Supplementary Information

Cu-Guanidine-Catalysed Asymmetric Protoboration of Internal 1,3-Dienes for One-Pot Access to Chiral Homoallylic Alcohols

Huangfeng Zhang, Ai Zhang, Tao Tang, Tao Jin, Chengzhi Wang, Yao Qin, Xiaoyan Ma, Jinghua Tang, Jinyu Liu and Yicen Ge*

College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu, Sichuan 610059, P. R. China. E-mail: geyicen@cdut.edu.cn

*Corresponding author.

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General Information

Commercially Available Reagents and Solvents

Commercially available chemicals were directly obtained from Merck, Aladdin, and Shanghai Titan Technology. The chemicals were used without further purification once delivered, unless otherwise noted. Solvents were purchased from Shanghai Titan Technology as A.R. grade. If an oxygen- and moisture-free system was required, the solvents were redistilled in the presence of CaH_2 or Na under N_2 atmosphere.

Glassware and Instruments

For reactions employing oxygen- or moisture-sensitive reagents, the glassware was dried at 110 °C in an oven overnight, or under high vacuum using Edwards oil-sealed rotary pumps. These reactions were carried out with Schlenk equipments. Reagents were injected into the reaction setup with microsyringes through a rubber septum, or added into the Schlenk reaction bottle under a N_2 counter-flow.

Thin layer chromatography (TLC) was performed on silica HPTLC plates bought from Yantai Jiangyou (8±2 μm ≥ 80%, HSGF254). Detection was carried out by fluorescence under UV light (wavelength, λ = 254 nm), I_2@silica stain, or $KMnO_4$ dip. The corresponding R_f values and eluting solvents used are listed in the experimental section. Column chromatography was performed with silica gel (grain size: 300–400 mesh, General-reagent®, Si60) under a pressure of approximately 1.5 atm. (air pump). The eluting ratios are listed with the respective experiments.

^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectra were acquired on Bruker Avance III 400 MHz NMR spectroscopy. Deuterated solvents were used ($CDCl_3$) and the residual solvent peaks were used as the internal references. Chemical shifts (δ) are reported in parts per million (ppm) related to the residual solvent signals ($CHCl_3$, 7.26 ppm; $CDCl_3$, 77.0 ppm). The following abbreviations are used to indicate the assignment of the signals and their multiplicities in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal; app, apparent. The given coupling constants *J* are listed as an average. All first-order splitting patterns were assigned on the basis of the appearance of the multiplets. Splitting patterns that could not be easily interpreted are designated as multiplets (m) or broad (br). $^{13}C\{^1H\}$ NMR experiments were carried out on a broad band decoupled mode.

GC conversions and selectivities of protoboration reactions were determined with Fuli GC 9720PLUS system (FID, Zhejiang Fuli Analytical Instruments Inc.) equipped with a Fuli RubyBond-5 fused silica capillary column (Length, 30 m; Inner diameter, 0.32 mm; Thin film, 0.25 μm) using biphenyl as an internal standard with N_2 as carrier gas.

High performance liquid chromatography (HPLC) analysis was performed on a Fuli LC5090 system (UV detector, Zhejiang Fuli Analytical Instruments Inc.) equipped with Daicel

CHIRALPAK columns as chiral stationary phases (IB N-5, IG and IF). Retention times (t) are given in minutes.

IR spectra were obtained by using Tianjin GangDong 650s FTIR spectroscopy. Samples were prepared as thin films on the KBr salt plate.

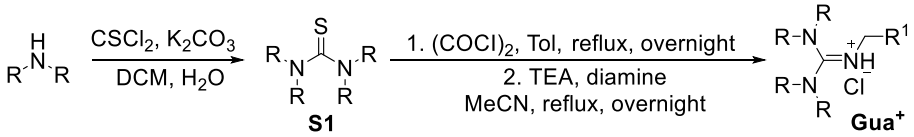
X-ray single crystal analysis ws performed on Bruker D8 VENTURE diffractometer equipped with Cu Kα X-ray.

High-resolution mass spectrometry (HRMS) results were recorded on an Agilent G6546AR Q-TOF (ESI) mass spectrometer and reported in units of mass to charge ratio (m/z).

Optical rotation power was measured with a DCM solution though a quartz cell on a Suoguang WZZ-2B polarimeter (Shanghai Suoguang Electric Technology Co., LTD) at 20 °C using a 10 mL cell with a 10 cm path length, reported as follows: $[\alpha]^{t}_{D}$.

Preparation and Characterization of Catalysts and Substrates

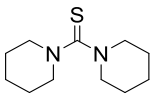
General Procedure A: Synthesis of Guanidiniums



The hydrochlorides of guanidines as ligand precursors were synthesized based on a similar procedure according to the previous literature.[1] A 250 mL round-bottom flask was charged with 30 mL DCM, 30 mL H_2O, 3.5 g K_2CO_3 (25 mmol, 5.0 equiv.), and secondary amine (12 mmol, 2.4 equiv.) in sequence. Then 0.4 mL thiophosgene (5 mmol, 1.0 equiv.) was added dropwise while the emulsion was kept stirring. After reacted overnight, the resulting biphasic system was separated, and the aqueous phase was extracted twice with DCM. The combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated in vacuum. The residual was further purified by column chromatography to give the desired thiourea.

To a dry 100 mL two-necked round-bottom flask under a N_2 counter-flow, 2.36 mmol thiourea (1.0 equiv.) dissolved in 8 mL toluene was charged. Later, 8 mL oxalyl chloride (94.4 mmol, 40 equiv.) was added via a syringe. After that, the reaction mixture was stirred and refluxed at 85 °C overnight, followed by concentration under vacuum to remove all toluene after cooled down. Next, 6 mL MeCN was used to dissolve the residual, before 1 mL triethylamine (7.21 mmol, 3.0 equiv.) and 0.944 mmol diamine (0.4 equiv.) in a minimal amount of MeCN were added into the reaction vessel under N_2. The resulting mixture was allowed to stir and reflux at around 88°C overnight. After the reaction was finished, triethylaminium chloride as a major side-product was removed by crystallization with DCM/Et_2O. The dark-brown filtrate was concentrated, and the desired guanidinium was successfully given after purification by column chromatography.

di(piperidin-1-yl)methanethione S1a



S1a was synthesized with piperidine following General Procedure A. Purification by column chromatography (*n*hexane/EA=100:0~10, column size 254 × 32 mm) within 30 min yielded a total of 795.5 mg (3.75 mmol, 75%) of product as a colorless crystalline solid.

TLC (*n*hexane:EA = 10:1, UV light), R_f =0.65.

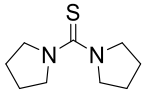
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 3.49 (t, *J* = 4.5 Hz, 8H), 1.66–1.59 (m, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 194.1, 52.7, 25.8, 24.6.

IR (thin film) ν_{max} (cm^{-1}): 3437, 2931, 2850, 1651, 1428, 1363, 1257, 1203, 1136, 1012, 899, 851, 734.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{22}N_2S^+$ [M+H$^+$]: 213.1420, found: 213.1416.

di(pyrrolidin-1-yl)methanethione S1b



S1b was synthesized following the general synthetic procedure A. Purification by column chromatography (*n*hexane/EA=100:0~10, column size 254 × 32 mm) yielded a total of 552.9 mg (3 mmol, 60%) of product as a colorless crystalline solid.

TLC (*n*hexane:EA = 1:1, UV light), R_f =0.65.

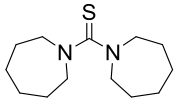
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 3.66 – 3.48 (m, 4H), 1.94 – 1.78 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 184.6, 52.8, 25.6.

IR (thin film) ν_{max} (cm^{-1}): 3044, 2973, 2878, 2361, 1436, 1358, 1319, 1294, 1266, 1227, 1185, 949, 876, 738, 704.

HRMS (ESI+/QTOF) calcd for $C_9H_{17}N_2S^+$ [M+H$^+$]: 185.1107, found: 185.1109.

di(azepan-1-yl)methanethione S1c



S1c was synthesized following the general synthetic procedure A. Purification by column chromatography (*n*hexane/EA=100:0~10, column size 254 × 32 mm) yielded a total of 480.8 mg (2 mmol, 40%) of product as a colorless crystalline solid.

TLC (*n*hexane:EA = 10:1, UV light), R_f =0.65.

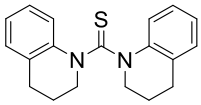
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 3.65 – 3.54 (m, 4H), 1.78 (dt, *J* = 7.8, 3.2 Hz, 4H), 1.60 (dt, *J* = 6.0, 2.8 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 194.7, 54.3, 27.9, 27.8.

IR (thin film) ν_{max} (cm^{-1}): 2931, 2856, 1446, 1413, 1371, 1298, 1265, 1222, 1202, 1181, 1143, 1100, 1014, 739, 703.

HRMS (ESI+/QTOF) calcd for $C_{13}H_{25}N_2S^+$ [M+H$^+$]: 241.1733, found: 241.1736.

bis(3,4-dihydroquinolin-1(2*H*)-yl)methanethione S1d



S1d was synthesized following the general synthetic procedure A. By recrystallization purification (DCM/*n*hexane), a total of 4.87 g (15.8 mmol, 79%) of product was obtained within 30 minutes, as a yellow crystalline solid.

TLC (*n*hexane:EA = 5:1, UV light), R_f =0.50.

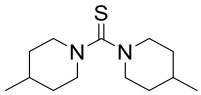
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.17 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.08 – 6.76 (m, 6H), 4.24 – 3.72 (m, 4H), 2.67 (q, *J* = 6.5 Hz, 4H), 2.18 – 1.84 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 188.3, 141.2, 130.8, 128.5, 126.0, 124.0, 121.8, 50.8, 26.8, 23.9.

IR (thin film) ν_{max} (cm^{-1}): 2943, 2359, 1650, 1488, 1455, 1371, 1332, 1198, 1180, 1141, 1074, 753.

HRMS (ESI+/QTOF) calcd for $C_{19}H_{21}N_2S^+$ [$M+H^+$]: 309.1420; found: 309.1425.

bis(4-methylpiperidin-1-yl)methanethione S1e



S1e was synthesized with piperidine following General Procedure A. Purification by column chromatography (*n*hexane/EA=100:0~10, column size 254 × 32 mm) within 30 min yielded a total of 1.61 g (6.7 mmol, 67%) of product as a yellow oil.

TLC (*n*hexane:EA = 10:1, UV light), R_f =0.50.

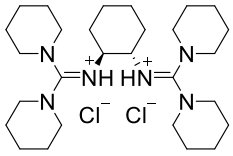
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 4.03 (dp, *J* = 13.4, 2.2 Hz, 4H), 2.91 (td, *J* = 12.7, 2.4 Hz, 4H), 1.69 – 1.52 (m, 6H), 1.22 (dtd, *J* = 12.5, 10.8, 4.1 Hz, 4H), 0.92 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 193.7, 52.1, 34.1, 31.2, 21.6.

IR (thin film) ν_{max} (cm^{-1}): 2921, 2845, 2359, 2341, 1416, 1301, 1278, 1190, 1035, 970, 886, 835.

HRMS (ESI+/QTOF) calcd for $C_{13}H_{25}N_2S^+$ [$M+H^+$]: 241.1733, found: 241.1740.

Gua-1$^+$



Gua-1$^+$ was synthesized with **S1a** and (1*S*,2*S*)-cyclohexane-1,2-diamine following general synthetic procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 258.0 mg (0.50 mmol, 50%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

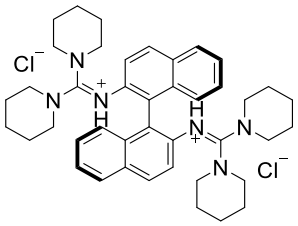
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.29 (d, *J* = 8.2 Hz, 2H), 4.20 (td, *J* = 11.9, 10.9, 5.9 Hz, 2H), 3.72 – 3.03 (m, 16H), 2.37 – 2.20 (m, 2H), 2.06 (s, 2H), 1.95 (d, *J* = 14.3 Hz, 2H), 1.86 – 1.47 (m, 26H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 160.6, 57.7, 50.3, 49.9, 32.3, 25.7, 25.2, 24.9, 23.7, 23.3.

IR (thin film) ν_{max} (cm^{-1}): 3407, 3191, 2937, 2860, 1589, 1547, 1446, 1371, 1331, 1270, 1072, 1024, 861, 730.

HRMS (ESI+/QTOF) calcd for $C_{28}H_{52}N_6^{2+}$ [M^{2+}]: 236.2121; found: 236.2124.

Gua-2$^+$



Gua-2$^+$ was synthesized with **S1a** and (*R*)-[1,1'-binaphthalene]-2,2'-diamine following general synthetic procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 258.0 mg (0.38 mmol, 38%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

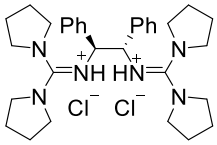
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.90 (dd, J = 30.5, 8.5 Hz, 4H), 7.40 – 7.24 (m, 4H), 7.20 – 6.86 (m, 4H), 3.12 (d, J = 222.7 Hz, 16H), 1.89 – 0.82 (m, 24H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 159.5, 132.9, 130.9, 129.8, 128.6, 126.4, 125.9, 125.8, 124.6, 50.0, 30.2, 29.7, 25.7, 24.8, 23.8.

IR (thin film) ν_{max} (cm^{-1}): 3374, 3053, 2935, 2854, 1592, 1526, 1447, 1368, 1331, 1256, 1222, 1132, 1094, 1020, 731.

HRMS (ESI+/QTOF) calcd for $C_{42}H_{54}N_6^{2+}$ [M^{2+}]: 321.2200; found: 321.2202.

Gua-3$^+$



Gua-3$^+$ was synthesized with **S1b** and (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine following general synthetic procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 236.6 mg (1 mmol, 40%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

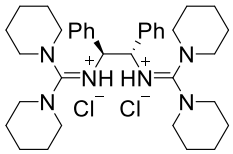
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.17 (s, 2H), 7.74 (s, 3H), 7.21 – 6.99 (m, 7H), 6.01 (d, *J* = 8.2 Hz, 2H), 3.47 (d, *J* = 6.2 Hz, 8H), 2.93 (h, *J* = 7.2 Hz, 8H), 1.83 (d, *J* = 45.5 Hz, 16H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 156.1, 138.3, 128.2, 128.0, 127.3, 64.3, 50.3, 50.1, 42.4, 25.6, 25.4, 11.3.

IR (thin film) ν_{max} (cm^{-1}): 3424, 3220, 2970, 2925, 1597, 1537, 1498, 1448, 1384, 1360, 1337, 1275, 1261, 1181, 1142, 1066, 750, 707.

HRMS (ESI+/QTOF) calcd for $C_{32}H_{46}N_6^{2+}$ [M^{2+}]: 257.1887; found: 257.1890.

Gua-4$^+$



Gua-4$^+$ was synthesized with **S1a** and (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine following General Procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 421 mg (0.66 mmol, 69%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

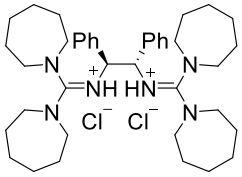
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.79 (s, 2H), 8.13 (s, 3H), 7.26 (s, 5H), 7.21–7.14 (m, 2H), 6.08 (s, 2H), 3.11 (d, *J* = 91.0 Hz, 16H), 1.59 (d, *J* = 41.5 Hz, 24H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 161.3, 137.9, 128.4, 127.6, 64.3, 53.4, 45.7, 25.5, 25.0, 23.5, 23.1, 8.5.

IR (thin film) ν_{max} (cm^{-1}): 3431, 2939, 2862, 1599, 1539, 1450, 1371, 1319, 1265, 1022, 852, 735.

HRMS (ESI+/QTOF) calcd for $C_{36}H_{54}N_6^{2+}$ [M^{2+}]: 285.2200; found: 285.2202.

Gua-5$^+$



Gua-5$^+$ was synthesized with **S1c** and (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine following general synthetic procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 923 mg (2 mmol, 66%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

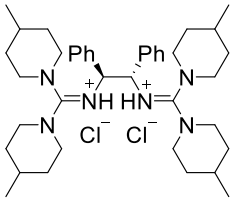
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.37 (d, *J* = 7.6 Hz, 2H), 7.86 (s, 3H), 7.22 (dt, *J* = 39.0, 7.3 Hz, 7H), 6.05 – 5.82 (m, 2H), 3.46 – 2.92 (m, 16H), 1.79 – 1.33 (m, 32H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 162.0, 138.0, 128.3, 127.7, 127.6, 64.6, 52.7, 52.0, 28.9, 28.8, 26.7.

IR (thin film) ν_{max} (cm^{-1}): 3190, 3051, 2936, 2860, 1576, 1525, 1465, 1449, 1393, 1317, 1265, 1238, 1207, 1196, 1143, 1067, 740, 703.

HRMS (ESI+/QTOF) calcd for $C_{40}H_{62}N_6^{2+}$ [M^{2+}]: 313.2513; found: 313.2517.

Gua-6$^+$



Gua-5$^+$ was synthesized with **S1e** and (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine following General Procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:0~20, column size 254 × 32 mm) within 1 h yielded a total of 1.32 g (1.9 mmol, 95%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

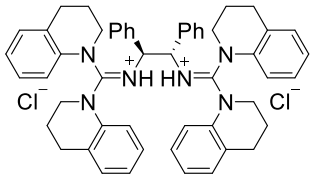
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.85 (s, 2H), 8.18 (s, 3H), 7.38 – 6.82 (m, 7H), 6.07 (s, 2H), 3.66 – 2.73 (m, 14H), 2.46 (s, 2H), 1.91 – 1.39 (m, 14H), 1.32 – 0.61 (m, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 161.0, 137.9, 128.4, 127.7, 127.5, 64.4, 49.4, 33.9, 30.4, 21.4.

IR (thin film) ν_{max} (cm^{-1}): 3386, 2926, 2869, 1590, 1540, 1452, 1379, 1247, 1142, 1084, 1061, 970, 732, 702.

HRMS (ESI+/QTOF) calcd for $C_{40}H_{62}N_6^{2+}$ [M^{2+}]: 313.2513; found: 313.2516.

Gua-7$^+$



Gua-7$^+$ was synthesized with **S1d** and (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine following General Procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:3~5, column size 254 × 32 mm) within 1 h yielded a total of 211.6 mg (0.25 mmol, 41%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

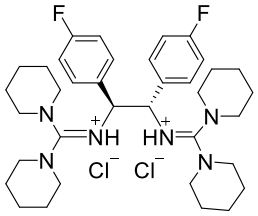
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.02 – 6.39 (m, 24H), 6.26 (m, 2H), 5.25 – 3.25 (m, 8H), 3.08 – 1.78 (m, 16H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 128.9, 128.0, 127.7, 127.2, 127.0, 126.7, 126.3, 120.8, 66.9, 47.9, 46.1, 31.6, 22.6, 14.1.

IR (thin film) ν_{max} (cm^{-1}): 3357, 3030, 2936, 2867, 1573, 1493, 1451, 1303, 1260, 1197, 1080, 1035, 754, 701.

HRMS (ESI+/QTOF) calcd for $C_{52}H_{54}ClN_6^+$ [M^+]: 797.4093; found: 797.4094

Gua-8$^+$



Gua-8$^+$ was synthesized with **S1a** and (1*S*,2*S*)-1,2-bis(4-fluorophenyl)ethane-1,2-diamine following general synthetic procedure A. Purification by recrystallization and column chromatography (DCM/MeOH=100:0~16, column size 254 × 32 mm) within 1 h yielded a total of 675.2 mg (0.99 mmol, 99%) of product as a yellow solid.

TLC (DCM:MeOH = 10:1, I_2@Silica), R_f =0.45.

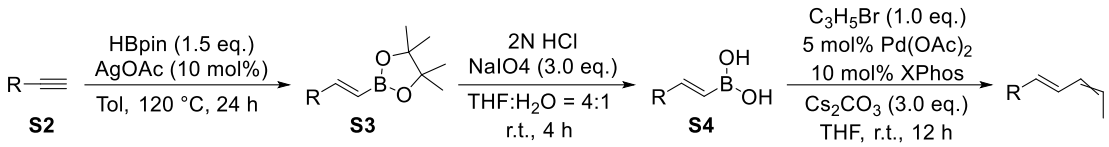
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.88 (d, J = 181.0 Hz, 2H), 8.28 (m, 3H), 7.01 (m, 5H), 6.08 (m, 2H), 3.23 (m, 16H), 2.30 (m, 2H), 1.61 (m, 22H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 163.3, 161.0 (d, J_{C-F} = 32.3 Hz), 133.8, 129.6, 115.3, 63.8, 50.4, 25.6, 25.1, 23.6, 23.2.

IR (thin film) ν_{max} (cm^{-1}): 3394, 2940, 2860, 1590, 1539, 1514, 1447, 1378, 1322, 1260, 1226, 1165, 853, 732.

HRMS (ESI+/QTOF) calcd for $C_{36}H_{52}F_2N_6^{2+}$ [M^{2+}]: 303.2106; found: 303.2108.

General Procedure B: Synthesis of 1,3-Conjugated Dienes

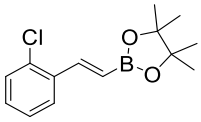


The conjugated dienes were synthesised with a modified procedure according to the literatures.[2,3] To a 100 mL dry Schlenk flask, 170.0 mg AgOAc (0.1 mmol, 10 mol%), arylacetylene **S2** (10.0 mmol, 1.0 equiv.), and 20 mL toluene were added. Then the reaction setup was purged with N_2 for three times, followed by slow addition of 2.0 g HBpin (15.0 mmol, 1.5 equiv.) via syringe over 1 minute. The resulting mixture was stirred in an oil bath at 120 °C for 24 h. After cooled down to room temperature, the reaction mixture was diluted with 30 mL of EA and filtered through a celite plug. The solvent of the resulting filtrate was evaporated under reduced pressure to leave a crude product, which was purified by column chromatography eluting with PE/EA to get **S3**.

S3 (6.0 mmol, 1.0 equiv.) was dissolved in 45 mL mixture of THF:H_2O (4:1), to which 3.42 g NaIO4 (18.0 mmol, 3.0 equiv.) was later added and stirred for 5 min. Then 1.8 mL aqueous solution of HCl (2.0 N) was added and stirred until the **S3** was completely consumed as monitored by TLC. The reaction mixture was extracted with EA. The combined organic layers were washed with brine, dried over Na_2SO_4 anhydrous, and filtered. The solvent of the resulting filtrate was evaporated to leave the crude product **S4**, which was used directly for the next step of the reaction without further purification.

To a 100 mL dry Schlenk flask, 86 μL 1-bromo-1-propene (1.0 mmol, 1.0 equiv.), 222 mg **S4** (1.5 mmol, 1.5 equiv.), 11.25 mg $Pd(OAc)_2$ (0.1 mmol, 5 mol%), and 975 mg Cs_2CO_3 (3.0 mmol, 3.0 equiv.) were added. Then the reaction setup was purged with N_2 for three times, followed by slow addition of 10 mL THF. The mixture was allowed to stir at room temperature for 12 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the crude product which was purified by column chromatography (eluting with petroleum ether and ethyl acetate) to obtain **1a-1p**.

(*E*)-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane S3a



S3a was synthesized with 1-chloro-2-ethynylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.1346 g (4.30 mmol, 43%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

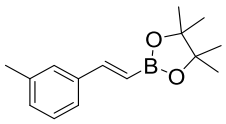
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.78 (d, *J* = 18.4 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.37 – 7.33 (m, 1H), 7.23 (ddd, *J* = 6.7, 3.9, 2.0 Hz, 2H), 6.17 (d, *J* = 18.3 Hz, 1H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 145.0, 135.6, 133.9, 129.8, 129.7, 127.0, 126.9, 83.5, 24.8.

IR (thin film) ν_{max} (cm^{-1}): 3064, 2979, 2930, 1621, 1565, 1468, 1440, 1348, 1270, 1209, 1144, 1045, 970, 849, 753, 707, 644.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{19}BClO_2^+$ [M+H$^+$]: 265.1162; found: 265.1163.

(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane S3b



S3b was synthesized with 1-ethynyl-3-methylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.5700 g (7.10 mmol, 71%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

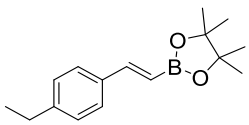
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.41 (d, *J* = 18.4 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 18.5 Hz, 1H), 2.38 (s, 3H), 1.35 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 149.7, 138.1, 137.5, 129.7, 128.5, 127.8, 124.3, 83.3, 24.8, 21.4.

IR (thin film) ν_{max} (cm^{-1}): 2978, 2927, 1625, 1585, 1423, 1351, 1270, 1246, 1199, 1145, 998, 849, 779, 693, 647.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{22}BO_2^+$ [M+H$^+$]: 245.1708; found: 245.1704.

(*E*)-2-(4-ethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane S3c



S3c was synthesized with 1-ethyl-4-ethynylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.9048 g (7.40 mmol, 74%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

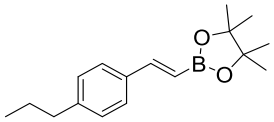
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.44 – 7.34 (m, 3H), 7.17 (d, J = 8.1 Hz, 2H), 6.12 (d, J = 18.4 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.31 (s, 12H), 1.23 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 149.5, 145.3, 135.0, 128.1, 127.1, 83.3, 28.7, 24.8, 15.4.

IR (thin film) ν_{max} (cm^{-1}): 3082, 2973, 2873, 1624, 1568, 1511, 1459, 1419, 1351, 1270, 1145, 1110, 1056, 997, 970, 851, 815, 677, 655, 545.

HRMS (ESI+/QTOF) calcd for $C_{16}H_{24}BO_2^+$ [M+H$^+$]: 259.1864; found: 259.1865.

(*E*)-4,4,5,5-tetramethyl-2-(4-propylstyryl)-1,3,2-dioxaborolane S3d



S3d was synthesized with 1-ethynyl-4-propylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 880.3 mg (3.40 mmol, 68%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

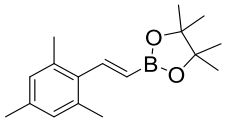
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.44 – 7.34 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 2.61 – 2.54 (m, 2H), 1.68 – 1.58 (m, 2H), 1.31 (s, 12H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 149.6, 143.8, 135.0, 128.7, 127.0, 83.3, 37.9, 24.8, 24.4, 13.8.

IR (thin film) ν_{max} (cm^{-1}): 2975, 2930, 2869, 1624, 1567, 1510, 1461, 1419, 1351, 1270, 1214, 1145, 1111, 997, 970, 900, 850, 812, 738, 646, 554, 499.

HRMS (ESI+/QTOF) calcd for $C_{17}H_{26}BO_2^+$ [M+H$^+$]: 273.2021; found: 273.2021.

(*E*)-4,4,5,5-tetramethyl-2-(2,4,6-trimethylstyryl)-1,3,2-dioxaborolane S3e



S3e was synthesized with 2-ethynyl-1,3,5-trimethylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.1718 g (4.30 mmol, 64%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.45.

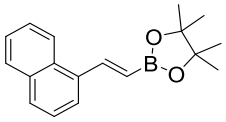
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.44 (d, J = 18.8 Hz, 1H), 6.86 (s, 2H), 5.69 (d, J = 18.9 Hz, 1H), 2.30 (s, 6H), 2.27 (s, 3H), 1.33 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 148.5, 136.7, 135.9, 135.2, 128.7, 83.3, 24.9, 21.0.

IR (thin film) ν_{max} (cm^{-1}): 2976, 2923, 1628, 1473, 1378, 1347, 1269, 1207, 1144, 1005, 970, 852, 652.

HRMS (ESI+/QTOF) calcd for $C_{17}H_{26}BO_2^+$ [M+H$^+$]: 273.2021; found: 273.2022.

(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane S3f



S3f was synthesized with 1-ethynylnaphthalene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 525 mg (1.85 mmol, 37%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

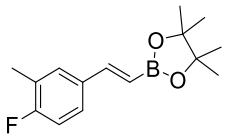
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.31 – 8.17 (m, 2H), 7.87 – 7.80 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.56 – 7.44 (m, 3H), 6.27 (d, J = 18.1 Hz, 1H), 1.36 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 146.5, 135.4, 133.6, 131.1, 129.1, 128.5, 126.2, 125.8, 125.6, 124.1, 123.8, 83.5, 24.9.

IR (thin film) ν_{max} (cm^{-1}): 3054, 2978, 2930,1616, 1509, 1452, 1356, 1329, 1266, 1213, 1143, 993, 970, 848, 796, 776, 660.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{22}BO_2^+$ [M+H$^+$]: 281.1708; found: 281.1708.

(*E*)-2-(4-fluoro-3-methylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane S3g



S3g was synthesized with 4-ethynyl-1-fluoro-2-methylbenzene and pinacol borane according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.8738 g (7.13 mmol, 95%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

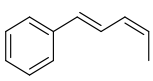
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.35 – 7.24 (m, 3H), 6.99 – 6.92 (m, 1H), 6.05 (d, J = 18.4 Hz, 1H), 2.26 (d, J = 2.0 Hz, 3H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 160.7 (d, $J_{C\text{-}F}$ = 247.6 Hz), 147.4, 132.4 (d, $J_{C\text{-}F}$ = 3.6 Hz), 129.1 (d, $J_{C\text{-}F}$ = 5.4 Hz), 125.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 123.9 (d, $J_{C\text{-}F}$ = 17.7 Hz), 114.1 (d, $J_{C\text{-}F}$ = 22.8 Hz), 82.3, 23.8, 13.6 (d, $J_{C\text{-}F}$ = 3.5 Hz)

IR (thin film) ν_{max} (cm^{-1}): 2979, 2929, 1627, 1500, 1454, 1413, 1349, 1292, 1249, 1192, 1145, 996, 896, 849, 811, 768, 651.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{21}BFO_2^+$ [M+H$^+$]: 263.1614; found: 263.1614.

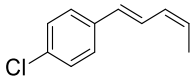
((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1a



(1*E*,3*Z*)-**1a** was synthesized with (*E*)-styrylboronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography

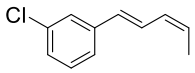
(*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 112.5 mg (0.78 mmol, 78%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 97:3.
TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.47 – 7.39 (m, 2H), 7.33 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.11 (ddd, *J* = 15.5, 11.1, 1.2 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.20 (tq, *J* = 10.9, 1.9 Hz, 1H), 5.62 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.91 – 1.83 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 136.7, 130.8, 128.6, 127.5, 126.3, 126.1, 125.3, 123.1, 12.6.
IR (thin film) ν_{max} (cm^{-1}): 3058, 3027, 2916, 1595, 1490, 1443, 1407, 1371, 980, 942, 757, 711, 620.
HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}^+$ [M+H$^+$]: 145.1012; found: 145.1012.

1-chloro-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1b



(1*E*,3*Z*)-**1b** was synthesized with (*E*)-(4-chlorostyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 146.5 mg (0.82 mmol, 82%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 95:5.
TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.40 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.06 (ddd, *J* = 15.6, 11.1, 1.2 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.17 (tq, *J* = 11.0, 1.9 Hz, 1H), 5.63 (dq, *J* = 11.4, 7.5 Hz, 1H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 135.1, 131.8, 129.4, 128.3, 127.7, 126.8, 126.4, 123.7, 12.7.
IR (thin film) ν_{max} (cm^{-1}): 3027, 2981, 2925, 1709, 1680, 1592, 1489, 1402, 1371, 1124, 1090, 976, 816, 728, 694.
HRMS (ESI+/QTOF) calcd for $C_{11}H_{12}Cl^+$ [M+H$^+$]: 179.0623; found: 179.0620.

1-chloro-3-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1c

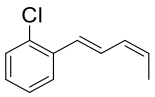


(1*E*,3*Z*)-**1c** was synthesized with (*E*)-(3-chlorostyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 140.0 mg (0.78 mmol, 78%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 97:3.
TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.40 (s, 1H), 7.30 – 7.15 (m, 3H), 7.08 (dd, *J* = 15.6, 11.1 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.17 (td, *J* = 11.0, 2.0 Hz, 1H), 5.65 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.6, 134.5, 130.3, 129.8, 129.2, 128.4, 127.2, 126.1, 125.5, 124.6, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3026, 2918, 1588, 1562, 1474, 1430, 1402, 1083, 979, 939, 882, 779, 721, 699.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{12}Cl^+$ [M+H$^+$]: 179.0623; found: 179.0621.

1-chloro-2-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1d



(1*E*,3*Z*)-**1d** was synthesized with (*E*)-(2-chlorostyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 95.0 mg (0.52 mmol, 52%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 92:8.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

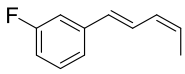
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.56 – 7.46 (m, 1H), 7.27 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.19 – 6.96 (m, 3H), 6.84 (d, *J* = 15.6 Hz, 1H), 6.17 (tq, *J* = 10.9, 1.8 Hz, 1H), 5.59 (dqt, *J* = 10.8, 7.2, 1.0 Hz, 1H), 1.83 – 1.74 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 135.7, 133.1, 131.9, 131.8, 131.7, 129.81, 129.77, 129.6, 128.4, 128.2, 128.0, 127.6, 126.80, 126.76, 126.6, 126.4, 126.1, 125.6, 18.4, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3025, 2918, 1587, 1467, 1439, 1407, 1122, 1034, 981, 943, 752, 731, 696, 621.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{12}Cl^+$ [M+H$^+$]: 179.0623; found: 179.0620.

1-fiuoro-3-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1e



(1*E*,3*Z*)-**1e** was synthesized with (*E*)-(3-fluorostyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 130.0 mg (0.80 mmol, 80%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 96:4.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

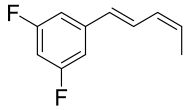
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.26 (td, *J* = 7.9, 6.1 Hz, 1H), 7.20 – 7.03 (m, 3H), 6.90 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 6.22 – 6.12 (m, 1H), 5.65 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 163.2 (d, $J_{C\text{-}F}$ = 244.8 Hz), 140.1 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.2, 128.3, 125.4, 122.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21.5 Hz), 112.5 (d, $J_{C\text{-}F}$ = 21.8 Hz), 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3030, 2918, 1607, 1579, 1485, 1443, 1405, 1260, 1142, 980, 943, 874, 780, 722, 680.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{12}F^+$ [M+H$^+$]: 163.0918; found: 163.0921.

1,3-difiuoro-5-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1f



(1*E*,3*Z*)-**1f** was synthesized with (*E*)-(3,5-difluorostyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 76.0 mg (0.42 mmol, 42%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 97:3.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

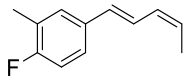
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.08 (ddd, *J* = 15.5, 11.1, 1.2 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.65 (tt, *J* = 8.9, 2.3 Hz, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 6.21 – 6.12 (m, 1H), 5.70 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.88 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 162.2 (dd, $J_{C\text{-}F}$ = 247.3, 13.2 Hz) 140.1 (t, $J_{C\text{-}F}$ = 9.6 Hz), 128.6 (t, $J_{C\text{-}F}$ = 3.1 Hz), 128.4, 127.8, 125.5, 107.8 (d, $J_{C\text{-}F}$ = 6.9 Hz), 107.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 101.4 (t, $J_{C\text{-}F}$ = 25.8 Hz), 12.7.

IR (thin film) ν_{max} (cm^{-1}): 3030, 2923, 1617, 1586, 1448, 1408, 1322, 1269, 1140, 1118, 980, 943, 872, 842, 725, 672.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{11}F_2^+$ [M+H$^+$]: 181.0824; found: 181.0821.

1-fluoro-2-methyl-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1g



(1*E*,3*Z*)-**1g** was synthesized with (*E*)-(4-fluoro-3-methylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 123.0 mg (0.70 mmol, 70%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 94:6.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

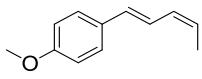
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.21 (ddd, *J* = 16.5, 7.7, 2.3 Hz, 2H), 7.03 – 6.88 (m, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.16 (ddt, *J* = 12.8, 10.9, 2.0 Hz, 1H), 5.59 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.28 (d, *J* = 2.1 Hz, 3H), 1.86 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 160.8 (d, $J_{C\text{-}F}$ = 245.8 Hz), 133.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 130.8 (d, $J_{C\text{-}F}$ = 1.4 Hz), 129.5, 129.2 (d, $J_{C\text{-}F}$ = 5.0 Hz), 127.0, 125.2 (d, $J_{C\text{-}F}$ = 7.9 Hz), 124.9 (d, $J_{C\text{-}F}$ = 17.7 Hz), 123.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 115.1 (d, $J_{C\text{-}F}$ = 22.8 Hz), 14.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 13.6.

IR (thin film) ν_{max} (cm^{-1}): 3025, 2924, 1499, 1441, 1252, 1234, 1206, 1115, 979, 940, 886, 814, 727.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{14}F^+$ [M+H$^+$]: 177.1075; found: 177.1069.

1-methoxy-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1h



(1*E*,3*Z*)-**1h** was synthesized with (*E*)-(4-methoxystyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 160.0 mg (0.91 mmol, 91%) of product as a yellow oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 91:9.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

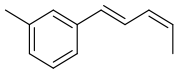
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.40 – 7.32 (m, 2H), 6.97 (ddd, *J* = 15.6, 11.0, 1.2 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.48 (d, *J* = 15.5 Hz, 1H), 6.25 – 6.12 (m, 1H), 5.62 – 5.49 (m, 1H), 3.82 (s, 3H), 1.89 – 1.78 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 159.1, 158.9, 132.0, 131.4, 130.5, 129.8, 129.3, 129.1, 127.5, 127.4, 127.3, 126.0, 122.3, 114.1, 114.0, 55.3, 18.4, 13.6.

IR (thin film) ν_{max} (cm^{-1}): 3026, 2931, 2836, 1603, 1509, 1460, 1301, 1249, 1175, 1035, 981, 924, 858, 824, 732, 704.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{15}O^+$ [M+H$^+$]: 175.1118; found: 175.1117.

1-methyl-3-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1i



(1*E*,3*Z*)-**1i** was synthesized with (*E*)-(3-methylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 120.0 mg (0.78 mmol, 78%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 95:5.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

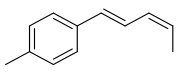
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.31 – 7.23 (m, 3H), 7.18 – 7.06 (m, 2H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.24 (tt, *J* = 10.9, 1.9 Hz, 1H), 5.65 (dtd, *J* = 10.9, 8.2, 7.7, 6.7 Hz, 1H), 2.41 (s, 3H), 1.92 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.1, 137.6, 132.0, 129.7, 128.5, 128.2, 127.0, 124.0, 123.5, 21.4, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3026, 2921, 2856, 1600, 1483, 1441, 1371, 979, 941, 779, 719.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{15}^+$ [M+H$^+$]: 159.1169; found: 159.1171.

1-methyl-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1j



(1*E*,3*Z*)-**1j** was synthesized with (*E*)-(4-methylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 130.0 mg (0.82 mmol, 82%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 94:6.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

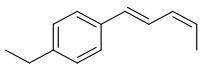
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.38 – 7.27 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 – 7.00 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.19 (tq, *J* = 10.9, 2.0 Hz, 1H), 5.59 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.35 (s, 3H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.2, 134.9, 131.8, 129.7, 129.3, 126.6, 126.3, 123.3, 21.3, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3023, 2919, 2861, 1681, 1607, 1511, 1502, 1447, 1405, 1371, 1121, 979, 942, 861, 807, 726, 515.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{15}^+$ [M+H$^+$]: 159.1169; found: 159.1163.

1-ethyl-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1k



(1*E*,3*Z*)-**1k** was synthesized with (*E*)-(4-ethylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 128.0 mg (0.74 mmol, 74%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 89:11.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

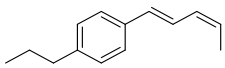
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.39 – 7.29 (m, 2H), 7.20 – 7.12 (m, 2H), 7.06 (ddd, *J* = 15.6, 11.1, 1.2 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.27 – 6.14 (m, 1H), 5.59 (dqt, *J* = 10.8, 7.1, 1.0 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.91 – 1.80 (m, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.6, 134.1, 130.9, 130.8, 128.71, 128.66, 127.4, 127.1, 127.0, 125.5, 125.3, 125.1, 122.3, 27.6, 17.3, 14.5, 12.6.

IR (thin film) ν_{max} (cm^{-1}): 3023, 2965, 2928, 2870, 1508, 1455, 1403, 1371, 979, 939, 863, 821, 726, 707.

HRMS (ESI+/QTOF) calcd for $C_{13}H_{17}^+$ [M+H$^+$]: 173.1325; found: 173.1331.

1-((1*E*,3*Z*)-penta-1,3-dien-1-yl)-4-propylbenzene (1*E*,3*Z*)-1l



(1*E*,3*Z*)-**1l** was synthesized with (*E*)-(4-propylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 166.0 mg (0.89 mmol, 89%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 93:7.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

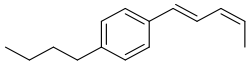
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.38 – 7.29 (m, 2H), 7.17 – 7.11 (m, 2H), 7.06 (ddd, *J* = 15.6, 11.0, 1.2 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.19 (tq, *J* = 10.9, 1.9 Hz, 1H), 5.58 (dtd, *J* = 10.8, 8.3, 7.8, 6.8 Hz, 1H), 2.62 – 2.56 (m, 2H), 1.87 (dd, *J* = 7.2, 1.7 Hz, 3H), 1.70 – 1.60 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 136.6, 131.7, 130.5, 129.4, 128.0, 127.8, 124.8, 121.0, 31.5, 29.7, 18.5, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3023, 2959, 2927, 2866, 1508, 1457, 1403, 1372, 979, 939. 864, 820, 730, 706.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{19}^+$ [M+H$^+$]: 187.1482; found: 187.1484.

1-butyl-4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1m



(1*E*,3*Z*)-**1m** was synthesized with (*E*)-(4-butylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 190.0 mg (0.95 mmol, 95%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 94:6.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

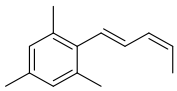
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.39 – 7.29 (m, 2H), 7.18 – 7.11 (m, 2H), 7.06 (ddd, *J* = 15.6, 11.0, 1.2 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.19 (tq, *J* = 10.9, 1.9 Hz, 1H), 5.63 – 5.54 (m, 1H), 2.64 – 2.58 (m, 2H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.64 – 1.55 (m, 2H), 1.41 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 141.3, 134.1, 130.8, 128.7, 127.6, 125.5, 125.2, 122.3, 34.4, 32.6, 21.3, 12.9, 12.6.

IR (thin film) ν_{max} (cm^{-1}): 3023, 2957, 2927, 2859, 1508, 1458, 1403, 1372, 979, 939, 862, 819, 729, 706.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{21}^+$ [M+H$^+$]: 201.1638; found: 201.1642.

1,3,5-trimethyl-2-((1*E*,3*Z*)-penta-1,3-dien-1-yl)benzene (1*E*,3*Z*)-1n



(1*E*,3*Z*)-**1n** was synthesized with (*E*)-(2,4,6-trimethylstyryl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 110.0 mg (0.60 mmol, 60%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 85:15.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

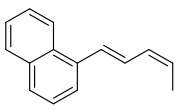
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 6.88 (d, *J* = 6.5 Hz, 2H), 6.71 – 6.38 (m, 2H), 6.32 – 6.17 (m, 1H), 5.64 – 5.54 (m, 1H), 2.31 (d, *J* = 12.9 Hz, 9H), 1.85 – 1.77 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 135.1, 134.94, 134.92, 134.88, 133.2, 133.1, 133.0, 131.2, 129.0, 128.7, 128.3, 128.0, 127.7, 127.6, 126.7, 125.0, 20.1, 20.0, 19.9, 17.2, 12.4.

IR (thin film) ν_{max} (cm^{-1}): 3013, 2918, 2858, 1609, 1508, 1442, 1404, 1373, 1029, 985, 947, 853, 708.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{19}^+$ [M+H$^+$]: 187.1482; found: 187.1482.

1-((1*E*,3*Z*)-penta-1,3-dien-1-yl)naphthalene (1*E*,3*Z*)-1o



(1*E*,3*Z*)-**1o** was synthesized with (*E*)-(2-(naphthalen-2-yl)vinyl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column

chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 127.0 mg (0.65 mmol, 65%) of product as a colorless oil. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 91:9.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

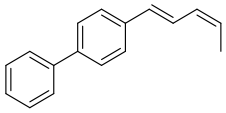
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.17 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.89 – 7.69 (m, 3H), 7.55 – 7.45 (m, 3H), 7.32 (d, *J* = 15.3 Hz, 1H), 7.16 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.36 (tq, *J* = 10.8, 2.0 Hz, 1H), 5.74 – 5.64 (m, 1H), 1.91 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 135.1, 133.7, 132.2, 131.2, 130.7, 129.9, 128.62, 128.59, 127.8, 127.6, 127.1, 126.0, 125.8, 125.7, 123.7, 123.3, 18.4, 13.7.

IR (thin film) ν_{max} (cm^{-1}): 3026, 2915, 2853, 1586, 1508, 1439, 1392, 982, 941, 795, 774, 721, 622, 552.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{15}^+$ [M+H$^+$]: 195.1169; found: 195.1169.

4-((1*E*,3*Z*)-penta-1,3-dien-1-yl)-1,1'-biphenyl (1*E*,3*Z*)-1p



(1*E*,3*Z*)-**1p** was synthesized with (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)boronic acid and *cis*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 200.0 mg (0.90 mmol, 90%) of product as a white soild. The 3*Z*/3*E* ratio was determined by ^{1}H NMR as 93:7.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

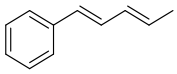
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.65 – 7.54 (m, 4H), 7.53 – 7.42 (m, 4H), 7.40 – 7.32 (m, 1H), 7.15 (ddd, *J* = 15.5, 11.1, 1.2 Hz, 1H), 6.58 (d, *J* = 15.5 Hz, 1H), 6.31 – 6.17 (m, 1H), 5.64 (dqt, *J* = 10.7, 7.1, 1.0 Hz, 1H), 1.90 (dd, *J* = 7.2, 1.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.7, 139.0, 135.7, 130.3, 128.6, 127.7, 126.3, 126.2, 125.9, 125.7, 123.2, 12.7.

IR (thin film) ν_{max} (cm^{-1}): 3024, 2920, 1508, 1401, 984, 943, 870, 827, 762, 731, 689.

HRMS (ESI+/QTOF) calcd for $C_{17}H_{17}^+$ [M+H$^+$]: 221.1325; found: 221.1329.

((1*E*,3*E*)-penta-1,3-dien-1-yl)benzene (1*E*,3*E*)-1a



(1*E*,3*E*)-**1a** was synthesized with (*E*)-styrylboronic acid and *trans*-1-bromo-1-propene according to the above experimental procedure. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 100.0 mg (0.69 mmol, 69%) of product as a colorless oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

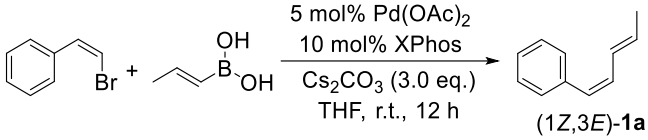
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.23 – 7.16 (m, 1H), 6.76 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.23 (ddq, *J* = 14.1, 10.5, 1.8 Hz, 1H), 5.84 (dq, *J* = 13.9, 6.8 Hz, 1H), 1.83 (dd, *J* = 6.8, 1.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.7, 131.9, 130.4, 129.7, 129.4, 128.6, 127.1, 126.1, 18.4.

IR (thin film) ν_{max} (cm^{-1}): 3029, 2983, 2929, 1679, 1493, 1450, 1371, 1268, 1127, 1072, 969, 749, 696.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}^+$ [M+H$^+$]: 145.1012; found: 145.1011.

Synthesis of ((1*Z*,3*E*)-penta-1,3-dien-1-yl)benzene (1*Z*,3*E*)-1a



(1*Z*,3*E*)-**1a** were performed with a modified procedure according to the literature.[2] To a 100 mL dry Schlenk flask, 128 µL (*Z*)-(2-bromovinyl)benzene (1.0 mmol, 1.0 equiv.), 129 mg (*E*)-prop-1-en-1-ylboronic acid (1.5 mmol, 1.5 equiv.), 11.25 mg $Pd(OAc)_2$ (0.1 mmol, 0.1 equiv.), and 975 mg Cs_2CO_3 (3.0 mmol, 3.0 equiv.) were added. Then the reaction setup was purged with N_2 for three times, followed by slow addition of 10 mL THF. The mixture was allowed to stir at room temperature for 12 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the crude product. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 110.0 mg (0.76 mmol, 76%) of title compound as a colorless oil. The 1*Z*/1*E* ratio was determined by ^{1}H NMR as 88:12.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

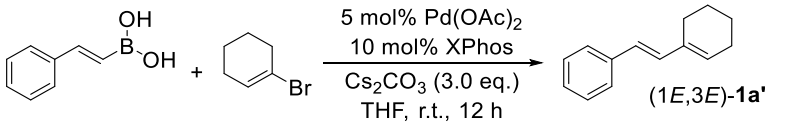
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.39 – 7.28 (m, 4H), 7.23 (m, 1H), 6.67 – 6.56 (m, 1H), 6.30 (d, *J* = 11.6 Hz, 1H), 6.21 (t, *J* = 11.2 Hz, 1H), 5.88 (dq, *J* = 13.6, 6.6 Hz, 1H), 1.80 (d, *J* = 6.9 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.9, 132.6, 131.9, 130.5, 130.4, 129.7, 129.4, 128.9, 128.6, 128.2, 127.9, 127.4, 127.1, 126.7, 126.1, 18.4.

IR (thin film) ν_{max} (cm^{-1}): 3058, 3028, 2983, 2932, 1717, 1678, 1493, 1449, 1371, 1331, 1270, 1159, 1125, 1071, 968, 749, 696.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}^+$ [M+H$^+$]: 145.1012; found: 145.1012.

Synthesis of (*E*)-(2-(cyclohex-1-en-1-yl)vinyl)benzene (1*E*,3*E*)-1a′



(1*E*,3*E*)-**1a′** was prepared with a modified procedure according to the literature.[2a] To a 100 mL dry Schlenk flask, 115 µL 1-bromocyclohex-1-ene (1.0 mmol, 1.0 equiv.), 222 mg (*E*)-styrylboronic acid (1.5 mmol, 1.5 equiv.), 11.3 mg $Pd(OAc)_2$ (0.1 mmol, 10 mol%), and 975 mg Cs_2CO_3 (3.0 mmol, 3.0 equiv.) were added. Then the reaction setup was purged with N_2 for

three times, followed by slow addition of 10 mL THF. The mixture was allowed to stir at room temperature for 12 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the residue. Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 180.0 mg (0.97 mmol, 97%) of the title compound as a colorless oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

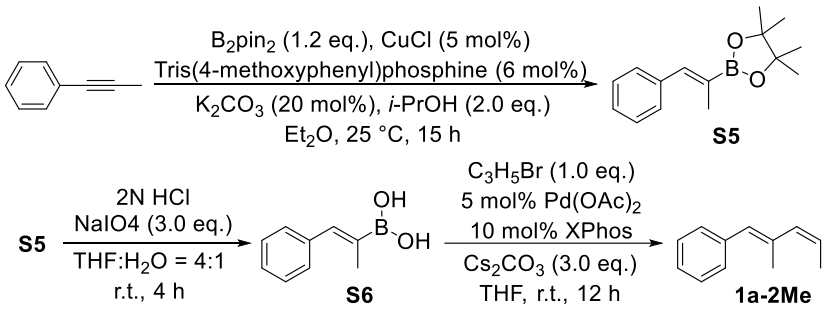
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.45 – 7.38 (m, 2H), 7.31 (m, 2H), 7.24 – 7.17 (m, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 5.95 – 5.88 (m, 1H), 2.32 – 2.16 (m, 4H), 1.74 (tdd, *J* = 8.4, 5.2, 2.7 Hz, 2H), 1.66 (dtt, *J* = 9.1, 5.9, 2.7 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.0, 134.8, 131.6, 129.8, 127.5, 125.8, 125.1, 123.6, 25.1, 23.5, 21.52, 21.48.

IR (thin film) ν_{max} (cm^{-1}): 3057, 3025, 2928, 2860, 2832, 1631, 1599, 1492, 1445, 1072, 960, 795, 745, 692.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{17}^+$ [M+H$^+$]: 185.1325; found: 185.1322.

Synthesis of ((1*E*,3*Z*)-2-methylpenta-1,3-dien-1-yl)benzene 1a-2Me



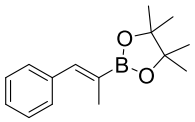
The conjugated diene was prepared with a modified procedure according to the literatures.[2,3] To a dry 100 mL two-necked round-bottom flask equipped with a magnetic stir bar, 276.4 mg K_2CO_3 (2.0 mmol, 20 mol%), 3.047 g B_2pin_2 (12.0 mmol, 1.2 equiv.), 50.0 mg CuCl (0.5 mmol, 5 mol%), and 211.4 mg Tris(4-methoxyphenyl)phosphine (0.6 mmol, 6 mol%) were added in sequence, followed by the addition of 40 mL Et_2O and stirring at 25 °C for 5 min. Then 1.6 mL *i*-PrOH (20.0 mmol, 2.0 equiv.) was added and stirred for 1 min, followed by the addition of 11.62 g prop-1-yn-1-ylbenzene (10.0 mmol, 1.0 equiv.). The resulting mixture was stirred in an oil bath at 25 °C for 15 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the crude product which was purified by column chromatography to obtain **S5**.

S5 (6.0 mmol) was dissolved in 45 mL mixture of THF:water (4:1). To this solution, 3.42 g NaIO4 (18.0 mmol, 3.0 equiv.) was added and stirred for 5 min. Then an aqueous solution of 1.8 mL HCl (2.0 N) was added and stirred until the **S5** was completely consumed as monitored by TLC.

The reaction mixture was extracted with EA. The combined organic layers were extracted with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the crude product **S6**, which was used directly for the next step without further purification.

To a 100 mL dry Schlenk flask, 86 μL *cis*-1-Bromo-1-propene (1.0 mmol, 1.0 equiv.), 243 mg **S6** (1.5 mmol, 1.5 equiv.), 11.25 mg $Pd(OAc)_2$ (0.1 mmol, 10 mol%), and 975 mg Cs_2CO_3 (3.0 mmol, 3.0 equiv.) were added. Then the reaction setup was purged with N_2 for three times, followed by slow addition of 10 mL THF. The mixture was allowed to stir at r.t. for 12 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the resulting filtrate was evaporated under reduced pressure to afford the residue which was purified by column chromatography (eluting with petroleum ether and ethyl acetate) to obtain **1a-2Me**.

(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane S5



Purification by column chromatography (*n*hexane/EA=100:2, column size 254 × 32 mm) within 30 min yielded a total of 1.3150 g (6.40 mmol, 64%) of product as a yellow oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.50.

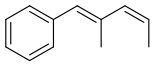
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.41 – 7.32 (m, 4H), 7.27 – 7.22 (m, 2H), 2.00 (d, *J* = 1.8 Hz, 3H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.4, 137.9, 129.4, 128.1, 127.1, 83.5, 24.9, 15.9.

IR (thin film) ν_{max} (cm^{-1}): 2978, 2931, 1617, 1489, 1449, 1370, 1312, 1272, 1209, 1147, 1106, 960, 864, 752, 697, 668.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{22}BO_2^+$ [M+H$^+$]: 245.1708; found: 245.1710.

((1*E*,3*Z*)-2-methylpenta-1,3-dien-1-yl)benzene 1a-2Me



Purification by column chromatography (*n*hexane/EA=100:0, column size 254 × 32 mm) within 30 min yielded a total of 130.0 mg (0.82 mmol, 82%) of product as a colorless oil.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.85.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.40 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 6.42 (s, 1H), 6.05 – 5.94 (m, 1H), 5.57 (dq, *J* = 11.4, 7.3 Hz, 1H), 2.04 (s, 3H), 1.90 (dd, *J* = 7.2, 1.9 Hz, 3H).

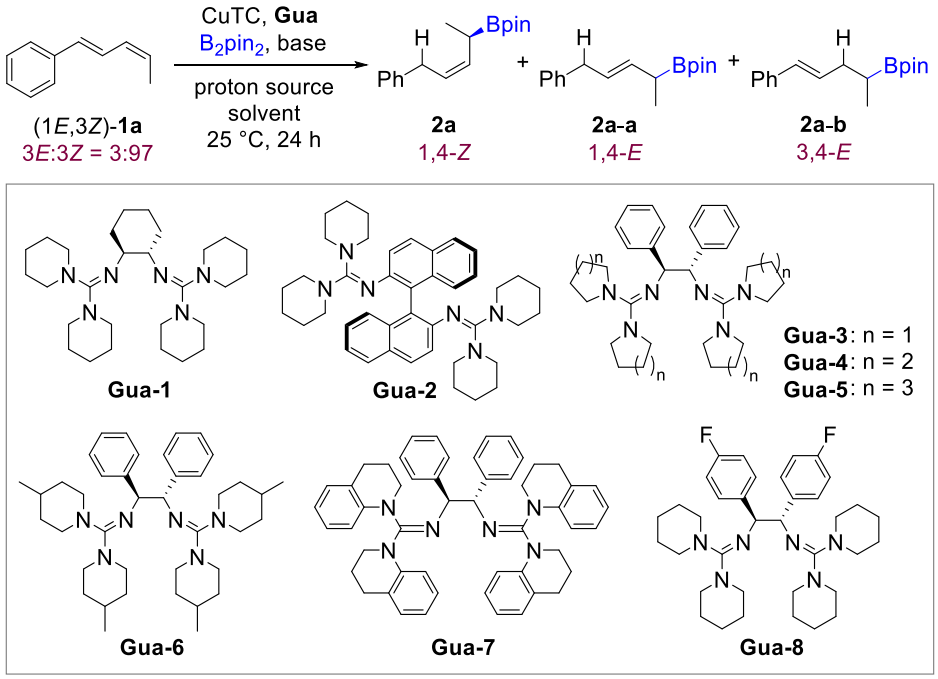
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.0, 135.3, 134.3, 129.7, 129.1, 128.1, 126.3, 125.4, 18.7, 15.0.

IR (thin film) ν_{max} (cm^{-1}): 3056, 3011, 2932, 2858, 1491, 1442, 1371, 999, 918, 865, 745, 699, 517.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{15}^+$ [M+H$^+$]: 159.1169; found: 159.1167.

Miscellaneous Optimization of Reaction Conditions

Table S1 Optimization of reaction conditions for the protoboration of acyclic internal 1,3-dienes.[a]



entry	solvent	Gua	base	H^+ source	conv. (%)[b]	protoboration (%)[c]			er (%)[d]
						2a (%)	**2a-a** (%)	**2a-b** (%)	
1	1,4-dioxane	**Gua-1**	KOMe	MeOH	7	85	3	12	58:42
2	1,4-dioxane	**Gua-2**	KOMe	MeOH	69	75	2	23	50:50
3	1,4-dioxane	**Gua-3**	KOMe	MeOH	15	92	3	5	85:15
4	1,4-dioxane	**Gua-4**	KOMe	MeOH	78	97	2	1	90:10
5	1,4-dioxane	**Gua-5**	KOMe	MeOH	33	98	2	-	91:9
6	1,4-dioxane	**Gua-6**	KOMe	MeOH	43	98	1	1	59:41
7	1,4-dioxane	**Gua-7**	KOMe	MeOH	68	94	2	4	74:26

8	1,4-dioxane	**Gua-8**	KOMe	MeOH	52	98	1	1	88:12
9	DME	**Gua-4**	KOMe	MeOH	18	99	-	-	88:12
10	THF	**Gua-4**	KOMe	MeOH	11	96	1	3	86:14
11	MTBE	**Gua-4**	KOMe	MeOH	49	97	2	1	87:13
12	DCM	**Gua-4**	KOMe	MeOH	23	99	-	-	93:7
13	Tol	**Gua-4**	KOMe	MeOH	3	98	1	1	91:9
14	MeCN	**Gua-4**	KOMe	MeOH	15	90	10	-	85:15
15	DCM	**Gua-4**	KOMe	H_2O	8	99	-	-	93:7
16	DCM	**Gua-4**	KOMe	*i*PrOH	15	99	-	-	93:7
17	DCM	**Gua-4**	KOMe	*t*BuOH	16	99	-	-	93:7
18	DCM	**Gua-4**	KOMe	EtOH	17	98	1	1	93:7
19	DCM	**Gua-4**	KO*t*Bu	MeOH	>99	99	-	-	97:3
20	DCM	**Gua-4**	KOH	MeOH	56	99	-	-	93:7
21	DCM	**Gua-4**	KOEt	MeOH	5	99	-	-	90:10
22	DCM	**Gua-4**	NaOEt	MeOH	13	99	-	-	91:9

[a] Reagents and conditions: (1*E*,3*Z*)-**1a** (0.2 mmol), B_2pin_2 (0.3 mmol), CuTC (0.01 mmol), **Gua** (0.01 mmol), base (0.3 mmol), H^+ source (0.3 mmol), solvent (2 mL), 25 °C, air, 24 h. The corresponding dihydrochlorides of **Gua-1** to **Gua-8** were used as ligand precursors.

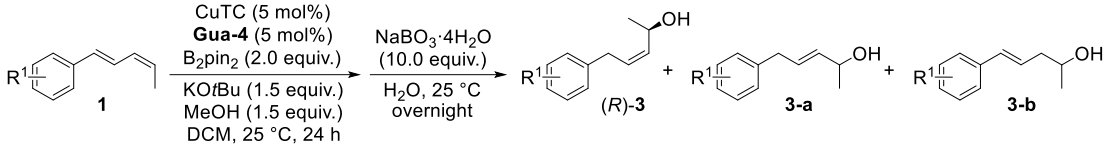
[b] Calibrated GC conversions of **1a** using biphenyl as an internal standard.

[c] The selectivity was determined by area normalization.

[d] Determinded by HPLC analysis of the corresponding alcohol after oxidation.

Preparation and Characterization of Allylic Alcohols

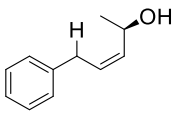
General Procedure C: Enantioselective Protoboration of Acyclic Internal 1,3-Dienes and Oxidation of Allylboronates



The allylboronates and allylic alcohols were prepared with a modified procedure according to the literatures.[4] To a dry 4 mL vial equipped with a magnetic stirrer bar, 33.7 mg KO*t*Bu (0.3 mmol, 1.5 equiv.), 102 mg B_2pin_2 (0.4 mmol, 2.0 equiv.), 1.9 mg Copper(I) thiophene-2-carboxylate (CuTC, 0.01 mmol, 5 mol%), and 6.4 mg **Gua-4**$^+$ (0.01 mmol, 5 mol%) were added in sequence, followed by the addition of 2 mL dry DCM and stirring at 25 °C for 5 min. Then 12.2 µL MeOH (0.3 mmol, 1.5 equiv.) was added and stirred for 1 min, followed by the addition of 0.2 mmol 1,3-diene (1.0 equiv.). The vial was then capped and sealed with parafilm. The reaction was allowed to stir vigorously at 25 °C for 24 h. The reaction progress was monitored by TLC.

Owing to the instability of allylboronates towards moisture and silica gel, most protoboration products were directly converted to the corresponding allylic alcohols via oxidation. When the borylation reaction was finished, 307 mg of $NaBO_3·4H_2O$ (2 mmol, 10 equiv.) and 0.5 mL of deionized water were added into the reaction vial. After overnight oxidation of the protoboration product (monitored by TLC), the resulting mixture was quenched with 1 mL of saturated brine, yielding an emulsion. 3 M NaOH aqueous solution was added to separate the organic phase, before the aqueous phase was extracted twice with 2 mL of EA. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was further purified by column chromatography to afford the desired *Z*-allylic alcohol. The absolute configuration and the geometry of the double bond for product **3a** were unambiguously determined by single-crystal X-ray diffraction analysis (**CCDC 2365198**) as reported by the previous literature.[1] The structures of the other products were determined by analogy to **3a**.

(*R*,*Z*)-5-phenylpent-3-en-2-ol 3a



3a was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 25.3 mg (0.16 mmol, 78%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.33 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 5.69 – 5.53 (m, 2H), 4.78 (dq, *J* = 7.9, 6.4 Hz, 1H), 3.53 – 3.40 (m, 2H), 1.31 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.2, 133.6, 128.3, 127.5, 127.3, 125.1, 62.9, 32.7, 22.6.

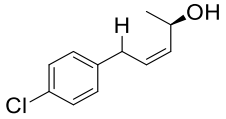
IR (thin film) ν_{max} (cm^{-1}): 3359, 3019, 2968, 2919, 1492, 1449, 1372, 1284, 1117, 1060, 922, 739, 699.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{15}O^+$[$M+H^+$]: 163.1118; found: 163.1121.

$[\alpha]^{20}_D$ (598 nm) = +18.3 (c = 1.7 in DCM, 97:3 er).

HPLC analysis of **3a** indicated an enantiomeric ratio of 97:3, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 18.25 min; minor enantiomer t_R = 23.21 min.

(*R*,*Z*)-5-(4-chlorophenyl)pent-3-en-2-ol 3b



3b was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 30.7 mg (0.16 mmol, 78%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.30 – 7.21 (m, 2H), 7.15 – 7.04 (m, 2H), 5.68 – 5.49 (m, 2H), 4.82 – 4.66 (m, 1H), 3.50 – 3.35 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.7, 135.0, 131.9, 129.7, 128.8, 128.6, 63.9, 33.1, 23.8.

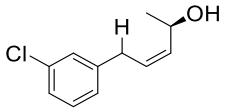
IR (thin film) ν_{max} (cm^{-1}): 3359, 3014, 2970, 2922, 1490, 1445, 1370, 1183, 1121, 1091, 1059, 1015, 917, 844, 804, 747, 661.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}ClNaO^+$[$M+Na^+$]: 219.0548; found: 219.0553.

$[\alpha]^{20}_D$ (598 nm) = +8.7 (c = 2.7 in DCM, 95:5 er).

HPLC analysis of **3b** indicated an enantiomeric ratio of 95:5, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 14.61 min; minor enantiomer t_R = 13.19 min.

(*R*,*Z*)-5-(3-chlorophenyl)pent-3-en-2-ol 3c



3c was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 29.8 mg (0.15 mmol, 76%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.49.

^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.26 – 7.15 (m, 3H), 7.06 (d, *J* = 7.1 Hz, 1H), 5.59 (t, *J* = 5.8 Hz, 2H), 4.81 – 4.68 (m, 1H), 3.49 – 3.36 (m, 2H), 1.31 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.3, 135.2, 134.3, 129.8, 128.5, 128.4, 126.5, 126.4, 63.9, 33.4, 23.8.

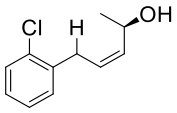
IR (thin film) ν_{max} (cm^{-1}): 3359, 3014, 2970, 2924, 1597, 1574, 1474, 1431, 1370, 1290, 1123, 1060, 922, 870, 778, 687.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}ClNaO^+$[M+Na^+]: 219.0548; found: 219.0551.

$[\alpha]^{20}_D$ (598 nm) = +18.3 (c = 2.3 in DCM, 92:8 er).

HPLC analysis of **3c** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 17.93 min; minor enantiomer t_R = 16.99 min.

(*R*,*Z*)-5-(2-chlorophenyl)pent-3-en-2-ol 3d



3d was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 33.8 mg (0.172 mmol, 86%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.35 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.25 – 7.13 (m, 3H), 5.63 – 5.53 (m, 2H), 4.86 – 4.77 (m, 1H), 3.64 – 3.49 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 136.8, 134.2, 132.8, 128.9, 128.5, 126.6, 126.5, 126.0, 62.8, 30.6, 22.5.

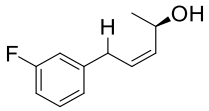
IR (thin film) ν_{max} (cm^{-1}): 3359, 3015, 2969, 2924, 1472, 1443, 1370, 1286, 1119, 1055, 924, 751, 685.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}ClNaO^+$[M+Na^+]: 219.0548; found: 219.0546.

$[\alpha]^{20}_D$ (598 nm) = +17.9 (c = 1.9 in DCM, 95:5 er).

HPLC analysis of **3d** indicated an enantiomeric ratio of 95:5, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 14.93 min; minor enantiomer t_R = 17.03 min.

(*R*,*Z*)-5-(3-fluorophenyl)pent-3-en-2-ol 3e



3e was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 33.7 mg (0.18 mmol, 89%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.45.

^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.28 – 7.21 (m, 1H), 6.98 – 6.83 (m, 3H), 5.66 – 5.51 (m, 2H), 4.82 – 4.68 (m, 1H), 3.51 – 3.39 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 163.0 (d, J_{C-F} = 245.7 Hz), 142.8 (d, J_{C-F} = 7.2 Hz), 135.2, 130.0 (d, J_{C-F} = 8.3 Hz), 128.5, 123.9 (d, J_{C-F} = 2.8 Hz), 115.2 (d, J_{C-F} = 21.2 Hz), 113.1 (d, J_{C-F} = 21.1 Hz), 63.9, 33.4 (d, J_{C-F} = 1.8 Hz), 23.7.

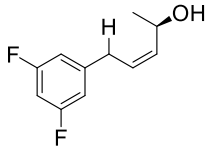
IR (thin film) ν_{max} (cm^{-1}): 3359, 3014, 2971, 2924, 1614, 1588, 1486, 1370, 1249, 1134, 1059, 948, 863, 777, 688.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{13}FNaO^+$[M+Na^+]: 203.0843; found: 203.0847.

$[\alpha]^{20}_D$ (598 nm) = +11.2 (c = 1.9 in DCM, 93:7 er).

HPLC analysis of **3e** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IF, *n*hexane:*i*-PrOH = 99:1, column flow rate = 0.5 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 26.66 min; minor enantiomer t_R = 27.76 min.

(*R*,*Z*)-5-(3,5-difluorophenyl)pent-3-en-2-ol 3f



3f was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 28.9 mg (0.15 mmol, 73%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.46.

^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 6.77 – 6.61 (m, 3H), 5.68 – 5.50 (m, 2H), 4.77 – 4.67 (m, 1H), 3.51 – 3.37 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C (ppm) 163.1 (dd, J_{C-F} = 248.2, 12.9 Hz), 144.1 (t, J_{C-F} = 8.9 Hz), 135.8, 127.6, 111.2 (d, J_{C-F} = 6.6 Hz), 111.0 (d, J_{C-F} = 6.6 Hz), 101.7 (t, J_{C-F} = 25.4 Hz), 63.9, 33.4, 23.8.

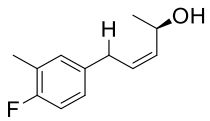
IR (thin film) ν_{max} (cm^{-1}): 3353, 3016, 2972, 2926, 1625, 1595, 1458, 1371, 1321, 1118, 1060, 991, 914, 848, 766, 677.

HRMS (ESI+/QTOF) calcd for $C_{11}H_{12}F_2NaO^+$[M+Na^+]: 221.0749; found: 221.0747.

$[\alpha]^{20}_D$ (598 nm) = +31.1 (c = 1.0 in DCM, 86:14 er).

HPLC analysis of **3f** indicated an enantiomeric ratio of 86:14, (Daicel Chiralcel IF, *n*hexane:*i*-PrOH = 95:5, column flow rate = 0.5 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 16.76 min; minor enantiomer t_R = 20.16 min.

(*R*,*Z*)-5-(4-fluoro-3-methylphenyl)pent-3-en-2-ol 3g



3g was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^1H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 34.6 mg (0.18 mmol, 89%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.49.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.04 – 6.82 (m, 3H), 5.70 – 5.41 (m, 2H), 4.84 – 4.67 (m, 1H), 3.46 – 3.27 (m, 2H), 2.25 (d, *J* = 2.0 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 159.9 (d, $J_{C\text{-}F}$ = 242.8 Hz), 135.6 (d, $J_{C\text{-}F}$ = 3.7 Hz), 134.6, 131.2 (d, $J_{C\text{-}F}$ = 5.0 Hz), 129.4, 126.9 (d, $J_{C\text{-}F}$ = 7.8 Hz), 124.8 (d, $J_{C\text{-}F}$ = 17.4 Hz), 114.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 63.9, 32.9, 23.7, 14.6 (d, $J_{C\text{-}F}$ = 3.6 Hz).

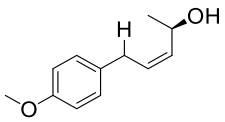
IR (thin film) ν_{max} (cm^{-1}): 3361, 3012, 2969, 2925, 1501, 1448, 1370, 1248, 1208, 1119, 1059, 925, 817, 755, 714.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{15}FNaO^+$[M+Na$^+$]:217.1000; found: 217.0999.

[α]$^{20}_D$ (598 nm) = +9.0 (c = 1.0 in DCM, 92:8 er).

HPLC analysis of **3g** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 10.37 min; minor enantiomer t_R = 11.26 min.

(*R*,*Z*)-5-(4-methoxyphenyl)pent-3-en-2-ol 3h



3h was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:10~15, column size 254 x 17 mm) within 30 min yielded a total of 26.2 mg (0.14 mmol, 68%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.12 – 7.07 (m, 2H), 6.87 – 6.82 (m, 2H), 5.66 – 5.50 (m, 2H), 4.77 (m, 1H), 3.79 (s, 3H), 3.47 – 3.34 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.0, 134.3, 132.3, 129.8, 129.2, 114.0, 63.9, 55.3, 32.9, 23.7.

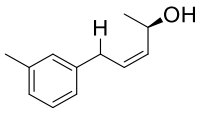
IR (thin film) ν_{max} (cm^{-1}): 3393, 3005, 2966, 2926, 2837, 1610, 1510, 1460, 1369, 1298, 1245, 1178, 1121, 1038, 845, 717.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{17}O_2^+$[M+H$^+$]:193.1224; found: 193.1216.

[α]$^{20}_D$ (598 nm) = +11.5 (c = 1.6 in DCM, 88:12 er).

HPLC analysis of **3h** indicated an enantiomeric ratio of 88:12, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 23.73 min; minor enantiomer t_R = 25.36 min.

(*R*,*Z*)-5-(*m*-tolyl)pent-3-en-2-ol 3i



3i was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography

(*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 25.0 mg (0.14 mmol, 71%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.19 (t, *J* = 7.4 Hz, 1H), 7.05 – 6.97 (m, 3H), 5.68 – 5.52 (m, 2H), 4.78 (m, 1H), 3.50 – 3.37 (m, 2H), 2.34 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.2, 137.2, 133.4, 128.5, 128.1, 127.4, 125.8, 124.2, 62.9, 32.6, 22.6, 20.4.

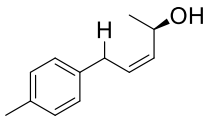
IR (thin film) ν_{max} (cm^{-1}): 3359, 2969, 2925, 2855, 1614, 1589, 1486, 1448, 1370, 1249, 1134, 1059, 948, 777, 688.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{17}O^+$[M+H$^+$]: 177.1274; found: 177.1275.

[α]$^{20}_D$ (598 nm) = +12.4 (c = 1.7 in DCM, 93:7 er).

HPLC analysis of **3i** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 16.29 min; minor enantiomer t_R = 25.03 min.

(*R*,*Z*)-5-(*p*-tolyl)pent-3-en-2-ol 3j



3j was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 19.7 mg (0.11 mmol, 56%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.10 (q, *J* = 8.0 Hz, 4H), 5.68 – 5.51 (m, 2H), 4.84 – 4.72 (m, 1H), 3.50 – 3.36 (m, 2H), 2.33 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.2, 135.7, 134.4, 129.7, 129.3, 128.2, 63.9, 33.3, 23.7, 21.0.

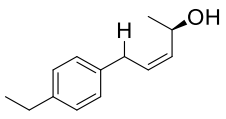
IR (thin film) ν_{max} (cm^{-1}): 3359, 3012, 2970, 2922, 1513, 1448, 1370, 1318, 1290, 1121, 1058, 916, 846, 801, 775, 717.

HRMS (ESI+/QTOF) calcd for $C_{12}H_{17}O^+$[M+H$^+$]: 177.1274; found: 177.1274.

[α]$^{20}_D$ (598 nm) = +13.5 (c = 2.4 in DCM, 91:9 er).

HPLC analysis of **3j** indicated an enantiomeric ratio of 91:9, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 14.35 min; minor enantiomer t_R = 19.02 min.

(*R*,*Z*)-5-(4-ethylphenyl)pent-3-en-2-ol 3k



3k was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography

(*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 30.4 mg (0.16 mmol, 79%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.48.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.17 – 7.09 (m, 4H), 5.69 – 5.50 (m, 2H), 4.86 – 4.70 (m, 1H), 3.52 – 3.35 (m, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.1, 137.4, 134.4, 129.6, 128.2, 128.1, 63.9, 33.4, 28.5, 23.7, 15.7.

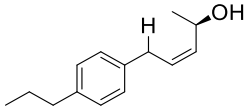
IR (thin film) ν_{max} (cm^{-1}): 3358, 3012, 2965, 2925, 1513, 1453, 1371, 1317, 1121, 1058, 915, 845, 815, 767.

HRMS (ESI+/QTOF) calcd for $C_{13}H_{18}NaO^+$[M+Na$^+$]: 213.1250; found: 213.1249.

[α]$^{20}_D$ (598 nm) = +24.4 (c = 1.6 in DCM, 90:10 er).

HPLC analysis of **3k** indicated an enantiomeric ratio of 90:10, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 12.64 min; minor enantiomer t_R = 16.67 min.

(*R*,*Z*)-5-(4-propylphenyl)pent-3-en-2-ol 3l



3l was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 30.6 mg (0.15 mmol, 74%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.11 (d, *J* = 2.0 Hz, 4H), 5.70 – 5.51 (m, 2H), 4.86 – 4.71 (m, 1H), 3.50 – 3.36 (m, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.64 (dtd, *J* = 15.0, 7.5, 1.2 Hz, 2H), 1.31 (dd, *J* = 6.3, 1.2 Hz, 3H), 0.94 (td, *J* = 7.4, 1.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.6, 137.4, 134.4, 129.7, 128.7, 128.1, 63.9, 37.7, 33.4, 24.7, 23.7, 13.9.

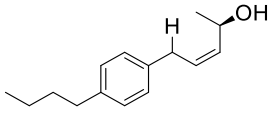
IR (thin film) ν_{max} (cm^{-1}): 3359, 3012, 2961, 2926, 2857, 1513, 1457, 1372, 1262, 1186, 1119, 1059, 914, 846, 800.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{20}NaO^+$[M+Na$^+$]: 227.1407; found: 227.1406.

[α]$^{20}_D$ (598 nm) = +6.7 (c = 1.2 in DCM, 92:8 er).

HPLC analysis of **3l** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 11.46 min; minor enantiomer t_R = 18.96 min.

(*R*,*Z*)-5-(4-butylphenyl)pent-3-en-2-ol 3m



3m was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 34.9 mg (0.16 mmol, 80%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.15 – 7.07 (m, 4H), 5.68 – 5.51 (m, 2H), 4.85 – 4.74 (m, 1H), 3.49 – 3.37 (m, 2H), 2.61 – 2.55 (m, 2H), 1.62 – 1.55 (m, 2H), 1.41 – 1.33 (m, 2H), 1.31 (d, *J* = 6.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.8, 137.4, 134.4, 129.6, 128.6, 128.2, 63.9, 35.2, 33.8, 33.4, 23.7, 22.4, 14.0.

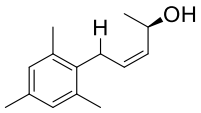
IR (thin film) ν_{max} (cm^{-1}): 3346, 3012, 2960, 2927, 2860, 1513, 1457, 1372, 1286, 1121, 1059, 925, 846, 804, 725.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{23}O^+$[M+H$^+$]: 219.1744; found: 219.1736.

[α]$^{20}_D$ (598 nm) = +23.3 (c = 1.8 in DCM, 92:8 er).

HPLC analysis of **3m** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 11.50 min; minor enantiomer t_R = 21.00 min.

(*R*,*Z*)-5-mesitylpent-3-en-2-ol 3n



3n was synthesized according to the general procedure C. ^{1}H NMR indicated that three major isomers were generated in a ratio of 84:13:3 (**3n**:**3n-a**:**3n-b**). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 22.5 mg (0.11 mmol, 52%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.45.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 6.85 (s, 2H), 5.47 (tq, *J* = 8.6, 1.8 Hz, 1H), 5.30 (dt, *J* = 10.7, 6.7 Hz, 1H), 4.95 – 4.77 (m, 1H), 3.52 – 3.35 (m, 2H), 2.27 (d, *J* = 7.1 Hz, 9H), 1.33 (dd, *J* = 6.3, 1.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 136.2, 135.6, 134.0, 133.8, 129.0, 128.8, 64.1, 27.9, 23.7, 20.8, 20.0.

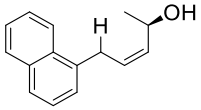
IR (thin film) ν_{max} (cm^{-1}): 3361, 3007, 2967, 2922, 2861, 1482, 1450, 1373, 1282, 1122, 1058, 921, 850, 725.

HRMS (ESI+/QTOF) calcd for $C_{14}H_{20}NaO^+$[M+Na$^+$]:227.1407; found: 227.1408.

[α]$^{20}_D$ (598 nm) = +35.7 (c = 1.4 in DCM, 92:8 er).

HPLC analysis of **3n** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 99:1, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 32.10 min; minor enantiomer t_R = 35.70 min.

(*R*,*Z*)-5-(naphthalen-1-yl)pent-3-en-2-ol 3o



3o was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 38.2 mg (0.18 mmol, 89%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.50.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.06 – 7.99 (m, 1H), 7.91 – 7.84 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.34 (dd, *J* = 7.0, 1.2 Hz, 1H), 5.75 (m, *J* = 10.9, 7.2, 1.0 Hz, 1H), 5.62 (m, *J* = 10.5, 8.5, 1.6 Hz, 1H), 4.94 – 4.82 (m, 1H), 4.00 – 3.79 (m, 2H), 1.34 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 136.4, 134.9, 133.9, 131.8, 129.1, 128.8, 127.1, 126.0, 125.69, 125.68, 125.66, 123.7, 64.0, 31.0, 23.7.

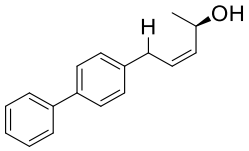
IR (thin film) ν_{max} (cm^{-1}): 3365, 3046, 3011, 2969, 2923, 1596, 1448, 1394, 1369, 1288, 1122, 1059, 921, 778, 736.

HRMS (ESI+/QTOF) calcd for $C_{15}H_{16}NaO^+$[M+Na^+]: 235.1094; found: 235.1095.

$[\alpha]^{20}_D$ (598 nm) = +12.7 (c = 2.8 in DCM, 93:7 er).

HPLC analysis of **3o** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 90:10, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 14.46 min; minor enantiomer t_R = 16.23 min.

(*R*,*Z*)-5-([1,1'-biphenyl]-4-yl)pent-3-en-2-ol 3p



3p was synthesized according to the general procedure C. The regioselectivity was determined to be > 99% by ^{1}H NMR analysis. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 42.9 mg (0.18 mmol, 90%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.45.

^{11}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.60 – 7.50 (m, 4H), 7.46 – 7.40 (m, 2H), 7.36 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 5.70 – 5.55 (m, 2H), 4.80 (m, 1H), 3.57 – 3.44 (m, 2H), 1.32 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.9, 138.3, 138.1, 133.7, 128.2, 127.71, 127.67, 126.3, 126.1, 126.0, 62.9, 32.4, 22.7.

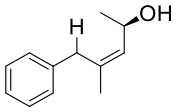
IR (thin film) ν_{max} (cm^{-1}): 3307, 3015, 2969, 2924, 1486, 1451, 1405, 1370, 1264, 1114, 1059, 844, 816, 755, 692.

HRMS (ESI+/QTOF) calcd for $C_{17}H_{18}NaO^+$[M+Na^+]: 261.1250; found: 261.1251.

$[\alpha]^{20}_D$ (598 nm) = +10.8 (c = 2.1 in DCM, 91:9 er).

HPLC analysis of **3p** indicated an enantiomeric ratio of 91:9, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 90:10, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 24.01 min; minor enantiomer t_R = 18.00 min.

(*R*,*Z*)-4-methyl-5-phenylpent-3-en-2-ol 3a-2Me



3a-2Me was synthesized according to the general procedure C. Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 12.3 mg (0.07 mmol, 36%) of product as a colorless liquid.

TLC (*n*hexane:EA = 2:1, UV light) R_f = 0.45.

^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm) 7.31 – 7.25 (m, 2H), 7.18 (m, 3H), 5.38 (d, *J* = 8.8 Hz, 1H), 4.71 (dq, *J* = 8.8, 6.3 Hz, 1H), 3.47 (d, *J* = 14.6 Hz, 1H), 3.38 (d, *J* = 14.6 Hz, 1H), 1.64 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz) δ_C (ppm) 139.4, 136.5, 131.0, 128.53, 128.50, 126.1, 64.7, 38.2, 24.0, 23.4.

IR (thin film) ν_{max} (cm^{-1}): 3333, 3026, 2968, 2922, 2362, 1449, 1371, 1282, 1119, 1058, 863, 734, 699.

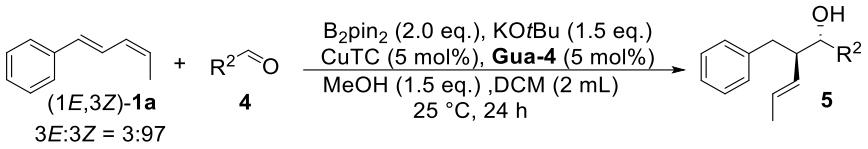
HRMS (ESI+/QTOF) calcd for $C_{12}H_{17}O^+$[M+H$^+$]: 177.1274; found: 177.1278.

$[\alpha]^{20}_D$ (598 nm) = +20.0 (c = 1.7 in DCM, 85:15 er).

HPLC analysis of **3a-2Me** indicated an enantiomeric ratio of 85:15, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 15.33 min; minor enantiomer t_R = 20.33 min.

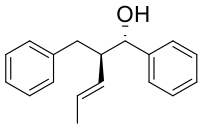
Preparation and Characterization of Homoallylic Alcohols

General Procedure D: One-pot Protoboration-Crotylboration of 1,3-Dienes with B_2pin_2 and Aldehydes



The homoallyl alcohols were prepared with a modified procedure according to the literature.[1] To a dry 4 mL vial equipped with a magnetic stirrer bar, 33.7 mg KO*t*Bu (0.3 mmol, 1.5 equiv.), 102 mg B_2pin_2 (0.4 mmol, 2.0 equiv.), 1.9 mg CuTC (0.01 mmol, 5 mol%), and 6.4 mg **Gua-4$^+$** (0.01 mmol, 5 mol%) were added in sequence, followed by the addition of 2 mL dry DCM and stirring at 25 °C for 5 min. Then 12.2 µL MeOH (0.3 mmol, 1.5 equiv.) was added and stirred for 1 min, followed by the addition of 28.8 mg (1*E*,3*Z*)-**1a** (0.2 mmol, 1.0 equiv.) and 0.4 mmol aldehyde (2.0 equiv.). The vial was then capped and sealed with parafilm. The reaction was allowed to stir vigorously at 25 °C for 24 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The crude material was concentrated in vacuo and purified by flash column chromatography to afford **5**. The absolute configuration and the geometry of the double bond for product **5a** were unambiguously determined by single-crystal X-ray diffraction analysis (**CCDC 2504333**). The structures of the other products were determined by analogy to **5a**.

(1*S*,2*R*,*E*)-2-benzyl-1-phenylpent-3-en-1-ol 5a



5a was synthesized according to the general procedure D with benzaldehyde (40.8 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 40.4 mg (0.16 mmol, 79%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.40 – 7.28 (m, 5H), 7.28 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H), 5.34 – 5.17 (m, 2H), 4.70 (d, *J* = 5.5 Hz, 1H), 2.86 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.53 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.07 (s, 1H), 1.56 (d, *J* = 5.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.5, 140.4, 130.0, 129.3, 128.6, 128.1, 127.4, 126.8, 125.7, 76.6, 51.6, 36.6, 18.1.

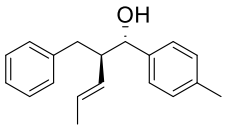
IR (thin film) ν_{max} (cm^{-1}): 3436, 3060, 3027, 2920, 2857, 1602, 1494, 1450, 1375, 1319, 1144, 1034, 969, 750, 701, 550.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{20}NaO^+$[M+Na^+]: 275.1407; found: 275.1414.

$[\alpha]^{20}_D$ (598 nm) = -31.1 (c = 3.5 in DCM, 96:4 er).

HPLC analysis of **5a** indicated an enantiomeric ratio of 96:4, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 13.23 min; minor enantiomer t_R = 19.30 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(*p*-tolyl)pent-3-en-1-ol 5b



5b was synthesized according to the general procedure D with 4-methylbenzaldehyde (47.2 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 45.3 mg (0.17 mmol, 86%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.29 – 7.08 (m, 9H), 5.36 – 5.13 (m, 2H), 4.67 (d, *J* = 5.5 Hz, 1H), 2.85 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.72 (m, 1H), 2.52 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.37 (s, 3H), 2.07 (s, 1H), 1.57 (d, *J* = 5.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.5, 139.4, 137.0, 130.1, 129.4, 128.8, 128.5, 128.0, 126.7, 125.7, 76.4, 51.5, 36.7, 21.2, 18.1.

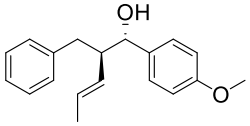
IR (thin film) ν_{max} (cm^{-1}): 3427, 3060, 3027, 2921, 2857, 1599, 1490, 1449, 1408, 1378, 1302, 1264, 1183, 1090, 1014, 969, 826, 744, 700, 548.

HRMS (ESI+/QTOF) calcd for $C_{19}H_{22}NaO^+$[M+Na^+]: 289.1563; found: 289.1567.

$[\alpha]^{20}_D$ (598 nm) = -25.1 (c = 3.5 in DCM, 93:7 er).

HPLC analysis of **5b** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 12.00 min; minor enantiomer t_R = 16.64 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(4-methoxyphenyl)pent-3-en-1-ol 5c



5c was synthesized according to the general procedure D with 4-methoxybenzaldehyde (48.5 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 39.5 mg (0.14 mmol, 71%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 10:1, UV light) R_f = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.26 – 7.20 (m, 4H), 7.18 – 7.13 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.91 – 6.84 (m, 2H), 5.32 – 5.13 (m, 2H), 4.63 (d, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 2.83 (dd, *J* = 13.5, 4.4 Hz, 1H), 2.69 (m, 1H), 2.51 (dd, *J* = 13.5, 9.4 Hz, 1H), 2.02 (s, 1H), 1.55 (d, *J* = 5.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.9, 140.4, 134.6, 130.0, 129.3, 128.5, 128.05, 127.95, 125.7, 113.4, 76.1, 55.3, 51.6, 36.8, 18.1.

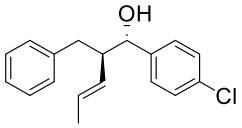
IR (thin film) ν_{max} (cm^{-1}): 3439, 3026, 2929, 2857, 1609, 1511, 1451, 1378, 1301, 1247, 1176, 1035, 969, 832, 745, 700, 552.

HRMS (ESI+/QTOF) calcd for $C_{19}H_{23}O_2^+$[$M+H^+$]: 283.1693; found: 283.1698.

$[\alpha]^{20}_D$ (598 nm) = -26.0 (c = 1.5 in DCM, 94:6 er).

HPLC analysis of **5c** indicated an enantiomeric ratio of 94:6, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 20.63 min; minor enantiomer t_R = 25.67 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(4-chlorophenyl)pent-3-en-1-ol 5d



5d was synthesized according to the general procedure D with 4-chlorobenzaldehyde (46.8 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 45.9 mg (0.16 mmol, 78%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.24 (d, *J* = 8.4 Hz, 2H), 7.16 (td, *J* = 8.5, 7.9, 3.2 Hz, 4H), 7.11 – 6.99 (m, 3H), 5.19 (dq, *J* = 15.3, 6.1 Hz, 1H), 5.08 (ddd, *J* = 15.3, 8.6, 1.7 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 1H), 2.73 (dd, *J* = 13.5, 4.3 Hz, 1H), 2.60 (m, 1H), 2.44 (dd, *J* = 13.5, 9.4 Hz, 1H), 2.02 (d, *J* = 3.4 Hz, 1H), 1.48 (d, *J* = 6.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 141.0, 140.1, 133.1, 129.6, 129.3, 129.0, 128.19, 128.17, 128.12, 125.8, 75.9, 51.5, 36.6, 18.1.

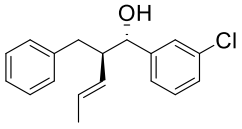
IR (thin film) ν_{max} (cm^{-1}): 3418, 3059, 3027, 2919, 2857, 1599, 1491, 1449, 1408, 1379, 1300, 1182, 1090, 1037, 1013, 969, 827, 745, 700, 548.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{20}ClO^+$[$M+H^+$]: 287.1198; found: 287.1193.

$[\alpha]^{20}_D$ (598 nm) = -45.0 (c = 1.2 in DCM, 93:7 er).

HPLC analysis of **5d** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 14.06 min; minor enantiomer t_R = 20.93 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(3-chlorophenyl)pent-3-en-1-ol 5e



5e was synthesized according to the general procedure D with 3-chlorobenzaldehyde (45.3 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 48.8 mg (0.17 mmol, 84%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.31 (m, 1H), 7.29 – 7.22 (m, 4H), 7.21 – 7.13 (m, 2H), 7.13 – 7.06 (m, 2H), 5.34 – 5.14 (m, 2H), 4.66 (d, *J* = 5.5 Hz, 1H), 2.82 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.69 (m, 1H), 2.55 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.14 (s, 1H), 1.63 – 1.52 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 144.7, 140.1, 134.0, 129.6, 129.3, 129.1, 128.1, 127.5, 127.0, 125.9, 124.9, 76.0, 51.5, 36.4, 18.1.

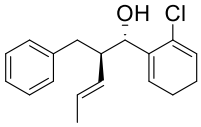
IR (thin film) ν_{max} (cm^{-1}): 3435, 3061, 3027, 2919, 2857, 1597, 1574, 1495, 1431, 1378, 1306, 1191, 1075, 1033, 969, 881, 784, 745, 699.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{19}ClNaO^+$[M+Na^+]: 309.1017; found: 309.1024.

[α]$^{20}_D$ (598 nm) = -19.5 (c = 3.8 in DCM, 94:6 er)

HPLC analysis of **5e** indicated an enantiomeric ratio of 94:6, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 13.20 min; minor enantiomer t_R = 21.66 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(2-chlorophenyl)pent-3-en-1-ol 5f



5f was synthesized according to the general procedure D with 2-methoxybenzaldehyde (45.1 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 48.8 mg (0.17 mmol, 87%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.56 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.21 (dd, *J* = 10.0, 4.6 Hz, 3H), 7.16 – 7.02 (m, 3H), 5.36 (ddd, *J* = 15.4, 8.3, 1.6 Hz, 1H), 5.30 – 5.21 (m, 1H), 5.19 (d, *J* = 5.5 Hz, 1H), 2.94 (dd, *J* = 13.6, 3.3 Hz, 1H), 2.80 (m, 1H), 2.60 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.07 (s, 1H), 1.52 (dd, *J* = 6.2, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.6, 140.3, 132.2, 130.4, 129.4, 129.3, 128.42, 128.39, 128.3, 128.0, 126.7, 125.6, 73.7, 49.9, 35.2, 18.1.

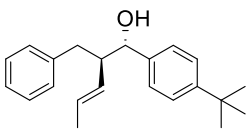
IR (thin film) ν_{max} (cm^{-1}): 3563, 3436, 3062, 3026, 2919, 2856, 1599, 1471, 1444, 1378, 1306, 1187, 1127, 1029, 968, 753, 701.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{19}ClNaO^+$[M+Na^+]: 309.1017; found: 309.1017.

[α]$^{20}_D$ (598 nm) = -44.7 (c = 3,0 in DCM, 93:7 er).

HPLC analysis of **5f** indicated an enantiomeric ratio of 93:7, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 11.30 min; minor enantiomer t_R = 12.60 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(4-(*tert*-butyl)phenyl)pent-3-en-1-ol 5g



5g was synthesized according to the general procedure D with 4-(*tert-butyl*)benzaldehyde (66.9 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size

254 x 17 mm) within 30 min yielded a total of 46.3 mg (0.15 mmol, 75%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.36 (m, 2H), 7.23 (m, 4H), 7.13 (m, 3H), 5.37 – 5.14 (m, 2H), 4.68 (d, *J* = 5.2 Hz, 1H), 2.83 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.73 (m, 1H), 2.51 (dd, *J* = 13.6, 9.4 Hz, 1H), 2.04 (s, 1H), 1.61 – 1.54 (m, 3H), 1.33 (d, *J* = 1.3 Hz, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 150.3, 140.5, 139.3, 129.3, 128.5, 128.0, 126.5, 125.7, 125.0, 76.3, 51.4, 36.5, 34.5, 31.4, 18.1.

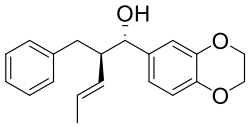
IR (thin film) ν_{max} (cm^{-1}): 3436, 3027, 2961, 2867, 1604, 1504, 1453, 1366, 1266, 1107, 1021, 969, 831, 744, 700, 574.

HRMS (ESI+/QTOF) calcd for $C_{22}H_{28}NaO^+$[M+Na^+]: 331.2033; found: 331.2036.

[α]$^{20}_D$ (598 nm) = -28.1 (c = 1.3 in DCM, 94:6 er).

HPLC analysis of **5g** indicated an enantiomeric ratio of 94:6, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 9.60 min; minor enantiomer t_R = 13.75 min.

(1*S*,2*R*,*E*)-2-benzyl-1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)pent-3-en-1-ol 5h



5h was synthesized according to the general procedure D with 1,4-benzodioxan-6-carboxaldehyde (65.7 mg, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:10~15, column size 254 x 17 mm) within 30 min yielded a total of 49.7 mg (0.16 mmol, 82%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 8:1, UV light) R_f = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.26 – 7.20 (m, 2H), 7.19 – 7.07 (m, 3H), 6.87 – 6.74 (m, 3H), 5.34 – 5.15 (m, 2H), 4.58 (d, *J* = 5.5 Hz, 1H), 4.26 (s, 4H), 2.84 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.51 (dd, *J* = 13.6, 9.6 Hz, 1H), 1.94 (s, 1H), 1.57 (d, *J* = 5.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 143.2, 142.8, 140.5, 135.9, 130.0, 129.3, 128.5, 128.0, 125.7, 119.9, 116.8, 115.7, 76.1, 64.40, 64.38, 51.4, 36.7, 18.1.

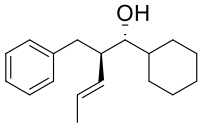
IR (thin film) ν_{max} (cm^{-1}): 3462, 3058, 3026, 2928, 2877, 1592, 1504, 1454, 1379, 1285, 1204, 1123, 1068, 969, 920, 886, 814, 746, 700.

HRMS (ESI+/QTOF) calcd for $C_{20}H_{22}NaO_3^+$[M+Na^+]: 333.1462; found: 333.1468.

[α]$^{20}_D$ (598 nm) = -17.0 (c = 3.7 in DCM, 92:8 er).

HPLC analysis of **5h** indicated an enantiomeric ratio of 92:8, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 95:5, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 23.10 min; minor enantiomer t_R = 29.50 min.

(1*R*,2*R*,*E*)-2-benzyl-1-cyclohexylpent-3-en-1-ol 5i



5i was synthesized according to the general procedure D with cyclohexanecarboxaldehyde (48.5 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 46.5 mg (0.18 mmol, 89%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.27 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 5.23 (dd, *J* = 5.9, 3.7 Hz, 2H), 3.29 (dd, *J* = 6.5, 4.9 Hz, 1H), 2.99 (dd, *J* = 13.3, 3.4 Hz, 1H), 2.54 (dd, *J* = 13.3, 9.9 Hz, 1H), 2.45 (m, 1H), 1.85 – 1.72 (m, 3H), 1.66 (d, *J* = 11.0 Hz, 1H), 1.58 (d, *J* = 4.2 Hz, 3H), 1.54 – 1.47 (m, 2H), 1.29 – 1.14 (m, 4H), 1.03 (m, *J* = 12.3, 3.4 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.9, 131.6, 129.5, 127.9, 126.9, 125.6, 78.7, 47.5, 40.3, 36.4, 30.3, 26.6, 26.54, 26.46, 26.1, 18.1.

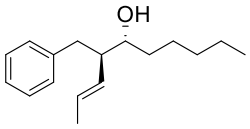
IR (thin film) ν_{max} (cm^{-1}): 3440, 3026, 2925, 2852, 1494, 1448, 1377, 1264, 1078, 1037, 970, 938, 744, 699.

HRMS (ESI+/QTOF) calcd for $C_{18}H_{27}O^+$[M+H$^+$]: 259.2057; found: 259.2049.

[α]$^{20}_D$ (598 nm) = -20.2 (c = 1.2 in DCM, 95:5 er).

HPLC analysis of **5i** indicated an enantiomeric ratio of 95:5, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 7.10 min; minor enantiomer t_R = 13.63 min.

(4*R*,5*R*,*E*)-4-benzyldec-2-en-5-ol 5j



5j was synthesized according to the general procedure D with 1-pentanecarbaldehyde (48.8 µL, 0.4 mmol). Purification by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 17 mm) within 30 min yielded a total of 25.1 mg (0.10 mmol, 51%) of product as a pale-yellow, viscous liquid (dr > 99:1).

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.26 (m, 2H), 7.20 – 7.07 (m, 3H), 5.43 – 5.21 (m, 2H), 3.57 – 3.43 (m, 1H), 2.84 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.59 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.40 (m, 1H), 1.62 (d, *J* = 5.8 Hz, 3H), 1.57 – 1.51 (m, 1H), 1.43 (m, 1H), 1.34 – 1.25 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.6, 130.7, 129.3, 128.2, 128.1, 125.7, 74.0, 51.1, 37.4, 33.7, 31.9, 25.7, 22.7, 18.1, 14.1.

IR (thin film) ν_{max} (cm^{-1}): 3371, 3027, 2924, 1492, 1455, 1372, 1318, 1144, 1074, 1030, 969, 935, 745, 699.

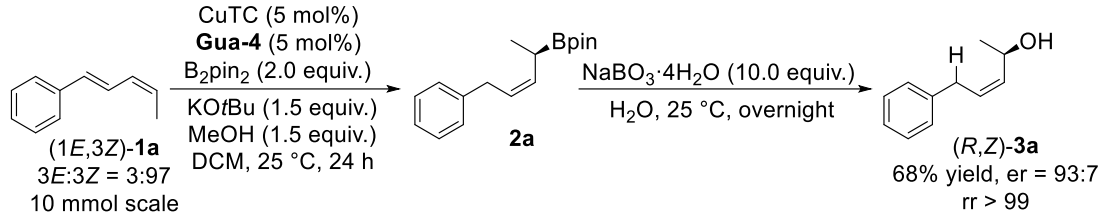
HRMS (ESI+/QTOF) calcd for $C_{17}H_{26}NaO^+$[M+Na$^+$]: 269.1876; found: 269.1874.

[α]$^{20}_D$ (598 nm) = -15.6 (c = 2.5 in DCM, 94:6 er).

HPLC analysis of **5j** indicated an enantiomeric ratio of 94:6, (Daicel Chiralcel IB N-5, *n*hexane:*i*-PrOH = 97:3, column flow rate = 1.0 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 7.05 min; minor enantiomer t_R = 12.79 min.

Scale-up Reaction & Derivatizations

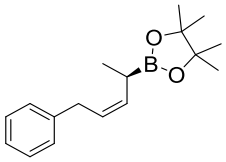
Gram-scale Synthesis of Allylboronate and Allylic Alcohols



To a 250 mL round-bottom flask, 1.685 g KO*t*Bu (15 mmol, 1.5 equiv.), 5.159 g B_2pin_2 (20 mmol, 2.0 equiv.), 95 mg CuTC (0.5 mmol, 5 mol%), and 321 mg **Gua-4**$^+$ (0.5 mmol, 5 mol%) were added in sequence, followed by the addition of 100 mL DCM and stirring at 25 °C for 5 min. ***Caution: The Combination of DCM and KOtBu in a Large Scale May Cause an Explosion!*** Then 608 μL MeOH (15 mmol, 1.5 equiv.) was added and stirred for 1 min, followed by the addition of 1.442 g (1*E*,3*Z*)-**1a** (10 mmol, 1.0 equiv.). After that, the flask was sealed and the reaction was allowed to stir vigorously at 25 °C for 24 h. The reaction progress was monitored by TLC. If the pure allylboronate was needed, saturated brine was added to quench the reaction when it was finished. Then the mixture was extracted with *n*hexane and the organic phase was separated and directly concentrated in vacuum. The residual was further purified by column chromatography as fast as possible to give the desired **2a**. Otherwise, for a scale-up reaction, the resulting mixture could also be centrifuged to collect the clear upper solution. After the supernatant was concentrated in vacuum, the residual was allowed to pass a short silica gel column with *n*hexane as eluant to remove most impurities, affording **2a** with a crude yield of 74% in gram scale.

For the preparation of the corresponding allylic alcohol **3a**, the mixture after protoboration was treated with 15.385 g $NaBO_3{\cdot}4H_2O$ (100 mmol, 10 equiv.) and 25 mL deionized water. The protoboration product was fully oxidized after overnight reaction, monitored by TLC. The resulting mixture was later quenched with 50 mL saturated brine to give an emulsion. 3 M NaOH aqueous solution was added to separate the organic phase, while the aqueous phase was extracted twice with 100 mL EA. The combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography (*n*hexane/EA=100:10~20, column size 254 x 32 mm) within 30 min to give a total of 1.11 g **3a** (6.8 mmol, 68%) as a colorless liquid. The regio- and E/Z-selectivity were determined to be >99% by ^{1}H NMR analysis.

(*R*,*Z*)-4,4,5,5-tetramethyl-2-(5-phenylpent-3-en-2-yl)-1,3,2-dioxaborolane 2a



2a was synthesized according to the general procedure. Probably due to their decomposition on silica, ^{1}H NMR analysis of the product indicated no existence of other isomeric impurities.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.40.

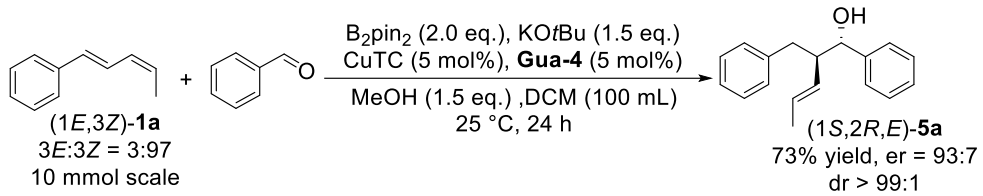
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.31 – 7.15 (m, 5H), 5.58 – 5.39 (m, 2H), 3.47 – 3.33 (m, 2H), 2.27 (p, *J* = 7.6 Hz, 1H), 1.24 (s, 12H), 1.12 (d, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 141.4, 133.3, 128.5, 128.3, 126.6, 125.7, 83.2, 33.8, 29.7, 16.1.

IR (thin film) ν_{max} (cm^{-1}): 3061, 2976, 2928, 2874, 1491, 1456, 1321, 1211, 1144, 1114, 966, 858, 743, 698, 673.

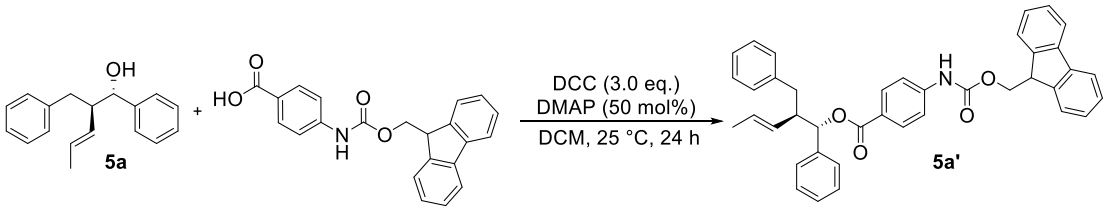
HRMS (ESI+/QTOF) calcd for $C_{17}H_{26}BO_2^+$[M+H$^+$]: 273.2021; found: 273.2020.

Gram-scale Synthesis of Homoallylic Alcohols



To a 250 mL round-bottom flask, 1.685 g KO*t*Bu (15 mmol, 1.5 equiv.), 5.159 g B_2pin_2 (20 mmol, 2.0 equiv.), 95 mg CuTC (0.5 mmol, 5 mol%) and 321 mg **Gua-4$^+$** (0.5 mmol, 5 mol%) were added in sequence, followed by the addition of 100 mL DCM and stirring at 25 °C for 5 min. ***Caution: The Combination of DCM and KOtBu in a Large Scale May Cause an Explosion!*** Then 608 μL MeOH (15 mmol, 1.5 equiv.) was added and stirred for 1 min, followed by the addition of 1.442 g (1*E*,3*Z*)-**1a** (10 mmol, 1.0 equiv.) and 2.04 mL benzaldehyde (20 mmol, 2.0 equiv.). After that, the flask was sealed and the reaction was allowed to stir vigorously at 25 °C for 24 h. After the reaction was finished, it was quenched by saturated brine and extracted with EA three times. The combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography (*n*hexane/EA=100:5~10, column size 254 x 32 mm) within 30 min to give a total of 1.84 g **5a** (7.3 mmol, 73%) as a pale-yellow and viscous liquid. ^{1}H NMR analysis indicated the diastereomeric ratio of >99:1.

Esterification of Chiral Homoallylic Alcohol



5a′ was synthesized with a modified procedure according to the literature.[5] To a 25 mL round-bottom flask, 125 mg **5a** (0.5 mmol, 1.0 equiv., 90% ee), 359.4 mg 4-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)benzoic acid (1.0 mmol, 2.0 equiv.), 310 mg *N*, *N*'-dicyclohexylcarbodiimide (DCC, 1.5 mmol, 3.0 equiv.), and 30.5 mg 4-dimethylaminopyridine (DMAP, 0.25 mmol, 50 mol%) were added, followed by the addition of 10 mL DCM and stirring at 25 °C for 24 h. After the reaction was finished, a large amount of deionized water was added. The mixture was stirred vigorously to remove the unreacted DCC and the corresponding

dicyclohexylurea (DCU). The aqueous phase was extracted three times with DCM, and the combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography (*n*hexane/EA=100:10~15, column size 254 x 32 mm) within 1 h to give a total of 166.1 mg **5a′** (0.43 mmol, 56%) as a white solid.

TLC (*n*hexane:EA = 5:1, UV light) R_f = 0.40.

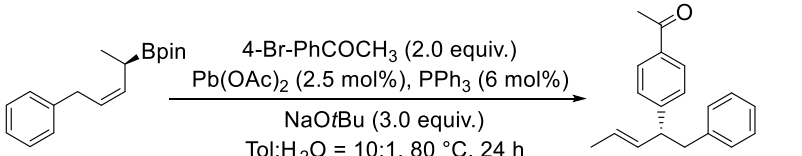
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.02 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.34 (m, 6H), 7.29 – 7.26 (m, 1H), 7.24 (m, 2H), 7.19 – 7.08 (m, 3H), 6.88 (d, *J* = 4.0 Hz, 1H), 5.94 (d, *J* = 6.3 Hz, 1H), 5.29 – 5.09 (m, 2H), 4.60 (d, *J* = 6.4 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.62 (m, *J* = 14.5, 10.2 Hz, 1H), 1.51 (d, *J* = 4.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 165.2, 152.9, 143.6, 142.1, 141.4, 140.0, 139.0, 131.0, 129.31, 129.25, 128.7, 128.13, 128.11, 127.9, 127.8, 127.22, 127.20, 125.9, 125.2, 124.9, 120.1, 117.7, 78.8, 67.1, 49.8, 47.1, 37.2, 18.0.

IR (thin film) ν_{max} (cm^{-1}): 3320, 3030, 2935, 1710, 1600, 1531, 1315, 1272, 1216, 1176, 1107, 740, 700.

HRMS (ESI+/QTOF) calcd for $C_{40}H_{35}KNO_4^+$ [M+K$^+$]: 632.2198; found: 632.2199.

Derivatization of Allylboronate: Suzuki-Miyaura Cross-Coupling for the Preparation of (*R*,*E*)-1-(4-(1-phenylpent-3-en-2-yl)phenyl)ethan-1-one 6a



2a **6a,** 50% yield, er = 94:6

6a was prepared with a modified procedure according to the literatures.[6] To a 25 mL Schlenk flask, 96 mg 1-(4-bromophenyl)ethan-1-one (0.48 mmol, 1.2 equiv.), 2.3 mg $Pb(OAc)_2$ (0.01 mmol, 2.5 mol%), 6.3 mg PPh_3 (0.024 mmol, 6 mol%), and 115 mg NaO*t*Bu (1.2 mmol, 3.0 equiv.) were added. The reaction setup was purged with N_2 for three times, before 2 mL mixture of toluene and H_2O (10:1) was added. After pre-stirring for 2 min, 108.9 mg **2a** (0.4 mmol, 1.0 equiv.) in 0.5 mL toluene was added dropwise into the mixture. Then the reaction was heated to 80 °C for 24 h. After that, the reaction was cooled to room temperature and quenched by 2 mL deionized water. The mixture was extracted with 5 mL EA twice. The combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography (*n*hexane/EA=100:10~20, column size 254 x 17 mm) within 1 h to give a total of 52.9 mg **6a** (0.20 mmol, 50% yield) as a colorless liquid.

TLC (*n*hexane:EA = 20:1, UV light) R_f = 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.88 – 7.83 (m, 2H), 7.25 – 7.13 (m, 5H), 7.05 – 6.98 (m, 2H), 5.65 (ddq, *J* = 15.1, 7.5, 1.5 Hz, 1H), 5.40 (dqd, *J* = 15.3, 6.4, 1.1 Hz, 1H), 3.59 (q, *J* = 7.6 Hz, 1H), 3.04 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.96 (dd, *J* = 13.4, 7.9 Hz, 1H), 2.57 (s, 3H), 1.65 (ddd, *J* = 6.4, 1.6, 0.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 196.9, 149.2, 138.7, 134.2, 132.3, 128.1, 127.5, 127.0, 126.9, 125.1, 124.9, 49.7, 41.5, 25.6, 17.0.

IR (thin film) ν_{max}(cm^{-1}): 3027, 2921, 2856, 1681, 1604, 1493, 1415, 1358, 1268, 1183, 963, 839, 745, 700, 600.

HRMS (ESI+/QTOF) calcd for $C_{19}H_{21}O^+$ [$M+H^+$]: 265.1587; found: 265.1586.

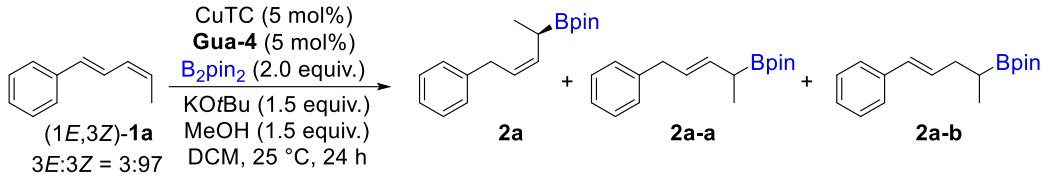
$[\alpha]^{20}_D$ (598 nm) = +27.8 (c = 1.8 in DCM, 94:6 er).

HPLC analysis of **6a** indicated an enantiomeric ratio of 94:6, (Daicel Chiralcel IG, *n*hexane:*i*-PrOH = 99:1, column flow rate = 0.3 mL/min, T = 25 °C, λ = 210 nm); major enantiomer t_R = 42.46 min; minor enantiomer t_R = 45.40 min.

Mechanistic Investigations

Control Experiments

Table S2 Control experiments of protoboration with varied reaction conditions.[a]



entry	variation from standard condition	conv. (%)[b]	protoboration (%)[c]			er (%)[d]
			2a (%)	**2a-a** (%)	**2a-b** (%)	
1	without KO*t*Bu	<5	-	-	-	-
2	without CuTC	<5	-	-	-	-
3	without **Gua-4**	64	90	0	10	50:50
4	with 1.0 equiv. Tempo	76	99	-	-	94:6
5	with 1.0 equiv. BHT	>99	98	-	2	97:3

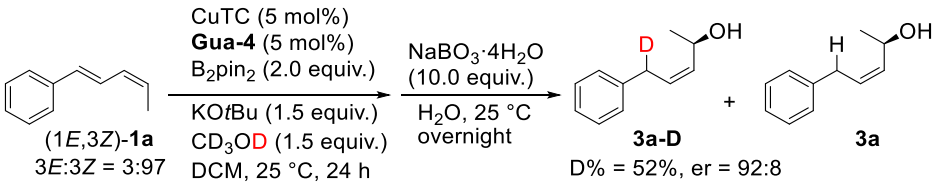
[a] Reagents and conditions: (1*E*,3*Z*)-**1a** (0.2 mmol), B_2pin_2 (0.3 mmol), CuTC (0.01 mmol), **Gua-4** (0.01 mmol), KO*t*Bu (0.3 mmol), MeOH (0.3 mmol), DCM (2 mL), 25 °C, air, 24 h. The corresponding dihydrochlorides of **Gua-4** was used as ligand precursor.

[b] Calibrated GC conversions of **1a** using biphenyl as an internal standard.

[c] The selectivity was determined by area normalization.

[d] Determinded by HPLC analysis of the corresponding alcohol after oxidation.

Deuterium Labeling Experiment



To a dry 8 mL vial equipped with a magnetic stir bar in a glove box under an argon protection, 67.4 mg KO*t*Bu (0.6 mmol, 1.5 equiv.), 202 mg B_2pin_2 (0.8 mmol, 2.0 equiv.), 3.8 mg CuTC (0.02 mmol, 5 mol%), and 12.8 mg **Gua-4**$^+$ (0.02 mmol, 5 mol%) were added in sequence, followed by the addition of 4 mL oxygen- and moisture-free DCM and stirring at 25 °C for 5 min. Then 24.4 μL CD_3OD (0.6 mmol, 1.5 equiv.) was added and stirred for 1 min, followed by the addition of 57.7 mg (1*E*,3*Z*)-**1a** (0.4 mmol, 1.0 equiv.). After that, the vial was sealed and the reaction was allowed to stir vigorously at 25 °C for 24 h.

When the reaction was finished, the reaction setup was removed from the glove box. Then 614 mg $NaBO_3$.$4H_2O$ (4 mmol, 10 equiv.) and 1 mL deionized water were added into the vial. The protoboration product was fully oxidized after overnight reaction. The resulting mixture was later quenched with saturated brine to give an emulsion. 3 M NaOH aqueous solution was added to separate the organic phase, while the aqueous phase was extracted twice with EA. The combined organic layers were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography to give the desired the product a

mixture (**3a** and **3a-D**, D% = 52%, er = 92:8) in 68% yield. The deuterium incorporation ratio of only 52% is most likely due to the hygroscopic nature of KO*t*Bu (containting HO*t*Bu), the intrinsic protons on **Gua-4**$^{+}$, and other competitive H^{+} source (H_2O) accompanied with the chemical reagents.

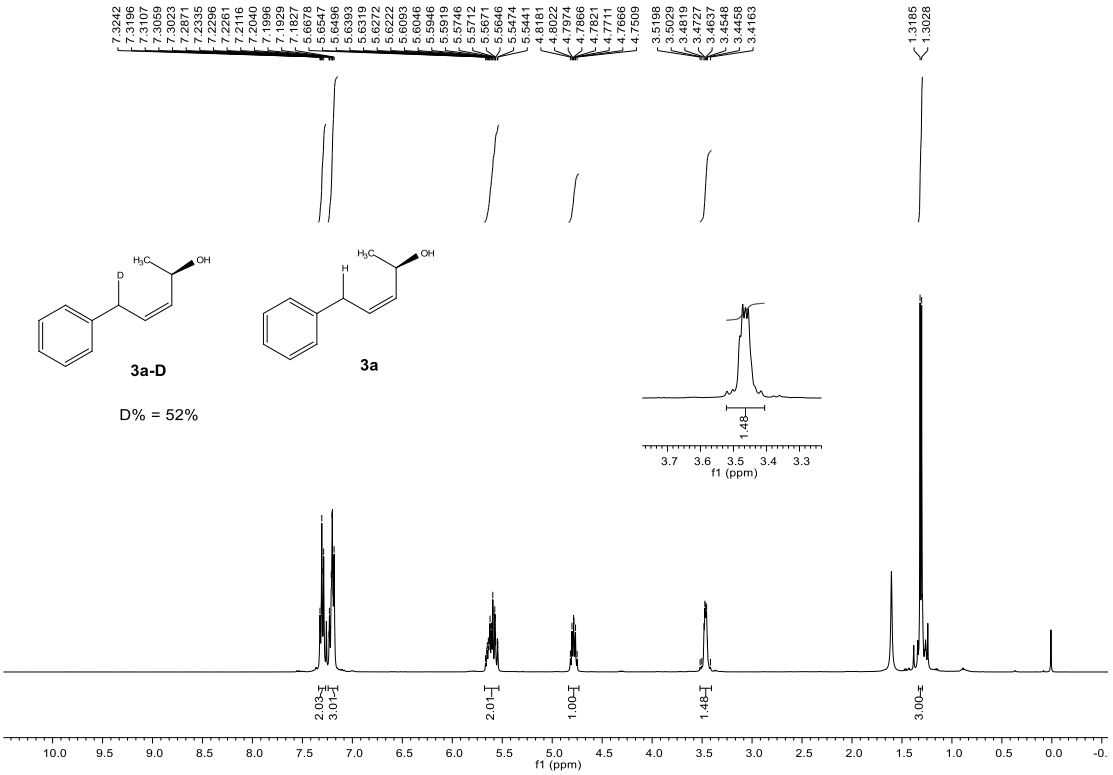
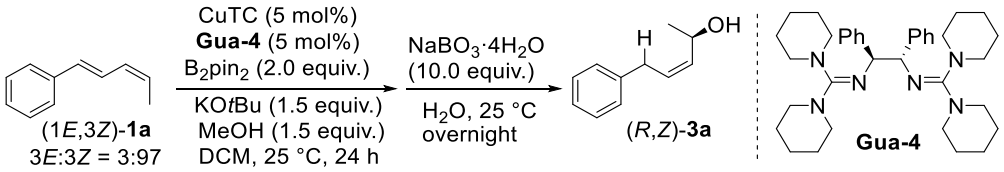
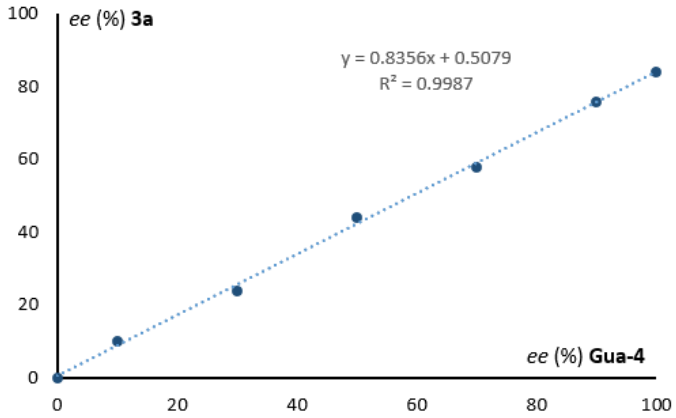


Figure S1 ^{1}H NMR spectra of protoboration/oxidation products in deuterium labelling experiment.

Investigation of Non-Linear Effect with Gua-4

Table S3 The NLE investigation of copper-guanidine-catalyzed protoboration.[a]





entry	ee of **Gua-4** (%)	Conv. of **1a** (%)[b]	er of **3a** (%)[c]
1	0	93	50:50
2	10	80	55:45
3	30	82	62:38
4	50	94	72:28
5	70	83	79:21
6	90	82	88:12
7	>99	91	92:8

[a] Reagents and conditions: (1*E*,3*Z*)-**1a** (0.2 mmol), B_2pin_2 (0.3 mmol), CuTC (0.01 mmol), **Gua-4** (0.01 mmol), KO*t*Bu (0.3 mmol), MeOH (0.3 mmol), DCM (2 mL), 25 °C, air, 24 h. The corresponding dihydrochlorides of **Gua-4** was used as ligand precursor.

[b] Calibrated GC conversions of **1a** using biphenyl as an internal standard.

[c] Determinded by HPLC analysis of the corresponding alcohol after oxidation.

Assignment of Stereochemistry

Due to the established retention of configuration at the boron-bound stereocenters after oxidation of boronates, the absolute (*R*/*S*) configurations of chiral allyl boronate **2a** and the corresponding allylic alcohol **3a** were assigned as *R*, according to the literature.[1] The absolute configurations of all other allylic compounds were assigned by analogy.

The absolute (*R*/*S*) configuration of the chiral homoallylic alcohol compound **5a** was revealed as 1*S*,2*R* by the crystal structure of its ester derivative **5a′**.

The configuration of the C=C bond in the chiral homoallylic alcohol compound **5a** was revealed as *E* by the crystal structure of its ester derivative **5a′**.

The absolute (*R*/*S*) configuration of the arylated derivative **6a** was assigned as *R*, according to the literature.[7]

X-ray Crystal Data

Crystal Structure Determination: The Esterification Derivative of Chiral *Z*-Homoallylic Alcohol 5a′

The crystal of **5a′** was grown in a 4 mL vial, with EtOH and *n*hexane as good and poor solvents, respectively. A colorless needle-like specimen of $C_{40}H_{35}NO_4$, approximate dimensions 0.21 mm x 0.13 mm x 0.1 mm, was used for the X-ray crystallographic analysis. The data was measured on a Bruker D8 VENTURE diffractometer using graphite-monochromated Cu Kα radiation. The crystal was kept at 193.00 K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using intrinsic phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal data for $C_{40}H_{35}NO_4$ (M =593.69 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.2097(2) Å, b = 11.8294(5) Å, c = 56.908(2) Å, V = 3507.1(2) Å^3, Z = 4, T = 193.00 K, μ(CuKα) = 0.571 mm^{-1}, *Dcalc* = 1.124 g/cm^3, 122533 reflections measured (6.212° ≤ 2Θ ≤ 137.524°), 6507 unique (R_{int} = 0.0973, R_{sigma} = 0.0365) which were used in all calculations. The final R_1 was 0.0386 (I > 2σ(I)) and wR_2 was 0.1015 (all data). More details are listed in the **Table S4** below. The ORTEP drawing of **5a′** is demonstrated in **Figure S2**.

CCDC 2504333 contains the supplementary crystallographic data for **5a′**. The data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S4 Sample and crystal data for **5a′**.

Identification code	cu_20251117_ZZ_CDLG_1S_2R_0m
Empirical formula	$C_{40}H_{35}NO_4$
Formula weight	593.69
Temperature/K	193.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.2097(2)
b/Å	11.8294(5)
c/Å	56.908(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3507.1(2)
Z	4
ρ_{calc}g/cm^3	1.124
μ/mm^{-1}	0.571
F(000)	1256.0
Crystal size/mm^3	0.21 × 0.13 × 0.1
Radiation	CuKα (λ= 1.54178)
2Θ range for data collection/°	6.212 to 137.524
Index ranges	-6 ≤ h ≤ 6, -14 ≤ k ≤ 14, -68 ≤ l ≤ 68

Reflections collected	122533
Independent reflections	6507 [R_{int} = 0.0973, R_{sigma} = 0.0365]
Data/restraints/parameters	6507/0/408
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.0974
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1015
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.13
Flack parameter	0.11(9)

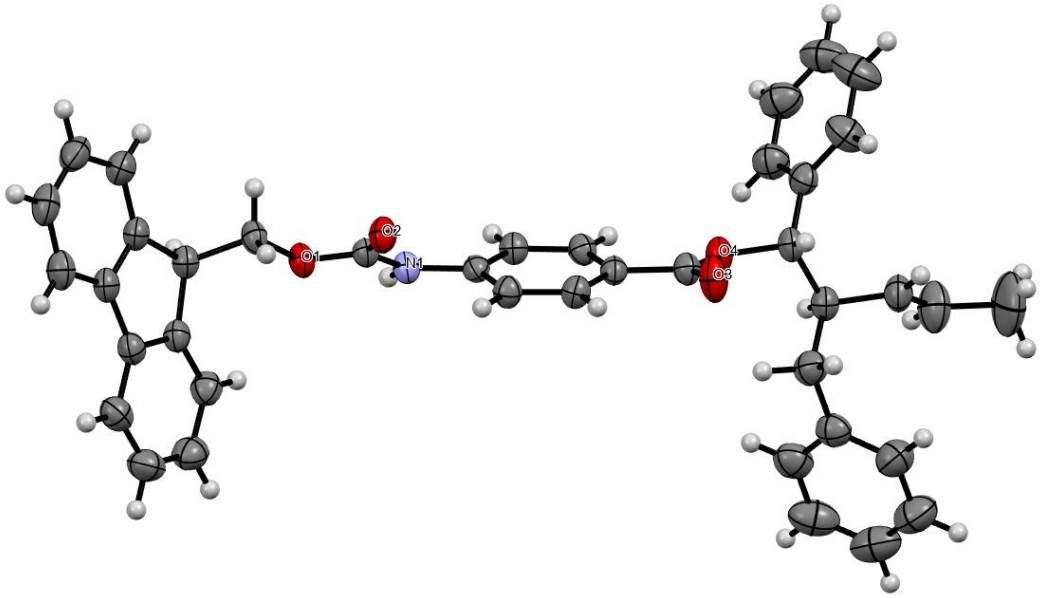


Figure S2 ORTEP drawing of Esterification product **5a′** with thermal ellipsoids at 50% probability levels. The labels of carbon and hydrogen atoms are omitted for clarity.

References

[1] A. Zhang, H. Zhang, T. Jin, L. Ge, X. Ma, J. Tang, J. Liu, C. H. Tan, R. Lee and Y. Ge, *Adv. Synth. Catal.* 2024, **367**, e202401322.

[2] (a) S. Park and S. J. Malcolmson, *ACS Catal.* 2018, **8**, 8468; (b) Y. Ma, B. R. P. Reddy and X. Bi, *Org. Lett.* 2019, **21**, 9860.

[3] W. Yuan and S. Ma, *Org. Biomol. Chem.* 2012, **10**, 7266.

[4] (a) Y. Ge, X. Y. Cui, S. M. Tan, H. Jiang, J. Ren, N. Lee, R. Lee and C. H. Tan, *Angew. Chem. Int. Ed.* 2019, **58**, 2382; (b) Q. Guan, Y. Ji, Q. Zhao and C. Zhang, *CCS Chem.* 2022, **4**, 1545.

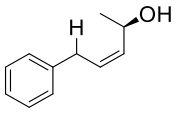
[5] W. Zhang, W. Xu, F. Zhang, J. Li, M. Liu and W. Li, *Res. Chem. Intermed.* 2011, **38**, 957.

[6] Y. Xi and J. F.Hartwig, *J. Am. Chem. Soc.* 2016, **138**, 6703.

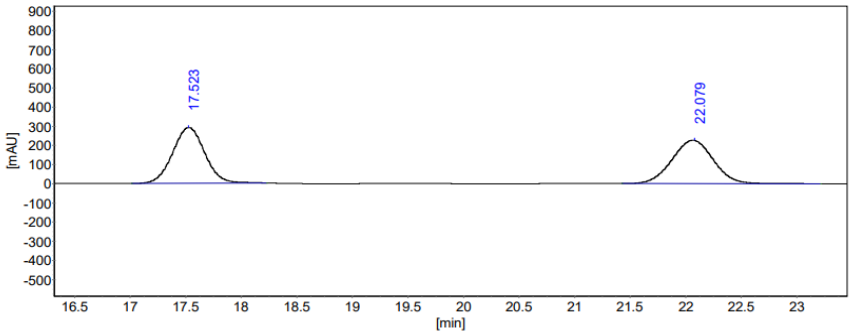
[7] L. Chausset-Boissarie, K. Ghozati, E. LaBine, J. L. Y. Chen, V. K. Aggarwal and C. M. Crudden, *Chem. - Eur. J.* 2013, **19**, 17698.

HPLC Traces of Chiral Compounds

Compound **3a**:



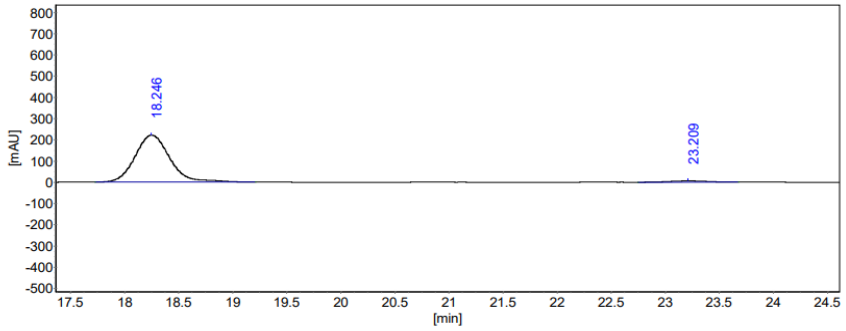
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		17.523	290150.4	5850018.3	49.8841	49.8841	+ BB
2		22.079	226379.0	5877206.6	50.1159	50.1159	+ BB
	Total:		**516529.4**	**11727224.9**	**100.0000**	**100.0000**	

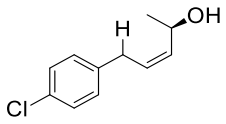
Chiral:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		18.246	220466.4	4895476.3	96.9861	96.9861	+ BB
2		23.209	6259.2	152127.8	3.0139	3.0139	+ BB
	Total:		**226725.6**	**5047604.1**	**100.0000**	**100.0000**	

Compound **3b**:



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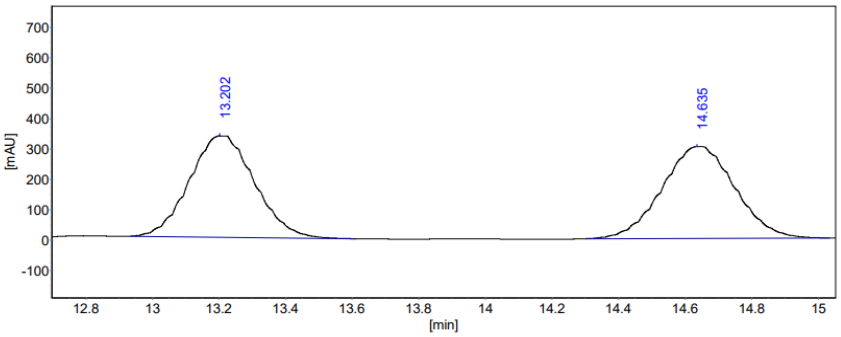
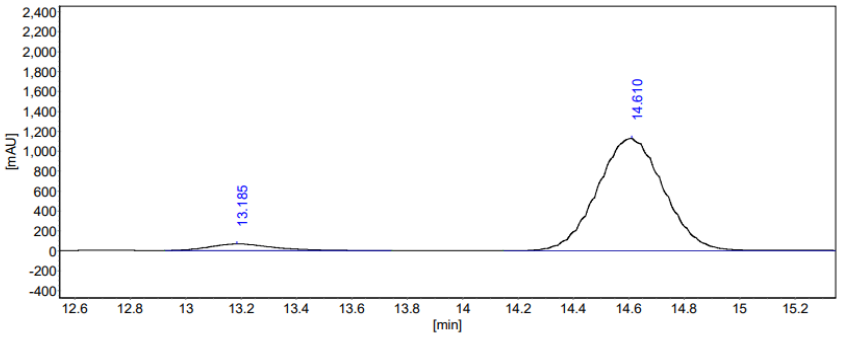


Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.202	333347.4	4514341.2	49.6612	49.6612	+ BB
2		14.635	301771.4	4575928.1	50.3388	50.3388	+ BB
	Total:		**635118.8**	**9090269.2**	**100.0000**	**100.0000**	

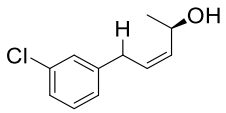
Chiral:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.185	65768.6	1042196.5	5.2471	5.2471	+ BB
2		14.610	1129951.8	18820274.2	94.7529	94.7529	+ BB
	Total:		**1195720.4**	**19862470.8**	**100.0000**	**100.0000**	

Compound **3c**:



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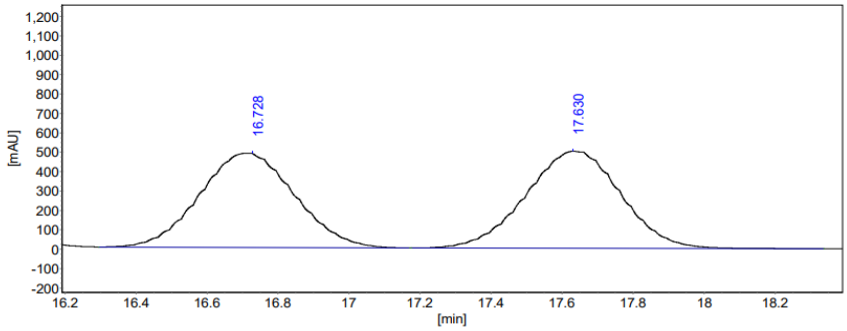
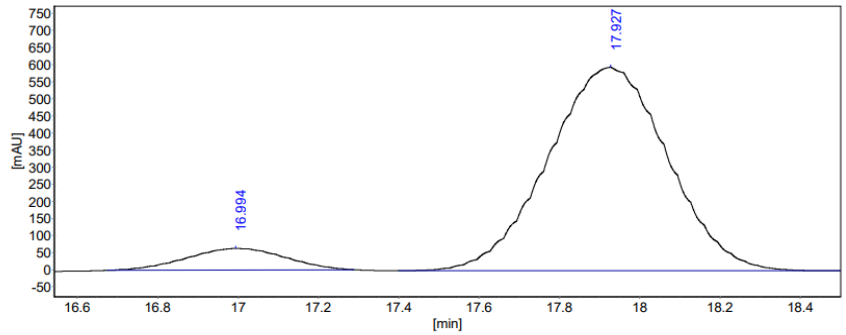


Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		16.728	485637.0	9028009.1	49.2069	49.2069	+ BB
2		17.630	500680.6	9319036.4	50.7931	50.7931	+ BB
	Total:		**986317.6**	**18347045.5**	**100.0000**	**100.0000**	

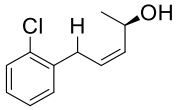
Chiral:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		16.994	63073.0	1073938.6	8.0380	8.0380	+ BB
2		17.927	595497.7	12286763.4	91.9620	91.9620	+ BB
	Total:		**658570.7**	**13360702.0**	**100.0000**	**100.0000**	

Compound **3d**:



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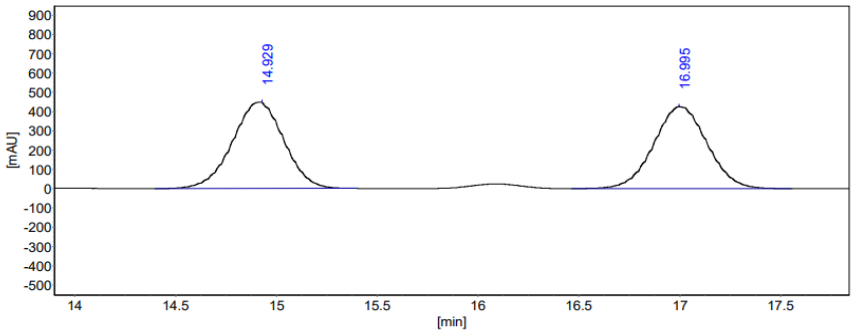
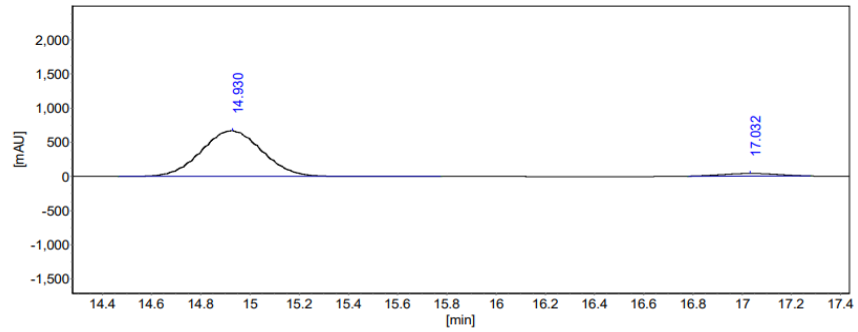


Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.929	447321.9	7956270.2	50.3946	50.3946	+ BB
2		16.995	425945.1	7831666.5	49.6054	49.6054	+ BB
	Total:		**873267.0**	**15787936.7**	**100.0000**	**100.0000**	

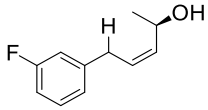
Chiral:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.930	669617.1	11530080.3	94.9374	94.9374	+ BB
2		17.032	39347.8	614847.3	5.0626	5.0626	+ BB
	Total:		**708964.9**	**12144927.6**	**100.0000**	**100.0000**	

Compound **3e**:



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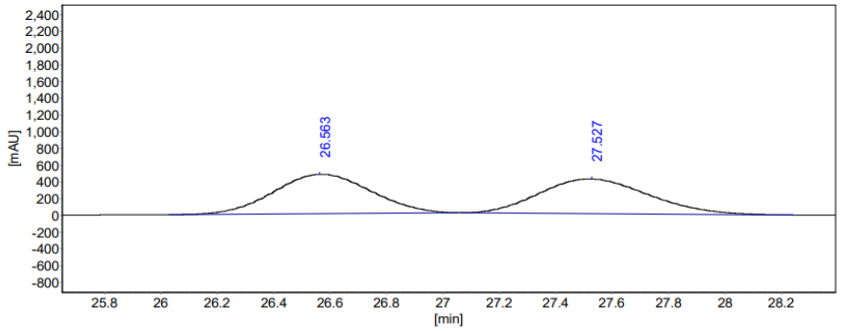
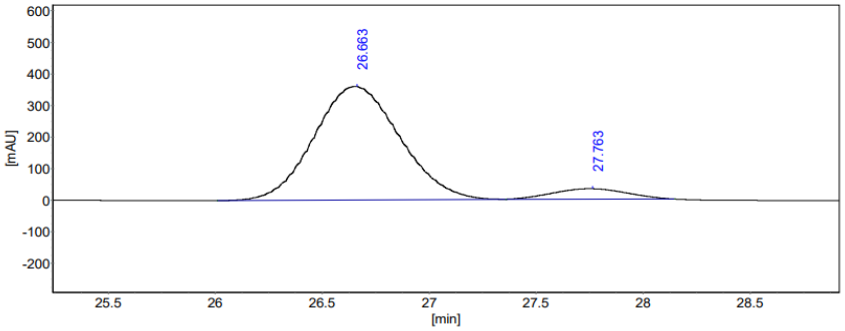


Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		26.563	470756.8	11298649.9	50.2769	50.2769	+ BB
2		27.527	414974.7	11174183.1	49.7231	49.7231	+ BB
	Total:		**885731.5**	**22472833.0**	**100.0000**	**100.0000**	

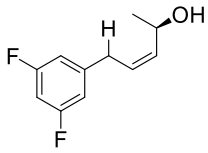
Chiral:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		26.663	359815.7	10005374.3	92.6595	92.6595	+ BB
2		27.763	33044.8	792631.8	7.3405	7.3405	+ BB
	Total:		**392860.5**	**10798006.1**	**100.0000**	**100.0000**	

Compound **3f**:



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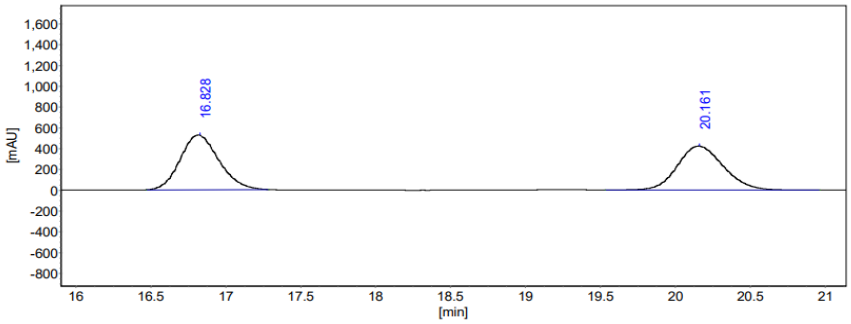
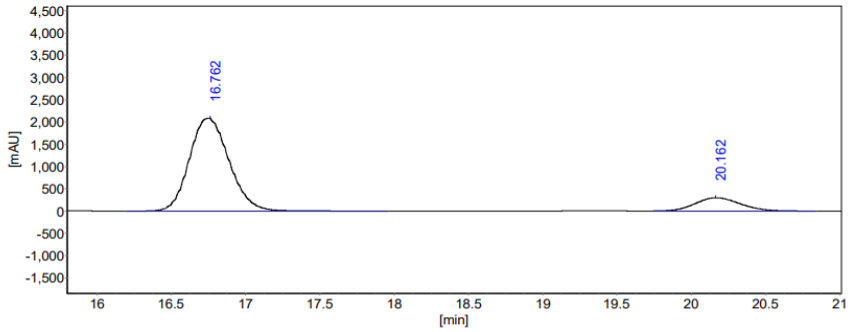


Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		16.828	527386.2	9438554.5	51.0021	51.0021	+ BB
2		20.161	424710.1	9067649.4	48.9979	48.9979	+ BB
	Total:		**952096.3**	**18506203.9**	**100.0000**	**100.0000**	

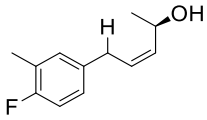
Chiral:



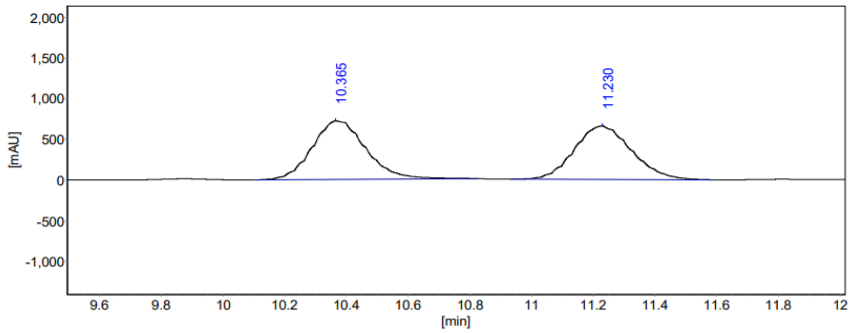
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		16.762	2086252.4	38691995.2	86.0698	86.0698	+ BB
2		20.162	298146.1	6262206.6	13.9302	13.9302	+ BB
	Total:		**2384398.5**	**44954201.8**	**100.0000**	**100.0000**	

Compound **3g**:



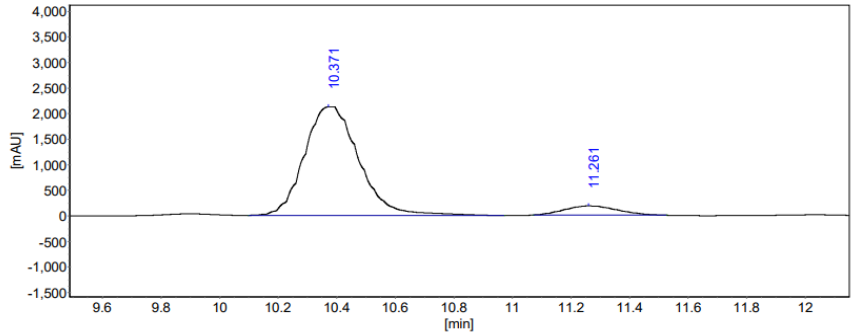
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		10.365	719282.8	8698902.0	50.6527	50.6527	+ BB
2		11.230	659205.5	8474711.6	49.3473	49.3473	+ BB
	Total:		**1378488.3**	**17173613.5**	**100.0000**	**100.0000**	

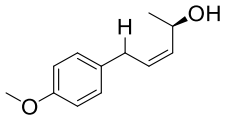
Chiral:



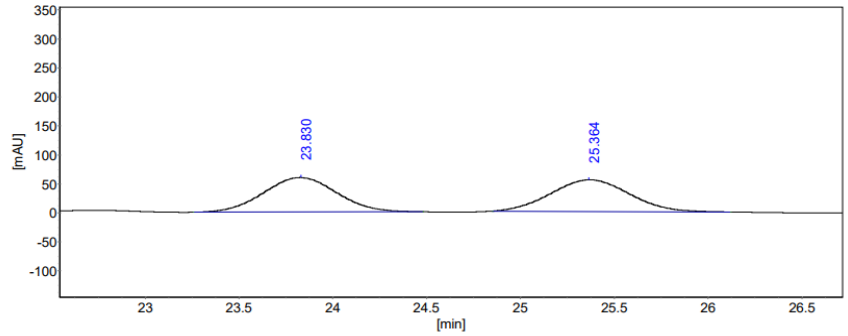
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		10.371	2125565.6	27459569.2	92.3811	92.3811	+ BB
2		11.261	180974.8	2264644.5	7.6189	7.6189	+ BB
	Total:		**2306540.4**	**29724213.6**	**100.0000**	**100.0000**	

Compound **3h**:



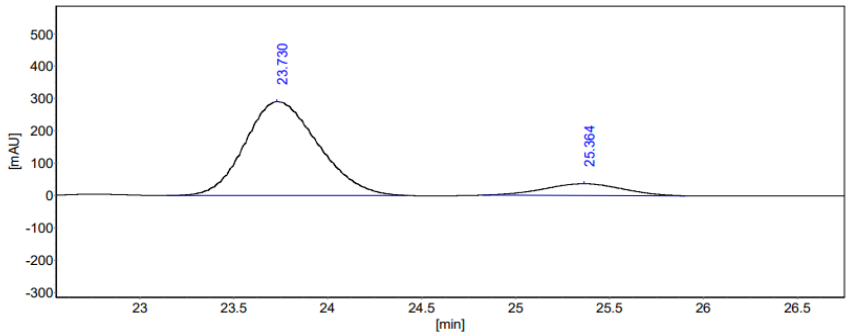
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		23.830	59553.1	1617964.0	50.4326	50.4326	+ BB
2		25.364	54536.7	1590208.3	49.5674	49.5674	+ BB
	Total:		**114089.8**	**3208172.3**	**100.0000**	**100.0000**	

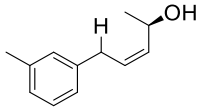
Chiral:



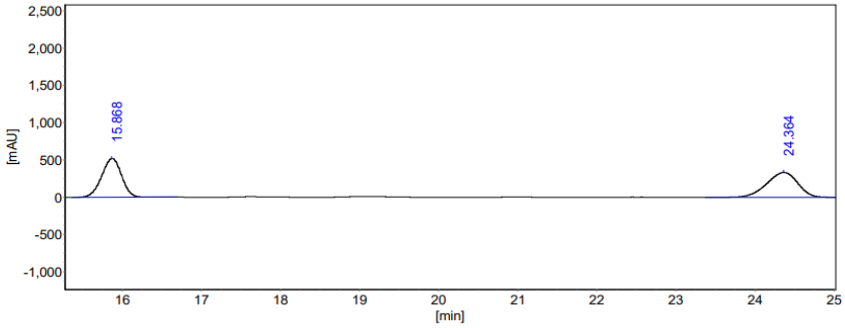
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		23.730	290708.9	7851209.2	88.2057	88.2057	+ BB
2		25.364	36220.2	1049810.1	11.7943	11.7943	+ BB
	Total:		**326929.1**	**8901019.3**	**100.0000**	**100.0000**	

Compound **3i**:



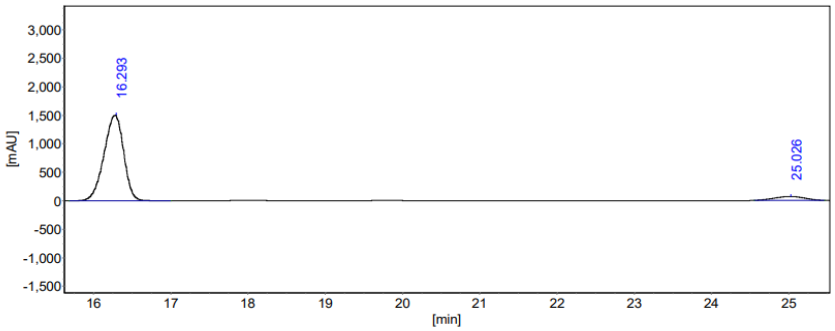
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		15.868	518411.5	9118637.3	49.9176	49.9176	+ BB
2		24.364	333829.9	9148724.9	50.0824	50.0824	+ BB
	Total:		**852241.4**	**18267362.2**	**100.0000**	**100.0000**	

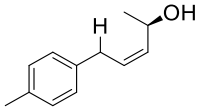
Chiral:



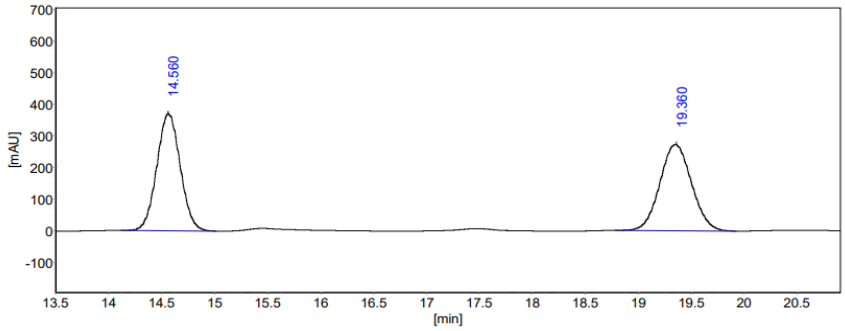
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		16.293	1500175.8	26561223.1	93.3929	93.3929	+ BB
2		25.026	69280.4	1879087.7	6.6071	6.6071	+ BB
	Total:		**1569456.2**	**28440310.7**	**100.0000**	**100.0000**	

Compound **3j**:



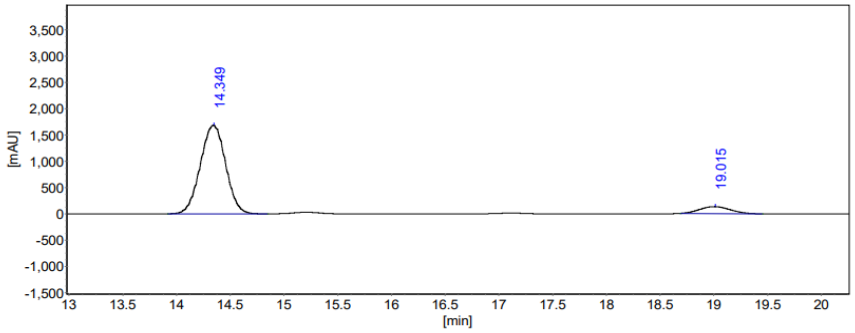
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.560	371476.9	5717408.8	50.1320	50.1320	+ BB
2		19.360	273787.5	5687295.5	49.8680	49.8680	+ BB
	Total:		**645264.4**	**11404704.3**	**100.0000**	**100.0000**	

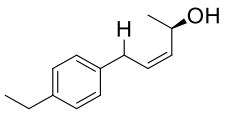
Chiral:



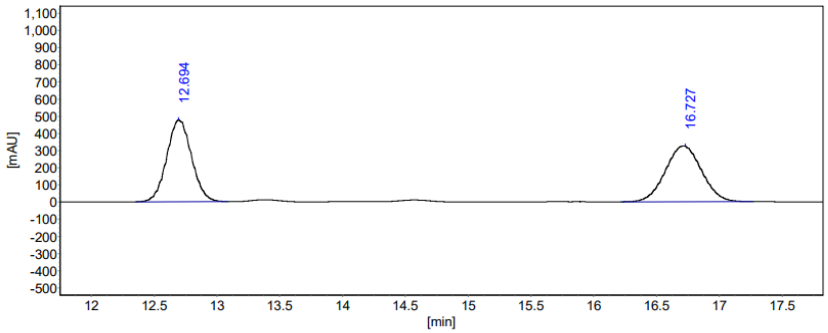
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.349	1688550.8	27521946.9	91.1640	91.1640	+ BB
2		19.015	134166.6	2667541.3	8.8360	8.8360	+ BB
	Total:		**1822717.4**	**30189488.2**	**100.0000**	**100.0000**	

Compound **3k**:



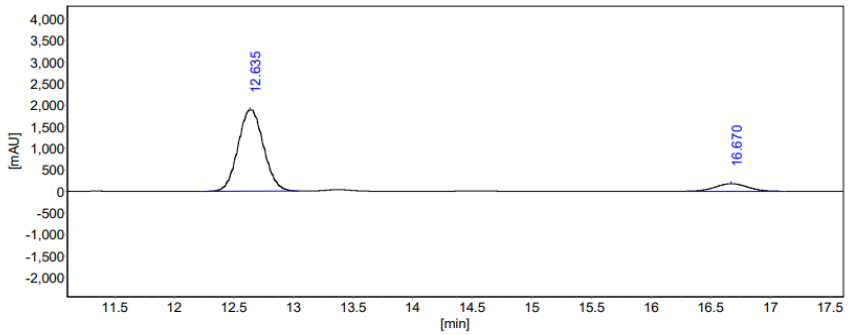
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		12.694	478224.2	6546171.6	50.1235	50.1235	+ BB
2		16.727	325485.1	6513912.2	49.8765	49.8765	+ BB
	Total:		**803709.3**	**13060083.8**	**100.0000**	**100.0000**	

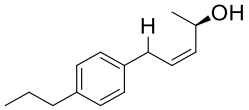
Chiral:



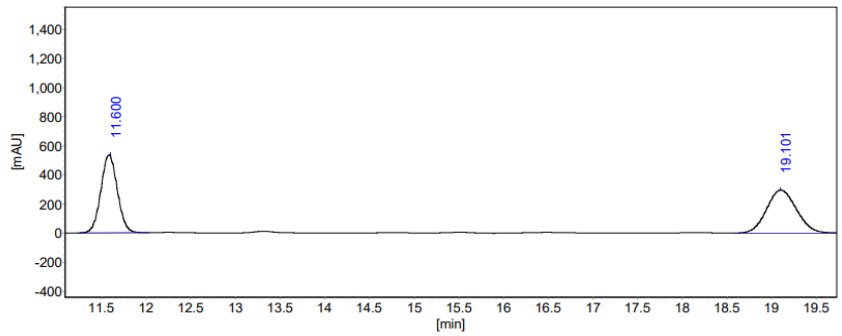
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		12.635	1883588.6	27955013.0	89.6011	89.6011	+ BB
2		16.670	175455.4	3244390.4	10.3989	10.3989	+ BB
	Total:		**2059044.0**	**31199403.5**	**100.0000**	**100.0000**	

Compound **3l**:



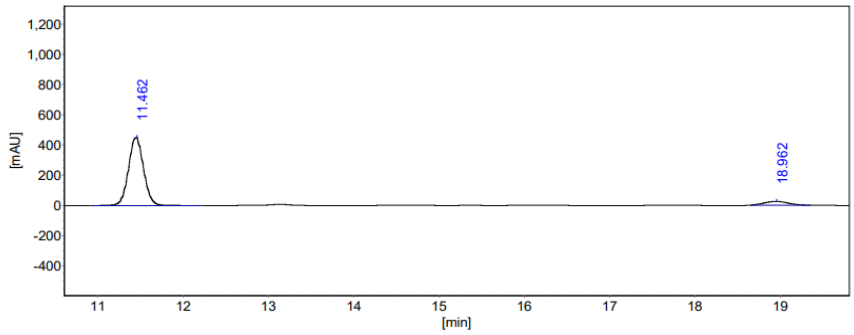
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.600	535537.2	6888580.9	49.9088	49.9088	+ BB
2		19.101	295405.1	6913743.9	50.0912	50.0912	+ BB
	Total:		**830942.3**	**13802324.8**	**100.0000**	**100.0000**	

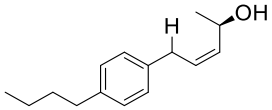
Chiral:



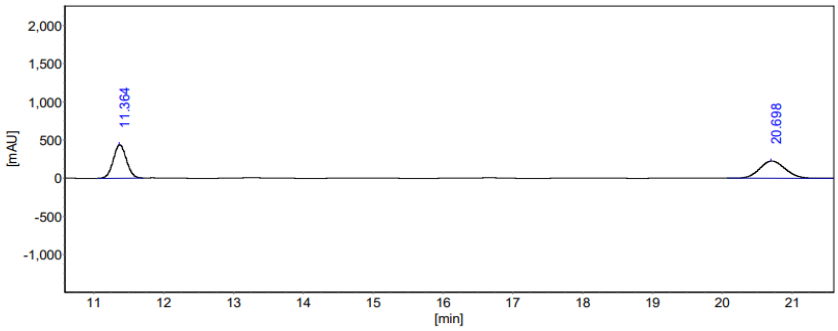
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.462	451412.4	5566085.5	91.9794	91.9794	+ BB
2		18.962	25011.8	485360.7	8.0206	8.0206	+ BB
	Total:		**476424.2**	**6051446.2**	**100.0000**	**100.0000**	

Compound **3m**:



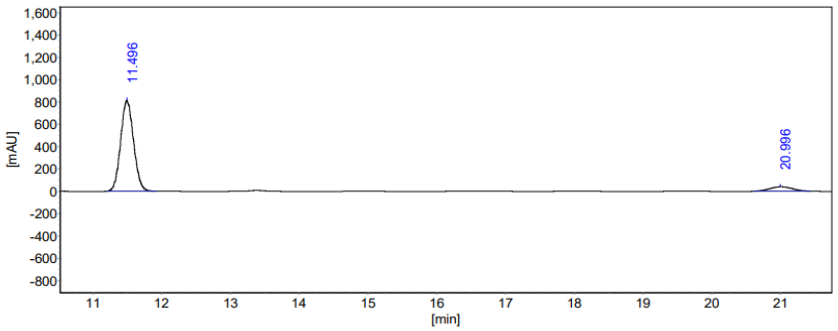
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.364	438867.0	5694992.6	49.5537	49.5537	+ BB
2		20.698	225835.6	5797567.8	50.4463	50.4463	+ BB
	Total:		**664702.6**	**11492560.4**	**100.0000**	**100.0000**	

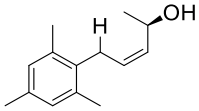
Chiral:



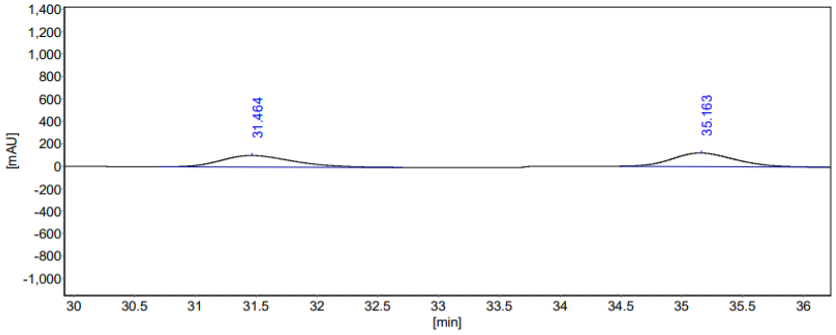
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.496	817849.4	10630977.8	91.9023	91.9023	+ BB
2		20.996	40723.8	936723.2	8.0977	8.0977	+ BB
	Total:		**858573.2**	**11567701.0**	**100.0000**	**100.0000**	

Compound **3n**:



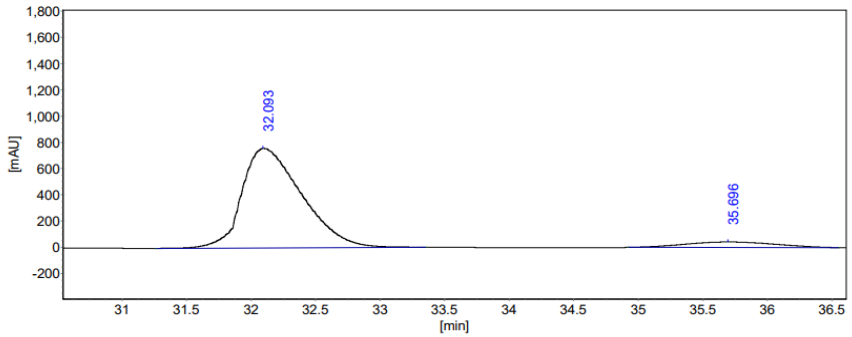
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		31.464	102776.7	4230533.4	49.6493	49.6493	+ BB
2		35.163	120579.5	4290296.4	50.3507	50.3507	+ BB
	Total:		**223356.2**	**8520829.8**	**100.0000**	**100.0000**	

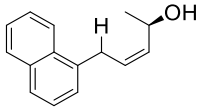
Chiral:



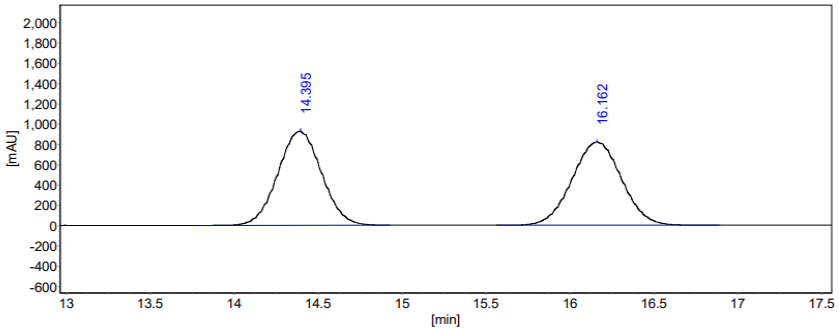
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		32.093	758508.0	24331171.9	92.0330	92.0330	+ BB
2		35.696	42732.5	2106283.5	7.9670	7.9670	+ BB
	Total:		**801240.5**	**26437455.4**	**100.0000**	**100.0000**	

Compound **3o**:



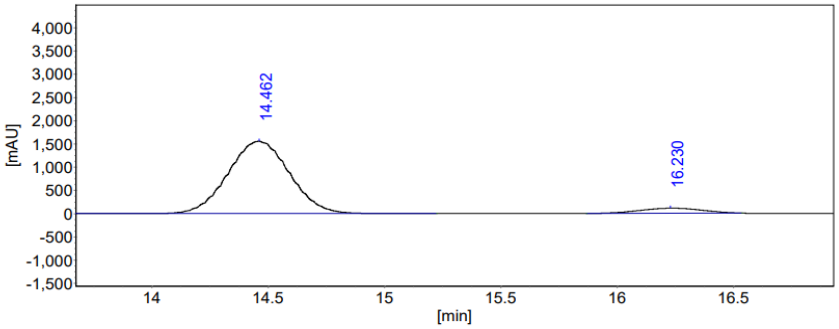
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.395	929184.0	16789416.2	49.8738	49.8738	+ BB
2		16.162	821998.1	16874395.6	50.1262	50.1262	+ BB
	Total:		**1751182.1**	**33663811.8**	**100.0000**	**100.0000**	

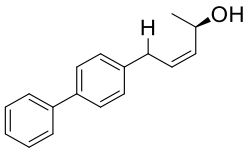
Chiral:



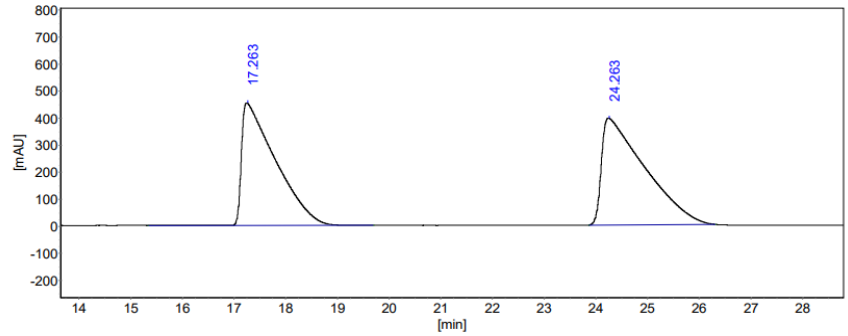
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.462	1561040.5	28738249.9	93.3201	93.3201	+ BB
2		16.230	110006.2	2057091.9	6.6799	6.6799	+ BB
	Total:		**1671046.7**	**30795341.8**	**100.0000**	**100.0000**	

Compound **3p**:



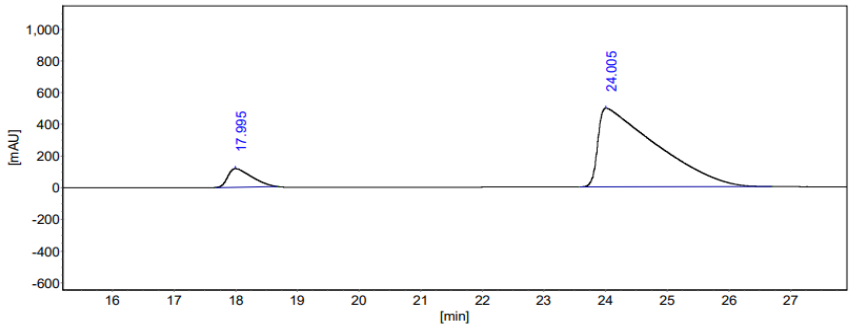
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		17.263	453194.6	20670600.7	47.3372	47.3372	+ BB
2		24.263	395280.7	22996092.2	52.6628	52.6628	+ BB
	Total:		**848475.3**	**43666692.9**	**100.0000**	**100.0000**	

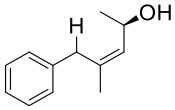
Chiral:



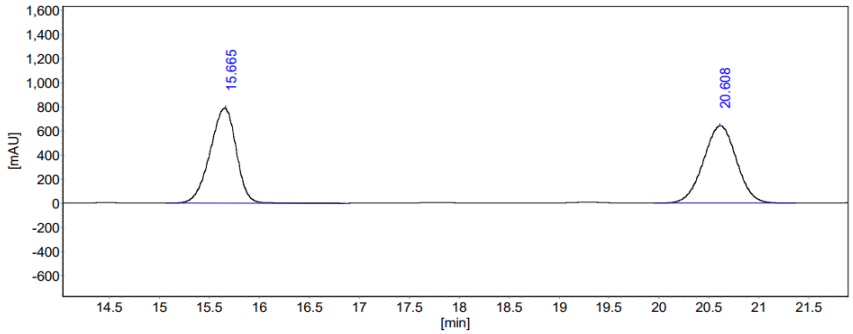
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		17.995	117751.1	3142835.6	8.8021	8.8021	+ BB
2		24.005	495143.2	32562642.2	91.1979	91.1979	+ BB
	Total:		**612894.3**	**35705477.7**	**100.0000**	**100.0000**	

Compound **3a-2Me**:



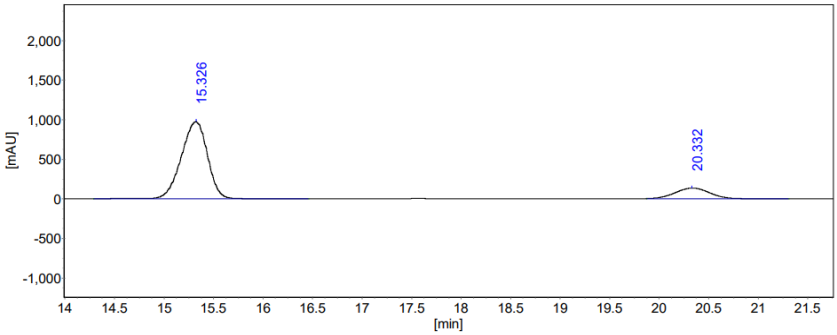
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		15.665	790142.4	14333358.3	49.1857	49.1857	+ BB
2		20.608	640613.9	14807974.9	50.8143	50.8143	+ BB
	Total:		**1430756.3**	**29141333.3**	**100.0000**	**100.0000**	

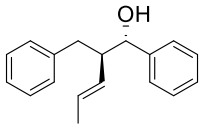
Chiral:



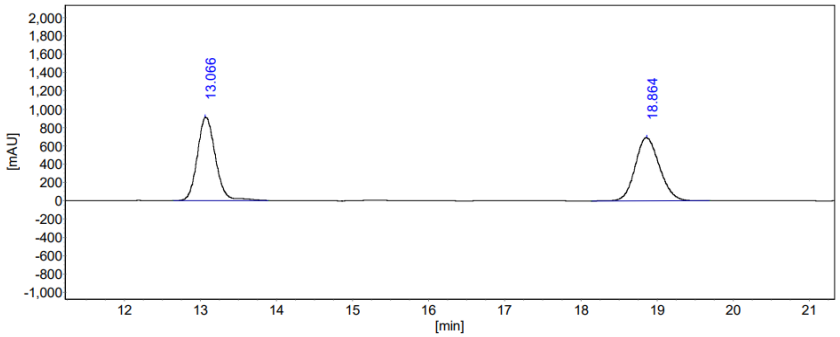
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		15.326	974562.4	17867795.7	84.7710	84.7710	+ BB
2		20.332	133810.6	3209926.0	15.2290	15.2290	+ BB
	Total:		**1108373.0**	**21077721.7**	**100.0000**	**100.0000**	

Compound **5a**:



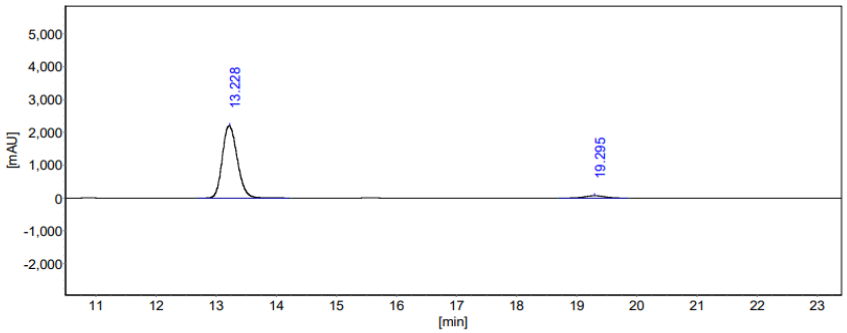
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.066	910238.2	15036591.0	49.5371	49.5371	+ BB
2		18.864	692086.0	15317613.4	50.4629	50.4629	+ BB
	Total:		**1602324.2**	**30354204.4**	**100.0000**	**100.0000**	

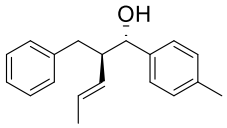
Chiral:



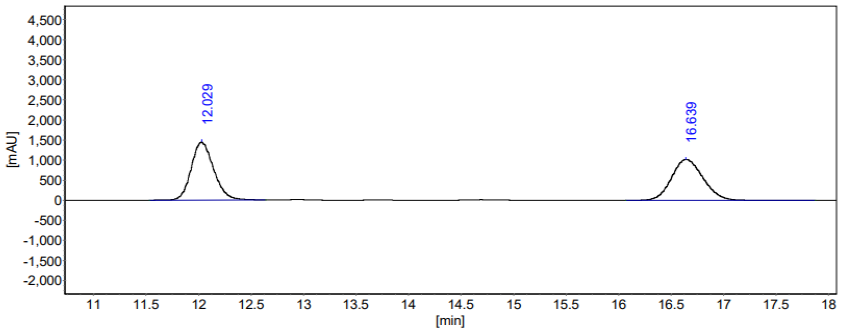
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.228	2203831.4	38122081.7	95.8025	95.8025	+ BB
2		19.295	72357.9	1670273.7	4.1975	4.1975	+ BB
	Total:		**2276189.3**	**39792355.4**	**100.0000**	**100.0000**	

Compound **5b**:



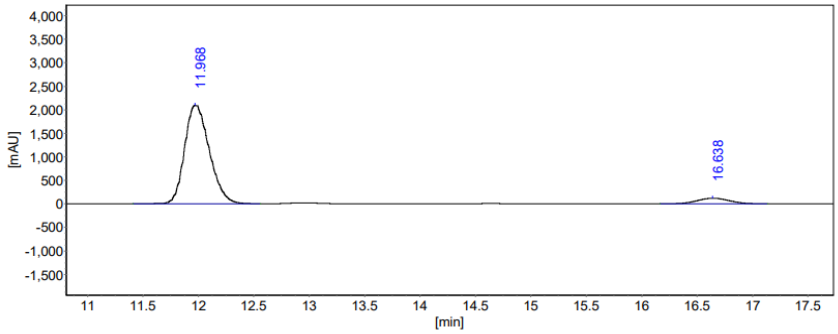
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		12.029	1448730.3	21543483.5	50.3871	50.3871	+ BB
2		16.639	1014459.8	21212473.4	49.6129	49.6129	+ BB
	Total:		**2463190.1**	**42755956.8**	**100.0000**	**100.0000**	

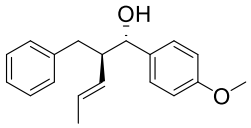
Chiral:



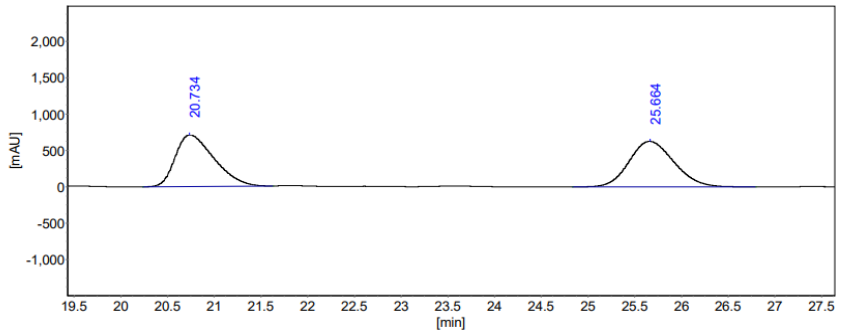
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.968	2089756.4	32470052.4	93.0594	93.0594	+ BB
2		16.638	119177.1	2421690.6	6.9406	6.9406	+ BB
	Total:		**2208933.5**	**34891743.0**	**100.0000**	**100.0000**	

Compound **5c**:



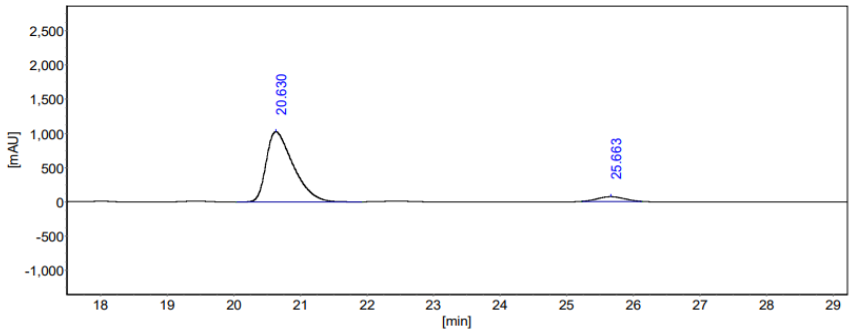
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		20.734	708974.0	20375721.8	49.4091	49.4091	+ BB
2		25.664	625818.3	20863055.2	50.5909	50.5909	+ BB
	Total:		**1334792.3**	**41238777.0**	**100.0000**	**100.0000**	

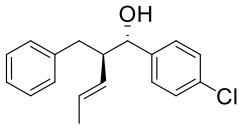
Chiral:



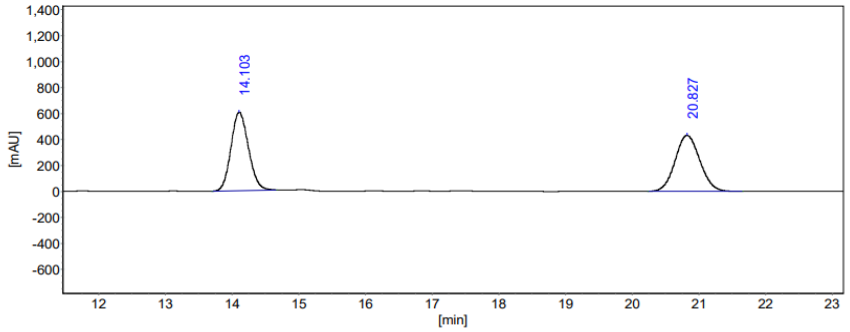
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		20.630	1028064.2	28871640.0	93.7850	93.7850	+ BB
2		25.663	69112.5	1913299.4	6.2150	6.2150	+ BB
	Total:		**1097176.7**	**30784939.3**	**100.0000**	**100.0000**	

Compound **5d**:



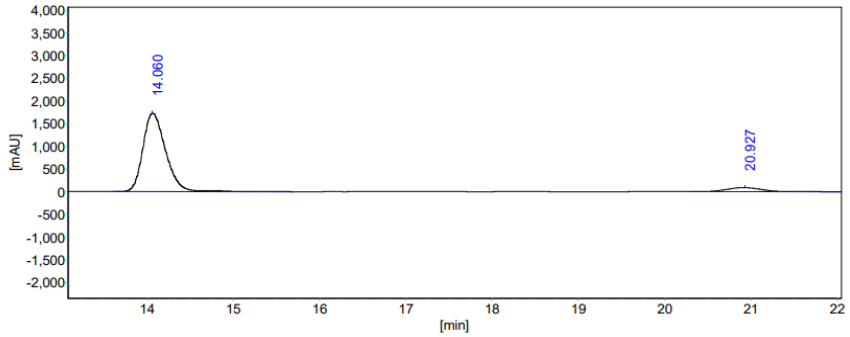
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.103	601918.3	11017982.6	49.7717	49.7717	+ BB
2		20.827	432365.0	11119070.4	50.2283	50.2283	+ BB
	Total:		**1034283.3**	**22137053.1**	**100.0000**	**100.0000**	

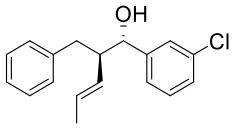
Chiral:



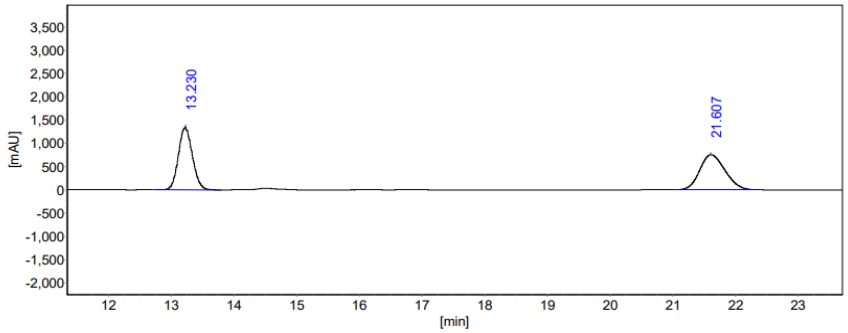
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		14.060	1730485.8	31768287.1	92.7974	92.7974	+ BB
2		20.927	89469.2	2465748.0	7.2026	7.2026	+ BB
	Total:		**1819955.0**	**34234035.2**	**100.0000**	**100.0000**	

Compound **5e**:



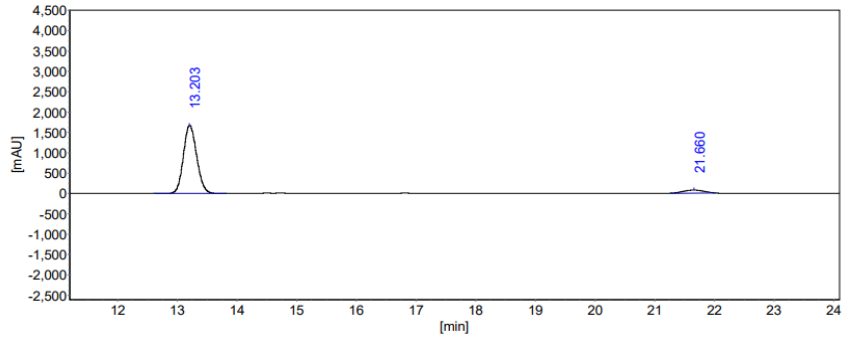
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.230	1341250.7	20773454.6	49.6166	49.6166	+ BB
2		21.607	753055.7	21094509.2	50.3834	50.3834	+ BB
	Total:		**2094306.4**	**41867963.8**	**100.0000**	**100.0000**	

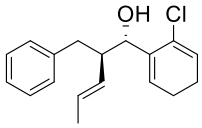
Chiral:



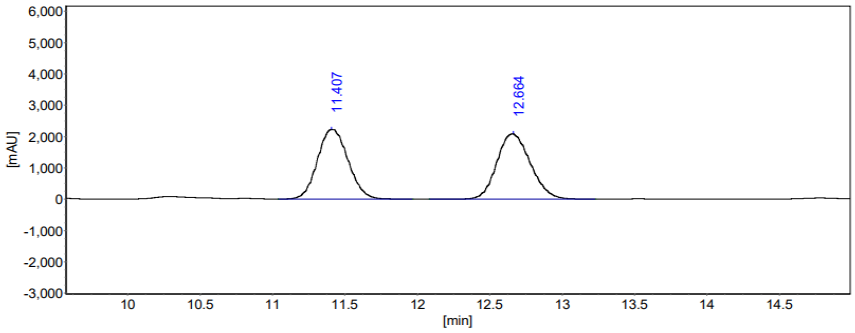
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		13.203	1668864.0	25947310.2	93.6201	93.6201	+ BB
2		21.660	74783.1	1768221.1	6.3799	6.3799	+ BB
	Total:		**1743647.1**	**27715531.3**	**100.0000**	**100.0000**	

Compound **5f**:



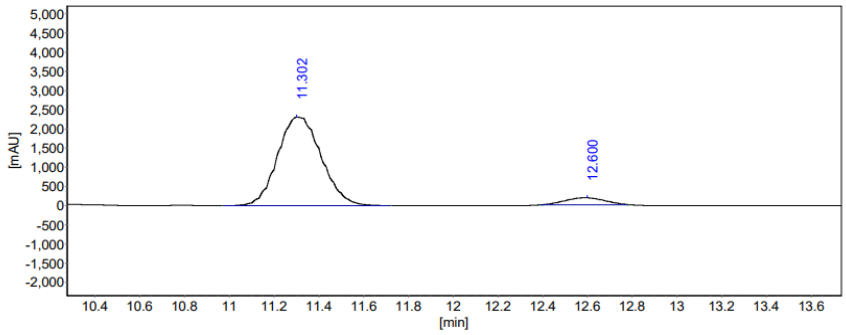
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.407	2222791.2	32644543.2	49.4017	49.4017	+ BB
2		12.664	2091121.2	33435268.6	50.5983	50.5983	+ BB
	Total:		**4313912.4**	**66079811.8**	**100.0000**	**100.0000**	

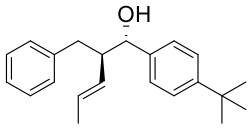
Chiral:



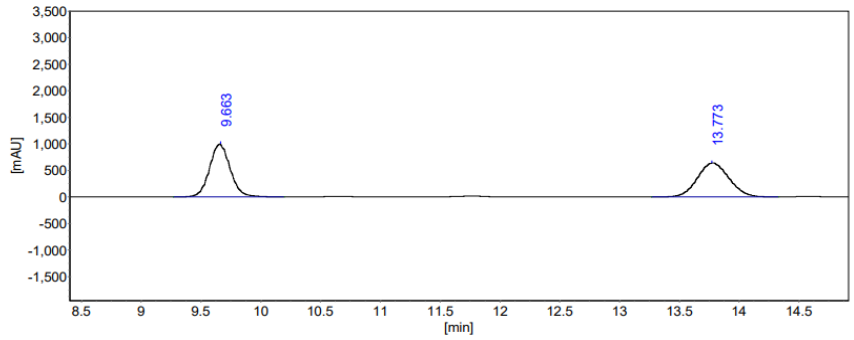
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		11.302	2313108.4	31217616.0	93.3296	93.3296	+ BB
2		12.600	183106.7	2231159.5	6.6704	6.6704	+ BB
	Total:		**2496215.1**	**33448775.5**	**100.0000**	**100.0000**	

Compound **5g**:



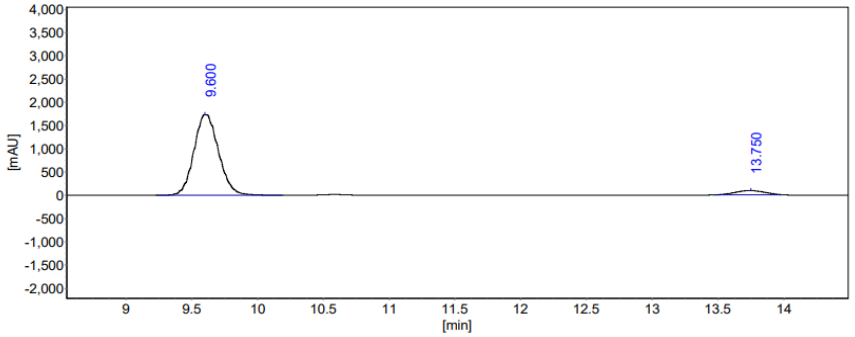
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		9.663	997313.9	11948770.6	50.4470	50.4470	+ BB
2		13.773	634467.2	11737008.6	49.5530	49.5530	+ BB
	Total:		**1631781.1**	**23685779.2**	**100.0000**	**100.0000**	

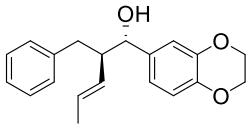
Chiral:



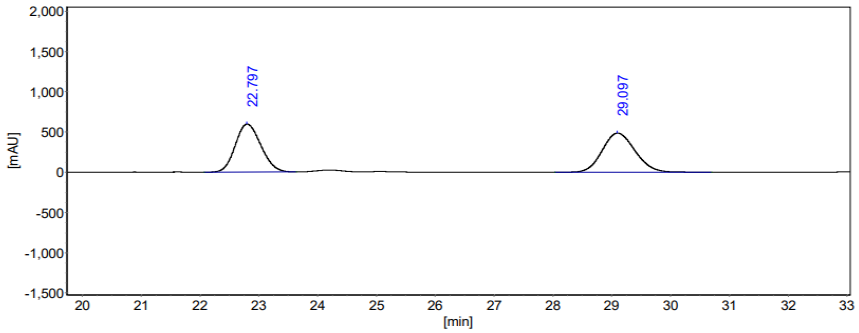
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		9.600	1735087.8	22557667.0	94.2119	94.2119	+ BB
2		13.750	90174.8	1385888.7	5.7881	5.7881	+ BB
	Total:		**1825262.6**	**23943555.7**	**100.0000**	**100.0000**	

Compound **5h**:



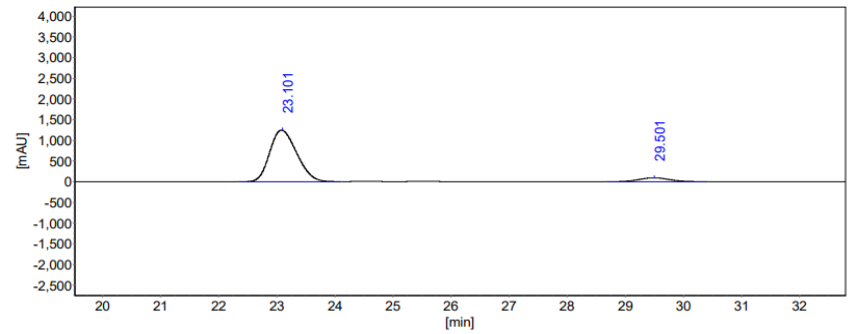
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		22.797	597574.6	18063883.2	48.9335	48.9335	+ BB
2		29.097	486311.3	18851288.5	51.0665	51.0665	+ BB
	Total:		**1083885.9**	**36915171.7**	**100.0000**	**100.0000**	

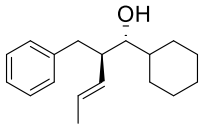
Chiral:



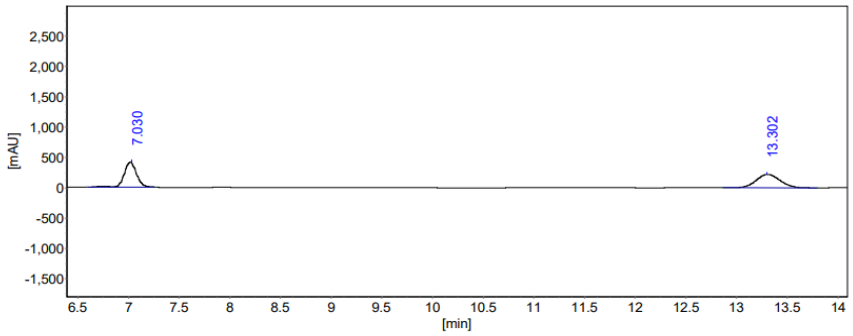
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		23.101	1244058.6	40180439.6	92.1635	92.1635	+ BB
2		29.501	92931.1	3416449.3	7.8365	7.8365	+ BB
	Total:		**1336989.7**	**43596888.9**	**100.0000**	**100.0000**	

Compound **5i**:



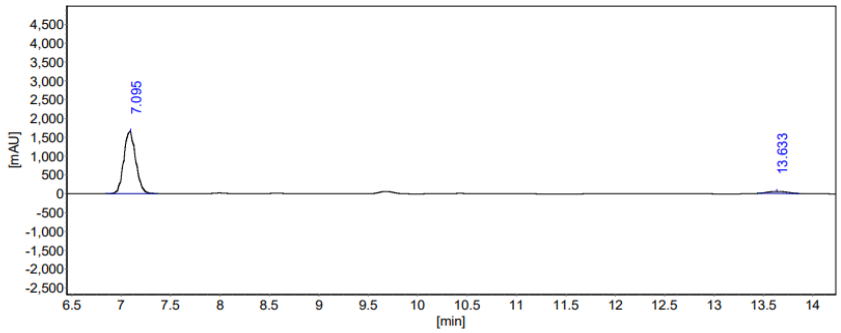
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		7.030	415462.3	3534230.5	49.5176	49.5176	+ BB
2		13.302	220334.0	3603091.1	50.4824	50.4824	+ BB
	Total:		**635796.3**	**7137321.6**	**100.0000**	**100.0000**	

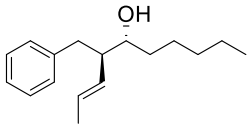
Chiral:



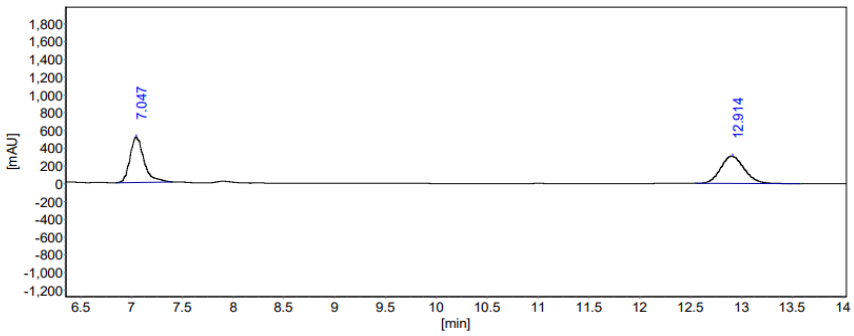
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		7.095	1660699.8	13871378.5	94.9520	94.9520	+ BB
2		13.633	55719.3	737446.8	5.0480	5.0480	+ BB
	Total:		**1716419.1**	**14608825.3**	**100.0000**	**100.0000**	

Compound **5j**:



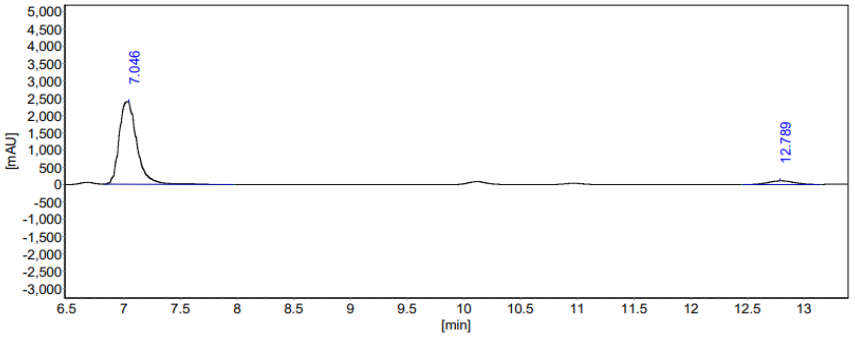
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		7.047	516090.4	4920271.0	49.4509	49.4509	+ BB
2		12.914	310335.1	5029540.6	50.5491	50.5491	+ BB
	Total:		**826425.5**	**9949811.5**	**100.0000**	**100.0000**	

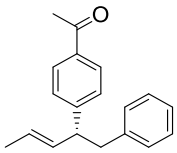
Chiral:



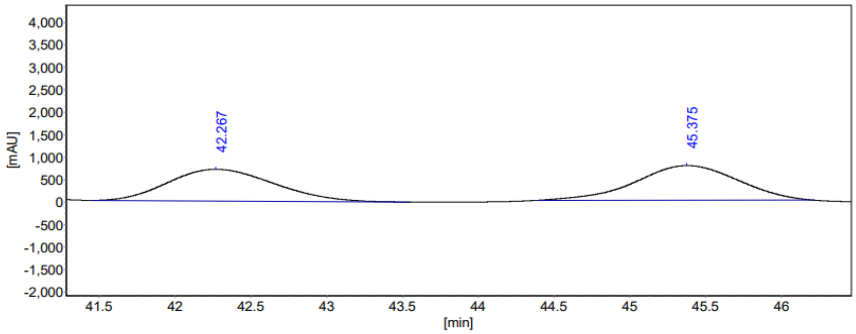
Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		7.046	2388489.6	25849202.7	93.9803	93.9803	+ BB
2		12.789	104676.1	1655721.9	6.0197	6.0197	+ BB
	Total:		**2493165.7**	**27504924.6**	**100.0000**	**100.0000**	

Compound **6a**:



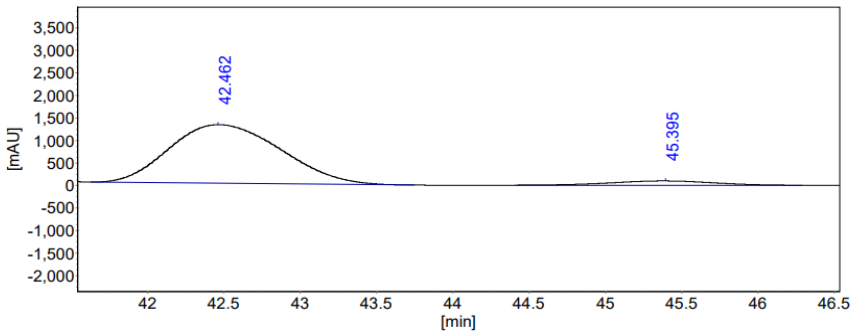
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		42.267	706199.4	34265400.5	48.4552	48.4552	+ BB
2		45.375	771922.6	36450166.1	51.5448	51.5448	+ BB
	Total:		**1478122.0**	**70715566.6**	**100.0000**	**100.0000**	

Chiral:

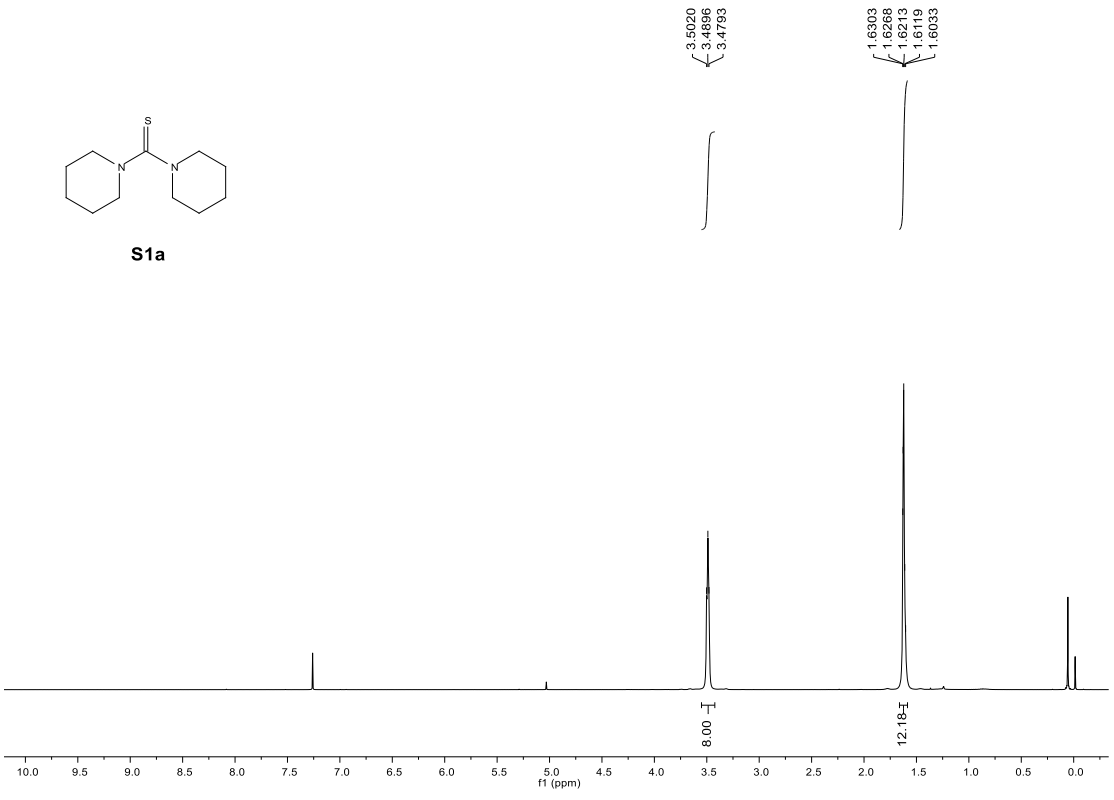


Analysis Results

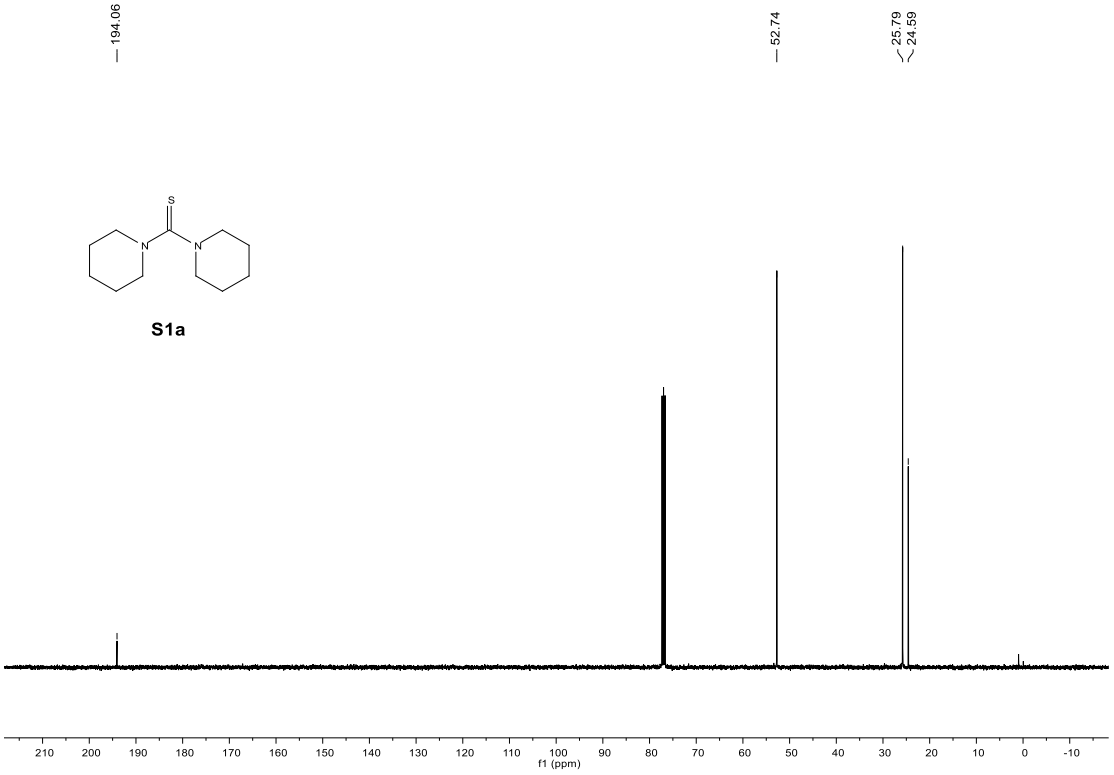
No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		42.462	1302270.4	66264650.2	93.6894	93.6894	+ BB
2		45.395	95107.8	4463355.6	6.3106	6.3106	+ BB
	Total:		**1397378.2**	**70728005.8**	**100.0000**	**100.0000**	

NMR Spectra

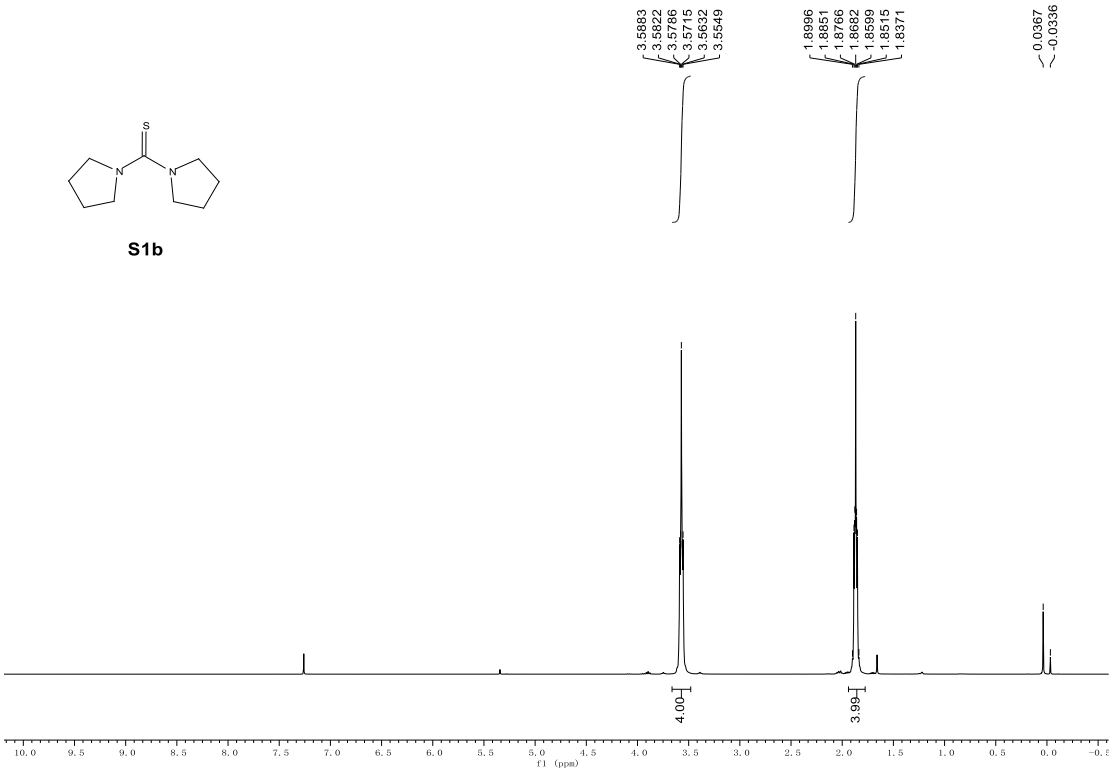
S1a ^{1}H NMR (400 MHz, $CDCl_3$)



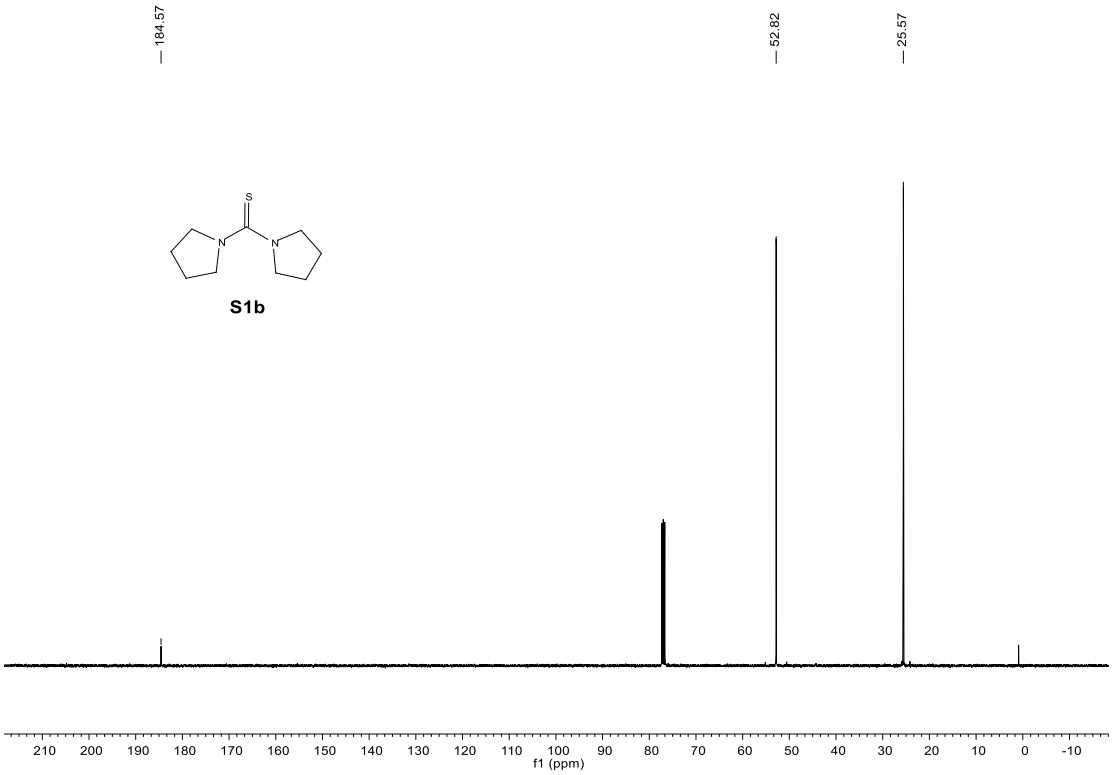
S1a $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



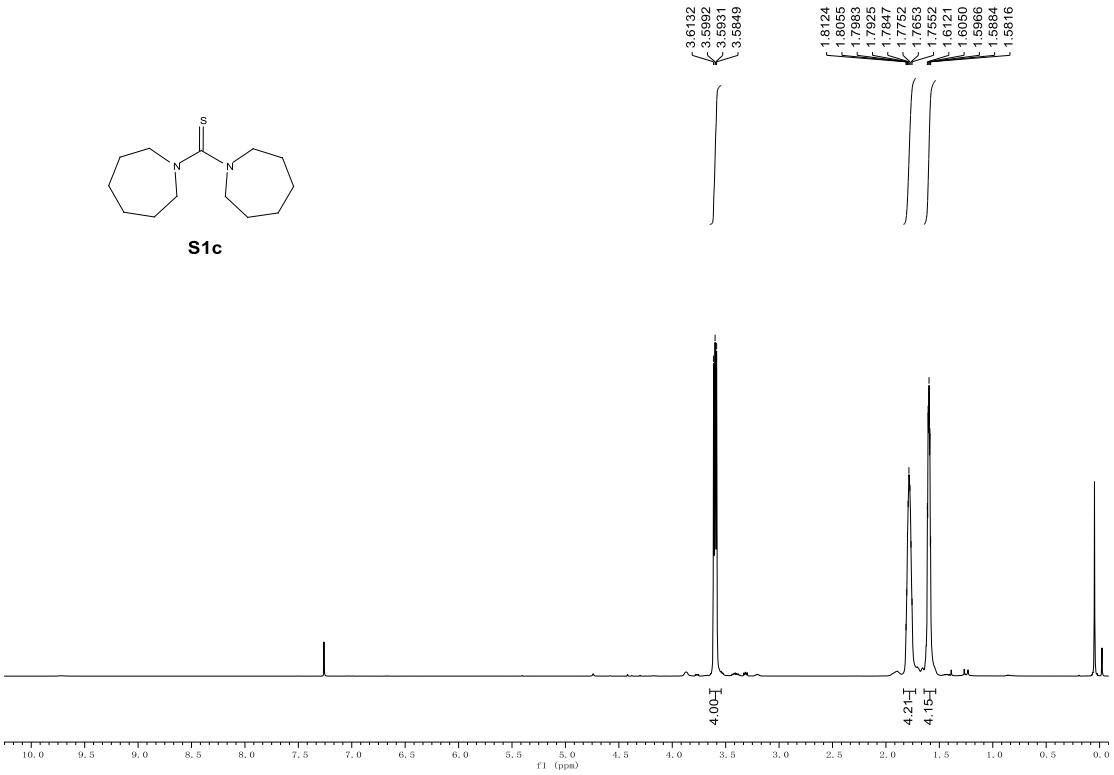
S1b ^{1}H NMR (400 MHz, $CDCl_3$)



S1b ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

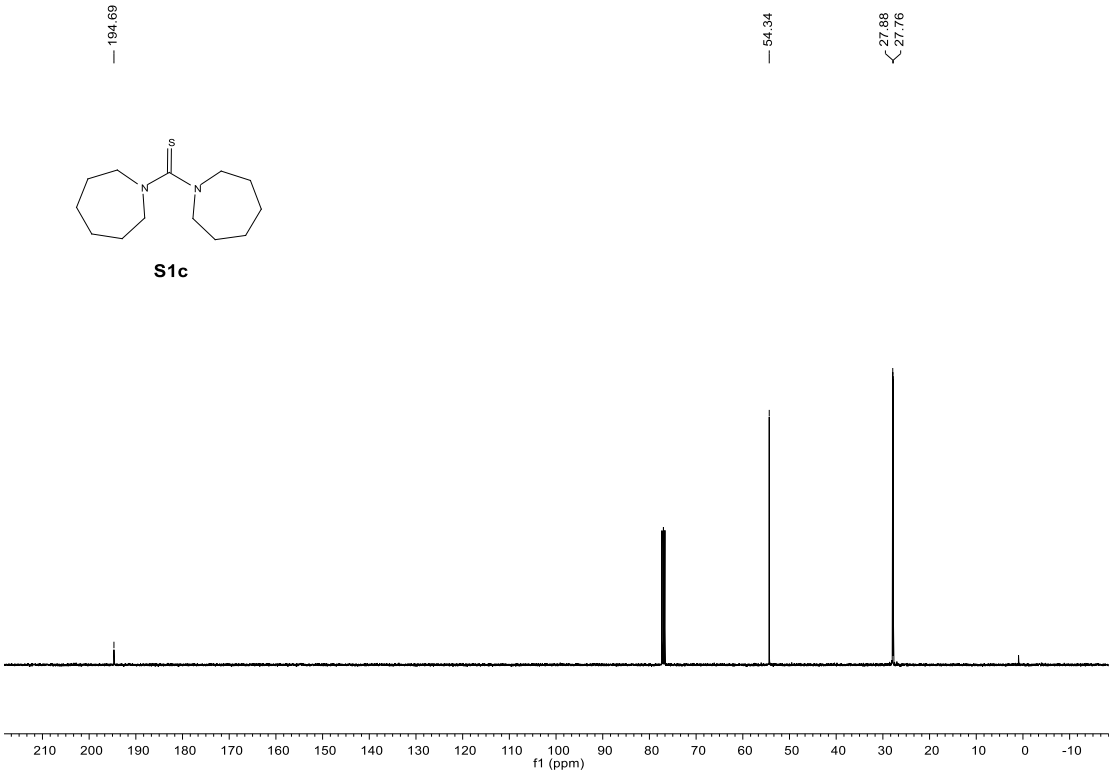


S1c ^{1}H NMR (400 MHz, $CDCl_3$)



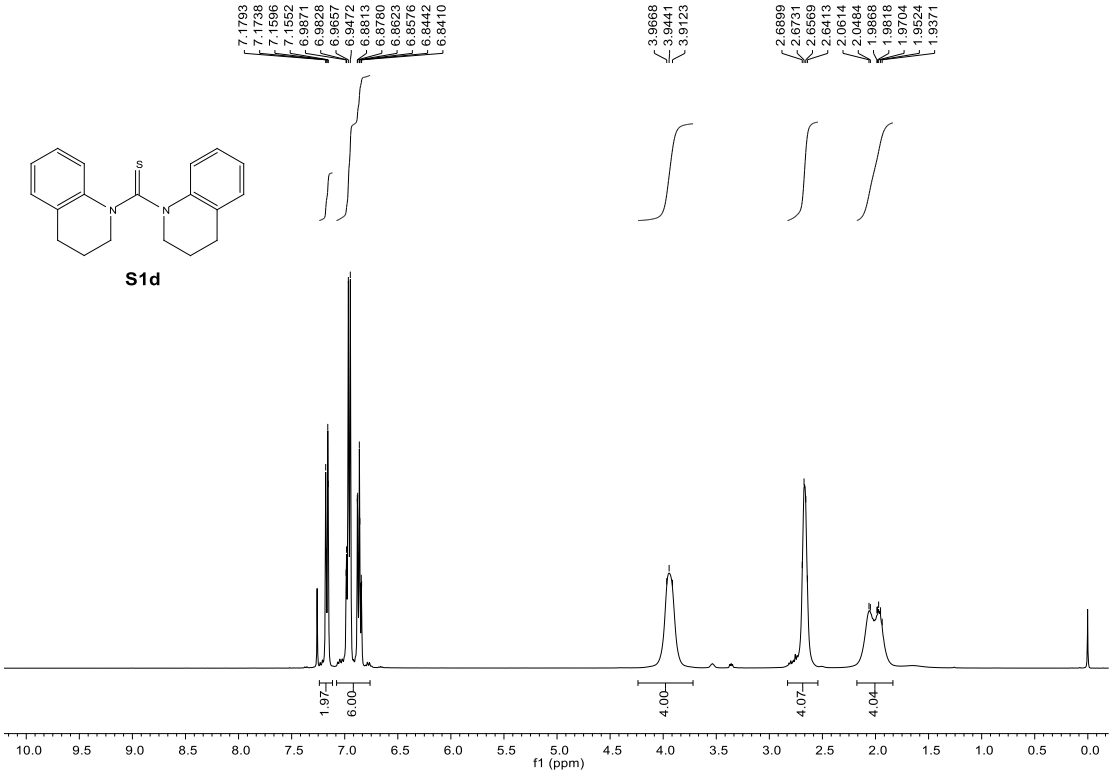
S1c

S1c ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

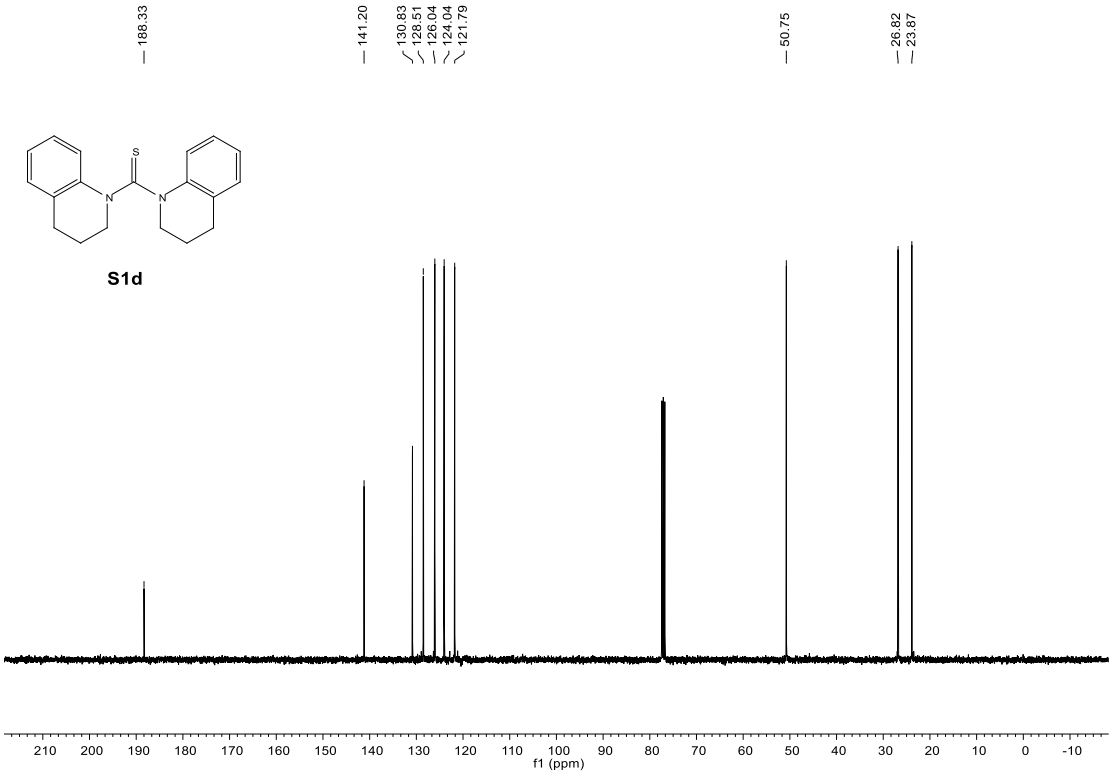


S1c

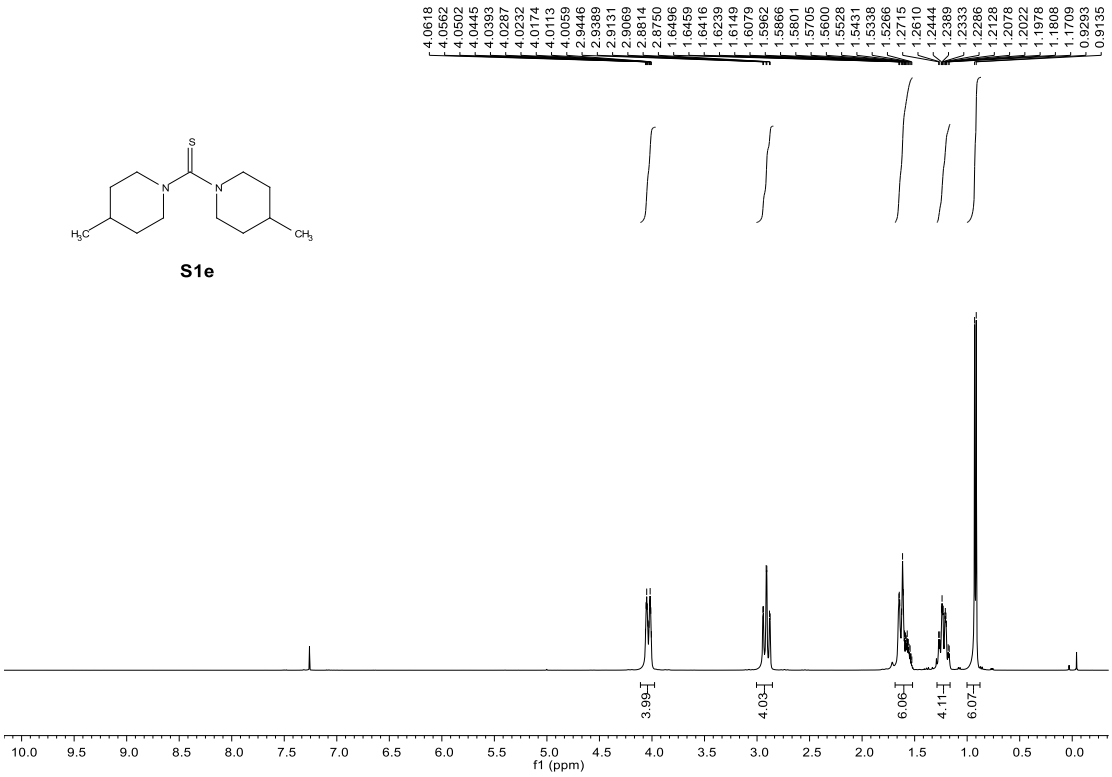
S1d ^{1}H NMR (400 MHz, $CDCl_3$)



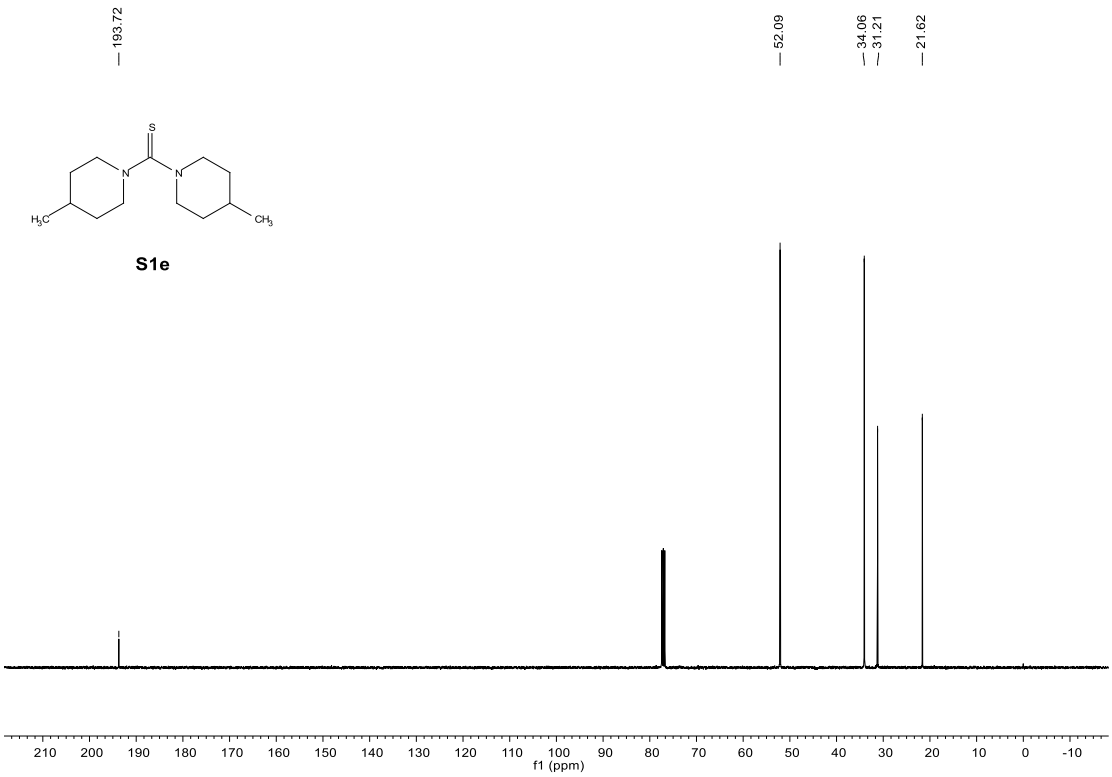
S1d ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



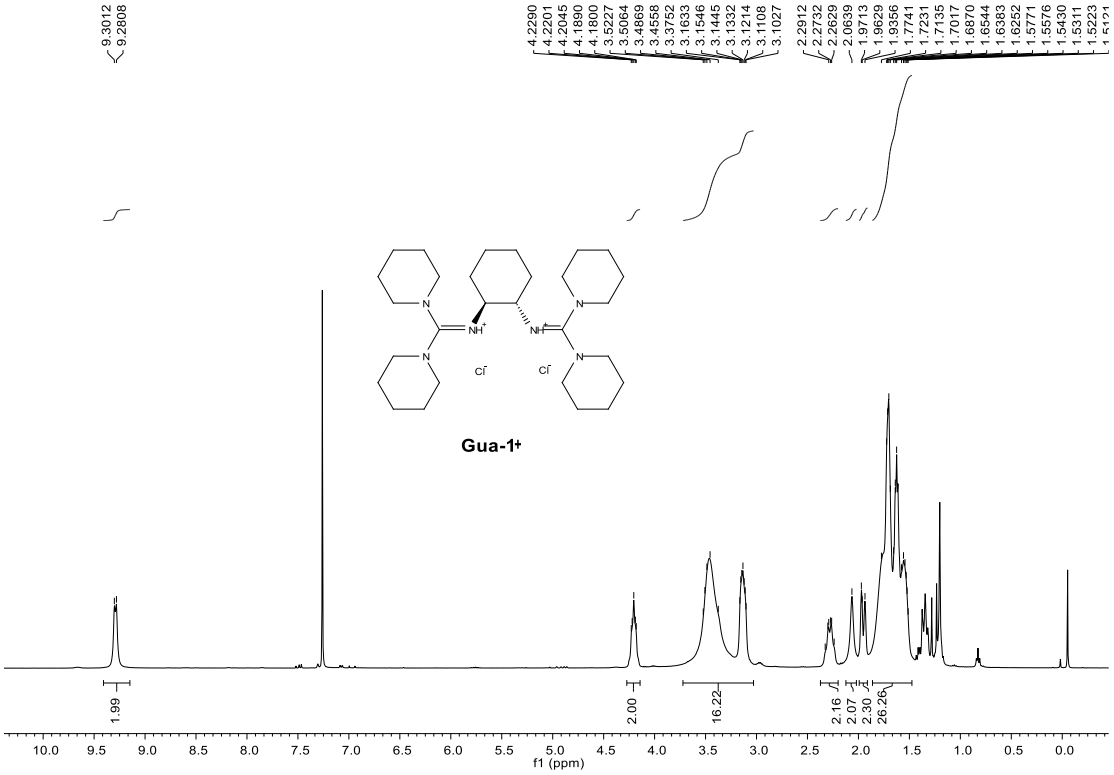
S1e ^{1}H NMR (400 MHz, $CDCl_3$)



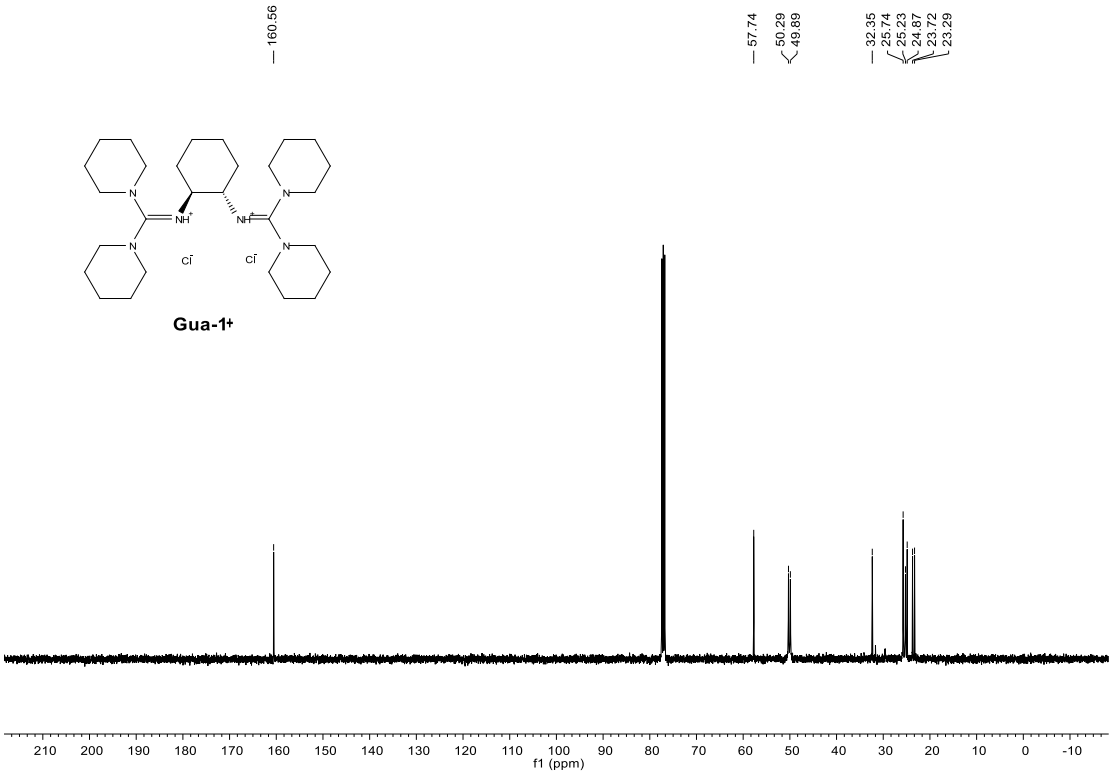
S1e ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



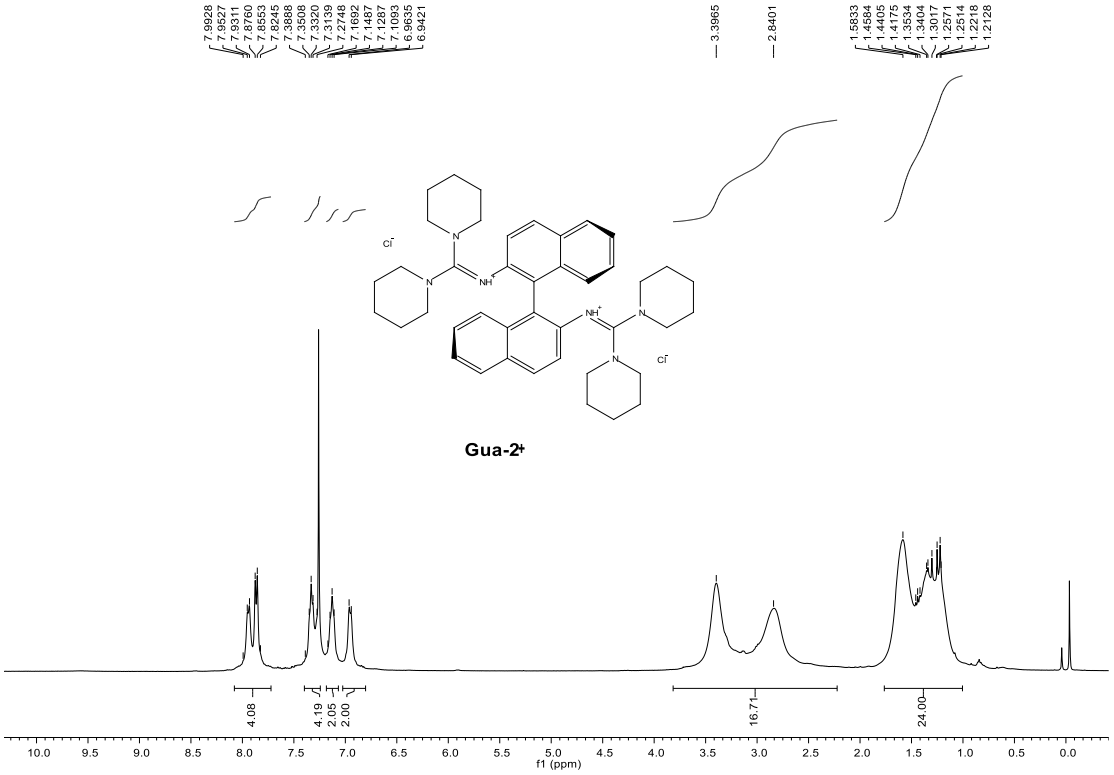
Gua-1⁺ ^{1}H NMR (400 MHz, $CDCl_3$)



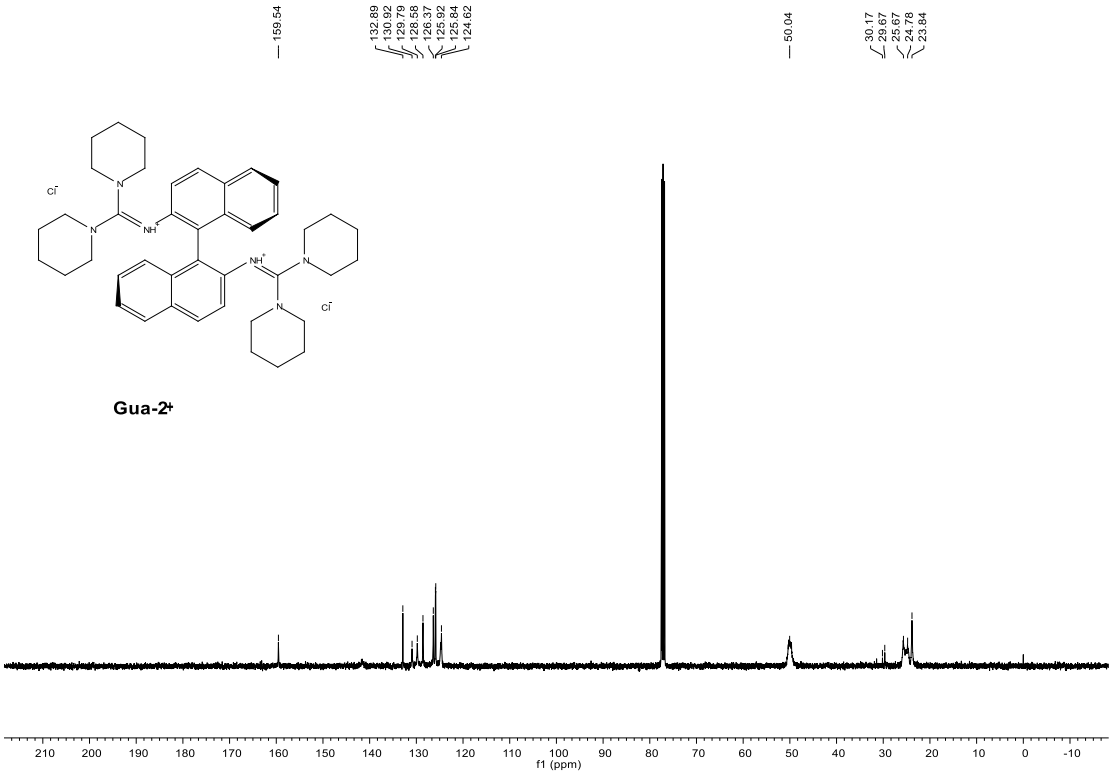
Gua-1⁺ $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



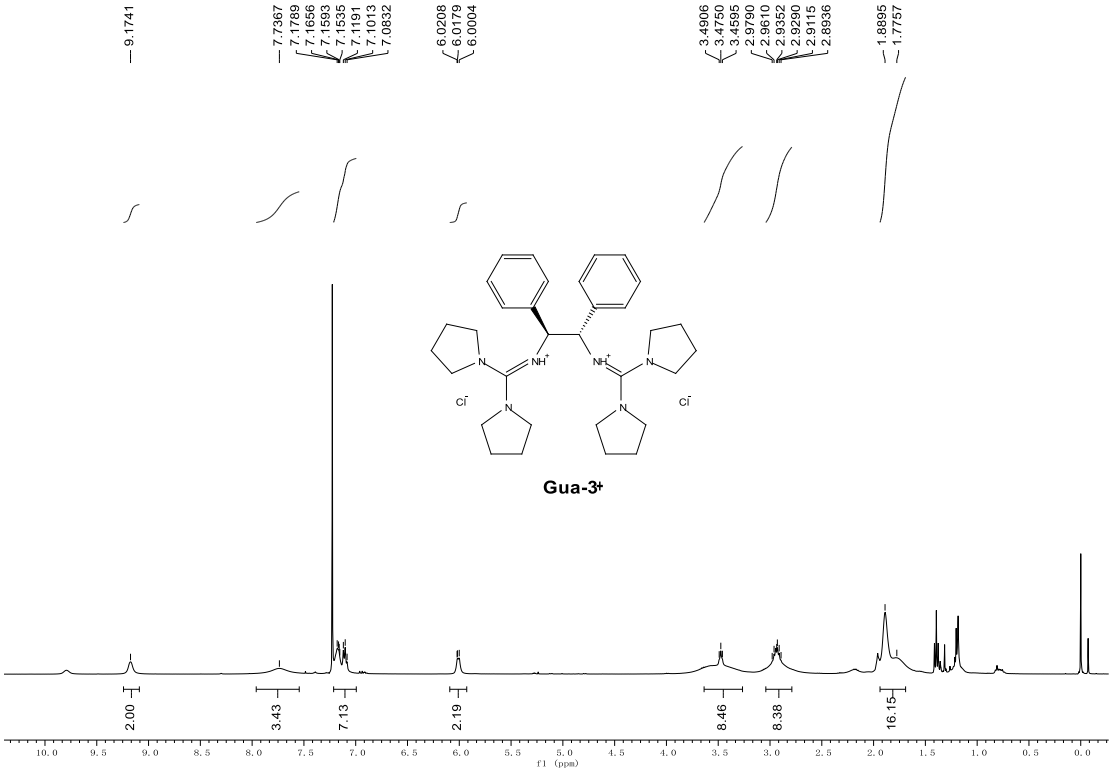
Gua-2$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



Gua-2$^+$ $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

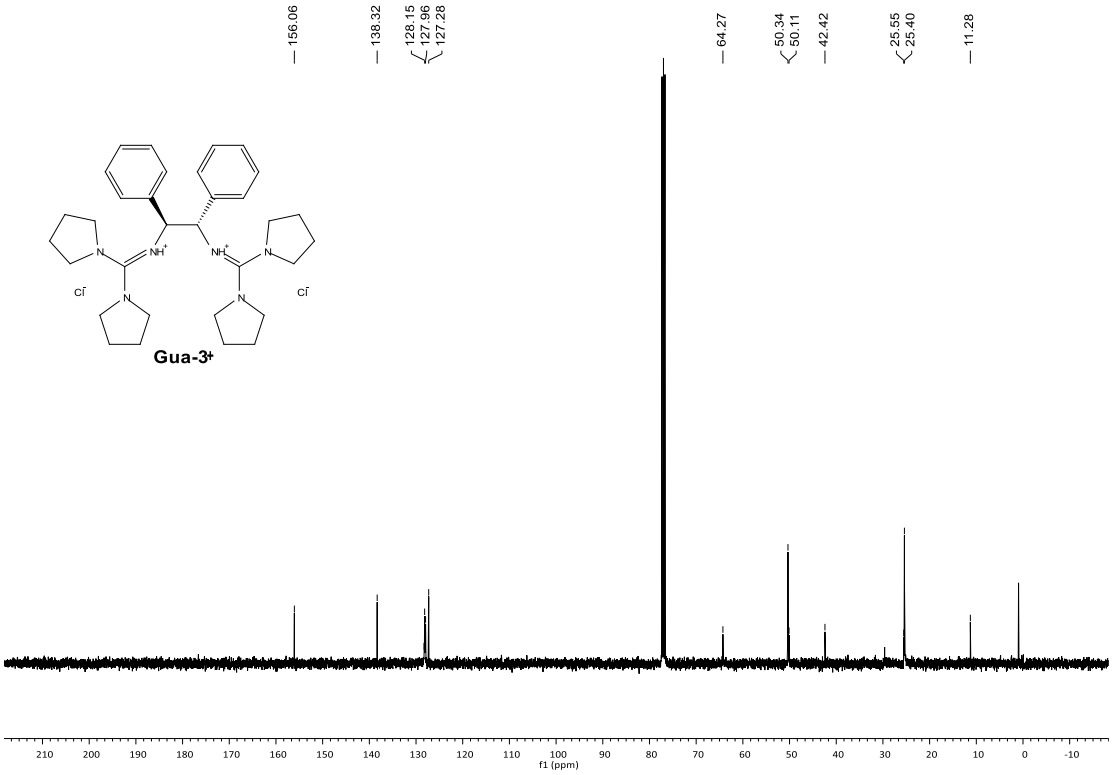


Gua-3$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



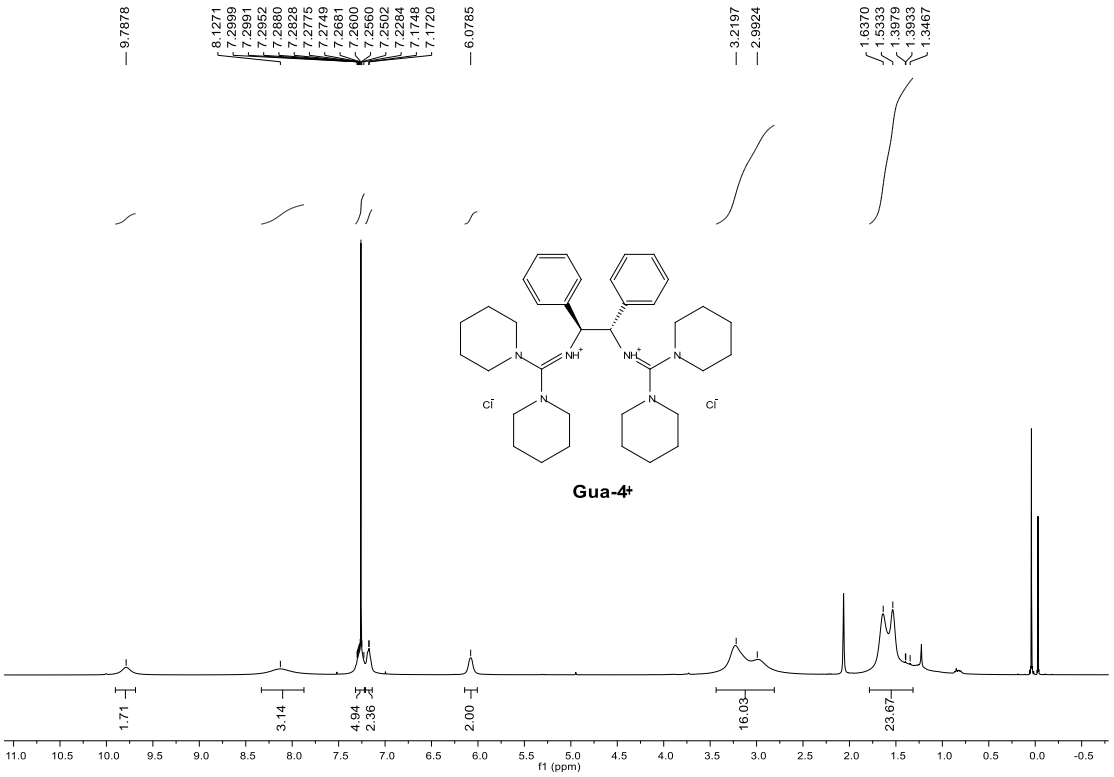
Gua-3$^+$

Gua-3$^+$ $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

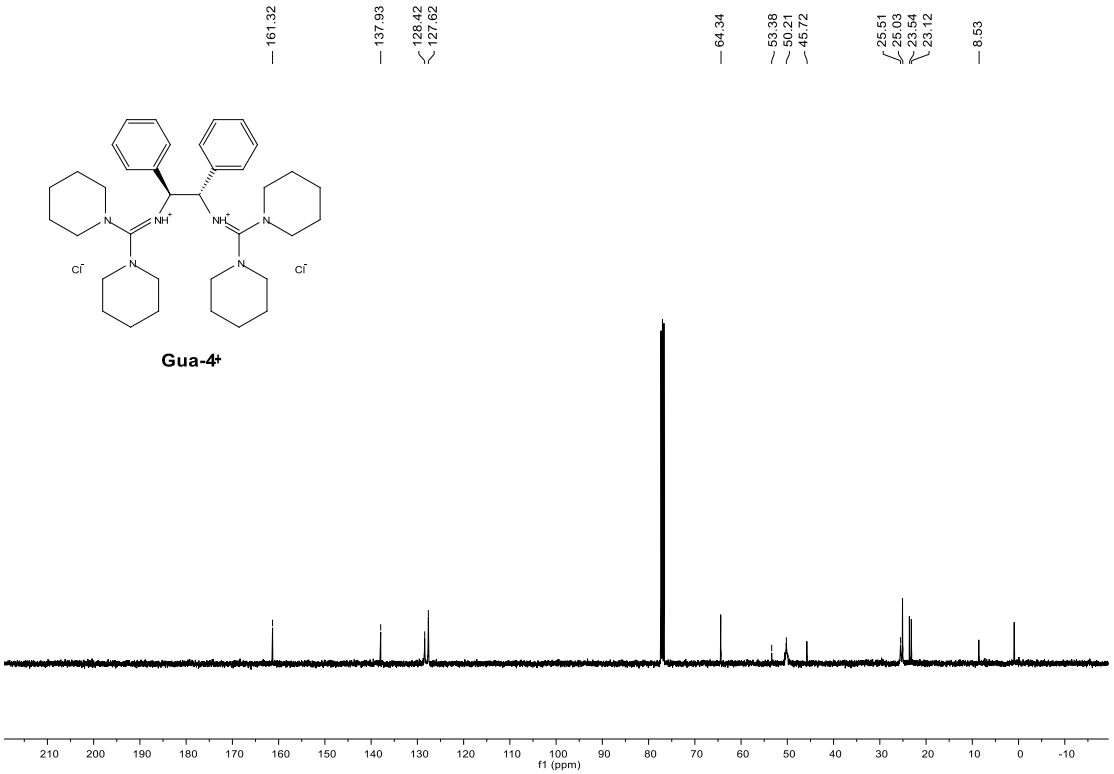


Gua-3$^+$

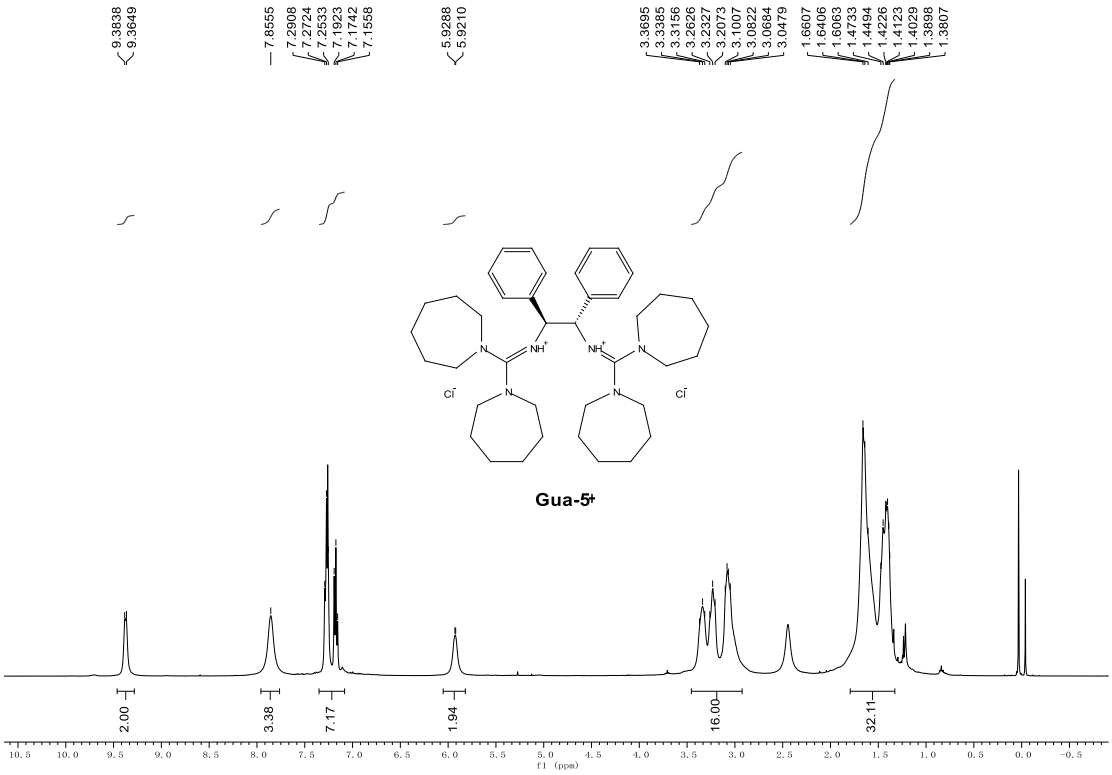
Gua-4$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



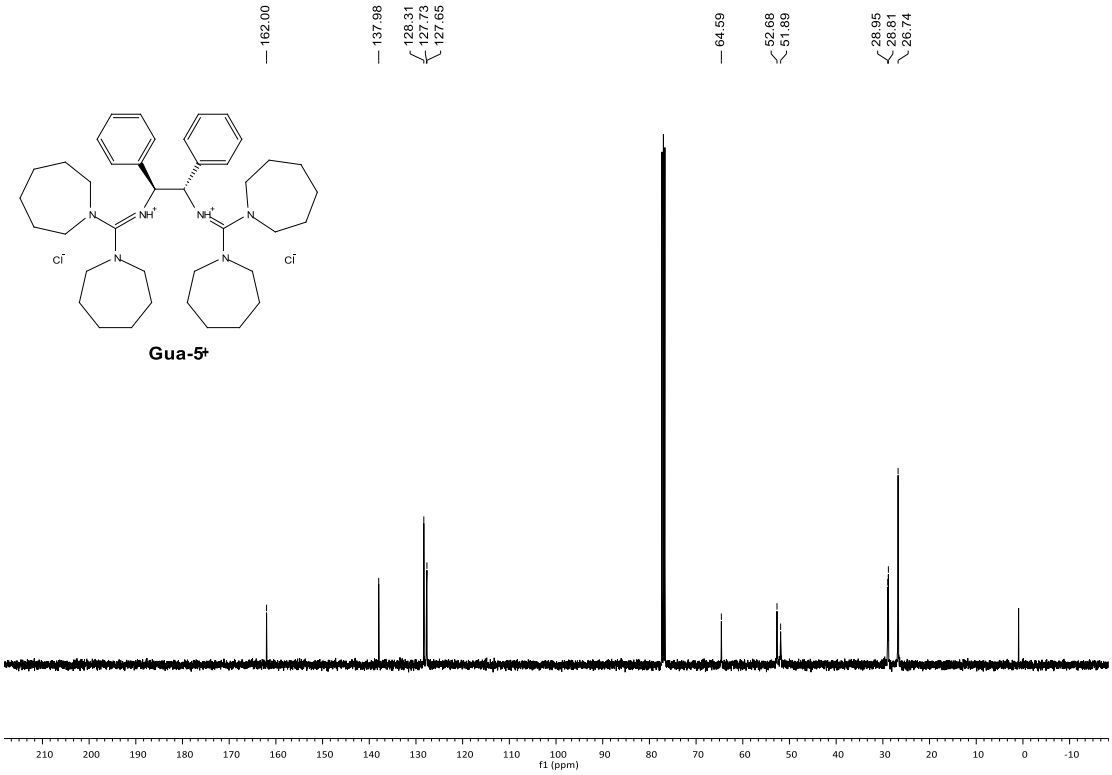
Gua-4$^+$ ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



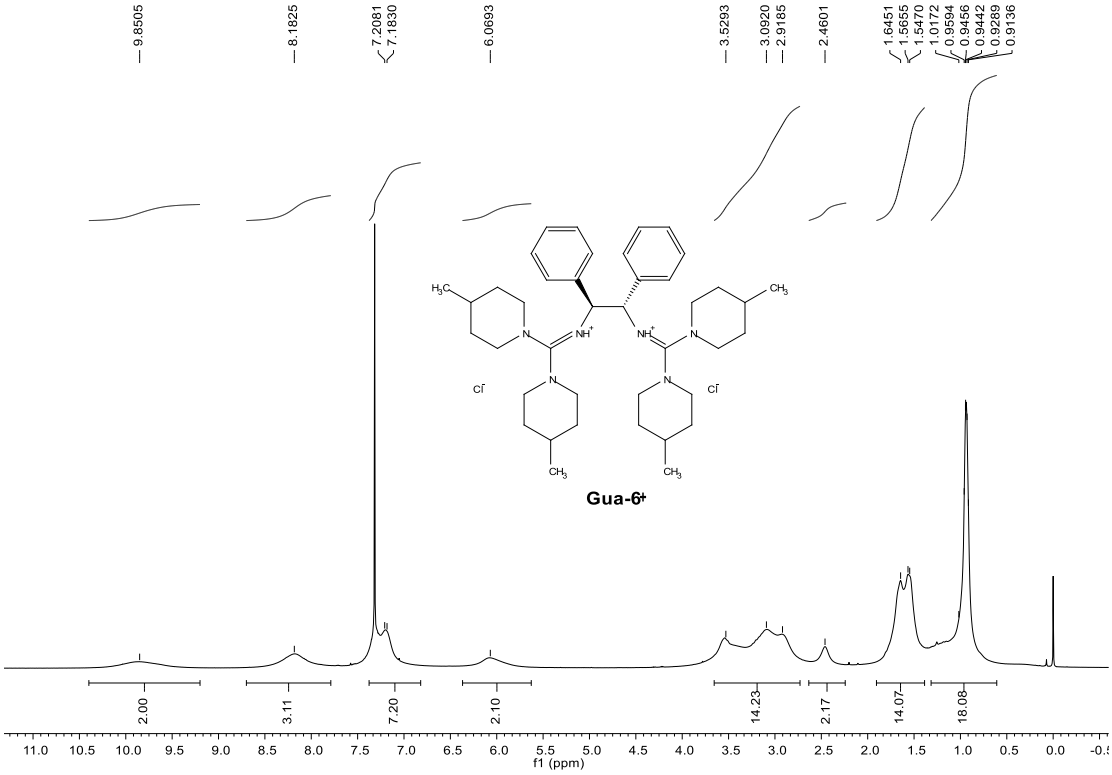
Gua-5$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



Gua-5$^+$ ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

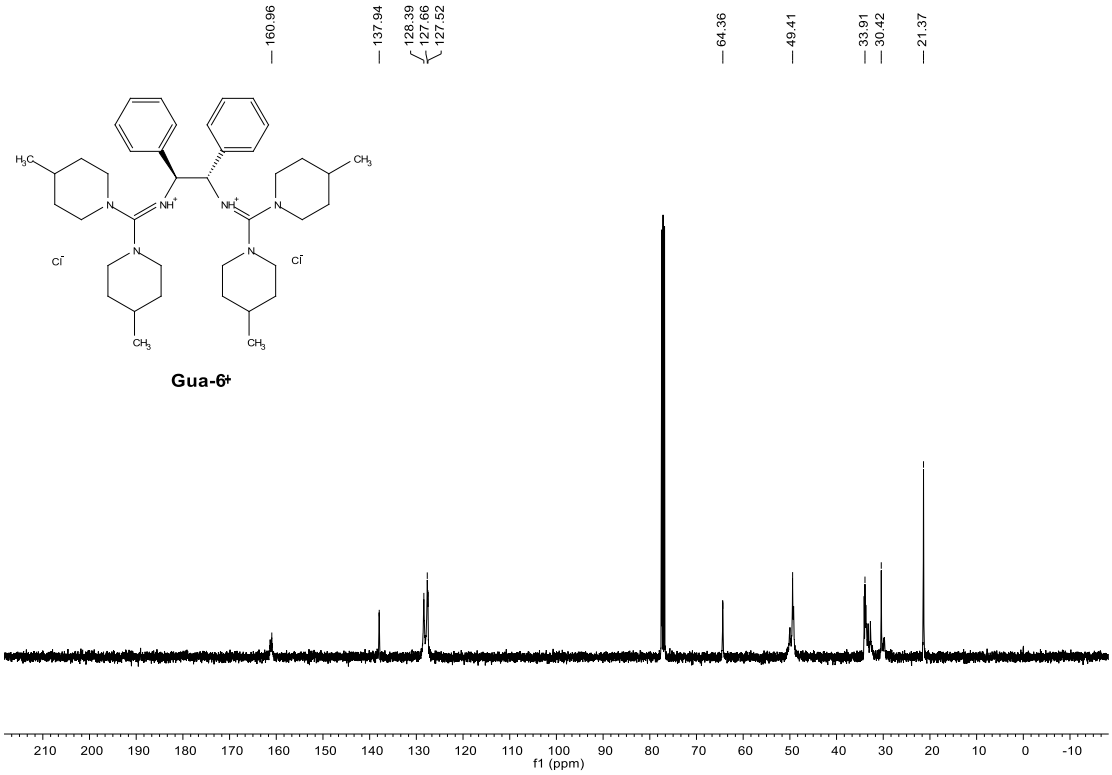


Gua-6$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



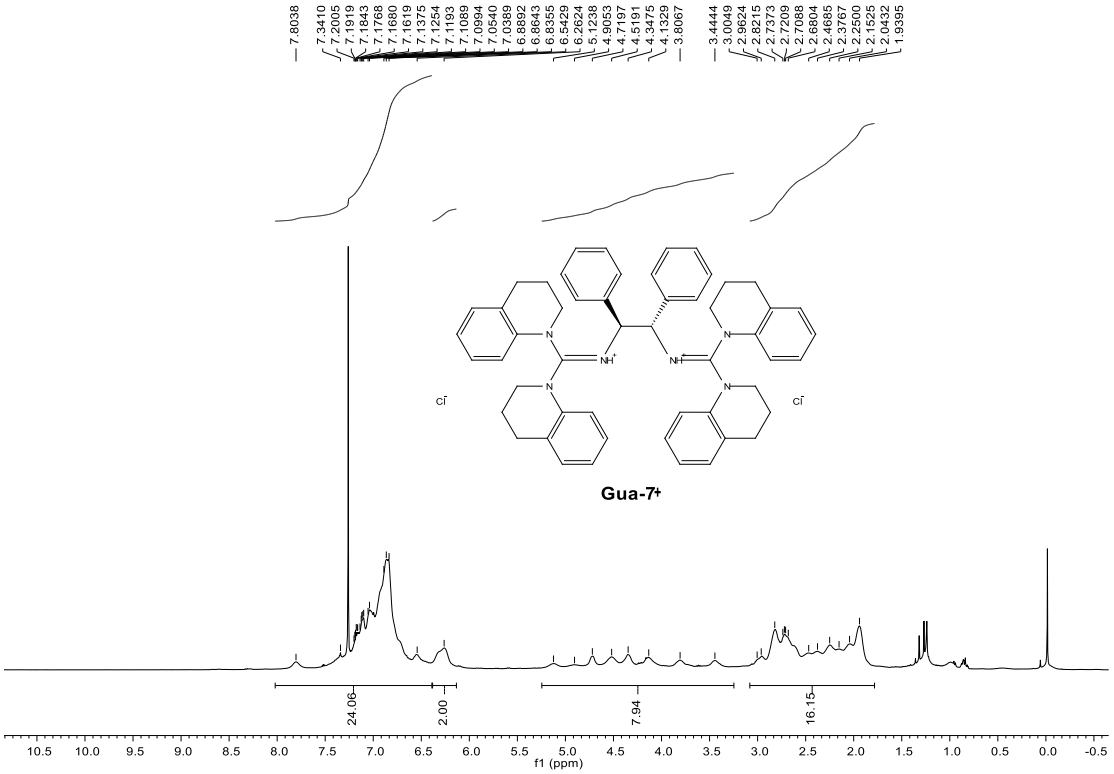
Gua-6$^+$

Gua-6$^+$ ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

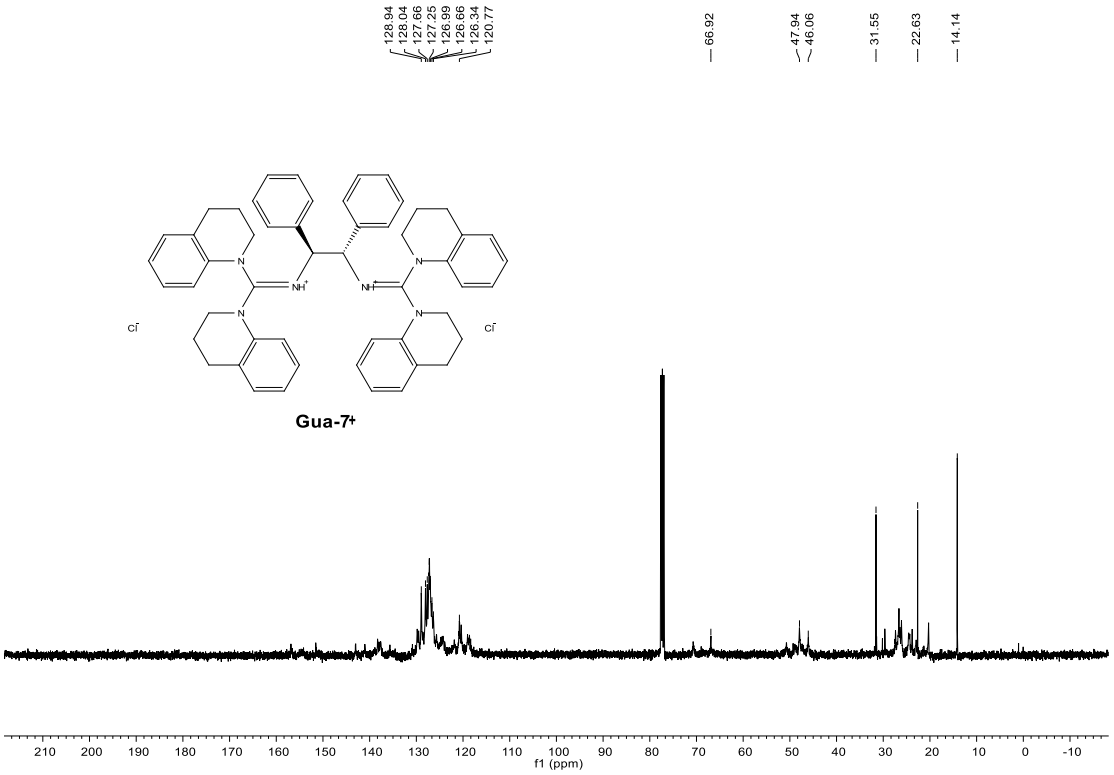


Gua-6$^+$

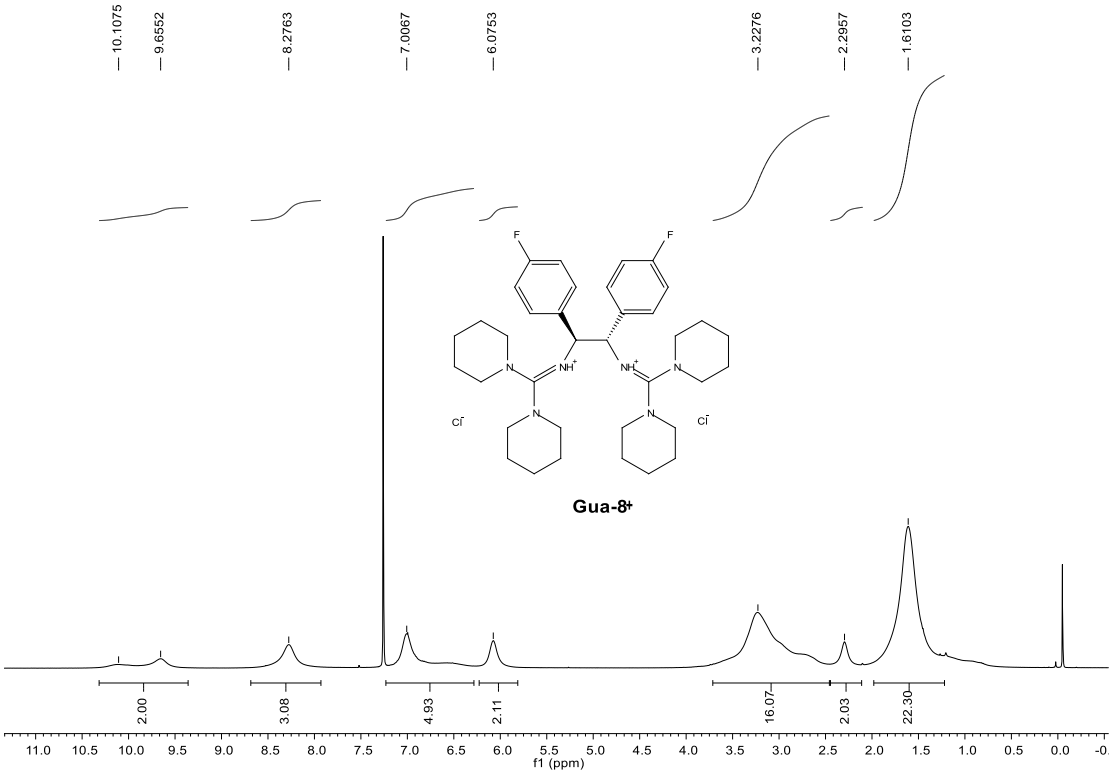
Gua-7$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



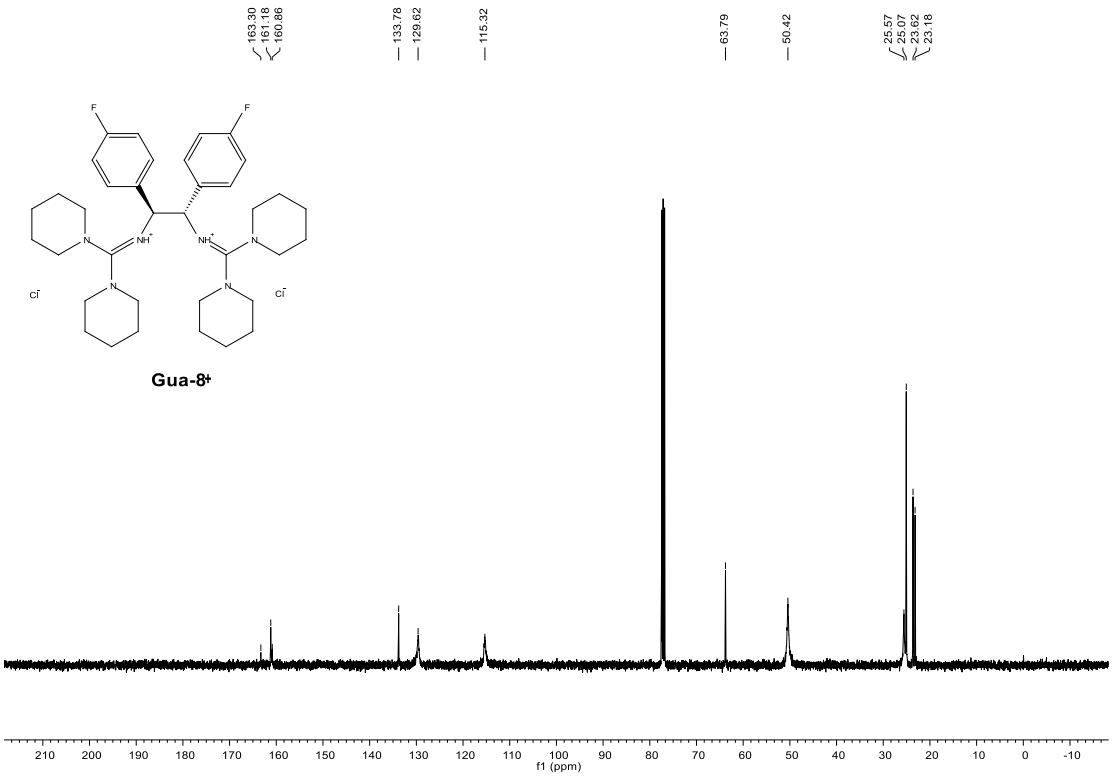
Gua-7$^+$ $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



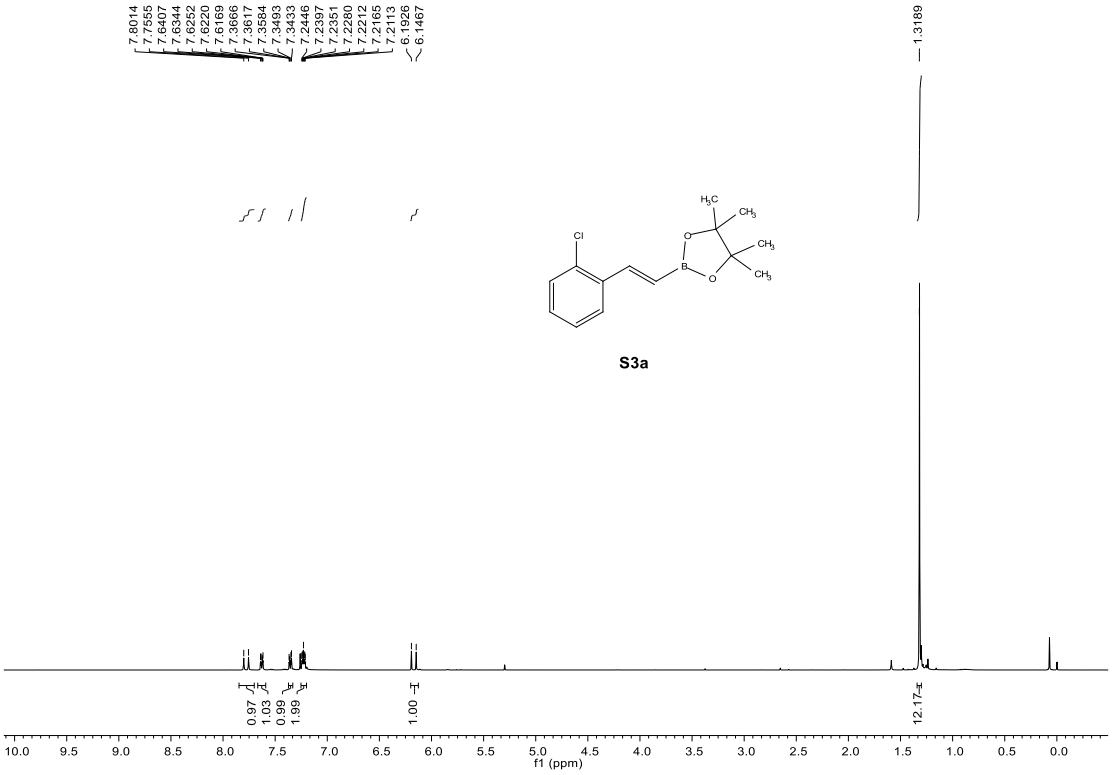
Gua-8$^+$ ^{1}H NMR (400 MHz, $CDCl_3$)



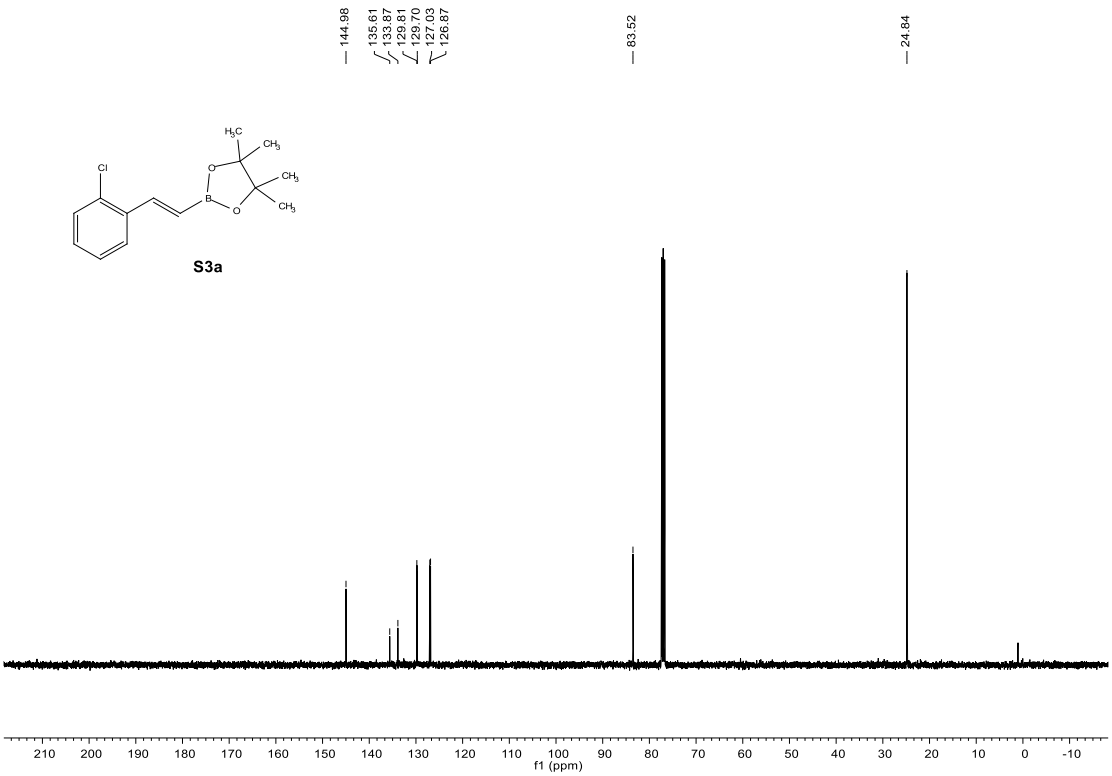
Gua-8$^+$ ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



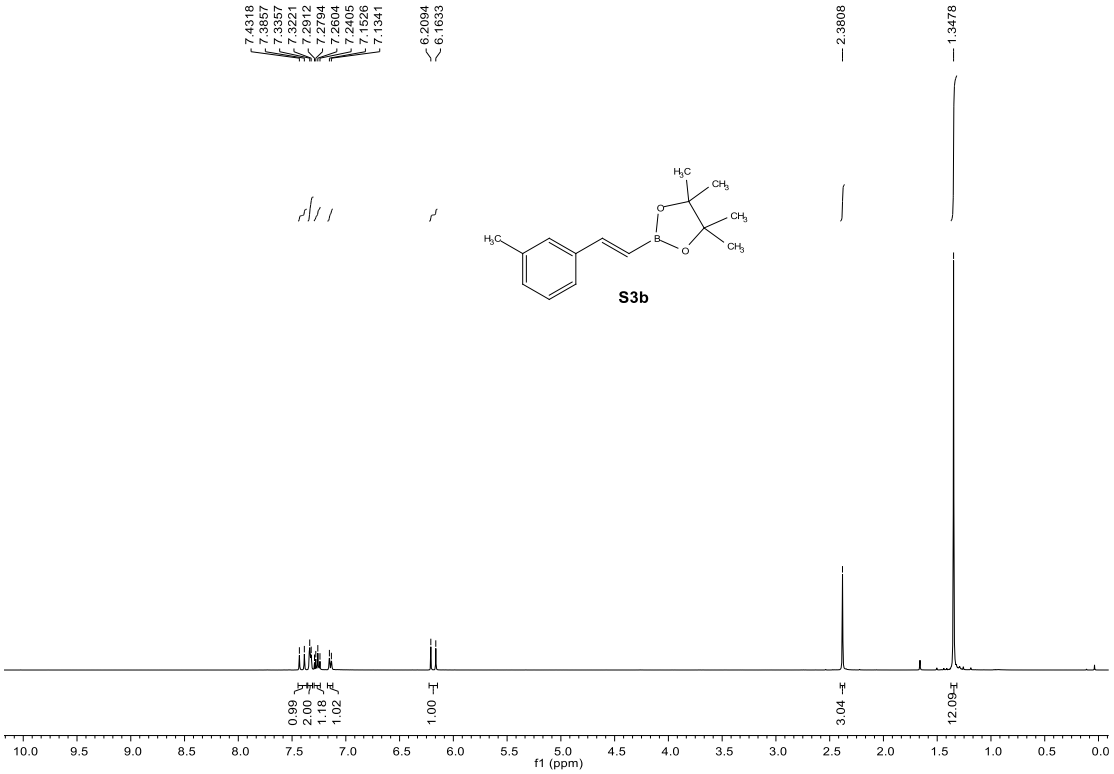
S3a ^{1}H NMR (400 MHz, $CDCl_3$)



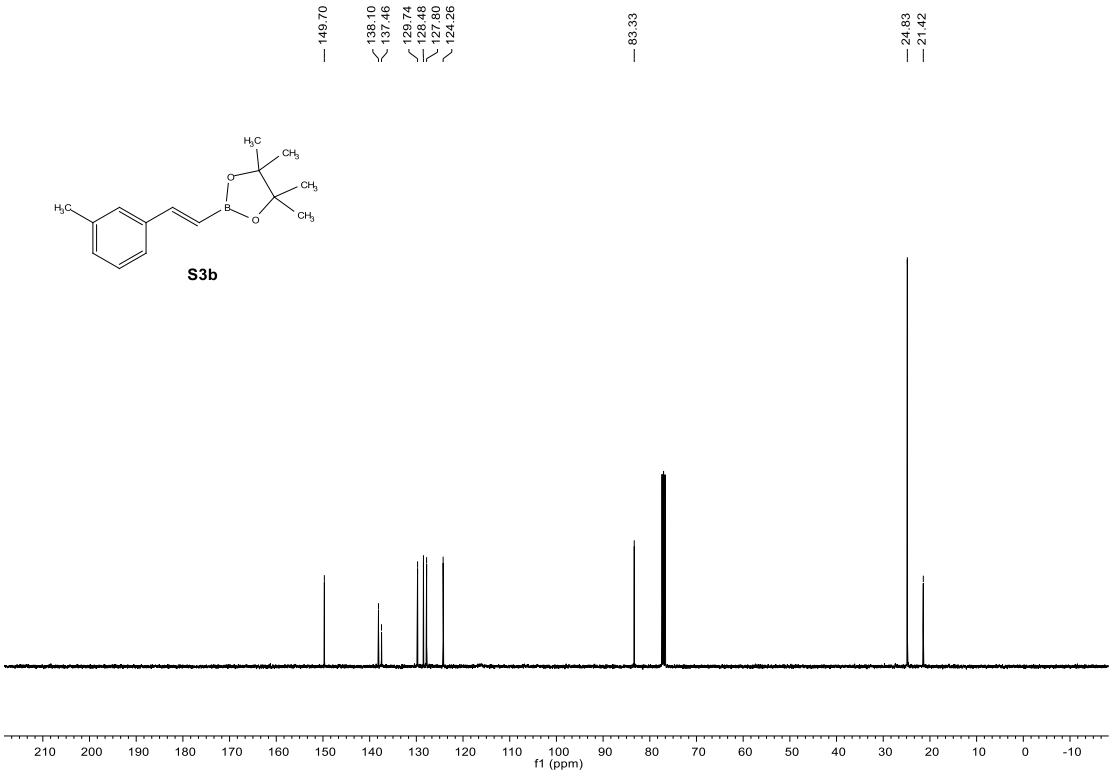
S3a $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



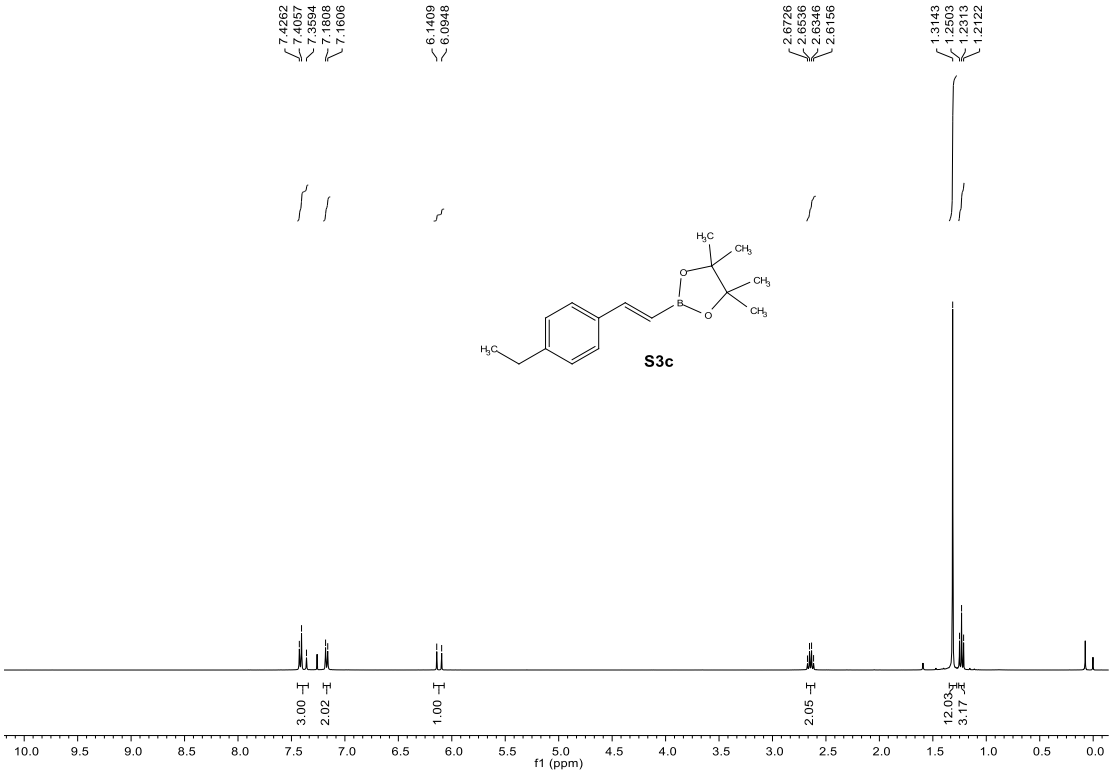
S3b ^{1}H NMR (400 MHz, $CDCl_3$)



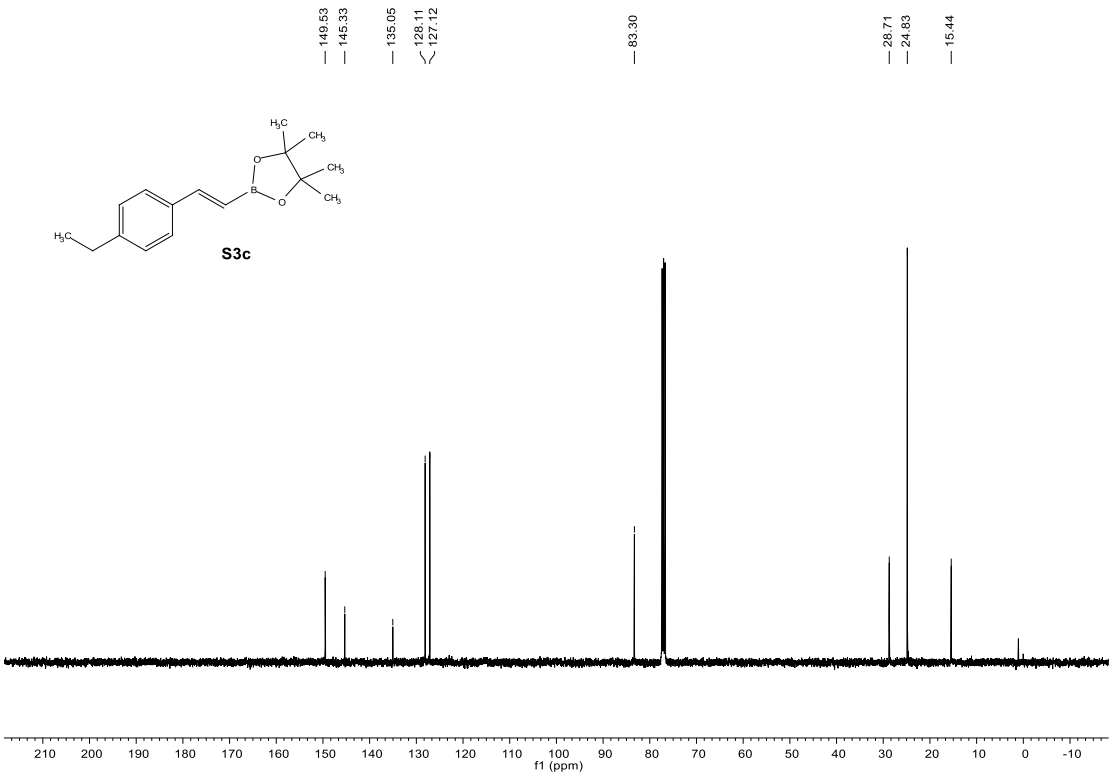
S3b $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



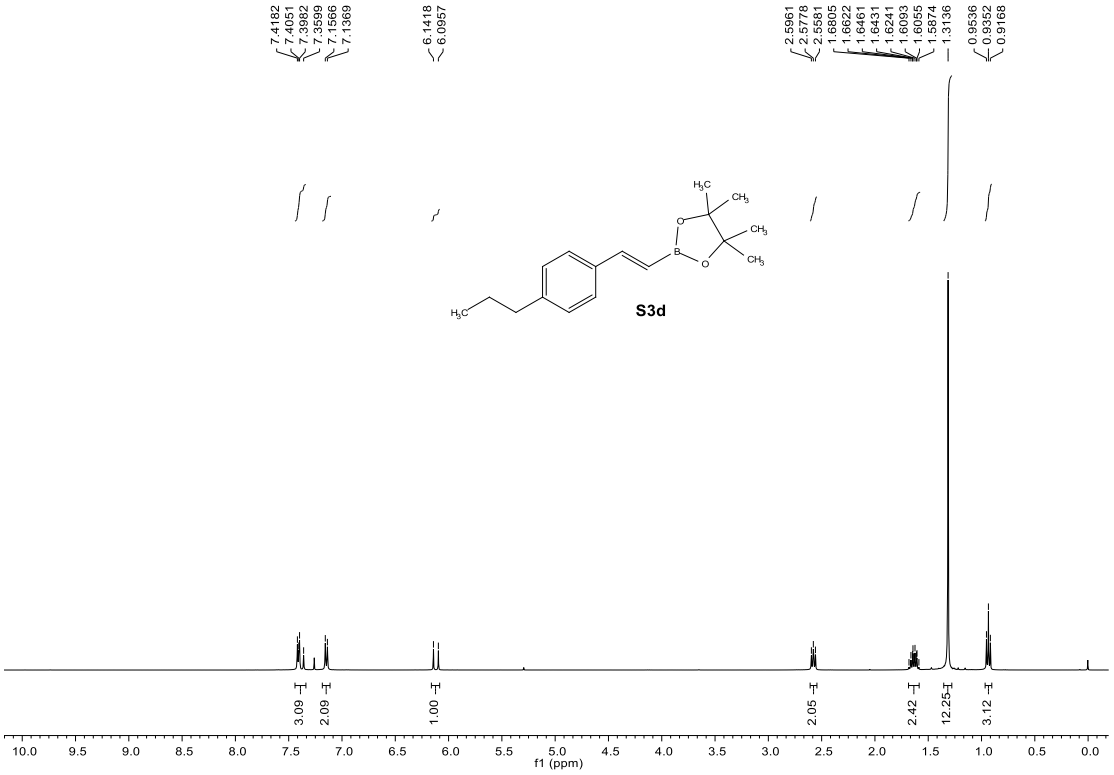
S3c ^{1}H NMR (400 MHz, $CDCl_3$)



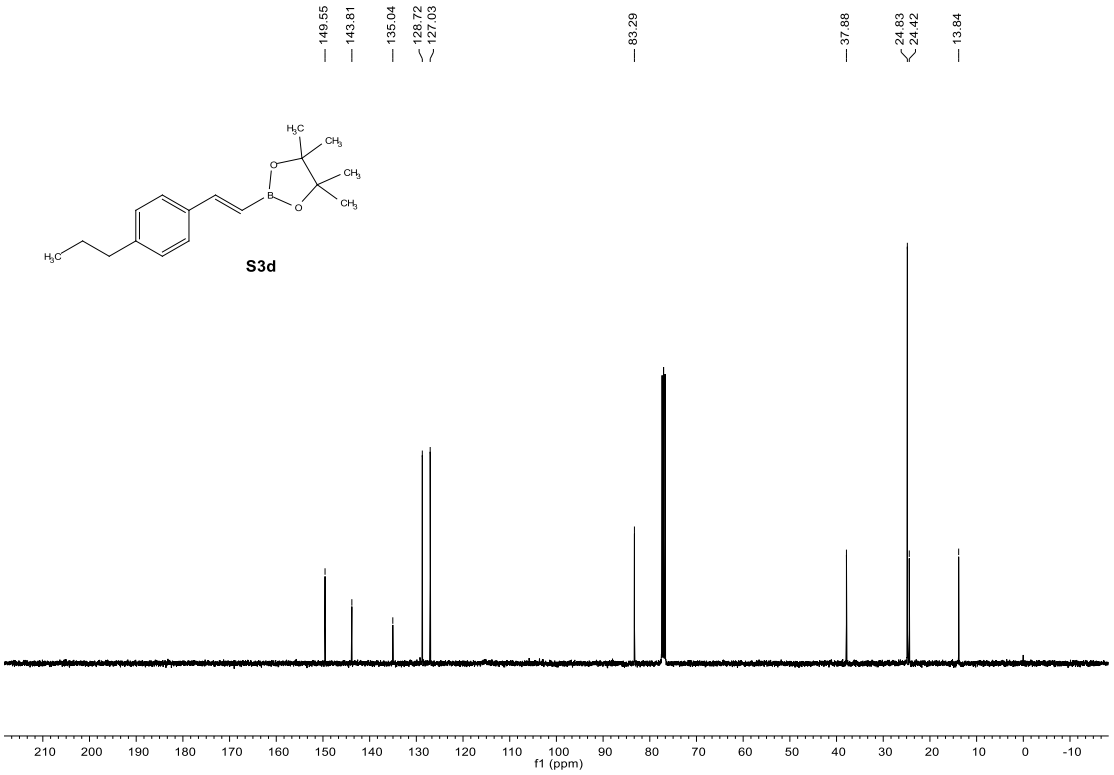
S3c ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



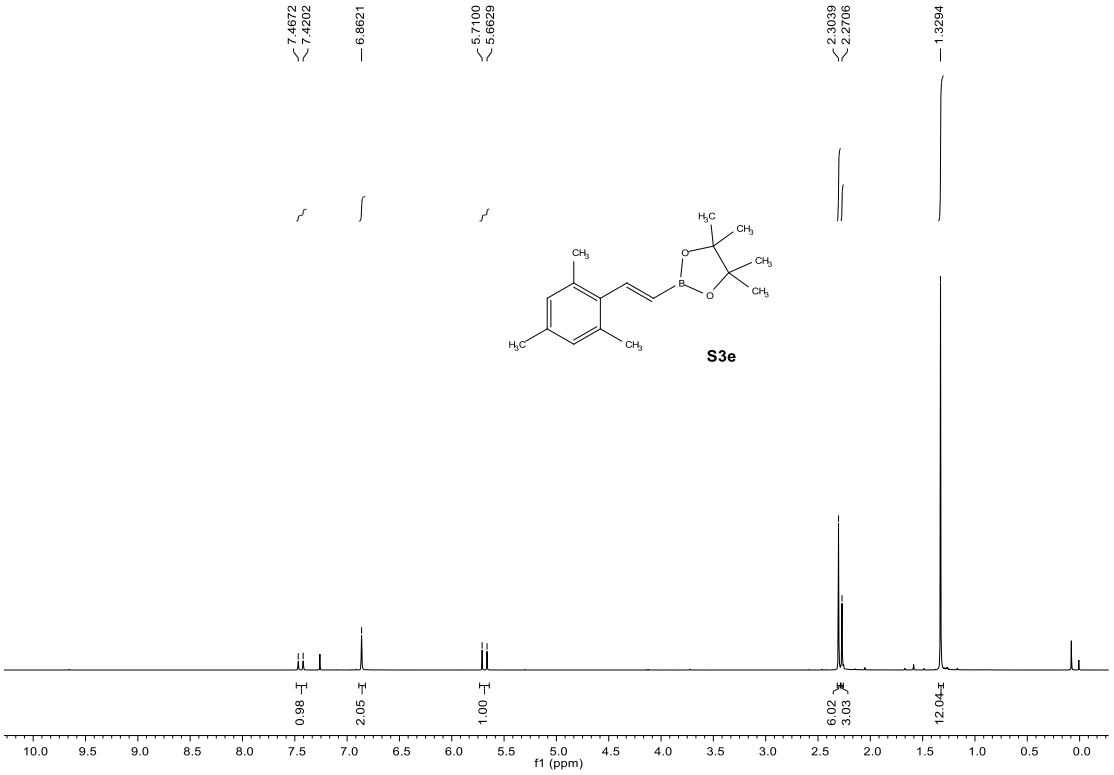
S3d ^{1}H NMR (400 MHz, $CDCl_3$)



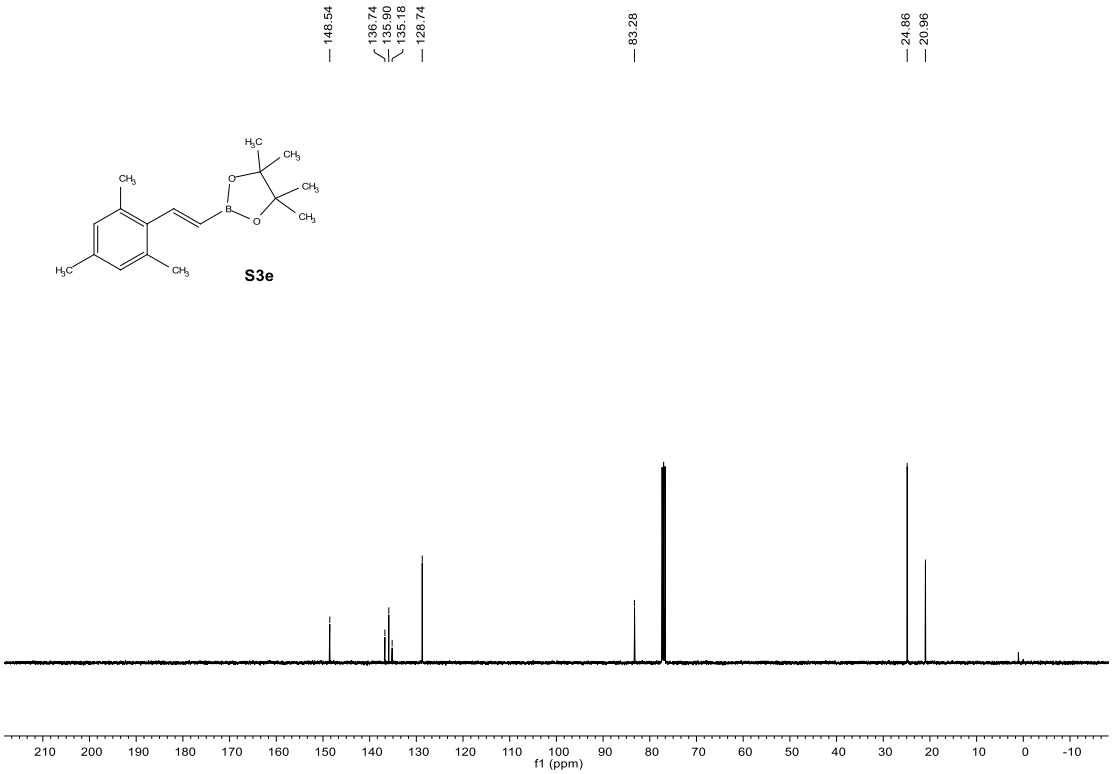
S3d $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



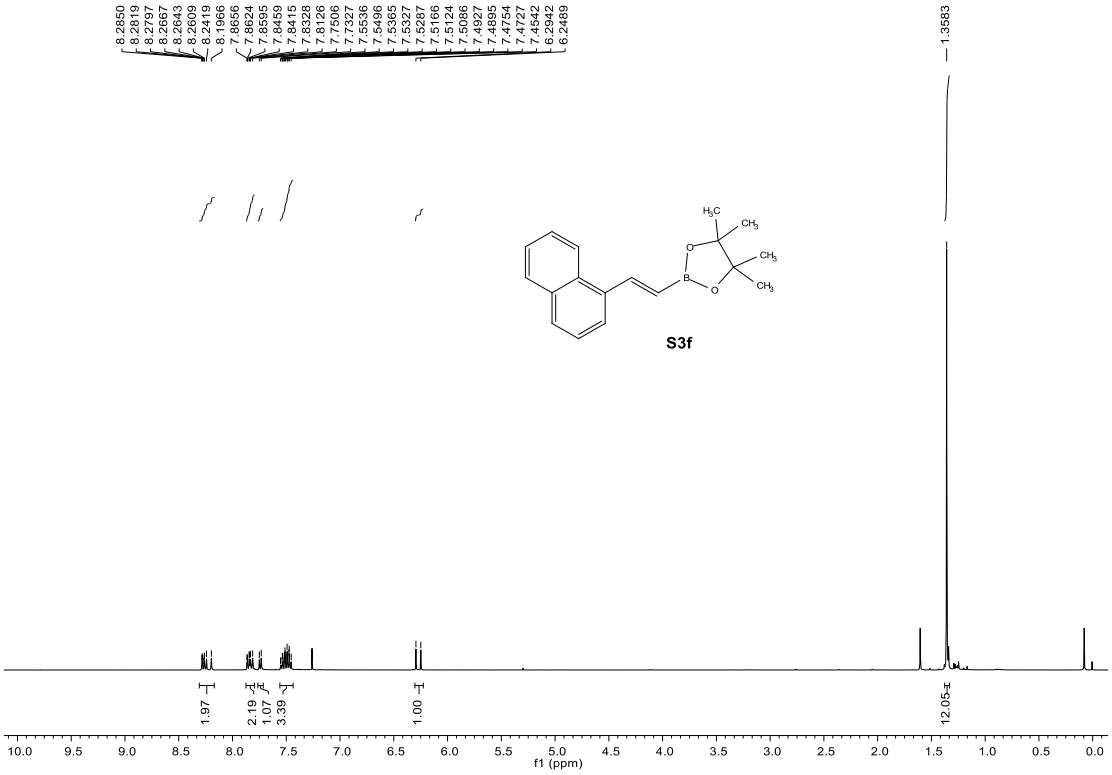
S3e ^{1}H NMR (400 MHz, $CDCl_3$)



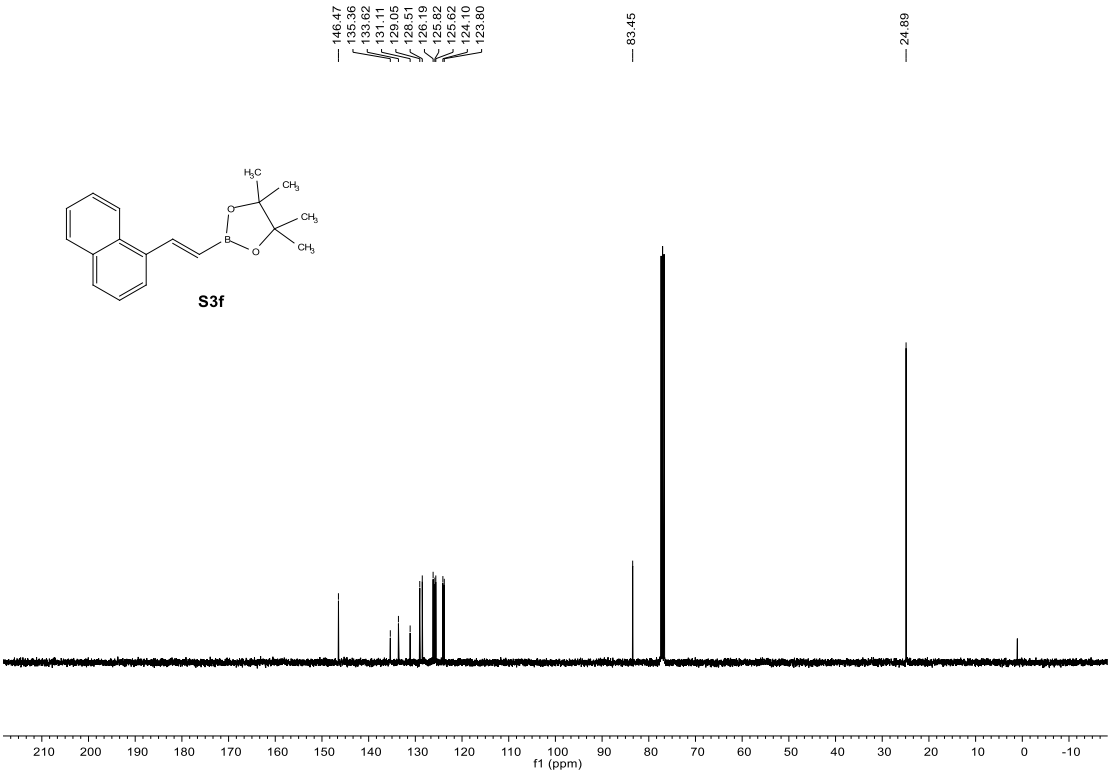
S3e ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



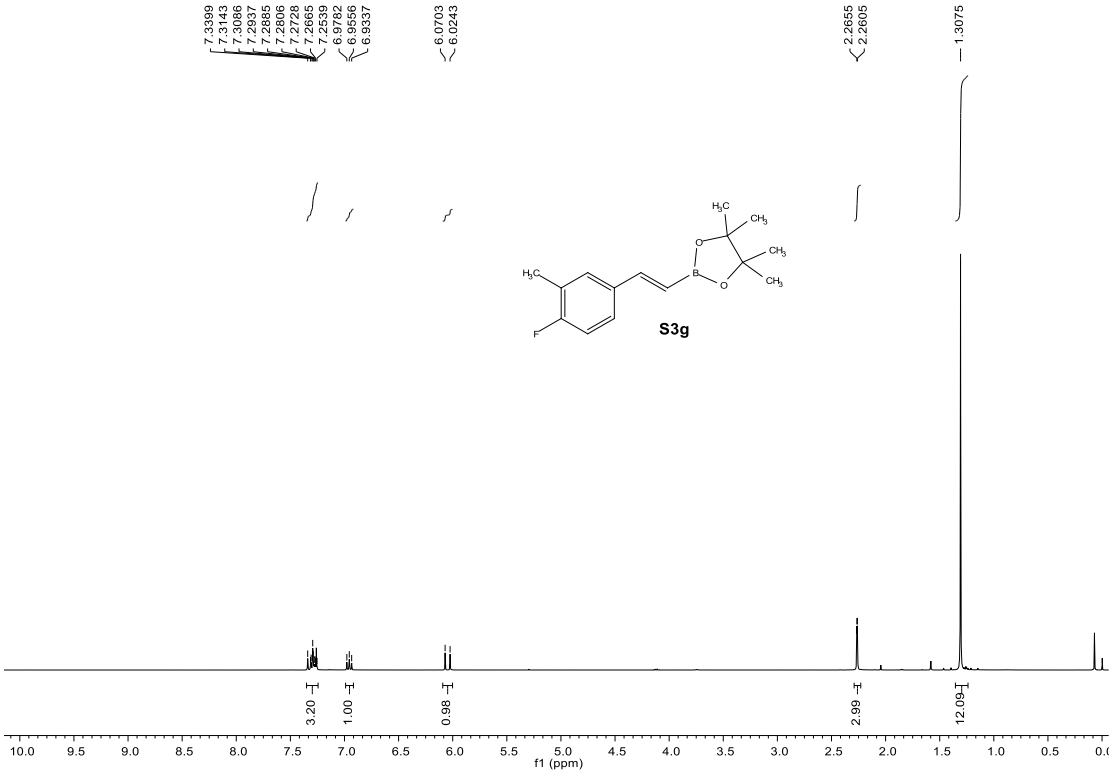
S3f ^{1}H NMR (400 MHz, $CDCl_3$)



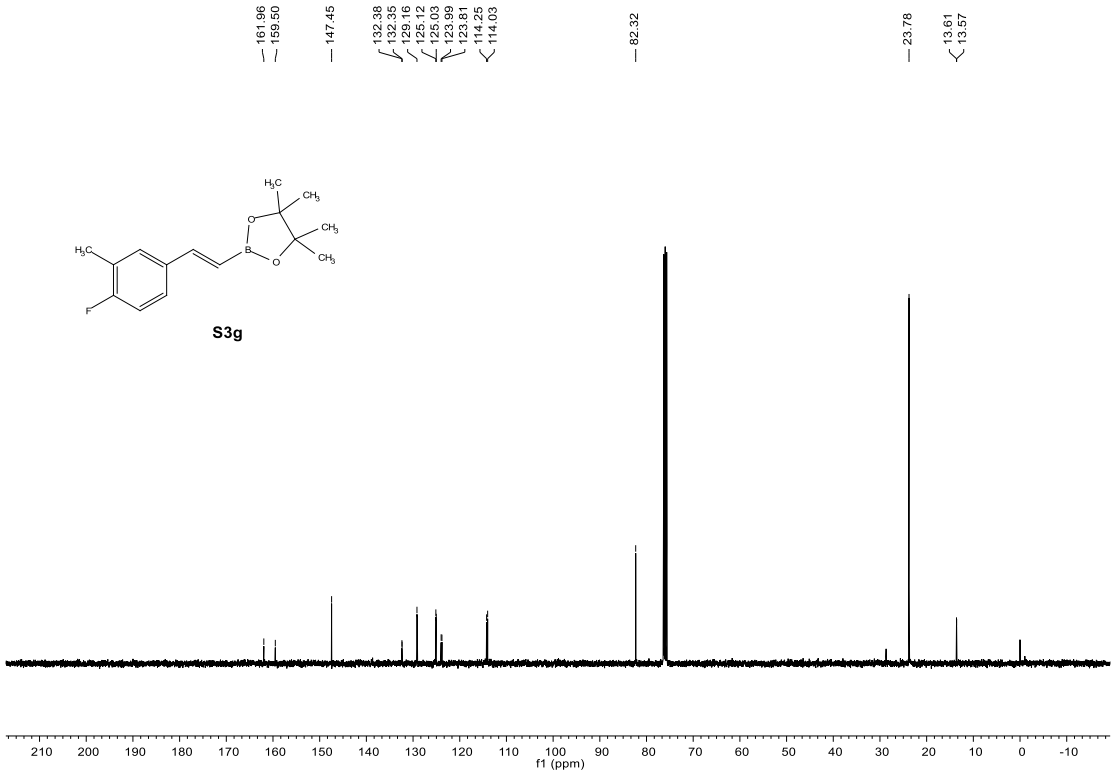
S3f $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



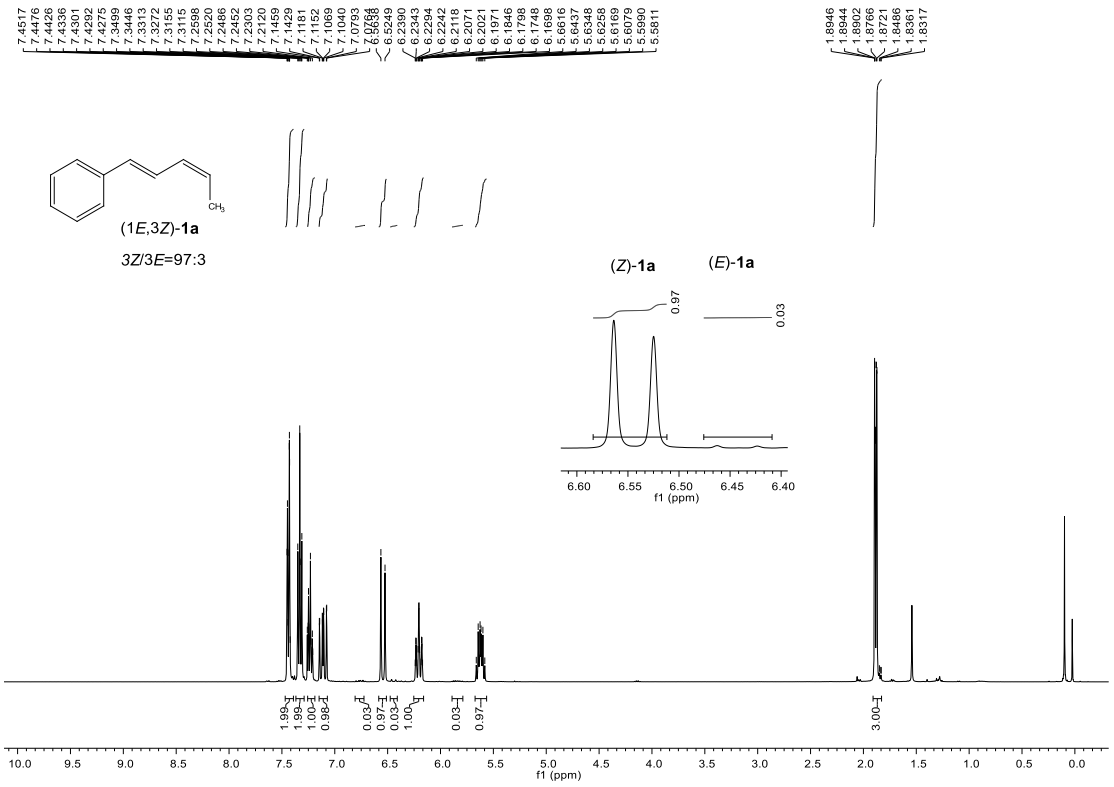
S3g ^{1}H NMR (400 MHz, $CDCl_3$)



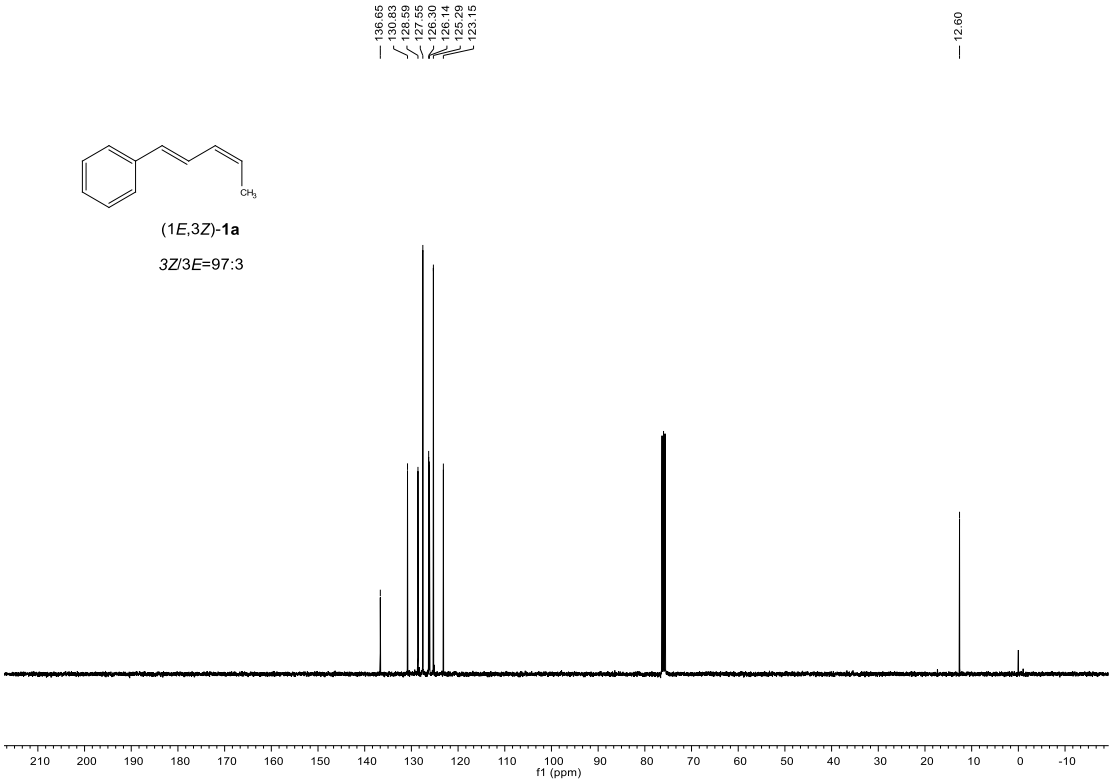
S3g ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



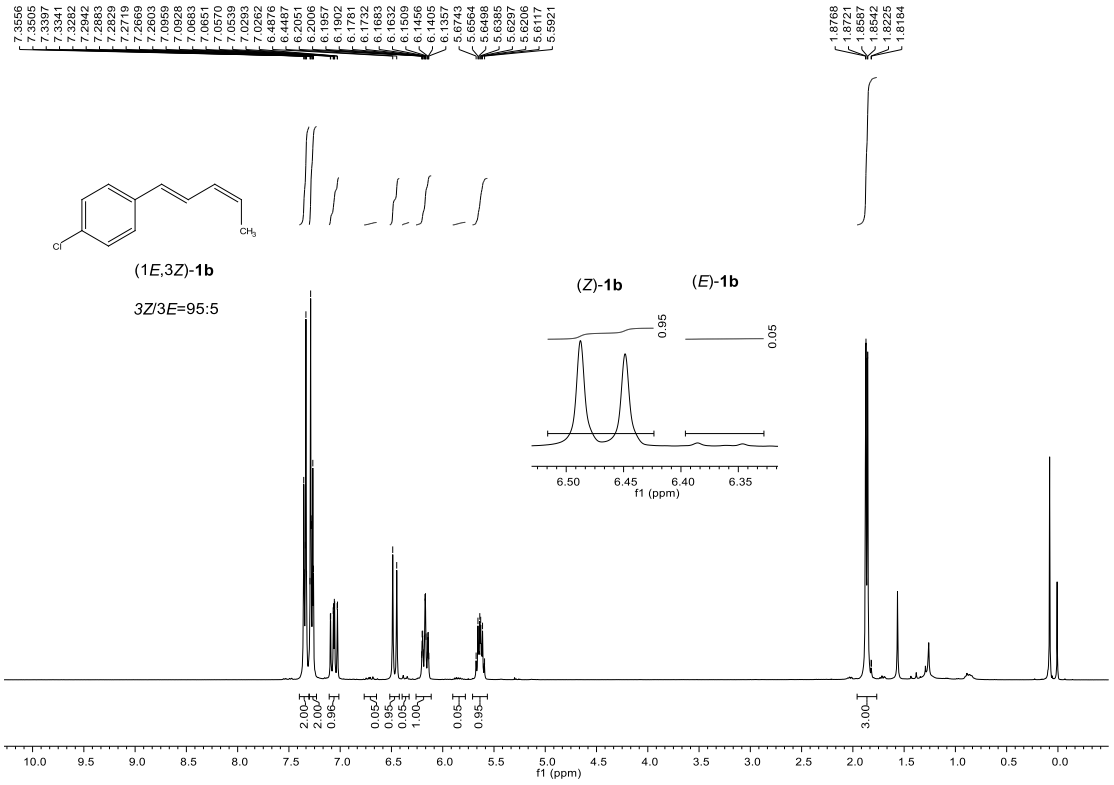
(1*E*,3*Z*)-**1a** ^{1}H NMR (400 MHz, $CDCl_3$)



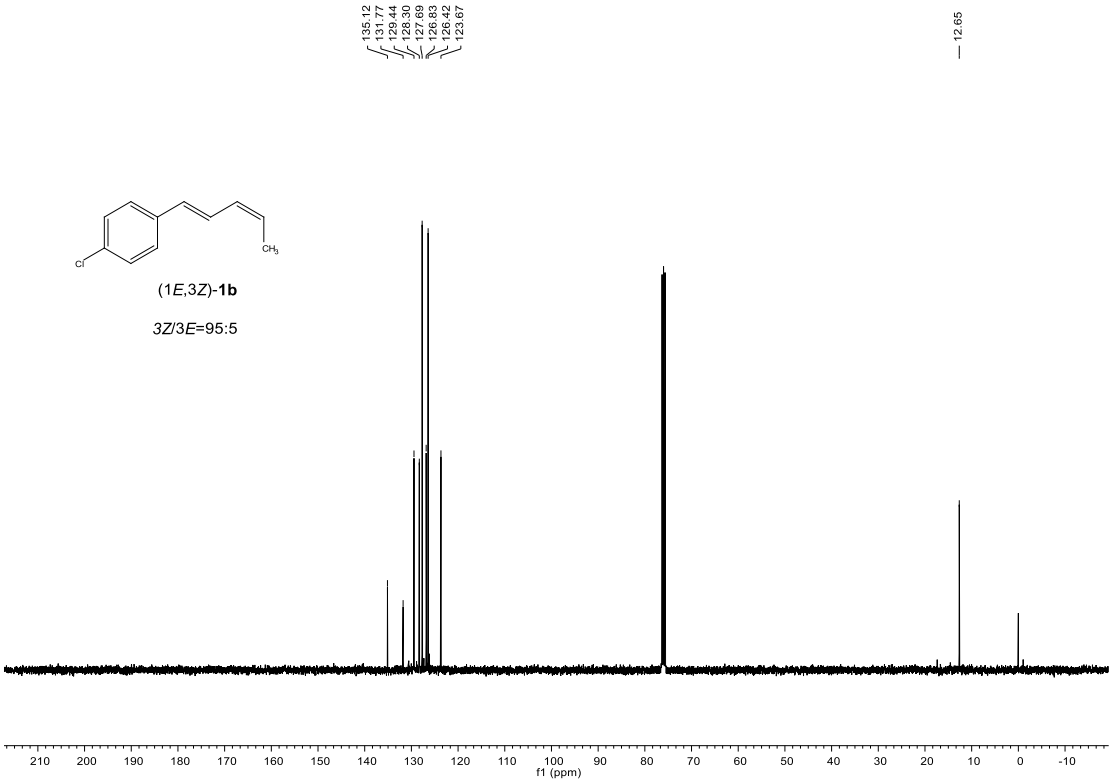
(1*E*,3*Z*)-**1a** $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



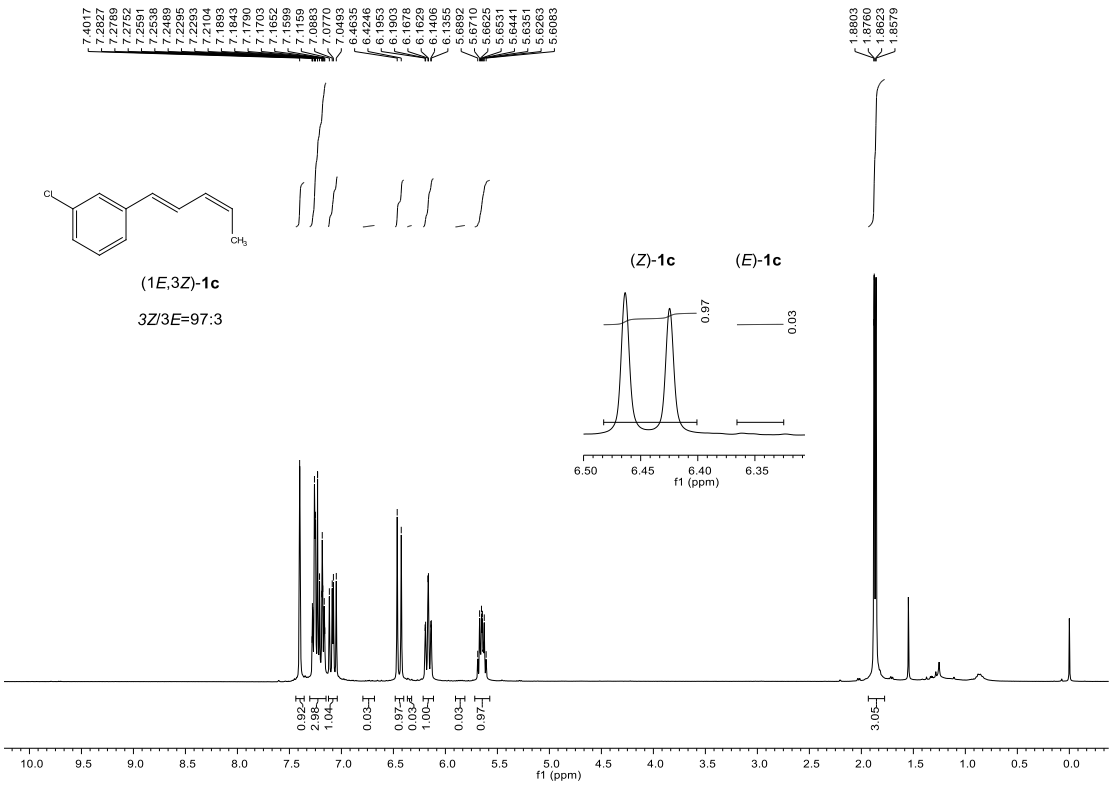
(1*E*,3*Z*)-**1b** ^{1}H NMR (400 MHz, $CDCl_3$)



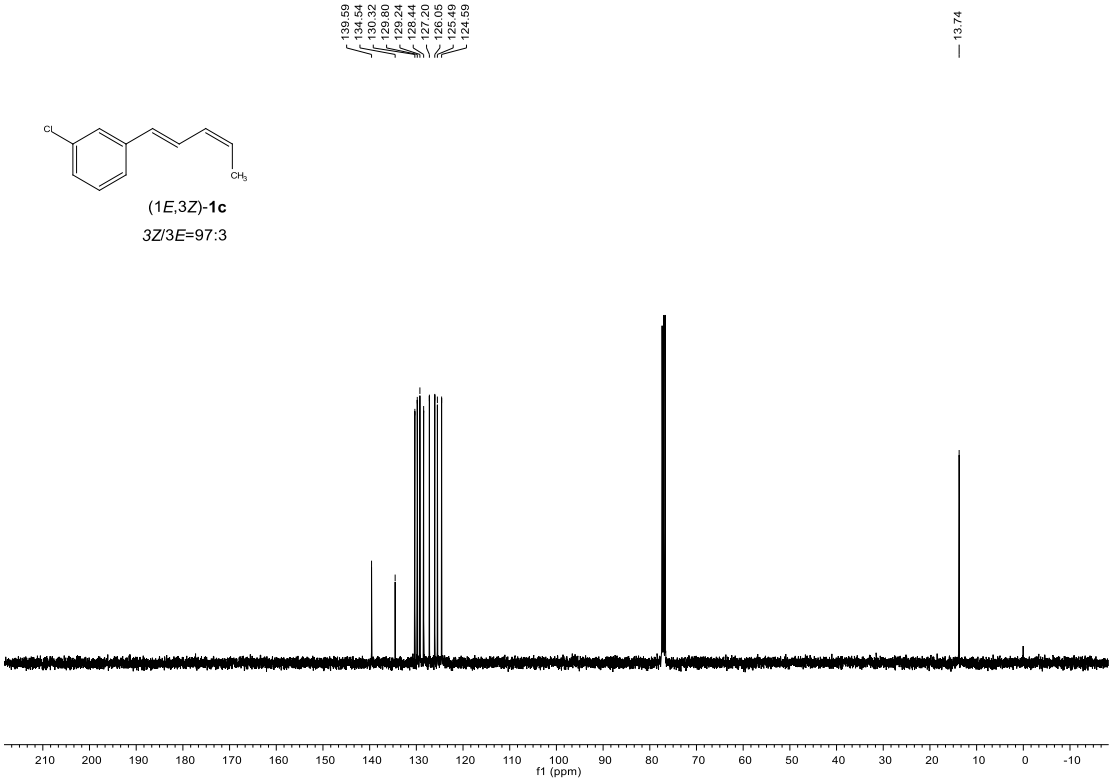
(1*E*,3*Z*)-**1b** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



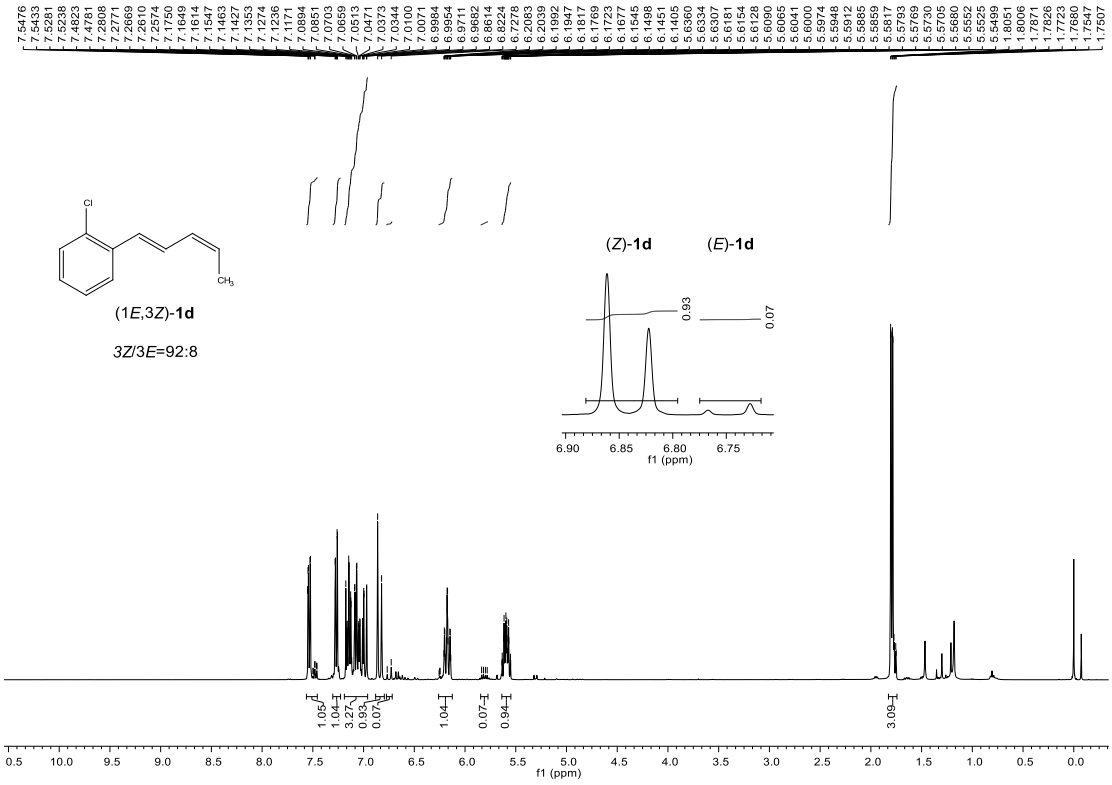
(1*E*,3*Z*)-**1c** ^{1}H NMR (400 MHz, $CDCl_3$)



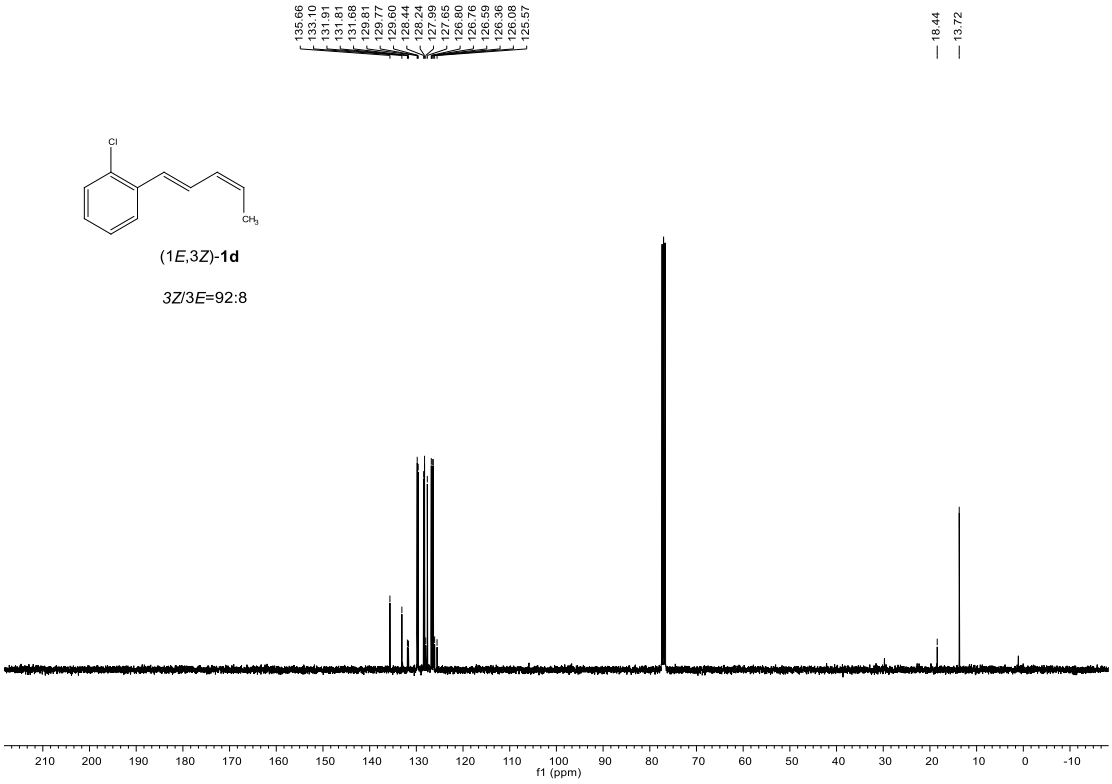
(1*E*,3*Z*)-**1c** $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



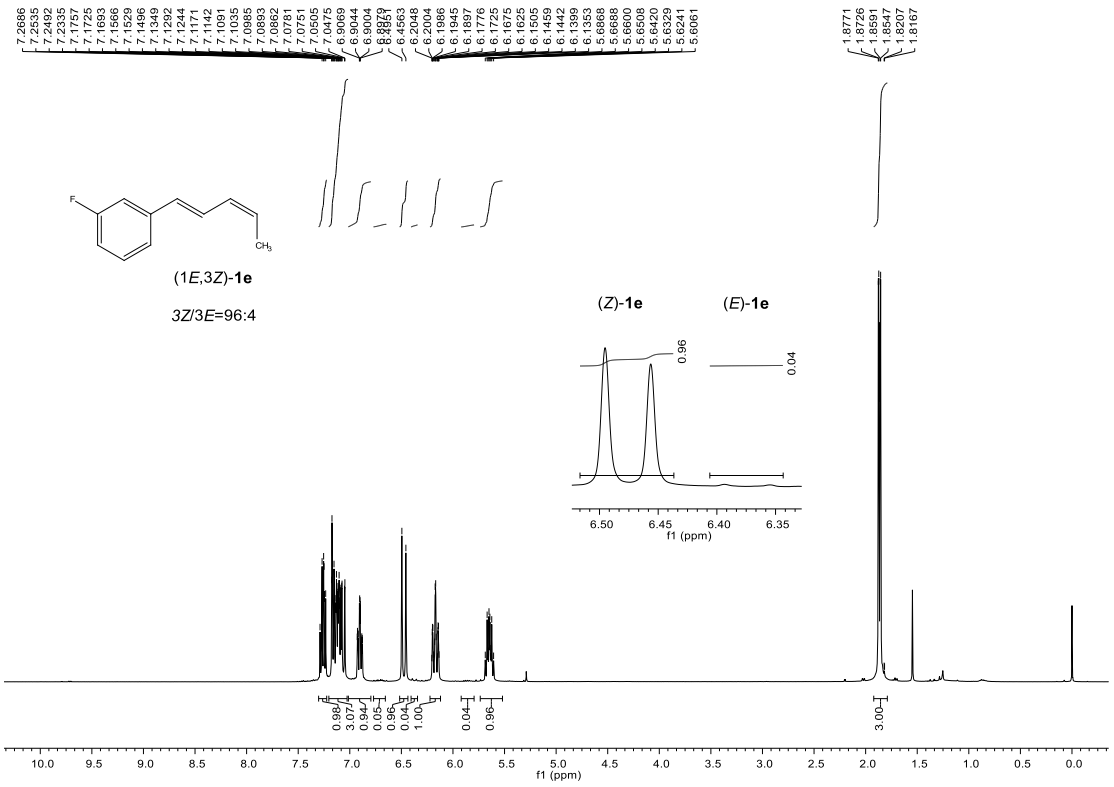
(1*E*,3*Z*)-**1d** ^{1}H NMR (400 MHz, $CDCl_3$)



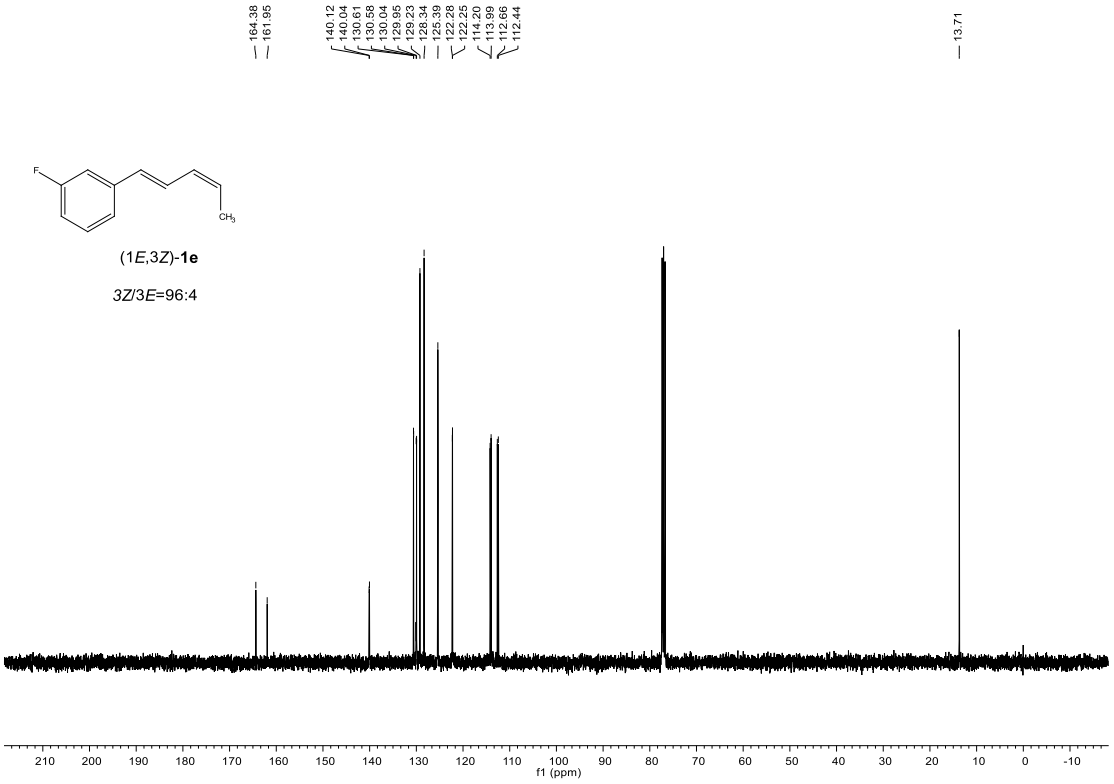
(1*E*,3*Z*)-**1d** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



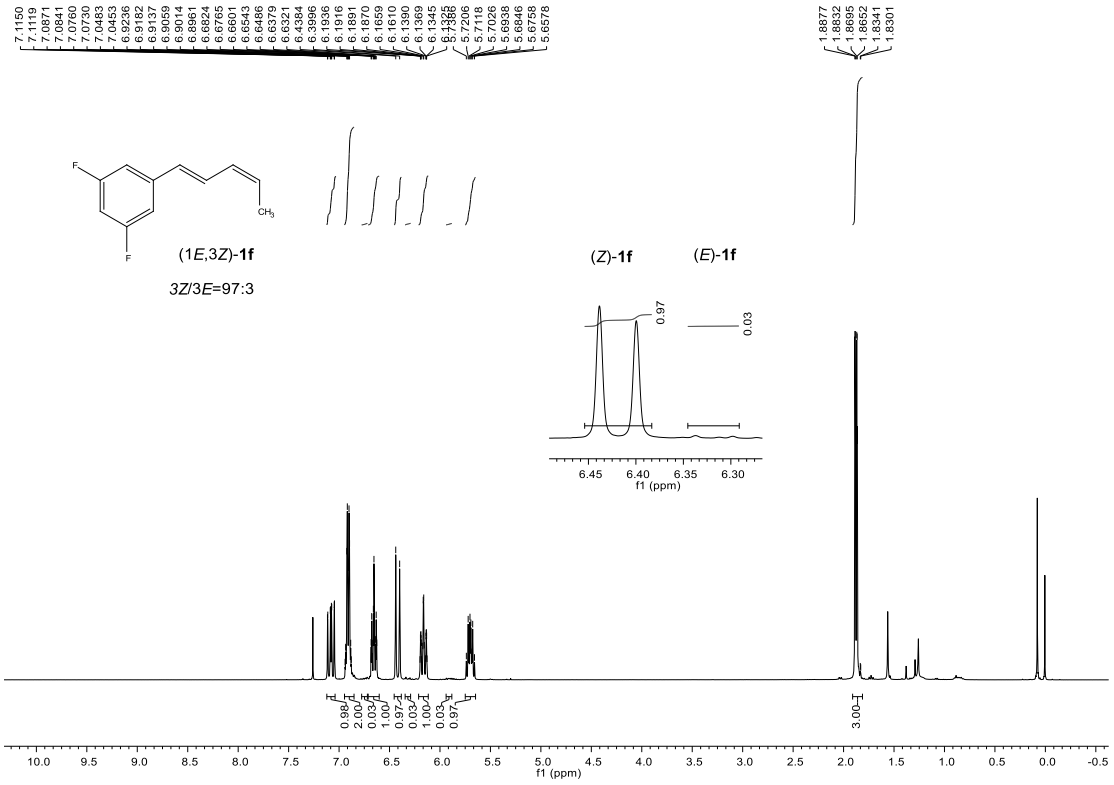
(1*E*,3*Z*)-**1e** ^{1}H NMR (400 MHz, $CDCl_3$)



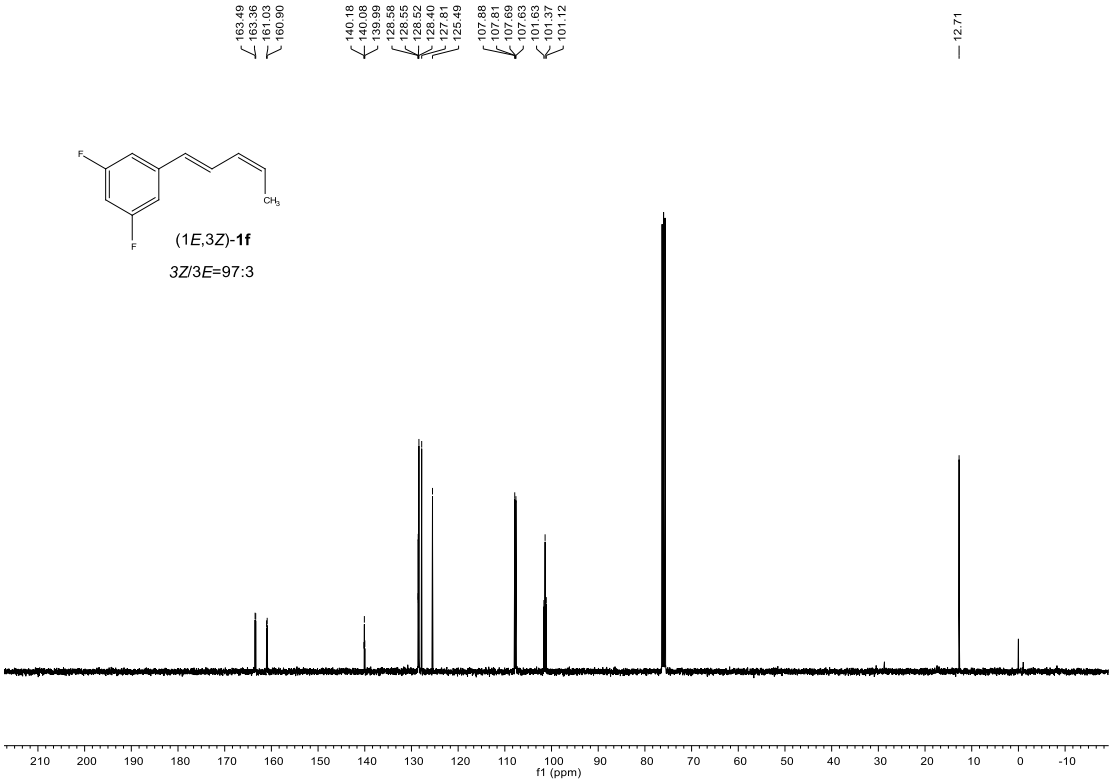
(1*E*,3*Z*)-**1e** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



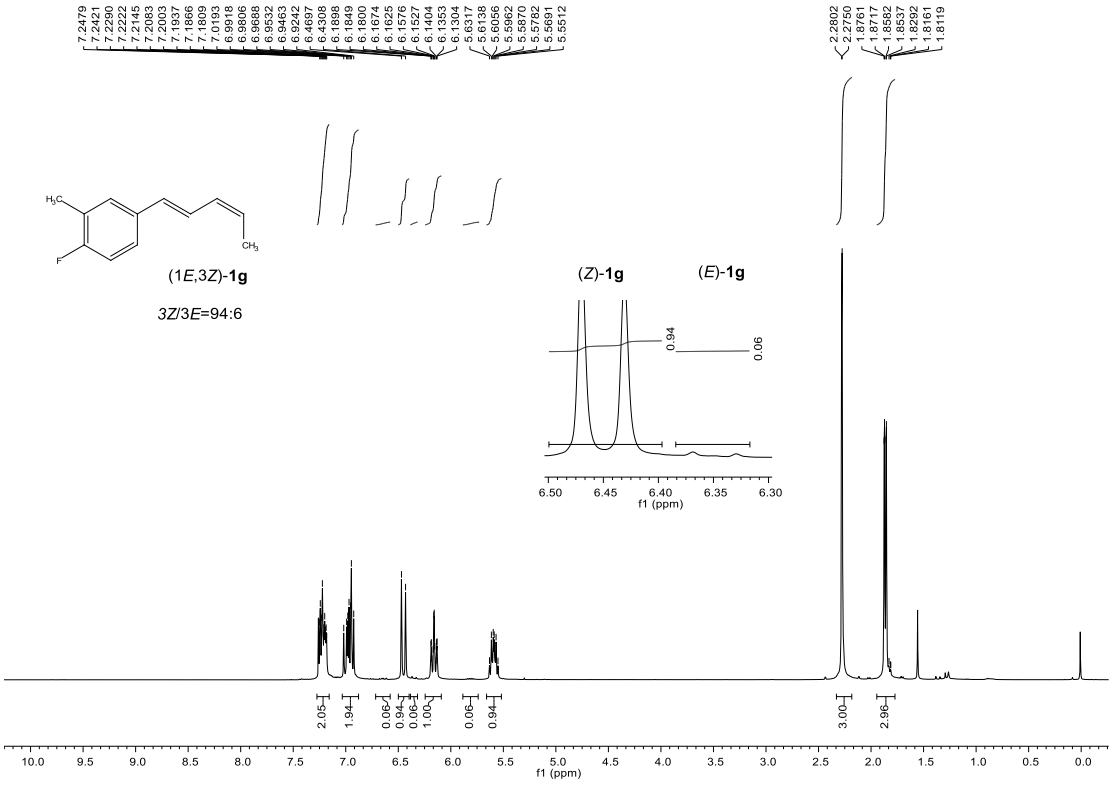
(1*E*,3*Z*)-**1f** ^{1}H NMR (400 MHz, $CDCl_3$)



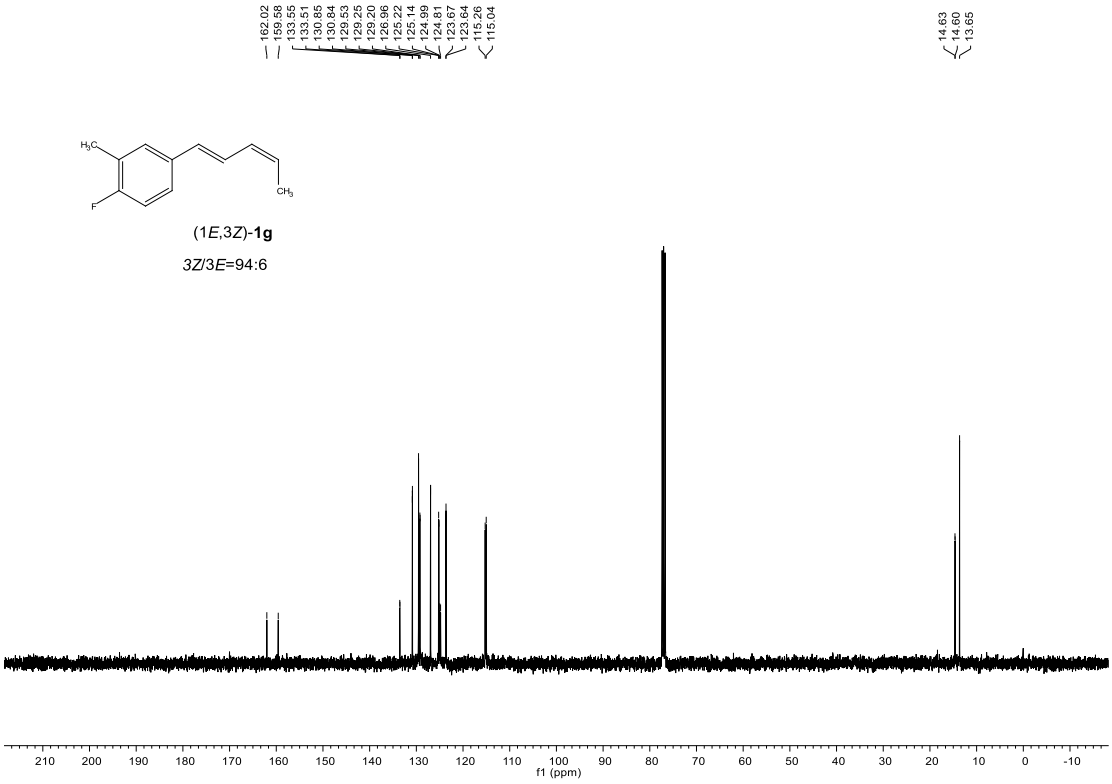
(1*E*,3*Z*)-**1f** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



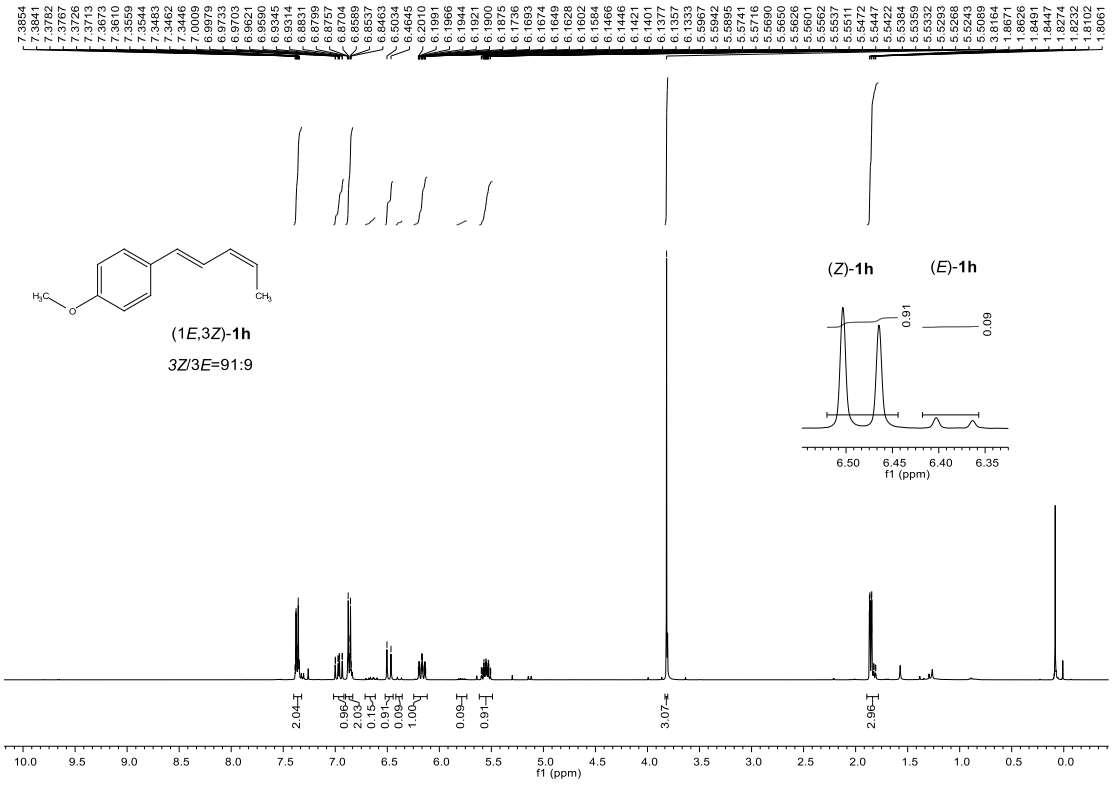
(1*E*,3*Z*)-**1g** ^{1}H NMR (400 MHz, $CDCl_3$)



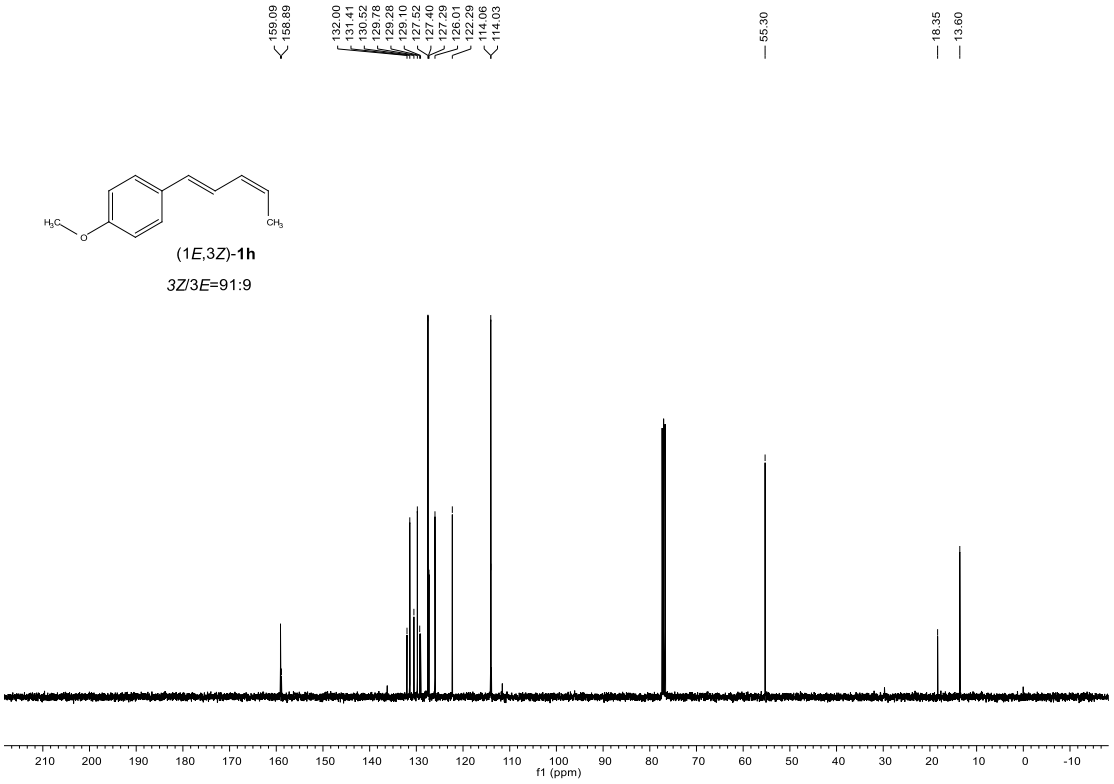
(1*E*,3*Z*)-**1g** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



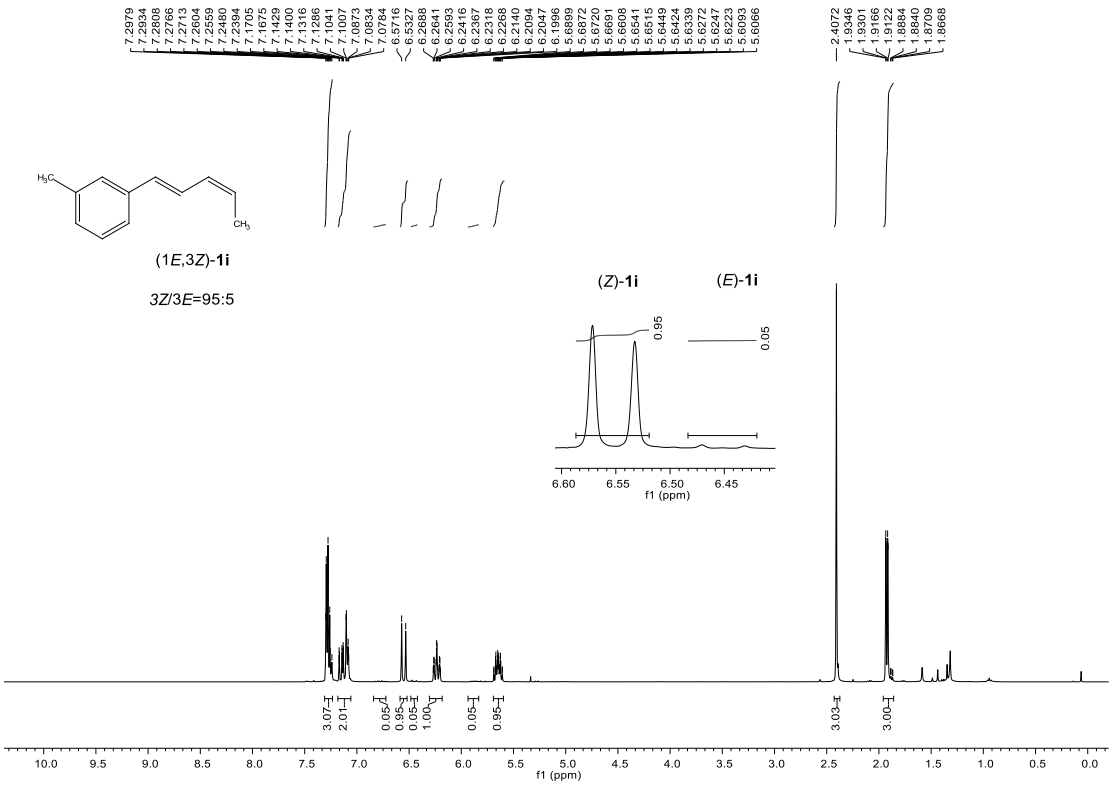
(1*E*,3*Z*)-**1h** ^{1}H NMR (400 MHz, $CDCl_3$)



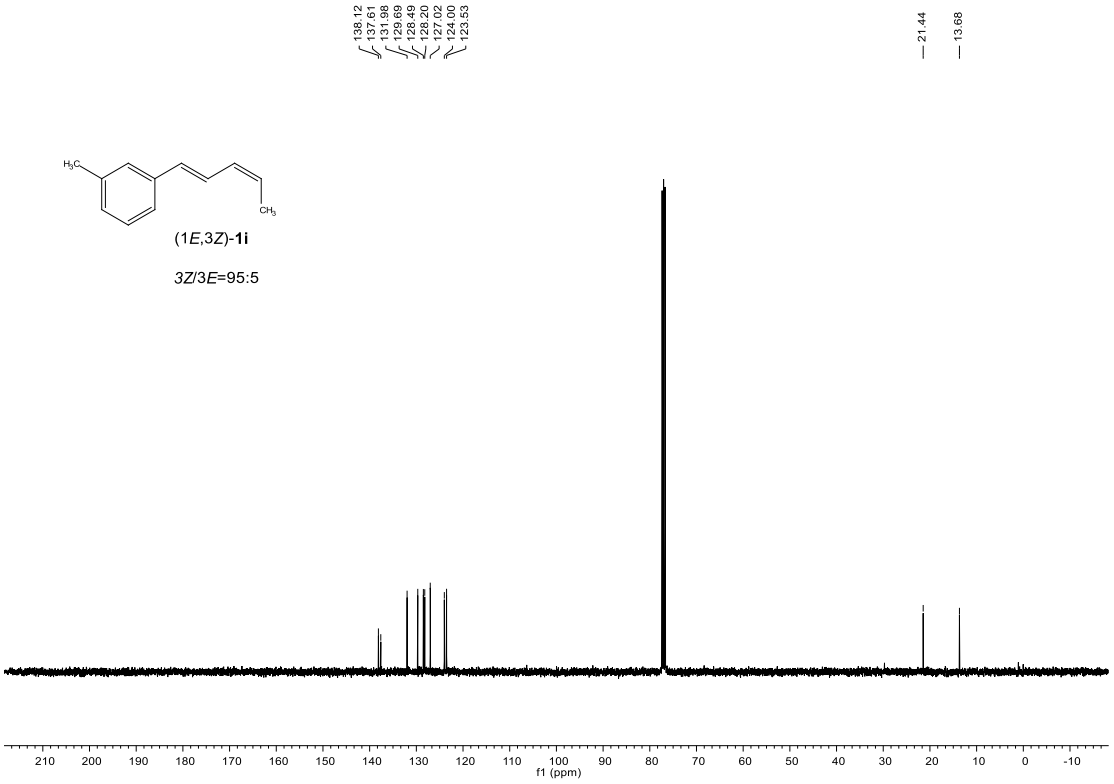
(1*E*,3*Z*)-**1h** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



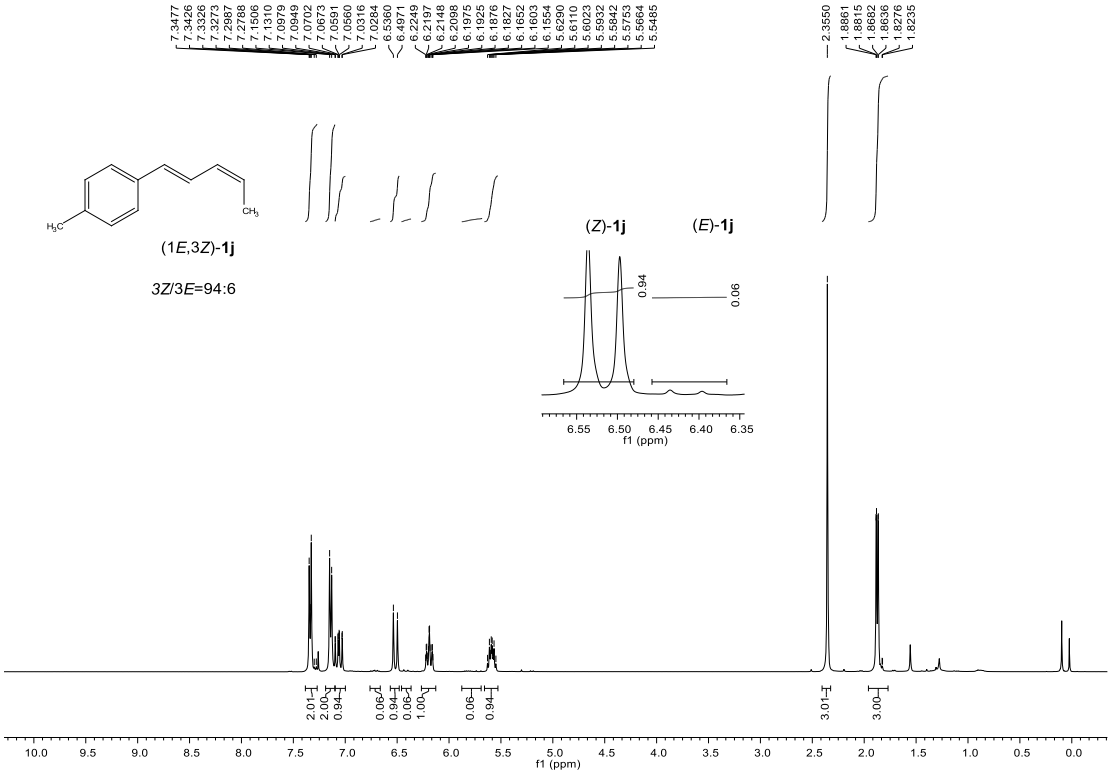
(1*E*,3*Z*)-**1i** ^{1}H NMR (400 MHz, $CDCl_3$)



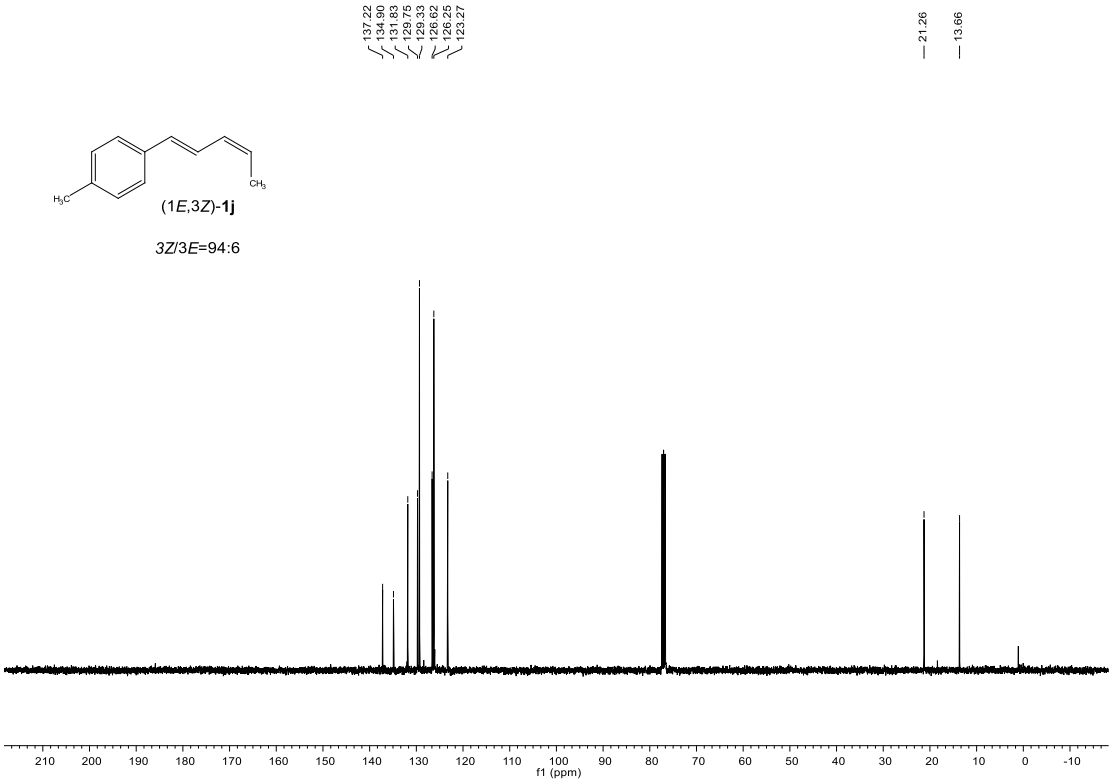
(1*E*,3*Z*)-**1i** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



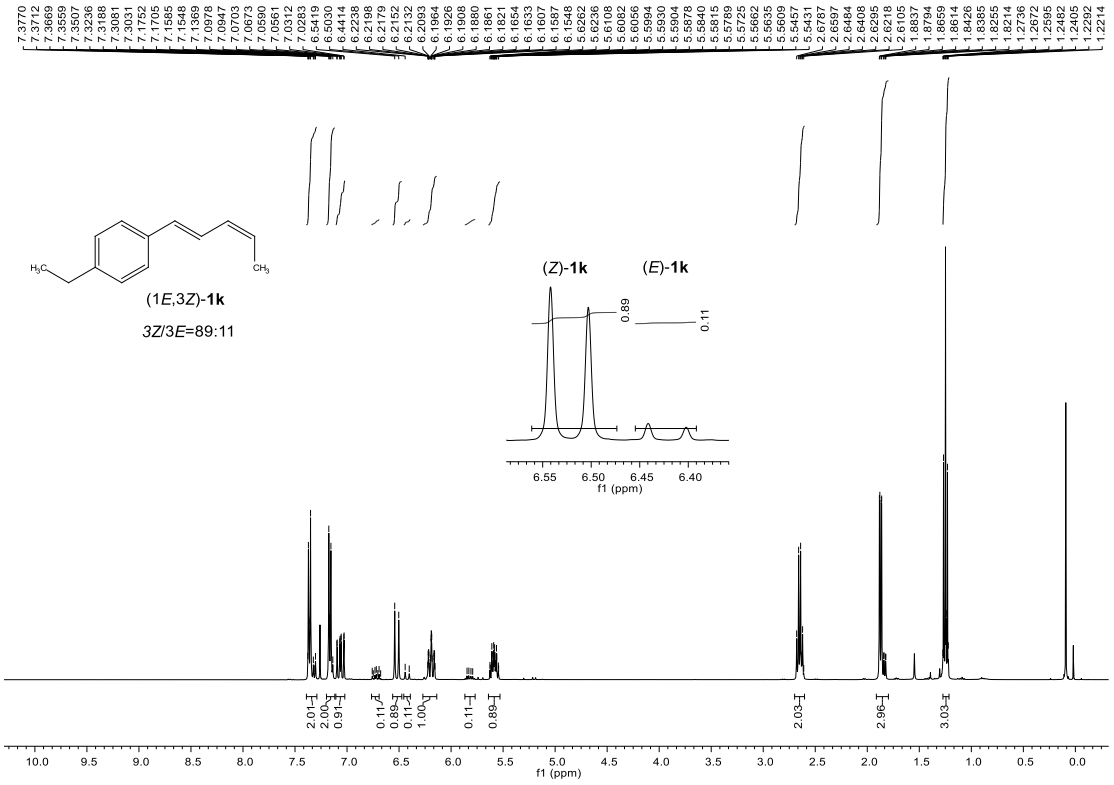
(1*E*,3*Z*)-**1j** ^{1}H NMR (400 MHz, $CDCl_3$)



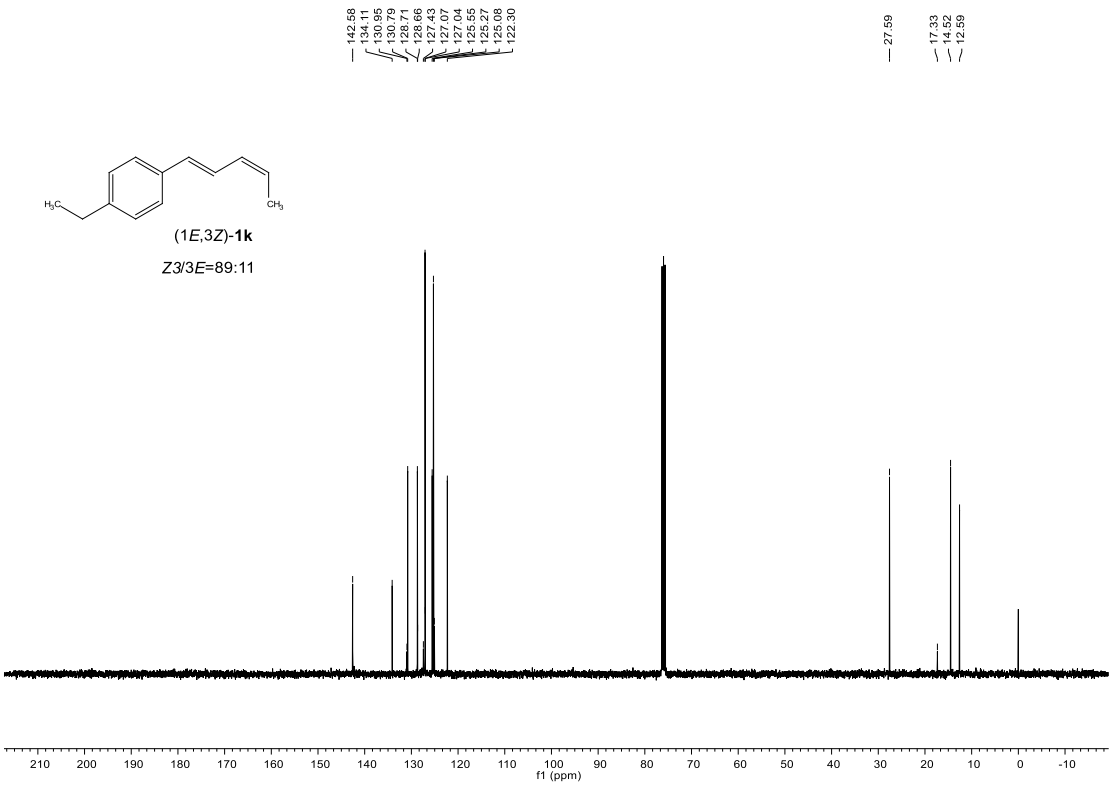
(1*E*,3*Z*)-**1j** $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



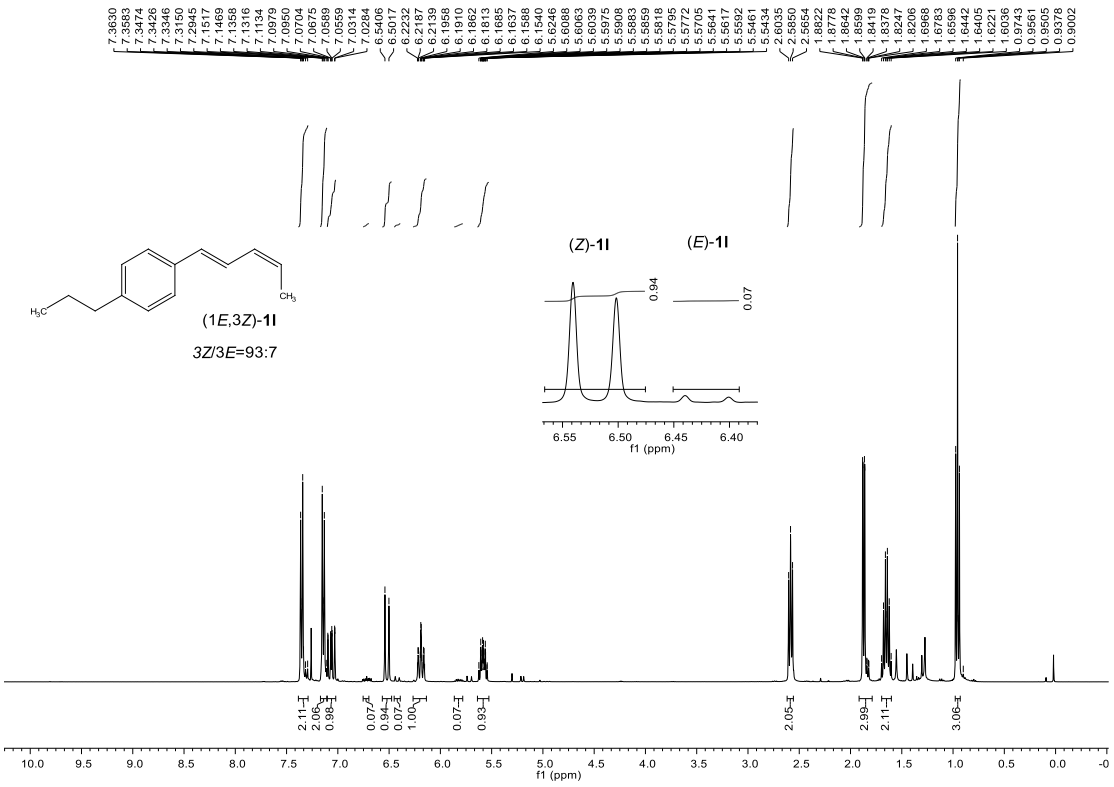
(1*E*,3*Z*)-**1k** ^{1}H NMR (400 MHz, $CDCl_3$)



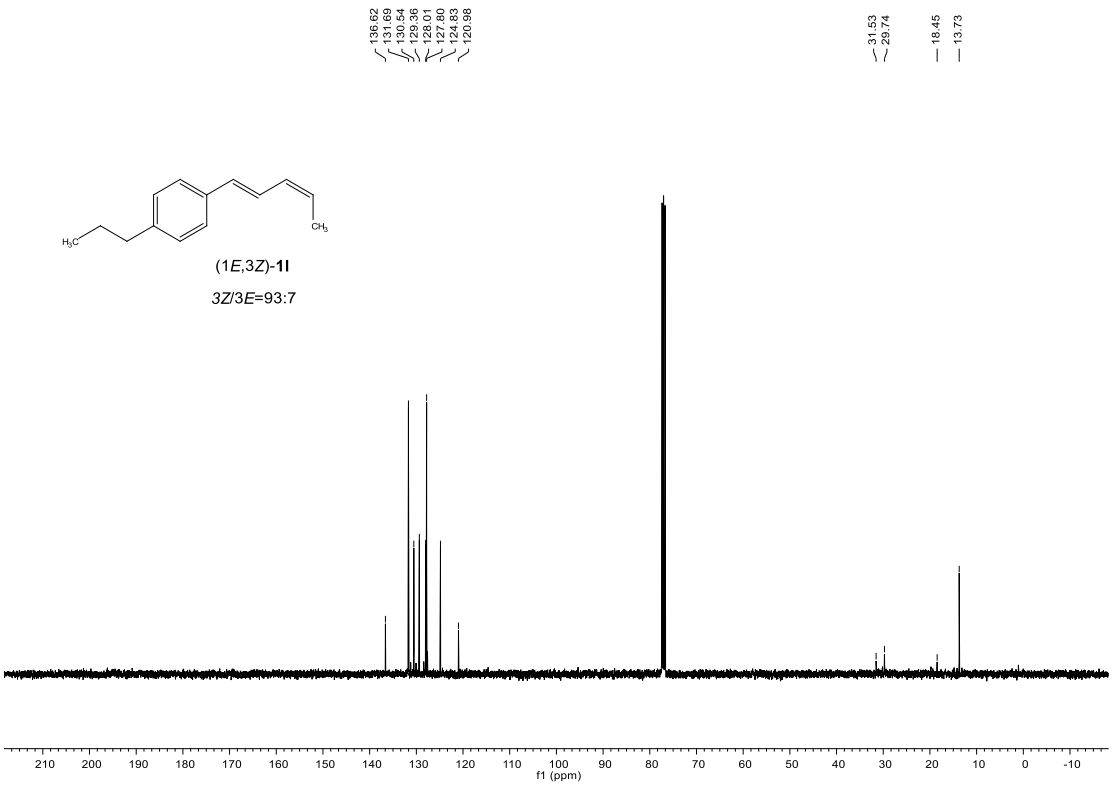
(1*E*,3*Z*)-**1k** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



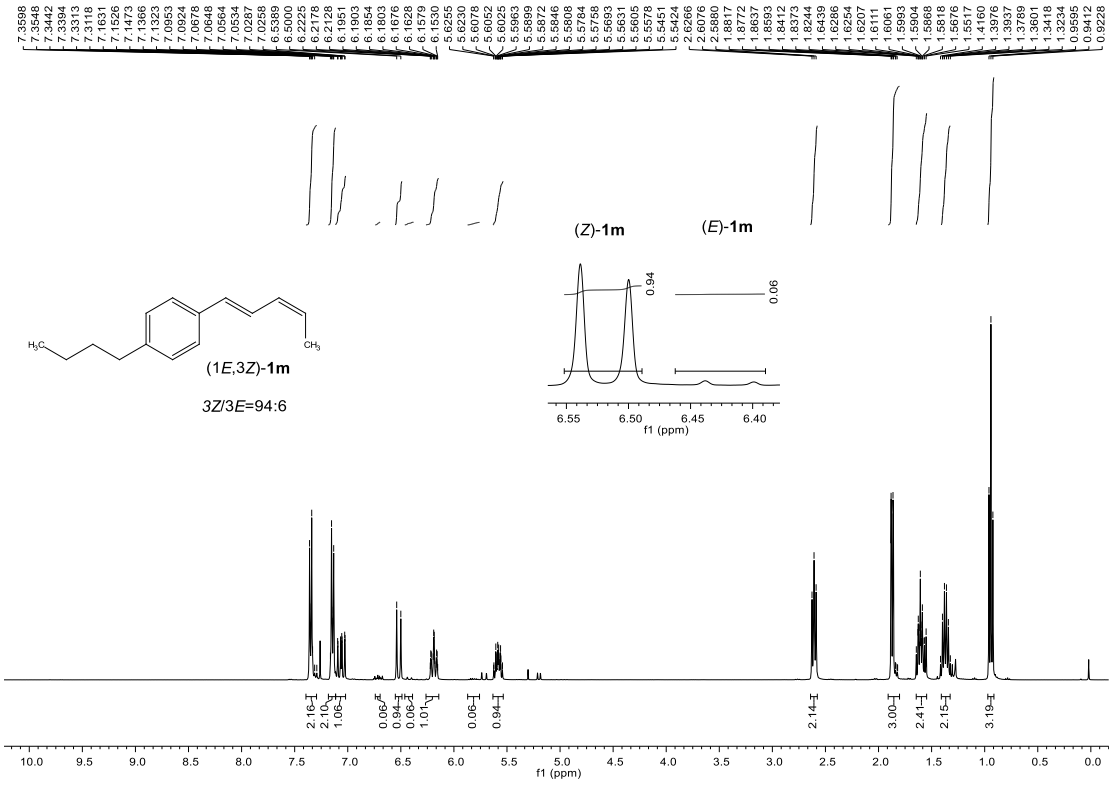
(1*E*,3*Z*)-**1l** ^{1}H NMR (400 MHz, $CDCl_3$)



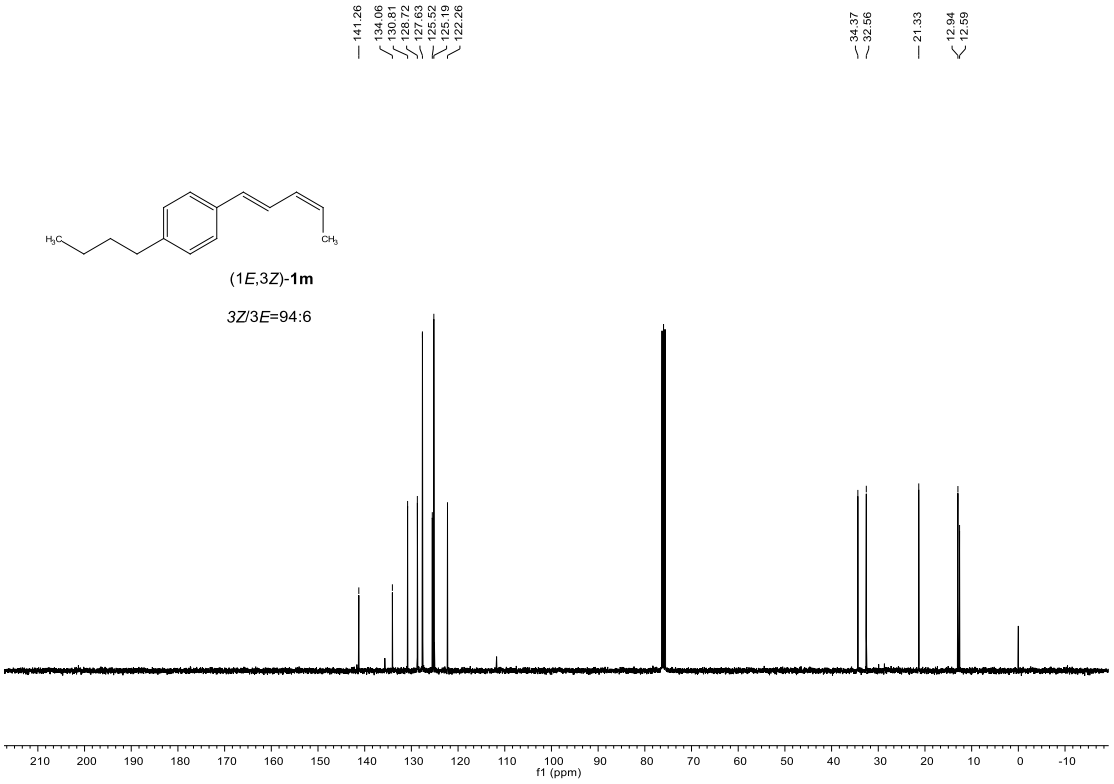
(1*E*,3*Z*)-**1l** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



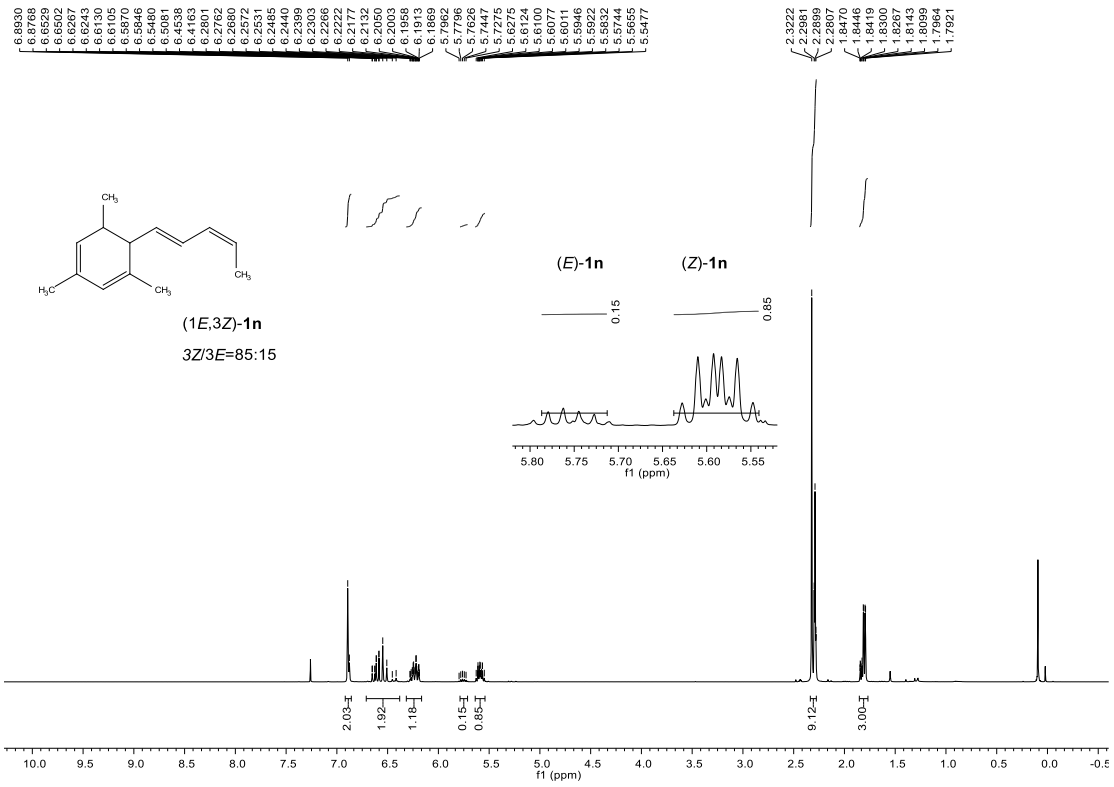
(1*E*,3*Z*)-**1m** ^{1}H NMR (400 MHz, $CDCl_3$)



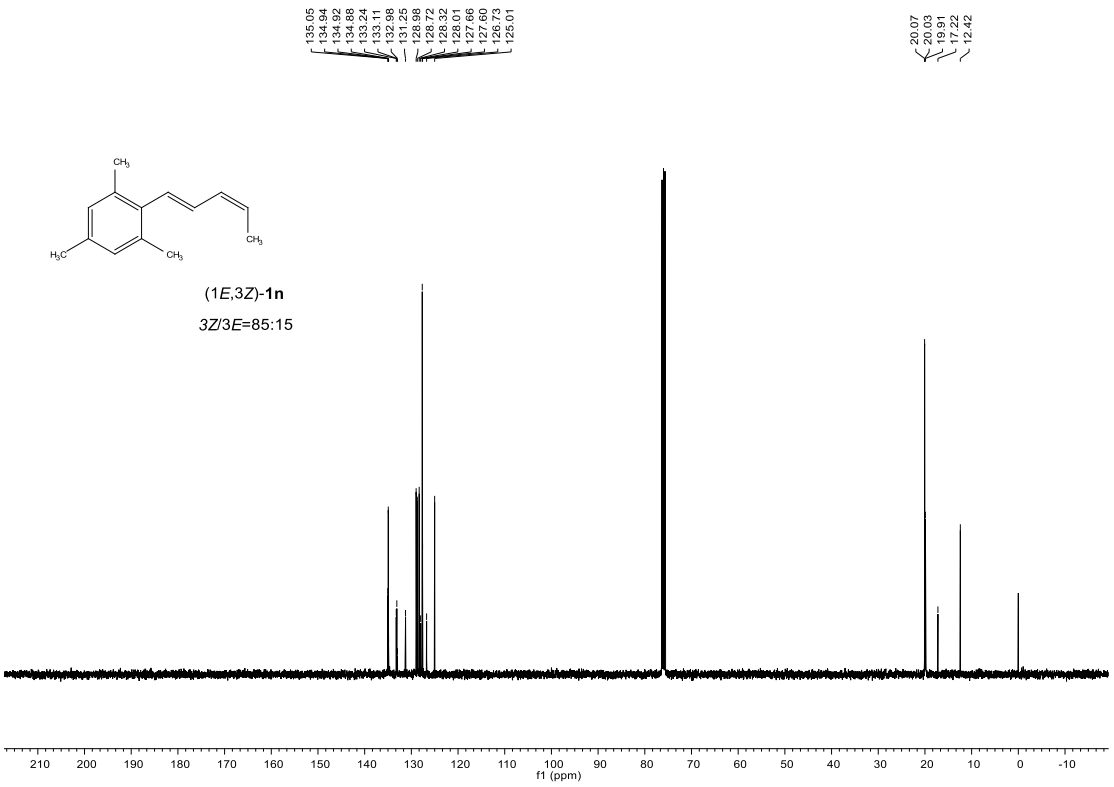
(1*E*,3*Z*)-**1m** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



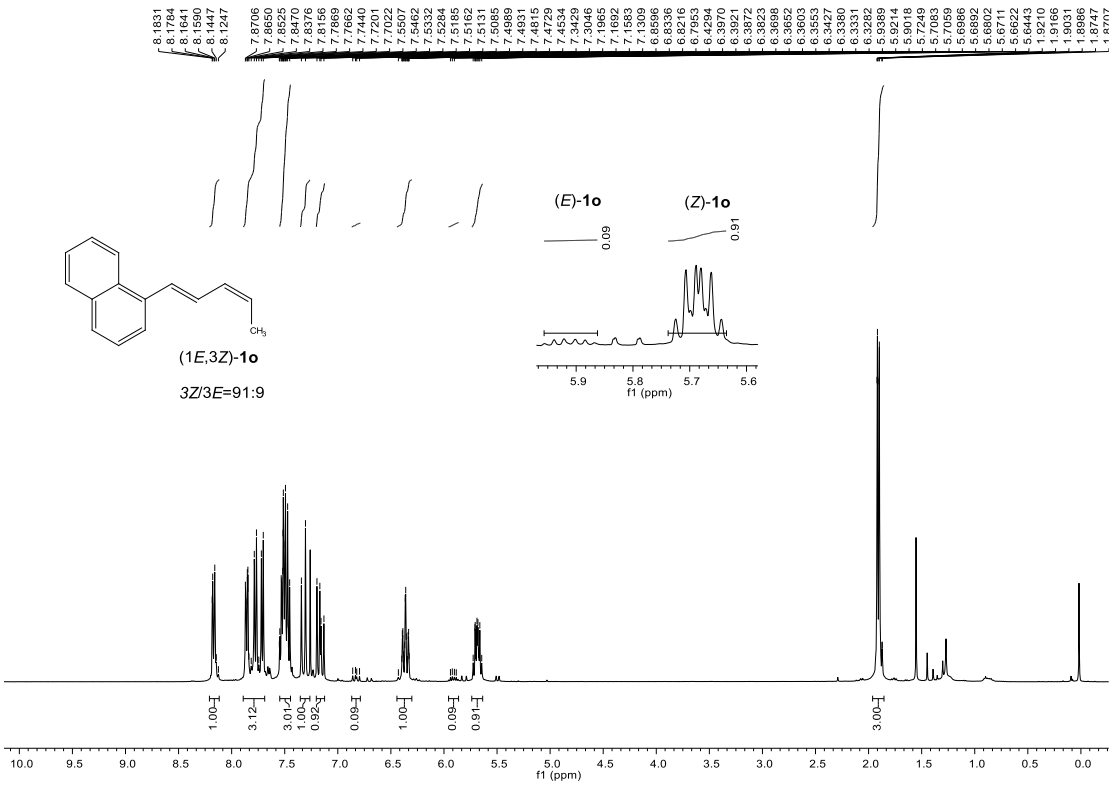
(1*E*,3*Z*)-**1n** ^{1}H NMR (400 MHz, $CDCl_3$)



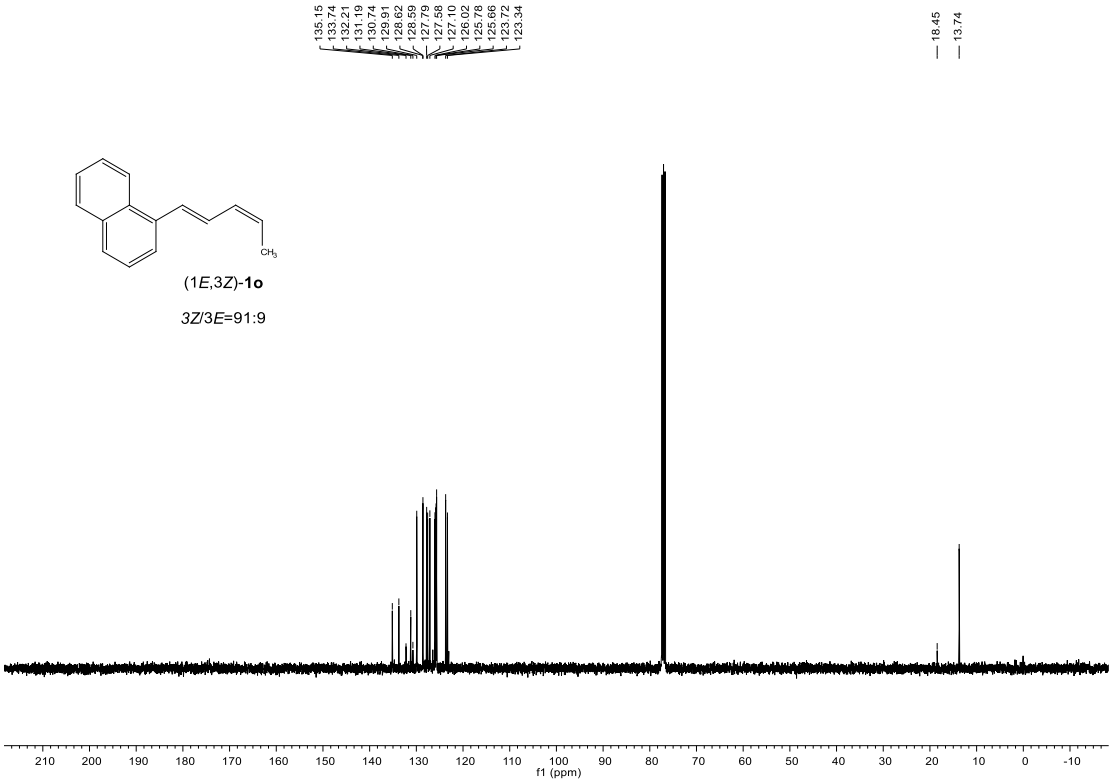
(1*E*,3*Z*)-**1n** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



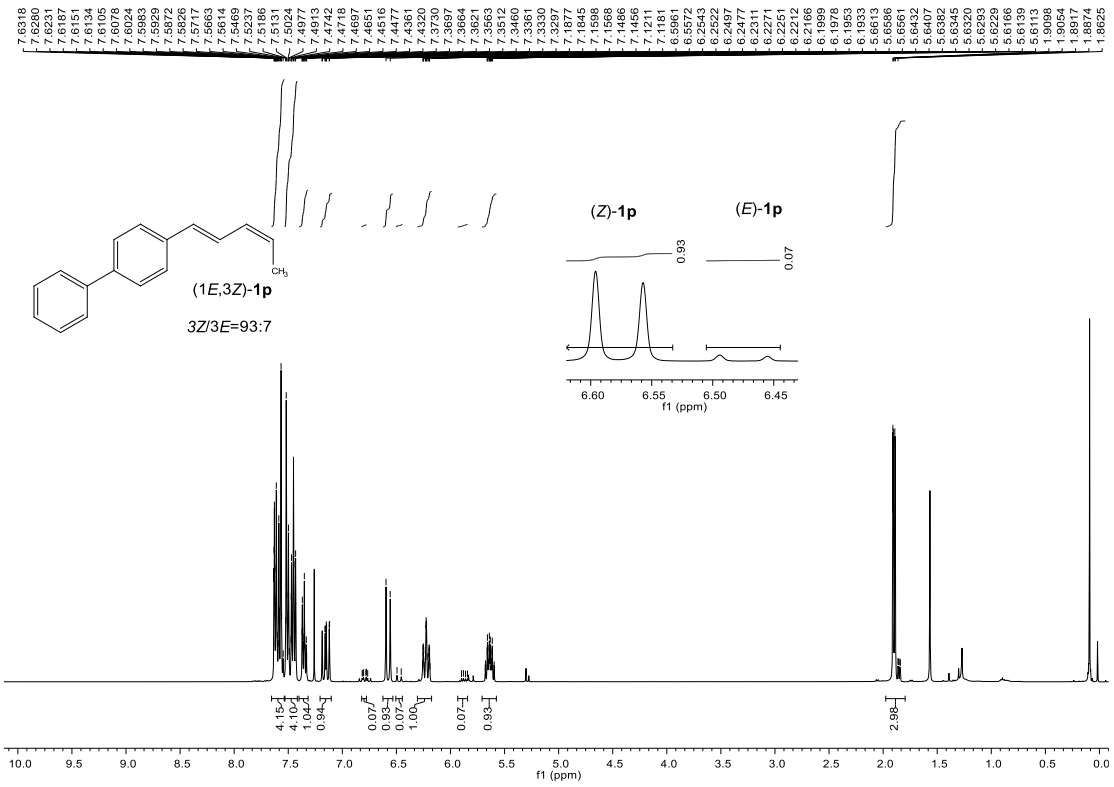
(1*E*,3*Z*)-**1o** ^{1}H NMR (400 MHz, $CDCl_3$)



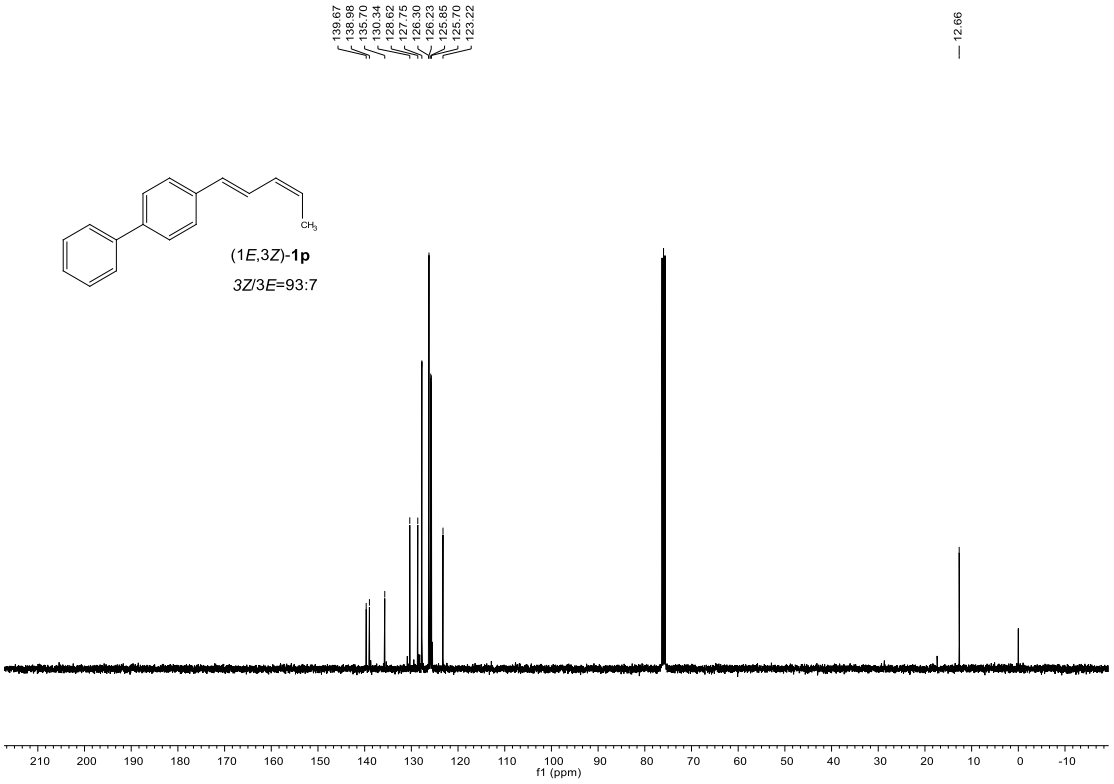
(1*E*,3*Z*)-**1o** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



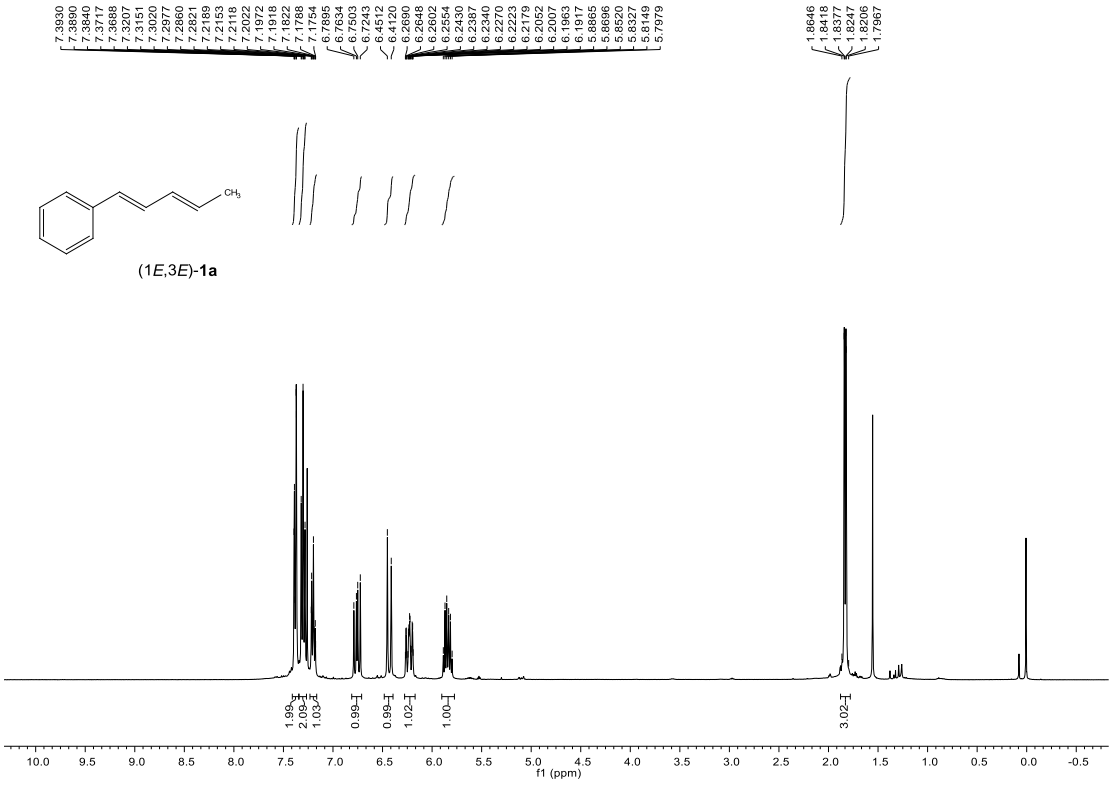
(1*E*,3*Z*)-**1p** ^{1}H NMR (400 MHz, $CDCl_3$)



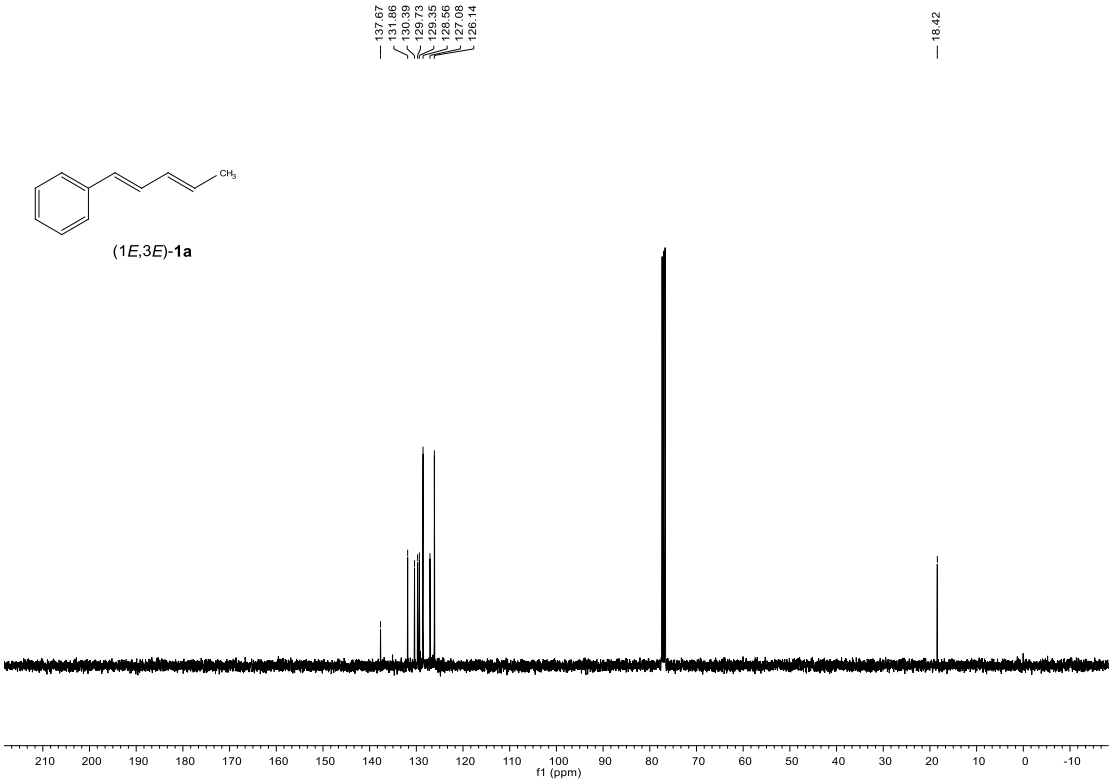
(1*E*,3*Z*)-**1p** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



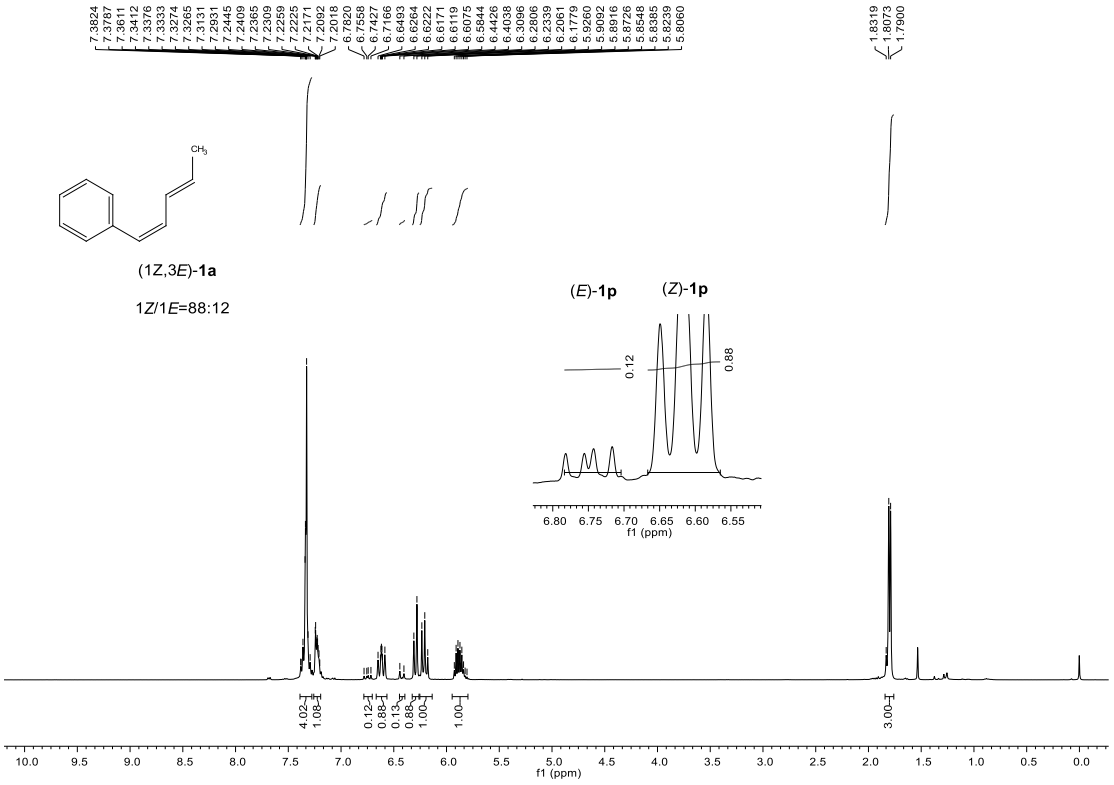
(1*E*,3*E*)-**1a** ^{1}H NMR (400 MHz, $CDCl_3$)



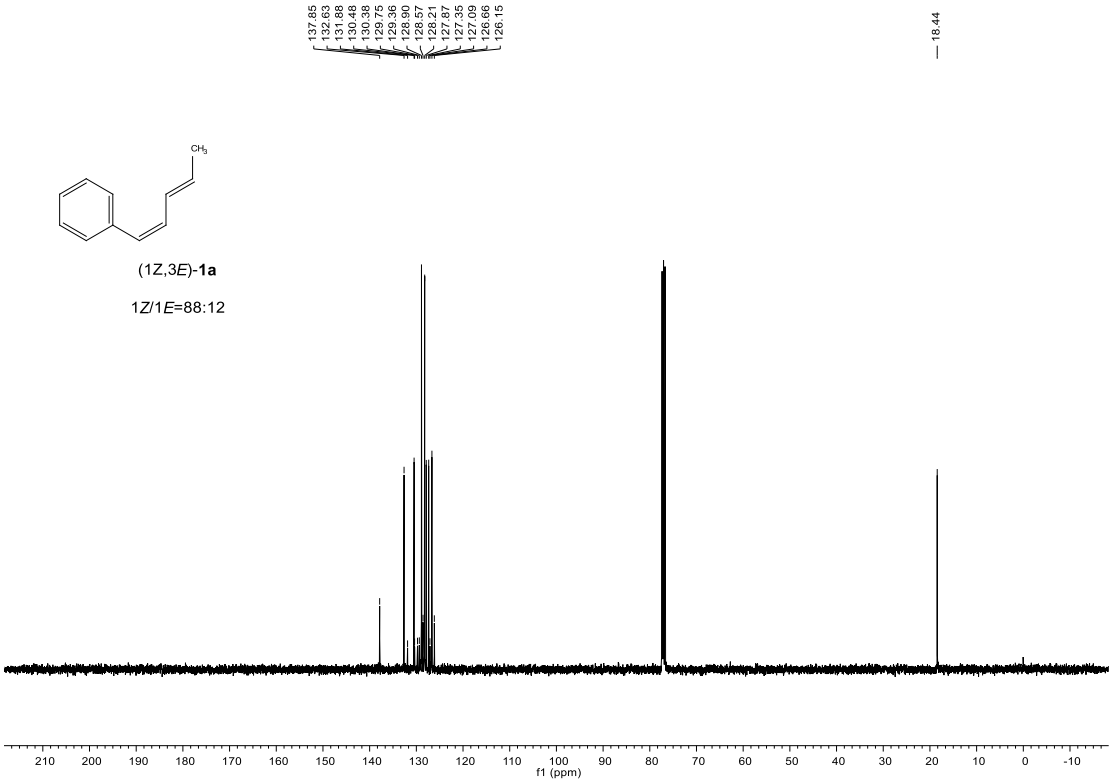
(1*E*,3*E*)-**1a** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



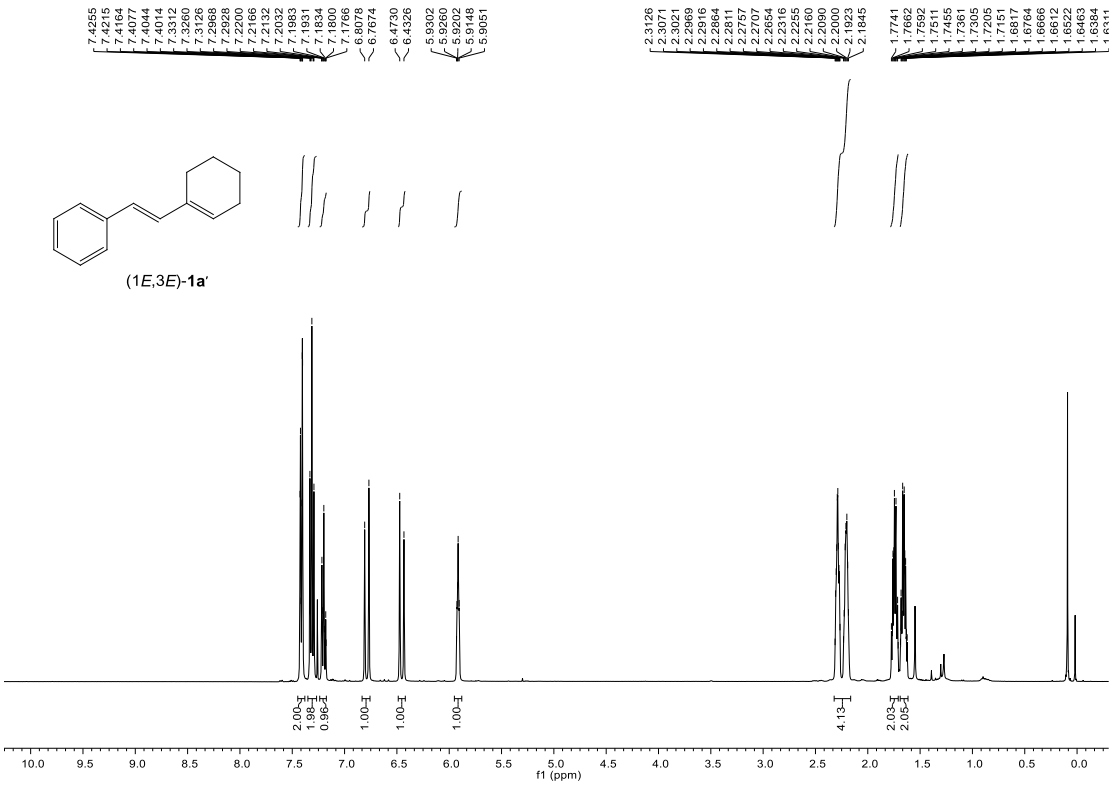
(1*Z*,3*E*)-**1a** ^{1}H NMR (400 MHz, $CDCl_3$)



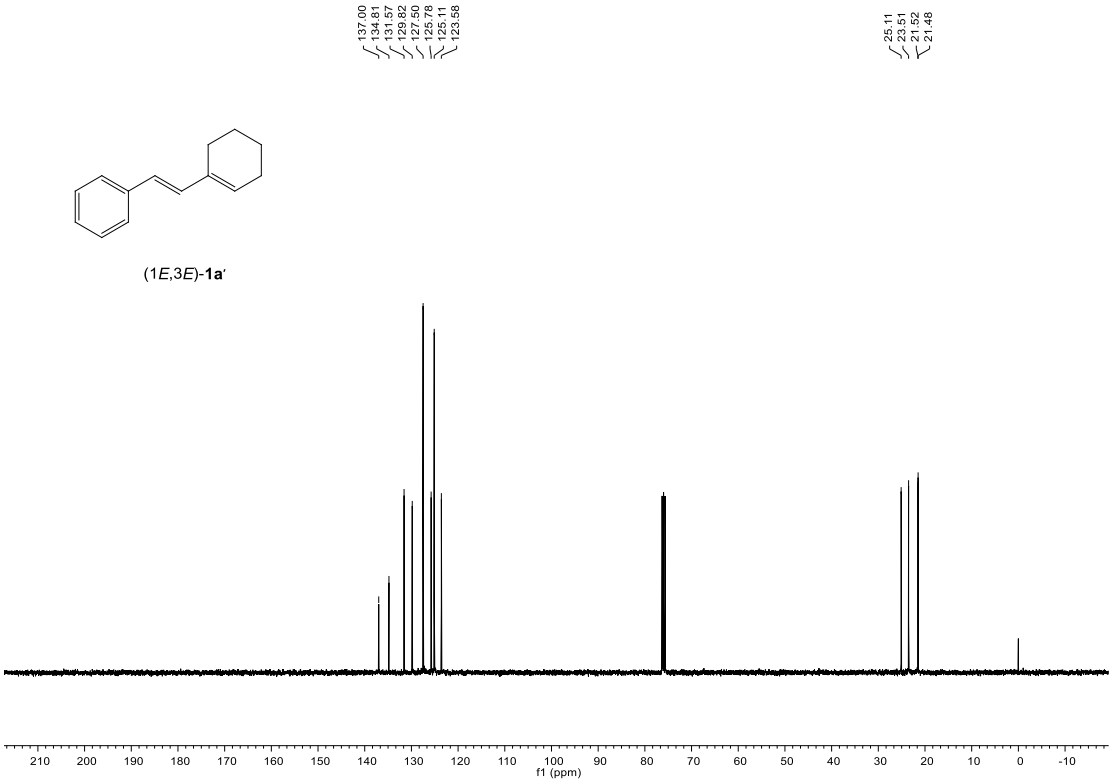
(1*Z*,3*E*)-**1a** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



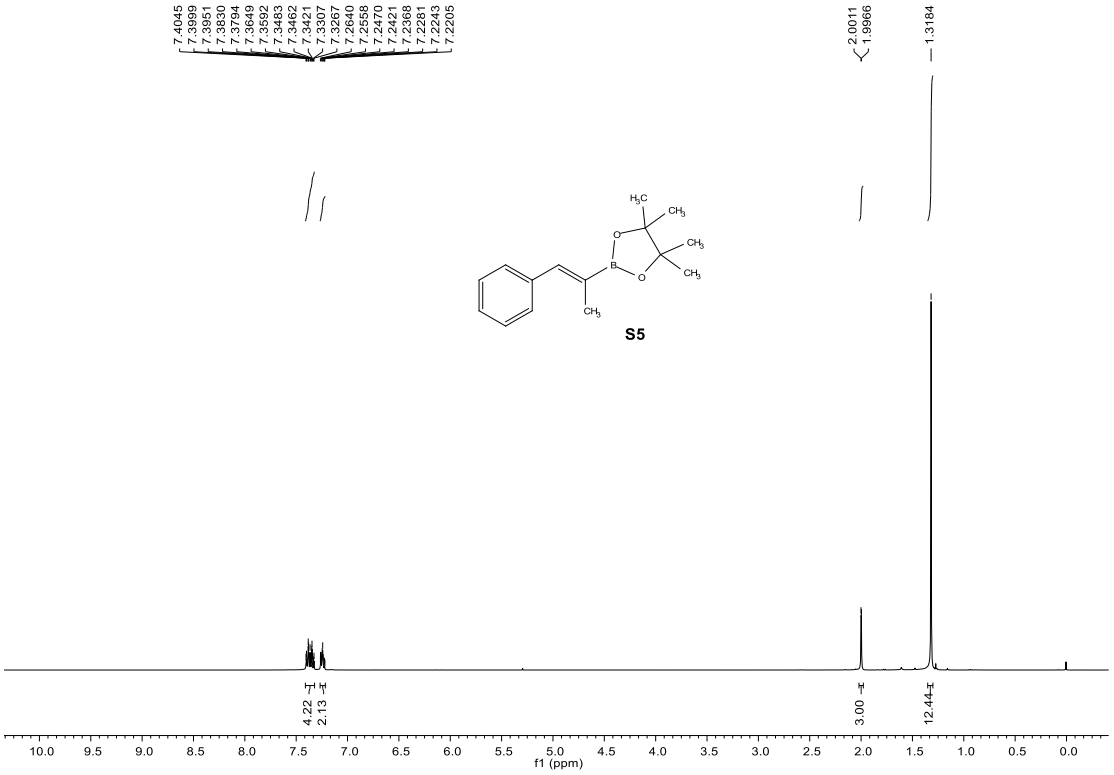
(1*E*,3*E*)-**1a′** ^{1}H NMR (400 MHz, $CDCl_3$)



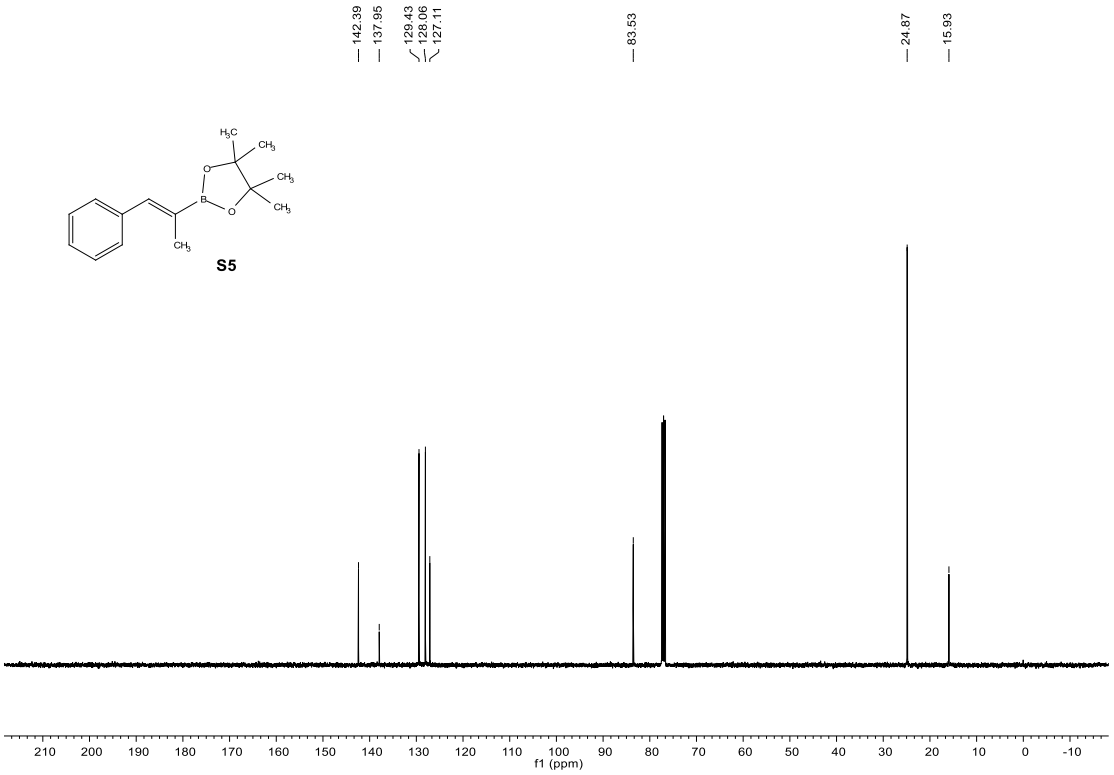
(1*E*,3*E*)-**1a′** ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



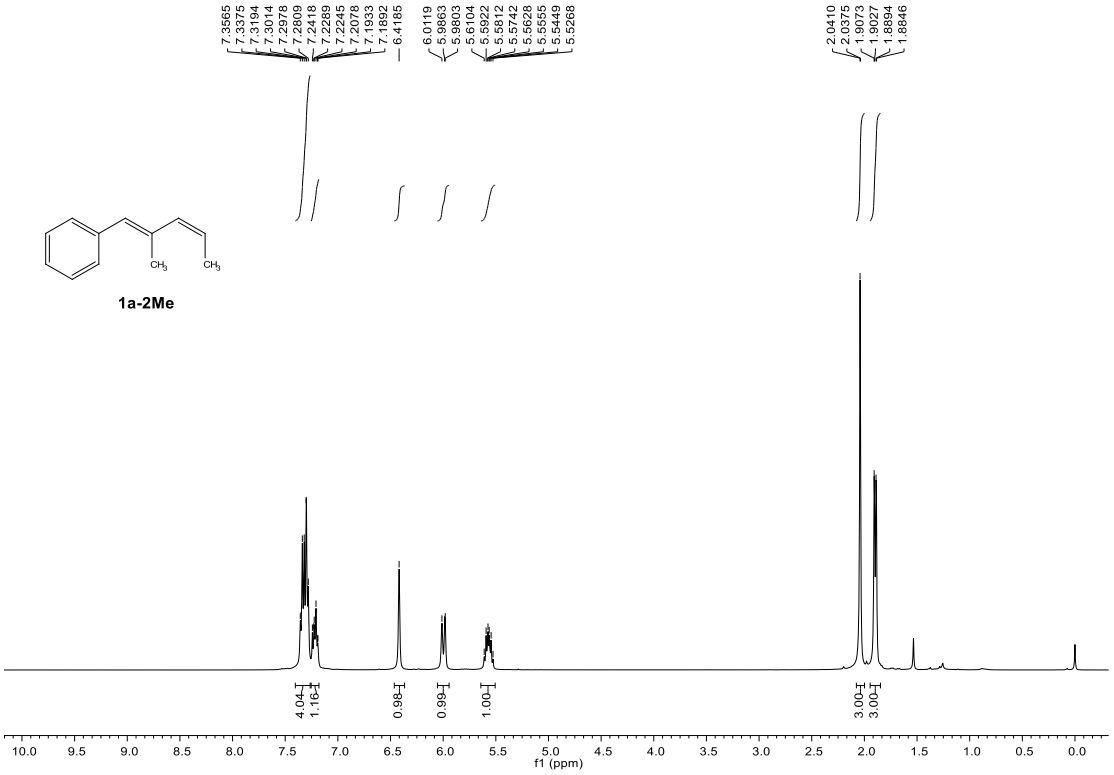
S5 ^{1}H NMR (400 MHz, $CDCl_3$)



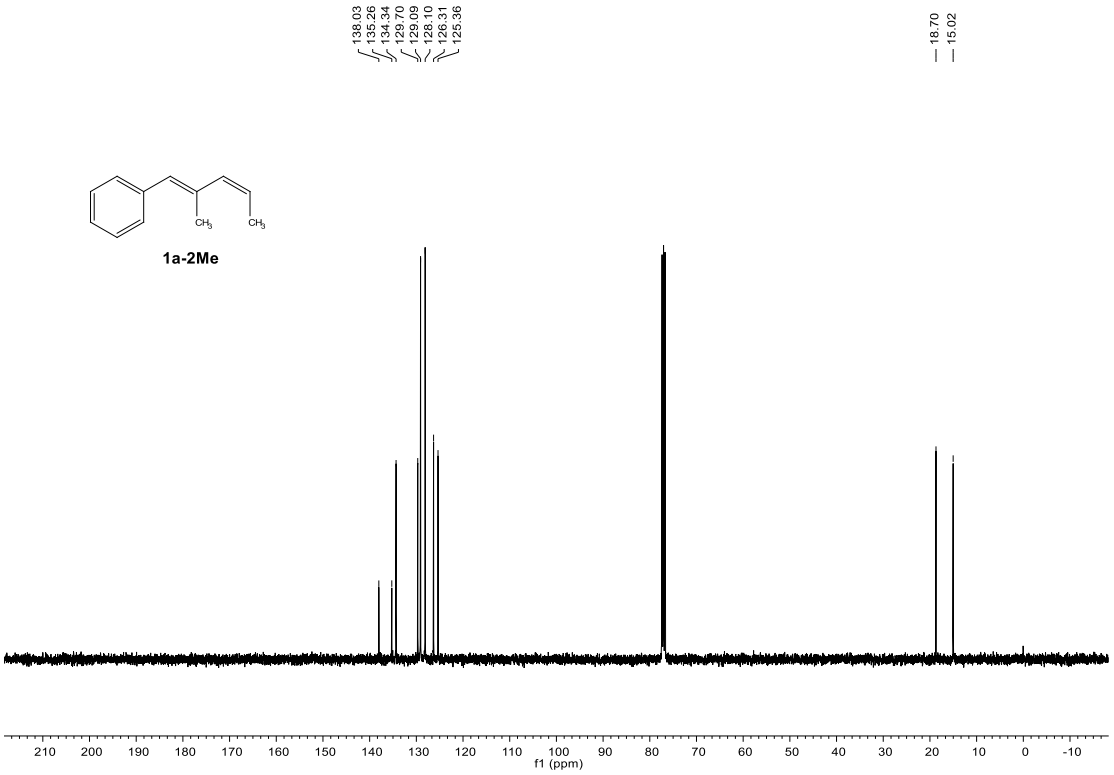
S5 ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



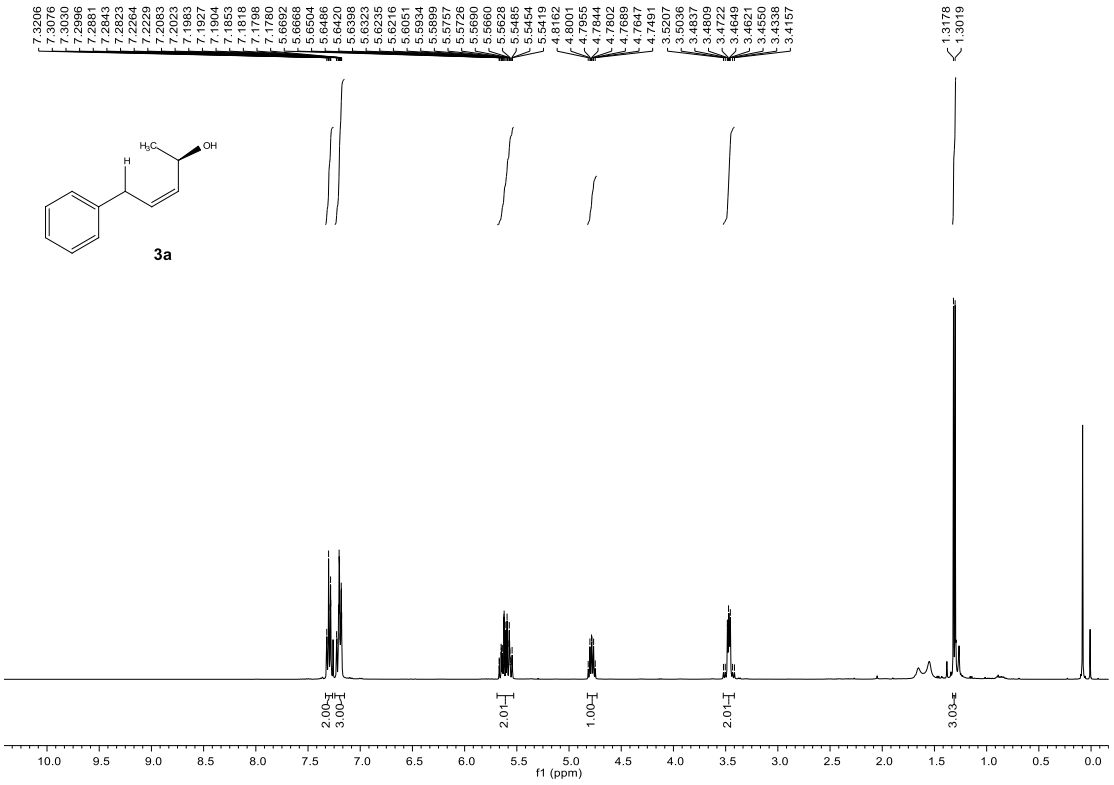
1a-2Me ^{1}H NMR (400 MHz, $CDCl_3$)



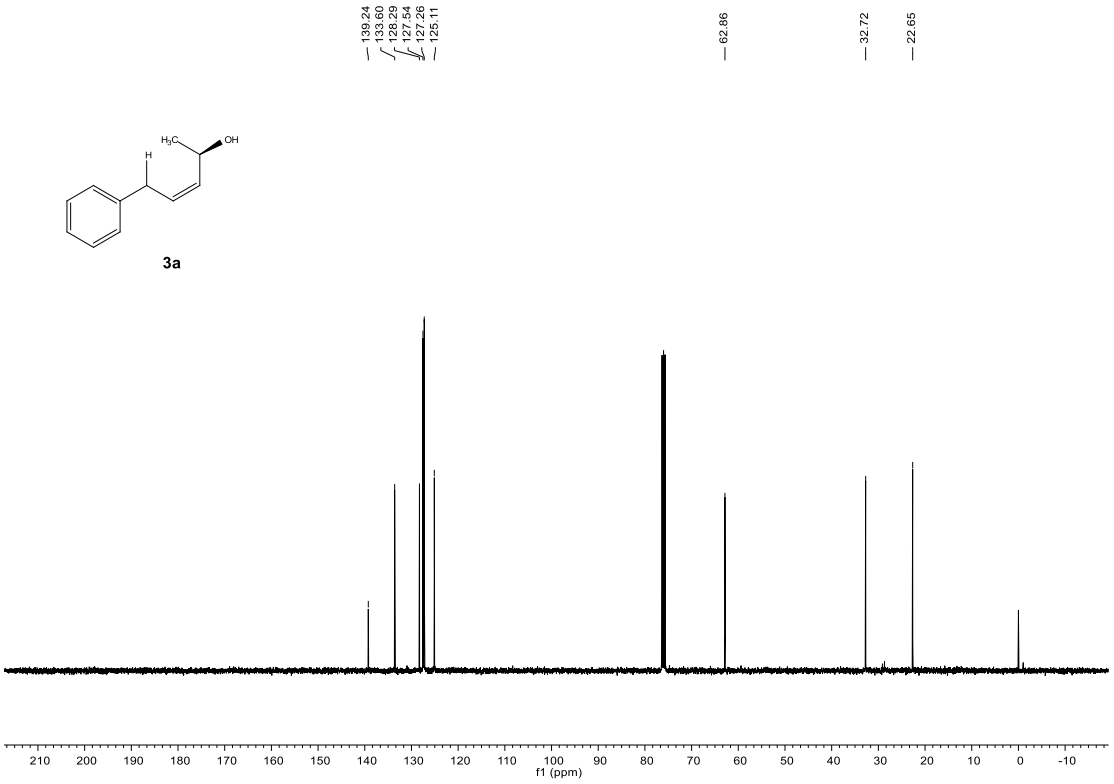
1a-2Me $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



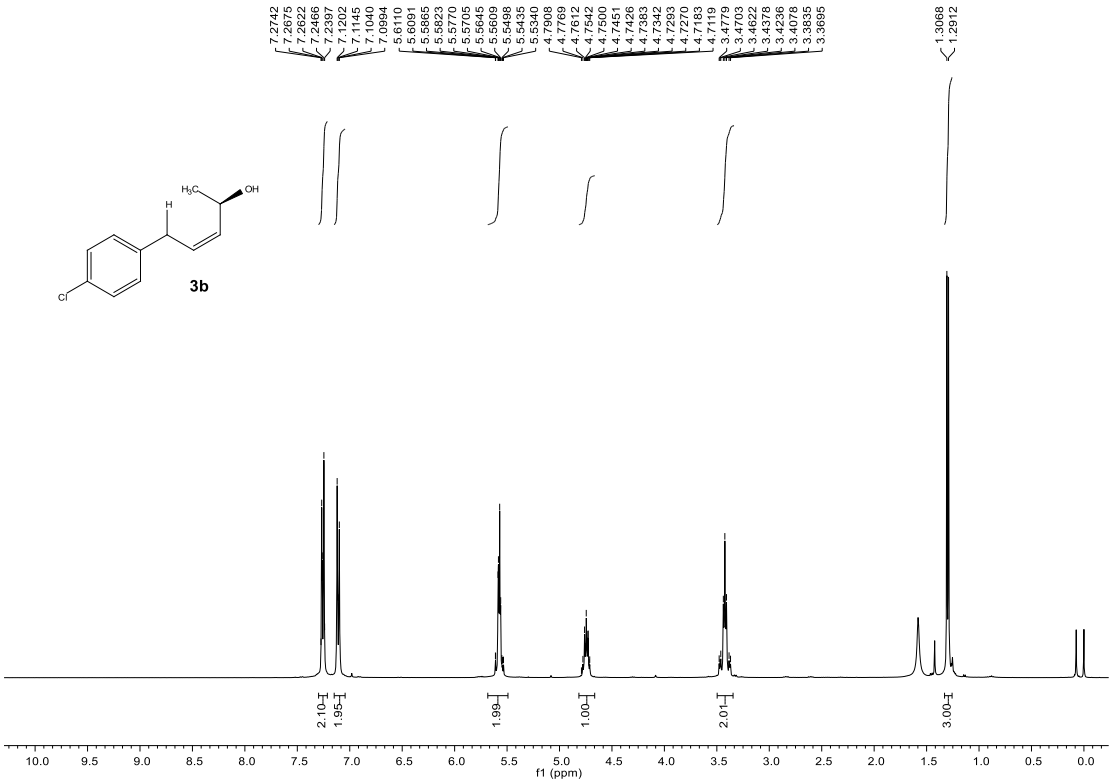
3a ^{1}H NMR (400 MHz, $CDCl_3$)



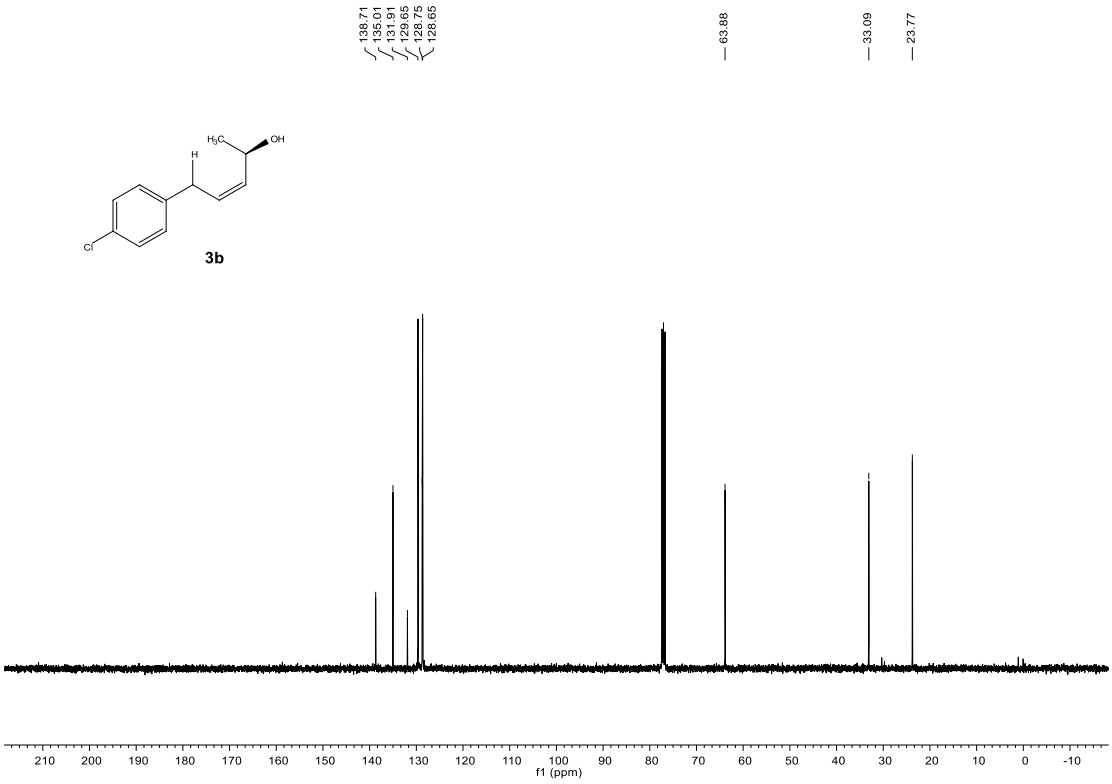
3a ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



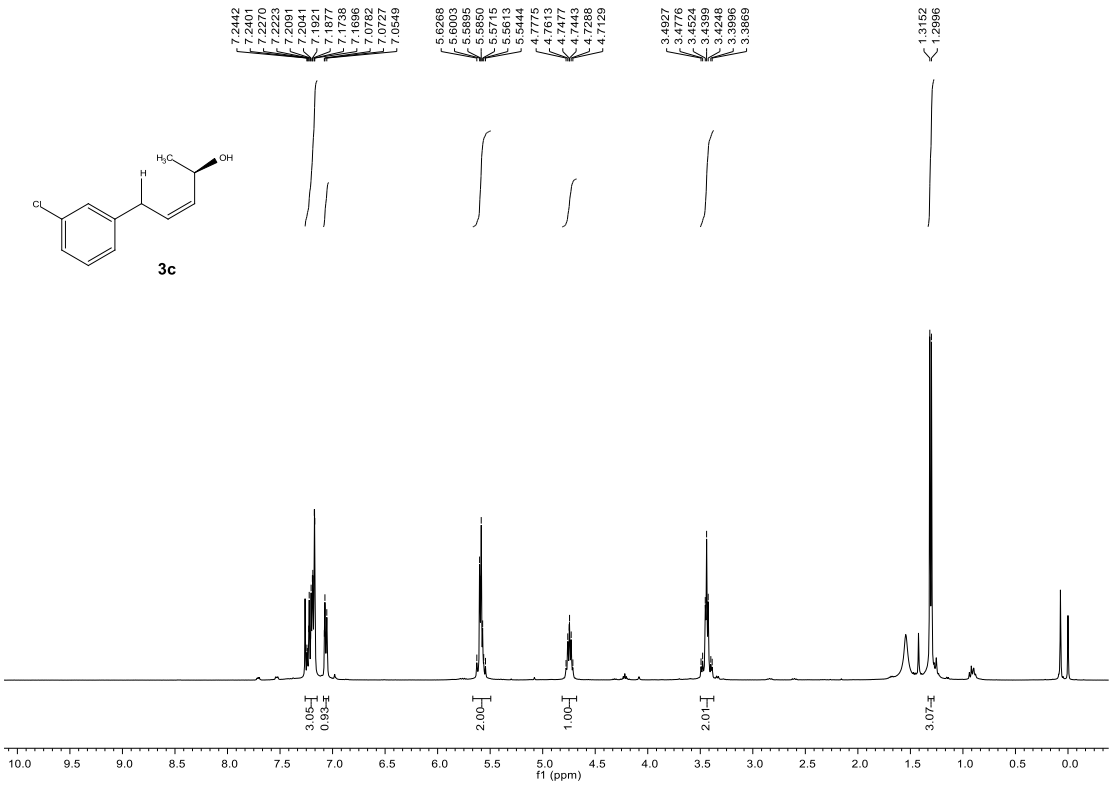
3b ^{1}H NMR (400 MHz, $CDCl_3$)



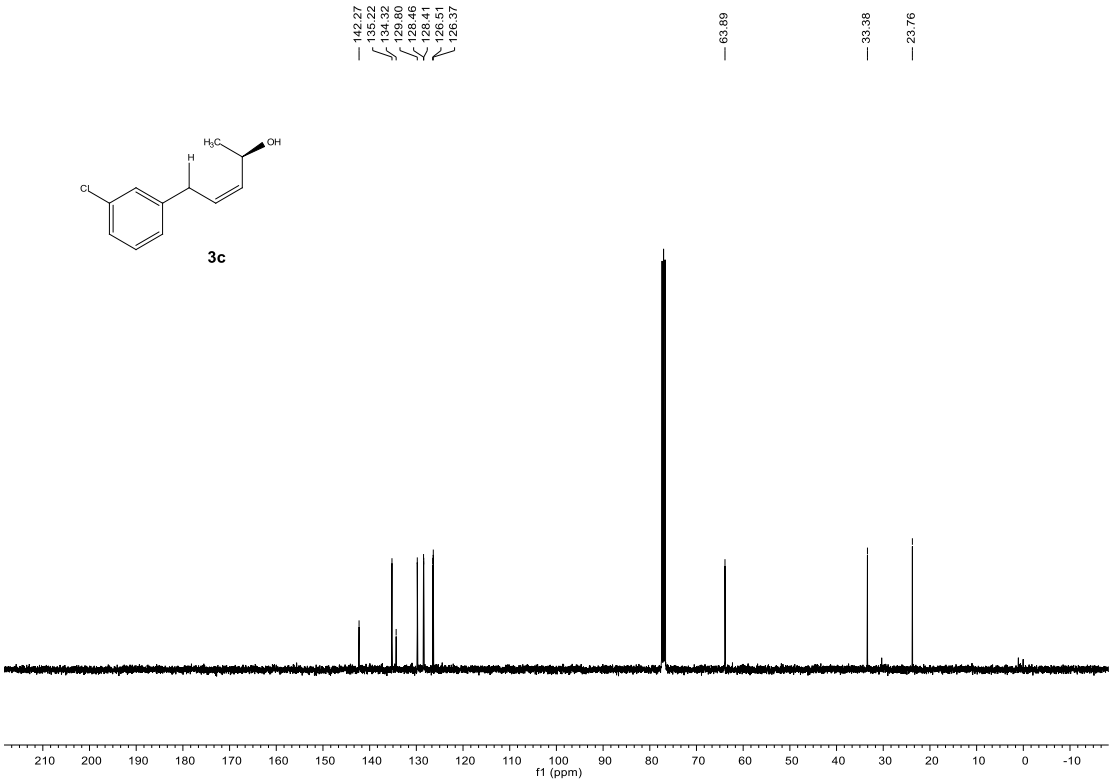
3b $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



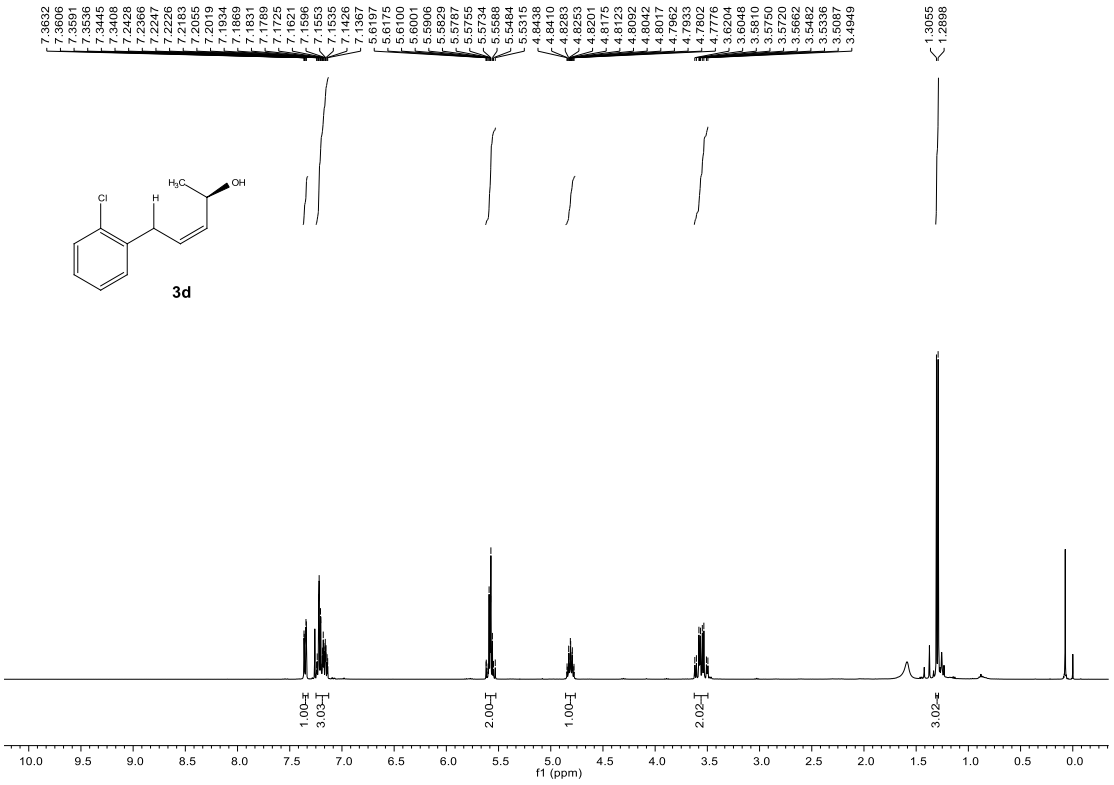
3c ^{1}H NMR (400 MHz, $CDCl_3$)



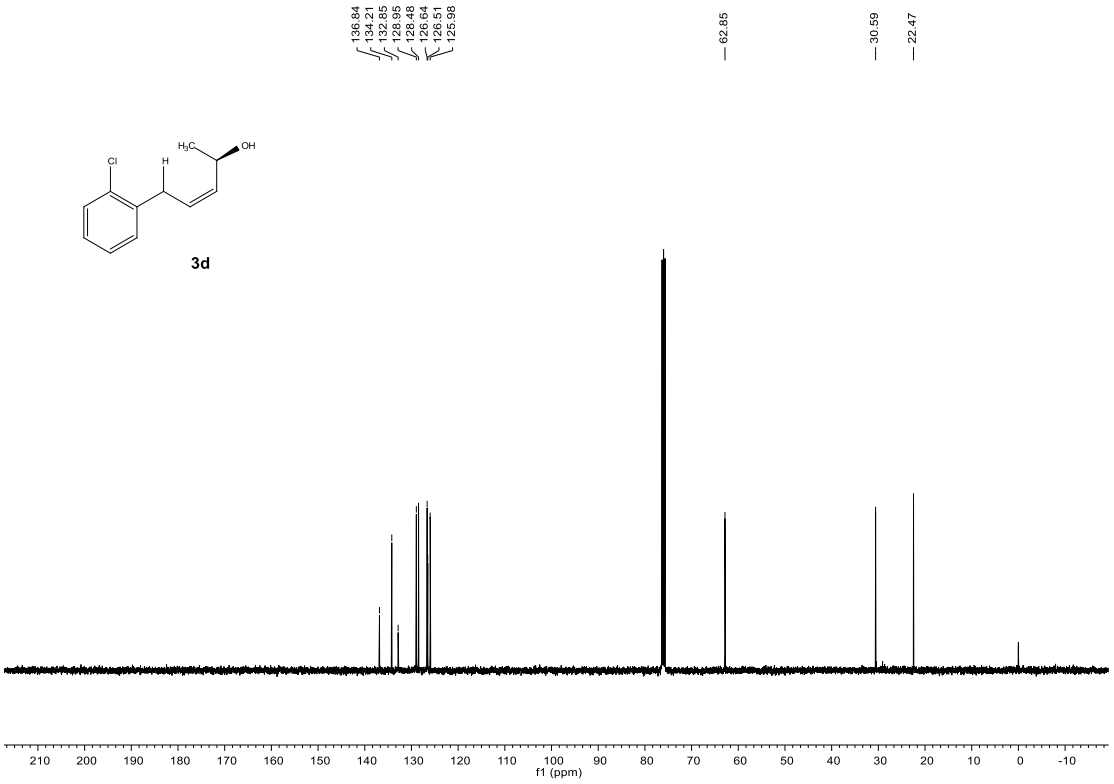
3c ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



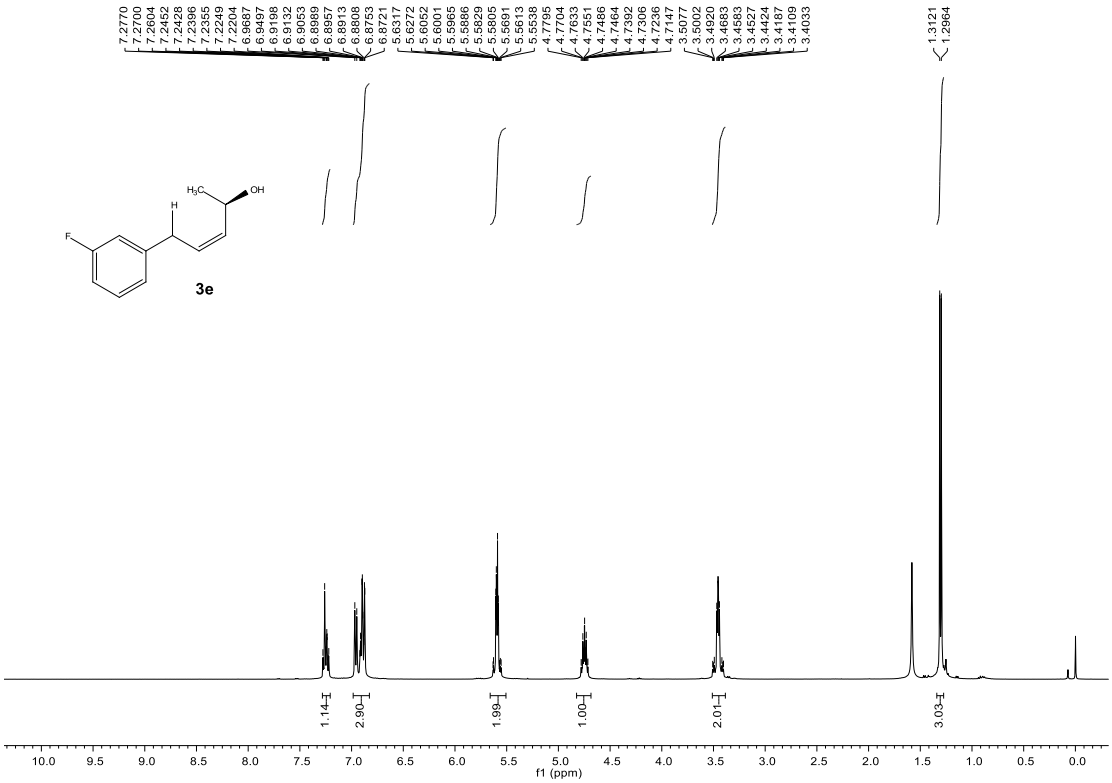
3d ^{1}H NMR (400 MHz, $CDCl_3$)



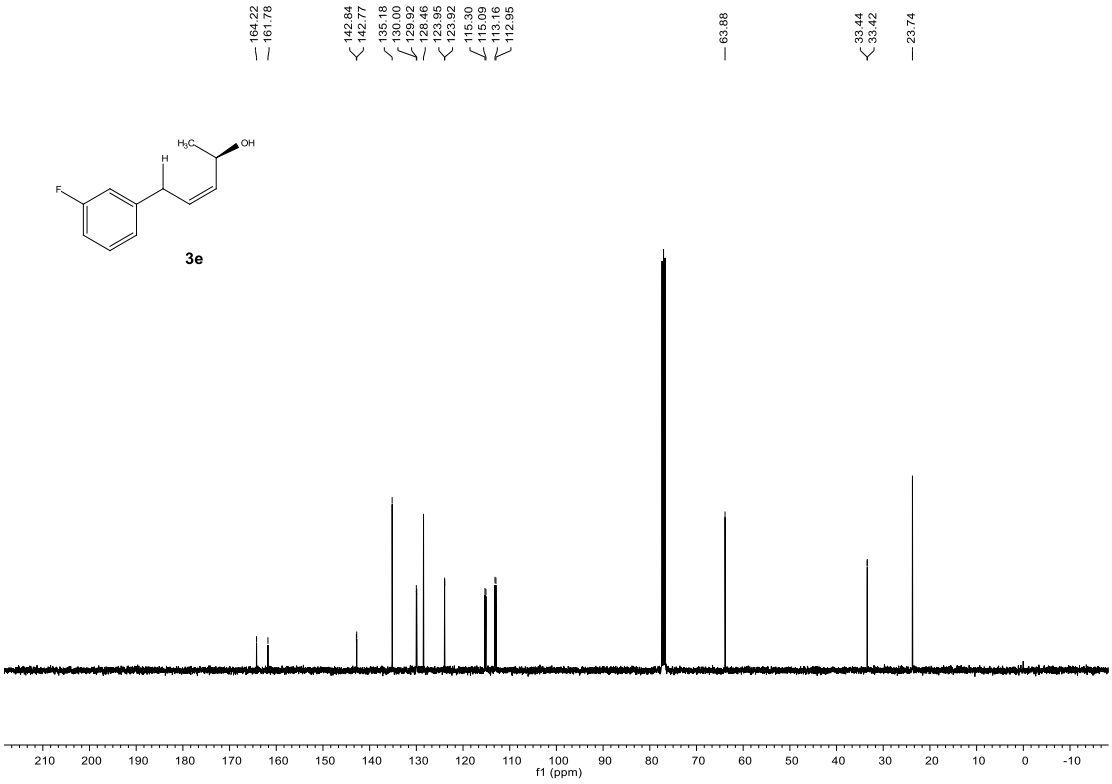
3d ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



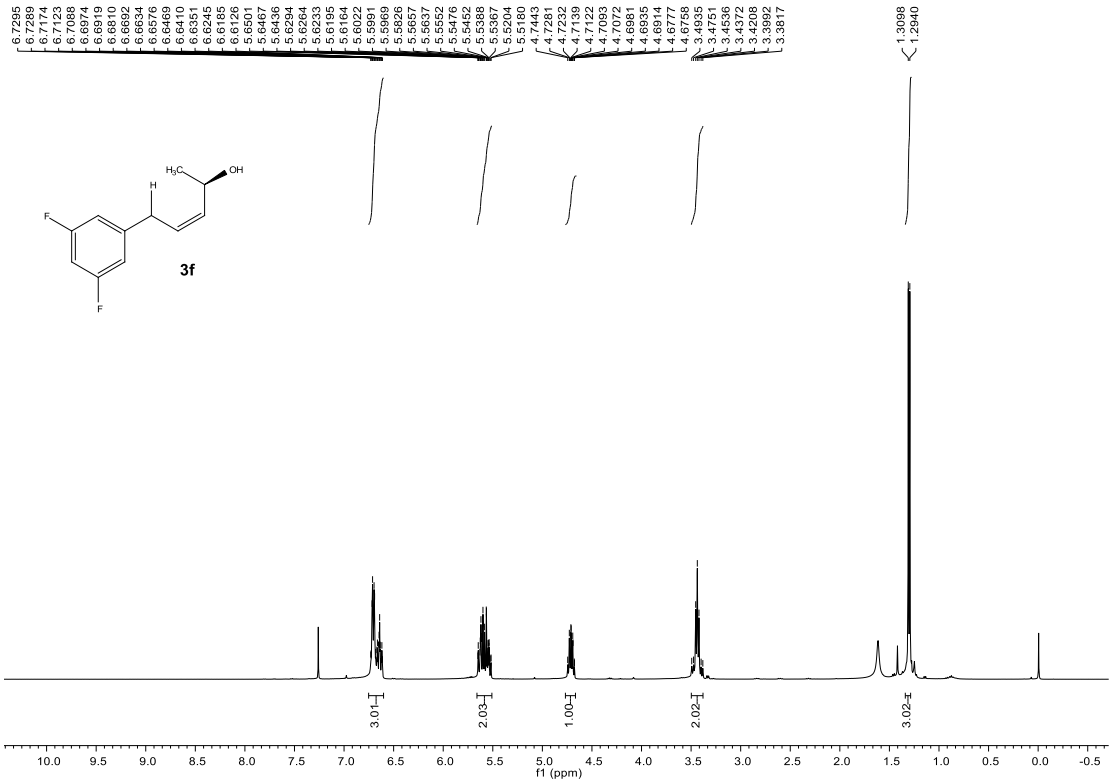
3e ^{1}H NMR (400 MHz, $CDCl_3$)



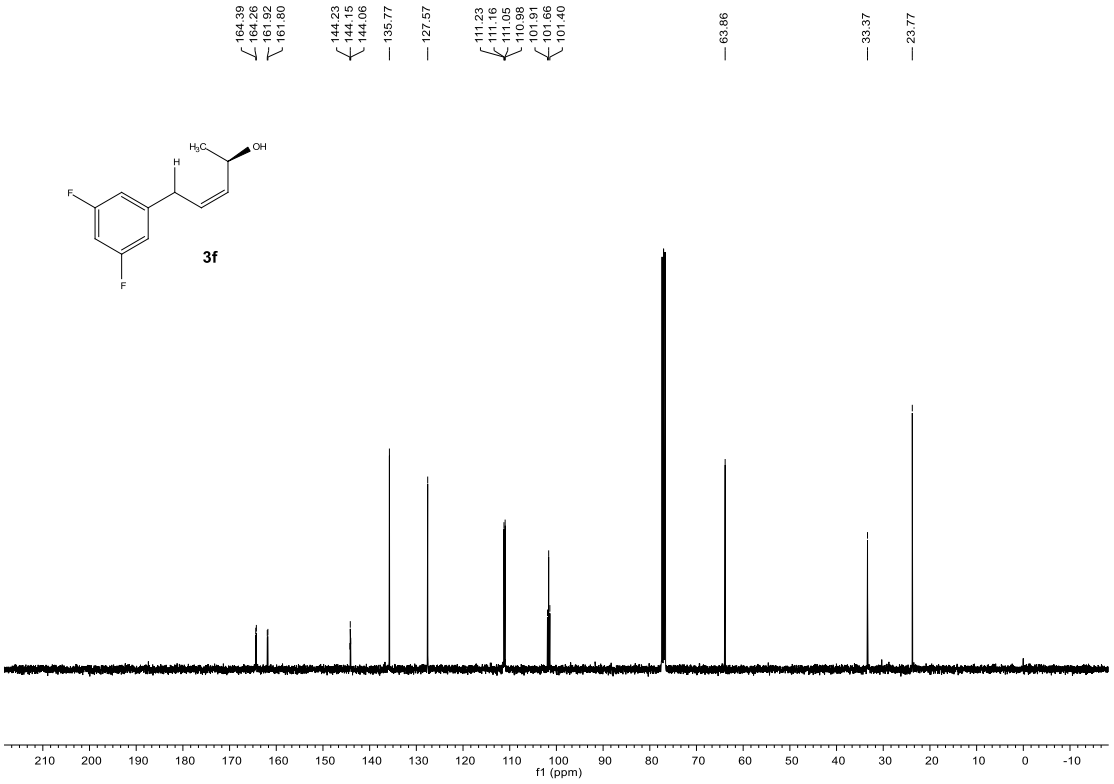
3e ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



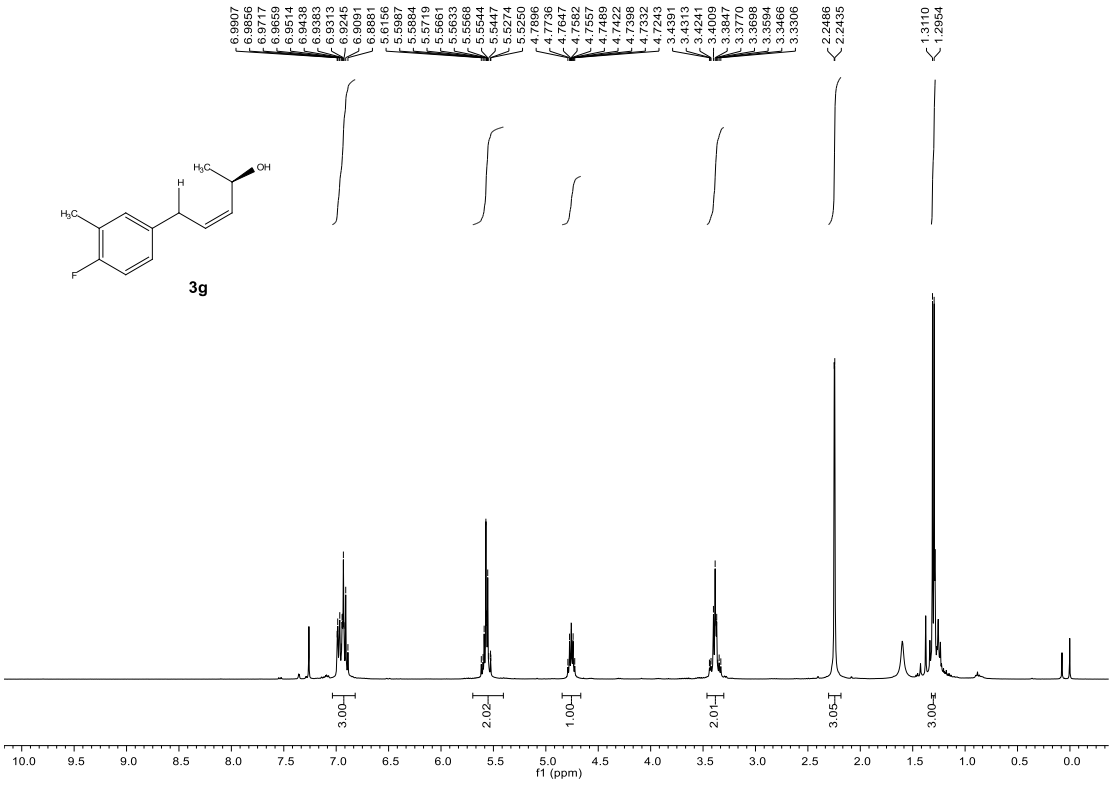
3f ^{1}H NMR (400 MHz, $CDCl_3$)



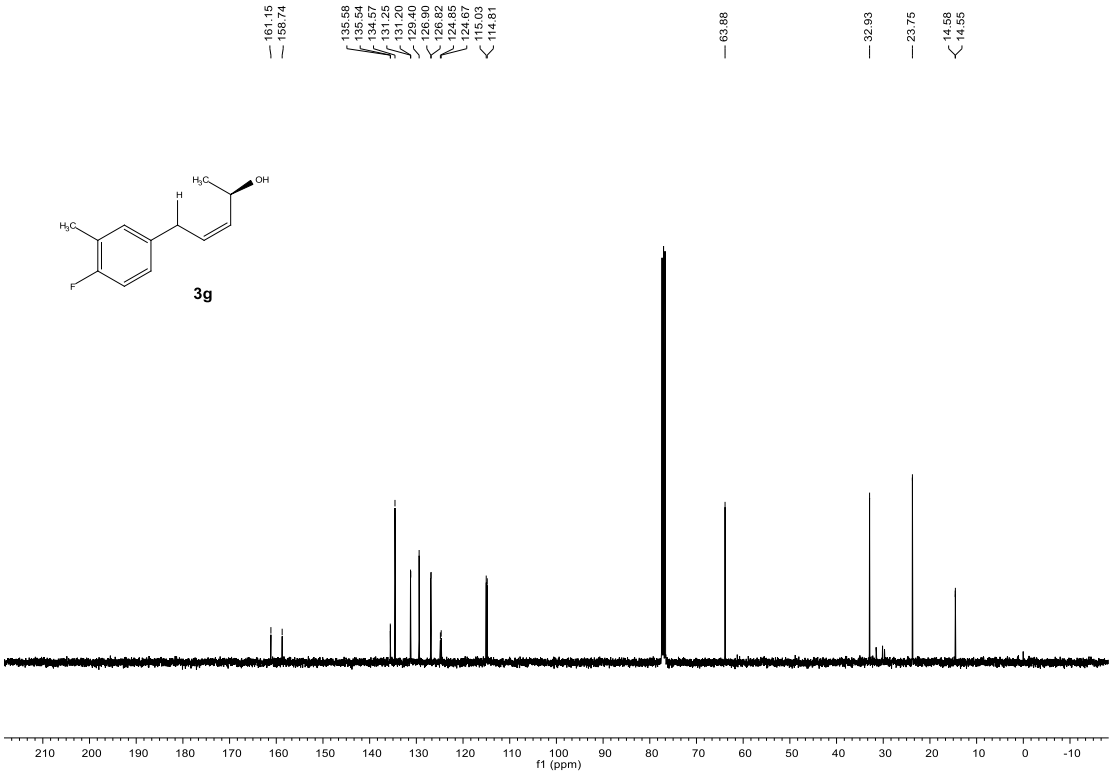
3f ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



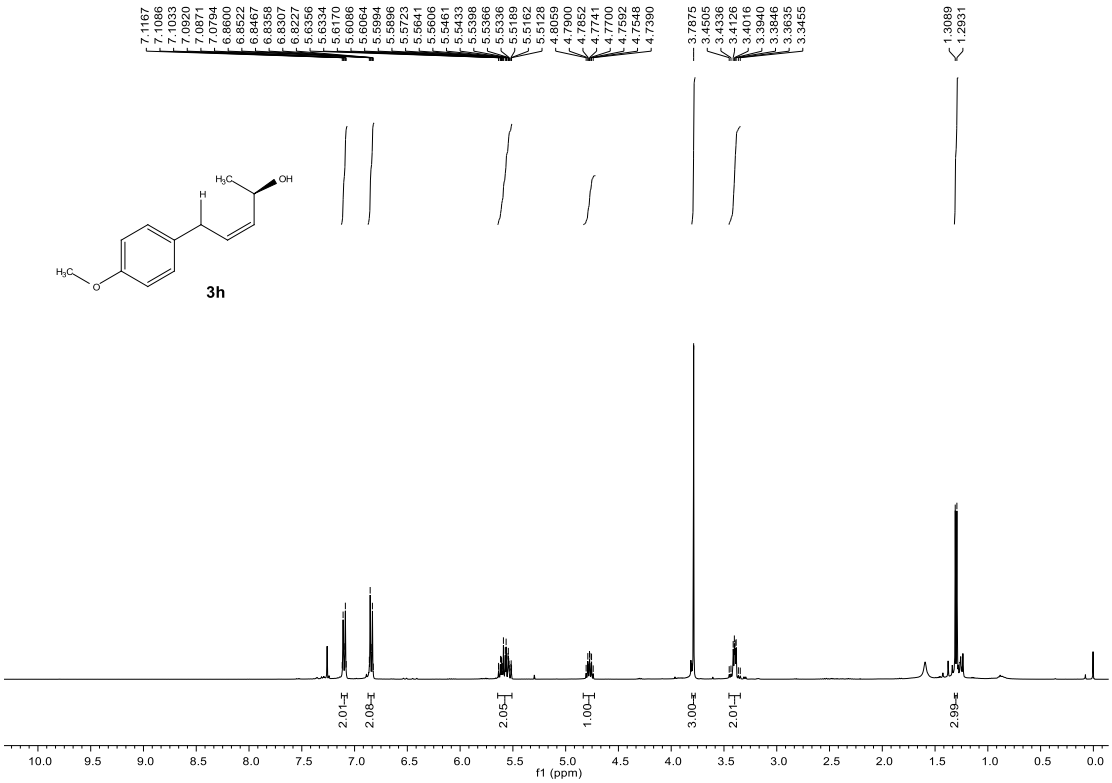
3g ^{1}H NMR (400 MHz, $CDCl_3$)



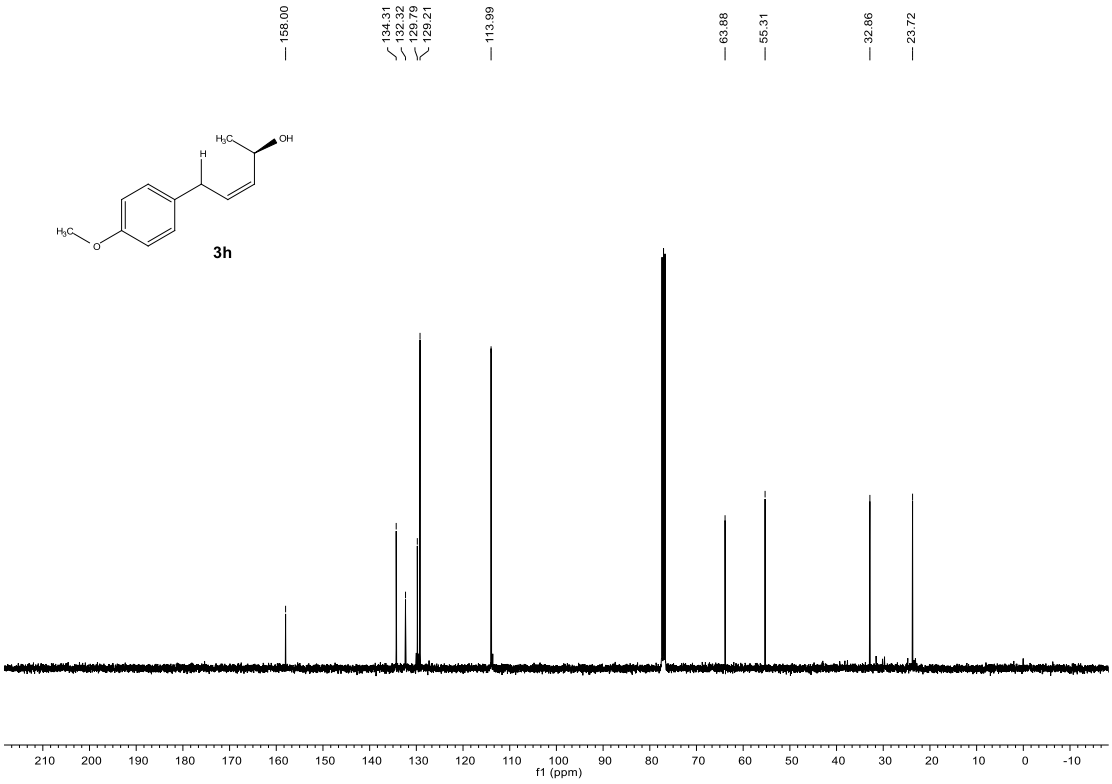
3g ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



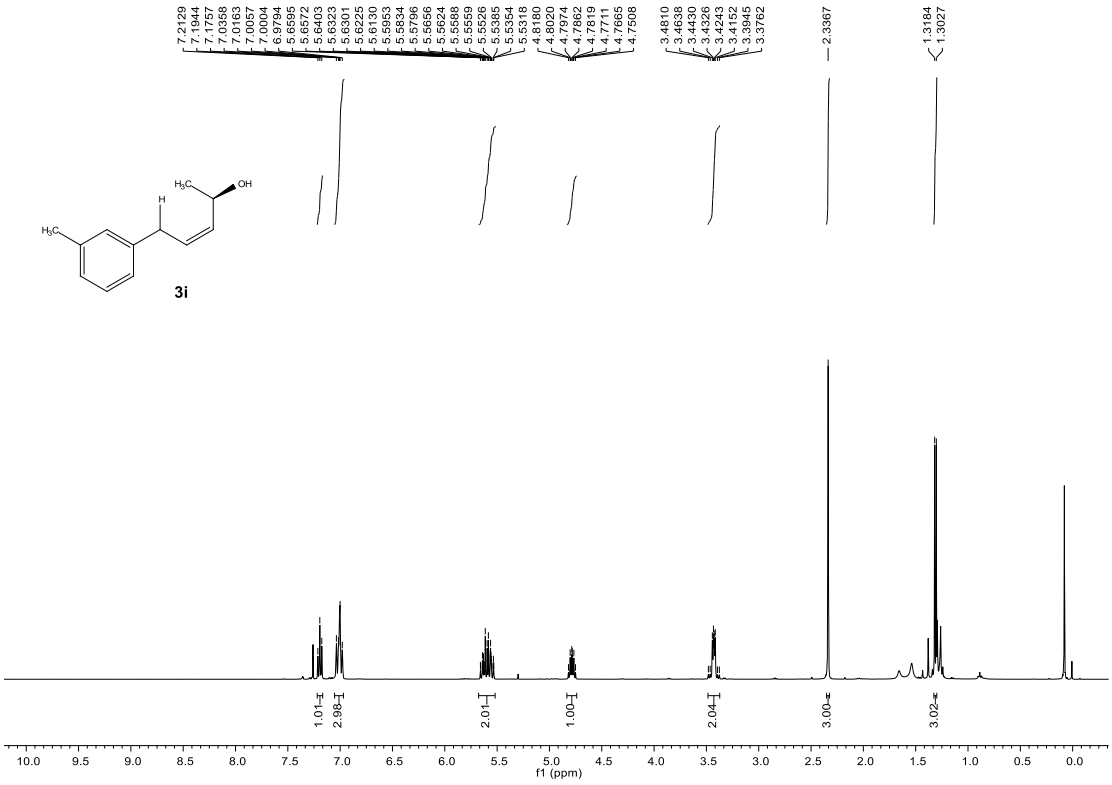
3h ^{1}H NMR (400 MHz, $CDCl_3$)



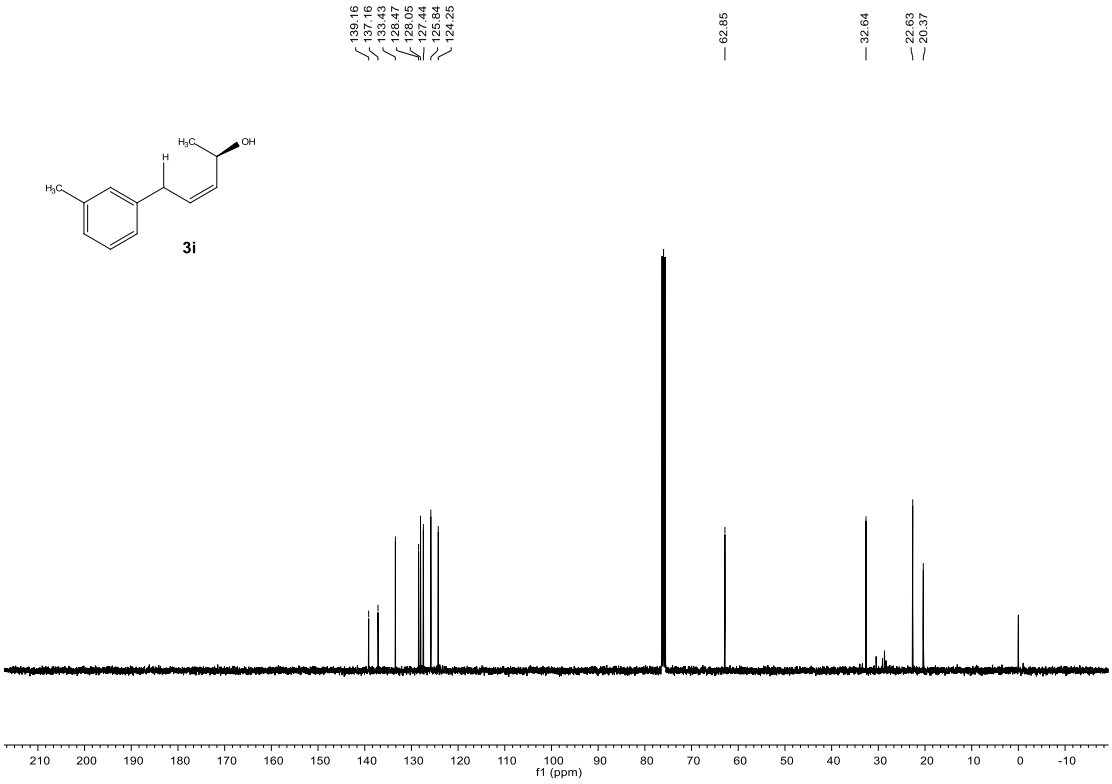
3h $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



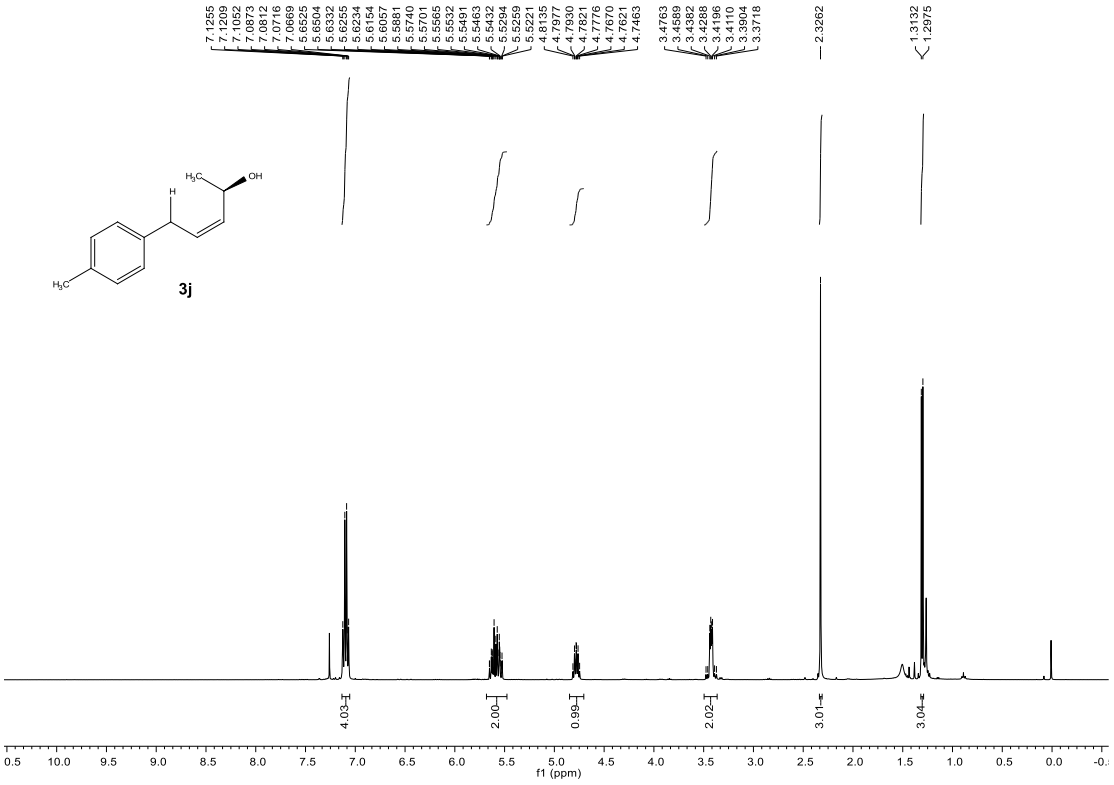
3i ^{1}H NMR (400 MHz, $CDCl_3$)



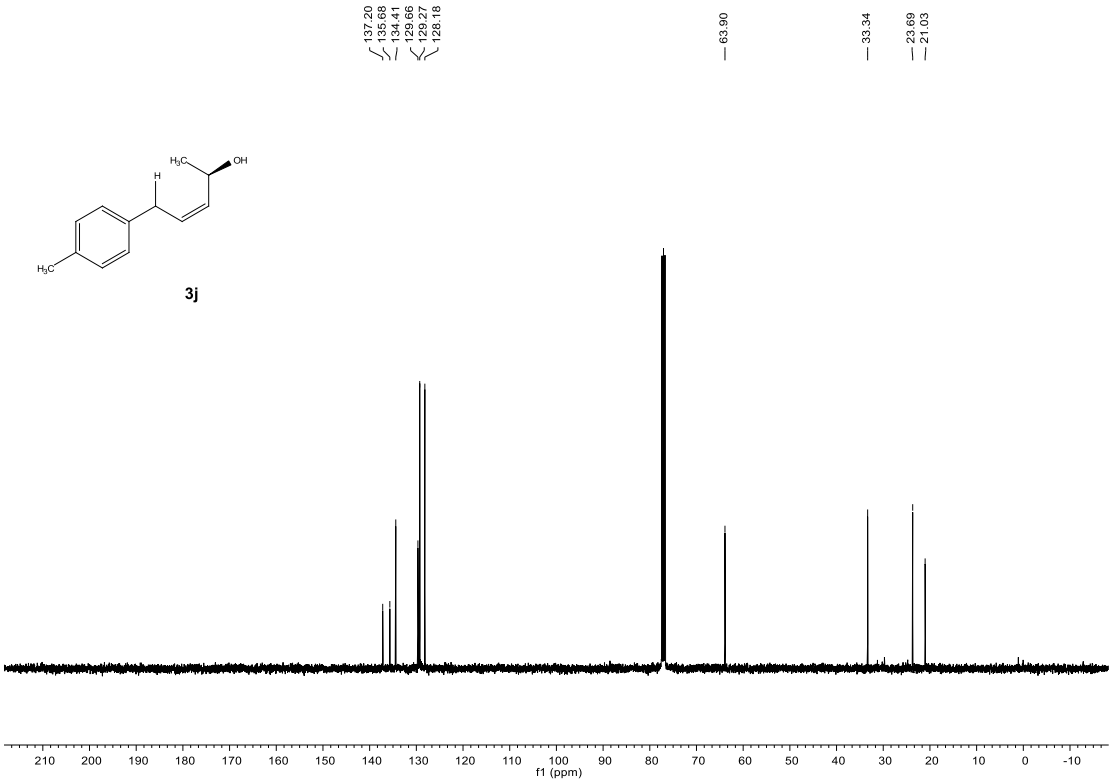
3i $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



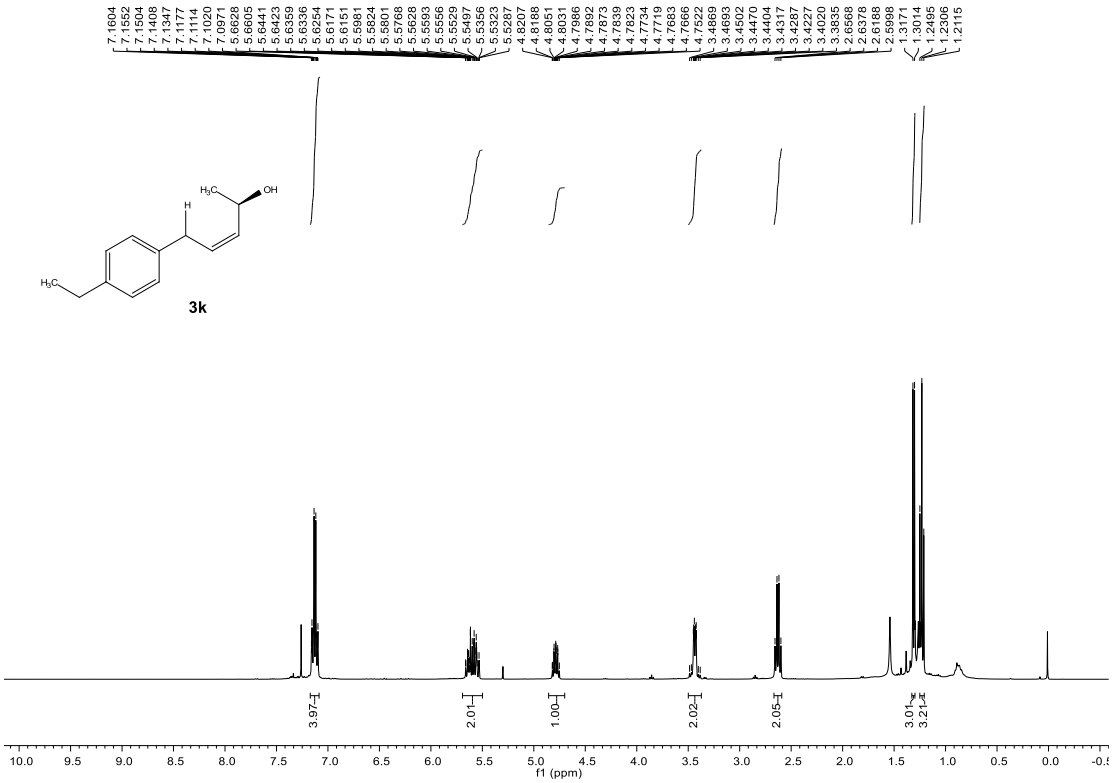
3j ^{1}H NMR (400 MHz, $CDCl_3$)



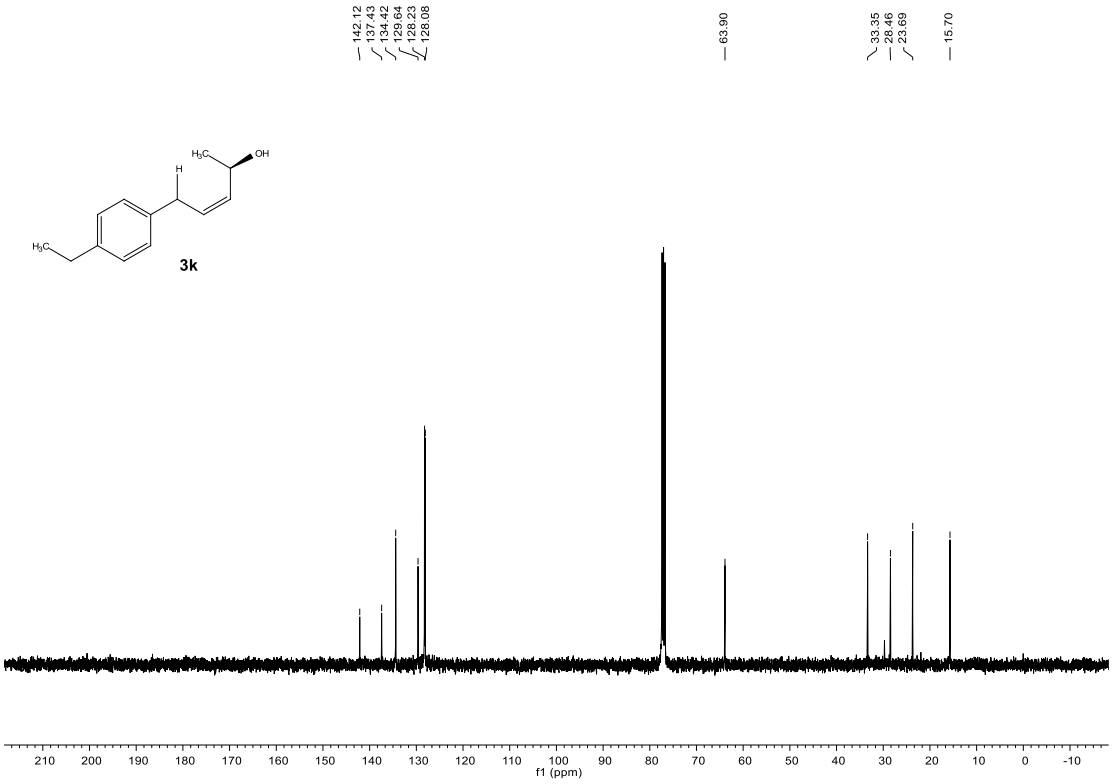
3j ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



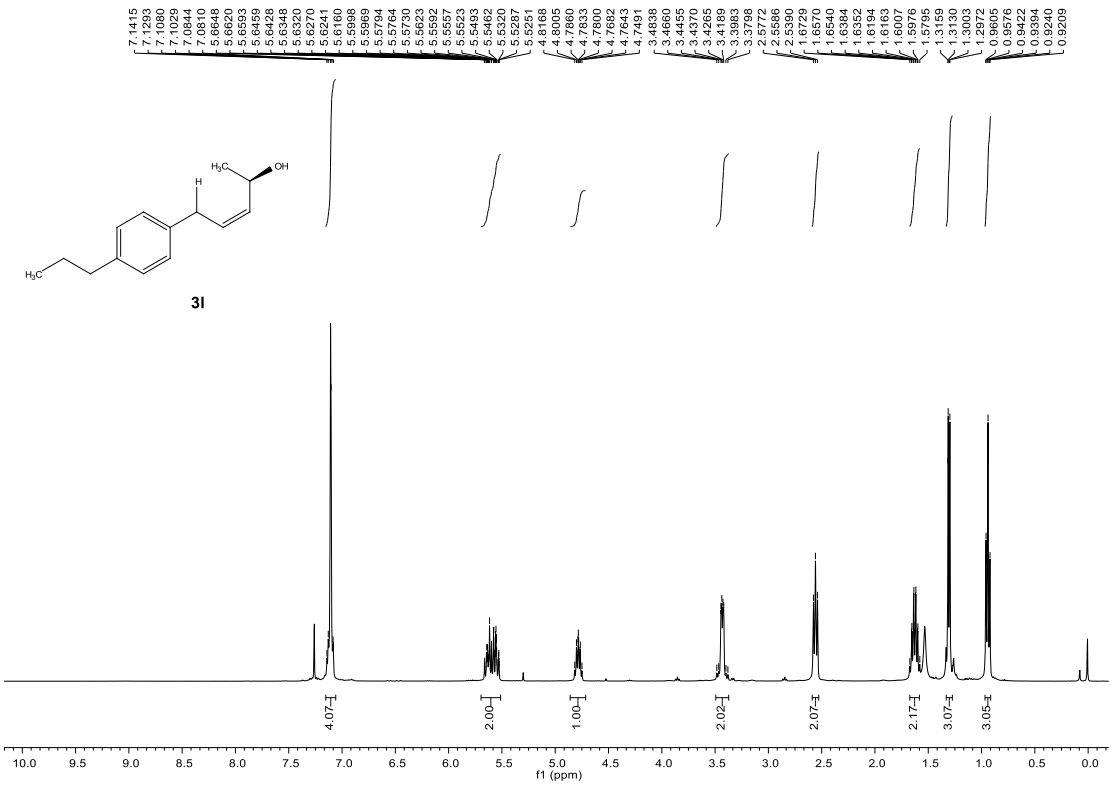
3k ^{1}H NMR (400 MHz, $CDCl_3$)



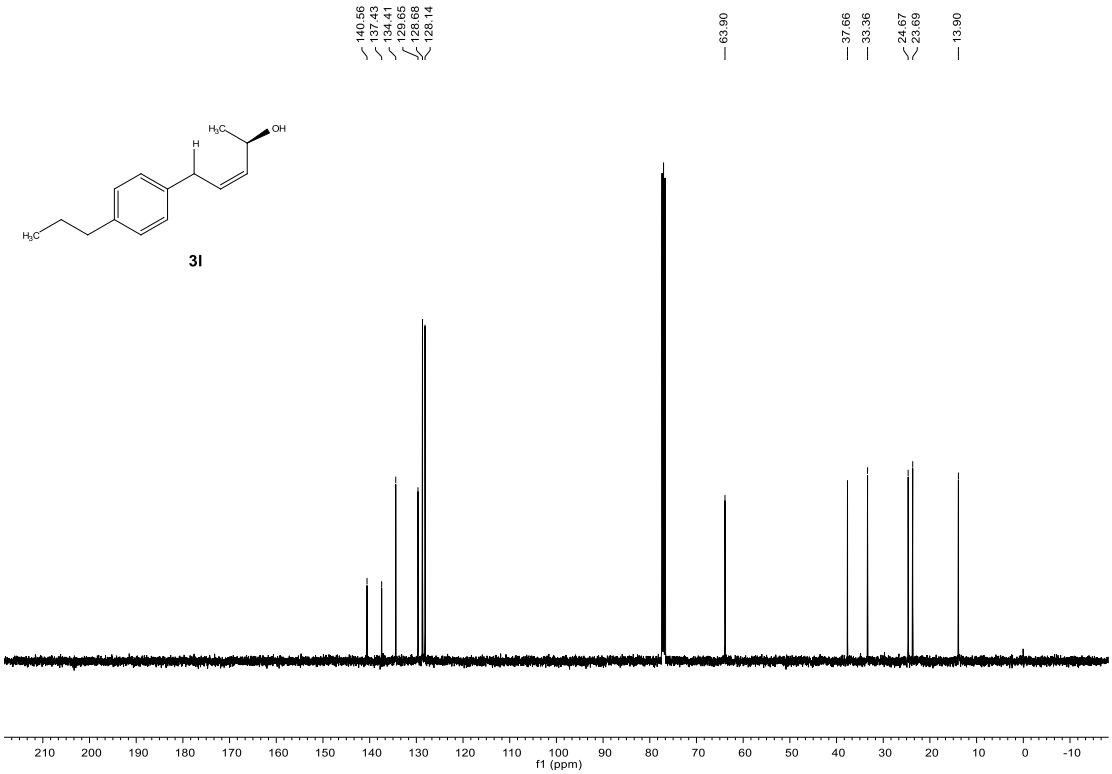
3k ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



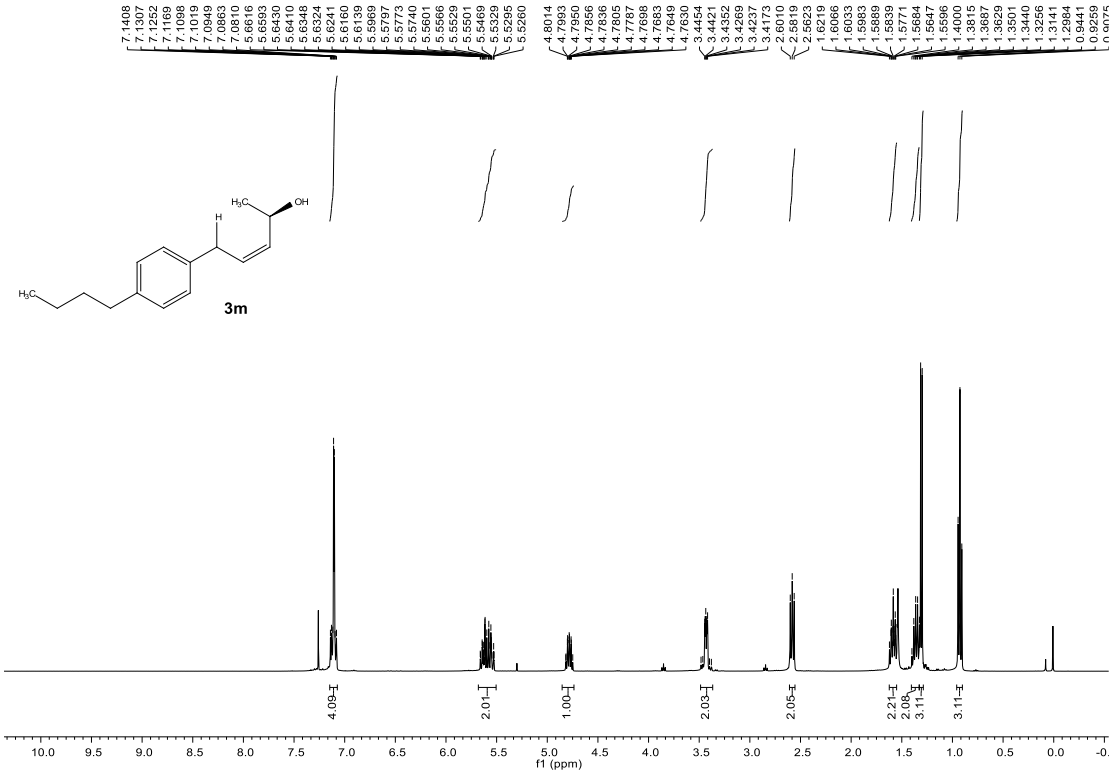
3l ^{1}H NMR (400 MHz, $CDCl_3$)



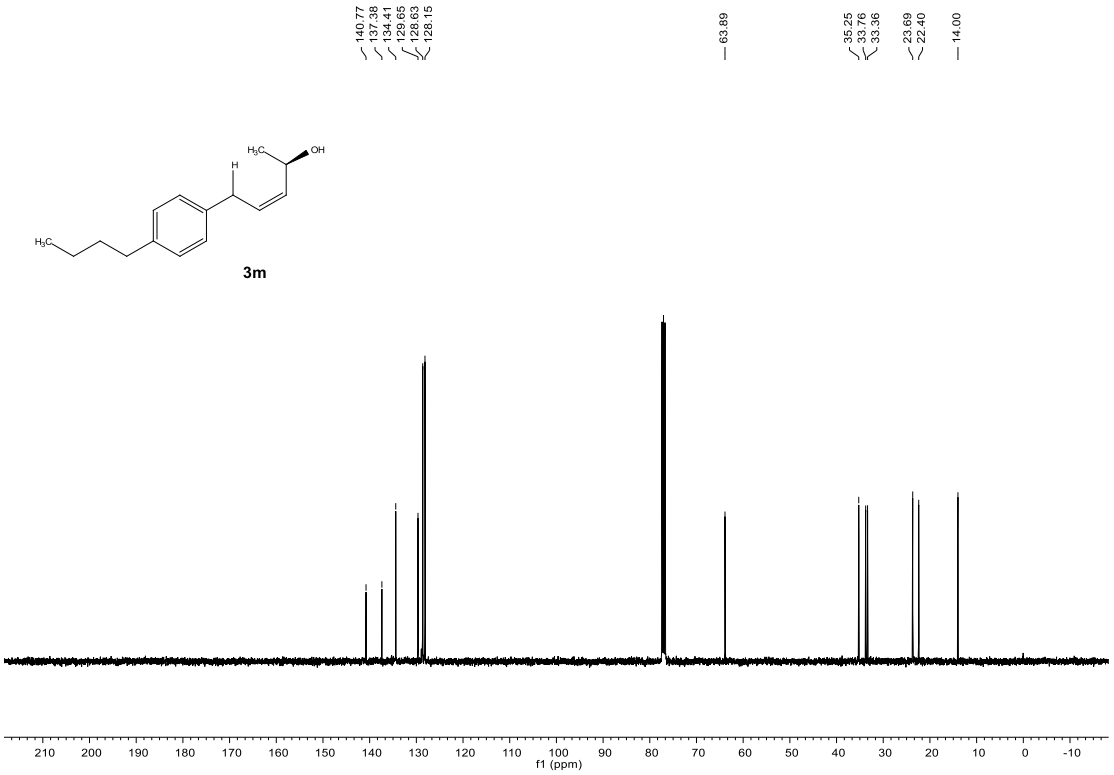
3l $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



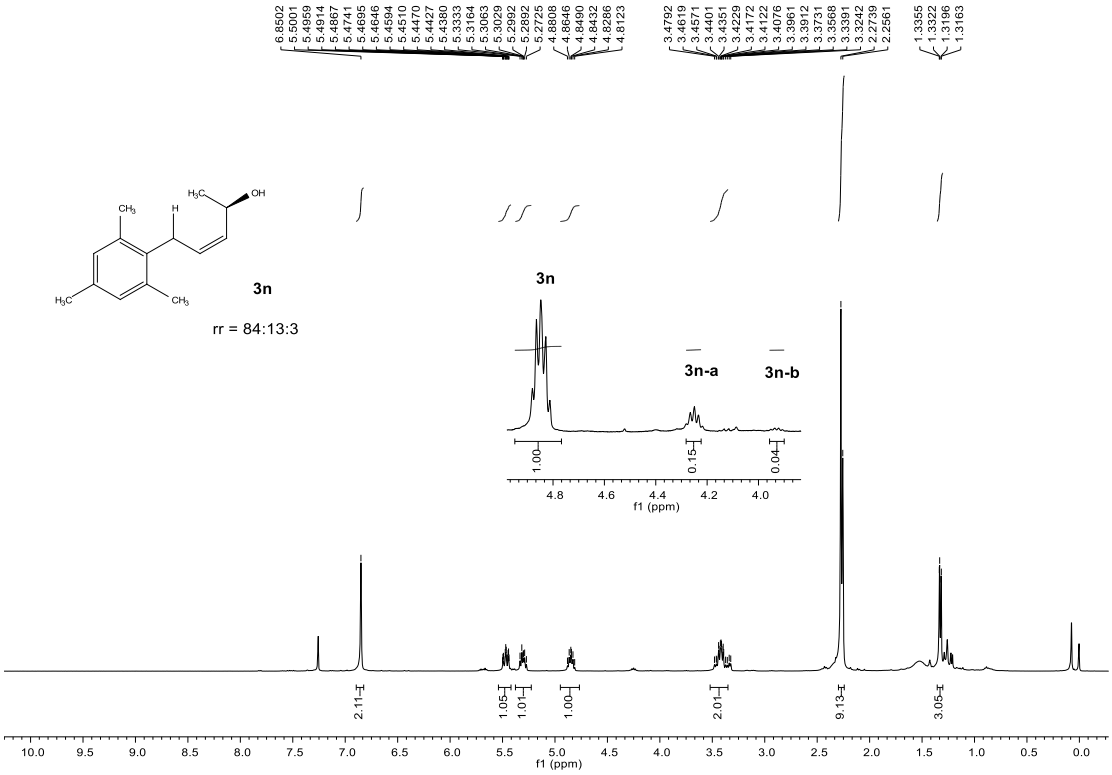
3m ^{1}H NMR (400 MHz, $CDCl_3$)



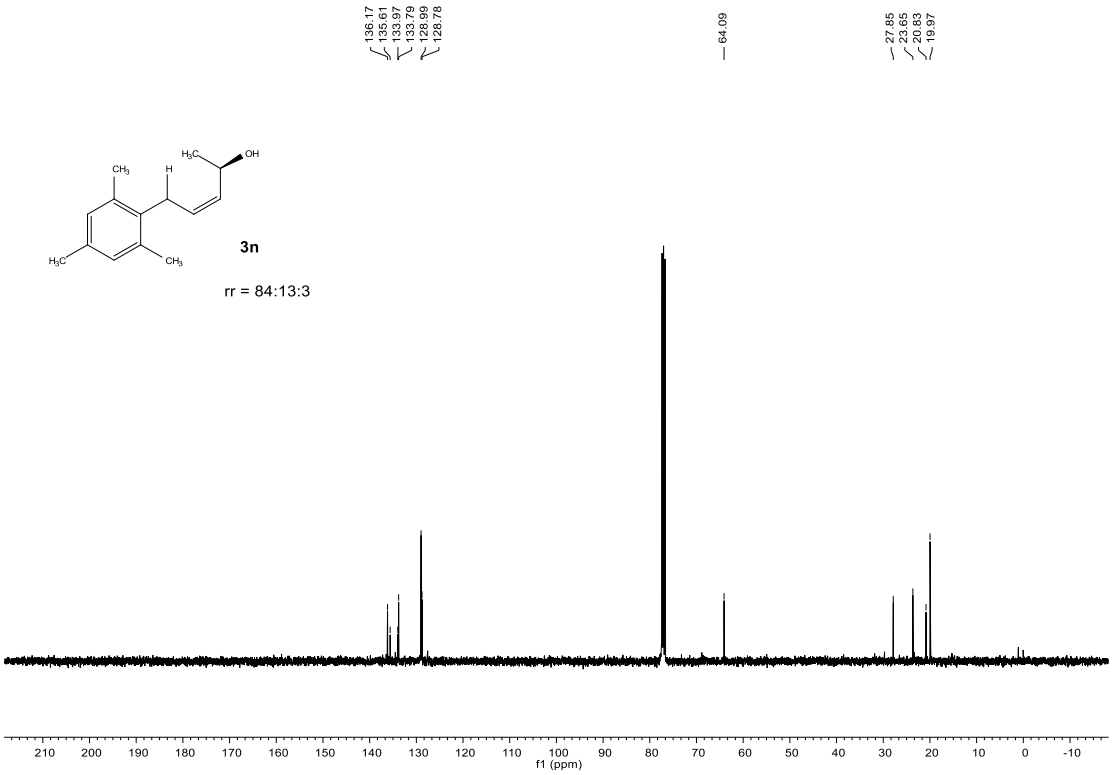
3m ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



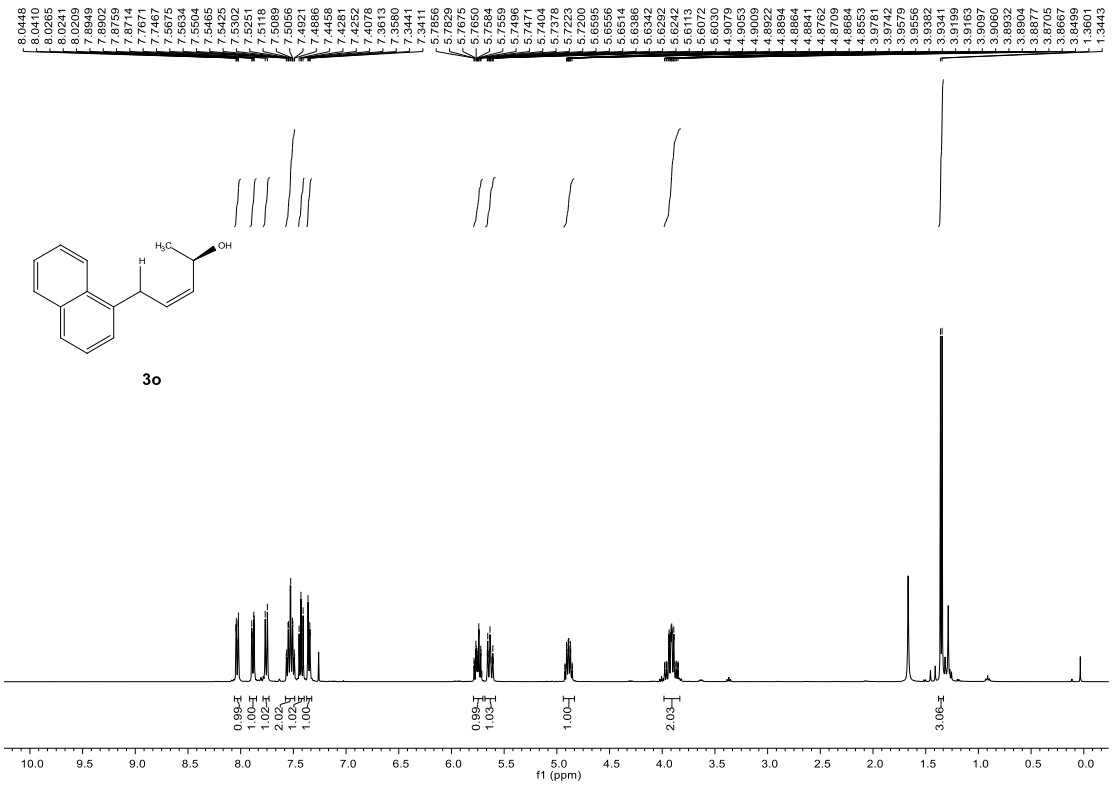
3n ^{1}H NMR (400 MHz, $CDCl_3$)



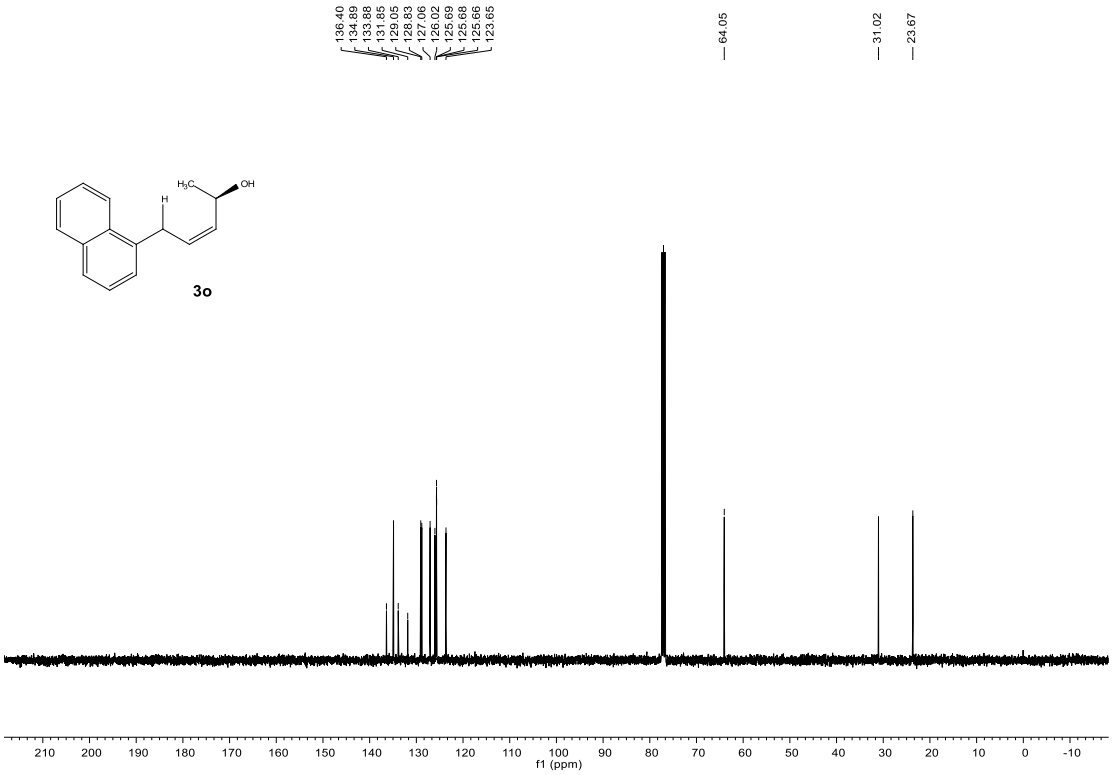
3n $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



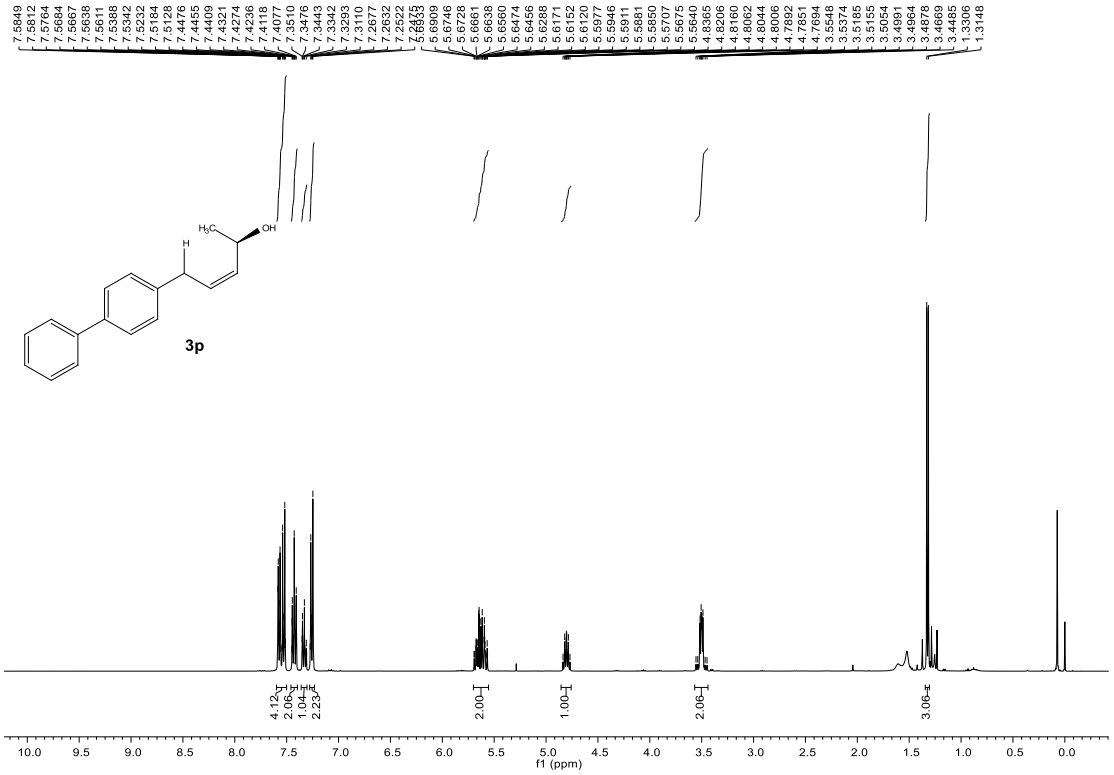
3o ^{1}H NMR (400 MHz, $CDCl_3$)



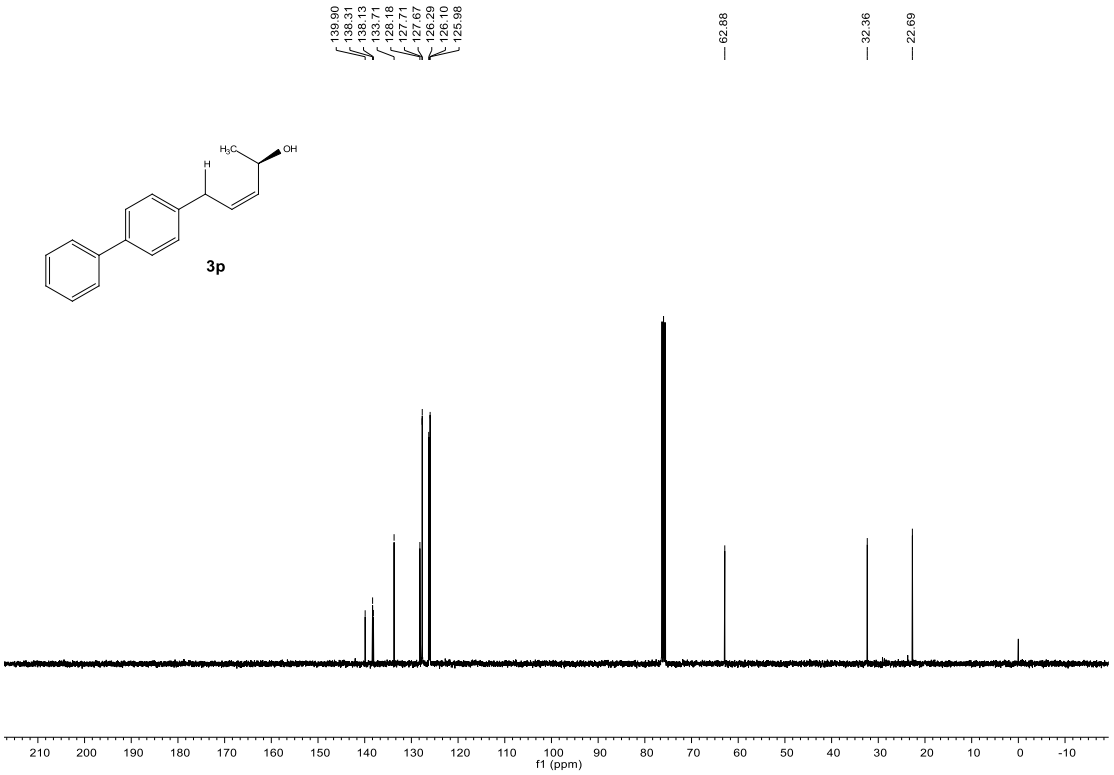
3o ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



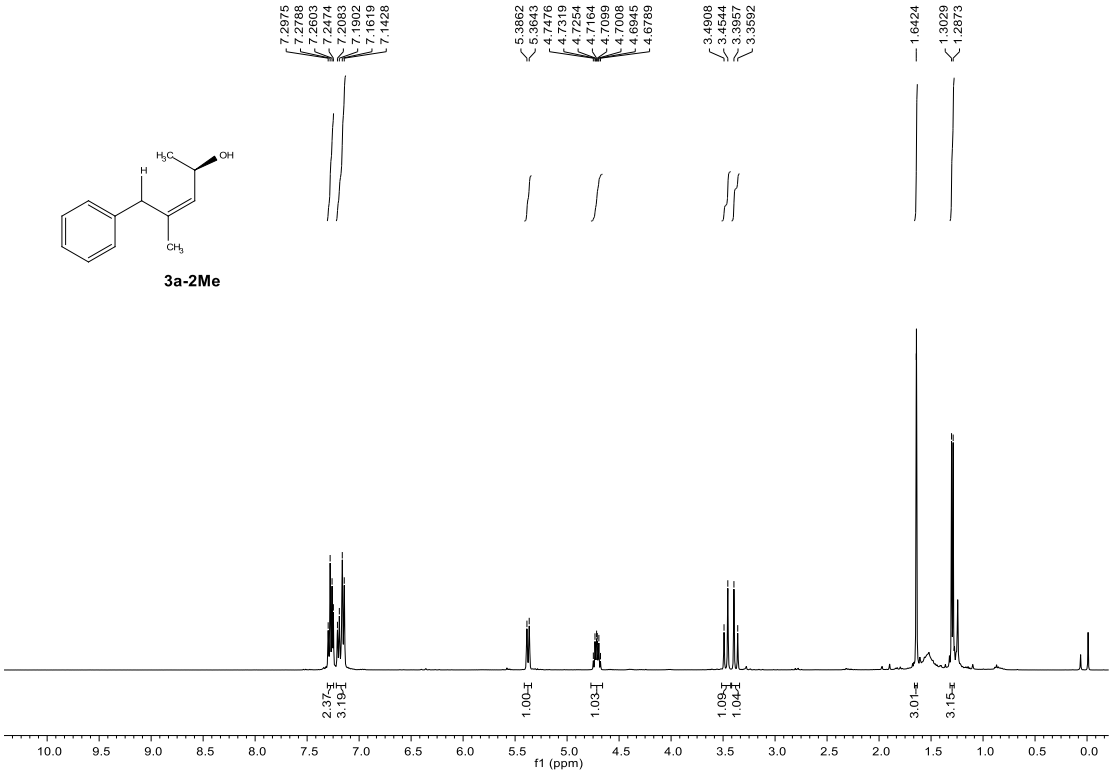
3p ^{1}H NMR (400 MHz, $CDCl_3$)



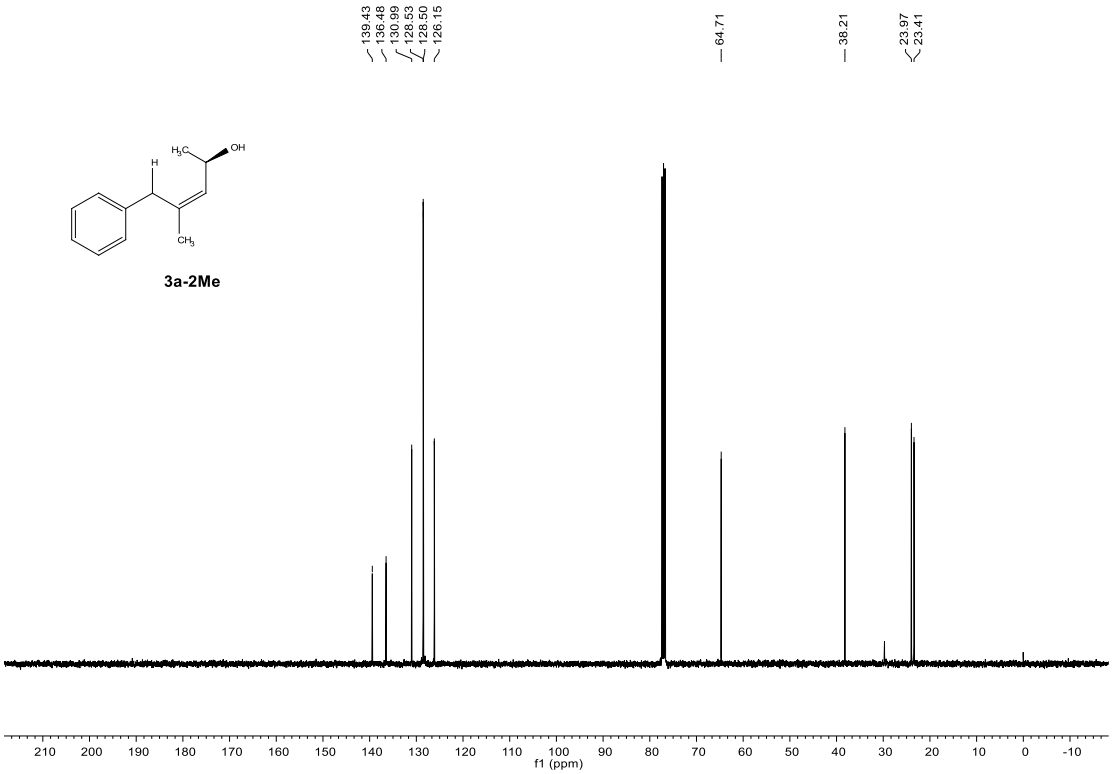
3p ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



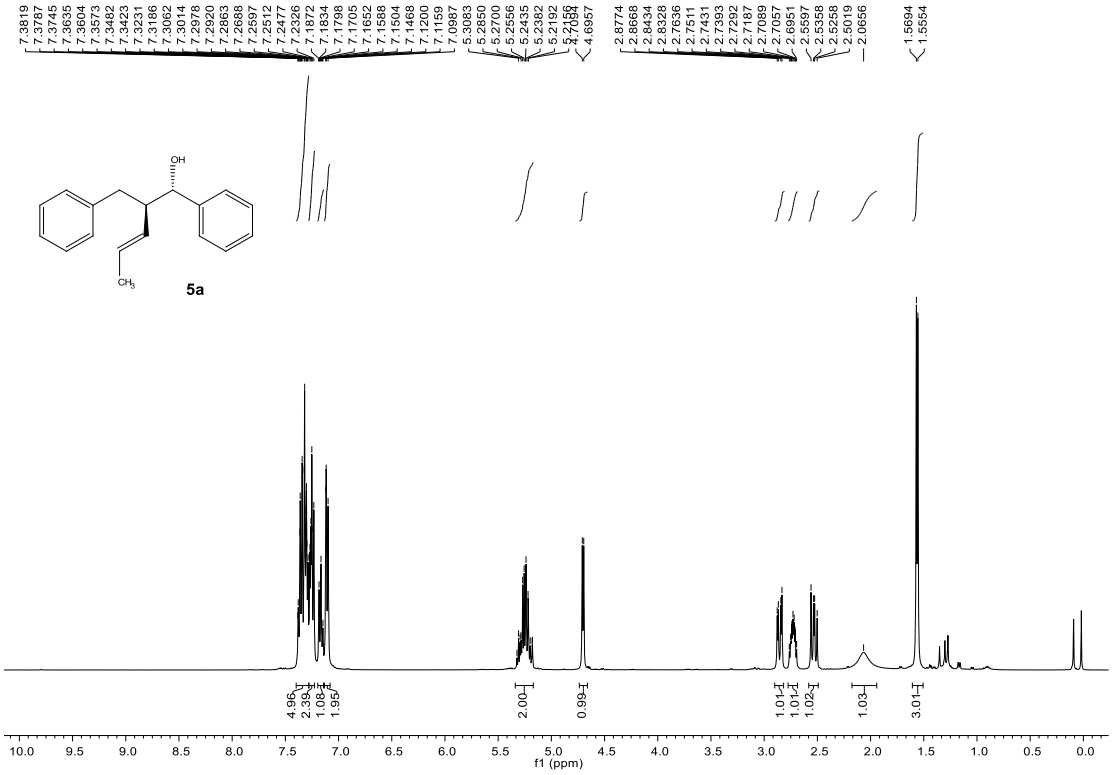
3a-2Me ^{1}H NMR (400 MHz, $CDCl_3$)



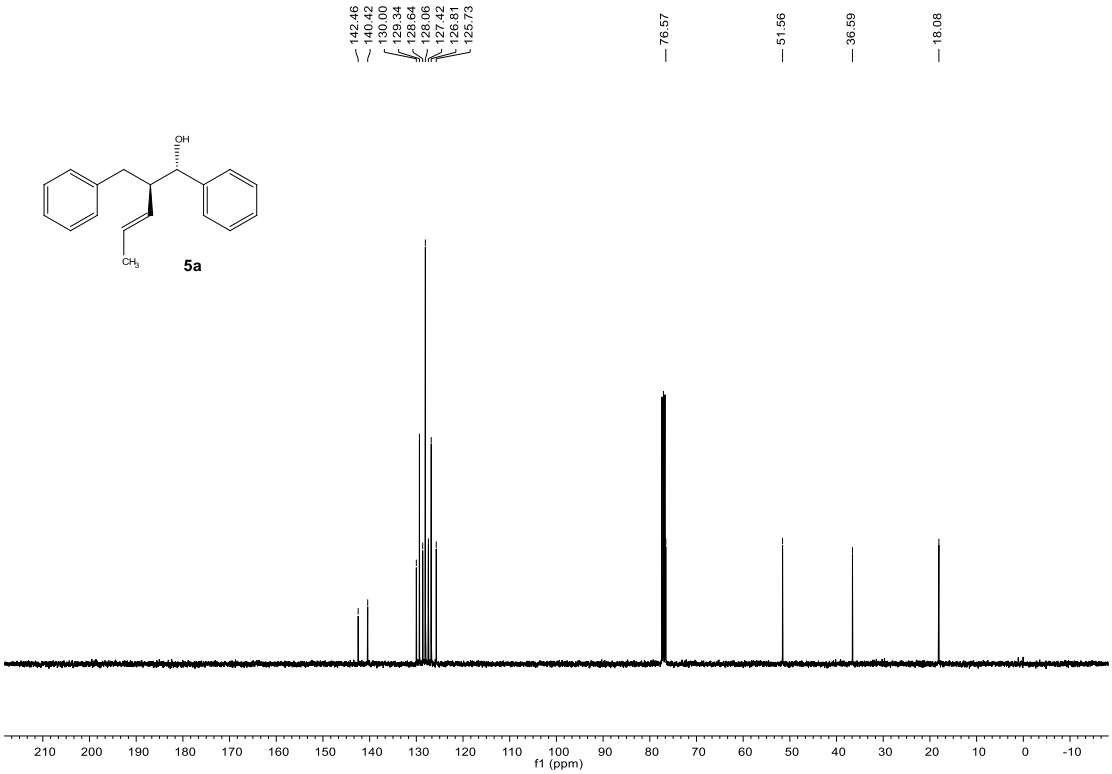
3a-2Me ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



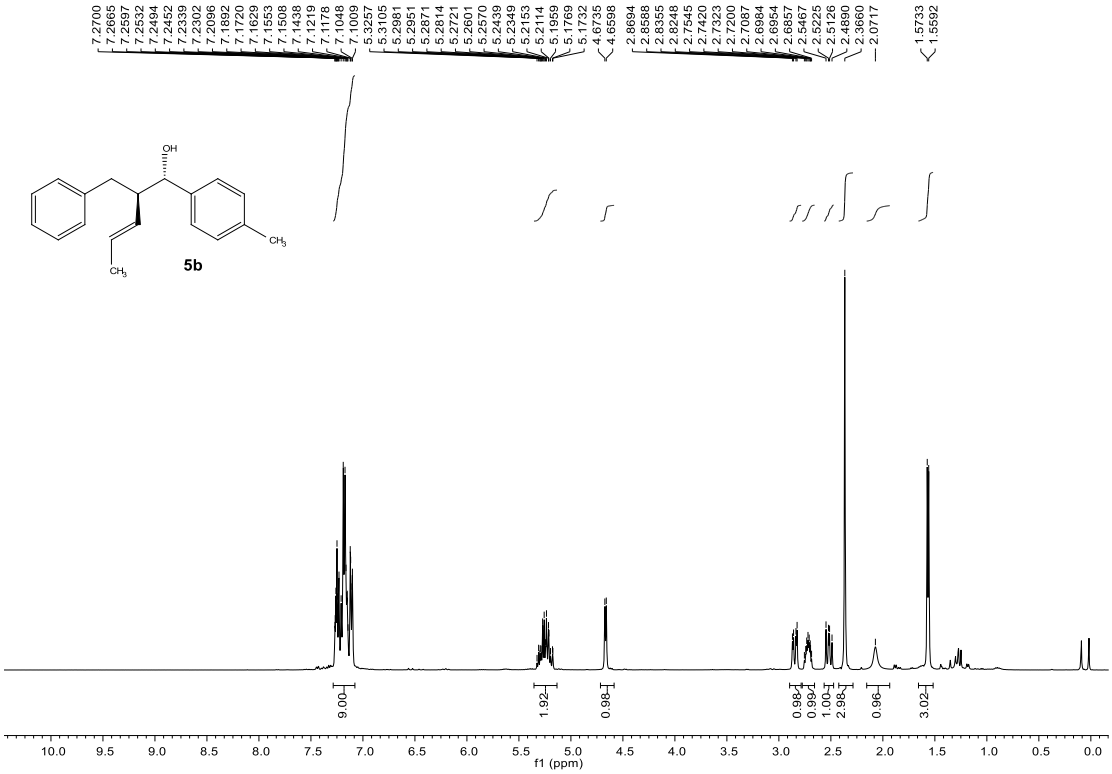
5a ^{1}H NMR (400 MHz, $CDCl_3$)



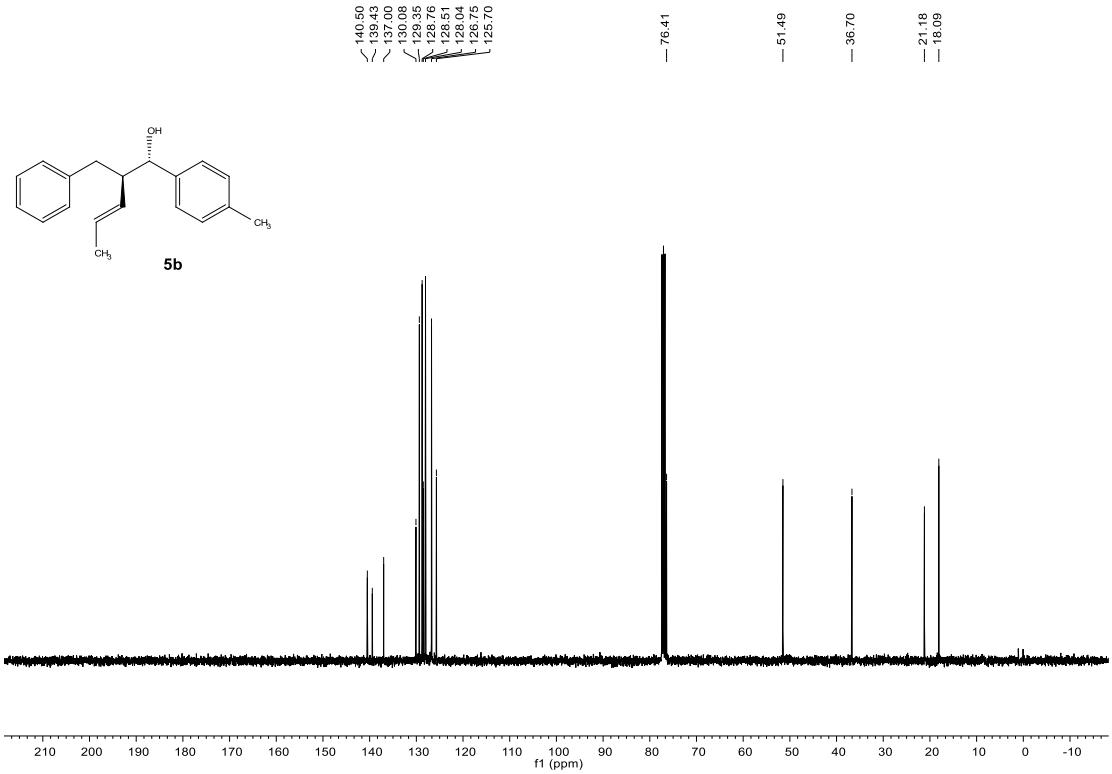
5a ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



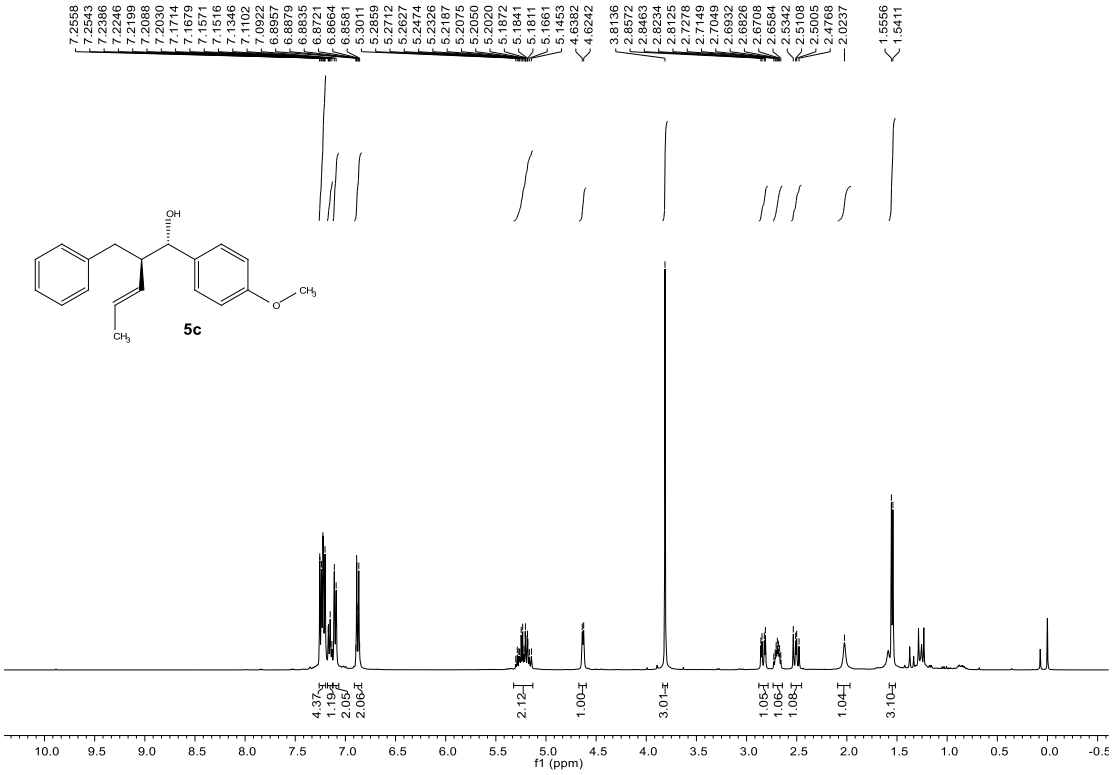
5b ^{1}H NMR (400 MHz, $CDCl_3$)



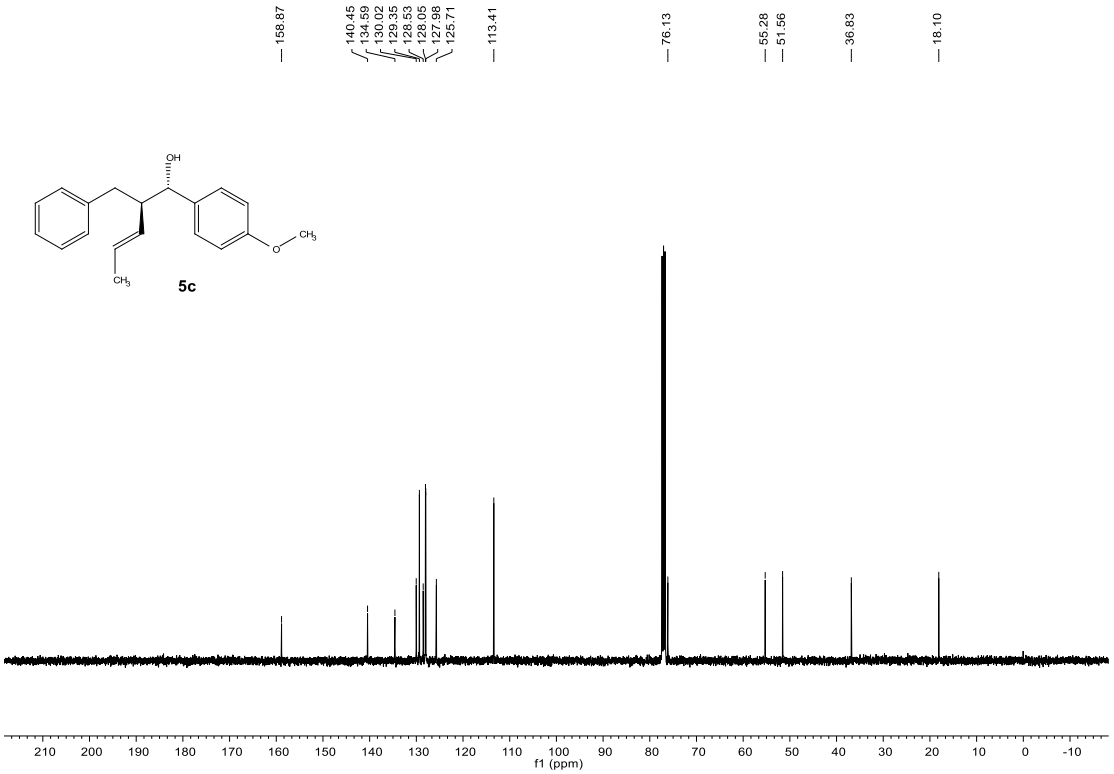
5b $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



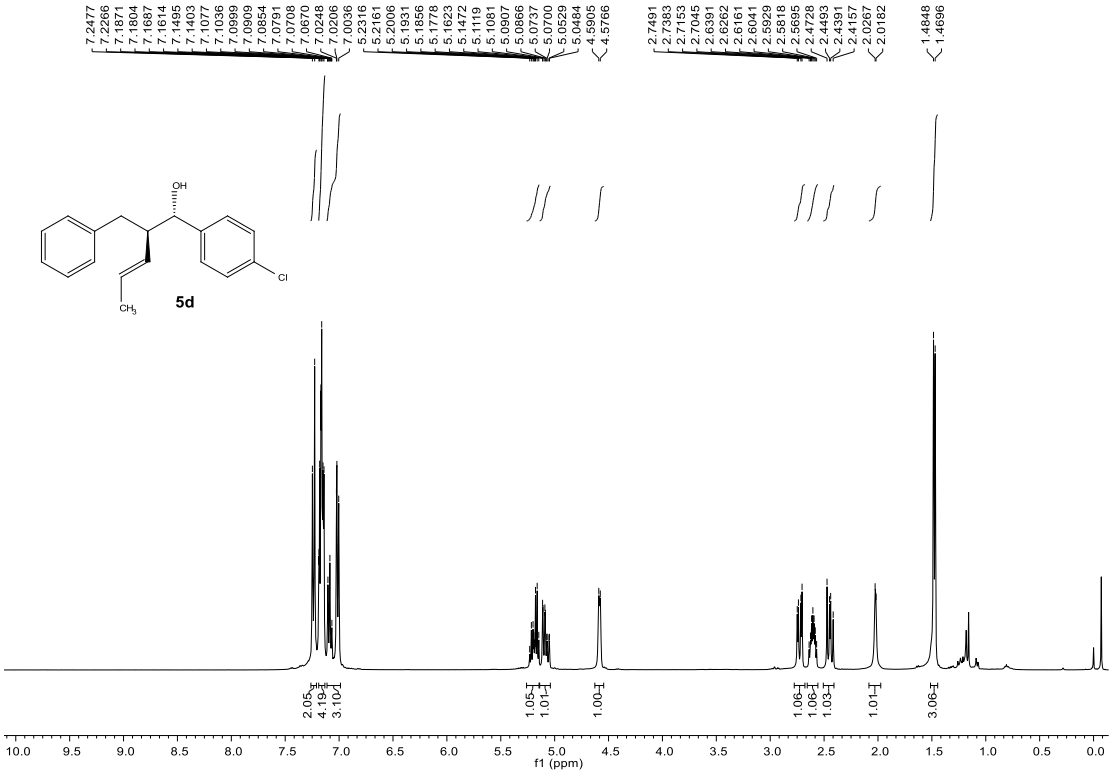
5c ^{1}H NMR (400 MHz, $CDCl_3$)



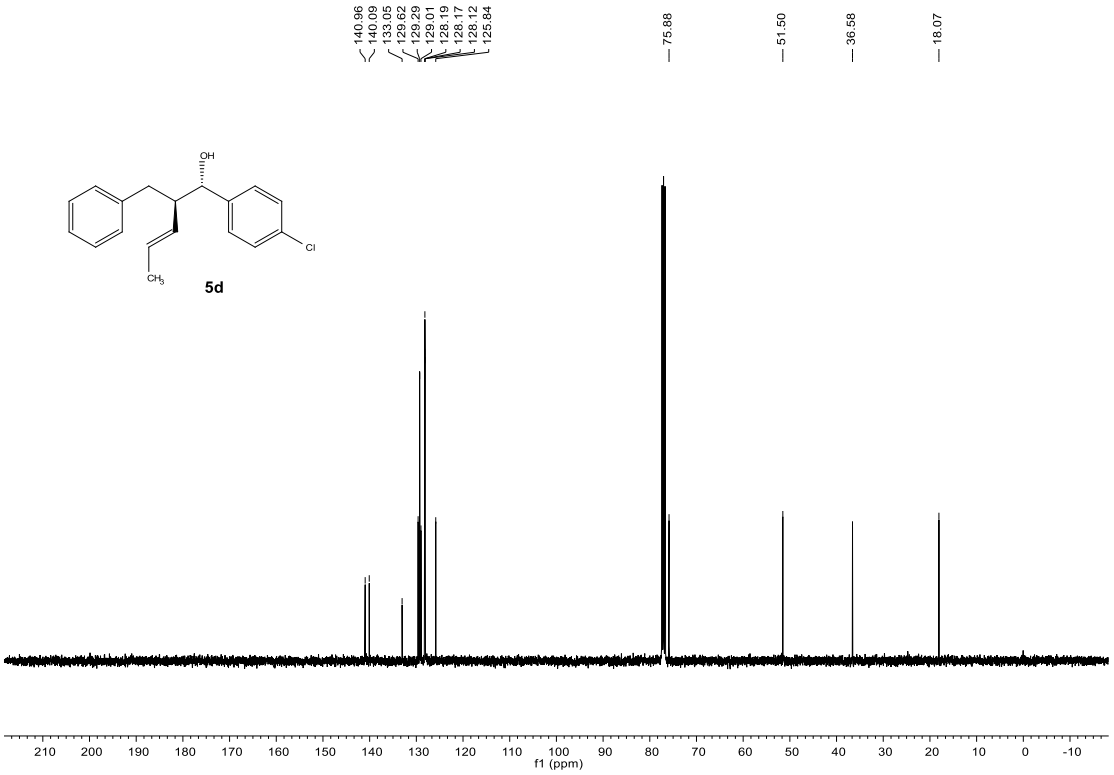
5c ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



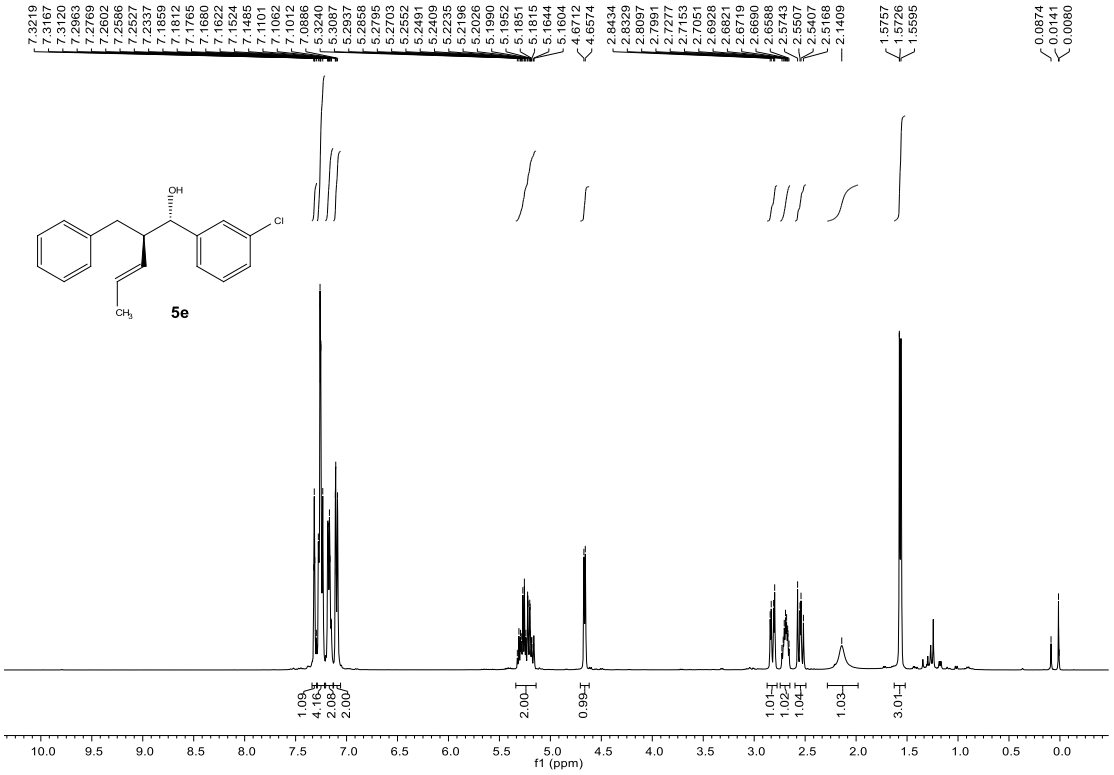
5d ^{1}H NMR (400 MHz, $CDCl_3$)



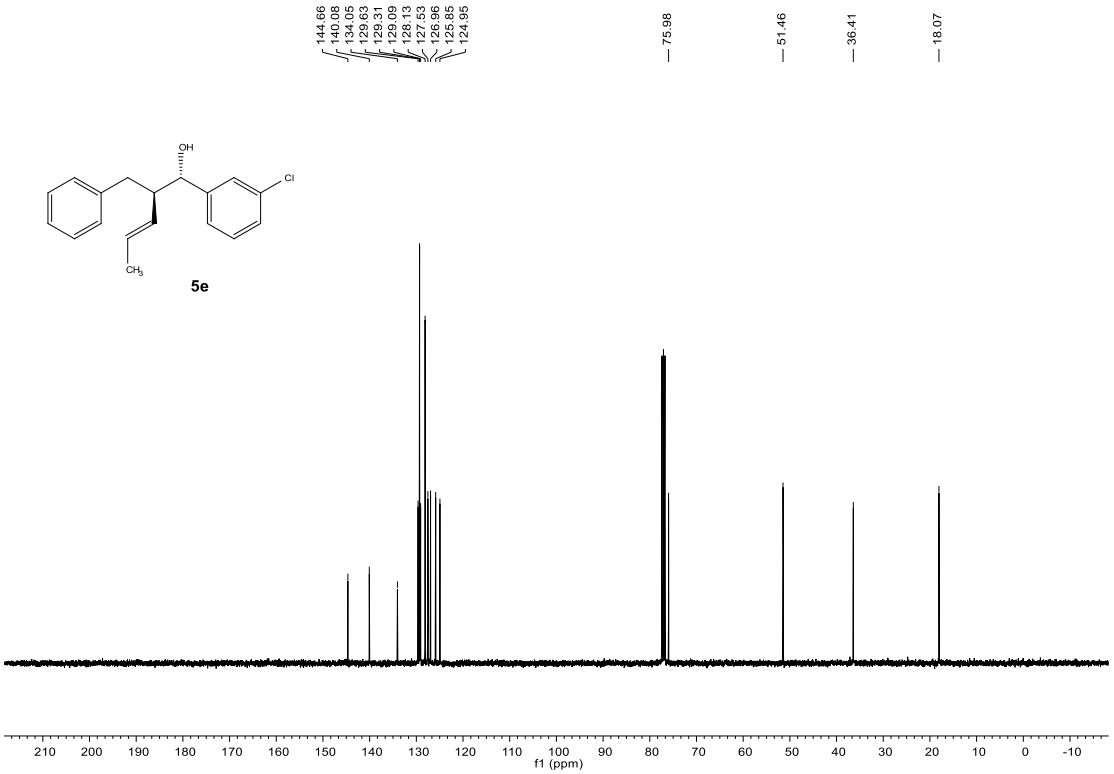
5d ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



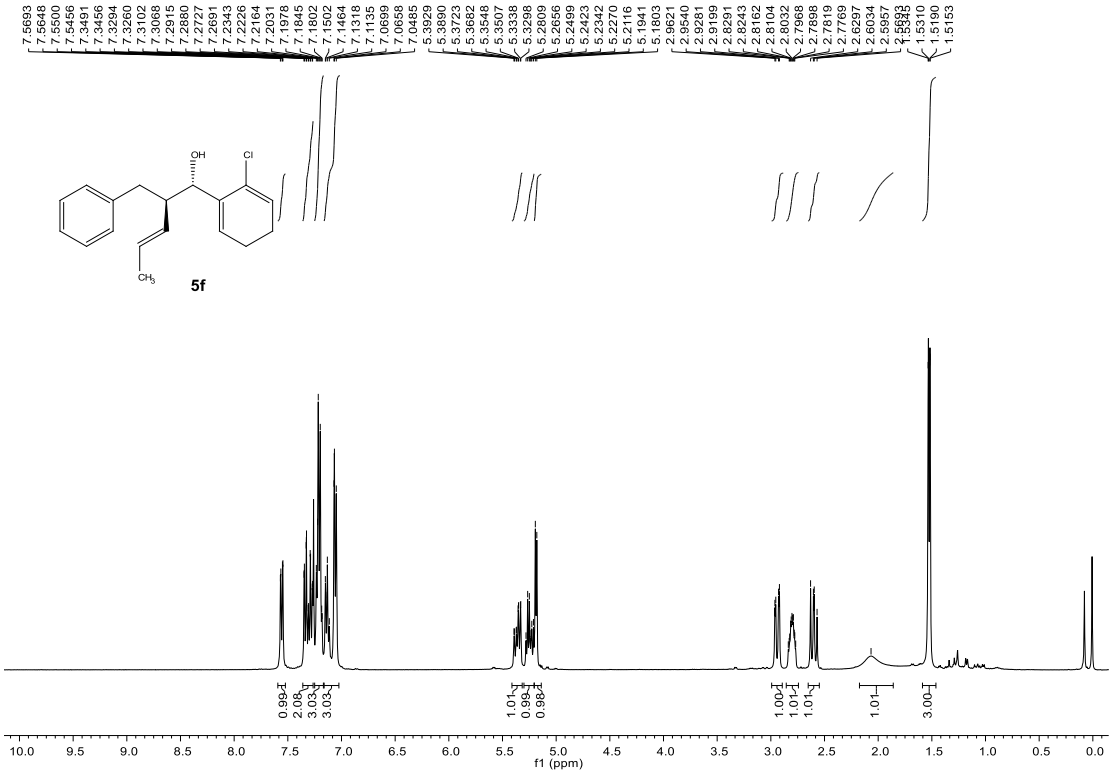
5e ^{1}H NMR (400 MHz, $CDCl_3$)



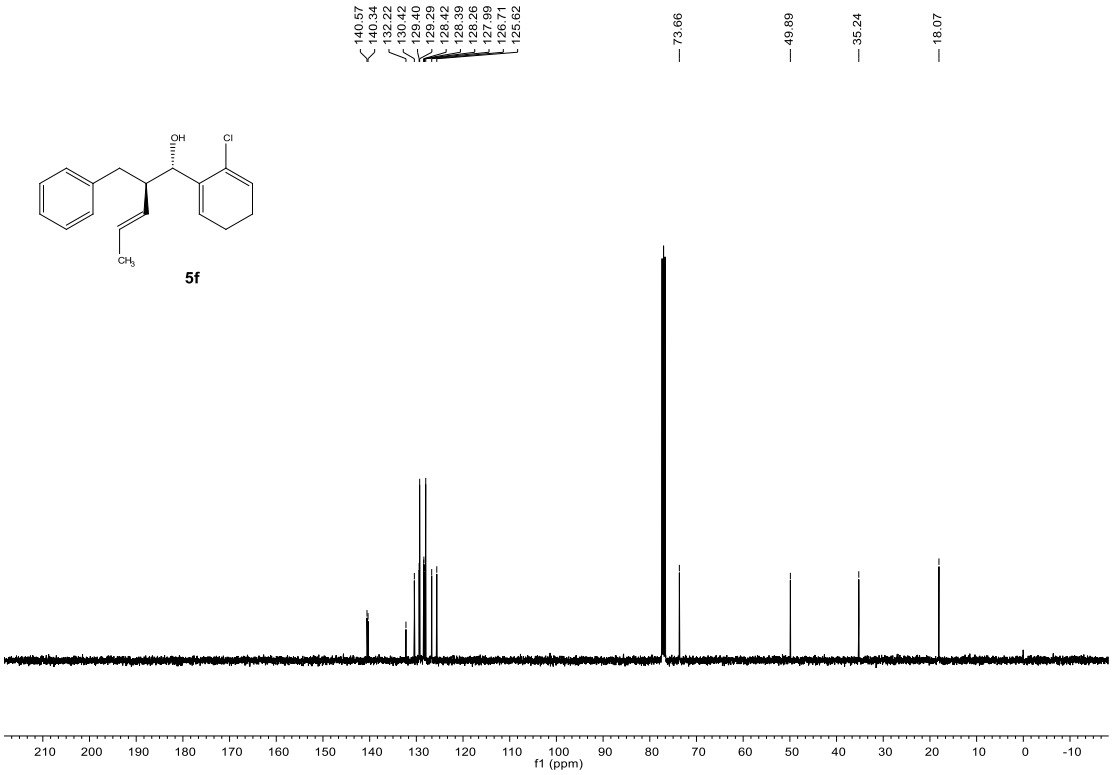
5e $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



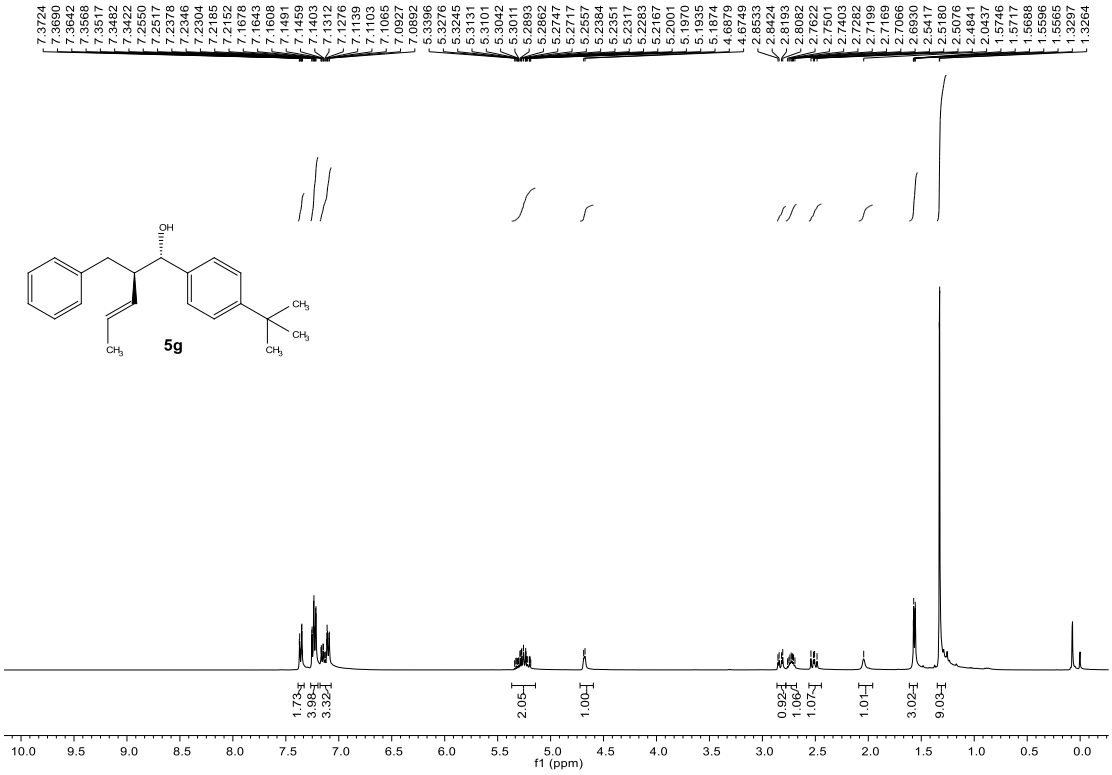
5f ^{1}H NMR (400 MHz, $CDCl_3$)



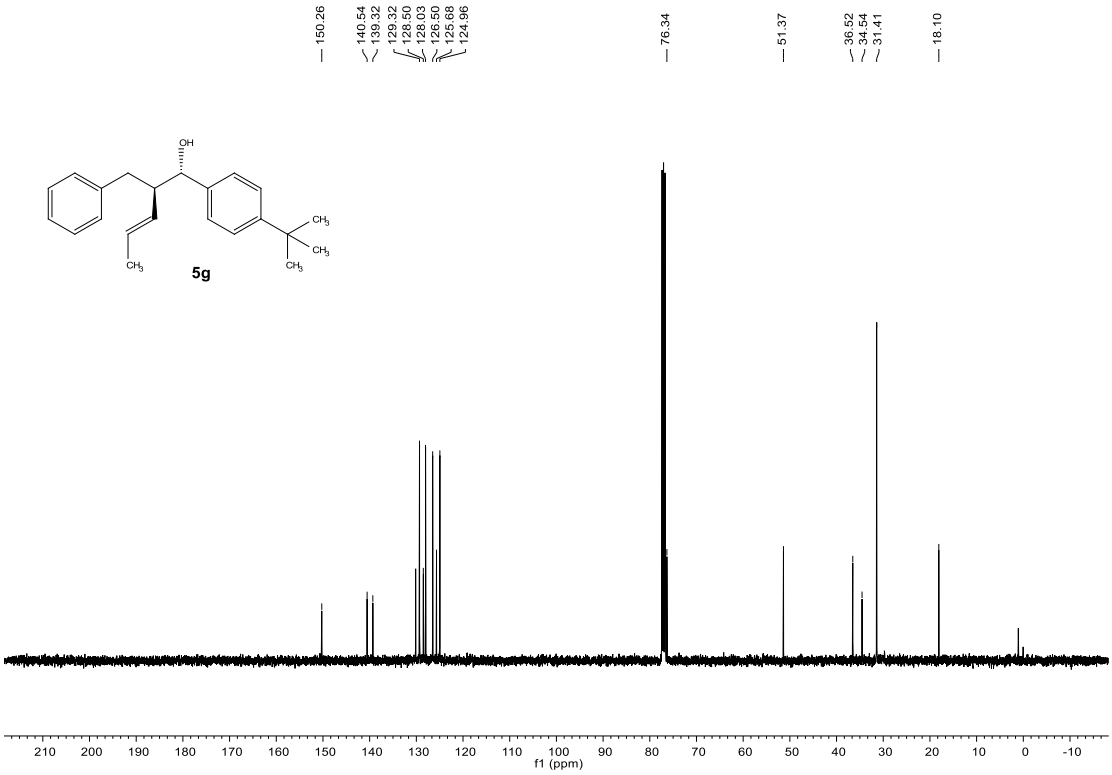
5f ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



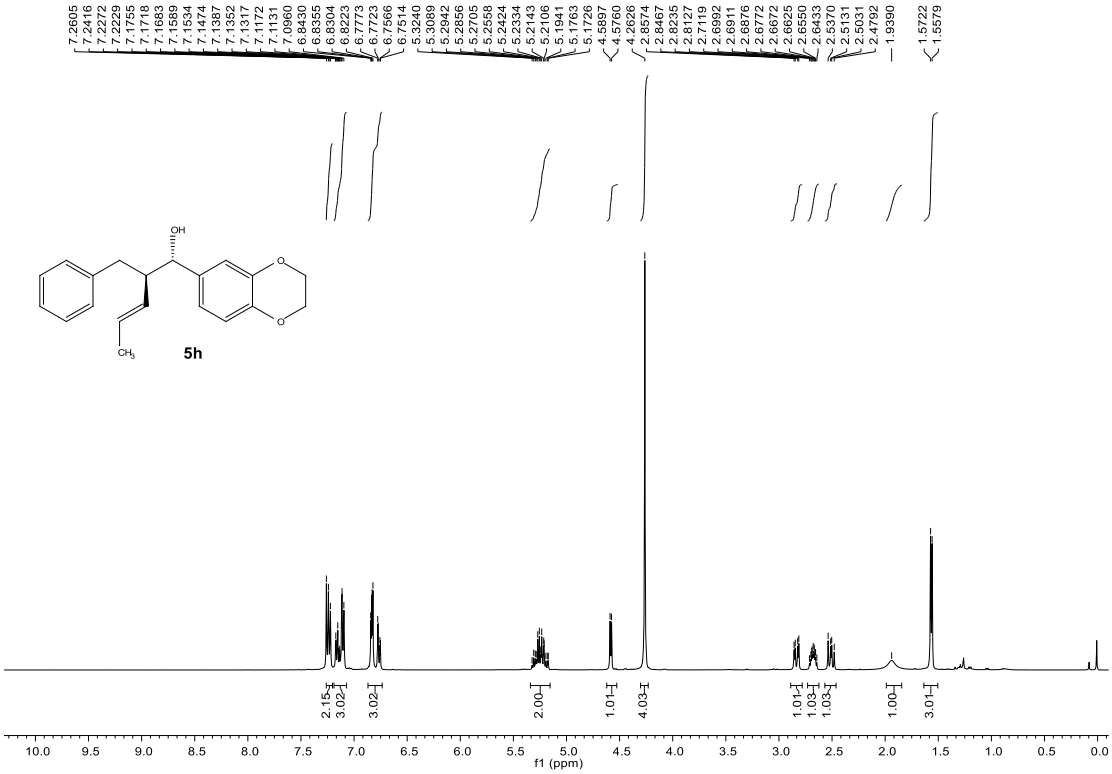
5g ^{1}H NMR (400 MHz, $CDCl_3$)



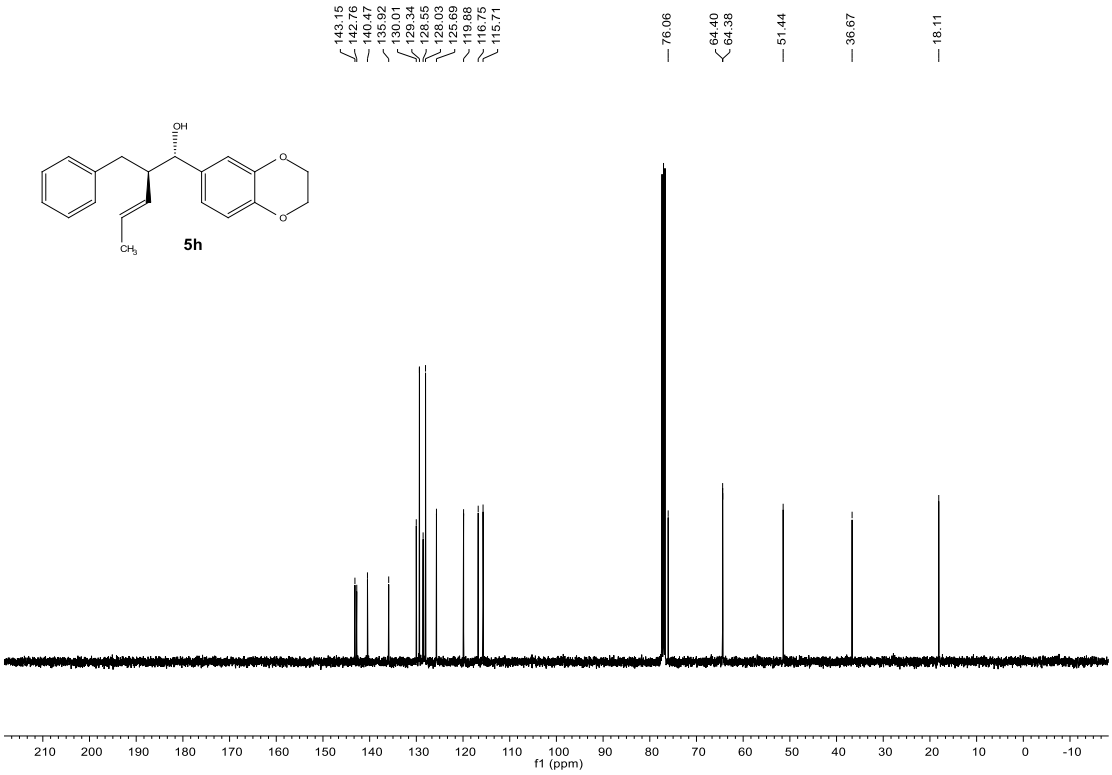
5g ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



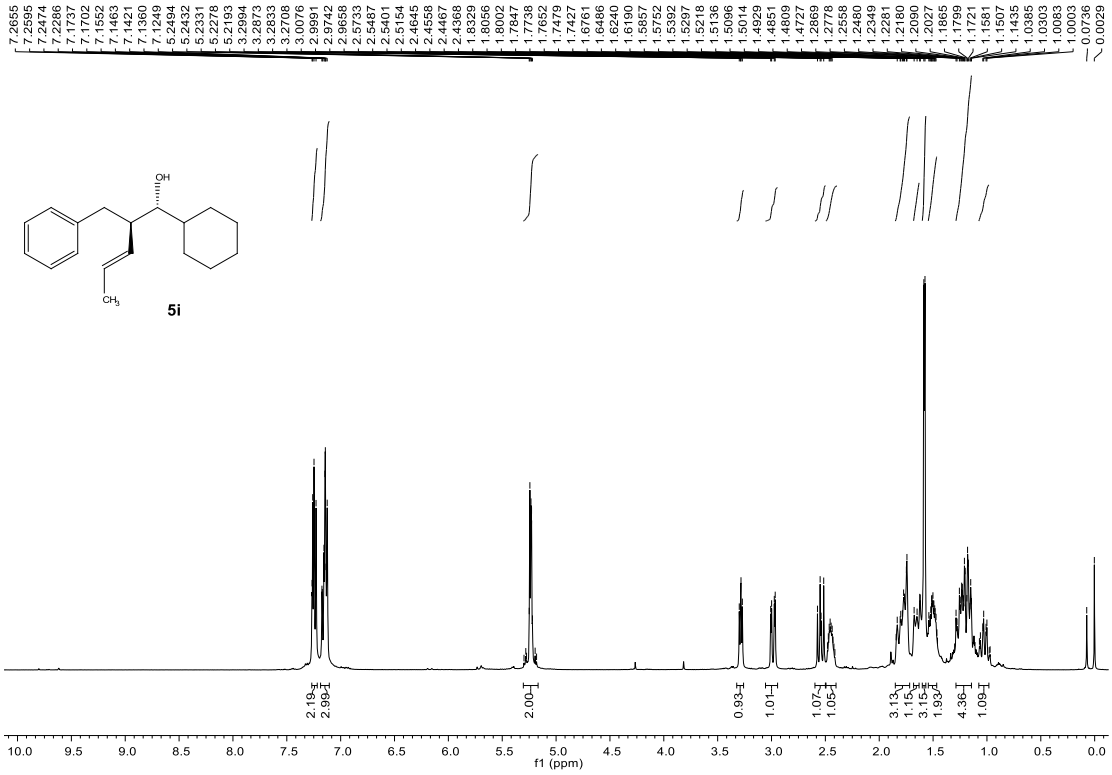
5h ^{1}H NMR (400 MHz, $CDCl_3$)



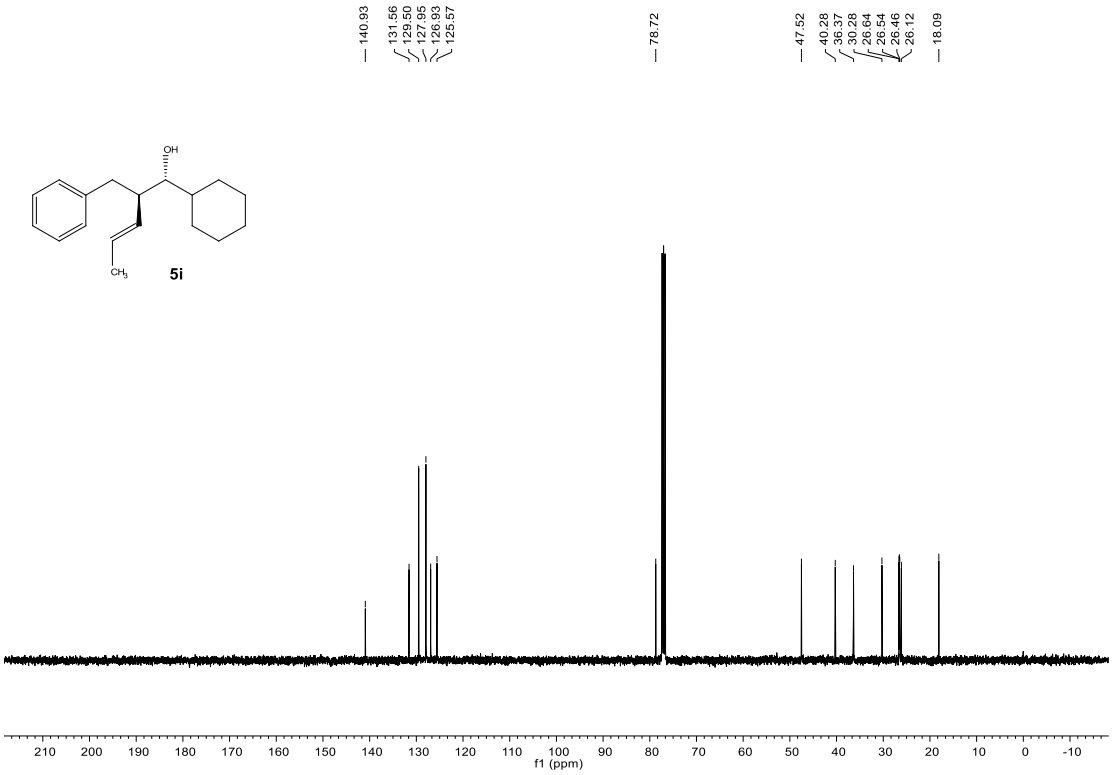
5h ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



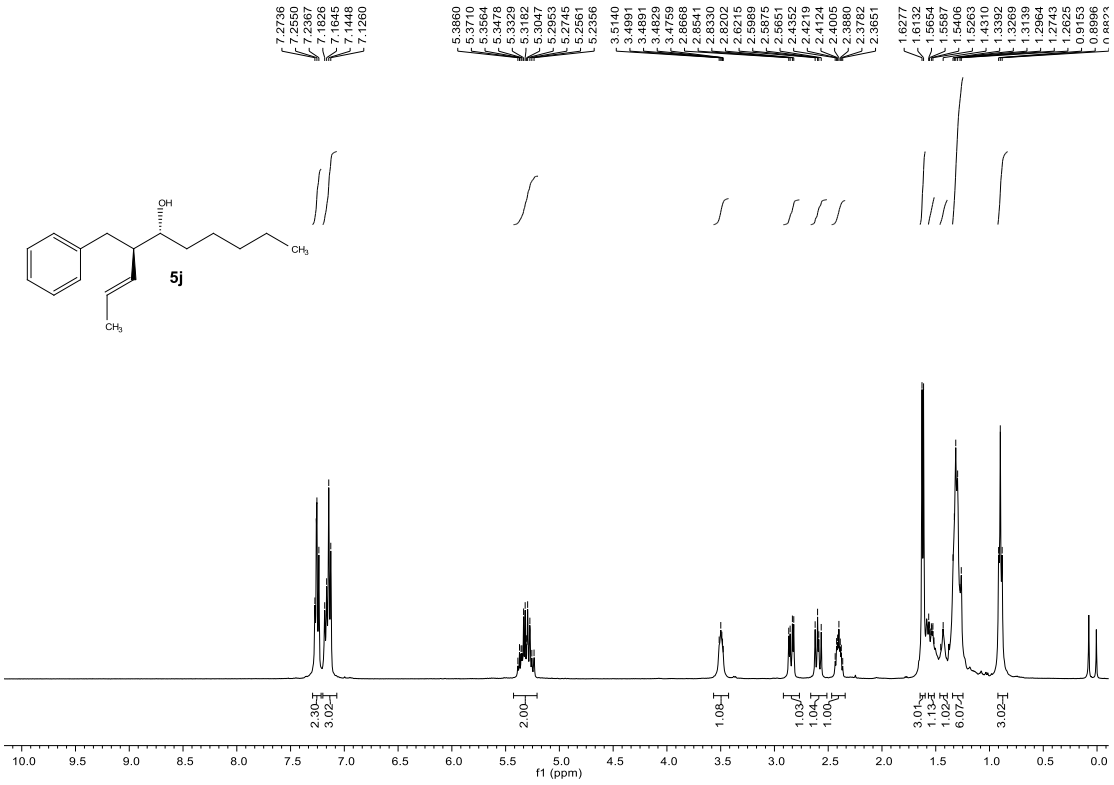
5i ^{1}H NMR (400 MHz, $CDCl_3$)



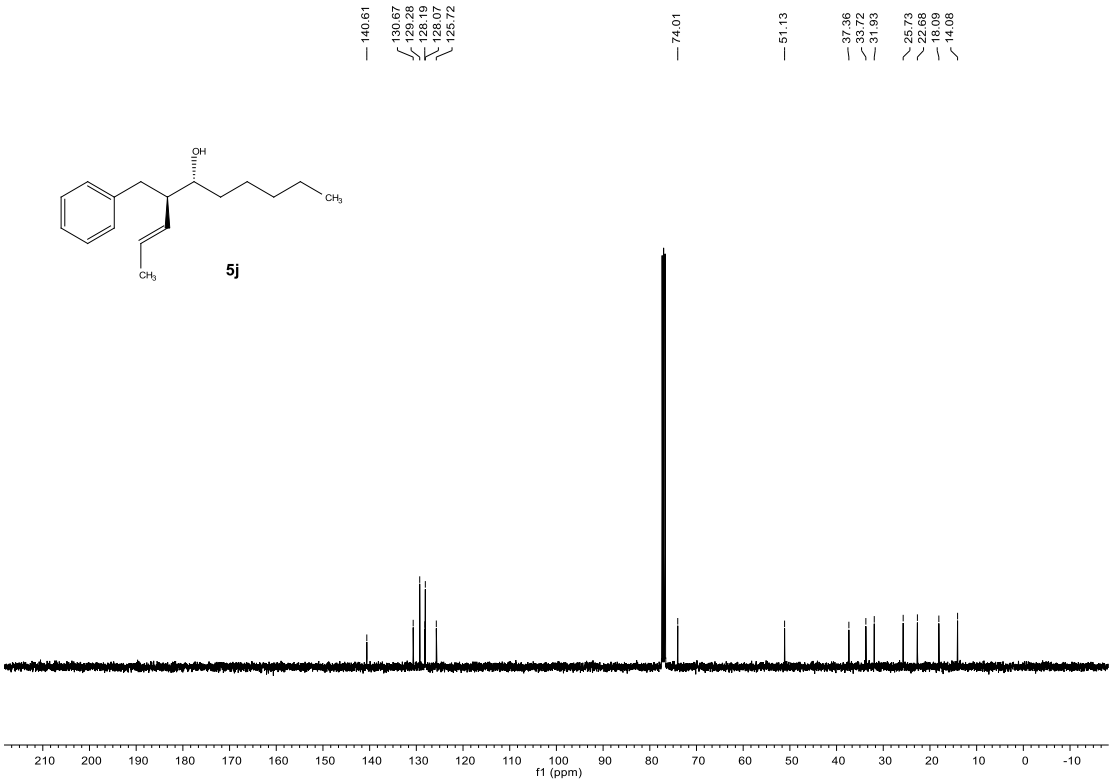
5i $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



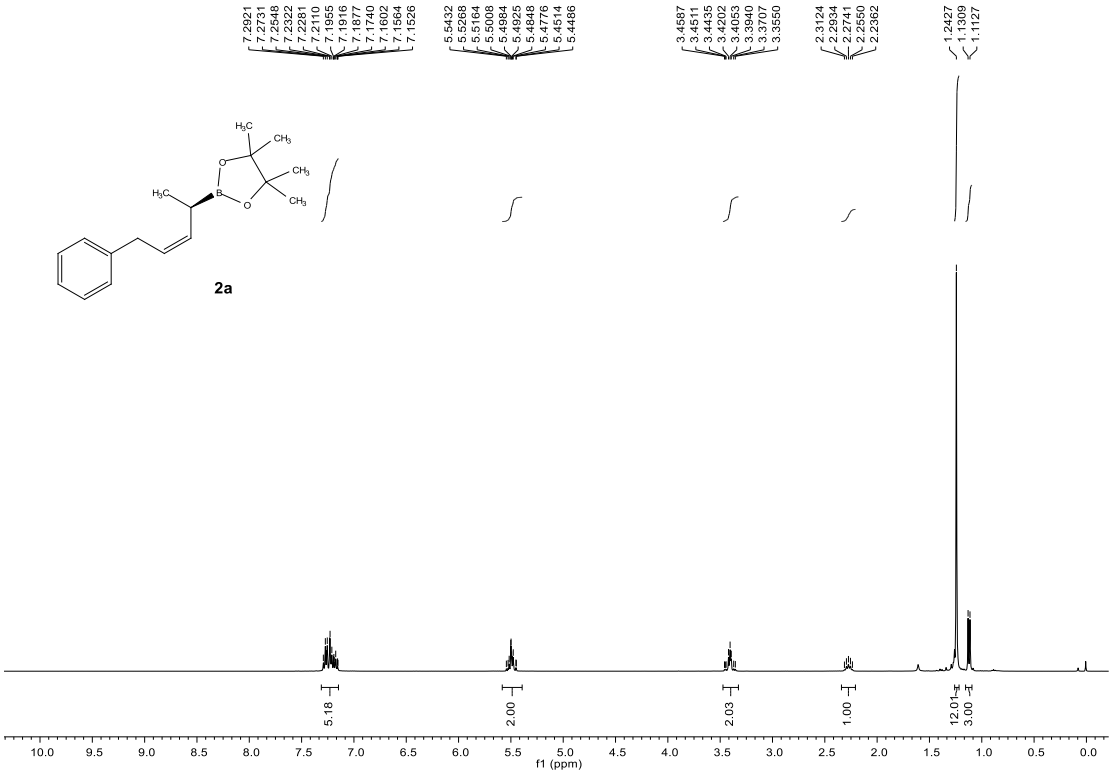
5j ^{1}H NMR (400 MHz, $CDCl_3$)



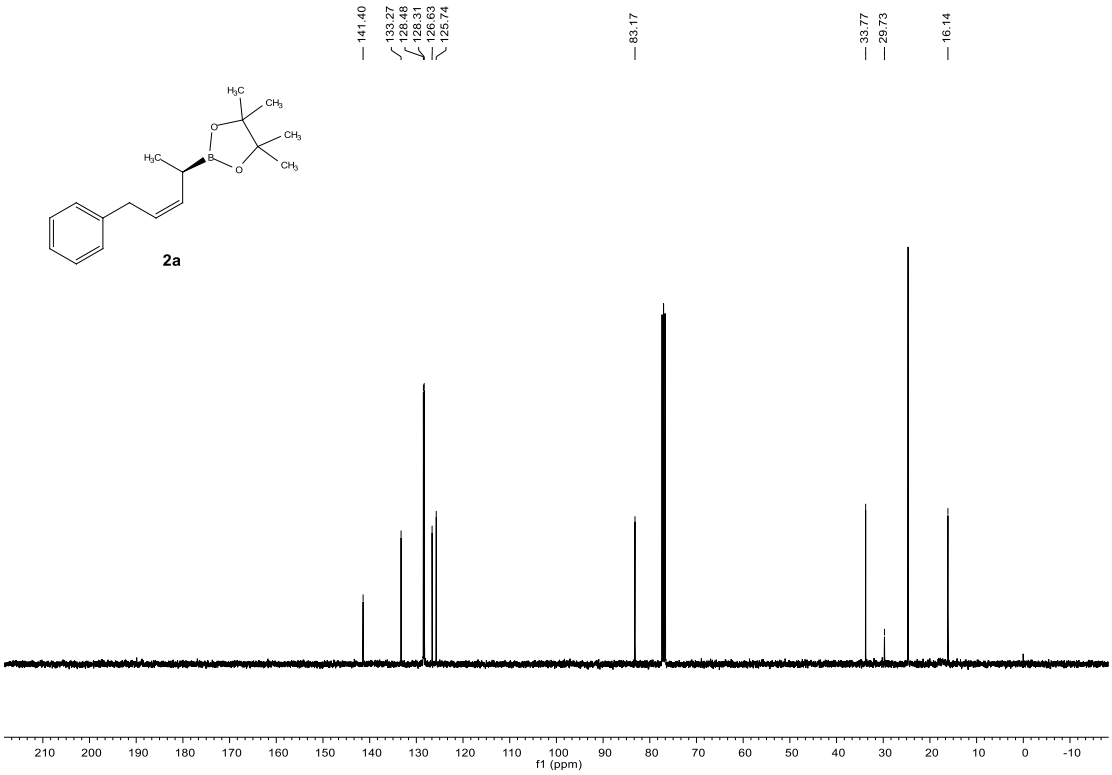
5j ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



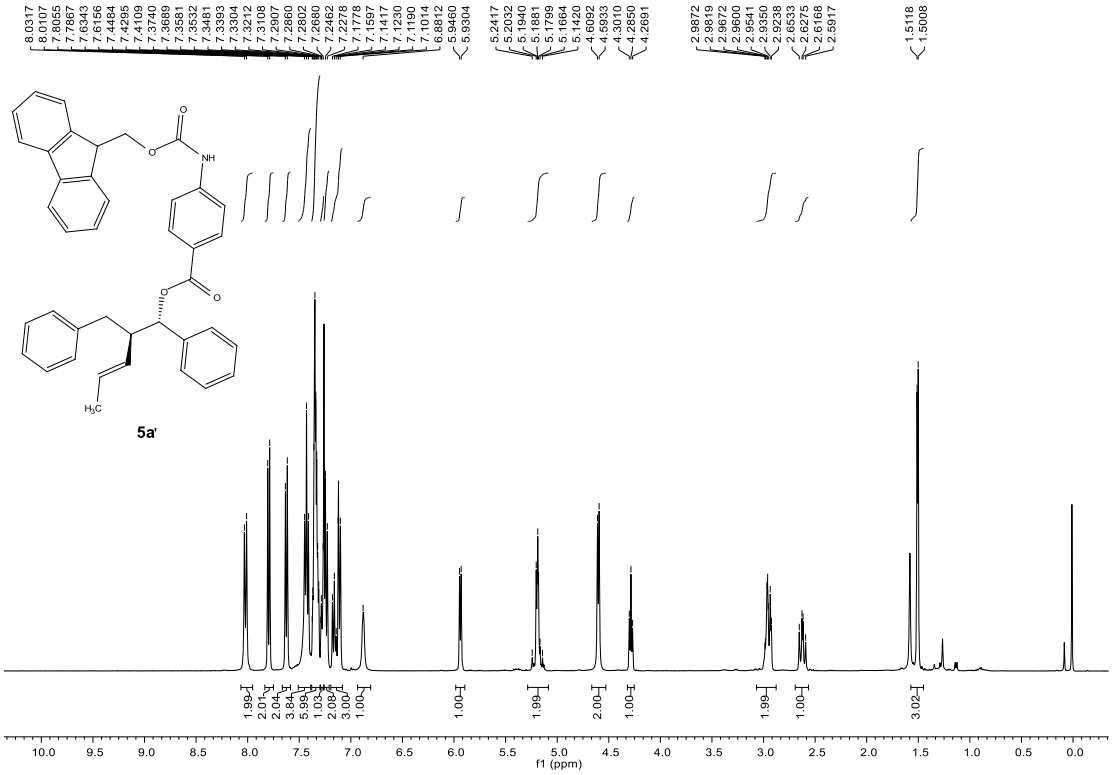
2a ^{1}H NMR (400 MHz, $CDCl_3$)



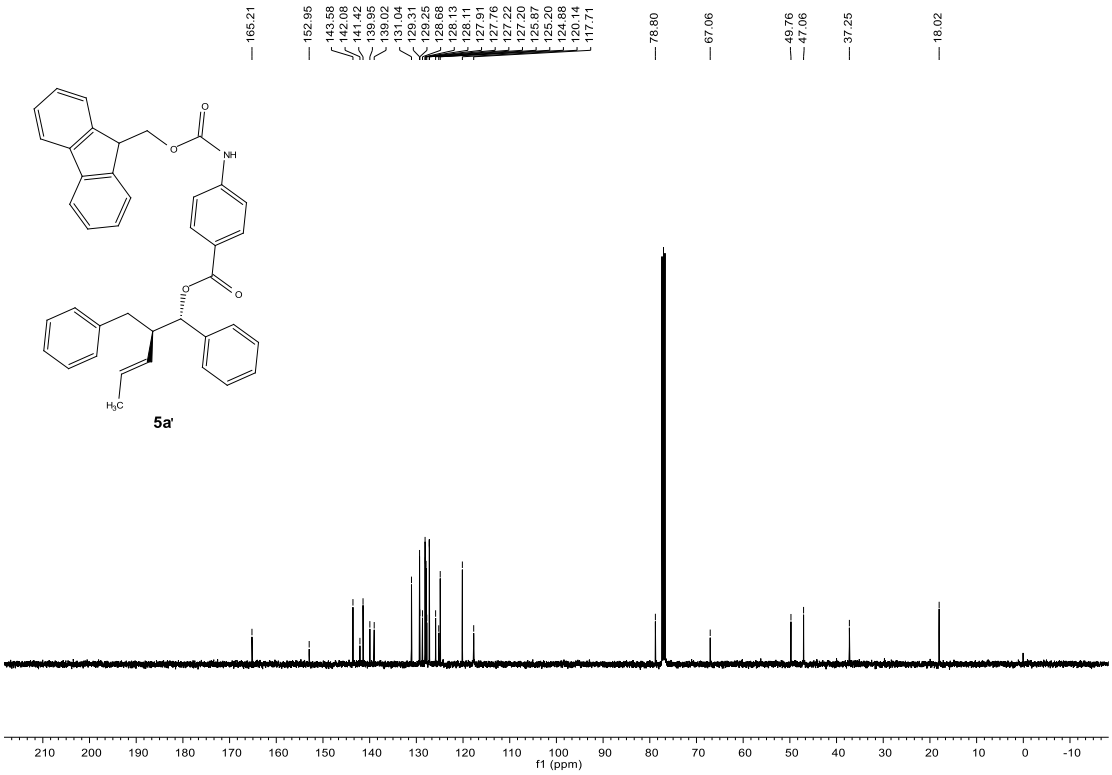
2a ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



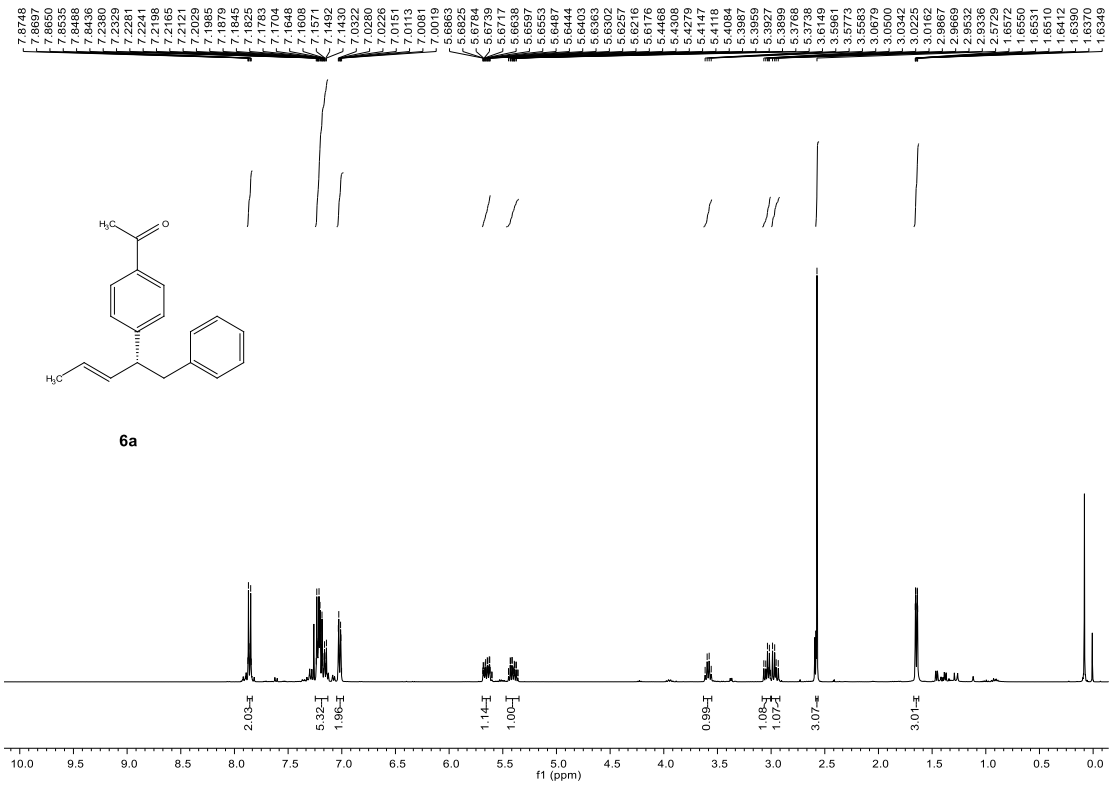
5a' ^{1}H NMR (400 MHz, $CDCl_3$)



5a' ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



6a ^{1}H NMR (400 MHz, $CDCl_3$)



6a ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)