Science
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Supplementary Materials for

Catalytic reductive [4 + 1]-cycloadditions of vinylidenes and dienes

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This PDF file includes:

Materials and Methods

1. General Information

General considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of N_2. Solvents were dried and degassed by passing through a column of activated alumina and sparging with Ar gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over activated 3 Å molecular sieves prior to use. All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted. Liquid reagents were degassed and stored over activated 3 Å molecular sieves prior to use. The [$^{i\text{-}Pr}$NDI]Ni$_2$(C_6H_6) complex **3** was prepared according to previously reported procedures (*28*). Zn powder (325 mesh, 99.9%) was purchased from Strem and used without further purification.

Physical methods. ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra were collected at room temperature on a Varian INOVA 300 MHz, Bruker AV400 HD or AV800 HD spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. UV–vis measurements were acquired on an Agilent Cary 6000i UV-Vis-NIR Spectrophotometer using a 1-cm two-window quartz cuvette. ATR-IR data were collected on a Thermo Scientific Nicolet Nexus spectrometer containing a MCT* detector and KBr beam splitter with a range of 350–7400 cm^{-1}. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. HPLC was performed on a Varian ProStar Series instrument equipped with a variable wavelength detector using chiral columns (Chiralpak OD-H, AD-H, 0.46 cm x 25 cm) purchased from Daicel.

X-ray crystallography. Single-crystal X-ray diffraction studies were carried out at the Purdue X-Ray Crystallography Facility using a Rigaku Rapid II diffractometer or a Bruker AXS D8 Quest CMOS diffractometer.

Procedure for XRD data collected using the Rigaku Rapid II instrument. Single crystal X-ray measurement was conducted on a Rigaku Rapid II curved image plate diffractometer with a Cu-Kα X-ray microsource (λ = 1.54178 Å) with a laterally graded multilayer (Goebel) mirror for monochromatization. Single crystals were mounted on Mitegen microloop mounts using a trace of mineral oil and cooled in-situ to 100(2) K for data collection. Data were collected using the dtrek option of CrystalClear-SM Expert 2.1 b32 (*29*). Data were processed using HKL3000 and data were corrected for absorption and scaled using Scalepack (*30*).

Procedure for XRD data collected using the Bruker Quest instrument. Single crystals were coated with fomblin and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 (*31*).

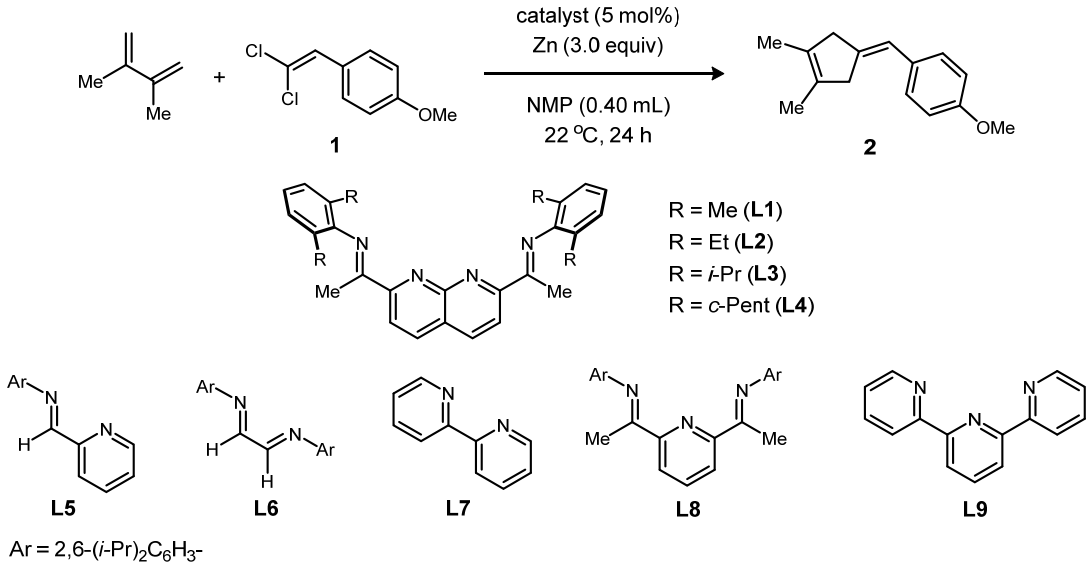
Structure Solution and Refinement. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs (*32*, *33*) and refined by full matrix least squares against F2 with all reflections using Shelxl2019 (*34*, *35*) using the graphical interface Shelxle (*36*). If not specified otherwise H atoms attached to carbon

and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for aromatic C-H and 1.00, 0.99, and 0.98 Å for aliphatic CH, CH_2 and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH_3, and 1.2 for CH units, respectively. Additional data collection and refinement details, including description of disorder and/or twinning (where present) can be found in Section 11.

2. Reaction Optimization Studies

General Procedure. In an N_2-filled glovebox, a 2-dram vial equipped with a magnetic stir bar was charged with ligand (5 mol%), Ni(DME)Br_2 (10 mol%), Zn powder (0.60 mmol, 3.0 equiv) and NMP (0.40 mL). The mixture was stirred at 22 °C for 15 min. To the mixture were sequentially added 2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv) and 1-(2,2-dichlorovinyl)-4-methoxybenzene (41 mg, 0.20 mmol, 1.0 equiv) by syringe. The vial was sealed, and the reaction mixture was stirred at 22 °C. After 24 h, mesitylene (17 mg, 20 μL) was added. An aliquot of the reaction mixture was removed and loaded directly onto a 2-cm pad of SiO_2 packed in a pipet. The mixture was eluted from the SiO_2 pad with $CDCl_3$ (approx. 1.5 mL). The conversion of **1** and yield of **2** were determined by ^{1}H NMR integration against mesitylene.

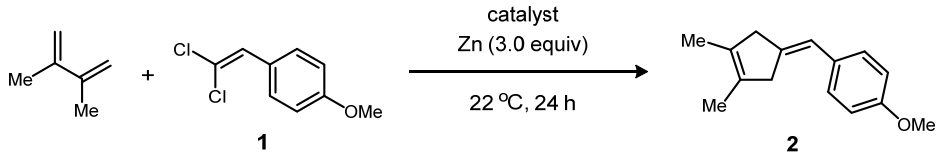
Table S1. Catalyst comparison studies.



entry	ligand	conversion (%)*	yield (%)*
1‡	**L1** + Ni(DME)Br_2	33	12
2‡	**L2** + Ni(DME)Br_2	46	22
3‡	**L3** + Ni(DME)Br_2	63	52
4‡	**L4** + Ni(DME)Br_2	>99	>99 (99)†
5§	**L5** + Ni(DME)Br_2	40	<2
6§	**L6** + Ni(DME)Br_2	43	<2
7§	**L7** + Ni(DME)Br_2	29	<2
8§	**L8** + Ni(DME)Br_2	29	<2
9§	**L9** + Ni(DME)Br_2	41	<2
10	(dppe)$NiCl_2$	6	<2
11	$(Ph_3P)_2NiCl_2$	2	<2
12	Ni(DME)Br_2	57	<2
13	--	<2	<2

*Conversions of **1** and yields of **2** were determined by ^{1}H NMR integration against an internal standard. †Isolated yield. ‡Ligand (5 mol%) and Ni(DME)Br_2 (10 mol%). §Ligand (5 mol%) and Ni(DME)Br_2 (5 mol%).

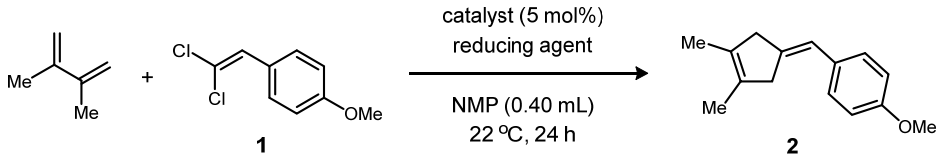
Table S2. Screen of reaction conditions. Reaction conditions: 1-(2,2-dichlorovinyl)-4-methoxybenzene (0.20 mmol), 2,3-dimethyl-butadiene (0.40 mmol), catalyst (5 mol%), Zn (0.60 mmol, 3.0 equiv), 24 h, 22 °C.



entry	catalyst	solvent (mL)	conversion (%)*	yield (%)*
1	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/DMA (1.6/0.2)	31	16
2	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/NMP (0.4/0.05)	33	14
3	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/NMP (0.8/0.1)	28	17
4	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/NMP (1.6/0.2)	34	26
5	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/NMP (3.2/0.4)	59	29
6†	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/NMP (1.6/0.2)	65	28
7	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	DCE/NMP (1.6/0.2)	23	6
8	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	EtOAc/NMP (1.6/0.2)	49	24
9	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	$(EtO)_2CO$/NMP (1.6/0.2)	39	12
10	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/EtOAc (1.6/0.2)	30	<2
11	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/$(EtO)_2CO$ (1.6/0.2)	30	<2
12	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Et_2O/DMSO (1.6/0.2)	35	22
13	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	THF (1.8)	21	11
14	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	DME (1.8)	23	<2
15	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	Dioxane (1.8)	28	<2
16	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	EtOAc (1.8)	20	<2
17	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	CH_3CN (1.8)	>95	<2
18	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	DMA (1.8)	42	21
19	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	NMP (1.8)	49	34
20‡	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	NMP (1.8)	73	43
21‡,§	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	NMP (1.8)	94	79 (73¶)
22‡,§	[$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) **3**	NMP (0.4)	91	76 (73¶)
23#	**L3** + Ni(DME)Br$_2$	NMP (1.8)	66	32
24#	**L3** + FeBr$_2$	NMP (1.8)	<5	<2
25#	**L3** + Co(DME)Br$_2$	NMP (1.8)	18	<2
26#	**L3** + Ni(DME)Br$_2$	NMP (0.4)	63	52
27#	**L4** + Ni(DME)Br$_2$	NMP (0.4)	99	>99 (99^e)

*Conversions and yields were determined by ^{1}H NMR integration against mesitylene. †Temperature: 50 °C. ‡10 mol% catalyst. §2,3-dimethylbutadiene (0.80 mmol). ¶Isolated yield. #Ligand (5 mol%) and metal salt (10 mol%).

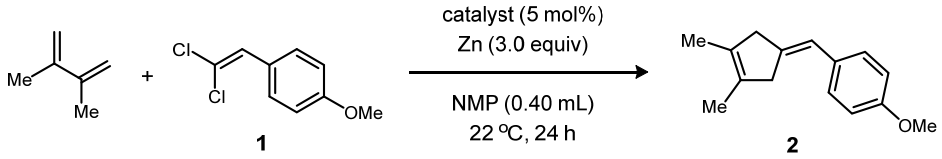
Table S3. Screen of reducing agents. Reaction conditions: 1-(2,2-dichlorovinyl)-4-methoxybenzene (0.20 mmol), 2,3-dimethyl-butadiene (0.40 mmol), **L4** (5 mol%), Ni(DME)Br_2 (10 mol%), reducing agent (x equiv), NMP (0.40 mL), 24 h, 22 °C.



entry	reducing agent	conversion (%)*	yield (%)*
1	Zn (1.5 equiv)	>99	96
2	Zn (3.0 equiv)	>99	>99
3†	Zn (3.0 equiv)	96	96
4‡	Zn (3.0 equiv)	74	44
5	Mn (3.0 equiv)	60	17

*Conversions and yields were determined by ^{1}H NMR integration against mesitylene. †Particle size of Zn power: ~100 mesh. ‡Particle size of Zn power: 20~30 mesh.

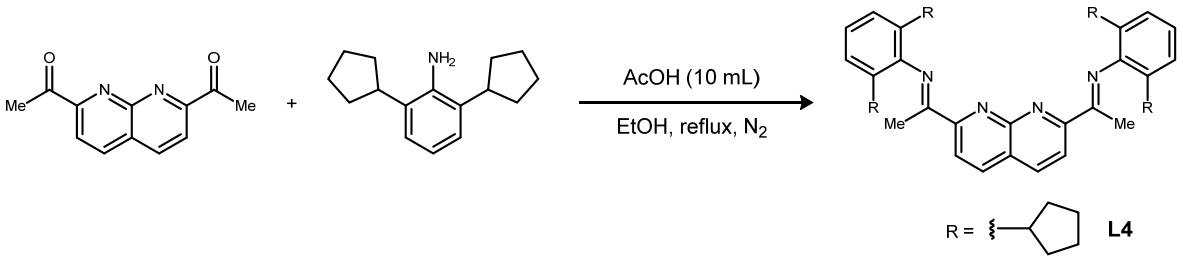
Table S4. Screen of substrate stoichiometry. Reaction conditions: 1-(2,2-dichlorovinyl)-4-methoxybenzene (**1**) (x mmol), 2,3-dimethyl-butadiene (y mmol), **L4** (5 mol%), Ni(DME)Br_2 (10 mol%), Zn (3.0 equiv), NMP (0.40 mL), 24 h, 22 °C.



entry	2,3-dimethylbutadiene/1 (mmol)	conversion (%)*	yield (%)*
1	0.80/0.20	83	85
2	0.40/0.20	>99	99 (99)†
3	0.30/0.20	98	95 (90)†
4	0.24/0.20	92	92
5	0.20/0.24	78	67

*Conversions and yields were determined by ^{1}H NMR integration against mesitylene. †Isolated yield.

3. Synthesis and Characterization of NDI Ligands and [NDI]Ni_2 Complexes



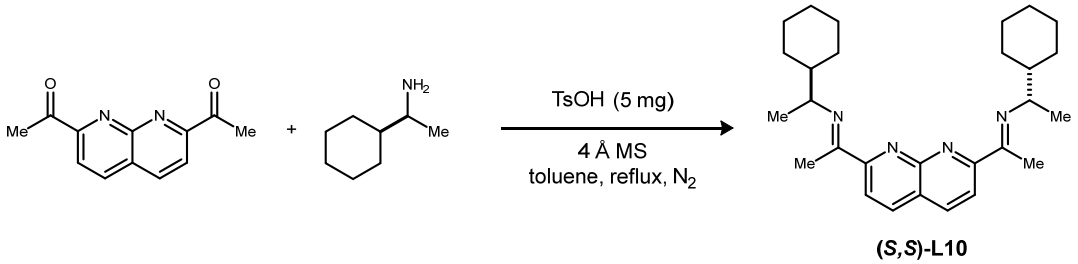
L4. 2,6-dicyclopentylaniline (0.48 g, 2.1 mmol, 2.1 equiv) and MeOH (10 mL) were added to a round bottom flask equipped with a reflux condenser and magnetic stir bar. 2,7-Diacetyl-1,8-naphthyridine (214 mg, 2.0 mmol, 1.0 equiv) was added followed by AcOH (10 μL). The reaction mixture was stirred at reflux under an atmosphere of N_2 for 48 h. The reaction mixture was cooled to room temperature and concentrated to dryness under reduced pressure. The residue was washed with four 2-mL portions of MeOH cooled to 0 °C. The solid material was dried under vacuum to provide **L4** as a yellow powder. 0.55 g, 86% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 4H), 7.10 (t, *J* = 7.7 Hz, 2H), 2.82 (ddd, *J* = 17.1, 9.3, 7.6 Hz, 4H), 2.45 (s, 6H), 2.00 (dtd, *J* = 13.7, 7.4, 3.8 Hz, 4H), 1.84 (dtd, *J* = 11.4, 7.3, 6.8, 3.3 Hz, 4H), 1.78 – 1.70 (m, 8H), 1.61 – 1.49 (m, 16H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 167.79, 159.76, 155.12, 148.11, 137.39, 133.61, 124.48, 123.90, 123.80, 120.78, 40.61, 34.01, 33.99, 25.82, 25.80, 17.76.

HRMS (ESI): calcd for $C_{44}H_{53}N_4^+$ $[M + H]^+$: 637.4265; found: 637.4268.

m.p.: 292 – 295 °C.



(*S*,*S*)-L10 (*37*)**.** (*S*)-1-cyclohexylethylamine (0.52 g, 4.1 mmol, 2.2 equiv), toluene (40 mL) and 4 Å MS (approximately 5.0 g) were added to a round bottom flask equipped with a reflux condenser and magnetic stir bar. 2,7-Diacetyl-1,8-naphthyridine (0.40 g mg, 1.9 mmol, 1.0 equiv) was added followed by TsOH (5.0 mg). The reaction mixture was stirred at reflux under an atmosphere of N_2 for 48 h. The reaction mixture was cooled to room temperature then filtered. The filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in pentane, and the mixture was filtered through a glass fiber pad. The filtrate was concentrated to dryness, and the crude residue was heated at 60 °C under vacuum for 10 h to provide **(*S*,*S*)-L10** as a red-brown solid. 0.73 g, 90% yield, $[\alpha]_D^{23}$ = 55.9 º (c 0.272, $CHCl_3$).

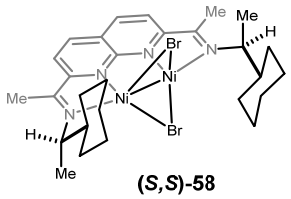
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 3.56 (p, *J* = 6.5 Hz, 2H), 2.55 (s, 6H), 1.87 (d, *J* = 12.9 Hz, 2H), 1.82 – 1.63 (m, 8H), 1.55 (tdt, *J* = 11.1,

6.8, 3.3 Hz, 2H), 1.36 – 1.09 (m, 8H), 1.87 (d, J = 6.4 Hz, 6H), 1.01 (dqd, J = 15.5, 12.3, 3.5 Hz, 4H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.18, 161.59, 154.81, 136.72, 123.27, 120.59, 61.89, 44.68, 30.01, 29.95, 26.84, 26.60, 26.52, 18.52, 14.09.

HRMS (APCI): calcd for $C_{28}H_{41}N_4^+$ $[M + H]^+$: 433.3326; found: 433.3328.

m.p.: 79 – 83 °C



(*S,S*)-58

(*S,S*)-58. In an N_2-filled glovebox, a Schlenk tube was charged with **(*S,S*)-L10** (130 mg, 1.0 equiv), $Ni(COD)_2$ (86 mg, 1.0 equiv), $Ni(DME)Br_2$ (97.0 mg, 1.05 equiv), and THF (15 mL). The tube was sealed, and the reaction mixture was stirred at 60 °C for 24 h, during which time a green color developed. The reaction vessel was cooled to room temperature and unsealed in the glovebox. The reaction mixture was filtered through a glass fiber pad, and the filtrate was concentrated to dryness. The solid residue was washed with pentane (2 x 2 ml) and benzene (2 x 2 ml). The solid was re-dissolved in a minimal amount of THF (approx. 2.5 mL), and the solution was filtered through a glass fiber pad. To the filtrate was added an equal volume of C_6H_6. Pentane (approximately 15 mL) was carefully layered on top of the THF/C_6H_6 solution. After the layers were allowed to slowly mix without agitation for 12 h, the mother liquor was decanted from the crystalline solid. The solid was washed with pentane (3 x 2 mL) and dried under reduced pressure to generate **(*S,S*)-58** (120.0 mg, 56% yield) as a dark green crystalline solid. Single crystals suitable for XRD were obtained by slow evaporation of a concentrated solution of **(*S,S*)-58** in THF.

^{1}H NMR (400 MHz, C_6D_6) δ 102.07, 64.89, 24.71, 10.53, 10.14, 4.57, 3.25, 3.04, 2.53, 1.91, 1.69, 1.15, -52.12.

UV–vis (THF, nm $\{M^{-1}\ cm^{-1}\}$): 261 {17421}, 352 {7960}, 568 {sh}, 671 {3666}.

μ_{eff} = 2.81 μ_B (Evans method, 296 K, TMS in THF-d_8).

Anal. Calcd for ($C_{28}H_{40}Br_2N_4Ni_2$): C 47.38, H 5.68, N 7.89; found: C 47.27, H 5.61, N 7.77.

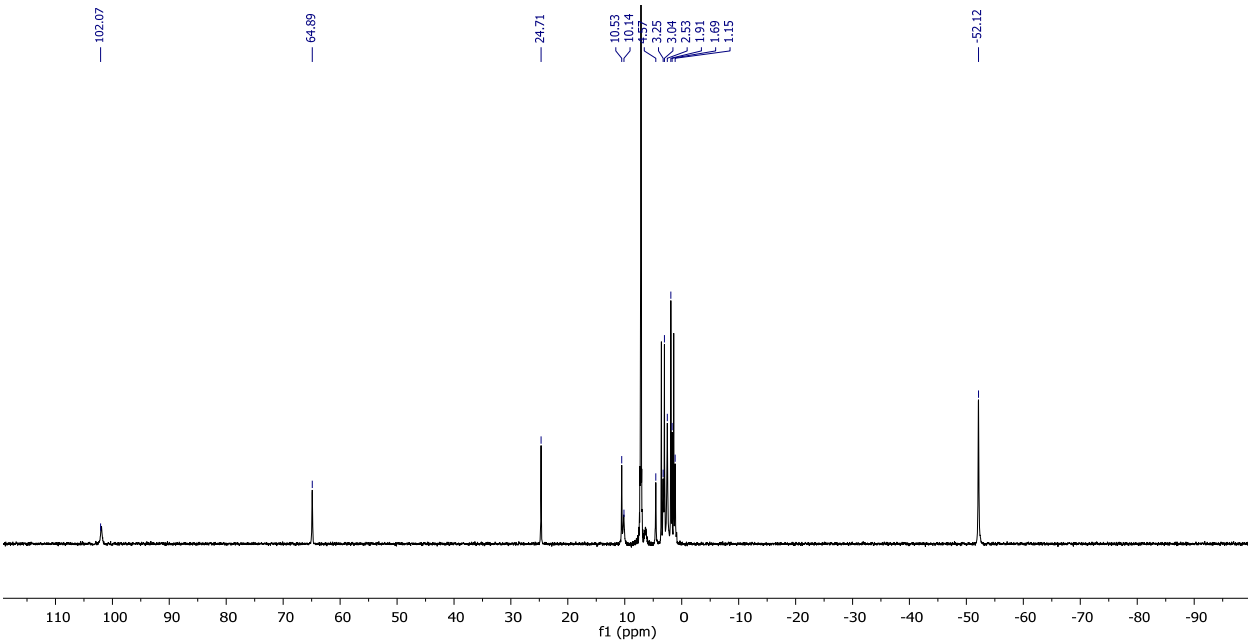


Fig. S1. ^{1}H NMR spectrum of **(*S*,*S*)-58** (C_6D_6, room temperature).

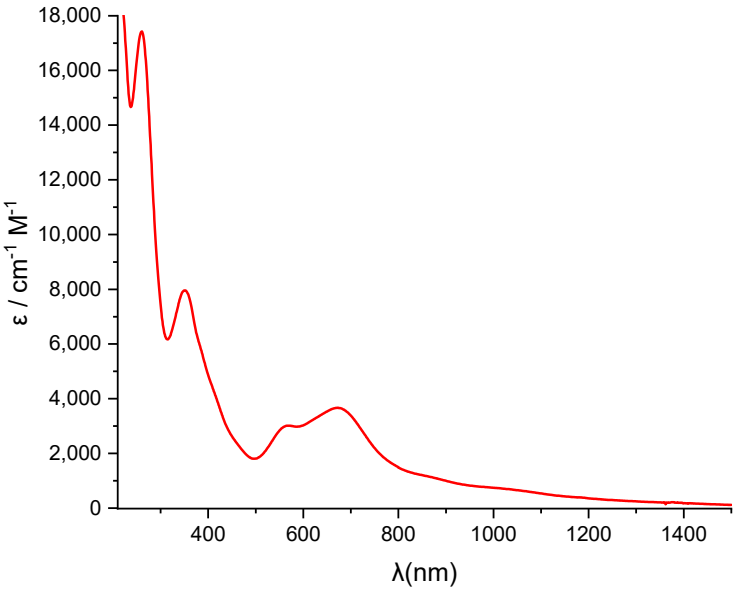


Fig. S2. UV-vis-NIR spectrum of **(*S*,*S*)-58** (0.74 mM in THF, room temperature).

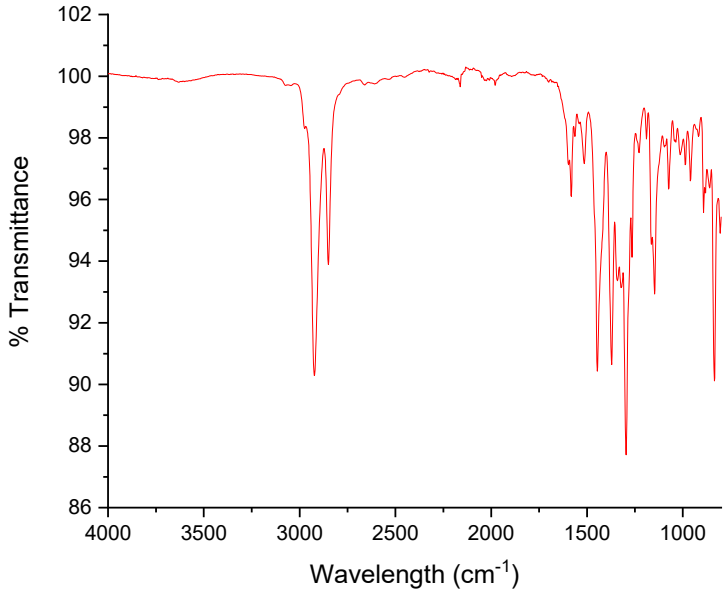
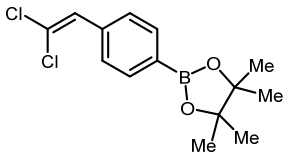


Fig. S3. ATR-IR spectrum of **(*S*,*S*)-58**.

4. Synthesis and Characterization of 1,1-Dichloroalkenes

General Procedure A (*38*)**.** Under an N_2 atmosphere, a 100-mL Schlenk flask equipped a magnetic stir bar was charged with Ph_3P (4.0 equiv) and MeCN (5 mL/mmol). With stirring, a solution of the aldehyde (1.0 equiv) and CCl_4 (2.0 equiv) in MeCN (2 mL/mmol) was added dropwise by syringe pump over 1 h. Following the addition, the reaction mixture was stirred for additional 2 h. The reaction mixture was then quenched by addition of H_2O (150 mL) The product was extracted with Et_2O (3 x 100 mL). The combined organic phases were dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography.

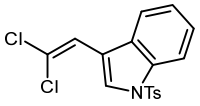


2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. According to General Procedure A: 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (1.62 g, 7.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, 1:9 to 1:3 CH_2Cl_2:hexane followed by 1:20 Et_2O/hexane). 1.06 g, 51% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.58 – 7.48 (m, 2H), 6.87 (s, 1H), 1.35 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 136.11, 134.97, 128.78, 127.98, 121.96, 84.09, 25.02.

HRMS (APCI): calcd for $C_{14}H_{17}BCl_2O_2^+$ M^+ : 297.0730; found: 297.0727.



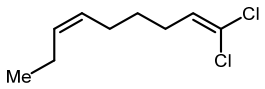
3-(2,2-dichlorovinyl)-1-tosyl-1H-indole. According to General Procedure A: 1-tosyl-1H-indole-3-carbaldehyde (2.10 g, 7.0 mmol, 1.0 equiv). The product was isolated as a pale yellow solid following purification by flash chromatography (SiO_2, hexane to 1:3 CH_2Cl_2/hexane). 1.57g, 61% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 0.8 Hz, 1H), 7.99 (dt, J = 8.3, 0.9 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.52 (dt, J = 7.8, 1.0 Hz, 1H), 7.36 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.22 (m, 2H), 6.93 (d, J = 0.8 Hz, 1H), 2.35 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.45, 135.10, 134.29, 130.16, 129.65, 127.05, 125.53, 125.38, 123.74, 121.66, 118.90, 118.65, 115.57, 113.84, 21.7.

HRMS (APCI): calcd for $C_{14}H_{13}Cl_2NO_2S^+$ $[M + H]^+$: 366.0117; found: 366.0114

m.p.: 145 – 148 °C

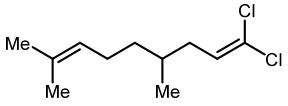


(*Z*)-1,1-dichlorononona-1,6-diene. According to General Procedure A: (*Z*)-oct-5-enal (1.52 g, 12.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, hexane). 1.00 g, 43% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 5.85 (t, *J* = 7.4 Hz, 1H), 5.44 – 5.38 (m, 1H), 5.33 – 5.28 (m, 1H), 2.18 (q, *J* = 7.5 Hz, 2H), 2.09 – 2.01 (m, 4H), 1.47 (p, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 132.67, 129.96, 128.19, 120.11, 29.34, 28.34, 26.65, 20.70, 14.47.

HRMS (APCI): calcd for $C_9H_{14}Cl_2^+$ M^+: 192.0467; found: 192.0465.

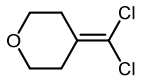


1,1-dichloro-4,8-dimethylnona-1,7-diene. According to General Procedure A: citronellal (0.63 g, 4.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash column chromatography (SiO_2, hexane). 0.83 g, 91% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 5.86 (t, *J* = 7.5 Hz, 1H), 5.08 (ddq, *J* = 8.5, 5.7, 1.4 Hz, 1H), 2.17 (ddd, *J* = 14.7, 7.3, 5.8 Hz, 1H), 2.08 – 1.92 (m, 3H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.61 (s, 3H), 1.60 – 1.56 (m, 1H), 1.34 (ddt, *J* = 13.5, 9.5, 6.1 Hz, 1H), 1.20 (dddd, *J* = 13.6, 9.5, 7.8, 5.9 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 131.65, 129.01, 124.56, 120.25, 36.88, 36.68, 32.46, 25.87, 25.67, 19.59, 17.81.

HRMS (APCI): calcd for $C_{11}H_{18}Cl_2^+$ M^+: 220.0780; found: 220.0782.

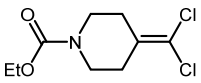


4-(dichloromethylene)tetrahydro-2H-pyran. According to General Procedure A: tetrahydro-4H-pyran-4-one (1.00 g, 10.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash column chromatography (SiO_2, 1:20 Et_2O/pentane). 1.14, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, *J* = 5.6 Hz, 4H), 3.50 (t, *J* = 5.6 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.12, 113.55, 67.51, 32.17.

HRMS (APCI): calcd for $C_6H_9Cl_2O^+$ $[M + H]^+$: 167.0025; found: 167.0026.



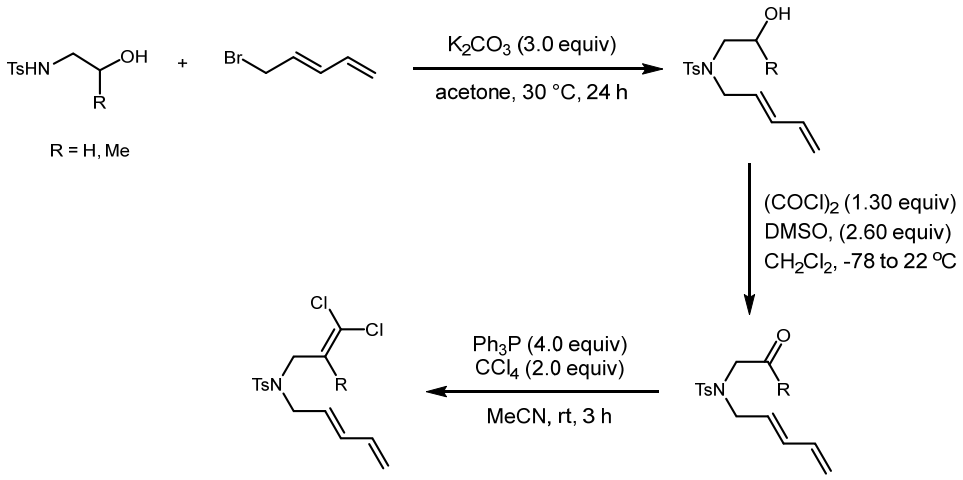
Ethyl 4-(dichloromethylene)piperidine-1-carboxylate. According to General Procedure A: ethyl 4-oxopiperidine-1-carboxylate (1.60 mL, 10.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash column chromatography (SiO_2, 1:12 EtOAc/hexane). 1.38 g, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 5.9 Hz, 4H), 2.48 (t, *J* = 5.9 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.54, 133.57, 114.28, 61.68, 43.39, 31.03, 14.83.

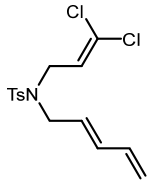
HRMS (ESI): calcd for $C_9H_{14}Cl_2NO_2^+$[M + H]$^+$: 239.0396; found: 239.0394.

m.p.: 50 – 52 °C



Step 1 (General Procedure B) (*39*)**.** A 100-mL round bottom flask was charged with *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide or *N*-(2-hydroxypropyl)-4-methylbenzene-sulfonamide (1.0 equiv), anhydrous acetone (1.5 mL/mmol) and K_2CO_3 (3.0 equiv). A solution of (*E*)-5-bromopenta-1,3-diene (1.05 equiv) dissolved in anhydrous acetone (0.5 mL/mmol) was added, and the reaction mixture was stirred at 30 °C under N_2. After 24 h, the mixture was filtered, and the precipitate was washed several times with acetone. The filtrate was concentrated under reduced pressure. Water (20 mL) was added to the residue, and the product was extracted with CH_2Cl_2 (100 mL). The organic phase was washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated to dryness under reduced pressure, and the crude product was carried forward into the next step without further purification.

Step 2 (General Procedure C). Under an N_2 atmosphere, a solution of oxalyl chloride (1.30 equiv) in CH_2Cl_2 (6 mL/mmol) was cooled to –78 °C (dry ice/acetone bath). A solution of DMSO (2.6 equiv) in CH_2Cl_2 (1.5 ml/mmol) was added dropwise over 10 min. Following the addition, the reaction mixture was stirred at –78 °C for 30 min. A solution of the alcohol (1.0 equiv) in CH_2Cl_2 (1.5 ml/mmol) was added dropwise over 10 min. The reaction was stirred for 1 h at –78 °C. Et_3N (5.2 equiv) was added dropwise over 10 min. After stirring for an additional 1 h at –78 °C, the reaction mixture was allowed to warm to room temperature. Once the reaction mixture reached room temperature, it was diluted with CH_2Cl_2 (30 mL) and washed with water (2 x 30 ml) then brine (30 ml). The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the crude product was carried forward into the next step without further purification.



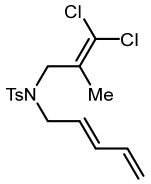
(*E*)-N-(3,3-dichloroallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide (48). According to General Procedure A: (*E*)-4-methyl-N-(2-oxoethyl)-N-(penta-2,4-dien-1-yl)benzenesulfonamide (2.80 g, 10.0 mmol, 1.0 equiv). The product was isolated as a white solid following purification by flash chromatography (SiO_2, 1:3 to 1:1 CH_2Cl_2/hexane). 1.79 g, 52% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.34 – 7.31 (m, 2H), 6.27 (dtd, *J* = 17.0, 10.3, 0.7 Hz, 1H), 6.13 (ddt, *J* = 15.2, 10.3, 0.7 Hz, 1H), 5.79 (t, *J* = 6.7 Hz, 1H), 5.49 (dtd, *J* = 15.2, 6.8, 0.7 Hz, 1H), 5.19 (ddt, *J* = 16.9, 1.4, 0.7 Hz, 1H), 5.11 (ddt, *J* = 10.1, 1.4, 0.7 Hz, 1H), 3.89 (d, *J* = 6.7 Hz, 2H), 3.81 (d, *J* = 6.7 Hz, 1H), 2.44 (s, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 143.84, 136.82, 135.78, 135.47, 129.99, 127.40, 127.37, 127.21, 125.30, 123.73, 118.66, 49.83, 45.78, 21.69.

HRMS (ESI): calcd for $C_{15}H_{17}Cl_2NO_2SNa^+$ [M + Na]$^+$: 368.0249/370.0221; found: 368.0247/370.0220.

m.p.: 48 – 50 °C



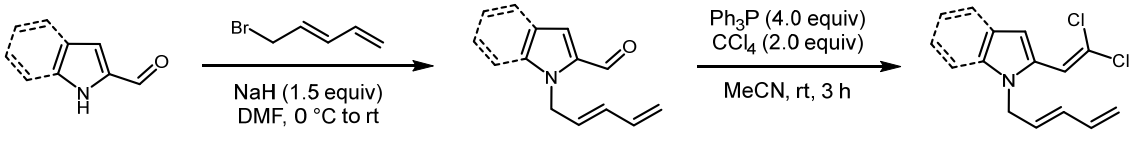
(*E*)-N-(3,3-dichloro-2-methylallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzene-sulfonamide (56). According to General Procedure A: (*E*)-4-methyl-N-(2-oxopropyl)-N-(penta-2,4-dien-1-yl)benzenesulfonamide (2.35 g, 8.0 mmol, 1.0 equiv). The product was isolated as a white solid following purification by flash chromatography (1:3 to 1:1 CH_2Cl_2/hexane). 2.10 g, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.34 – 7.29 (m, 2H), 6.25 – 6.04 (m, 2H), 5.46 – 5.36 (m, 1H), 5.20 – 5.14 (m, 1H), 5.10 – 5.06 (m, 1H), 3.95 (s, 2H), 3.74 (dt, *J* = 7.0, 0.8 Hz, 2H), 2.44 (s, 3H), 1.92 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.73, 136.81, 135.80, 135.38, 131.01, 129.95, 127.40, 126.86, 118.52, 118.38, 50.39, 50.04, 21.67, 18.07.

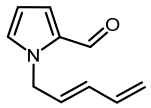
HRMS (APCI): calcd for $C_{16}H_{20}Cl_2NO_2S^+$[M + H]$^+$: 360.0586; found: 360.0590.

m.p.: 50 – 53 °C



General Procedure D. Under an N_2 atmosphere, NaH (1.5 equiv, 60% wt. in mineral oil) was suspended in dry DMF (1.5 ml/mmol). A solution of the aldehyde (1.0 equiv) in DMF (1.5

ml/mmol) was added dropwise over 30 min at 0 °C. After stirring for 1 h at 0 °C, (*E*)-5-bromopenta-1,3-diene (1.5 equiv) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h at room temperature. The reaction mixture was cooled to 0 °C, and the reaction was carefully quenched by slow addition of water (20 mL). The reaction mixture was extracted with Et_2O (3 x 50 mL). The combined organic phases were washed with water (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 1:9 to 1:4 EtOAc/hexane) to provide the corresponding aldehydes as pale yellow oils.

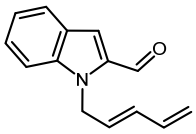


(*E*)-1-(penta-2,4-dien-1-yl)-1H-pyrrole-2-carbaldehyde. According to the General Procedure D: 1.20 g, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, *J* = 1.1 Hz, 1H), 6.97 – 6.94 (m, 2H), 6.37 – 6.28 (m, 1H), 6.25 (dd, *J* = 4.0, 2.5 Hz, 1H), 6.11 – 6.02 (m, 1H), 5.84 (dtd, *J* = 15.2, 6.1, 0.7 Hz, 1H), 5.19 (ddt, *J* = 17.0, 1.5, 0.7 Hz, 1H), 5.10 (ddt, *J* = 10.2, 1.5, 0.7 Hz, 1H), 5.02 – 4.97 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.57, 136.01, 133.49, 131.47, 131.00, 129.18, 124.82, 118.35, 110.08, 50.20.

HRMS (ESI): calcd for $C_{10}H_{12}NO^+$ $[M + H]^+$: 162.0913; found: 162.0911.

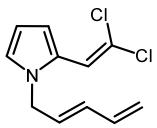


(*E*)-1-(penta-2,4-dien-1-yl)-1H-indole-2-carbaldehyde. According to General Procedure D: 0.48 g, 33% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.75 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.29 (s, 1H), 7.19 (ddd, *J* = 8.0, 5.5, 2.4 Hz, 1H), 6.26 (dt, *J* = 16.9, 10.2 Hz, 1H), 6.03 (ddtd, *J* = 14.8, 10.2, 1.5, 0.7 Hz, 1H), 5.91 – 5.79 (m, 1H), 5.29 – 5.24 (m, 2H), 5.12 (ddt, *J* = 16.9, 1.5, 0.7 Hz, 1H), 5.04 (ddt, *J* = 10.1, 1.5, 0.7 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.72, 140.42, 136.09, 135.24, 132.71, 129.01, 127.22, 126.66, 123.61, 121.25, 118.21, 117.90, 110.96, 46.07.

HRMS (ESI): calcd for $C_{14}H_{14}NO^+$ $[M + H]^+$: 212.1070; found: 212.1069.

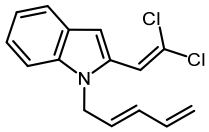


(*E*)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-pyrrole (50). According to General Procedure A: (*E*)-1-(penta-2,4-dien-1-yl)-1H-pyrrole-2-carbaldehyde (1.20 g, 8.0 mmol, 1.0 equiv). The product was isolated as a colorless oil following purification by flash column chromatography (SiO_2, 1:20 to 1:9 CH_2Cl_2/hexane). 0.44 g, 24% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.82 (m, 1H), 6.70 (dd, *J* = 2.7, 1.6 Hz, 1H), 6.65 (s, 1H), 6.33 (dt, *J* = 17.0, 10.2 Hz, 1H), 6.24 (dd, *J* = 3.9, 2.7 Hz, 1H), 5.99 – 5.89 (m, 1H), 5.76 (dt, *J* = 15.3, 5.4 Hz, 1H), 5.23 – 5.17 (m, 1H), 5.15 – 5.10 (m, 1H), 4.54 (dd, *J* = 5.4, 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.72, 133.01, 128.83, 125.84, 123.25, 118.61, 117.73, 117.42, 111.96, 108.93, 48.64.

HRMS (ESI): calcd for $C_{11}H_{12}Cl_2N^+$ $[M + H]^+$: 228.0341; found: 228.0340.



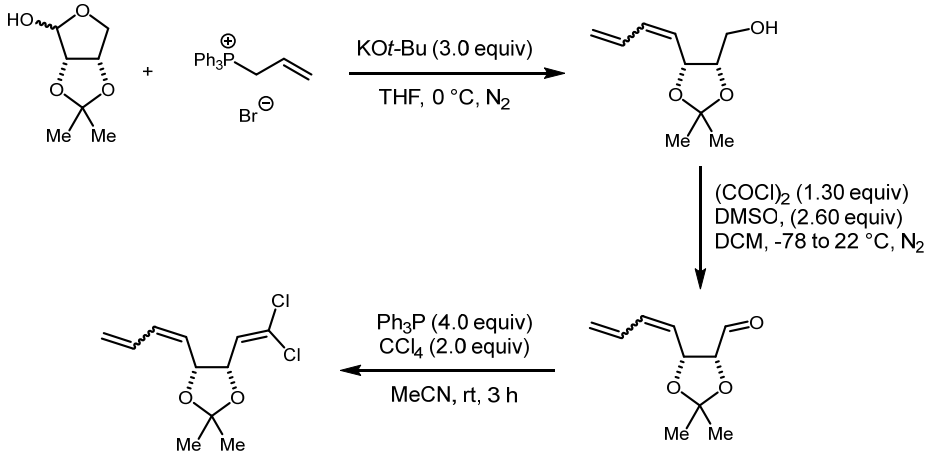
(*E*)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-indole (52). According to General Procedure A: (*E*)-1-(penta-2,4-dien-1-yl)-1H-indole-2-carbaldehyde. (0.48 g, 2.25 mmol, 1.0 equiv). The product was isolated as a white solid following purification by flash column chromatography (SiO_2, 1:9 to 1:4 CH_2Cl_2/hexane). 0.15 g, 24% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.30 – 7.21 (m, 3H), 7.16 – 7.10 (m, 2H), 6.84 (d, *J* = 0.8 Hz, 1H), 6.29 (dt, *J* = 17.0, 10.1 Hz, 1H), 5.95 – 5.84 (m, 1H), 5.78 (dt, *J* = 15.4, 4.7 Hz, 1H), 5.17 – 5.03 (m, 2H), 4.79 (d, *J* = 4.5 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.82, 135.70, 132.43, 131.78, 128.36, 127.79, 123.27, 122.36, 121.42, 120.46, 118.38, 118.17, 109.59, 104.77, 44.69.

HRMS (ESI): calcd for $C_{15}H_{14}Cl_2N^+$ $[M + H]^+$: 278.0498; found: 278.0496.

m.p.: 43 – 45 °C



Step 1 (*40*)**. ((4S,5R)-5-(buta-1,3-dien-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl)methanol.** Under an N_2 atmosphere, triphenylallylphosphonium bromide (12.65 g, 33 mmol, 3.3 equiv) was stirred in THF (50 mL). KO*t*-Bu (3.37 g, 30 mmol, 3.0 equiv) was added as a solid at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. A solution of (3a*S*,6a*S*)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (*41*) (1.60 g, 10.0 mmol, 1.0 equiv) in THF (50 mL) added dropwise over 30 min, and the mixture was stirred for an additional 6 h at 0 °C. The reaction was quenched with saturated NH_4Cl (aq). The aqueous phase was extracted with EtOAc (2 x 100 mL), and the combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by flash

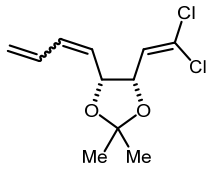
chromatograph (SiO_2, 1:20 to 1:3 EtOAc/hexane) to afford a mixture of *Z* and *E* isomers as a colorless oil. 1.30 g, 71% yield, *E*:*Z* = 1:6.6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (dddd, *J* = 16.7, 11.2, 10.1, 1.1 Hz, 1H, *Z*), 6.42 – 6.28 (m, 2H, *E*), 6.21 (t, *J* = 11.2, 1H, *Z*), 5.71 (dd, *J* = 14.2, 7.7 Hz, 1H, *E*), 5.51 (t, *J* = 9.8, 1H, *Z*), 5.36 – 5.27 (m, 1H, *Z*), 5.25 (dd, *J* = 10.1, 1.8 Hz, 1H, *E*/*Z*), 5.14 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1H, *E*/*Z*), 4.69 (t, *J* = 7.3 Hz, 1H, *E*), 4.29 (dt, *J* = 6.8, 5.6 Hz, 1H, *Z*), 3.57 (t, *J* = 5.9 Hz, 2H, *E*/*Z*), 1.87 – 1.78 (m, 1H, *E*/*Z*), 1.52 (s, 3H, *E*/*Z*), 1.41 (s, 3H, *Z*), 1.39 (s, 3H, *E*).

Z isomer: ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.25, 131.27, 126.17, 120.76, 108.98, 78.63, 73.35, 62.21, 28.00, 25.32.

HRMS (ESI): calcd for $C_{10}H_{15}O_3^+$ [M - H]$^+$: 183.1016; found: 183.1017.

Step 2. (4R,5R)-5-(buta-1,3-dien-1-yl)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde. Following General Procedure C for the Swern Oxidation. The crude product was carried forward into the next step without further purification.



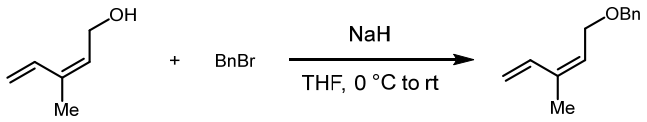
(4*R*,5*S*)-4-(buta-1,3-dien-1-yl)-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane (54). According to General Procedure A: (4*R*,5*R*)-5-(buta-1,3-dien-1-yl)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (1.29 g, 7.0 mmol, *E*:*Z* = 1:7.0). The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, 1:9 to 1:3 CH_2Cl_2/pentane, then 1:20 Et_2O/pentane). 0.77 g, 44% yield, *E*:*Z* = 1:6.6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dddd, *J* = 16.7, 11.3, 10.1, 1.1 Hz, 1H, *Z*), 6.40 – 6.29 (m, 2H, *E*), 6.29 – 6.18 (m, 1H, *Z*), 5.93 (d, *J* = 8.5 Hz, 1H, *E*), 5.89 (d, *J* = 8.7 Hz, 1H, *Z*), 5.60 – 5.53 (m, 1H, *E*), 5.45 (ddq, *J* = 10.8, 8.5, 1.1 Hz, 1H, *E*), 5.39 – 5.29 (m, 2H, *Z*), 5.25 (dtd, *J* = 10.1, 1.6, 0.8 Hz, 1H, *Z*), 5.15 (ddd, *J* = 8.5, 6.2, 1.3 Hz, 1H, *Z*), 4.94 (dd, *J* = 8.7, 6.2 Hz, 1H, *Z*), 4.75 – 4.70 (m, 1H, *E*), 4.65 (td, *J* = 8.4, 1.2 Hz, 1H, *E*), 4.48 (t, *J* = 8.3 Hz, 1H, *E*), 1.51 (s, 3H, *Z*), 1.46 (s, 3H, *E*), 1.44 (s, 3H, *E*), 1.41 (d, *J* = 0.8 Hz, 3H, *Z*).

Z isomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.92, 131.34, 126.78, 125.27, 120.87, 109.64, 76.52, 74.43, 28.25, 25.69.

HRMS (APCI): calcd for $C_{11}H_{13}Cl_2O_2^+$ [M - H]$^+$: 247.0287; found: 247.0286

5. Synthesis and Characterization of 1,3-Dienes

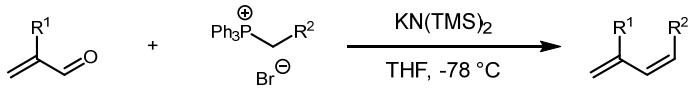


(*Z*)-(((3-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene (*42*)**.** Under an N_2 atmosphere, (Z)-3-methylpenta-2,4-dien-1-ol (0.16 g, 1.60 mmol, 1.0 equiv) was stirred in dry THF (5 mL) at 0 °C. Solid NaH (0.13 g, 3.2 mmol, 2.0 equiv, 60% wt. in mineral oil) was added, and the reaction mixture was stirred at 0 °C for 1 h. Benzyl bromide (2.4 mmol, 0.30 mL, 1.5 equiv) was added dropwise, and stirring was continued for 30 min at 0 °C. The reaction was warmed to room temperature and stirred for an additional 1 h. The reaction mixture was cooled to 0 °C and quenched with saturated NH_4Cl (aq). The aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 1:9 to 1:4 EtOAc/hexane) to provide the diene as a colorless oil. 0.28 g, 93% yield.

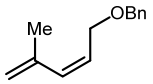
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.70 (dd, *J* = 10.8, 6.4 Hz, 1H), 5.60 (t, *J* = 6.8 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.16 (dt, *J* = 10.8, 1.6 Hz, 2H), 4.52 (s, 2H), 4.18 (d, *J* = 6.9 Hz, 2H), 1.88 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.49, 136.38, 133.33, 128.53, 127.98, 127.75, 126.52, 115.46, 72.35, 65.64, 19.87.

HRMS (APCI): calcd for $C_{13}H_{15}O^+$ [M - H]$^+$: 187.1117; found: 187.1119.



General Procedure E (*43*)**.** Under an N_2 atmosphere, a frame-dried round bottom flask was charged with a magnetic stir bar, the phosphonium salt (1.0 equiv), and THF (20 mL/mmol). The suspension was stirred at –78 °C. K[N(TMS)$_2$] (1.0 equiv) was added, and the resulting orange solution was stirred at –78 °C for 1 h. A second flame-dried round bottom flask was charged with the aldehyde (1.5 equiv) and THF (10 mL/mmol). The aldehyde solution was cooled to –78 °C then slowly transferred via cannula to the orange solution of the ylide. The reaction mixture was stirred for 1 h at –78 °C then for 1 h at room temperature. The reaction volume was concentrated to 1/4 of the original volume. The crude mixture was diluted with pentane (150 mL) and washed with water (2 x 50 ml) and brine (50 mL). The organic phase was dried over $NaSO_4$, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by flash column chromatography.

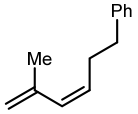


(*Z*)-(((4-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene. According to the General Procedure E: 1.29 g, 69% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 4H), 7.31 – 7.28 (m, 1H), 6.02 (d, *J* = 11.9 Hz, 1H), 5.67 (dt, *J* = 12.2, 6.2 Hz, 2H), 5.00 (s, 1H), 4.77 (s, 1H), 4.53 (s, 2H), 4.28 (d, *J* = 6.3 Hz, 2H), 1.85 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 141.17, 138.45, 133.51, 128.51, 128.24, 127.95, 127.75, 116.51, 72.48, 67.14, 23.08.

HRMS (APCI): calcd for $C_{13}H_{17}NO^+$ $[M + H]^+$: 189.1274; found: 189.1272.

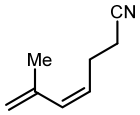


(*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (59). According to the General Procedure E: 1.40 g, 81% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.87 (d, *J* = 11.8 Hz, 1H), 5.49 – 5.43 (m, 1H), 4.94 (s, 1H), 4.82 (s, 1H), 2.73 – 2.70 (m, 2H), 2.63 – 2.57 (m, 2H), 1.85 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 142.00, 141.89, 131.52, 130.70, 128.59, 128.46, 125.99, 115.41, 36.50, 30.60, 23.46.

HRMS (APCI): calcd for $C_{13}H_{17}^+$ $[M + H]^+$: 173.1325; found: 173.1324.

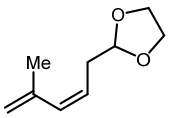


(*Z*)-6-methylhepta-4,6-dienenitrile. According to the General Procedure E: 0.43 g, 36% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.00 (dq, *J* = 11.6, 1.6 Hz, 1H), 5.39 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.02 (p, *J* = 1.7 Hz, 1H), 4.84 (s, 1H), 2.62 (qd, *J* = 7.3, 1.8 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.87 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 141.07, 134.26, 126.29, 119.39, 116.24, 24.55, 23.31, 17.93.

HRMS (APCI): calcd for $C_{13}H_{16}N^+$ $[M+ H]^+$: 122.0964; found: 122.0962.

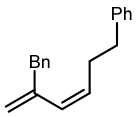


(*Z*)-2-(4-methylpenta-2,4-dien-1-yl)-1,3-dioxolane. According to the General Procedure E: 0.91 g, 59% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dq, *J* = 11.9, 1.7 Hz, 1H), 5.49 (dt, *J* = 11.8, 7.3 Hz, 1H), 4.98 (p, *J* = 1.8 Hz, 1H), 4.92 (t, *J* = 4.7 Hz, 1H), 4.89 (s, 1H), 4.04 – 3.94 (m, 2H), 3.92 – 3.82 (m, 2H), 2.68 (ddd, *J* = 7.0, 4.8, 1.9 Hz, 2H), 1.88 (t, *J* = 1.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 141.50, 133.72, 124.01, 115.95, 104.13, 65.12, 33.62, 23.38.

HRMS (APCI): calcd for $C_9H_{13}O_2^+$ $[M - H]^+$: 153.0910; found: 153.0907.



(*Z*)-(2-methylenehex-3-ene-1,6-diyl)dibenzene. According to the General Procedure E: 0.95 g, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 4H), 7.24 – 7.08 (m, 6H), 5.79 (dq, *J* = 11.7, 1.6 Hz, 1H), 5.48 (dt, *J* = 11.6, 7.1 Hz, 1H), 5.00 – 4.99 (m, 1H), 4.93 (s, 1H), 3.39 (s, 2H), 2.63 – 2.57 (m, 2H), 2.55 – 2.47 (m, 2H).

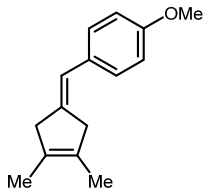
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.49, 142.00, 139.63, 131.81, 130.14, 129.06, 128.58, 128.42, 128.41, 126.22, 125.95, 115.42, 43.82, 36.26, 30.67.

HRMS (ESI): calcd for $C_{19}H_{19}^{+}$ $[M - H]^{+}$: 247.1481; found: 247.1479.

6. Intermolecular [4 + 1]-Cycloadditions

General Procedure F. In an N_2-filled glovebox, a 3-dram vial was charged with the [NDI] ligand (5–10 mol%), Ni(DME)Br_2 (10–20 mol%), Zn powder (0.60 mmol), and a magnetic stir bar. The reaction solvent was added, and the resulting suspension was stirred for 15 min, during which time the catalyst solution turned purple. The diene and 1,1-dichloroalkene were successively added to the catalyst/reductant mixture. The vial was sealed, and the reaction mixture was stirred at room temperature. After 24 h, the reaction vial was opened to ambient atmosphere. The crude reaction mixture was directly loaded onto a SiO_2 column for purification.

General Procedure G. In an N_2-filled glovebox, a 3-dram vial was charged with the [$^{i\text{-}Pr}$NDI]$Ni_2(C_6H_6)$ complex **3** (5–10 mol%), Zn powder (0.60 mmol), the reaction solvent, and a magnetic stir bar. The diene and 1,1-dichloroalkene were successively added to the catalyst/reductant mixture. The vial was sealed, and the reaction mixture was stirred at room temperature. After 24 h, the reaction vial was opened to ambient atmosphere. The crude reaction mixture was concentrated under reduced pressure, and the residue was directly loaded onto a SiO_2 column for purification.



1-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)-4-methoxybenzene (2). According to General Procedure F: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexanes). 42.7 mg, 99% yield.

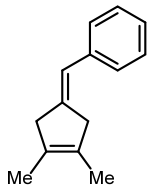
Benchtop Reaction: A 3-dram vial was charged with Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%), **L4** ligand (6.4 mg, 0.01 mmol, 5 mol%), Zn powder (39.2 mg, 0.60 mmol), and a magnetic stir bar. After sealing with a rubber septum, the vial was evacuated and back-filled with N_2 three times. Dry NMP (0.40 mL) was added by syringe, and the resulting suspension was stirred for 15 min, during which time the catalyst solution turned purple. 2,3-Dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv) and 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv) were successively added to the catalyst/reductant mixture. The reaction mixture was stirred at room temperature under N_2. After 24 h, the reaction vial was opened to ambient atmosphere. The crude reaction mixture was directly loaded onto a SiO_2 column for purification. The product (**2**) was isolated as a white solid. 37.3 mg, 88% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 2H), 6.92 – 6.84 (m, 2H), 6.30 (p, J = 2.4 Hz, 1H), 3.81 (s, 3H), 3.24 (s, br, 2H), 3.21 (s, br, 2H), 1.68 (m, 6H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 157.78, 140.11, 131.50, 130.17, 129.62, 129.18, 121.16, 113.81, 55.40, 47.02, 43.61, 13.88, 13.54.

HRMS (APCI): calcd for $C_{15}H_{17}O^+$ $[M - H]^+$: 213.1274; found: 213.1276.

m.p.: 58 – 60 °C

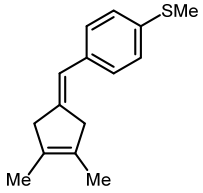


((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzene (4). According to General Procedure F: (2,2-dichlorovinyl)benzene (34.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 µL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 33.6 mg, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.20 -7.16 (m, 1H), 6.37 (q, J = 2.3 Hz, 1H), 3.29 (s, br, 1H), 3.25 (s, br, 1H), 1.77 – 1.65 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.52, 138.57, 130.16, 129.51, 128.35, 128.07, 125.89, 121.85, 47.12, 43.70, 13.85, 13.52.

HRMS (APCI): calcd for $C_{14}H_{15}^+$ $[M - H]^+$: 183.1168; found: 183.1165.

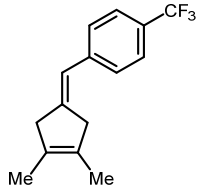


(4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)phenyl)(methyl)sulfane (5). According to General Procedure F: (4-(2,2-dichlorovinyl)phenyl)(methyl)sulfane (43.8 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene(45 µL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 45.4 mg, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4H), 6.31 (p, J = 2.4 Hz, 1H), 3.25 (s, br, 2H), 3.22 (s, br, 2H), 2.49 (s, 3H), 1.75 – 1.65 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.26, 135.73, 135.52, 130.10, 129.55, 128.49, 126.86, 121.24, 47.14, 43.75, 16.25, 13.86, 13.51.

HRMS (APCI): calcd for $C_{15}H_{17}S^+$ $[M - H]^+$: 229.1046; found: 229.1048.



1-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)-4-(trifluoromethyl)benzene (6). According to General Procedure F: 1-(2,2-dichlorovinyl)-4-(trifluoromethyl)benzene (48.2 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 µL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL).

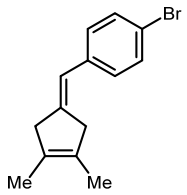
The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 37.0 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 6.39 (p, J = 2.5 Hz, 1H), 3.27 (s, br, 1H), 3.26 (s, br, 1H), 1.69 (dhept, J = 2.2, 1.0 Hz, 6H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 145.79, 141.98, 129.95, 129.51, 129.04, 128.09, 127.66 (q, J = 32.2 Hz) 125.28 (q, J = 4.0 Hz), 120.87, 47.25, 43.80, 13.83, 13.49.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.83.

HRMS (APCI): calcd for $C_{15}H_{14}F_3^+$ $[M - H]^+$: 251.1042; found: 251.1044.



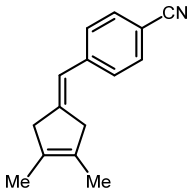
1-bromo-4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzene (7). According to General Procedure F: 1-bromo-4-(2,2-dichlorovinyl)benzene (50.4 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 µL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and $Ni(DME)Br_2$ (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, pentane). 44.0 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.19 – 7.13 (m, 2H), 6.29 (p, J = 2.4 Hz, 1H), 3.38 – 3.04 (m, 4H), 1.68 (ddq, J = 3.3, 2.2, 1.1 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.64, 137.44, 131.42, 129.99, 129.61, 129.54, 120.82, 119.54, 47.15, 43.68, 13.84, 13.50.

HRMS (APCI): calcd for $C_{14}H_{16}Br^+$[M + H]$^+$: 263.0430; found: 263.0428.

m.p.: 69 – 71 °C



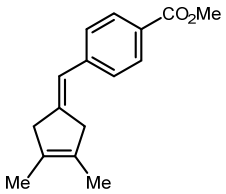
4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzonitrile (8). According to General Procedure F: 4-(2,2-dichlorovinyl)benzonitrile (39.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 µL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 24.0 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.39 – 7.34 (m, 2H), 6.37 (p, J = 2.4 Hz, 1H), 3.26 (s, br, 4H), 1.88 – 1.58 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.64, 142.99, 132.20, 129.80, 129.47, 128.40, 120.81, 119.45, 108.98, 47.43, 43.95, 13.79, 13.45.

HRMS (APCI): calcd for $C_{15}H_{14}N^+$ $[M - H]^+$: 208.1121; found: 208.1123

m.p.: 98 – 102 °C



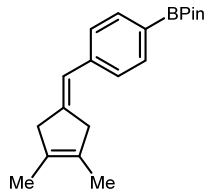
methyl 4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzoate (9). According to General Procedure F: methyl 4-(2,2-dichlorovinyl)benzoate (46.2 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 μL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 3:4 CH_2Cl_2/pentane). 43.7 mg, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.39 – 7.32 (m, 2H), 6.40 (p, J = 2.4 Hz, 1H), 3.91 (s, 3H), 3.29 (s, br, 2H), 3.26 (s, br, 2H), 1.73 – 1.66 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.23, 146.06, 143.10, 129.99, 129.74, 129.44, 127.84, 127.29, 121.36, 52.12, 47.38, 43.94, 13.83, 13.48.

HRMS (APCI): calcd for $C_{16}H_{17}O_2^+$ [M – H]$^+$: 241.1223; found: 241.1225.

m.p.: 74 – 76 °C

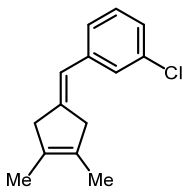


2-(4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10). According to General Procedure F: 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59.8 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as colorless oil following purification by column chromatography (SiO_2, 1:2:50 Et_2O/CH_2Cl_2/pentane). 61.5 mg, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.34 – 7.27 (m, 2H), 6.37 (p, J = 2.4 Hz, 1H), 3.28 (s, br, 2H), 3.24 (s, br, 2H), 1.68 (m, 6H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.01, 141.34, 134.88, 130.16, 129.43, 127.37, 122.04, 83.80, 47.26, 43.80, 25.02, 13.85, 13.50.

HRMS (ESI): calcd for $C_{20}H_{26}BO_2^+$ [M – H]$^+$: 308.2057; found: 308.2065.



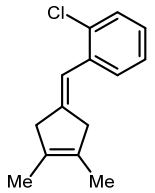
1-chloro-3-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzene (11). According to General Procedure F: 1-chloro-3-(2,2-dichlorovinyl)benzene (41.5 mg, 0.20 mmol, 1.0 equiv);

2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 39.2 mg, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 1.9 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 6.30 (p, *J* = 2.5 Hz, 1H), 3.25 (s, br, 2H), 3.23 (s, br, 2H), 1.72 – 1.67 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.44, 140.36, 134.25, 130.01, 129.54, 129.47, 127.86, 126.24, 125.87, 120.71, 47.15, 43.66, 13.84, 13.49.

HRMS (APCI): calcd for $C_{14}H_{14}Cl^+$ $[M - H]^+$: 217.0779; found: 217.0782.

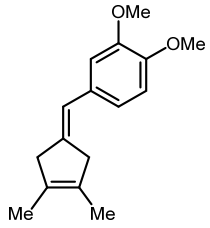


1-chloro-2-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzene (12). According to General Procedure F: 1-chloro-2-(2,2-dichlorovinyl)benzene (41.5 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 37.5 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1H), 7.12 (td, *J* = 7.6, 1.7 Hz, 1H), 6.60 (p, *J* = 2.4 Hz, 1H), 3.26 (s, 2H), 3.17 (s, 2H), 1.68 (tq, *J* = 2.1, 1.1 Hz, 3H), 1.66 (tq, *J* = 2.2, 1.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.78, 136.39, 133.35, 129.97, 129.68, 129.54, 129.22, 127.28, 126.41, 118.37, 46.74, 43.09, 13.80, 13.55.

HRMS (ESI): calcd for $C_{14}H_{14}Cl^+$ $[M - H]^+$: 217.0779; found: 217.0778.

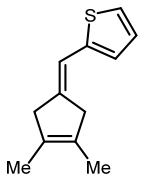


4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)-1,2-dimethoxybenzene (13). According to General Procedure F: 4-(2,2-dichlorovinyl)-1,2-dimethoxybenzene (46.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as an off-white solid following purification by column chromatography (SiO_2, 1:3 CH_2Cl_2/pentane). 41.1 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.78 (m, 3H), 6.30 (p, *J* = 2.4 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.25 (s, br, 2H), 3.22 (s, br, 2H), 1.68 (m, 6H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 148.74, 147.36, 140.55, 131.84, 130.06, 129.66, 121.45, 120.51, 111.53, 111.21, 56.04, 55.97, 47.03, 43.55, 13.89, 13.54.

HRMS (APCI): calcd for $C_{16}H_{21}O_2^+$ [M + H]$^+$: 245.1536; found: 245.1533
m.p.: 70 – 73 °C

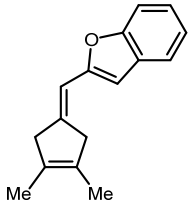


2-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)thiophene (14). According to General Procedure F: 2-(2,2-dichlorovinyl)thiophene (36.0 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 µL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.8 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a yellow oil following purification by column chromatography (SiO_2, pentane). 22.8 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 5.1 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.60 (p, *J* = 2.5 Hz, 1H), 3.23 – 3.20 (m, 4H), 1.72 (m, 3H), 1.68 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.80, 141.04, 129.91, 129.70, 126.97, 124.75, 124.08, 115.37, 46.23, 44.21, 13.90, 13.56.

HRMS (APCI): calcd for $C_{12}H_{15}S^+$ [M + H]$^+$: 191.0889; found: 191.0888.

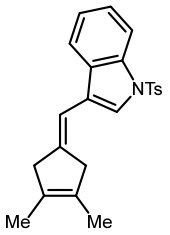


2-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)benzofuran (15). According to General Procedure F: 2-(2,2-dichlorovinyl)benzofuran (43.0 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 µL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a pale yellow oil following purification by column chromatography (SiO_2, 1:9 CH_2Cl_2/hexane). 37.1 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.45 – 7.42 (m, 1H), 7.25 – 7.15 (m, 2H), 6.48 (s, 1H), 6.37 (p, *J* = 2.4 Hz, 1H), 3.40 (s, br, 2H), 3.27 (s, br, 2H), 1.74 (tq, *J* = 2.3, 1.1 Hz, 3H), 1.70 (tq, *J* = 2.3, 1.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.12, 154.31, 146.41, 130.13, 129.48, 129.30, 123.63, 122.71, 120.55, 111.01, 110.96, 102.97, 46.45, 44.63, 13.84, 13.53.

HRMS (ESI): calcd for $C_{16}H_{17}O^+$ [M + H]$^+$: 225.1274; found: 225.1276



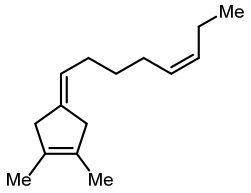
3-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)-1-tosyl-1H-indole (16). According to General Procedure F: 3-(2,2-dichlorovinyl)-1-tosyl-1H-indole (73.0 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 μL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a pale yellow solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexane). 53.4 mg, 71% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.2, 0.9 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.58 (dt, J = 7.7, 1.0 Hz, 1H), 7.44 (s, 1H), 7.32 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.21 – 7.18 (m, 2H), 6.46 (p, J = 2.4 Hz, 1H), 3.27 (s, 2H), 3.20 (s, 2H), 2.32 (s, 3H), 1.75 (dq, J = 2.3, 1.1 Hz, 3H), 1.70 (dq, J = 2.2, 1.1 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.94, 144.25, 135.35, 129.96, 126.86, 124.96, 123.29, 122.23, 120.70, 119.46, 113.78, 110.06, 46.25, 44.97, 21.69, 13.94, 13.61.

HRMS (APCI): calcd for $C_{23}H_{24}NO_2S^+$ $[M + H]^+$: 378.1522; found: 378.1518.

m.p.: 173 – 176 °C

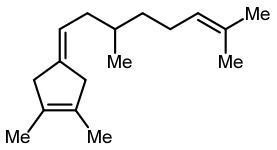


(*Z*)-1,2-dimethyl-4-(oct-5-en-1-ylidene)cyclopent-1-ene (17). According to General Procedure F: (*Z*)-1,1-dichlorononа-1,6-diene (38.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 μL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 28.2 mg, 69% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.29 (m, 2H), 5.26 (tp, J = 7.2, 2.4 Hz, 1H), 2.98 (tt, J = 2.6, 1.3 Hz, 2H), 2.91 (ddp, J = 3.6, 2.4, 1.2 Hz, 2H), 2.10 – 1.92 (m, 6H), 1.65 -1.61 (m, 6H), 1.45 – 1.37 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.62, 131.89, 130.29, 129.76, 129.29, 121.32, 44.61, 41.37, 29.78, 29.33, 26.98, 20.68, 14.53, 13.88, 13.72.

HRMS (APCI): calcd for $C_{15}H_{25}^+$ $[M + H]^+$: 205.1951; found: 205.1950.

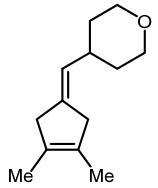


4-(3,7-dimethyloct-6-en-1-ylidene)-1,2-dimethylcyclopent-1-ene (18). According to General Procedure F: 1,1-dichloro-4,8-dimethylnona-1,7-diene (44.2 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene (68 μL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 32.2 mg, 69% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 5.28 (tp, J = 7.2, 2.3 Hz, 1H), 5.10 (ddq, J = 8.5, 5.7, 1.4 Hz, 1H), 3.00 (dq, J = 2.5, 1.2 Hz, 2H), 2.91 (ddq, J = 3.7, 2.6, 1.2 Hz, 2H), 2.05 – 1.89 (m, 3H), 1.85 – 1.75 (m, 1H), 1.68 (q, J = 1.3 Hz, 3H), 1.64-1.61 (m, 6H), 1.61 (s, br, 3H), 1.54 – 1.44 (m, 1H), 1.36 (dddd, J = 13.2, 9.5, 6.3, 5.5 Hz, 1H), 1.14 (dddd, J = 13.6, 9.5, 7.8, 6.0 Hz, 1H), 0.88 (d, J = 6.7 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.99, 131.14, 130.28, 129.81, 125.20, 120.20, 44.66, 41.60, 37.06, 36.98, 33.29, 25.91, 25.88, 19.77, 17.79, 13.88, 13.72.

HRMS (APCI): calcd for $C_{17}H_{27}^+$ $[M + H]^+$: 231.2107; found: 231.2105.

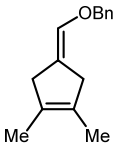


4-((3,4-dimethylcyclopent-3-en-1-ylidene)methyl)tetrahydro-2H-pyran (19). According to General Procedure F: 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (36.2 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene(68 μL, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 35.4 mg, 92% yield.

^1H NMR (800 MHz, $CDCl_3$) δ 5.12 (dp, J = 9.2, 2.4 Hz, 1H), 3.94 (ddd, J = 11.5, 4.5, 2.1 Hz, 2H), 3.42 (td, J = 11.7, 2.2 Hz, 2H), 2.98 (q, J = 2.0 Hz, 2H), 2.96 (dq, J = 2.7, 1.4 Hz, 2H), 2.26 (dddd, J = 15.4, 11.2, 8.5, 4.1 Hz, 1H), 1.64 (tt, J = 2.3, 1.2 Hz, 3H), 1.62 (tt, J = 2.3, 1.1 Hz, 3H), 1.54 (ddq, J = 13.2, 4.2, 2.1 Hz, 2H), 1.42 (dtd, J = 13.5, 11.6, 4.4 Hz, 2H).

$^{13}C\{^1H\}$ NMR (201 MHz, $CDCl_3$) δ 137.95, 130.38, 129.59, 125.80, 68.01, 44.68, 41.15, 36.08, 32.71, 13.85, 13.70.

HRMS (APCI): calcd for $C_{13}H_{20}O^+$ M^+: 192.1514; found: 192.1515.



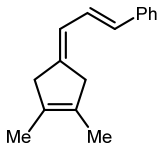
(((3,4-dimethylcyclopent-3-en-1-ylidene)methoxy)methyl)benzene (20). According to General Procedure F: (((2,2-dichlorovinyl)oxy)methyl)benzene (41.0 mg, 0.20 mmol, 1.0 equiv);

2,3-dimethylbutadiene (45 μL, 0.40 mmol, 2.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 11.2 mg, 26% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.06 – 6.03 (m, 1H), 4.78 (s, 2H), 3.04 (ddq, *J* = 3.3, 2.2, 1.1 Hz, 2H), 2.94 (pd, *J* = 2.2, 1.0 Hz, 2H), 1.64 (tq, *J* = 2.0, 1.0 Hz, 3H), 1.62 (tq, *J* = 2.2, 1.0 Hz, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 138.32, 137.80, 129.89, 129.75, 128.57, 127.83, 127.44, 117.16, 73.56, 40.50, 40.08, 13.82, 13.78.

HRMS (APCI): calcd for $C_{15}H_{19}O^+$ $[M + H]^+$: 215.1430; found: 215.1429.



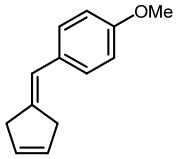
(*E*)-(3-(3,4-dimethylcyclopent-3-en-1-ylidene)prop-1-en-1-yl)benzene (21). According to General Procedure F: (*E*)-(4,4-dichlorobuta-1,3-dien-1-yl)benzene (40.0 mg, 0.20 mmol, 1.0 equiv); 2,3-dimethylbutadiene(45 μL, 0.40 mmol, 2.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, pentane). 34.5 mg, 82% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.16 (m, 1H), 6.85 (dd, *J* = 15.6, 10.9 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.14 – 6.10 (m, 1H), 3.21 (d, *J* = 3.3 Hz, 2H), 3.14 – 3.13 (m, 2H), 1.69 (tq, *J* = 2.2, 1.1 Hz, 3H), 1.66 (tq, *J* = 2.2, 1.1 Hz, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 144.29, 138.22, 129.96, 129.52, 129.27, 128.68, 127.05, 126.23, 121.71, 45.28, 42.10, 13.85, 13.69.

HRMS (ESI): calcd for $C_{16}H_{17}^+$ $[M – H]^+$: 209.1330; found: 209.1333.

m.p.: 49 – 52 °C



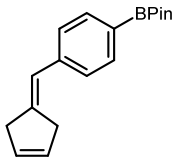
1-(cyclopent-3-en-1-ylidenemethyl)-4-methoxybenzene (22). According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); butadiene (13.5 mL of gas, 0.60 mmol, 3.0 equiv); [i-^{Pr}NDI]$Ni_2(C_6H_6)$ **3** (5 mol%); rt for 24 h in THF (1.80 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexanes). 33.3 mg, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 6.93 – 6.84 (m, 2H), 6.39 (p, *J* = 2.6 Hz, 1H), 5.85 (s, 2H), 3.82 (s, 3H), 3.31 (d, *J* = 2.6 Hz, 2H), 3.29 (d, *J* = 2.2 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.89, 140.33, 131.30, 129.89, 129.42, 129.19, 122.07, 113.85, 55.41, 41.44, 37.87.

HRMS (APCI): calcd for $C_{13}H_{13}O^+$ $[M – H]^+$: 185.0961; found: 185.0962.

m.p.: 51 – 53 °C

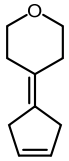


2-(4-(cyclopent-3-en-1-ylidenemethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23). According to General Procedure G: 2-(4-(2,2-dichlorovinyl)-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59.8 mg, 0.20 mmol, 1.0 equiv); butadiene (13.5 mL of gas, 0.60 mmol, 3.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) (5 mol%); rt for 24 h in THF (1.80 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:10:50 Et_2O/CH_2Cl_2/hexanes). 46.7 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.34 – 7.29 (m, 2H), 6.47 (p, *J* = 2.5 Hz, 1H), 5.85 (s, 2H), 3.35 (d, *J* = 2.6 Hz, 2H), 3.32 (d, *J* = 2.1 Hz, 2H), 1.35 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.22, 141.12, 134.92, 129.87, 129.21, 127.36, 122.92, 83.82, 41.70, 38.14, 25.02.

HRMS (APCI): calcd for $C_{18}H_{24}B^{10}O_2^+$ [M + H]$^+$: 282.1900; found: 282.1897.

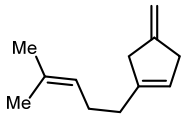


4-(cyclopent-3-en-1-ylidene)tetrahydro-2H-pyran (24). According to General Procedure F: 4-(dichloromethylene)tetrahydro-2H-pyran (33.4 mg, 0.20 mmol, 1.0 equiv); butadiene (13.5 mL of gas, 0.60 mmol, 3.0 equiv); ***(S,S)*- L10** (4.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%; rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:25 Et_2O/hexanes). 13.8 mg, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (m, 2H), 3.67 (t, *J* = 5.6, 4H), 3.10 – 2.94 (m, 4H), 2.22 (ddq, *J* = 6.8, 4.1, 1.4 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.07, 129.83, 125.61, 68.68, 36.33, 32.12.

HRMS (ESI): calcd for $C_{10}H_{15}O^+$ [M + H]$^+$: 151.1117; found: 151.1116.

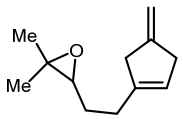


4-methylene-1-(4-methylpent-3-en-1-yl)cyclopent-1-ene (25). According to General Procedure F: 1,1-dichloroethene (16.0 µL, 0.20 mmol, 1.0 equiv); myrcene (70 µL, 0.40 mmol, 2.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 19.2 mg, 59% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (ddt, *J* = 3.6, 2.4, 1.4 Hz, 1H), 5.12 (tdd, *J* = 6.7, 3.0, 1.5 Hz, 1H), 4.94 (dddp, *J* = 4.7, 3.6, 2.3, 1.2 Hz, 2H), 3.06 (h, *J* = 2.2 Hz, 2H), 3.00 (qd, *J* = 2.2, 1.1 Hz, 2H), 2.20 – 2.02 (m, 4H), 1.69 (d, *J* = 1.5 Hz, 3H), 1.69 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.22, 143.82, 131.74, 124.41, 122.46, 106.70, 41.69, 39.27, 31.61, 26.38, 25.84, 17.84.

HRMS (ESI): calcd for $C_{12}H_{17}^+$ $[M - H]^+$: 161.1325; found: 161.1327.

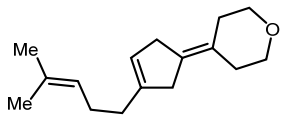


2,2-dimethyl-3-(2-(4-methylenecyclopent-1-en-1-yl)ethyl)oxirane (26). According to General Procedure F: 1,1-dichloroethene (16.0 µL, 0.20 mmol, 1.0 equiv); 2,2-dimethyl-3-(3-methylenepent-4-en-1-yl)oxirane (60 µL, 0.40 mmol, 2.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:20 Et_2O/pentane). 15.5 mg, 44% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (ddt, J = 3.6, 2.4, 1.4 Hz, 1H), 4.95 (dddp, J = 4.7, 3.5, 2.3, 1.2 Hz, 2H), 3.06 (h, J = 2.2 Hz, 2H), 3.02 (tp, J = 2.2, 1.0 Hz, 2H), 2.73 (t, J = 6.2 Hz, 1H), 2.31 – 2.14 (m, 2H), 1.69 (td, J = 7.7, 6.2 Hz, 2H), 1.31 (s, 3H), 1.26 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.75, 142.81, 123.14, 106.99, 64.26, 58.52, 41.62, 39.25, 28.26, 27.15, 25.02, 18.88.

HRMS (ESI): calcd for $C_{14}H_{19}O^+$ $[M + H]^+$: 179.1430; found: 179.1433.

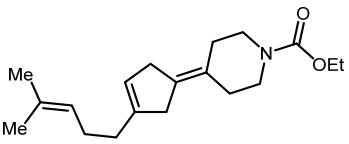


4-(3-(4-methylpent-3-en-1-yl)cyclopent-3-en-1-ylidene)tetrahydro-2H-pyran (27). According to General Procedure F: 4-(dichloromethylene) tetrahydro-2H-pyran (33.4 mg, 0.20 mmol, 1.0 equiv); myrcene (70 µL, 0.60 mmol, 3.0 equiv); **(*S,S*)- L10** (4.4 mg, 0.01 mmol, 5 mol%) and $Ni(DME)Br_2$ (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:25 Et_2O/hexanes). 32.3 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.40 (m, 1H), 5.12 (m, 1H), 3.67 (td, J = 5.5, 2.5 Hz, 4H), 3.00 (s, 2H), 2.95 (s, 2H), 2.21 (q, J = 5.8 Hz, 4H), 2.17 – 2.07 (m, 4H), 1.69 (s, 3H), 1.61 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.54, 131.74, 125.34, 124.42, 122.36, 68.70, 38.97, 36.46, 32.06, 31.79, 31.70, 26.42, 25.84, 17.85.

HRMS (ESI): calcd for $C_{10}H_{25}O^+$ $[M + H]^+$: 233.1900; found: 233.1902.



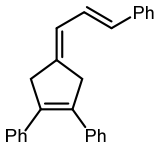
ethyl 4-(3-(4-methylpent-3-en-1-yl)cyclopent-3-en-1-ylidene)piperidine-1-carboxylate (28). According to General Procedure F: 4-(dichloromethylene)tetrahydro-2H-pyran (47.6 mg, 0.20 mmol, 1.0 equiv); myrcene (70 µL, 0.40 mmol, 2.0 equiv); **(*S,S*)- L10** (4.4 mg, 0.01 mmol,

5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a pale yellow oil following purification by column chromatography (SiO_2, 1:25 Et_2O/hexanes). 30.5 mg, 50% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.38 (m, 1H), 5.16 – 5.07 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.40 (m, 4H), 3.00 (s, 2H), 2.95 (s, 2H), 2.23 – 2.05 (m, 8H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.61 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.81, 143.52, 132.70, 131.77, 125.74, 124.39, 122.34, 61.33, 44.52, 39.16, 36.65, 31.67, 30.66, 30.38, 26.41, 25.84, 17.86, 14.88.

HRMS (ESI): calcd for $C_{19}H_{29}NO_2^+$ $[M - H]^+$: 302.2115; found: 302.2109.



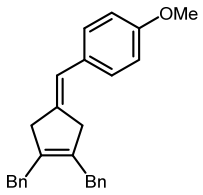
(*E*)-(4-(3-phenylallylidene)cyclopent-1-ene-1,2-diyl)dibenzene (29). According to General Procedure F: (*E*)-(4,4-dichlorobuta-1,3-dien-1-yl)benzene (40.0 mg, 0.20 mmol, 1.0 equiv); 2,3-diphenyl-butadiene (124.0 mg, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, pentane). 30.3 mg, 45% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.34 - 7.30 (m, 2H), 7.28 – 7.17 (m, 11H), 6.93 (dd, *J* = 15.6, 10.9 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.27 (dp, *J* = 11.0, 2.4 Hz, 1H), 3.86 (d, *J* = 2.6 Hz, 2H), 3.79 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.70, 138.00, 137.88, 137.71, 136.07, 135.72, 130.22, 128.74, 128.36, 128.33, 128.28, 128.25, 127.29, 127.11, 127.08, 126.47, 126.35, 122.70, 45.79, 42.73.

HRMS (APCI): calcd for $C_{26}H_{23}^+$ $[M + H]^+$: 335.1794; found: 335.1797.

m.p.: 149 – 152 °C



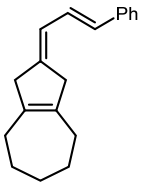
((4-(4-methoxybenzylidene)cyclopent-1-ene-1,2-diyl)bis(methylene))dibenzene (30). According to General Procedure F: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); 2,3-dibenzyl-butadiene (140.0 mg, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexanes). 37.6 mg, 51% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.23 – 7.19 (m, 2.5 Hz, 6H), 7.17 – 7.11 (m, 2H), 6.85 – 6.80 (m, 2H), 6.24 (p, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 3.61 (d, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.79, 139.90, 139.78, 138.98, 134.43, 134.39, 131.19, 129.12, 128.81, 128.72, 128.64, 128.58, 126.19, 121.79, 113.80, 55.37, 44.65, 41.19, 34.94, 34.76.

HRMS (ESI): calcd for $C_{27}H_{25}O^+$ $[M - H]^+$: 365.1900; found: 365.1904.

m.p.: 79 – 81 °C

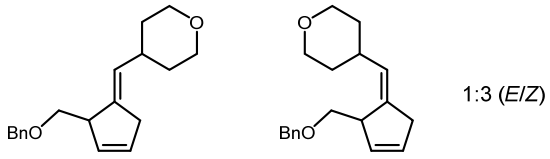


(*E*)-2-(3-phenylallylidene)-1,2,3,4,5,6,7,8-octahydroazulene (31). According to General Procedure F: (*E*)-(4,4-dichlorobuta-1,3-dien-1-yl)benzene (40.0 mg, 0.20 mmol, 1.0 equiv); 1,2-dimethylenecycloheptane (73.2 mg, 0.60 mmol, 3.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (0.40 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, pentane). 50.7 mg, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 6.83 (dd, *J* = 15.6, 10.9 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.12 – 6.04 (m, 1H), 3.27 (s, 2H), 3.20 (s, 2H), 2.19 – 2.08 (m, 4H), 1.74 – 1.66 (m, 2H), 1.64 - 1.57 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.25, 138.25, 136.23, 135.79, 129.18, 128.68, 127.07, 127.02, 126.23, 121.62, 46.65, 43.43, 30.75, 30.29, 30.08, 27.72.

HRMS (ESI): calcd for $C_{19}H_{21}^+$ $[M - H]^+$: 249.1638; found: 249.1634.

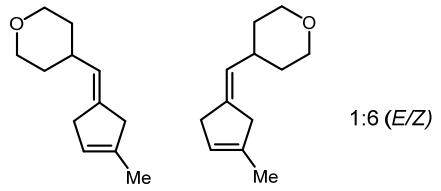


4-((2-((benzyloxy)methyl)cyclopent-3-en-1-ylidene)methyl)tetrahydro-2H-pyran (32). According to General Procedure G: 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (36.2 mg, 0.20 mmol, 1.0 equiv); (*Z*)-((penta-2,4-dien-1-yloxy)methyl)benzene (69.6 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (14.6 mg, 10 mol%); rt for 24 h in Et_2O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:19 Et_2O/pentane). 35.3 mg, 62% yield (*E*/*Z* = 1:3).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 4H, ***E***/***Z***), 7.30 - 7.27 (m, 1H, ***E***/***Z***), 5.95 – 5.80 (m, 2H ***E***/***Z***), 5.27 (dd, *J* = 9.0, 2.4 Hz, 1H, ***E***), 5.20 (dd, *J* = 9.9, 2.2 Hz, 1H ***Z***), 4.56 – 4.49 (m, 2H, ***E***/***Z***), 3.95 (ddd, *J* = 11.5, 4.4, 2.1 Hz, 2H, ***E***), 3.91 (ddd, *J* = 11.4, 4.7, 1.9 Hz, 1H, ***Z***), 3.83 (ddd, *J* = 11.5, 4.5, 2.0 Hz, 1H, ***Z***), 3.59 (ddd, *J* = 7.9, 5.8, 2.2 Hz, 1H, ***Z***), 3.50 (dt, *J* = 8.9, 5.6 Hz, 1H, ***E***/***Z***), 3.47 – 3.41 (m, 3H, ***E***), 3.39 – 3.33 (m, 1H, ***E***/***Z***), 3.29 (t, *J* = 8.5 Hz, 1H, ***Z***), 3.22 (td, *J* = 11.7, 2.6 Hz, 1H, ***Z***), 3.11 (dq, *J* = 20.4, 2.4 Hz, 1H, ***Z***), 3.08 – 3.00 (m, 2H, ***E***), 2.91 (dq, *J* = 20.4, 2.0 Hz, 1H, ***Z***), 2.38 (qt, *J* = 10.9, 4.2 Hz, 1H, ***Z***), 2.29 (dddd, *J* = 15.3, 11.1, 8.5, 4.1 Hz, 1H, ***E***), 1.57 – 1.52 (m, 2H, ***E***), 1.49 (ddq, *J* = 13.5, 4.2, 2.2 Hz, 1H, ***Z***), 1.47 – 1.42 (m, 2H, ***E***), 1.42 – 1.32 (m, 3H, ***Z***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 139.61(***E***), 138.75(***E***), 138.69, 138.51, 132.73, 132.56, 130.89, 129.91(***E***), 129.11, 128.49, 127.81, 127.74, 127.65(***E***), 127.62(***E***), 75.11(***E***), 73.94, 73.29, 73.25(***E***), 67.92(***E***), 67.79, 67.65, 50.19(***E***), 47.73, 38.95, 36.23(***E***), 35.77(***E***), 35.64, 33.39, 33.03, 32.69(***E***), 32.51(***E***).

HRMS (ESI): calcd for $C_{19}H_{25}O_2^+$ $[M + H]^+$: 285.1849; found: 285.1851.

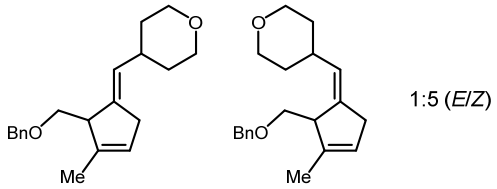


4-((3-methylcyclopent-3-en-1-ylidene)methyl)tetrahydro-2H-pyran (33). According to General Procedure G: 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (36.2 mg, 0.20 mmol, 1.0 equiv); isoprene (60 µL, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (14.6 mg, 10 mol%); rt for 24 h in Et_2O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:4 to 1:1 CH_2Cl_2/pentane). 34.9 mg, 98% yield (*E*/*Z* = 1:6).

^{1}H NMR (800 MHz, $CDCl_3$) δ 5.36 (dp, *J* = 3.9, 1.9 Hz, 1H, ***Z***), 5.35-5.34 (m, 1H, ***E***), 5.17 – 5.13 (m, 1H, ***E***/***Z***), 3.94 (m, 2H, ***E***/***Z***), 3.44 – 3.40 (m, 2H, ***E***/***Z***), 3.02 (h, *J* = 2.3 Hz, 2H, ***Z***), 2.99 (h, *J* = 2.4 Hz, 2H, ***E***), 2.95 (s, 2H, ***E***), 2.93 (s, 2H, ***Z***), 2.29 – 2.24 (m, 1H, ***E***/***Z***), 1.74 (tq, *J* = 2.5, 1.2 Hz, 3H, ***Z***), 1.72 (tt, *J* = 2.4, 1.2 Hz, 3H, ***E***), 1.57-1.53 (m, 2H, ***E***/***Z***), 1.45 – 1.40 (m, 2H, ***E***/***Z***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 139.71(***E***), 139.55, 138.89, 126.35, 123.62, 122.89 (***E***), 67.99, 43.25(***E***), 39.78, 39.40, 36.28, 35.98(***E***), 35.82(***E***), 32.66, 16.98, 16.86(***E***).

HRMS (APCI): calcd for $C_{12}H_{18}O^+$ M^+: 178.1358; found: 178.1355.



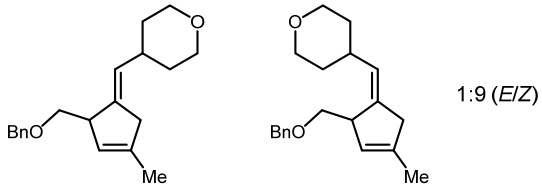
4-((2-((benzyloxy)methyl)-3-methylcyclopent-3-en-1-ylidene)methyl)tetrahydro-2H-pyran (34). According to General Procedure G: 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (36.2 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(((3-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene (75.2 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (14.6 mg, 10 mol%); rt for 24 h in Et_2O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:19 Et_2O/pentane). 37.3 mg, 62% yield (*E*/*Z* = 1:5).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H, ***E***/***Z***), 7.28 - 7.27 (m, 1H, ***E***/***Z***), 5.48 – 5.46 (m, 1H, ***E***/***Z***), 5.26 (dq, *J* = 8.9, 2.5 Hz, 1H, ***E***), 5.13 (dq, *J* = 9.9, 1.9 Hz, 1H, ***Z***), 4.56 – 4.46 (m, 2H, ***E***/***Z***), 3.95 (dtt, *J* = 9.9, 4.0, 2.3 Hz, 2H, ***E***), 3.91 (ddd, *J* = 11.4, 4.6, 2.0 Hz, 1H, ***Z***), 3.80 (ddd, *J* = 11.4, 4.4, 2.2 Hz, 1H, ***Z***), 3.56 – 3.46 (m, 2H, ***E***/***Z***), 3.43 (tt, *J* = 11.7, 2.5 Hz, 2H, ***E***), 3.36 (td, *J* = 11.8, 2.3 Hz, 1H, ***Z***), 3.33 (t, *J* = 5.4 Hz, 1H, ***Z***), 3.20 (td, *J* = 11.5, 2.9 Hz, 1H, ***Z***), 3.18 (t, *J* = 5.3 Hz, 1H, ***E***), 3.08 (ddq, *J* = 19.8, 5.0, 2.6 Hz, 1H, ***Z***), 2.98 (qh, *J* = 22.8, 20.5, 18.1, 2.4 Hz, 2H, ***E***), 2.81 (dp, *J* = 19.7, 2.0 Hz, 1H, ***Z***), 2.41 (dtd, *J* = 15.0, 10.9, 4.3 Hz, 1H, ***Z***),

2.30 (dddd, *J* = 16.1, 14.3, 7.9, 3.7 Hz, 1H, ***E***), 1.80 (dp, *J* = 2.7, 0.9 Hz, 3H, ***Z***), 1.77 (dp, *J* = 2.4, 1.2 Hz, 3H, ***E***), 1.58 – 1.53 (m, 2H, ***E***), 1.49 (ddq, *J* = 13.4, 4.1, 2.1 Hz, 1H, ***Z***), 1.47 – 1.41 (m, 2H, ***E***), 1.41 – 1.31 (m, 3H, ***Z***)

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 141.34(***E***), 141.15(***Z***), 141.12(***E***), 140.72(***Z***), 138.81(***E***), 138.57(***Z***), 128.46(***Z***), 128.44(***E***), 128.25(***Z***), 127.80(***Z***), 127.68(***Z***), 127.63(***E***), 127.56(***E***), 127.22(***E***), 124.94(***Z***), 124.07(***E***), 73.57(***E***), 73.37(***Z***), 73.30(***E***), 73.17(***Z***), 67.96(***E***), 67.83(***Z***), 67.72(***Z***), 53.00(***E***), 50.70(***Z***), 38.73(***Z***), 35.93(***E***), 35.32(***Z***), 35.08(***E***), 33.25(***Z***), 33.07(***Z***), 32.74(***E***), 32.61(***E***), 16.29(***Z***), 15.92(***E***).

HRMS (ESI): calcd for $C_{20}H_{27}O_2^+$ $[M + H]^+$: 299. 2006; found: 299.2009.

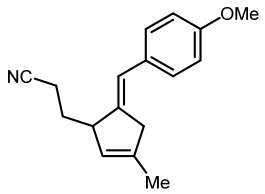


4-((2-((benzyloxy)methyl)-4-methylcyclopent-3-en-1-ylidene)methyl)tetrahydro-2H-pyran (35). According to General Procedure G: 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (36.2 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(((4-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene (75.2 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (14.6 mg, 10 mol%); rt for 24 h in Et_2O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO_2, 1:19 Et_2O/pentane). 44.2 mg, 74% yield (*E*/*Z* = 9/1).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 4H, ***E***/***Z***), 7.30 – 7.27 (m, 1H, ***E***/***Z***), 5.50 – 5.48 (m, 1H, ***Z***), 5.48 (hept, *J* = 1.7 Hz, 1H, ***E***), 5.22 (dq, *J* = 8.9, 2.3 Hz, 1H, ***E***), 5.15 (dd, *J* = 9.9, 2.1 Hz, 1H, ***Z***), 4.53 (d, *J* = 2.6 Hz, 2H, ***E***), 4.50 (d, *J* = 11.2 Hz, 2H, ***Z***), 3.95 (ddt, *J* = 11.7, 3.8, 1.5 Hz, 2H, ***E***), 3.90 (ddd, *J* = 11.4, 4.7, 1.9 Hz, 1H, ***Z***), 3.82 (ddd, *J* = 11.5, 4.5, 2.2 Hz, 1H, ***Z***), 3.55 (ddt, *J* = 6.0, 3.8, 1.9 Hz, 1H, ***Z***), 3.48 – 3.40 (m, 4H, ***E***), 3.36 (td, *J* = 11.7, 2.3 Hz, 1H, ***Z***), 3.33 (dd, *J* = 8.5, 7.5 Hz, 1H, ***E***), 3.28 (dd, *J* = 8.9, 8.0 Hz, 1H, ***Z***), 3.21 (td, *J* = 11.5, 2.8 Hz, 1H, ***Z***), 3.09 – 3.04 (m, 1H, ***Z***), 3.01 – 2.90 (m, 2H, ***E***), 2.79 – 2.76 (m, 1H, ***Z***), 2.37 (dtd, *J* = 15.0, 10.8, 4.2 Hz, 1H, ***Z***), 2.28 (dddd, *J* = 15.3, 11.2, 8.5, 4.1 Hz, 1H, ***E***), 1.77 (p, *J* = 1.2 Hz, 3H, ***E***), 1.75 (p, *J* = 1.4 Hz, 3H, ***Z***), 1.58 – 1.51 (m, 2H, ***E***), 1.49 (ddd, *J* = 9.2, 4.7, 2.1 Hz, 1H, ***Z***), 1.47 – 1.41 (m, 2H, ***E***), 1.40 – 1.32 (m, 3H, ***Z***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 140.72(***Z***), 140.62(***E***), 139.68(***Z***), 139.65(***E***), 138.85(***E***), 138.61(***Z***), 128.73(***Z***), 128.47(***E***), 127.80(***Z***), 127.70(***Z***), 127.66(***E***), 127.58(***E***), 127.42(***E***), 126.28(***E***), 126.07(***Z***), 75.35(***E***), 74.15(***Z***), 73.22(***E***), 67.95(***E***), 67.81(***Z***), 67.67(***Z***), 50.57(***E***), 48.13(***Z***), 43.05(***Z***), 40.00(***E***), 36.22(***E***), 35.41(***Z***), 33.40(***Z***), 33.06(***Z***), 32.73(***E***), 32.55(***E***), 17.00(***E***), 16.98(***Z***).

HRMS (ESI): calcd for $C_{20}H_{27}O_2^+$ $[M + H]^+$: 299. 2006; found: 299.2010.

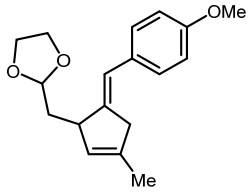


(*E*)-3-(5-(4-methoxybenzylidene)-3-methylcyclopent-2-en-1-yl)propanenitrile (36). According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); (*Z*)-6-methylhepta-4,6-dienenitrile (48.5 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-}Pr}$NDI]Ni$_2$(C$_6$H$_6$) **3** (14.6 mg, 10 mol%); rt for 24 h in Et$_2$O/NMP (0.80 mL/0.10 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO$_2$, 1:4 CH$_2$Cl$_2$/hexanes). 30.8 mg, 61% yield (*E*/*Z* = 13/1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.23 (m, 2H), 6.92 – 6.87 (m, 2H), 6.29 (q, *J* = 2.4 Hz, 1H), 5.37 (p, *J* = 1.9 Hz, 1H), 3.82 (s, 3H), 3.56 – 3.45 (m, 1H), 3.28 – 3.15 (m, 2H), 2.40 – 2.24 (m, 2H), 2.03 – 1.86 (m, 2H), 1.83 – 1.81 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.28, 142.43, 141.13, 130.53, 129.47, 125.17, 122.92, 120.38, 113.94, 55.42, 50.79, 42.37, 31.27, 16.91, 13.77.

HRMS (APCI): calcd for C$_{17}$H$_{20}$NO$^+$ [M + H]$^+$: 254.1545; found: 254.1547.

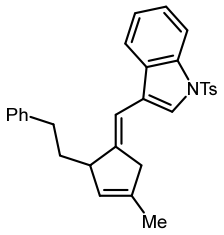


(*E*)-2-((5-(4-methoxybenzylidene)-3-methylcyclopent-2-en-1-yl)methyl)-1,3-dioxolane (37). According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); (*Z*)-2-(4-methylpenta-2,4-dien-1-yl)-1,3-dioxolane (61.6 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-}Pr}$NDI]Ni$_2$(C$_6$H$_6$) **3** (14.6 mg, 10 mol%); rt for 24 h in Et$_2$O/NMP (0.80 mL/0.10 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO$_2$, 1:9 Et$_2$O/hexanes). 34.3 mg, 60% yield (*E*/*Z* = 16/1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.22 (m, 2H), 6.87 (dd, *J* = 9.3, 2.6 Hz, 2H), 6.32 (q, *J* = 2.4 Hz, 1H), 5.54 (p, *J* = 1.8 Hz, 1H), 4.99 (t, *J* = 5.0 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.91 – 3.84 (m, 2H), 3.81 (s, 3H), 3.49 (ddd, *J* = 9.6, 5.1, 2.2 Hz, 1H), 3.32 – 3.11 (m, 2H), 1.99 (dt, *J* = 13.8, 5.1 Hz, 1H), 1.80 – 1.78 (m, 3H), 1.78 – 1.73 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 157.97, 144.94, 138.79, 131.15, 129.39, 127.26, 122.07, 113.82, 103.85, 65.04, 64.90, 55.40, 48.19, 41.91, 40.85, 16.95.

HRMS (ESI): calcd for C$_{18}$H$_{21}$O$_3^+$ [M – H]$^+$: 285.1485; found: 285.1491.

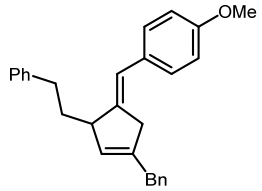


(*E*)-3-((4-methyl-2-phenethylcyclopent-3-en-1-ylidene)methyl)-1-tosyl-1H-indole (38). According to General Procedure G: 3-(2,2-dichlorovinyl)-1-tosyl-1H-indole (73.0 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (68.8 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (14.6 mg, 10 mol%); rt for 24 h in THF/NMP (1.60 mL/0.20 mL). The product was isolated as a pale yellow solid following purification by column chromatography (SiO$_2$, 1:4 DCM/hexane). 68.9 mg, 74% yield (*E*/*Z* = 16/1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.46 (s, 1H), 7.36 – 7.14 (m, 9H), 6.46 (q, *J* = 2.5 Hz, 1H), 5.55 (p, *J* = 1.8 Hz, 1H), 3.47 (tt, *J* = 5.3, 2.6 Hz, 1H), 3.28 – 3.11 (m, 2H), 2.76 – 2.61 (m, 2H), 2.33 (s, 3H), 2.07 – 1.95 (m, 1H), 1.89 (s, 3H), 1.82 (dddd, *J* = 13.6, 10.3, 6.0, 3.9 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 149.42, 144.99, 142.82, 138.81, 135.35, 134.73, 130.79, 129.99, 128.54, 128.47, 127.35, 126.89, 125.83, 125.02, 123.31, 122.35, 120.46, 119.46, 113.75, 110.42, 51.31, 43.80, 38.19, 33.18, 21.70, 17.05.

HRMS (ESI): calcd for C$_{30}$H$_{30}$NO$_2$S$^+$ [M + H]$^+$: 468.1992; found: 468.1982.

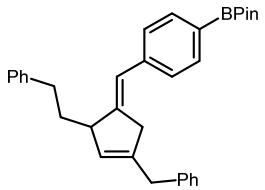


(*E*)-1-((4-benzyl-2-phenethylcyclopent-3-en-1-ylidene)methyl)-4-methoxybenzene (39). According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(2-methylenehex-3-ene-1,6-diyl)dibenzene (99.2 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (7.3 mg, 5 mol%); rt for 24 h in Et$_2$O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO$_2$, 1:4 DCM/hexanes). 65.7 mg, 86% yield (*E*/*Z* = 25/1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.27 (m, *J* = 9.6, 6.5, 5.7, 2.8 Hz, 4H), 7.24 – 7.14 (m, 8H), 6.89 – 6.83 (m, 2H), 6.31 (q, *J* = 2.4 Hz, 1H), 5.55 (h, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 3.49 (s, 2H), 3.47 – 3.39 (m, 1H), 3.34 – 3.09 (m, 2H), 2.66 (ddd, *J* = 9.6, 6.4, 3.1 Hz, 2H), 1.97 (dddd, *J* = 13.3, 9.7, 6.8, 5.0 Hz, 1H), 1.88 – 1.77 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 157.95, 144.57, 142.99, 142.32, 139.52, 131.14, 129.35, 128.94, 128.55, 128.54, 128.45, 128.41, 126.25, 125.78, 122.04, 113.85, 55.41, 51.73, 40.37, 38.24, 38.15, 32.97.

HRMS (ESI): calcd for C$_{28}$H$_{29}$O$^+$ [M + H]$^+$: 381.2213; found: 381.2218.

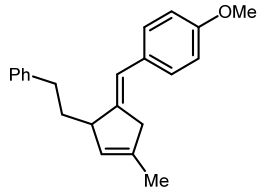


(*E*)-2-(4-((4-benzyl-2-phenethylcyclopent-3-en-1-ylidene)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40). According to General Procedure G: 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59.8 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(2-methylenehex-3-ene-1,6-diyl)dibenzene (99.2 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (7.3 mg, 5 mol%); rt for 24 h in Et$_2$O/NMP (1.60 mL/0.20 mL). The product was isolated as a colorless oil following purification by column chromatography (SiO$_2$, 1:3 CH$_2$Cl$_2$/hexanes to 1:10:30 Et$_2$O/CH$_2$Cl$_2$/hexanes). 71.7 mg, 75% yield (*E*/*Z* = 32/1).

^{1}H NMR (800 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.32 – 7.26 (m, 6H), 7.24 – 7.15 (m, 6H), 6.38 (q, *J* = 2.4 Hz, 1H), 5.54 (h, *J* = 1.7 Hz, 1H), 3.49 (s, 2H), 3.45 (tt, *J* = 4.4, 2.3 Hz, 1H), 3.29 (dt, *J* = 21.1, 2.4 Hz, 1H), 3.19 (dt, *J* = 21.1, 2.1 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.01 – 1.94 (m, 1H), 1.84 (dddd, *J* = 13.4, 10.4, 7.7, 5.8 Hz, 1H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (201 MHz, CDCl$_3$) δ 148.40, 142.86, 142.38, 141.03, 139.43, 134.89, 128.95, 128.57, 128.54, 128.47, 128.09, 127.53, 126.28, 125.82, 122.88, 83.82, 51.92, 40.57, 38.21, 38.05, 32.98, 25.03, 25.00.

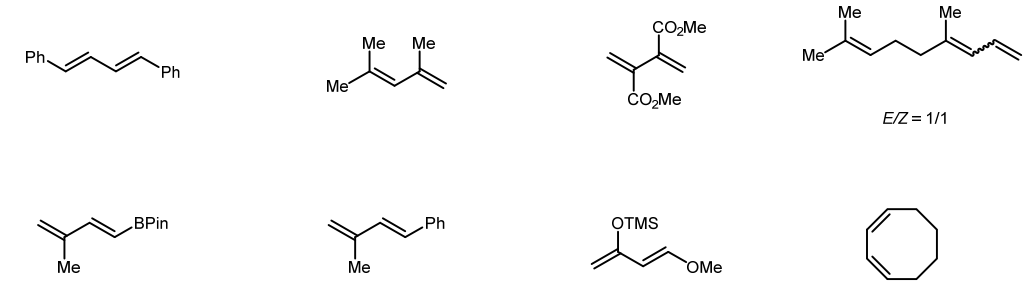
HRMS (APCI): calcd for C$_{33}$H$_{38}$B^{10}O$_2^+$ [M + H]$^+$: 476.2996; found: 476.2991.



(*E*)-1-methoxy-4-((4-methyl-2-phenethylcyclopent-3-en-1-ylidene)methyl)benzene(41). According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); (*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (**59**) (69.5 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (7.3 mg, 5 mol%); rt for 24 h in Et$_2$O/NMP (1.60 mL/0.20 mL). The product was isolated as a yellow oil following purification by column chromatography (SiO$_2$, 1:4 DCM/hexanes). 65.7 mg, 86% yield (*E*/*Z* = 25/1).

Gram Scale Reaction: According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (1.015 g, 5.0 mmol, 1.0 equiv); (*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (**59**) (1.720 g, 10.0 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (185.0 mg, 5 mol%); rt for 24 h in Et$_2$O/NMP (40 mL/5 mL). The product **(41)** was isolated as a yellow oil following purification by column chromatography (SiO$_2$, 1:4 DCM/hexanes). 1.010 g, 66% yield (*E*/*Z* = 21/1).

Examples of 1,3-dienes that did not undergo [4 + 1]-cycloaddition:



Examples of 1,3-dienes that exhibited low yields and/or provided inseperable byproducts:

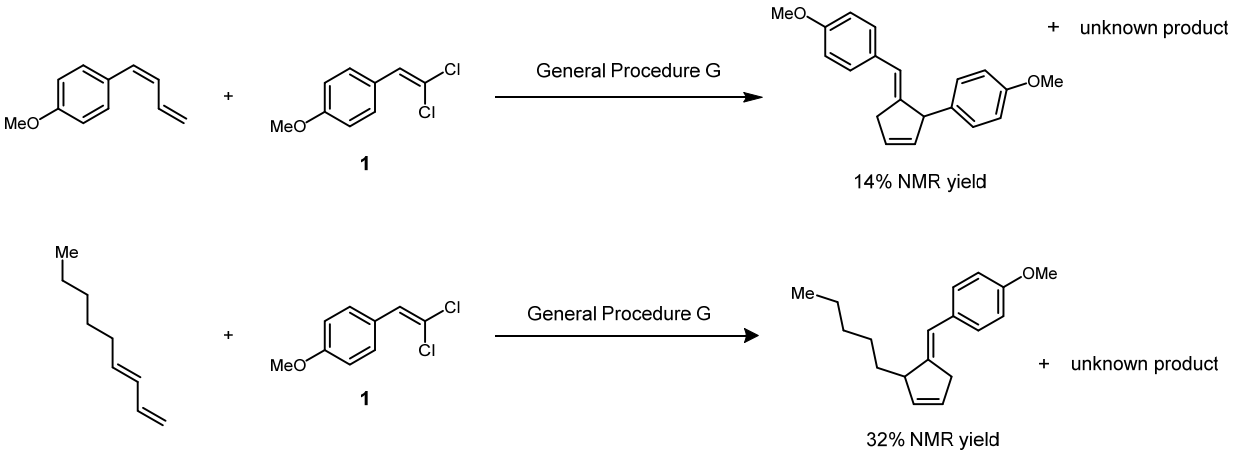
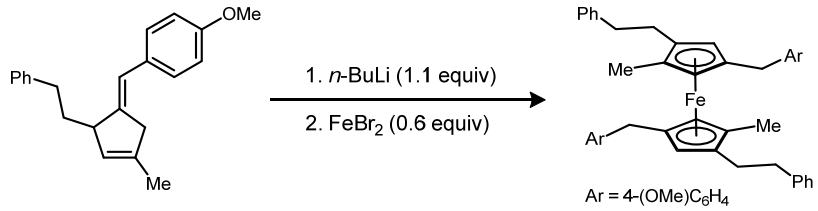


Fig S4. Limitations of the catalytic [4 + 1]-cycloaddition.

7. Synthetic Applications of the [4 + 1]-Cycloadditions Products



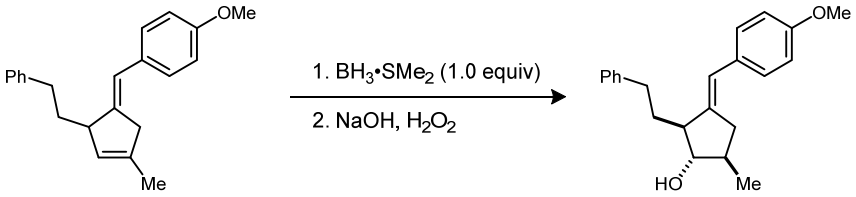
41 **42** 60% Yield

Under an N_2 atmosphere, a solution of **41** (20 mg, 0.066 mmol, 1.0 equiv) dissolved in THF (0.50 mL) was cooled to –30 °C. The solution was stirred, and *n*-BuLi (32 µL, 0.080 mmol, 2.5 M in hexane, 1.2 equiv) was added. The resulting reaction mixture was allowed to warm to room temperature. After 7 h, the reaction mixture was cooled to –30 °C, and $FeBr_2$ (8.5 mg, 0.040 mmol, 0.6 equiv) was added as a solution in THF (0.50 mL). The reaction mixture was stirred for 3 h at room temperature then 21 h at 65 °C. The solvent was removed under reduced pressure, and the product was isolated as an orange solid following purification by column chromatography (SiO_2, 1:19 Et_2O/hexane). 13.0 mg, 60% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 - 7.23 (m, 4H), 7.20 - 7.14 (m, 4H), 7.09 - 7.06 (m, 8 H), 6.81 – 6.76 (m, 4 H), 3.764 (s, 3H), 3.764 (s, 3H), 3.71 (s, *br*, 2H), 3.67 (s, *br*, 2H), 3.57 (s, *br*, 4H), 2.59-2.43 (m, 8H), 1.93 (s, 6H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 157.90, 142.52, 134.13, 129.32, 129.30, 128.49, 128.44, 125.93, 113.80, 86.07, 85.25, 82.09, 72.15, 71.14, 55.41, 37.79, 32.85, 29.90, 14.16.

HRMS (ESI): calcd for $C_{44}H_{46}Fe^{54}O_2^+$ $[M]^+$: 660.2888; found: 660.2881.



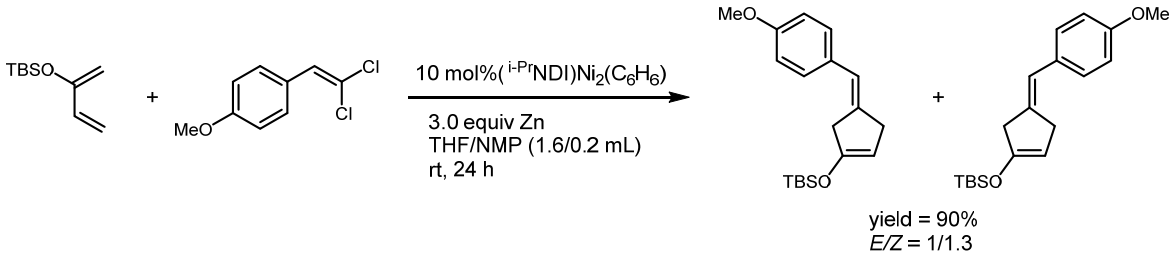
41 **43** 65% Yield

3-((*E*)-4-Methoxybenzylidene)-5-methyl-2-phenethylcyclopentan-1-ol (43). Under an N_2 atmosphere, BH_3·Me_2S (10 µL, 0.10 mmol) was added to a solution of **41** (31.0 mg, 0.10 mmol) in THF (1.0 mL) cooled to 0 °C. After 1 h, the mixture was cooled to –10 °C, and NaOH (60 µL, 10% aq) was added dropwise followed by H_2O_2 (20 µL, 30% aq). After stirring for 15 min at –10 °C, the mixture was diluted with Et_2O and washed with H_2O. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The product was isolated as a white solid following purification by flash chromatography (SiO_2, 1:4 EtOAc/hexane). 21.0 mg, 65% yield, dr = 18/1, E/Z = 7/1.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2H, ***E/Z***), 7.27 – 7.24 (m, 2H, ***E/Z***), 7.23 – 7.21 (m, 2H, ***E/Z***), 7.20 – 7.18 (m, 1H, ***E/Z***), 6.89 – 6.85 (m, 2H, ***E/Z***), 6.23 (q, *J* = 2.2 Hz, 1H, ***Z***), 6.21 (q, *J* = 2.5 Hz, 1H, ***E***), 3.81 (s, 3H, ***E/Z***), 3.46 (td, *J* = 8.8, 5.6 Hz, 1H, ***E/Z***), 2.92 – 2.83 (m, 1H, ***E/Z***), 2.79 (ddd, *J* = 13.8, 10.9, 6.0 Hz, 1H, ***E/Z***), 2.57 – 2.53 (m, 1H, ***E/Z***), 2.18 – 2.08 (m, 1H, ***E/Z***), 1.93 (dddd, *J* = 14.0, 10.9, 7.2, 5.3 Hz, 1H, ***E/Z***), 1.88 – 1.82 (m, 1H, ***E/Z***), 1.53 (d, *J* = 6.0 Hz, 1H, ***E/Z***), 1.15 (d, *J* = 6.5 Hz, 3H, ***E/Z***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 157.99, 142.93, 142.26, 131.19, 129.52, 128.57, 128.55, 125.91, 121.59, 113.82, 83.54, 55.42, 52.65, 41.58, 37.52, 34.38, 32.95, 17.53.

HRMS (ESI): calcd for $C_{22}H_{27}O_2^+$ $[M + H]^+$: 323.2006; found: 323.2002.

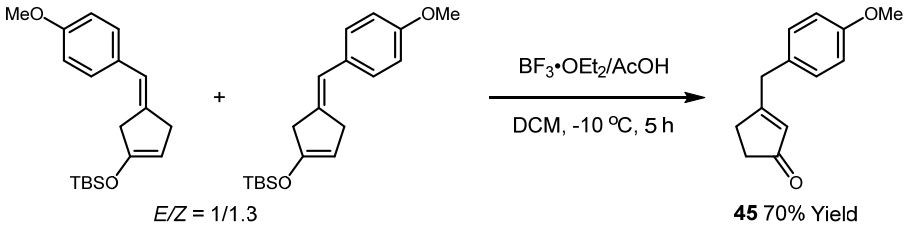


***tert*-Butyl((4-(4-methoxybenzylidene)cyclopent-1-en-1-yl)oxy)dimethylsilane.** According to General Procedure G: 1-(2,2-dichlorovinyl)-4-methoxybenzene (40.6 mg, 0.20 mmol, 1.0 equiv); (buta-1,3-dien-2-yloxy)(*tert*-butyl)dimethylsilane (74.0 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]Ni$_2$(C$_6$H$_6$) **3** (14.6 mg, 10 mol%); rt for 24 h in THF/NMP (1.6 mL/0.20 mL). The product was isolated as a pale yellow oil following purification by column chromatography (SiO_2,1:9 CH_2Cl_2/hexanes). 57.0 mg, 90% yield (*E*/*Z* = 1/1.3)

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H, ***E***/***Z***), 6.90 – 6.86 (m, 2H, ***E***/***Z***), 6.30 (p, *J* = 2.5 Hz, 1H, ***E***), 6.28 (p, *J* = 2.4 Hz, 1H, ***Z***), 4.72 – 4.70 (m, 1H, ***E***/***Z***), 3.81 (s, 3H, ***Z***), 3.81 (s, 3H, ***E***), 3.27 (t, *J* = 2.5 Hz, 2H, ***E***), 3.25 (t, *J* = 2.3 Hz, 2H, ***Z***), 3.21 (m, 2H, ***E***/***Z***), 0.94 (s, 9H, ***E***/***Z***), 0.19 (s, 6H, ***Z***), 0.18 (s, 6H, ***E***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 157.95, 157.91, 153.29, 153.25, 138.14, 137.61, 131.09, 131.03, 129.28, 129.14, 122.70, 122.39, 113.90, 113.84, 101.57, 100.63, 55.40, 42.22, 39.51, 38.25, 35.45, 25.83, 25.82, 18.29, 18.27, -4.39, -4.42.

HRMS (ESI): calcd for $C_{20}H_{27}O_2^+$ $[M + H]^+$: 317.1931; found: 317.1927.

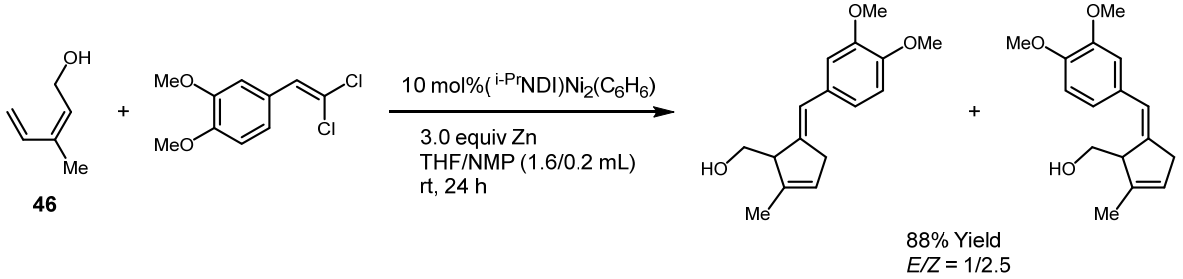


3-(4-methoxybenzyl)cyclopent-2-en-1-one (45). A 2-dram vial was charged with tert-butyl((4-(4-methoxybenzylidene)cyclopent-1-en-1-yl)oxy)dimethylsilane (16.0 mg, 0.05 mmol, 1.0 equiv) and CH_2Cl_2 (2.0 mL). The solution was cooled to –10 °C. $BF_3{\cdot}Et_2O$ (1 µL, 0.005, 0.10 equiv) and AcOH (3 µL, 0.05, 1.0 equiv) were added sequentially. The reaction mixture was stirred at -10 °C. After 5 h, the reaction was allowed to warm to room temperature and quenched with saturated aq. $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, 1:4 EtOAc/hexane). 71.0 mg, 70% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.10 – 7.09 (m, 2H), 6.88 – 6.84 (m, 2H), 5.89 (s, 1H), 3.80 (s, 3H), 3.66 (s, 2H), 2.57 – 2.53 (m, 2H), 2.42 – 2.38 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 209.96, 181.65, 158.74, 130.61, 130.11, 129.03, 114.32, 55.45, 39.39, 35.70, 31.12.

HRMS (ESI): calcd for $C_{13}H_{15}O_2^+$ $[M + H]^+$: 203.1067; found: 203.1065.

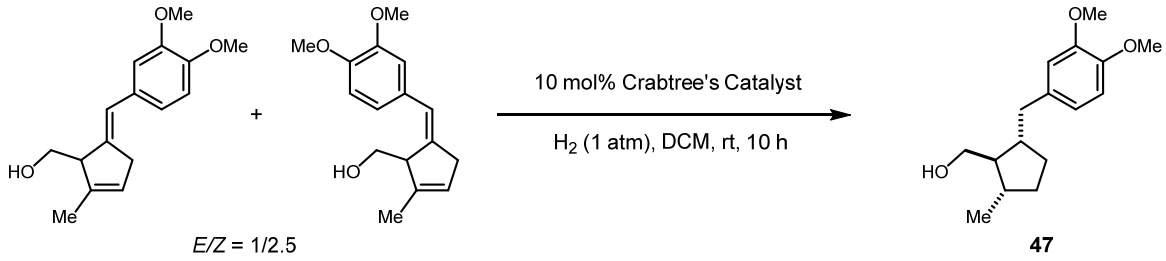


(5-(3,4-dimethoxybenzylidene)-2-methylcyclopent-2-en-1-yl)methanol. According to General Procedure G: 4-(2,2-dichlorovinyl)-1,2-dimethoxybenzene (46.6 mg, 0.20 mmol, 1.0 equiv); (Z)-3-methylpenta-2,4-dien-1-ol (40.0 mg, 0.40 mmol, 2.0 equiv); [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (14.6 mg, 10 mol%); rt for 24 h in THF/NMP (1.6 mL/0.20 mL). The product was isolated as a pale yellow oil following purification by column chromatography (SiO_2, 3:7 EtOAc/hexanes). 46.0 mg, 88% yield (*E*/*Z* = 1/2.5).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.92 – 6.89 (m, 2H, ***E***/***Z***), 6.86 – 6.82 (m, 1H, ***E***/***Z***), 6.45 (q, *J* = 2.2 Hz, 1H, ***Z***), 6.41 (q, *J* = 2.5 Hz, 1H, ***E***), 5.63 (s, 1H, ***E***/***Z***). 3.895 (s, 3H, ***E***), 3.888 (s, 3H, ***E***), 3.881 (s, 3H, ***Z***), 3.877 (s, 3H, ***Z***), 3.79 – 3.61 (m, 3H, ***E***/***Z***), 3.34 – 3.10 (m, 3H, ***E***/***Z***), 1.81 (s, *br*, 3H, ***E***/***Z***).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 148.88 (***Z***), 148.80(***E***), 147.81(***Z***), 142.88(***Z***), 142.51(***E***), 139.69(***Z***), 138.88(***E***), 130.96(***E***), 130.81(***Z***), 125.55(***Z***), 125.53(***E***), 123.88(***Z***), 123.16(***E***), 121.01(***E***), 120.55(***Z***), 111.71(***E***), 111.55(***Z***), 111.29(***Z***), 111.22(***E***), 64.00(***E***), 62.04(***Z***), 57.58(***E***), 56.05(***E***), 56.02(***Z***), 55.97(***E***), 53.13(***Z***), 41.09(***Z***), 37.82(***E***), 15.52(***Z***), 15.18(***E***).

HRMS (ESI): calcd for $C_{16}H_{21}O_3^+$ $[M + H]^+$: 261.1485; found: 261.1487.



2-(3,4-Dimethoxybenzyl)-5-methylcyclopentyl)methanol (47). A 2-dram vial was charged with (5-(3,4-dimethoxybenzylidene)-2-methylcyclopent-2-en-1-yl)methanol (13.0 mg, 0.050 mmol, *E*/*Z* = 1/2.5) and dry CH_2Cl_2 (1.0 mL). After sealing with a rubber septum, the reaction vial was evacuated and back-filled with H_2 three times. A solution of $[Ir(cod)(PCy_3)(py)]PF_6$ (4.1 mg, 0.005, 0.10 equiv) dissolved in CH_2Cl_2 (1.0 mL) was added, and the reaction was stirred under an H_2 atmosphere (balloon pressure). After 10 h, the solution was filtered through celite, eluting with EtOAc (20 mL). The solvent was removed under reduced pressure, and the product was isolated as a pale yellow solid following purification by flash chromatography (SiO_2, 3:7 EtOAc/hexane). 12.1 mg, 92% yield, dr = 18/1.

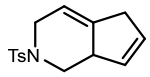
^{1}H NMR (800 MHz, CD_3OD) δ 6.86 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.55 – 3.50 (m, 2H), 2.82 (dd, *J* = 13.5, 5.6 Hz, 1H), 2.43 (dd, *J* = 13.4, 9.4 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.85 – 1.80 (m, 1H), 1.75 (dtd, *J* = 12.3, 7.4, 5.9 Hz, 1H), 1.61 (dq, *J* = 12.9, 7.5 Hz, 1H), 1.40 (ddt, *J* = 12.8, 7.9, 6.1 Hz, 1H), 1.28 (dt, *J* = 12.3, 7.7 Hz, 1H), 1.24 (ddt, *J* = 10.7, 7.9, 4.0 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 148.92, 147.33, 134.47, 120.89, 112.29, 111.23, 65.11, 56.00, 55.74, 44.30, 42.03, 37.39, 33.35, 31.02, 20.73.

HRMS (ESI): calcd for $C_{16}H_{23}O_2^+$ $[M - H_2O]^+$: 247.1693; found: 247.1689.

8. Intramolecular [4 + 1]-Cycloadditions

General Procedure H. In an N_2-filled glovebox, a 3-dram vial was charged with the [NDI] ligand (5–10 mol%), Ni(DME)Br_2 (10–20 mol%), Zn powder (0.60 mmol, 3.0 equiv), and a magnetic stir bar. The reaction solvent was added, and the resulting suspension was stirred for 15 min, during which time the catalyst solution turned purple. The substrate was added to the catalyst/reductant mixture. The vial was sealed, and the reaction mixture was stirred at room temperature. The reaction mixture was diluted with Et_2O (40 mL) and washed with water (2 x 20 mL) and brine (20 mL). The organic phase was concentrated under reduced pressure, and the crude residue was purified by column chromatography.

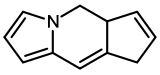


2-tosyl-2,3,5,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (49). According to General Procedure H: (*E*)-N-(3,3-dichloroallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide **48** (69.0 mg, 0.20 mmol, 1.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (4.0 mL). The product was isolated as a white solid following purification by flash chromatography (SiO_2, 1:19 EtOAc/hexane). 35.0 mg, 64% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.32 – 7.29 (m, 2H), 5.87 (dq, *J* = 6.1, 2.3 Hz, 1H), 5.67 (ddtd, *J* = 6.1, 2.7, 1.8, 0.8 Hz, 1H), 5.37 (ddt, *J* = 5.4, 4.1, 2.0 Hz, 1H), 4.17 (dd, *J* = 10.7, 5.2 Hz, 1H), 4.10 – 4.05 (m, 1H), 3.35 (ddp, *J* = 10.7, 5.3, 2.6 Hz, 1H), 3.23 (dqd, *J* = 16.4, 3.2, 1.4 Hz, 1H), 3.09 – 3.04 (m, 1H), 2.89 (dq, *J* = 19.2, 1.7 Hz, 1H), 2.42 (s, 3H), 2.05 (t, *J* = 10.7 Hz, 1H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 143.52, 141.56, 134.09, 132.03, 130.37, 129.76, 127.63, 113.94, 46.92, 45.55, 44.80, 38.09, 21.65.

HRMS (ESI): calcd for $C_{15}H_{17}NO_2SNa^+$ $[M + Na]^+$:298.0872; found: 298.0874.

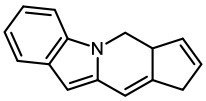


5a,8-dihydro-5*H*-cyclopenta[*f*]indolizine (51). According to General Procedure H: (*E*)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-pyrrole **50** (45.6 mg, 0.20 mmol, 1.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 18 h in THF/NMP (3.60 mL/0.40 mL). The product was isolated as a pale yellow oil following purification by flash chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 25.0 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 2.7, 1.6 Hz, 1H), 6.29 (tt, *J* = 2.7, 1.2 Hz, 1H), 6.11 (dd, *J* = 3.5, 2.7 Hz, 1H), 6.02 (dq, *J* = 6.0, 2.3 Hz, 1H), 5.98 (dd, *J* = 3.5, 1.5 Hz, 1H), 5.77 (dddd, *J* = 7.1, 2.9, 2.0, 1.0 Hz, 1H), 4.20 (dd, *J* = 11.4, 6.5 Hz, 1H), 3.74 (ddq, *J* = 13.9, 6.9, 2.4 Hz, 1H), 3.51 (dd, *J* = 14.0, 11.4 Hz, 1H), 3.20 (qq, *J* = 21.3, 2.2 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.99, 133.27, 130.56, 129.67, 120.73, 112.18, 107.93, 104.84, 49.31, 46.55, 37.01.

HRMS (ESI): calcd for $C_{11}H_{12}N^+$ $[M + H]^+$: 158.0964; found: 158.0961.



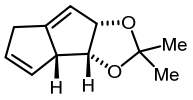
3a,4-dihydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole (53). According to General Procedure H: (*E*)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-indole **52** (55.6 mg, 0.20 mmol, 1.0 equiv); **L4** (6.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 21 h in THF/NMP (3.60 mL/0.40 mL). The product was isolated as a white solid following purification by flash chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 33.7 mg, 81% yield.

Single crystals for X-ray diffraction analysis were obtained from slow evaporation of solution of **53** hexane and THF (2:1).

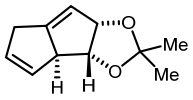
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.17 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.05 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.47 (dp, *J* = 2.7, 1.2 Hz, 1H), 6.33 (s, 1H), 6.07 (dq, *J* = 6.0, 2.3 Hz, 1H), 5.91 – 5.85 (m, 1H), 4.60 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.83 (ddq, *J* = 13.7, 7.0, 2.4 Hz, 1H), 3.46 (dd, *J* = 13.3, 11.2 Hz, 1H), 3.29 (qq, *J* = 21.4, 2.2 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.34, 136.85, 136.31, 132.92, 129.88, 129.24, 121.60, 120.66, 119.55, 112.44, 108.70, 98.48, 46.29, 45.16, 37.47.

HRMS (ESI): calcd for $C_{15}H_{14}N^+$ $[M + H]^+$: 208.1121; found: 208.1123.



cis



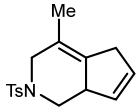
trans

(3a*R*,7a*S*)-2,2-dimethyl-3a,3b,6,7a-tetrahydropentaleno[1,2-*d*][1,3]dioxole (55). According to General Procedure H: (4*R*,5*S*)-4-(buta-1,3-dien-1-yl)-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane **54** (49.8 mg, 0.20 mmol, 1.0 equiv, *E*/*Z* = 5/1); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (4.0 mL). The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, 1:20 Et_2O/pentane). 16.1 mg, 45% yield (*trans*/*cis* = 1.3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 – 5.99 (m, 1H, ***trans***), 5.98 – 5.96 (m, 1H, ***cis***), 5.93 (dq, *J* = 6.1, 2.1 Hz, 1H, ***cis***), 5.83 (dq, *J* = 6.3, 2.3 Hz, 1H, ***trans***), 5.56 (tdt, *J* = 2.9, 2.0, 1.1 Hz, 1H, ***trans***), 5.40 (s, 1H, ***cis***), 5.34 – 5.32 (m, 1H, ***cis***), 5.16 – 5.08 (m, 1H, ***trans***), 4.77 (t, *J* = 4.6 Hz, 1H, ***cis***), 4.59 (dd, *J* = 6.3, 4.1 Hz, 1H, ***trans***), 3.79 – 3.76 (m, 1H, ***trans***), 3.57 (d, *J* = 4.7 Hz, 1H, ***cis***), 2.86 – 2.83 (m, 2H, ***trans***), 1.56 (s, 3H, ***trans***), 1.36 (s, 2H, ***trans***), 1.34 (s, 3H***, cis***), 1.30 (s, 3H, ***cis***).

trans isomer: ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.38, 133.05, 132.55, 117.48, 113.76, 87.23, 84.72, 62.19, 32.93, 27.79, 25.76.

HRMS (ESI): calcd for $C_{11}H_{15}O_2^+$ $[M + H]^+$: 179.1067; found: 179.1063.



4-methyl-2-tosyl-2,3,5,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (57). According to General Procedure H: (*E*)-N-(3,3-dichloro-2-methylallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide **56** (72.0 mg, 0.20 mmol, 1.0 equiv); **L4** (12.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 24 h in NMP (4.0 mL). The product was isolated an off-white solid following purification by flash chromatography (SiO_2, 1:19 EtOAc/hexane). 7.0 mg, 12% yield.

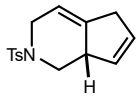
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.33 – 7.29 (m, 2H), 5.87 (dq, *J* = 6.1, 2.3 Hz, 1H), 5.68 (dq, *J* = 6.1, 2.0 Hz, 1H), 4.14 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.32 (dt, *J* = 8.0, 2.4 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.98 – 2.86 (m, 2H), 2.42 (s, 3H), 2.04 (t, *J* = 10.7 Hz, 1H), 1.58 (tq, *J* = 1.9, 0.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.48, 134.25, 134.04, 131.72, 130.56, 129.76, 127.66, 120.07, 48.48, 46.99, 45.66, 35.78, 21.65, 16.66.

HRMS (APCI): calcd for $C_{16}H_{20}NO_2S^+$ $[M + H]^+$: 290.1209; found: 290.1211.

9. Catalytic Asymmetric [4 + 1]-Cycloadditions

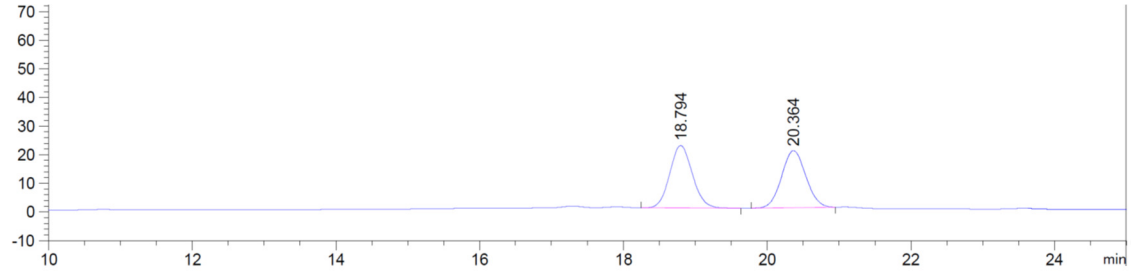
General Procedure I. In an N_2-filled glovebox, a 3-dram vial was charged with the **(*S*,*S*)-L10** ligand (5–10 mol%), Ni(DME)Br_2 (10–20 mol%), Zn powder (0.60 mmol, 3.0 equiv), and a magnetic stir bar. The reaction solvent was added, and the resulting suspension was stirred for 15 min, during which time the catalyst solution turned purple. The substrate (0.20 mmol, 1.0 equiv) was added to the catalyst/reductant mixture. The vial was sealed, and the reaction mixture was stirred at room temperature. The reaction mixture was diluted with Et_2O (40 mL) and washed with water (2 x 20 mL) and brine (20 mL). The organic phase was concentrated under reduced pressure, and the crude residue was purified by column chromatography.



(*S*)-2-tosyl-2,3,5,7a-tetrahydro-1H-cyclopenta[*c*]pyridine (49). According to General Procedure I: (*E*)-N-(3,3-dichloroallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide **48** (69.0 mg, 0.20 mmol, 1.0 equiv); **(*S*,*S*)-L10** (8.8 mg, 0.02 mmol, 10 mol%) and $Ni(DME)Br_2$ (12.4 mg, 0.04 mmol, 20 mol%); rt for 17 h in NMP (4.0 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:19 EtOAc/hexane). 34.8 mg, 65% yield. $[\alpha]_D^{23} = -47.3°$ (c 1.052, $CHCl_3$).

Spectroscopic and mass spectrometry data were identical to those of the racemic product.

HPLC: Chiralpak® AD-H column (hexane/IPA = 90:10, 0.75 mL/min, $\lambda = 254$ nm) t_r = 18.69 min (minor), 20.21 min (major): 5:95 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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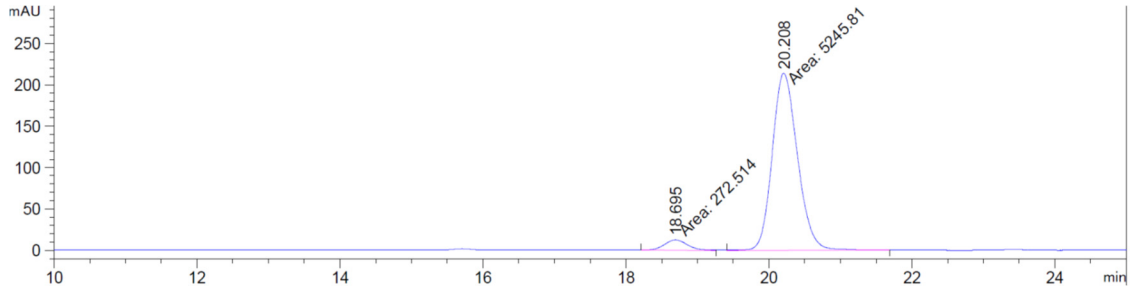
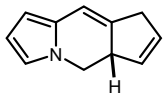
2	20.364	BB	0.3627	463.78186	19.91669	49.2971



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.694	BB	0.3396	270.69772	12.35617	4.9138
2	20.208	BB	0.3788	5238.22510	213.80522	95.0862

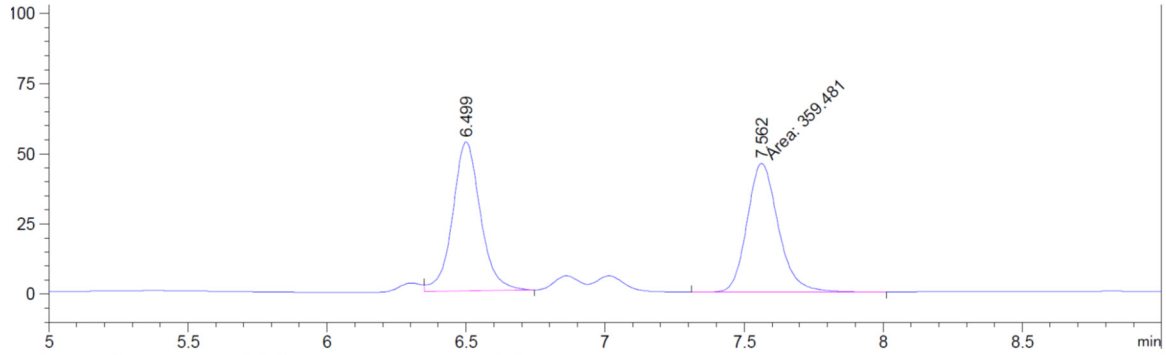
Fig. S5. HPLC data for the asymmetric [4 + 1]-cycloaddition of **48** (racemate, top; enantioselective reaction, bottom).



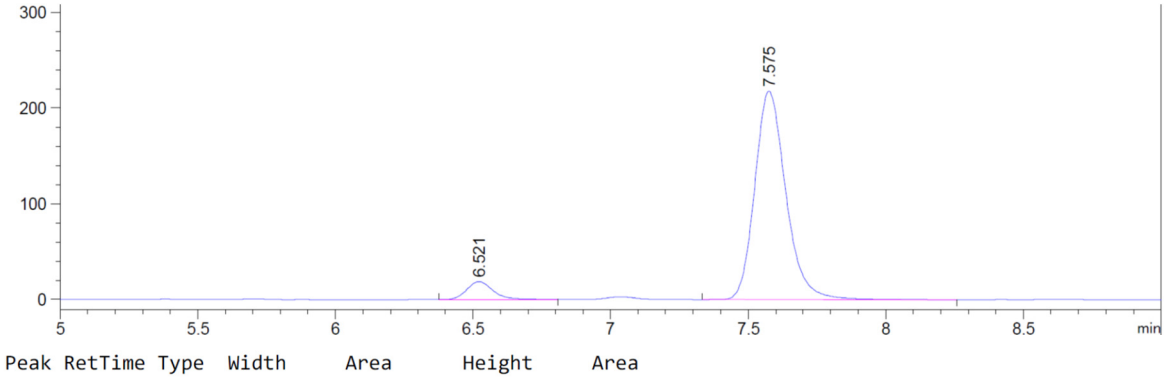
(*S*)-5a,8-dihydro-5*H*-cyclopenta[*f*]indolizine (51). According to General Procedure I: (*E*)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-pyrrole **50** (45.6 mg, 0.20 mmol, 1.0 equiv); **(*S*,*S*)-L10** (4.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 18 h in THF/NMP (3.60 mL/0.40 mL). The product was isolated as a pale-yellow oil following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2 /pentane). 29.0 mg, 92% yield, $[\alpha]_D^{23}$ = –158.0° (c 0.694, $CHCl_3$).

Spectroscopic and mass spectrometry data were identical to those of the racemic product.

HPLC: Chiralpak® OD-H column (hexane/IPA = 95:5, 0.75 mL/min, λ = 254 nm) t_r = 6.52 min (minor), 7.58 min (major): 7:93 er.

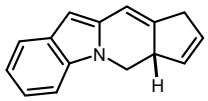


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.499	VB R	0.1064	370.26581	53.08019	50.7390
2	7.562	MM	0.1306	359.48083	45.87210	49.2610



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.521	VV	0.1047	130.37755	18.85746	7.0631
2	7.575	BB	0.1209	1715.50659	217.79767	92.9369

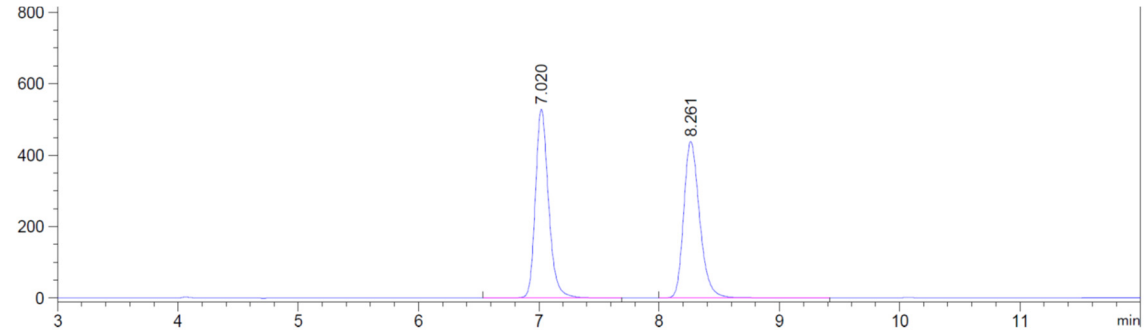
Fig. S6. HPLC data for the asymmetric [4 + 1]-cycloaddition of **50** (racemate, top; enantioselective reaction, bottom).



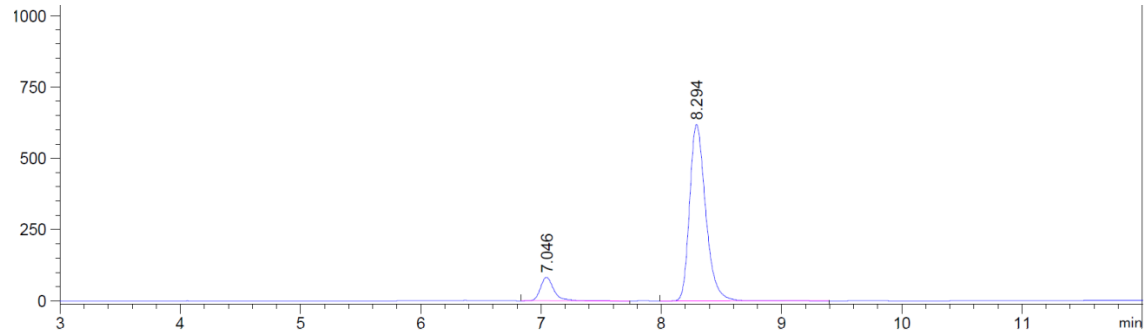
(*S*)-3a,4-dihydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole (53). According to General Procedure I: (***E***)-2-(2,2-dichlorovinyl)-1-(penta-2,4-dien-1-yl)-1H-indole **52** (55.6 mg, 0.20 mmol, 1.0 equiv); **(*S*,*S*)-L10** (4.4 mg, 0.01 mmol, 5 mol%) and Ni(DME)Br_2 (6.2 mg, 0.02 mmol, 10 mol%); rt for 21 h in THF/NMP (3.60 mL/0.40 mL). The product was isolated as a white solid following purification by column chromatography (SiO_2, 1:4 CH_2Cl_2/pentane). 38.0 mg, 91% yield, $[\alpha]_D^{23} = -64.1°$ (c 1.388, $CHCl_3$).

Spectroscopic and mass spectrometry data were identical to those of the racemic product.

HPLC: Chiralpak® OD-H column (hexane/IPA = 95:5, 0.75 mL/min, λ = 254 nm) t_r = 7.05 min (minor), 8.29 min (major): 10:90 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.020	BB	0.1167	4018.88745	528.79926	49.8881
2	8.261	BB	0.1405	4036.91235	438.19009	50.1119

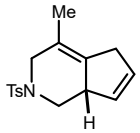


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.046	BV	0.1184	639.25708	82.51818	10.0254
2	8.294	BB	0.1423	5737.09326	618.12408	89.9746

Fig. S7. HPLC data for the asymmetric [4 + 1]-cycloaddition of **52** (racemate, top; enantioselective reaction, bottom).

cis *trans*

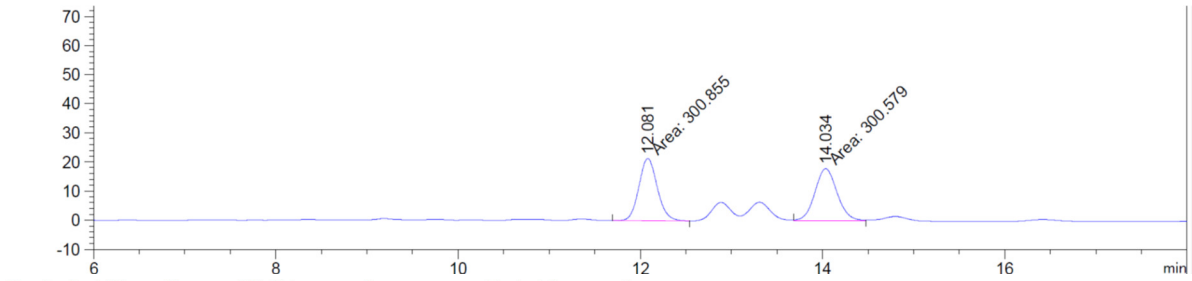
(3a*R*,3b*S*,7a*S*)-2,2-dimethyl-3a,3b,6,7a-tetrahydropentaleno[1,2-*d*][1,3]dioxole (55). According to General Procedure I: (4*R*,5*S*)-4-(buta-1,3-dien-1-yl)-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane **54** (49.8 mg, 0.20 mmol, 1.0 equiv, *E*/*Z* = 5/1); **(*S*,*S*)-L10** (8.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); 50 ºC for 24 h in NMP/THF (0.40/3.6 mL). The product was isolated as a colorless oil following purification by flash chromatography (SiO_2, 1:20 Et_2O/pentane). 17.1 mg, 48% yield (*trans*/*cis* = 18/1), $[\alpha]_D^{23}$ = 65.6° (c 0.596, $CHCl_3$).



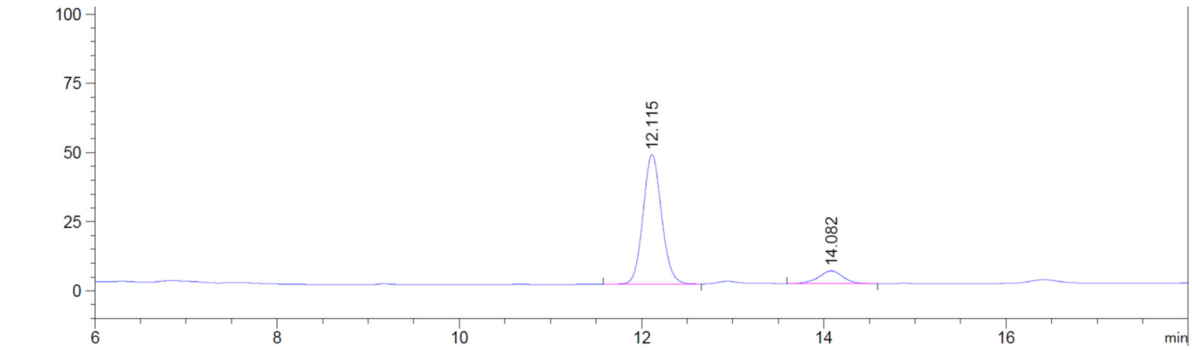
(*S*)-4-methyl-2-tosyl-2,3,5,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (57). According to General Procedure I: (*E*)-N-(3,3-dichloro-2-methylallyl)-4-methyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide **56** (72.0 mg, 0.20 mmol, 1.0 equiv); **(*S*,*S*)-L10** (8.8 mg, 0.02 mmol, 10 mol%) and Ni(DME)Br_2 (12.4 mg, 0.04 mmol, 20 mol%); rt for 12 h in NMP (4.0 mL). The product was isolated an off-white solid following purification by column chromatography (SiO_2, 1:19 EtOAc/hexane). 52.5 mg, 91% yield, $[\alpha]_D^{23} = -23.2°$ (c 1.148, $CHCl_3$). Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of a concentrated solution of **57** in hexane/Et_2O (2:1).

Spectroscopic and mass spectrometry data were identical to those of the racemic product.

HPLC: Chiralpak® AD-H column (hexane/IPA = 90:10, 0.75 mL/min, $\lambda = 254$ nm) t_r = 12.12 min (major), 14.08 min (minor): 89:11 er.



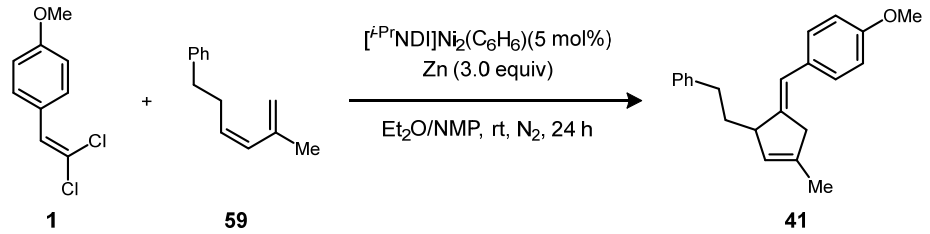
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.081	MM	0.2342	300.85541	21.40866	50.0230
2	14.034	MM	0.2806	300.57898	17.85100	49.9770



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.115	BB	0.2193	663.41620	46.80946	88.6456
2	14.082	MM	0.3075	84.97575	4.60553	11.3544

Fig. S8. HPLC data for the asymmetric [4 + 1]-cycloaddition of **56** (racemate, top; enantioselective reaction, bottom).

10. Mechanistic Studies

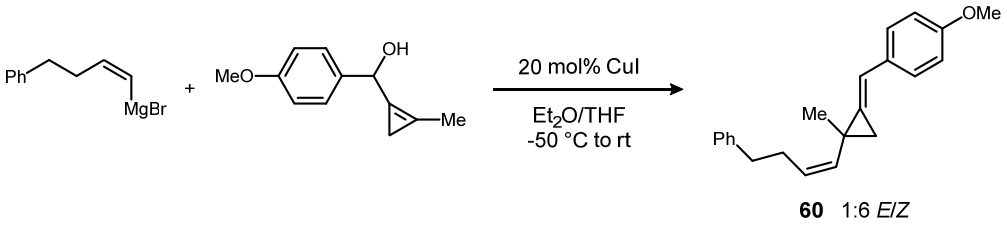


In an N_2-filled glovebox, a 3-dram vial was charged with the [$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) complex **3** (7.3 mg, 0.01 mmol, 5 mol%), Zn powder (39.2 mg, 0.60 mmol 3.0 equiv), Et_2O (1.60 mL), NMP (0.20 mL), and a magnetic stir bar. (*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (**59**) (69.5 mg, 0.40 mmol, 2.0 equiv) and 1-(2,2-dichlorovinyl)-4-methoxybenzene (**1**) (40.6 mg, 0.20 mmol, 1.0 equiv) were successively added to the catalyst/reductant mixture. The vial was sealed, and the reaction mixture was stirred at room temperature. After 24 h, The reaction mixture was concentrated under reduced pressure, and the crude residue was purified by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexane). Colorless oil, 46.0 mg, 76% yield (*E*/*Z* = 25/1).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 4H), 7.22 – 7.19 (m, 2H), 7.18 (td, *J* = 7.3, 1.4 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.31 (q, *J* = 2.4 Hz, 1H), 5.51 (hept, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 3.40 (ddq, *J* = 6.9, 4.3, 2.1 Hz, 1H), 3.31 – 3.27 (m, 1H), 3.19 (d, *J* = 20.9, 1H), 2.67 (dddd, *J* = 38.8, 13.7, 10.8, 5.6 Hz, 2H), 1.96 (dddd, *J* = 13.4, 11.0, 6.0, 4.9 Hz, 1H), 1.83 (s, 3H), 1.80 (dddd, *J* = 13.3, 10.8, 8.0, 5.3 Hz, 1H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 157.93, 145.27, 143.07, 139.08, 131.32, 129.37, 128.55, 128.42, 127.09, 125.73, 121.68, 113.85, 55.42, 51.94, 42.48, 38.27, 33.08, 16.99.

HRMS (ESI): calcd for $C_{22}H_{23}O^+$ [M - H]$^+$: 303.1749; found: 303.1746.

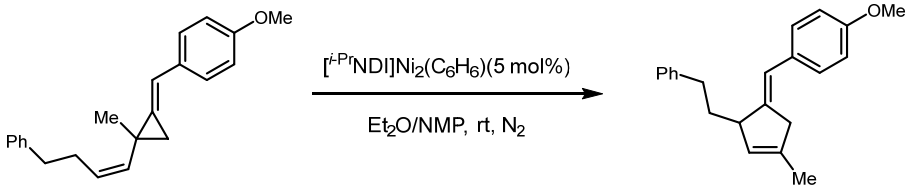


1-methoxy-4-((2-methyl-2-((Z)-4-phenylbut-1-en-1-yl)cyclopropylidene)methyl)-benzene (60) (*44*)**.** Under an N_2 atmosphere, a round bottom flask was charged with (4-methoxyphenyl)(2-methylcycloprop-1-en-1-yl)methanol (0.40 g, 2.1 mmol, 1.0 equiv) and Et_2O (50 mL). CuI (80.0 mg, 0.42, 0.2 equiv) was added as a solid, and the mixture was cooled to –50 °C. A solution of (*Z*)-(4-phenylbut-1-en-1-yl)magnesium bromide (*44*) freshly prepared from (*Z*)-(4-bromobut-3-en-1-yl)benzene (1.90 g, 9.0 mmol) and Mg (0.32 g, 13.5 mmol) in THF (20 mL) was added dropwise over 10 min. Following the addition, the reaction mixture was gradually warmed to room temperature, and stirring was continued overnight. The reaction was quenched with a saturated NH_4Cl (aq) and stirred until the aqueous phase turned blue. The aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic phases were wash with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 1:9 to 1:4 CH_2Cl_2/hexane). Colorless oil, 0.48 g, 75% yield, *E*/*Z* = 5.7:1.0.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H, ***E***), 7.37 – 7.16 (m, 5H, ***E***/***Z***), 7.12 – 7.07 (m, 2H, ***Z***), 6.92 – 6.85 (m, 2H, ***E***/***Z***), 6.75 (t, *J* = 2.4 Hz, 1H, ***E***), 6.62 (t, *J* = 2.0 Hz, 1H, ***Z***), 5.61 – 5.52 (m, 1H, ***E***/***Z***), 5.47 – 5.36 (m, 1H, ***E***/***Z***), 3.62 (s, 3H, ***E***/***Z***), 2.72 – 2.65 (m, 2H, ***E***), 2.65 – 2.56 (m, 2H, ***E***/***Z***), 2.54 – 2.44 (m, 1H, ***Z***), 1.42 (ddd, *J* = 21.8, 8.7, 2.6 Hz, 2H, ***E***/***Z***), 1.28 (s, 3H, ***E***/***Z***).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.77(***E***), 142.19(***E***), 133.15(***E***), 132.82(***E***), 132.11(***Z***), 131.76(***E***), 131.18(***E***), 130.68(***Z***), 128.64(***E***), 128.57(***Z***), 128.45(***E***), 128.38(***Z***), 128.25(***Z***), 127.81(***E***), 125.97(***E***), 125.90(***Z***), 116.87(***E***), 114.15(***Z***), 114.04(***E***), 55.44(***Z***), 36.38(***Z***), 36.25(***E***), 35.78(***Z***), 30.21(***E***), 29.66(***Z***), 24.52(***E***), 23.86(***Z***), 19.89(***E***), 19.39(***Z***), 17.79(***E***).

HRMS (APCI): calcd for $C_{22}H_{25}O^+$ $[M + H]^+$: 305.1900; found: 305.1902.

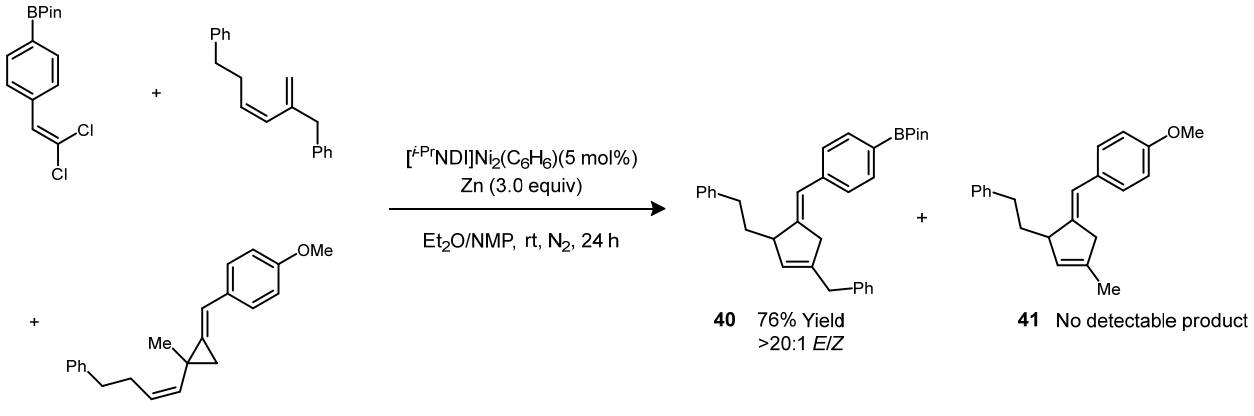


60 1:6 *E*/*Z*

41

24 h: conversion = 3%,
No detectable product

In an N_2-filled glovebox, a 2-dram vial was charged with [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (3.7 mg, 0.05 mmol, 5 mol%) and a magnetic stir bar. A solution of 1-methoxy-4-((2-methyl-2-((Z)-4-phenylbut-1-en-1-yl)cyclopropylidene)methyl)benzene (**60**) (30.4 mg, 0.10 mmol) in Et_2O/NMP (0.80 mL/0.10 mL) was added followed by mesitylene (17.2 mg, 20 µL). The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy. After 24 h, an aliquot of reaction was directly loaded onto a 2-cm pad of SiO_2 packed in a pipet. The produce mixture was eluted from the SiO_2 pad with $CDCl_3$ (approximately 1.5 mL). The conversion of **60** and yield of **41** were determined by ^{1}H NMR integration against mesitylene.



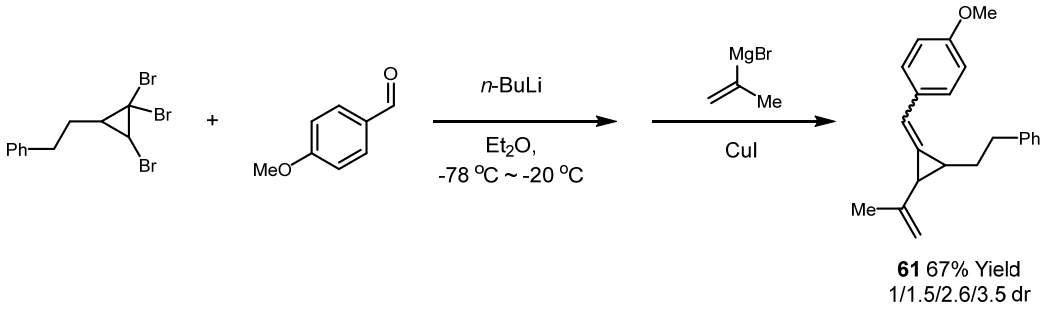
60 1:6 *E*/*Z*

82% Recovery

40 76% Yield
>20:1 *E*/*Z*

41 No detectable product

In an N_2-filled glovebox, a 2-dram vial was charged with the [$^{i\text{-Pr}}$NDI]Ni$_2$(C_6H_6) complex **3** (7.3 mg, 0.01 mmol, 5 mol%), Zn powder (39.2 mg, 0.60 mmol, 3.0 equiv), Et_2O/NMP (0.80 mL/0.15 mL), and a magnetic stir bar. (*Z*)-(2-methylenehex-3-ene-1,6-diyl)dibenzene (99.2 mg, 0.40 mmol, 2.0 equiv) was added by syringe followed by a solution of 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59.6 mg, 0.20 mmol, 1.0 equiv) dissolved in Et_2O (0.40 mL). After 30 min, a solution of 1-methoxy-4-((2-methyl-2-((Z)-4-phenylbut-1-en-1-yl)cyclopropylidene)methyl)benzene (**60**) (30.4 mg, 0.10 mmol, 0.50 equiv) dissolved in Et_2O/NMP (0.40 mL/0.05 mL) was added followed by mesitylene (17.2 mg, 20 µL). The mixture was stirred at 22 °C. After 24 h, an aliquot of the reaction mixture was removed, and the substrate conversion, the yield of product, and the ratio of *E*/*Z* diastereomers were determined by ^{1}H NMR integration against mesitylene.



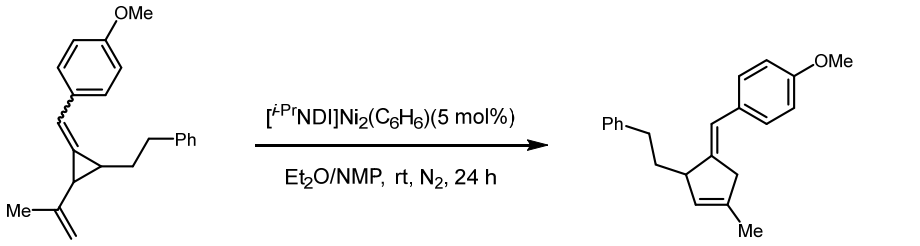
61 67% Yield
1/1.5/2.6/3.5 dr

1-Methoxy-4-((2-phenethyl-3-(prop-1-en-2-yl)cyclopropylidene)methyl)benzene (61) (*45*)**.** Under an N_2 atmosphere, *n*-BuLi in hexane (8.8 mmol, 3.6 mL, 2.5 M, 2.0 equiv) was added dropwise to a stirred solution of *cis*-(2-(2,2,3-tribromocyclopropyl)ethyl)benzene (1.33 g, 4.4 mmol, 1.0 equiv) in Et_2O (50 mL) cooled to –78 °C. The mixture was allowed to warm to –20 °C, and stirring was continued for 1 h. The reaction mixture was cooled to –50 °C, and 4-methoxybenzaldehyde (0.55 mL, 5.0 mmol, 1.0 equiv) was added. The reaction was allowed to warm to –20 °C, and stirring was continued 2.5 h. The reaction mixture was cooled to –50 °C, and CuI (0.167 g, 0.88 mmol, 0.20 equiv) was added followed by 2-methylallylmagnesium bromide solution (35.2 mL, 17.6 mmol, 0.5 M in THF, 4.0 equiv). The reaction mixture was slowly warmed to room temperature and stirring was continued overnight. The reaction was quenched with sat. aq. NH_4Cl and stirred until the aqueous phase became blue. The aqueous phase was extracted with diethyl ether (3 x 30 mL). The combined organic phases were washed with brine (1 x 30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 1:4 CH_2Cl_2/hexane) to obtain **61** as a pale yellow oil (0.89 g, 67% yield). The product was found to be a mixture of four isomers (**a**, **b**, **c**, **d**): 1/1.5/2.6/3.5 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.39 – 6.84 (m, 9H, Aromatic, **a, b, c, d**), 6.71 (t, *J* = 2.1 Hz, 1H, -C=CH-, **b**), 6.70 (t, *J* = 2.1 Hz, 1H, -C=CH-, **a**), 6.63 (t, *J* = 2.0 Hz, 1H, -C=CH-, **d**), 6.60 (t, *J* = 1.9 Hz, 1H, -C=CH-, **c**), 4.93 – 4.91 (m, 1H, -MeC=CH_2, **a**), 4.86 - 4.85 (m, 1H, -MeC=CH_2, **c**), 4.80 – 4.79 (m, 2H, -MeC=CH_2, **b, d**), 4.78 - 4.77 (m, 1H, -MeC=CH_2, **d**), 4.73-4.72 (m, 2H, -MeC=CH_2, **a, b**), 4.40-4.39 (m, 1H, -MeC=CH_2, **c**), 3.81 (s, 3H, -OCH_3, **b**), 3.81 (s, 3H, -OCH_3, **a**), 3.80 (s, 3H, -OCH_3, **c**), 3.80 (s, 3H, -OCH_3, **d**), 2.86 – 1.25 (aliphatic, 6H, **a, b, c, d**), 1.93 (t, *J* = 1.1 Hz, 3H, -CH_3, **a**), 1.88 (t, *J* = 1.2 Hz, 3H, -CH_3, **c**), 1.68 (dd, *J* = 1.5, 0.8 Hz, 3H, -CH_3, **b**), 1.57 (dd, *J* = 1.5, 0.8 Hz, 3H, -CH_3, **d**).

$^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 158.69, 158.61, 144.70, 144.17, 142.33, 142.25, 141.95, 141.88, 140.77, 139.65, 130.93, 130.64, 130.54, 130.48, 129.36, 128.84, 128.59, 128.56, 128.49, 128.38, 128.36, 128.33, 128.11, 128.02, 127.93, 125.86, 125.80, 125.76, 119.27, 119.20, 119.13, 118.78, 113.99, 113.95, 113.80, 113.70, 113.09, 112.20, 110.31, 109.46, 55.32, 55.28, 55.25, 36.00, 35.96, 35.75, 35.27, 34.77, 33.78, 31.09, 28.15, 27.90, 27.67, 27.18, 24.94, 24.41, 24.26, 24.00, 23.34, 21.99, 20.57, 20.34, 19.72.

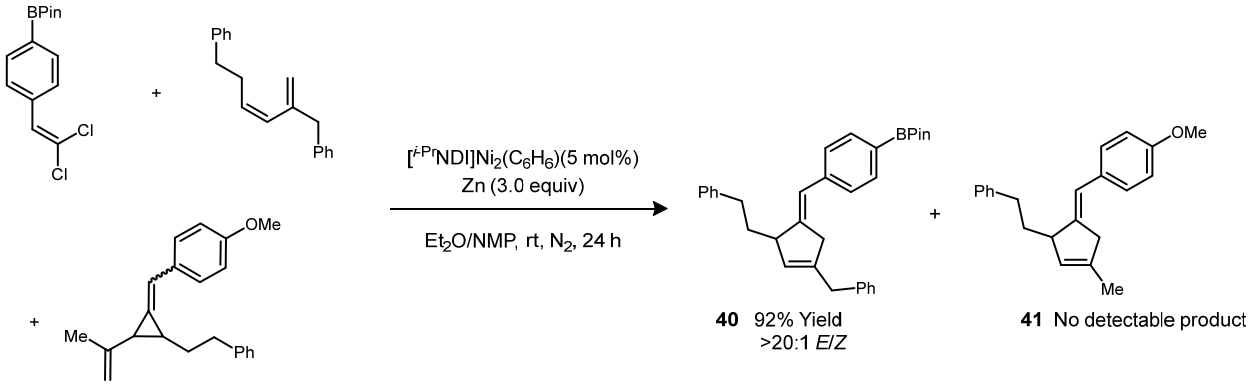
HRMS (ESI): calcd for $C_{22}H_{25}O^+$ $[M + H]^+$: 305.1900; found:305.1898.



61
1/1.5/2.6/3.5 dr

41
conversion = 4%, No detactable product

In an N_2-filled glovebox, a 2-dram vial was charged with [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **3** (3.7 mg, 0.05 mmol, 5 mol%) and a magnetic stir bar. A solution of 1-methoxy-4-((2-phenethyl-3-(prop-1-en-2-yl)cyclopropylidene)methyl)benzene (**61**) (30.4 mg, 0.10 mmol) in Et_2O/NMP (0.80 mL/0.10 mL) was added followed by mesitylene (17.2 mg, 20 µL). The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy. After 24 h, an aliquot of reaction was directly loaded onto a 2-cm pad of SiO_2 packed in a pipet. The produce mixture was eluted from the SiO_2 pad with $CDCl_3$ (approximately 1.5 mL). The conversion of **61** and yield of **41** were determined by ^{1}H NMR integration against mesitylene.



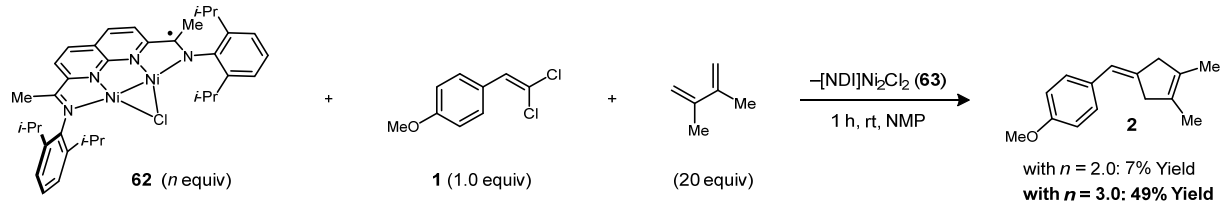
61
1/1.5/2.6/3.5 dr
90% Recovery

40 92% Yield
>20:1 *E/Z*

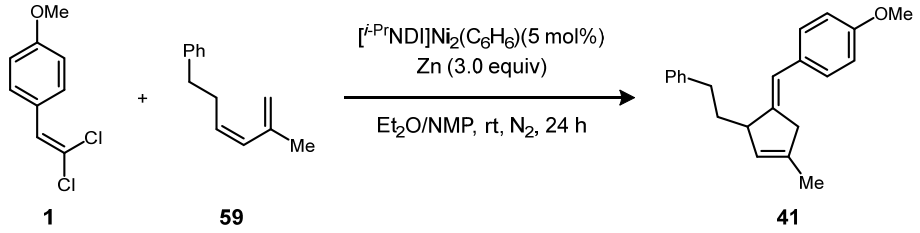
41 No detectable product

In an N_2-filled glovebox, a 2-dram vial was charged with the [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ complex **3** (7.3 mg, 0.01 mmol, 5 mol%), Zn powder (39.2 mg, 0.60 mmol, 3.0 equiv), Et_2O/NMP (0.80 mL/0.15 mL), and a magnetic stir bar. (*Z*)-(2-methylenehex-3-ene-1,6-diyl)dibenzene (99.2 mg, 0.40 mmol, 2.0 equiv) was added by microsyringe followed by a solution of 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59.6 mg, 0.20 mmol, 1.0 equiv) dissolved in Et_2O (0.40 mL). After 30 min, a solution of 1-methoxy-4-((2-phenethyl-3-(prop-1-

en-2-yl)cyclopropylidene)methyl)benzene (**61**) (30.4 mg, 0.10 mmol, 0.50 equiv) dissolved in Et_2O/NMP (0.40 mL/0.05 mL) was added followed by mesitylene (17.2 mg, 20 μL). The mixture was stirred at 22 °C. After 24 h, an aliquot of the reaction mixture was removed, and the substrate conversion, the yield of product, and the ratio of *E*/*Z* diastereomers were determined by ^{1}H NMR integration against mesitylene.



Stoichiometric [4 + 1]-cycloaddition using an isolable low-valent [NDI]Ni_2Cl complex. In an N_2-filled glovebox, the [$^{i\text{-Pr}}$NDI]Ni_2Cl complex **62** (20.6 mg, 0.030 mmol) was dissolved in NMP (0.1 mL) in a 2-dram vial, generating a dark purple solution. 2,3-Dimethylbutadiene (23 μL, 0.20 mmol or 27 μL, 0.30 mmol, 20 equiv) was added by microsyringe. A solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (2.0 mg, 0.010 mmol, or 3.1 mg, 0.015 mmol, 1.0 equiv) in NMP (0.10 mL) was added. The reaction mixture was stirred at room temperature. After 1 h, an aliquot of product mixture was removed, diluted with C_6D_6 and analyzed by ^{1}H NMR spectroscopy. The yield of the [4+1] product was determined by ^{1}H NMR integration against mesitylene.



Dependence of product distribution on conversion. In an N_2-filled glovebox, a 3-dram vial was charged with the [$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ complex **3** (7.3 mg, 0.01 mmol, 5 mol%), Zn powder (39.2 mg, 0.60 mmol 3.0 equiv), Et_2O (1.60 mL), NMP (0.20 mL), and a magnetic stir bar. (*Z*)-(5-methylhexa-3,5-dien-1-yl)benzene (**59**) (69.5 mg, 0.40 mmol, 2.0 equiv), 1-(2,2-dichlorovinyl)-4-methoxybenzene (**1**) (40.6 mg, 0.20 mmol, 1.0 equiv) and mesitylene (20 μL) were successively added to the catalyst/reductant mixture by microsyringe. The vial was sealed, and the reaction mixture was stirred at room temperature. At the indicated time points, an aliquot of the reaction mixture was removed and loaded directly onto a 2-cm pad of SiO_2 packed in a pipet. The mixture was eluted from the SiO_2 pad with $CDCl_3$ (approx. 1.5 mL). The conversion of **1**, yield of products and selectivity were determined by ^{1}H NMR integration against mesitylene.

30 min, 27% conversion of **1**, 28% yield of **41**, *E*/*Z* > 20:1, no detectable **60** or **61**.
2 h, 59% conversion of **1**, 56% yield of **41**, *E*/*Z* > 20:1, no detectable **60** or **61**.
5 h, 77% conversion of **1**, 69% yield of **41**, *E*/*Z* > 20:1, no detectable **60** or **61**.
10 h, 84% conversion of **1**, 75% yield of **41**, *E*/*Z* > 20:1, no detectable **60** or **61**.

11. X-Ray Diffraction Data

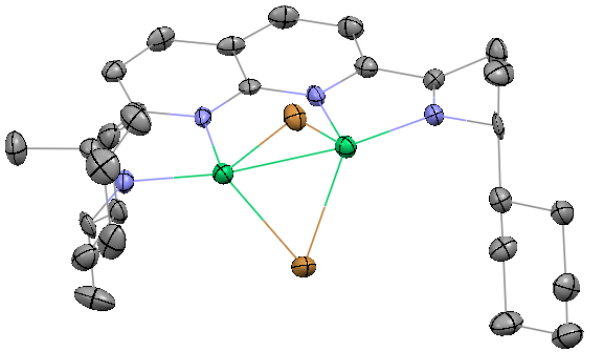


Fig. S9. Solid-state structure of **(*S*,*S*)-58.**

Table S5. Crystallographic information for **(*S*,*S*)-58** (*30–35*).

Crystal data	
Chemical formula	$C_{28}H_{40}Br_2N_4Ni_2 \cdot 2(C_6H_6)$
M_r	866.09
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	13.8800 (2), 14.2983 (2), 19.6591 (3)
V (Å^3)	3901.55 (10)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.84
Crystal size (mm)	0.23 × 0.19 × 0.11
Data collection	
Diffractometer	Rigaku Rapid II curved image plate diffractometer
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.555, 0.677
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38055, 7509, 7441
R_{int}	0.034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618

Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.096, 1.18
No. of reflections	7509
No. of parameters	438
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + 13.6065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.89, -0.90
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.02 (3)

Refined as a 2-component inversion twin.

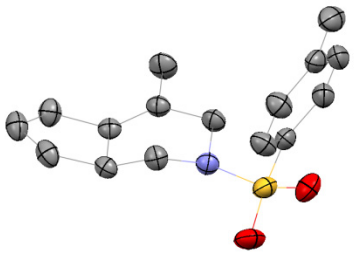


Fig. S10. Solid-state structure of **57.**

Table S6. Crystallographic information for **57** (*30–35*).

Crystal data	
Chemical formula	$C_{16}H_{19}NO_2S$
M_r	289.38
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, b, c (Å)	12.5776 (8), 8.6526 (6), 13.9394 (9)
β (°)	100.008 (2)
V (Å^3)	1493.93 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.22
Crystal size (mm)	0.34 × 0.25 × 0.09
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.672, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	55729, 10508, 9499
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.751
Refinement	

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.111, 1.03
No. of reflections	10508
No. of parameters	448
No. of restraints	391
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.43, -0.45
Absolute structure	Flack x determined using 4106 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.016 (11)

The structure exhibits pseudo-centrosymmetric symmetry, emulating space group P2(1)/c. The pseudo-inversion symmetry is broken by the geometry around C7, which is always S, and by partial rotation of the bicyclic moiety in one of the two molecules. The two disordered moieties were restrained to have similar geometries as the not disordered equivalent moiety of the other molecule. Uij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.692(4) to 0.308(4).

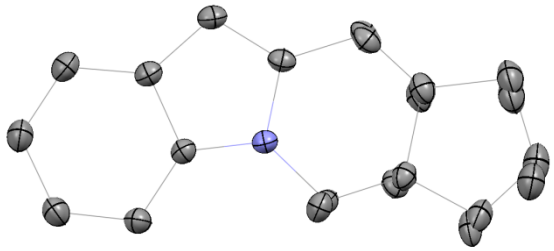


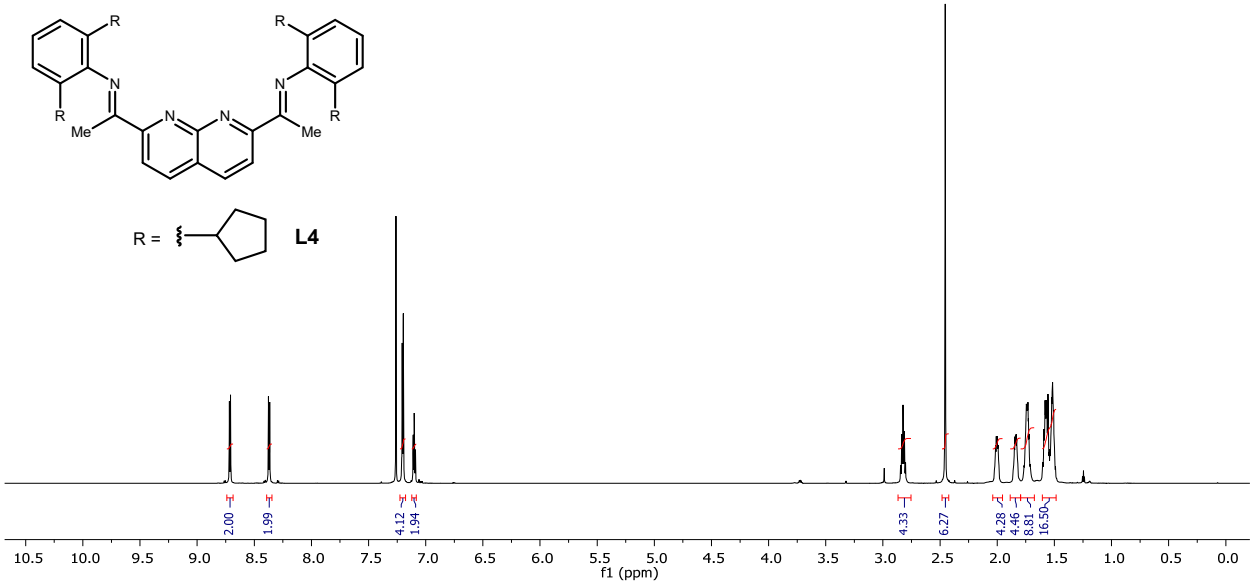
Fig. S11. Solid-state structure of **53.**

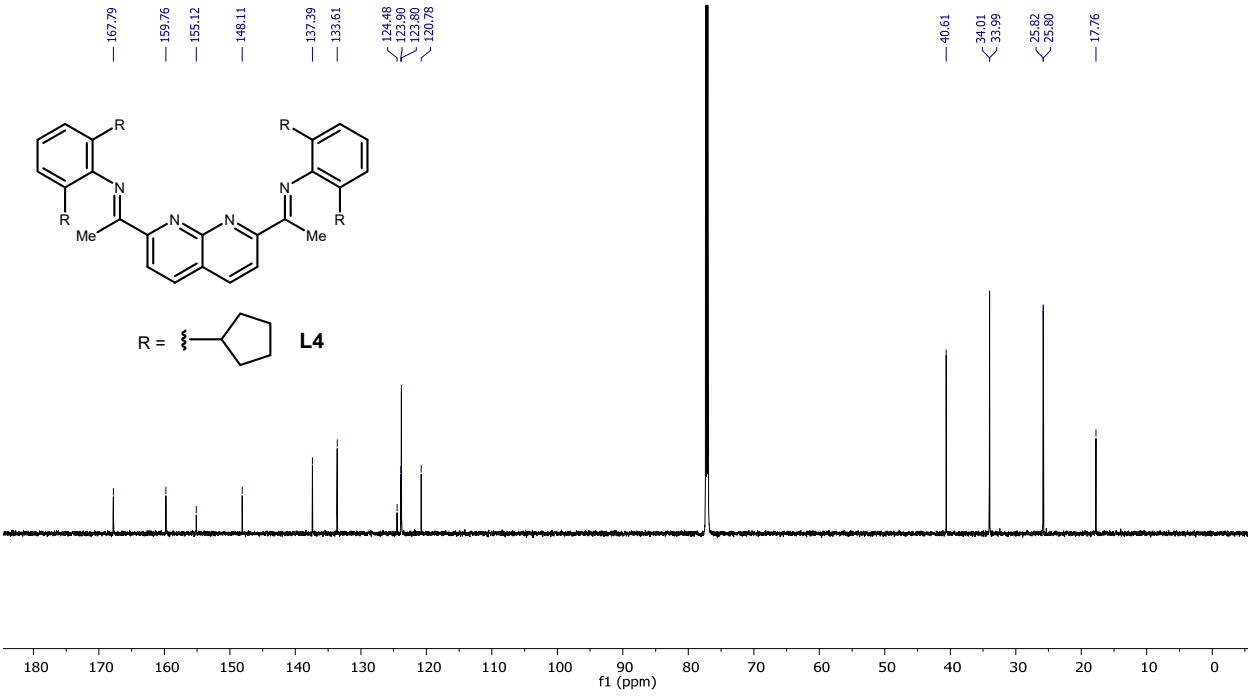
Table S7. Crystallographic information for **53** (*30–35*).

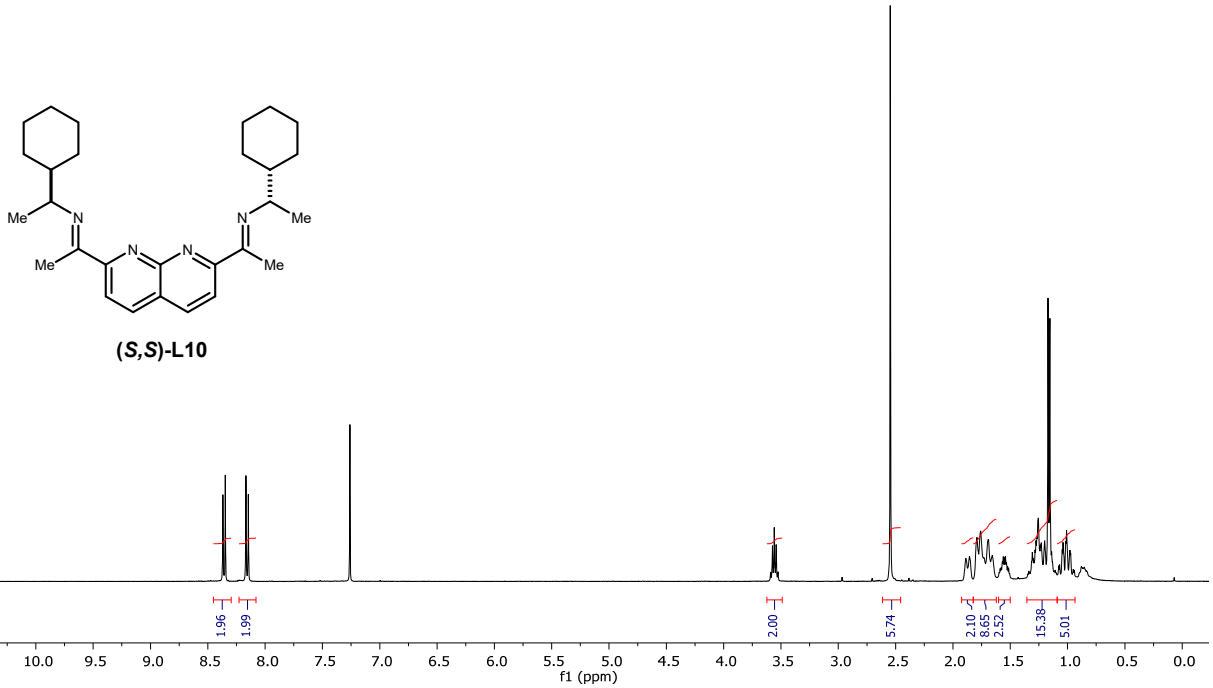
Crystal data	
Chemical formula	$C_{60}H_{52}N_4$
M_r	829.05
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	7.6190 (3), 6.0888 (2), 23.0370 (9)
β (°)	95.4168 (19)
V (Å^3)	1063.93 (7)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.60 × 0.20 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.695, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36353, 3877, 3090
R_{int}	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.769
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.120, 1.04

No. of reflections	3877
No. of parameters	191
No. of restraints	228
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.37, -0.25

12. NMR Spectra



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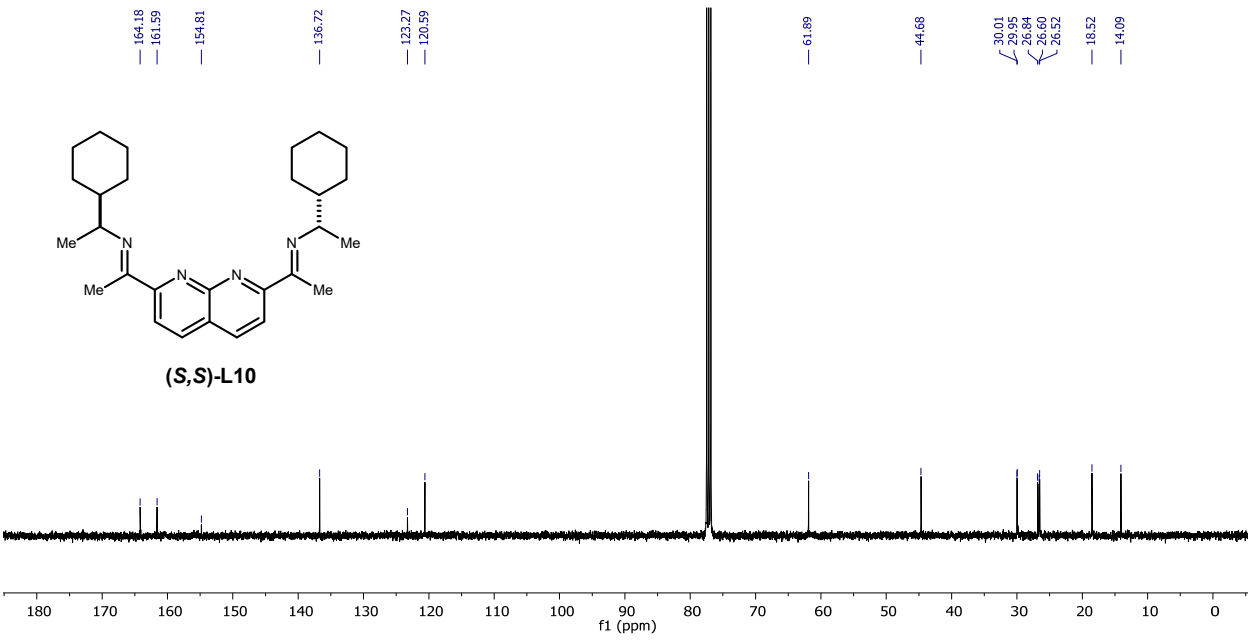
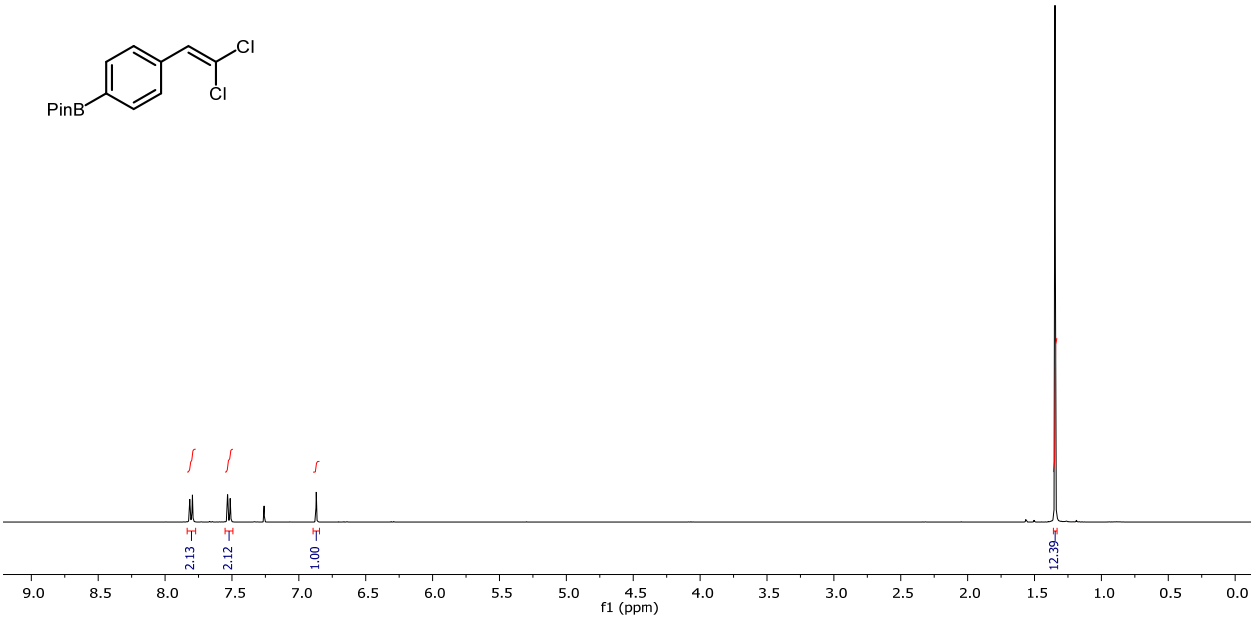
N
N
N
N
Me
Me
Me
1.96
1.99
2.00
5.74
2.10
8.65
2.52
15.38
5.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(*S*,*S*)-L10


164.18
161.59
154.81
136.72
123.27
120.59
61.89
44.68
30.01
29.95
26.84
26.60
26.52
18.52
14.09
Me
N
N
N
N
Me
Me
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(*S*,*S*)-L10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Cl
PinB
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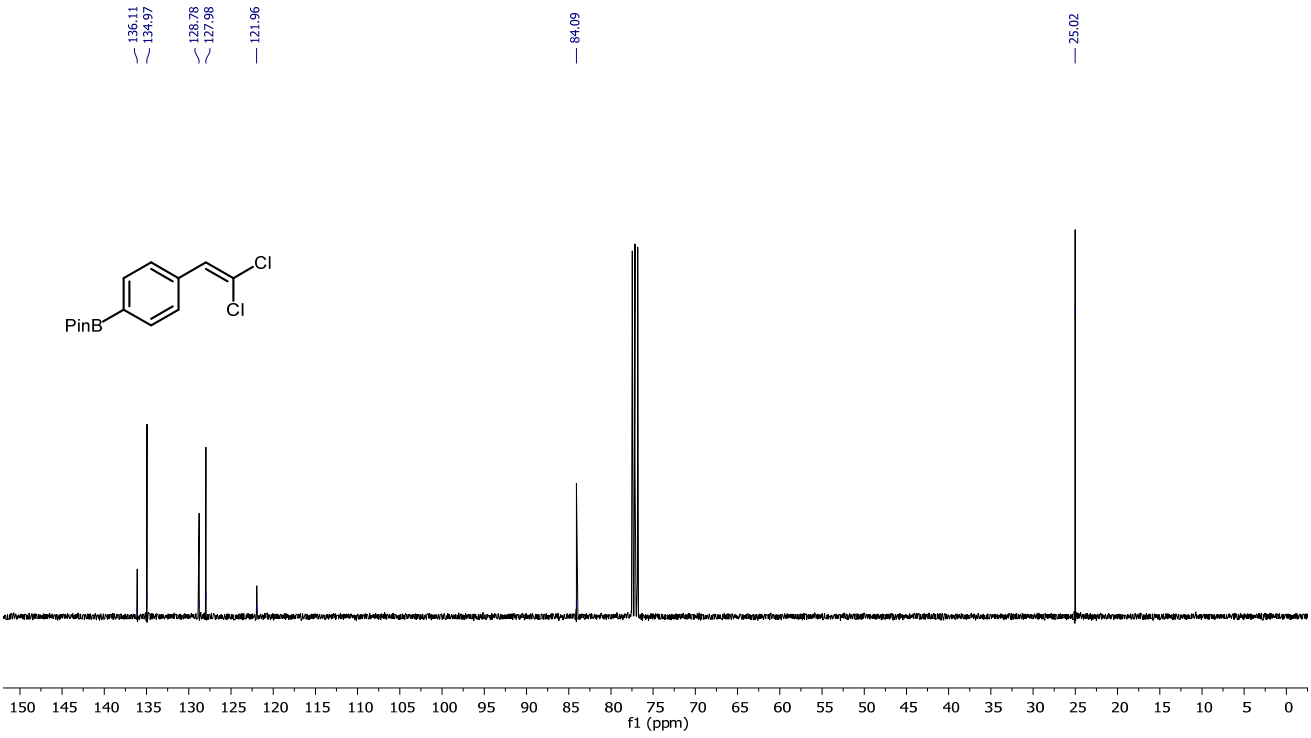
2.12
1.00
12.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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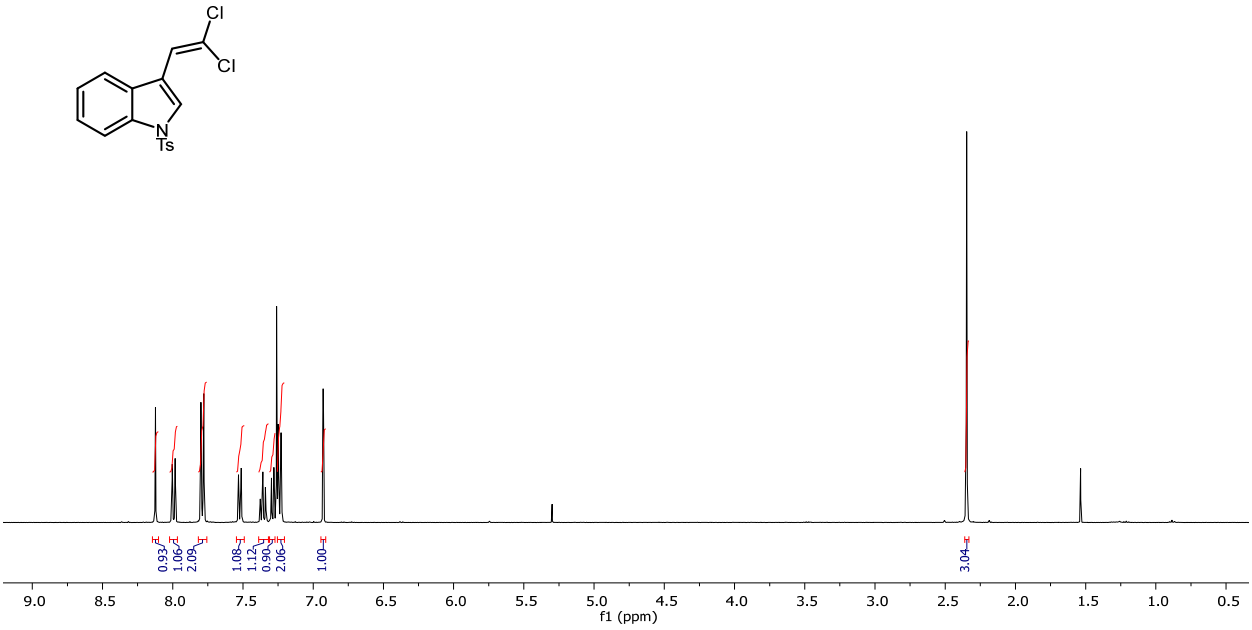
134.97
128.78
127.98
121.96
84.09
25.02
Cl
Cl
PinB
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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Cl
N
Ts
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1.06
2.09
1.08
1.12
0.90
2.06
1.00
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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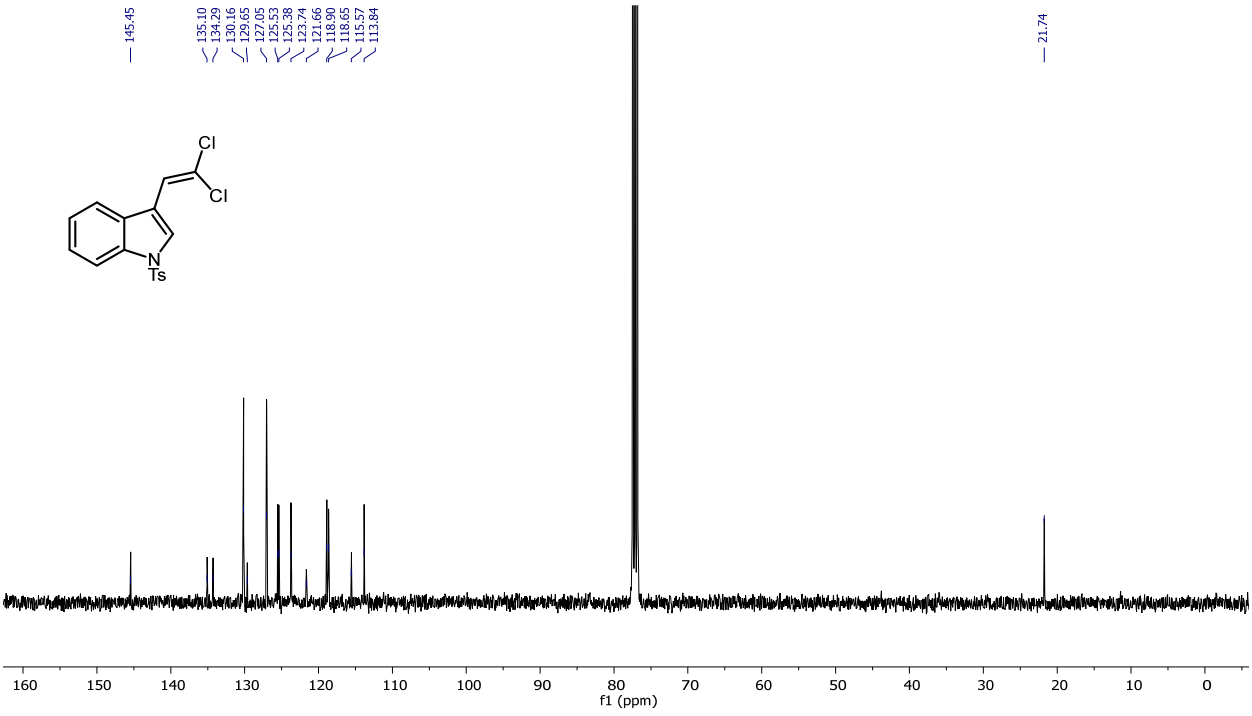
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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135.10
134.29
130.16
129.65
127.05
125.53
125.38
123.74
121.66
118.90
118.65
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113.84
21.74
Cl
Cl
N
Ts
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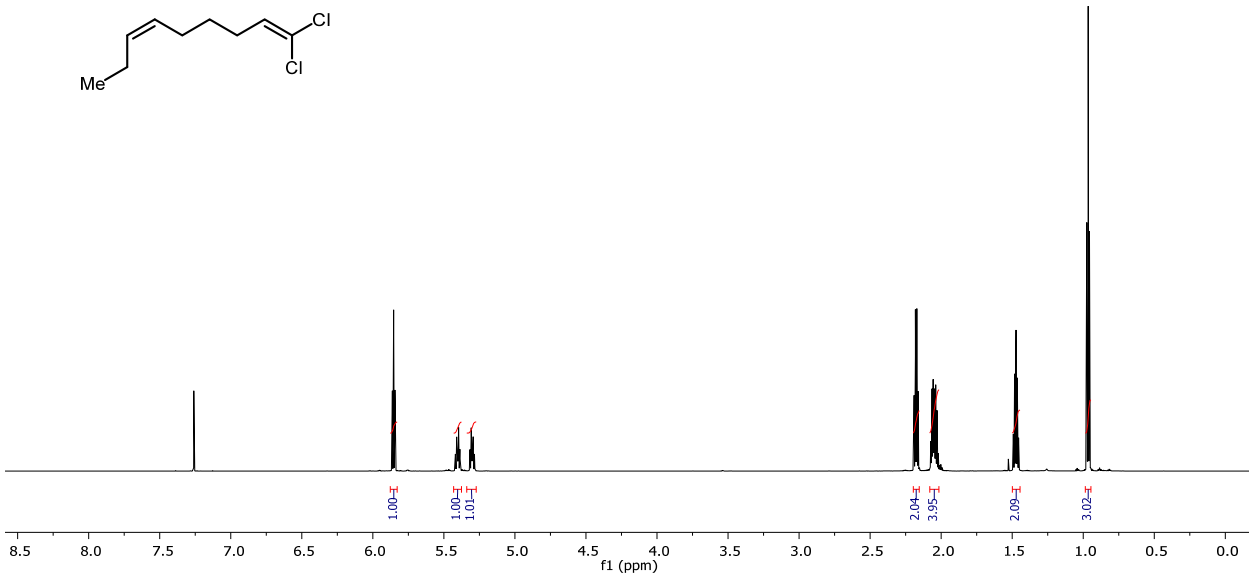
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Cl
Me
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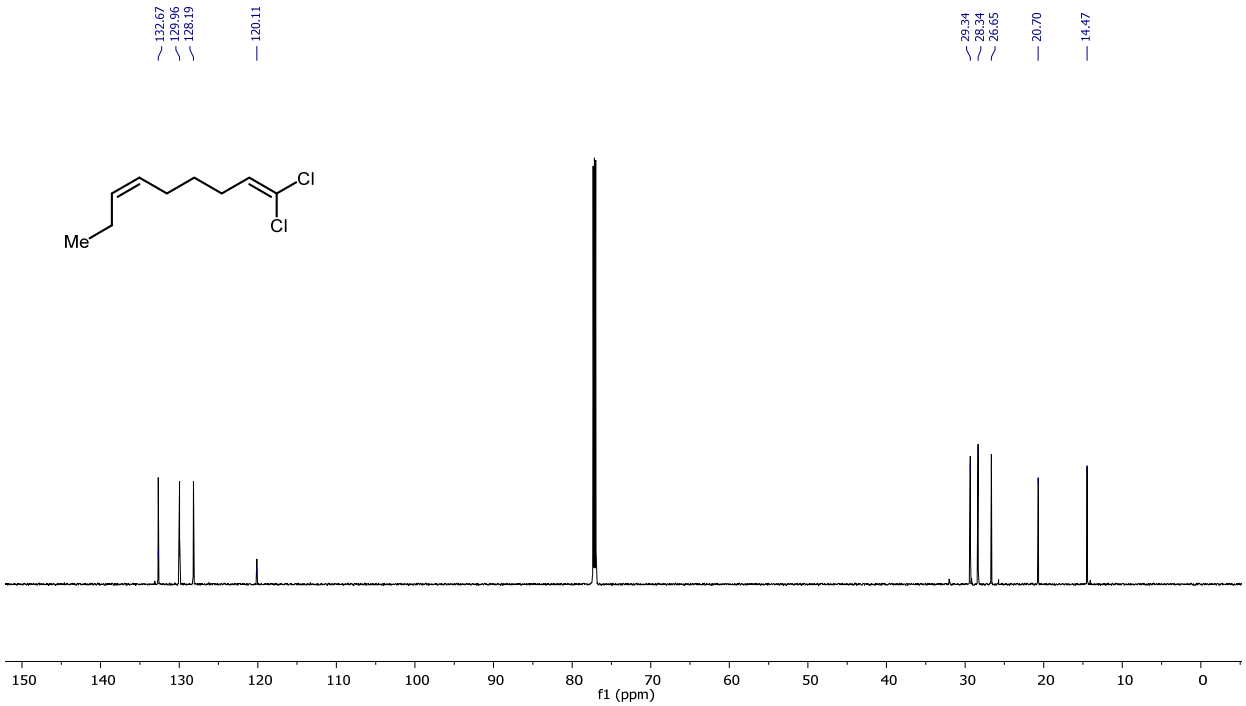
1.00
1.01
2.04
3.95
2.09
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.96
128.19
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29.34
28.34
26.65
20.70
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Cl
Me
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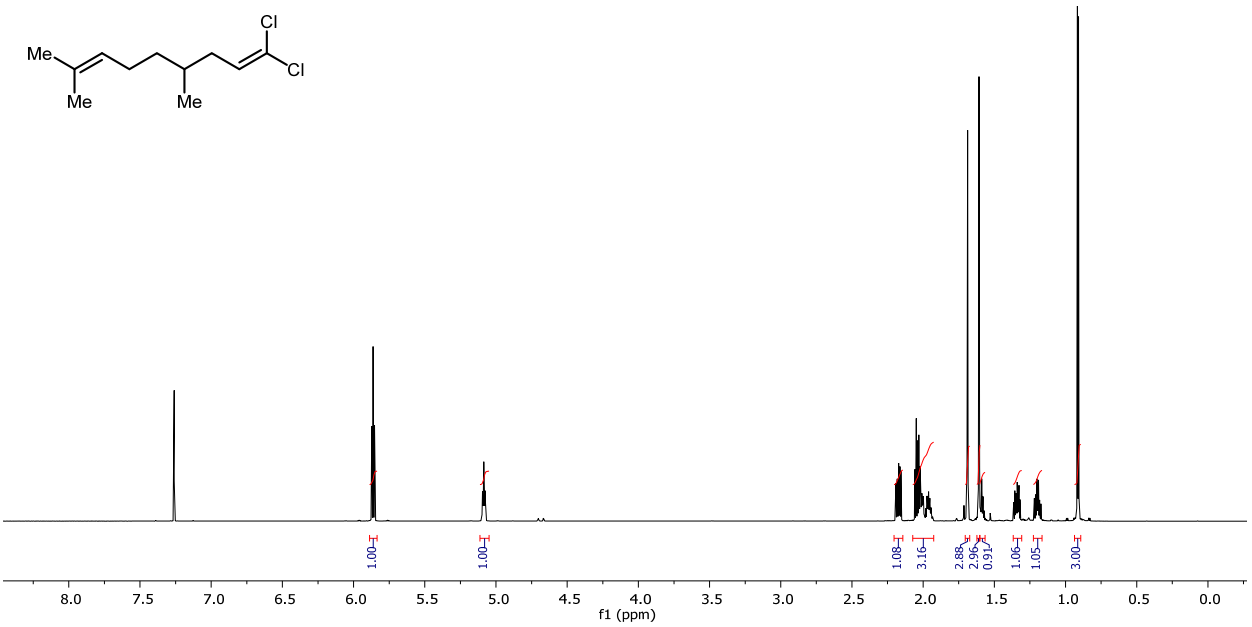
f1 (ppm)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Me
Me
Cl
Cl
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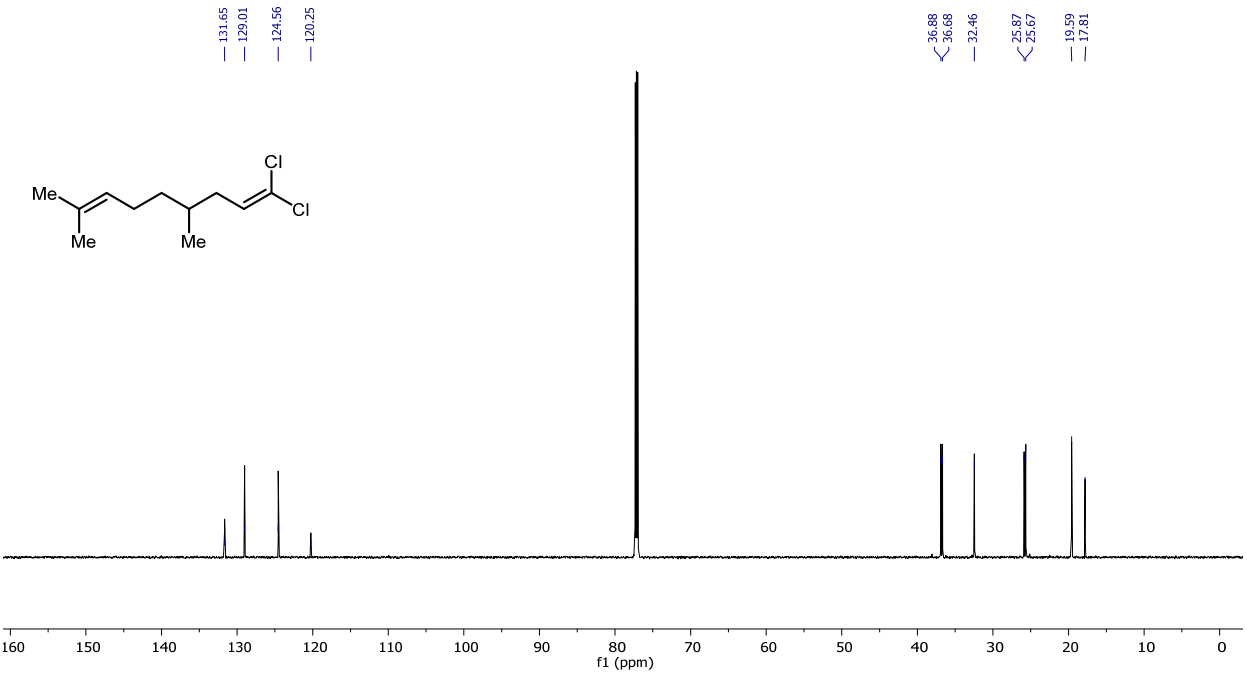
1.00
1.08
3.16
2.88
2.96
0.91
1.06
1.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.01
124.56
120.25
36.88
36.68
32.46
25.87
25.67
19.59
17.81
Me
Me
Me
Cl
Cl
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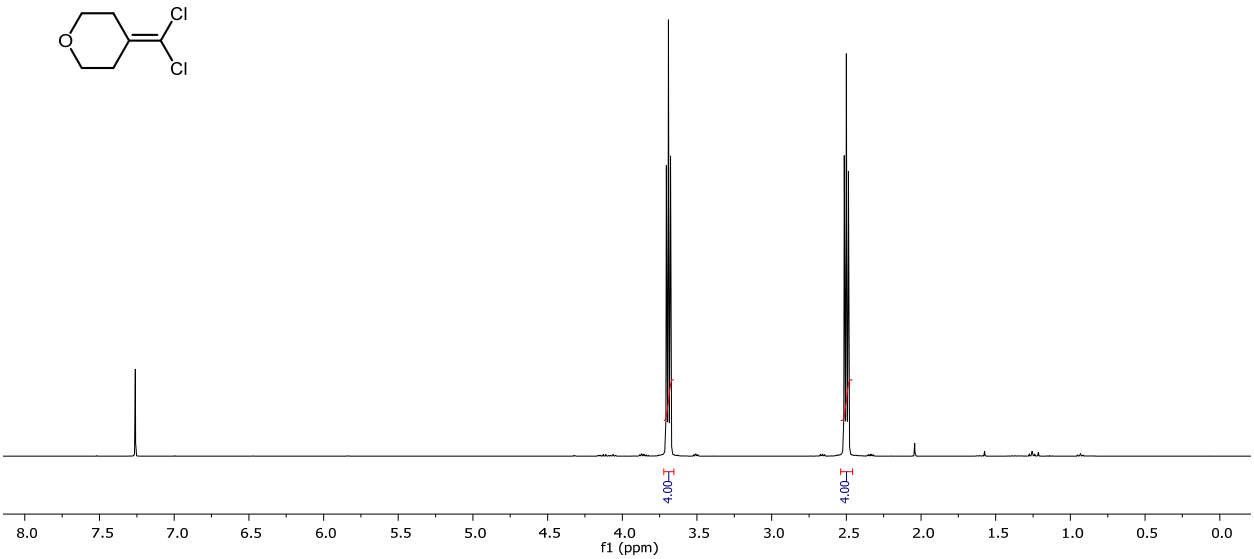
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Cl
O
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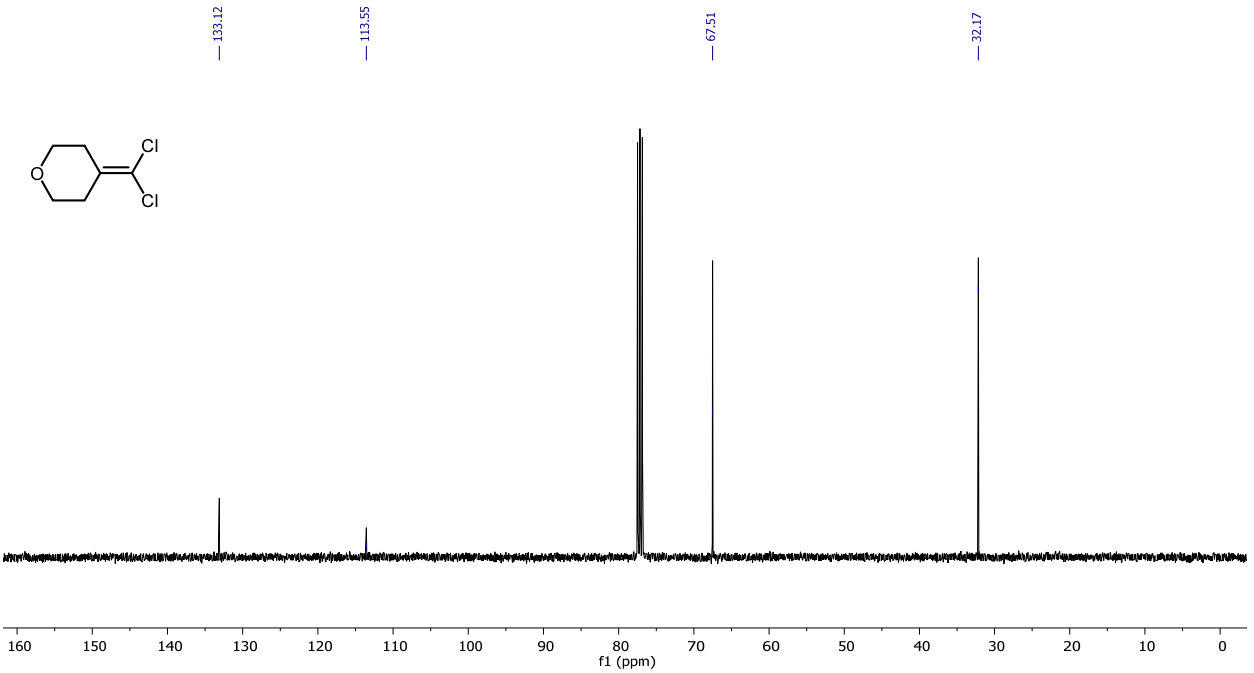
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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67.51
32.17
Cl
Cl
O
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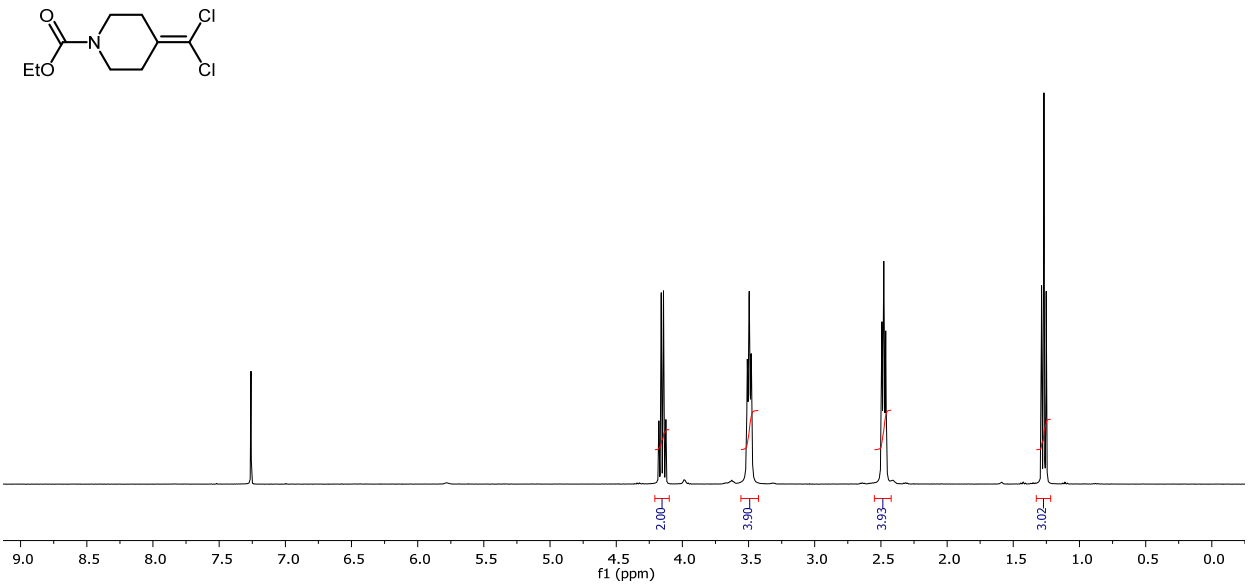
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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N
Cl
EtO
Cl
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3.90
3.93
3.02
9.0
8.5
8.0
7.5
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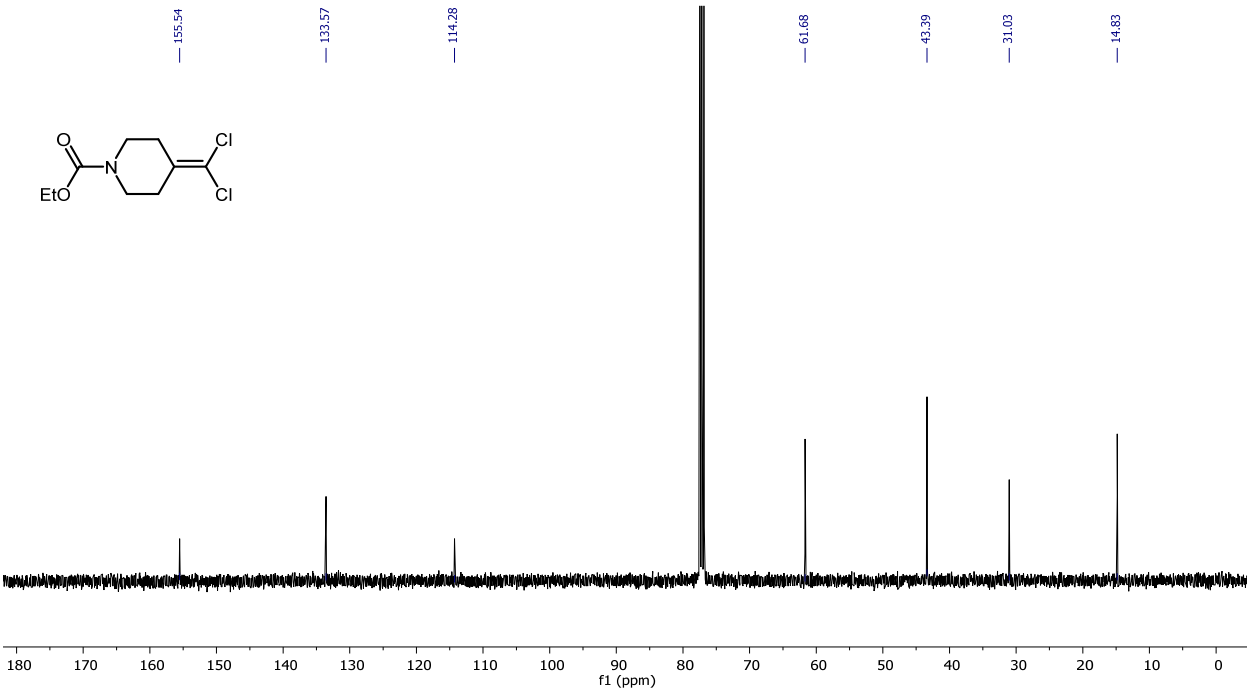
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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114.28
61.68
43.39
31.03
14.83
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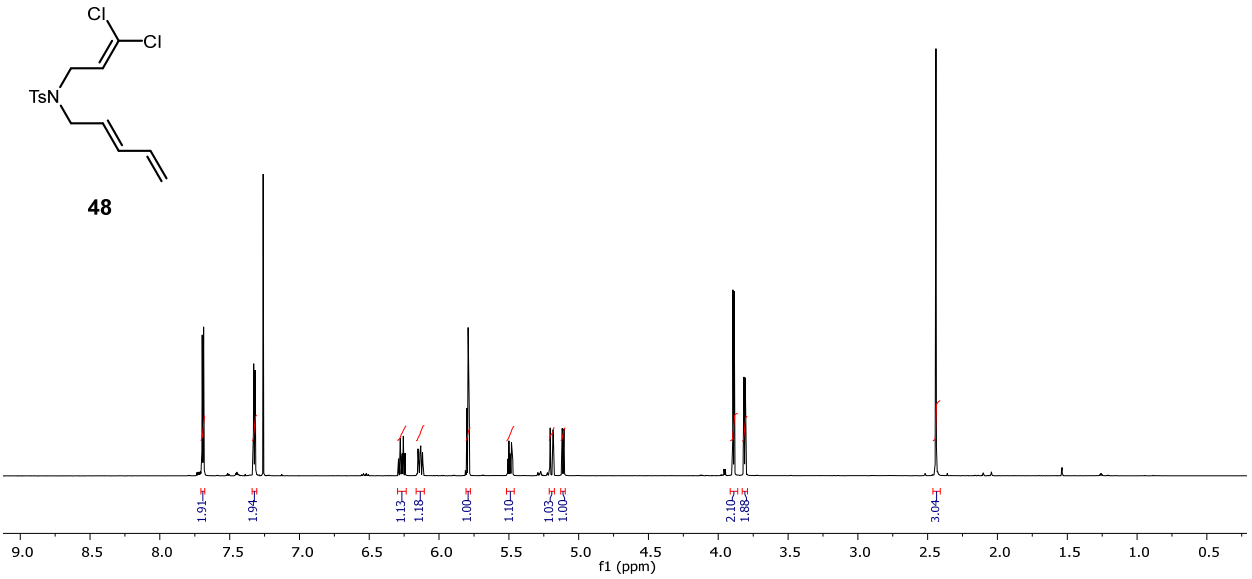
N
Cl
EtO
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Cl
TsN
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1.00
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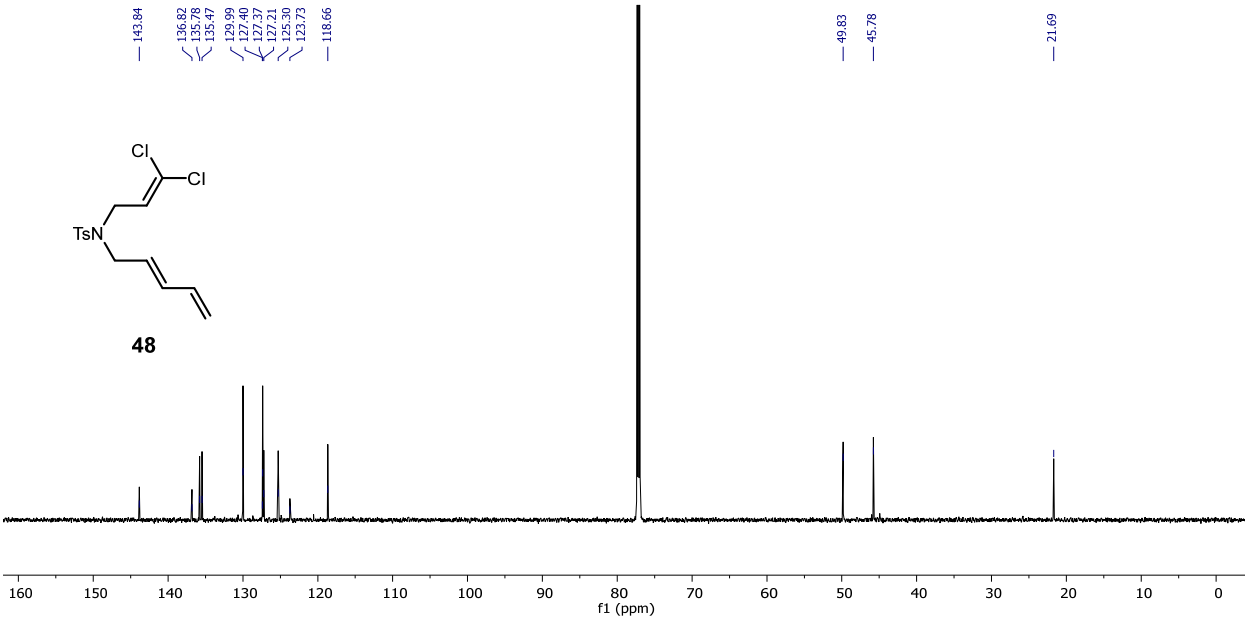
1.88
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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135.47
129.99
127.40
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127.21
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123.73
118.66
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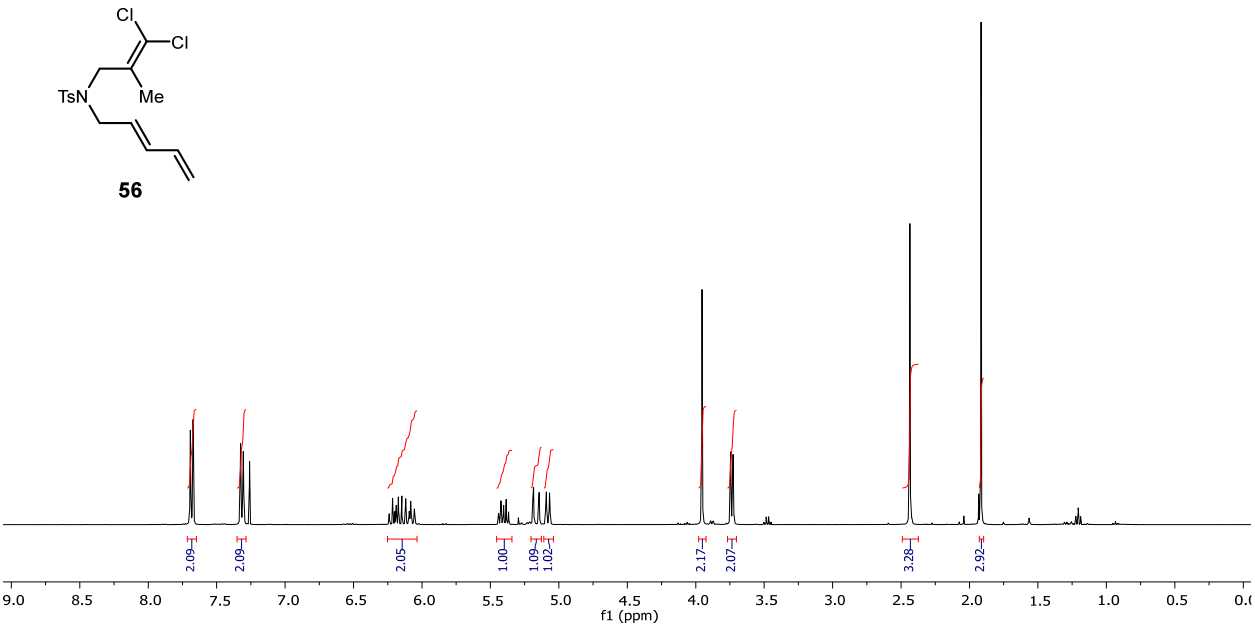
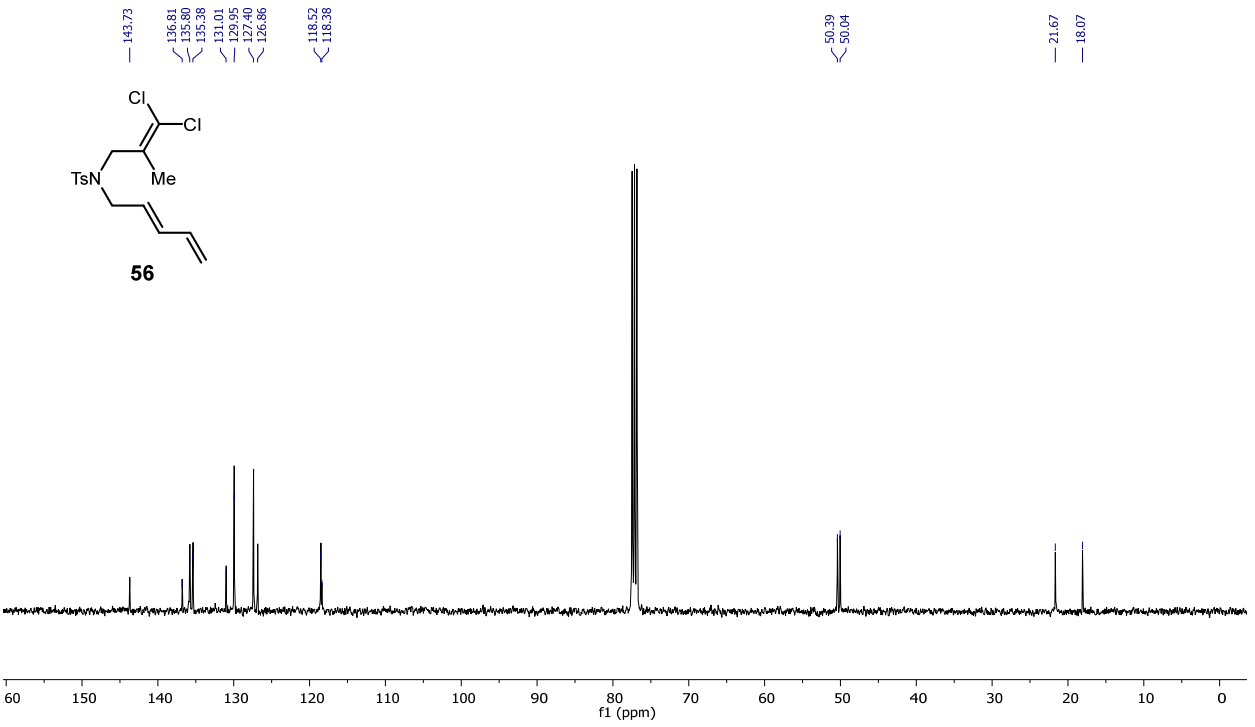
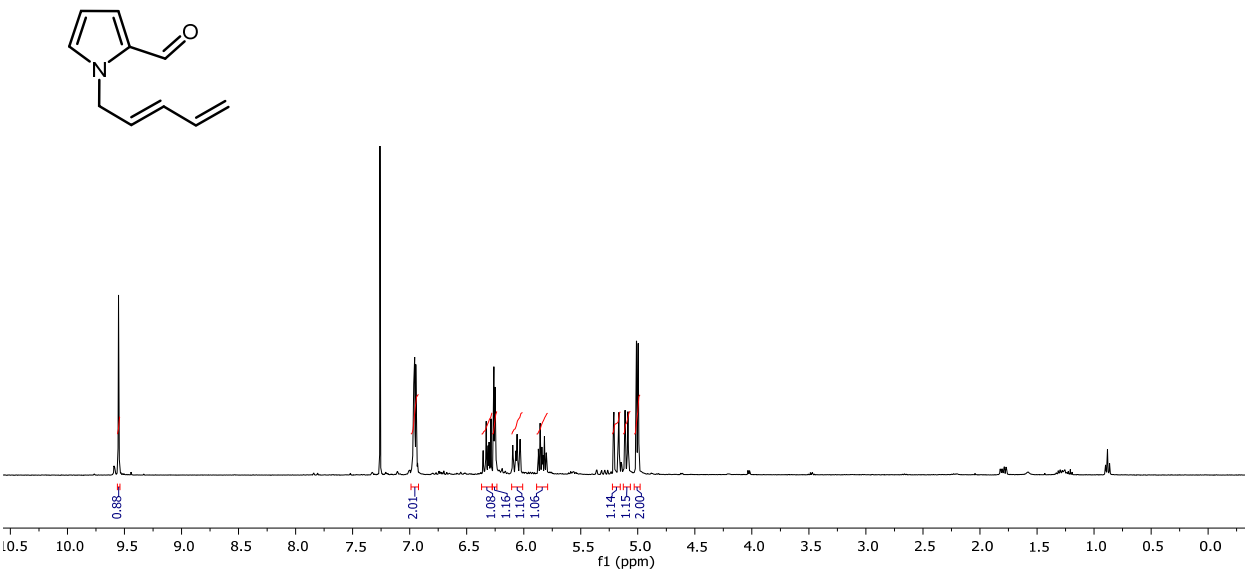
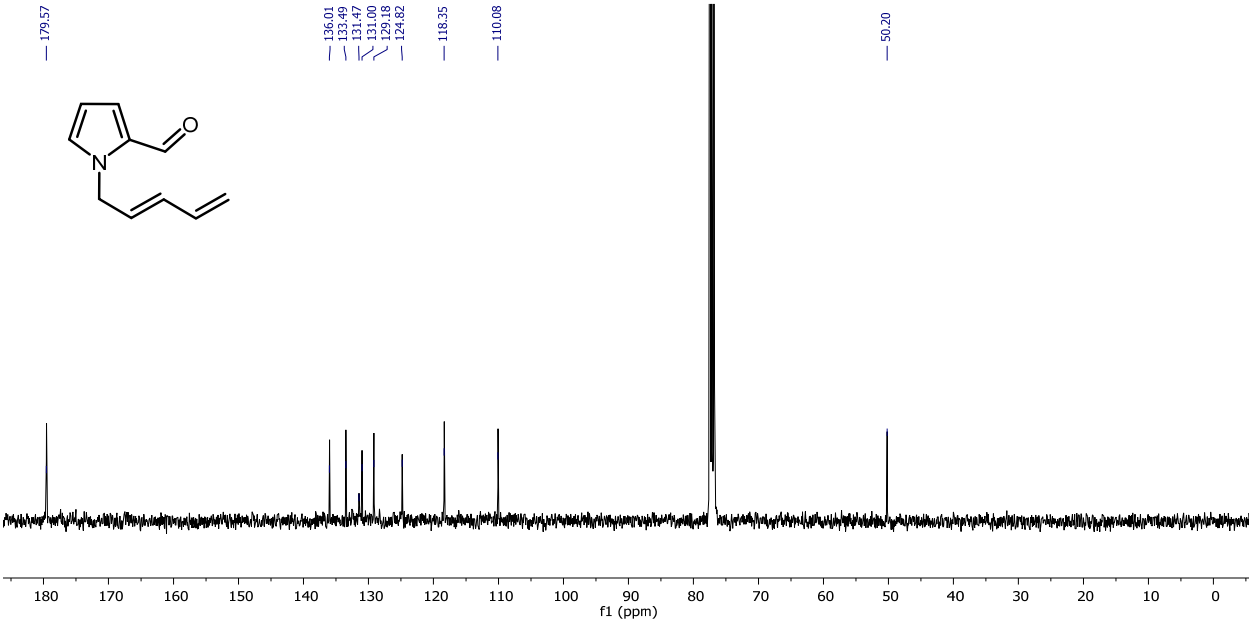
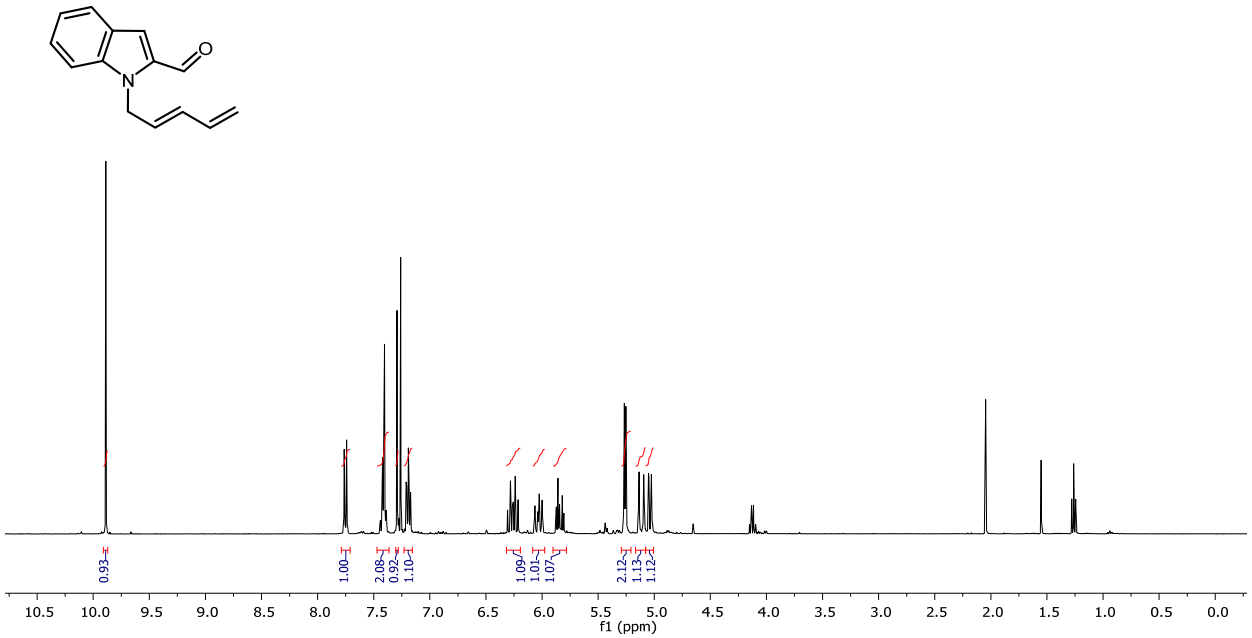
21.69
Cl
Cl
TsN
48
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

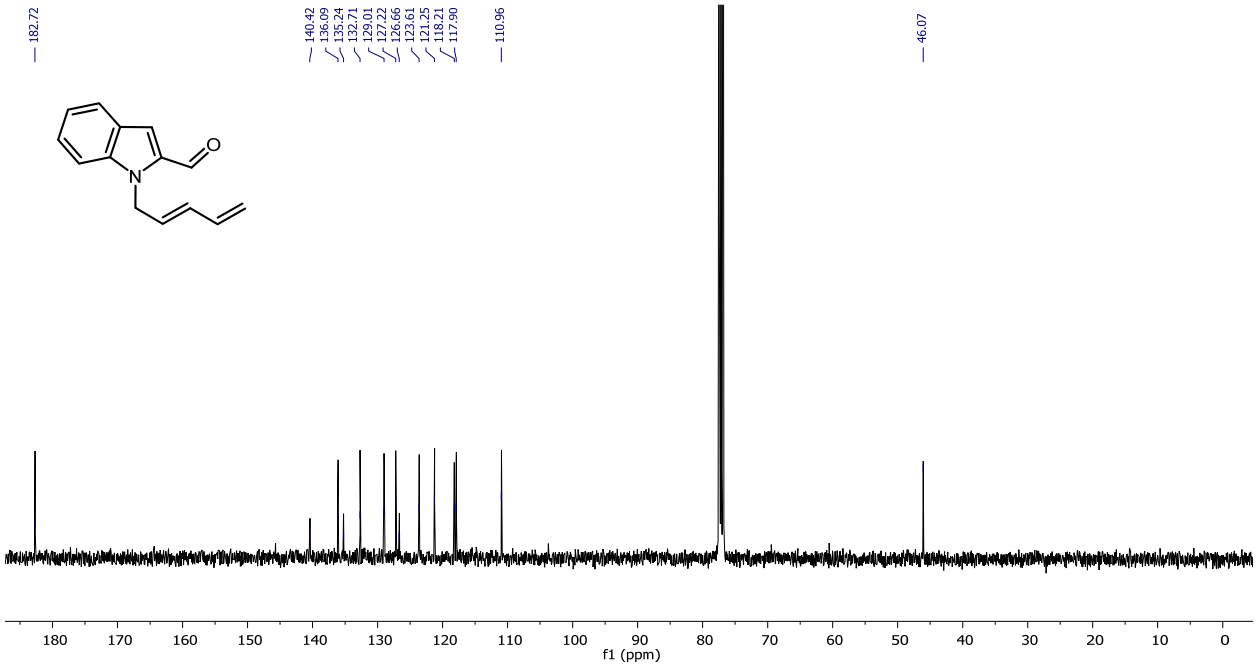

Cl
Cl
TsN
Me
56
2.09
2.09
2.05
1.00
1.09
1.02
2.17
2.07
3.28
2.92
f1 (ppm)

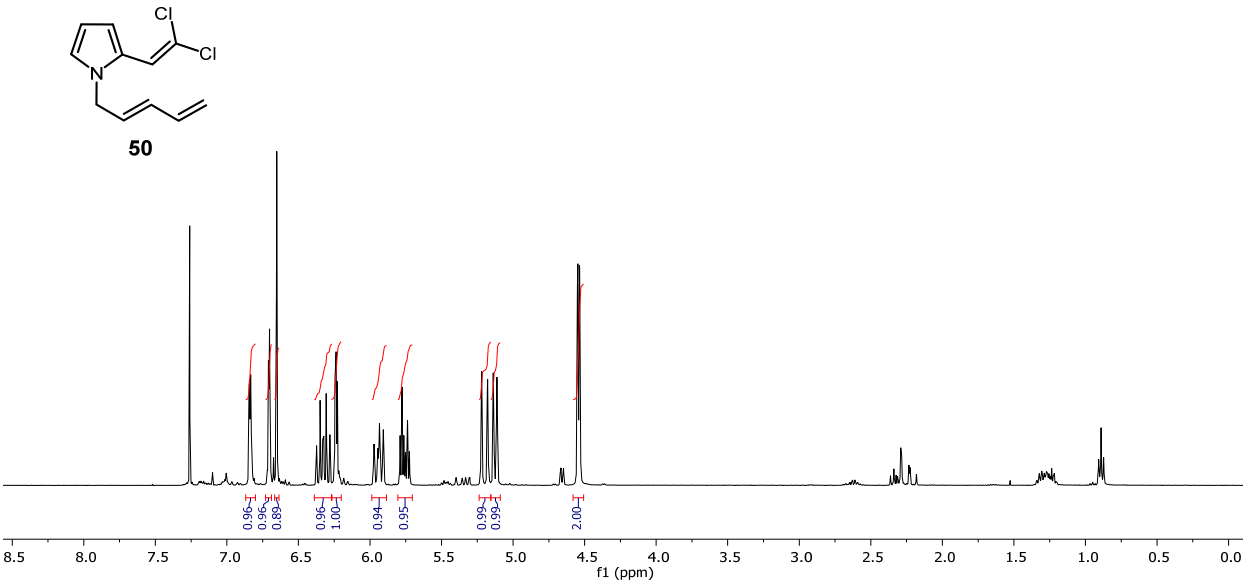

143.73
136.81
135.80
135.38
131.01
129.95
127.40
126.86
118.52
118.38
50.39
50.04
21.67
18.07
Cl
Cl
TsN
Me
56
f1 (ppm)

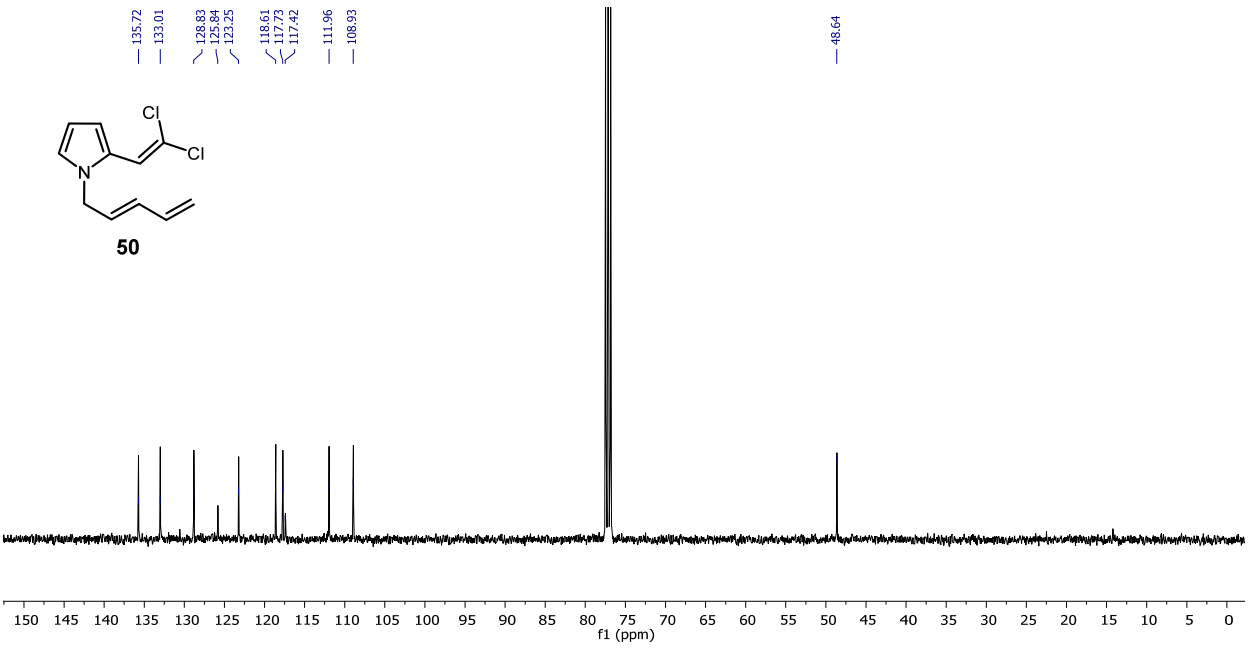

O
N
0.88
2.01
1.08
1.16
1.10
1.06
1.14
1.15
2.00
f1 (ppm)

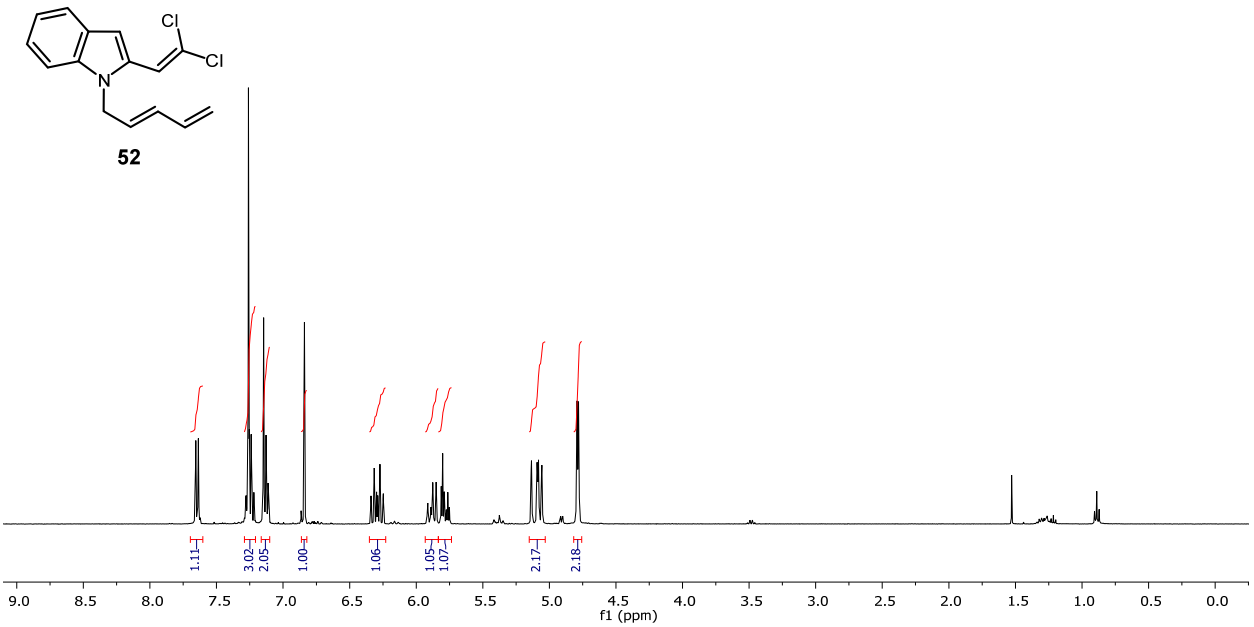

179.57
136.01
133.49
131.47
131.00
129.18
124.82
118.35
110.08
50.20
O
N
f1 (ppm)

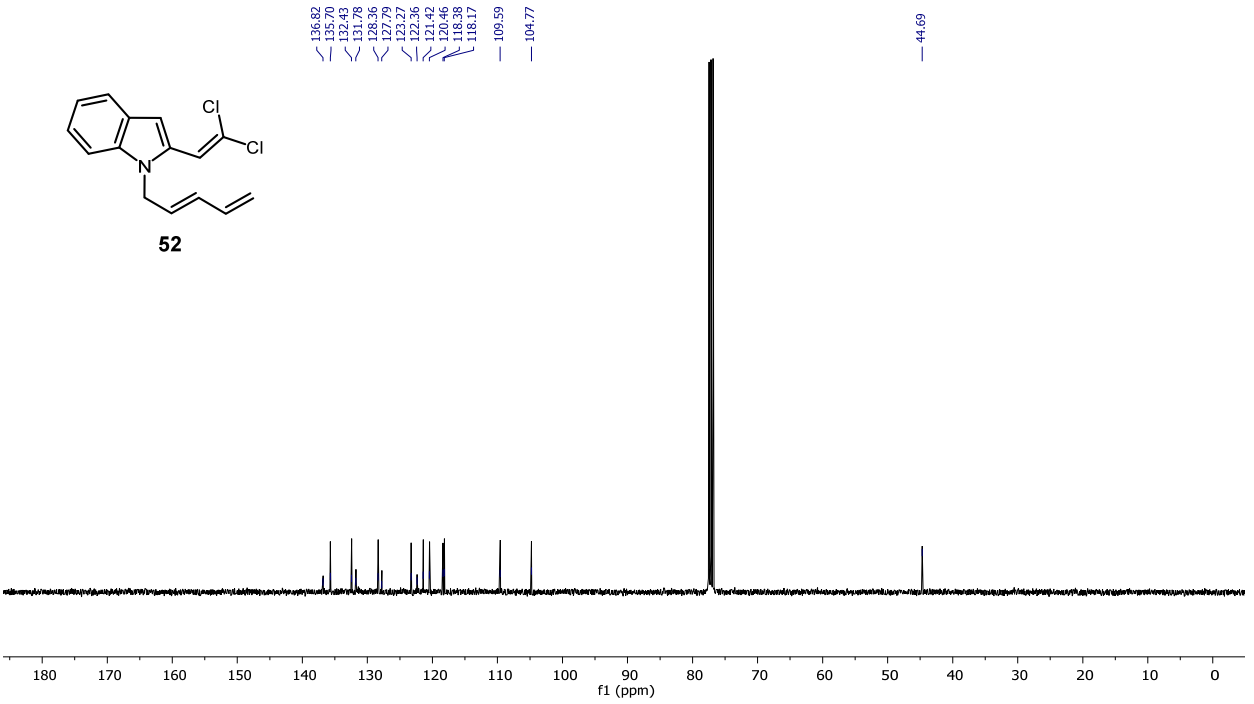

O
N
0.93
1.00
2.08
0.92
1.10
1.09
1.01
1.07
2.12
1.13
1.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

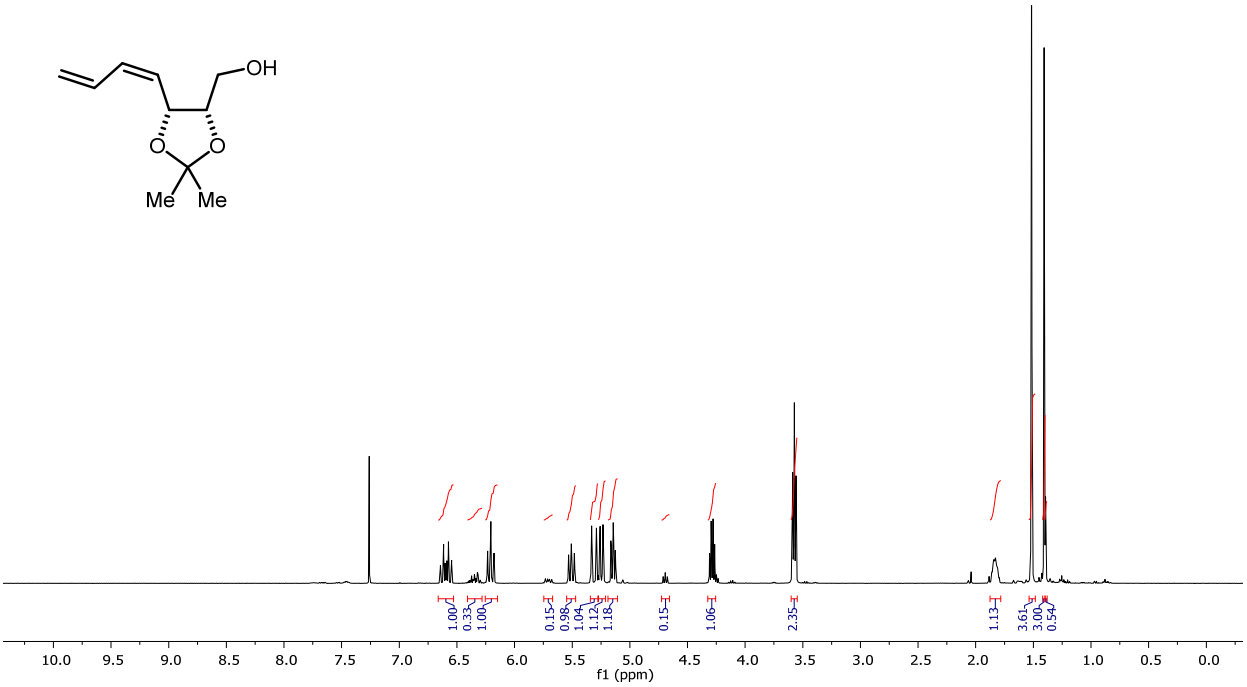

182.72
140.42
136.09
135.24
132.71
129.01
127.22
126.66
123.61
121.25
118.21
117.90
110.96
46.07
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

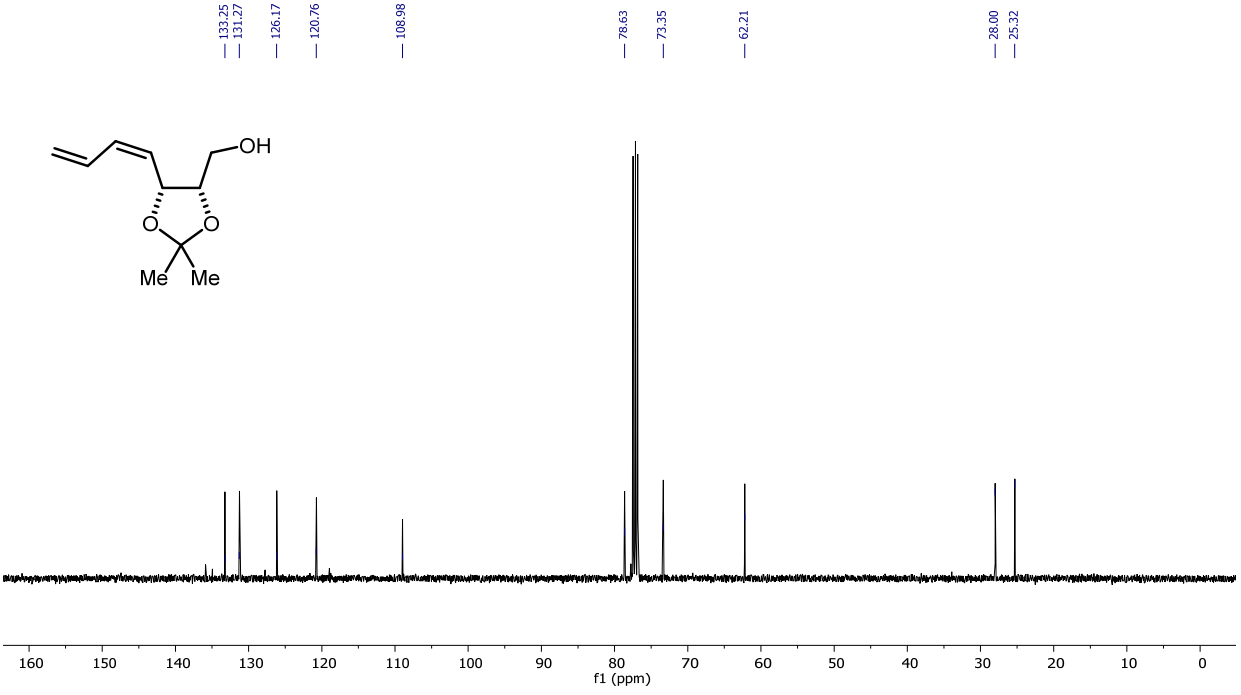

Cl
Cl
N
50
0.96
0.96
0.89
0.96
1.00
0.94
0.95
0.99
0.99
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

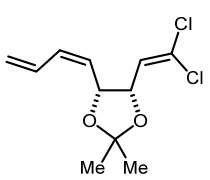

135.72
133.01
128.83
125.84
123.25
118.61
117.73
117.42
111.96
108.93
48.64
Cl
Cl
N
50
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


Cl
Cl
N
52
1.11
3.02
2.05
1.00
1.06
1.05
1.07
2.17
2.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


136.82
135.70
132.43
131.78
128.36
127.79
123.27
122.36
121.42
120.46
118.38
118.17
109.59
104.77
44.69
Cl
Cl
N
52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

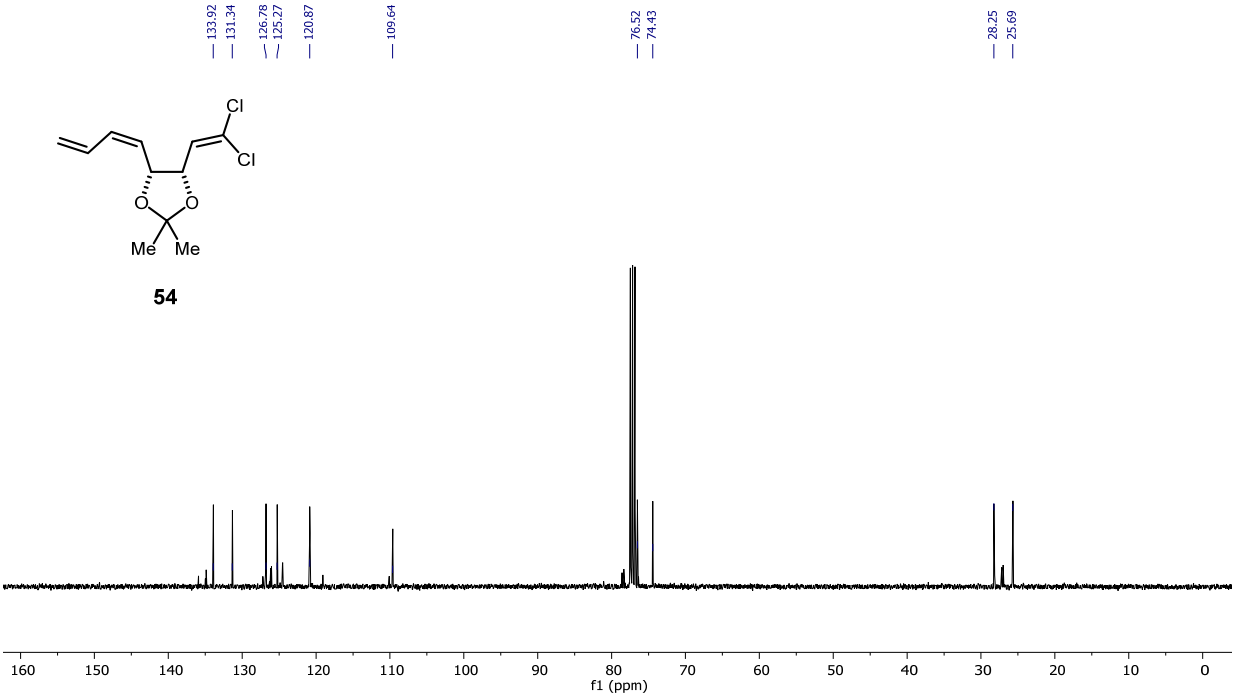

OH
O
O
Me
Me
1.00
0.33
1.00
0.15
0.98
1.04
1.12
1.18
0.15
1.06
2.35
1.13
3.61
3.00
0.54
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


133.25
131.27
126.17
120.76
108.98
78.63
73.35
62.21
28.00
25.32
OH
O
O
Me
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
Cl
O
O
Me
Me

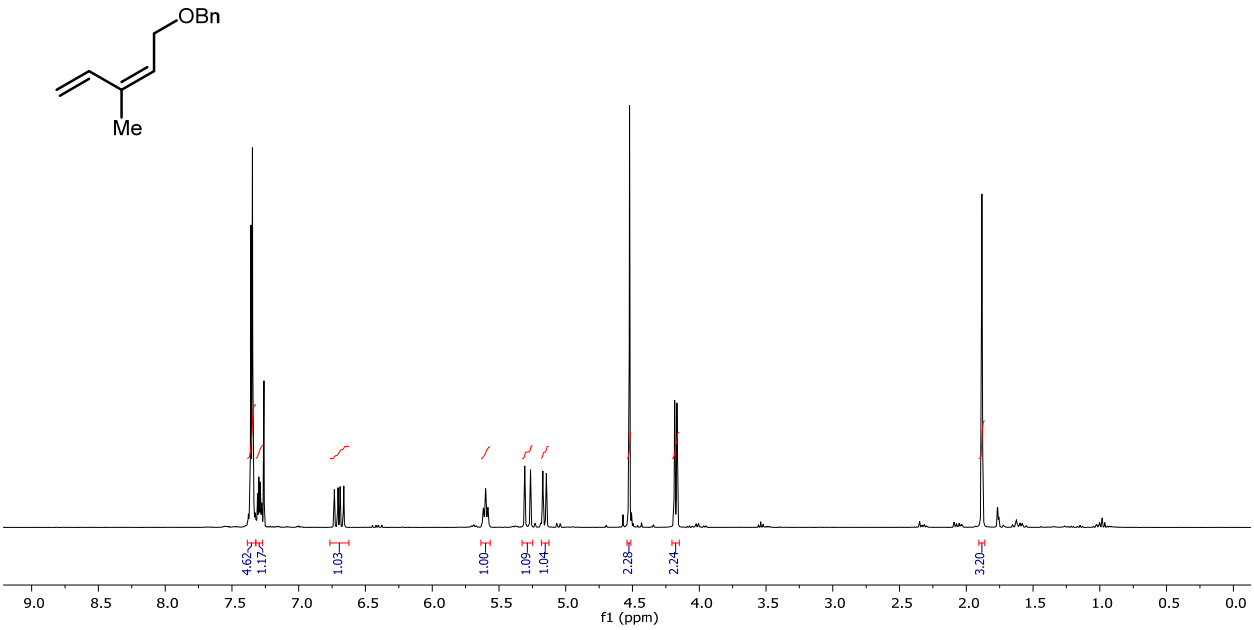
54

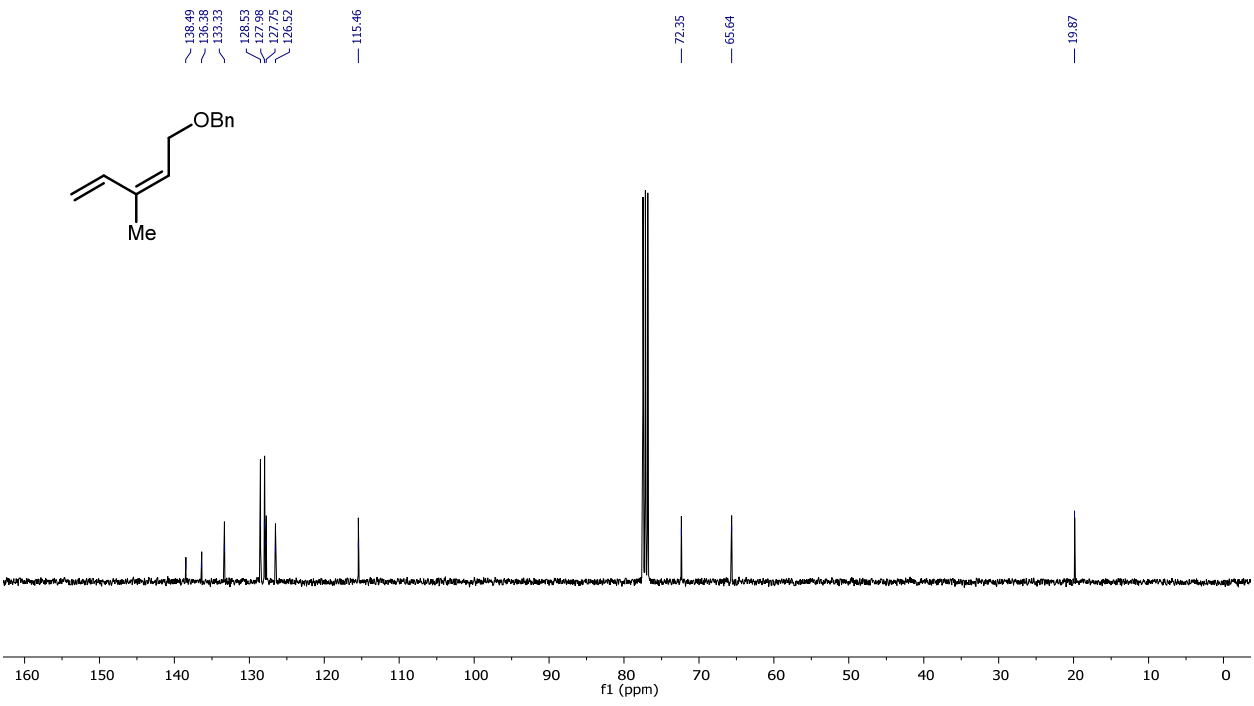
1.00
0.29
0.99
0.18
0.84
0.12
0.18
1.94
1.13
1.03
0.88
0.13
0.19
0.20
2.99
0.65
0.55
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

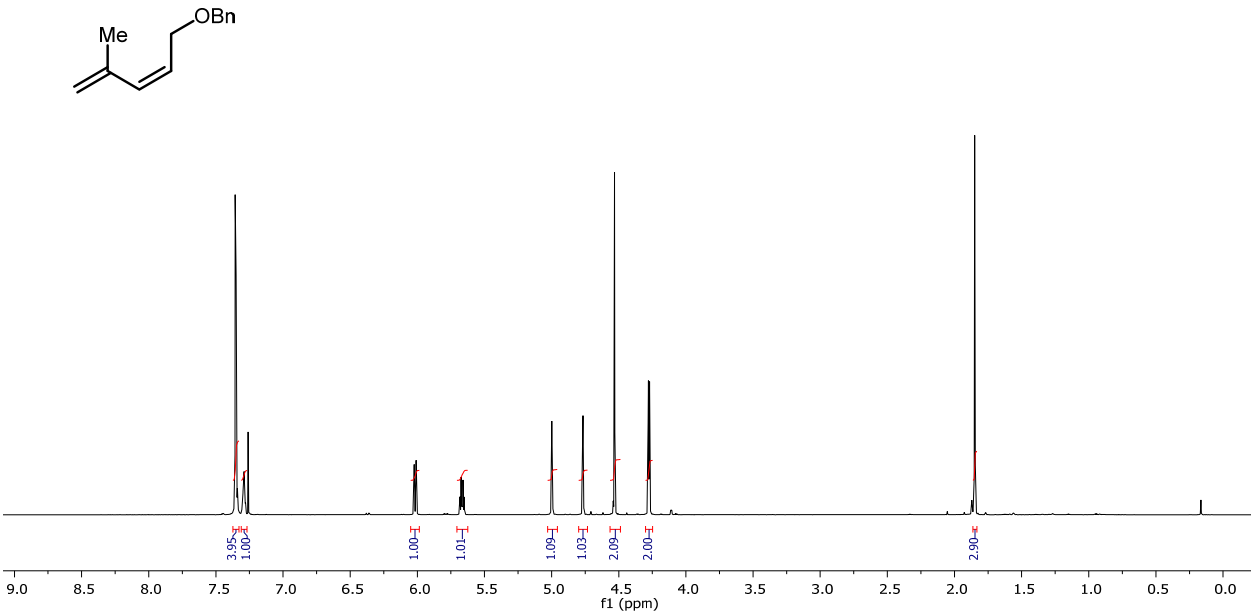

133.92
131.34
126.78
125.27
120.87
109.64
76.52
74.43
28.25
25.69
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

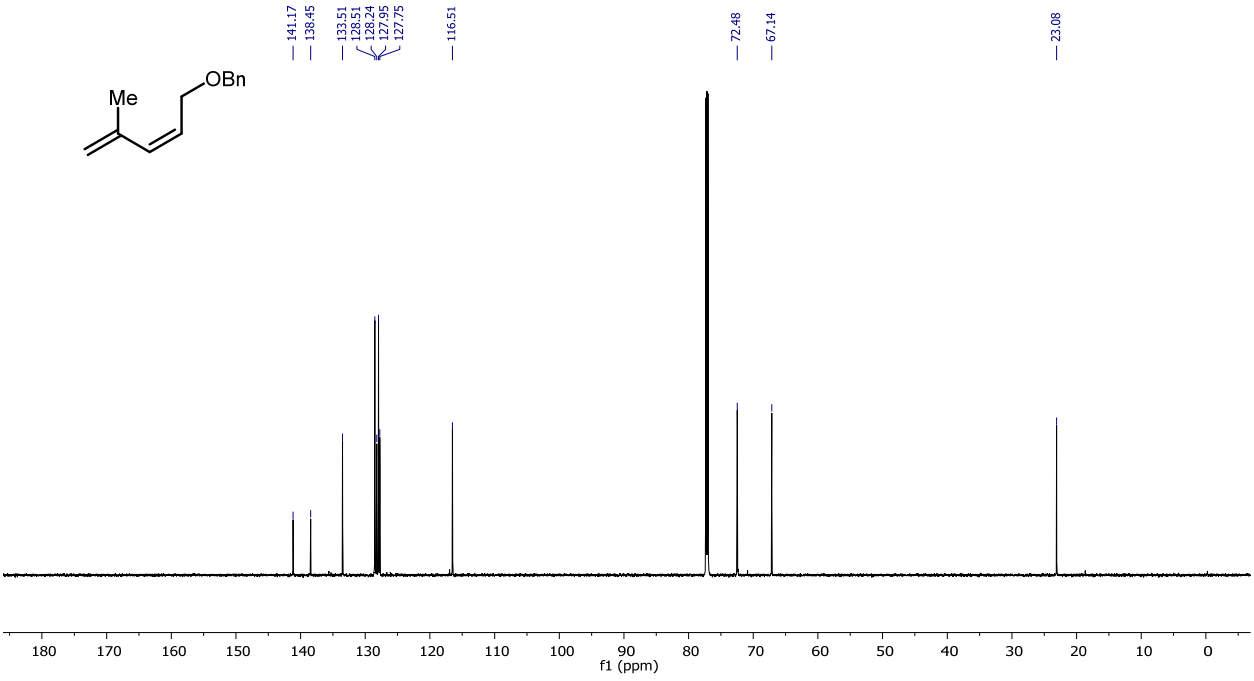
Cl
Cl
O
O
Me
Me

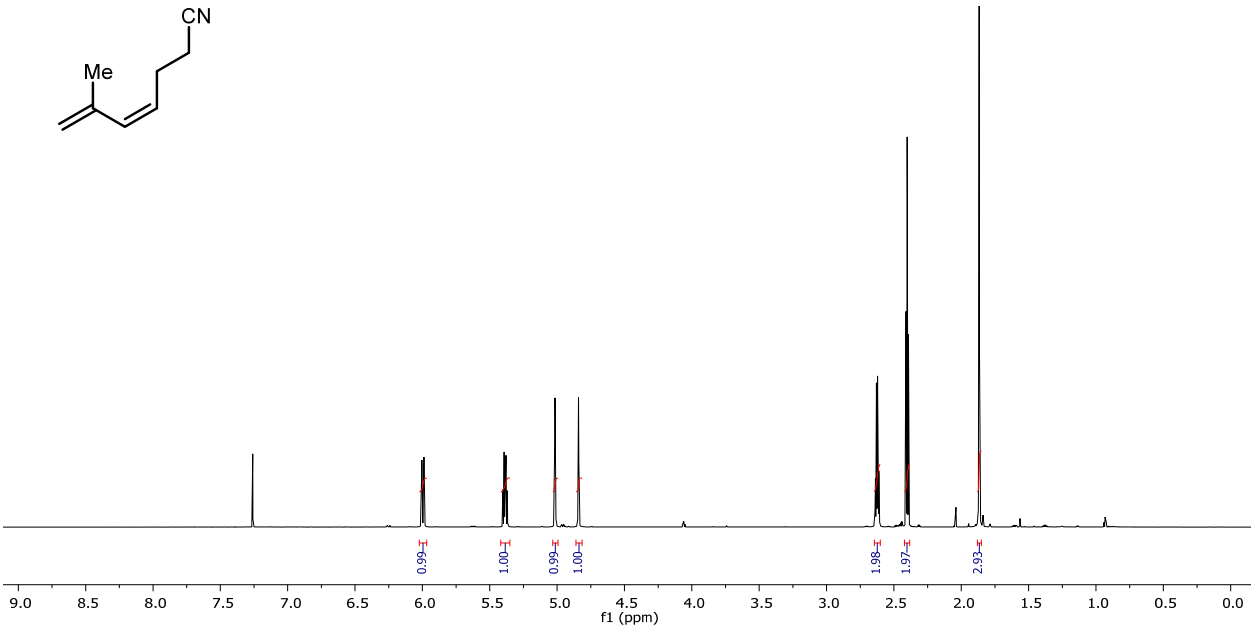
54

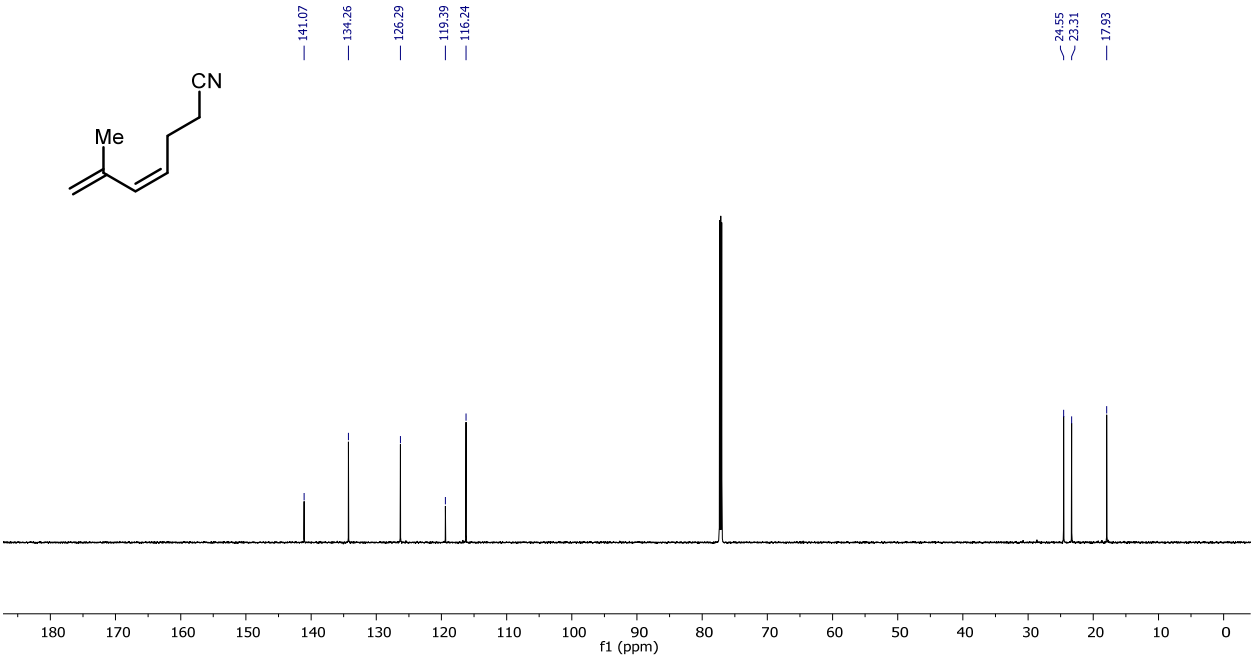

OBn
Me
4.62
1.17
1.03
1.00
1.09
1.04
2.28
2.24
3.20
f1 (ppm)

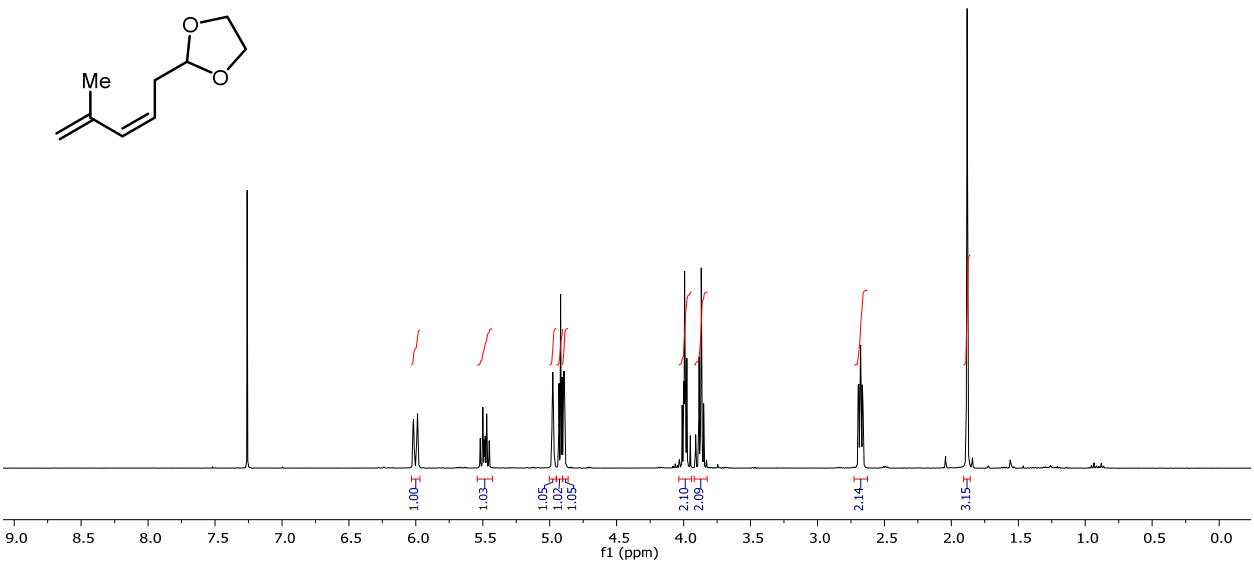

138.49
136.38
133.33
128.53
127.98
127.75
126.52
115.46
72.35
65.64
19.87
OBn
Me
f1 (ppm)

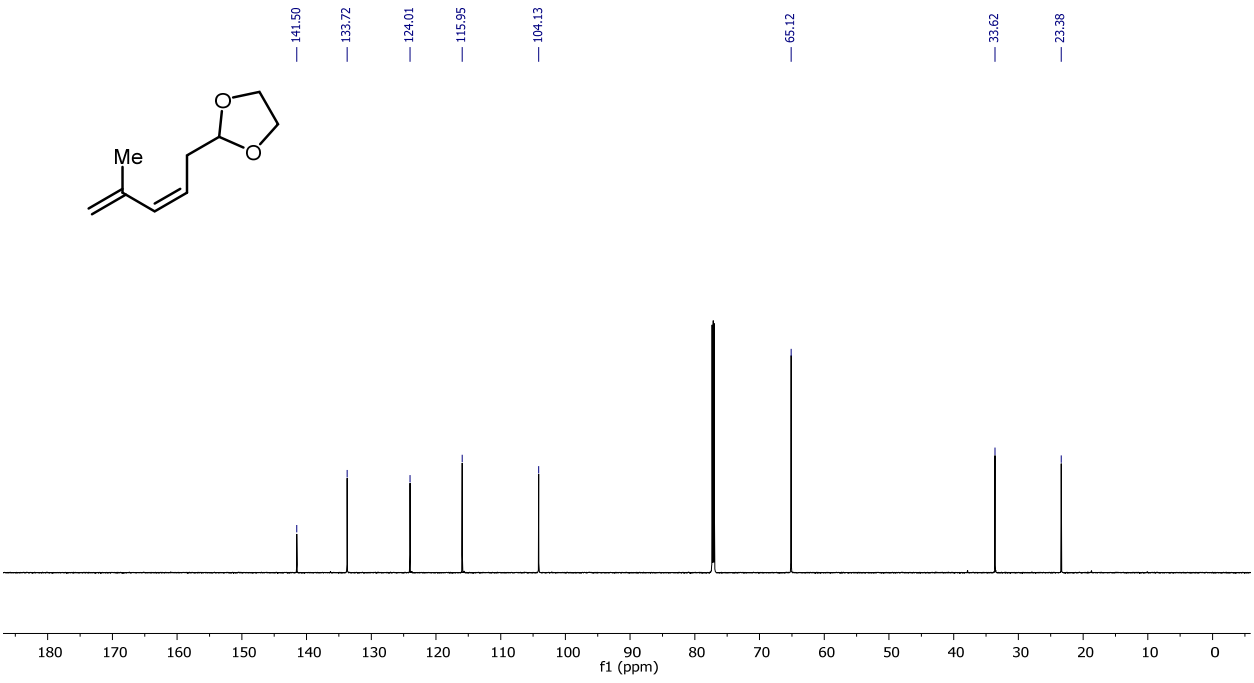

Me
OBn
3.95
1.00
1.00
1.01
1.09
1.03
2.09
2.00
2.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

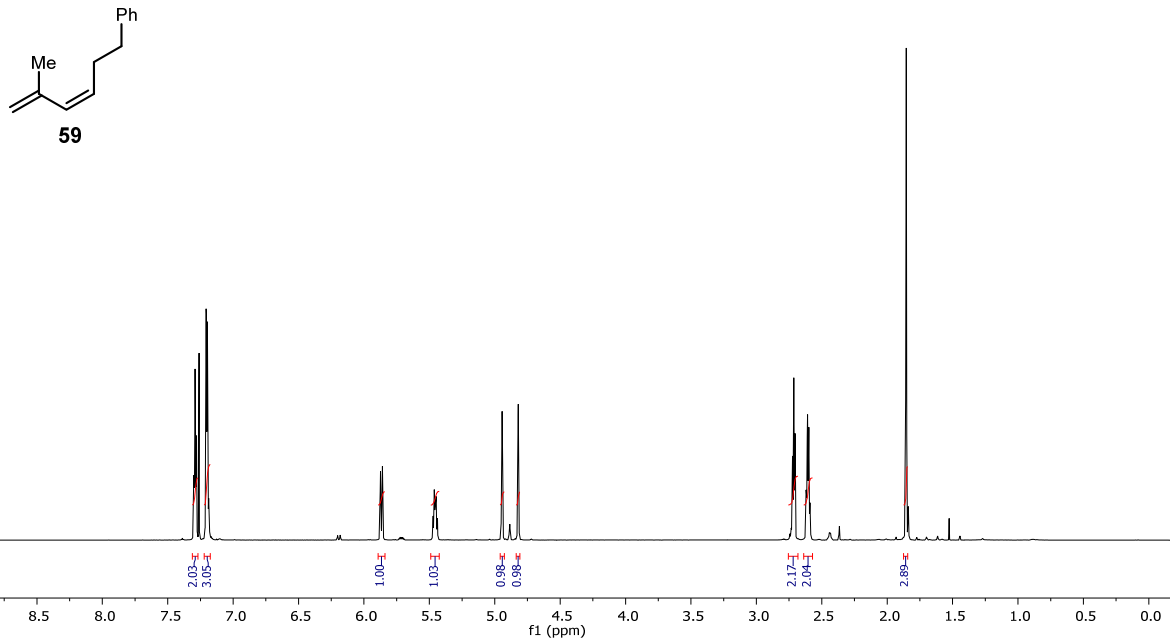

141.17
138.45
133.51
128.51
128.24
127.95
127.75
116.51
72.48
67.14
23.08
Me
OBn
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

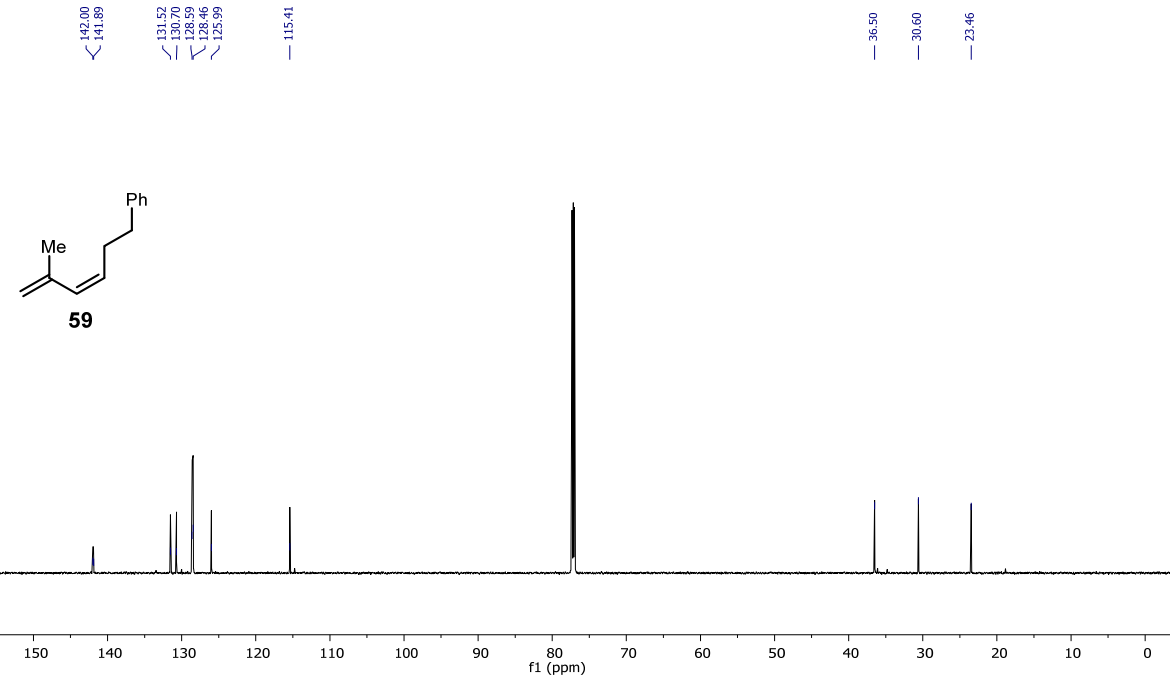

CN
Me
0.99
1.00
0.99
1.00
1.98
1.97
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

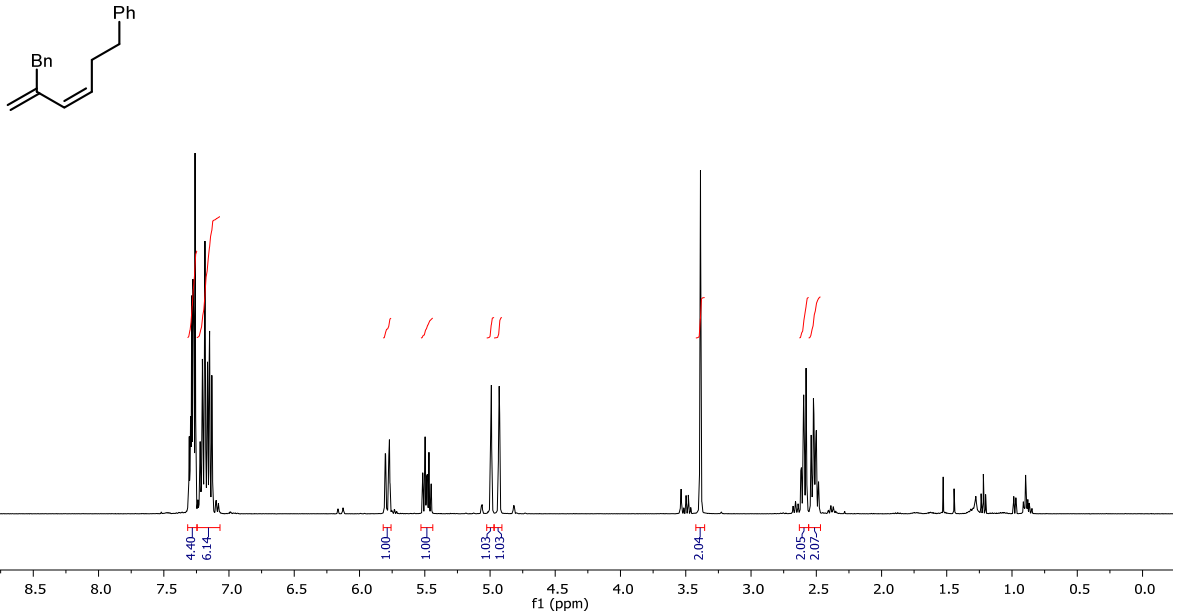

141.07
134.26
126.29
119.39
116.24
24.55
23.31
17.93
CN
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

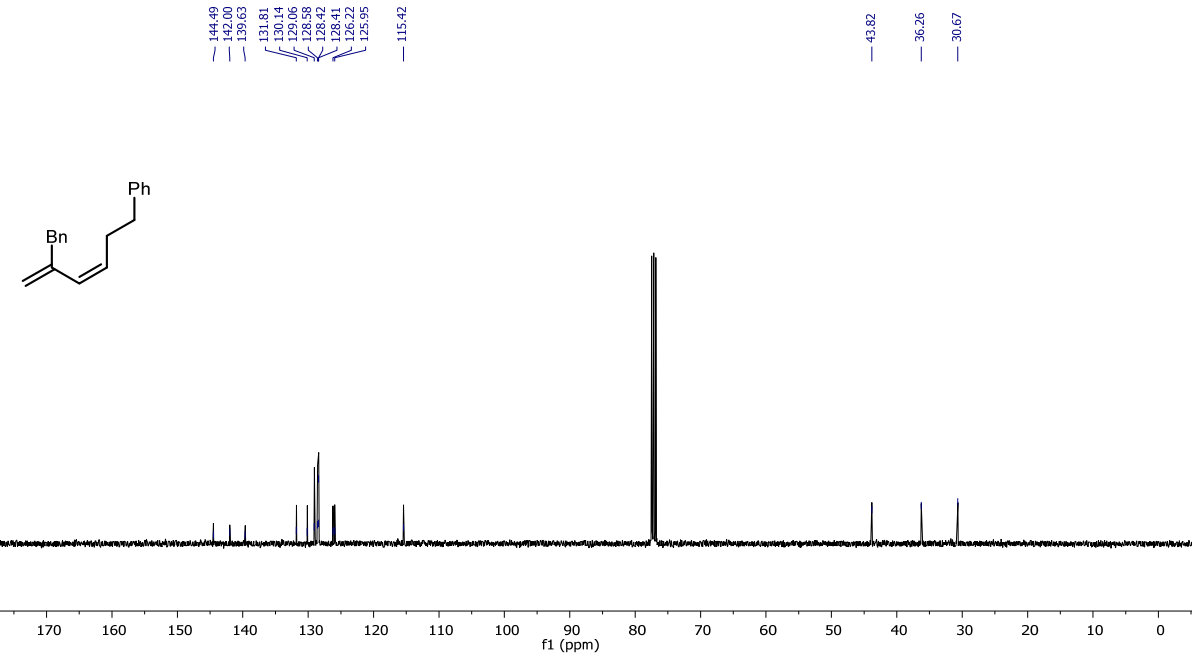

Me
1.00
1.03
1.05
1.02
1.05
2.10
2.09
2.14
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

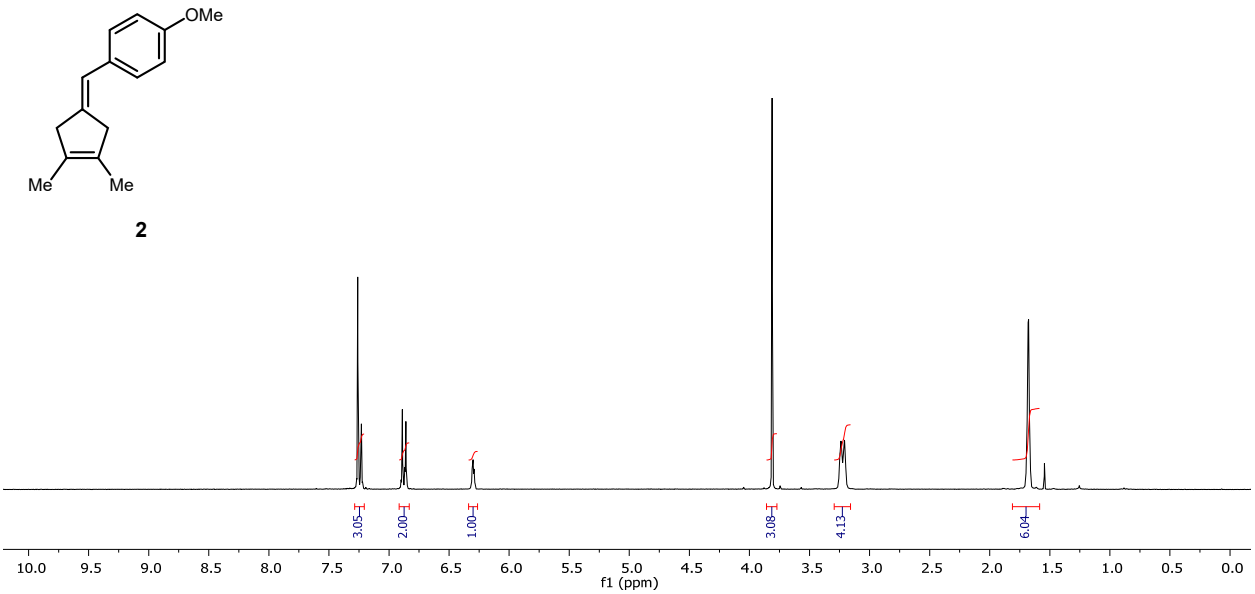

141.50
133.72
124.01
115.95
104.13
65.12
33.62
23.38
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Me
59
2.03
3.05
1.00
1.03
0.98
0.98
2.17
2.04
2.89
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

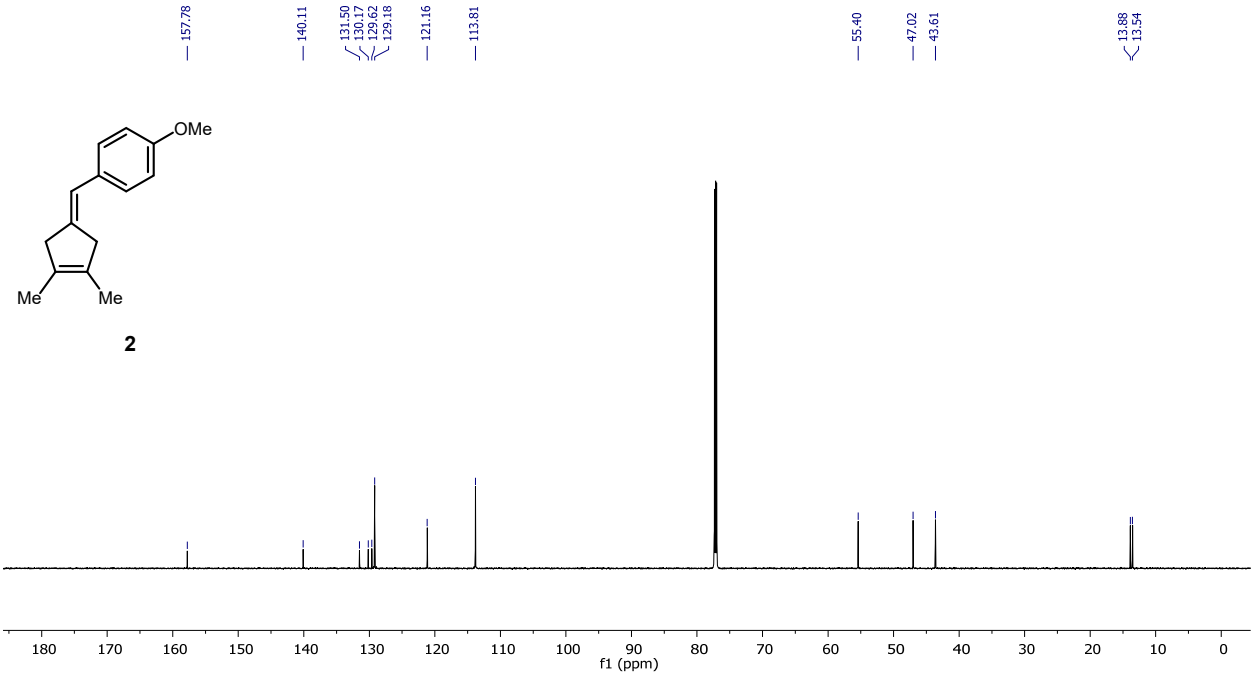

142.00
141.89
131.52
130.70
128.59
128.46
125.99
115.41
36.50
30.60
23.46
Ph
Me
59
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Bn
4.40
6.14
1.00
1.00
1.03
1.03
2.04
2.05
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

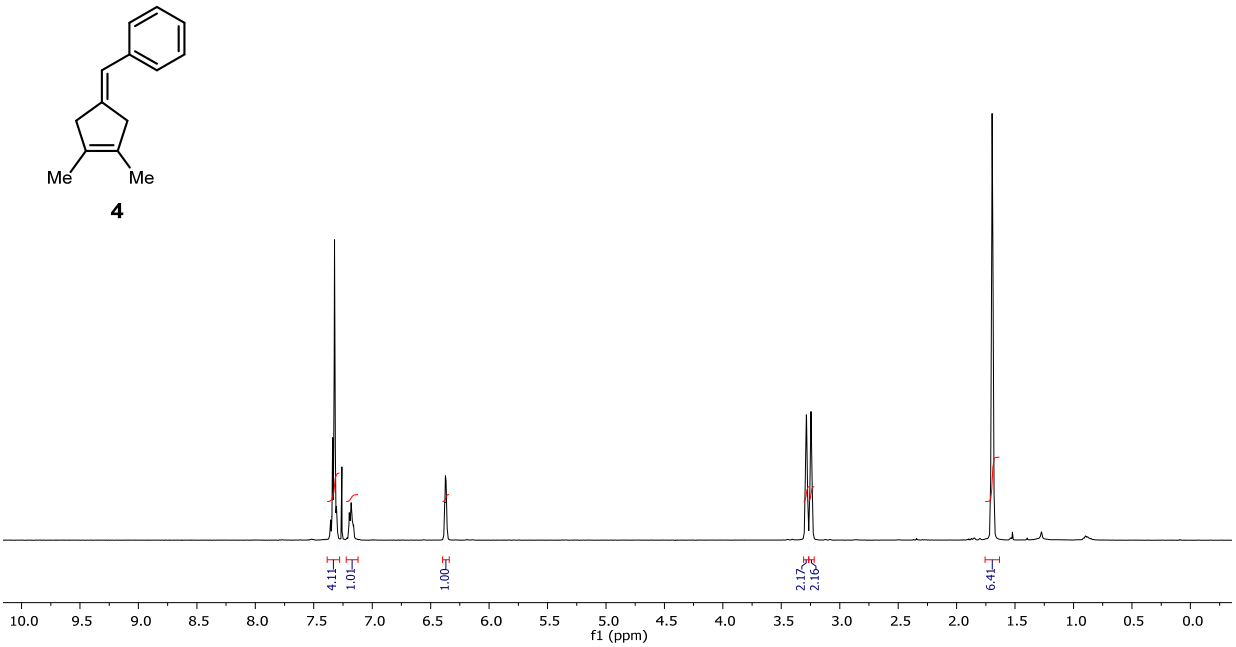

144.49
142.00
139.63
131.81
130.14
129.06
128.58
128.42
128.41
126.22
125.95
115.42
43.82
36.26
30.67
Ph
Bn
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

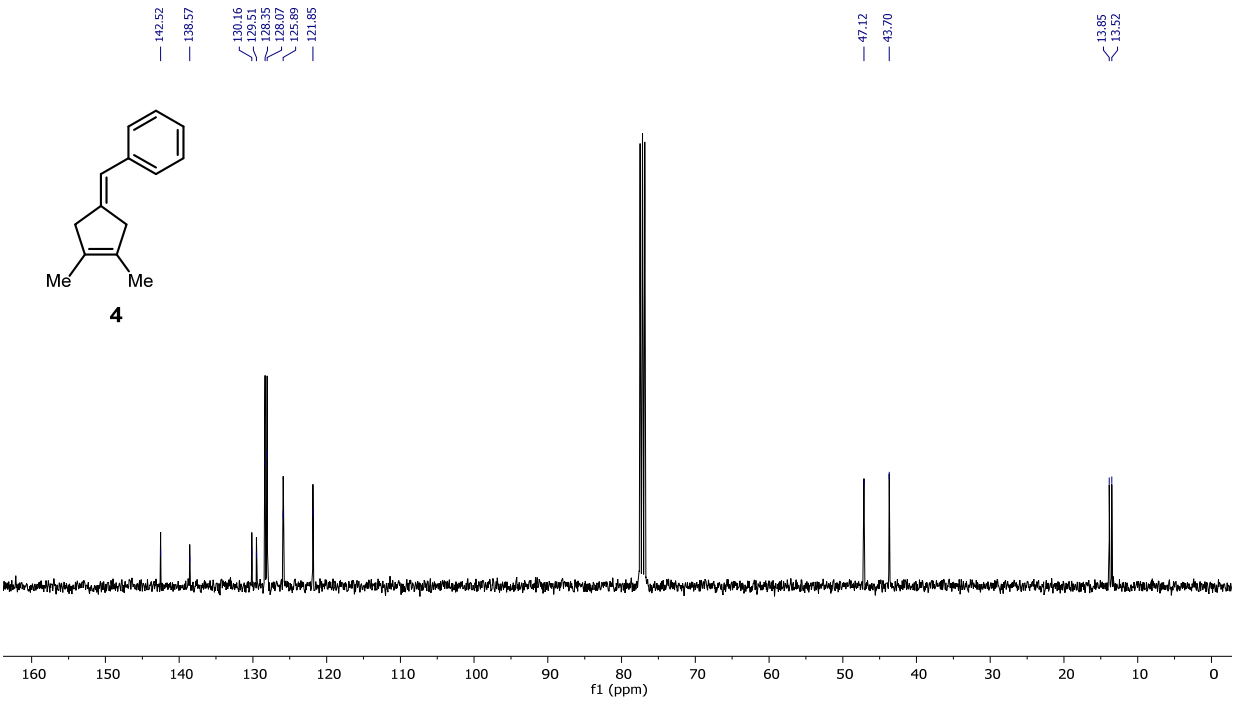

OMe
Me
Me
3.05
2.00
1.00
3.08
4.13
6.04
f1 (ppm)

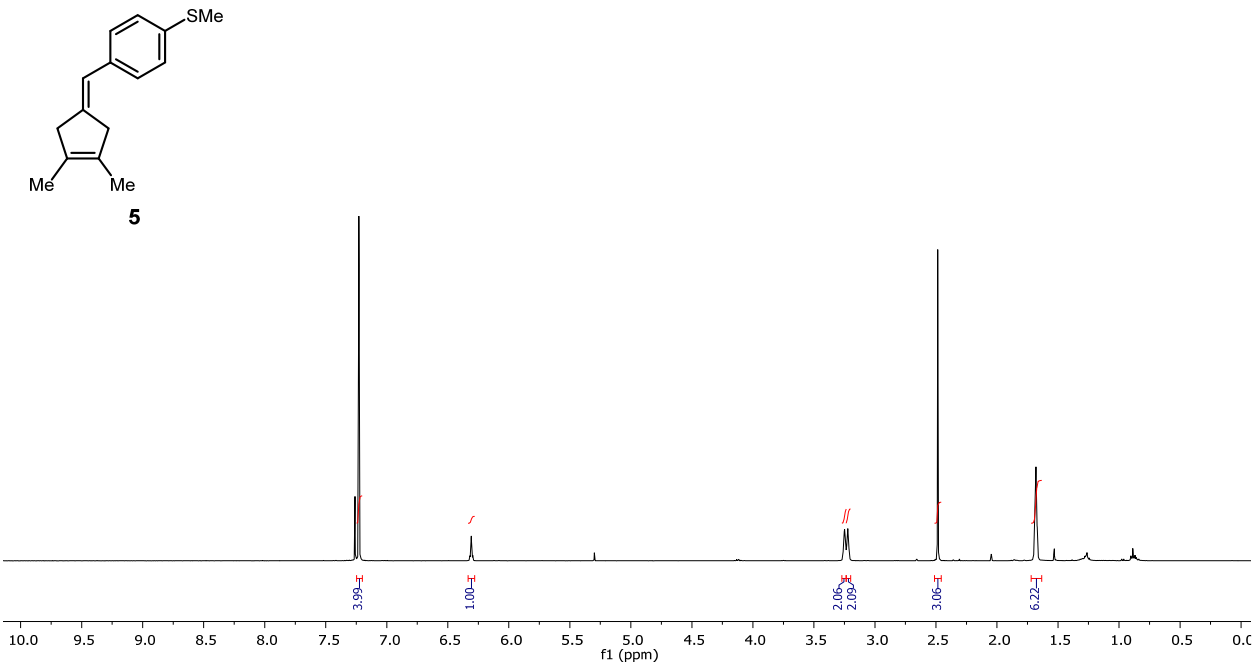
2

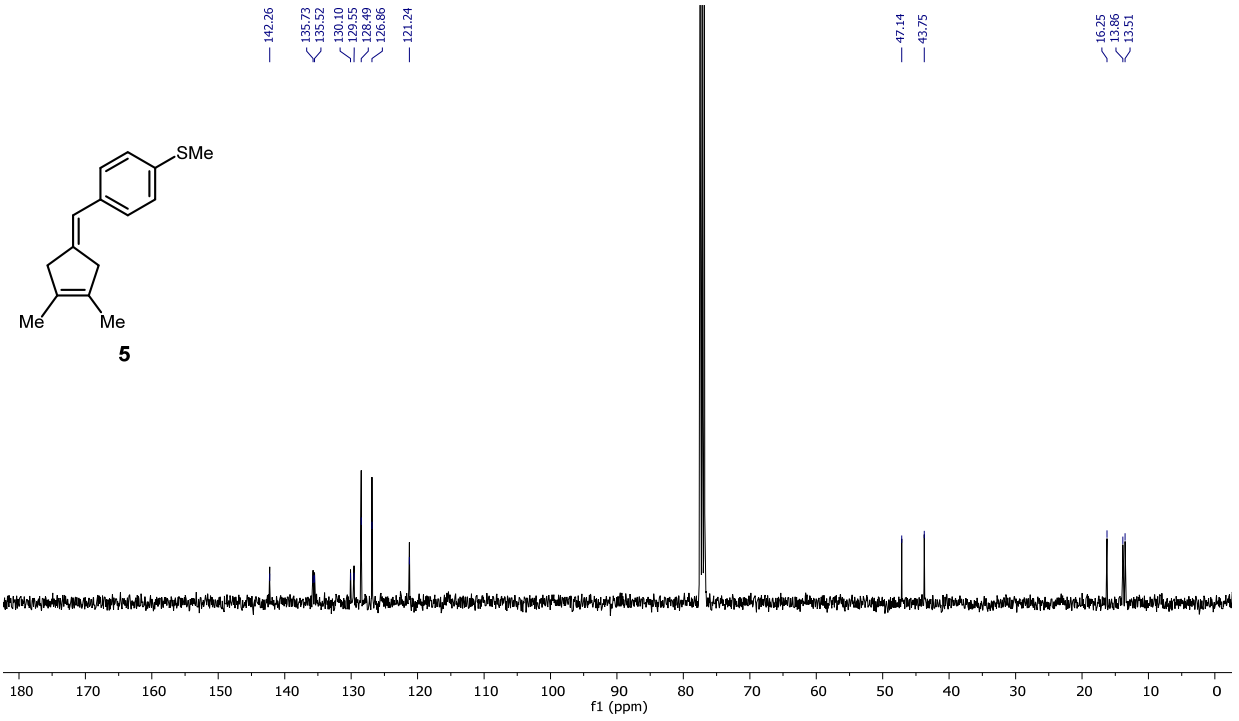

157.78
140.11
131.50
130.17
129.62
129.18
121.16
113.81
55.40
47.02
43.61
13.88
13.54
OMe
Me
Me
f1 (ppm)

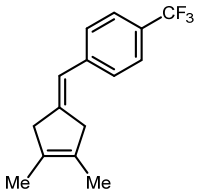
2


Me
Me
4
4.11
1.01
1.00
2.17
2.16
6.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

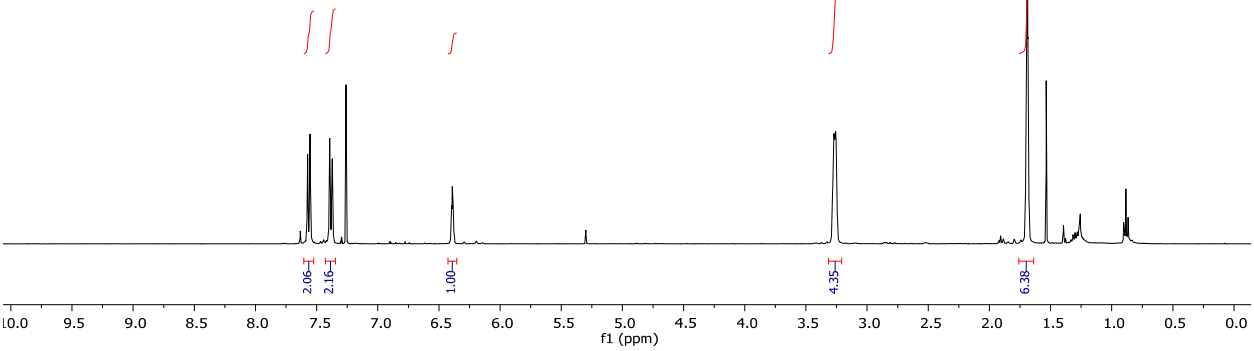

142.52
138.57
130.16
129.51
128.35
128.07
125.89
121.85
47.12
43.70
13.85
13.52
Me
Me
4
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SMe
Me
Me
5
3.99
1.00
2.06
2.09
3.06
6.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.26
135.73
135.52
130.10
129.55
128.49
126.86
121.24
47.14
43.75
16.25
13.86
13.51
SMe
Me
Me
5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

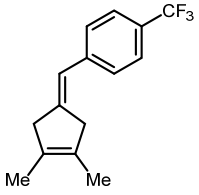

CF3
Me
Me

6


2.06
2.16
1.00
4.35
6.38
f1 (ppm)

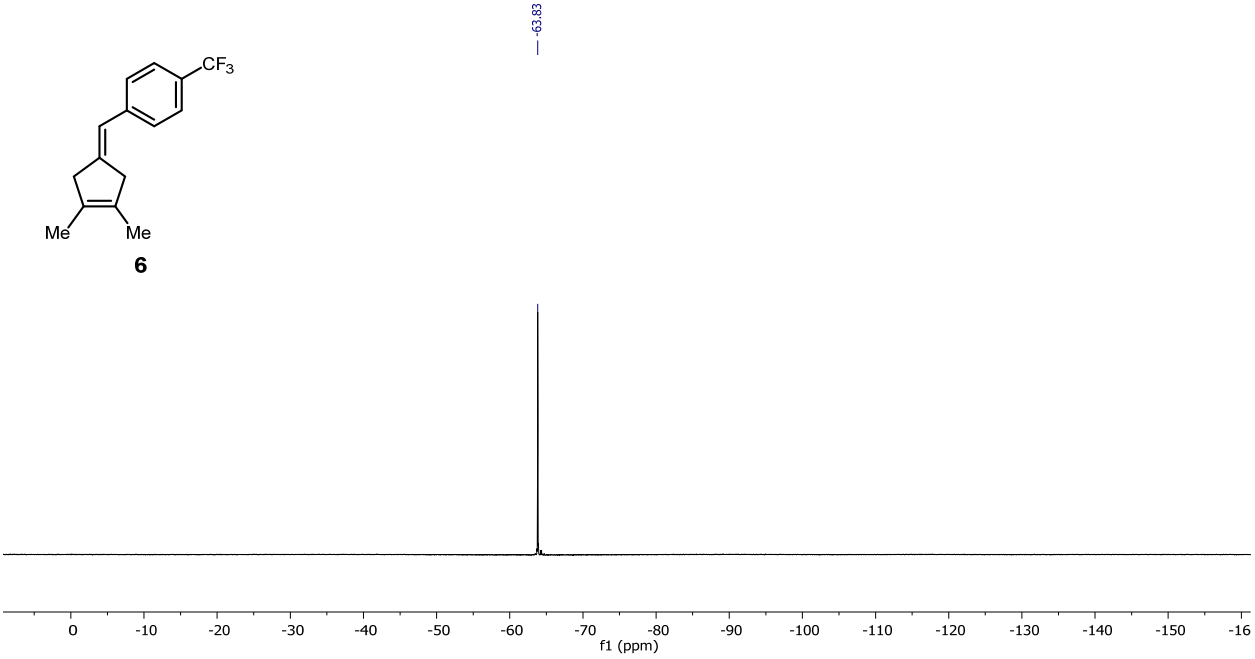

145.79
141.98
129.95
129.51
129.04
128.09
127.90
127.74
127.58
127.42
125.30
125.29
125.27
125.25
120.87


47.25
43.80
13.83
13.49

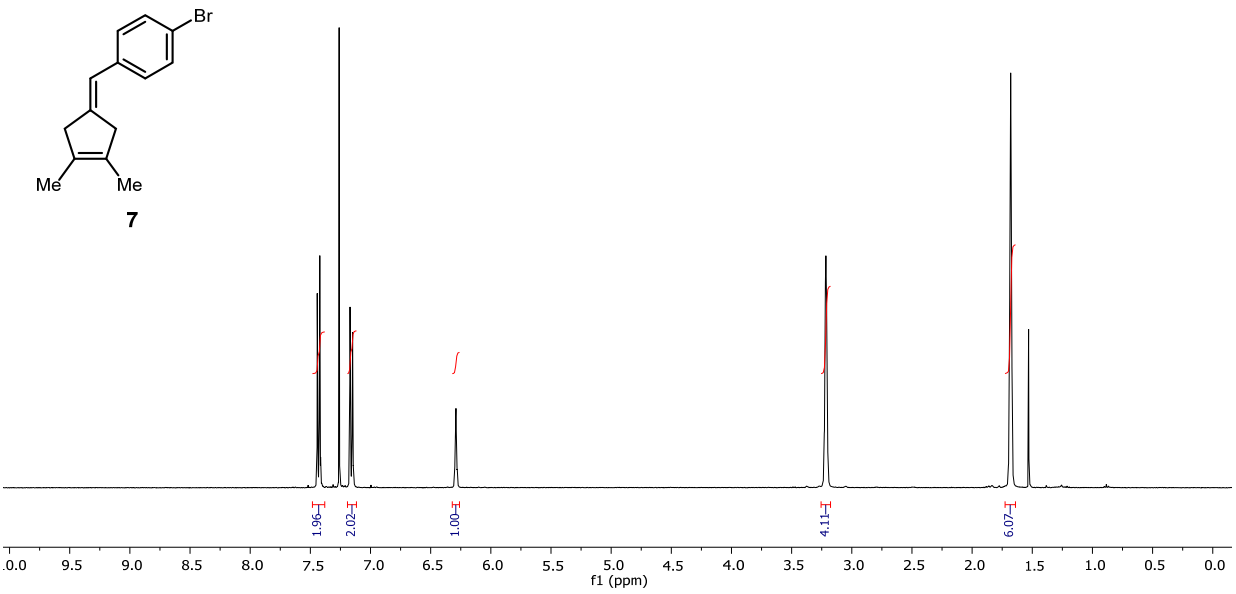

CF3
Me
Me

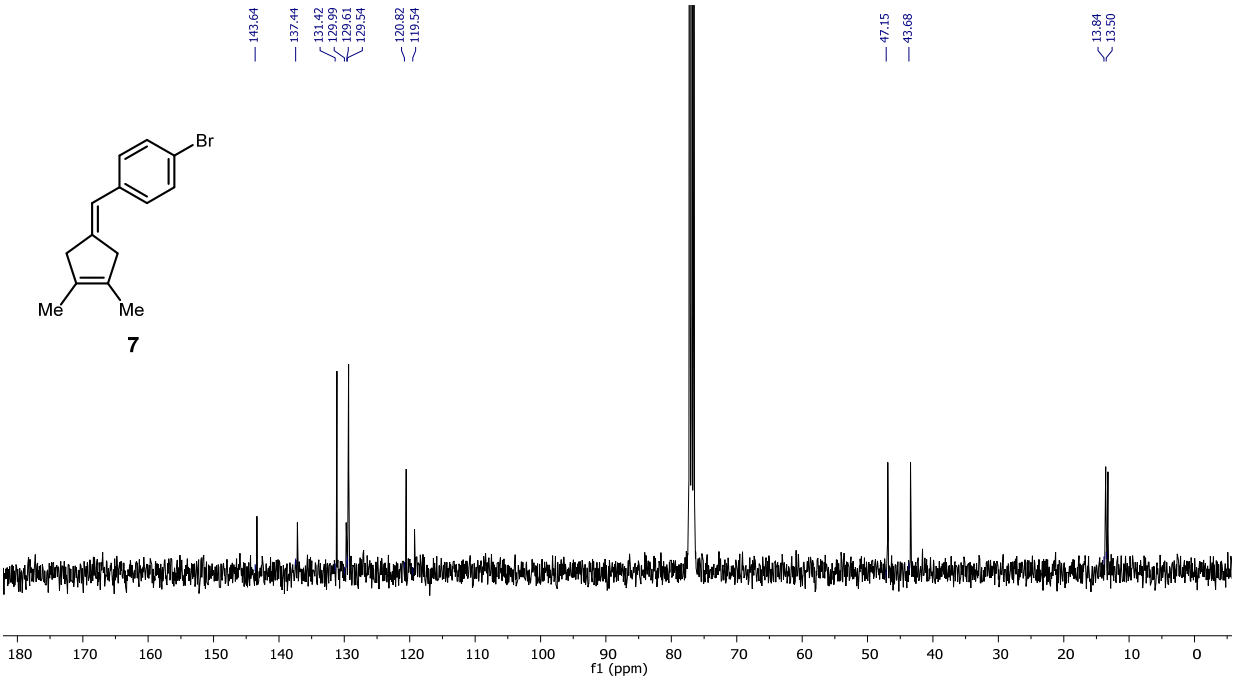
6

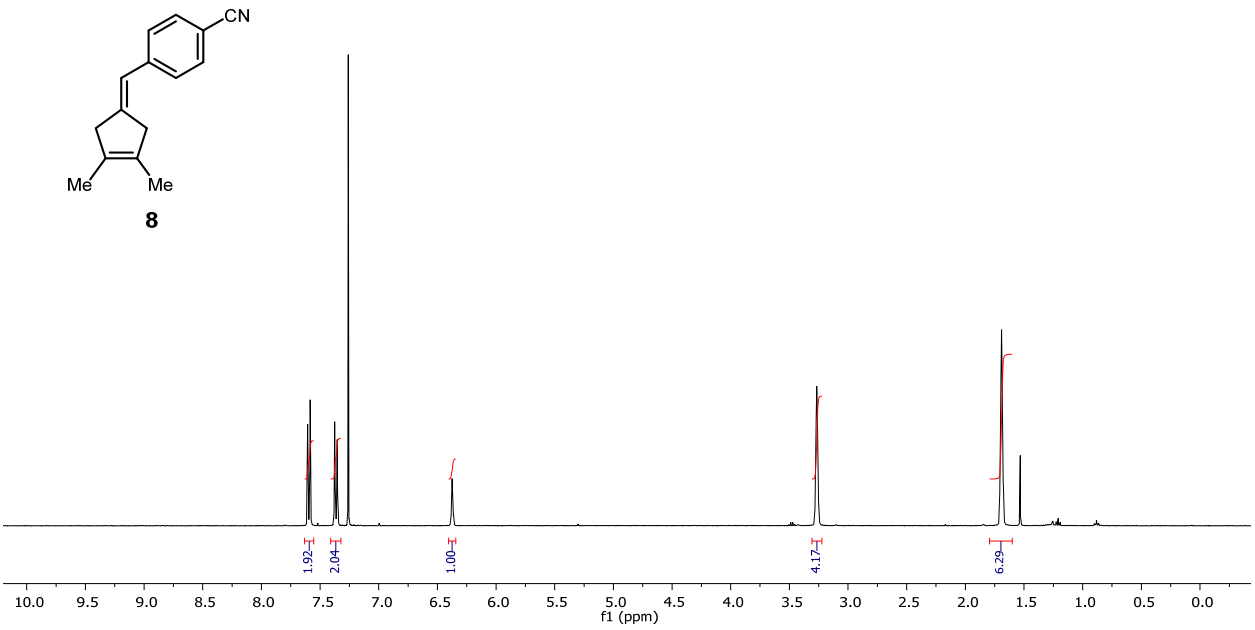
f1 (ppm)

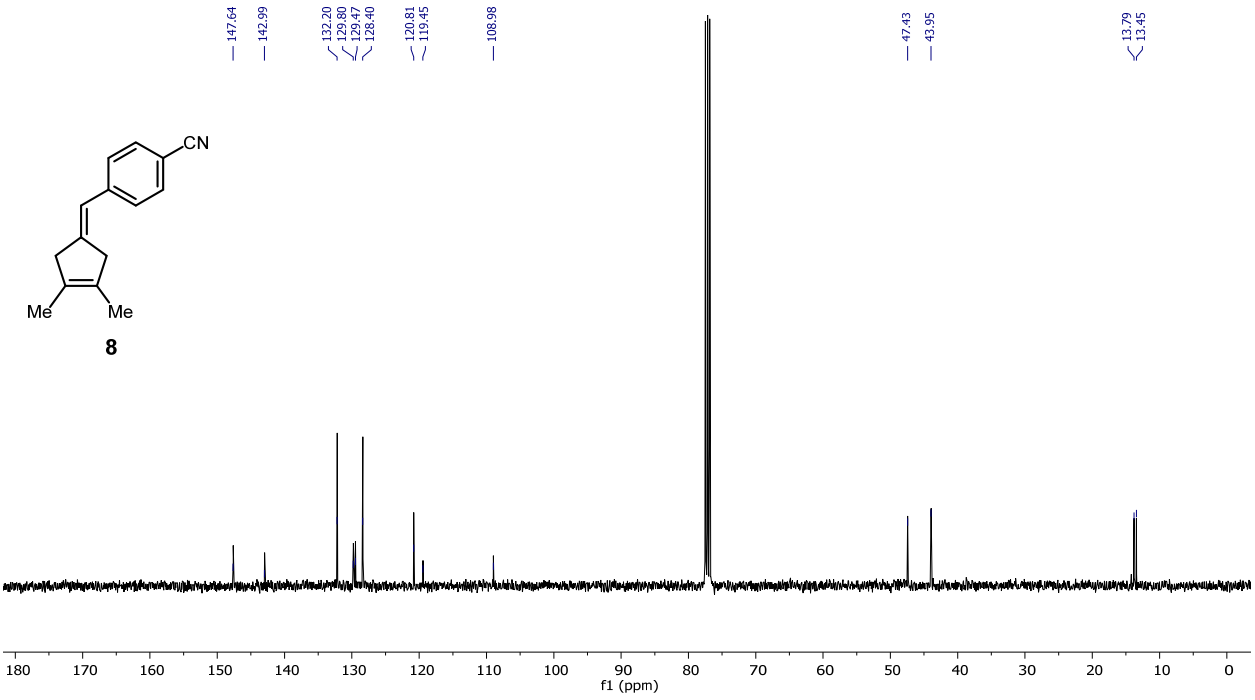

CF3
Me
Me
-63.83
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-16
f1 (ppm)

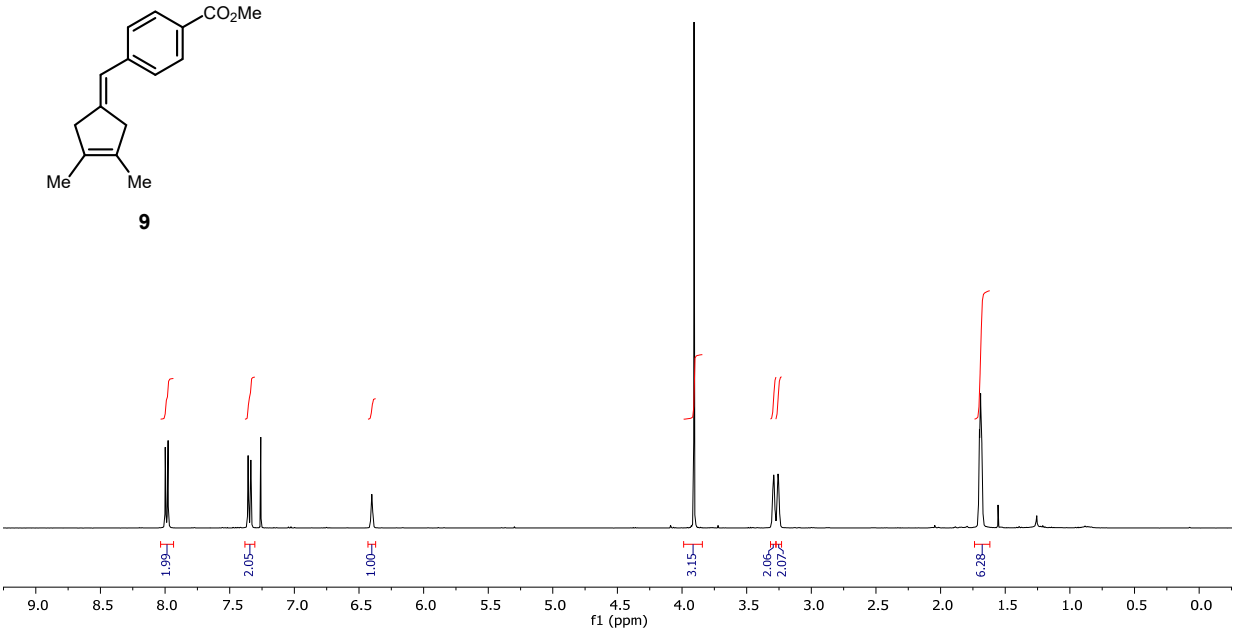
6

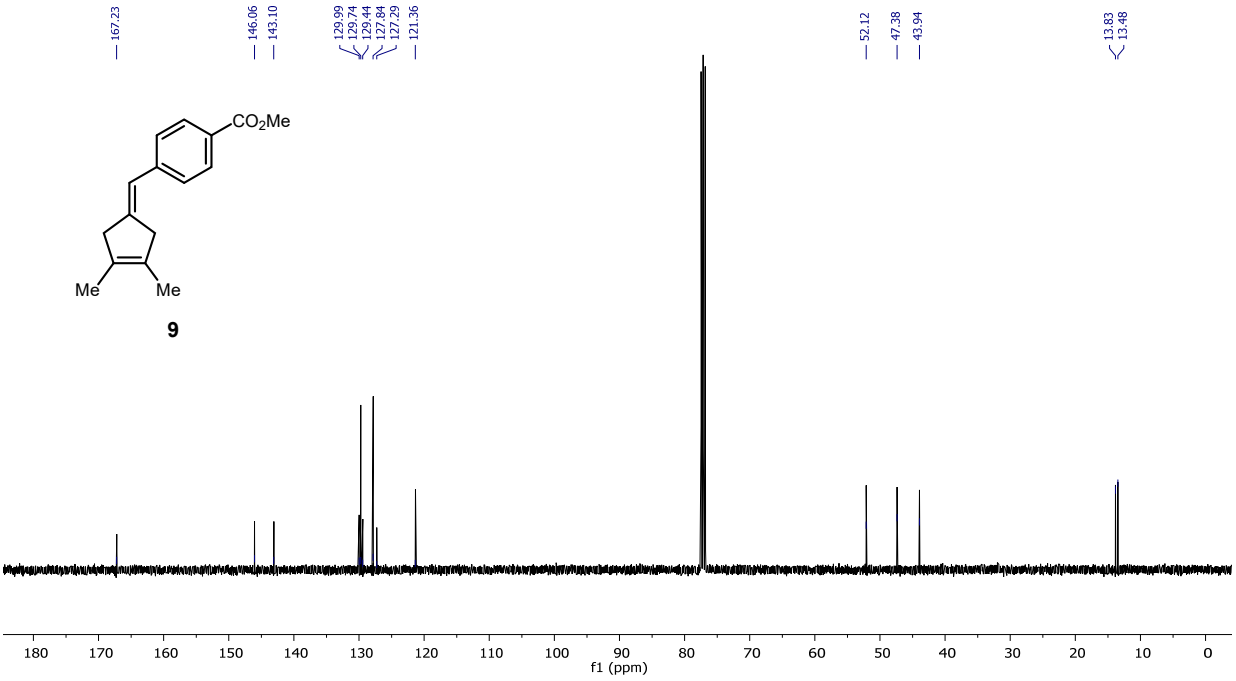

Br
Me
Me
7
1.96
2.02
1.00
4.11
6.07
f1 (ppm)

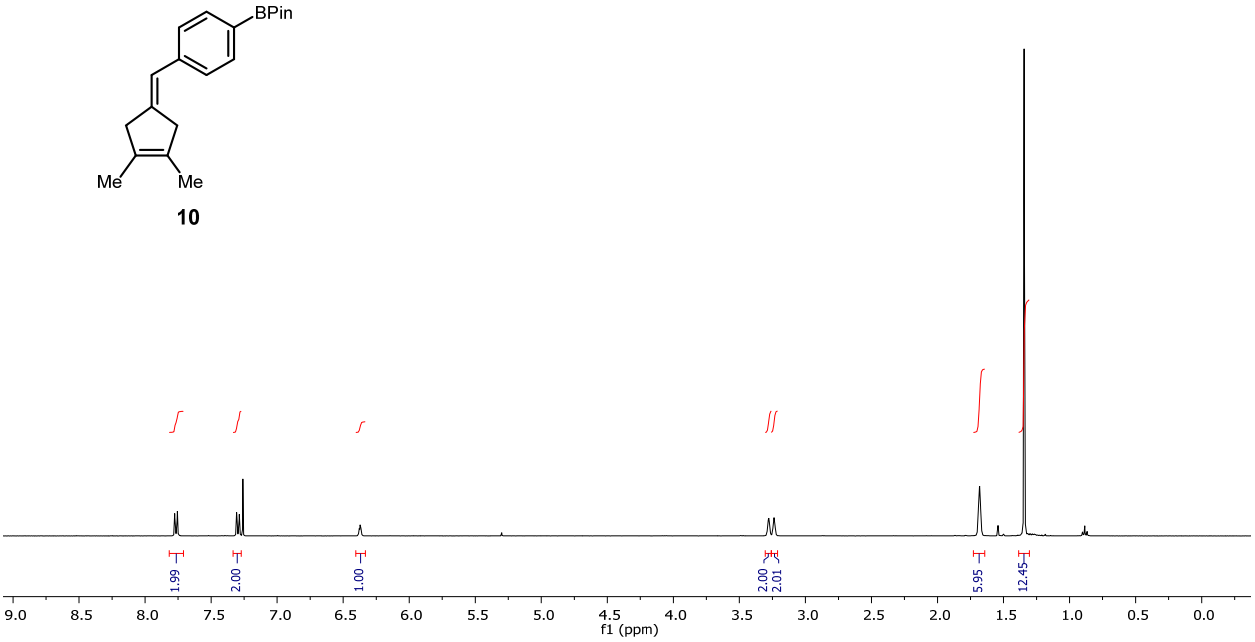

143.64
137.44
131.42
129.99
129.61
129.54
120.82
119.54
47.15
43.68
13.84
13.50
Br
Me
Me
7
f1 (ppm)

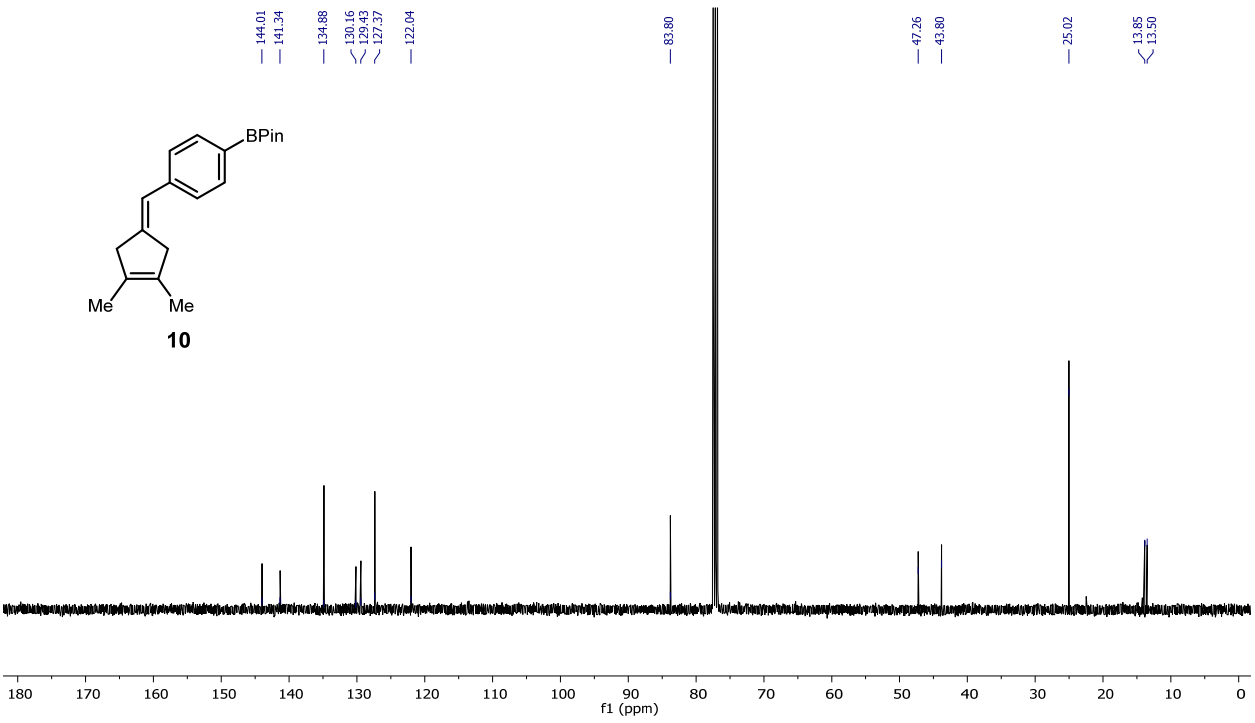

CN
Me
Me
8
1.92
2.04
1.00
4.17
6.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

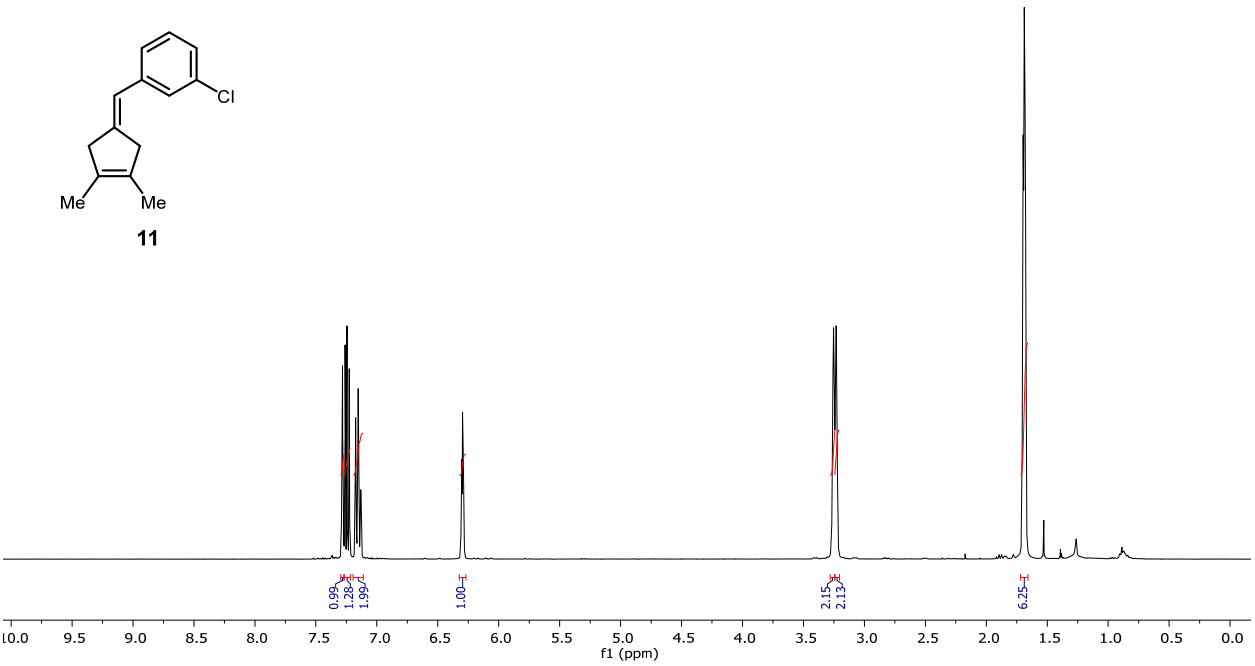

147.64
142.99
132.20
129.80
129.47
128.40
120.81
119.45
108.98
47.43
43.95
13.79
13.45
CN
Me
Me
8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

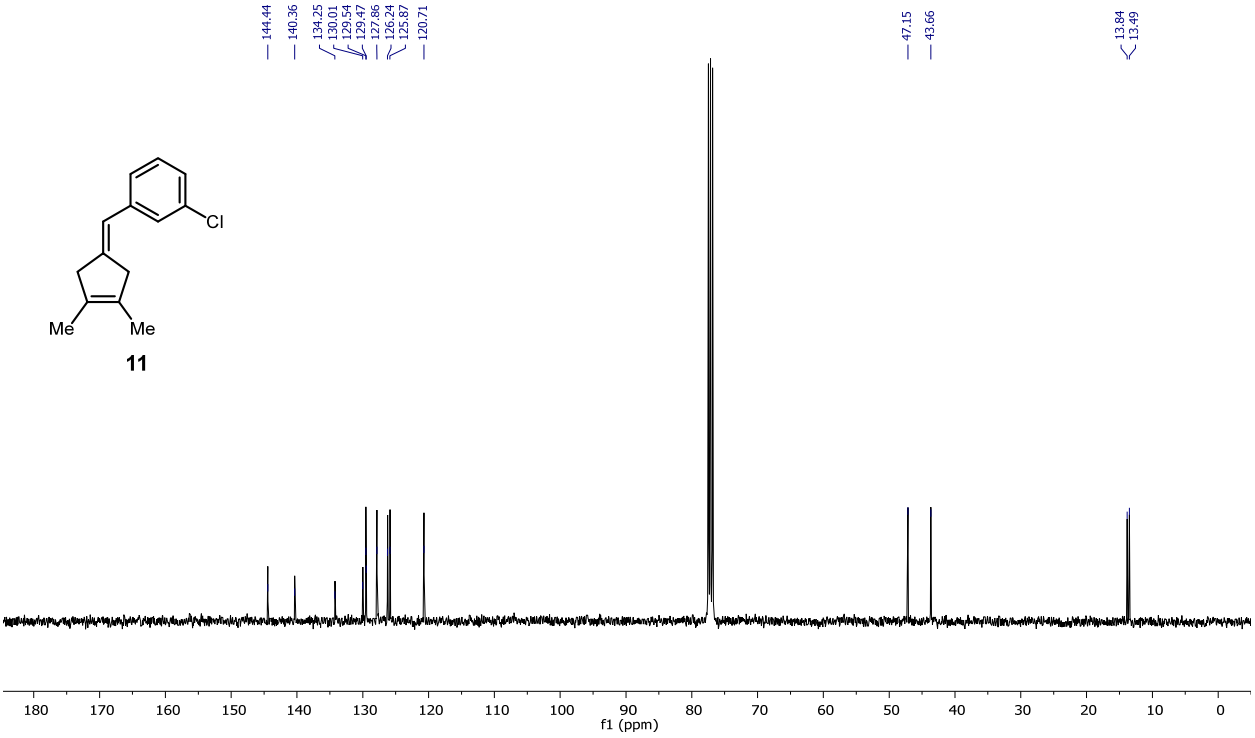

CO2Me
Me
Me
9
1.99
2.05
1.00
3.15
2.06
2.07
6.28
f1 (ppm)

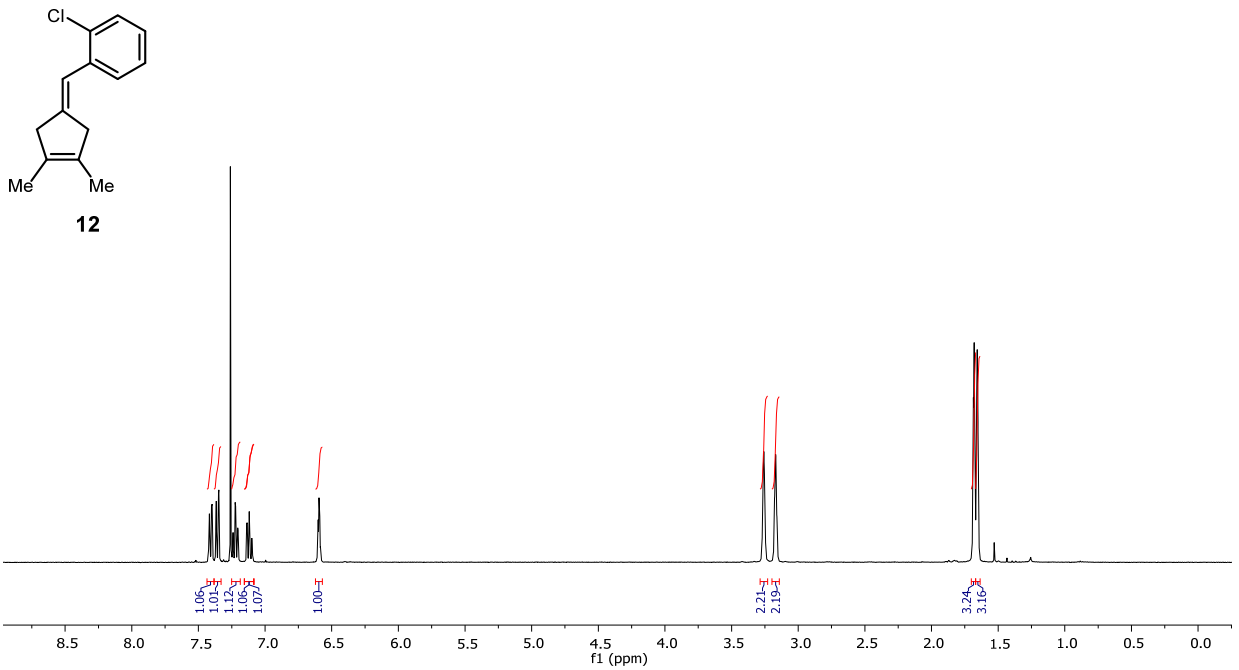

167.23
146.06
143.10
129.99
129.74
129.44
127.84
127.29
121.36
52.12
47.38
43.94
13.83
13.48
CO2Me
Me
Me
9
f1 (ppm)

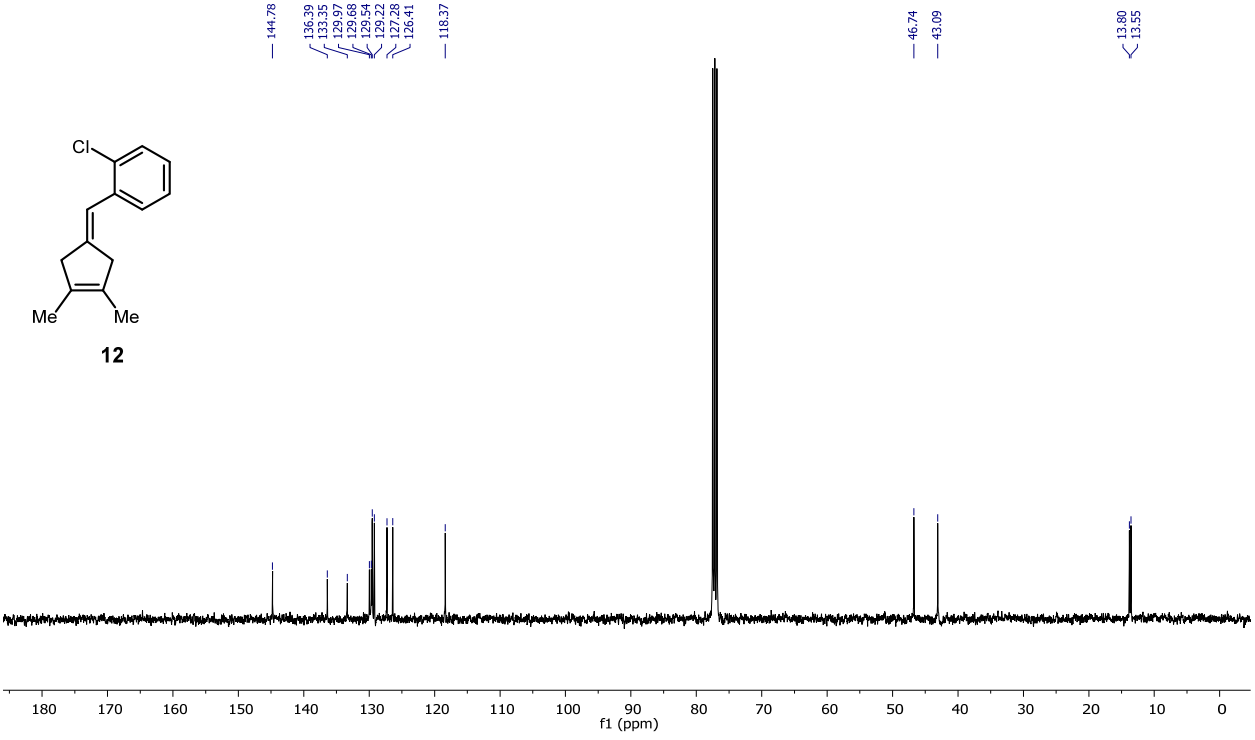

BPin
Me
Me
10
1.99
2.00
1.00
2.00
2.01
5.95
12.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

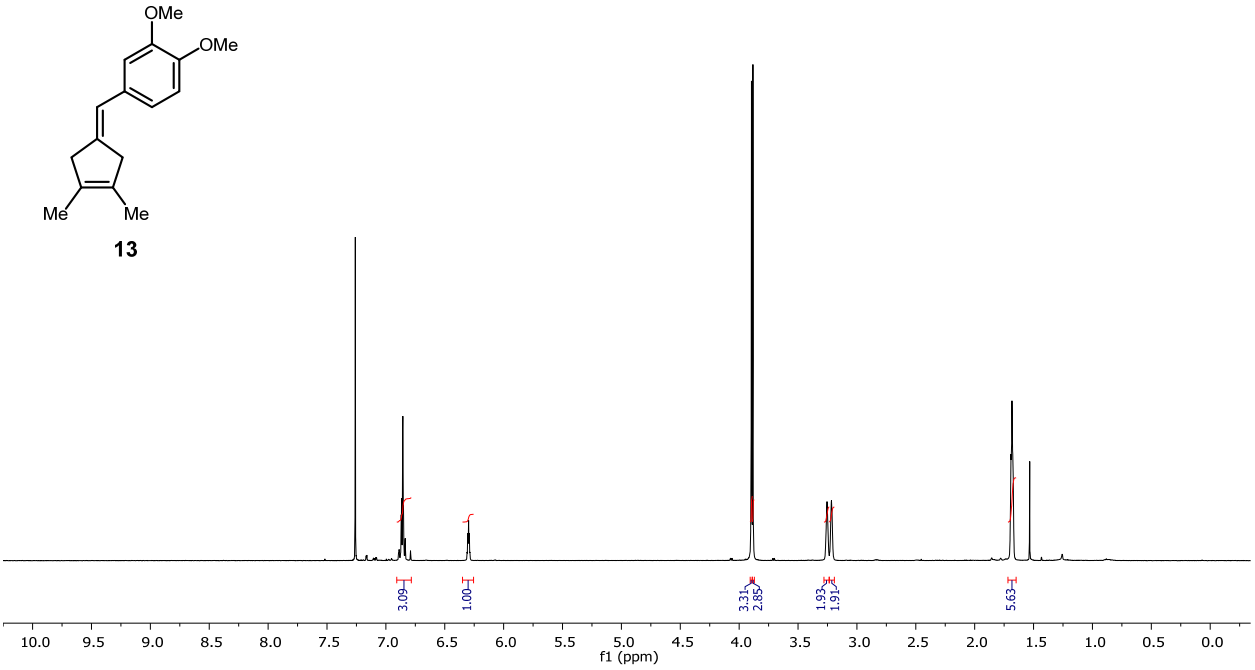

144.01
141.34
134.88
130.16
129.43
127.37
122.04
83.80
47.26
43.80
25.02
13.85
13.50
BPin
Me
Me
10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

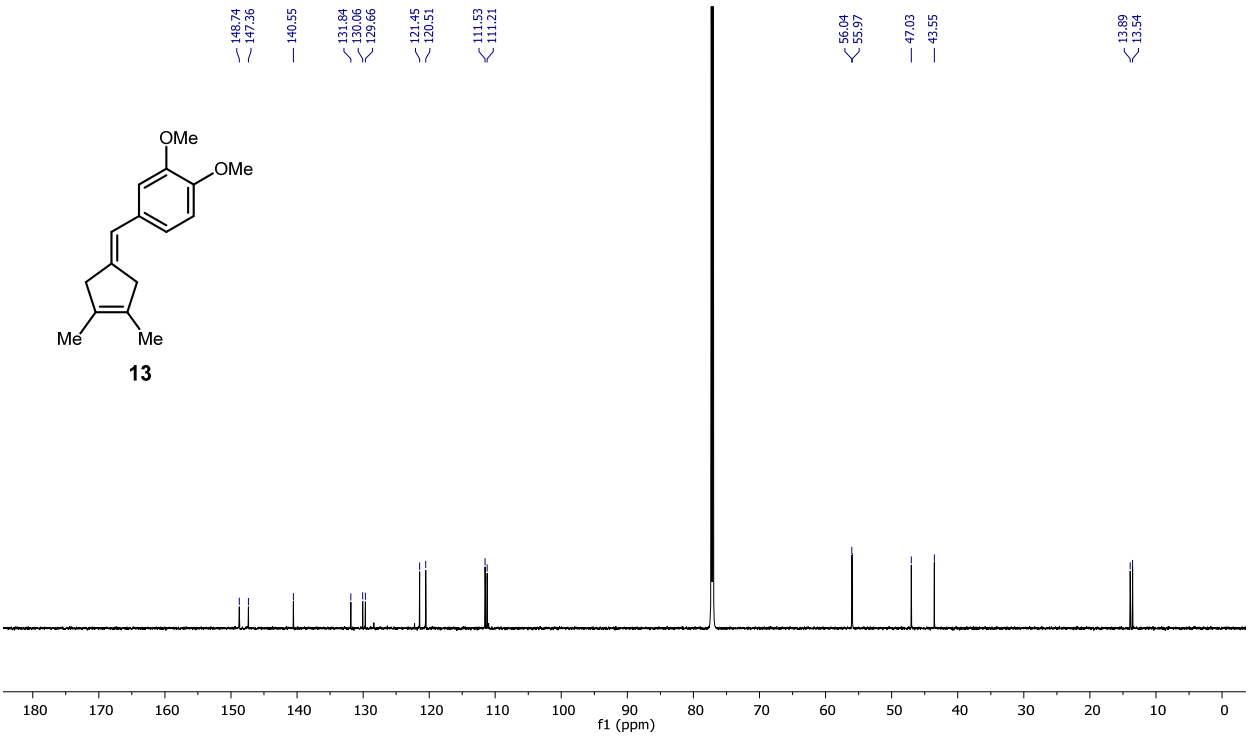

Cl
Me
Me
11
0.99
1.28
1.99
1.00
2.15
2.13
6.25
f1 (ppm)

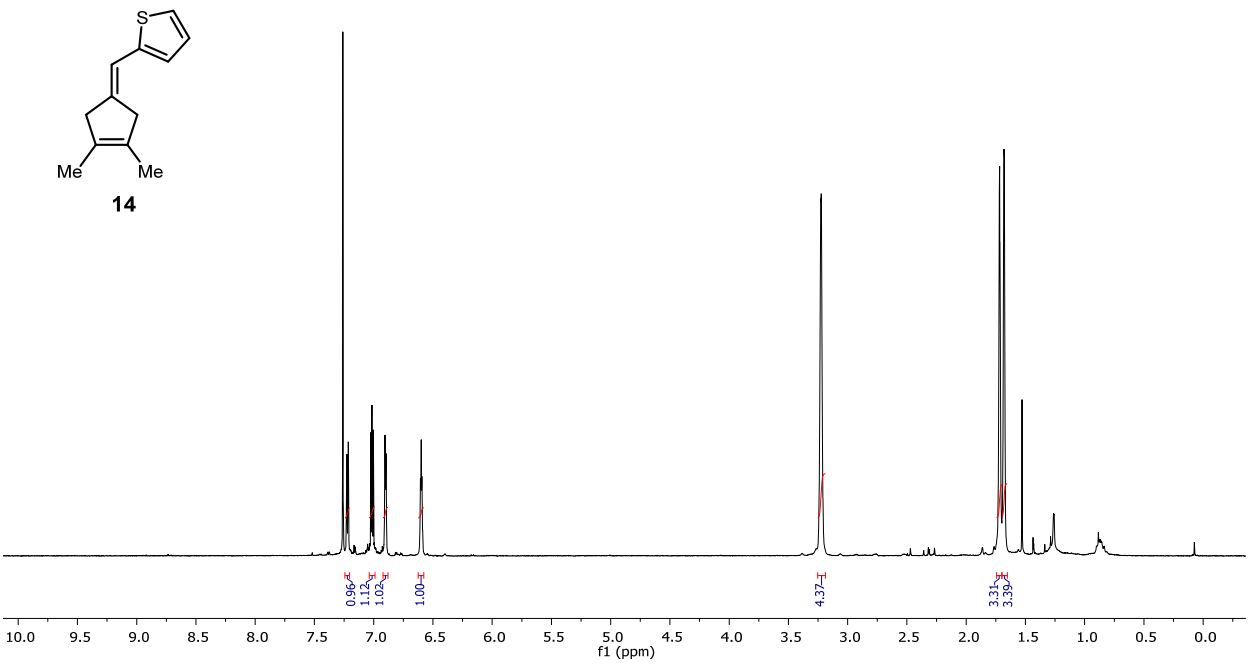

144.44
140.36
134.25
130.01
129.54
129.47
127.86
126.24
125.87
120.71
47.15
43.66
13.84
13.49
Cl
Me
Me
11
f1 (ppm)

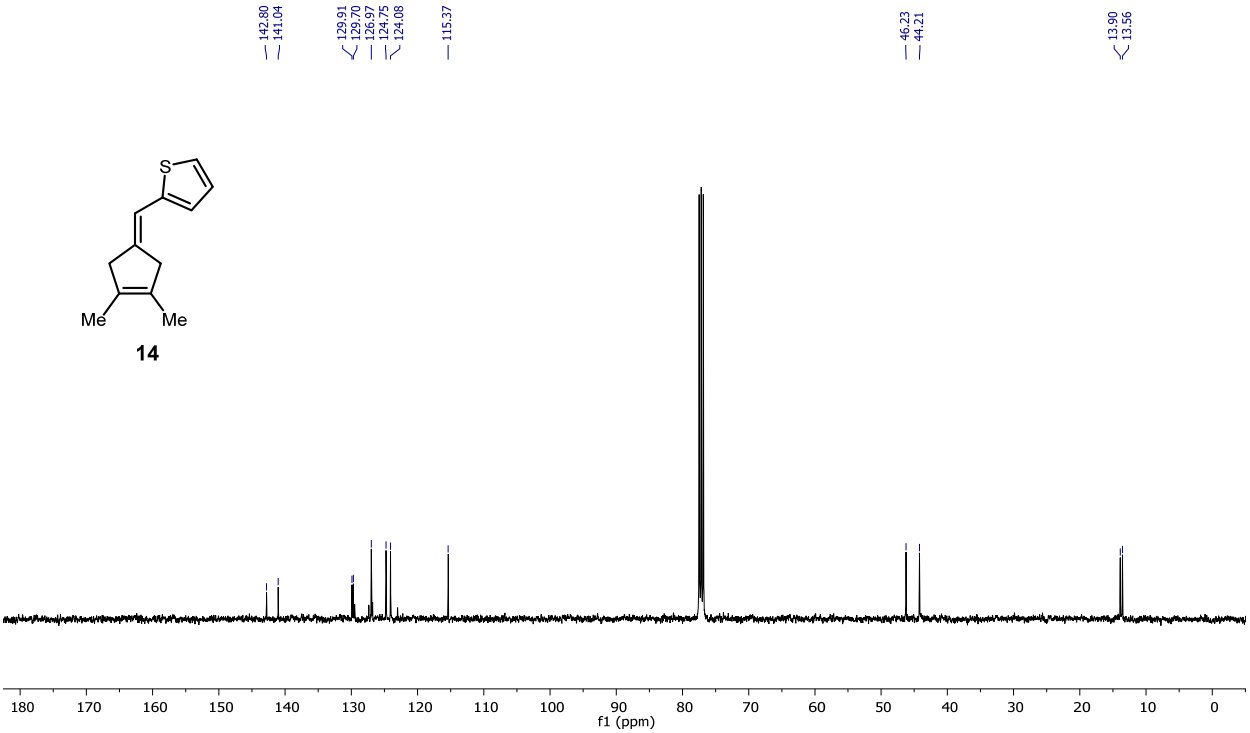

Cl
Me
Me
12
1.06
1.01
1.12
1.06
1.07
1.00
2.21
2.19
3.24
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

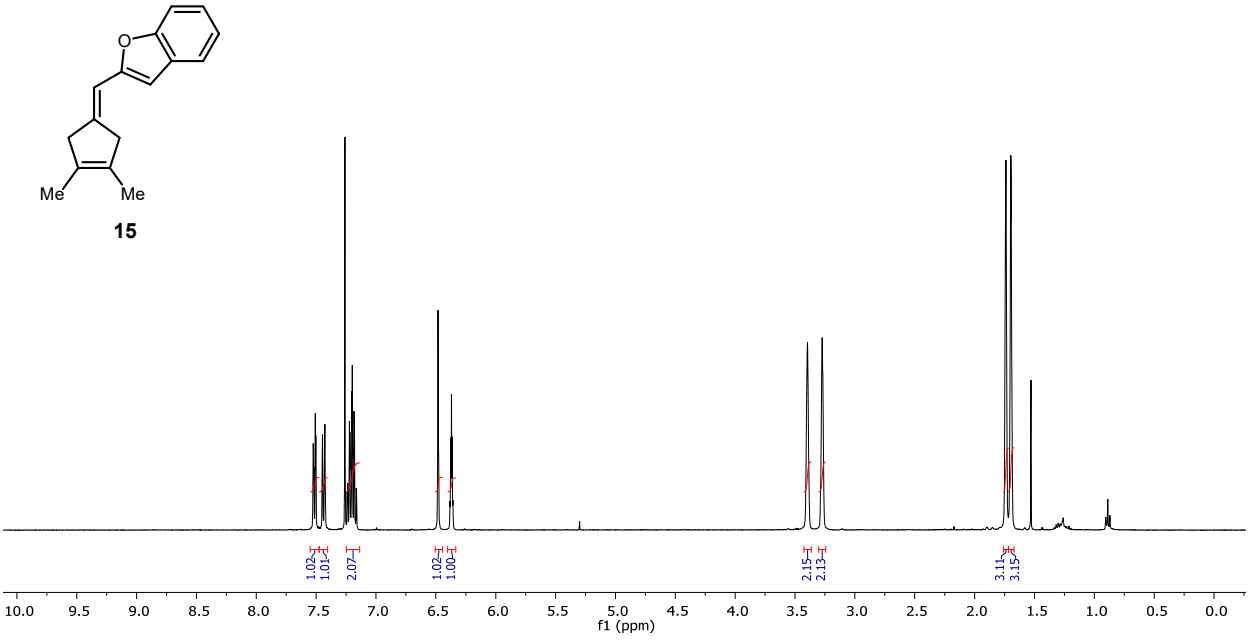

144.78
136.39
133.35
129.97
129.68
129.54
129.22
127.28
126.41
118.37
46.74
43.09
13.80
13.55
Cl
Me
Me
12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

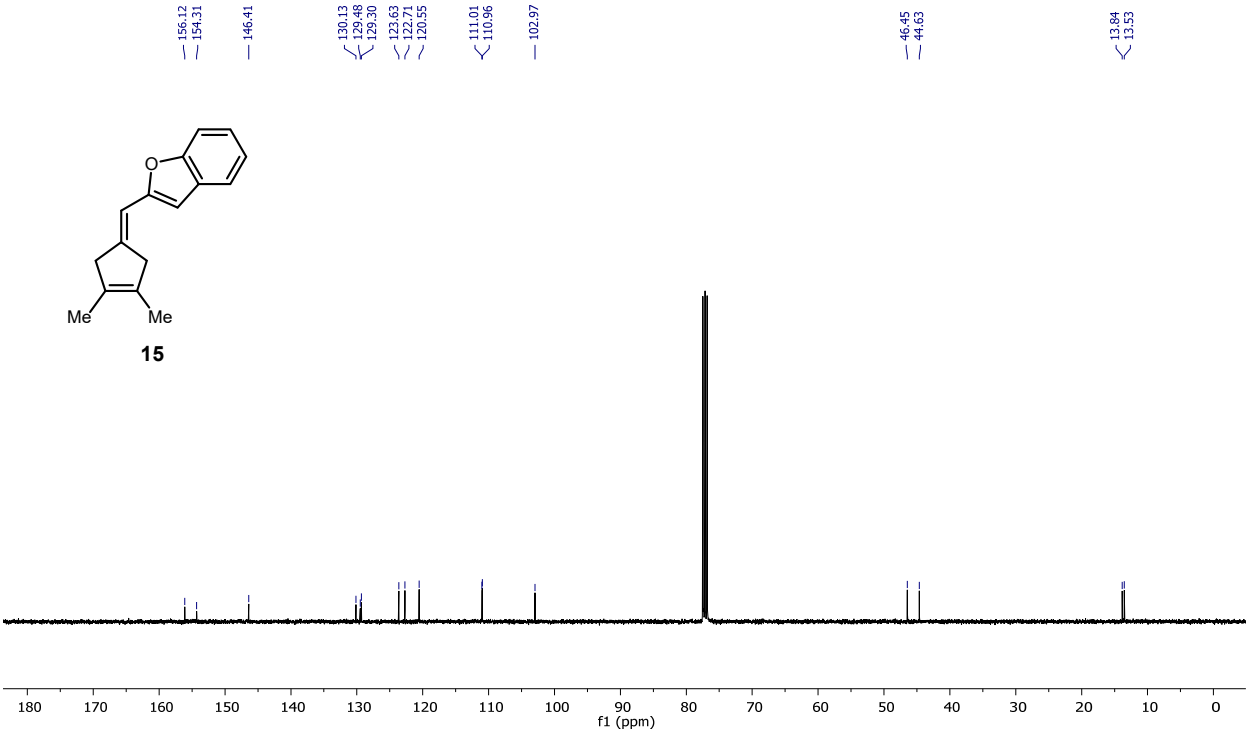

OMe
OMe
Me
Me
13
3.09
1.00
3.31
2.85
1.93
1.91
5.63
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

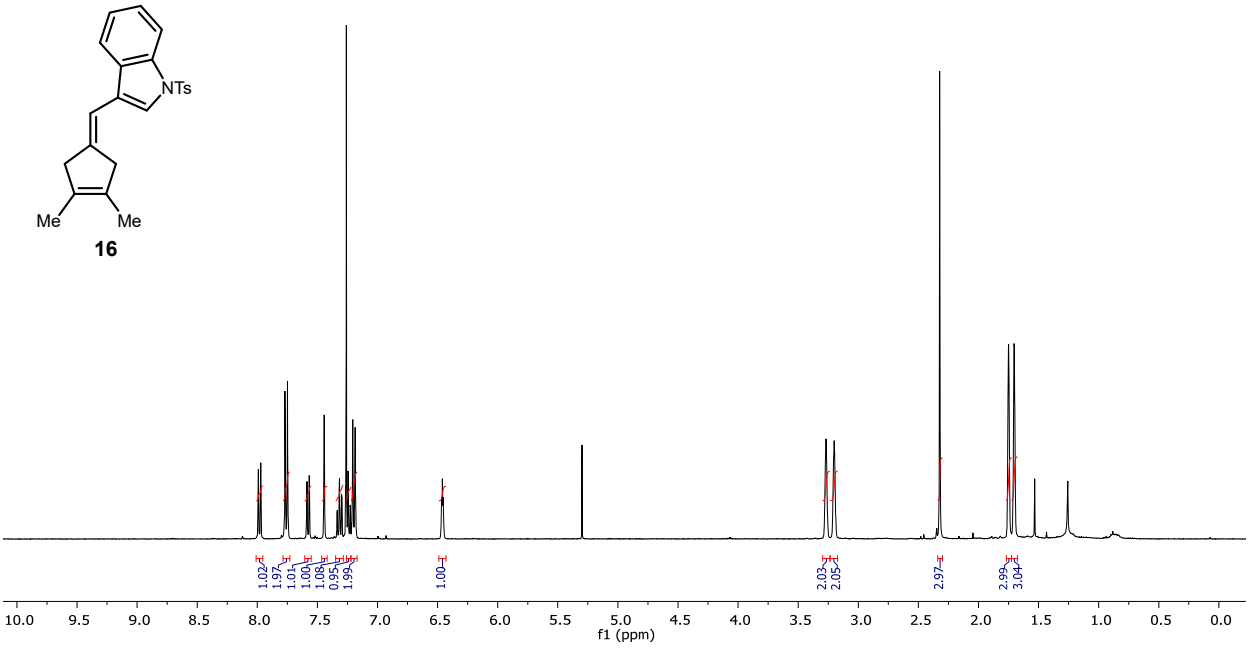

148.74
147.36
140.55
131.84
130.06
129.66
121.45
120.51
111.53
111.21
56.04
55.97
47.03
43.55
13.89
13.54
OMe
OMe
Me
Me
13
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

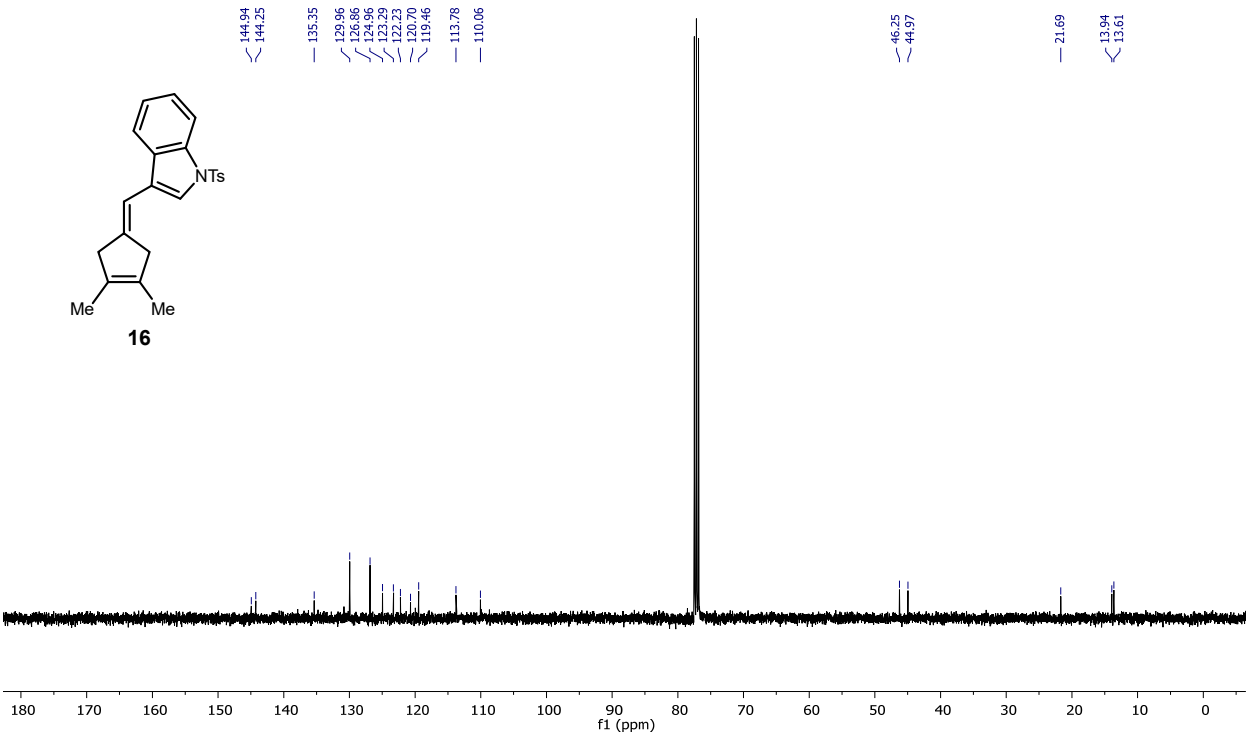

S
Me
Me
14
0.96
1.12
1.02
1.00
4.37
3.31
3.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

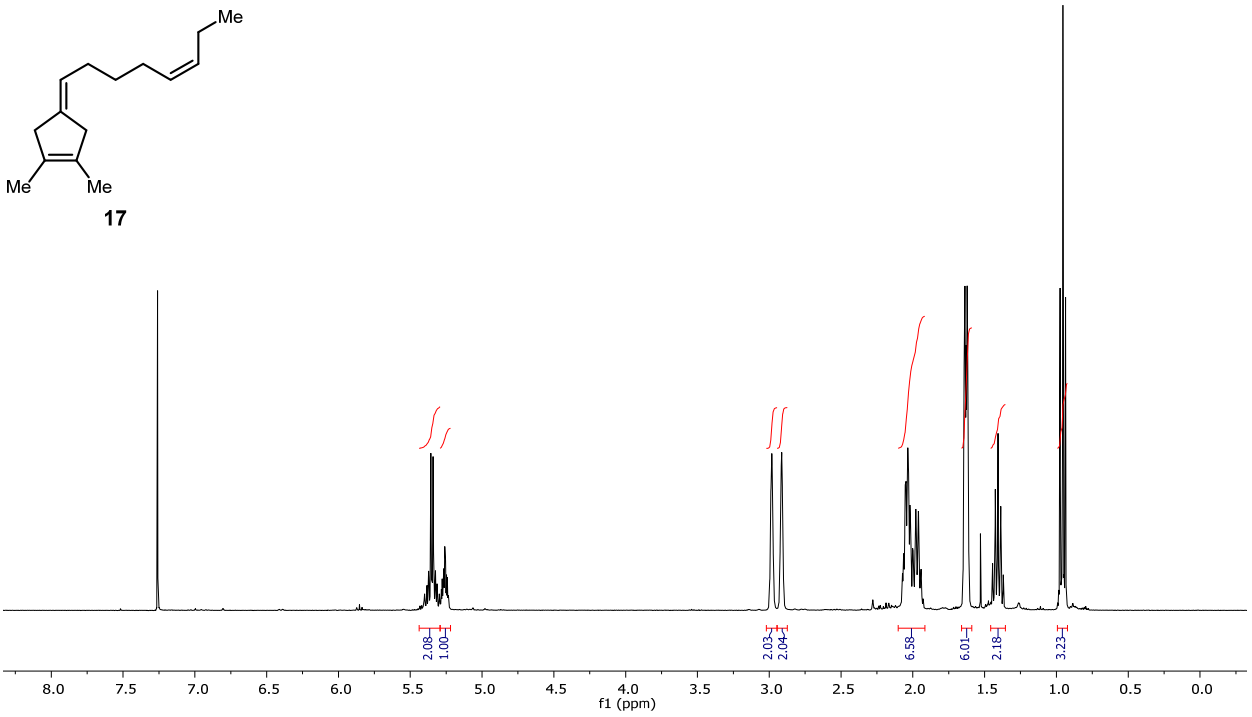

142.80
141.04
129.91
129.70
126.97
124.75
124.08
115.37
46.23
44.21
13.90
13.56
S
Me
Me
14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

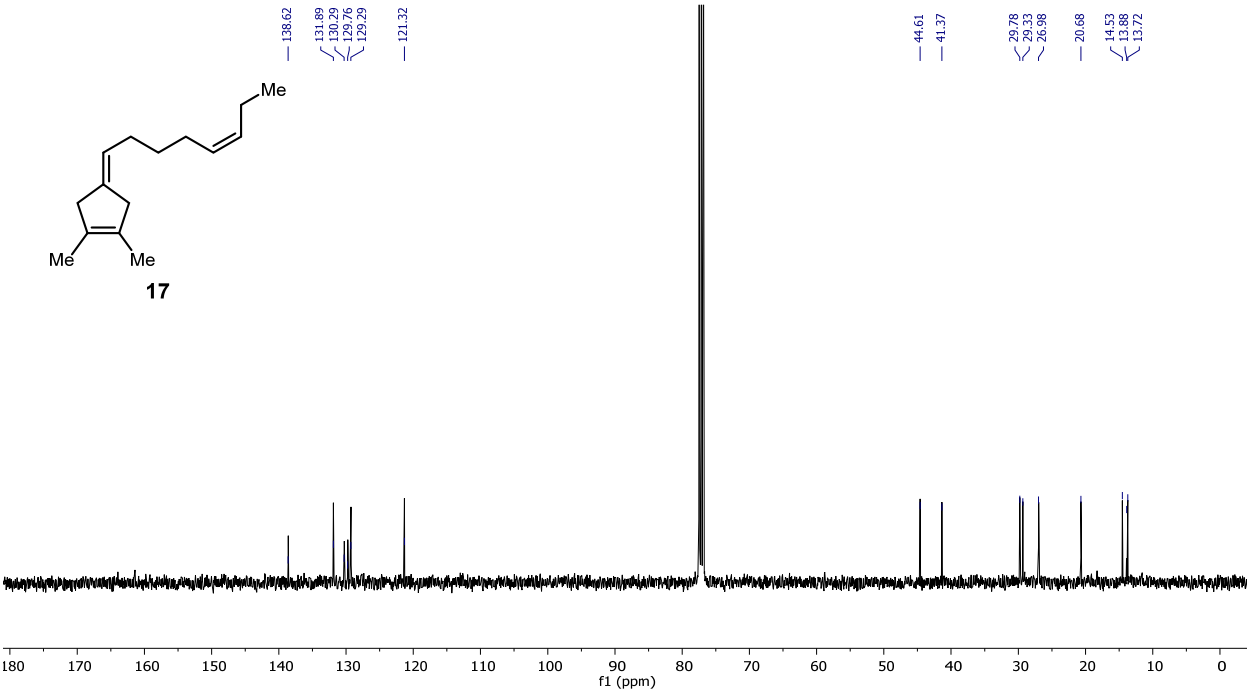

O
Me
Me
15
1.02
1.01
2.07
1.02
1.00
2.15
2.13
3.11
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

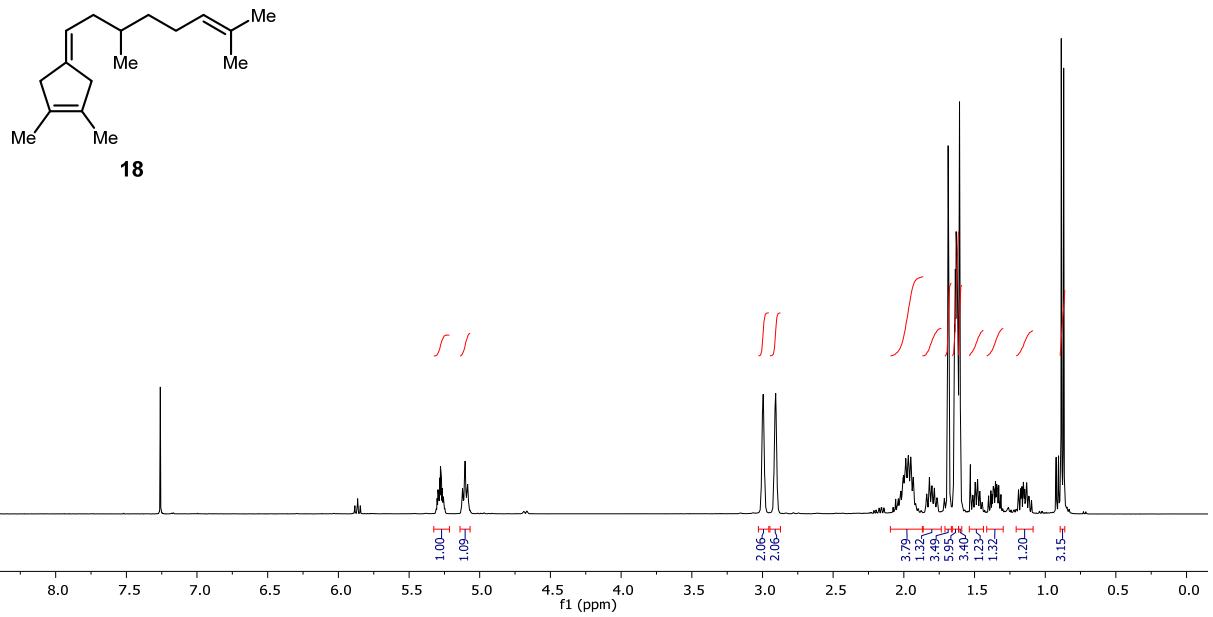

156.12
154.31
146.41
130.13
129.48
129.30
123.63
122.71
120.55
111.01
110.96
102.97
46.45
44.63
13.84
13.53
O
Me
Me
15
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

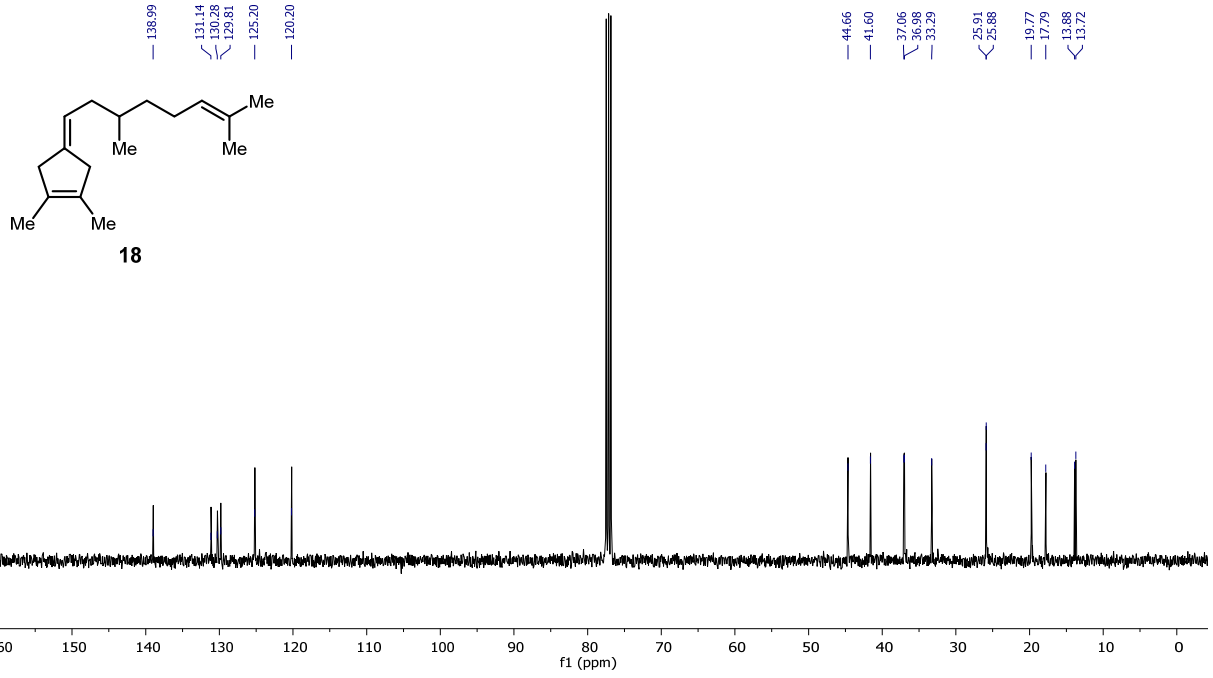

NTs
Me
Me
16
1.02
1.97
1.01
1.00
1.08
0.95
1.99
1.00
2.03
2.05
2.97
2.99
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

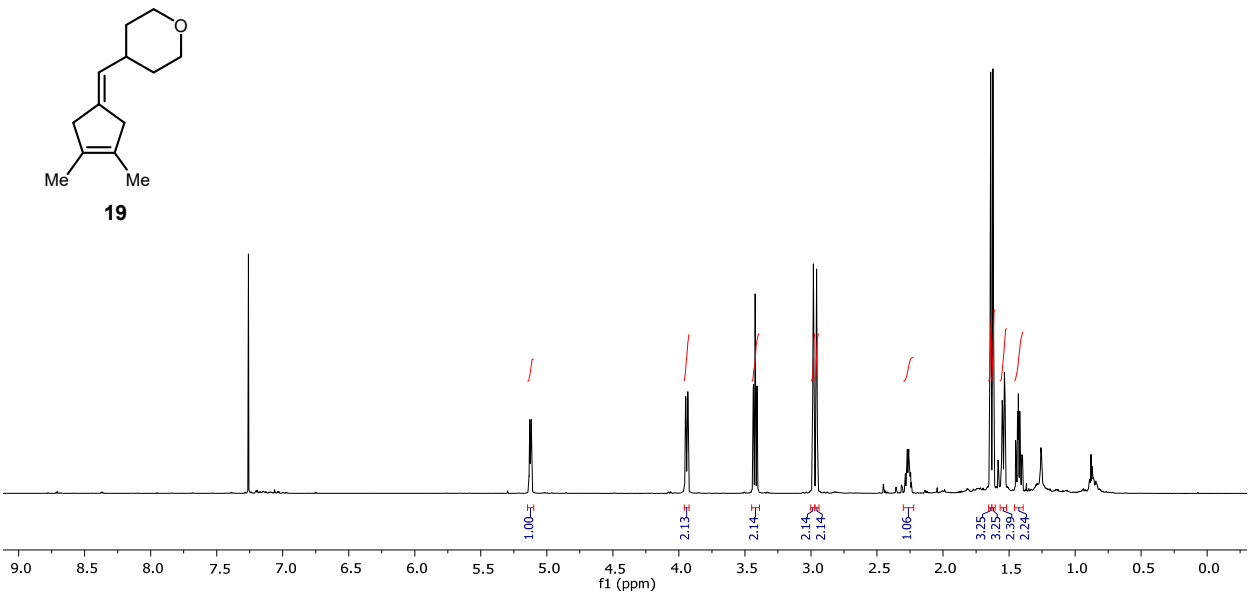

144.94
144.25
135.35
129.96
126.86
124.96
123.29
122.23
120.70
119.46
113.78
110.06
46.25
44.97
21.69
13.94
13.61
NTs
Me
Me
16
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

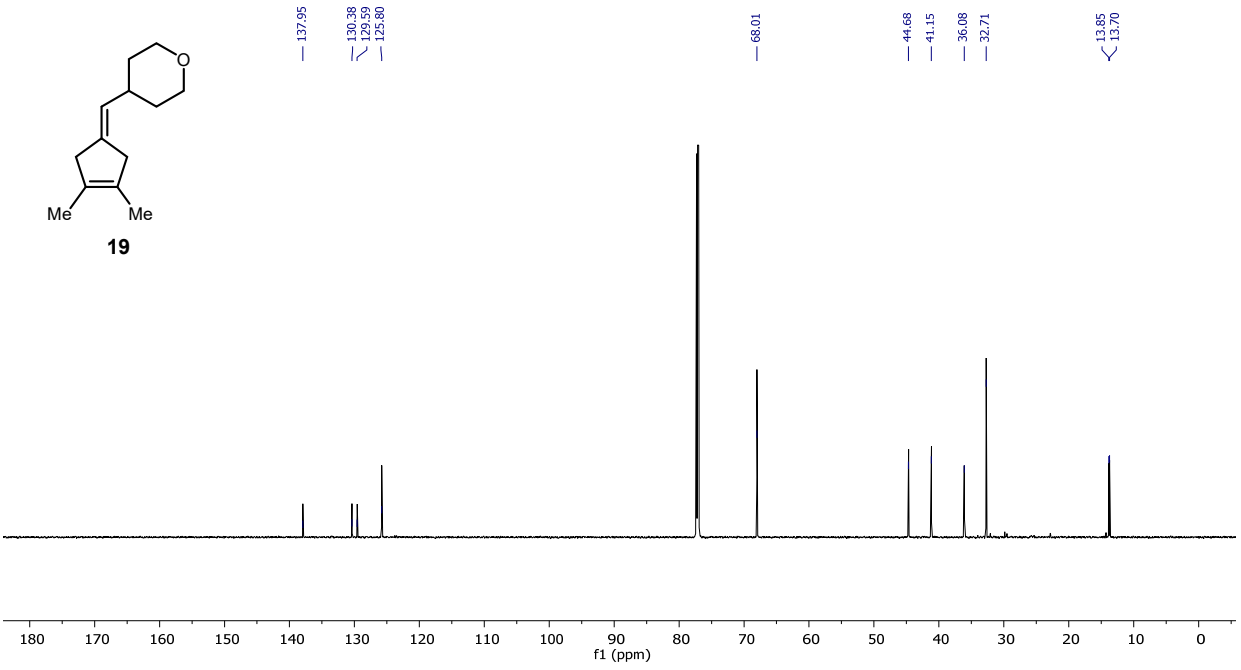

Me
Me
Me
17
2.08
1.00
2.03
2.04
6.58
6.01
2.18
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

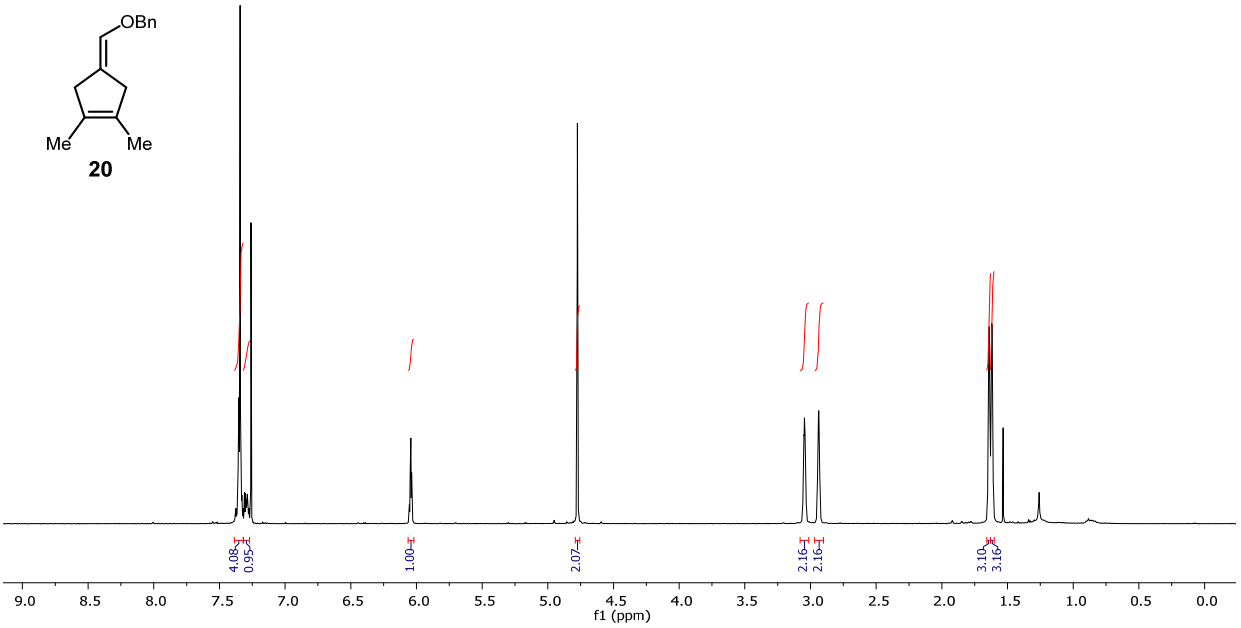

138.62
131.89
130.29
129.76
129.29
121.32
44.61
41.37
29.78
29.33
26.98
20.68
14.53
13.88
13.72
Me
Me
Me
17
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

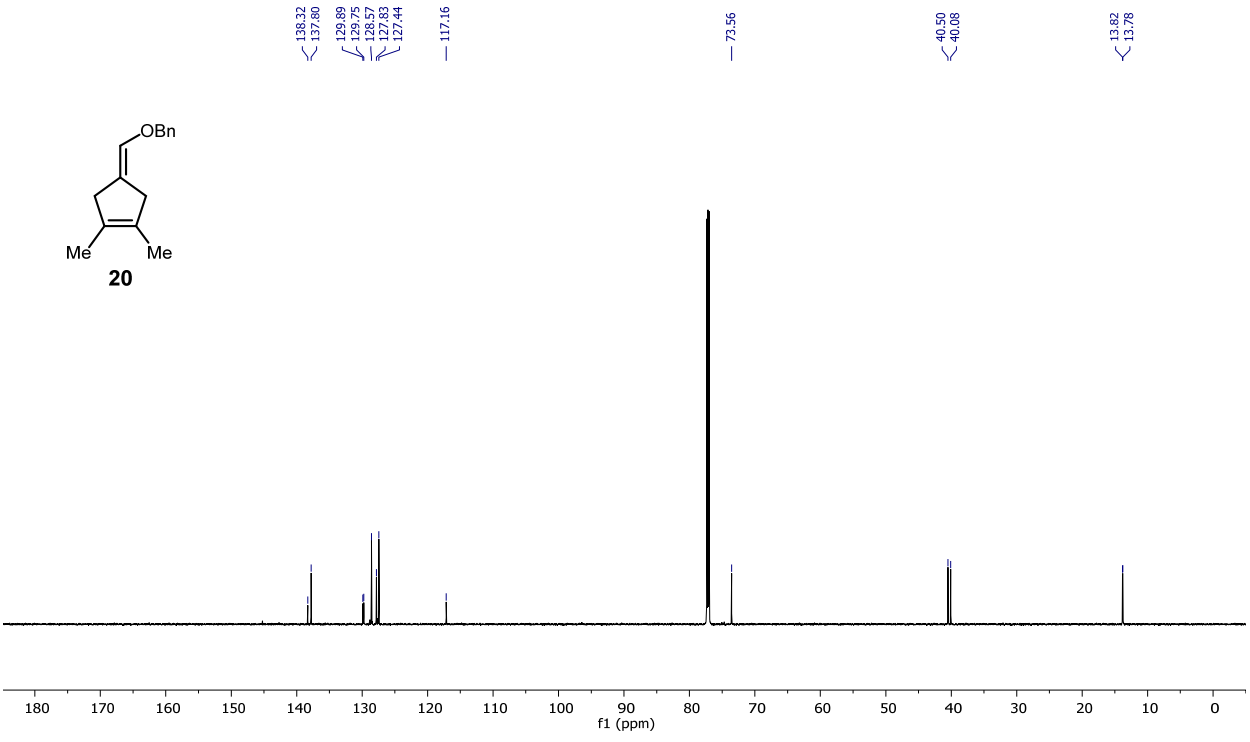

Me
Me
Me
Me
Me
18
1.00
1.09
2.06
2.06
3.79
1.32
3.49
5.95
3.40
1.23
1.32
1.20
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

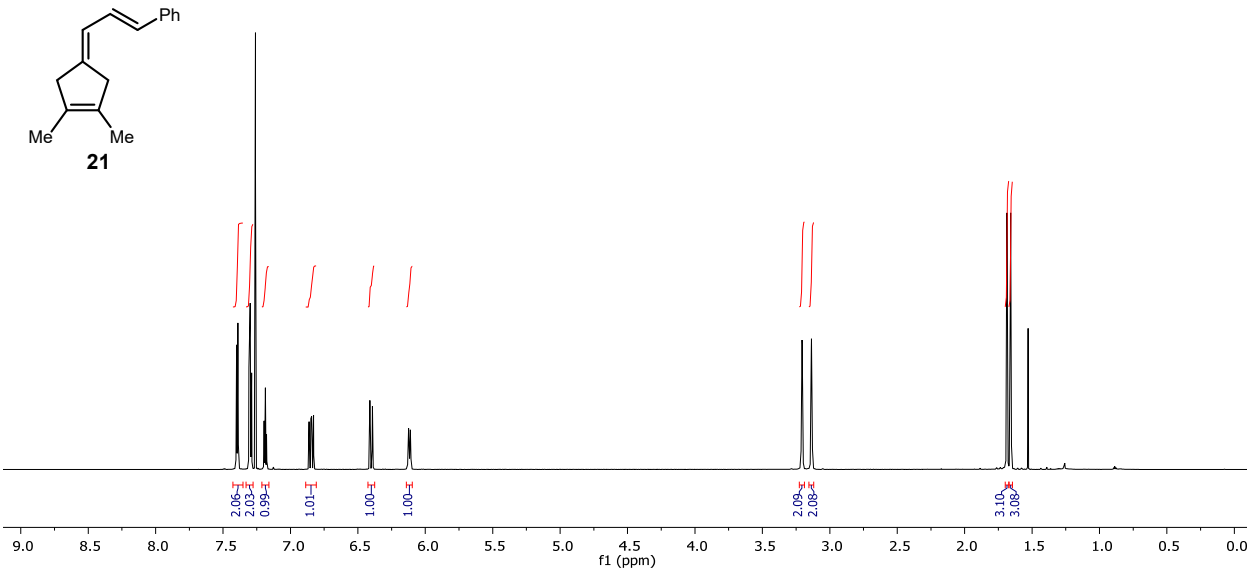

138.99
131.14
130.28
129.81
125.20
120.20
44.66
41.60
37.06
36.98
33.29
25.91
25.88
19.77
17.79
13.88
13.72
Me
Me
Me
Me
Me
18
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

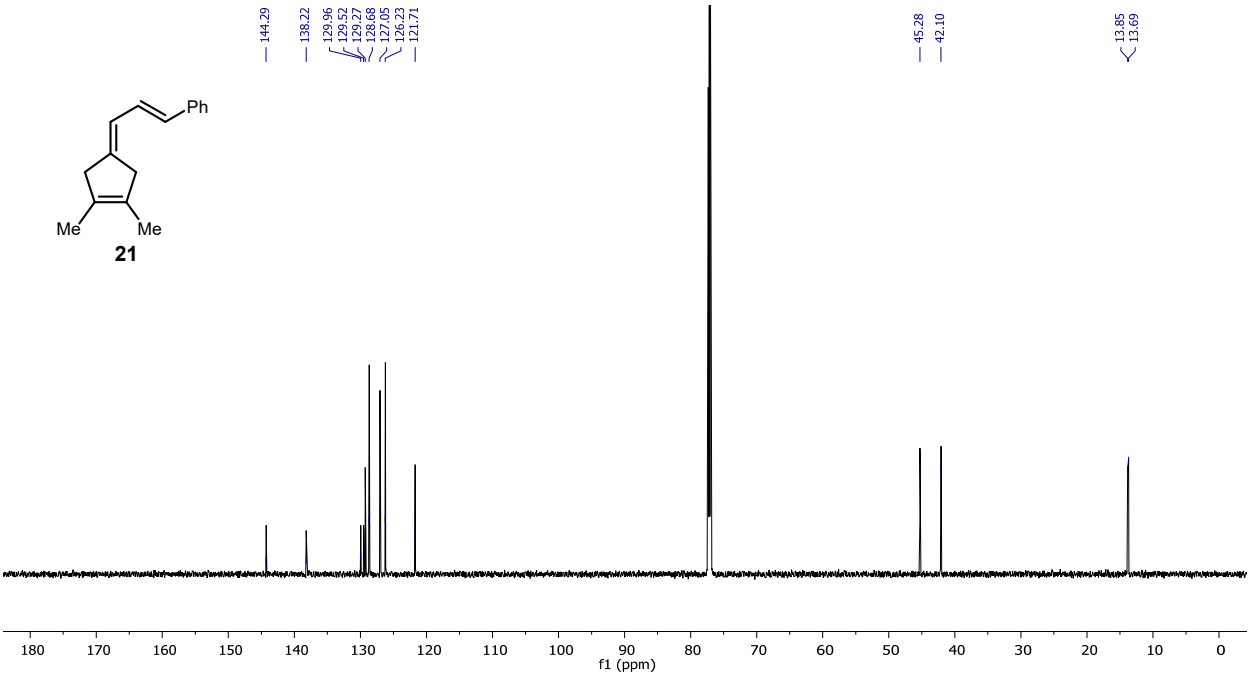

O
Me
Me
19
1.00
2.13
2.14
2.14
2.14
1.06
3.25
3.25
2.39
2.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

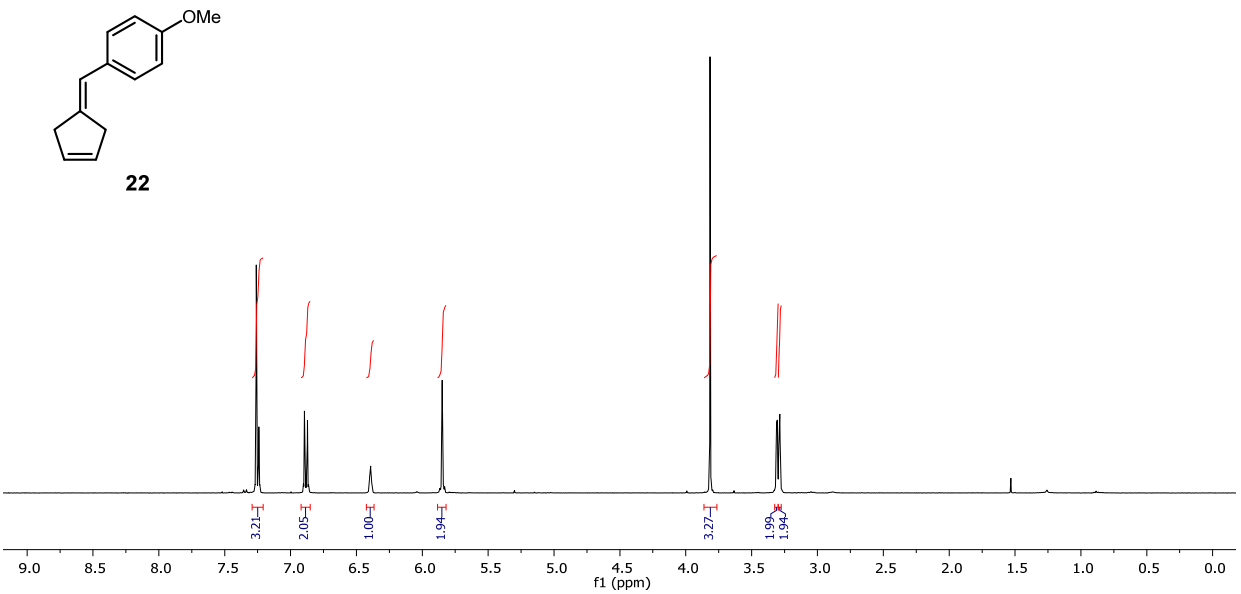

O
Me
Me
19
137.95
130.38
129.59
125.80
68.01
44.68
41.15
36.08
32.71
13.85
13.70
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

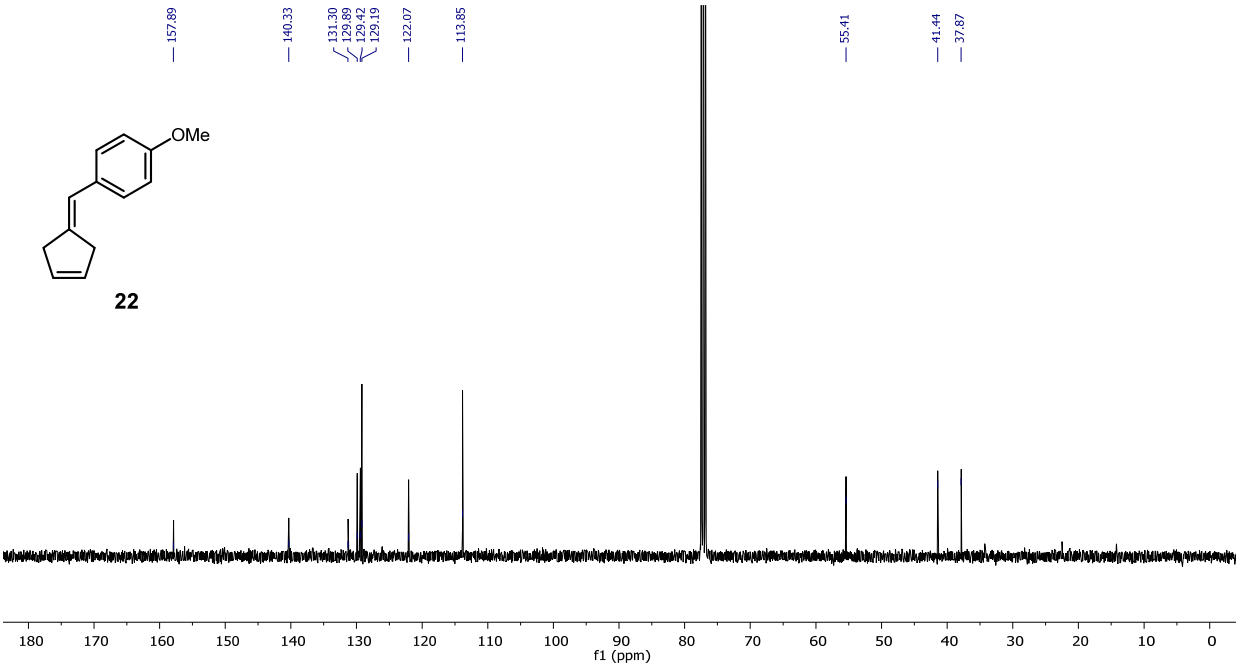

OBn
Me
Me
20
4.08
0.95
1.00
2.07
2.16
2.16
3.10
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

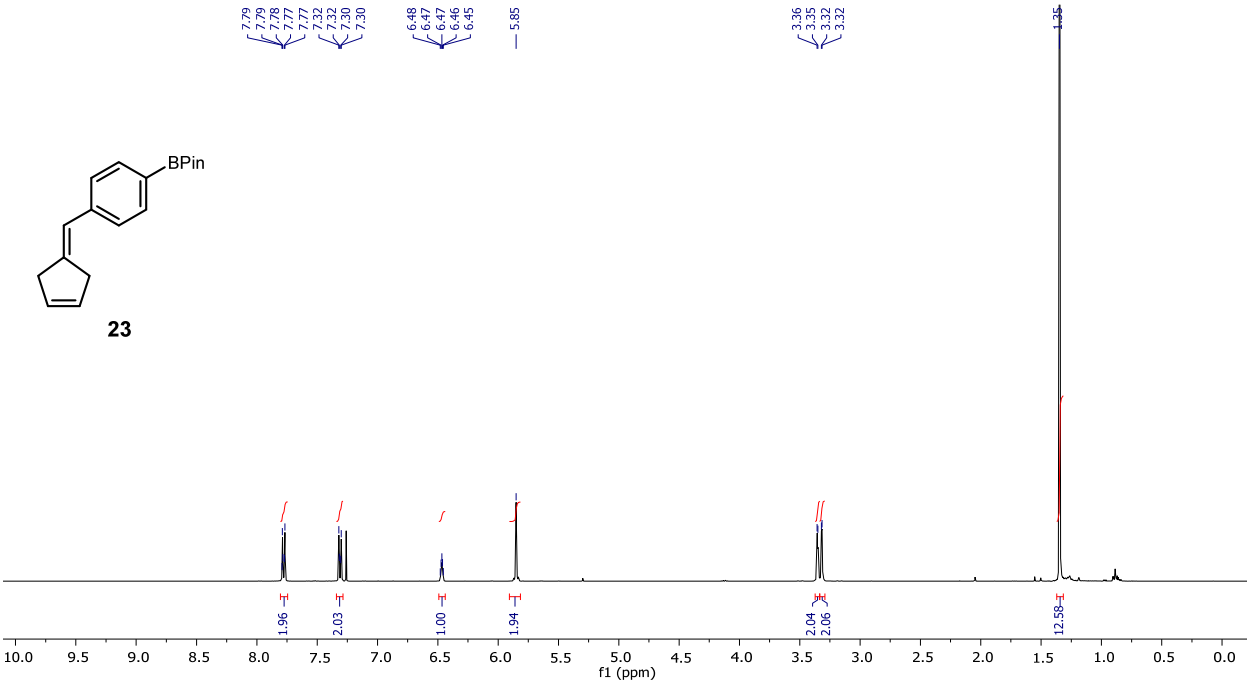

138.32
137.80
129.89
129.75
128.57
127.83
127.44
117.16
73.56
40.50
40.08
13.82
13.78
OBn
Me
Me
20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

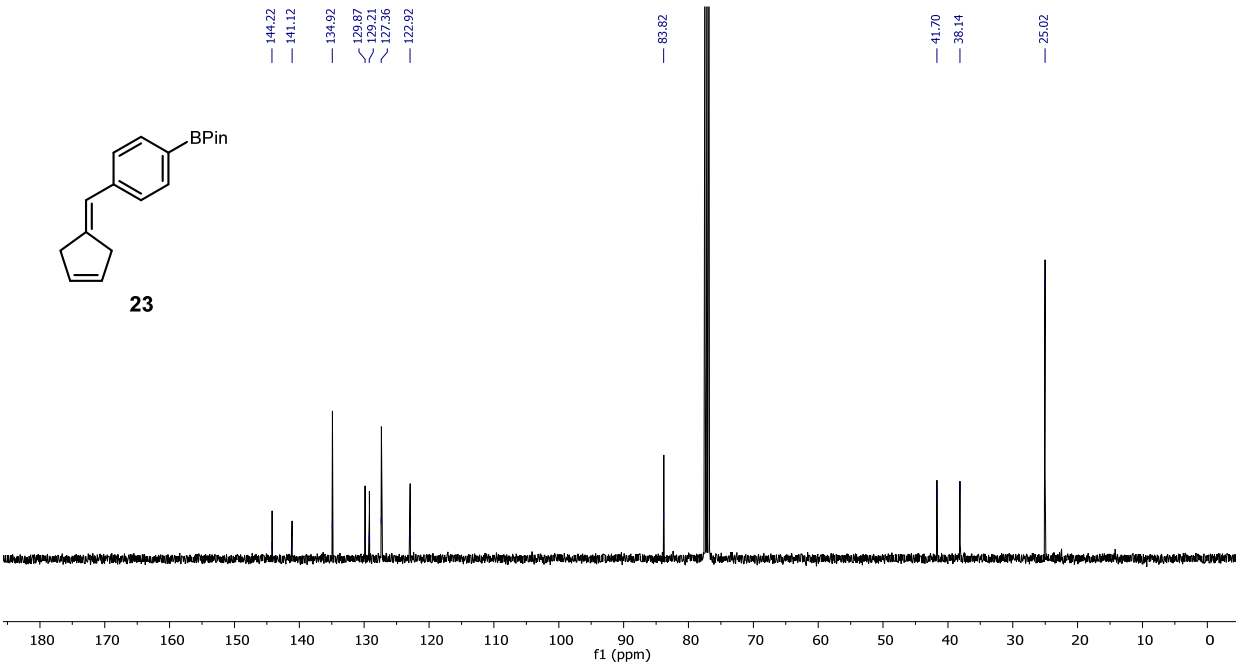

Ph
Me
Me
21
2.06
2.03
0.99
1.01
1.00
1.00
2.09
2.08
3.10
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

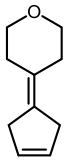

144.29
138.22
129.96
129.52
129.27
128.68
127.05
126.23
121.71
45.28
42.10
13.85
13.69
Ph
Me
Me
21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
22
3.21
2.05
1.00
1.94
3.27
1.99
1.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

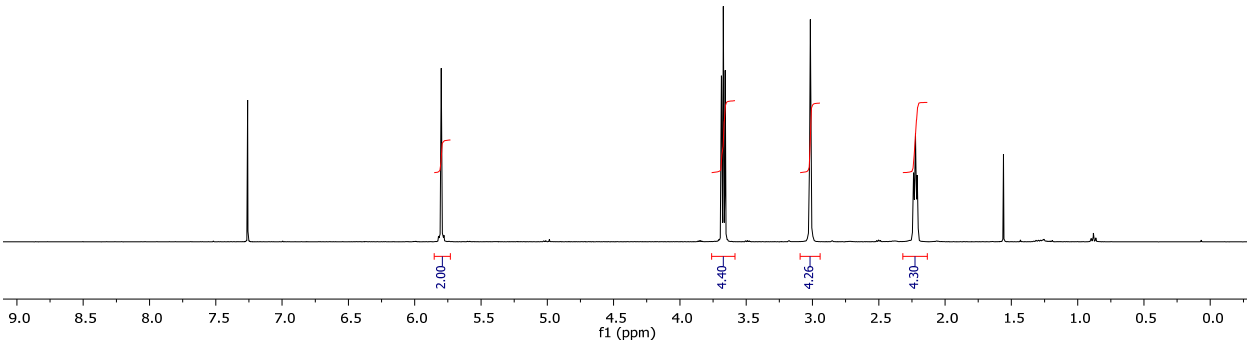

157.89
140.33
131.30
129.89
129.42
129.19
122.07
113.85
55.41
41.44
37.87
OMe
22
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

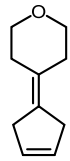

7.79
7.79
7.78
7.77
7.77
7.32
7.32
7.30
7.30
6.48
6.47
6.47
6.46
6.45
5.85
3.36
3.35
3.32
3.32
1.35
BPin
23
1.96
2.03
1.00
1.94
2.04
2.06
12.58
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.22
141.12
134.92
129.87
129.21
127.36
122.92
83.82
41.70
38.14
25.02
BPin
23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



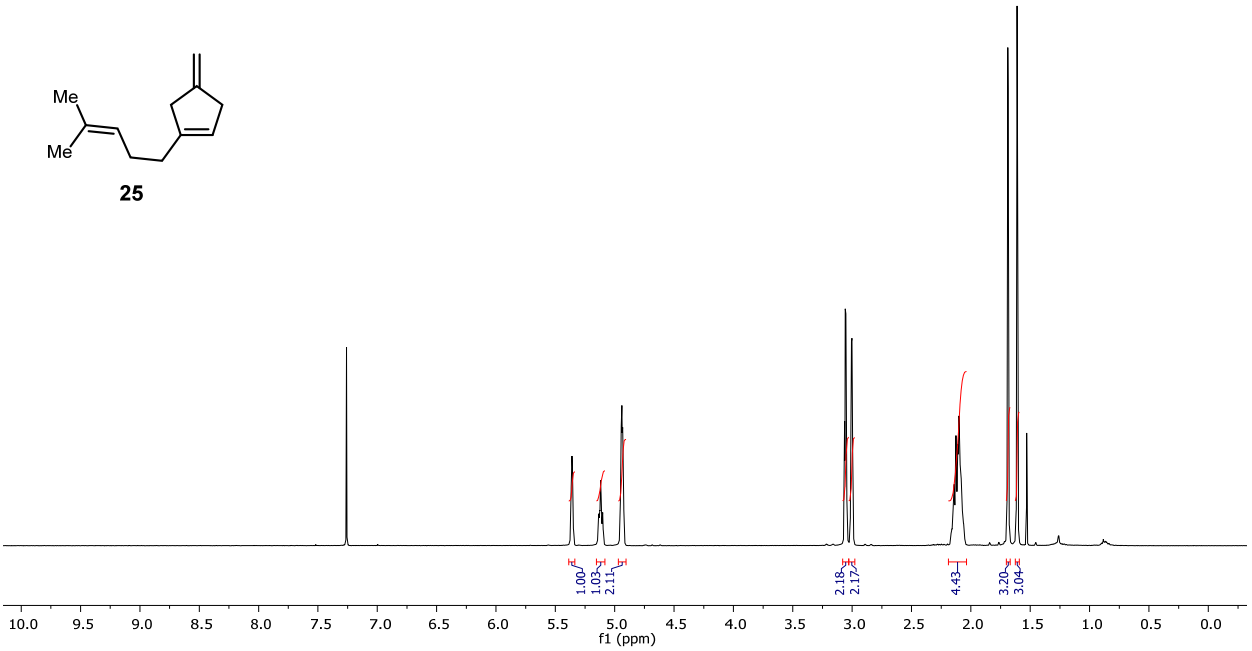
24

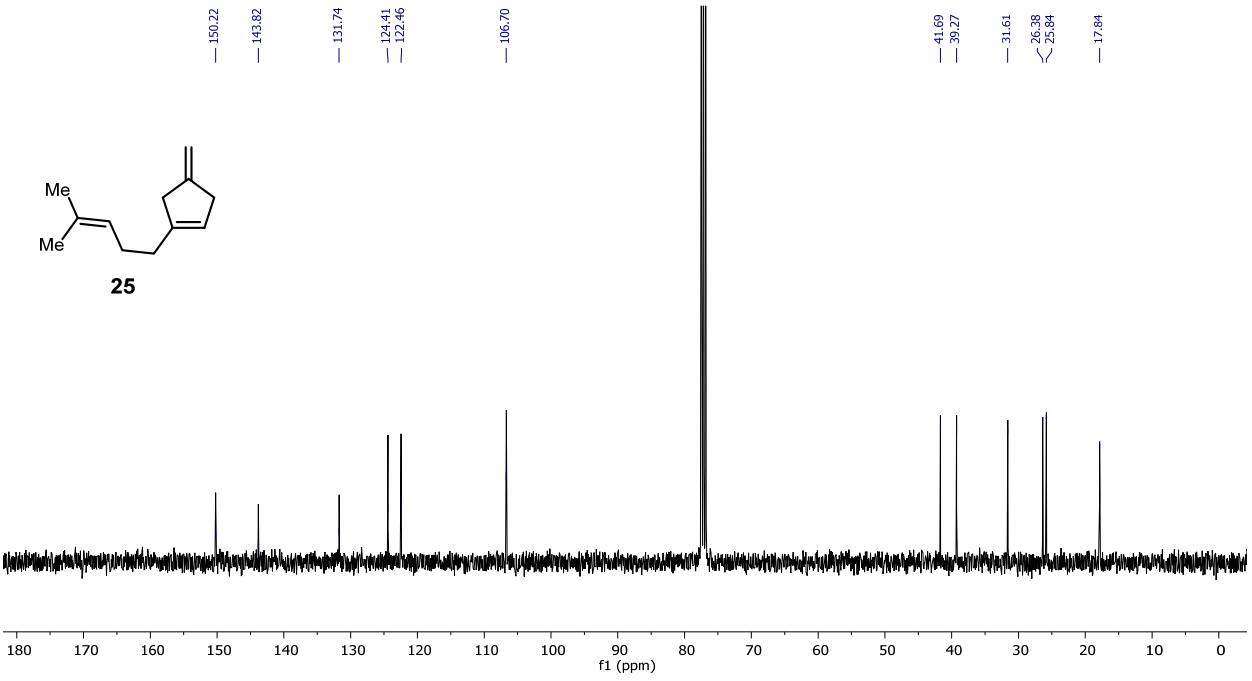

2.00
4.40
4.26
4.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

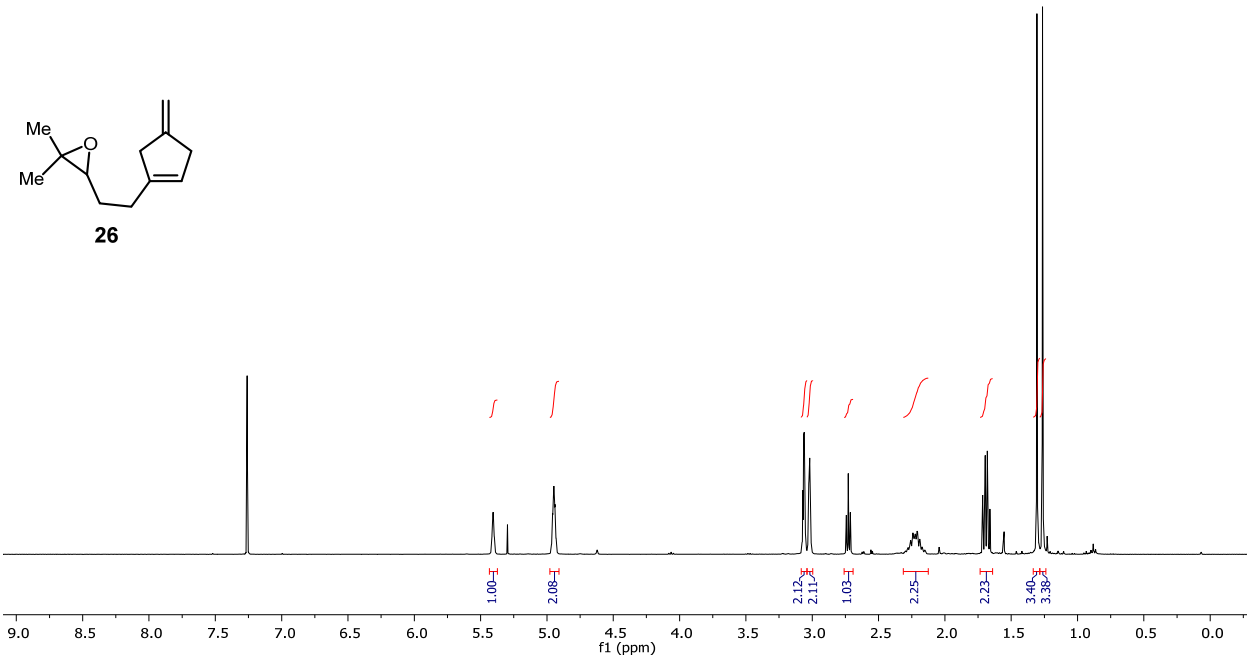


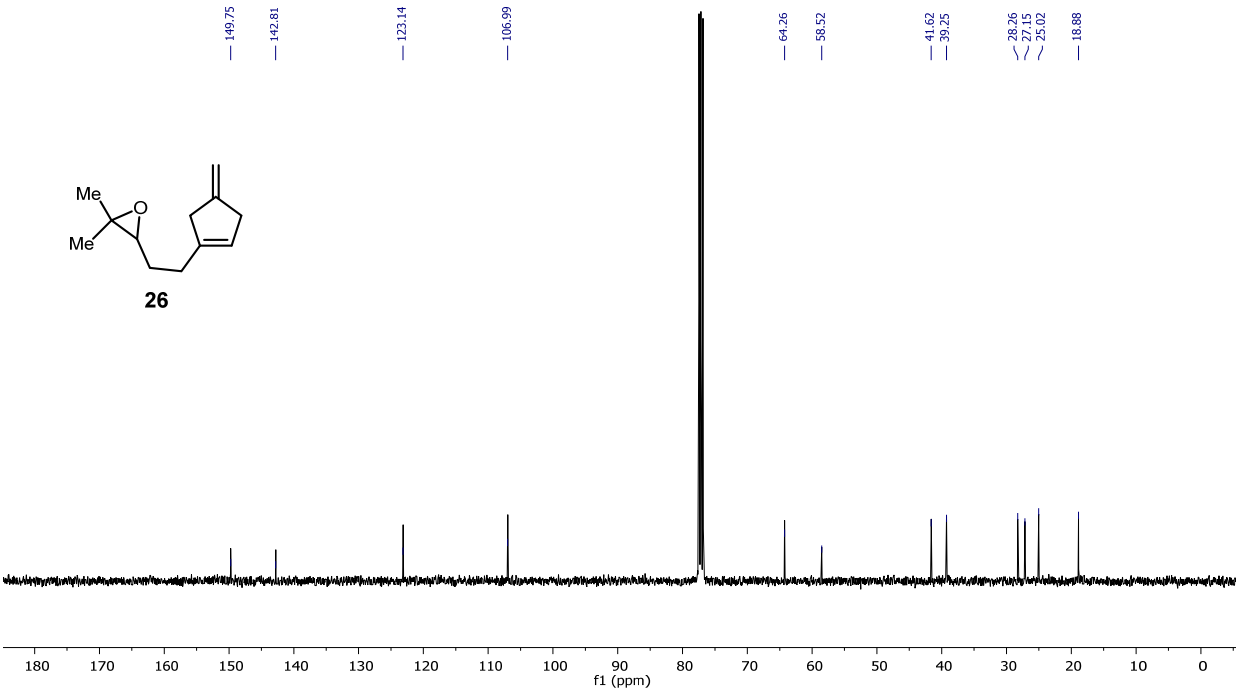
24

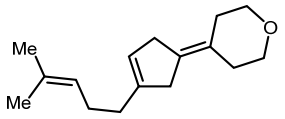
131.07
129.83
125.61
68.68
36.33
32.12
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
25
1.00
1.03
2.11
2.18
2.17
4.43
3.20
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.22
143.82
131.74
124.41
122.46
106.70
41.69
39.27
31.61
26.38
25.84
17.84
Me
Me
25
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
Me
26
1.00
2.08
2.12
2.11
1.03
2.25
2.23
3.40
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

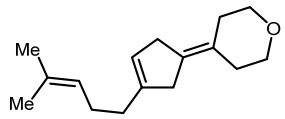

149.75
142.81
123.14
106.99
64.26
58.52
41.62
39.25
28.26
27.15
25.02
18.88
Me
O
Me
26
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
O

27

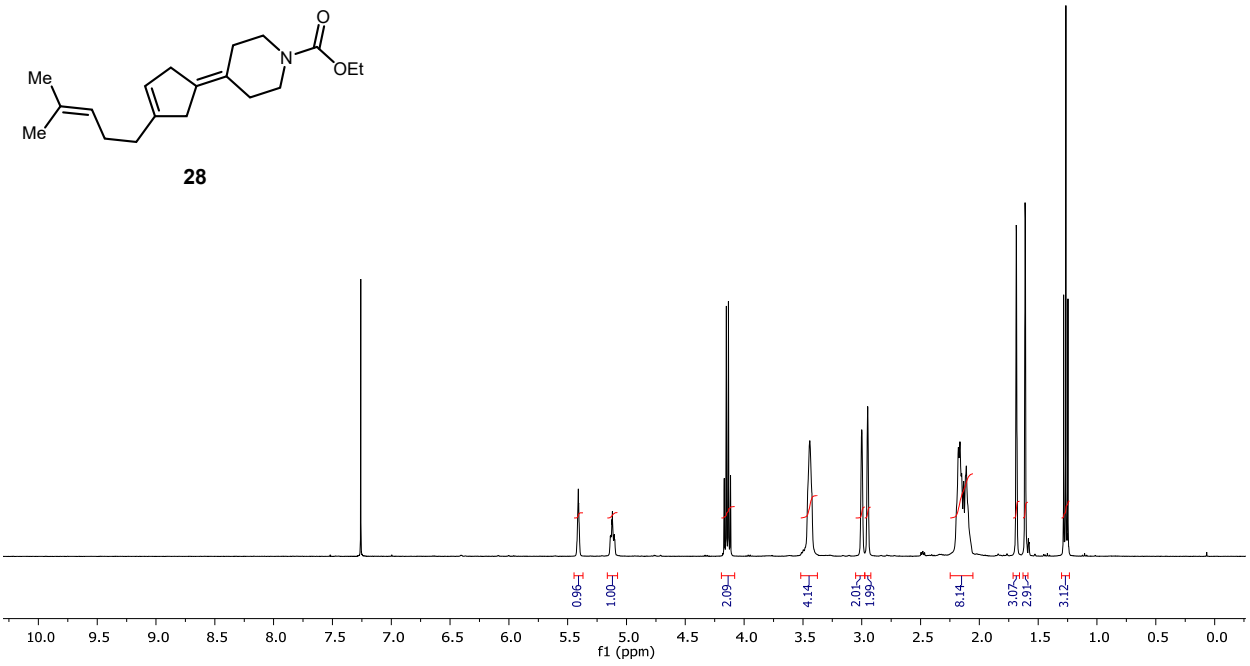
1.00
1.01
4.27
2.09
2.07
4.28
4.25
3.09
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

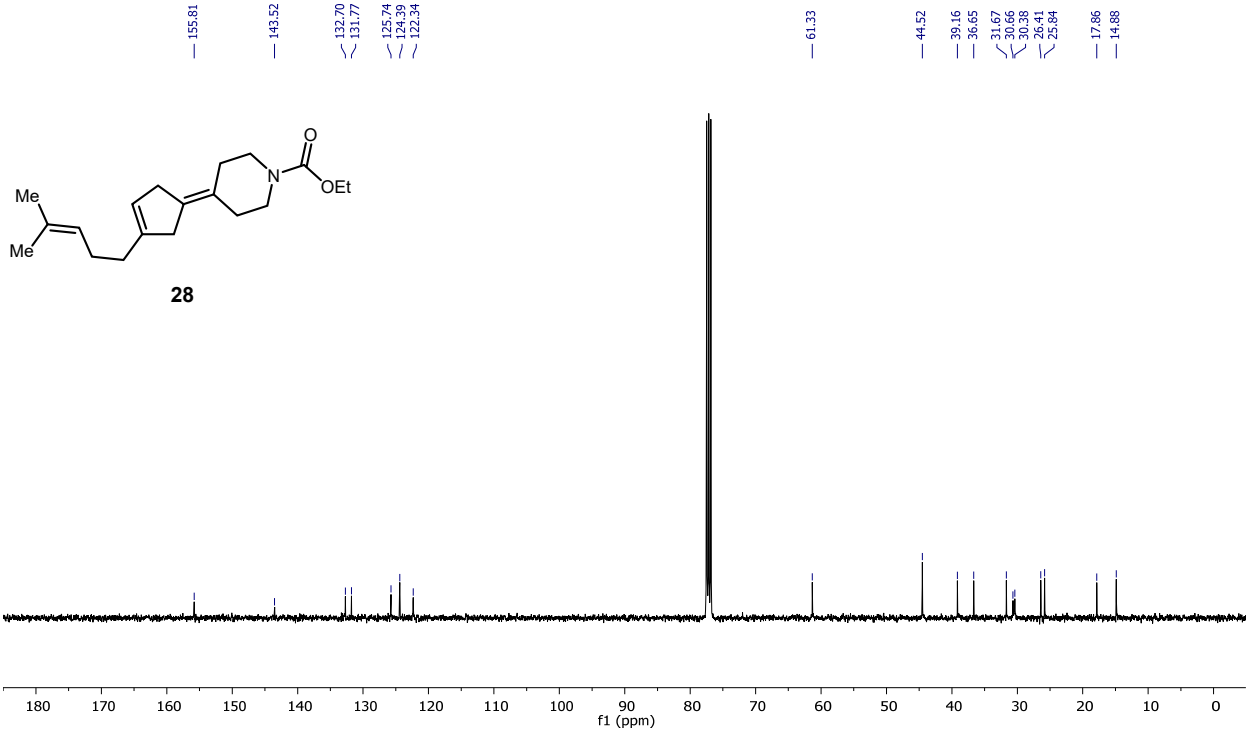

143.54
131.74
125.34
124.42
122.36
68.70
38.97
36.46
32.06
31.79
31.70
26.42
25.84
17.85

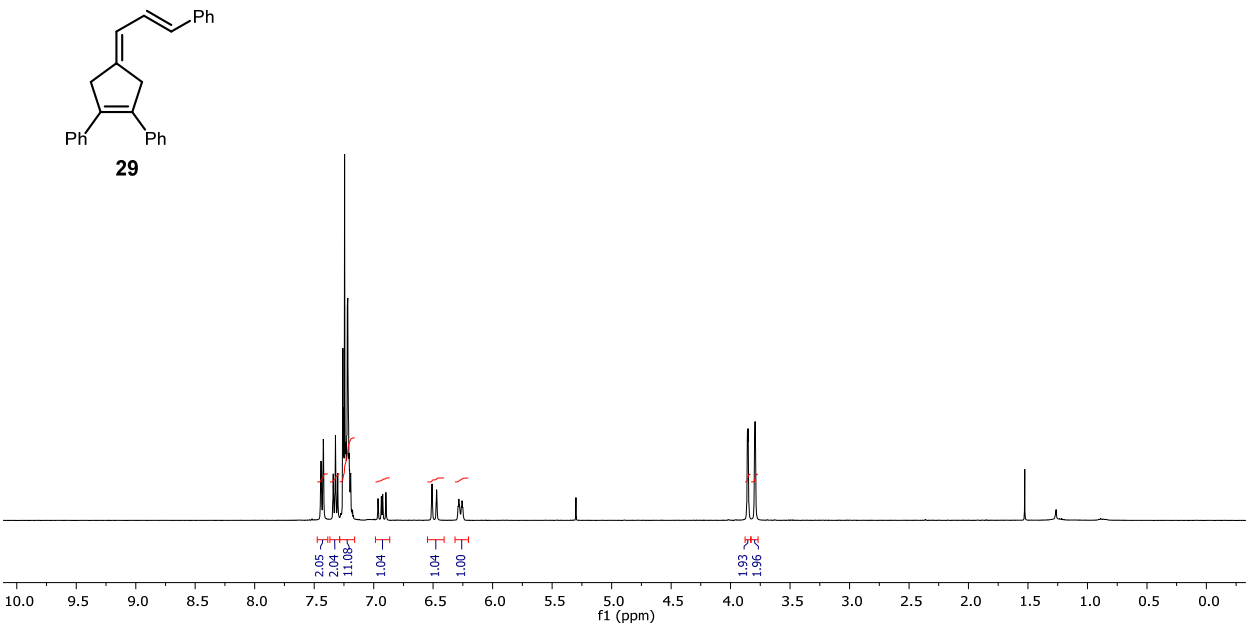

Me
Me
O

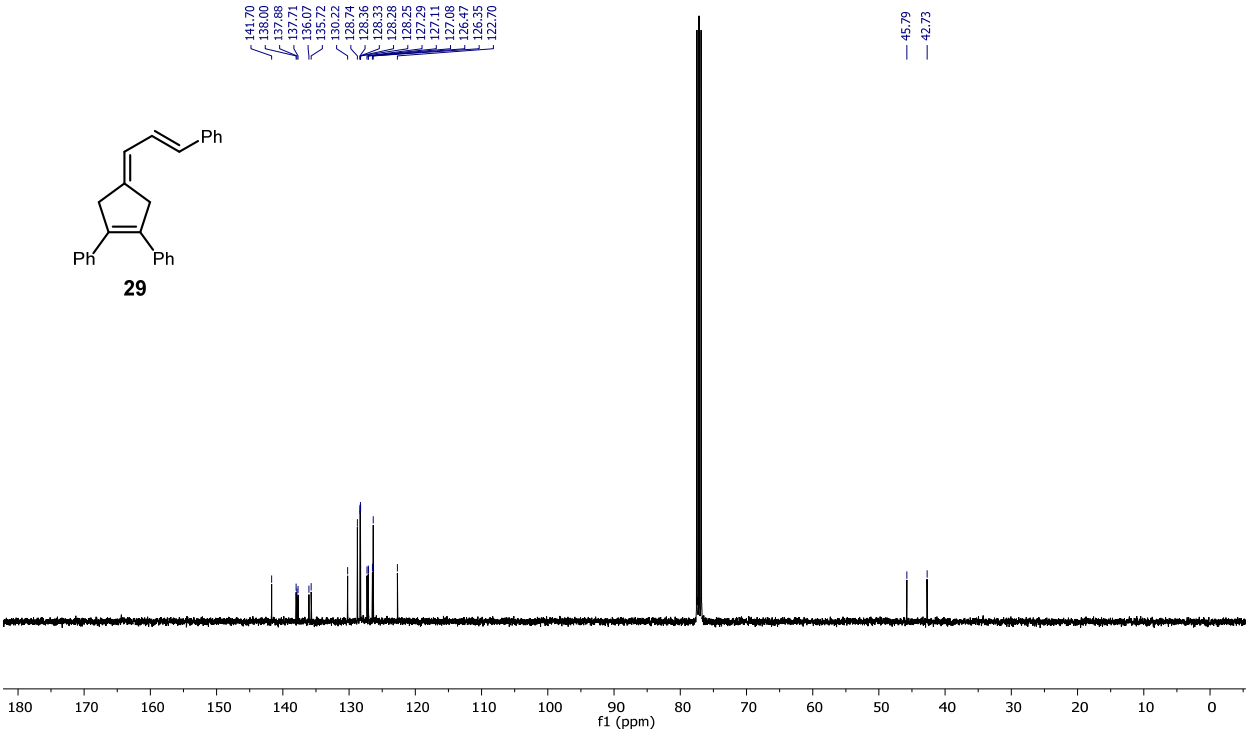
27

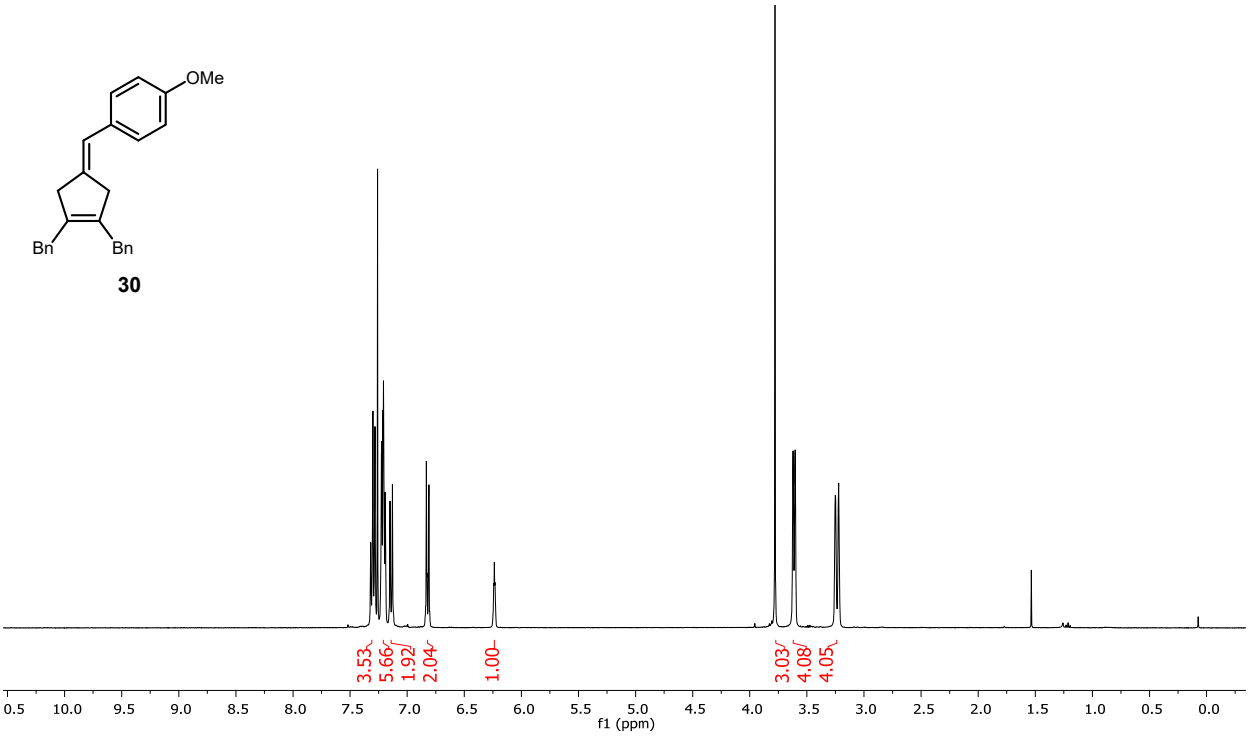
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

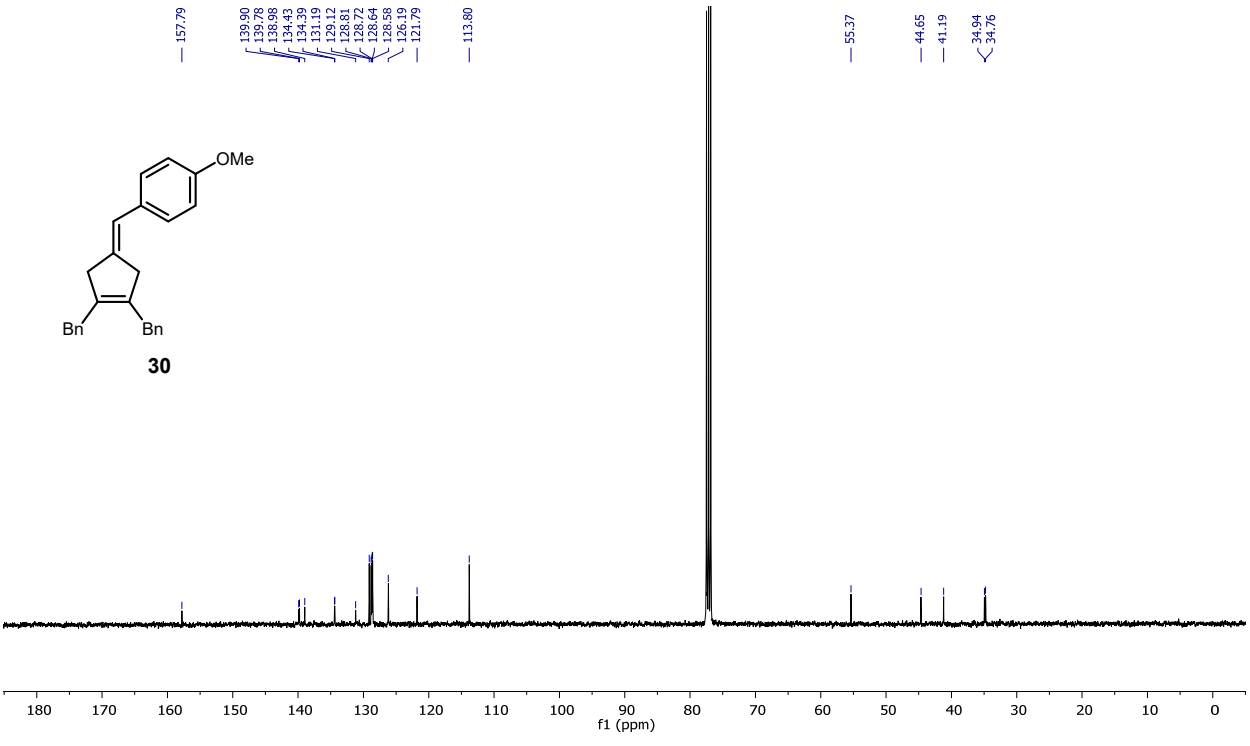

Me
Me
N
O
OEt
28
0.96
1.00
2.09
4.14
2.01
1.99
8.14
3.07
2.91
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

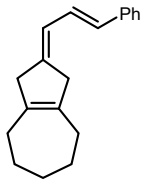

155.81
143.52
132.70
131.77
125.74
124.39
122.34
61.33
44.52
39.16
36.65
31.67
30.66
30.38
26.41
25.84
17.86
14.88
Me
Me
N
O
OEt
28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Ph
29
2.05
2.04
11.08
1.04
1.04
1.00
1.93
1.96
f1 (ppm)

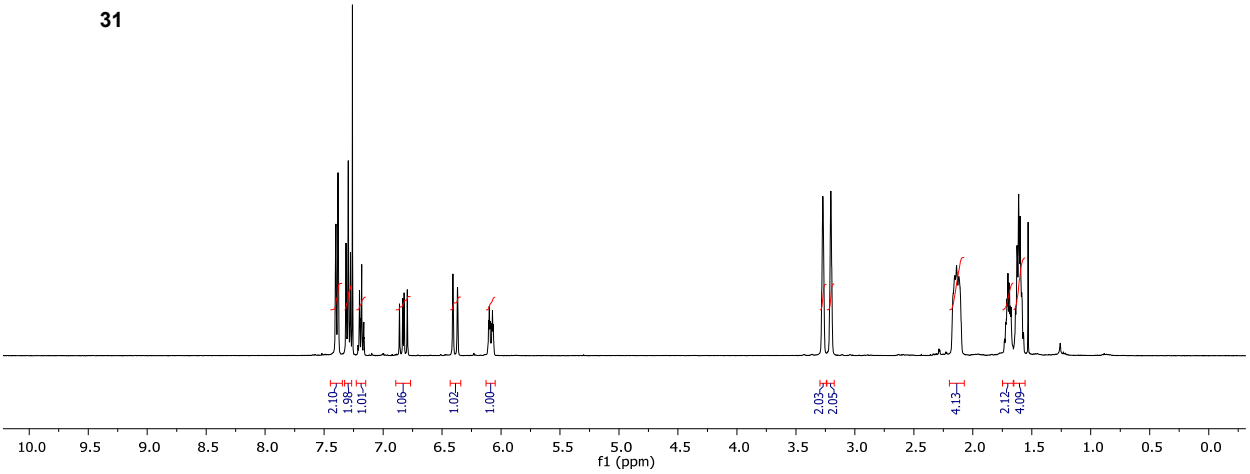

141.70
138.00
137.88
137.71
136.07
135.72
130.22
128.74
128.36
128.33
128.28
128.25
127.29
127.11
127.08
126.47
126.35
122.70
45.79
42.73
Ph
Ph
Ph
29
f1 (ppm)


OMe
Bn
Bn
30
3.53
5.66
1.92
2.04
1.00
3.03
4.08
4.05
f1 (ppm)

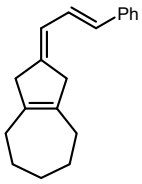

157.79
139.90
139.78
138.98
134.43
134.39
131.19
129.12
128.81
128.72
128.64
128.58
126.19
121.79
113.80
55.37
44.65
41.19
34.94
34.76
OMe
Bn
Bn
30
f1 (ppm)


Ph

31

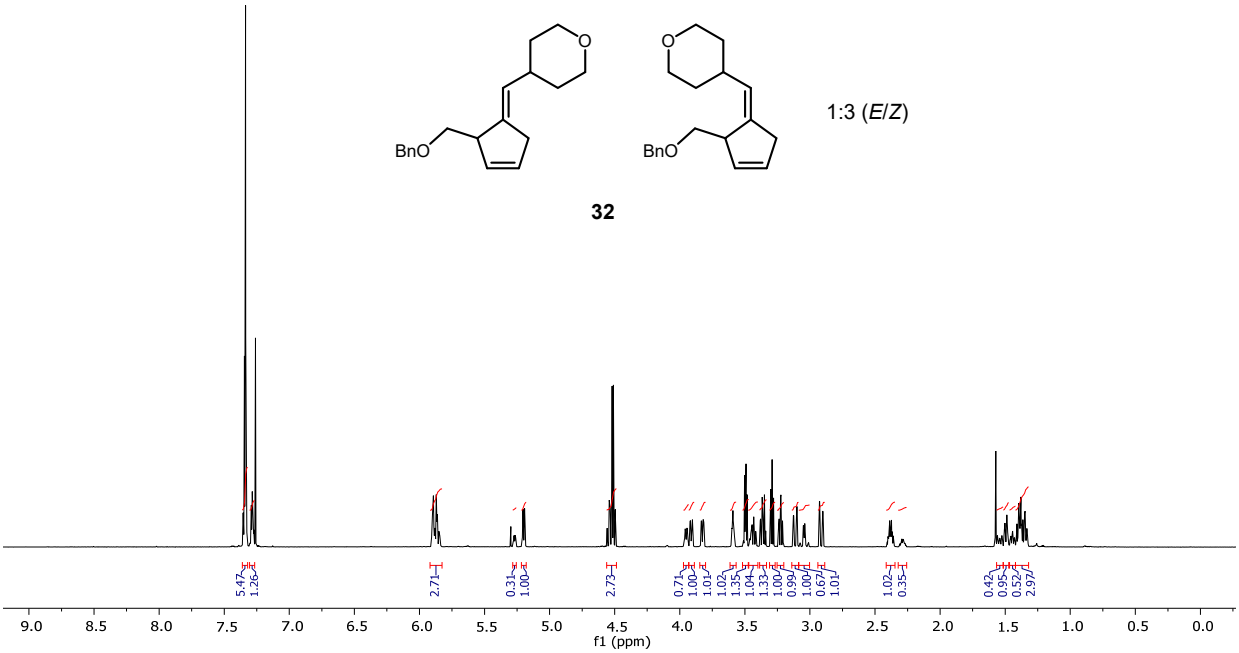

2.10
1.98
1.01
1.06
1.02
1.00
2.03
2.05
4.13
2.12
4.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

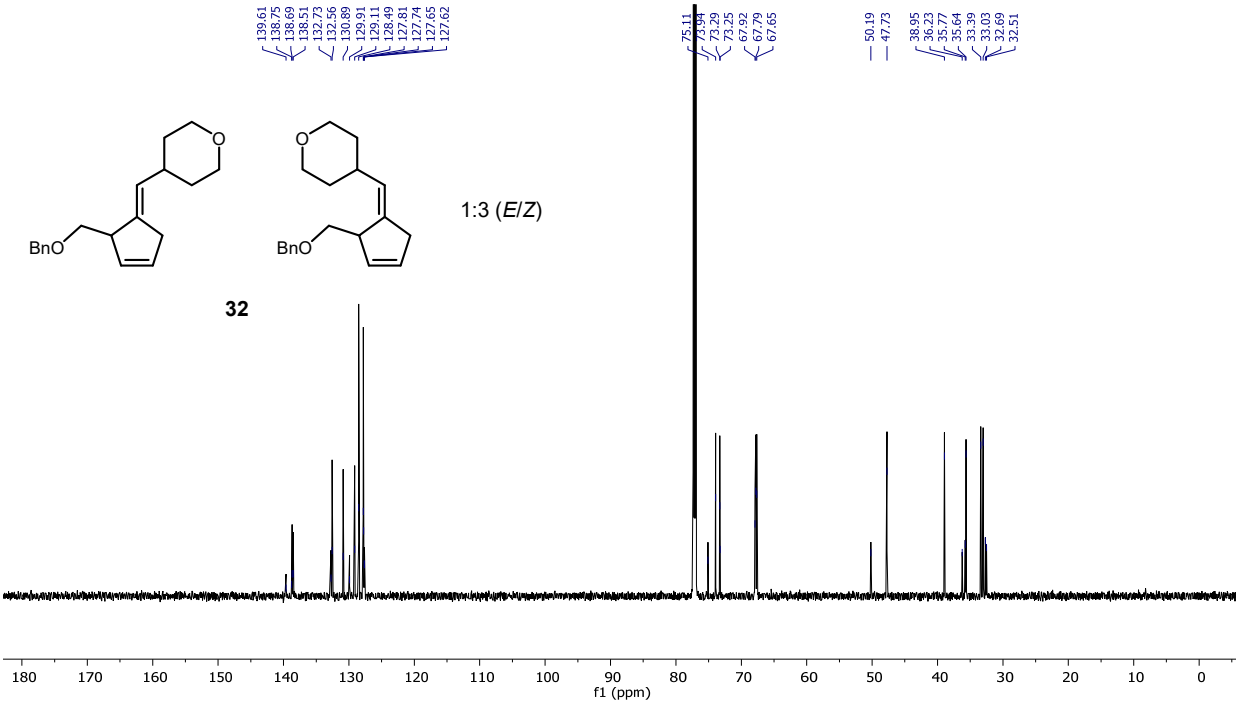

145.25
138.25
136.23
135.79
129.18
128.68
127.07
127.02
126.23
121.62
46.65
43.43
30.75
30.29
30.08
27.72

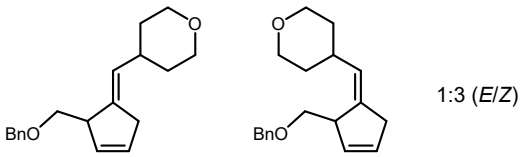

Ph

31

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


BnO
BnO
1:3 (E/Z)
32
f1 (ppm)

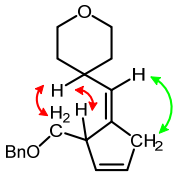

BnO
BnO
1:3 (E/Z)
32
f1 (ppm)


BnO
BnO

1:3 (*E*/*Z*)

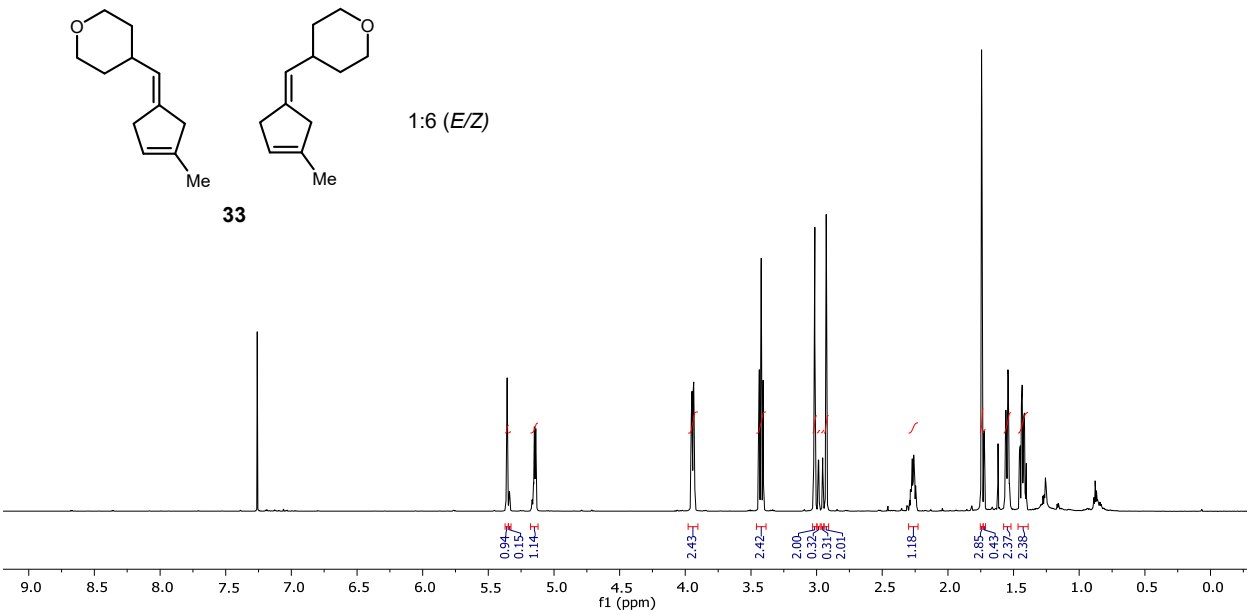
32


YYZ10-045-1-800M.4.ser
H1 gradient-COSY standard parameters, cryoprobe.
NS = 1. Turn spinning OFF.
f2 (ppm)
f1 (ppm)

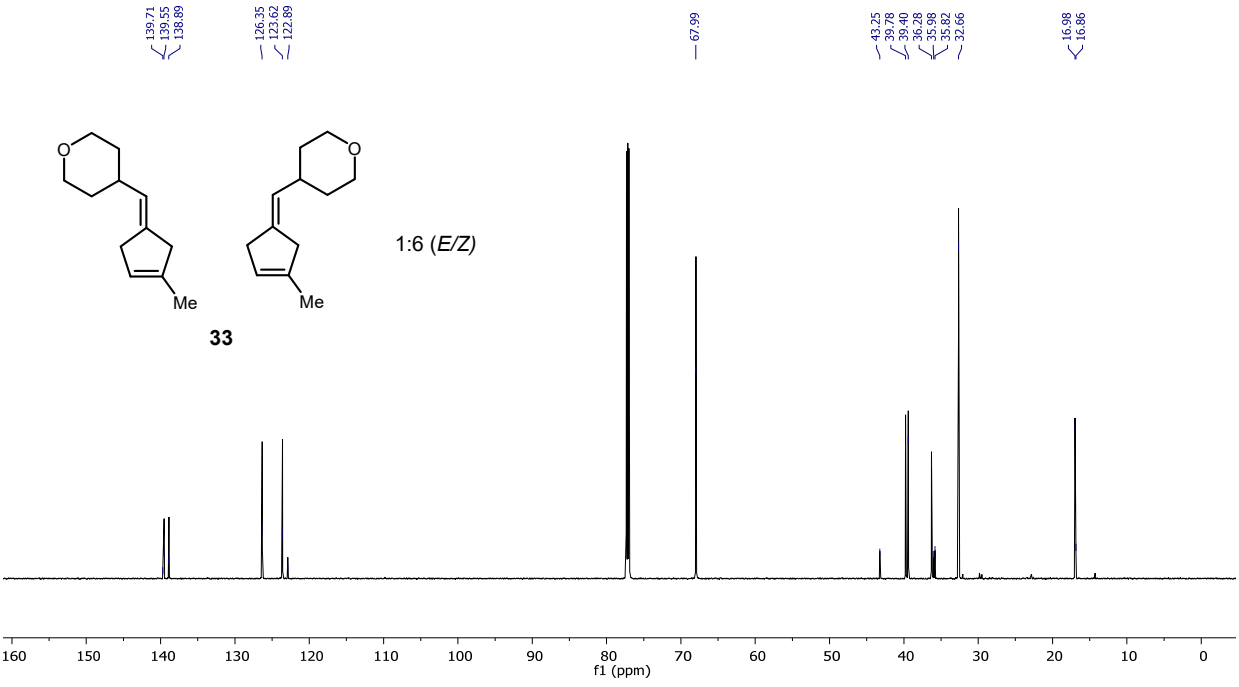

O
H
H
H2
H
C
BnO
CH2

32-*Z*

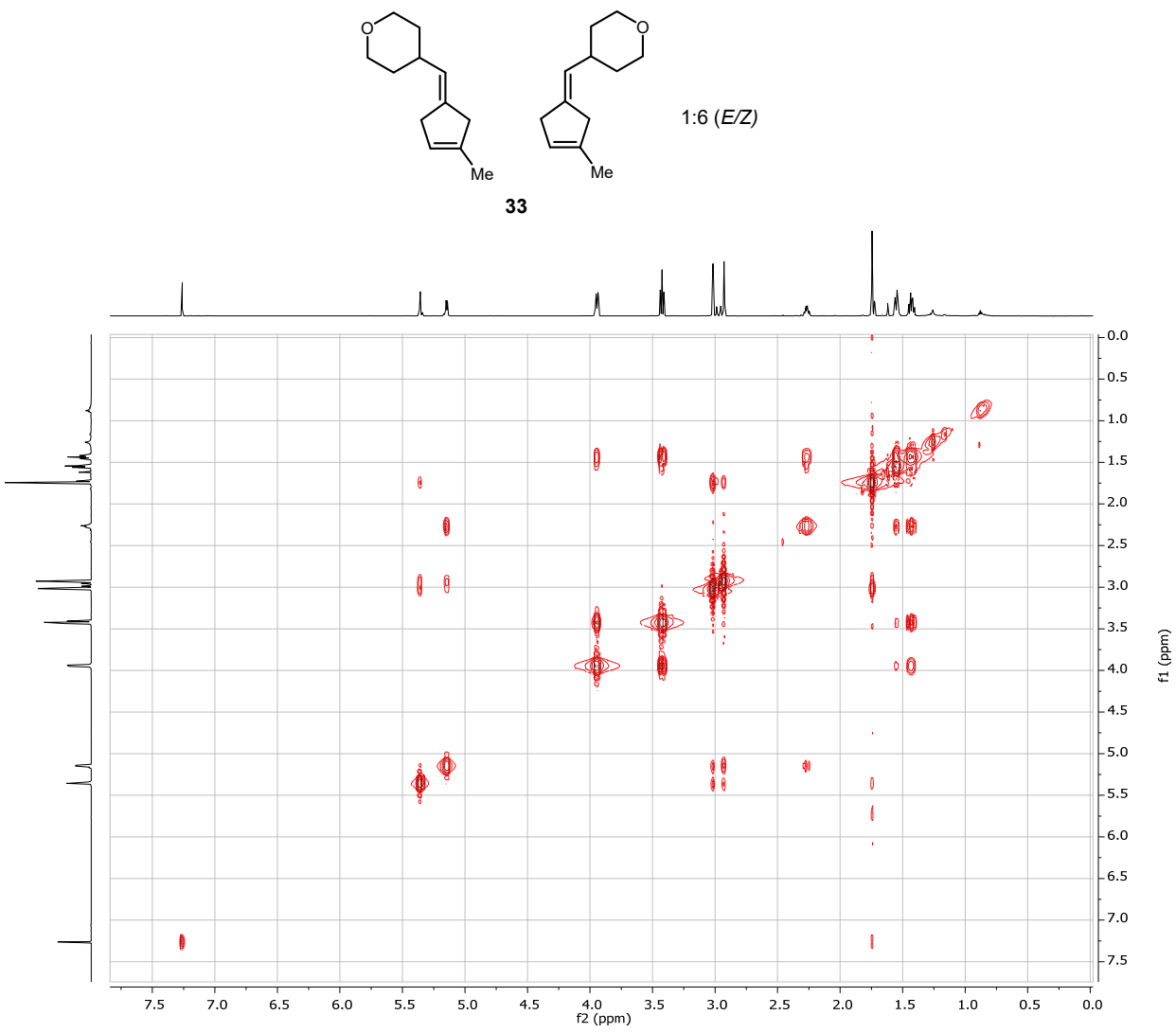

YYZ10-045-1-800M.5.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
f2 (ppm)
f1 (ppm)


O
Me
O
Me
1:6 (E/Z)
0.94
0.15
1.14
2.43
2.42
2.00
0.32
0.31
2.01
1.18
2.85
0.43
2.37
2.38
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

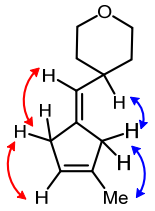
33


139.71
139.55
138.89
126.35
123.62
122.89
67.99
43.25
39.78
39.40
36.28
35.98
35.82
32.66
16.98
16.86
O
Me
O
Me
1:6 (E/Z)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

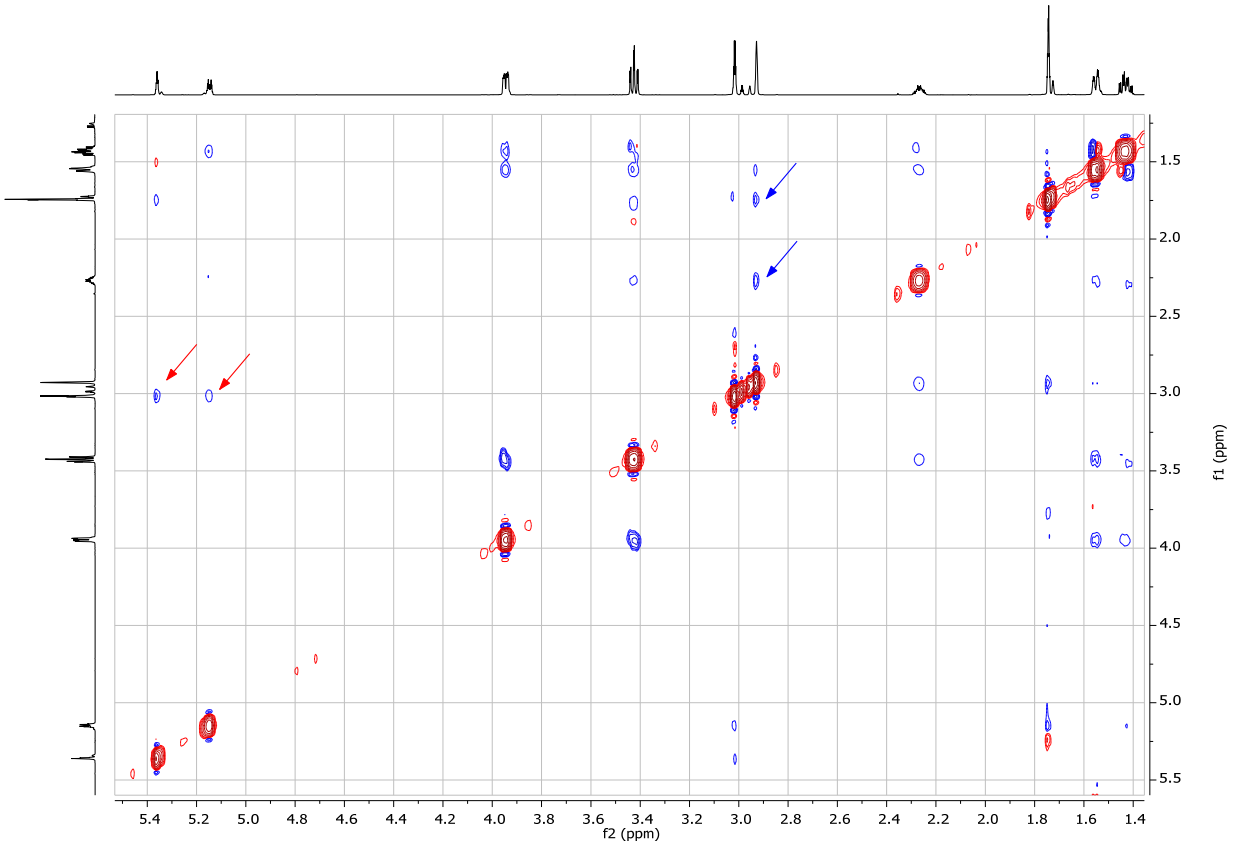
33

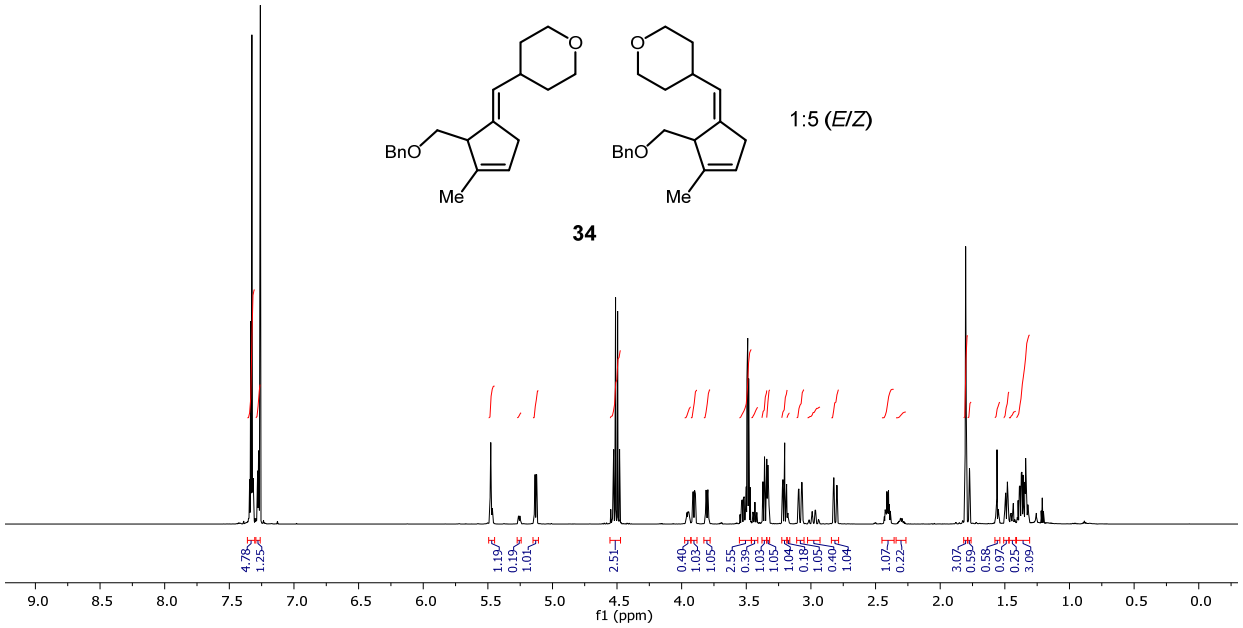


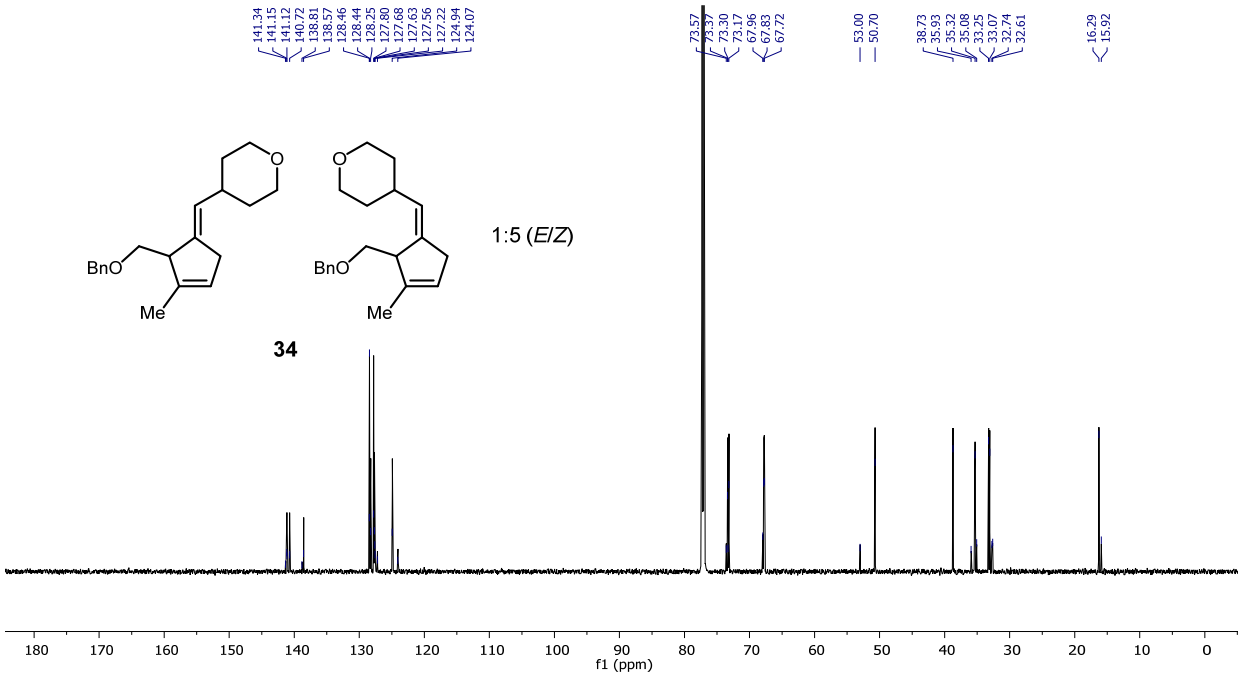
33

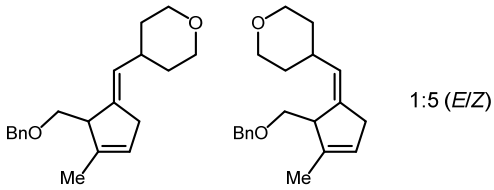

O
H
H
H
H
H
H
H
H
Me

33-*Z*


5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)


BnO
Me
O
BnO
Me
O
1:5 (E/Z)
34
4.78
1.25
1.19
0.19
1.01
2.51
0.40
1.03
1.05
2.55
0.39
1.03
1.05
1.04
0.18
1.05
0.40
1.04
1.07
0.22
3.07
0.59
0.58
0.97
0.25
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

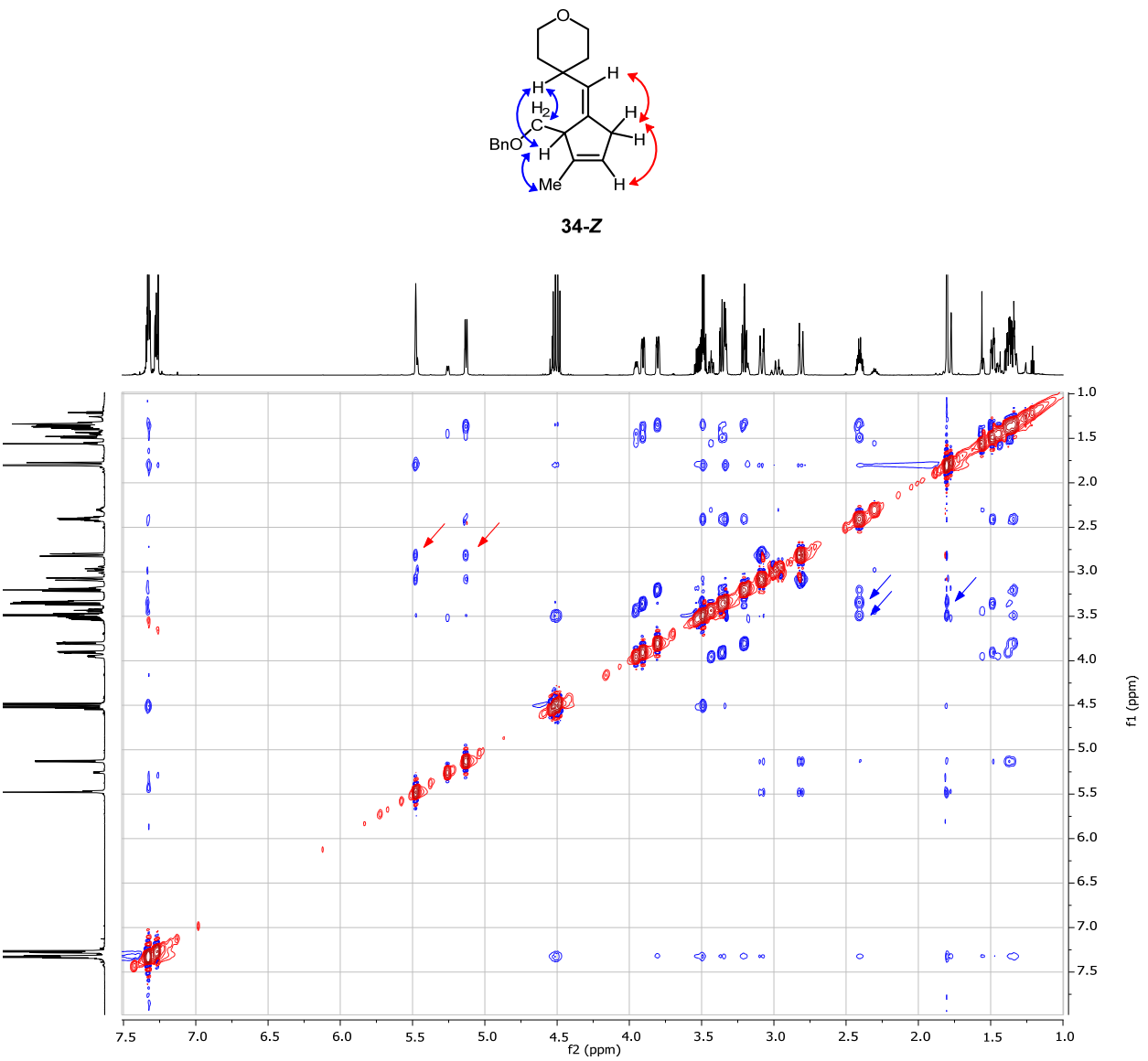

141.34
141.15
141.12
140.72
138.81
138.57
128.46
128.44
128.25
127.80
127.68
127.63
127.56
127.22
124.94
124.07
73.57
73.37
73.30
73.17
67.96
67.83
67.72
53.00
50.70
38.73
35.93
35.32
35.08
33.25
33.07
32.74
32.61
16.29
15.92
BnO
Me
O
BnO
Me
O
1:5 (E/Z)
34
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


BnO
Me
O
BnO
Me
O

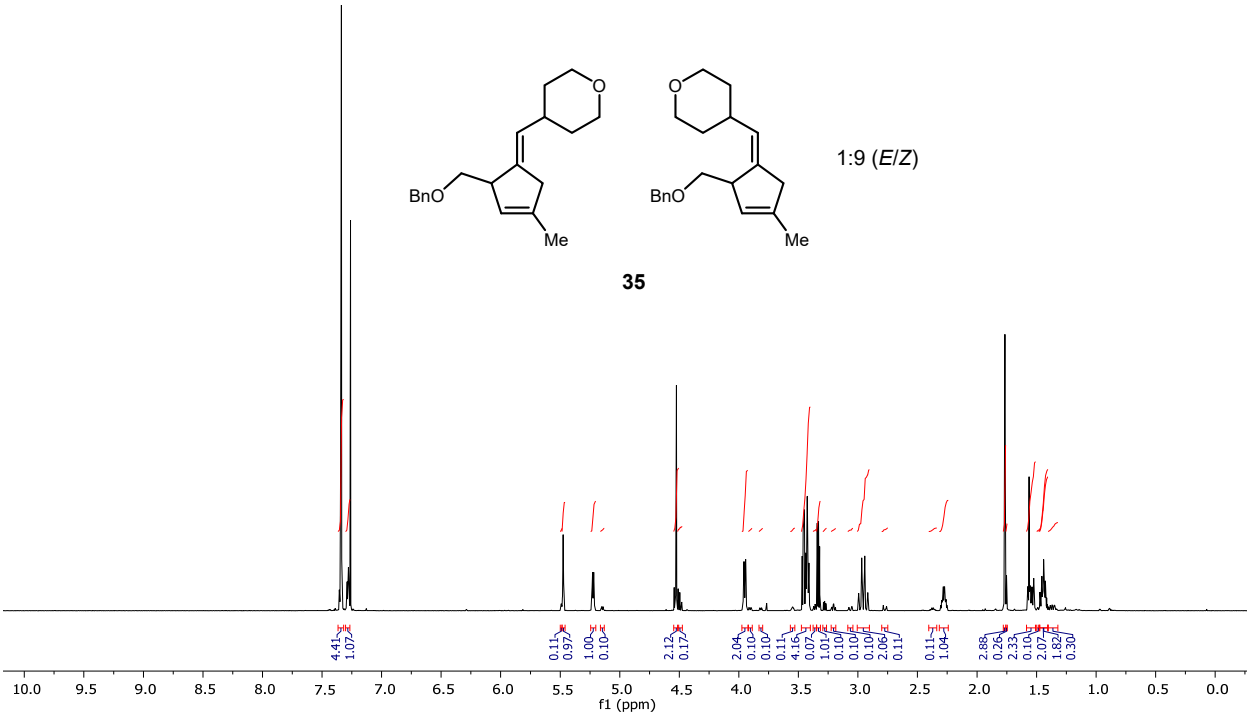
1:5 (*E*/*Z*)

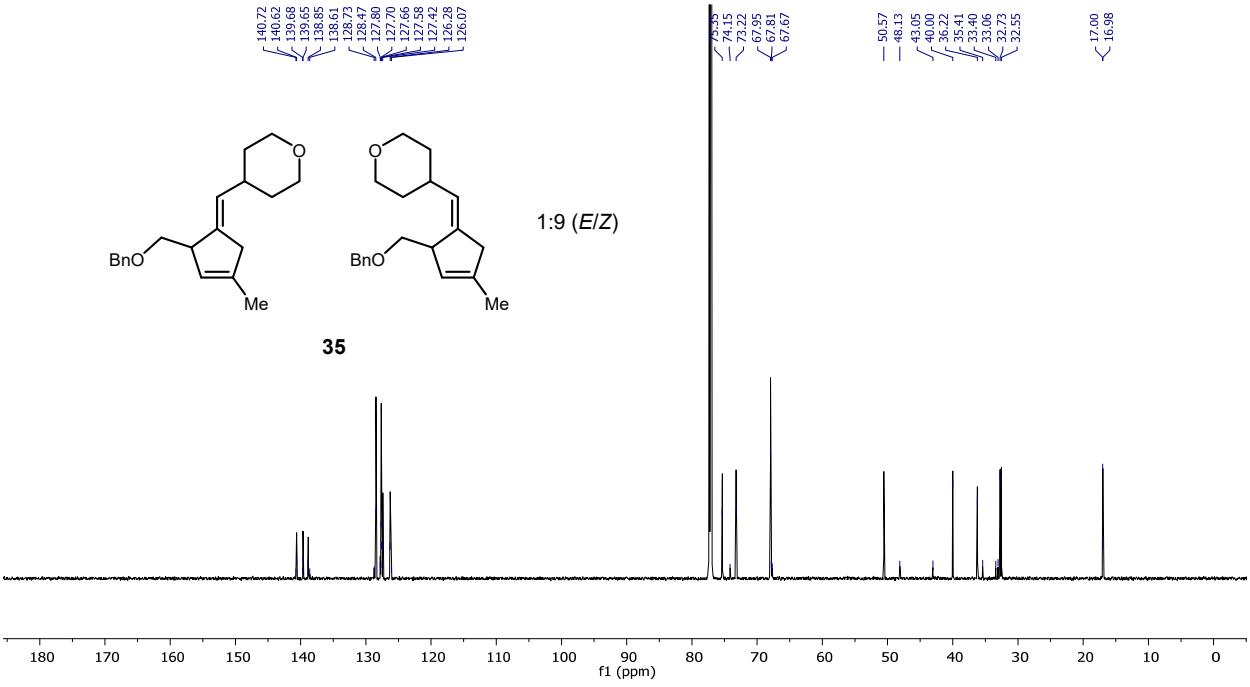
34

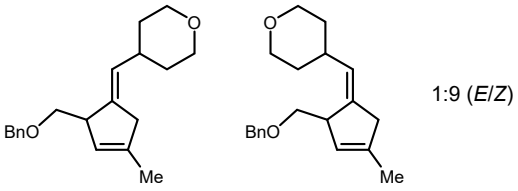

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)



34-*Z*

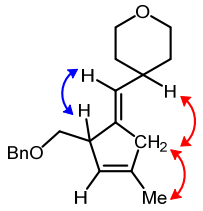

BnO
Me
O
1:9 (E/Z)
35
f1 (ppm)


BnO
Me
O
1:9 (E/Z)
35
f1 (ppm)

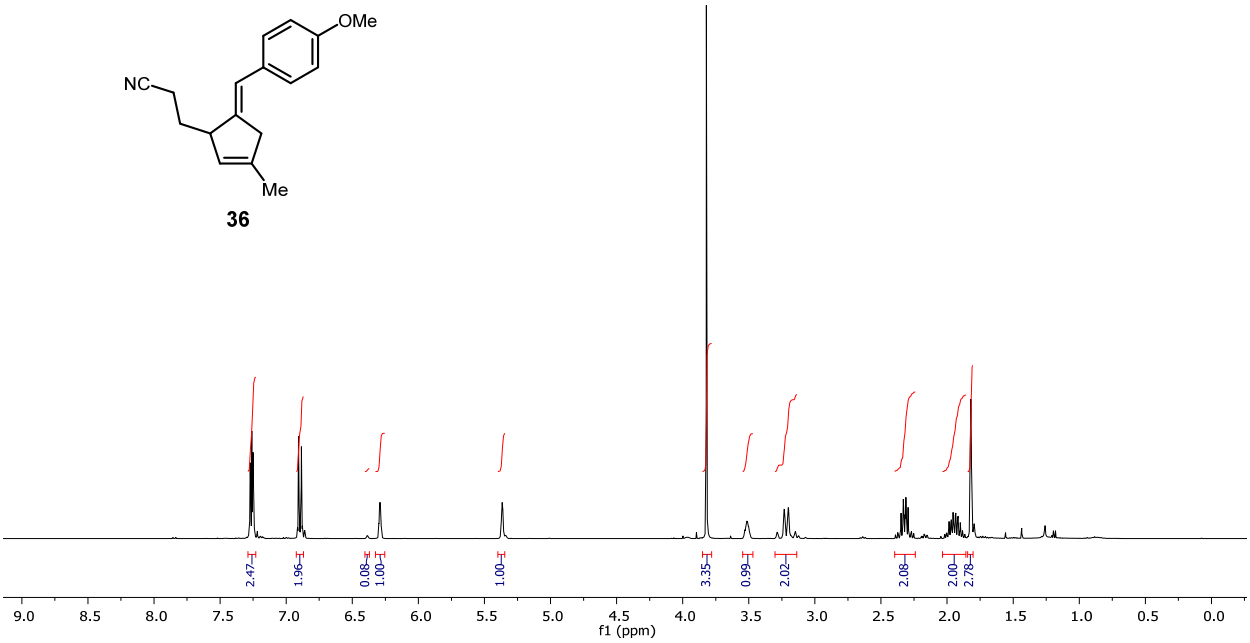


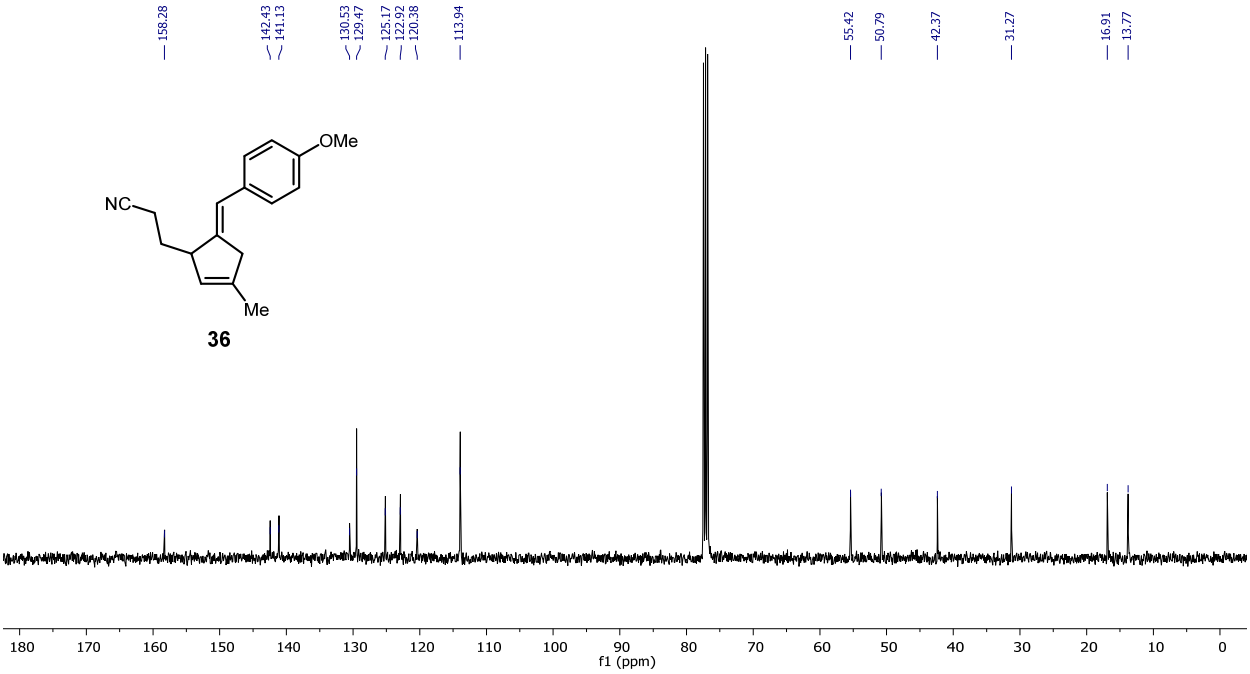
1:9 (*E*/*Z*)

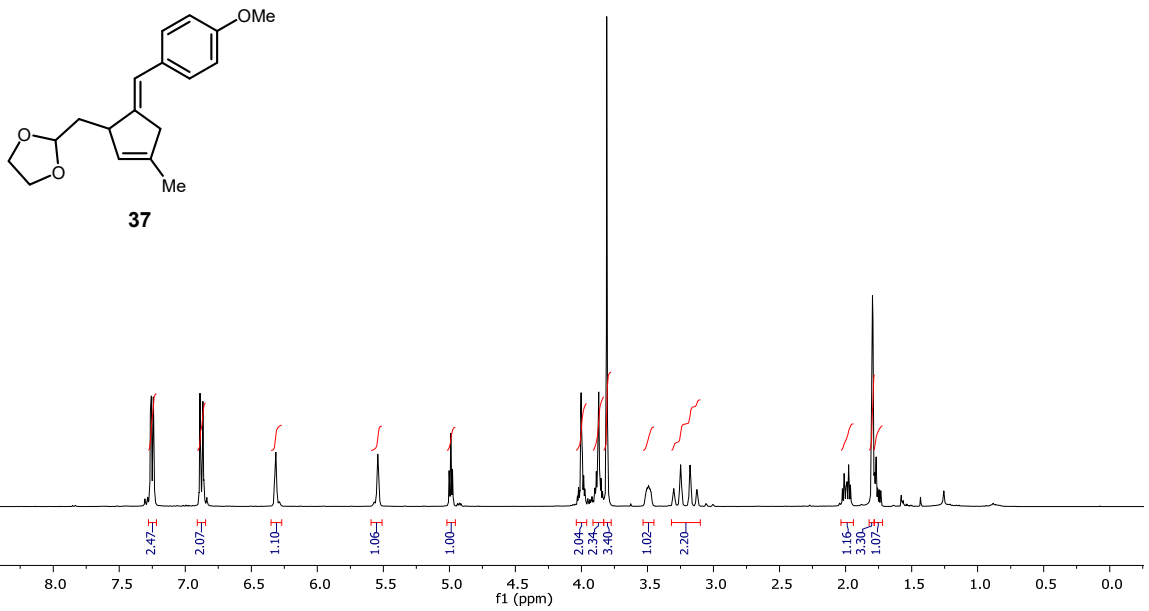
35

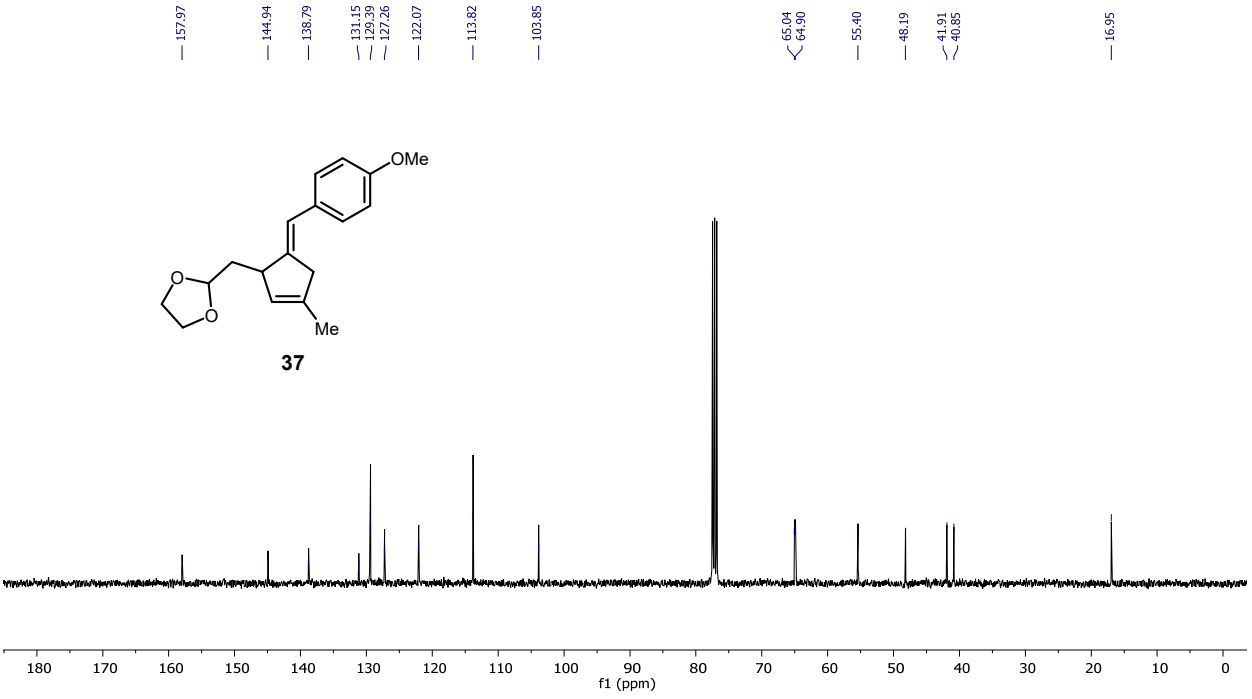


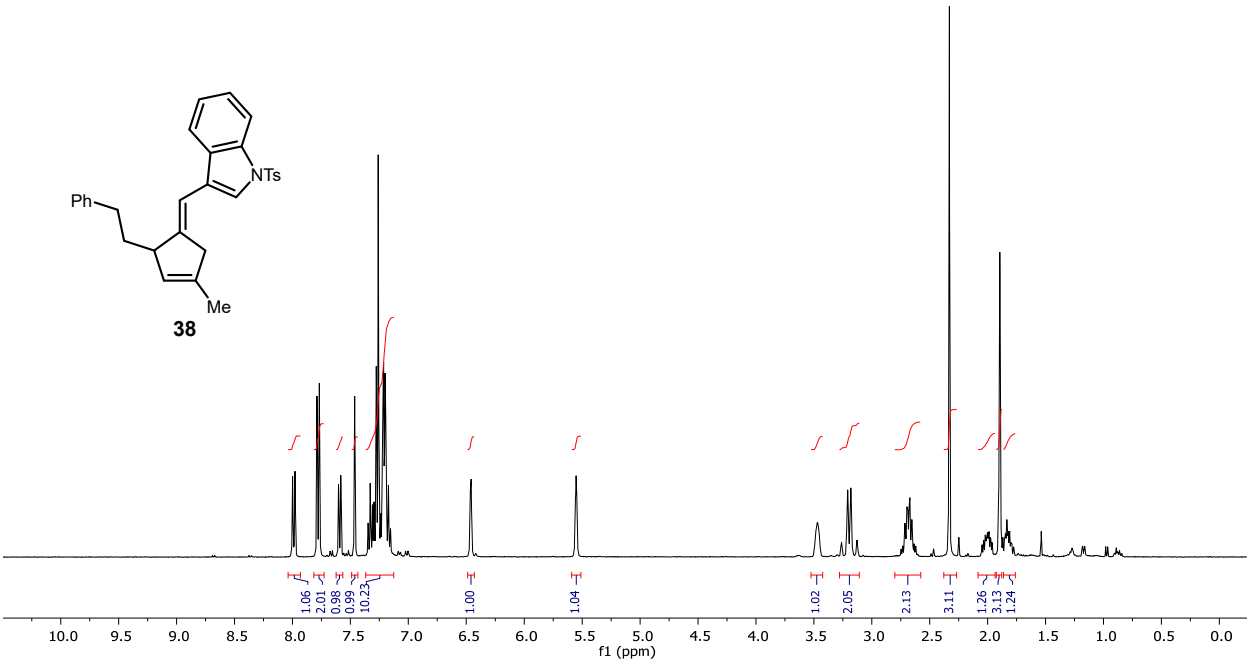
35-*E*

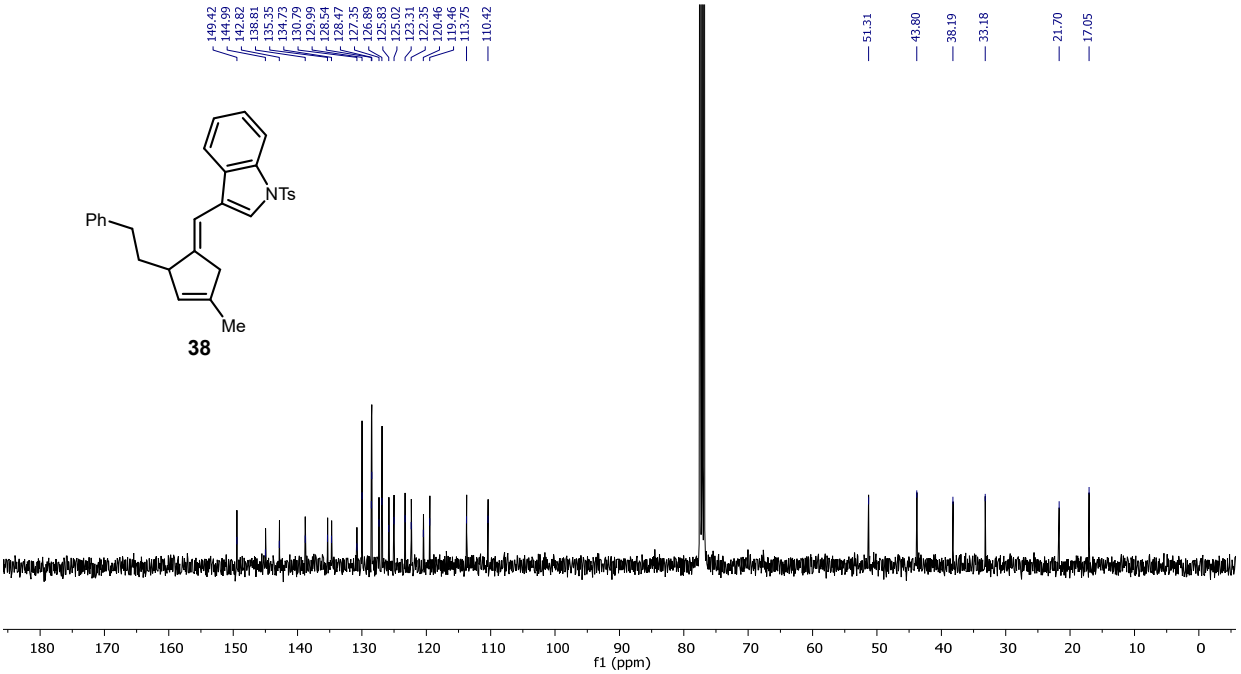

OMe
NC
Me
36
2.47
1.96
0.08
1.00
1.00
3.35
0.99
2.02
2.08
2.00
2.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

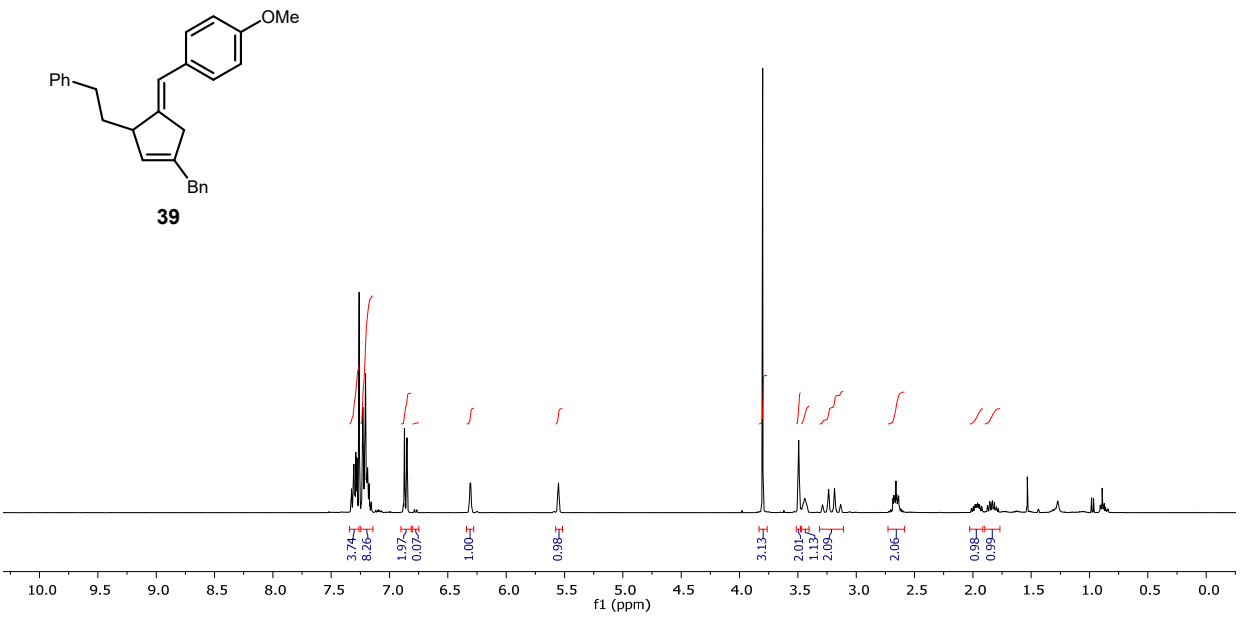

158.28
142.43
141.13
130.53
129.47
125.17
122.92
120.38
113.94
55.42
50.79
42.37
31.27
16.91
13.77
OMe
NC
Me
36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

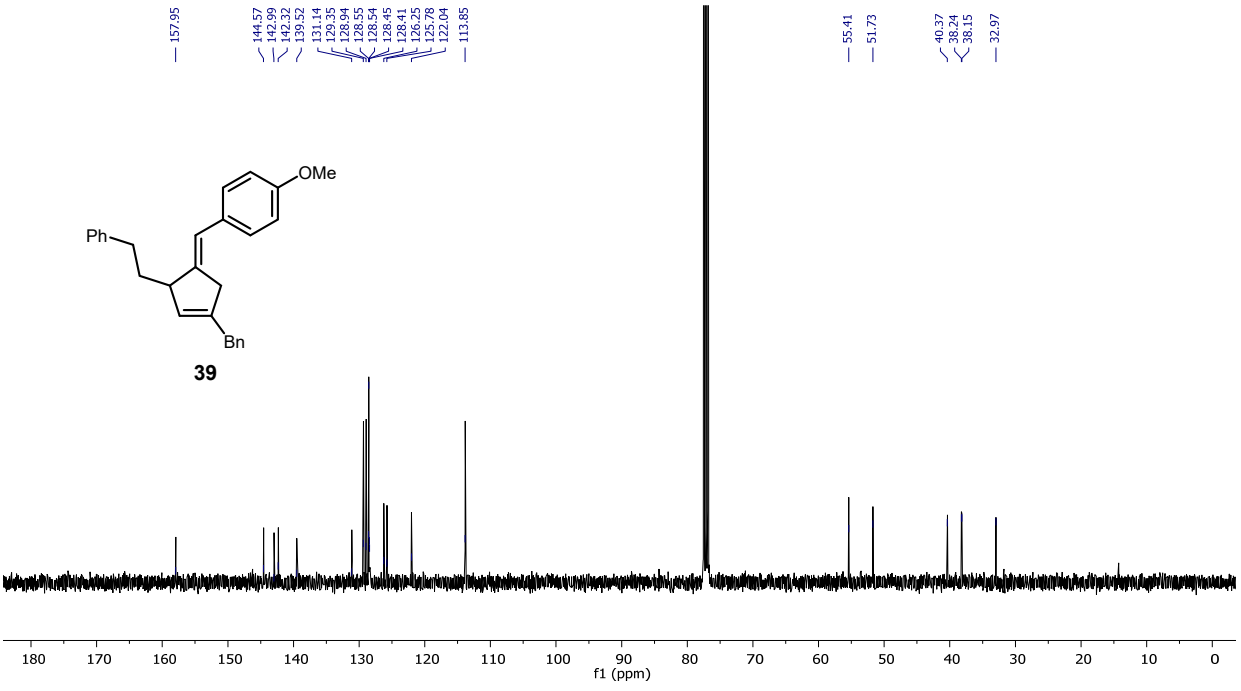

OMe
O
O
Me
37
2.47
2.07
1.10
1.06
1.00
2.04
2.34
3.40
1.02
2.20
1.16
3.30
1.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

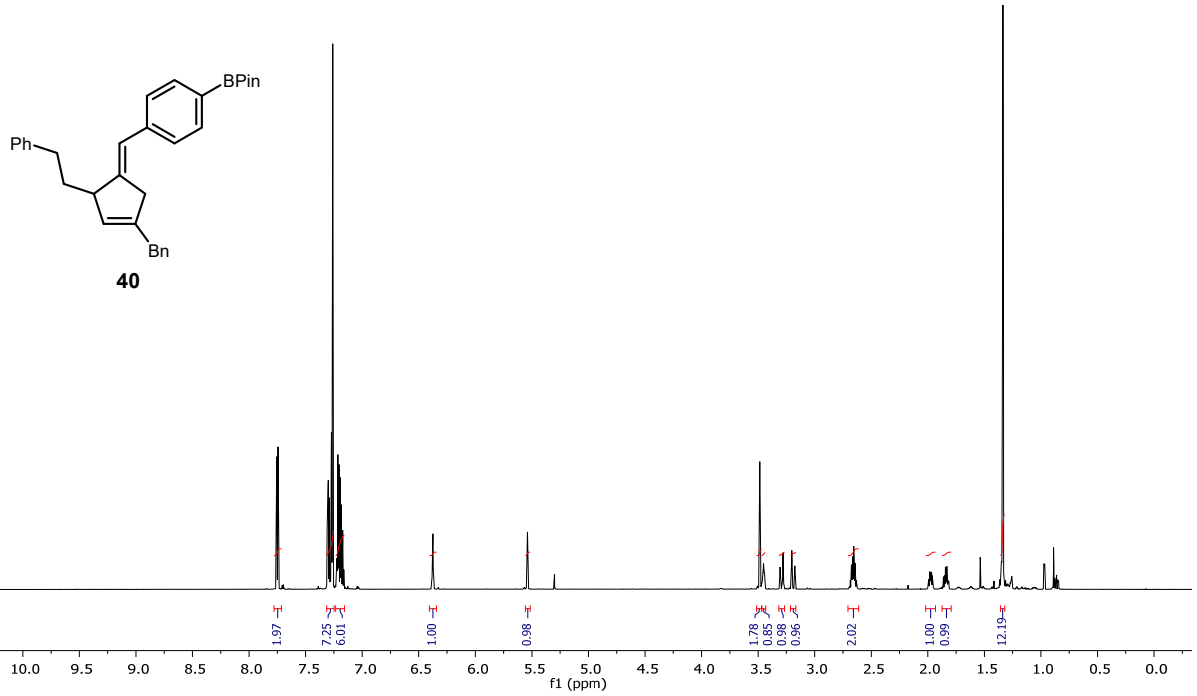

157.97
144.94
138.79
131.15
129.39
127.26
122.07
113.82
103.85
65.04
64.90
55.40
48.19
41.91
40.85
16.95
OMe
O
O
Me
37
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

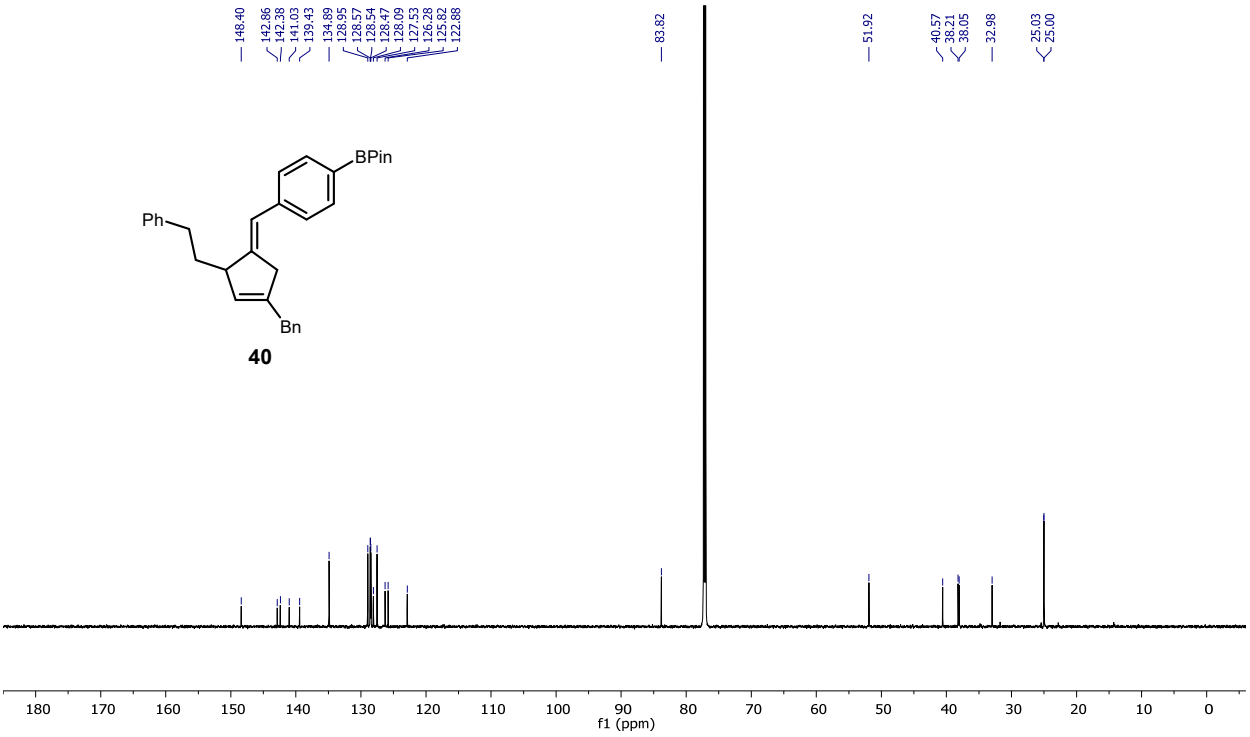

NTs
Ph
Me
38
1.06
2.01
0.98
0.99
10.23
1.00
1.04
1.02
2.05
2.13
3.11
1.26
3.13
1.24
f1 (ppm)

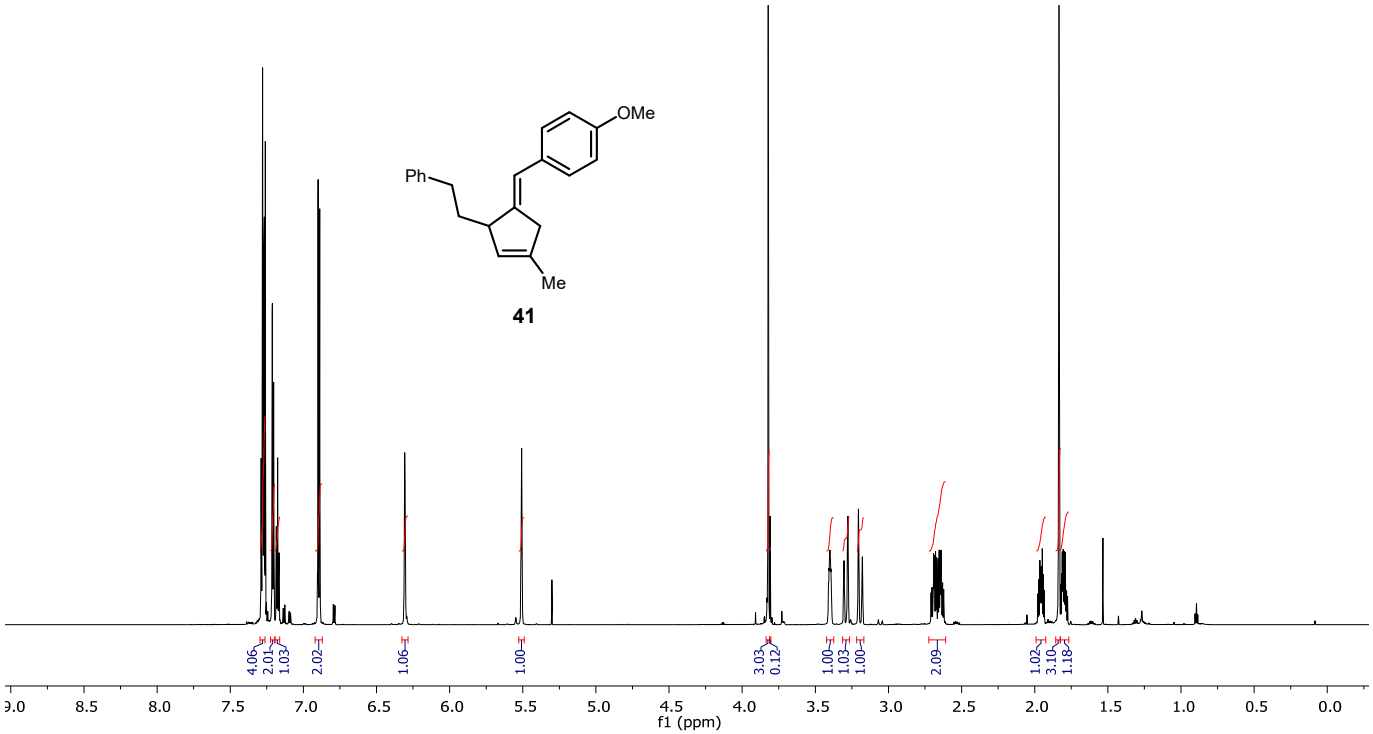

149.42
144.99
142.82
138.81
135.35
134.73
130.79
129.99
128.54
128.47
127.35
126.89
125.83
125.02
123.31
122.35
120.46
119.46
113.75
110.42
51.31
43.80
38.19
33.18
21.70
17.05
NTs
Ph
Me
38
f1 (ppm)

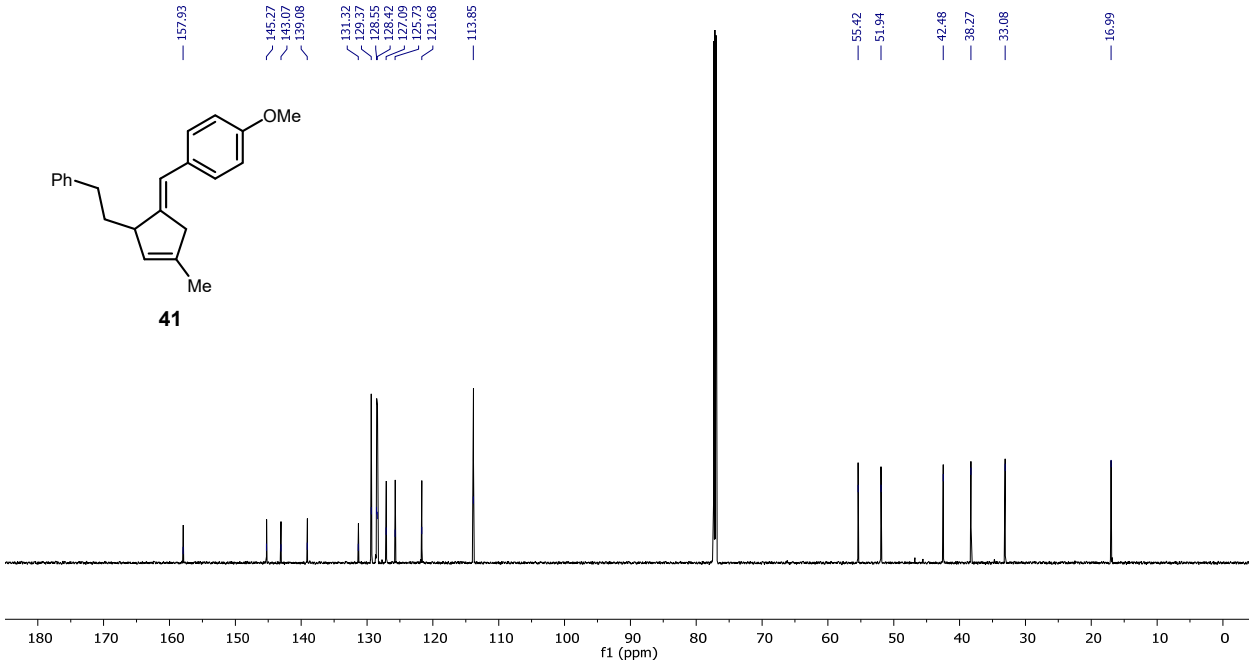

OMe
Ph
Bn
39
3.74
8.26
1.97
0.07
1.00
0.98
3.13
2.01
1.13
2.09
2.06
0.98
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

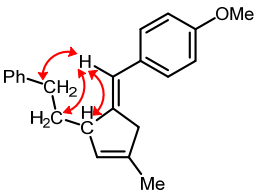

157.95
144.57
142.99
142.32
139.52
131.14
129.35
128.94
128.55
128.54
128.45
128.41
126.25
125.78
122.04
113.85
55.41
51.73
40.37
38.24
38.15
32.97
OMe
Ph
Bn
39
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


BPin
Ph
Bn
40
1.97
7.25
6.01
1.00
0.98
1.78
0.85
0.98
0.96
2.02
1.00
0.99
12.19
f1 (ppm)

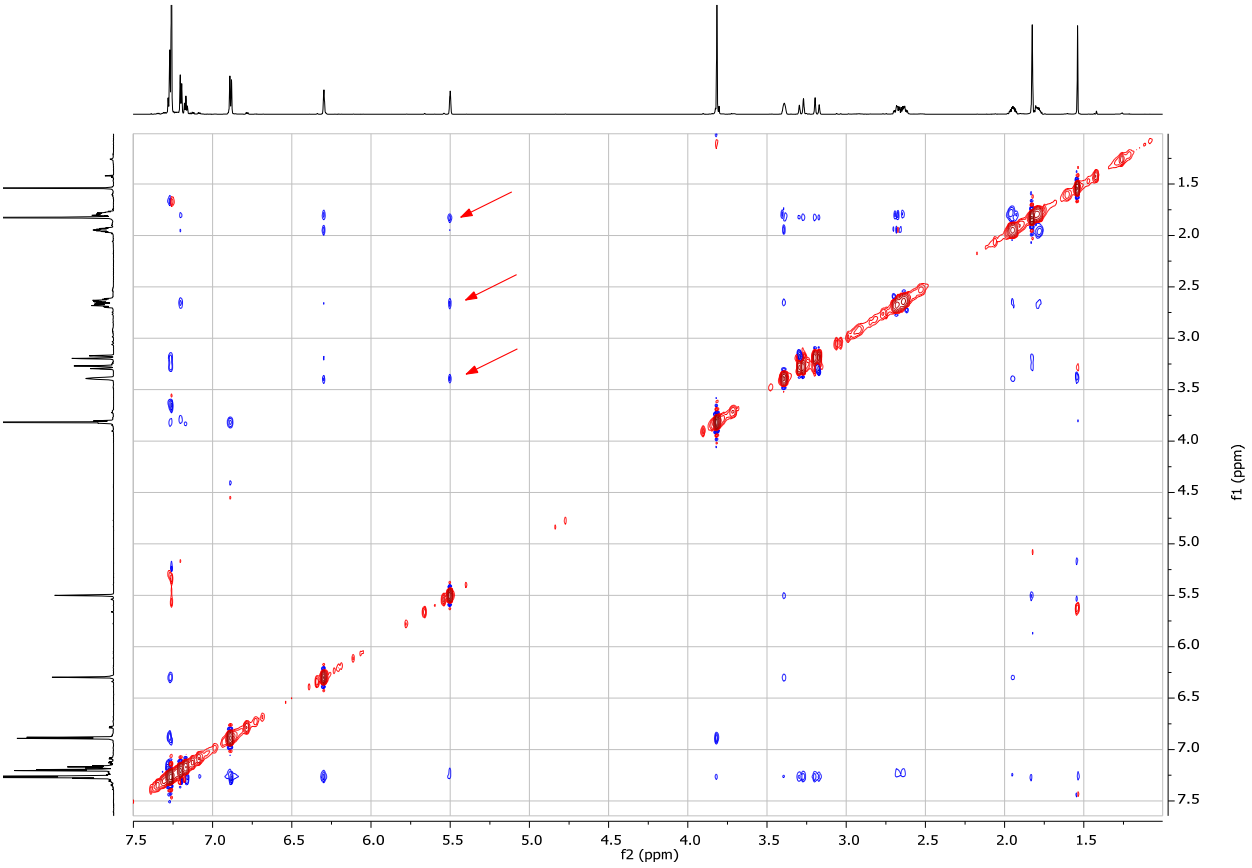

148.40
142.86
142.38
141.03
139.43
134.89
128.95
128.57
128.54
128.47
128.09
127.53
126.28
125.82
122.88
83.82
51.92
40.57
38.21
38.05
32.98
25.03
25.00
BPin
Ph
Bn
40
f1 (ppm)

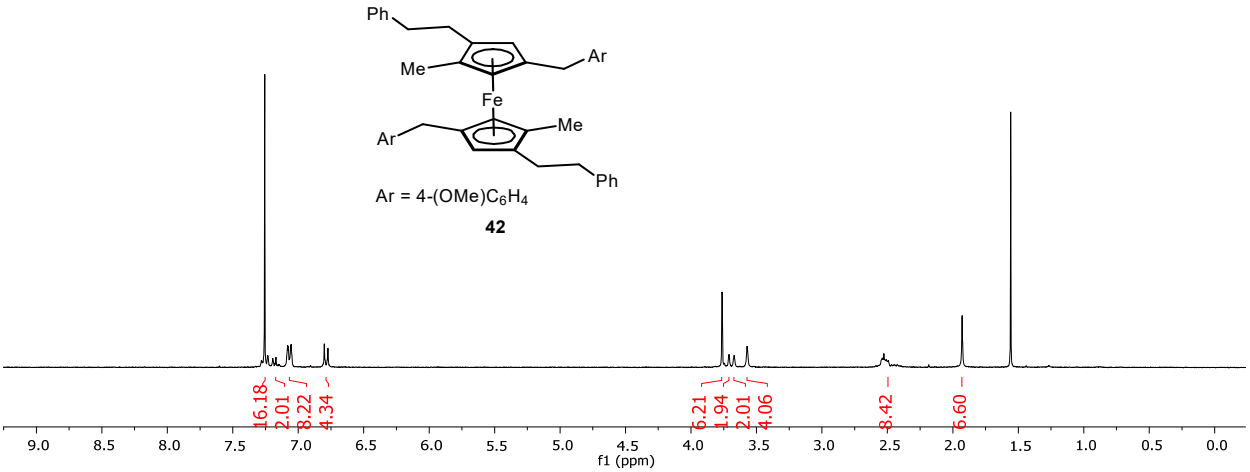

OMe
Ph
Me
41
4.06
2.01
1.03
2.02
1.06
1.00
3.03
0.12
1.00
1.03
1.00
2.09
1.02
3.10
1.18
f1 (ppm)

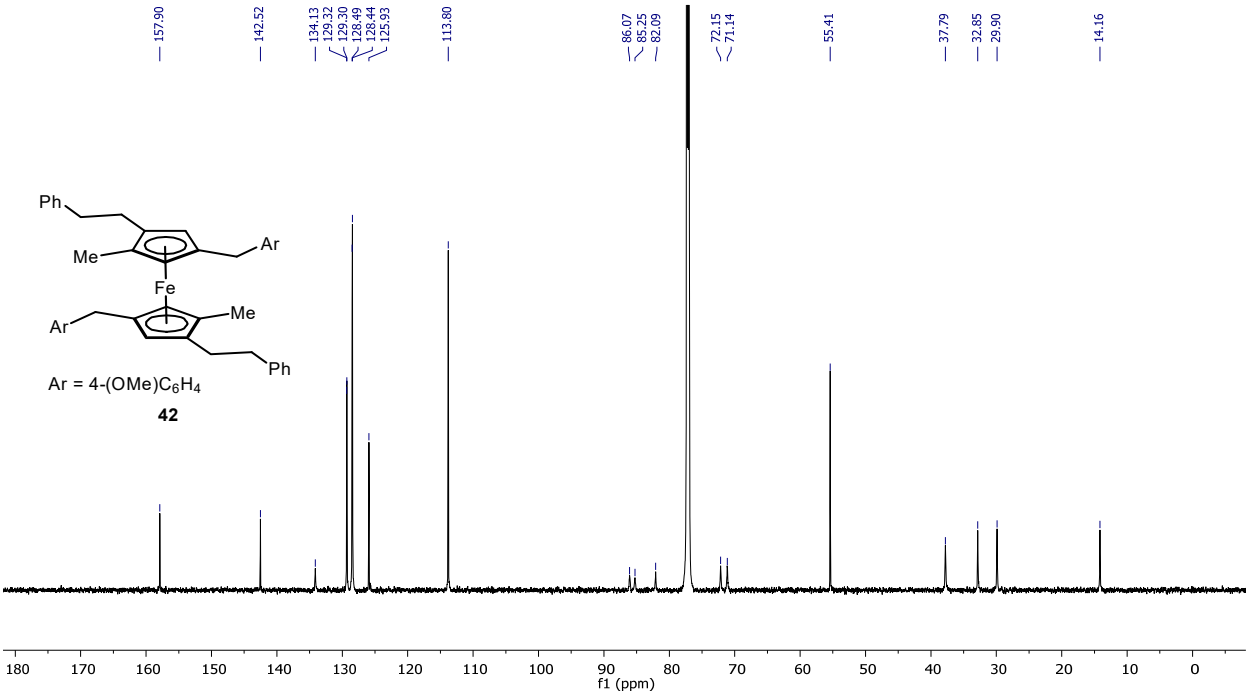

157.93
145.27
143.07
139.08
131.32
129.37
128.55
128.42
127.09
125.73
121.68
113.85
55.42
51.94
42.48
38.27
33.08
16.99
OMe
Ph
Me
41
f1 (ppm)

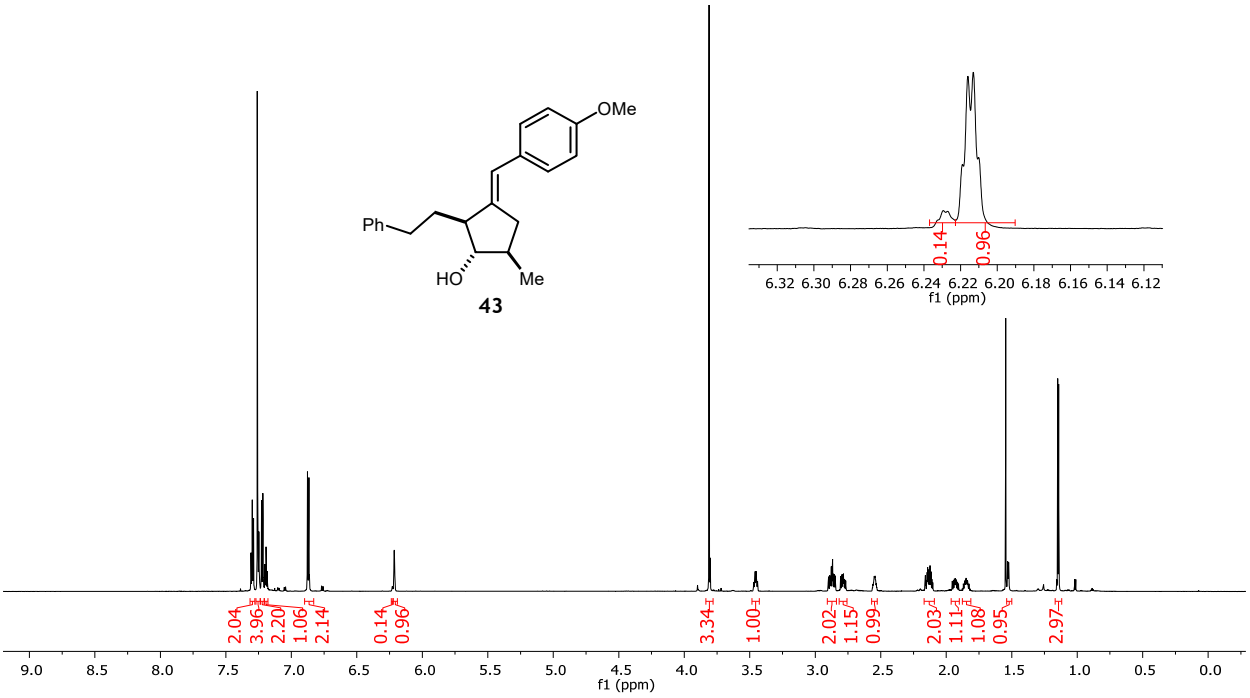

OMe
H
Ph
CH2
H2C
H
C
Me

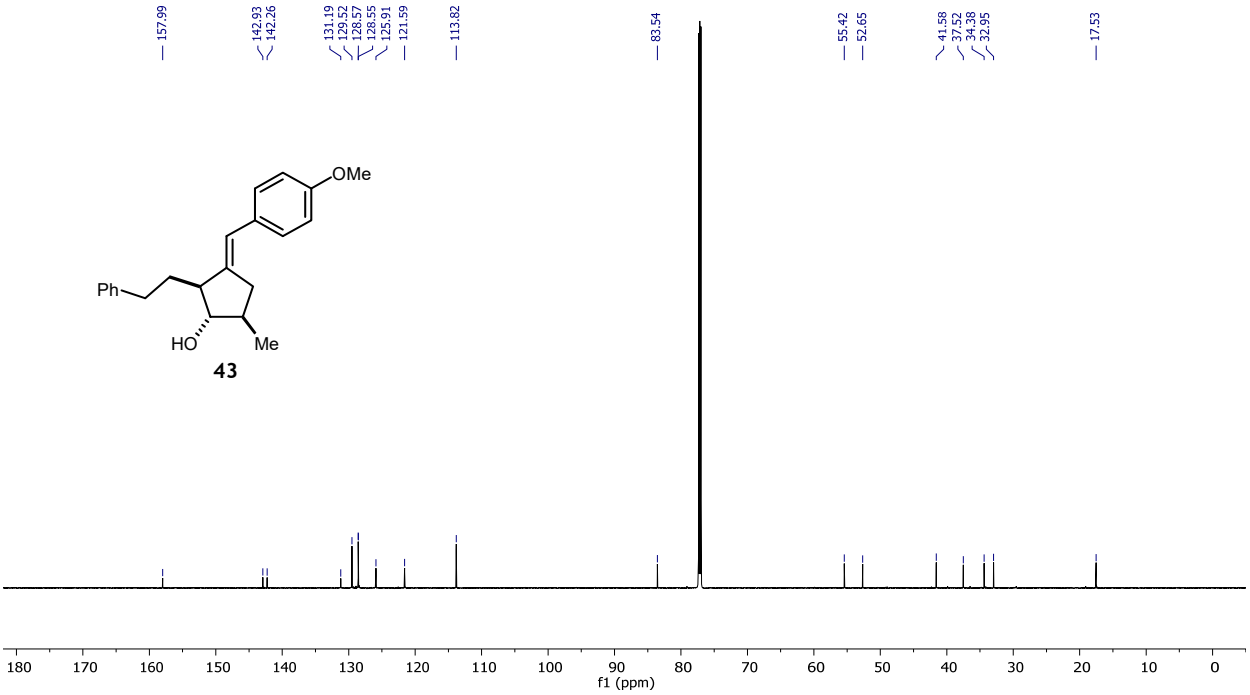
41-*E*

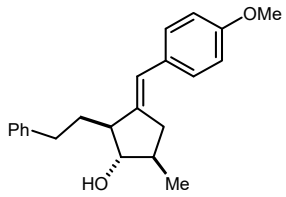

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)


Ph
Me
Ar
Fe
Ar
Me
Ph
Ar = 4-(OMe)C6H4
42
16.18
2.01
8.22
4.34
6.21
1.94
2.01
4.06
8.42
6.60
f1 (ppm)

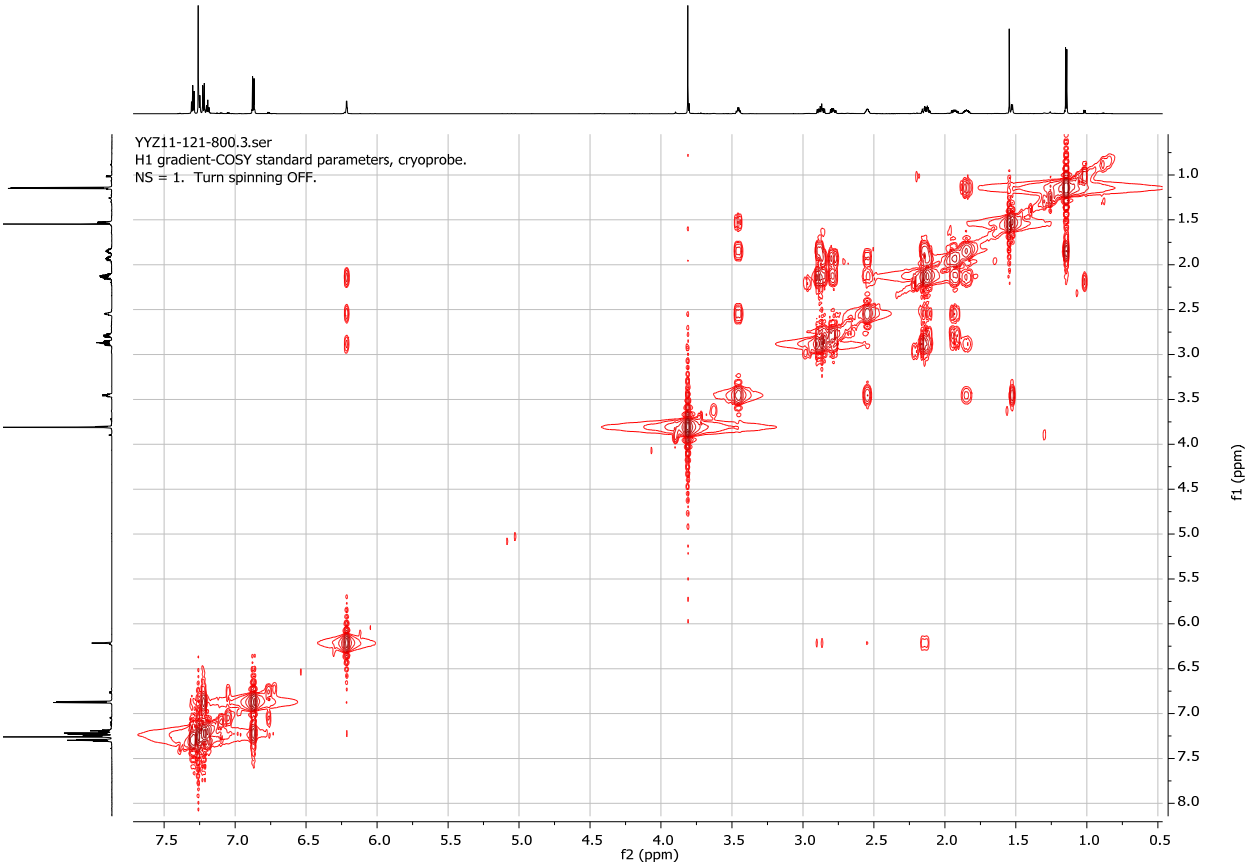

157.90
142.52
134.13
129.32
129.30
128.49
128.44
125.93
113.80
86.07
85.25
82.09
72.15
71.14
55.41
37.79
32.85
29.90
14.16
Ph
Me
Ar
Fe
Ar
Me
Ph
Ar = 4-(OMe)C6H4
42
f1 (ppm)

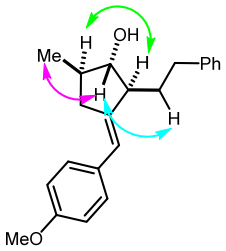

OMe
Ph
HO
Me
43
0.14
0.96
6.32 6.30 6.28 6.26 6.24 6.22 6.20 6.18 6.16 6.14 6.12
f1 (ppm)
2.04
3.96
2.20
1.06
2.14
0.14
0.96
3.34
1.00
2.02
1.15
0.99
2.03
1.11
1.08
0.95
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.99
142.93
142.26
131.19
129.52
128.57
128.55
125.91
121.59
113.82
83.54
55.42
52.65
41.58
37.52
34.38
32.95
17.53
OMe
Ph
HO
Me
43
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

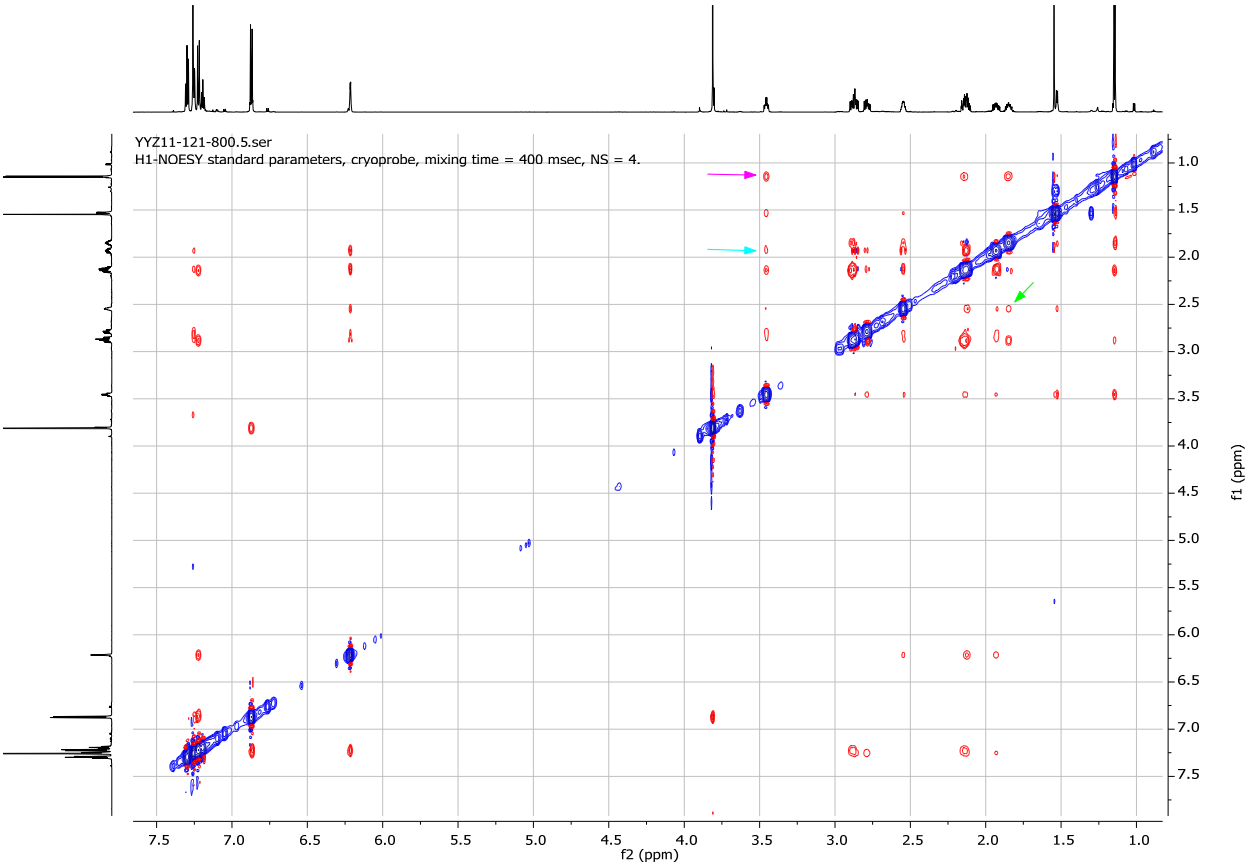

OMe
Ph
HO
Me

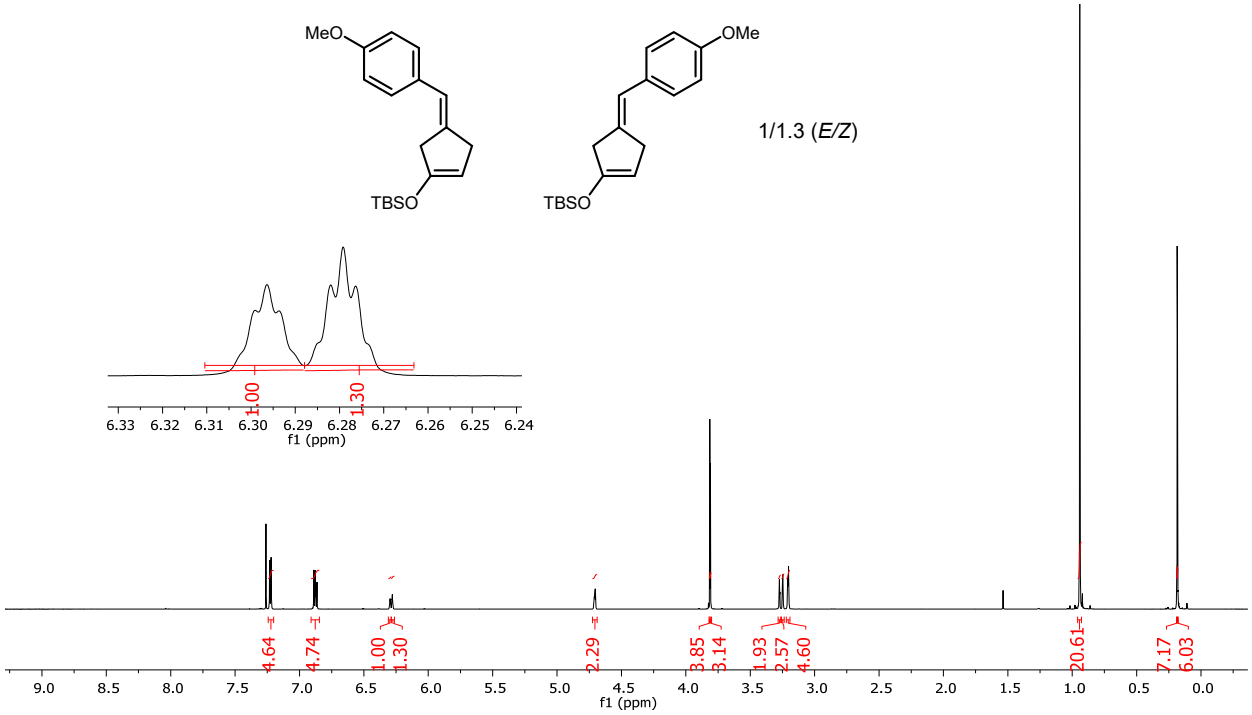
43

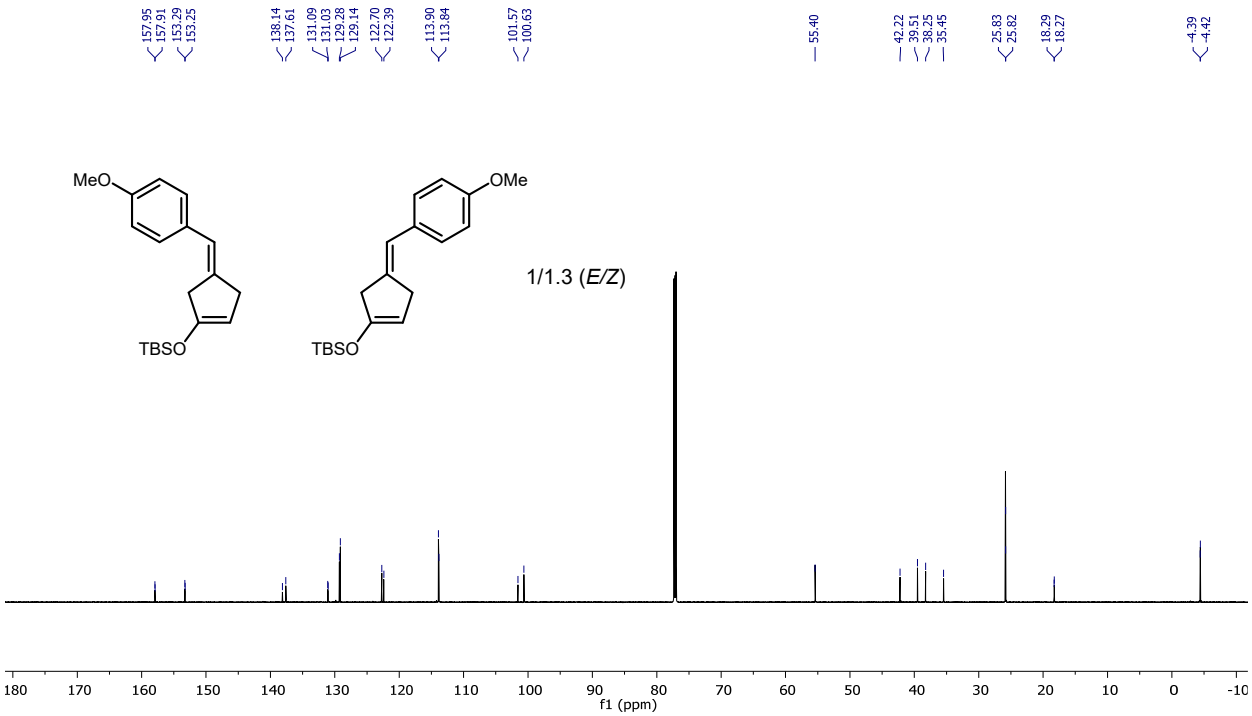

YYZ11-121-800.3.ser
H1 gradient-COSY standard parameters, cryoprobe.
NS = 1. Turn spinning OFF.
f2 (ppm)
f1 (ppm)

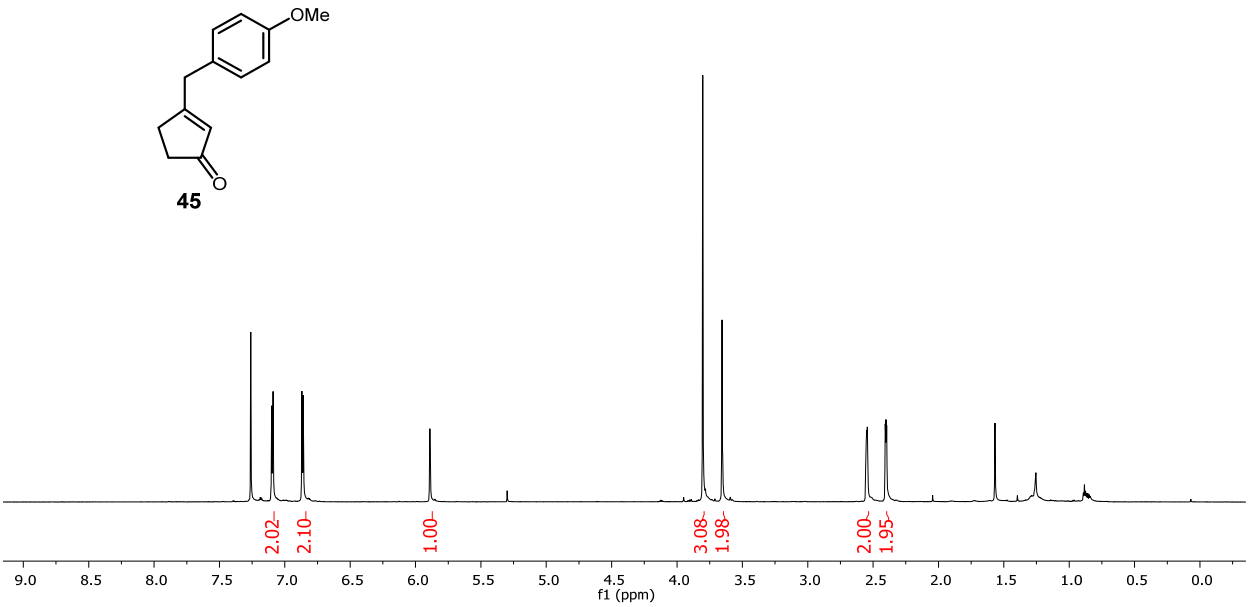

OH
H
Me
H
Ph
H
H
MeO

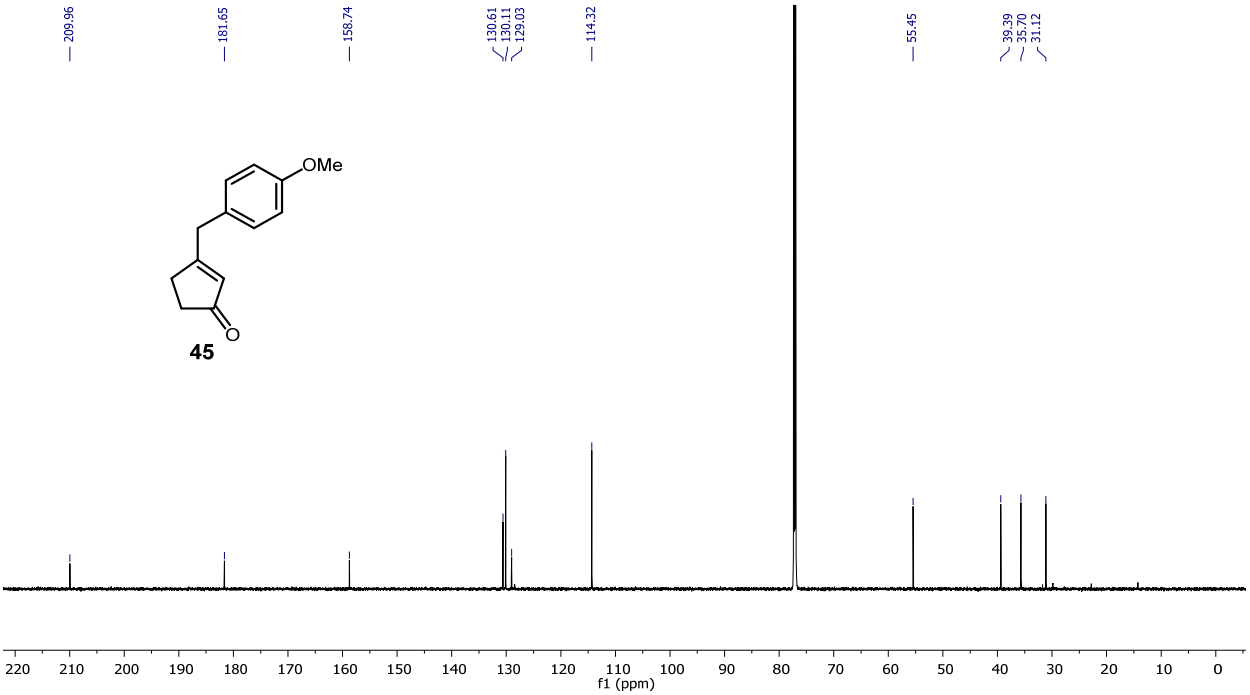
43

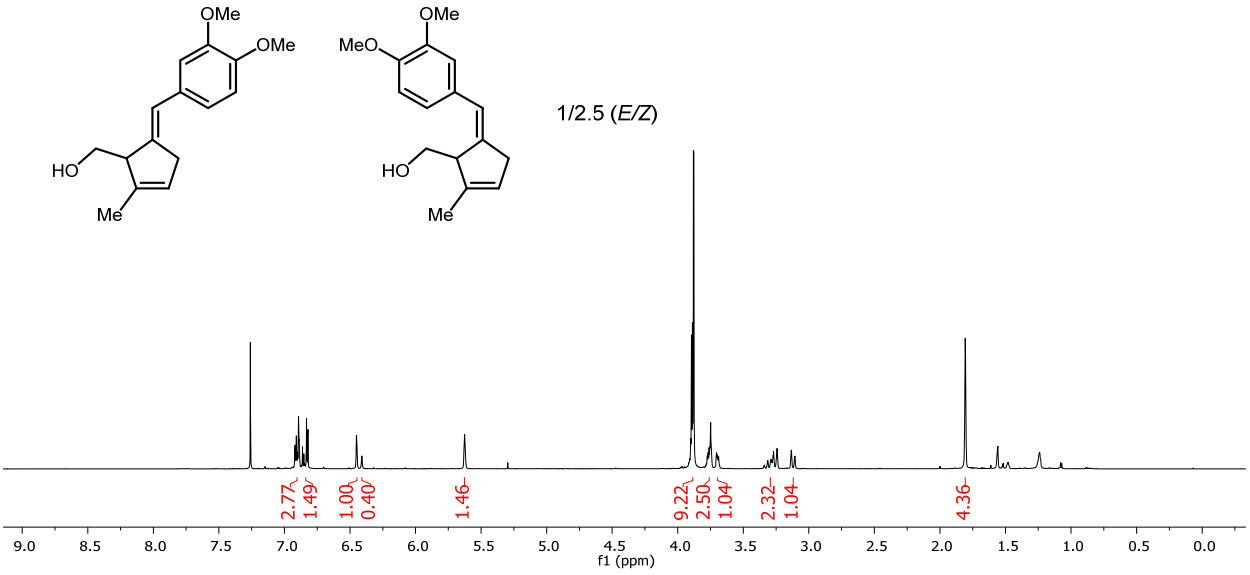

YYZ11-121-800.5.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
f2 (ppm)
f1 (ppm)

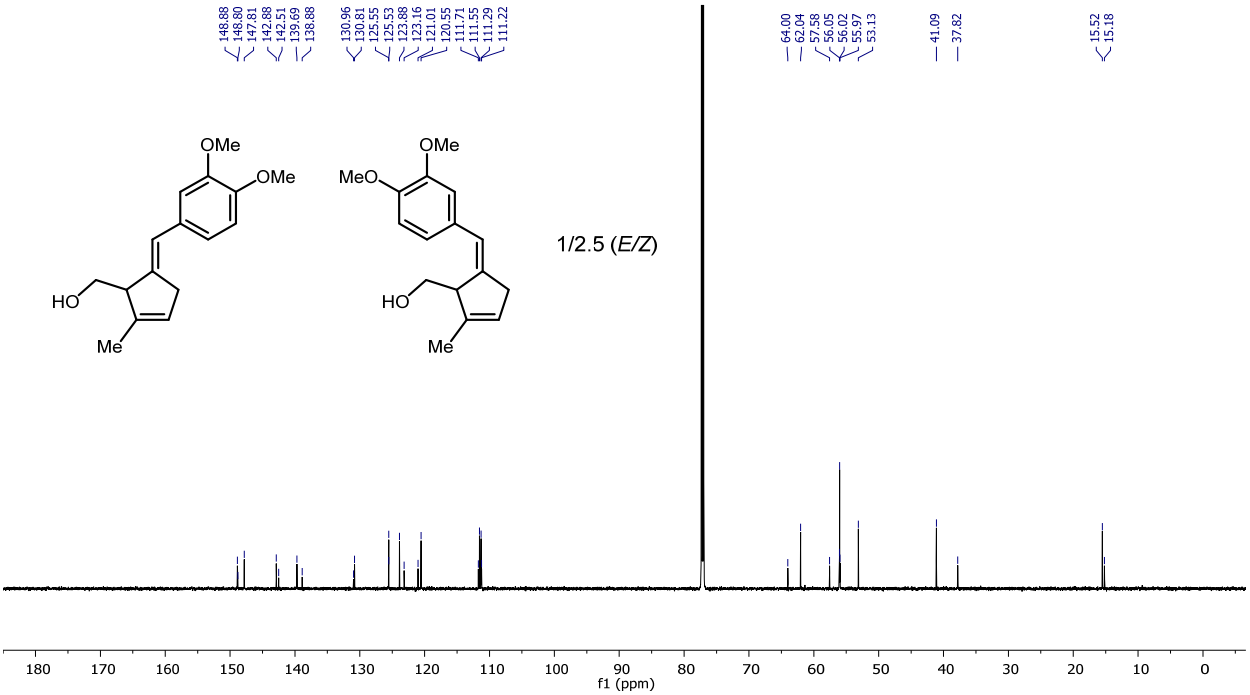

MeO
TBSO
OMe
TBSO
1/1.3 (E/Z)
1.00
1.30
6.33 6.32 6.31 6.30 6.29 6.28 6.27 6.26 6.25 6.24
f1 (ppm)
4.64
4.74
1.00
1.30
2.29
3.85
3.14
1.93
2.57
4.60
20.61
7.17
6.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

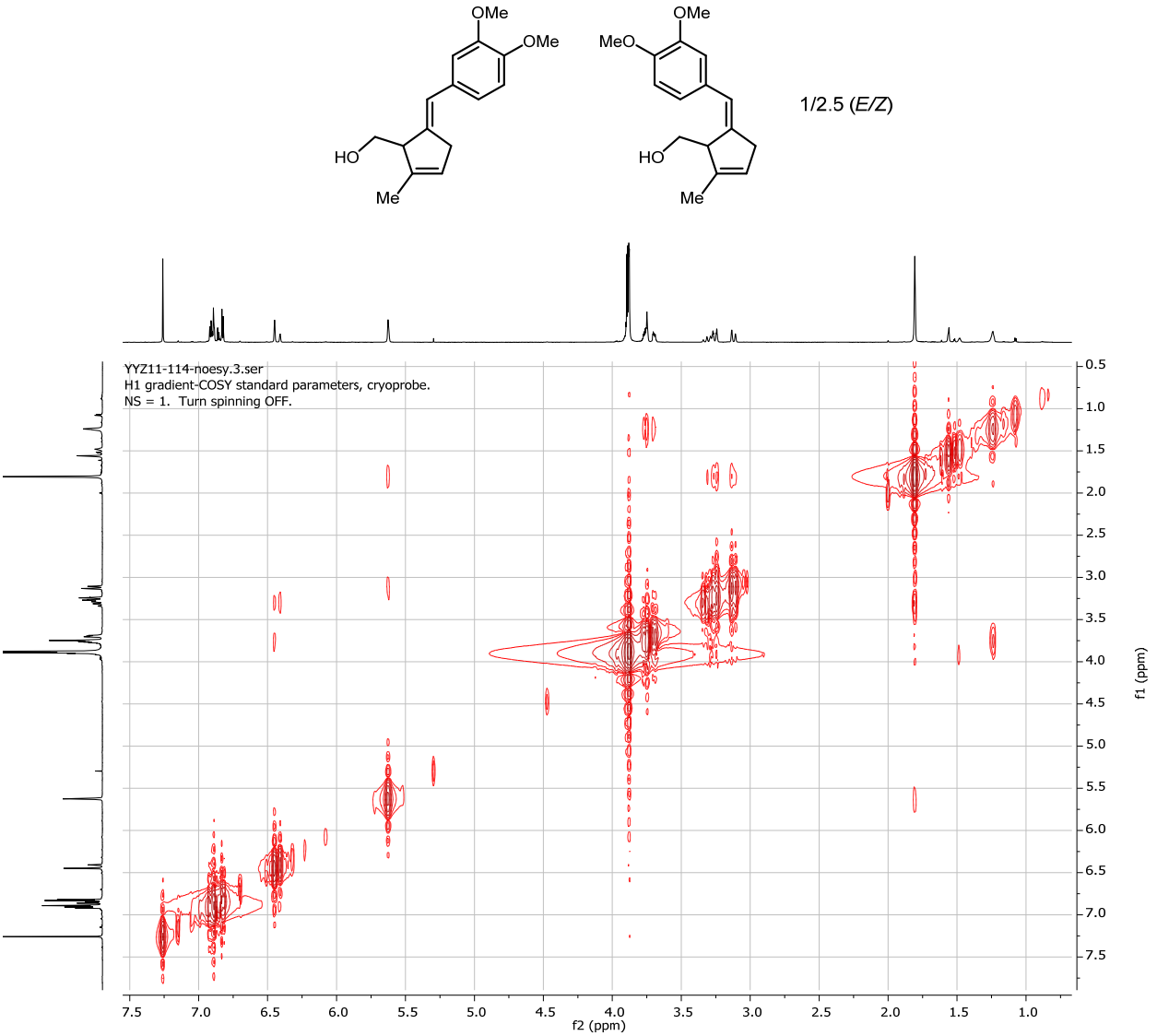

157.95
157.91
153.29
153.25
138.14
137.61
131.09
131.03
129.28
129.14
122.70
122.39
113.90
113.84
101.57
100.63
55.40
42.22
39.51
38.25
35.45
25.83
25.82
18.29
18.27
-4.39
-4.42
MeO
TBSO
OMe
TBSO
1/1.3 (E/Z)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

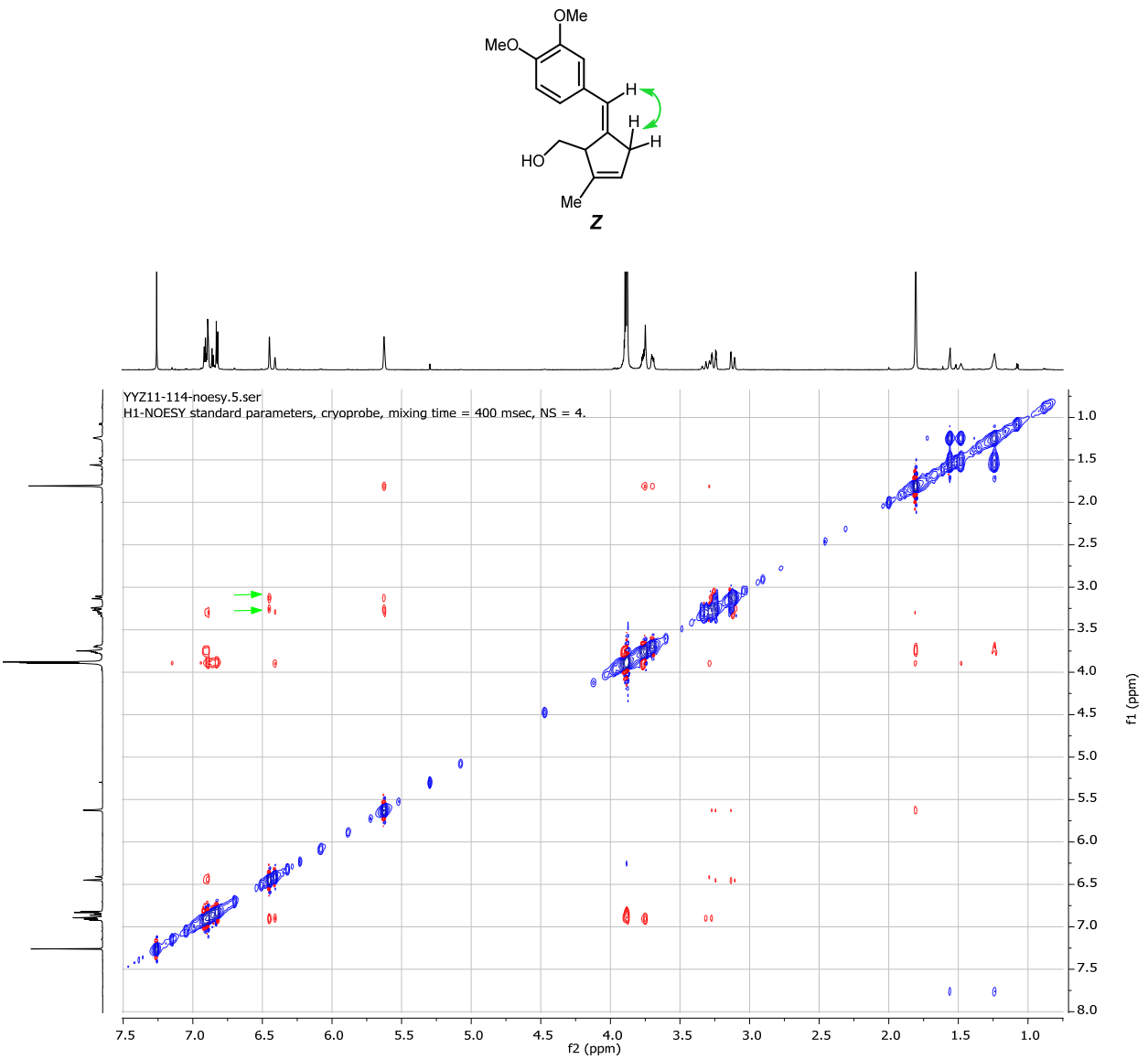

OMe
O
45
2.02
2.10
1.00
3.08
1.98
2.00
1.95
f1 (ppm)

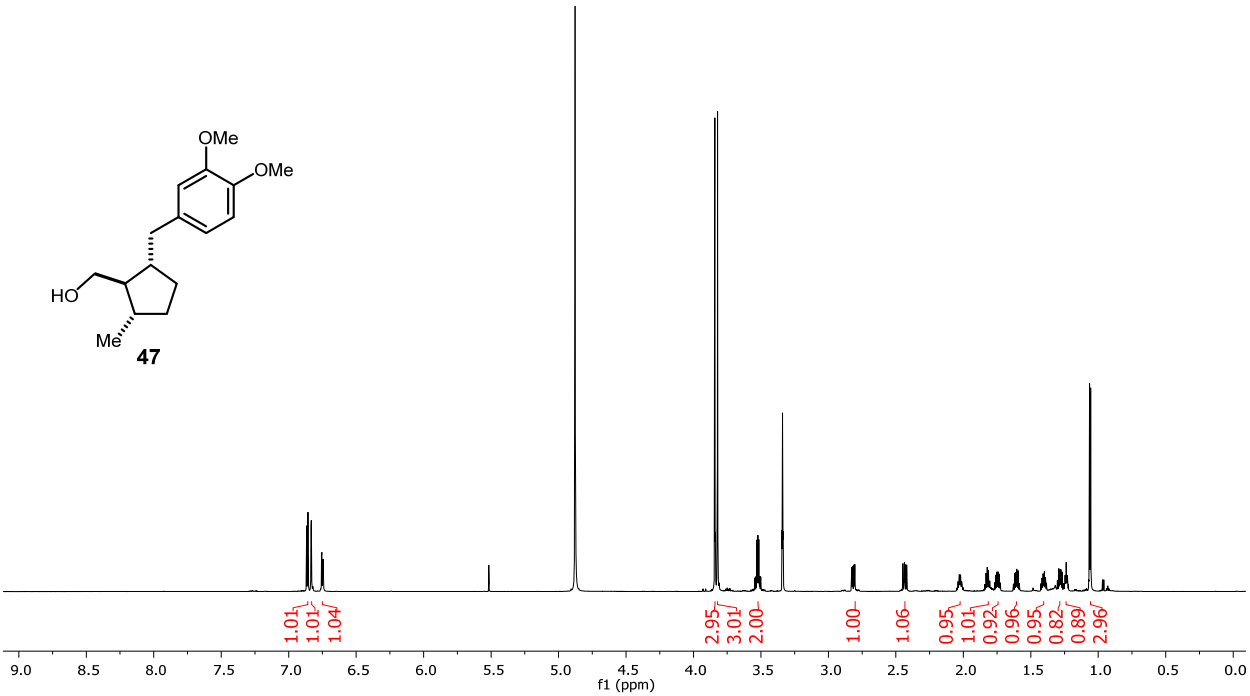

209.96
181.65
158.74
130.61
130.11
129.03
114.32
55.45
39.39
35.70
31.12
OMe
O
45
f1 (ppm)

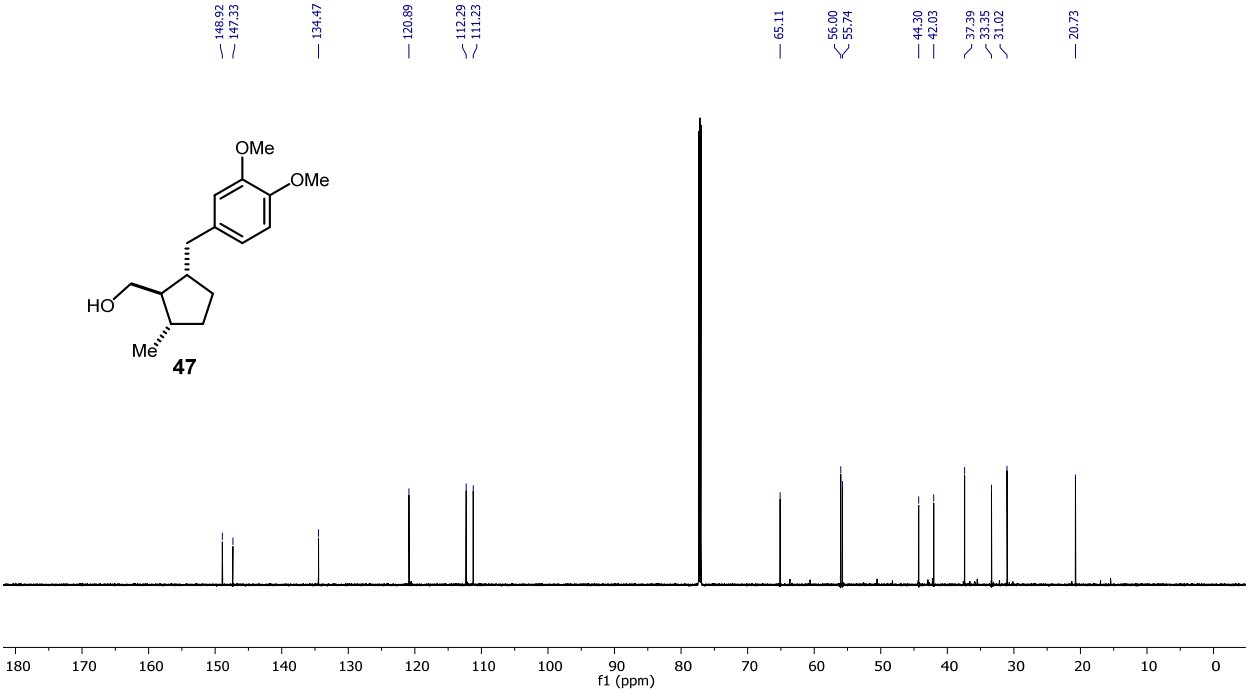

OMe
OMe
HO
Me
OMe
MeO
HO
Me
1/2.5 (E/Z)
2.77
1.49
1.00
0.40
1.46
9.22
2.50
1.04
2.32
1.04
4.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

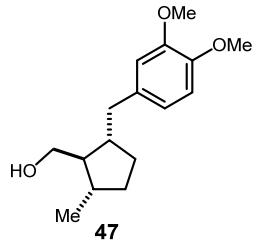

148.88
148.80
147.81
142.88
142.51
139.69
138.88
130.96
130.81
125.55
125.53
123.88
123.16
121.01
120.55
111.71
111.55
111.29
111.22
64.00
62.04
57.58
56.05
56.02
55.97
53.13
41.09
37.82
15.52
15.18
OMe
OMe
HO
Me
OMe
MeO
HO
Me
1/2.5 (E/Z)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
OMe
HO
Me
OMe
MeO
HO
Me
1/2.5 (E/Z)
YYZ11-114-noesy.3.ser
H1 gradient-COSY standard parameters, cryoprobe.
NS = 1. Turn spinning OFF.
f2 (ppm)
f1 (ppm)

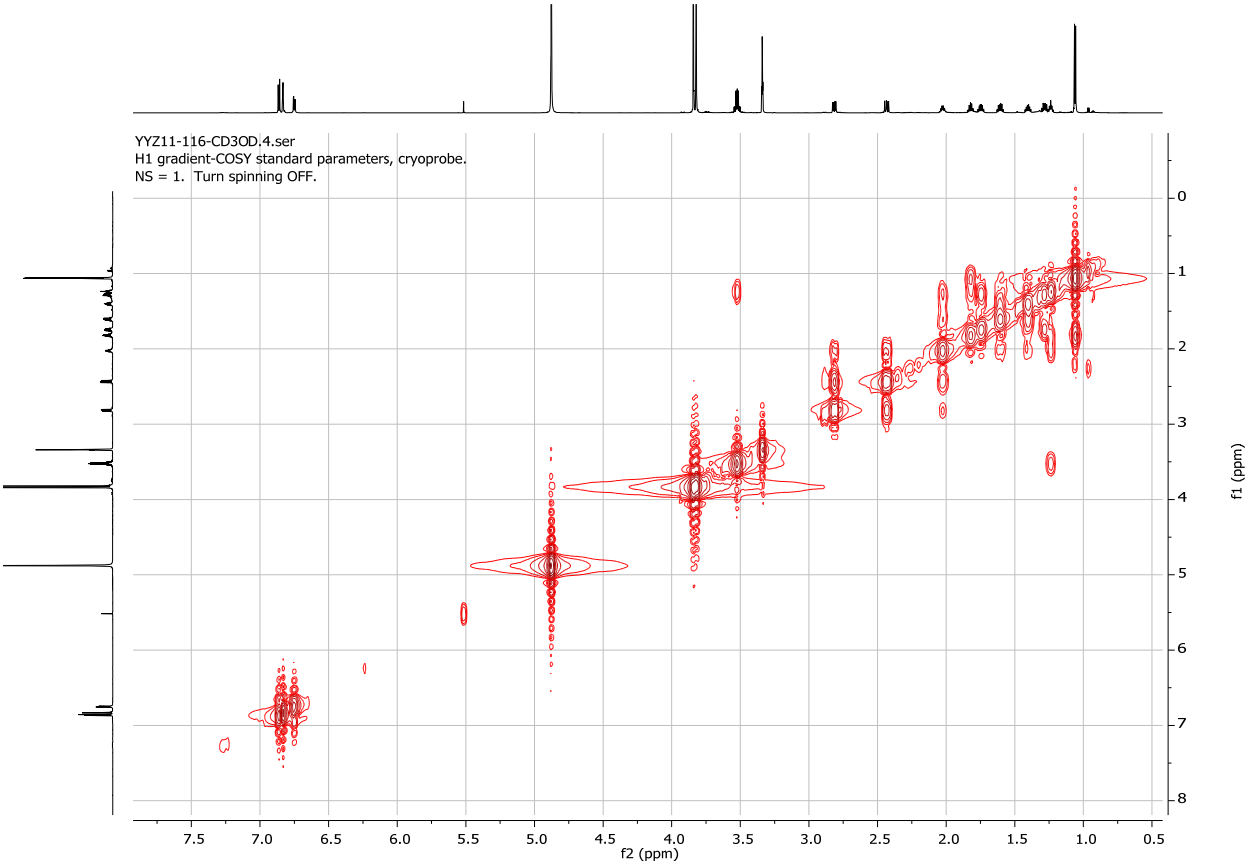

OMe
MeO
H
H
H
HO
Me
Z
YYZ11-114-noesy.5.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
f2 (ppm)
f1 (ppm)

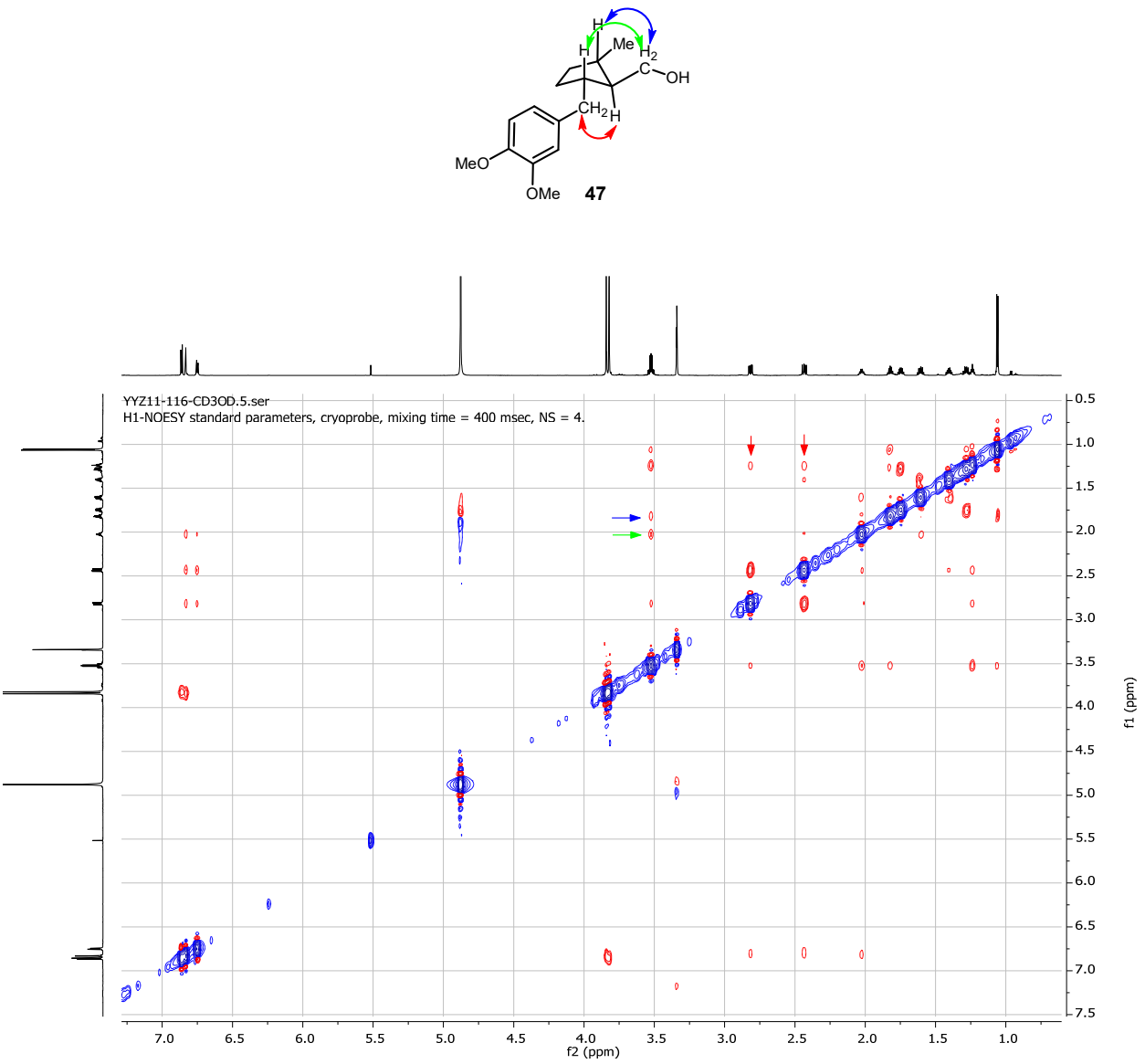

OMe
OMe
HO
Me
47
1.01
1.01
1.04
2.95
3.01
2.00
1.00
1.06
0.95
1.01
0.92
0.96
0.95
0.82
0.89
2.96
f1 (ppm)

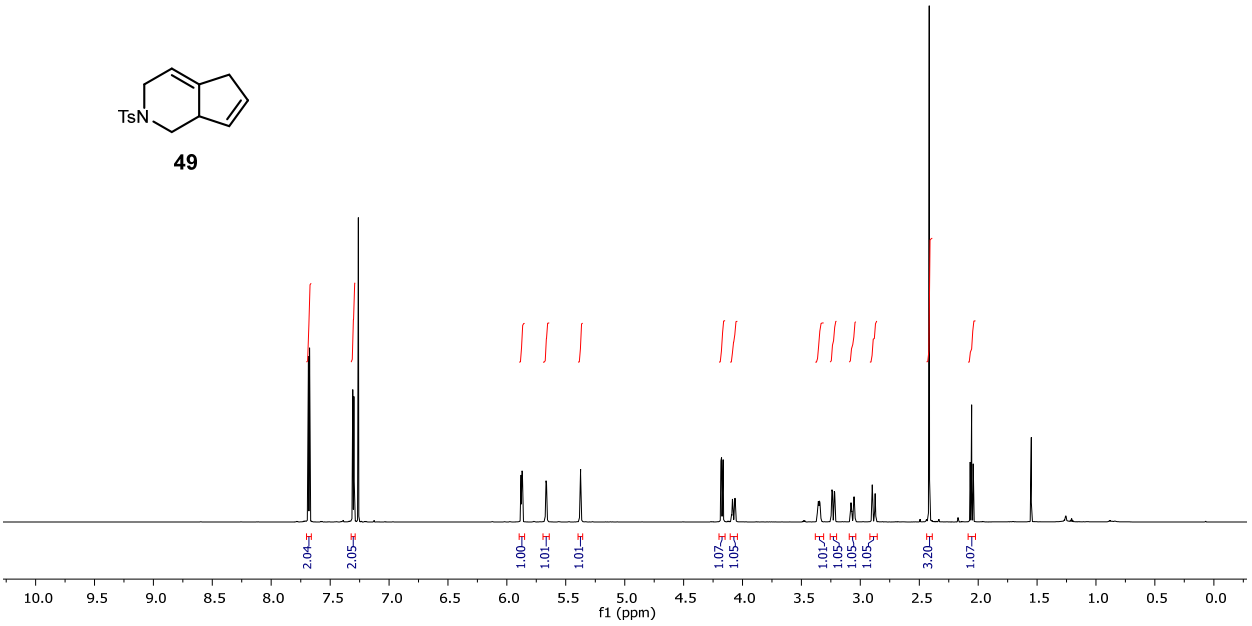

148.92
147.33
134.47
120.89
112.29
111.23
65.11
56.00
55.74
44.30
42.03
37.39
33.35
31.02
20.73
OMe
OMe
HO
Me
47
f1 (ppm)

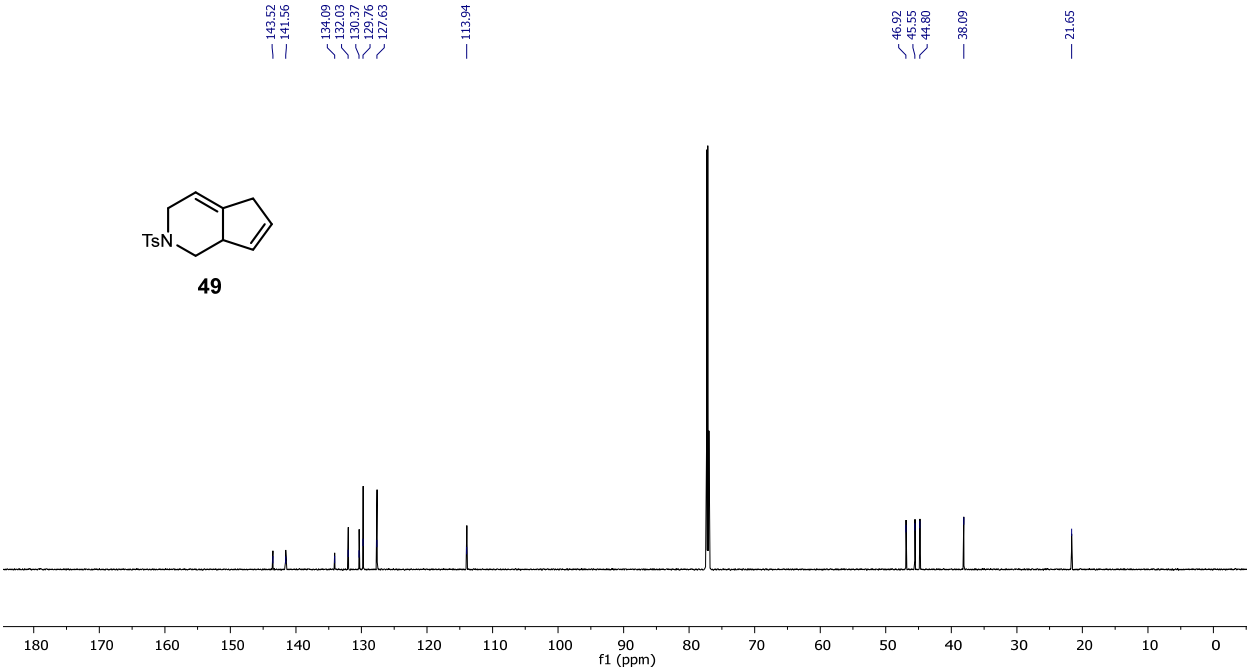

OMe
OMe
HO
Me

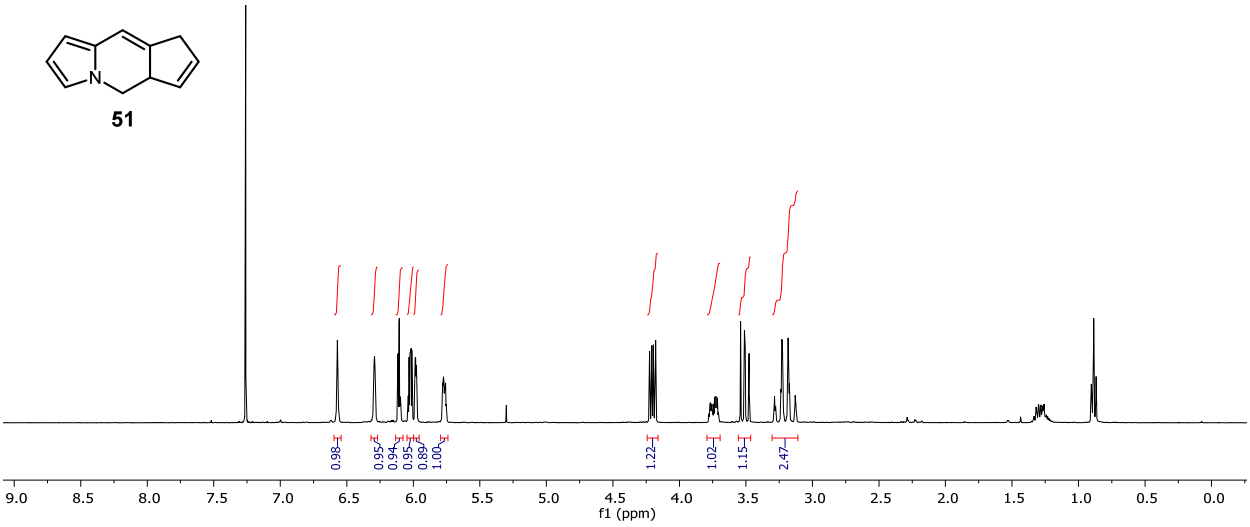
47

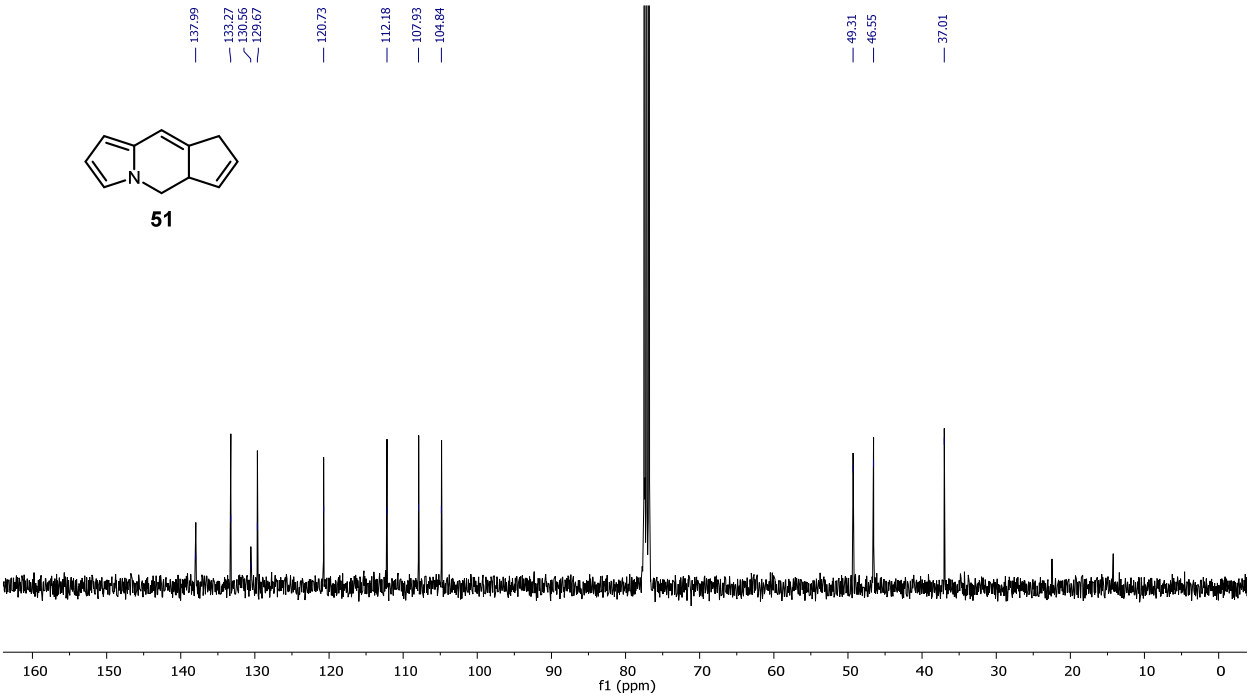

YYZ11-116-CD3OD.4.ser
H1 gradient-COSY standard parameters, cryoprobe.
NS = 1. Turn spinning OFF.
f2 (ppm)
f1 (ppm)

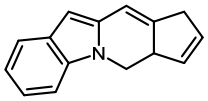

H
H
Me
H2
C
OH
CH2H
MeO
OMe
47
YYZ11-116-CD3OD.5.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
f2 (ppm)
f1 (ppm)


TsN
49
2.04
2.05
1.00
1.01
1.01
1.07
1.05
1.01
1.05
1.05
1.05
3.20
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

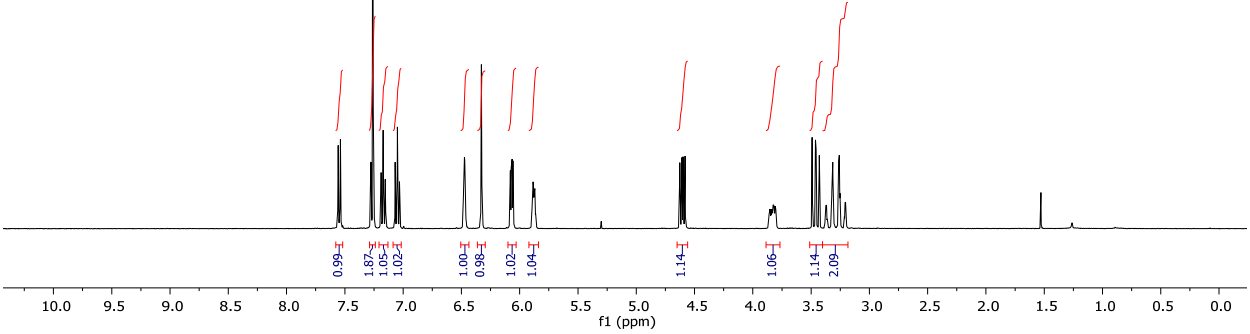

143.52
141.56
134.09
132.03
130.37
129.76
127.63
113.94
46.92
45.55
44.80
38.09
21.65
TsN
49
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

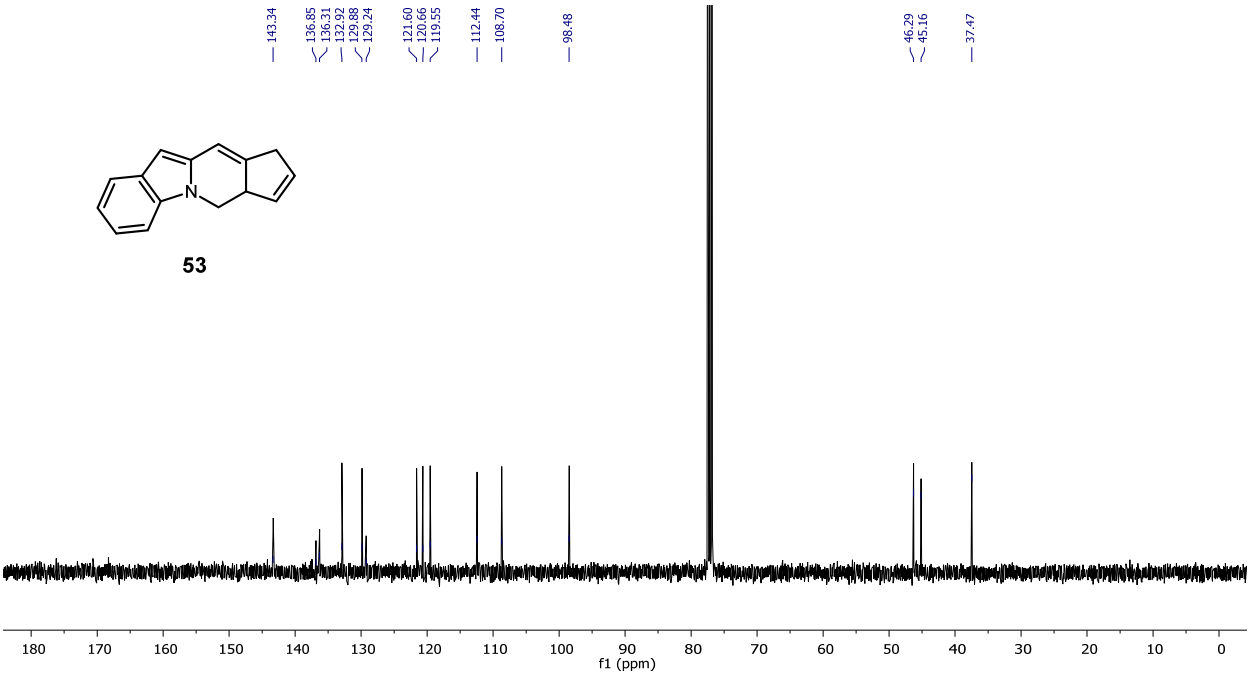

51
0.98
0.95
0.94
0.95
0.89
1.00
1.22
1.02
1.15
2.47
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.99
133.27
130.56
129.67
120.73
112.18
107.93
104.84
49.31
46.55
37.01
51
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

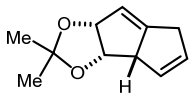


53


0.99
1.87
1.05
1.02
1.00
0.98
1.02
1.04
1.14
1.06
1.14
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.34
136.85
136.31
132.92
129.88
129.24
121.60
120.66
119.55
112.44
108.70
98.48
46.29
45.16
37.47
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

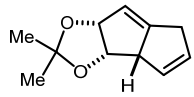
53


Me
O
Me
O
H

55

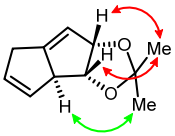
0.95
0.02
1.01
0.96
0.05
0.05
1.04
0.06
1.00
0.98
0.05
2.02
3.24
3.10
0.14
0.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.38
133.05
132.55
117.48
113.76
87.23
84.72
62.19
32.93
27.79
25.76

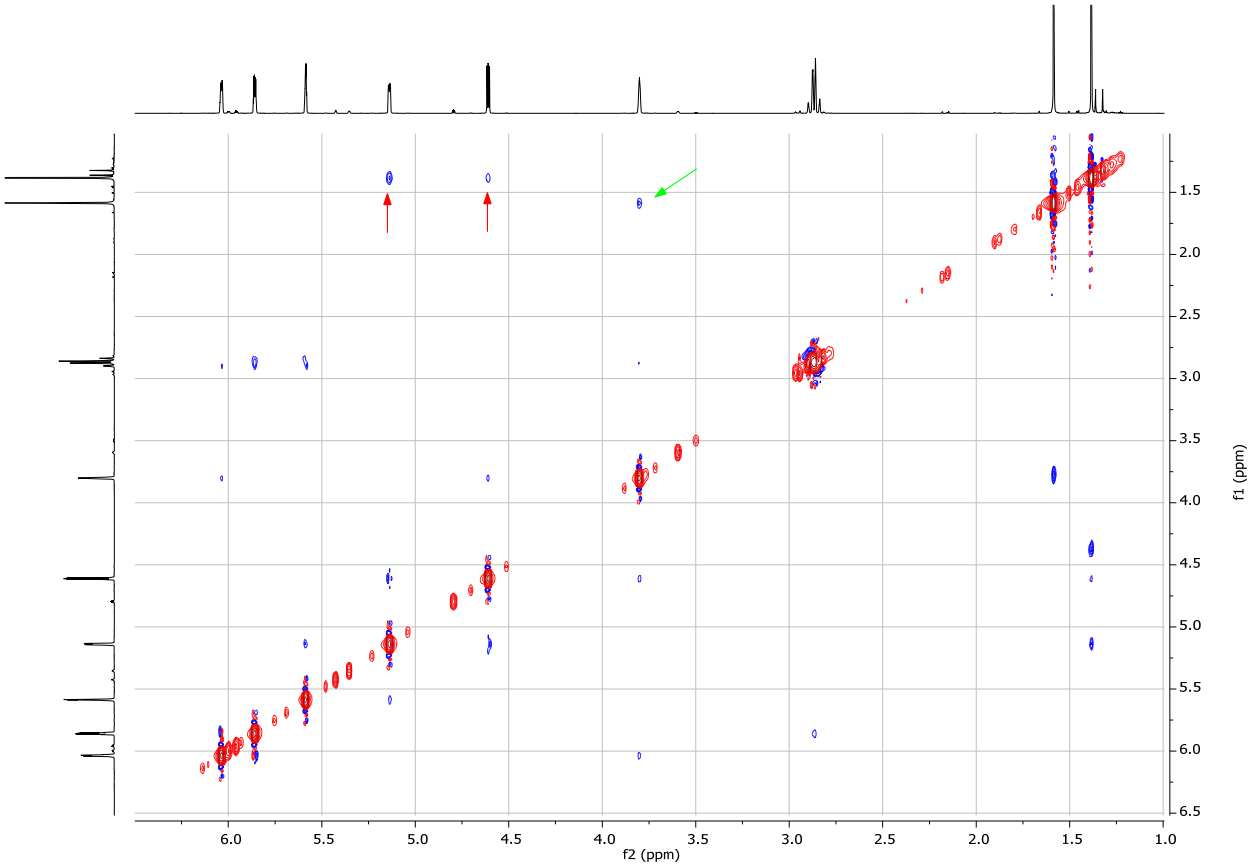

Me
O
Me
O
H

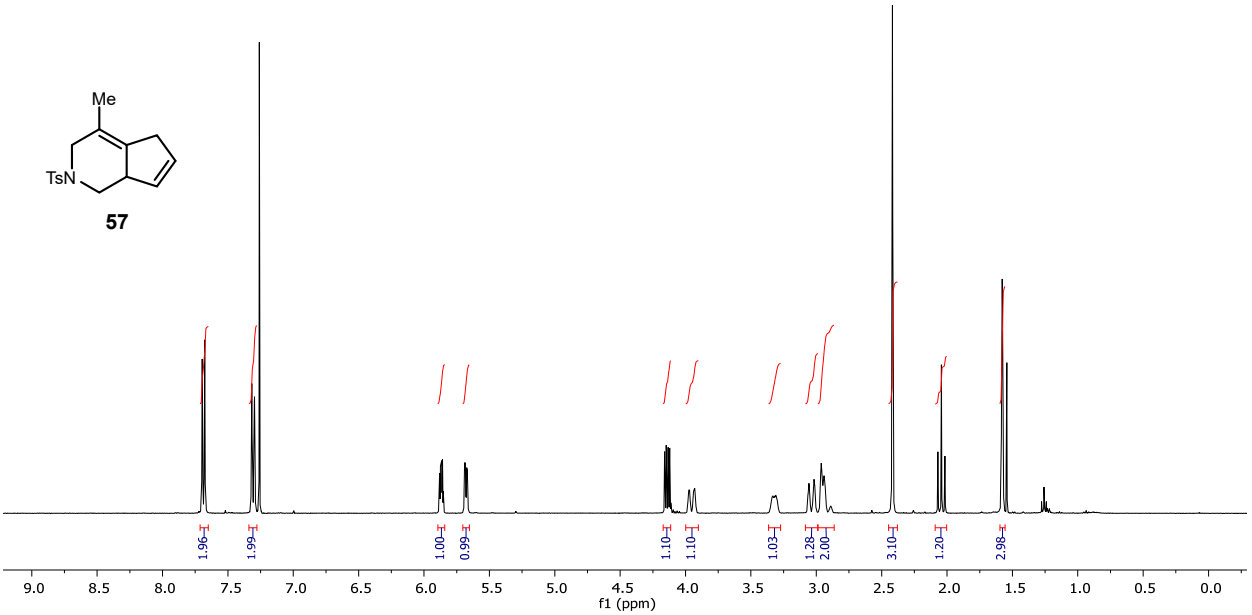
55

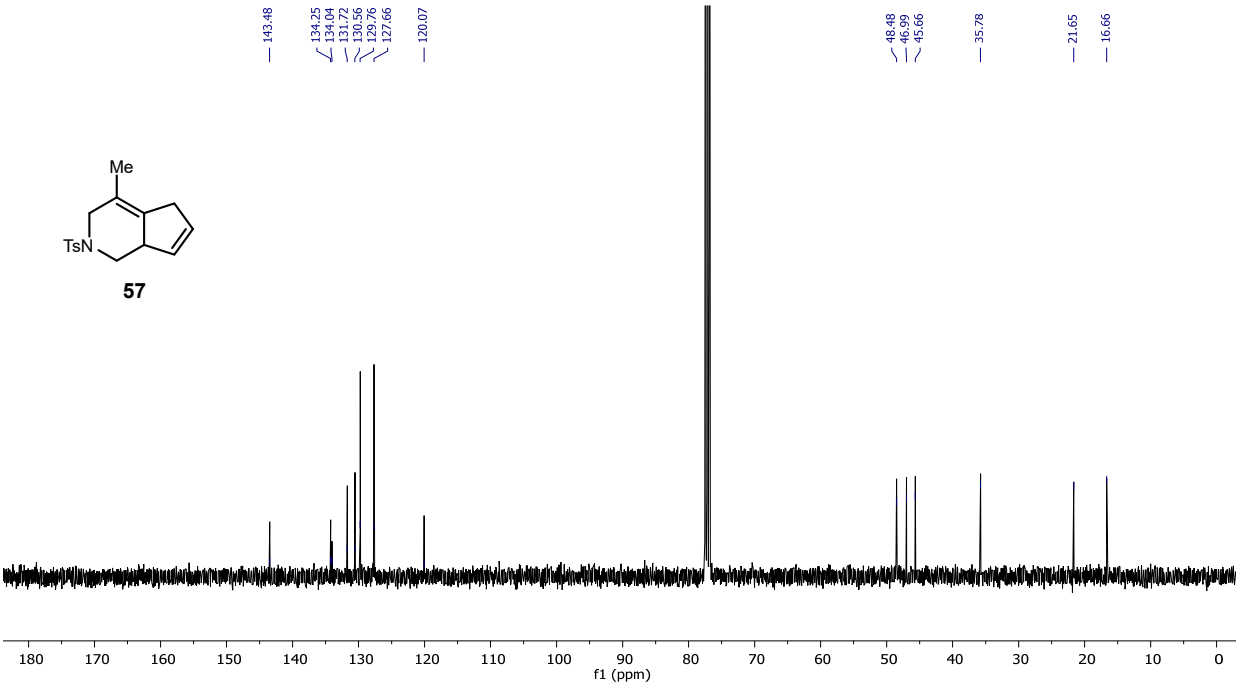
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

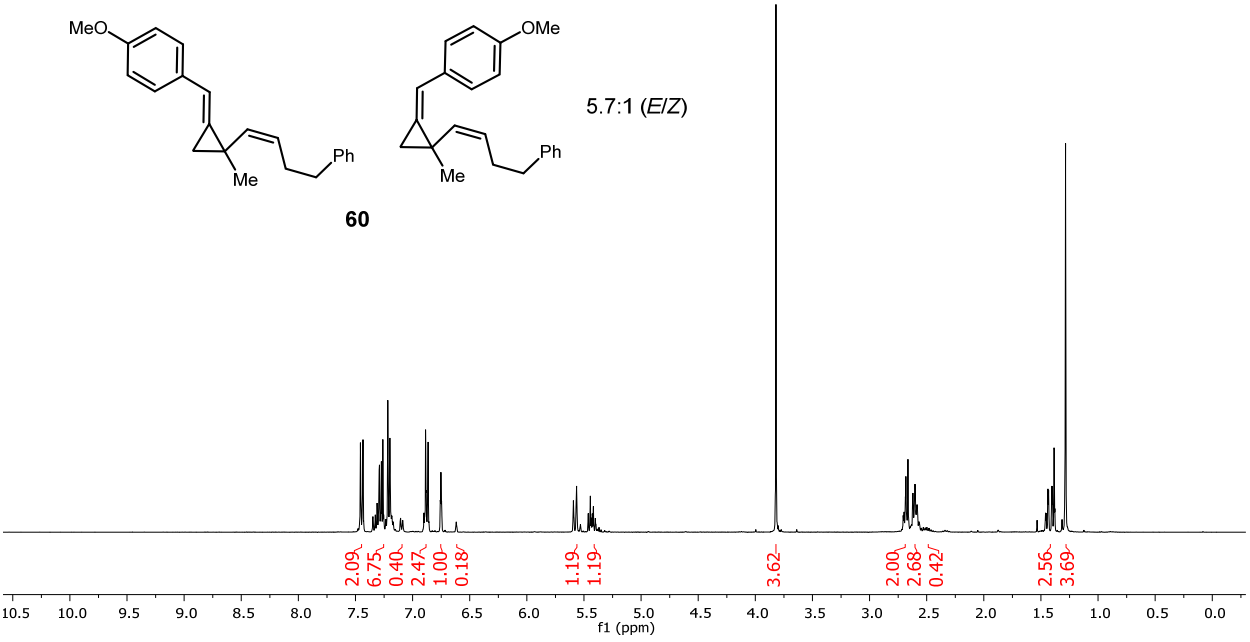

H
H
O
Me
O
Me
H

55

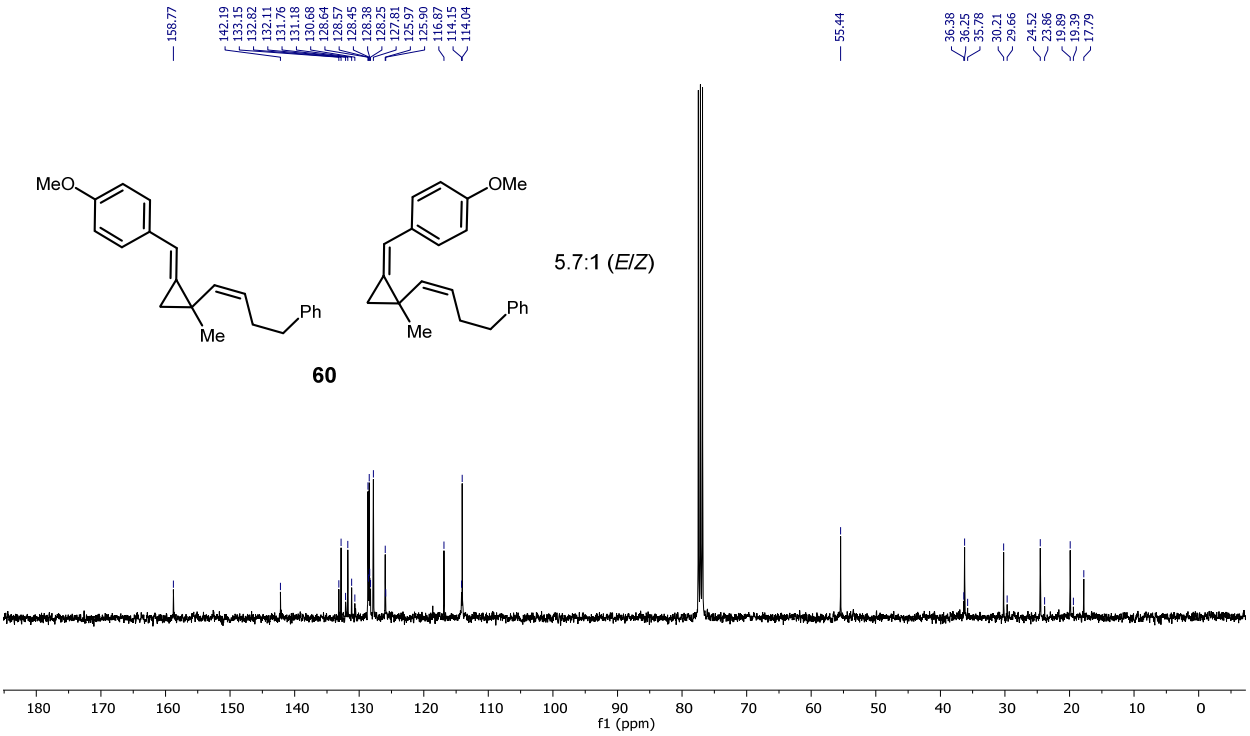

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)


Me
TsN
57
1.96
1.99
1.00
0.99
1.10
1.10
1.03
1.28
2.00
3.10
1.20
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

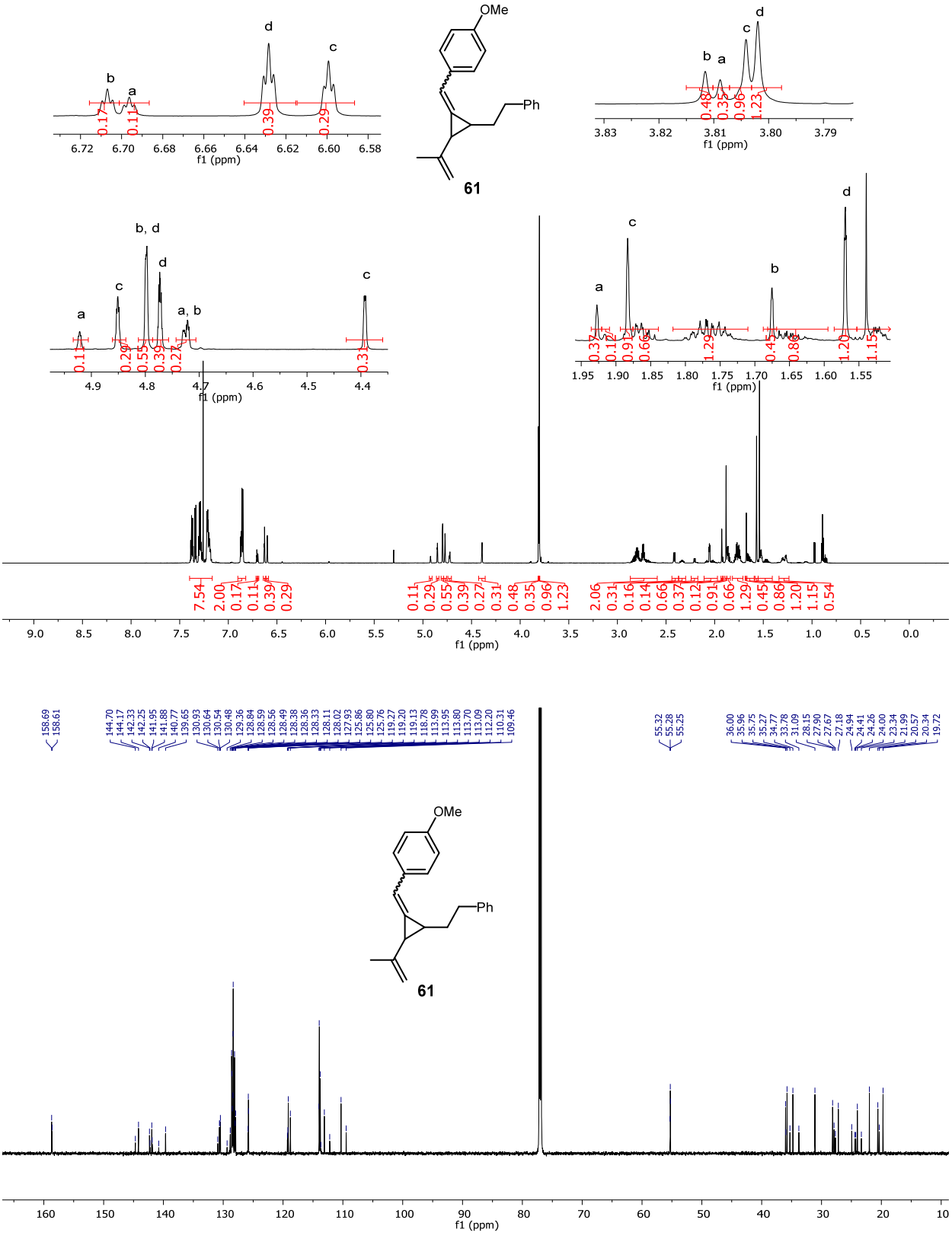

143.48
134.25
134.04
131.72
130.56
129.76
127.66
120.07
48.48
46.99
45.66
35.78
21.65
16.66
Me
TsN
57
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
Ph
Me
OMe
Ph
Me
5.7:1 (E/Z)
2.09
6.75
0.40
2.47
1.00
0.18
1.19
1.19
3.62
2.00
2.68
0.42
2.56
3.69
f1 (ppm)

60


158.77
142.19
133.15
132.82
132.11
131.76
131.18
130.68
128.64
128.57
128.45
128.38
128.25
127.81
125.97
125.90
116.87
114.15
114.04
55.44
36.38
36.25
35.78
30.21
29.66
24.52
23.86
19.89
19.39
17.79
MeO
Ph
Me
OMe
Ph
Me
5.7:1 (E/Z)
f1 (ppm)

60


OMe
Ph
61
f1 (ppm)

13. DFT Calculations

Computational Methods. Geometry optimizations were performed using the Gaussian 09 (*46*) software package. All geometries were fully optimized at the M06-L/6-31G(d,p) (*47*) level of DFT. Stationary points were verified by frequency analysis. The catalyst was modeled with 2,6-Me_2Ph- substituents on the imines.

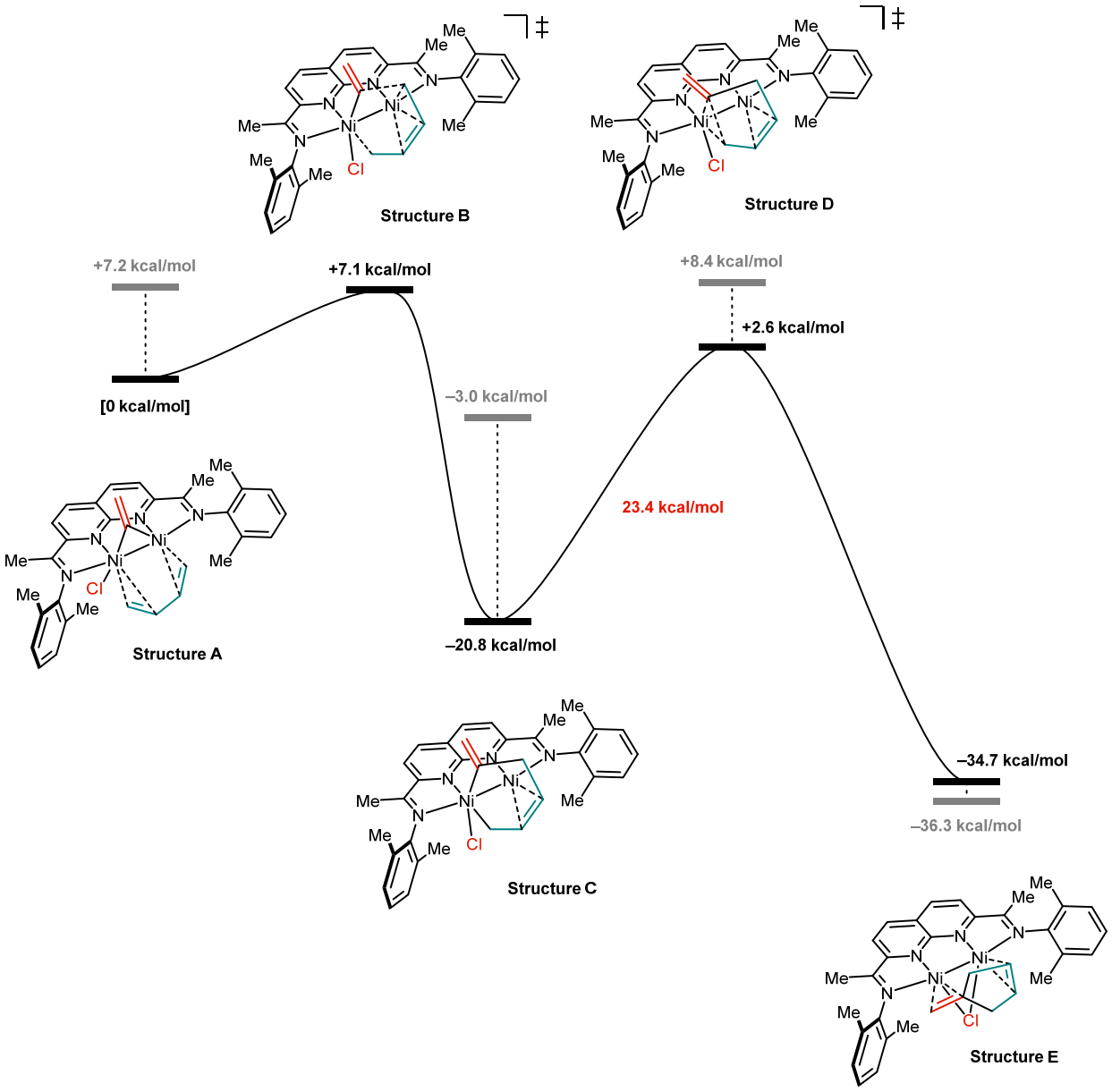


Figure S12. Calculated [4 + 1]-cycloaddition pathway. Uncorrected electronic energies are shown in kcal/mol and are relative to the energy of Structure A (S = 1/2). Black = doublet surface; gray = quartet surface.

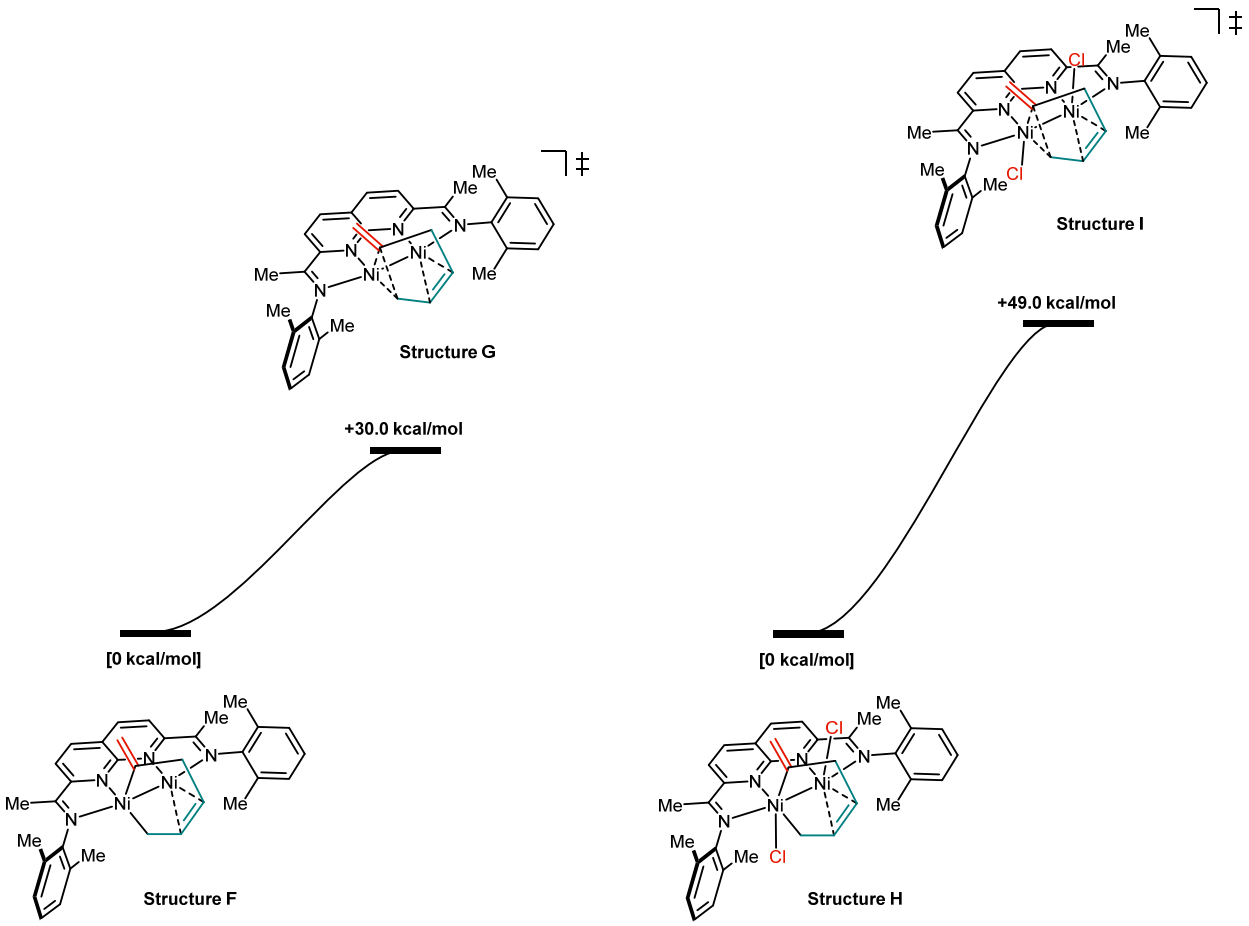
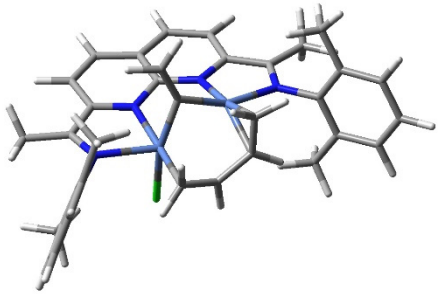


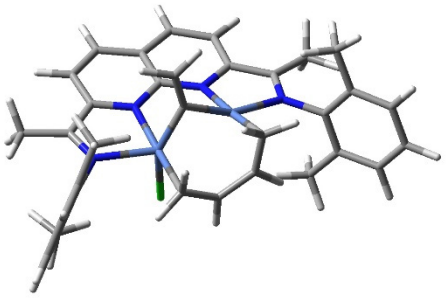
Figure S13. Dependence of the C–C reductive elimination barriers on the oxidation state of the [NDI]Ni_2 catalyst. The reductive elimination with one Cl bound to the catalyst is 23.4 kcal/mol (see Figure S12).



Structure A
Charge = 0; Multiplicity = 2
Imaginary Frequencies = 0
Electronic Energy = -5012.66162325
Electronic Energy + ZPE = -5012.040577
Free Energy (298 K) = -5012.109562

C	2.37014300	3.66820100	-0.30011500
C	1.21180200	4.42217800	-0.20735300
C	-0.04101200	3.79108400	-0.11086200
C	-0.05126200	2.36077000	-0.13256100
C	2.28767800	2.27454700	-0.24480100
H	-1.30644300	5.54073500	0.08594100
H	3.33612200	4.15126200	-0.40291000
H	1.25702100	5.50773900	-0.21784200
C	-1.28516200	4.45653600	0.03019000
C	-2.39876500	2.31387600	0.05332800
C	-2.43843200	3.71481600	0.13978200
H	-3.39608000	4.20246600	0.29720000
N	-1.20595700	1.64651400	-0.15081000
N	1.08635000	1.66194000	-0.11564200
C	3.42213100	1.37110900	-0.29913800
C	-3.51201300	1.44868700	0.17318400
C	4.80225400	1.93819700	-0.38472700
H	4.87002100	2.65246100	-1.21124400
H	5.06392100	2.47987900	0.53061300
H	5.54463300	1.15473900	-0.54059200
C	-4.88386900	1.97039700	0.45536100
H	-5.19978700	2.68840400	-0.30933300
H	-5.61959300	1.16527000	0.48634600
H	-4.91974800	2.49505600	1.41653500
N	3.14386800	0.09431600	-0.28339100
N	-3.22240300	0.15470100	0.01651400
C	4.16546600	-0.87852400	-0.14154900
C	4.93556000	-0.95709600	1.03854000
C	4.33405400	-1.82113400	-1.17828900
C	5.83588100	-2.02046800	1.16388700
C	5.25413200	-2.85227100	-1.00974100
C	5.99622000	-2.96531100	0.16152200
H	6.41971700	-2.09329600	2.07902700
H	5.38606100	-3.57146400	-1.81518400
H	6.70099600	-3.78243200	0.28688900
C	-4.24058200	-0.81935800	0.17303500
C	-4.43660800	-1.40612100	1.43662300
C	-4.99702000	-1.21300600	-0.94557900
C	-5.39569100	-2.41450800	1.55457200
C	-5.94897800	-2.22048400	-0.78092900
C	-6.14566800	-2.82293300	0.45728100
H	-5.55174200	-2.87829800	2.52601700
H	-6.53876600	-2.53141200	-1.64040900
H	-6.88536700	-3.61065400	0.56731700
C	-4.79135000	-0.53847700	-2.26672800

H	-3.72890900	-0.49681100	-2.53488400
H	-5.33277200	-1.05221000	-3.06439300
H	-5.13849900	0.50196200	-2.24725600
C	-3.66086800	-0.92642000	2.62588200
H	-2.60584000	-0.74284100	2.39095400
H	-4.05206800	0.02808700	2.99932600
H	-3.71434000	-1.64216400	3.44954100
C	3.57684800	-1.67264000	-2.45751400
H	2.49736900	-1.61122400	-2.28876400
H	3.85024900	-0.74519500	-2.97708000
H	3.77677200	-2.50529500	-3.13622500
C	4.85458700	0.04992500	2.14486900
H	3.91343900	0.60193900	2.15359100
H	4.93967800	-0.44350900	3.11649500
H	5.68562500	0.76489600	2.08025300
Ni	-1.37830700	-0.21254000	-0.49920400
Ni	1.10468100	-0.29516600	0.11172000
C	0.19363100	-0.22875200	-1.50696700
C	-1.31882700	-2.11406800	0.11667800
H	-2.14062100	-2.23807800	0.81977800
C	-1.63173300	-2.06060600	-1.25663900
H	-2.66641100	-2.24326200	-1.53936600
H	-0.89099900	-2.31317400	-2.00768800
C	-0.00695000	-2.11074600	0.71542900
H	0.00167900	-2.04359900	1.80006600
C	1.22339900	-2.30325500	0.08007600
H	2.08498000	-2.55870000	0.69371800
H	1.24408600	-2.66077300	-0.94769800
Cl	1.42177900	0.02183000	2.42373900
C	0.50752500	-0.00526500	-2.77382700
H	1.53040900	0.18087600	-3.10371200
H	-0.25566200	0.01767800	-3.55329000

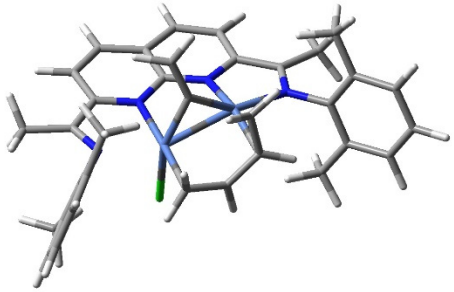


Structure A
Charge = 0; Multiplicity = 4
Imaginary Frequencies = 0
Electronic Energy = -5012.65018958

Electronic Energy + ZPE = -5012.031475
Free Energy (298 K) = -5012.104044

C	2.42550900	3.69276500	-0.24507200
C	1.26712500	4.44473500	-0.16845800
C	0.01309700	3.80589800	-0.08267900
C	-0.00167700	2.37496900	-0.10138700
C	2.34345200	2.29623400	-0.20111000
H	-1.25996800	5.55227600	0.05509200
H	3.39550400	4.17545500	-0.31114100
H	1.30940400	5.53039500	-0.16694100
C	-1.23062800	4.46660000	0.03398000
C	-2.33277000	2.32275300	0.07690800
C	-2.38799400	3.72169100	0.13755400
H	-3.34937900	4.21313800	0.25095700
N	-1.14731500	1.65639400	-0.07752800
N	1.14256400	1.67509000	-0.11888800
C	3.47356800	1.39134900	-0.19681000
C	-3.48558500	1.46570900	0.17193900
C	4.86218900	1.93597800	-0.28020300
H	4.97533700	2.56878500	-1.16686800
H	5.09370300	2.56077900	0.58897300
H	5.59951000	1.13379400	-0.33175300
C	-4.83199200	2.03643400	0.48177100
H	-5.13786700	2.75692700	-0.28457000
H	-5.59094100	1.25471200	0.53535900
H	-4.82410600	2.57384000	1.43576900
N	3.17642700	0.11649400	-0.14462800
N	-3.25370100	0.18377200	-0.01697400
C	4.19272100	-0.86843200	-0.03500500
C	4.86849900	-1.05204100	1.18735400
C	4.44678100	-1.69539000	-1.14499500
C	5.78954800	-2.09913100	1.27283800
C	5.38328500	-2.71987800	-1.01284400
C	6.04738000	-2.93062300	0.19015100
H	6.30839100	-2.25481900	2.21620100
H	5.58675200	-3.35619000	-1.87136900
H	6.76669500	-3.73937200	0.28274100
C	-4.28245700	-0.77158400	0.16688800
C	-4.46258100	-1.32988000	1.44525200
C	-5.03599800	-1.19897100	-0.93917800
C	-5.41980900	-2.33579000	1.59240800
C	-5.98450300	-2.20429200	-0.74513400
C	-6.17605400	-2.77251600	0.50990900
H	-5.56609700	-2.77881100	2.57498900
H	-6.57391700	-2.54174700	-1.59486700

H	-6.91333600	-3.55864200	0.64395900
C	-4.81856800	-0.56724400	-2.27919400
H	-3.75460400	-0.55982800	-2.54912700
H	-5.36811900	-1.09356300	-3.06290800
H	-5.14167500	0.48097400	-2.29370400
C	-3.65747900	-0.83314000	2.60751300
H	-2.59820100	-0.70243300	2.35441600
H	-4.00638400	0.14925800	2.95001200
H	-3.72798700	-1.51484000	3.45818500
C	3.74201900	-1.45002600	-2.44003800
H	2.65422000	-1.48763900	-2.31808300
H	3.96522300	-0.45172900	-2.83802900
H	4.03124800	-2.18440000	-3.19560000
C	4.62214800	-0.15806400	2.36167000
H	3.55202200	-0.00693900	2.54481000
H	5.07215400	-0.57730600	3.26470300
H	5.06791800	0.83421100	2.21501200
Ni	-1.36143300	-0.25467400	-0.60368900
Ni	1.16360400	-0.26280000	-0.00098500
C	0.23837000	-0.27512200	-1.61626900
C	-1.29346500	-2.25046100	0.14879500
H	-2.08848900	-2.33659600	0.88742200
C	-1.66331700	-2.10658500	-1.21125000
H	-2.71176600	-2.27266600	-1.45982100
H	-0.96136000	-2.40168900	-1.98822500
C	0.03049900	-2.36869100	0.64543400
H	0.12821600	-2.37132000	1.72750400
C	1.21605000	-2.35006000	-0.09801200
H	2.13501000	-2.61822500	0.42253600
H	1.18353600	-2.61664400	-1.15273000
Cl	1.04479500	-0.01841200	2.39280300
C	0.44330800	-0.10562000	-2.91469900
H	1.43071600	0.09906500	-3.33247800
H	-0.37352800	-0.14762900	-3.63923000

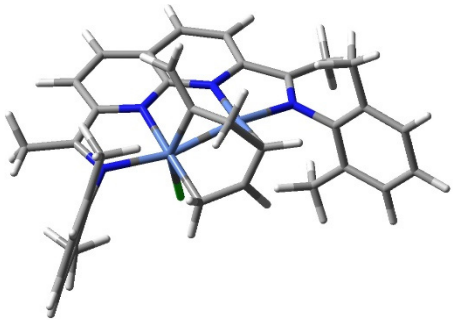


Structure B
Charge = 0; Multiplicity = 2

Imaginary Frequencies = 1
Electronic Energy = -5012.65029076
Electronic Energy + ZPE = -5012.030786
Free Energy (298 K) = -5012.100469

C	2.36741600	3.68131700	-0.32348400
C	1.21338300	4.44420400	-0.23281400
C	-0.04430100	3.82103600	-0.11441700
C	-0.05697100	2.39382400	-0.10829100
C	2.28090900	2.28716200	-0.25893300
H	-1.32405700	5.56397600	0.04021800
H	3.33597200	4.15901100	-0.43071200
H	1.26684200	5.52904000	-0.25883000
C	-1.29339800	4.47875400	0.01328100
C	-2.40691500	2.33358200	0.07847500
C	-2.44936700	3.73724900	0.12781300
H	-3.40497100	4.23707000	0.25106700
N	-1.20363200	1.67987800	-0.07632200
N	1.07386600	1.68354500	-0.12123500
C	3.39637200	1.36596000	-0.30346400
C	-3.49872500	1.43411300	0.17634200
C	4.78809200	1.89819400	-0.40540200
H	4.86503900	2.60906200	-1.23428300
H	5.07196300	2.43707200	0.50504900
H	5.51070800	1.09709200	-0.56596500
C	-4.90463300	1.85923500	0.43269400
H	-5.30160600	1.36722000	1.32771800
H	-4.98784600	2.93693200	0.57610900
H	-5.56950200	1.57435200	-0.39042400
N	3.08731500	0.09126500	-0.26996400
N	-3.16241200	0.14794800	0.03904300
C	4.08785400	-0.90748100	-0.14897900
C	4.85527500	-1.02259300	1.02897100
C	4.23451000	-1.83213200	-1.20408800
C	5.73873000	-2.10202000	1.13201300
C	5.14016200	-2.88014200	-1.05777000
C	5.88300500	-3.02755200	0.10879900
H	6.32071000	-2.20463000	2.04550400
H	5.25862300	-3.58644200	-1.87671100
H	6.57470400	-3.85837300	0.21595700
C	-4.17423800	-0.83968300	0.14746600
C	-4.38136300	-1.45857900	1.39465100
C	-4.89210000	-1.22910100	-0.99586600
C	-5.33404900	-2.47427100	1.47864900
C	-5.83599300	-2.25100100	-0.86624400
C	-6.05838700	-2.86999800	0.35828100

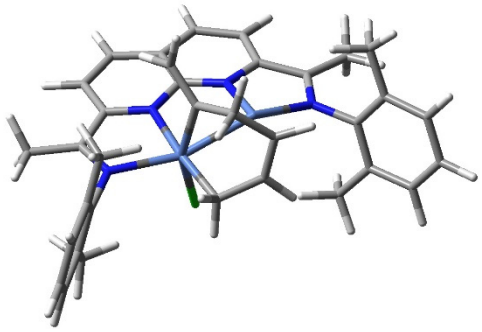
H	-5.50097600	-2.95988000	2.43755000
H	-6.39748100	-2.56136700	-1.74484300
H	-6.79283600	-3.66612500	0.43963100
C	-4.66349200	-0.54593300	-2.31034700
H	-5.16811500	0.42749800	-2.35768700
H	-3.60124600	-0.34196300	-2.48472900
H	-5.04569600	-1.14527400	-3.14042900
C	-3.58478400	-1.02388300	2.58558400
H	-2.50547300	-1.04622700	2.38697800
H	-3.80141300	0.01357000	2.86570300
H	-3.78942400	-1.65389000	3.45384200
C	3.46966500	-1.65431100	-2.47649500
H	2.38788200	-1.61763400	-2.30842600
H	3.72137000	-0.70500900	-2.96615600
H	3.68511800	-2.46043900	-3.18216800
C	4.77165100	-0.03529400	2.15207200
H	4.95249700	-0.53020900	3.10958900
H	5.54089900	0.74146500	2.04974600
H	3.79340200	0.44752500	2.21736500
Ni	-1.29871800	-0.19167600	-0.32637600
Ni	1.08716400	-0.24587300	0.11011200
C	-1.30018600	-2.13896900	-0.04285200
H	-2.25448800	-2.38521100	0.41418000
C	-1.19350600	-1.91744600	-1.45989000
H	-2.11665600	-1.93341000	-2.04031900
H	-0.36988900	-2.38150000	-1.99392700
C	-0.13568700	-2.12484000	0.77327400
H	-0.28182700	-2.07883200	1.84995400
C	1.19249000	-2.20657000	0.30353800
H	1.96719200	-2.40466300	1.04144900
H	1.36969200	-2.64965100	-0.67758900
Cl	1.28952700	0.09606400	2.45863500
C	0.44942400	0.09729700	-2.75273600
H	1.39351300	0.59672000	-2.96783100
H	-0.22071600	-0.05842400	-3.59755000
C	0.14810400	-0.30822600	-1.52168400



Structure C
Charge = 0; Multiplicity = 2
Imaginary Frequencies = 0
Electronic Energy = -5012.69476665
Electronic Energy + ZPE = -5012.072531
Free Energy (298 K) = -5012.141977

C	2.41641900	3.69099200	-0.11831800
C	1.26287200	4.46498000	-0.06693900
C	-0.00815600	3.85615000	-0.09039700
C	-0.03026200	2.43731500	-0.21766600
C	2.30835400	2.29815200	-0.19566200
H	-1.30548500	5.58247800	0.12991900
H	3.39471300	4.15928200	-0.07007600
H	1.33278300	5.54595200	0.01743200
C	-1.26625600	4.50165300	0.02976600
C	-2.37243500	2.35140400	-0.05678700
C	-2.42560100	3.75048100	0.06484700
H	-3.38552200	4.23863300	0.20431400
N	-1.17038300	1.72531300	-0.25599200
N	1.09232000	1.71402000	-0.27868400
C	3.39503400	1.33441000	-0.12940300
C	-3.44792200	1.42032800	0.07218700
C	4.81030400	1.80799100	-0.10809400
H	5.00833800	2.47203300	-0.95569300
H	5.01546700	2.38399800	0.80119000
H	5.50977000	0.97158800	-0.14703400
C	-4.83670500	1.83241700	0.42433200
H	-5.06273100	2.83480500	0.05376700
H	-5.57080600	1.13529300	0.01291900
H	-4.98590300	1.84548400	1.51126200
N	3.02681200	0.07830200	-0.07788500
N	-3.08792000	0.14773700	-0.08105500
C	3.97715400	-0.96240100	0.09091800
C	4.54762200	-1.18483100	1.35832700
C	4.26235000	-1.80016900	-1.00211600
C	5.42065100	-2.26526000	1.50222300
C	5.14951300	-2.85966300	-0.81106800
C	5.72562000	-3.09723000	0.43163900
H	5.86251500	-2.44780100	2.47929900
H	5.38448200	-3.50259600	-1.65664500
H	6.40910500	-3.93098300	0.56569800
C	-3.99131200	-0.89723800	0.23313600
C	-4.05235700	-1.34859100	1.56410100
C	-4.72773400	-1.51006700	-0.79421500
C	-4.88396700	-2.43437300	1.84628100
C	-5.54916100	-2.58913100	-0.46464400

C	-5.62805500	-3.05028500	0.84548800
H	-4.93950500	-2.79824400	2.86991200
H	-6.12556100	-3.07175100	-1.25100900
H	-6.26601500	-3.89592800	1.08594900
C	-4.61426100	-0.99943600	-2.19673800
H	-3.56547300	-0.93741200	-2.51440600
H	-5.15228000	-1.63942500	-2.89999200
H	-5.01404000	0.01695700	-2.29627800
C	-3.24435100	-0.67763500	2.63206700
H	-2.18180000	-0.58337900	2.36748500
H	-3.58733800	0.34772900	2.81743800
H	-3.31298500	-1.22053000	3.57736100
C	3.63701300	-1.54320300	-2.33612900
H	2.54926100	-1.67351200	-2.30210800
H	3.79154400	-0.51115400	-2.67269600
H	4.03978500	-2.21580500	-3.09726600
C	4.22499500	-0.29754000	2.52011400
H	3.14535900	-0.13737100	2.62732900
H	4.60601500	-0.72573000	3.45017700
H	4.68091200	0.69543800	2.41499000
Ni	-1.23675400	-0.15787800	-0.45551500
Ni	1.00510700	-0.19799100	-0.06310100
C	0.28991200	-0.43499900	-1.86943300
C	-1.26725500	-2.02721100	-1.05042900
H	-2.28085000	-2.40628400	-1.16314000
C	-0.37059400	-1.76598000	-2.22347800
H	-0.93344500	-1.67897800	-3.16007700
H	0.37727500	-2.56526400	-2.37017500
C	-0.61648700	-2.06011500	0.19506100
H	-1.20406800	-2.25563800	1.09329900
C	0.83274700	-2.08015600	0.28597700
H	1.23514800	-2.27811600	1.27799000
H	1.34079900	-2.65093900	-0.49894500
Cl	0.59933000	0.22711700	2.27400600
C	0.58301800	0.43171500	-2.86313900
H	0.34033600	0.19436500	-3.90078700
H	1.05765700	1.39372300	-2.69379100

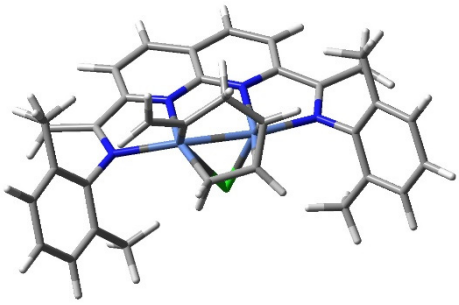


Structure C
Charge = 0; Multiplicity = 4
Imaginary Frequencies = 0
Electronic Energy = -5012.66634089
Electronic Energy + ZPE = -5012.045929
Free Energy (298 K) = -5012.117894

C	2.42334600	3.68907700	-0.11258200
C	1.27681300	4.47003200	-0.05161200
C	0.00429100	3.86304600	-0.05575700
C	-0.02663500	2.44169600	-0.18617200
C	2.31031700	2.29517700	-0.17297600
H	-1.27556400	5.59653500	0.18940600
H	3.40498500	4.15215300	-0.08433200
H	1.35196500	5.55136300	0.02429400
C	-1.24517200	4.51554500	0.08668300
C	-2.35691100	2.37269300	0.01746500
C	-2.40839200	3.76689800	0.15467000
H	-3.36198800	4.25495700	0.33535100
N	-1.17408400	1.74247900	-0.23821900
N	1.09391600	1.70790500	-0.23147800
C	3.41324500	1.34635000	-0.11034600
C	-3.45935500	1.45787100	0.20501000
C	4.81880900	1.85273200	-0.07945300
H	5.01109200	2.50507000	-0.93765400
H	5.00228800	2.44980300	0.82045400
H	5.53572100	1.03050400	-0.09788600
C	-4.83035300	1.95762800	0.52135900
H	-5.14121000	2.73864400	-0.17975600
H	-5.56280600	1.14873300	0.48803900
H	-4.86357600	2.39835300	1.52436600
N	3.07378000	0.08586700	-0.07830700
N	-3.14029600	0.18229200	0.12913200
C	4.03709600	-0.93658400	0.10670800
C	4.61664700	-1.13496300	1.37562000
C	4.33061100	-1.79027300	-0.97338700

C	5.49709300	-2.20738400	1.53442800
C	5.22636000	-2.83911800	-0.76770000
C	5.80569800	-3.05471300	0.47758500
H	5.94268600	-2.37039500	2.51325300
H	5.46637200	-3.49151700	-1.60462300
H	6.49553800	-3.88121500	0.62336200
C	-4.06774000	-0.85811700	0.34902100
C	-4.07628300	-1.48623500	1.60783700
C	-4.85701200	-1.32423000	-0.71674800
C	-4.91563200	-2.58731300	1.78346800
C	-5.67937400	-2.43014600	-0.49565100
C	-5.71278100	-3.05813700	0.74480700
H	-4.93484900	-3.08079400	2.75292400
H	-6.29415600	-2.79990100	-1.31372300
H	-6.35515800	-3.92017300	0.90039900
C	-4.78826200	-0.64671900	-2.05065800
H	-3.75416700	-0.58792300	-2.41692300
H	-5.38294200	-1.17715100	-2.79801600
H	-5.15168900	0.38751400	-2.00948300
C	-3.20488300	-0.96600800	2.70829200
H	-2.15733600	-0.85461900	2.39583000
H	-3.51811700	0.03365600	3.03366200
H	-3.23524600	-1.62145300	3.58166200
C	3.71135700	-1.55782300	-2.31446000
H	2.62459500	-1.69551600	-2.28557600
H	3.86368000	-0.53069200	-2.66630700
H	4.12361100	-2.23994400	-3.06199500
C	4.30017600	-0.23192600	2.52693100
H	3.22180800	-0.06661700	2.63204000
H	4.67719000	-0.65371600	3.46154600
H	4.76515800	0.75571900	2.41268500
Ni	-1.28588900	-0.17983900	-0.57004500
Ni	0.97842800	-0.23340800	-0.03409700
C	0.40062700	-0.44946200	-1.93621800
C	-1.29245600	-2.08596700	-1.34497400
H	-2.30575300	-2.40529900	-1.58190000
C	-0.28676400	-1.73917500	-2.40396300
H	-0.75830600	-1.59270500	-3.38410100
H	0.46369800	-2.54042600	-2.52988800
C	-0.77967000	-2.19097600	-0.06111700
H	-1.44422300	-2.47514900	0.75708700
C	0.66724900	-2.13395700	0.18379600
H	0.95779000	-2.39744800	1.19977900
H	1.25539600	-2.68652000	-0.56003300
Cl	0.68971600	0.07381600	2.25081200
C	0.73212800	0.45796500	-2.87771800

H	0.50286300	0.29345400	-3.93439300
H	1.23603900	1.39406300	-2.64837500

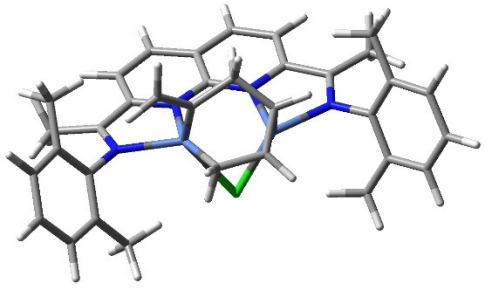


Structure D
Charge = 0; Multiplicity = 2
Imaginary Frequencies = 1
Electronic Energy = -5012.65754439
Electronic Energy + ZPE = -5012.035848
Free Energy (298 K) = -5012.103909

C	-2.34074500	3.74178400	-0.09068400
C	-1.18728900	4.50304500	-0.09179500
C	0.06944900	3.86071600	-0.03863800
C	0.06944200	2.43929200	0.09131300
C	-2.26787300	2.34552700	0.00546500
H	1.36551800	5.58199500	-0.22539600
H	-3.31081900	4.22034600	-0.18242200
H	-1.23371500	5.58481300	-0.17835900
C	1.32585600	4.50017500	-0.13458000
C	2.40764000	2.35077900	-0.06066800
C	2.48464500	3.74584400	-0.16277700
H	3.45073200	4.22553000	-0.28787600
N	1.21113600	1.72702400	0.13073600
N	-1.06734700	1.71130300	0.16431000
C	-3.39422600	1.45707600	-0.12332300
C	3.51418200	1.43336000	-0.16559300
C	-4.76447300	2.01847000	-0.33264600
H	-4.76423000	2.72762500	-1.16600500
H	-5.48750800	1.23271800	-0.55463900
H	-5.11407100	2.56301200	0.55161000
C	4.91679600	1.94170800	-0.23317600
H	5.20110300	2.47000800	0.68385700
H	5.62777300	1.13074300	-0.39707700
H	5.02009100	2.65830700	-1.05479000
N	-3.10823300	0.17091300	-0.12500300
N	3.17776500	0.16006500	-0.23781300
C	-4.12717800	-0.80650800	-0.21973900

C	-4.12239800	-1.65079600	-1.35007900
C	-5.07635200	-0.98131500	0.81043200
C	-5.05067700	-2.68888100	-1.41240300
C	-5.98599100	-2.03680600	0.70182700
C	-5.97477000	-2.89072800	-0.39318500
H	-5.04717200	-3.33882700	-2.28456000
H	-6.70796000	-2.18540900	1.50224900
H	-6.68587900	-3.70982100	-0.45358100
C	4.14348400	-0.86730700	-0.14429400
C	4.28192800	-1.75172200	-1.23331600
C	4.86059700	-1.06680700	1.05401800
C	5.16703400	-2.82124200	-1.11021100
C	5.72353500	-2.16276700	1.13428400
C	5.88332400	-3.03239500	0.06361700
H	5.28620600	-3.49908600	-1.95258500
H	6.26978000	-2.33001100	2.06033600
H	6.55920200	-3.87888800	0.14542400
C	4.70353000	-0.14901700	2.22979400
H	3.69211200	0.26587200	2.30026300
H	4.92103900	-0.67454000	3.16345300
H	5.39305800	0.70288600	2.17924500
C	3.50417200	-1.52162400	-2.48767100
H	2.42569200	-1.47521300	-2.29381700
H	3.75069600	-0.55670200	-2.94568300
H	3.69673200	-2.30602100	-3.22319000
C	-5.12600200	-0.08047200	2.00890600
H	-5.43422900	-0.63728800	2.89833600
H	-4.15569000	0.37629600	2.22296800
H	-5.85439700	0.72921100	1.87578600
C	-3.19729300	-1.38201500	-2.49222000
H	-2.19566200	-1.08426700	-2.16954600
H	-3.11170000	-2.24904100	-3.15136800
H	-3.56071900	-0.54238100	-3.09827500
Ni	1.20770200	-0.18656100	-0.06270500
Ni	-1.11168300	-0.22178100	0.16831400
C	-1.04163200	-1.16669700	1.81390400
C	1.35540700	-1.37375500	1.46200800
H	2.38042600	-1.51853200	1.79984000
C	0.30705100	-1.05314300	2.48690600
H	0.44376200	-0.04416100	2.90165500
H	0.37218700	-1.74972300	3.33956100
C	0.89162400	-2.05868900	0.30844300
H	1.52787700	-2.74716300	-0.25004800
C	-0.59410800	-2.17198700	0.22189500
H	-0.96130200	-2.08580100	-0.81406500
H	-1.04451300	-3.07551400	0.63357300

Cl	0.17469300	-0.06218800	-2.20454100
C	-2.13930300	-1.51261300	2.51365400
H	-3.08441000	-1.75767300	2.04321100
H	-2.09787200	-1.58063400	3.59967000

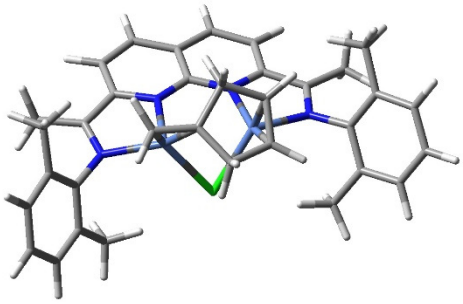


Structure D
Charge = 0; Multiplicity = 4
Imaginary Frequencies = 1
Electronic Energy = -5012.64816860
Electronic Energy + ZPE = -5012.027964
Free Energy (298 K) = -5012.098031

C	-2.35430500	3.70258100	-0.25042400
C	-1.19494200	4.44611900	-0.15838000
C	0.04995300	3.78982600	-0.09207900
C	0.05722900	2.35314900	-0.11070900
C	-2.28793900	2.30640400	-0.22695700
H	1.30515400	5.54378100	0.03103100
H	-3.31930100	4.19350100	-0.32767100
H	-1.22413100	5.53215400	-0.14793600
C	1.28977500	4.45805800	-0.00539600
C	2.40534400	2.32978900	-0.03884800
C	2.45805000	3.72672500	0.02876900
H	3.42064300	4.22472500	0.09629600
N	1.21414000	1.65295500	-0.11426300
N	-1.09425100	1.64252100	-0.12605100
C	-3.45029600	1.45851300	-0.30081800
C	3.56680700	1.48745400	-0.05210000
C	-4.80089700	2.06342400	-0.52006000
H	-4.79165400	2.70747400	-1.40476000
H	-5.56140800	1.29484700	-0.66328600
H	-5.10494200	2.68930200	0.32603200
C	4.93924200	2.07446600	0.02760200
H	5.10436500	2.58715700	0.98197100
H	5.70527900	1.30549600	-0.08253000
H	5.08651000	2.81944300	-0.76085600
N	-3.22430800	0.16584500	-0.21148800

N	3.31875600	0.19807000	-0.17535900
C	-4.28025800	-0.76762700	-0.13319500
C	-4.37920900	-1.75375800	-1.13650000
C	-5.15359900	-0.77112000	0.97663800
C	-5.35638400	-2.74032200	-1.00882600
C	-6.11185900	-1.78336600	1.06159500
C	-6.21866500	-2.76236600	0.08235900
H	-5.43766400	-3.49811700	-1.78516400
H	-6.77605500	-1.79907300	1.92321300
H	-6.96780800	-3.54385500	0.17114200
C	4.32134100	-0.78465000	-0.04861200
C	4.55853200	-1.63519400	-1.14814800
C	4.97355300	-0.99067800	1.18482800
C	5.48553400	-2.66534900	-1.00569300
C	5.88677000	-2.04341000	1.28252100
C	6.15121100	-2.87130800	0.19906700
H	5.68092800	-3.31468000	-1.85632100
H	6.38722500	-2.21281000	2.23371300
H	6.86504200	-3.68422400	0.29615300
C	4.69410800	-0.12549800	2.37752300
H	3.65693000	0.22584200	2.39977500
H	4.88896900	-0.66981300	3.30531300
H	5.32914900	0.76887000	2.39584800
C	3.83657900	-1.39936900	-2.43632500
H	2.75681300	-1.27837400	-2.28079400
H	4.16585200	-0.47126900	-2.91843100
H	3.99412700	-2.21887000	-3.14089400
C	-5.06357500	0.25511200	2.06644000
H	-5.37944900	-0.17238700	3.02212800
H	-4.04559800	0.63525300	2.19208500
H	-5.71839000	1.11406900	1.87369900
C	-3.49346300	-1.69246900	-2.34112000
H	-2.47350600	-1.38028400	-2.09381400
H	-3.44856200	-2.65496100	-2.85643000
H	-3.85667800	-0.94979900	-3.06214400
Ni	1.40424700	-0.31786800	-0.33292200
Ni	-1.26756400	-0.32273600	-0.00228400
C	-1.05679500	-0.99733500	1.75890900
C	1.33876900	-1.36078200	1.35998700
H	2.35668000	-1.52805700	1.70970100
C	0.33340600	-0.76416900	2.30853700
H	0.52163200	0.30742500	2.47218300
H	0.42534200	-1.24439900	3.29519000
C	0.80751200	-2.15120800	0.33453900
H	1.41052300	-2.91384500	-0.16199500
C	-0.68153900	-2.23644900	0.26285500

H	-1.04955000	-2.28717900	-0.77571400
H	-1.12012800	-3.08101100	0.79498400
Cl	0.10867600	-0.42074500	-2.26496800
C	-2.08980400	-1.28235100	2.57322900
H	-3.05925700	-1.59366100	2.19625000
H	-1.98319900	-1.21588100	3.65513300

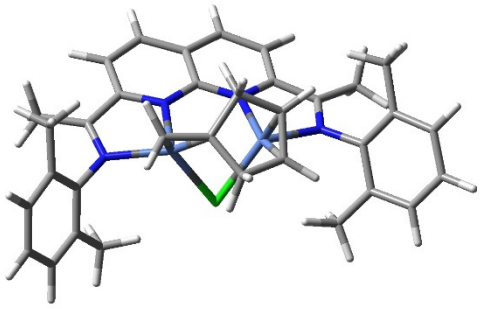


Structure E
Charge = 0; Multiplicity = 2
Imaginary Frequencies = 1
Electronic Energy = -5012.71687719
Electronic Energy + ZPE = -5012.092769
Free Energy (298 K) = -5012.162151

C	2.43277300	3.71248500	-0.03230300
C	1.27416000	4.45026800	0.06130800
C	0.03536900	3.78259700	0.15347600
C	0.02041000	2.35113200	0.02818700
C	2.37047100	2.31452800	-0.08393800
H	-1.18998400	5.52754500	0.48006300
H	3.40025900	4.20450700	-0.03354400
H	1.29955300	5.53448200	0.12546900
C	-1.18548500	4.44492700	0.38766400
C	-2.30060700	2.31979900	0.40079600
C	-2.34341200	3.71198500	0.53308900
H	-3.28634600	4.20431500	0.74829900
N	-1.13770800	1.65582200	0.09966700
N	1.16657200	1.64413100	-0.16125600
C	3.53480200	1.48587700	0.03915700
C	-3.46533700	1.48425100	0.53874100
C	4.90298900	2.09218700	0.07245800
H	4.97247100	2.86144700	0.84753300
H	5.66237100	1.33752900	0.28151000
H	5.15675800	2.57241600	-0.87961600
C	-4.79945600	2.09838400	0.82498300
H	-5.14020400	2.74253000	0.00697500
H	-5.55814700	1.33342700	0.99487100

H	-4.74329300	2.72489200	1.72086100
N	3.30035500	0.19392700	0.17934900
N	-3.25741700	0.18685700	0.43622200
C	4.35774700	-0.74520500	0.27908900
C	4.49803200	-1.43639700	1.50092300
C	5.19409400	-1.03608600	-0.81665600
C	5.46664200	-2.43337100	1.59732800
C	6.14127200	-2.05562600	-0.67693200
C	6.27818900	-2.75476200	0.51363300
H	5.58103200	-2.96000200	2.54228000
H	6.77957200	-2.29326300	-1.52571200
H	7.02064800	-3.54284000	0.60186600
C	-4.32258400	-0.73148100	0.31365200
C	-4.36652100	-1.80979000	1.22484800
C	-5.23586600	-0.65721400	-0.76017900
C	-5.35216700	-2.78069100	1.06731100
C	-6.19397200	-1.66756500	-0.88761000
C	-6.26391200	-2.71640100	0.01723100
H	-5.39294000	-3.60346400	1.77779500
H	-6.89101600	-1.62036900	-1.72191800
H	-7.01844800	-3.48899400	-0.09944300
C	-5.21599600	0.44501600	-1.77784900
H	-4.24759700	0.94757400	-1.84664900
H	-5.46102700	0.05433400	-2.76982400
H	-5.96259500	1.21671000	-1.55280300
C	-3.36014700	-1.89815500	2.32541000
H	-2.34351900	-1.99801800	1.92445100
H	-3.34106600	-0.99155400	2.93945500
H	-3.55888800	-2.75240100	2.97662000
C	5.12234000	-0.27663600	-2.10826200
H	5.16170100	-0.95366700	-2.96718100
H	4.21307700	0.32086700	-2.19473200
H	5.97227500	0.40997000	-2.20836000
C	3.65457600	-1.06195400	2.67728800
H	2.58488700	-1.16386200	2.46651700
H	3.89517800	-1.67916200	3.54594400
H	3.80449800	-0.01226300	2.95600700
Ni	-1.38115400	-0.29746800	-0.04424500
Ni	1.42893100	-0.32890800	-0.25856900
C	0.52052000	-1.37192700	-1.75450100
C	-1.76402100	-0.88051700	-1.85470200
H	-2.72770900	-0.57270100	-2.25426400
C	-0.48556800	-0.62243000	-2.60523300
H	-0.23682400	0.43791800	-2.73574600
H	-0.51774700	-1.06894800	-3.61626600
C	-1.60316700	-2.00490400	-1.00178000

H	-2.43662900	-2.62941200	-0.68164900
C	-0.21727800	-2.57347300	-1.19160300
H	0.23126400	-2.97774000	-0.27685200
H	-0.22248300	-3.38843600	-1.93731200
Cl	0.14430900	-0.92866600	1.69760900
C	1.90253000	-1.26069900	-1.92874900
H	2.56949500	-2.07856200	-1.64524000
H	2.28925600	-0.60302100	-2.70547100

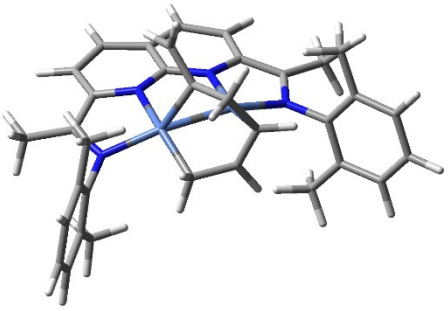


Structure E
Charge = 0; Multiplicity = 4
Imaginary Frequencies = 1
Electronic Energy = -5012.71945264
Electronic Energy + ZPE = -5012.095618
Free Energy (298 K) = -5012.165660

C	2.42696100	3.70863800	-0.03476700
C	1.26552900	4.44589400	0.03657000
C	0.02712700	3.77885100	0.13583500
C	0.01663600	2.34523800	0.03014900
C	2.36633700	2.31058800	-0.06764000
H	-1.20443800	5.52518300	0.43369000
H	3.39342200	4.20276500	-0.03846700
H	1.28861600	5.53148200	0.07373000
C	-1.19583400	4.44141100	0.35812600
C	-2.30550000	2.31216500	0.40228000
C	-2.35034000	3.70510800	0.51669300
H	-3.29441400	4.19632600	0.73022100
N	-1.13959600	1.64406000	0.11278500
N	1.16410800	1.63989000	-0.13669200
C	3.53415200	1.48329900	0.06756600
C	-3.46597400	1.47673300	0.56228800
C	4.89490500	2.10302000	0.14267000
H	4.94456600	2.84176300	0.94856100
H	5.66040300	1.34889400	0.32970900
H	5.15176600	2.62486600	-0.78619200

C	-4.78957300	2.08568100	0.90340600
H	-5.15061700	2.74797300	0.10863900
H	-5.54491600	1.31713500	1.07270900
H	-4.70955000	2.69240400	1.81097700
N	3.31173900	0.19008500	0.17888400
N	-3.26539400	0.18331800	0.41473200
C	4.37509800	-0.74088300	0.27874200
C	4.51417500	-1.44724900	1.49168300
C	5.21818000	-1.01213600	-0.81716100
C	5.48887600	-2.43898300	1.57955000
C	6.17136200	-2.02715100	-0.68622800
C	6.30756800	-2.74105800	0.49565800
H	5.60240900	-2.97705800	2.51818000
H	6.81483700	-2.24947700	-1.53524200
H	7.05450000	-3.52559800	0.57697700
C	-4.33259100	-0.73211500	0.31221100
C	-4.36387900	-1.82236000	1.20939200
C	-5.26727700	-0.64031200	-0.74202700
C	-5.35460400	-2.78902300	1.05602700
C	-6.23171800	-1.64474300	-0.86443900
C	-6.28698000	-2.70749400	0.02552500
H	-5.38449000	-3.62105900	1.75634700
H	-6.94593700	-1.58191100	-1.68310900
H	-7.04620200	-3.47602000	-0.08714800
C	-5.25893400	0.47801300	-1.74207700
H	-4.28326000	0.96340000	-1.83089000
H	-5.54174900	0.10924900	-2.73231200
H	-5.98242000	1.26068300	-1.48161700
C	-3.34136700	-1.92547300	2.29382100
H	-2.33241300	-2.03866500	1.87772200
H	-3.30117900	-1.01984100	2.90854400
H	-3.54007400	-2.77807900	2.94723200
C	5.14659000	-0.23226800	-2.09634700
H	5.24955100	-0.88902500	-2.96547600
H	4.20926300	0.31757800	-2.20056000
H	5.96022100	0.50149400	-2.15753500
C	3.66233000	-1.09432100	2.66870000
H	2.59503600	-1.21011200	2.45385200
H	3.90850100	-1.71520800	3.53311800
H	3.79561700	-0.04481800	2.95673500
Ni	-1.37059500	-0.30328700	-0.05289800
Ni	1.41731200	-0.33851900	-0.24699400
C	0.51688100	-1.35950200	-1.77668600
C	-1.76983100	-0.89228400	-1.87312900
H	-2.73891100	-0.57894200	-2.25445600
C	-0.49517700	-0.61365900	-2.62277800

H	-0.25764500	0.45031900	-2.74396100
H	-0.52173500	-1.05120500	-3.63813200
C	-1.59640400	-2.01598500	-1.02981200
H	-2.42477100	-2.63999500	-0.69656100
C	-0.20702100	-2.57227400	-1.22236500
H	0.24571300	-2.97578400	-0.30899200
H	-0.20339600	-3.38481200	-1.97080400
Cl	0.15138100	-0.93228200	1.68234800
C	1.89777900	-1.23343300	-1.94665500
H	2.57292500	-2.04761000	-1.67263700
H	2.27834100	-0.56000500	-2.71246000

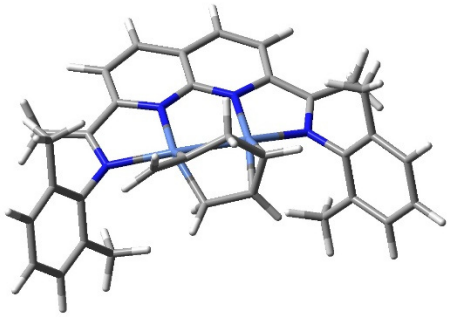


Structure F
Charge = 0; Multiplicity = 1
Imaginary Frequencies = 0
Electronic Energy = -4552.46530961
Electronic Energy + ZPE = -4551.845475
Free Energy (298 K) = -4551.911878

C	-2.53795600	3.68793600	-0.20350500
C	-1.38363000	4.45761800	-0.31030200
C	-0.11108300	3.85418600	-0.24628800
C	-0.07686500	2.45148600	0.05627500
C	-2.43325400	2.31816700	0.03344900
H	1.15273300	5.54603100	-0.71931000
H	-3.51075600	4.14365500	-0.36243500
H	-1.45279600	5.52010600	-0.52653700
C	1.13013700	4.48318500	-0.49706000
C	2.26828900	2.35825600	-0.28040100
C	2.29377400	3.73089100	-0.53953600
H	3.23301800	4.20660100	-0.80763400
N	1.07686000	1.76041100	0.12536100
N	-1.19764200	1.76115800	0.28727000
C	-3.44307100	1.32238900	-0.12332300
C	3.30525100	1.41933300	-0.45810500
C	-4.89564300	1.64225800	-0.22655100
H	-5.08349000	2.71511300	-0.16865700

H	-5.32770000	1.26270200	-1.15909700
H	-5.45172600	1.15653100	0.58339300
C	4.70461400	1.78213900	-0.82076600
H	5.41695900	1.44376700	-0.05913000
H	5.00898900	1.29617000	-1.75527800
H	4.82904200	2.85919000	-0.94030200
N	-2.98668900	0.06969400	-0.19177200
N	2.92250300	0.13346100	-0.32652600
C	-3.89144300	-1.00504000	-0.37573800
C	-4.25468900	-1.37439000	-1.68193400
C	-4.33639100	-1.73320900	0.74118100
C	-5.09987100	-2.47238300	-1.85105500
C	-5.17723800	-2.82620000	0.52851600
C	-5.56273300	-3.19407700	-0.75638900
H	-5.38636900	-2.76411800	-2.85940100
H	-5.52766600	-3.39401200	1.38801600
H	-6.21755000	-4.04818800	-0.90478200
C	3.88309200	-0.89911000	-0.44179600
C	3.98270000	-1.59899200	-1.65712500
C	4.66716700	-1.25730000	0.67154000
C	4.89219300	-2.65479600	-1.74588900
C	5.56245700	-2.31987900	0.54266500
C	5.67879200	-3.01463300	-0.65716200
H	4.97751900	-3.19837800	-2.68466600
H	6.16855800	-2.60518600	1.39993900
H	6.37830000	-3.84163400	-0.74117700
C	4.50544400	-0.52150600	1.96533900
H	3.44922400	-0.47387800	2.26202900
H	5.07226100	-0.99703600	2.76922200
H	4.83682600	0.52154200	1.89482900
C	3.14111900	-1.19027000	-2.82614500
H	2.08582600	-1.09509100	-2.54673000
H	3.43250800	-0.20541600	-3.21067400
H	3.22424900	-1.90652200	-3.64720500
C	-3.88702100	-1.34091500	2.11335500
H	-2.79386000	-1.39630000	2.20179200
H	-4.14338500	-0.30214400	2.35324300
H	-4.32767500	-1.98443300	2.87857100
C	-3.71644400	-0.61263400	-2.85298600
H	-2.62084200	-0.58118300	-2.83435800
H	-4.03317900	-1.06087600	-3.79779200
H	-4.04238100	0.43450300	-2.85598100
Ni	1.16253600	-0.09414600	0.40130600
Ni	-1.15792100	-0.14101800	0.41195800
C	-0.09358900	-0.24063700	2.01518400
C	-0.45345800	0.65799500	2.95721400

C	1.32094900	-1.91741400	1.17484200
H	2.34763100	-2.27389000	1.21608400
C	0.54594600	-1.56521800	2.40665100
H	1.19378900	-1.44568200	3.28194100
H	-0.21247300	-2.32641100	2.66211800
C	0.57185500	-2.03041500	-0.00483700
H	1.09182100	-2.34056300	-0.91395500
C	-0.88897100	-1.99297400	0.01284000
H	-1.35636100	-2.23710800	-0.94575500
H	-1.32902000	-2.60442300	0.81323500
H	-0.87258300	1.62957800	2.71656800
H	-0.30645300	0.43543700	4.01521300



Structure G
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Electronic Energy + ZPE = -4551.797301
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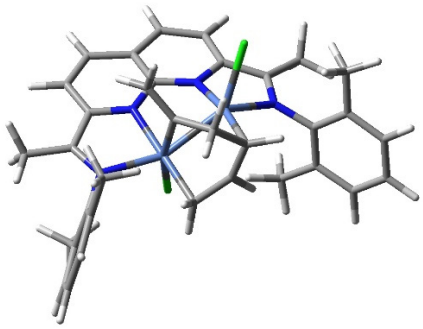
C	1.19387400	4.52959800	0.16403000
C	-0.06460100	3.90244900	0.09603000
C	-0.06753000	2.47549000	-0.06369200
C	2.28275400	2.37820300	0.03598500
H	-1.36310300	5.61670000	0.32103700
H	3.32144300	4.23998600	0.27984500
H	1.24597200	5.60877400	0.27699500
C	-1.32275200	4.53748400	0.20594400
C	-2.43380300	2.39350400	0.10791600
C	-2.48489400	3.78125900	0.23139100
H	-3.44710000	4.26763800	0.36789500
N	-1.20974000	1.76726900	-0.12336000
N	1.06296200	1.75759300	-0.16754800
C	3.37477000	1.47529300	0.20281100
C	-3.50447400	1.47908300	0.24299500
C	4.75528300	2.01049400	0.42971900

H	4.76924500	2.68137400	1.29479600
H	5.47358900	1.21059400	0.61287900
H	5.10492500	2.59522000	-0.42789500
C	-4.91979200	1.92676000	0.40835900
H	-5.54923500	1.11596500	0.78269900
H	-4.99100100	2.76289700	1.11011300
H	-5.35393700	2.27135300	-0.53829300
N	3.06050700	0.18491200	0.23934800
N	-3.13410200	0.19084800	0.25914400
C	4.08068500	-0.78315900	0.37237200
C	4.13900200	-1.54152200	1.55846800
C	4.98532100	-1.03065800	-0.68313000
C	5.09320000	-2.55408900	1.66324100
C	5.92019000	-2.05727000	-0.53721700
C	5.97627800	-2.82058100	0.62297700
H	5.14266300	-3.13321900	2.58311300
H	6.60800800	-2.25795100	-1.35631700
H	6.70910300	-3.61666900	0.71870500
C	-4.07191900	-0.85844100	0.31629000
C	-4.13578500	-1.62375100	1.49814000
C	-4.84167200	-1.20693000	-0.81154200
C	-4.98161500	-2.73206300	1.53598600
C	-5.67363100	-2.32583900	-0.73269100
C	-5.74743800	-3.08531300	0.42928300
H	-5.03539000	-3.32235800	2.44848600
H	-6.26381500	-2.60351300	-1.60365800
H	-6.39565400	-3.95606400	0.47021400
C	-4.75132700	-0.40290400	-2.07210300
H	-3.72036500	-0.09099100	-2.27665800
H	-5.11943800	-0.97096100	-2.93040700
H	-5.34655300	0.51679400	-2.01657000
C	-3.32118200	-1.21950200	2.68680600
H	-2.27616800	-1.03872800	2.40717000
H	-3.67801400	-0.27468500	3.11416400
H	-3.35396600	-1.97836900	3.47253000
C	4.92290400	-0.23094700	-1.94836700
H	5.41794700	-0.75838300	-2.76784400
H	3.88636300	-0.03337000	-2.24268800
H	5.41864100	0.74235100	-1.84696400
C	3.22875900	-1.23064200	2.70603500
H	2.18575900	-1.48891900	2.49156800
H	3.52447500	-1.78277600	3.60164300
H	3.23084100	-0.16211300	2.94569500
Ni	-1.25987400	-0.09184200	-0.21161900
Ni	1.05870000	-0.13565100	-0.26512000
C	0.98085700	-1.48577300	-1.57949500

C	2.09310300	-2.07844500	-2.05288100
C	-1.40354900	-1.68247700	-1.31269900
H	-2.42223800	-1.90939500	-1.62432600
C	-0.31943400	-1.56022500	-2.33977200
H	-0.46020300	-0.67329300	-2.97266700
H	-0.32558200	-2.42950300	-3.01818300
C	-0.98151000	-2.00757000	-0.00956100
H	-1.64084900	-2.50550500	0.70293800
C	0.48179100	-1.92159400	0.23193300
H	0.69431700	-1.34978700	1.17043400
H	1.05928000	-2.84807800	0.30574500
H	2.11714800	-2.46523100	-3.07095700
H	2.99898900	-2.19348000	-1.46909100



Structure H
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Electronic Energy + ZPE = -5472.264703
Free Energy (298 K) = -5472.334421

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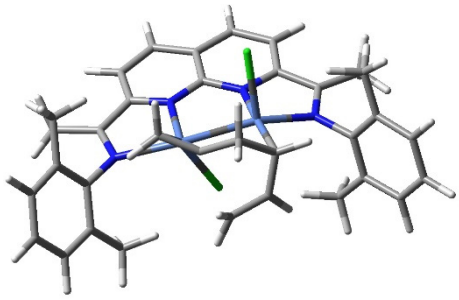
C	-1.28315100	4.41391900	-0.38144700
C	-0.01618000	3.78855400	-0.39343100
C	0.00107000	2.39867300	-0.11784100
C	-2.31497600	2.27160800	0.02188100
H	1.27543400	5.45526800	-0.90835400
H	-3.40307000	4.13222400	-0.20547700
H	-1.35348400	5.48342900	-0.55973900
C	1.23066700	4.39156600	-0.69363200
C	2.29534600	2.23094000	-0.47909800
C	2.36659000	3.61346900	-0.75289100
H	3.32288000	4.05677100	-1.01307500
N	1.12892600	1.66237500	-0.12864300
N	-1.11806700	1.68835400	0.09561800
C	-3.43493600	1.31816000	0.04938400
C	3.37840200	1.26386200	-0.60154500

C	-4.83226200	1.83922300	0.04661200
H	-4.98810200	2.50894200	0.89940100
H	-5.03423300	2.42356800	-0.85780500
H	-5.55745400	1.02655800	0.10038900
C	4.71852000	1.68104000	-1.10186300
H	5.18416500	2.38316700	-0.40111300
H	5.37935900	0.82007300	-1.21445200
H	4.64288200	2.19052000	-2.06835800
N	-3.09947100	0.06133500	0.03356500
N	3.04052300	0.04369900	-0.28254200
C	-4.08153100	-0.95498500	-0.14996700
C	-4.64381200	-1.13452100	-1.43047000
C	-4.41410400	-1.80122000	0.92325200
C	-5.53219800	-2.19663000	-1.61234200
C	-5.32066600	-2.83657400	0.69100300
C	-5.87094100	-3.04579500	-0.56712400
H	-5.96078400	-2.34725400	-2.60040100
H	-5.59217700	-3.48306000	1.52250000
H	-6.56593700	-3.86440700	-0.73063500
C	3.87744600	-1.06990700	-0.55263800
C	3.67976800	-1.72239300	-1.78581800
C	4.78599200	-1.54812500	0.40718500
C	4.40674500	-2.88821800	-2.03247400
C	5.48967800	-2.71744900	0.10944500
C	5.30038900	-3.38923200	-1.09288400
H	4.26148700	-3.40123700	-2.98053700
H	6.19759800	-3.09750600	0.84258200
H	5.85444600	-4.30041900	-1.30018300
C	5.00349400	-0.81202000	1.68985900
H	4.07139100	-0.65273100	2.24382500
H	5.71439700	-1.34016000	2.32960900
H	5.39700200	0.19680300	1.51434700
C	2.73627100	-1.15999300	-2.80165200
H	1.73563200	-0.96092200	-2.39504000
H	3.08943700	-0.19611600	-3.19019200
H	2.62839300	-1.83475800	-3.65376300
C	-3.84908300	-1.58695300	2.29046100
H	-2.78894300	-1.85599400	2.34420200
H	-3.88914600	-0.53614000	2.59693000
H	-4.38743000	-2.18433100	3.03048700
C	-4.31082000	-0.22580800	-2.57288200
H	-3.23091500	-0.06667600	-2.66716600
H	-4.67978700	-0.64295700	-3.51250400
H	-4.77818800	0.76117700	-2.46046900
Ni	1.23340100	-0.06429000	0.62906700
Ni	-1.04620300	-0.25797300	0.12391300

C	-0.69364600	-0.33024000	2.01665600
C	-1.28403500	0.54144800	2.83996400
H	-1.15773000	0.45855400	3.92007100
C	1.16329300	-1.79908300	1.50784700
H	2.16296300	-2.13838700	1.77460400
C	0.13742700	-1.47913300	2.55835800
H	0.61926400	-1.16697100	3.49004800
H	-0.49551400	-2.35729900	2.78043500
C	0.64007400	-2.01325000	0.21203900
H	1.31845000	-2.31195200	-0.58971100
C	-0.79069200	-2.15251800	0.00448700
H	-1.09911900	-2.47635500	-0.98815300
H	-1.33097600	-2.66149400	0.80859100
Cl	2.14673000	1.02339300	2.60030200
Cl	-0.75100100	-0.07556300	-2.24273900
H	-1.87589700	1.38884100	2.50283300



Structure I
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Electronic Energy + ZPE = -5472.188673
Free Energy (298 K) = -5472.258402

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C	-1.34188200	4.49553400	-0.47812300
C	-0.09002500	3.86586000	-0.33894500
C	-0.08295700	2.45233000	-0.13209000
C	-2.39576700	2.33960100	-0.29938700
H	1.18600700	5.59948700	-0.56307600
H	-3.45572700	4.18469600	-0.66509500
H	-1.38761400	5.57213000	-0.61589800
C	1.15879600	4.52178100	-0.42982300
C	2.24892800	2.38470500	-0.25983000
C	2.31747000	3.78194400	-0.39701200
H	3.28557800	4.26238900	-0.49627700
N	1.06378400	1.74736100	-0.09306300

N	-1.22087900	1.73030200	-0.02827600
C	-3.52685900	1.43587200	-0.39459400
C	3.37278000	1.49305000	-0.32555500
C	-4.89312800	2.00392400	-0.61660800
H	-4.89513900	2.62398700	-1.51892700
H	-5.19952400	2.65069300	0.21226200
H	-5.64039800	1.22044700	-0.74088100
C	4.75062800	2.01570100	-0.56128900
H	5.46537700	1.20518400	-0.70783500
H	5.08911300	2.61648500	0.29075800
H	4.77967500	2.66466600	-1.44241400
N	-3.24180000	0.16108800	-0.34086900
N	3.06831700	0.21596400	-0.18963900
C	-4.29330700	-0.78576100	-0.26768200
C	-5.13656900	-0.82365900	0.86433500
C	-4.40733900	-1.74526900	-1.29332400
C	-6.09614100	-1.83589100	0.94302500
C	-5.39321000	-2.72463000	-1.17684700
C	-6.23218700	-2.77711800	-0.06815600
H	-6.73649500	-1.87956600	1.82114100
H	-5.49410000	-3.45844700	-1.97331100
H	-6.98482600	-3.55638600	0.01014300
C	4.08923500	-0.76732900	-0.30933200
C	4.87779100	-1.10686300	0.80394700
C	4.23580800	-1.40848500	-1.55081500
C	5.81603600	-2.12905500	0.65166600
C	5.19049300	-2.42239300	-1.65553200
C	5.97095500	-2.78693300	-0.56433500
H	6.42859800	-2.40683700	1.50641300
H	5.31507200	-2.92614600	-2.61153900
H	6.70361700	-3.58308800	-0.66179800
C	3.41602800	-0.97236400	-2.72494000
H	3.49781900	-1.68341000	-3.55051600
H	3.74917000	0.00425200	-3.09978700
H	2.35657800	-0.84743100	-2.46828000
C	4.70045200	-0.38923900	2.10418200
H	3.65766700	-0.39928000	2.44594000
H	4.96051700	0.67326900	2.01952700
H	5.33083000	-0.82287200	2.88377600
C	-3.51187100	-1.67800800	-2.48666400
H	-2.45260700	-1.66229100	-2.20545500
H	-3.66667200	-0.75170300	-3.05233800
H	-3.68892900	-2.51878100	-3.16145900
C	-5.00958400	0.16634900	1.98340000
H	-3.97945300	0.51102800	2.11886700
H	-5.34499100	-0.27297500	2.92635200

H	-5.62703900	1.05713300	1.81383400
Ni	1.25696000	-0.09309100	0.45003900
Ni	-1.18954500	-0.22279100	0.23078400
C	-0.73389200	-1.65403300	1.24694500
C	-1.91847500	-1.18423700	1.79754900
H	-2.89429300	-1.55441200	1.49328200
C	1.12852900	-2.61993900	-0.24204600
H	1.70856900	-2.50775800	-1.15745000
C	-0.15617800	-3.14992000	-0.29240400
H	-0.65944700	-3.27425800	-1.24757300
H	-0.54034400	-3.75942600	0.52057100
C	1.56600100	-2.01440500	0.97352900
H	2.60953100	-2.08417500	1.27763900
C	0.47033100	-2.14559100	1.98321800
H	0.30029500	-3.18062200	2.33209100
Cl	1.27867500	0.81235200	2.64685900
Cl	-0.20388900	-0.39648500	-1.93350300
H	0.62678300	-1.52419500	2.86987600
H	-1.87208500	-0.77839200	2.81385100

14. References

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