Cobalt Catalyzed Reductive Dimethylcyclopropanation of 1,3-Dienes

Jacob Werth and Christopher Uyeda

Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

Correspondence: cuyeda@purdue.edu

Supporting Information

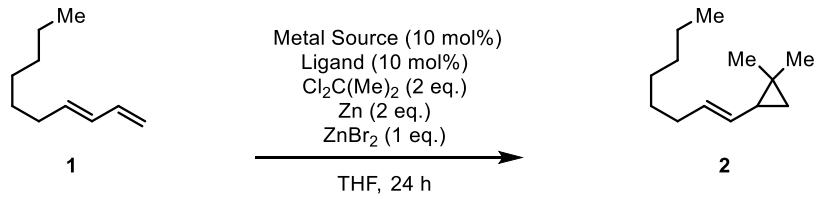
1. General Information

General considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of N_2. THF was dried and degassed by passage through a column of activated alumina and sparging with Ar gas. $CDCl_3$ was 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. PDI ligands were synthesized according to reported methods.[1,2] Zn powder (325 mesh, 99.9%) and $CoBr_2$ were purchased from Strem. $ZnBr_2$ was purchased from Sigma-Aldrich. $CoBr_2$ was dried in the oven and stored in the glovebox.

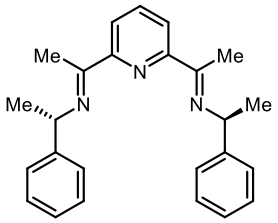
Physical methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were collected at room temperature on a Varian INOVA 300 MHz spectrometer, Bruker Avance 400 MHz spectrometer, or Bruker Avance 500 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High-resolution mass data were obtained using an Agilent 6320 Trap LC/MS, Agilent 5975C GC/MS, or Thermo Electron Corporation MAT 95XP-Trap instrument. ATR-IR data were collected on a Thermo Scientific Nicolet Nexus spectrometer.

2. Reaction Optimization Studies

General Procedure for Optimization Study. In an N_2-filled glovebox, a 2-dram vial was charged with the metal salt (0.014 mmol, 0.10 equiv), ligand (0.014 mmol, 0.10 equiv), THF (0.5 mL) and a magnetic stir bar. The metal complex was allowed to form by stirring at room temperature for 24 h. Then, Zn powder (18 mg, 0.28 mmol, 2.0 equiv), $ZnBr_2$ (18 mg, 0.28 mmol, 1.0 equiv), and a stock solution of the substrate (0.14 mmol, 1.0 equiv) and a mesitylene standard dissolved in THF (0.5 mL) were added. The reaction mixture was stirred at room temperature for approximately 15 min, during which time a deep violet color developed. Me_2CCl_2 (31.6 mg, 0.28 mmol, 2.0 equiv) was added, and stirring was continued at room temperature. After 24 h, the reaction mixture was diluted with CH_2Cl_2, and an aliquot was analyzed by GC (FID detector).



Entry	Metal Source	Ligand	Yield **2** [%]
1	–	–	< 1
2	–	2-*t*-BuPDI (**L1**)	< 1
3	$CoBr_2$	–	< 1
4	$CoBr_2$	2-*t*-BuPDI (**L1**)	93
5	$CoBr_2$	2,4,6-MePDI (**L2**)	77
6	$CoBr_2$	3,5-*t*-BuPDI (**L3**)	8
7	$CoBr_2$	2,6-*i*-PrPDI (**L4**)	2
8	$NiBr_2$	2-*t*-BuPDI (**L1**)	5
9	$FeBr_2$	2-*t*-BuPDI (**L1**)	4
10	$CoBr_2$	2,6-*i*-PrIP (**L5**)	2
11	$CoBr_2$	2,6-*i*-PrDAD (**L6**)	<1
12	$CoBr_2$	bpy (**L7**)	4
13	$CoBr_2$	terpy (**L8**)	1
14	$CoBr_2$	Chiral PDI (**L9**)	9
15	$CoBr_2$	Chiral PDI (**L10**)	17
16[b]	$CoBr_2$	2-*t*-BuPDI (**L1**)	87
17[c]	$CoBr_2$	2-*t*-BuPDI (**L1**)	78
18[d]	$CoBr_2$	2-*t*-BuPDI (**L1**)	79
19[e]	$CoBr_2$	2-*t*-BuPDI (**L1**)	26
20[f]	$CoBr_2$	2-*t*-BuPDI (**L1**)	>99
21[g]	$CoBr_2$	2-*t*-BuPDI (**L1**)	7
22[h]	$CoBr_2$	2-*t*-BuPDI (**L1**)	11



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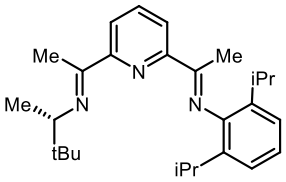
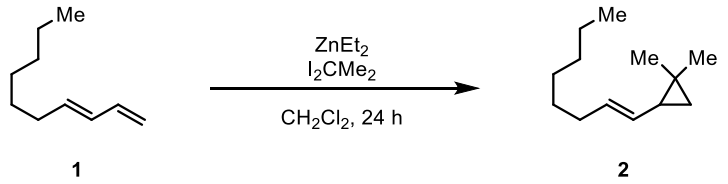


L10

Figure S1. Optimization studies probing metal and ligand sources. [b] Modifications from standard conditions: without $ZnBr_2$. [c] Modifications from standard conditions: 1.1 equiv of Me_2CCl_2. [d] Modifications from standard conditions: 2.0 equiv of Me_2CBr_2. [e] Modifications from standard conditions: 2.0 equiv of I_2CMe_2. [f] Modifications from standard conditions: 1.1 equiv of Zn. [g] Modifications from standard conditions: 1 equiv of $MgBr_2$ (No $ZnBr_2$). [h] Modifications from standard conditions: 1 equiv of LiCl (No $ZnBr_2$).



General Procedure for Zinc Carbenoid Dimethylcyclopropanation.[3] In an N_2-filled glovebox, a 2-dram vial was charged with **1** (0.14 mmol, 1.0 equiv), CH_2Cl_2 (1.0 mL), mesitylene, and a magnetic stir bar. Et_2Zn (69 mg, 0.56 mmol, 4.0 equiv) was added dropwise to the solution at –30 °C. I_2CMe_2[4] (166 mg, 0.56 mmol, 4.0 equiv) was added dropwise, and the reaction was allowed to warm to room temperature and stirred for 24 h. The crude reaction mixture was diluted with CH_2Cl_2, and an aliquot was analyzed by GC (FID detector). Conversion of **1**: 70%. Yield of **2**: 45%.

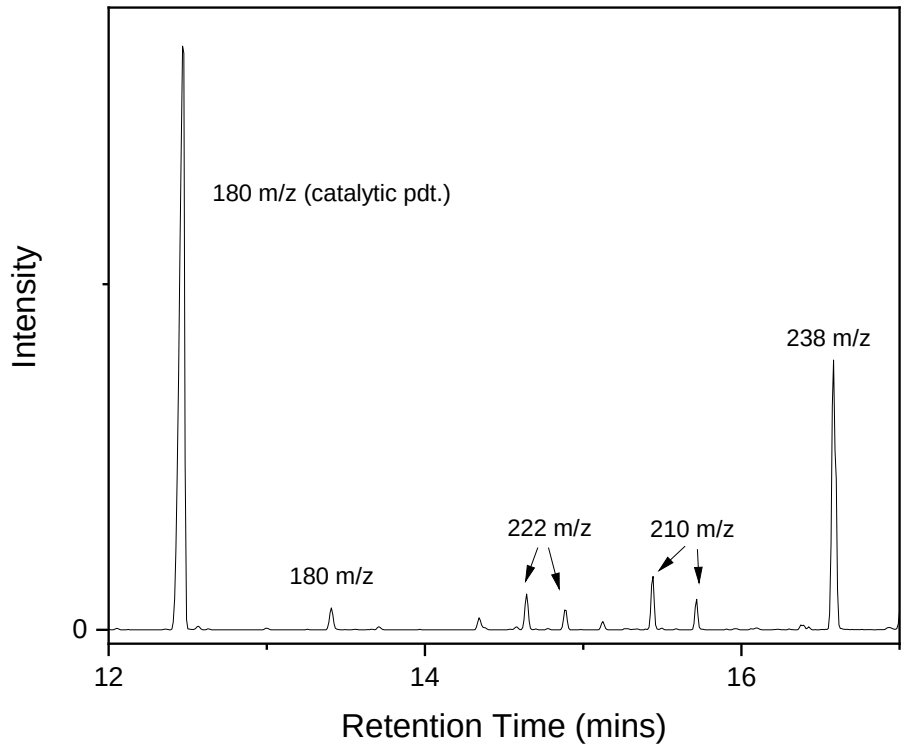


Figure S2. GC/MS analysis of the crude reaction mixture (**1** + I_2CMe_2/Et_2Zn). Additional products correspond to isomers of **2**, products containing two Me_2C fragments, and products containing additional Et groups.

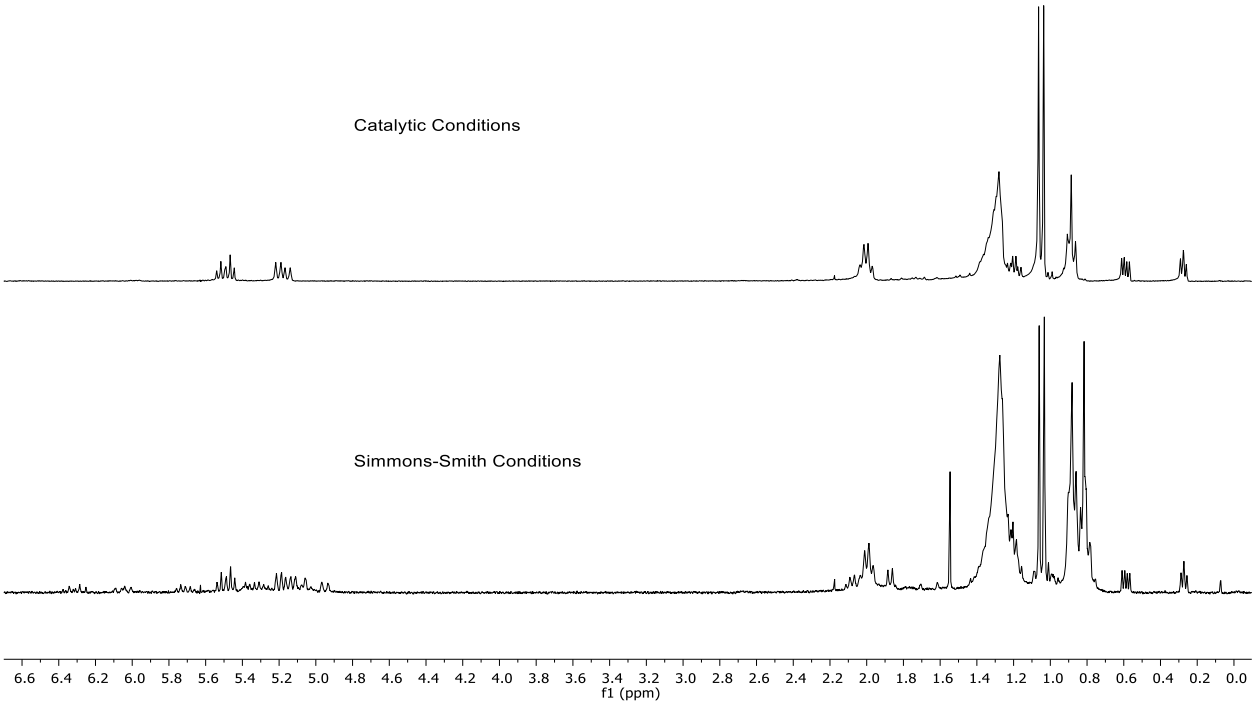


Figure S3. A ^{1}H NMR comparison of the crude reaction mixtures for the cobalt-catalyzed cyclopropanation of **1** (top) and the non-catalytic Furukawa-type Simmons–Smith reaction of **1** (bottom).

3. Procedures for the Dimethylcyclopropanation of 1,3-Dienes

Preparation of [$^{2\text{-}t\text{Bu}}$PDI]$CoBr_2$ (3). In an N_2-filled glovebox, a 5-dram vial was charged with $^{2\text{-}t\text{Bu}}$PDI[5] (100 mg, 0.23 mmol, 1.0 equiv), $CoBr_2$ (anhydrous) (50.1 mg, 0.23 mmol, 1.0 equiv), THF (7.0 mL) and a magnetic stir bar. The mixture was stirred at room temperature for 24 h. After 24 h, the mixture was concentrated to dryness under vacuum to produce a mustard-yellow solid.

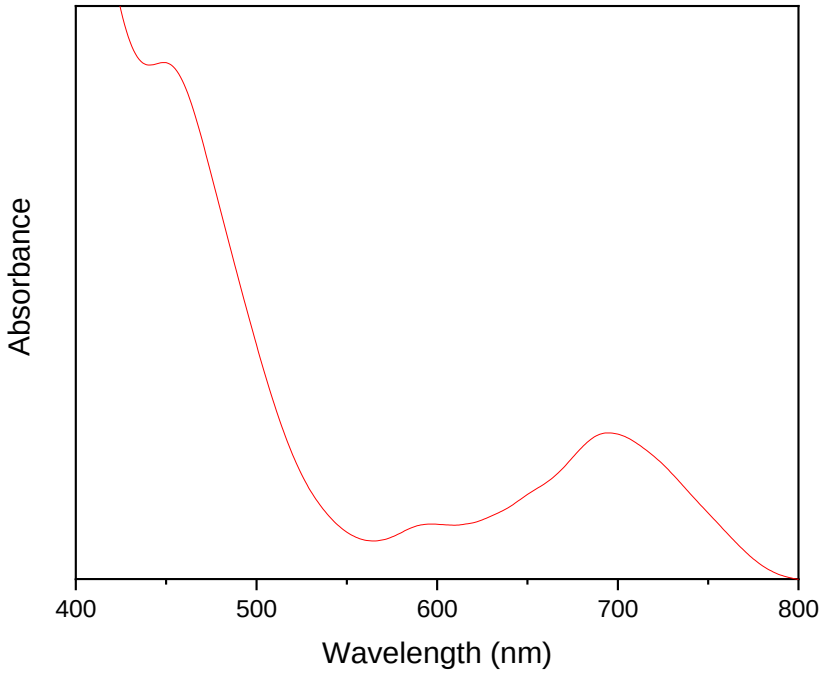
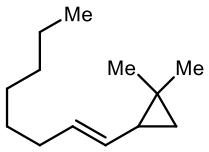


Figure S4. UV-Vis spectrum of [$^{2\text{-}t\text{Bu}}$PDI]$CoBr_2$ **(3)**.

General procedure for the dimethylcyclopropanation of 1,3-dienes. In an N_2-filled glovebox, a 2-dram vial was charged with the [$^{2\text{-}t\text{Bu}}$PDI]$CoBr_2$ catalyst **3** (9.0 mg, 0.014 mmol, 0.10 equiv), the substrate (0.14 mmol, 1.0 equiv), Zn powder (18 mg, 0.28 mmol, 2.0 equiv), $ZnBr_2$ (31 mg, 0.14 mmol, 1.0 equiv), THF (1.0 mL), and a magnetic stir bar. The reaction mixture was stirred at room temperature for approximately 15 min during which time a deep violet color developed. Me_2CCl_2 (31.6 mg, 0.28 mmol, 2.0 equiv) was added, and stirring was continued at room temperature. After 24 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly loaded onto a SiO_2 column for purification.



(2). The reaction was conducted using (*E*)-deca-1,3-diene[6] without modification from the general procedure to provide **2** as a colorless oil.

Run 1: 24.7 mg (98% yield). Run 2: 22.2 mg (88% yield).

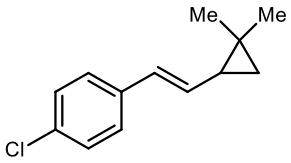
Purification: SiO_2 column; pentane.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54-5.44 (m, 1H), 5.22-5.14 (m, 1H), 2.00 (q, *J* = 6.52 Hz, 2H), 1.36-1.26 (m, 8H), 1.23-1.16 (m, 1H), 1.06 (s, 3H), 1.04 (s, 3H), 0.89 (t, *J* = 6.97 Hz, 3H), 0.61-0.57 (m, 1H), 0.28 (t, *J* = 4.71 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 130.3, 130.1, 32.8, 31.8, 29.8, 28.9, 27.5, 27.0, 22.7, 21.0, 20.5, 18.0, 14.1.

HRMS (ESI) calc. for $C_{13}H_{23}$: m/z=179.1794, found: m/z=179.1792

IR (film): 3052, 3001, 2952, 2915, 2851, 1452, 1365, 963 cm^{-1}



(4). The reaction was conducted using (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene[7] without modification from the general procedure to provide **4** as a colorless oil.

Run 1: 27.8 mg (96% yield). Run 2: 27.2 mg (94% yield).

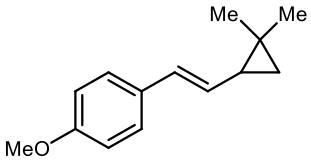
Purification: SiO_2 column; pentane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 4H), 6.42 (d, *J* = 15.70 Hz, 1H), 6.01-5.92 (m, 1H), 1.47-1.39 (m, 1H), 1.15 (s, 6H), 0.83-0.79 (m, 1H), 0.52 (t, *J* = 4.87 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 136.5, 132.5, 131.9, 128.6, 128.0, 126.8, 28.6, 27.1, 22.5, 20.8, 19.9.

HRMS (ESI) calc. for $C_{13}H_{14}Cl$: m/z=205.0779, found: m/z=205.0781

IR (film): 3001, 2944, 2858, 1645, 1487, 1444, 1085, 971 cm^{-1}



(5). The reaction was conducted using (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene[8] without modification from the general procedure to provide **5** as a colorless oil.

Run 1: 26.6 mg (94% yield). Run 2: 26.9 mg (95% yield).

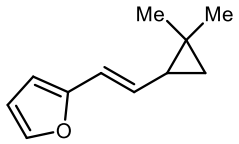
Purification: SiO_2 column; CH_2Cl_2

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.50 Hz, 2H), 6.84 (d, *J* = 8.44 Hz, 2H), 6.43 (d, *J* = 15.69 Hz, 1H), 5.86 (dd, *J* = 8.87, 6.54 Hz, 1H), 3.81 (s, 3H), 1.45-1.37 (m, 1H), 1.14 (s, 6H), 0.79-0.75 (m, 1H), 0.48 (t, *J* = 4.78 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.4, 130.9, 129.4, 128.6, 126.7, 113.9, 55.3, 28.5, 27.1, 22.1, 20.8, 19.4.

HRMS (ESI) calc. for $C_{14}H_{17}O$: m/z=201.1274, found: m/z=201.1277

IR (film): 2995, 2958, 1609, 1509, 1236, 1164, 1049, 934 cm^{-1}



(6). The reaction was conducted using (*E*)-2-(buta-1,3-dien-1-yl)furan[9] without modification from the general procedure to provide **6** as a colorless oil.

Run 1: 16.8 mg (74% yield). Run 2: 15.9 mg (70% yield).

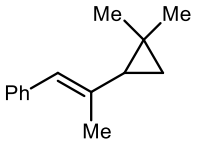
Purification: SiO_2 column; CH_2Cl_2

^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.62 Hz, 1H), 6.34 (dd, *J* = 1.84, 1.42 Hz, 1H), 6.29 (d, *J* = 15.73 Hz, 1H), 6.10 (d, *J* = 3.23 Hz, 1H), 5.94 (dd, *J* = 9.24, 6.48 Hz, 1H), 1.41-1.33 (m, 1H), 1.13-1.12 (m, 6H), 0.80-0.76 (m, 1H), 0.49 (t, *J* = 4.78 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.5, 140.9, 130.8, 117.8, 111.1, 105.2, 28.4, 27.0, 22.5, 20.8, 19.9.

HRMS (ESI) calc. for $C_{11}H_{13}O$: m/z=161.0961, found: m/z=161.0960

IR (film): 2995, 2944, 2865, 1444, 1150, 1006, 949, 906 cm^{-1}



(7). The reaction was conducted using (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene[10] without modification from the general procedure to provide **7** as a colorless oil.

Run 1: 23.7 mg (91% yield). Run 2: 23.0 mg (88% yield).

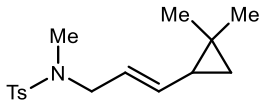
Purification: SiO_2 column; pentane

^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.27 (m, 3H), 7.27-7.17 (m, 2H), 6.19 (s, 1H),
1.95 (s, 3H), 1.36 (t, *J* = 6.97 Hz, 1H), 1.21 (s, 3H), 1.02 (s, 3H), 0.70 (t, *J* = 5.0 Hz, 1H), 0.60-0.56 (m, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.6, 138.0, 128.8, 128.0, 125.8, 125.0, 34.4, 27.5, 20.1, 19.3, 18.4, 17.8.

HRMS (ESI) calc. for $C_{14}H_{17}$: m/z=185.1325, found: m/z=185.1323

IR (film): 3073, 2937, 2851, 1652, 1595, 1452, 1372, 1071, 913 cm^{-1}



(8). The reaction was conducted using (*E*)-N,4-dimethyl-N-(penta-2,4-dien-1-yl)benzenesulfonamide[11] without modification from the general procedure to provide **8** as a yellow oil.

Run 1: 23.4 mg (57% yield). Run 2: 20.5 mg (50% yield).

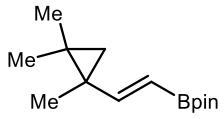
Purification: SiO_2 column; hexane/EtOAc (80:20)

^1H NMR (300 MHz, $CDCl_3$) δ7.67 (d, *J* = 8.29 Hz, 2H), 7.32 (d, *J* = 8.44 Hz, 2H), 5.42-5.26 (m, 2H), 3.63-3.51 (m, 2H), 2.64 (s, 3H), 2.43 (s, 3H), 1.26-1.17 (m, 1H), 1.05 (s, 3H), 0.99 (s, 3H), 0.67-0.62 (m, 1H), 0.30 (t, *J* = 4.89 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.2, 136.5, 134.6, 129.6, 127.5, 123.2, 52.5, 33.9, 27.2, 26.9, 21.6, 21.5, 20.5, 18.9.

HRMS (ESI) calc. for $C_{16}H_{23}NO_2SNa$: m/z=316.1342, found: m/z=316.1346

IR (film): 2966, 2915, 2872, 1430, 1336, 1164, 1078, 956, 906 cm^{-1}



(9). The reaction was conducted using (*E*)-4,4,5,5-tetramethyl-2-(3-methylbuta-1,3-dien-1-yl)-1,3,2-dioxaborolane[12] without modification from the general procedure to provide **9** as a colorless oil.

Run 1: 29.8 mg (90% yield). Run 2: 30.1 mg (91% yield).

Purification: SiO_2 column; CH_2Cl_2

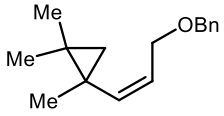
^1H NMR (300 MHz, $CDCl_3$) δ 6.54 (d, *J* = 18.07 Hz, 1H), 5.41 (d, *J* = 18.05 Hz, 1H), 1.25 (s, 12H), 1.19 (s, 3H), 1.13 (s, 6H), 0.79 (d, *J* = 4.38 Hz, 1H), 0.51 (d, *J* = 4.37 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.1, 82.8, 29.9, 28.2, 24.8, 24.4, 22.8, 22.7, 17.4.

^{11}B NMR (96 MHz, $CDCl_3$) δ 29.85.

HRMS (ESI) calc. for $C_{14}H_{25}BO_2$: m/z=236.2057, found: m/z=236.2054

IR (film): 2973, 2937, 1609, 1344, 1307, 1164, 956 cm^{-1}



(10). The reaction was conducted using (*Z*)-(((4-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene without modification from the general procedure to provide **10** as a colorless oil.

Run 1: 31.0 mg (96% yield). Run 2: 31.0 mg (96% yield).

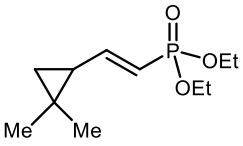
Purification: SiO_2 column; CH_2Cl_2

^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 5.75-5.71 (m, 1H), 5.67-5.60 (m, 1H), 4.55 (s, 2H), 4.27-4.21 (m, 1H), 4.15-4.09 (m, 1H), 1.12 (s, 3H), 1.09 (s, 3H), 1.01 (s, 3H), 0.38 (d, *J* = 4.04 Hz, 1H), 0.33 (d, *J* = 4.04 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.4, 137.0, 128.8, 128.4, 127.9, 127.6, 72.6, 66.9, 28.1, 23.8, 23.3, 21.3, 21.2, 20.1.

HRMS (ESI) calc. for $C_{16}H_{23}O$: m/z=231.1743, found: m/z=231.1741

IR (film): 3030, 2980, 2944, 2851, 1452, 1350, 1064, 1021, 934 cm^{-1}



(11). The reaction was conducted using diethyl (*E*)-buta-1,3-dien-1-ylphosphonate[14] without modification from the general procedure to provide **11** as a colorless oil.

Run 1: 30.2 mg (93% yield). Run 2: 29.6 mg (91% yield).

Purification: SiO_2 column; EtOAc

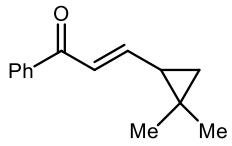
^1H NMR (300 MHz, $CDCl_3$) δ 6.71-6.55 (m, 1H), 5.65 (dd, *J* = 16.82, 5.6 Hz, 1H), 4.20-4.08 (m, 4H), 1.47-1.38 (m, 1H), 1.32 (t, *J* = 7.66 Hz, 6H), 1.17 (s, 3H), 1.11 (s, 3H), 0.94-0.90 (m, 1H), 0.75 (t, *J* = 4.85 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.3, 111.9 (d, *J* = 194.2 Hz), 62.9, 30.4, 30.2, 26.9, 24.4, 22.7, 20.9, 16.3.

^{31}P NMR (121 MHz, $CDCl_3$) δ 20.8

HRMS (ESI) calc. for $C_{11}H_{22}O_3P$: m/z=233.1301, found: m/z=233.1303

IR (film): 2980, 2865, 1616, 1207, 1021, 956, 826 cm^{-1}



(12). The reaction was conducted using (*E*)-1-phenylpenta-2,4-dien-1-one[13] without modification from the general procedure to provide **12** as a colorless oil.

Run 1: 14.0 mg (50% yield). Run 2: 15.1 mg (54% yield).

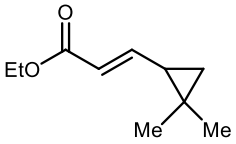
Purification: SiO_2 column; hexane/EtOAc (95:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.58-7.52 (m, 1H), 7.49-7.43 (m, 2H), 7.03 (d, *J* = 15.05 Hz, 1H), 6.90-6.82 (m, 1H), 1.61-1.54 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H), 1.06-1.01 (m, 1H), 0.79 (t, *J* = 4.75 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 189.7, 152.8, 138.3, 132.4, 128.4, 128.4 124.4, 29.5, 27.0, 25.2, 23.3, 21.1.

HRMS (APCI) calc. for $C_{14}H_{17}O$: m/z=201.1274, found: m/z=201.1276

IR (film): 3059, 2958, 2872, 1667, 1602, 1279, 1178, 1006, 920 cm^{-1}



(13). The reaction was conducted using ethyl (*E*)-penta-2,4-dienoate[14] without modification from the general procedure to provide **13** as a colorless oil.

Run 1: 21.0 mg (89% yield). Run 2: 21.4 mg (91% yield).

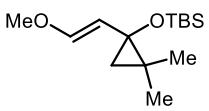
Purification: SiO_2 column; hexane:CH_2Cl_2 (1:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (dd, *J* = 14.80, 10.92 Hz, 1H), 5.88 (d, *J* = 15.35 Hz, 1H), 4.17 (q, *J* = 8.02 Hz, 2H), 1.46-1.38 (m, 1H), 1.28 (td, *J* = 7.13, 1.24 Hz, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 0.94-0.90 (m, 1H), 0.66 (t, *J* = 4.92 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 166.7, 151.3, 119.6, 60.0, 28.3, 26.9, 24.3, 22.3, 20.9, 14.3.

HRMS (ESI) calc. for $C_{10}H_{17}O_2$: m/z=169.1223, found: m/z=169.1221

IR (film): 2973, 2944, 2865, 1724, 1630, 1221, 1143, 1035 cm^{-1}



(14). The reaction was conducted using *trans*-3-(*tert*-Butyldimethylsilyloxy)-1-methoxy-1,3-butadiene

without modification from the general procedure to provide **14** as a colorless oil.

Run 1: 24.3 mg (68% yield). Run 2: 25.6 mg (72% yield).

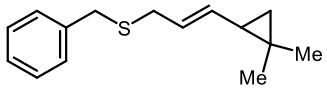
Purification: SiO_2 column; CH_2Cl_2

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (d, *J* = 12.7 Hz, 1H), 5.04 (d, *J* = 12.6 Hz, 1H), 3.55 (s, 3H), 1.19 (s, 3H), 0.94 (s, 3H), 0.86 (s, 9H), 0.60 (d, *J* = 5.3 Hz, 1H), 0.42 (d, *J* = 5.3 Hz, 1H), 0.09 (d, *J* = 3.6 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.6, 104.3, 61.5, 56.0, 25.9, 24.3, 22.3, 21.4, 20.2, 18.1.

HRMS (ESI) calc. for $C_{14}H_{27}O_2Si$: m/z=255.1775, found: m/z=255.1774

IR (film): 2952, 2923, 2844, 1645, 1458, 1258, 1135, 941 cm^{-1}



(15). The reaction was conducted using (*E*)-benzyl(penta-2,4-dien-1-yl)sulfane[15] without modification from the general procedure to provide **15** as a colorless oil.

Run 1: 25.7 mg (79% yield). Run 2: 27 mg (83% yield).

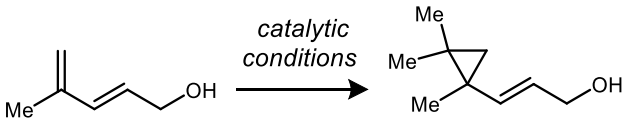
Purification: SiO_2 column; CH_2Cl_2

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 5.50 (dt, *J* = 14.6, 7.2 Hz, 1H), 5.26 (dd, *J* = 15.0, 9.5 Hz, 1H), 3.68 (s, 2H), 3.03 (d, *J* = 7.2 Hz, 2H), 1.30 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.10 (s, 3H), 1.08 (s, 3H), 0.69 (dd, *J* = 8.7, 4.3 Hz, 1H), 0.36 (t, *J* = 4.9 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.5, 134.2, 128.9, 128.3, 126.7, 125.0, 34.8, 33.4, 27.3, 26.9, 21.5, 20.6, 18.6.

HRMS (ESI) calc. for $C_{15}H_{21}S$: m/z=233.1359, found: m/z=233.1358

IR (film): 3030, 2930, 2865, 1501, 1437, 963, 913 cm^{-1}



(18). The reaction was conducted using (*E*)-4-methylpenta-2,4-dien-1-ol **16**[16] without modification from the general procedure to provide **18** as a yellow oil.

Run 1: 11.2 mg (57% yield). Run 2: 11.4 mg (58% yield).

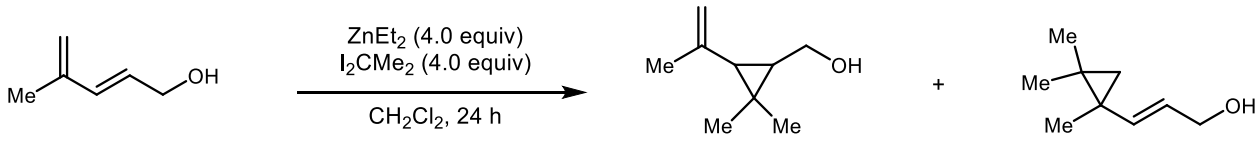
Purification: SiO_2 column; hexane/EtOAc (90:10)

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64-5.62 (m, 2H), 4.14-4.11 (m, 2H), 1.24-1.22 (m, 1H), 1.20 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H), 0.60 (d, *J* = 4.55 Hz, 1H), 0.42 (d, *J* = 4.39 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.3, 126.5, 64.2, 28.4, 25.4, 22.9, 22.6, 22.3, 18.5.

HRMS (ESI) calc. for $C_9H_{15}O$: m/z=139.1117, found: m/z=139.1120

IR (film): 3324, 2980, 2923, 2858, 1659, 1452, 1379, 1085, 956, 906 cm^{-1}



16 **17** **18**

4:1 rr (35% combined yield)

Non-Catalytic Furukawa-Type Simmons–Smith Cyclopropanation of 16. In an N_2-filled glovebox, a 2-dram vial was charged with **16** (0.14 mmol, 1.0 equiv), CH_2Cl_2 (1.0 mL), and a magnetic stir bar. Et_2Zn (69 mg, 0.56 mmol, 4.0 equiv) was added dropwise to the solution at –30 °C. I_2CMe_2 (166 mg, 0.56 mmol, 4.0

equiv) was added dropwise, and the reaction was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was concentrated under reduced pressure, and the crude residue was directly loaded onto a SiO_2 column to obtain a mixture of **16**, **17**, and **18**. Combined Yield of **17 + 18**: 35%. Ratio **17**:**18** = 4:1.

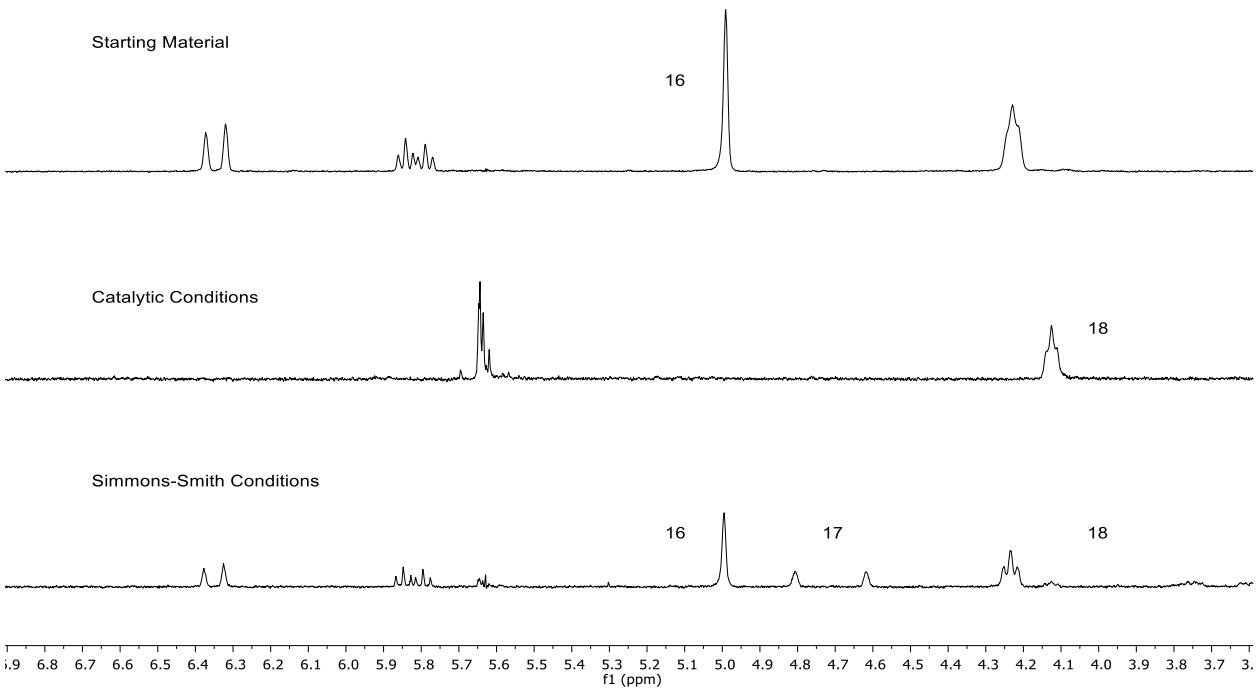
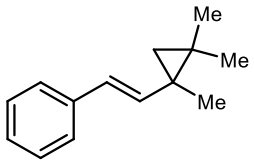


Figure S5. ^{1}H NMR comparison of product **18** obtained from the catalytic dimethylcyclopropanation (middle) and the mixture of **17**, **18**, and recovered starting material (**16**) obtained under the Furukawa-type Simmons–Smith conditions (bottom).



(26). The reaction was conducted using (*E*)-(3-methylbuta-1,3-dien-1-yl)benzene[10] without modification from the general procedure to provide **26** as a colorless oil.

Run 1: 25.8 mg (99% yield). Run 2: 25.3 mg (97% yield).

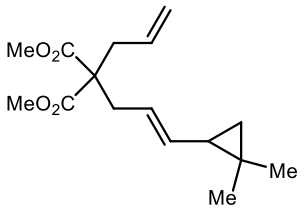
Purification: SiO_2 column; pentane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H), 7.22-7.17 (m, 1H), 6.39 (d, *J* = 15.97 Hz, 1H), 6.24 (d, *J* = 15.97 Hz, 1H), 1.33 (s, 3H), 1.22 (s, 3H), 1.17 (s, 3H), 0.79 (d, *J* = 4.34 Hz, 1H), 0.53 (d, *J* = 4.41 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.3, 137.0, 128.5, 127.4, 126.5, 125.7, 28.8, 26.4, 23.3, 23.1, 22.5, 18.7.

HRMS (ESI) calc. for $C_{14}H_{17}$: m/z=185.1325, found: m/z=185.1322

IR (film): 3016, 2987, 2944, 2865, 1630, 1444, 1114, 1064, 971 cm^{-1}



(28). The reaction was conducted using dimethyl (*E*)-2-allyl-2-(penta-2,4-dien-1-yl)malonate[17] without modification from the general procedure to provide **28** as a yellow oil.

Run 1: 35.7mg (91% yield). Run 2: 34.5 mg (88% yield).

Purification: SiO_2 column; hexane/EtOAc (95:5)

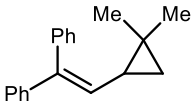
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72-5.57 (m, 1H), 5.27 (t, *J* = 5.99 Hz, 2H), 5.11 (d, *J* = 5.81 Hz, 1H), 5.06 (s, 1H), 3.70 (s, 6H), 2.65-2.59 (m, 4H), 1.22-1.15 (m, 1H), 1.04 (s, 3H), 1.01 (s, 3H), 0.63-0.59 (m, 1H), 0.27 (t, *J* = 4.67 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.3, 135.7, 132.5, 122.6, 119.0, 58.0, 52.3, 36.8, 35.9, 27.5, 27.0, 21.4, 20.6, 18.5.

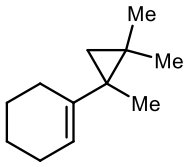
HRMS (ESI) calc. for $C_{16}H_{25}O_4$: m/z=281.1747, found: m/z=281.1746

IR (film): 2987, 2958, 2858, 1724, 1437, 1200, 963, 920 cm^{-1}

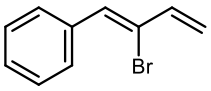
Additional Substrates Exhibiting Modest Yields:



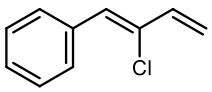
^{1}H NMR Yield: 9%



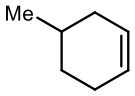
^{1}H NMR Yield: 19%



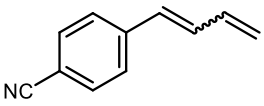
Messy NMR



Messy NMR

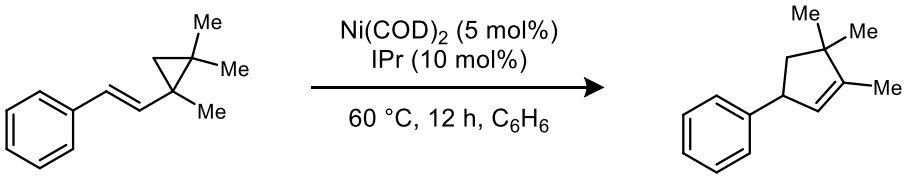


Low Conversion



Low Conversion

4. Procedures for the Vinylcyclopropane Ring-Opening Reactions



(27). The reaction was conducted using the procedure reported by Louie using **26** to provide **27** as a colorless oil (65% yield, 10.2 mg).[18]

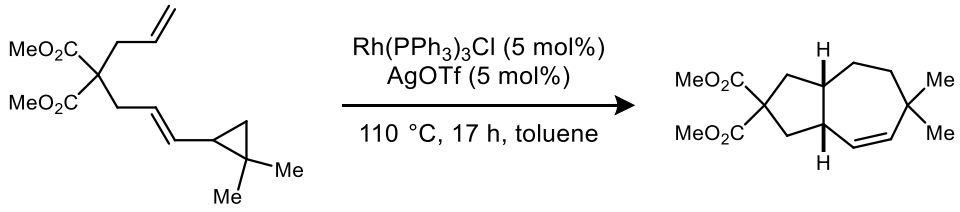
Purification: SiO_2 column; pentane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.15 (m, 3H), 5.29 (t, *J* = 1.46 Hz, 1H), 3.88-3.78 (m, 1H), 2.25 (dd, *J* = 12.58, 8.01 Hz, 1H), 1.71 (dd, *J* = 1.55, 0.81, Hz, 3H), 1.61 (dd, *J* = 8.30, 4.25, Hz, 1H), 1.08 (s, 3H), 1.08 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.3, 147.0, 128.3, 127.3, 126.2, 125.8, 51.2, 48.0, 46.2, 27.6, 26.0, 12.3.

HRMS (APCI) calc. for $C_{14}H_{17}$: m/z=185.1325, found: m/z=185.1326

IR (film): 3023, 2944, 2930, 2844, 1602, 1501, 1444, 1358, 1035, 834 cm^{-1}



(29). The reaction was conducted using the procedure reported by Wender using **28** to provide **29** as a colorless oil (77% yield, 28.1 mg).[19]

Purification: SiO_2 column; hexane/EtOAc (95:5)

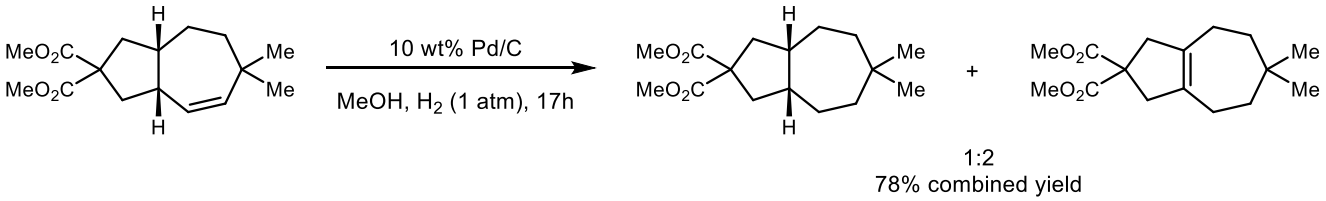
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18-5.14 (m, 2H), 3.71 (s, 6H), 2.86 (qd, *J* = 7.64, 2.48 Hz, 1H), 2.50-2.39 (m, 2H), 2.26-2.18 (m, 1H), 2.11 (dd, *J* = 7.95, 5.62 Hz, 1H), 1.95 (dd, *J* = 8.17, 5.12 Hz, 1H), 1.74 (d, *J* = 4.28 Hz, 1H), 1.66-1.60 (m, 1H), 1.51-1.48 (m, 2H), 0.99 (s, 3H), 0.96 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.2, 172.9, 139.6, 126.6, 59.0, 52.7, 52.7, 43.9, 41.4, 41.3, 40.8, 38.7, 37.5, 31.2, 29.8, 26.9.

HRMS (ESI) calc. for $C_{16}H_{25}O_4$: m/z=281.1747, found: m/z=281.1752.

IR (film): 3009, 2958, 2858, 1724, 1437, 1250, 1207, 1150, 1064 cm^{-1}

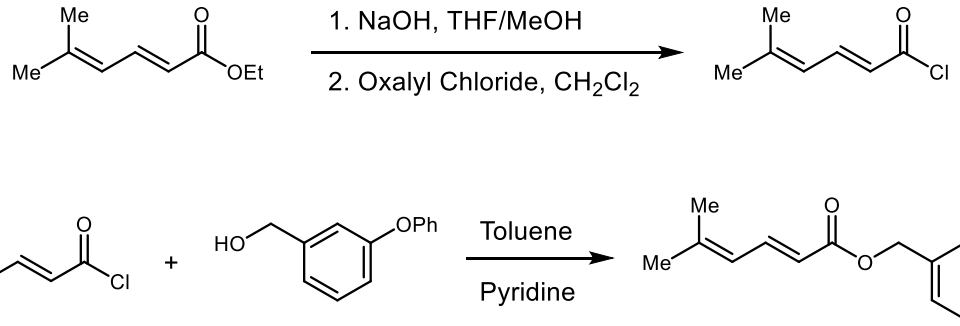
Stereochemical Assignment for 29. The relative stereochemistry of the ring fusion was assigned as cis by analogy to the products obtained by Wender. Additionally, **29** was hydrogenated using a Pd/C catalyst to obtain a mixture of the hydrogenated product and an alkene migration product. The hydrogenated product was assigned as the cis diastereomer based on the non-equivalency ^{1}H NMR signals corresponding to the two methyl groups and the two methyl esters.



1:2
78% combined yield

5. Synthesis and Characterization of Dienoic Esters

Procedure A[20,21]:



Step 1: A 100-mL round bottom flask was charged with the dienoic ester[25] (4.1 mmol) and a THF/MeOH (1:2, 70 mL) solvent mixture. An aqueous solution of 2 M NaOH (19 mL) was added dropwise. The reaction mixture was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was dissolved in water (50 mL), and the aqueous phase was washed with Et_2O (3 × 20 mL). The aqueous phase was acidified with concentrated HCl (aq) and extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with water (2 × 25 mL) then saturated aqueous NaCl (2 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under vacuum to give provide the dienoic acid[22] (460 mg, 89% yield), which was carried forward without purification.

Step 2: To a solution of the dienoic acid (460 mg, 3.6 mmol) dissolved in anhydrous CH_2Cl_2 (20 mL) was added oxalyl chloride (0.65 mL, 7.2 mmol). The mixture was stirred at room temperature for 12 h. The solvent was evaporated under vacuum to provide the acid chloride (**S1**) (505 mg, 97%) as a yellow oil. The crude product was carried forward without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 14.60, 11.72 Hz, 1H), 6.08 (d, *J* = 11.78 Hz, 1H), 5.98 (d, *J* = 14.55 Hz, 1H), 1.97 (s, 3H), 1.95 (s, 3H).

Step 3: To a solution of 3-phenoxy-benzenemethanol (505 mg, 3.5 mmol) in dry toluene (10 mL) was added pyridine (0.5 mL). Acid chloride **S1** was added dropwise, and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with water (10 mL) and extracted with Et_2O (3 × 20 mL). The organic phase was washed with 1 M HCl then saturated NaCl (aq). The organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was purified by column chromatography (hexane/CH_2Cl_2) to afford **S2** in an isomerically pure form (452 mg, 43% yield).

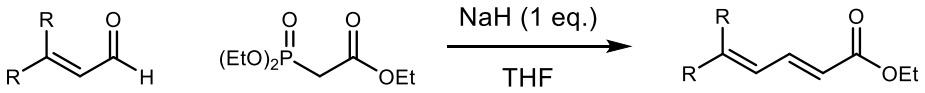
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 10.82, 3.56 Hz, 1H), 7.34 (q, *J* = 7.53 Hz, 3H), 7.15-7.09 (m, 2H), 7.05-7.01 (m, 3H), 6.97-6.93 (m, 1H), 6.00 (d, *J* = 11.61 Hz, 1H), 5.82 (d, *J* = 15.18 Hz, 1H), 5.17 (s, 2H), 1.89 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.4, 157.5, 157.0, 146.9, 141.7, 138.4, 129.8, 123.7, 123.4, 122.6, 119.0, 118.2, 118.0, 65.4, 26.6, 19.0.

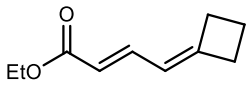
HRMS (ESI) calc. for $C_{20}H_{20}O_3$: m/z=309.1485, found: m/z=309.1481.

IR (film): 3052, 2901, 1695, 1566, 1466, 1258, 1207, 1121, 985 cm^{-1}

Procedure B:[23]



The following dienoic esters were synthesized using the Horner—Wadsworth—Emmons reaction following the literature procedure:



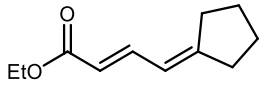
(S3). The reaction was conducted using 2-cyclobutylideneacetaldehyde[24] without modification from procedure B to provide **S3** as a colorless oil (56% yield)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 15.32, 11.47, Hz, 1H), 5.97-5.86 (m, 1H), 5.70 (dt, *J* = 15.30, 0.81 Hz, 1H), 4.19 (q, *J* = 7.13 Hz, 2H), 2.89 (t, *J* = 7.99 Hz, 2H), 2.80 (t, *J* = 7.92 Hz, 2H), 2.05 (tt, *J* = 8.20, 7.39 Hz, 2H), 1.28 (t, *J* = 7.14 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.6, 157.3, 140.8, 119.5, 117.5, 60.1, 32.1, 30.7, 16.9, 14.3.

HRMS (ESI) calc. for $C_{10}H_{15}O_2$: m/z=167.1067, found: m/z=167.1068

IR (film): 2973, 2937, 2908, 1716, 1652, 1616, 1258, 1186, 1129, 971 cm^{-1}



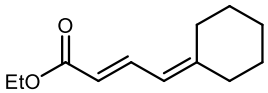
(S4). The reaction was conducted using 2-cyclopentylideneacetaldehyde[25] without modification from procedure B to provide **S4** as a colorless oil (41% yield)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 15.17, 11.66, Hz, 1H), 6.09 (d, *J* = 11.60 Hz, 1H), 5.71 (d, *J* = 15.24 Hz, 1H), 4.20 (q, *J* = 7.13 Hz, 2H), 2.49 (t, *J* = 6.85 Hz, 2H), 2.39 (t, *J* = 6.97 Hz, 2H), 1.74 (quintet, *J* = 6.78 Hz, 2H), 1.68 (quintet, *J* = 6.59 Hz, 2H), 1.29 (t, *J* = 7.12 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.7, 159.1, 142.5, 119.1, 117.7, 60.1, 34.8, 30.2, 26.2, 26.0, 14.4.

HRMS (ESI) calc. for $C_{11}H_{17}O_2$: m/z=181.1223, found: m/z=181.1222.

IR (film): 2966, 2880, 1702, 1630, 1372, 1258, 1200, 1129, 963 cm^{-1}



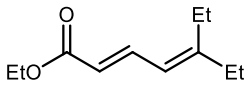
(S5). The reaction was conducted using 2-cyclohexylideneacetaldehyde[25] without modification from procedure B to provide **S5** as a colorless oil (38% yield)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 15.20, 11.70, Hz, 1H), 5.93 (d, *J* = 11.56 Hz, 1H), 5.79 (d, *J* = 15.17 Hz, 1H), 4.20 (q, *J* = 7.12 Hz, 2H), 2.42-2.36 (m, 2H), 2.24-2.18 (m, 2H), 1.63-1.57 (m, 6H), 1.29 (t, *J* = 7.11 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.8, 154.3, 140.4, 120.5, 118.8, 60.1, 37.8, 29.8, 28.5, 27.9, 26.5, 14.4.

HRMS (ESI) calc. for $C_{12}H_{19}O_2$: m/z=195.1380, found: m/z=195.1377

IR (film): 2930, 2844, 1702, 1624, 1301, 1272, 1164, 1129, 977, 870 cm^{-1}



(S6). The reaction was conducted using 3-ethylpent-2-enal[26] without modification from procedure B to provide **S6** as a colorless oil (54% yield)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, *J* =15.12, 11.64, Hz, 1H), 5.94 (d, *J* = 11.78 Hz, 1H), 5.80 (d, *J* = 15.14 Hz, 1H), 4.21 (q, *J* = 7.13 Hz, 2H), 2.32 (q, *J* = 7.58 Hz, 2H), 2.19 (q, *J* = 7.49 Hz, 2H), 1.30 (dt, *J* = 7.13, 1.51 Hz, 3H), 1.06 (dq, *J* = 3.98, 1.49 Hz, 6H).

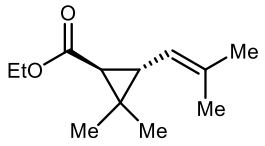
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.7, 157.4, 140.7, 121.3, 119.0, 60.1, 30.0, 24.4, 14.4, 13.8, 12.4.

HRMS (ESI) calc. for $C_{11}H_{19}O_2$: m/z=183.1380, found: m/z=183.1379.

IR (film): 2980, 2937, 2837, 1702, 1630, 1358, 1272, 1135, 985, 877 cm^{-1}

6. Procedures for the Dimethylcyclopropanation of Dienoic Esters

General procedure for the dimethylcyclopropanation of dienoic esters. In an N_2-filled glovebox, a 2-dram vial was charged with the [$^{2\text{-}tBu}$PDI]$CoBr_2$ catalyst **3** (9.0 mg, 0.014 mmol, 0.10 equiv), the substrate (0.14 mmol, 1.0 equiv), Zn powder (18 mg, 0.28 mmol, 2.0 equiv), $ZnBr_2$ (31 mg, 0.14 mmol, 1.0 equiv), 1,2-dichloroethane (1.0 mL), and a magnetic stir bar. The reaction mixture was stirred at room temperature for approximately 15 min during which time a deep violet color developed. Me_2CBr_2 (56.5 mg, 0.28 mmol, 2.0 equiv) was added, and stirring was continued at room temperature. After 24 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly loaded onto a SiO_2 column for purification.



(19). The reaction was conducted using ethyl (*E*)-5-methylhexa-2,4-dienoate[27] without modification from the general procedure to provide **19** as a colorless oil.

Run 1: 17.9 mg (65% yield, >19:1 trans/cis). Run 2: 16.2 mg (59% yield, 13:1 trans/cis).

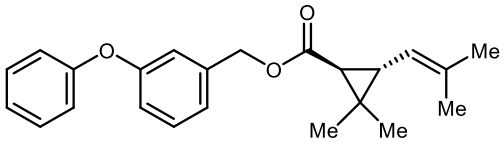
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88 (d, *J* = 9.44 Hz, 1H), 4.17-4.07 (m, 2H), 2.06-2.02 (m, 1H), 1.73-1.67 (m, 6H), 1.37 (d, *J* = 5.34 Hz, 1H), 1.25 (t, *J* = 7.25 Hz, 6H), 1.13 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.5, 135.4, 121.2, 60.2, 34.8, 32.6, 28.5, 25.6, 22.2, 20.4, 18.5, 14.4.

HRMS (ESI) calc. for $C_{12}H_{21}O_2$: m/z=197.1536, found: m/z=197.1538.

IR (film): 2958, 2915, 2880, 1731, 1150 cm^{-1}



(20). The reaction was conducted using **S2** without modification from the general procedure to provide **20** as a colorless oil.

Run 1: 27.5 mg (56% yield, >19:1 trans/cis). Run 2: 26.5 mg (54% yield, 11:1 trans/cis).

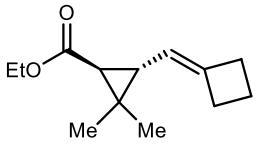
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 3H), 7.11 (q, *J* = 8.56 Hz, 2H), 7.03-7.01 (m, 3H), 6.95 (d, *J* = 7.96 Hz, 1H), 5.09 (s, 2H), 4.89 (d, *J* = 7.86 Hz, 1H), 2.09-2.07 (m, 1H), 1.72 (s, 3H), 1.70 (s, 3H), 1.45 (d, *J* = 5.33 Hz, 1H), 1.26 (s, 3H), 1.13 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.3, 157.5, 157.0, 138.4, 135.6, 129.8, 129.8, 123.4, 122.7, 121.0, 119.0, 118.3, 118.2, 65.6, 34.7, 33.0, 28.9, 25.6, 22.2, 20.5, 18.5.

HRMS (ESI) calc. for $C_{23}H_{27}O_3$: m/z=351.1955, found: m/z=351.1958.

IR (film): 3030, 2944, 2923, 2865, 1724, 1573, 1487, 1473, 1243, 1121 cm^{-1}



(21). The reaction was conducted using **S3** without modification from the general procedure to provide **21** as a colorless oil.

Run 1: 23.3 mg (80% yield, 8:1 trans/cis). Run 2: 21.9 mg (75% yield, 9:1 trans/cis).

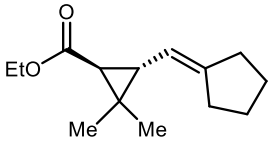
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^1H NMR (500 MHz, $CDCl_3$) δ 4.85-4.81 (m, 1H), 4.14-4.08 (m, 2H), 2.75-2.69 (m, 2H), 2.66 (t, *J* = 8.76 Hz, 2H), 1.96 (quintet, *J* = 7.84 Hz, 2H), 1.88 (dd, *J* = 8.86, 5.27, Hz, 1H), 1.41 (d, *J* = 5.31 Hz, 1H), 1.26 (d, *J* = 8.13 Hz, 3H), 1.24 (s, 3H), 1.14 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.4, 143.2, 117.1, 60.2, 34.4, 32.7, 31.2, 29.7, 28.2, 22.2, 20.3, 17.1, 14.4.

HRMS (ESI) calc. for $C_{13}H_{21}O_2$: m/z=209.1536, found: m/z=209.1532

IR (film): 2973, 2937, 2865, 1716, 1272, 1221, 1172, 841 cm^{-1}



(22). The reaction was conducted using **S4** without modification from the general procedure to provide **22** as a colorless oil.

Run 1: 22.1 mg (71% yield, 13:1 trans/cis). Run 2: 23.7 mg (76% yield, 12:1 trans/cis).

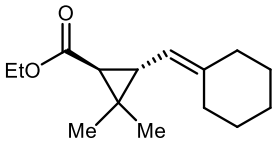
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^1H NMR (300 MHz, $CDCl_3$) δ 5.02 (dt, *J* = 2.20, 8.53 Hz, 1H), 4.12 (dq, *J* = 7.10, 2.87, Hz, 2H), 2.31-2.22 (m, 4H), 1.99 (dd, *J* = 8.55, 5.34, Hz, 1H), 1.70-1.57 (m, 4H), 1.39 (d, *J* = 5.32 Hz, 1H), 1.26 (t, *J* = 7.13 Hz, 6H), 1.14 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.5, 146.8, 116.6, 60.1, 34.8, 34.0, 33.8, 29.3, 28.4, 26.5, 26.4, 22.3, 20.5, 14.4.

HRMS (ESI) calc. for $C_{14}H_{23}O_2$: m/z=223.1693, found: m/z=223.1691

IR (film): 2952, 2858, 1710, 1365, 1236, 1172, 1135, 1028 cm^{-1}



(23). The reaction was conducted using **S5** without modification from the general procedure to provide **23** as a colorless oil.

Run 1: 23.2 mg (70% yield, 13:1 trans/cis). Run 2: 22.5 mg (68% yield, 13:1 trans/cis).

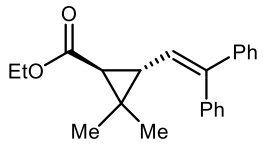
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^1H NMR (300 MHz, $CDCl_3$) δ 4.82 (d, *J* = 7.83 Hz, 1H), 4.17-4.05 (m, 2H), 2.21-2.16 (m, 2H), 2.08-2.04 (m, 3H), 1.57-1.48 (m, 6H), 1.36 (d, *J* = 5.23 Hz, 1H), 1.25 (t, *J* = 3.34 Hz, 6H), 1.12 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.6, 143.5, 117.8, 60.1, 36.8, 34.9, 31.7, 29.4, 28.6, 28.5, 27.7, 26.8, 22.2, 20.4, 14.4.

HRMS (ESI) calc. for $C_{15}H_{25}O_2$: m/z=237.1849, found: m/z=237.1847

IR (film): 2930, 2851, 1731, 1423, 1372, 1207, 1150, 1121, 834 cm^{-1}



(24). The reaction was conducted using ethyl (*E*)-5,5-diphenylpenta-2,4-dienoate[28] without modification from the general procedure to provide **24** as a colorless oil.

Run 1: 9.9 mg (22% yield, >19:1 trans/cis). Run 2: 8.5 mg (19% yield, 16:1 trans/cis).

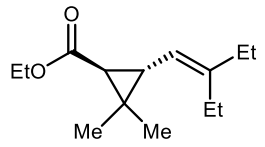
Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.29 (m, 4H), 7.24-7.21 (m, 6H), 6.50 (d, *J* =9.45 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 1.86 (t, *J* = 8.87 Hz, 1H), 1.68 (d, *J* = 8.56 Hz, 1H), 1.38 (s, 3H), 1.28 (t, *J* = 7.11 Hz, 3H), 1.14 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.2, 143.4, 142.6, 140.2, 130.4, 128.1, 128.1, 127.4, 127.0, 126.9, 123.8, 60.0, 34.0, 32.7, 28.3, 28.0, 15.1, 14.4.

HRMS (ESI) calc. for $C_{22}H_{25}O_2$: m/z=321.1849, found: m/z=321.1854

IR (film): 3052, 3030, 2952, 1724, 1200, 1143, 1100 cm^{-1}



(25). The reaction was conducted using **S6** without modification from the general procedure to provide **25** as a colorless oil.

Run 1: 17.6 mg (56% yield, >19:1 trans/cis). Run 2: 15.1 mg (48% yield, >19:1 trans/cis).

Purification: SiO_2 column; (1:1) CH_2Cl_2:Hexane

^1H NMR (300 MHz, $CDCl_3$) δ 4.82 (d, *J* = 8.07 Hz, 1H), 4.16 – 4.09 (m, 2H), 2.16-2.09 (m, 5H), 1.39 (d, *J* = 5.34 Hz, 1H), 1.26 (t, *J* = 7.25 Hz, 6H), 1.13 (s, 3H), 0.98 (td, *J* = 7.50, 1.92 Hz, 6H)

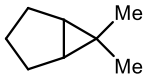
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.5, 146.9, 119.2, 60.1, 35.1, 32.2, 29.2, 28.5, 23.9, 22.2, 20.4, 14.4, 13.2, 12.8.

HRMS (ESI) calc. for $C_{16}H_{25}O_2$: m/z=225.1849, found: m/z=225.1851

IR (film): 2958, 2930, 2887, 1716, 1458, 1365, 1200, 1150, 1100, 1035, 841 cm^{-1}

7. Procedure for the Dimethylcyclopropanation of Activated Alkenes

General procedure for the dimethylcyclopropanation of activated alkenes. In an N_2-filled glovebox, a 2-dram vial was charged with the [$^{2\text{-}tBu}$PDI]$CoBr_2$ catalyst **3** (9.0 mg, 0.014 mmol, 0.10 equiv), the substrate (0.14 mmol, 1.0 equiv), Zn powder (18 mg, 0.28 mmol, 2.0 equiv), $ZnBr_2$ (31 mg, 0.14 mmol, 1.0 equiv), THF (1.0 mL), and a magnetic stir bar. The reaction mixture was stirred at room temperature for approximately 15 min during which time a deep violet color developed. Me_2CCl_2 (31.6 mg, 0.28 mmol, 2.0 equiv) was added, and stirring was continued at room temperature. After 24 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly loaded onto a SiO_2 column for purification.



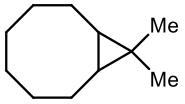
(30). The reaction was conducted using cyclopentene without modification from the general procedure to provide **30** as a colorless oil.

Purification: SiO_2 column; pentane

^{1}H NMR Yield. Run 1: 88%; Run 2: 85%

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85-1.75 (m, 2H), 1.52-1.27 (m, 4H), 1.05 (d, *J* = 4.3 Hz, 2H), 0.95 (s, 3H), 0.90 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 31.5, 28.0, 27.8, 25.3, 14.5, 14.1.



(31). The reaction was conducted using cyclooctene without modification from the general procedure to provide **31** as a colorless oil.

Purification: SiO_2 column; pentane

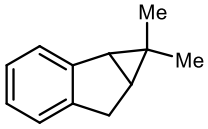
Yield 1: 83%, 17.7 mg; Yield 2: 78%, 16.6 mg

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76-1.55 (m, 6H), 1.40-1.29 (m, 4H), 1.08-1.02 (m, 1H), 1.01 (s, 3H), 0.99-0.97 (m, 1H), 0.92 (s, 3H), 0.34-0.25 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 29.7, 29.2, 26.6, 26.5, 22.4, 16.4, 15.1.

HRMS (APCI) calc. for $C_{11}H_{20}$: m/z=152.1560, found: m/z=152.1557

IR (film): 2923, 2844, 1452, 1372 cm^{-1}



(32). The reaction was conducted using indene without modification from the general procedure to provide **32** as a colorless oil.

Purification: SiO_2 column; pentane

Yield 1: 75%, 16.7 mg; Yield 2: 82%, 18.3 mg

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.22 (m, 1H), 7.12-7.07 (m, 3H), 3.10 (dd, *J* = 17.43, 7.26 Hz, 1H), 2.77 (d, *J* = 17.40 Hz, 1H), 2.24 (dd, *J* = 6.36, 1.23 Hz, 1H), 1.60 (t, *J* = 6.86 Hz, 1H),1.16 (s, 3H) 0.63 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.0, 143.8, 125.8, 125.2, 124.3, 124.0, 37.2, 32.0, 29.1, 26.8, 21.4, 13.8.

HRMS (ESI) calc. for $C_{12}H_{15}$: m/z=159.1168, found: m/z=159.1166

IR (film): 3023, 2944, 2908, 2858, 1480, 1372, 1114, 884 cm^{-1}

(33). The reaction was conducted using norbornene without modification from the general procedure to provide **33** as a colorless oil.

Purification: SiO_2 column; pentane

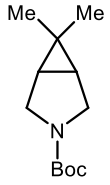
Yield 1:66%, 12.7 mg; Yield 2: 67%, 12.8 mg

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 2H), 1.46-1.35 (m, 3H), 1.25-1.19 (m, 2H), 1.17 (s, 3H), 0.88 (s, 3H), 0.64 (d, *J* = 10.64 Hz, 1H), 0.43 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 36.0, 31.1, 31.0, 30.8, 30.5, 18.6, 16.1.

HRMS (APCI) calc. for $C_{10}H_{17}$: m/z=137.1325, found: m/z=137.1320

IR (film): 2958, 2908, 2844, 1444 cm^{-1}



(35). The reaction was conducted using *N*-Boc-2,5-dihydro-1*H*-pyrrole without modification from the general procedure to provide **35** as a yellow oil.

Run 1: 26.2 mg (89% yield). Run 2: 26.6 mg (91% yield).

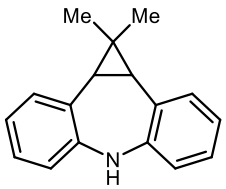
Purification: SiO_2 column; Hexane/EtOAc (80:20)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48-3.38 (m, 2H), 3.35-3.24 (m, 2H), 1.42 (s, 9H), 1.29-1.27 (m, 2H), 1.00 (s, 3H), 0.90 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.9, 79.0, 46.1, 45.9, 28.5, 27.9, 27.1, 26.3, 18.9, 12.4.

HRMS (ESI) calc. for $C_{12}H_{21}NO_2Na$: m/z=234.1465, found: m/z=234.1467

IR (film): 2966, 2930, 2880, 1702, 1409, 1379, 1178, 1107, 870 cm^{-1}



(37). The reaction was conducted using iminostilbene without modification from the general procedure to provide **37** as a white solid.

Run 1: 30.6 mg (93% yield). Run 2: 32.5 mg (99% yield).

Purification: SiO_2 column; hexane/EtOAc (95:5)

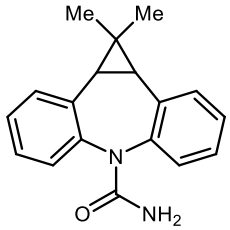
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.44, 1.18, Hz, 2H), 7.07 (td, *J* = 7.66, 1.67 Hz, 2H), 6.92 (td, *J* = 7.44, 1.28 Hz, 2H), 6.81 (dd, *J* = 7.93, 1.26 Hz, 2H), 5.55 (br s, 1H), 2.30 (s, 2H), 1.50 (s, 3H), 0.59 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 133.3, 126.4, 125.7, 121.0, 119.5, 30.9, 28.7, 27.8, 18.5.

HRMS (ESI) calc. for $C_{17}H_{18}N$: m/z=236.1434, found: m/z=236.1436

IR (film): 3367, 2966, 2937, 2865, 1587, 1480, 1329, 1250, 1107, 1028, 913 cm^{-1}

m.p.: 133-136°C



(38). The reaction was conducted using **37** under previously reported conditions[29] to provide **38** as a white solid.

Run 1: 23.3 mg (64% yield)

Purification: SiO_2 column; 100% EtOAc

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.28-7.25 (m, 2H), 7.24-7.21 (m, 4H), 7.19-7.14 (m, 2H), 5.65 (br s, 2H), 2.20 (s, 2H), 1.40 (s, 3H), 0.42 (s, 3H).

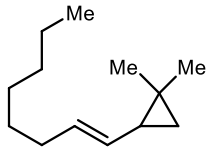
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 157.5, 143.5, 135.4, 132.7, 129.3, 127.8, 127.4, 28.6, 28.1, 19.6, 19.0.

HRMS (ESI) calc. for $C_{18}H_{19}N_2O$: m/z=279.1492, found: m/z=279.1491

IR (film): 3475, 3318, 3203, 2930, 1673, 1581, 1480, 1393, 920 cm^{-1}

m.p.: 176-177 °C

8. NMR Spectra



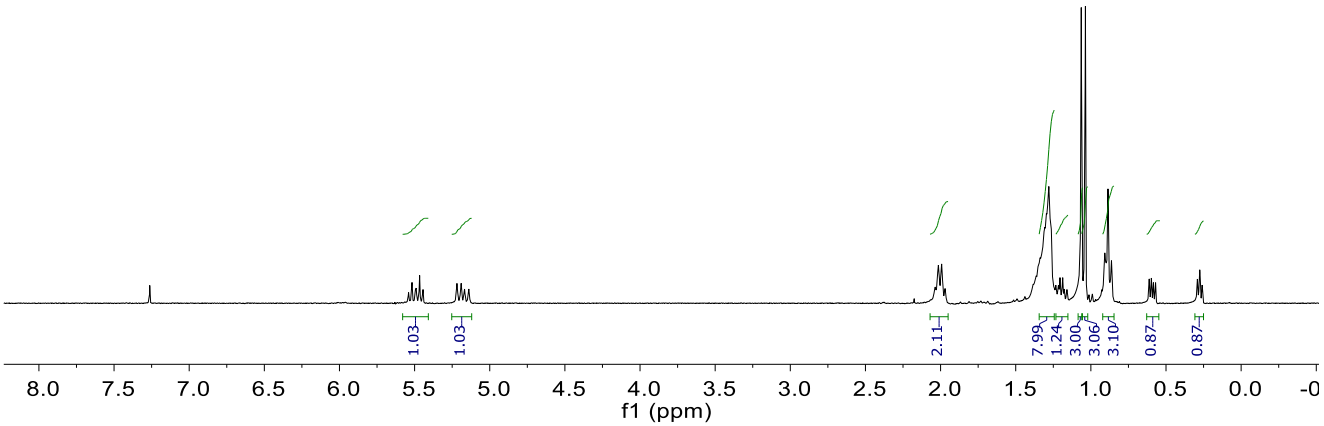


Figure S6. ^{1}H NMR spectrum for **2** ($CDCl_3$, 295 K)

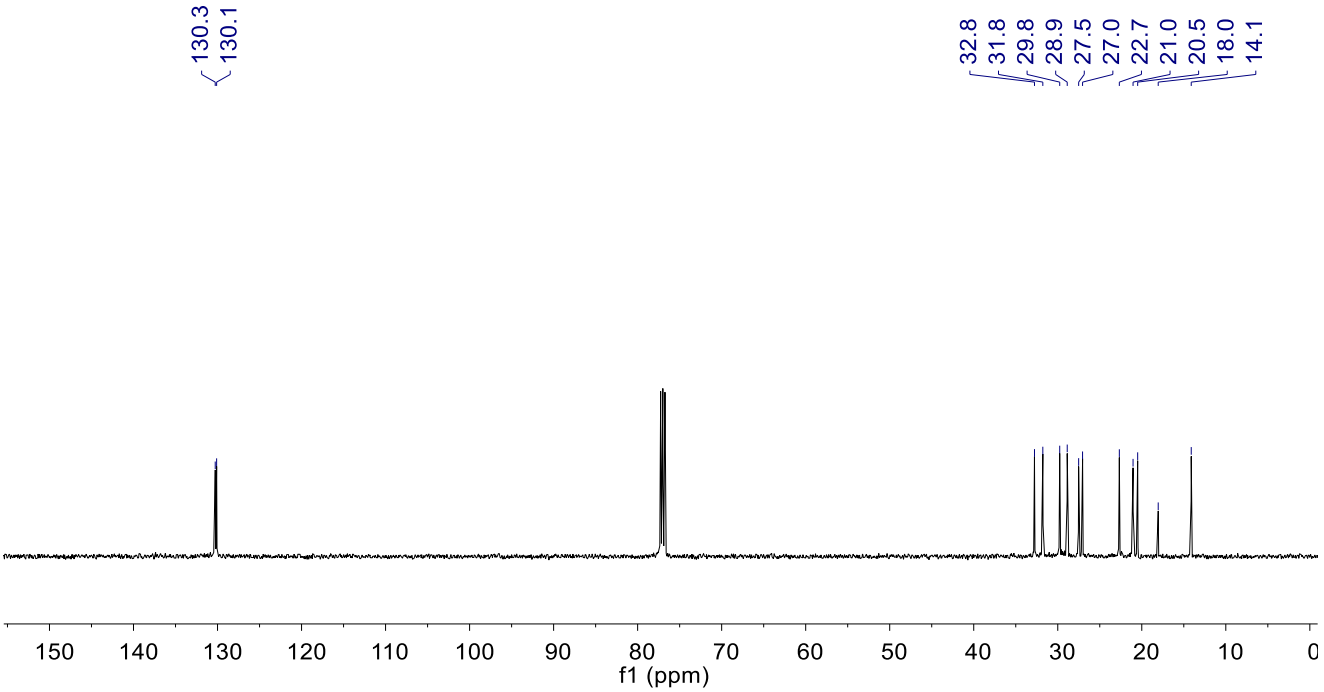


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum for **2** ($CDCl_3$, 295 K)

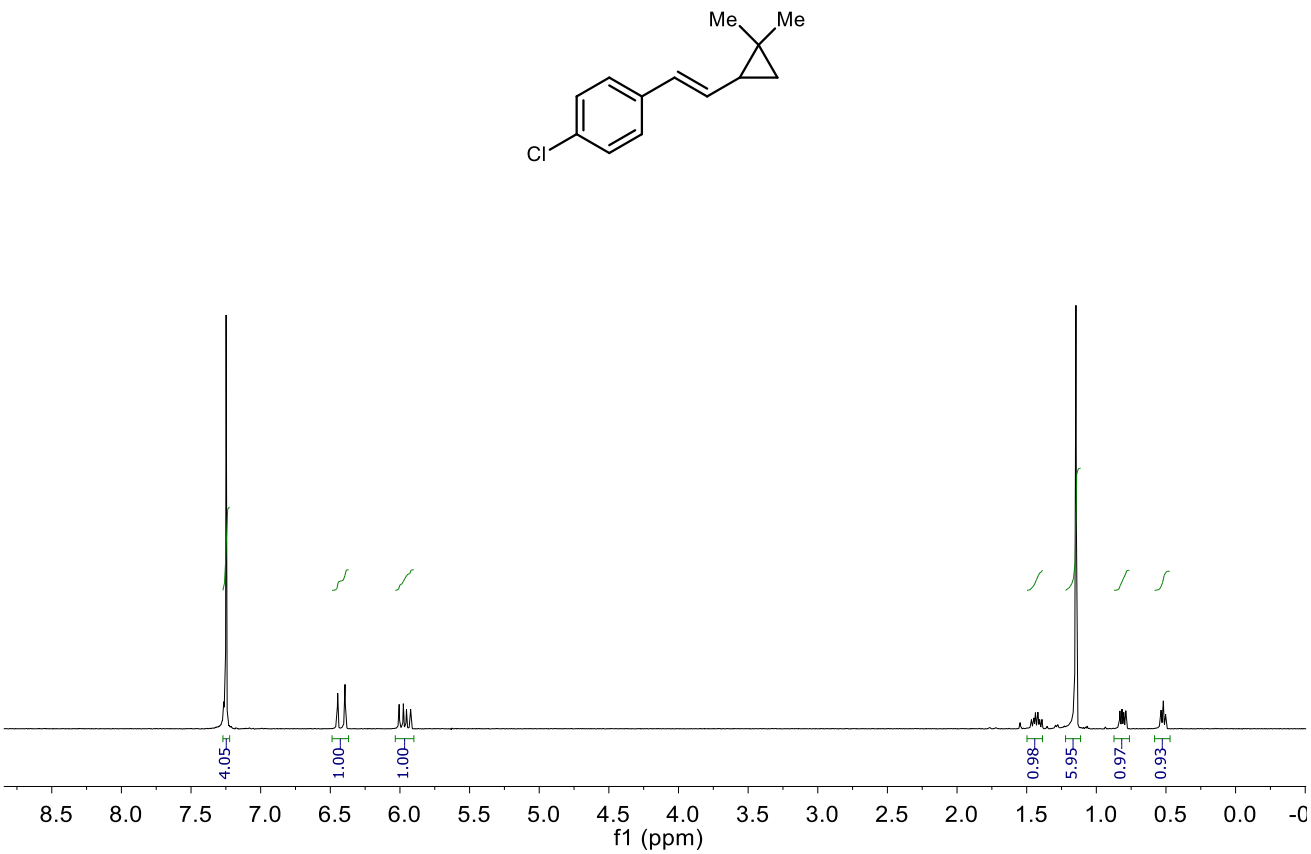


Figure S8: ^{1}H NMR spectrum for **4** ($CDCl_3$, 295 K)

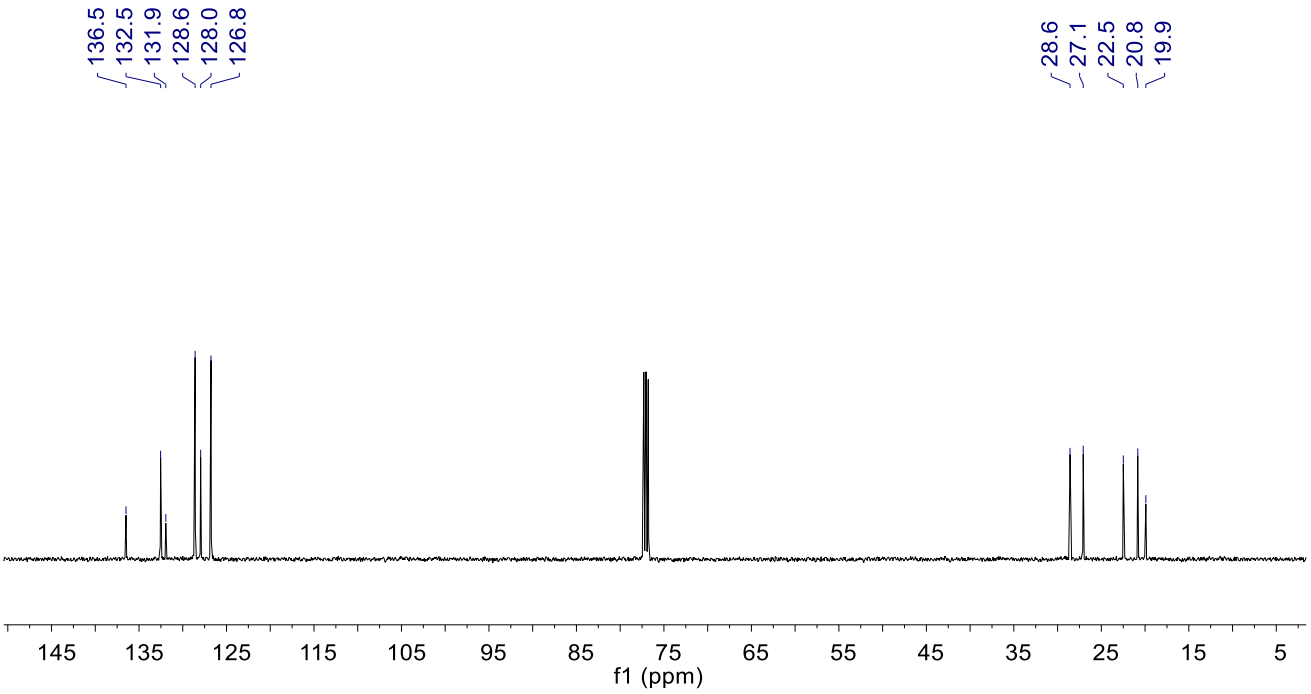
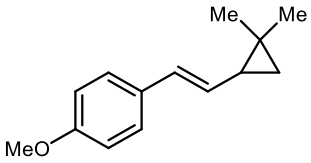


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum for **4** ($CDCl_3$, 295 K)



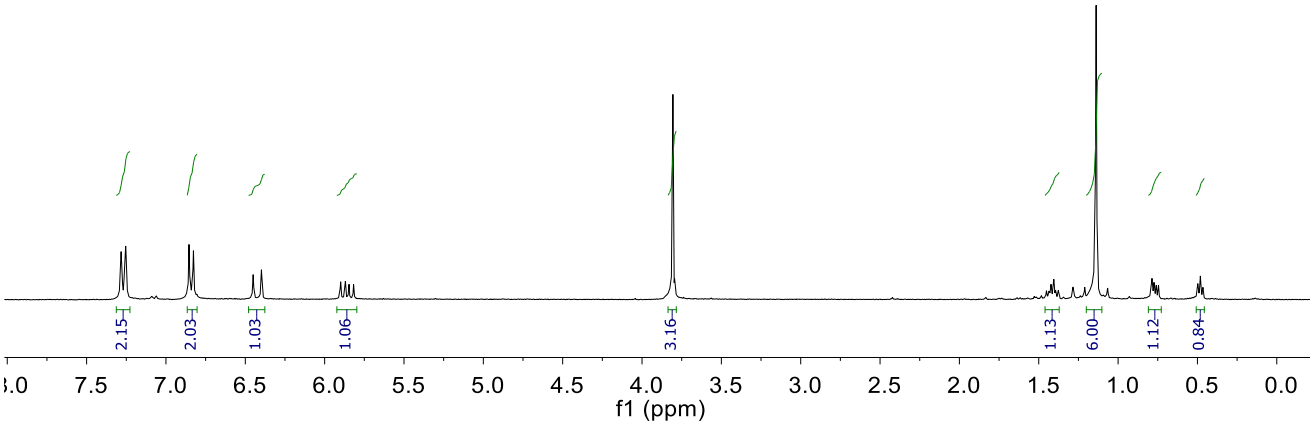


Figure S10: ^{1}H NMR spectrum for **5** ($CDCl_3$, 295 K)

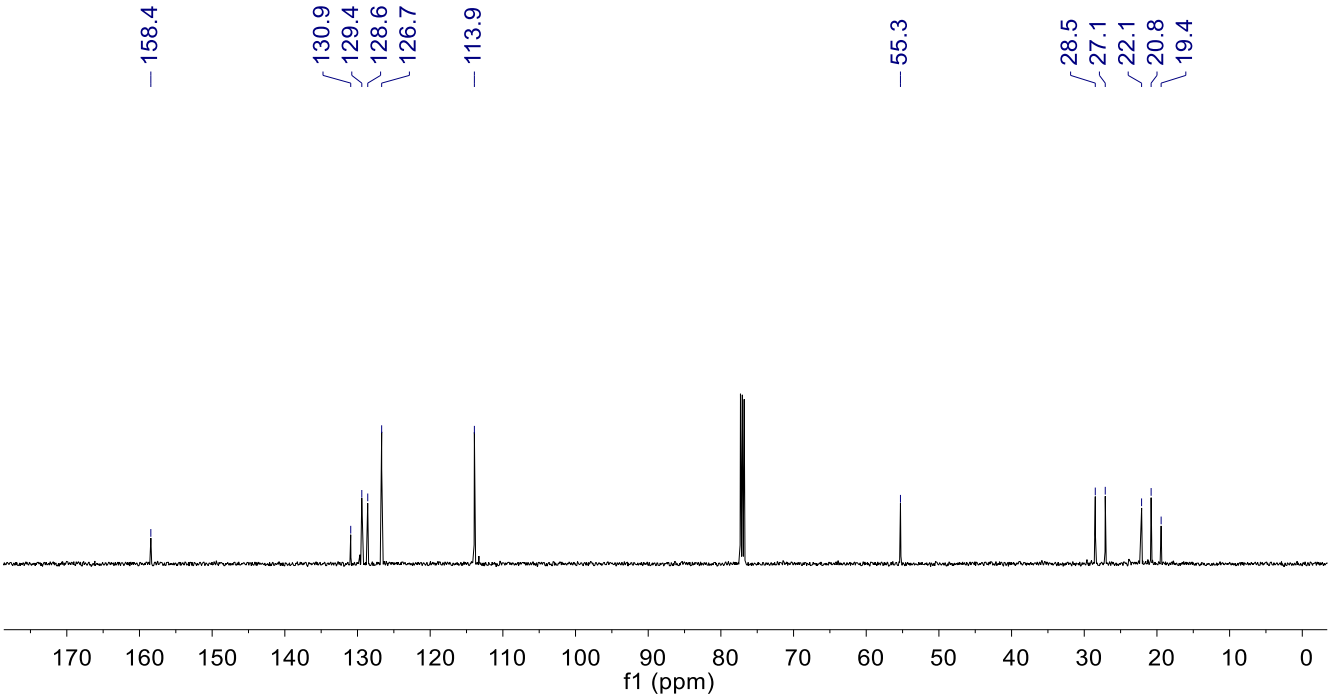


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum for **5** ($CDCl_3$, 295 K)

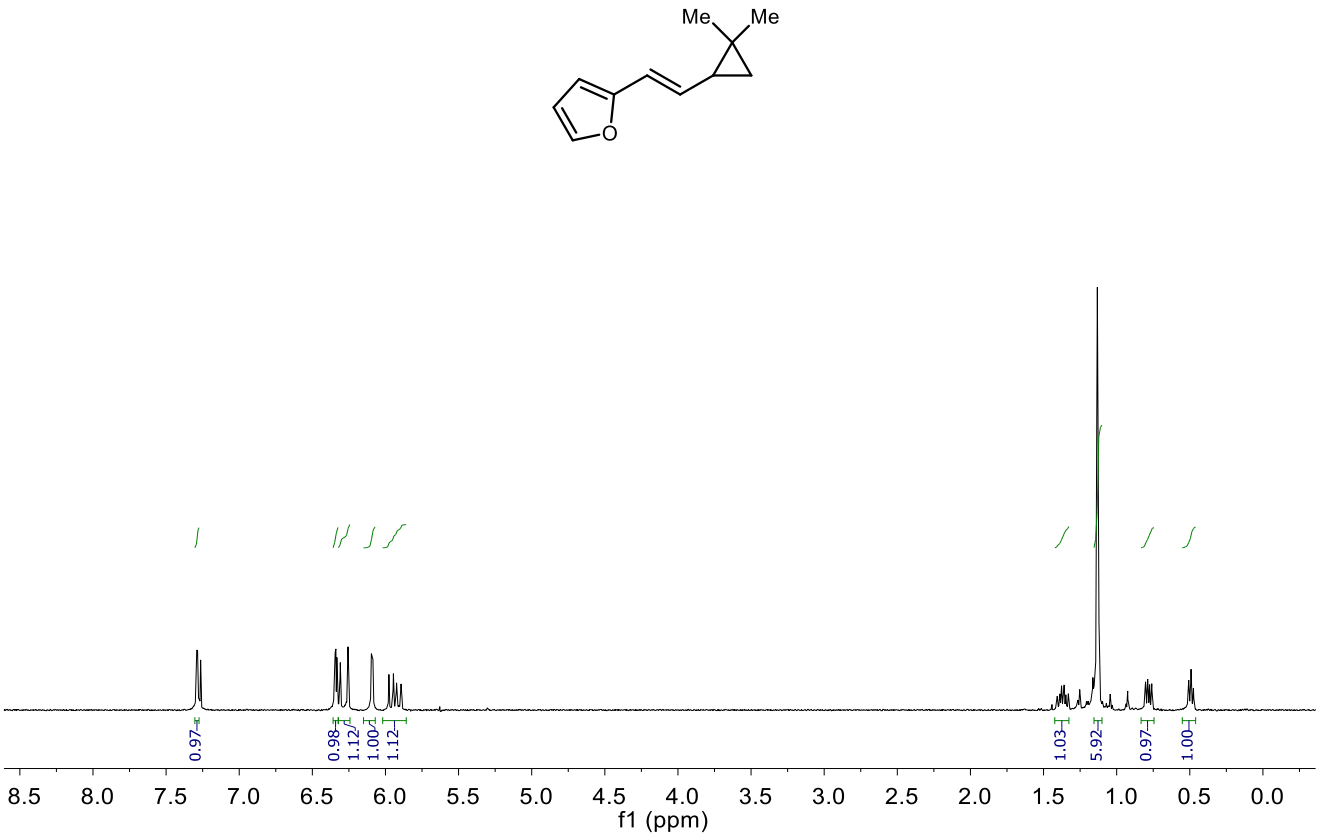


Figure S12: ^{1}H NMR spectrum for **6** ($CDCl_3$, 295 K)

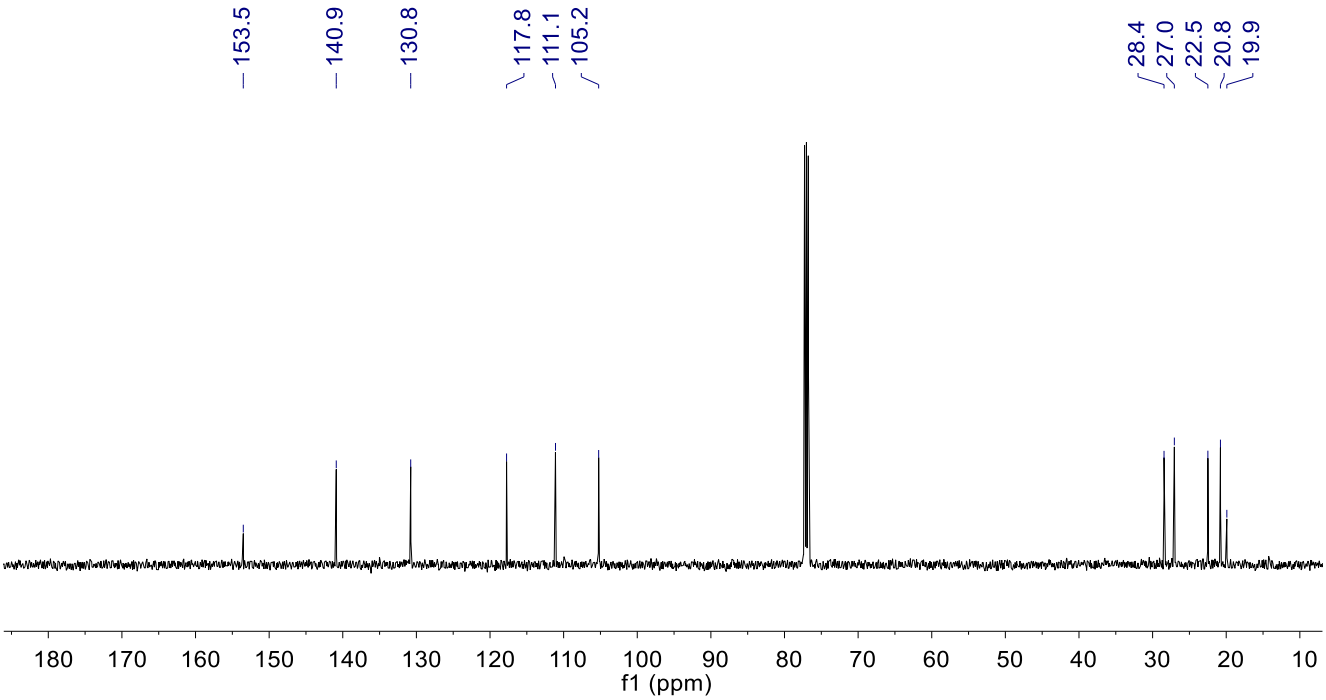
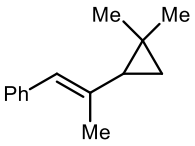


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum for **6** ($CDCl_3$, 295 K)



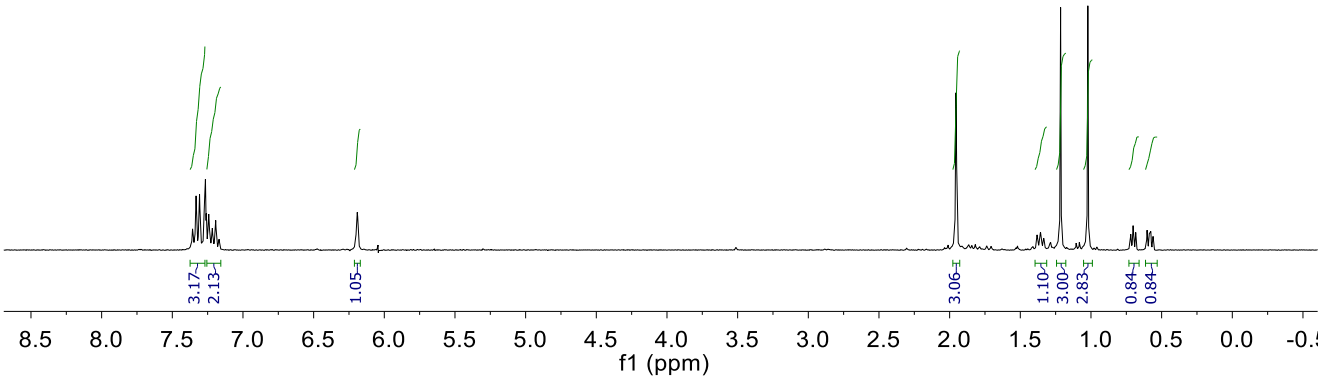


Figure S14: ^{1}H NMR spectrum for **7** ($CDCl_3$, 295 K)

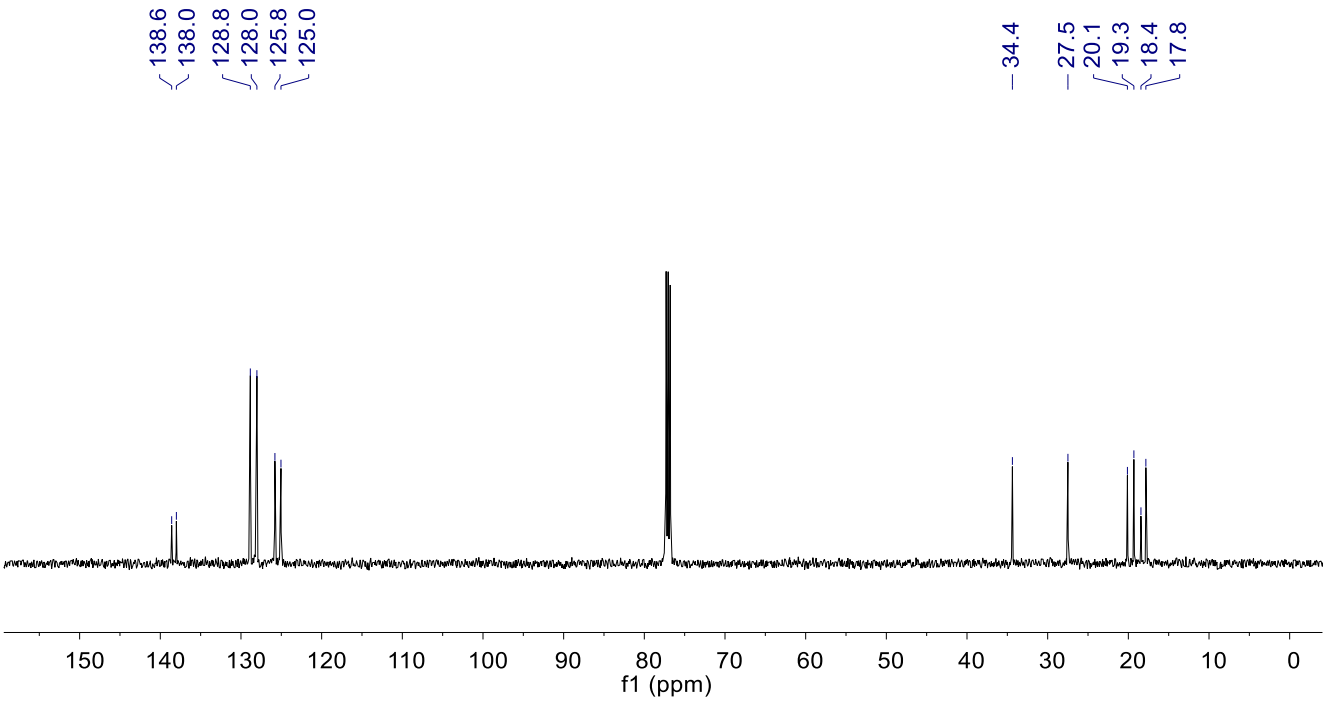
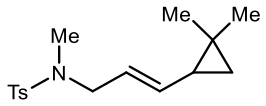


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum for **7** ($CDCl_3$, 295 K)



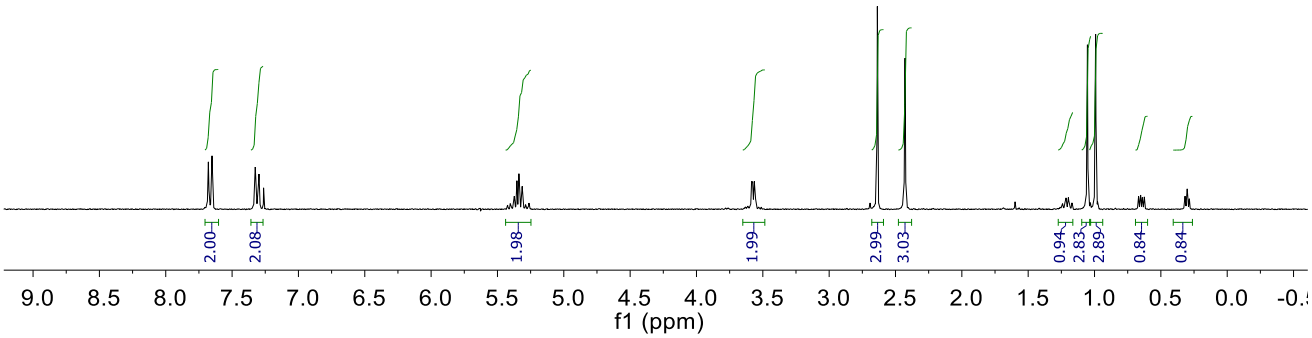


Figure S16: ^{1}H NMR spectrum for **8** ($CDCl_3$, 295 K)

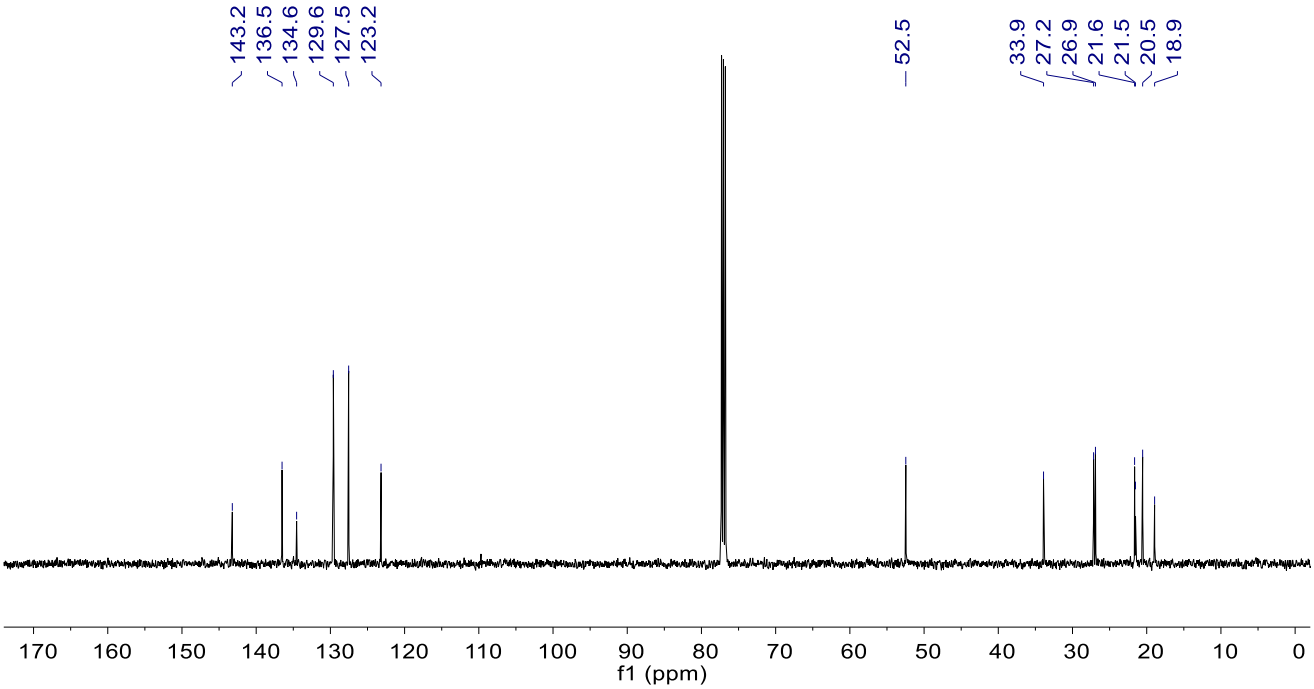


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum for **8** ($CDCl_3$, 295 K)

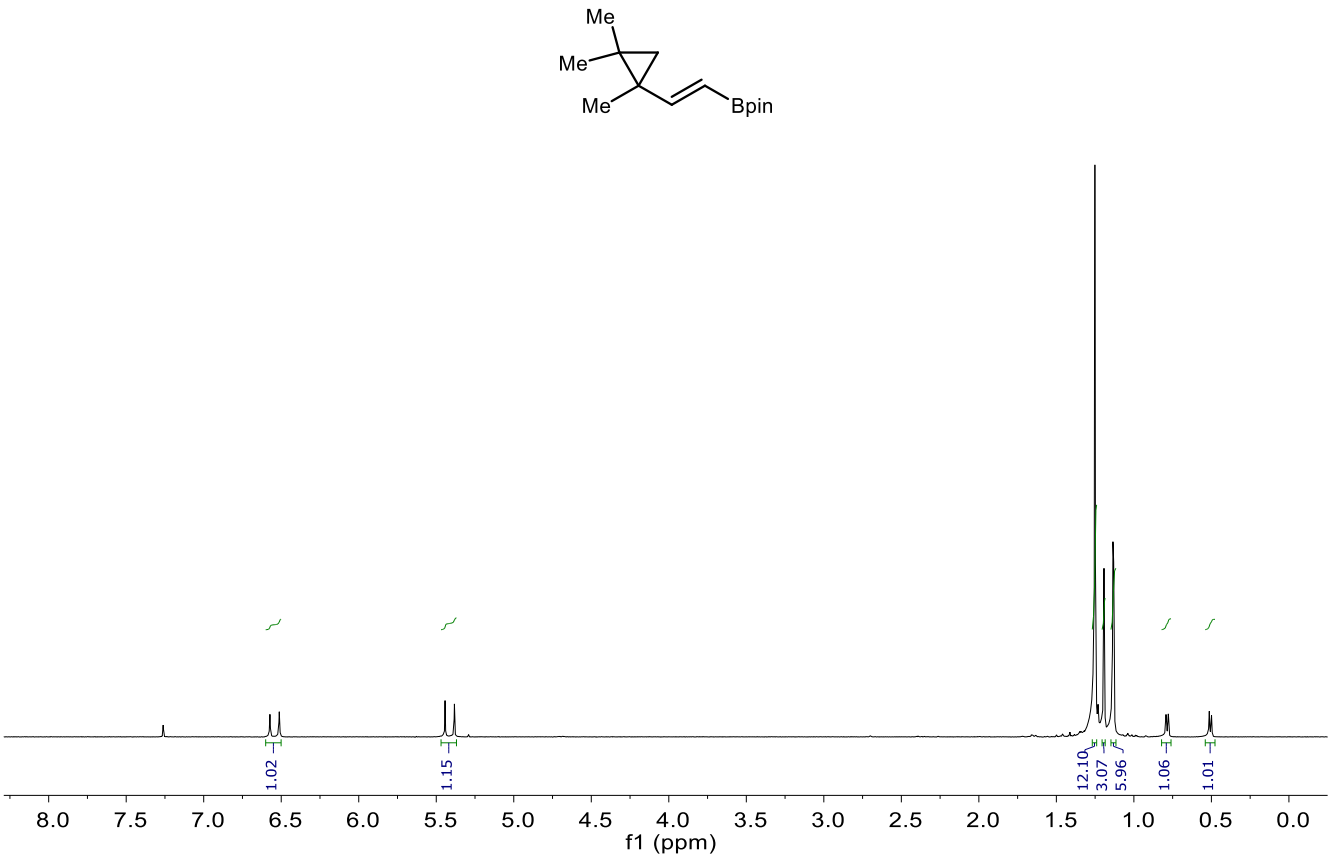


Figure S18: ^{1}H NMR spectrum for **9** ($CDCl_3$, 295 K)

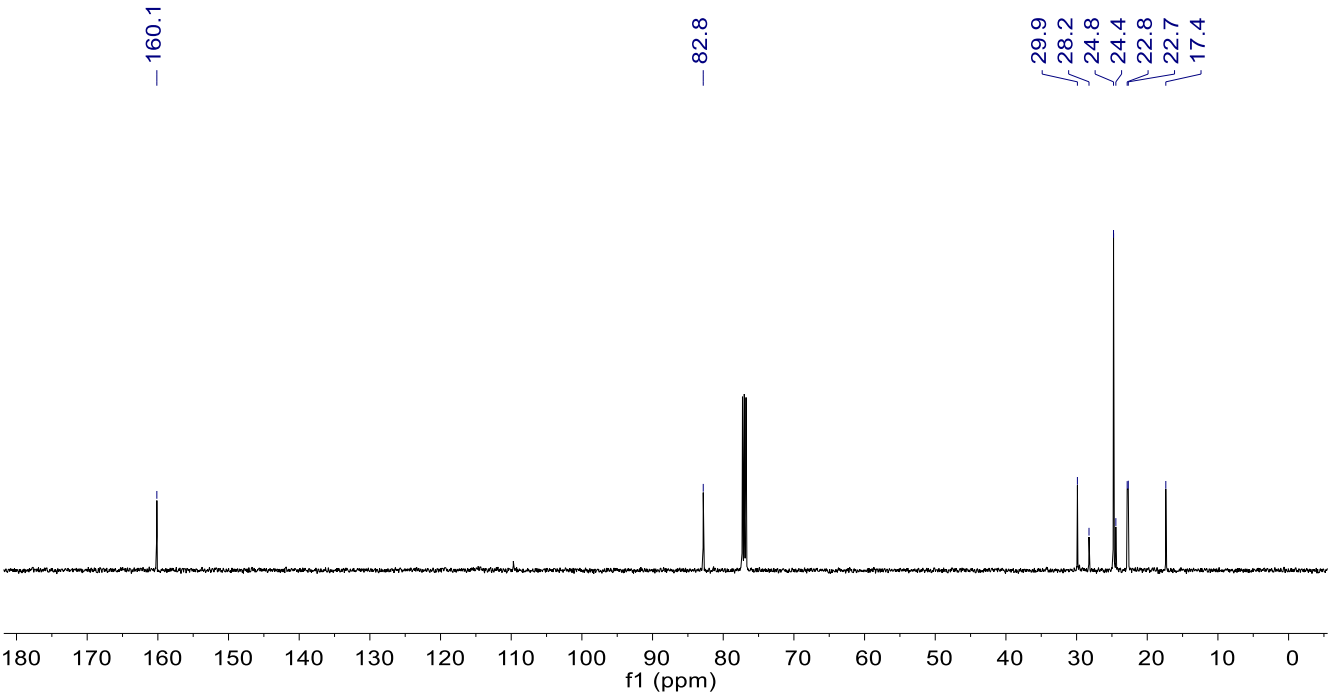


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum for **9** ($CDCl_3$, 295 K)

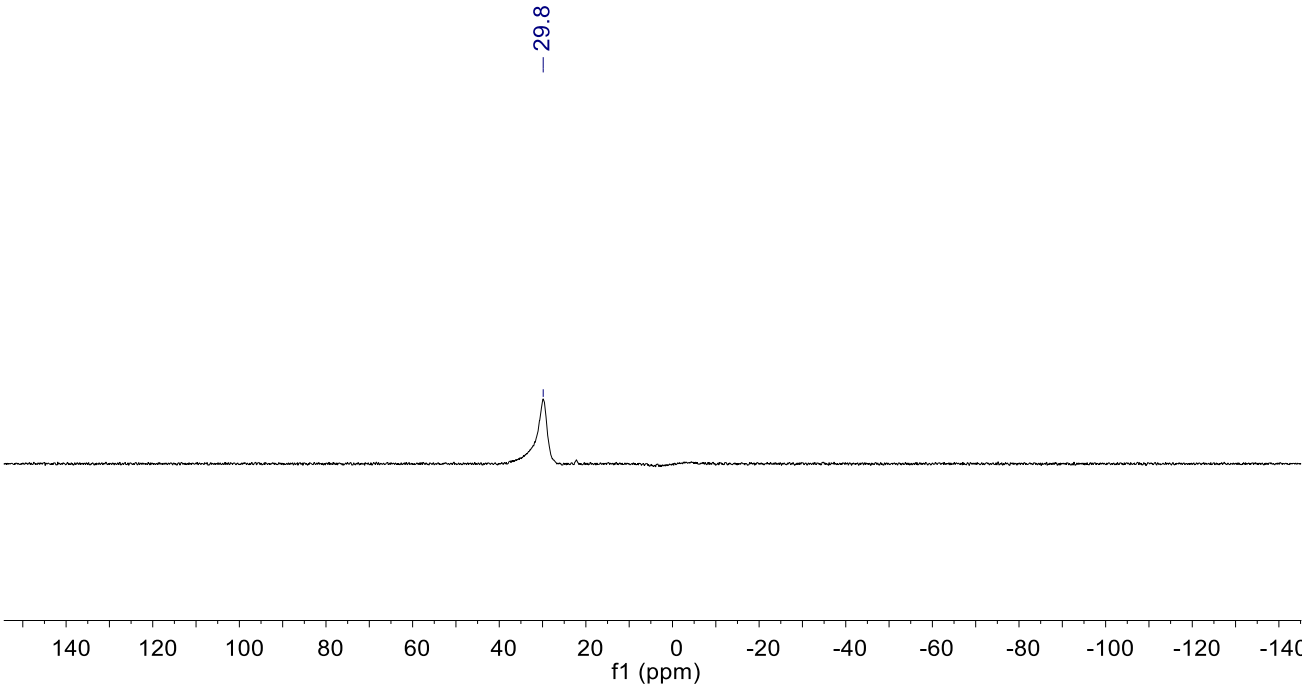
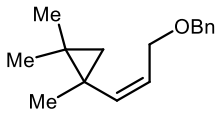


Figure S20: ^{11}B NMR spectrum for **9** ($CDCl_3$, 295 K)



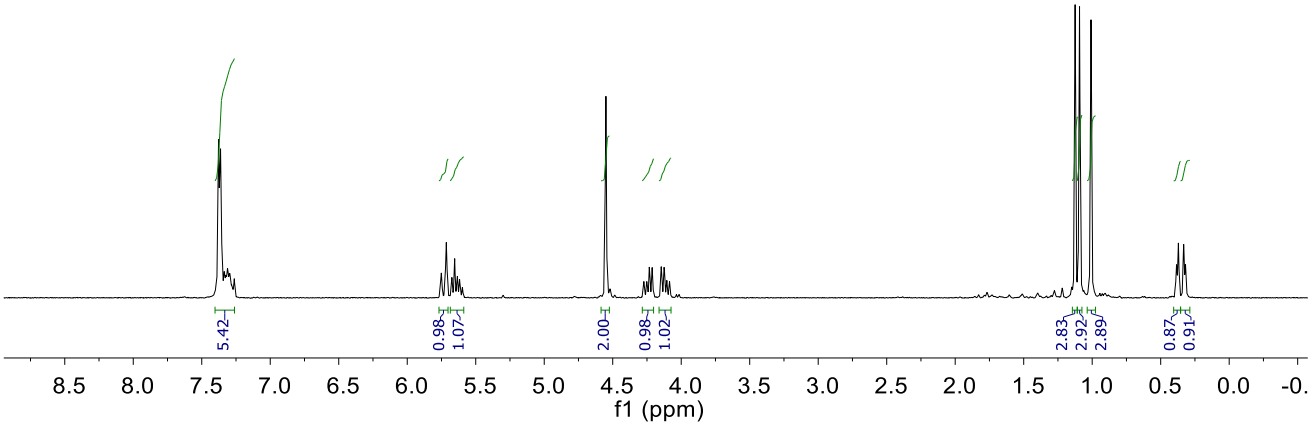


Figure S21: ^{1}H NMR spectrum for **10** ($CDCl_3$, 295 K)

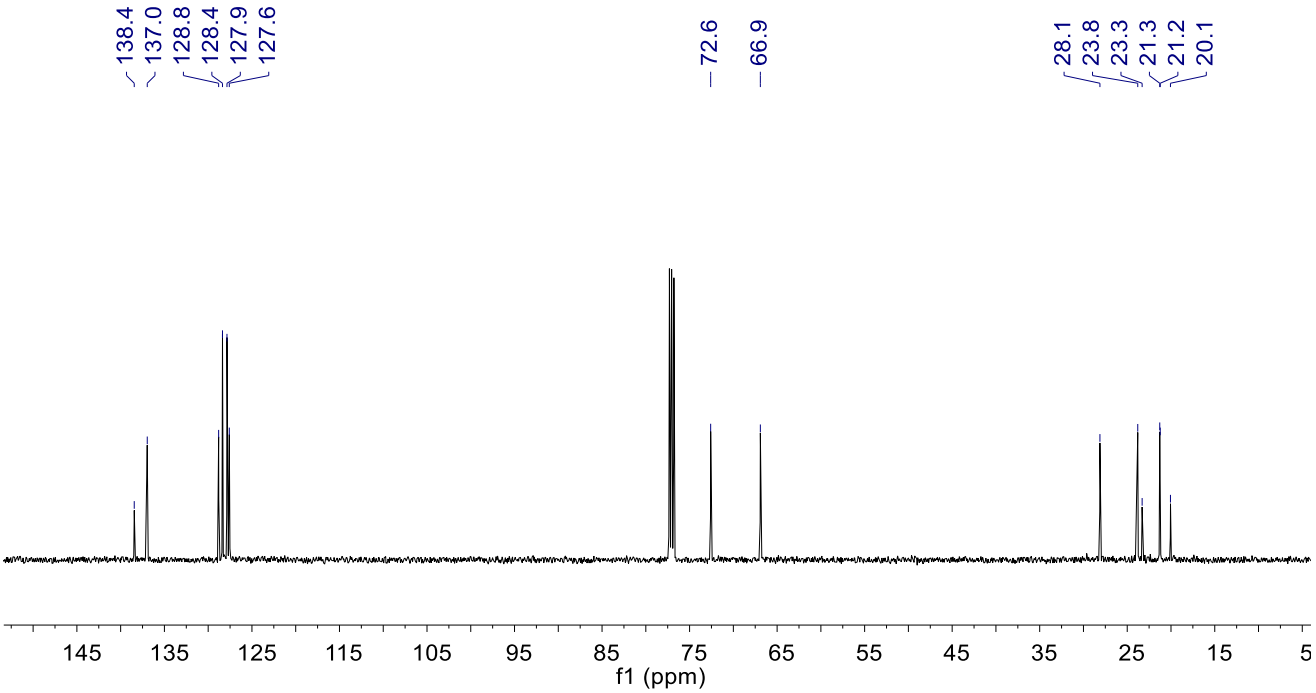
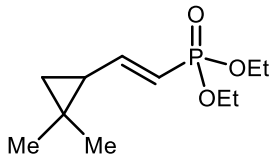


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum for **10** ($CDCl_3$, 295 K)



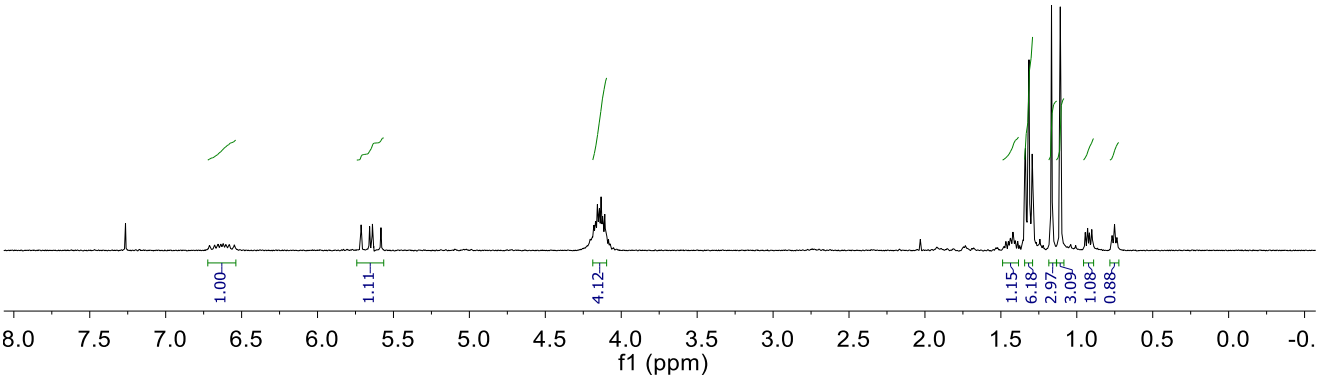


Figure S23: ^{1}H NMR spectrum for **11** ($CDCl_3$, 295 K)

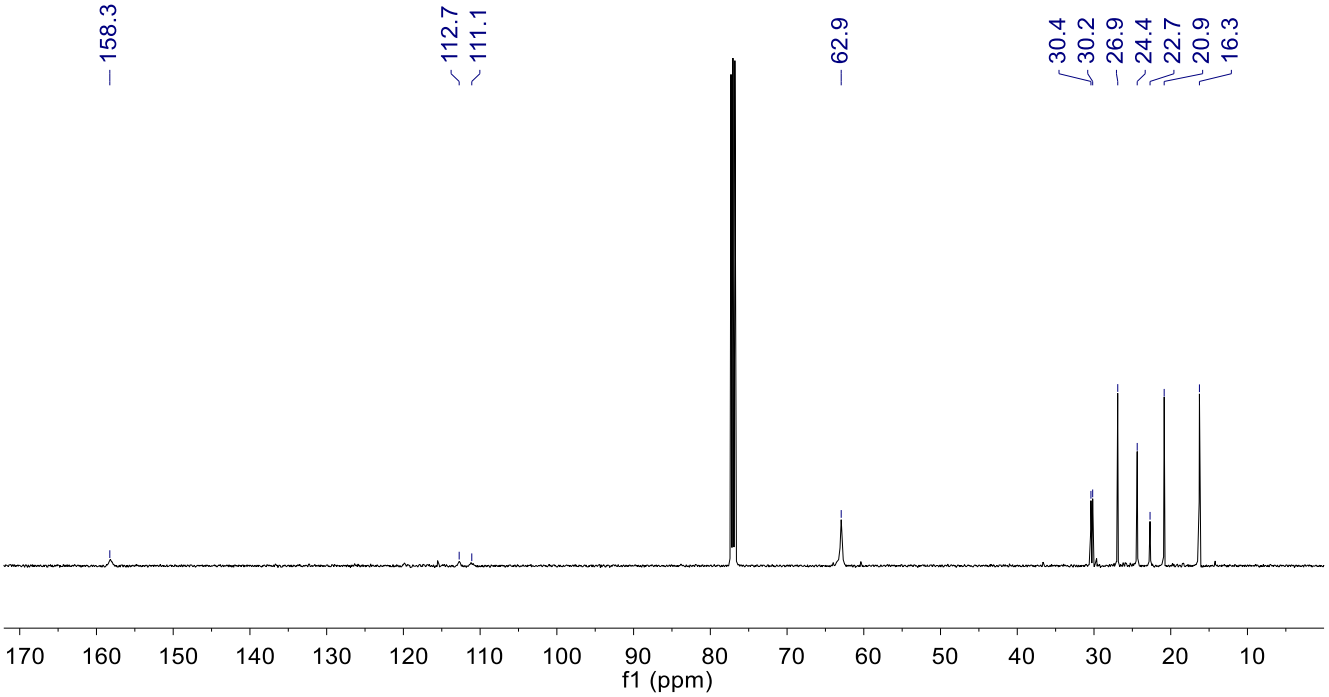


Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum for **11** ($CDCl_3$, 295 K)

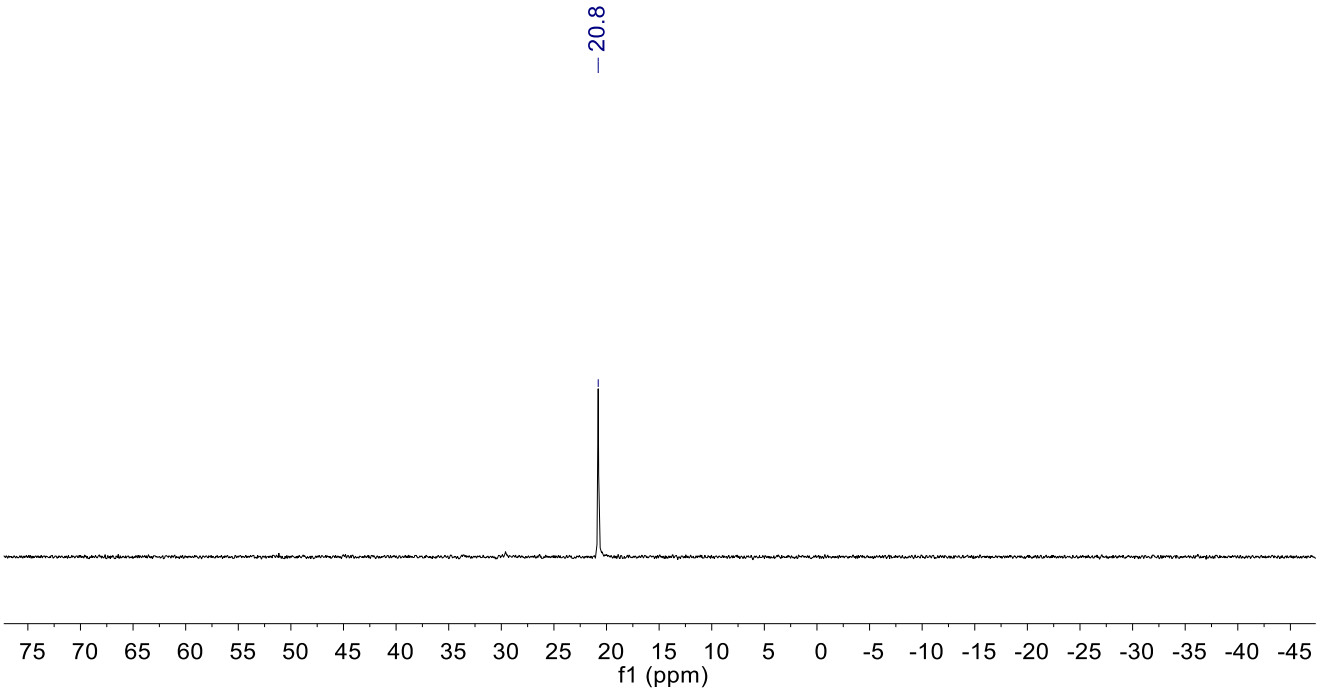


Figure S25: ^{31}P NMR spectrum for **11** ($CDCl_3$, 295 K)

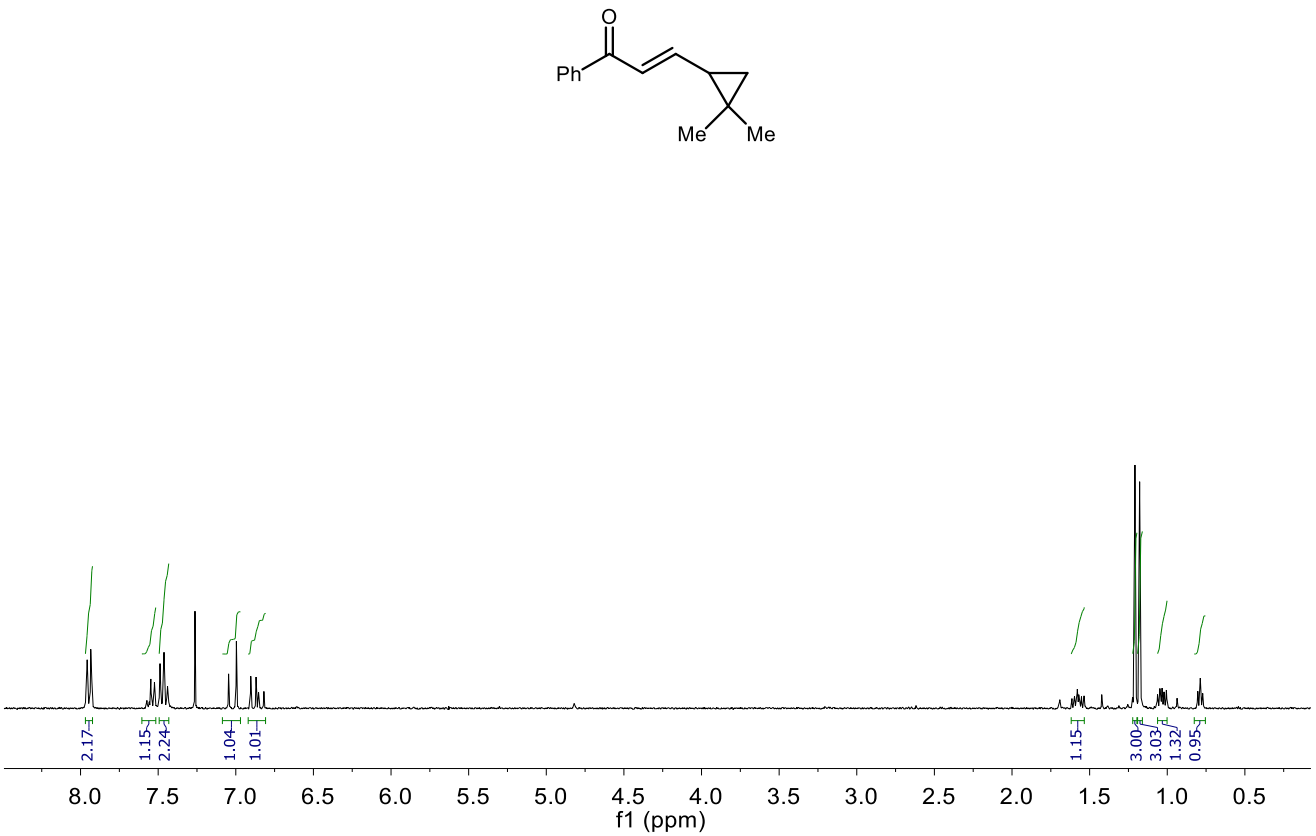


Figure S26: ^{1}H NMR spectrum for **12** ($CDCl_3$, 295 K)

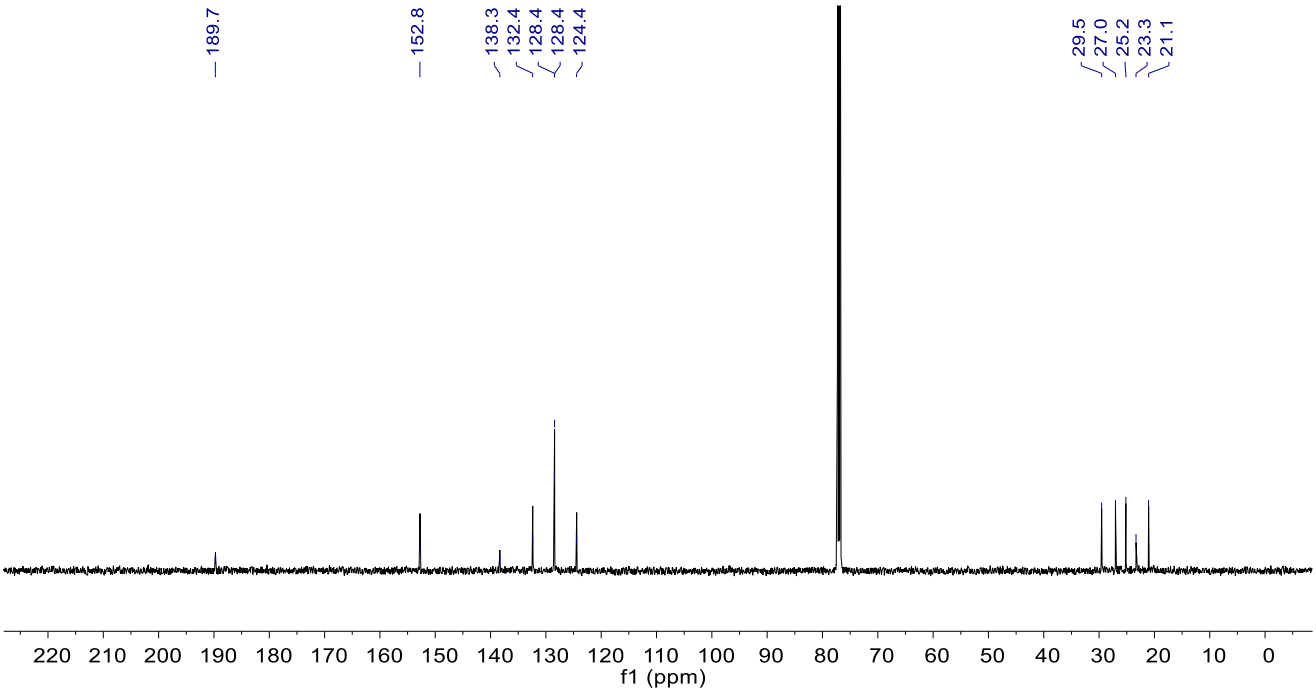
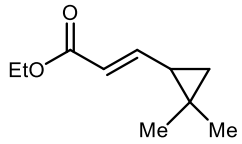


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum for **12** ($CDCl_3$, 295 K)



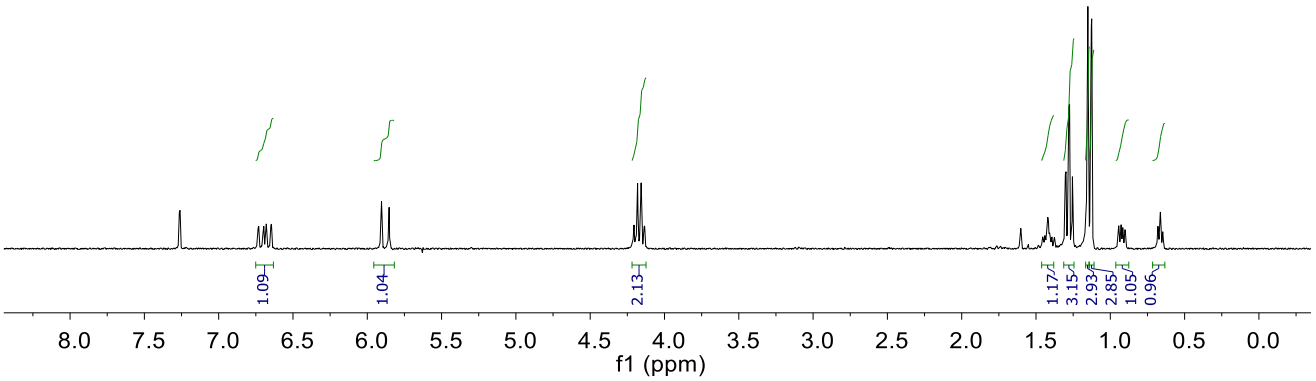


Figure S28: ^{1}H NMR spectrum for **13** ($CDCl_3$, 295 K)

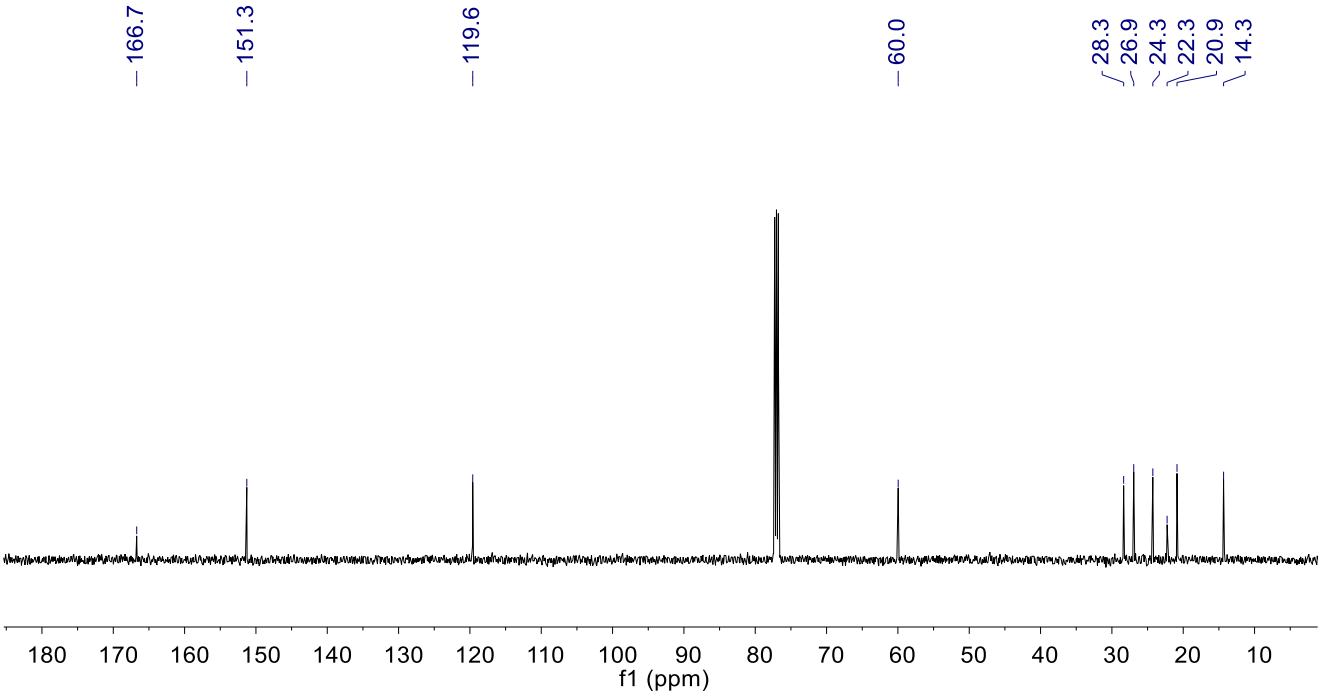


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum for **13** ($CDCl_3$, 295 K)

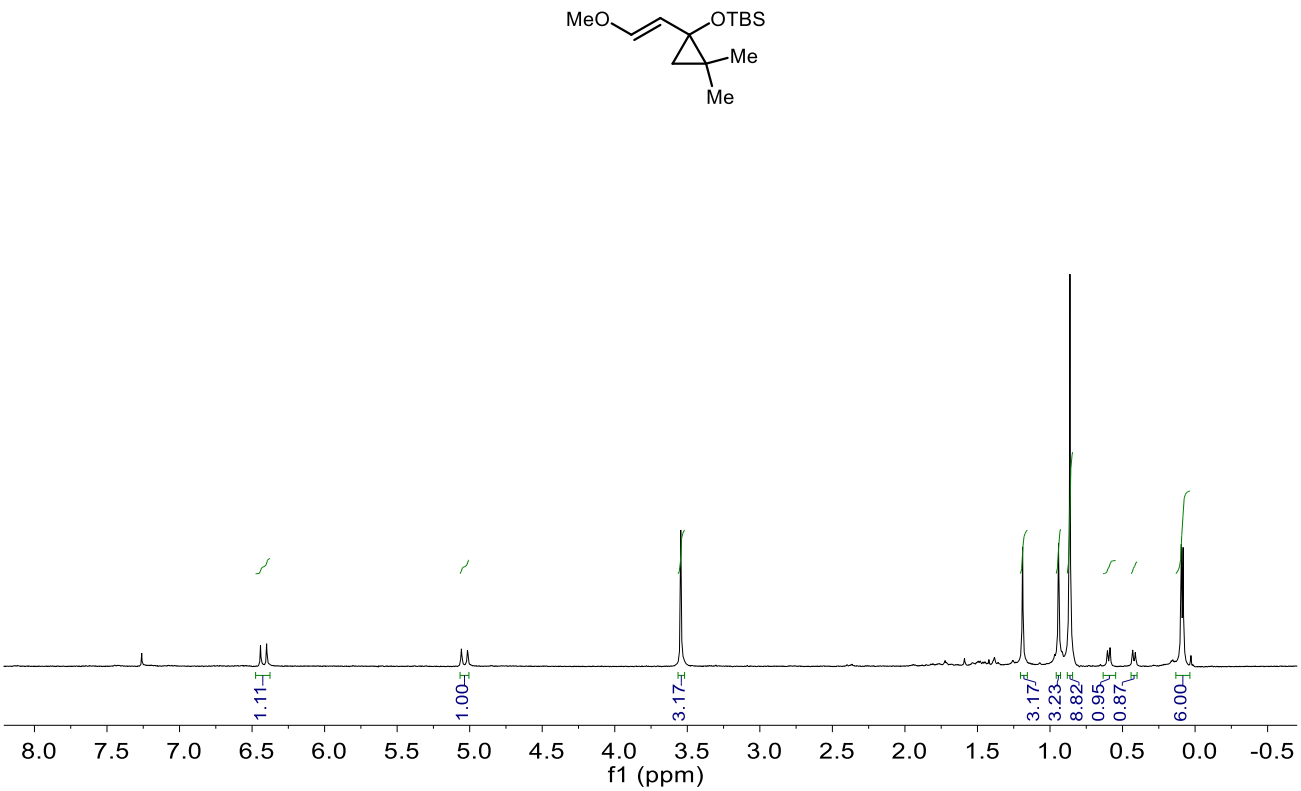


Figure S30: ^{1}H NMR spectrum for **14** ($CDCl_3$, 295 K)

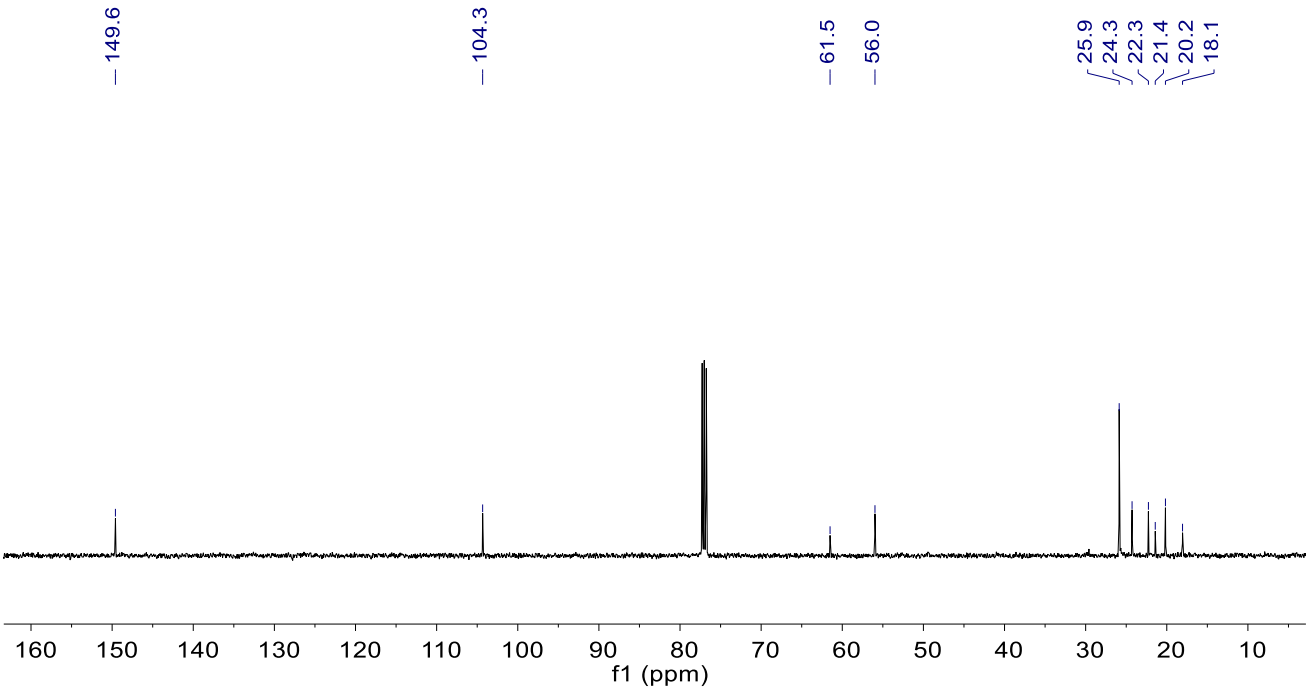
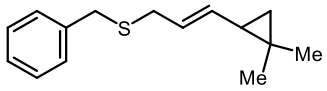


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum for **14** ($CDCl_3$, 295 K)



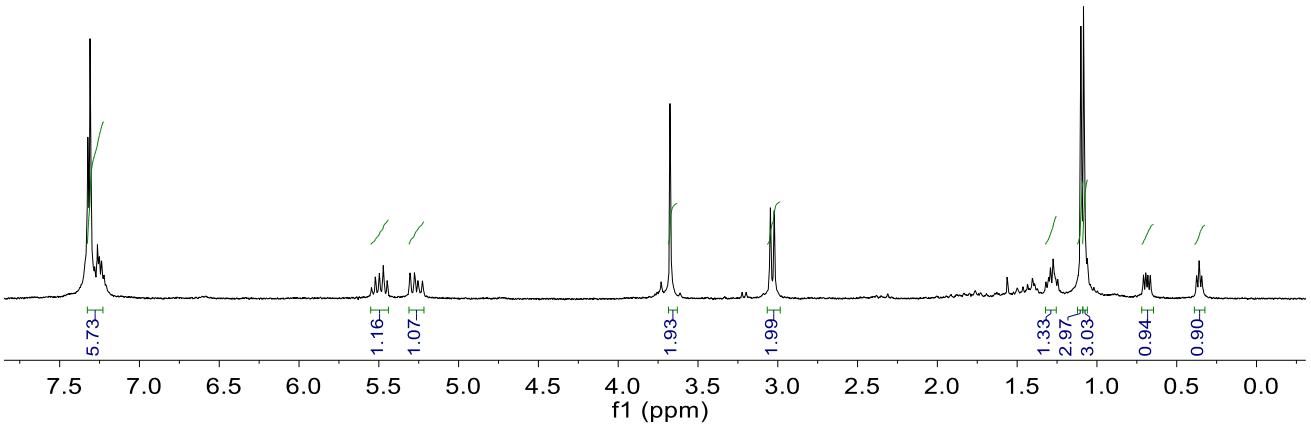


Figure S32: ^{1}H NMR spectrum for **15** ($CDCl_3$, 295 K)

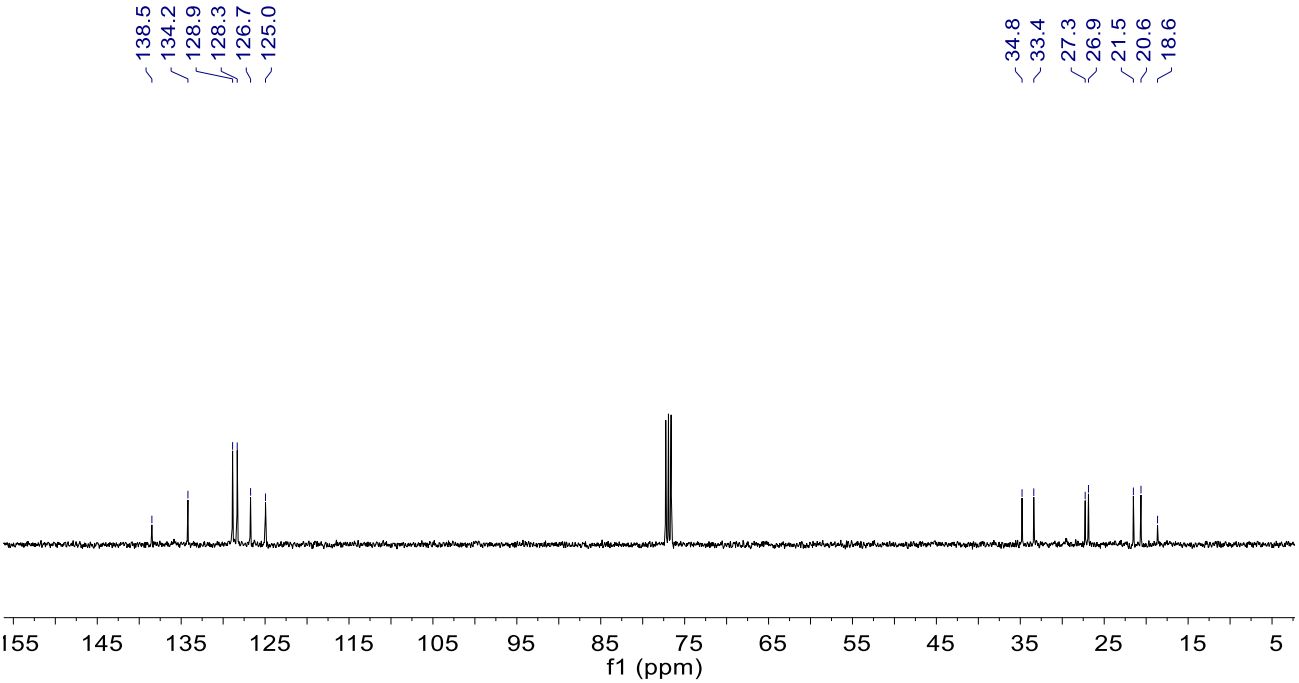
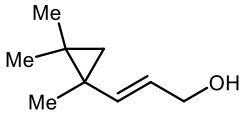


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum for **15** ($CDCl_3$, 295 K)



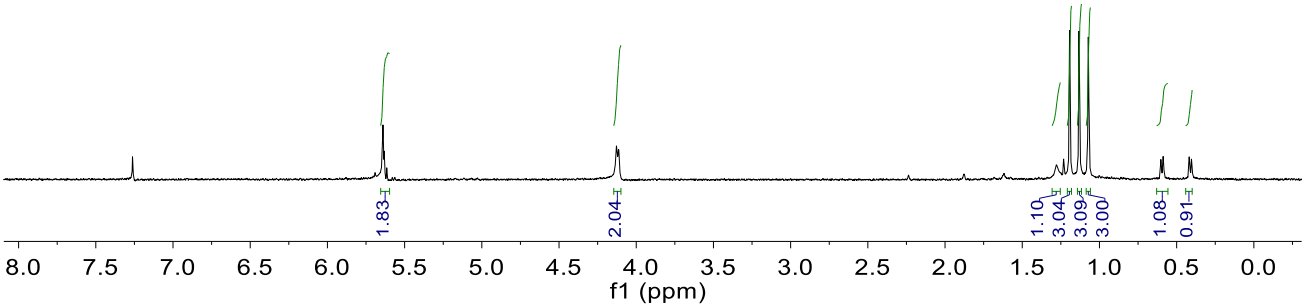


Figure S34: ^{1}H NMR spectrum for **18** ($CDCl_3$, 295 K)

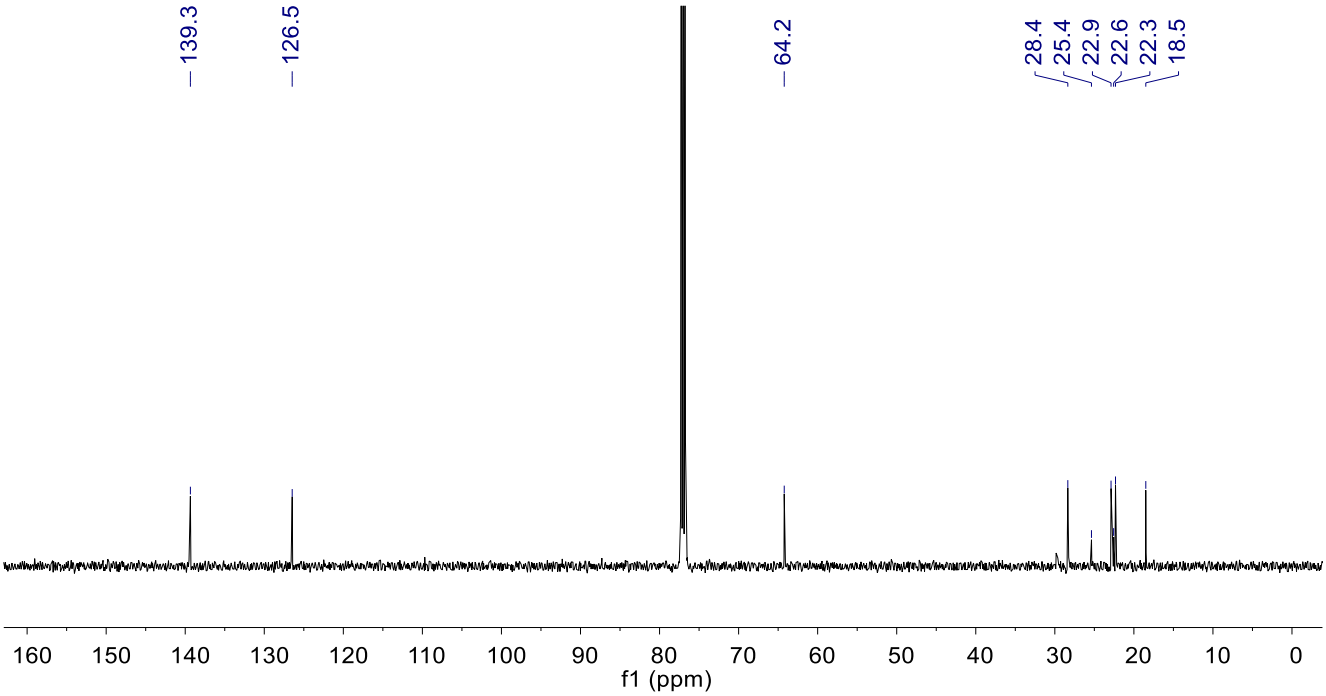
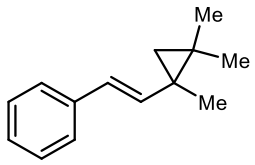


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum for **18** ($CDCl_3$, 295 K)



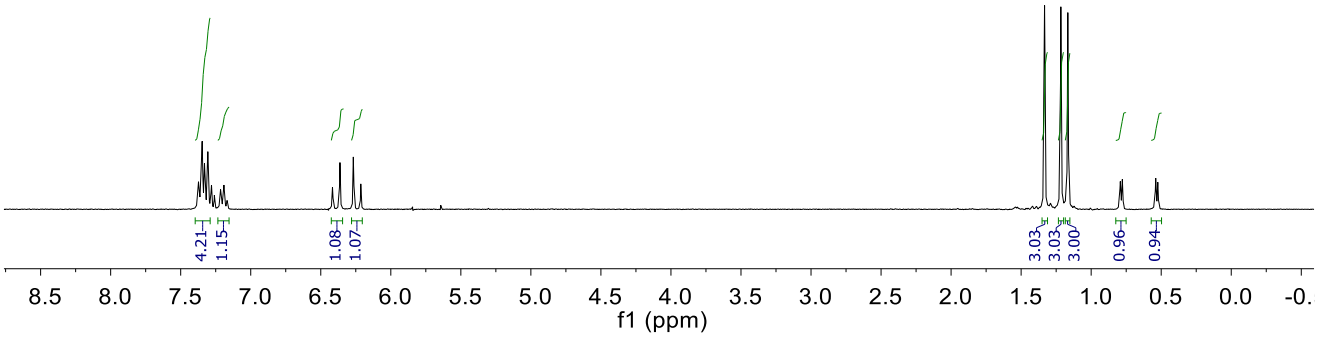


Figure S36: ^{1}H NMR spectrum for **26** ($CDCl_3$, 295 K)

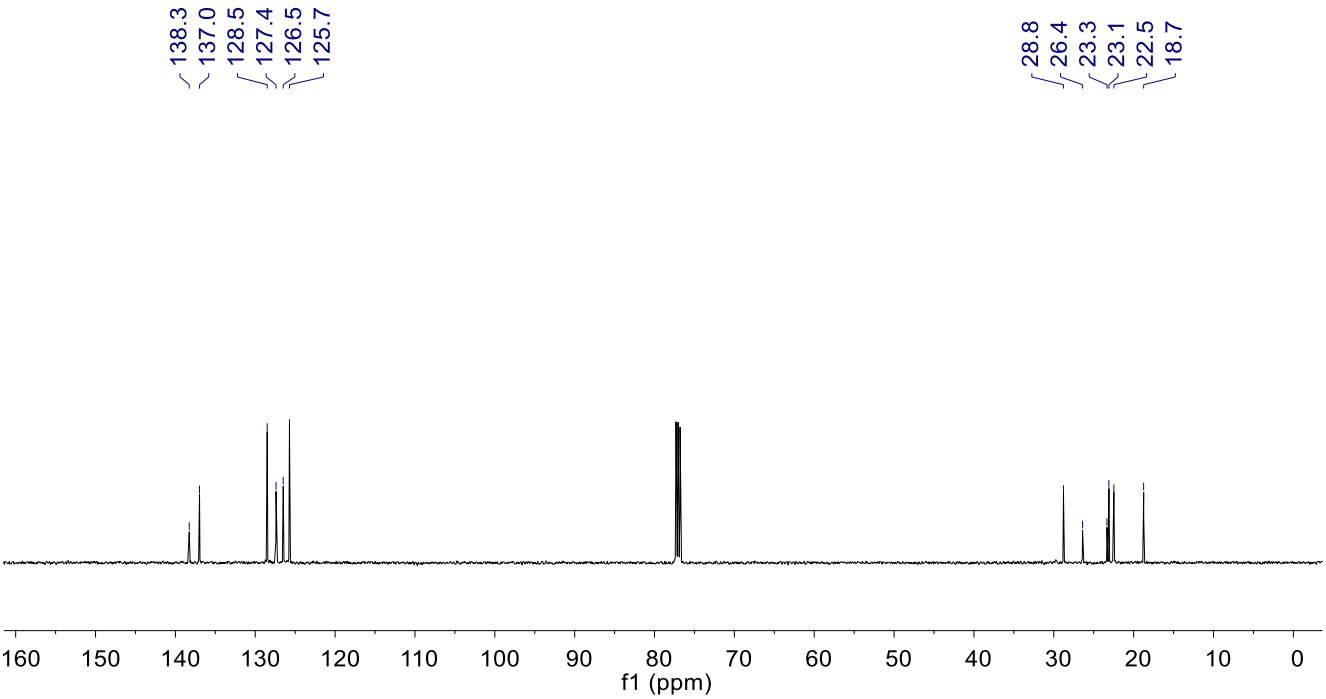


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum for **26** ($CDCl_3$, 295 K)

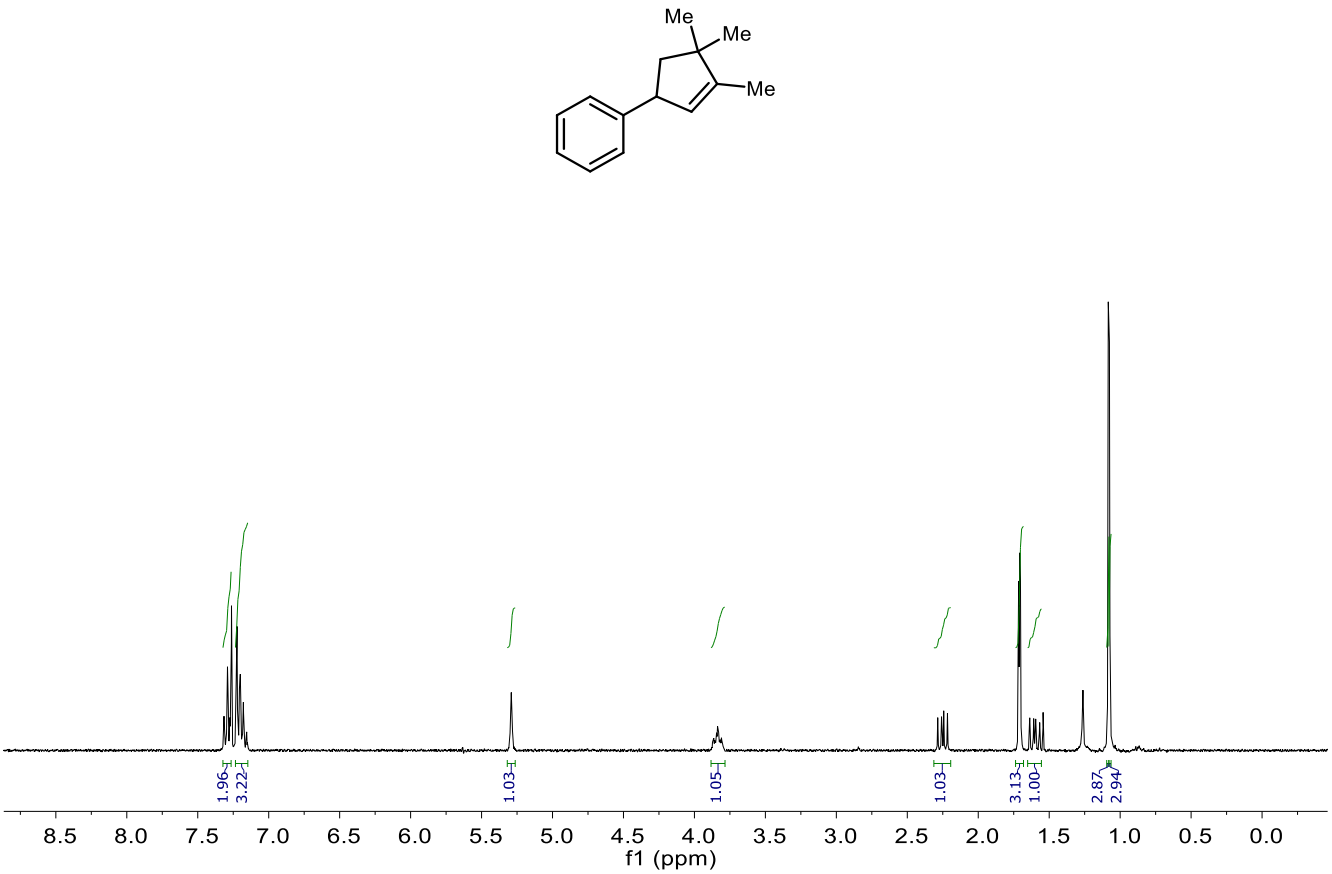


Figure S38: ^{1}H NMR spectrum for **27** ($CDCl_3$, 295 K)

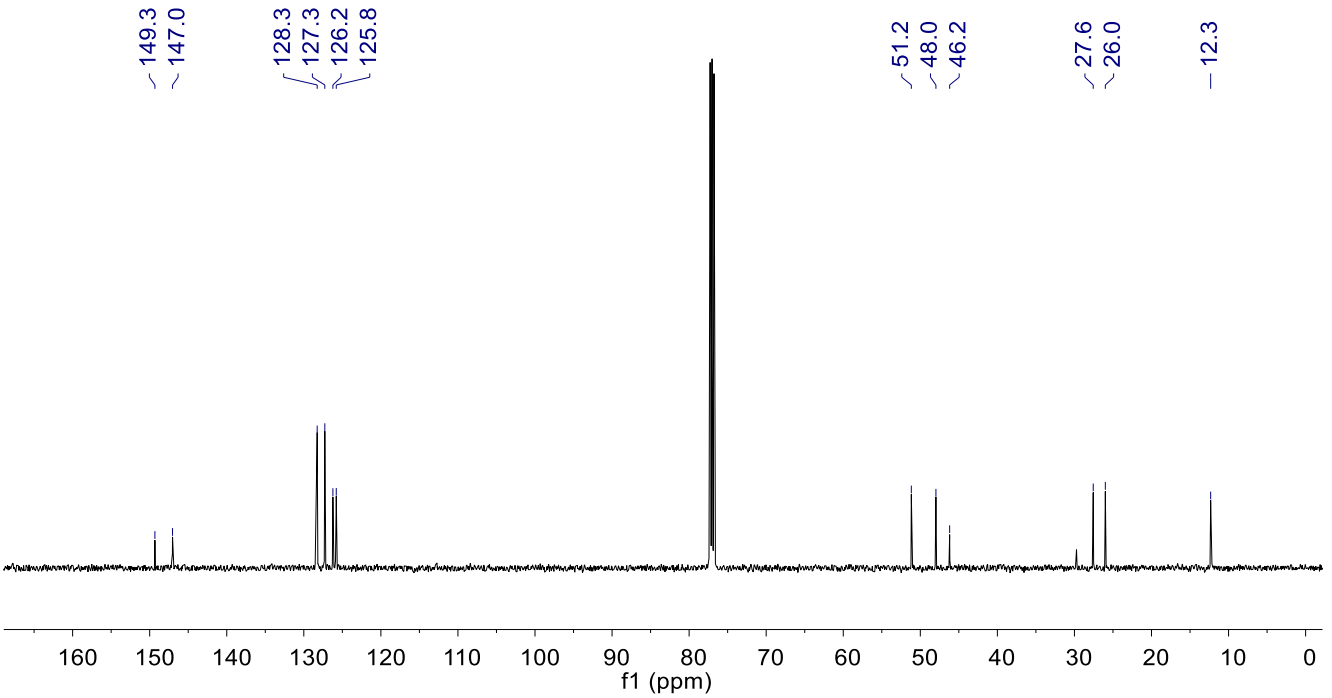


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum for **27** ($CDCl_3$, 295 K)

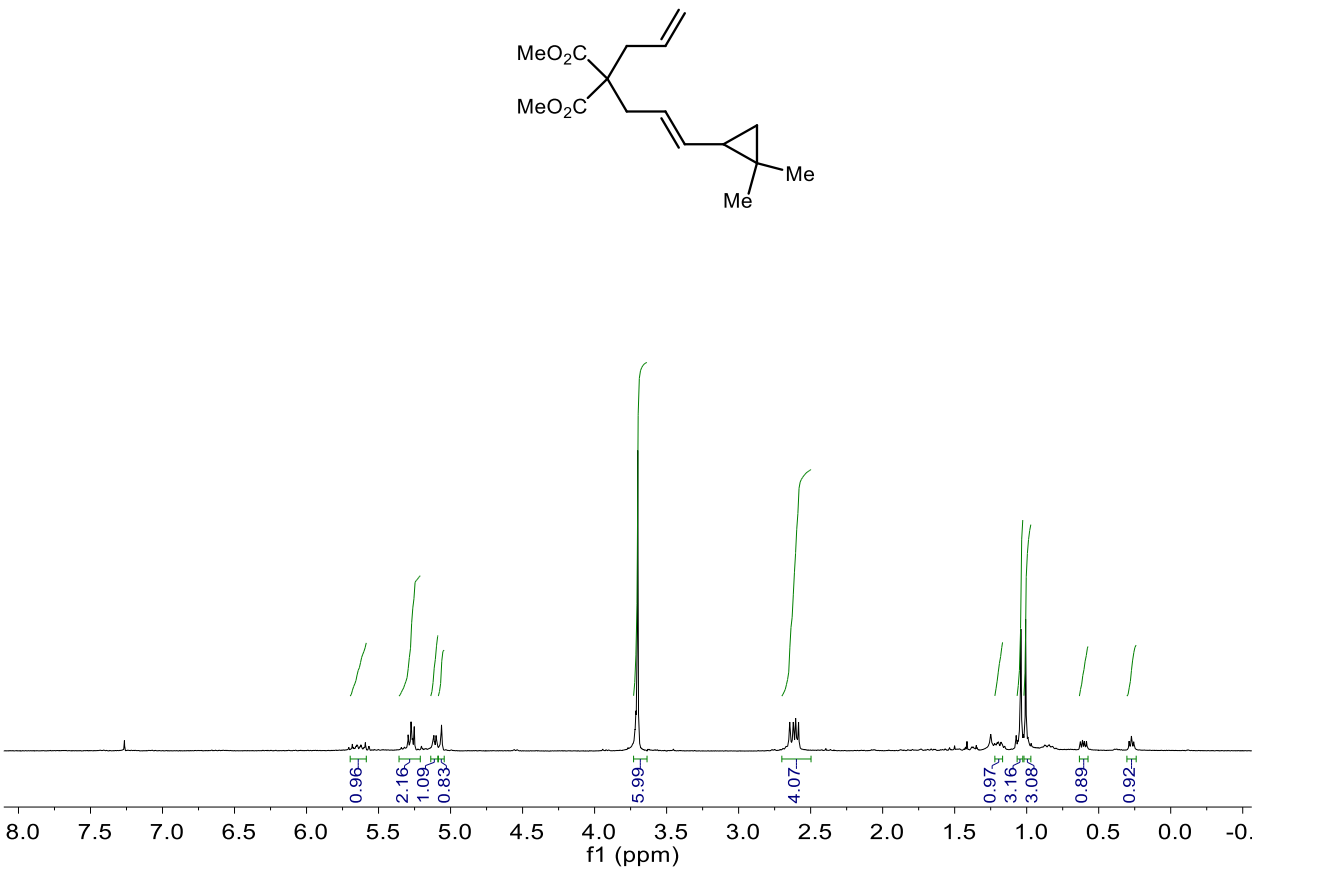


Figure S40: ^{1}H NMR spectrum for **28** ($CDCl_3$, 295 K)

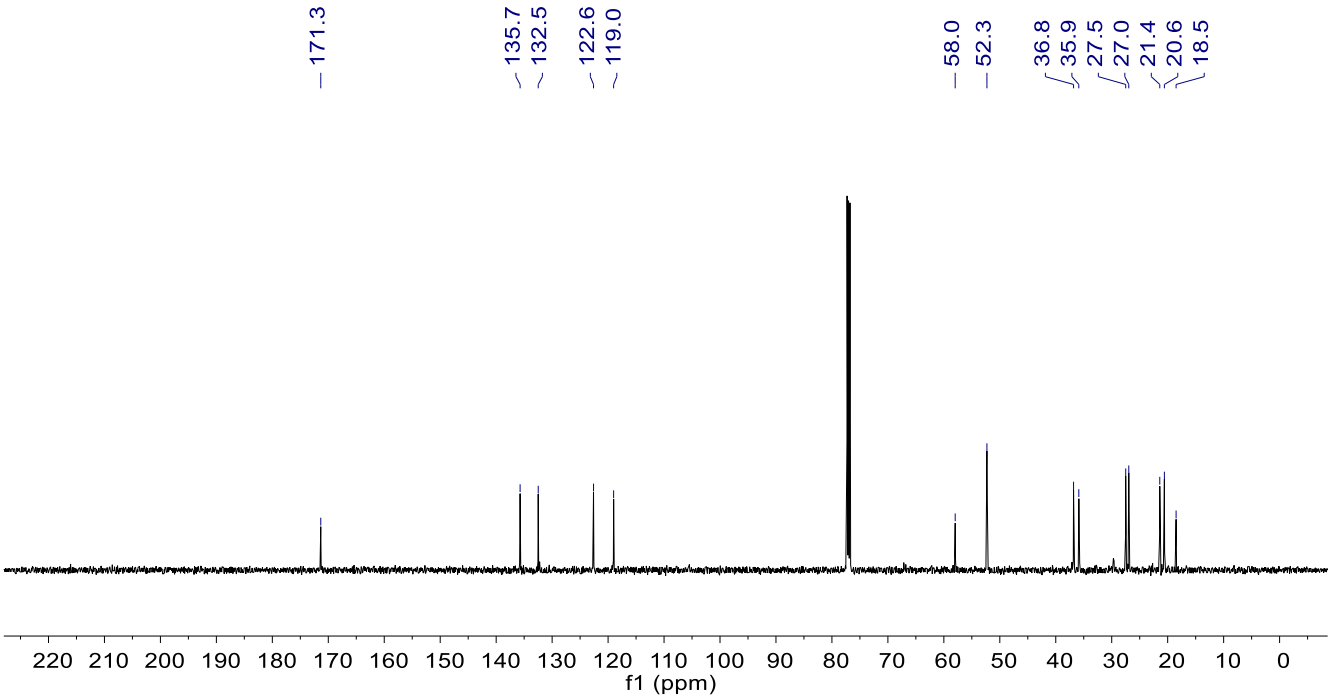
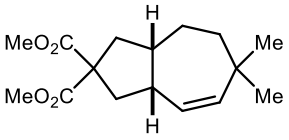


Figure S41: $^{13}C\{^{1}H\}$ NMR spectrum for **28** ($CDCl_3$, 295 K)



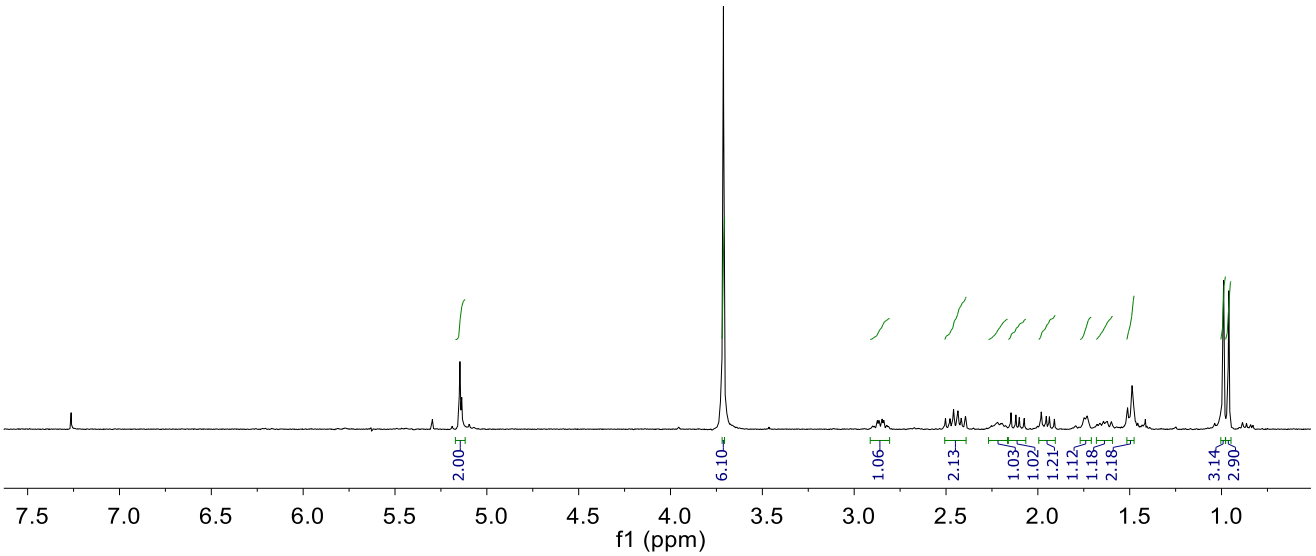


Figure S42: ^{1}H NMR spectrum for **29** ($CDCl_3$, 295 K)

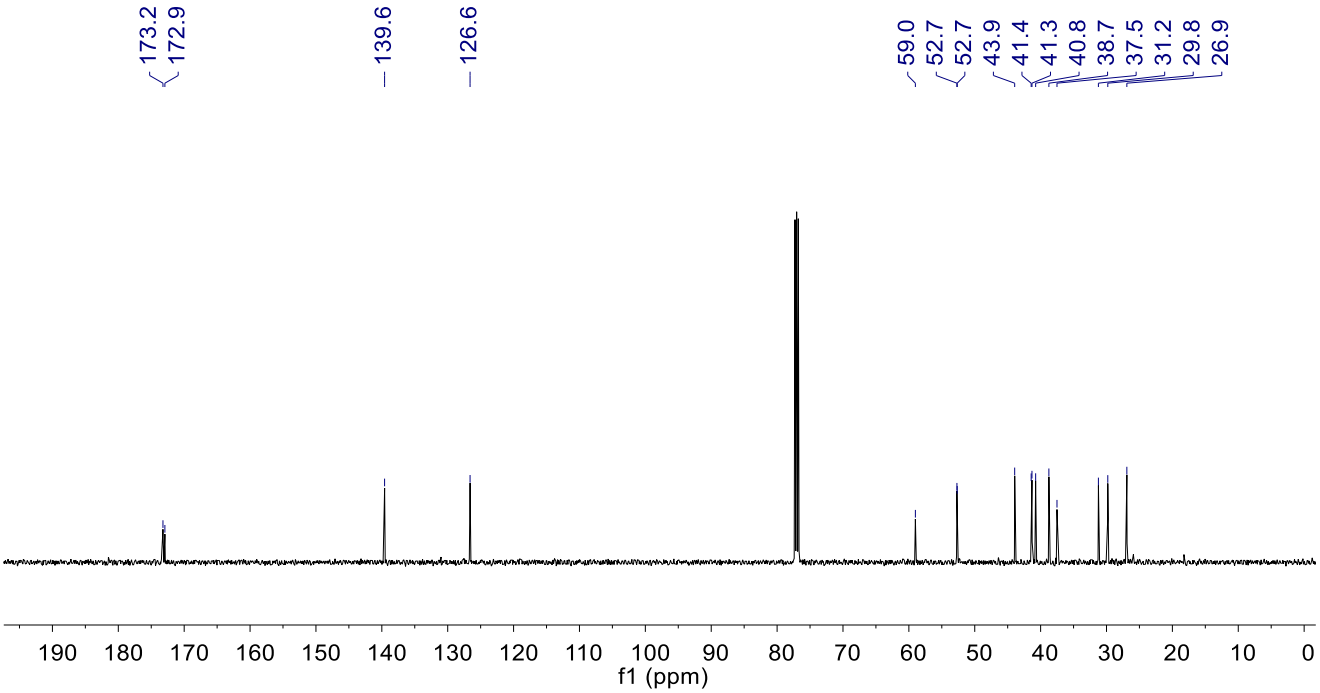


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum for **29** ($CDCl_3$, 295 K)

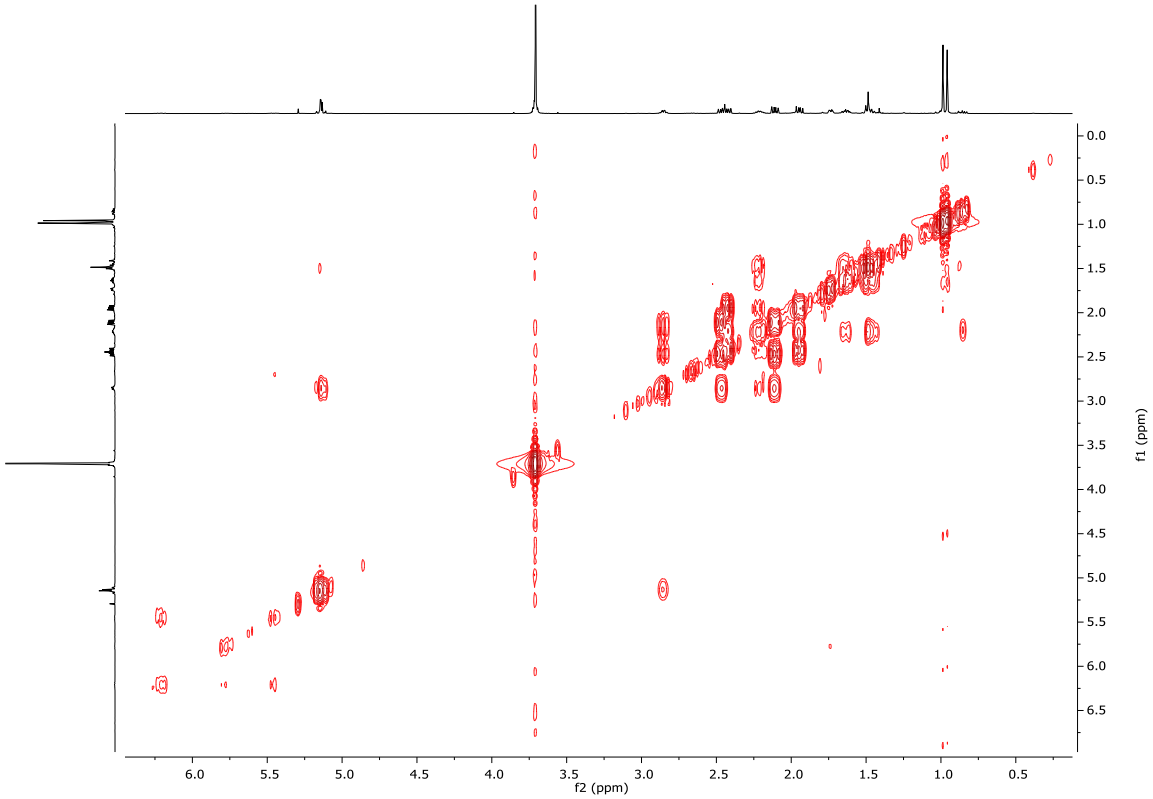


Figure S44: COSY spectrum for **29** ($CDCl_3$, 295 K)

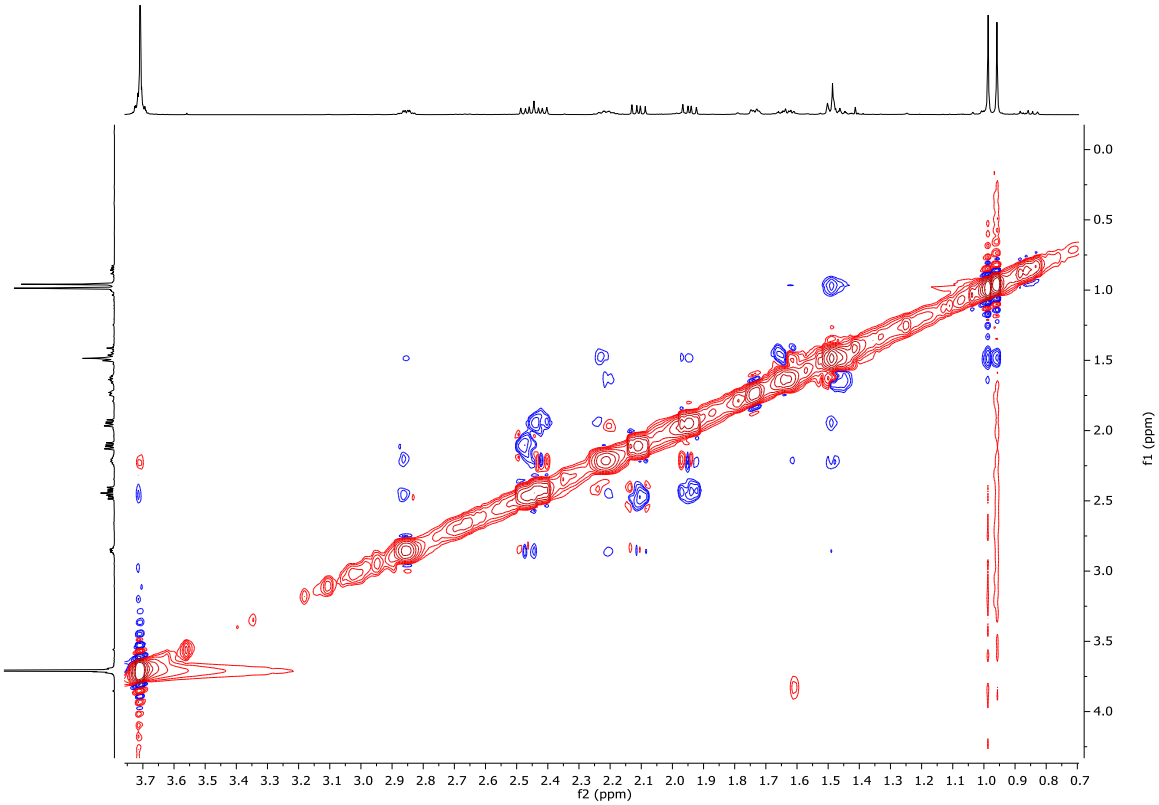
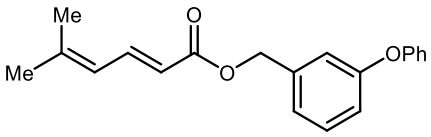


Figure S45: NOESY spectrum for **29** ($CDCl_3$, 295 K)



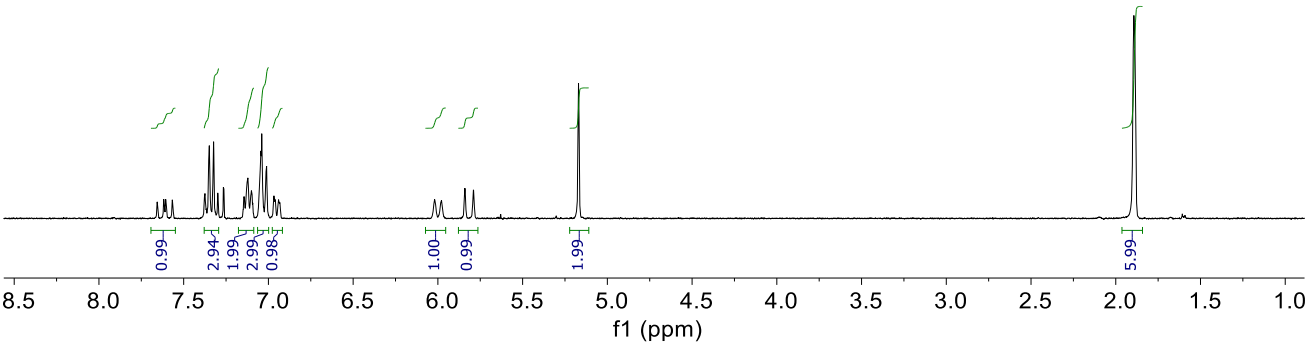


Figure S46: ^{1}H NMR spectrum for **S2** ($CDCl_3$, 295 K)

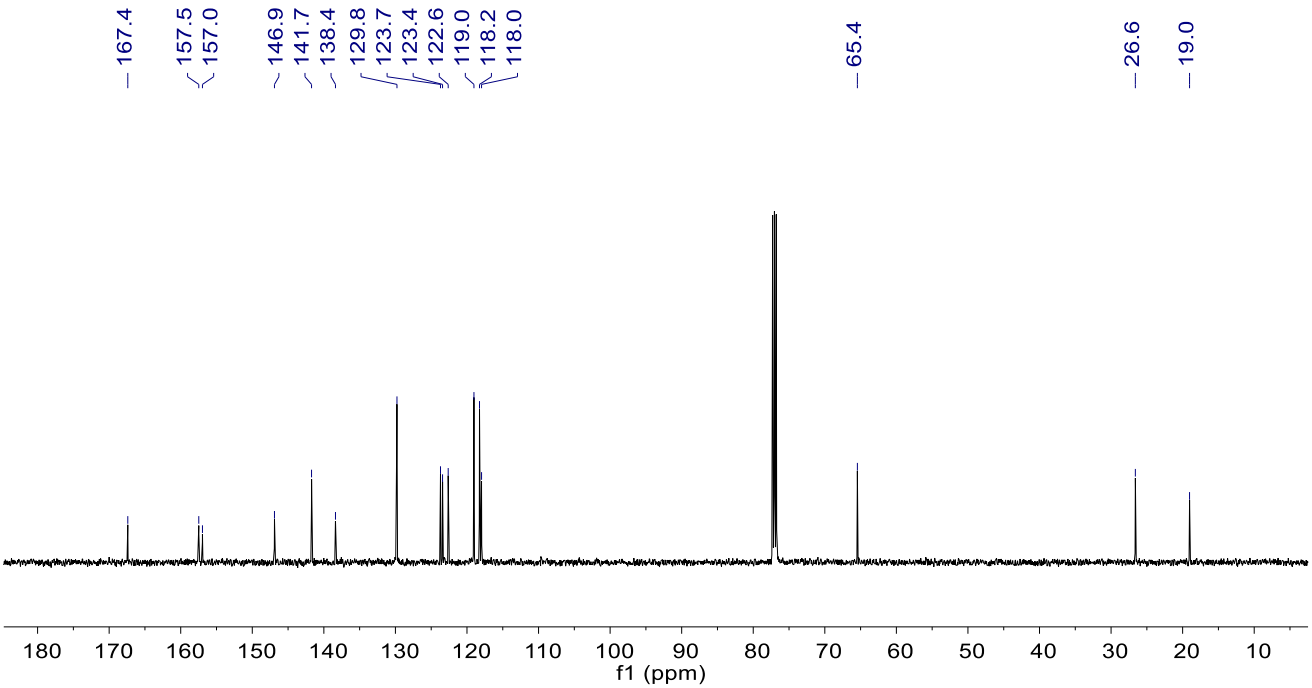
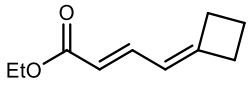


Figure S47: $^{13}C\{^{1}H\}$ NMR spectrum for **S2** ($CDCl_3$, 295 K)



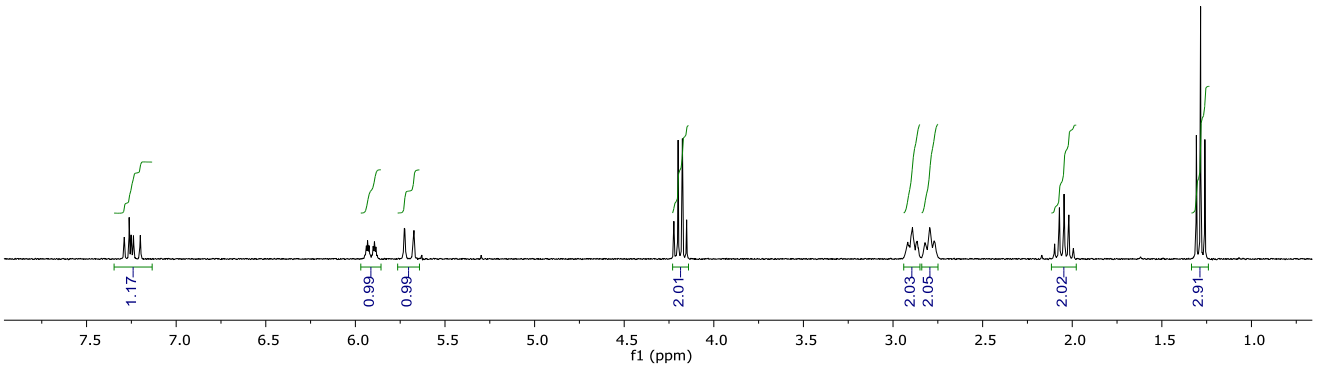


Figure S48: ^{1}H NMR spectrum for **S3** ($CDCl_3$, 295 K)

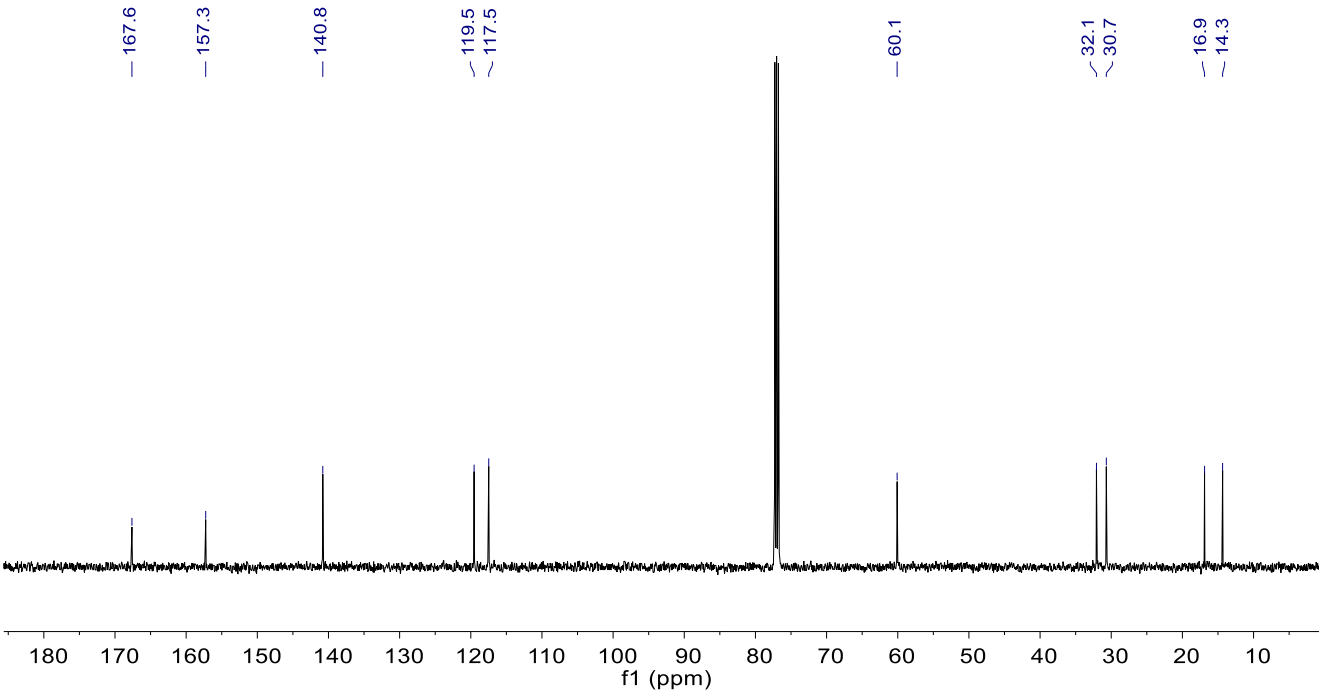
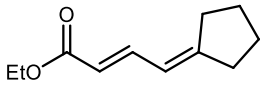


Figure S49: $^{13}C\{^{1}H\}$ NMR spectrum for **S3** ($CDCl_3$, 295 K)



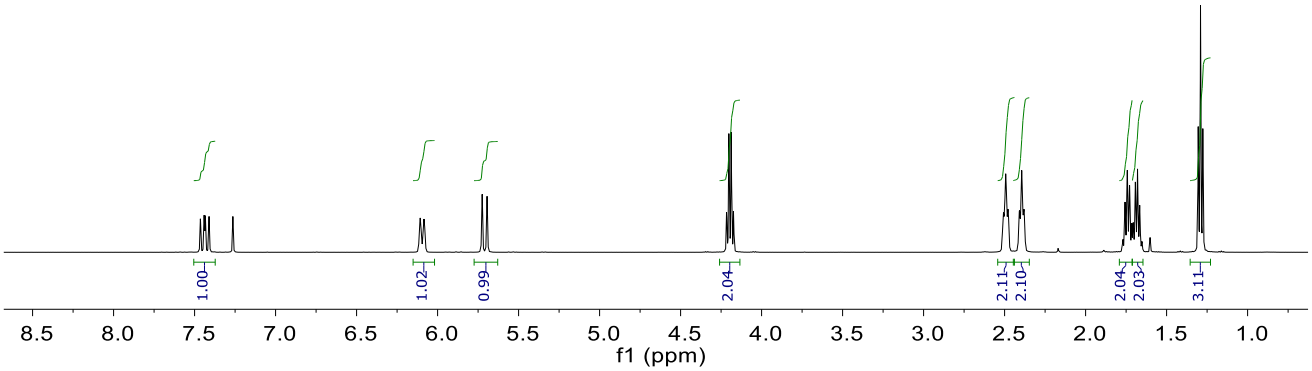


Figure S50: ^{1}H NMR spectrum for **S4** ($CDCl_3$, 295 K)

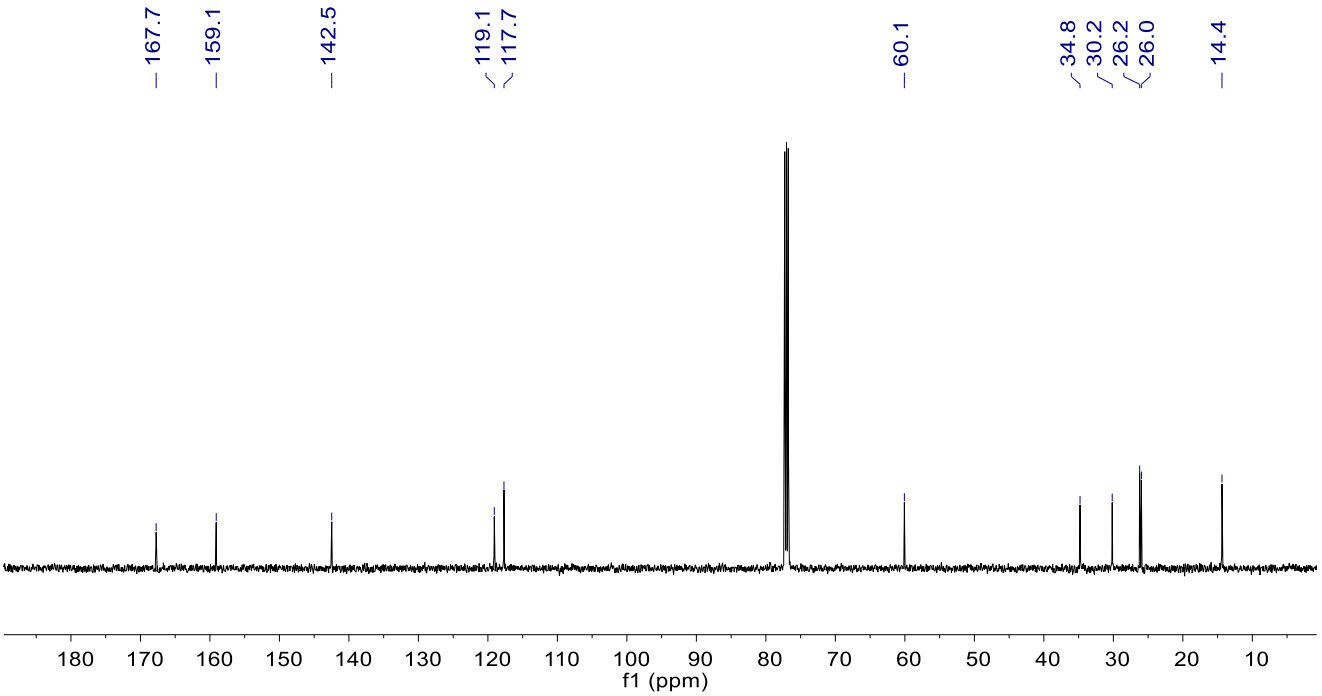
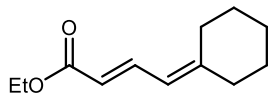


Figure S51: $^{13}C\{^{1}H\}$ NMR spectrum for **S4** ($CDCl_3$, 295 K)



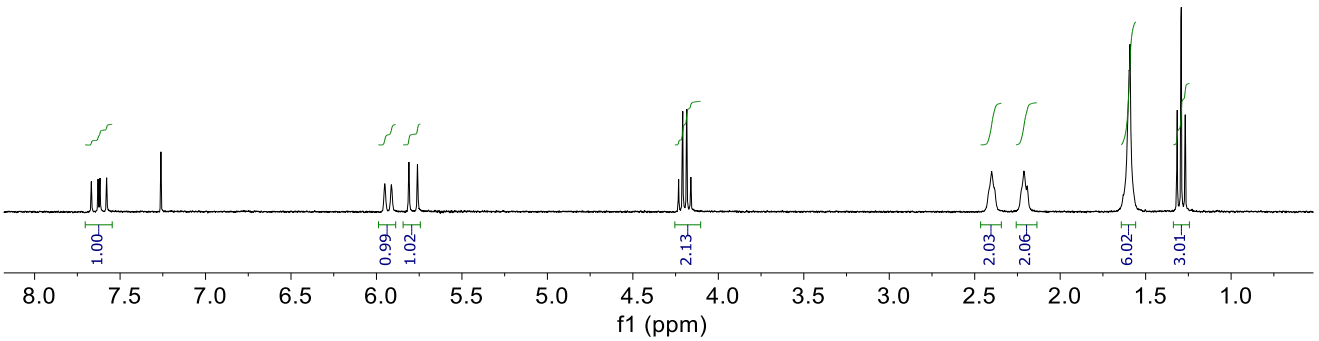


Figure S52: ^{1}H NMR spectrum for **S5** ($CDCl_3$, 295 K)

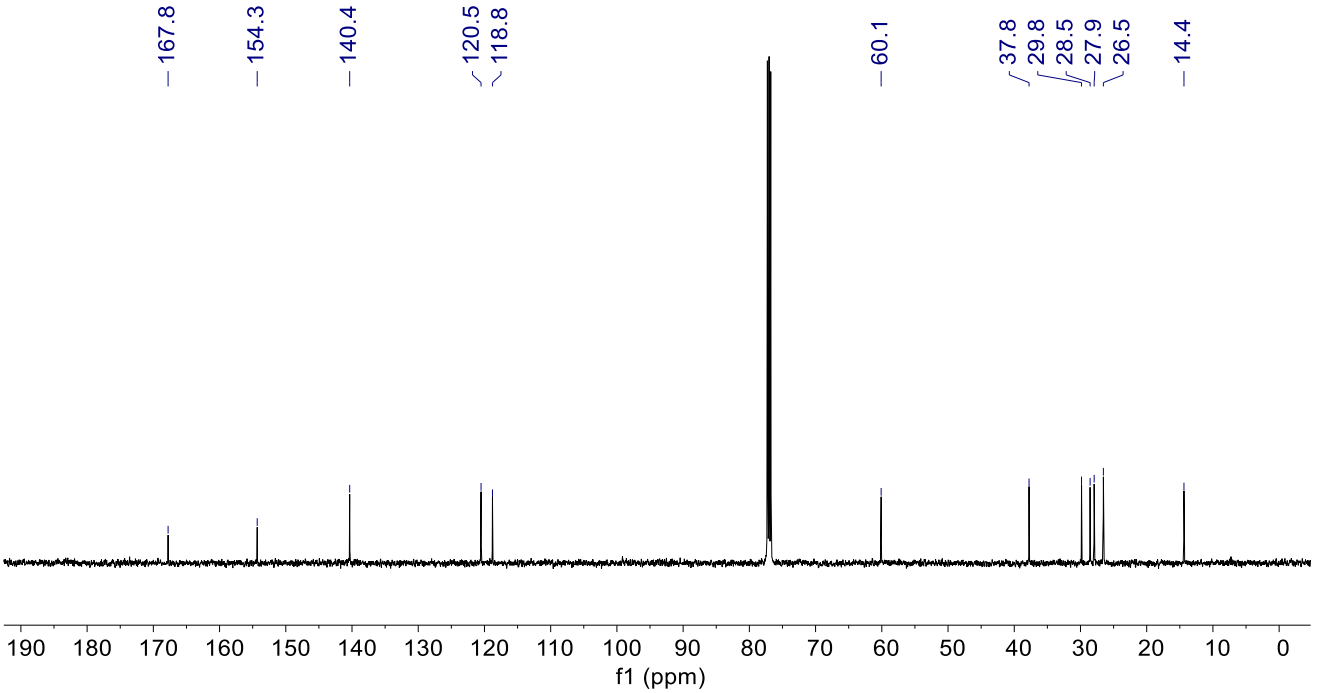
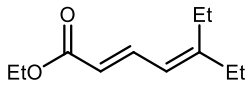


Figure S53: $^{13}C\{^{1}H\}$ NMR spectrum for **S5** ($CDCl_3$, 295 K)



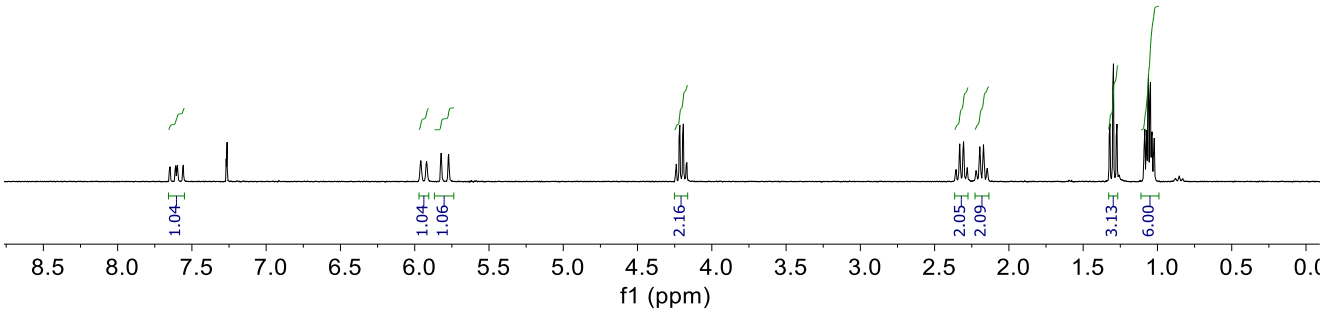


Figure S54: ^{1}H NMR spectrum for **S6** ($CDCl_3$, 295 K)

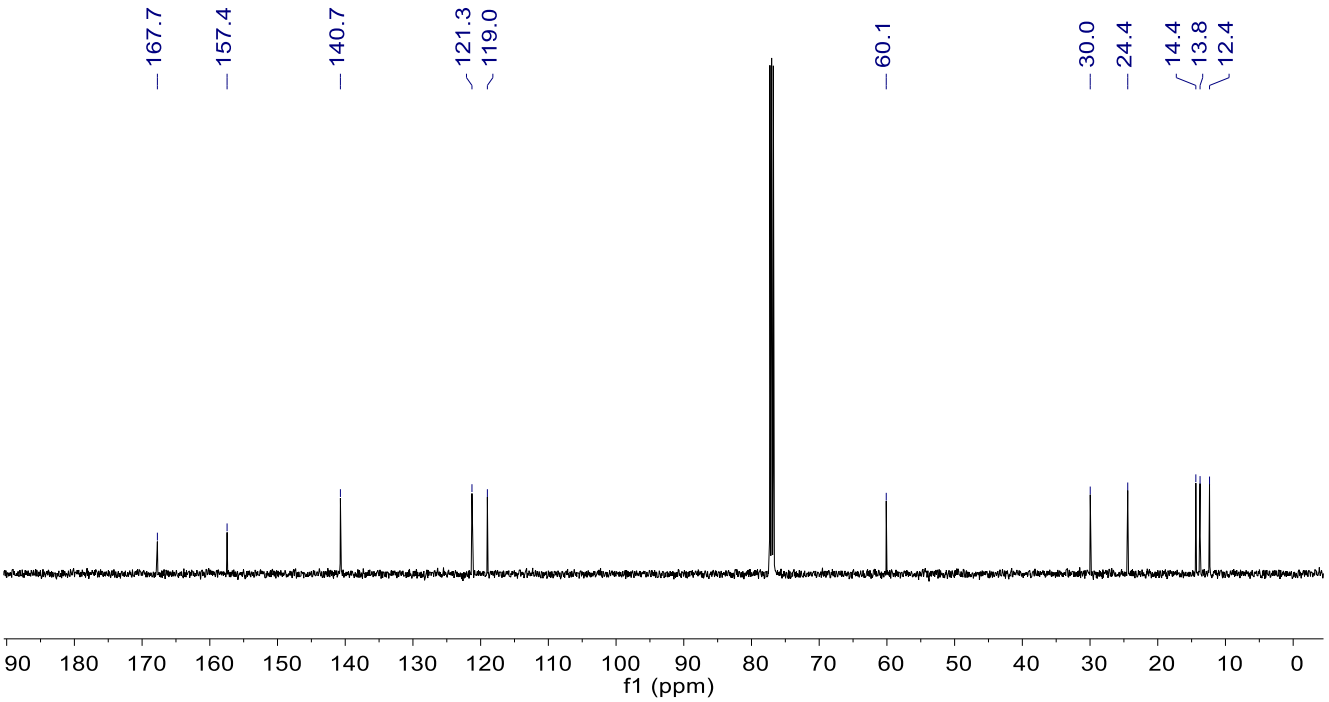


Figure S55: $^{13}C\{^{1}H\}$ NMR spectrum for **S6** ($CDCl_3$, 295 K)

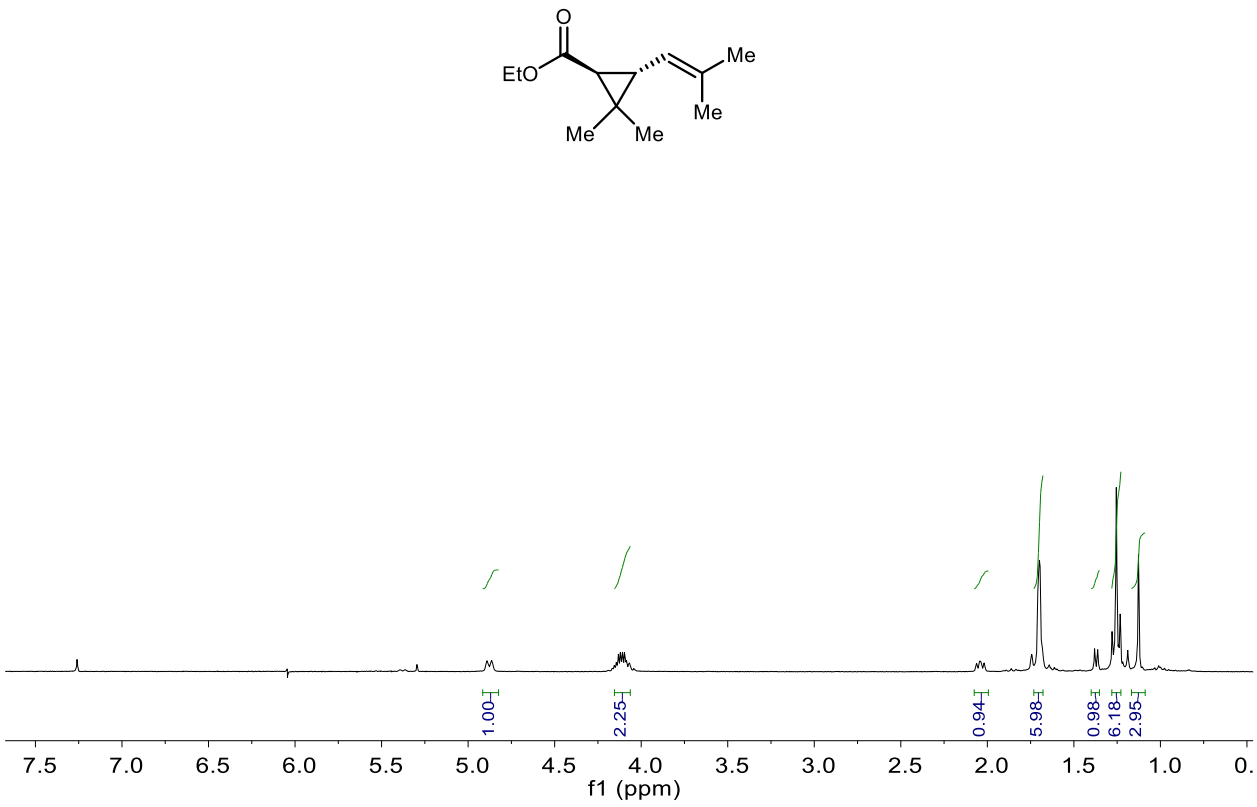


Figure S56: ^{1}H NMR spectrum for **19** ($CDCl_3$, 295 K)

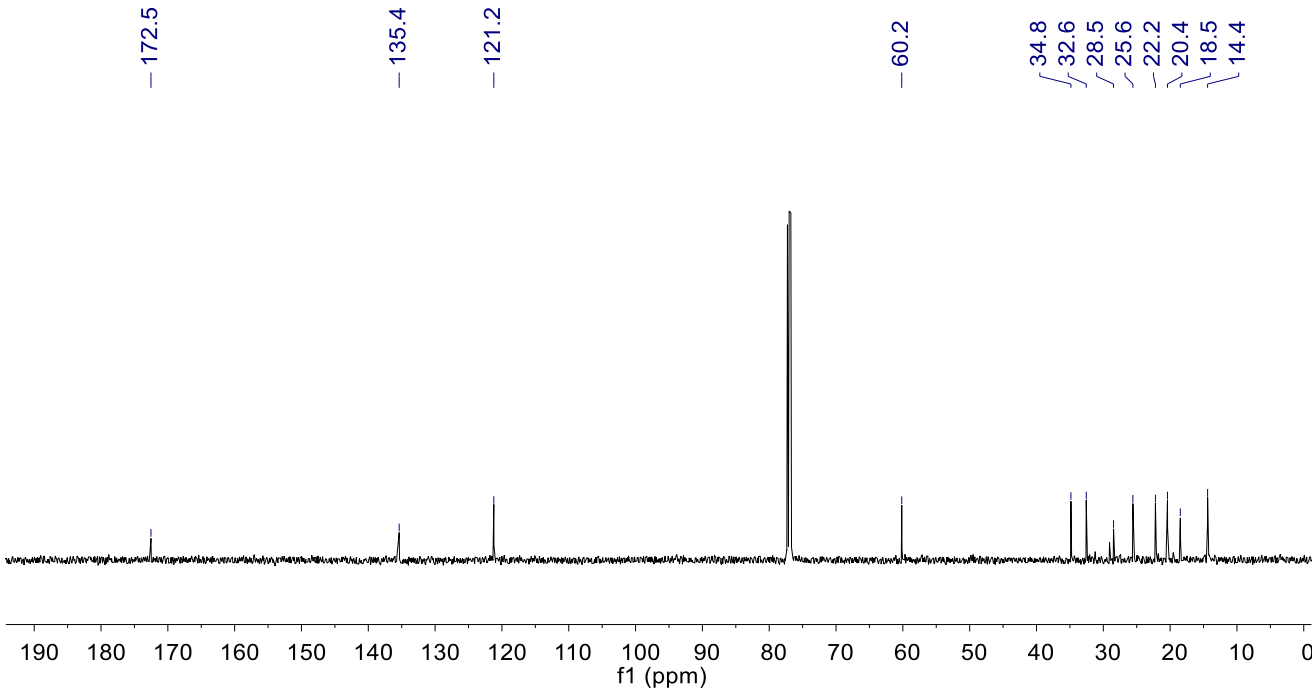
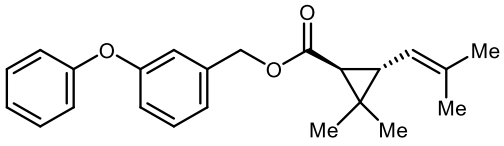


Figure S57: $^{13}C\{^{1}H\}$ NMR spectrum for **19** ($CDCl_3$, 295 K)



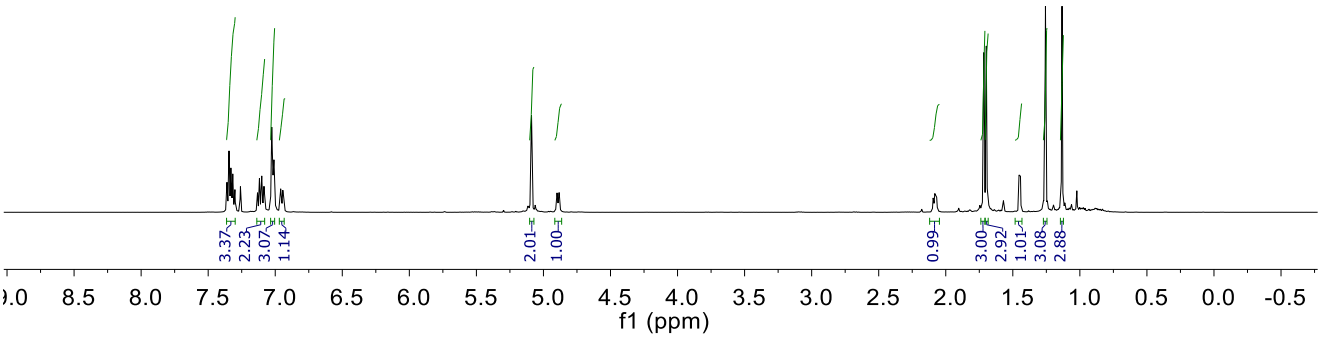


Figure S58: ^{1}H NMR spectrum for **20** ($CDCl_3$, 295 K)

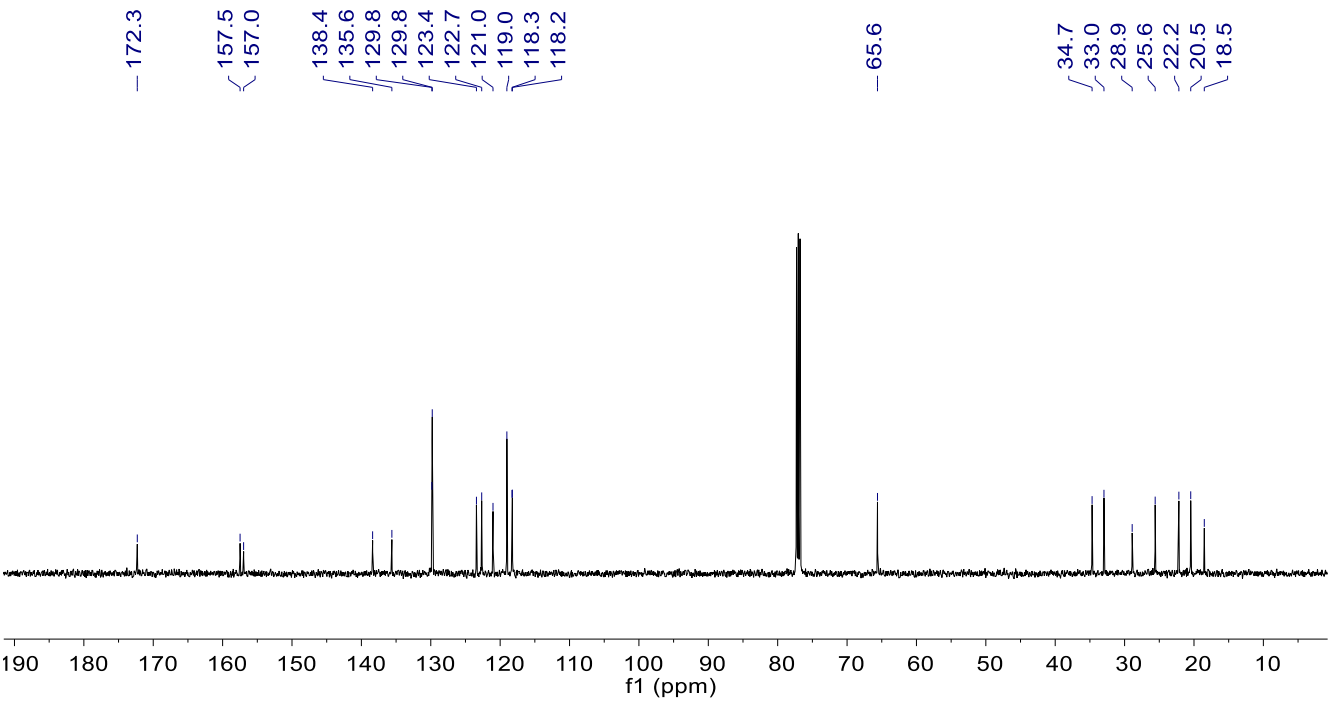


Figure S59: $^{13}C\{^{1}H\}$ NMR spectrum for **20** ($CDCl_3$, 295 K)

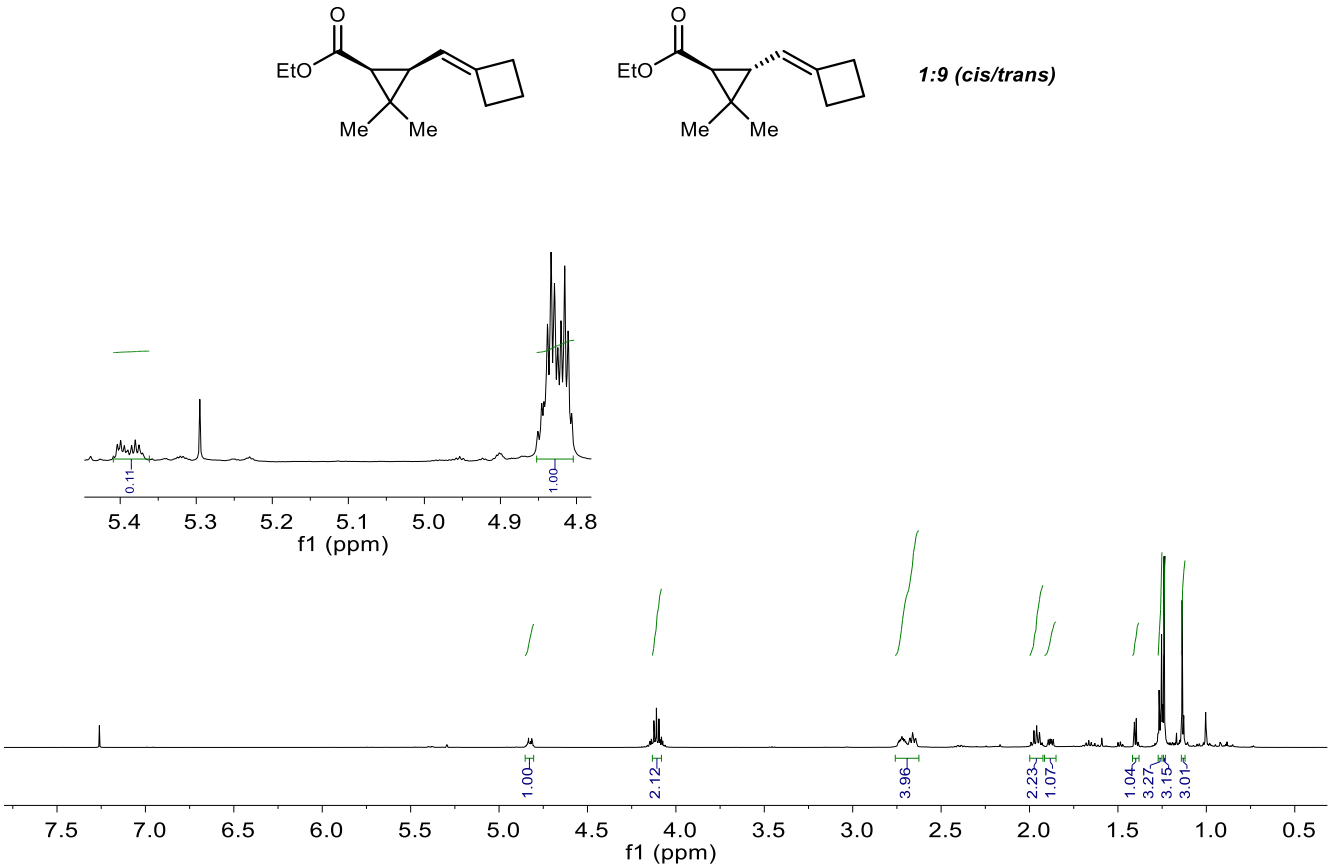


Figure S60: ^{1}H NMR spectrum for **21** ($CDCl_3$, 295 K)

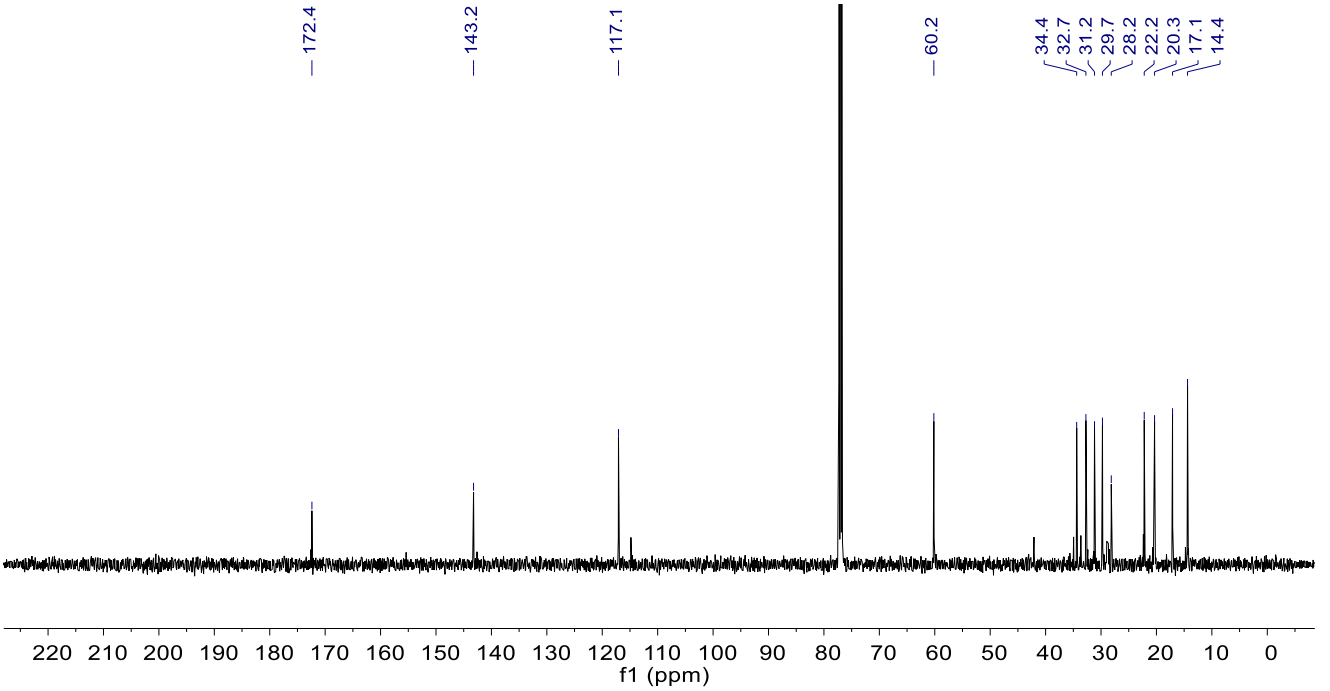


Figure S61: $^{13}C\{^{1}H\}$ NMR spectrum for **21** ($CDCl_3$, 295 K)

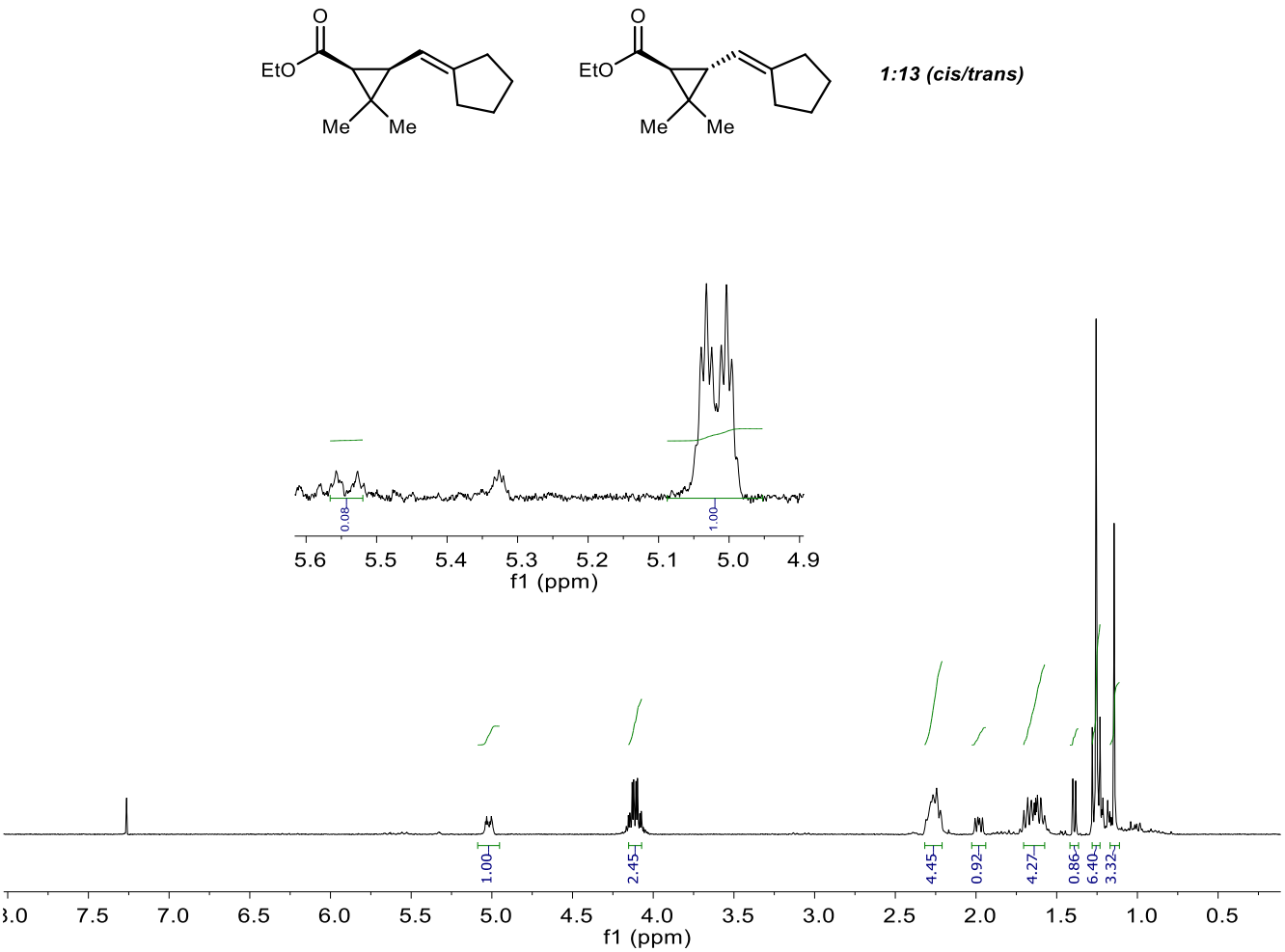


Figure S62: ^{1}H NMR spectrum for **22** ($CDCl_3$, 295 K)

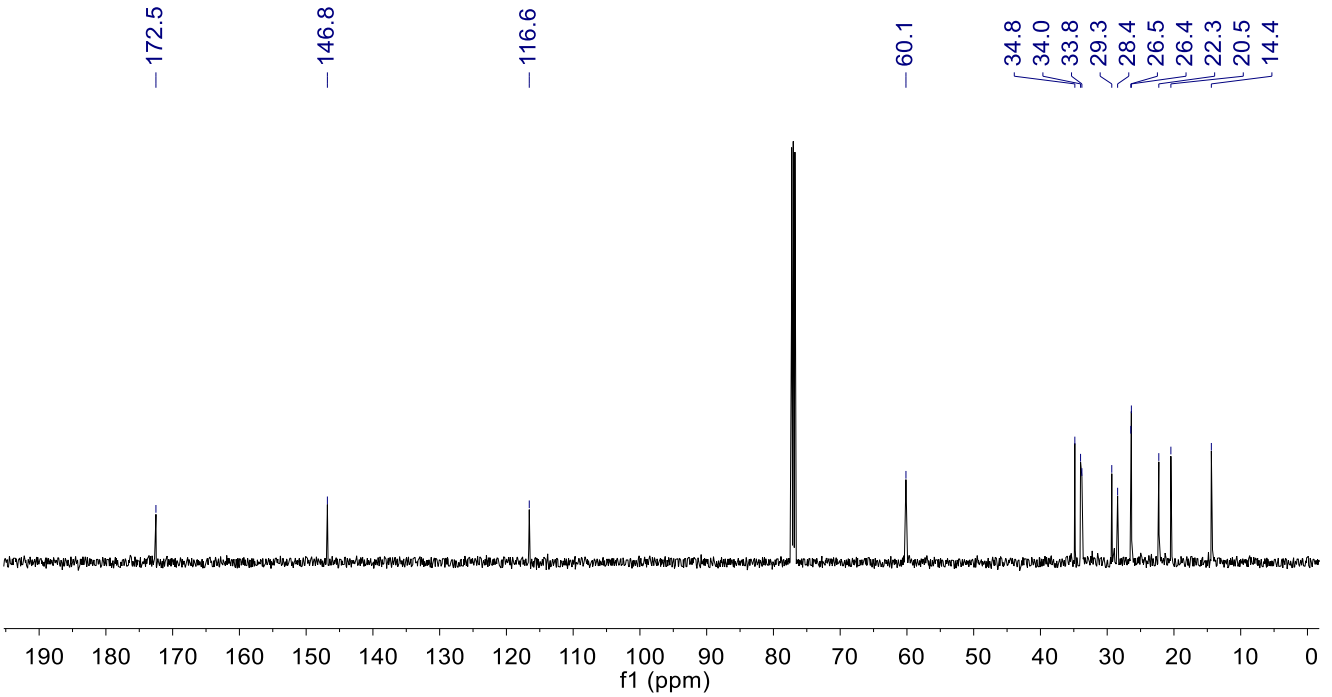


Figure S63: $^{13}C\{^{1}H\}$ NMR spectrum for **22** ($CDCl_3$, 295 K)

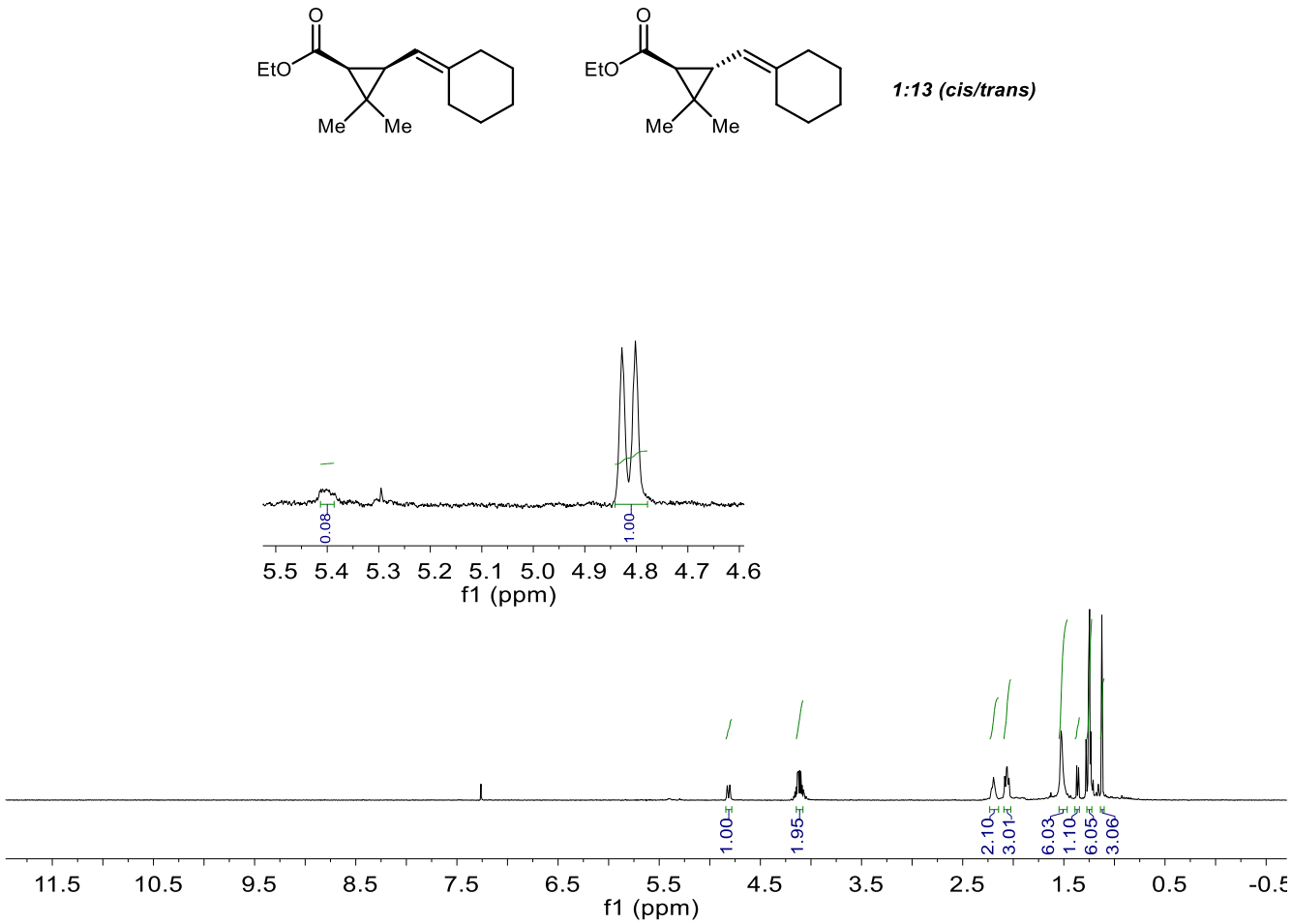


Figure S64: ^{1}H NMR spectrum for **23** ($CDCl_3$, 295 K)

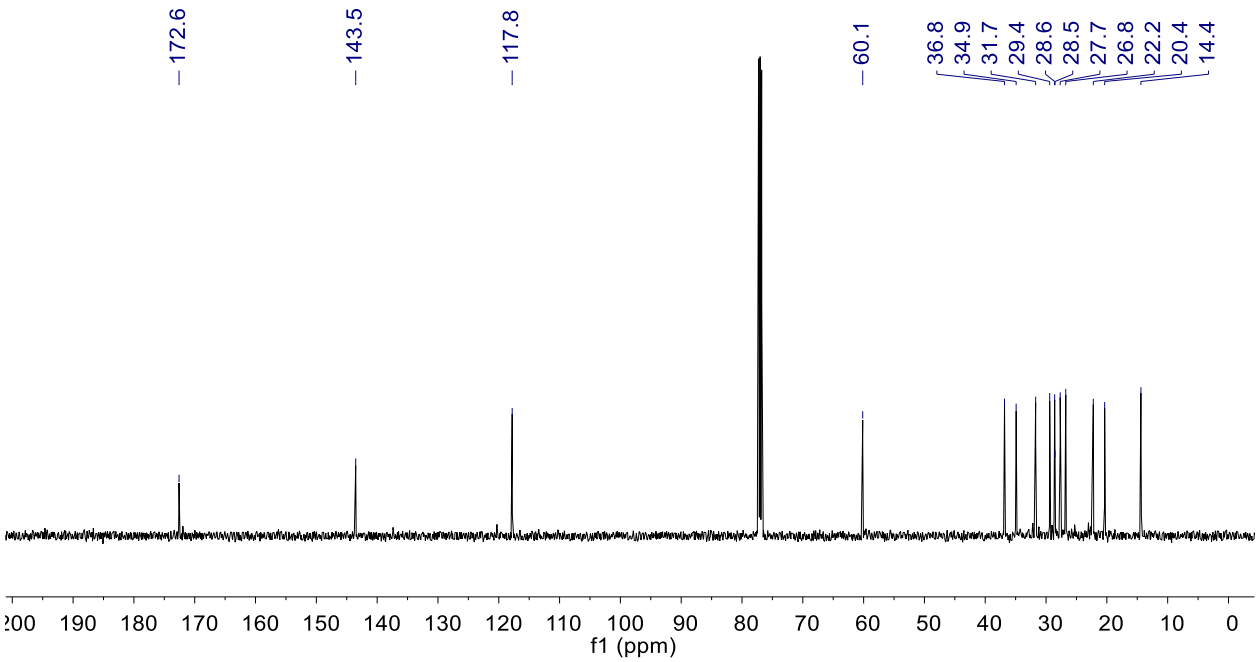
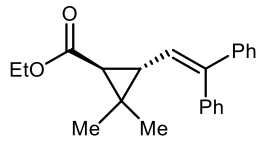


Figure S65: $^{13}C\{^{1}H\}$ NMR spectrum for **23** ($CDCl_3$, 295 K)



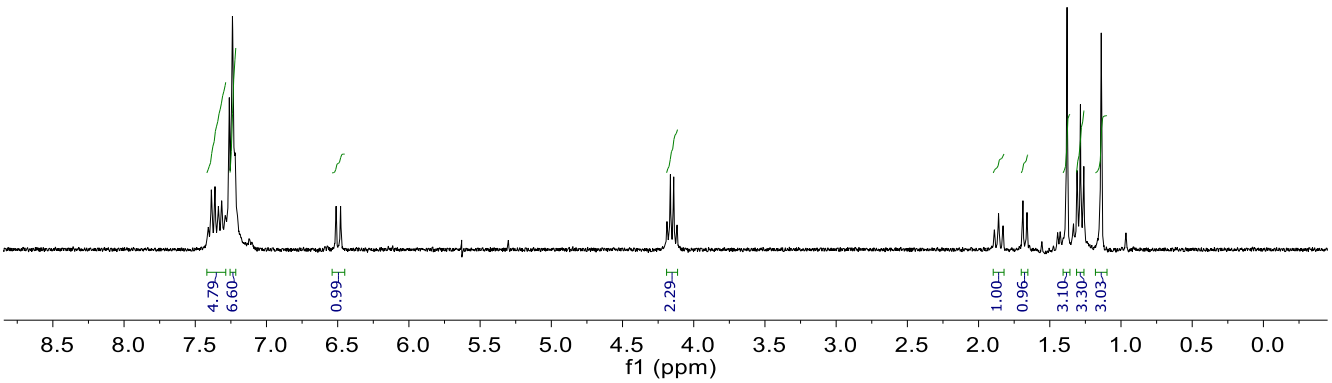


Figure S66: ^{1}H NMR spectrum for **24** ($CDCl_3$, 295 K)

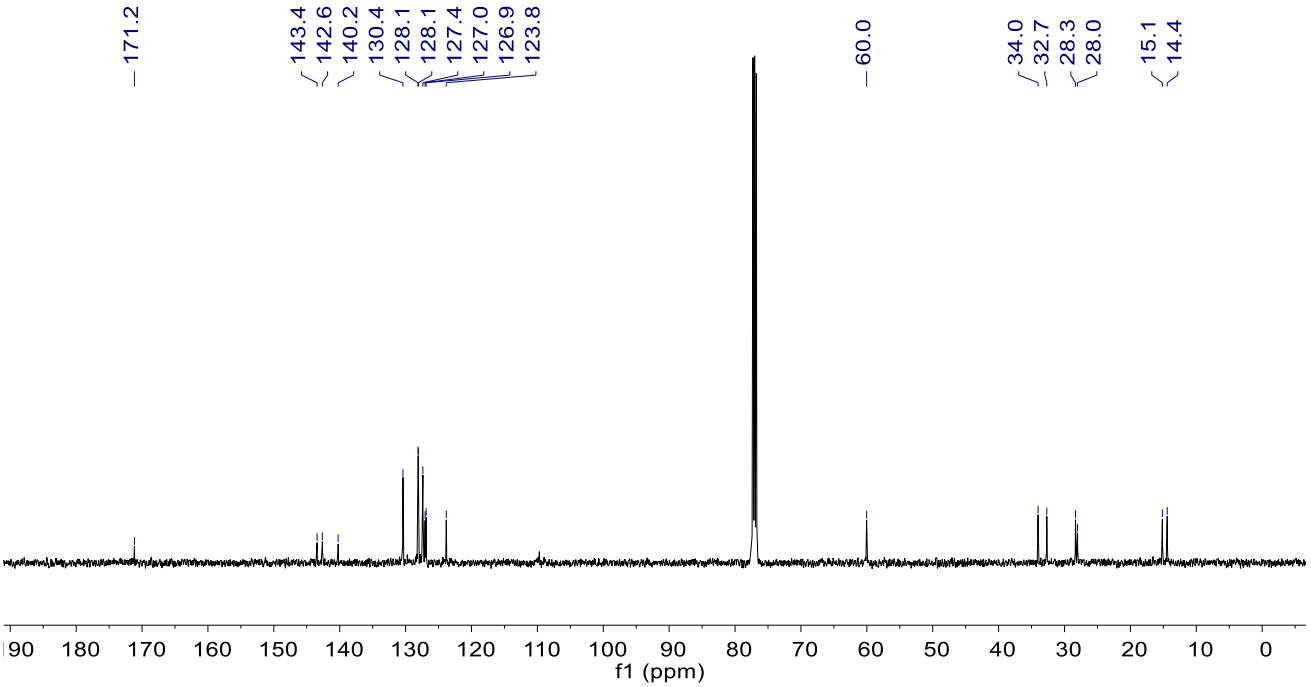
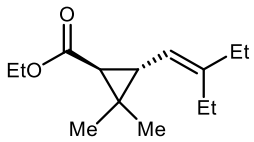


Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum for **24** ($CDCl_3$, 295 K)



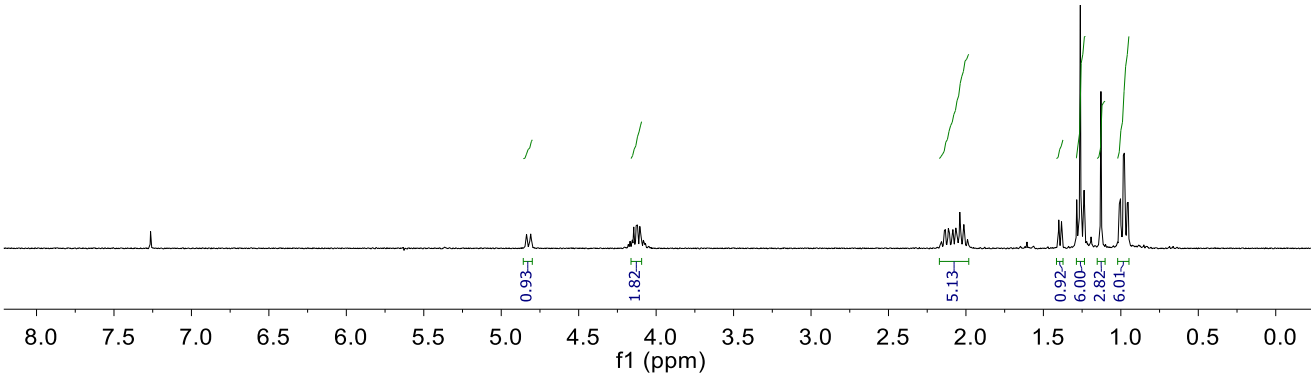


Figure S68: ^{1}H NMR spectrum for **25** ($CDCl_3$, 295 K)

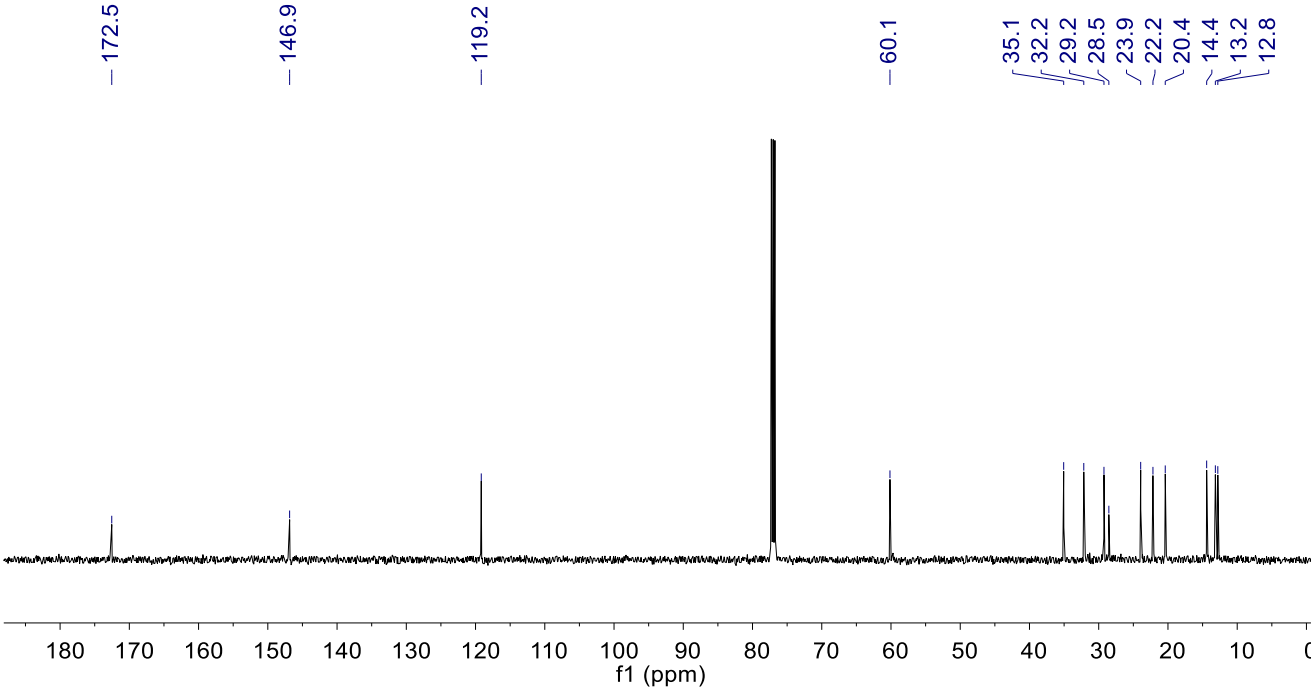


Figure S69: $^{13}C\{^{1}H\}$ NMR spectrum for **25** ($CDCl_3$, 295 K)

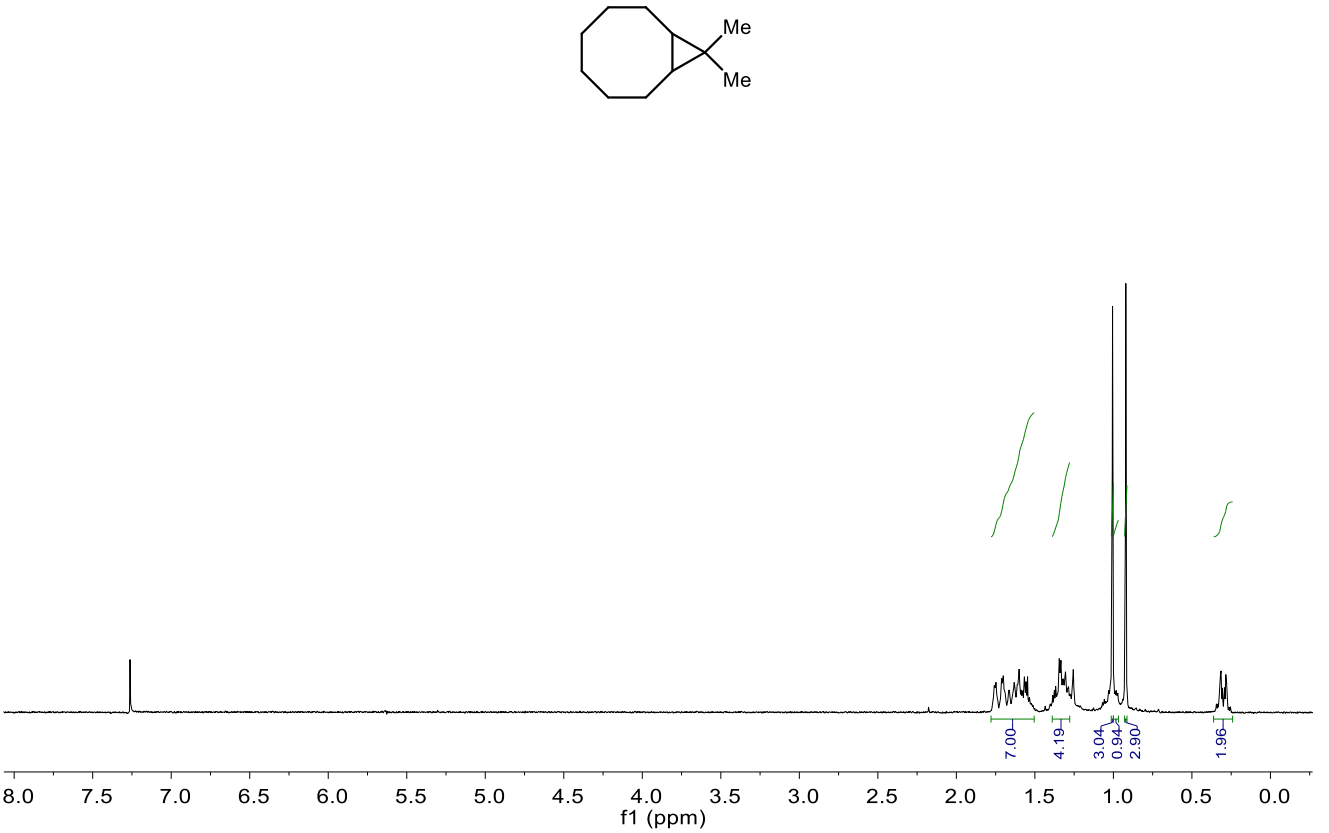


Figure S70: ^{1}H NMR spectrum for **31** ($CDCl_3$, 295 K)

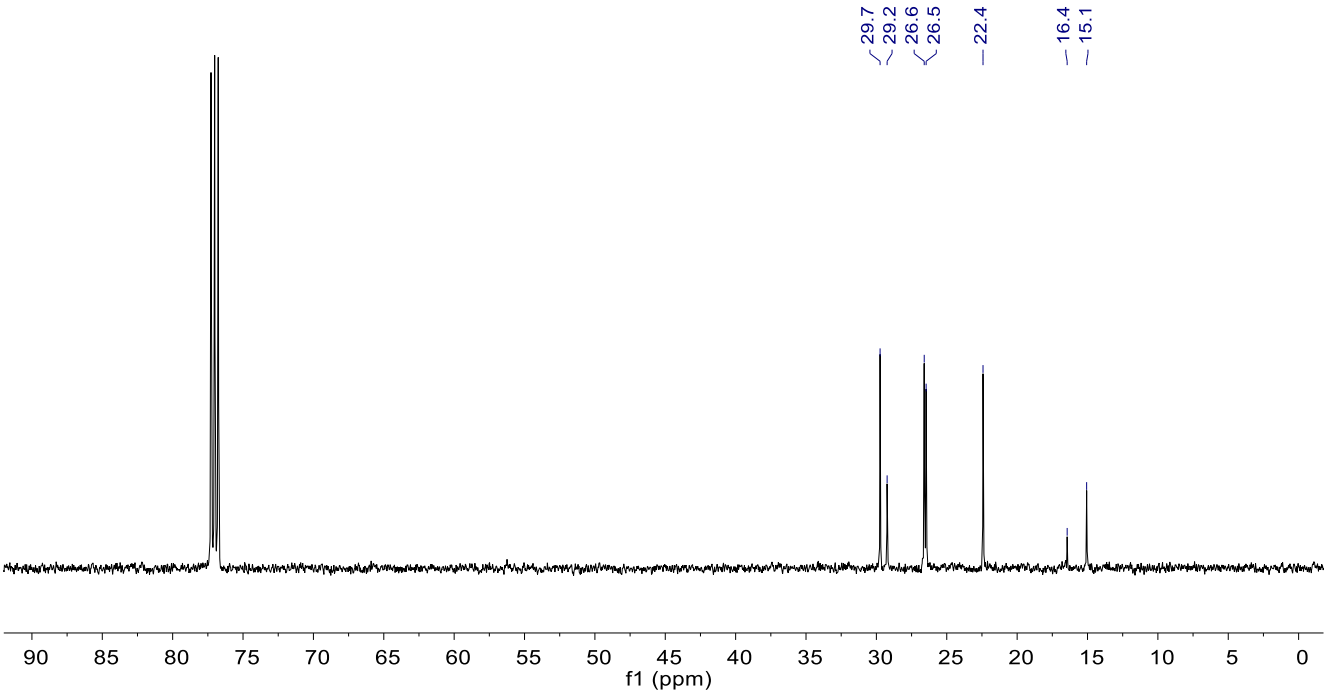


Figure S71: $^{13}C\{^{1}H\}$ NMR spectrum for **31** ($CDCl_3$, 295 K)

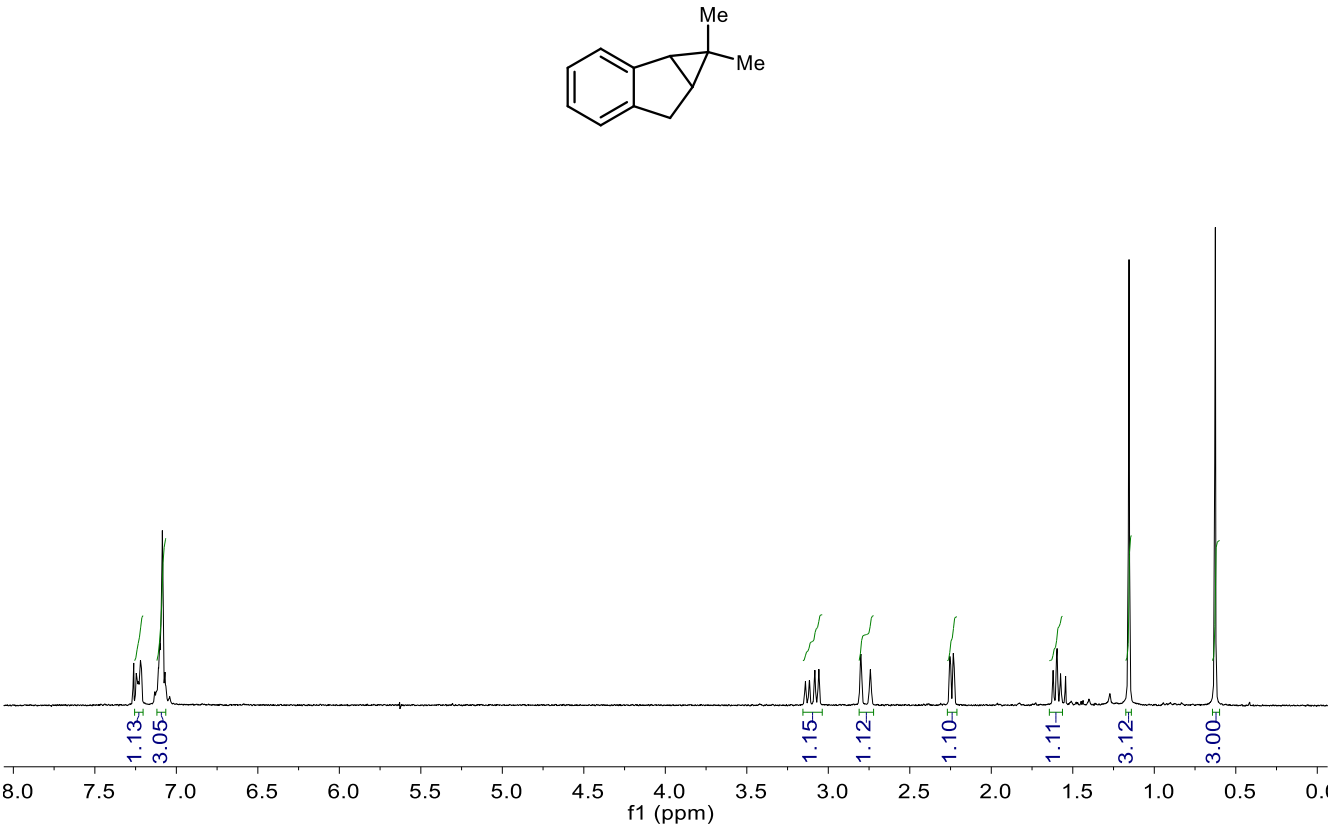


Figure S72: ^{1}H NMR spectrum for **32** ($CDCl_3$, 295 K)

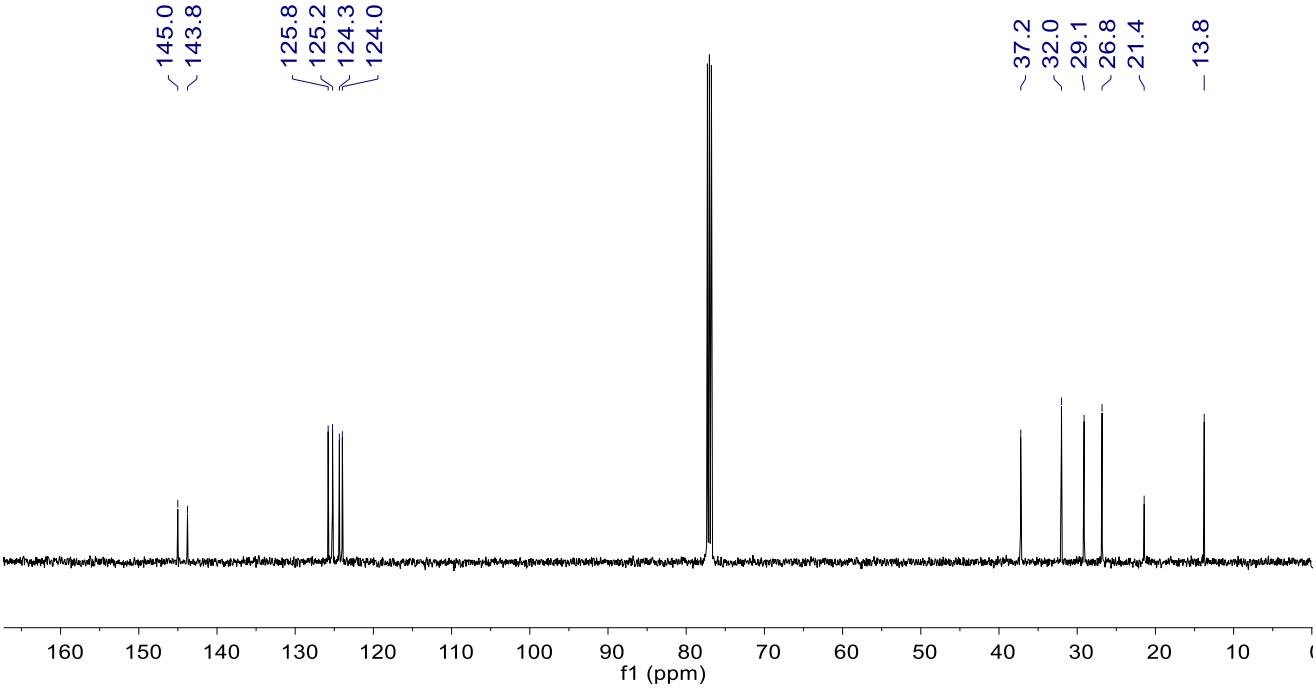


Figure S73: $^{13}C\{^{1}H\}$ NMR spectrum for **32** ($CDCl_3$, 295 K)

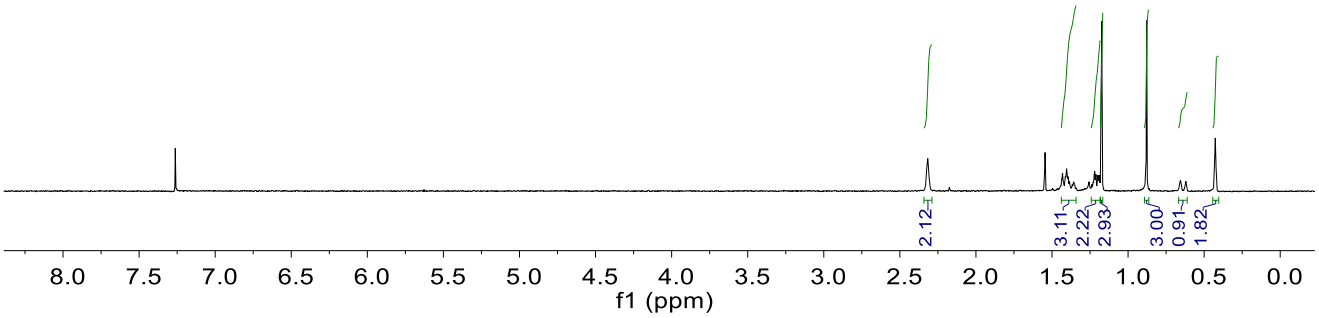


Figure S74: ^{1}H NMR spectrum for **33** ($CDCl_3$, 295 K)

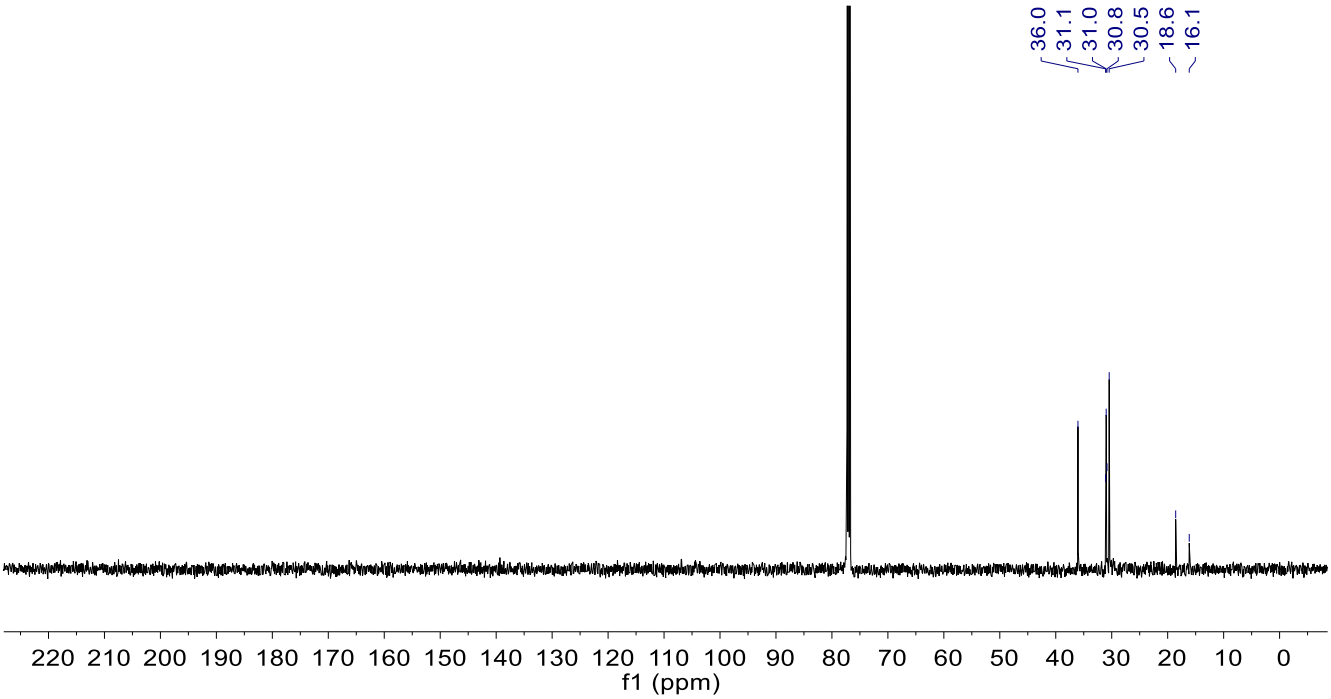
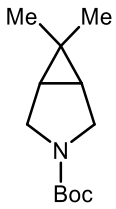


Figure S75: $^{13}C\{^{1}H\}$ NMR spectrum for **33** ($CDCl_3$, 295 K)



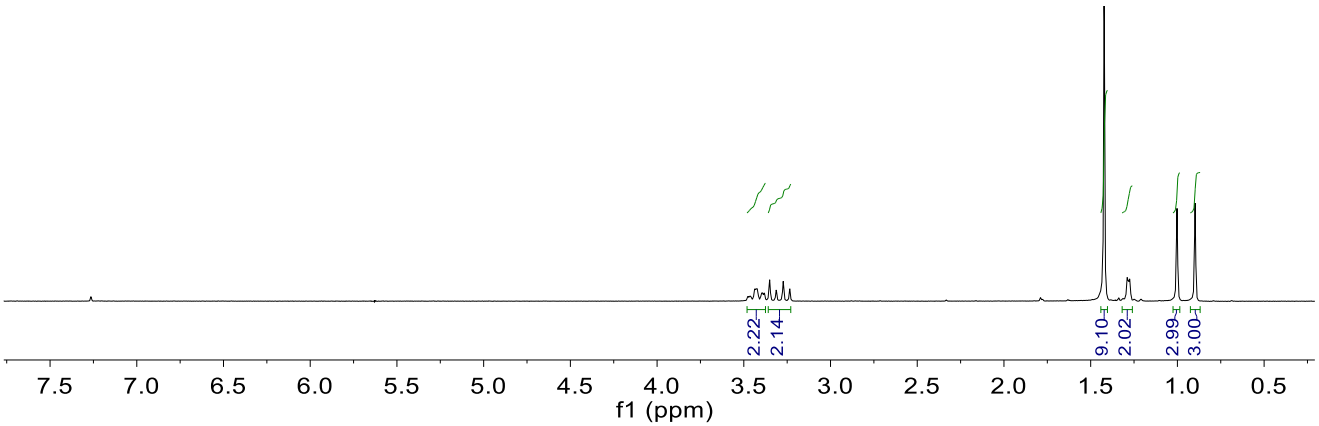


Figure S76: ^{1}H NMR spectrum for **35** ($CDCl_3$, 295 K)

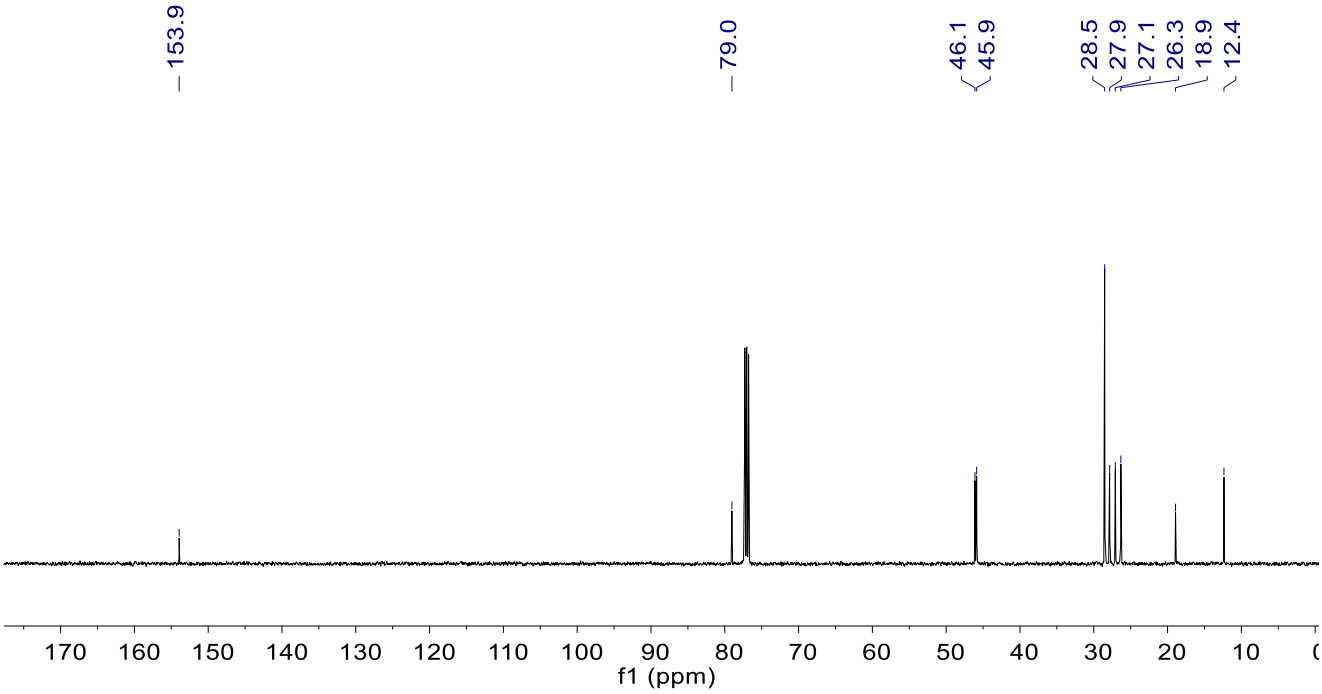
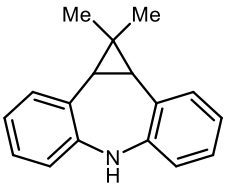


Figure S77: $^{13}C\{^{1}H\}$ NMR spectrum for **35** ($CDCl_3$, 295 K)



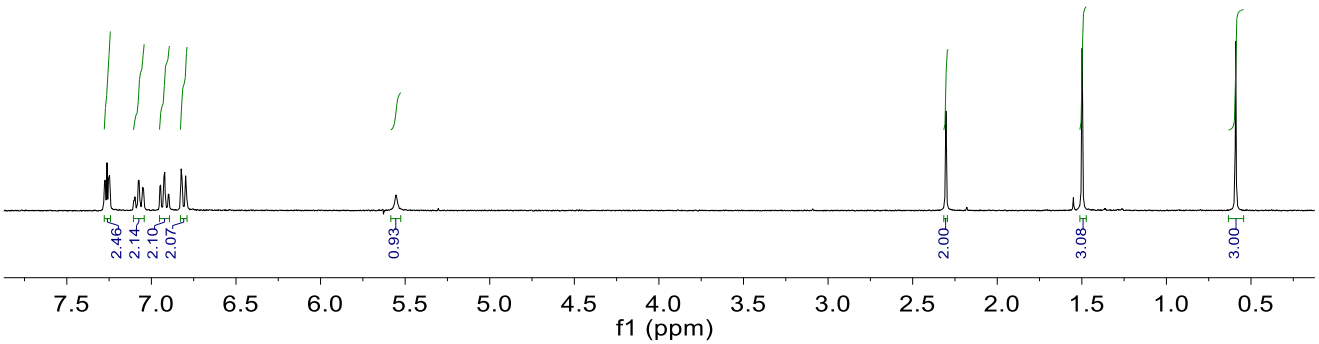


Figure S78: ^{1}H NMR spectrum for **37** ($CDCl_3$, 295 K)

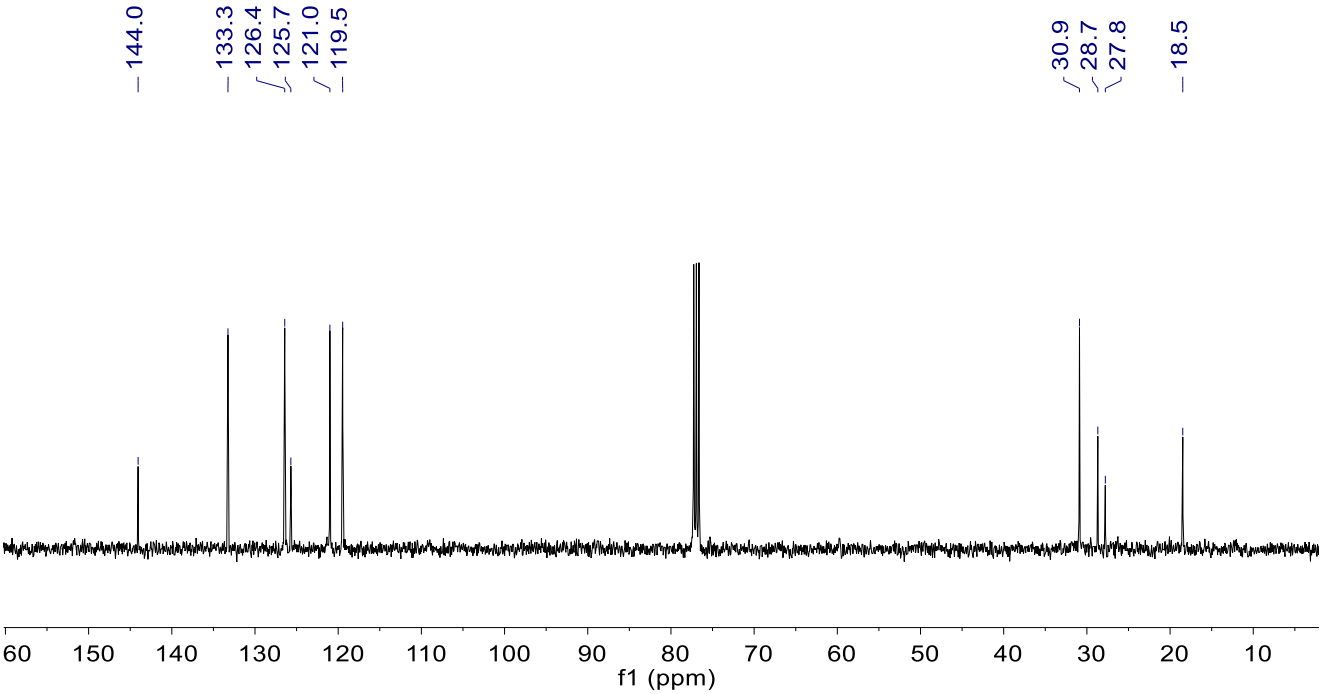
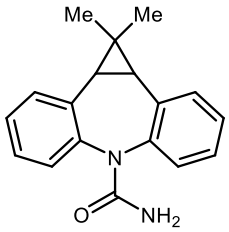


Figure S79: $^{13}C\{^{1}H\}$ NMR spectrum for **37** ($CDCl_3$, 295 K)



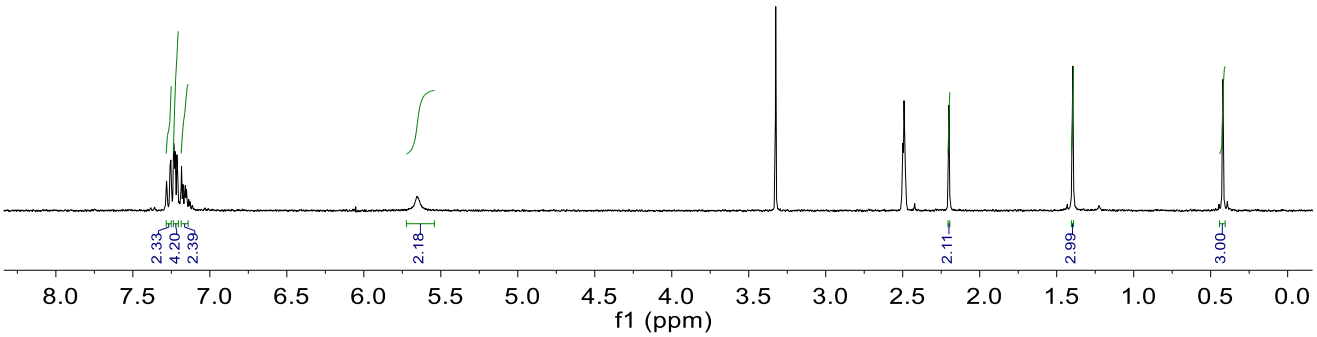


Figure S80: ^{1}H NMR spectrum for **38** (DMSO-d_6, 295 K)

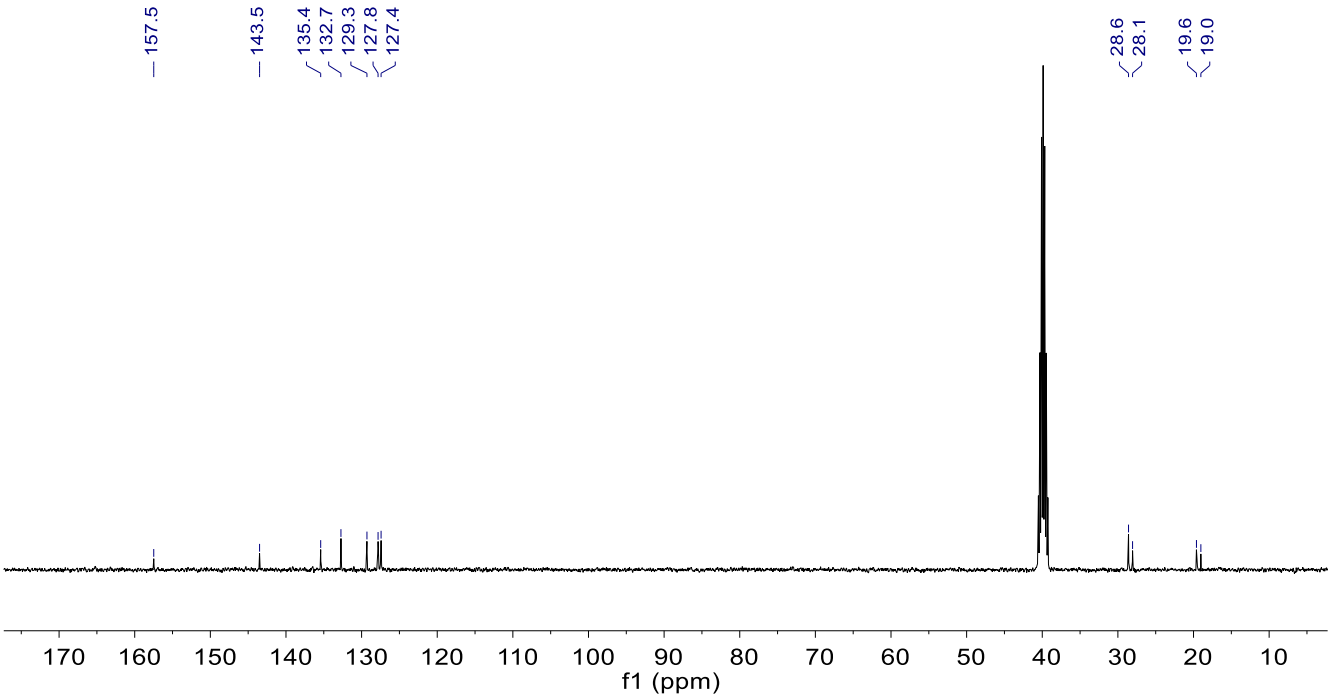
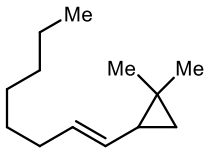


Figure S81: $^{13}C\{^{1}H\}$ NMR spectrum for **38** (DMSO-d_6, 295 K)

9. IR Spectra



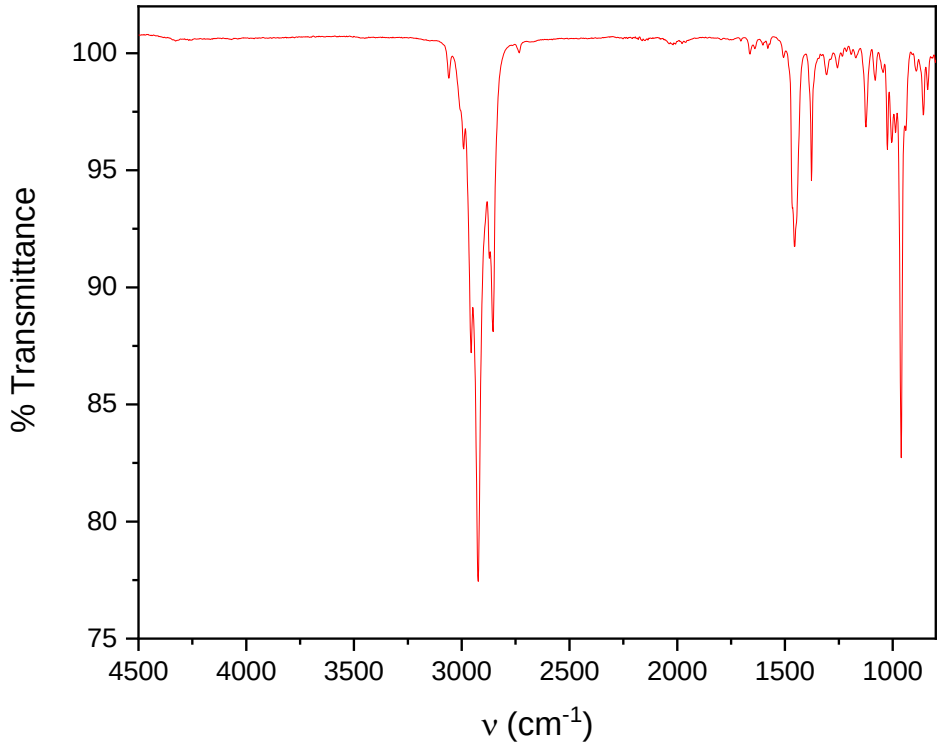


Figure S82: ATR-IR spectrum for **2**

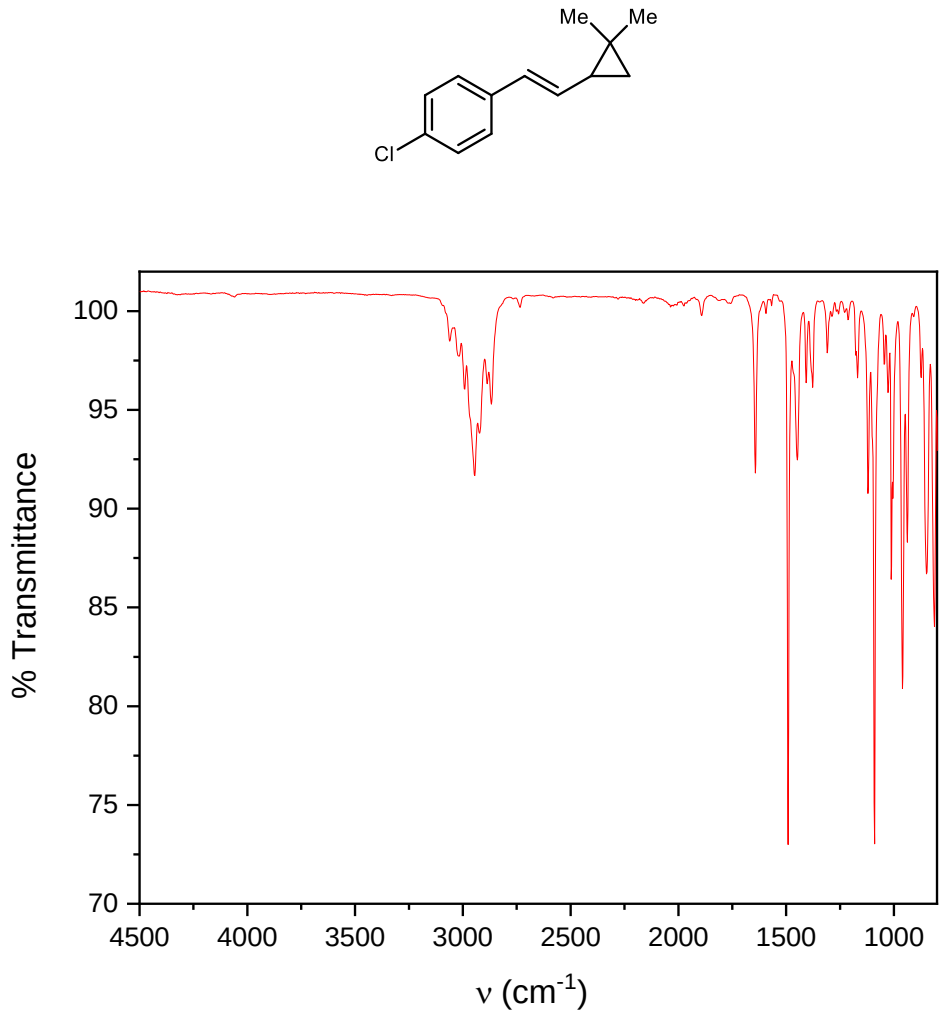


Figure S83: ATR-IR spectrum for **4**

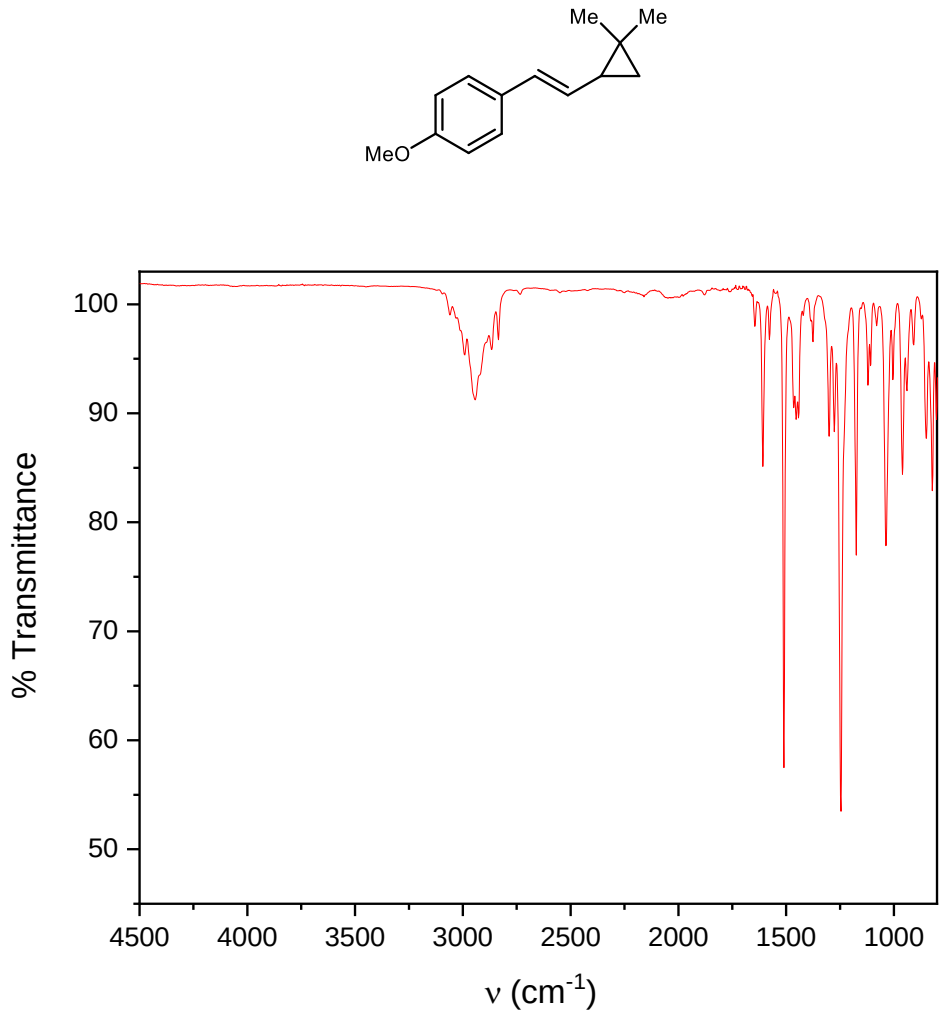


Figure S84: ATR-IR spectrum for **5**

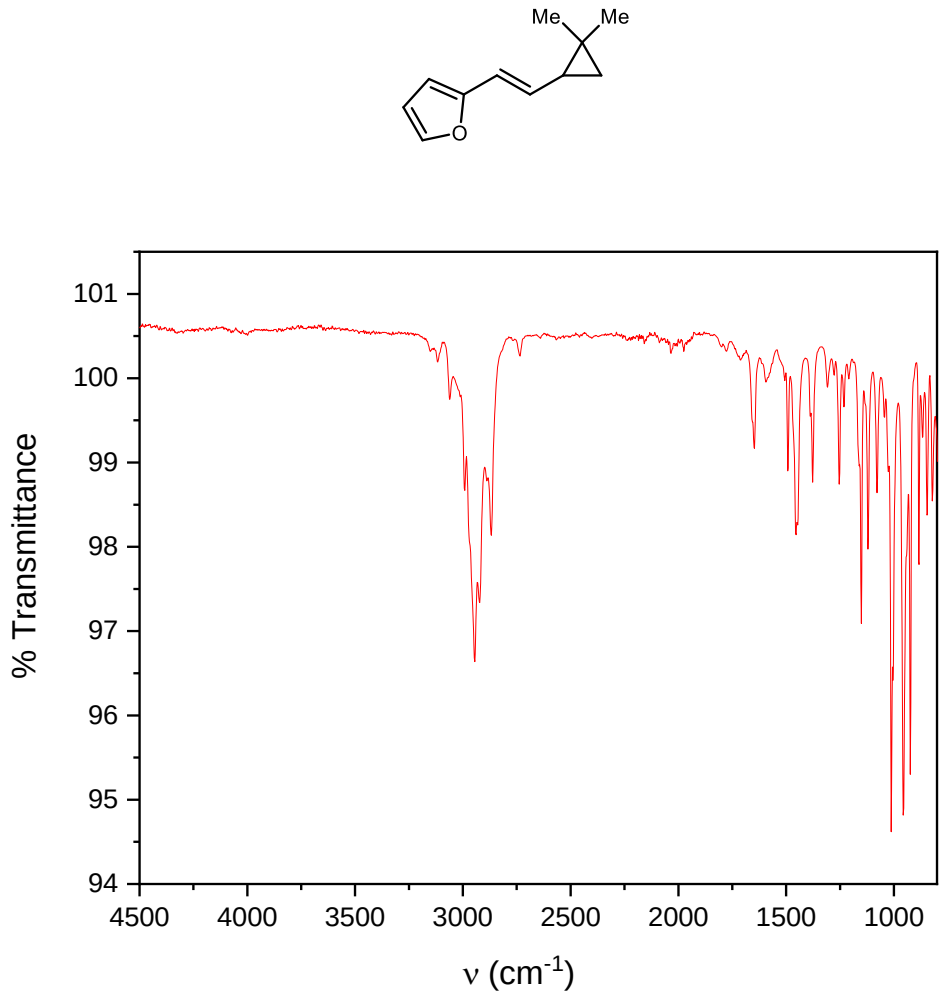
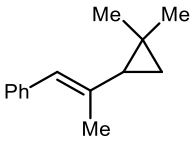


Figure S85: ATR-IR spectrum for **6**



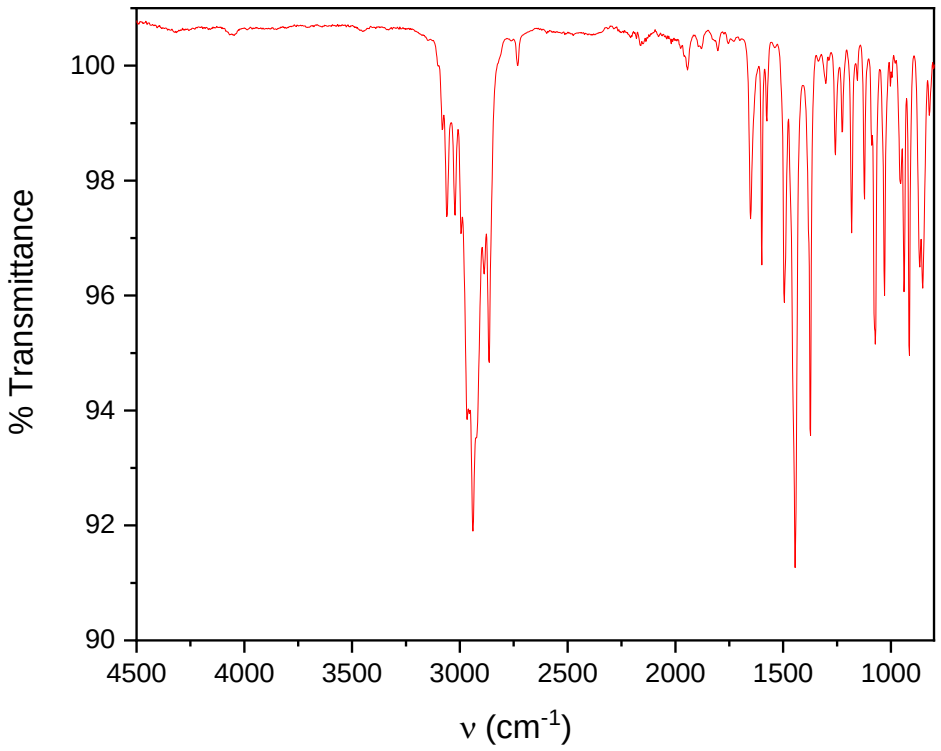


Figure S86: ATR-IR spectrum for **7**

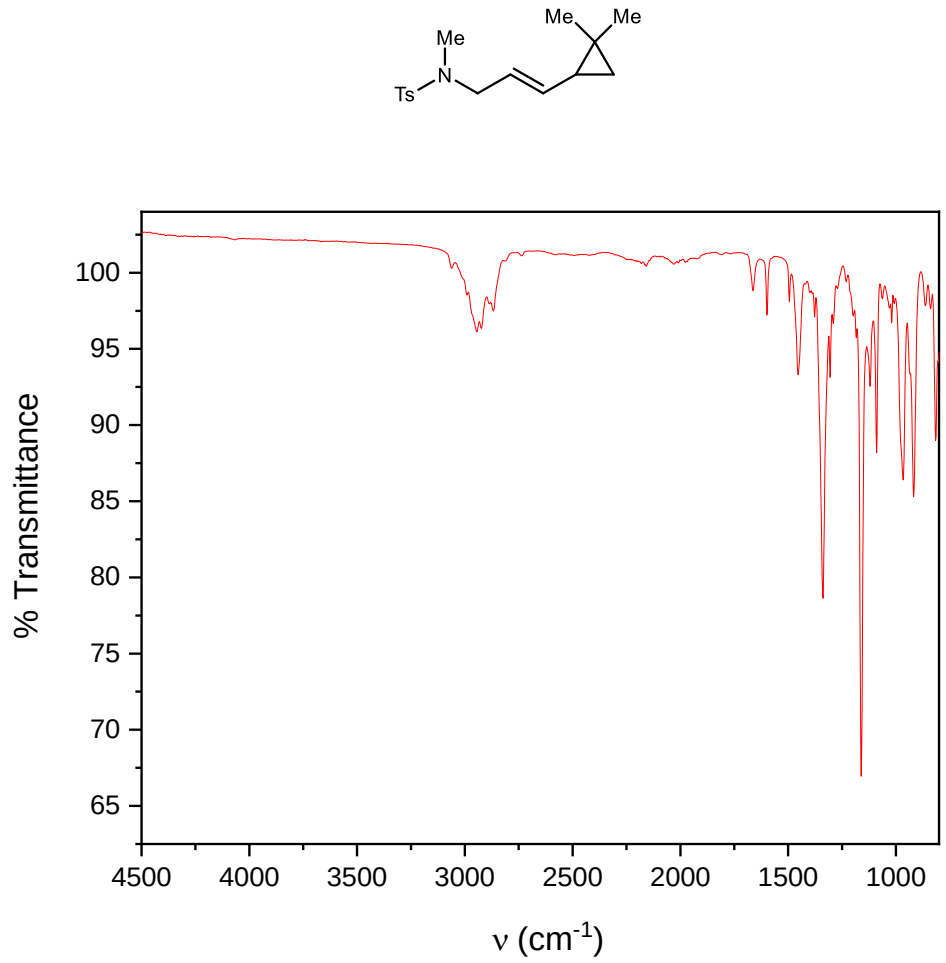
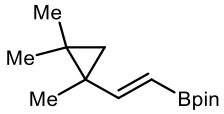


Figure S87: ATR-IR spectrum for **8**



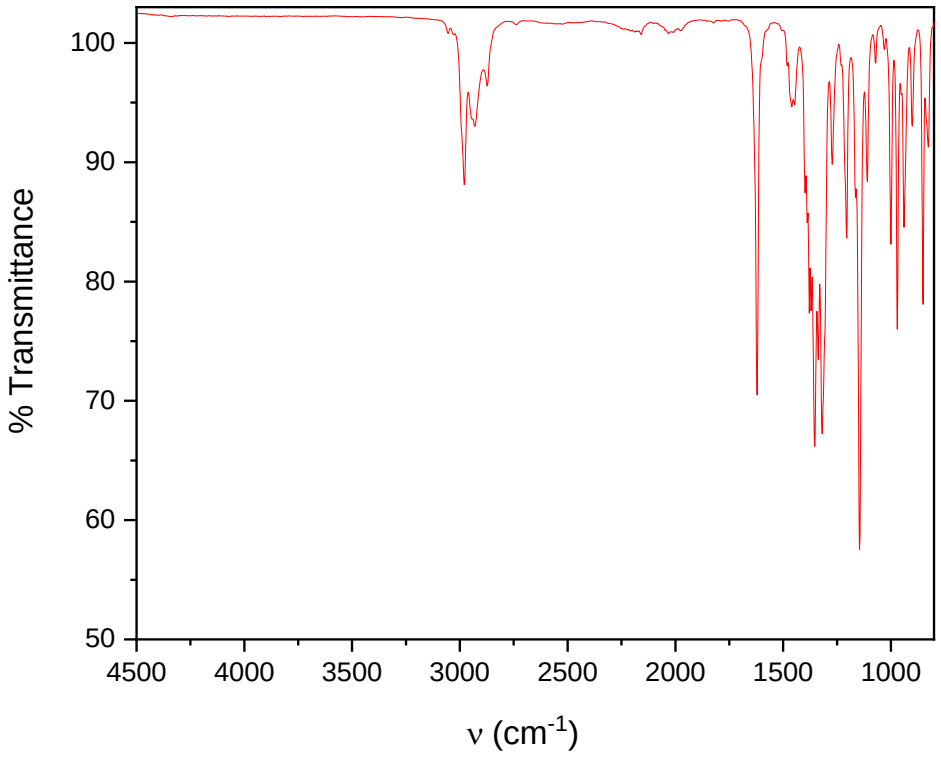
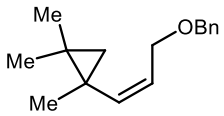


Figure S88: ATR-IR spectrum for **9**



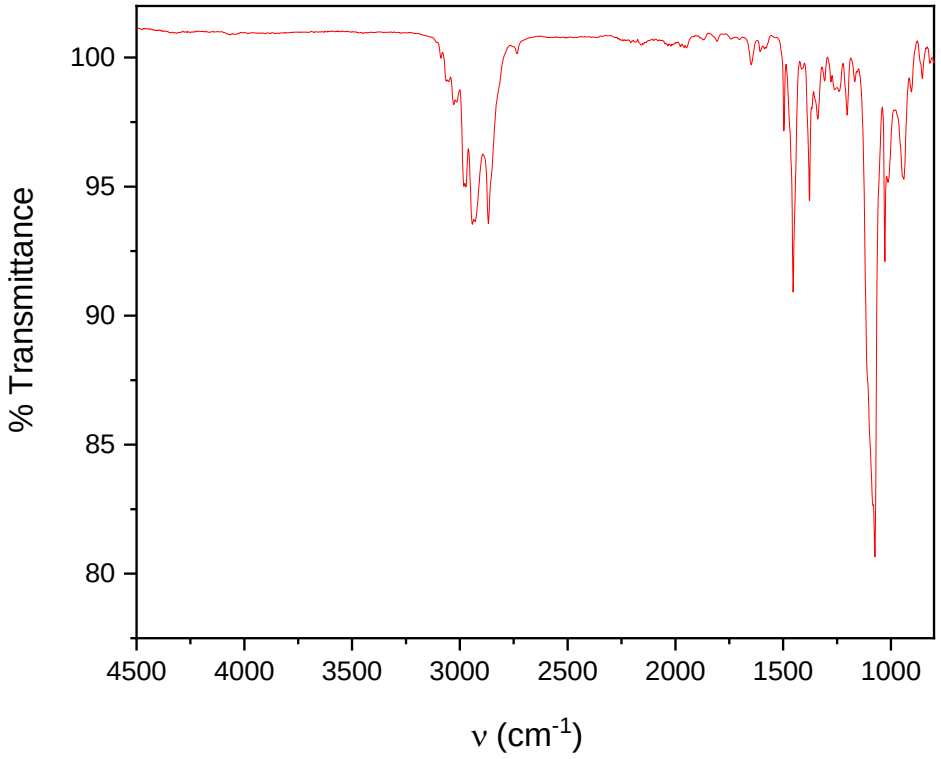
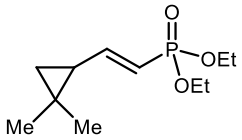


Figure S89: ATR-IR spectrum for **10**



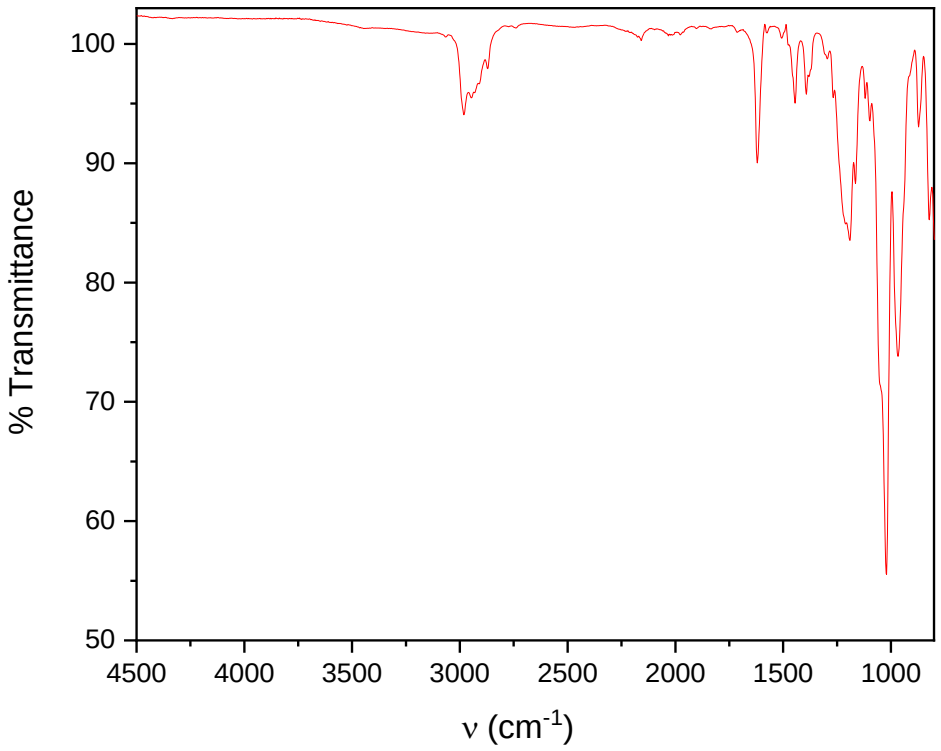


Figure S90: ATR-IR spectrum for **11**

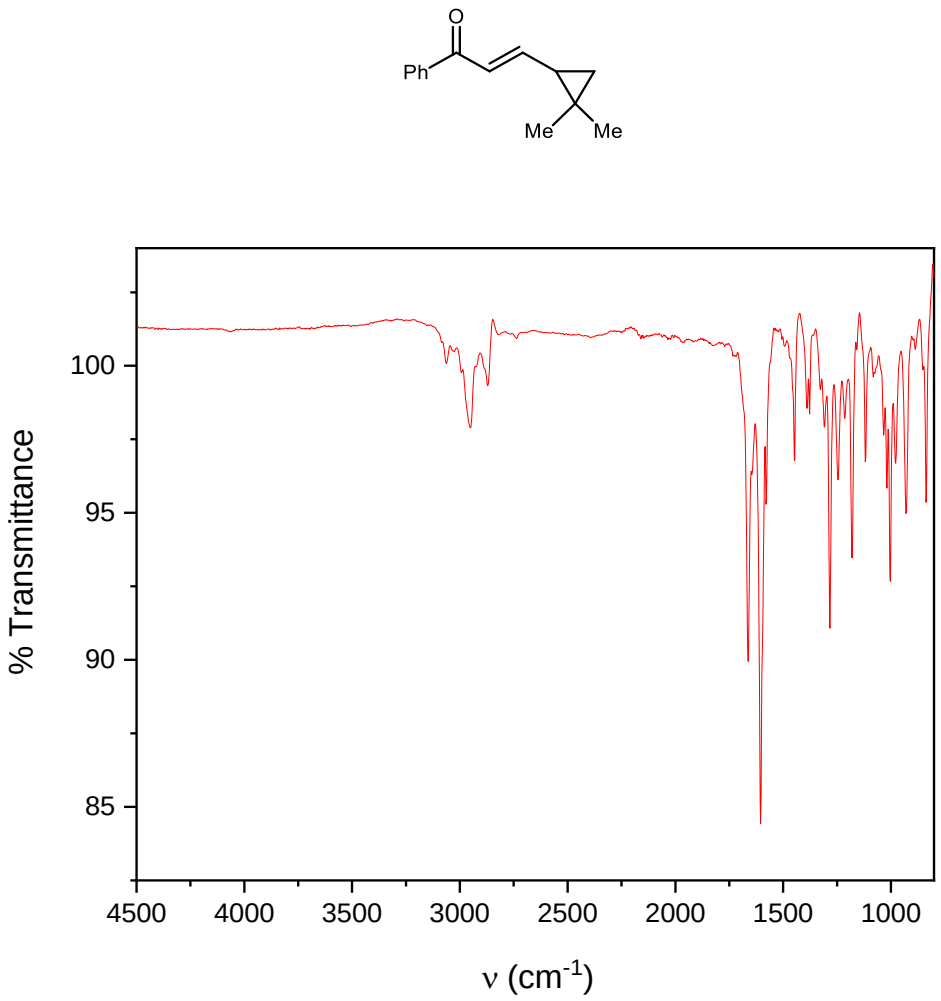
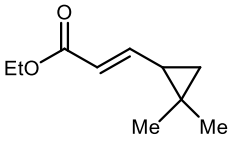


Figure S91: ATR-IR spectrum for **12**



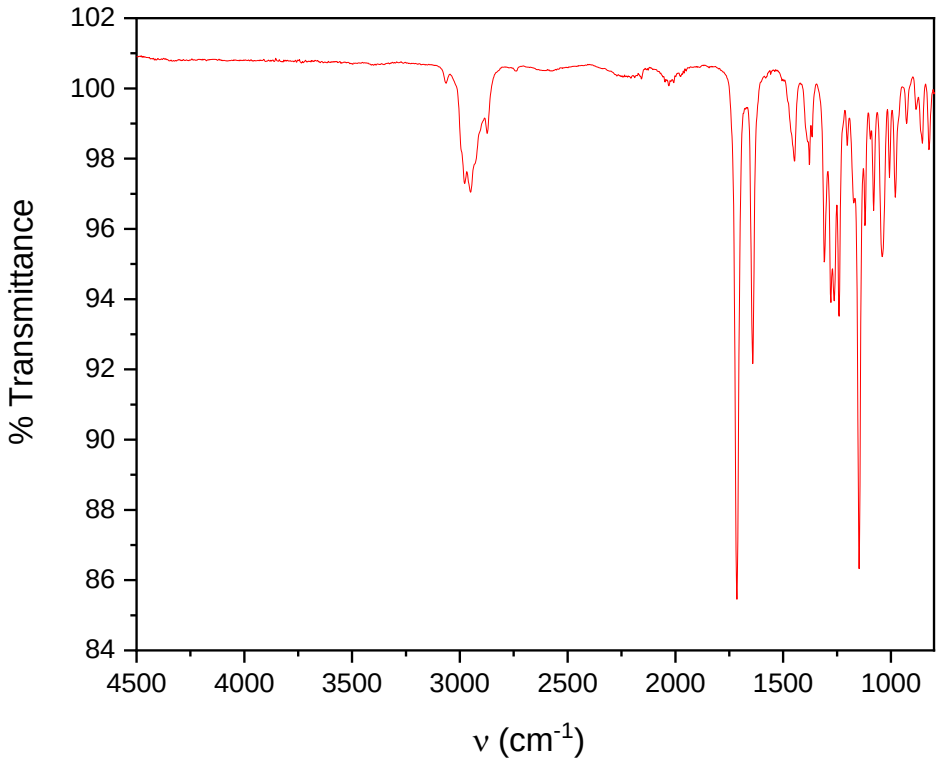


Figure S92: ATR-IR spectrum for **13**

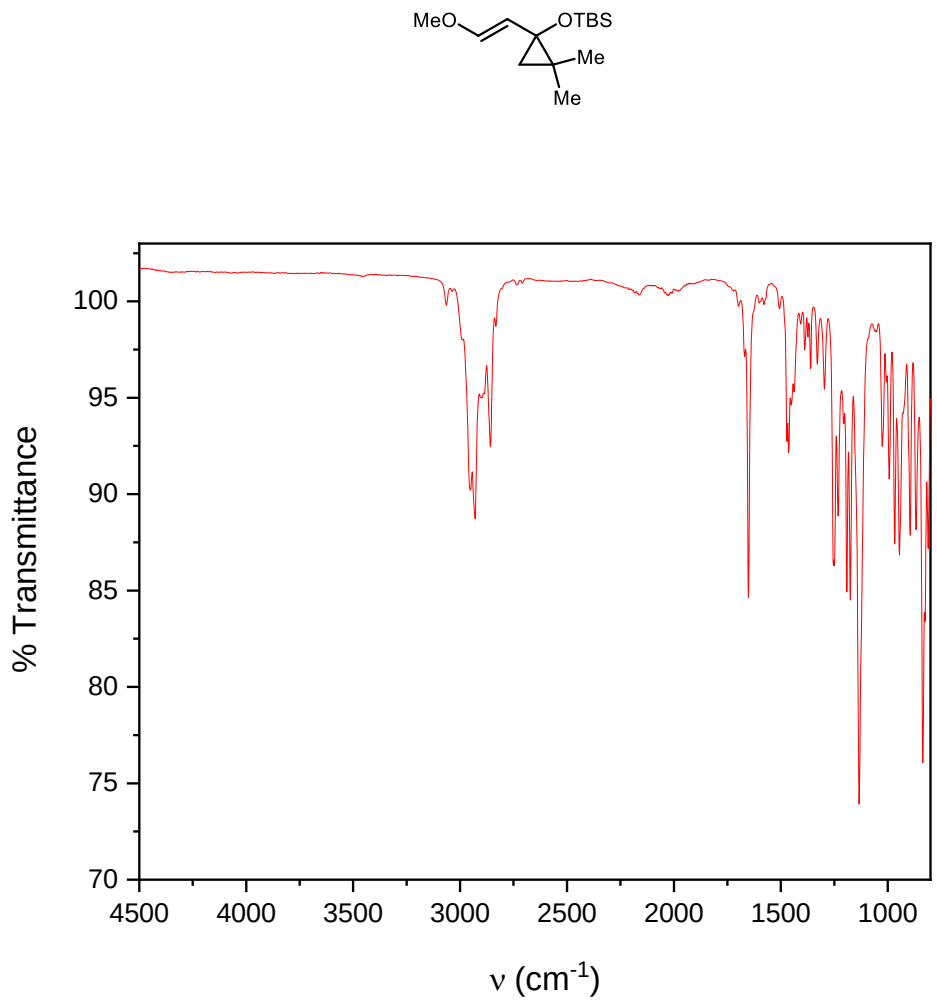
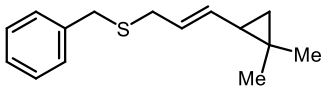


Figure S93: ATR-IR spectrum for **14**



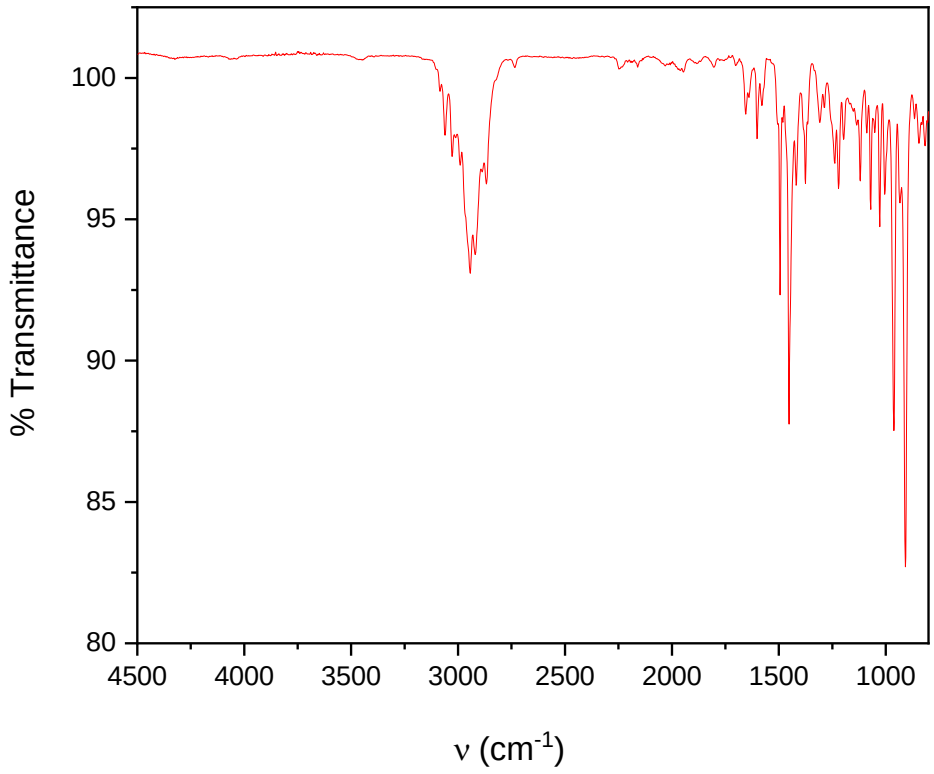


Figure S94: ATR-IR spectrum for **15**

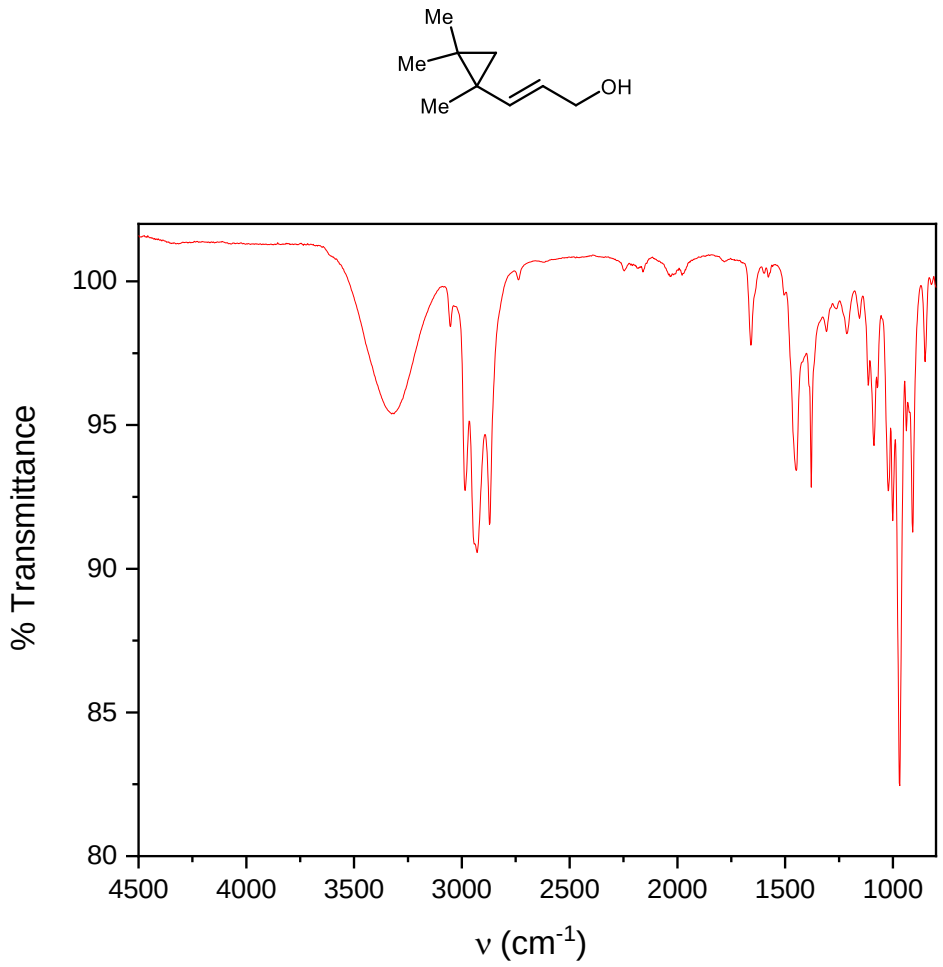


Figure S95: ATR-IR spectrum for **18**

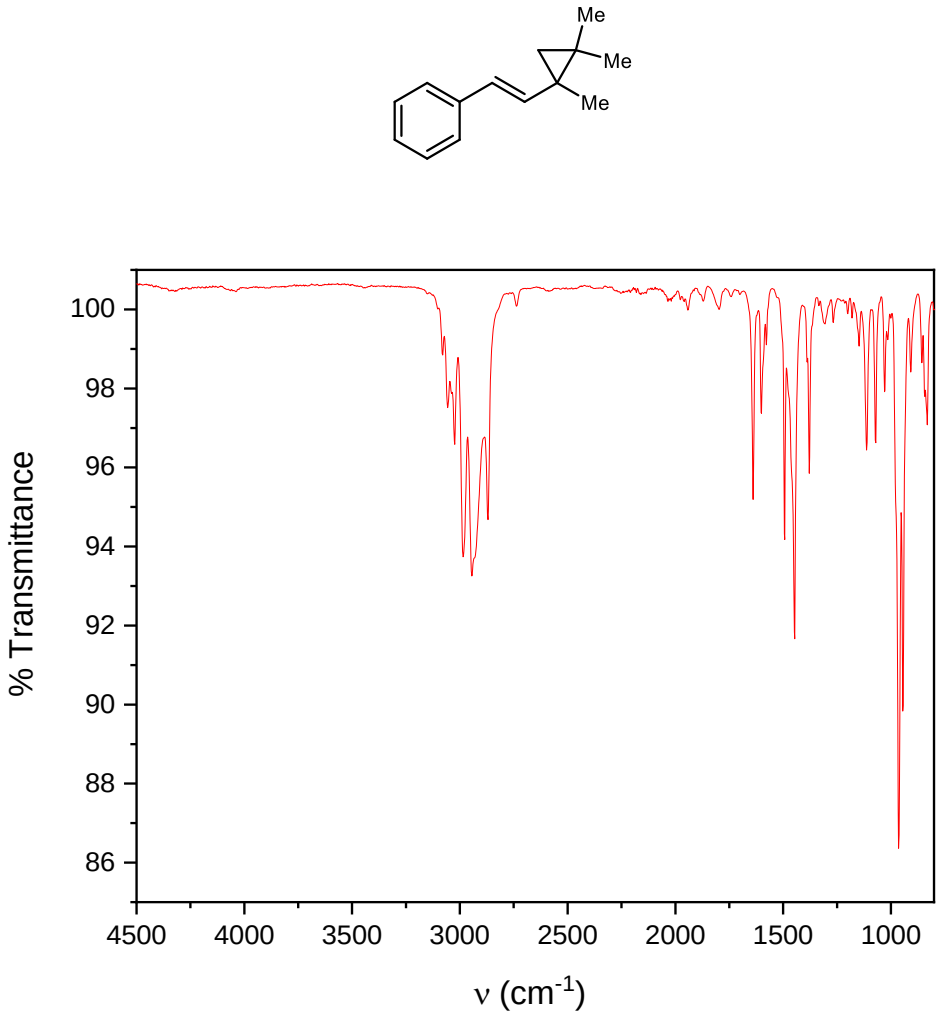


Figure S96: ATR-IR spectrum for **26**

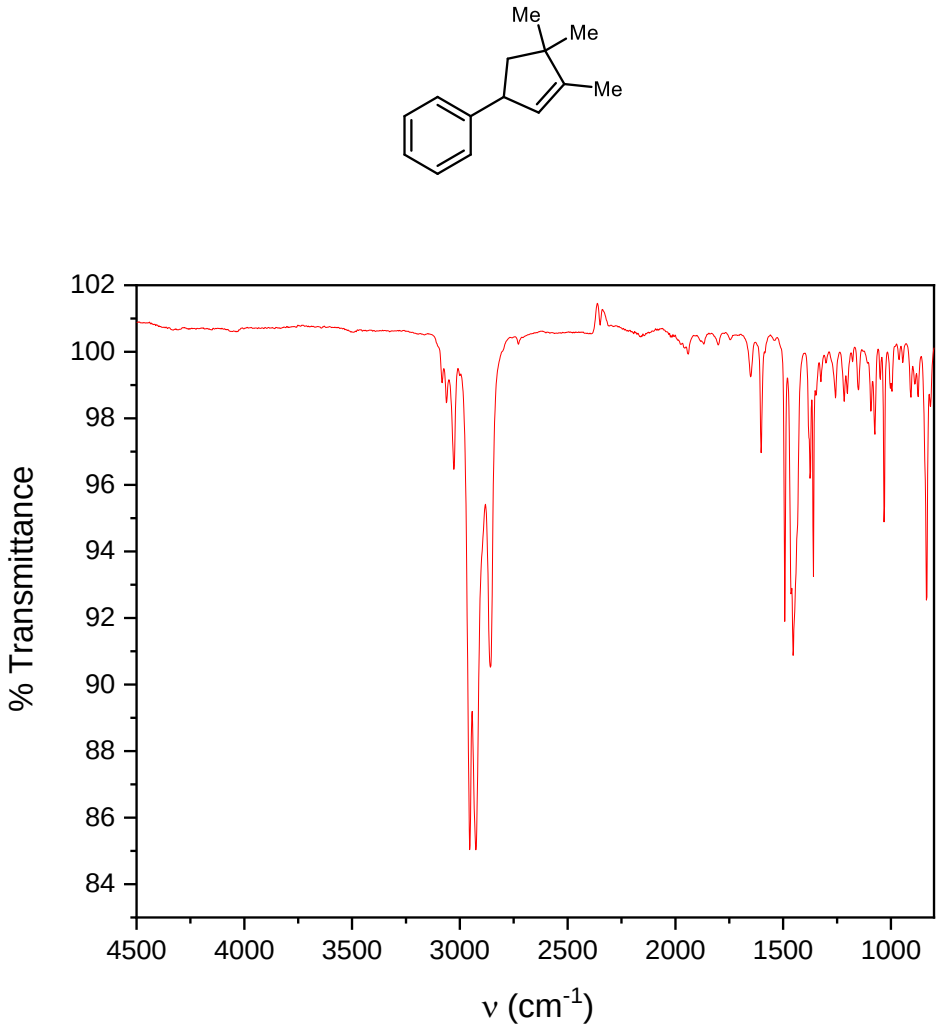


Figure S97: ATR-IR spectrum for **27**

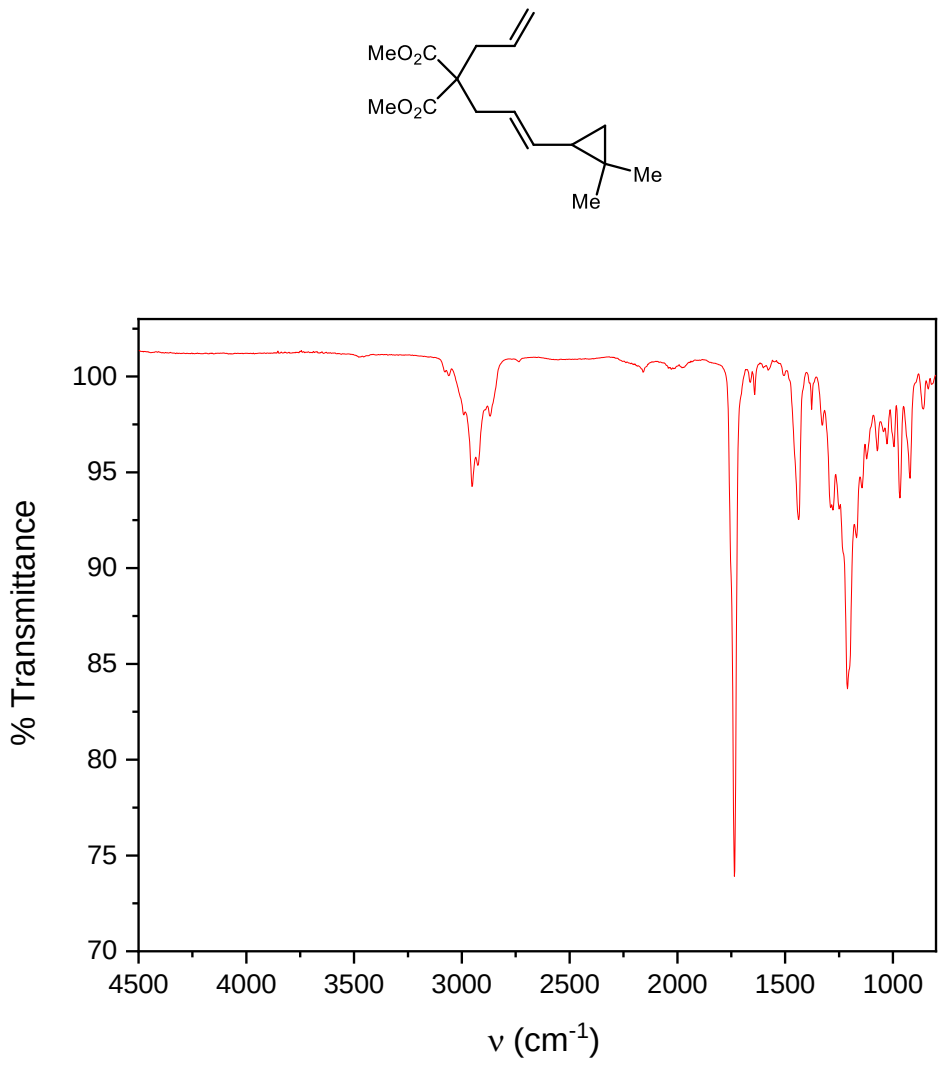
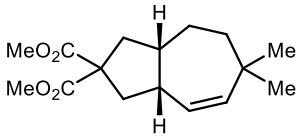


Figure S98: ATR-IR spectrum for **28**



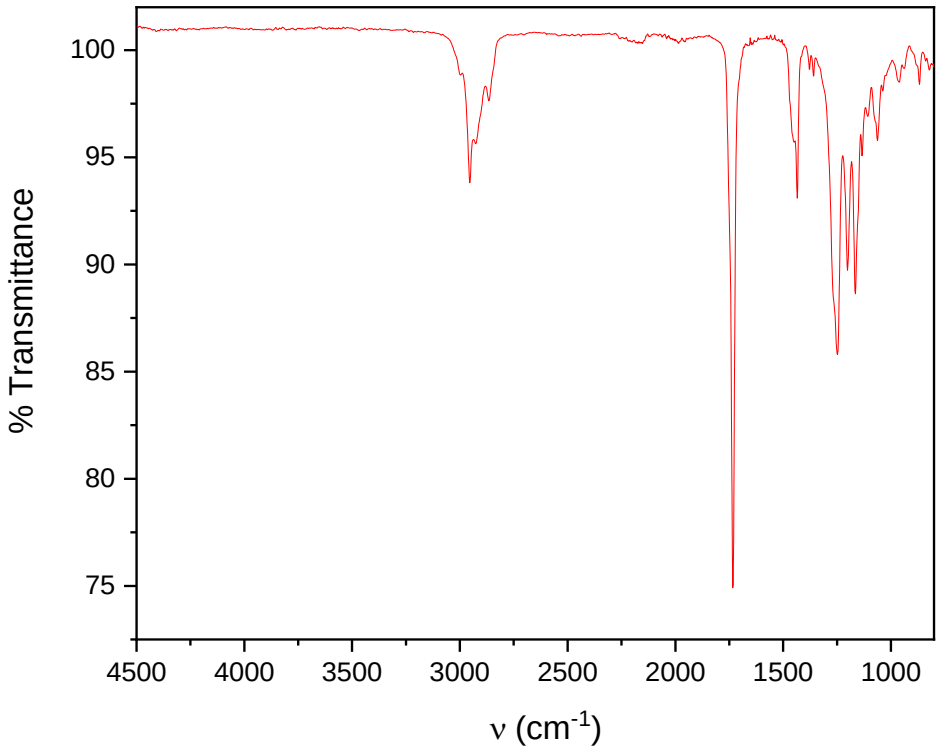


Figure S99: ATR-IR spectrum for **29**

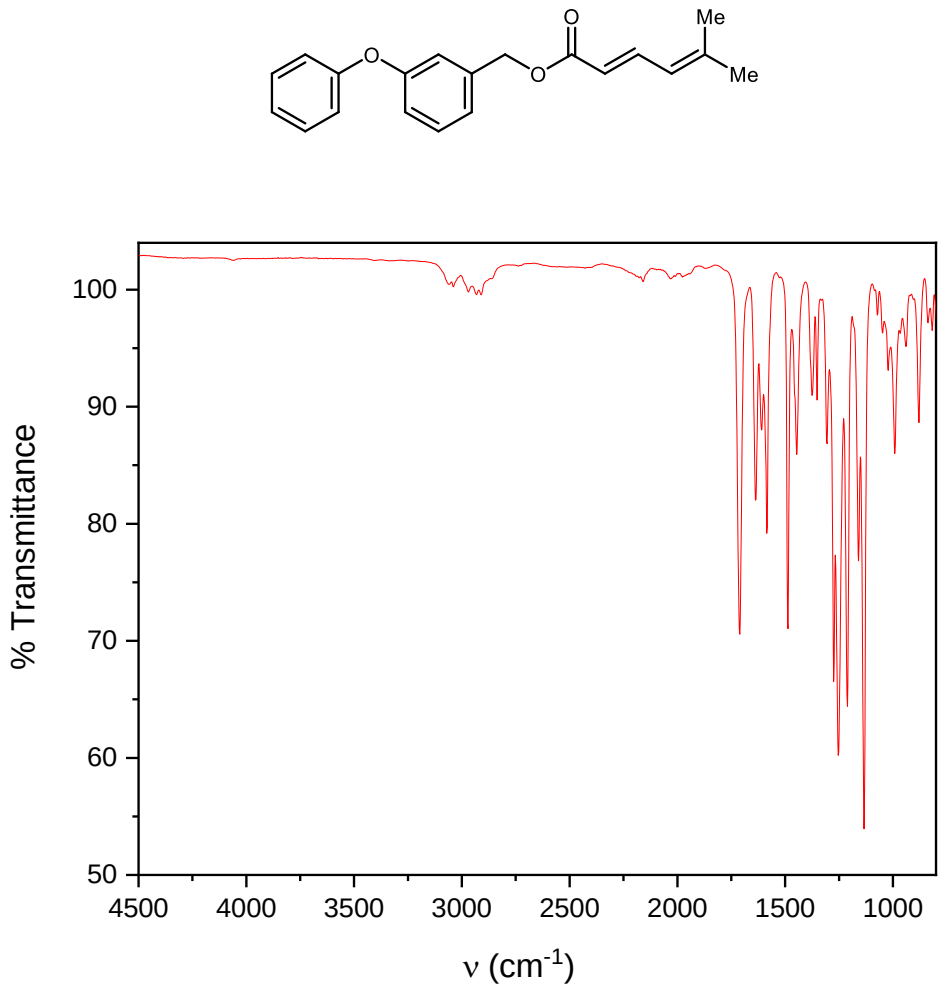


Figure S100: ATR-IR spectrum for **S2**

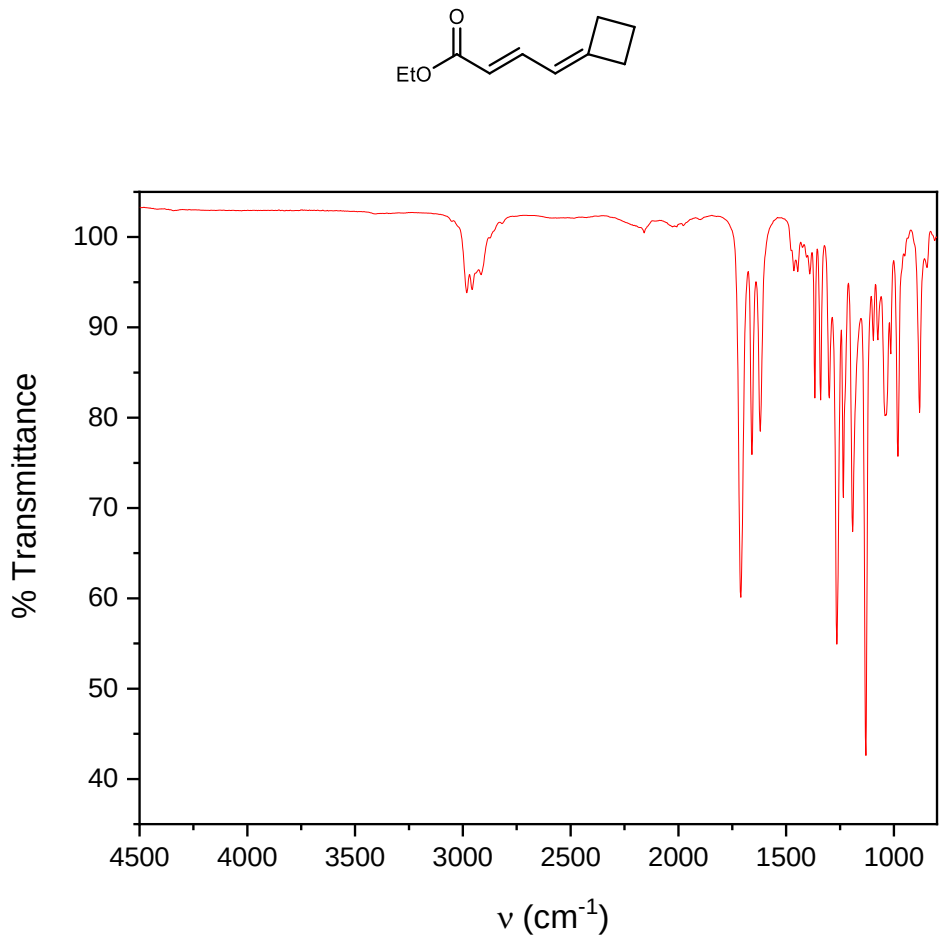


Figure S101: ATR-IR spectrum for **S3**

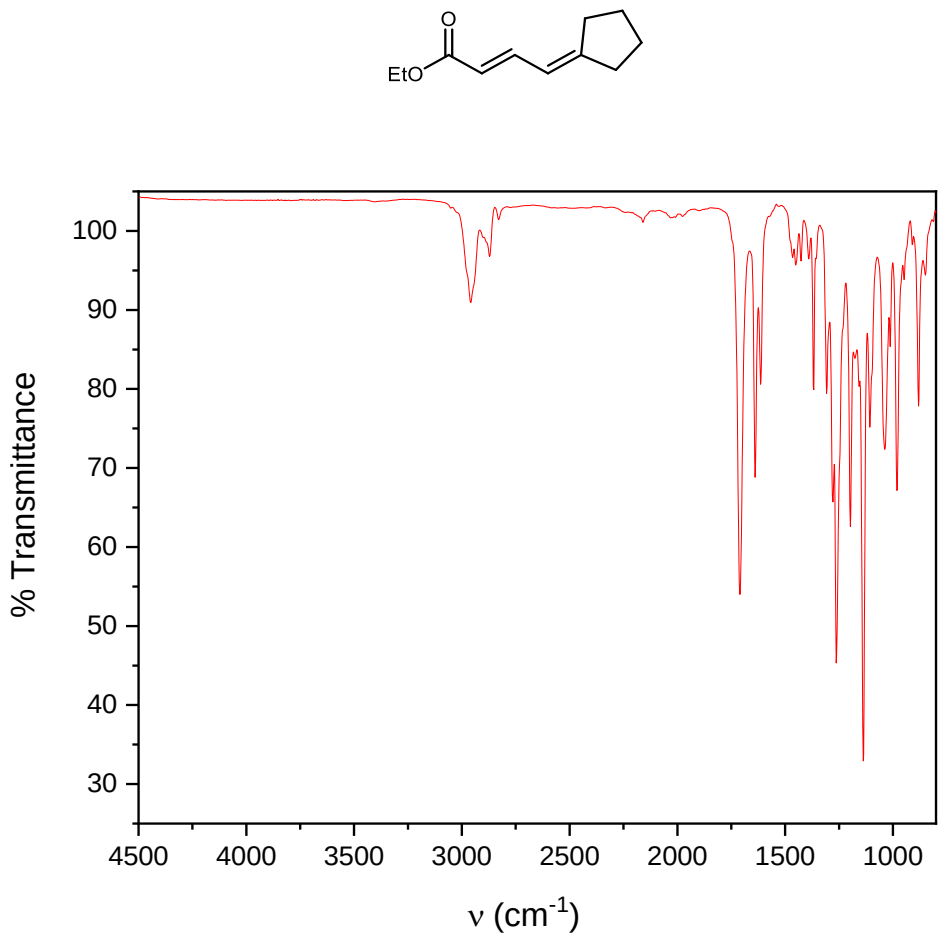


Figure S102: ATR-IR spectrum for **S4**

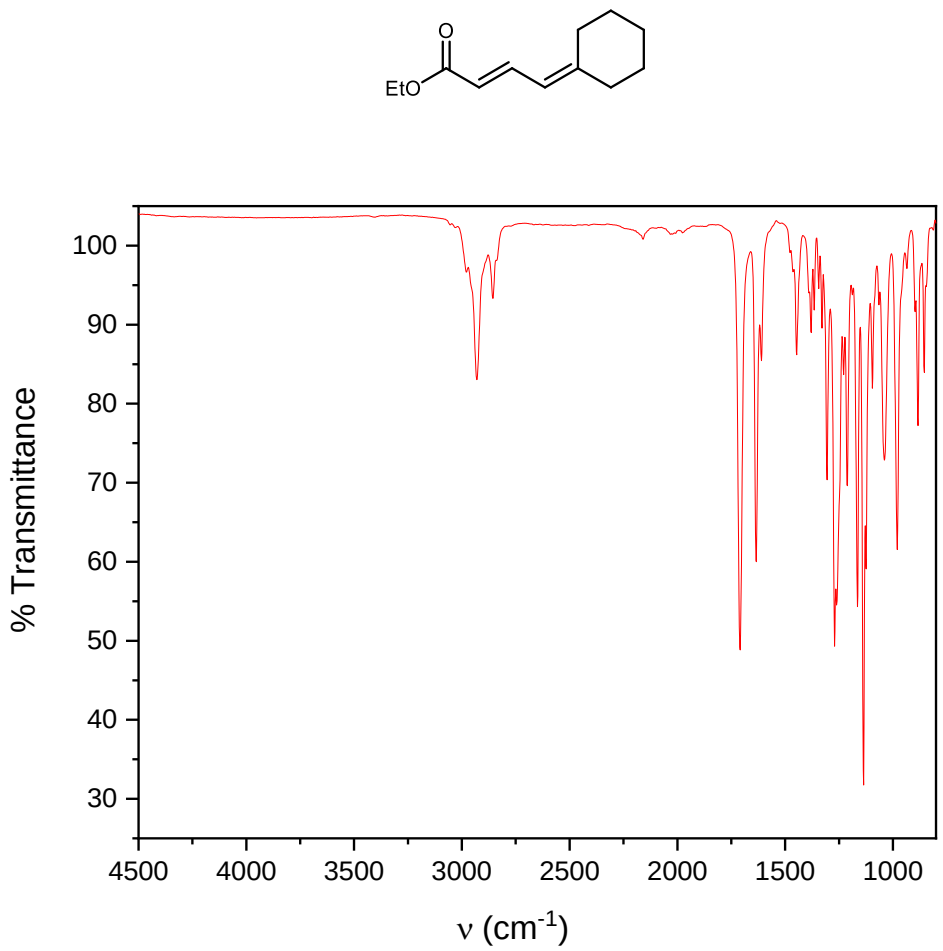


Figure S103: ATR-IR spectrum for **S5**

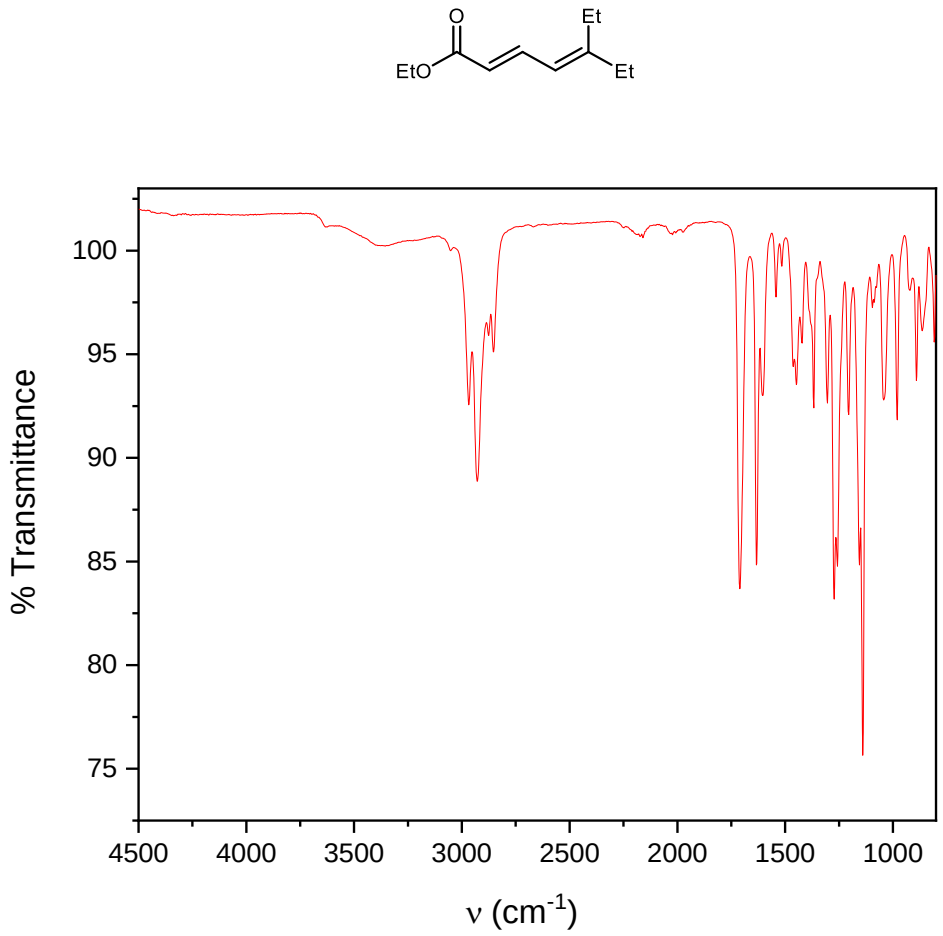
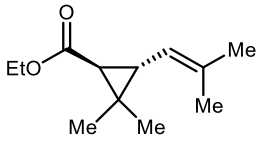


Figure S104: ATR-IR spectrum for **S6**



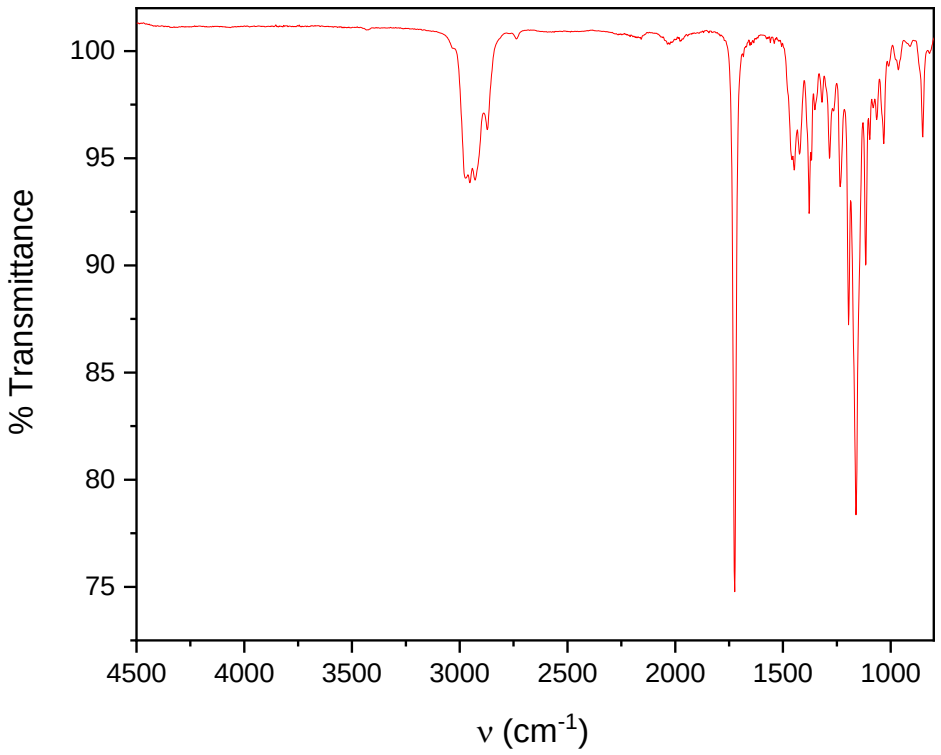


Figure S105: ATR-IR spectrum for **19**

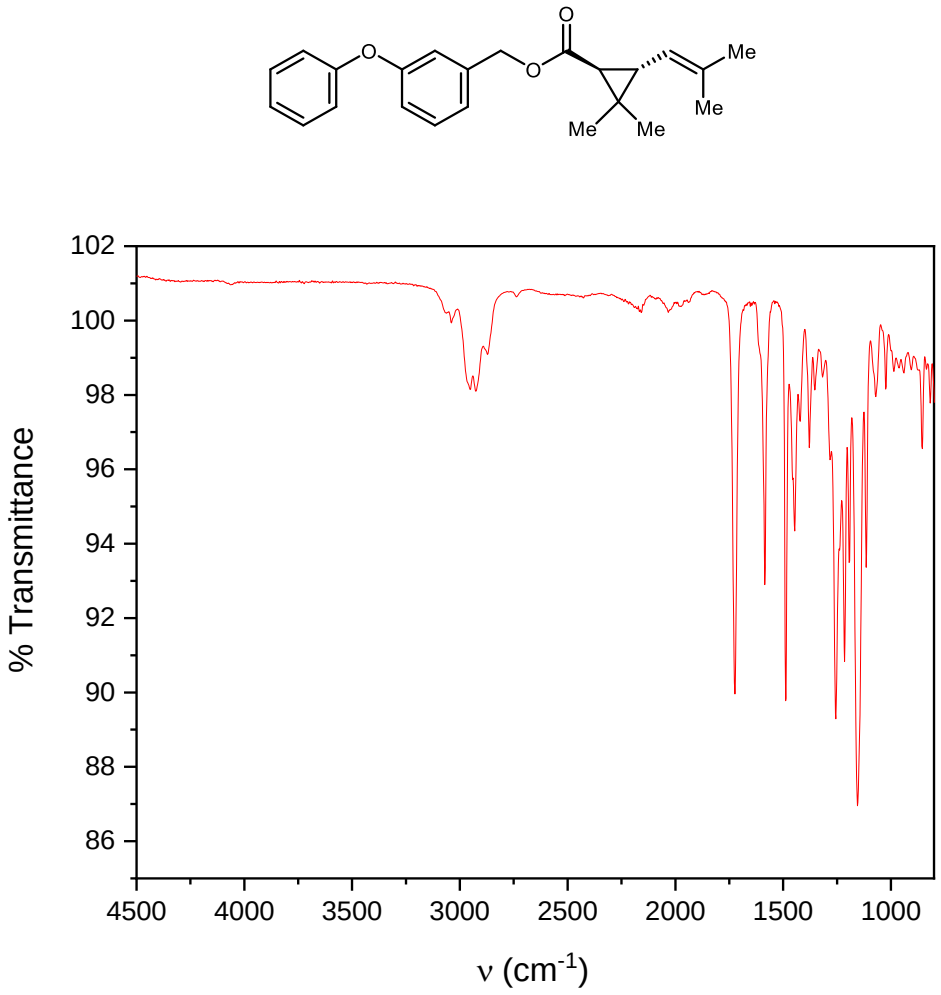
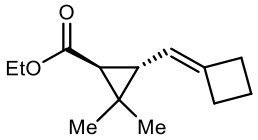


Figure S106: ATR-IR spectrum for **20**



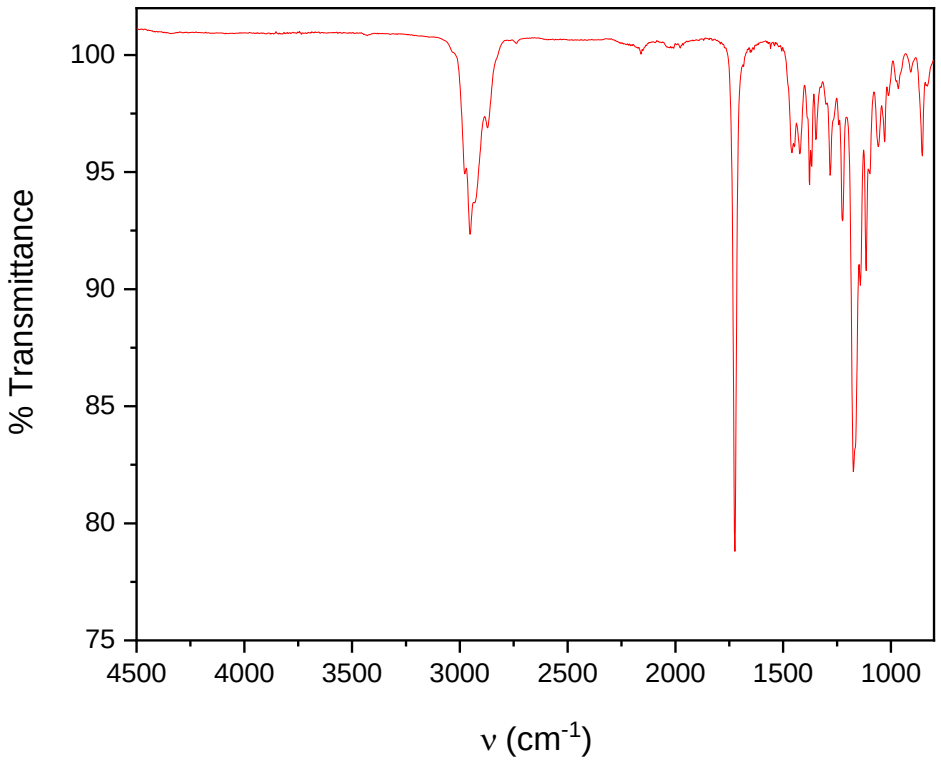


Figure S107: ATR-IR spectrum for **21**

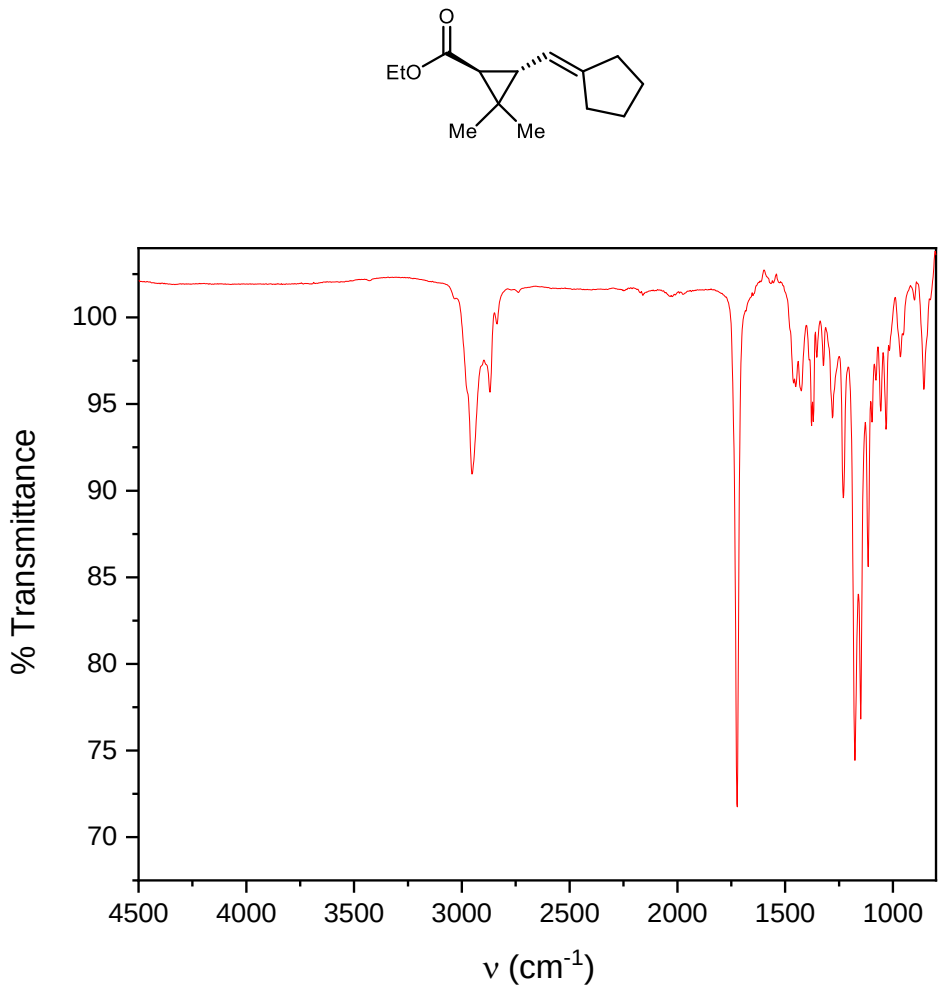


Figure S108: ATR-IR spectrum for **22**

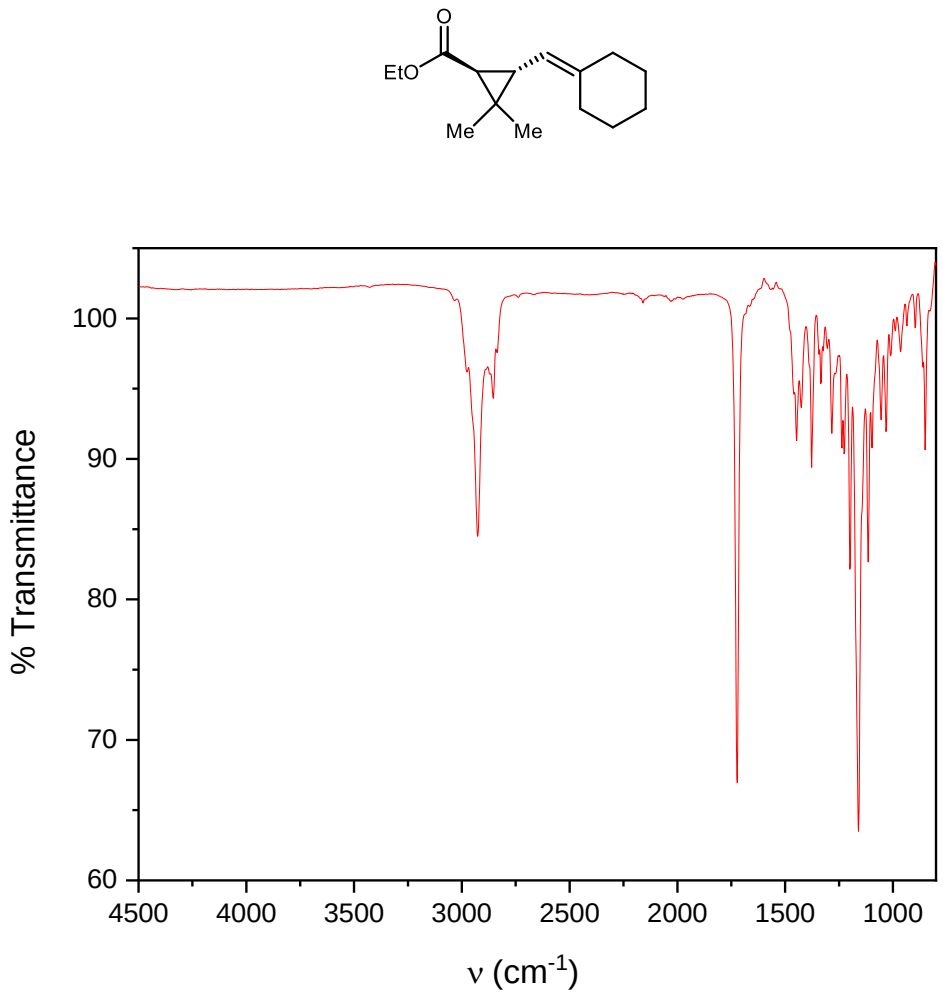
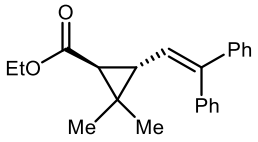


Figure S109: ATR-IR spectrum for **23**



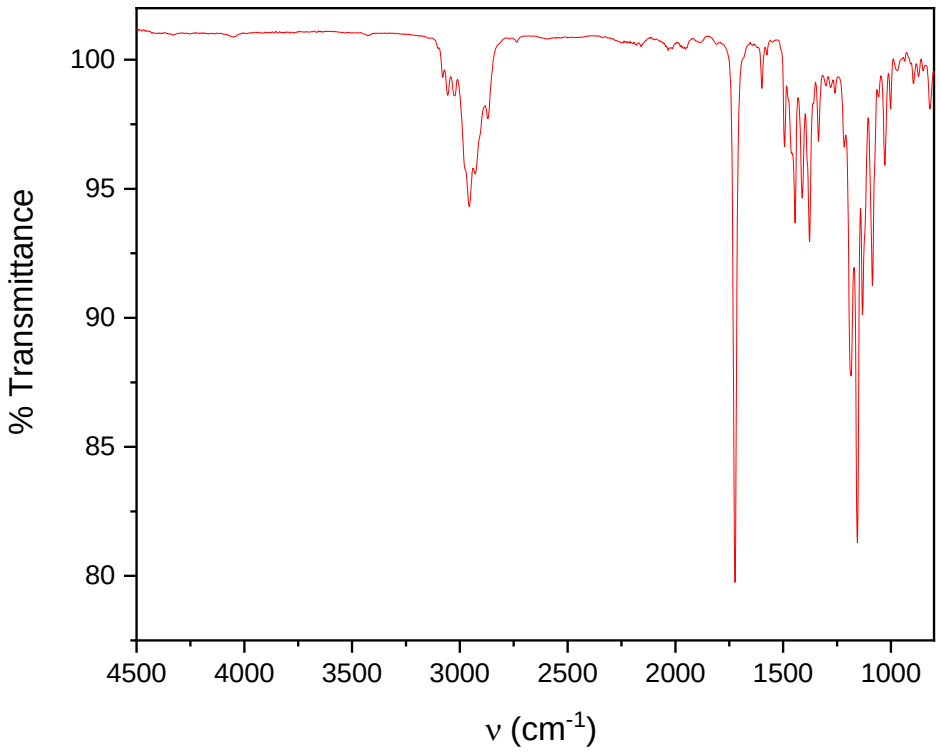
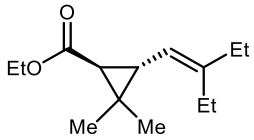


Figure S110: ATR-IR spectrum for **24**



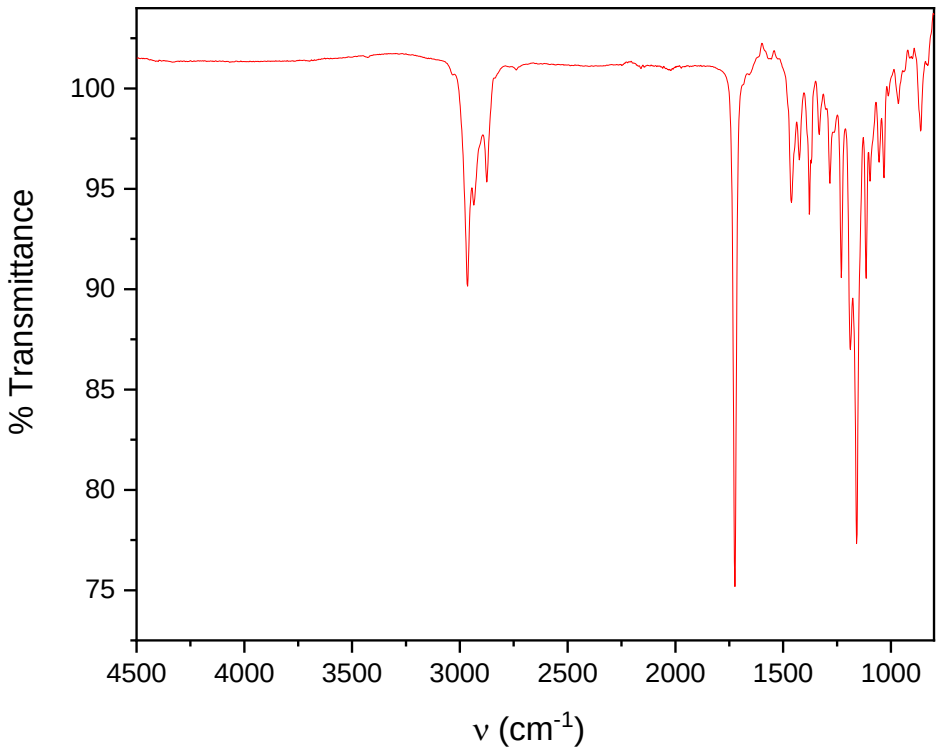


Figure S111: ATR-IR spectrum for **25**

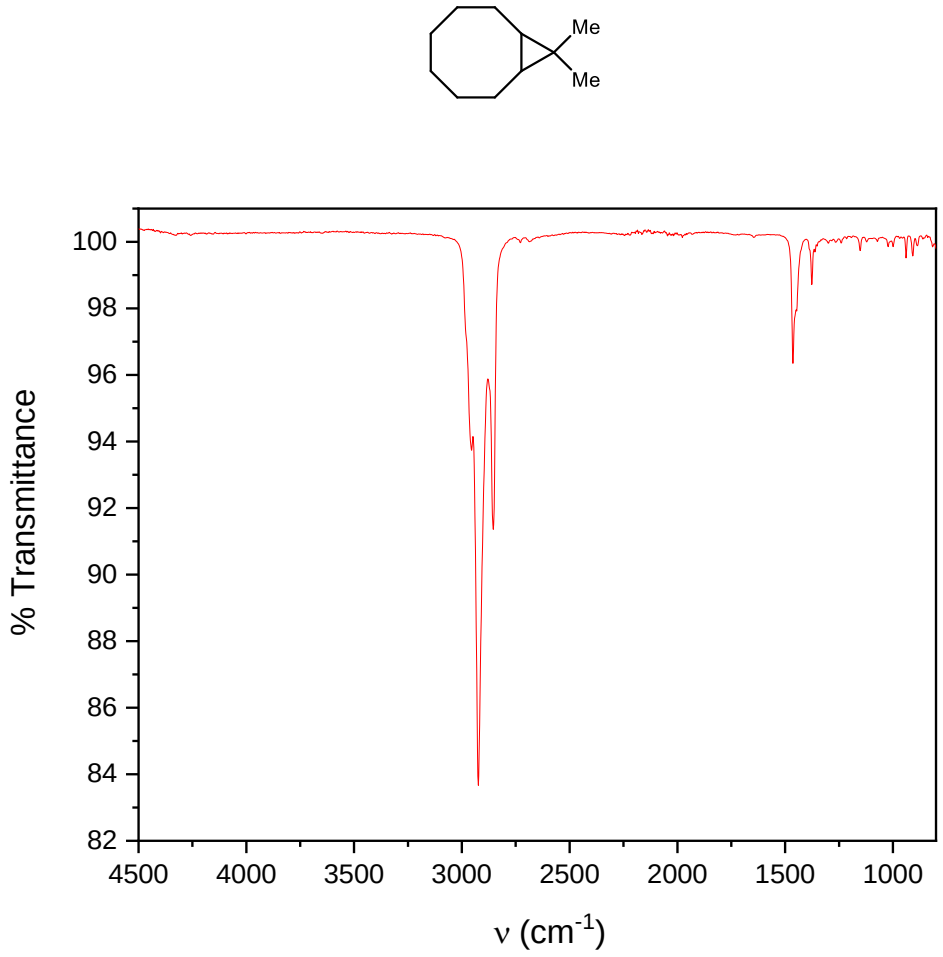
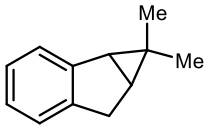


Figure S112: ATR-IR spectrum for **31**



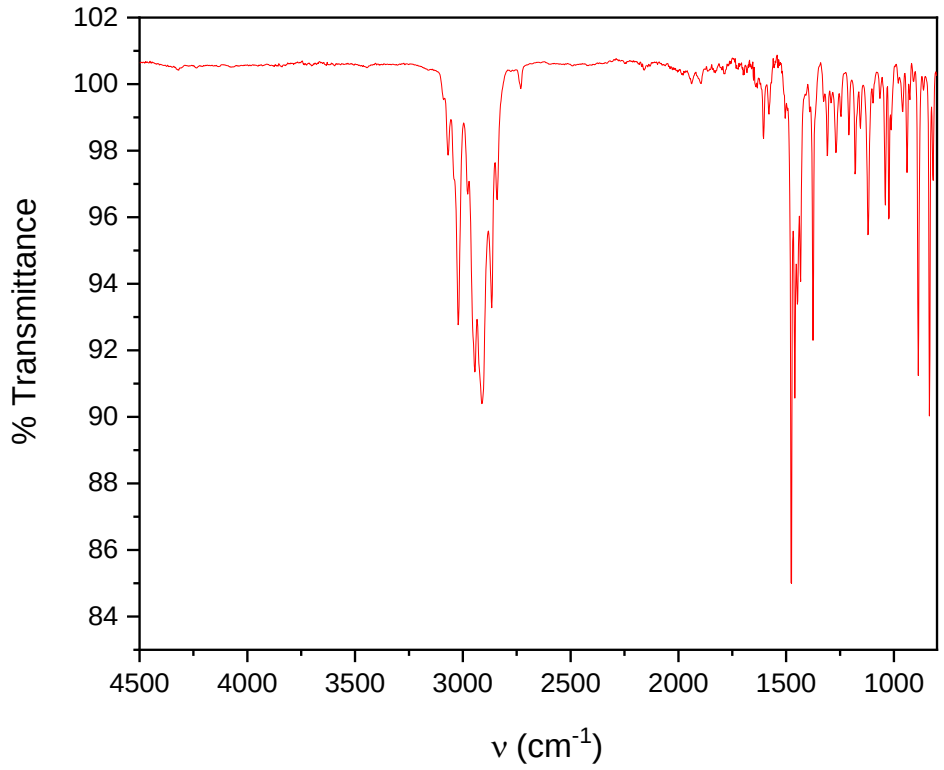


Figure S113: ATR-IR spectrum for **32**

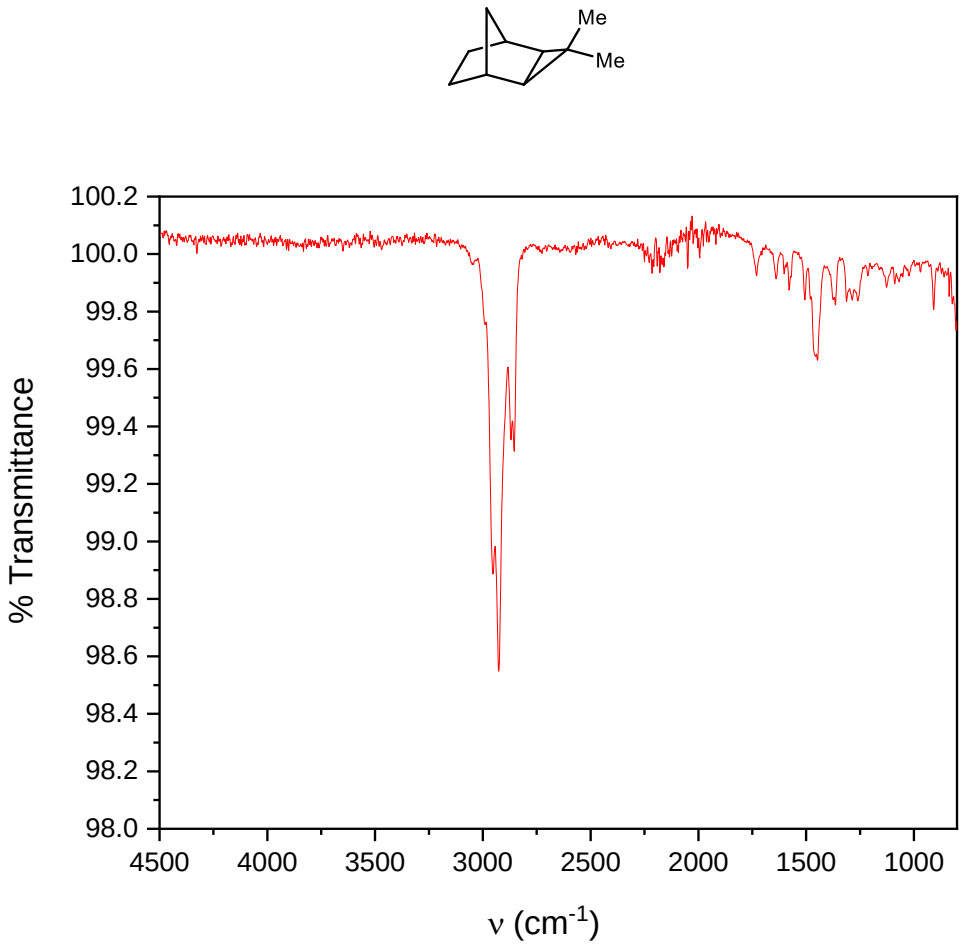


Figure S114: ATR-IR spectrum for **33**

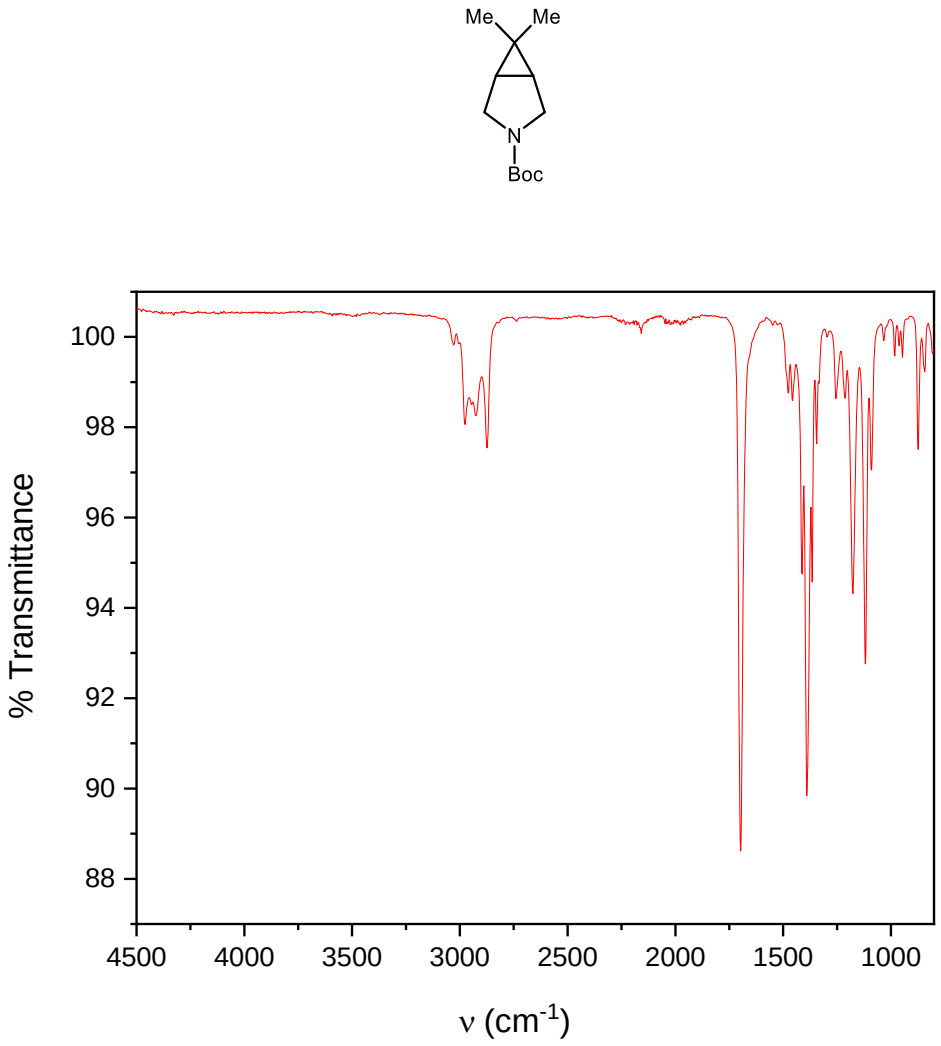
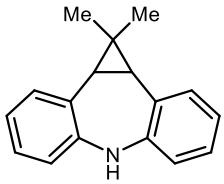


Figure S115: ATR-IR spectrum for **35**



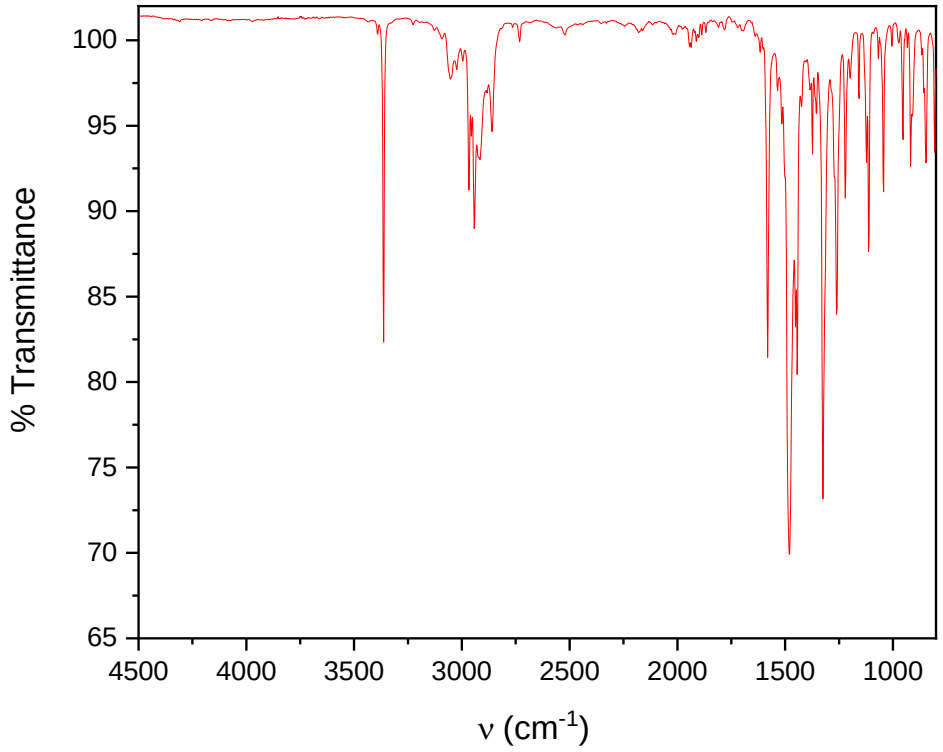
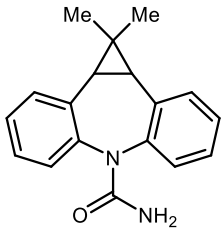


Figure S116: ATR-IR spectrum for **37**



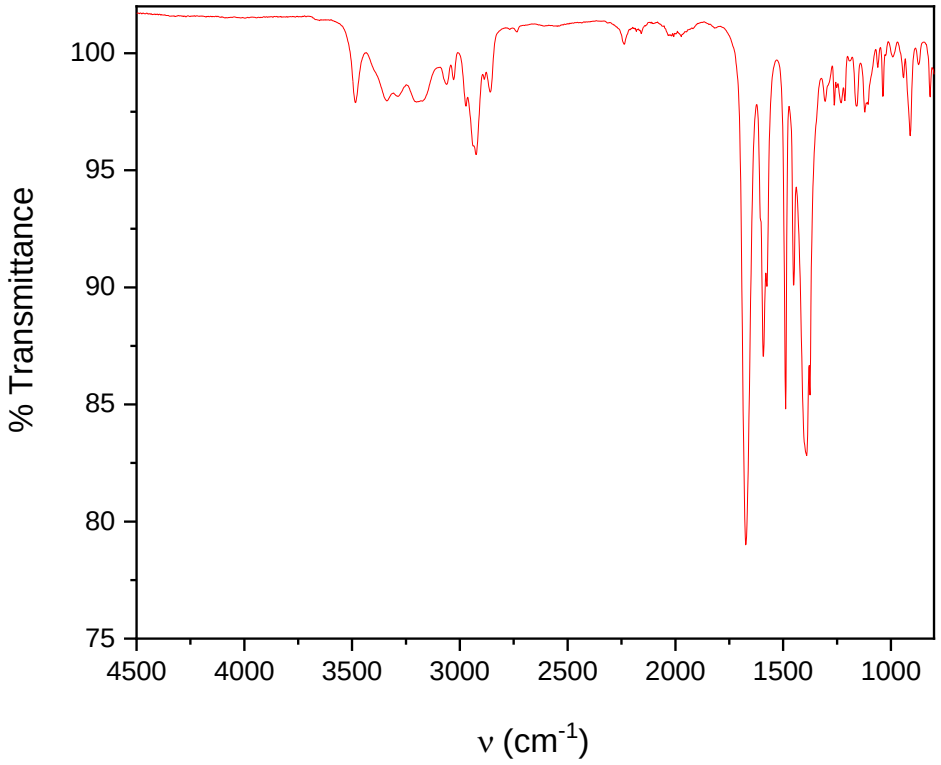


Figure S117: ATR-IR spectrum for **38**

10. References

[1] Wei, L.; Yang, Y.; Fan, R.; Wang, P.; Li, L.; Yu, J.; Yang, B.; Cao, W. *RSC Adv*. **2013**. 3, 25908-25916.
[2] A. M. A. Bennett (DuPont), *WO Pat*., 98/27124, 1998.
[3] Charette, A. B.; Wilb, N.; *Synlett*, **2002**, 1, 0176-0178.
[4] Redies, K. M.; Fallon, T.; Oestreich, M. *Organometallics*, **2014**, 33, 3235-3238.
[5] Britovsek, G.J.P.; Bruce, M.; Gibson, V.C.; Kimberley, B.S.; Maddox, P.J.; MastroIannni, S.; McTavish, S.J.; Redshaw, C.; Solan, G.A.; Stromberg, S.; White, A.J.P.; Williams, D.J. *J. Am. Chem. Soc.* **1999**, *121*, 8728-8740.
[6] Ardolino, M.J.; Morken, J.P. *J. Am. Chem. Soc.* **2012**, 134, 8770-8773.
[7] Marcum, J.S.; Roberts, C.; Manan, R.S.; Cervarich, T.N.; Meek, S.M. *J. Am. Chem. Soc*. **2017**, 139, 15580-15583.
[8] Sun, X.; Li, X.; Song, S.; Zhu, Y.; Lilang, Y.; Jiao, N. *J. Am. Chem. Soc*. **2015**, 137, 6059-6066.
[9] Sargent, B.T.; Alexanian, E.J.; *J. Am. Chem. Soc*. **2017**, 139, 12438-12440.
[10] Sarrdini, S.R.; Brown, K. *J. Am. Chem. Soc.* **2017**, 139, 9823-9826.
[11] Kimura, M.; Ezoe, A.; Mori, M.; Tamaru, T. *J. Am. Chem. Soc*. **2005**, 127, 201-209.
[12] Cannillo, A.; Norsikian, S.; Retailleau, P.; Dau, M. E.; Iorga, B. I.; Beau, J.M. *Chem. Eur. J*. **2013**, 19, 9127-9131.
[13] Yu, Y.; Lin, R.; Zhang, Y. *Tetrahedron, Lett.* **1993**, 34, 4547-4550.
[14] Zhao, D.; Lied, F.; Glorius, F. *Chem. Sci*. **2014**, 5, 2869-2873.
[15] Turos, E.; Parvez, M.; Garigipati, R.S.; Weinreb, S. M. *J. Org. Chem*. **1988**, *53*, 1116-1118.
[16] Stevenson, S. M.; Higgins, R. F.; Shores, M. P.; Ferreira, E. M. *Chem. Sci.* **2017**, 8, 654-660.
[17] Wender, P. A.; Christy, J.P. *J. Am. Chem. Soc*. **2006**, 128, 5354-5355.
[18] Zuo, G.; Louie, J. *Angew. Chem. Int. Ed*. **2004**, 43, 2277-2279.
[19] Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J.A. *J. Am. Chem. Soc*. **1998**, 120, 1940-1941.
[20] Pohjala, L.; Alakurtti, S.; Ahola, T.; Yli-Kauhaluoma, J.; Tamella, P. *J. Nat. Prod*. **2009**. 72, 1917-1926.
[21] Hatch, C.E.; Baum, J.S.; Takashima, T.; Kondo, K. *J. Org. Chem.* **1980**, 45, 3281-3285.
[22] Abarbri, M.; Parrain, J.; Cintrat, J.; Duchene, ,A. *Synthesis*. **1996**, 1, 82-86.
[23] Jiang, Y.; Thomson, R.J.; Schaus, S.E. *Angew. Chem. Int. Ed*. **2017**, 56, 16631-16635.
[24] Wickham, G.; Wells, G.J.; Waykole, L.; Paquette, L.A. *J. Org. Chem.* **1985**, 50, 3485-3489.
[25] Pettigrew, J.D.; Cadieux, J.A.; So, S.S.S.; Wilson, P.D. *Org. Lett.* **2005**, 7, 467-470.
[26] Chuit, C.; Foulon, J.P.; Normant, J.F. *Tetrahedron*. **1980**, 36, 2305-2310.
[27] Garayalde, D.; Gomez-Bengoa, E.; Huang, X.; Goeke, A.; Nevado, C. *J. Am. Chem. Soc.* **2010**, 132, 4720-4730.
[28] Wint, L. T.; McCarthyl, P.A. *J. Label. Compd*. *Radiopharm.* **1988**, 25, 1289-1297.
[29] Ravinder, B.; Reddy, S.R.; Sridhar, M.; Mohan, M.M.; Srinivas, K.; Reddy, A.P.; Bandichhor, R. *Tetrahedron Lett*. **2013**, *54*, 2841-2844.