Dimeric Boroles: Effective Sources of Monomeric Boroles for Heterocycle Synthesis

Xiaojun Su, J. J. Baker, and Caleb D. Martin*

Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX 76798, USA

E-mail: caleb_d_martin@baylor.edu

-Supporting Information-

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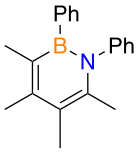
General Details. All manipulations were performed under an inert nitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glovebox. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 4 Å molecular sieves. Silica gel (40-63 μM) was purchased from SiliCycle Inc. 1-Phenyl-2,3,4,5-tetramethylborole dimer and diphenylketene were prepared *via* the corresponding literature procedures.[1] Benzophenone, 3-hexyne, and elemental sulfur were purchased from Alfa Aesar and used as received. $Cr(CH_3CN)_3(CO)_3$ was purchased from Sigma Aldrich and used as received. $CDCl_3$ and C_6D_6 for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled, and stored over 4 Å molecular sieves. THF-d_8 for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and used as received. All reactions were conducted at 100 °C and monitored by in situ ^{1}H and ^{11}B NMR spectroscopy. The reaction times reflect the time upon which dimeric boroles (**C**$_2$, **D**$_2$ and **E**$_2$) were completely consumed. The reaction times differ for substrates suggesting that the substrate influences the reaction times. Multinuclear NMR spectra were recorded on a Bruker 600 MHz or 400 MHz spectrometer. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High-resolution mass spectra (HRMS) were acquired at Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI and the University of Texas at Austin Mass Spectrometry Center with CI. Melting points were measured with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Elemental analyses (C, H, and N) were performed by Atlantic Microlab, Inc. (Norcross, GA). UV-Vis spectra were recorded using an Agilent 8453 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer with excitation at the absorbance λ_{max}. Solutions were prepared in a N_2 filled glovebox and measured in screw capped quartz cuvettes for both UV-Vis and fluorescence. Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures produced using OLEX2.[2-3]



Synthesis of **1**: Phenyl azide (60.0 mg, 0.503 mmol) was added to a toluene (5 mL) solution of **C**$_2$ (99.0 mg, 0.251 mmol) in a pressure tube and heated for 12 h at 100 °C. The volatiles were removed *in vacuo* and the remaining residue was purified through a silica gel plug with hexanes:Et_2O (10:1). The volatiles were removed *in vacuo* to give **1** as a yellow powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion of an Et_2O solution of **1** into toluene at -35 °C.

Yield: 101.0 mg, 70%

m.p. 97-100 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.14 (m, 2H), 7.11-7.09 (m, 1H), 7.07-6.99 (m, 5H), 6.94-6.92 (m, 2H), 2.28 (s, 3H), 2.22 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H)

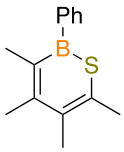
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 151.14 ($Ar_{quaternary}$), 145.77 ($Ar_{quaternary}$), 137.99 ($Ar_{quaternary}$), 132.60 (Ar_{CH}), 128.54 (Ar_{CH}), 128.20 (Ar_{CH}), 126.54 (Ar_{CH}), 126.17 (Ar_{CH}), 125.58 (Ar_{CH}), 116.94 ($Ar_{quaternary}$), 18.88 (CH_3), 18.26 (CH_3), 17.47 (CH_3), 16.56 (CH_3). Note: the signals for the two carbon atoms bound to boron are not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ 35.5

FT-IR (cm^{-1} (ranked intensity)): 2914 (12), 1587 (6), 1488 (3), 1428 (14), 1338 (5), 1292 (13), 1260 (9), 1217 (11), 1028 (7), 770 (8), 742 (2), 696 (1), 605 (4), 638 (15), 517 (10)

HRMS chemical ionization (CI): calcd for $C_{20}H_{22}BN$ $[M]^+$, 287.1845; found 287.1848

Elemental Analysis: calculated for $C_{20}H_{22}BN$: C 83.64, H 7.72, N 4.88. Found: C 83.41, H 7.81, N 4.69



Synthesis of **2**: Elemental sulfur (4.62 g, 18.061 mmol) was added to a solution of **C2** (395.0 mg, 1.008 mmol) in toluene (20 mL) in a pressure tube and heated to 100 °C for 24 h. The solution was cooled to room temperature (23 °C) and excess elemental sulfur was removed by filtration. The volatiles were stripped from the filtrate *in vacuo* at 40 °C to give a yellow oil. The oil was dissolved in hexanes (10 mL) and stored at -35 °C in the glovebox freezer overnight to precipitate excess elemental sulfur. Once filtered, the solvent was removed *in vacuo*, and the yellow oil was dissolved in toluene (20 mL). Copper powder (3.00 g) was added to the toluene solution in a pressure tube and heated to 100 °C for 12 h. After cooling to room temperature the solution was filtered to remove copper and copper sulfide. The volatiles were removed and the remaining yellow oil was dissolved in *n*-pentane and filtered through a silica gel plug. The solvent was removed *in vacuo* to give **2** as a yellow oil.

Note: This reaction is temperature dependent. Conducting the reaction at 60 °C in toluene only results in 25% conversion after 18 days. At 70 °C in toluene, only 90% consumption of **C2** was observed after 26 d.

Yield: 224.0 mg, 49%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.43-7.41 (m, 3H), 2.57 (s, 3H), 2.36 (s, 3H), 2.31 (s, 6H)

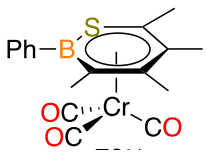
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.34 ($Ar_{quaternary}$), 135.92 ($Ar_{quaternary}$), 133.03 (Ar_{CH}), 132.75 ($Ar_{quaternary}$), 128.07 (Ar_{CH}), 127.73 (Ar_{CH}), 25.62 (CH_3), 19.86 (CH_3), 19.75 (CH_3), 18.65 (CH_3). Note: the signals for the two carbon atoms bound to boron are not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ 49.8

FT-IR (cm^{-1} (ranked intensity)): 2915 (12), 1566 (11), 1429 (7), 1330 (6), 1256 (3), 1208 (13), 1054 (10), 980 (14), 924 (15), 892 (4), 743 (2), 699 (1), 609 (9), 578 (5), 502 (8)

HRMS chemical ionization (CI): calcd for $C_{14}H_{17}BS$ $[M]^+$, 228.1144; found 228.1143

Elemental Analysis: calculated for $C_{14}H_{17}BS$: C 73.70, H 7.51. Found: C 74.89, H 7.72



Synthesis of **2•Cr(CO)$_3$**: **2** (110.0 mg, 0.482 mmol), Cr(CH$_3$CN)$_3$(CO)$_3$ (395.0 mg, 1.446 mmol), and THF (5 mL) were combined and the suspension stirred for 24 hours at 23 °C. The volatiles were removed *in vacuo* to give a red solid, which was extracted with CH_2Cl_2 (5 × 3 mL). The volatiles were removed and the remaining solid was purified through a silica gel plug with CH_2Cl_2:*n*-pentane (1:9). The red band was collected and the solvent was removed *in vacuo* to give **2•Cr(CO)$_3$** as a red solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a *n*-pentane solution of **2•Cr(CO)$_3$** into toluene.

Yield: 133.0 mg, 76%

m.p. 143-147 °C

^{1}H NMR (600 MHz, THF-d_8): δ 7.59-7.57 (m, 2H), 7.41-7.38 (m, 3H), 2.60 (s, 3H), 2.52 (s, 3H), 2.44 (s, 3H), 2.17 (s, 3H)

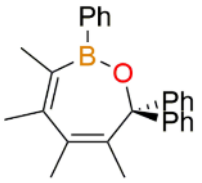
^{13}C{^{1}H} NMR (150 MHz, THF-d_8): δ 229.83 (*C*O), 133.81 (Ar$_{CH}$), 128.72 (Ar$_{CH}$), 127.69 (Ar$_{CH}$), 120.64 (Ar$_{quaternary}$), 103.22 (Ar$_{quaternary}$), 102.77 (Ar$_{quaternary}$), 24.83 (*C*H$_3$), 20.16 (*C*H$_3$), 17.75 (*C*H$_3$), 17.51 (*C*H$_3$). Note: the signals for the two carbon atoms bound to boron are not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ 29.1

FT-IR (cm^{-1} (ranked intensity)): 1964 (3), 1908 (6), 1873 (1), 1431 (14), 1376 (9), 1261 (15), 878 (10), 753 (7), 704 (8), 661 (2), 615 (12), 602 (4), 547 (13), 521 (5), 488 (11)

HRMS chemical ionization (CI): calcd for $C_{17}H_{17}BCrO_3S$ $[M]^+$, 364.0397; found 364.0402

Elemental Analysis: calculated for $C_{17}H_{17}BO_3SCr$: C 56.07, H 4.71. Found: C 56.11, H 4.98



3

Synthesis of **3**: Benzophenone (265.0 mg, 1.455 mmol) was added to a toluene (5 mL) solution of **C**$_2$ (298.0 mg, 0.7125 mmol) in a pressure tube and heated to 100 °C for 1 h. The solvent was removed *in vacuo* and the residue washed with hexanes (3 × 3 mL). The volatiles were removed to provide **3** as an off-white solid. Single crystals for X-ray diffraction were grown from a saturated solution of **3** in hexanes at -35 °C.

Yield: 506.0 mg, 94%

m.p. 35-39 °C

$_1$H NMR (400 MHz, $CDCl_3$, -40 °C): δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.49 (q, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25-7.08 (m, 6H), 6.71 (d, *J* = 8.0 Hz, 1H), 1.83 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H)

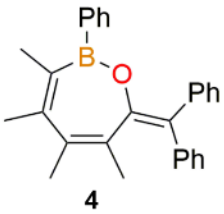
$_{13}$C{$_1$H} NMR (101 MHz, $CDCl_3$): δ 149.86 ($C_{quaternary}$), 148.22 ($C_{quaternary}$), 147.64 ($C_{quaternary}$), 138.08 (B-$C_{quaternary}$), 137.00 ($C_{quaternary}$), 136.37 ($C_{quaternary}$), 135.57 (ArCH), 130.76 (ArCH), 128.51 (ArCH), 127.86 (ArCH), 126.78 (ArCH), 126.56 (ArCH), 126.50 (ArCH), 126.01 (ArCH), 125.15 (ArCH), 86.28 ($Alkyl_{quaternary}$), 20.13 (CH_3), 18.84 (CH_3), 17.41 (CH_3), 17.01 (CH_3). Note: a signal for one of the carbon atoms bound to boron is not observed.

$_{11}$B NMR (128 MHz, $CDCl_3$): δ 43.6

FT-IR (cm^{-1} (ranked intensity)): 1596 (8), 1490 (14), 1436 (4), 1335 (7), 1274 (2), 1180 (9), 999 (5), 913 (15), 756 (3), 743 (12), 692 (1), 656 (10), 617 (11), 601 (6), 546 (13)

HRMS chemical ionization (CI): calcd for $C_{27}H_{27}BO$ $[M]^+$, 378.2155; found 378.2168

Elemental Analysis: calculated for $C_{27}H_{27}BO$: C 85.72, H 7.19. Found: C 84.61, H 7.11



4

Synthesis of **4**. Diphenylketene (58.0 mg, 0.300 mmol) was added to a toluene (5 mL) solution of **C2** (58.0 mg, 0.150 mmol) in a pressure tube and heated to 100 °C for 12 h. The solvent was removed *in vacuo* and the remaining yellow oil was dissolved in hexanes and purified through a silica gel plug. The volatiles were removed *in vacuo* to give **4** as a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of Et_2O solution of **4** into toluene at -35 °C.

Yield: 98.0 mg, 84%

m.p. 95-97 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 6.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.37-7.33 (m, 1H), 7.31-7.28 (m, 4H), 7.21-7.14 (m, 4H), 7.09-7.07 (m, 2H), 1.98 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H), 1.54 (s, 3H)

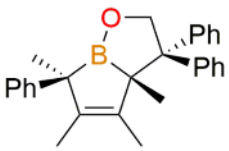
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 151.08 ($C_{quaternary}$), 150.17 ($C_{quaternary}$), 140.24 ($C_{quaternary}$), 139.74 ($C_{quaternary}$), 138.05 ($C_{quaternary}$), 135.27 (Ar_{CH}), 131.13 ($C_{quaternary}$), 130.67 (Ar_{CH}), 130.32 (Ar_{CH}), 130.27 ($C_{quaternary}$), 127.72 (Ar_{CH}), 127.59 (Ar_{CH}), 127.54 (Ar_{CH}), 126.55 (Ar_{CH}), 126.30 (Ar_{CH}), 123.15, 18.51 (CH_3), 18.08 (CH_3), 17.48 (CH_3), 16.61 (CH_3). Note: the signals for the two carbon atoms bound to boron are not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ 43.2

FT-IR (cm^{-1} (ranked intensity)): 1601 (8), 1442 (5), 1337 (12), 1287 (14), 1260 (2), 1157 (10), 844 (15), 769 (3), 691 (1), 666 (11), 649 (6), 625 (13), 580 (4), 557 (9), 453 (7)

Elemental Analysis: calculated for $C_{28}H_{27}BO$: C 86.16, H 6.97. Found: C 83.26, H 7.04*

*Note: The elemental analysis value of carbon was low, likely due to the decomposition. The purity of compound **4** is established from the multinuclear NMR data.



5

Synthesis of **5**: 1,1-Diphenylethylene oxide (98.0 mg, 0.500 mmol) was added to a toluene (8 mL) solution of **C**$_2$ (98.0 mg, 0.250 mmol) in a pressure tube and heated to 100 °C for 12 h. The volatiles were removed *in vacuo* and the residue was purified by dissolving in hexanes and passing through a silica gel plug with hexanes:Et$_2$O (1:10). The volatiles were removed *in vacuo* to give **5** as a colorless solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of an Et$_2$O solution of **5** into toluene.

Yield: 147.0 mg, 75%

m.p. 115-118 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.36 (m, 2H), 7.32-7.23 (m, 9H), 7.19-7.10 (m, 4H), 5.23-5.16 (dd, *J* = 9.2 Hz, *J* = 9.2 Hz, 4H), 1.79 (s, 3H), 1.53 (s, 3H), 1.44 (s, 3H), 0.92 (s, 3H)

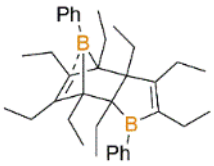
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 145.75 ($Ar_{quaternary}$), 144.61 ($Ar_{quaternary}$), 143.09 ($Ar_{quaternary}$), 141.63 (C=$C_{quaternary}$), 138.20 (C=$C_{quaternary}$), 129.44 (Ar_{CH}), 128.42 (Ar_{CH}), 128.16 (Ar_{CH}), 127.89 (Ar_{CH}), 127.51 (Ar_{CH}), 126.94 (Ar_{CH}), 126.19 (Ar_{CH}), 126.06 (Ar_{CH}), 125.01 (Ar_{CH}), 85.77 (O-CH_2), 62.41 (C-CPh_2), 48.64 (B-$C_{quaternary}$), 39.72 (B-$C_{quaternary}$), 19.14 (CH_3), 17.06 (CH_3), 13.81 (CH_3), 11.58 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ 61.0

FT-IR (cm^{-1} (ranked intensity)): 2959 (11), 1697 (8), 1493 (14), 1443 (5), 1405 (6), 1304 (2), 1029 (4), 976 (10), 932 (12), 748 (3), 699 (1), 602 (13), 574 (7), 523 (9), 494 (15)

HRMS chemical ionization (CI): calcd for $C_{28}H_{29}BO$ $[M]^+$, 392.2311; found 392.2296.

Elemental Analysis: calculated for $C_{28}H_{29}BO$: C 85.72, H 7.45. Found: C 85.65, H 7.63



Synthesis of **D2**: A THF solution (30 mL) of Cp_2ZrCl_2 (2.923 g, 10.0 mmol) and 3-hexyne (1.642 g, 19.99 mmol) was cooled to -78 °C. *n*-BuLi (7.78 mL, 2.57 M in hexanes, 19.99 mmol) was added dropwise and the reaction stirred for 30 min at -78 °C and the bath removed. After 3 h, the volatiles were removed *in vacuo* and the red solid was transferred to glovebox. The zirconacycle was extracted with toluene (3 × 10 mL). The volatiles were removed *in vacuo* and the red residue dissolved in hexanes (30 mL). $PhBCl_2$ (1.56 mL, 11.728 mmol) was added slowly to the solution upon which the color changed from red to brown with the formation of a precipitate. The reaction was stirred for 2 d at room temperature and the suspension centrifuged to remove the brown precipitate. The volatiles were removed *in vacuo* and the crude product purified by passing a through a silica gel plug with *n*-pentane:Et_2O (10:1). The volatiles were removed *in vacuo* to give **D2** as a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a hexanes solution of **D2** into toluene at -35 °C.

Yield: 1.89 g, 75%

m.p. 120-122 °C

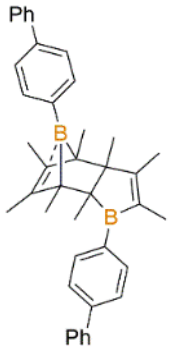
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.58 (m, 2H), 7.28-7.34 (m, 3H), 7.19-7.21 (m, 2H), 7.03-7.05 (m, 3H), 2.52-2.61 (m, 1H), 2.38-2.45 (m, 1H), 2.26-2.33 (m, 2H), 1.91-2.22 (m, 9H), 1.67-1.75 (m, 2H), 1.57-1.58 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 8.6 Hz, 3H), 0.90-0.94 (m, 9H), 0.72 (t, *J* = 8.6 Hz, 3H), 0.59-0.67 (m, 6H)

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 149.29 ($Ar_{quaternary}$), 142.87 ($Ar_{quaternary}$), 139.08 ($Ar_{quaternary}$), 134.77 (Ar_{CH}), 132.74 ($Ar_{quaternary}$), 132.64 (Ar_{CH}), 129.97 ($Ar_{quaternary}$), 128.44 (Ar_{CH}), 127.24 (Ar_{CH}), 126.39 (Ar_{CH}), 125.62 (Ar_{CH}), 63.18 ($Alkyl_{quaternary}$), 61.42 ($Alkyl_{quaternary}$), 56.27 ($Alkyl_{quaternary}$), 34.29 ($Alkyl_{quaternary}$), 24.59 (CH_2), 23.69 (CH_2), 23.16 (CH_2), 22.17 (CH_2), 22.08 (CH_2), 21.62 (CH_2), 21.21 (CH_2), 20.76 (CH_2), 15.68 (CH_3), 15.41 (CH_3), 15.00 (CH_3), 14.23 (CH_3), 13.70 (CH_3), 13.47 (CH_3), 12.60 (CH_3). Note: a signal for one of the carbon atoms bound to boron is not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ -2.7, 68.5

FT-IR (cm^{-1} (ranked intensity)): 3037 (3), 2024 (1), 1594 (2), 1562 (15), 1203 (7), 1156 (4), 1048 (10), 972 (5), 934 (12), 730 (9), 610 (11), 592 (8), 569 (13), 494 (14), 451 (6)

Elemental Analysis: calculated for $C_{36}H_{50}B_2$: C 85.72, H 9.99. Found: C 85.42, H 9.66



Synthesis of **E2**: A THF solution (6 mL) of Cp_2ZrCl_2 (584.0 mg, 1.998 mmol) and 2-butyne (216.0 mg, 3.993 mmol) was cooled to -78 °C. *n*-BuLi (1.56 mL, 2.57 M in hexanes, 4.009 mmol) was added dropwise and the reaction stirred at -78 °C for 30 min. The bath was removed and the reaction stirred for 3 h. The volatiles were removed *in vacuo* and the red solid was transferred to glovebox. The zirconacycle was extracted with toluene (3 × 10 mL). The volatiles were removed *in vacuo* and red residue was dissolved in hexanes (30 mL). *p*-$PhC_6H_4BCl_2$ (515.0 mg, 2.201 mmol) was added slowly to the solution and the color changed from red to brown with the formation of a brown precipitate. The reaction was stirred at room temperature for 2 d and the suspension centrifuged to remove the brown precipitate. The volatiles were removed *in vacuo* and the crude product was purified by passing through a silica gel plug with *n*-pentane: Et_2O (10:1). The volatiles were removed *in vacuo* to give **E2** as a white solid.

Yield: 492.0 mg, 90%

m.p. 68-71 °C

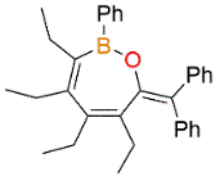
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.89 (m, 3H), 7.64 (s, 1H), 7.55-7.59 (m, 4H), 7.38-7.48 (m, 6H), 7.28-7.37 (m, 2H), 7.18-7.20 (d, *J* = 8.0 Hz, 2H), 1.92 (s, 3H), 1.88 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 0.87 (s, 3H)

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 142.31 ($Ar_{quaternary}$), 141.55 ($Ar_{quaternary}$), 141.37 ($Ar_{quaternary}$), 141.22 ($Ar_{quaternary}$), 140.88 ($Ar_{quaternary}$), 139.42 ($Ar_{quaternary}$), 133.74 (Ar_{CH}), 132.44 (Ar_{CH}), 129.22 ($Ar_{quaternary}$), 128.88 (Ar_{CH}), 128.78 (Ar_{CH}), 127.37 (Ar_{CH}), 127.32 ($Ar_{quaternary}$), 127.20 (Ar_{CH}), 127.11 (Ar_{CH}), 127.05 (Ar_{CH}), 126.21 (Ar_{CH}), 126.10 (Ar_{CH}), 125.55 ($Ar_{quaternary}$), 57.15 ($Alkyl_{quaternary}$), 54.44 ($Alkyl_{quaternary}$), 52.91 ($Alkyl_{quaternary}$), 34.29 ($Alkyl_{quaternary}$), 19.47 (CH_3), 15.89 (CH_3), 15.17 (CH_3), 13.58 (CH_3), 13.30 (CH_3), 13.17 (CH_3), 12.86 (CH_3), 12.40 (CH_3). Note: a signal for one of the carbon atoms bound to boron is not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ -5.8, 70.4

FT-IR (cm^{-1} (ranked intensity)): 3025 (3), 2956 (6), 1599 (11), 1578 (4), 1543 (2), 1516 (1), 1484 (9), 1444 (8), 1157 (5), 1074 (15), 995 (10), 942 (13), 909 (7), 621 (12), 551 (14)

Elemental Analysis: calculated for $C_{40}H_{42}B_2$: C 88.25, H 7.78. Found: C 87.90, H 7.80



Synthesis of **6**: Diphenylketene (39.0 mg, 0.201 mmol) was added to a toluene solution (5 mL) of **D2** (50.0 mg, 0.099 mmol) in a pressure tube and heated to 100 °C for 1 h. The solvent was removed *in vacuo* and the yellow oil was purified through a silica gel plug with *n*-pentane. The volatiles were removed *in vacuo* to give **6** as a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a hexanes solution of **6** into toluene at -35 °C.

Yield: 80 mg, 89%

m.p. 123-125 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.63 (m, 2H), 7.42-7.45 (m, 2H), 7.38-7.40 (m, 1H), 7.31-7.35 (m, 4H), 7.19-7.23 (m, 6H), 2.48-2.60 (m, 2H), 2.32-2.43 (m, 2H), 2.19-2.27 (m, 3H), 1.63-1.72 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.61 (t, *J* = 7.6 Hz, 3H)

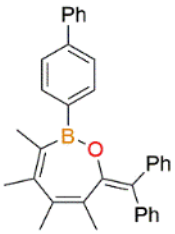
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 151.74 ($Ar_{quaternary}$), 149.21 ($Ar_{quaternary}$), 143.64 ($Ar_{quaternary}$), 142.85 ($Ar_{quaternary}$), 140.20 ($Ar_{quaternary}$), 140.13 ($Ar_{quaternary}$), 139.13 ($Ar_{quaternary}$), 137.21 ($Ar_{quaternary}$), 135.01 (Ar_{CH}), 130.71 (Ar_{CH}), 130.68 (Ar_{CH}), 130.12 (Ar_{CH}), 127.73 (Ar_{CH}), 127.69 (Ar_{CH}), 126.65 (Ar_{CH}), 126.44 (Ar_{CH}), 123.62 ($Ar_{quaternary}$), 25.01 (CH_2), 25.00 (CH_2), 23.11 (CH_2), 22.24 (CH_2), 15.96 (CH_3), 15.17 (CH_3), 14.88 (CH_3), 14.19 (CH_3). Note: a signal for one of the carbon atoms bound to boron is not observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ 44.9

FT-IR (cm^{-1} (ranked intensity)): 3051 (2), 2098 (1), 1569 (4), 1494 (5), 1373 (9), 1356 (10), 1072 (13), 1034 (11), 938 (3), 917 (8), 810 (14), 638 (15), 525 (7), 479 (12), 446 (6)

HRMS chemical ionization (CI): calcd for $C_{30}H_{36}BNa$ $[M+Na]^+$, 469.2679; found 469.2670

Elemental Analysis: calculated for $C_{32}H_{35}BO$: C 86.09, H 7.90. Found: C 85.35, H 7.96



Synthesis of **7**: Diphenylketene (39.0 mg, 0.201 mmol) was added to a toluene solution (5 mL) of **E2** (54.0 mg, 0.099 mmol) in a pressure tube and heated to 100 °C for 8 h. The volatiles were removed *in vacuo* and the yellow oil was purified through a silica gel plug with *n*-pentane:Et_2O (10:1). The volatiles were removed *in vacuo* to give **7** as a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of hexanes solution of **7** into toluene at -35 °C.

Yield: 79 mg, 85%

m.p. 105-108 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.76 (d, *J* = 8.0 Hz, 2H), 7.57-7.82 (m, 4H), 7.42-7.48 (m, 4H), 7.32-7.37 (m, 3H), 7.20-7.25 (m, 4H), 7.11-7.14 (m, 2H), 2.04 (s, 3H), 1.91 (s, 3H), 1.79 (s, 3H), 1.59 (s, 3H)

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 151.34 ($Ar_{quaternary}$), 150.39 ($Ar_{quaternary}$), 143.50 ($Ar_{quaternary}$), 141.29 ($Ar_{quaternary}$), 140.42 ($Ar_{quaternary}$), 139.95 ($Ar_{quaternary}$), 138.26 ($Ar_{quaternary}$), 136.01 (Ar_{CH}), 131.36 ($Ar_{quaternary}$), 130.52 (Ar_{CH}), 130.46 (Ar_{CH}), 128.91 (Ar_{CH}), 128.90 ($Ar_{quaternary}$), 128.84 (Ar_{CH}), 127.92 (Ar_{CH}), 127.80 (Ar_{CH}), 127.79 ($Ar_{quaternary}$), 127.62 (Ar_{CH}), 127.36 (Ar_{CH}), 126.76 (Ar_{CH}), 126.51 (Ar_{CH}), 123.37 ($Ar_{quaternary}$), 18.74 (CH_3), 18.28 (CH_3), 17.70 (CH_3), 16.82 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ 43.7

FT-IR (cm^{-1} (ranked intensity)): 3024 (6), 2912 (5), 2096 (1), 1813 (2), 1707 (4), 1643 (3), 1567 (7), 1493 (13), 1391 (9), 1110 (8), 906 (15), 546 (14), 516 (12), 493 (11), 454 (10)

HRMS chemical ionization (CI): calcd for $C_{34}H_{31}BO$ $[M]^+$, 489.2366; found 489.2365

Elemental Analysis: calculated for $C_{34}H_{31}BO$: C 87.55, H 6.70. Found: C 83.46, H 6.66

*Note: The elemental analysis value of carbon was low, likely due to decomposition. The purity of compound **7** is established from the multinuclear NMR data.

Figure S1. $_1$H NMR spectrum of **1** in $CDCl_3$.

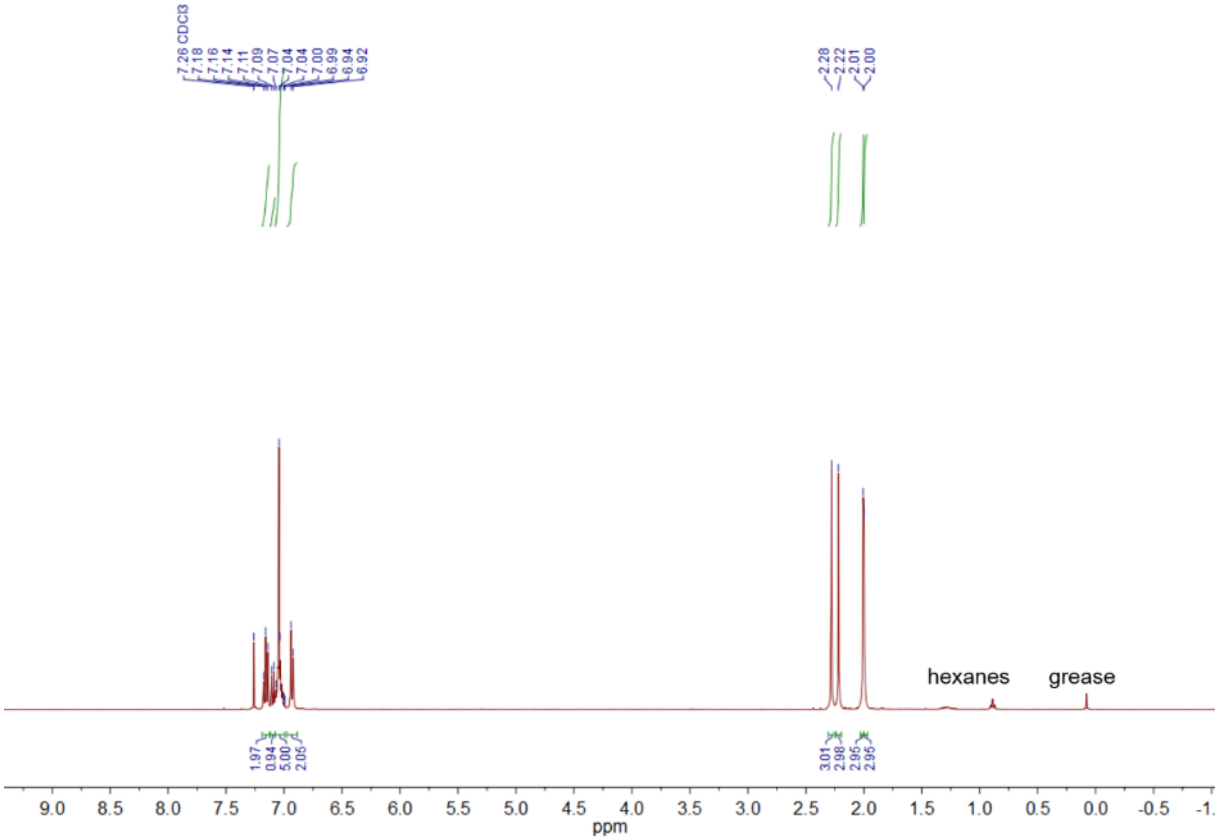


Figure S2. Expansion of $_1$H NMR spectrum of **1** in $CDCl_3$ (aryl region).

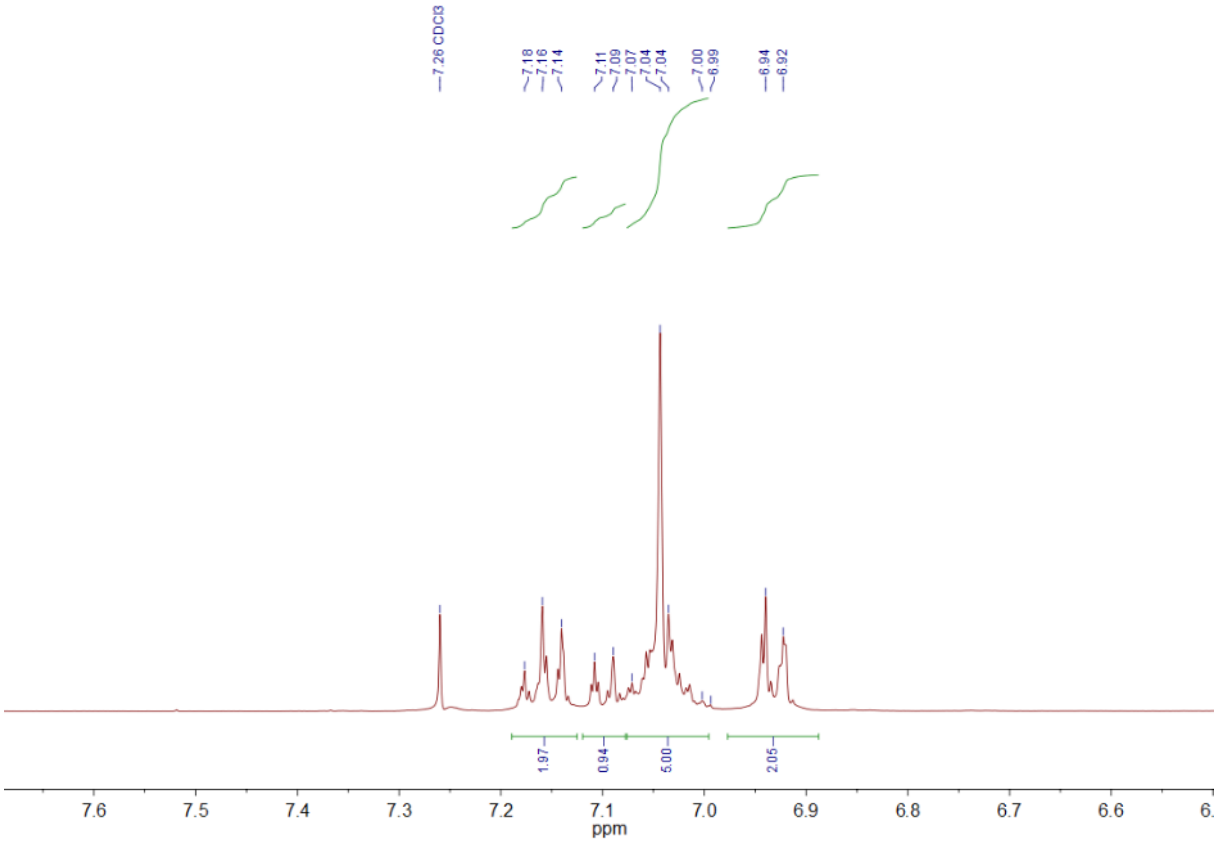


Figure S3. Expansion of $_{1}$H NMR spectrum of **1** in $CDCl_3$ (aliphatic region).

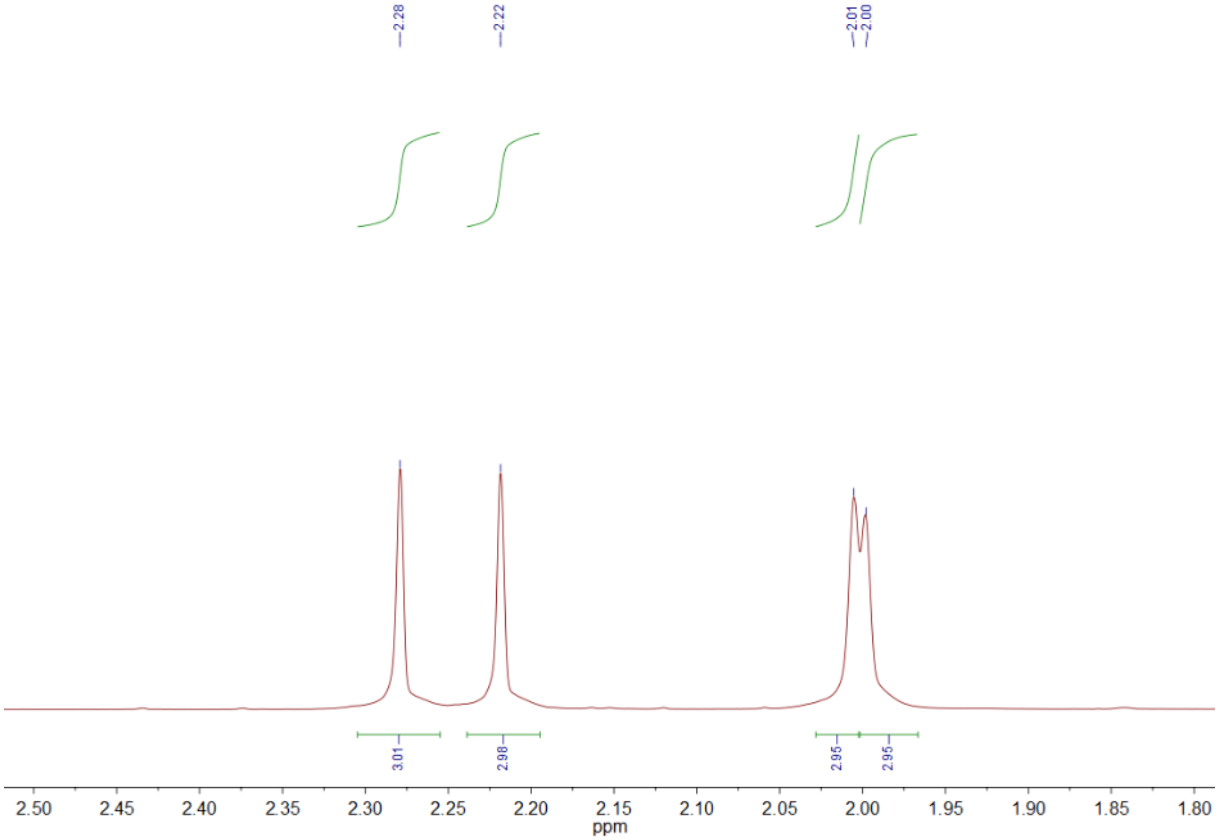


Figure S4. $_{13}$C{$_{1}$H} NMR Spectrum of **1** in $CDCl_3$.

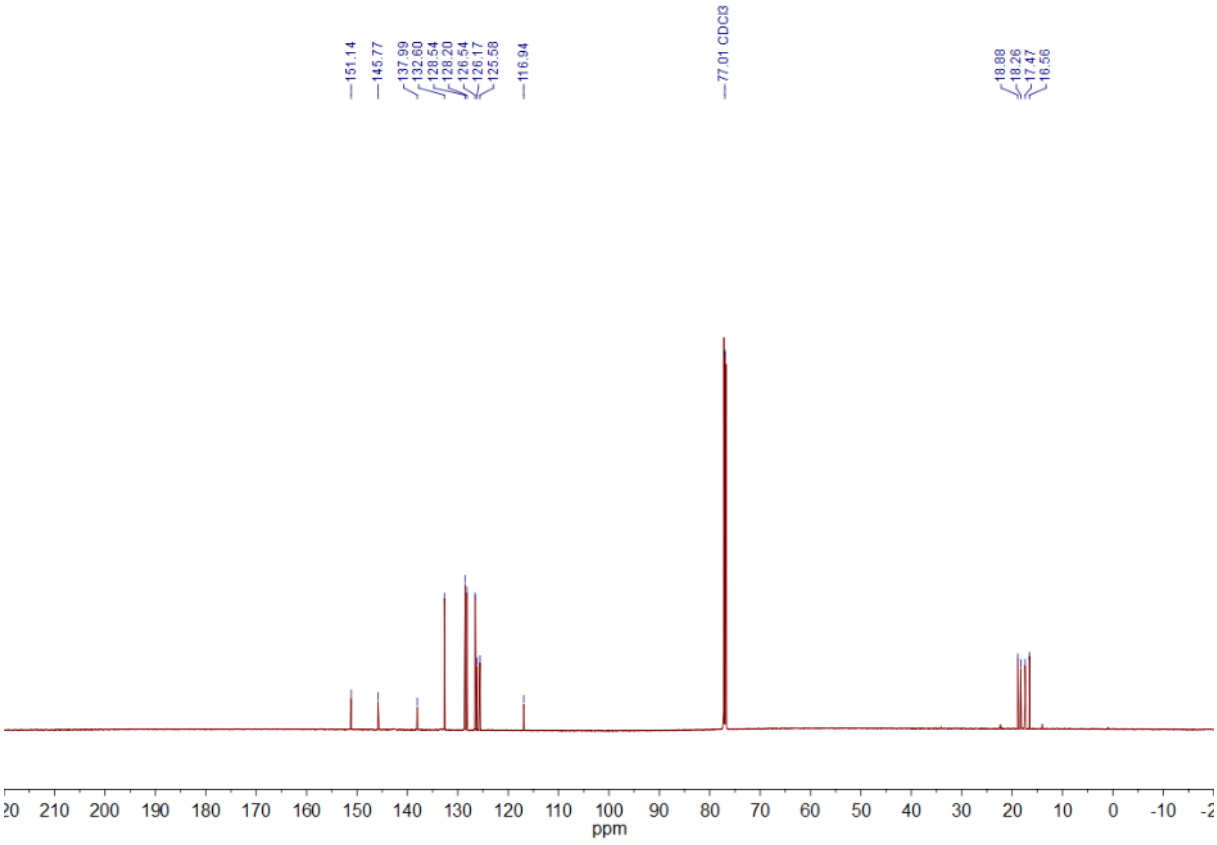


Figure S5. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **1** in $CDCl_3$ (aryl region).

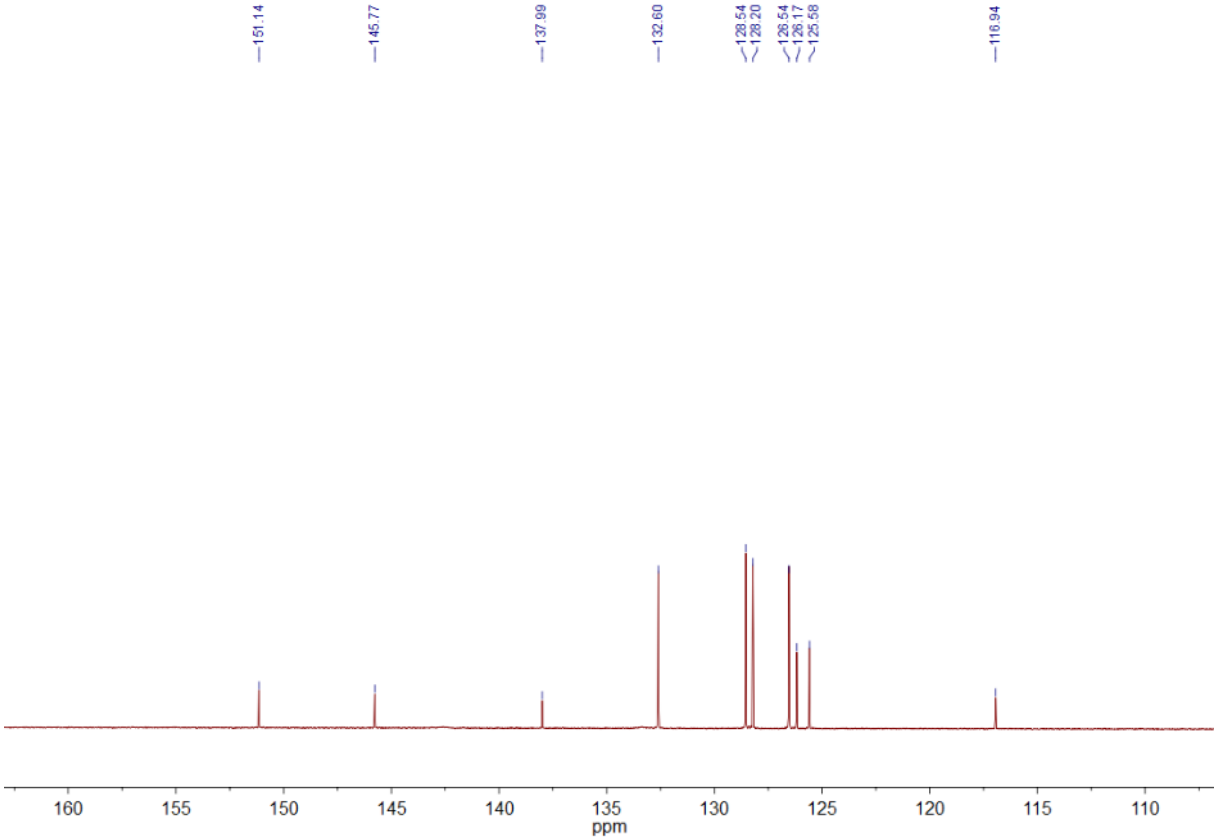


Figure S6. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **1** in $CDCl_3$ (aliphatic region).

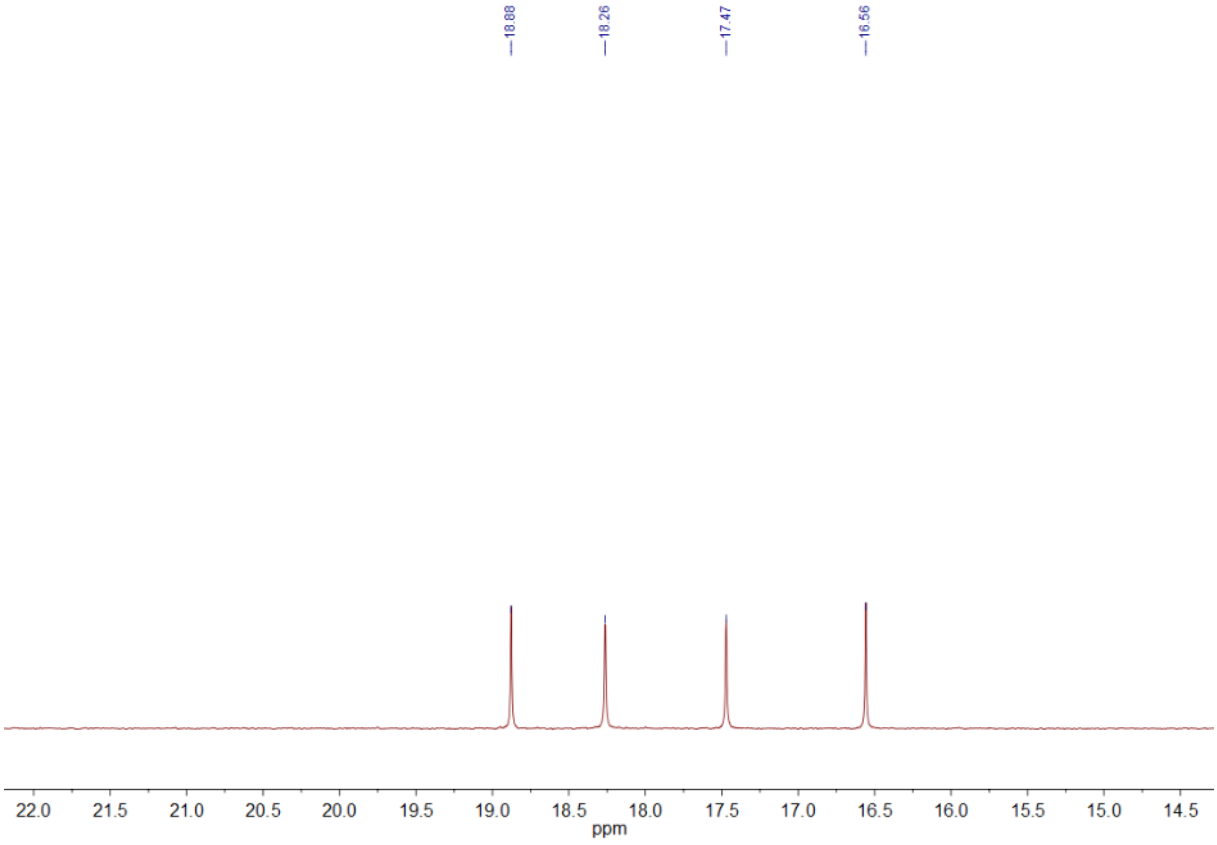


Figure S7. ^{13}C DEPT135 NMR Spectrum of **1** in $CDCl_3$.

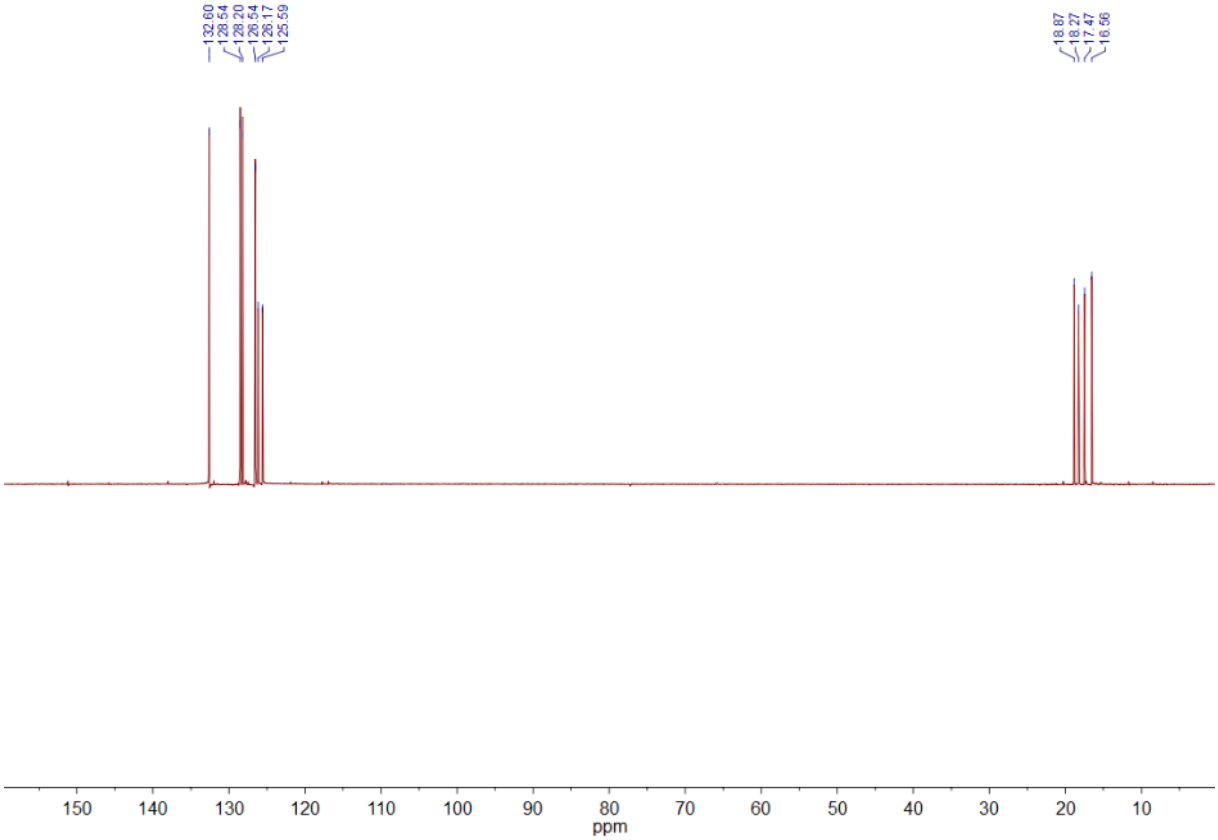


Figure S8. ^{11}B NMR Spectrum of **1** in $CDCl_3$.

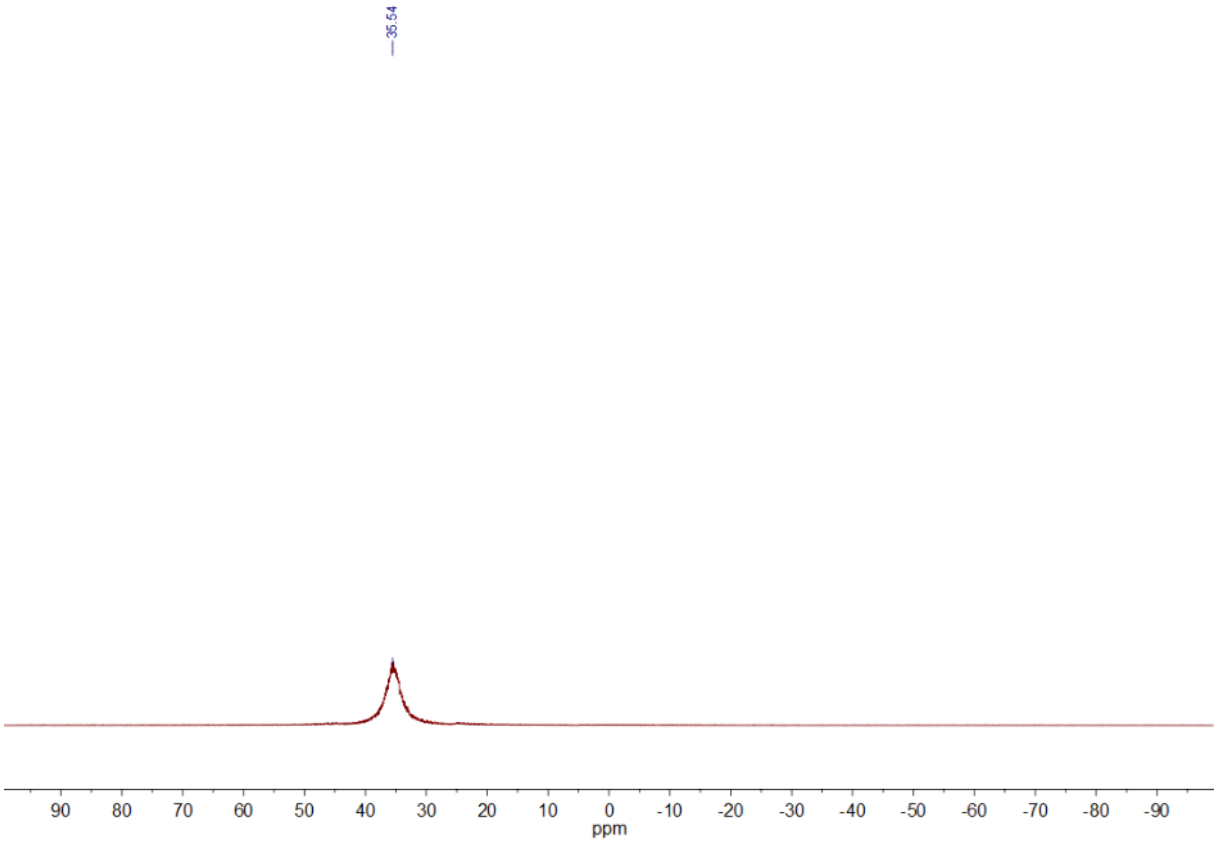


Figure S9. FT-IR Spectrum of **1**.

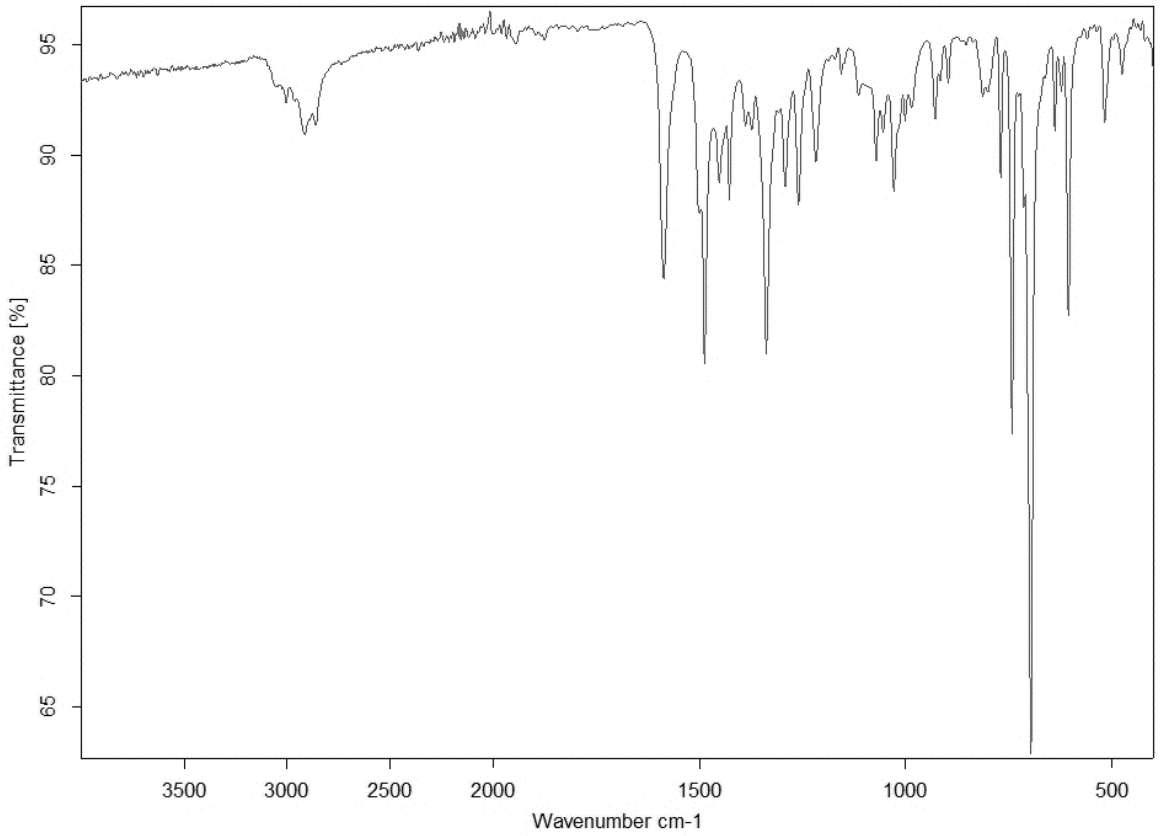
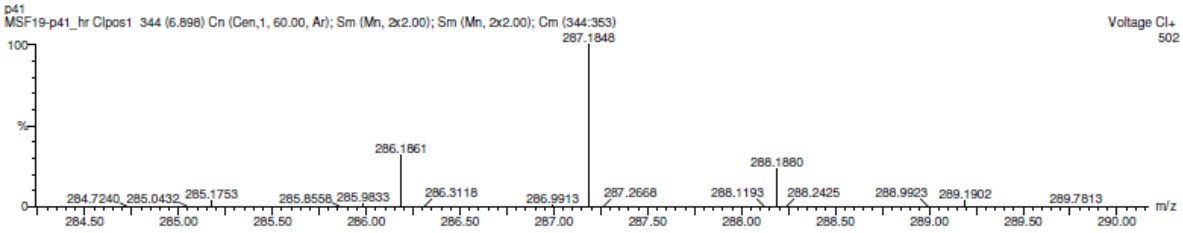


Figure S10. High Resolution Mass Spectrum (CI+) of **1**.

Multiple Mass Analysis: 3 mass(es) processed - displaying only valid results
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
138 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 1-1 O: 1-3 10B: 0-1 11B: 0-1



Minimum:	20.00				-1.5		
Maximum:	100.00		5.0	5.0	70.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
288.1880	22.90	288.1886	-0.6	-2.1	6.0	2773068.3	C16 H24 N O3 10B

Figure S11. $_1$H NMR spectrum of **2** in $CDCl_3$.

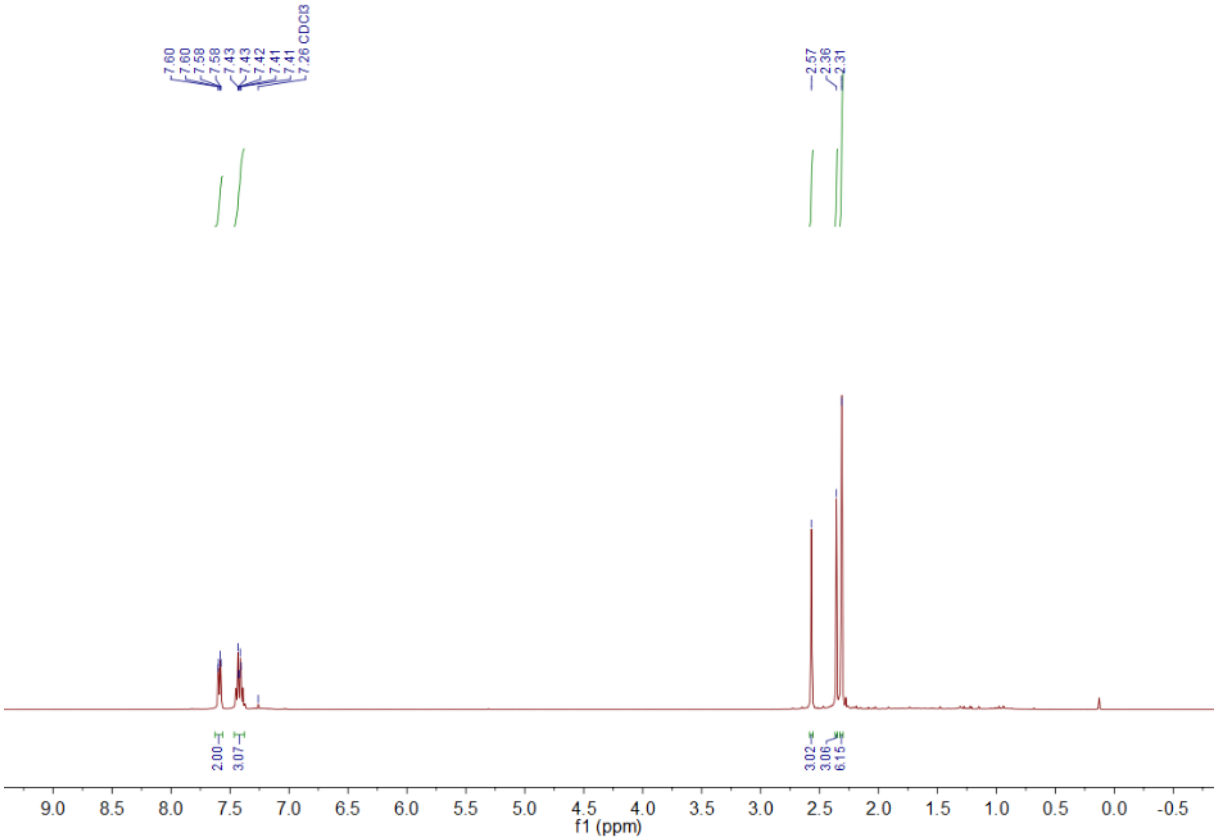


Figure S12. Expansion of $_1$H NMR spectrum of **2** in $CDCl_3$ (aryl region).

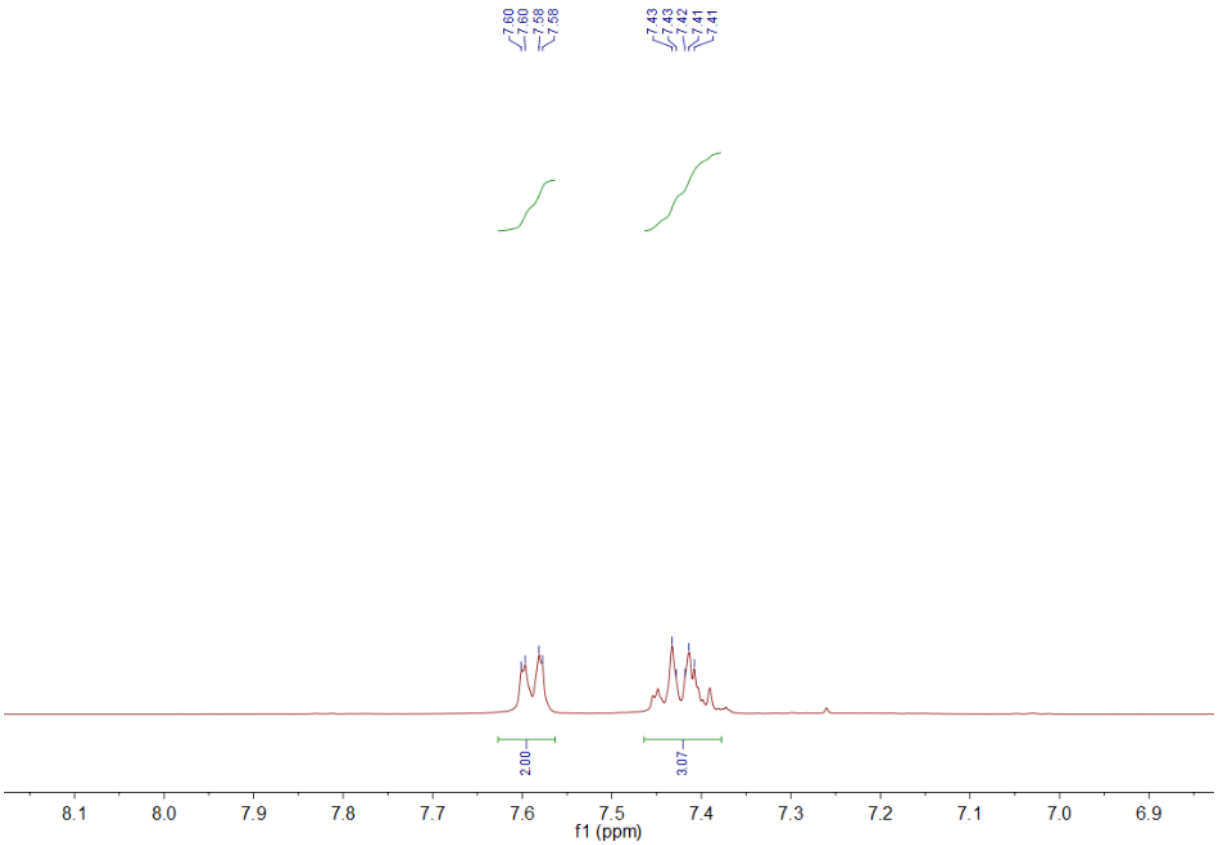


Figure S13. Expansion of ^{1}H NMR spectrum of **2** in $CDCl_3$ (aliphatic region).

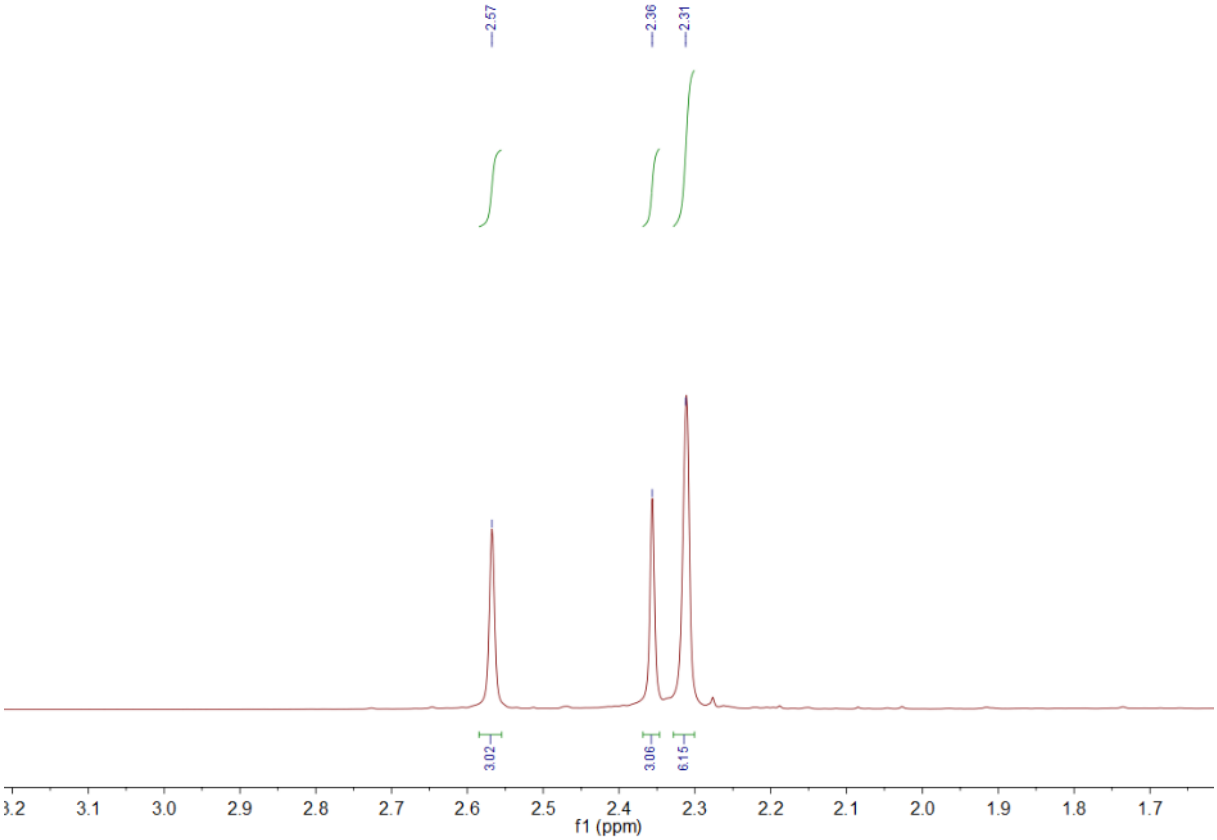


Figure S14. $^{13}C\{^{1}H\}$ NMR Spectrum of **2** in $CDCl_3$.

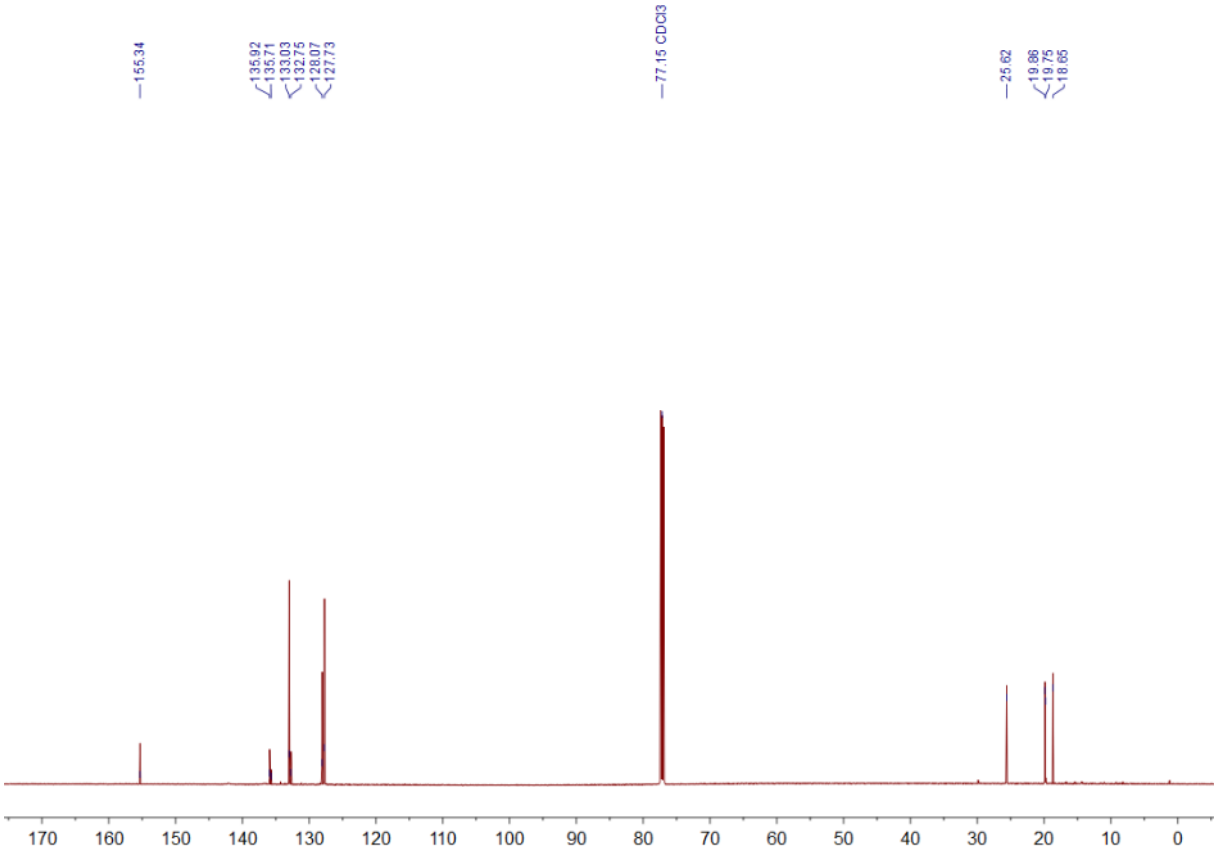


Figure S15. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **2** in $CDCl_3$ (aryl region).

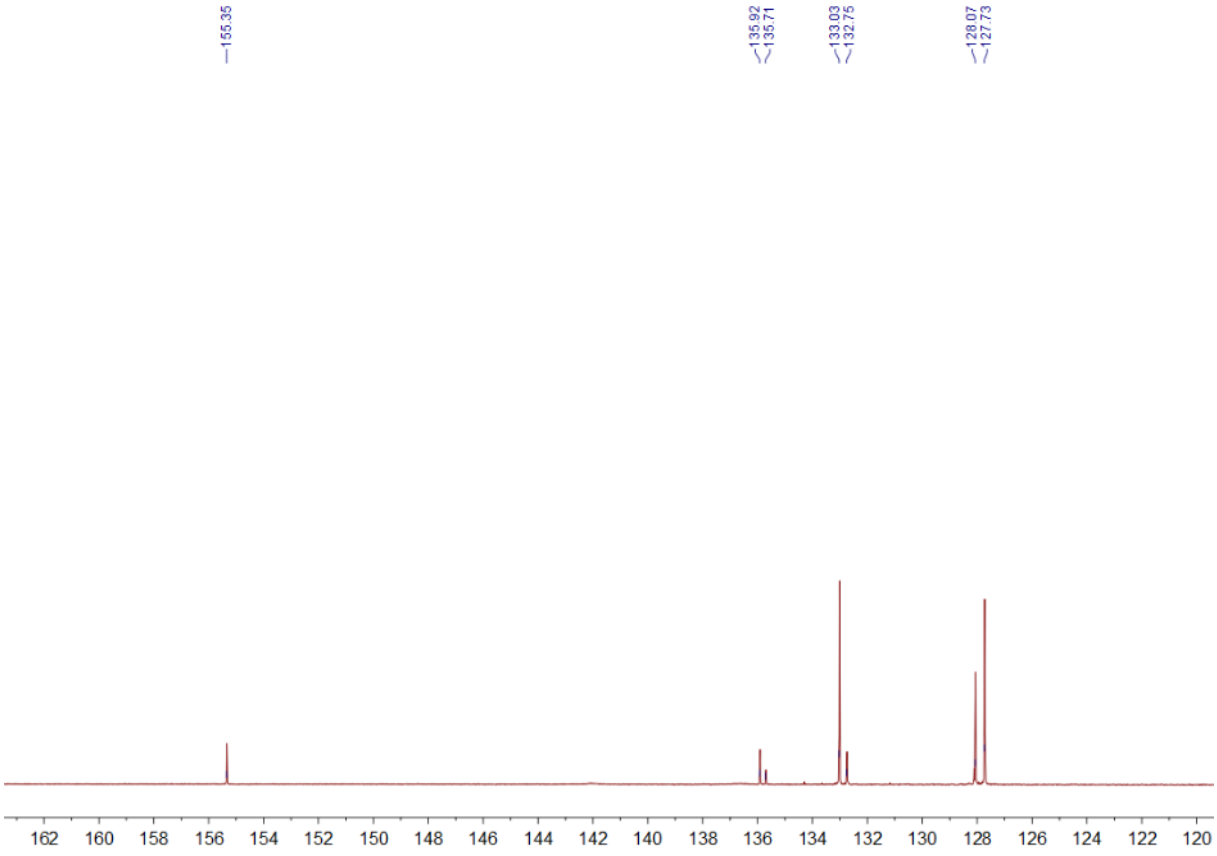


Figure S16. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **2** in $CDCl_3$ (aliphatic region).

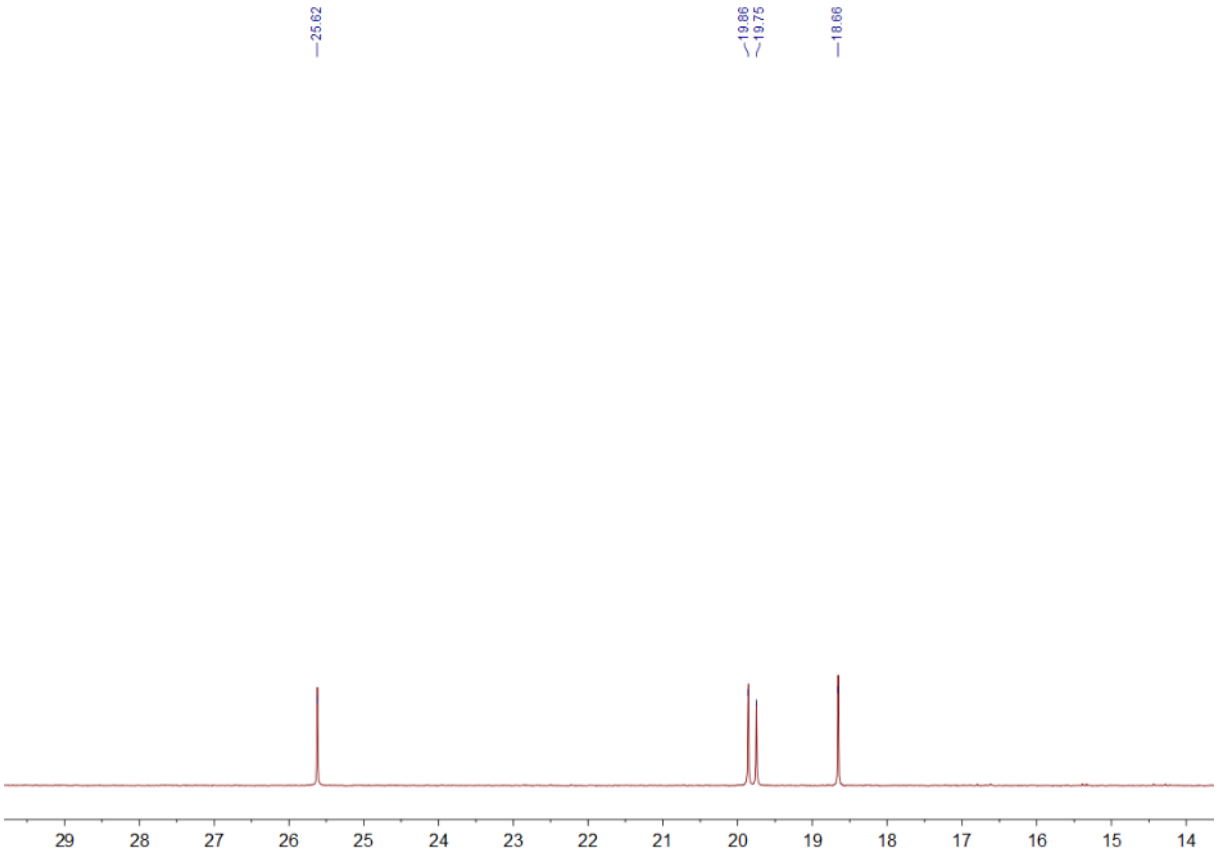


Figure S17. ^{13}C DEPT135 NMR Spectrum of **2** in $CDCl_3$.

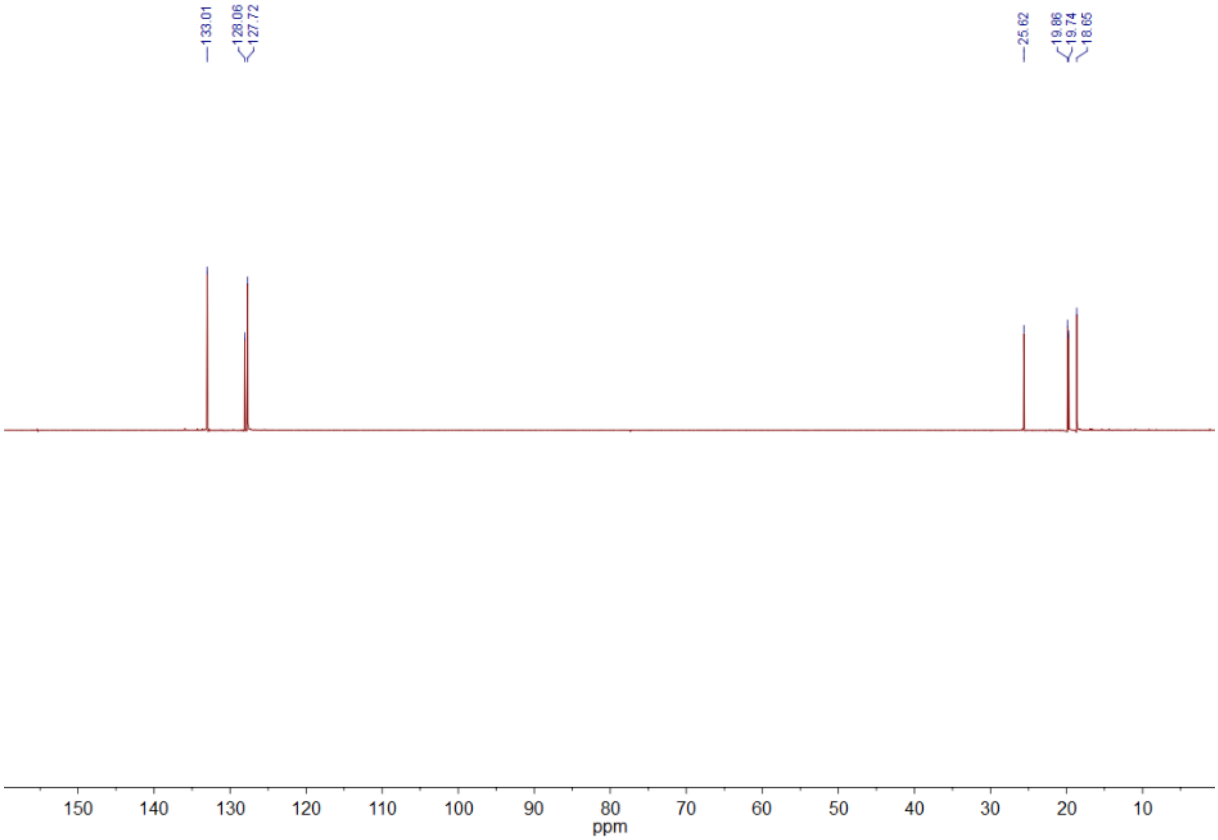


Figure S18. ^{11}B NMR Spectrum of **2** in $CDCl_3$.

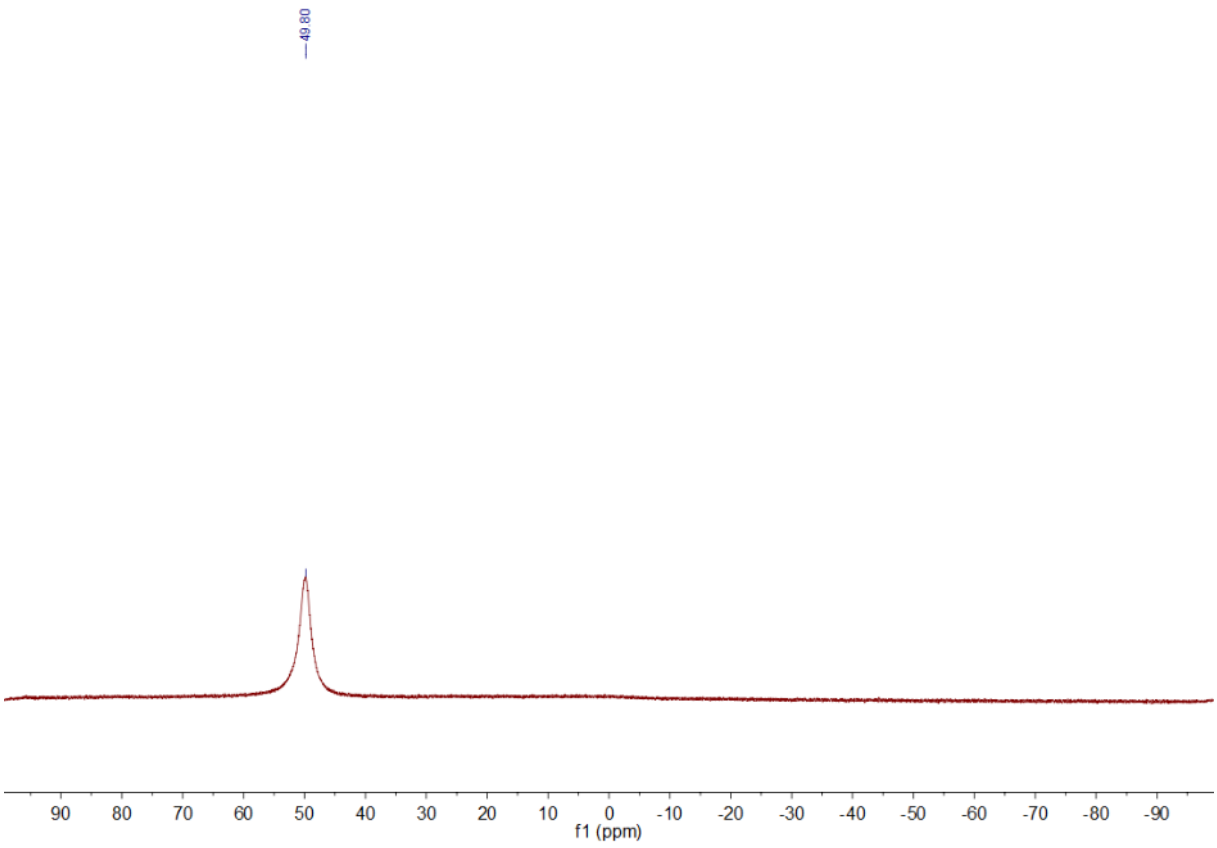


Figure S19. FT-IR Spectrum of **2**.

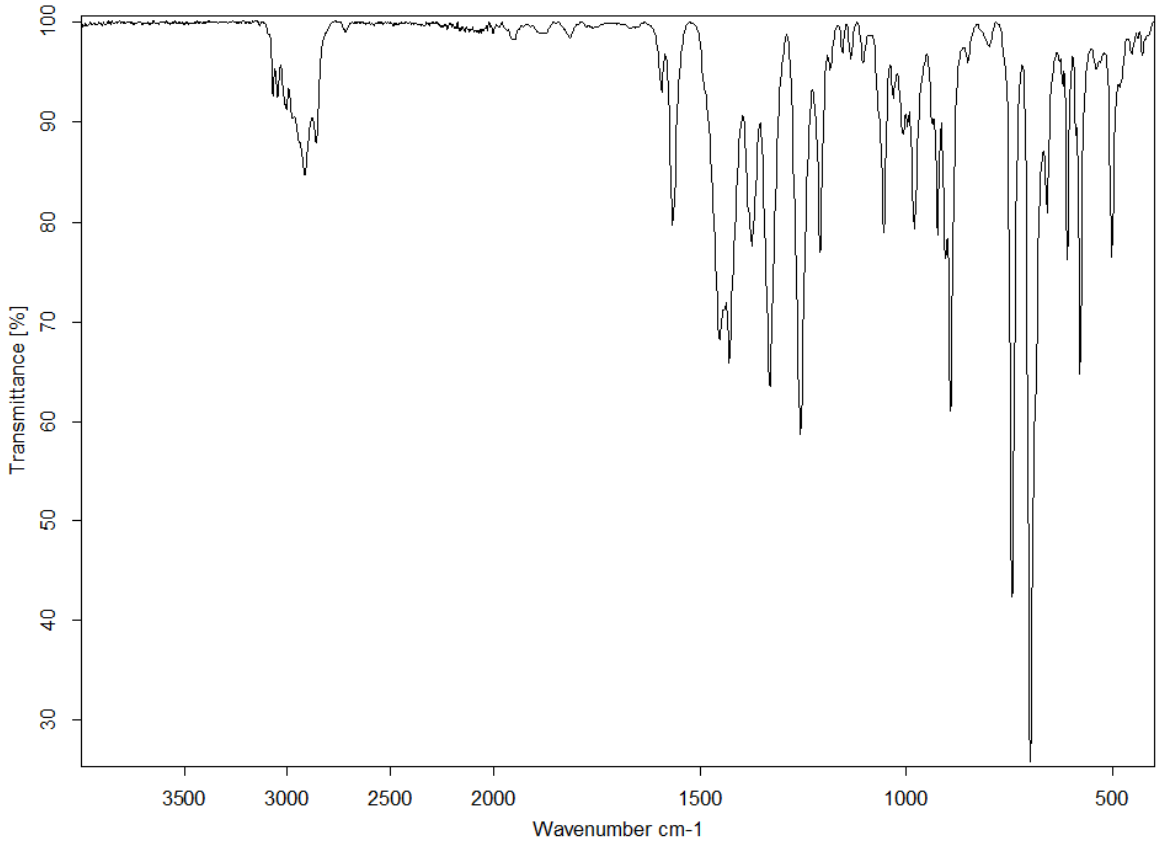


Figure S20. High Resolution Mass Spectrum (CI+) of **2**.

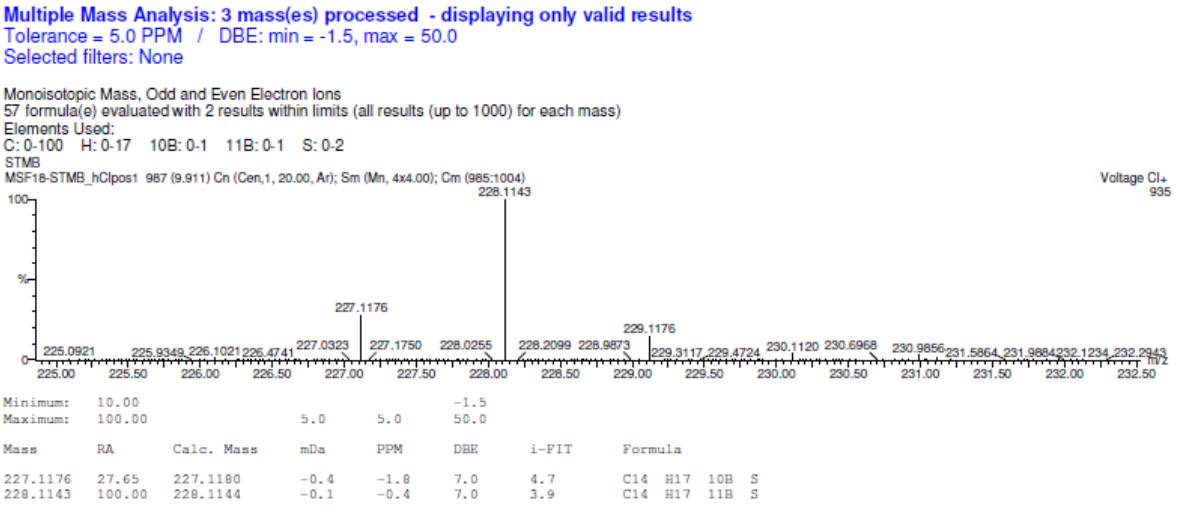


Figure S21. ^{1}H NMR spectrum of **2•Cr(CO)$_3$** in THF-d_8.

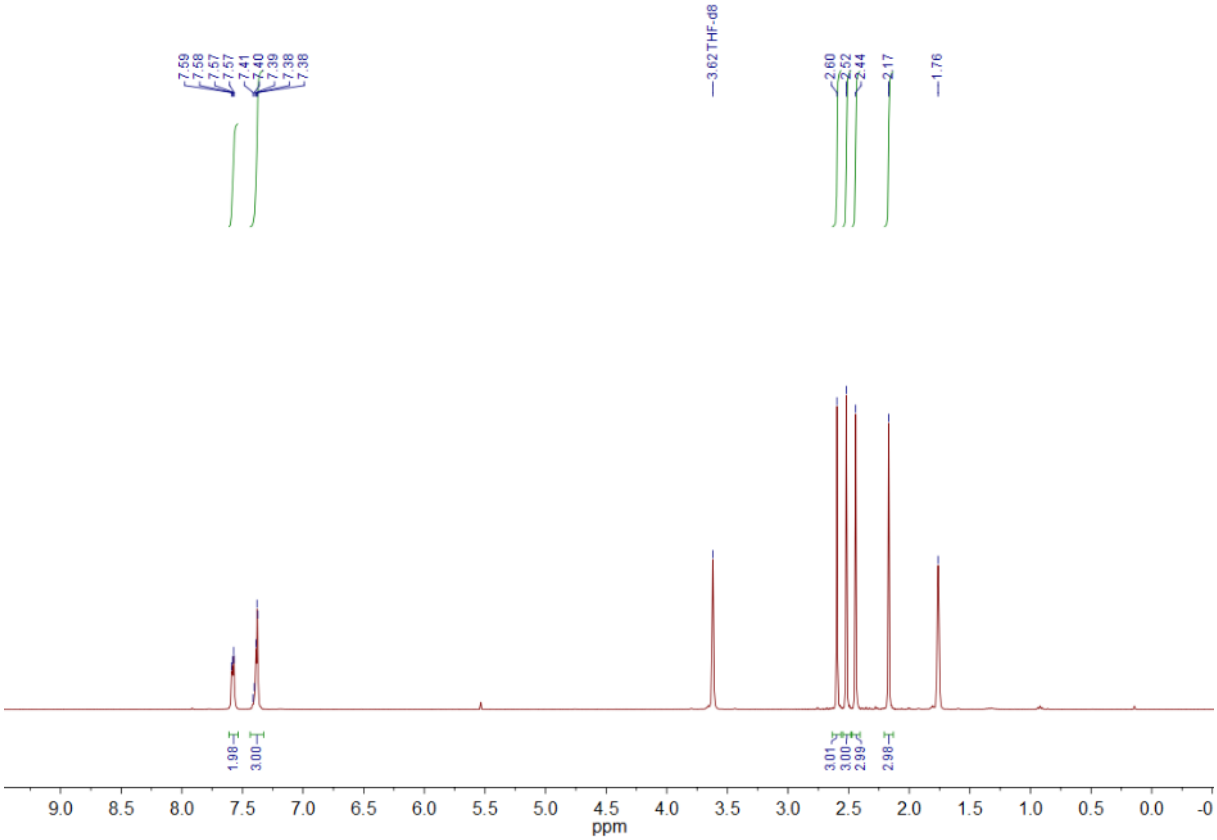


Figure S22. Expansion of ^{1}H NMR spectrum of **2•Cr(CO)$_3$** in THF-d_8 (aryl region).

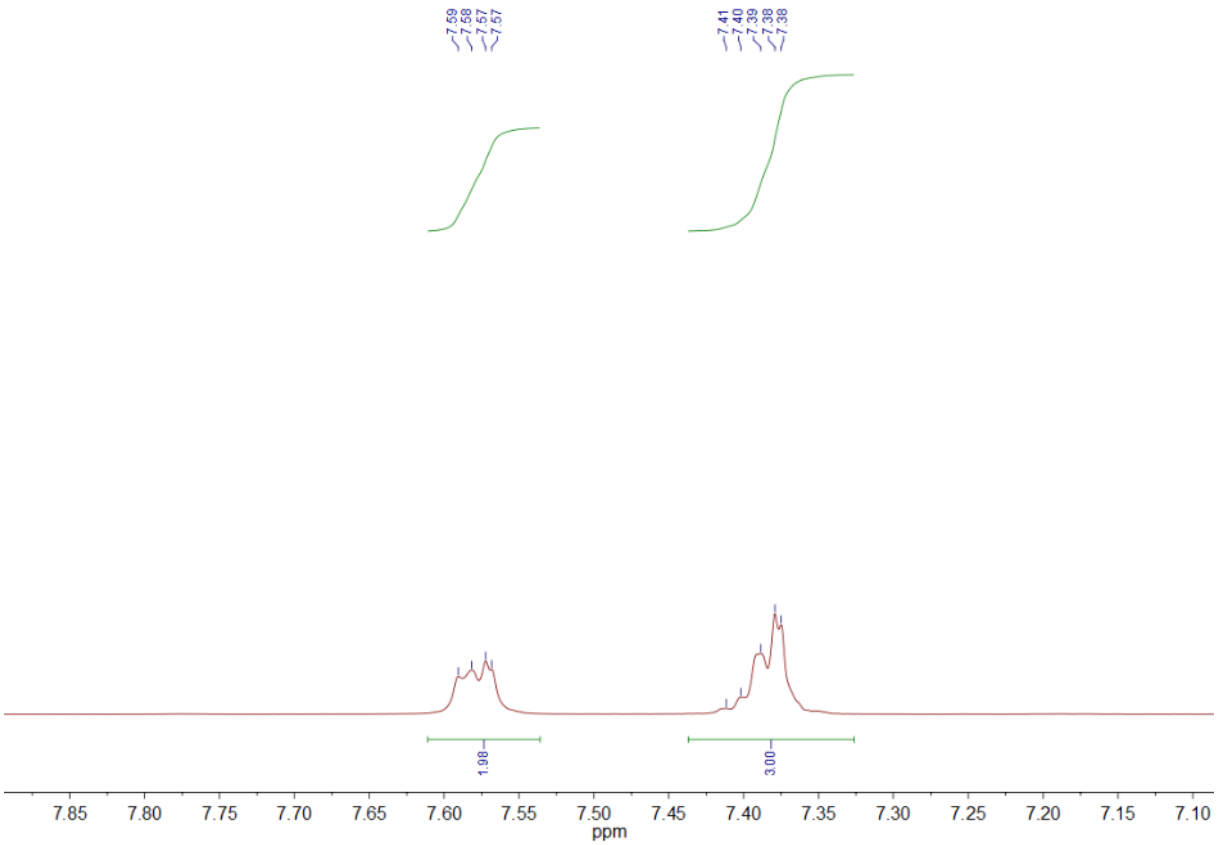


Figure S23. Expansion of ^{1}H NMR spectrum of **2•Cr(CO)$_3$** in THF-d_8 (aliphatic region).

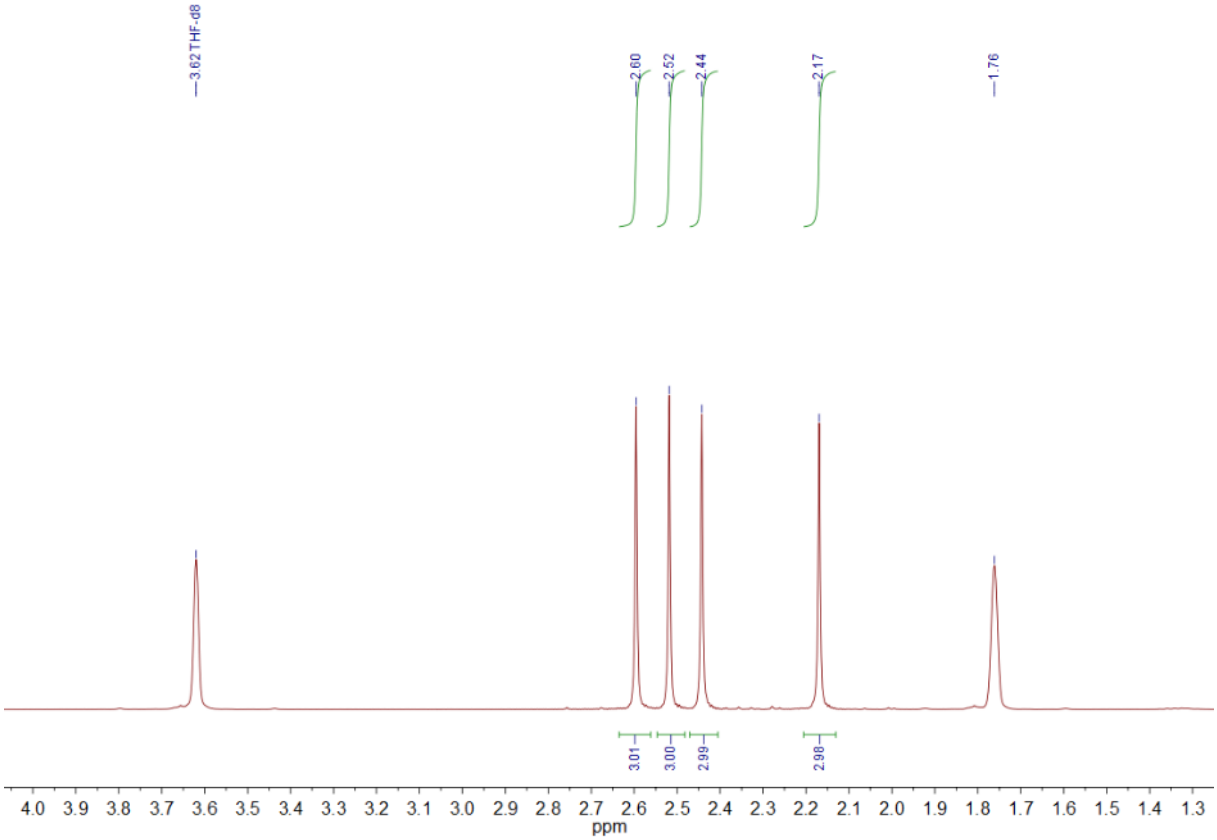


Figure S24. ^{13}C{^{1}H} NMR Spectrum of **2•Cr(CO)$_3$** in THF-d_8.

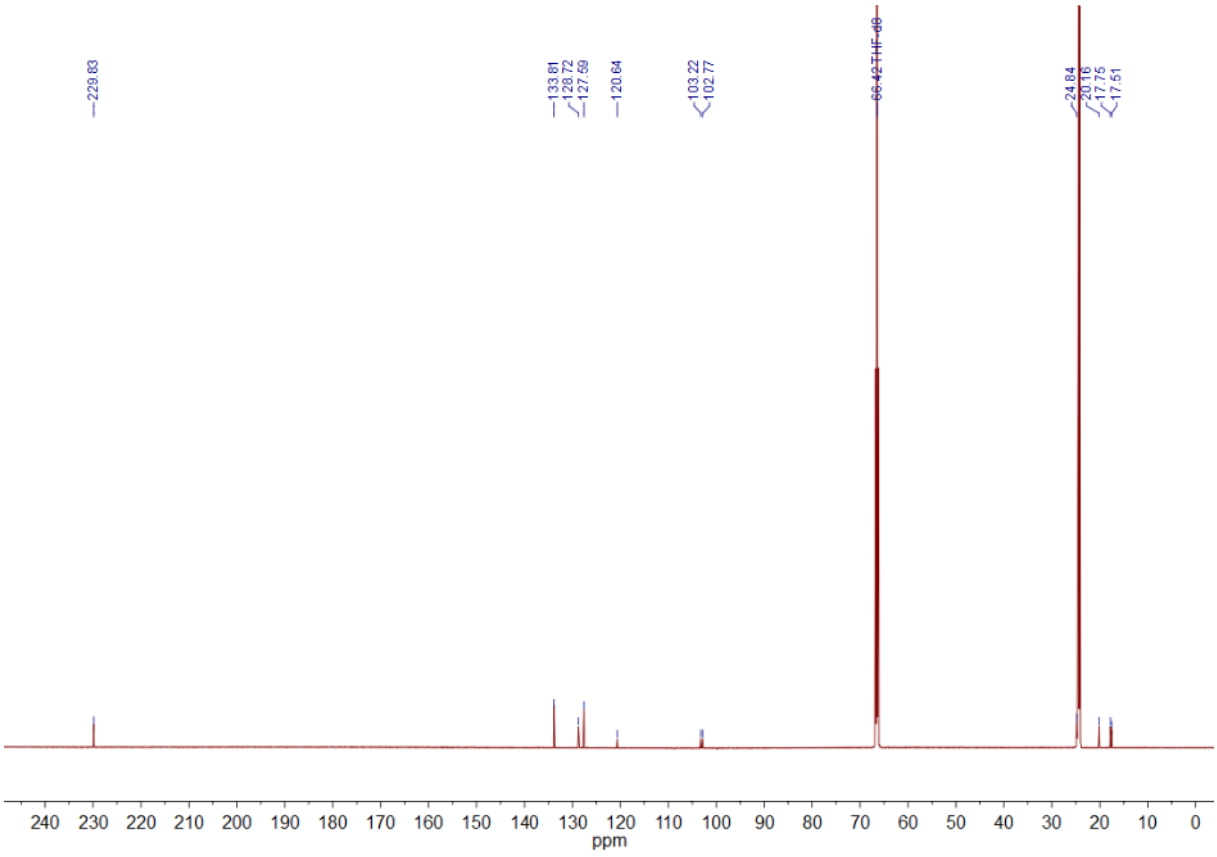


Figure S25. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **2•Cr(CO)$_3$** in THF-d_8 (aryl region).

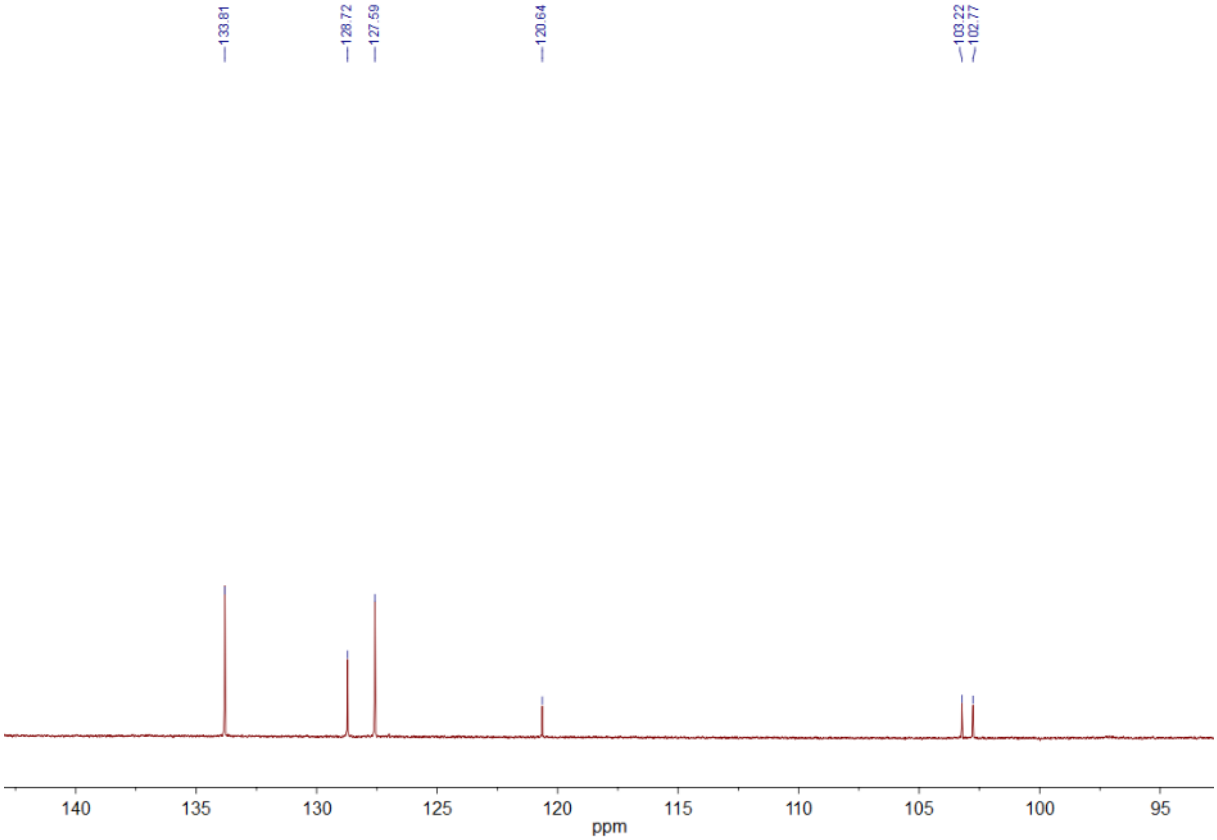


Figure S26. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **2•Cr(CO)$_3$** in THF-d_8 (aliphatic region).

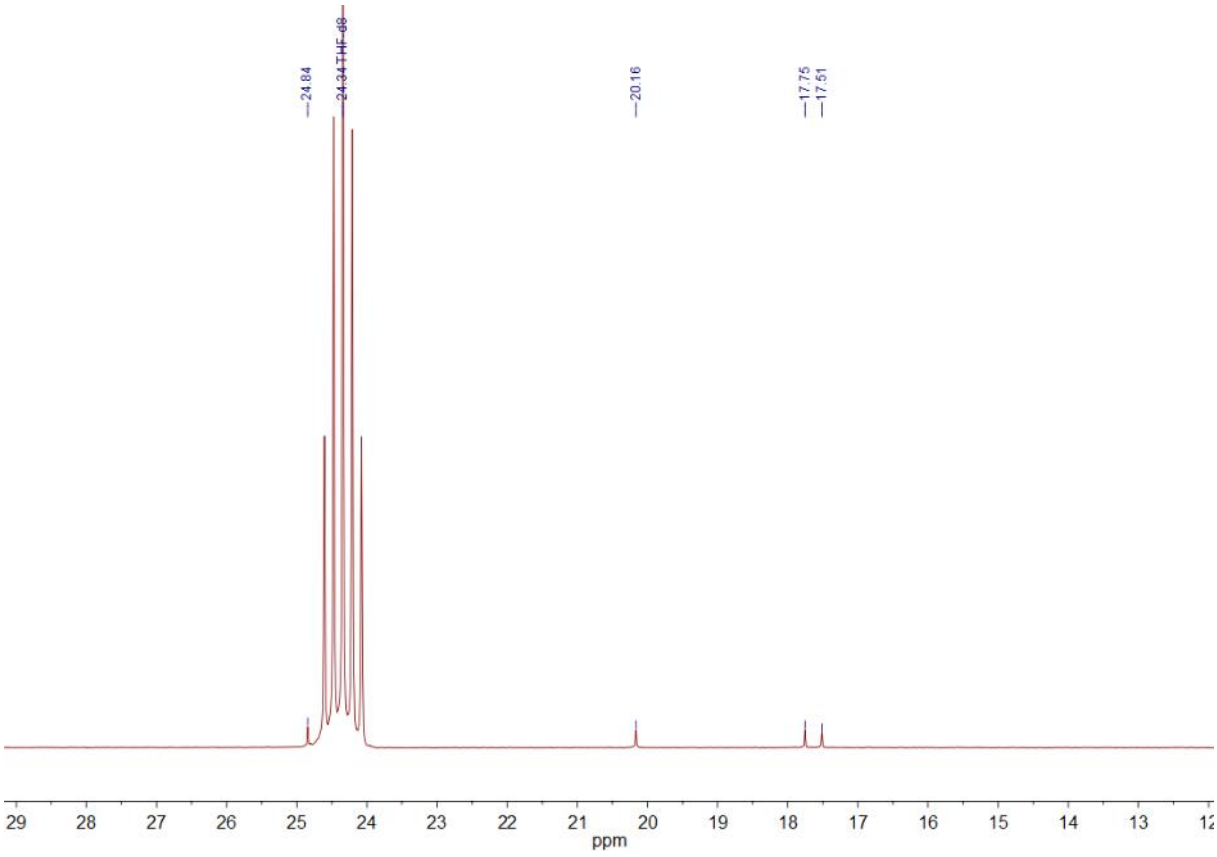


Figure S27. ^{13}C DEPT135 NMR Spectrum of **2•Cr(CO)$_3$** in THF-*d*$_8$.

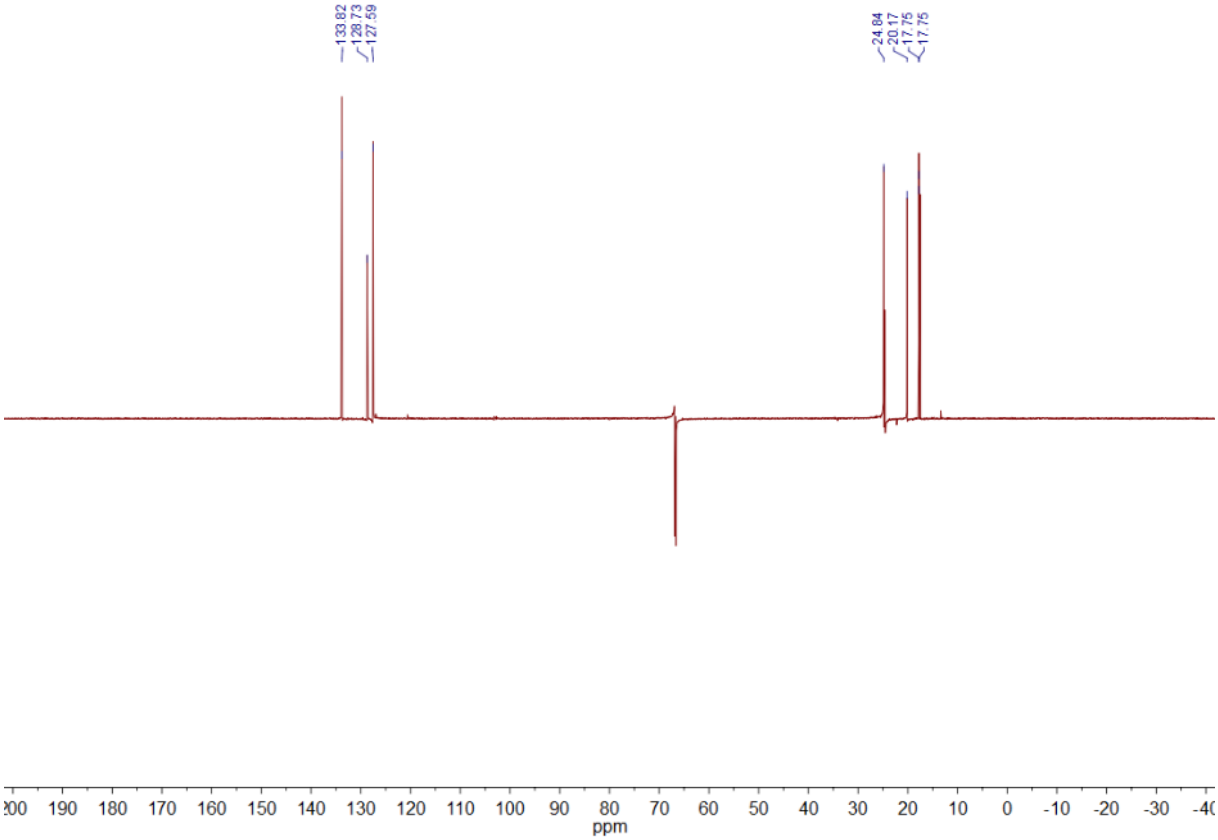


Figure S28. ^{11}B NMR Spectrum of **2•Cr(CO)$_3$** in THF-*d*$_8$.

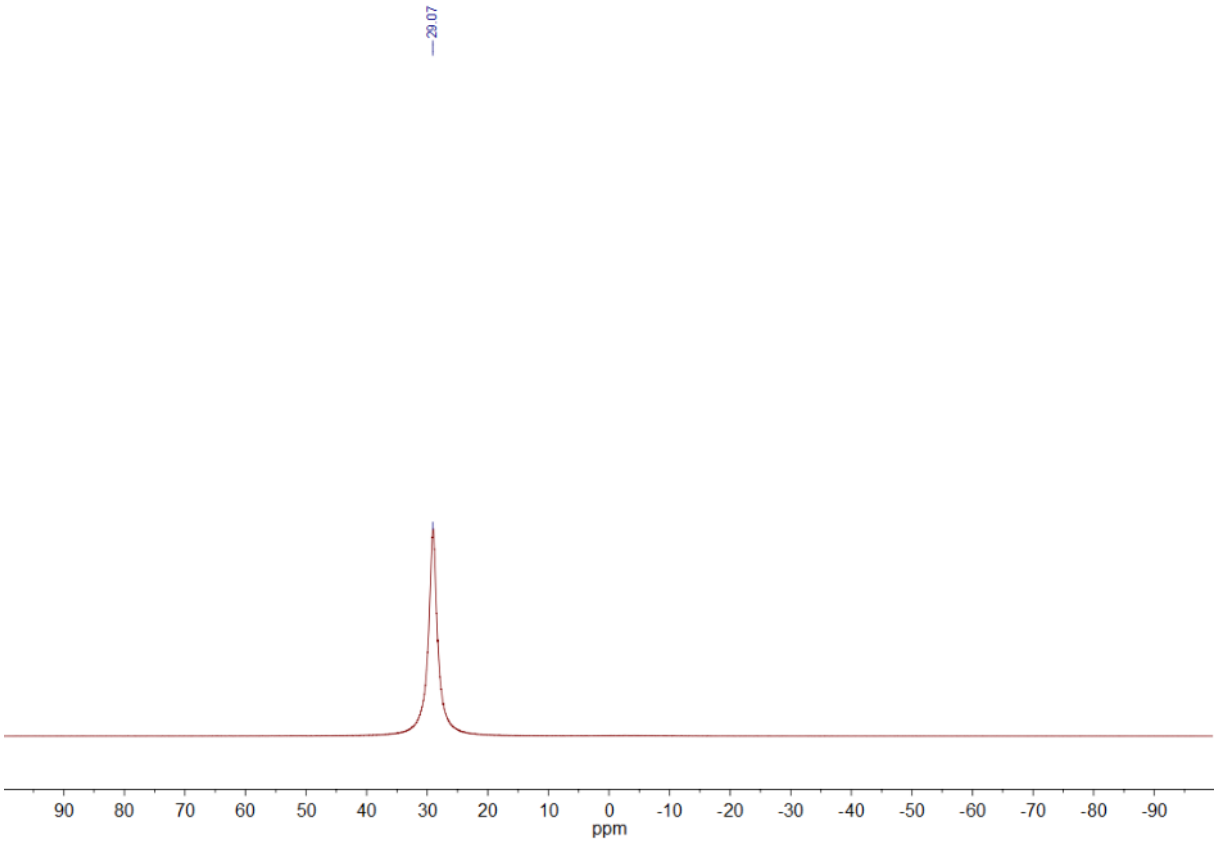


Figure S29. FT-IR Spectrum of **2•Cr(CO)$_3$**.

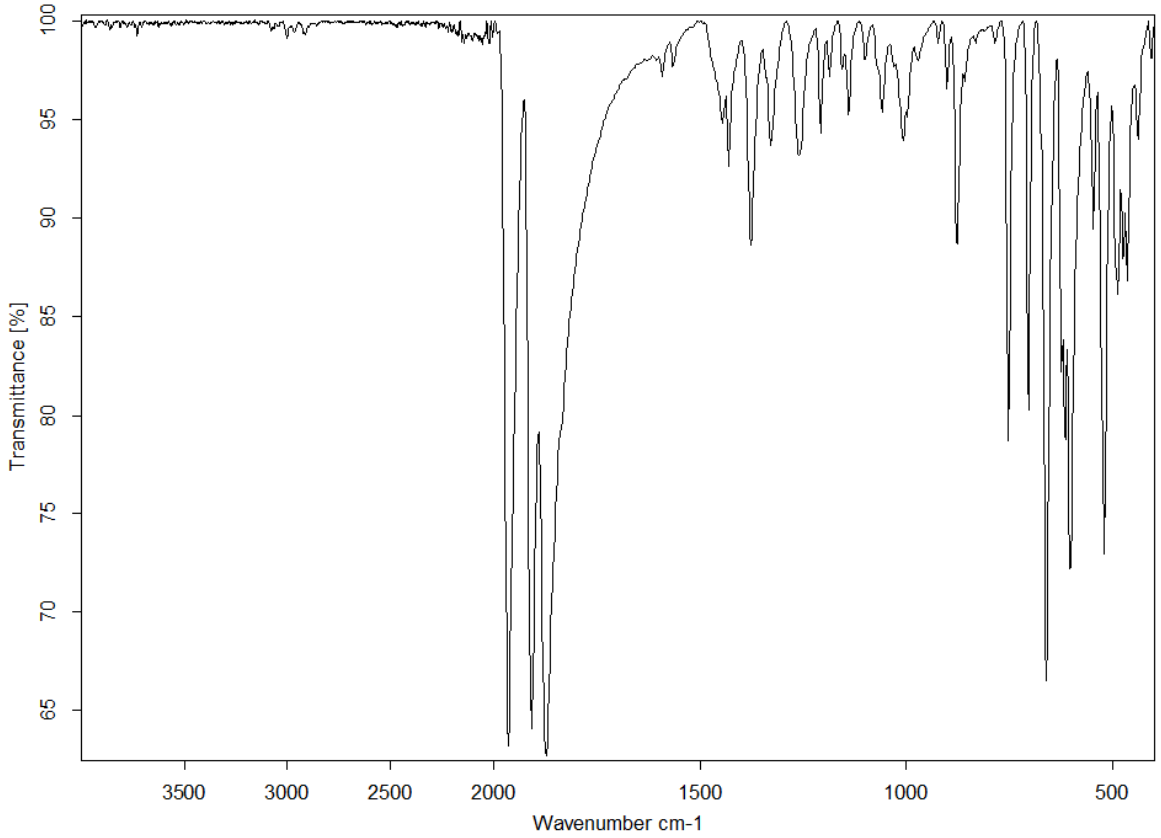


Figure S30. High Resolution Mass Spectrum (CI+) of **2•Cr(CO)$_3$**.

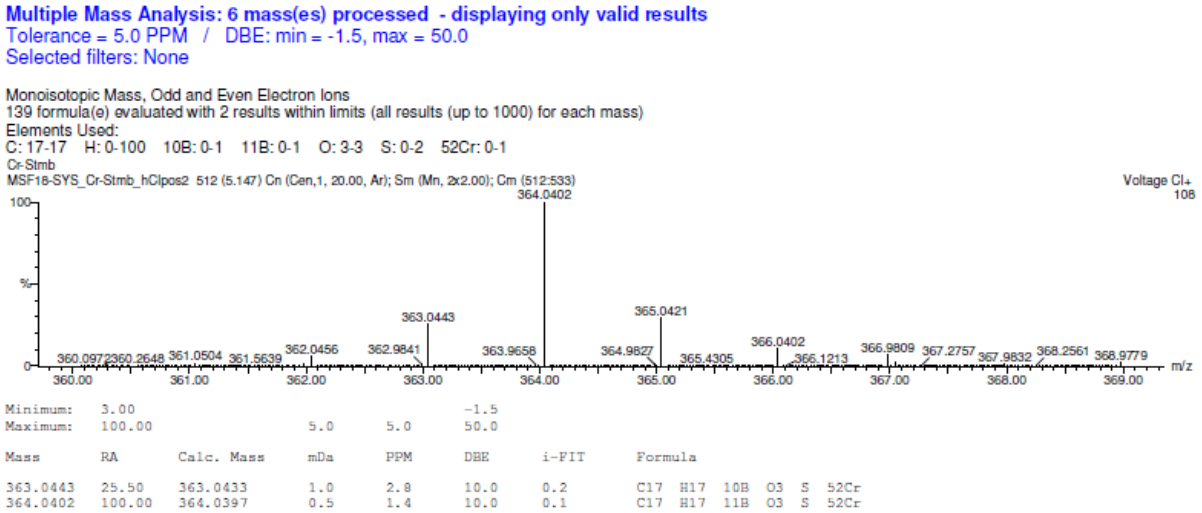


Figure S31. $_1$H NMR spectrum of **3** in $CDCl_3$ at -40 °C.

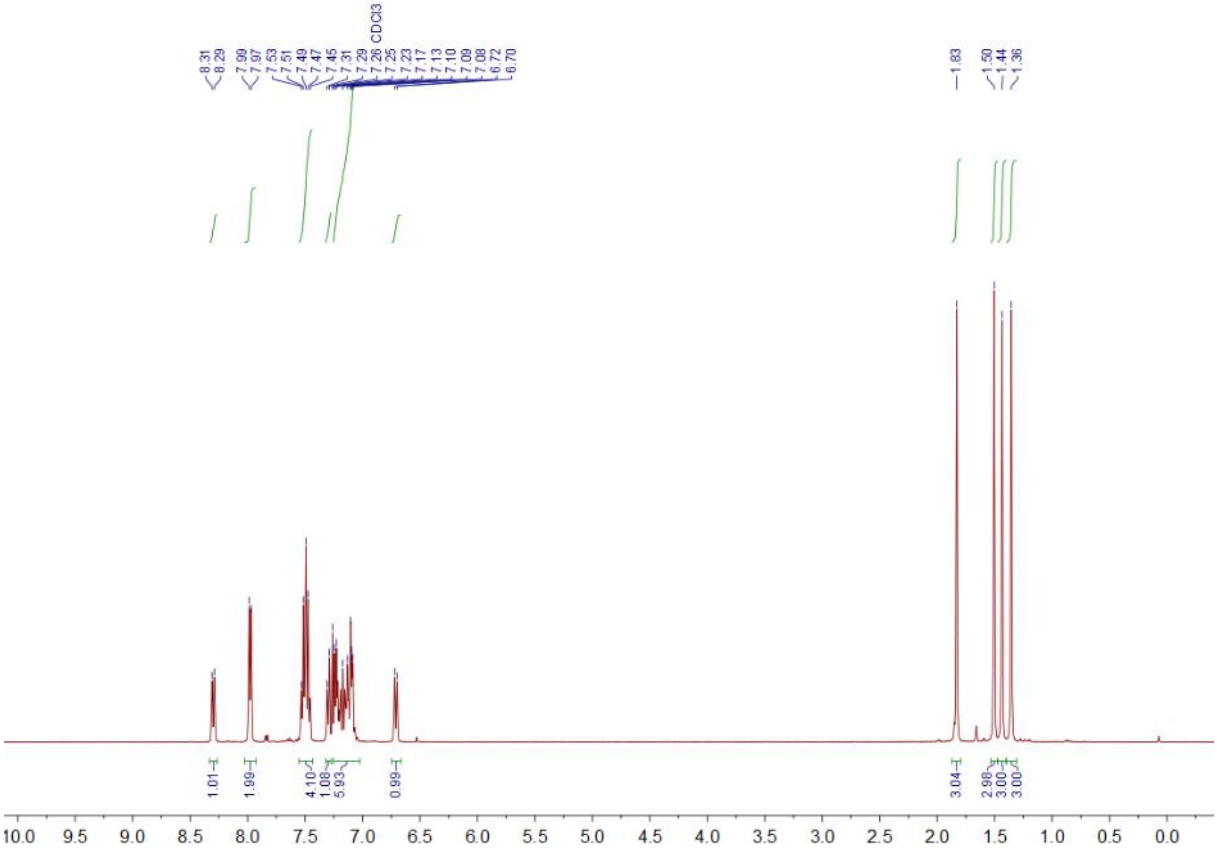


Figure S32. Expansion of $_1$H NMR spectrum of **3** in $CDCl_3$ at -40 °C (aryl region).

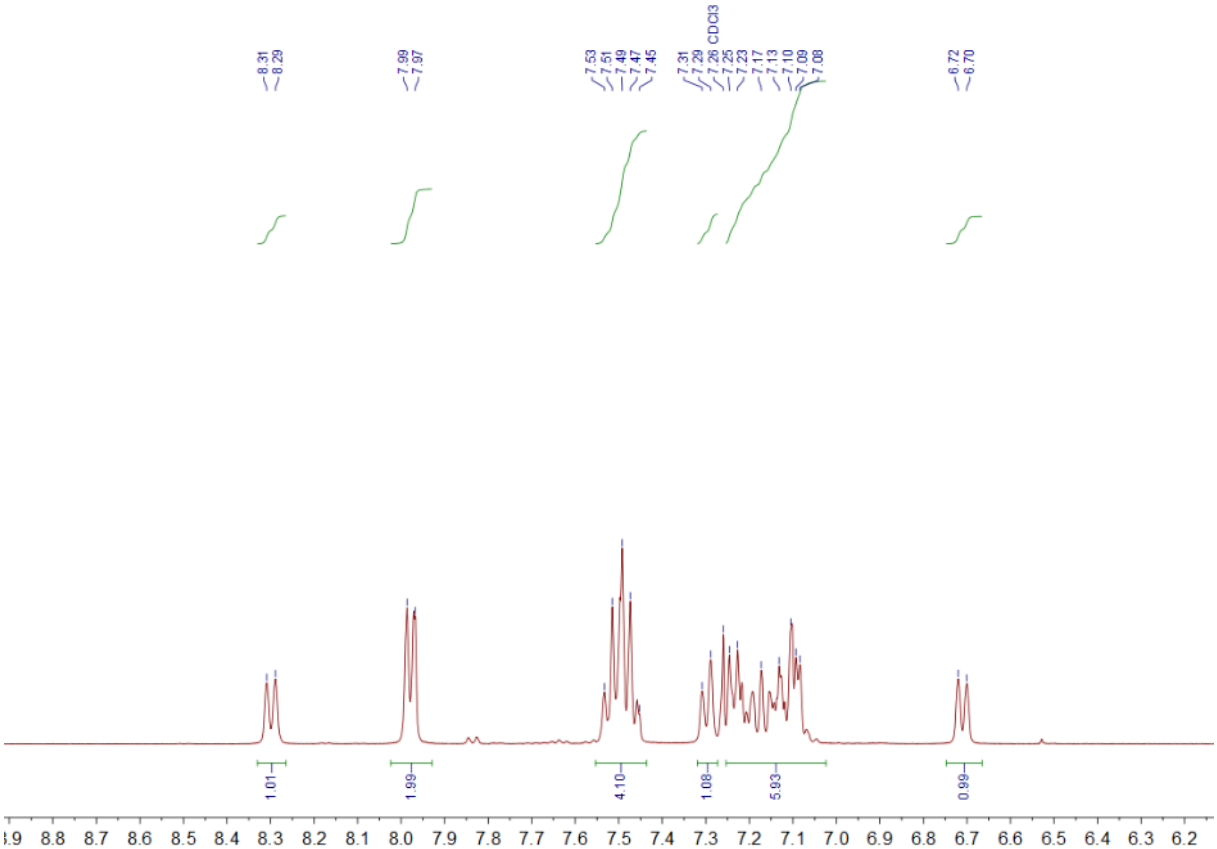


Figure S33. Expansion of ^{1}H NMR spectrum of **3** in $CDCl_3$ at -40 °C (aliphatic region).

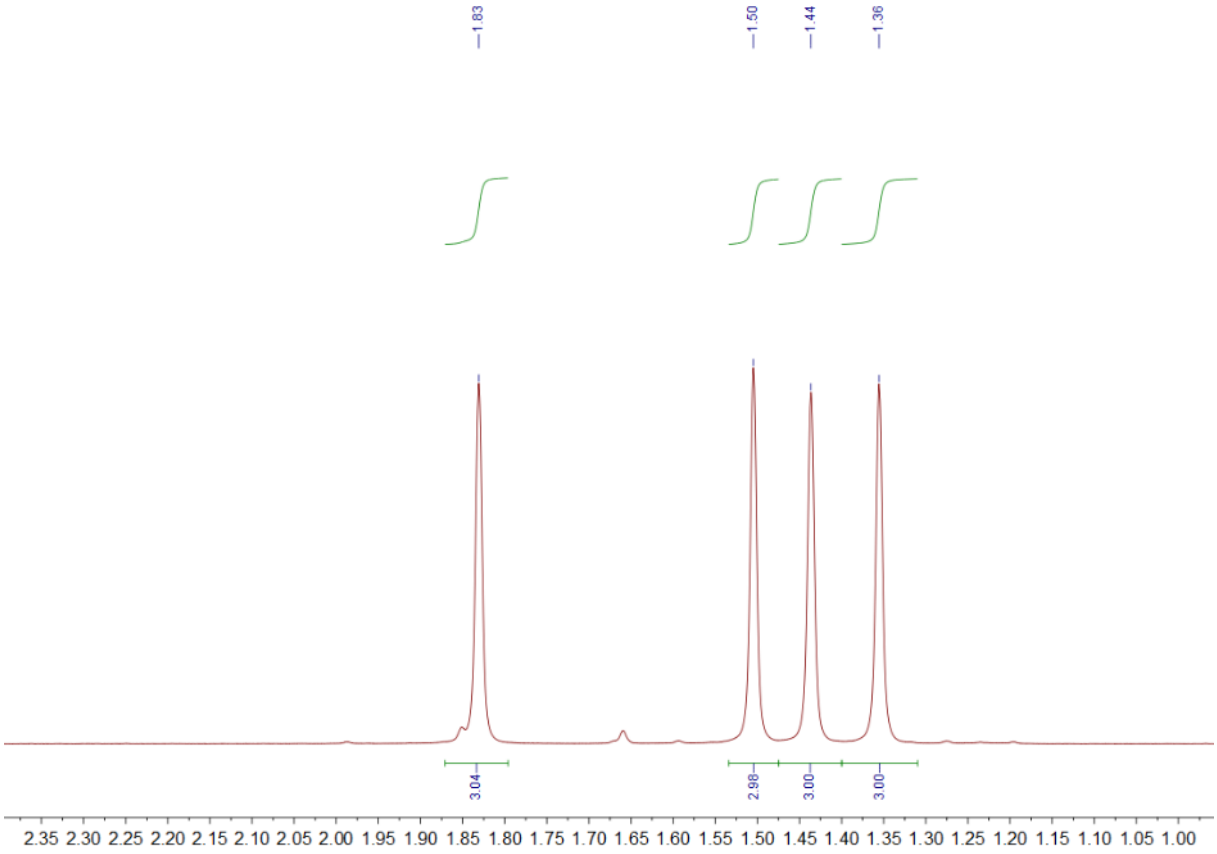


Figure S34. $^{13}C\{^{1}H\}$ NMR Spectrum of **3** in $CDCl_3$.

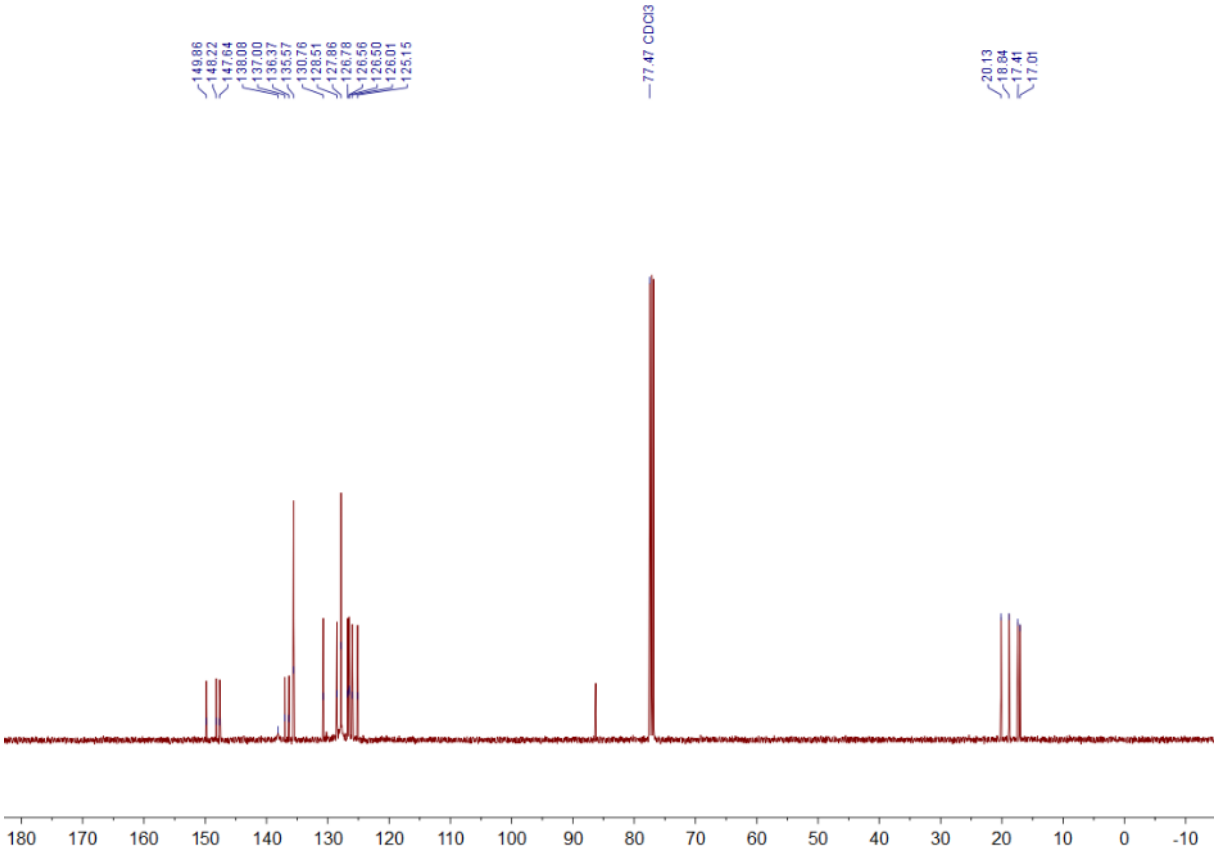


Figure S35. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **3** in $CDCl_3$ (aryl region).

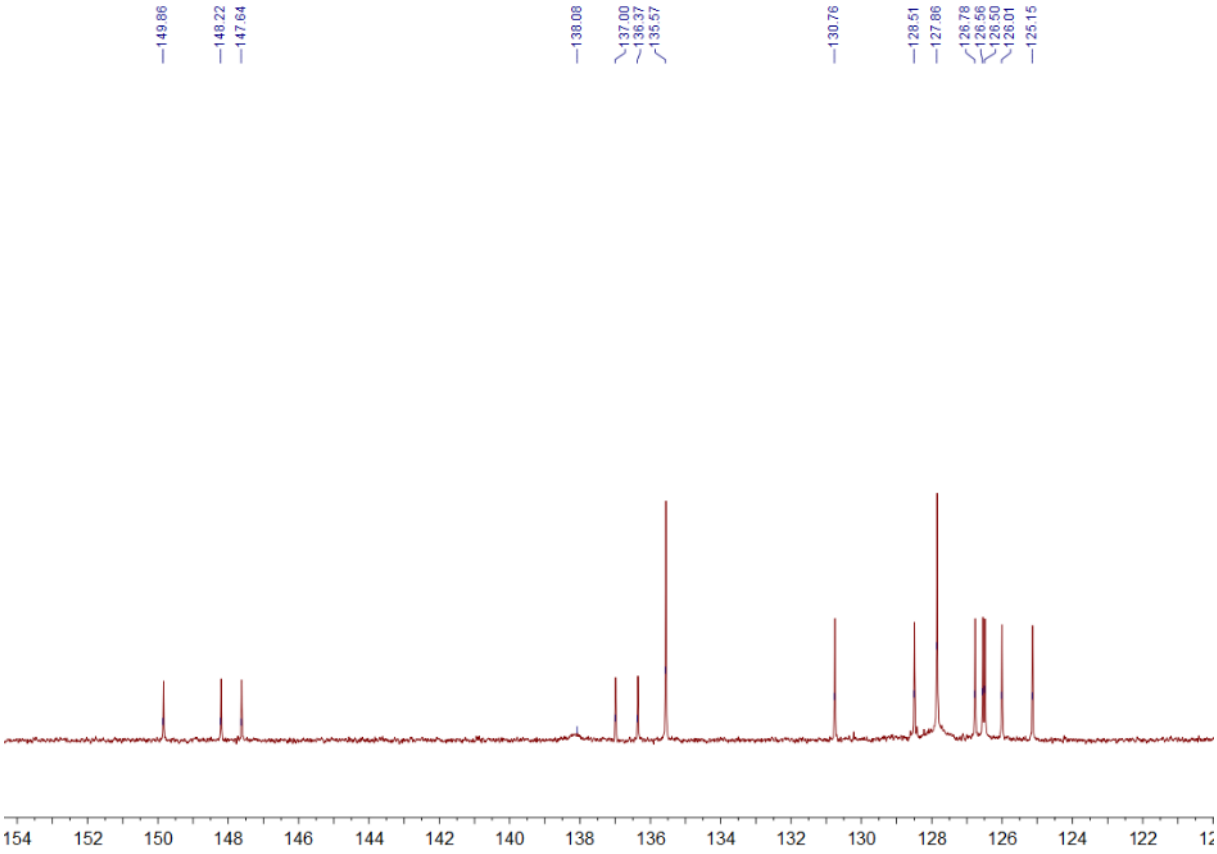


Figure S36. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **3** in $CDCl_3$ (aliphatic region).

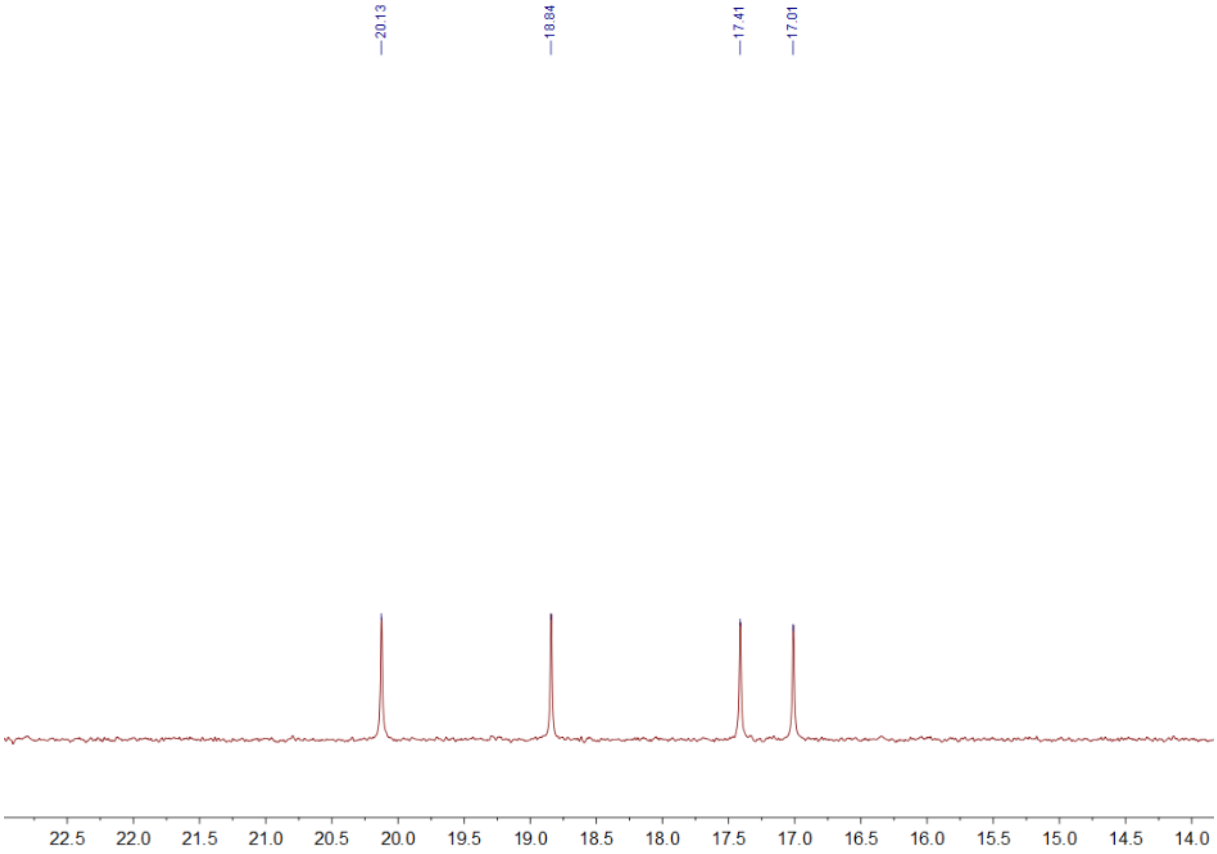


Figure S37. ^{13}C DEPT135 NMR Spectrum of **3** in $CDCl_3$.

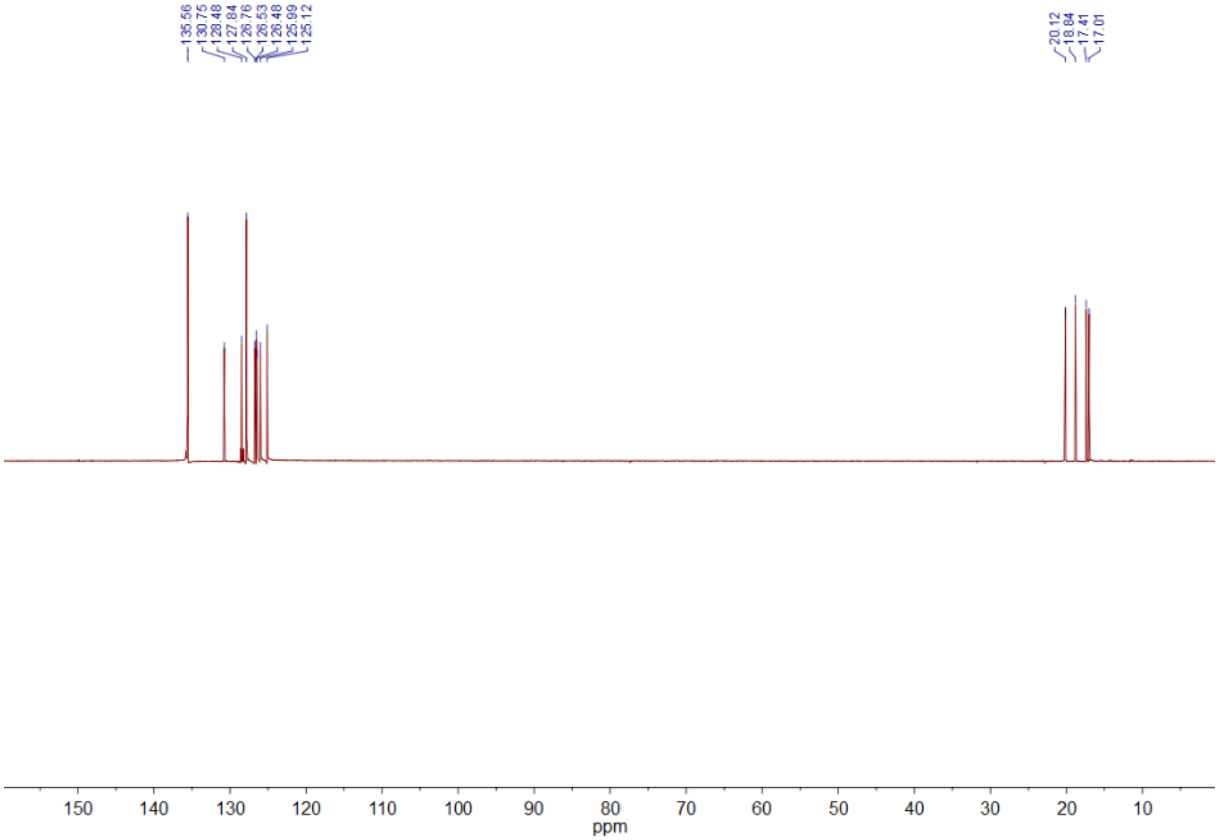


Figure S38. ^{11}B NMR Spectrum of **3** in $CDCl_3$.

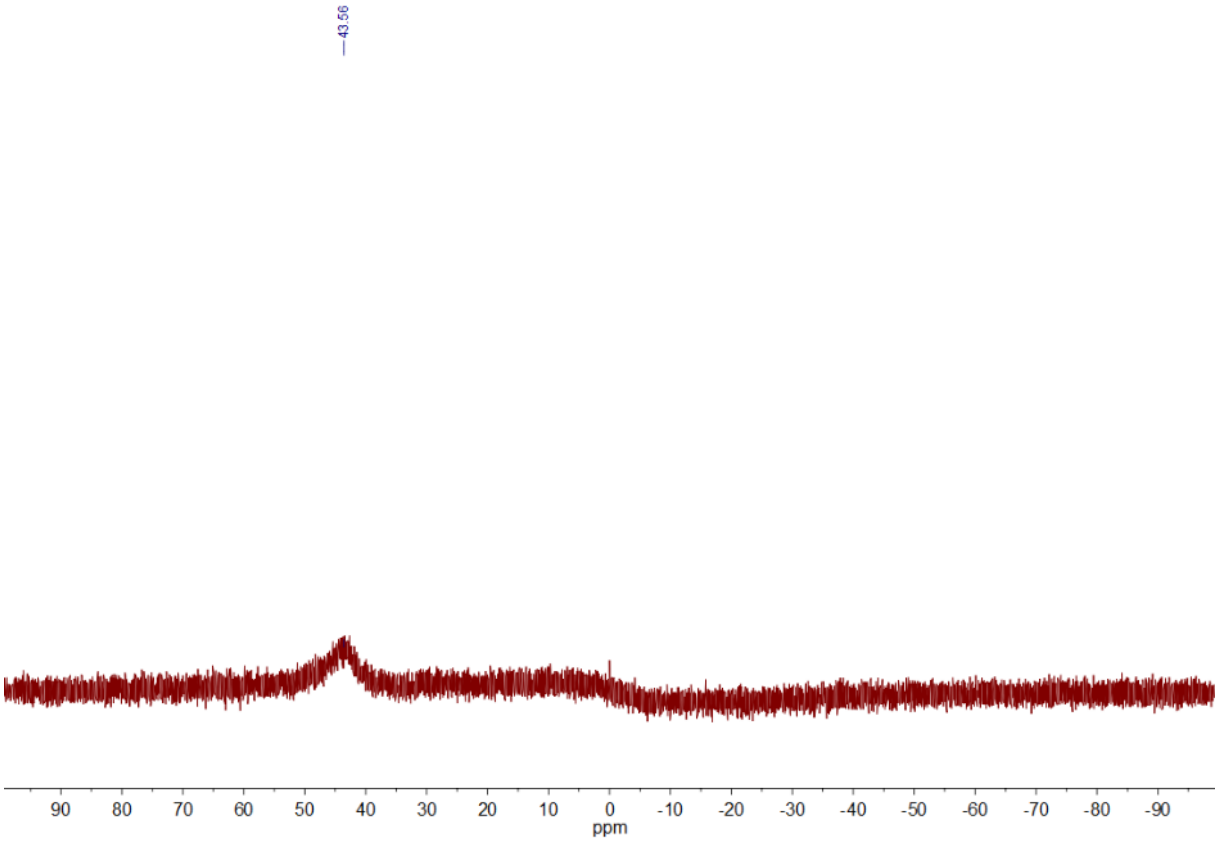


Figure S39. FT-IR Spectrum of **3**.

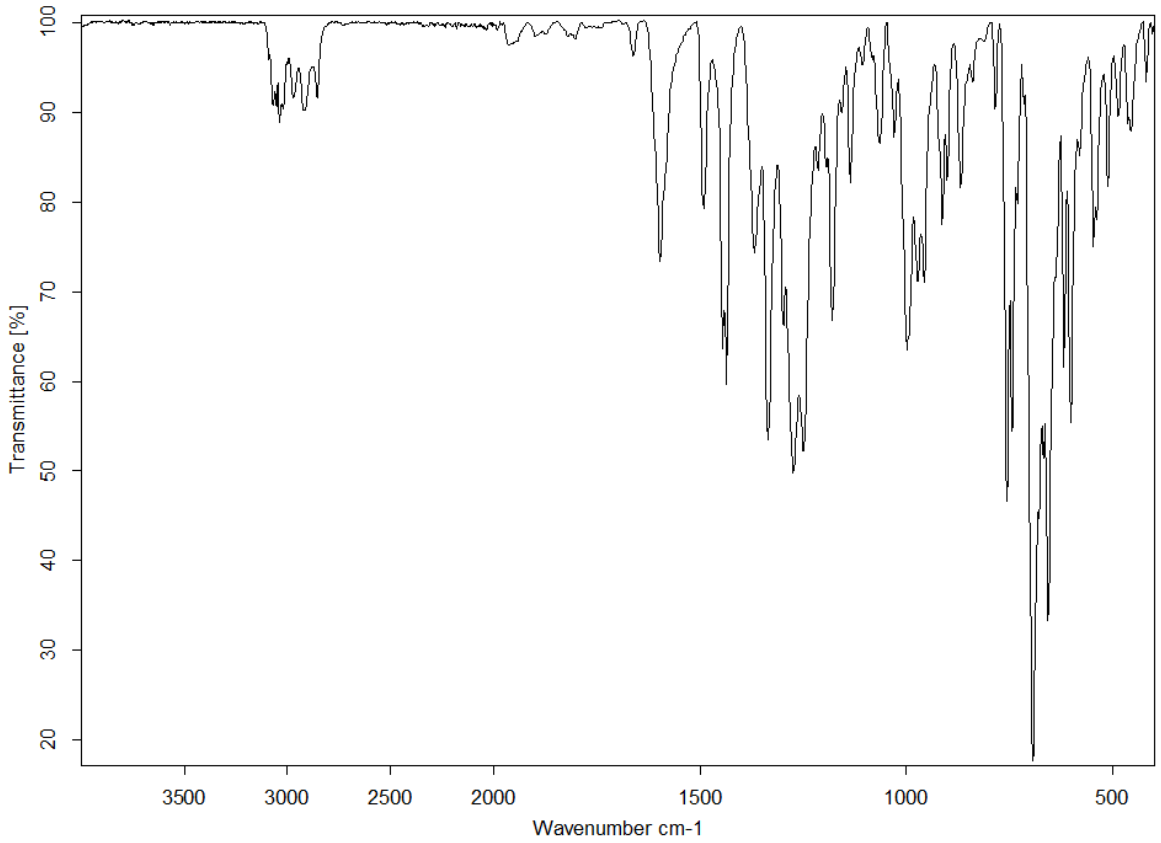


Figure S40. High Resolution Mass Spectrum (CI+) of **3**.

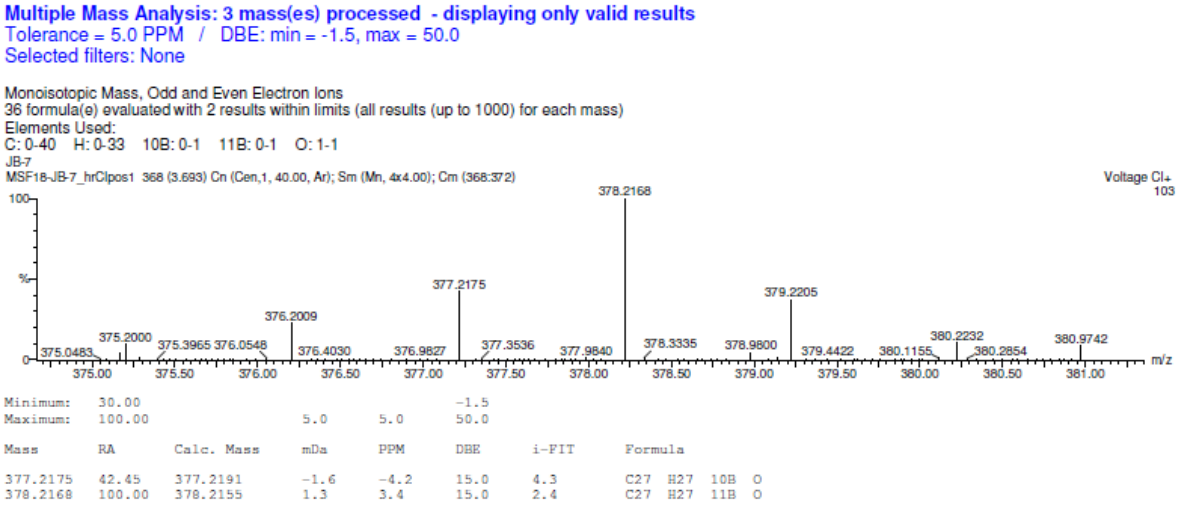


Figure S41. $_1$H NMR spectrum of **4** in $CDCl_3$.

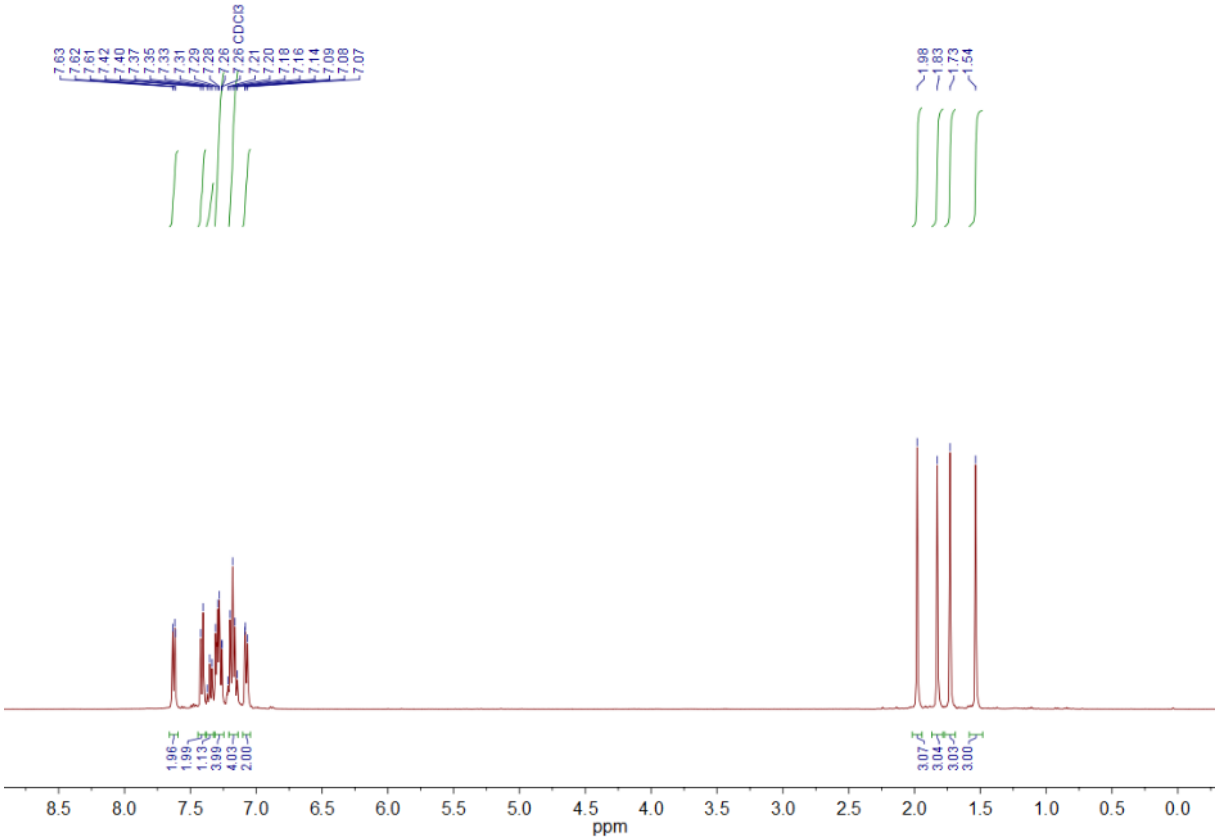


Figure S42. Expansion of $_1$H NMR spectrum of **4** in $CDCl_3$ (aryl region).

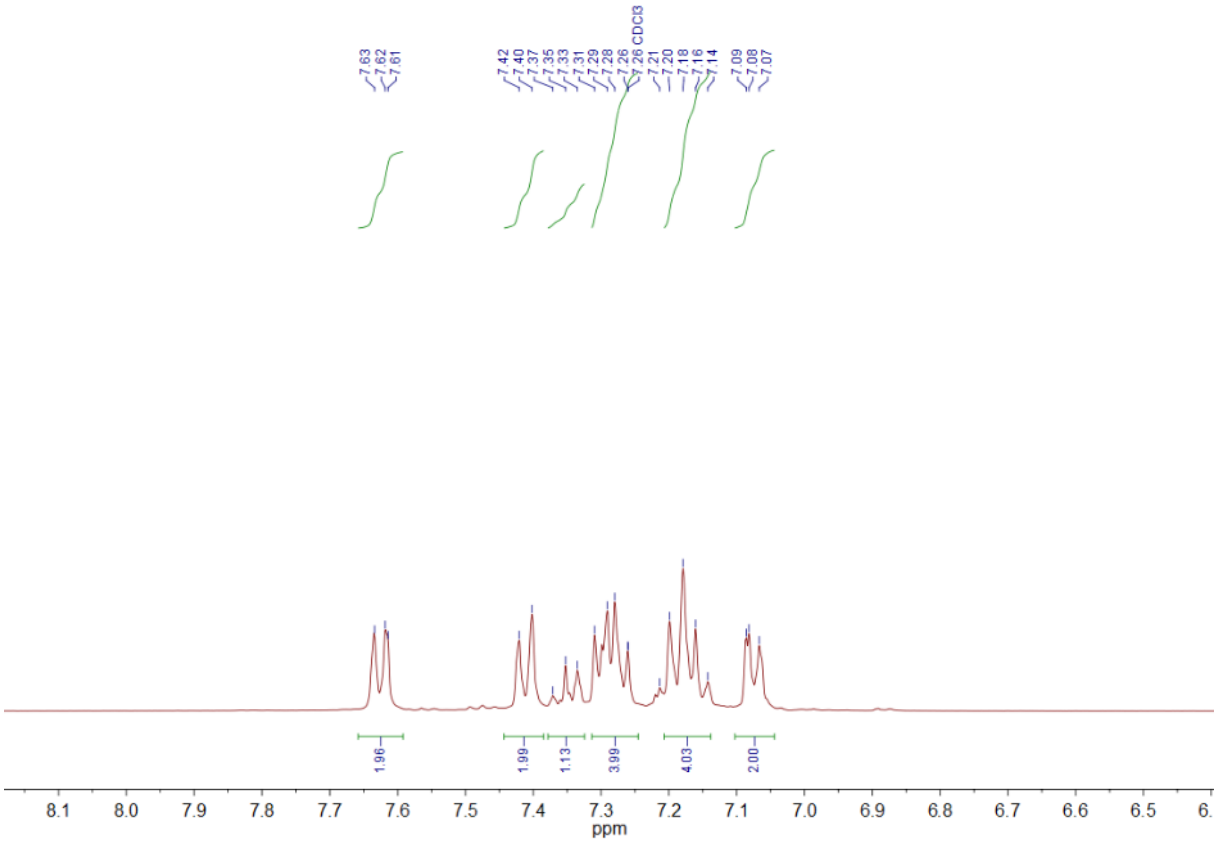


Figure S43. Expansion of $_{1}$H NMR spectrum of **4** in $CDCl_3$ (aliphatic region).

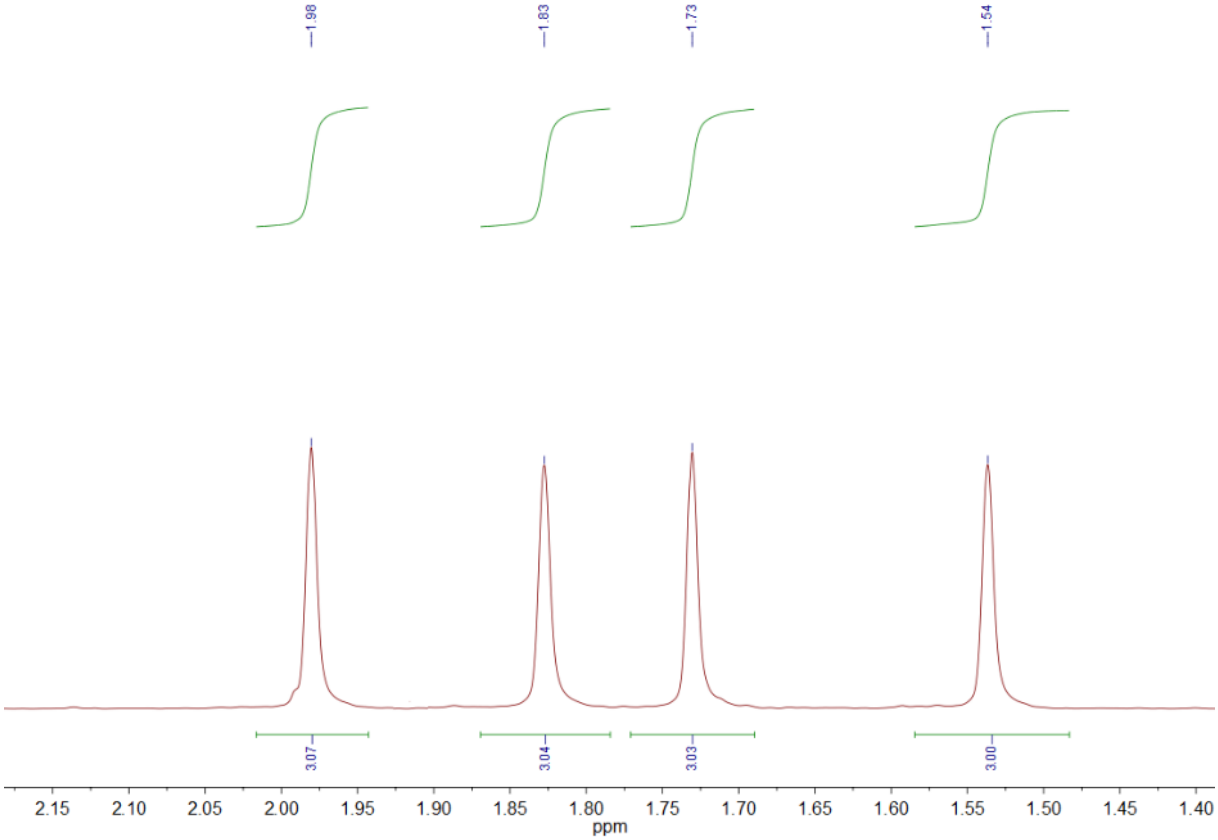


Figure S44. $_{13}$C{$_{1}$H} NMR Spectrum of **4** in $CDCl_3$.

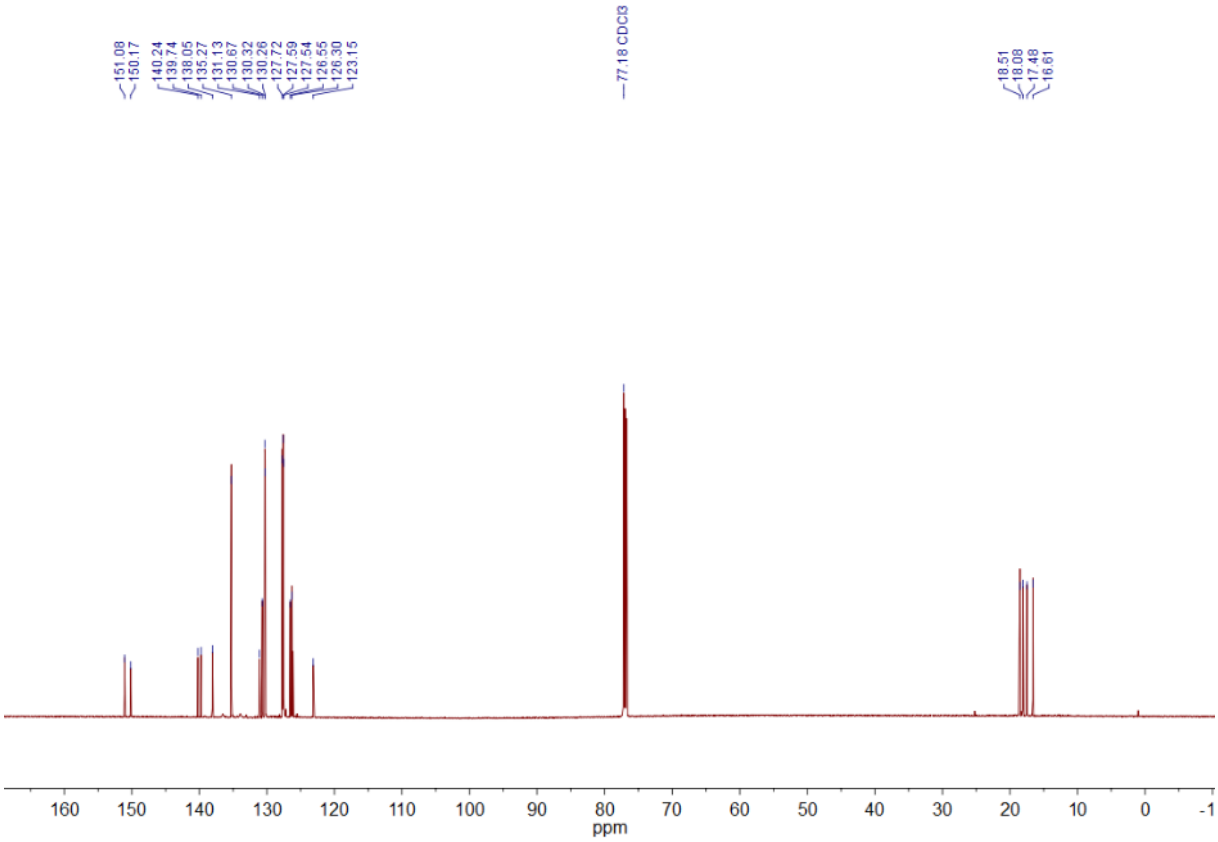


Figure S45. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **4** in $CDCl_3$ (aryl region).

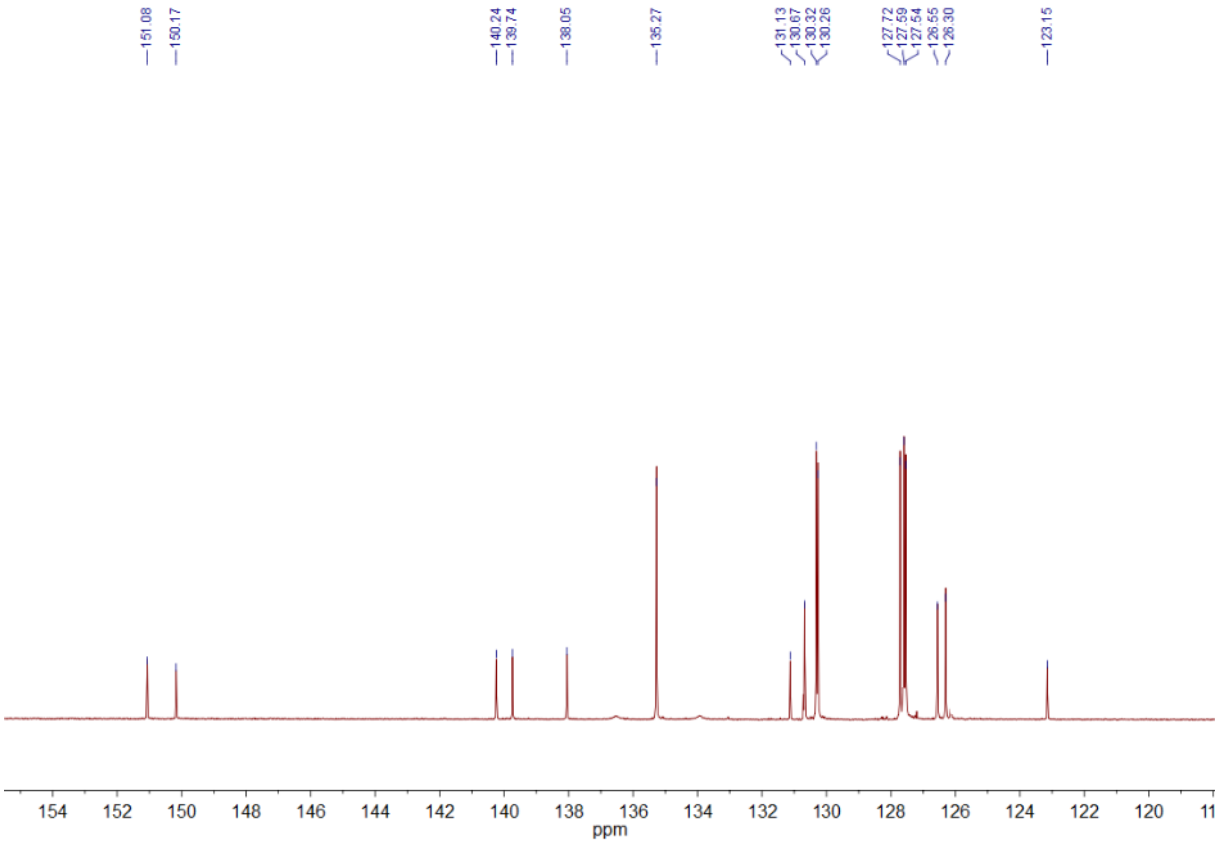


Figure S46. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **4** in $CDCl_3$ (aliphatic region).

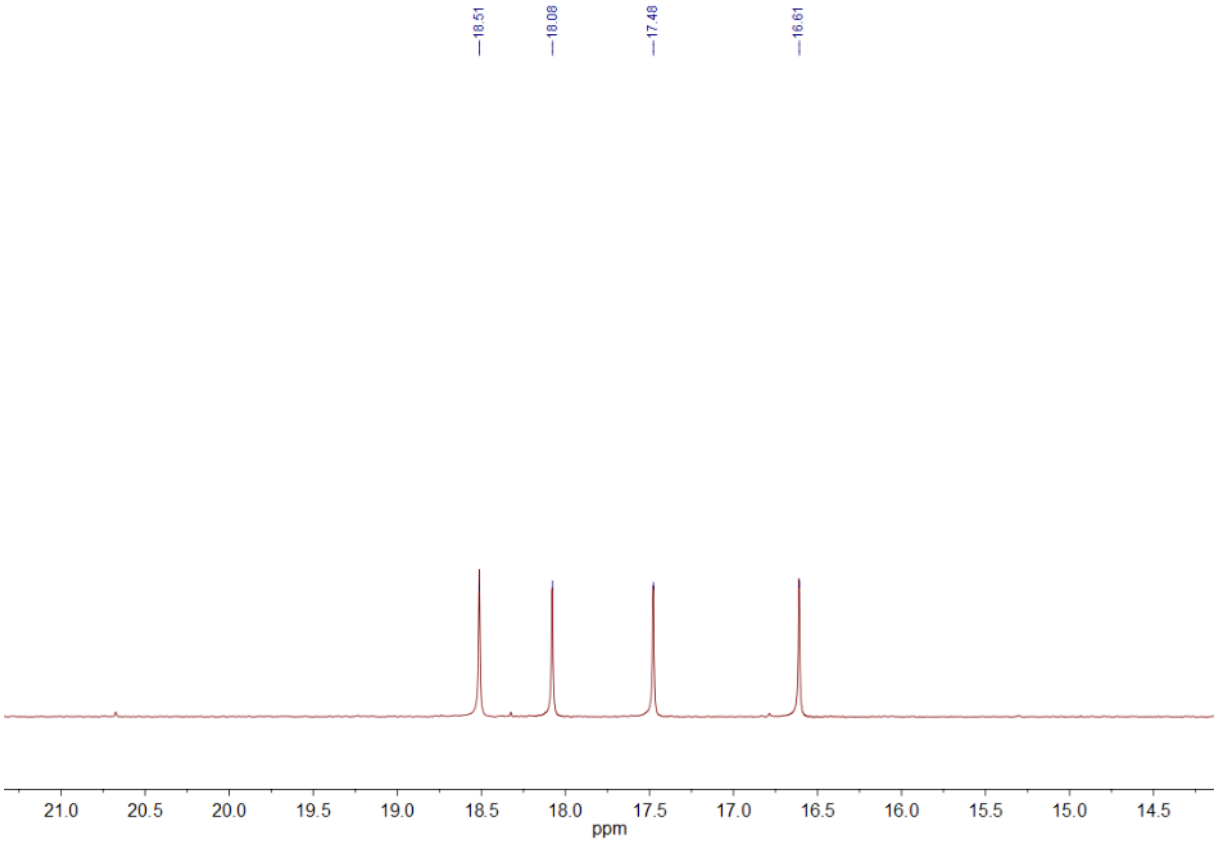


Figure S47. ^{13}C DEPT135 NMR Spectrum of **4** in $CDCl_3$.

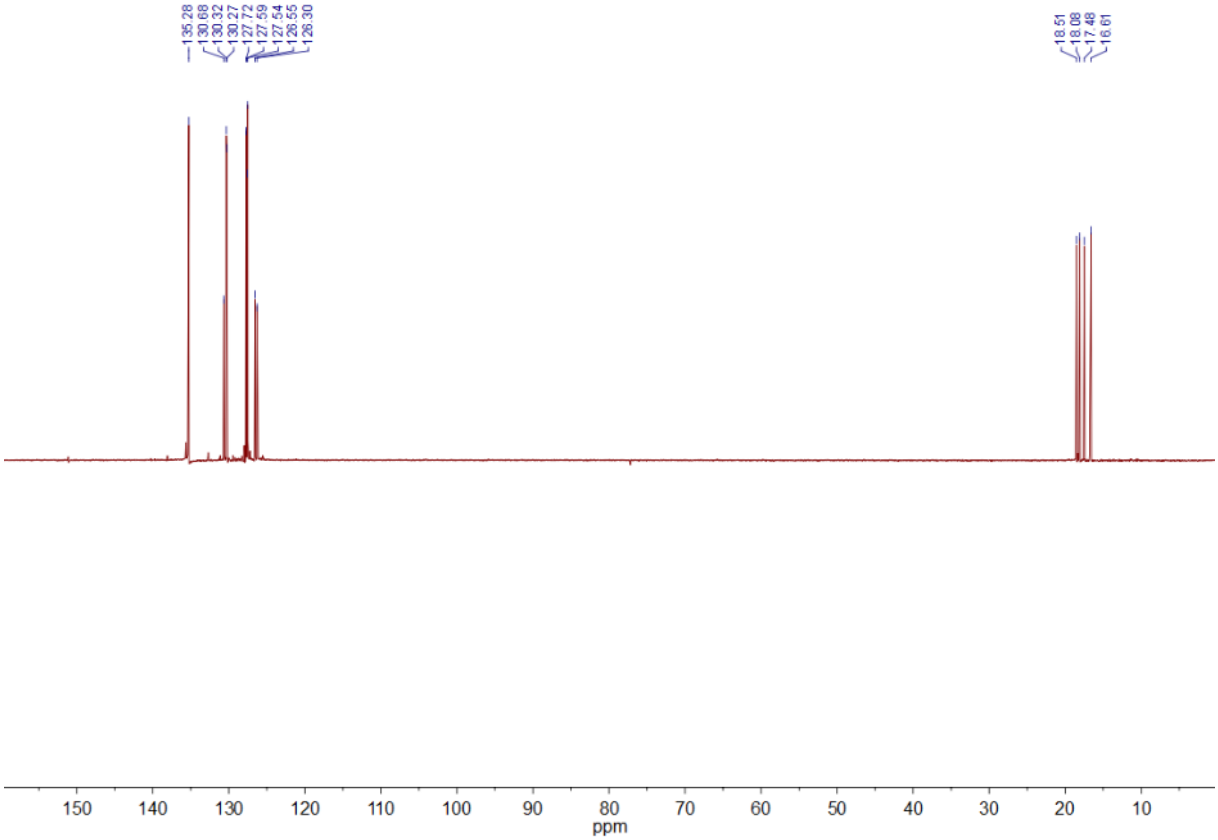


Figure S48. ^{11}B NMR Spectrum of **4** in $CDCl_3$.

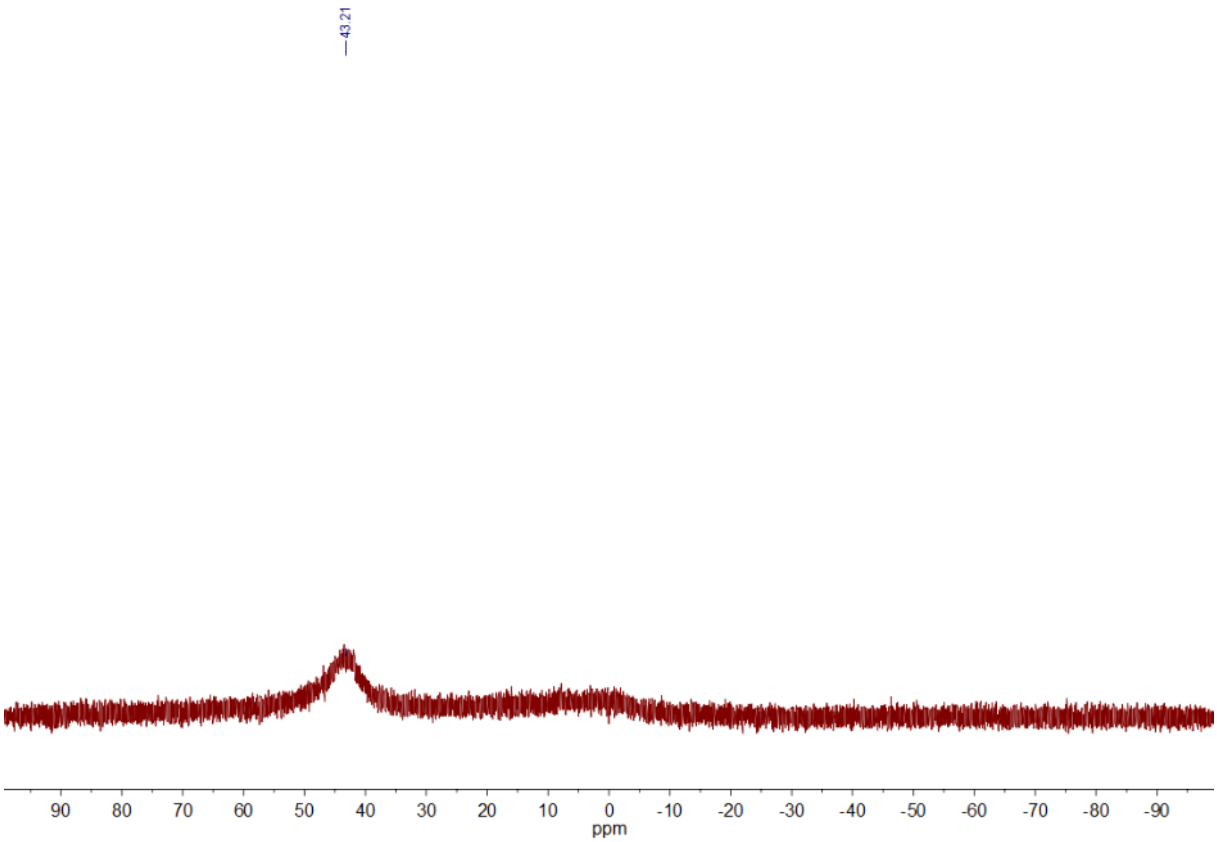


Figure S49. FT-IR Spectrum of **4**.

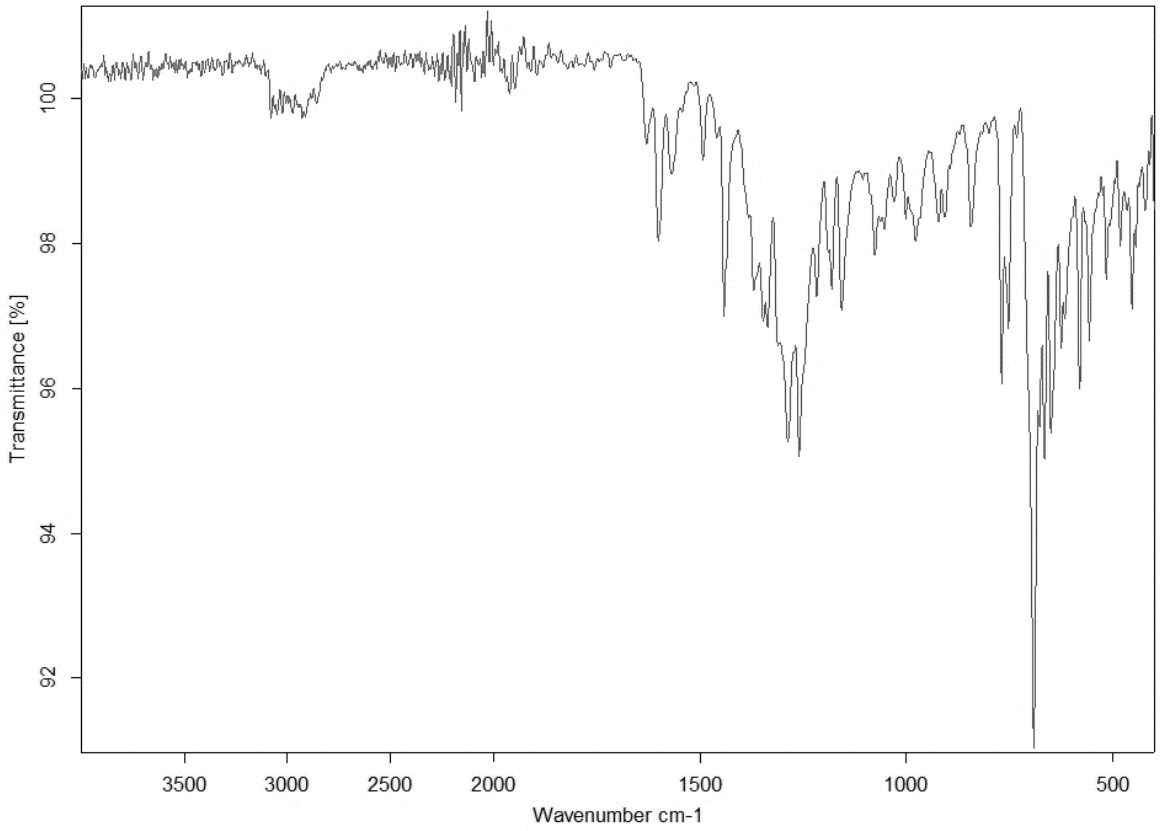


Figure S50. ^{1}H NMR spectrum of **5** in $CDCl_3$.

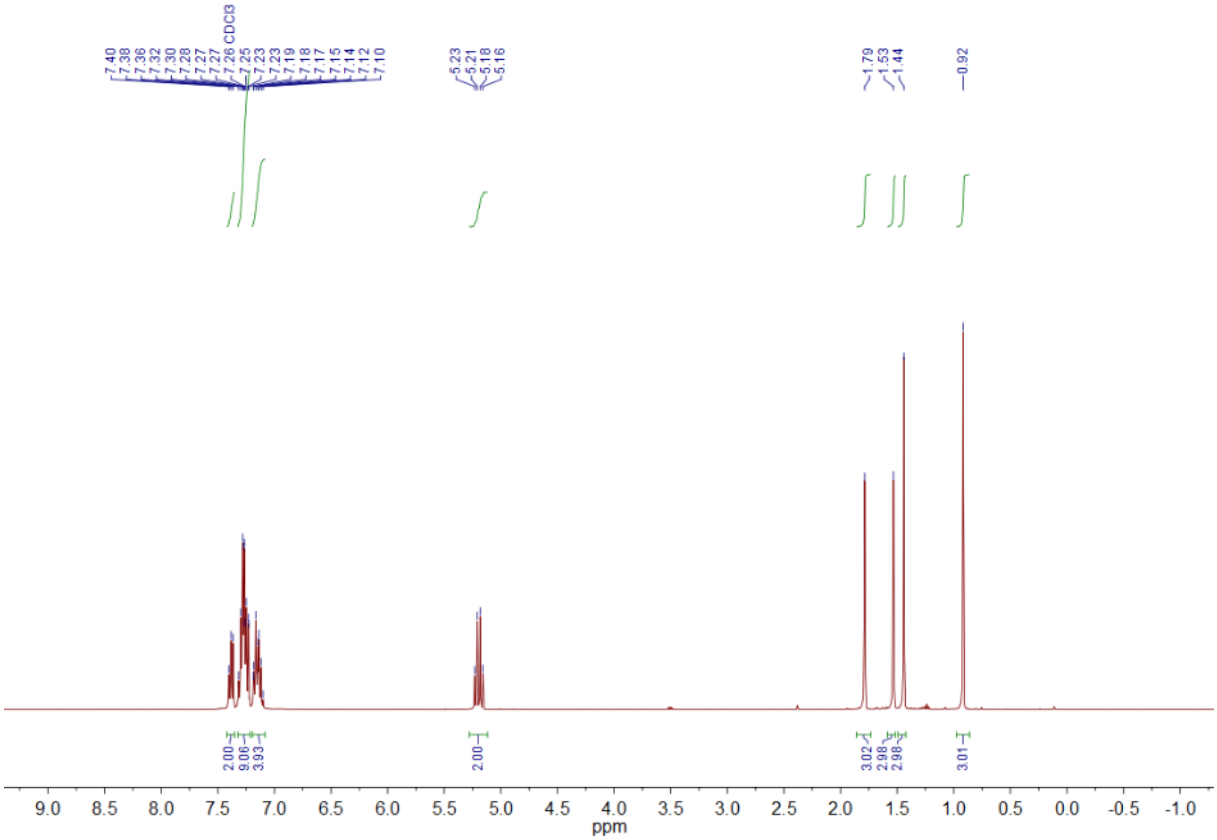


Figure S51. Expansion of ^{1}H NMR spectrum of **5** in $CDCl_3$ (aryl region).

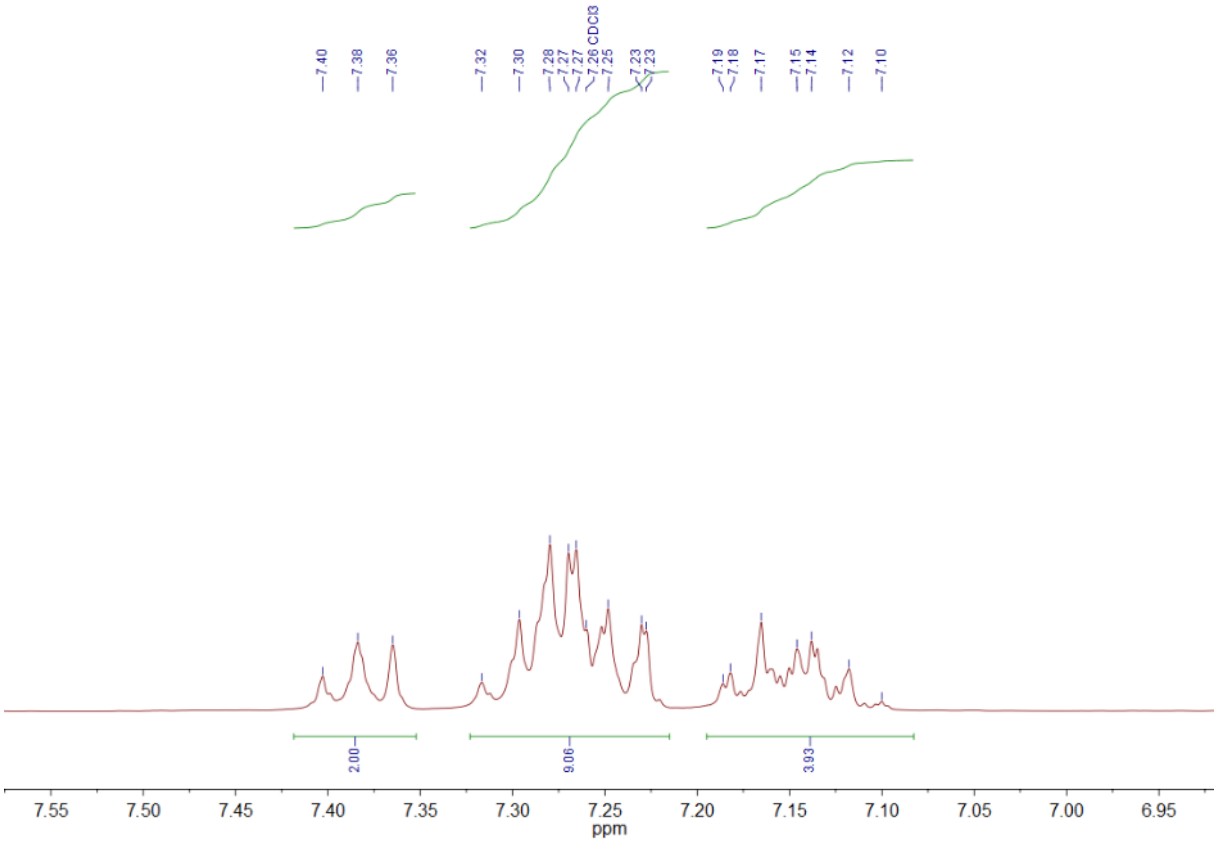


Figure S52. Expansion of ^{1}H NMR spectrum of **5** in $CDCl_3$ (aliphatic region).

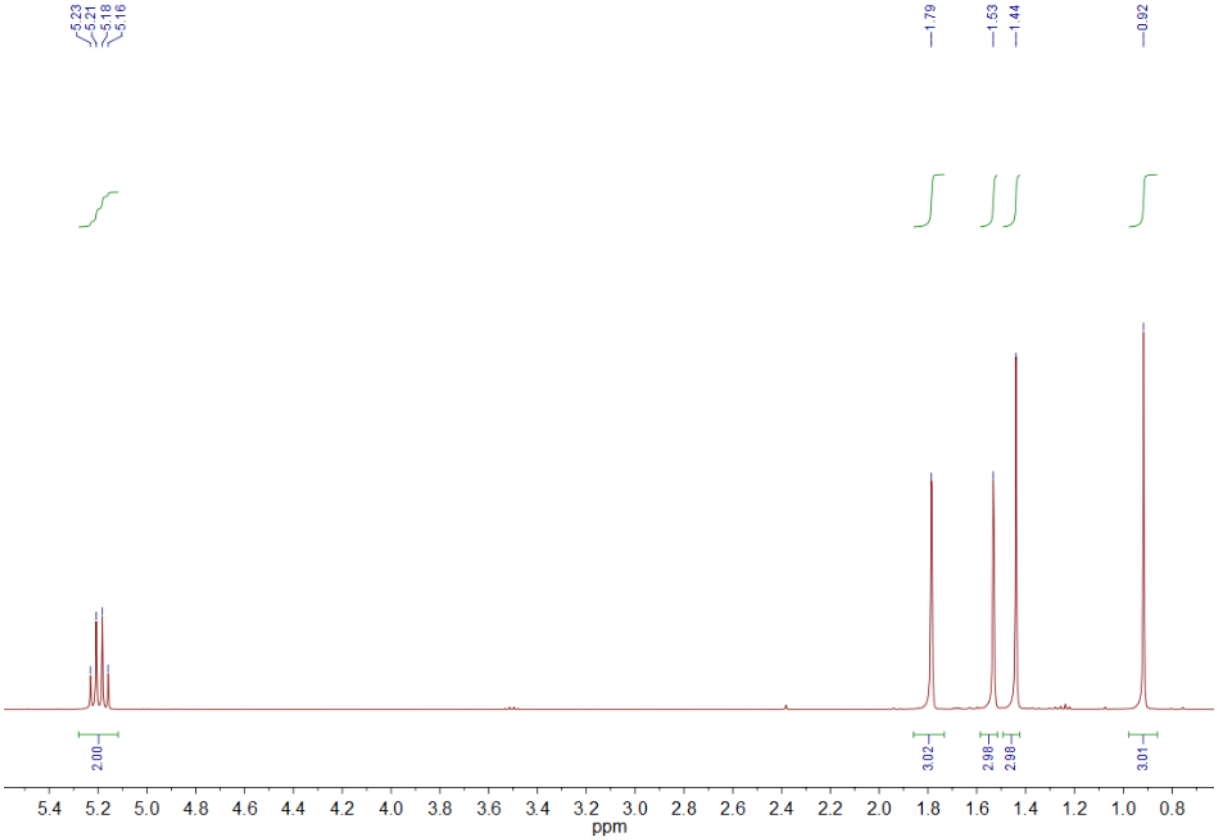


Figure S53. $^{13}C\{^{1}H\}$ NMR Spectrum of **5** in $CDCl_3$.

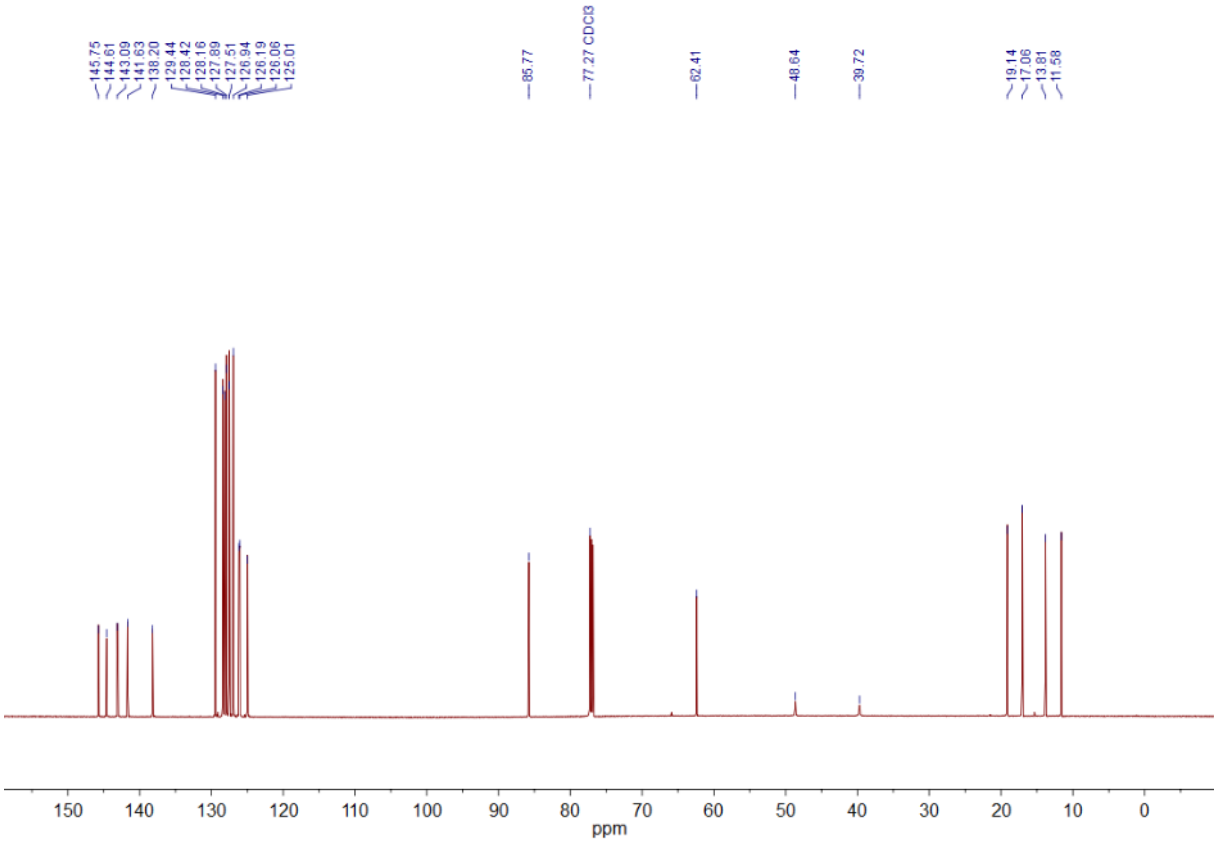


Figure S54. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **5** in $CDCl_3$ (aryl region).

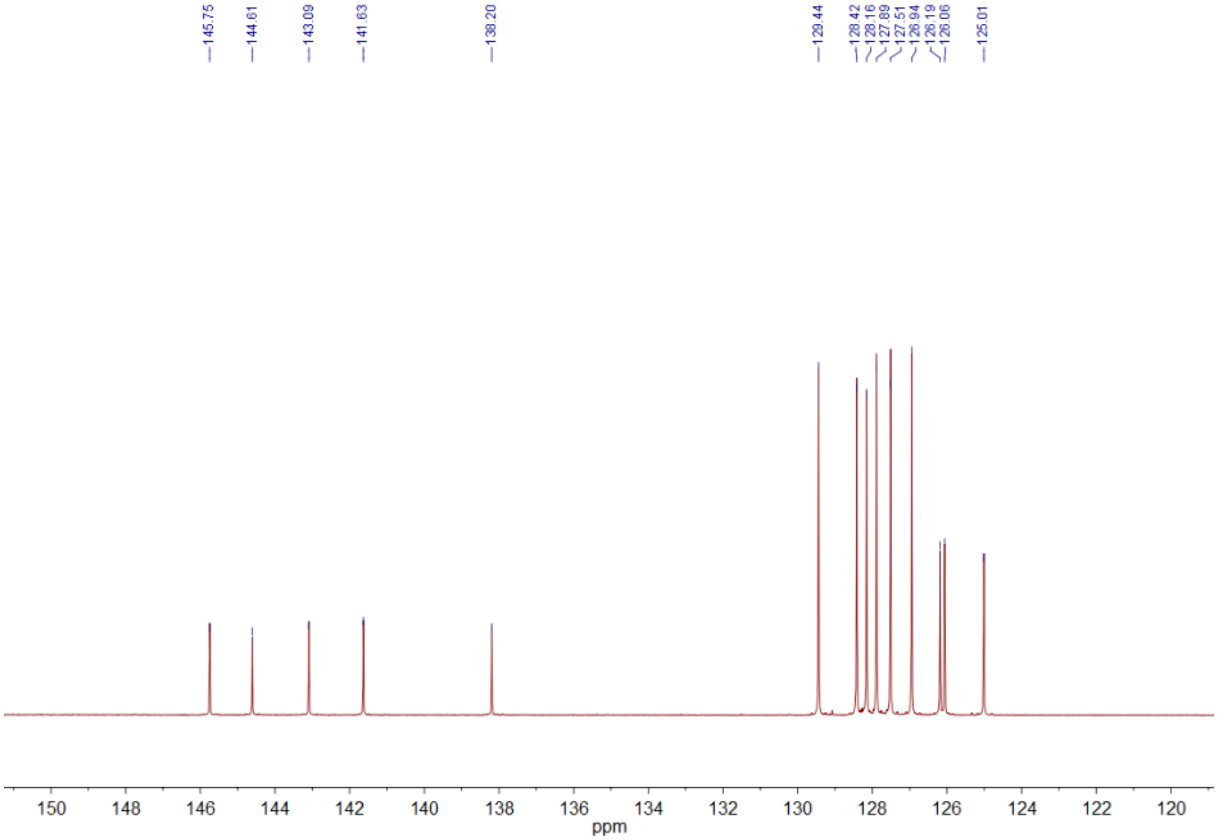


Figure S55. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **5** in $CDCl_3$ (aliphatic region).

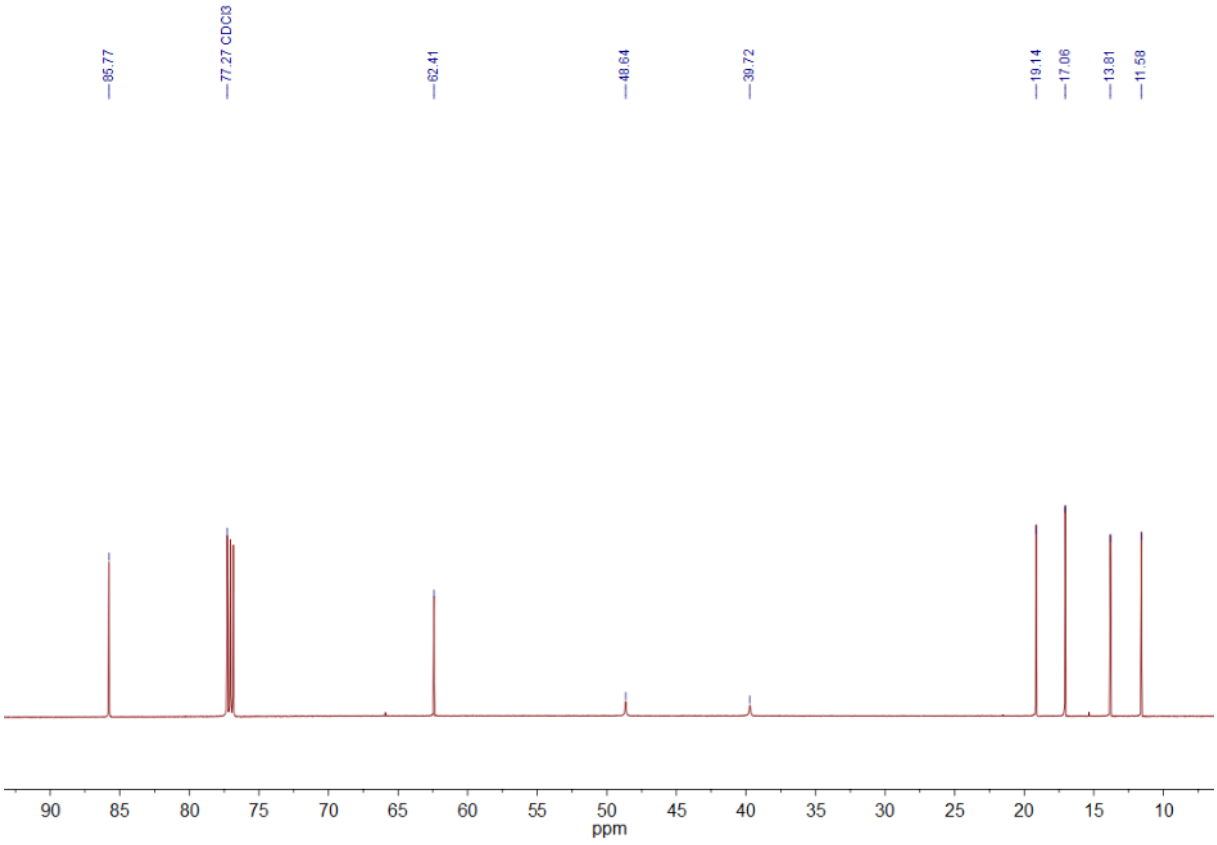


Figure S56. ^{13}C DEPT135 NMR Spectrum of **5** in $CDCl_3$.

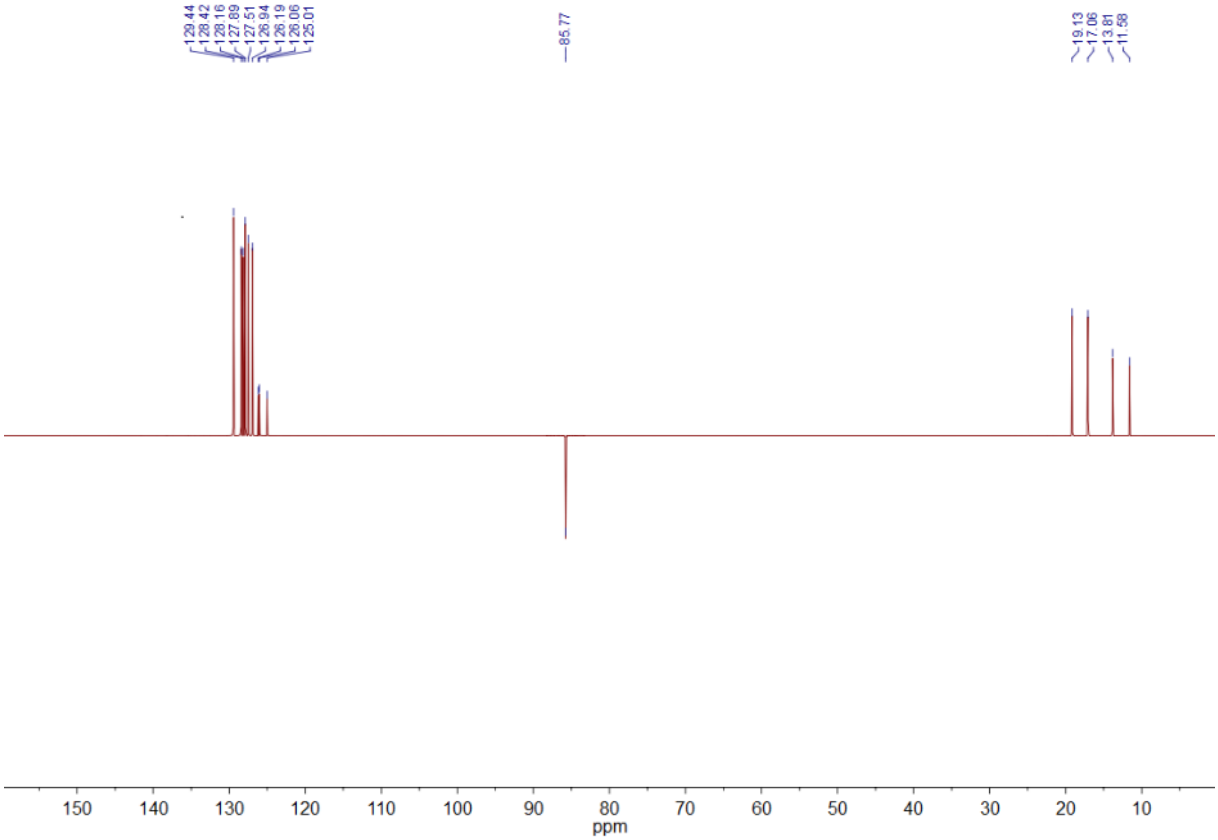


Figure S57. $^{11}B\{^{1}H\}$ NMR Spectrum of **5** in $CDCl_3$.

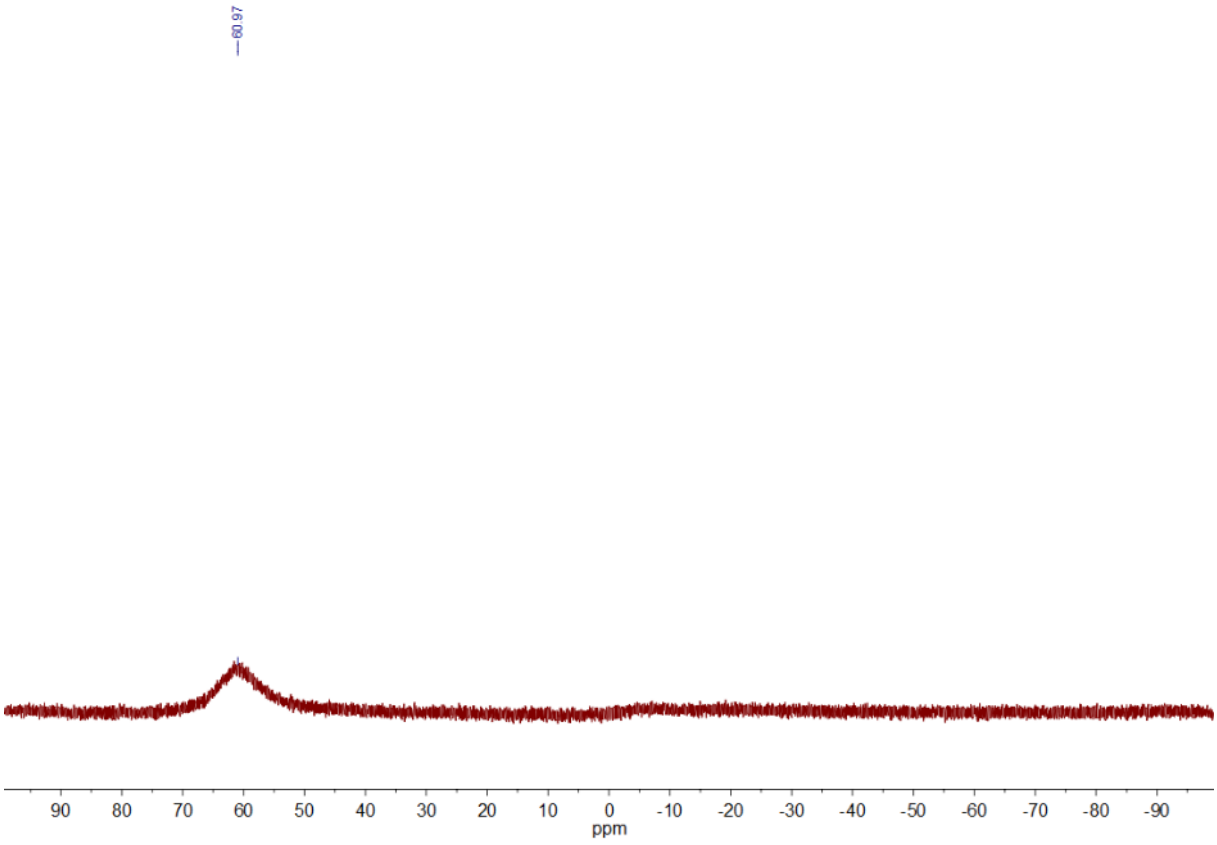


Figure S58. FT-IR Spectrum of **5**.

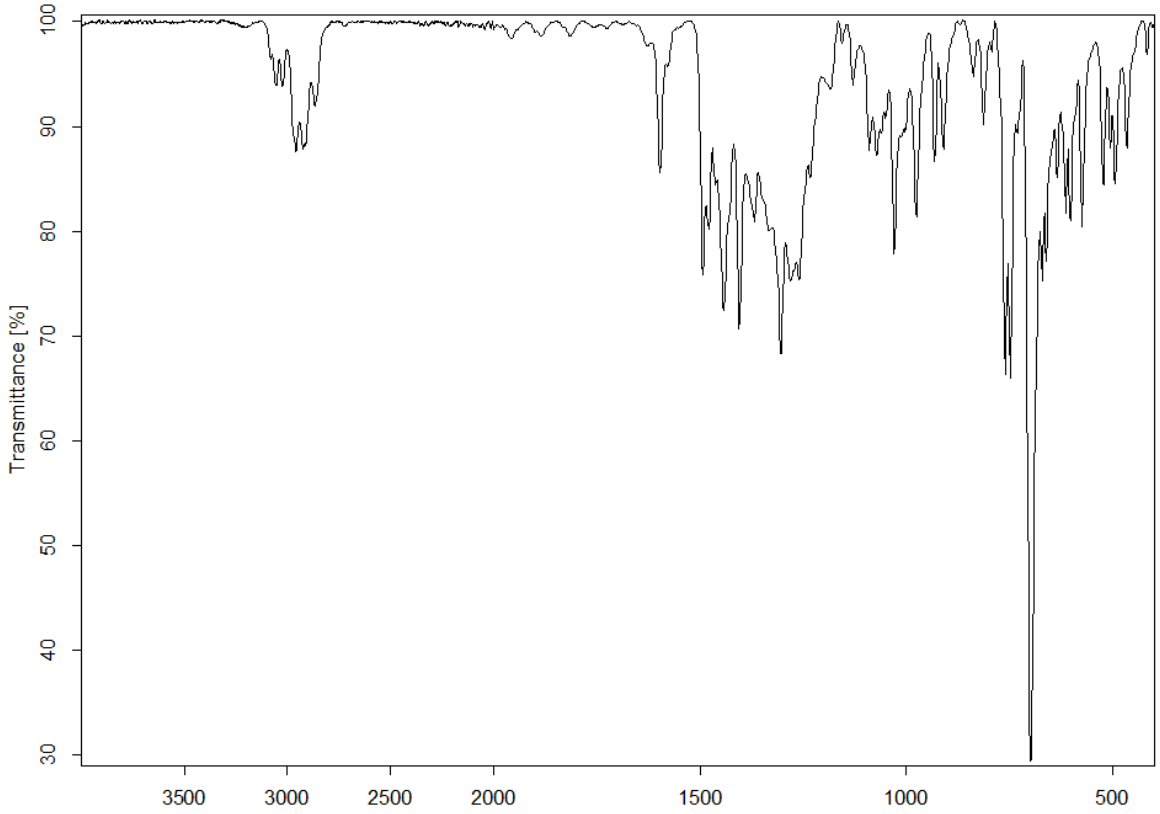
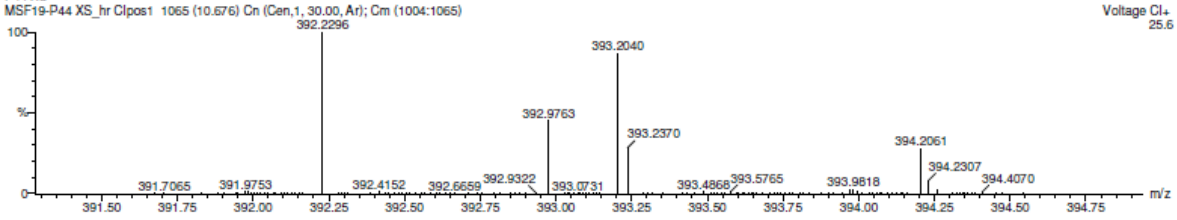


Figure S59. High Resolution mass spectrum (CI+) of **5**.

Multiple Mass Analysis: 3 mass(es) processed - displaying only valid results
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 70.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
65 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 11B: 0-1 O: 1-2
P44 XS
MSF19-P44 XS_hr CIpos1 1065 (10.676) Cn (Cen,1, 30.00, Ar); Cm (1004:1065)



Minimum:	30.00				-1.5		
Maximum:	100.00		5.0	10.0	70.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
392.2296	100.00	392.2311	-1.5	-3.8	15.0	0.2	C28 H29 11B O
393.2040	86.92	393.2026	1.4	3.6	15.5	2773012.5	C27 H26 11B O2

Figure S60. ^{1}H NMR spectrum of **D2** in $CDCl_3$.

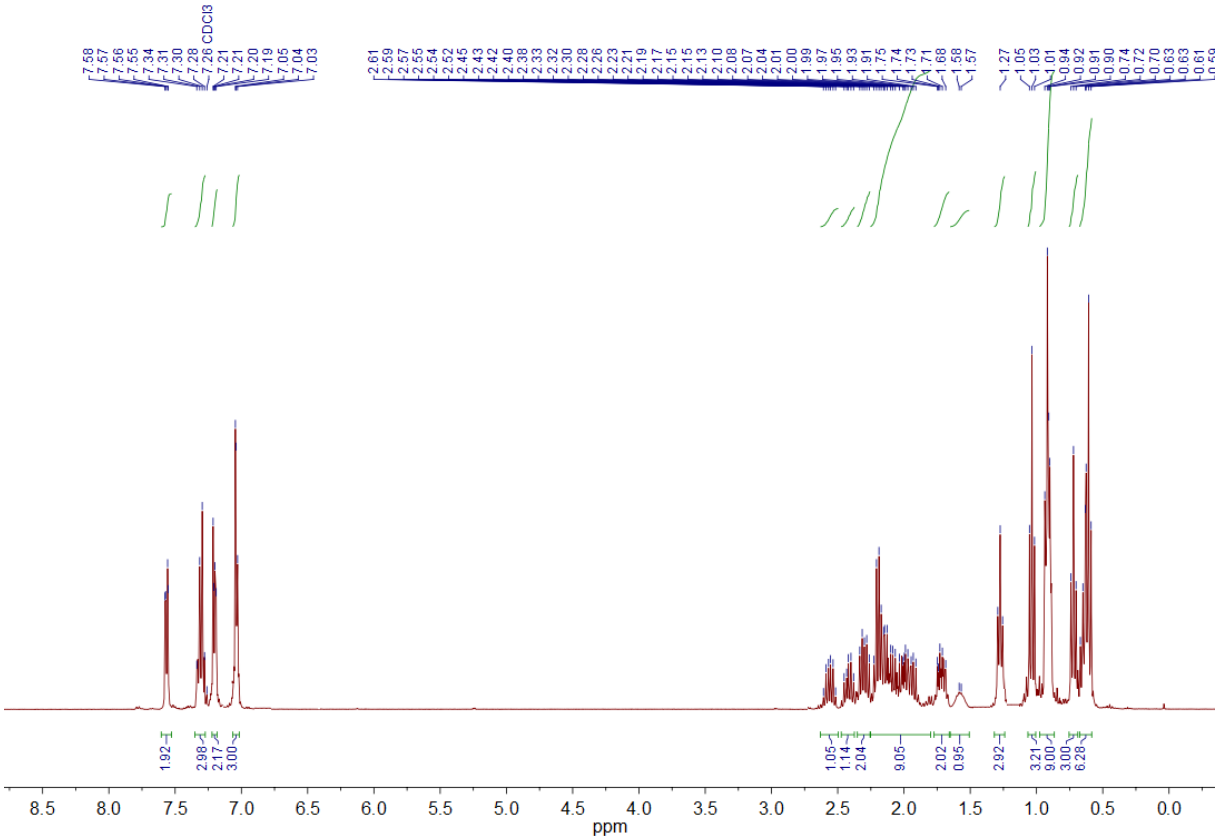


Figure S61. Expansion of ^{1}H NMR spectrum of **D2** in $CDCl_3$ (aryl region).

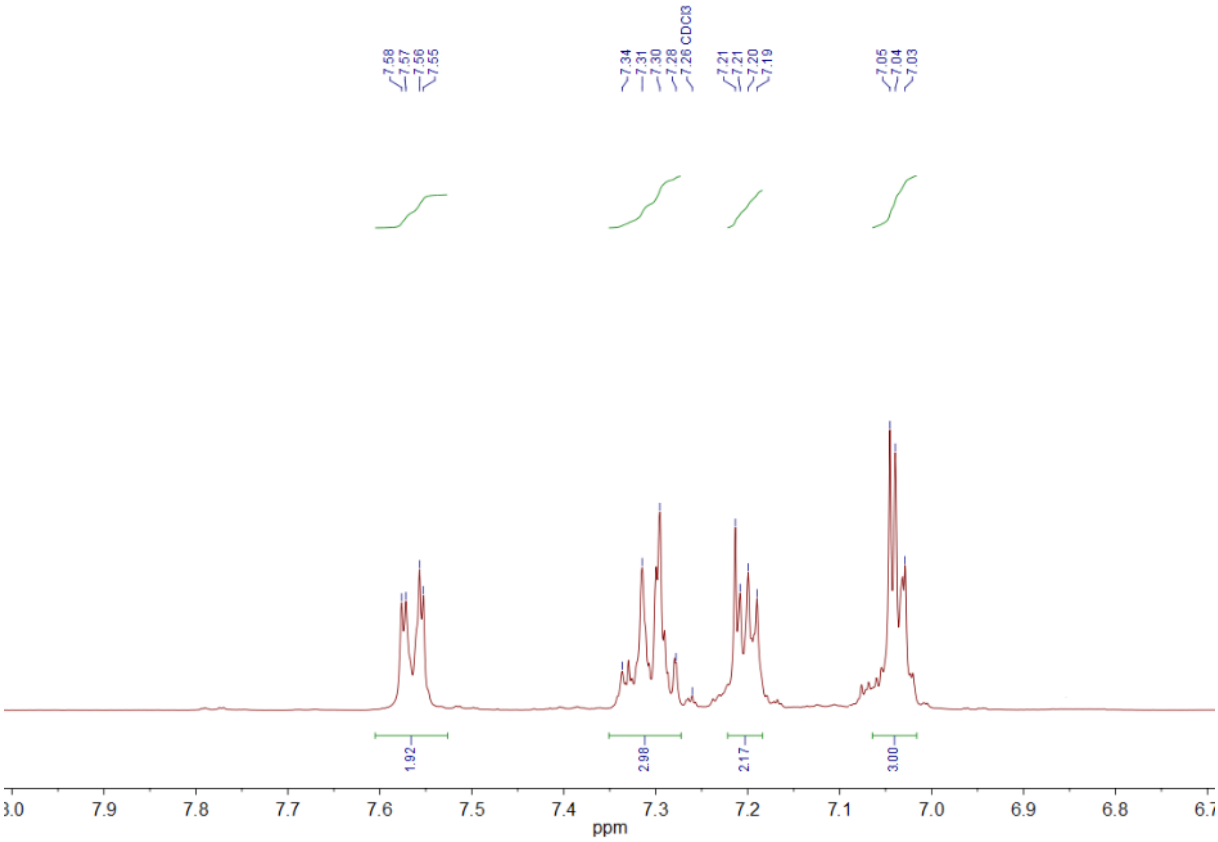


Figure S62. Expansion of ^{1}H NMR spectrum of **D2** in $CDCl_3$ (aliphatic region).

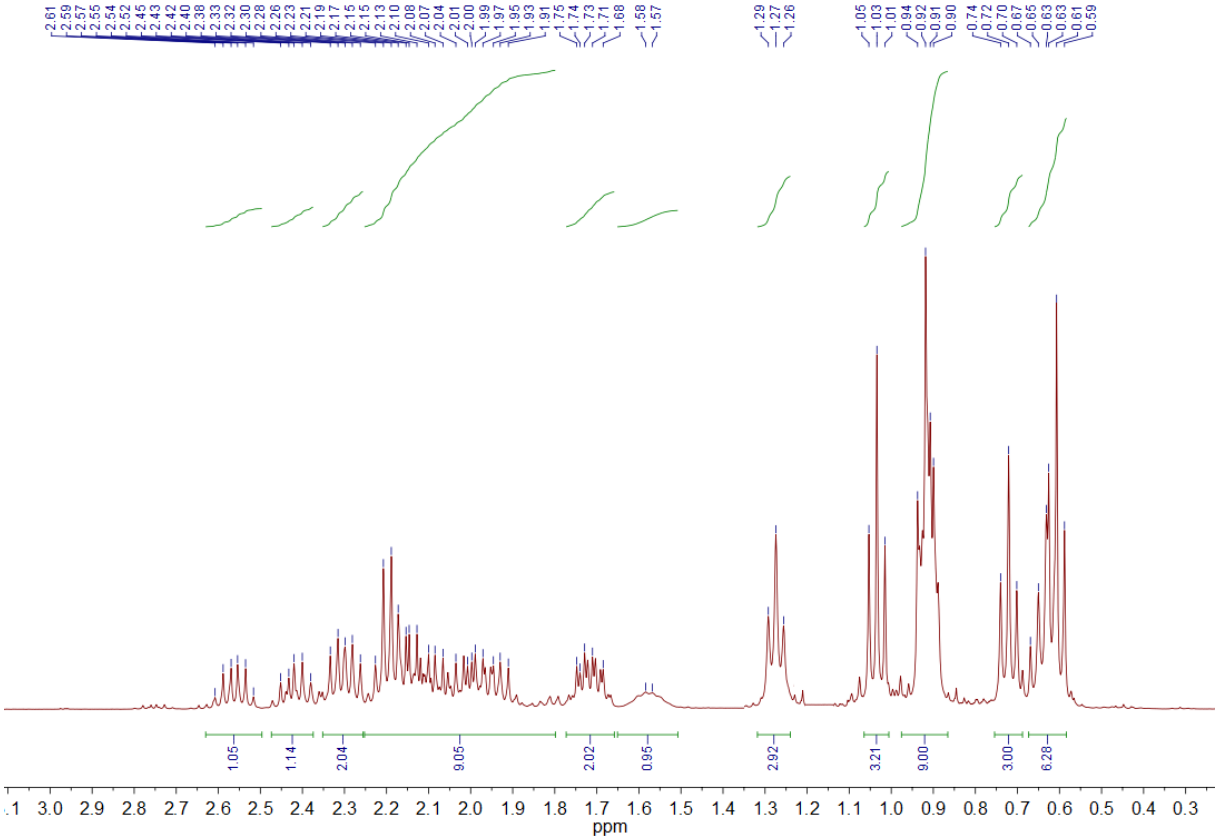


Figure S63. $^{13}C\{^{1}H\}$ NMR Spectrum of **D2** in $CDCl_3$.

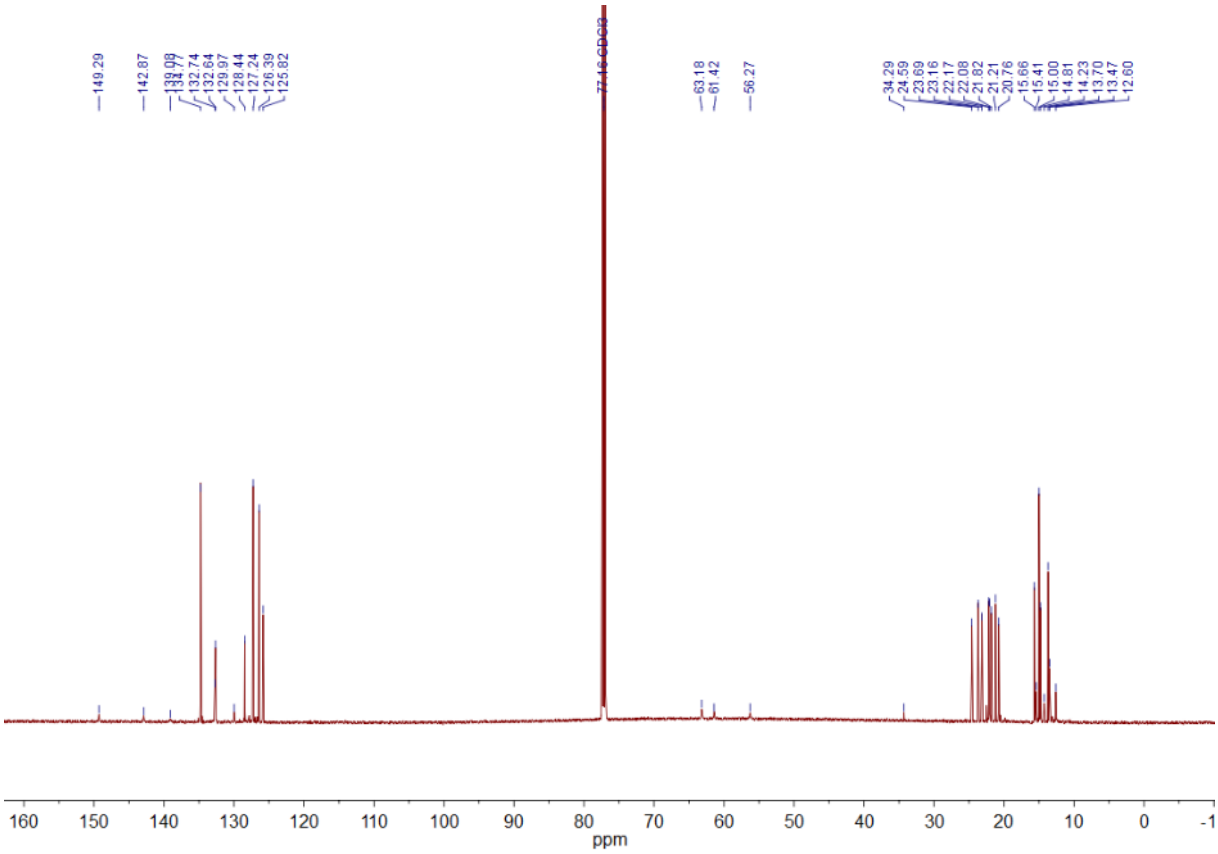


Figure S64. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **D2** in $CDCl_3$ (aryl region).

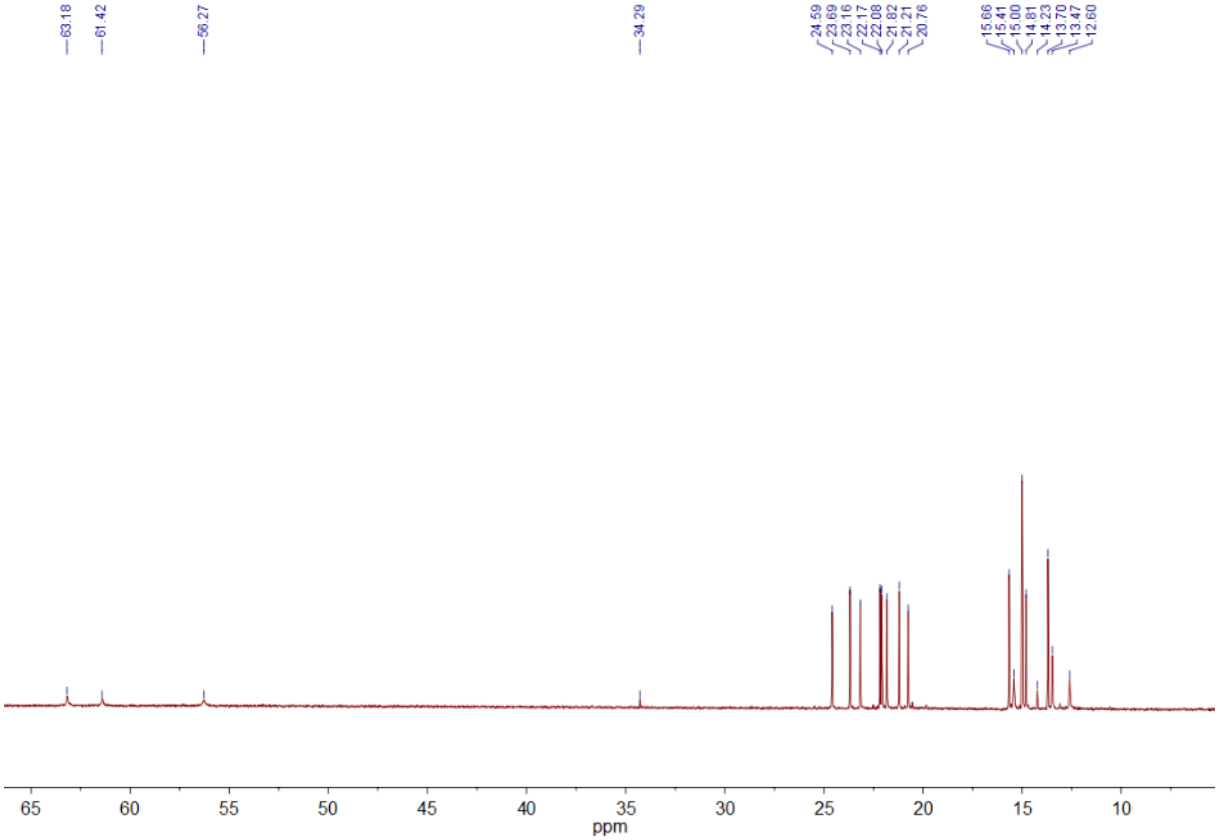


Figure S65. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **D2** in $CDCl_3$ (aliphatic region).

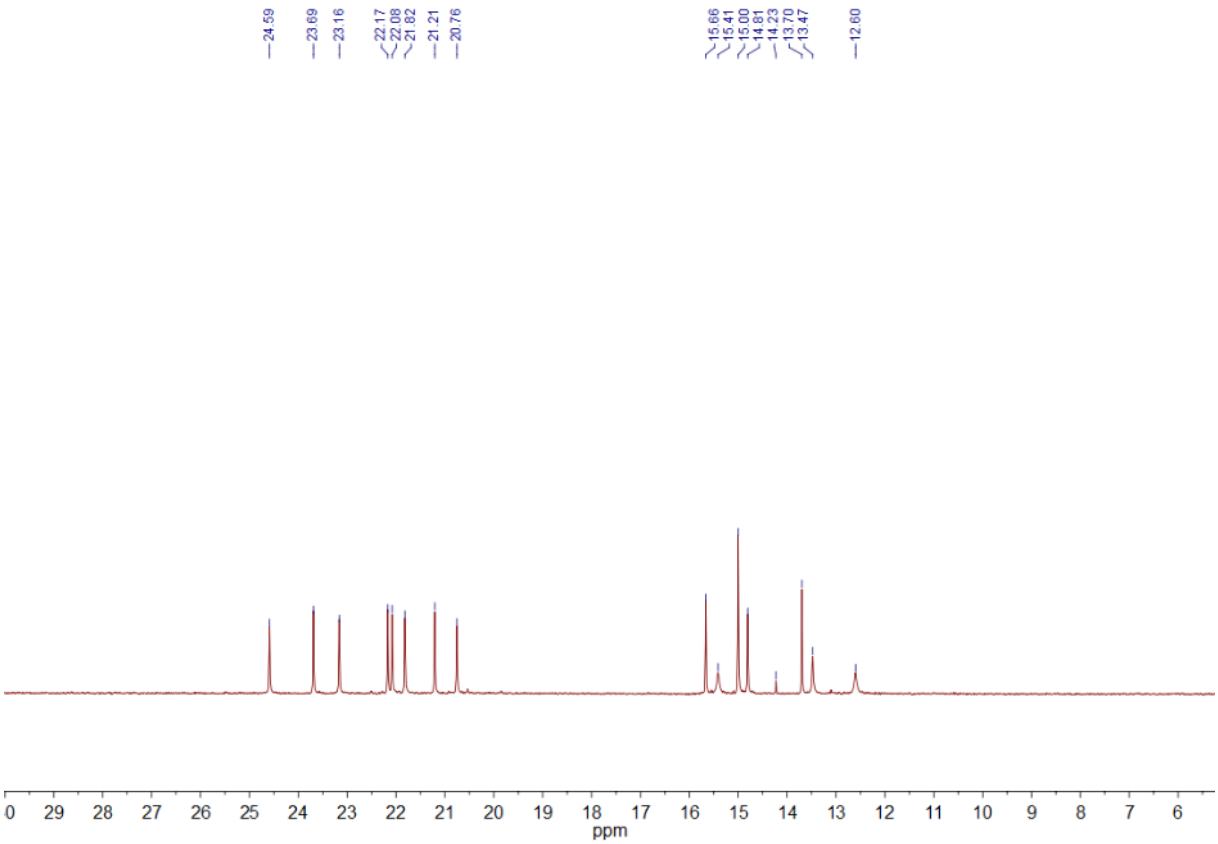


Figure S66. ^{13}C DEPT135 NMR Spectrum of **D2** in $CDCl_3$.

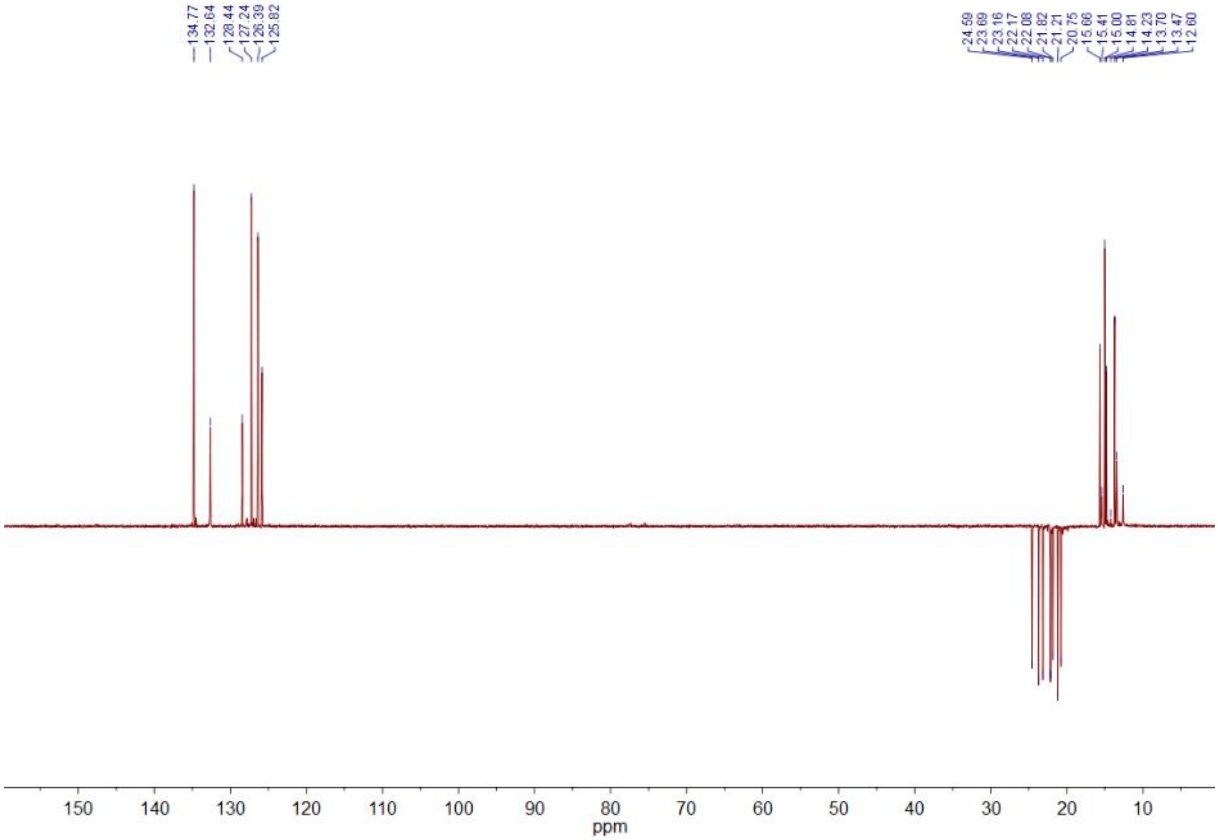


Figure S67. ^{11}B NMR Spectrum of **D2** in $CDCl_3$.

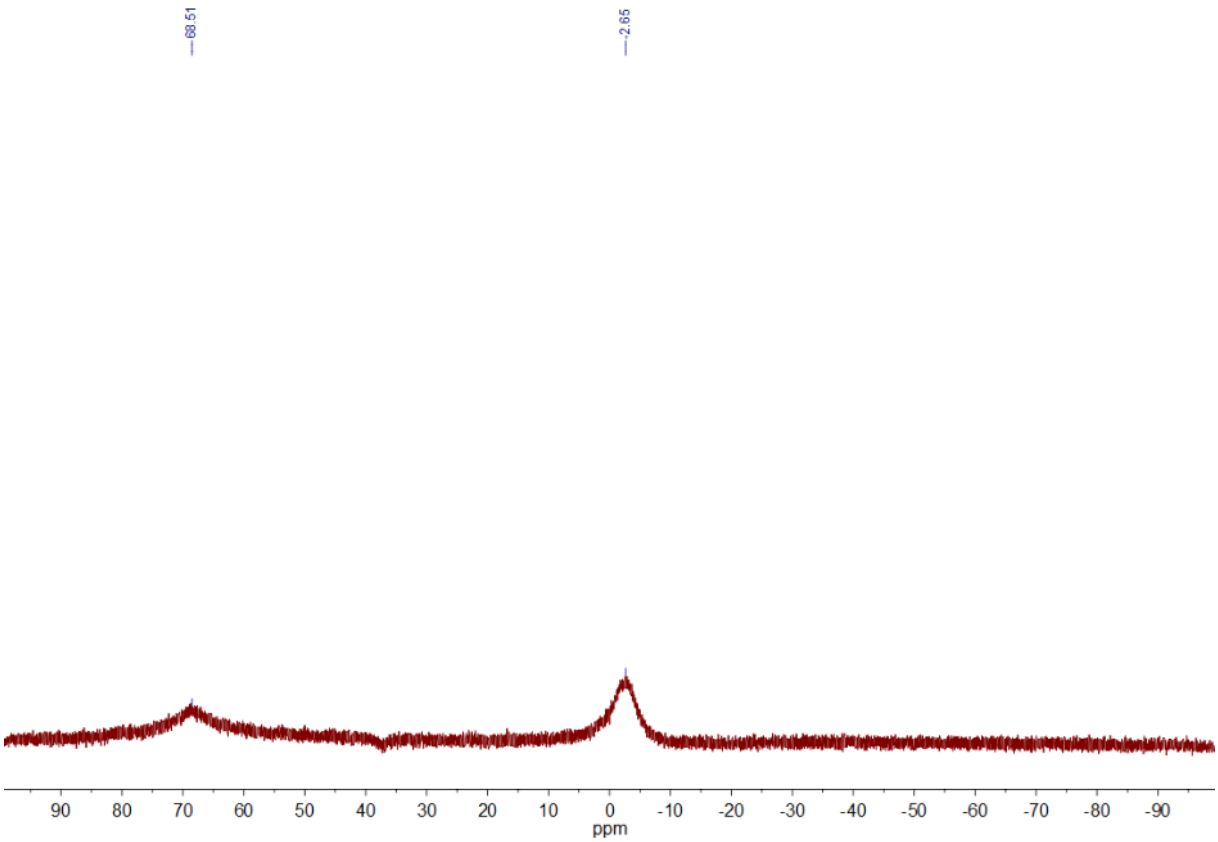


Figure S68. FT-IR Spectrum of **D2**.

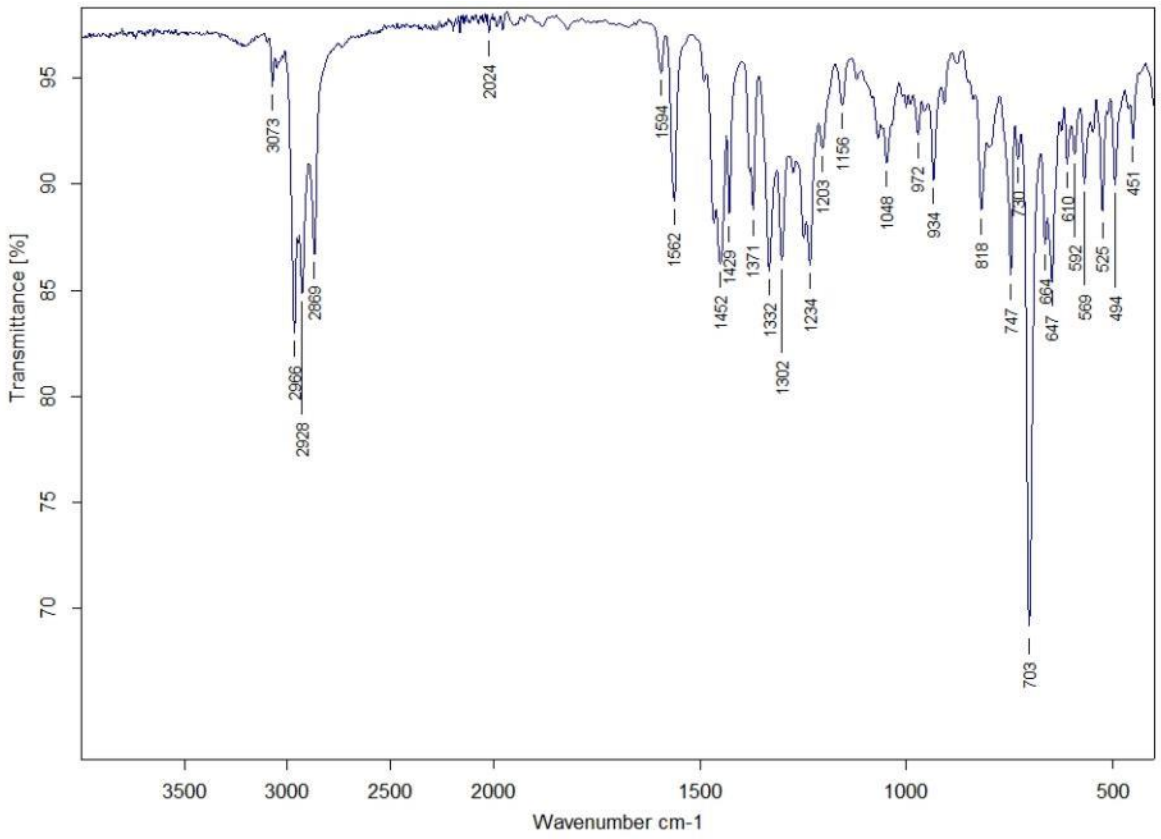


Figure S69. ^{1}H NMR spectrum of **E2** in $CDCl_3$.

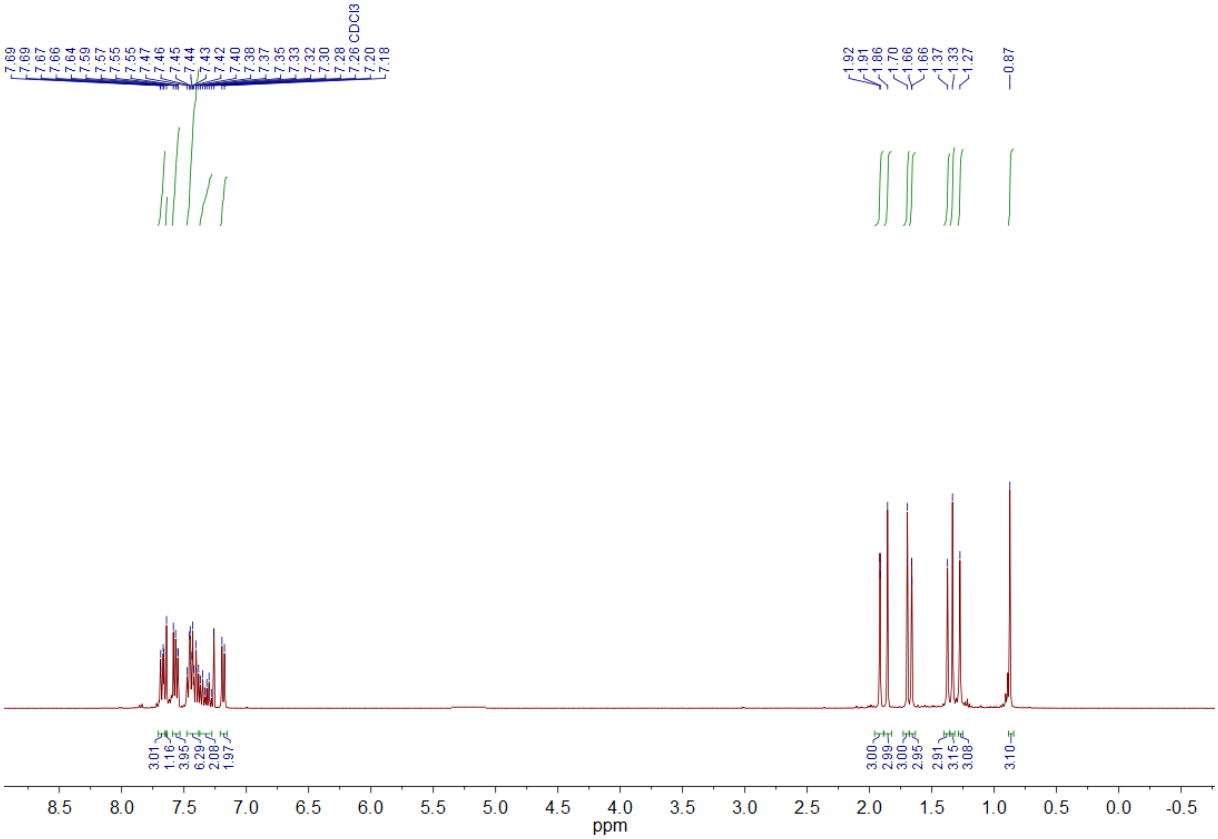


Figure S70. Expansion of ^{1}H NMR spectrum of **E2** in $CDCl_3$ (aryl region).

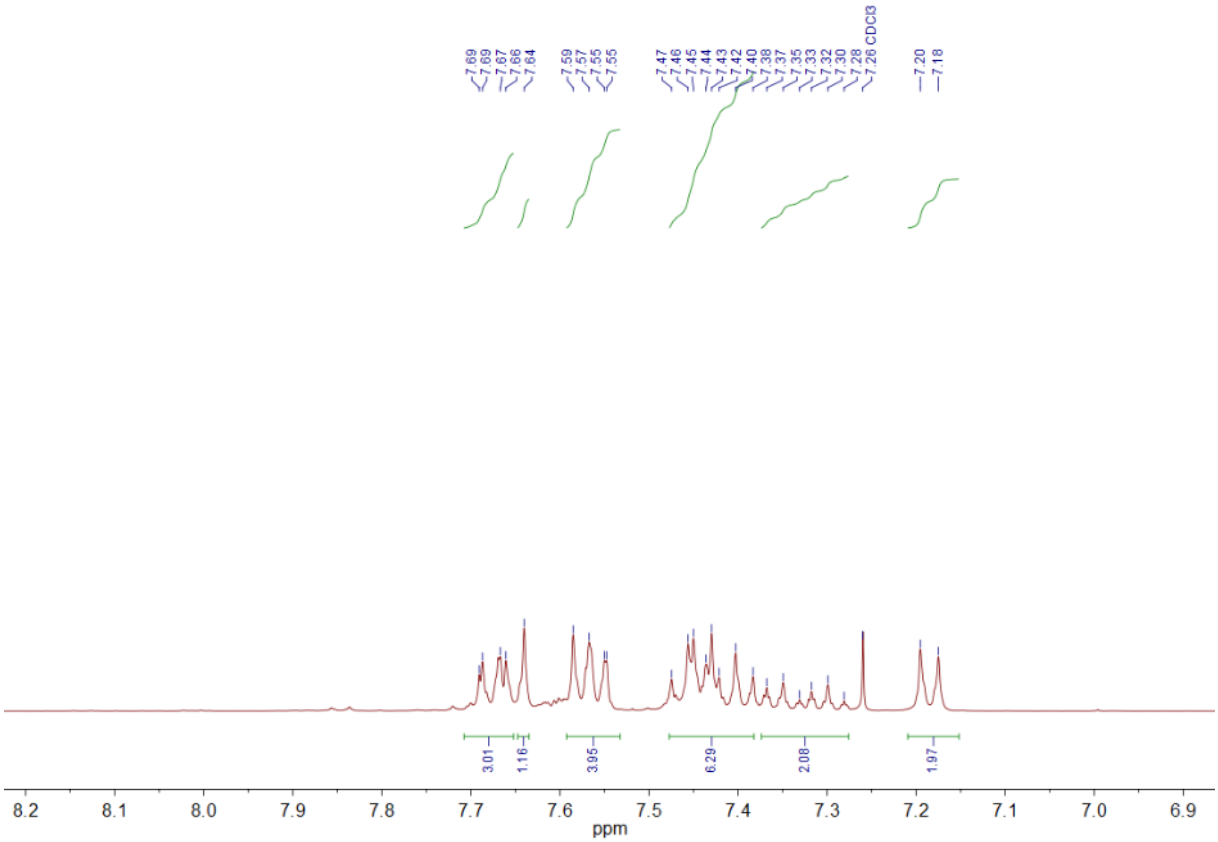


Figure S71. Expansion of ^{1}H NMR spectrum of **E2** in $CDCl_3$ (aliphatic region).

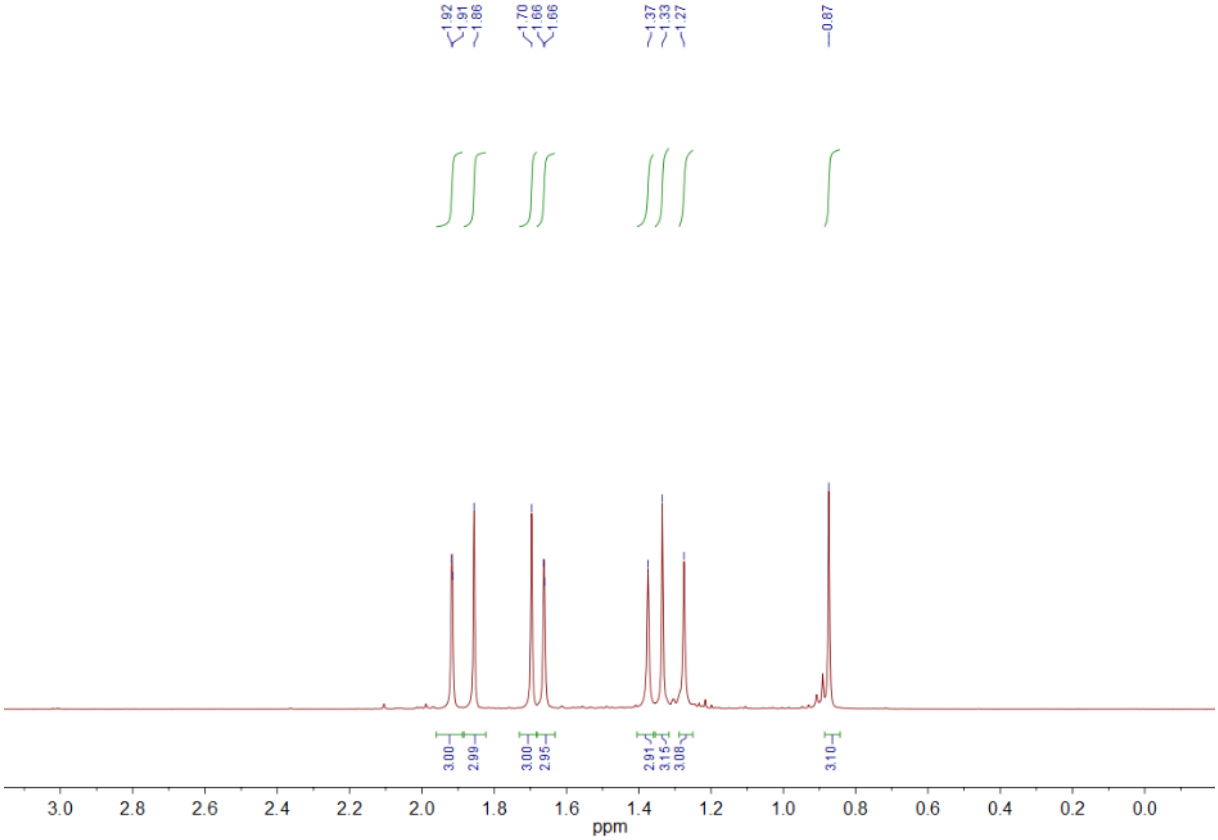


Figure S72. $^{13}C\{^{1}H\}$ NMR Spectrum of **E2** in $CDCl_3$.

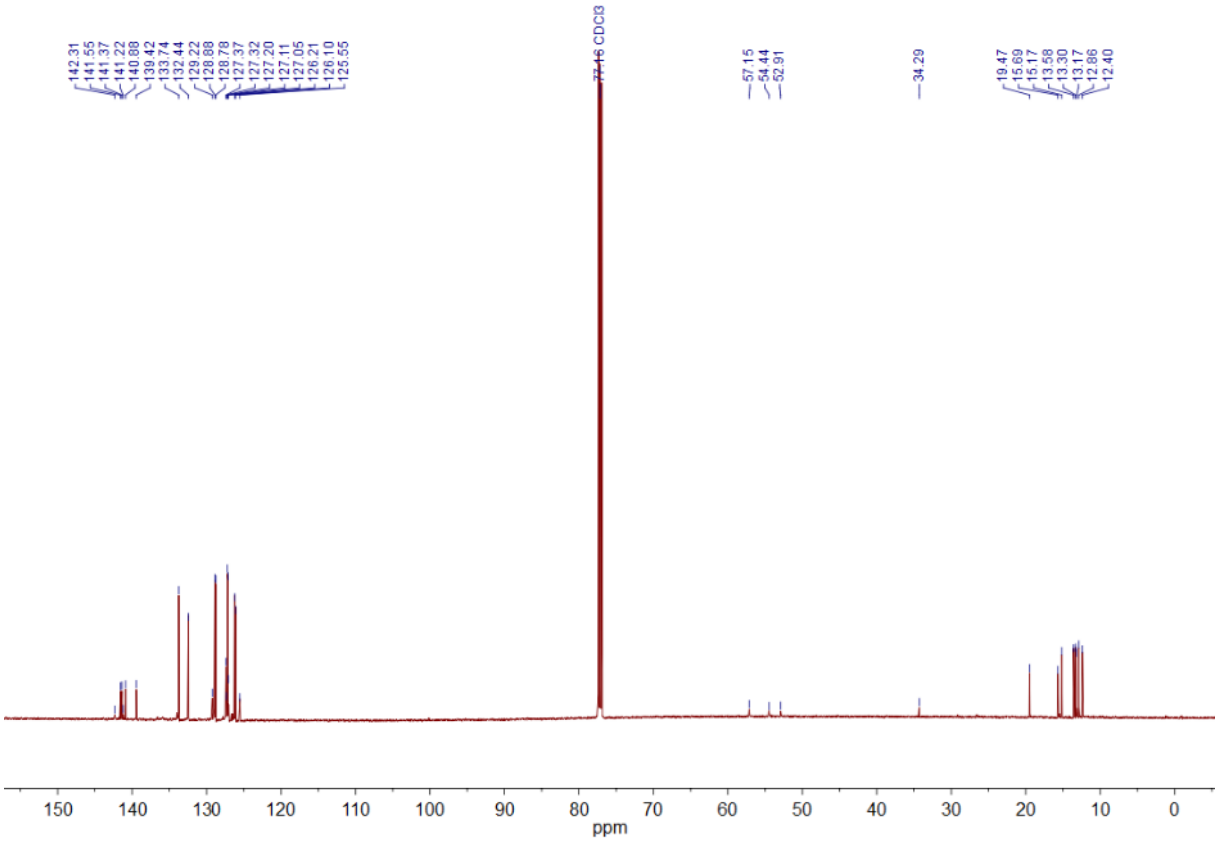


Figure S73. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **E2** in $CDCl_3$ (aryl region).

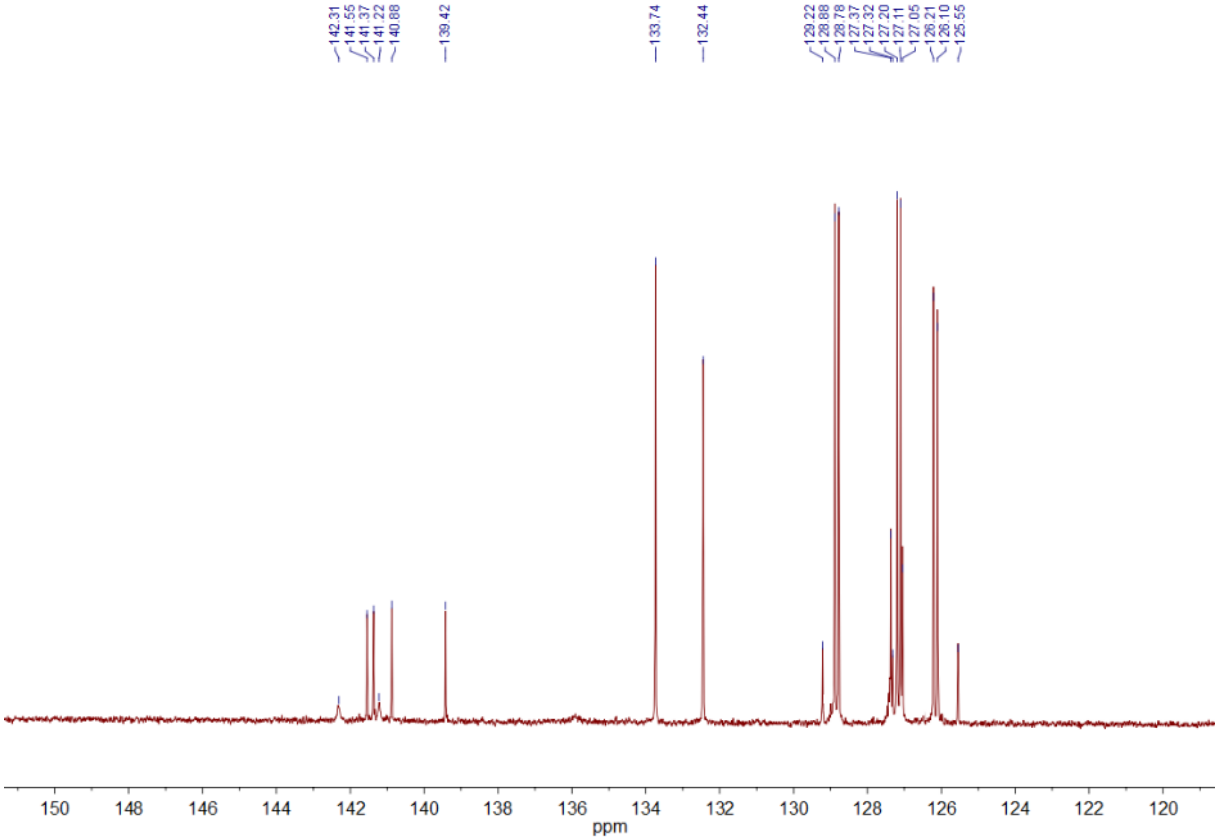


Figure S74. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **E2** in $CDCl_3$ (aliphatic region).

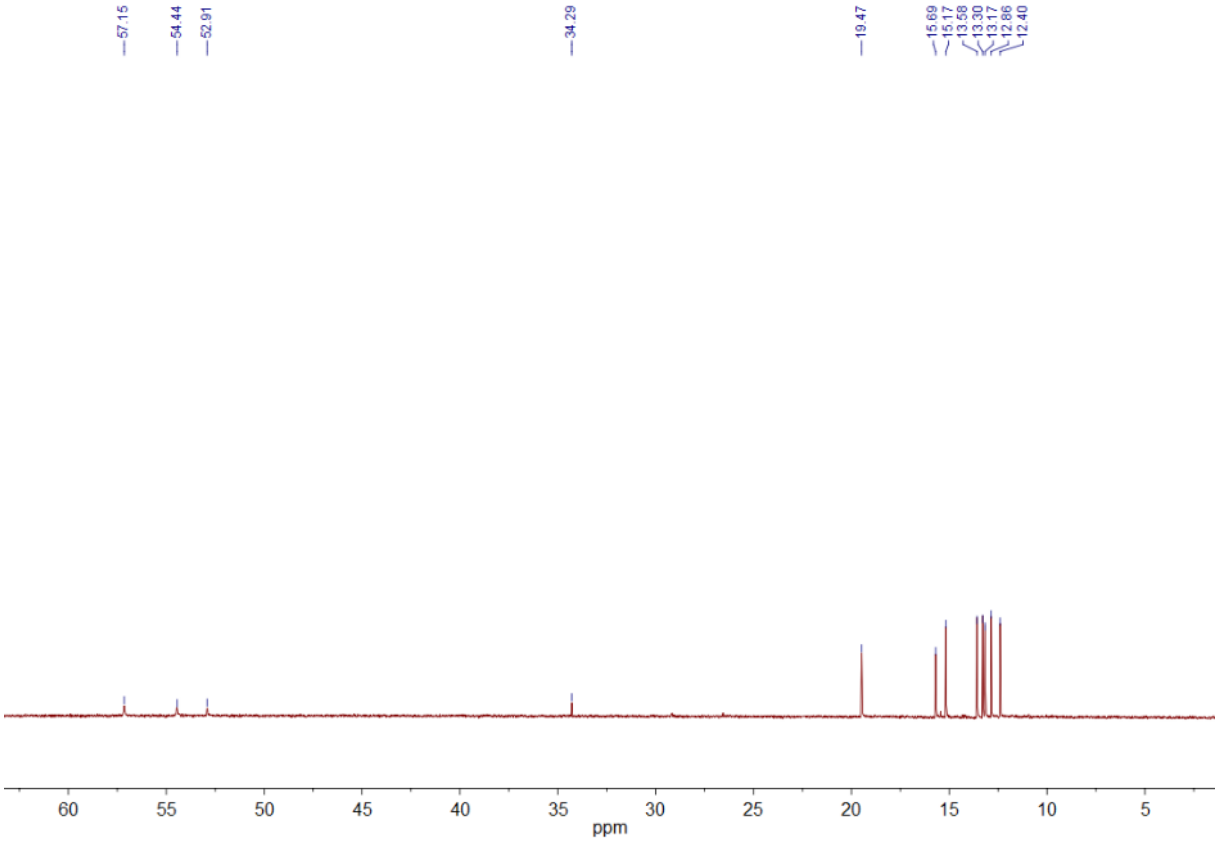


Figure S75. ^{13}C DEPT135 NMR Spectrum of **E2** in $CDCl_3$.

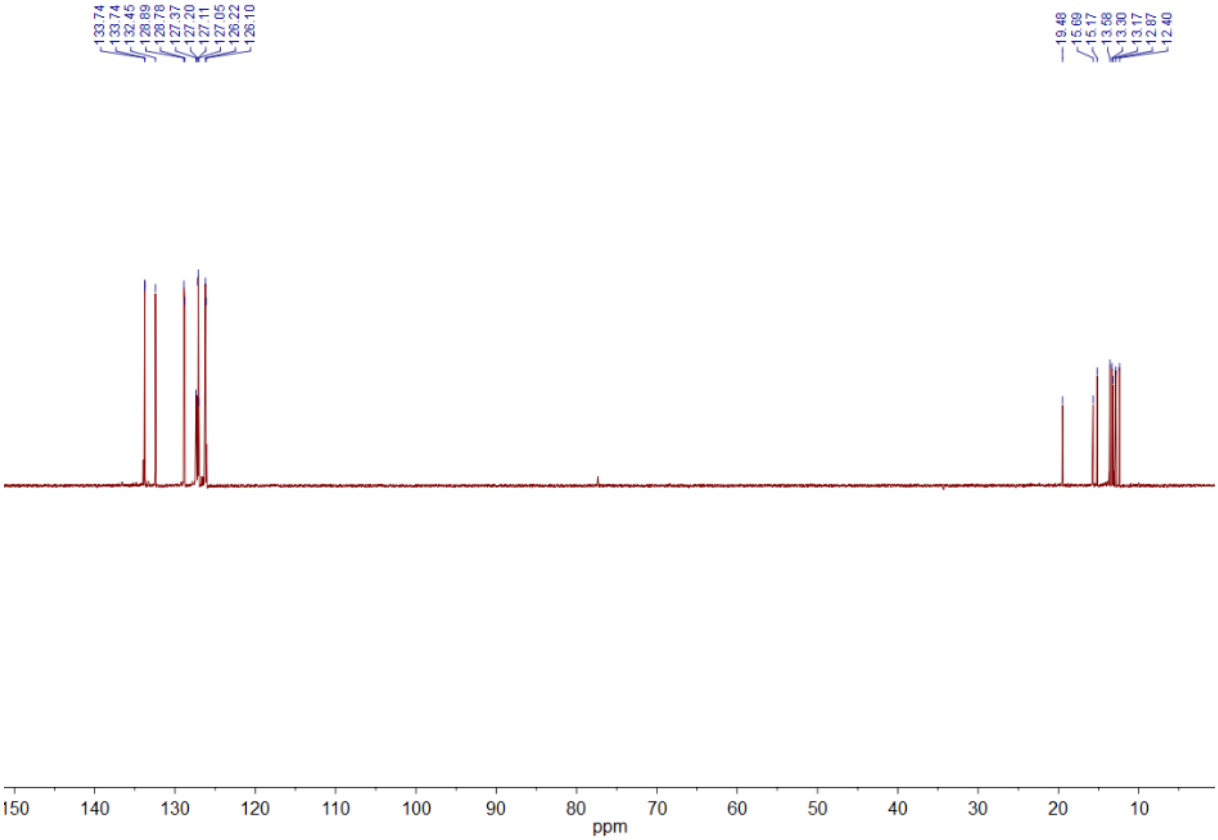


Figure S76. ^{11}B NMR Spectrum of **E2** in $CDCl_3$.

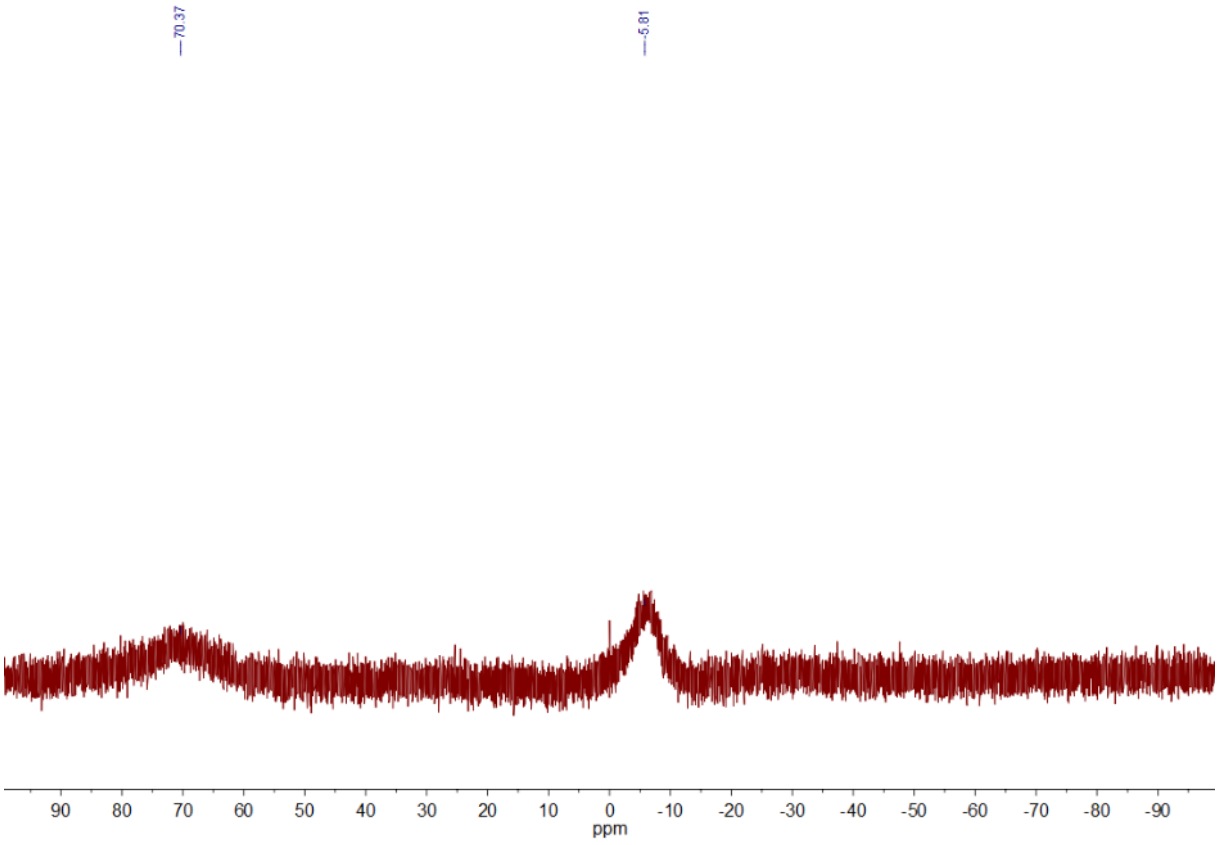


Figure S77. FT-IR Spectrum of **E2**.

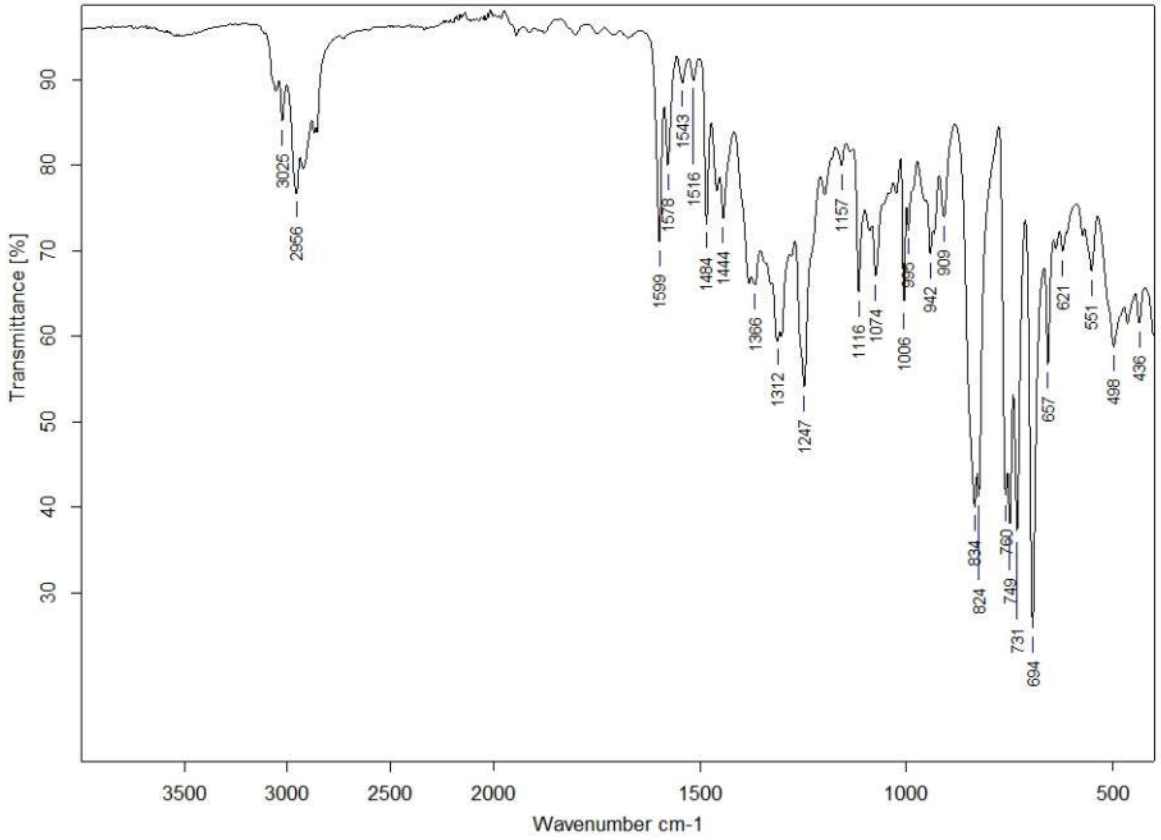


Figure S78. $_1$H NMR spectrum of **6** in $CDCl_3$.

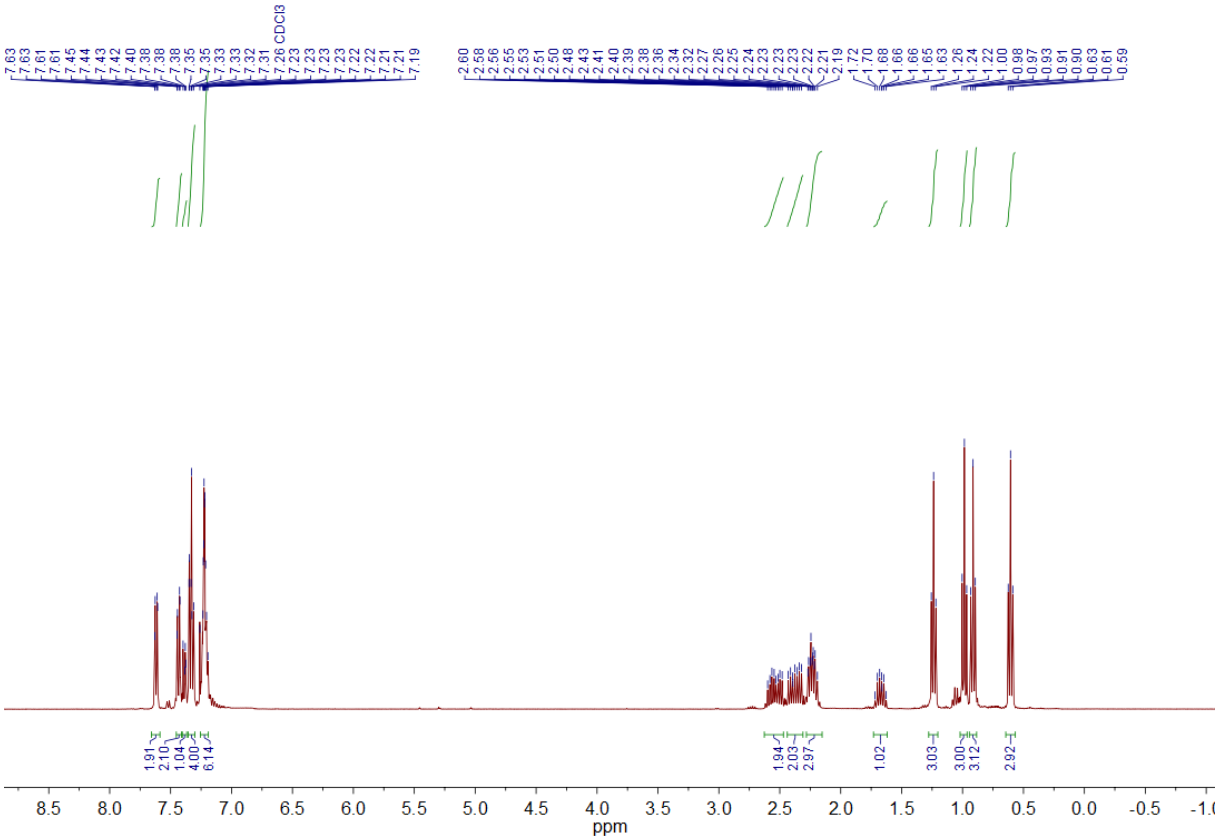


Figure S79. Expansion of $_1$H NMR spectrum of **6** in $CDCl_3$ (aryl region).

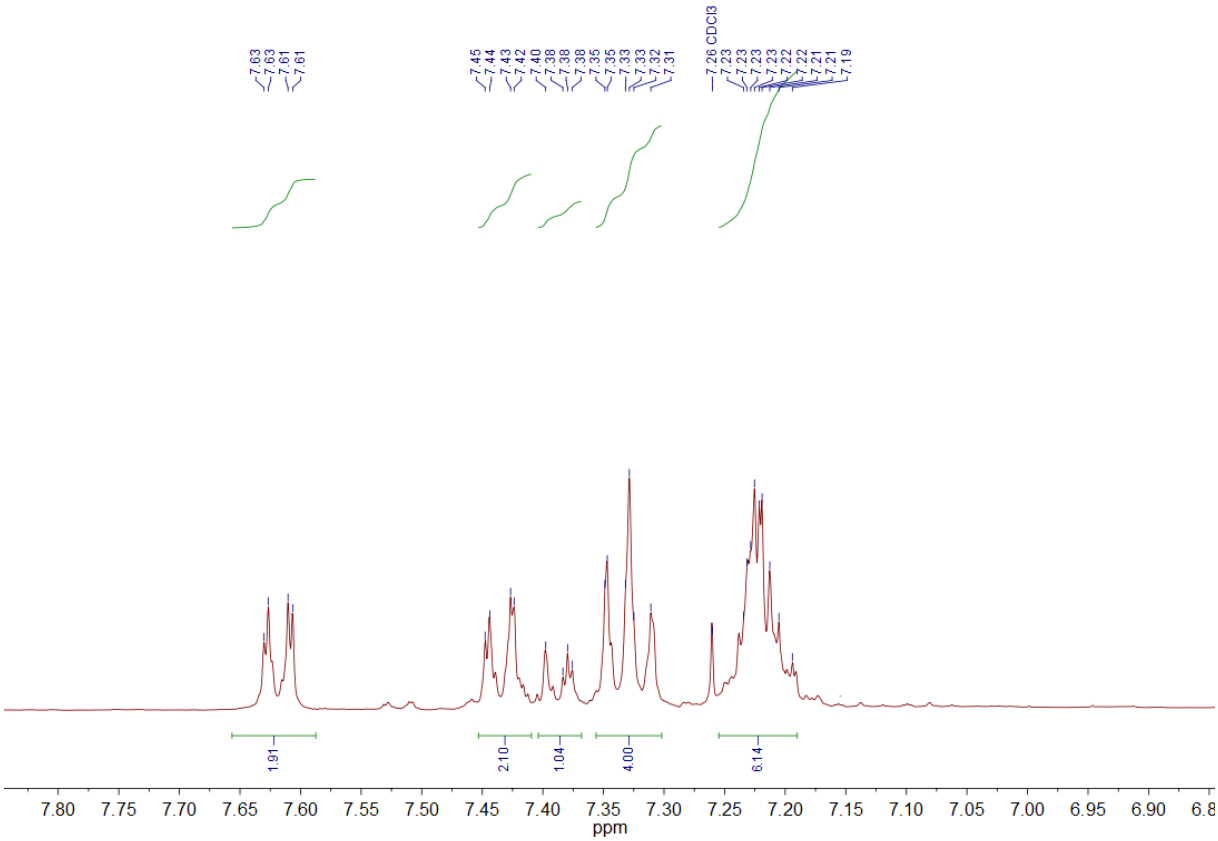


Figure S80. Expansion of ^{1}H NMR spectrum of **6** in $CDCl_3$ (aliphatic region).

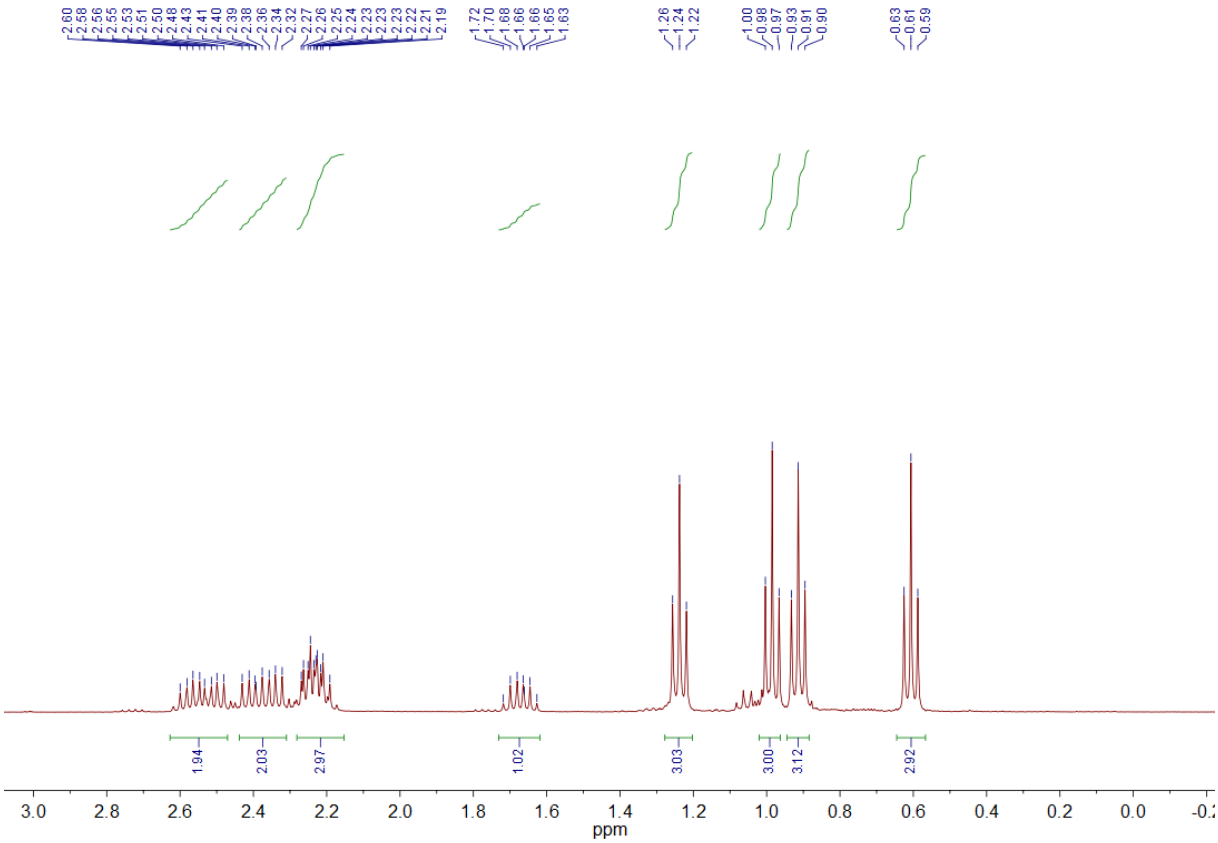


Figure S81. $^{13}C\{^{1}H\}$ NMR Spectrum of **6** in $CDCl_3$.

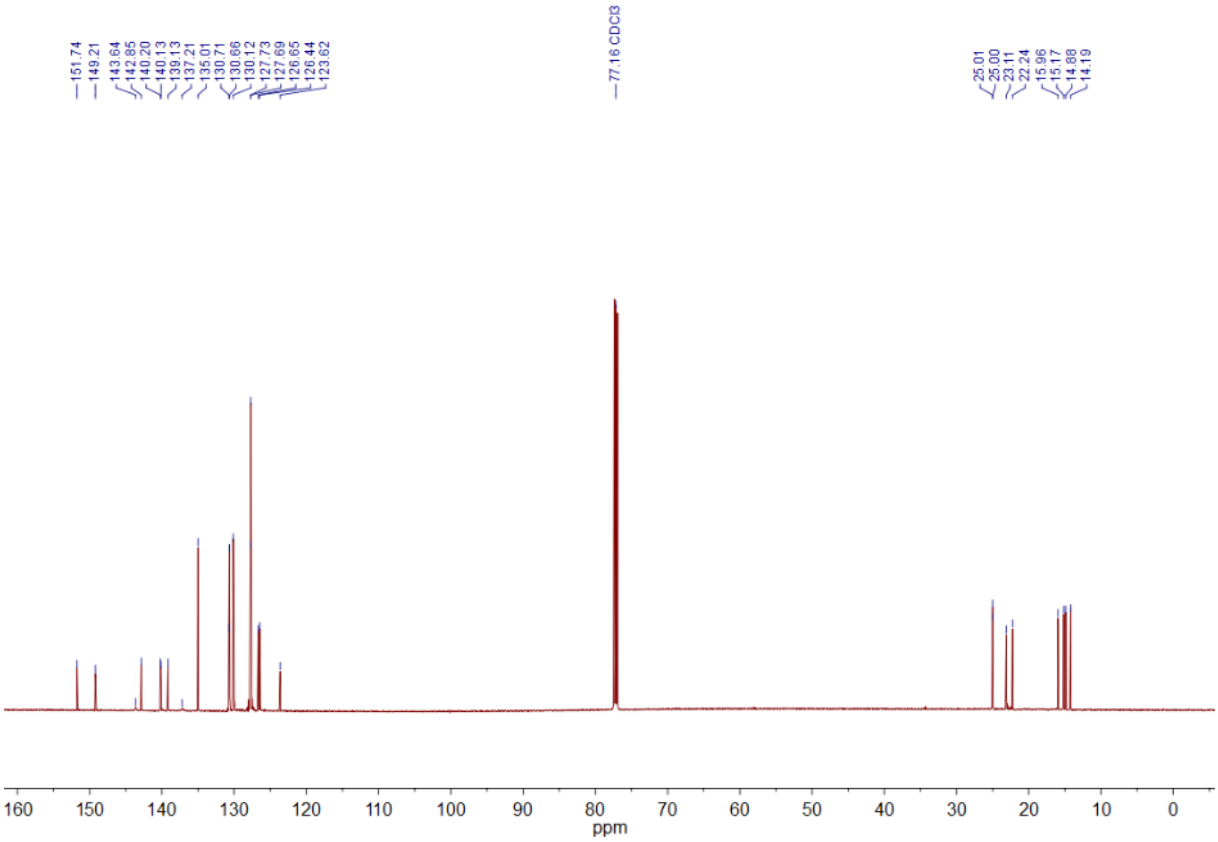


Figure S82. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **6** in $CDCl_3$ (aryl region).

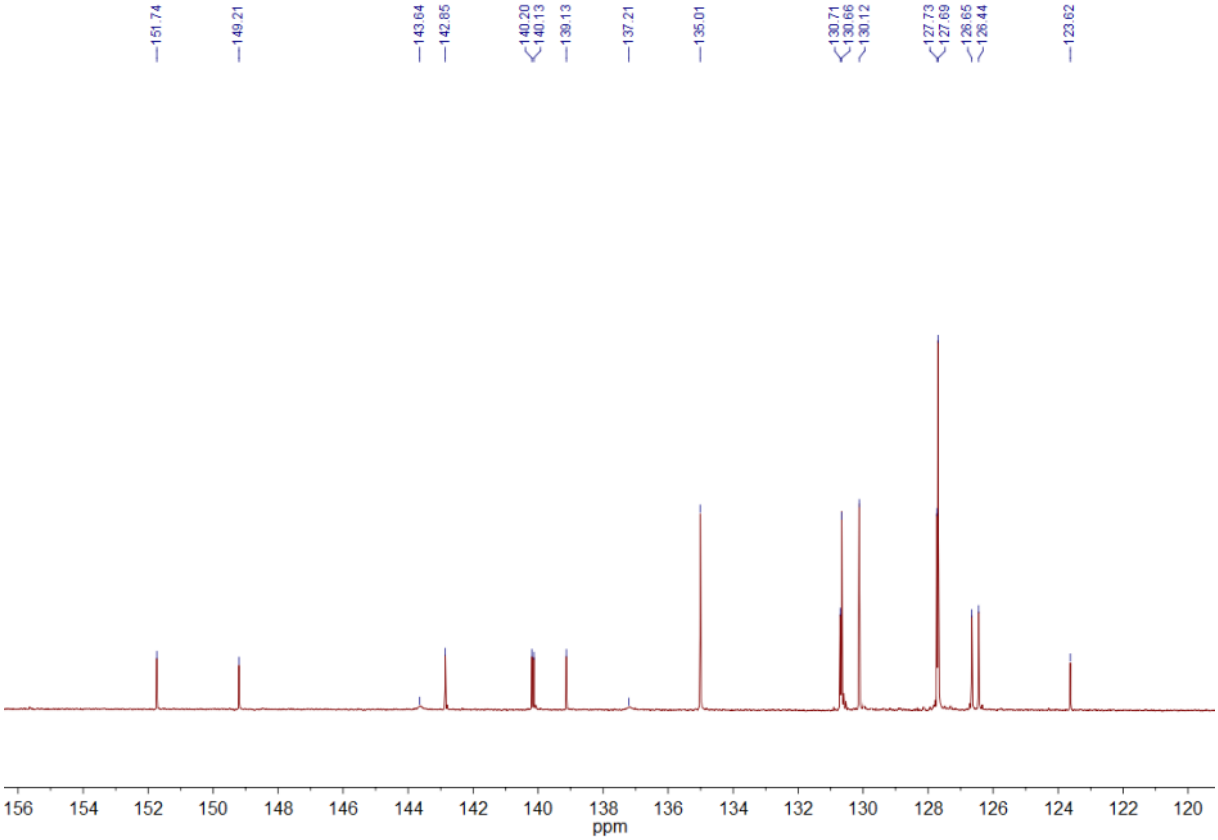


Figure S83. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **6** in $CDCl_3$ (aliphatic region).

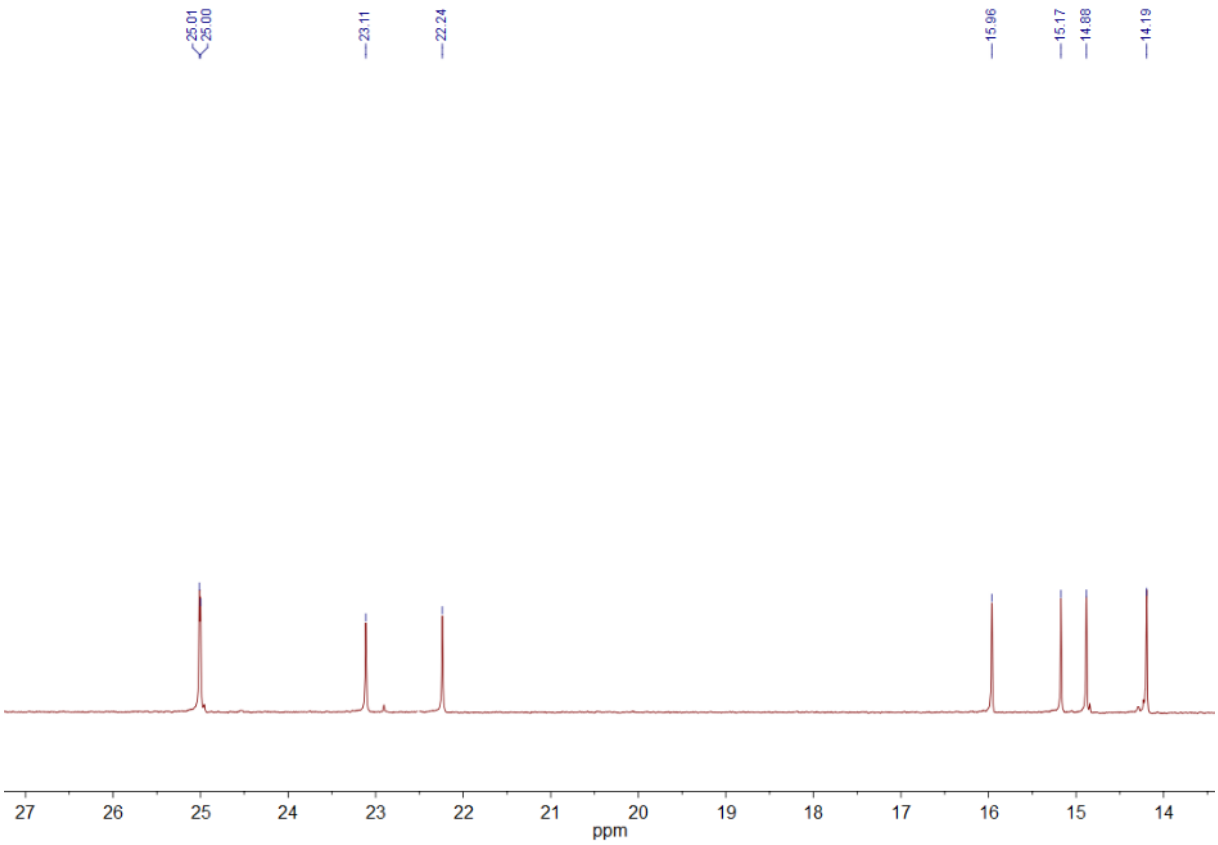


Figure S84. ^{13}C DEPT135 NMR Spectrum of **6** in $CDCl_3$.

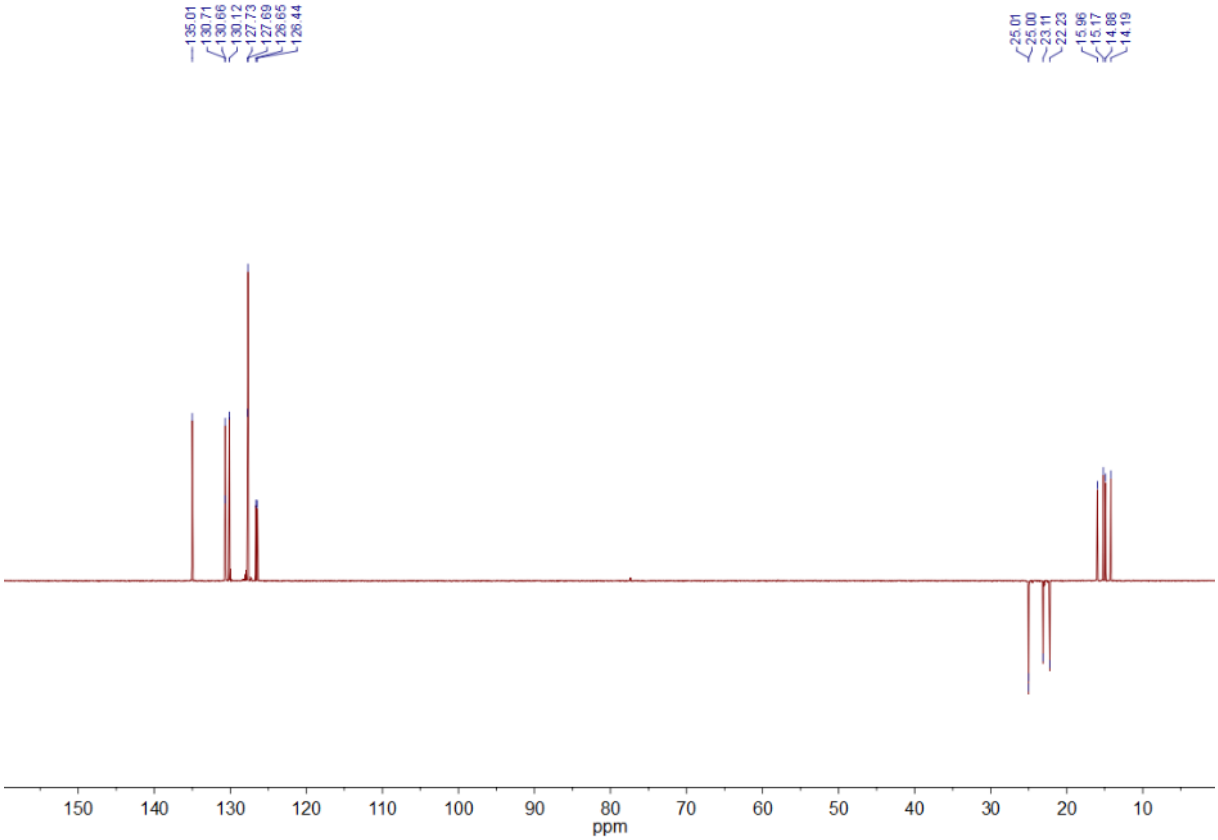


Figure S85. ^{11}B NMR Spectrum of **6** in $CDCl_3$.

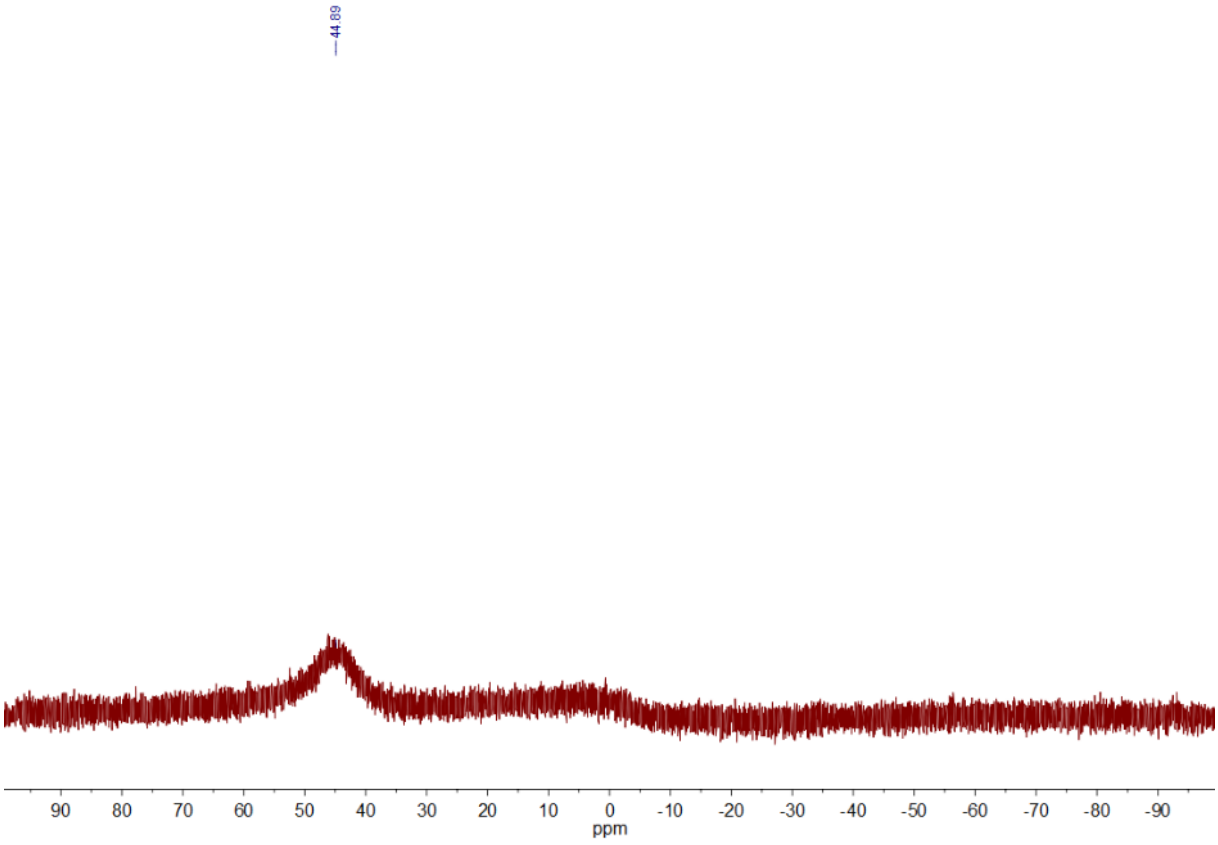


Figure S86. FT-IR Spectrum of **6**.

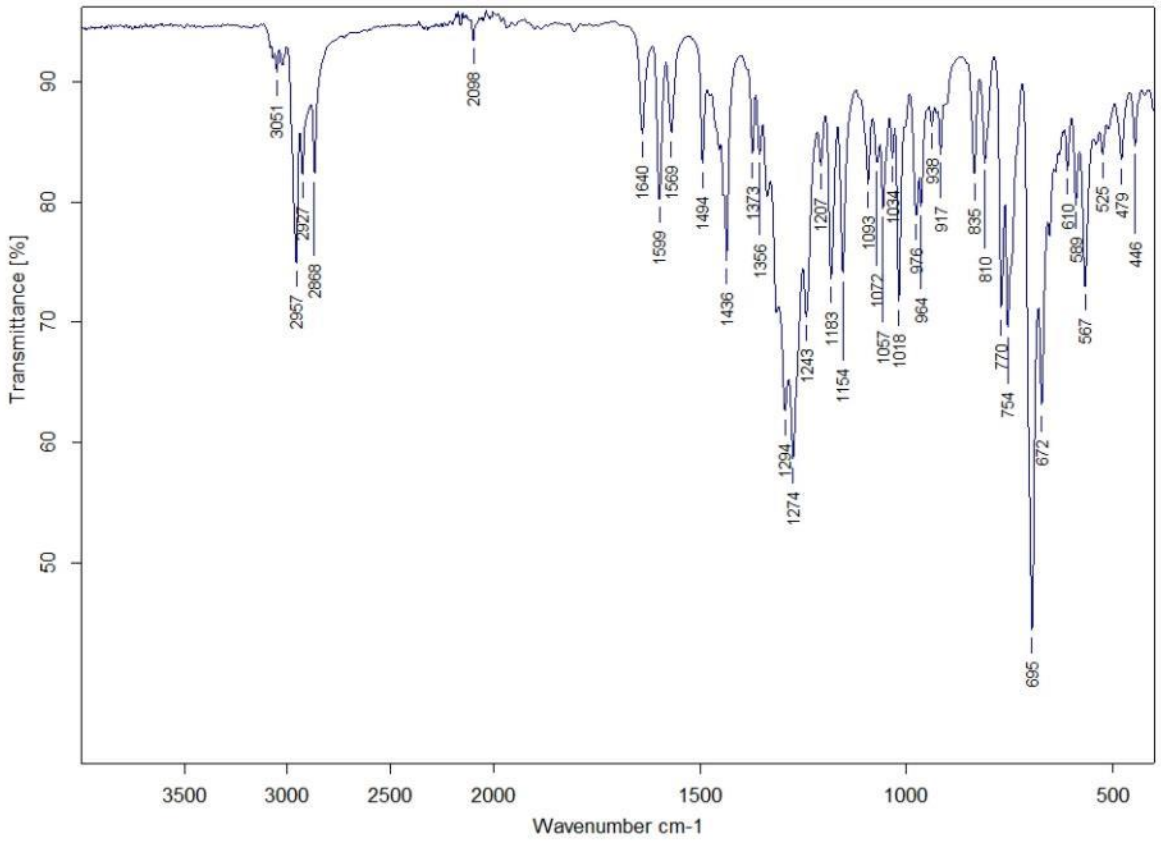


Figure S87. High Resolution Mass Spectrum (ESI+) of **6**.

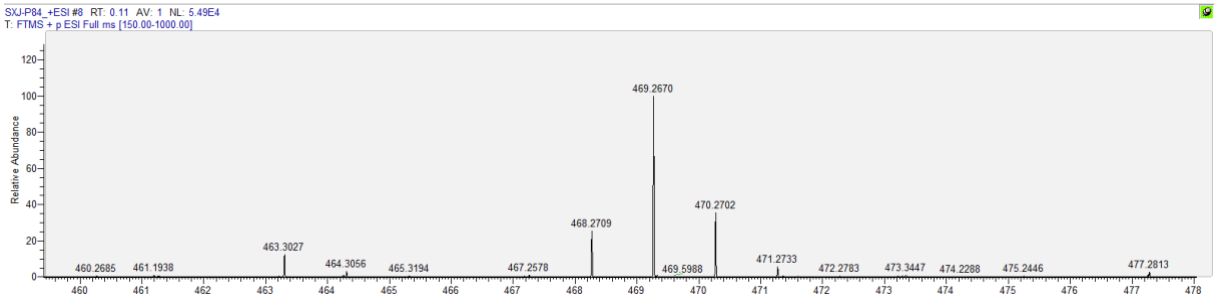


Figure S88. $_1$H NMR spectrum of **7** in $CDCl_3$.

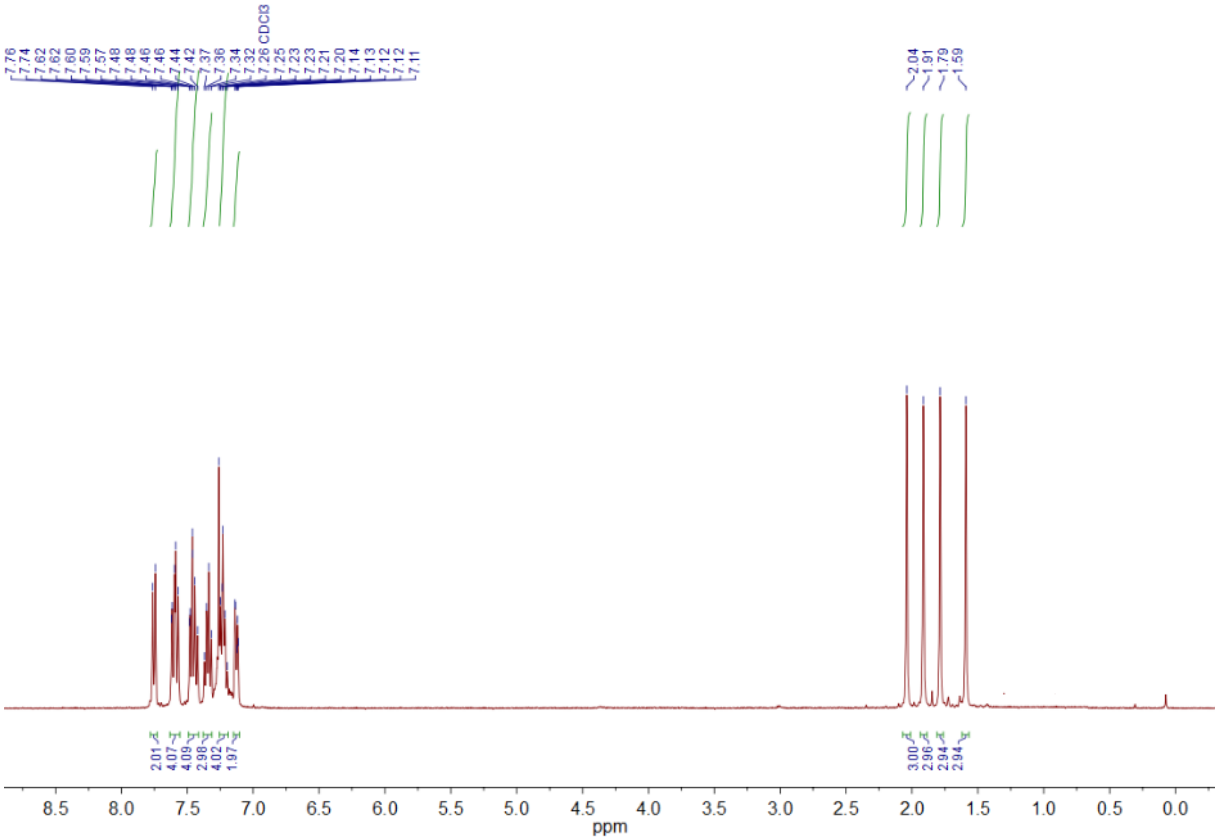


Figure S89. Expansion of $_1$H NMR spectrum of **7** in $CDCl_3$ (aryl region).

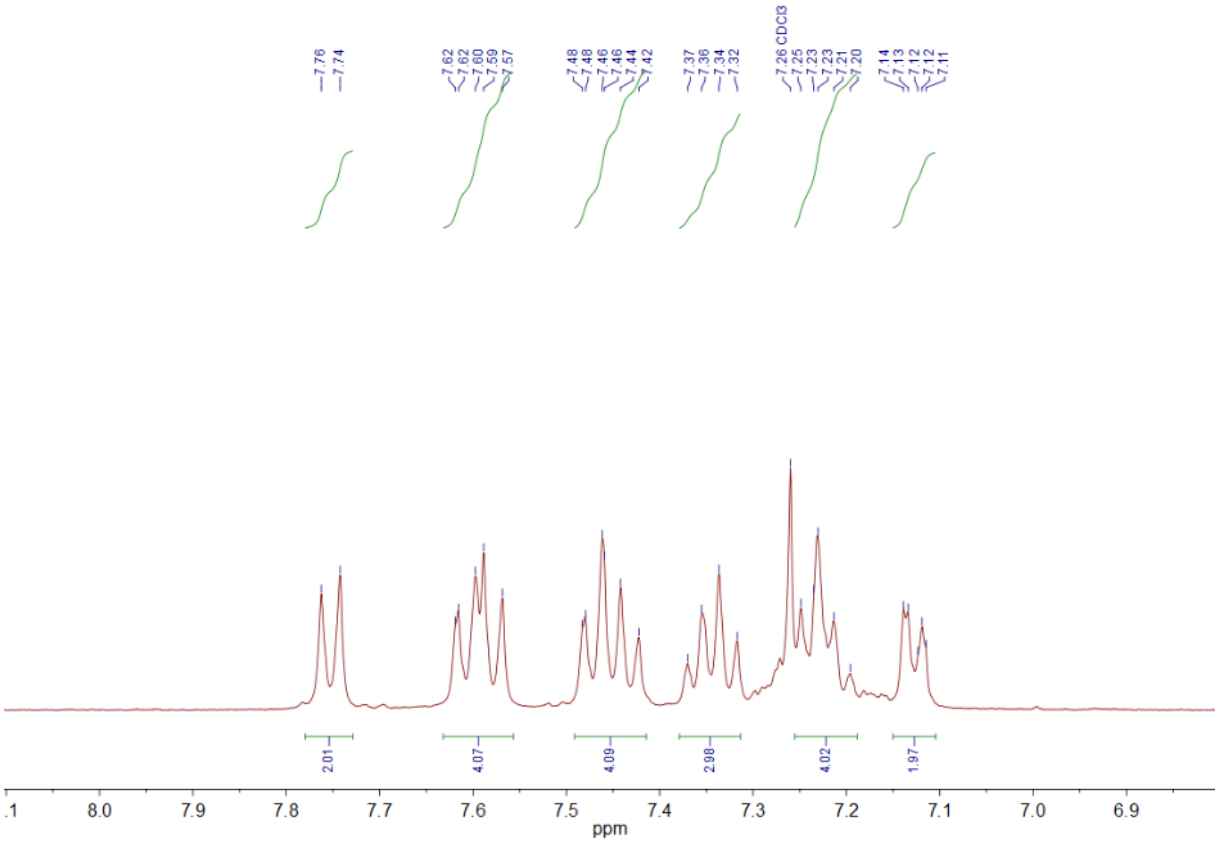


Figure S90. Expansion of ^{1}H NMR spectrum of **7** in $CDCl_3$ (aliphatic region).

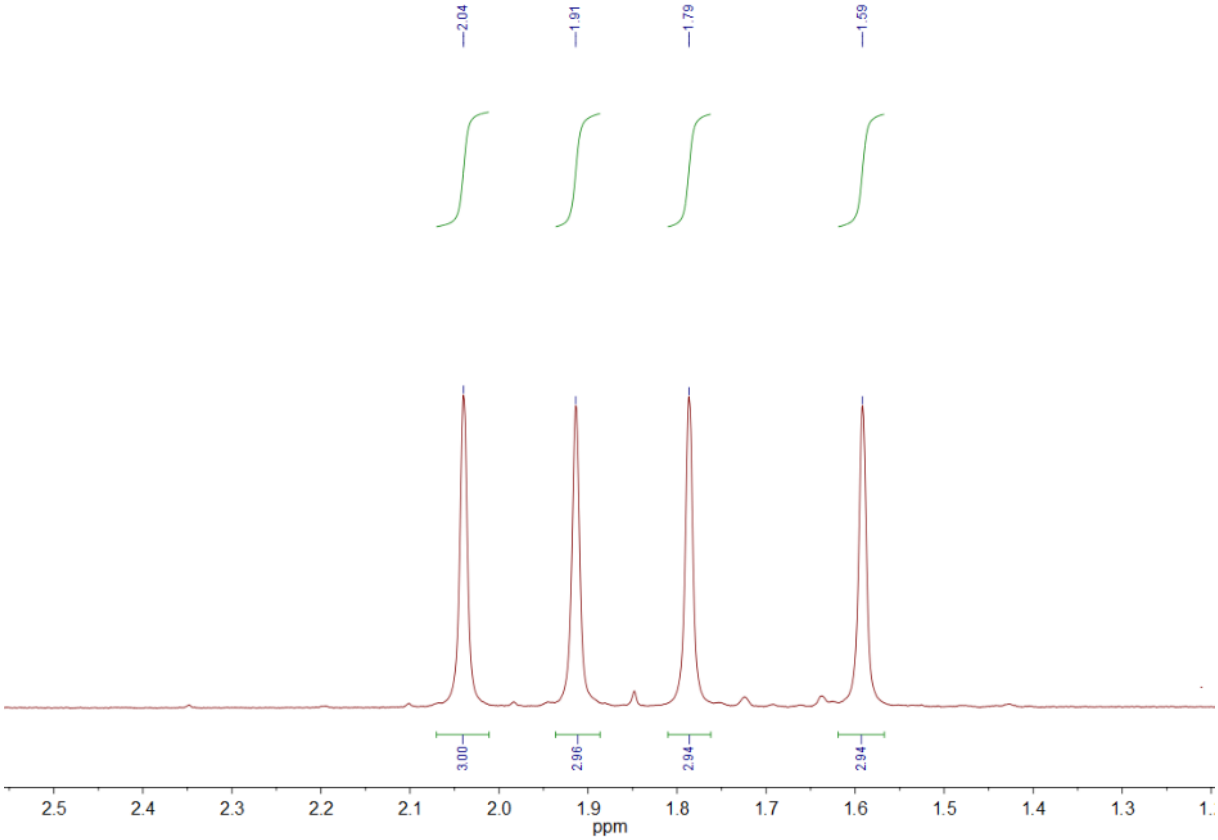


Figure S91. $^{13}C\{^{1}H\}$ NMR Spectrum of **7** in $CDCl_3$.

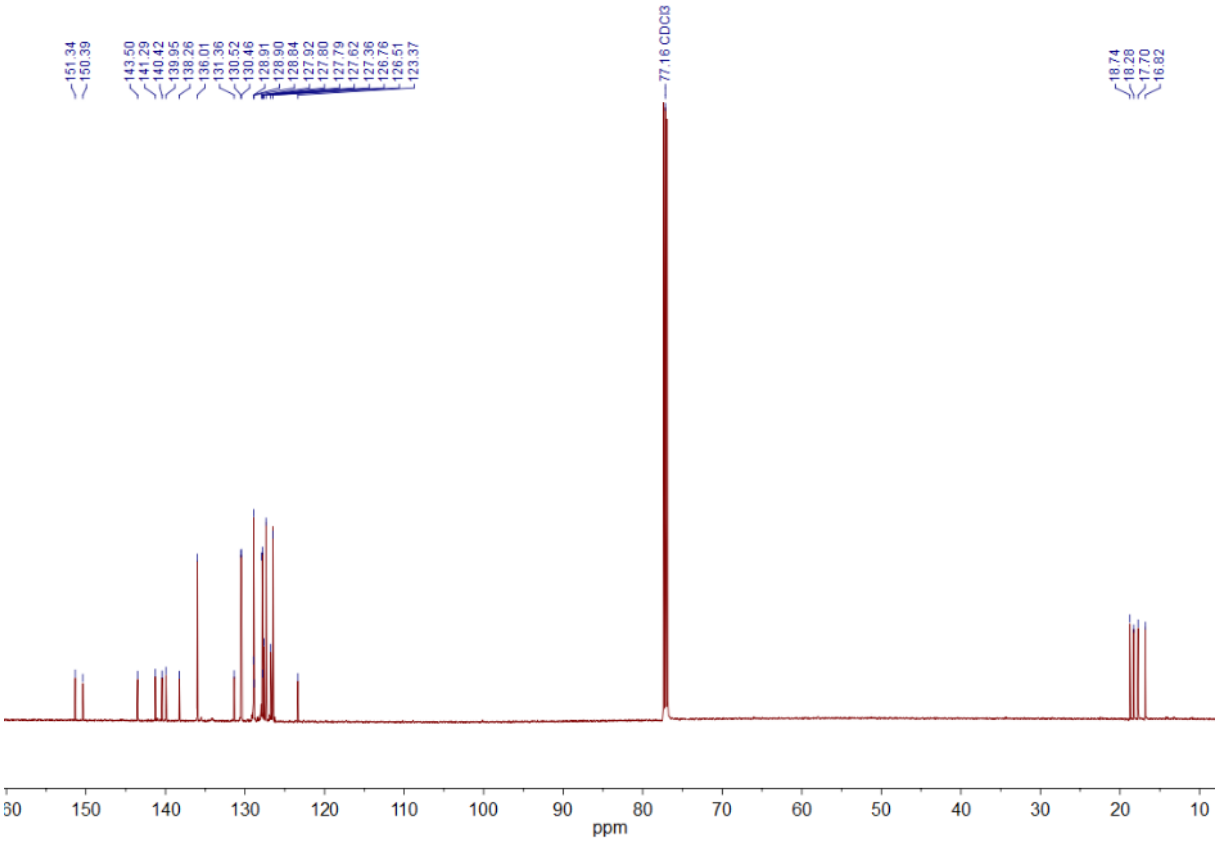


Figure S92. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **7** in $CDCl_3$ (aryl region).

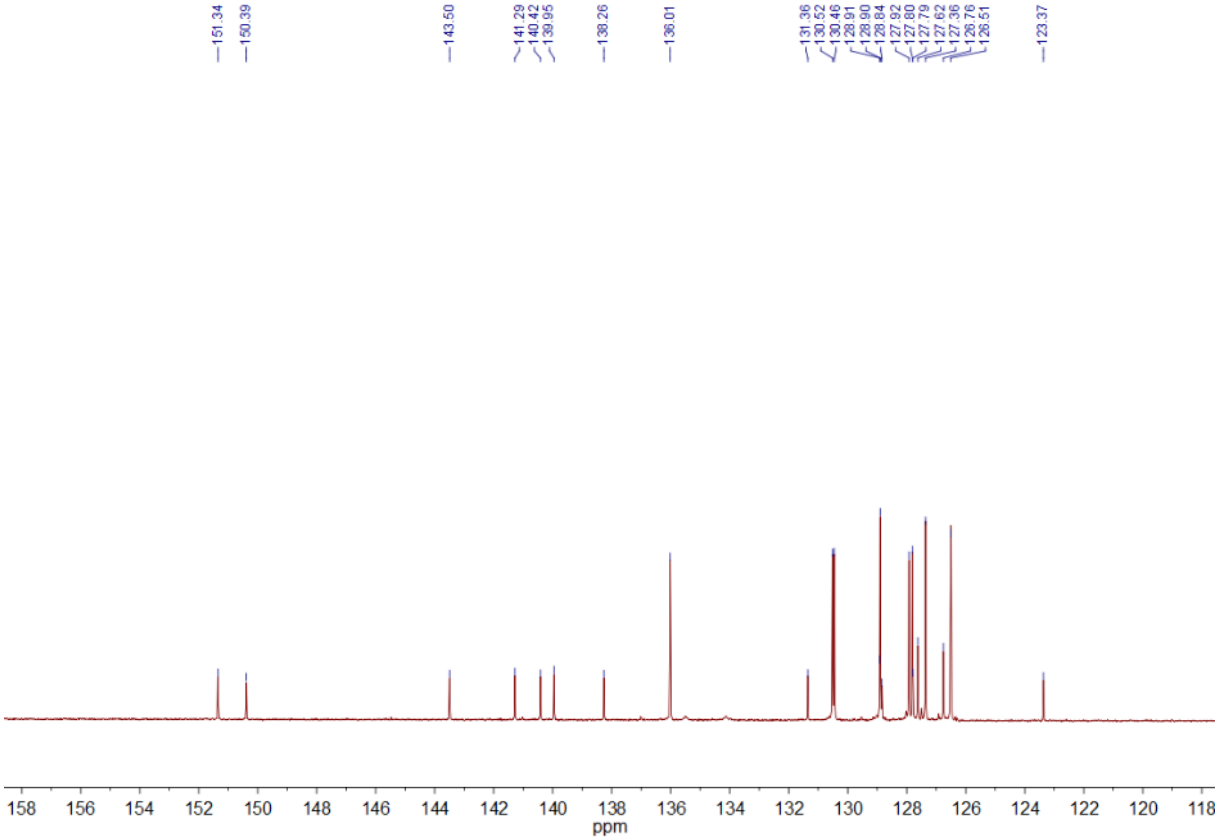


Figure S93. Expansion of $^{13}C\{^{1}H\}$ NMR Spectrum of **7** in $CDCl_3$ (aliphatic region).

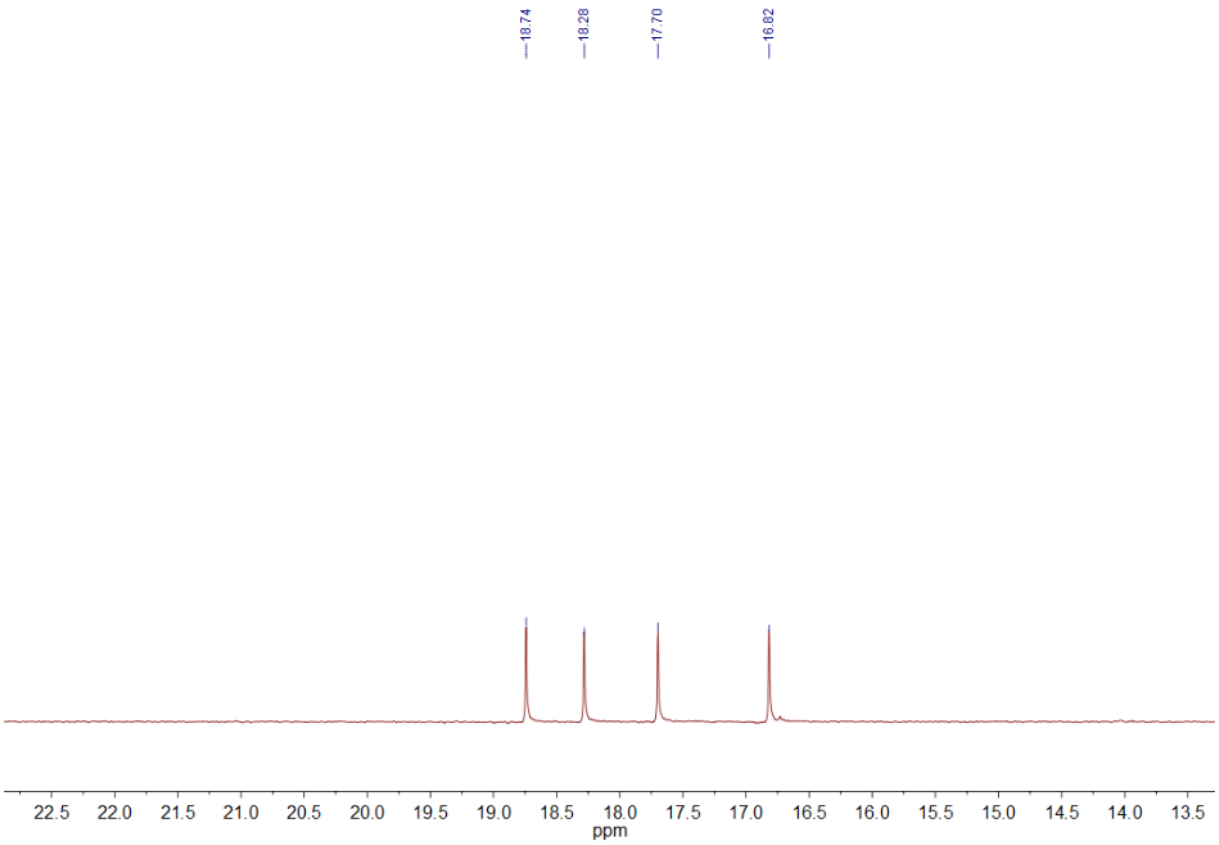


Figure S94. ^{13}C DEPT135 NMR Spectrum of **7** in $CDCl_3$.

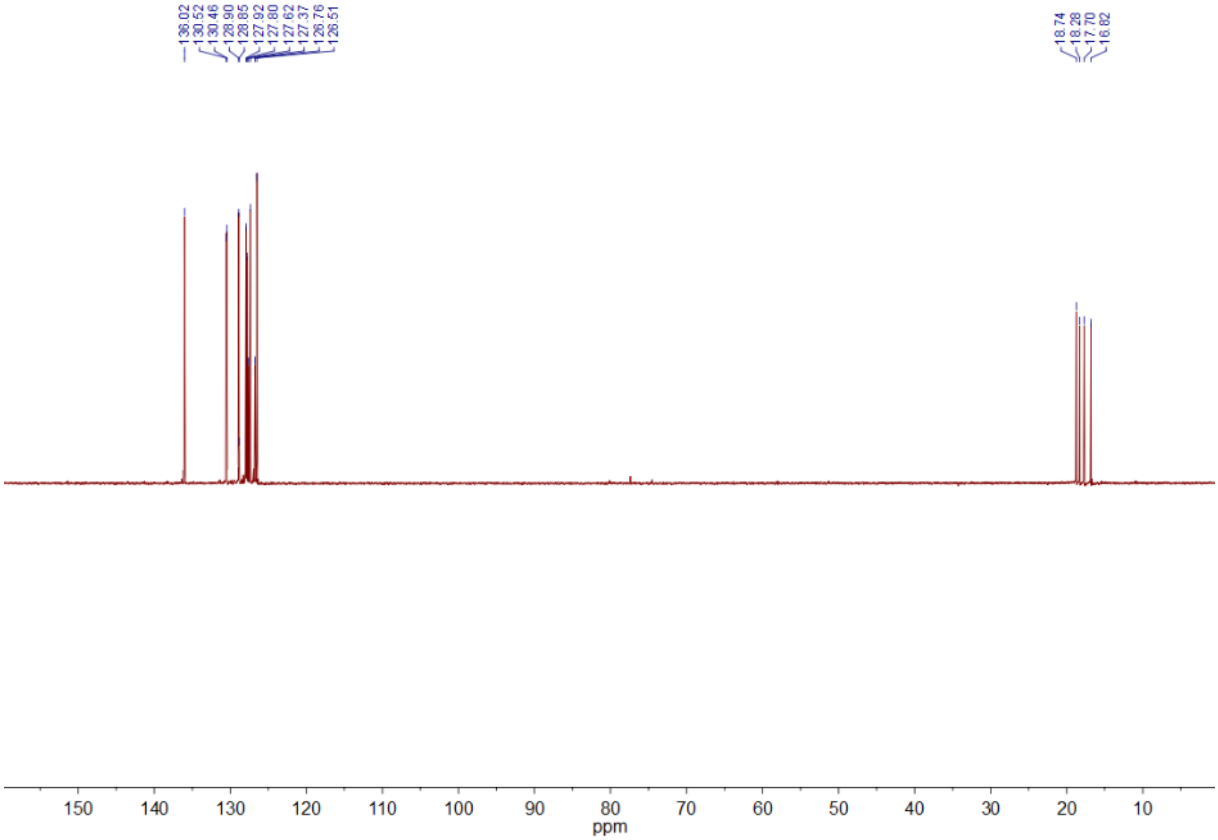


Figure S95. ^{11}B NMR Spectrum of **7** in $CDCl_3$.

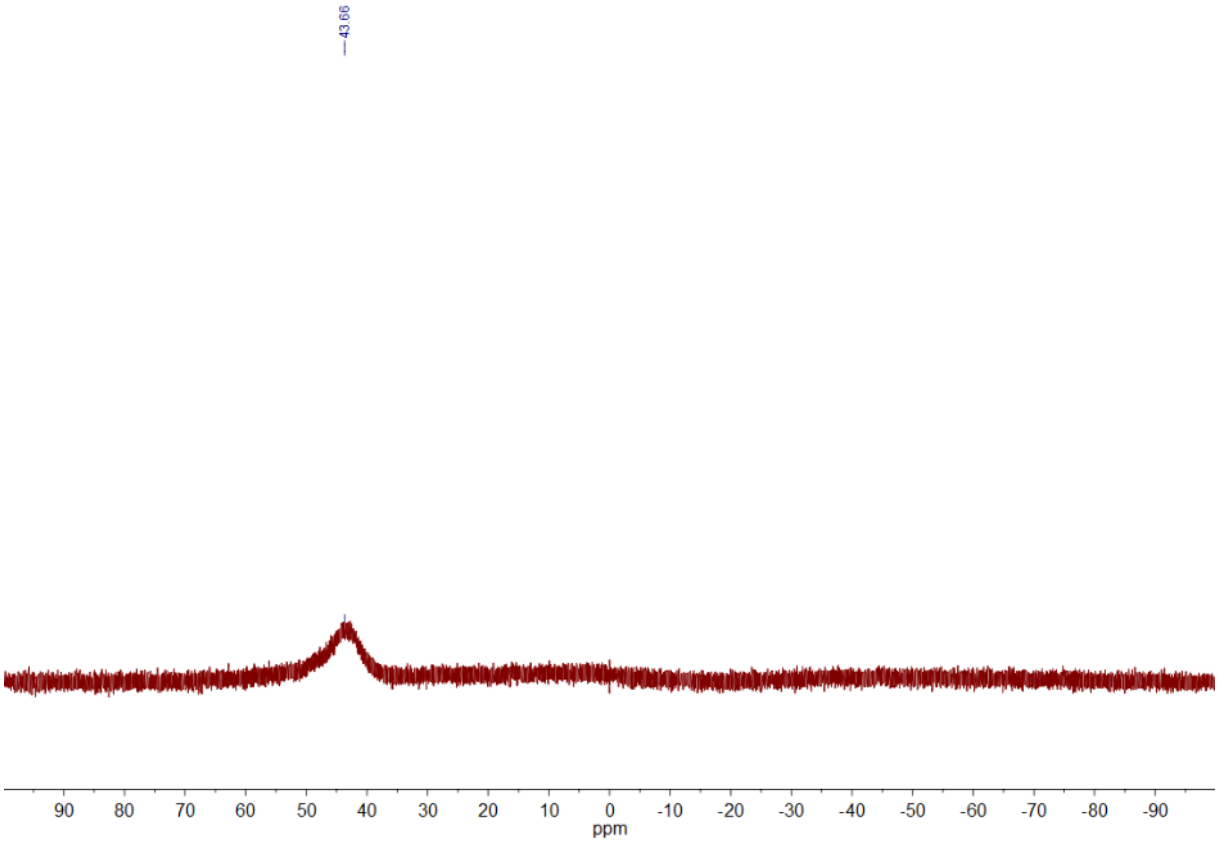


Figure S96. FT-IR Spectrum of **7**.

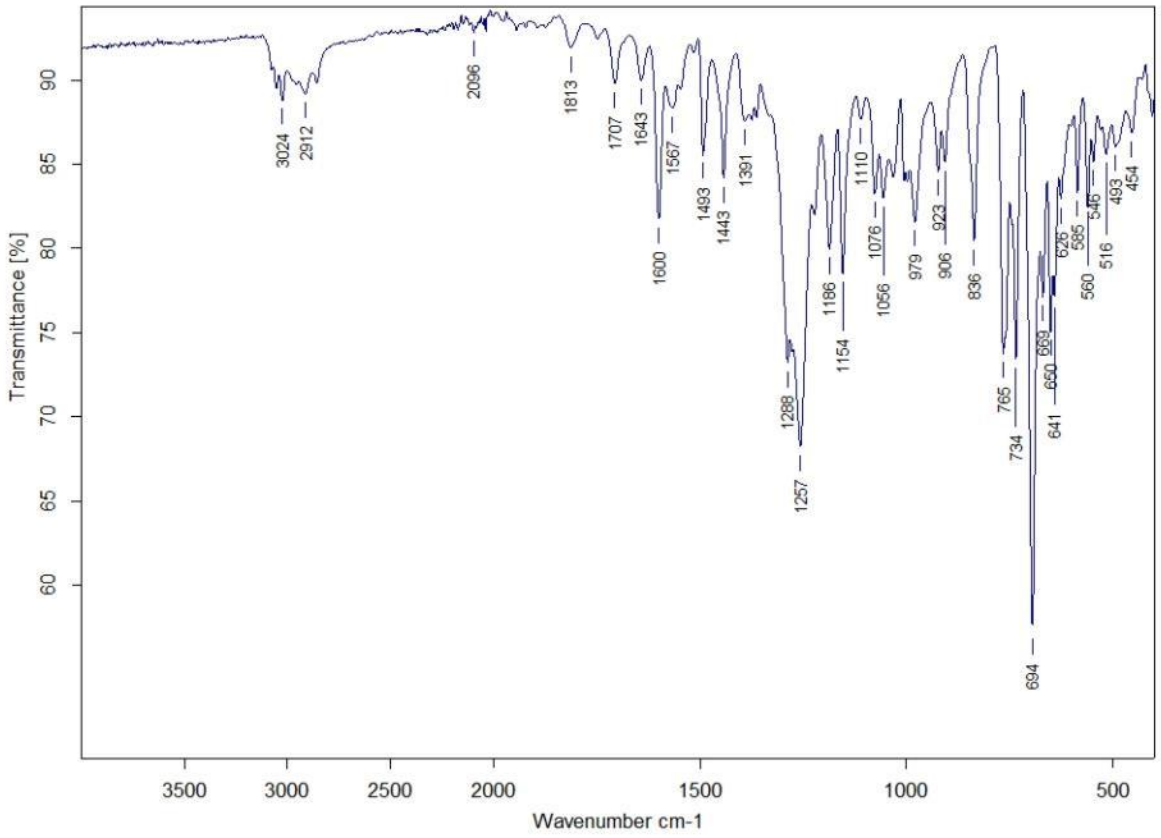


Figure S97. High Resolution Mass Spectrum (ESI+) of **7**.

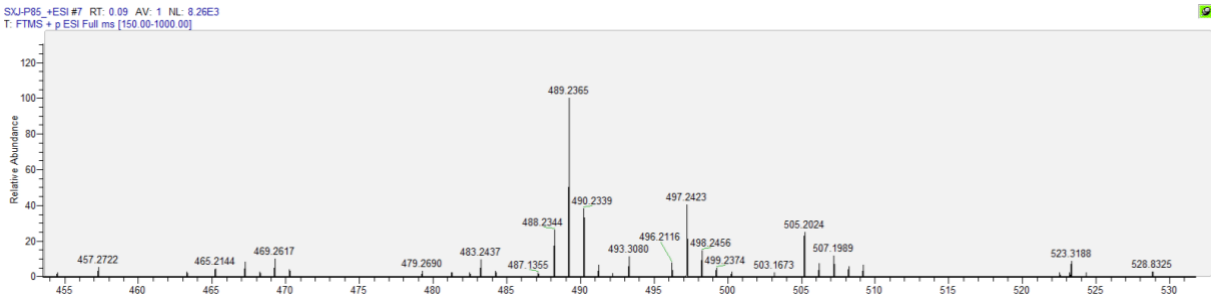


Figure S98. ^{1}H NMR spectrum of **C2** in $CDCl_3$.

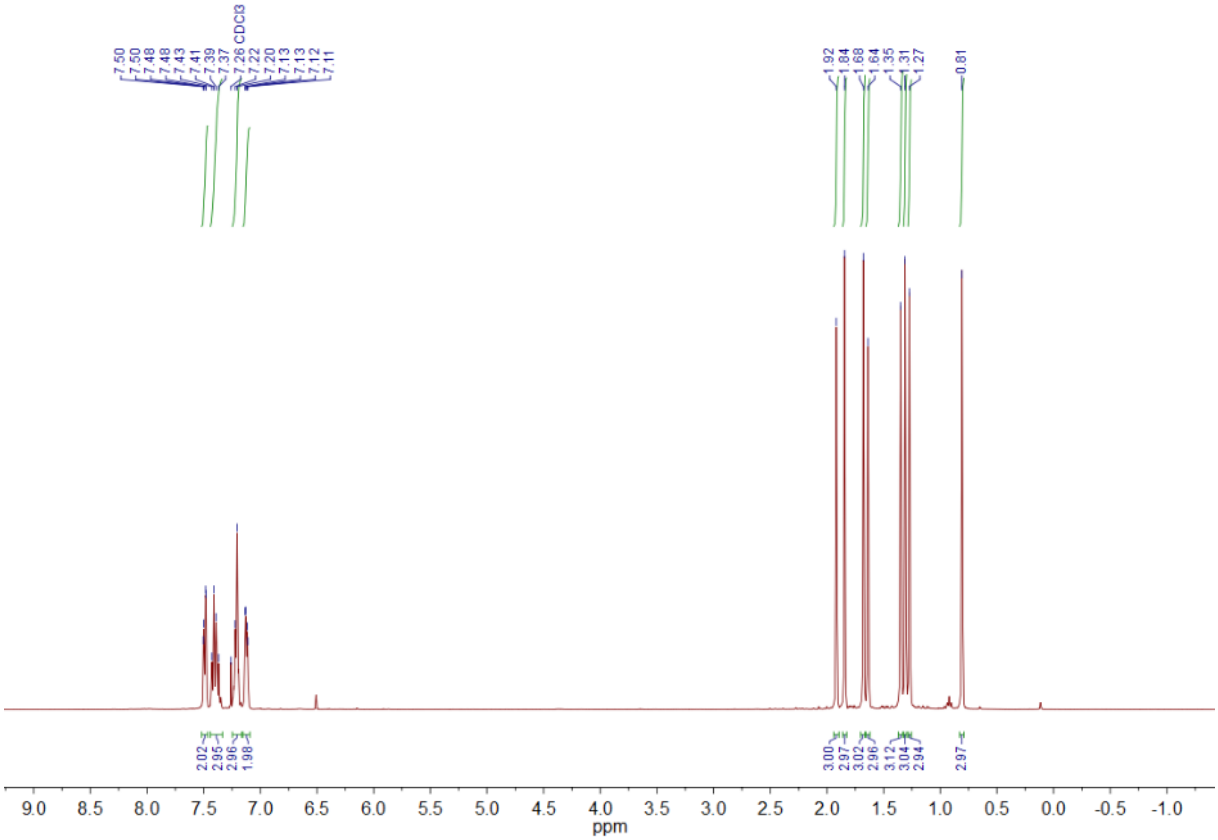


Figure S99. ^{11}B NMR spectrum of **C2** in $CDCl_3$.

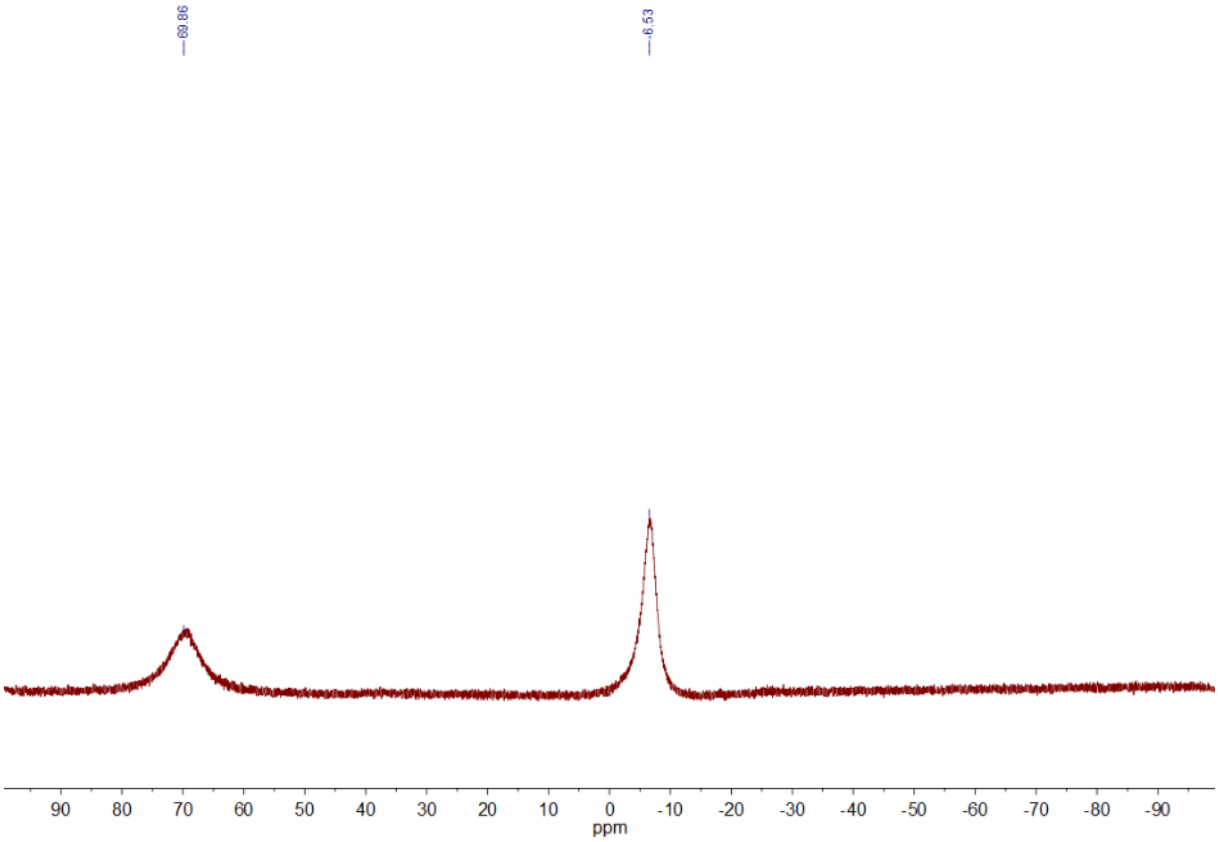


Figure S100. ^{1}H NMR spectrum of **C2** in Toluene-*d*$_8$.

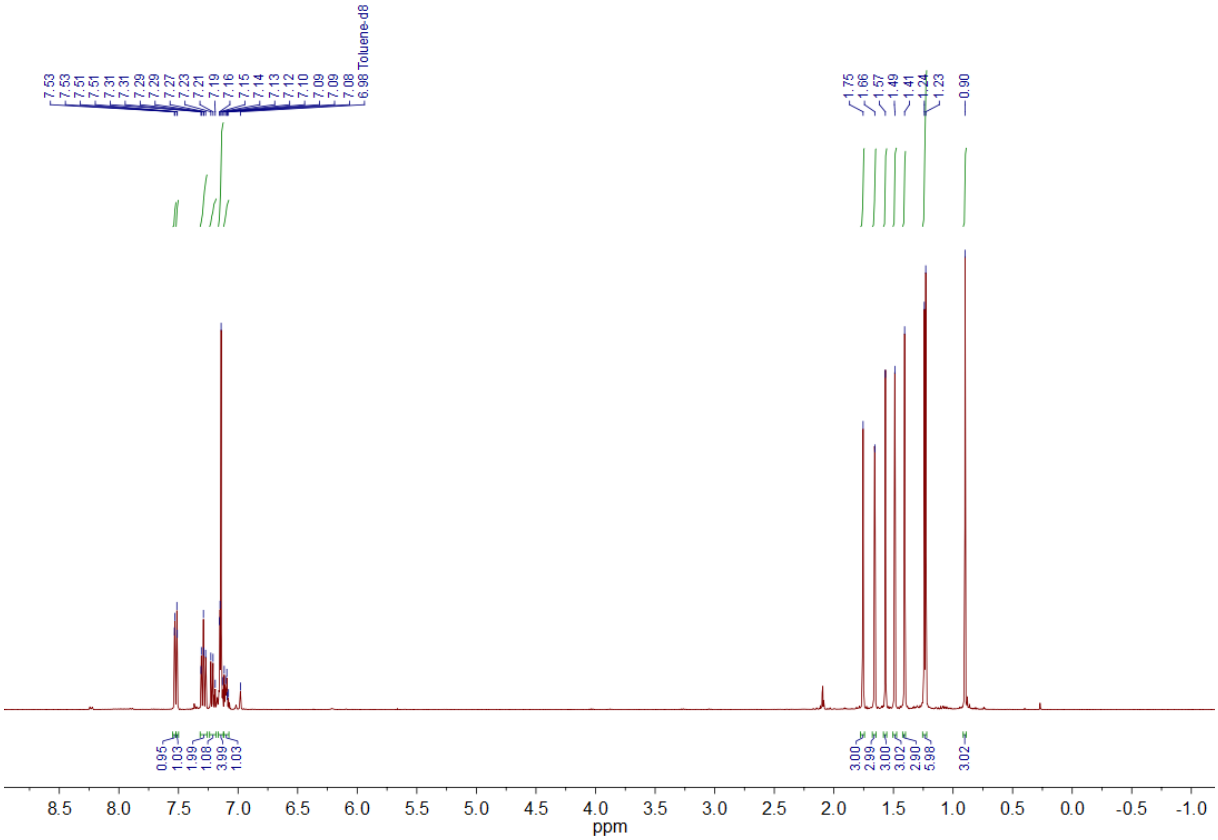


Figure S101. ^{11}B NMR spectrum of **C2** in Toluene-*d*$_8$.

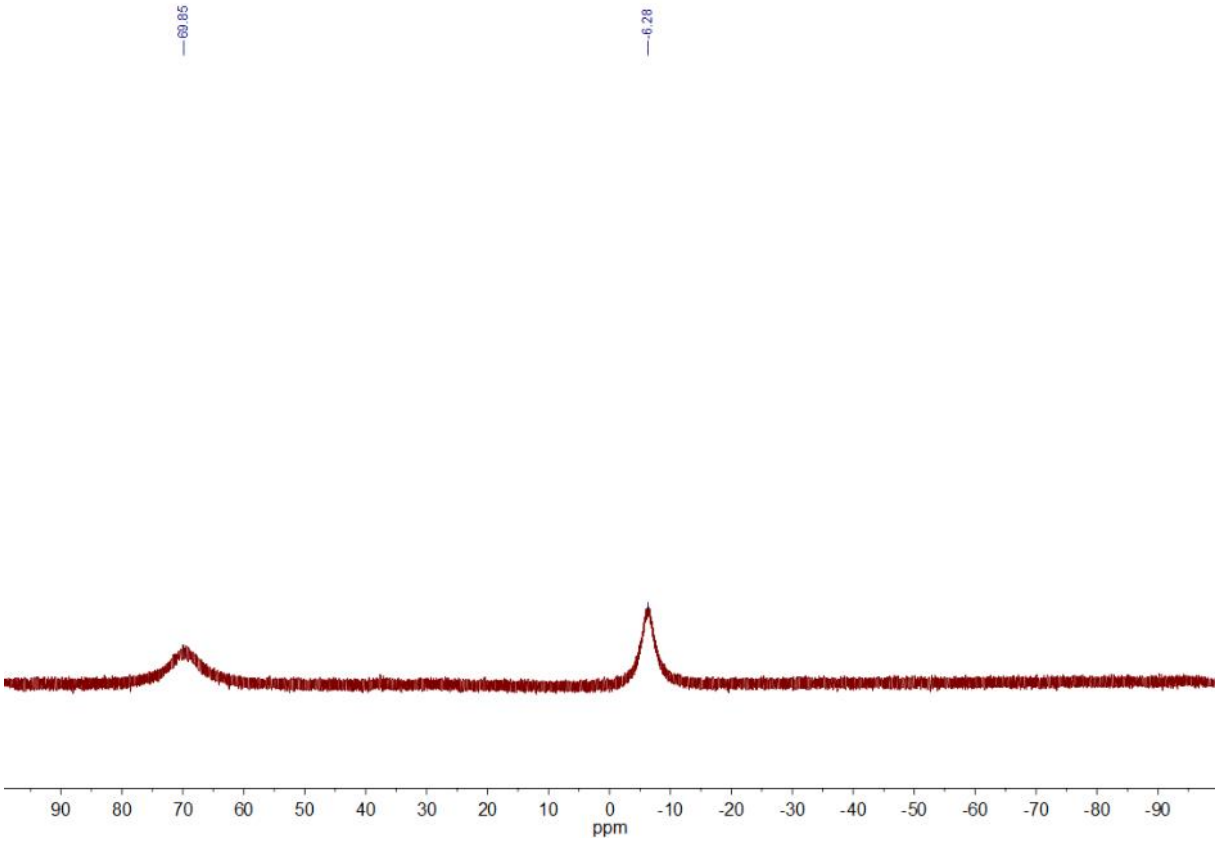


Figure S102. ^{1}H NMR spectra of **C2** in Toluene-*d*$_8$ at 27, 40, 50 ,60, 70 and 80 °C (bottom to top).

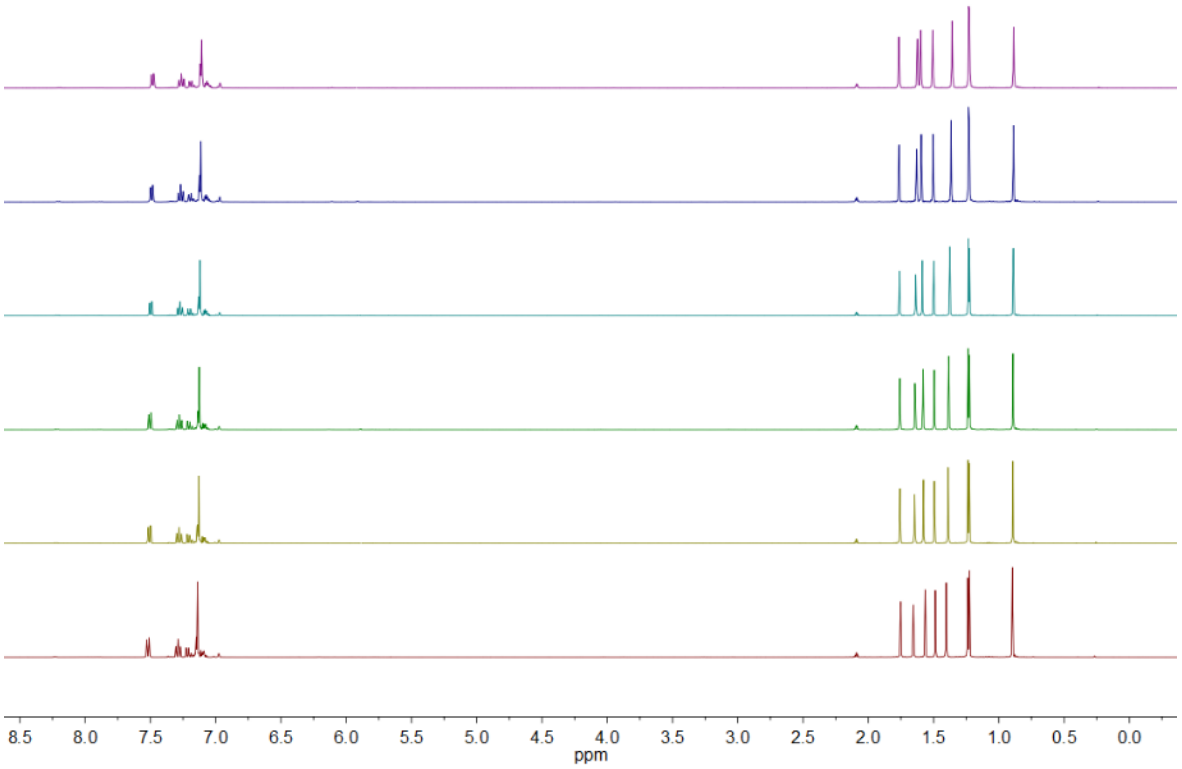


Figure S103. ^{11}B NMR spectra of **C2** in Toluene-*d*$_8$ at 27, 40, 50 ,60, 70 and 80 °C (bottom to top).

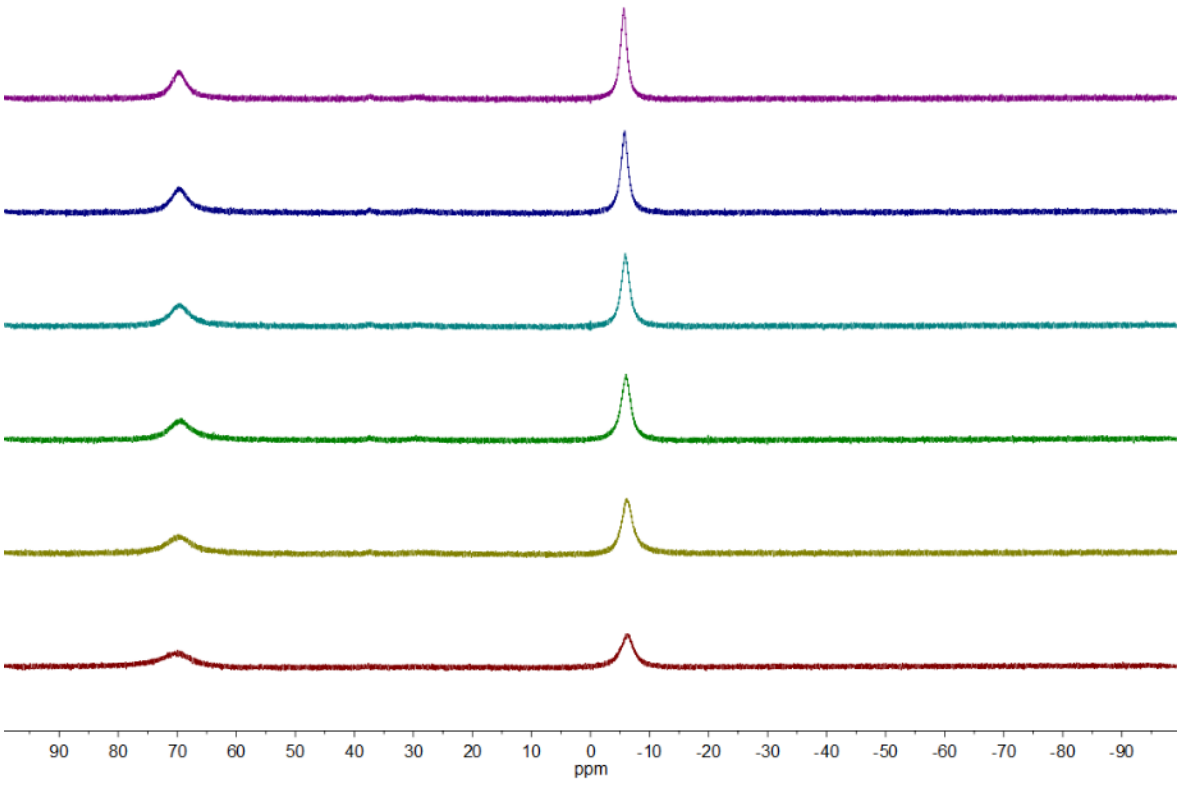


Figure S104. ^{1}H NMR spectra of **D2** in Toluene-*d*$_8$ at 27, 35, 45 ,60, 70 and 80 °C (bottom to top).

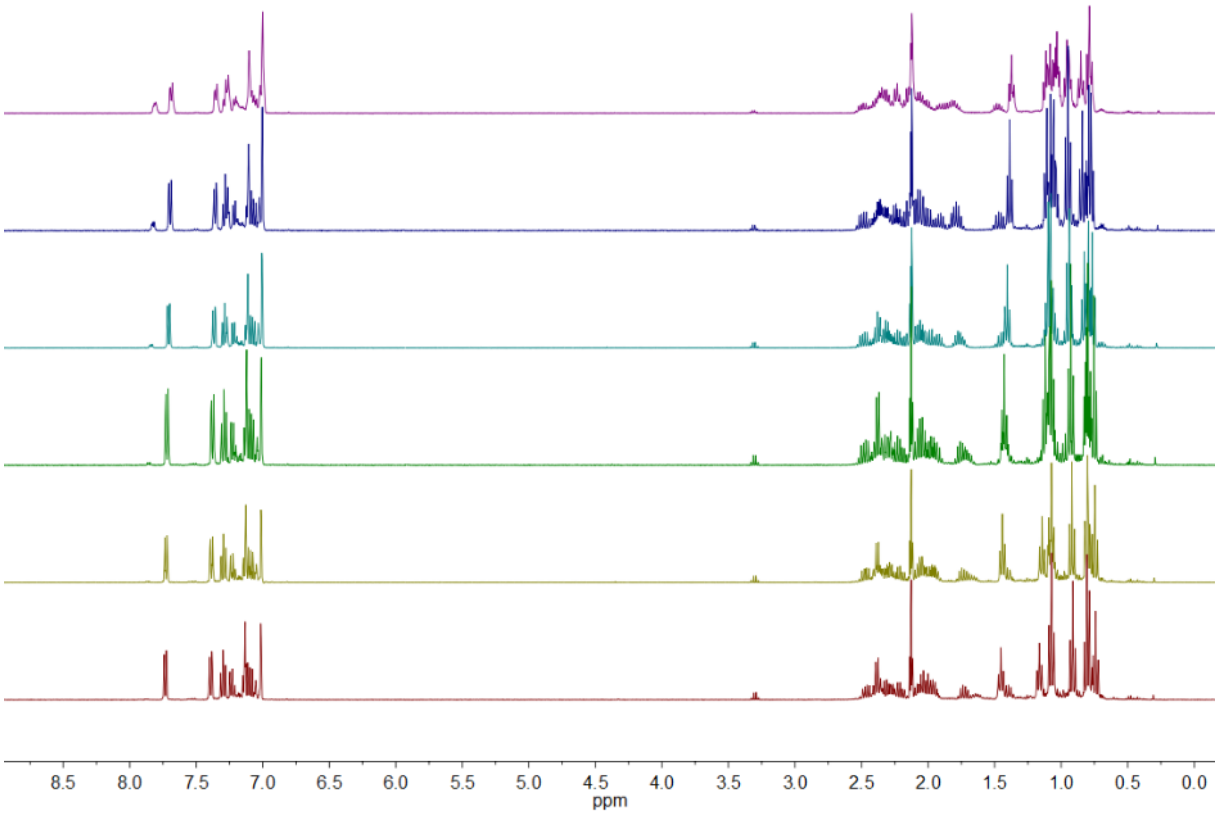


Figure S105. ^{11}B NMR spectra of **D2** in Toluene-*d*$_8$ at 27, 45 ,60, 70 and 80 °C (bottom to top).

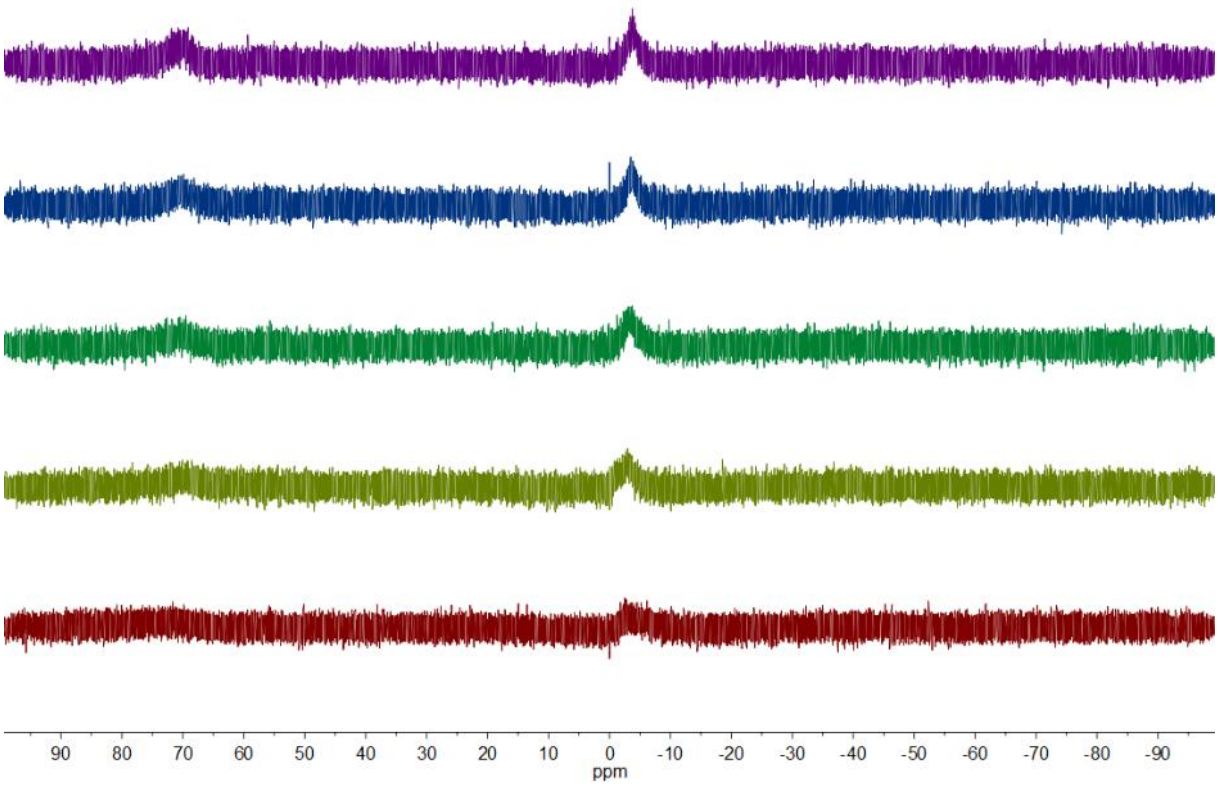


Figure S106. ^{1}H NMR spectra of **E2** in Toluene-*d*$_8$ at 27, 35, 50 ,65 and 80 °C (bottom to top).

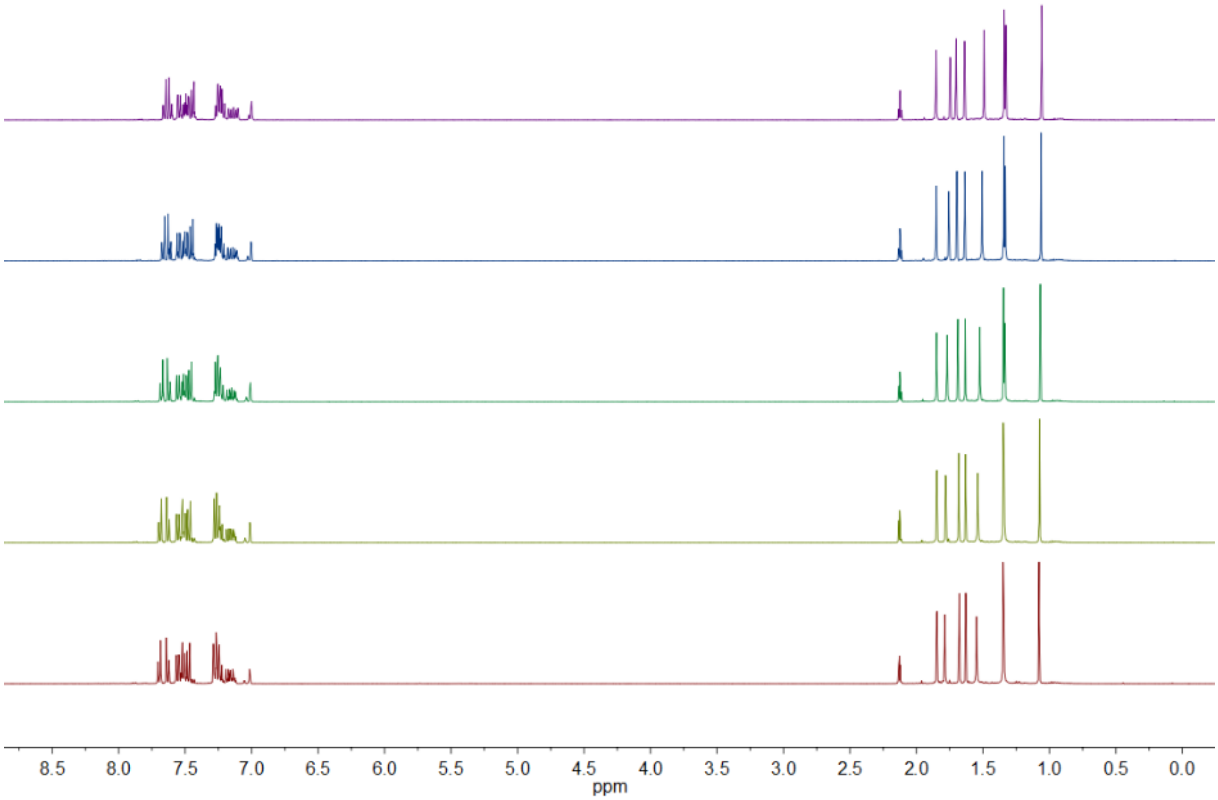


Figure S107. ^{11}B NMR spectra of **E2** in Toluene-*d*$_8$ at 27, 35 ,50, 65 and 80 °C (bottom to top).

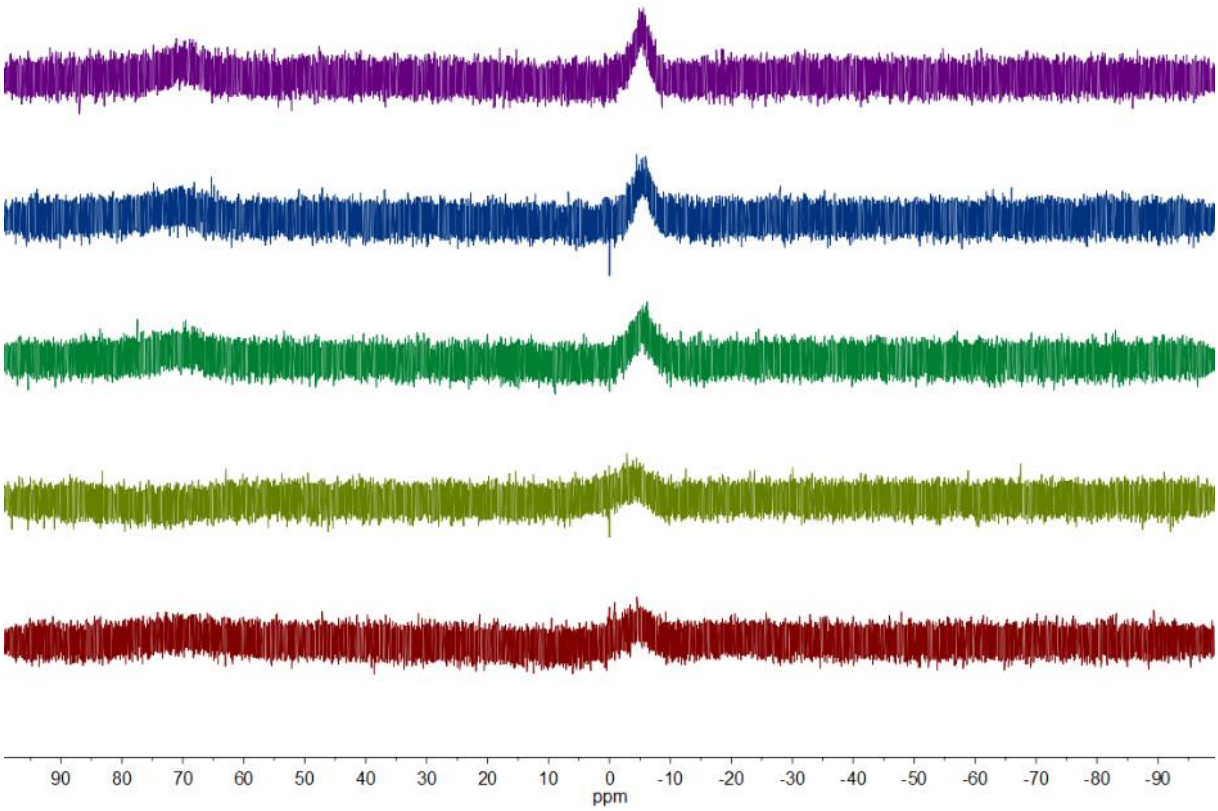
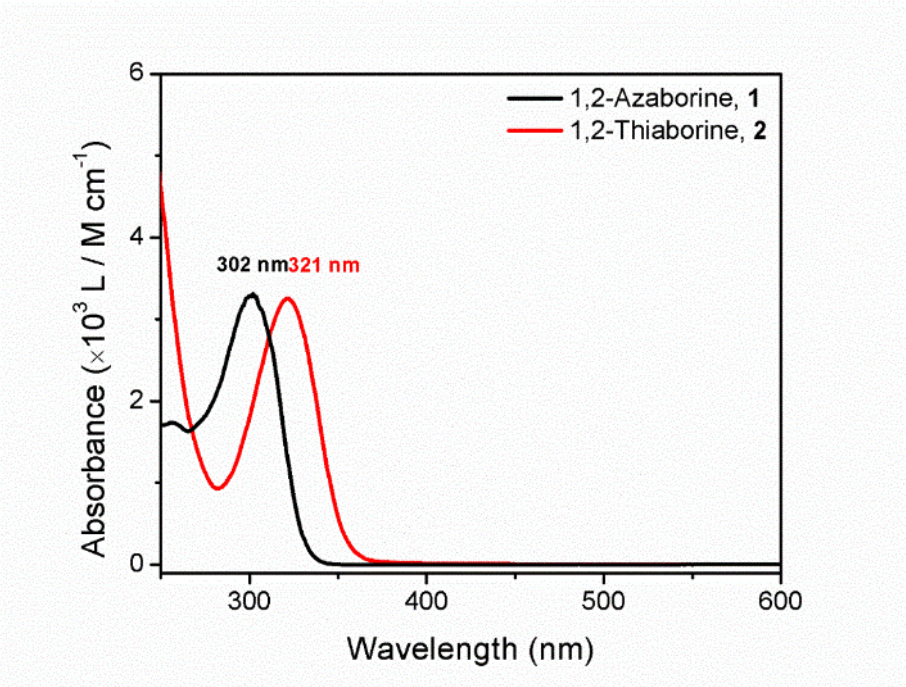


Table S1: Reactions of 1,2-thiaborine **2** with metal precursors to attempt to prepare η_1-coordination complexes.

Precursor	Dry Solvent, N_2 atm	Temperature	Time (h)	Result
$(Ph_3P)AuCl$	DCM	23 °C	24	NR
(THT)AuCl	DCM	23 °C	24	NR
Me_2SAuCl	DCM	23 °C	12	Unstable species*
Me_2SAuCl + AgOTf	DCM	23 °C	24	NR
Me_2SAuCl + $AgBF_4$	DCM/CH_3CN (1:1)	23 °C	24	NR
$HgCl_2$	DCM/Et_2O	23 °C	24	NR
$W(CO)_5(CH_3CN)$	$CHCl_3$	23 °C	12	NR
$W(CO)_5(CH_3CN)$	THF	60 °C	3	NR

Note: NR indicates no reaction was observed by ^{11}B NMR spectroscopy. *A new boron peak at 11.9 ppm was observed by in situ ^{11}B NMR spectroscopy but this species is unstable and we have been unable to isolate or characterize it.

Figure S108. UV absorption spectra of **1** and **2** in CH_2Cl_2.



1 (302 nm): ε = 3311 $Lmol^{-1}$ cm^{-1}; **2** (321 nm): ε = 3253 $Lmol^{-1}$ cm^{-1}

Figure S109. Normalized emission spectra of **1** and **2** in CH_2Cl_2 (compounds excited at 302 and 321 nm respectively). Concentrations of samples **1**: 5.22 × 10^{-6} M; **2**: 4.82 × 10^{-6} M.

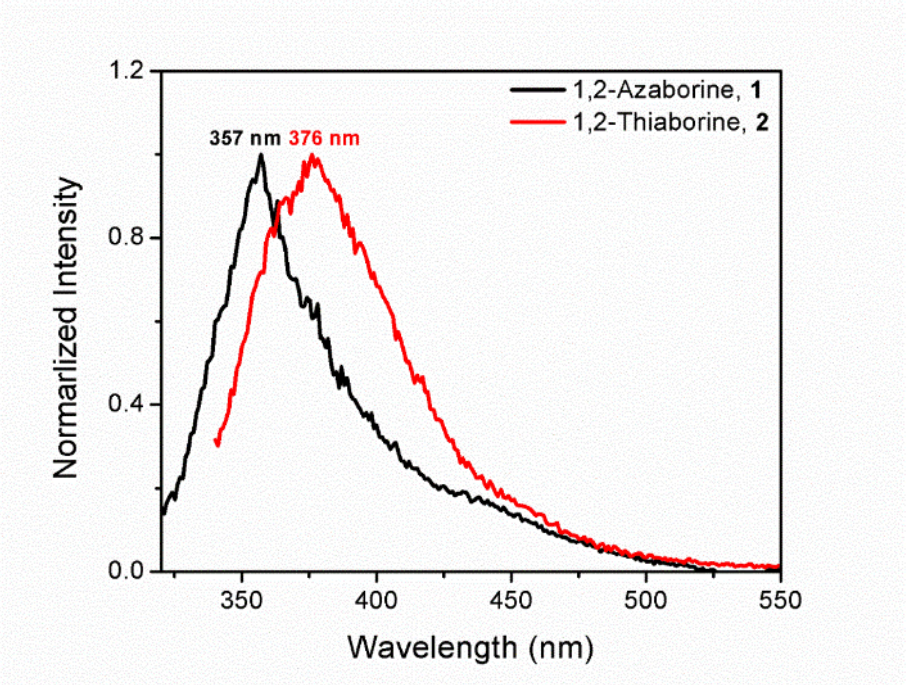


Figure S110. (a) Solid-state structure of **3**. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å): B(1)–O(1) 1.366(5), O(1)–C(1) 1.452(5), C(1)–C(2) 1.542(5), C(2)–C(3) 1.348(5), C(3)–C(4) 1.486(5), C(4)–C(5) 1.347(5), C(5)–B(1) 1.563(5); (b) View of the seven-membered ring; (c) Diagram illustrating the θ_{prow} and θ_{stern} defining the deviation of the ring from planarity into a boat-like confirmation.

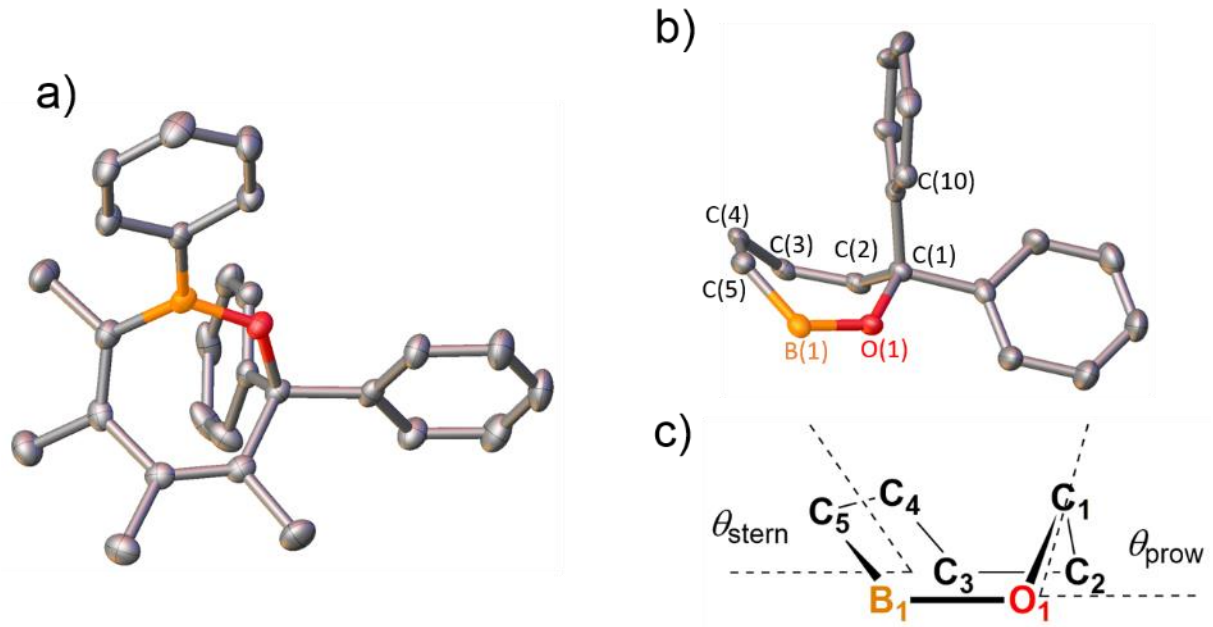


Figure S111. (a) Solid-state structure of **4**. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å): B(1)–O(1) 1.368(2), O(1)–C(1) 1.392(3), C(1)–C(2) 1.484(2), C(2)–C(3) 1.346(2), C(3)–C(4) 1.489(2), C(4)–C(5) 1.353(3), C(5)–B(1) 1.558(3), C(1)–C(10) 1.345(3); (b) View of the seven-membered ring; (c) Diagram illustrating the θ_{prow} and θ_{stern} defining the deviation of the ring from planarity into a boat-like confirmation.

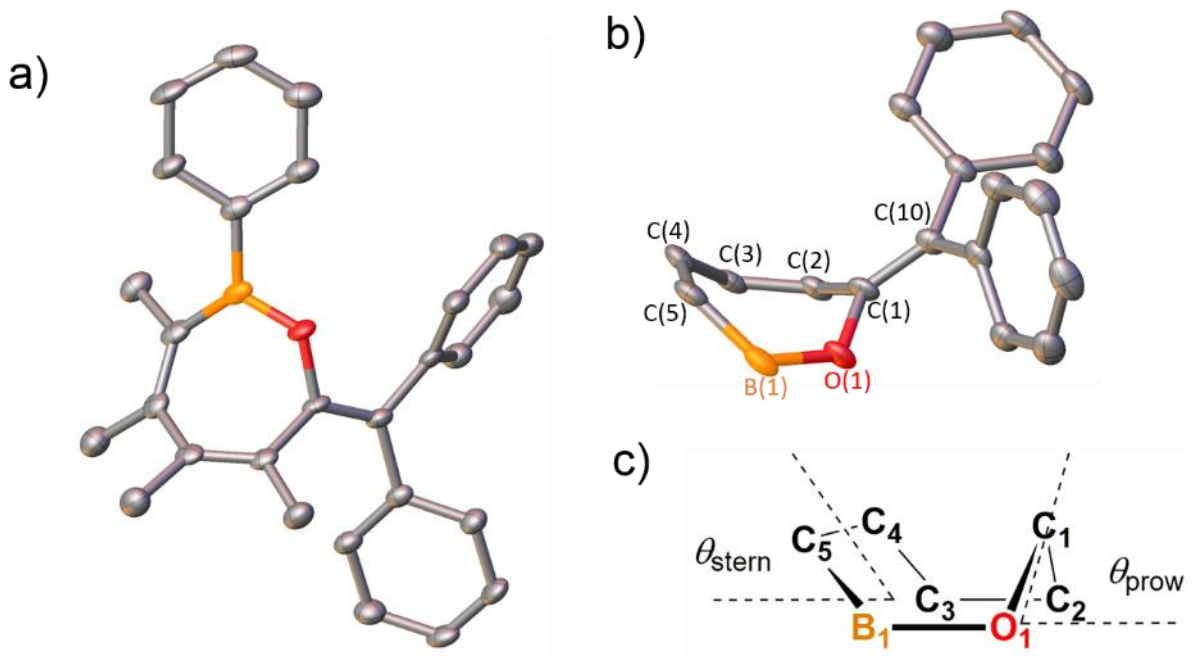


Figure S112. (a) Solid-state structure of **6**. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å): B(1)–O(1) 1.368(2), O(1)–C(1) 1.398(2), C(1)–C(2) 1.489(2), C(2)–C(3) 1.351(2), C(3)–C(4) 1.500(2), C(4)–C(5) 1.351(2), C(5)–B(1) 1.561(1), C(1)–C(10) 1.345(2); (b) View of the seven-membered ring; (c) Diagram illustrating the θ_{prow} and θ_{stern} defining the deviation of the ring from planarity into a boat-like confirmation.

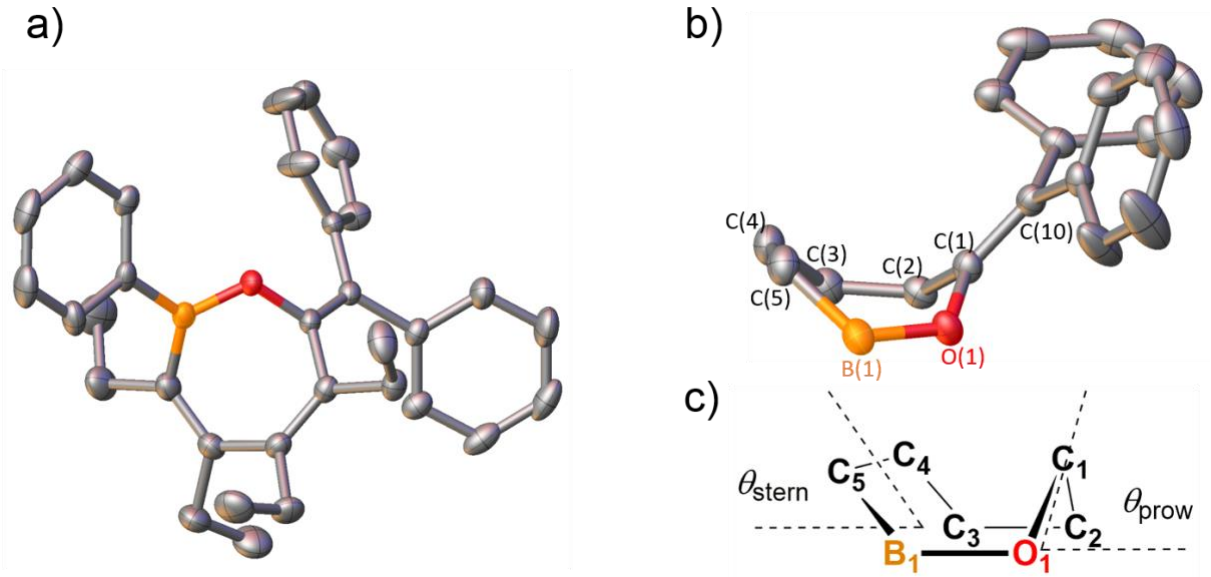


Figure S113. (a) Solid-state structure of **7**. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å): B(1)–O(1) 1.372(2), O(1)–C(1) 1.398(2), C(1)–C(2) 1.483(2), C(2)–C(3) 1.341(2), C(3)–C(4) 1.482(2), C(4)–C(5) 1.355(2), C(5)–B(1) 1.563(2), C(1)–C(10) 1.340(2); (b) View of the seven-membered ring; (c) Diagram illustrating the θ_{prow} and θ_{stern} defining the deviation of the ring from planarity into a boat-like confirmation.

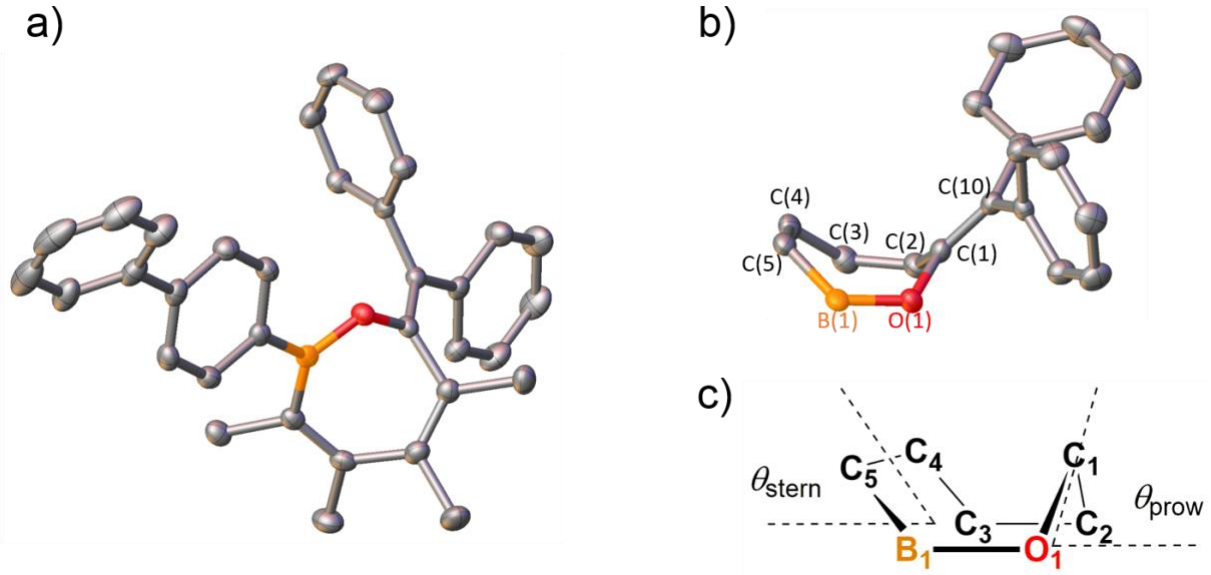


Table S2: X-ray crystallographic details for compounds **1**, **2•Cr(CO)$_3$**, **3-7**, and **D$_2$**.

Compound	**1**	**2•Cr(CO)$_3$**	**3**	**4**	**5**	**6**	**7**	**D$_2$**
CCDC #	1942996	1942997	1942998	1942999	1943000	1960238	1960239	1960237
Empirical Formula	$C_{20}H_{22}BN$	$C_{17}H_{17}BCrO_3S$	$C_{27}H_{27}BO$	$C_{28}H_{27}BO$	$C_{28}H_{29}BO$	$C_{32}H_{35}BO$	$C_{34}H_{31}BO$	$C_{36}H_{50}B_2$
FW (g/mol)	287.19	364.17	378.29	390.30	392.32	446.41	466.40	504.38
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space Group	F d d 2	P 2$_1$/c	C c	P -1	P 2$_1$/n	P 2$_1$/c	P b c a	P -1
a (Å)	39.763(2)	11.6050(5)	13.4410(8)	8.7781(9)	14.454(2)	10.6036(3)	10.0358(4)	9.0350(4)
b (Å)	37.788(2)	9.0305(5)	13.1854(8)	10.9283(11)	7.2349(7)	17.5824(5)	12.1076(6)	12.0924(6)
c (Å)	8.9491(5)	15.7985(8)	24.0772(16)	12.3004(12)	21.474(3)	17.4460(5)	43.226(2)	14.7514(7)
α (deg)	90	90	90	70.809(4)	90	90	90	92.899(2)
β (deg)	90	102.1274(16)	94.762(2)	87.538(5)	100.708(4)	125.621(1)	90	103.022(2)
ɣ (deg)	90	90	90	79.597(5)	90	90	90	103.134(2)
V (Å$_3$)	13446.6(12)	1618.72(14)	4252.4(5)	1095.91(19)	2206.6(5)	2643.98	5252.3(4)	1520.32(13)
Z	32	4	8	2	4	4	8	2
D$_c$ (Mg m^{-3})	1.135	1.494	1.182	1.183	1.181	1.121	1.180	1.102
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0
R1[I>2σ]	0.0468	0.0325	0.0437	0.0472	0.0553	0.0561	0.0542	0.0708
wR2(F$_2$)	0.1391	0.0778	0.1127	0.1213	0.1356	0.1426	0.1484	0.2090
GOF (S)	1.075	1.053	1.098	1.049	1.006	1.075	1.190	1.224

References

1. a) P. J. Fagan, E. G. Burns, J. C. Calabrese. *J. Am. Chem. Soc*. **1988**, *110*, 2979; b) E. C. Taylor, A. McKillop, G. H. Hawks. *Org. Synth*. **1972**, *52*, 36.

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