Rh-Catalyzed *trans*-Divinylcyclopropane Rearrangement: An Approach to 1,5-Disubstituted 1,4-Cycloheptadienes

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I. General information

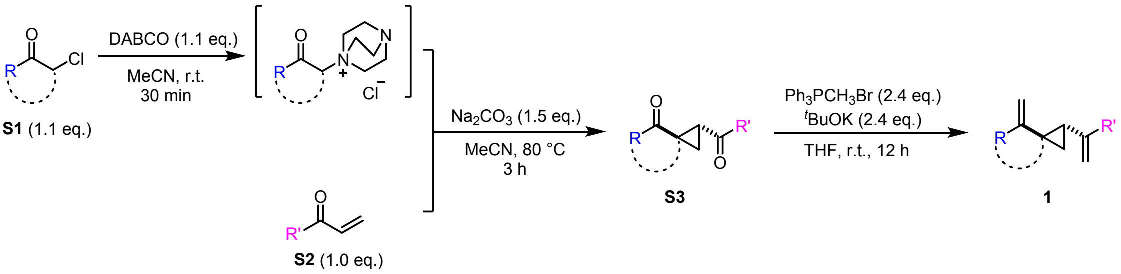
Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stirring bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Solvents (A. R.) were used without purification. $[Rh(CO)_2Cl]_2$ was purchased from J&K, and was used without further purification. Other synthetic reagents were purchased from Adamas, BidePharm, D&B, Energy, and Heowns, and were used without purification. 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. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

High-resolution mass spectra (HRMS) were measured on ThermoFisher Q Exactive GC hybrid quadrupole-orbitrap GC-MS/MS system (EI) or on Bruker Solarix XR Fourier-transform ion cyclotron resonance mass spectrometer (ESI). NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) or on Bruker AVANCE III (^{1}H at 500 MHz, ^{13}C at 126 MHz, ^{19}F at 471 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H 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).

Abbreviations:
acac = acetylacetonate
cod = 1,5-cyclooctadiene
coe = cyclooctene
Cy = cyclohexyl
DABCO = 1,4-diazabicyclo[2.2.2]octane
DCE = 1,2-dichloroethane
DCM = dichloromethane
DME = 1,2-dimethoxyethane
DVCP = divinylcyclopropane
EA = ethyl acetate
PE = petroleum ether
r.t. = room temperature
THF = tetrahydrofuran
TLC = thin layer chromatography

II. Preparation of substrates

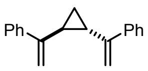
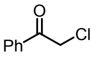
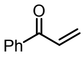
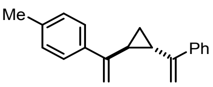
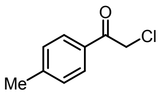
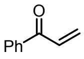
General procedure for the synthesis of 1a-q:

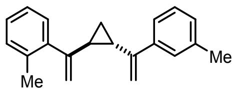
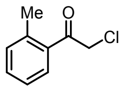
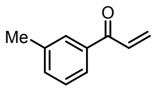
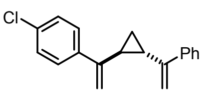
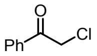
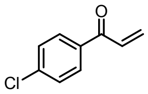
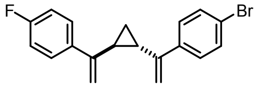
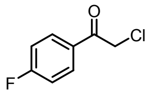
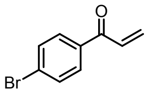
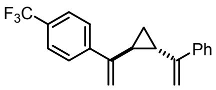
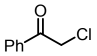
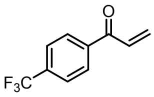
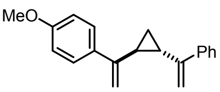
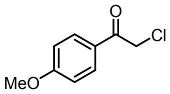
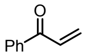
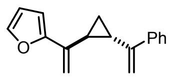
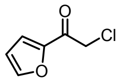
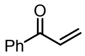
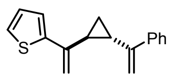
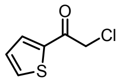
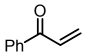


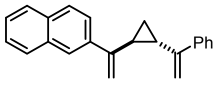
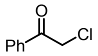
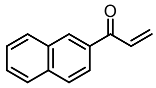
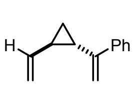
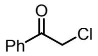
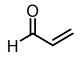
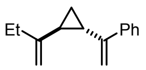
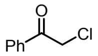
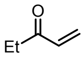
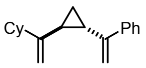
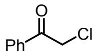
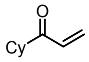
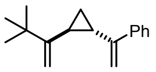
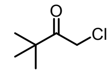
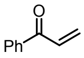
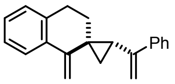
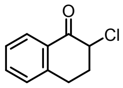
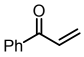
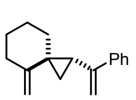
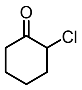
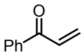
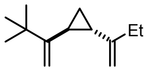
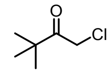
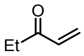
S3 was prepared following a modified procedure from Gaunt:[1] DABCO (0.36 g, 3.2 mmol, 1.1 eq. to **S2**) was added to stirred solution of **S1** (3.2 mmol, 1.1 eq. to **S2**) in MeCN (10 mL). The resulting mixture was stirred at room temperature for 30 min, during which the *in situ* formed ammonium salt may precipitate. Na_2CO_3 (0.48 g, 4.5 mmol, 1.5 eq.) was added, followed by a solution of **S2** (3.0 mmol, 1.0 eq.) in MeCN (2 mL). The resulting mixture was stirred at 80 °C for 3 h, quenched with saturated NH_4Cl aq. (10 mL), and extracted with EA (3×10 mL). The combined organic phase was washed with 1M HCl (10 mL) and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford crude **S3**. Unless otherwise stated, the crude product was directly used in the followed Wittig reaction without further purification.

Wittig reaction (**S3a→1a** as an example): Under N_2 protection, dry THF (6.5 mL) was added to a stirred mixture of Ph_3PCH_3Br (1.69 g, 4.73 mmol, 2.4 eq. to **S3a**) and ^{t}BuOK (0.53 g, 4.7 mmol, 2.4 eq. to **S3a**). The resulting bright yellow slurry was stirred at room temperature for 20 min, and then the crude **S3a** obtained in the previous step (0.49 g, 2.0 mmol, 1.0 eq.) was dissolved in dry THF (1.5 mL) and added slowly via syringe. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed *in vacuo*, and the residue was dispersed in DCM (1 mL). After that, PE (10 mL) was added to precipitate Ph_3PO, and the slurry was filtered through a short pad of silica gel. The filter residue was washed with 50:1 PE/EA until TLC indicated no product **1a** remaining. The filtrate was concentrated *in vacuo*, and the residue was subjected to column chromatography (silica gel, PE as eluent) to give **1a** (0.44 g, 89% yield).

The starting materials for the synthesis of **1a-q**, as well as the yields for cyclopropanation reaction and Wittig reaction are given below. **S1** and **S2** are either commercially available or easily accessible by reported methods (the relevant references are shown in the table).

1	**S1**	**S2**	Step 1 (**S2→S3**)	Step 2 (**S3→1**)
 **1a**	 **S1a** [#] 0.49 g (3.2 mmol)	 **S2a** [2] 0.40 g (3.0 mmol)	3 h Crude product 0.49 g (67%)	12 h Pure product 0.44 g (89%)
 **1b**	 **S1b** [3] 0.54 g (3.2 mmol)	 **S2a** [2] 0.40 g (3.0 mmol)	2.5 h Crude product 0.74 g (93%)	12 h Pure product 0.51 g (71%)

1	**S1**	**S2**	Step 1 (**S2**→**S3**)	Step 2 (**S3**→**1**)
 **1c**	 **S1c**[4] 0.51 g (3.0 mmol)	 **S2c**[5] 0.38 g (2.6 mmol)	2.5 h Crude product 0.68 g (92%)	12 h Pure product 0.41 g (62%)
 **1d**	 **S1a**[#] 0.49 g (3.2 mmol)	 **S2d**[6] 0.50 g (3.0 mmol)	3 h Crude product 0.52 g (60%)	12 h Pure product 0.27 g (53%)
 **1e**	 **S1e**[#] 0.72 g (4.2 mmol)	 **S2e**[7] 0.85 g (4.0 mmol)	3 h Crude product 1.24 g (90%)	12 h Pure product 0.83 g (67%)
 **1f**	 **S1a**[#] 0.49 g (3.2 mmol)	 **S2f**[8] 0.60 g (3.0 mmol)	3.5 h Pure product[†] 0.17 g (18%)	18 h Pure product 0.11 g (68%)
 **1g**	 **S1g**[9] 0.58 g (3.1 mmol)	 **S2a**[2] 0.40 g (3.0 mmol)	2.5 h Crude product 0.73 g (87%)	12 h Pure product 0.69 g (96%)
 **1h**	 **S1h**[4] 0.46 g (3.2 mmol)	 **S2a**[2] 0.40 g (3.0 mmol)	3 h Crude product 0.61 g (83%)	12 h Pure product 0.43 g (72%)
 **1i**	 **S1i**[4] 0.51 g (3.2 mmol)	 **S2a**[2] 0.40 g (3.0 mmol)	3 h Crude product 0.76 g (100%)	12 h Pure product 0.47 g (62%)

1	**S1**	**S2**	Step 1 (**S2**→**S3**)	Step 2 (**S3**→**1**)
 **1j**	 **S1a** [#] 0.45 g (2.9 mmol)	 **S2j** [10] 0.50 g (2.7 mmol)	3 h Crude product 0.86 g (107%)	12 h Pure product 0.54 g (62%)
 **1k**	 **S1a** [#] 0.78 g (5.0 mmol)	 **S2k** [#] 0.42 g (7.5 mmol)	4 h Crude product 0.59 g (68%) [$]	12 h Pure product 0.24 g (41%)
 **1l**	 **S1a** [#] 0.49 g (3.2 mmol)	 **S2l** [#] 0.25 g (3.0 mmol)	3.5 h Crude product 0.55 g (90%)	12 h Pure product 0.42 g (78%)
 **1m**	 **S1a** [#] 0.53 g (3.4 mmol)	 **S2m** [11] 0.45 g (3.3 mmol)	3 h Crude product 0.57 g (67%)	12 h Pure product 0.44 g (79%)
 **1n**	 **S1n** [#] 0.44 g (3.3 mmol)	 **S2a** [2] 0.40 g (3.0 mmol)	3 h Crude product 0.50 g (73%)	12 h Pure product 0.13 g (25%)
 **1o**	 **S1o** [12] 0.75 g (4.1 mmol)	 **S2a** [2] 0.52 g (3.9 mmol)	3.5 h Pure product [†] 0.26 g (24%)	24 h Pure product 0.19 g (78%)
 **1p**	 **S1p** [#] 0.43 g (3.2 mmol)	 **S2a** [2] 0.40 g (3.0 mmol)	4 h Crude product 0.69 g (100%)	12 h Pure product 51.2 mg (8%)
 **1q**	 **S1n** [#] 1.08 g (8.02 mmol)	 **S2l** [#] 0.61g (7.3 mmol)	3 h Crude product (~100%) [‡]	12 h Pure product 0.84 g (65%)

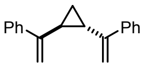
[#] These compounds are commercially available.

[†] These products were purified by column chromatography (silica gel, PE/EA = 100:1~50:1).

[$] Due to its volatile nature, acrolein (**S2k**) was added in an excess amount (1.5 eq. to **S1a**), and the crude yield was based on **S1a**.

[‡] This product was not weighed and was directly used in the next step assuming 100% yield.

Characterization data for substrates 1a-q:

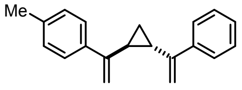


1a

Colorless oil, TLC R_f = 0.8 (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.37 – 7.27 (m, 6H), 5.34 (s, 2H), 5.06 (s, 2H), 1.93 – 1.87 (m, 2H), 1.24 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 141.4, 128.4, 127.7, 126.4, 109.6, 25.7, 15.3.

HRMS (EI): calcd. for $C_{19}H_{18}$ ([M·]$^+$): 246.1403, found 246.1404.

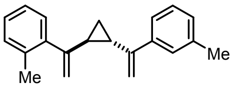


1b

Colorless oil, TLC R_f = 0.8 (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.37 – 7.27 (m, 3H), 7.17 – 7.13 (m, 2H), 5.34 (d, *J* = 0.9 Hz, 1H), 5.31 (d, *J* = 0.9 Hz, 1H), 5.05 (s, 1H), 5.01 (s, 1H), 2.36 (s, 3H), 1.93 – 1.85 (m, 2H), 1.22 – 1.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 148.6, 141.5, 138.6, 137.4, 129.1, 128.4, 127.7, 126.4, 126.3, 109.5, 108.8, 25.7, 25.6, 21.3, 15.3.

HRMS (EI): calcd. for $C_{20}H_{20}$ ([M·]$^+$): 260.1560, found 260.1559.

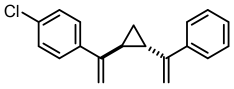


1c

Colorless oil, TLC R_f = 0.6 (PE/EA = 50:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.24 – 7.08 (m, 6H), 5.29 – 5.24 (m, 2H), 4.94 – 4.90 (m, 2H), 2.36 (s, 3H), 2.32 (s, 3H), 1.81 – 1.74 (m, 1H), 1.73 – 1.66 (m, 1H), 1.19 – 1.12 (m, 1H), 0.94 – 0.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 148.7, 141.4, 141.2, 137.8, 135.6, 130.0, 129.1, 128.4, 128.2, 127.2, 127.1, 125.4, 123.4, 112.1, 109.5, 28.3, 24.9, 21.7, 20.1, 13.9.

HRMS (EI): calcd. for $C_{21}H_{22}$ ([M·]$^+$): 274.1716, found 274.1722.

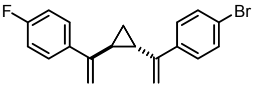


1d

Colorless oil, TLC R_f = 0.7 (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.48 – 7.44 (m, 2H), 7.37 – 7.27 (m, 5H), 5.34 (s, 1H), 5.32 (s, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 1.91 – 1.79 (m, 2H), 1.23 – 1.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.7, 141.4, 139.9, 133.5, 128.5, 128.4, 127.8, 127.7, 126.4, 110.1, 109.8, 25.8, 25.5, 15.2.

HRMS (EI): calcd. for $C_{19}H_{17}Cl$ ([M·]$^+$): 280.1013, found 280.1010.

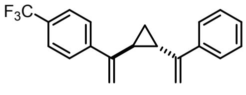


1e

Colorless oil, TLC R_f = 0.7 (PE/EA = 50:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 4H), 7.41 – 7.36 (m, 2H), 7.05 – 6.97 (m, 2H), 5.33 (s, 1H), 5.28 (s, 1H), 5.06 (s, 1H), 5.02 (s, 1H), 1.86 – 1.78 (m, 2H), 1.22 – 1.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.6 Hz), 147.64, 147.59, 140.3, 137.4 (d, *J* = 3.3 Hz), 131.5, 128.0, 127.9 (d, *J* = 7.8 Hz), 121.8, 115.2 (d, *J* = 21.3 Hz), 110.3, 109.7 (d, *J* = 1.1 Hz), 25.7, 25.4, 15.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.9.

HRMS (EI): calcd. for $C_{19}H_{16}BrF$ ([M·]$^+$): 342.0414, found 342.0403.

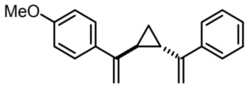


1f

Colorless oil, TLC R_f = 0.8 (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.54 (m, 2H), 7.39 – 7.30 (m, 3H), 5.43 (s, 1H), 5.38 (s, 1H), 5.18 (s, 1H), 5.08 (s, 1H), 1.96 – 1.86 (m, 2H), 1.30 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.8, 145.0 (q, *J* = 1.1 Hz), 141.3, 129.7 (q, *J* = 32.5 Hz), 128.4, 127.8, 126.7, 126.4, 125.3 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.8 Hz), 111.6, 109.9, 25.9, 25.4, 15.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5.

HRMS (EI): calcd. for $C_{20}H_{17}F_3$ ([M·]$^+$): 314.1277, found 314.1275.

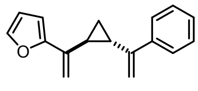


1g

Colorless oil, TLC R_f = 0.7 (PE/EA = 10:1). Column chromatography eluent: PE/EA = 100:1~50:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.36 – 7.27 (m, 3H), 6.89 – 6.84 (m, 2H), 5.33 (d, *J* = 1.0 Hz, 1H), 5.27 (d, *J* = 1.0 Hz, 1H), 5.05 (s, 1H), 4.97 (s, 1H), 3.82 (s, 3H), 1.91 – 1.83 (m, 2H), 1.23 – 1.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.9, 148.0, 141.5, 134.0, 128.4, 127.7, 127.5, 126.4, 113.7, 109.5, 108.0, 55.4, 25.7, 25.6, 15.3.

HRMS (ESI): calcd. for $C_{20}H_{21}O$ ([M+H]$^+$): 277.1587, found 277.1587.

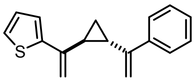


1h

Colorless oil, TLC R_f = 0.8 (PE/EA = 10:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.41 (d, *J* = 3.4 Hz, 1H), 6.38 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.52 (s, 1H), 5.34 (s, 1H), 5.05 (s, 1H), 4.95 (s, 1H), 1.91 – 1.82 (m, 2H), 1.23 – 1.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 148.7, 142.1, 141.3, 138.1, 128.4, 127.7, 126.4, 111.3, 109.7, 106.9, 106.7, 25.0, 23.1, 14.3.

HRMS (ESI): calcd. for $C_{17}H_{17}O$ ([M+H]$^+$): 237.1274, found 237.1272.

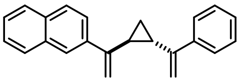


1i

Colorless oil, TLC $R_f = 0.7$ (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.37 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 6.98 (dd, J = 5.0, 3.8 Hz, 1H), 5.41 (s, 1H), 5.35 (s, 1H), 5.08 (s, 1H), 4.97 (s, 1H), 2.01 – 1.95 (m, 1H), 1.95 – 1.89 (m, 1H), 1.23 (ddd, J = 8.7, 5.8, 4.5 Hz, 1H), 1.16 (ddd, J = 8.6, 5.9, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 145.6, 142.2, 141.4, 128.4, 127.7, 127.5, 126.4, 124.5, 124.1, 109.8, 108.6, 25.3, 25.2, 15.0.

HRMS (EI): calcd. for $C_{17}H_{16}S$ ([M·]$^+$): 252.0967, found 252.0969.

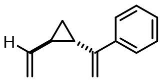


1j

Colorless oil, TLC $R_f = 0.7$ (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 1H), 7.84 – 7.79 (m, 2H), 7.78 – 7.74 (m, 1H), 7.70 (dd, J = 8.6, 1.9 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.49 – 7.44 (m, 2H), 7.37 – 7.28 (m, 3H), 5.50 (s, 1H), 5.39 (s, 1H), 5.17 (s, 1H), 5.12 (s, 1H), 2.04 – 1.95 (m, 2H), 1.31 – 1.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 148.6, 141.5, 138.6, 133.5, 133.0, 128.5, 128.4, 127.9, 127.7, 127.6, 126.5, 126.2, 126.0, 125.3, 124.7, 110.2, 109.8, 25.9, 25.8, 15.1.

HRMS (EI): calcd. for $C_{23}H_{20}$ ([M·]$^+$): 296.1560, found 296.1552.

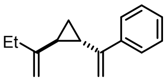


1k

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.57 (ddd, J = 17.1, 10.4, 8.6 Hz, 1H), 5.33 (s, 1H), 5.18 (dd, J = 16.9, 1.9 Hz, 1H), 5.00 (dd, J = 10.2, 1.5 Hz, 1H), 4.95 (s, 1H), 1.73 – 1.66 (m, 1H), 1.58 – 1.49 (m, 1H), 1.23 – 1.16 (m, 1H), 0.99 – 0.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 141.2, 141.0, 128.4, 127.7, 126.2, 113.0, 109.4, 26.1, 25.4, 14.0.

HRMS (EI): calcd. for $C_{13}H_{14}$ ([M·]$^+$): 170.1090, found 170.1086.

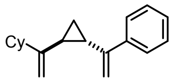


1l

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.30 (s, 1H), 4.96 (s, 1H), 4.75 – 4.73 (m, 2H), 2.10 (q, J = 7.4 Hz, 2H), 1.80 – 1.73 (m, 1H), 1.53 – 1.47 (m, 1H), 1.10 (t, J = 7.5 Hz, 3H), 1.09 – 1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 148.9, 141.5, 128.3, 127.6, 126.3, 109.3, 105.8, 28.5, 27.1, 24.8, 14.1, 12.8.

HRMS (EI): calcd. for $C_{15}H_{18}$ ([M·]$^+$): 198.1403, found 198.1399.

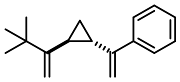


1m

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

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.51 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.29 (s, 1H), 4.96 (s, 1H), 4.69 (s, 1H), 4.62 (s, 1H), 1.98 (tt, J = 11.5, 3.4 Hz, 1H), 1.87 – 1.64 (m, 6H), 1.46 (dt, J = 8.7, 5.4 Hz, 1H), 1.32 – 1.14 (m, 5H), 1.05 (ddd, J = 8.7, 5.8, 4.4 Hz, 1H), 1.00 (ddd, J = 8.5, 5.9, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.9, 149.1, 141.5, 128.3, 127.6, 126.3, 109.2, 104.3, 45.3, 32.84, 32.81, 26.9 (2C), 26.5, 25.5, 25.4, 15.2.

HRMS (EI): calcd. for $C_{19}H_{24}$ ([M·]$^+$): 252.1873, found 252.1870.

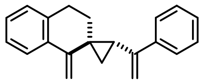


1n

Colorless oil, TLC R_f = 0.8 (PE/EA = 20:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.49 (m, 2H), 7.36 – 7.27 (m, 3H), 5.27 (s, 1H), 4.97 (s, 1H), 4.76 (s, 1H), 4.57 (s, 1H), 1.77 – 1.70 (m, 1H), 1.59 – 1.53 (m, 1H), 1.15 (s, 9H), 1.06 (ddd, J = 8.7, 5.8, 4.3 Hz, 1H), 1.01 (ddd, J = 8.6, 6.0, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.9, 149.3, 141.6, 128.3, 127.6, 126.4, 109.0, 102.7, 36.8, 29.7, 26.1, 23.0, 16.6.

HRMS (EI): calcd. for $C_{17}H_{22}$ ([M·]$^+$): 226.1716, found 226.1713.

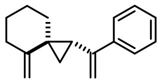


1o

Colorless oil, TLC R_f = 0.6 (PE/EA = 50:1). Column chromatography eluent: PE.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.68 (m, 1H), 7.53 – 7.48 (m, 2H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.17 (m, 2H), 7.10 – 7.06 (m, 1H), 5.65 (s, 1H), 5.57 (s, 1H), 5.06 (s, 1H), 4.97 (s, 1H), 2.76 (ddd, J = 16.1, 8.4, 5.1 Hz, 1H), 2.66 (ddd, J = 16.1, 6.7, 4.9 Hz, 1H), 2.28 (ddd, J = 8.3, 6.5, 1.4 Hz, 1H), 1.70 (ddd, J = 13.3, 8.4, 4.9 Hz, 1H), 1.62 (ddd, J = 13.3, 6.8, 5.1 Hz, 1H), 1.17 (dd, J = 8.4, 4.8 Hz, 1H), 1.11 (dd, J = 6.5, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.0, 145.1, 141.1, 137.9, 135.3, 129.1, 128.4, 127.69, 127.67, 126.07, 126.06, 124.5, 112.0, 103.9, 31.8, 29.4, 28.6, 26.8, 19.9.

HRMS (EI): calcd. for $C_{21}H_{20}$ ([M·]$^+$): 272.1560, found 272.1562.

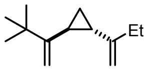


1p

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

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.56 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 5.54 (s, 1H), 4.97 (s, 1H), 4.74 (s, 1H), 4.68 (s, 1H), 2.35 – 2.20 (m, 2H), 2.09 (ddd, J = 8.2, 6.0, 1.3 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.54 – 1.37 (m, 4H), 1.34 – 1.27 (m, 1H), 0.90 (dd, J = 8.2, 4.5 Hz, 1H), 0.81 (dd, J = 5.9, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.0, 145.7, 142.0, 128.4, 127.5, 126.3, 112.7, 104.7, 35.5, 31.2, 30.8, 28.8, 28.1, 25.4, 17.2.

HRMS (EI): calcd. for $C_{17}H_{20}$ ([M·]$^+$): 224.1560, found 224.1555.



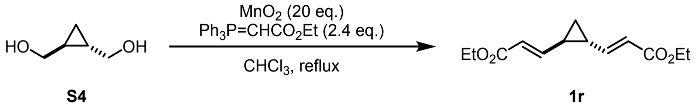
1q

Colorless oil, TLC R_f = 0.8 (PE). Column chromatography eluent: *n*-Pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 1H), 4.67 – 4.65 (m, 1H), 4.64 (s, 1H), 4.48 (s, 1H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.48 – 1.42 (m, 1H), 1.31 – 1.25 (m, 1H), 1.13 (s, 9H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.93 – 0.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 152.1, 105.1, 102.6, 36.7, 29.8, 28.4, 28.1, 22.6, 14.4, 12.8.

HRMS (EI): calcd. for $C_{13}H_{22}$ ($[M\cdot]^+$): 178.1716, found 178.1713.

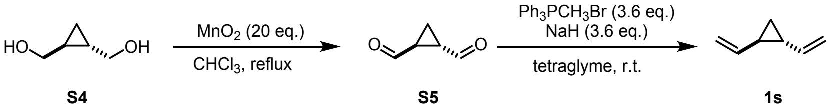
Synthesis of compound 1r:



Compound **1r** was synthesized following a reported procedure.[13] 0.21 g (2.0 mmol) of **S4** [13] gave 0.22 g (0.92 mmol) of **1r** as a white solid, yield 46%.

Characterization data for **1r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (dd, *J* = 15.4, 9.5 Hz, 2H), 5.90 (d, *J* = 15.4 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 1.86 – 1.77 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H), 1.24 (t, *J* = 6.8 Hz, 2H, overlapping signal). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 149.6, 120.1, 60.4, 25.3, 17.6, 14.4. Consistent with previous report.[13]

Synthesis of compound 1s:



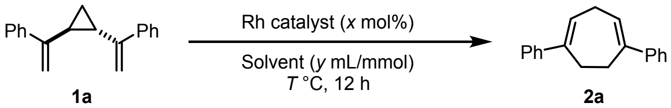
To a solution of **S4** [13] (1.03 g, 10.1 mmol) in $CHCl_3$ (50 mL) was added activated MnO_2 (17.24 g, 198.3 mmol). The mixture was refluxed for 18 h and then filtered through Celite. The filter residue was washed with Et_2O until TLC indicated no **S5** remaining, and the combined filtrate was evaporated at 10 °C to give crude **S5** as a yellow oil (0.80 g, 81% crude yield), which was directly used in the next step without further purification.

To a mixture of Ph_3PCH_3Br (10.61 g, 29.70 mmol) and NaH (60% dispersion in mineral oil, 1.19 g, 29.8 mmol) under N_2 atmosphere was added tetraglyme (30 mL). The mixture was heated at 60 °C for 12 h, during which the reaction system turned yellow. The mixture was cooled to room temperature and a solution of **S5** (0.80 g, 8.2 mmol) in tetraglyme (10 mL) was added slowly. After 4 h of stirring at room temperature, the system was heated to 60 °C and all volatile components were evacuated into a cold trap (dry ice / acetone). This gave 0.29 g of a colorless oil, which was found to be a mixture of **1s** and benzene (1:0.52 molar ratio) by ^{1}H NMR. As this molar ratio corresponded to 70 wt% of **1s**, the corrected yield for **1s** was 26%.

Characterization data for **1s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 – 5.36 (m, 2H), 5.07 (dd, *J* = 17.0, 1.6 Hz, 2H), 4.90 (dd, *J* = 10.2, 1.6 Hz, 2H), 1.50 – 1.42 (m, 2H), 0.87 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 112.4, 24.7, 15.1. Consistent with previous report.[14]

III. Reaction optimization

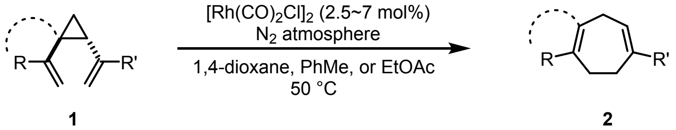
Below is the full list of reaction conditions that were evaluated during reaction optimization. All reactions were carried out on 0.10 mmol scale under N_2 atmosphere. After 12 h, the reaction mixture was concentrated *in vacuo* and ^1H NMR analysis ($CDCl_3$ as solvent) was performed. The conversion was determined by comparing the integrals of **1a** (δ = 5.34, s, 2H) and **2a** (δ = 3.14, tt, 2H), assuming 100% mass balance.



Entry	Rh catalyst	*x*	Solvent	*y*	*T* (°C)	Conversion
0	$[Rh(CO)_2Cl]_2$	5	PhMe	20	30	25%
1	$[Rh(CO)_2Cl]_2$	5	PhMe	20	40	76%
2	$[Rh(CO)_2Cl]_2$	5	DCE	20	40	55%
3	$[Rh(CO)_2Cl]_2$	5	1,4-dioxane	20	40	90%
4	$[Rh(CO)_2Cl]_2$	5	THF	20	40	60%
5	$[Rh(CO)_2Cl]_2$	5	MeCN	20	40	5%
6	$[Rh(CO)_2Cl]_2$	5	MeOH	20	40	10%
7	$[Rh(CO)_2Cl]_2$	5	EtOAc	20	40	84%
8	$[Rh(CO)_2Cl]_2$	5	DME	20	40	68%
9	$[Rh(CO)_2Cl]_2$	5	acetone	20	40	74%
10	$[Rh(CO)_2Cl]_2$	5	1,4-dioxane	10	40	99%
11	**$[Rh(CO)_2Cl]_2$**	**2.5**	**1,4-dioxane**	**10**	**50**	**100%**
12	$[Rh(cod)Cl]_2$	5	PhMe	20	40	0
13	$[Rh(coe)_2Cl]_2$	5	PhMe	20	40	0
14	$[Rh(C_2H_4)_2Cl]_2$	5	PhMe	20	40	0
15	$Rh(CO)_2(acac)$	10	PhMe	20	40	0
16	$Rh(C_2H_4)_2(acac)$	10	PhMe	20	40	0
17	$[Rh(cod)_2]BF_4$	10	PhMe	20	40	0
18	$Rh(PPh_3)_3Cl$	10	PhMe	20	40	0

IV. General procedure and experimental details of Rh-catalyzed DVCP rearrangement

General procedure for substrates 1a-r:



A reaction vessel (20~25 mL) was charged with substrate **1** (0.20 mmol, 1.0 eq.) and $[Rh(CO)_2Cl]_2$ (2.5 mol%, 5 mol%, or 7 mol% as indicated below). The reaction vessel was sealed with a rubber septum, evacuated, and refilled with N_2. Solvent (1,4-dioxane, toluene, or ethyl acetate as indicated below, 2.0 mL) was added to dissolve the substrate and the catalyst, resulting in a yellowish solution. The reaction mixture was stirred at 50 °C (oil bath) until full conversion of the substrate as judged by TLC. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel) to give product **2**.

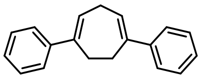
Notes:

(1) $[Rh(CO)_2Cl]_2$ can be safely stored and weighed outside a glovebox. Substrate **1** is stable enough to be handled in open air, but does slowly polymerize if left to stand for several days; for optimum yield immediate use of substrate **1** after isolation is suggested.

(2) For column chromatography the eluent system of PE/DCM is recommended over PE/EA, as the latter may partially elute the catalyst and result in red impurities in the product.

(3) This reaction can be carried out without inert gas protection. See Section V for details.

Experimental details and characterization data:



2a

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 100:1.

Run 1: 49.4 mg (0.201 mmol) of **1a** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 49.3 mg of **2a**, 100% yield.

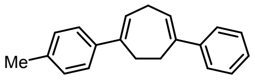
Run 2: 49.4 mg (0.201 mmol) of **1a** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 49.2 mg of **2a**, 100% yield.

Average yield: 100%

Colorless oil, TLC $R_f = 0.4$ (PE/EA = 50:1).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.35 (m, 4H), 7.33 – 7.27 (m, 4H), 7.25 – 7.19 (m, 2H), 6.09 (t, J = 5.9 Hz, 2H), 3.14 (tt, J = 5.8, 1.6 Hz, 2H), 2.85 (t, J = 1.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 142.1, 128.4, 126.8, 125.9, 125.8, 29.7, 27.5.

HRMS (EI): calcd. for $C_{19}H_{18}$ ($[M\cdot]^+$): 246.1403, found 246.1402.



2b

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 50:1.

Run 1: 52.1 mg (0.200 mmol) of **1b** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 51.3

mg of **2b**, 98% yield.

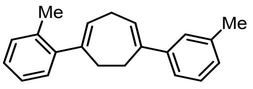
Run 2: 52.1 mg (0.200 mmol) of **1b** and 2.0 mg (5.1 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 50.9 mg of **2b**, 98% yield.

Average yield: 98%

Colorless oil, TLC R_f = 0.6 (PE/EA = 50:1).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.25 (m, 4H), 7.24 – 7.19 (m, 1H), 7.14 – 7.10 (m, 2H), 6.09 (t, *J* = 5.8 Hz, 1H), 6.06 (t, *J* = 5.8 Hz, 1H), 3.12 (tt, *J* = 5.8, 1.6 Hz, 2H), 2.86 – 2.80 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 142.1, 141.9, 141.1, 136.4, 129.1, 128.4, 126.7, 126.0, 125.8, 125.7, 125.1, 29.74, 29.72, 27.5, 21.2.

HRMS (EI): calcd. for $C_{20}H_{20}$ ([M·]$^+$): 260.1560, found 260.1558.



2c

Reaction performed in 1,4-dioxane for 48 h. Column chromatography eluent: PE.

Run 1: 54.9 mg (0.200 mmol) of **1c** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 48.9 mg of **2c**, 89% yield.

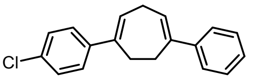
Run 2: 54.8 mg (0.200 mmol) of **1c** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 47.1 mg of **2c**, 86% yield.

Average yield: 88%

Colorless oil, TLC R_f = 0.5 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.06 (m, 8H), 6.13 (t, *J* = 5.9 Hz, 1H), 5.61 (t, *J* = 5.6 Hz, 1H), 3.15 – 3.08 (m, 2H), 2.89 – 2.84 (m, 2H), 2.63 – 2.57 (m, 2H), 2.38 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 144.0, 143.1, 142.4, 137.9, 135.0, 130.1, 128.6, 128.3, 127.5, 126.7, 126.6, 126.4, 126.1, 125.7, 122.9, 32.1, 29.8, 27.6, 21.7, 20.0.

HRMS (EI): calcd. for $C_{21}H_{22}$ ([M·]$^+$): 274.1716, found 274.1718.



2d

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 100:1.

Run 1: 56.1 mg (0.200 mmol) of **1d** and 2.0 mg (5.1 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 55.4 mg of **2d**, 99% yield.

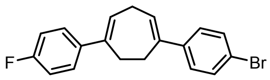
Run 2: 56.2 mg (0.200 mmol) of **1d** and 2.0 mg (5.1 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 53.2 mg of **2d**, 95% yield.

Average yield: 97%

Colorless oil, TLC R_f = 0.6 (PE/EA = 50:1).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.26 (m, 6H), 7.25 – 7.19 (m, 1H), 6.09 (t, *J* = 5.9 Hz, 1H), 6.08 (t, *J* = 5.9 Hz, 1H), 3.15 – 3.10 (m, 2H), 2.87 – 2.78 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 142.4, 142.1, 140.9, 132.5, 128.42, 128.38, 127.1, 126.8, 126.4, 125.8, 125.7, 29.63, 29.57, 27.5.

HRMS (EI): calcd. for $C_{19}H_{17}Cl$ ([M·]$^+$): 280.1013, found 280.1012.



2e

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 50:1.

Run 1: 68.8 mg (0.200 mmol) of **1e** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 67.3 mg of **2e**, 98% yield.

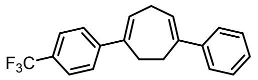
Run 2: 68.7 mg (0.200 mmol) of **1e** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 66.5 mg of **2e**, 97% yield.

Average yield: 98%

Colorless oil, TLC $R_f = 0.6$ (PE/EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.03 – 6.94 (m, 2H), 6.07 (t, J = 5.9 Hz, 1H), 6.01 (t, J = 5.9 Hz, 1H), 3.11 (tt, J = 5.9, 1.6 Hz, 2H), 2.80 (t, J = 1.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, J = 245.3 Hz), 142.8, 141.1, 141.0, 139.9 (d, J = 3.4 Hz), 131.4, 127.5, 127.3 (d, J = 7.8 Hz), 126.6, 125.7 (d, J = 1.0 Hz), 120.6, 115.1 (d, J = 21.3 Hz), 29.8, 29.5, 27.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.3.

HRMS (EI): calcd. for $C_{19}H_{16}BrF$ ($[M\cdot]^+$): 342.0414, found 342.0406.



2f

Reaction performed in 1,4-dioxane for 36 h. Column chromatography eluent: PE.

Run 1: 63.0 mg (0.200 mmol) of **1f** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 58.0 mg of **2f**, 92% yield.

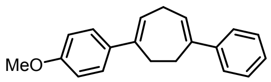
Run 2: 62.9 mg (0.200 mmol) of **1f** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 61.2 mg of **2f**, 97% yield.

Average yield: 94%

Colorless oil, TLC $R_f = 0.6$ (PE).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 6.20 (t, J = 5.9 Hz, 1H), 6.12 (t, J = 5.9 Hz, 1H), 3.18 (tt, J = 5.9, 1.7 Hz, 2H), 2.92 – 2.84 (m, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.0 (q, J = 1.3 Hz), 144.1, 142.5, 141.3, 128.74 (q, J = 32.2 Hz), 128.69, 128.6, 127.2, 126.4, 126.0, 125.9, 125.6 (q, J = 3.8 Hz), 125.0 (q, J = 271.6 Hz), 29.83, 29.80, 27.8. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -62.7.

HRMS (EI): calcd. for $C_{20}H_{17}F_3$ ($[M\cdot]^+$): 314.1277, found 314.1274.



2g

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 8:1~5:1.

Run 1: 55.2 mg (0.200 mmol) of **1g** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 51.7 mg of **2g**, 94% yield.

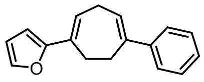
Run 2: 55.4 mg (0.200 mmol) of **1g** and 2.0 mg (5.1 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 52.7 mg of **2g**, 95% yield.

Average yield: 94%

Colorless oil, TLC $R_f = 0.4$ (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 4H), 7.17 – 7.12 (m, 1H), 6.80 – 6.75 (m, 2H), 6.00 (t, *J* = 5.8 Hz, 1H), 5.93 (t, *J* = 5.9 Hz, 1H), 3.73 (s, 3H), 3.06 – 2.99 (m, 2H), 2.75 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 144.0, 142.0, 141.5, 136.6, 128.4, 126.8, 126.7, 126.1, 125.8, 124.5, 113.7, 55.4, 29.8, 29.7, 27.5.

HRMS (ESI): calcd. for $C_{20}H_{21}O$ ($[M+H]^+$): 277.1587, found 277.1586.



2h

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 50:1.

Run 1: 47.3 mg (0.200 mmol) of **1h** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 46.0 mg of **2h**, 97% yield.

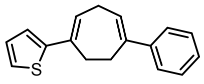
Run 2: 47.4 mg (0.201 mmol) of **1h** and 2.0 mg (5.1 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 45.2 mg of **2h**, 95% yield.

Average yield: 96%

Colorless viscous oil, TLC R_f = 0.5 (PE/EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.25 – 7.20 (m, 1H), 6.41 (t, *J* = 6.0 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.22 (d, *J* = 3.3 Hz, 1H), 6.07 (t, *J* = 5.8 Hz, 1H), 3.15 (tt, *J* = 6.0, 1.6 Hz, 2H), 2.87 – 2.80 (m, 2H), 2.75 – 2.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 143.8, 142.4, 141.4, 131.5, 128.4, 126.8, 126.1, 125.8, 122.9, 111.1, 104.2, 29.4, 27.1, 27.0.

HRMS (ESI): calcd. for $C_{17}H_{17}O$ ($[M+H]^+$): 237.1274, found 237.1274.



2i

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 50:1.

Run 1: 50.5 mg (0.200 mmol) of **1i** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 49.7 mg of **2i**, 98% yield.

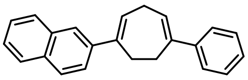
Run 2: 50.5 mg (0.200 mmol) of **1i** and 2.0 mg (5.1 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 50.4 mg of **2i**, 100% yield.

Average yield: 99%

Colorless viscous oil, TLC R_f = 0.6 (PE/EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.20 (m, 1H), 7.11 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.29 (t, *J* = 6.0 Hz, 1H), 6.09 (t, *J* = 5.9 Hz, 1H), 3.15 – 3.09 (m, 2H), 2.90 – 2.82 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.6, 142.3, 135.5, 128.4, 127.4, 126.8, 126.0, 125.8, 124.5, 123.2, 121.8, 29.7, 29.3, 27.2.

HRMS (EI): calcd. for $C_{17}H_{16}S$ ($[M\cdot]^+$): 252.0967, found 252.0964.



2j

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE/DCM = 100:1.

Run 1: 59.6 mg (0.201 mmol) of **1j** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 59.4 mg of **2j**, 100% yield.

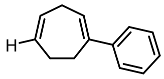
Run 2: 59.4 mg (0.200 mmol) of **1j** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 58.3 mg of **2j**, 98% yield.

Average yield: 99%

Colorless viscous oil, TLC R_f = 0.4 (PE/EA = 50:1).

^1H NMR (400 MHz, CD_2Cl_2) δ 7.85 – 7.77 (m, 4H), 7.58 (dd, J = 8.6, 1.9 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 6.28 (t, J = 5.9 Hz, 1H), 6.12 (t, J = 5.9 Hz, 1H), 3.20 (tt, J = 6.0, 1.6 Hz, 2H), 3.01 – 2.95 (m, 2H), 2.93 – 2.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 142.2, 142.0, 141.1, 133.6, 132.5, 128.4, 128.1, 127.9, 127.6, 126.8, 126.6, 126.2, 125.9, 125.8, 125.6, 124.7, 124.0, 29.8, 29.7, 27.7.

HRMS (EI): calcd. for $C_{23}H_{20}$ ([M·]$^+$): 296.1560, found 296.1559.



2k

Reaction performed in 1,4-dioxane for 12 h. Column chromatography eluent: PE.

Run 1: 34.2 mg (0.201 mmol) of **1k** and 1.9 mg (4.9 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 31.1 mg of **2k**, 91% yield.

Run 2: 34.2 mg (0.201 mmol) of **1k** and 2.0 mg (5.1 µmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 32.1 mg of **2k**, 94% yield.

Average yield: 92%

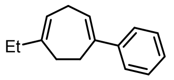
Note: This compound is potentially volatile and prolonged evacuation may lead to reduced yields.

Colorless oil, TLC R_f = 0.6 (PE).

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 6.11 (t, J = 6.0 Hz, 1H), 5.75 – 5.68 (m, 1H), 5.68 – 5.61 (m, 1H), 3.02 – 2.95 (m, 2H), 2.86 – 2.78 (m, 2H), 2.39 – 2.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.2, 130.7, 128.3, 127.7, 126.9, 126.6, 125.7, 30.0, 27.7, 27.0.

HRMS (EI): calcd. for $C_{13}H_{14}$ ([M·]$^+$): 170.1090, found 170.1085.

A previous work[15] claimed of synthesis of this compound, but what the authors actually obtained was 1-phenylcyclohepta-1,3-diene.[16,17]



2l

Reaction performed in toluene for 18 h. Column chromatography eluent: PE.

Run 1: 39.6 mg (0.200 mmol) of **1l** and 3.9 mg (10 µmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 37.6 mg of **2l**, 95% yield.

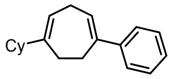
Run 2: 39.6 mg (0.200 mmol) of **1l** and 3.9 mg (10 µmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 36.7 mg of **2l**, 93% yield.

Average yield: 94%

Colorless oil, TLC R_f = 0.6 (PE).

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 6.07 (t, J = 5.9 Hz, 1H), 5.48 (t, J = 5.7 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.76 – 2.70 (m, 2H), 2.37 – 2.31 (m, 2H), 2.01 (q, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.9, 142.3, 128.3, 127.1, 126.6, 125.7, 120.0, 32.4, 30.1, 29.5, 27.1, 12.9.

HRMS (EI): calcd. for $C_{15}H_{18}$ ([M·]$^+$): 198.1403, found 198.1398.



2m

Reaction performed in toluene for 48 h. Column chromatography eluent: PE.

Run 1: 50.5 mg (0.200 mmol) of **1m** and 3.9 mg (10 μmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 45.0 mg of **2m**, 89% yield.

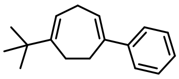
Run 2: 50.4 mg (0.200 mmol) of **1m** and 3.9 mg (10 μmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 45.9 mg of **2m**, 91% yield.

Average yield: 90%

Colorless oil, TLC R_f = 0.6 (PE).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.27 (m, 4H), 7.23 – 7.18 (m, 1H), 5.99 (t, *J* = 5.8 Hz, 1H), 5.50 (t, *J* = 5.7 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.67 – 2.62 (m, 2H), 2.42 – 2.36 (m, 2H), 1.90 – 1.80 (m, 1H), 1.80 – 1.64 (m, 5H), 1.33 – 1.08 (m, 5H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.0, 144.5, 141.7, 128.3, 126.6, 126.4, 125.8, 120.1, 47.3, 32.1, 30.1, 28.6, 27.2, 26.9, 26.6.

HRMS (EI): calcd. for $C_{19}H_{24}$ ([M·]$^+$): 252.1873, found 252.1868.



2n

Reaction performed in toluene for 96 h. Column chromatography eluent: PE.

Run 1: 45.4 mg (0.200 mmol) of **1n** and 5.5 mg (14 μmol, 7 mol%) of $[Rh(CO)_2Cl]_2$ gave 45.0 mg of **2n**, 99% yield.

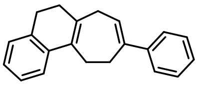
Run 2: 45.3 mg (0.200 mmol) of **1n** and 5.5 mg (14 μmol, 7 mol%) of $[Rh(CO)_2Cl]_2$ gave 43.2 mg of **2n**, 95% yield.

Average yield: 97%

Colorless oil, TLC R_f = 0.6 (PE).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 5.94 (t, *J* = 5.7 Hz, 1H), 5.67 (t, *J* = 5.9 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.60 – 2.52 (m, 4H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 151.4, 144.9, 140.9, 128.2, 126.6, 125.8, 125.5, 120.0, 36.5, 30.6, 28.9, 27.1, 26.3.

HRMS (EI): calcd. for $C_{17}H_{22}$ ([M·]$^+$): 226.1716, found 226.1712.



2o

Reaction performed in 1,4-dioxane for 48 h. Column chromatography eluent: PE~200:1 PE/EA.

Run 1: 54.4 mg (0.200 mmol) of **1o** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 41.2 mg of **2o**, 76% yield.

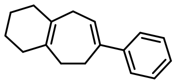
Run 2: 54.4 mg (0.200 mmol) of **1o** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ gave 43.1 mg of **2o**, 79% yield.

Average yield: 78%

Colorless oil, TLC R_f = 0.6 (PE).

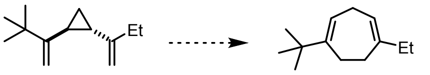
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.27 (m, 5H), 7.24 – 7.18 (m, 2H), 7.14 – 7.08 (m, 2H), 6.01

(tt, $J = 5.8, 1.3$ Hz, 1H), 3.19 (d, $J = 5.8$ Hz, 2H), 2.95 – 2.90 (m, 2H), 2.80 – 2.73 (m, 4H), 2.33 (tt, $J = 8.1, 1.3$ Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 141.6, 137.7, 136.5, 135.4, 131.3, 128.3, 127.4, 126.8, 126.5, 125.9, 125.8, 124.7, 121.7, 34.3, 31.3, 29.6, 29.1, 26.3.
HRMS (EI): calcd. for $C_{21}H_{20}$ ([M·]$^+$): 272.1560, found 272.1561.



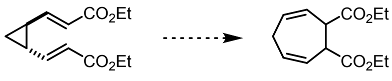
2p

Reaction performed in ethyl acetate for 60 h. Column chromatography eluent: PE.
Run 1: 44.7 mg (0.199 mmol) of **1p** and 3.8 mg (9.8 μmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 21.0 mg of **2p**, 47% yield.
Run 2: 44.9 mg (0.200 mmol) of **1p** and 3.9 mg (10 μmol, 5 mol%) of $[Rh(CO)_2Cl]_2$ gave 21.5 mg of **2p**, 48% yield.
Average yield: 48%
Colorless oil, TLC $R_f = 0.3$ (PE).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 6.05 (t, $J = 6.1$ Hz, 1H), 2.86 (d, $J = 6.1$ Hz, 2H), 2.68 – 2.63 (m, 2H), 2.32 – 2.26 (m, 2H), 2.02 – 1.95 (m, 4H), 1.61 – 1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.7, 132.1, 130.5, 128.3, 126.6, 126.2, 125.7, 33.5, 32.4, 32.2, 31.4, 29.4, 23.5, 23.2.
HRMS (EI): calcd. for $C_{17}H_{20}$ ([M·]$^+$): 224.1560, found 224.1554.



1q **2q** (N. D.)

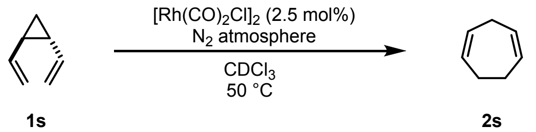
The reaction was performed with 35.6 mg (0.200 mmol) of **1q** and 1.9 mg (4.9 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ in 1,4-dioxane (2.0 mL). After 24 h of stirring at 50 °C, ^{1}H NMR indicated that no reaction occurred.



1r **2r** (N. D.)

The reaction was performed with 47.7 mg (0.200 mmol) of **1r** and 2.0 mg (5.1 μmol, 2.5 mol%) of $[Rh(CO)_2Cl]_2$ in 1,4-dioxane (2.0 mL). After 12 h of stirring at 50 °C, ^{1}H NMR indicated that no reaction occurred. The same experiment at 70 °C also resulted in no conversion. We did not test the Rh-catalyzed reaction at an even higher temperature, because **1r** had been reported to undergo thermal rearrangement at 100 °C.[18]

Procedure for substrate 1s:



1s **2s**

A 20-mL reaction vessel was charged with $[Rh(CO)_2Cl]_2$ (1.9 mg, 2.5 mol%), sealed with a rubber septum, evacuated, and refilled with N_2. **1s** (70 wt% in benzene, 27.0 mg, 0.201 mmol, 1.0

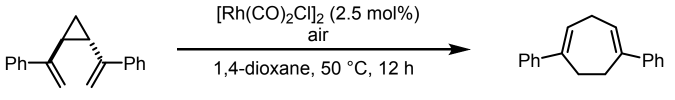
eq.) was dissolved in $CDCl_3$ (2.0 mL) and added via syringe. The resulting pale yellow solution was stirred at 50 °C. After 12 h, 0.6 mL of the reaction mixture was withdrawn from the system and directly subjected to ^1H NMR, which indicated that **1s** had been fully converted to **2s**.

As **2s** was too volatile, its isolated yield could not be determined. Instead, we estimated the NMR yield of **2s** using benzene as internal standard. In the ^1H NMR spectrum for the substrate, the integration for benzene (δ = 7.36, s, 6H) was 3.11 after **1s** had been normalized. After the reaction, the integration of benzene changed to 3.13 with the integration of **2s** normalized. Assuming the amount of benzene was unchanged, the yield of **2s** was 3.11/3.13 = 99% (See Section VIII for the original spectra).

Characterization data for **2s**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (d, J = 10.1 Hz, 2H), 5.64 (dt, J = 10.2, 4.9 Hz, 2H), 2.87 (tt, J = 5.1, 1.7 Hz, 2H), 2.27 (br s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.3, 128.5, 28.7, 27.1. Consistent with previous report.[19,20]

V. Unprotected reactions: 0.2 mmol scale, gram scale, and reduced catalyst loading

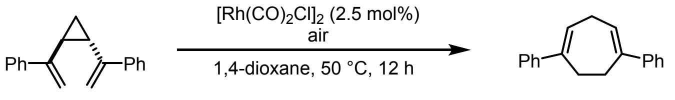
Unprotected reaction at 0.2 mmol scale:



1a **2a**

In open air (28 °C, 41% relative humidity), a reaction vessel (20 mL) was charged with substrate **1a** (49.2 mg, 0.200 mmol, 1.0 eq.) and $[Rh(CO)_2Cl]_2$ (1.9 mg, 4.9 µmol, 2.5 mol%). The reaction vessel was sealed with a rubber septum. 1,4-Dioxane (2.0 mL) was added via syringe to dissolve the substrate and the catalyst, resulting in a yellowish solution. The reaction mixture was stirred at 50 °C (oil bath) for 12 h, concentrated *in vacuo*, and subjected to column chromatography (silica gel, PE/DCM = 50:1) to give product **2a** (48.8 mg, 99% yield) as a colorless oil. The completeness of the reaction was confirmed by ^{1}H NMR.

Unprotected reaction at gram scale:

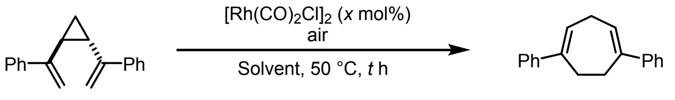


1a **2a**

In open air (27 °C, 70% relative humidity), a round-bottomed flask (100 mL) was charged with substrate **1a** (1.11 g, 4.49 mmol, 1.0 eq.), $[Rh(CO)_2Cl]_2$ (43.6 mg, 0.112 mmol, 2.5 mol%), and 1,4-dioxane (45 mL). The flask was sealed with a rubber septum. The reaction mixture was stirred at 50 °C (oil bath) for 12 h, concentrated *in vacuo*, and subjected to column chromatography (silica gel, PE/DCM = 50:1) to give product **2a** (1.10 g, 99% yield) as a colorless oil. The completeness of the reaction was confirmed by ^{1}H NMR.

Note: Even though the reaction can be safely carried out without inert gas protection, we recommend to seal the reaction system with a rubber septum. Otherwise, the reaction will proceed with a somewhat slower rate, possibly due to gradual loss of CO.

Unprotected reaction with reduced catalyst loading:



1a **2a**

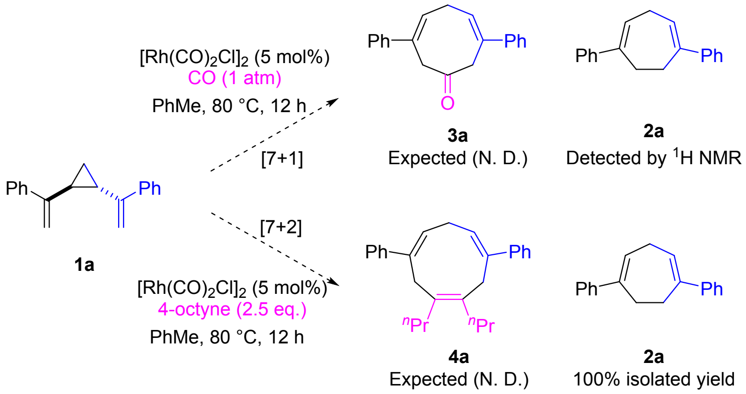
General procedure: In open air, a reaction vessel (20 mL) was charged with substrate **1a** (123.2/*x* mg, 0.5/*x* mmol, 1.0 eq.) and $[Rh(CO)_2Cl]_2$ (1.9 mg, 4.9 µmol, *x* mol%). The vessel was sealed with a rubber septum. Solvent (2.0 mL) was added via syringe. The resulting yellowish solution was stirred at 50 °C for *t* hours, concentrated *in vacuo*, and subjected to ^{1}H NMR analysis ($CDCl_3$ as solvent). The conversion was determined by comparing the integrals of **1a** ($\delta = 5.34$, s, 2H) and **2a** ($\delta = 3.14$, tt, 2H), assuming 100% mass balance (the NMR spectra were extremely clean and no by-product could be observed).

Entry	***x***	**Solvent**	***t* (h)**	**Conversion**
1	2.5	1,4-dioxane	12	100%
2	2.0	1,4-dioxane	36	75%
3	1.5	1,4-dioxane	36	65%
4	2.0	EtOAc	12 18	99% 100%
5	1.5	EtOAc	18	100%
6	1.0	EtOAc	18 24	98% 100%

We noticed that when 1,4-dioxane was used as solvent, 2.5 mol% of $[Rh(CO)_2Cl]_2$ seemed to be the lower limit of catalyst loading. Further reducing $[Rh(CO)_2Cl]_2$ to 2.0 mol% or 1.5 mol% resulted in incomplete conversion, even after 36 hours of stirring (Entries 2-3). It seemed that the Rh catalyst was deactivated after around 20 turnovers.

Nevertheless, by changing the solvent to EtOAc, it was possible to reduce the catalyst loading (at the expense of extended reaction time). With 2.0 mol% of $[Rh(CO)_2Cl]_2$, the reaction was almost complete in 12 h, and 18 h was enough to guarantee full conversion (Entry 4). With 1.5 mol% of $[Rh(CO)_2Cl]_2$, the reaction was also complete in 18 h (Entry 5). With 1.0 mol% of $[Rh(CO)_2Cl]_2$, the reaction proceeded with 98% conversion in 18 h, and 24 h was enough to guarantee full conversion (Entry 6). It seems that further decrease of catalyst loading is still possible, provided that one doesn’t mind the reaction time.

VI. Failed attempt of [7+1] and [7+2] cycloadditions



Attempt of [7+1] reaction: A reaction vessel (20 mL) was charged with **1a** (24.7 mg, 0.100 mmol), [Rh(CO)$_2$Cl]$_2$ (1.9 mg, 4.9 µmol) and PhMe (2.0 mL). The system was sealed with a rubber septum, bubbled with CO (1 atm) for 10 min, and then stirred at 80 °C (oil bath) under CO atmosphere for 12 h. ^{1}H NMR of the crude reaction mixture indicated that the only product formed was **2a**.

Attempt of [7+2] reaction: A reaction vessel (25 mL) was charged with **1a** (24.6 mg, 99.9 µmol) and [Rh(CO)$_2$Cl]$_2$ (1.9 mg, 4.9 µmol). The vessel was sealed with a rubber septum, evacuated, and refilled with N$_2$. 4-Octyne (27.6 mg, 0.250 mmol) was dissolved in PhMe (2.0 mL) and added via syringe. The reaction mixture was stirred at 80 °C (oil bath) for 12 h, evaporated, and subjected to column chromatography (silica gel, PE/DCM = 100:1) to give **2a** (24.7 mg, 100% yield).

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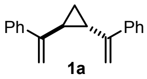
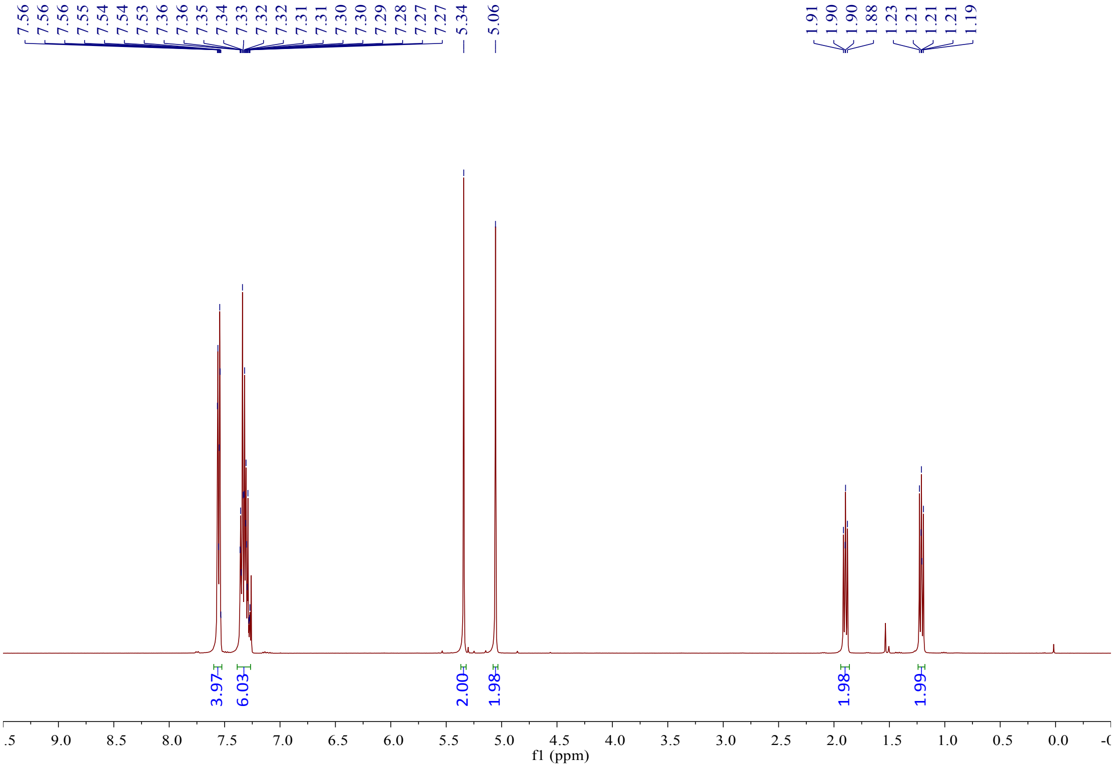
VIII. NMR Spectra

Substrates

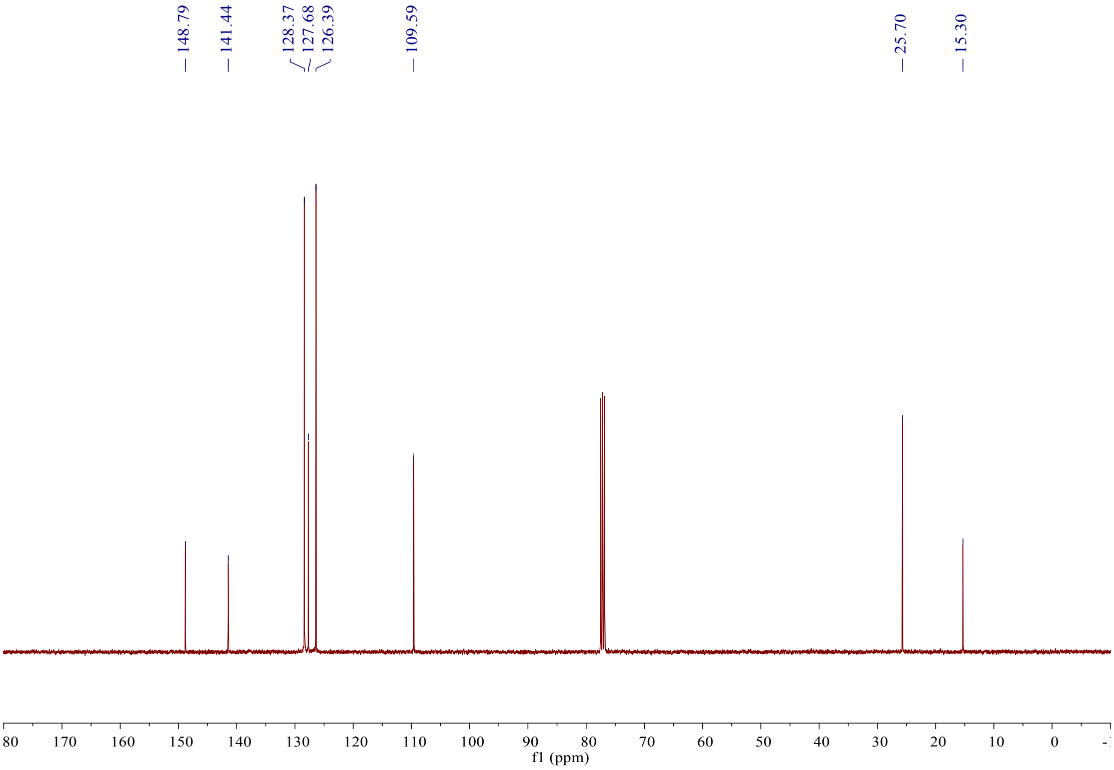


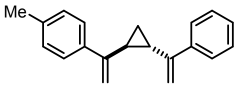
1a

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



^{13}C NMR spectrum (CDCl$_3$, 101 MHz):





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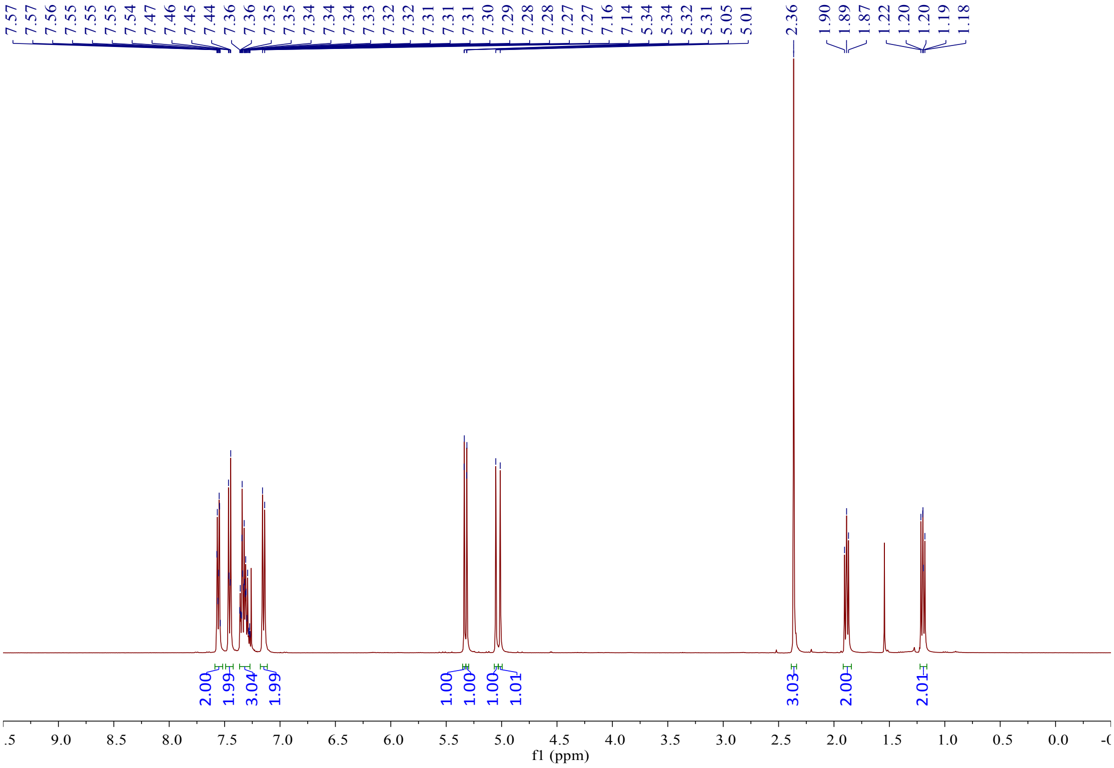
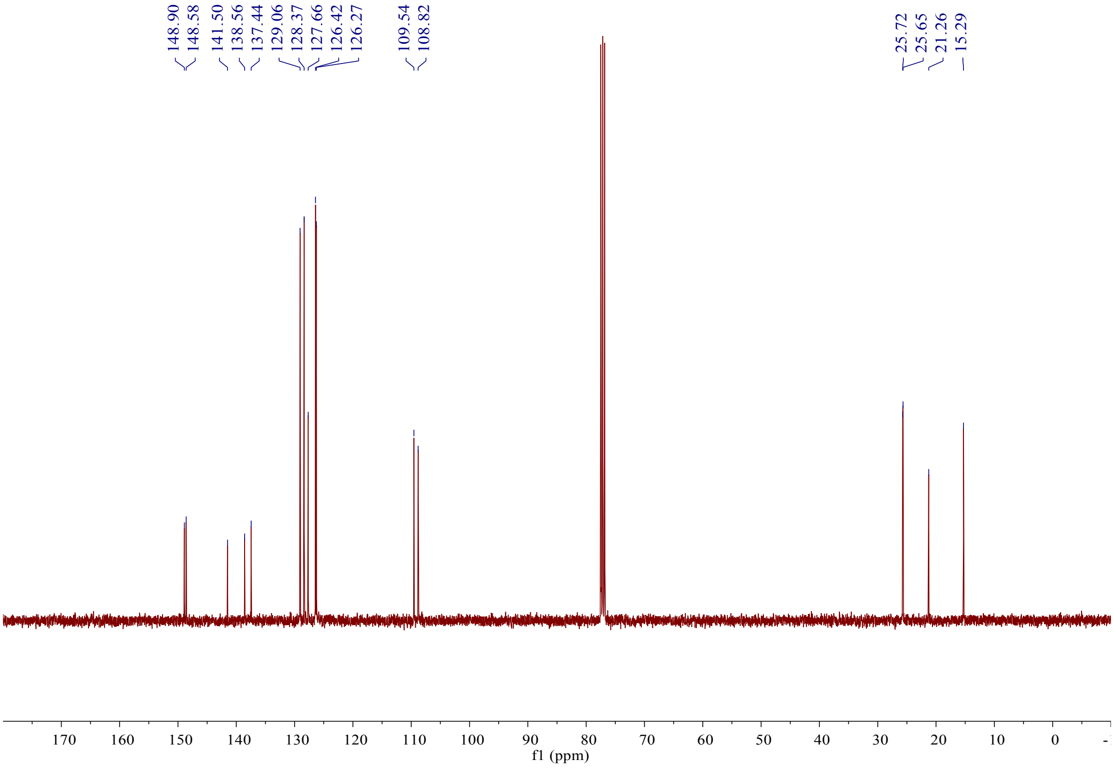
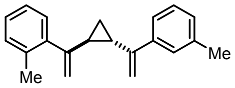
^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



^{13}C NMR spectrum (CDCl$_3$, 101 MHz):





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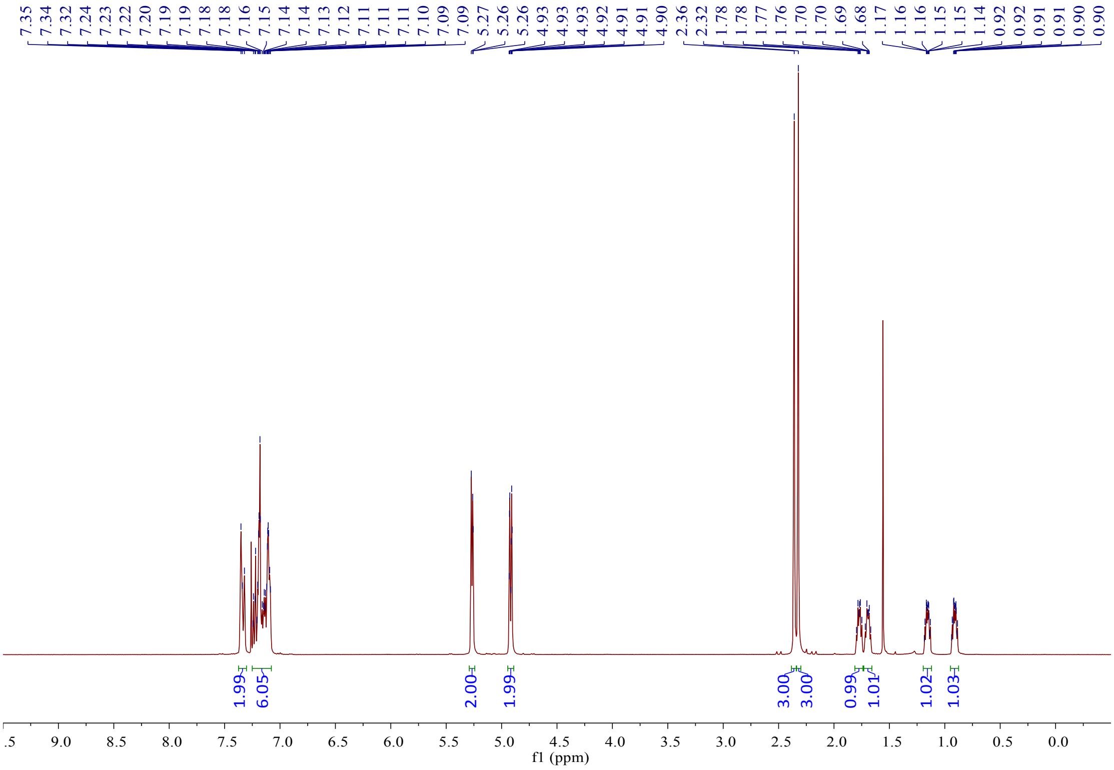
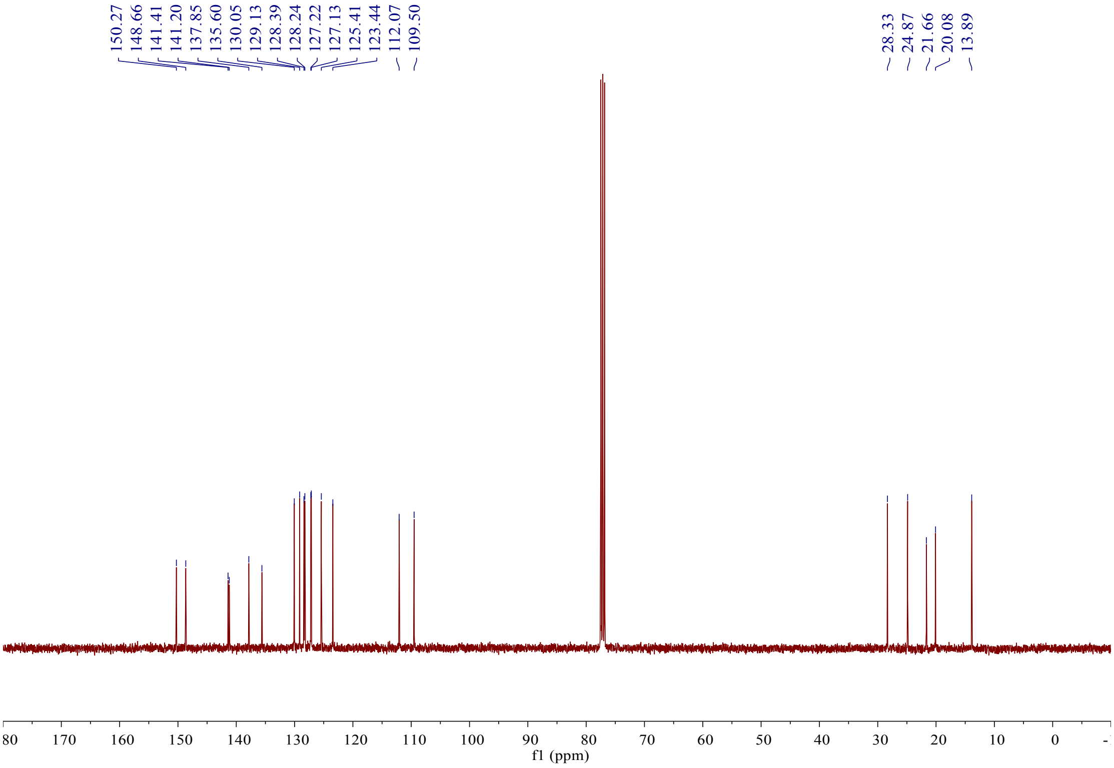
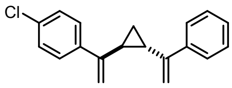
^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



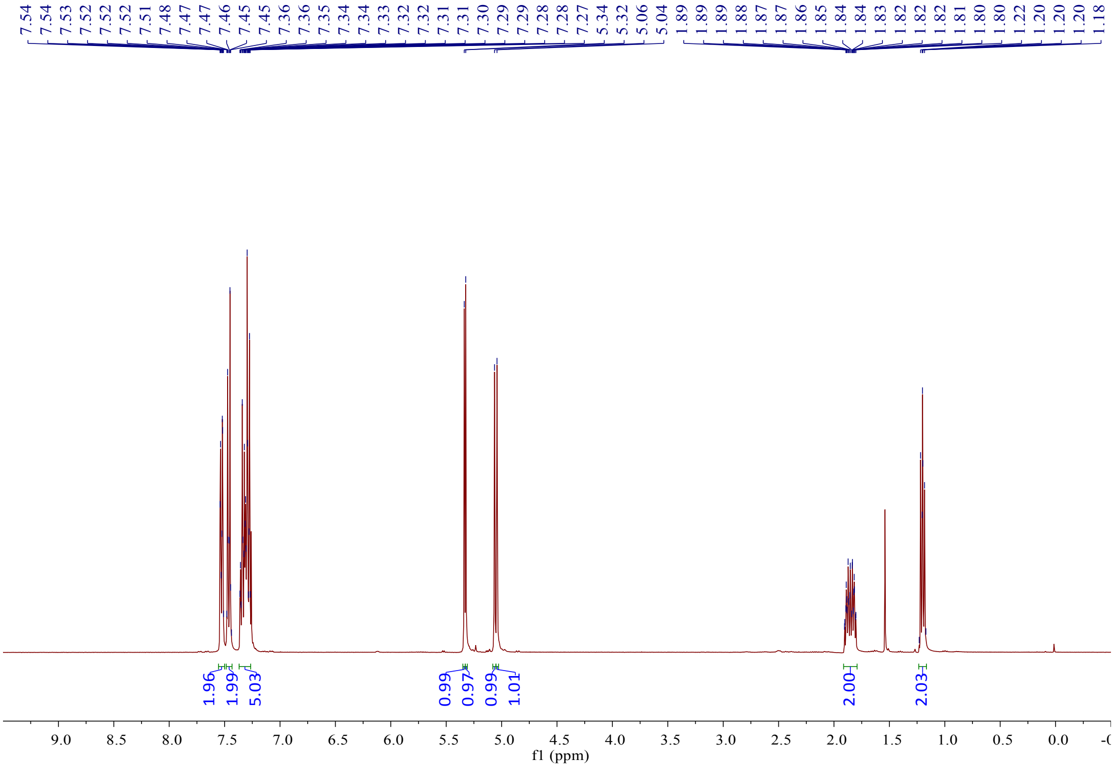
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



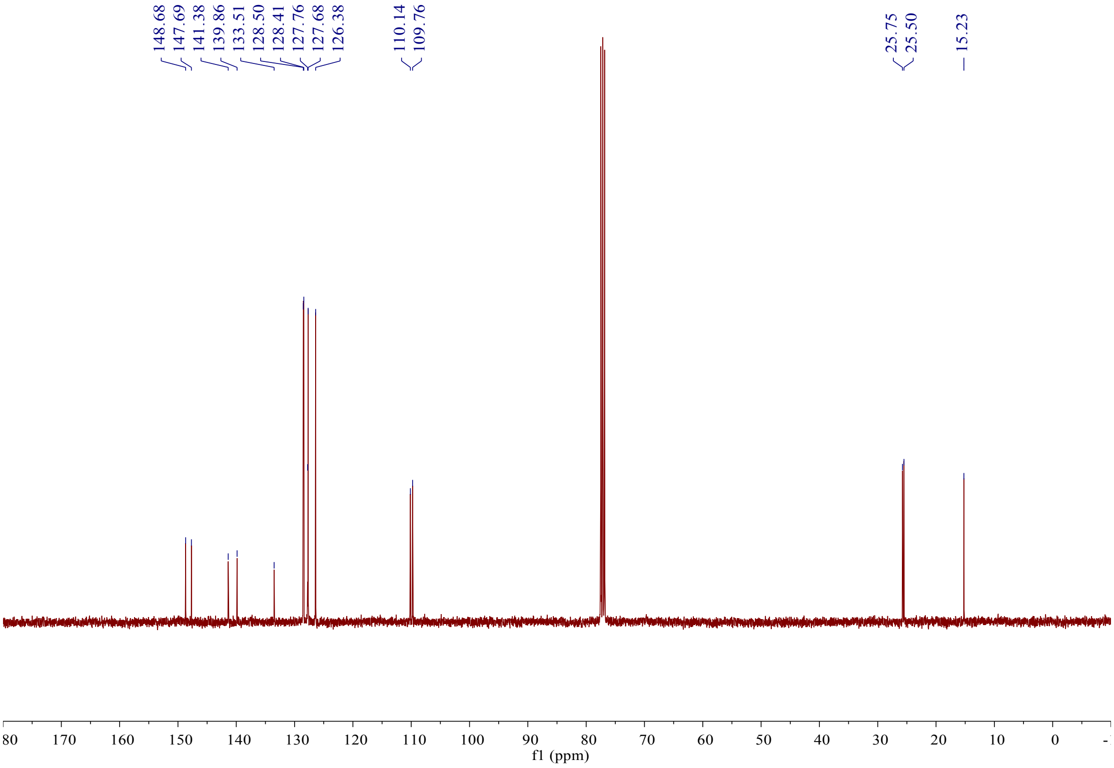


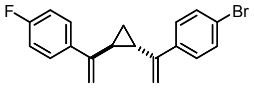
1d

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



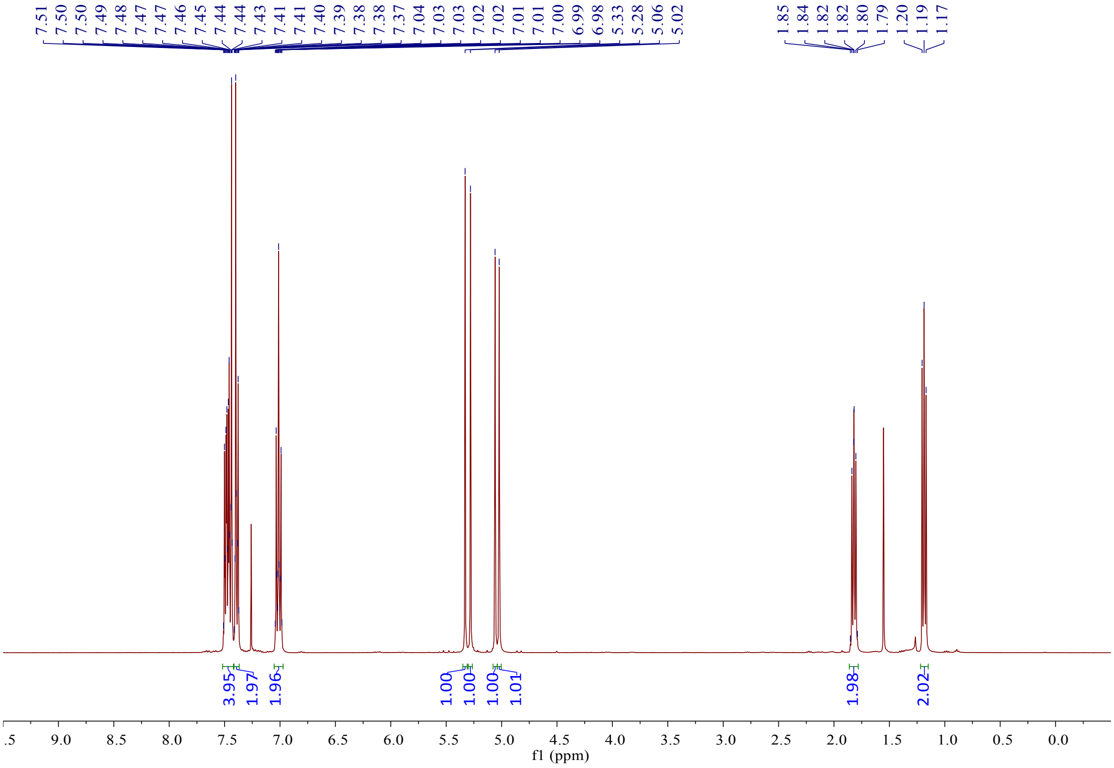
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



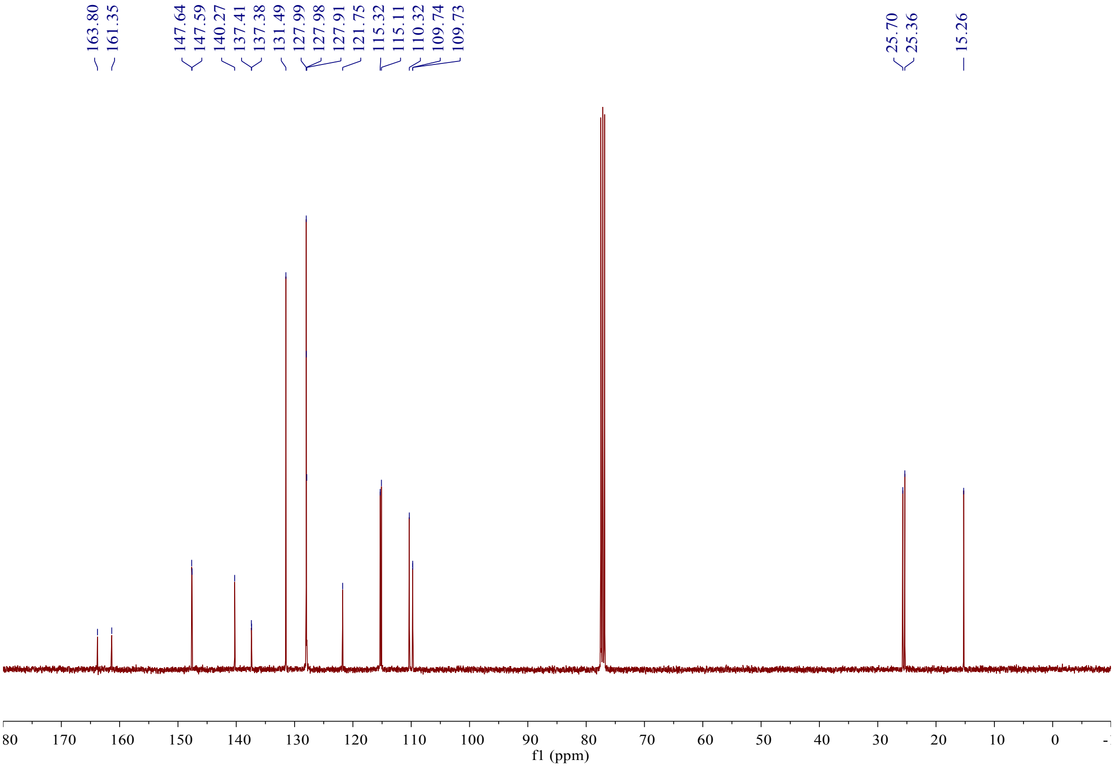


1e

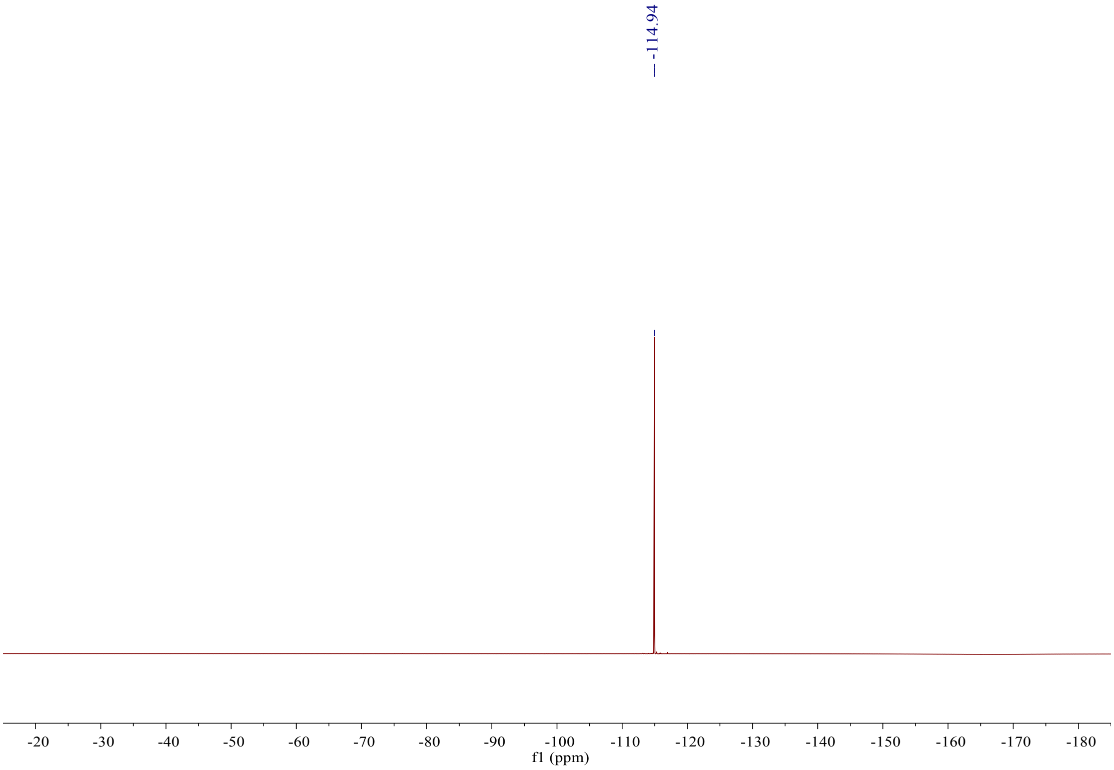
^{1}H NMR spectrum ($CDCl_3$, 400 MHz):

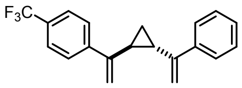


^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



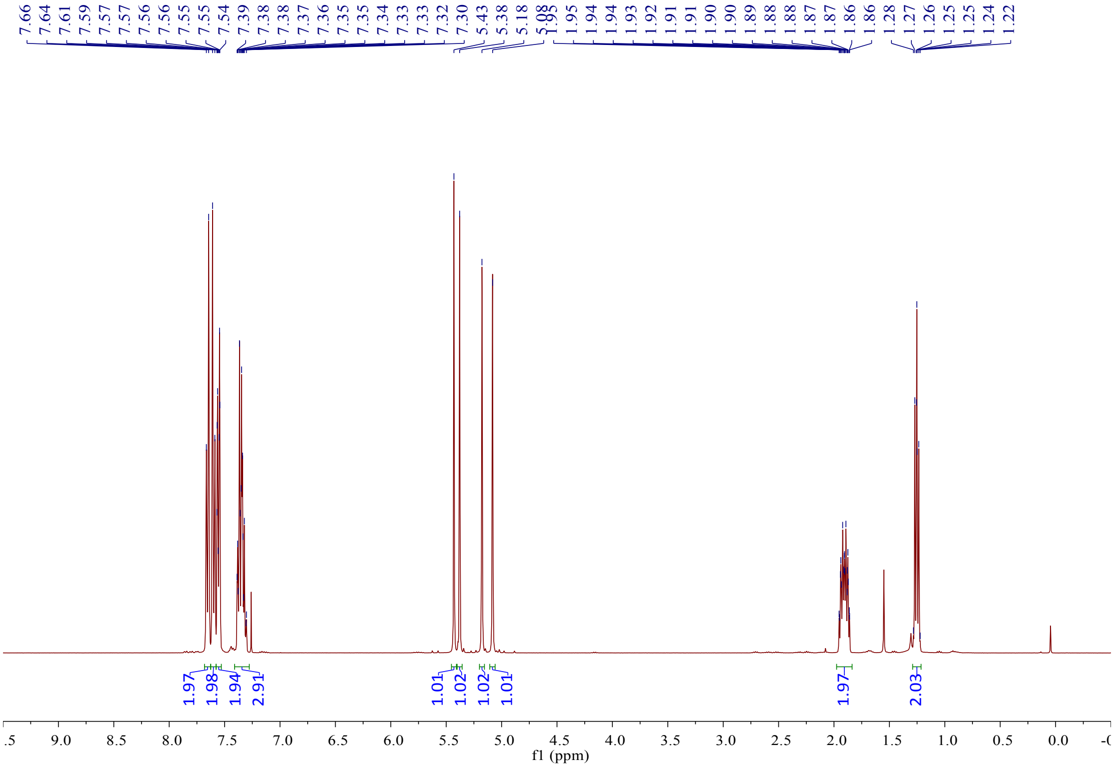
^{19}F NMR spectrum ($CDCl_3$, 471 MHz):



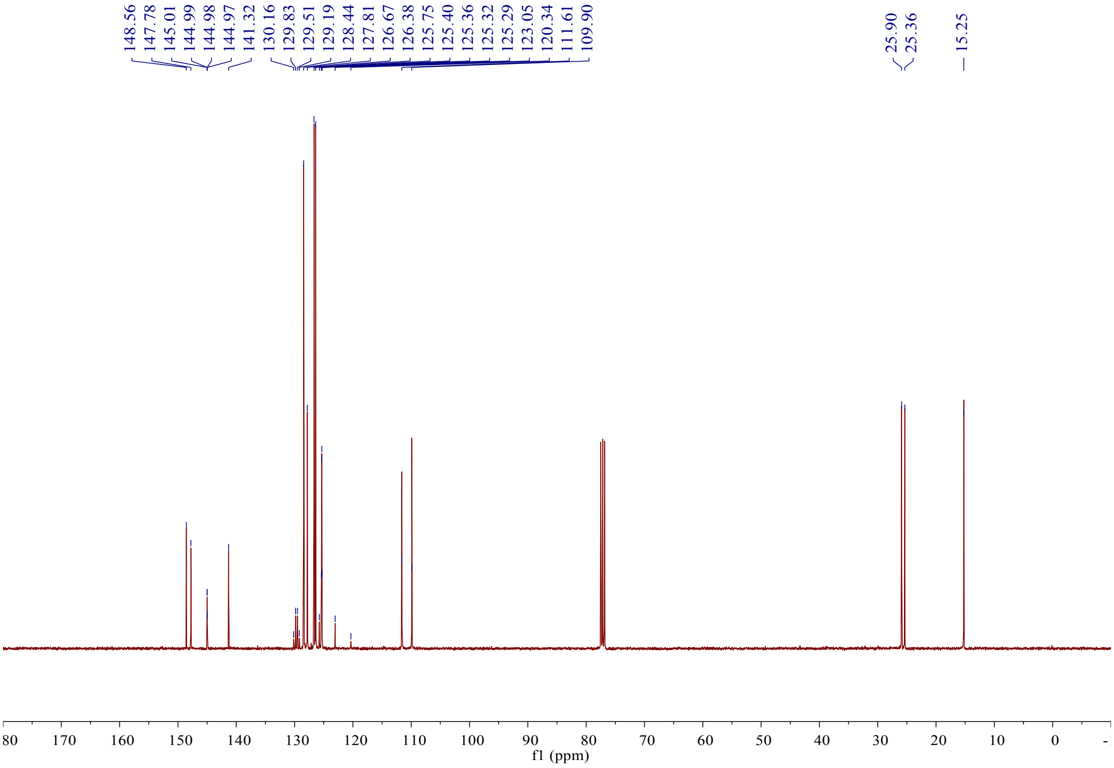


1f

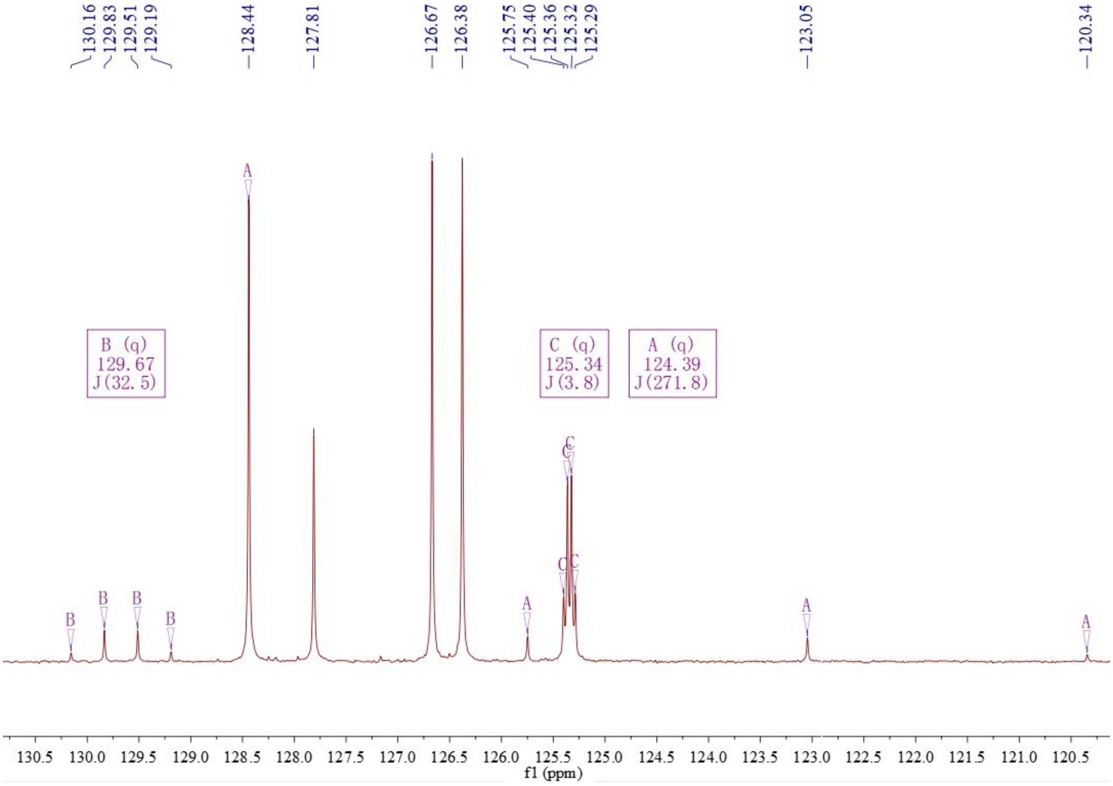
^{1}H NMR spectrum ($CDCl_3$, 400 MHz):



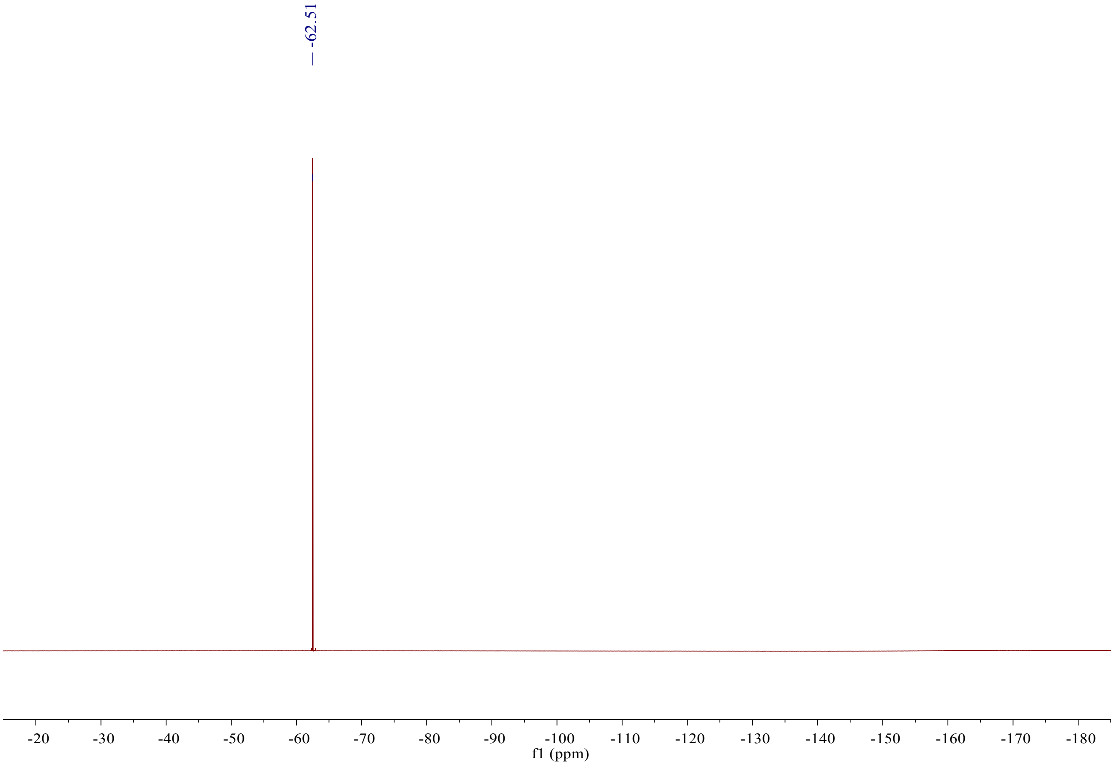
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):

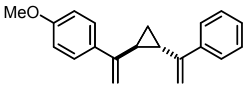


^{13}C NMR spectrum zoomed in (131-120 ppm; A, B, and C indicate different multiplets; the leftmost peak in quartet A overlaps with the peak at 128.44 ppm):



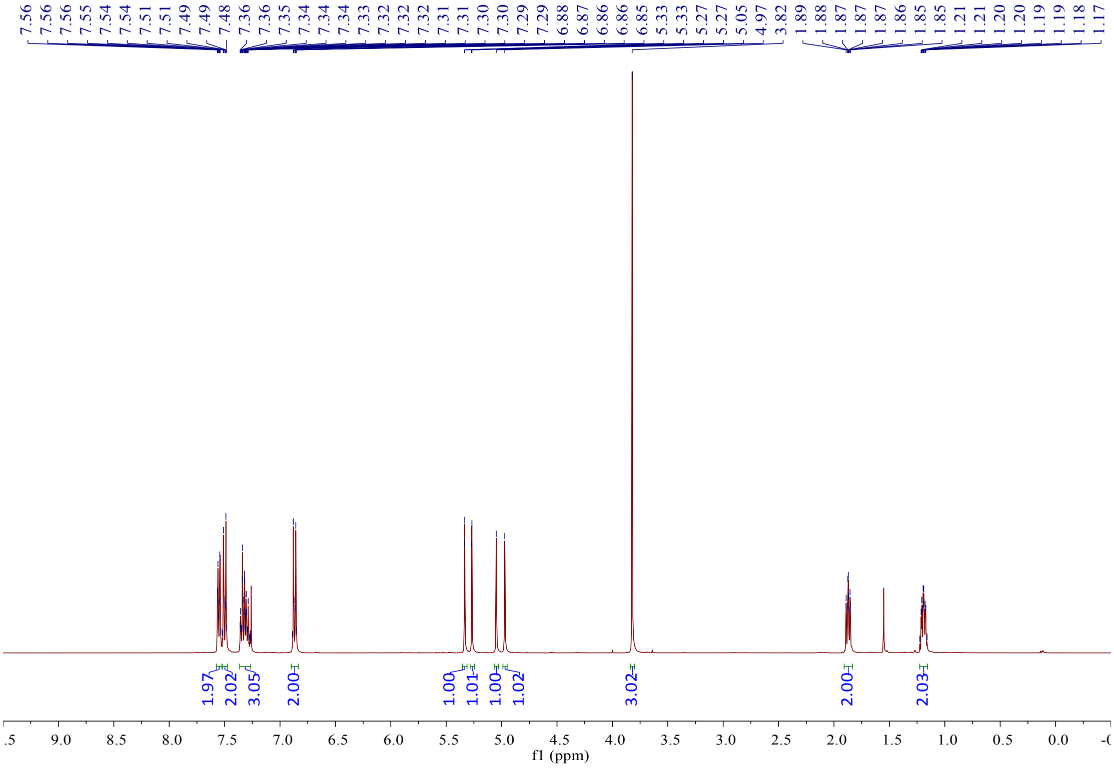
^{19}F NMR spectrum ($CDCl_3$, 471 MHz):



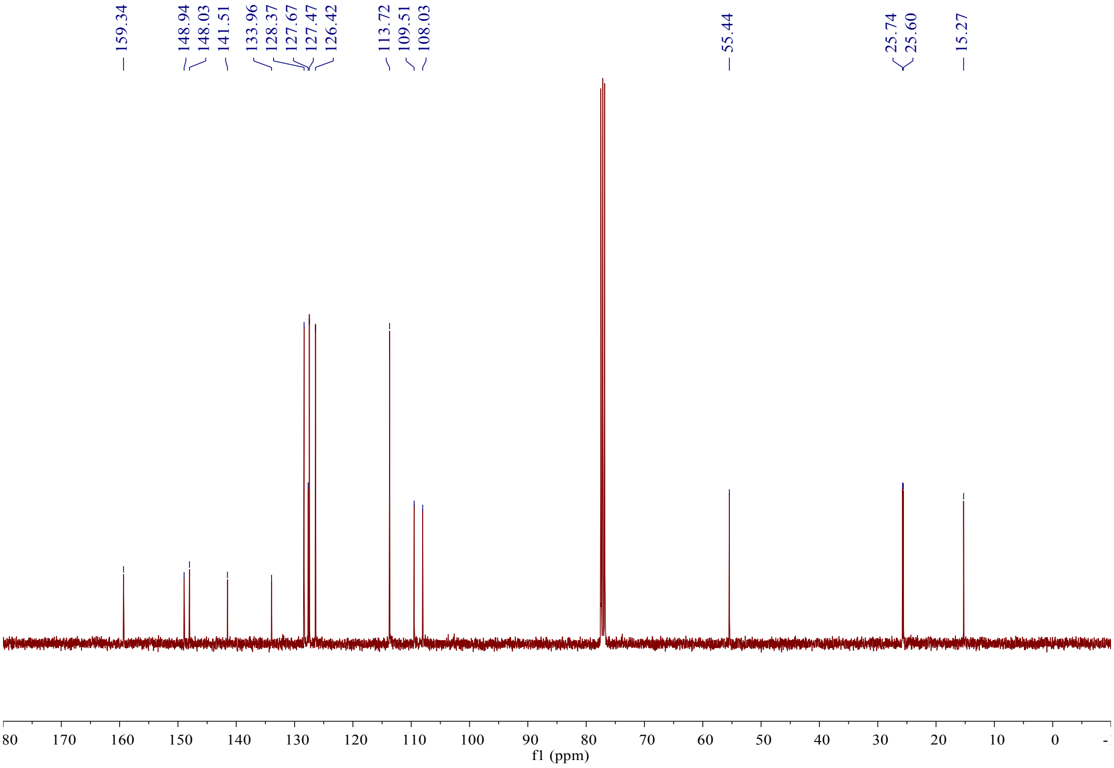


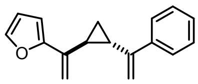
1g

^{1}H NMR spectrum ($CDCl_3$, 400 MHz):



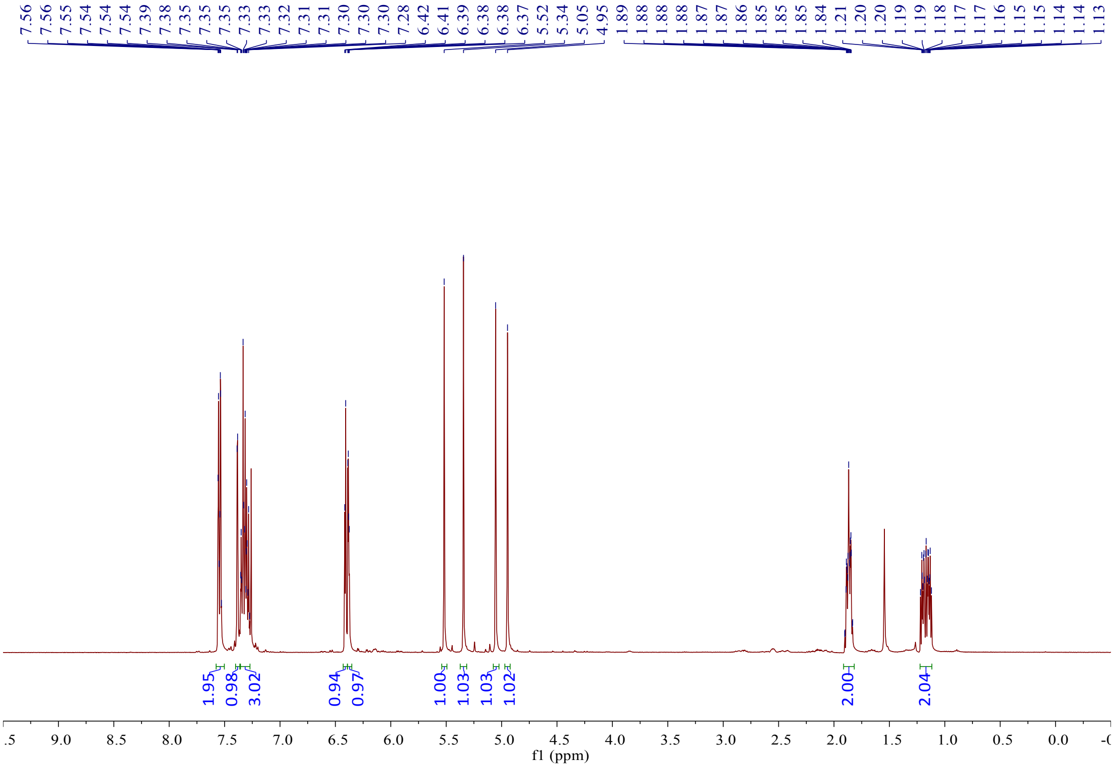
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



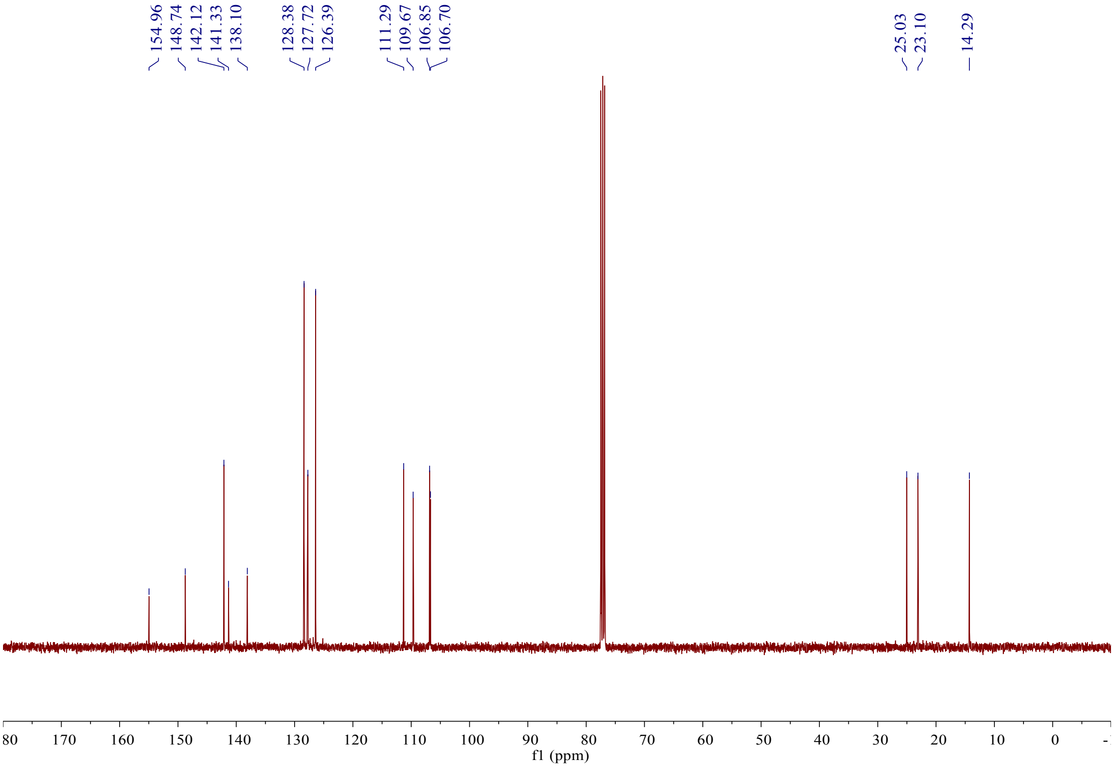


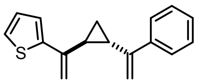
1h

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



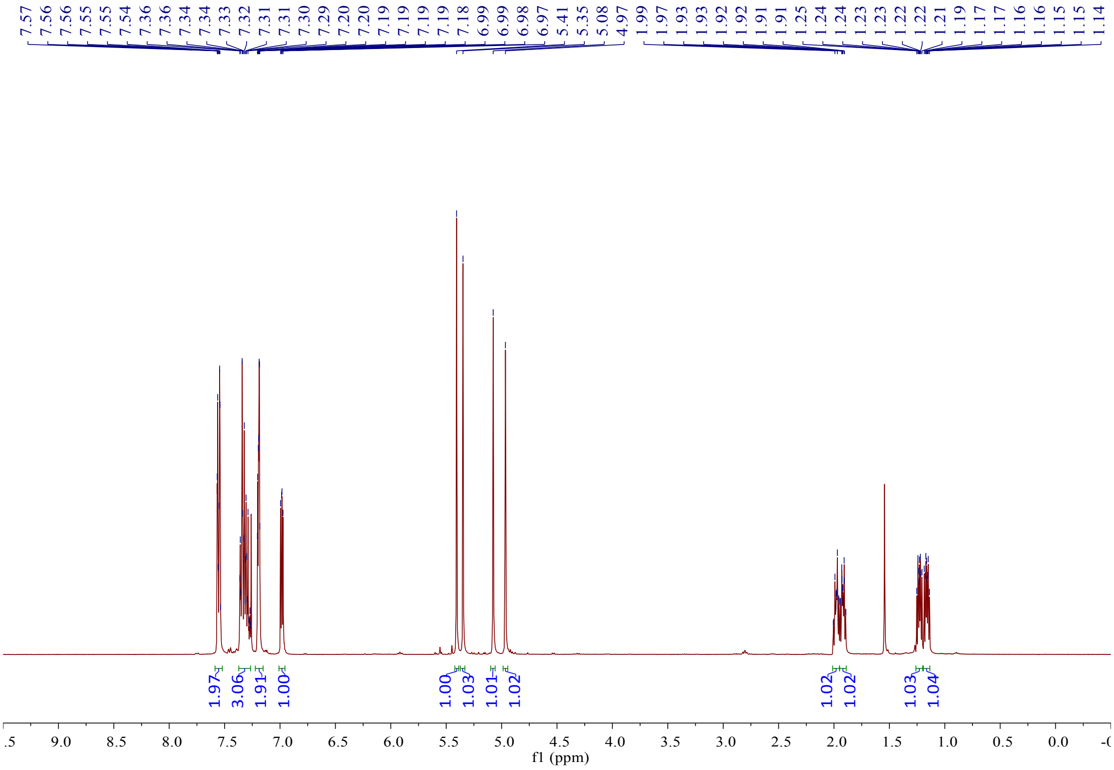
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



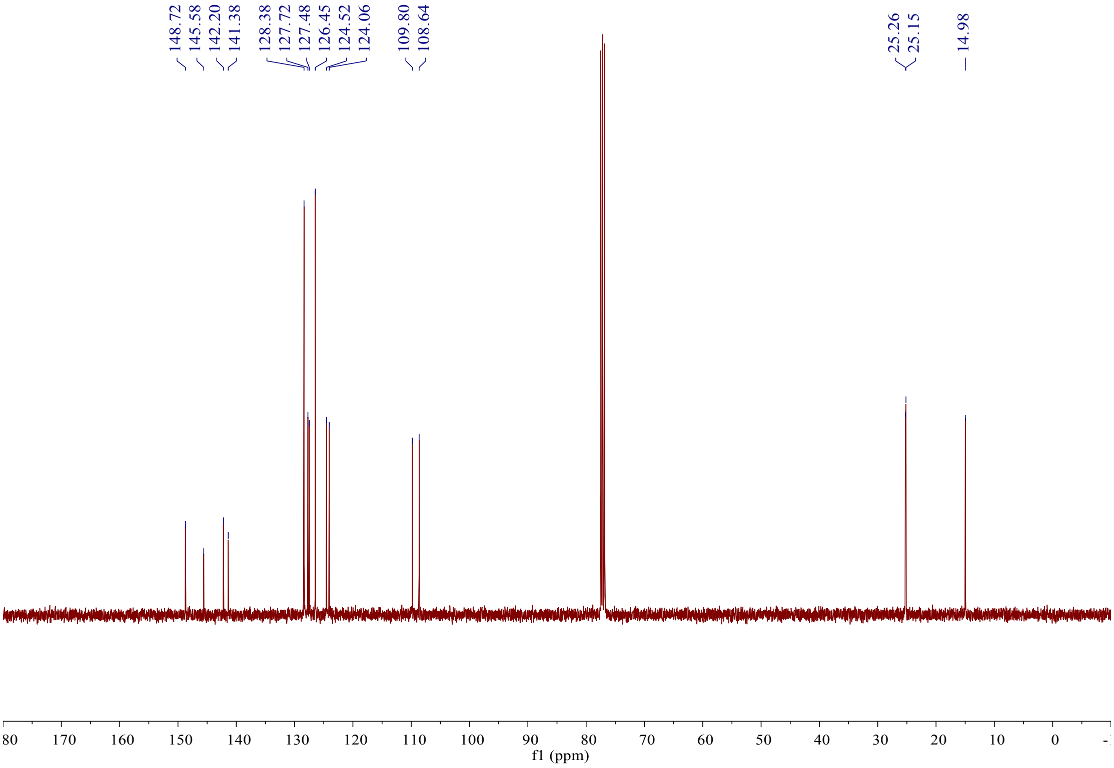


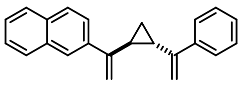
1i

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



^{13}C NMR spectrum (CDCl$_3$, 101 MHz):





1j

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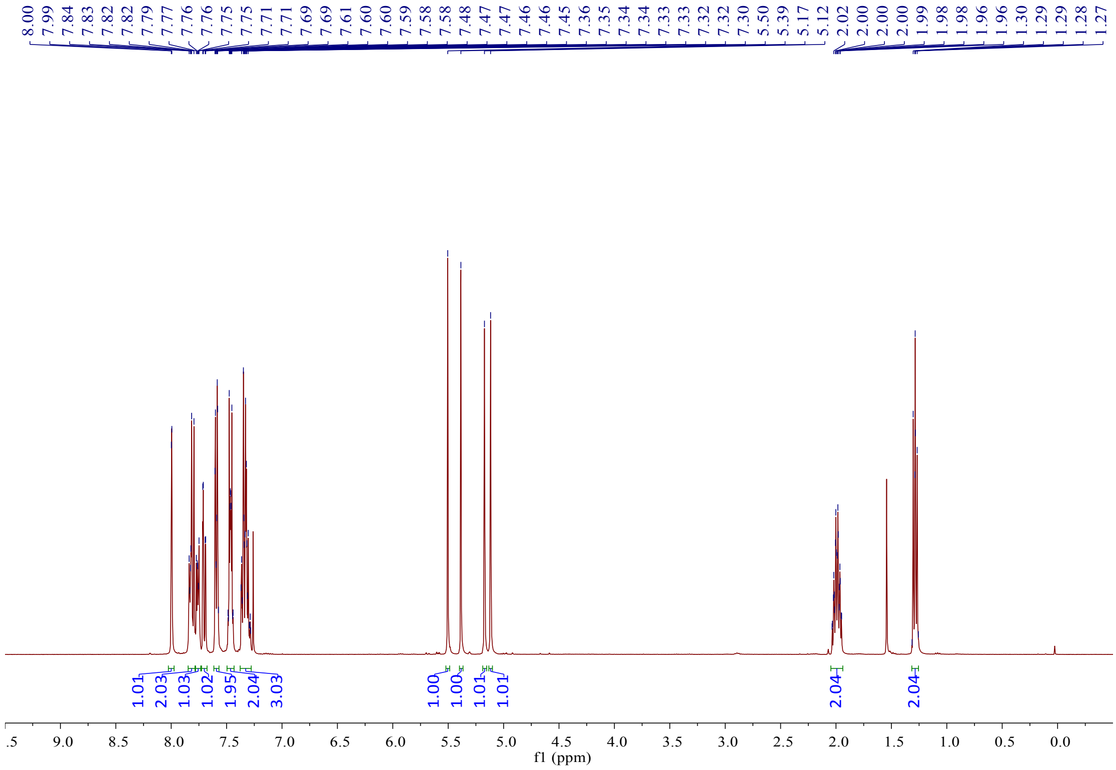

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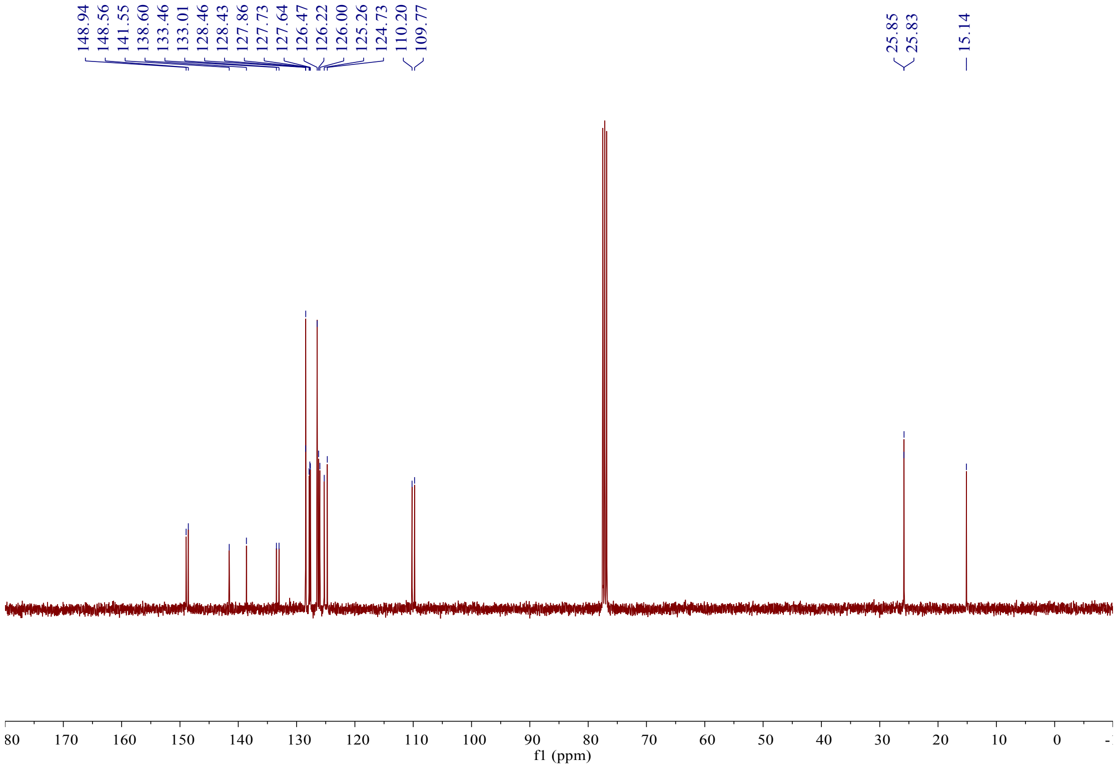

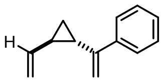

1k

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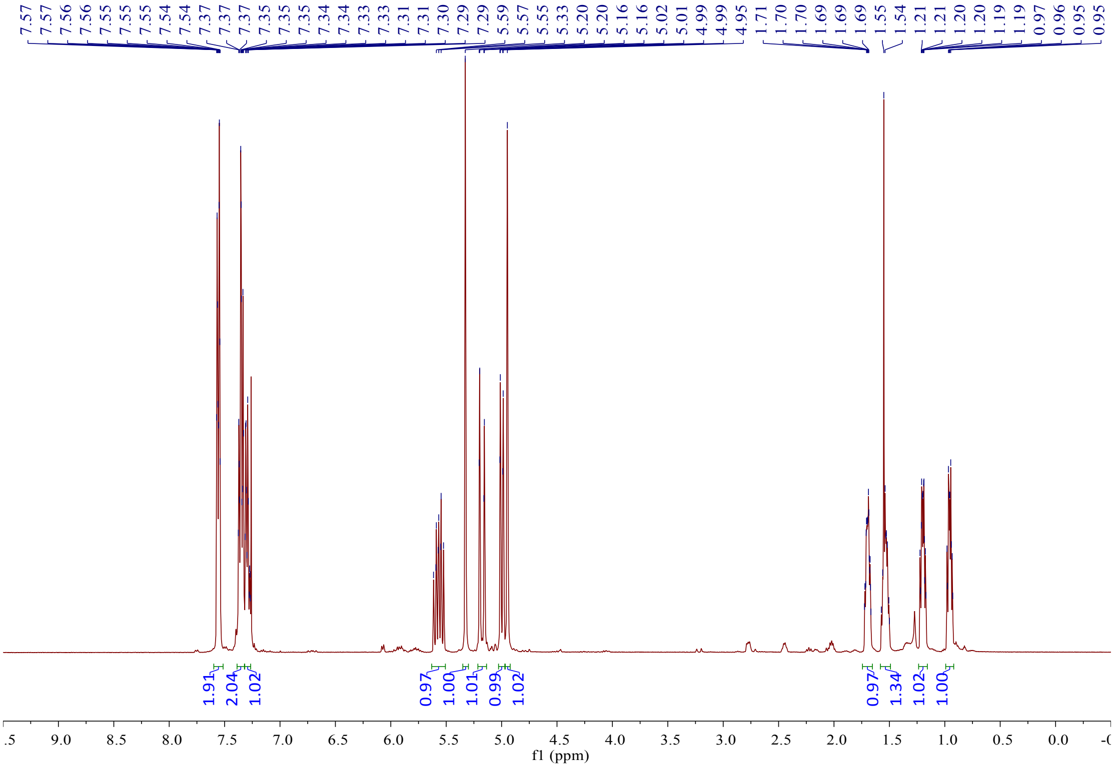
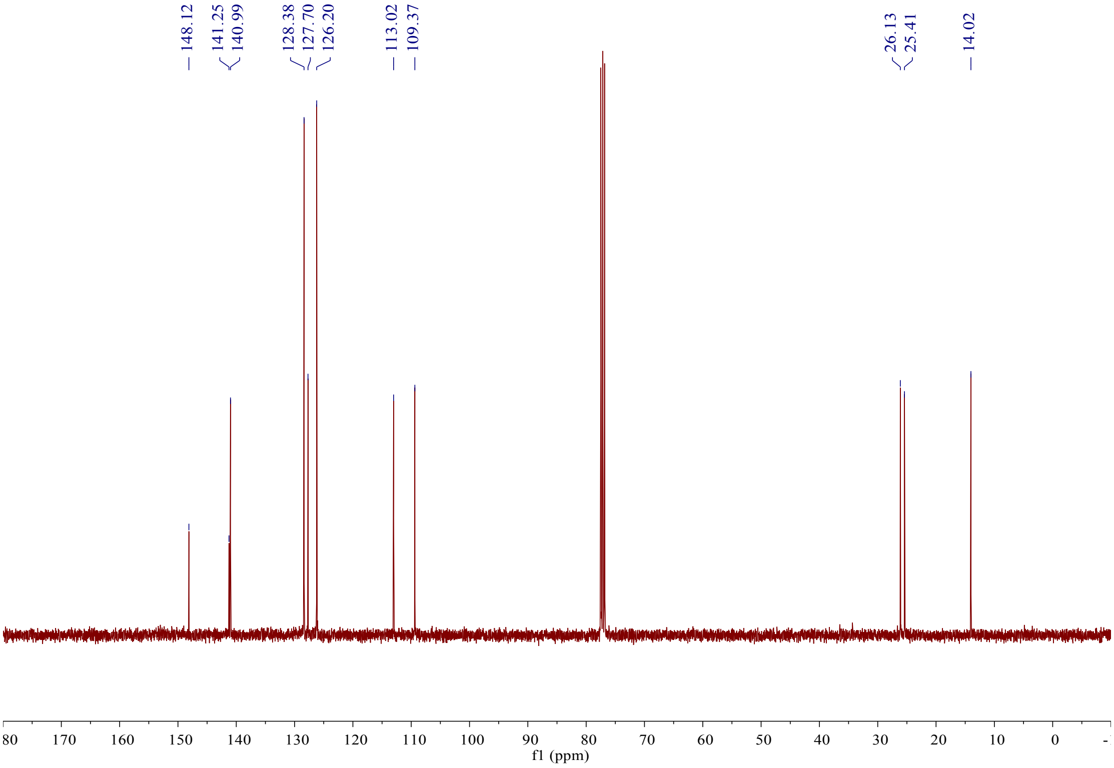
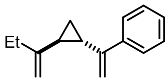


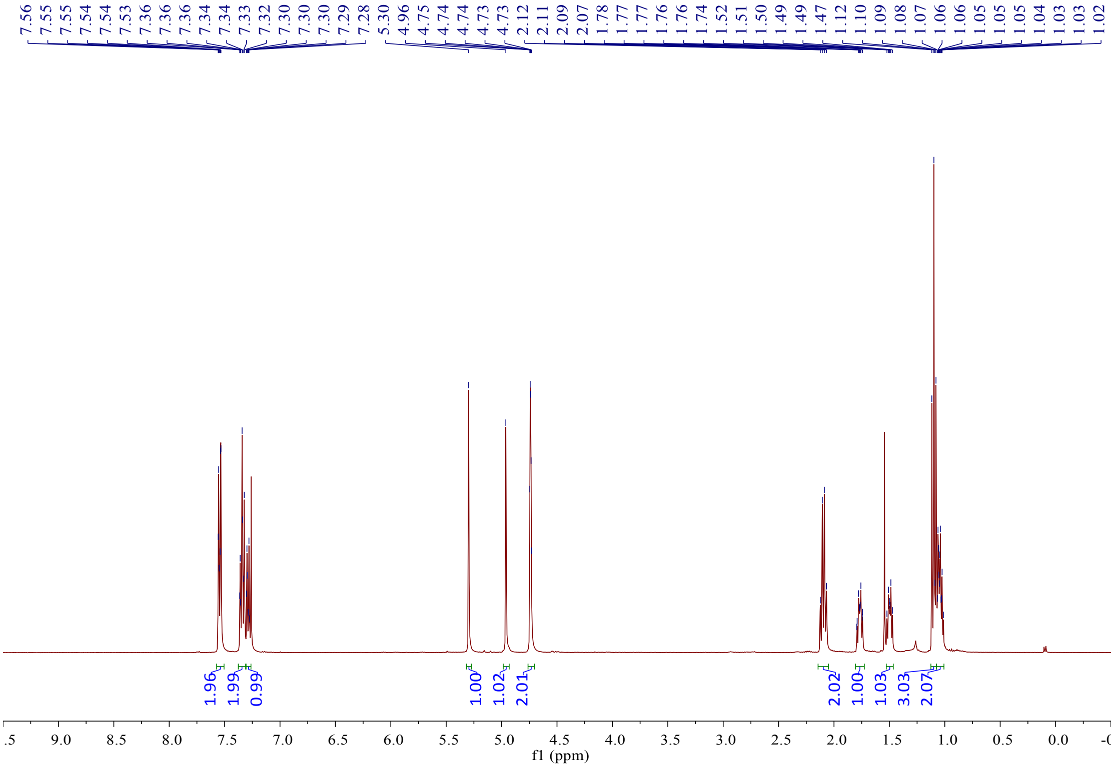
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



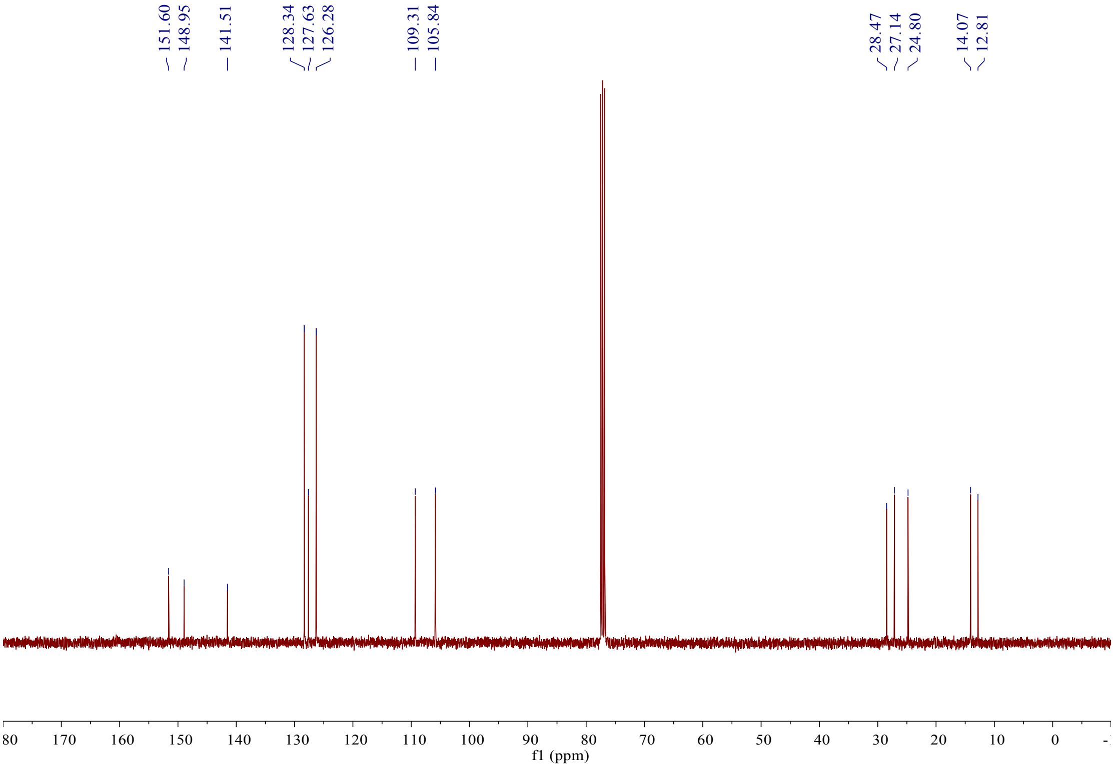


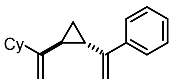
1l

¹H NMR spectrum (CDCl$_3$, 400 MHz):



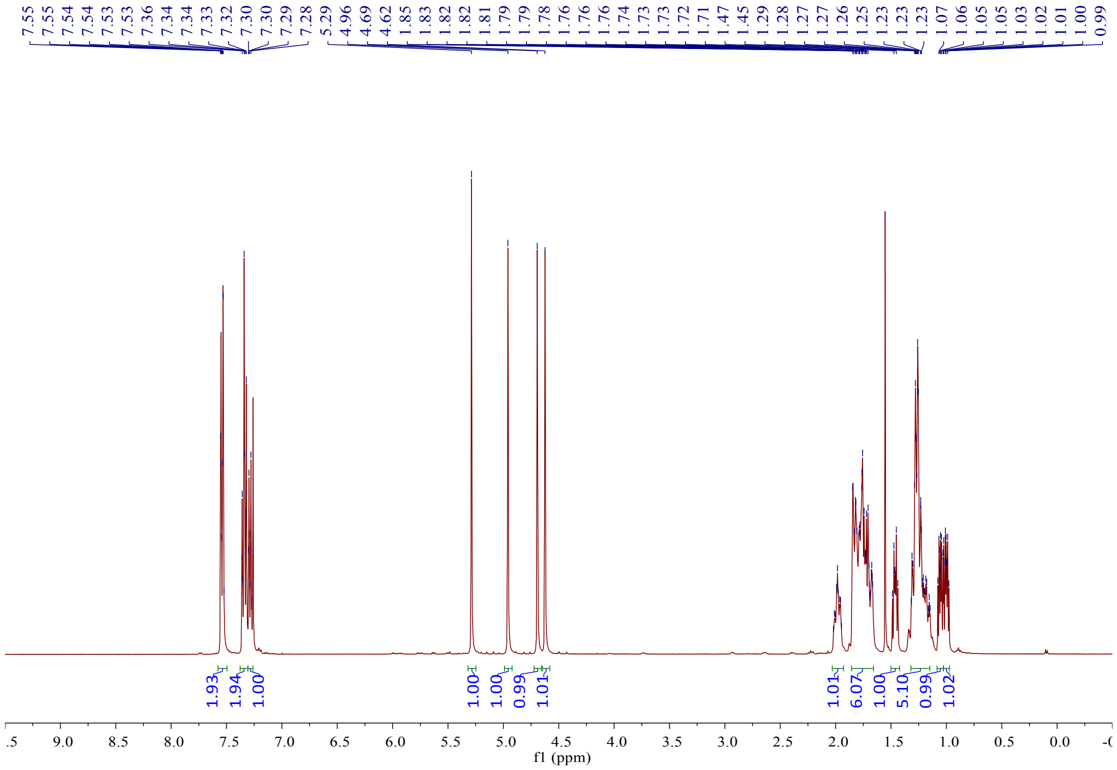
¹³C NMR spectrum (CDCl$_3$, 101 MHz):



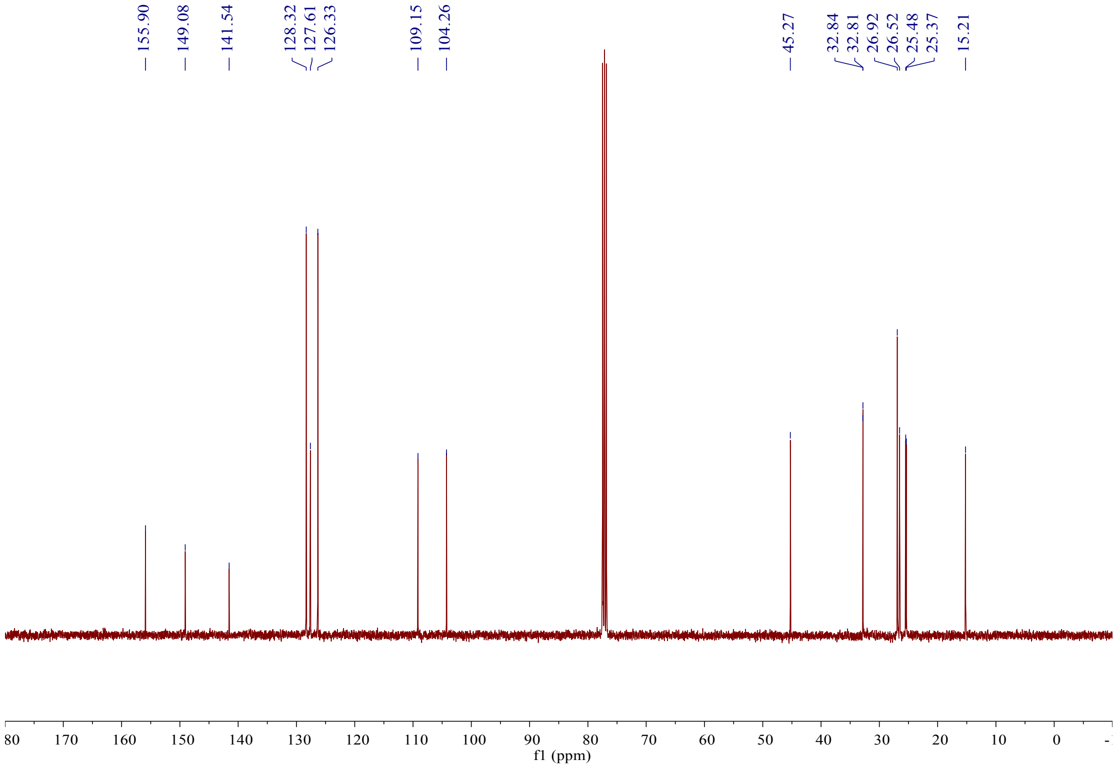


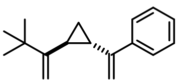
1m

^{1}H NMR spectrum ($CDCl_3$, 400 MHz):



^{13}C NMR spectrum ($CDCl_3$, 101 MHz):





1n

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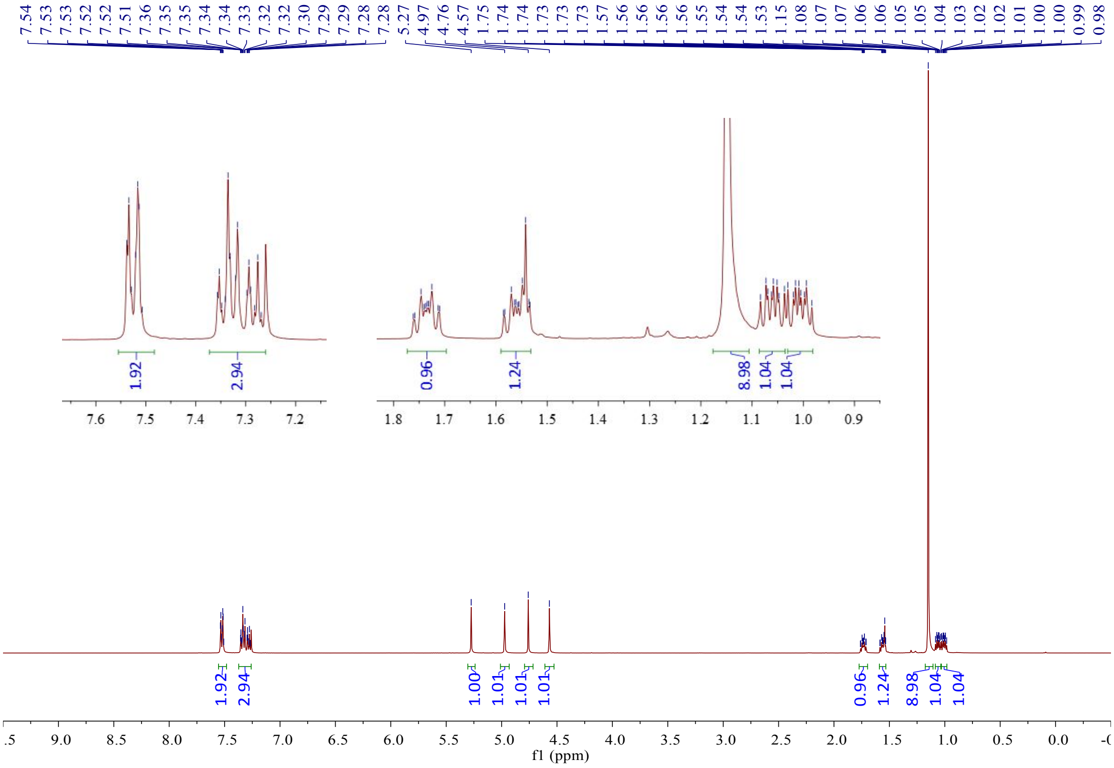

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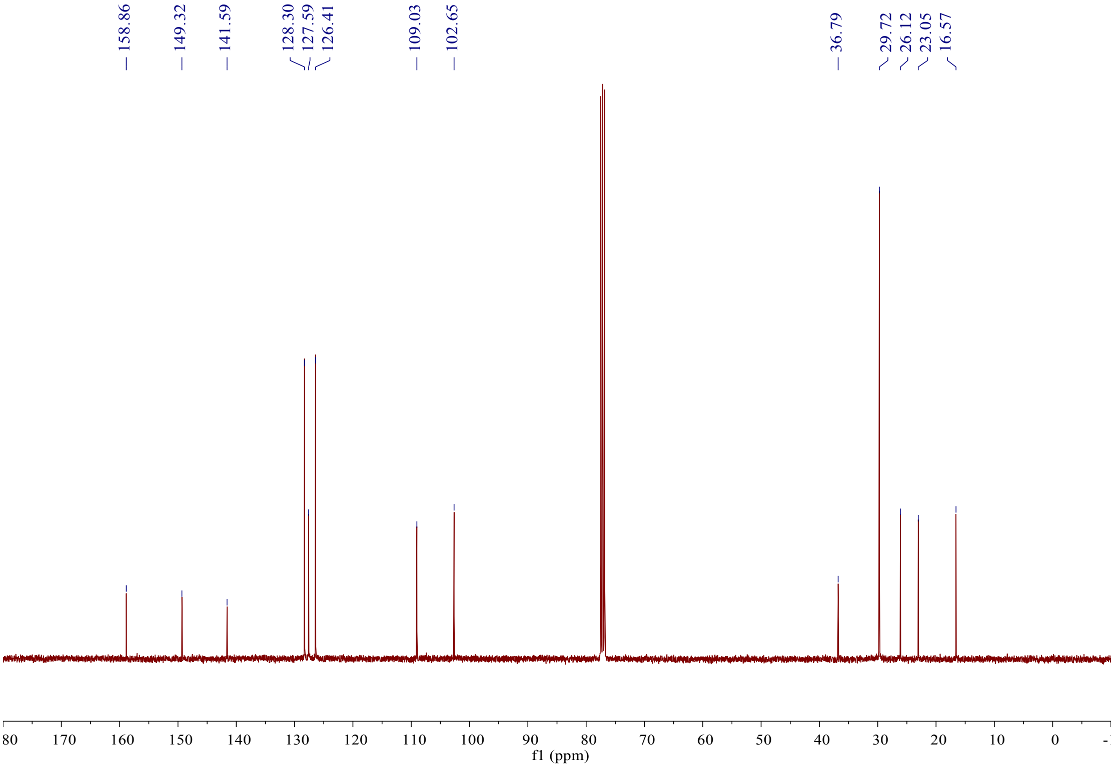

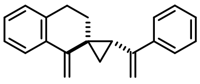

1o

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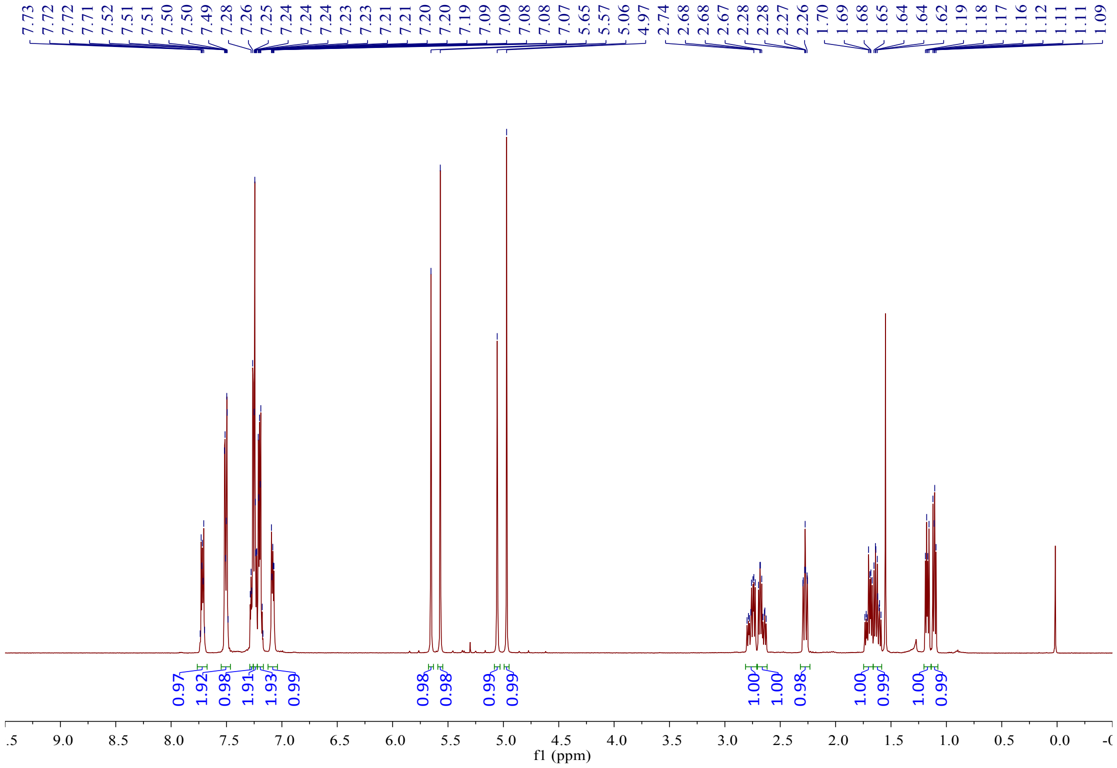

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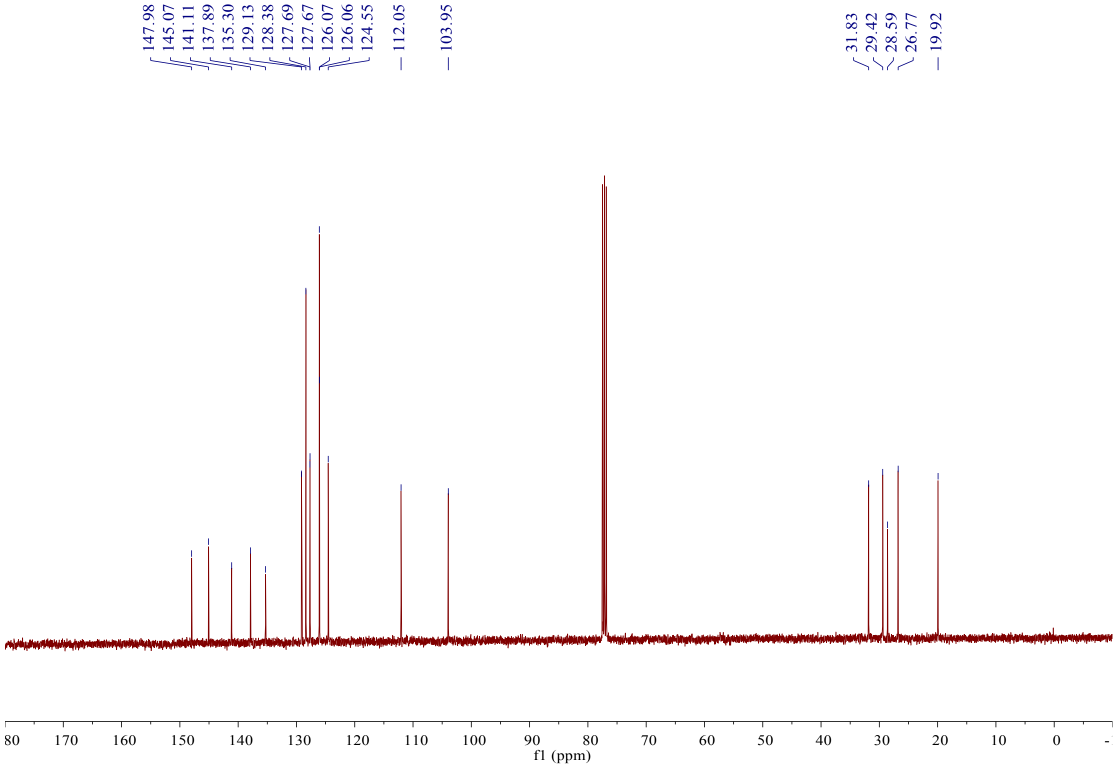
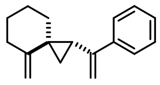
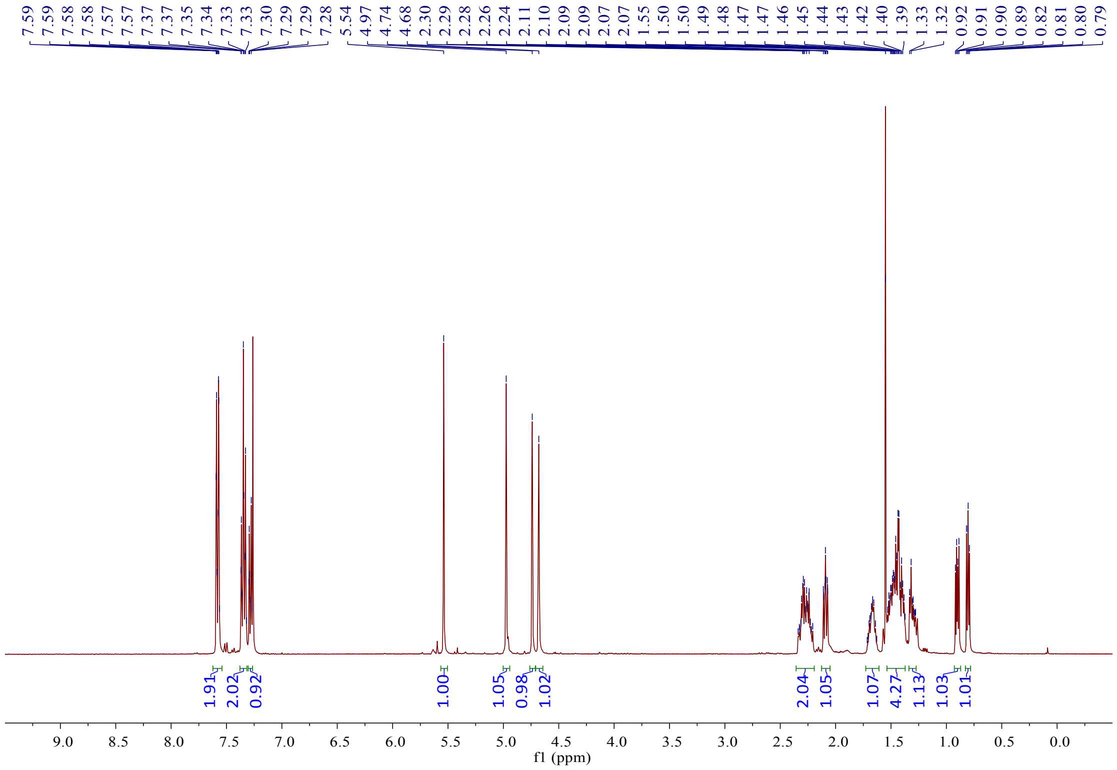




1p

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



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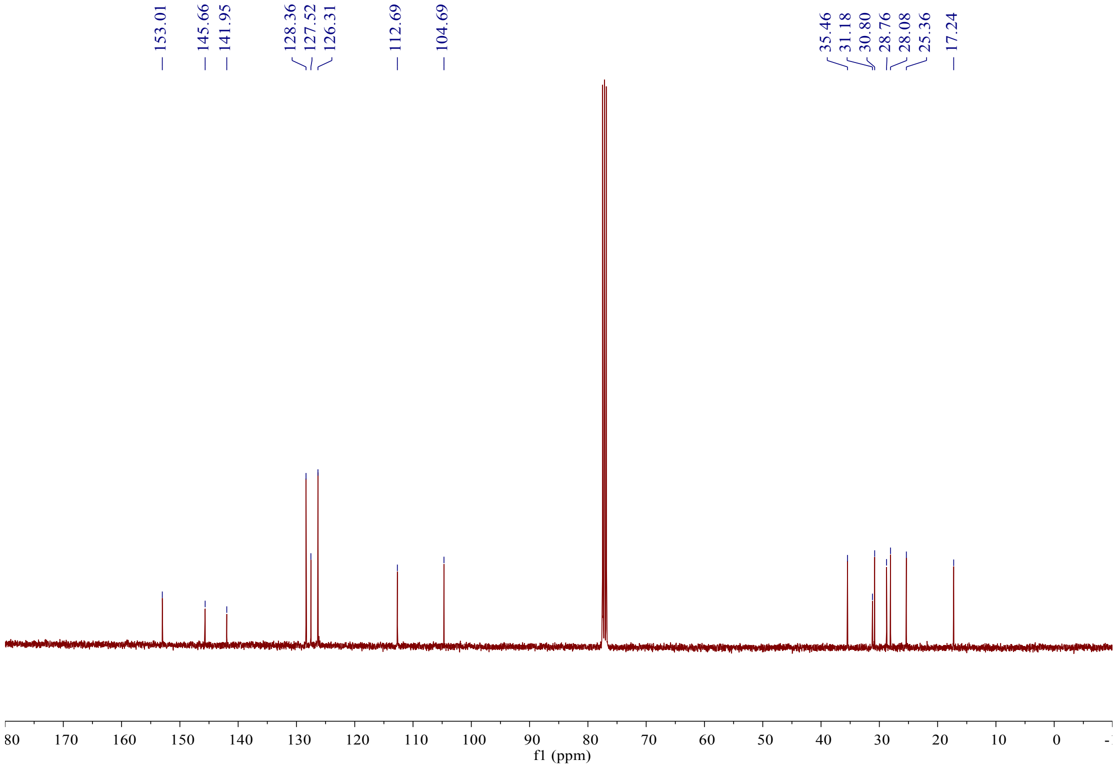
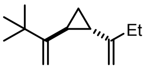
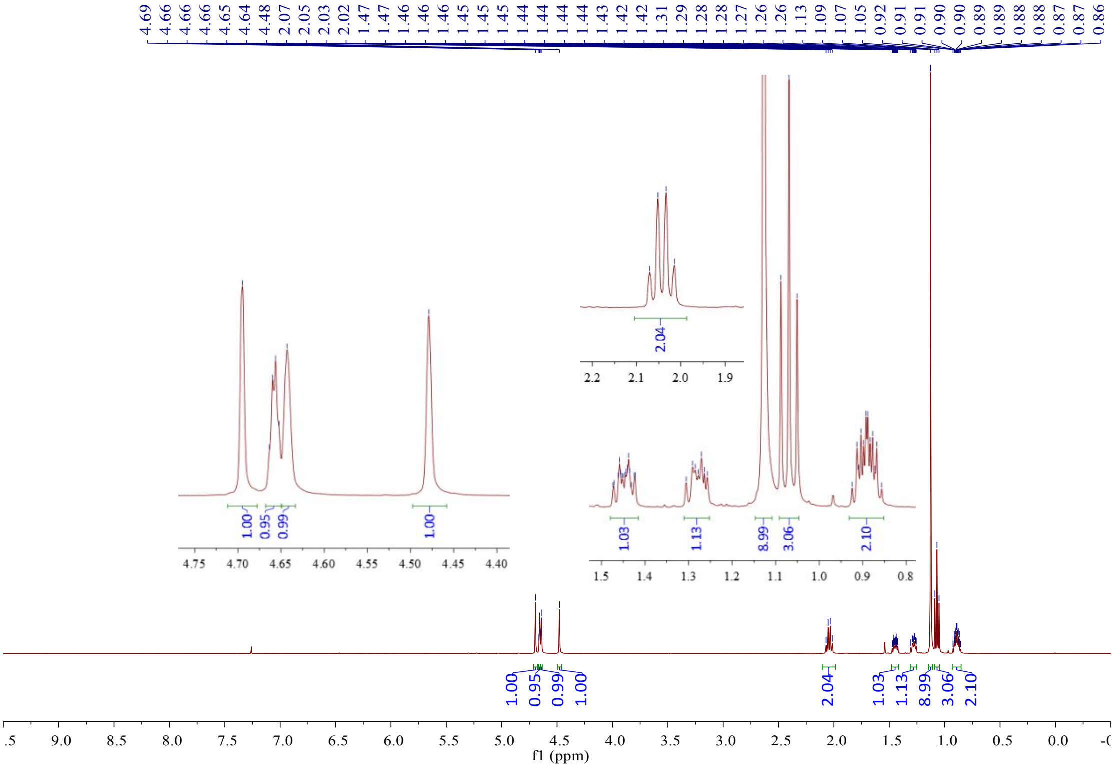




1q

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



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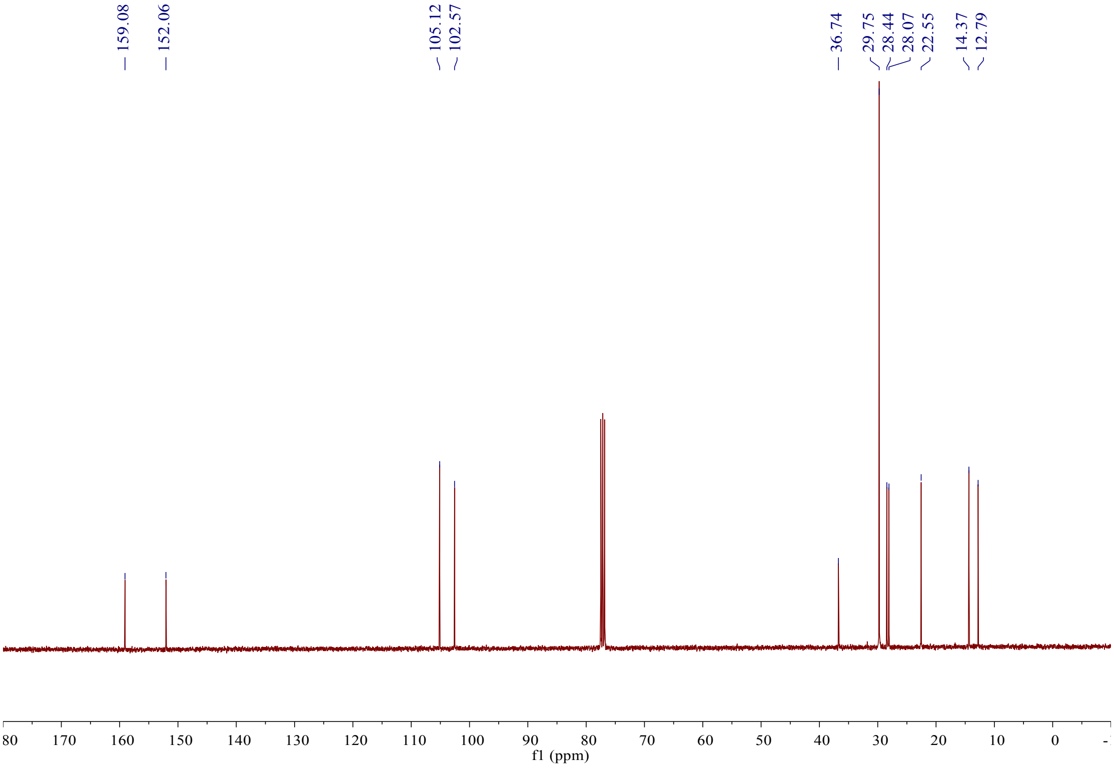

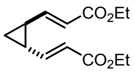

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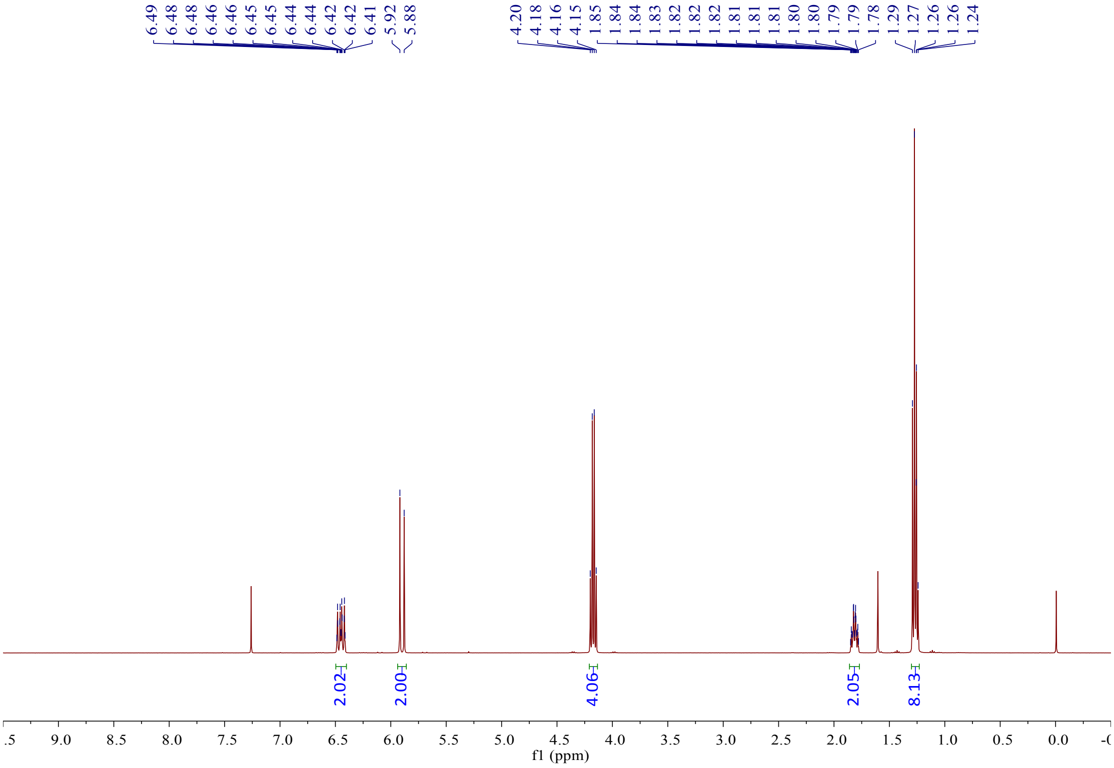
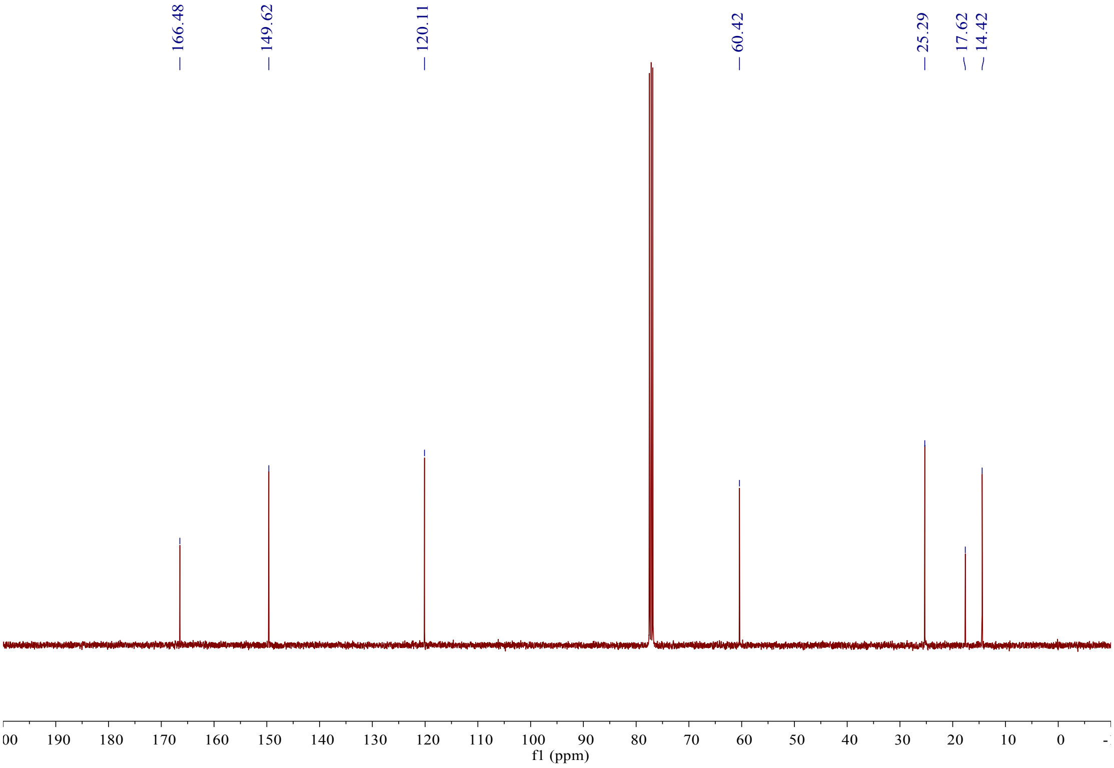
^{1}H NMR spectrum (CDCl$_3$, 400 MHz):

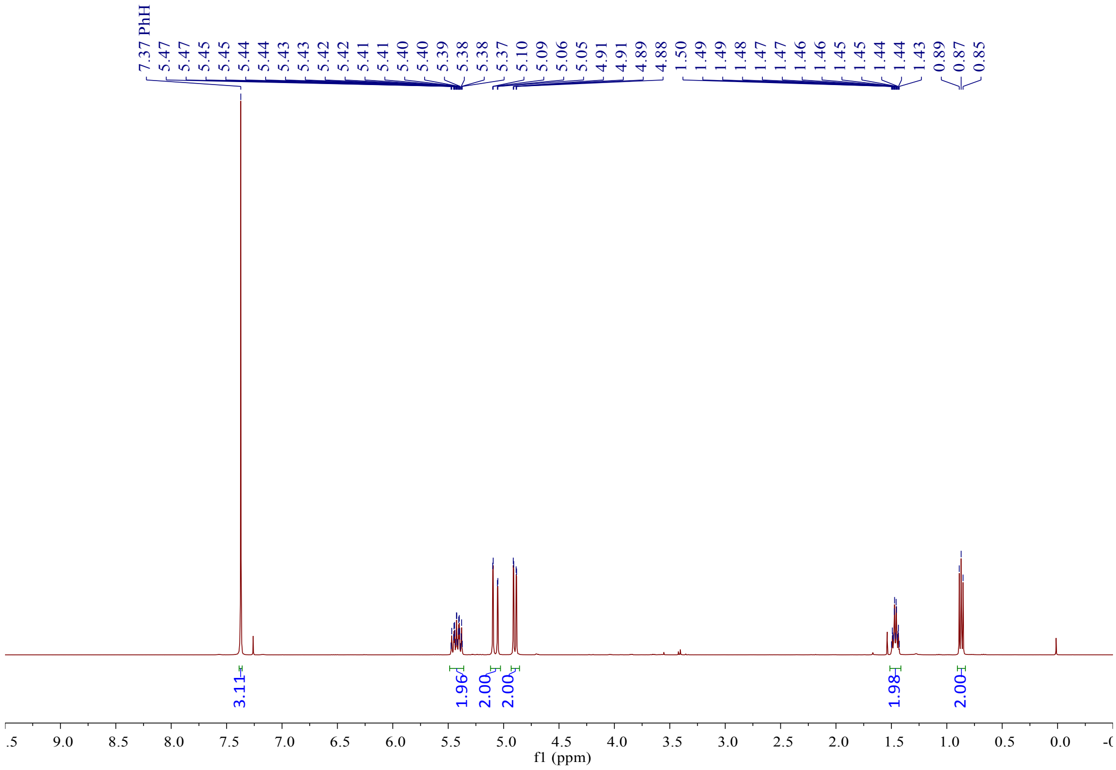


^{13}C NMR spectrum (CDCl$_3$, 101 MHz):

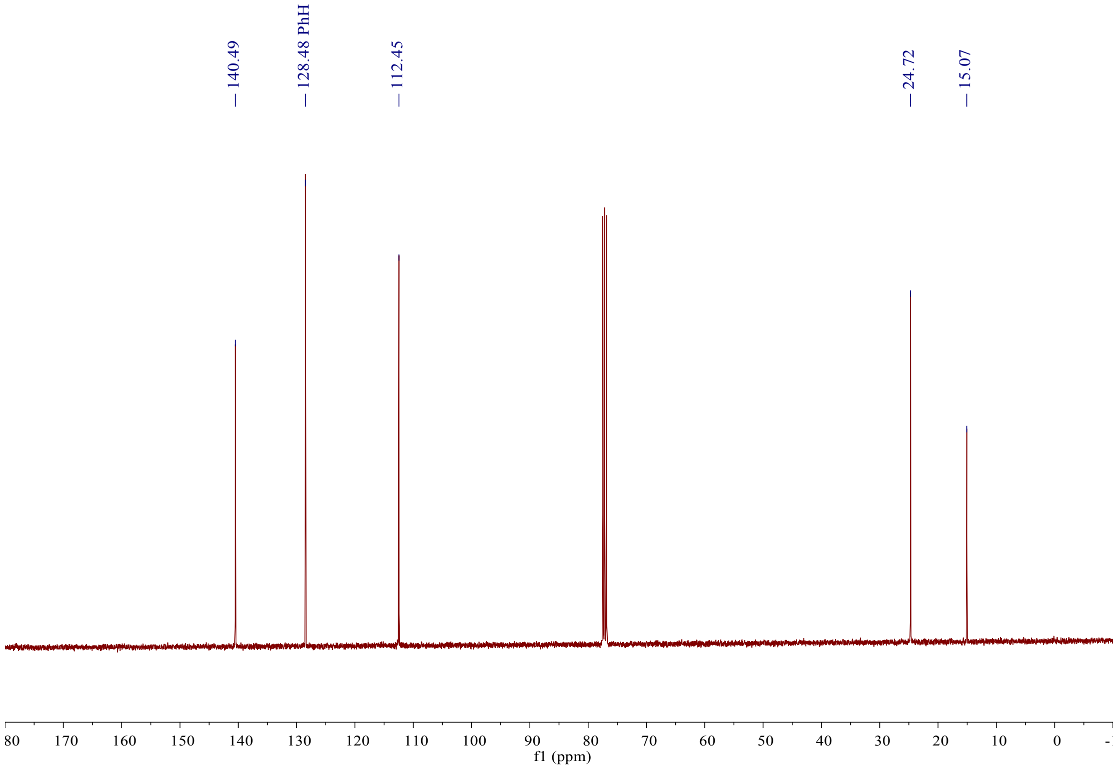


1s

^{1}H NMR spectrum (CDCl$_3$, 400 MHz, **1s**:benzene = 1:0.52):



^{13}C NMR spectrum (CDCl$_3$, 101 MHz, **1s**:benzene = 1:0.52):



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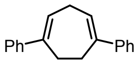

2a

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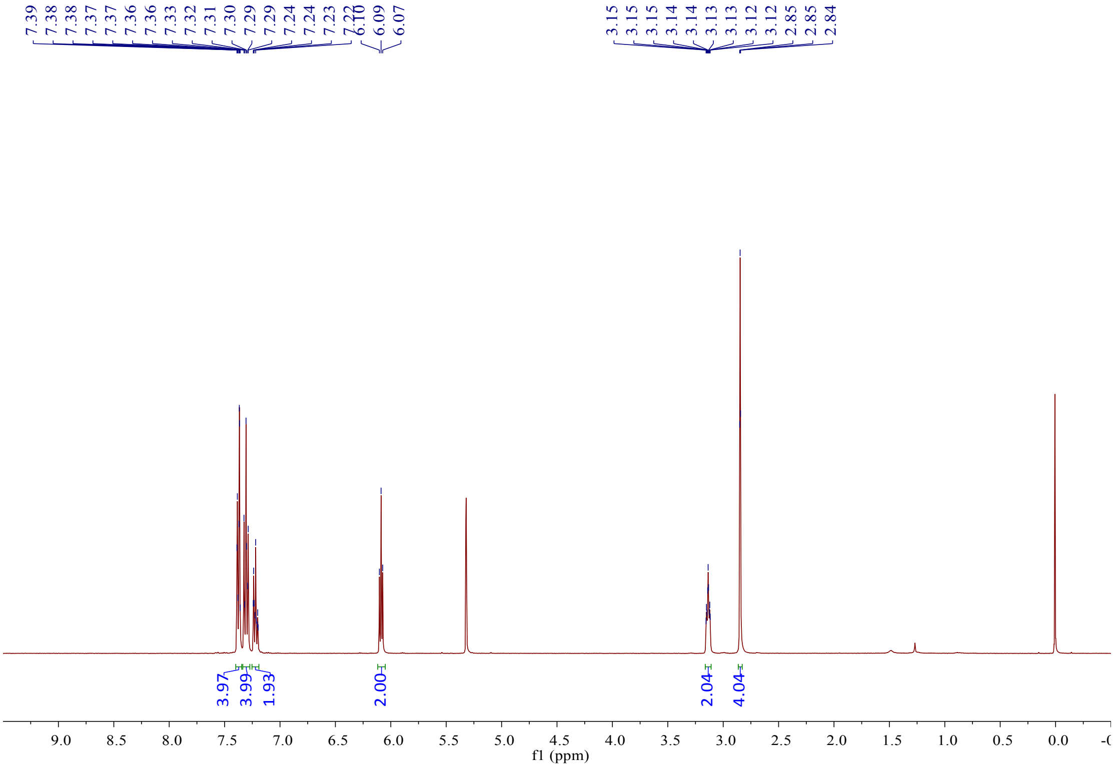
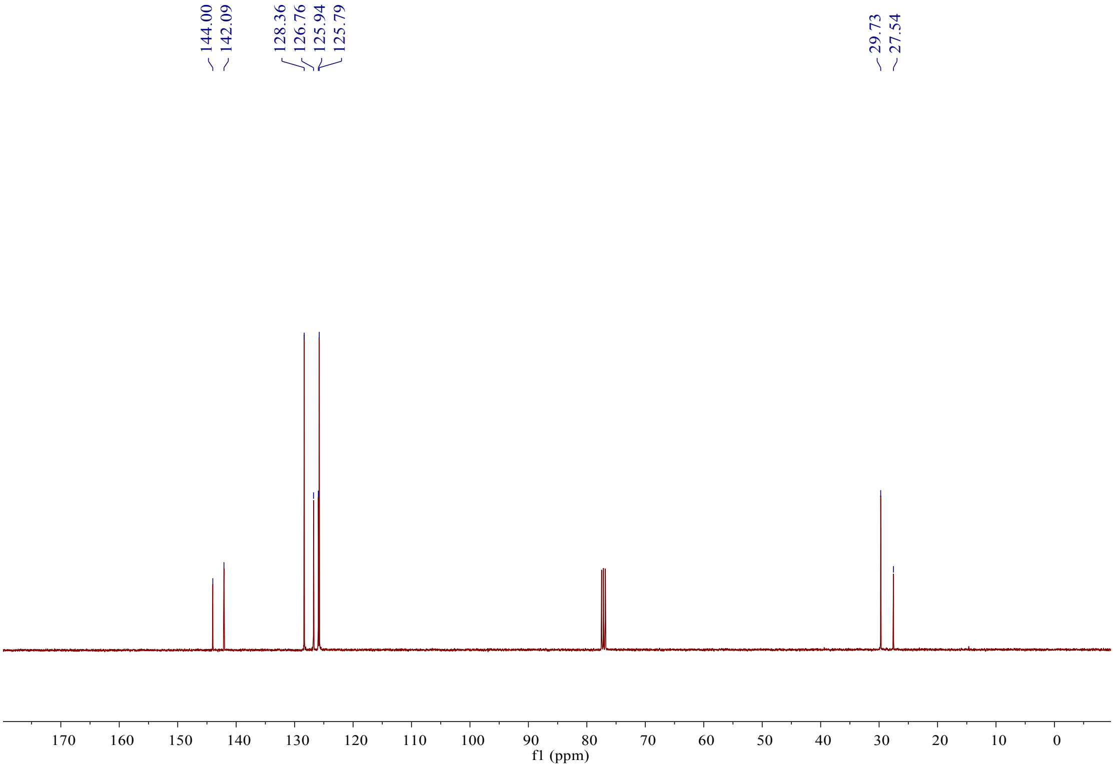
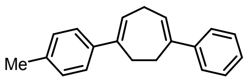


^{13}C NMR spectrum ($CDCl_3$, 101 MHz):





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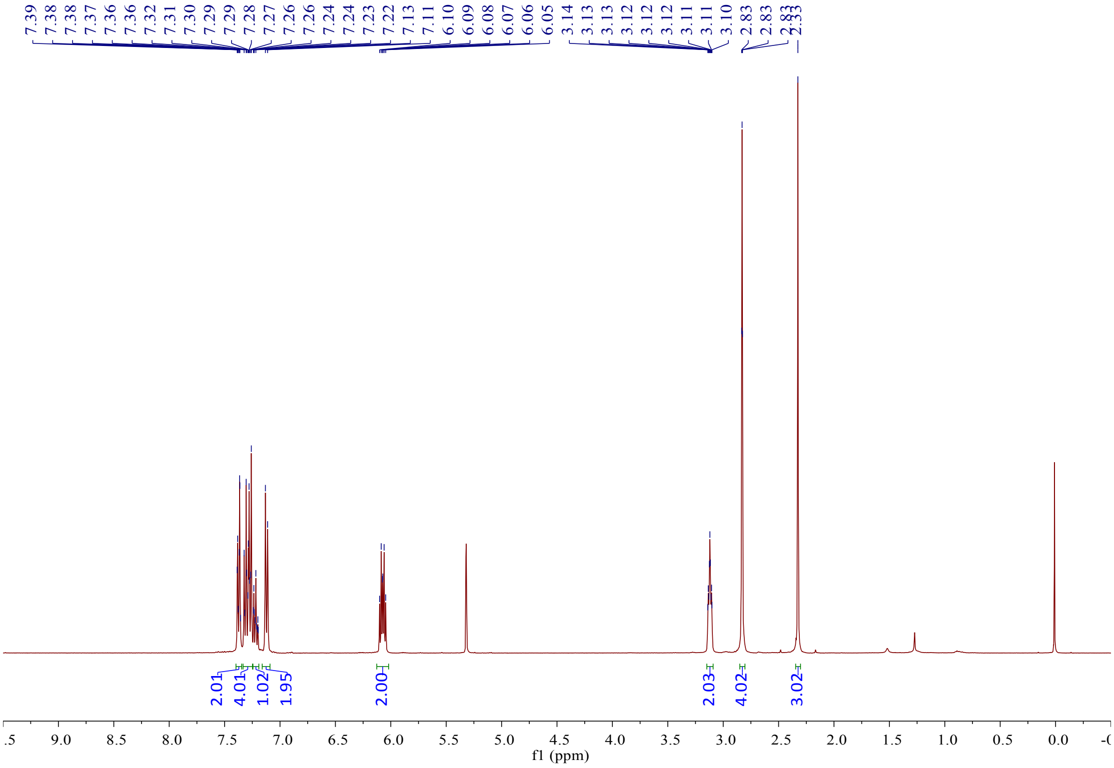
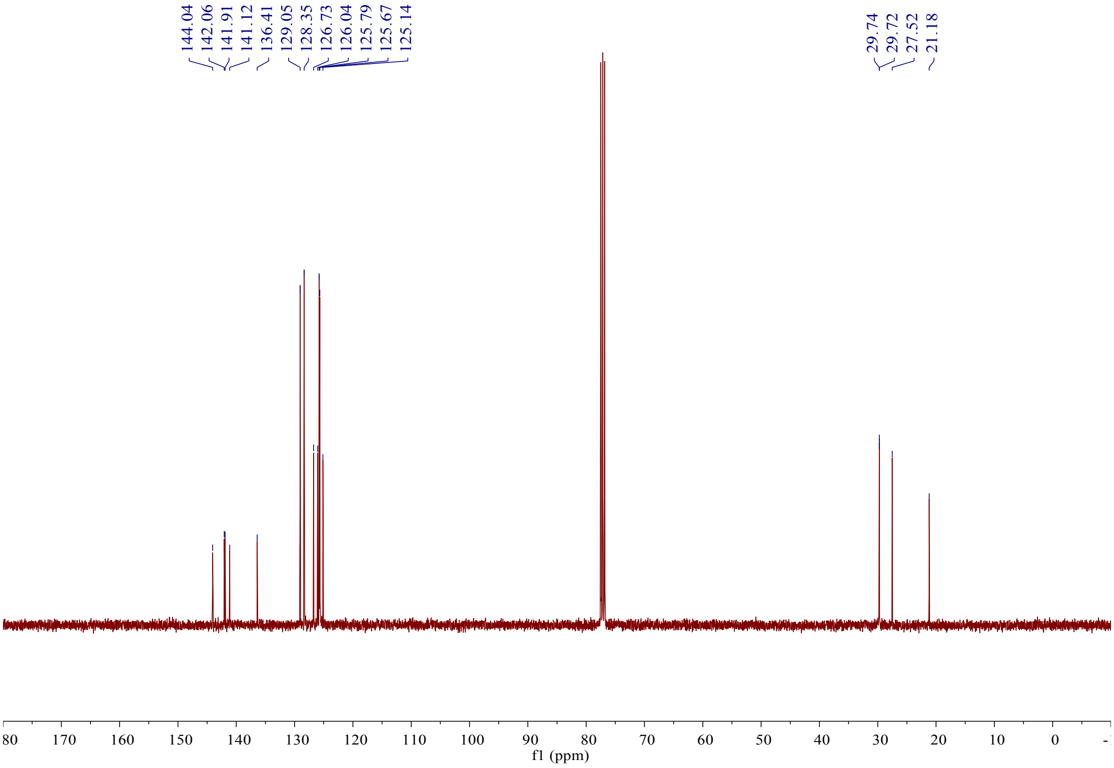
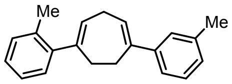


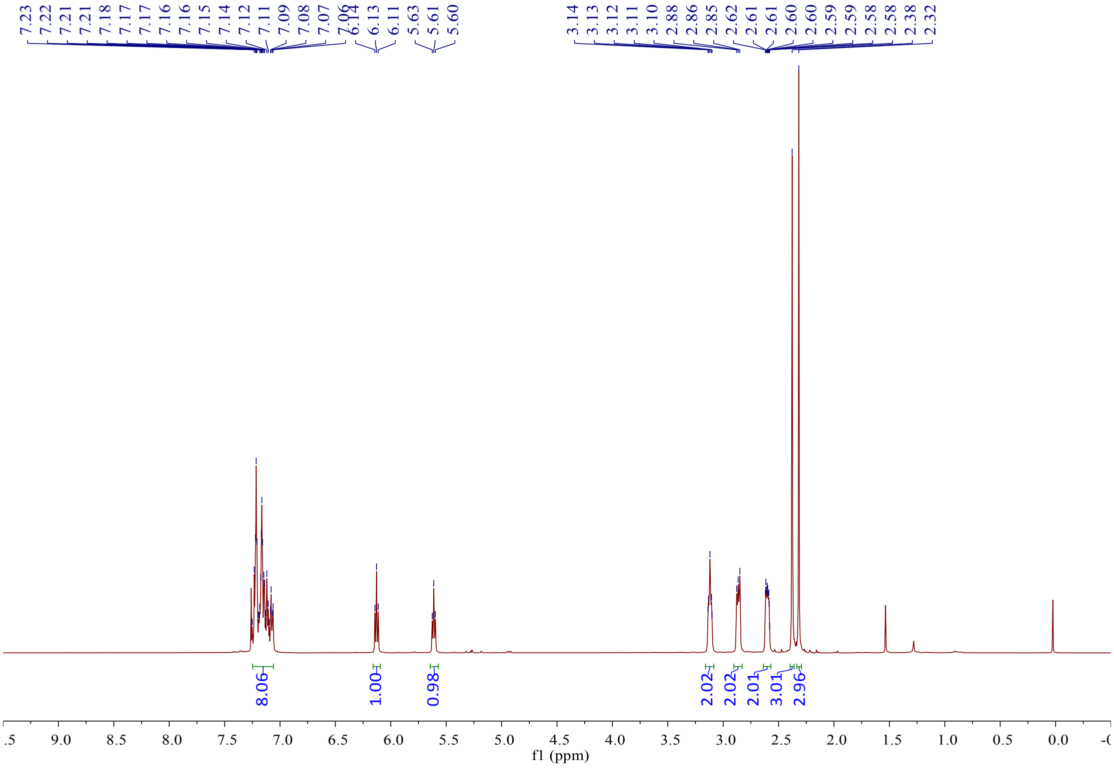
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



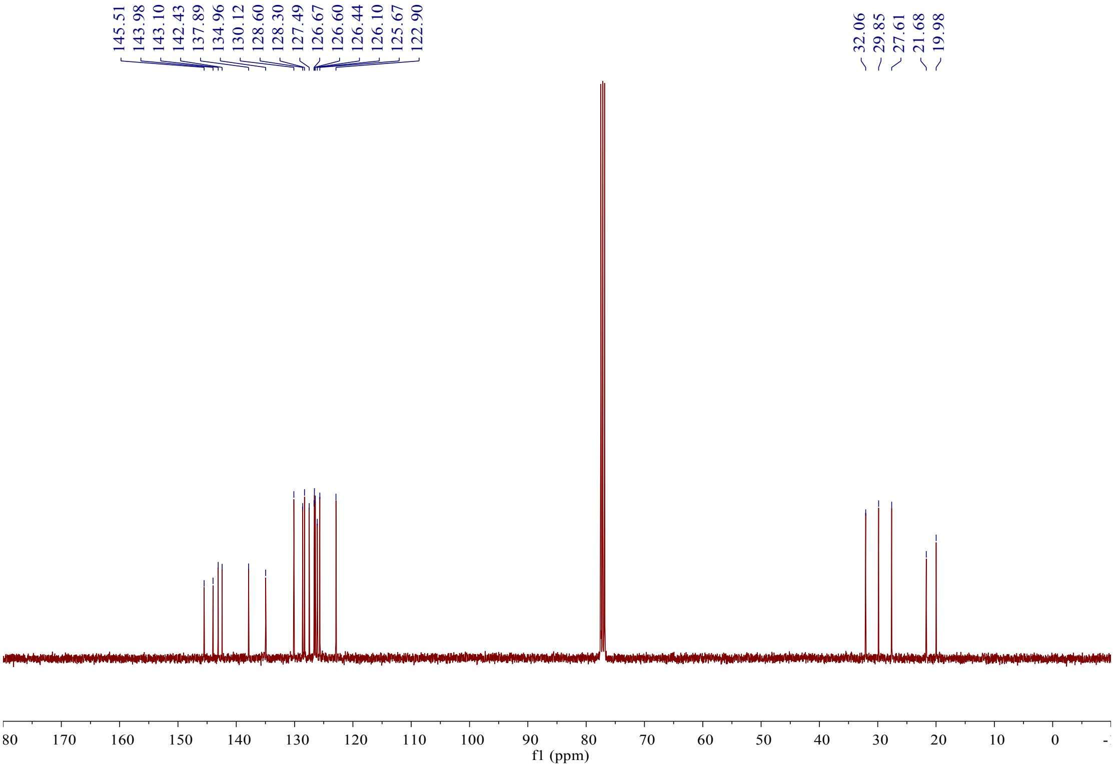


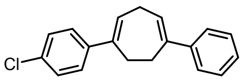
2c

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



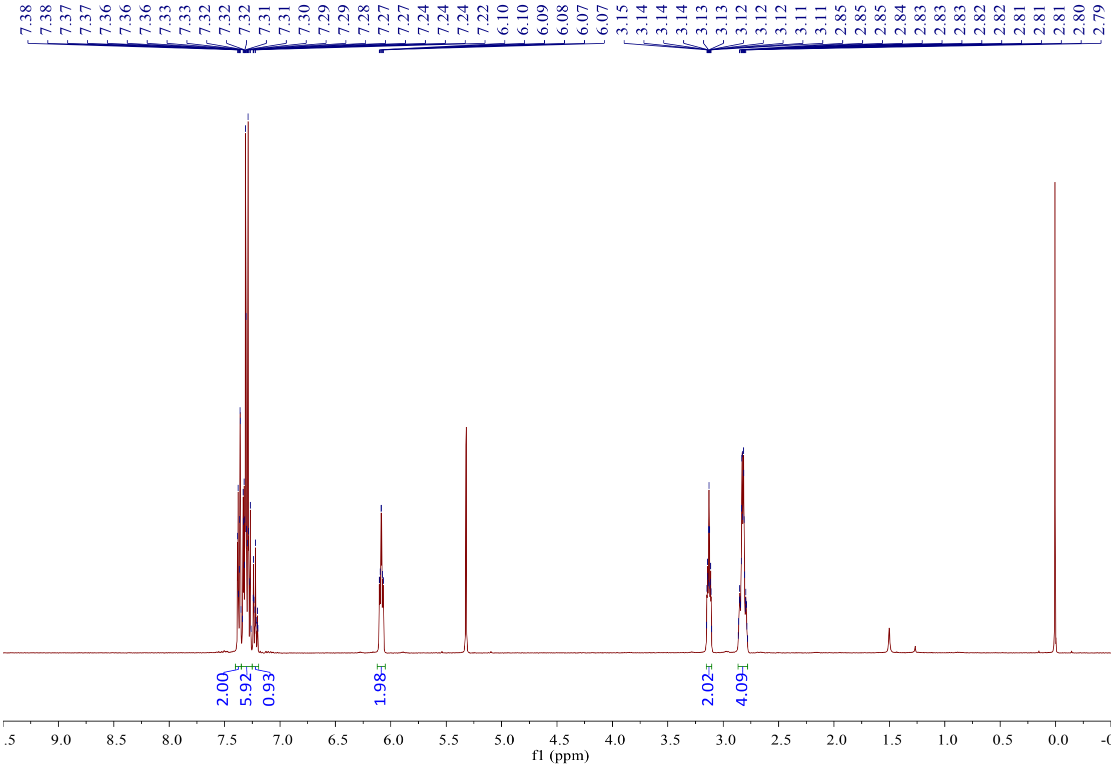
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



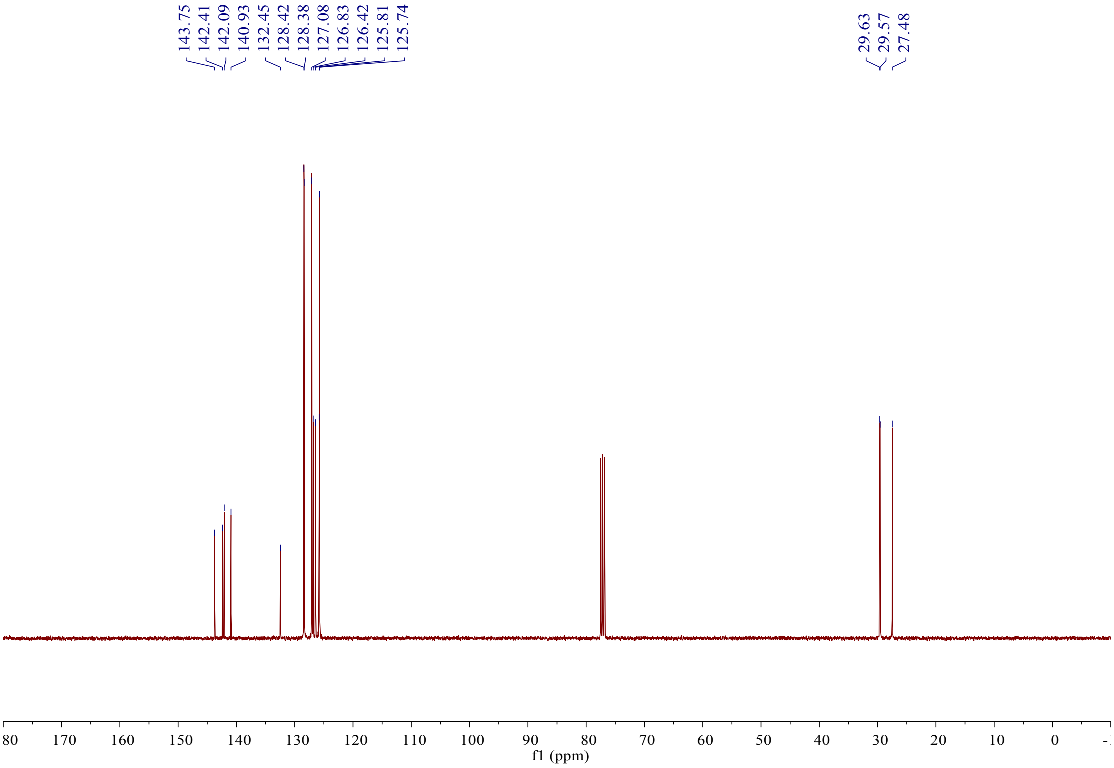


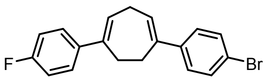
2d

^{1}H NMR spectrum (CD_2Cl_2, 400 MHz):



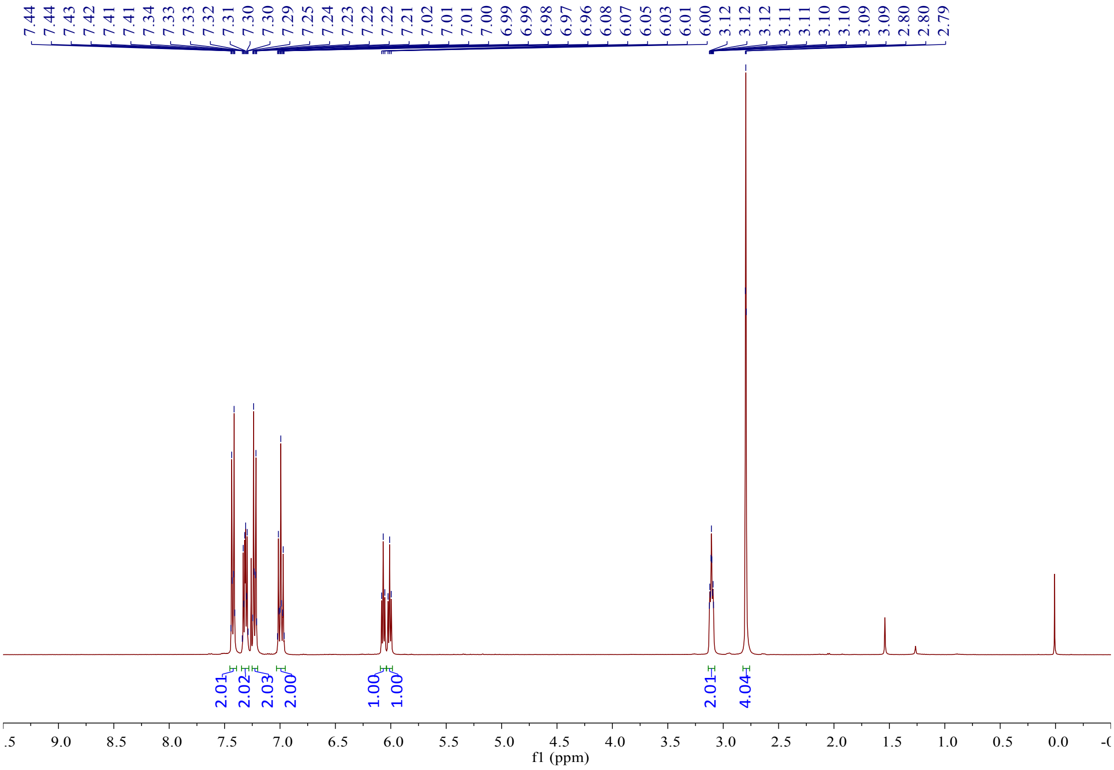
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



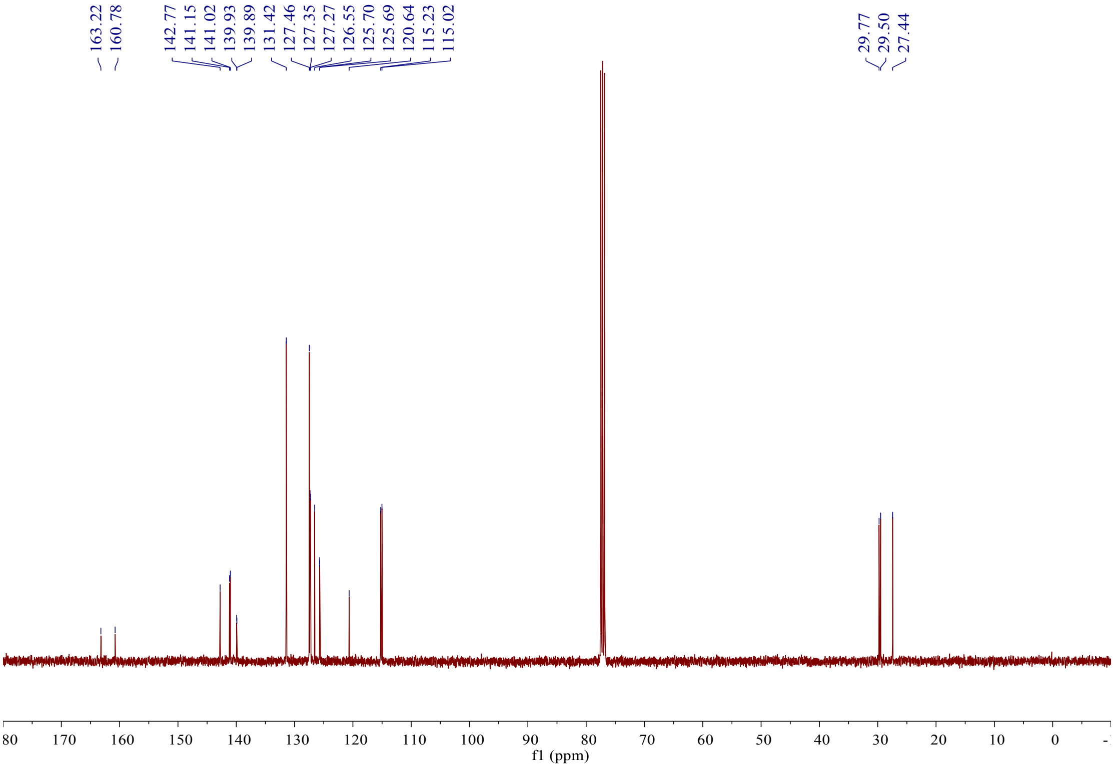


2e

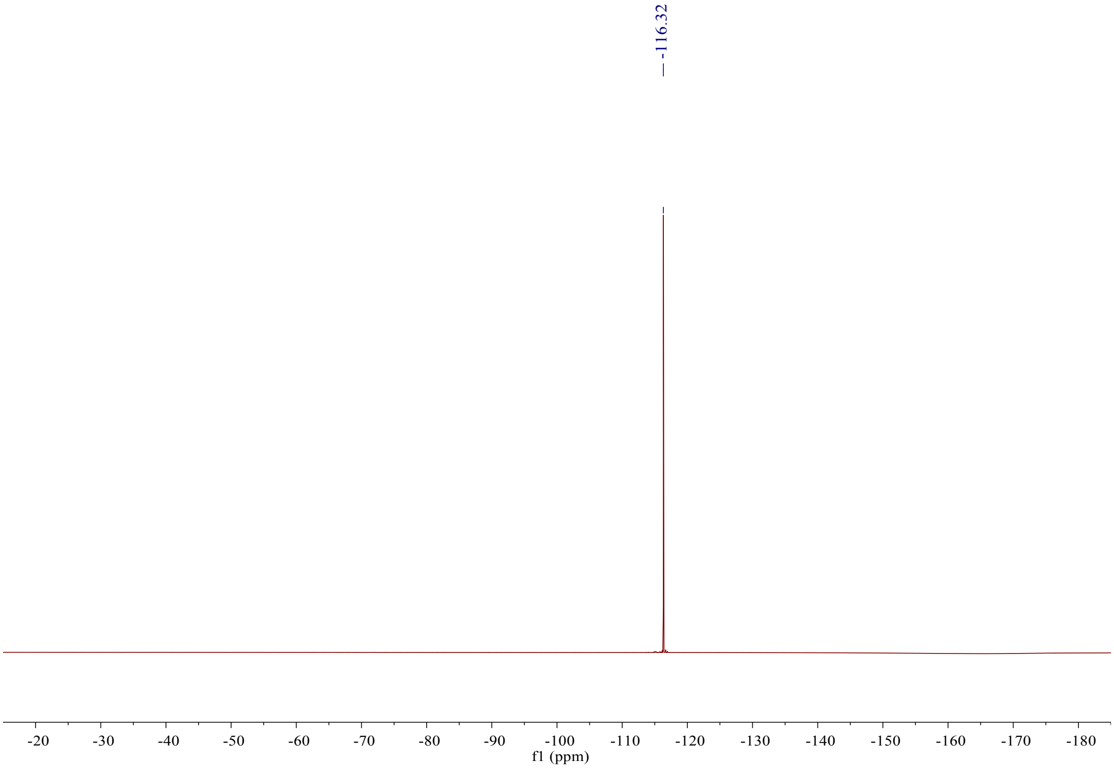
^{1}H NMR spectrum (CDCl$_3$, 400 MHz):

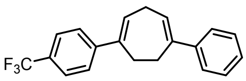


^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



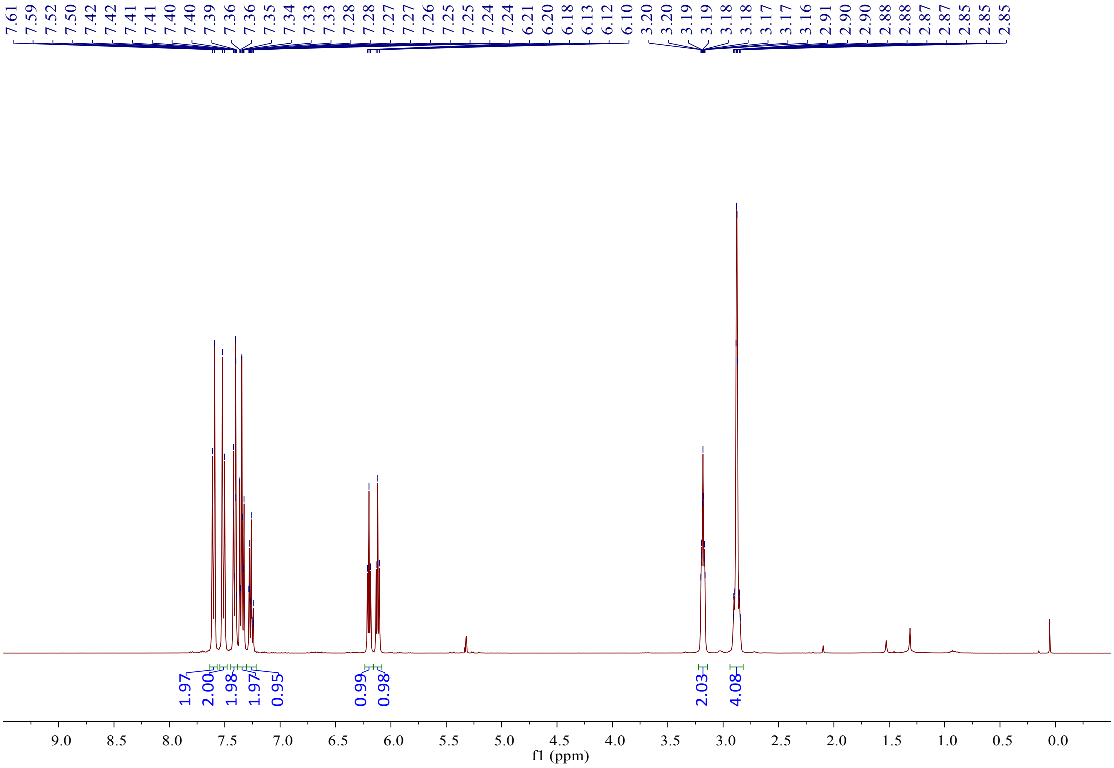
^{19}F NMR spectrum ($CDCl_3$, 471 MHz):



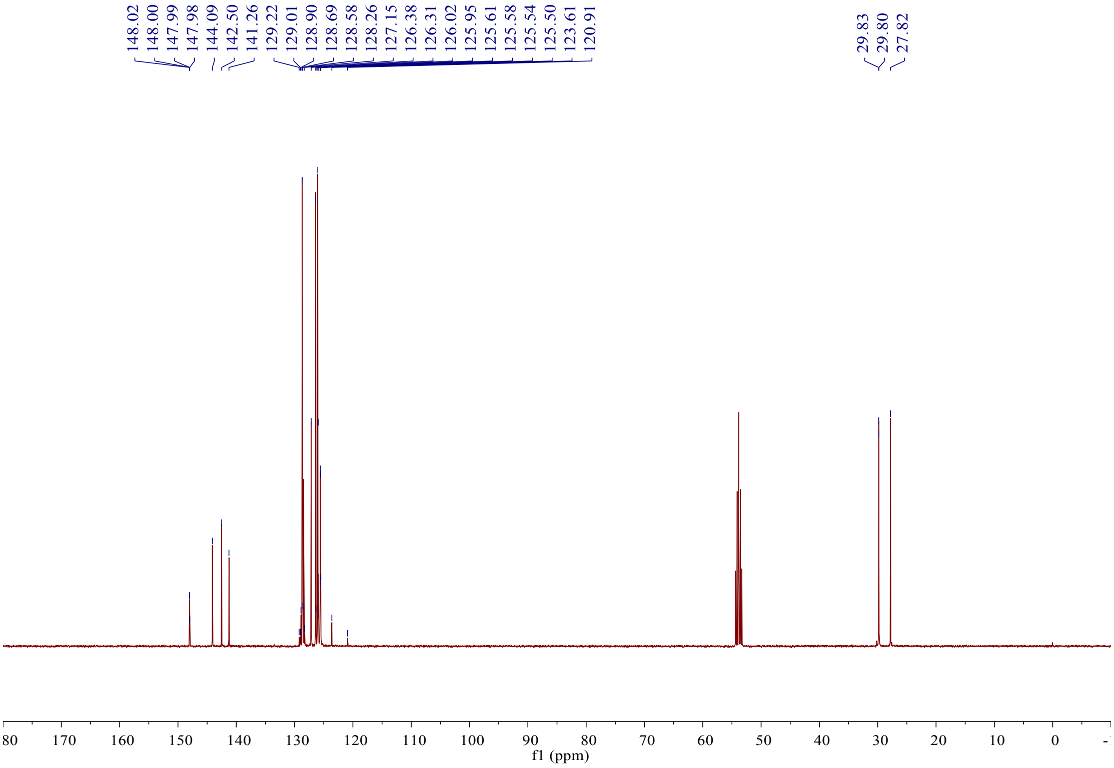


2f

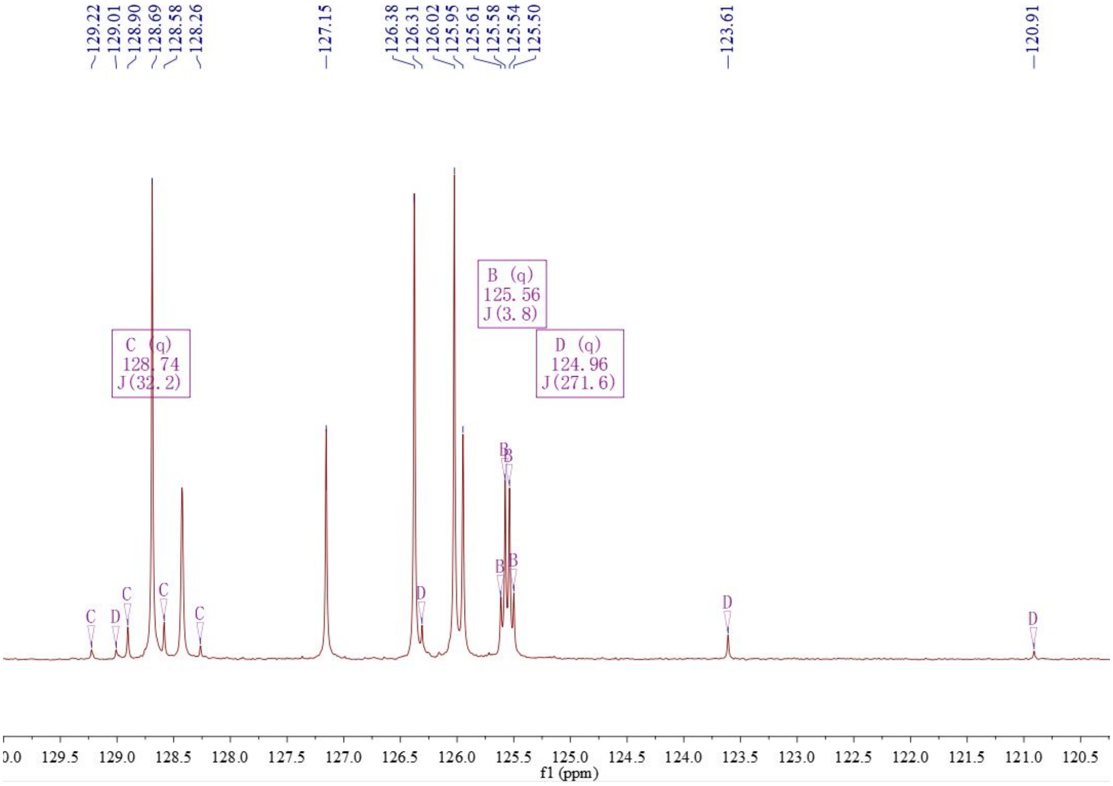
^{1}H NMR spectrum (CD$_2$Cl$_2$, 400 MHz):



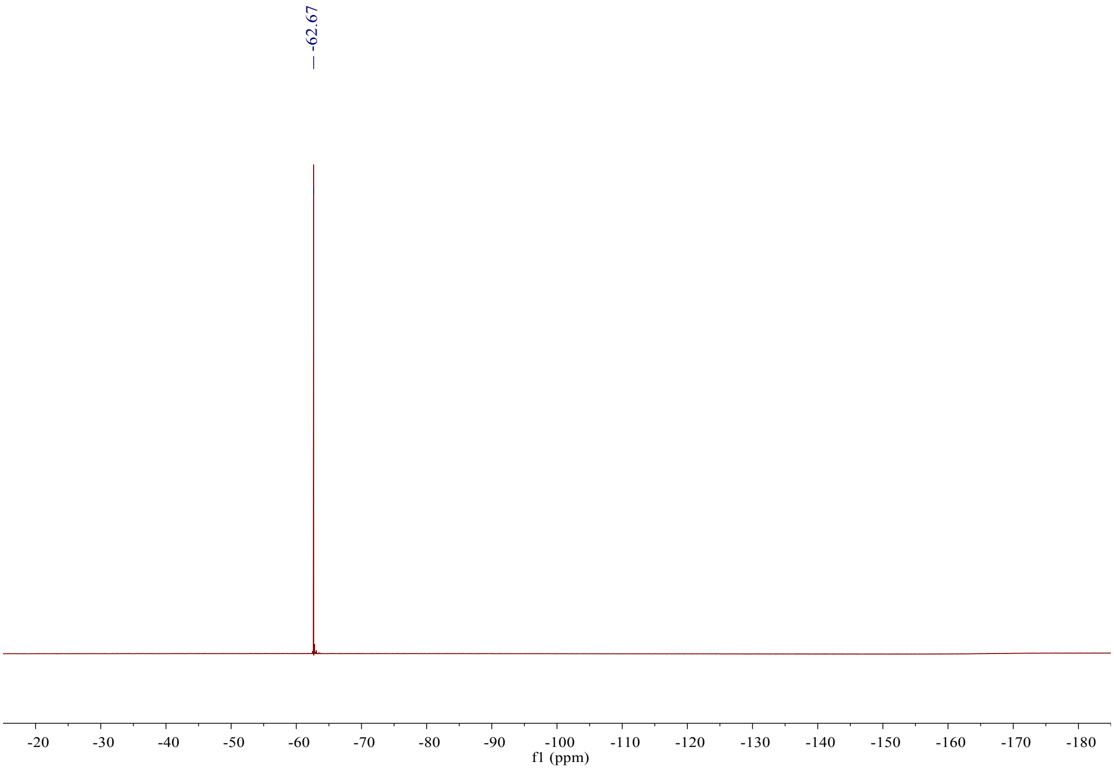
^{13}C NMR spectrum (CD$_2$Cl$_2$, 101 MHz):

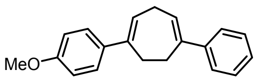


^{13}C NMR spectrum zoomed in (130-120 ppm; B, C, and D indicate different multiplets):



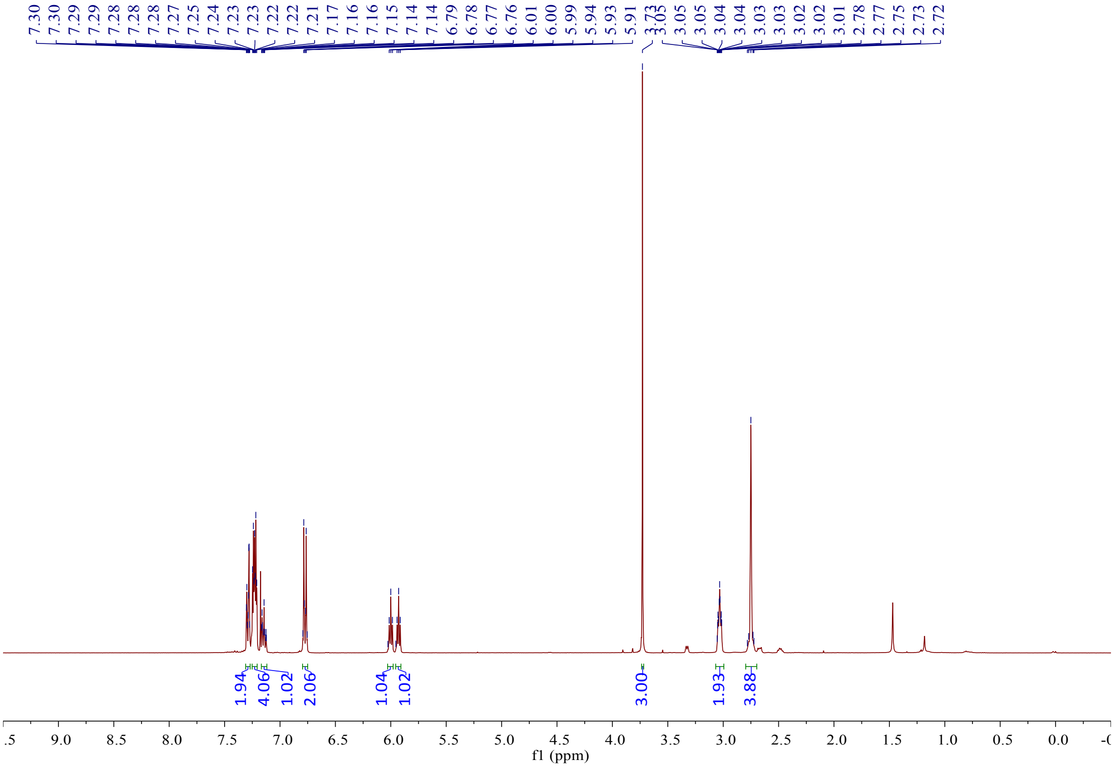
^{19}F NMR spectrum (CD$_2$Cl$_2$, 471 MHz):



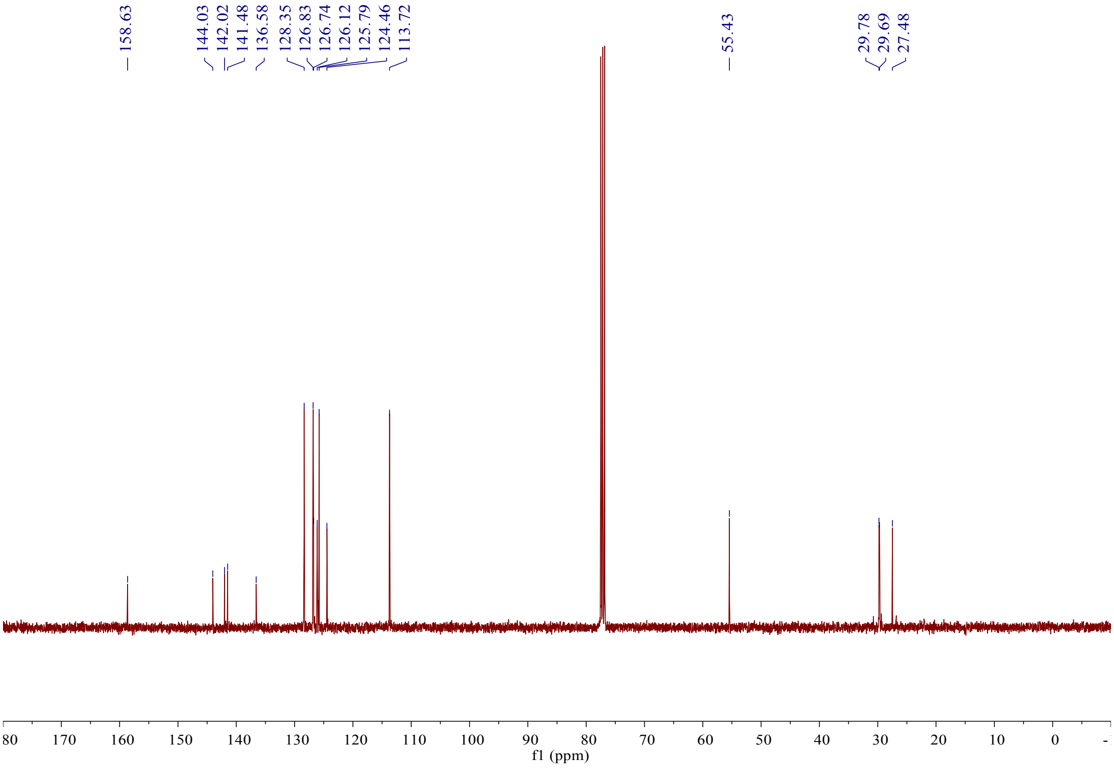


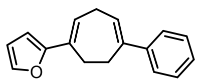
2g

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



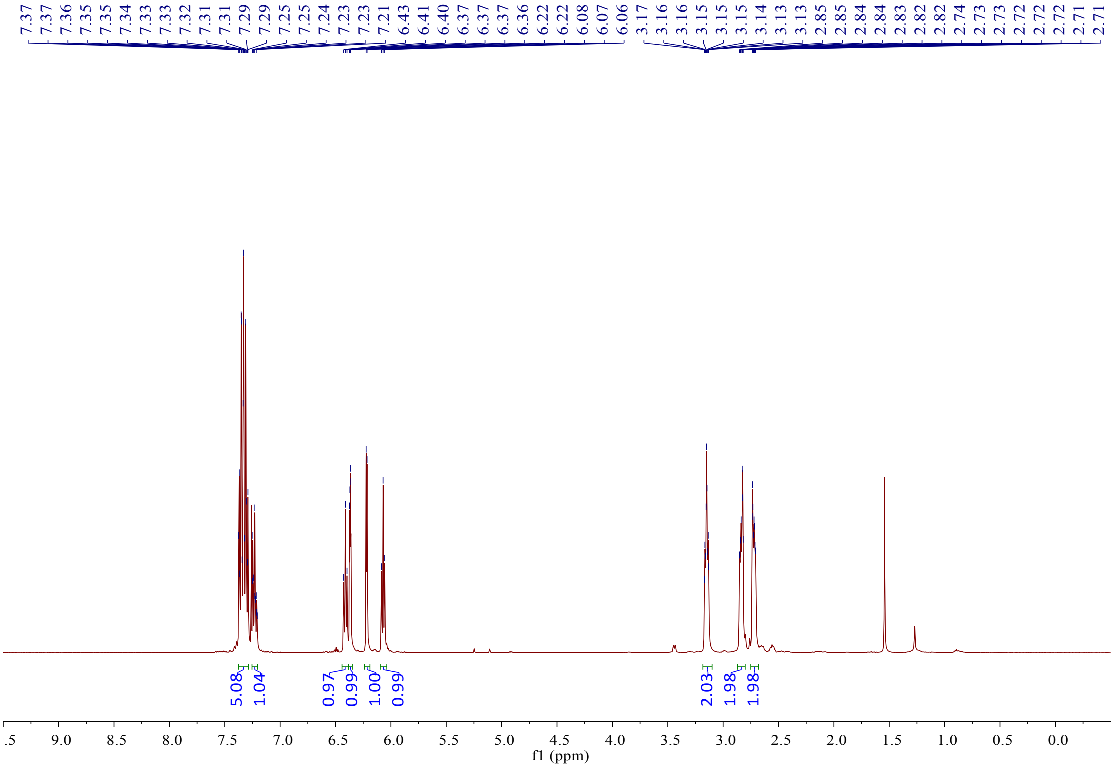
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



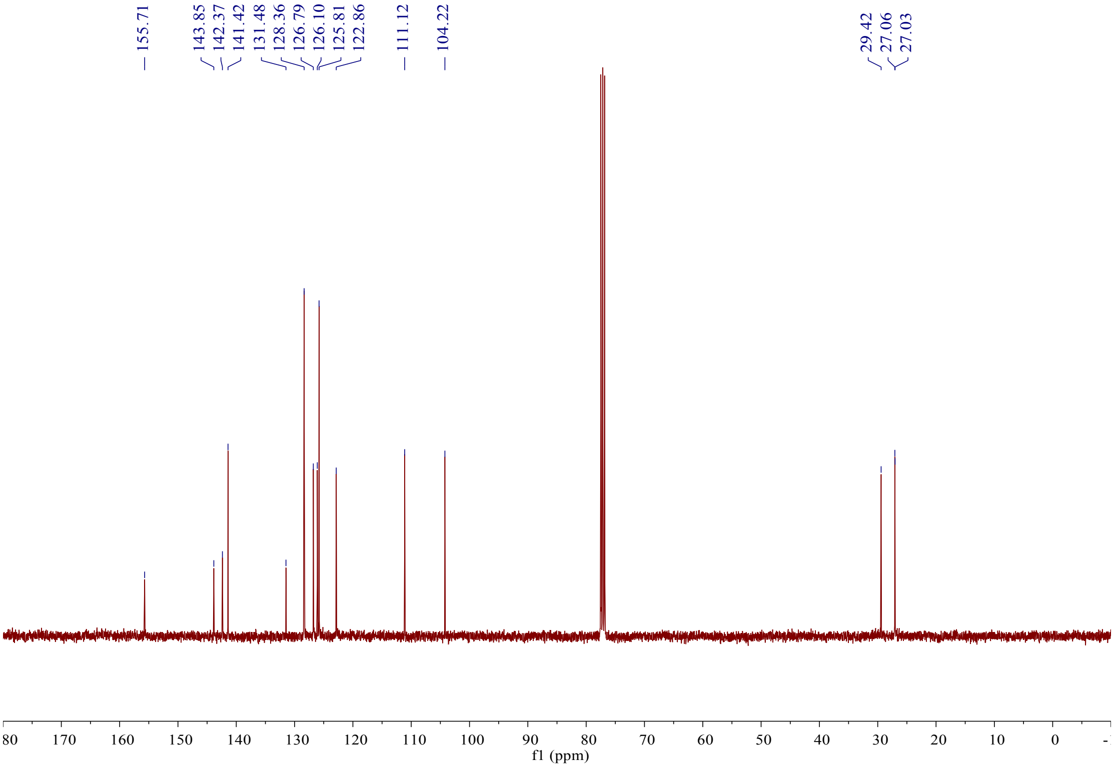


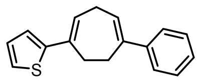
2h

^{1}H NMR spectrum ($CDCl_3$, 400 MHz):



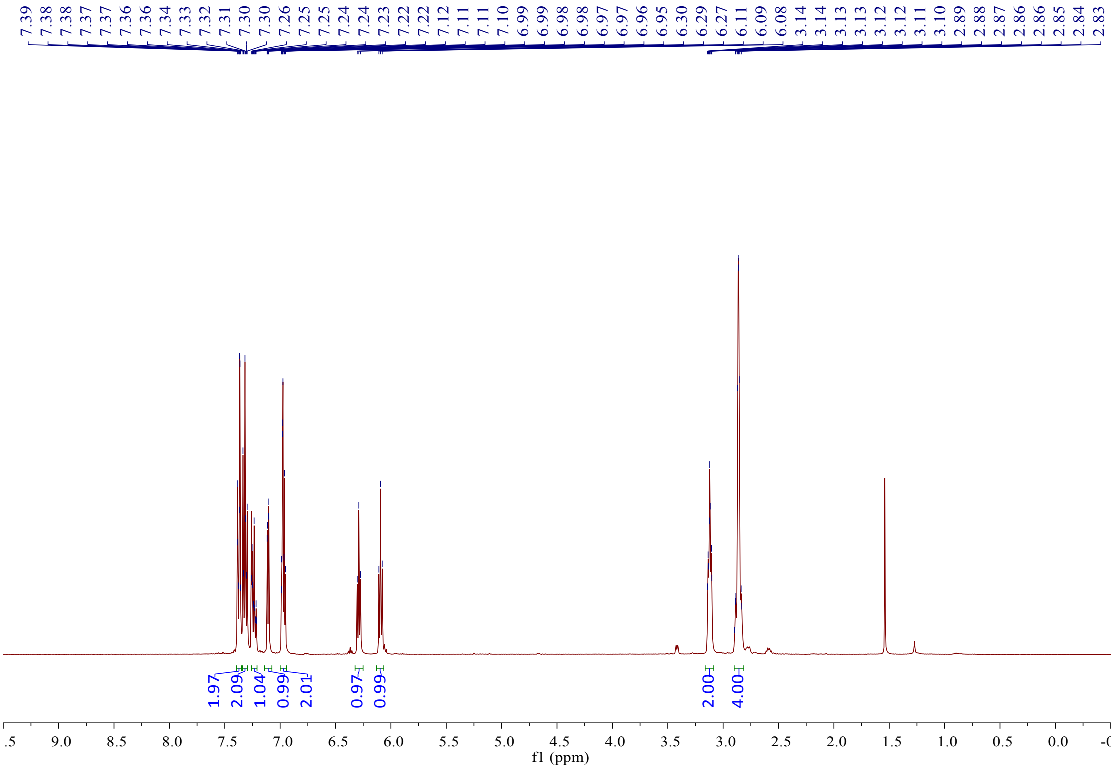
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



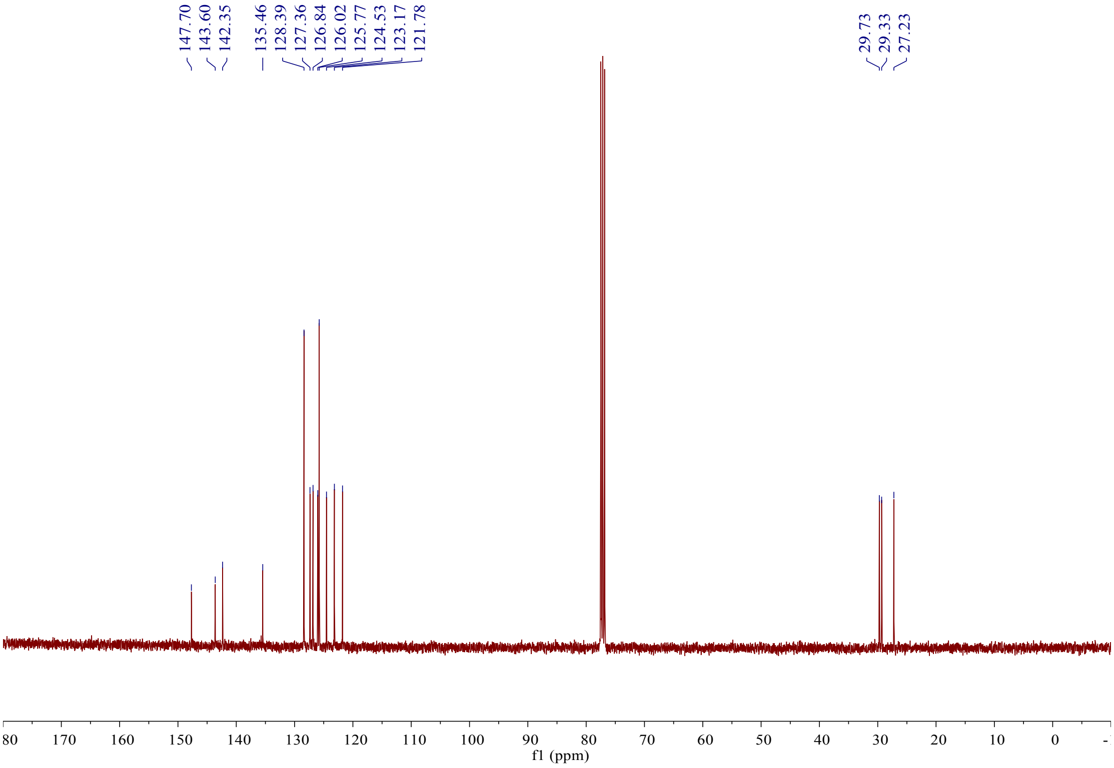


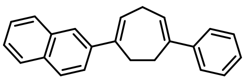
2i

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



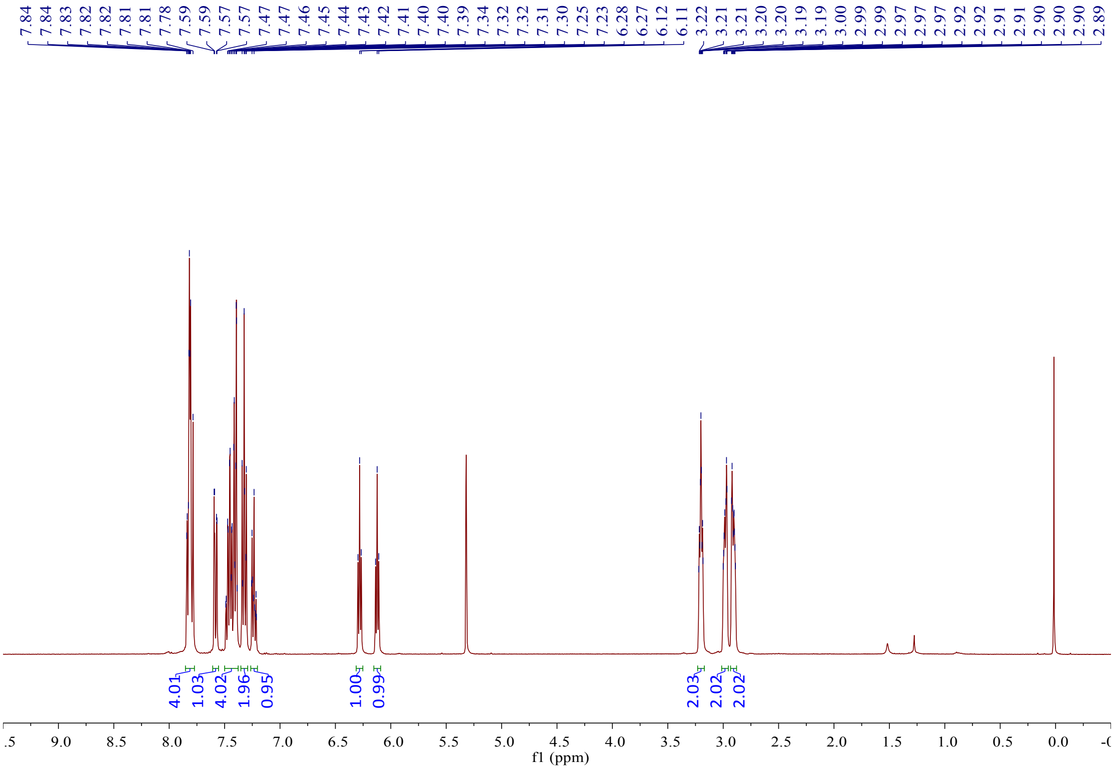
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



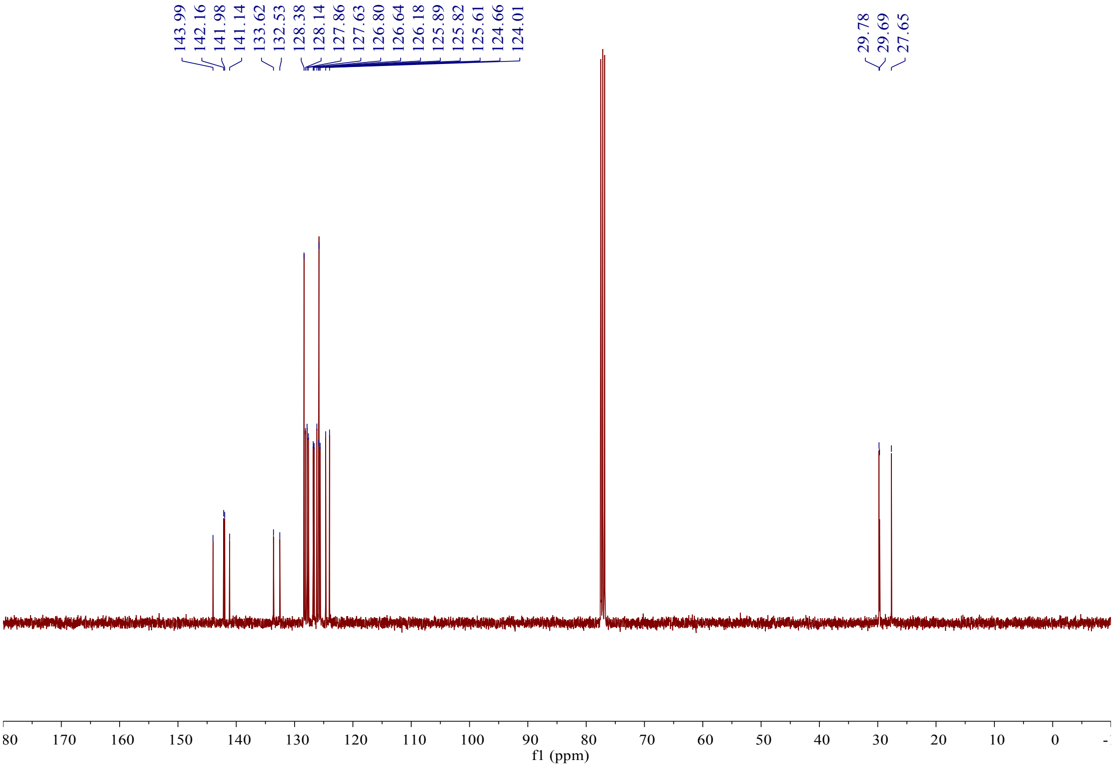


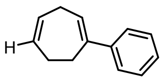
2j

^{1}H NMR spectrum (CD_2Cl_2, 400 MHz):



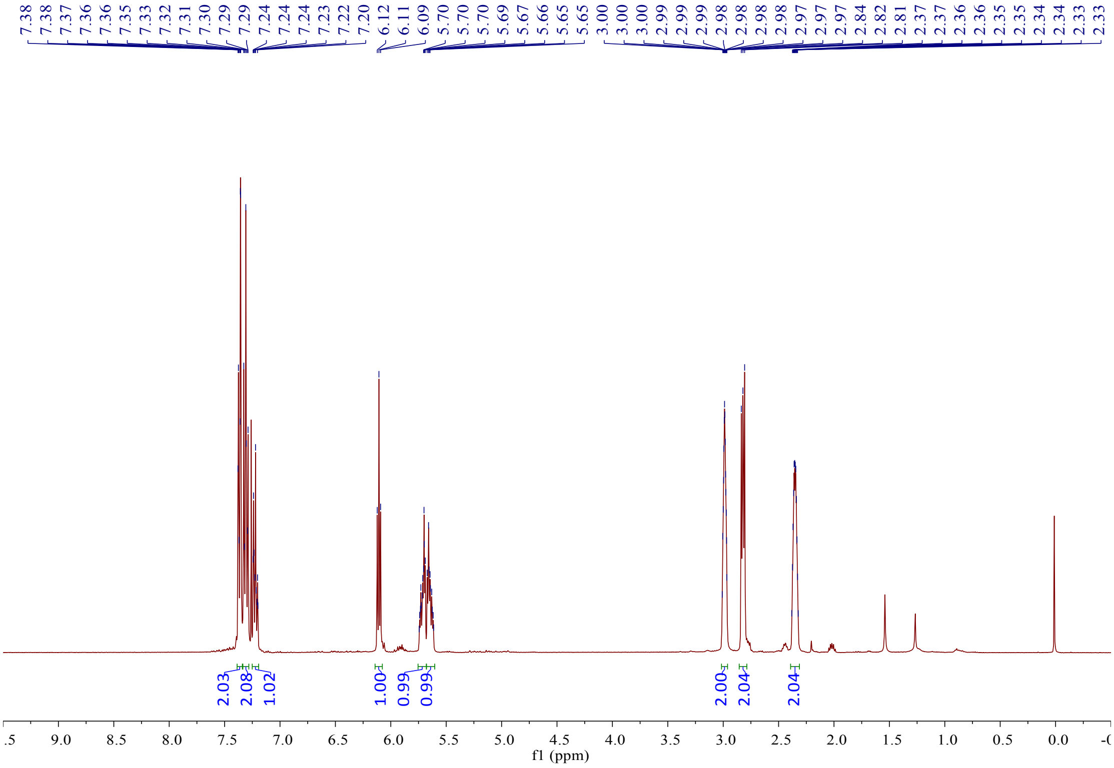
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



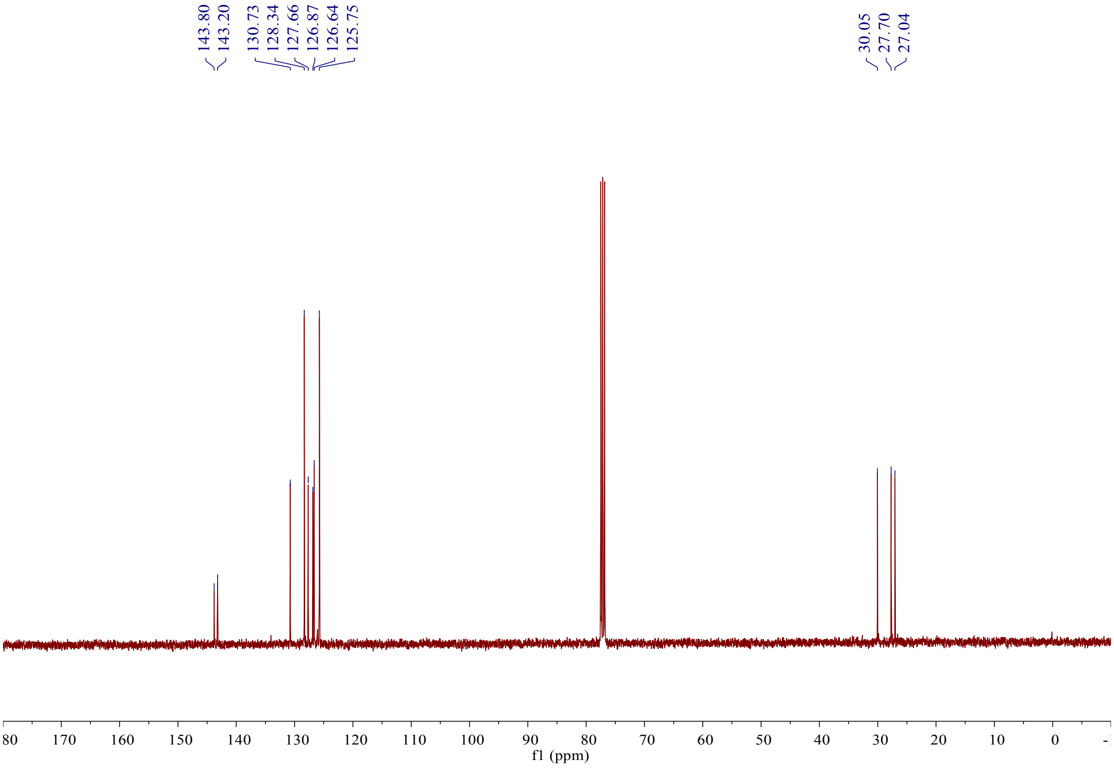


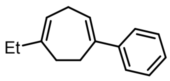
2k

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



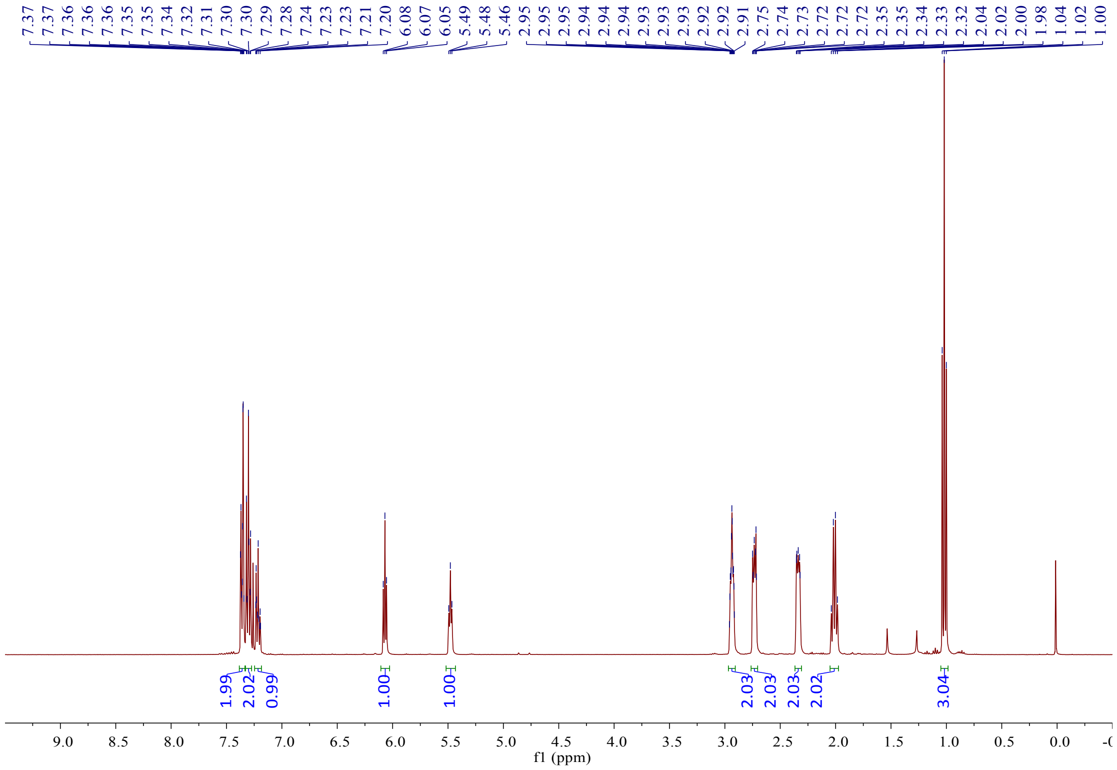
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



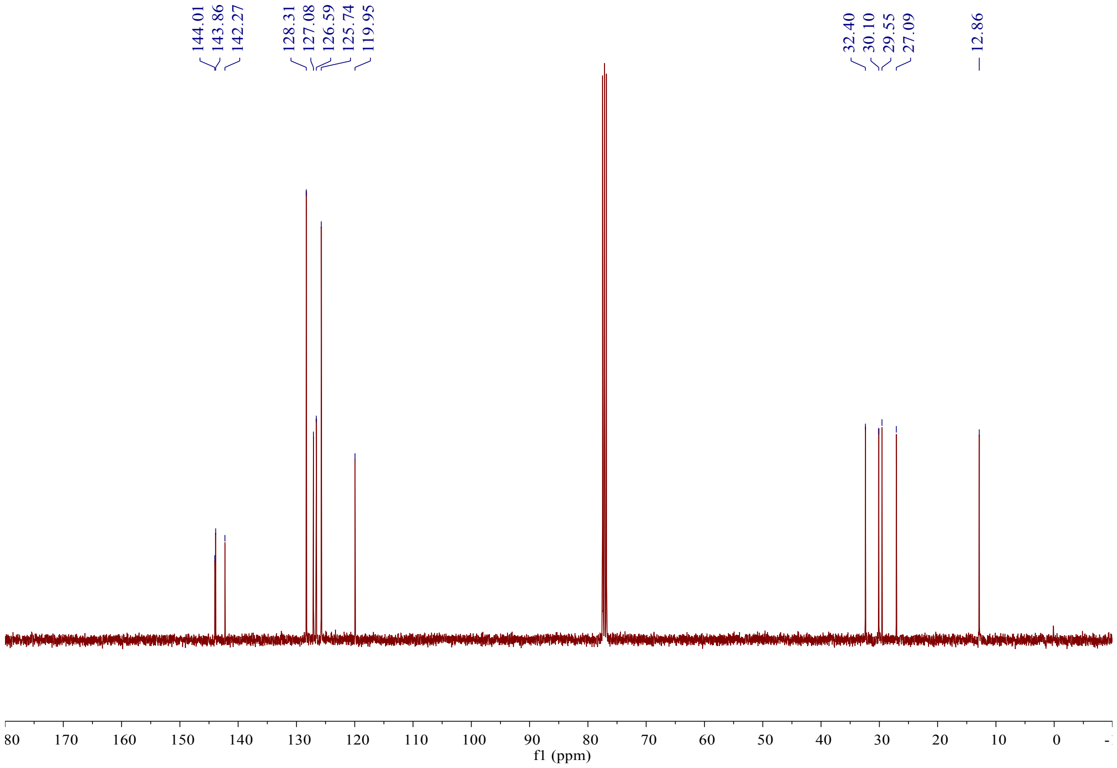


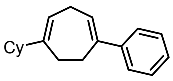
2l

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



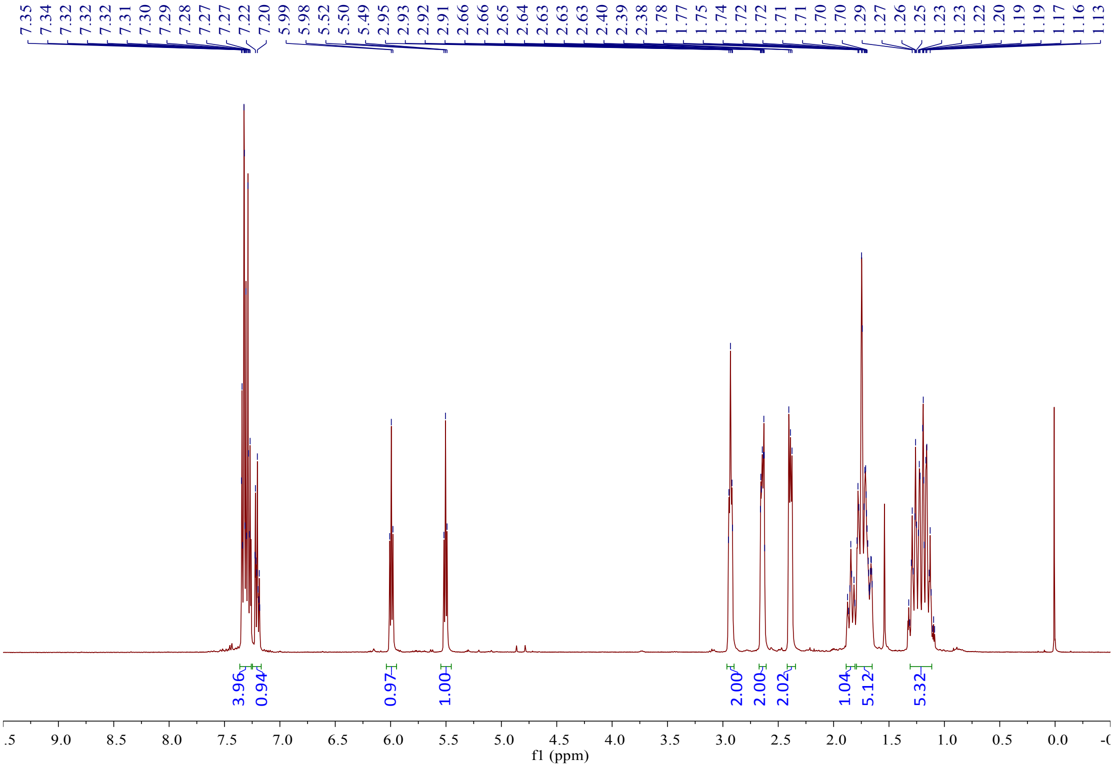
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



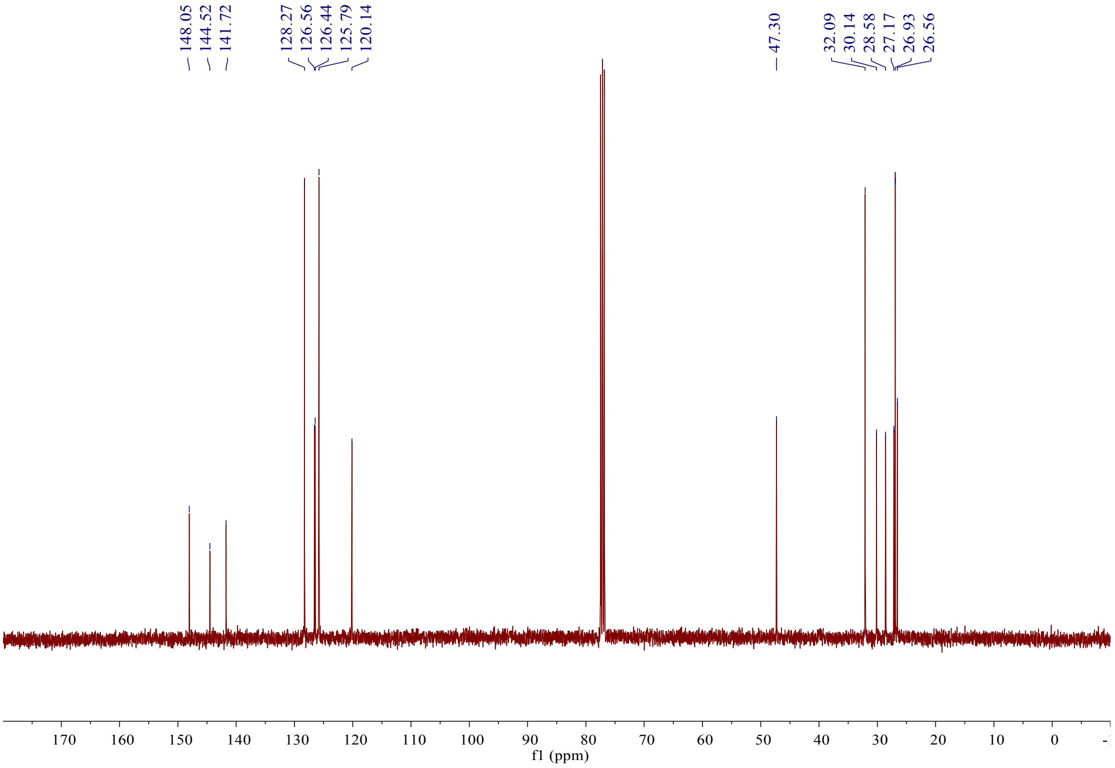


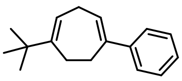
2m

^{1}H NMR spectrum ($CDCl_3$, 400 MHz):



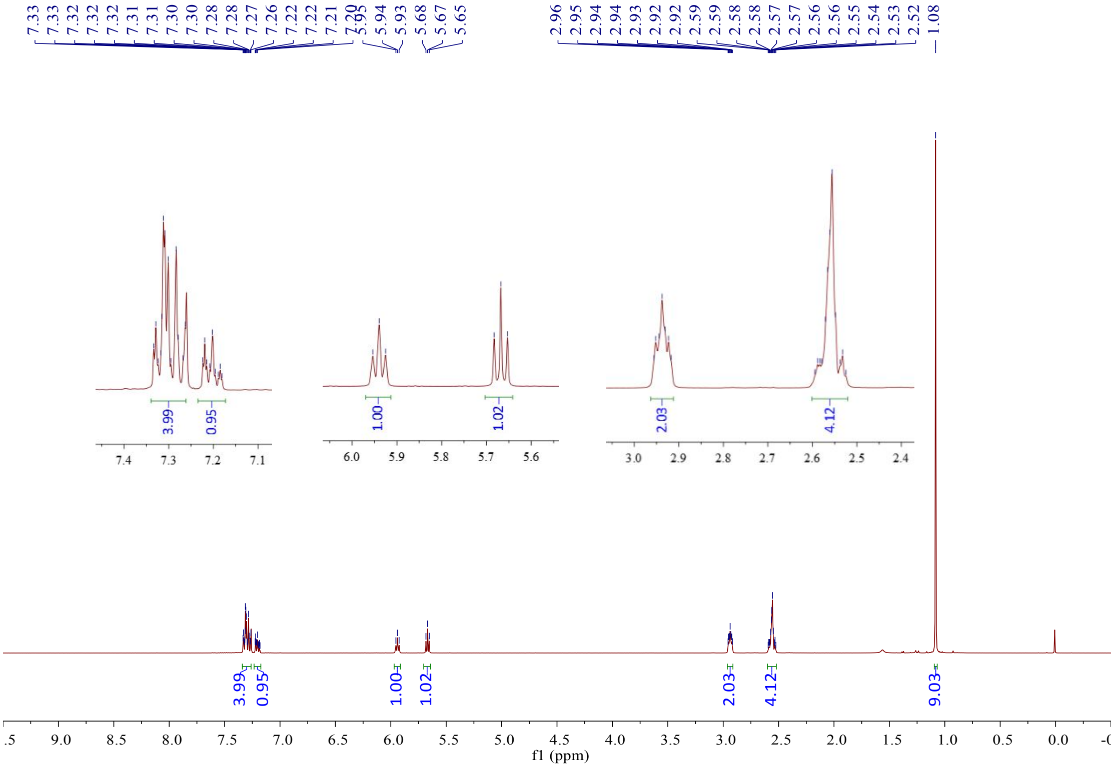
^{13}C NMR spectrum ($CDCl_3$, 101 MHz):



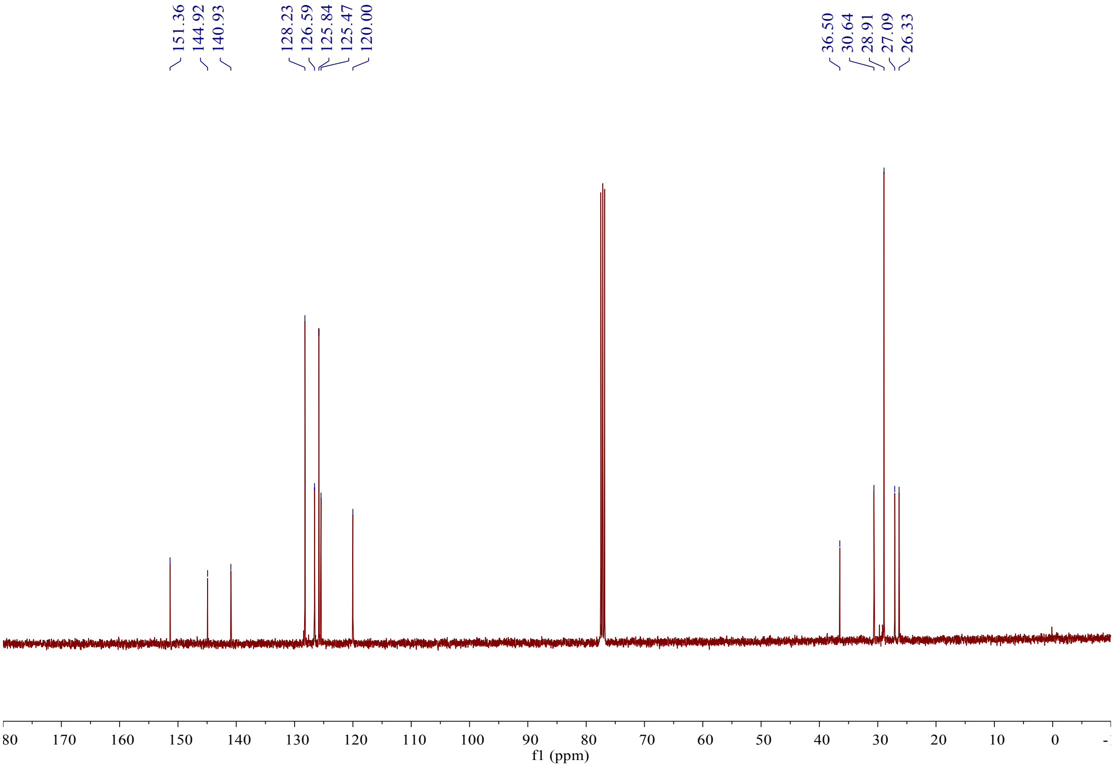


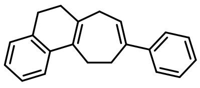
2n

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



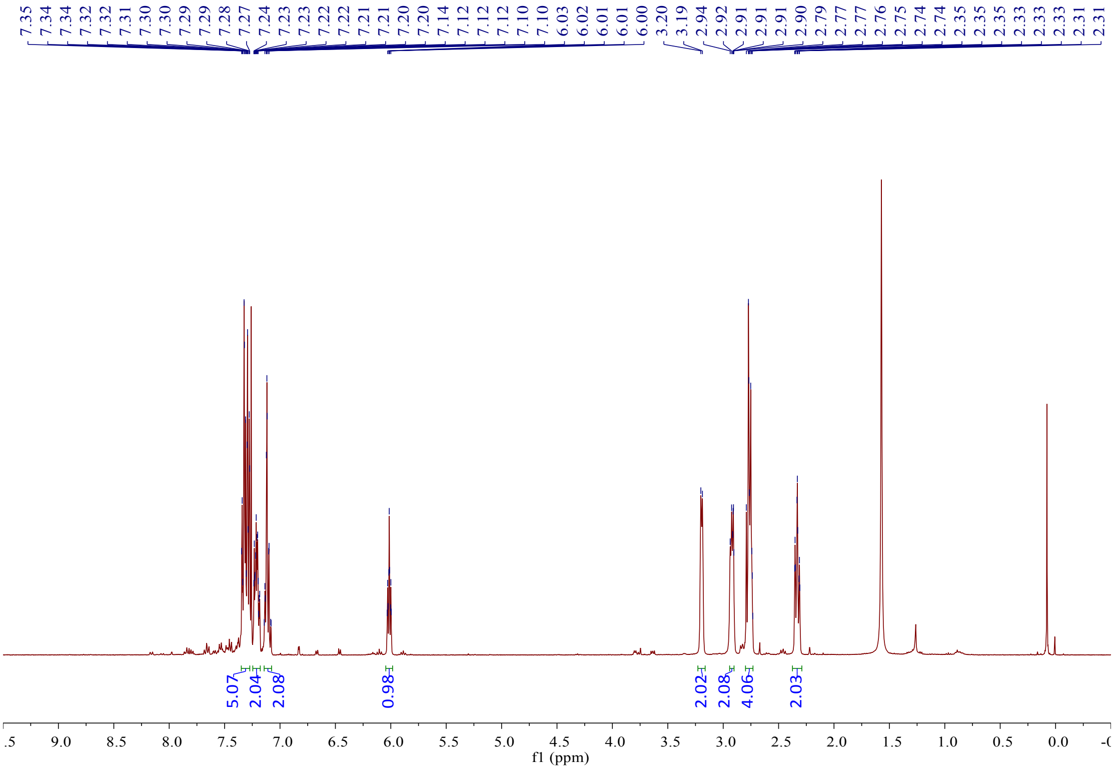
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



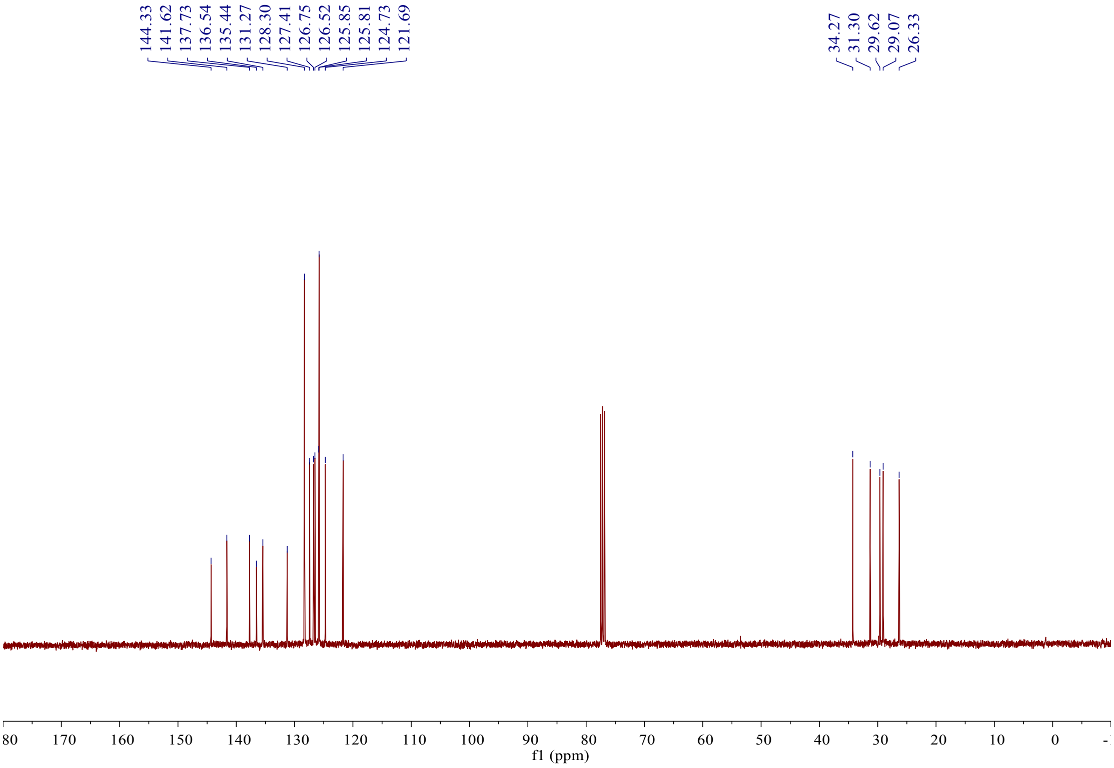


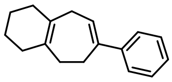
2o

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



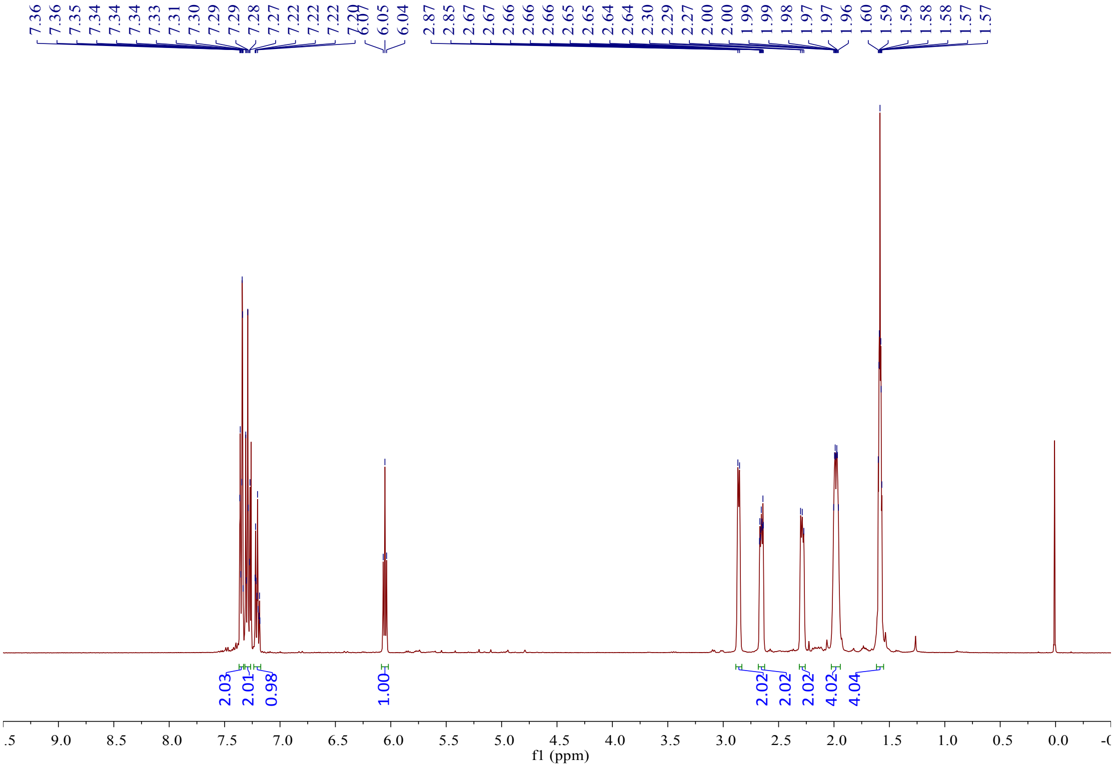
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):



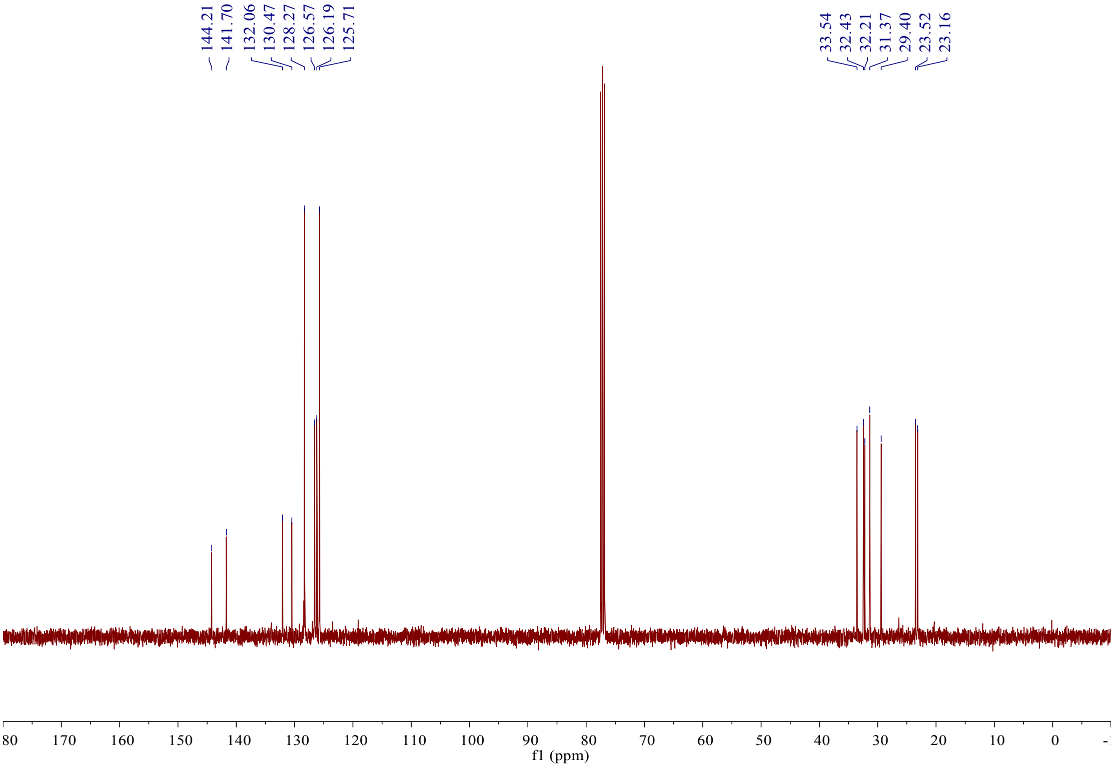


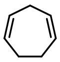
2p

^{1}H NMR spectrum (CDCl$_3$, 400 MHz):



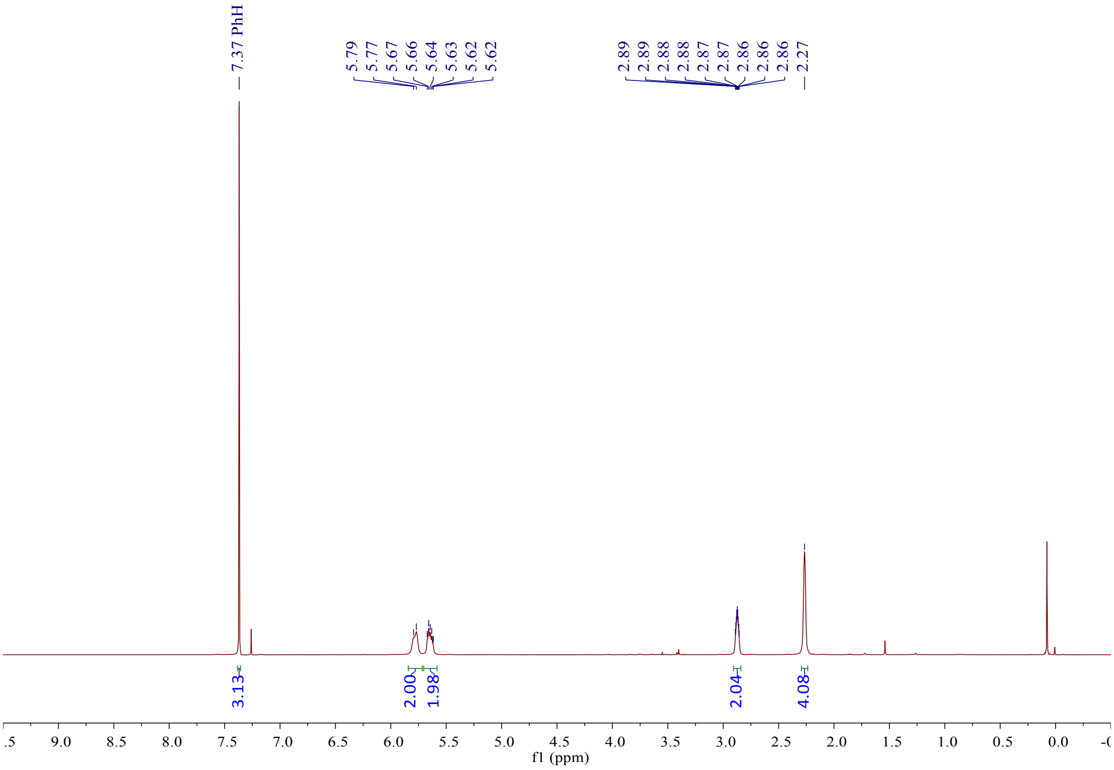
^{13}C NMR spectrum (CDCl$_3$, 101 MHz):





2s

^{1}H NMR spectrum (CDCl$_3$, 400 MHz, **2s**:benzene = 1:0.52):



^{13}C NMR spectrum (CDCl$_3$, 101 MHz, **2s**:benzene = 1:0.52):