Rh-Catalyzed [4+1] Reaction of Cyclopropyl-Capped Dienes (but not Common Dienes) and Carbon Monoxide: Reaction Development and Mechanistic Study

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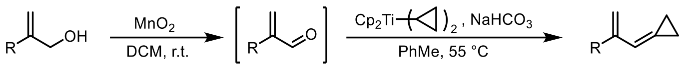
I. General Information

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stirring bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Solvents for the [4+1] cycloaddition were distilled prior to use. $[Rh(cod)Cl]_2$ was purchased from J&K and TCI, and was used without further purification. Other synthetic reagents were purchased from J&K and Acros, and were used without further purification unless otherwise stated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with $KMnO_4$ stain or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.
NMR spectra were measured on Bruker ARX 400 (^1H at 400 MHz, ^{13}C at 101 MHz) and Bruker AVANCE III (^1H at 500 MHz, ^{13}C at 126 MHz, ^{19}F at 471 MHz) nuclear magnetic resonance spectrometers. Data for ^1H NMR spectra were reported as follows: chemical shift (ppm, referenced to residual solvent peak ($CDCl_3$ = δ 7.26 ppm, CD_2Cl_2 = δ 5.32 ppm, $(CD_3)_2SO$ = δ 2.50 ppm; s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, tt = triplet of triplets, tq = triplet of quartets, m = multiplet, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR were reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$ = δ 77.16 ppm, CD_2Cl_2 = δ 53.84 ppm, $(CD_3)_2SO$ = δ 39.52 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI or EI) with an FT-ICR analyzer.

Abbreviations:
cod = 1,5-cyclooctadiene
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
DCE = 1,2-dichloroethane
DCM = dichloromethane
EA = ethyl acetate
IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
m.p. = melting point
MS = molecular sieves
PE = petroleum ether
r.t. = room temperature
TBS = *tert*-butyldimethylsilyl
TMS = trimethylsilyl
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

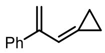
II. Preparation of Substrates

General procedure A:



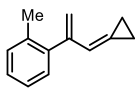
S1 **S2** **1**

Allylic alcohol **S1** (4.0 mmol) was dissolved in DCM (40 mL). Activated MnO_2 (7.0 g, 80 mmol) was added, and the mixture was stirred in open air until TLC indicated complete consumption of the alcohol (Typically 4~6 hours). The resulting mixture was filtered through a short pad of silica gel and eluted with Et_2O. To the filtrate was added PhMe (60 mL), and then the mixture was concentrated *in vacuo* at 5 °C to remove DCM and Et_2O. To the resulting solution of **S2** in PhMe was added $NaHCO_3$ (0.77 g, 9.2 mmol) and subsequently a solution of dicyclopropyltitanocene[1] (2.39 g, 9.2 mmol) in PhMe (20 mL) under N_2 protection. The resulting mixture was stirred at 55 °C until TLC showed complete consumption of the aldehyde (Typically 0.5~4 hours). The solvent was removed *in vacuo* and the residue was subjected to column chromatography (silica gel, PE as eluent) to give **1**. Note that 2-arylacroleins (**S2** where R = aryl) readily dimerize under neat condition at room temperature,[2] and should always be kept in dilute solution. **1** is unstable in air, and should be used immediately after isolation.



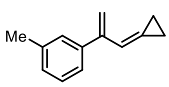
1a

36% yield from **S1a** [3], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 4H), 7.30 – 7.28 (m, 1H), 6.66 (apparent p, J = 2.1 Hz, 1H), 5.36 (s, 1H), 5.21 (s, 1H), 1.10 – 1.05 (m, 2H), 0.95 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.0, 141.6, 128.3, 128.2, 127.6, 127.6, 119.4, 114.8, 5.1, 1.5.
HRMS (EI): calcd. for $C_{12}H_{12}$ ($[M\cdot]^+$): 156.0934, found 156.0933.



1b

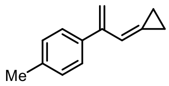
50% yield from **S1b** [4], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 3H), 7.09 – 7.05 (m, 1H), 6.65 (apparent p, J = 2.1 Hz, 1H), 5.38 (d, J = 2.1 Hz, 1H), 5.02 (d, J = 2.1 Hz, 1H), 2.17 (s, 3H), 1.01 – 0.94 (m, 2H), 0.54 – 0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 141.7, 135.8, 129.4, 129.3, 127.3, 127.0, 125.3, 120.3, 115.5, 19.6, 3.8, 1.2.
HRMS (EI): calcd. for $C_{13}H_{14}$ ($[M\cdot]^+$): 170.1090, found 170.1088.



1c

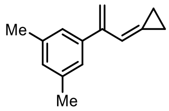
27% yield from **S1c** [4], yellow oil, TLC R_f = 0.7 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.21 (m, 1H), 7.19 – 7.11 (m, 3H), 6.67 (apparent t, J = 2.2 Hz, 1H), 5.38 (s, 1H), 5.23 (s, 1H), 2.38 (s, 3H), 1.12 – 1.08 (m, 2H), 0.99 – 0.95 (m, 2H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 147.6, 141.2, 137.4, 128.8, 128.0, 127.8, 127.1, 125.1, 119.4, 114.5, 21.6, 4.9, 1.5.
HRMS (EI): calcd. for $C_{13}H_{14}$ ($[M\cdot]^+$): 170.1090, found 170.1089.



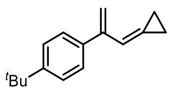
1d

59% yield from **S1d** [4], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.66 (apparent p, J = 2.1 Hz, 1H), 5.34 (d, J = 1.8 Hz, 1H), 5.20 (d, J = 1.8 Hz, 1H), 2.37 (s, 3H), 1.11 – 1.06 (m, 2H), 1.00 – 0.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 138.4, 137.0, 128.6, 127.9, 127.0, 119.4, 114.2, 21.3, 5.0, 1.5.
HRMS (EI): calcd. for $C_{13}H_{14}$ ($[M\cdot]^+$): 170.1090, found 170.1090.



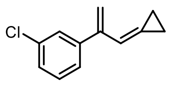
1e

34% yield from **S1e** [5], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.94 (s, 1H), 6.64 (apparent p, J = 2.2 Hz, 1H), 5.35 (d, J = 1.9 Hz, 1H), 5.21 (d, J = 1.9 Hz, 1H), 2.32 (s, 6H), 1.12 – 1.07 (m, 2H), 1.00 – 0.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 141.2, 137.3, 128.9, 126.9, 125.8, 119.3, 114.3, 21.5, 4.9, 1.4.
HRMS (EI): calcd. for $C_{14}H_{16}$ ($[M\cdot]^+$): 184.1247, found 184.1247.



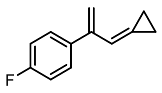
1f

34% yield from **S1f** [6], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.31 – 7.29 (m, 2H), 6.66 (apparent p, J = 2.1 Hz, 1H), 5.38 (s, 1H), 5.24 (s, 1H), 1.35 (s, 9H), 1.12 – 1.09 (m, 2H), 1.03 – 0.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 147.0, 138.3, 127.5, 126.9, 124.8, 119.2, 114.0, 34.6, 31.5, 4.9, 1.5.
HRMS (EI): calcd. for $C_{16}H_{20}$ ($[M\cdot]^+$): 212.1560, found 212.1559.



1g

28% yield from **S1g** [4], yellow oil, TLC R_f = 0.7 (PE/EA = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.25 – 7.22 (m, 2H), 7.21 – 7.18 (m, 1H), 6.62 (apparent p, J = 2.1 Hz, 1H), 5.35 (s, 1H), 5.19 (s, 1H), 1.10 – 1.06 (m, 2H), 0.93 – 0.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 143.1, 133.7, 129.1, 128.4, 127.8, 127.3, 126.4, 119.0, 115.6, 5.0, 1.5.
HRMS (EI): calcd. for $C_{12}H_{11}Cl$ ($[M\cdot]^+$): 190.0544, found 190.0542.

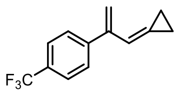


1h

45% yield from **S1h** [5], yellow oil, TLC R_f = 0.9 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.03 – 6.96 (m, 2H), 6.64 (apparent p, *J* = 2.1 Hz, 1H), 5.33 (d, *J* = 1.7 Hz, 1H), 5.16 (d, *J* = 1.7 Hz, 1H), 1.10 – 1.04 (m, 2H), 0.92 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.3 Hz), 146.8, 137.3 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 7.9 Hz), 127.5, 119.5, 115.0, 114.7 (d, *J* = 21.2 Hz), 5.0, 1.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.8.

HRMS (EI): calcd. for $C_{12}H_{11}F$ ($[M\cdot]^+$): 174.0839, found 174.0838.

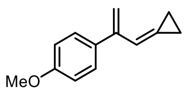


1i

31% yield from **S1i** [5], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.68 (apparent p, *J* = 2.1 Hz, 1H), 5.42 (s, 1H), 5.23 (s, 1H), 1.13 – 1.07 (m, 2H), 0.93 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.73, 145.03, 129.42 (q, *J* = 32.3 Hz), 128.54, 128.09, 124.84 (q, *J* = 3.8 Hz), 124.48 (d, *J* = 271.9 Hz), 118.94, 116.19, 5.02, 1.56. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.

HRMS (EI): calcd. for $C_{13}H_{11}F_3$ ($[M\cdot]^+$): 224.0807, found 224.0810.

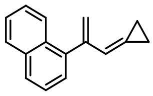


1j

29% yield from **S1j** [3], yellow oil, TLC R_f = 0.8 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.64 (apparent p, *J* = 2.1 Hz, 1H), 5.30 (d, *J* = 1.8 Hz, 1H), 5.16 (d, *J* = 1.8 Hz, 1H), 3.82 (s, 3H), 1.12 – 1.05 (m, 2H), 1.01 – 0.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.9, 133.8, 129.1, 127.0, 119.6, 113.8, 113.3, 55.4, 5.0, 1.5.

HRMS (EI): calcd. for $C_{13}H_{14}O$ ($[M\cdot]^+$): 186.1039, found 186.1038.

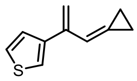


1k

47% yield from **S1k** [3], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.30 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.82 (apparent p, *J* = 2.1 Hz, 1H), 5.59 (d, *J* = 2.0 Hz, 1H), 5.22 (d, *J* = 2.0 Hz, 1H), 0.94 – 0.87 (m, 2H), 0.17 – 0.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 140.0, 133.4, 132.3, 128.2, 128.1, 127.3, 126.4, 126.2, 125.7, 125.5, 125.3, 120.9, 117.0, 3.8, 1.3.

HRMS (EI): calcd. for $C_{16}H_{14}$($[M\cdot]^+$): 206.1090, found 206.1088.

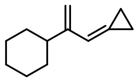


1l

20% yield from **S1l** [7], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.24 (m, 1H), 7.23 – 7.20 (m, 1H), 7.16 – 7.13 (m, 1H), 6.64 (apparent p, J = 2.1 Hz, 1H), 5.35 (s, 1H), 5.30 (s, 1H), 1.10 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 141.5, 127.6, 126.8, 124.9, 121.7, 118.8, 113.5, 4.8, 1.6.

HRMS (EI): calcd. for $C_{10}H_{10}S$ ([M·]$^+$): 162.0498, found 162.0496.

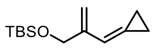


1m

32% yield from **S1m** [7], yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (apparent p, J = 2.1 Hz, 1H), 4.99 (s, 1H), 4.89 (s, 1H), 2.48 (tt, J = 11.6, 3.0 Hz, 1H), 1.84 – 1.76 (m, 4H), 1.75 – 1.68 (m, 1H), 1.38 – 1.26 (m, 4H), 1.23 – 1.13 (m, 3H), 1.07 – 1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 122.4, 120.9, 110.7, 40.4, 33.2, 27.1, 26.7, 4.6, 0.7.

HRMS (EI): calcd. for $C_{12}H_{18}$ ([M·]$^+$): 162.1403, found 162.1401.



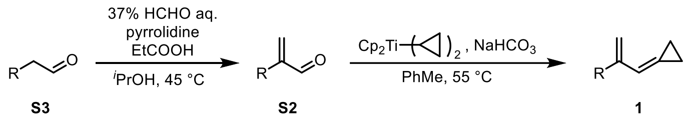
1n

35% yield from **S1n** [8], yellow oil, TLC R_f = 0.8 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (apparent p, J = 2.1 Hz, 1H), 5.28 (s, 1H), 5.10 (s, 1H), 4.48 (s, 2H), 1.25 – 1.20 (m, 2H), 1.11 – 1.05 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 122.9, 118.8, 111.7, 63.4, 26.1, 18.6, 4.7, 1.4, -5.2.

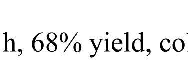
HRMS (EI): calcd. for $C_{13}H_{24}OSi$ ([M·]$^+$): 224.1591, found 224.1592.

General procedure B:



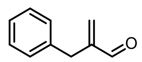
*Preparation of substituted acrolein **S2**:*

Following a reported procedure by Pihko,[9] to a mixture of 37% HCHO aq. (0.55 g, 6.8 mmol) and aldehyde **S3** (6.0 mmol) in ^{i}PrOH (0.6 mL) were added propionic acid (45.7 mg, 0.6 mmol) and pyrrolidine (42.7 mg, 0.6 mmol). The reaction mixture was stirred at 45 °C for 1~4 h (as indicated below). Saturated $NaHCO_3$ aq. (10 mL) was added, and the mixture was extracted with DCM (3×10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and filtered through a short pad of silica gel (DCM as eluent). The filtrate was concentrated *in vacuo* to give **S2**.



S2o

4 h, 68% yield, colorless oil, TLC R_f = 0.5 (PE/EA = 20:1).

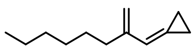


S2p

1 h, 74% yield, pale yellow oil, TLC R_f = 0.4 (PE/EA = 20:1).

*Preparation of substrates **1o** and **1p**:*

To a mixture of **S2** (3.1 mmol) and $NaHCO_3$ (0.59 g, 7.0 mmol) in PhMe (40 mL) was added a solution of dicyclopropyltitanocene[1] (1.84 g, 7.1 mmol) in PhMe (20 mL) under N_2 protection. The resulting mixture was stirred at 55 °C for 3.5 hours. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was subjected to column chromatography (silica gel, PE as eluent) to give **1**.

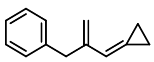


1o

54% yield, yellow oil, TLC R_f = 0.9 (PE/EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (apparent t, J = 2.2 Hz, 1H), 4.98 (s, 1H), 4.90 (s, 1H), 2.33 (t, J = 7.7 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.33 – 1.23 (m, 8H), 1.09 – 1.02 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 123.3, 121.1, 113.1, 33.3, 32.0, 29.5, 29.2, 22.8, 14.3, 4.7, 0.8.

HRMS (EI): calcd. for $C_{12}H_{20}$ ([M·]$^+$): 164.1560, found 164.1559.



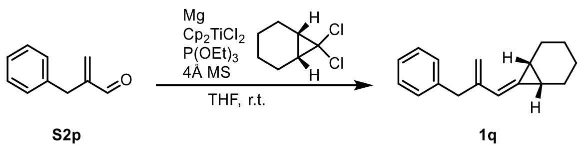
1p

60% yield, yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 6.53 (apparent t, J = 2.2 Hz, 1H), 5.17 (s, 1H), 4.83 (s, 1H), 3.69 (s, 2H), 1.16 – 1.10 (m, 2H), 1.04 – 0.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 140.4, 128.9, 128.3, 125.9, 124.5, 120.8, 115.9, 39.5, 4.9, 1.0.

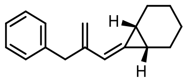
HRMS (EI): calcd. for $C_{13}H_{14}$ ([M·]$^+$): 170.1090, found 170.1090.

Preparation of substrate 1q:



S2p **1q**

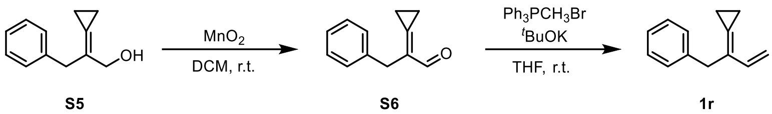
Substrate **1q** was synthesized following a modified procedure from Takeda.[10] A 250 mL round-bottomed flask was charged with 4Å MS (1.34 g). The flask was dried with a heat gun under vacuum and then cooled to room temperature. This procedure was repeated for three times, and then the flask was refilled with argon. Mg turnings (0.34 g, 14.0 mmol) and Cp_2TiCl_2 (3.17 g, 12.7 mmol) were then added rapidly. The system was again subjected to argon protection, before addition of superdry THF (25 mL) and $P(OEt)_3$ (4.4 mL, 25 mmol) via syringe. The resulting red mixture was then stirred at room temperature. Within 15 min, the system turned briefly dark green and then black with an evolution of heat. After 3 h, 7,7-dichlorobicyclo[4.1.0]heptane (0.71 g, 4.30 mmol) in THF (5 mL) was added via syringe, and the reaction mixture was further stirred for 30 min. To the mixture was added dropwise **S2p** (0.27 g, 1.87 mmol) in THF (5 mL). After 1.5 h of stirring, the reaction mixture was diluted with PE (30 mL). The precipitates were filtered off through a short pad of silica gel, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, PE as eluent) to give **1q** (72.8 mg, 17% yield).



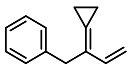
1q

Yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 6.53 (apparent t, J = 2.1 Hz, 1H), 5.16 (s, 1H), 4.76 (s, 1H), 3.70 (d, J = 16.0 Hz, 1H), 3.60 (d, J = 16.0 Hz, 1H), 1.87 – 1.74 (m, 3H), 1.65 – 1.55 (m, 2H), 1.46 – 1.41 (m, 1H), 1.29 – 1.18 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 146.3, 140.3, 136.1, 129.0, 128.3, 126.0, 120.5, 115.1, 39.5, 23.6, 23.1, 21.7, 21.3, 14.9, 11.1.
HRMS (EI): calcd. for $C_{17}H_{20}$ ([M·]$^+$): 224.1560, found 224.1557.

Preparation of substrate 1r:



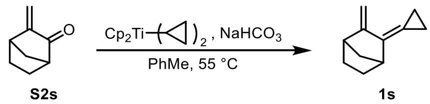
To a solution of **S5** [11] (0.35 g, 2.0 mmol) in DCM (20 mL) was added activated MnO_2 (3.72 g, 42.8 mmol). The reaction mixture was stirred at room temperature for 13 h, filtered through a short pad of silica gel and eluted with DCM. The filtrate was concentrated *in vacuo* to give **S6** (317.0 mg, 92% yield) as a yellow oil, which was directly used in the next step.
To a stirred mixture of Ph_3PCH_3Br (0.88 g, 2.5 mmol) and ^{t}BuOK (266.9 mg, 2.38 mmol) was added dry THF (15 mL). The resulting bright-yellow suspension was stirred at room temperature for 5 min. **S6** (317.0 mg, 1.84 mmol) in THF (5 mL) was then added via syringe, and the reaction mixture was further stirred at room temperature for 2.5 h. The resulting mixture was concentrated to 2 mL via rotary evaporation, and then diluted with PE (20 mL) to precipitate $Ph_3P=O$. The slurry was filtered through a short pad of silica gel and eluted with 50:1 PE/EA. The filtrate was concentrated *in vacuo*, and subjected to column chromatography (silica gel, PE as eluent) to give **1s** (235.0 mg, 75% yield).



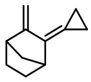
1r

Pale yellow oil, TLC R_f = 0.7 (PE/EA = 20:1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 6.62 (dd, J = 17.7, 10.8 Hz, 1H), 5.22 (d, J = 17.7 Hz, 1H), 5.04 (d, J = 10.8 Hz, 1H), 3.74 (s, 2H), 1.20 (dd, J = 8.9, 5.8 Hz, 2H), 1.09 (dd, J = 8.6, 5.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.6, 137.5, 128.8, 128.3, 127.3, 126.5, 125.9, 112.3, 37.4, 3.0, 2.6.
HRMS (EI): calcd. for $C_{13}H_{14}$ ([M·]$^+$): 170.1090, found 170.1085.

Preparation of substrate 1s:



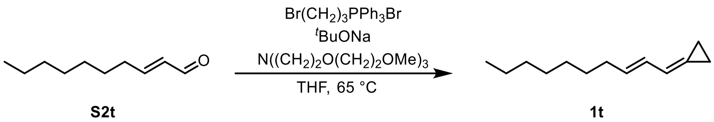
To a mixture of **S2s** (184.4 mg, 1.64 mmol) and $NaHCO_3$ (0.33 g, 3.9 mmol) in PhMe (20 mL) was added a solution of dicyclopropyltitanocene[1] (0.93 g, 3.6 mmol) in PhMe (15 mL) under N_2 protection. The resulting mixture was stirred at 55 °C for 4 h. After cooling to room temperature, the solvent was removed *in vacuo*, and the residue was subjected to column chromatography to give **1s** (36.4 mg, 15% yield).



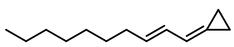
1s

Pale yellow oil, TLC R_f = 0.9 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1H), 4.77 (s, 1H), 2.98 – 2.95 (m, 1H), 2.89 – 2.85 (m, 1H), 1.76 – 1.73 (m, 1H), 1.73 – 1.71 (m, 1H), 1.58 – 1.53 (m, 1H), 1.52 – 1.48 (m, 1H), 1.41 – 1.39 (m, 1H), 1.38 – 1.37 (m, 1H), 1.20 – 1.13 (m, 2H), 1.03 – 0.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 133.1, 110.0, 99.4, 46.1, 44.4, 40.1, 29.0, 28.5, 2.9, -0.7.
HRMS (EI): calcd. for $C_{11}H_{14}$ ([M·]$^+$): 146.1090, found 146.1090.

Preparation of substrate 1t:



Following a modified procedure from McMurry,[12] to a mixture of $Br(CH_2)_3PPh_3Br$ (1.52 g, 3.27 mmol) and ^{t}BuONa (625.9 mg, 6.51 mmol) was added dry THF (11 mL) under N_2 protection. The resulting yellow suspension was stirred at 65 °C for 3 h. **S2t** (0.39 g, 2.5 mmol) and $N((CH_2)_2O(CH_2)_2OMe)_3$ (93.3 mg, 0.29 mmol) were then dissolved in dry THF (4 mL) and added via syringe. The resulting mixture was further stirred at 65 °C for 13 h. After cooling to room temperature, the reaction mixture was diluted with PE (30 mL) to precipitate Ph_3P=O. The slurry was filtered through a short pad of silica gel and eluted with PE. The filtrate was concentrated *in vacuo*, and the residue was subjected to column chromatography (silica gel, PE as eluent) to give **1t** (433.0 mg, 97% yield).

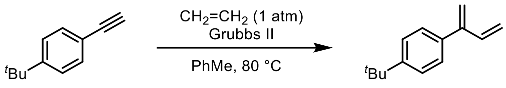


1t

Pale yellow oil, TLC R_f = 0.7 (100% PE).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.35 (apparent dp, J = 10.4, 2.1 Hz, 1H), 6.18 (ddt, J = 13.3, 10.4, 1.6 Hz, 1H), 5.68 (dt, J = 14.7, 7.0 Hz, 1H), 2.09 (apparent q, J = 7.1 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.24 (m, 10H), 1.11 – 1.08 (m, 2H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 133.4, 129.8, 124.2, 119.3, 33.2, 32.3, 30.0, 29.64, 29.63, 23.1, 14.3, 2.6, 2.4.
HRMS (EI): calcd. for $C_{13}H_{22}$ ([M·]$^+$): 178.1716, found 178.1713.

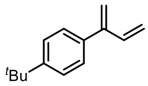
Preparation of common diene 3 and cyclobutyl-capped diene 4

Common diene **3** and cyclobutyl-capped diene **4** were prepared by enyne metathesis, following the procedures of Mori and Diver.[13,14] Note that 2-(4-*tert*-butylphenyl)-1,3-butadiene was used instead of 2-phenyl-1,3-butadiene to reduce the volatility.



S7 **3**

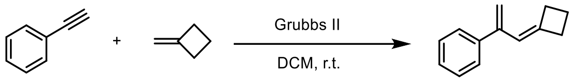
4-*tert*-Butylphenylacetylene (193.0 mg, 1.22 mmol) and Grubbs II catalyst (41.4 mg, 49 μmol) were dissolved in PhMe (4 mL). The solution was bubbled with ethylene for 10 min, and then stirred at 80 °C for 4 h under ethylene atmosphere. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, 100% PE) to give **3** (120.2 mg, 53% yield).



3

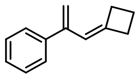
Colorless oil, TLC R_f = 0.8 (100% PE), a known compound.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.29 – 7.24 (m, 2H), 6.61 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.30 – 5.17 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 148.1, 138.3, 136.9, 128.0, 125.2, 117.1, 116.5, 34.7, 31.5.



S8 **S9** **4**

Under N_2 protection, to a solution of Grubbs II catalyst (29.9 mg, 35 μmol) in DCM (5 mL) was added via syringe phenylacetylene (71.5 mg, 0.70 mmol, dissolved in 1 mL of DCM) and methylenecyclobutane (168 mg, 2.5 mmol, dissolved in 1 mL of DCM). The solution was stirred at room temperature for 3.5 h. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, 100% PE) to give **4** (101.7 mg, 85% yield).



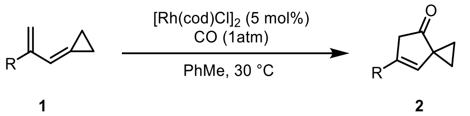
4

Colorless oil, TLC R_f = 0.6 (100% PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 5.92 (apparent p, *J* = 2.4 Hz, 1H), 5.17 (s, 1H), 5.07 (s, 1H), 2.84 – 2.74 (m, 2H), 2.50 – 2.40 (m, 2H), 1.93 (apparent p, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 146.1, 141.9, 128.1, 127.5, 127.3, 121.0, 113.6, 32.6, 32.5, 18.0.

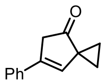
HRMS (EI): calcd. for $C_{13}H_{14}$ ($[M\cdot]^+$): 170.1090, found 170.1088.

III. General Procedure and Experimental Details of Rh(I)-Catalyzed [4+1] Cycloaddition



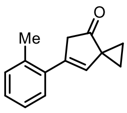
General procedure:

PhMe (4.0 mL) was added to a mixture of **1** (0.20 mmol) and $[Rh(cod)Cl]_2$ (4.9 mg, 10 μmol). The resulting yellow solution was bubbled with CO (1 atm) for 10 min, during which the solution faded to pale yellow or colorless. The mixture was then stirred at 30 °C under CO atmosphere until TLC indicated complete consumption of the starting material. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel to afford **2**.



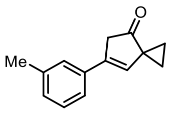
2a

Run 1: Following the general procedure, 33.0 mg of **1a** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.1 mg of **2a** was obtained in 85% yield.
Run 2: Following the general procedure, 31.4 mg of **1a** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 31.7 mg of **2a** was obtained in 86% yield.
Average yield: 86%.
Pale yellow solid, m.p. 96~97 °C, TLC R_f = 0.4 (PE/EA = 10:1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 1H), 6.22 (t, *J* = 1.9 Hz, 1H), 3.37 (d, *J* = 1.9 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.26 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.4, 136.7, 135.2, 128.7, 128.4, 127.8, 124.9, 43.6, 37.3, 18.6.
HRMS (ESI): calcd. for $C_{13}H_{13}O$ ($[M+H]^+$): 185.0961, found 185.0963.



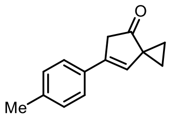
2b

Run 1: Following the general procedure, 34.0 mg of **1b** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 30.9 mg of **2b** was obtained in 78% yield.
Run 2: Following the general procedure, 34.1 mg of **1b** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 32.5 mg of **2b** was obtained in 82% yield.
Average yield: 80%
Yellow oil, TLC R_f = 0.4 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 5.83 (t, *J* = 2.0 Hz, 1H), 3.39 (d, *J* = 2.0 Hz, 2H), 2.43 (s, 3H), 1.49 – 1.44 (m, 2H), 1.27 – 1.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.9, 137.5, 136.2, 135.6, 132.3, 131.1, 128.1, 127.5, 126.1, 46.3, 37.0, 21.6, 18.5.
HRMS (ESI): calcd. for $C_{14}H_{15}O$ ($[M+H]^+$): 199.1117, found 199.1115.



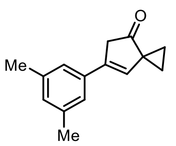
2c

Run 1: Following the general procedure, 34.4 mg of **1c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 23.5 mg of **2c** was obtained in 59% yield.
Run 2: Following the general procedure, 34.0 mg of **1c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 23.9 mg of **2c** was obtained in 60% yield.
Average yield: 60%
Pale yellow solid, m.p. 63~64 °C, TLC R_f = 0.5 (PE/EA = 10:1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.29 – 7.24 (m, 3H), 7.12 – 7.08 (m, 1H), 6.21 (t, J = 1.9 Hz, 1H), 3.35 (d, J = 1.9 Hz, 2H), 2.37 (s, 3H), 1.42 – 1.37 (m, 2H), 1.26 – 1.21 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 216.2, 138.7, 137.0, 135.5, 128.8, 128.7, 128.5, 125.9, 122.3, 43.9, 37.3, 21.6, 18.5.
HRMS (ESI): calcd. for $C_{14}H_{15}O$ ([M+H]$^+$): 199.1117, found 199.1121.



2d

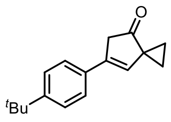
Run 1: Following the general procedure, 33.5 mg of **1d** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.5 mg of **2d** was obtained in 86% yield.
Run 2: Following the general procedure, 34.1 mg of **1d** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.1 mg of **2d** was obtained in 83% yield.
Average yield: 84%
Pale yellow solid, m.p. 126~128 °C, TLC R_f = 0.3 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.12 (t, J = 1.9 Hz, 1H), 3.37 (d, J = 1.9 Hz, 2H), 2.36 (s, 3H), 1.49 – 1.41 (m, 2H), 1.27 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.8, 137.7, 136.6, 132.5, 129.4, 127.3, 124.9, 43.7, 37.2, 21.3, 18.6.
HRMS (ESI): calcd. for $C_{14}H_{15}O$ ([M+H]$^+$): 199.1117, found 199.1118.



2e

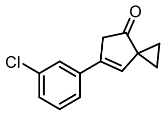
Run 1: Following the general procedure, 37.9 mg of **1e** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 39.6 mg of **2e** was obtained in 91% yield.
Run 2: Following the general procedure, 38.2 mg of **1d** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 38.6 mg of **2e** was obtained in 88% yield.
Average yield: 90%
Pale yellow solid, m.p. 66~67 °C, TLC R_f = 0.5 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.93 (s, 1H), 6.16 (t, J = 1.9 Hz, 1H), 3.37 (d, J = 1.9 Hz, 2H), 2.34 (s, 6H), 1.48 – 1.43 (m, 2H), 1.25 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.7, 138.2, 136.8, 135.1, 129.5, 128.0, 122.9, 43.8, 37.2, 21.5, 18.6.

HRMS (ESI): calcd. for $C_{15}H_{17}O$ ($[M+H]^+$): 213.1274, found 213.1273.



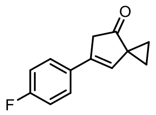
2f

Run 1: Following the general procedure, 42.3 mg of **1f** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 31.0 mg of **2f** was obtained in 65% yield.
Run 2: Following the general procedure, 43.4 mg of **1f** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 34.1 mg of **2f** was obtained in 70% yield.
Average yield: 68%
Pale yellow solid, m.p. 107~108 °C, TLC R_f = 0.4 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 4H), 6.14 (t, J = 1.9 Hz, 1H), 3.38 (d, J = 1.9 Hz, 2H), 1.47 – 1.44 (m, 2H), 1.34 (s, 9H), 1.26 – 1.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.8, 151.0, 136.5, 132.5, 127.5, 125.7, 124.7, 43.7, 37.2, 34.7, 31.4, 18.6.
HRMS (ESI): calcd. for $C_{17}H_{21}O$ ($[M+H]^+$): 241.1587, found 241.1583.



2g

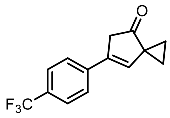
Run 1: Following the general procedure, 37.6 mg of **1g** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 23.7 mg of **2g** was obtained in 55% yield.
Run 2: Following the general procedure, 38.0 mg of **1g** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 24.4 mg of **2g** was obtained in 56% yield.
Average yield: 56%
Pale yellow solid, m.p. 107~108 °C, TLC R_f = 0.4 (PE/EA = 10:1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.41 (m, 1H), 7.36 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 6.26 (t, J = 1.9 Hz, 1H), 3.34 (d, J = 1.9 Hz, 2H), 1.44 – 1.40 (m, 2H), 1.28 – 1.24 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 215.4, 137.5, 135.7, 134.9, 130.6, 130.3, 127.8, 125.3, 123.4, 43.7, 37.5, 18.8.
HRMS (ESI): calcd. for $C_{13}H_{12}ClO$ ($[M+H]^+$): 219.0571, found 219.0571.



2h

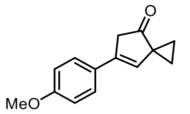
Run 1: Following the general procedure, 34.6 mg of **1h** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 31.7 mg of **2h** was obtained in 79% yield.
Run 2: Following the general procedure, 34.8 mg of **1h** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 31.2 mg of **2h** was obtained in 77% yield.
Average yield: 78%
Pale yellow solid, m.p. 101~102 °C, TLC R_f = 0.3 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.11 – 7.02 (m, 2H), 6.10 (t, J = 1.9 Hz, 1H), 3.35 (d, J = 1.9 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.25 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

216.2, 162.4 (d, J = 247.5 Hz), 135.6, 131.5 (d, J = 3.5 Hz), 128.1 (d, J = 2.1 Hz), 126.6 (d, J = 8.0 Hz), 115.7 (d, J = 21.7 Hz), 43.7, 37.3, 18.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.0.
HRMS (ESI): calcd. for $C_{13}H_{12}FO$ ($[M+H]^+$): 203.0867, found 203.0868.



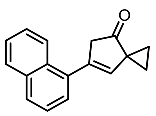
2i

Run 1: Following the general procedure, 45.0 mg of **1i** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 32.4 mg of **2i** was obtained in 64% yield.
Run 2: Following the general procedure, 45.1 mg of **1i** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.8 mg of **2i** was obtained in 67% yield.
Average yield: 66%
White solid, m.p. 104~105 °C, TLC R_f = 0.3 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 6.32 (t, J = 2.0 Hz, 1H), 3.39 (d, J = 2.0 Hz, 2H), 1.53 – 1.48 (m, 2H), 1.32 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 138.4, 135.5, 131.3, 130.0 (q, J = 32.6 Hz), 125.8 (q, J = 3.9 Hz), 125.1, 124.2 (q, J = 271.8 Hz), 43.4, 37.5, 19.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5.
HRMS (ESI): calcd. for $C_{14}H_{12}F_3O$ ($[M+H]^+$): 253.0835, found 253.0836.



2j

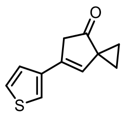
Run 1: Following the general procedure, 37.3 mg of **1j** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 26.1 mg of **2j** was obtained in 61% yield.
Run 2: Following the general procedure, 37.0 mg of **1j** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 27.9 mg of **2j** was obtained in 65% yield.
Average yield: 63%
White solid, m.p. 138~140 °C, TLC R_f = 0.2 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.03 (t, J = 1.9 Hz, 1H), 3.82 (s, 3H), 3.35 (d, J = 1.9 Hz, 2H), 1.45 – 1.40 (m, 2H), 1.22 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.8, 159.3, 136.1, 128.1, 126.2, 126.1, 114.1, 55.4, 43.8, 37.2, 18.5.
HRMS (ESI): calcd. for $C_{14}H_{15}O_2$ ($[M+H]^+$): 215.1067, found 215.1064.



2k

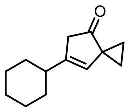
Run 1: Following the general procedure, 41.3 mg of **1k** was used, 22 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 38.1 mg of **2k** was obtained in 81% yield.
Run 2: Following the general procedure, 41.4 mg of **1k** was used, 22 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 39.2 mg of **2k** was obtained in 83% yield.
Average yield: 82%

Colorless oil, TLC R_f = 0.4 (PE/EA = 10:1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.28 – 8.18 (m, 1H), 7.94 – 7.85 (m, 1H), 7.83 – 7.79 (m, 1H), 7.53 – 7.50 (m, 2H), 7.48 (d, J = 8.1 Hz, 1H), 7.42 (dd, J = 7.1, 1.4 Hz, 1H), 6.03 (t, J = 2.0 Hz, 1H), 3.50 (d, J = 2.0 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.34 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 216.4, 136.7, 135.6, 134.4, 133.8, 131.5, 128.9, 128.1, 126.5, 126.3, 125.7, 125.7, 125.5, 47.4, 37.2, 18.4.
HRMS (ESI): calcd. for $C_{17}H_{15}O$ ($[M+H]^+$): 235.1117, found 235.1114.



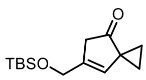
2l

Run 1: Following the general procedure, 34.1 mg of **1l** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 24.3 mg of **2l** was obtained in 61% yield.
Run 2: Following the general procedure, 33.0 mg of **1l** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 22.4 mg of **2l** was obtained in 58% yield.
Average yield: 60%
Pale yellow solid, m.p. 111~112 °C, TLC R_f = 0.2 (PE/EA = 20:1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.35 (dd, J = 5.1, 2.9 Hz, 1H), 7.31 (dd, J = 5.1, 1.3 Hz, 1H), 7.14 (dd, J = 2.9, 1.3 Hz, 1H), 6.03 (t, J = 1.9 Hz, 1H), 3.33 (d, J = 1.9 Hz, 2H), 1.40 – 1.35 (m, 2H), 1.24 – 1.17 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 215.9, 138.3, 132.7, 128.2, 126.6, 124.9, 120.8, 44.3, 36.9, 18.4.
HRMS (ESI): calcd. for $C_{11}H_{11}OS$ ($[M+H]^+$): 191.0525, found 191.0529.



2m

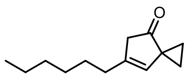
Run 1: Following the general procedure, 32.1 mg of **1m** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 27.7 mg of **2m** was obtained in 74% yield.
Run 2: Following the general procedure, 32.5 mg of **1m** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 30.6 mg of **2m** was obtained in 80% yield.
Average yield: 77%
Pale yellow oil, TLC R_f = 0.4 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (t, J = 1.8 Hz, 1H), 2.94 (d, J = 1.8 Hz, 2H), 2.14 – 2.02 (m, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.74 (m, 2H), 1.72 – 1.66 (m, 1H), 1.36 – 1.29 (m, 1H), 1.29 – 1.25 (m, 3H), 1.23 – 1.15 (m, 3H), 1.05 – 1.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.3, 144.6, 124.8, 43.8, 40.2, 35.8, 31.6, 26.4, 26.3, 17.7.
HRMS (ESI): calcd. for $C_{13}H_{19}O$ ($[M+H]^+$): 191.1430, found 191.1426.



2n

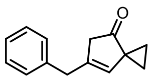
Run 1: Following the general procedure, 44.7 mg of **1n** was used, 72 h. After flash column

chromatography on silica gel (eluted with PE/EA, 50:1), 36.6 mg of **2n** was obtained in 73% yield.
Run 2: Following the general procedure, 44.9 mg of **1n** was used, 72 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 37.7 mg of **2n** was obtained in 75% yield.
Average yield: 74%
Pale yellow oil, TLC R_f = 0.2 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (t, J = 2.0 Hz, 1H), 4.30 (s, 2H), 2.98 (d, J = 2.0 Hz, 2H), 1.33 – 1.29 (m, 2H), 1.12 – 1.07 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.2, 138.7, 127.7, 62.6, 43.2, 35.9, 26.0, 18.5, 17.8, -5.2.
HRMS (ESI): calcd. for $C_{14}H_{25}O_2Si$ ($[M+H]^+$): 253.1618, found 253.1618.



2o

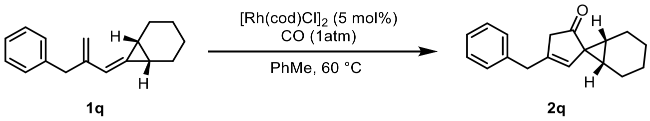
Run 1: Following the general procedure, 32.8 mg of **1o** was used, 72 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 22.9 mg of **2o** was obtained in 60% yield.
Run 2: Following the general procedure, 32.8 mg of **1o** was used, 72 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 23.3 mg of **2o** was obtained in 61% yield.
Average yield: 60%
Pale yellow oil, TLC R_f = 0.2 (PE/EA = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (t, J = 1.9 Hz, 1H), 2.91 (d, J = 1.9 Hz, 2H), 2.18 (t, J = 7.6 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.36 – 1.24 (m, 9H), 1.06 – 1.00 (m, 2H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 139.7, 126.7, 45.4, 35.9, 32.0, 31.8, 29.2, 27.4, 22.7, 17.6, 14.2.
HRMS (ESI): calcd. for $C_{13}H_{21}O$ ($[M+H]^+$): 193.1587, found 193.1585.



2p

Run 1: Following the general procedure, 34.0 mg of **1p** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 27.5 mg of **2p** was obtained in 69% yield.
Run 2: Following the general procedure, 34.1 mg of **1p** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 28.1 mg of **2p** was obtained in 71% yield.
Average yield: 70%
Yellow oil, TLC R_f = 0.2 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.28 – 7.18 (m, 3H), 5.37 (t, J = 1.9 Hz, 1H), 3.52 (s, 2H), 2.91 (d, J = 1.9 Hz, 2H), 1.32 – 1.25 (m, 2H), 1.09 – 1.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.5, 138.53, 138.49, 129.0, 128.7, 128.6, 126.5, 45.2, 38.8, 36.1, 17.7.
HRMS (ESI): calcd. for $C_{14}H_{15}O$ ($[M+H]^+$): 199.1117, found 199.1117.

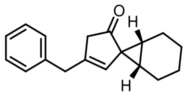
Procedure for substrate 1q:



1q **2q**

PhMe (2.6 mL) was added to a mixture of **1q** (0.13 mmol) and $[Rh(cod)Cl]_2$ (3.2 mg, 6.5 μmol). The resulting yellow solution was bubbled with CO (1 atm) for 10 min, and then stirred at 60 °C for

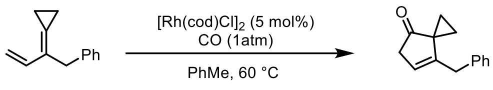
72 h under CO atmosphere. After cooling to room temperature, the solvent was removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, PE/EA = 20:1) to afford **2q**. Run 1: 29.1 mg of **1q** gave 18.6 mg of **2q**, 57% yield; Run 2: 29.3 mg of **1q** gave 18.5 mg of **2q**, 56% yield.
Average yield: 56%



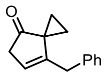
2q

Yellow oil, TLC R_f = 0.2 (PE/EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 5.73 (t, *J* = 1.8 Hz, 1H), 3.58 (s, 2H), 2.83 (d, *J* = 1.8 Hz, 2H), 1.98 – 1.86 (m, 2H), 1.75 – 1.67 (m, 2H), 1.59 – 1.50 (m, 2H), 1.40 – 1.26 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.1, 140.6, 138.7, 128.9, 128.7, 126.5, 124.6, 45.7, 44.7, 39.4, 28.6, 21.9, 20.2.
HRMS (ESI): calcd. for $C_{18}H_{21}O$ ($[M+H]^+$): 253.1587, found 253.1588.

Procedure for substrate 1r:



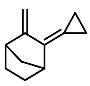
PhMe (4.0 mL) was added to a mixture of **1r** (0.20 mmol) and $[Rh(cod)Cl]_2$ (4.9 mg, 10 μmol). The resulting yellow solution was bubbled with CO (1 atm) for 10 min, during which the solution faded to pale yellow. The reaction mixture was then stirred at 60 °C for 30 h under CO atmosphere. After cooling to room temperature, the solvent was removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, PE/EA = 20:1) to afford **2r**. Run 1: 34.3 mg of **1r** gave 11.2 mg of **2r**, 28% yield; Run 2: 34.5 mg of **1r** gave 12.7 mg of **2r**, 32% yield.
Average yield: 30%



2r

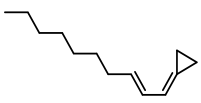
Yellow oil, TLC R_f = 0.3 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 5.63 (apparent p, *J* = 2.0 Hz, 1H), 3.20 (apparent q, *J* = 2.2 Hz, 2H), 2.99 (apparent q, *J* = 2.4 Hz, 2H), 1.23 – 1.18 (m, 2H), 1.13 – 1.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.0, 143.5, 138.0, 129.1, 128.6, 126.6, 120.8, 42.3, 37.3, 34.5, 15.9.
HRMS (ESI): calcd. for $C_{14}H_{15}O$ ($[M+H]^+$): 199.1117, found 199.1119.

Unsuccessful substrates for [4+1] cycloaddition:



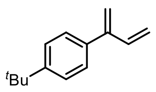
1s

A solution of **1s** (31.2 mg, 0.213 mmol) and $[Rh(cod)Cl]_2$ (5.4 mg, 11 μmol) in PhMe (4.0 mL) was bubbled with CO (1 atm) for 10 min. Stirring under CO atmosphere at 30 °C for 89 h led to a complex mixture.



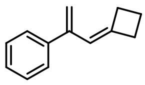
1t

A solution of **1t** (35.9 mg, 0.201 mmol) and $[Rh(cod)Cl]_2$ (5.0 mg, 10 μmol) in PhMe (4.0 mL) was bubbled with CO (1 atm) for 10 min. Stirring under CO atmosphere at 30 °C for 48 h led to recovery of the starting material. The same experiment performed at 60 °C resulted in full decomposition of **1t** after 24 h. No [4+1] product was detected in either case.



3

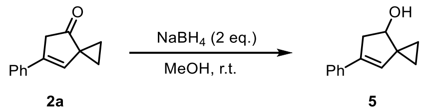
A solution of **3** (37.7 mg, 0.202 mmol) and $[Rh(cod)Cl]_2$ (5.1 mg, 10 μmol) in PhMe (4.0 mL) was bubbled with CO (1 atm) for 10 min. Stirring under CO atmosphere at 30 °C or 80 °C for 24 h led to recovery of the starting material. The same experiment performed at 100 °C for 48 h resulted in partial decomposition of **3**. However, no [4+1] product was detected.



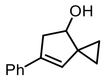
4

A solution of **4** (34.6 mg, 0.203 mmol) and $[Rh(cod)Cl]_2$ (5.0 mg, 10 μmol) in PhMe (4.0 mL) was bubbled with CO (1 atm) for 10 min. Stirring under CO atmosphere at 30 °C or 80 °C for 24 h led to recovery of the starting material. The same experiment performed at 100 °C for 40 h resulted in partial decomposition of **4**. However, no [4+1] product was detected.

IV. Derivatization of the [4+1] Cycloadduct

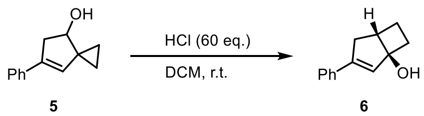


To a solution of **2a** (0.20 mmol) in MeOH (4 mL) was added $NaBH_4$ (14.9 mg, 0.39 mmol). The solution was stirred at room temperature for 2.5 h. MeOH was removed *in vacuo*, and the residue was taken up in DCM. The suspension was filtered through a short pad of silica gel and concentrated *in vacuo* to give **5**. Run 1: 37.1 mg of **2a** gave 35.2 mg of **5**, 94% yield; Run 2: 36.9 mg of **2a** gave 35.6 mg of **5**, 96% yield.
Average yield: 95%

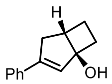


5

Colorless oil, TLC R_f = 0.2 (PE/EA = 5:1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 5.69 (t, *J* = 1.6 Hz, 1H), 4.04 (dd, *J* = 6.6, 2.0 Hz, 1H), 3.23 (ddd, *J* = 16.6, 6.6, 2.3 Hz, 1H), 2.78 (dt, *J* = 16.8, 1.7 Hz, 1H), 1.81 (br s, 1H), 1.12 – 1.06 (m, 1H), 0.93 – 0.87 (m, 1H), 0.86 – 0.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 136.1, 130.0, 128.5, 127.1, 125.2, 76.7, 43.2, 37.2, 13.5, 7.9.
HRMS (EI): calcd. for $C_{13}H_{14}O$ ($[M\cdot]^+$): 186.1039, found 186.1036.

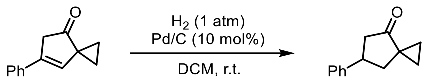


To a solution of **5** (0.19 mmol) in DCM (1 mL) was added 12 M HCl (1 mL, 12 mmol). The mixture was stirred at room temperature for 24 h, during which the system turned purple. The reaction mixture was quenched with saturated $NaHCO_3$ aq. (5 mL) and extracted with DCM (3×10 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was subjected to column chromatography (silica gel, PE/EA = 5:1) to give **6**. Run 1: 34.7 mg of **5** gave 26.9 mg of **6**, 77% yield; Run 2: 35.6 mg of **5** gave 27.5 mg of **6**, 77% yield.
Average yield: 77%



6

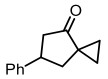
Yellow oil, TLC R_f = 0.2 (PE/EA = 5:1). This compound has the same R_f as **5**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.14 (apparent p, *J* = 1.1 Hz, 1H), 3.08 (ddd, *J* = 16.6, 6.9, 2.2 Hz, 1H), 2.78 (dt, *J* = 9.3, 7.1 Hz, 1H), 2.50 (dd, *J* = 16.7, 1.5 Hz, 1H), 2.39 – 2.28 (m, 2H), 2.10 (dtd, *J* = 11.6, 9.3, 4.0 Hz, 1H), 1.90 (br s, 1H), 1.19 (dtd, *J* = 11.6, 9.1, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 136.1, 128.5, 128.2, 128.2, 126.4, 86.7, 44.7, 39.5, 34.5, 20.2.
HRMS (EI): calcd. for $C_{13}H_{14}O$ ($[M\cdot]^+$): 186.1039, found 186.1036.



2a **7**

A mixture of **2a** (0.29 mmol) and 10% Pd/C (32.6 mg, containing 0.03 mmol of Pd) in DCM (5 mL) was stirred under an atmosphere of H_2 at room temperature for 2.5 h. The resulting mixture was filtered through a short pad of silica gel and eluted with EA. The filtrate was concentrated *in vacuo* to give **7**. Run 1: 53.9 mg of **2a** gave 51.9 mg of **7**, 95% yield; Run 2: 54.1 mg of **2a** gave 52.9 mg of **7**, 97% yield.

Average yield: 96%

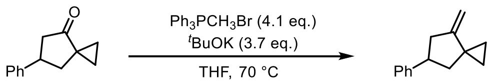


7

Colorless oil, TLC R_f = 0.3 (PE/EA = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 3.59 (tt, *J* = 10.6, 7.1 Hz, 1H), 2.80 (dd, *J* = 17.7, 7.5 Hz, 1H), 2.57 (dd, *J* = 17.7, 11.1 Hz, 1H), 2.35 (dd, *J* = 12.7, 10.1 Hz, 1H), 2.23 (dd, *J* = 12.7, 7.1 Hz, 1H), 1.40 – 1.30 (m, 1H), 1.27 – 1.17 (m, 1H), 1.00 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.2, 143.5, 128.7, 126.9, 126.7, 46.5, 40.5, 40.0, 30.2, 20.3, 15.9.

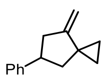
HRMS (ESI): calcd. for $C_{13}H_{15}O$ ($[M+H]^+$): 187.1117, found 187.1122.



7 **8**

To a stirred mixture of Ph_3PCH_3Br (390.6 mg, 1.1 mmol) and ^{t}BuOK (112.5 mg, 1.0 mmol) was added dry THF (10 mL) under N_2 protection. The resulting bright-yellow suspension was stirred at 70 °C for 2 h. **7** (0.27 mmol) was dissolved in dry THF (2 mL), and was added via syringe. The reaction mixture was further stirred at 70 °C for 1h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with EA (3×10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and subjected to column chromatography (silica gel, PE as eluent) to give **8**. Run 1: 49.6 mg of **7** gave 42.9 mg of **8**, 88% yield; Run 2: 56.2 mg of **7** gave 50.5 mg of **8**, 91% yield.

Average yield: 90%

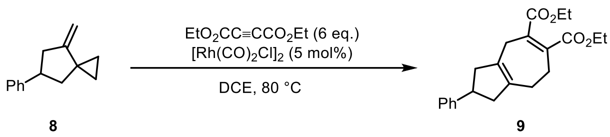


8

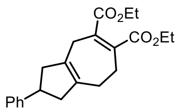
Colorless oil, TLC R_f = 0.9 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.23 – 7.18 (m, 1H), 4.63 (s, 1H), 4.32 (s, 1H), 3.34 (tt, *J* = 10.8, 6.6 Hz, 1H), 2.92 (dd, *J* = 15.8, 7.2 Hz, 1H), 2.65 (ddt, *J* = 16.2, 10.8, 2.9 Hz, 1H), 2.14 (t, *J* = 11.4 Hz, 1H), 1.88 (dd, *J* = 12.3, 6.6 Hz, 1H), 0.92 – 0.78 (m, 3H), 0.75 – 0.68 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 144.9, 128.5, 127.2, 126.2, 97.6, 44.4, 43.9, 42.8, 25.3, 20.8, 15.4.

HRMS (EI): calcd. for $C_{14}H_{16}$ ($[M\cdot]^+$): 184.1247, found 184.1246.

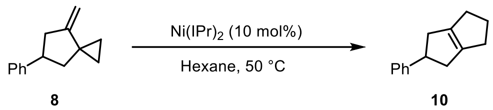


Following a modified procedure from Wender,[16] to a solution of **8** (0.10 mmol) in DCE (2 mL) was added $[Rh(CO)_2Cl]_2$ (2.1 mg, 5 µmol). The solution was bubbled with N_2 for 1 min, and then diethyl acetylenedicarboxylate (104.6 mg, 0.61 mmol) was added via syringe. The resulting mixture was stirred at 80 °C for 3 h. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, PE/EA = 20:1) to give **9**. Run 1: 18.4 mg of **8** gave 21.1 mg of **9**, 60% yield; Run 2: 18.4 mg of **8** gave 22.7 mg of **9**, 64% yield.
Average yield: 62%

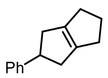


9

Colorless oil, TLC R_f = 0.1 (PE/EA = 20:1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.35 – 7.08 (m, 5H), 4.19 (q, *J* = 7.3 Hz, 2H), 4.17 (q, *J* = 7.3 Hz, 2H), 3.38 (ddd, *J* = 16.1, 9.0, 7.1 Hz, 1H), 3.15 (s, 2H), 2.91 – 2.59 (m, 4H), 2.58 – 2.47 (m, 1H), 2.46 – 2.34 (m, 1H), 2.31 – 2.14 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.9, 168.3, 147.8, 139.5, 138.5, 135.4, 128.9, 128.7, 127.2, 126.1, 61.5, 61.4, 48.3, 47.8, 41.5, 29.1, 28.0, 27.0, 14.3, 14.2.
HRMS (ESI): calcd. for $C_{22}H_{27}O_4$ ($[M+H]^+$): 355.1904, found 355.1898.



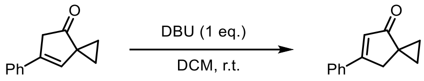
Note: This reaction is highly air- and water-sensitive, and Louie's original procedure[17] resulted in no conversion. We found it necessary to add Zn powder to prevent catalyst deactivation.
Preparation of the $Ni(IPr)_2$ catalyst: In a glovebox, superdry hexane (3.0 mL) was added to a mixture of $Ni(cod)_2$ (8.3 mg, 30 µmol), IPr (23.3 mg, 60 µmol) and Zn powder (3.1 mg, 47 µmol). The resulting black mixture was stirred inside the glovebox for 5 h, and the supernatant was suitable for use in the cycloisomerization.
Cycloisomerization of 8: A reaction vessel equipped with a high-vacuum valve was charged with **8** (0.10 mmol). The vessel was degassed under vacuum for 20 min, refilled with N_2, and moved into the glovebox. The above $Ni(IPr)_2$ solution (1.0 mL, containing 10 µmol of $Ni(IPr)_2$) was added, and the reaction vessel was properly sealed before being moved out of the glovebox. The resulting black solution was stirred at 50 °C for 24 h. After cooling to room temperature, the reaction mixture was directly subjected to column chromatography (silica gel, PE as eluent) to give **10**. Run 1: 17.9 mg of **8** gave 16.3 mg of **10**, 91% yield; Run 2: 18.4 mg of **8** gave 17.3 mg of **10**, 94% yield.
Average yield: 92%



10

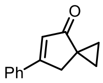
Colorless oil, TLC R_f = 0.4 (100% PE)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 – 7.23 (m, 4H), 7.19 – 7.14 (m, 1H), 3.85 (tt, *J* = 8.9, 6.4 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.31 – 2.19 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 144.9, 128.5, 127.0, 125.9, 49.3, 38.7, 29.6, 28.3.
HRMS (EI): calcd. for $C_{14}H_{16}$ ($[M\cdot]^+$): 184.1247, found 184.1243.



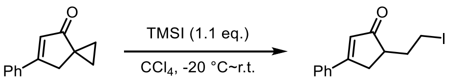
2a **11**

To **2a** (0.50 mmol) was added a solution of DBU (77.4 mg, 0.50 mmol) in DCM (4 mL). The resulting mixture was stirred at room temperature for 20 min and subjected to column chromatography (silica gel, PE/EA = 5:1) to give **11**. Run 1: 92.6 mg of **2a** gave 91.1 mg of **11**, 98% yield; Run 2: 93.1 mg of **2a** gave 92.8 mg of **11**, 100% yield.
Average yield: Quantitative



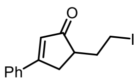
11

White solid, m.p. 108 ~ 109 °C, TLC R_f = 0.4 (PE/EA = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.47 – 7.42 (m, 3H), 6.69 (t, *J* = 1.7 Hz, 1H), 3.14 (d, *J* = 1.7 Hz, 2H), 1.38 – 1.32 (m, 2H), 1.12 – 1.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 171.6, 134.3, 131.1, 129.0, 127.5, 126.7, 38.9, 28.8, 16.8.
HRMS (ESI): calcd. for $C_{13}H_{13}O$ ($[M+H]^+$): 185.0961, found 185.0960.



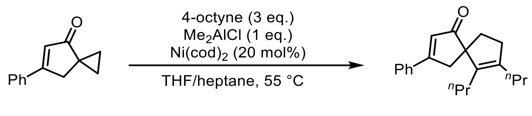
11 **12**

Following a procedure from Miller,[18] to a stirred solution of **11** (0.25 mmol) in CCl_4 (1 mL) was added iodotrimethylsilane (40 µL, 0.28 mmol) at -20 °C. After being stirred at that temperature for 1 h, the reaction mixture was warmed to room temperature and further stirred for 4 h. The solution was diluted with Et_2O (20 mL) and washed with saturated Na_2SO_3 aq. (10 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated in *vacuo* to give **12**. Run 1: 45.4 mg of **11** gave 74.8 mg of **12**, 98% yield; Run 2: 45.6 mg of **11** gave 76.7 mg of **12**, 100% yield.
Average yield: Quantitative

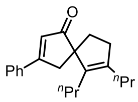


12

Yellow solid, m.p. 55~56 °C, TLC R_f = 0.4 (PE/EA = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.49 – 7.43 (m, 3H), 6.55 (s, 1H), 3.49 – 3.40 (m, 1H), 3.38 – 3.27 (m, 2H), 2.78 – 2.65 (m, 2H), 2.49 – 2.34 (m, 1H), 2.01 – 1.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 172.3, 133.9, 131.6, 129.1, 127.0, 126.7, 47.0, 35.7, 35.1, 4.0.
HRMS (ESI): calcd. for $C_{13}H_{14}IO$ ($[M+H]^+$): 313.0084, found 313.0082.

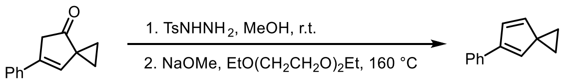


Following a modified procedure from Ogoshi,[19] under N_2 protection, to a solution of **11** (0.24 mmol) in dry THF (0.25 mL) was added consecutively 4-octyne (95.1 mg, 0.86 mmol) and Me_2AlCl (1.0 M in heptane, 0.25 mL, 0.25 mmol) via syringe. The reaction vessel was then moved into a glovebox. $Ni(cod)_2$ (13.8 mg, 50 µmol) was added, and the reaction vessel was properly sealed before being moved out of the glovebox. The resulting brown solution was stirred at 55 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with 1 M HCl (8 mL) and extracted with Et_2O (3×10 mL). The combined organic phase was washed with saturated $NaHCO_3$ aq. and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, PE/EA = 10:1) to give **13** and the unreacted starting material. Run 1: 44.9 mg of **11** gave 42.2 mg of **13** (59% yield) and 7.7 mg of **11** (17% recovery); Run 2: 45.4 mg of **11** gave 41.0 mg of **13** (57% yield) and 6.6 mg of **11** (15% recovery).
Note: We have attempted to elongate the reaction time to 48 h, but the conversion of **11** was not improved. However, it was possible to fully convert **11** in 24 h when $Ni(cod)_2$ was increased to 50 mol%. Unfortunately, the yield of **13** was even lower than using 20 mol% of $Ni(cod)_2$.
Average yield: 58%



13

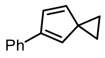
Yellow oil, TLC R_f = 0.2 (PE/EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.50 – 7.43 (m, 3H), 6.59 (apparent t, *J* = 1.8 Hz, 1H), 3.13 (dd, *J* = 18.4, 1.8 Hz, 1H), 2.98 (dd, *J* = 18.4, 1.8 Hz, 1H), 2.48 – 2.36 (m, 2H), 2.32 – 2.23 (m, 1H), 2.16 – 2.07 (m, 2H), 2.00 – 1.91 (m, 1H), 1.83 – 1.71 (m, 2H), 1.55 – 1.41 (m, 2H), 1.32 – 1.19 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 171.7, 141.3, 136.8, 134.2, 131.3, 129.0, 127.0, 126.7, 64.5, 43.0, 36.7, 33.9, 31.1, 28.5, 22.9, 21.4, 14.7, 14.3.
HRMS (ESI): calcd. for $C_{21}H_{27}O$ ($[M+H]^+$): 295.2056, found 295.2061.



Preparation of the tosylhydrazone: To a solution of **2a** (148.1 mg, 0.804 mmol) in MeOH (4 mL) was added $TsNHNH_2$ (169.6 mg, 0.911 mmol). The solution was stirred at room temperature for 48 h. The solvent was removed *in vacuo*, and the residue was purified by column chromatrography (DCM as eluent) to give the corresponding tosylhydrazone (280.2 mg, 99% yield) as a yellow solid.
Bamford-Stevens olefination: To a mixture of the above tosylhydrazone (0.20 mmol) and NaOMe (76.3 mg, 1.41 mmol) was added diethylene glycol diethyl ether (1.0 mL) under N_2 protection. The mixture was stirred at room temperature for 3 min, and then at 160 °C for 20 min. After cooling to room temperature, the reaction mixture was quenched with water (10 mL) and extracted with PE (3×10 mL). The combined organic phase was washed with water and brine, dried over Na_2SO_4, and

concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, 50:1 PE/EA) to give **14**. Run 1: 70.3 mg of tosylhydrazone gave 19.3 mg of **14**, 58% yield; Run 2: 70.7 mg of tosylhydrazone gave 20.4 mg of **14**, 60% yield.

Average yield: 59%



14

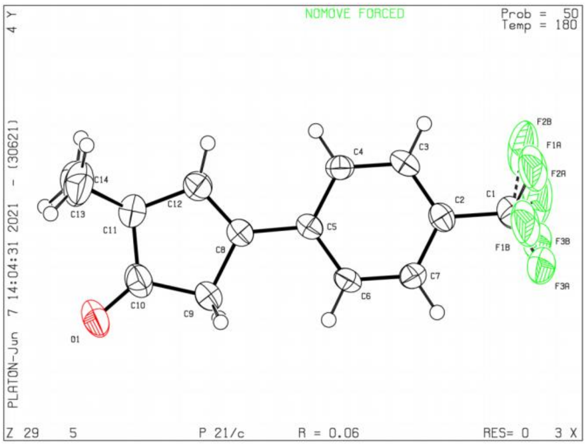
White solid, m.p. 55~56 °C, TLC R_f = 0.2 (100% PE)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.34 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.26 – 7.17 (m, 1H), 6.89 (dd, *J* = 5.2, 1.8 Hz, 1H), 6.34 (apparent t, *J* = 2.0 Hz, 1H), 6.23 (dd, *J* = 5.2, 2.2 Hz, 1H), 1.69 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.8, 136.3, 133.4, 128.9, 128.7, 126.9, 125.8, 38.8, 13.9.

HRMS (EI): calcd. for $C_{13}H_{12}$ ($[M\cdot]^+$): 168.0934, found 168.0930.

V. X-Ray Crystallography

Crystallographic data of compound **2i**



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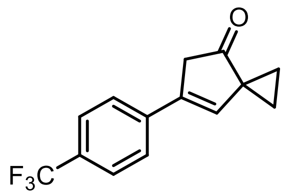


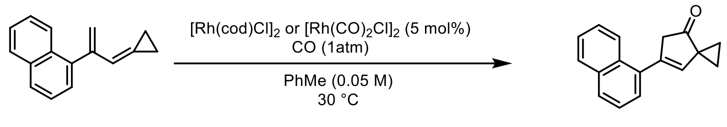
2i

CCDC number: 2250702

Table S1 Crystal data and structure refinement for compound **2i**

Crystal data	
Chemical formula	$C_{14}H_{11}F_3O$
M_r	252.23
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, *b*, *c* (Å)	11.2755 (8), 14.7009 (9), 7.0873 (5)
β (°)	94.179 (6)
V (Å^3)	1171.67 (14)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.12
Crystal size (mm)	0.45 × 0.18 × 0.02
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.165, 1.05
No. of reflections	4599
No. of parameters	174
No. of restraints	21
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.23

VI. NMR Monitoring of Reaction Progress



1k **2k**

Substrate **1k** (51.8 mg, 0.25 mmol), Rh catalyst (0.013 mmol, 6.5 mg for $[Rh(cod)Cl]_2$ and 4.9 mg for $[Rh(CO)_2Cl]_2$) and internal standard 1,3,5-trimethoxybenzene (6.9 mg, 0.041 mmol) were dissolved in PhMe (5.0 mL). The solution was bubbled with CO (1 atm) for 3 min, and then stirred at 30 °C under CO atmosphere. Every 1 h, 0.6 mL of crude reaction mixture was withdrawn from the reaction system and quickly concentrated by rotary evaporation. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR. As the substrate is unstable, we used the product to determine the kinetic profile. The concentration of product **2k** was determined by the integral of the alkenyl hydrogen (δ 6.03) compared to that of the aromatic hydrogens (δ 6.12) of 1,3,5-trimethoxybenzene.

Table S2 Concentration of **2k** vs. time, using $[Rh(CO)_2Cl]_2$ and $[Rh(cod)Cl]_2$ as catalyst

t/h	[**2k**]/M	
	$[Rh(CO)_2Cl]_2$	$[Rh(cod)Cl]_2$
1	0.00388	0.00369
2	0.00560	0.00574
3	0.00758	0.00796
4	0.00966	0.00976
5	0.01155	0.01157
6	0.01318	0.01337

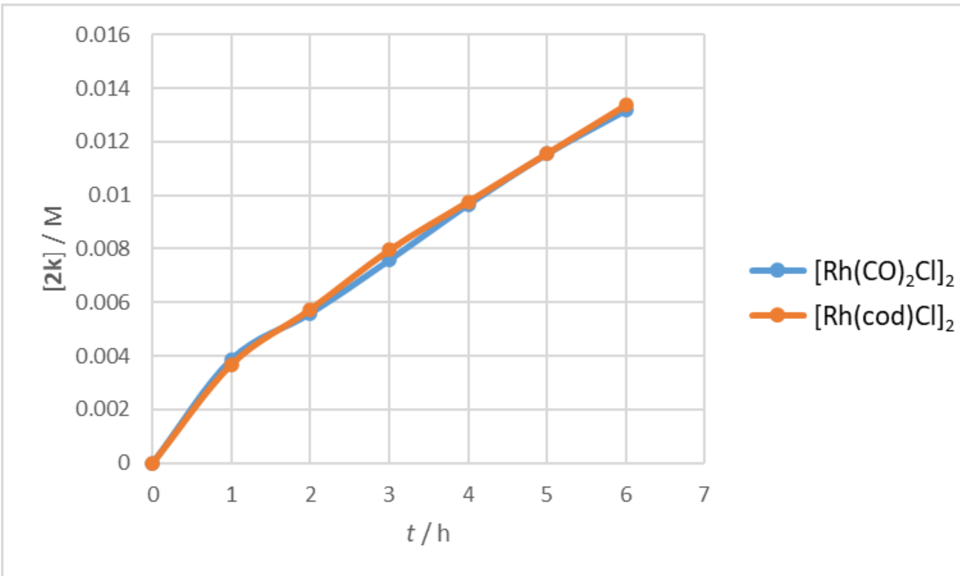


Figure S1 Concentration of **2k** vs. time, using $[Rh(CO)_2Cl]_2$ and $[Rh(cod)Cl]_2$ as catalyst

VII. DFT Calculations

Gibbs energy profile for [4+1] cycloaddition of cyclobutyl-capped diene

Below is the computed free energy surface (Figure S2) for cyclobutyl-capped diene and CO, showing that the transition state for oxidative cyclization is just 2.4 kcal/mol lower than that in the reaction of common diene, and the overall activation free energy for this [4+1] reaction is 1.7 kcal/mol higher than that for the [4+1] reaction of common diene and CO, explaining why cyclobutyl-capped diene cannot participate in the [4+1] reaction.

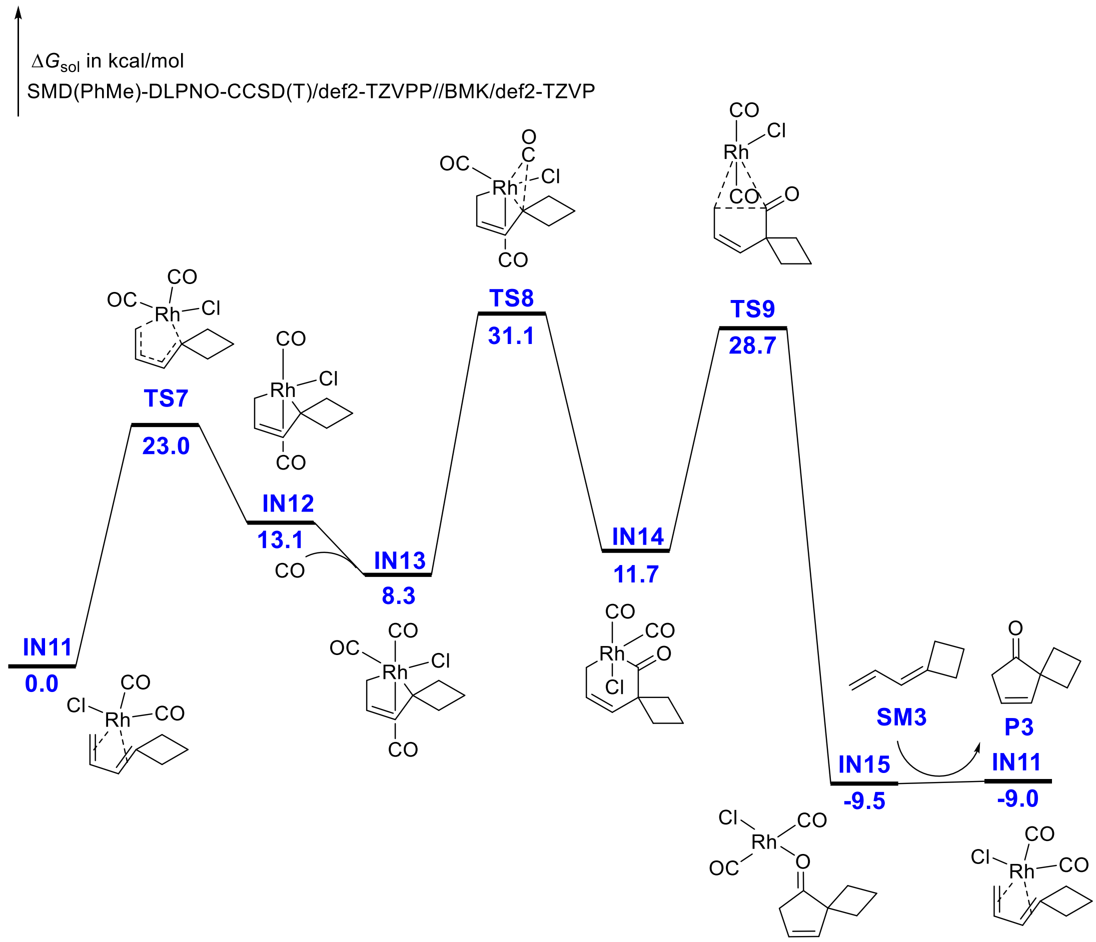


Figure S2 Gibbs energy profile for [4+1] cycloaddition of cyclobutyl-capped diene and CO

It is possible that for CP-capped dienes, there is a donor effect due to the CP group with respect to the diene. It will be helpful to compare the Gibbs energy profile of CP-capped diene (Figure 3a in the main text) and cyclobutyl-capped diene (Figure S2). Cyclobutyl-capped diene could have the donor effect if CP-capped diene has. But the activation free energy (31.1 kcal/mol) for cyclobutyl-capped diene is much higher than that for CP-capped diene, and even higher than unsubstituted common diene (29.4 kcal/mol, Figure 3b in the main text). Therefore, we conclude the donor effect is not the key for making CP-capped diene reactive in [4+1] cycloaddition.

Gibbs energy profile for [4+1] cycloaddition of terminally-substituted CP-capped diene and CO

Here we computed the free energy surface for the [4+1] reaction of substrate with a methyl group in the terminal position of the CP-capped diene (Figure S3). The computed activation free energy here is only 1.0 kcal/mol higher than that for CP-capped diene shown in Figure 3 of the main text. This [4+1] reaction could happen for **1t** in terms of the computed results, but experimentally it failed. We hypothesized that some side reaction with lower activation free energy could happen for **1t**. It was interesting to find that, the yellow solution of catalyst and every successful substrate became nearly colorless when bubbled with CO, while the color of the solution of **1t** with catalyst stayed unchanged in the presence of CO, implying that **1t** and catalyst cannot easily form the reactive species (maybe this is the steric reason, due to the presence of an additional substituent in **1t** compared to the successful substrates).

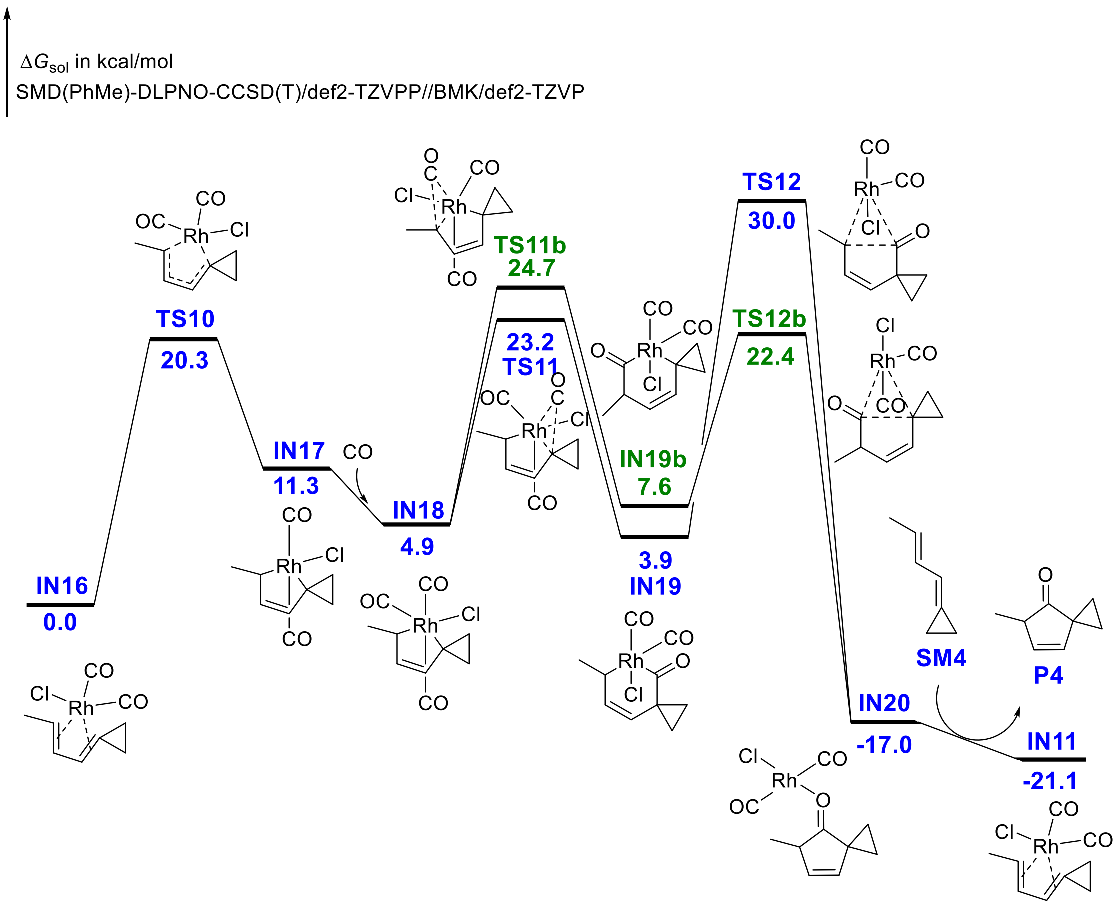


Figure S3 Gibbs energy profile for [4+1] cycloaddition of terminally-substituted CP-capped diene and CO

Energy data

Table S3 Computed energies (in a. u.) of all stationary points

	E [a]	TCH [a]	TCG [a]	E_{PhMe} [b]	E_{DLPNO} [c]	Final G [d]
CO	-113.309610	0.008513	-0.013900	-113.305142	-113.157893	-113.168920 [e]
H_2	-1.168278	0.013526	-0.001262	N/A	-1.172386	-1.173648 [f]
IN1	-1030.190245	0.154742	0.098925	-1030.202040	-1029.493601	-1029.406471
IN2	-1030.168506	0.154179	0.096690	-1030.182686	-1029.472784	-1029.390273

IN3	-1143.506101	0.165688	0.104617	-1143.516620	-1142.664690	-1142.570592
IN4	-1143.506400	0.166917	0.106510	-1143.521405	-1142.661079	-1142.569574
IN4b	-1143.500962	0.167161	0.106871	-1143.515926	-1142.656513	-1142.564607
IN5	-1143.551909	0.168023	0.106914	-1143.565129	-1142.697614	-1142.603921
IN6	-952.841373	0.119335	0.068039	-952.850288	-952.259888	-952.200763
IN7	-952.805923	0.118597	0.064151	-952.818551	-952.224130	-952.172607
IN8	-1066.143798	0.129875	0.071849	-1066.153172	-1065.416319	-1065.353844
IN9	-1066.145600	0.131254	0.075135	-1066.158592	-1065.416096	-1065.353953
IN10	-1066.185696	0.132281	0.075072	-1066.197499	-1065.446754	-1065.383485
IN11	-1069.501769	0.186071	0.128217	-1069.514605	-1068.747241	-1068.631859
IN12	-1069.474152	0.185005	0.124816	-1069.489171	-1068.720782	-1068.610985
IN13	-1182.806960	0.196081	0.131646	-1182.818145	-1181.907983	-1181.787523
IN14	-1182.806793	0.197929	0.135532	-1182.821087	-1181.903422	-1181.782184
IN15	-1182.852642	0.199117	0.135582	-1182.865768	-1181.938395	-1181.815939
IN16	-1069.489281	0.184566	0.125433	-1069.501559	-1068.738006	-1068.624852
IN17	-1069.464661	0.183919	0.122804	-1069.479769	-1068.714536	-1068.606840
IN18	-1182.800658	0.195518	0.131557	-1182.812538	-1181.905630	-1181.785953
IN19	-1182.802707	0.196463	0.132282	-1182.818461	-1181.904059	-1181.787530
IN19b	-1182.799601	0.196846	0.133667	-1182.814708	-1181.900177	-1181.781617
IN20	-1182.850420	0.197974	0.133767	-1182.863778	-1181.941294	-1181.820886
IN21	-990.900525	0.124842	0.071192	-990.909836	-990.260663	-990.198781
IN22	-990.886686	0.124445	0.068360	-990.898183	-990.247047	-990.190183
IN23	-1104.222274	0.135617	0.075311	-1104.231526	-1103.437142	-1103.371083
IN24	-1104.219477	0.137277	0.078933	-1104.233041	-1103.432239	-1103.366871
IN25	-1104.255666	0.138217	0.079694	-1104.268125	-1103.462716	-1103.395481
TS1	-1030.151879	0.153401	0.098592	-1030.164259	-1029.458558	-1029.372346
TS2	-1143.480761	0.164793	0.105592	-1143.493381	-1142.633888	-1142.540916
TS2b	-1143.473215	0.164199	0.104243	-1143.488207	-1142.626866	-1142.537615
TS3	-1143.479097	0.164719	0.105678	-1143.494241	-1142.628151	-1142.537618
TS3b	-1143.478881	0.165703	0.108008	-1143.493445	-1142.633603	-1142.540159
TS4	-952.796362	0.117902	0.067502	-952.806397	-952.217778	-952.160311
TS5	-1066.115871	0.128634	0.072930	-1066.128179	-1065.383488	-1065.322866
TS6	-1066.120149	0.130016	0.076380	-1066.132300	-1065.387584	-1065.323354
TS7	-1069.460250	0.184260	0.128240	-1069.473729	-1068.710015	-1068.595255
TS8	-1182.776680	0.195789	0.134496	-1182.790833	-1181.871518	-1181.751175
TS9	-1182.784680	0.196165	0.136123	-1182.798300	-1181.877602	-1181.755099
TS10	-1069.450785	0.183010	0.125541	-1069.464955	-1068.703829	-1068.592459
TS11	-1182.775399	0.194522	0.132310	-1182.789649	-1181.874913	-1181.756854
TS11b	-1182.771447	0.194176	0.131152	-1182.785191	-1181.871817	-1181.754409
TS12	-1182.767632	0.195199	0.133680	-1182.781745	-1181.865520	-1181.745953
TS12b	-1182.777576	0.195258	0.133976	-1182.792177	-1181.877381	-1181.758006
TS13	-990.871398	0.123617	0.071028	-990.881495	-990.234525	-990.173594
TS14	-1104.192615	0.134535	0.076809	-1104.204786	-1103.402845	-1103.338206

TS15	-1104.193640	0.135426	0.078719	-1104.207544	-1103.400897	-1103.336082
SM1	-233.271422	0.126544	0.089399	-233.279319	-232.924288	-232.842786 -232.834889 [f]
SM2	-155.925623	0.091282	0.059264	-155.929512	-155.697375	-155.642000
SM2'	-234.527097	0.150762	0.111241	N/A	-234.184952	-234.073711 [f]
SM3	-272.592362	0.157620	0.117901	-272.600672	-272.184662	-272.075071 -272.066761 [f]
SM4	-272.569795	0.155359	0.115440	-272.579305	-272.165350	-272.059420
SM5	-193.979731	0.096419	0.061617	-193.984845	-193.690578	-193.634076
P1	-346.637712	0.139725	0.100819	-346.649059	-346.134993	-346.045521
P2	-269.272753	0.104049	0.069104	-269.282584	-268.886099	-268.826826
P3	-385.939128	0.170649	0.129177	-385.950515	-385.376105	-385.258316
P4	-385.936013	0.169592	0.127204	-385.947512	-385.377654	-385.261949
P5	-307.349549	0.110172	0.073541	-307.359059	-306.904660	-306.840629
PH1	-234.512496	0.150961	0.112656	N/A	-234.168231	-234.055575 [f]
PH2'	-235.749217	0.174582	0.133926	N/A	-235.409484	-235.275558 [f]
PH3	-273.817261	0.181891	0.141166	N/A	-273.412306	-273.271140 [f]
PH5	-195.227397	0.121040	0.085216	N/A	-194.941560	-194.856344 [f]

[a] Computed at BMK/def2-TZVP level

[b] Single-point energy computed at BMK-SMD(PhMe)/def2-TZVP level

[c] Single-point energy computed at DLPNO-CCSD(T)/def2-TZVPP level

[d] Unless otherwise stated, final $G = E_{DLPNO} + TCG + E_{PhMe} - E$

[e] For CO, the standard state is shifted to 7.5 mM, thus final $G = E_{DLPNO} + TCG + E_{PhMe} - E + RT\ln(0.0075\times24.6)$

[f] In gas phase, final $G = E_{DLPNO} + TCG$

Cartesian coordinates of all stationary points

CO

C	0.000000	0.000000	-0.640016
O	0.000000	0.000000	0.480012

H_2

H	0.000000	0.000000	0.370715
H	0.000000	0.000000	-0.370715

IN1

Rh	-0.224863	-0.048559	-0.013050
Cl	-2.583755	-0.472633	-0.519274
C	-0.643529	1.861048	-0.465784
O	-0.915842	2.916065	-0.729515
C	-0.560802	-0.001647	1.908838
O	-0.745408	-0.021731	3.017314
C	1.337870	-0.428568	-1.494052
C	1.832752	0.101953	-0.238355
C	2.912277	1.114473	0.011897
H	3.588920	1.359717	-0.799297
H	2.706325	1.934663	0.688538
C	3.006675	-0.294535	0.624777
H	2.856518	-0.387192	1.693494
H	3.742145	-0.973488	0.209319
H	1.417746	0.105161	-2.434677
C	0.529545	-1.578234	-1.386728
C	0.318861	-2.108018	-0.067293
H	1.178943	-2.251313	0.575955
H	-0.478568	-2.832576	0.045619
H	-0.081255	-1.888544	-2.226207

IN2

Rh	-0.327403	-0.000523	0.496363
C	-0.234284	-1.977582	0.483797
O	-0.143397	-3.092487	0.460246
C	-0.242488	1.977521	0.483344
O	-0.156709	3.092808	0.459666
Cl	-2.566825	-0.005033	-0.358957
C	1.423370	0.002403	1.656013
H	1.446868	-0.870097	2.318521
H	1.443646	0.874271	2.319421
C	2.611435	0.004821	0.730471
H	3.620306	0.006998	1.134611
C	2.387908	0.004148	-0.580022
H	3.186213	0.005459	-1.319226
C	0.980595	0.001463	-1.055319
C	0.614849	0.764250	-2.326308
C	0.617585	-0.762511	-2.326302
H	-0.358860	1.235475	-2.382988
H	-0.354525	-1.237025	-2.382989
H	1.414088	1.289089	-2.837329
H	1.418457	-1.284737	-2.837441

IN3

Rh	0.389471	-0.163402	0.000421
C	0.137952	-0.135497	1.949564
O	-0.081771	-0.097585	3.046046
C	2.394219	-0.616283	0.001732
O	3.493633	-0.823064	0.001583
Cl	1.080645	2.202570	-0.001519
C	0.141032	-0.140040	-1.948577
O	-0.076749	-0.104672	-3.045548
C	-0.237200	-2.178053	0.002878
H	0.159241	-2.704753	0.876914
H	0.160988	-2.707735	-0.868516
C	-1.744299	-2.190182	0.001571
H	-2.267376	-3.143016	0.002312
C	-2.408755	-1.036818	-0.000279
H	-3.496821	-1.002677	-0.000924
C	-1.658190	0.245557	-0.001339
C	-2.271908	1.432621	-0.759543
C	-2.272732	1.434544	0.753134
H	-1.597876	2.128966	-1.243172
H	-1.598934	2.131914	1.235650
H	-3.208302	1.255265	-1.276399
H	-3.209718	1.258898	1.269500

IN4

Rh	-0.797176	0.430320	0.006909
Cl	-1.768561	-0.431149	1.937414
C	-0.129400	1.380683	-1.508210
O	0.248431	1.974938	-2.385936
C	0.664354	-0.918005	-0.231438
O	0.306241	-1.998101	-0.582764
C	-2.202367	-0.882992	-0.997040
O	-2.958970	-1.590826	-1.414318
C	2.552178	0.797341	0.359569
C	2.103296	-0.580291	0.035043
C	2.879109	-1.758338	0.693192
H	3.643558	-1.464674	1.400184
H	2.283836	-2.620704	0.962591
C	3.086460	-1.476904	-0.759723
H	2.639758	-2.157946	-1.471222
H	4.003301	-0.993766	-1.071911
H	3.613123	0.969501	0.206101
C	1.801434	1.793998	0.830284
C	0.344895	1.704073	1.159554
H	-0.120962	2.694770	1.101143
H	0.210042	1.350671	2.185450
H	2.300428	2.741817	1.017483

IN4b

Rh	-0.385324	0.159520	-0.347203
Cl	-0.881192	2.006792	0.989826
C	0.093021	-1.270249	-1.531604
O	0.415217	-2.091981	-2.226837
C	-0.423466	-1.154339	1.172348
O	-1.354578	-1.874590	1.289045
C	2.471640	-0.642879	0.364075
C	1.659431	0.440067	-0.249002
C	2.277613	1.158098	-1.461133
H	3.224026	0.790850	-1.844523
H	1.611643	1.544637	-2.226706
C	2.250576	1.852905	-0.114127

H	1.564525	2.676709	0.027969
H	3.186427	1.939130	0.425562
H	3.445323	-0.856021	-0.074086
C	2.080968	-1.343929	1.429044
C	0.765179	-1.092994	2.132605
H	0.742694	-0.087405	2.567598
H	0.575441	-1.827248	2.915949
H	2.716231	-2.119558	1.838813
C	-2.525203	0.044712	-0.533418
O	-3.641267	0.053654	-0.572985

IN5

Rh	-1.351902	0.110961	-0.088359
C	-3.164015	-0.296881	0.080336
O	-4.254062	-0.570513	0.180782
C	-1.649586	1.899408	0.434209
O	-1.821963	2.973843	0.746303
Cl	-0.939386	-2.094017	-0.742165
O	0.750677	0.520305	-0.341907
C	1.709702	0.000211	0.201950
C	3.118855	0.258235	-0.179816
C	3.933751	-0.524934	0.785084
C	3.157901	-1.201206	1.633661
C	1.688540	-0.980150	1.357234
H	1.127419	-0.556355	2.197306
H	1.148706	-1.880766	1.041738
H	3.512699	-1.848815	2.423406
H	5.015802	-0.531400	0.773403
C	3.499719	1.628064	-0.774166
C	3.448412	0.438836	-1.679479
H	4.377421	-0.006442	-2.010706
H	2.606253	0.344215	-2.353293
H	4.465295	2.016647	-0.477530
H	2.694649	2.349394	-0.836850

IN6

Rh	0.097435	0.006397	-0.096255
Cl	-1.399462	-0.421378	1.778877
C	-1.079832	1.591663	-0.443317
O	-1.759649	2.469730	-0.599581
C	-0.796412	-1.311177	-1.235765
O	-1.278775	-2.101727	-1.872293
C	1.906078	0.016234	1.103519
C	1.605521	-1.308010	0.631836
H	1.845108	0.272820	2.153915
C	1.993050	1.039125	0.133759
C	1.767431	0.652002	-1.242581
H	2.302830	-0.204009	-1.637944
H	1.655430	1.456654	-1.960535
H	2.057182	2.074691	0.445256
H	1.305856	-2.033434	1.378515
H	2.172262	-1.714212	-0.198368

IN7

Rh	-0.236020	-0.003630	-0.229184
C	-0.140050	-1.971938	-0.206684
O	-0.051728	-3.087216	-0.173228
C	-0.172834	1.972931	-0.207381
O	-0.105516	3.089447	-0.174286
Cl	-2.550408	-0.016530	0.327385
C	0.893135	0.004903	1.491817
H	0.611135	-0.874830	2.076984
H	0.593544	0.878563	2.077380
C	2.356841	0.019262	1.149592
H	3.083519	0.026813	1.958372
C	2.714126	0.021720	-0.128874
H	3.760395	0.031452	-0.424959
C	1.635537	0.010374	-1.179630
H	1.725105	0.882142	-1.837547
H	1.741579	-0.861125	-1.835397

IN8

Rh	0.124472	-0.000384	0.073100
C	-0.058498	-1.949141	-0.061569
O	-0.209424	-3.050839	-0.190064
C	-0.057699	1.949171	-0.061891
O	-0.208270	3.050917	-0.190103
Cl	1.842857	0.000412	-1.682500
C	1.651784	-0.000243	1.446891
O	2.512220	-0.000283	2.161845
C	-1.456505	-0.000805	-1.321681
H	-1.374163	-0.867895	-1.982415
H	-1.372579	0.865584	-1.983139
C	-2.749841	0.000630	-0.552747

H	-3.689327	0.000850	-1.100976
C	-2.732020	0.001455	0.776544
H	-3.655884	0.002522	1.350764
C	-1.416702	0.000574	1.513413
H	-1.337897	0.872449	2.170810
H	-1.339266	-0.871452	2.170769

IN9

Rh	0.327398	0.105077	-0.449170
Cl	1.299573	-2.011188	-0.502140
C	-0.502233	1.823459	-0.580711
O	-1.009932	2.821826	-0.682013
C	-0.396765	-0.076547	1.421736
O	0.161342	0.464396	2.311590
C	-2.676396	-0.297230	-0.556744
C	-1.422030	-0.658311	-1.286765
H	-3.511499	0.116806	-1.114863
C	-2.793979	-0.457550	0.763275
C	-1.637675	-0.976104	1.582384
H	-1.322323	-1.970907	1.248024
H	-1.863498	-1.009705	2.648053
H	-3.702630	-0.187771	1.286712
C	2.250011	0.733534	0.290415
O	3.269585	0.970240	0.680045
H	-1.463693	-0.347161	-2.334436
H	-1.255585	-1.738729	-1.262948

IN10

Rh	-1.023153	0.081199	-0.133060
C	-2.736004	-0.466769	0.365119
O	-3.761312	-0.824526	0.670404
C	-1.475078	1.897194	0.116230
O	-1.743573	2.986518	0.264819
Cl	-0.425418	-2.154136	-0.455549
O	0.972830	0.639422	-0.747339
C	2.037348	0.324160	-0.258478
C	2.251649	-0.428608	1.038760
C	3.753571	-0.408816	1.184695
C	4.359263	0.176054	0.152871
C	3.378439	0.669195	-0.883380
H	3.465732	0.158384	-1.848824
H	3.434639	1.743198	-1.086101
H	5.429455	0.289374	0.043250
H	4.260734	-0.841577	2.036597
H	1.819191	-1.431645	0.937450
H	1.705535	0.062840	1.851685

IN11

C	-0.034618	2.124319	-0.360726
C	0.221353	1.414738	-1.584626
H	0.792803	2.440852	0.259786
H	-0.888774	2.790952	-0.360993
H	-0.406780	1.557916	-2.455828
C	1.090806	0.304065	-1.531464
C	1.662317	-0.027871	-0.236275
H	1.171915	-0.360446	-2.385550
C	2.577584	-1.255776	-0.089877
H	2.657023	-1.920108	-0.953171
H	2.332037	-1.847555	0.793447
C	2.720267	0.838935	0.493653
H	2.516326	0.925025	1.562133
H	2.927934	1.826322	0.083418
C	3.754040	-0.280611	0.188024
H	4.315895	-0.063131	-0.720585
H	4.446118	-0.549245	0.985447
Rh	-0.435309	0.059955	-0.014535
C	-0.725760	0.237560	1.910477
O	-0.884691	0.386026	3.013798
C	-0.769944	-1.901397	-0.208488
O	-1.009733	-2.990268	-0.331470
Cl	-2.829204	0.271271	-0.535107

IN12

C	0.170059	-0.000797	2.264292
C	1.665924	-0.000648	2.107122
H	-0.157590	-0.871890	2.842659
H	-0.157717	0.869828	2.843288
H	2.307485	-0.000920	2.985342
C	2.179820	-0.000172	0.882429
C	1.265690	0.000220	-0.310765
H	3.253626	-0.000046	0.703054
C	1.630339	1.084575	-1.369566
H	2.134679	1.979807	-1.002311
H	0.766602	1.359104	-1.976763

C	1.630309	-1.083358	-1.370355
H	0.766533	-1.357358	-1.977733
H	2.134609	-1.978898	-1.003794
C	2.474396	0.000857	-2.093538
H	3.510345	0.000734	-1.755691
H	2.446072	0.001255	-3.182144
Rh	-0.678627	-0.000161	0.345350
C	-0.643488	-1.975293	0.421759
O	-0.614208	-3.092208	0.494862
Cl	-2.059351	0.000307	-1.628001
C	-0.643887	1.975057	0.422992
O	-0.614846	3.091929	0.496783

IN13

C	0.385127	2.218531	0.005775
C	-1.086432	2.535282	0.007476
H	0.879332	2.660939	-0.865237
H	0.880332	2.656239	0.878590
H	-1.403737	3.575767	0.010652
C	-1.977341	1.548436	0.005079
C	-1.542355	0.108480	0.000469
H	-3.045759	1.760393	0.006239
C	-2.307859	-0.738803	1.073682
H	-2.637126	-0.211086	1.971465
H	-1.739782	-1.628421	1.349593
C	-2.308826	-0.731681	-1.077752
H	-1.741314	-1.619504	-1.360405
H	-2.638913	-0.197837	-1.971604
C	-3.365344	-1.087437	-0.002719
H	-4.200153	-0.386059	-0.000049
H	-3.753580	-2.105530	-0.005922
Rh	0.575107	0.121612	0.000144
Cl	0.759030	-2.338803	-0.005909
C	0.370927	0.181470	-1.952001
C	2.646781	0.113768	0.000002
O	3.763928	0.053408	-0.000063
O	0.211364	0.223547	-3.059380
C	0.371476	0.170807	1.952495
O	0.212268	0.206684	3.060143

IN14

C	0.408947	-1.630606	1.432558
C	-1.078072	-1.783258	1.549380
H	0.810332	-1.362993	2.417882
H	0.838428	-2.607162	1.182442
H	-1.415187	-2.460991	2.331854
C	-2.031404	-1.196310	0.829781
C	-1.906438	-0.218769	-0.304786
H	-3.063468	-1.426332	1.079777
C	-3.081891	-0.361789	-1.329664
H	-3.544007	-1.347287	-1.382435
H	-2.762809	-0.050013	-2.322575
C	-2.497641	1.197876	0.063983
H	-2.009276	1.989498	-0.505710
H	-2.478140	1.448901	1.121524
C	-3.837889	0.760528	-0.579708
H	-4.533069	0.367603	0.162194
H	-4.353675	1.500287	-1.190280
Rh	1.084411	-0.081304	0.231304
C	1.841089	-1.447411	-0.879065
O	2.269329	-2.284201	-1.495239
C	-0.531616	-0.132865	-0.966061
O	-0.369122	-0.010232	-2.134889
C	1.821507	1.603394	-0.759630
O	2.183683	2.551577	-1.228350
Cl	0.376571	1.459133	1.836692

IN15

Rh	-1.568622	0.139561	-0.104919
C	-3.402103	-0.202208	-0.063574
O	-4.505415	-0.436806	-0.041015
C	-1.833017	1.919872	0.462991
O	-1.987802	2.988008	0.804087
Cl	-1.197010	-2.057256	-0.808238
O	0.562679	0.460889	-0.220095
C	1.454310	-0.118604	0.368927
C	2.916991	0.078386	0.039929
C	3.595882	-0.730538	1.111889
C	2.730323	-1.364308	1.902357
C	1.296404	-1.101368	1.509106
H	0.676162	-0.665325	2.299958
H	0.758924	-1.983960	1.141444
H	2.998784	-2.010523	2.727393
H	4.674282	-0.784172	1.199221
C	3.433076	1.533124	-0.201628

C	3.346603	-0.231208	-1.438752
H	3.796769	-1.208331	-1.608666
H	2.497340	-0.090847	-2.108567
H	3.955716	2.000571	0.632575
H	2.608484	2.168101	-0.528670
C	4.266089	1.013501	-1.398877
H	5.282488	0.754386	-1.100479
H	4.305151	1.636577	-2.290847

IN16

Rh	-0.141773	0.181986	-0.014785
Cl	-2.524000	0.456484	-0.551803
C	-0.041760	2.141715	-0.372026
O	-0.021996	3.243687	-0.579968
C	-0.476334	0.206544	1.910417
O	-0.662942	0.186271	3.019213
C	1.273329	-0.512336	-1.509138
C	1.886192	-0.177281	-0.238692
C	3.180444	0.528465	0.042517
H	3.896216	0.635198	-0.765163
H	3.182632	1.343855	0.755356
C	2.927162	-0.886293	0.594594
H	2.759785	-0.984794	1.660323
H	3.474673	-1.705681	0.143507
H	1.482168	0.022123	-2.429014
C	0.219650	-1.450029	-1.444693
C	-0.122905	-1.989693	-0.162617
H	0.709413	-2.277076	0.471695
H	-0.446376	-1.568528	-2.293075
C	-1.379331	-2.819317	-0.007631
H	-1.195779	-3.847824	-0.335015
H	-1.693574	-2.856561	1.036324
H	-2.200544	-2.400605	-0.589333

IN17

Rh	-0.359884	-0.177932	0.187830
C	-0.322691	1.644206	0.996542
O	-0.262492	2.646590	1.489807
C	-0.251133	-1.977423	-0.599599
O	-0.161666	-2.992709	-1.062556
Cl	-2.671574	-0.466657	0.726586
C	0.000069	0.610207	-1.696613
H	-0.271275	-0.194504	-2.388891
C	1.465297	0.924699	-1.834372
H	1.807080	1.434943	-2.732049
C	2.292972	0.545959	-0.864855
H	3.367692	0.711269	-0.915332
C	1.701012	-0.135745	0.312820
C	2.508024	-1.265114	0.962707
C	2.379319	0.067453	1.678455
H	1.972341	-2.107745	1.386505
H	1.760857	0.094652	2.569067
H	3.465465	-1.521848	0.523350
H	3.247904	0.715201	1.719458
C	-0.922213	1.797892	-1.982851
H	-0.653370	2.673799	-1.387990
H	-0.828642	2.083105	-3.037326
H	-1.967206	1.547373	-1.792522

IN18

Rh	0.351064	-0.098742	0.064578
C	0.257195	0.426473	-1.829880
O	0.117026	0.680829	-2.910642
C	2.397230	-0.225154	0.209045
O	3.507274	-0.348252	0.275928
Cl	0.430026	-2.477128	-0.611692
C	-0.060827	-0.608364	1.916332
O	-0.374260	-0.902222	2.949572
C	0.256860	1.927974	0.671532
H	0.618977	1.975929	1.705586
C	-1.199162	2.322387	0.647896
H	-1.463286	3.343250	0.917862
C	-2.129256	1.437312	0.296926
H	-3.186605	1.695842	0.274298
C	-1.725922	0.056868	-0.072103
C	-2.679704	-1.089099	0.300418
C	-2.552939	-0.667238	-1.146195
H	-2.244776	-2.045427	0.564191
H	-2.037654	-1.354356	-1.806174
H	-3.582241	-0.823087	0.839013
H	-3.368704	-0.112779	-1.596295
C	1.124254	2.905872	-0.142000
H	0.813249	2.951155	-1.188642
H	1.032258	3.919672	0.263551
H	2.183761	2.639308	-0.111333

IN19

Rh	0.783989	0.222892	-0.076542
C	-0.730514	-1.078874	-0.277595
O	-0.420843	-2.203668	-0.508142
C	-2.540062	0.785865	-0.206897
C	-2.156481	-0.641721	-0.045275
C	-3.201832	-1.724442	-0.335857
H	-4.163275	-1.363595	-0.678911
H	-2.841671	-2.631341	-0.802042
C	-2.818816	-1.477253	1.094687
H	-2.185013	-2.203620	1.587036
H	-3.495957	-0.926412	1.733744
H	-3.516112	0.968832	-0.643445
C	-1.763898	1.813704	0.143610
C	-0.424868	1.666430	0.792707
H	-0.561717	1.276011	1.804996
H	-2.129647	2.821346	-0.045490
C	0.364406	2.980710	0.863792
H	-0.175848	3.725027	1.459888
H	1.337372	2.833144	1.339105
H	0.527595	3.415031	-0.127394
C	0.346165	0.972007	-1.777976
O	0.109787	1.433403	-2.777021
Cl	1.455217	-0.447445	2.051109
C	2.228936	-1.258745	-0.744010
O	2.982035	-2.050244	-0.976719

IN19b

Rh	-0.562761	0.433790	0.131273
C	-0.013147	-1.502386	0.139104
O	-0.733742	-2.301986	0.629455
C	2.462812	0.218118	0.362237
C	1.373650	1.117898	-0.101529
C	1.751359	2.057652	-1.257807
H	2.761387	1.973029	-1.641673
H	0.999217	2.280214	-2.001892
C	1.576464	2.622960	0.138501
H	0.700449	3.240503	0.311635
H	2.455411	2.938344	0.691403
H	3.316911	0.668048	0.865927
C	2.447769	-1.101841	0.173771
C	1.324405	-1.817809	-0.554755
H	3.262890	-1.721416	0.531431
C	1.541450	-3.331724	-0.640016
H	2.469546	-3.532771	-1.178219
H	1.613917	-3.767725	0.357835
H	0.719412	-3.817082	-1.165630
H	1.219267	-1.387323	-1.557343
C	-2.632105	-0.120042	0.299478
O	-3.711248	-0.408178	0.300081
C	-0.133678	0.526114	1.996997
O	0.151666	0.603203	3.081088
Cl	-1.061262	0.496921	-2.149508

IN20

Rh	1.419609	0.142401	-0.133274
C	3.232861	-0.283608	-0.072761
O	4.324737	-0.567321	-0.043377
O	-0.682059	0.606642	-0.304596
C	-1.692357	0.017747	0.040141
C	-3.057356	0.418859	-0.378255
C	-3.969195	-0.528493	0.312725
C	-3.281506	-1.412543	1.036483
C	-1.785372	-1.196116	0.954051
H	-1.278267	-2.021320	0.438189
H	-3.715322	-2.209278	1.626420
H	-5.046194	-0.487651	0.214598
C	-3.255477	0.951637	-1.815460
C	-3.353645	1.903590	-0.665973
H	-4.330932	2.255480	-0.361918
H	-2.528787	2.584917	-0.499425
H	-4.164106	0.634649	-2.310392
H	-2.362721	0.978712	-2.427316
C	-1.091306	-0.964405	2.308809
H	-1.195786	-1.853936	2.931432
H	-0.025808	-0.773854	2.160209
H	-1.536782	-0.118139	2.835989
C	1.736487	1.833249	0.643944
O	1.921362	2.849318	1.107268
Cl	0.993598	-1.938015	-1.109825

IN21

C	0.720038	-1.932031	0.602650

C	0.985862	-1.799467	-0.803364
H	1.539282	-1.782713	1.296765
H	-0.014060	-2.673367	0.894606
H	0.490643	-2.419939	-1.540843
C	1.694058	-0.651131	-1.209919
C	1.973039	0.289167	-0.147880
H	1.840957	-0.427124	-2.260816
Rh	-0.030188	-0.026342	0.008832
C	-0.520563	0.527537	1.812841
O	-0.784791	0.805402	2.868358
C	-0.609840	1.618334	-0.992687
O	-0.968213	2.518350	-1.555261
Cl	-2.285523	-0.863332	-0.466119
C	3.004555	0.961930	0.330895
H	4.010210	0.794711	-0.043219
H	2.886448	1.694433	1.120101

IN22

Rh	0.314128	0.000390	0.076797
C	0.228894	-1.978506	0.082479
O	0.144798	-3.093707	0.078388
C	0.224806	1.978905	0.082312
O	0.138069	3.093912	0.078105
Cl	2.689845	0.001946	0.007033
C	-0.670535	-0.000532	-1.736469
H	-0.333500	-0.877149	-2.297673
H	-0.335329	0.876817	-2.297626
C	-2.158514	-0.002068	-1.531784
H	-2.813771	-0.002861	-2.398563
C	-2.619900	-0.002389	-0.279912
H	-3.679147	-0.003424	-0.036947
C	-1.608152	-0.001241	0.781088
C	-1.886731	-0.001323	2.087273
H	-2.913481	-0.002311	2.447131
H	-1.110048	-0.000430	2.846387

IN23

Rh	-0.183184	0.000015	-0.023937
C	-0.032924	1.958606	-0.155617
O	0.089233	3.063290	-0.280899
C	-0.032445	-1.958020	-0.162377
O	0.089988	-3.062240	-0.291436
Cl	-2.278179	0.002090	-1.303626
C	1.004597	0.003145	-1.761396
H	0.762743	0.871583	-2.380225
H	0.762857	-0.863147	-2.383269
C	2.446602	0.002506	-1.337998
H	3.224506	0.003859	-2.097443
C	2.747879	0.000283	-0.036327
H	3.774633	-0.000262	0.321752
C	1.647636	-0.001484	0.938824
C	1.866164	-0.003753	2.258714
H	2.880008	-0.004352	2.653097
H	1.070317	-0.005080	2.994175
C	-1.374535	-0.003030	1.661017
O	-2.071796	-0.004589	2.535046

IN24

C	-1.112796	-1.321924	-1.782815
C	-2.441836	-0.988048	-1.154866
H	-1.210258	-1.435021	-2.864875
H	-0.737543	-2.266243	-1.366259
H	-3.294759	-1.429549	-1.658495
C	-2.658087	-0.253223	-0.060444
C	-1.641470	0.411997	0.753651
H	-3.687855	-0.127155	0.267579
Rh	0.340819	0.207067	0.346658
C	0.010494	-0.313629	-1.558276
O	0.713825	0.095953	-2.418925
C	0.242820	2.052241	-0.192836
O	0.137070	3.125726	-0.503913
Cl	0.336772	-1.957690	1.214570
C	-2.000974	1.111514	1.838673
H	-3.038787	1.158902	2.161539
H	-1.286758	1.636975	2.465167
C	2.451411	-0.109852	0.125783
O	3.536183	-0.360383	0.039694

IN25

C	-0.770836	-0.352832	1.742801
C	-1.462018	-0.530376	0.569945
C	-1.714363	-1.743657	-0.217782
Rh	0.772828	0.127573	0.145152
C	0.326840	1.972729	0.084833

O	0.152302	3.086864	0.050094
H	-1.186442	-2.670549	-0.049110
C	-2.656007	-1.525066	-1.146748
C	-3.184114	-0.113355	-1.137546
H	-4.258818	-0.050094	-0.944175
C	-2.412452	0.526444	0.017584
O	-2.543310	1.635862	0.443212
H	-2.990888	0.428723	-2.068397
H	-3.013039	-2.277015	-1.838201
H	-0.289825	-1.185877	2.239634
H	-0.923278	0.564696	2.300154
C	2.447312	0.462699	-0.759698
O	3.435319	0.617378	-1.271431
Cl	1.534375	-2.085354	0.301936

TS1

Rh	0.372955	0.121314	-0.075685
C	-0.060791	1.792220	-0.756583
O	-0.368726	2.792465	-1.178355
C	2.440642	0.253987	0.032718
O	3.559163	0.263001	0.054605
Cl	0.885516	-2.142874	-0.622772
C	-0.001851	0.965452	1.778655
H	-0.512245	1.927423	1.717384
H	0.920602	1.088997	2.345551
C	-0.892122	-0.122400	2.293291
H	-0.828169	-0.438346	3.329568
C	-1.733811	-0.698271	1.421831
H	-2.407906	-1.496457	1.724352
C	-1.646230	-0.292572	-0.003883
C	-2.420580	-1.070359	-1.052213
C	-2.865977	0.338251	-0.694780
H	-1.948315	-1.234052	-2.012226
H	-2.704302	1.124871	-1.422262
H	-3.027421	-1.900560	-0.707951
H	-3.768146	0.456300	-0.105689

TS2

Rh	0.426430	-0.162086	-0.043531
Cl	1.099266	2.150961	-0.534207
C	2.004753	-0.807533	-0.935987
O	2.890911	-1.186849	-1.510744
C	-0.944587	-0.170092	-1.334651
O	-1.426871	-0.281647	-2.382264
C	1.307442	0.166459	1.897947
O	1.772023	0.403522	2.886701
C	-2.370306	-1.052964	0.670688
C	-1.804184	0.203036	0.095870
C	-1.885257	1.532058	0.967090
H	-2.311571	1.363904	1.948804
H	-1.054004	2.221688	0.905389
C	-2.748643	1.375654	-0.224916
H	-2.510678	1.955292	-1.108465
H	-3.799223	1.147721	-0.090900
H	-3.425441	-1.062749	0.928775
C	-1.600233	-2.126972	0.827233
C	-0.144973	-2.123275	0.438566
H	0.013742	-2.812103	-0.396902
H	0.465452	-2.502313	1.263785
H	-2.027726	-3.042322	1.229342

TS2b

Rh	0.343541	-0.031972	-0.013133
Cl	2.680776	-0.725739	0.158244
C	0.871202	1.431319	1.502515
O	1.206135	2.177319	2.263696
C	-0.250324	-1.677181	-0.706913
O	-0.526958	-2.462766	-1.508085
C	0.739803	1.055222	-1.547819
O	0.972123	1.635079	-2.479834
C	-2.444801	-0.454729	0.855288
C	-1.662117	0.516126	0.039225
C	-2.126882	1.980585	0.105093
H	-2.938271	2.221492	0.782747
H	-1.387074	2.766220	0.008586
C	-2.447422	1.150280	-1.121255
H	-1.926163	1.369190	-2.044499
H	-3.473570	0.831703	-1.262831
H	-3.484587	-0.209134	1.064412
C	-1.932927	-1.606100	1.289218
C	-0.490922	-1.927358	1.011767
H	-0.223663	-2.982041	0.987169
H	0.188901	-1.499644	1.764146
H	-2.532156	-2.327501	1.832176

TS3

Rh	0.794173	0.096677	0.269153
Cl	2.446513	1.231146	-0.912829
C	1.963017	-1.543513	0.102233
O	2.647736	-2.420366	-0.010310
C	-0.897565	-1.000181	-0.209368
O	-0.610600	-2.009898	-0.803372
C	-0.054204	1.856967	0.416066
O	-0.445619	2.906401	0.472025
C	-2.709402	0.235576	0.862119
C	-2.187014	-0.227737	-0.437045
C	-2.337265	0.565048	-1.747343
H	-2.870309	1.506190	-1.692402
H	-1.483952	0.550902	-2.414978
C	-3.104095	-0.720011	-1.555595
H	-2.756684	-1.599072	-2.083553
H	-4.169458	-0.663319	-1.372670
H	-3.620803	0.818019	0.927725
C	-1.981366	-0.134582	1.915693
C	-0.726360	-0.906953	1.619094
H	-0.807598	-1.984409	1.762041
H	0.095413	-0.583767	2.281563
H	-2.241731	0.118759	2.936607

TS3b

Rh	-0.593477	0.174302	-0.218502
Cl	-1.710169	-1.890711	0.020516
C	-2.371338	0.878515	0.152813
O	-3.392588	1.246583	0.440615
C	0.846731	-0.075398	1.346998
O	0.493688	-0.830894	2.182483
C	2.552879	0.196417	-0.591288
C	1.387126	-0.713935	-0.434681
C	1.685212	-2.212007	-0.278595
H	2.731205	-2.479156	-0.187780
H	0.999572	-2.746834	0.369928
C	1.163578	-1.765592	-1.600166
H	0.152175	-2.037271	-1.864596
H	1.855940	-1.648191	-2.426433
H	3.172931	0.125134	-1.479739
C	2.791516	1.088416	0.367314
C	1.875908	1.044262	1.555434
H	1.347542	1.988490	1.724034
H	2.410065	0.799099	2.477349
H	3.595588	1.811678	0.322084
C	0.057158	1.881804	-0.749813
O	0.346611	2.903143	-1.130489

TS4

Rh	0.094195	0.137136	-0.169506
C	-0.542457	1.816724	-0.656713
O	-0.959303	2.814775	-0.977882
C	1.944049	0.620472	0.635333
O	2.967991	0.824395	1.037335
Cl	1.213399	-1.874847	-0.765566
C	-0.966732	0.417821	1.585884
H	-1.626944	1.286364	1.560308
H	-0.283893	0.524452	2.428963
C	-1.715254	-0.881820	1.581445
H	-1.904041	-1.401631	2.515718
C	-2.088451	-1.382865	0.399138
H	-2.597421	-2.340370	0.335158
C	-1.715752	-0.634466	-0.851898
H	-1.529033	-1.300942	-1.694126
H	-2.487144	0.084841	-1.138389

TS5

Rh	-0.168483	0.002157	0.084415
Cl	-1.690715	-1.134356	-1.452745
C	-1.329817	1.756439	-0.425530
O	-1.992573	2.607181	-0.718345
C	1.190474	-1.285774	-0.068661
O	1.808478	-2.231335	0.175129
C	-1.196178	-0.509234	1.624251
O	-1.760657	-0.857797	2.529118
C	2.451148	1.329684	0.493561
C	1.182390	1.086370	1.274523
H	3.199111	1.984594	0.934623
C	2.696482	0.755405	-0.681568
C	1.659593	-0.131258	-1.314692
H	2.026553	-0.892127	-2.000748
H	0.930514	0.436245	-1.911318
H	3.636327	0.904378	-1.201501
H	1.427459	0.560440	2.202295

H	0.737399	2.039269	1.576141

TS6

Rh	-0.559613	-0.040104	-0.276848
Cl	0.255996	-2.230655	-0.392451
C	-2.131040	-0.882609	0.488814
O	-2.990751	-1.398652	0.994746
C	1.001473	0.823975	0.883679
O	0.767590	1.887808	1.358490
C	2.696753	0.192913	-0.893511
C	1.340009	0.811534	-1.063743
H	3.349051	0.123311	-1.756967
C	3.050832	-0.287055	0.293108
C	2.064085	-0.140888	1.415142
H	2.500422	0.330759	2.298344
H	1.623356	-1.101293	1.689435
H	4.001022	-0.775415	0.469305
C	-1.379940	1.698859	-0.371900
O	-1.867340	2.707177	-0.469106
H	1.364766	1.894017	-1.186962
H	0.863024	0.383397	-1.965889

TS7

Rh	0.573664	-0.021715	0.331661
C	-0.214015	0.247571	1.996162
O	-0.655663	0.364174	3.028863
C	1.008436	1.924349	-0.234029
O	1.350114	2.947191	-0.534522
Cl	2.530149	-0.461801	-0.979401
C	-1.322505	-0.092510	-0.497226
C	-1.116244	-1.381401	-1.243494
H	-1.547429	-1.494975	-2.235041
C	-0.356155	-2.332243	-0.688894
H	-0.137769	-3.249683	-1.228194
C	0.280618	-2.058372	0.641838
H	-0.369391	-2.341951	1.472939
H	1.240369	-2.562613	0.755654
C	-1.834623	1.061608	-1.393925
H	-1.604045	2.042235	-0.973998
H	-1.548136	1.037642	-2.446191
C	-2.671422	-0.026462	0.278783
H	-2.648263	0.691001	1.100224
H	-3.086266	-0.972436	0.626286
C	-3.273875	0.635089	-0.990100
H	-4.003904	1.429641	-0.839584
H	-3.679498	-0.107760	-1.676431

TS8

C	-0.380053	1.846262	1.167638
C	1.064931	1.929753	1.580275
H	-1.022340	1.827792	2.052765
H	-0.648352	2.752754	0.616348
H	1.327173	2.651495	2.351118
C	2.033965	1.195173	1.038035
C	1.785398	0.137808	-0.009932
H	3.065741	1.334945	1.349109
C	3.052508	-0.201237	-0.857220
H	3.742760	0.629393	-1.005897
H	2.767741	-0.616912	-1.823207
C	1.917720	-1.338436	0.563690
H	1.349153	-2.051319	-0.032197
H	1.671071	-1.446327	1.620862
C	3.405983	-1.317877	0.154053
H	4.048672	-0.955269	0.956391
H	3.821400	-2.238966	-0.251892
Rh	-0.656438	0.120912	0.018559
Cl	-0.972528	-1.950019	-1.254239
C	-1.493097	-1.013055	1.673298
C	-2.254452	0.841145	-0.715446
O	-3.172745	1.286004	-1.184333
O	-1.979196	-1.646303	2.455800
C	0.685288	0.817034	-1.114831
O	1.032007	1.415581	-2.049446

TS9

C	-0.160806	-1.139972	1.613945
C	-1.463078	-0.606700	2.130211
H	0.664269	-0.792547	2.264233
H	-0.103590	-2.227486	1.579349
H	-1.629603	-0.573156	3.201023
C	-2.356672	-0.132971	1.268219
C	-2.034522	-0.209193	-0.188425
H	-3.298356	0.304038	1.581221
C	-3.184767	-0.803656	-1.064288

H	-3.906806	-1.433198	-0.544664
H	-2.767872	-1.347729	-1.911379
C	-2.198143	1.124038	-0.988407
H	-1.493950	1.162273	-1.821470
H	-2.117782	2.039477	-0.407665
C	-3.600509	0.640610	-1.437087
H	-4.385293	1.022447	-0.783369
H	-3.882824	0.823937	-2.472777
Rh	1.110345	0.033393	0.216393
C	2.041375	-1.563274	-0.323259
O	2.620774	-2.487038	-0.597416
C	-0.715028	-0.984468	-0.283517
O	-0.557978	-1.943368	-0.969232
C	2.090865	1.170022	-1.010235
O	2.584515	1.856304	-1.750332
Cl	0.309736	2.067380	1.047690

TS10

Rh	-0.256910	0.094645	-0.251311
C	0.087770	-1.152539	-1.583990
O	0.346178	-1.898263	-2.391215
C	-2.308272	0.329030	-0.465993
O	-3.392091	0.557608	-0.627001
Cl	-0.438496	2.416839	0.311824
C	-0.272064	-1.527477	1.055807
C	0.621322	-0.893593	2.076967
H	0.406551	-1.027396	3.133681
C	1.646085	-0.142848	1.644151
H	2.324132	0.349365	2.337712
C	1.755725	0.095236	0.184594
C	2.774059	1.090939	-0.339517
C	2.995939	-0.393026	-0.581934
H	2.488600	1.713644	-1.177483
H	2.869387	-0.770934	-1.589552
H	3.403740	1.588421	0.389925
H	3.770581	-0.894017	-0.012907
C	-1.651222	-1.922235	1.568357
H	-2.273497	-2.341544	0.775477
H	-1.550309	-2.686578	2.347046
H	-2.171268	-1.069163	2.011180
H	0.218743	-2.382780	0.587995

TS11

Rh	-0.363012	-0.110178	-0.131147
Cl	-0.429643	-2.556081	0.194731
C	-1.935515	-0.225284	-1.234675
O	-2.813291	-0.304426	-1.929843
C	1.105093	-0.194013	-1.307236
O	1.659716	-0.326636	-2.316368
C	-1.354331	-0.062839	1.785321
O	-1.849655	-0.165383	2.782397
C	2.062499	1.630001	0.292284
C	1.866058	0.155510	0.179586
C	2.149127	-0.740952	1.462560
H	2.413007	-0.154239	2.334350
H	1.509017	-1.598004	1.623791
C	3.082572	-0.777688	0.314115
H	3.083131	-1.658286	-0.316563
H	4.031752	-0.260594	0.387202
H	3.049716	1.992938	0.564183
C	1.057368	2.462312	0.033394
C	-0.313710	1.982581	-0.374122
H	-0.444987	2.209818	-1.438100
H	1.214639	3.537263	0.106667
C	-1.408277	2.746184	0.393955
H	-1.335424	3.821560	0.196306
H	-2.410609	2.427662	0.098648
H	-1.310241	2.609953	1.474113

TS11b

Rh	0.126274	-0.355533	-0.050902
Cl	-0.853283	-2.599815	-0.027933
C	1.139624	-0.956654	1.753134
O	1.659785	-1.318687	2.673374
C	-1.232629	0.374387	-1.110972
O	-1.850690	0.736936	-2.008255
C	1.518315	-0.932662	-1.264115
O	2.271594	-1.260636	-2.028249
C	-0.179412	2.475356	0.703485
C	0.853411	1.585408	0.103256
C	2.314921	1.912301	0.450470
H	2.496440	2.720620	1.149925
H	3.028689	1.100404	0.522510
C	1.775278	2.266971	-0.921149
H	2.118670	1.695875	-1.774548

H	1.593200	3.313083	-1.138222
H	0.112980	3.498353	0.934431
C	-1.430500	2.070814	0.922382
C	-1.833353	0.649949	0.645662
H	-2.188099	2.749447	1.302337
C	-3.320857	0.375740	0.404181
H	-3.878648	0.625052	1.310189
H	-3.700437	0.977749	-0.422287
H	-3.481177	-0.680170	0.180096
H	-1.552474	0.004874	1.488052

TS12

Rh	-0.887560	-0.030238	0.140576
C	-1.797565	1.346642	-0.840252
O	-2.362155	2.152495	-1.387075
C	0.969060	0.678257	-0.797576
O	0.736085	1.291791	-1.794557
C	2.692538	0.043122	0.799596
C	2.196563	-0.164979	-0.568427
C	2.297838	-1.511782	-1.296388
H	2.759853	-2.317329	-0.740606
H	1.440902	-1.796734	-1.893776
C	3.136400	-0.352360	-1.766748
H	2.841894	0.155634	-2.676253
H	4.196157	-0.353861	-1.546337
H	3.557481	-0.495633	1.165711
C	1.981256	0.894348	1.532319
C	0.750369	1.501427	0.924128
H	0.960225	2.442495	0.412814
H	2.206776	1.100059	2.572555
C	-0.294469	1.838571	2.031132
H	-1.177797	2.351398	1.650940
H	-0.597694	0.961471	2.605697
H	0.203552	2.527023	2.723485
Cl	-0.046062	-1.782607	1.451952
C	-2.079227	-1.387644	-0.483643
O	-2.722012	-2.222176	-0.879394

TS12b

Rh	-0.780712	-0.188677	-0.219371
Cl	-2.030067	1.657964	0.557342
C	-2.331594	-1.173459	0.425835
O	-3.208843	-1.712535	0.874642
C	0.950666	0.071975	1.012721
O	0.721078	0.677183	1.999901
C	2.172171	0.266326	-1.265102
C	0.983298	0.984383	-0.734367
C	1.145150	2.481537	-0.440290
H	2.147528	2.878743	-0.546812
H	0.579429	2.844145	0.411276
C	0.377759	2.117537	-1.664285
H	-0.691034	2.274742	-1.657411
H	0.863565	2.190330	-2.630985
H	2.562491	0.527737	-2.244189
C	2.715201	-0.694193	-0.521263
C	2.120562	-0.921800	0.841067
H	1.696471	-1.930322	0.920483
H	3.561719	-1.288857	-0.842906
C	-0.097060	-1.713461	-1.130931
O	0.197176	-2.630525	-1.717692
C	3.141642	-0.724823	1.974225
H	2.666454	-0.861880	2.945361
H	3.952436	-1.447590	1.867358
H	3.562058	0.280944	1.934255

TS13

Rh	-0.184318	0.003568	-0.202715
C	0.789968	-0.849220	-1.525792
O	1.397331	-1.338062	-2.340313
C	-1.263709	-1.576187	0.613394
O	-1.886782	-2.396043	1.048466
Cl	-2.254721	1.168882	-0.018410
C	1.630644	1.080796	1.451744
H	2.000033	1.244395	2.459852
C	1.259164	2.089339	0.640354
H	1.275215	3.118427	0.987710
C	0.794122	1.757365	-0.745356
H	1.633120	1.646492	-1.434320
H	0.083064	2.477563	-1.146235
C	1.454240	-0.283786	0.939076
C	2.121519	-1.379540	1.293373
H	2.927485	-1.319972	2.019457
H	1.905570	-2.358213	0.882717

TS14

C	-2.618808	-0.508966	1.029729
H	-3.514928	-0.914334	1.484983
C	-2.615490	0.681261	0.420729
H	-3.515852	1.290090	0.395825
Rh	0.220682	-0.033649	-0.010940
C	-0.843674	-1.460118	-0.624566
O	-1.289742	-2.238896	-1.348395
C	-1.357990	-1.320177	1.072413
C	1.109608	0.628868	-1.588358
O	1.599508	0.962426	-2.539784
Cl	2.095793	-1.497091	0.526295
C	-1.413239	1.199157	-0.256959
C	-1.456476	2.380029	-0.887067
H	-0.610071	2.804725	-1.413764
H	-2.368659	2.972190	-0.897532
H	-1.470526	-2.392880	1.212896
H	-0.687484	-1.007713	1.886628
C	1.095998	1.365643	1.383201
O	1.591330	2.078779	2.085868

TS15

C	1.213521	-1.872992	1.598266
C	1.379966	-0.800351	0.811139
C	2.555623	0.089918	0.881094
Rh	-0.491417	0.120662	0.142318
C	-1.592867	-1.572166	0.065057
O	-2.262232	-2.466776	0.010077
H	3.056378	0.281763	1.823287
C	2.950210	0.593232	-0.290191
C	2.150383	0.135998	-1.478819
H	2.755928	-0.453804	-2.172821
C	1.040068	-0.793373	-0.948714
O	0.677713	-1.786524	-1.524336
Cl	-2.513764	1.226243	-0.208137
H	1.712838	0.962748	-2.046848
H	3.795352	1.260374	-0.403627
H	1.903693	-2.087173	2.409889
H	0.413176	-2.585694	1.442334
C	0.233728	1.933987	0.265902
O	0.537842	3.010841	0.346681

P1

O	-0.000024	2.035456	-0.000097
C	0.376321	0.897543	-0.000052
C	-0.500739	-0.325982	-0.000296
C	0.430774	-1.481265	-0.000196
C	1.705525	-1.084860	-0.000064
C	1.836922	0.420531	0.000196
H	2.354766	0.814727	-0.879555
H	2.354710	0.814750	0.879946
H	2.558522	-1.750467	0.000012
H	0.095284	-2.510899	-0.000413
C	-1.839451	-0.267484	-0.751236
C	-1.839085	-0.267764	0.751606
H	-2.143621	-1.167191	1.271178
H	-2.047973	0.668535	1.254574
H	-2.144460	-1.166535	-1.271181
H	-2.048646	0.669115	-1.253541

P2

O	-2.052350	0.000018	-0.000098
C	-0.857522	0.000038	0.000019
C	0.039572	-1.248344	0.000045
C	1.430379	-0.666565	-0.000046
C	1.430477	0.666456	-0.000050
C	0.039676	1.248346	0.000105
H	-0.180576	1.861604	-0.879365
H	-0.180802	1.862013	0.879190
H	2.323126	1.278936	-0.000025
H	2.323115	-1.278952	-0.000288
H	-0.180961	-1.862090	-0.878949
H	-0.180595	-1.861237	0.879781

P3

O	0.771927	2.043847	0.000195
C	0.878495	0.851636	0.000070
C	-0.293728	-0.132052	-0.000008
C	0.394846	-1.467310	-0.000149
C	1.724579	-1.367771	-0.000048
C	2.196912	0.065520	-0.000054
H	2.790682	0.333003	-0.879647
H	2.790914	0.332910	0.879401
H	2.404832	-2.209936	0.000023

H	-0.152690	-2.402952	-0.000143
C	-1.406143	0.085180	-1.076609
C	-1.406205	0.084605	1.076679
H	-1.357798	-0.549306	1.962209
H	-1.427343	1.135750	1.369788
H	-1.357723	-0.548080	-1.962607
H	-1.427200	1.136546	-1.368934
C	-2.473853	-0.230206	-0.000098
H	-2.745747	-1.286667	-0.000373
H	-3.382758	0.370340	0.000024

P4

O	-0.099581	-1.910168	-0.278555
C	-0.190476	-0.714967	-0.239501
C	0.932422	0.251940	0.018771
C	0.300100	1.594535	0.017468
C	-1.010359	1.518910	-0.224565
C	-1.486515	0.096331	-0.424534
H	-1.833561	-0.063659	-1.452414
H	-1.680247	2.368341	-0.272697
H	0.854390	2.508354	0.192591
C	2.325841	-0.070612	-0.544939
C	2.085164	-0.183507	0.934215
H	2.499575	0.574081	1.586975
H	1.993372	-1.177933	1.353740
H	2.904482	0.765991	-0.915086
H	2.396118	-0.988838	-1.115081
C	-2.584967	-0.368009	0.545545
H	-3.508316	0.188962	0.376013
H	-2.782864	-1.431017	0.399212
H	-2.273558	-0.210663	1.580423

P5

C	1.950900	-0.895309	0.000484
C	0.656120	-0.576210	-0.000051
C	-0.536851	-1.426558	-0.000425
H	-0.498945	-2.508099	-0.001006
C	-1.658349	-0.693146	-0.000314
C	-1.380359	0.790700	0.000773
H	-1.774808	1.305152	0.882124
C	0.154672	0.850390	-0.000030
O	0.826020	1.841136	-0.000734
H	-1.776314	1.307384	-0.878534
H	-2.660443	-1.101882	-0.000814
H	2.290506	-1.924177	0.000668
H	2.695049	-0.106666	0.000804

PH1

C	2.908212	-0.000146	0.239887
H	2.799080	-0.001944	1.325827
H	3.493509	-0.878728	-0.047757
C	1.565785	0.000208	-0.439213
H	1.570919	0.000545	-1.527167
C	0.394260	-0.000019	0.194162
H	0.380412	-0.000662	1.283732
C	-0.929756	0.000426	-0.467834
C	-2.092589	-0.758271	0.177015
H	-2.784159	-1.271430	-0.478275
H	-1.892189	-1.265865	1.112291
C	-2.092505	0.757949	0.177798
H	-1.892559	1.264562	1.113729
H	-2.784129	1.271846	-0.476881
H	-0.903995	0.000889	-1.551491
H	3.492668	0.879901	-0.044908

PH2'

C	2.888416	0.000008	0.178432
H	2.840873	-0.000584	1.268672
H	3.455702	-0.878858	-0.142077
C	1.509653	-0.000098	-0.424698
H	1.457482	0.000105	-1.512017
C	0.373770	-0.000251	0.267258
H	0.418054	-0.000544	1.357283
C	-1.013485	0.000039	-0.326914
H	-0.917557	0.000066	-1.417393
H	3.455033	0.879637	-0.141148
C	-1.782684	1.264404	0.097336
H	-2.788854	1.268219	-0.329276
H	-1.878891	1.304263	1.186500
H	-1.264162	2.167680	-0.229765
C	-1.783073	-1.264200	0.097259
H	-1.879228	-1.304090	1.186428
H	-2.789271	-1.267746	-0.329290
H	-1.264768	-2.167554	-0.229957

H	3.124825	0.000103	0.986875
H	3.457773	-0.000145	-0.757632

PH3

C	-3.353648	-0.000055	-0.191463
H	-3.295561	-0.000578	-1.281176
H	-3.923836	-0.879043	0.123749
C	-1.981391	0.000202	0.424905
H	-1.939222	0.000647	1.512524
C	-0.837571	-0.000173	-0.256475
H	-0.872348	-0.000936	-1.346441
C	0.529159	0.000145	0.348384
C	1.558457	-1.075709	-0.114501
H	1.647068	-1.982680	0.483874
H	1.378358	-1.350611	-1.156474
C	1.558503	1.075668	-0.114927
H	1.378464	1.350352	-1.156969
H	1.647096	1.982785	0.483232
H	0.461085	0.000444	1.439245
H	-3.923574	0.879358	0.122951
C	2.669802	-0.000028	-0.004883

PH5

C	2.467936	-0.216488	0.000010
H	2.394980	-1.305067	0.000061
H	3.042300	0.091862	-0.878875
C	1.108072	0.419956	-0.000010
H	1.079429	1.507689	-0.000021
C	-0.049776	-0.247563	-0.000028
H	-0.040897	-1.335613	-0.000037
H	3.042273	0.091910	0.878916
C	-2.521259	-0.261781	0.000013
H	-3.469513	0.260291	0.000028
H	-2.552542	-1.346108	0.000000
C	-1.360527	0.397598	0.000000
H	-1.362708	1.484707	0.000017

VIII. References

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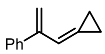
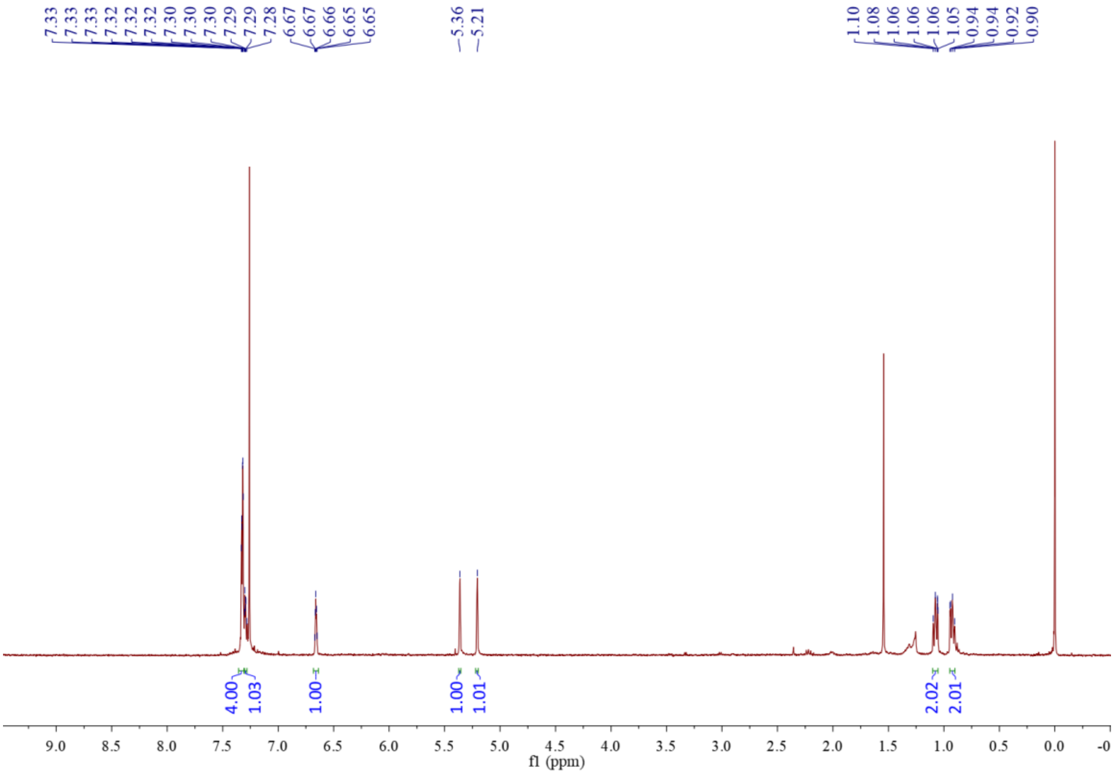
IX. NMR Spectra

NMR spectra for substrates of [4+1] cycloaddition, including unsuccessful substrates



1a

^{1}H NMR spectrum in $CDCl_3$:



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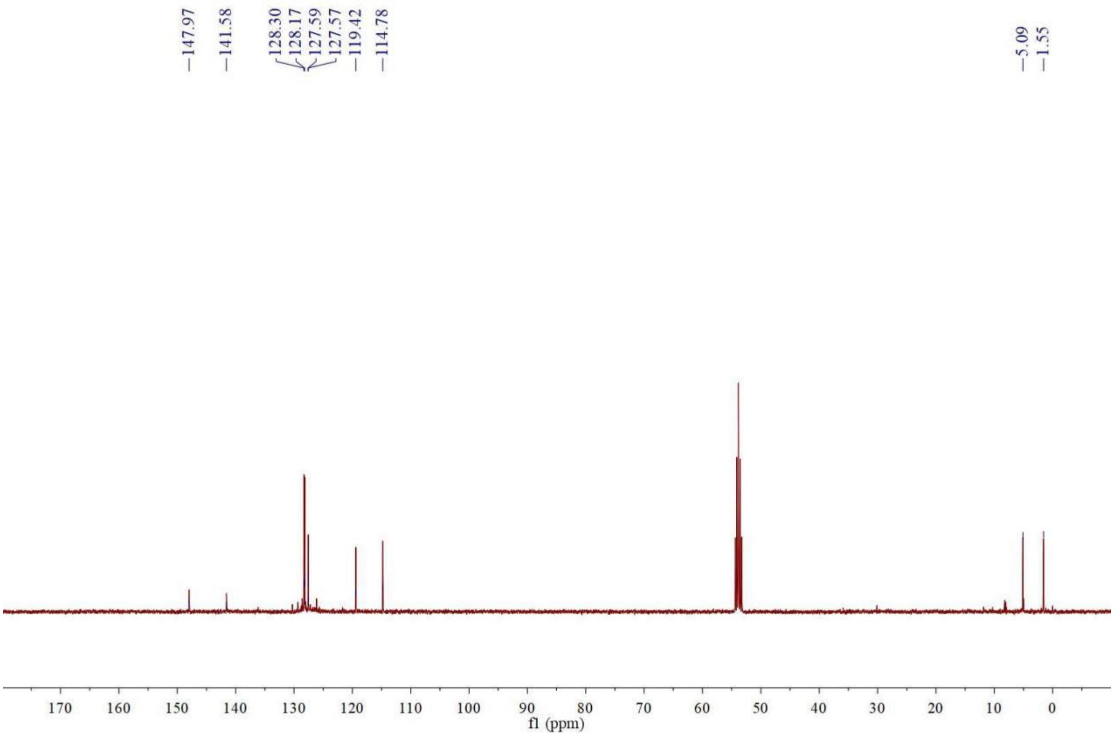

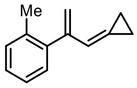

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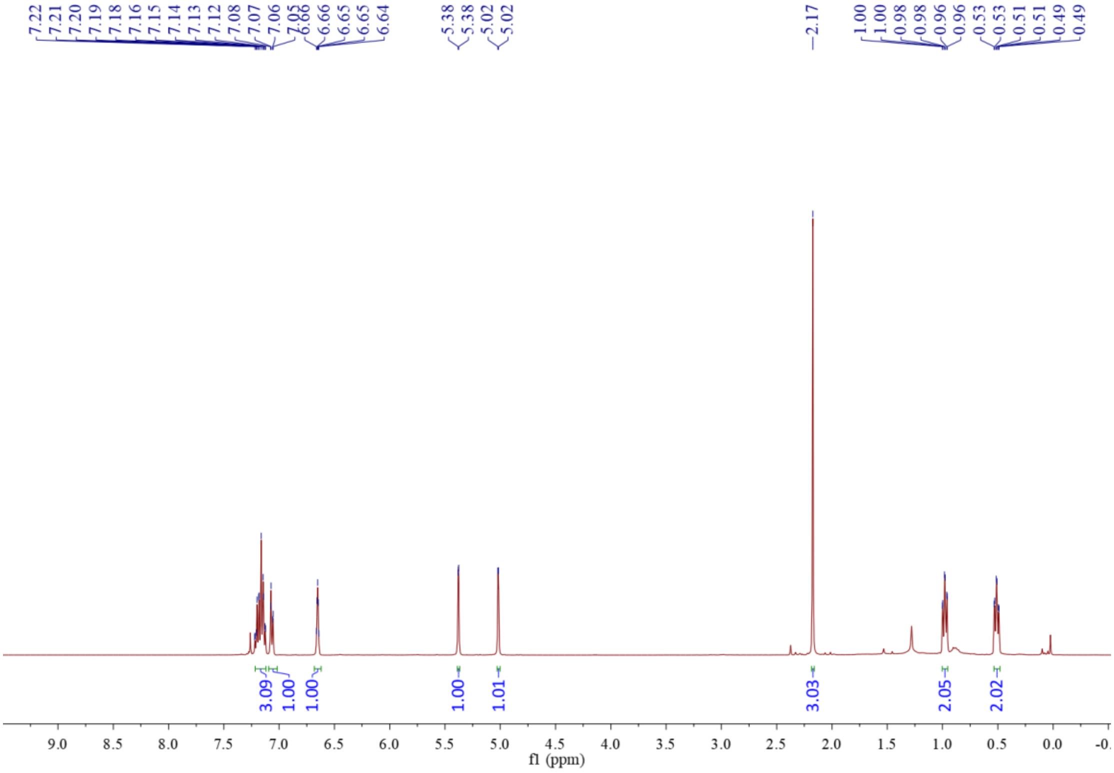

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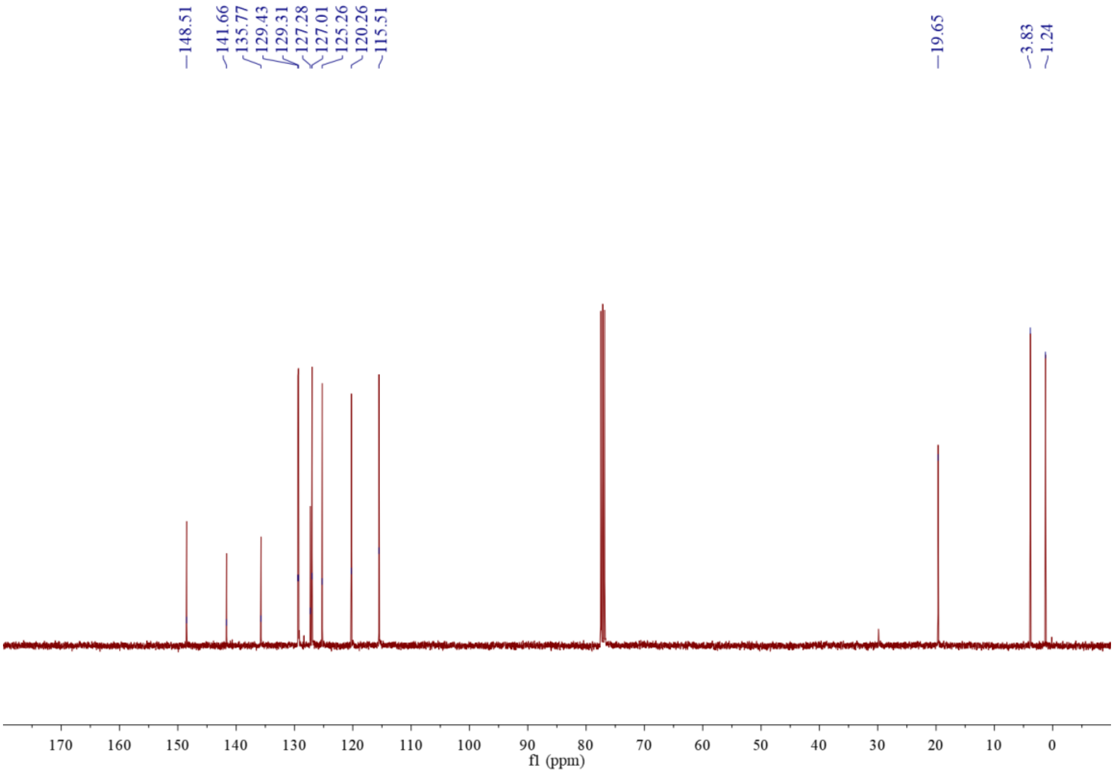

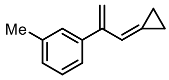

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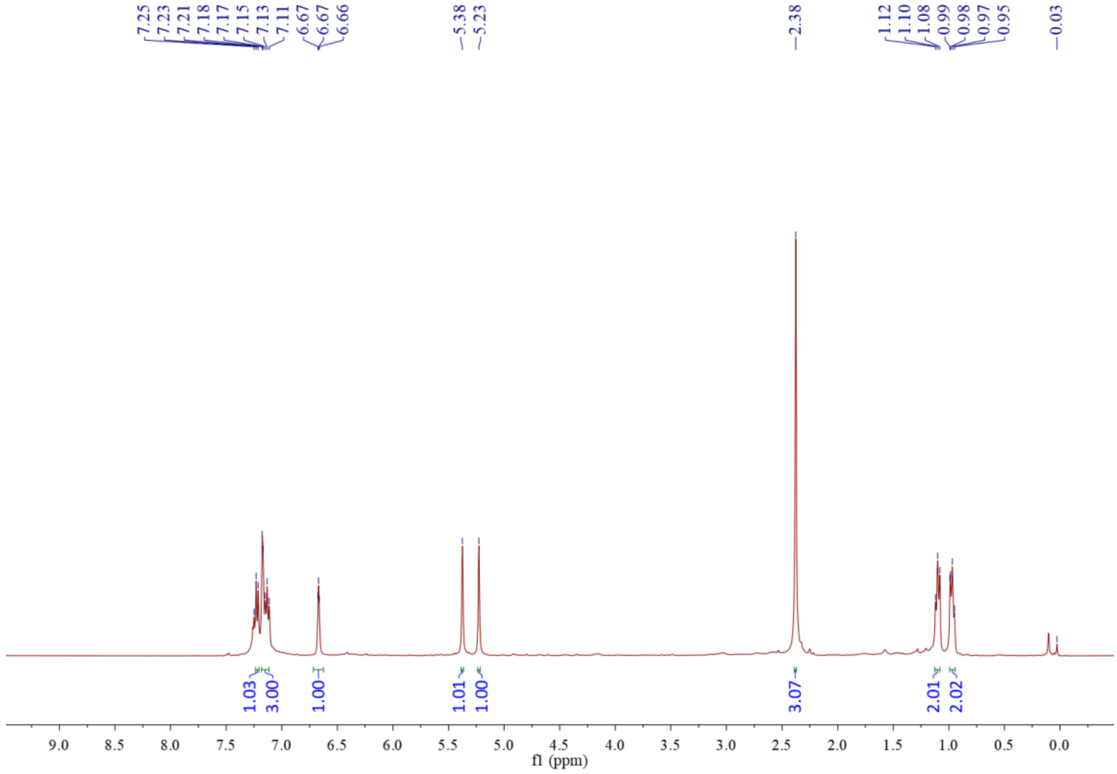

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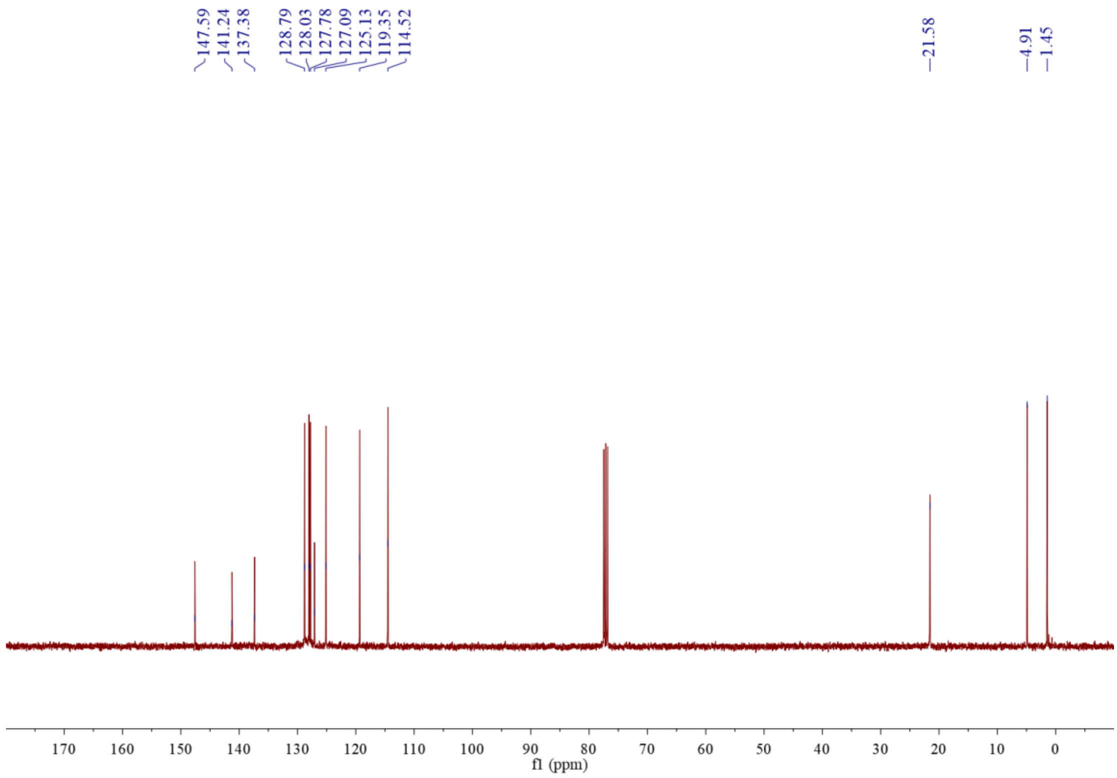

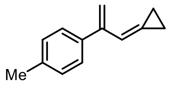

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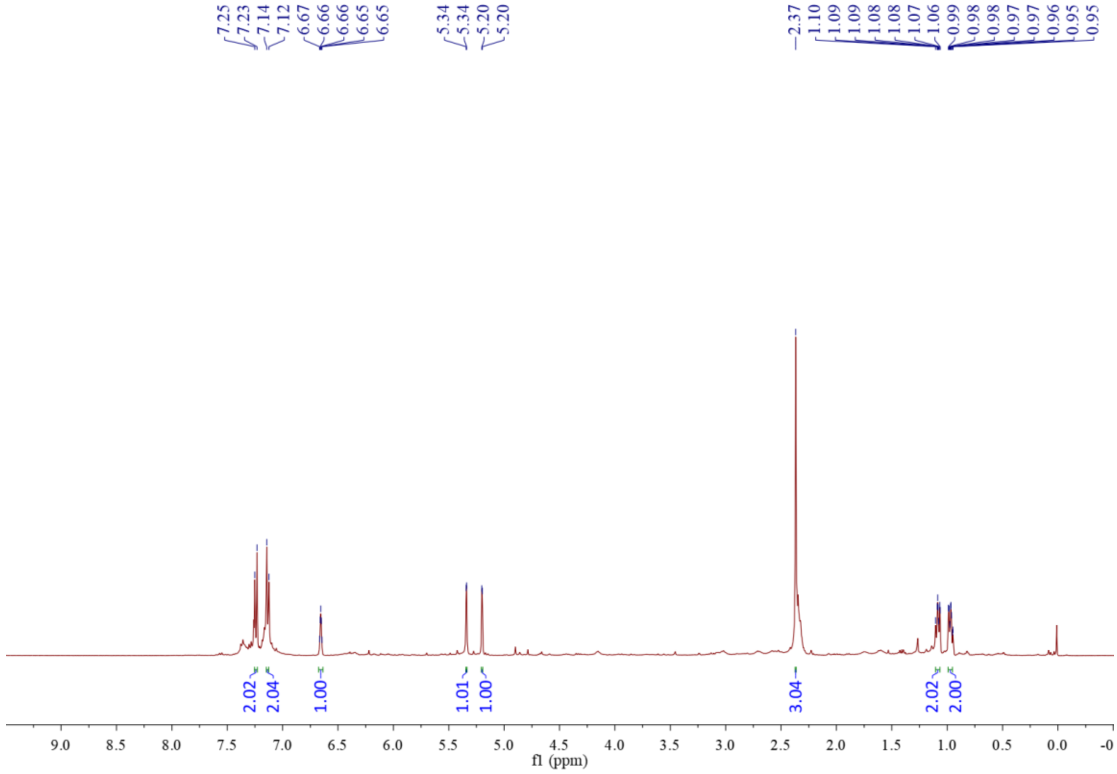

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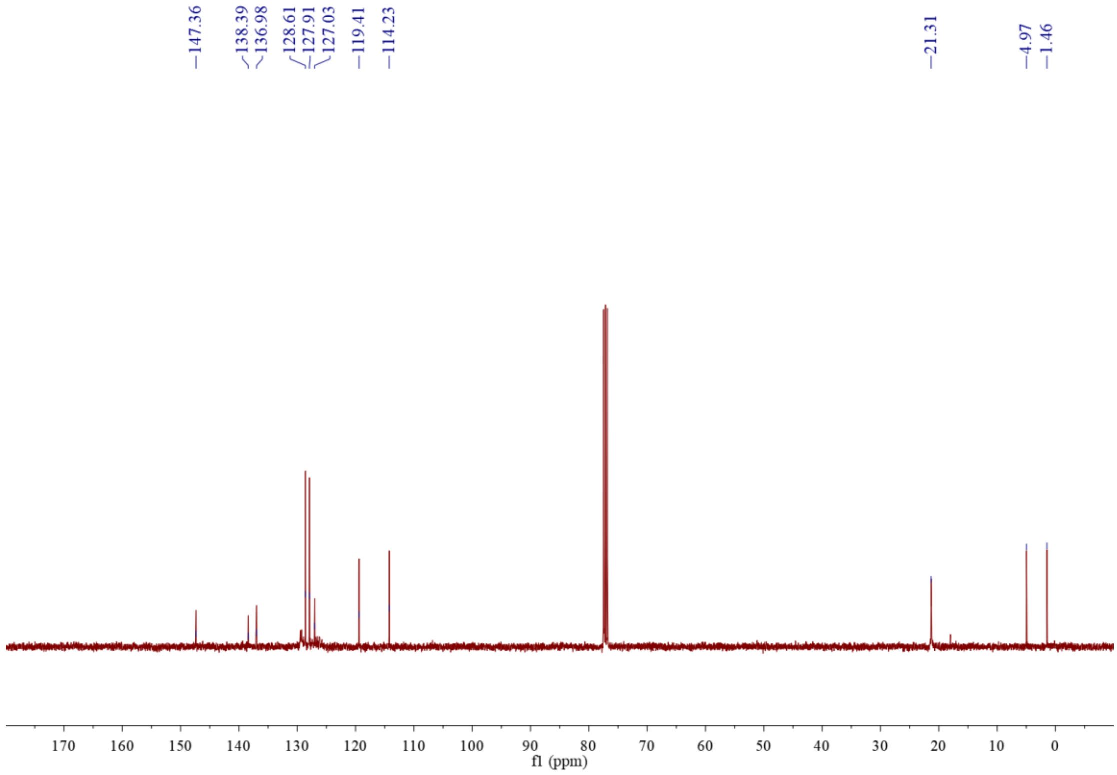

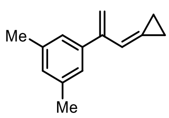

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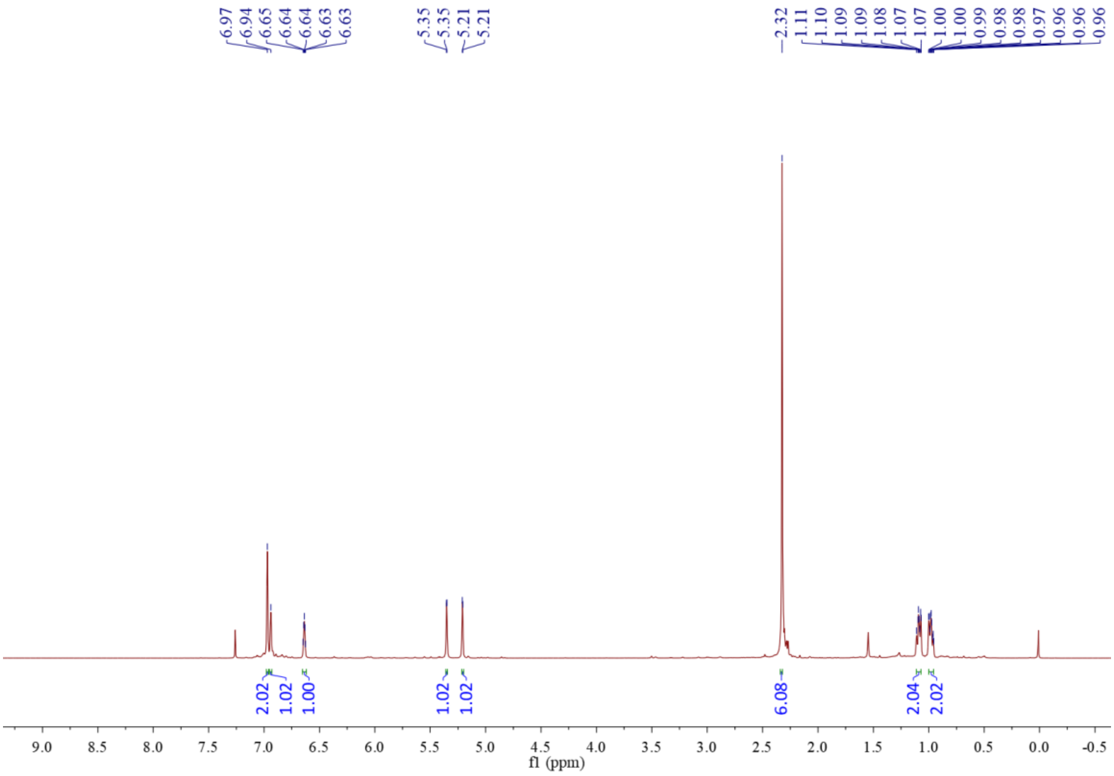

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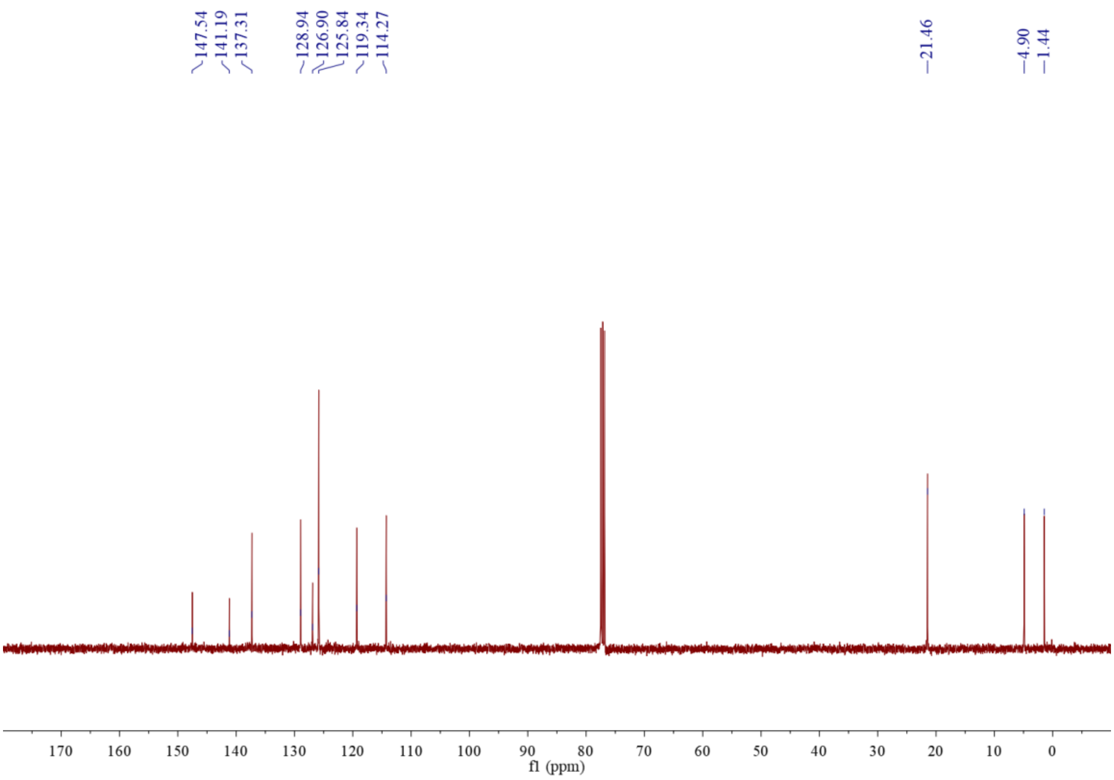

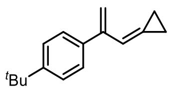

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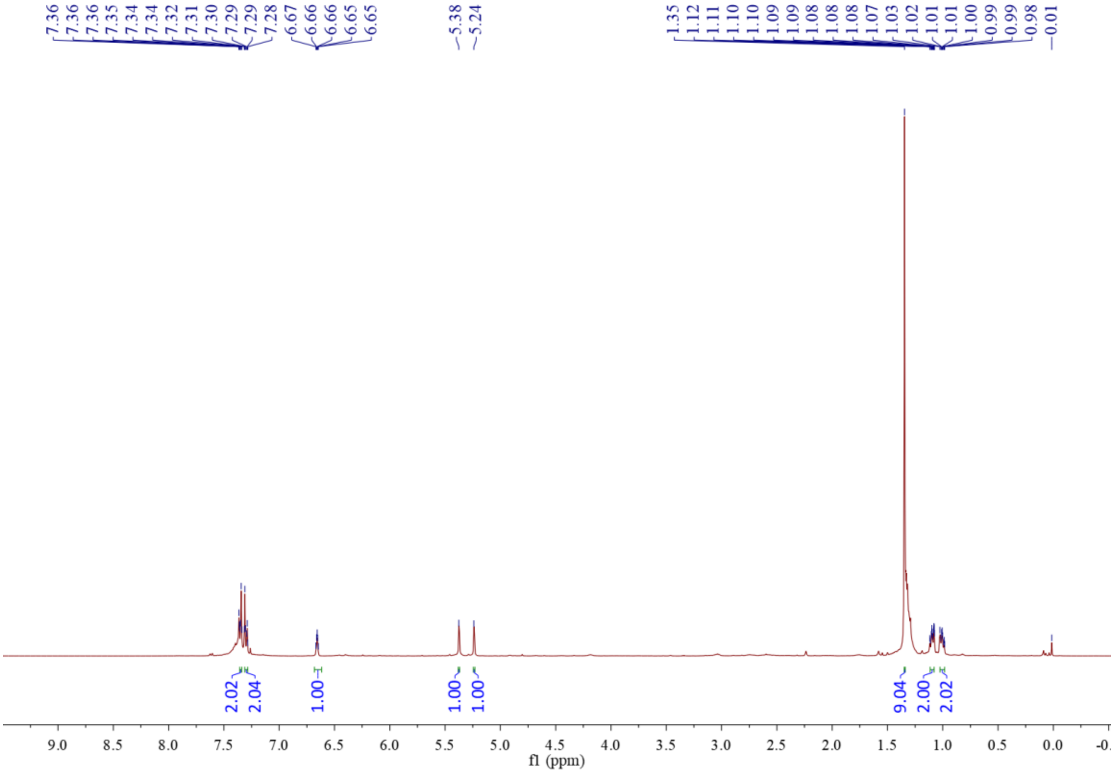

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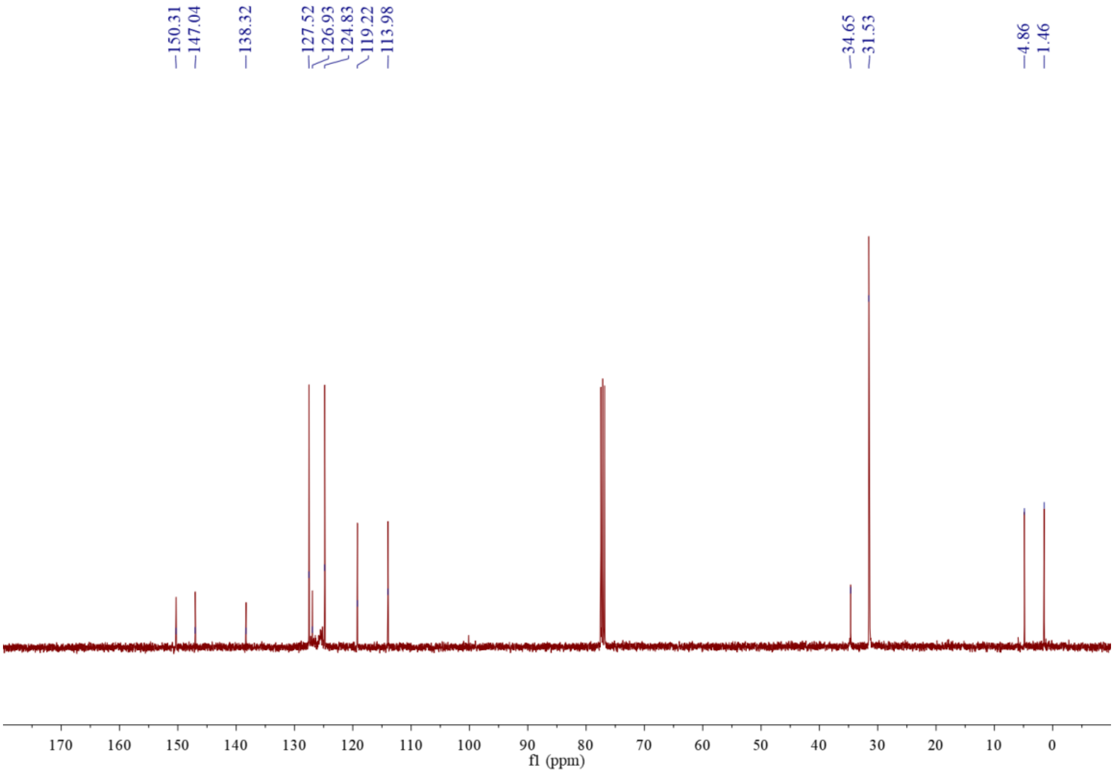

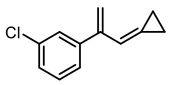

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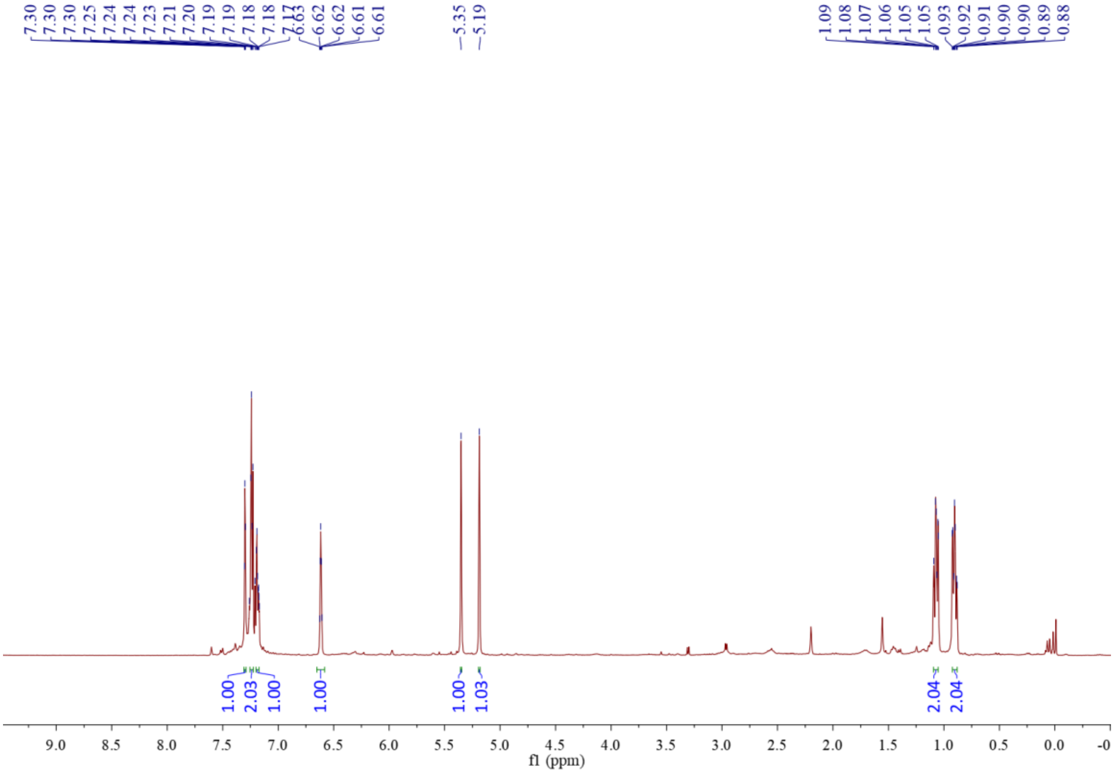

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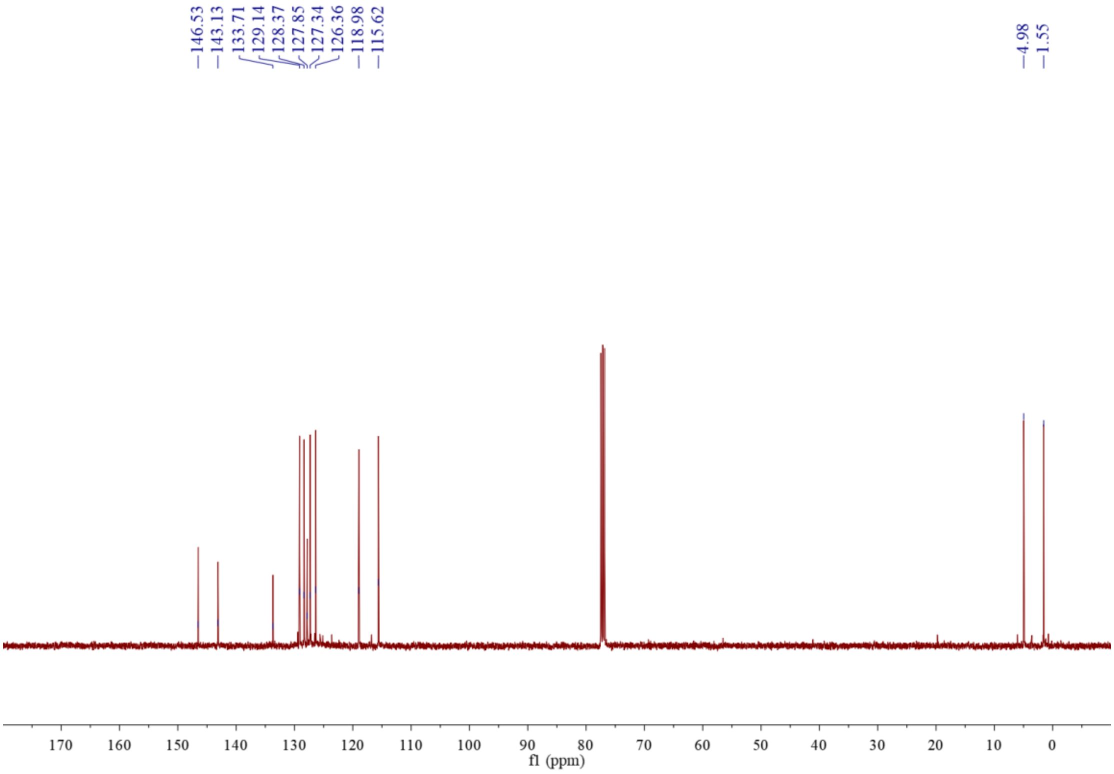

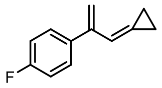

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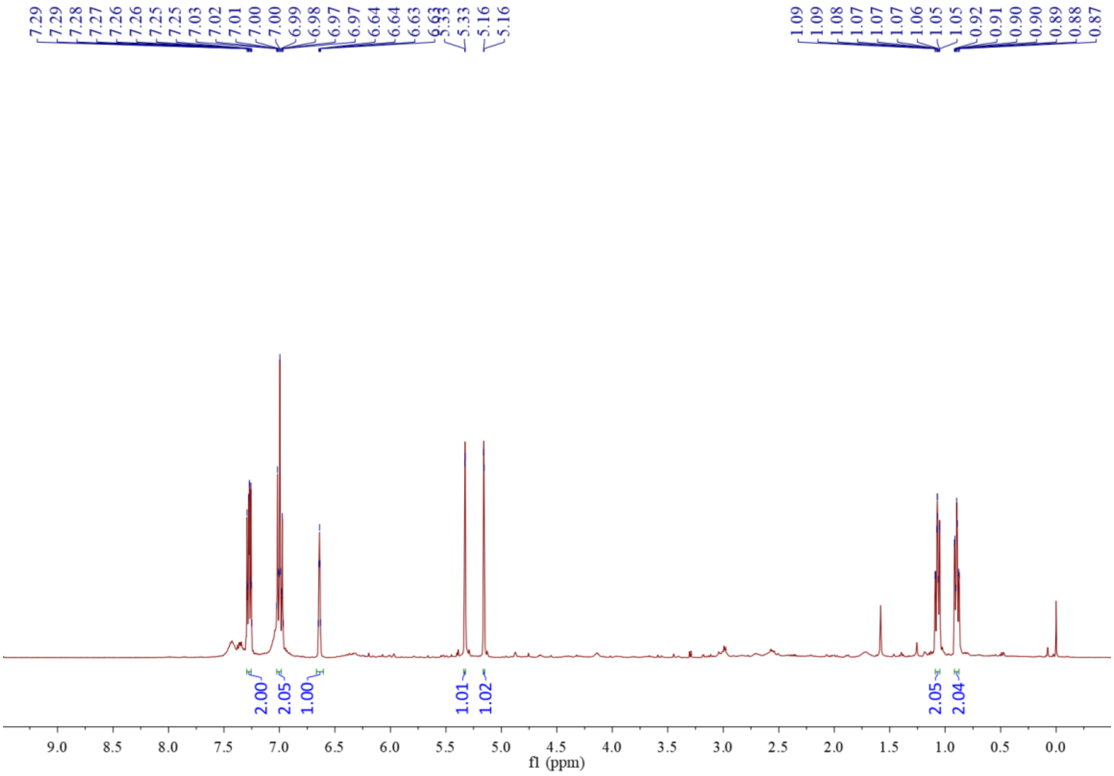

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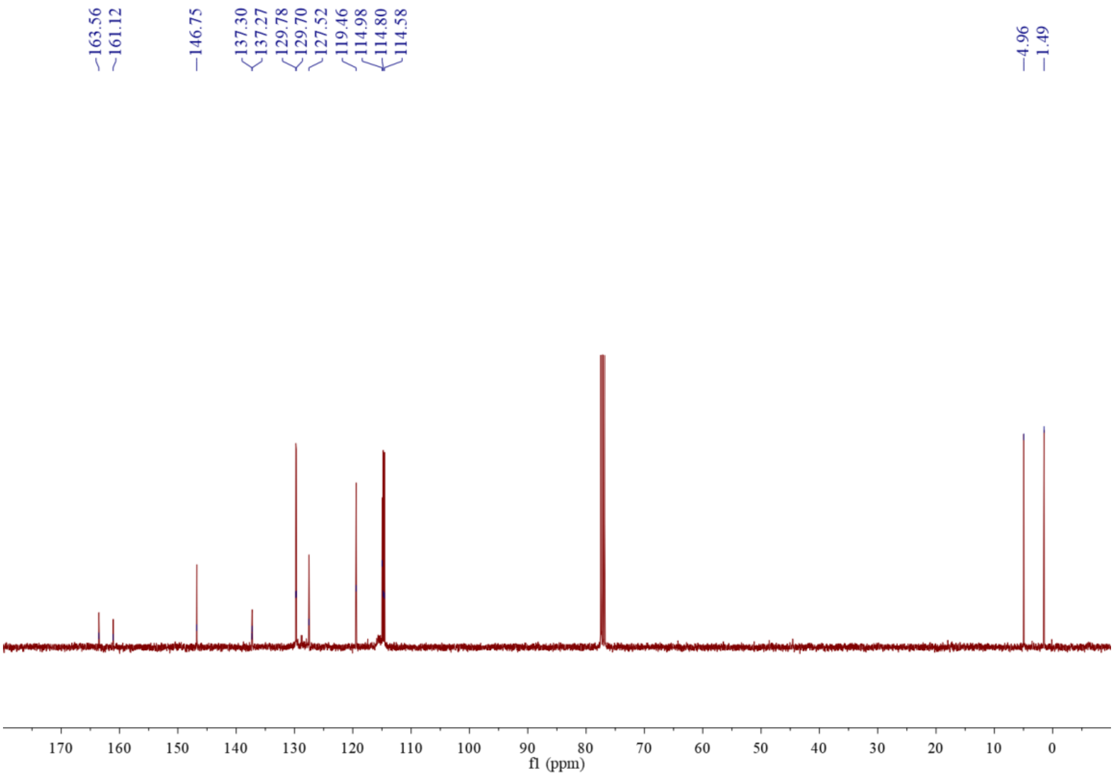

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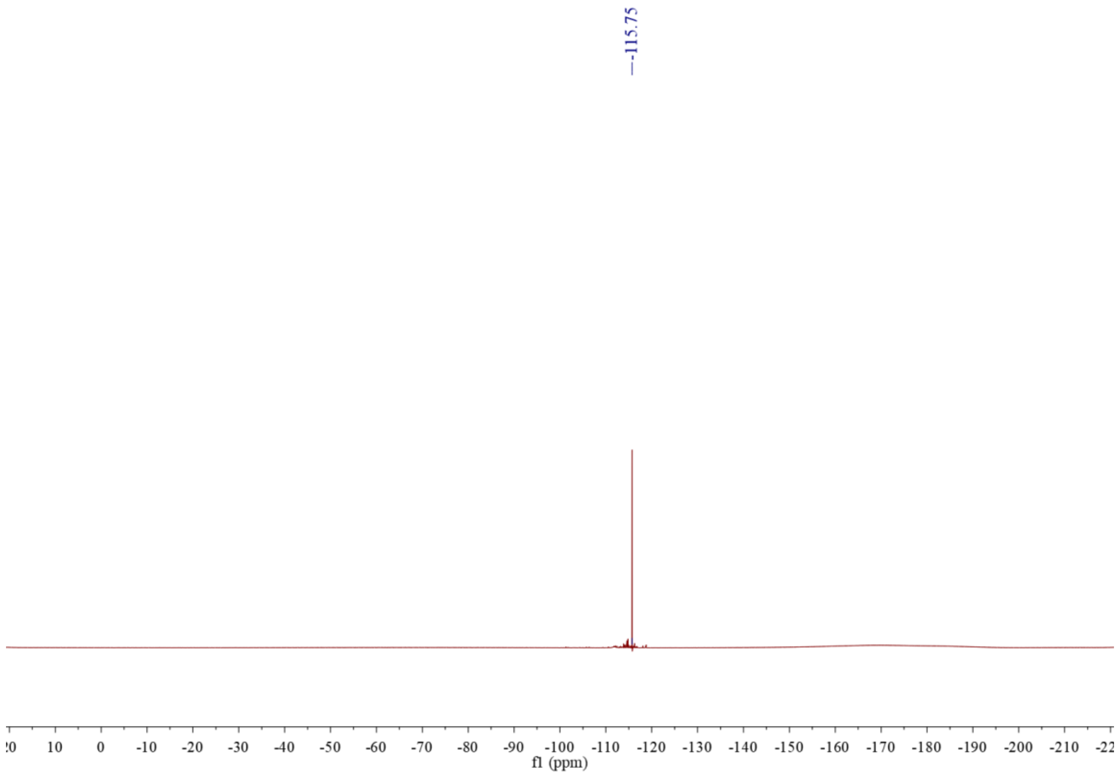

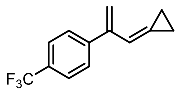

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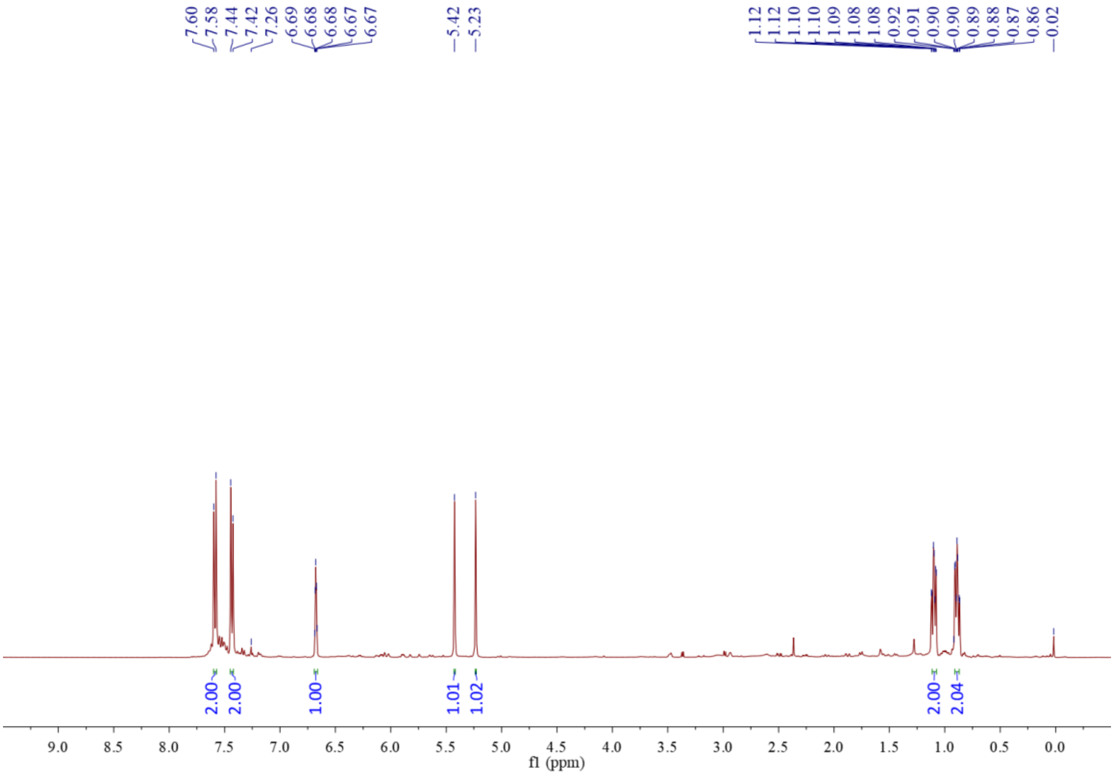
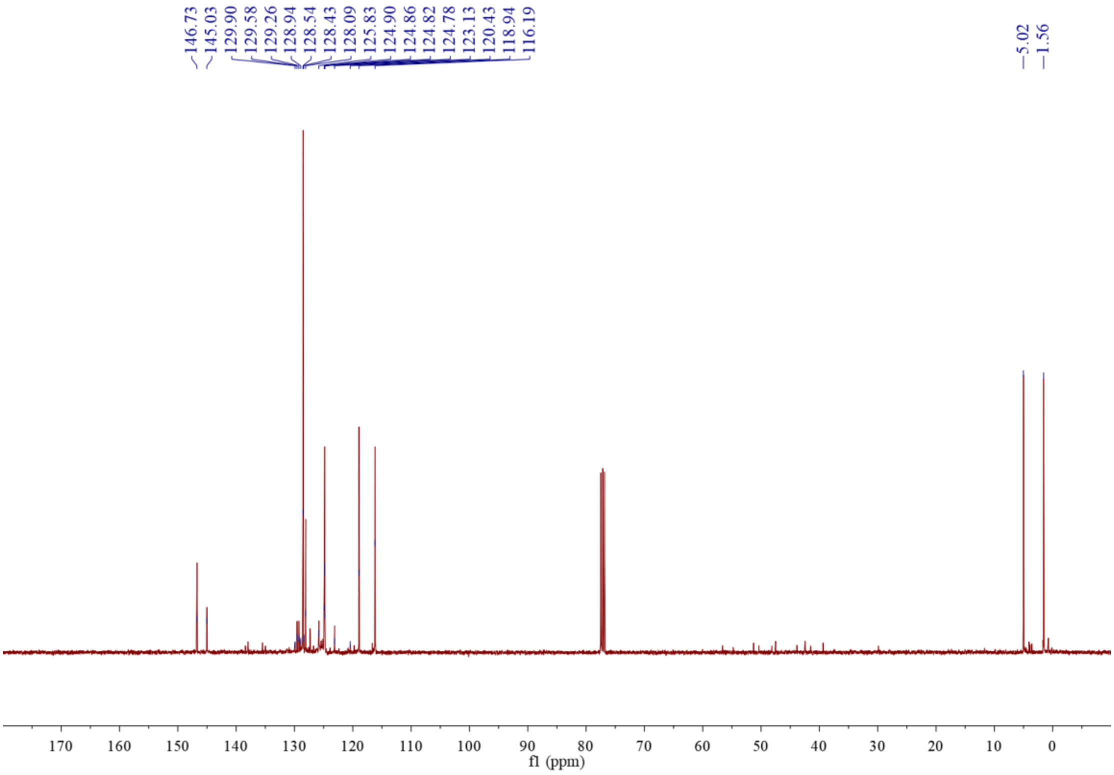
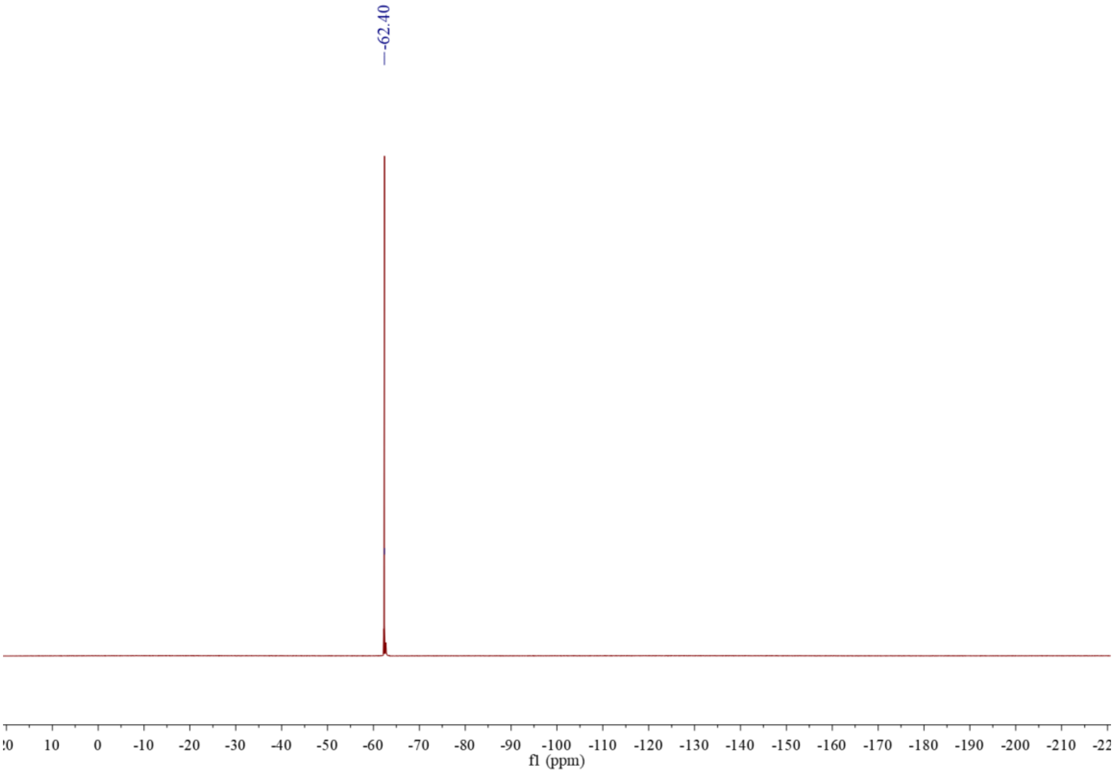
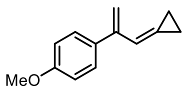


^{13}C NMR spectrum in $CDCl_3$:



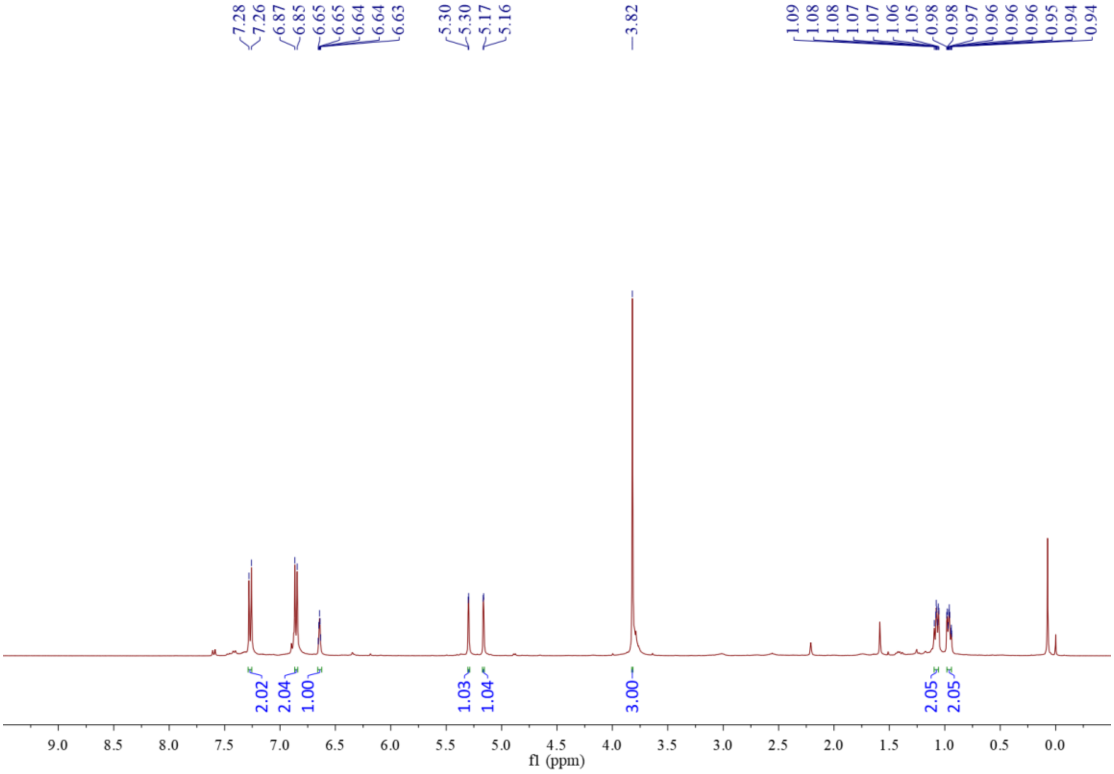
^{19}F NMR spectrum in $CDCl_3$:



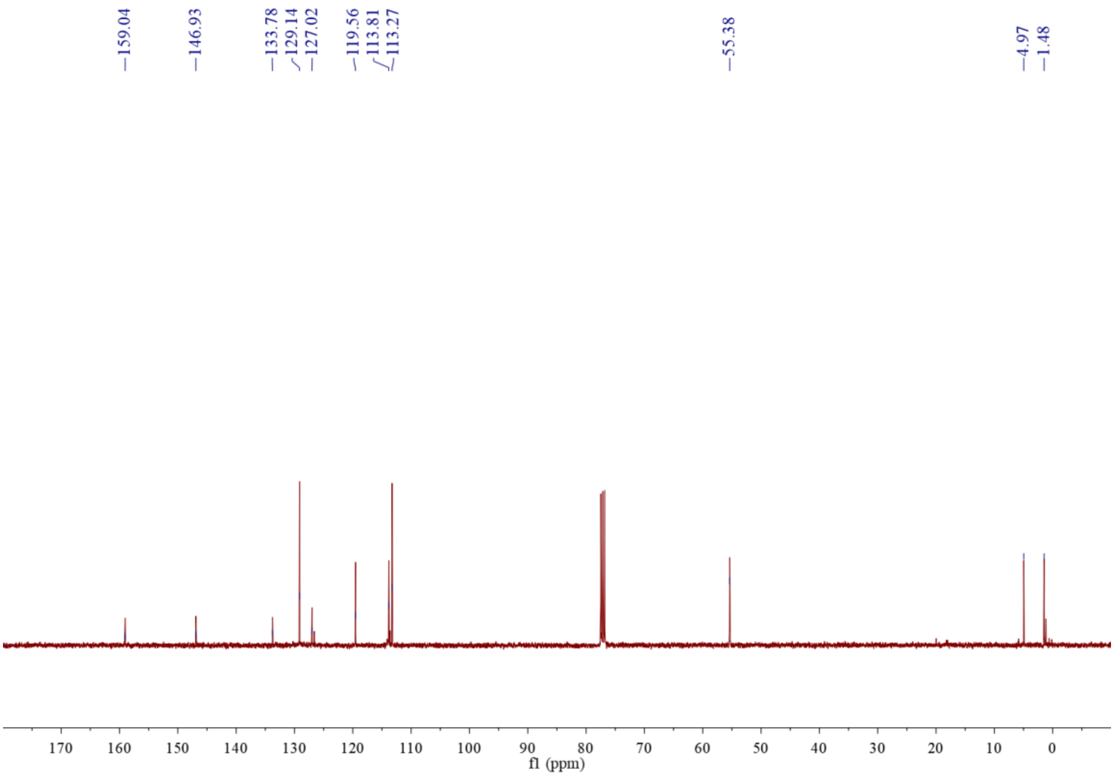


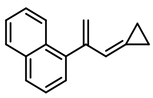
1j

^{1}H NMR spectrum in $CDCl_3$:



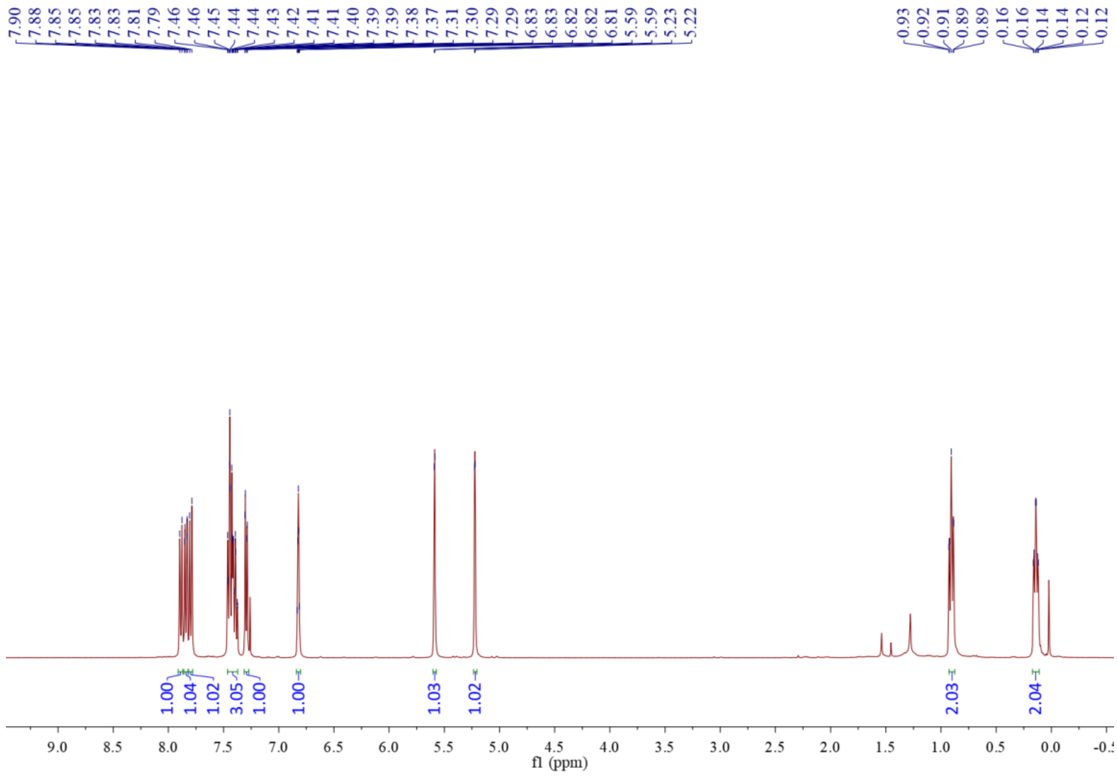
^{13}C NMR spectrum in $CDCl_3$:



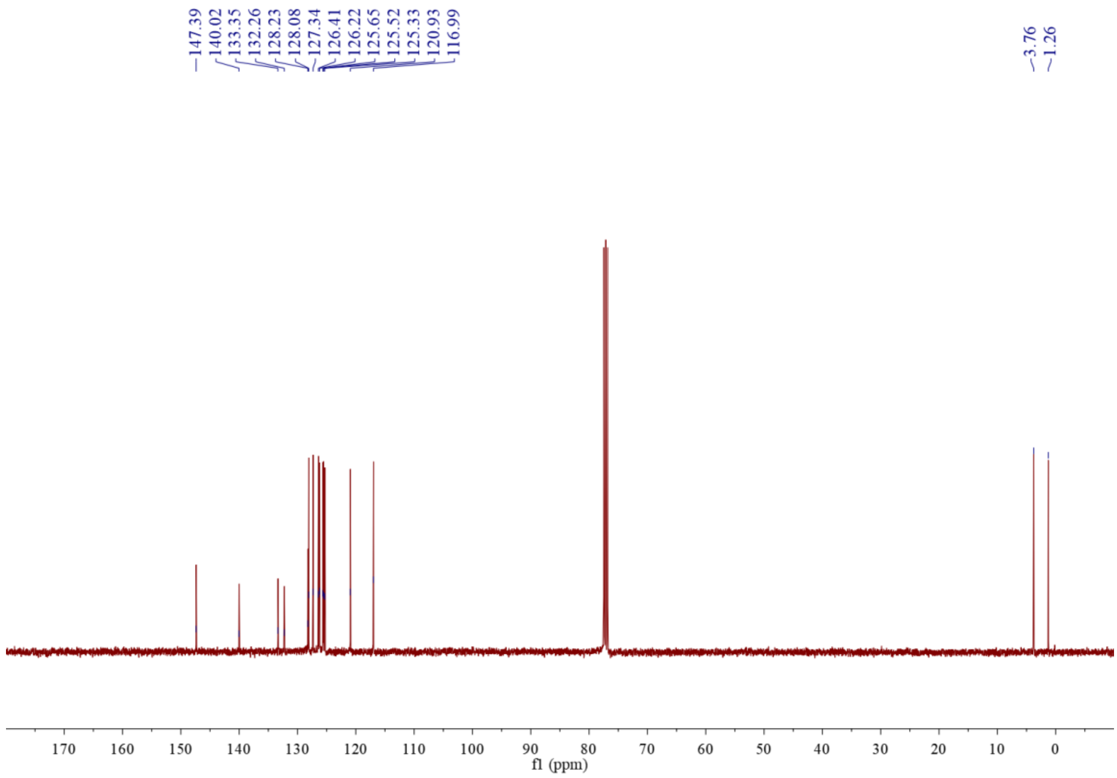


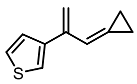
1k

^{1}H NMR spectrum in $CDCl_3$:



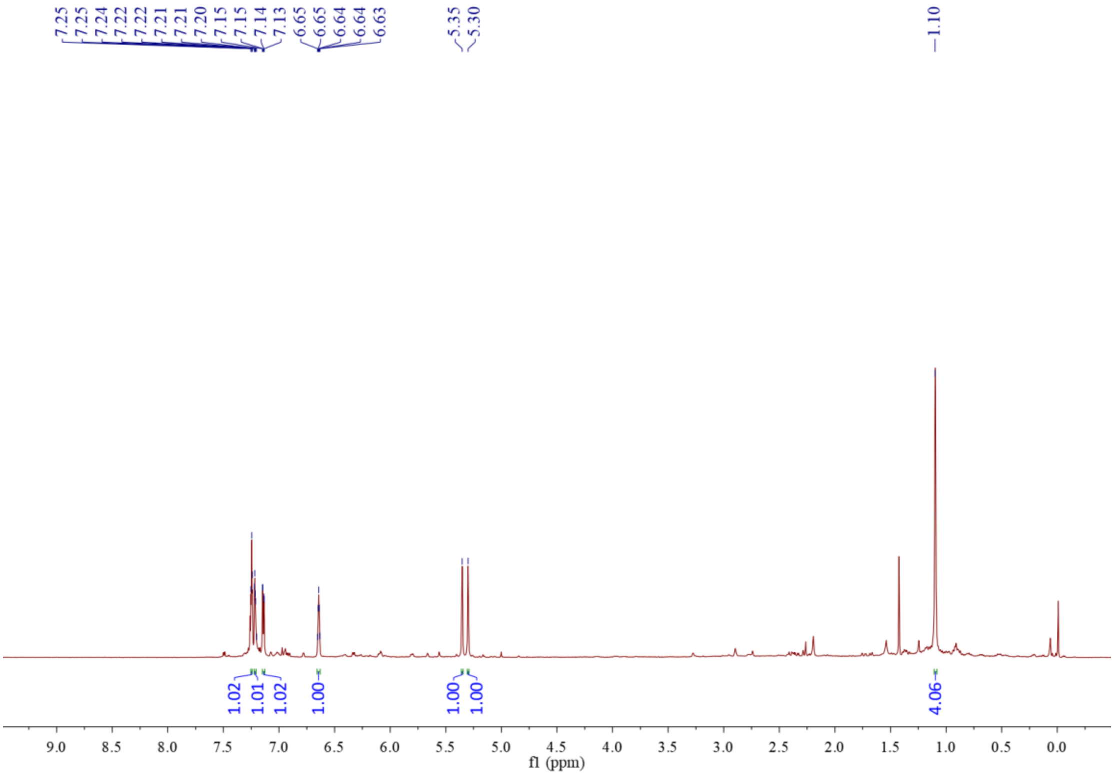
^{13}C NMR spectrum in $CDCl_3$:



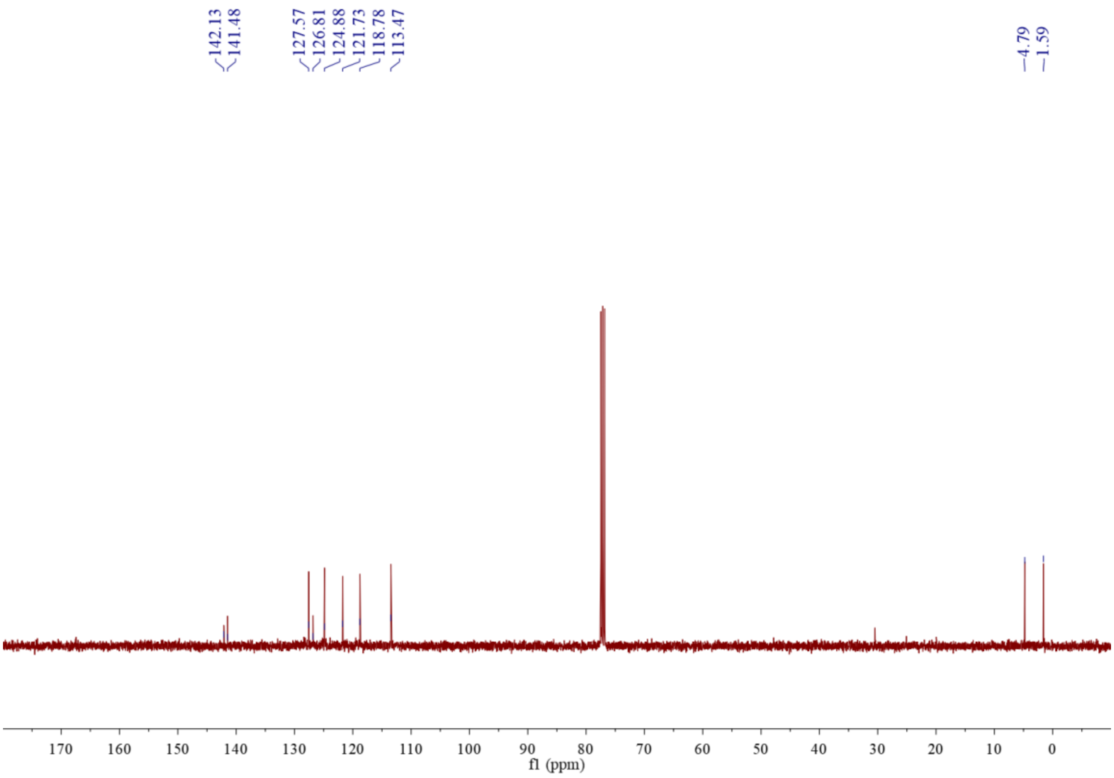


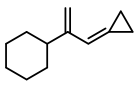
1l

^{1}H NMR spectrum in $CDCl_3$:



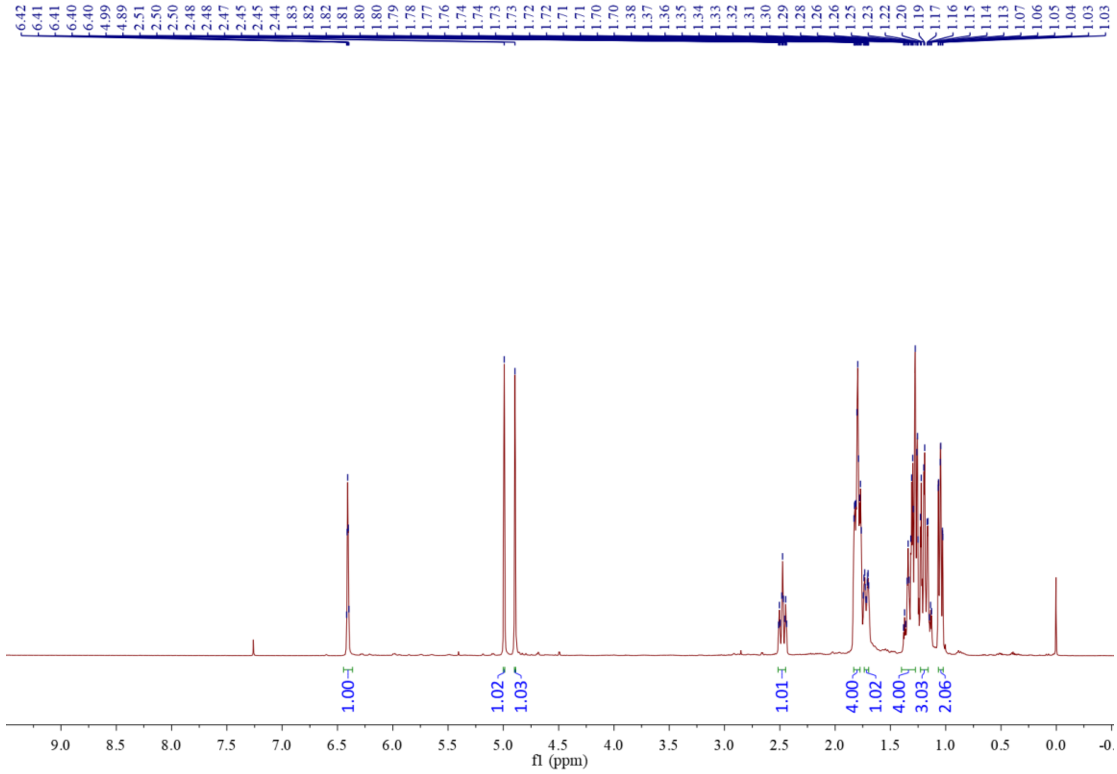
^{13}C NMR spectrum in $CDCl_3$:



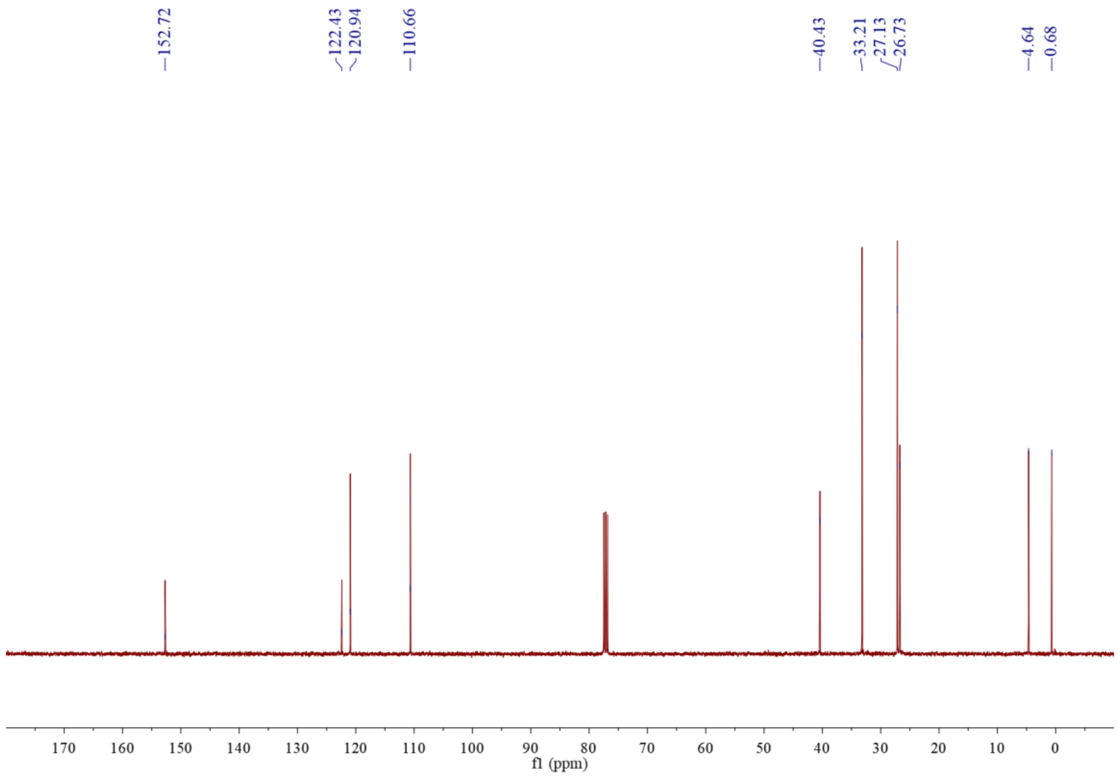


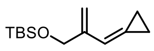
1m

^{1}H NMR spectrum in $CDCl_3$:



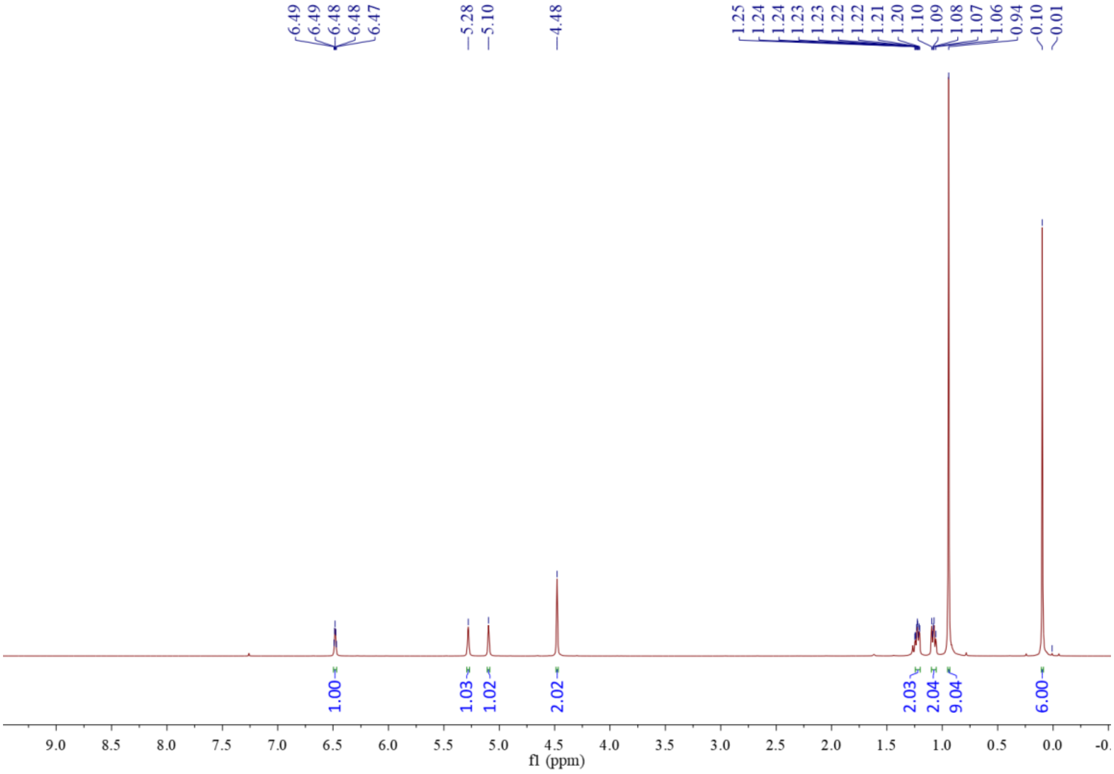
^{13}C NMR spectrum in $CDCl_3$:



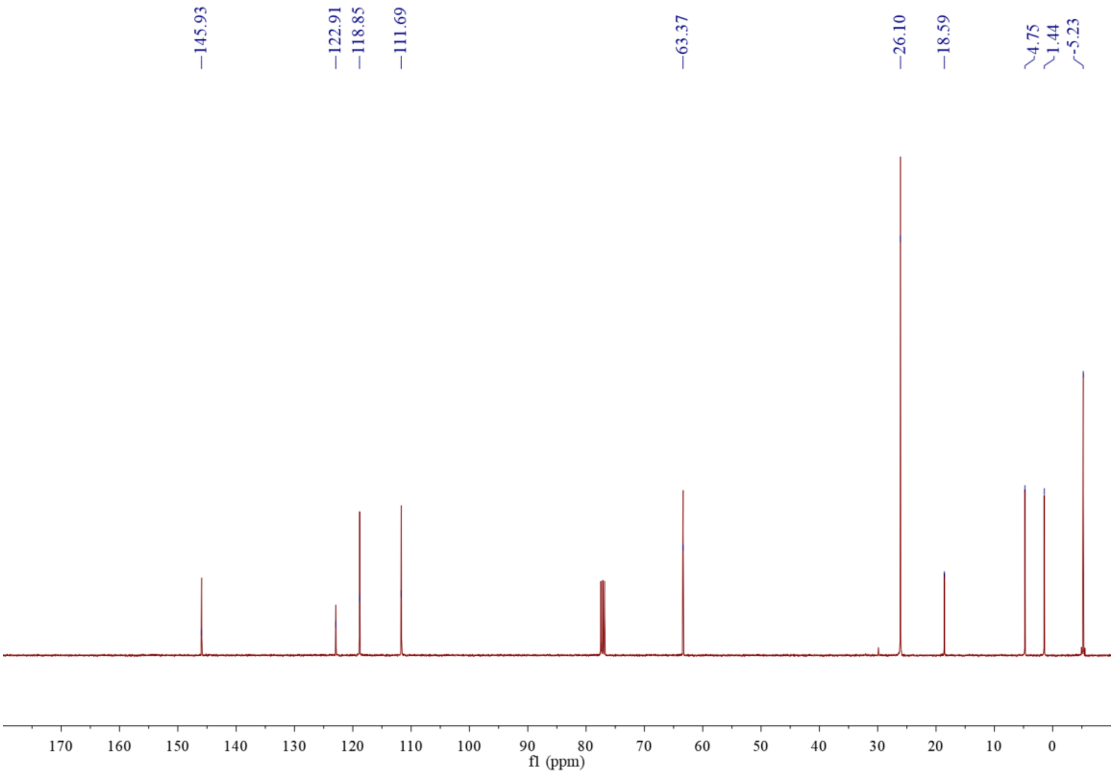


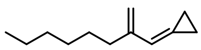
1n

¹H NMR spectrum in $CDCl_3$:



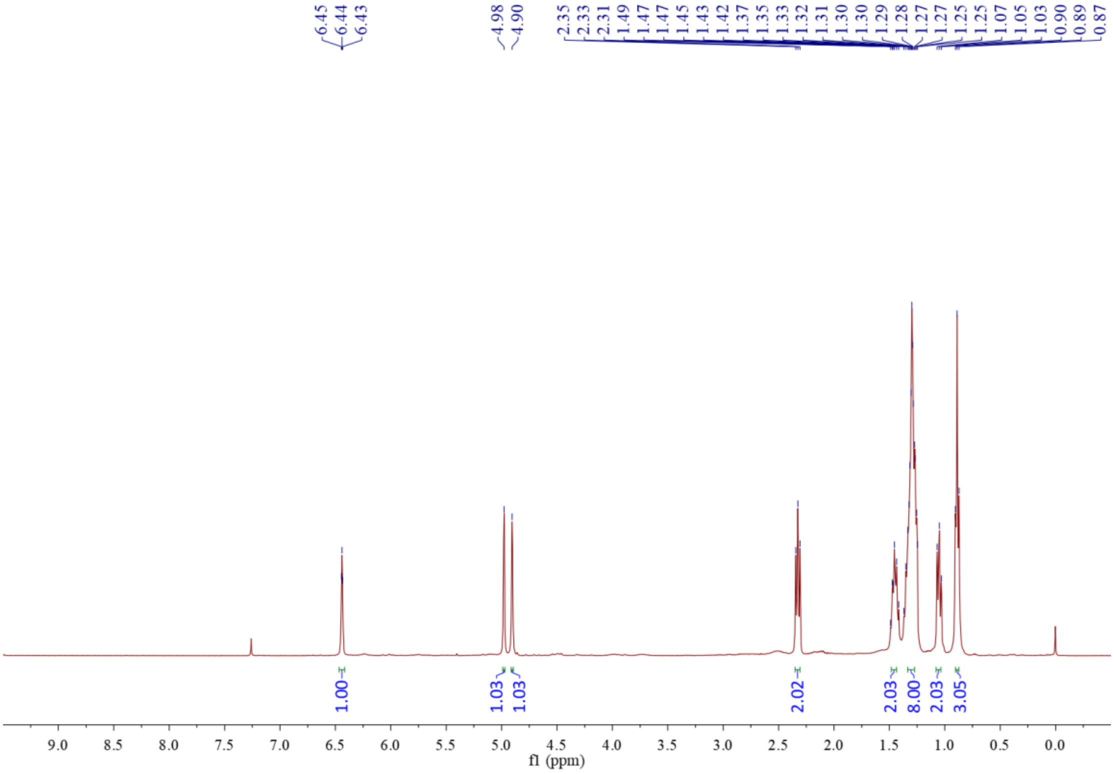
¹³C NMR spectrum in $CDCl_3$:



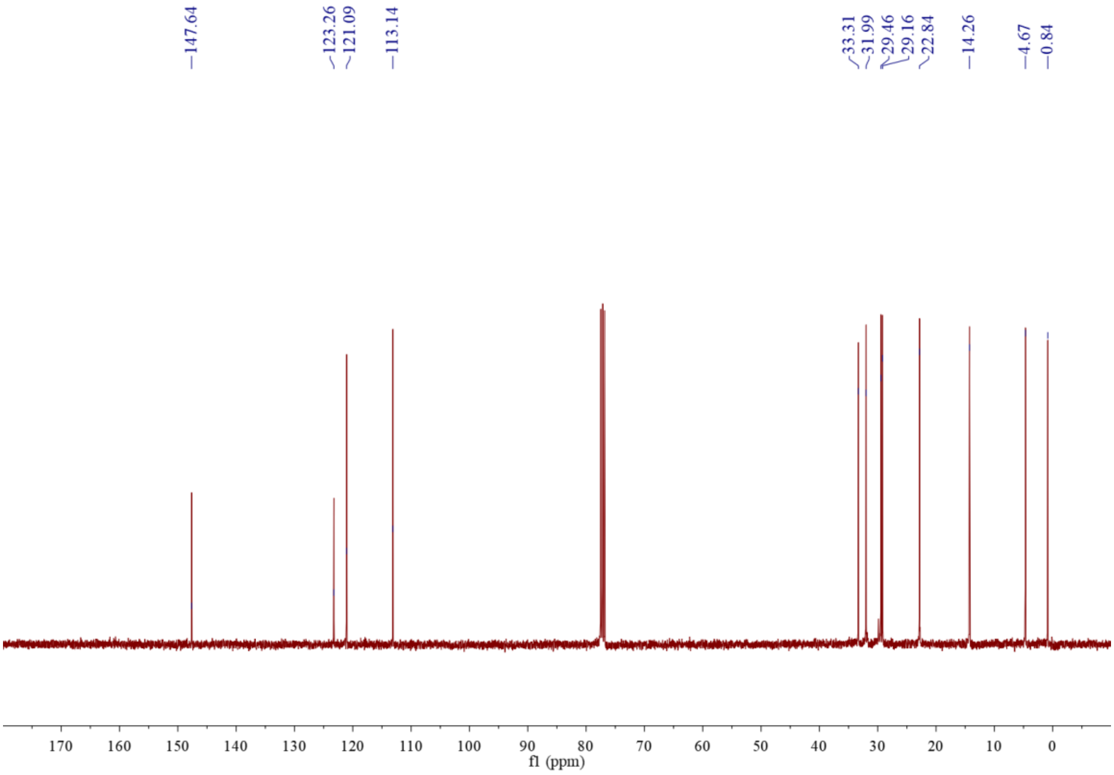


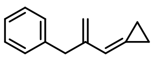
1o

^{1}H NMR spectrum in $CDCl_3$:



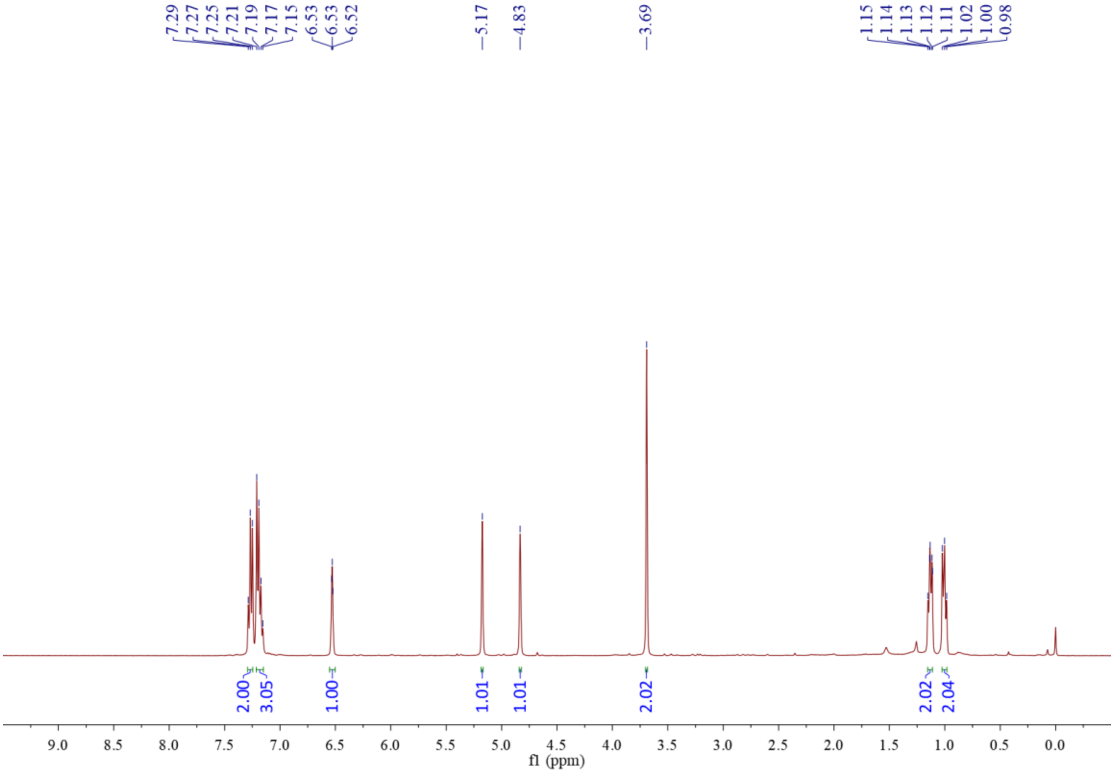
^{13}C NMR spectrum in $CDCl_3$:



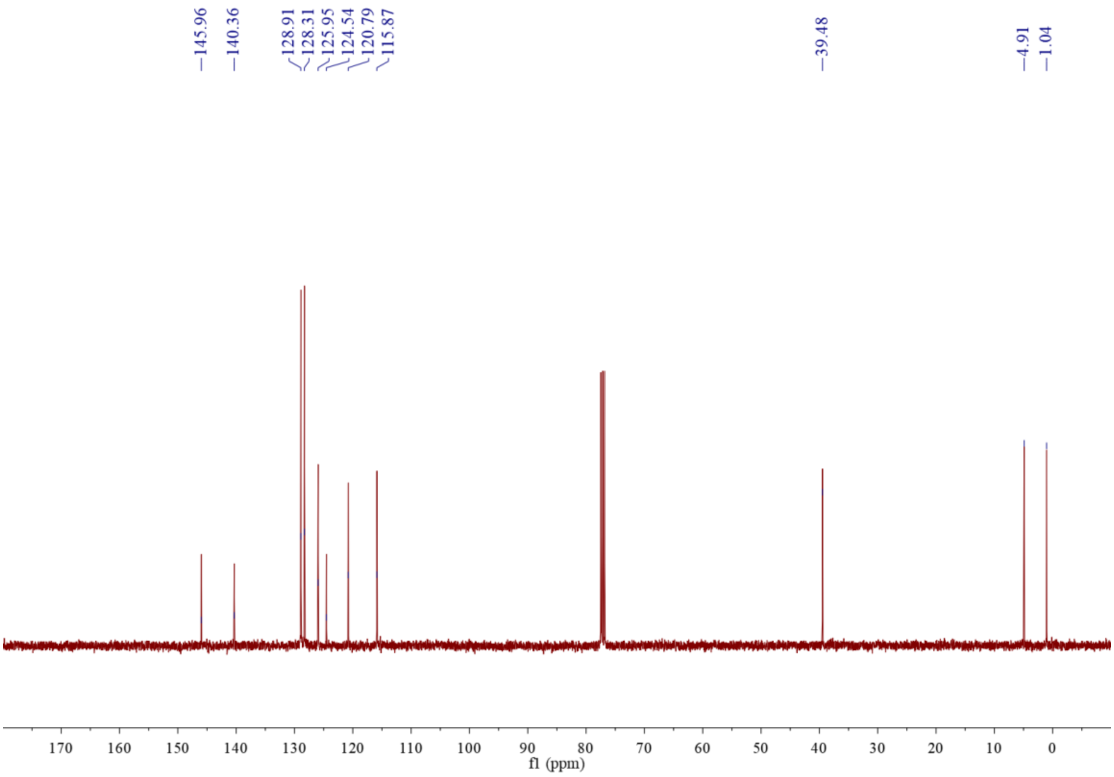


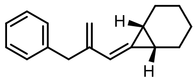
1p

^{1}H NMR spectrum in $CDCl_3$:



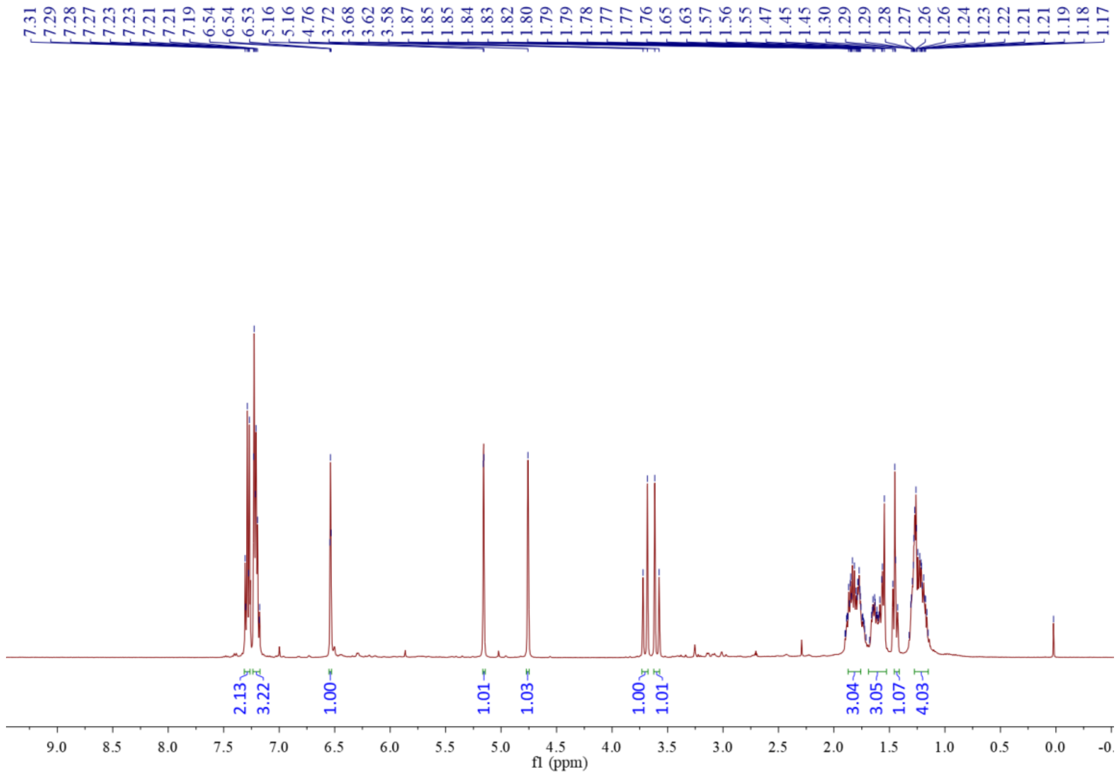
^{13}C NMR spectrum in $CDCl_3$:



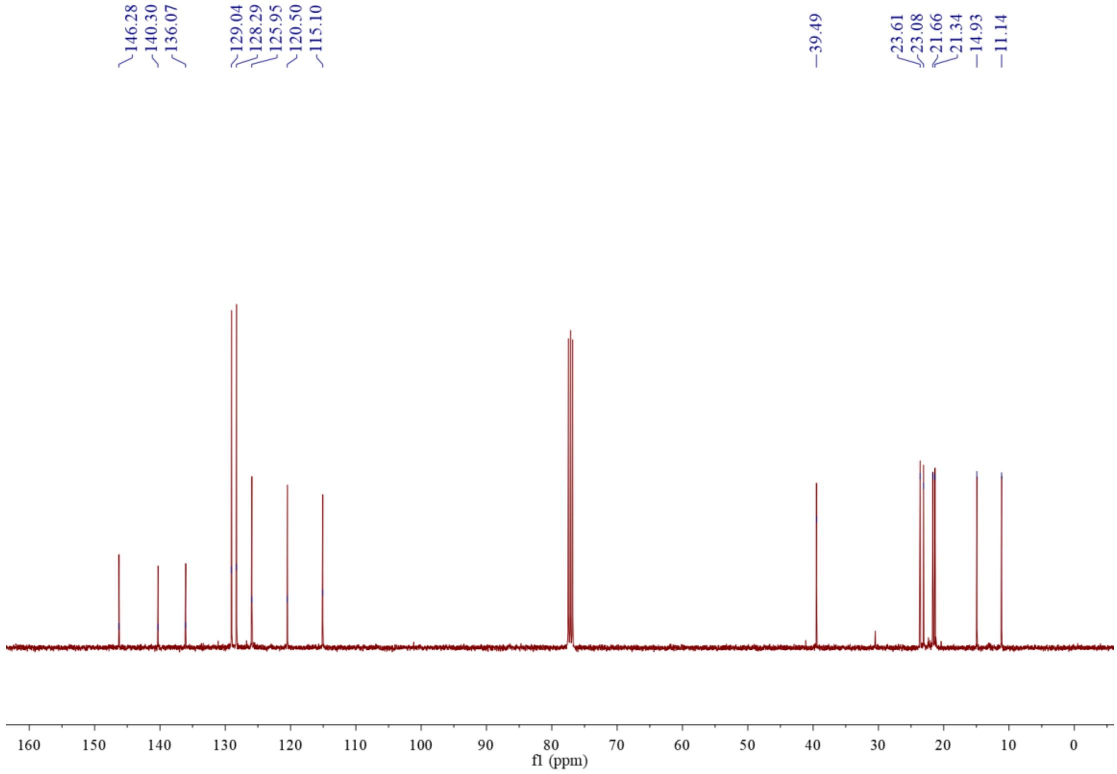


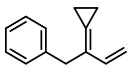
1q

[1]H NMR spectrum in $CDCl_3$:



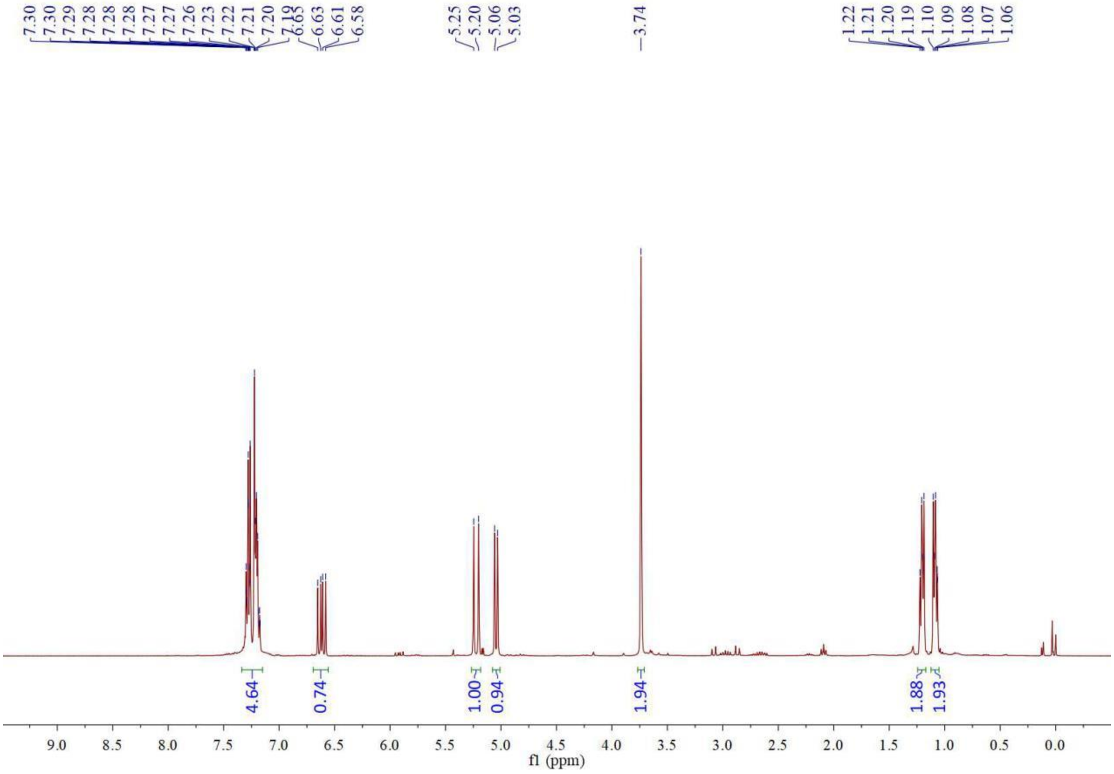
[13]C NMR spectrum in $CDCl_3$:



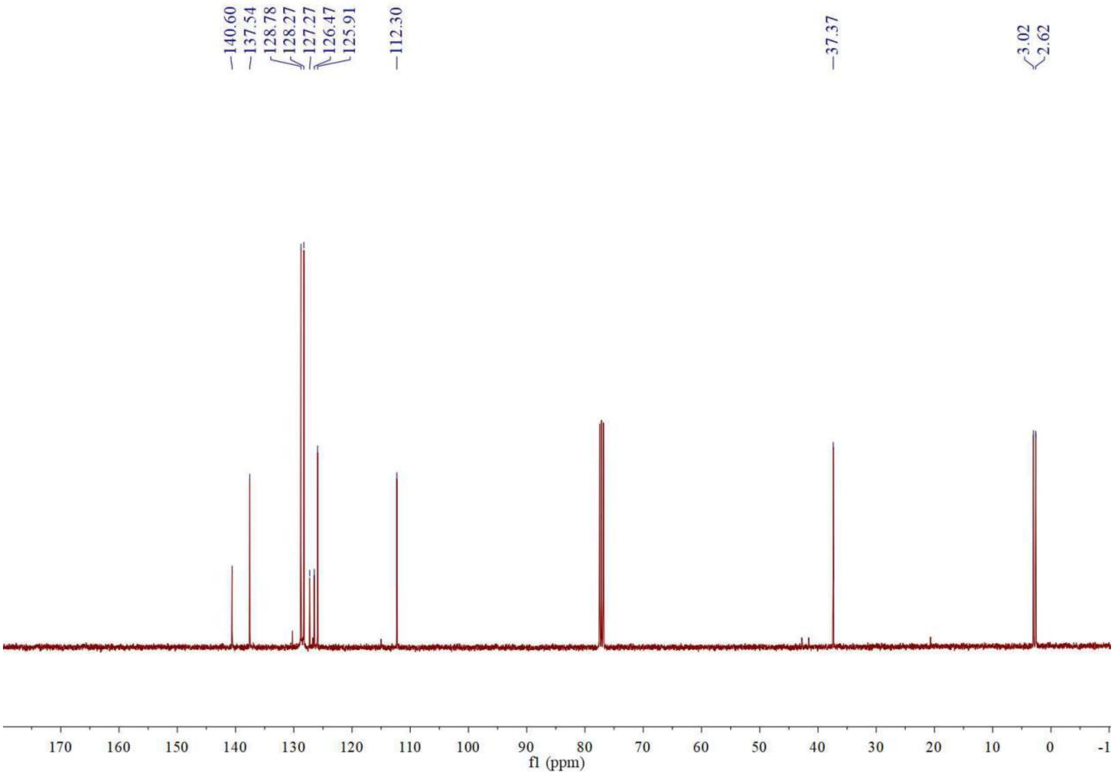


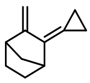
1r

^{1}H NMR spectrum in $CDCl_3$:



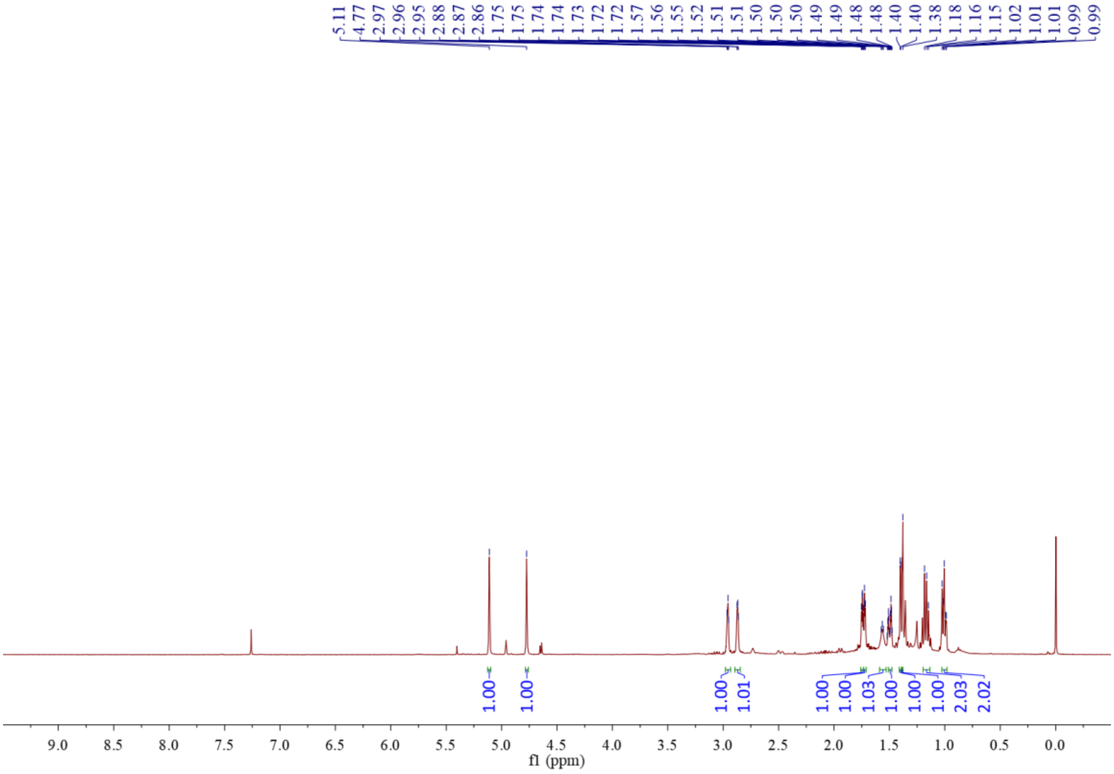
^{13}C NMR spectrum in $CDCl_3$:



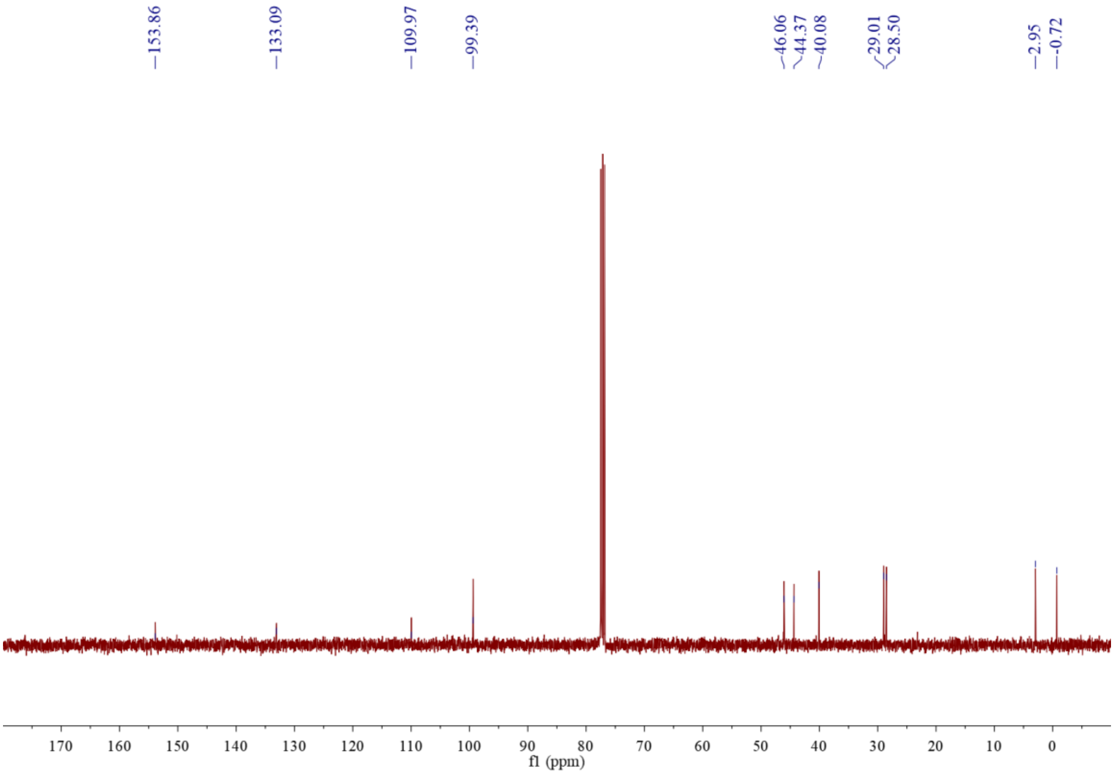


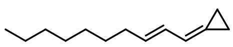
1s

^{1}H NMR spectrum in $CDCl_3$:



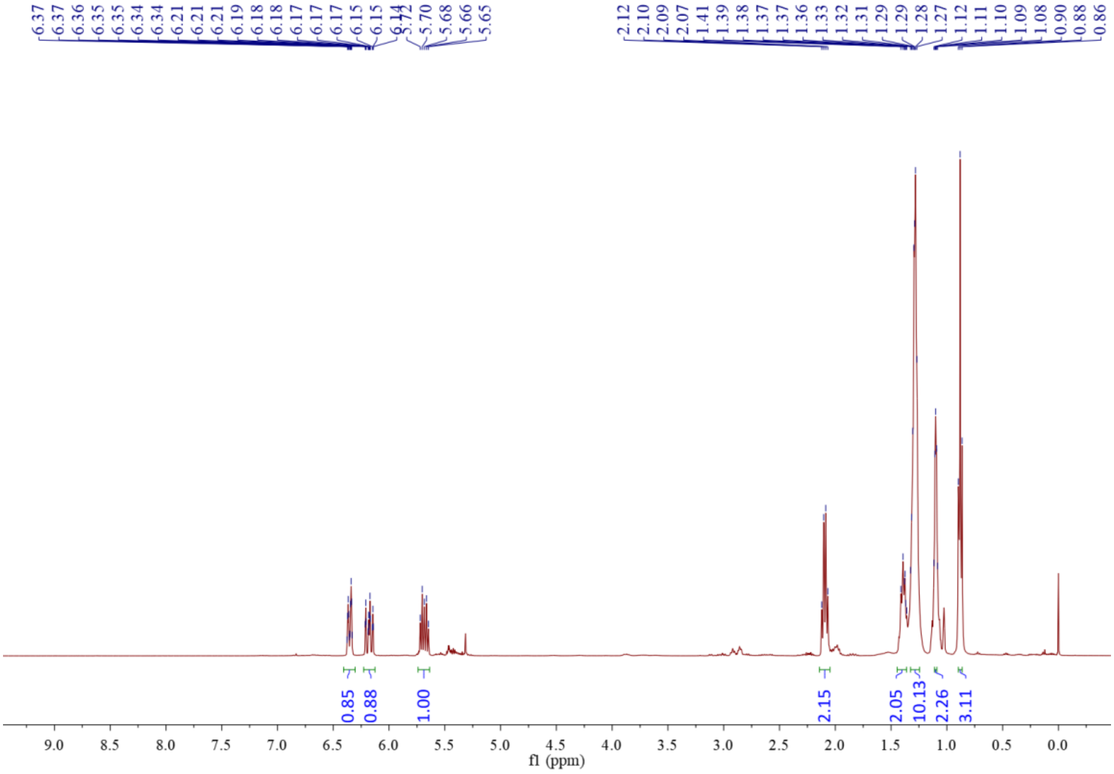
^{13}C NMR spectrum in $CDCl_3$:



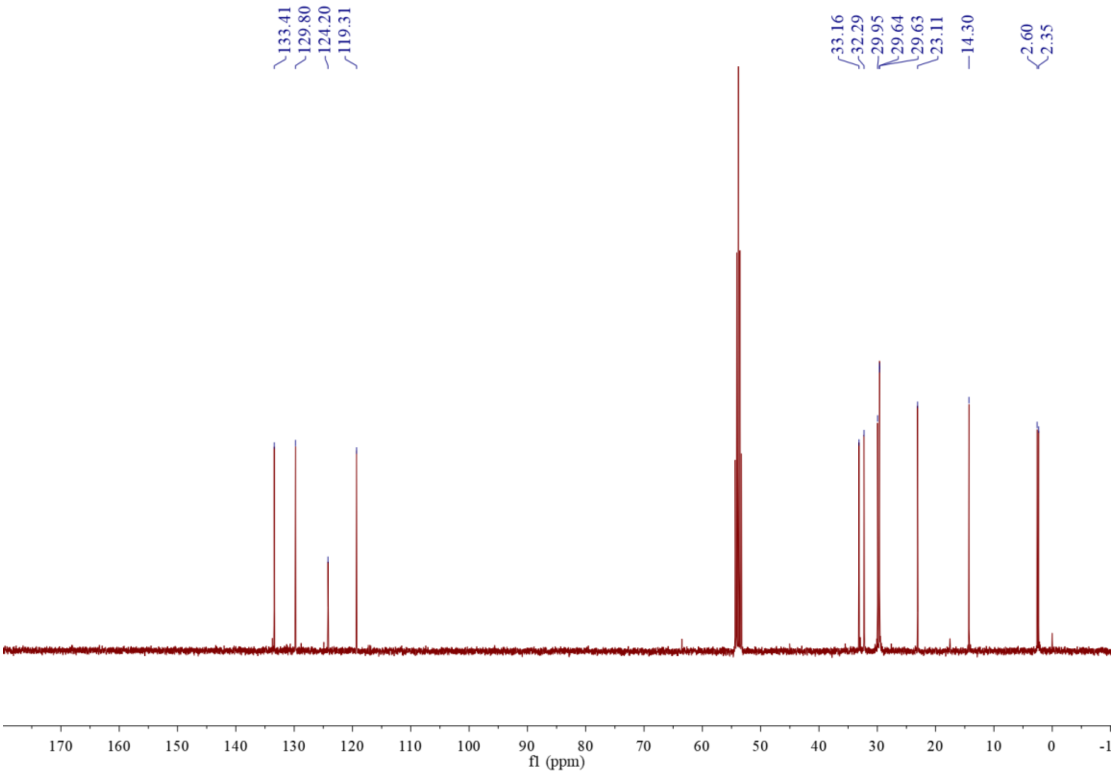


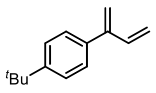
1t

^{1}H NMR spectrum in CD_2Cl_2:



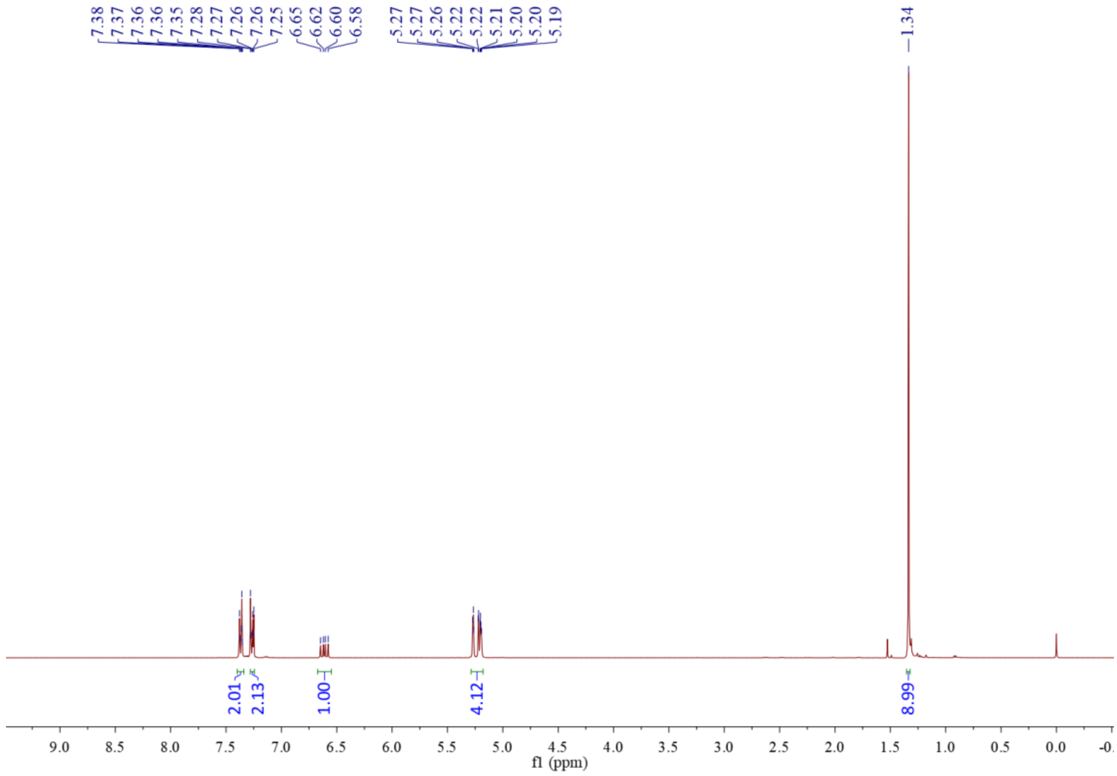
^{13}C NMR spectrum in CD_2Cl_2:



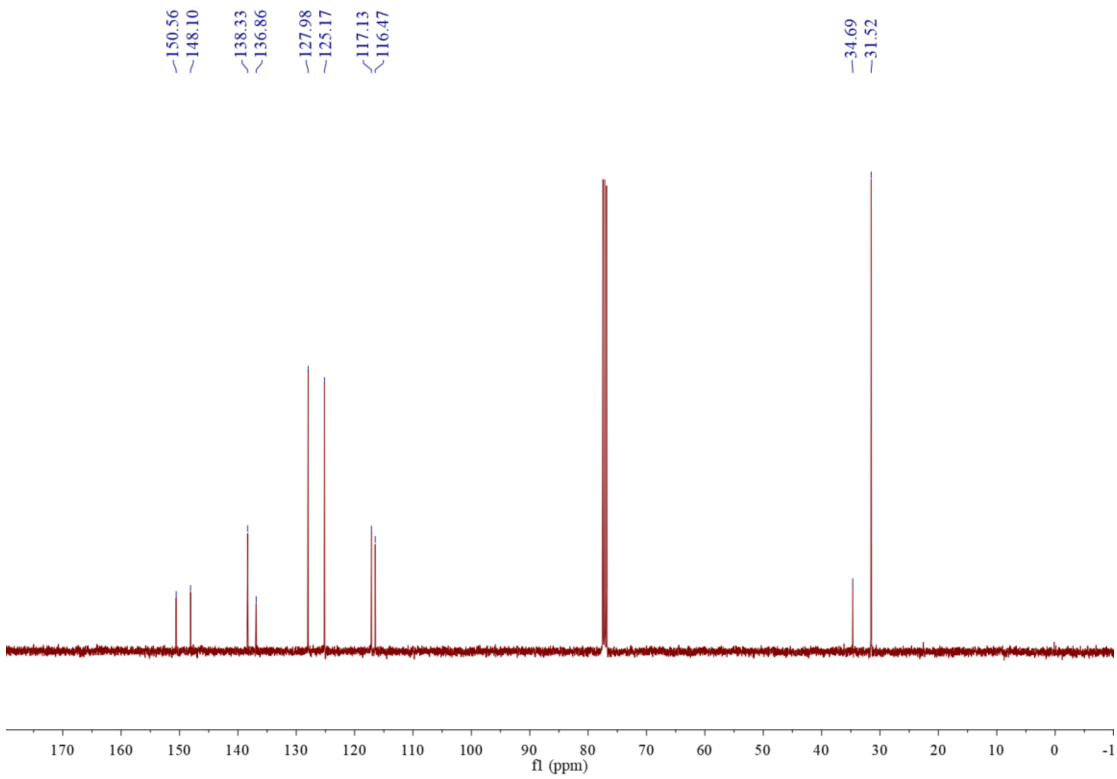


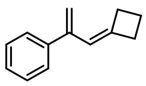
3

^{1}H NMR spectrum in $CDCl_3$:



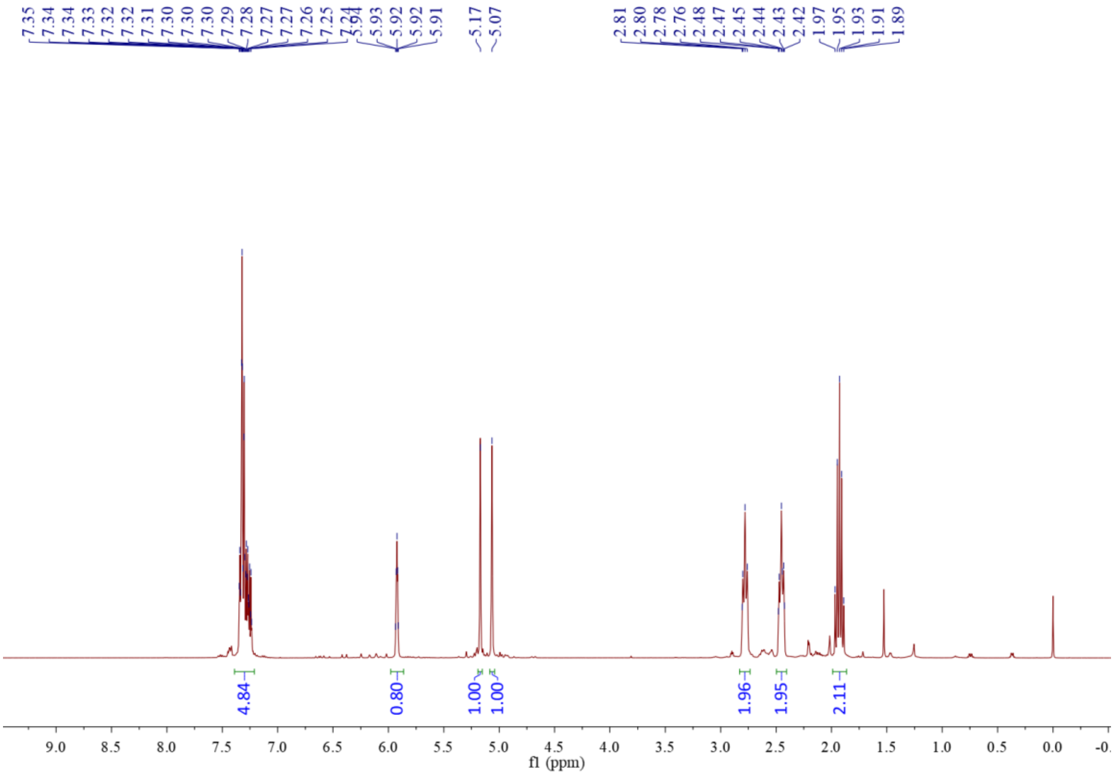
^{13}C NMR spectrum in $CDCl_3$:



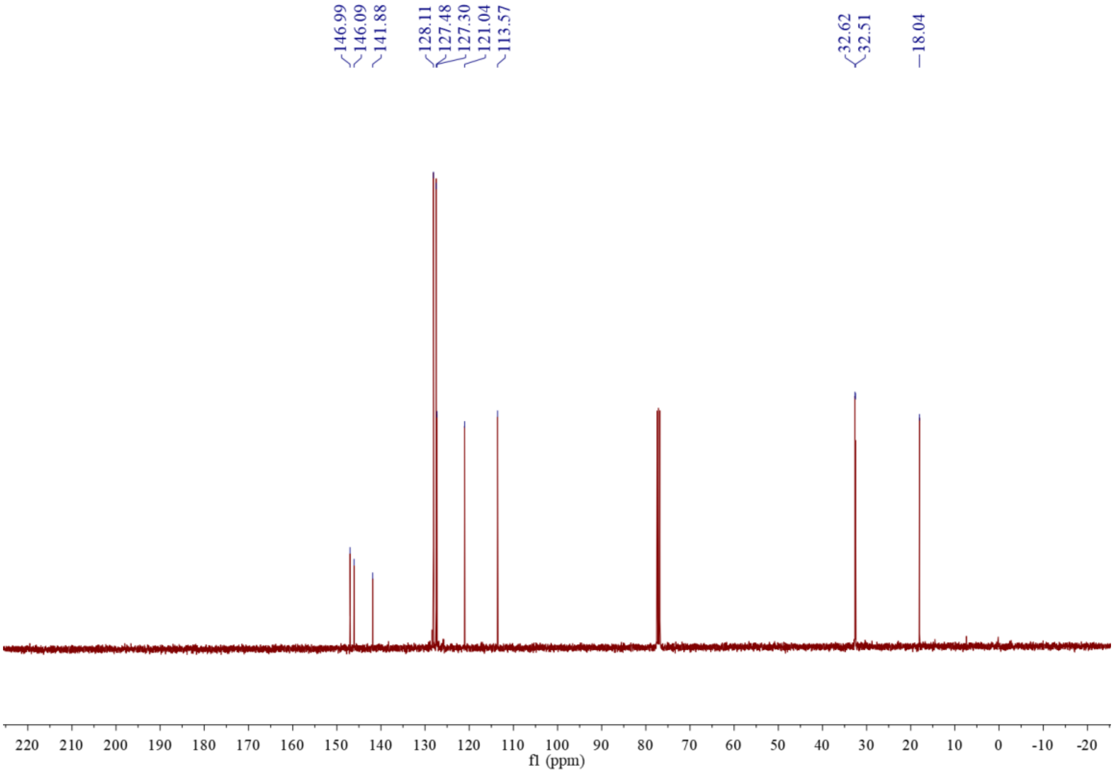


4

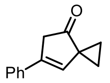
[1]H NMR spectrum in $CDCl_3$:



[13]C NMR spectrum in $CDCl_3$:

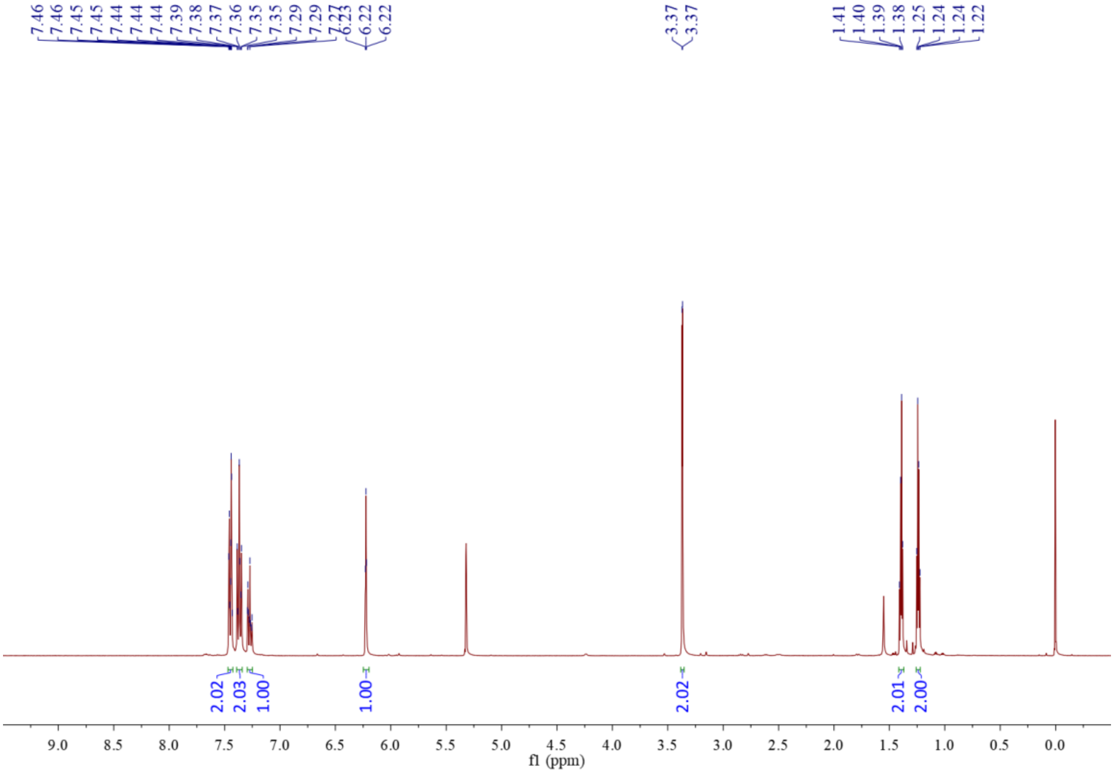


NMR spectra for [4+1] cycloadducts

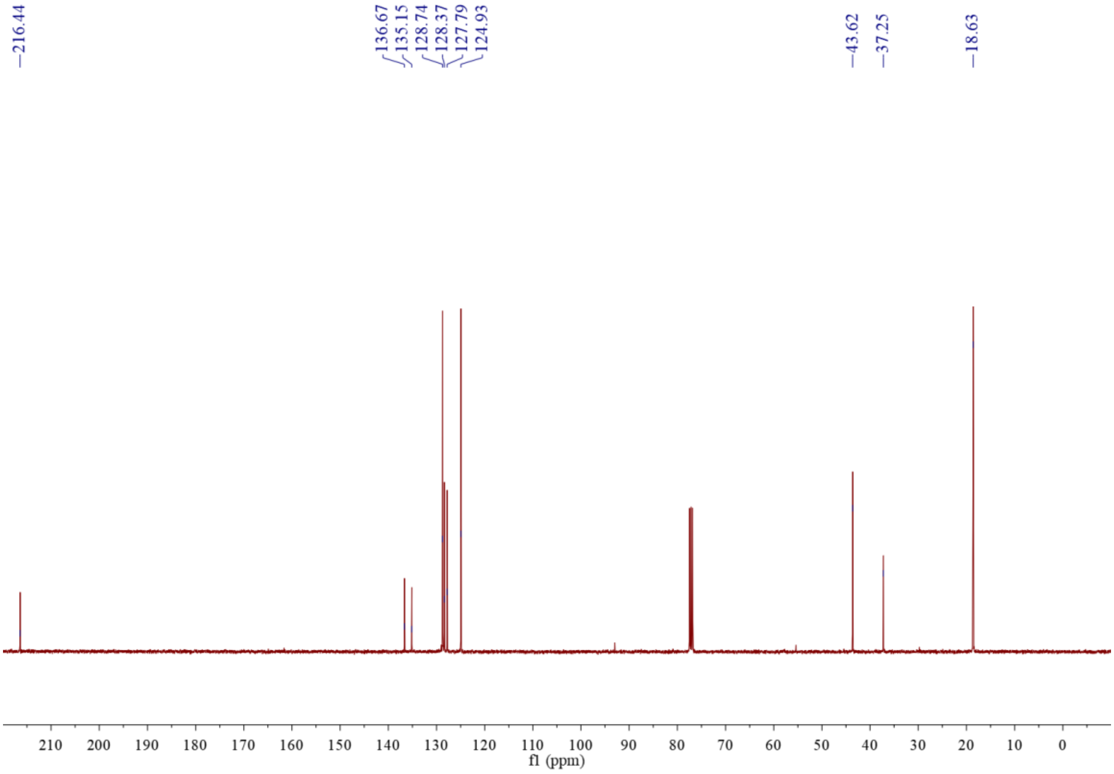


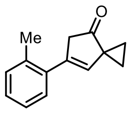
2a

[1]H NMR spectrum in CD_2Cl_2:



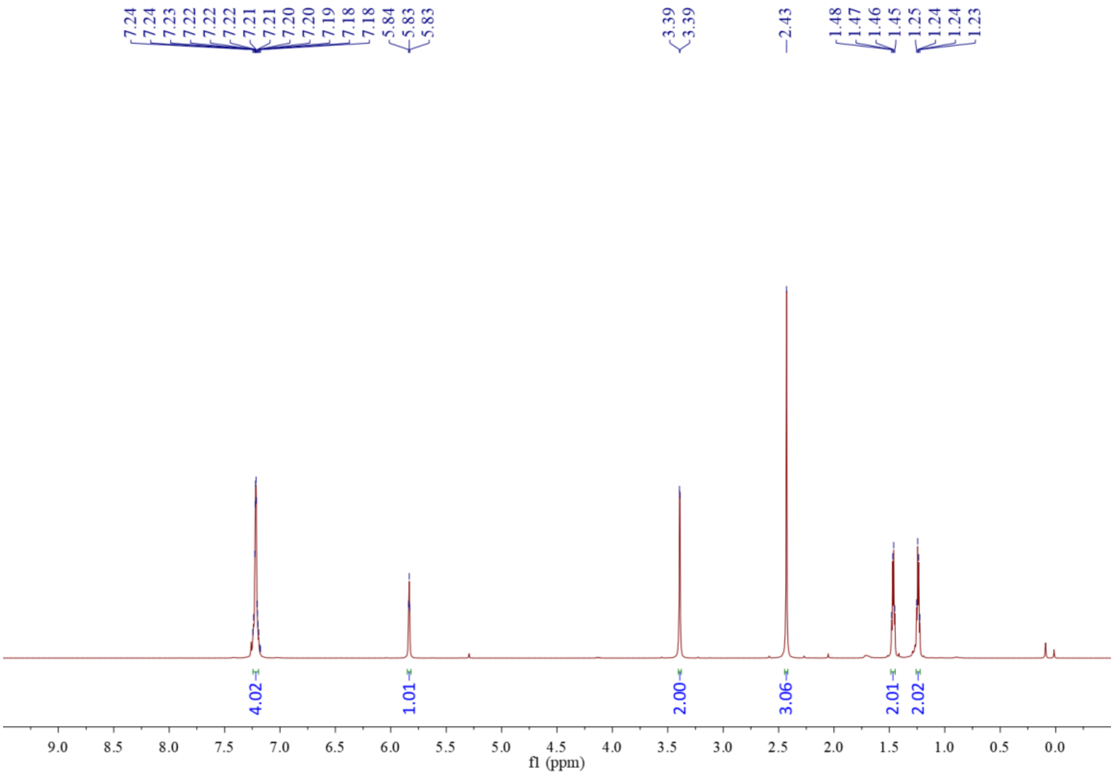
[13]C NMR spectrum in $CDCl_3$:



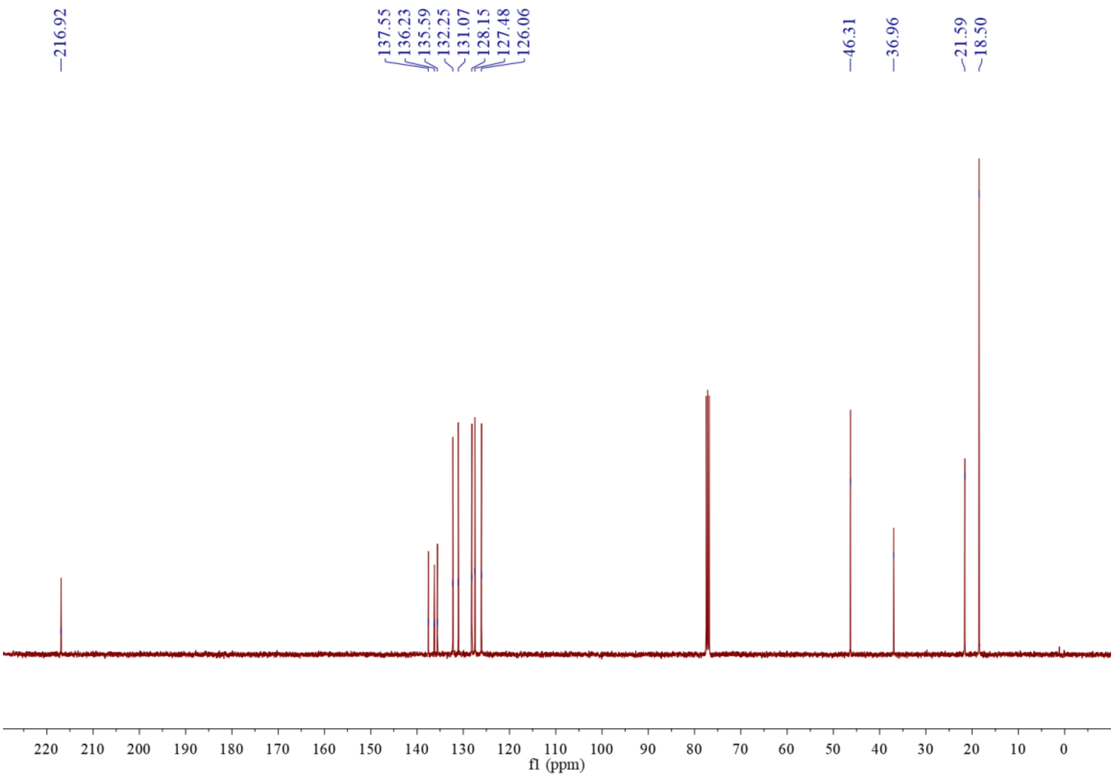


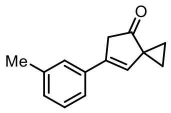
2b

^1H NMR spectrum in $CDCl_3$:



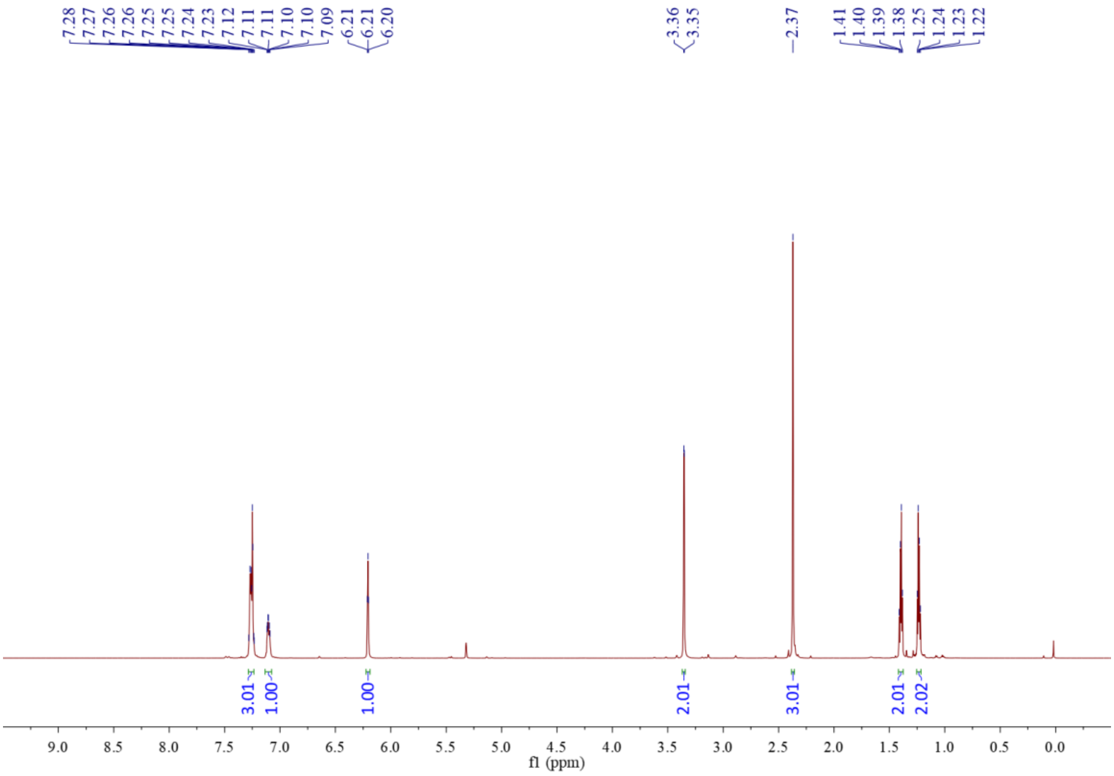
^{13}C NMR spectrum in $CDCl_3$:



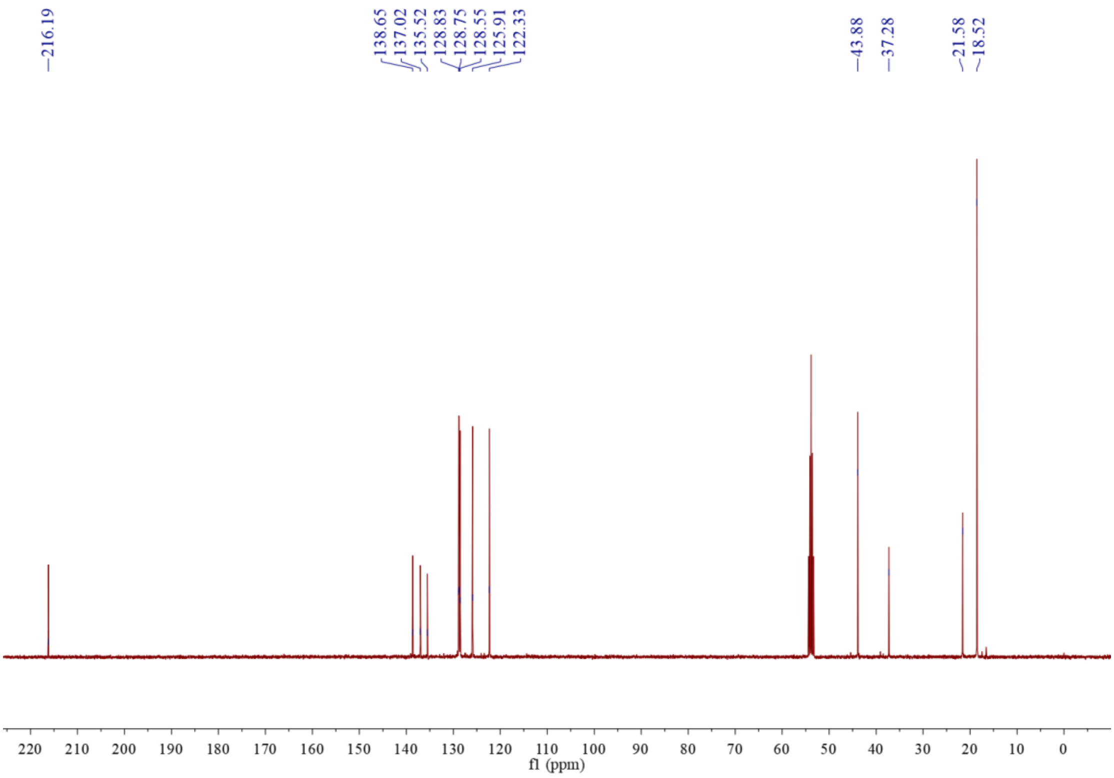


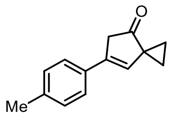
2c

^{1}H NMR spectrum in CD_2Cl_2:



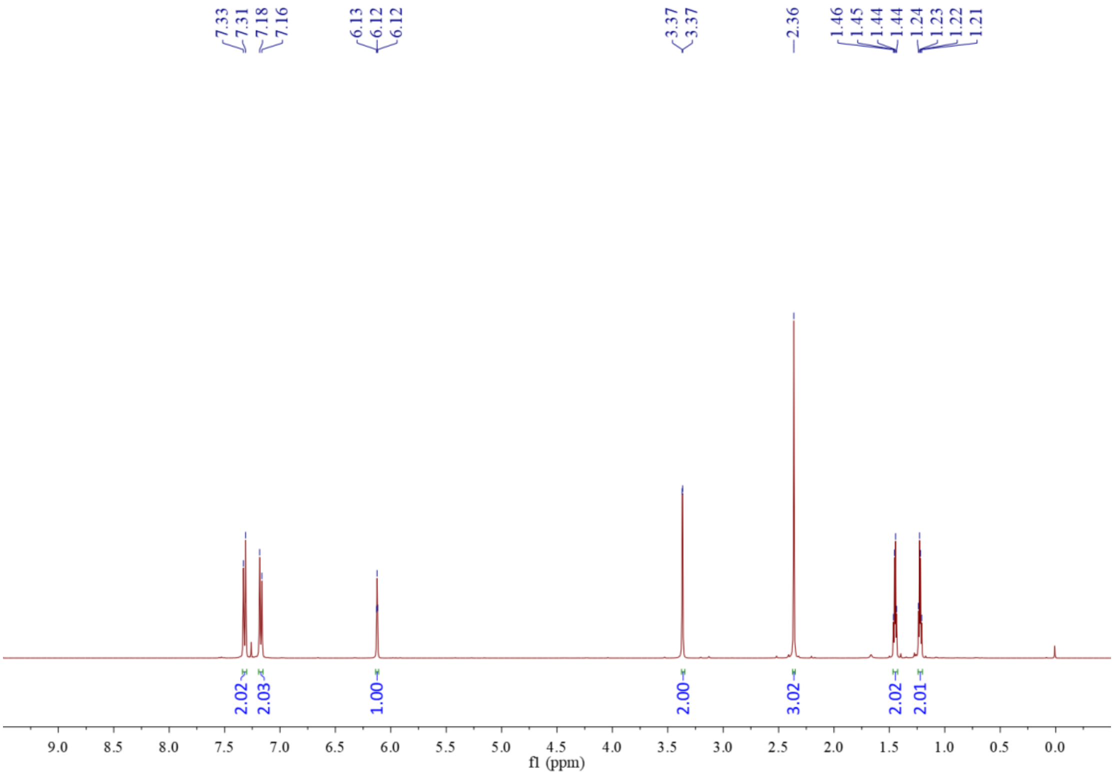
^{13}C NMR spectrum in CD_2Cl_2:



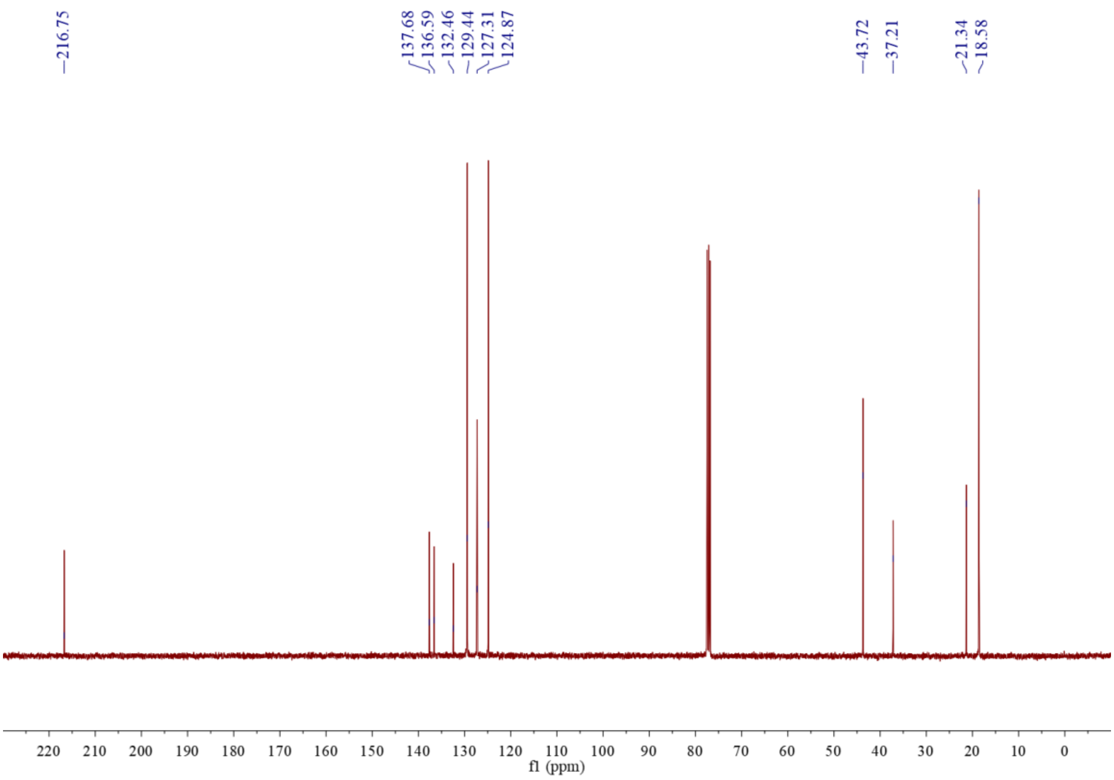


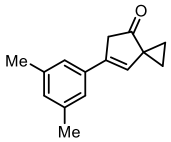
2d

^{1}H NMR spectrum in $CDCl_3$:



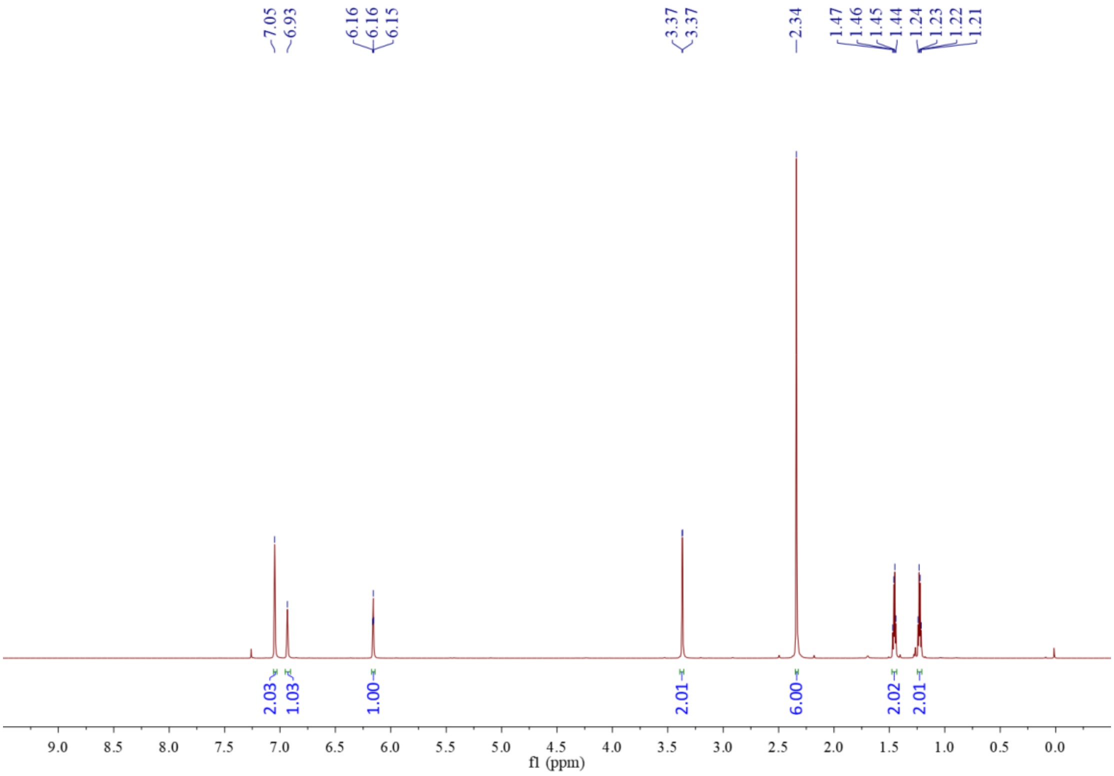
^{13}C NMR spectrum in $CDCl_3$:



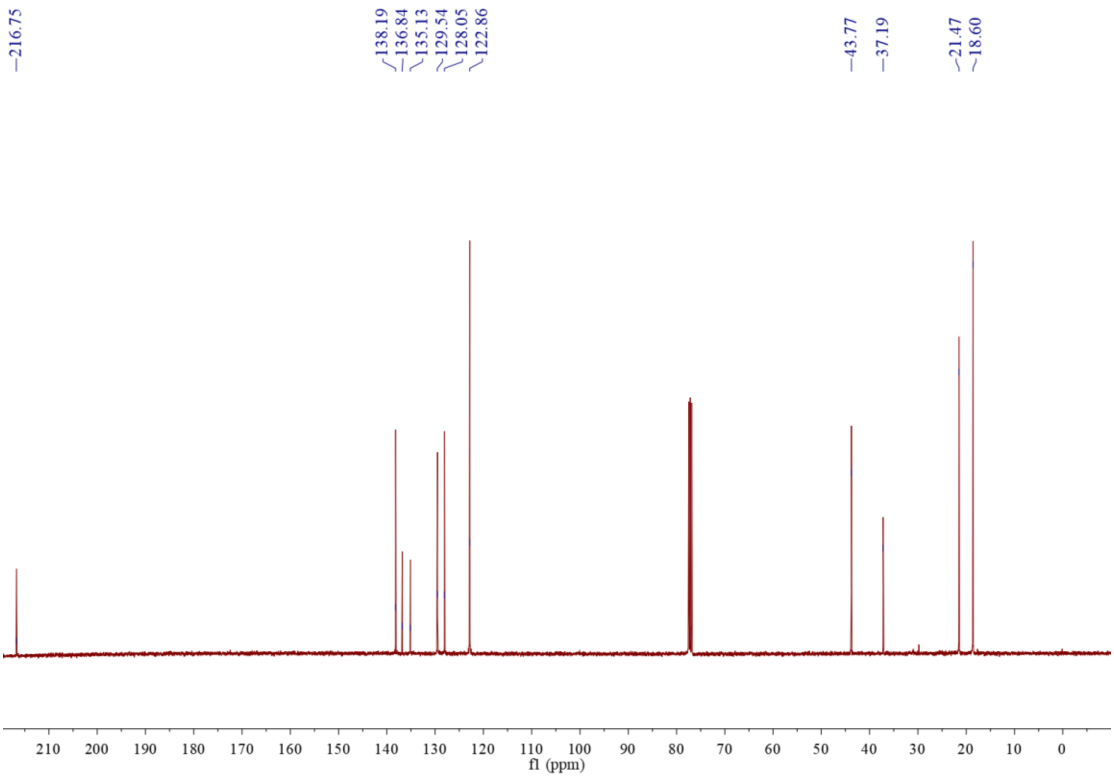


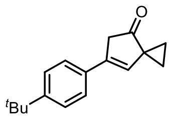
2e

^{1}H NMR spectrum in $CDCl_3$:



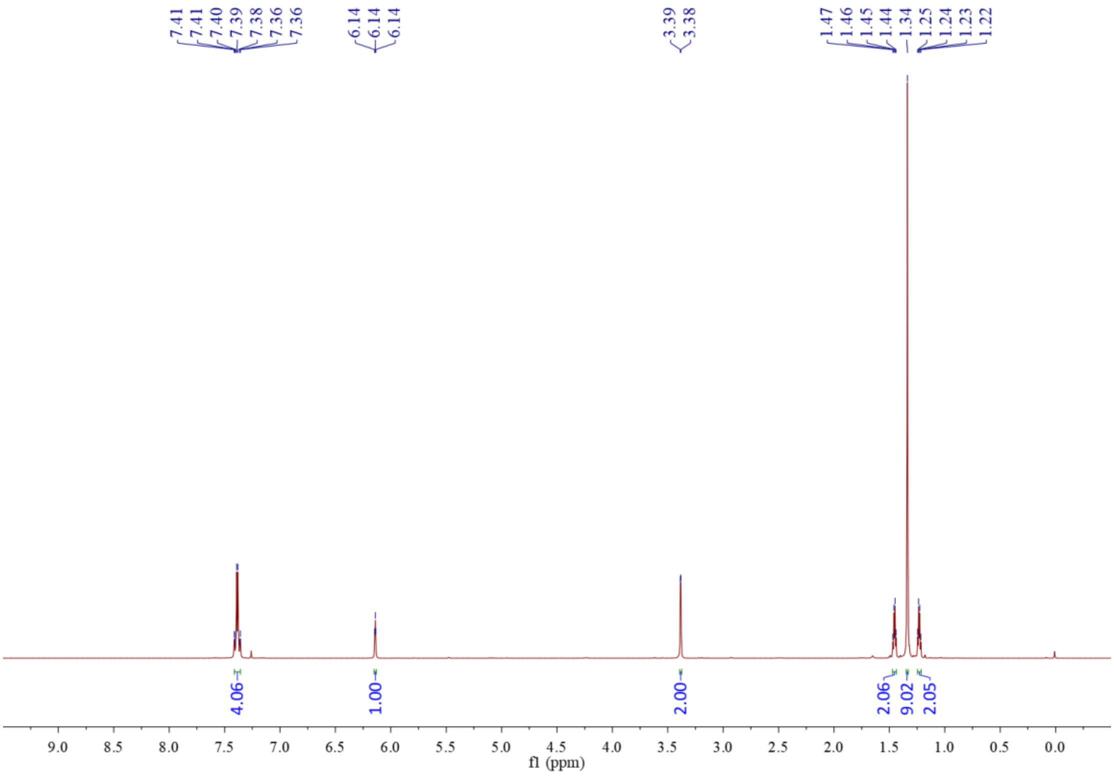
^{13}C NMR spectrum in $CDCl_3$:



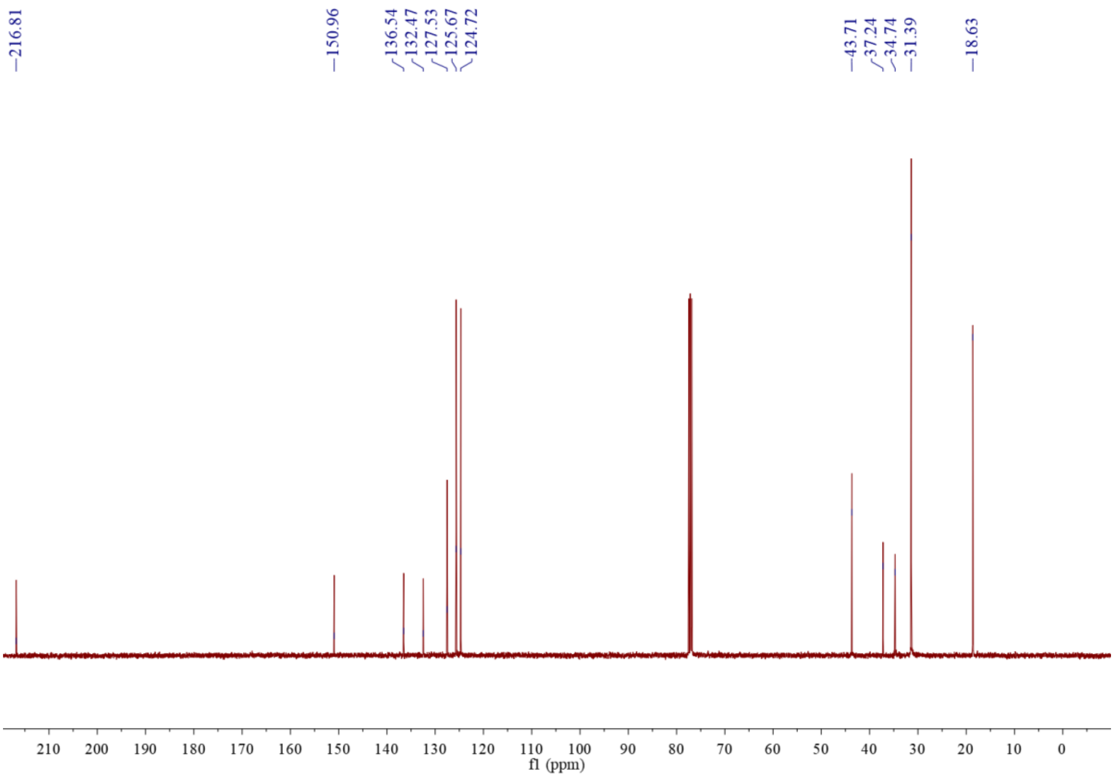


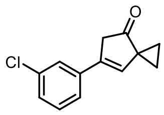
2f

^{1}H NMR spectrum in $CDCl_3$:



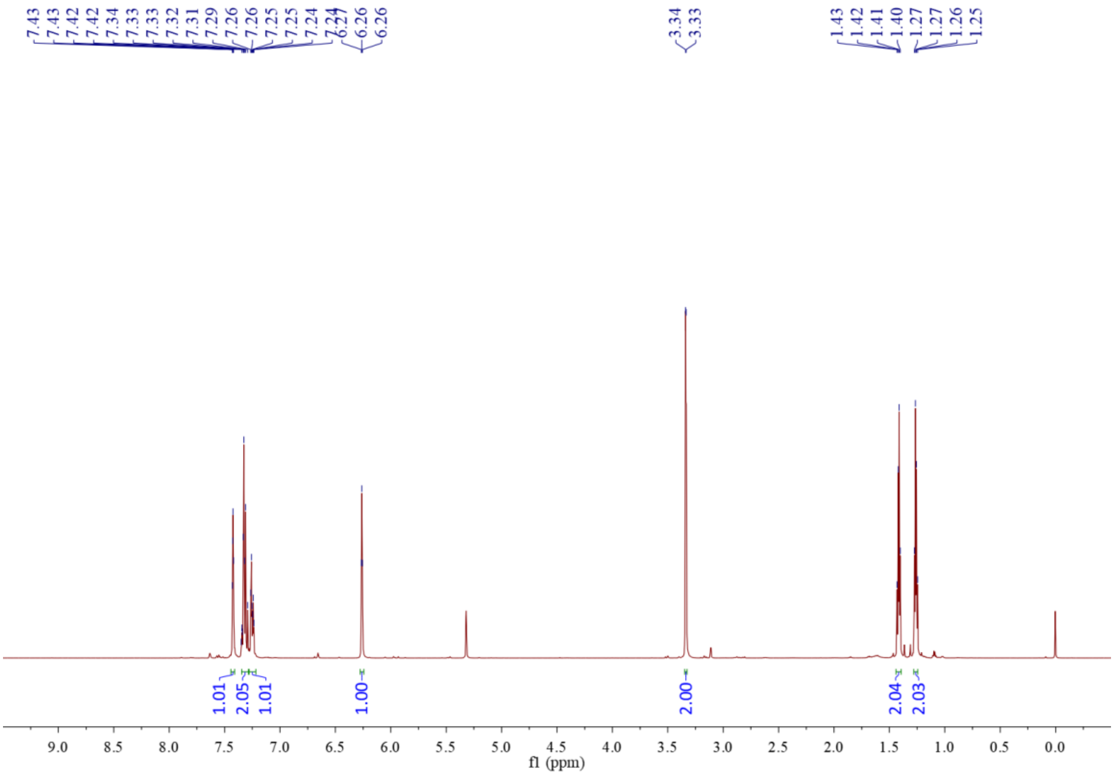
^{13}C NMR spectrum in $CDCl_3$:



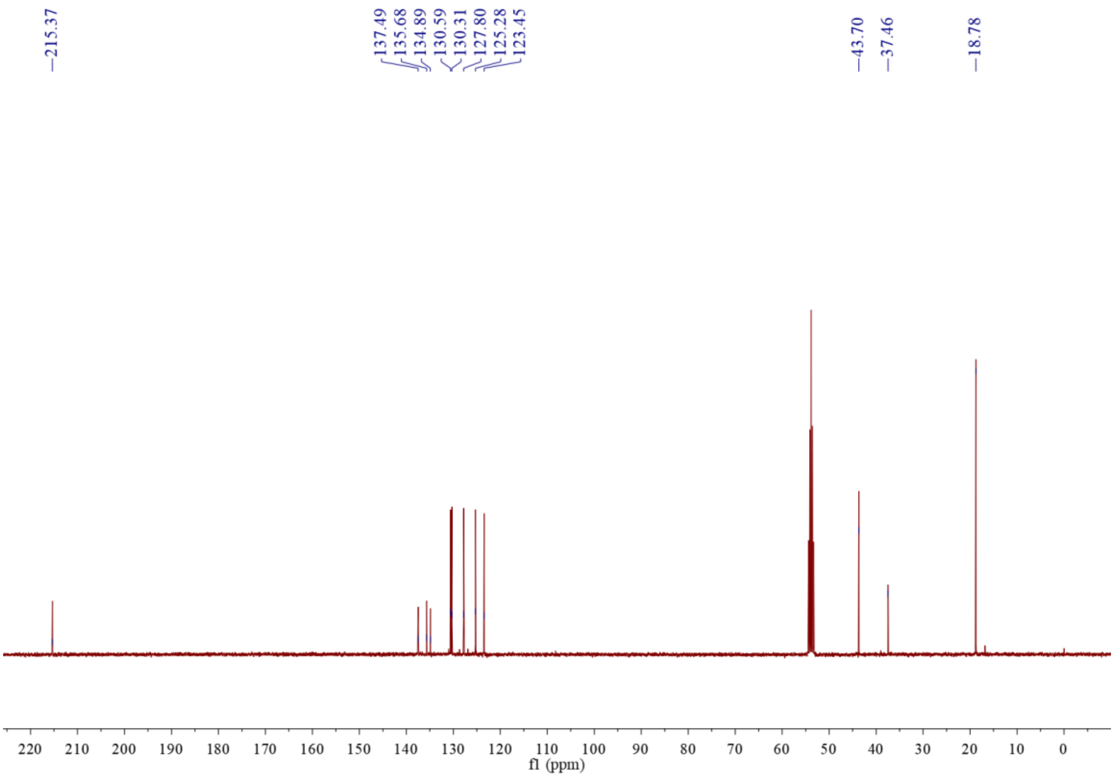


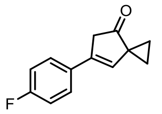
2g

^{1}H NMR spectrum in CD_2Cl_2:



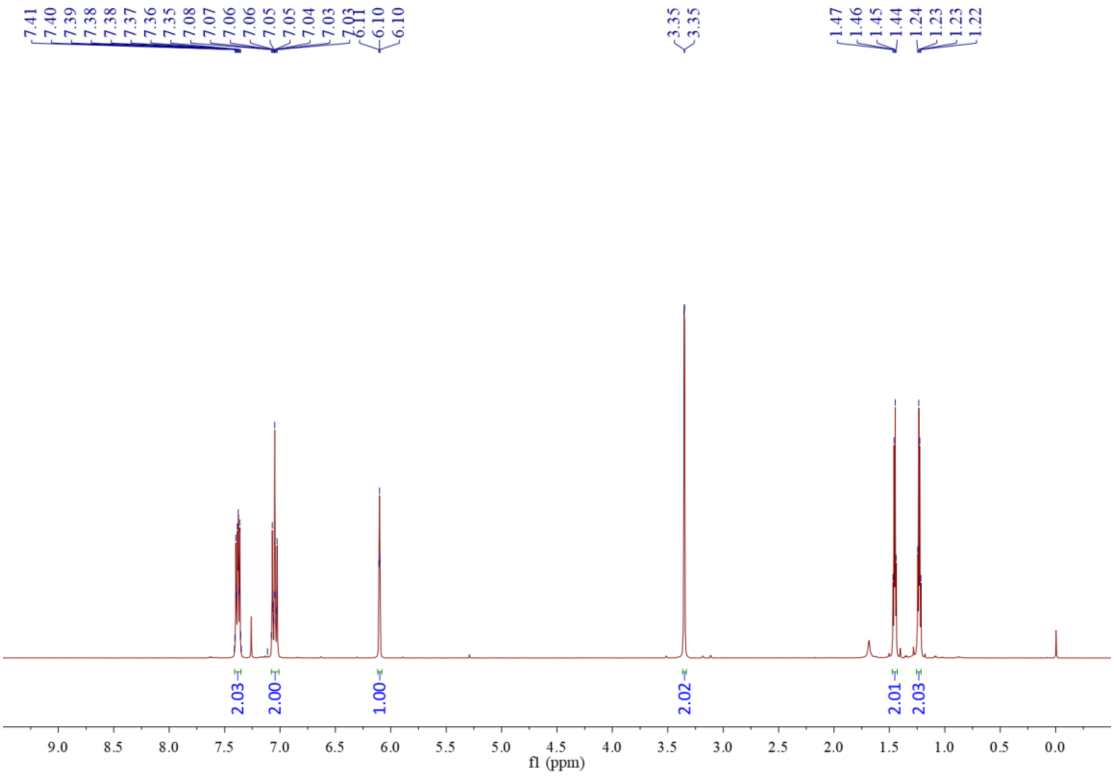
^{13}C NMR spectrum in CD_2Cl_2:



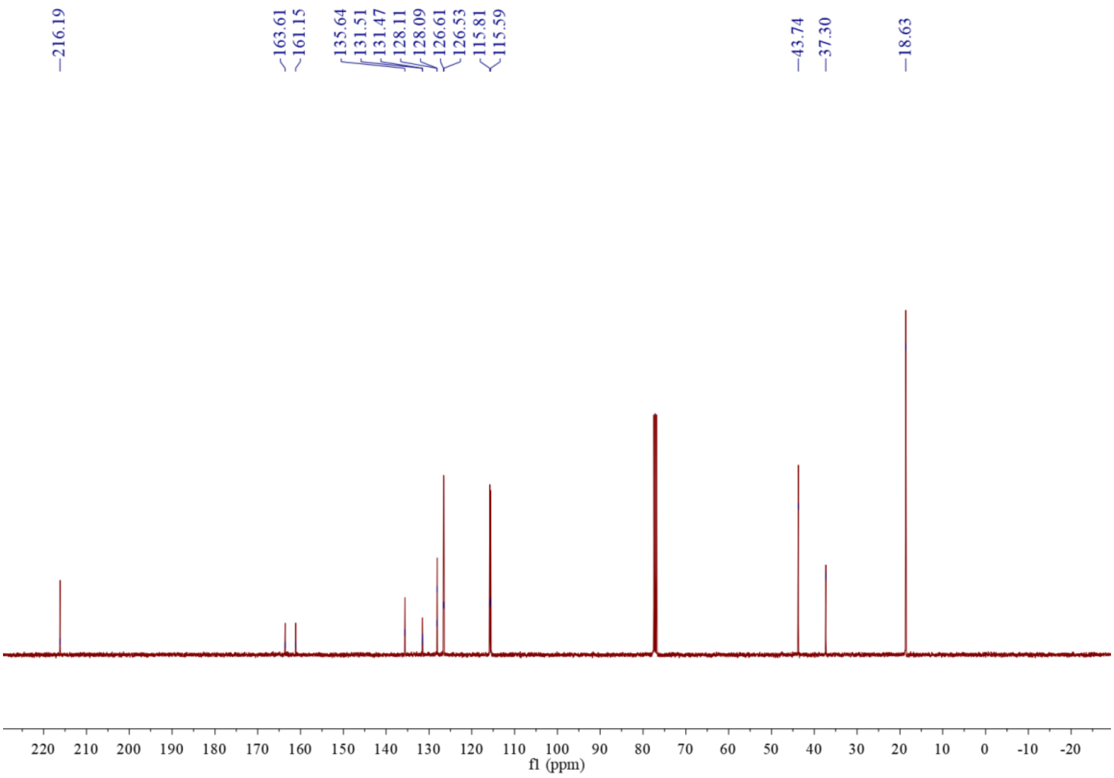


2h

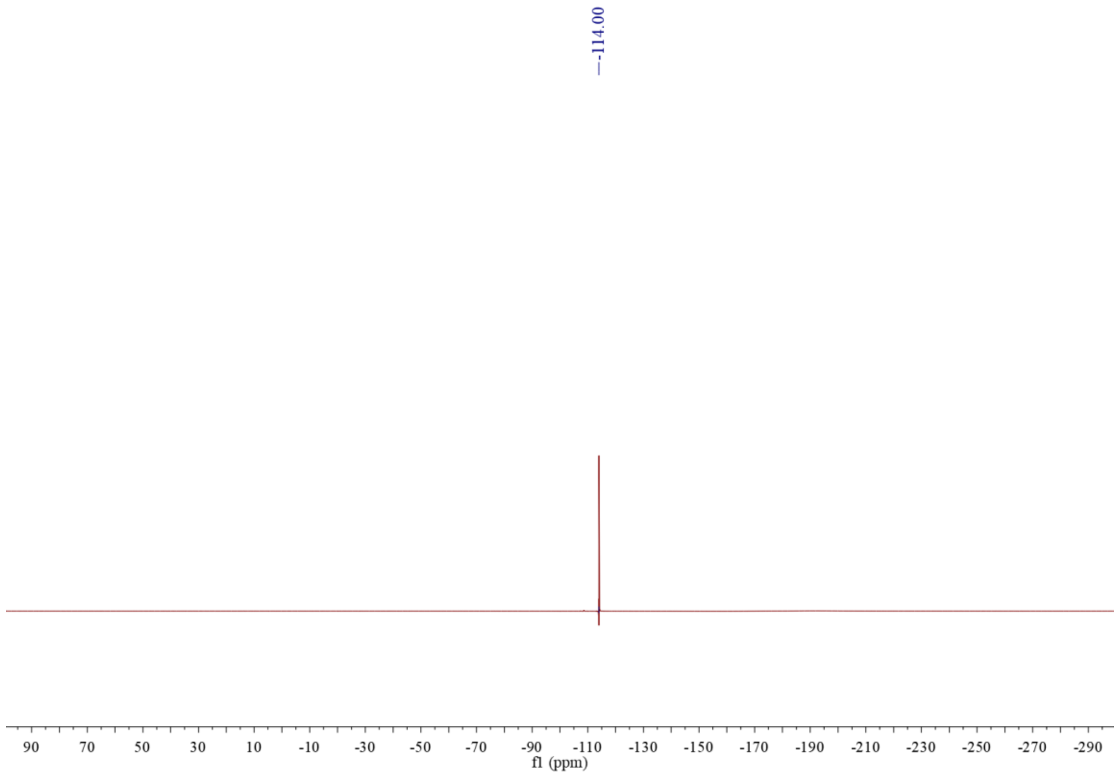
^{1}H NMR spectrum in $CDCl_3$:

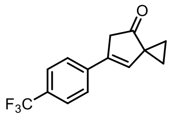


^{13}C NMR spectrum in $CDCl_3$:



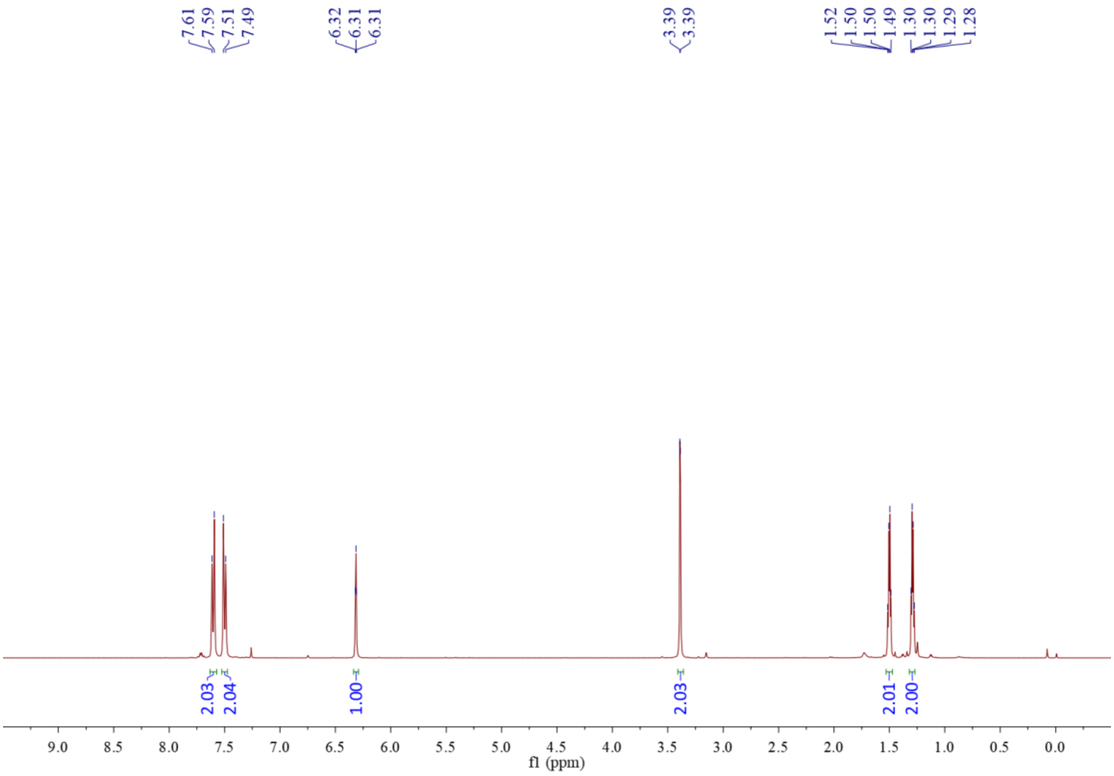
^{19}F NMR spectrum in $CDCl_3$:



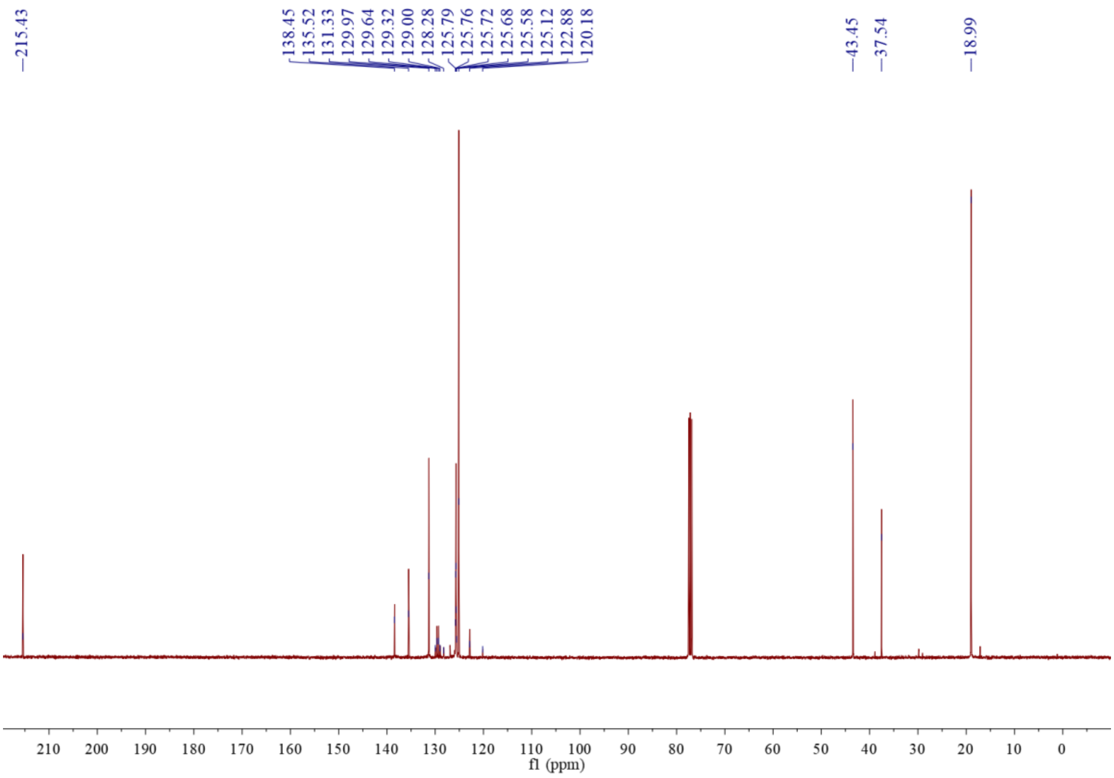


2i

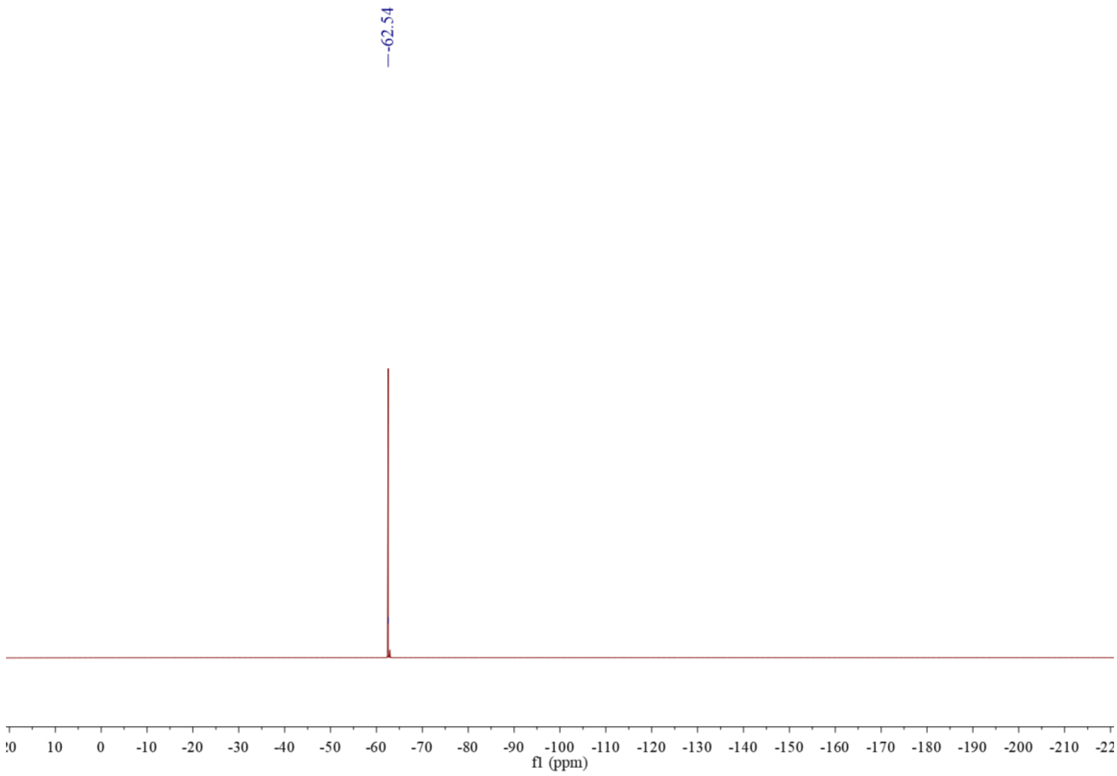
[1]H NMR spectrum in $CDCl_3$:

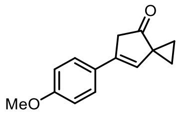


[13]C NMR spectrum in $CDCl_3$:



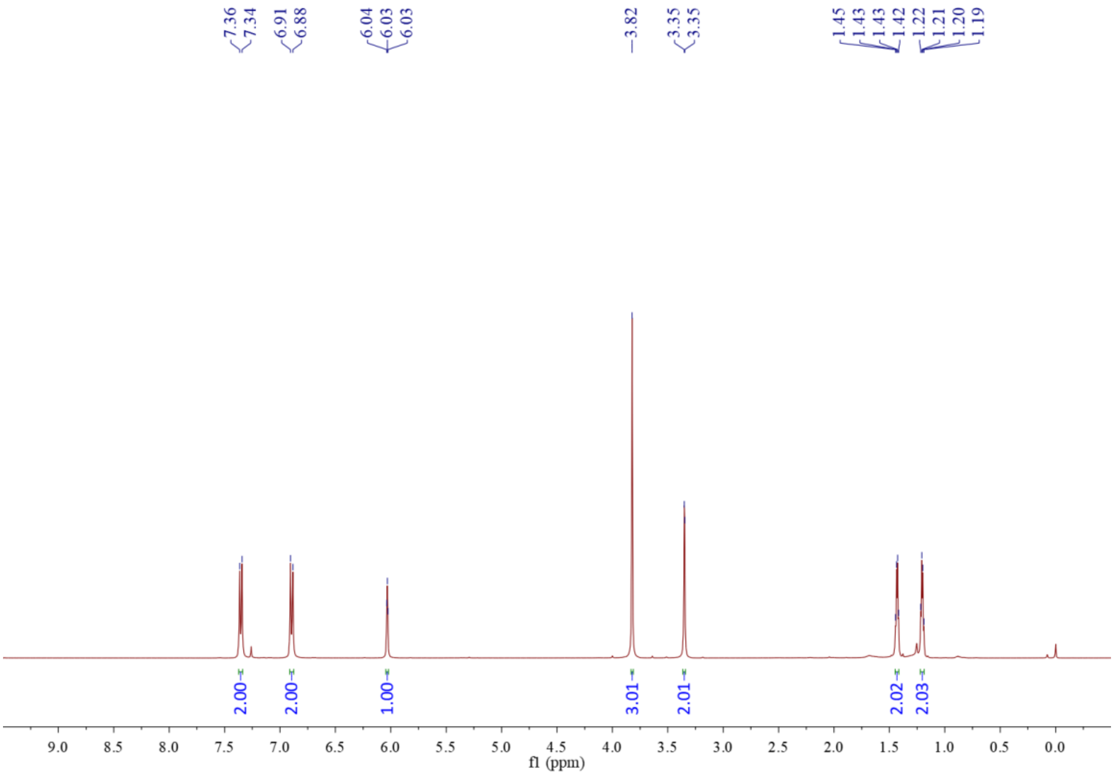
^{19}F NMR spectrum in $CDCl_3$:



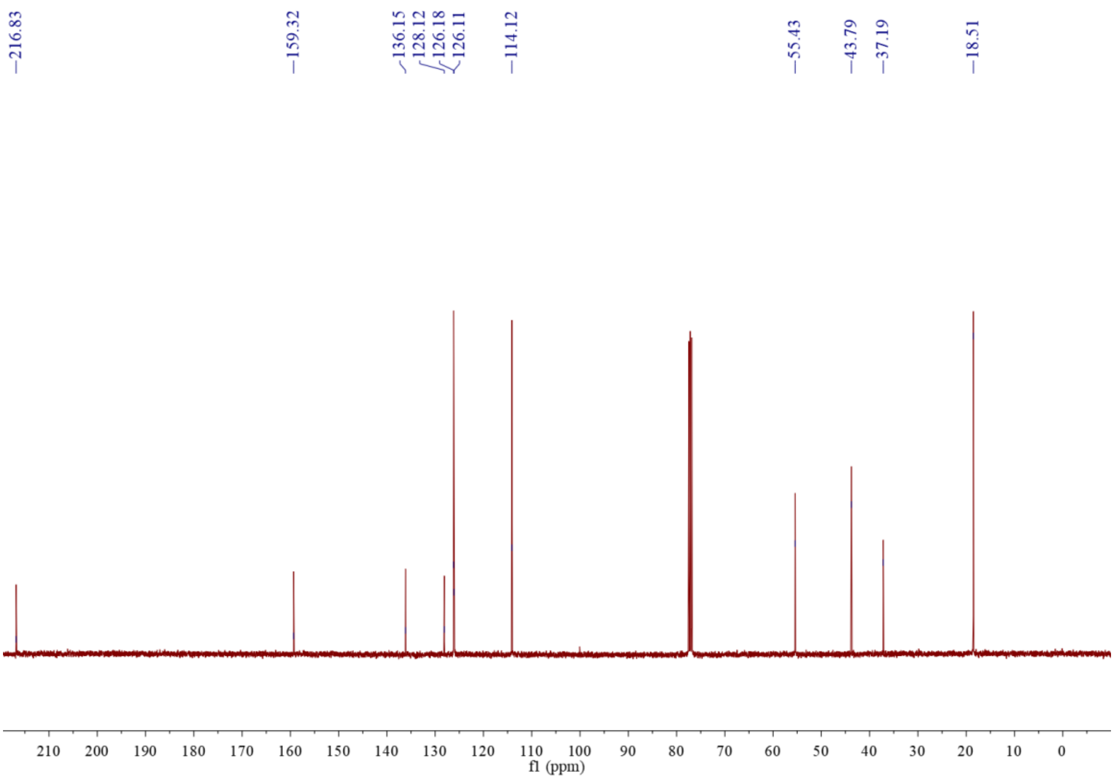


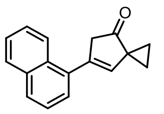
2j

^{1}H NMR spectrum in $CDCl_3$:



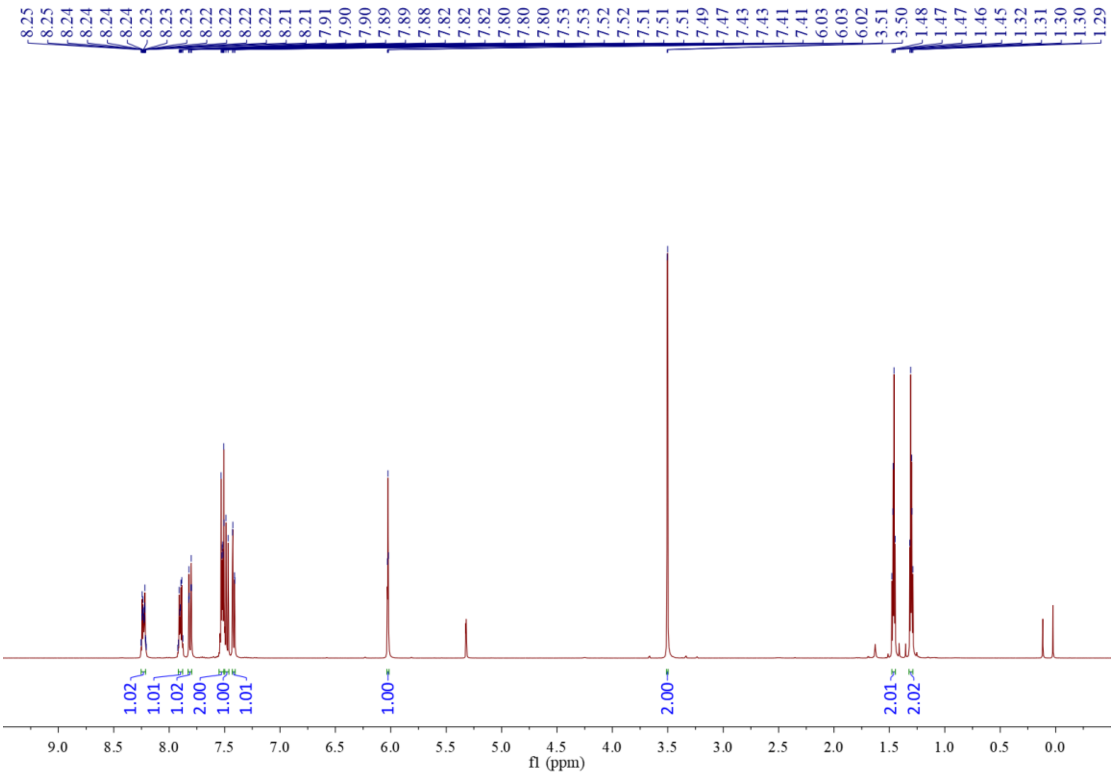
^{13}C NMR spectrum in $CDCl_3$:



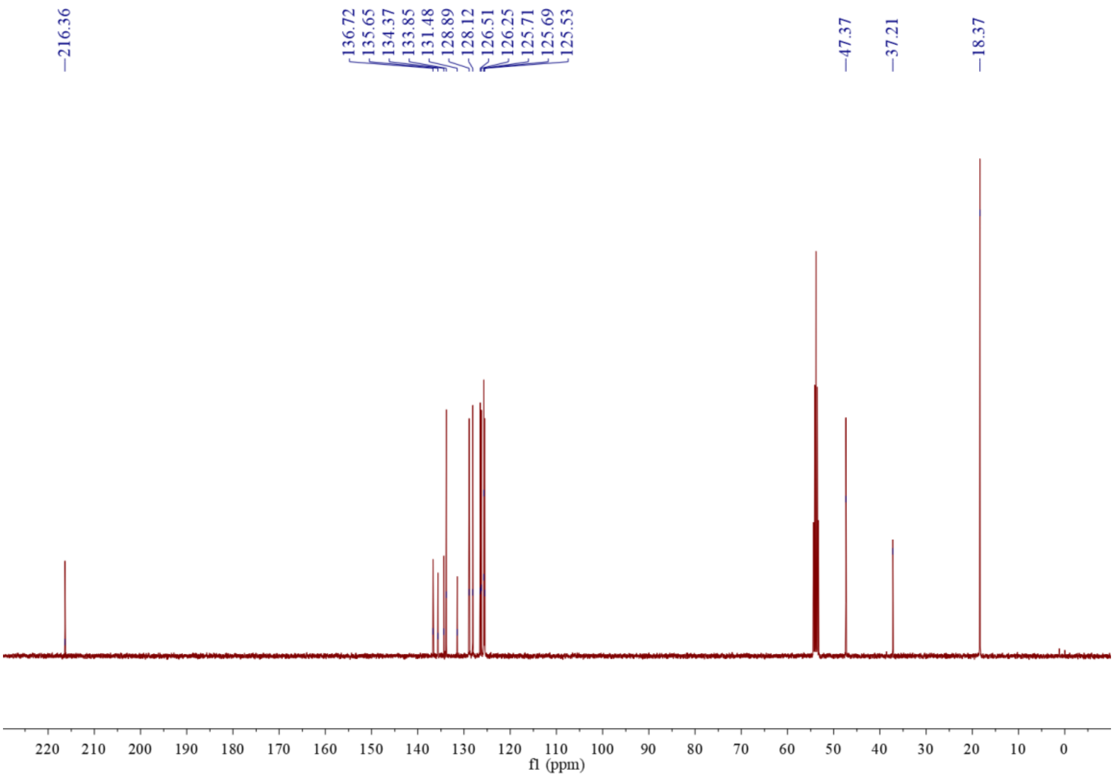


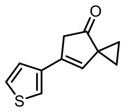
2k

^{1}H NMR spectrum in CD_2Cl_2:



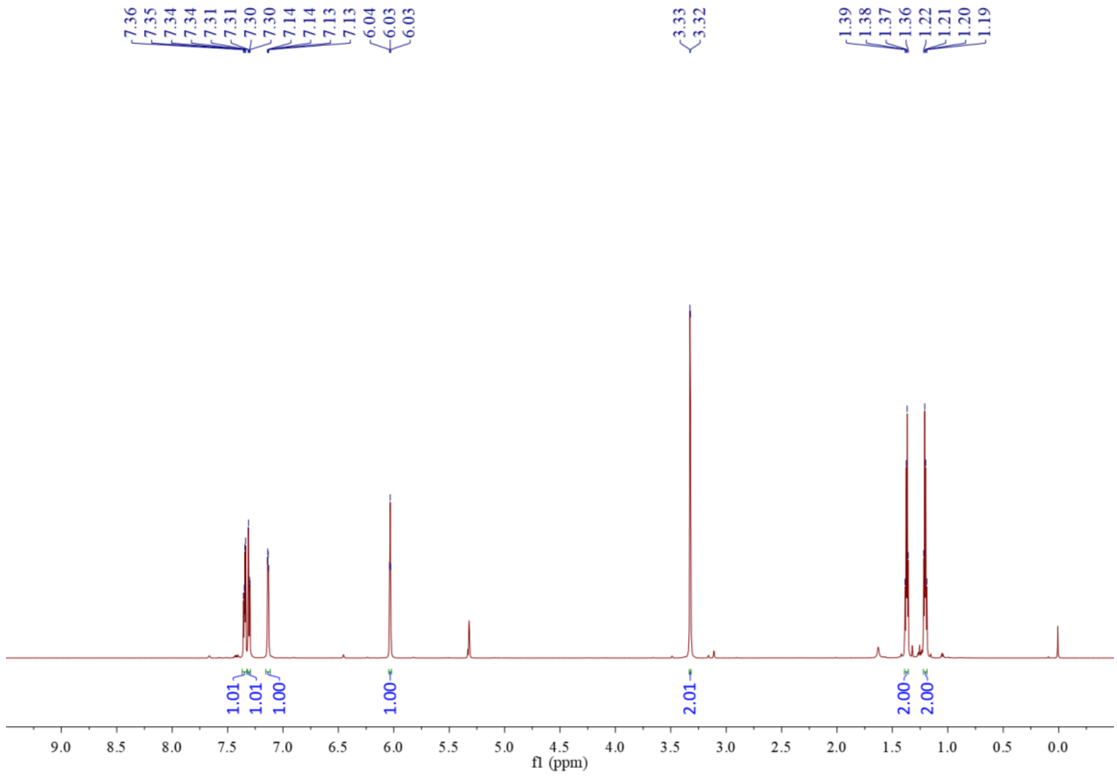
^{13}C NMR spectrum in CD_2Cl_2:



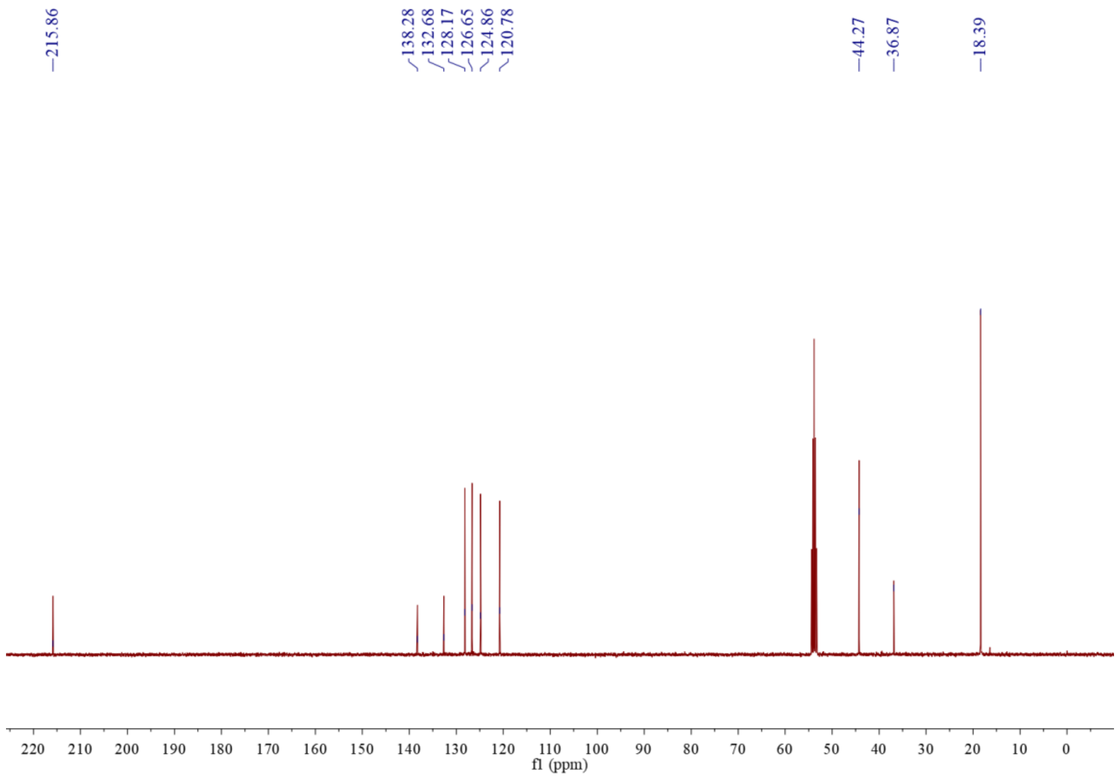


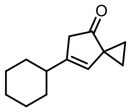
2l

^{1}H NMR spectrum in CD_2Cl_2:



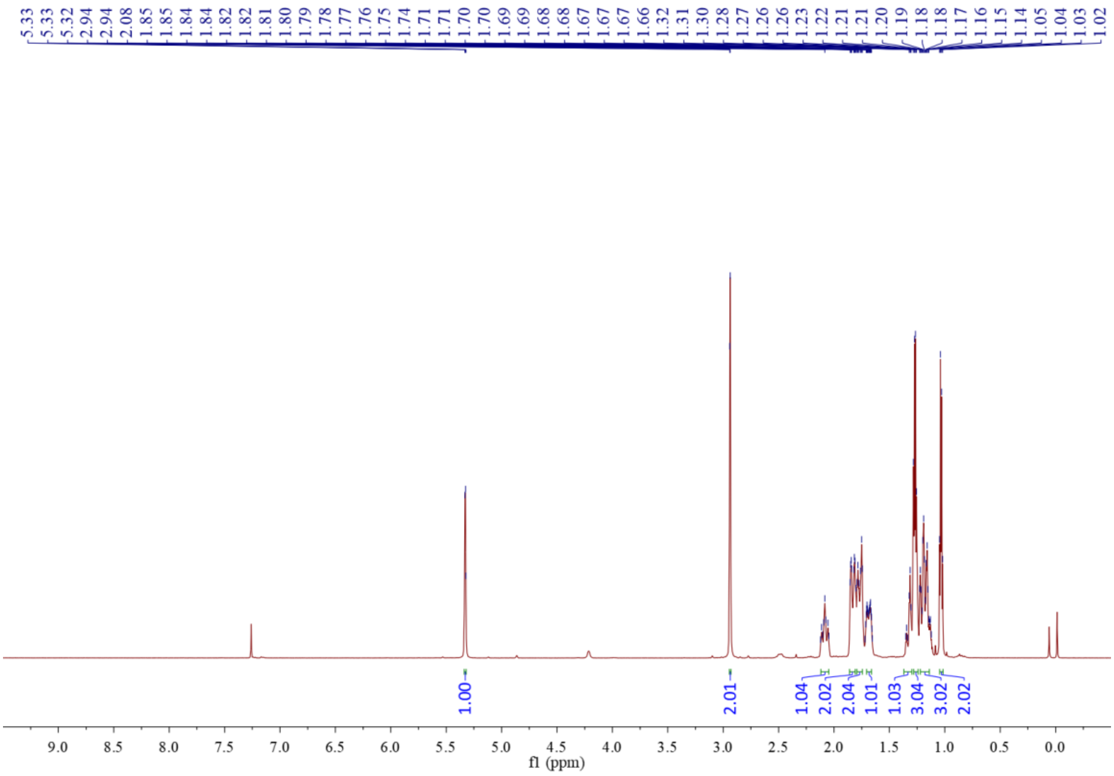
^{13}C NMR spectrum in CD_2Cl_2:



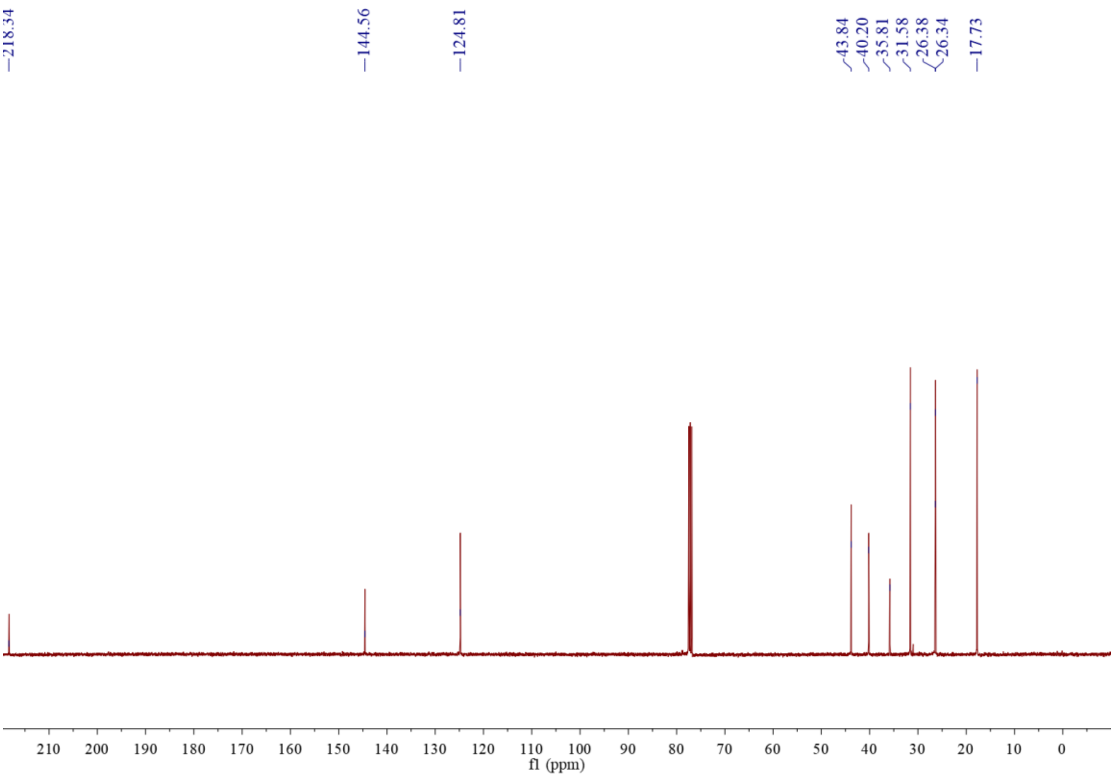


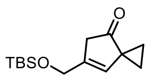
2m

[1]H NMR spectrum in $CDCl_3$:



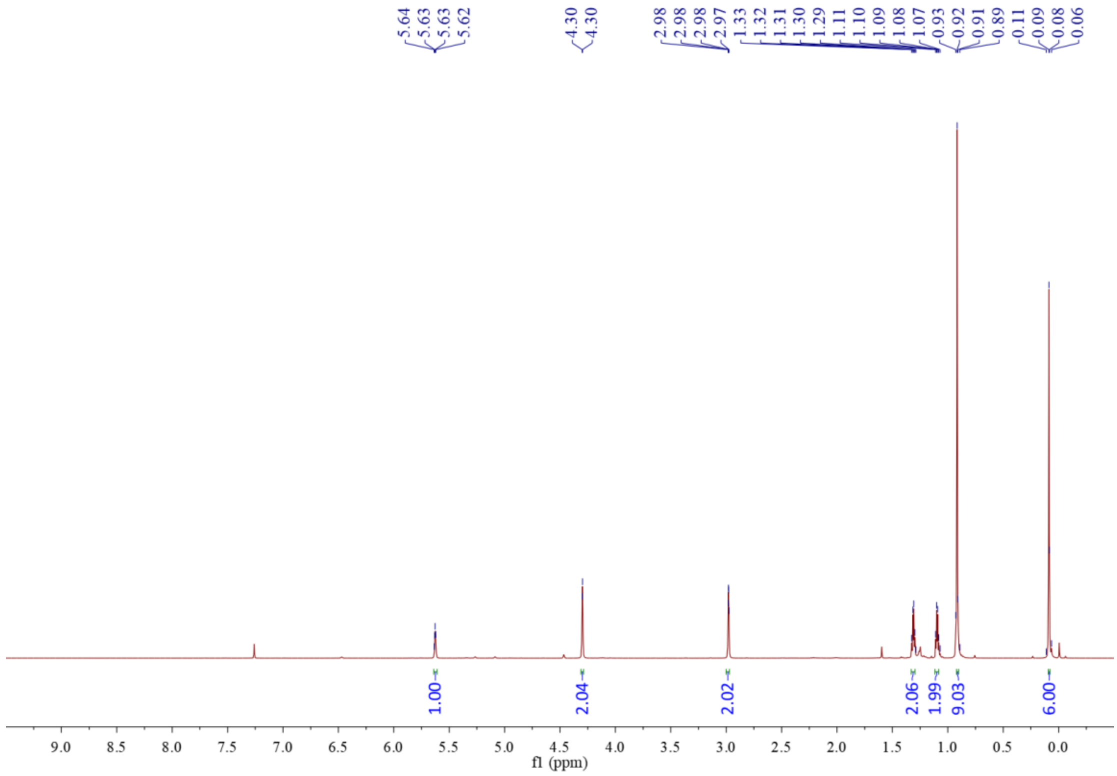
[13]C NMR spectrum in $CDCl_3$:



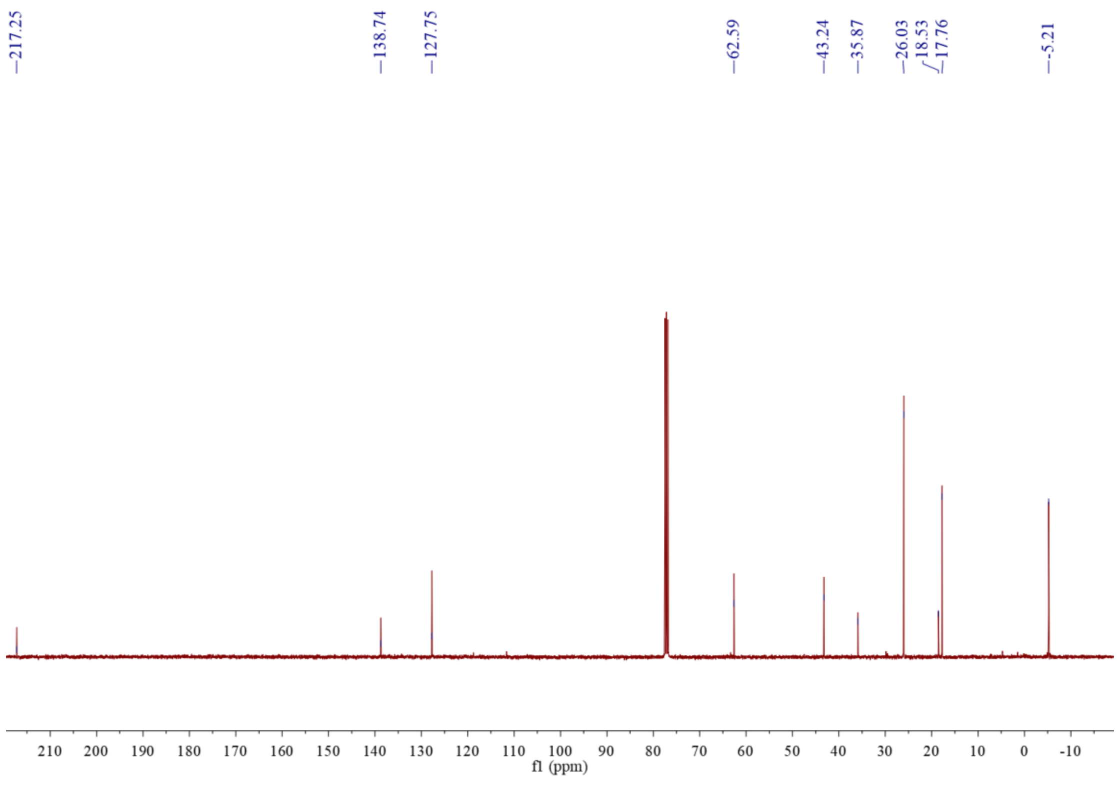


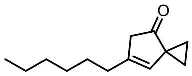
2n

^{1}H NMR spectrum in $CDCl_3$:



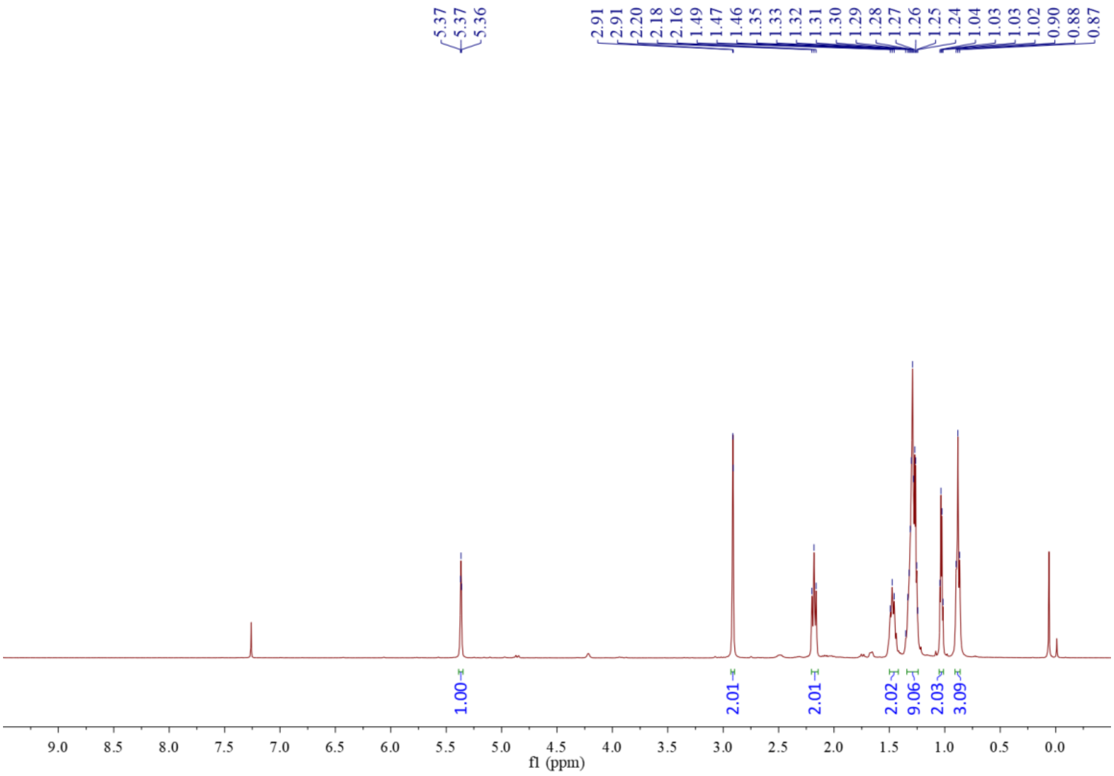
^{13}C NMR spectrum in $CDCl_3$:



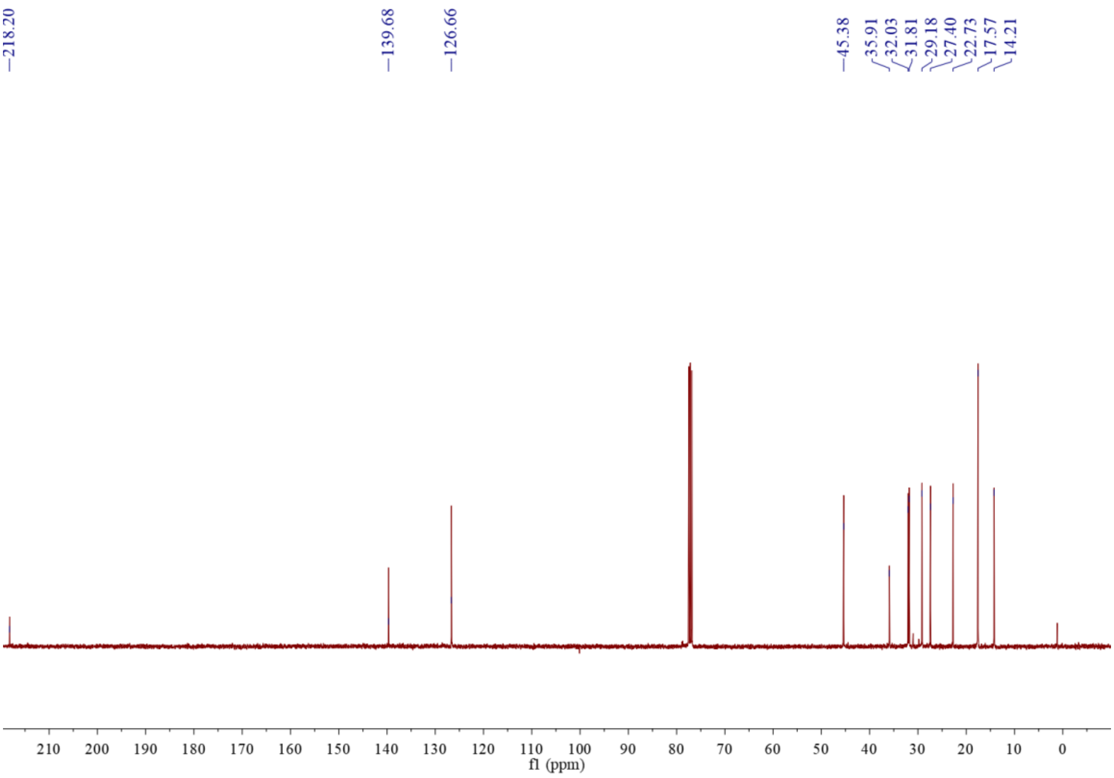


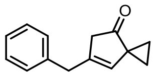
2o

^{1}H NMR spectrum in $CDCl_3$:



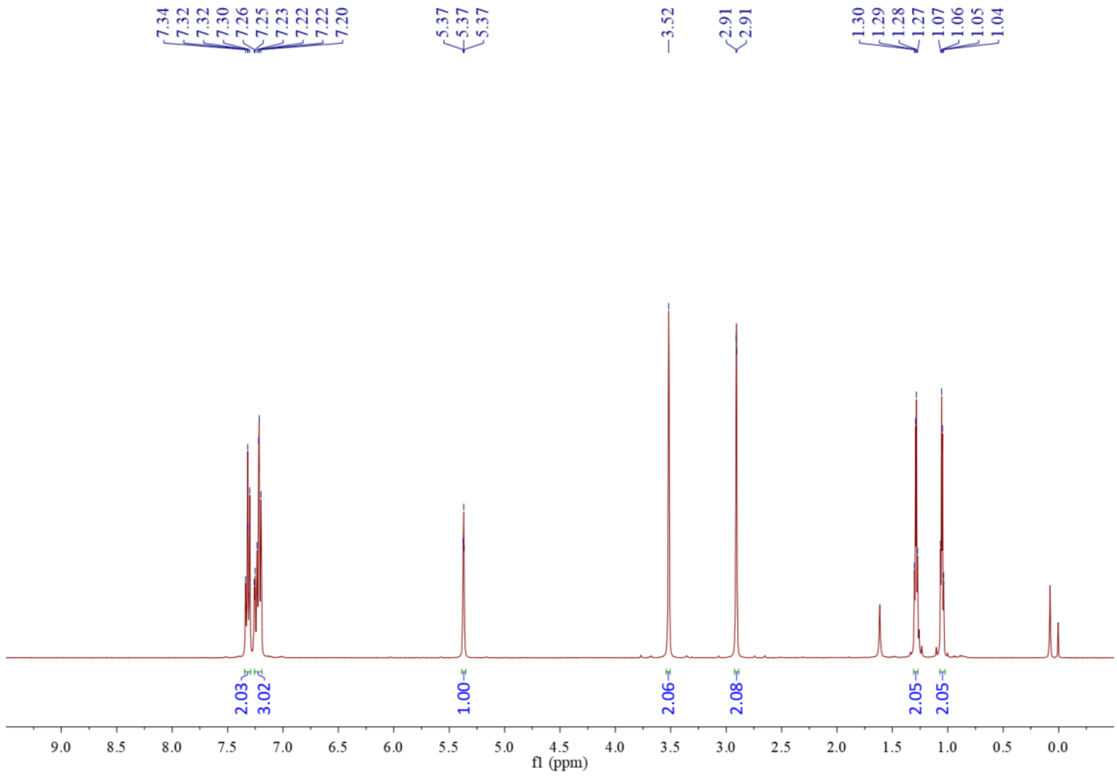
^{13}C NMR spectrum in $CDCl_3$:



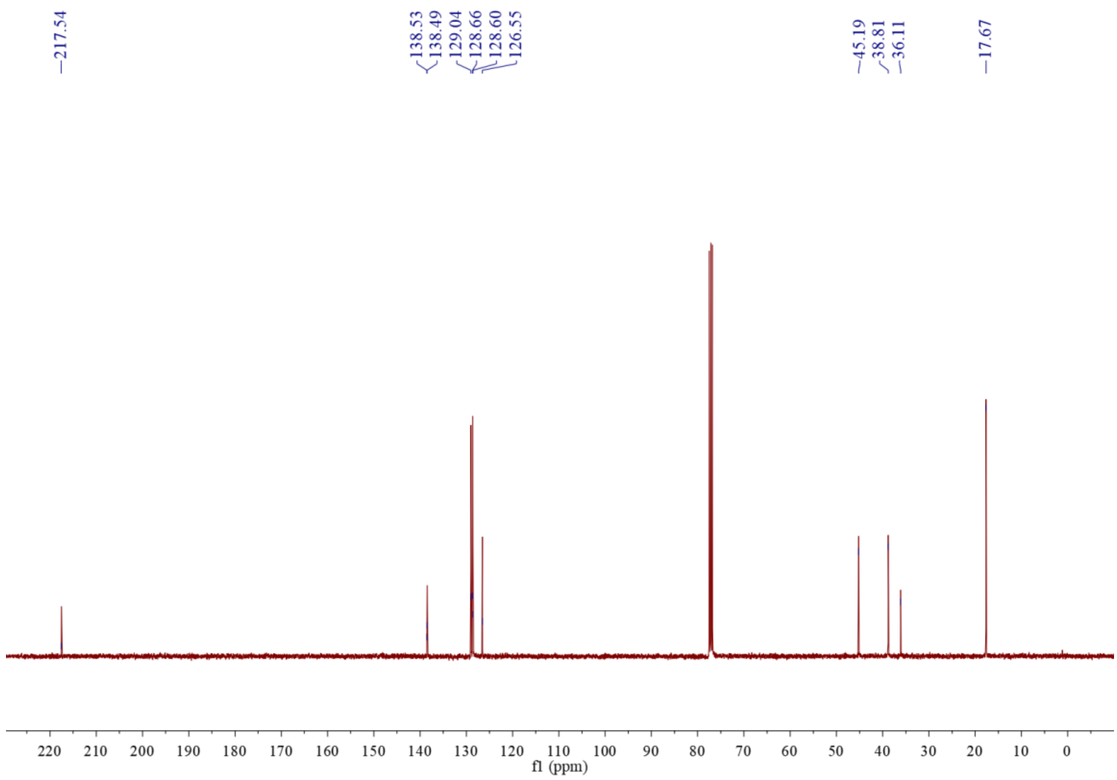


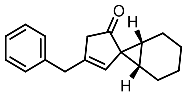
2p

^{1}H NMR spectrum in $CDCl_3$:



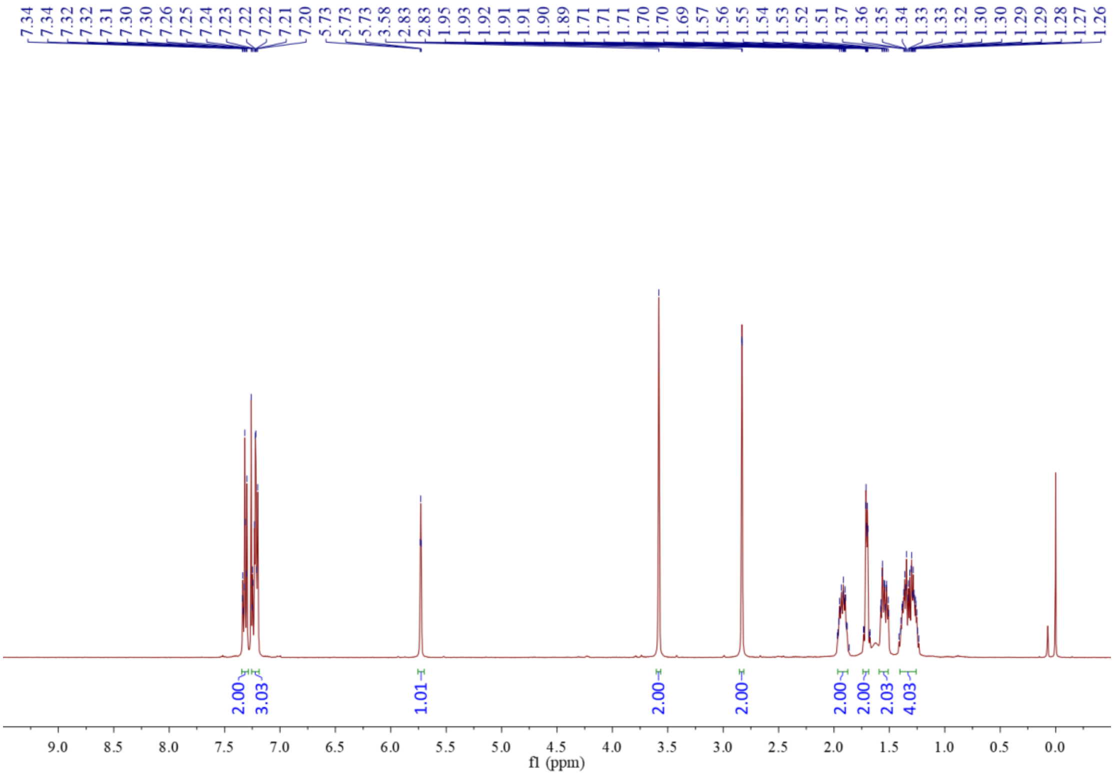
^{13}C NMR spectrum in $CDCl_3$:



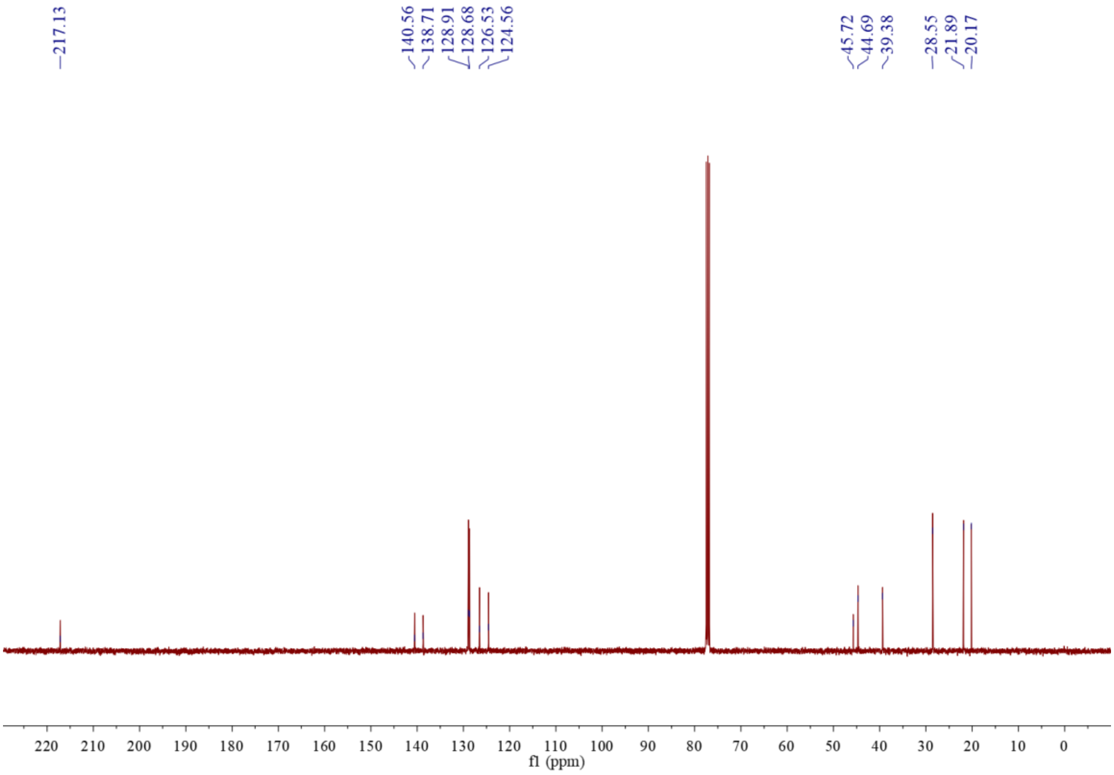


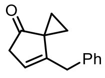
2q

^{1}H NMR spectrum in $CDCl_3$:



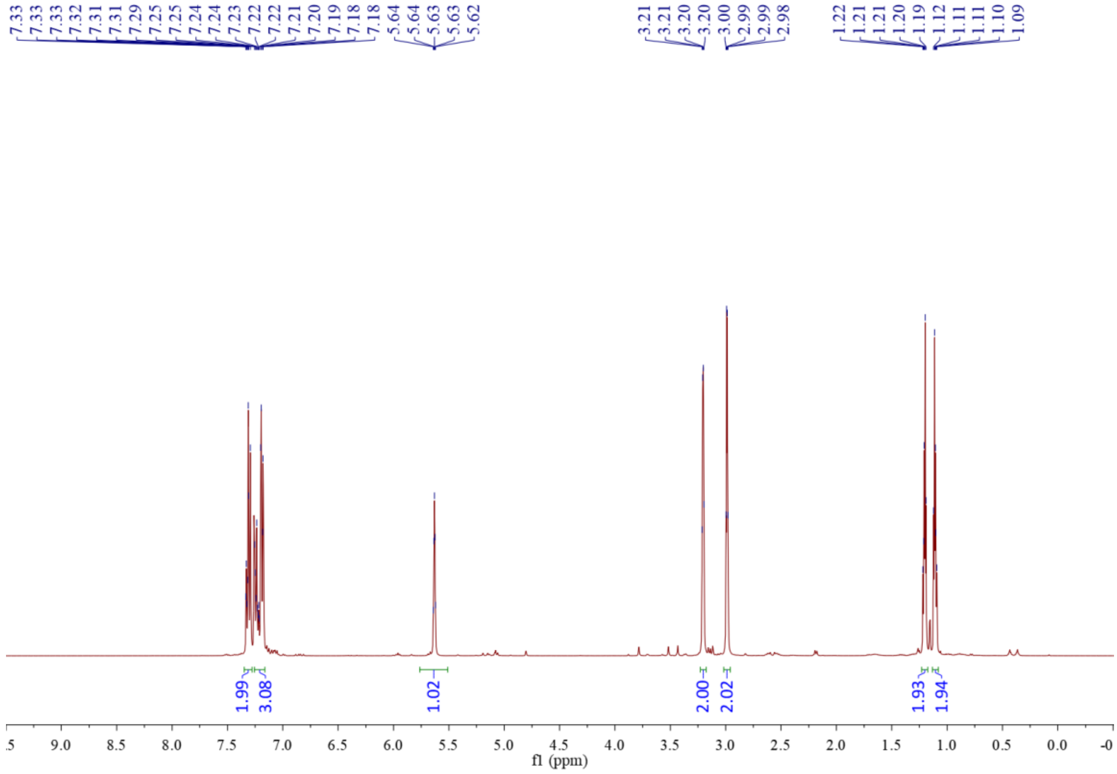
^{13}C NMR spectrum in $CDCl_3$:



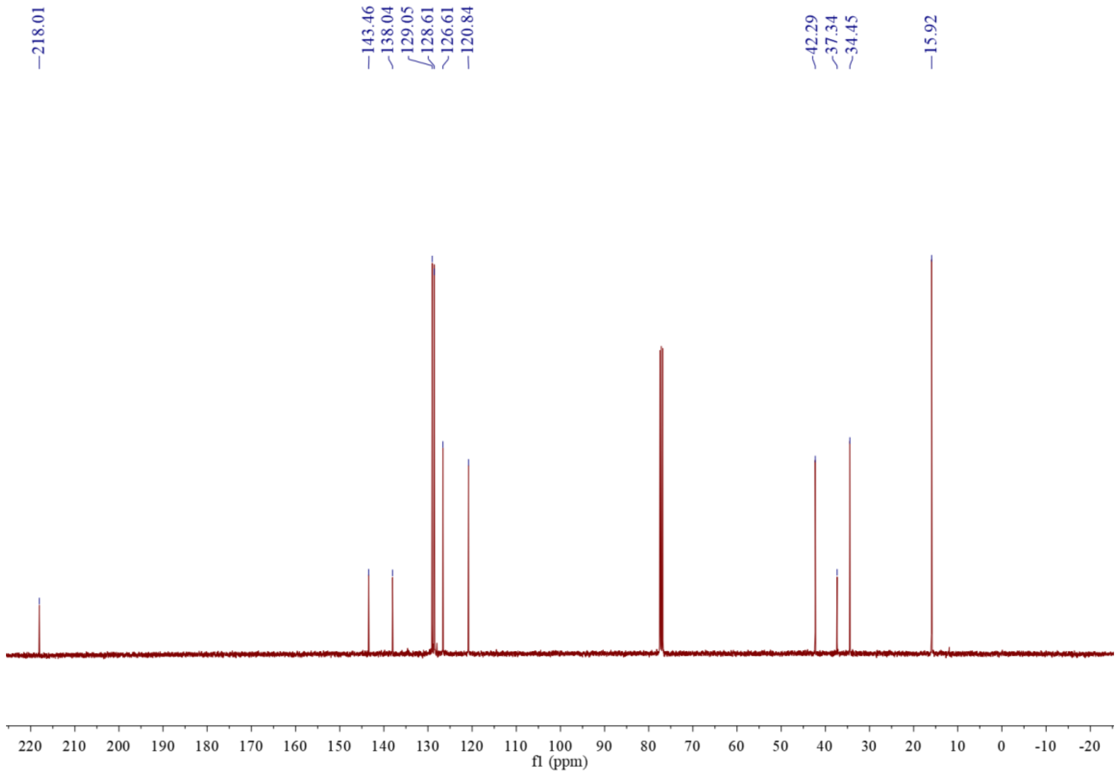


2r

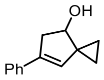
[1]H NMR spectrum in $CDCl_3$:



[13]C NMR spectrum in $CDCl_3$:

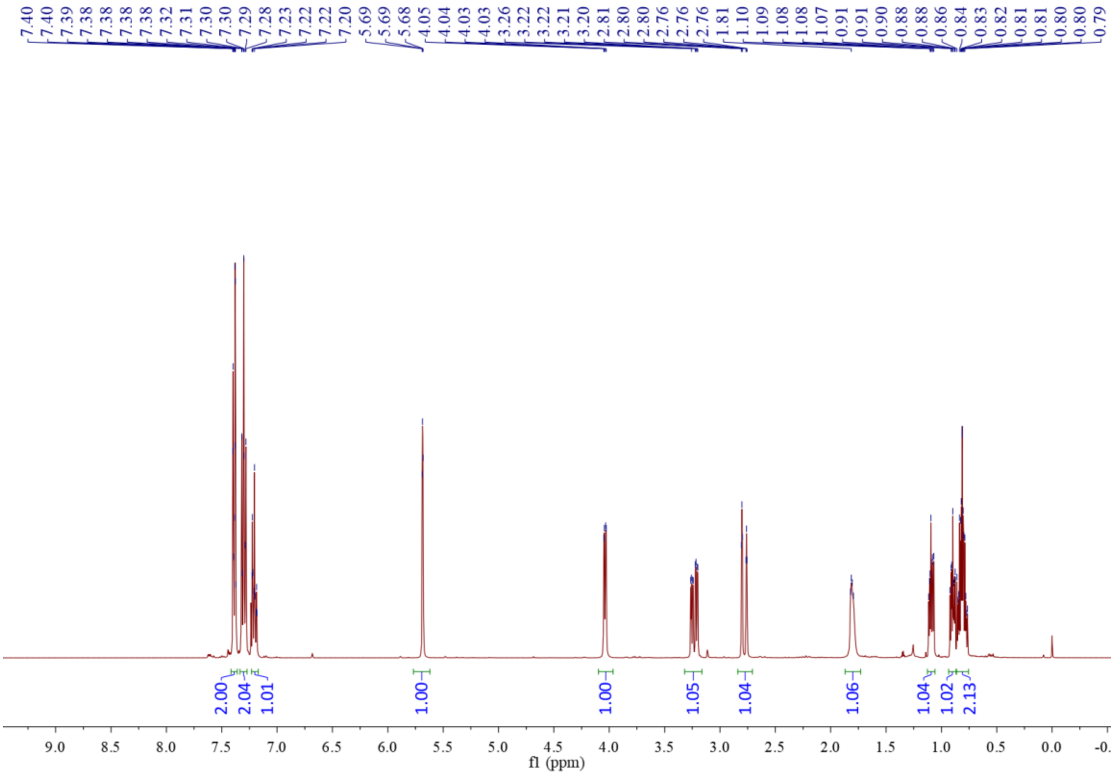


NMR spectra for derivatization products

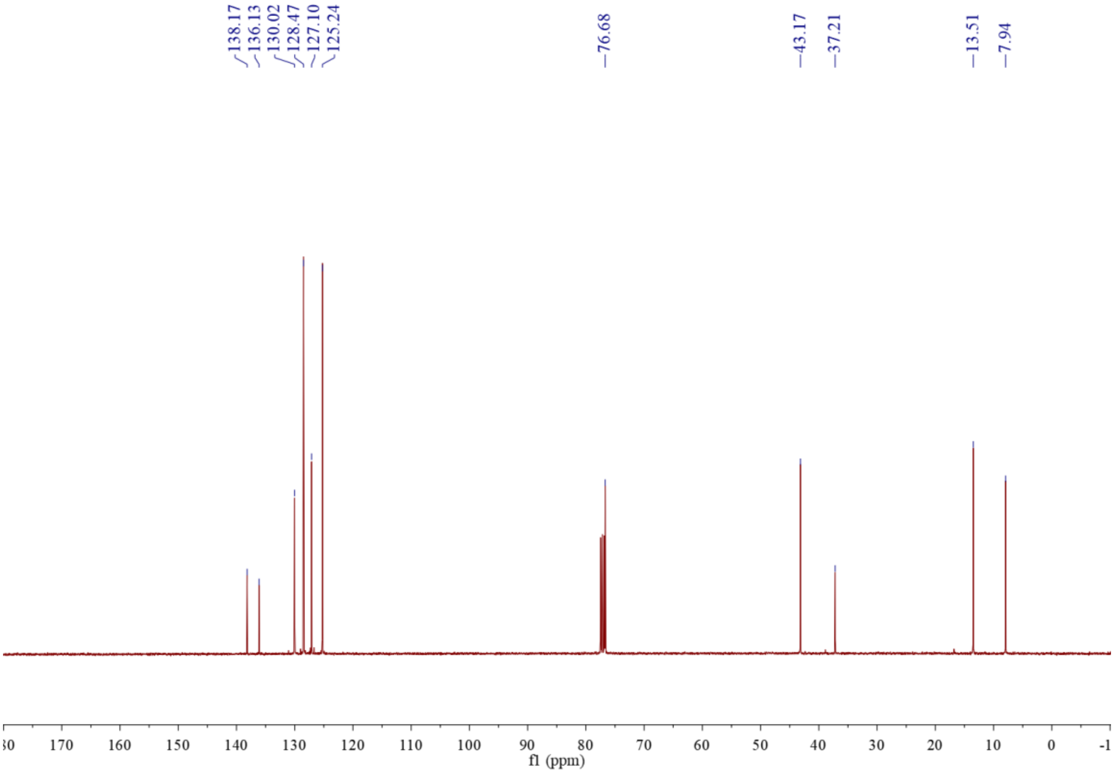


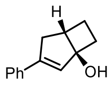
5

[1]H NMR spectrum in $CDCl_3$:



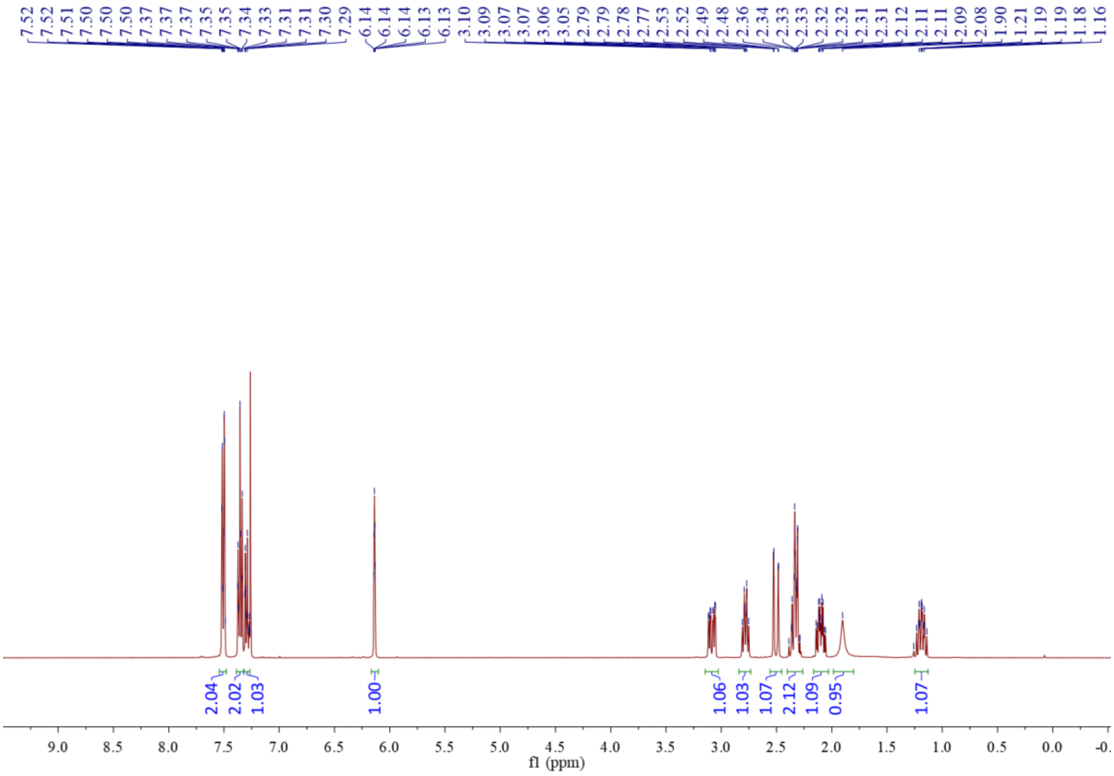
[13]C NMR spectrum in $CDCl_3$:



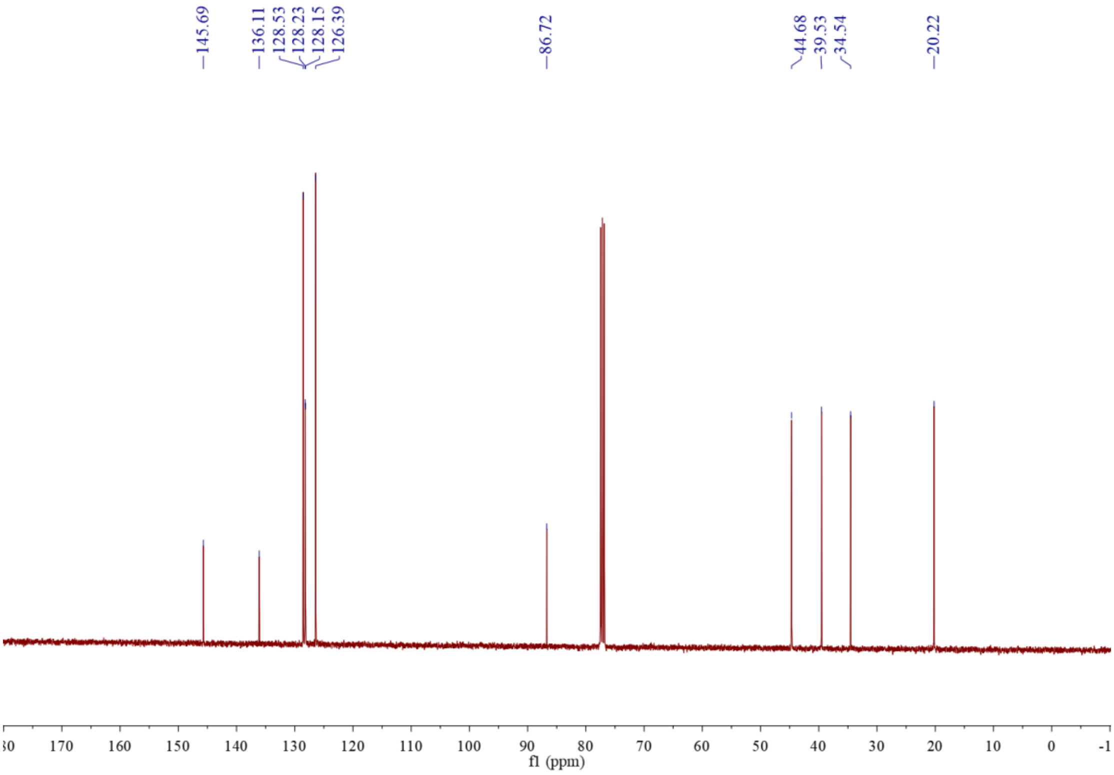


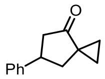
6

^{1}H NMR spectrum in $CDCl_3$:



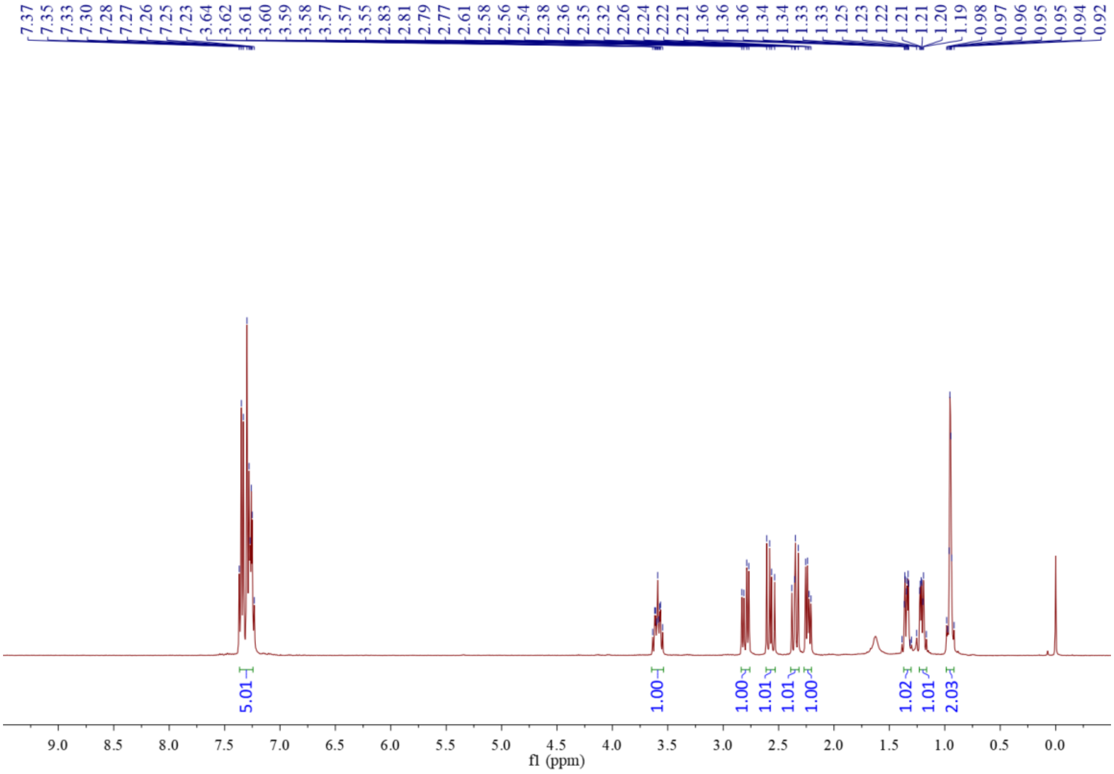
^{13}C NMR spectrum in $CDCl_3$:



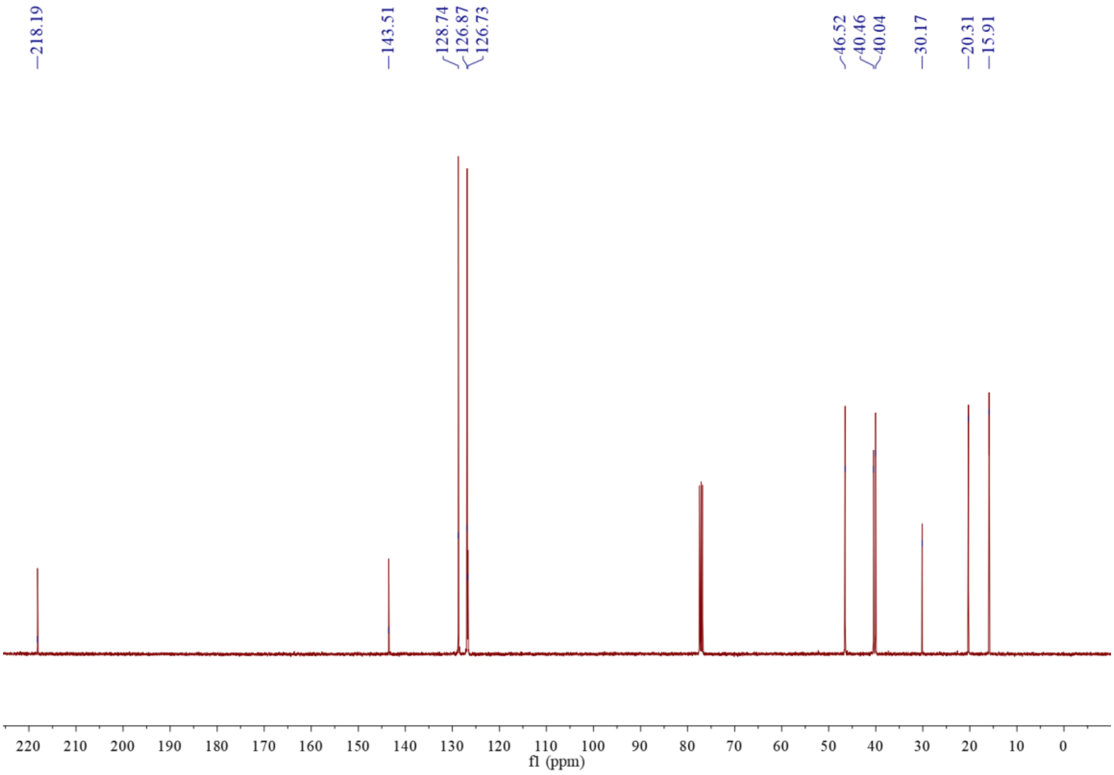


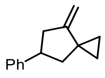
7

[1]H NMR spectrum in $CDCl_3$:



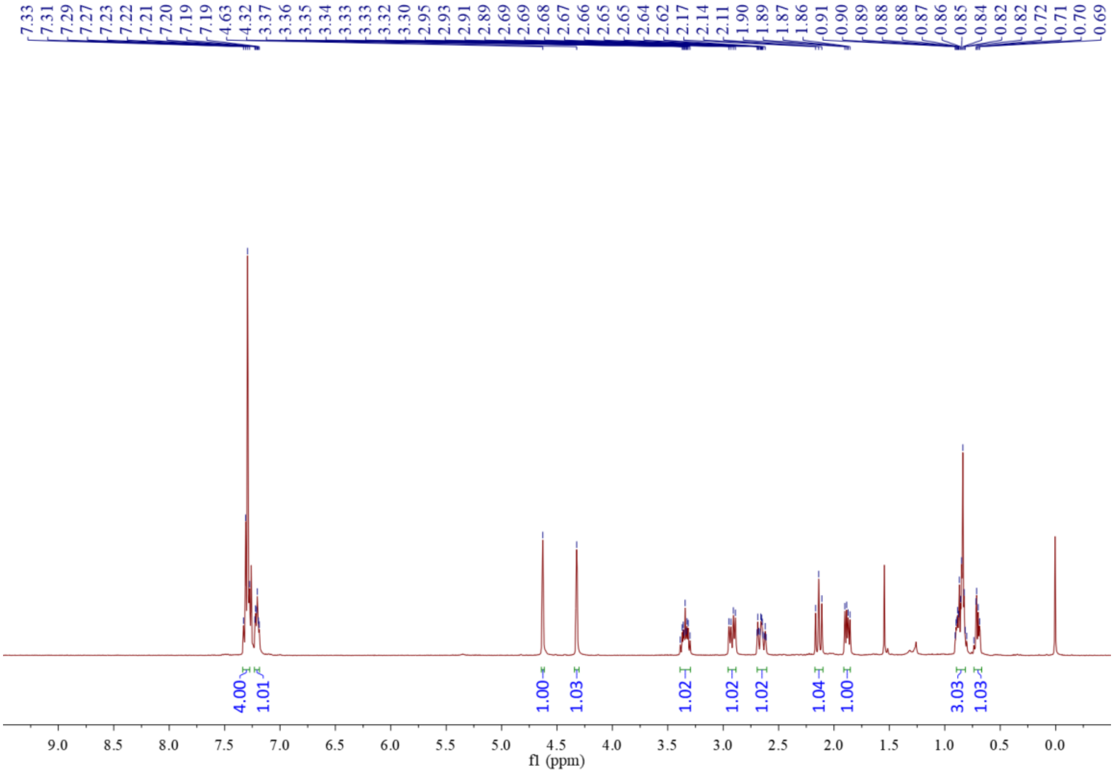
[13]C NMR spectrum in $CDCl_3$:



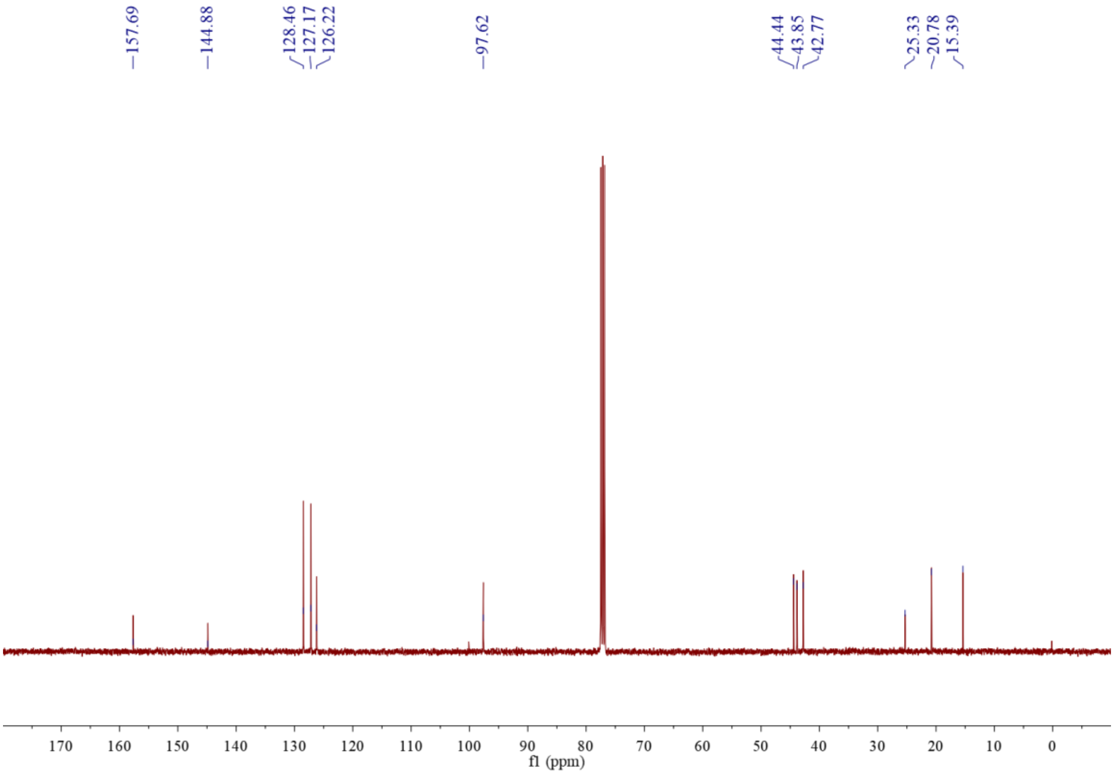


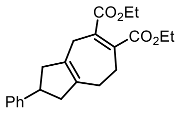
8

^{1}H NMR spectrum in $CDCl_3$:



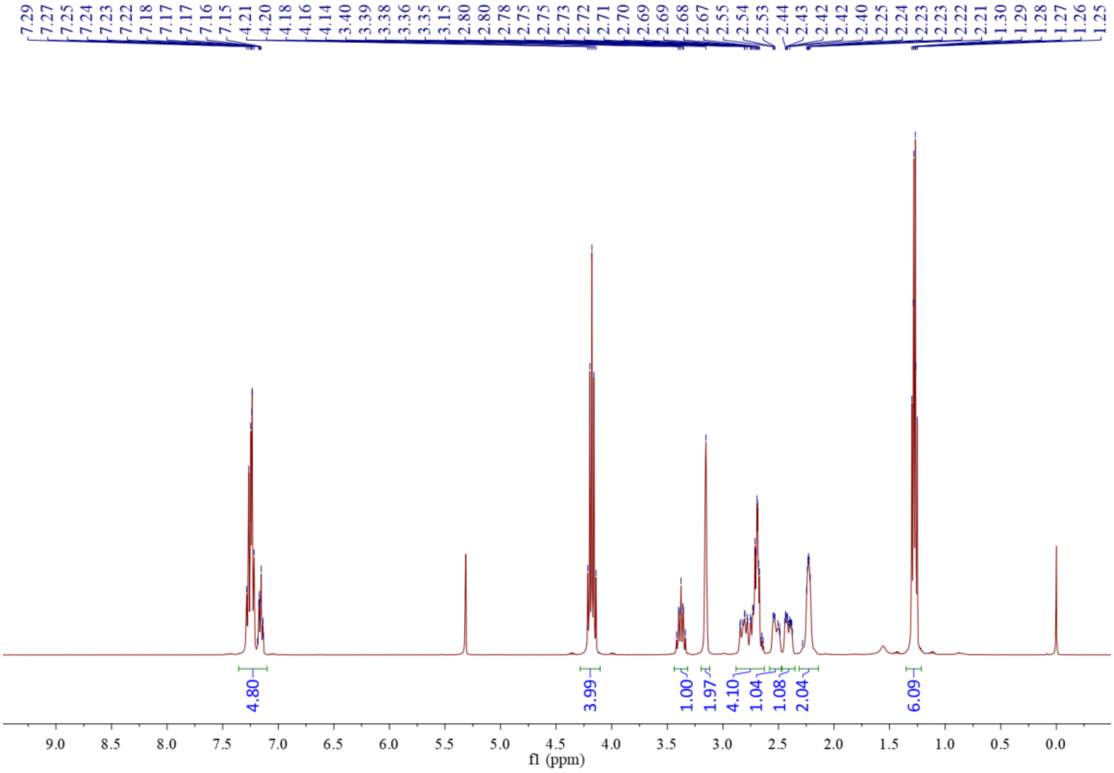
^{13}C NMR spectrum in $CDCl_3$:



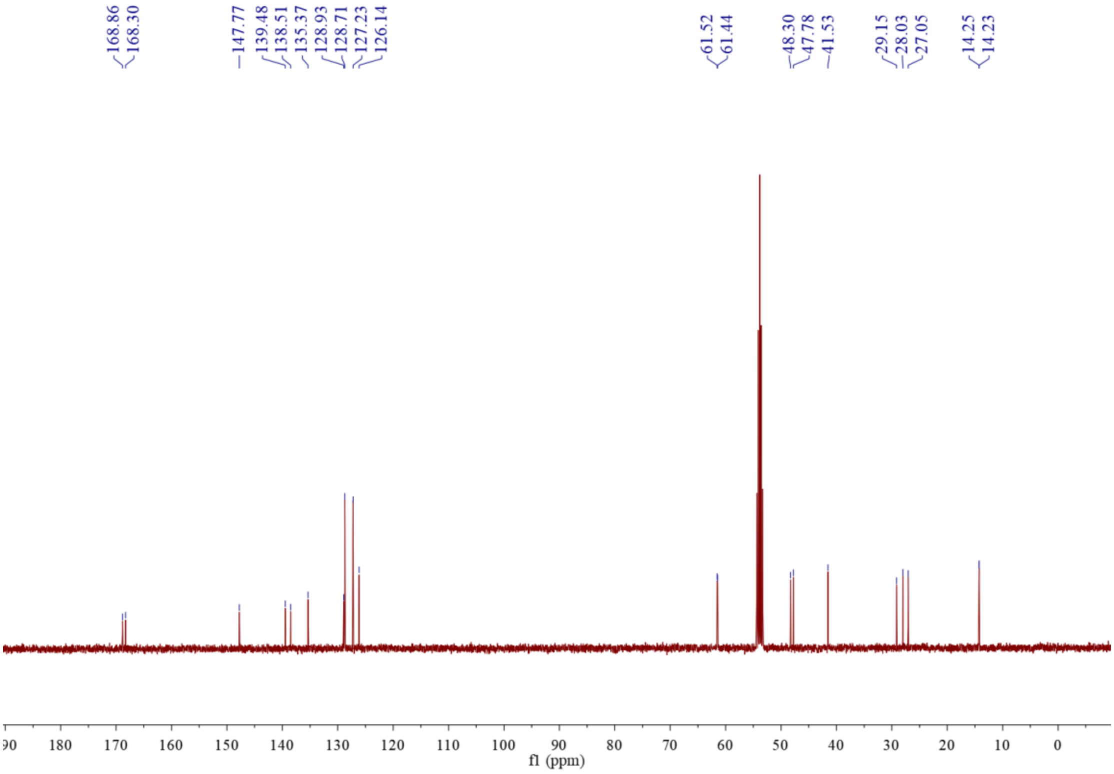


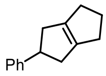
9

^{1}H NMR spectrum in CD_2Cl_2:



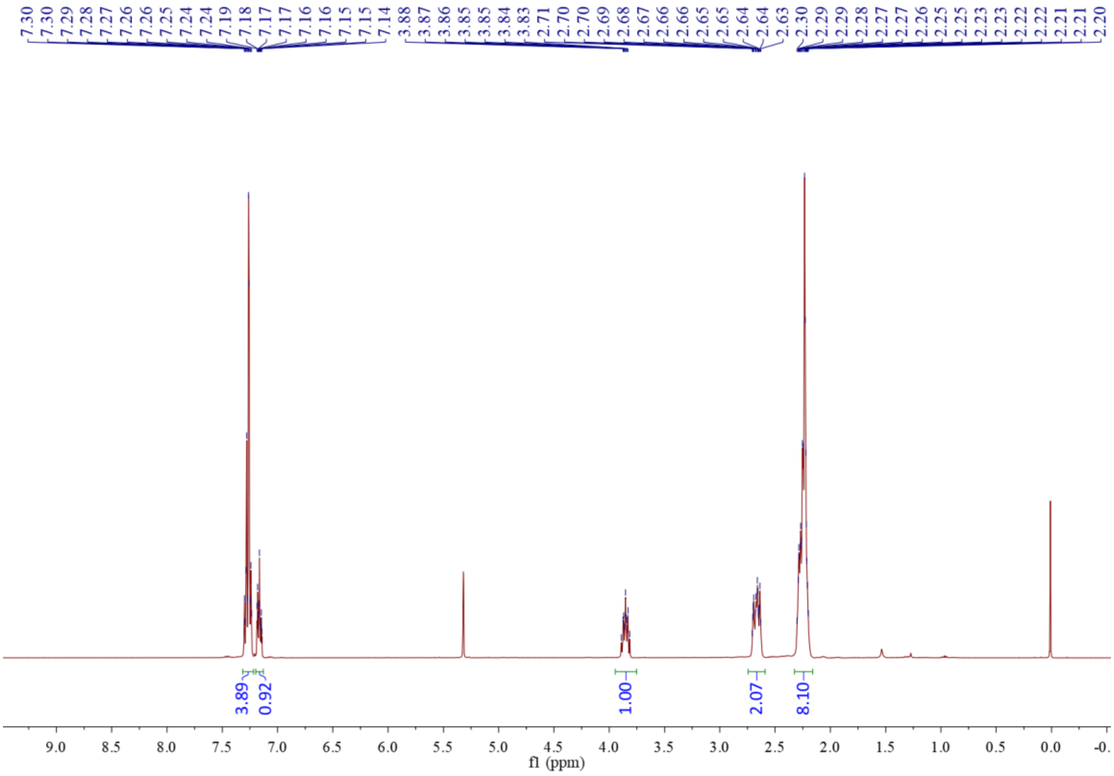
^{13}C NMR spectrum in CD_2Cl_2:



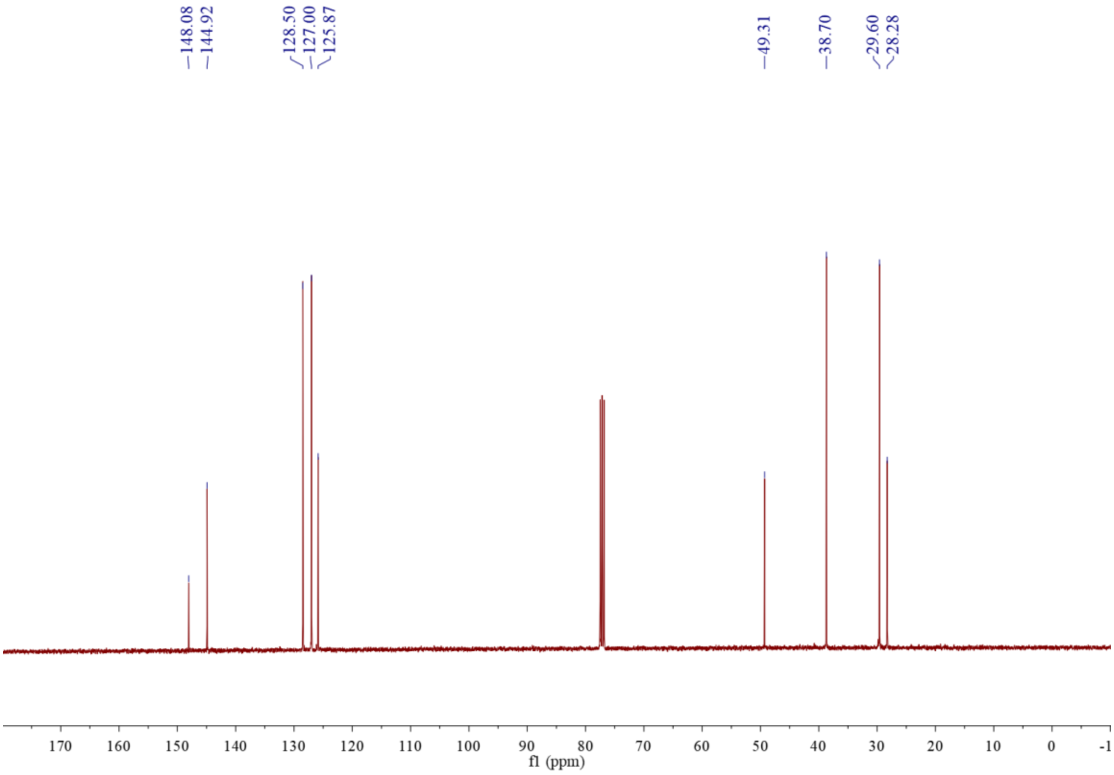


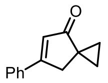
10

[1]H NMR spectrum in CD_2Cl_2:



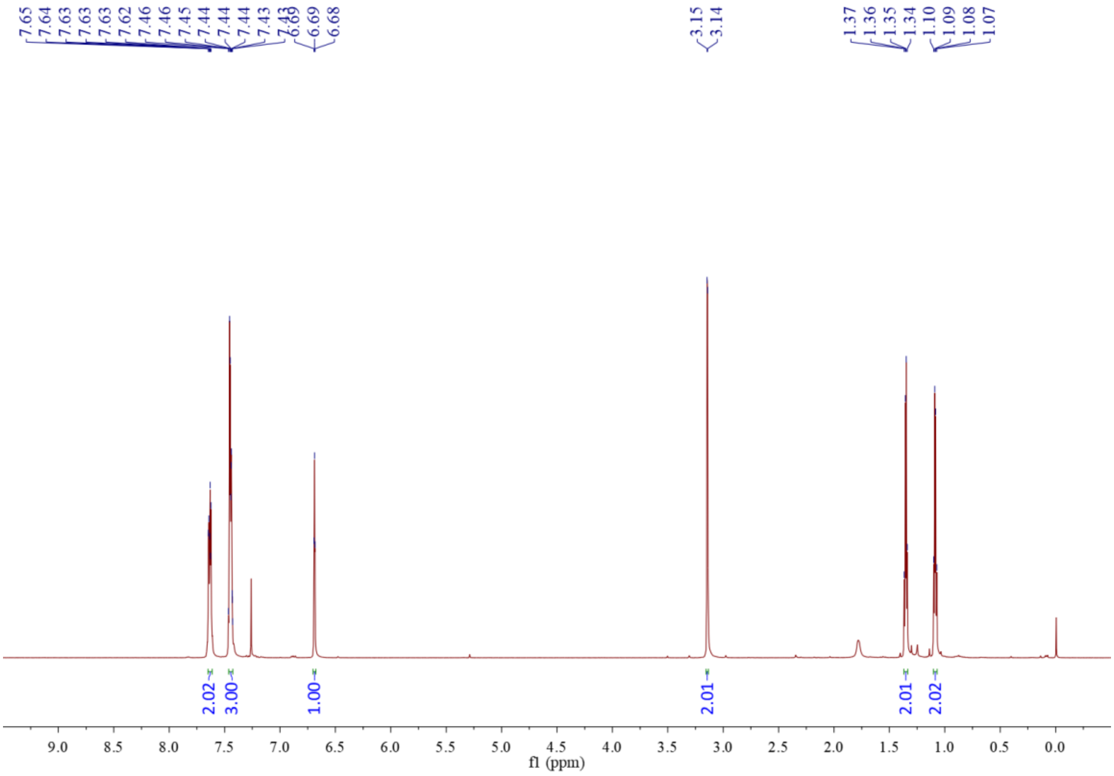
[13]C NMR spectrum in $CDCl_3$:



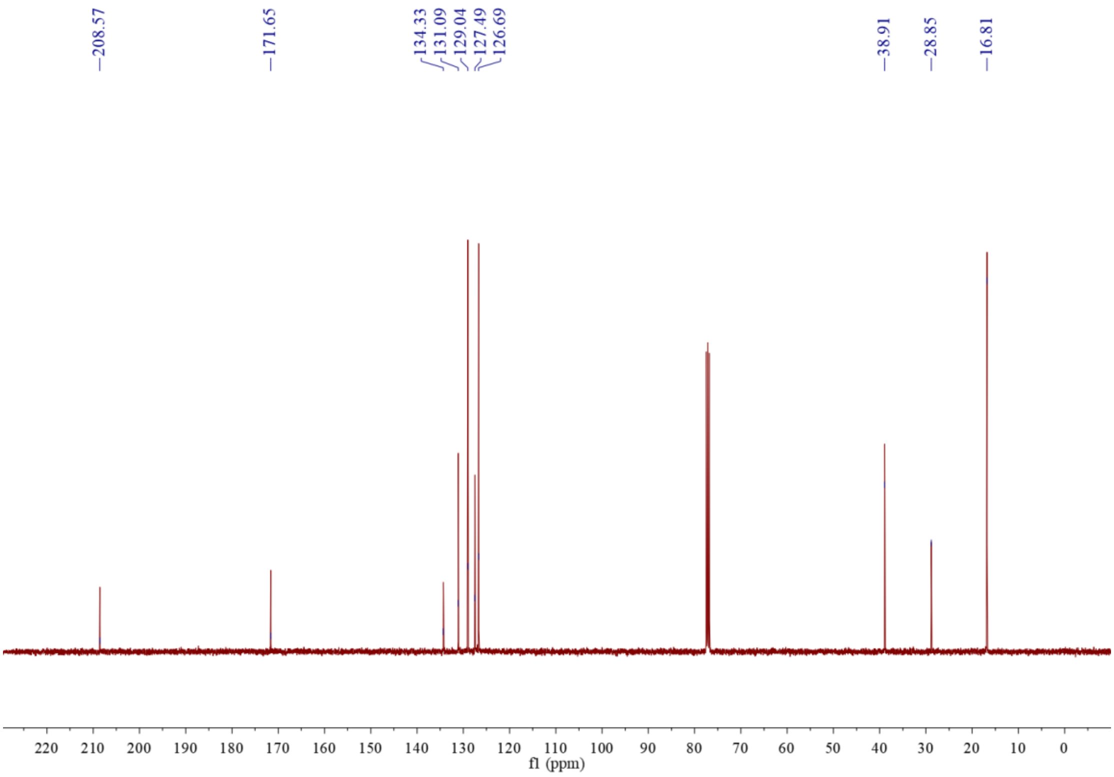


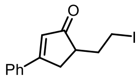
11

[1]H NMR spectrum in $CDCl_3$:



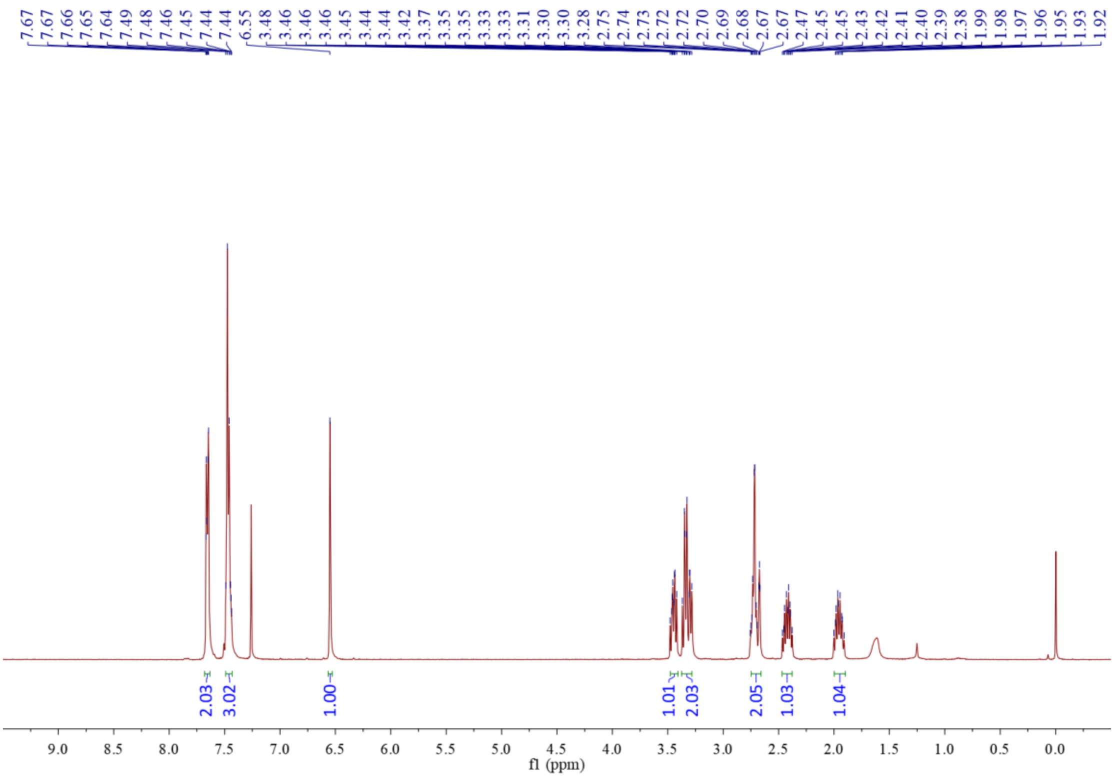
[13]C NMR spectrum in $CDCl_3$:



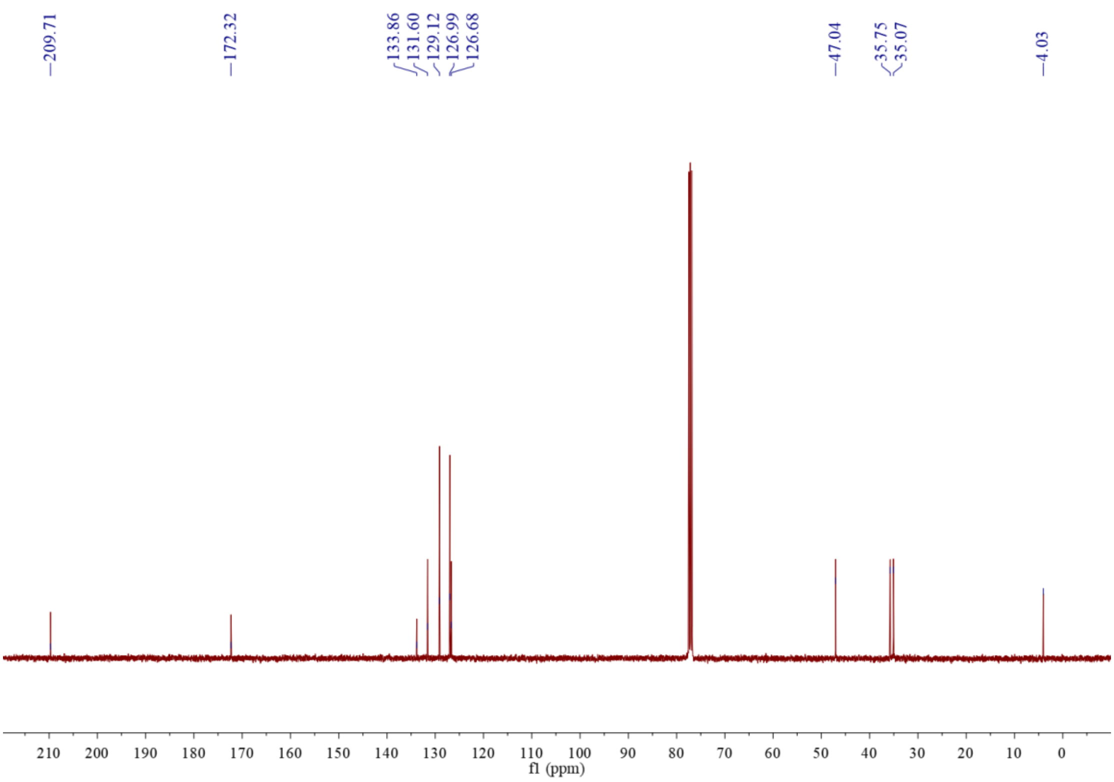


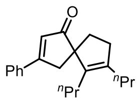
12

[1]H NMR spectrum in $CDCl_3$:



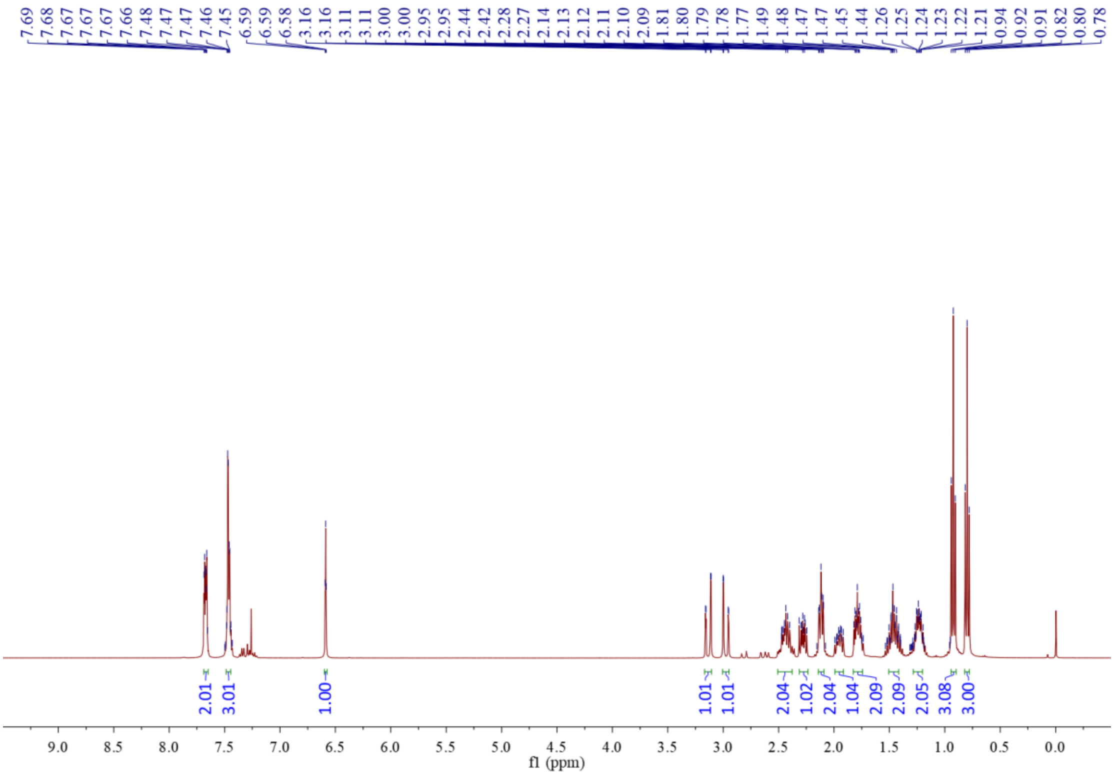
[13]C NMR spectrum in $CDCl_3$:



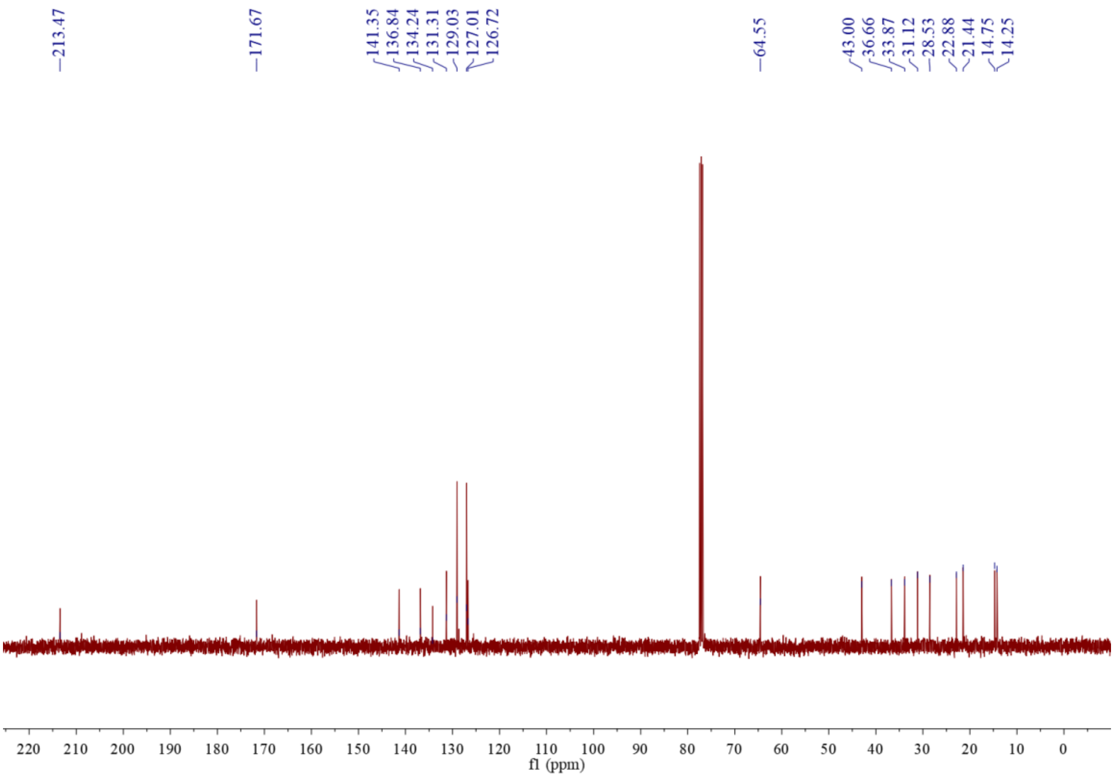


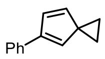
13

^{1}H NMR spectrum in $CDCl_3$:



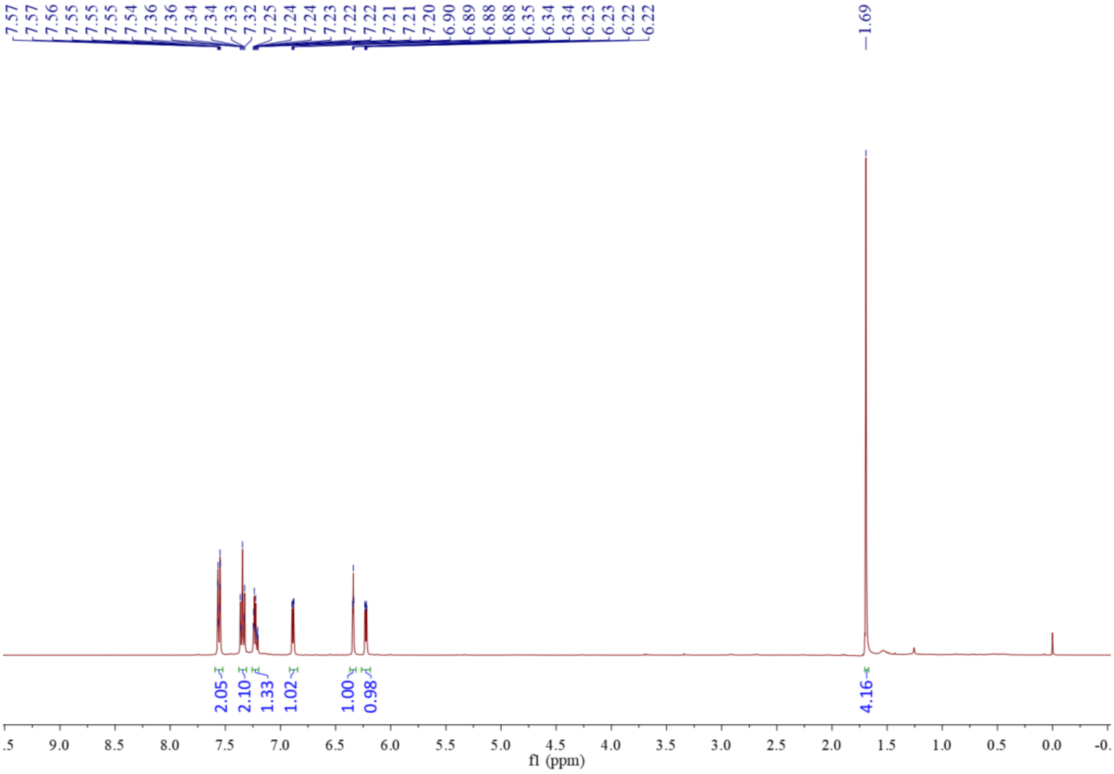
^{13}C NMR spectrum in $CDCl_3$:





14

^{1}H NMR spectrum in $CDCl_3$:



^{13}C NMR spectrum in $CDCl_3$: