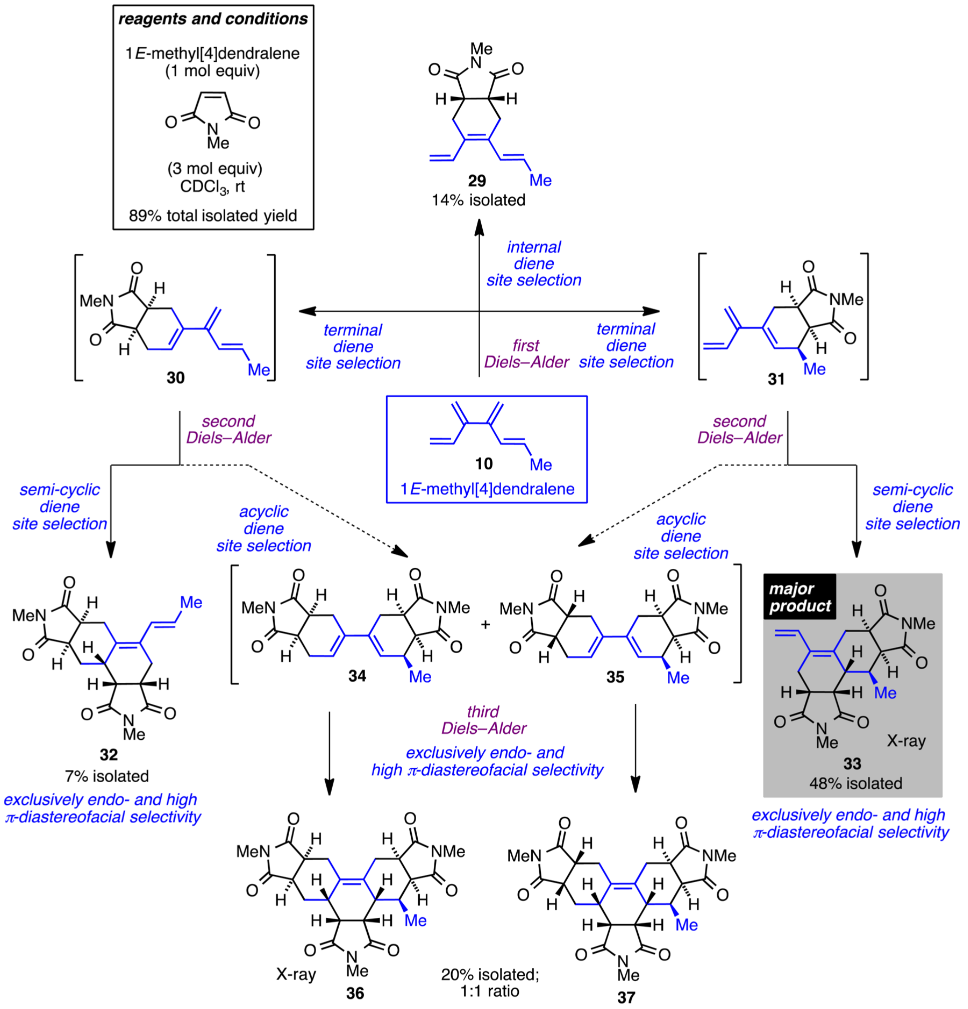
Scheme 4. Diels–Alder Reaction of 1*E*-Methyl[4]dendralene (10) with an Excess of NMM at Room Temperature

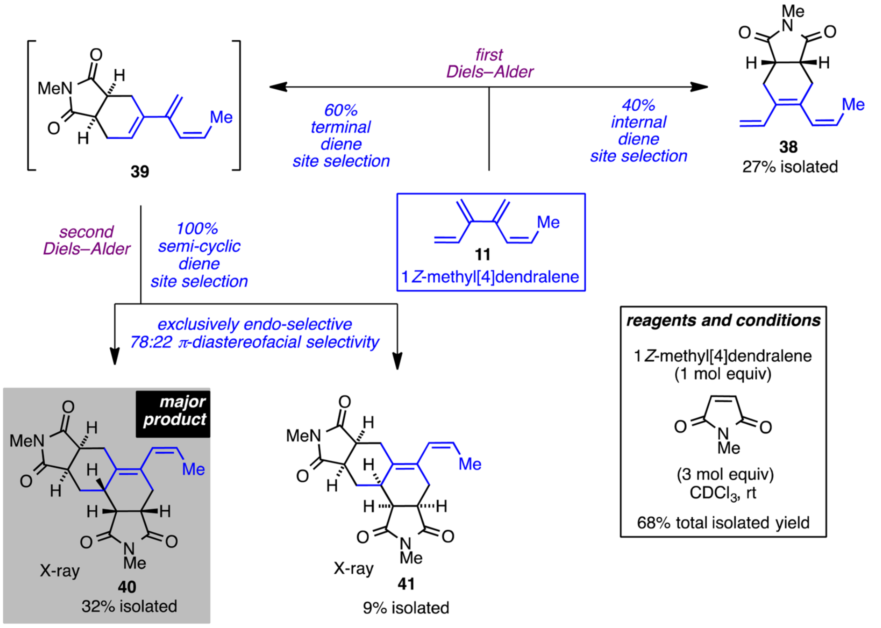


monoadduct **30**, we can deduce that the methyl-substituted terminal diene site is favored over the unsubstituted diene terminus by at least ca. 2:1. Bis-adduct **33**, the major product of the reaction, can only be formed from an initial addition to the more substituted terminal 1,3-butadiene site and a second addition to the semicyclic diene site of monoadduct **31**. The stereochemistry of this product reveals two successive *endo*-mode cycloadditions, with the second Diels–Alder event (**31** → **33**) proceeding with complete π-diastereofacial selectivity. This enhancement relative to the unsubstituted [4]dendralene (cf. Scheme 2, **2** → **4** + **5**) is presumably due to the additional steric blocking influence brought to bear by the methyl group. (The lack of detection of a minor diastereomer from the pathway **30** → **32** is presumably due to the very small amount of such a product being formed.)

Mirroring the sequence for the unsubstituted [4]dendralene **1**, the minor pathway for the second Diels–Alder reaction proceeds with a lack of π-diastereofacial selectivity, delivering *terminal–terminal* bis-adducts **34** and **35** in equal measure, which ultimately give rise to tris-adducts **36** and **37** in a 1:1 ratio through highly stereoselective final additions. The presence of the *C*-methyl group in *syn-terminal–terminal* bis-adduct **34** would be expected to reinforce the already strong (cf. Scheme 2, **6** → **8**) preference for dienophile approach from the bottom face during the third cycloaddition, thus forming tris-adduct **36** exclusively. In the case of *anti-terminal–terminal* bis-adduct **35**, the *C*-methyl group directs approach from the face of the diene opposite to it, thereby generating tris-adduct **37** in high selectivity.

Overall, the product distribution obtained from reaction of 1*E*-methyl[4]dendralene (**10**) with NMM correlates closely with that of the parent [4]dendralene (**1**). Similar yields of analogous products are obtained, in spite of the additional complexity brought to bear on the system by the methyl substituent. Overall, the presence of the *outside* methyl substituent at C1 only marginally increases the terminal site selectivity of the first Diels–Alder reaction (compare the *terminal*:*internal* ratio of ca. 78:22 for **1** with ca. 84:16 for **10**).

Scheme 5. Diels–Alder Reaction of 1*Z*-Methyl[4]dendralene (11) with an Excess of NMM at Room Temperature



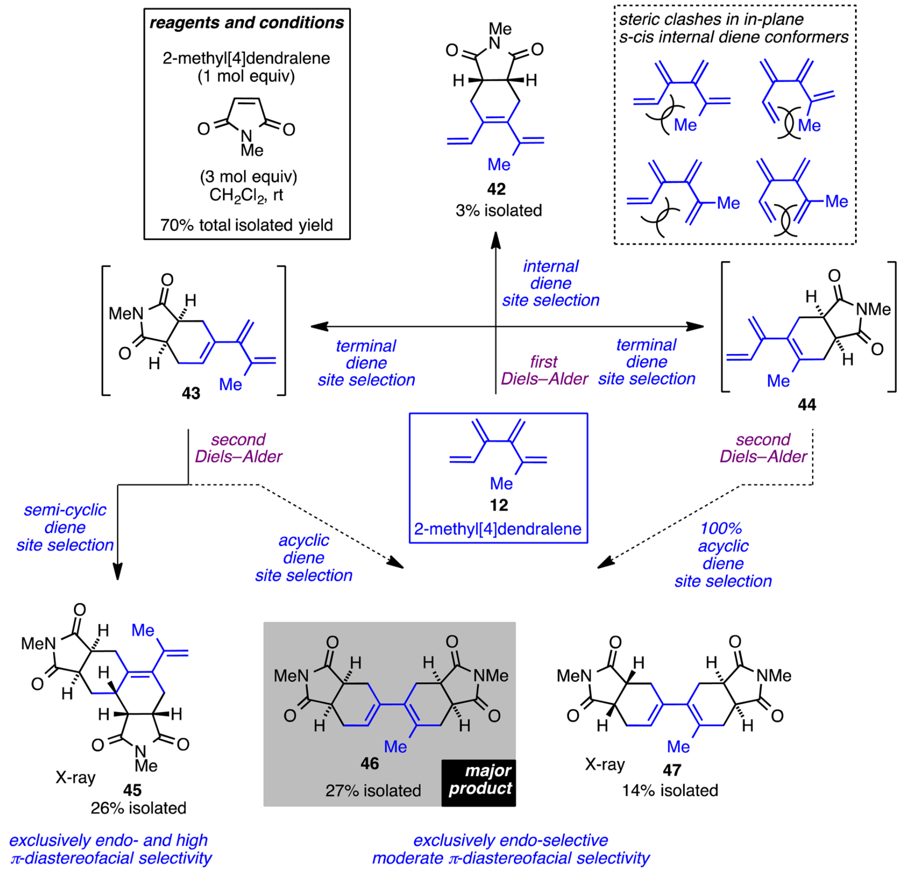
The significant preference (at least 2:1) for the 1*E*-methyl-substituted butadiene terminus over the unsubstituted one is interesting, in light of the very mild influence of the methyl group. We presume that more activating 1*E*-substituents will give a much stronger preference for this site.

Exposure of 1*Z*-methyl[4]dendralene (**11**) to an excess[30] (3 mol equiv) of NMM at room temperature gave three products: internal monoadduct **38** in 27% yield, and two diastereomeric bis-adducts **40** and **41** in 32% and 9% yields, respectively (Scheme 5).[32] From this product distribution it is evident that the presence of the *inside*-methyl substituent prevents cycloaddition to the more substituted terminal diene site. Of the two remaining diene sites, we can deduce a ca. 60:40 site selectivity in favor of the less substituted *terminal* diene site, which is consistent with the *terminal*:*internal* ratio of 78:22 ratio observed with [4]dendralene (**1**) (Scheme 2). ([4]Dendralene (**1**) has two degenerate unsubstituted terminal diene sites and one internal site, whereas 1*Z*-methyl[4]dendralene (**11**) has one of each.) The *inside*-methyl substituent blocks addition to the acyclic diene site of monoadduct **39**, hence only bis-adducts **40** and **41** resulting from a second Diels–Alder reaction to the semicyclic diene site of **39** are seen. The π-diastereofacial selectivity of this second cycloaddition favors *anti*-bis-adduct **40**, qualitatively consistent with previous findings, albeit with slightly diminished selectivity in this case.

Thus, 1*Z*-methyl[4]dendralene (**11**) delivers significantly fewer products than both the parent system and the 1*E*-substituted congener, due to the blocking influence of the *inside* methyl substituent, which prevents the formation of tris-adducts. Evidently, this substitution alone will not be enough to engender synthetic utility upon the system, since two products are formed in roughly equal amounts in this reaction. Nevertheless, if terminal *Z*-substituents were present at both ends of the structure, we can safely predict the exclusive formation of the internal monoadduct.

When 2-methyl[4]dendralene (**12**) was treated with an excess[30] (3 mol equiv) of NMM at room temperature, four products were isolated: internal monoadduct **42** in 3% yield, and three bis-adducts **45**, **46**, and **47** in 26, 27, and 14% yields, respectively (Scheme 6).[32] It is clear that the presence of the methyl substituent at C2 has the effect of disfavoring the initial addition to the internal diene site. This is, presumably, a conformational effect, inasmuch as the methyl substituent either (a) disfavors the *s-cis* conformation of the internal diene through steric effects (Scheme 6, dashed box), and/or, as a result of this steric clash, (b) blocks dienophile approach due to the vinyl or 2-propenyl substituents being rotated out of the plane of the internal *cisoid* diene. Disappointingly, the site selectivity between the two dissimilar terminal diene sites cannot be determined, since it is not possible to establish the order of cycloaddition events leading to *terminal*–*terminal* bis-adducts **46** and **47**. Thus, both putative monoadducts **43** or **44** could, in principle, give rise to *terminal*–*terminal* bis-adducts **46** and **47**. Only monoadduct **43** can, however, give rise to bis-adduct **45** and, consistent with results described herein for the other substrates, the π-diastereofacial selectivity of this second Diels–Alder addition to the semicyclic diene site of monoadduct **43** is high. If regioisomeric monoadduct **44** is generated, then it must undergo a second addition exclusively to the remaining terminal diene site, a conclusion that seems reasonable in light of the presence of the *inside* methyl substituent, which would disfavor the *s-cis* conformation of the semicyclic diene of **44**. That the *terminal*–*terminal* bis-adduct **46** is preferred over its diastereomer **47** is interesting, since it indicates a moderate level of π-diastereofacial selectivity in the cycloaddition to the acyclic diene site(s) of monoadducts **43**/**44**. The lack of tris-adducts from *terminal*–*terminal* bis-adducts **46** and **47** is presumably, once again, the result of a disfavored *s-cis* conformation due to the presence of an *inside* methyl group.

Scheme 6. Diels–Alder Reaction of 2-Methyl[4]dendralene (12) with an Excess of NMM at Room Temperature



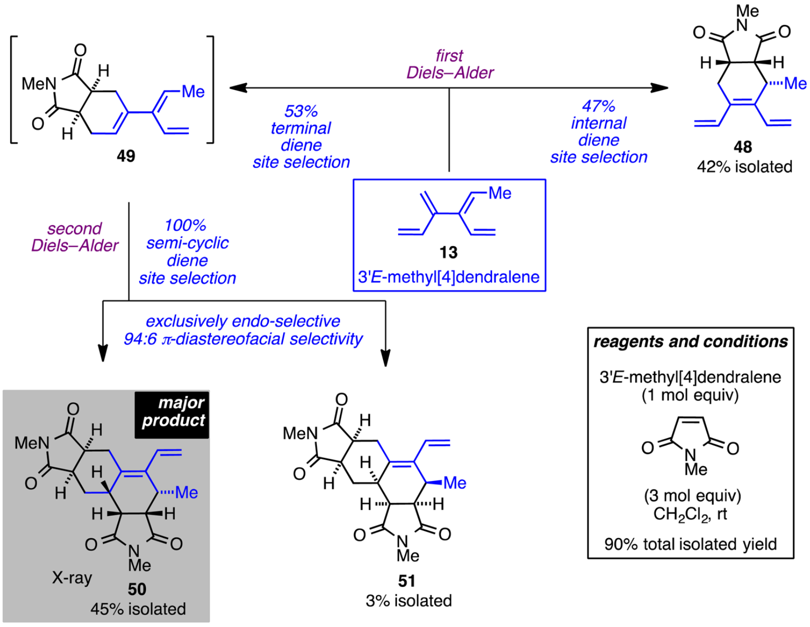
In terms of future synthetic applications, the most important—and surprising—observation with 2-methyl[4]dendralene (**12**) is that addition to its internal diene site is disfavored. A more detailed analysis of the experimental findings is thwarted by an inability to attribute products to specific pathways. Nonetheless, a significant hurdle toward future applications is that the 2-methyl substituent (and presumably other groups in this position) leads to the formation of different regioisomeric bis-adducts in significant amounts.

Exposure of 3′*E*-methyl[4]dendralene (**13**) to an excess[30] (3 mol equiv) of NMM at room temperature resulted in three products: internal monoadduct **48** in 42% yield, and diastereomeric bis-adducts **50** and **51** in 45% and 3% yields (Scheme 7).[31] The impact of the 3′-methyl substituent is clear from the first cycloaddition reaction, with no addition occurring to the terminal diene site to which it is attached, and addition to the remaining internal and terminal sites occurring in roughly equal measure. The presence of the *outside* methyl group leads to a modest enhancement upon the reactivity of the internal diene site of **13**, as evidenced by the increased quantity of the internal adduct (*terminal*:*internal* ratio = 53:47) relative to 1*Z*-methyl[4]dendralene (**11**) (Scheme 5, *terminal*:*internal* ratio = 60:40), a substrate which also has only one reactive internal and terminal diene but lacks a methyl substituent on either. While the internal monoadduct **48** is inert toward further reaction, terminal monoadduct **49** undergoes a highly site-selective and stereoselective cycloaddition reaction with more dienophile. Again, the methyl substituent of putative monoadduct **49** blocks addition to the acyclic diene site, hence steering the reaction path to bis-adducts **50** and **51**, with a strong π-diastereofacial selectivity in favor of the former, for reasons discussed in previous cases.

Hence, only two compounds (**48**+**50**) account for 87% of the isolated yield in the Diels–Alder reaction of 3′*E*-methyl[4]dendralene (**13**) with NMM. These two products are, however, the result of dienophile additions to two different diene sites in the precursor.

Reaction of 3′*Z*-methyl[4]dendralene (**14**) with an excess[30] (3 mol equiv) of NMM at room temperature delivered a mixture of five products: two diastereomeric bis-adducts **54** and **55** in 11% and in 8% yields and three diastereomeric tris-adducts **58**, **59** and **60** in 23, 18, and 10% yields, respectively (Scheme 8).[33] Unsurprisingly, none of the internal monoadduct is observed from this reaction, presumably due to the *inside*-methyl substituent attached to the internal 1,3-butadiene unit of **14**. The first cycloaddition, therefore, proceeds with complete site selectivity in favor of the two terminal diene sites. As was the case with 2-methyl[4]dendralene (**12**) (Scheme 6), it is not possible to determine the selectivity for one of these

Scheme 7. Diels–Alder Reaction of 3′*E*-Methyl[4]dendralene (13) with an Excess of NMM at Room Temperature



terminal sites over the other, since the three tris-adducts **58**, **59** and **60** can, in principle, be derived from either of the two monoadducts, **52** or **53**. It is certain that addition occurs to the more substituted terminal diene site to generate monoadduct **52**, since two diastereomeric products (**54** and **55**) of addition to the semicyclic diene site of **52** are isolated. What is curious about this cycloaddition to the semicyclic diene site of **52** is its low level of π-diastereofacial selectivity. The methyl substituent would be expected to reinforce the preference for diastereomer **54**, by further shielding dienophile approach to the concave face of **52** (cf. **31** → **33**, Scheme 4). Consistent with this finding (but also surprising) is the relatively mild π-diastereofacial selectivity seen in the conversion of putative *anti-terminal–terminal* bis-adduct **57** into tris-adducts **59** and **60**. Not surprisingly, the diastereomeric *syn-terminal–terminal* bis-adduct **56** forms tris-adduct **58** exclusively. If monoadduct **53** is formed, then it reacts exclusively at the other terminal diene site to form *terminal–terminal* bis-adducts **56** and **57** and not at the semicyclic diene site, again due to the presence of the *inside*-methyl substituent.

■ SUMMARY AND CONCLUSIONS

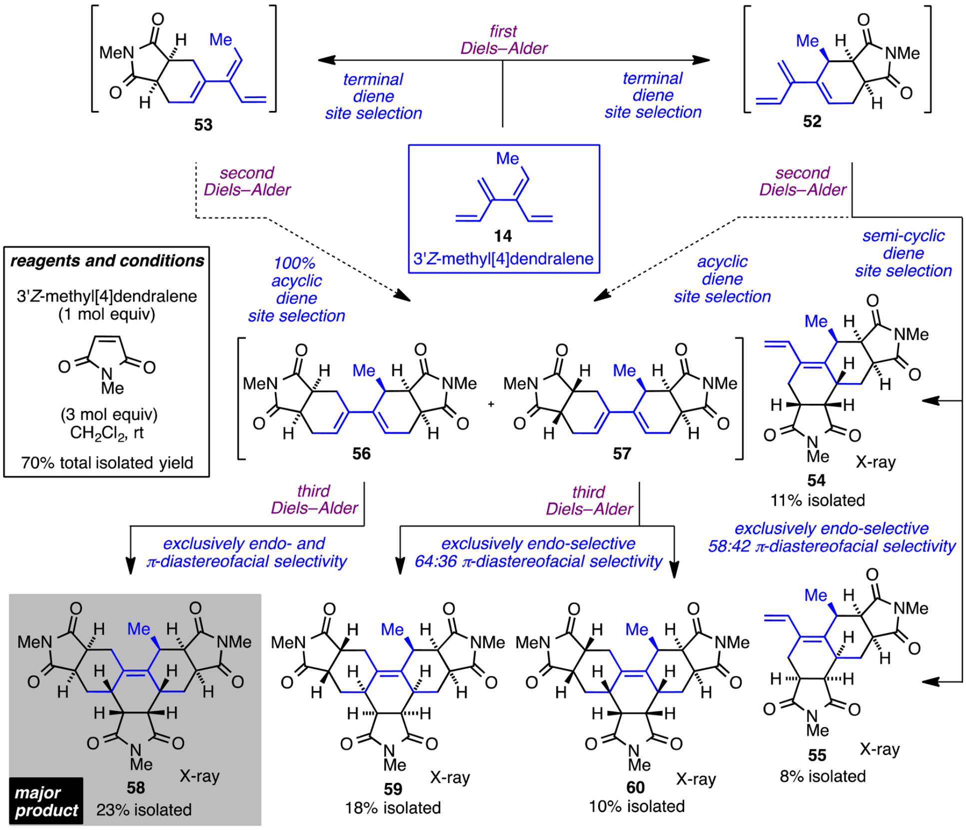
In summary, two distinct synthetic strategies have been devised in order to access all five possible monomethylated [4]-dendralenes. Applications and extensions of these synthetic pathways can be envisioned for the preparation of other monosubstituted, as well as multisubstituted [4]dendralenes. These syntheses also serve as a stepping stone toward the synthesis of the as yet unknown monosubstituted higher [*n*]dendralenes (i.e., *n* > 4).

An exploratory investigation into the cycloaddition chemistry of these hydrocarbons has demonstrated that, in comparison with the unsubstituted [4]dendralene, each of the five possible monomethylated [4]dendralenes behaves differently on reaction with a dienophile. Thus, competing and complex sequences of cycloaddition reactions give rise to different distributions of mono-, bis- and tris-addition products. These reactions could not be easier to carry out, since they involve simply mixing the tetraene hydrocarbon with the dienophile at ambient temperature in a common solvent, yet they bring about some of the most striking examples of rapid complexity generation, with three new carbocycles, six new C–C bonds, and nine new stereocenters being generated.

Analysis of the outcomes of the Diels–Alder reactions of the five different substituted [4]dendralenes and comparisons with prior findings with the unsubstituted hydrocarbon has allowed the identification of recurring themes and the attribution of specific reactivity to substituent location. Some of our observations were predictable on the basis of known findings with substituted 1,3-butadienes.[34] Thus, the presence of an *inside*-methyl substituent on a 1,3-butadiene portion of the dendralene completely prevents Diels–Alder reaction at that site, whereas an *outside*-methyl substituent on a 1,3-butadiene unit leads to a moderate reactivity increase.[35] In this respect, the dendralene behaves as if it were simply a mixture of different substituted dienes. Other influences are less predictable, as exemplified by the case of the 2-methyl substituent, which inhibits dienophile addition to the adjacent, *internal* site in a [4]dendralene (**12**, Figure 3), whereas the same substituent promotes addition to the adjacent site in a [3]dendralene (Figure 1).

In all cases, an initial Diels–Alder addition of a dienophile to the internal site of a [4]dendralene results in formation of a product that resists further reaction at ambient temperature. Boosting the yield of the internal adduct is of interest since it will allow the rapid, high yield construction of downstream products. For example, 6π-electrocyclization of the internal adduct has been demonstrated previously with the parent [4]dendralene, along with cycloaddition to the resulting 1,3-cyclohexadiene structure, as has direct dienophile addition to

Scheme 8. Diels–Alder Reaction of 3′Z-Methyl[4]dendralene (14) with an Excess of NMM at Room Temperature



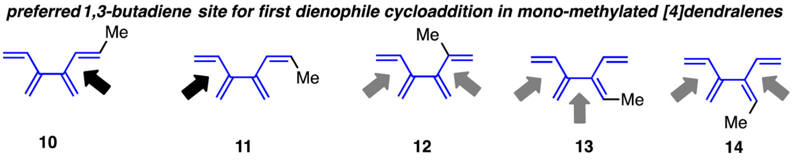


Figure 3. Site selection in dienophile additions to monosubstituted [4]dendralenes (darker shading indicates stronger selectivity).

the internal adduct under high pressure conditions.[3] Similar processes can be envisioned with the substituted systems.

An initial dienophile addition to a terminal 1,3-butadiene site gives rise to a substituted [3]dendralene, which can in turn react with another dienophile at either the acyclic or semicyclic diene site. A third Diels–Alder addition occurs to the product of addition to the acyclic site but, at ambient temperature, the semicyclic addition product does not react on. (Further addition is possible, however, under high pressure.[3]) The presence of a methyl group blocks reaction as an *inside*-substituent and mildly enhances reactivity as an *outside*-substituent. In general, the π-diastereofacial selectivities of these reactions are predictable through consideration of steric effects.

The purpose of this work was to develop ways to prepare substituted [4]dendralenes and to document their Diels–Alder reactivity, in the hope of promoting synthetic applications. The reactions described herein are of marginal direct use in total synthesis due to their propensity to generate complex mixtures. These findings do, however, form the foundations for directed, future studies toward specific product structures. The methyl substituent is neither a particularly sterically bulky group, nor is it strongly electron donating. For these reasons, it is likely that other substituents will exhibit higher selectivities. Thus, larger groups and those with more potent electronic characteristics will have a much greater influence, and the deployment of multiple substituents that operate cooperatively are likely to deliver significantly more selective domino cycloaddition sequences. The deployment of catalysts can also influence the site selectivity of Diels–Alder processes.[3] It is most likely the case that a combination of these tactics will be ultimately successful in achieving the highest level of control in multicycloaddition sequences to dendralenes. This work serves to highlight the significant challenges that need to be met, in order for these extraordinarily step economic processes to be applied in total synthesis.

■ EXPERIMENTAL SECTION

General Methods. See the Supporting Information.

*Chloroprene (**62**).*[36] The title compound **62** was prepared following the patented procedure.[36]

*Buta-1,3-dien-2-ylmagnesium chloride (**15**).*[37] The title compound **15** was prepared following modification of the procedure reported by Nunomoto and Yamashita.[37]

*2-Chloro[3]dendralene (**17**).*[21] The title compound **17** was prepared following modification of the published procedure.[21]

*(3-Methylenepenta-1,4-dien-2-yl)magnesium chloride (**63**).*[21] The title compound **63** was prepared following modification of the published procedure.[21] A 3-necked round bottomed flask equipped with a condenser and dropping funnel was charged with oven-dried magnesium powder (3.7 g, 0.15 mol, 2.9 mol equiv) and flushed with argon for 1 h. To this was added THF (45 mL) followed by portionwise addition of 1,2-dibromoethane (1.8 mL, 21 mmol, 0.40 mol equiv) (***Caution!** Exothermic*). After refluxing had subsided, ZnBr$_2$ (0.59 g, 2.6 mmol, 0.050 mol equiv) was added and the sides of the reaction flask were rinsed with THF (5.0 mL). The reaction mixture was then heated to reflux and a solution of 2-chloro[3]dendralene (**17**) (6.0 g, 26% (w/w) solution in THF, 53 mmol, 1.0 mol equiv) and 1,2-dibromoethane (2.8 mL, 32 mmol, 0.60 mol equiv) in THF (40 mL) was added dropwise over 30 min. After the addition was complete, the reaction mixture was stirred at reflux for a further 10 min. The title compound **63** was obtained as a dark black solution (0.10 L, 0.22 M solution in THF, 22 mmol, 42%) and was used immediately in the next reaction.

*1E-Methyl[4]dendralene (**10**).* A freshly prepared solution of (3-methylenepenta-1,4-dien-2-yl)magnesium chloride (**63**) (25 mL, 0.16 M solution in THF, 4.0 mmol, 1.6 mol equiv) was added slowly into a stirred solution of ZnBr$_2$ (0.92 g, 4.1 mmol, 1.6 mol equiv) and THF (5.0 mL) at 0 °C. Once the addition was complete, the reaction mixture was allowed to warm to 25 °C and stirred for a further 20 min. To this was added 1*E*-bromopropene (**19**) (0.22 mL, 2.6 mmol, 1.0 mol equiv) followed by addition of Pd(PPh$_3$)$_4$ (0.15 g, 0.13 mmol, 0.050 mol equiv) and the reaction mixture was stirred at 25 °C for 16 h with the exclusion of light. The resulting solution was poured into water (0.15 L), stirred for 15 min and petroleum ether (30−40 °C) (0.15 L) was added. The organic phase was separated and aqueous phase was then extracted with petroleum ether (30−40 °C) (2 × 0.10 L). The organic phases were combined, washed with brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure (50 mbar, 0 °C). Purification by flash column chromatography (SiO$_2$, petroleum ether (30−40 °C)) gave the title compound **10** (0.11 g, 0.92 mmol, 35%) as a colorless oil. R_f 0.56 (petroleum ether (30−40 °C)); ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.41 (ddd, J = 17.4, 10.5, 0.8 Hz, 1H), 6.13 (ddd, J = 15.5, 1.9, 0.7 Hz, 1H), 5.65 (dq, J = 15.6, 5.0 Hz, 1H), 5.24−5.14 (m, 2H), 5.12−5.01 (m, 3H), 4.89 (dd, J = 2.2, 0.8 Hz, 1H), 1.74 (ddt, J = 6.7, 1.5, 0.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 147.5 (C), 146.4 (C), 137.7 (CH), 132.1 (CH), 128.5 (CH), 117.4 (CH$_2$), 116.5 (CH$_2$), 115.0 (CH$_2$), 18.2 (CH$_3$) ppm; IR (thin film) ν_{max} = 3083, 2954, 2923, 2852, 1635, 1456 cm^{-1}; LRMS (70 eV, EI) m/z (%) 120 ([M]$^{+\bullet}$, 15%), 105 (100), 91 (44), 79 (34); HRMS calc for C$_9$H$_{12}$ [M]$^{+\bullet}$ 120.0939, found 120.0938.

*(Z)-Prop-1-en-1-ylmagnesium bromide (**20**).*[22] The title compound **20** was prepared following the procedure reported by Prieto et al.[22]

*1Z-Methyl[4]dendralene (**11**).* To a stirred solution of 2-chloro[3]dendralene (**17**) (3.6 g, 32 mmol, 1.0 mol equiv) and Ni(dppp)Cl$_2$ (0.69 g, 1.3 mmol, 0.040 mol equiv) in THF (12 mL) at −20 °C was added dropwise a solution of (*Z*)-prop-1-en-1-ylmagnesium bromide (**20**) (0.24 L, 0.20 M solution in THF, 47 mmol, 1.5 mol equiv) over 25 min. The reaction mixture was then allowed to warm to 25 °C and stirred for 2.5 h. The resulting solution was poured into a mixture of ice-cold petroleum ether (30−40 °C) (0.60 L) and water (0.60 L) and stirred for 15 min before a solution of aqueous HCl (40 mL, 1.0 M) was added. The organic phase was separated, washed with a solution of saturated aqueous NaHCO$_3$ (0.10 L) followed by brine (0.10 L), dried over MgSO$_4$, filtered, and concentrated under reduced pressure (45 mbar, 0 °C). Purification by flash column chromatography (SiO$_2$, petroleum ether (30−40 °C)) afforded the title compound **11** (2.2 g, 18 mmol, 58%) as a colorless oil along with a small amount of the *E* isomer **10** and homocoupled byproduct **65** (**11**:**10**:**65** = 87:6:7 ratio). R_f 0.57 (petroleum ether (30−40 °C)); ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.45 (ddd, J = 17.3, 10.7, 0.9 Hz, 1H), 5.99 (ddt, J = 11.6, 3.0, 1.7 Hz, 1H), 5.61 (dq, J = 11.6, 7.0 Hz, 1H), 5.31 (dd, J = 17.4, 1.7 Hz, 1H), 5.21 (d, J = 2.3 Hz, 1H), 5.17−5.08 (m, 4H), 1.74 (dd, J = 7.1, 1.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 148.7 (C), 144.0 (C), 137.3 (CH), 129.8 (CH), 127.3 (CH), 117.4 (CH$_2$), 116.6 (CH$_2$), 115.7 (CH$_2$), 14.5 (CH$_3$) ppm; IR (thin film) ν_{max} = 3087, 3012, 2916, 1801, 1633, 1593, 1439 cm^{-1}; LRMS (70 eV, EI) m/z (%) 120 ([M]$^{+\bullet}$, 17%), 108 (3), 105 (100); HRMS calc for C$_9$H$_{12}$ [M]$^{+\bullet}$ 120.0939, found 120.0944.

*Prop-1-en-2-ylmagnesium bromide (**21**).*[38] The title compound **21** was prepared following modification of the procedure reported by Slater et al.[38] 2-Bromopropene (**66**) (1.5 mL, 17 mmol, 1.0 mol equiv) was added to a stirred mixture of oven-dried magnesium powder (0.44 g, 18 mmol, 1.1 mol equiv) in degassed THF (25 mL) at 25 °C (***Caution!** Exothermic*). After the addition was complete, the reaction mixture was heated to 40 °C and stirred for 75 min. The title compound **21** was obtained as pale yellow solution (25 mL, 0.39 M solution in THF, 9.8 mmol, 57%).

*2-Methyl[4]dendralene (**12**).* To a stirred solution of 2-chloro[3]dendralene (**17**) (0.50 g, 4.4 mmol, 1.0 mol equiv) and Ni(dppp)Cl$_2$ (95 mg, 0.14 mmol, 0.04 mol equiv) in THF (2.0 mL) at −20 °C was added dropwise a solution of prop-1-en-2-ylmagnesium bromide (**21**) (17 mL, 0.39 M solution in THF, 0.66 mmol, 1.5 mol equiv) over 7 min. The reaction mixture was allowed to warm to 25 °C and stirred for 2 h. The resulting mixture was poured into a stirred mixture of ice-cold petroleum ether (30−40 °C) (60 mL) and water (40 mL) and stirred for 15 min before a solution of aqueous HCl (10 mL, 1.0 M) was added. The organic phase was separated and washed with a solution of saturated aqueous NaHCO$_3$ (20 mL) followed by brine (20 mL). The organic phase was dried over MgSO$_4$, filtered and concentrated under reduced pressure (45 mbar, 0 °C). Purification by flash column chromatography (SiO$_2$, petroleum ether (30−40 °C) afforded the title compound **12** (0.14 g, 1.2 mmol, 27%) as a colorless oil. R_f 0.66 (petroleum ether (30−40 °C)); ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.43 (dd, J = 17.3, 10.5 Hz, 1H), 5.30−5.27 (m, 1H), 5.23−5.20 (m, 1H), 5.16−5.09 (m, 1H), 5.08−4.98 (m, 5H), 1.96−1.94 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 148.7 (C), 148.7 (C), 141.8 (C), 138.2 (CH), 117.7 (CH$_2$), 116.3 (CH$_2$), 116.1 (CH$_2$), 114.4 (CH$_2$), 20.3 (CH$_3$) ppm; IR (thin film) ν_{max} = 3092, 3006, 2974, 2948, 1586, 1458, 1440 cm^{-1}; LRMS (70 eV, EI) m/z (%) 120 ([M]$^{+\bullet}$, 12%), 119 (31), 115 (13), 107.1 (100); HRMS calc for C$_9$H$_{12}$ [M]$^{+\bullet}$ 120.0939, found 120.0939.

*Pent-2-yne-1,4-diol (**22**).*[39] The title compound **22** was prepared following the procedure reported by Takahashi and Matsumoto.[40]

*(E)-Diethyl-3-ethylidene-4-methylenehexanedioate (**23**) and (Z)-Diethyl-3-ethylidene-4-methylenehexanedioate (**24**).* The title compounds **23** and **24** were prepared following modification of the procedure reported by Srikrishna and Nagaraju.[41] A microwave reactor vial was charged with a solution of pent-2-yne-1,4-diol (**22**) (1.7 g, 17 mmol, 1.0 mol equiv), triethyl orthoacetate (25 g, 0.15 mol, 9.1 mol equiv) and propionic acid (0.63 g, 8.5 mmol, 0.52 mol equiv) in dry DMF (30 mL). The reaction mixture was heated to 180 °C using microwave irradiation (300 W) for 25 min. The resulting mixture was diluted with Et$_2$O (60 mL) and washed with a solution of aqueous HCl (1.0 M) followed by a solution of aqueous LiCl (5% (w/w) in water). The organic phase was dried over MgSO$_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO$_2$, EtOAc:hexane (5:95)) gave the title compound **23** (1.4 g, 5.8 mmol, 35%) as a yellow oil and the title compound **24** (1.5 g, 6.3 mmol, 38%) as a yellow oil.

*(E)-Diethyl-3-ethylidene-4-methylenehexanedioate (**23**).* R_f 0.37 (EtOAc:hexane (10:90)); ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.87 (q, J = 6.7 Hz, 1H), 5.20 (s, 1H), 5.04 (s, 1H), 4.13 (dtd, J = 7.8, 6.8, 2.4 Hz, 4H), 3.33 (s, 2H), 3.28 (s, 2H), 1.77 (d, J = 6.9 Hz, 3H), 1.23 (tt, J = 7.1, 0.6 Hz, 6H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 171.7 (C), 171.4

(C), 140.8 (C), 132.4 (C), 126.7 (CH), 115.0 (CH_2), 60.7 (CH_2) (two coincident signals), 40.7 (CH_2), 33.9 (CH_2), 14.6 (CH_3), 14.2 (CH_3) (two coincident signals) ppm; IR (thin film) ν_{max} = 3096, 2982, 2938, 1732, 1610, 1446 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 240 ($[M]^{+\bullet}$, 42%), 225 (6), 194 (72), 166 (58), 93 (100); HRMS calc for $C_{13}H_{20}O_4$ $[M]^+$ 240.1362, found 240.1357.

(Z)-Diethyl-3-ethylidene-4-methylenehexanedioate (24). R_f 0.43 (EtOAc:hexane (10:90)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (qt, *J* = 6.9, 1.3 Hz, 1H), 5.21 (q, *J* = 1.5 Hz, 1H), 4.98 (d, *J* = 1.8 Hz, 1H), 4.09 (qd, *J* = 7.0, 1.5 Hz, 4H), 3.16 (d, 2H), 3.10 (t, *J* = 1.2 Hz, 2H), 1.69 (dt, *J* = 8.6, 1.0 Hz, 3H), 1.22 (td, *J* = 7.2, 1.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6 (C), 171.0 (C), 139.1 (C), 134.1 (C), 127.1 (CH), 118.8 (CH_2), 60.7 (CH_2), 60.6 (CH_2), 42.3 (CH_2), 41.2 (CH_2), 14.9 (CH_3), 14.3 (CH_3), 14.2 (CH_3) ppm; IR (thin film) ν_{max} = 3086, 2983, 2938, 1737, 1634, 1446 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 240 ($[M]^{+\bullet}$, 40%), 225 (12), 194 (78), 166 (68), 93 (100); HRMS calc for $C_{13}H_{20}O_4$ $[M]^{+\bullet}$ 240.1362, found 240.1362.

(E)-3-Ethylidene-4-methylenehexane-1,6-diol (25). A solution of (*E*)-diethyl 3-ethylidene-4-methylenehexanedioate (**23**) (4.7 g, 20 mmol, 1.0 mol equiv) in dry Et_2O (60 mL) was slowly added into a stirred suspension of $LiAlH_4$ (1.5 g, 39 mmol, 2.0 mol equiv) in dry Et_2O (40 mL) at 0 °C. The resulting mixture was stirred for 30 min and then allowed to warm to 25 °C and stirred further overnight. The resulting reaction mixture was cooled to 0 °C and carefully quenched by dropwise addition of water (25 mL) followed by addition of Et_2O (25 mL). The resulting mixture was then stirred at 25 °C for 1 h. The resulting reaction mixture was poured into a stirred saturated solution of aqueous NH_4Cl (0.10 L) before a solution of aqueous HCl (1.0 M, 0.10 L) was added. The organic phase was separated and the aqueous layer was extracted with Et_2O (4 × 0.10 L). The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (70:30)) gave the title compound **25** (3.0 g, 19 mmol, 97% yield) as a yellow oil. R_f 0.32 (EtOAc:hexane (70:30)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (q, *J* = 6.9 Hz, 1H), 5.11–5.09 (m, 1H), 4.99–4.97 (m, 1H), 3.68 (td, *J* = 6.4, 5.1 Hz, 4H), 2.59 (t, *J* = 6.6 Hz, 2H), 2.54 (td, *J* = 6.2, 1.0 Hz, 2H), 1.96 (br s, 2H), 1.76 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1 (C), 135.8 (C), 124.9 (CH), 113.1 (CH_2), 61.5 (CH_2), 61.2 (CH_2), 37.8 (CH_2), 31.0 (CH_2), 14.2 (CH_3) ppm; IR (thin film) ν_{max} = 3329, 2954, 2883, 1458, 1042 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 156 ($[M]^{+\bullet}$, 12%), 141 (11), 125 (36), 111 (69), 97 (100); HRMS calc for $C_9H_{16}O_2$ $[M]^{+\bullet}$ 156.1150, found 156.1150.

(E)-6-Bromo-3-(2-bromoethyl)-4-methylenehex-2-ene (27). *N*-Bromosuccinimide (5.3 g, 30 mmol, 2.0 mol equiv) was added portionwise to a stirred mixture of (*E*)-3-ethylidene-4-methylenehexane-1,6-diol (**25**) (2.3 g, 15 mmol, 1.0 mol equiv) and triphenylphosphine (7.8 g, 30 mmol, 1.0 mol equiv) in CH_2Cl_2 (0.10 L) at −78 °C. The reaction mixture was then allowed to warm to 25 °C and stirred overnight. The resulting mixture was poured into petroleum ether (30–40 °C) (0.10 L) and stirred for 30 min, filtered and concentrated under reduced pressure (45 mbar, 0 °C). The resulting mixture was again diluted with petroleum ether (30–40 °C) (0.10 L), filtered and concentrated under reduced pressure (45 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave the title compound **27** (1.6 g, 5.7 mmol, 40% yield) as a colorless oil. R_f 0.56 (petroleum ether (40–60 °C)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (q, *J* = 7.0 Hz, 1H), 5.09 (s, 1H), 4.99 (s, 1H), 3.43 (t, *J* = 7.5 Hz, 2H), 3.35 (t, *J* = 7.9 Hz, 2H), 2.81 (dt, *J* = 15.4, 7.9 Hz, 4H), 1.77 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3 (C), 136.0 (C), 125.3 (CH), 113.2 (CH_2), 37.9 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 30.8 (CH_2), 14.3 (CH_3) ppm; IR (thin film) ν_{max} = 3090, 2967, 2919, 2857, 1439 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 284 ($[M^{81}Br^{81}Br]^{+\bullet}$, 26%), 282 ($[M^{81}Br^{79}Br]^{+\bullet}$, 48%), 280 ($[M^{79}Br^{79}Br]^{+\bullet}$, 27%), 203 (99), 201 (100), 121 (74); HRMS calc for $C_9H_{14}{}^{81}Br_2$ $[M]^{+\bullet}$ 283.9421, found 283.9420; calc for $C_9H_{14}{}^{81}Br^{79}Br$ $[M]^{+\bullet}$ 281.9442, found 281.9424; $C_9H_{14}{}^{79}Br_2$ $[M]^{+\bullet}$ 279.9462, found 279.9461.

3′E-Methyl[4]dendralene (13). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (3.5 g, 23 mmol, 6.4 mol equiv) was added dropwise into a stirred solution of (*E*)-6-bromo-3-(2-bromoethyl)-4-methylenehex-2-ene (**27**) (1.0 g, 3.6 mmol, 1.0 mol equiv) in anhydrous DMSO (3.0 mL) at 25 °C and stirred for 15 min. The resulting reaction mixture was then subjected to vacuum distillation at 65 mbar for 2 h and then at 20 mbar for a further 2 h (trap at −78 °C). The title compound **13** (0.26 g, 2.2 mmol, 60%) was isolated from the receiving flask as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (dd, *J* = 17.3, 10.8 Hz, 1H), 6.41 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.56–5.47 (m, 1H), 5.24–4.97 (m, 6H), 1.83 (d, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4 (C), 138.5 (C), 138.1 (CH), 131.7 (CH), 127.0 (CH), 117.8 (CH_2), 116.3 (CH_2), 116.2 (CH_2), 13.4 (CH_3) ppm; IR (thin film) ν_{max} = 3090, 3016, 2918, 1597, 1586 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 120 ($[M]^{+\bullet}$, 10%), 119 (26), 105 (31), 78 (86), 63 (100); HRMS calc for C_9H_{11} $[M^{+\bullet}{-}H]$ 119.0861, found 119.0857; calc for C_8H_9 $[M^{+\bullet}{-}CH_3]$ 105.0704, found 105.0702.

(Z)-3-Ethylidene-4-methylenehexane-1,6-diol (26). A solution of (*Z*)-diethyl-3-ethylidene-4-methylenehexanedioate (**24**) (4.3 g, 18 mmol, 1.0 mol equiv) in dry Et_2O (60 mL) was slowly added into a stirred suspension of $LiAlH_4$ (1.4 g, 36 mmol, 2.0 mol equiv) in dry Et_2O (40 mL) at 0 °C. The reaction mixture was stirred for 30 min and then allowed to warm to 25 °C and stirred further overnight. The resulting reaction mixture was cooled to 0 °C and carefully quenched by dropwise addition of water (25 mL) followed by addition of Et_2O (25 mL). The resulting mixture was then stirred at 25 °C for 1 h. The resulting reaction mixture was poured into a stirred saturated solution of aqueous NH_4Cl (0.10 L) before a solution of aqueous HCl (1.0 M, 0.10 L) was added. The organic phase separated and the aqueous layer was extracted with Et_2O (4 × 0.10 L). The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (70:30)) gave the title compound **26** (2.5 g, 16 mmol, 91% yield) as a yellow oil. R_f 0.26 (EtOAc:hexane (70:30)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43 (q, *J* = 6.9 Hz, 1H), 5.11 (d, *J* = 1.3 Hz, 1H), 4.81 (d, *J* = 2.3 Hz, 1H), 3.62 (dt, *J* = 13.2, 6.3 Hz, 4H), 2.42 (br s, 2H), 2.38 (t, *J* = 6.5 Hz, 2H), 2.32 (t, *J* = 6.3 Hz, 2H), 1.63 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1 (C), 138.5 (C), 124.1 (CH), 115.9 (CH_2), 60.9 (CH_2), 60.8 (CH_2), 39.6 (CH_2), 38.6 (CH_2), 14.7 (CH_3) ppm; IR (thin film) ν_{max} = 3339, 2936, 2882, 1441, 1045 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 156 ($[M]^{+\bullet}$, 4%), 138 (10), 126 (36), 111 (71), 97 (100); HRMS calc for $C_9H_{16}O_2$ $[M]^{+\bullet}$ 156.1150, found 156.1150.

(Z)-6-Bromo-3-(2-bromoethyl)-4-methylenehex-2-ene (28). *N*-Bromosuccinimide (1.1 g, 6.4 mmol, 2.0 mol equiv) was added portionwise to a stirred mixture of (*Z*)-3-ethylidene-4-methylenehexane-1,6-diol (**26**) (0.50 g, 3.2 mmol, 1.0 mol equiv) and triphenylphosphine (1.7 g, 6.4 mmol, 2.0 mol equiv) in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was then allowed to warm to 25 °C and stirred overnight. The resulting mixture was poured into petroleum ether (30–40 °C) (30 mL) and stirred for 30 min, filtered and concentrated under reduced pressure (45 mbar, 0 °C). The resulting mixture was again diluted with petroleum ether (30–40 °C) (30 mL), filtered and concentrated under reduced pressure (45 mbar, 0 °C). Purification by flash column chromatography (SiO_2, petroleum ether (30–40 °C)) gave the title compound **28** (0.44 g, 1.6 mmol, 49% yield) as a colorless oil. R_f 0.46 (petroleum ether (40–60 °C)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (q, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 1.6 Hz, 1H), 4.91 (d, *J* = 1.9 Hz, 1H), 3.39 (t, *J* = 7.3 Hz, 2H), 3.35 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.67 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7 (C), 137.7 (C), 125.8 (CH), 117.3 (CH_2), 39.4 (CH_2), 38.6 (CH_2), 31.6 (CH_2), 30.5 (CH_2), 14.8 (CH_3) ppm; IR (thin film) ν_{max} = 3080, 2965, 2937, 2916, 2857, 1443, 1431 cm^{-1}; LRMS (70 eV, EI) *m/z* (%) 284 ($[M^{81}Br^{81}Br]^{+\bullet}$, 17%), 282 ($[M^{81}Br^{79}Br]^{+\bullet}$, 34%), 280 ($[M^{79}Br^{79}Br]^{+\bullet}$, 18%), 203 (91), 201 (94), 121 (66), 93 (100); HRMS calc for $C_9H_{14}{}^{81}Br_2$ $[M]^{+\bullet}$ 283.9421, found 283.9436; calc for $C_9H_{14}{}^{81}Br^{79}Br$ $[M]^{+\bullet}$ 281.9442, found 281.9445; calc for $C_9H_{14}{}^{79}Br_2$ $[M]^{+\bullet}$ 279.9462, found 279.9462.

3′Z-Methyl[4]dendralene (14). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1.8 g, 12 mmol, 6.4 mol equiv) was added dropwise into a stirred solution of (*Z*)-6-bromo-3-(2-bromoethyl)-4-methylenehex-2-

ene (**28**) (0.50 g, 1.8 mmol, 1.0 mol equiv) in anhydrous DMSO (2.5 mL) at 25 °C and stirred for 15 min. The resulting reaction mixture was then subjected to vacuum distillation at 65 mbar for 2 h and then at 20 mbar for a further 2 h (trap at −78 °C). The title compound **14** (0.17 g, 1.4 mmol, 77%) was isolated from the receiving flask as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (dd, J = 10.5, 6.4 Hz, 1H), 6.38 (dd, J = 10.7, 6.6 Hz, 1H), 5.75 (q, J = 6.9 Hz, 1H), 5.39 (d, J = 2.3 Hz, 1H), 5.11−4.87 (m, 5H), 1.61 (d, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1 (C), 139.9 (C), 139.1 (CH), 137.0 (CH), 128.3 (CH), 118.9 (CH_2), 115.9 (CH_2), 112.9 (CH_2), 14.8 (CH_3) ppm; IR (thin film) ν_{max} = 3089, 3004, 2914, 1583 cm^{-1}; LRMS (70 eV, EI) m/z (%) 120 ([M]$^{+\bullet}$, 4%), 78 (84), 63 (100); HRMS calc for C_9H_{12} [M]$^{+\bullet}$ 120.0939, found 120.0938.

*Reaction between 1E-Methyl[4]dendralene (**10**) and NMM.* A solution of 1*E*-methyl[4]dendralene (**10**) (66 mg, 0.55 mmol, 1.0 mol equiv) and NMM (0.18 g, 1.6 mmol, 3.0 mol equiv) in $CDCl_3$ (1.9 mL) was stirred for 21 h at room temperature. The solvent was then removed under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (35:65 to 75:25)) gave the compound **29** (18 mg, 0.076 mmol, 14%) as a colorless oil, **32** (14 mg, 0.041 mmol, 7%) as a colorless oil, **33** (91 mg, 0.27 mmol, 48%) as a colorless solid, and a mixture of compounds **36** and **37** (70 mg). Further purification of the mixture of **36** and **37** by flash column chromatography (SiO_2, EtOAc:hexane (90:10)) afforded compound **36** (24 mg, 0.054 mmol, 10%) as a colorless solid and **37** (24 mg, 0.053 mmol, 10%) as a colorless oil.

*Monoadduct **29**.* R_f 0.36 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (dd, J = 17.3, 11.0 Hz, 1H), 6.56 (dd, J = 15.5, 1.8 Hz, 1H), 5.86 (dq, J = 15.6, 6.7 Hz, 1H), 5.31 (d, J = 17.3 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 3.18−3.07 (m, 2H), 3.00−2.91 (m, 2H), 2.90 (s, 3H), 2.30 (dt, J = 14.3, 6.4 Hz, 2H), 1.82 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7 (C) (two coincident signals), 132.8 (C), 131.9 (CH), 130.0 (C), 126.9 (CH), 126.8 (CH), 113.6 (CH_2), 39.5 (CH) (two coincident signals), 25.3 (CH_2), 25.0 (CH_3), 24.1 (CH_2), 19.0 (CH_3) ppm; IR (thin film) ν_{max} = 2931, 1702, 1438, 1384, 1285, 1096 cm^{-1}; LRMS (70 eV, EI) m/z (%) 231 ([M]$^{+\bullet}$, 100%), 216 (67), 145 (65), 131 (91); HRMS calc for $C_{14}H_{17}NO_2$ [M]$^{+\bullet}$ 231.1259, found 231.1255.

*Bis-adduct **32**.* R_f 0.13 (EtOAc:hexane (50:50)); ^{1}H NMR (800 MHz, $CDCl_3$) δ 6.27 (d, J = 15.6 Hz, 1H), 5.78 (dq, J = 15.8, 6.6 Hz, 1H), 3.21 (ddd, J = 9.6, 5.7, 2.6 Hz, 1H), 3.18 (dd, J = 15.0, 2.2 Hz, 1H), 3.13 (ddd, J = 9.6, 6.3, 2.2 Hz, 1H), 3.11−3.05 (m, 2H), 3.00 (dd, J = 8.7, 5.5 Hz, 1H), 2.92 (s, 3H), 2.86 (s, 3H), 2.76 (ddd, J = 14.1, 13.4, 5.6 Hz, 1H), 2.38 (ddd, J = 14.2, 4.9, 2.6 Hz, 1H), 2.20−2.16 (m, 1H), 2.16−2.11 (m, 1H), 1.99−1.93 (m, 1H), 1.77 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.1 (C), 179.7 (C), 179.0 (C), 178.0 (C), 131.8 (C), 128.8 (C), 126.8 (CH), 126.4 (CH), 43.5 (CH), 39.9 (CH), 39.5 (CH), 39.0 (CH), 34.4 (CH), 25.2 (CH_2), 25.1 (CH_3), 25.0 (CH_3), 23.9 (CH_2), 23.6 (CH_2), 18.7 (CH_3) ppm; IR (thin film) ν_{max} = 2944, 1773, 1694, 1436, 1384, 1283, 1020 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ([M]$^{+\bullet}$, 100%), 315 (9), 301 (7), 256 (12), 242 (13), 216 (18); HRMS calc for $C_{19}H_{22}N_2O_4$ [M]$^{+\bullet}$ 342.1580, found 342.1582.

*Bis-adduct **33**.* An analytic sample of **33** was obtained by recrystallization from EtOAc/hexane to give colorless needles, mp 163−165 °C; R_f 0.19 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.59 (dd, J = 17.2, 11.0 Hz, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 3.27 (dd, J = 8.7, 5.4 Hz, 1H), 3.22−3.01 (m, 5H), 3.00−2.91 (m, 1H), 2.87 (s, 3H), 2.85 (s, 3H), 2.24−2.12 (m, 1H), 2.00−1.86 (m, 2H), 1.56 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4 (C), 178.9 (C), 178.5 (C), 177.5 (C), 132.4 (C), 132.1 (C), 131.4 (CH), 115.0 (CH_2), 44.2 (CH), 41.5 (CH), 40.5 (CH), 40.4 (CH), 39.8 (CH), 29.2 (CH), 24.9 (CH_3), 24.8 (CH_3), 24.1 (CH_2), 24.1 (CH_2), 16.3 (CH_3) ppm; IR (KBr disc) ν_{max} = 2963, 1770, 1693, 1438, 1385, 1285, 1094 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ([M]$^{+\bullet}$, 100%), 327 (6), 313 (12), 257 (15), 112 (42); HRMS calc for $C_{19}H_{22}N_2O_4$ [M]$^{+\bullet}$ 342.1580, found 342.1584.

*Tris-adduct **36**.* An analytic sample of **36** was obtained by recrystallization from EtOAc/hexane to give colorless needles, mp 255−257 °C; R_f 0.20 (EtOAc, 100%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.22 (dd, J = 8.6, 5.9 Hz, 1H), 3.19−3.07 (m, 3H), 3.04−2.91 (m, 5H), 2.90 (s, 6H), 2.86 (s, 3H), 2.65 (ddd, J = 14.1, 13.4, 5.4 Hz, 1H), 2.35 (ddd, J = 14.3, 5.0, 2.5 Hz, 1H), 2.16−2.05 (m, 2H), 2.03−1.91 (m, 1H), 1.85−1.74 (m, 1H), 1.54 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7 (C), 178.5 (C), 178.4 (C), 178.3 (C), 177.0 (C), 176.6 (C), 130.8 (C), 130.8 (C), 44.4 (CH), 43.4 (CH), 40.8 (CH), 40.6 (CH), 40.3 (CH), 39.2 (CH), 38.8 (CH), 33.7 (CH), 29.0 (CH), 25.0 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 24.7 (CH_2), 24.4 (CH_2), 23.1 (CH_2), 16.5 (CH_3) ppm; IR (KBr disc) ν_{max} = 2961, 2948, 2842, 1770, 1695, 1435, 1383, 1286 cm^{-1}; LRMS (70 eV, EI) m/z (%) 453 ([M]$^{+\bullet}$, 100%), 438 (7), 342 (33), 256 (14), 112 (39); HRMS calc for $C_{24}H_{27}N_3O_6$ [M]$^{+\bullet}$ 453.1900, found 453.1905.

*Tris-adduct **37**.* R_f 0.31 (EtOAc 100%); ^{1}H NMR (800 MHz, $CDCl_3$) δ 3.27 (dd, J = 8.5, 5.6 Hz, 1H), 3.17 (ddd, J = 9.4, 6.2, 2.0 Hz, 1H), 3.08 (dd, J = 9.5, 5.2 Hz, 1H), 3.05 (dd, J = 8.5, 6.0 Hz, 1H), 3.01−2.97 (m, 2H), 2.99 (s, 3H), 2.96−2.89 (m, 1H), 2.86 (s, 3H), 2.84 (s, 3H), 2.71−2.64 (m, 2H), 2.35 (dt, J = 13.8, 4.6 Hz, 1H), 2.26 (q, J = 13.1 Hz, 1H), 2.21−2.14 (m, 2H), 1.84−1.76 (m, 2H), 1.55 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$) δ 179.3 (C), 178.7 (C), 178.6 (C), 178.3 (C), 176.7 (C), 176.6 (C), 132.2 (C), 129.8 (C), 44.3 (CH), 43.3 (CH), 41.1 (CH), 41.0 (CH), 40.7 (CH), 40.0 (CH), 39.5 (CH), 36.8 (CH), 29.5 (CH), 24.9 (CH_2), 24.9 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 24.4 (CH_2), 23.8 (CH_2), 16.1 (CH_3) ppm; IR (thin film) ν_{max} = 2946, 1770, 1694, 1435, 1383, 1285 cm^{-1}; MS (70 eV, EI) m/z (%) 453 ([M]$^{+\bullet}$, 100%), 438 (5), 368 (7), 342 (73), 256 (26), 112 (48); HRMS calc for $C_{24}H_{27}N_3O_6$ [M]$^{+\bullet}$ 453.1900, found 453.1908.

*Reaction of 1Z-Methyl[4]dendralene (**11**) with NMM.* A solution of 1*Z*-methyl[4]dendralene (**11**) (in 95:5 ratio *Z*:*E* mixture) (0.10 g, 0.86 mmol, 1.0 mol equiv) and NMM (0.29 g, 2.6 mmol, 3.0 mol equiv) in $CDCl_3$ (3.0 mL) was stirred for 21 h at room temperature. The solvent was then removed under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (25:75 to 60:40) afforded compounds **38** (52 mg, 0.22 mmol, 27%) as a colorless oil, **40** (90 mg, 0.26 mmol, 32%) as a colorless solid, **41** (24 mg, 0.070 mmol, 9%) as a colorless solid. Analytical sample of compound **38** was obtained by a reversed phase HPLC (t_R = 16.2 min, XBridge C18 column, 5 μm, 4.6 × 150 mm, eluting with THF:H_2O (25:75), flow rate = 1 mL/min).

*Monoadduct **38**.* R_f 0.42 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) 6.45 (dd, J = 17.5, 10.9 Hz, 1H), 5.92−5.82 (m, 1H), 5.59 (dq, J = 11.4, 7.0 Hz, 1H), 5.30 (d, J = 17.5 Hz, 1H), 5.05 (d, J = 10.9 Hz, 1H), 3.24−3.07 (m, 2H), 3.00 (dd, J = 14.9, 2.9 Hz, 1H), 2.91 (s, 3H), 2.64 (dd, J = 15.0, 2.8 Hz, 1H), 2.50−2.37 (m, 1H), 2.33−2.18 (m, 1H), 1.45 (dd, J = 7.0, 1.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8 (C), 179.7 (C), 134.4 (CH), 133.6 (C), 131.7 (C), 128.2 (CH), 127.7 (CH), 112.9 (CH_2), 39.6 (CH), 39.6 (CH), 29.8 (CH_2), 25.1 (CH_3), 23.4 (CH_2), 15.0 (CH_3) ppm; IR (thin film) ν_{max} = 2932, 1772, 1697, 1433, 1381, 1286 cm^{-1}; LRMS (70 eV, EI) m/z (%) 231 ([M]$^{+\bullet}$, 94%), 230 (99), 216 (100), 145 (66), 131 (94); HRMS calc for $C_{14}H_{17}NO_2$ [M]$^{+\bullet}$ 231.1259, found 231.1254.

*Bis-adduct **40**.* An analytic sample of **40** was obtained by recrystallization from dichloromethane/hexane to give colorless prism, mp 152−154 °C; R_f 0.14 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (d, J = 11.4 Hz, 1H), 5.51 (dq, J = 11.3, 6.9 Hz, 1H), 3.22 (ddd, J = 9.7, 5.6, 2.6 Hz, 1H), 3.12−2.98 (m, 3H), 2.93 (s, 3H), 2.85 (s, 3H), 2.83−2.70 (m, 2H), 2.63 (dd, J = 14.2, 1.6 Hz, 1H), 2.38 (ddd, J = 14.1, 4.7, 2.6 Hz, 1H), 2.25−2.01 (m, 3H), 1.33 (dd, J = 6.9, 1.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2 (C), 179.6 (C), 179.1 (C), 178.0 (C), 131.3 (C), 130.7 (C), 127.5 (CH), 127.0 (CH), 43.6 (CH), 39.8 (CH), 39.3 (CH), 39.1 (CH), 33.9 (CH), 29.5 (CH_2), 25.7 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 23.8 (CH_2), 14.6 (CH_3) ppm; IR (thin film) ν_{max} = 2951, 1772, 1692, 1436, 1383, 1283, 1020 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ([M]$^{+\bullet}$, 100%), 327 (9), 313 (2), 301 (2), 256 (9), 242 (10), 216 (12); HRMS calc for $C_{19}H_{22}N_2O_4$ [M]$^{+\bullet}$ 342.1580, found 342.1584.

*Bis-adduct **41**.* An analytic sample of **41** was obtained by recrystallization from EtOAc/hexane to give colorless needles, mp 217−219 °C; R_f 0.09 (EtOAc:hexane (50:50)); ^{1}H NMR (800 MHz,

$CDCl_3$) δ 5.81 (d, J = 11.4 Hz, 1H), 5.54 (dq, J = 11.3, 6.9 Hz, 1H), 3.16 (t, J = 7.6 Hz, 1H), 3.10 (dd, J = 8.7, 5.4 Hz, 1H), 3.00 (s, 3H), 2.85 (s, 3H), 2.84–2.75 (m, 3H), 2.71 (d, J = 14.5 Hz, 1H), 2.45–2.38 (m, 2H), 2.38–2.34 (m, 1H), 2.33–2.29 (m, 1H), 1.91–1.84 (m, 1H), 1.39 (dd, J = 7.0, 1.7 Hz, 3H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$) δ 179.2 (C), 179.1 (C), 179.0 (C), 177.8 (C), 132.1 (C), 130.3 (C), 127.7 (CH), 127.2 (CH), 43.7 (CH), 40.3 (CH), 40.1 (CH), 39.0 (CH), 36.8 (CH), 29.7 (CH_2), 25.5 (CH_2), 25.2 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 14.7 (CH_3) ppm; IR (thin film) ν_{max} = 2951, 1775, 1699, 1691, 1437, 1384, 1284, 1027 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 327 (2), 313 (2), 300 (8), 257 2(9), 242 (13), 216 (15); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1579.

*Reaction of 2-Methyl[4]dendralene (**12**) with NMM.* A solution of 2-methyl[4]dendralene (**12**) (0.41 g, 3.4 mmol, 1.0 mol equiv) and NMM (1.1 g, 10 mmol, 3.0 mol equiv) in CH_2Cl_2 (4.0 mL) was stirred at room temperature for 14 h. The solvent was then removed under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (40:60 to 60:40)) afforded compounds **42** (22 mg, 0.095 mmol, 3%) as a colorless oil, **45** (0.16 g, 0.47 mmol, 26%) as a colorless solid, **47** (88 mg, 0.26 mmol, 14%) as a colorless solid and **46** (0.17 g, 0.49 mmol, 27%) as a colorless oil. Analytical sample of compound **47** was obtained by a reversed phase HPLC (t_R = 16.5 min, Altima C18 column, 5 μm, 10 × 250 mm, eluting with $CH_3CN:H_2O$ (30:70), flow rate = 4.7 mL/min).

*Monoadduct **42**.* R_f 0.74 (EtOAc:hexane (75:25)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (dd, J = 17.6, 11.0 Hz, 1H), 5.27 (d, J = 17.6 Hz, 1H), 5.04–4.95 (m, 2H), 4.57 (dd, J = 1.5, 0.7 Hz, 1H), 3.20–3.07 (m, 2H), 3.03–2.97 (m, 1H), 2.91 (s, 3H), 2.67 (dd, J = 15.0, 2.5 Hz, 1H), 2.37 (dd, J = 15.0, 6.3 Hz, 1H), 2.18 (dd, J = 14.2, 5.2 Hz, 1H), 1.74–1.70 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7 (C), 179.5 (C), 143.2 (C), 139.7 (C), 134.0 (CH), 130.3 (C), 115.6 (CH_2), 112.7 (CH_2), 39.6 (CH), 39.6 (CH), 28.6 (CH_2), 24.9 (CH_3), 23.3 (CH_2), 21.6 (CH_3) ppm; IR (thin film) ν_{max} = 3087, 2955, 2914, 2853, 1693, 1434 cm^{-1}; LRMS (70 eV, EI) m/z (%) 231 ($[M]^{+\bullet}$, 74%), 230 (100), 216 (49), 131 (57), 119 (59); HRMS calc for $C_{14}H_{17}NO_2$ $[M]^{+\bullet}$ 231.1259, found 231.1257.

*Bis-adduct **45**.* An analytic sample of **45** was obtained by recrystallization from EtOAc/hexane to give colorless needles, mp 186–188 °C; R_f 0.39 (EtOAc:hexane (75:25)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88 (dq, J = 3.0, 1.5 Hz, 1H), 4.44 (dd, J = 2.1, 0.9 Hz, 1H), 3.21 (ddd, J = 9.2, 5.5, 2.5 Hz, 1H), 3.15–3.04 (m, 3H), 3.00 (dd, J = 8.6, 5.1 Hz, 1H), 2.93 (s, 3H), 2.89 (s, 3H), 2.79 (ddd, J = 6.9, 6.9, 2.9 Hz, 1H), 2.65 (dd, J = 14.5, 1.4 Hz, 1H), 2.36 (ddd, J = 14.1, 4.9, 2.5 Hz, 1H), 2.23–1.97 (m, 3H), 1.63 (dd, J = 1.4, 0.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.1 (C), 179.5 (C), 179.1 (C), 177.9 (C), 142.6 (C), 137.8 (C), 128.7 (C), 114.1 (CH_2), 43.3 (CH), 39.9 (CH), 39.6 (CH), 39.1 (CH), 33.8 (CH), 28.6 (CH_2), 24.9 (CH_2), 24.9 (CH_3), 24.7 (CH_3), 23.5 (CH_2), 21.7 (CH_3) ppm; IR (KBr disc) ν_{max} = 3075, 2960, 2946, 1687, 1435, 1384 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 242 (12), 231 (9), 112 (21); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1579.

*Bis-adduct **46**.* R_f 0.42 (EtOAc:hexane (75:25)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45–5.37 (m, 1H), 3.10–2.99 (m, 4H), 2.92 (s, 3H), 2.86 (s, 3H), 2.64 (ddd, J = 15.2, 7.2, 1.8 Hz, 1H), 2.53–2.38 (m, 3H), 2.20–2.04 (m, 4H), 1.54–1.51 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.1 (C), 179.9 (C), 179.8 (C), 179.5 (C), 138.7 (C), 132.4 (C), 130.2 (C), 124.5 (CH), 39.9 (CH), 39.7 (CH), 39.4 (CH), 39.4 (CH), 30.8 (CH_2), 27.9 (CH_2), 26.9 (CH_2), 24.9 (CH_3), 24.9 (CH_3), 24.4 (CH_2), 20.4 (CH_3) ppm; IR (thin film) ν_{max} = 3057, 2949, 2849, 1774, 1694, 1434 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 242 (7), 112 (19); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1581.

*Bis-adduct **47**.* An analytic sample of **47** was obtained by recrystallization from EtOAc/hexane to give colorless needles, mp 185–187 °C; R_f 0.36 (EtOAc:hexane (75:25)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54–5.47 (m, 1H), 3.14–3.01 (m, 4H), 2.96 (s, 6H), 2.70 (ddd, J = 15.2, 7.1, 2.0 Hz, 1H), 2.54 (dtd, J = 14.7, 8.9, 2.1 Hz, 3H), 2.29–2.12 (m, 4H), 1.65 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2 (C), 180.0 (C), 179.8 (C), 179.7 (C), 139.6 (C), 132.2 (C), 130.8 (C), 124.3 (CH), 39.9 (CH), 39.8 (CH), 39.2 (CH), 39.1 (CH), 30.9 (CH_2), 28.2 (CH_2), 27.4 (CH_2), 25.1 (CH_3), 25.0 (CH_3), 24.3 (CH_2), 21.0 (CH_3) ppm; IR (KBr disc) ν_{max} = 3026, 2944, 2848, 1769, 1963, 1439 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 242 (8), 112 (26); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1580.

*Reaction of 3′E-Methyl[4]dendralene (**13**) with NMM.* A solution of 3′*E*-methyl[4]dendralene (**13**) (0.21 g, 1.8 mmol, 1.0 mol equiv) and NMM (0.58 g, 5.2 mmol, 3.0 mol equiv) in CH_2Cl_2 (7.5 mL) was stirred at room temperature overnight. The solvent was then removed under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (30:70)) afforded compound **48** (0.17 g, 0.74 mmol, 42%) as a colorless oil, compound **50** (0.27 g, 0.79 mmol, 45%) as a colorless solid, and compound **51** (16 mg, 0.047 mmol, 3%) as a colorless solid.

*Monoadduct **48**.* R_f 0.78 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (dd, J = 17.5, 11.1 Hz, 1H), 6.88 (dd, J = 15.8, 9.6 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H), 5.21 (d, J = 2.7 Hz, 1H), 5.17 (d, J = 2.7 Hz, 1H), 3.38 (p, J = 7.1 Hz, 1H), 3.15–2.94 (m, 3H), 3.02 (s, 3H), 2.38–2.24 (m, 1H), 0.89 (d, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.4 (C), 178.8 (C), 138.1 (C), 132.6 (CH), 131.4 (C), 131.3 (CH), 114.5 (CH_2), 114.4 (CH_2), 43.3 (CH), 38.3 (CH), 29.8 (CH), 24.7 (CH_3), 21.9 (CH_2), 13.8 (CH_3) ppm; IR (thin film) ν_{max} = 3090, 2970, 2941, 1775, 1697, 1433, 1382 cm^{-1}; LRMS (70 eV, EI) m/z (%) 231 ($[M^{+\bullet}]$, 25%), 230 (100), 216 (5), 204 (8), 145 (48); HRMS calc for $C_{14}H_{16}NO_2$ $[M^{+\bullet}-H]$ 230.1181, found 230.1180.

*Bis-adduct **50**.* An analytic sample of **50** was obtained by recrystallization from dichloromethane/petroleum ether (40–60 °C) to give colorless needles, mp 182–184 °C; R_f 0.27 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08–5.93 (m, 1H), 5.24 (dd, J = 11.2, 2.1 Hz, 1H), 4.89 (dd, J = 17.6, 2.1 Hz, 1H), 3.28–3.18 (m, 2H), 3.10 (ddd, J = 9.7, 6.4, 2.1 Hz, 1H), 2.99 (dd, J = 8.4, 5.3 Hz, 1H), 2.94 (s, 3H), 2.92–2.85 (m, 1H), 2.84 (s, 3H), 2.78 (dd, J = 13.3, 5.5 Hz, 1H), 2.39 (ddd, J = 14.1, 5.0, 2.5 Hz, 2H), 2.28–2.17 (m, 1H), 2.16–2.03 (m, 1H), 1.39 (d, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2 (C), 179.7 (C), 177.6 (C), 177.1 (C), 138.0 (C), 132.3 (CH), 130.5 (C), 119.8 (CH_2), 45.4 (CH), 44.0 (CH), 39.6 (CH), 39.0 (CH), 34.2 (CH), 34.0 (CH), 25.5 (CH_2), 25.1 (CH_3), 24.7 (CH_3), 23.4 (CH_2), 14.9 (CH_3) ppm; IR (KBr disc) ν_{max} = 3093, 2934, 2946, 1769, 1697, 1433 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 257 (12), 230 (9), 112 (37); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1573.

*Bis-adduct **51**.* Colorless solid, mp 166–168 °C; R_f 0.20 (EtOAc:hexane (50:50)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.15–6.01 (m, 1H), 5.28 (dd, J = 11.1, 2.1 Hz, 1H), 4.82 (dd, J = 17.5, 2.1 Hz, 1H), 3.26 (dd, J = 14.7, 6.4 Hz, 1H), 3.07 (dd, J = 8.4, 4.8 Hz, 1H), 3.03–2.96 (m, 1H), 3.00 (s, 3H), 2.86–2.72 (m, 3H), 2.83 (s, 3H), 2.62–2.48 (m, 1H), 2.46–2.30 (m, 2H), 2.05–1.89 (m, 1H), 1.45 (d, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2 (C), 179.1 (C), 177.4 (C), 177.0 (C), 136.9 (C), 132.5 (C), 132.3 (CH), 120.1 (CH_2), 45.7 (CH), 44.2 (CH), 40.0 (CH), 39.5 (CH), 36.9 (CH), 34.3 (CH), 25.2 (CH_2), 25.1 (CH_2), 24.9 (CH_3), 24.6 (CH_3), 15.0 (CH_3) ppm; IR (KBr disc) ν_{max} = 3081, 2938, 2849, 1770, 1696, 1435 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 327 (6), 313 (11), 257 (19), 112 (45); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1577.

*Reaction of 3′Z-Methyl[4]dendralene (**14**) with NMM.* A solution of 3′*Z*-methyl[4]dendralene (**14**) (0.42 mg, 3.5 mmol, 1.0 mol equiv) and NMM (1.2 g, 11 mmol, 3.0 mol equiv) in CH_2Cl_2 (15 mL) was stirred at room temperature overnight. The solvent was then removed under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc:hexane (30:70)) afforded compound **54** (0.13 g, 0.38 mmol, 11%) as a colorless solid, compound **55** (95 mg, 0.28 mmol, 8%) as a colorless solid, compound **58** (0.37 g, 0.82 mmol, 23%) as a colorless solid, compound **59** (0.28 g, 0.62 mmol, 18%) as a colorless solid, compound **60** (0.16 g, 0.35 mmol, 10%) as a colorless solid. Analytical samples of tris-adducts **58**, **59**, and **60** were isolated by a reversed phase HPLC (retention times: for **58**, t_R = 9.1 min; for **59**, t_R = 12.5 min; for **60**, t_R = 11.3 min, Altima C18 column, 5 μm, 4.6 × 250

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mm, eluting with $CH_3CN:H_2O$ (30:70) to CH_3CN (100%), flow rate = 1.0 mL/min).

Bis-adduct ***54***. An analytic sample of **54** was obtained by recrystallization from dichloromethane/petroleum ether (40–60 °C) to give colorless needles, mp 173–175 °C; R_f 0.56 (EtOAc:hexane (70:30)); ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (dd, J = 17.2, 11.0 Hz, 1H), 5.36 (d, J = 17.2 Hz, 1H), 5.13 (dd, J = 10.9, 1.1 Hz, 1H), 3.67 (q, J = 9.9 Hz, 1H), 3.48 (p, J = 7.2 Hz, 1H), 3.26–3.09 (m, 3H), 2.98 (s, 3H), 2.86 (s, 3H), 2.74–2.63 (m, 2H), 2.56 (dd, J = 9.6, 5.8 Hz, 1H), 2.30 (ddd, J = 15.2, 10.6, 8.4 Hz, 1H), 2.03 (dd, J = 15.4, 6.8 Hz, 1H), 0.88 (d, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.0 (C), 178.9 (C), 178.9 (C), 178.8 (C), 137.3 (C), 131.1 (CH), 130.4 (C), 115.1 (CH_2), 46.1 (CH), 43.2 (CH), 40.4 (CH), 35.9 (CH), 34.0 (CH), 30.7 (CH), 25.0 (CH_3), 24.6 (CH_3), 24.2 (CH_2), 22.2 (CH_2), 17.1 (CH_3) ppm; IR (KBr disc) ν_{max} = 3080, 2926, 2842, 1773, 1690, 1435 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 324 (65), 112 (74); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1579.

Bis-adduct ***55***. An analytic sample of **55** was obtained by recrystallization from dichloromethane/petroleum ether (40–60 °C) to give colorless prism, mp 164–166 °C; R_f 0.31 (EtOAc:hexane (70:30)); ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (dd, J = 17.0, 11.0 Hz, 1H), 5.39 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.8 Hz, 1H), 3.58 (p, J = 7.3 Hz, 1H), 3.31–3.17 (m, 2H), 3.11 (dd, J = 9.6, 4.8 Hz, 1H), 3.02 (s, 3H), 2.98–2.87 (m, 2H), 2.85 (s, 3H), 2.69–2.36 (m, 3H), 2.05 (dd, J = 14.8, 6.7 Hz, 1H), 0.80 (d, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4 (C), 178.8 (C), 178.3 (C), 177.7 (C), 138.2 (C), 131.2 (CH), 130.5 (C), 115.2 (CH_2), 43.7 (CH), 42.4 (CH), 40.2 (CH), 38.6 (CH), 36.8 (CH), 29.8 (CH), 28.7 (CH_3), 24.8 (CH_3), 24.1 (CH_2), 23.2 (CH_2), 17.6 (CH_3) ppm; IR (KBr disc) ν_{max} = 2925, 2853, 1768, 1695, 1435 cm^{-1}; LRMS (70 eV, EI) m/z (%) 342 ($[M]^{+\bullet}$, 100%), 257 (37), 112 (62); HRMS calc for $C_{19}H_{22}N_2O_4$ $[M]^{+\bullet}$ 342.1580, found 342.1582.

Tris-adduct ***58***. An analytic sample of **58** was obtained by recrystallization from dichloromethane/petroleum ether (40–60 °C) to give colorless prism, mp 244–246 °C; R_f 0.34 (EtOAc:hexane (75:25)); ^1H NMR (300 MHz, $CDCl_3$) δ 3.51 (q, J = 9.9 Hz, 1H), 3.33–3.11 (m, 3H), 3.11–2.99 (m, 3H), 2.98 (s, 3H), 2.91 (s, 3H), 2.86 (s, 3H), 2.78 (dd, J = 13.9, 5.3 Hz, 1H), 2.67 (dd, J = 15.1, 9.7 Hz, 1H), 2.58–2.43 (m, 2H), 2.37 (ddd, J = 14.3, 4.8, 2.2 Hz, 1H), 2.32–2.13 (m, 2H), 2.06–1.90 (m, 1H), 0.77 (br s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8 (C), 179.8 (C), 179.5 (C), 178.7 (C), 178.1 (C), 177.1 (C), 135.8 (C), 129.1 (C), 45.7 (CH), 43.9 (CH), 43.4 (CH), 39.4 (CH), 38.9 (CH), 35.7 (CH), 34.0 (CH), 33.4 (CH), 31.2 (CH), 25.0 (CH_3), 24.9 (CH_3), 24.6 (CH_3), 24.3 (CH_2), 23.5 (CH_2), 21.6 (CH_2), 17.1 (CH_3) ppm; IR (KBr disc) ν_{max} = 2938, 2875, 2854, 1769, 1688, 1435 cm^{-1}; LRMS (70 eV, EI) m/z (%) 453 ($[M]^{+\bullet}$, 100%), 438 (13), 424 (8), 394 (7), 329 (17), 112 (40); HRMS calc for $C_{24}H_{27}N_3O_6$ $[M]^{+\bullet}$ 453.1900, found 453.1895.

Tris-adduct ***59***. An analytic sample of **59** was obtained by recrystallization from dichloromethane/petroleum ether (40–60 °C) to give colorless prism, mp 231–233 °C; R_f 0.19 (EtOAc:hexane (75:25)); ^1H NMR (300 MHz, $CDCl_3$) δ 3.35 (p, J = 7.5 Hz, 1H), 3.29–3.20 (m, 1H), 3.20–3.11 (m, 1H), 3.07–3.05 (m, 3H), 2.99 (s, 3H), 2.90 (s, 3H), 2.97–2.76 (m, 3H), 2.83 (s, 3H), 2.42–2.32 (m, 4H), 2.24–2.15 (m, 1H), 2.02 (d, J = 11.7 Hz, 1H), 0.72 (d, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9 (C), 179.4 (C), 179.2 (C), 177.9 (C), 177.2 (C), 176.6 (C), 136.6 (C), 129.6 (C), 43.8 (CH), 43.8 (CH), 42.6 (CH), 39.5 (CH), 39.0 (CH), 38.8 (CH), 36.1 (CH), 33.9 (CH), 28.8 (CH), 25.1 (CH_3), 24.8 (CH_3), 24.7 (CH_3), 23.7 (CH_2), 23.6 (CH_2), 23.2 (CH_2), 17.8 (CH_3) ppm; IR (KBr disc) ν_{max} = 2924, 1771, 1694, 1435 cm^{-1}; LRMS (70 eV, EI) m/z (%) 453 ($[M]^{+\bullet}$, 100%), 424 (9), 342 (29), 329 (13), 112 (49); HRMS calc for $C_{24}H_{27}N_3O_6$ $[M]^{+\bullet}$ 453.1900, found 453.1900.

Tris-adduct ***60***. An analytic sample of **60** was obtained by recrystallization from chloroform/petroleum ether (40–60 °C) to give colorless prism, mp 144–146 °C; R_f 0.21 (EtOAc:hexane (75:25)); ^1H NMR (300 MHz, $CDCl_3$) δ 3.55 (q, J = 9.6 Hz, 1H), 3.38–3.23 (m, 1H), 3.20–3.05 (m, 3H), 3.02 (s, 3H), 2.99 (s, 3H), 2.85 (s, 3H), 2.84–2.66 (m, 3H), 2.66–2.19 (m, 6H), 1.92 (t, J = 13.4 Hz, 1H), 0.92 (br s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9 (C), 178.7 (C) (two coincident signals), 178.6 (C), 178.1 (C), 176.9 (C), 134.4 (C), 130.8 (C), 46.0 (CH), 44.1 (CH), 43.5 (CH), 39.9 (CH), 39.5 (CH), 36.8 (CH), 35.9 (CH), 33.8 (CH), 31.4 (CH), 25.0 (CH_3), 25.0 (CH_3), 24.8 (CH_3), 24.6 (CH_2), 23.9 (CH_2), 21.7 (CH_2), 17.8 (CH_3) ppm; IR (KBr disc) ν_{max} = 2923, 2852, 1771, 1694, 1434 cm^{-1}; LRMS (70 eV, EI) m/z (%) 453 ($[M]^{+\bullet}$, 100%), 342 (57), 329 (7), 112 (65); HRMS calc for $C_{24}H_{27}N_3O_6$ $[M]^{+\bullet}$ 453.1900, found 453.1902.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02583.

Crystal data for compounds **33**, **36**, **40**, **41**, **45**, **47**, **50**, **54**, **55**, **58**, **59**, and **60** (CCDC nos. 1421657, 1421658, 1421659, 1421660, 1421661, 1421662, 1421663, 1421664, 1421665, 1421666, 1421667, and 1421668, respectively). (CIF)

^1H and ^{13}C NMR spectra for all new compounds, anisotropic displacement ellipsoid plots for above compounds. (PDF)

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Notes

The authors declare no competing financial interest.

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(23) The Kumada−Tamao−Corriu type cross-coupling reaction between 2-chloro[3]dendralene (**17**) and the Grignard reagent of 1*Z*-bromopropene (**20**) was performed on gram scale and gave a *Z*:*E* product ratio of 95:5. The *E*- and *Z*- isomers **10** and **11** could not be separated chromatographically.

(24) Several unsuccessful variations on the cross-coupling themes were trialed, and the most instructive observations are summarized here. Interestingly, whereas the generation of the Grignard reagent of 1*Z*-propenyl bromide (**20**) proceeded relatively smoothly and with stereoretention, formation of the Grignard reagent of 1*E*-propenyl bromide (**19**) was capricious, and significant geometrical isomerization was observed during its cross-coupling. (*E*/*Z* isomerization has previously been reported during cross-couplings of the Grignard reagents of *E*- and *Z*-propenyl bromides: Zembayashi, M.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1975**, *16*, 1719−1722). Switching the nucleophile and electrophile allowed the formation of **10** but not by way of Kumada−Tamao−Corriu type cross-coupling, or Suzuki−Miyaura cross-coupling. Only the Negishi method between **18** and **19** depicted in Scheme 3 gave the desired product **10** in appreciable yield. Intriguingly, an attempted Negishi cross-coupling between trienylzinc species **18** and 1*Z*-bromopropene failed.

(25) This final step is reminiscent of the final step in our gram-scale synthesis of the parent [3]dendralene: Bradford, T. A.; Payne, A. D.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. *J. Org. Chem.* **2010**, *75*, 491−494.

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(29) The outcomes of these reactions were found to exhibit no significant solvent dependence. Thus, in test experiments between unsubstituted [4]dendralene (**1**) and *N*-methylmaleimide (NMM) in THF, CH_2Cl_2 and $CDCl_3$ (both dried/base-treated and used as received), the variance in product ratios was less than 5%. Details of these experiments are provided in the Supporting Information.

(30) The Diels−Alder reaction between monomethyl-substituted [4]dendralenes and 1 mol equiv of *N*-methylmaleimide (NMM) at room temperature resulted in the generation of a complex mixture of monoadducts and bis-adducts along with unreacted starting material.

(31) The estimated product ratio based upon analysis of crude ^{1}H NMR spectra was very similar to isolated product ratios.

(32) The estimated product ratio based upon analysis of the ^{1}H NMR spectrum of the crude product mixture was similar but not identical to that based upon isolated product yields: crude product ratio (^{1}H NMR) for the Diels−Alder reaction of 1*Z*-methyl[4]dendralene (**11**): **38**:**40**:**41** = 41:43:16; percentage ratio based upon isolated yields = 40:47:13, respectively; for the Diels−Alder reaction of 2-methyl[4]dendralene (**12**): **42**:**45**:**46**:**47** = 8:26:37:29; percentage ratio based upon isolated yields = 4:37:39:20, respectively. We attribute this discrepancy to selective losses of **40** and **45** during chromatographic purification.

(33) The high complexity of the ^{1}H NMR spectrum of the crude product precluded the estimation of a crude product ratio.

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Supporting Information for:

Synthesis and Diels–Alder Reactivity of Substituted [4]Dendralenes

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1. Experimental Section

1.1 General Methods

Reactions were performed under a positive pressure of dry nitrogen in oven or flame dried glassware, unless otherwise specified. Anhydrous THF was dried over sodium wire and distilled from sodium benzophenone ketyl. Other anhydrous solvents were dried using a solvent purification system outlined in the procedure by Grubbs et al.[1] Commercially available chemicals were used as purchased or purified by standard procedures.[2] Grignard reagents were titrated against salicylaldehyde phenylhydrazone according to the procedure of Love and Jones.[3] Microwave reactions were performed using a CEM Discovery instrument.

Chromatography

Analytical thin-layer chromatography (TLC) was performed with silica gel plates, precoated with silica gel 60 F_{254} (0.2 mm) on aluminium sheets and visualized using UV fluorescence (λ_{max} = 254 nm) and flash column chromatography employed using 230–400 mesh silica gel. Analytical high performance liquid chromatography (HPLC) was performed using on a 5µm, 4.6 × 150 mm, C18 column or a 5µm, 10 × 250 mm, C18 column.

NMR Spectroscopy

^{1}H and ^{13}C NMR spectra were recorded at 298 K using either 300, 400, or 800 MHz spectrometers. Residual chloroform ($CHCl_3$ in $CDCl_3$) (δ = 7.26 ppm) was used for ^{1}H NMR spectra and the central line of the deuterochloroform ($CDCl_3$) triplet (δ = 77.1 ppm) was used for ^{13}C NMR spectra as an internal reference. Assignment of proton and carbon signals were assisted by DEPT, COSY, HSQC or HMBC experiments where necessary.

Infrared Spectroscopy

Infrared spectra were recorded on a FT-IR spectrometer as neat films on NaCl plates for oils or as KBr disks for solids.

Mass Spectroscopy

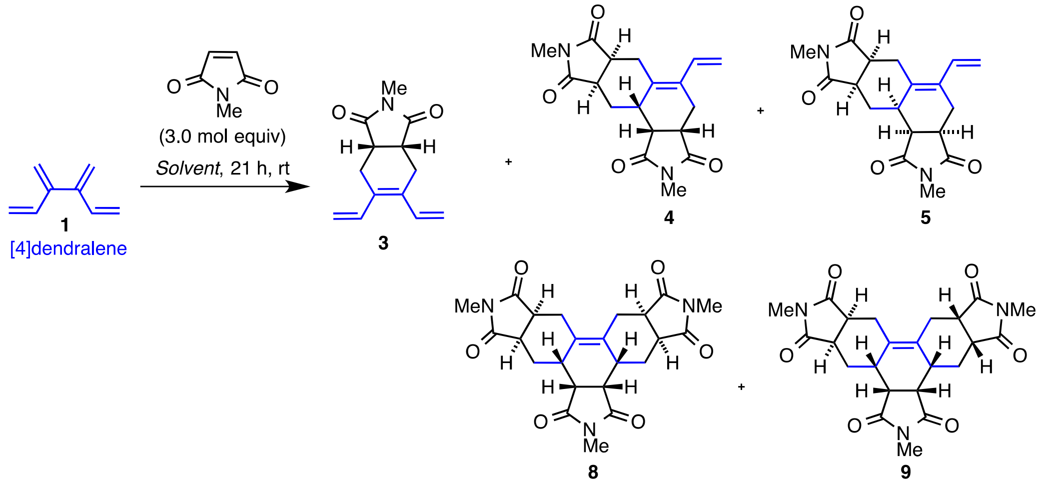
Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were recorded on a magnetic sector mass spectrometer using electron impact (EI^+) ionization mode at 70 eV. LRMS were reported with intensities quoted as percentages of the base peak.

Melting Points

Melting points were measured on a hot stage melting points apparatus and are uncorrected.

1.2 Diels–Alder Reaction Between [4]Dendralene (1) and *N*-Methylmaleimide (NMM) in Various Solvents

The solvent dependence of the Diels–Alder reaction between parent [4]dendralene (**1**) and excess NMM (3 mol equiv) was examined. The product distribution obtained from reactions performed in THF, CH_2Cl_2 and $CDCl_3$ were the same, demonstrating no significant solvent influence.



Scheme S1: Diels–Alder reaction between [4]dendralene (**1**) and excess NMM (3 mol equiv) in different solvents (THF, CH_2Cl_2 and $CDCl_3$) at room temperature.

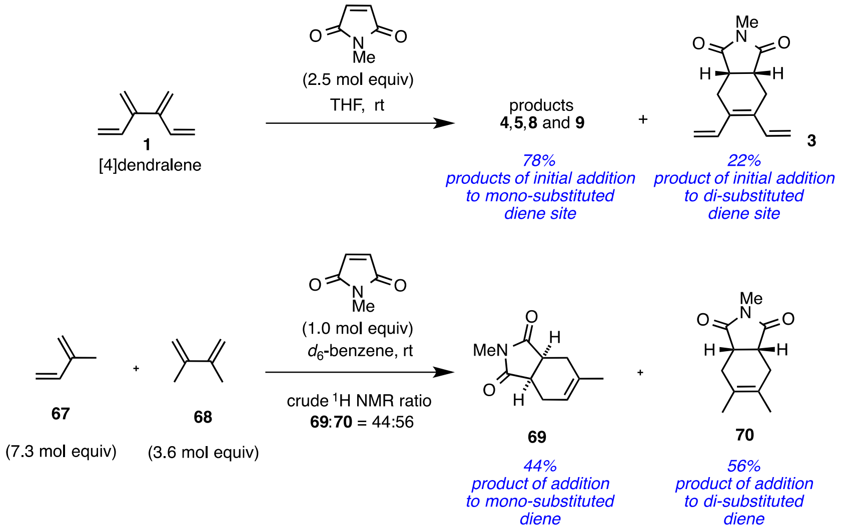
Experimental procedure: A reaction vessel was charged with [4]dendralene (**1**) (15 mg, 0.14 mmol, 1.0 mol equiv), solvent (0.50 mL), and NMM (47 mg, 0.42 mmol, 3.0 mol equiv) and then capped. The reaction mixture was stirred for 21 hours at room temperature. The product composition was determined by analysis of the ^{1}H NMR spectra (800 MHz, at 25 °C, in $CDCl_3$) (Table S1). In the case of the $CDCl_3$ reactions, direct analyses of the reaction mixtures by ^{1}H NMR spectroscopy was carried out. With runs in THF and CH_2Cl_2, the solvent was removed under reduced pressure before $CDCl_3$ (0.5 mL) was added and the ^{1}H NMR spectrum was recorded.

	Product Ratio[(a)]				
Solvent	**3**	**4**	**5**	**8**	**9**
$CDCl_3$[(b)]	24	42	6	14	14
$CDCl_3$[(c)]	26	42	6	13	13
CH_2Cl_2	24	44	6	13	13
THF	21	49	7	11	12

Table S1: Diels–Alder reaction between parent [4]dendralene (**1**) and excess (3 mol equiv) of NMM in different solvents at room temperature. ***(a)*** The crude product ratio was calculated based upon analysis of the crude ^{1}H NMR spectra (800 MHz, at 25 °C, in $CDCl_3$), ***(b)*** Commercial $CDCl_3$ was used directly as received. ***(c)*** $CDCl_3$ was stored over K_2CO_3 and 3Å molecular sieves before use.

1.3 Competition Experiment: Diels–Alder Reaction Between a 2:1 (Isoprene (67) : 2,3-Dimethyl-1,3-butadiene (68)) Mixture and *N*-Methylmaleimide (NMM)

The outcome of the reaction between the parent [4]dendralene (**1**) and excess NMM is shown in Scheme 2 of the main manuscript. Of the five products formed, four are the result of addition to the mono-substituted diene site and the remaining one product results from addition to the di-substituted diene site. The mono-substituted diene site of [4]dendralene (**1**) is preferred over the di-substituted diene site in a ratio of 78:22 (Scheme S2, top). To test if this outcome is simply the result of a preference for addition to a 2-substituted diene over a 2,3-disubstituted diene, a competition experiment was performed in which NMM was treated with a 2:1 mixture of isoprene (**67**) and 2,3-dimethyl-1,3-butadiene (**68**). This experiment gave a slight preference for the more substituted diene (Scheme S2, bottom), demonstrating that [4]dendralene (**1**) does not behave as a simple mixtures of 1,3-butadienes.



Scheme S2: A comparison of (top equation) the reactivity of [4]dendralene with NMM with (bottom equation) a 2:1 (isoprene (**67**) : 2,3-dimethyl-1,3-butadiene (**68**)) mixture with NMM.

Experimental procedure: An NMR tube was charged with a 2:1 mixture of isoprene (**67**) (38 mg, 0.56 mmol, 7.3 mol equiv) and 2,3-dimethyl-1,3-butadiene (**68**) (23 mg, 0.28 mmol, 3.6 mol equiv), anisole (internal standard, 19 mg) and d_6-benzene. To this was added a solution of *N*-methylmaleimide (8.6 mg, 0.077 mmol, 1.0 mol equiv) in d_6-benzene (0.30 mL). The resulting solution was allowed to stand for 16 hours at room temperature. The reaction progression was monitored by ^{1}H NMR spectroscopy and the reaction was deemed complete when NMM could no longer be observed. The ratio of the corresponding products **69**[4] and **70**[5] (44:56) was obtained from integration of the ^{1}H NMR spectrum of the reaction mixture.

2. Crystallography Section

2.1 Crystallographic Data for 33, 36, 40, 41, 45, 47, 50, 54, 55, 58, 59, and 60.

Compound 33: $C_{19}H_{22}N_2O_4$, *M* = 342.39, *T* = 200 K, monoclinic, space group $P2_1$, *Z* = 2, *a* = 9.2230(4), *b* = 10.8655(2), *c* = 9.4767(3) Å, β = 115.290(2) °; *V* = 858.67(6) $Å^3$, D_x = 1.324 g cm^{-3}, 2067 unique data ($2\theta_{max}$ = 55 °), *R* = 0.041 [for 1933 reflections with $I > 2.0\sigma(I)$]; *Rw* = 0.104 (all data), *S* = 1.01.

Compound 36: $C_{24}H_{27}N_3O_6$, *M* = 453.49, *T* = 150 K, monoclinic, space group $P2_1/n$, *Z* = 12, *a* = 10.1654(2), *b* = 23.4039(7), *c* = 27.8440(7) Å, β = 97.1260(15) °; *V* = 6573.2(3) $Å^3$, D_x = 1.375 g cm^{-3}, 11573 unique data ($2\theta_{max}$ = 50 °), *R* = 0.076 [for 6910 reflections with $I > 2.0\sigma(I)$]; *Rw* = 0.156 (all data), *S* = 1.03.

Compound 40: $C_{19}H_{22}N_2O_4$, *M* = 342.39, *T* = 200 K, monoclinic, space group $P2_1/n$, *Z* = 12, *a* = 25.4459(4), *b* = 7.8587(1), *c* = 26.2588(4) Å, β = 93.5300(7) °; *V* = 5241.05(13) $Å^3$, D_x = 1.302 g cm^{-3}, 9266 unique data ($2\theta_{max}$ = 50 °), *R* = 0.048 [for 5989 reflections with $I > 2.0\sigma(I)$]; *Rw* = 0.120 (all data), *S* = 0.97.

Compound 41: $C_{19}H_{22}N_2O_4$, *M* = 342.39, *T* = 200 K, monoclinic, space group $P2_1/a$, *Z* = 4, *a* = 8.1469(2), *b* = 21.0989(6), *c* = 10.1495(3) Å, β = 91.2076(17) °; *V* = 1744.22(8) $Å^3$, D_x = 1.304 g cm^{-3}, 3999 unique data ($2\theta_{max}$ = 55 °), *R* = 0.048 [for 2569 reflections with $I > 2.0\sigma(I)$]; *Rw* = 0.115 (all data), *S* = 0.96.

Compound 45: $C_{19}H_{22}N_2O_4$, M = 342.39, T = 200 K, monoclinic, space group $P2_1$, Z = 2, a = 8.7713(4), b = 8.2519(3), c = 12.8289(5) Å, β = 104.4285(19) °; V = 899.27(6) Å^3, D_x = 1.264 g cm^{-3}, 2208 unique data ($2\theta_{\max}$ = 55 °), R = 0.035 [for 2033 reflections with $I > 2.0\sigma(I)$]; Rw = 0.086 (all data), S = 1.01.

Compound 47: $C_{19}H_{22}N_2O_4$, M = 342.39, T = 200 K, monoclinic, space group $P2_1/n$, Z = 4, a = 6.5131(4), b = 15.578(1), c = 17.3470(11) Å, β = 99.532(4) °; V = 1735.75(19) Å^3, D_x = 1.310 g cm^{-3}, 3970 unique data ($2\theta_{\max}$ = 55 °), R = 0.060 [for 2851 reflections with $I > 2.0\sigma(I)$]; Rw = 0.155 (all data), S = 1.05.

Compound 50: $C_{19}H_{22}N_2O_4$, M = 342.39, T = 200 K, monoclinic, space group $P2_1/a$, Z = 4, a = 8.1146(1), b = 15.1903(3), c = 14.0567(3) Å, β = 105.3616(10) °; V = 1670.77(5) Å^3, D_x = 1.361 g cm^{-3}, 4873 unique data ($2\theta_{\max}$ = 60 °), R = 0.038 [for 3534 reflections with $I > 2.0\sigma(I)$]; Rw = 0.106 (all data), S = 0.91.

Compound 54: $C_{19}H_{22}N_2O_4$, M = 342.39, T = 200 K, monoclinic, space group $P2_1/c$, Z = 4, a = 6.8438(2), b = 9.8978(2), c = 24.5997(6) Å, β = 97.1851(10) °; V = 1653.26(7) Å^3, D_x = 1.376 g cm^{-3}, 3752 unique data ($2\theta_{\max}$ = 55 °), R = 0.071 [for 2980 reflections with $I > 2.0\sigma(I)$]; Rw = 0.216 (all data), S = 1.00.

Compound 55: $C_{19}H_{22}N_2O_4 \bullet 0.5(CH_2Cl_2)$, M = 384.86, T = 200 K, monoclinic, space group $P2_1/a$, Z = 4, a = 8.6793(2), b = 22.8503(4), c = 9.6857(2) Å, β = 91.2144(9) °; V = 1920.48(5)

Å^3, D_x = 1.331 g cm^{-3}, 4392 unique data ($2\theta_{max}$ = 55 °), R = 0.049 [for 2309 reflections with $I >$ $2.0\sigma(I)$]; Rw = 0.133 (all data), S = 0.81.

Compound 58: $C_{24}H_{27}N_3O_6$•CH_2Cl_2, M = 538.43, T = 200 K, monoclinic, space group $P2_1/a$, Z = 8, a = 12.8137(1), b = 20.3565(2), c = 19.3212(2) Å, β = 94.2880(6) °; V = 5025.67(8) Å^3, D_x = 1.423 g cm^{-3}, 11540 unique data ($2\theta_{max}$ = 55 °), R = 0.038 [for 7015 reflections with $I >$ $2.0\sigma(I)$]; Rw = 0.093 (all data), S = 0.82.

Compound 59: $C_{24}H_{27}N_3O_6$•H_2O, M = 471.51, T = 200 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 7.6862(3), b = 10.4995(5), c = 28.4514(11) Å; V = 2296.06(15) Å^3, D_x = 1.364 g cm^{-3}, 2345 unique data ($2\theta_{max}$ = 50 °), R = 0.058 [for 1644 reflections with $I > 2.0\sigma(I)$]; Rw = 0.158 (all data), S = 0.99.

Compound 60: $C_{24}H_{27}N_3O_6$•$CHCl_3$, M = 572.87, T = 200 K, monoclinic, space group Cc, Z = 4, a = 13.2299(2), b = 13.6070(2), c = 14.5131(3) Å, β = 91.0006(11) °; V = 2612.24(8) Å^3, D_x = 1.457 g cm^{-3}, 5906 unique data ($2\theta_{max}$ = 55 °), R = 0.042 [for 5203 reflections with $I > 2.0\sigma(I)$]; Rw = 0.111 (all data), S = 1.04.

2.2 Structure Determination

Images were measured on a Nonius Kappa CCD diffractometer (MoKα, graphite monochromator, λ = 0.71073 Å) and data extracted using the DENZO package.[6] Structure solution was by direct methods (SIR92).[7] The structures were refined using the CRYSTALS program package.[8] Atomic coordinates, bond lengths and angles, and displacement parameters for compounds **33**, **36**, **40**, **41, 45**, **47**, **50, 54, 55, 58, 59**, and **60** have been deposited at the Cambridge Crystallographic Data Centre (CCDC nos. 1421657 – 1421668, respectively). These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. The CIFs are available as SI of this paper. The individual CIFs also contain details of refinement procedures used for that particular structure.

2.3 Anisotropic Displacement Ellipsoid Plots for 33, 36, 40, 41, 45, 47, 50, 54, 55, 58, 59, and 60.

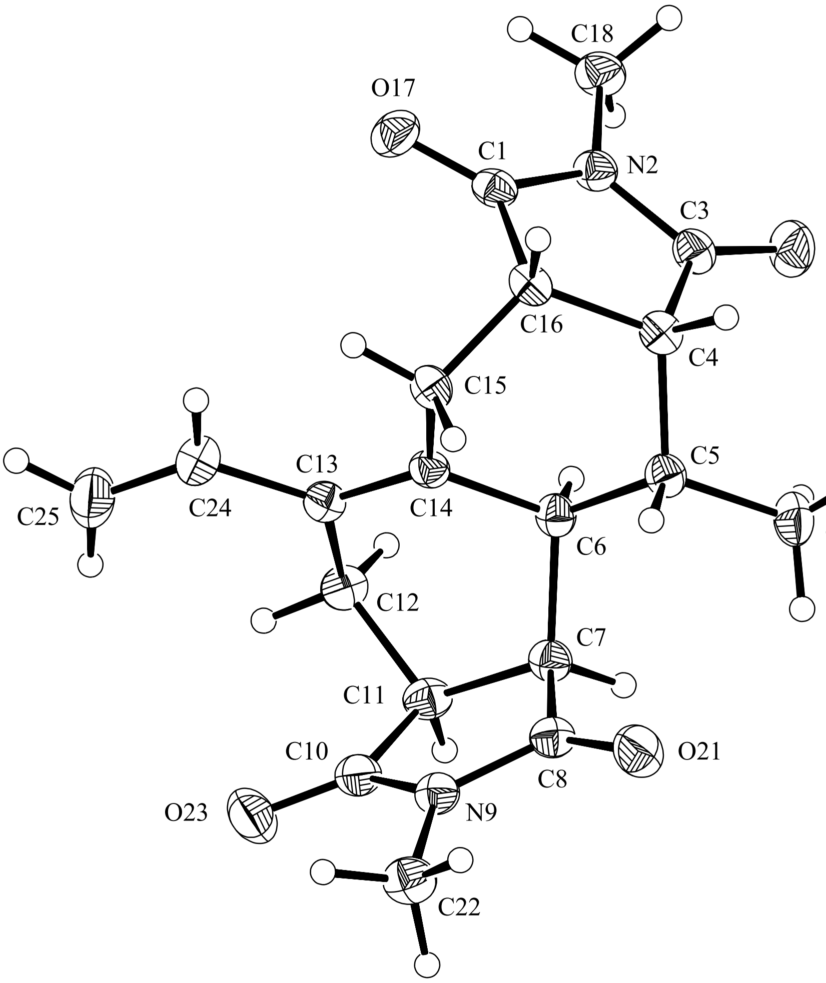


Figure S1: Molecular structure of **33** (CCDC 1421657) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

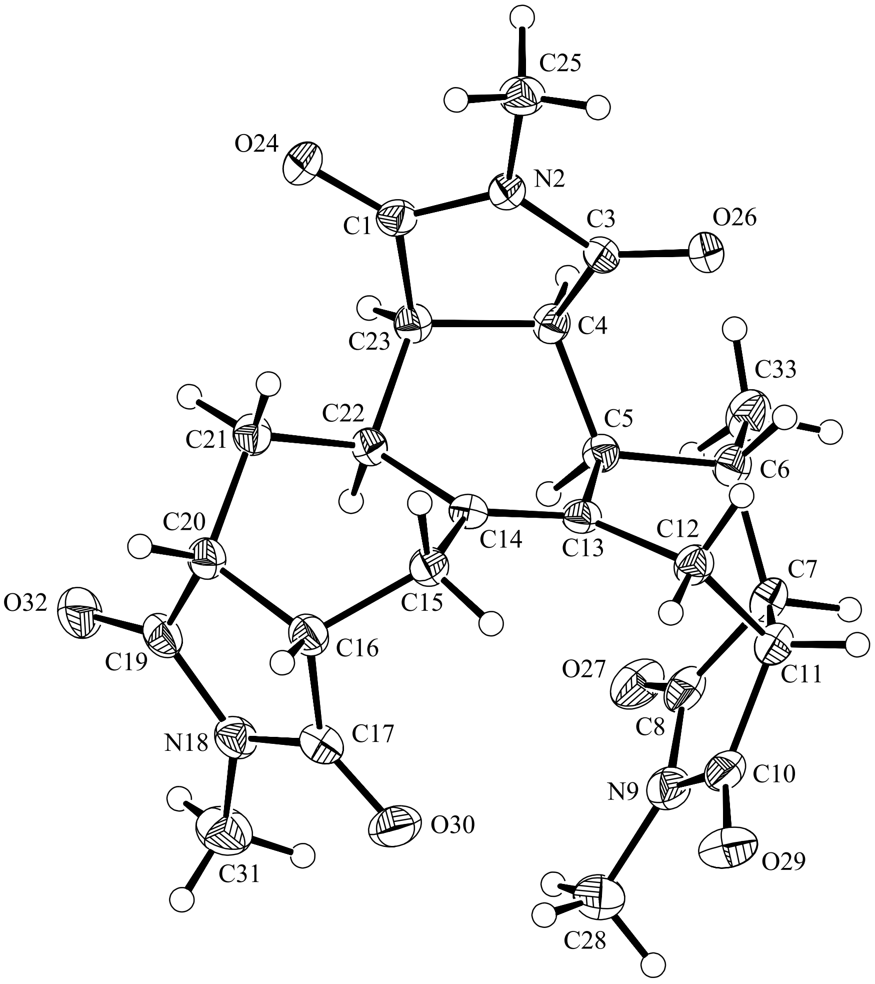


Figure S2: Molecular structure of **36** (CCDC 1421658) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

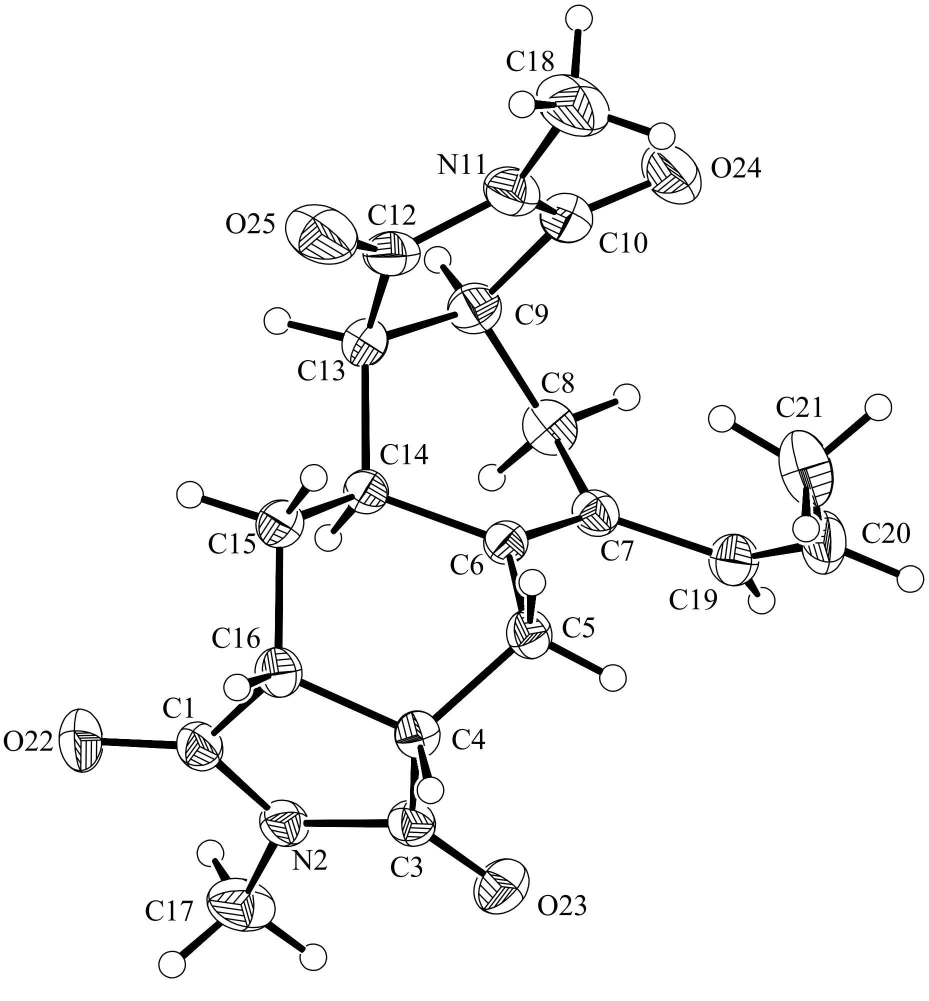


Figure S3: Molecular structure of **40** (CCDC 1421659) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

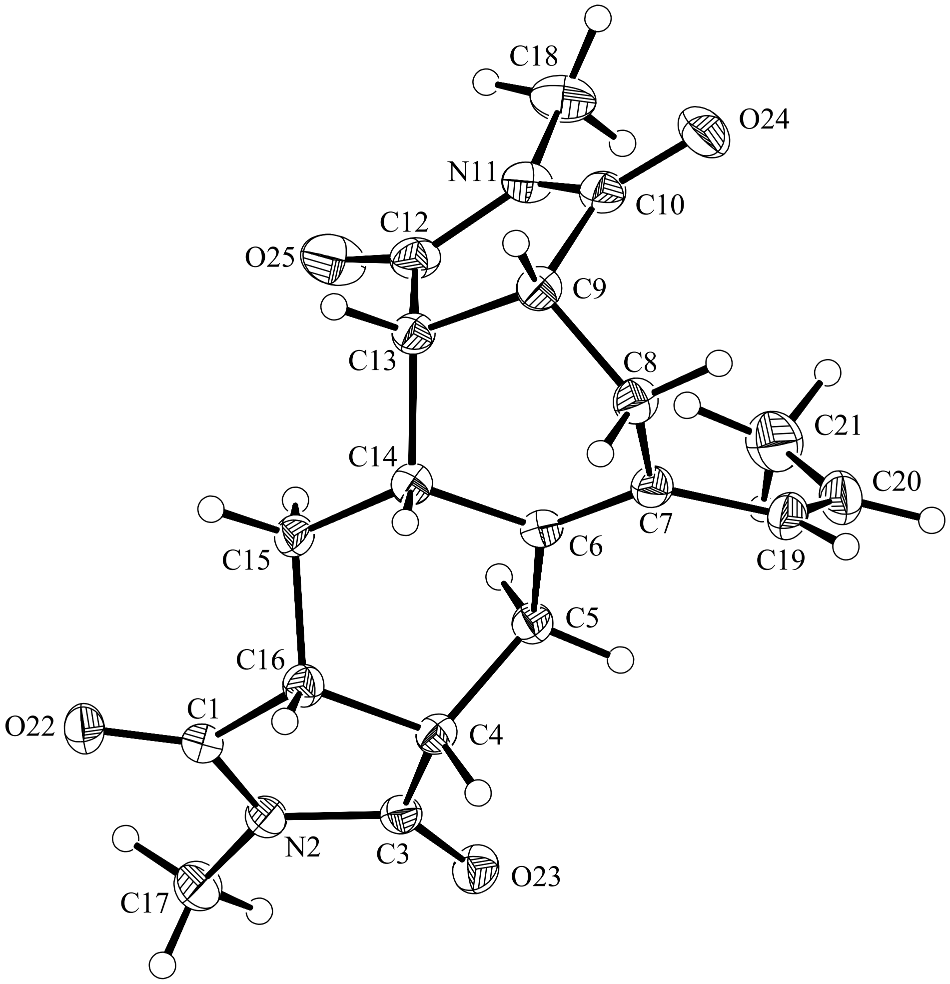


Figure S4: Molecular structure of **41** (CCDC 1421660) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

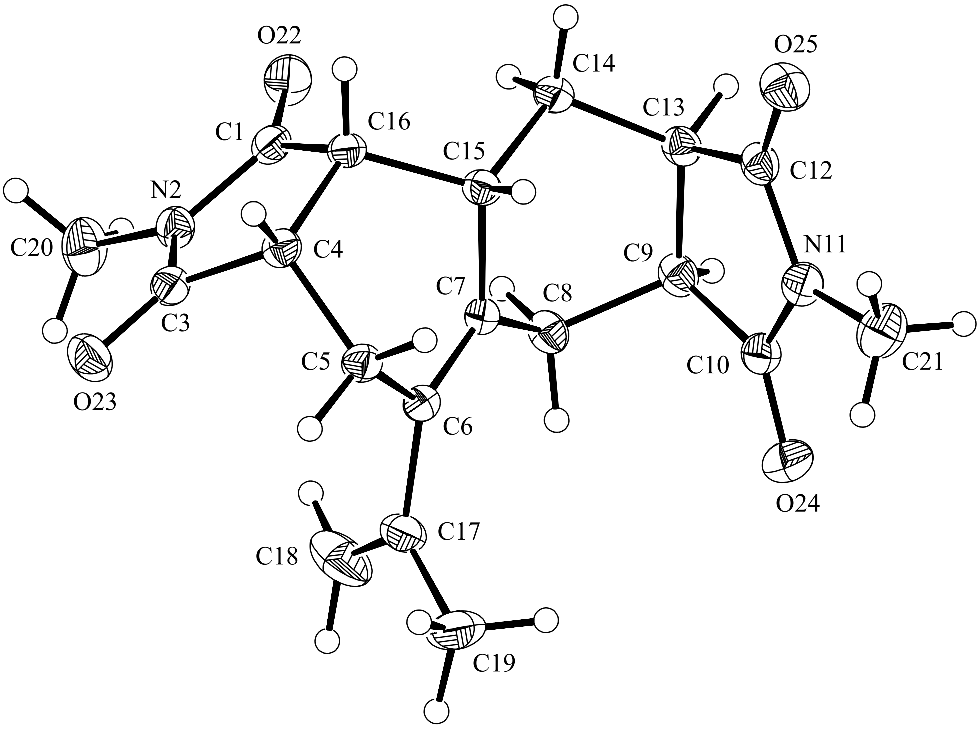


Figure S5: Molecular structure of **45** (CCDC 1421661) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

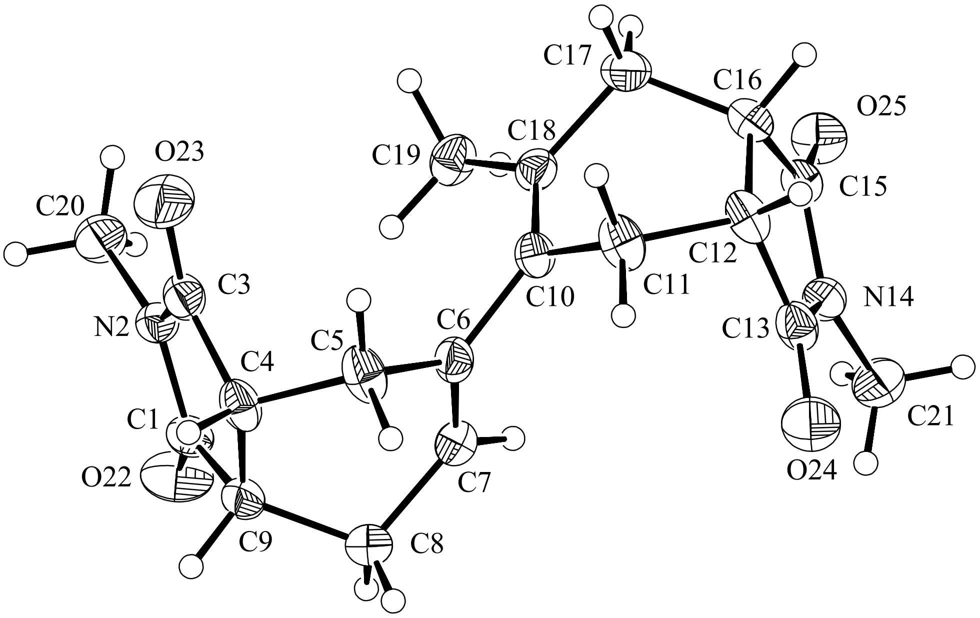


Figure S6: Molecular structure of **47** (CCDC 1421662) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

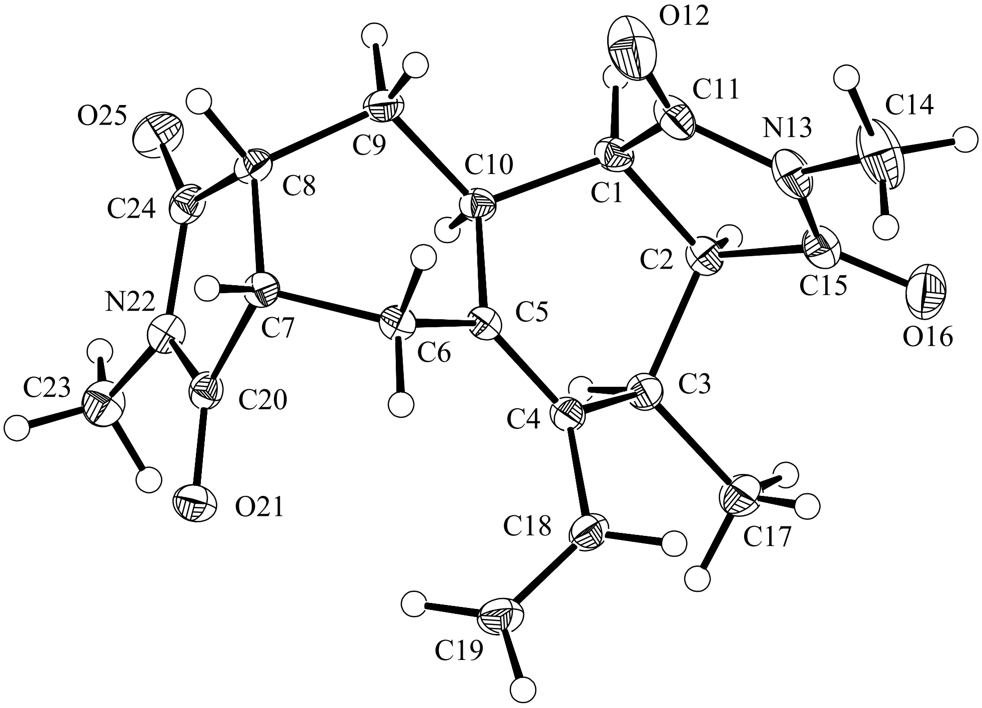


Figure S7: Molecular structure of **50** (CCDC 1421663) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

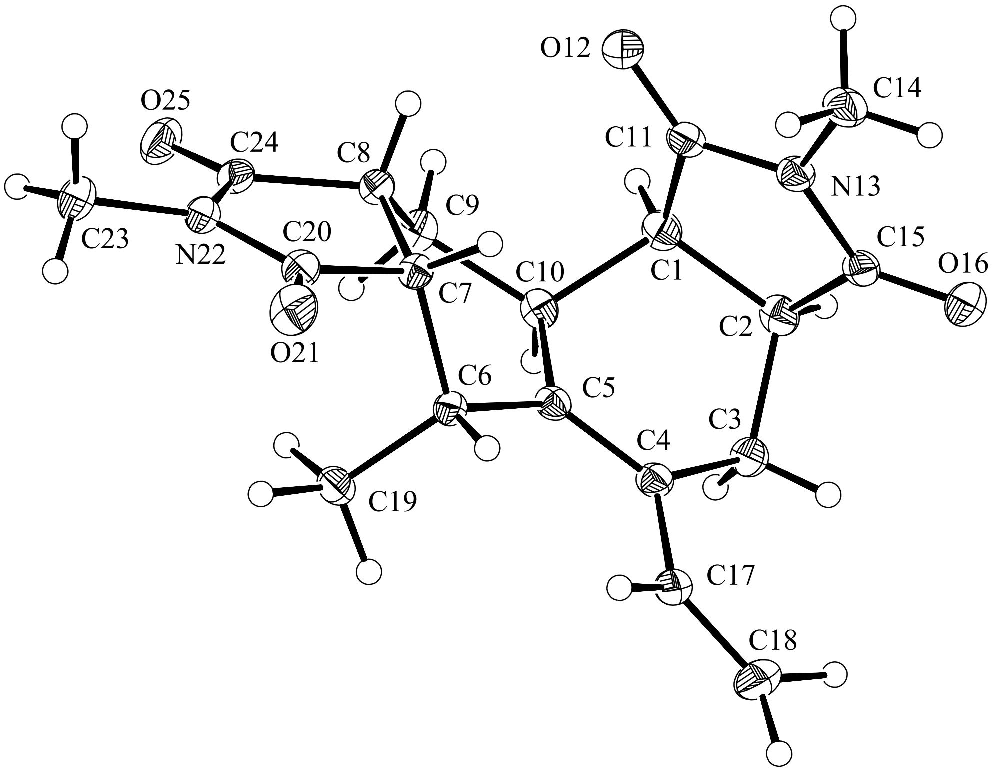


Figure S8: Molecular structure of **54** (CCDC 1421664) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

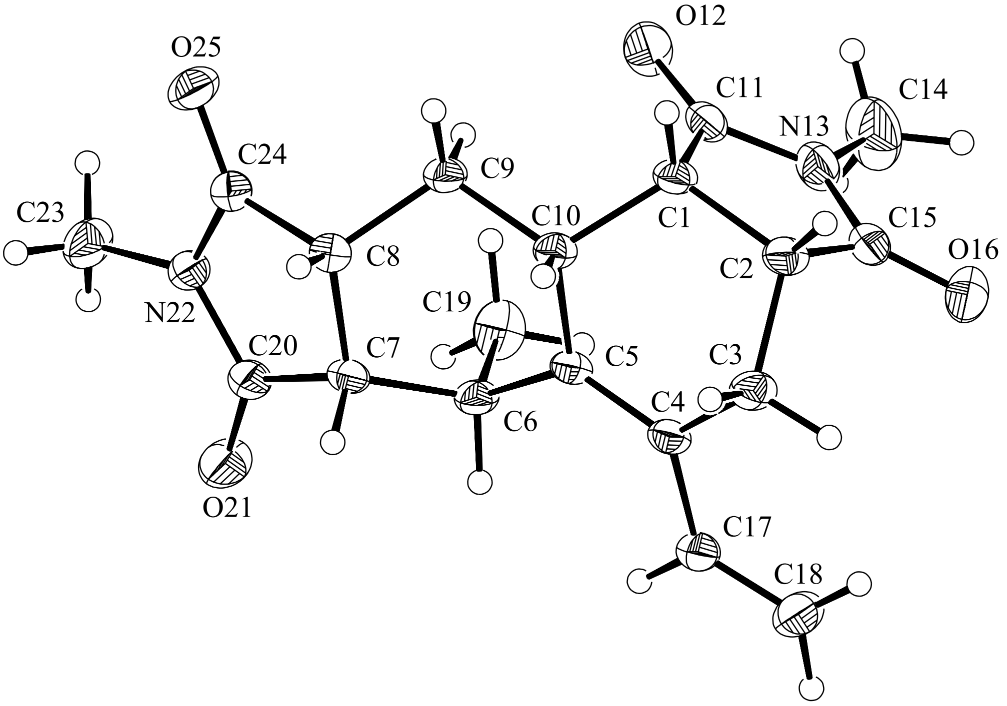


Figure S9: Molecular structure of **55** (CCDC 1421665) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

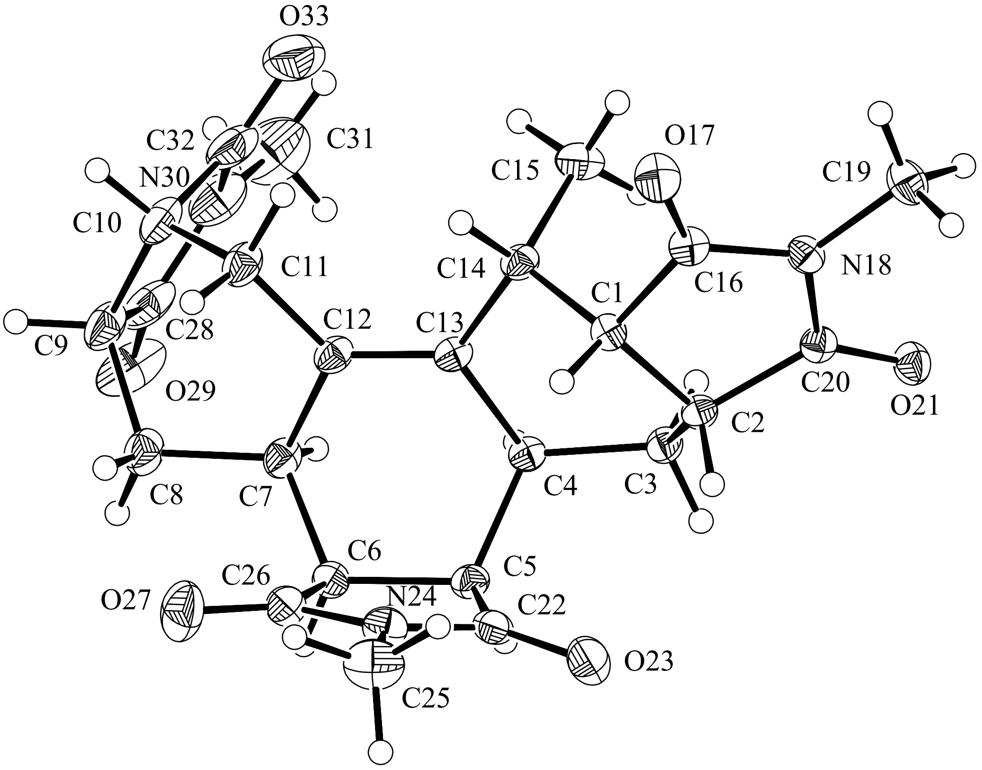


Figure S10: Molecular structure of **58** (CCDC 1421666) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

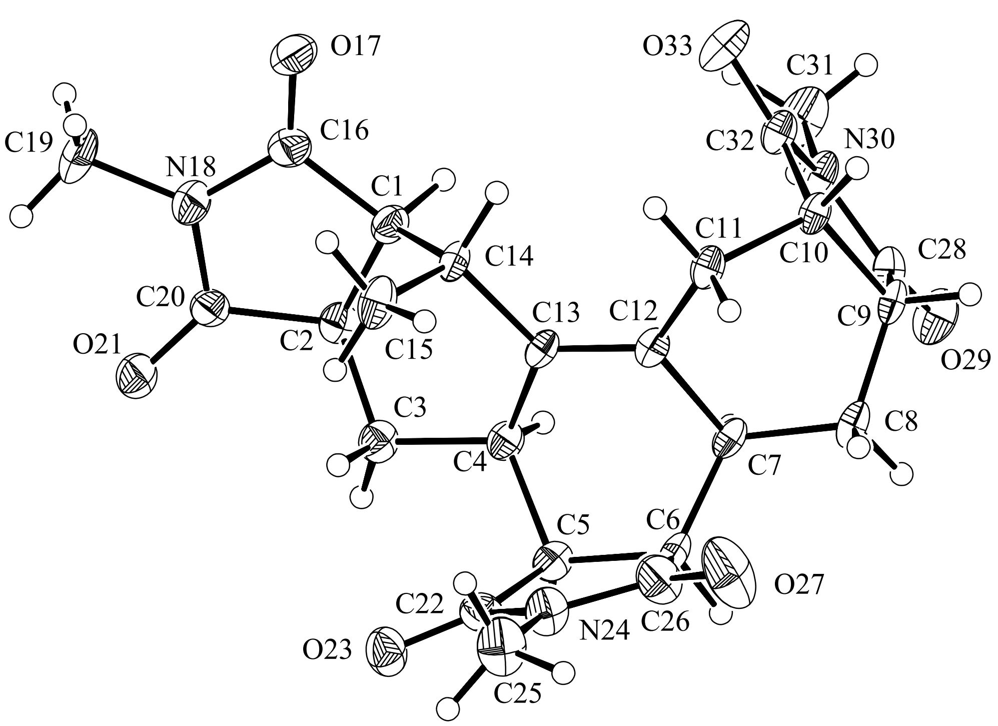


Figure S11: Molecular structure of **59** (CCDC 1421667) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

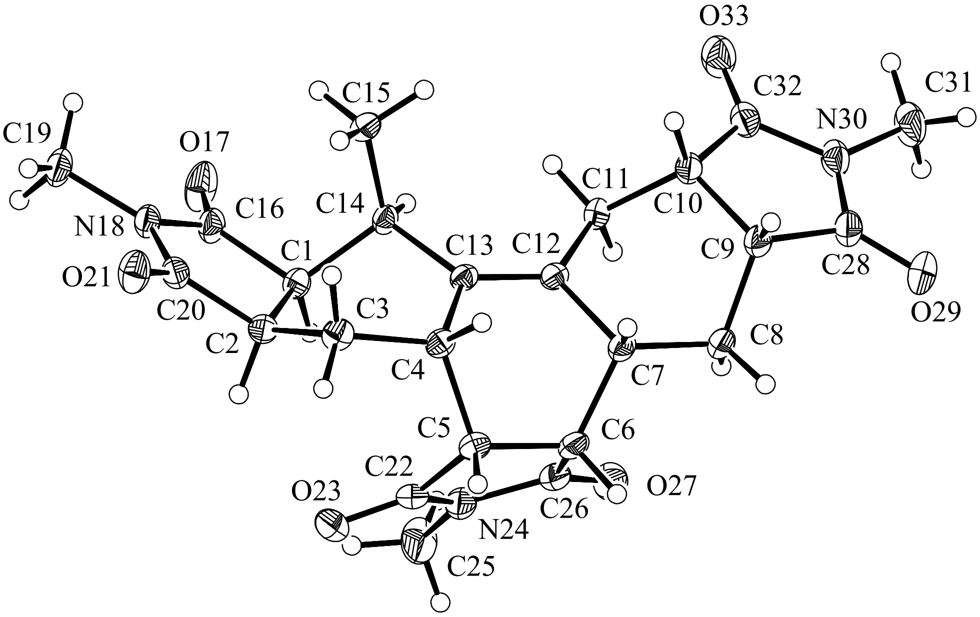
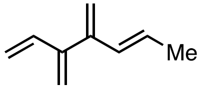


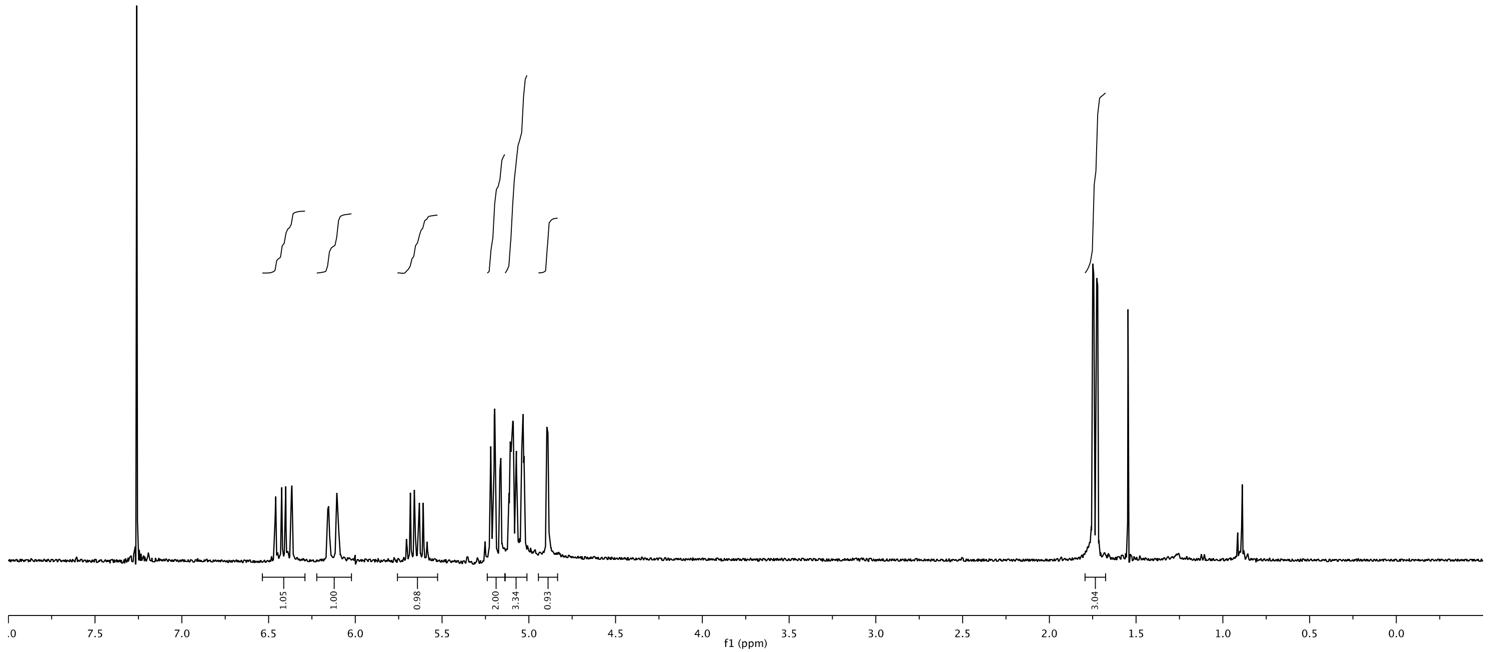
Figure S12: Molecular structure of **60** (CCDC 1421668) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. H atoms are drawn as circles with small radii.

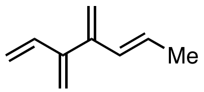
3. ^{1}H and ^{13}C NMR Spectra



10

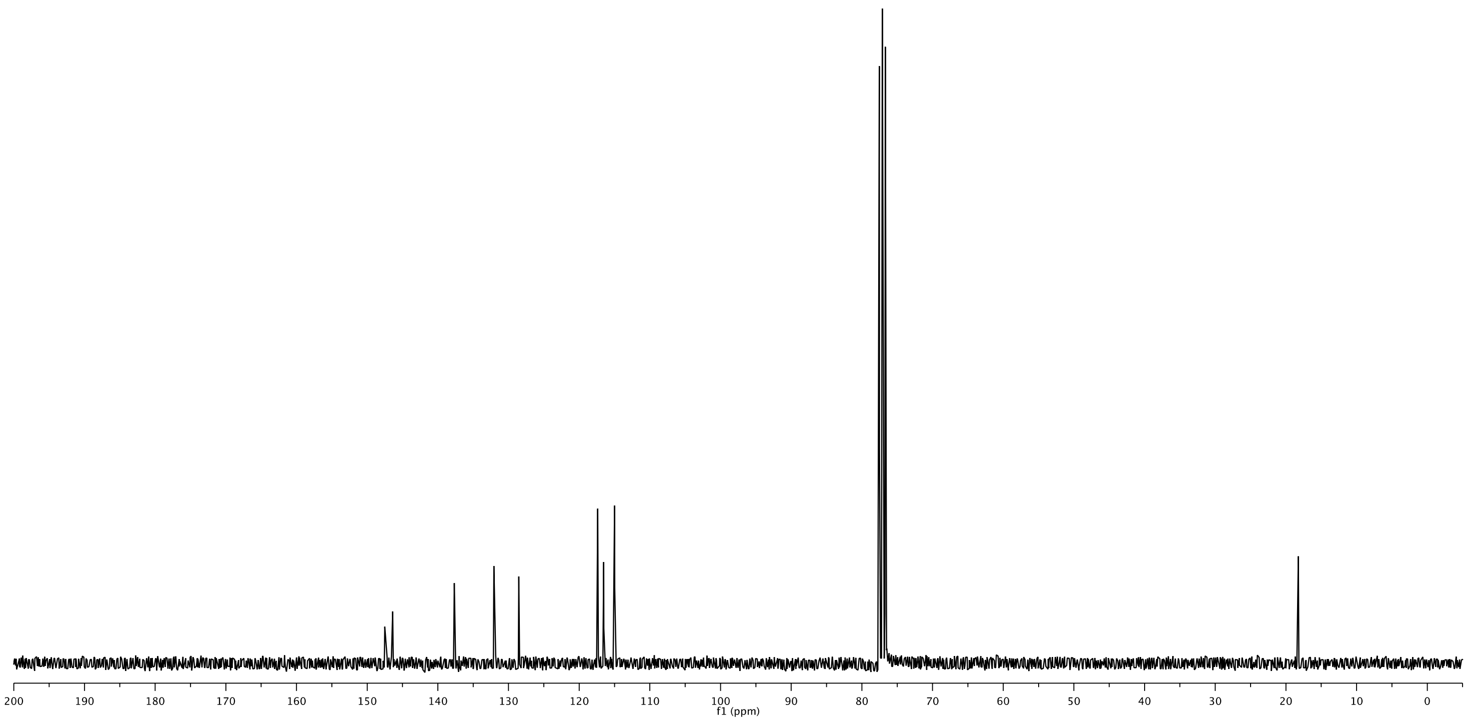
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

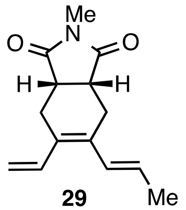




10

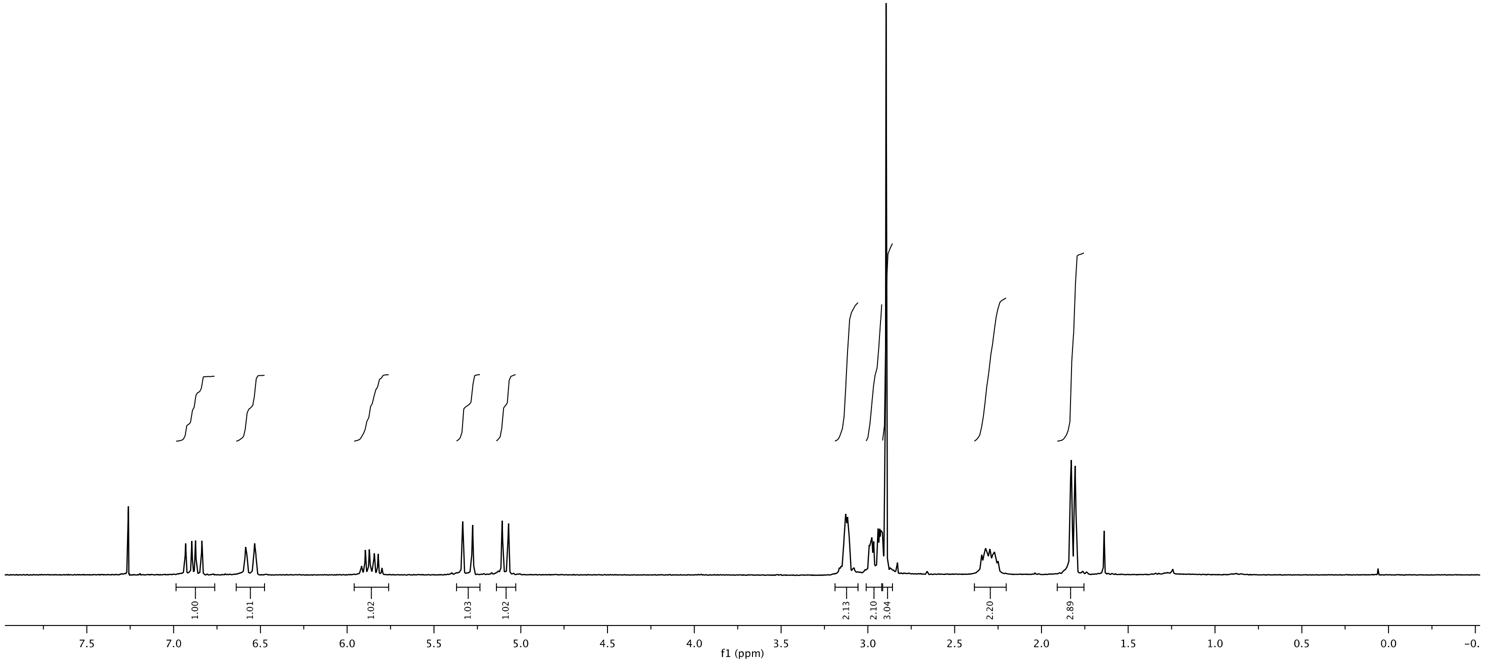
^{13}C NMR spectrum
75 MHz, in CDCl$_3$

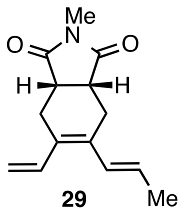




29

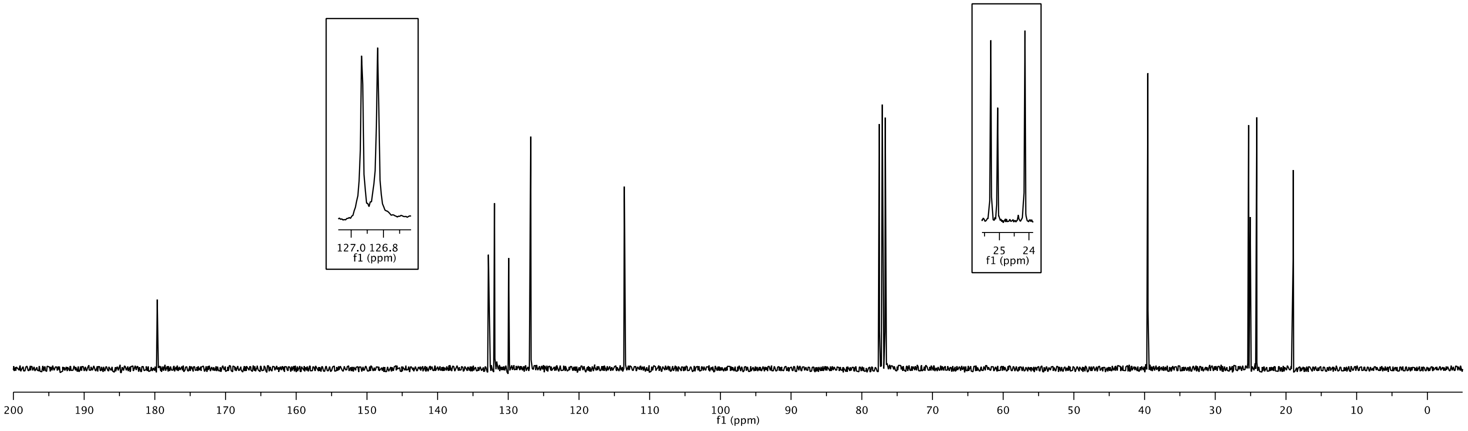
^1H NMR spectrum
300 MHz, in $CDCl_3$

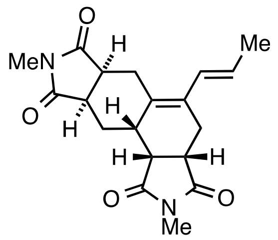




29

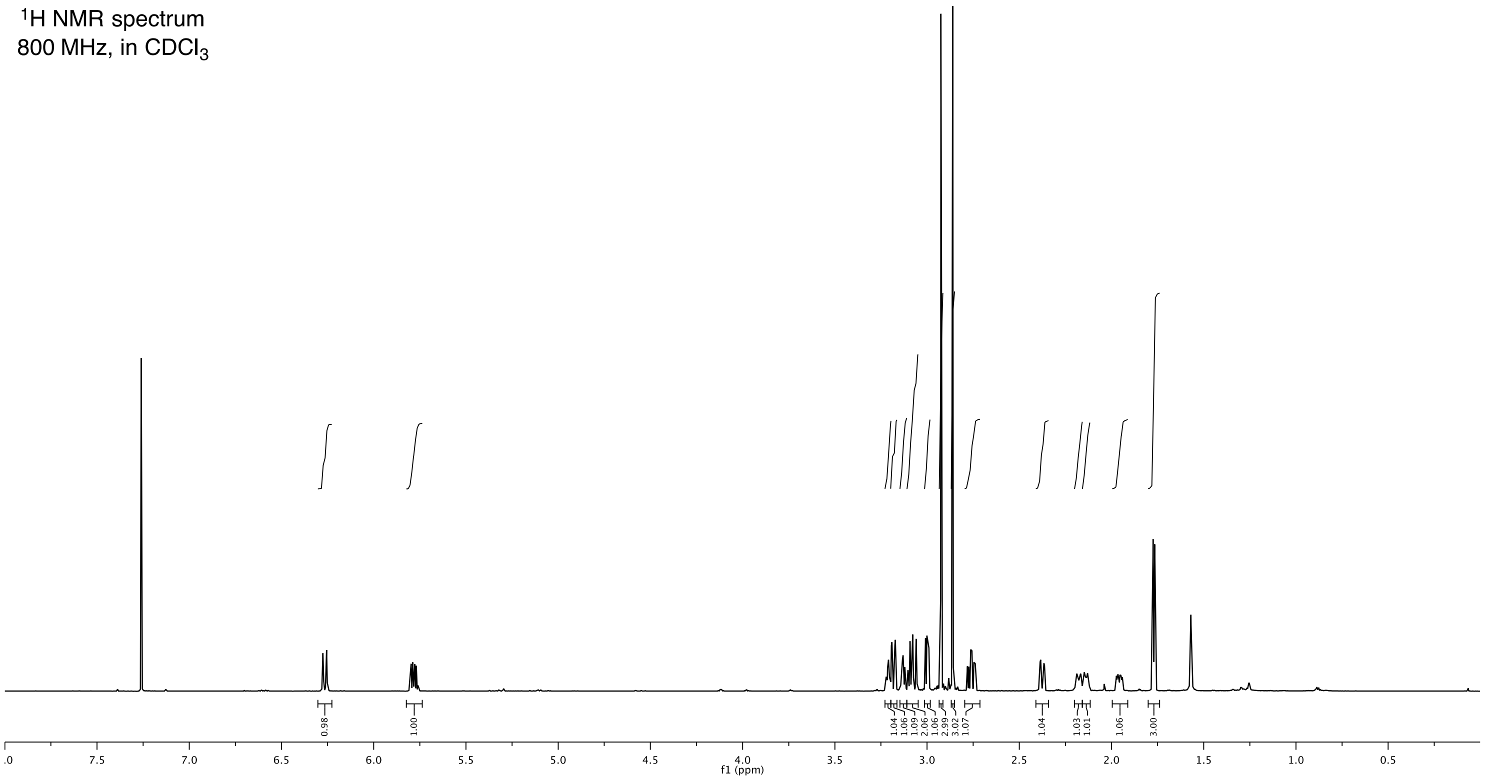
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

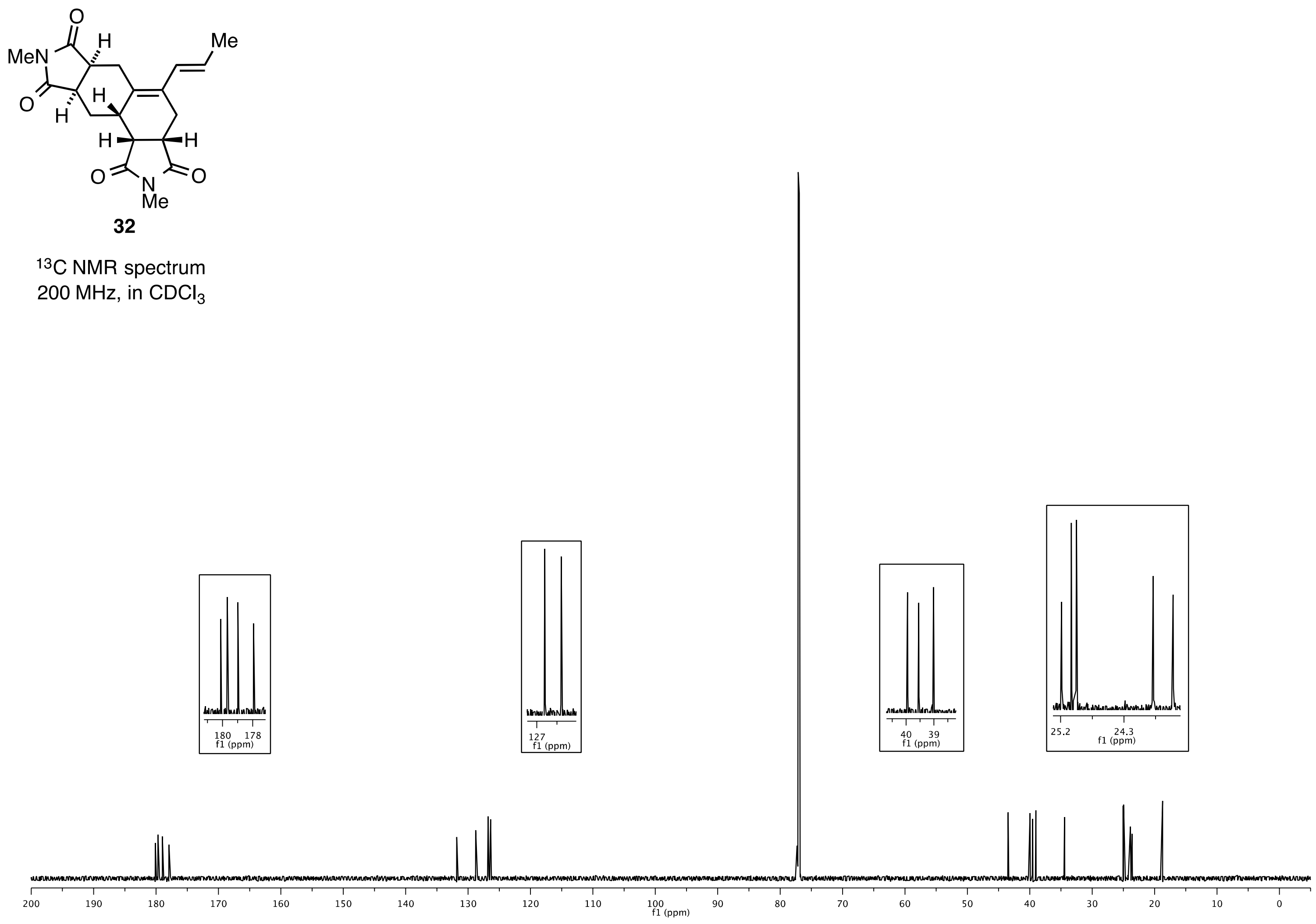




32

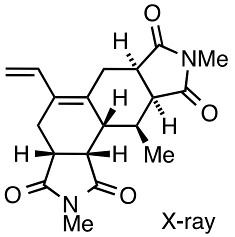
^{1}H NMR spectrum
800 MHz, in $CDCl_3$





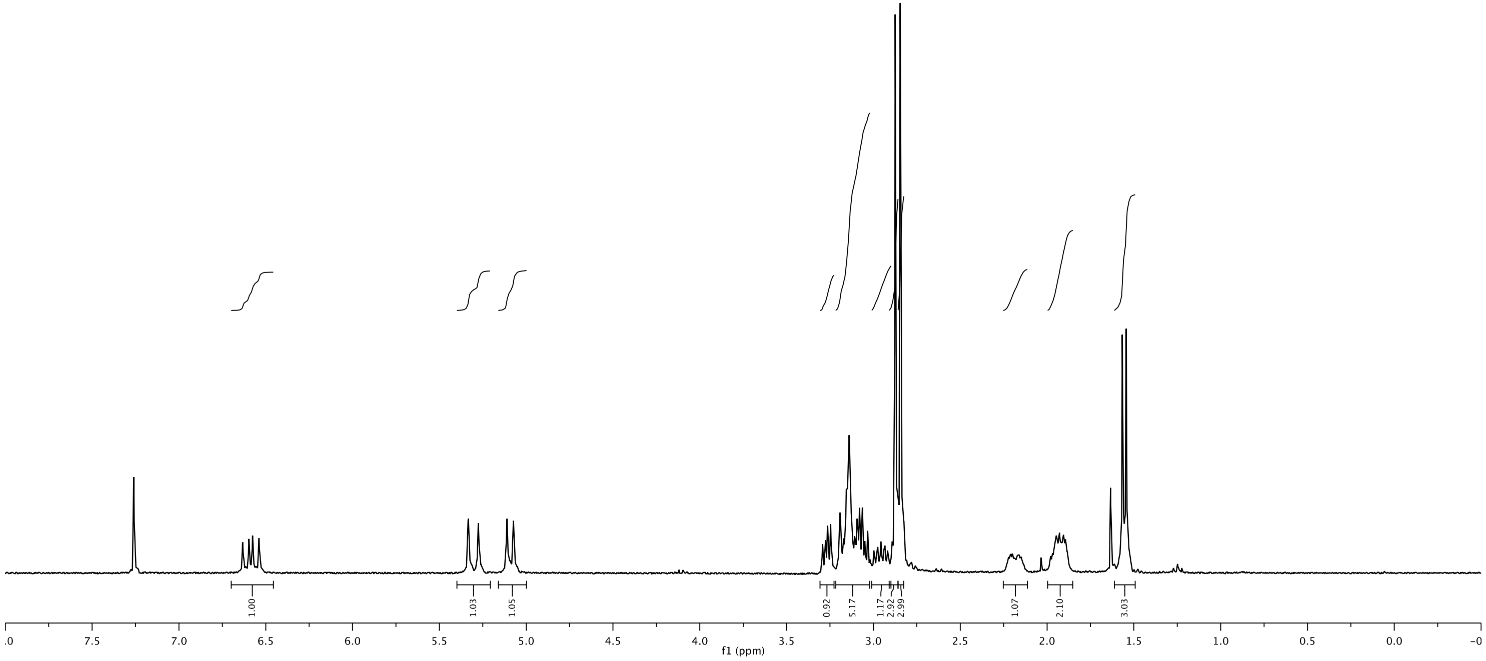
32

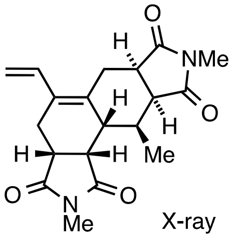
^{13}C NMR spectrum
200 MHz, in $CDCl_3$



33

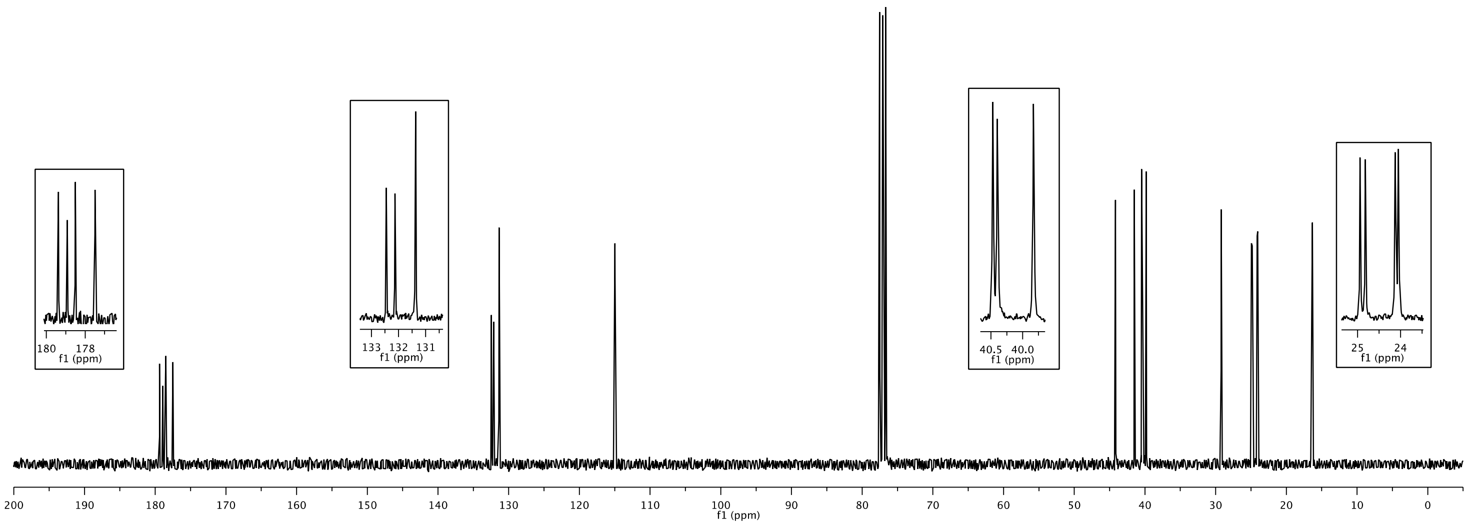
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

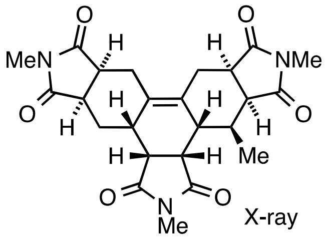




33

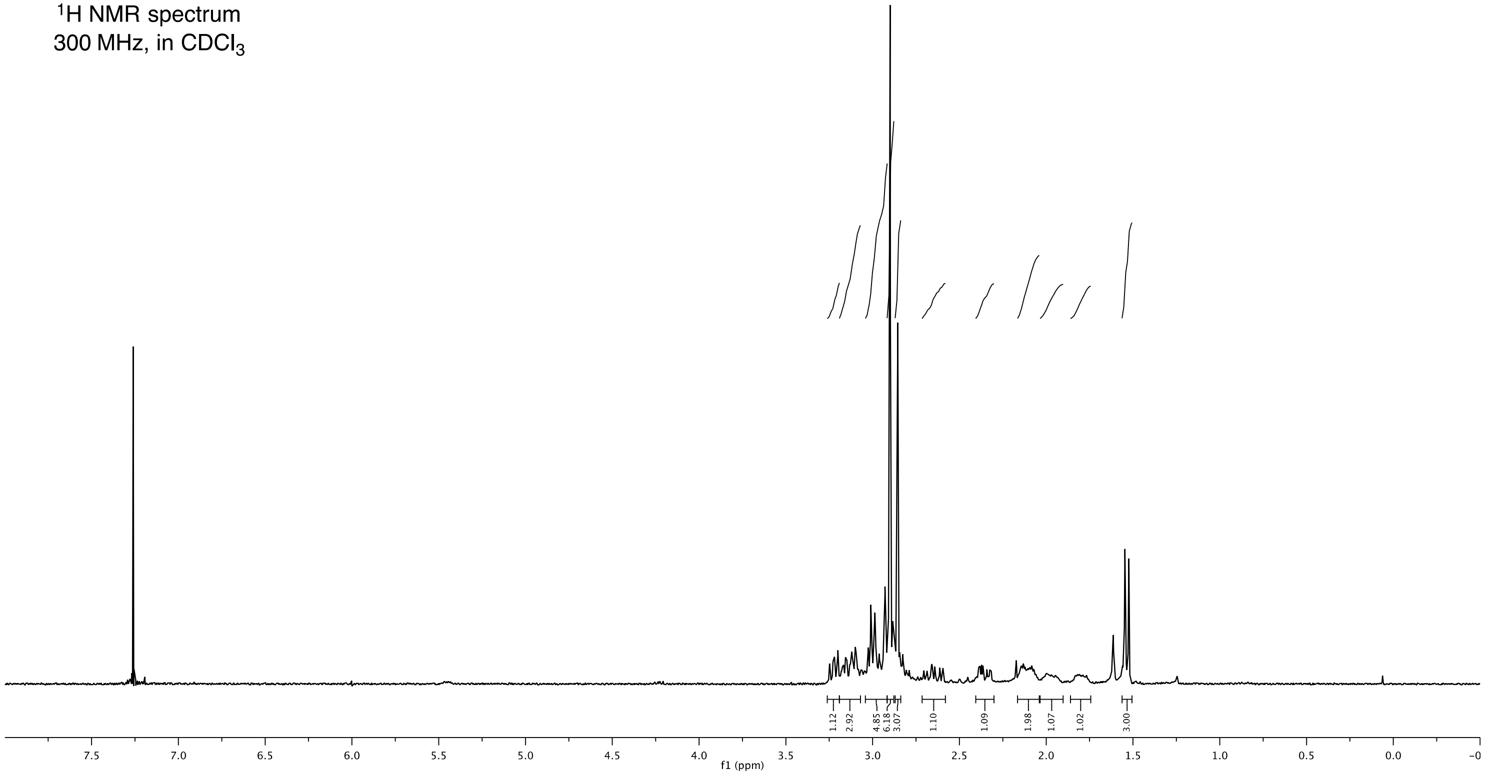
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

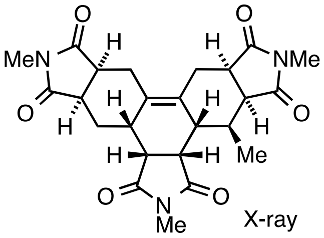




36

^{1}H NMR spectrum
300 MHz, in CDCl$_3$

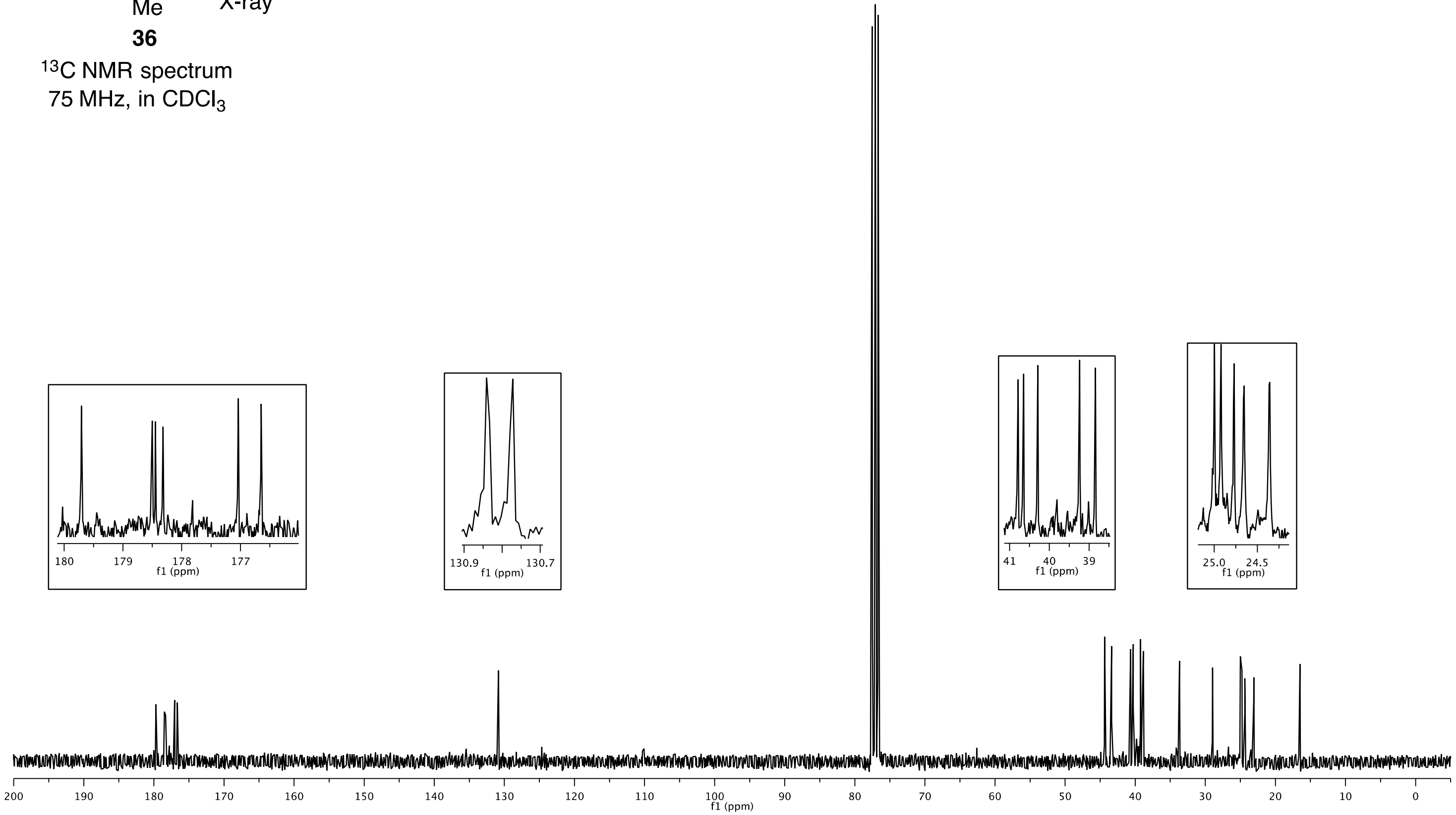


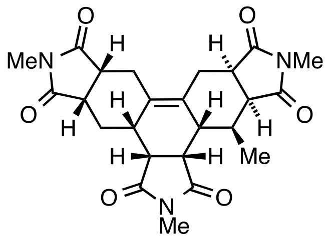


X-ray

36

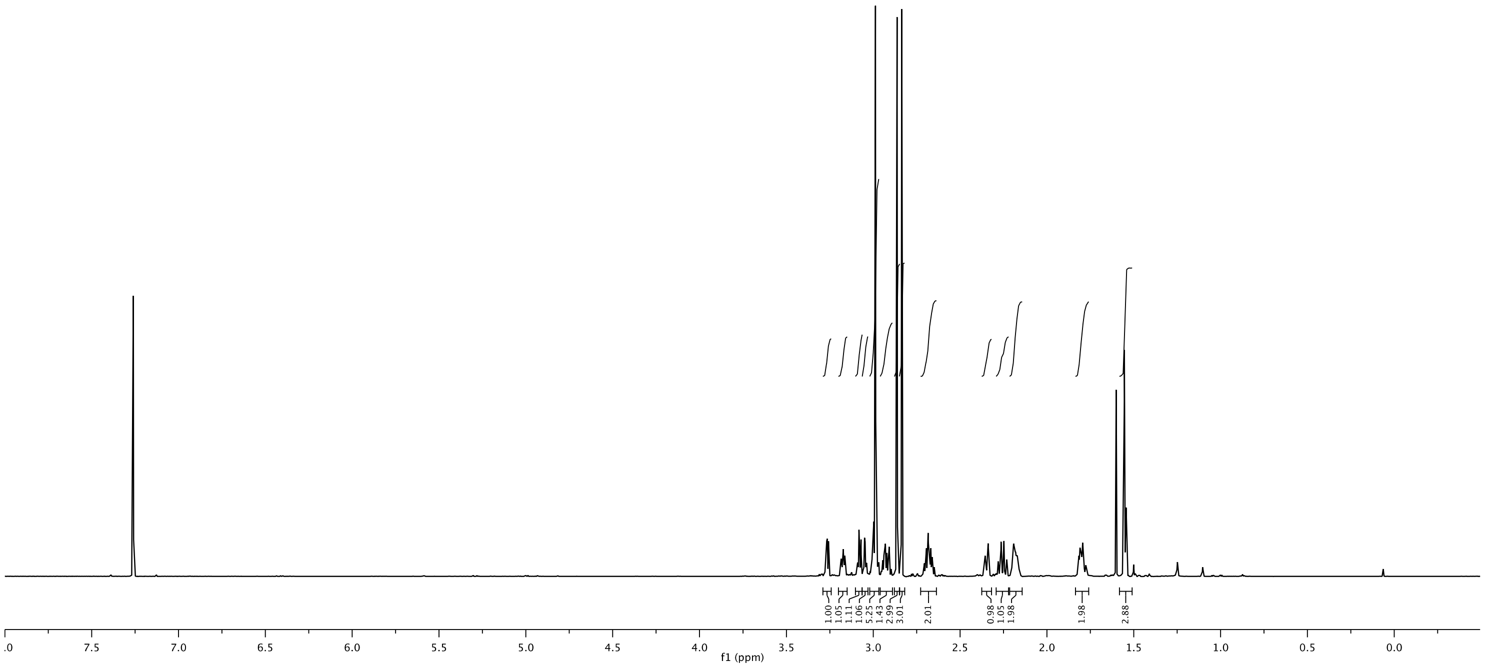
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

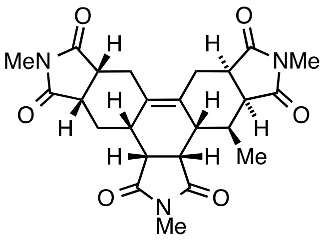




37

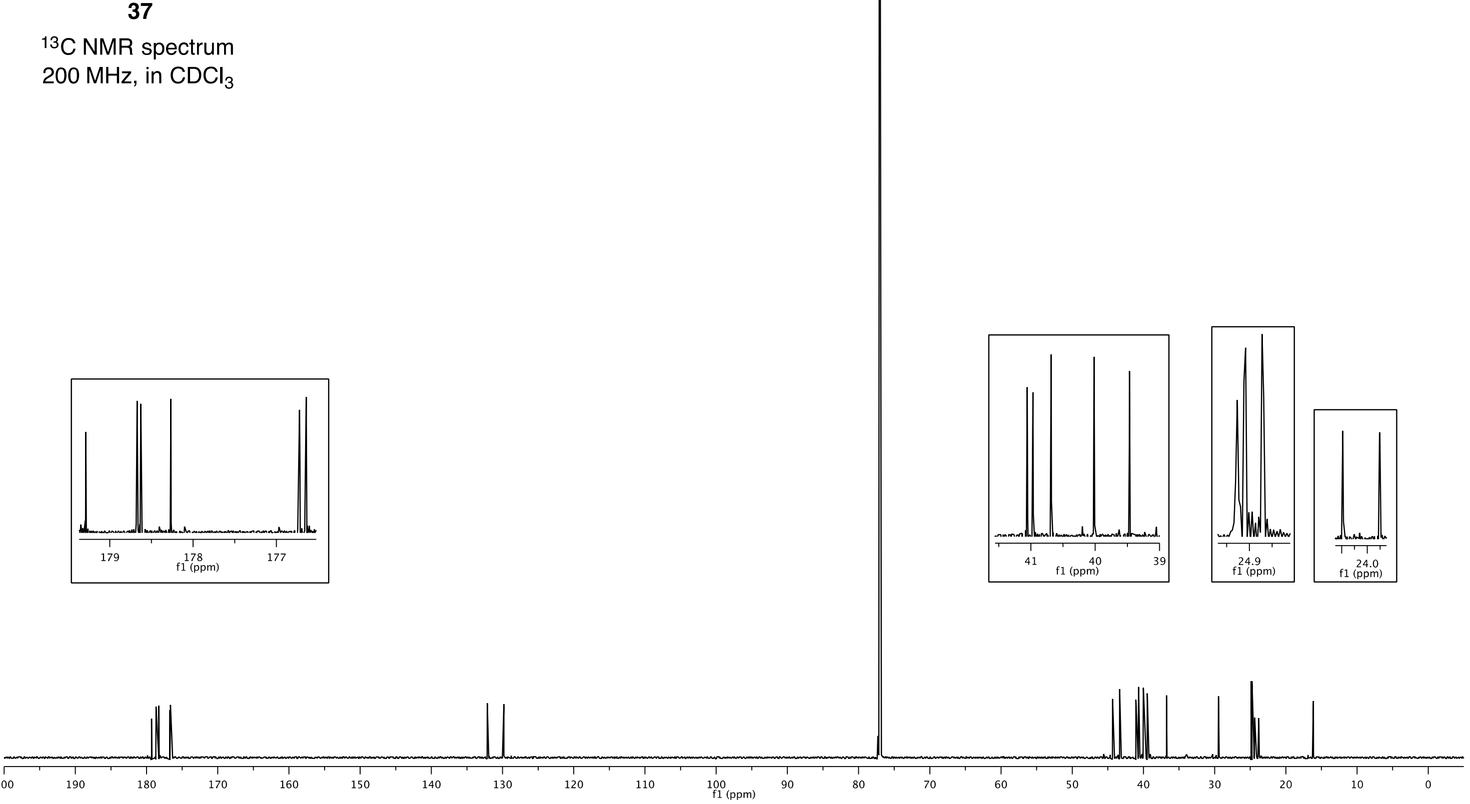
^1H NMR spectrum
800 MHz, in $CDCl_3$

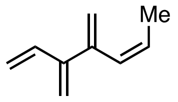




37

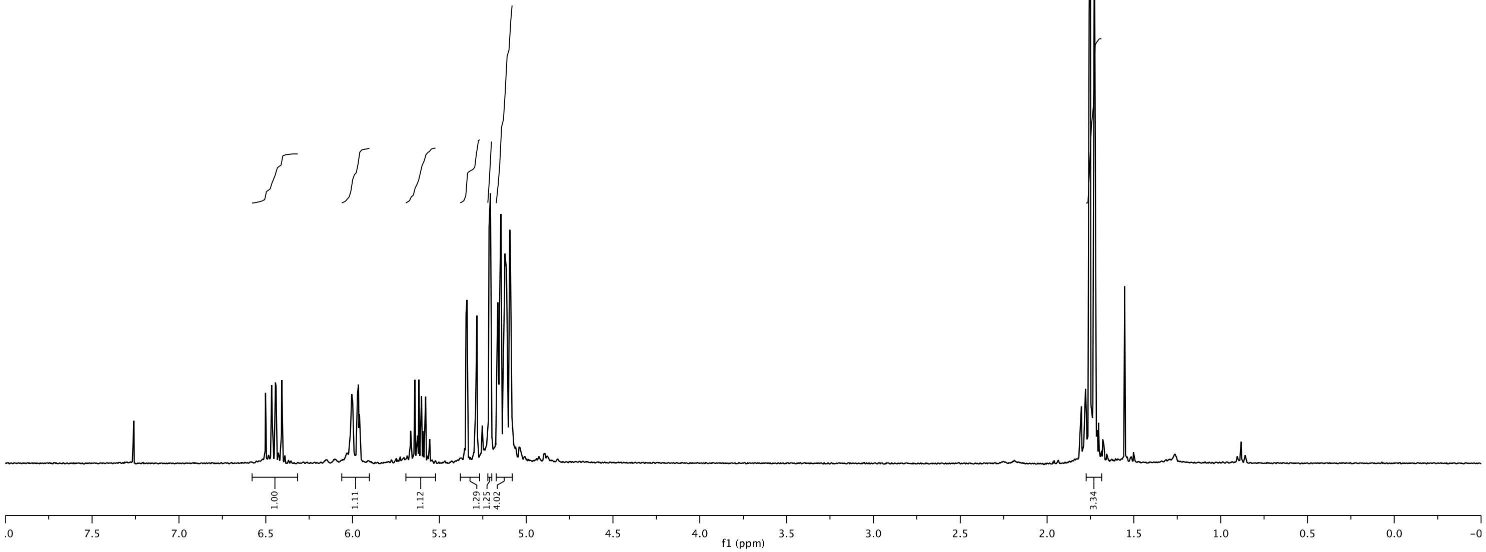
^{13}C NMR spectrum
200 MHz, in CDCl$_3$

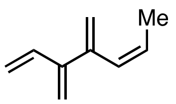




11

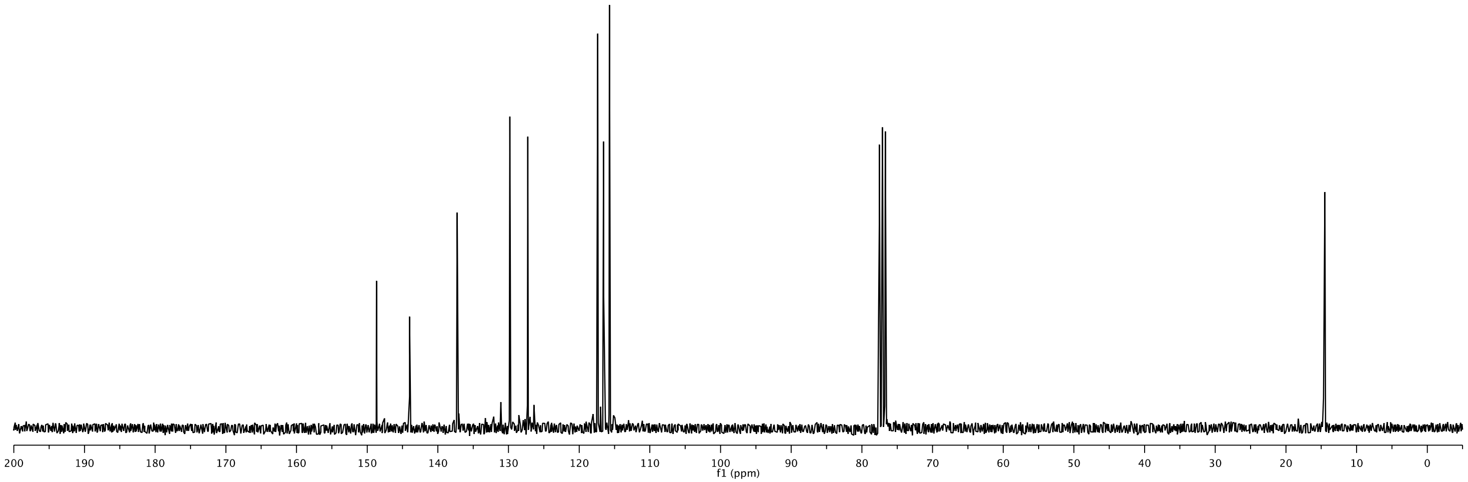
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

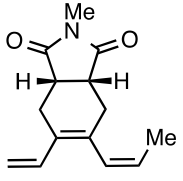




11

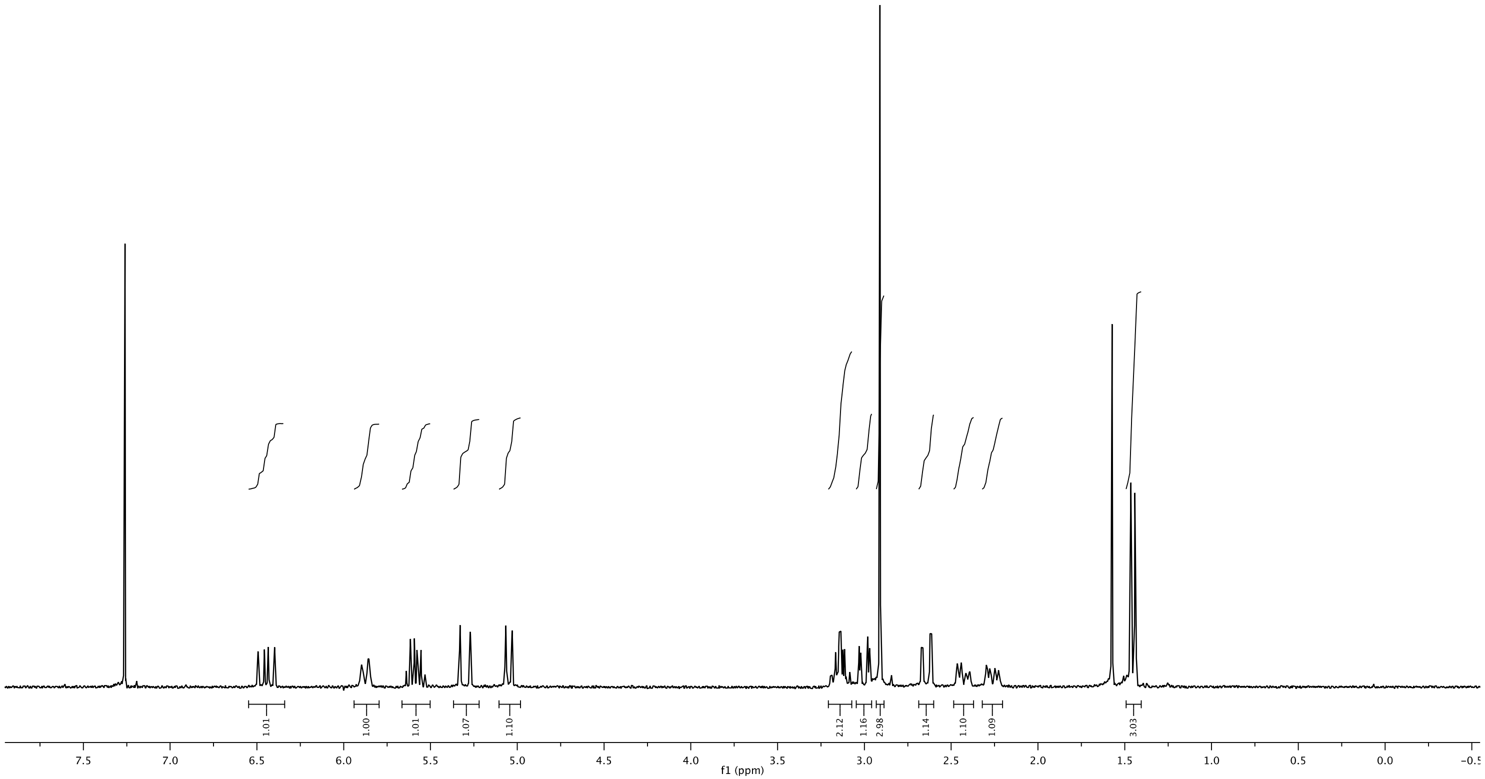
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

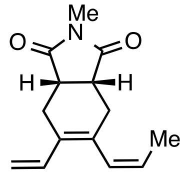




38

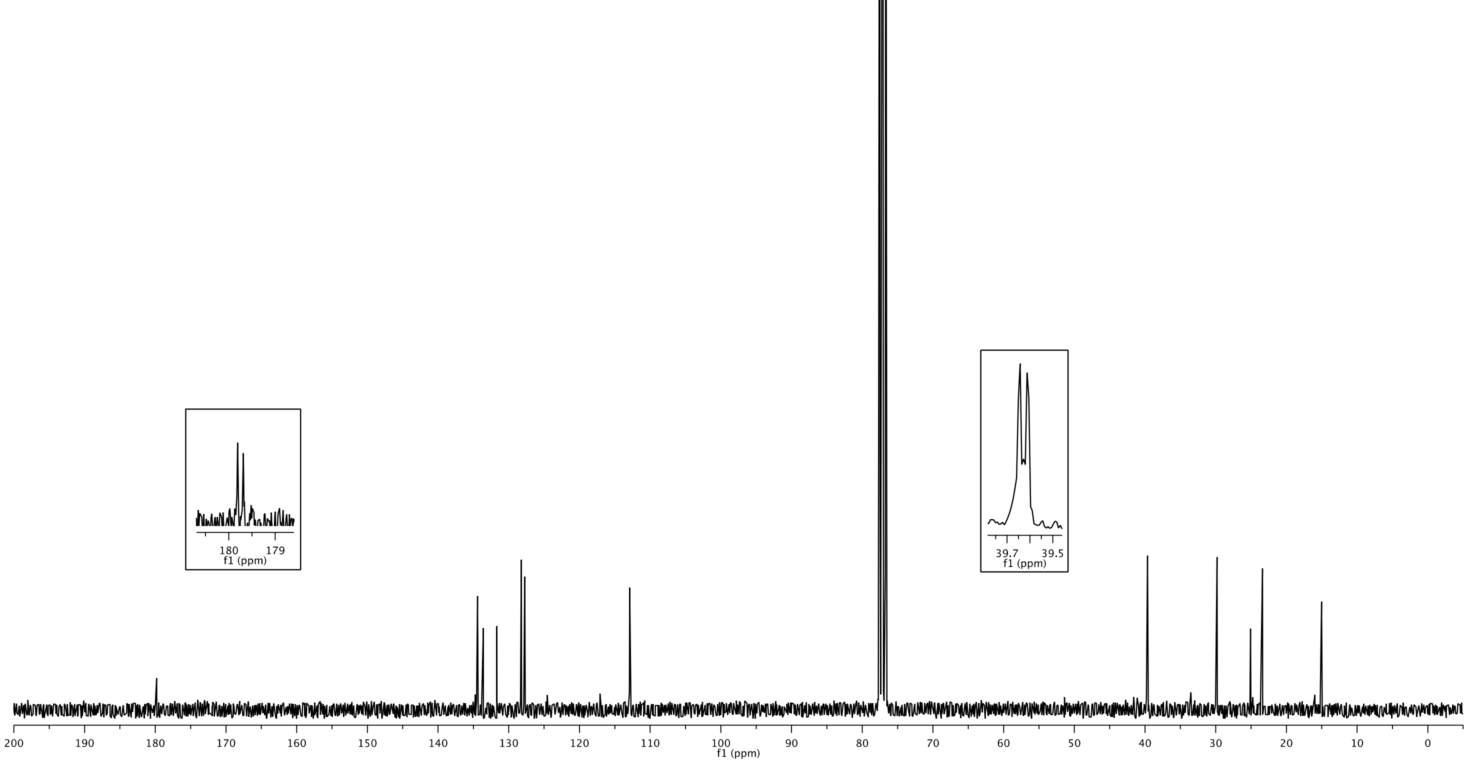
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

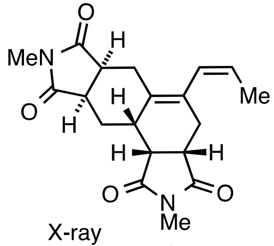




38

^{13}C NMR spectrum
75 MHz, in $CDCl_3$

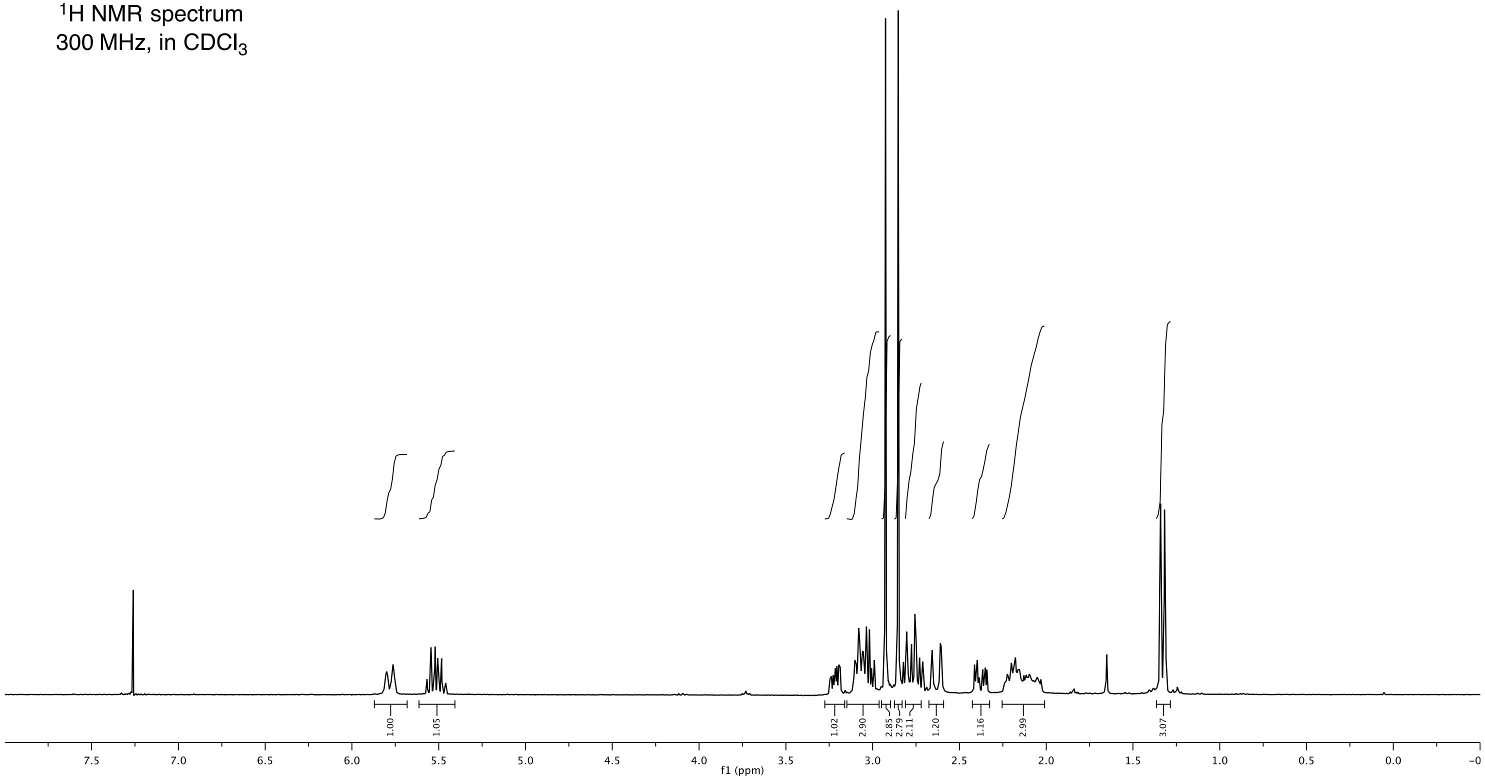


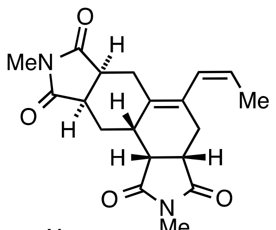


X-ray

40

^{1}H NMR spectrum
300 MHz, in $CDCl_3$

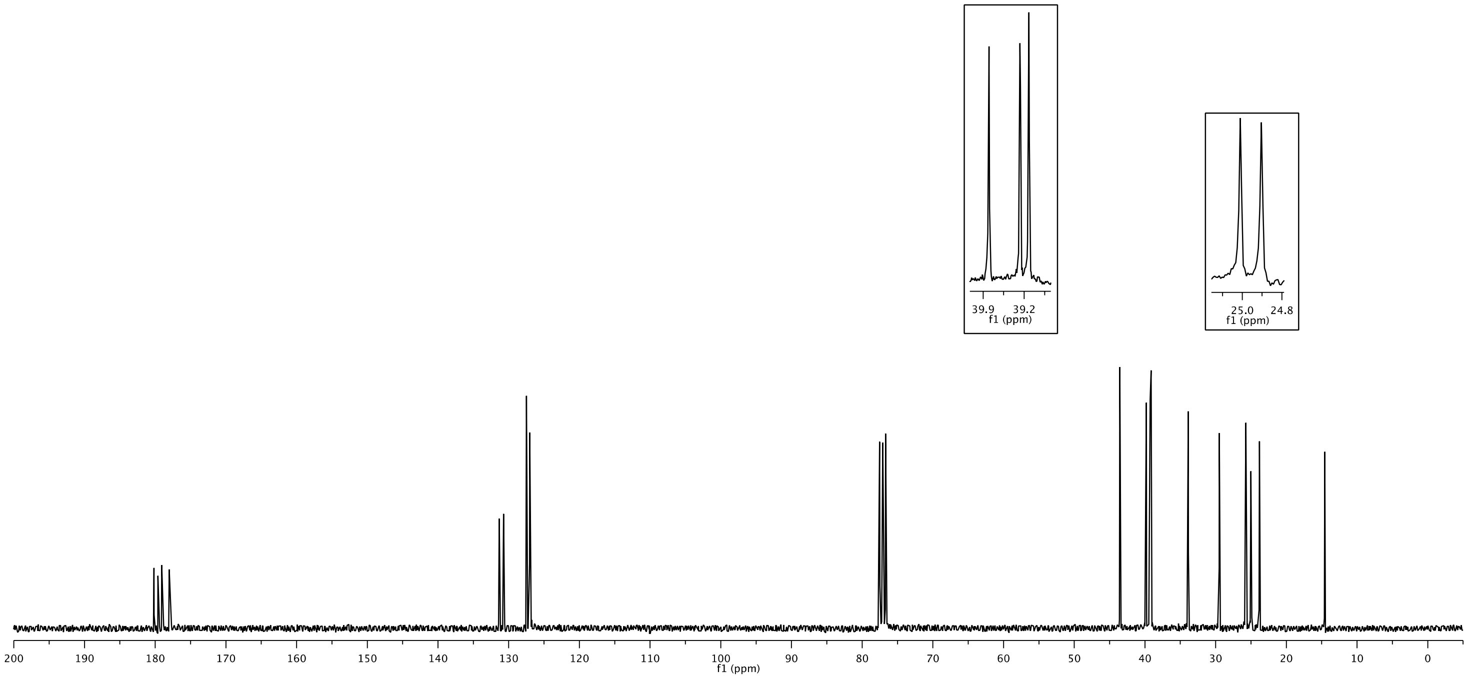


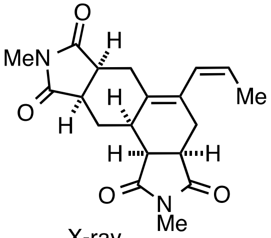


X-ray

40

^{13}C NMR spectrum
75 MHz, in CDCl$_3$

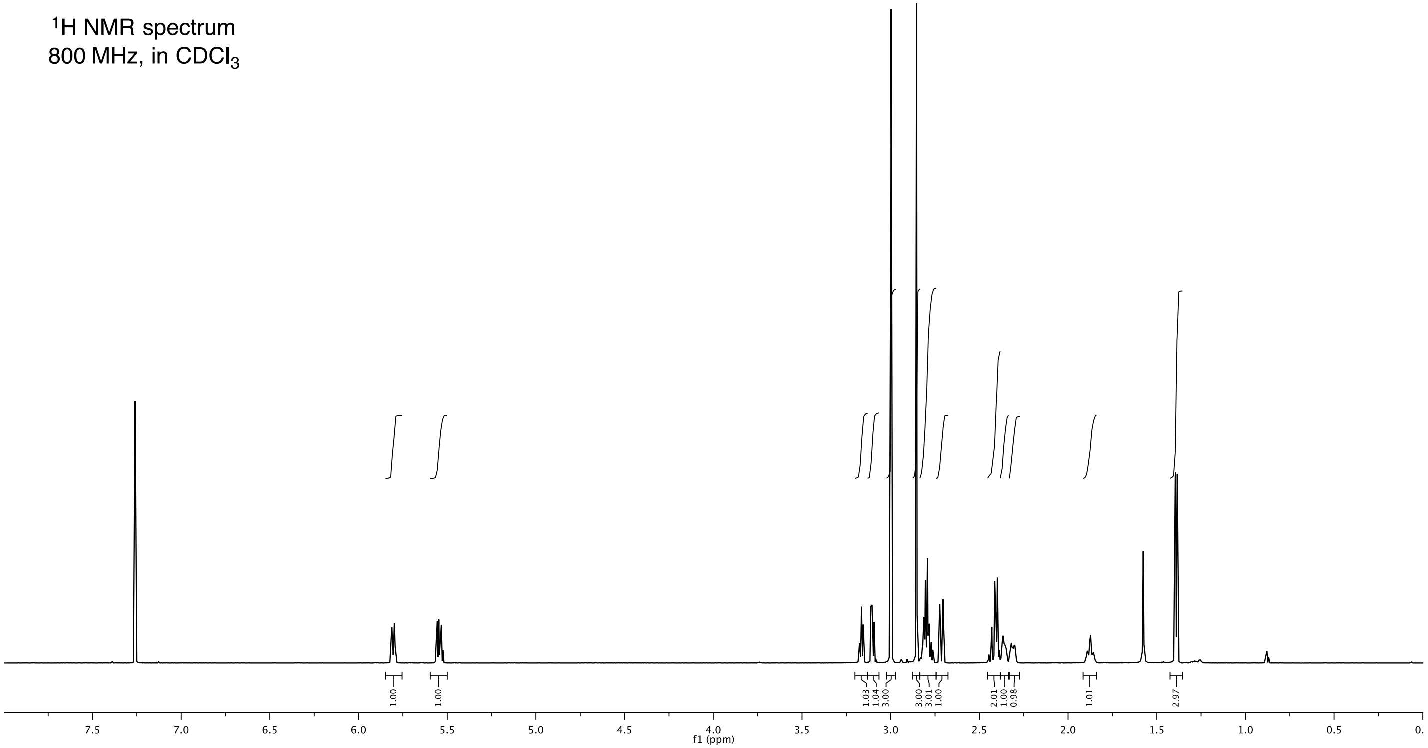


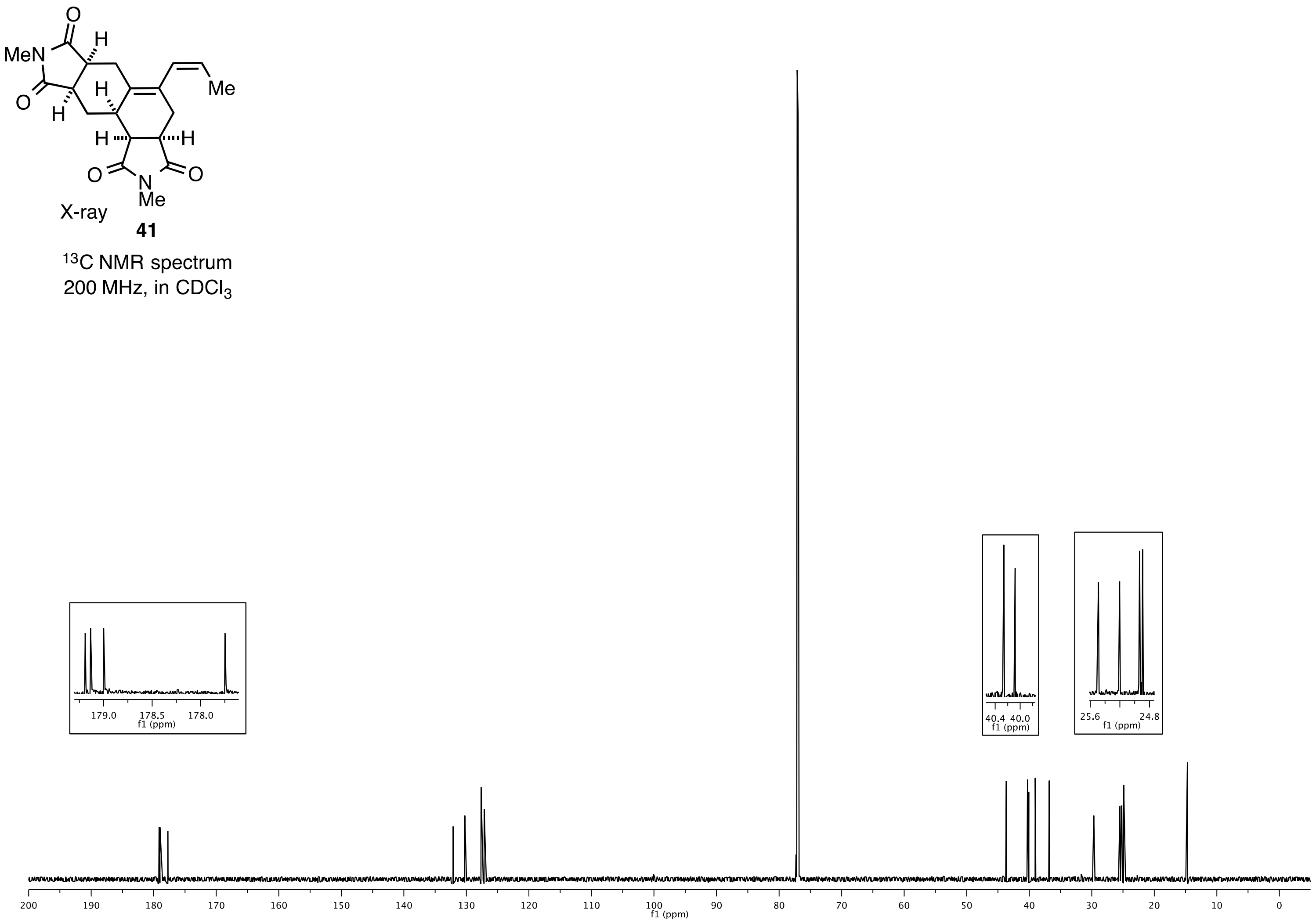


X-ray

41

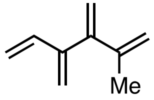
^{1}H NMR spectrum
800 MHz, in CDCl$_3$





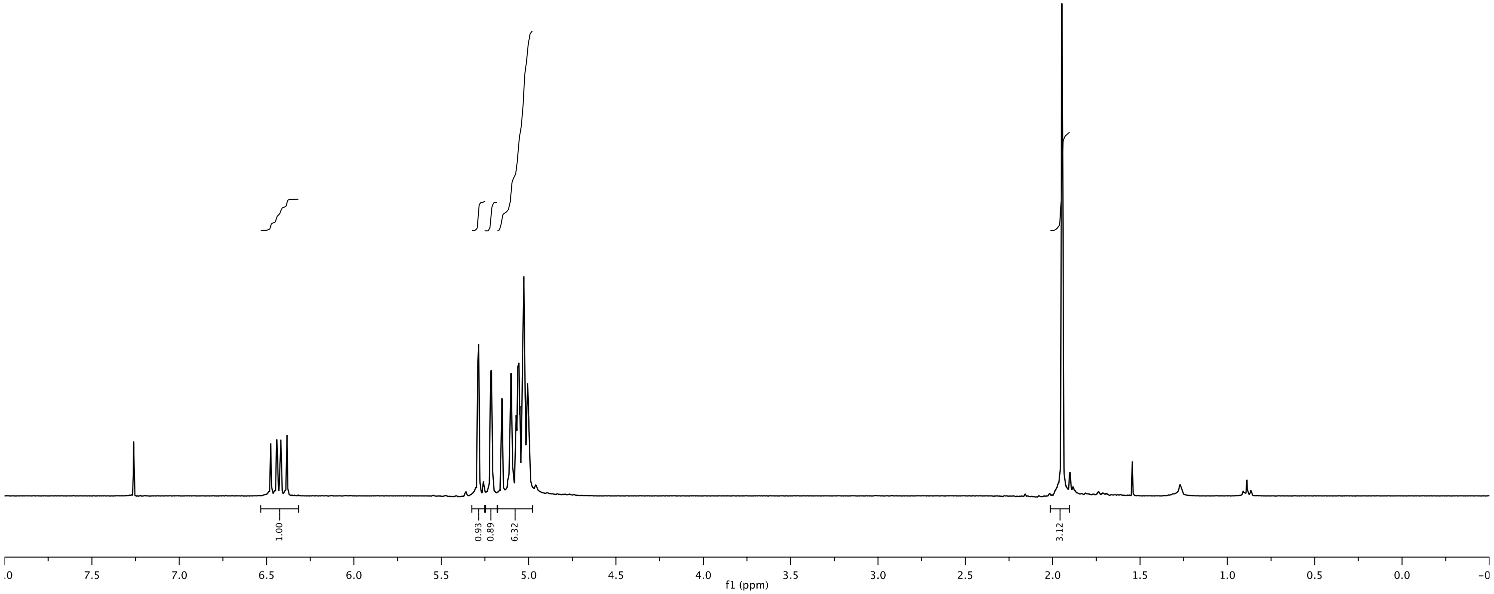
X-ray **41**

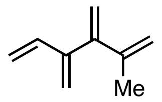
^{13}C NMR spectrum
200 MHz, in $CDCl_3$



12

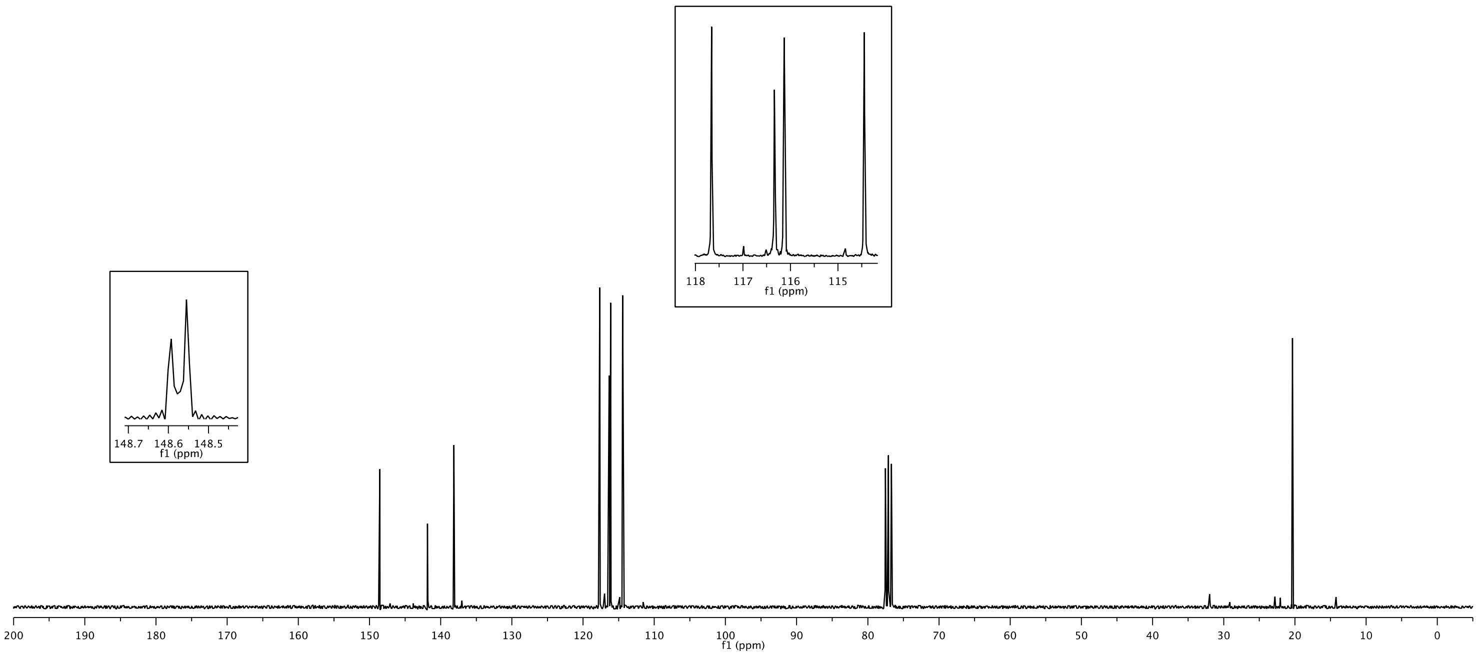
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

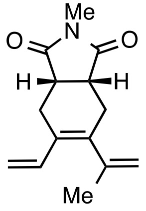




12

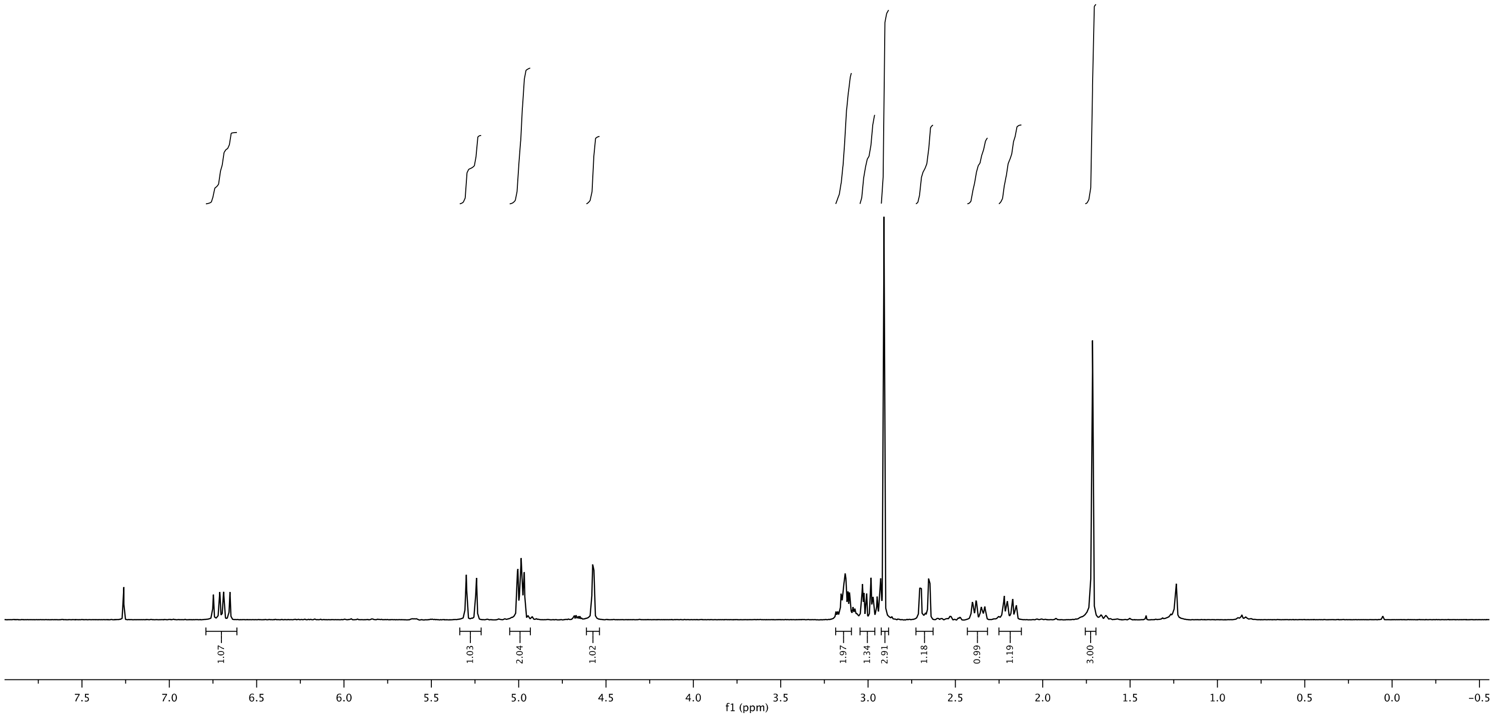
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

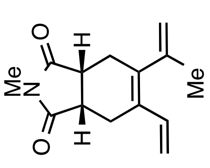




42

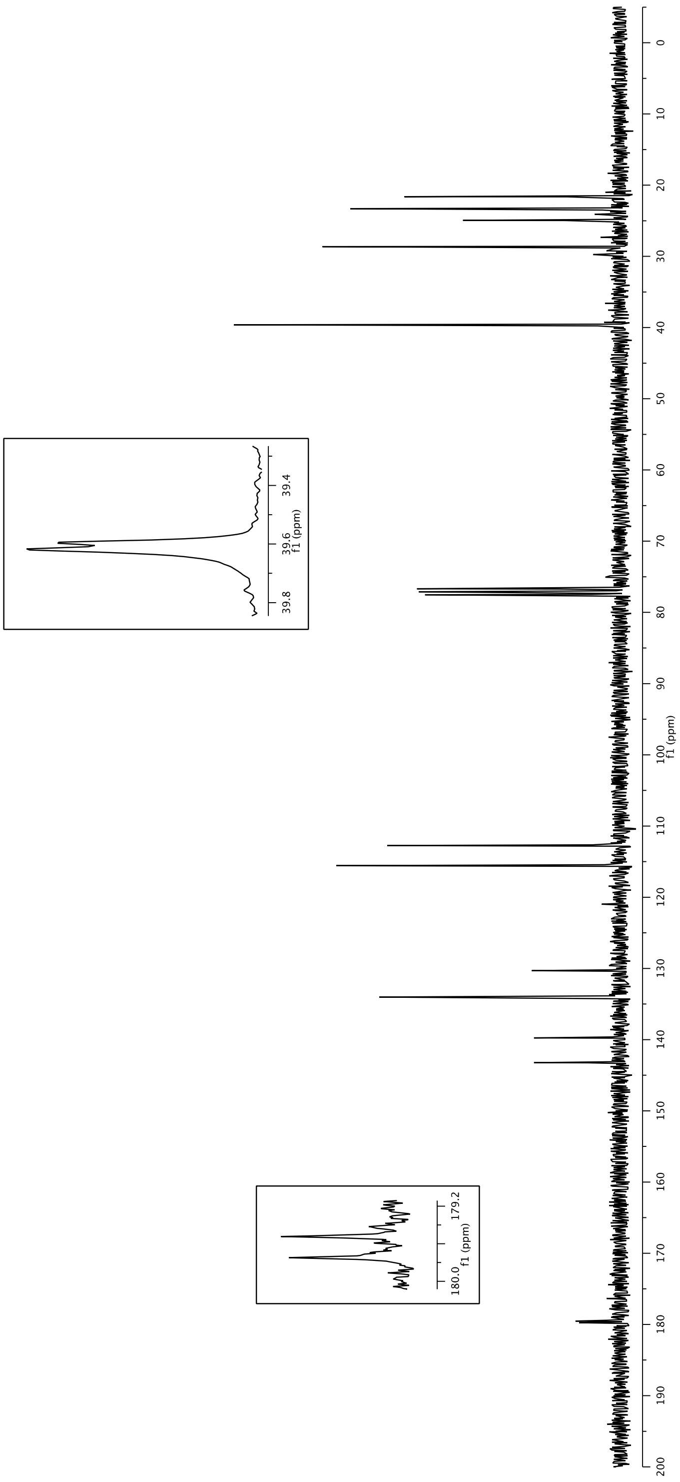
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

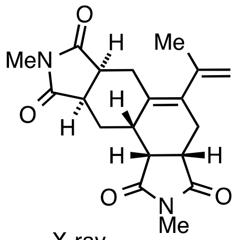




42

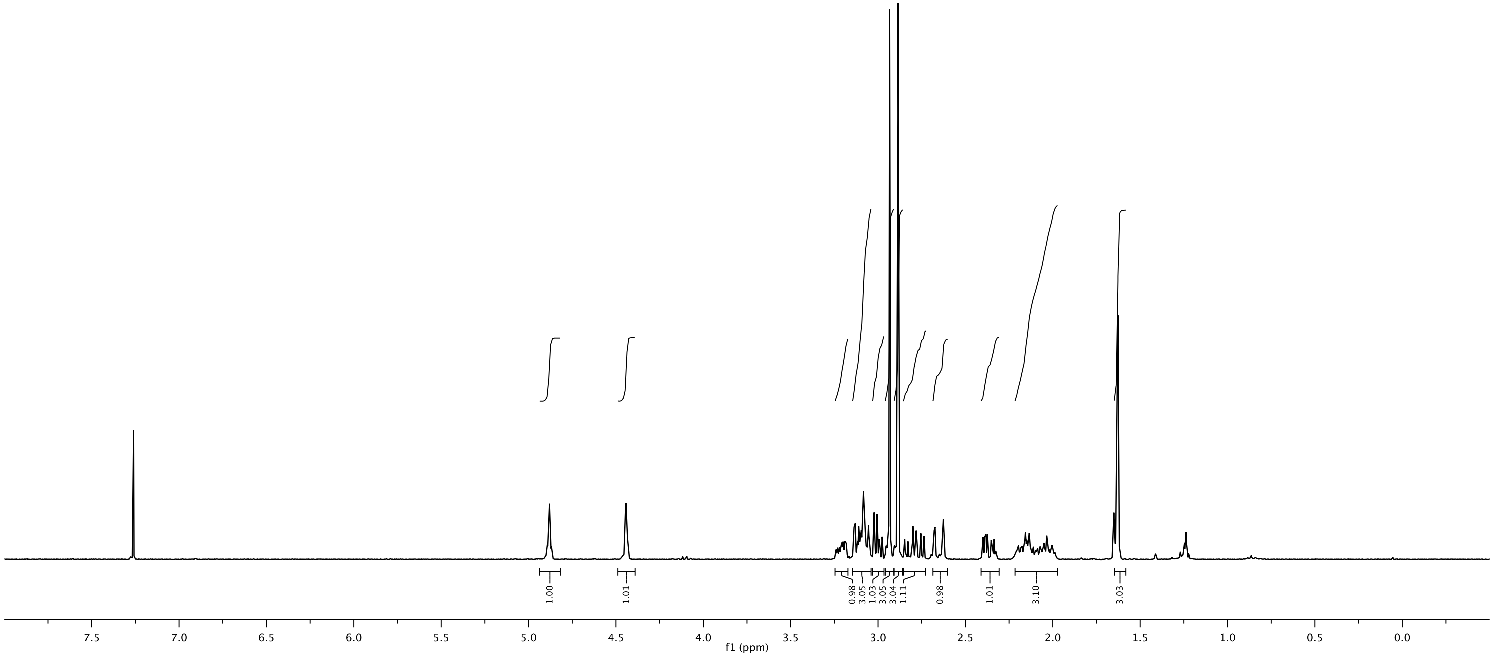
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

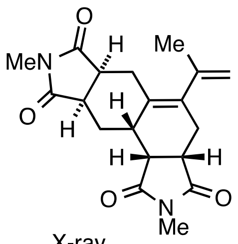




X-ray **45**

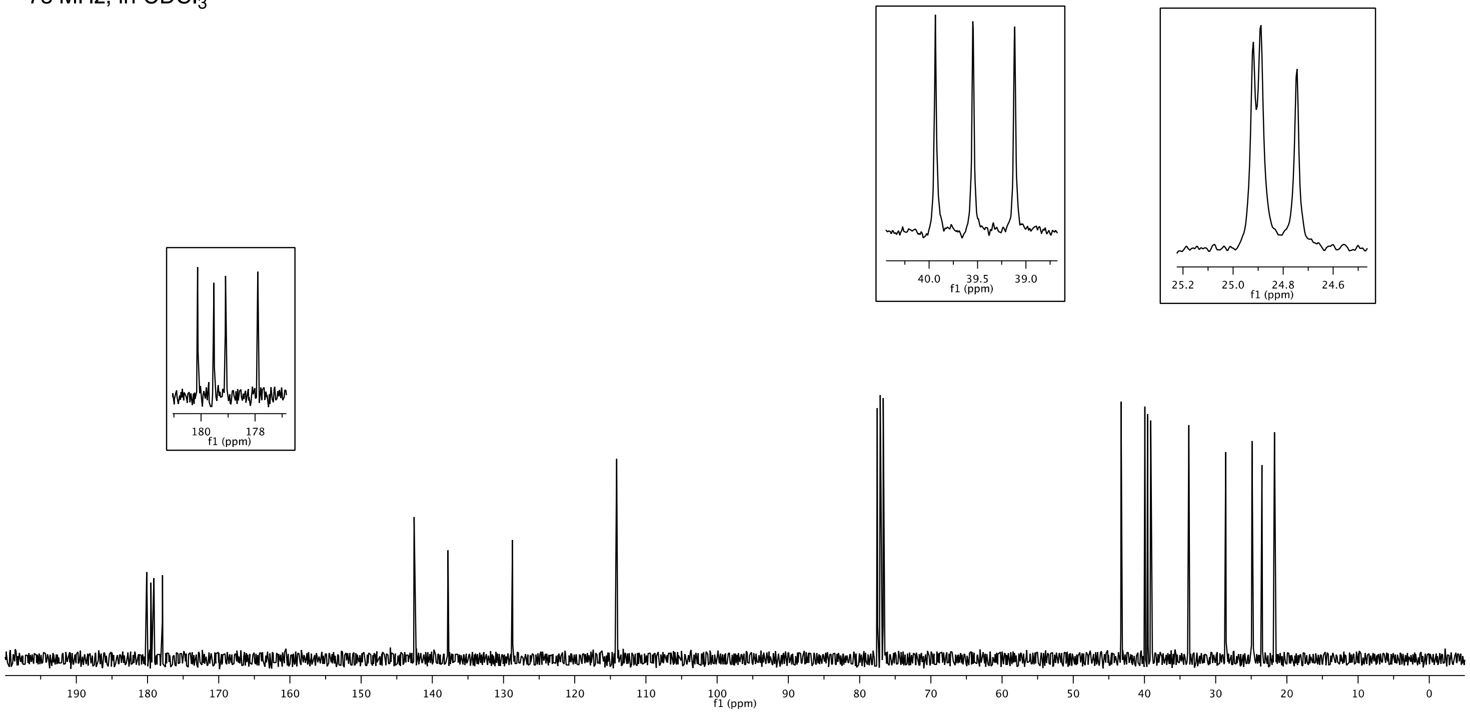
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

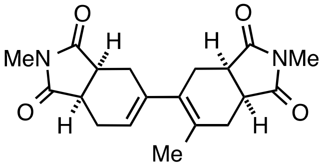




X-ray **45**

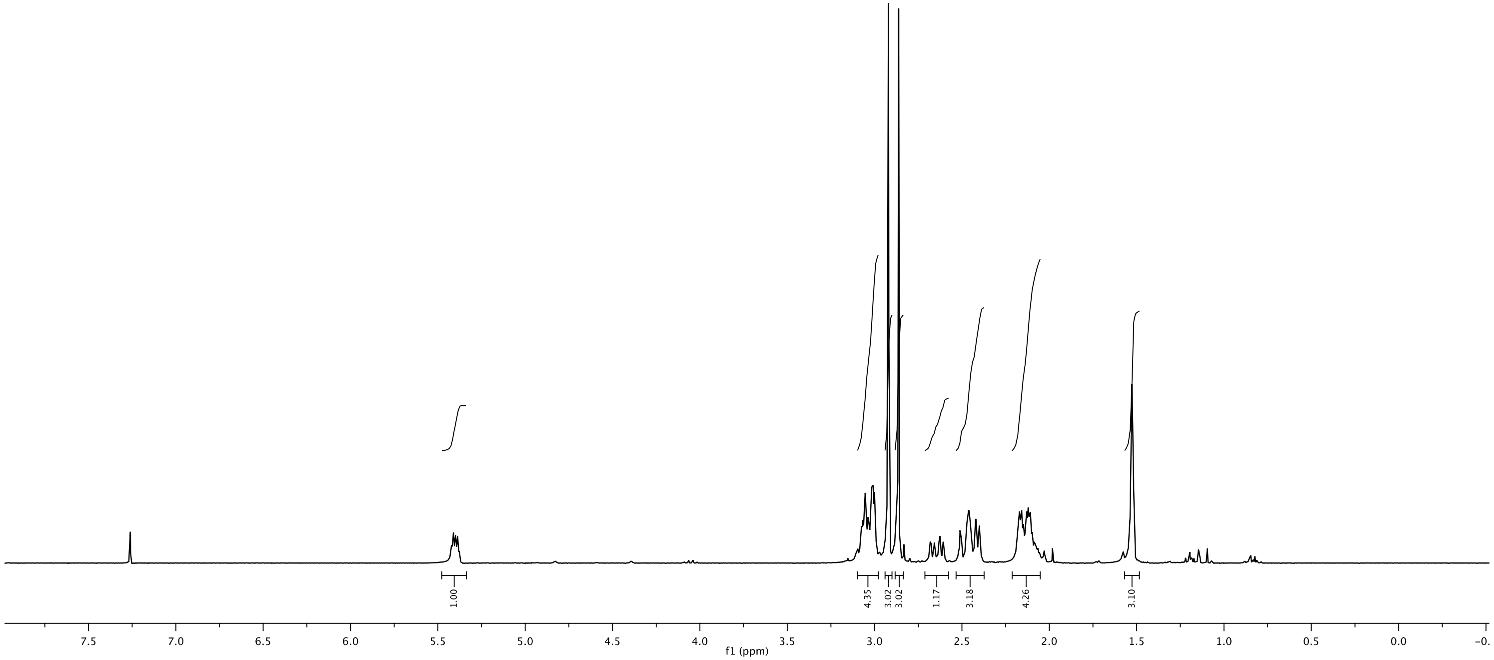
^{13}C NMR spectrum
75 MHz, in CDCl$_3$

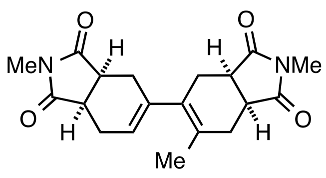




46

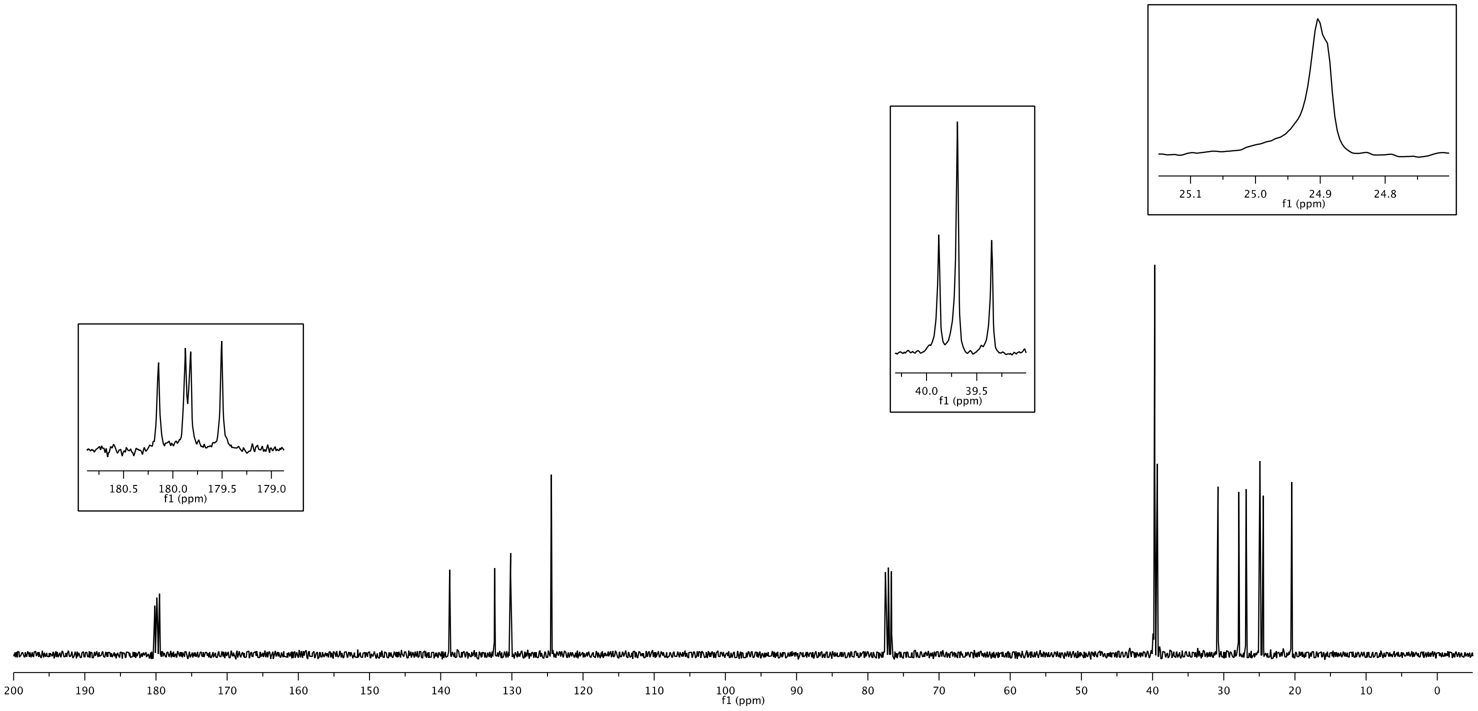
^1H NMR spectrum
300 MHz, in $CDCl_3$

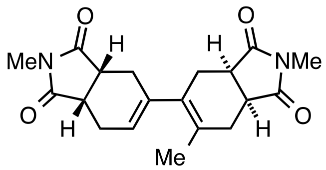




46

^{13}C NMR spectrum
75 MHz, in $CDCl_3$

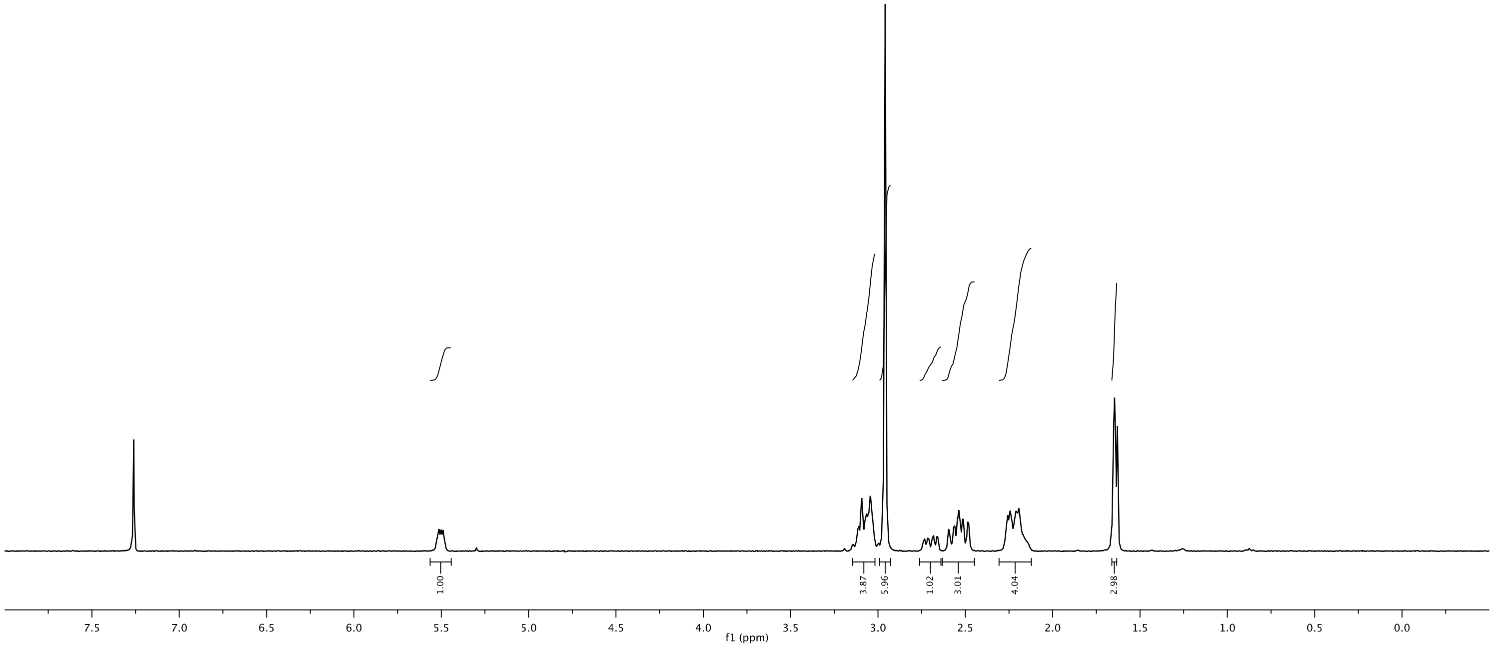


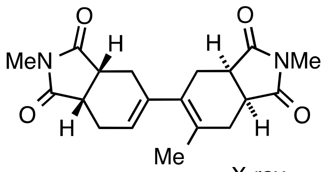


47

X-ray

^{1}H NMR spectrum
300 MHz, in $CDCl_3$

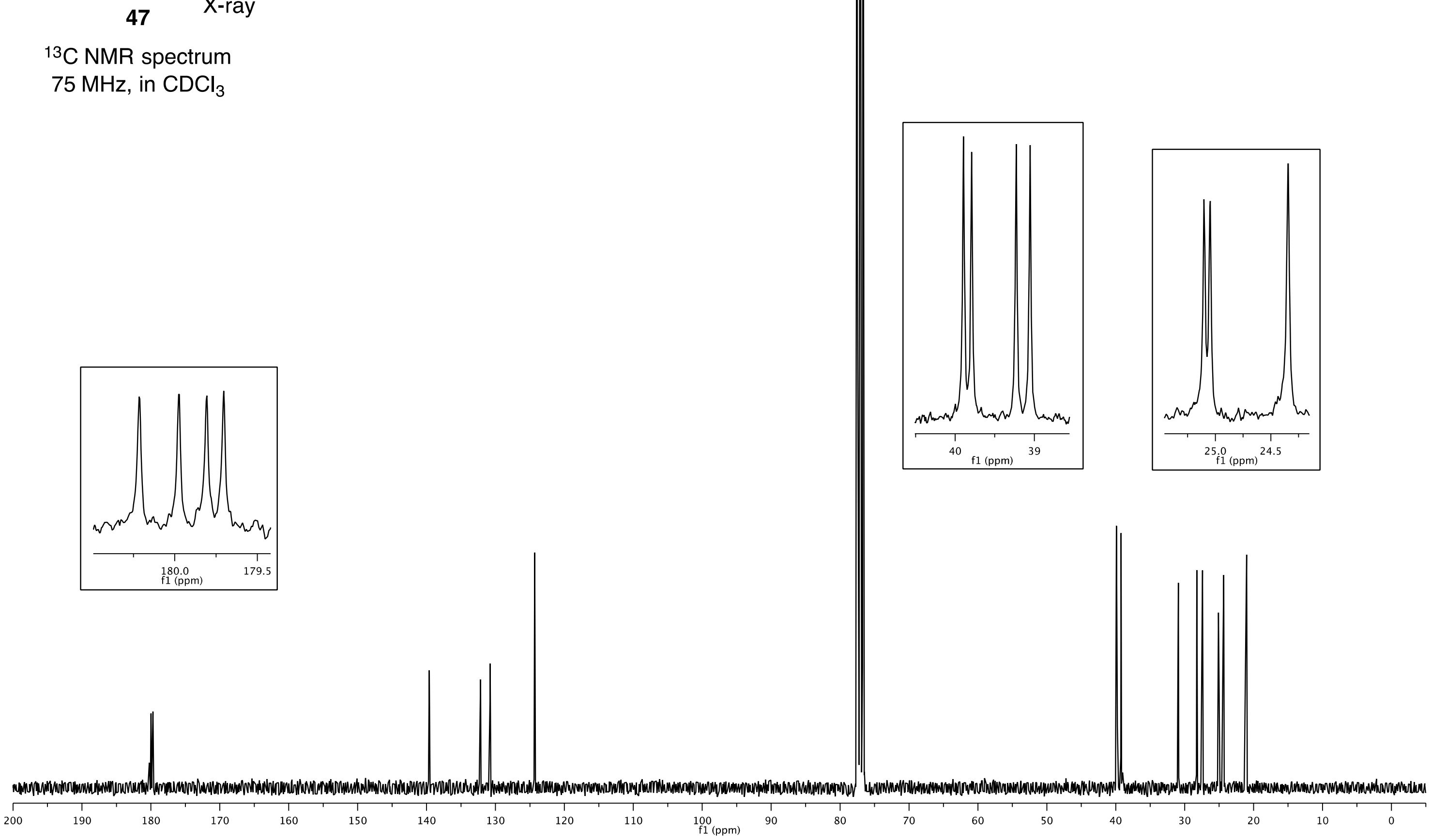


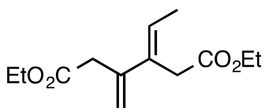


47

X-ray

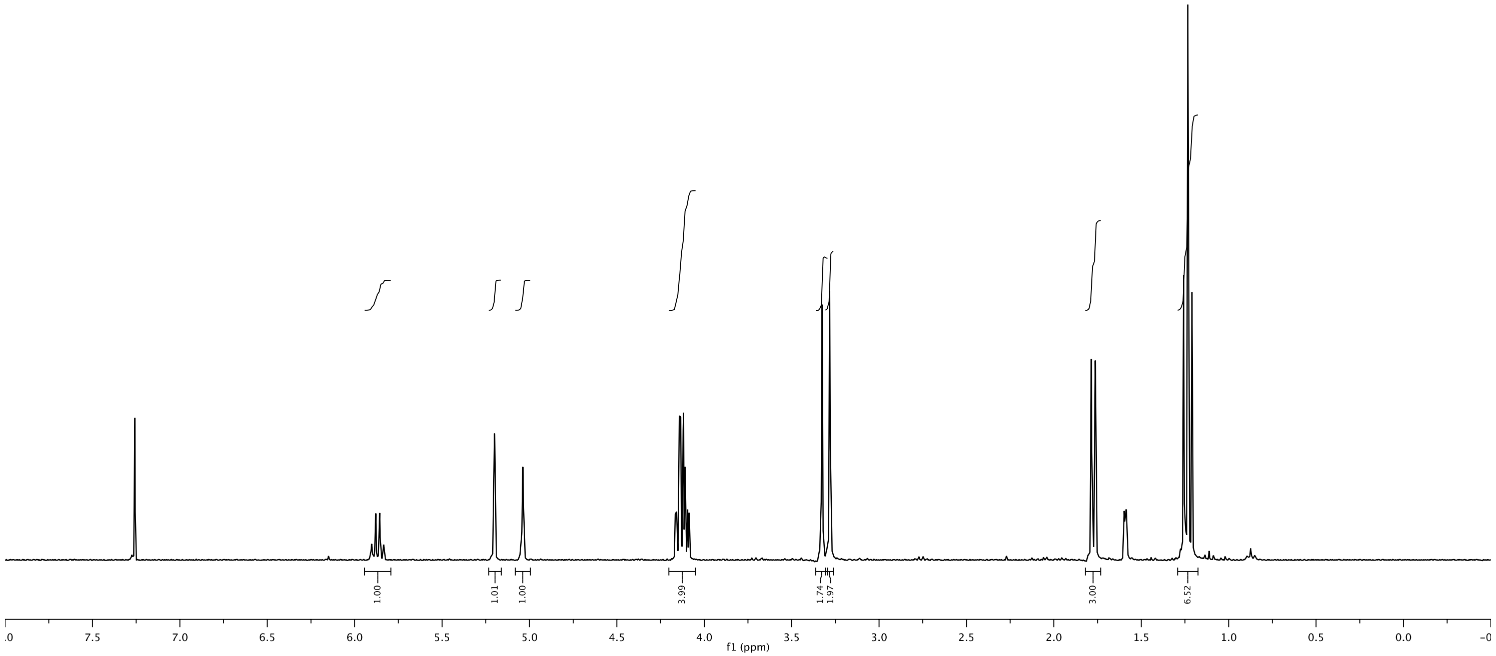
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

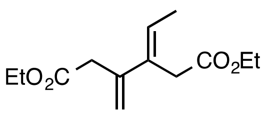




23

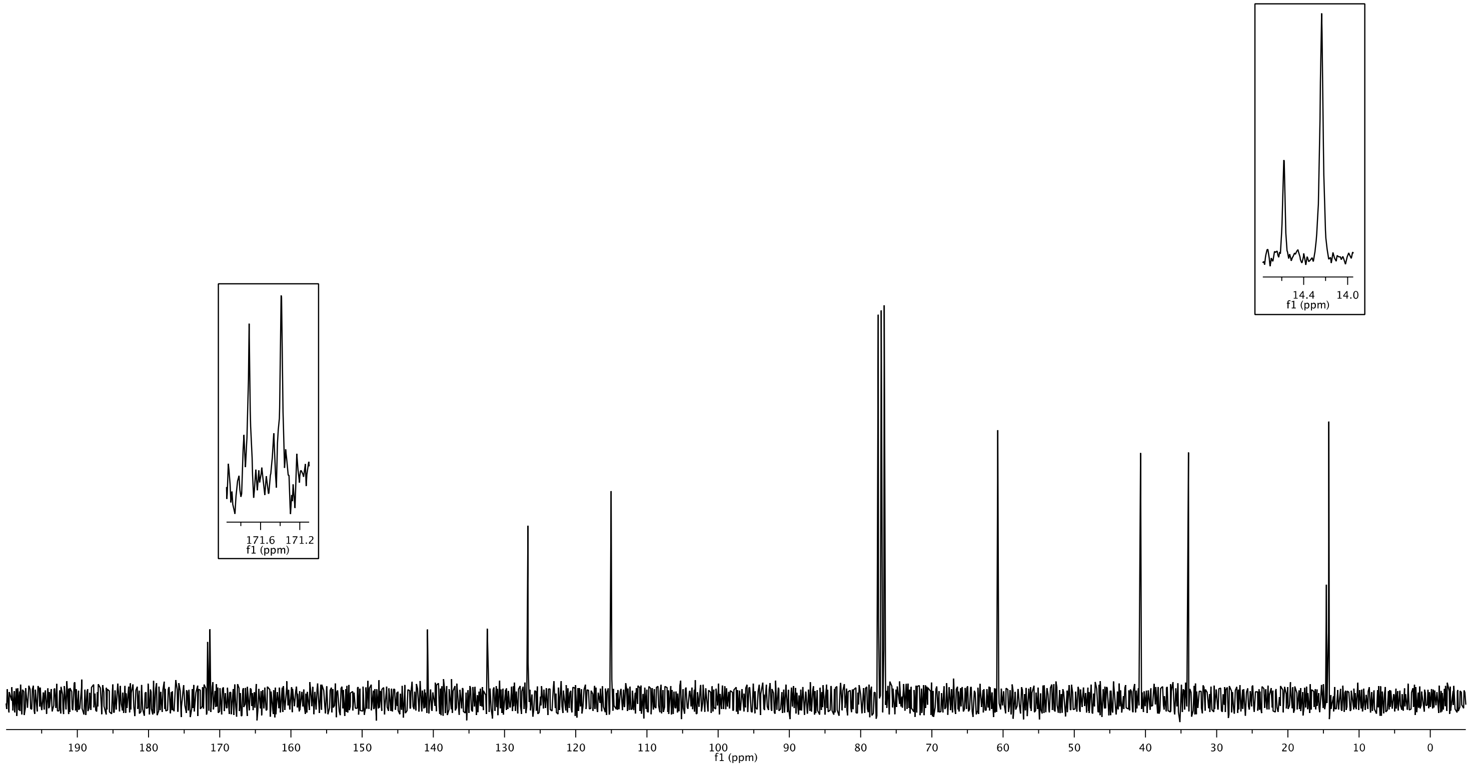
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

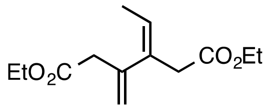




23

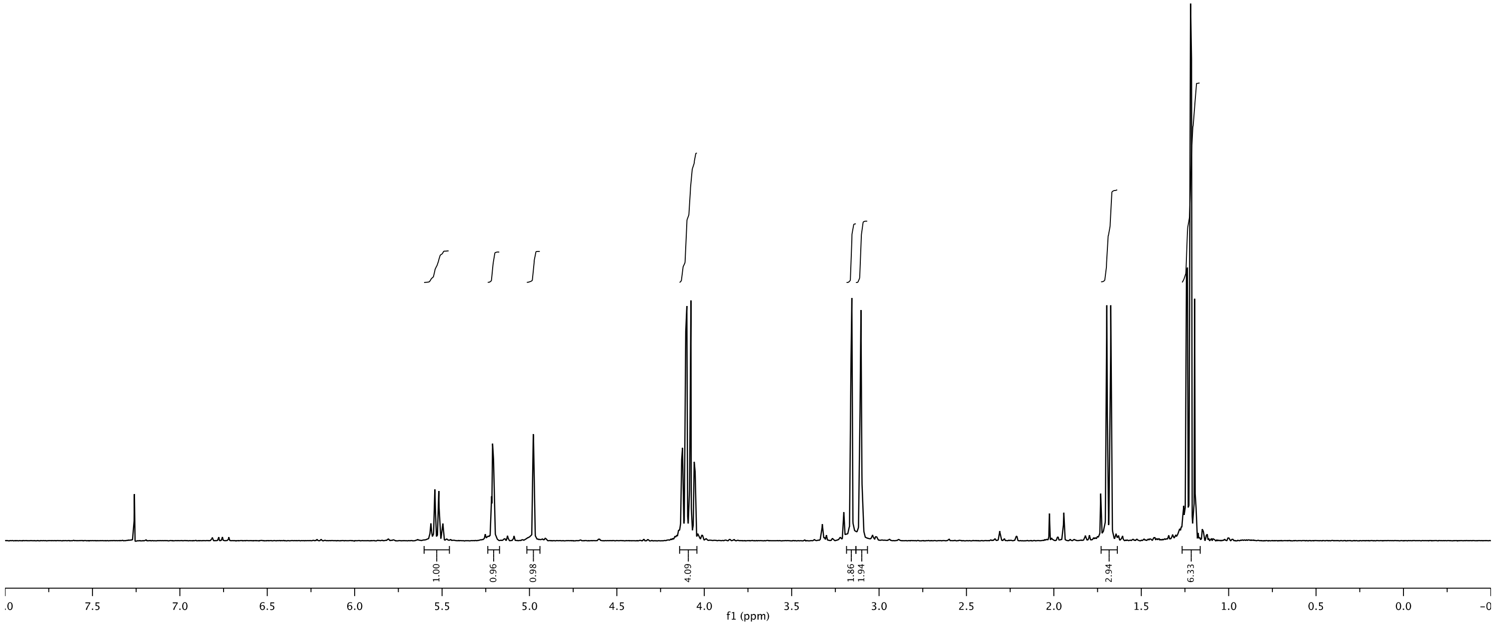
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

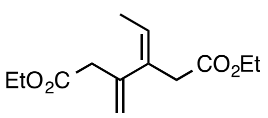




24

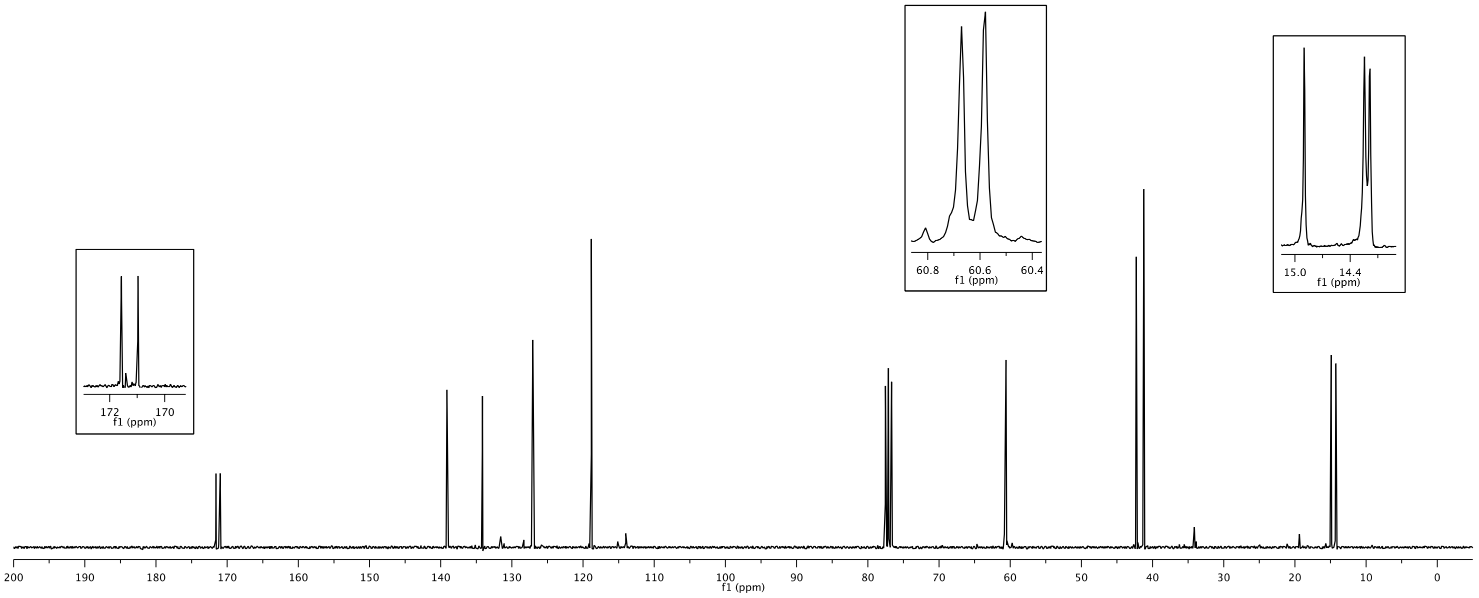
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

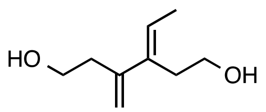




24

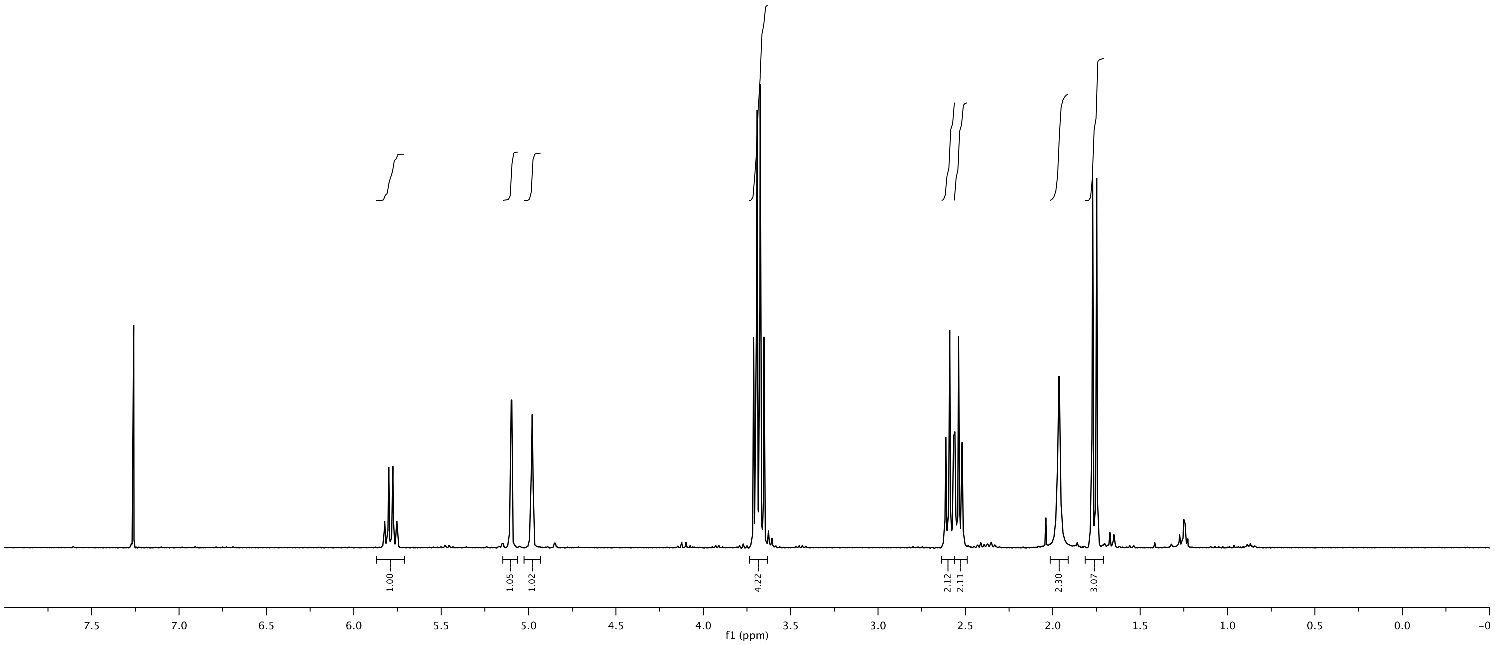
^{13}C NMR spectrum
75 MHz, in CDCl$_3$

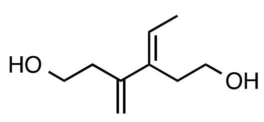




25

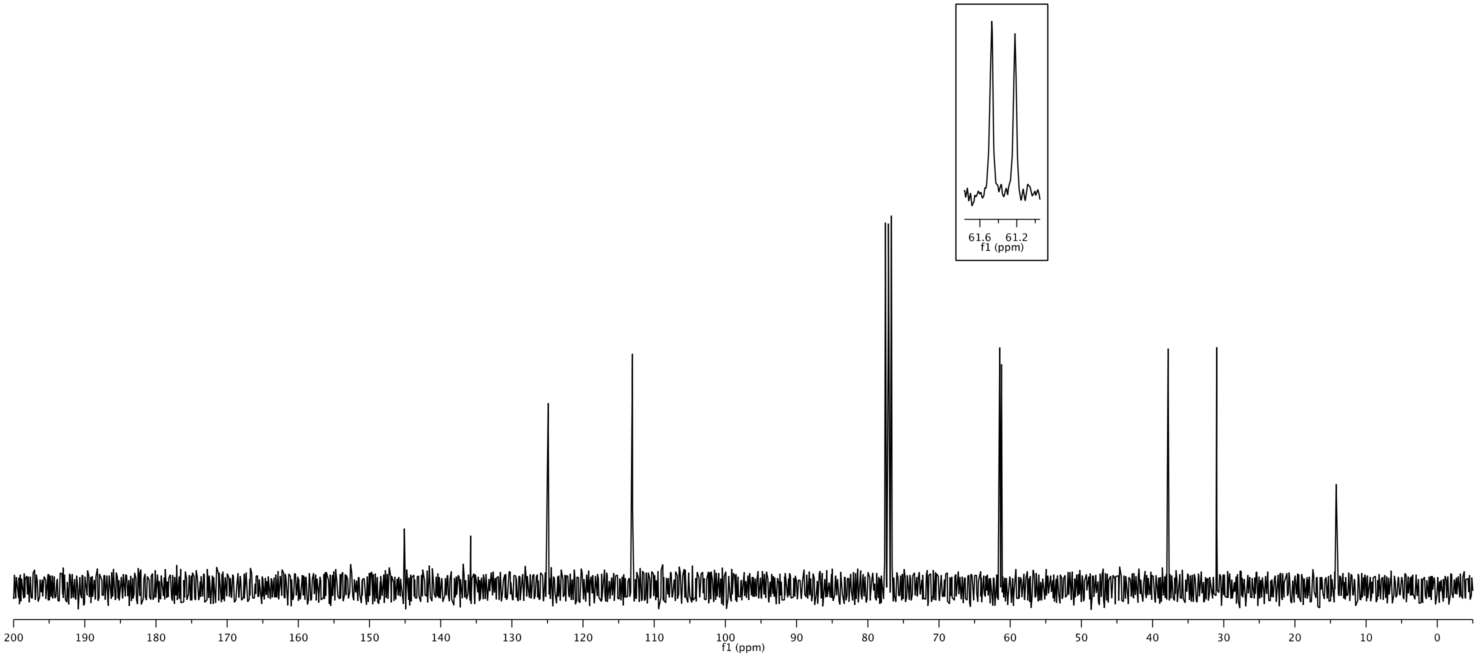
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

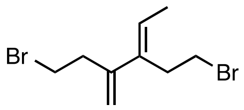




25

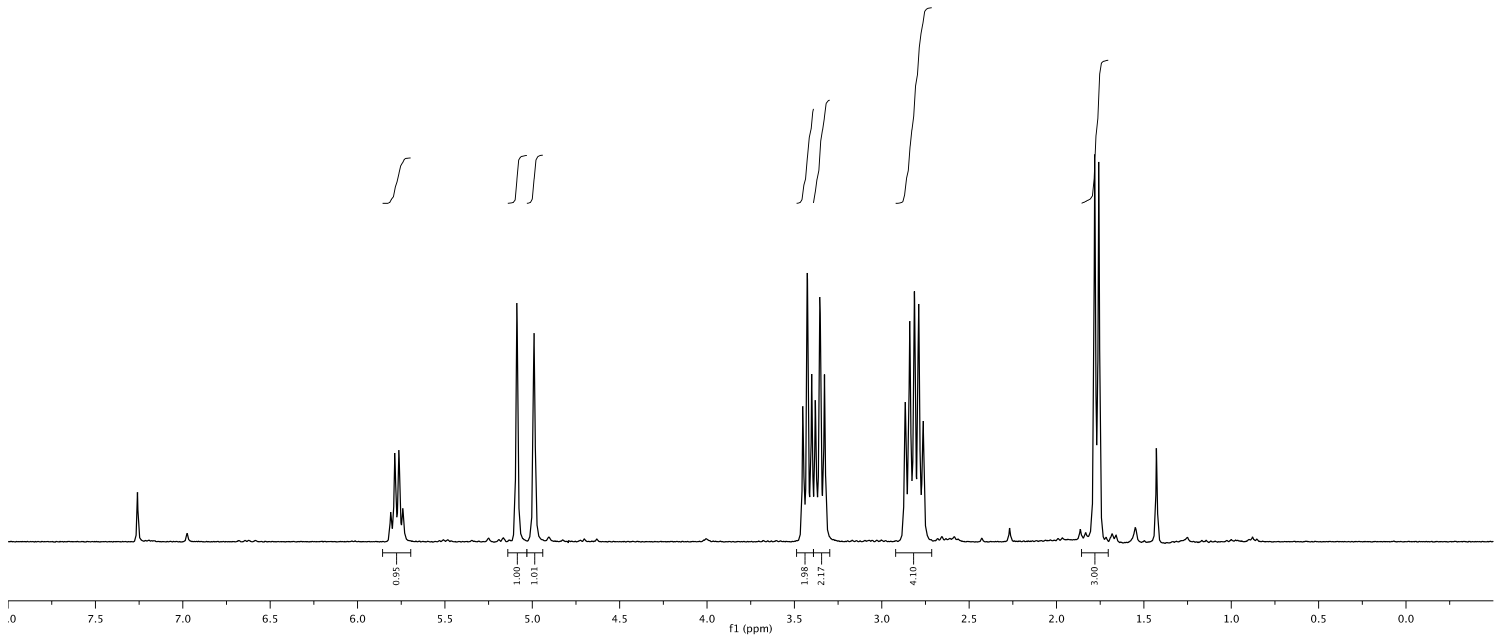
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

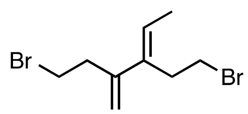




27

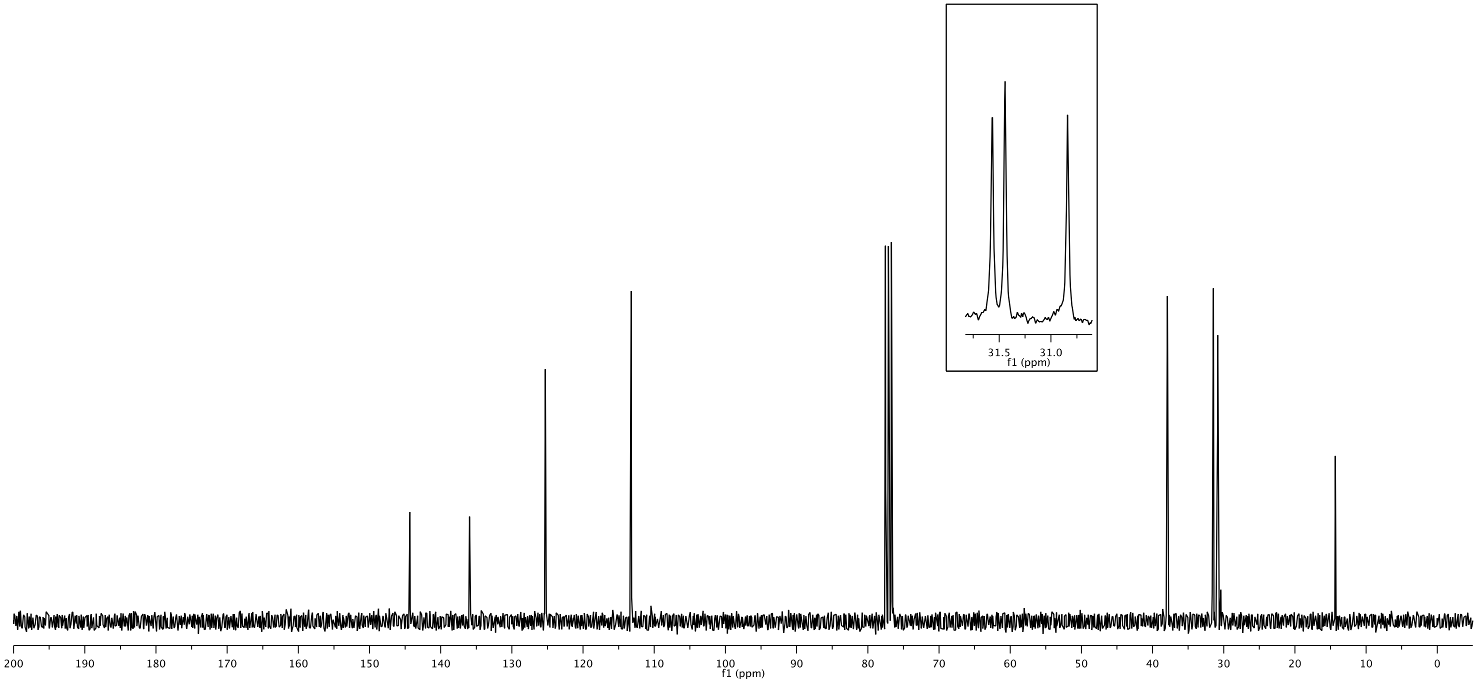
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

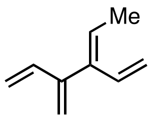




27

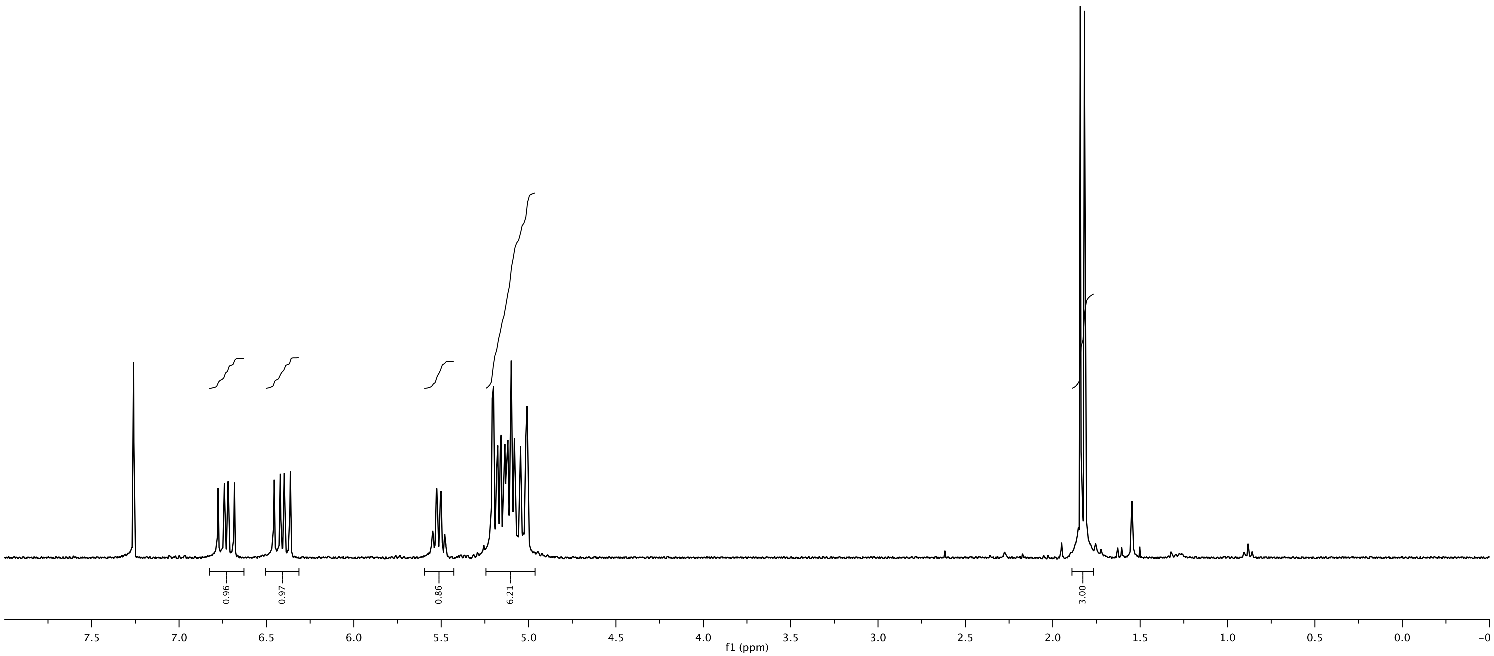
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

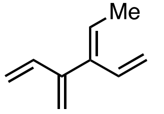




13

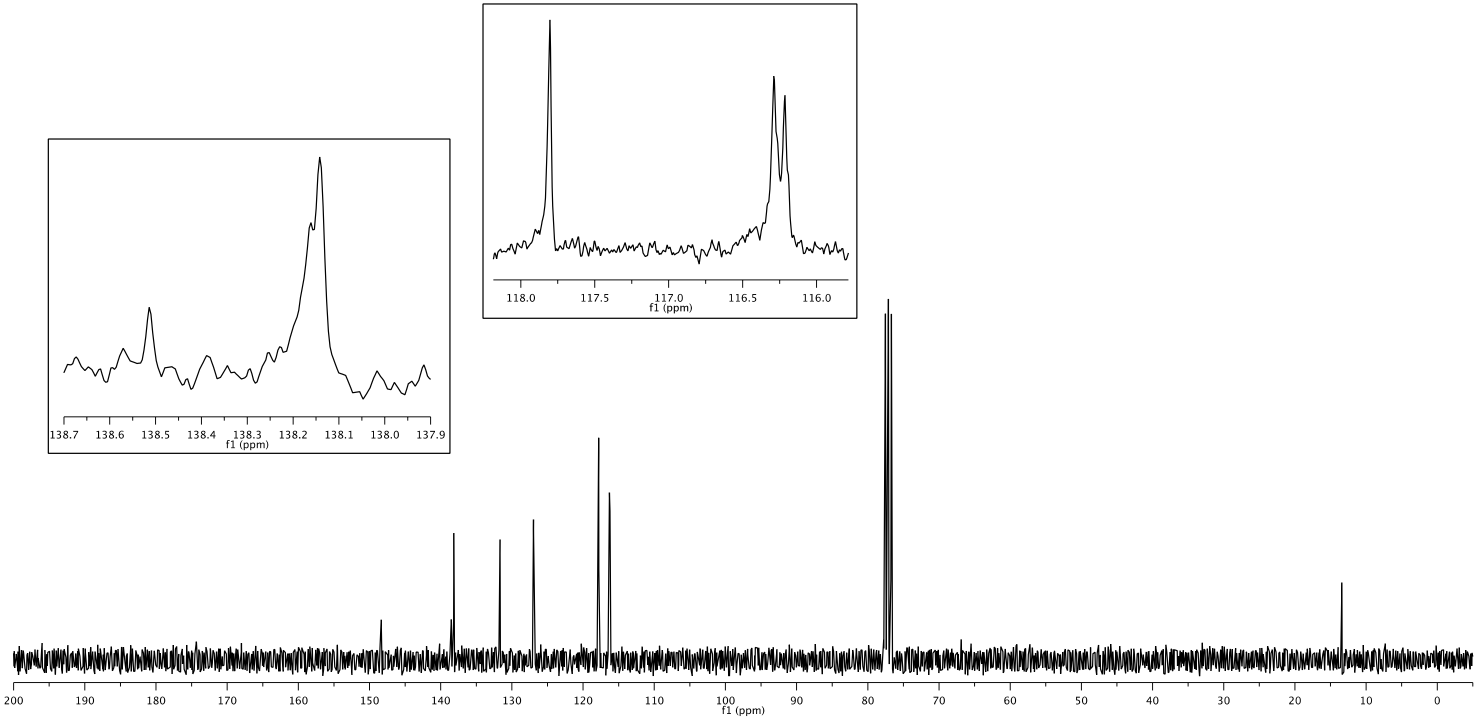
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

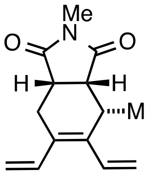




13

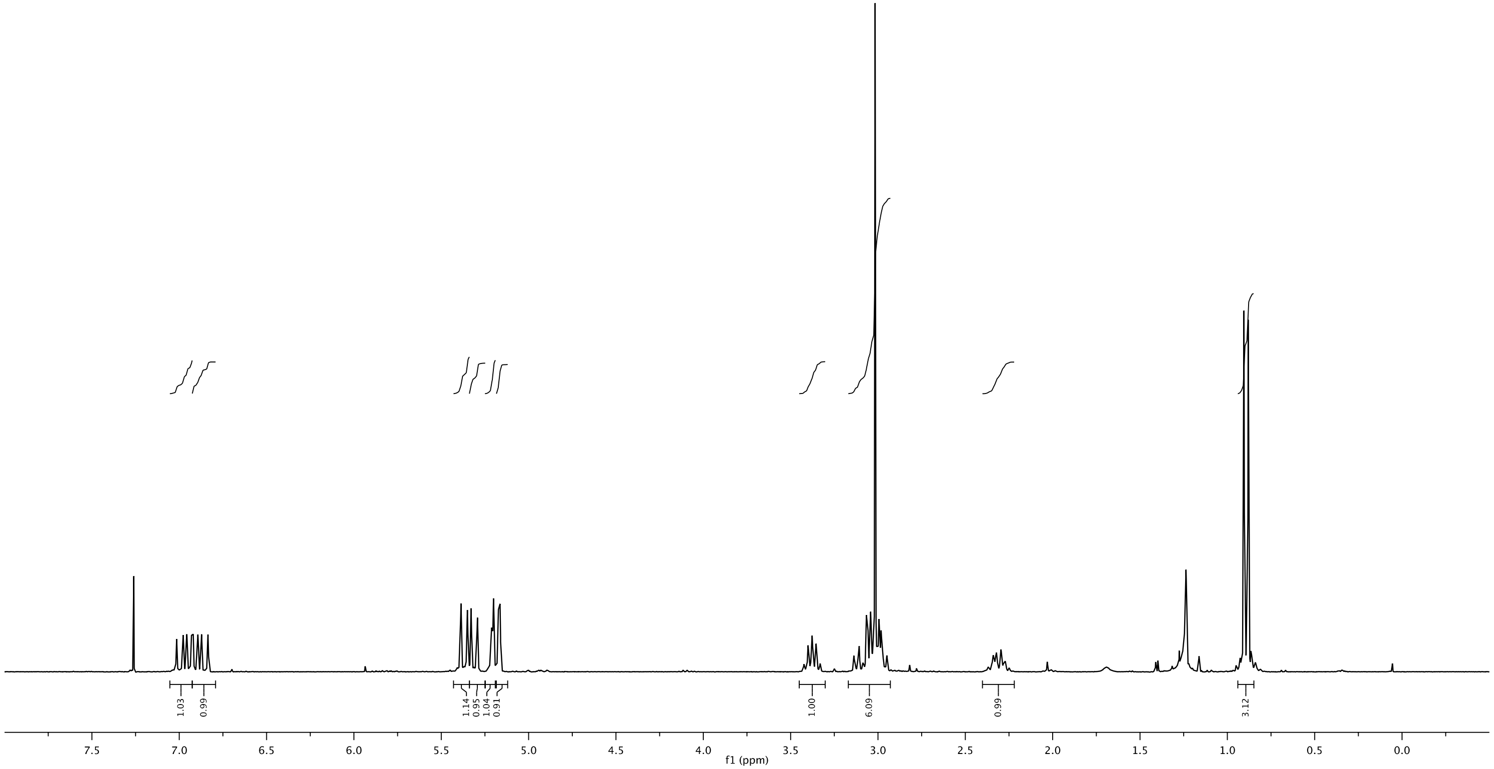
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

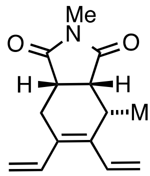




48

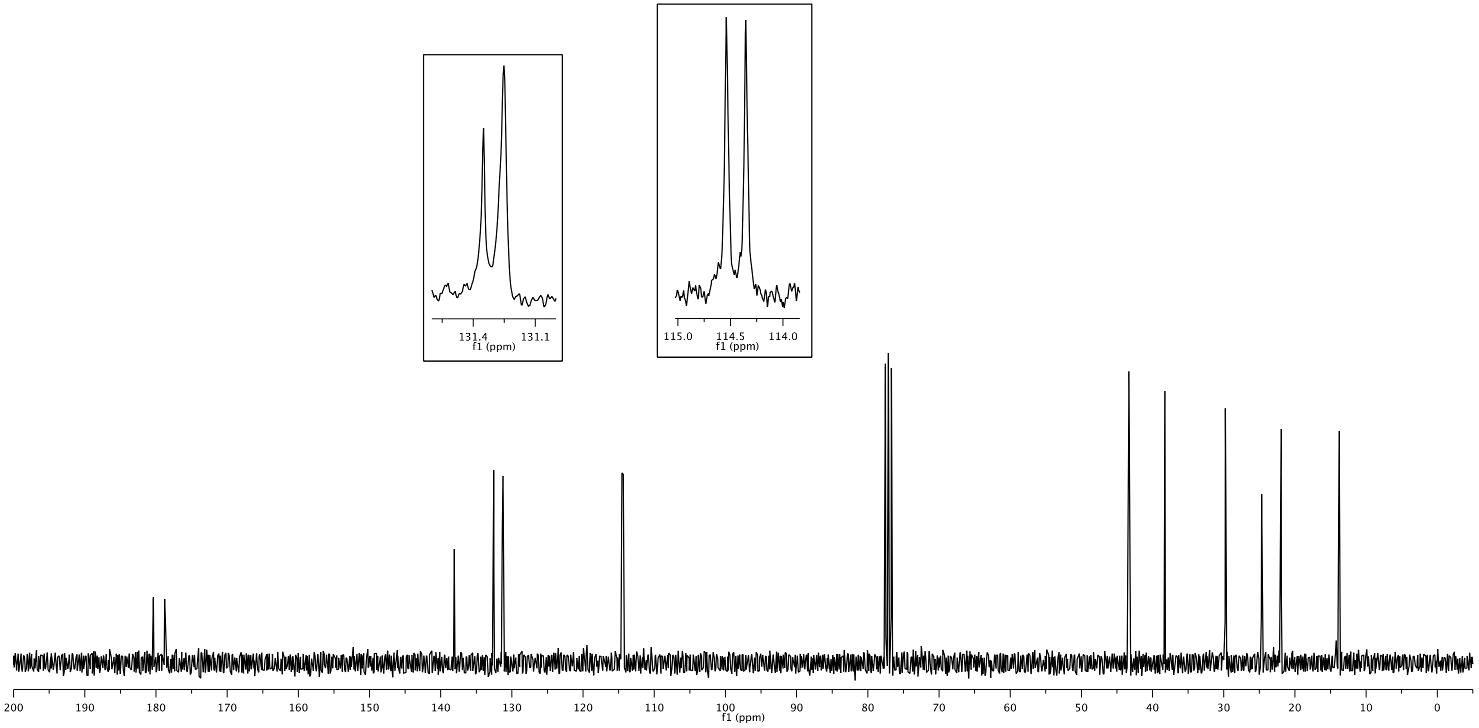
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

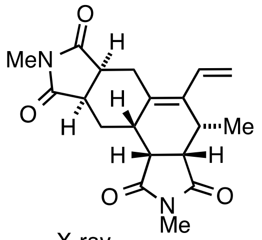




48

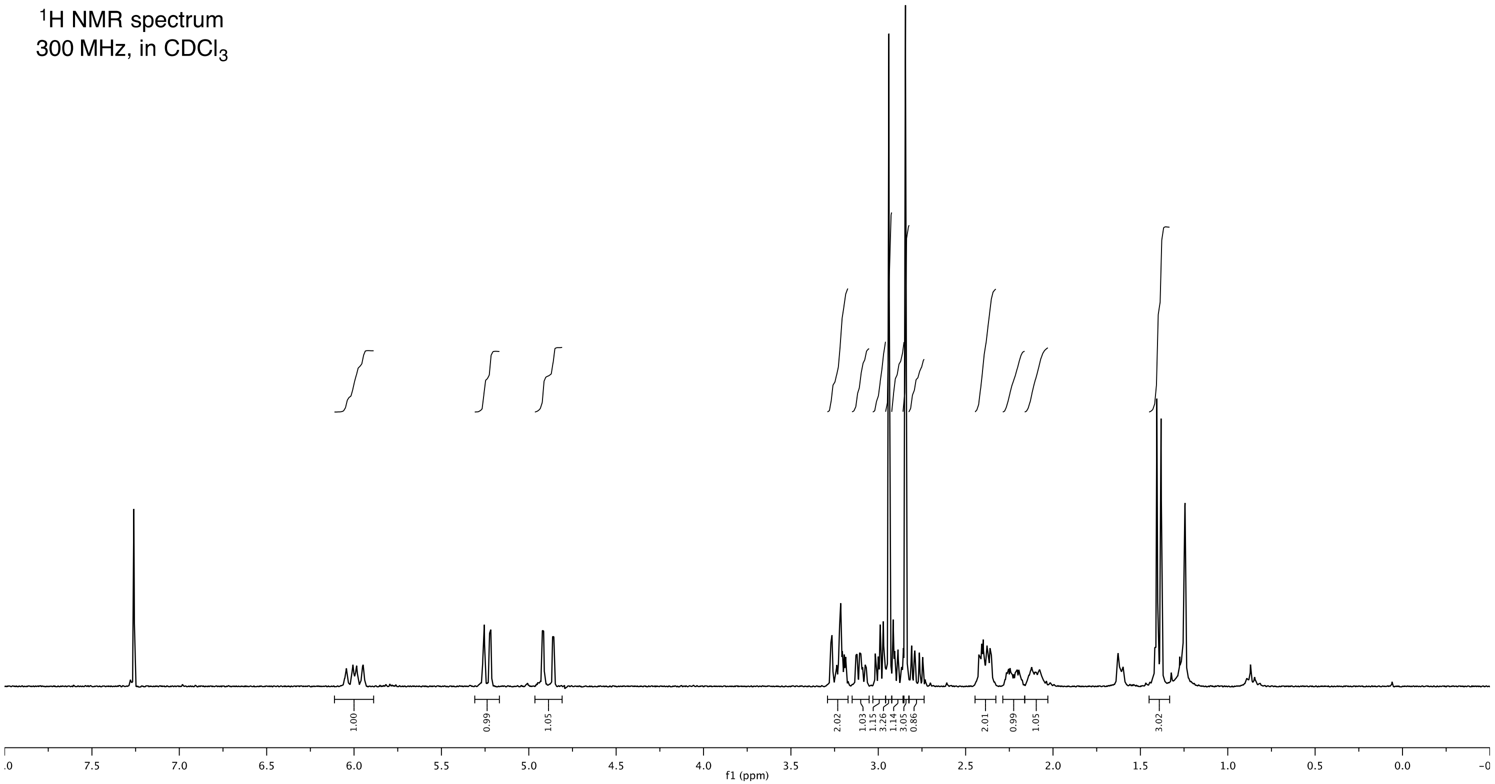
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

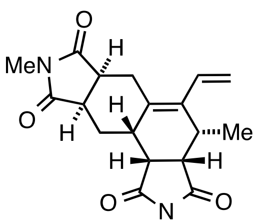




X-ray **50**

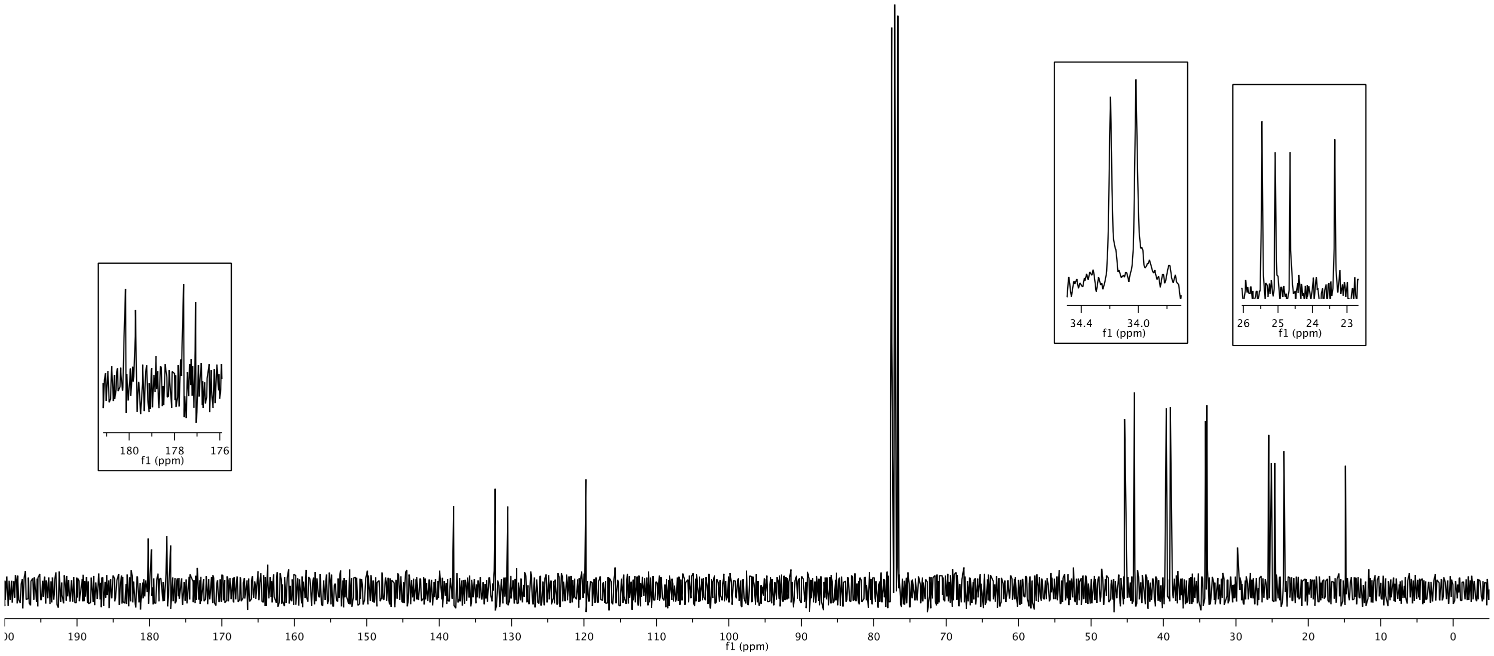
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

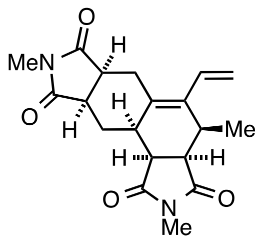




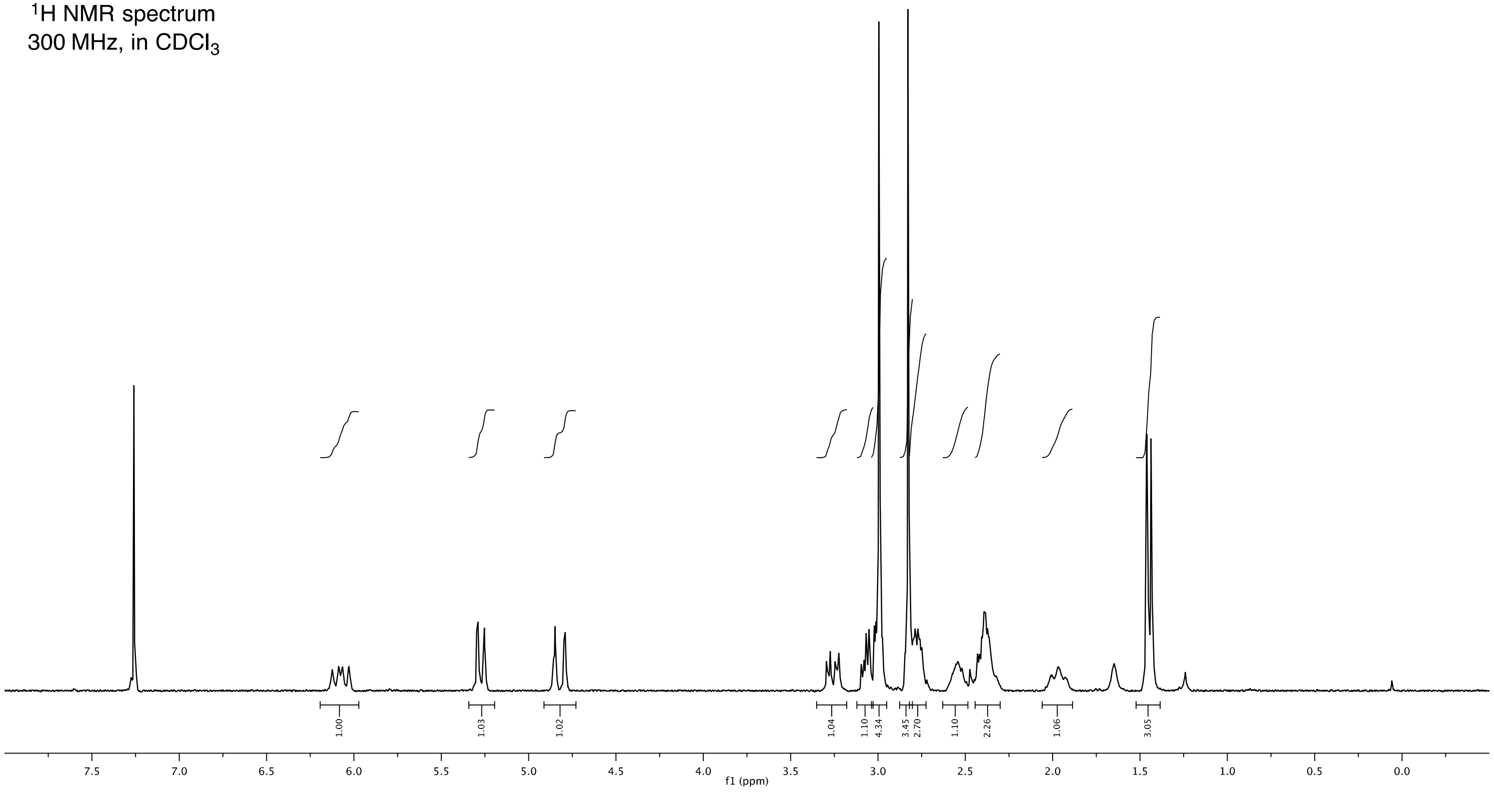
X-ray **50**

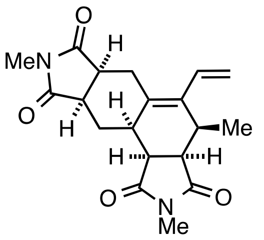
^{13}C NMR spectrum
75 MHz, in CDCl$_3$





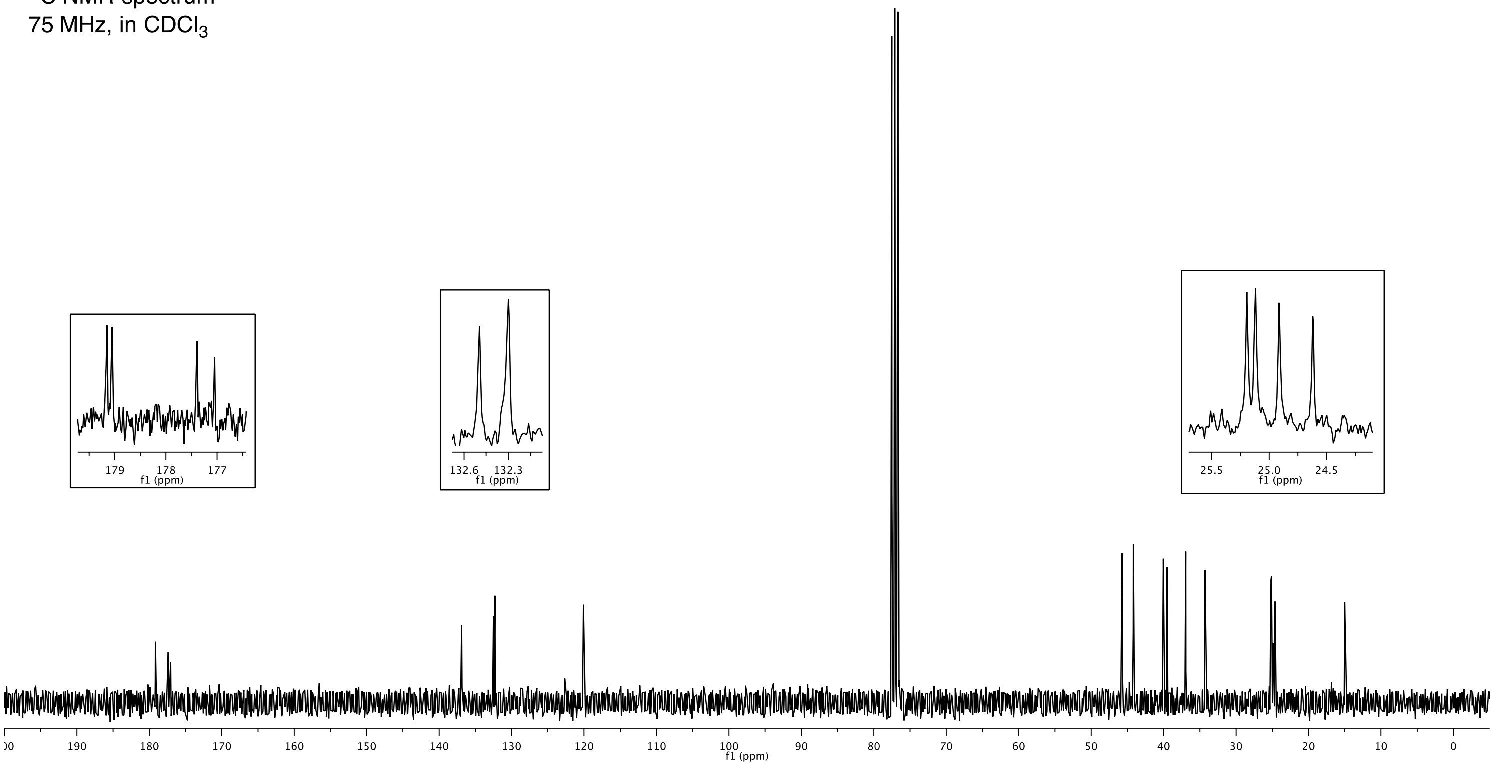
51
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

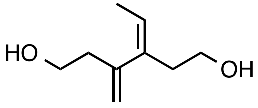




51

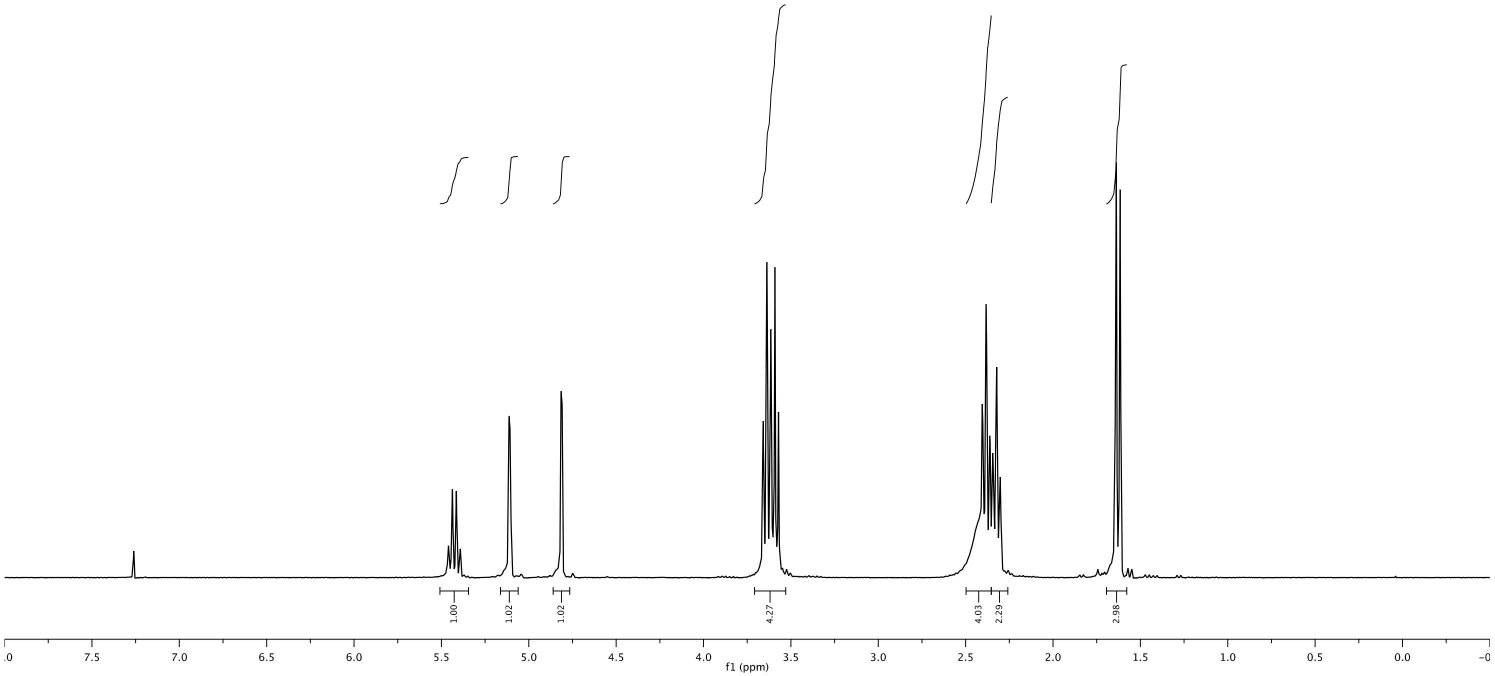
^{13}C NMR spectrum
75 MHz, in CDCl$_3$

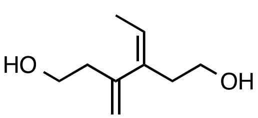




26

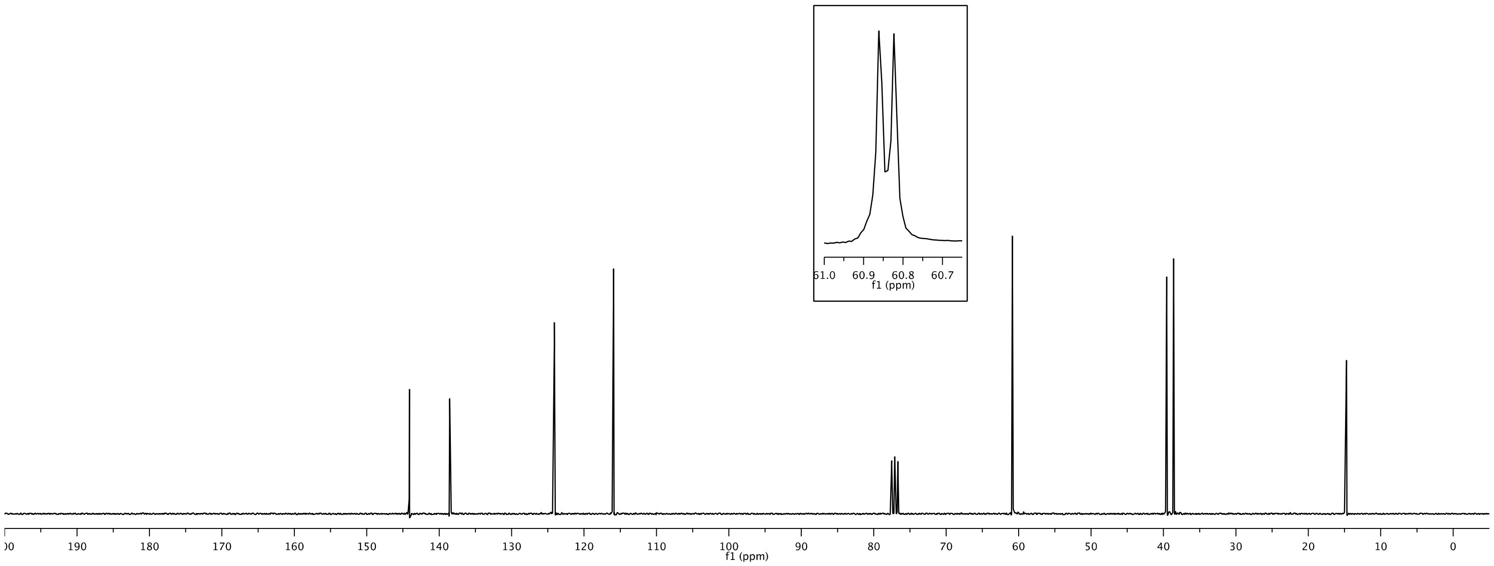
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

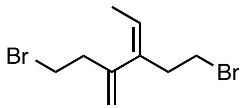




26

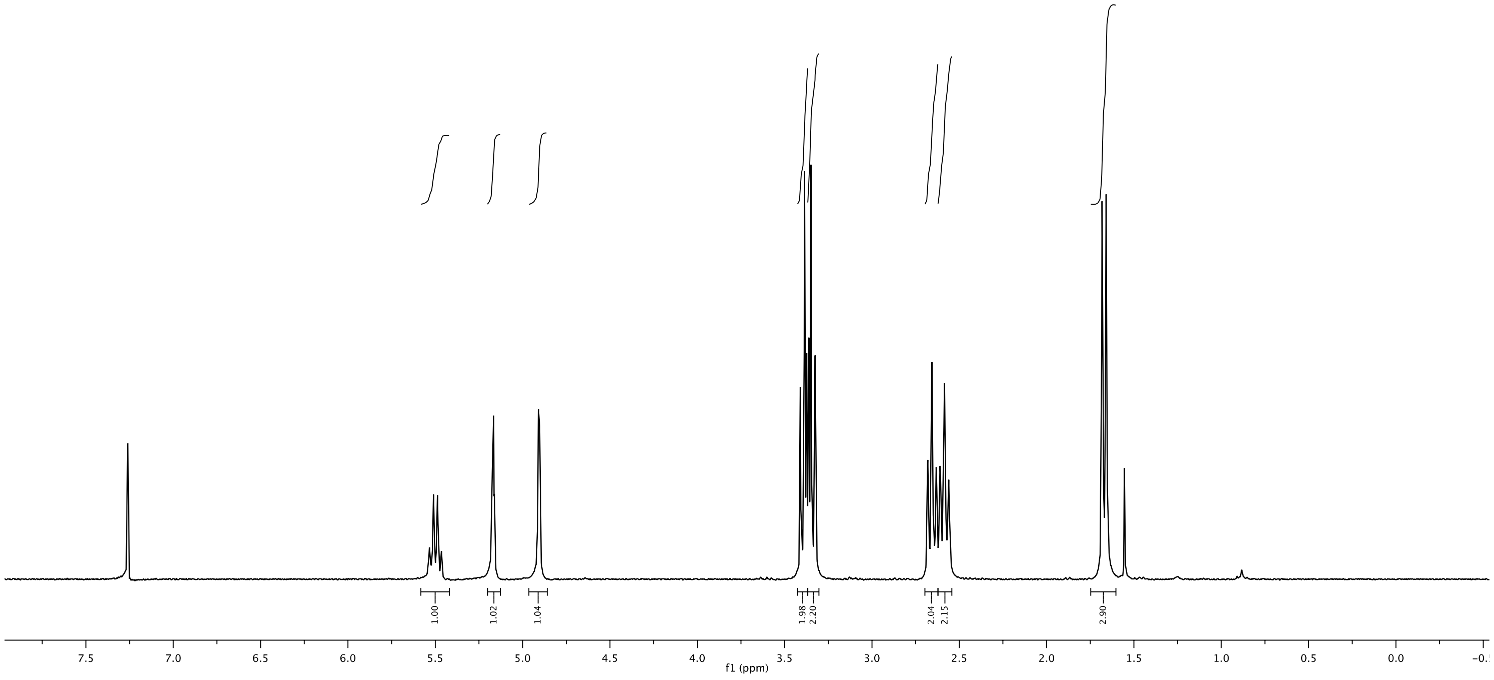
^{13}C NMR spectrum
75 MHz, in CDCl$_3$

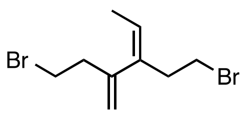




28

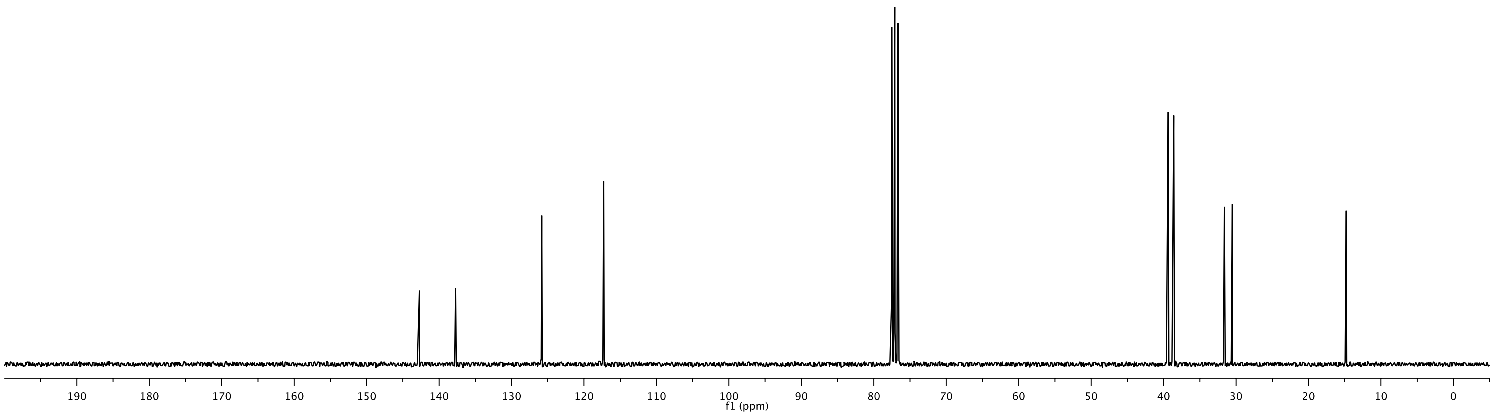
^{1}H NMR spectrum
300 MHz, in CDCl$_3$

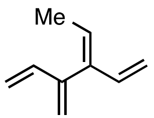




28

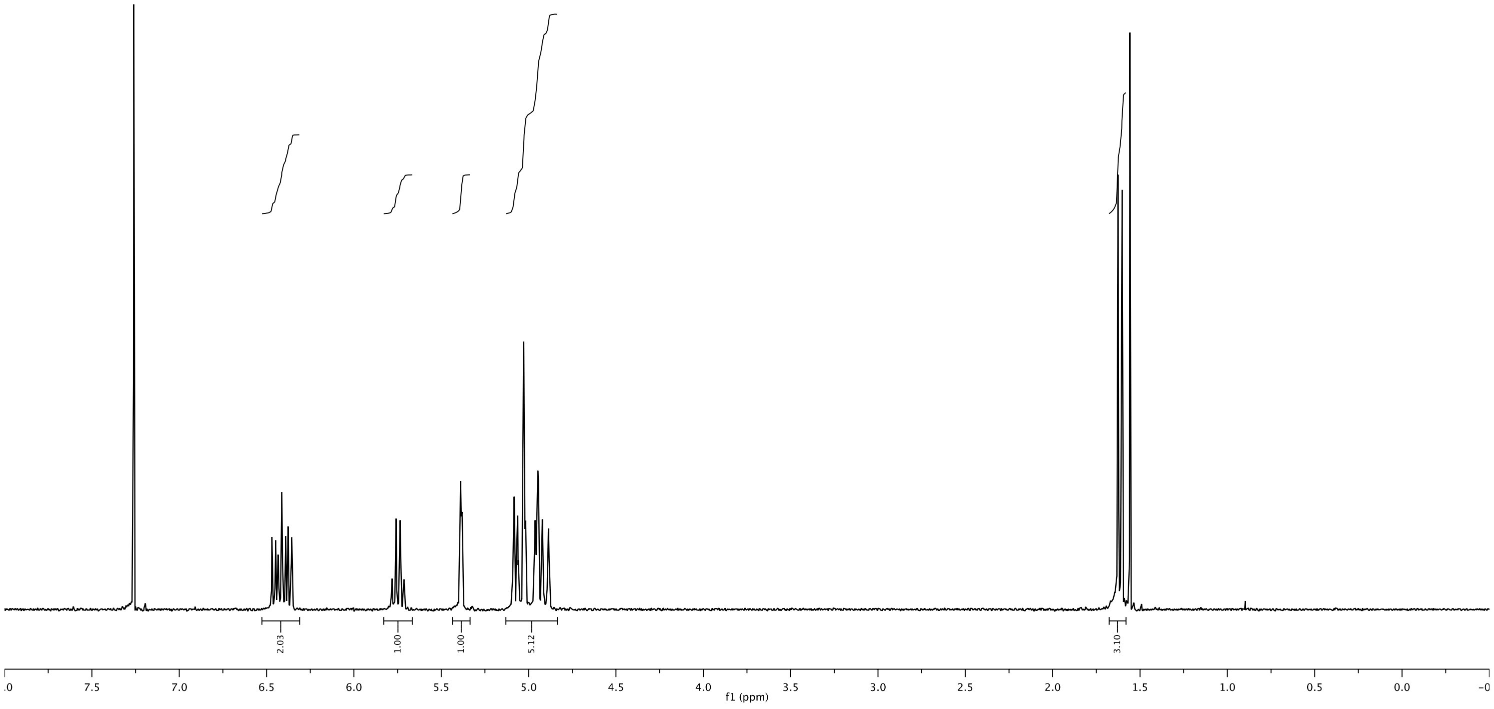
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

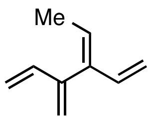




14

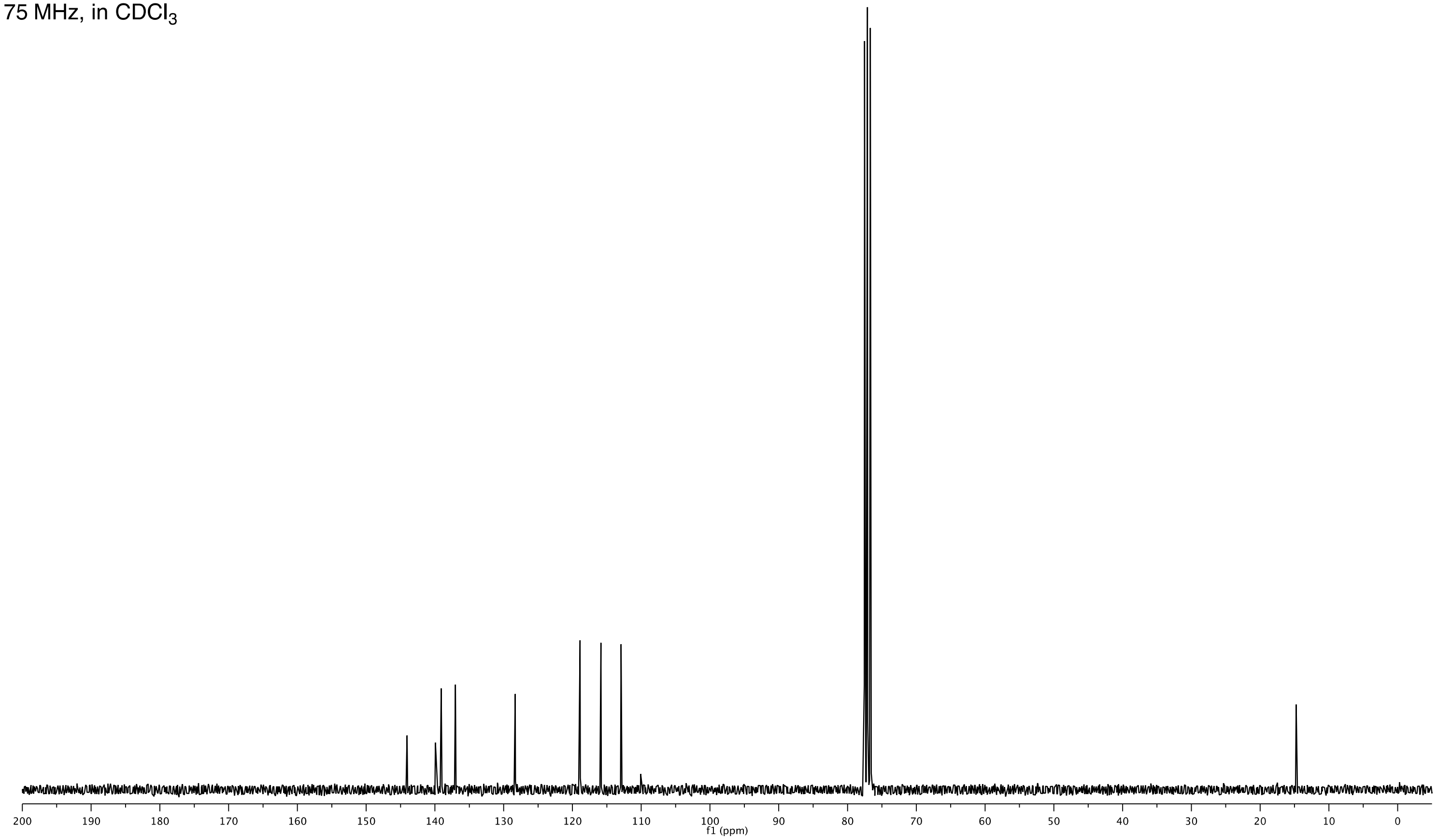
^{1}H NMR spectrum
300 MHz, in $CDCl_3$

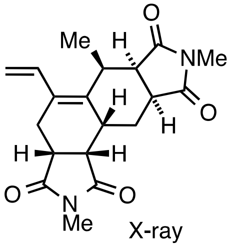




14

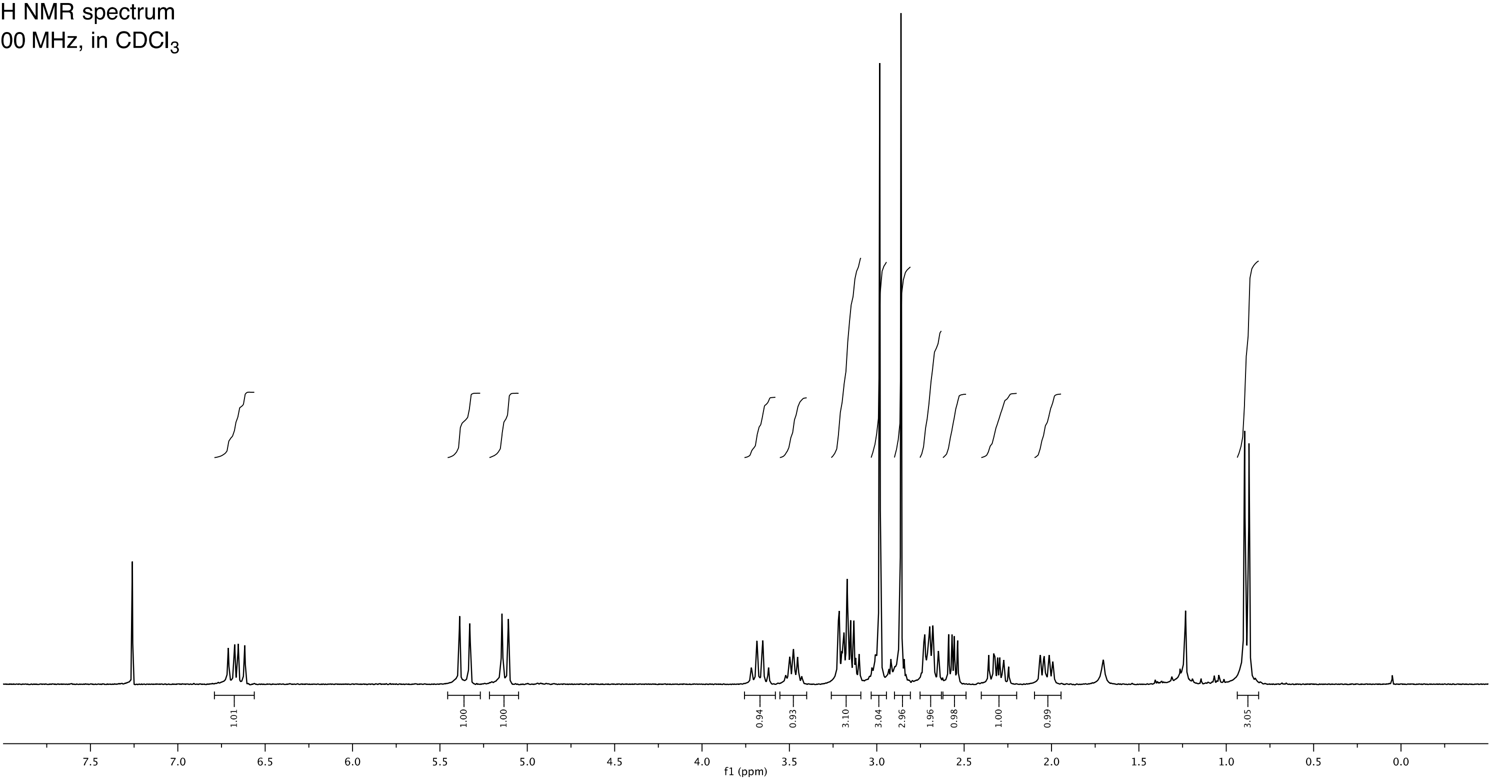
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

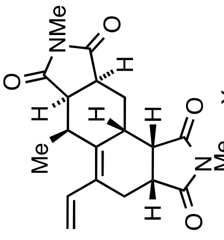



X-ray

54

^{1}H NMR spectrum
300 MHz, in $CDCl_3$

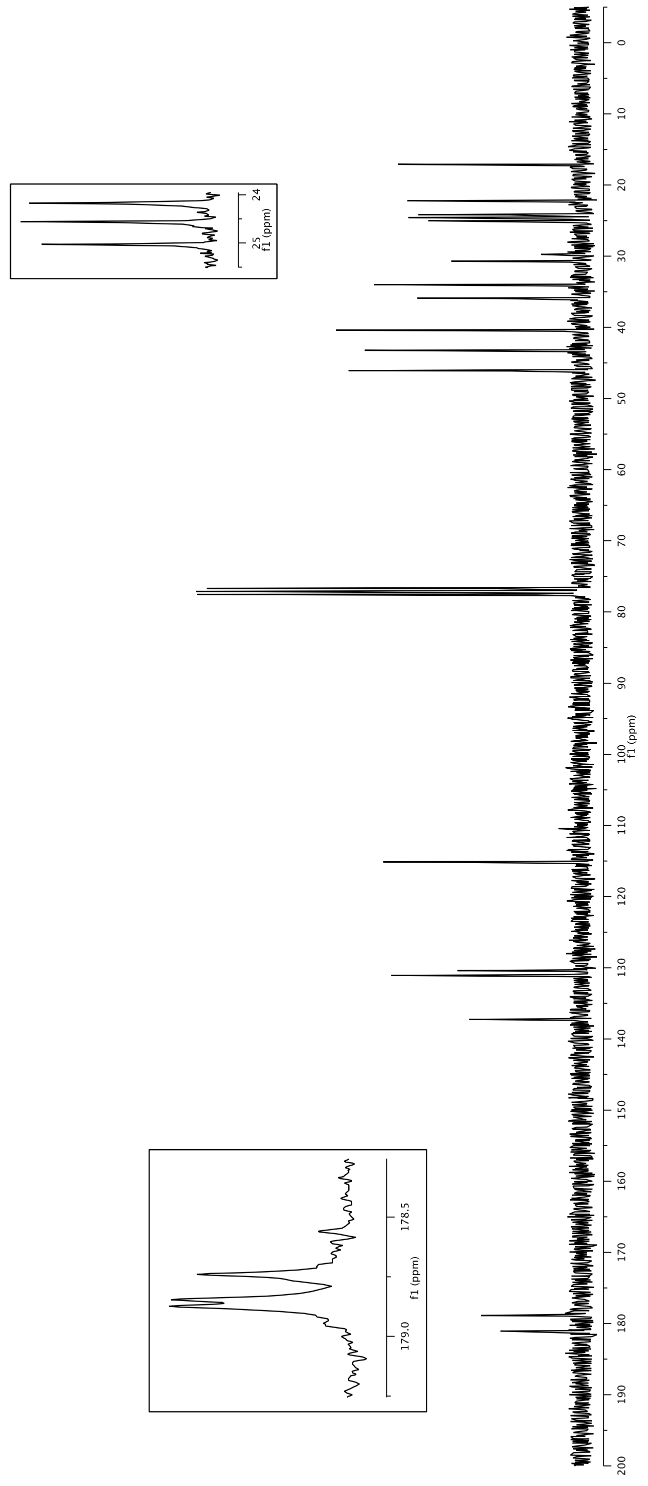


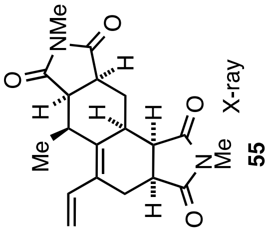


54

X-ray

^{13}C NMR spectrum
75 MHz, in CDCl$_3$

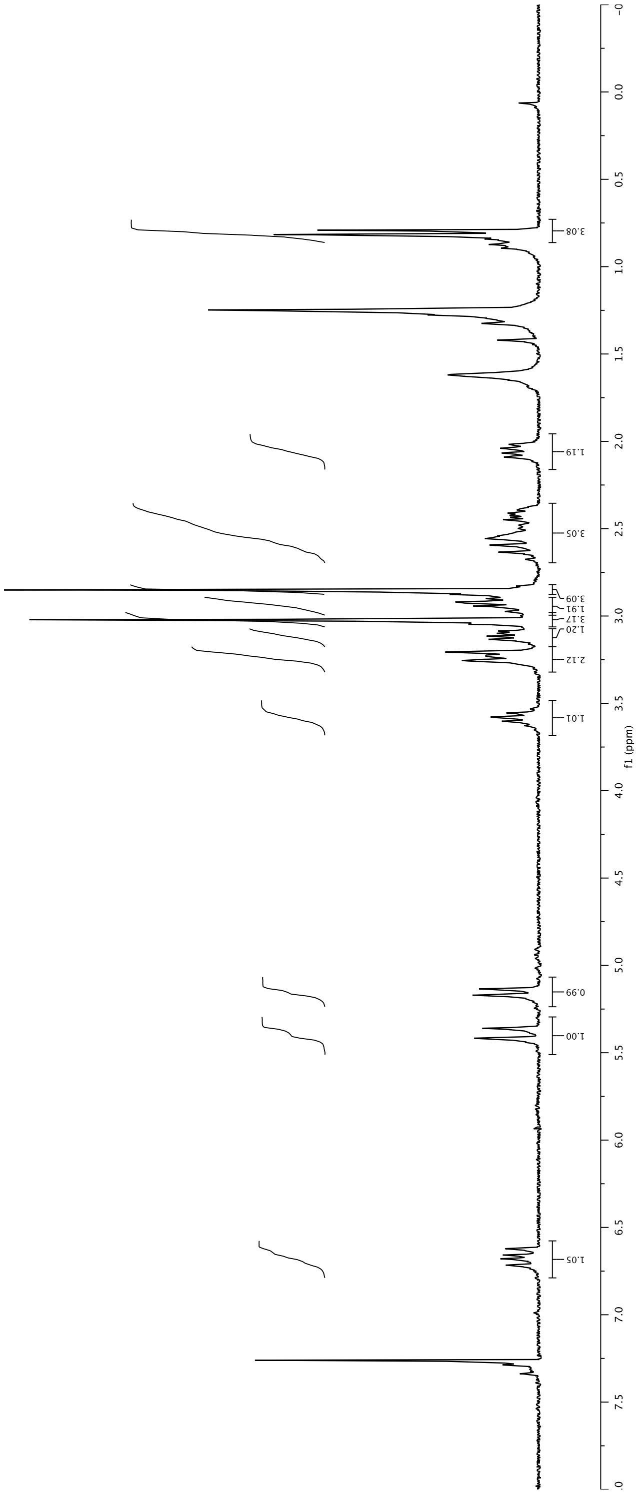


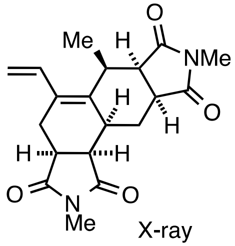


X-ray

55

^{1}H NMR spectrum
300 MHz, in $CDCl_3$

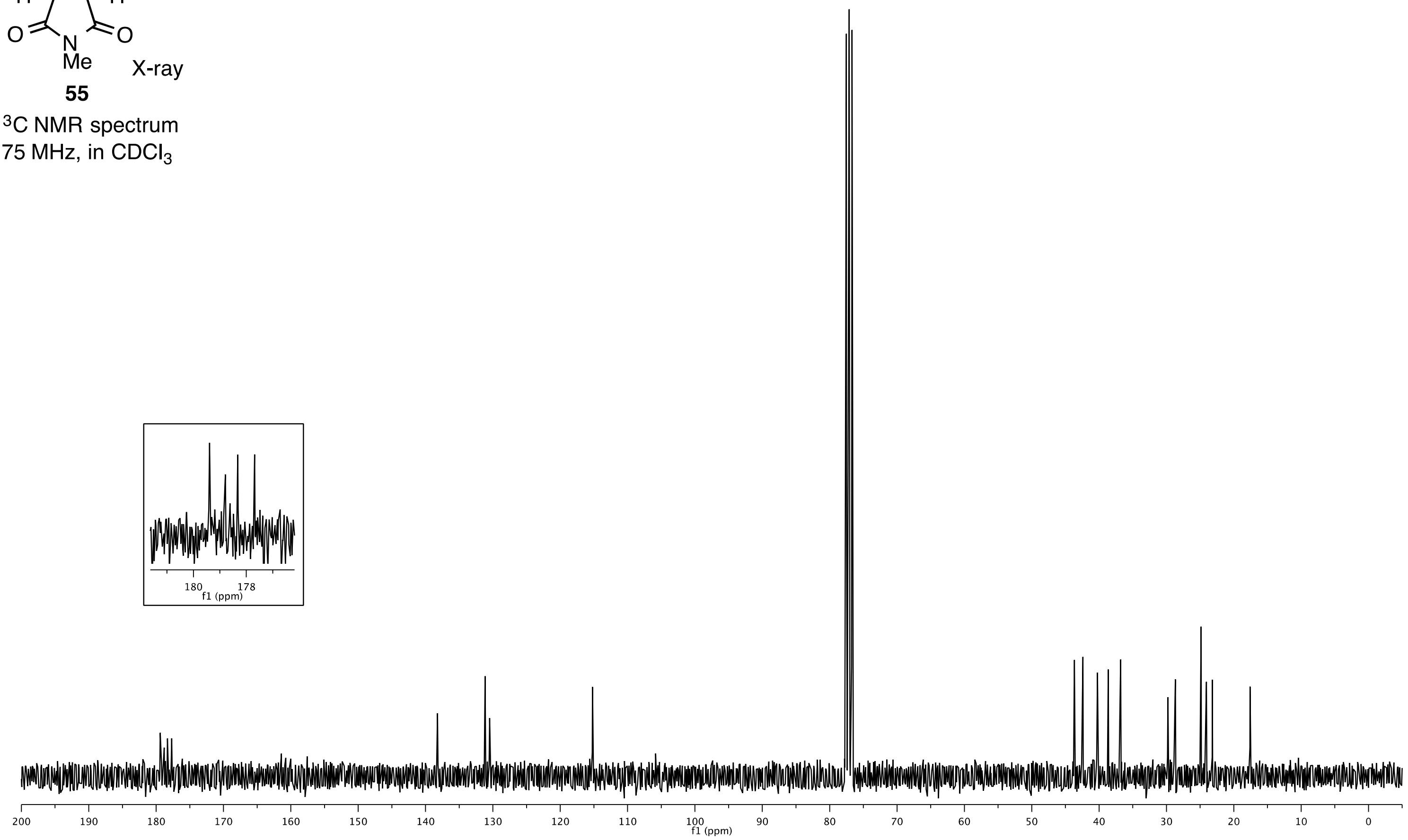


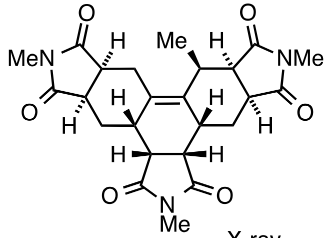


X-ray

55

^{13}C NMR spectrum
75 MHz, in CDCl$_3$

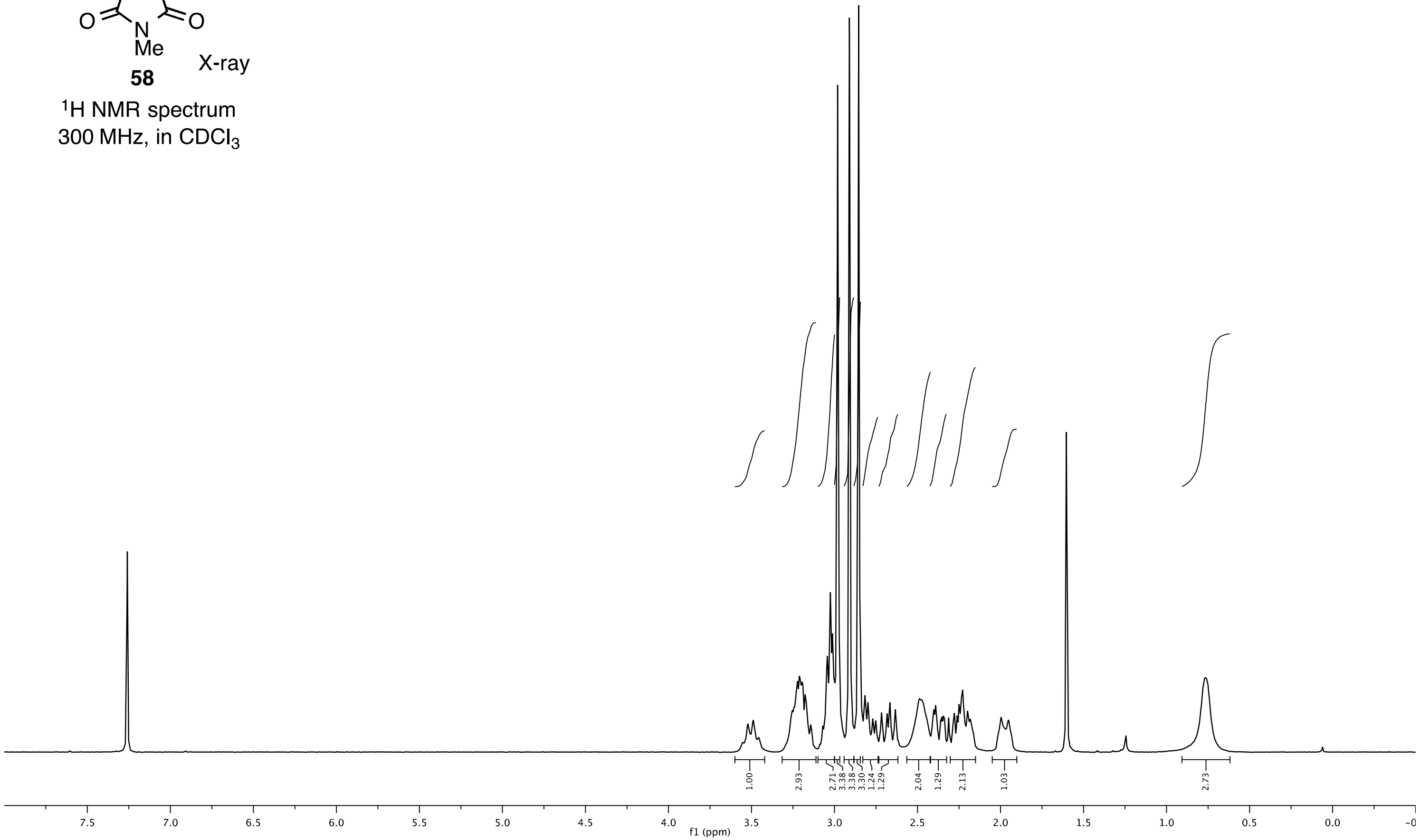


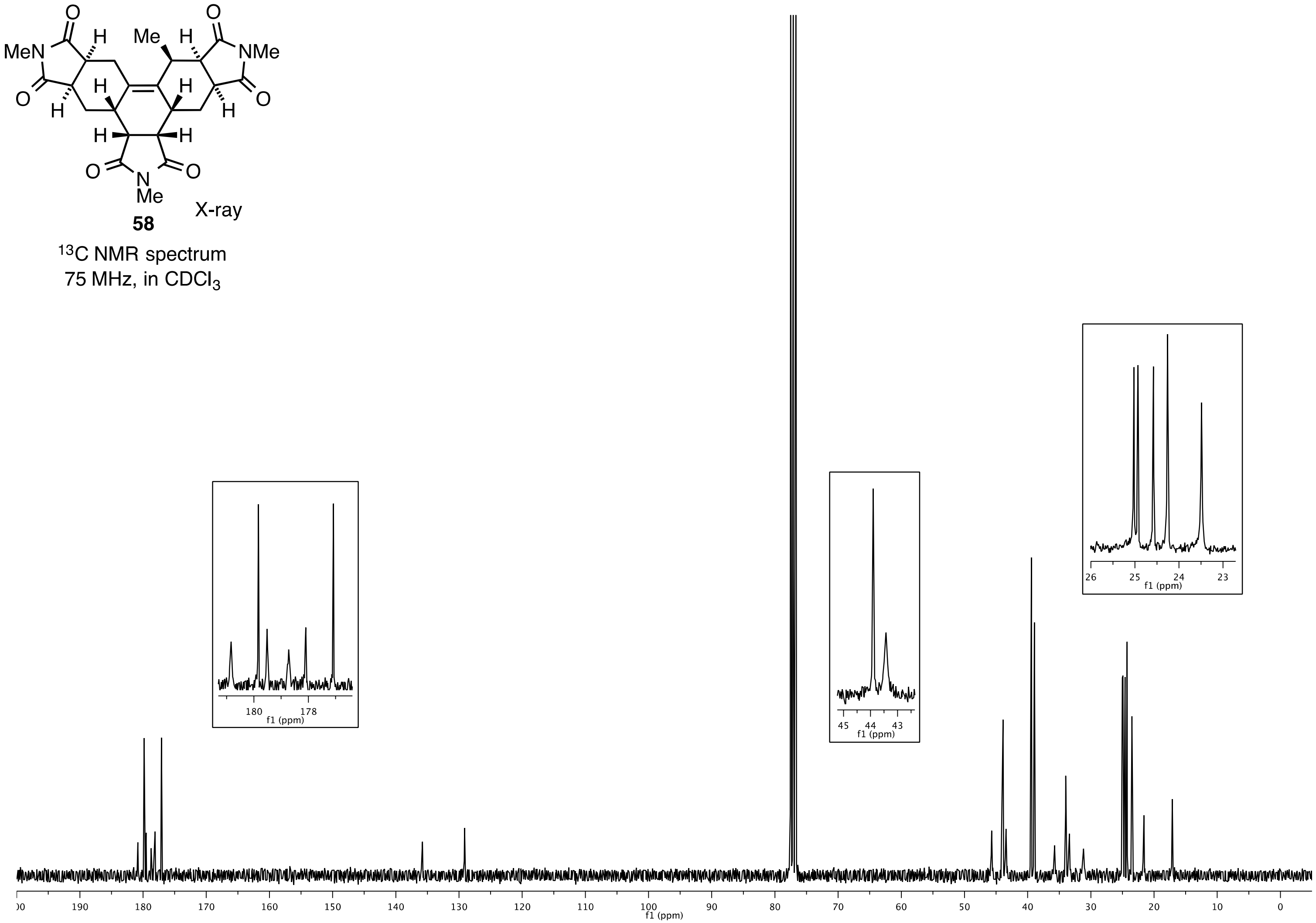


X-ray

58

^{1}H NMR spectrum
300 MHz, in $CDCl_3$

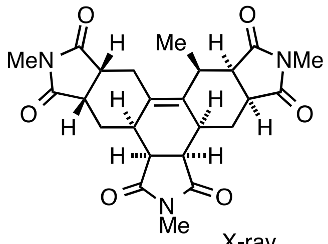




58

X-ray

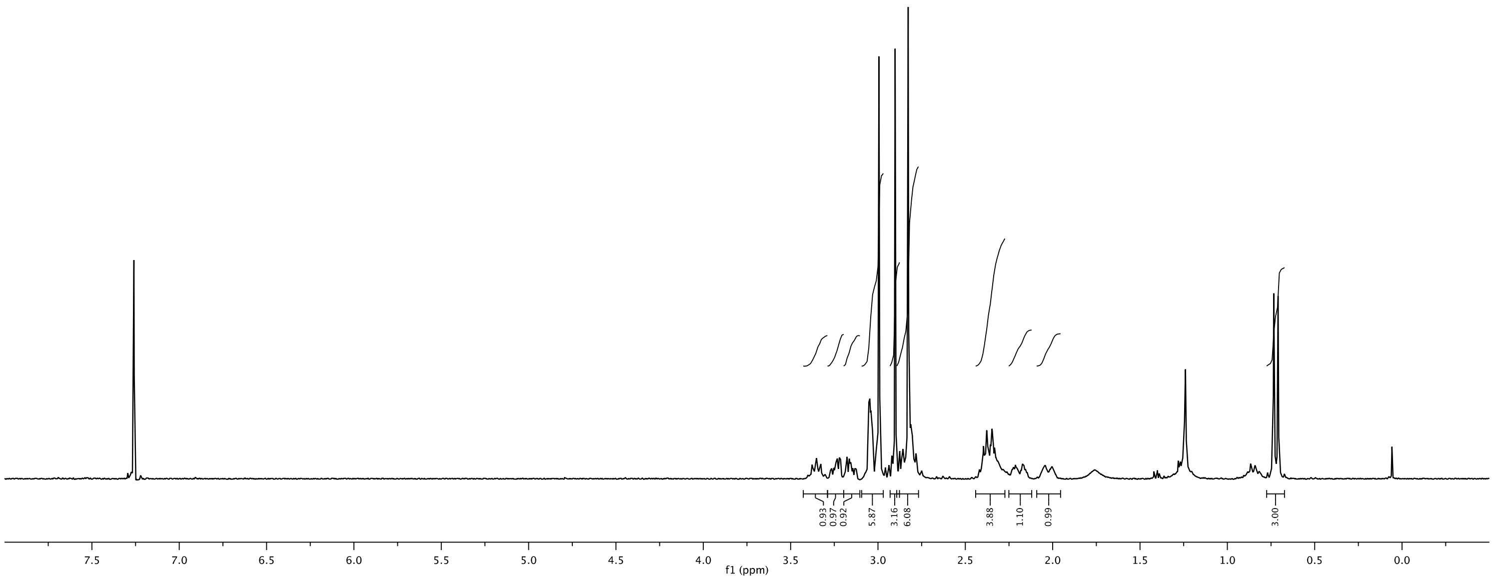
^{13}C NMR spectrum
75 MHz, in $CDCl_3$

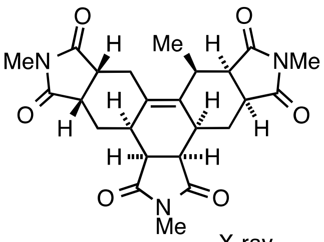


X-ray

59

^{1}H NMR spectrum
300 MHz, in CDCl$_3$

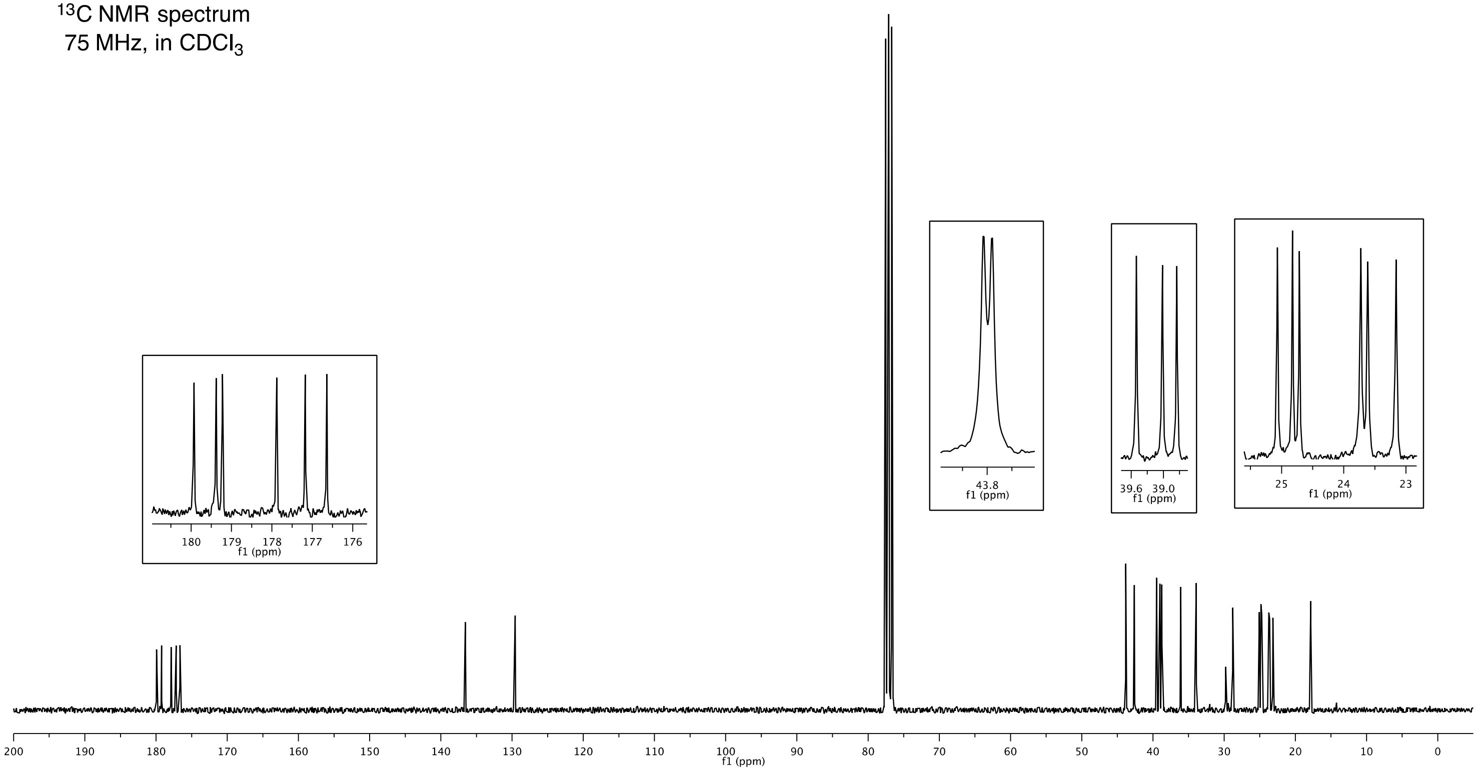


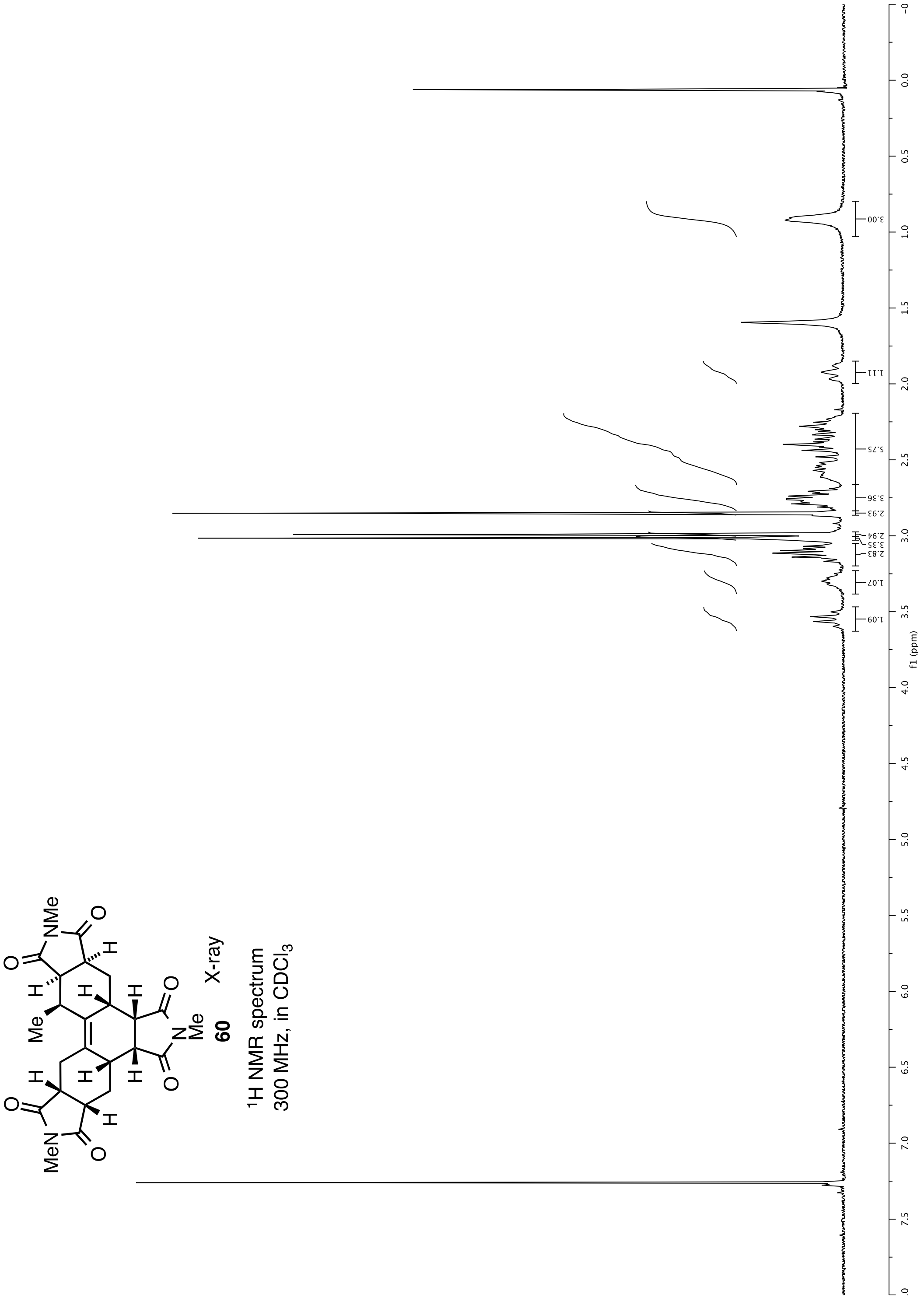


59

X-ray

^{13}C NMR spectrum
75 MHz, in CDCl$_3$

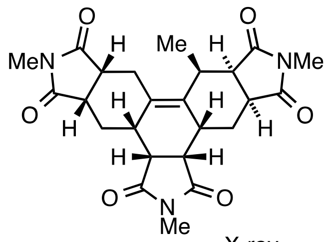




60

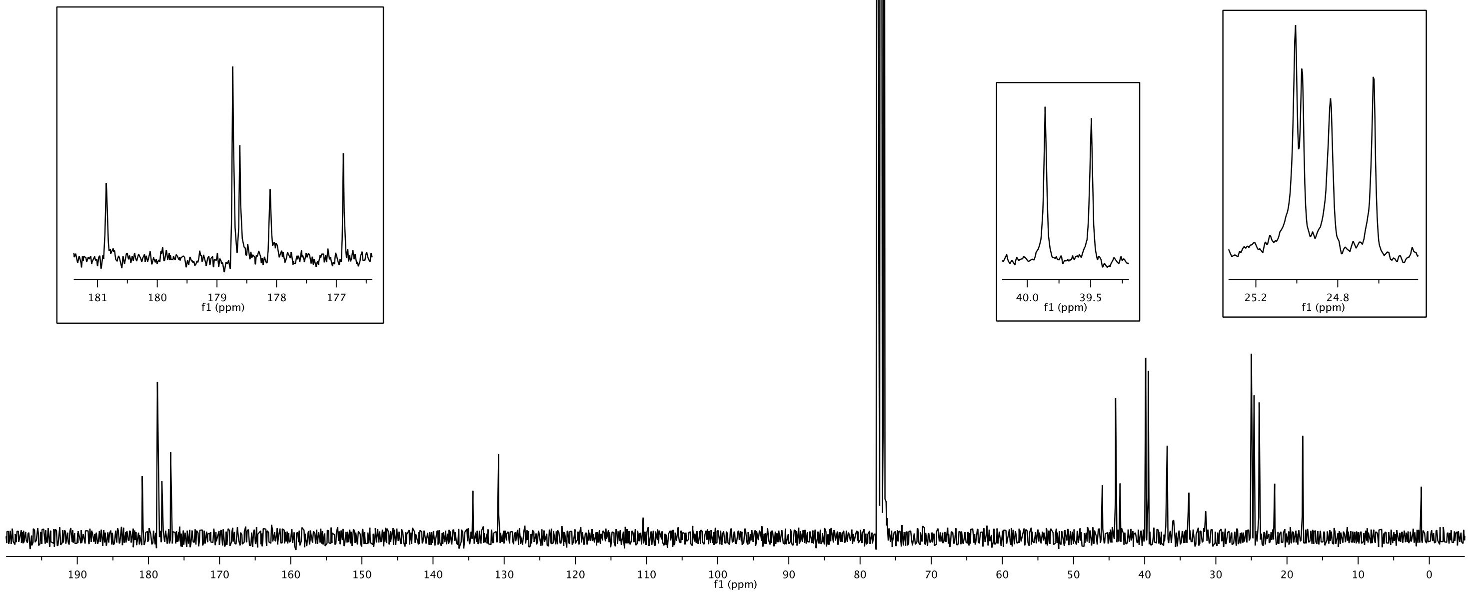
X-ray

^{1}H NMR spectrum
300 MHz, in $CDCl_3$



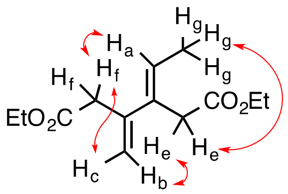
60 X-ray

^{13}C NMR spectrum
75 MHz, in $CDCl_3$



4. Stereochemical Assignments for 13, 14, 23, 24, 32, 37, 46, and 51.

The stereochemistry of **23** was secured through 2D NMR experiments. The ^{1}H – ^{1}H NOESY spectrum is shown in Figure S13.



23

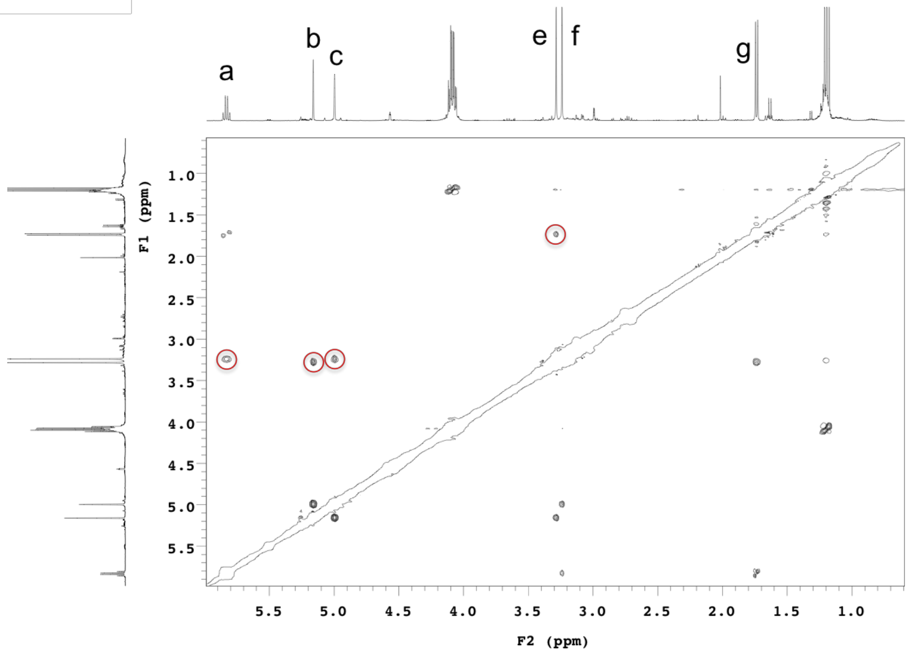
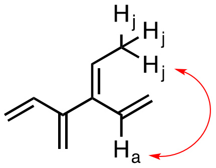


Figure S13: ^{1}H – ^{1}H NOESY NMR (400 MHz, in $CDCl_3$) spectrum of **23**.

The stereochemistry of **13** was secured through 2D NMR experiments. The $^1H - ^1H$ NOESY spectrum is shown in Figure S14.



13

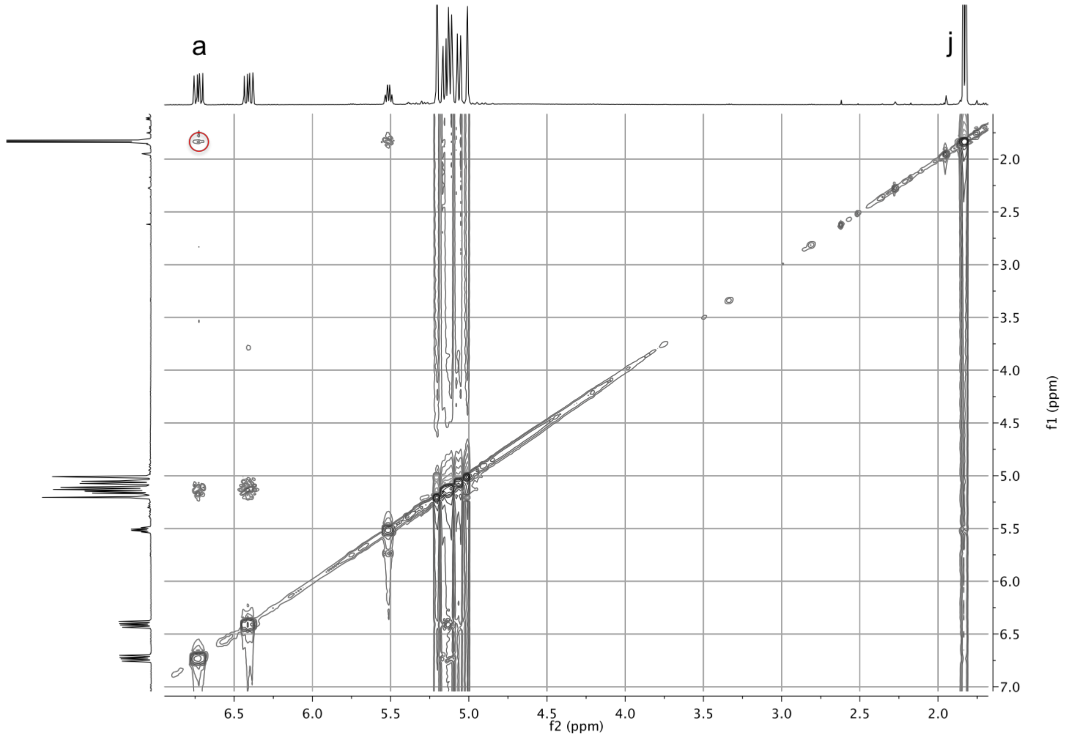


Figure S14: $^1H - ^1H$ NOESY NMR (500 MHz, in $CDCl_3$) spectrum of **13**.

The stereochemistries of **25** and **27** were assigned by comparison of ^{1}H NMR spectra with **23** and **13**. Similarities between ^{1}H NMR spectra of **23**, **25**, **27**, and **13** are highlighted in Figure S15.

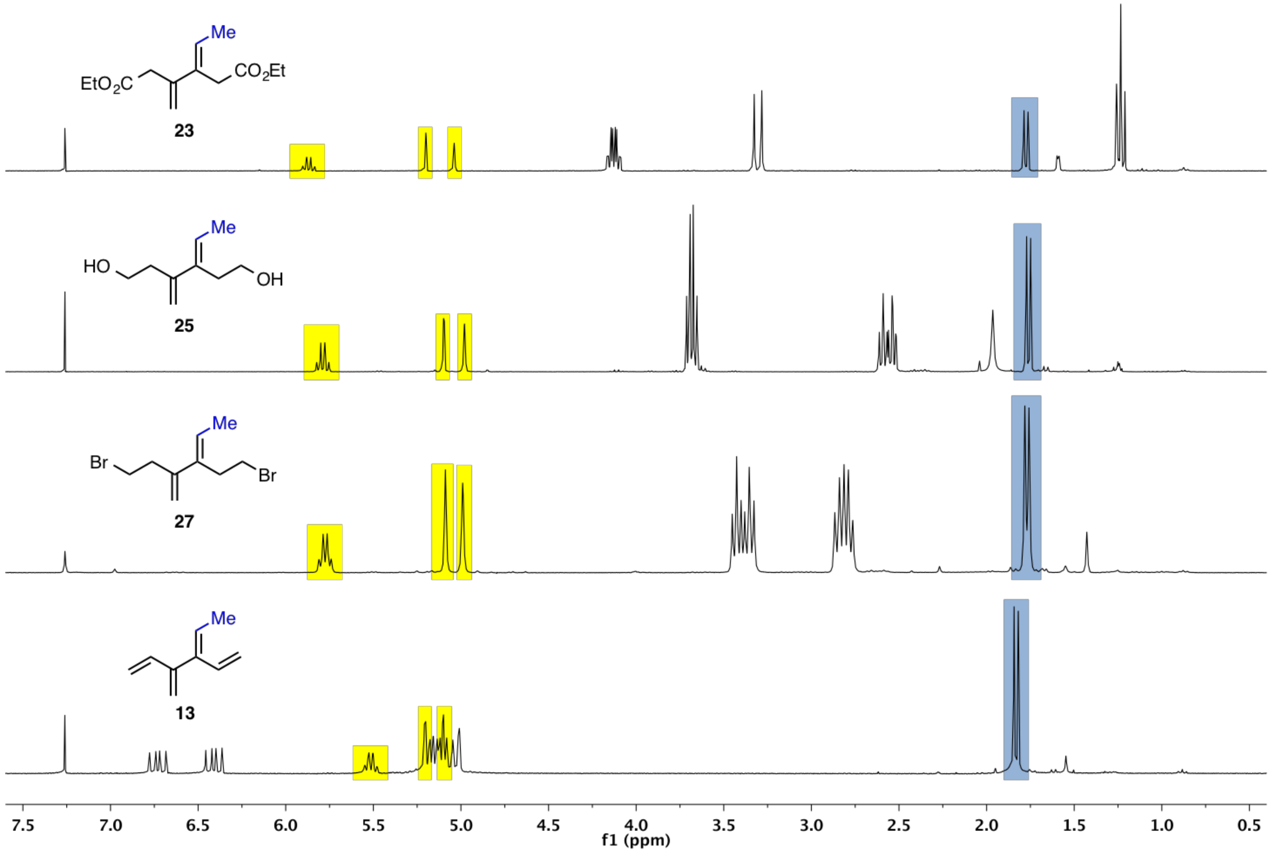
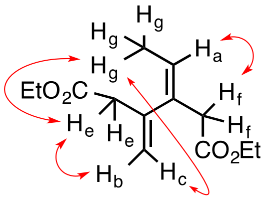


Figure S15: ^{1}H NMR spectra (300 MHz, in $CDCl_3$) of **23**, **25**, **27**, and **13**.

The stereochemistry of **24** was secured through 2D NMR experiments. The ^1H – ^1H NOESY spectrum is shown in Figure S16.



24

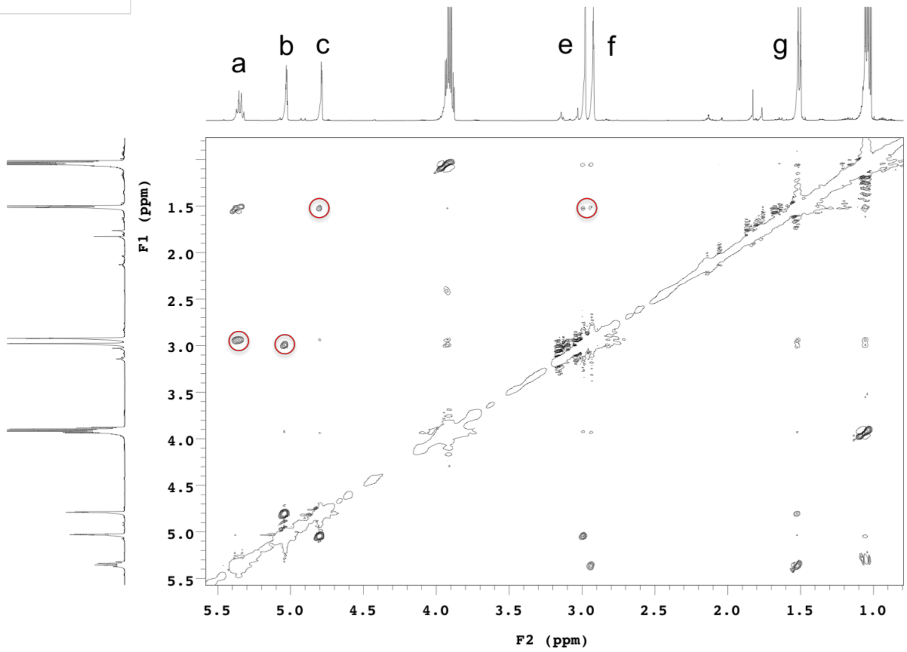
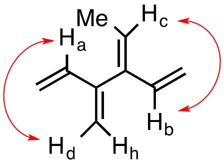


Figure S16: ^1H – ^1H NOESY NMR (400 MHz, in $CDCl_3$) spectrum of **24**.

The stereochemistry of **14** was secured through 2D NMR experiments. The ^{1}H – ^{1}H NOESY spectrum is shown in Figure S17.



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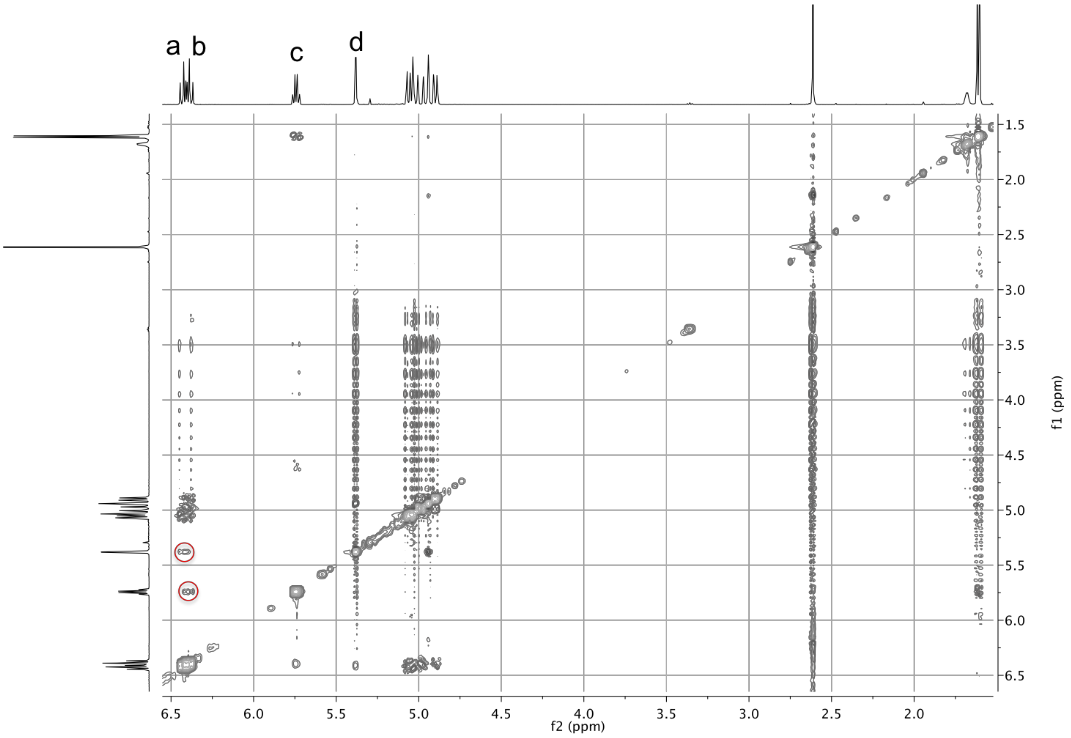


Figure S17: ^{1}H – ^{1}H NOESY NMR (500 MHz, in $CDCl_3$) spectrum of **14**.

The stereochemistries of **26**, and **28** were assigned by comparison of ^{1}H NMR spectra with **24** and **14**. Similarities between ^{1}H NMR spectra of **24**, **26**, **28**, and **14** are highlighted in Figure S18.

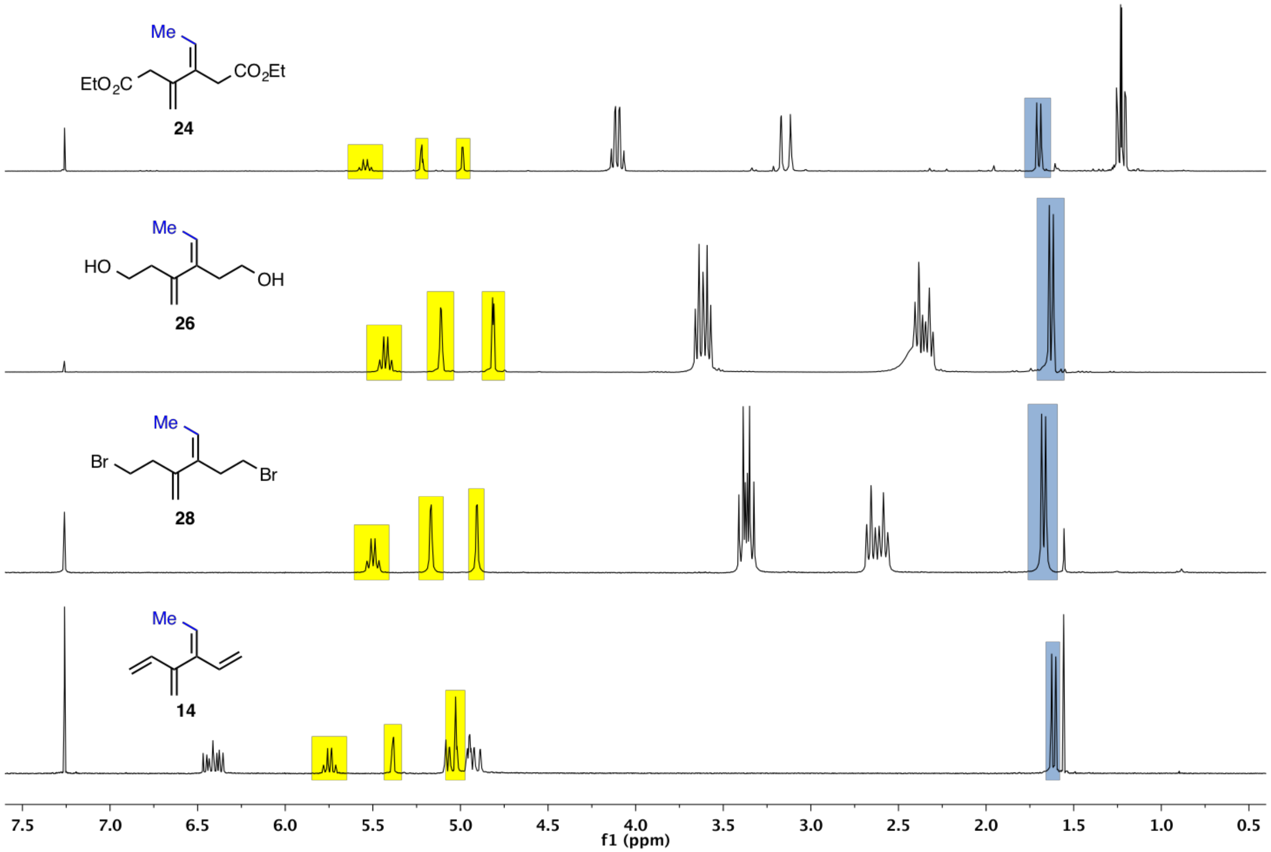
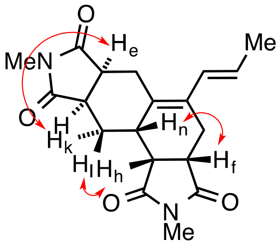


Figure S18: ^{1}H NMR spectra (300 MHz, in CDCl$_3$) of **24**, **26**, **28**, and **14**.

The stereochemistry of **32** was assigned through 2D NMR experiments. The ^{1}H – ^{1}H NOESY spectrum is shown in Figure S19.



32

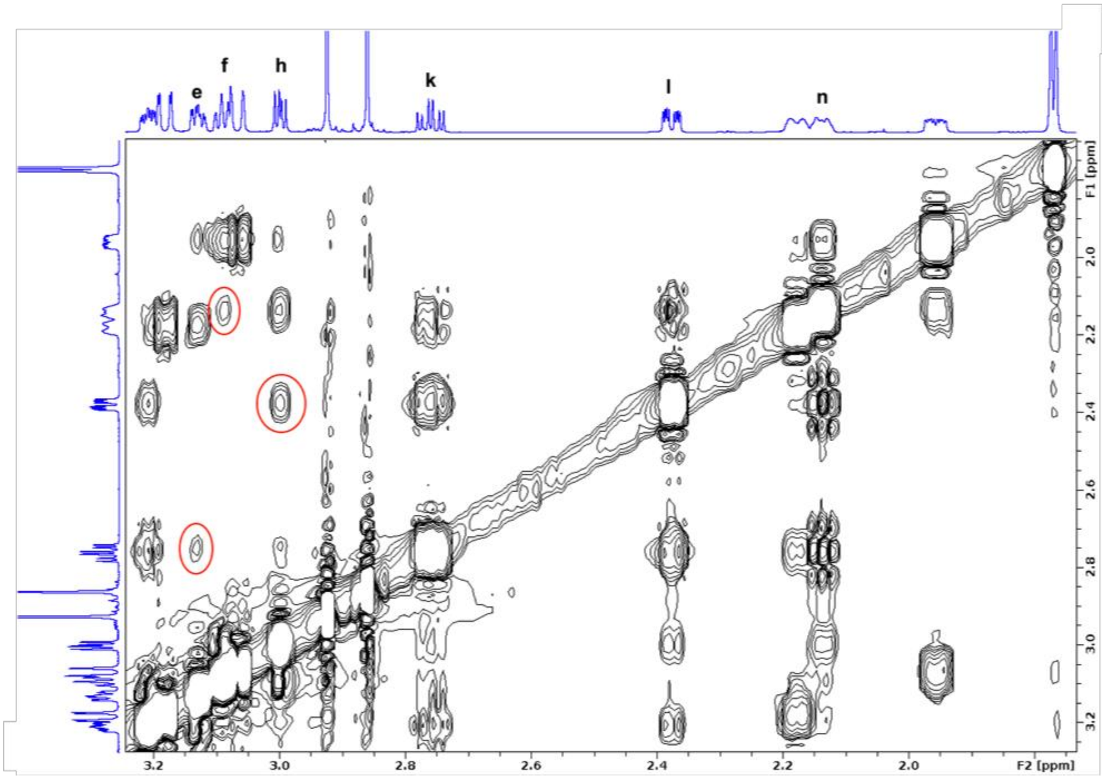


Figure S19: ^{1}H – ^{1}H NOESY NMR spectrum (800 MHz, in CDCl$_3$) of **32**.

Similarities between ^{1}H NMR spectra of **50**, **45**, **40**, **32**, and **4** are highlighted in Figure S20. Single crystal X-ray analysis of **50** (Figure S7), **45** (Figure S5), **40** (Figure S3) and **4**[9] secured the stereochemical assignments of compound **32**.

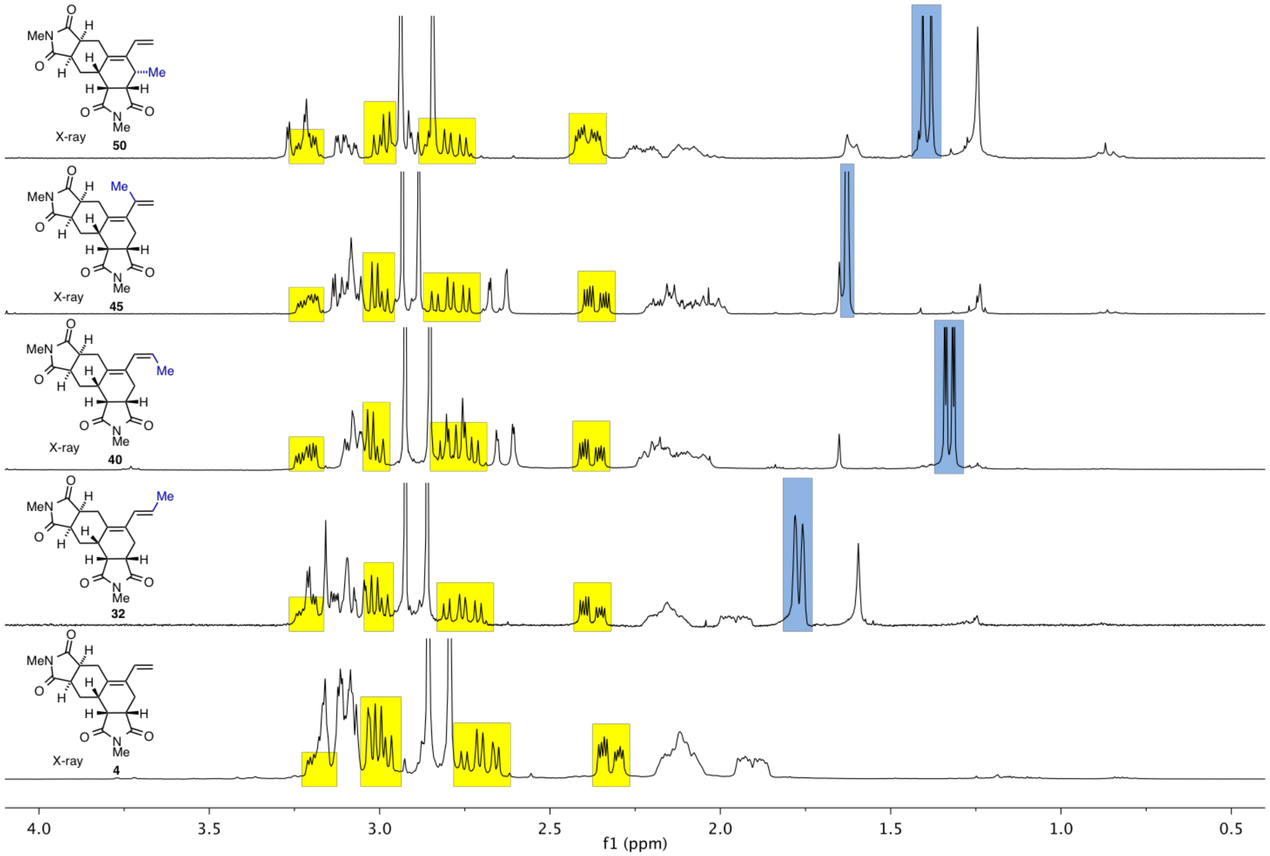
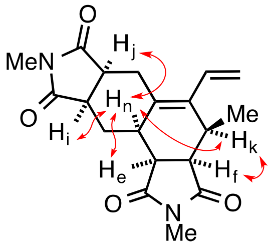


Figure S20: ^{1}H NMR spectra (300 MHz, in $CDCl_3$) of **50**, **45**, **40**, **32** and parent [4]dendralene bis-adduct **4**.[9]

The stereochemistry of **53** was assigned through 2D NMR experiments. The ^1H – ^1H NOESY spectrum is shown in Figure S21.



51

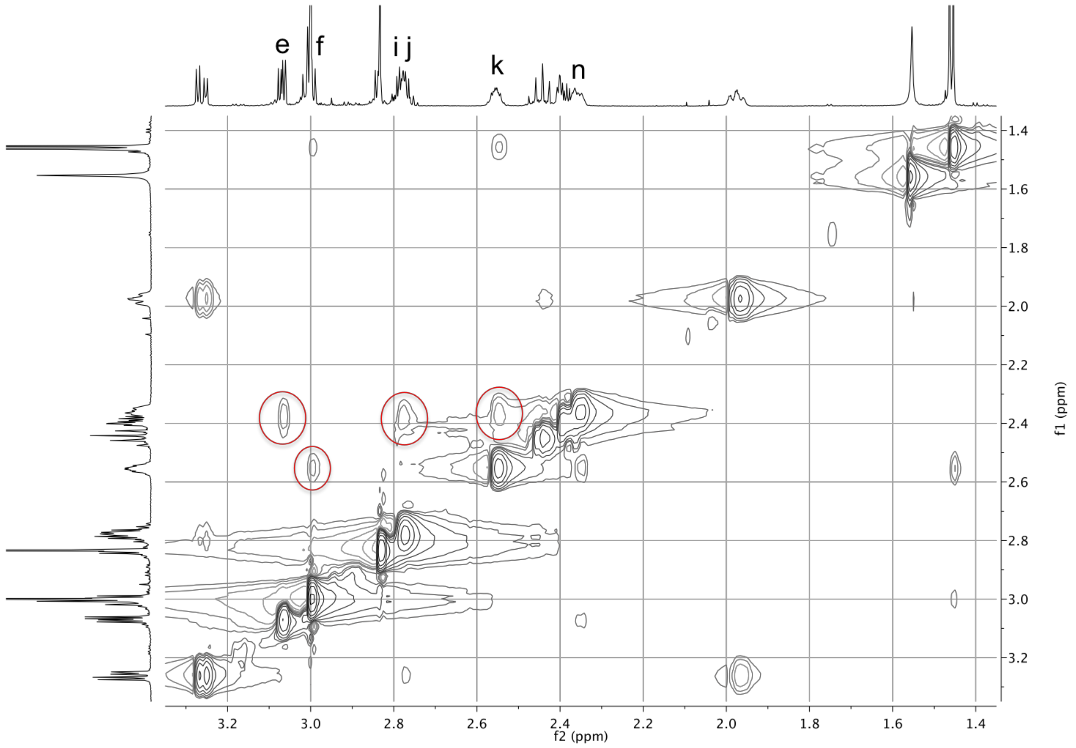


Figure S21: ^1H – ^1H NOESY NMR spectrum (800 MHz, in $CDCl_3$) of **53**.

The stereochemistry of minor bis-adduct **51** was also assigned by comparison of ^{1}H NMR spectra with minor bis-adduct **41**. Similarities between ^{1}H NMR spectra of **51** and **41** are highlighted in Figure S22. Single crystal X-ray analysis of **41** (see Figure S4) secured the stereochemical assignments of compound **51**.

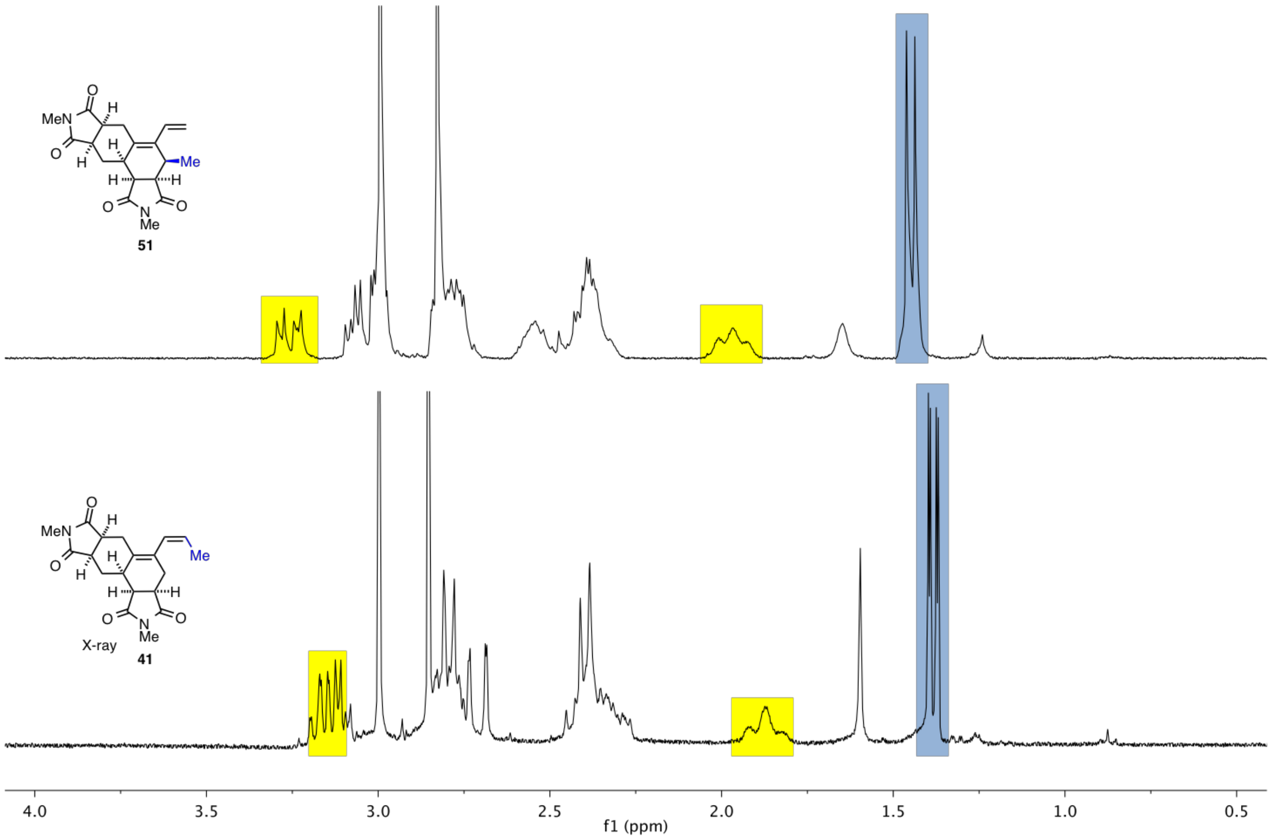


Figure S22: ^{1}H NMR spectra (300 MHz, in $CDCl_3$) of **51** and **41**.

Similarities between ^{1}H NMR spectra of **47** and parent [6]dendralene terminal-terminal bis-adduct **B1**[10] are highlighted in Figure S23. Single crystal X-ray analysis of **47** (see Figure S6) and **B1**[10] secured the stereochemical assignments of these compounds.

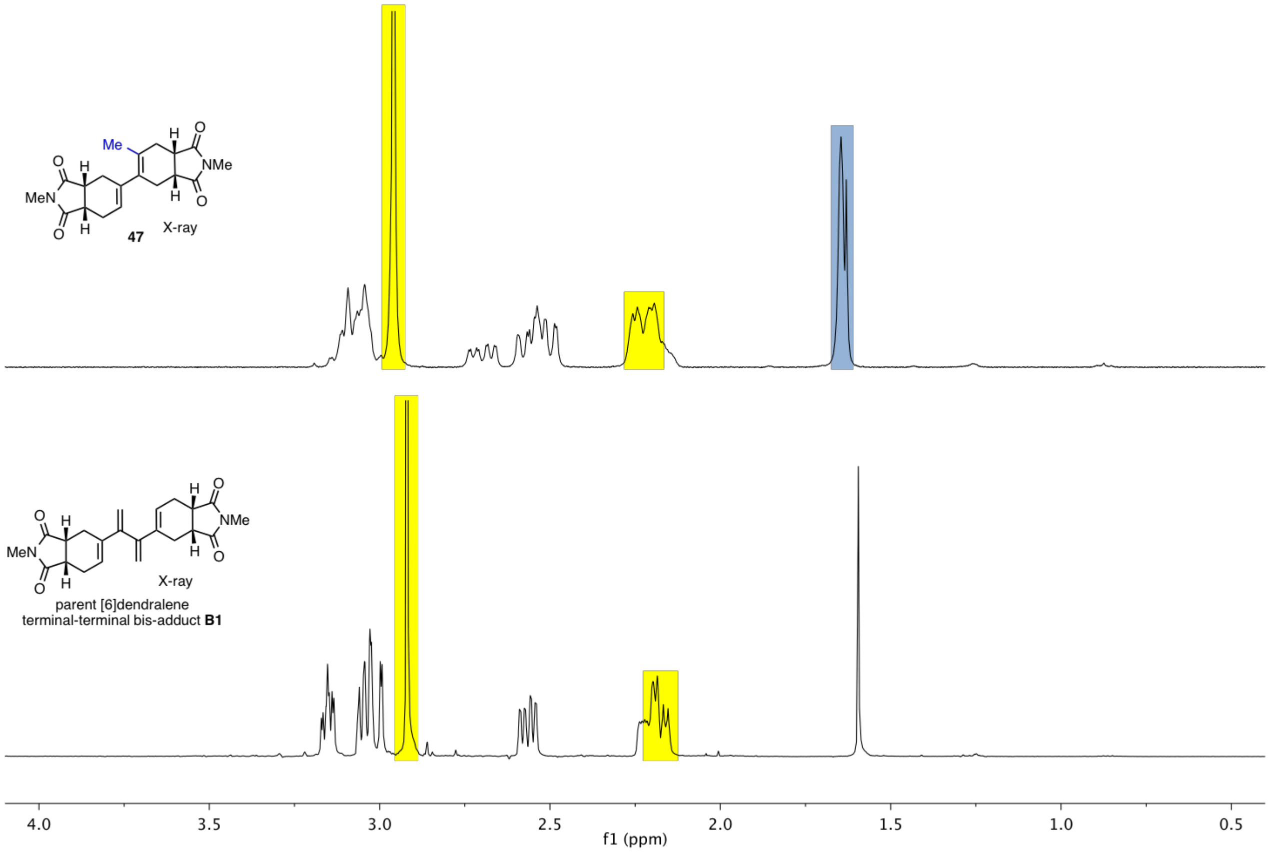


Figure S23: ^{1}H NMR spectra of **47** (300 MHz, in $CDCl_3$) and **B1**[10] (500 MHz, in $CDCl_3$).

Similarities between ^{1}H NMR spectra of **46** and parent [6]dendralene terminal-terminal bis-adduct **B2**[10] are highlighted in Figure S24. Tentative stereochemical assignment of compound **46** was made by ^{1}H NMR in analogy to similar compound **B2**.

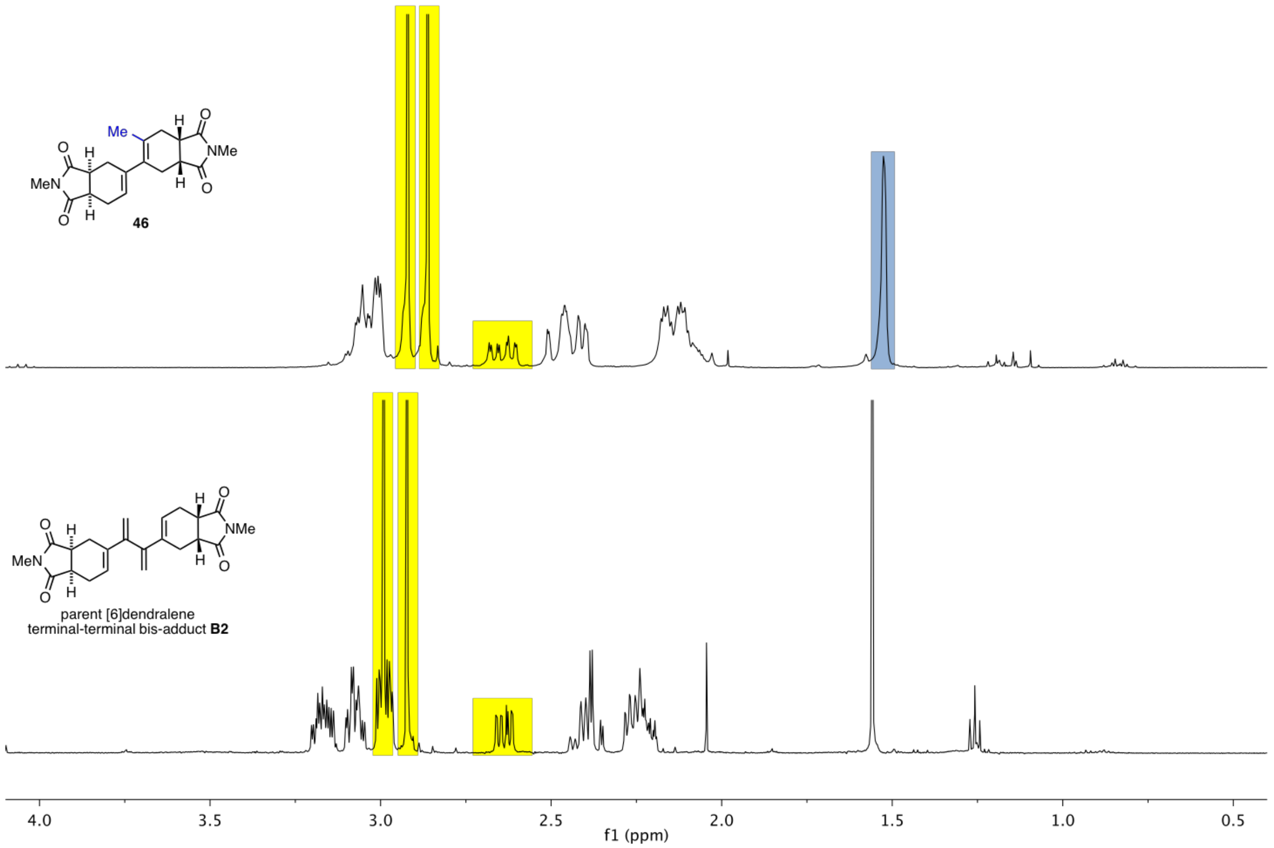


Figure S24: ^{1}H NMR spectra of **46** (300 MHz, in $CDCl_3$) and **B2**[10] (500 MHz, in $CDCl_3$).

The stereochemistry of tris-adduct **37** was assigned by comparison of ^{1}H NMR spectra with tris-adduct **9**. Similarities between ^{1}H NMR spectra of **37** and **9** are highlighted in Figure S25. Single crystal X-ray analysis of **9**[9] secured the stereochemical assignments of compound **37**.

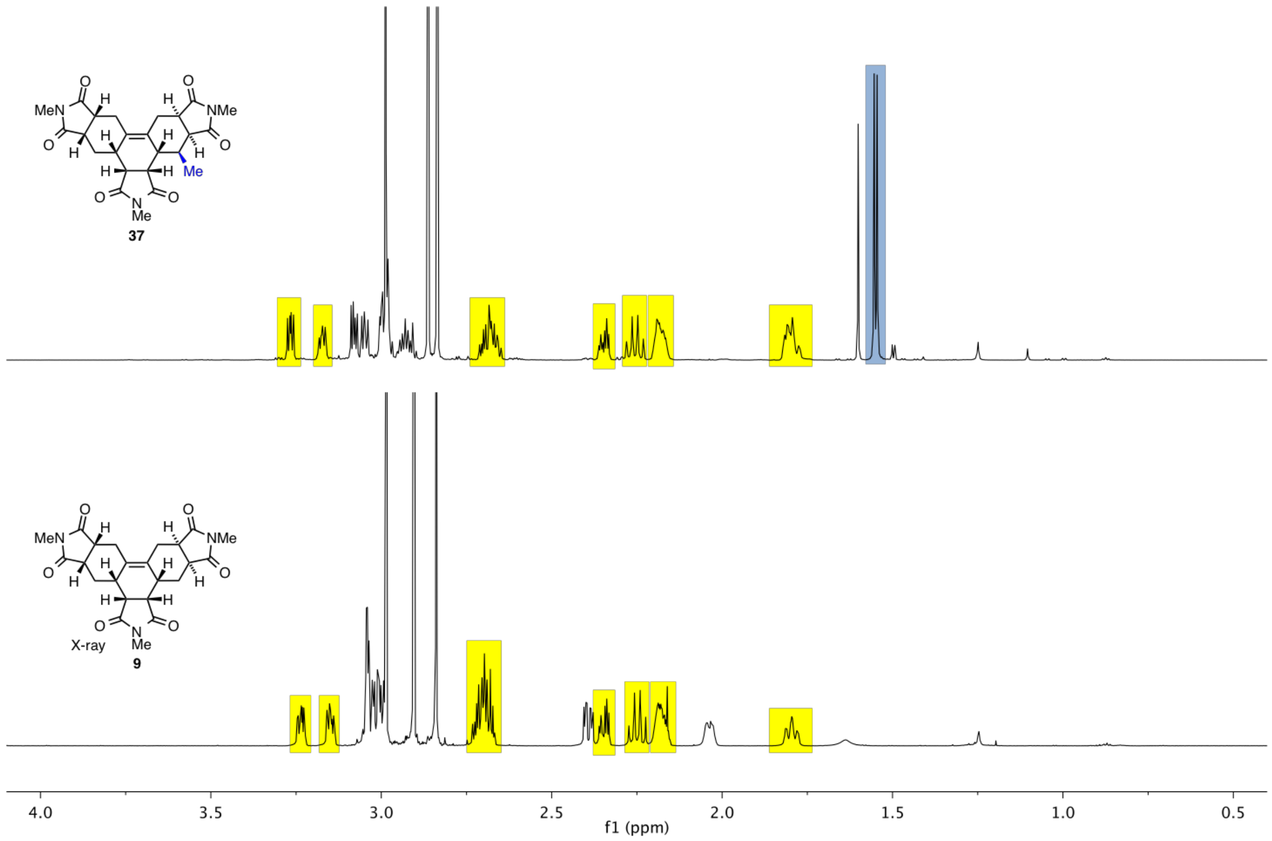


Figure S25: ^{1}H NMR spectra (800 MHz, in $CDCl_3$) of **37** and parent [4]dendralene tris-adduct **9**.[9]

5. References

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