Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supporting Information

Metal-Catalyzed B–H Acylmethylation of Pyridylcarboranes: Access to Carborane-Fused Indoliziniums and Quinoliziniums

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1. General considerations

o-Carborane containing starting materials[1] and sulfoxonium ylides[2] were synthesized according to literature methods. Unless otherwise noted, all the solvents and commercially available reagents were purchased from commercial sources and used directly. Toluene, THF, and Et_2O were refluxed and distilled over sodium/benzophenone under nitrogen. CH_2Cl_2, 1,2-dichloroethane (DCE) and CH_3CN were refluxed and distilled over CaH_2 under nitrogen. All manipulations were carried out under standard Schlenk techniques or in a glove box, unless otherwise stated. Glass-backed Silica Gel 60 thin-layer chromatography (TLC) plates were used as received. Column chromatography was performed on Silica Gel 60 (200–300 or 300–400 mesh). TLC samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6 M HCl and were developed with heating using a heat gun.

Spectroscopic Measurements. ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers in ambient conditions unless otherwise stated. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. Note that H_2O resonances are often present due to high humidity. ^{11}B chemical shifts were measured utilizing external $BF_3 \cdot Et_2O$ ($\delta^{11}B = 0.00$ ppm) as reference. ^{19}F NMR spectra were referenced to fluorobenzene ($\delta = -113.15$ ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d =doublet, t = triplet, q = quartet and m = multiplet), coupling constant (*J* values) in Hz and integration. The high-resolution mass spectra (HRMS) were recorded on a Thermo Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ Mass Spectrometer for ESI-MS. Fluorescence spectral measurements were carried out by using a Hitachi F-4600 fluorescence spectrophotometer. Electronic absorption spectra were recorded with Shimadzu UV-2550 spectrophotometers.

X-ray Crystallography. X-ray diffraction data of **3a**, **3p**, **5m**, **6e**, **7h**, **12** **13a** and **14** (CCDC No. 2004239-2004241, 2025251, 2110467, 2088268-2088269 and 2089805) were collected on a Bruker APEX2 microsource diffractometer or Bruker D8 Quest diffractometer by means of graphitemonochromated Mo Kα radiation. During the collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption by using the SADABS program.[3] The structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL or Olex2 crystallographic software package.[4] All non-hydrogen atom positions were determined utilizing the difference Fourier synthesis. The hydrogen atoms were placed at geometrically calculated positions, which were refined using a riding model. All calculations were performed by applying the Bruker SMART program. X-ray data can be obtained from the Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures/.

2. Experimental section

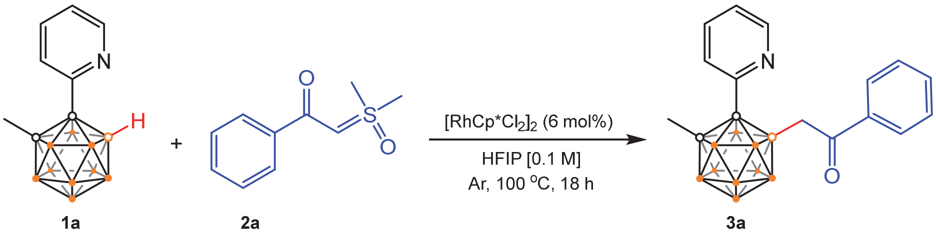
2.1 General procedure for preparation of sulfoxonium ylides

Scheme S1. Synthesis of sulfoxonium ylide **2a**.

A representative procedure. To a stirred solution of potassium tert-butoxide (3.0 g, 27.2 mmol) in THF (30 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture was refluxed for 2h under argon. Then reaction mixture was cooled to 0 °C, followed by addition of acyl chlorides (7 mmol) in THF (5 mL). The reaction was warmed to room temperature and stirred for 3 h. Next, the solvent was evaporated, then water (15 mL) and ethyl acetate (20 mL) were added to the resulting slurry. The layers were separated, and then the aqueous layer was washed with ethyl acetate (2 x 30 mL) and the organic layers were combined. The organic solution was dried over anhydrous sodium sulphate (Na_2SO_4), filtered over a sintered funnel, and then evaporated to dryness. The crude product was purified by flash chromatography over silica gel by using EtOAc/MeOH (95:5) to afford the corresponding sulfoxonium ylides.

2.2 Optimization of reaction conditions

Table S1. Reaction development for the preparation of **3**[a]

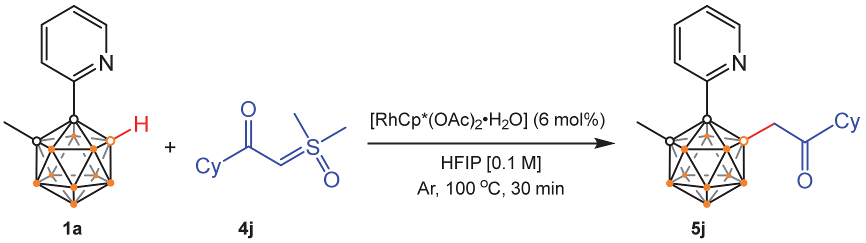


Entry	Variation from the standard conditions	Yield [%][b] of **3a**
1	none	77 (72[c])
2	RhCp* $(OAc)_2 \cdot H_2O$ instead of $[RhCp^*Cl_2]_2$	59
3	$RhCl_3$ instead of $[RhCp^*Cl_2]_2$	0
4	$[Rh(COD)Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$	0
5	CoCp* $(CO)I_2$ instead of $[RhCp^*Cl_2]_2$	0
6	$[IrCp^*Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$	0
7	[Ru(*p*-cymene)$Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$	63
8	$Cu(CH_3CN)_4PF_6$ instead of $[RhCp^*Cl_2]_2$	0
9	with 1.0 equiv. NaOAC	58
10	with 1.0 equiv. PivOH	40
11	with 16 mol% $AgSbF_6$	74
12	36 h instead of 18h	76
13	12 h instead of 18h	65
14	120 °C instead of 100 °C	74
15	80 °C instead of 100 °C	65
16	toluene instead of HFIP	n.d.
17	CH_3CN instead of HFIP	n.d.

18	THF instead of HFIP	n.d.
19	DCE instead of HFIP	n.d.
20	TFA instead of HFIP	n.d.
21	DMSO instead of HFIP	n.d.
22	1,4-dixone instead of HFIP	n.d.
34	NMP instead of HFIP	n.d.
24	TFE instead of HFIP	6
25	1.5 equiv. **2a**, 36 h	73
26	3 mol % $[RhCp^*Cl_2]_2$	60
27	without $[RhCp^*Cl_2]_2$	n.d.
28	under air	63

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv.), $[RhCp^*Cl_2]_2$ (6 mol%), HFIP (1.0 mL), 100 °C, 18 h, Ar atmosphere. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield. HFIP: hexafluoroisopropanol. THF: tetrahydrofuran. DCE: dichloroethane. TFA: trifluoroacetic acid. DMSO: dimethyl sulfoxide. NMP: 1-methyl-2-pyrrolidinone. TFE: 2,2,2-trifluoroethanol. n.d. = not detected.

Table S2. Reaction development for the preparation of **5**.[a]



Entry	Variation from the standard conditions	Yield [%][b] **5j**
1	none	97 (95[c])
2	3 mol% $[RhCp^*Cl_2]_2$	73
3	5 min instead of 30 min	89
4	80 °C instead of 100 °C	79
5	1.2 equiv. **4j**, 12 h	76
6	without $RhCp^*(OAc)_2 \cdot H_2O$	n.d.
7	in air	71

[a] Reaction conditions: **1a** (0.1 mmol), **4j** (2.0 equiv.), $RhCp^*(OAc)_2 \cdot H_2O$ (6 mol%), HFIP (1.0 mL), 100 °C, sealed under Ar atmosphere, 30 min. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield.

2.3 General procedure for the preparation of mono-acylmethylated carboranes.

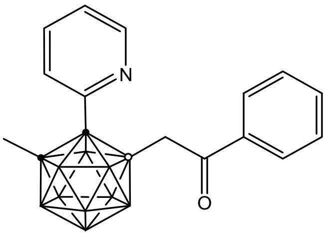
General procedure for the preparation of 3. 1a (23.5mg, 0.1 mmol), sulfoxonium ylide **2** (2.0 equiv., 0.2 mmol), $[RhCp^*Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 18 h. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford the desired product.

General procedure for the preparation of 5. A representative procedure. 1a (23.5mg, 0.1 mmol), sulfoxonium ylide **4** (2.0 equiv., 0.2 mmol), $RhCp^*(OAc)_2 \cdot H_2O$ (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 30 min. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford the desired product.

General procedure for the preparation of 6. A representative procedure. 1b (31.1mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 0.2 mmol), $RhCp^*(OAc)_2 \cdot H_2O$ (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 30 min. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford the desired product.

General procedure for the preparation of 7. 1-(2-pyridyl)-*o*-carboranes or 1-(2-pyridyl)-*p*-carboranes (0.1 mmol), sulfoxonium ylide (2.0 equiv., 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 18 h. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford the desired product.

Compound data:



3a: Yield 72%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.6, 1.3 Hz, 1H), 7.90 – 7.79 (m, 4H), 7.54 – 7.47 (m, 1H), 7.45 – 7.36 (m, 3H) (aryl C−**H**), 2.67 (d, *J* = 12.7 Hz, 1H), 2.45 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.75 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.4 (4B), -11.2 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 200.4 (**C**=O), 149.6, 147.8, 137.6, 132.8, 128.9, 128.4, 126.9, 125.0 (aryl−**C**), 81.0, 77.8 (cage−**C**), 28.8 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{24}$ [M+H$^+$]: 354.2856. Found: 354.2849.

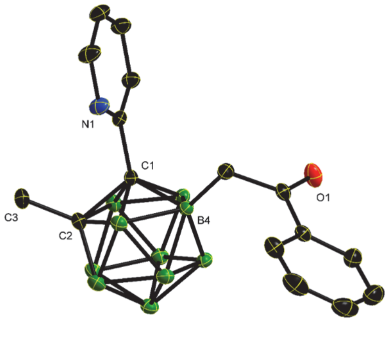
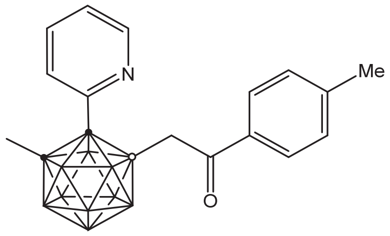
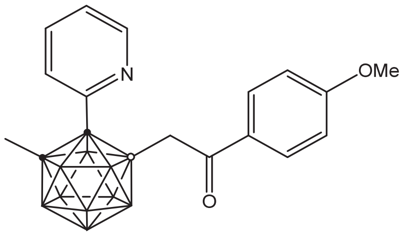


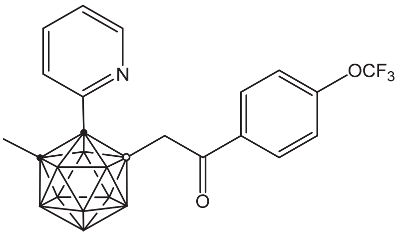
Figure S1. Molecular structure of compound **3a** (ellipsoids at 30% probability and H atoms omitted for clarity).



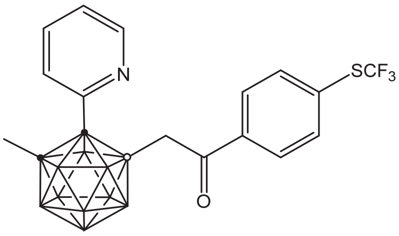
3b: Yield 79%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.74 – 8.61 (m, 1H), 7.87 – 7.79 (m, 2H), 7.76 – 7.70 (m, 2H), 7.41 (ddd, *J* = 6.7, 4.7, 2.2 Hz, 1H), 7.22 – 7.15 (m, 2H) (aryl C−**H**), 2.63 (d, *J* = 12.6 Hz, 1H), 2.42 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 2.38 (s, 3H) (Ph−C**H**$_3$), 1.74 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 200.0 (**C**=O), 149.6, 147.8, 143.5, 137.5, 135.1, 129.1, 129.0, 126.9, 125.0 (aryl−**C**), 81.0, 77.7 (cage−**C**), 28.8 (Ph−**C**H$_3$), 23.5 (**C**H$_2$), 21.7 (cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NOH_{26}$ [M+H$^+$]: 368.3012. Found: 368.3001.



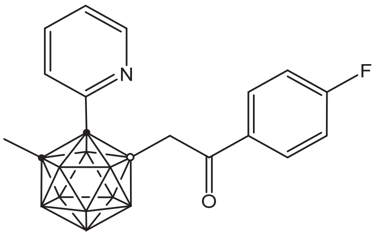
3c: Yield 86%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.68 (dt, *J* = 4.5, 1.4 Hz, 1H), 8.03 – 7.68 (m, 4H), 7.41 (ddd, *J* = 6.8, 4.7, 1.9 Hz, 1H), 6.93 – 6.73 (m, 2H) (aryl C−**H**), 3.84 (s, 3H) (OC**H**$_3$), 2.60 (d, *J* = 12.7 Hz, 1H), 2.39 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 198.9 (**C**=O), 163.3, 149.6, 147.8, 137.5, 131.2, 130.6, 126.9, 125.0, 113.5 (aryl−**C**), 81.0, 77.7 (cage−**C**), 55.5 (O**C**H$_3$), 28.4 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NO_2H_{26}$ [M+H$^+$]: 384.2961. Found: 384.2955.



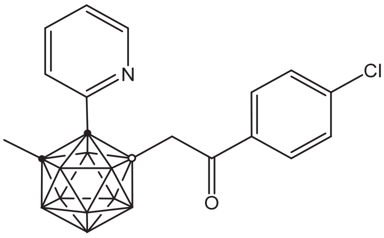
3d: Yield 91%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (m, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.85 – 7.78 (m, 2H), 7.42 (h, *J* = 4.4 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H) (aryl C−**H**), 2.66 (d, J = 12.7 Hz, 1H), 2.44 (d, J = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 198.8 (**C**=O), 152.4, 149.6, 147.8, 137.6, 135.8, 130.8, 126.9, 125.1, 121.5 (), 120.2, 119.4 (aryl−**C** and **C**F$_3$), 81.0, 77.9 (cage−**C**), 28.7 (**C**H$_2$), 23.6 (**C**H$_3$), *The signal of CF_3 group could not be detected clearly since this is a known issue*; **^{19}F NMR (471 MHz, Chloroform-*d*)**: δ -57.5. **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NO_2F_3H_{22}$ [M+H$^+$]: 439.2642. Found: 439.2646.



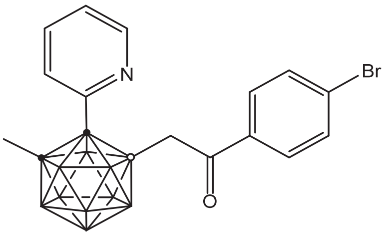
3e: Yield 59%. Light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.65 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.92 – 7.76 (m, 4H), 7.69 – 7.61 (m, 2H), 7.45 – 7.37 (m, 1H) (aryl C−**H**), 2.68 (d, *J* = 12.7 Hz, 1H), 2.46 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.3 (**C**=O), 149.6, 147.8, 139.1, 137.61, 135.6, 129.6, 126.9, 125.1 (aryl−**C** and **C**F$_3$), 81.0, 78.0 (cage−**C**), 28.8 (**C**H$_2$), 23.6 (**C**H$_3$), *The signal of CF_3 group could not be detected clearly since this is a known issue*; **^{19}F NMR (471 MHz, Chloroform-*d*)**: δ -41.8. **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}F_3NOSH_{22}$ [M+H$^+$]: 453.2450. Found: 453.2444.



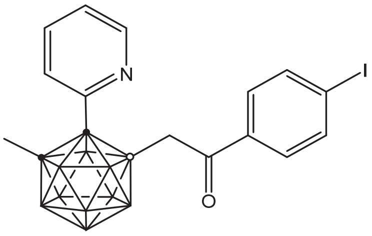
3f: Yield 63%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.94 – 7.74 (m, 4H), 7.42 (h, *J* = 4.6 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 2H) (aryl C−**H**), 2.64 (d, *J* = 12.7 Hz, 1H), 2.41 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.4 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 198.7 (**C**=O), 165.7 (d, J_{CF} = 254.0 Hz), 149.6, 147.8, 137.6, 134.0 (d, J_{CF} = 3.0 Hz), 131.5 (d, J_{CF} = 9.3 Hz), 126.9, 125.0, 115.5 (d, *J* = 21.8 Hz) (aryl−**C**), 81.0, 77.9 (cage−**C**), 28.8 (**C**H$_2$), 23.6 (**C**H$_3$); **^{19}F NMR (471 MHz, Chloroform-*d*)**: δ -106.2. **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}FNOH_{23}$ [M+H$^+$]: 372.2761. Found: 372.2764.



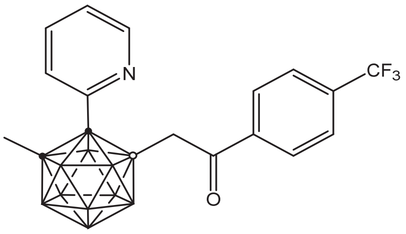
3g: Yield 61%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.79 – 7.73 (m, 2H), 7.42 (m, 1H), 7.39 – 7.32 (m, 2H) (aryl C−**H**), 2.64 (d, *J* = 12.6 Hz, 1H), 2.41 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.1 (**C**=O), 149.6, 147.8, 139.2, 137.6, 135.9, 130.3, 128.7, 126.9, 125.0(aryl−**C**), 81.0, 77.9 (cage−**C**), 29.0 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): m/z calcd for $C_{16}B_{10}ClNOH_{23}$ [M+H$^+$]: 388.2466. Found: 388.2463.



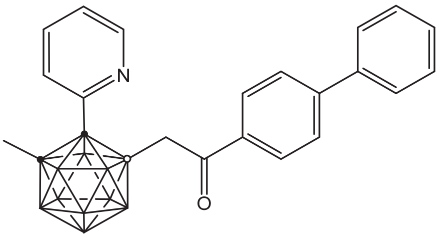
3h: Yield 51%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.72 – 7.65 (m, 2H), 7.56 – 7.50 (m, 2H), 7.42 (ddd, *J* = 5.9, 4.8, 2.6 Hz, 1H) (aryl C−**H**), 2.64 (d, *J* = 12.7 Hz, 1H), 2.41 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.0 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.2 (**C**=O), 149.6, 147.8, 137.6, 136.3, 131.7, 130.4, 128.0, 126.8, 125.0 (aryl−**C**), 81.0, 77.9 (cage−**C**), 28.7 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}BrNOH_{23}$ [M+H$^+$]: 433.1924. Found: 433.1916.



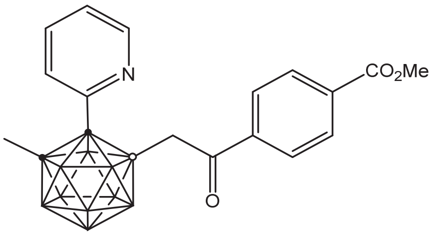
3i: Yield 50%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.82 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.40 (m, 1H) (aryl C−**H**), 2.63 (d, *J* = 12.7 Hz, 1H), 2.40 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (s, 4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 199.5 (**C**=O), 149.6, 147.8, 137.7, 137.6, 136.8, 130.4, 126.9, 125.0, 100.8 (aryl−**C**), 81.0, 77.9 (cage−**C**), 28.7 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}INOH_{23}$ [M+H$^+$]: 479.1858. Found: 479.1851.



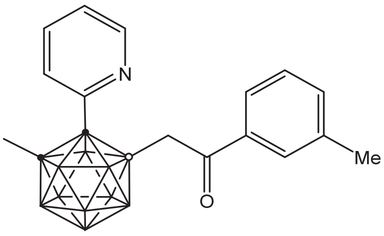
3j: Yield 56%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.68 (dt, *J* = 4.8, 1.6 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.83 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.43 (ddd, *J* = 6.2, 4.8, 2.4 Hz, 1H) (aryl−**H**), 2.71 (d, *J* = 12.6 Hz, 1H), 2.47 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.75 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.6 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.3 (**C**=O), 149.7, 147.8, 140.3, 137.6, 129.2, 126.9, 125.55, 125.51, 125.1 (aryl−**C**), 81.0, 78.0 (cage−**C** and **C**F$_3$), 29.1 (**C**H$_2$), 23.6 (**C**H$_3$), *The signal of CF$_3$ group could not be detected clearly since this is a known issue*; **^{19}F NMR (376 MHz, Chloroform-*d*)**: δ -63.0. **HRMS** (ESI, positive mode): *m/z* calcd for C$_{17}$B$_{10}$NOF$_3$H$_{23}$ [M+H$^+$]: 422.2729. Found: 422.2724.



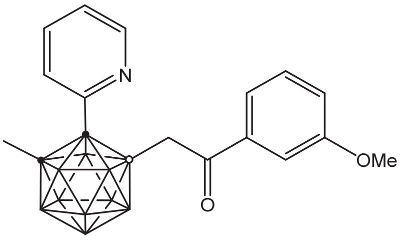
3k: Yield 65%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.73 – 8.64 (m, 1H), 7.93 – 7.88 (m, 2H), 7.88 – 7.81 (m, 2H), 7.66 – 7.59 (m, 4H), 7.49 – 7.36 (m, 4H) (aryl−**H**), 2.70 (d, *J* = 12.7 Hz, 1H), 2.49 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.76 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.4 (1B), -9.4 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.9 (**C**=O), 149.6, 147.8, 145.4, 140.1, 137.6, 136.3, 129.5, 129.0, 128.2, 127.4, 127.1, 126.9, 125.0 (aryl−**C**), 81.0, 77.8 (cage−**C**), 28.8 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for C$_{22}$B$_{10}$NOH$_{28}$ [M+H$^+$]: 430.3169. Found: 430.3160.



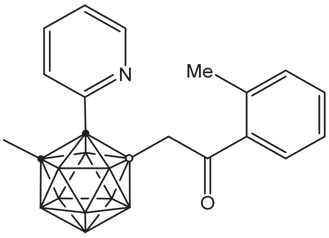
3l: Yield 40%. Light yellow solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (d, *J* = 4.7 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 6.4 Hz, 2H), 7.42 (t, *J* = 5.5 Hz, 1H) (aryl C−**H**), 3.93 (s, 3H) (CO_2CH_3), 2.70 (d, *J* = 12.6 Hz, 1H), 2.47 (d, *J* = 12.6 Hz, 1H) (CH_2), 1.74 (s, 3H) (B−CH_3); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (3B), -11.1 (4B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 199.8 (**C**=O), 166.5, 149.7, 147.8, 140.9, 137.7, 133.6, 129.7, 128.8, 126.9, 125.1 (aryl−**C**), 81.0, 77.9 (cage−C), 52.6 (CO_2CH_3), 29.2 (CH_2), 23.6 (B−CH_3). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NO_3H_{26}$ [M+H$^+$]: 413.2874. Found: 413.2866.



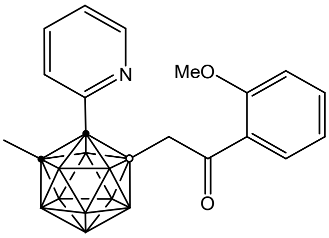
3m: Yield 82%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.66 (t, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 7.4, 1.7 Hz, 1H) , 7.41 (ddd, *J* = 6.4, 4.8, 2.4 Hz, 1H), 7.33 – 7.24 (m, 2H) (aryl C−**H**), 2.65 (d, *J* = 12.7 Hz, 1H), 2.44 (d, *J* = 12.7 Hz, 1H) (CH_2), 2.37 (s, 3H) (Ph−CH_3), 1.75 (s, 3H) (cage−CH_3); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.4 (4B), -11.2 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 200.5 (**C**=O), 149.6, 147.9, 138.1, 137.6, 137.5, 133.6, 129.4, 128.3, 126.9, 126.2, 125.0 (aryl−**C**), 81.0, 77.7 (cage−**C**), 28.7 (Ph−CH_3), 23.6 (CH_2), 21.5 (cage−CH_3). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NOH_{26}$ [M+H$^+$]: 368.3012. Found: 368.3001.



3n: Yield 83%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.6, 1.3 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.40 (m, 3H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.08 – 7.03 (m, 1H) (aryl C−**H)**, 3.83 (s, 3H) (OC**H**$_3$), 2.65 (d, *J* = 12.7 Hz, 1H), 2.44 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*):** δ 200.1 (**C**=O), 159.7, 149.6, 147.8, 139.0, 137.6, 129.4, 126.9, 125.0, 121.7, 119.5, 112.8 (aryl−**C)**, 81.0, 77.8 (cage−**C**), 55.5 (O−**C**H$_3$), 28.9 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NO_2H_{26}$ [M+H$^+$]: 384.2961. Found: 384.2955.



3o: Yield 80%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.64 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.46 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.38 (ddd, *J* = 5.9, 4.8, 2.9 Hz, 1H), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 – 7.09 (m, 2H) (aryl C−**H)**, 2.59 (d, *J* = 13.0 Hz, 1H) (C**H**$_2$), 2.47 (s, 3H) (Ph−C**H**$_3$), 2.46 (d, 1H) (C**H**$_2$), 1.73 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 203.7 (**C**=O), 149.6, 147.9, 138.7, 138.4, 137.5, 132.0, 131.1, 129.7, 126.7, 125.4, 124.9 (aryl−**C**), 81.0, 77.6 (cage−**C**), 31.6 (Ph−**C**H$_3$), 23.6 (**C**H$_2$), 21.7 (cage−CH$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NOH_{26}$ [M+H$^+$]: 368.3012. Found: 368.3004.



3p: Yield 86%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.63 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.56 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.43 – 7.34 (m, 2H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H) (aryl C−**H**), 3.78 (s, 3H) (OC**H**$_3$), 2.79 (d, *J* = 12.6 Hz, 1H), 2.65 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.72 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.4 (2B), -4.5 (1B), -9.4 (4B), -11.2 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 202.2 (**C**=O), 158.4, 149.5, 147.9, 137.3, 133.1, 131.0, 129.1, 126.7, 124.8, 120.5, 111.4 (aryl−**C**), 80.9, 77.4 (cage−**C**), 55.4 (O**C**H$_3$), 33.4 (**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}NO_2H_{26}$ [M+H$^+$]: 384.2961. Found: 384.2957.

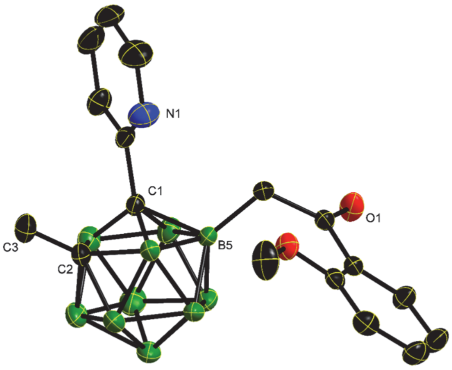
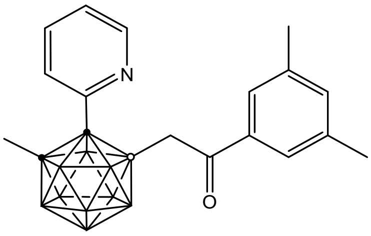
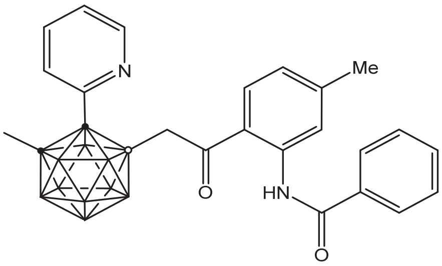


Figure S2. Molecular structure of compound **3p** (ellipsoids at 30% probability and H atoms omitted for clarity).

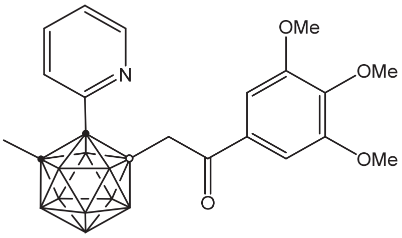


3q: Yield 83%. pale-yellow sticky solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.67 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.44 (s, 2H), 7.41 (ddd, *J* = 6.7, 4.7, 2.2

Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 1H) (aryl C−**H**), 2.64 (d, *J* = 12.6 Hz, 1H), 2.42 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 2.33 (s, 6H) (Ph−C**H**$_3$), 1.74 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.5 (s, 4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 200.7 (**C**=O), 149.6, 147.9, 137.9, 137.7, 137.5, 134.5, 126.9, 126.8, 124.9 (aryl−**C**), 81.0, 77.7 (cage−**C**), 29.1 (**C**H$_2$), 23.6 (cage−**C**H$_3$), 21.4 (Ph−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NOH_{28}$ [M+H$^+$]: 384.3169. Found: 3844.3172.

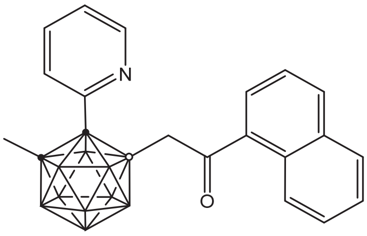


3r: Yield 90%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 12.69 (s, 1H) (N**H**), 8.77 (s, 1H), 8.61 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.76 – 7.67 (m, 3H), 7.58 – 7.48 (m, 3H), 7.31 (ddd, *J* = 7.3, 4.7, 1.3 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.7 Hz, 1H) (aryl C−**H**), 2.78 (d, *J* = 12.8 Hz, 1H), 2.51 (d, *J* = 13.0 Hz, 1H) (C**H**$_2$), 2.42 (s, 3H) (Ph−C**H**$_3$), 1.73 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.5 (1B), -9.4 (s, 4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 204.9 (**C**=O), 166.1, 149.5, 147.8, 146.3, 141.5, 137.5, 135.2, 132.7, 131.9, 128.8, 127.6, 126.7, 124.9, 123.3, 121.0, 120.0 (aryl−**C**), 80.6, 78.0 (cage−**C**), 30.6 (**C**H$_2$), 23.5 (cage−**C**H$_3$), 22.3 (Ph−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{24}B_{10}N_2O_2H_{31}$ [M+H$^+$]: 487.3383. Found: 487.3375.

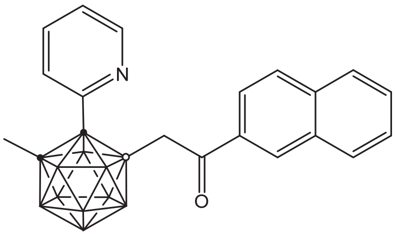


3s: Yield 87%. Light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.72 – 8.62 (m, 1H), 7.90 – 7.79 (m, 2H), 7.42 (ddd, *J* = 6.7, 4.8, 1.8 Hz, 1H), 7.15 (s, 2H) (aryl

C−**H**), 3.90 (s, 3H), 3.89 (s, 6H) (OC**H**3), 2.62 (d, *J* = 12.7 Hz, 1H), 2.40 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.50 (4B), -11.0 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.1 (**C**=O), 152.8, 149.6, 147.8, 142.3, 137.6, 132.7, 126.9, 125.0, 106.4 (aryl−**C**), 81.1, 77.9 (cage−**C**), 61.0, 56.3 (O**C**H$_3$), 28.7 (**C**H$_2$), 23.6 (cage−**C**H$_3$). **HRMS (ESI, positive mode)**: *m/z* calcd for $C_{19}B_{10}NO_4H_{30}$ [M+H$^+$]: 444.3173. Found: 444.3171.

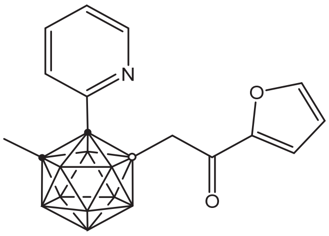


3t: Yield 78%. **White solid.** **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.65 – 8.52 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.83 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 (m, 3H), 7.60 – 7.47 (m, 2H), 7.37 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.33 (ddd, *J* = 7.1, 4.7, 1.5 Hz, 1H) (aryl C−**H**), 2.77 (d, *J* = 13.0 Hz, 1H), 2.67 (d, *J* = 13.0 Hz, 1H) (C**H**$_2$), 1.72 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.4 (1B), -9.3 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 203.7 (**C**=O), 149.5, 147.8, 137.4, 136.4, 134.1, 132.6, 130.5, 128.6, 128.4, 127.7, 126.7, 126.5, 126.3, 124.9, 124.3 (aryl−**C**), 80.9, 77.6 (cage−**C**), 32.1 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}NOH_{26}$ [M+H$^+$]: 404.3012. Found: 404.3009.

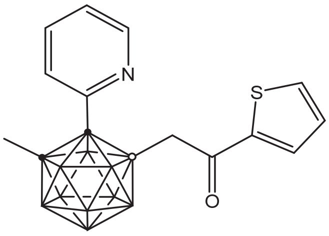


3u: Yield 70%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.68 (d, *J* = 4.6 Hz, 1H), 8.32 (s, 1H), 7.98 – 7.89 (m, 2H), 7.84 (m, 3H), 7.81 – 7.76 (m, 1H), 7.55 (m, 2H), 7.38 (ddd, *J* = 7.3, 4.7, 1.2 Hz, 1H) (aryl C−**H)**, 2.81 (d, *J* = 12.7 Hz, 1H), 2.59 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.75 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-**

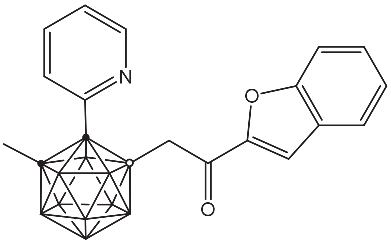
d): δ -2.2 (2B), -4.3 (1B), -9.3 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 200.23 (**C**=O), 149.60, 147.83, 137.53, 135.55, 134.91, 132.57, 130.72, 129.78, 128.33, 128.21, 127.81, 126.86, 126.61, 125.00, 124.62 (aryl−**C**), 80.99,77.80 (cage−**C**), 28.81 (**C**H$_2$), 23.56 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}NOH_{26}$ [M+H$^+$]: 404.3012. Found: 404.3007.



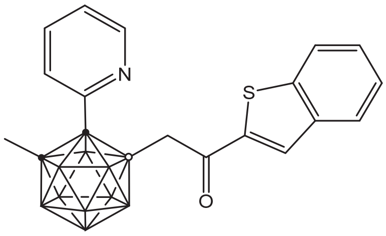
3v: Yield 97%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.65 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.53 – 7.45 (m, 1H), 7.44 – 7.36 (m, 1H), 7.03 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.45 (dd, *J* = 3.5, 1.7 Hz, 1H) (aryl C−**H**), 2.51 (d, *J* = 12.6 Hz, 1H), 2.31 (d, *J* = 12.5 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.4 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 188.9 (**C**=O), 152.9, 149.6, 147.8, 146.2, 137.5, 126.9, 125.0, 117.3, 112.2 (aryl−**C**), 81.0, 77.8, (cage−**C**), 28.9 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}NO_2H_{22}$ [M+H$^+$]: 384.2687. Found: 384.2624.



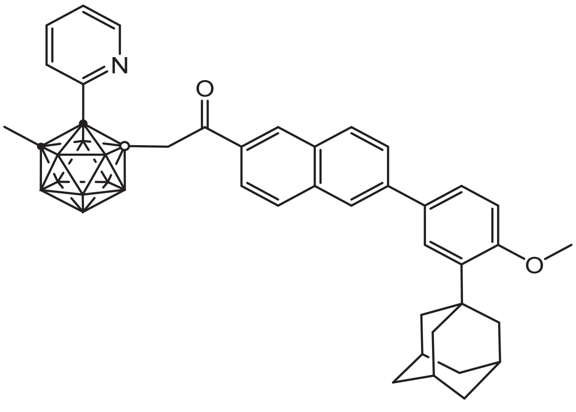
3w: Yield 85%. Light yellow solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (d, *J* = 4.7 Hz, 1H), 7.82 (m, 2H), 7.56 (d, *J* = 4.9 Hz, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.41 (t, *J* = 5.7 Hz, 1H), 7.04 (t, *J* = 4.3 Hz, 1H) (aryl C−**H)**, 2.57 (d, *J* = 12.7 Hz, 1H), 2.38 (d, *J* = 12.7 Hz, 1H) (C**H**$_2$), 1.74 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.3 (1B), -9.4 (4B), -11.0 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 192.9 (**C**=O), 149.6, 147.7, 145.3, 137.6, 133.7, 132.6, 128.0, 126.9, 125.0 (aryl−**C**), 81.0, 77.8 (cage−**C**), 29.8 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}NOSH_{22}$ [M+H$^+$]: 362.2462. Found: 362.2457.



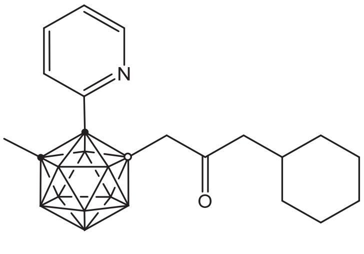
3x: Yield 60%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.69 – 8.59 (m, 1H), 7.90 – 7.75 (m, 2H), 7.67 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.52 (dq, *J* = 8.4, 1.0 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.33 (d, *J* = 0.9 Hz, 1H), 7.31 – 7.25 (m, 1H) (aryl C−**H**), 2.67 (d, *J* = 12.6 Hz, 1H), 2.46 (d, *J* = 12.6 Hz, 1H) (C**H**$_2$), 1.75 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.4 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 190.6 (**C**=O), 155.7, 152.9, 149.6, 147.8, 137.6, 128.0, 127.4, 126.9, 125.0, 123.8, 123.3, 113.2, 112.6 (aryl−**C**), 80.9, 77.9 (cage−**C**), 29.2 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NO_2H_{24}$ [M+H$^+$]: 394.2805. Found: 394.2801.



3y: Yield 72%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.70 – 8.64 (m, 1H), 7.87 – 7.77 (m, 4H), 7.69 (s, 1H), 7.48 – 7.35 (m, 3H) (aryl C−**H**), 2.69 (d, *J* = 12.8 Hz, 1H), 2.51 (d, *J* = 12.8 Hz, 1H) (C**H**$_2$), 1.75 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (s, 2B), -4.4 (s, 1B), -9.4 (s, 4B), -11.1 (s, 3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 194.4 (**C**=O), 149.6, 147.7, 144.8, 142.9, 139.3, 137.6, 129.7, 127.2, 127.0, 126.0, 125.1, 124.9, 123.1 (aryl−**C**), 80.9, 77.9 (cage−**C**), 29.6 (**C**H$_2$), 23.5 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NOSH_{24}$ [M+H$^+$]: 410.2576. Found: 410.25762.

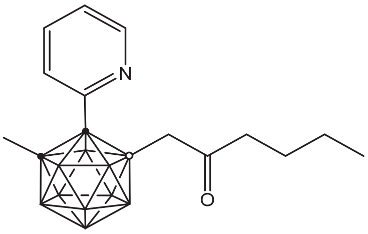


3z: Yield 82%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.69 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.32 (s, 1H), 7.98 (s, 1H), 7.97 – 7.91 (m, 2H), 7.89 – 7.83 (m, 2H), 7.83 – 7.74 (m, 2H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.54 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.39 (ddd, *J* = 7.3, 4.8, 1.3 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H) (aryl C−**H**), 3.91 (s, 3H) (OC**H**$_3$), 2.81 (d, *J* = 12.8 Hz, 1H), 2.60 (d, *J* = 12.5 Hz, 1H) (B−C**H**$_2$), 2.19 (d, *J* = 3.0 Hz, 6H), 2.11 (s, 3H), 1.81 (d, *J* = 3.2 Hz, 6H), 1.75 (s, 3H) (adamantly C−**H**); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.3 (1B), -9.3 (4B), -11.0 (3B); **^{13}C NMR (126 MHz, CDCl$_3$)**: δ 200.16 (**C**=O), 159.04, 149.62, 147.90, 141.53, 139.12, 137.54, 135.99, 134.56, 132.80, 131.32, 130.54, 130.15, 128.30, 126.90, 126.45, 126.13, 125.86, 125.01, 124.84, 112.25 (aryl **C**), 80.99, 77.79 (cage−**C**), 55.31 (OC**H**$_3$), 40.74, 37.34, 37.27, 29.25 (adamantly **C**), 28.7 (B−CH$_2$), 23.57(cage−CH$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{37}B_{10}NO_2H_{46}$ [M+H$^+$]: 644.4526. Found: 644.4519.

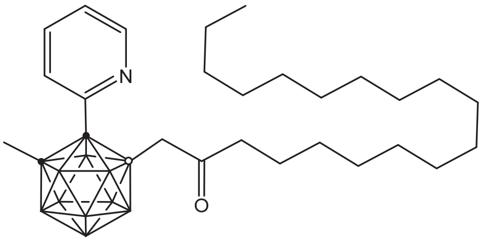


5a: Yield 89%. Colorless sticky solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.65 (dt, *J* = 4.7, 1.4 Hz, 1H), 8.02 – 7.57 (m, 2H), 7.40 (ddd, *J* = 6.6, 4.7, 1.8 Hz, 1H) (aryl C−**H**), 2.23 (d, *J* = 7.1 Hz, 2H) (COC**H**$_2$CH), 2.07 (d, *J* = 12.2 Hz, 1H), 1.89 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.72 – 1.55 (m, 6H), 1.29 – 1.15 (m, 2H), 1.14 – 1.03 (m, 1H), 0.92 – 0.78 (m, 2H) (Cyclohexyl−C**H**); **^{11}B{^{1}H} NMR (160

MHz, Chloroform-*d*): δ -2.4 (2B), -4.5 (1B), −9.6 (4B), −11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 210.28 (**C**=O), 149.57, 147.74, 137.52, 126.74, 124.95 (aryl−**C**), 80.87, 77.72 (cage−**C**), 51.53 (CO**C**H$_2$CH), 33.81, 33.40, 33.32, 26.37, 26.24, 26.22 (Cyclohexyl−**C**), 23.52 (cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{32}$ [M+H$^+$]: 363.3445. Found: 363.3439.

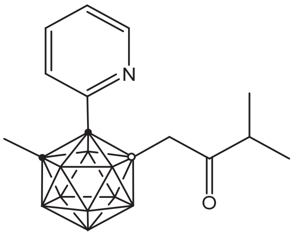


5b: Yield 63%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.8, 1.6 Hz, 1H), 8.04 – 7.58 (m, 2H), 7.40 (ddd, *J* = 6.6, 4.8, 1.9 Hz, 1H) (aryl C−**H**), 2.44 – 2.29 (m, 2H) (^{n}Bu−C**H**$_2$), 2.11 (d, *J* = 12.2 Hz, 1H), 1.91 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.51 – 1.40 (m, 2H) (^{n}Bu−C**H**$_2$), 1.26 (h, *J* = 7.3 Hz, 2H) (^{n}Bu−C**H**$_2$), 0.86 (t, *J* = 7.3 Hz, 3H) (^{n}Bu−C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 210.74 (**C**=O), 149.59, 147.78, 137.53, 126.75, 124.95 (aryl−**C**), 80.87, 77.76 (cage−**C**), 43.53 (^{n}Bu−**C**H$_2$), 33.42 (B−**C**H$_2$), 25.94 (^{n}Bu−**C**H$_2$), 23.55 (cage−**C**H$_3$), 22.44, 14.05 (^{n}Bu−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}NOH_{28}$ [M+H$^+$]: 335.3132. Found: 335.3131.

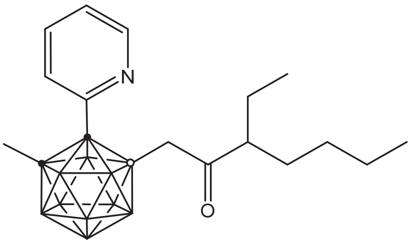


5c: Yield 67%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.66 (d, *J* = 4.6 Hz, 1H), 7.81 (m, 2H), 7.45 – 7.37 (m, 1H) (aryl C−**H**), 2.43 – 2.27 (m, 2H) (C17−chain−**H**), 2.11 (d, *J* = 12.3 Hz, 1H), 1.91 (d, *J* = 12.1 Hz, 1H) (B−C**H**$_2$), 1.75 (s, 3H) (cage−C**H**$_3$), 1.46 (p, *J* = 7.2 Hz, 2H), 1.24 (m, 27H), 0.88 (t, *J* = 6.7 Hz, 4H)

(C17−chain−**H**); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.2 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.7 (**C**=O), 149.6, 147.8, 137.5, 126.7, 124.9 (aryl−**C**), 80.9, 77.8 (cage−**C**), 43.8 (C17−chain−**C**), 33.4 (B−**C**H$_2$), 32.1, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.3, 23.8 (C17−chain−**C**), 23.5 (cage−**C**H$_3$), 22.8, 14.3 (C17−chain−**C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{27}B_{10}NOH_{54}$ [M+H$^+$]: 516.5203. Found: 512.5208.

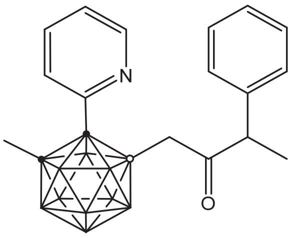


5d: Yield 63%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.40 (hept, *J* = 4.4 Hz, 1H) (aryl C−**H**), 2.63 (hept, *J* = 6.9 Hz, 1H) (C**H**), 2.16 (d, *J* = 12.4 Hz, 1H), 1.96 (d, *J* = 12.4 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 0.99 (dd, *J* = 10.4, 6.9 Hz, 6H) (^{i}Pr−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 214.3 (**C**=O), 149.6, 147.8, 137.5, 126.8, 125.0 (aryl−**C**), 81.0, 77.7 (cage−**C**), 41.1 (^{i}Pr−**C**H), 30.7 (B−CH$_2$), 23.6 (cage−**C**H$_3$), 18.4, 18.0 (^{i}Pr −CH$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{13}B_{10}NOH_{26}$ [M+H$^+$]: 320.3012. Found: 320.3009.

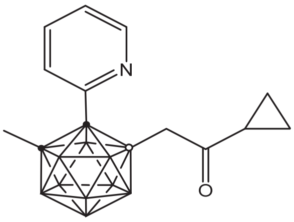


5e: Yield 44%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.77 – 8.53 (m, 1H), 7.93 – 7.74 (m, 2H), 7.40 (ddd, *J* = 6.7, 4.7, 1.6 Hz, 1H) (aryl C−**H**), 2.42 – 2.32 (m, 1H) (C**H**), 2.10 (d, *J* = 13.0 Hz, 1H), 1.96 (d, *J* = 12.5 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.58 – 1.45 (m, 2H), 1.42 – 1.28 (m, 2H), 1.24 – 1.19 (m, 2H), 1.19

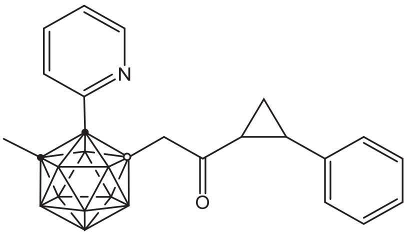
– 1.07 (m, 2H) (alkyl chain−C**H**$_2$), 0.85 (td, *J* = 7.2, 2.7 Hz, 3H), 0.79 (td, *J* = 7.5, 1.6 Hz, 3H) (alkyl chain−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.2 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 213.5 (**C**=O), 149.6, 147.9, 137.5, 126.8, 124.9 (aryl−**C**), 81.0, 77.6 (cage−**C**), 53.7 (**C**H), 31.7 (B−**C**H$_2$), 30.0, 29.6, 29.4 (alkyl chain−**C**H$_2$), 23.6 (cage−**C**H$_3$), 23.1 (alkyl chain−**C**H$_2$), 14.1, 11.8 (alkyl chain−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{34}$ [M+H$^+$]: 364.3638. Found: 364.3632.



5f: Yield 54%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Conformer I : Conformer II** = 63 : 37, **Conformer I**: δ 8.64 (d, *J* = 4.8 Hz, 1H), 7.90 – 7.68 (m, 2H), 7.38 (m, 1H), 7.25 – 7.03 (m, 5H) (aryl C−**H**), 3.75 (q, *J* = 6.9 Hz, 1H) (C**H**), 2.30 (d, *J* = 12.3 Hz, 1H), 2.14 (d, *J* = 12.4 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.32 (d, *J* = 6.9 Hz, 3H) (CHC**H**$_3$)]; **Conformer II**: δ 8.61 (d, *J* = 4.9 Hz, 1H), 7.90 – 7.68 (m, 2H), 7.38 (m, 1H), 7.25 – 7.03 (m, 5H) (aryl C−**H**), 3.90 (q, *J* = 6.8 Hz, 1H) (C**H**), 2.30 (d, *J* = 12.3 Hz, 1H), 2.14 (d, *J* = 12.4 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.29 (d, *J* = 6.9 Hz, 3H) (CHC**H**$_3$). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.6 (4B), -10.9 (3B); mixture: **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 209.9, 209.7 (**C**=O), 149.8, 149.5, 147.7, 141.2, 141.0, 137.6, 137.5, 128.9, 128.9, 128.2, 128.2, 127.0, 126.9, 126.4, 124.9 (aryl−**C**), 81.1, 80.9, 77.9, 77.7 (cage−**C**), 53.4, 52.9 (**C**H), 32.0 (B−**C**H$_2$), 23.6, 23.5 (cage−**C**H$_3$), 17.6, 17.5 (CH**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NOH_{28}$ [M+H$^+$]: 383.3132. Found: 383.3129.

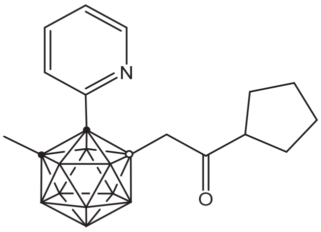


5g: Yield 99%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.66 (d, *J* = 4.7 Hz, 1H), 7.80 (m, 2H), 7.40 (m, 1H) (aryl C−**H**), 2.26 (d, *J* = 12.2 Hz, 1H), 2.07 (d, *J* = 12.2 Hz, 1H) ($\mathrm{C}\mathbf{H}_2$), 1.85 (tt, *J* = 8.3, 4.7 Hz, 1H) (cyclopropyl−C**H**), 1.76 (s, 3H) ($\mathrm{C}\mathbf{H}_3$), 0.94 (t, *J* = 4.3 Hz, 2H), 0.81 (t, *J* = 4.0 Hz, 2H) (cyclopropyl−$\mathrm{C}\mathbf{H}_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), -9.4 (4B), -11.0 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.5 (**C**=O), 149.6, 147.8, 137.5, 126.7, 124.9 (aryl−**C**), 80.9, 77.8 (cage−**C**), 34.8 (B−$\mathbf{C}\mathrm{H}_2$), 23.6 (cage−$\mathbf{C}\mathrm{H}_3$), 21.4 (cyclopropyl−CH), 11.4, 11.4 (cyclopropyl−$\mathbf{C}\mathrm{H}_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{13}B_{10}NOH_{24}$ [M+H^{+}]: 318.2856. Found: 318.2853.

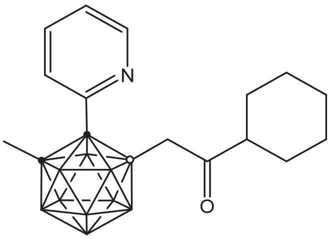


5h Yield 97%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**, **Conformer I : Conformer II** = 50 : 50, δ 8.65 (dq, *J* = 4.6, 1.5 Hz, 1H), 7.87 – 7.78 (m, 1H), 7.77 – 7.69 (m, 1H), 7.45 – 7.35 (m, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.18 (m, 1H), 7.09 (m, 2H) (aryl C−**H**), 2.47 (m, 1H) (cyclopropyl−C**H**), 2.37 (d, *J* = 12.2 Hz, 0.5H), 2.27 (d, *J* = 12.2 Hz, 0.5H), 2.18 (d, *J* = 12.1 Hz, 0.5H) (B−$\mathrm{C}\mathbf{H}_2$), 2.09 (ddt, *J* = 7.9, 5.3, 3.8 Hz, 1.5H) (B−$\mathrm{C}\mathbf{H}_2$ and cyclopropyl−C**H**), 1.77 (d, *J* = 6.6 Hz, 3H) (cage−$\mathbf{C}\mathrm{H}_3$), 1.60 (dddd, *J* = 9.3, 6.7, 5.3, 4.2 Hz, 1H), 1.34 (tdd, *J* = 8.2, 6.6, 4.1 Hz, 1H) (cyclopropyl−$\mathrm{C}\mathbf{H}_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (2B), -4.4 (1B), -9.4 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 208.4, 208.3 (**C**=O), 149.6, 149.5, 147.7, 140.8, 140.7, 137.5, 137.5, 128.5, 128.5, 126.7, 126.6, 126.4, 126.4, 126.2, 126.2, 124.9, 124.9 (aryl−**C**), 80.8, 80.8, 77.8, 77.8 (cage−**C**), 35.1 (B−$\mathbf{C}\mathrm{H}_2$), 33.3, 33.1, 29.4, 29.3

(cyclopropyl−**C**), 23.5 (cage−**C**H_3), 19.5, 19.4 (cyclopropyl−**C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}NOH_{28}$ [M+H$^+$]: 394.3619. Found: 394.3618.

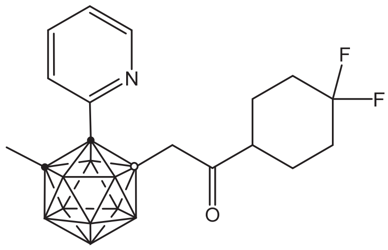


5i: Yield 95%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.95 – 7.78 (m, 2H), 7.45 – 7.32 (m, 1H) (aryl C−**H**), 2.90 (h, *J* = 7.8, 7.3 Hz, 1H) (cyclopentyl−C**H**), 2.15 (d, *J* = 12.3 Hz, 1H), 1.97 (d, *J* = 12.3 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−**C**H_3), 1.69 – 1.45 (m, 8H) (cyclopentyl−C**H**$_2$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.4 (1B), −9.6 (4B), −11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 212.8 (**C**=O), 149.6, 147.8, 137.5, 126.8, 124.9 (aryl−**C**), 81.0, 77.7 (cage−**C**), 51.9 (cyclopentyl−**C**H), 32.4 (B−**C**H_2), 29.3, 28.6, 26.1 (cyclopentyl −**C**H_2), 23.6 (cage−**C**H_3). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}NOH_{28}$ [M+H$^+$]: 346.3169. Found: 346.3166.

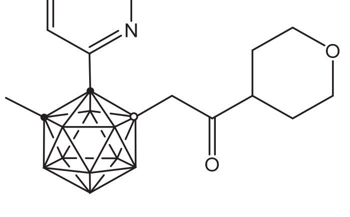


5j: Yield 95%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.92 – 7.74 (m, 2H), 7.47 – 7.36 (m, 1H) (aryl C−**H**), 2.36 – 2.34 (m, 1H) (Cyclohexy−C**H**), 2.13 (d, *J* = 12.4 Hz, 1H), 1.95 (d, *J* = 12.4 Hz, 1H) (B−C**H**$_2$), 1.80 – 1.69 (m, 8H) (Cyclohexy−C**H**$_2$ and cage−C**H**$_3$), 1.65 – 1.60 (m, 1H), 1.26 – 1.14 (m, 4H) (Cyclohexy−C**H**$_2$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.4 (2B), -4.6 (1B), −9.6 (4B), −11.2 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 213.7 (**C**=O), 149.6, 147.8, 137.5, 126.7, 124.9 (aryl−**C**), 80.9, 77.7 (cage−**C**), 51.1 (Cyclohexy−**C**H), 31.3 (B−**C**H_2), 28.6, 28.3, 26.0, 25.9, 25.8 (Cyclohexy−**C**H_2), 23.5 (cage−**C**H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{30}$ [M+H$^+$]: 360.3289. Found: 360.3257.

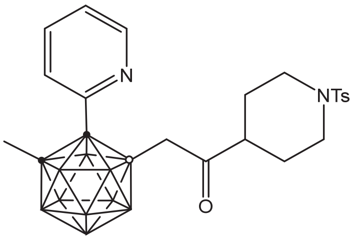


5k: Yield 62%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.73 – 8.58 (m, 1H), 7.89 – 7.72 (m, 2H), 7.40 (m, 1H) (aryl C−**H**), 2.43 (m, 1H) (C**H**), 2.25 (d, *J* = 12.2 Hz, 0.64H), 2.18 (d, *J* = 12.3 Hz, 0.36H), 2.06 (d, *J* = 12.2 Hz, 0.64H), 1.95 (d, *J* = 12.3 Hz, 0.36H) (B−C**H**$_2$), 1.84 (m, 2H) ($CF_2C\mathbf{H}_2CH_2$), 1.75 (s, 3H) (cage−CH_3), 1.71 – 1.54 (m, 2H) ($CF_2C\mathbf{H}_2CH_2$), 0.95 – 0.91 (m, 2H), 0.82 – 0.76 (m, 2H) ($CF_2CH_2C\mathbf{H}_2$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.33 (2B), -4.42 (1B), -9.53 (4B), -11.12 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 211.5, 210.4 (**C**=O), 149.6, 149.6, 147.8, 137.6, 137.5, 126.7, 126.7, 125.0, 124.9 (aryl−**C** and **C**F_2), 81.0, 80.9, 78.0, 77.8 (cage−**C**), 48.2 (**C**H), 35.1 (B−**C**H_2), 32.9 (m), 24.9 (d, J_{CF} = 9.7 Hz), 24.5 (d, J_{CF} = 9.5 Hz) ($CF_2\mathbf{C}H_2CH_2$), 23.6, 21.4 (cage−**C**H_3), 11.4, 11.4 ($CF_2CH_2\mathbf{C}H_2$). **^{19}F NMR (376 MHz, Chloroform-*d*)**: δ -93.2 (d, J_{FF} = 235.4 Hz, 1F), -100.6 (d, J_{FF} = 236.4 Hz, 1F). HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOF_2H_{28}$ [M+H$^+$]: 397.3100. Found: 397.3103.



5l: Yield 65%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.87 – 7.72 (m, 2H), 7.41 (ddd, *J* = 6.6, 4.7, 1.9 Hz, 1H) (aryl C−**H**), 3.94 (m, 2H), 3.42 – 3.31 (m, 2H) (OC**H**$_2$), 2.56 (m, 1H) (C**H**), 2.16 (d, *J* = 12.5 Hz, 1H), 1.94 (d, *J* = 12.1 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.68 (m, 1H), 1.63 – 1.53

(m, 3H) (CHC**H**$_2$) ; **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.4 (2B), -4.6 (1B), -9.7 (4B), -11.1 (3B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 211.5 (**C**=O), 149.6, 147.7, 137.6, 126.8, 125.0 (aryl−**C**), 81.0, 77.9 (cage−**C**), 67.5, 67.4 (O**C**H$_2$), 47.8 (**C**H), 31.0 (B−**C**H$_2$), 28.5, 28.0 (CH**C**H$_2$), 23.6 (cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}NO_2H_{28}$ [M+H$^+$]: 362.3118. Found: 362.3113.



5m: Yield 97%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.70 – 8.56 (m, 1H), 7.87 – 7.73 (m, 2H), 7.68 – 7.57 (m, 2H), 7.39 (ddd, *J* = 7.2, 4.7, 1.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H) (aryl C−**H**), 3.71 – 3.62 (m, 2H) (NC**H**$_2$), 2.43 (s, 3H) (Ts−C**H**$_3$), 2.37 – 2.28 (m, 2H), 2.26 (d, *J* = 7.4 Hz, 1H) (C**H**), 2.12 (d, *J* = 12.4 Hz, 1H), 1.88 (d, *J* = 12.5 Hz, 1H) (B−C**H**$_2$), 1.86 – 1.79 (m, 2H) (NC**H**$_2$), 1.79 – 1.73 (m, 2H) (CHC**H**$_2$), 1.72 (s, 3H) (cage−C**H**$_3$), 1.65 – 1.56 (m, 2H) (CHC**H**$_2$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.4 (2B), -4.7 (1B), -9.6 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.97 (**C**=O), 149.64, 147.62, 143.70, 137.63, 133.21, 129.81, 127.82, 126.72, 125.05 (aryl−**C**), 80.99, 78.00 (cage−**C**), 47.53 (**C**H), 45.85, 45.74 ((N**C**H$_2$)), 31.35 (B−**C**H$_2$), 27.29, 26.83 (CH**C**H$_2$), 23.52 (cage−**C**H$_3$), 21.67 (Ts−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{22}B_{10}N_2O_2S_2H_{35}$ [M+H$^+$]: 531.3138. Found: 531.3130.

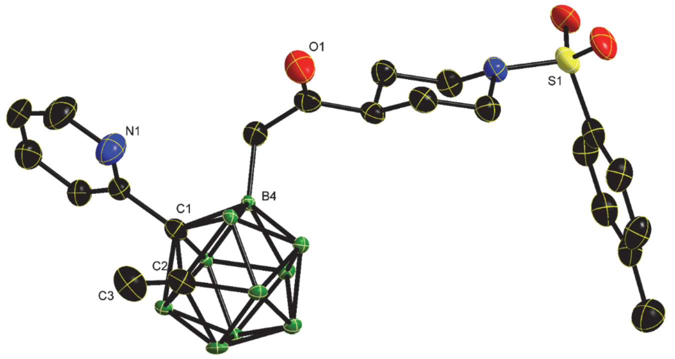
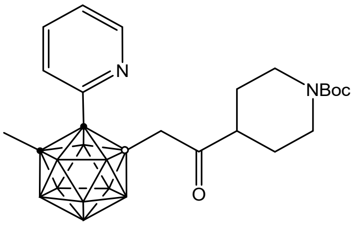
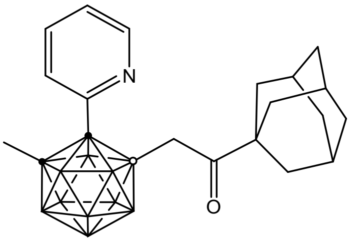


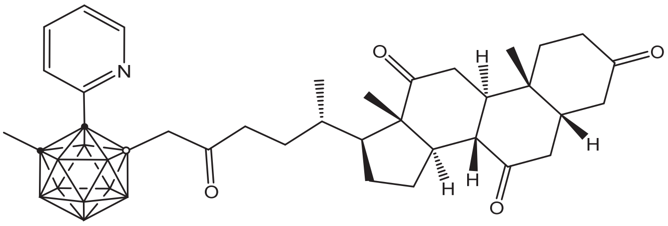
Figure S3. Molecular structure of compound **5m** (ellipsoids at 30% probability, solvent $CDCl_3$ and H atoms omitted for clarity**).**



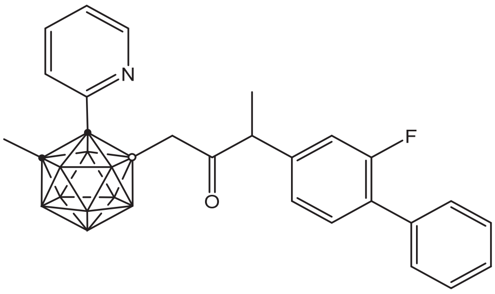
5n: Yield 65%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.70 – 8.63 (m, 1H), 7.88 – 7.77 (m, 2H), 7.41 (ddd, *J* = 6.7, 4.7, 2.1 Hz, 1H) (aryl C−**H**), 4.05 (s, 2H), 2.76 – 2.67 (m, 2H) (NC**H**$_2$), 2.54 – 2.42 (m, 1H) (C**H**), 2.15 (d, *J* = 12.4 Hz, 1H), 1.95 (d, *J* = 12.4 Hz, 1H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$), 1.67 (m, 2H) (CHC**H**$_2$), 1.43 (s, 9H) (Boc−C**H**$_3$), 1.40 – 1.32 (m, 2H) (CHC**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.0 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 211.7 (BCH$_2$−**C**=O), 154.8 (Boc−**C**=O), 149.6, 147.8, 137.6, 126.8, 125.0 (aryl−**C**), 81.0 (cage−**C**), 79.6 (tBu−**C**Me3), 77.9 (cage−**C**), 48.8 (br, **C**H), 43.45 (N**C**H$_2$), 31.5 (B−**C**H$_2$), 28.56 (tBu−**C**H$_3$), 27.76, 27.35 (CH**C**H$_2$), 23.55 (cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}N_2O_3H_{37}$ [M+H^{+}]: 462.3766. Found: 462.3769.



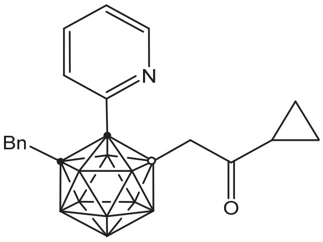
5o: Yield 42%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 4.5 Hz, 1H) (aryl C−**H**), 2.03 (s, 3H) (B−C**H**$_2$ and adamantly C−**H**), 1.91 (s, 6H) (adamantly C−**H**), 1.74 (d, *J* = 9.4 Hz, 11H) (cage−C**H**$_3$ and adamantly C−**H**); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ 5.8 (1B), -16.5 (1B), -18.4 (1B), -21.2 (1B), -22.2 (1B), -22.9 (1B), -23.5 (1B), -24.3 (1B), -25.3 (1B), -30.1 (1B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 182.85 (**C**=O), 149.77, 148.51, 137.73, 126.25, 124.91 (aryl−**C**), 77.97, 74.28 (cage−**C**), 40.54, 38.74, 36.67 (adamantly **C**), 29.85 (B−**C**H$_2$), 27.96 (adamantly **C**), 23.40 (cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}NOH_{34}$ [M+H$^+$]: 413.3602. Found: 413.3606.



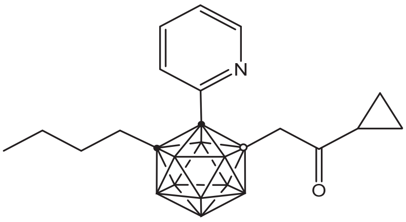
5p: Yield 71%. Colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.89 – 7.64 (m, 2H), 7.40 (ddd, *J* = 6.7, 4.8, 1.8 Hz, 1H) (aryl C−**H**), 2.93 (dd, *J* = 12.9, 6.1 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.74 (d, *J* = 12.6 Hz, 1H), 2.61 (q, *J* = 4.5 Hz, 2H), 2.50 – 2.36 (m, 2H), 2.35 – 2.14 (m, 6H), 2.11 – 2.03 (m, 2H), 2.01 – 1.84 (m, 6H) (alkyl C−**H**), 1.79 (m, 3H) (C**H**$_3$), 1.74 (s, 3H) (C**H**$_3$), 1.71 – 1.47 (m, 5H), 1.35 (s, 3H) (C**H**$_3$), 1.31 – 1.16 (m, 5H) (alkyl C−**H**), 1.02 (d, *J* = 1.0 Hz, 3H) (C**H**$_3$), 0.80 – 0.74 (m, 3H) (alkyl C−**H**); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.6 (4B), -11.1 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 212.9, 210.8, 210.2, 209.9 (**C**=O), 149.61, 147.8, 137.6, 126.7, 125.0 (aryl **C**), 80.9, 70.8 (cage−**C**), 58.0, 57.0, 52.0, 49.2, 45.7, 45.5, 45.2, 44.2, 40.8, 38.8, 36.0, 35.4, 34.8, 33.2, 29.2, 27.7, 25.3, 23.5, 22.7, 19.0, 12.0 (alkyl **C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{33}B_{10}NO_4H_{52}$ [M+H$^+$]: 635.4848. Found: 635.4953. In this case, diastereoisomers are formed from coupling at B(4) and B(5), and d.r. value could not be determined.



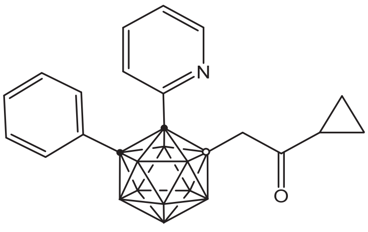
5q, Yield 60%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Conformer I : Conformer II** = 41 : 59, **Conformer I**: δ 8.63 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.56 – 7.28 (m, 7H), 7.05 – 6.84 (m, 2H) (aryl C−**H**), 3.95 (q, *J* = 6.8 Hz, 1H) (C**H**CH$_3$), 2.33 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.76 (s, 3H) (cage−C**H**$_3$), 1.70 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.33 (d, *J* = 6.9 Hz, 3H) (CHC**H**$_3$); **Conformer II**: δ 8.66 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.56 – 7.28 (m, 7H), 7.05 – 6.84 (m, 2H) (aryl C−**H**), 3.79 (q, *J* = 6.9 Hz, 1H) (C**H**CH$_3$), 2.16 (d, *J* = 12.2 Hz, 1H), 1.84 (d, *J* = 12.5 Hz, 1H) (B−C**H**$_2$), 1.75 (s, 3H) (cage−C**H**$_3$), 1.36 (d, *J* = 6.9 Hz, 3H) (CHC**H**$_3$). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.8 (4B), -11.0 (3B); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)**, **Conformer I**: δ 209.0 (**C**=O), 161.1, 158.6, 149.5, 147.7, 142.5, 137.6, 135.6, 131.1, 129.0, 127.8, 126.9, 124.2, 115.9 (d, *J* = 23.4 Hz) (aryl **C**), 80.9, 78.0 (cage−**C**), 52.3 (**C**HCH$_3$), 32.5 (B−**C**H$_2$), 23.6 (cage−**C**H$_3$), 17.4 (**C**HCH$_3$); **Conformer II**: **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 209.1 (**C**=O), 161.1, 158.6, 149.8, 147.7, 142.4, 137.5, 135.6, 131.1, 128.6, 127.8, 126.5, 125.0, 115.8 (d, *J* = 23.2 Hz) (aryl **C**), 81.1, 77.8 (cage−**C**), 52.8 (**C**HCH$_3$), 32.5 (B−**C**H$_2$), 23.6 (cage−**C**H$_3$), 17.5 (**C**HCH$_3$). **^{19}F NMR (376 MHz, Chloroform-*d*)**: δ -117.56 (q, *J* = 10.1 Hz). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{24}B_{10}FNOH_{31}$ [M+H$^+$]: 477.3351. Found: 477.3348.



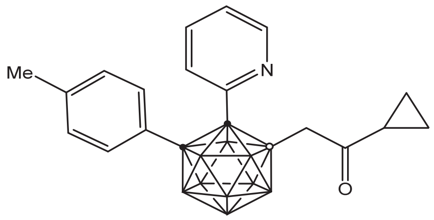
6b: Yield 95%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.76 (dt, *J* = 5.0, 1.3 Hz, 1H), 7.89 – 7.75 (m, 2H), 7.46 (ddd, *J* = 7.2, 4.8, 1.5 Hz, 1H), 7.26 – 7.16 (m, 3H), 6.91 – 6.75 (m, 2H) (aryl C−**H**), 3.26 (d, *J* = 14.9 Hz, 1H), 3.12 (d, *J* = 14.9 Hz, 1H) (Bn−C**H**$_2$), 2.29 (d, *J* = 12.2 Hz, 1H), 2.07 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.85 (tt, *J* = 7.8, 4.5 Hz, 1H) (Cyclopropyl−C**H**), 0.96 – 0.89 (m, 2H), 0.84 – 0.76 (m, 2H) (Cyclopropyl−C**H**$_2$) ; **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*):** δ -2.5 (3B), -10.2 (7B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.5 (**C**=O), 149.7, 147.8, 137.7, 135.4, 130.2, 128.4, 127.9, 127.4, 125.2 (aryl−**C**), 82.7, 82.1 (cage−**C**), 41.0 (Bn−**C**H$_2$), 35.0 (B−**C**H$_2$), 21.4 (Cyclopropyl−**C**H), 11.4, 11.4 (Cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}NOH_{28}$ [M+H$^+$]: 394.3169. Found: 394.3169.



6c: Yield 99%. Light yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.69 – 8.60 (m, 1H), 7.84 – 7.73 (m, 2H), 7.39 (ddd, *J* = 6.7, 4.8, 1.7 Hz, 1H) (aryl C−**H**), 2.25 (d, *J* = 12.2 Hz, 1H), 2.05 (d, *J* = 12.1 Hz, 1H) (B−CH$_2$), 1.89 – 1.79 (m, 2H) (Cyclopropyl−C**H** and nBu−C−**H**), 1.52 – 1.36 (m, 1H), 1.31 – 1.15 (m, 2H), 1.13 – 0.99 (m, 2H), 0.96 – 0.89 (m, 2H) (nBu−C−**H**), 0.84 – 0.75 (m, 2H) (Cyclopropyl−C**H**$_2$), 0.71 (t, *J* = 7.3 Hz, 3H) (nBu−C−**H** and Cyclopropyl−C**H**). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.7 (3B), -11.2 (7B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.5 (**C**=O), 149.5, 147.7, 137.5, 126.8, 124.9 (aryl−**C**), 83.2, 82.2 (cage−**C**), 35.1 (nBu−**C** and B−**C**H$_2$), 31.5, 22.2 (nBu−**C**), 21.4 (Cyclopropyl−**C**H), 13.6, 11.4 (nBu−**C**), 11.3 (Cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{30}$ [M+H$^+$]: 361.3289. Found: 361.3282.



6d: Yield 99%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.38 (d, *J* = 4.8 Hz, 1H), 7.53 (d, *J* = 4.3 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.03 (m, 3H) (aryl C−**H**), 2.29 (d, *J* = 12.2 Hz, 1H), 2.18 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 1.88 (tt, *J* = 8.1, 4.5 Hz, 1H) (Cyclopropyl−**C**H), 1.16 – 0.59 (m, 4H) (Cyclopropyl−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.9 (3B), -9.6 (3B), -10.9 (4B); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 210.5 (**C**=O), 149.5, 147.7, 137.5, 126.8, 124.9 (aryl−**C**), 83.2, 82.2 (cage−**C**), 35.1 (nBu−**C** and B−**C**H$_2$), 31.5, 22.2 (nBu−**C**), 21.4 (Cyclopropyl−**C**H), 13.6, 11.4 (nBu−**C**), 11.3 (Cyclopropyl−**C**H$_2$). **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.5 (**C**=O), 149.2, 147.1, 136.8, 130.9, 130.6, 130.3, 128.2, 126.0, 124.6 (aryl−**C**), 85.6, 84.3 (cage−**C**), 35.4 (B−**C**H$_2$), 21.5 (Cyclopropyl−**C**H), 11.4 (Cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NOH_{26}$ [M+H$^+$]: 380.3012. Found: 380.3013.



6e: Yield 95%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.40 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.36 – 7.29 (m, 2H), 7.16 (ddd, *J* = 6.1, 4.8, 2.5 Hz, 1H), 6.94 – 6.83 (m, 2H) (aryl C−**H**), 2.28 (d, *J* = 12.2 Hz, 1H) (B−C**H**$_2$), 2.20 (s, 3H) (Ph−C**H**$_3$), 2.17 (d, *J* = 12.3 Hz, 1H) (B−C**H**$_2$), 1.88 (tt, *J* = 7.8, 4.5 Hz, 1H) (Cyclopropyl−C**H**), 0.99 – 0.93 (m, 2H), 0.86 – 0.79 (m, 2H) (Cyclopropyl−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.1 (3B), -11.1 (7B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.6 (**C**=O), 149.2, 147.2, 140.6, 136.8, 130.7, 128.9, 127.9, 126.0, 124.6 (aryl−**C**), 85.9, 84.3 (cage−**C**), 35.1 (B−**C**H$_2$), 21.5 (Cyclopropyl−**C**H), 21.1 (Ph−**C**H$_3$), 11.4 (Cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}NOH_{28}$ [M+H$^+$]: 395.3132. Found: 395.3131.

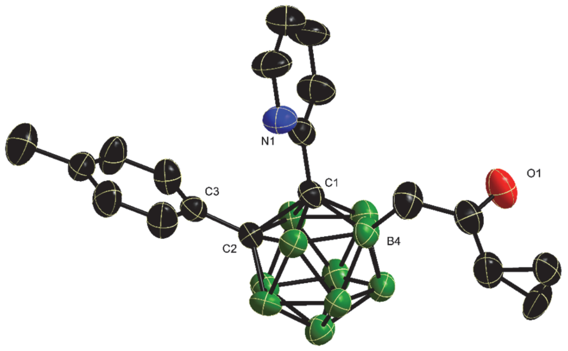
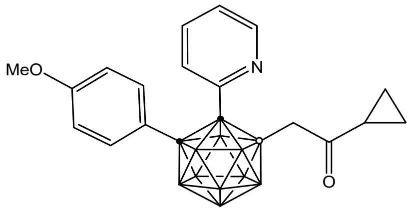
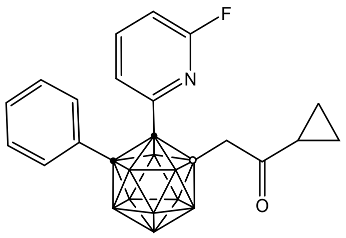


Figure S4. Molecular structure of compound **6e** (ellipsoids at 30% probability and H atoms omitted for clarity).

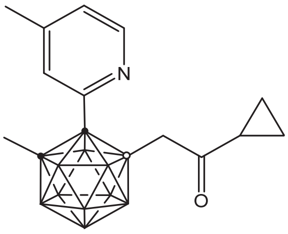


6f: Yield 99%. Yellow sticky solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.41 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.61 – 7.47 (m, 2H), 7.43 – 7.33 (m, 2H), 7.16 (ddd, *J* = 6.2, 4.8, 2.4 Hz, 1H), 6.65 – 6.55 (m, 2H) (aryl C−**H**), 3.70 (s, 3H) (O−C**H**$_3$), 2.28 (d, *J* = 12.2 Hz, 1H), 2.17 (d, *J* = 12.1 Hz, 1H) (B−C**H**$_2$), 1.88 (tt, *J* = 7.8, 4.6 Hz, 1H) (Cyclopropyl−C**H**), 0.95 (m, 2H), 0.87 – 0.77 (m, 2H) (Cyclopropyl−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.0 (3B), -10.6 (7B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.5 (**C**=O), 161.0, 149.2, 147.21, 136.8, 132.3, 126.0, 124.6, 122.9, 113.4 (aryl−**C**), 86.2, 84.5 (cage−**C**), 55.4 (O−**C**H$_3$), 35.2 (B−**C**H$_2$), 21.5 (Cyclopropyl−**C**H), 11.4 (Cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}NO_2H_{28}$ [M+H$^+$]: 410.3118. Found: 410.3122.

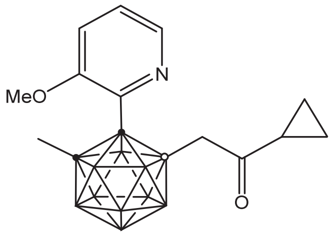


6g: Yield 99%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.65 (q, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.16

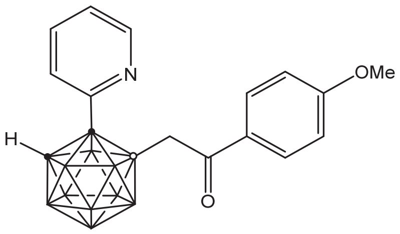
(t, *J* = 7.7 Hz, 2H), 6.81 (dd, *J* = 8.2, 3.1 Hz, 1H) (aryl C−**H**), 2.33 (d, *J* = 12.3 Hz, 1H), 2.21 (d, *J* = 12.3 Hz, 1H) (B−C**H**$_2$), 1.92 (m, 1H) (Cyclopropyl−C**H**), 0.97 (t, *J* = 4.9 Hz, 2H), 0.85 (t, J = 6.3 Hz, 2H) (Cyclopropyl−C**H**$_2$). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.0 (3B), -9.6 (2B), -10.9 (5B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.36 (**C**=O, 163.0, 160.6, 145.8, 145.6, 141.9, 141.9, 130.9, 130.5, 130.3, 128.4, 123.7, 123.7, 111.5, 111.1 (aryl−**C**), 85.9, 82.5 (cage−**C**), 35.0 (B−**C**H$_2$), 21.6 (cyclopropyl−**C**H), 11.5, 11.5 (cyclopropyl−**C**H$_2$). **^{19}F NMR (471 MHz, Chloroform-*d*)**: δ -65.2. **HRMS** (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}NOFH_{25}$ [M+H$^+$]: 398.2918. Found: 398.2915.



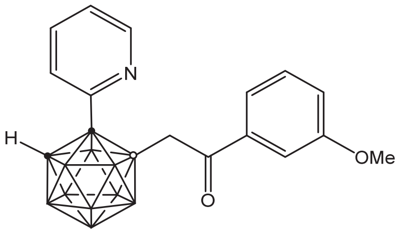
6h: Yield 99%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.51 (dd, *J* = 4.6, 1.8 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.32 – 7.26 (m, 1H) (aryl C−**H**), 2.68 (s, 3H) (Pyridyl−C**H**$_3$), 2.34 (d, *J* = 11.9 Hz, 1H), 1.96 (d, *J* = 12.1 Hz, 1H) (B−C**H**$_2$), 1.84 (tt, *J* = 7.8, 4.6 Hz, 1H) (cyclopropyl−C**H**), 1.70 (s, 3H) (cage−C**H**$_3$), 0.99 – 0.84 (m, 2H), 0.81 – 0.73 (m, 2H) (cyclopropyl−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.3 (1B), -2.3 (1B), -4.9 (1B), −7.2 (1B), −8.8 (1B), −10 (5B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.7 (**C**=O), 146.7, 143.7, 142.6, 136.6, 124.6 (aryl−**C**), 23.9 (cage−**C**H$_3$), 22.4 (Pyridyl−**C**H$_3$), 21.2 (cyclopropyl−**C**H), 11.4, 11.2 (cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}NOH_{26}$ [M+H$^+$]: 332.3012. Found: 332.3003.



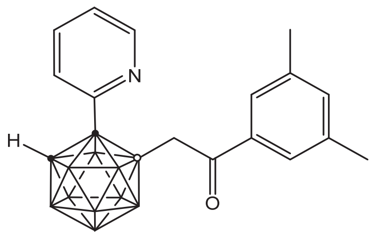
6i: Yield 99%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.27 (dd, *J* = 3.9, 1.9 Hz, 1H), 7.42 – 7.33 (m, 2H) (aryl C−**H**), 3.88 (s, 3H) (OC**H**$_3$), 2.32 (d, *J* = 12.0 Hz, 1H), 2.00 (d, *J* = 12.0 Hz, 1H) (B−C**H**$_2$), 1.85 (tt, *J* = 7.8, 4.6 Hz, 1H) (cyclopropyl−C**H**), 1.70 (s, 3H) (cage−C**H**$_3$), 0.92 – 0.85 (m, 2H), 0.81 – 0.74 (m, 2H) (Cyclopropyl−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.4 (1B), -2.3 (1B), -5.3 (1B), −9.2 (4B), −11.3 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 210.7 (**C**=O), 157.0, 141.0, 134.6, 126.4, 121.2 (aryl−**C**), 79.8, 78.6 (cage−**C**), 55.7 (O**C**H$_3$), 35.7 (B−**C**H$_2$), 23.7 (cage−**C**H$_3$), 21.1 (cyclopropyl−**C**H), 11.3, 11.2 (cyclopropyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}NO2H_{26}$ [M+H$^+$]: 370.2781. Found: 370.2788.



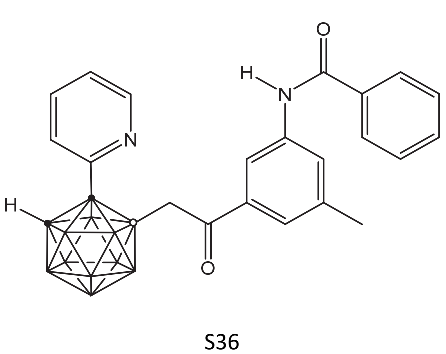
7a: Yield 73%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.46 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H), 7.55 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.32 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.94 – 6.84 (m, 2H) (aryl C−**H**), 5.07 (s, 1H) (cage−C**H**), 3.86 (s, 3H) (O−C**H**$_3$), 2.57 (d, *J* = 13.5 Hz, 1H), 2.31 (d, *J* = 13.5 Hz, 1H) (B−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -3.8 (3B), -8.2 (1B), -10.8 (4B), −12.8 (1B), −13.9 (1B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 197.4 (**C**=O), 163.6, 145.0, 149.1, 137.6, 131.1, 130.5, 124.5, 122.7, 113.8 (aryl−**C**), 76.0, 58.1 (cage−**C**H), 55.6 (O−**C**H$_3$), 27.4 (B−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NO_2H_{24}$ [M+H$^+$]: 370.2808. Found: 370.2805.



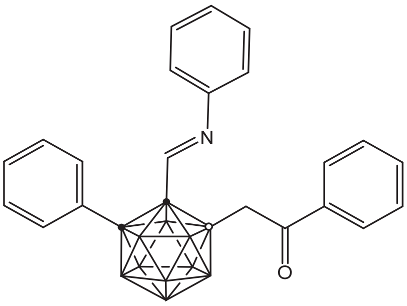
7b: Yield 71%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.44 (ddt, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.80 – 7.70 (m, 1H), 7.55 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.39 (dt, *J* = 4.5, 1.6 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.14 – 7.04 (m, 1H) (aryl C−**H**), 5.07 (s, 1H) (cage−C**H**), 3.84 (s, 3H) (O−C**H**$_3$), 2.61 (d, *J* = 13.5 Hz, 1H), 2.38 (d, *J* = 13.5 Hz, 1H) (B−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -3.8 (3B), -8.1 (1B), -10.7 (4B), −12.8 (1B), −13.8 (1B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 198.7 (**C**=O), 159.9, 149.9, 149.1, 138.8, 137.7, 129.6, 124.5, 122.7, 121.5, 119.8, 112.8 (aryl−**C**), 76.0, 58.0 (cage−**C**H), 55.6 (O−**C**H$_3$), 27.8 (B−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NO_2H_{24}$ [M+H$^+$]: 370.2812. Found: 370.2805.



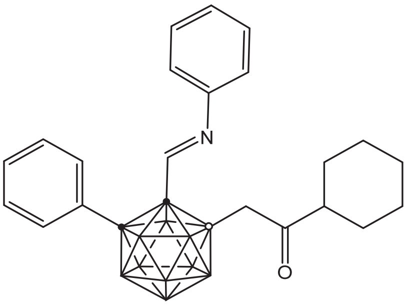
7c: Yield 72%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.44 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.55 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.44 (s, 2H), 7.31 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.17 (s, 1H) (aryl C−**H**), 5.07 (s, 1H) (cage−C**H**), 2.61 (d, *J* = 13.5 Hz, 1H), 2.37 (d, *J* = 13.5 Hz, 1H) (B−C**H**$_2$), 2.35 (s, 6H) (C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -1.9 (3B), -6.1 (1B), -8.7 (4B), −10.7 (1B), −11.8 (1B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.2 (**C**=O), 149.9, 149.0, 138.2, 137.6, 137.5, 134.9, 126.6, 124.5, 122.7 (aryl−**C**), 76.0, 58.0 (cage−**C**H), 27.5 (B−**C**H$_2$), 21.4 (**C**H$_3$). **HRMS** (ESI, positive mode)**:** *m/z* calcd for $C_{17}B_{10}NOH_{26}$ [M+H$^+$]: 368.3016. Found: 368.3012.



7d: Yield 86%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 12.53 (s, 1H) (N**H**), 8.72 (s, 1H), 8.35 (dt, *J* = 4.7, 1.5 Hz, 1H), 8.00 – 7.90 (m, 2H), 7.64 – 7.54 (m, 2H), 7.54 – 7.40 (m, 4H), 7.22 – 7.14 (m, 1H), 6.84 (dd, *J* = 8.3, 1.7 Hz, 1H) (aryl C−**H**), 4.99 (s, 1H) (cage−C**H**), 2.58 (d, *J* = 13.5 Hz, 1H), 2.46 (d, *J* = 13.6 Hz, 1H) (B−C**H**$_2$), 2.36 (s, 3H) (C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -3.7 (3B), -8.1 (1B), -10.7 (4B), −12.8 (1B), −13.7 (1B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 203.3, 166.1 (**C**=O), 149.7, 149.0, 146.9, 141.7, 137.6, 135.1, 132.3, 132.1, 128.9, 128.9, 127.6, 124.6, 123.5, 122.7, 121.3, 120.0 (aryl C−**H**), 75.8, 58.1 (cage−**C**H), 29.3 (B−**C**H$_2$), 22.4 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{23}B_{10}N_2O_2H_{29}$ [M+H$^+$]: 473.3230. Found: 473.3227.



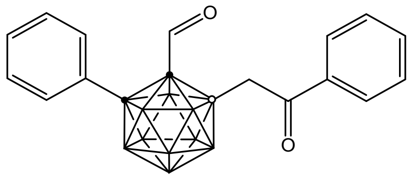
7e: Yield 43%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.01 – 7.94 (m, 2H), 7.69 – 7.61 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.39 (m, 4H), 7.37 – 7.30 (m, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 6.85 – 6.75 (m, 2H) (Ph−**H** and C**H**=N), 3.00 (d, *J* = 13.1 Hz, 1H), 2.95 (d, *J* = 13.0 Hz, 1H) (C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.0 (1B), -2.5 (2B), -9.3 (1B), -10.6 (6B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 200.6 (**C**=O), 150.9 (**C**H=N), 149.3, 137.2, 133.1, 131.2, 130.7, 130.3, 129.2, 129.0, 128.6, 128.5, 127.4, 120.5 (Ph−**C**), 84.8, 78.6 (cage−**C**), 29.1 (B−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{23}B_{10}NOH_{28}$ [M+H$^+$]: 442.3169. Found: 442.3164.



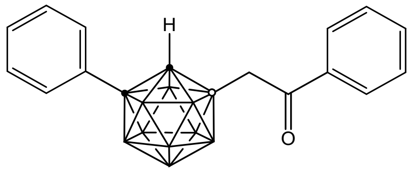
7f: Yield 59%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.67 – 7.62 (m, 2H), 7.46 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 1H), 6.81 – 6.68 (m, 2H) (Ph−**H** and C**H**=N), 2.53 – 2.41 (m, 3H) (cyclopropyl−C**H** and B−C**H**$_2$), 1.93 – 1.84 (m, 2H), 1.81 – 1.75 (m, 2H), 1.71 – 1.60 (m, 2H), 1.30 (m, 4H) (cyclopropyl−C**H**); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -0.9 (1B), -2.5 (2B), -9.2 (2B), -10.6 (5B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 214.0 (**C**=O), 150.9 (**C**H=N), 149.3, 131.2, 130.7, 130.3, 128.6, 127.3, 120.5 (Ph−**C**), 84.9, 78.5 (cage−**C**), 31.4 (B−**C**H$_2$), 28.5, 28.4, 26.0, 25.8 (cyclopropyl−**C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{23}B_{10}NOH_{34}$ [M+H$^+$]: 448.3638. Found: 448.3635.

Removal of directing group. **7e** (44.8 mg, 0.1 mmol), HOAc (0.4 mL) and HFIP (0.6 mL) were added into a 10 mL Schlenk tube and allowed to stir at 120 °C for 24h under argon. Then, the reaction mixture was cooled to room temperature and concentrated in *vacuo*. The residue was purified on preparative TLC by using petroleum ether/CH_2Cl_2 as the eluent to afford the desired product **7g** (29.7 mg, 81%).

A 10 mL reaction tube with a magnetic stir bar was charged with **7g** (36.6 mg, 0.1 mmol), THF (1 mL). A H_2O solution (1 mL) of KMnO4 (1.0 equiv. 15.8 mg) and Na_2HPO_4 (1.0 equiv. 14.2 mg) was added into the solution. The reaction mixture was allowed to stir at room temperature for 24h. Upon completion, the reaction mixture was treated with 5 mL of water. The organic layer was extracted with ethyl acetate for three times (3 × 10 mL). The crude reaction mixture was purified on preparative TLC using petroleum ether/CH_2Cl_2 as the eluent to afford the desired product **7h** (31.8 mg, 94%).



7g: Yield 81%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 9.04 (s, 1H) (C**HO**), 8.02 – 7.21 (m, 2H), 7.68 – 7.55 (m, 3H), 7.52 – 7.42 (m, 3H), 7.40 – 7.31 (m, 2H) (Ph−**H**), 3.00 (d, *J* = 13.7 Hz, 1H), 2.83 (d, *J* = 13.7 Hz, 1H) (C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ 0.6 (1B), -2.4 (2B), -8.5 (1B), -10.2 (2B), -11.1 (4B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 182.3 (**C**=O), 133.3, 131.2, 130.8, 129.9, 129.0, 128.8, 128.6, 127.5 (Ph−**C**), 29.3 (**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{21}$ $[M-H]^-$: 365.2550. Found: 365.2554.



7h: Yield 94%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.04 – 7.93 (m, 2H), 7.58 (m, 1H), 7.51 – 7.42 (m, 4H), 7.42 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H) (Ph−**H**), 4.39 (s, 1H) (cage−C**H**), 2.98 (d, J = 13.5 Hz, 1H); 2.92 (d, J = 13.5 Hz, 1H) (C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.2 (1B), -3.7 (1B), -5.1 (1B), -8.5 (1B), -9.3 (1B), -11.0 (4B), -13.4 (1B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 201.7 (**C**=O), 137.5, 133.4,, 130.0, 129.0, 128.82, 128.79, 127.6, 125.2 (Ph−**C**), 61.2 (cage−**C**), 28.7 (**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{21}$ $[M-H]^-$: 337.2601. Found: 337.2607.

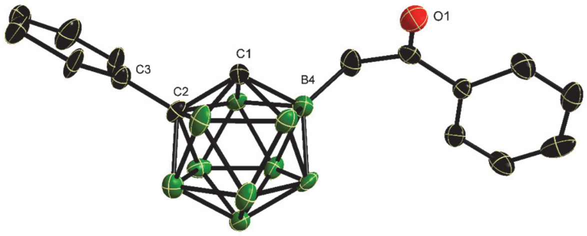
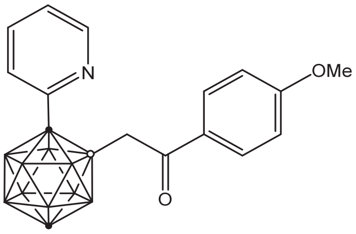
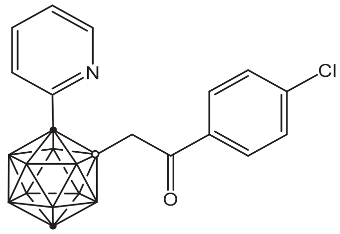


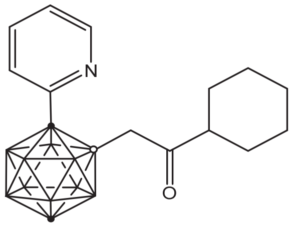
Figure S5. Molecular structure of compound **7h** (ellipsoids at 30% probability and H atoms omitted for clarity).



***p*-CB-a**: Yield 72%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.48 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.91 – 7.76 (m, 2H), 7.60 (td, *J* = 7.8, 1.9 Hz, 1H), 7.28 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.21 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H), 7.01 – 6.81 (m, 2H) (aryl C−**H**), 3.86 (s, 3H) (O−C**H**$_3$), 2.82 (s, 1H) (cage−C**H**), 2.46 (s, 2H) (B−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -4.6 (1B), -11.7 – -12.4 (4B), −14.7 (2B), −16.2 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.0 (**C**=O), 163.3, 152.2, 148.9, 136.8, 131.1, 130.5, 123.4, 122.2, 113.5 (aryl−**C**), 87.6, 61.5 (cage−**C**H), 55.4 (O−**C**H$_3$), 27.3 (B−CH$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NO_2H_{24}$ [M+H$^+$]: 370.2803. Found: 370.2805.



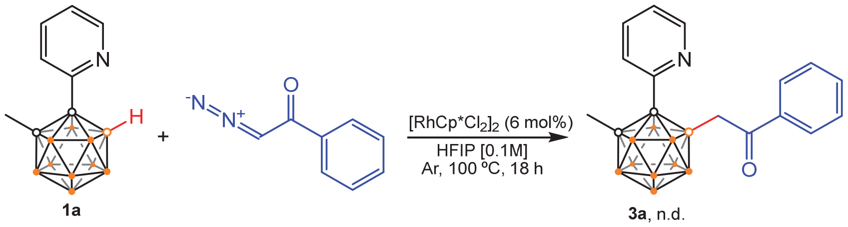
***p*-CB-b**: Yield 58%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.44 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.57 (td, *J* = 7.8, 1.9 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.23 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H) (aryl C−**H**), 2.81 (s, 1H) (cage−C**H**), 2.48 (s, 2H) (B−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -4.9 (1B), -11.8 – -12.5 (4B), −14.8 (2B), −16.2 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.3 (**C**=O), 152.3, 149.0, 139.3, 136.9, 136.0, 130.3, 128.8, 123.57, 122.3 (aryl−**C**), 87.5, 61.7 (cage−**C**H), 27.6 (B−CH$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}NOClH_{21}$ [M+H$^+$]: 347.2305. Found: 347.2309.



***p*-CB-c**: Yield 83%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.47 (d, *J* = 4.3 Hz, 1H), 7.60 (td, *J* = 7.8, 1.9 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 7.6, 4.8 Hz, 1H) (aryl C−**H**), 2.89 (s, 1H) (cage−C**H**), 2.21 (t, *J* = 10.9 Hz, 1H), 2.02 (s, 3H), 1.78 – 1.70 (m, 4H), 1.61 (s, 2H), 1.31 – 1.09 (m, 6H) (cyclopropyl−C**H** and B−C**H**$_2$). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -4.8 (1B), -11.7 (2B), -12.5 (2B), −14.7 (2B), −16.3 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 213.7 (**C**=O), 152.4, 149.0, 136.9, 123.5, 122.2 (aryl−**C**), 61.7, 51.4 (cage−**C**), 30.1 (B−**C**H$_2$), 28.5, 26.1, 25.9 (cyclopropyl−**C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}NOH_{28}$ [M+H$^+$]: 346.3169. Found: 346.3169.

2.4 Comparison of diazoketone and sulfoxonium ylide, intermolecular competition experiments

2.4.1 Comparison of diazoketone and sulfoxonium ylide

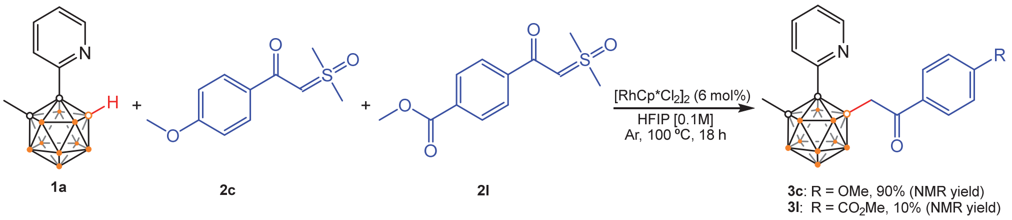


Scheme S2. Reaction of **1a** and diazoketone.

Reaction of diazoketone 6a and 1a. 1a (23.5 mg, 0.1 mmol), diazoketone (2.0 equiv., 29.2 mg, 0.2 mmol), RhCp*(OAc)$_2$•H$_2$O (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 18 h under argon. After cooling to room temperature, no desired product was detected. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography by using petroleum ether/DCM to afford the start material **1a** (22.8 mg, yield: 97%).

2.4.2 Intermolecular competition experiments

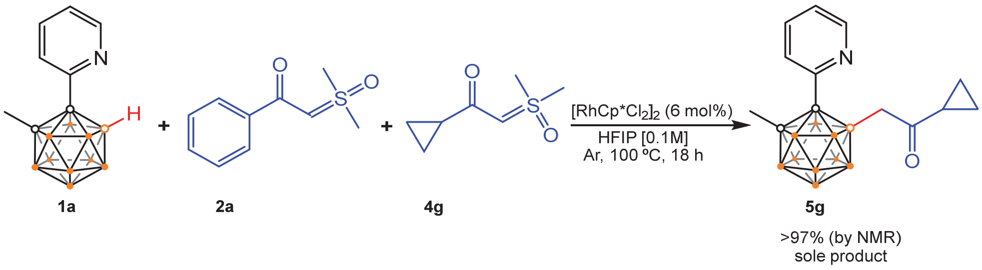
2.4.2.1 Intermolecular competition experiment between electron-rich and electron-deficient phenylsulfoxonium ylides



Scheme S3. Competition experiment of **2c** and **2l**.

Intermolecular competition experiment of 2c and 2l. 1a (23.5 mg, 0.1 mmol), **2c** (2.0 equiv., 45.3 mg, 0.2 mmol), **2l** (2.0 equiv., 50.9 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 18 h under argon. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was test by ^{1}H NMR in $CDCl_3$.

2.4.2.2 Intermolecular competition experiment between arylated and alkylated sulfoxonium ylides

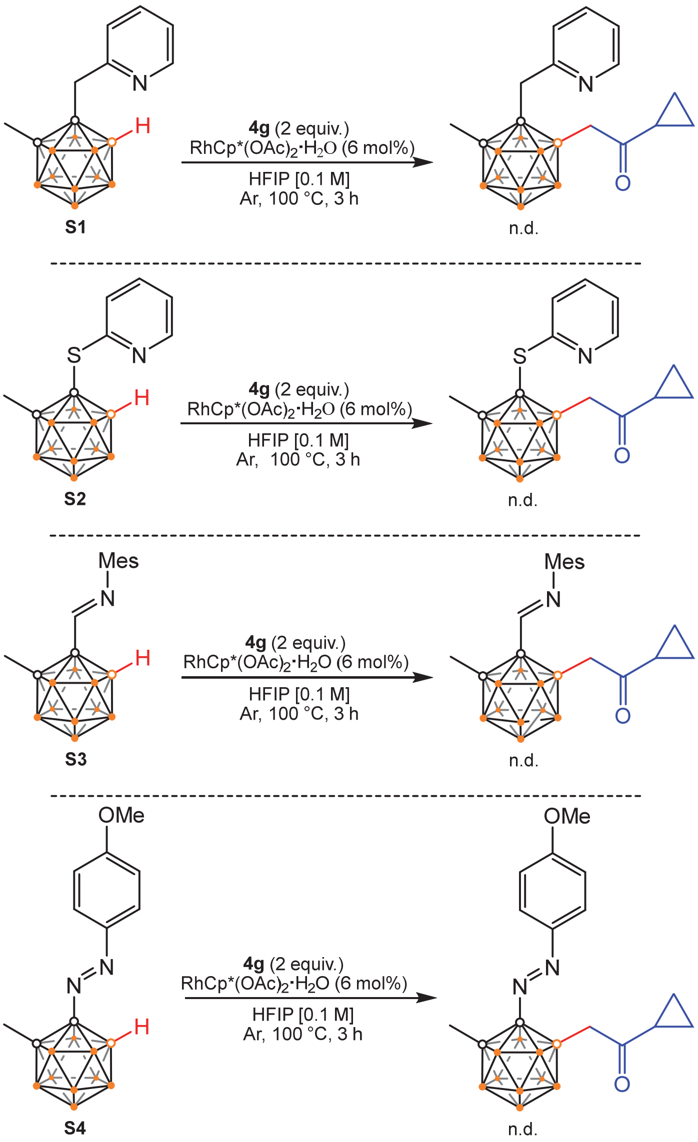


Scheme S4. Competition experiment of **2a** and **4g**.

Intermolecular competition experiment of 2a and 4g. 1a (23.5 mg, 0.1 mmol), **2a** (2.0 equiv., 39.2 mg, 0.2 mmol), **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 18 h under argon. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was test by ^1H NMR in $CDCl_3$.

2.5 Attempts with other substrates

2.5.1 Attempts with other directing groups

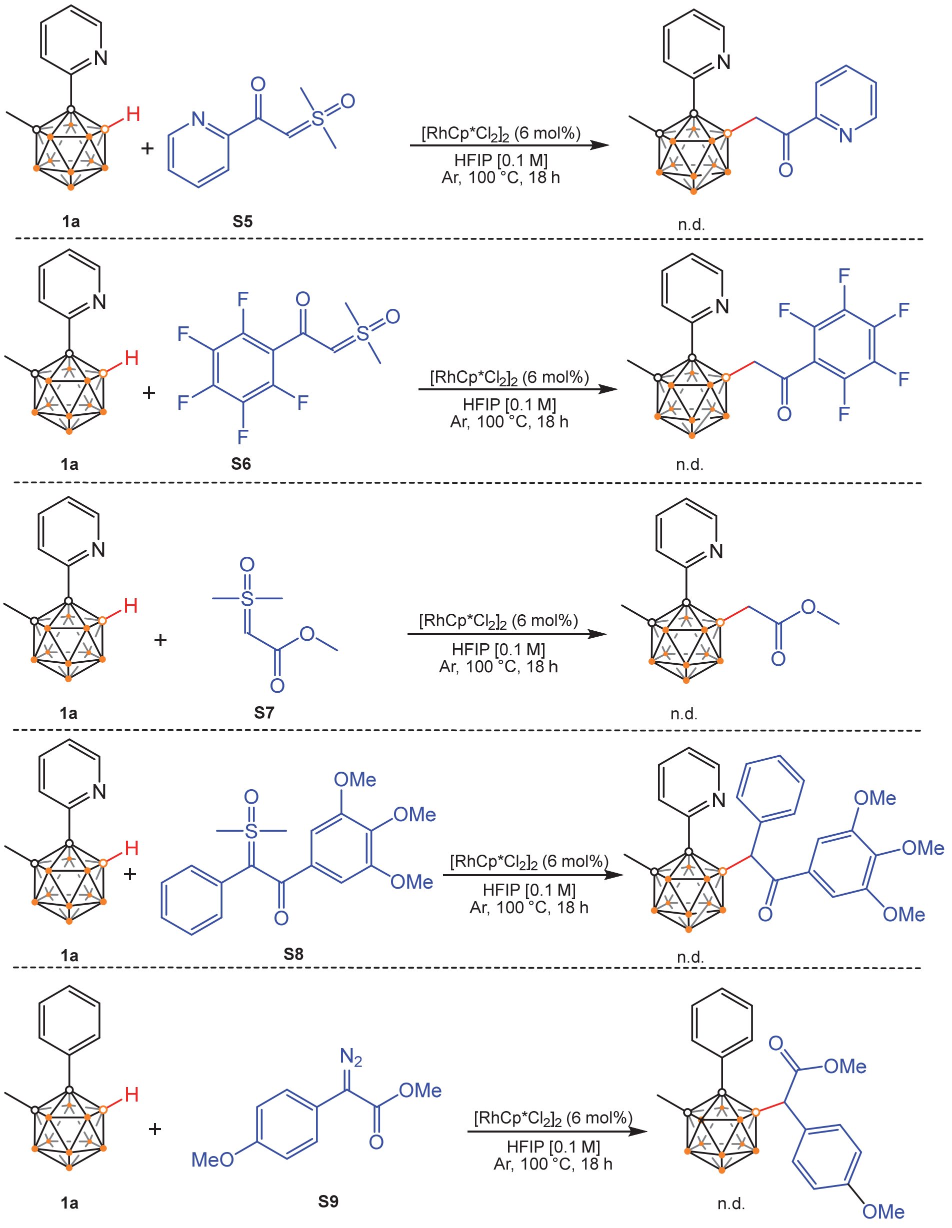


>95% Carborane starting materials were recovered in all cases.

Scheme S5. Attempts with other directing groups.

S1/S2/S3/S4 (0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), RhCp*$(OAc)_2$•H_2O (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 3 h under argon.

2.5.2 Attempts with other carbene precursors



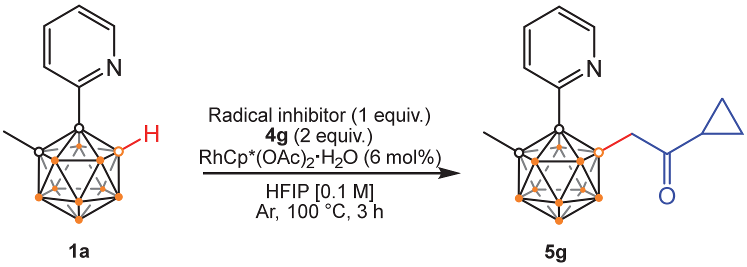
>95% Carborane starting materials were recovered in all cases!

Scheme S6. Attempts with other carbene precursors.

1a (23.5 mg, 0.1 mmol), sulfoxonium ylide **S5/S6/S7/S8/S9** (2.0 equiv., 0.2 mmol), $[RhCp^*Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 18 h under argon.

3 Mechanistic study

3.1 Reactions with radical inhibitor



Radical inhibitor	Yield of **5g**
TEMPO	70%
1,4–cyclohexadiene	96%

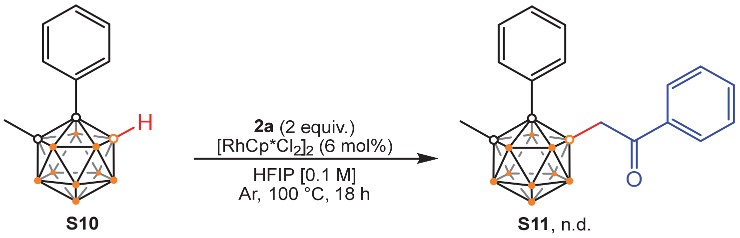
Scheme S7. Reactions with radical inhibitor.

Note: The reactions in the presence of radical quenchers TEMPO or 1,1-diphenylethylene still provided the product 5ag in high yields, implying that radical intermediates should not be involved.

Reaction in the presence of TEMPO. 1a (23.5 mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), RhCp*$(OAc)_2$•H_2O (6 mol%, 2.2 mg, 0.006 mmol), TEMPO (1.0 equiv., 15.6 mg, 0.1 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 3 h. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford compound **5g** (70%).

Reaction in the presence of 1,1-diphenylethylene. 1a (23.5 mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), RhCp*$(OAc)_2$•H_2O (6 mol%, 2.2 mg, 0.006 mmol), 1,1-diphenylethylene (1.0 equiv., 18.8 mg, 0.1 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 3 h. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford compound 5**g** (96%).

3.2 Reaction without directing group

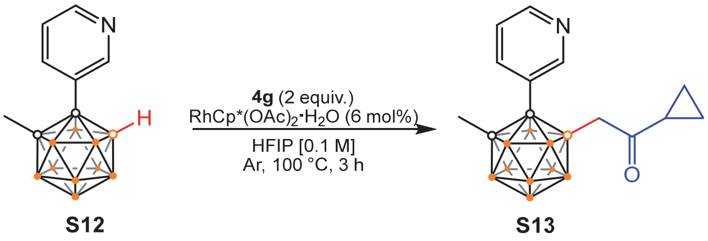


Scheme S8. Attempts without directing group.

Note: The reaction of S10 and 2a does not proceed, implying that the directing group is essential.

S10 (23.4 mg, 0.1 mmol), sulfoxonium ylide **2a** (2.0 equiv., 39.2 mg, 0.2 mmol), $[RhCp^{*}Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 18 h. Then, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. No product was detected. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum as the eluent to afford compound **S10** as a white solid (22.9 mg, 98%).

3.3 Influence of the electronic property from pyridyl



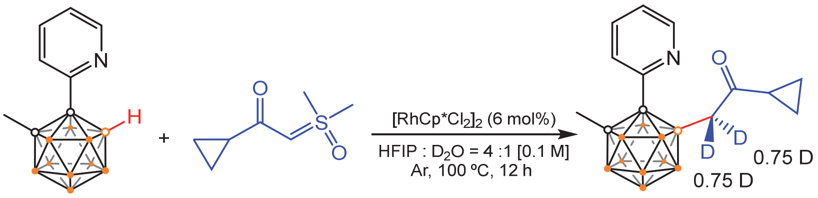
Scheme S9. Reaction of **S12** and **4g**.

Note: The reaction of S12 and 4g does not proceed, indicating that the B(4) site

regioselectivity is controlled by the directing function of 2-pyridyl.

S12 (23.5 mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), RhCp*$(OAc)_2$•H_2O (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 18 h under argon. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL EtOAc. No product was detected. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on preparative TLC by using petroleum ether/EtOAc as the eluent to afford compound **S12** as a white solid (23.0 mg, 98%).

3.4 Deuterium labeling experiments



1a   **4g** (2.0 equiv.)   **5g-D2**

Scheme S10. Deuterium labeling experiments

1a (23.5 mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (6 mol%, 3.7 mg, 0.006 mmol), HFIP (0.8 mL) and D_2O (0.2 mL) were mixed in a 10 mL Schlenk tube. The resulting mixture was stirred at 100 °C for 12 h under argon. Upon completion, the reaction mixture was cooled to room temperature. Then, ethyl acetate and brine were added and the aqueous layer was reextracted with ethyl acetate. The combined organic layers were washed with water then brine, dried over MgSO4, filtered and concentrated under reduced pressure. The crude reaction mixture was purified on preparative TLC by using petroleum/ethyl acetate as the eluent to afford compound **5g-D2** as a white solid (23.1 mg, 73%). **^{1}H {^{11}B} NMR (500 MHz, Chloroform-*d*)**: δ 8.66 (d, *J* = 4.1 Hz, 1H), 7.82-7.76 (m, 2H), 7.39 (ddd, *J* = 6.7, 4.6, 2.0 Hz, 1H) (aryl C−**H**), 3.07 (s, 1H), 2.62 (s, 1H), 2.51 (s, 1H), 2.42 (s, 2H), 2.33 (s, 1H), 2.31 (s, 2H) (B**H**), 2.23 (s, 0.25H) (C**H**$_2$), 2.20 (s, 1H) (B**H**), 2.04 (s, 0.25H) (C**H**$_2$), 1.84 (tt, *J* = 8.0, 4.6 Hz, 1H) (cyclopropyl−C**H**), 1.76 (s, 3H) (C**H**$_3$), 0.93 (t, *J* = 4.3 Hz, 2H), 0.81-0.78 (m, 2H) (cyclopropyl−C**H**$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{13}B_{10}NOH_{21}D_2$ [M+H$^+$]: 319.3000. Found: 319.3000. The deuterium content was 0.75 D.

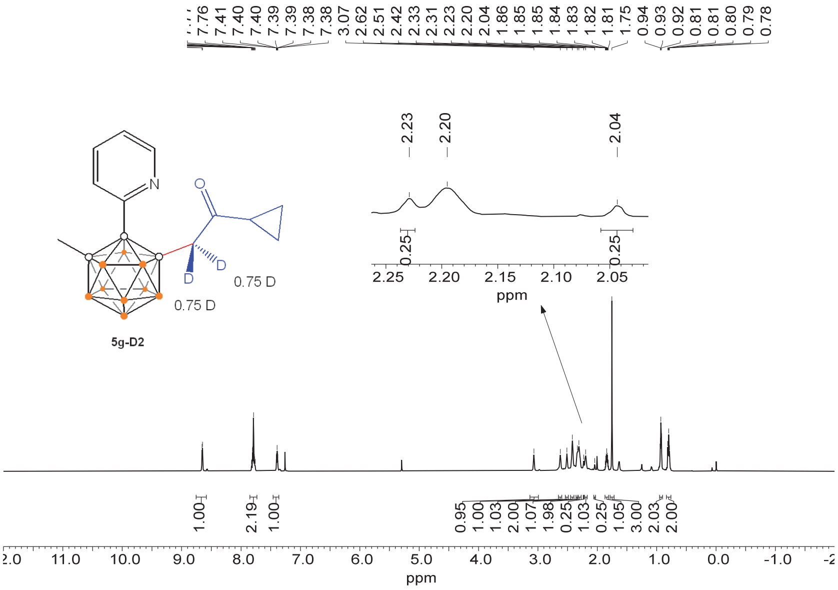
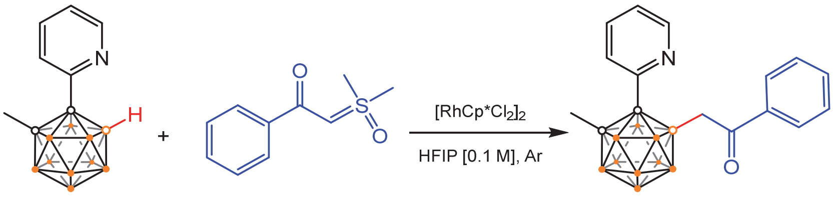


Figure S6. $^1H\{^{11}B\}$ NMR of **5g-D2**.

3.5 *in situ* HRMS and NMR studies of the reaction mechanism under different conditions

3.5.1 *in situ* HRMS and NMR studies on the reaction of 1a and less reactive 2a in HFIP

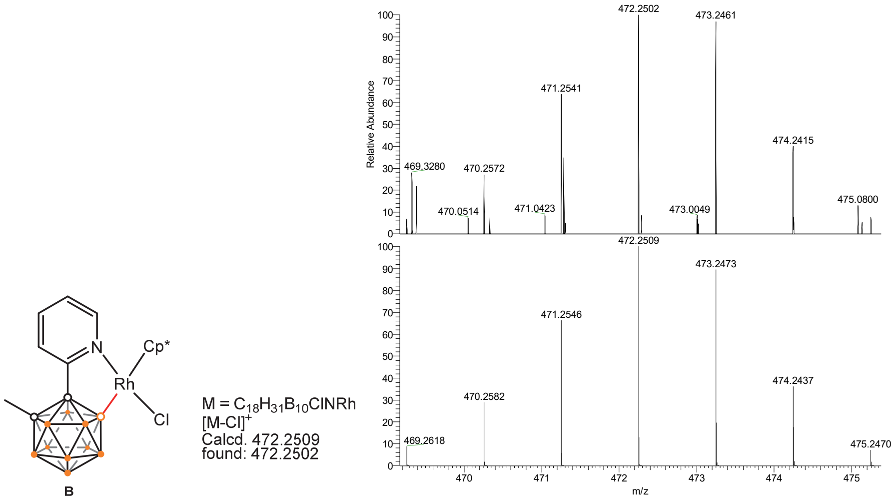


1a **2a** **3a**

Scheme S11. Reaction of **1a** and **2a**.

1a (11.8 mg, 0.05 mmol), sulfoxonium ylide **2a** (2.0 equiv., 19.6 mg, 0.1 mmol), $[RhCp^*Cl_2]_2$ (12.5 mol%, 3.9 mg, 0.006 mmol) and HFIP (0.5 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at variable temperature. The reaction system was directly analyzed by ESI-HRMS or ^1H NMR at different time and temperature. Part of the mixture was taken out and analyzed after being heated at 40 °C for 40 min. The mass spectrum indicated the formation of intermediates **B**. Then, the left mixture was heated at 60 °C for 60 min and the mass spectrum indicated the formation of rhodium intermediates **D** besides **B**. When heated at 60 °C for 120 min, the mass spectrum of the mixture indicated the formation of product **3a** besides **B** and **D**. When heated at 100 °C for 24h, the mass spectrum of the mixture still showed the product **3a** besides **B** and **D**. The starting materials **1a**, **2a** and $[RhCp^*Cl_2]_2$ were also detected during the reaction with different time. Examples of the NMR spectra collected over time and temperature are presented in Figure S16. When the mixture was heated at 100 °C for 270 min, the ^1H NMR spectrum indicated a new pyridyl signal at 8.60 ppm (☐) and the formation of the product **3a** (△). Two new pyridyl signals appeared at 8.41 (○) and 8.60 ppm (☐) at 100 °C for 24h.

a) *in situ* HRMS of the reaction mixture at 40 °C for 40 min

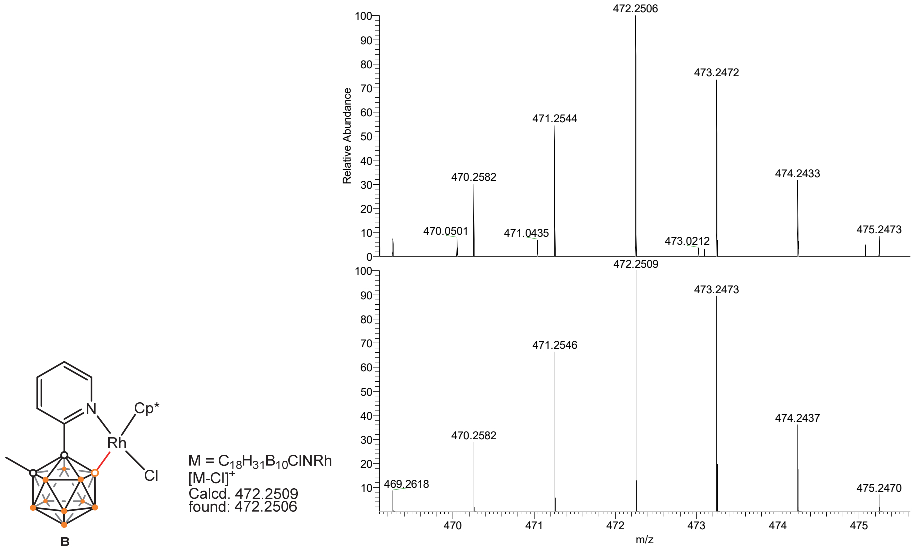


M = $C_{18}H_{31}B_{10}ClNRh$
$[M-Cl]^+$
Calcd. 472.2509
found: 472.2502

Figure S7. HRMS of **B**. Up: experimental MS. Down: calculated MS.

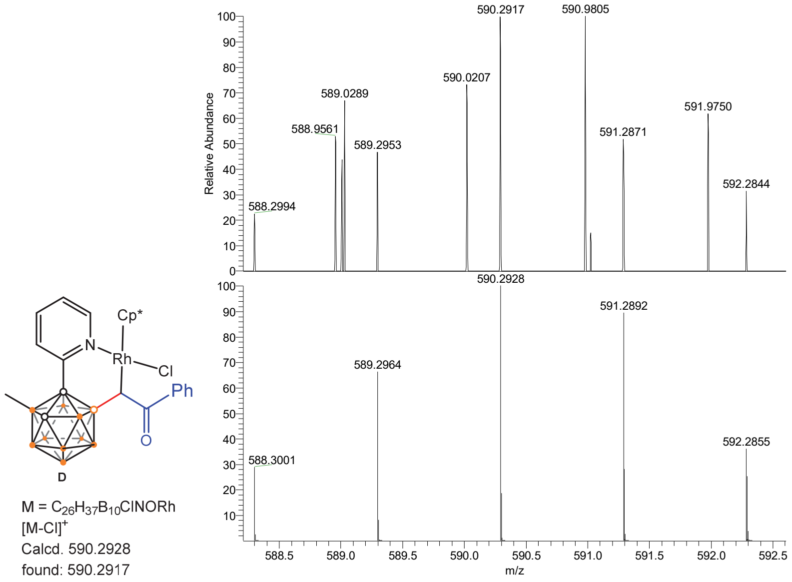
Note: The mass spectrum indicated the formation of rhodium intermediates B at early stage.

b) *in situ* HRMS of the reaction mixture at 60 °C for 60 min



M = $C_{18}H_{31}B_{10}ClNRh$
$[M-Cl]^+$
Calcd. 472.2509
found: 472.2506

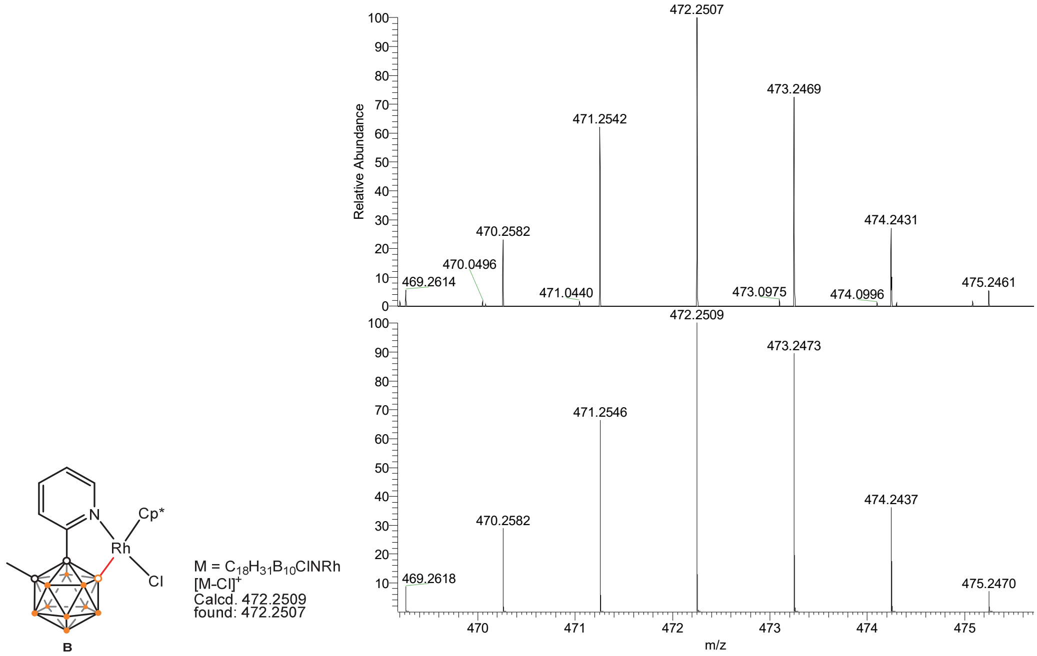
Figure S8. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{26}H_{37}B_{10}ClNORh$
$[M-Cl]^+$
Calcd. 590.2928
found: 590.2917

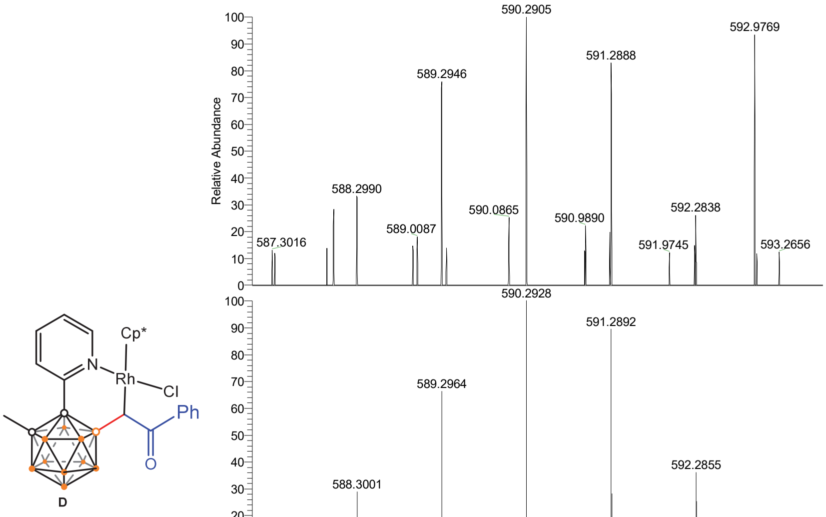
Figure S9. HRMS of **D**. Up: experimental MS. Down: calculated MS.

c) *in situ* HRMS of the reaction mixture at 60 °C for 120 min



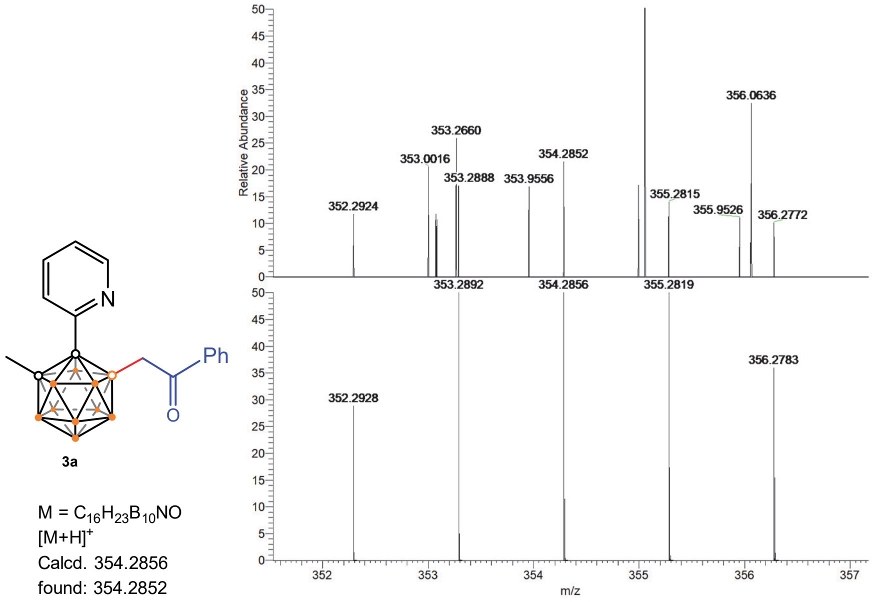
M = $C_{18}H_{31}B_{10}ClNRh$
$[M-Cl]^+$
Calcd. 472.2509
found: 472.2507

Figure S10. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{26}H_{37}B_{10}ClNORh$
$[M-Cl]^+$
Calcd. 590.2928
found: 590.2905

Figure S11. HRMS of **D**. Up: experimental MS. Down: calculated MS.

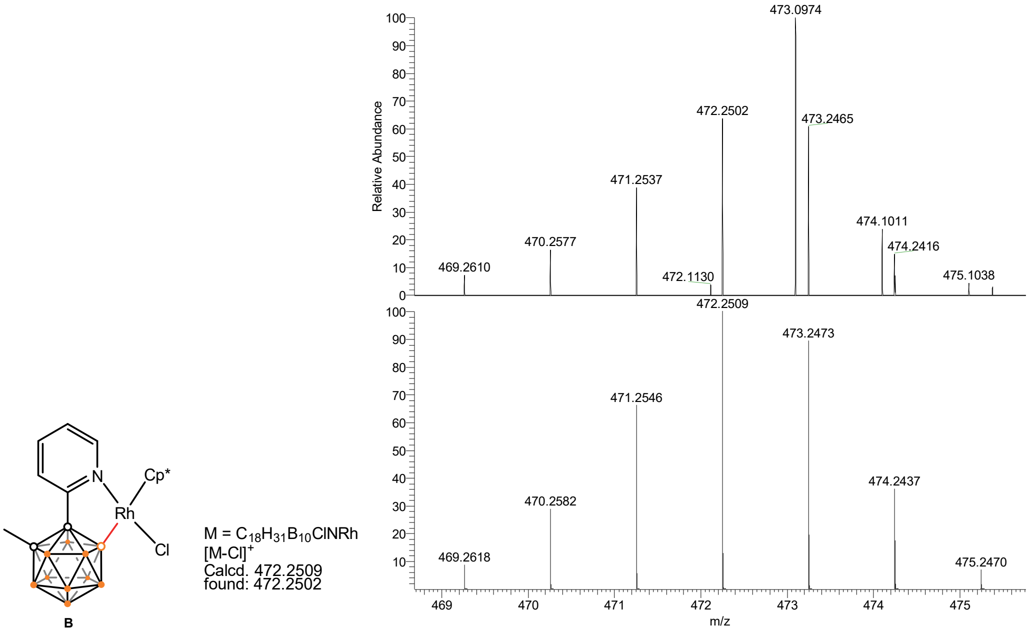


3a

M = $C_{16}H_{23}B_{10}NO$
$[M+H]^+$
Calcd. 354.2856
found: 354.2852

Figure S12. HRMS of product **3a**. Up: experimental MS. Down: calculated MS.

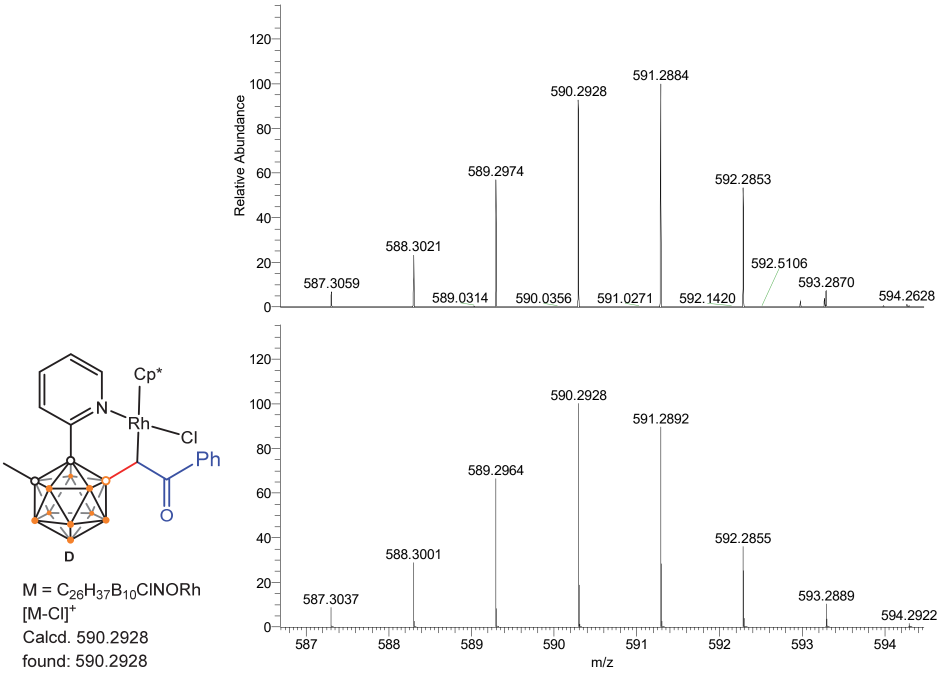
d) *in situ* HRMS of the reaction mixture at 100 °C for 24h



B

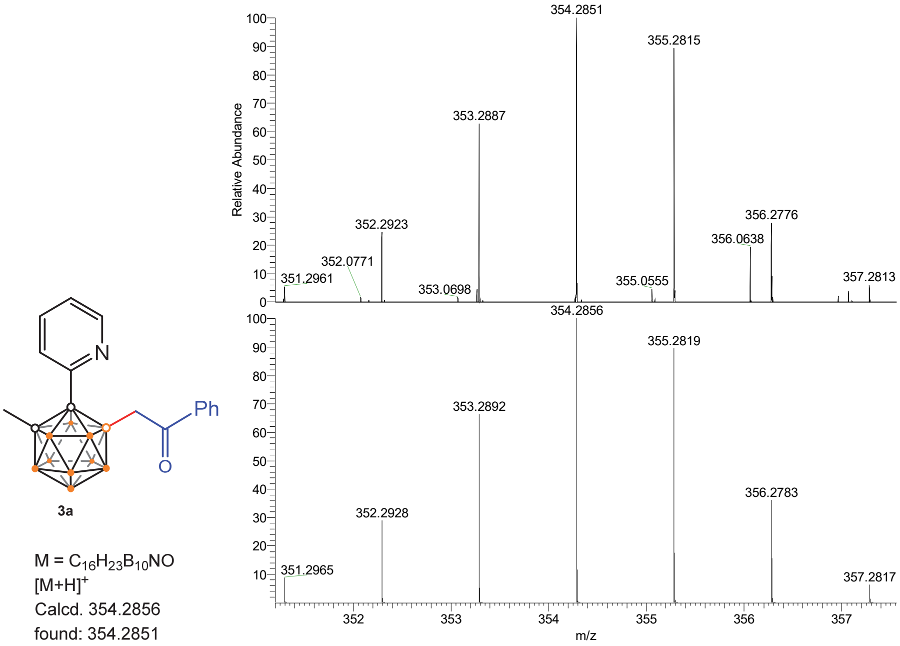
M = $C_{18}H_{31}B_{10}ClNRh$
$[M-Cl]^+$
Calcd. 472.2509
found: 472.2502

Figure S13. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{26}H_{37}B_{10}ClNORh$
$[M-Cl]^+$
Calcd. 590.2928
found: 590.2928

Figure S14. HRMS of **D**. Up: experimental MS. Down: calculated MS.



M = $C_{16}H_{23}B_{10}NO$
$[M+H]^+$
Calcd. 354.2856
found: 354.2851

Figure S15. HRMS of product **3a**. Up: experimental MS. Down: calculated MS.

e) *in situ* ^{1}H NMR study of the reaction

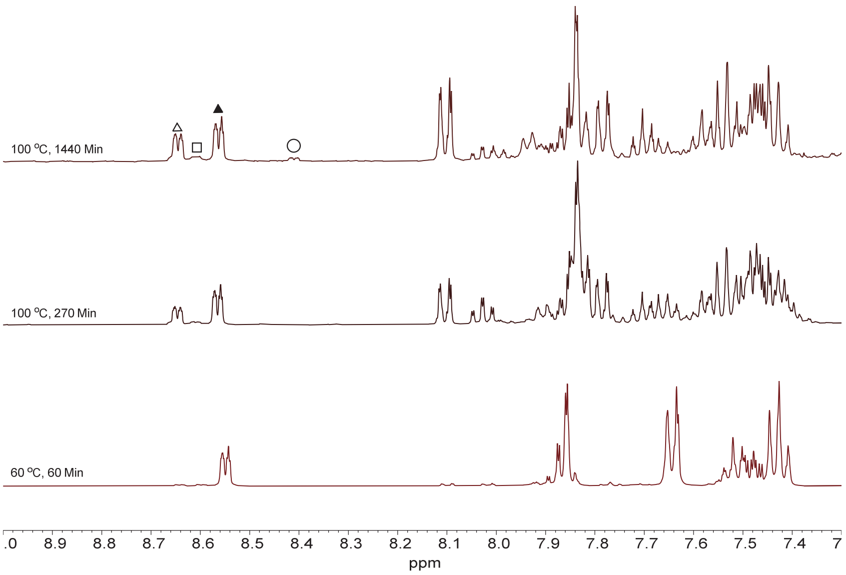
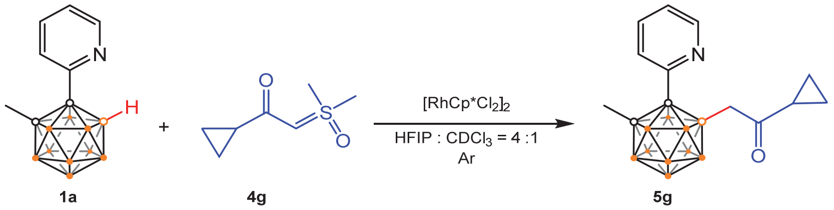


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, 7.3 to 9 ppm region) spectra of the reaction of **1a** and **2a** catalyzed by $[RhCp^*Cl_2]_2$ (12.5 mol%) in HFIP. ▲ = **1a**, △ = **3a**. ○ and ☐ represent new species.

Note: By using this less reactive sulfoxonium ylide 2a, HRMS monitoring the reaction can stepwisely detect the intermediates which greatly help understand the reaction mechanism.

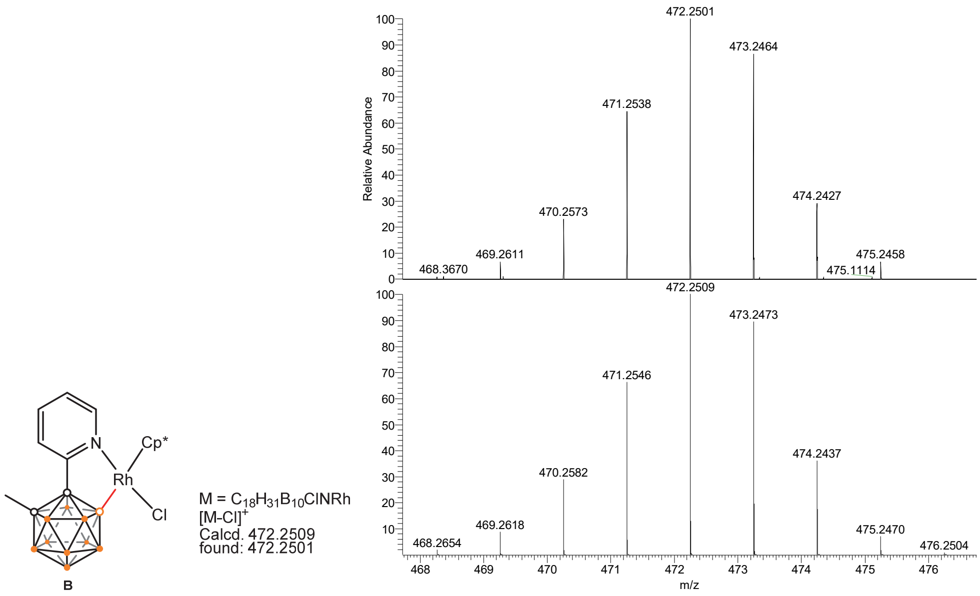
3.5.2 *in situ* HRMS and NMR studies on the reaction of 1a and highly reactive 4g in mixed solvents $CDCl_3$ and HFIP



Scheme S12. Reaction of **1a** and **4g**.

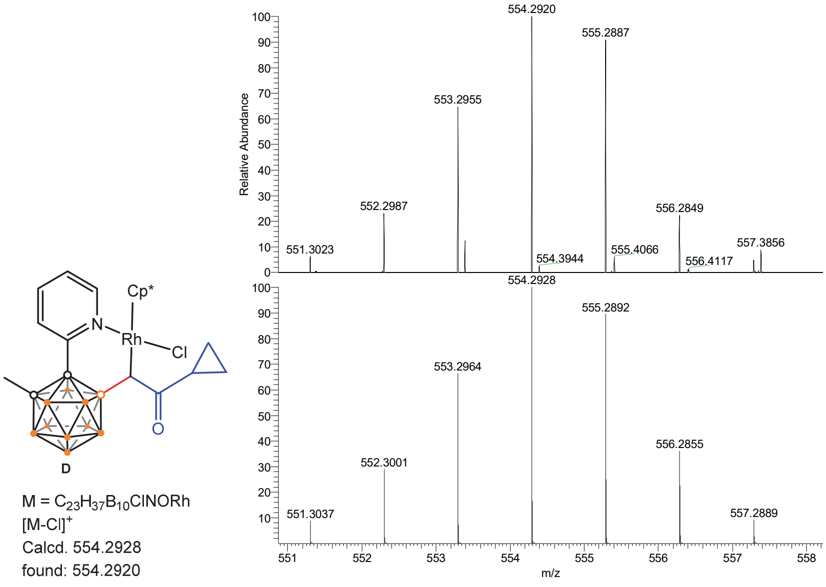
1a (5.9 mg, 0.025 mmol), $[RhCp^*Cl_2]_2$ (12.5 mol%, 1.9 mg, 0.003 mmol), sulfoxonium ylide **4g** (2.0 equiv, 8.0 mg, 0.05 mmol), HFIP (0.4 mL) and $CDCl_3$ (0.1 mL) were mixed in a J-Young NMR tube under argon. The resulting mixture was monitored by HRMS and ^{1}H NMR.

a) ***in situ*** HRMS of the reaction mixture at 35 °C for 14.5 h



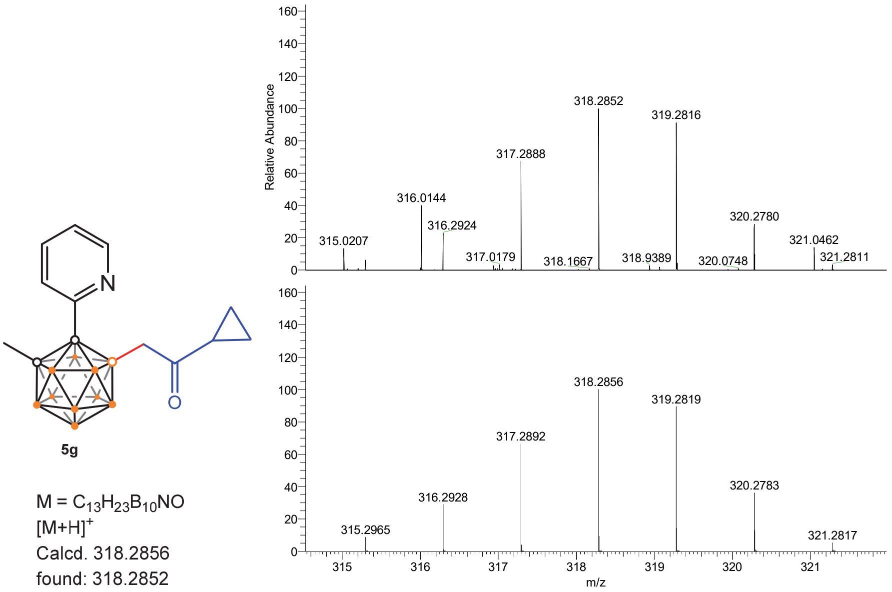
M = $C_{18}H_{31}B_{10}ClNRh$
$[M\text{-}Cl]^+$
Calcd. 472.2509
found: 472.2501

Figure S17. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{23}H_{37}B_{10}ClNORh$
$[M\text{-}Cl]^+$
Calcd. 554.2928
found: 554.2920

Figure S18. HRMS of **D**. Up: experimental MS. Down: calculated MS.

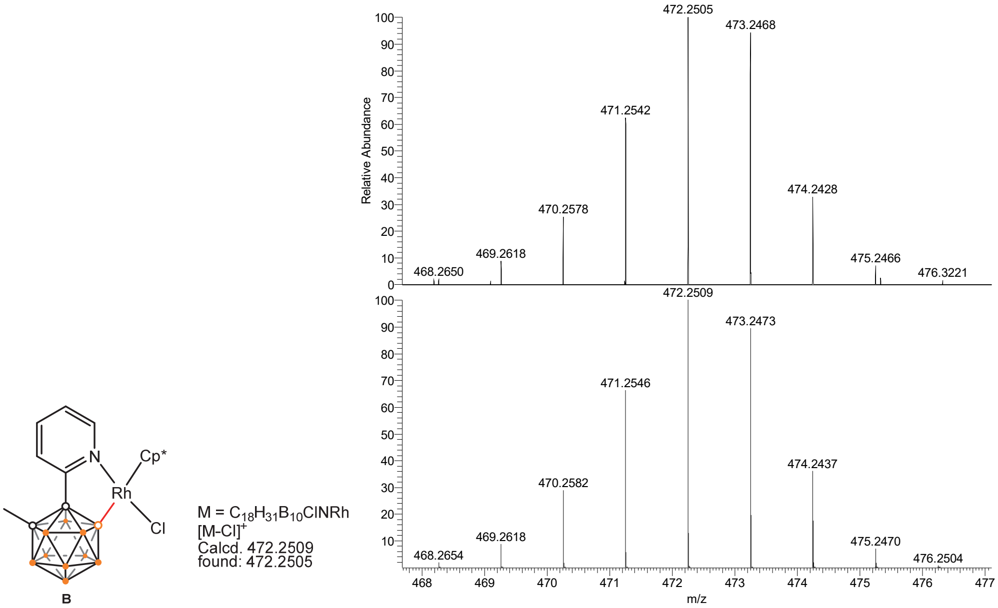


5g

M = $C_{13}H_{23}B_{10}NO$
$[M+H]^+$
Calcd. 318.2856
found: 318.2852

Figure S19. HRMS of product **5g**. Up: experimental MS. Down: calculated MS.

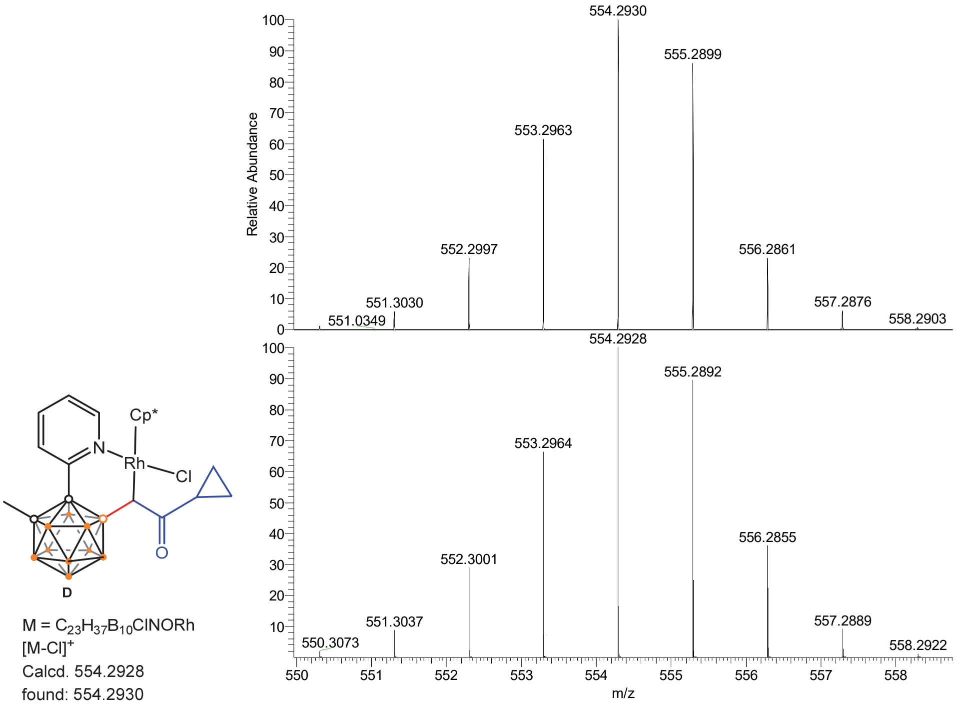
b) *in situ* HRMS of the reaction mixture at 35 °C for 34.5 h



B

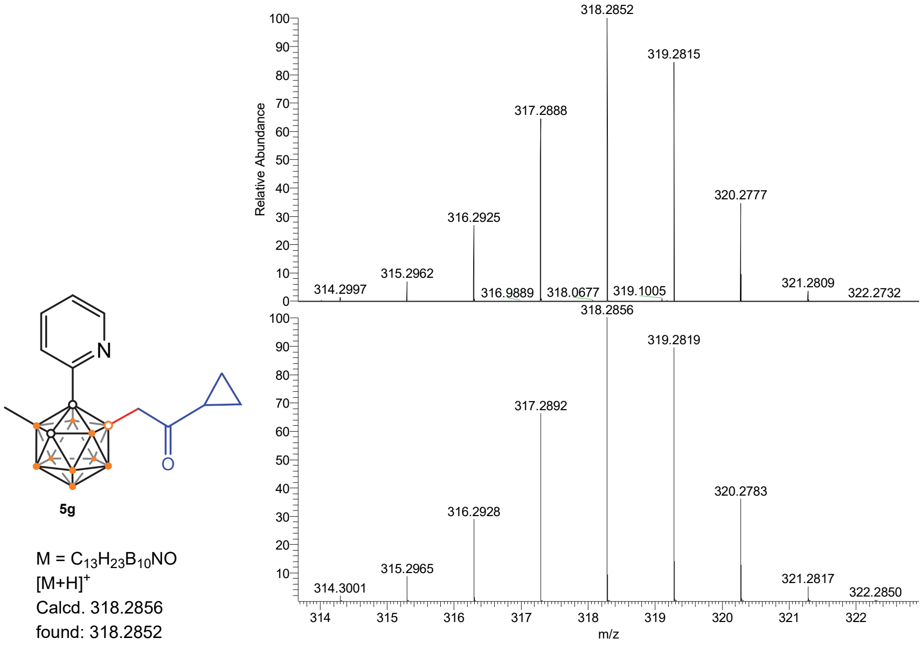
M = $C_{18}H_{31}B_{10}ClNRh$
$[M-Cl]^+$
Calcd. 472.2509
found: 472.2505

Figure S20. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{23}H_{37}B_{10}ClNORh$
$[M-Cl]^+$
Calcd. 554.2928
found: 554.2930

Figure S21. HRMS of **D**. Up: experimental MS. Down: calculated MS.



M = $C_{13}H_{23}B_{10}NO$
$[M+H]^+$
Calcd. 318.2856
found: 318.2852

Figure S22. HRMS of product **5g**. Up: experimental MS. Down: calculated MS.

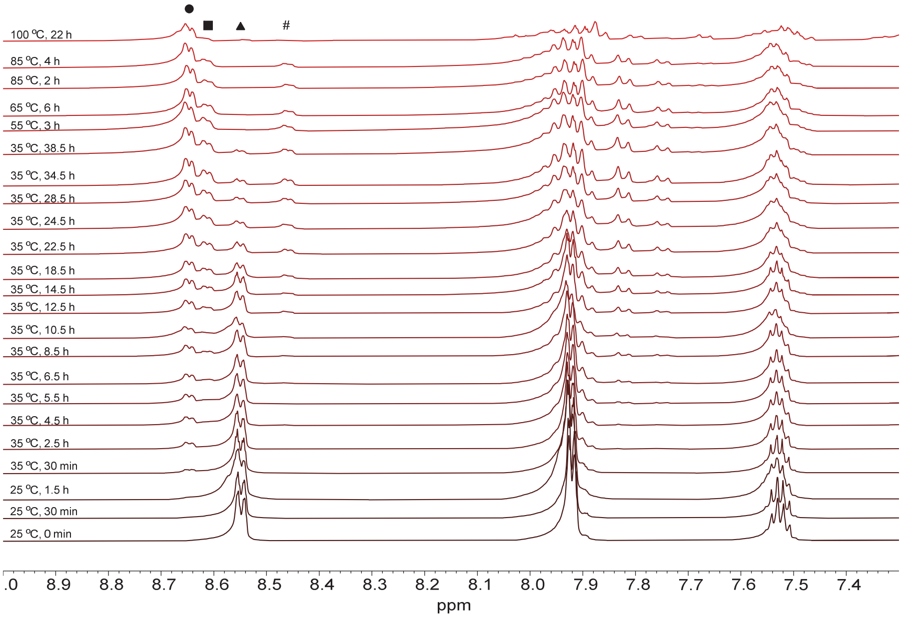


Figure S23. ^{1}H NMR (400 MHz, CDCl$_3$, 7.30 to 9.00 ppm region) spectra of the reaction of **1a** and **4g** catalyzed by [RhCp*Cl$_2$]$_2$ (12.5 mol%) in HFIP. ▲ = **1a**, ● = **5g**. # and ■ represent two new species.

Note: Two new pyridyl signals appeared at 8.46 (#) and 8.62 ppm (■). Both increase first and then decrease with time, finally disappear. They may correspond the two rhodium intermediates B and D observed by HRMS. Trials to isolated these intermediates failed.

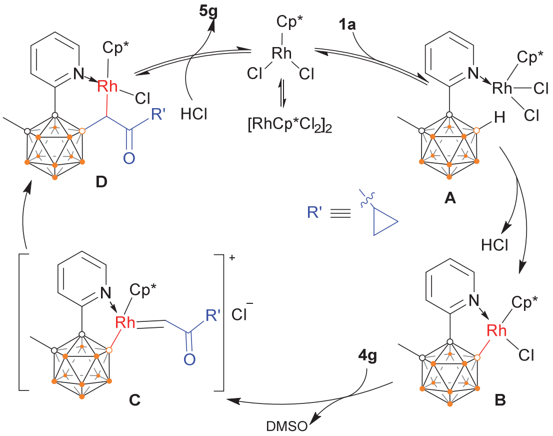
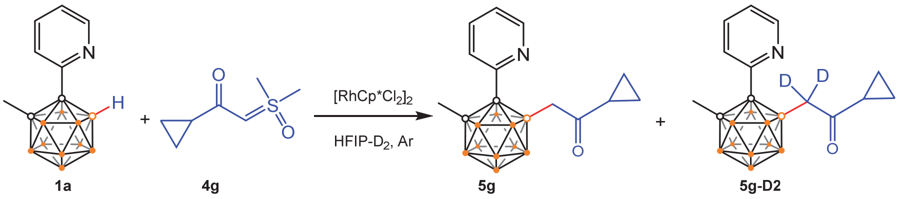


Figure S24. Proposed reaction mechanism (**1a** and **4g** as examples).

3.5.3 *in situ* HRMS and NMR studies on the reaction of 1a and highly reactive 4g in the deuterated HFIP-D$_2$



Scheme S13. Reaction of **1a** and **4g**.

1a (11.8 mg, 0.05 mmol), sulfoxonium ylide **4g** (2.0 equiv., 16.0 mg, 0.1 mmol), [RhCp*Cl$_2$]$_2$ (12.5 mol%, 3.9 mg, 0.006 mmol) and HFIP-D$_2$ (0.5 mL) were mixed in a J-Young NMR tube under argon, then kept at room temperature. The resulting mixture was monitored by HRMS and ^{1}H NMR. The mass spectra have detected the rhodium intermediates **B**, **D**, the products **5g**, **5g-**D$_2$ and the starting materials **1a**, **4g** and [RhCp*Cl$_2$]$_2$.

a) *in situ* HRMS of the reaction mixture at 25 °C for 5 h

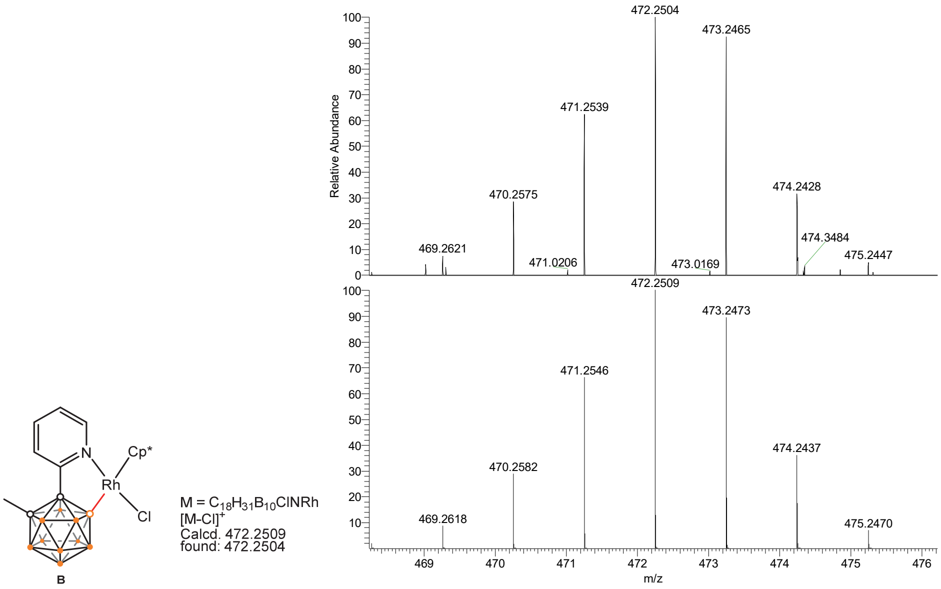
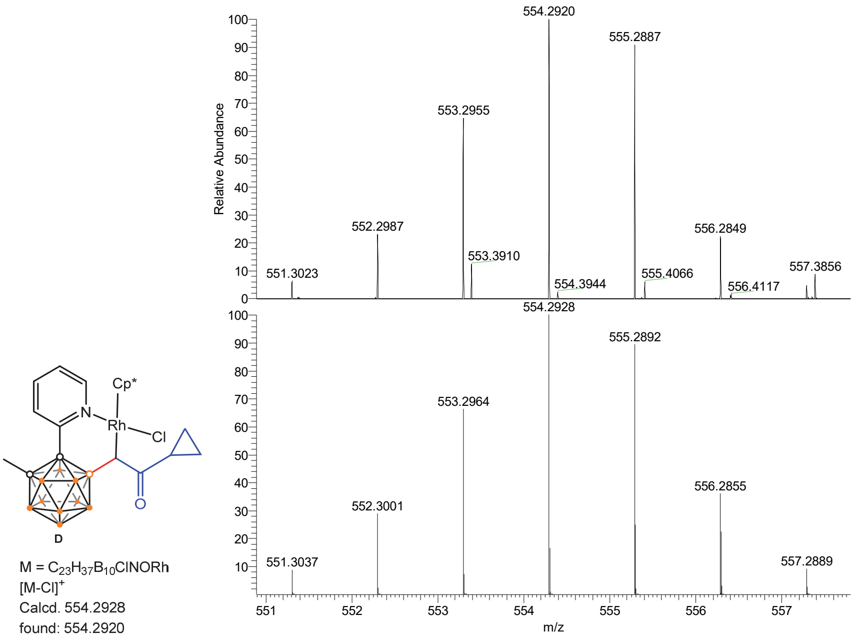
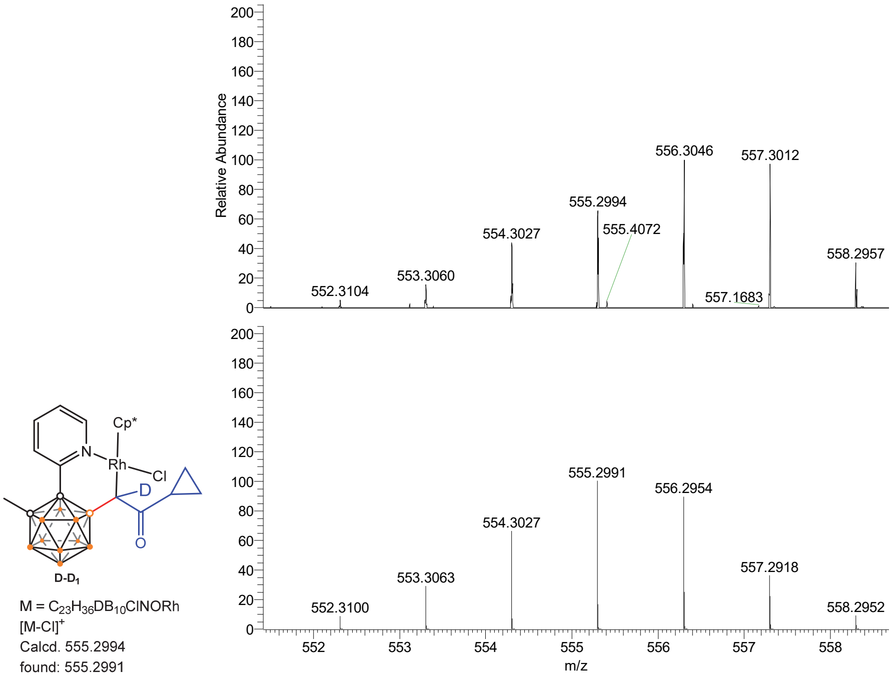


Figure S25. HRMS of **B**. Up: experimental MS. Down: calculated MS.



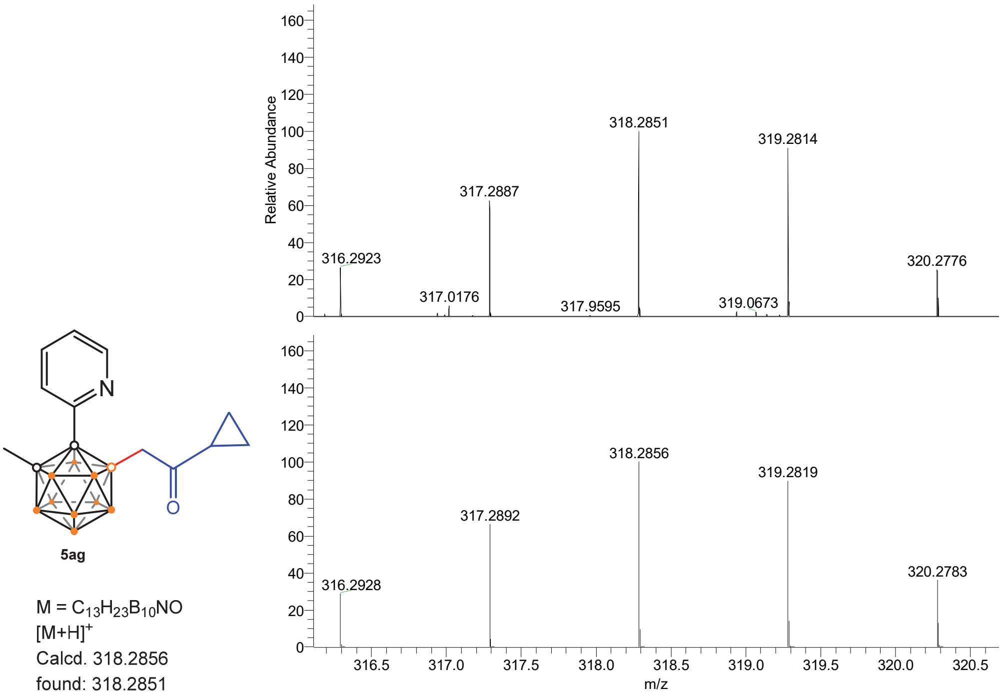
M = $C_{23}H_{37}B_{10}ClNORh$
$[M-Cl]^+$
Calcd. 554.2928
found: 554.2920

Figure S26. HRMS of **D**. Up: experimental MS. Down: calculated MS.



M = $C_{23}H_{36}DB_{10}ClNORh$
$[M-Cl]^+$
Calcd. 555.2994
found: 555.2991

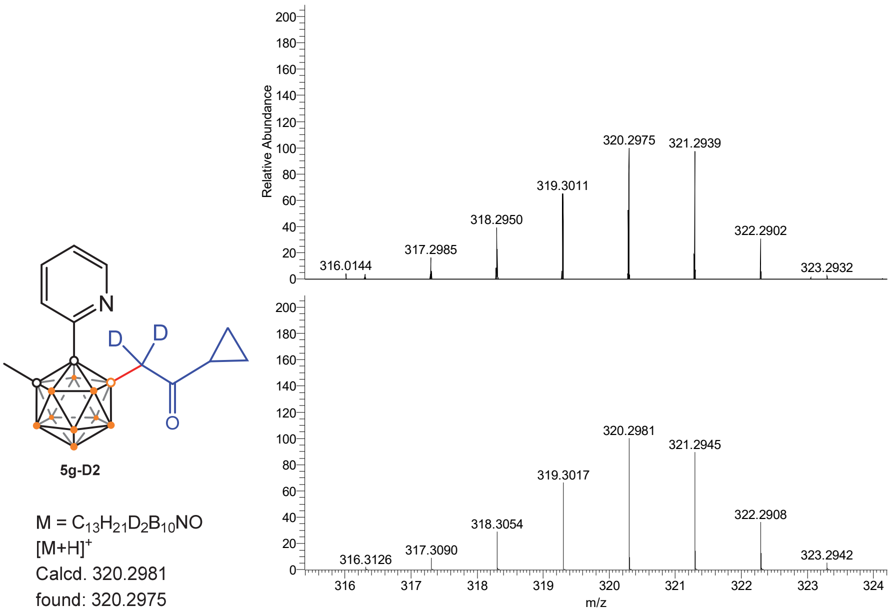
Figure S27. HRMS of **D-D$_1$**. Up: experimental MS. Down: calculated MS.



5ag

M = $C_{13}H_{23}B_{10}NO$
$[M+H]^+$
Calcd. 318.2856
found: 318.2851

Figure S28. HRMS of product **5g**. Up: experimental MS. Down: calculated MS.



5g-D2

M = $C_{13}H_{21}D_2B_{10}NO$
$[M+H]^+$
Calcd. 320.2981
found: 320.2975

Figure S29. HRMS of product **5g-D$_2$**. Up: experimental MS. Down: calculated MS.

Note: The identification of D-D$_1$, 5g-D$_2$ demonstrates H-D exchange at the enolizable α-carbon position in the presence of rhodium catalyst.

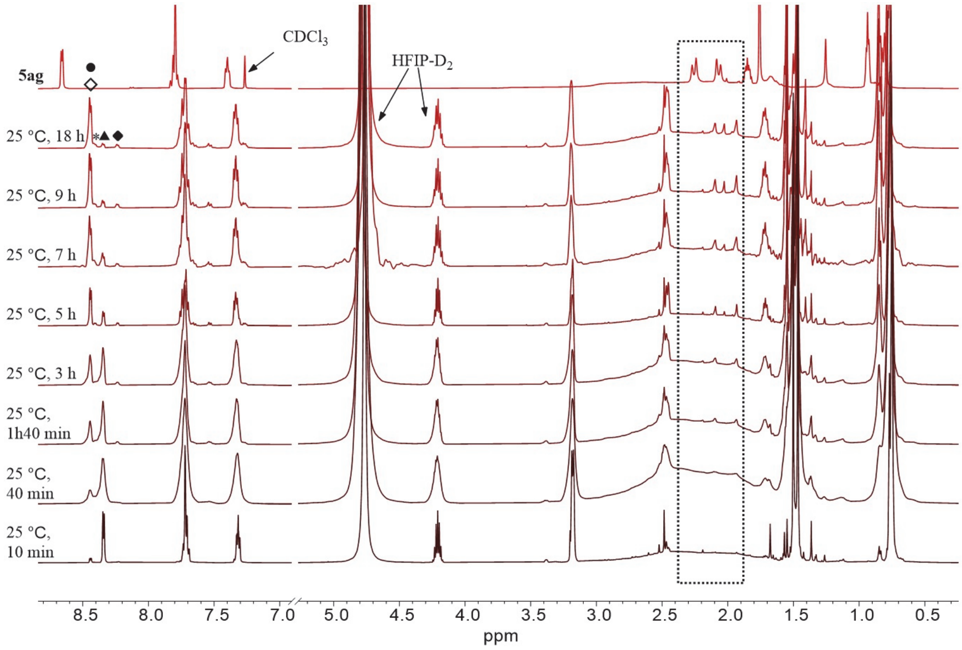
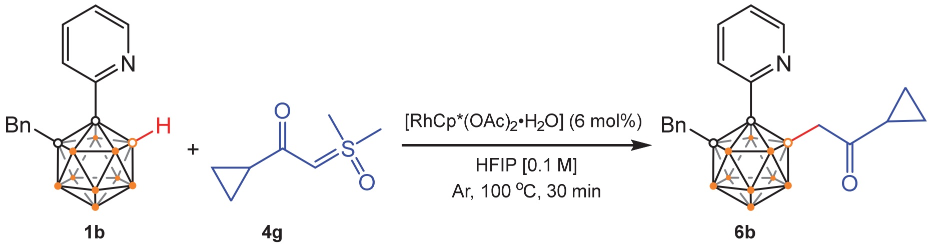


Figure S30. Time-dependent ^{1}H NMR spectra for the reaction of **1a** with **4g** in HFIP-D$_2$ at 25 °C. ▲ = **1a**, ● = **5g**, ◇ = **5g**-D$_2$. ◆ and * represent two new intermediates. Top spectrum represents **5g** in CDCl$_3$.

Note: Two new pyridyl signals appeared at 8.22 (◆) and 8.40 ppm (*) in HFIP-D$_2$. The dotted box showed the newly generated CH$_2$ of two products* 5g *(minor)* and 5g-D$_2$ *(major).

These monitoring experiments demonstrate that HRMS is a powerful tool to detect intermediates apart from the stable products and the starting materials. The combination of HRMS and NMR to explore the reaction course demonstrates that the key intermediates in this reaction are stable enough for in situ detection.

3.6 Detection of DMSO lost from sulfoxonium ylide



Scheme S14. Reaction of **1c** and **4g**.

1b (31.1 mg, 0.1 mmol), sulfoxonium ylide **4g** (2.0 equiv., 32.0 mg, 0.2 mmol), $RhCp^*(OAc)_2 \cdot H_2O$ (6 mol%, 2.2 mg, 0.006 mmol) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under argon. The resulting mixture was stirred at 100 °C for 30 min under argon. After cooling to room temperature, the mixture was concentrated in *vacuo*.

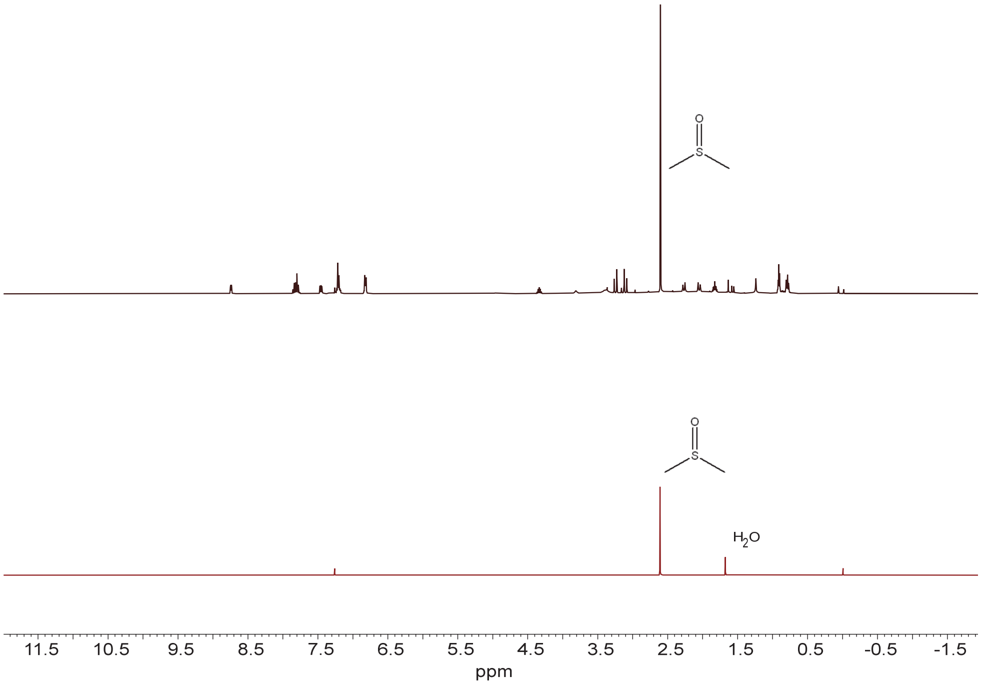
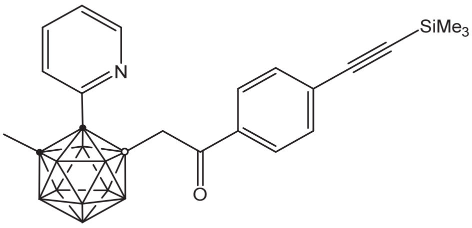


Figure S31. Up: ^{1}H NMR ($CDCl_3$) spectrum for the reaction of **1b** with **4g** in HFIP at 100 °C; down: ^{1}H NMR ($CDCl_3$) for pure DMSO for comparison.

Note: The reaction of 1c with 4g confirms the formation of 6b and DMSO.

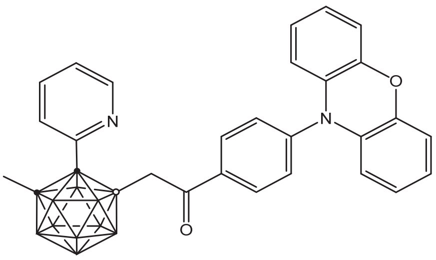
4 Transformations and synthetic applications.

Transformation of 3h to 8. Compound **3h** (54.0 mg, 0.1 mmol), TMSCCH (2.0 equiv., 19.6 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%, 3.5 mg, 0.005 mmol), CuI (10 mol%, 1.9 mg, 0.01mmol) were mixed in Et_3N (0.5 mL). The resulting mixture was heated at 70 °C for 24 h under argon. After hydrolysis with water (5 mL) and extraction with diethyl ether (5 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel by using petroleum ether/EtOAc as eluent to give the product **8**.



8: Yield 98%. Sticky colorless solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.66 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (m, 1H) (aryl C−**H**), 2.65 (d, *J* = 12.6 Hz, 1H), 2.42 (d, *J* = 12.6 Hz, 1H) (B−C**H**$_2$), 1.73 (s, 3H) (cage−C**H**$_3$), 0.25 (s, 9H) (SiMe$_3$−**H**); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -10.1 (3B); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 199.5 (**C**=O), 149.6, 147.8, 137.6, 136.9, 132.0, 128.7, 127.5, 126.8, 125.0 (aryl−**C**), 104.4, 97.8 (**C**=**C**), 80.9, 77.8 (cage−**C**), 28.8 (B−**C**H$_2$), 23.5 (cage−**C**H$_3$), 0.0 (SiMe$_3$−**C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{21}B_{10}NOSiH_{32}$ [M+H$^+$]: 450.3251. Found: 450.3257.

Transformation of 3h to 9. Compound **3h** (54.0 mg, 0.1 mmol), phenoxazine (1.0 equiv., 18.3 mg, 0.1 mmol), $Pd(OAc)_2$ (5 mol%, 1.1 mg, 0.005mmol), P^tBu_3 (15 mol%, 3.0 mg, 0.015 mmol) and K_2CO_3 (3.0 equiv., 41.5 mg, 0.3 mmol) were mixed in toluene (2.5 mL). The resulting mixture was heated at 120 °C for 12 h under argon. After hydrolysis with water (5 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel by using petroleum ether/EtOAc as eluent to give the product **9**.



9: Yield 90%. Yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.70 (dt, *J* = 4.8, 1.4 Hz, 1H), 8.10 – 7.99 (m, 2H), 7.92 – 7.81 (m, 2H), 7.44 (ddd, *J* = 6.7, 4.8, 2.3 Hz, 1H), 7.41 – 7.35 (m, 4H), 6.73 – 6.55 (m, 7H), 5.92 (dd, *J* = 7.9, 1.5 Hz, 2H) (aryl C−**H**), 2.73 (d, *J* = 12.7 Hz, 1H), 2.49 (d, *J* = 12.6 Hz, 1H) (B−C**H**$_2$), 1.77 (s, 3H) (cage−C**H**$_3$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.3 (2B), -4.5 (1B), -9.5 (4B), -11.0 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 199.3 (**C**=O), 149.7, 147.9, 144.1, 143.2, 137.7, 137.5, 133.9, 131.6, 130.8, 126.9, 125.1, 123.4, 121.9, 115.8, 113.5 (aryl **C**), 81.1, 78.0 (cage−**C**), 28.2 (B−**C**H$_2$), 23.6 (**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{28}B_{10}N_2O_2H_{31}$ [M+H$^+$]: 535.3384. Found: 535.3389.

Photophysical properties of 9.

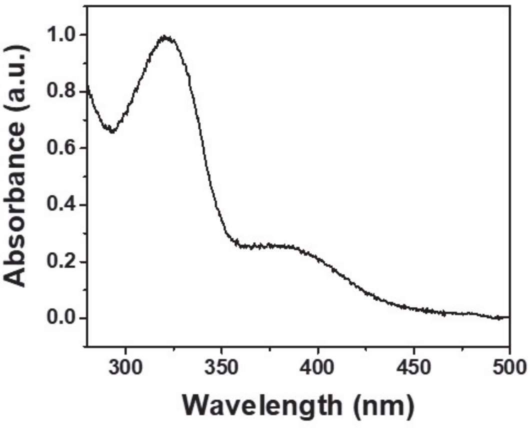


Figure S32. The normalized absorption spectral of **9** in THF (1.0 × 10^{-5} M) at room temperature.

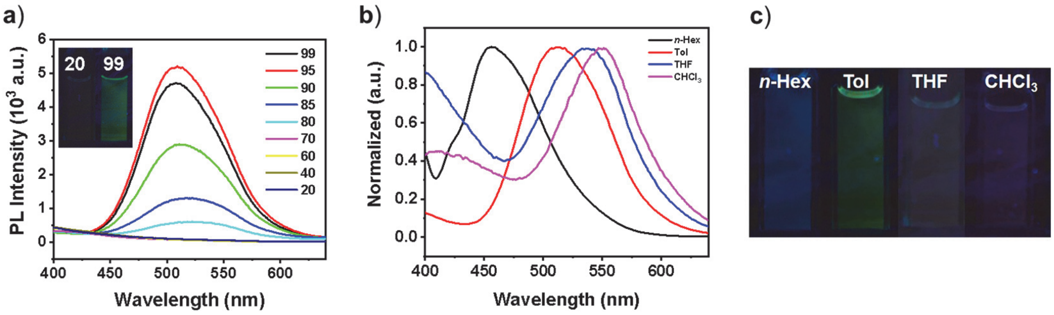
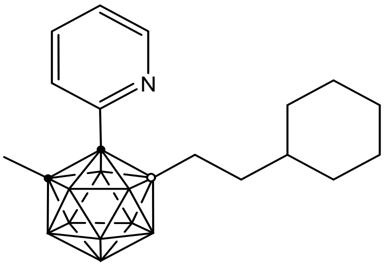


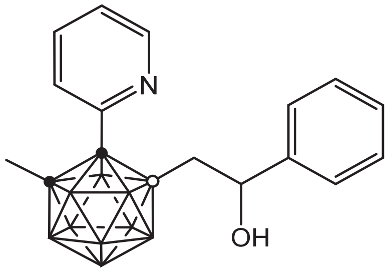
Figure S33. Photophysical properties of **9**. a): Luminescent photographs taken under UV light (365 nm) and fluorescence spectra with different water volume fraction (V_{H2O} / V_{THF} %) of **9** (1.0×10^{-5} M, $\lambda_{ex} = 323$ nm) under ambient condition; b): Fluorescence spectra of **9** observed in different solvents (1.0×10^{-5} M, $\lambda_{ex} = 323$ nm) under ambient condition; c): Luminescence photographs of **9** in different solvents taken under UV light (365 nm) according to b).

Transformation of 5j to 10. A solution of THF·BH_3 (1.0 M; 0.5 mL, 5.0 equiv., 0.5 mmol) was added by syringe to a solution of **5j** (1.0 equiv., 46.8 mg, 0.1 mmol) in THF (1 mL), and then the reaction mixture was refluxed for 12 h under argon. Next, the mixture was cooled to 0 °C, and the reaction was quenched by the addition of MeOH (0.25 mL). The solvent was evaporated, an aqueous of HCl (2N, 1.0 mL) was added to the residue, refluxed for 1 h. The reaction mixture was made basic through the addition of K_2CO_3 and extracted with $CHCl_3$ (5 mL x 3). The compound organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography by using petroleum ether/DCM to afford compound **10**.



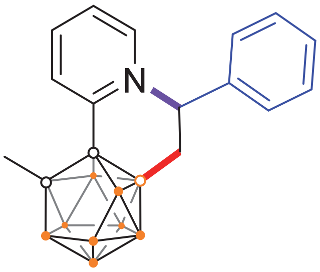
10: Yield 99%. Colorless oil. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.65 (ddt, *J* = 7.7, 4.8, 1.4 Hz, 1H), 7.89 – 7.72 (m, 2H), 7.46 – 7.35 (m, 1H) (aryl C−**H**), 1.75 (s, 2H) (BC**H**$_2$CH$_2$), 1.71 (s, 2H) (BCH$_2$C**H**$_2$), 1.67 – 1.52 (m, 4H) (Cyclohexyl C−**H**), 1.25 (s, 3H) (cage−C**H**$_3$), 1.17 – 1.00 (m, 4H), 0.89 – 0.80 (m, 2H), 0.64 (dd, *J* = 15.6, 9.7 Hz, 1H) (Cyclohexyl C−**H**); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -0.5 (2B), -2.7 (1B), -4.0 (1B), -4.8 (1B), -9.9 (3B), -11.6 (2B); **^{13}C NMR (126 MHz, Chloroform-*d*)**: δ 149.6, 149.4, 148.4, 148.2, 137.9, 137.5, 126.8, 126.5, 125.1, 124.8 (aryl−**C**), 75.9, 75.8 (cage−**C**), 45.1 (B**C**H$_2$CH$_2$), 44.5 (BCH$_2$**C**H$_2$), 29.9 (cage−**C**H$_3$), 29.4, 29.0, 27.7, 27.6, 26.8, 26.7, 26.5, 26.5, 26.4, 26.3, 23.6, 23.5 (Cyclohexyl **C**). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}NH_{32}$ [M+H$^+$]: 335.3496. Found: 335.3495.

Transformation of 3a to 11. To a solution of **3a** (35.3 mg, 0.1 mmol) in THF (2 mL) was added NaBH$_4$ (3 equiv., 11.4 mg, 0.3 mmol) carefully at room temperature. Then the mixture was stirred at 35°C for 24 h before quenched with water. The mixture was extracted with ethyl acetate (5 mL x 3), and the combined organic extracts were washed with water and brine, and dried over Na$_2$SO$_4$. The solvent was evaporated under the reduced pressure and the residue was purified by silica gel chromatography by using petroleum ether/EtOAc to afford compound **11**.



11: Yield 99%. Light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Diastereomer I : Diastereomer II = 29 : 71**, **Diastereomer I**: δ 8.76 – 8.69 (m, 1H), 7.89 – 7.80 (m, 2H), 7.47 (ddd, *J* = 7.3, 4.8, 1.3 Hz, 1H) (Pyridyl C−**H**), 7.32 – 7.15 (m, 5H) (Ph−**H**), 4.87 (dd, *J* = 10.0, 3.2 Hz, 1H) (C**H**OH), 2.89 (s, 2H) (B−C**H**$_2$), 1.72 (s, 3H) (cage−C**H**$_3$); **Diastereomer II**: δ 8.66 – 8.62 (m, 1H), 7.80 – 7.71 (m, 2H), 7.38 (ddd, *J* = 7.3, 4.8, 1.4 Hz, 1H) (Pyridyl C−**H**), 7.32 – 7.15 (m, 5H) (Ph−**H**), 4.81 (dd, *J* = 8.5, 4.9 Hz, 1H) (C**H**OH), 2.89 (s, 2H) (B−C**H**$_2$), 1.74 (s, 3H) (cage−C**H**$_3$). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**, **Diastereomer I**: δ -0.7 (2B), -3.6 (1B), -11.2 (7B); **Diastereomer II**: δ -2.3 (2B), -4.5 (1B), -9.6 (7B). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$), Diastereomer I**: δ 149.6, 148.0, 146.5, 138.1, 127.3, 126.8, 125.7, 125.3, 124.9 (aryl−**C**), 81.0, 74.3 (cage−**C**), 74.1 (**C**HOH), 29.8 (B**C**H$_2$CH), 23.5 (cage−**C**H$_3$); **Diastereomer II**: δ 149.5, 148.3, 145.9, 137.5, 128.4, 127.2, 126.5, 126.0, 125.3 (aryl−**C**), 81.0, 74.3 (cage−**C**), 74.1 (**C**HOH), 29.8 (B**C**H$_2$CH), 23.6 (cage−**C**H$_3$). 2575. **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOH_{26}$ [M+H$^+$]: 357.3090. Found: 357.3082.

Transformation of 11 to 12. The alcohol **11** (35.5 mg, 0.1 mmol) was dissolved in toluene (0.4 mL) and PBr$_3$ (0.67 equiv., 18.1 mg, 0.067 mmol) was added dropwise at 0 °C under argon. After 24 h at 65 °C the reaction was stopped by addition of water. The organic phase was washed with saturated aqueous NaHCO$_3$, dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography by using petroleum ether/CH$_2$Cl$_2$ to afford compound **12**.



12: Yield 38%. light yellow solid. **^{1}H NMR (400 MHz, Methylene Chloride-*d*$_2$), Diastereomer I: Diastereomer II** = 11 : 89, **Diastereomer I**: δ 8.17 (m, 1H), 7.83 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.62 – 7.47 (m, 3H), 7.45 – 7.38 (m, 2H), 7.31 (td, *J* = 7.0, 1.7 Hz, 1H) (aryl C−**H**), 5.94 (d, *J* = 13.8 Hz, 1H) (C**H**−N), 2.12 – 1.98 (m, 2H) (B−C**H**$_2$), 1.54 (s, 3H) (C**H**$_3$), -2.28 (br, 1H, B−**H**−B); **Diastereomer II**: δ 8.08 (m, 1H), 7.83 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.62 – 7.47 (m, 3H), 7.45 – 7.38 (m, 2H), 7.31 (td, *J* = 7.0, 1.7 Hz, 1H) (aryl C−**H**), 5.77 (dd, *J* = 12.2, 5.0 Hz, 1H) (C**H**−N), 2.12 – 1.98 (m, 2H) (B−C**H**$_2$), 1.53 (s, 3H) (C**H**$_3$), -2.28 (br, 1H, B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Methylene Chloride-*d*$_2$)**: δ -2.7, -10.1, -10.9, -12.7, -14.8, -18.6, -21.0, -31.4, -34.4; **^{13}C NMR** plus **^{13}C−^{1}H HSQC (101 MHz, Methylene Chloride-*d*$_2$)**: δ 142.3, 141.7, 131.8, 130.8, 130.7, 129.9, 123.1 (aryl−**C**), 73.9 (**C**H−N),,24.0 (**C**H$_3$), 23.8 (B−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_9NH_{24}Na$ [M+Na$^+$]: 351.2675. Found: 351.2673.

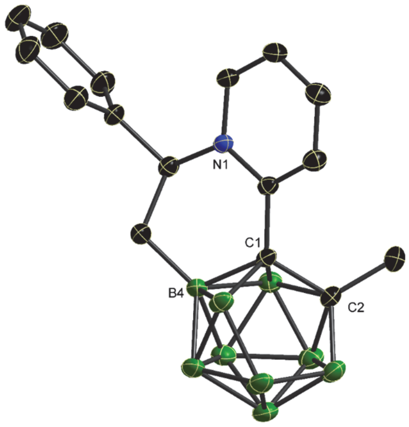


Figure S34. Molecular structure of compound **12** (ellipsoids at 30% probability and H atoms omitted for clarity).

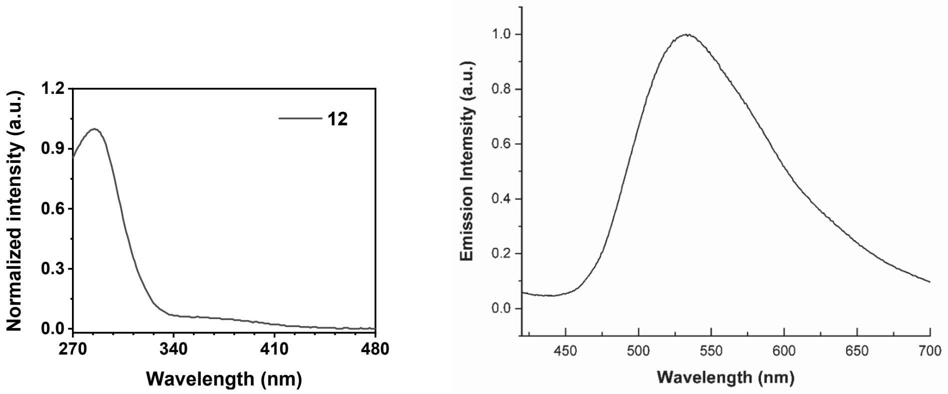
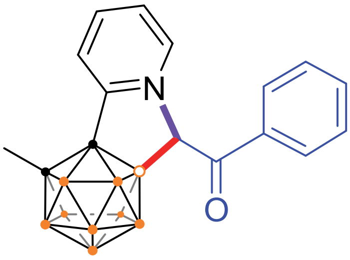


Figure S35. Photophysical properties of **12**. Left: Normalized absorption spectrum in THF (1.0 × 10^{-5} M) under ambient condition; Right: Fluorescence spectrum observed in the crystalline state under ambient condition (λ_{ex} = 365 nm).

Transformation of 3 to 13. Compound **3** (0.1 mmol) and Py·HBr$_3$(1.1 equiv., 35.2 mg, 0.11 mmol) were mixed in ethyl acetate (1.0 mL). Then, the resulting mixture was heated at 60 °C for 18 h under argon. After diluting with CH_2Cl_2 (2 mL), the solvent was evaporated under the reduced pressure and the residue was purified by silica gel chromatography by using petroleum ether/CH_2Cl_2 as eluent to give the product.



13a: Yield 82%. light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Diastereomer I: Diastereomer II** = 27 : 73, **Diastereomer I**: δ 8.33 – 8.07 (m, 4H), 7.73 – 7.47 (m, 5H) (aryl C−**H**), 6.57 (s, 1H) (B−C**H**−N), 1.77 (s, 3H) (C**H**$_3$), 2.50 (br, 1H) (B−**H**−B); **Diastereomer II**: δ 8.33 – 8.07 (m, 4H), 7.73 – 7.47 (m, 5H) (aryl C−**H**), 6.13 (s, 1H) (B−C**H**−N), 1.76 (s, 3H) (C**H**$_3$), 2.86 (br, 1H) (B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.9, -7.0, -11.1, -14.6, -19.3, -24.5, -32.0, -34.2; **^{13}C NMR (400 MHz, Chloroform-*d*)**: δ 145.8, 145.2, 144.2, 134.4, 129.2, 129.0, 128.8, 128.7, 123.0, 122.4 (aryl−**C**), 22.0 (**CH$_3$**). **HRMS** (ESI, positive mode): *m/z* calcd for calcd for $C_{16}B_9NOH_{22}Na$ [M+Na$^+$]: 364.2504. Found: 364.2508.

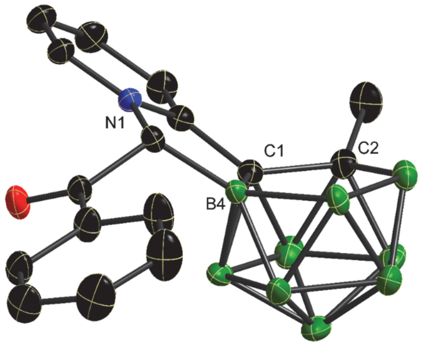


Figure S36. Molecular structure of compound **13a** (ellipsoids at 30% probability and H atoms omitted for clarity).

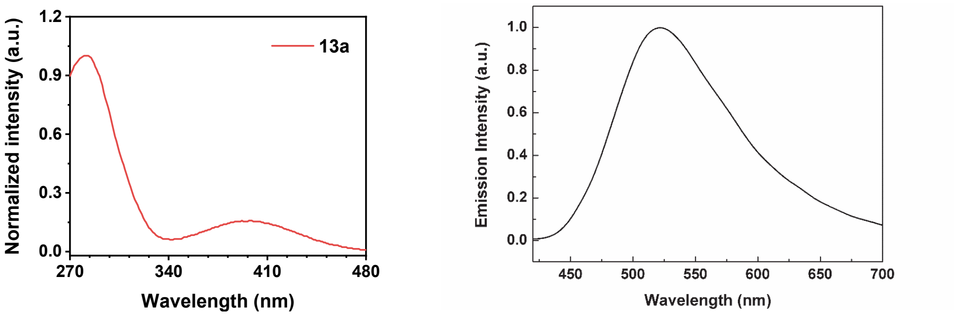
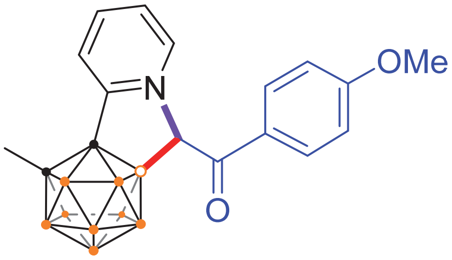
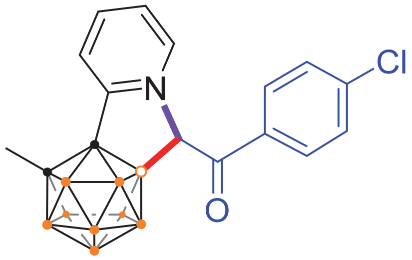


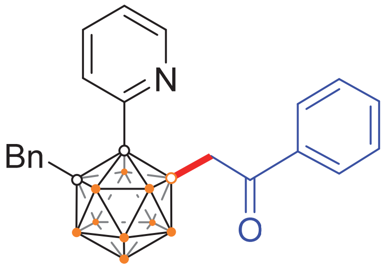
Figure S37. Photophysical properties of **13a**. Left: Normalized absorption spectrum in THF (1.0×10^{-5} M) under ambient condition; Right: Fluorescence spectrum observed in the crystalline state under ambient condition ($\lambda_{ex} = 365$ nm).



13b: Yield 86%. light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Diastereomer I: Diastereomer II** = 66 : 34, **Diastereomer I**: δ 8.31 – 8.00 (m, 4H), 7.74 – 7.50 (m, 2H), 7.06 – 6.93 (m, 2H) (aryl C−**H**), 6.50 (s, 1H) (B−C**H**−N), 3.88 (s, 3H) (OC$\mathbf{H}_3$), 1.77 (s, 3H) (Cage−C$\mathbf{H}_3$), 2.51 (br, 1H) (B−**H**−B); **Diastereomer II**: δ 8.31 – 8.00 (m, 4H), 7.74 – 7.50 (m, 2H), 7.06 – 6.93 (m, 2H) (aryl C−**H**), 6.07 (s, 1H) (B−C**H**−N), 3.90 (s, 3H), (OC$\mathbf{H}_3$), 1.76 (s, 3H) (Cage−C$\mathbf{H}_3$), 2.90 (br, 1H) (B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.3, -7.2, -10.9, -15.0, -20.2, -24.5, -32.0, -34.2; **^{13}C NMR** plus **^{13}C−^{1}H HSQC (400 MHz, Chloroform-*d*)**: δ 191.2 (**C**=O), 166.1, 146.1, 145.4, 144.2, 144.1, 131.7, 131.5, 127.5, 123.1, 122.4, 114.2, 114.0 (aryl−**C**), 73.8 (B−**C**H−N), 55.7 (O$\mathbf{C}$H$_3$), 22.1 (Cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{17}B_9NO_2H_{24}Na$ [M+Na$^+$]: 394.2609. Found: 394.2611.

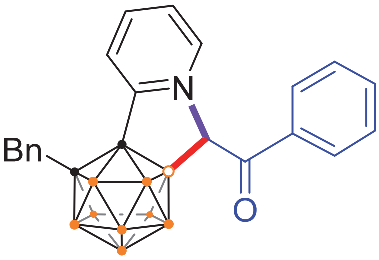


13c: Yield 71%. light yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**, **Diastereomer I: Diastereomer II** = 55 : 45, **Diastereomer I**: δ 8.32 – 8.19 (m, 2H), 8.18 – 8.04 (m, 2H), 7.71 – 7.55 (m, 2H), 7.53 – 7.42 (m, 2H) (aryl C−**H**), 6.51 (s, 1H) (B−C**H**−N), 1.77 (s, 3H) (Cage−C**H**$_3$), -2.53 (br, 1H) (B−**H**−B); **Diastereomer II**: δ 8.32 – 8.19 (m, 2H), 8.18 – 8.04 (m, 2H), 7.71 – 7.55 (m, 2H), 7.53 – 7.42 (m, 2H) (aryl C−**H**), 6.08 (s, 1H) (B−C**H**−N), 1.76 (s, 3H) (Cage−C**H**$_3$), -2.83 (br, 1H) (B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.0, -6.9, -10.9, -14.5, -19.3, -21.1, -24.5, -32.0, -34.2; **^{13}C NMR** plus **^{13}C−^{1}H HSQC (400 MHz, Chloroform-*d*)**: δ 192.9, 190.8 (**C**=O), 145.8, 145.2, 144.3, 144.2, 140.9, 140.6, 132.6, 132.3, 130.6, 130.4, 129.2, 129.0, 123.2, 123.1, 122.5, 122.4 (aryl−**C**), 21.94, 21.92 (Cage−**C**H$_3$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_9NOClH_{21}Na$ [M+Na$^+$]: 399.2078. Found: 399.2079.

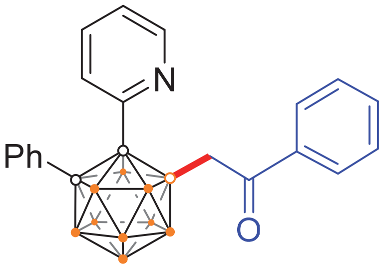


3ba was prepared by the same procedures to **3a**. Yield 71%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.78 (dt, *J* = 4.9, 1.5 Hz, 1H), 7.90 – 7.79 (m, 4H), 7.55 – 7.45 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.91 – 6.75 (m, 2H) (aryl C−**H**), 3.26 (d, *J* = 14.9 Hz, 1H), 3.11 (d, *J* = 14.9 Hz, 1H) (Bn−C**H**$_2$), 2.70 (d, *J* = 12.7 Hz, 1H), 2.46 (d, *J* = 12.7 Hz, 1H) (B−CH$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -2.6 (3B), -9.3 – 10.8 (7B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 200.4 (**C**=O), 149.76, 147.82, 137.7, 137.6, 135.4, 132.8, 130.2, 128.9, 128.4, 127.9, 127.5, 125.3

(aryl−**C**), 82.6, 82.2 (cage−**C**), 41.0 (Bn−CH$_2$), 28.3 (B−**C**H$_2$). HRMS (ESI, positive mode): *m/z* calcd for $C_{22}B_{10}NOH_{28}$ [M+H$^+$]: 431.3132. Found: 431.3136.

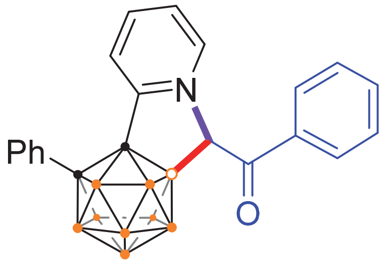


13d: Yield 91%. light yellow solid. **^{1}H NMR (400 MHz, Dichloromethane-*d*$_2$)**, **Diastereomer I: Diastereomer II** = 36 : 64, **Diastereomer I**: δ 8.33 – 8.09 (m, 3H), 7.98 – 7.52 (m, 4H), 7.49 – 6.97 (m, 6H), 6.93 – 6.85 (m, 1H) (aryl C−**H**), 6.67 (s, 1H) (B−C**H**−N), 3.66 – 3.47 (m, 2H) (Bn−C**H**$_2$), -2.24 (br, 1H, B−**H**−B); **Diastereomer II**: δ 8.33 – 8.09 (m, 3H), 7.98 – 7.52 (m, 4H), 7.49 – 6.97 (m, 6H), 6.93 – 6.85 (m, 1H) (aryl C−**H**), 6.18 (s, 1H) (B−C**H**−N), 3.66 – 3.47 (m, 2H) (Bn−C**H**$_2$), 2.56 (br, 1H, B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.0, -7.0, -10.4, -15.3, -19.0, -20.5, -23.3, -32.0, -34.0; **^{13}C NMR** plus **^{13}C−^{1}H HSQC (400 MHz, Chloroform-*d*)**: δ 194.2, 192.5 (**C**=O), 162.4, 161.5, 145.0, 144.1, 143.3, 140.5, 140.2, 134.7, 134.4, 134.3, 134.2, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 126.2, 126.1, 123.3, 122.9, 122.4, 122.4, 122.4 (aryl−**C**), 74.5, 73.1 (br, B−**C**H−N), 68.3 (br), 54.1 (br), 53.1 (br) (Cage−**C**), 41.8, 41.7 (Bn−CH$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{22}B_9NOH_{26}Na$ [M+Na$^+$]: 441.2780. Found: 441.2787.

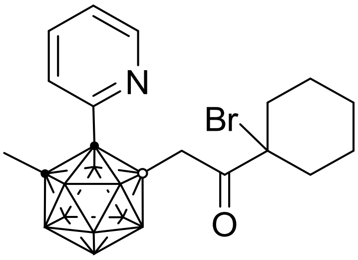


3da was prepared by the same procedures to **3a**. Yield 73%. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 8.40 (m, 1H), 7.90 – 7.83 (m, 2H), 7.62 – 7.49 (m, 3H), 7.48

– 7.36 (m, 4H), 7.24 – 7.18 (m, 1H), 7.16 (m, 1H), 7.14 – 7.07 (m, 2H) (aryl C−**H**), 2.67 (d, *J* = 12.7 Hz, 1H), 2.61 (d, *J* = 12.8 Hz, 1H) (B−C**H**$_2$); **^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)**: δ -1.8 (3B), -9.7 (3B), -11.0 (4B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 200.4 (**C**=O), 149.3, 147.1, 137.7, 136.8, 132.8, 130.9, 130.6, 130.3, 128.9, 128.5, 128.4, 128.2, 126.2, 124.6 (aryl−**C**), 85.6, 84.4 (cage−**C**), 29.0 (B−**C**H$_2$). HRMS (ESI, positive mode): *m/z* calcd for $C_{21}B_{10}NOH_{26}$ [M+H$^+$]: 416.3012. Found: 416.3008.



13e: Yield 89%. light yellow solid. **^{1}H NMR (400 MHz, Acetone-*d*$_6$), Diastereomer I: Diastereomer II** = 18 : 72, **Diastereomer I**: δ 8.96 (m, 1H), 8.27 – 8.22 (m, 2H), 8.16 – 8.08 (m, 1H), 7.88 – 7.81 (m, 1H), 7.76 – 7.53 (m, 3H), 7.39 – 7.19 (m, 5H) (aryl C−**H**), 6.68 (s, 1H) (B−C**H**−N), 6.24 (dt, *J* = 8.2, 1.1 Hz, 1H) (aryl C−**H**), -2.43 (br, 1H) (B−**H**−B); **Diastereomer II**: δ 8.88 (m, *J* = 6.3, 1.5, 0.7 Hz, 1H), 8.22 – 8.16 (m, 2H), 8.16 – 8.08 (m, 1H), 7.88 – 7.81 (m, 1H), 7.76 – 7.53 (m, 3H), 7.39 – 7.19 (m, 5H) (aryl C−**H**), 7.08 (s, 1H) (B−C**H**−N), 6.21 (dt, *J* = 8.2, 1.1 Hz, 1H) (aryl C−**H**), -1.80 (br, 1H) (B−**H**−B). **^{11}B{^{1}H} NMR (128 MHz, Acetone-*d*$_6$)**: δ -0.9, -6.3, -10.6, -12.8, -16.3, -21.3, -25.1, -31.3, -34.1; **^{13}C NMR** plus **^{13}C−^{1}H HSQC (400 MHz, Acetone-*d*$_6$)**: δ 191.8 (**C**=O), 147.6, 146.9, 145.2, 144.7, 139.6, 136.2, 134.6, 134.3, 129.8, 129.6, 129.5, 129.3, 129.0, 128.8, 128.4, 128.2, 124.5, 124.0, 123.4 (aryl−**C**), 75.3 74.2 (br, B−**C**H−N). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{21}B_9NOH_{24}Na$ [M+Na $^+$]: 426.2660. Found: 426.2665.



14: Yield 73%. White solid. **^{1}H NMR (500 MHz, Chloroform-*d*)**: δ 8.69 (m, 1H), 7.90 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.84 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42 (m, *J* = 7.5, 4.7, 1.1 Hz, 1H) (aryl C−**H**), 2.39 (d, *J* = 14.8 Hz, 1H), 2.32 (d, *J* = 14.7 Hz, 1H) (B−C**H**$_2$), 2.17 – 2.12 (m, 1H), 2.10 – 2.04 (m, 1H) (Cyclohexy−C**H**$_2$), 1.80 – 1.60 (m, 13H) (Cyclohexy−C**H**$_2$ and cage−C**H**$_3$); **^{11}B{^{1}H} NMR (160 MHz, Chloroform-*d*)**: δ -2.5 (2B), -4.3 (1B), −9.5 (4B), −11.2 (3B); **^{13}C NMR (101 MHz, Chloroform-*d*)**: δ 204.0 (**C**=O), 149.7, 148.0, 137.6, 126.8, 124.9 (aryl−**C**), 81.3, 74.0 (cage−**C**), 35.8, 35.7 (Cyclohexyl−**C**H$_2$), 26.2 (B−**C**H$_2$), 25.1 (Cyclohexyl−**C**H$_2$), 23.6 (cage−**C**H$_3$), 22.8, 22.8 (Cyclohexyl−**C**H$_2$). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NOBrH_{29}$ [M+H$^+$]: 442.2337. Found: 442.2343.

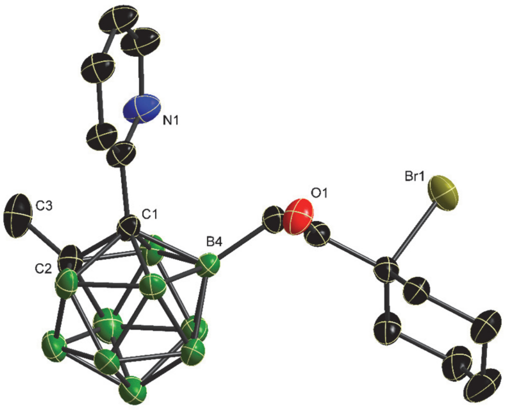


Figure S38. Molecular structure of compound **14** (ellipsoids at 30% probability and H atoms omitted for clarity).

5. References

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6. Crystallographic data

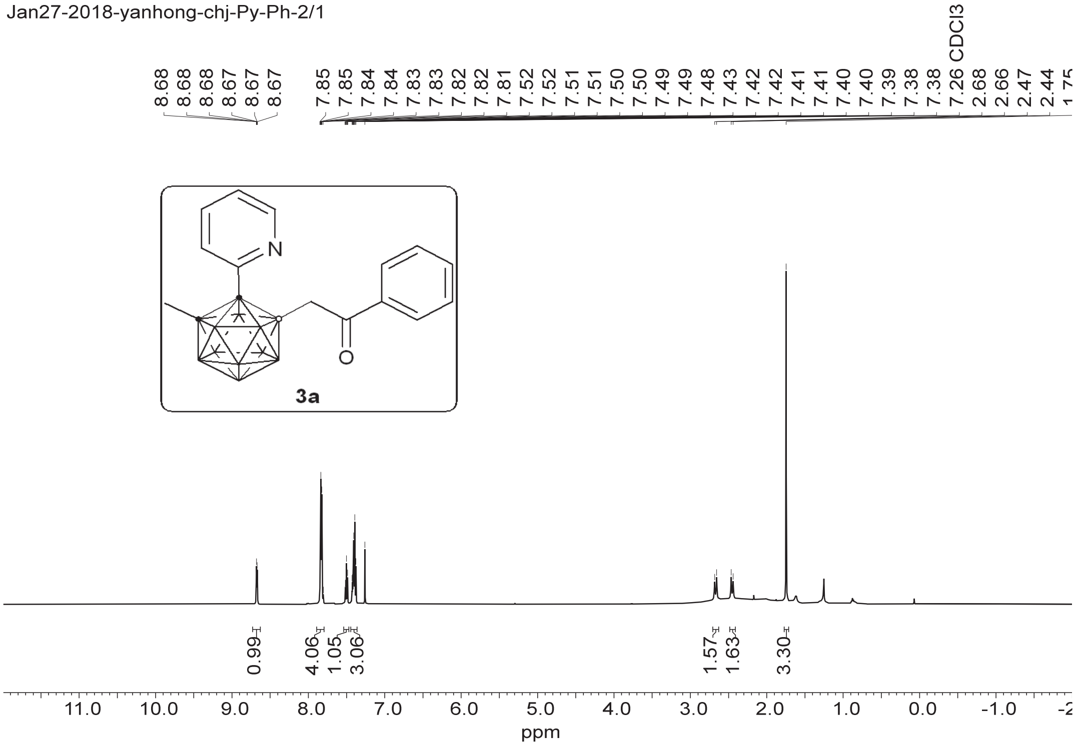
Table S3. Crystallographic data of compounds **3a**, **3p**, **5m**, **6e**, **7h**, **12**, **13a** and **14**.

	3a	**3p**	**5m**	**6e**
Empirical formula	$C_{16}H_{23}B_{10}NO$	$C_{17}H_{25}B_{10}NO_2$	$C_{23}H_{35}B_{10}Cl_3N_2O_3S$	$C_{114}H_{162}B_{60}N_6O_6$
Formula weight	353.45	383.48	635.04	2361.09
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/n	P2(1)/n	P1	P-1
a/ Å	10.075(2)	7.9346(7)	10.5400(11)	11.866(5)
b/ Å	10.417(2)	33.245(3)	12.1568(14)	24.030(9)
c/ Å	19.182(4)	8.0629(10)	14.1284(14)	24.784(9)
α/deg	90	90	71.811(3)	79.345(6)
β/deg	102.788(3)	97.9930(10)	76.438(3)	88.967(7)
γ/deg	90	90	65.487(3)	89.790(7)
V/ $Å^3$	1963.2(7)	2106.2(3)	1553.3(3)	6944(5)
Z	4	4	2	2
ρ_{calcd} (g cm^{-3})	1.196	1.209	1.358	1.129
μ (mm^{-1})	0.064	0.069	0.393	0.061
F(000)	736.0	800	656.0	2472.0
θ range (deg)	2.117/29.88	2.451/27.865	2.128/27.411	1.307/27.445
no. of rflns collected	20626	19455	13290	64306
no. of indep rflns	5592	4983	9387	31397
GoF on F^2	1.032	1.051	1.040	0.858
R1/wR2 (I> 2σ(I))	0.0519/ 0.1427	0.0540/0.1437	0.0461/0.0996	0.0833/0.1684
R1/wR2 (all data)	0.0741/ 0.1585	0.0659/0.1520	0.0667/0.1089	0.3408/0.2763
largest peak/hole (e $Å^{-1}$)	0.25/−0.23	0.3/−0.28	0.43/−0.29	0.19/−0.22

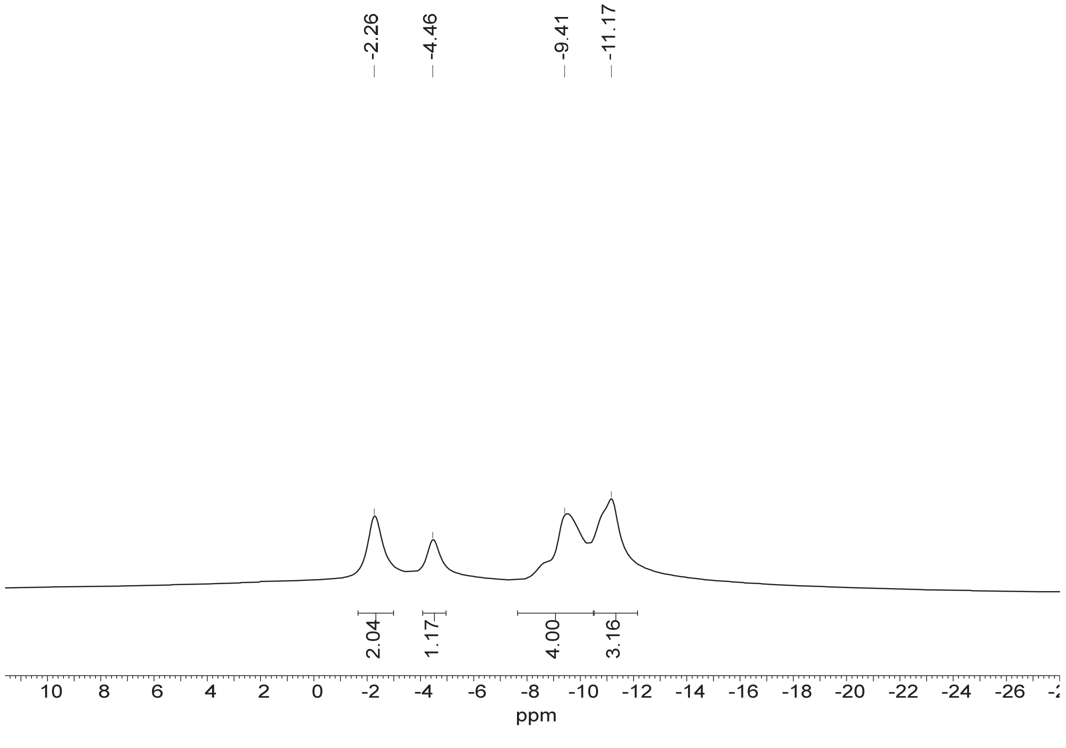
	7h	**12**	**13a**	**14**
Empirical formula	$C_{16}H_{22}B_{10}O$	$C_{16}H_{22}B_9NO$	$C_{16}H_{24}B_9N$	$C_{16}H_{28}B_{10}BrNO$
Formula weight	338.43	341.63	327.65	438.40
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P1	Aea2	Pc	P2(1)/n
a/ Å	12.097(8)	12.6535(5)	7.670(2)	7.829
b/ Å	13.280(10)	21.2265(9)	7.489(2)	29.804
c/ Å	13.603(9)	15.7104(6)	16.814(3)	9.584
α/deg	70.744(18)	90	90.00(3)	90
β/deg	72.905(18)	90	102.92(3)	93.06
γ/deg	70.884(19)	90	90.00(3)	90
V/ Å^3	1907(2)	4219.6(3)	941.3(4)	2233.1
Z	4	8	1	4
ρ_{calcd} (g cm^{-3})	1.179	1.076	1.268	1.304
μ (mm^{-1})	0.062	0.059	0.077	1.848
F(000)	704.0	1424.0	361.0	896.0
θ range (deg)	2.011/27.687	1.919/27.522	2.911/27.5	2.235/27.557
no. of rflns collected	13580	19061	8417	17903
no. of indep rflns	10731	4149	3461	5074
GoF on F^2	0.987	1.050	1.044	1.042
R1/wR2 (I> 2σ(I))	0.1150/0.26204	0.0597/ 0.1577	0.0409/ 0.1035	0.0942/ 0.2705
R1/wR2 (all data)	0.2331/0.3313	0.0710/ 0.1661	0.0465/ 0.1088	0.1473/ 0.3114
largest peak/hole (e Å^{-1})	0.48/−0.35	0.23/−0.23	0.17/−0.15	0.99/−0.54

7. NMR Spectra

^{1}H NMR (500 MHz, CDCl$_3$)



^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



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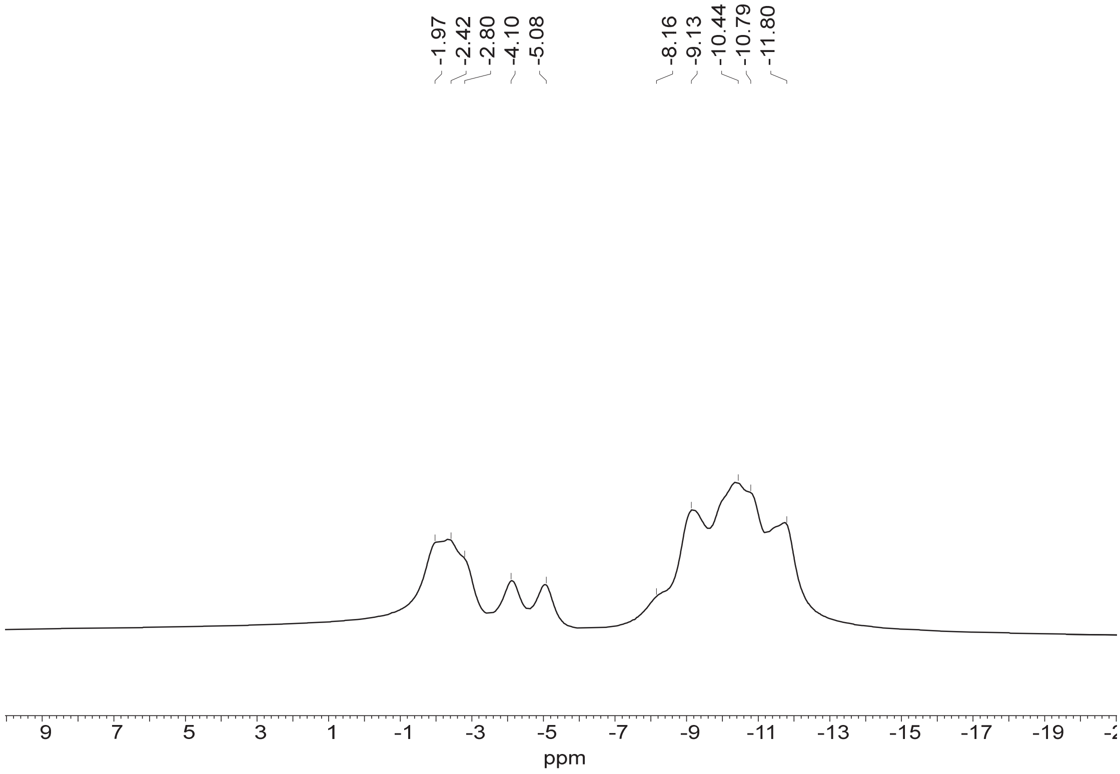
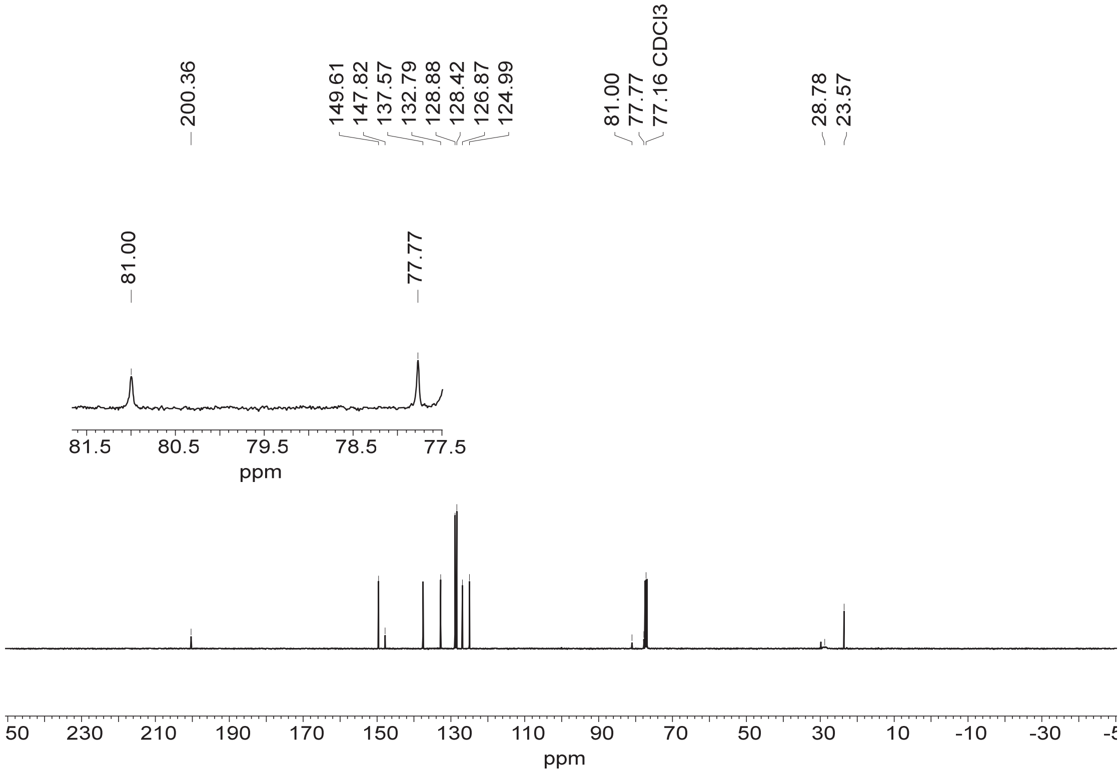


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



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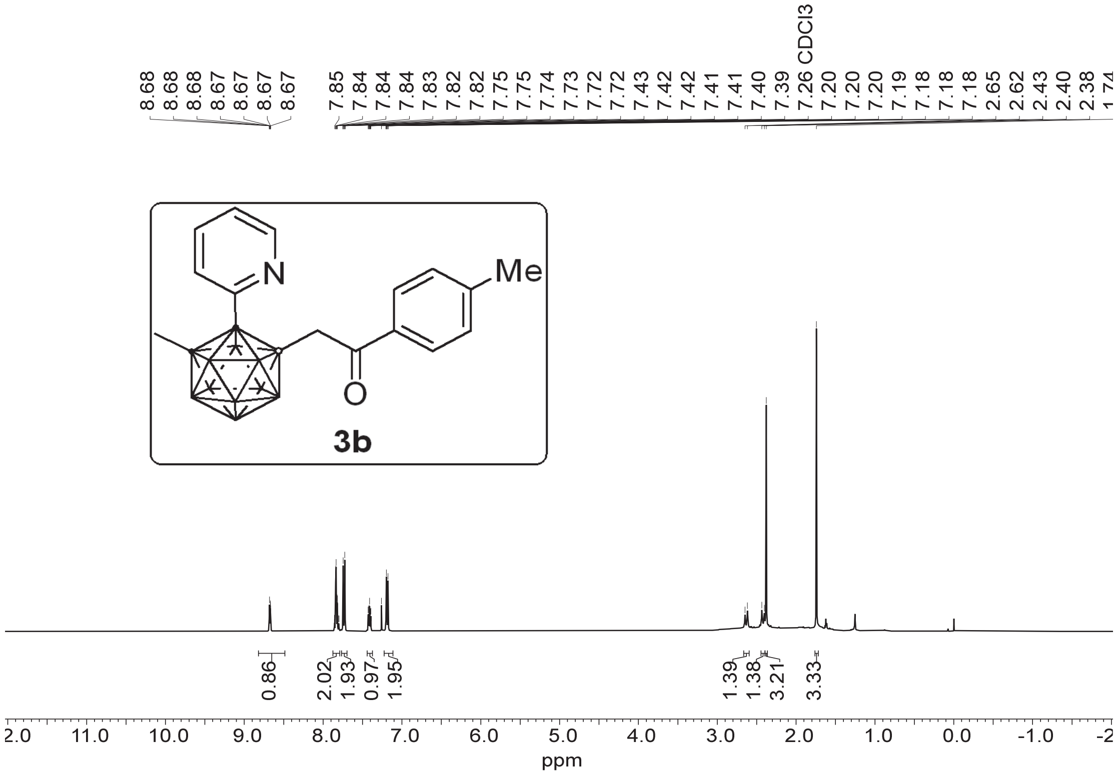

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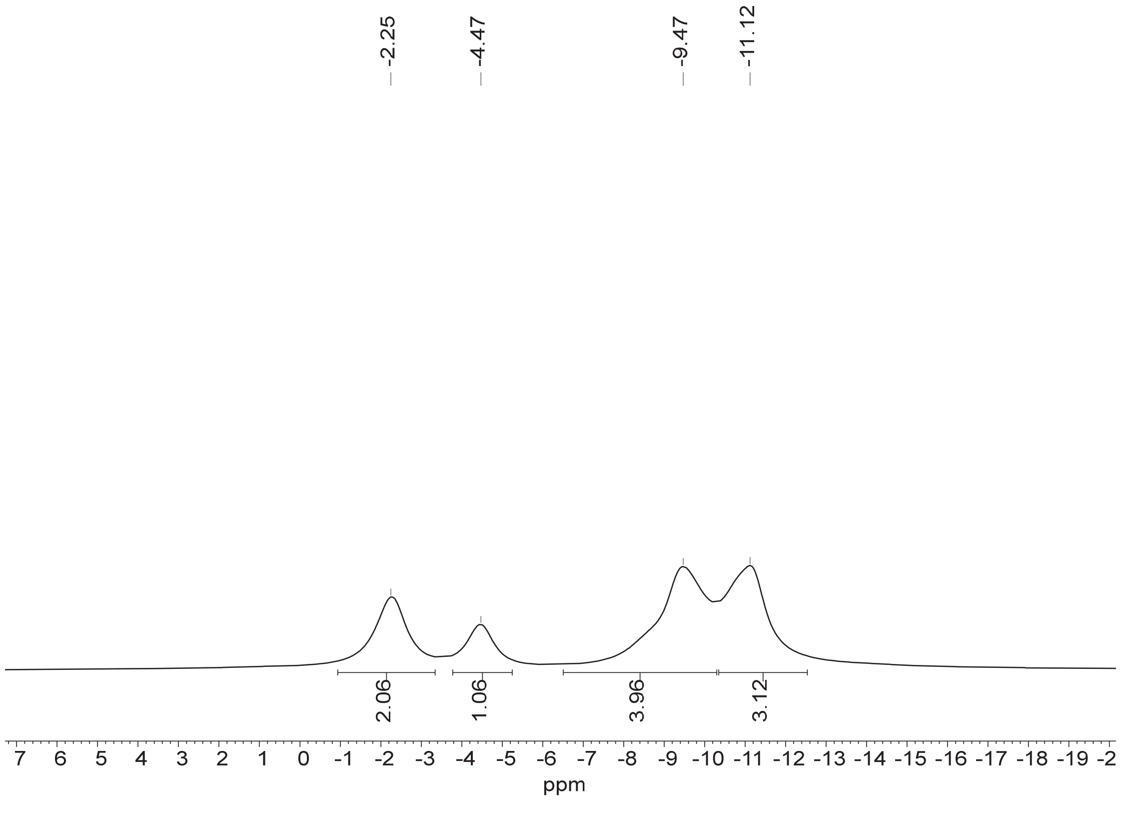

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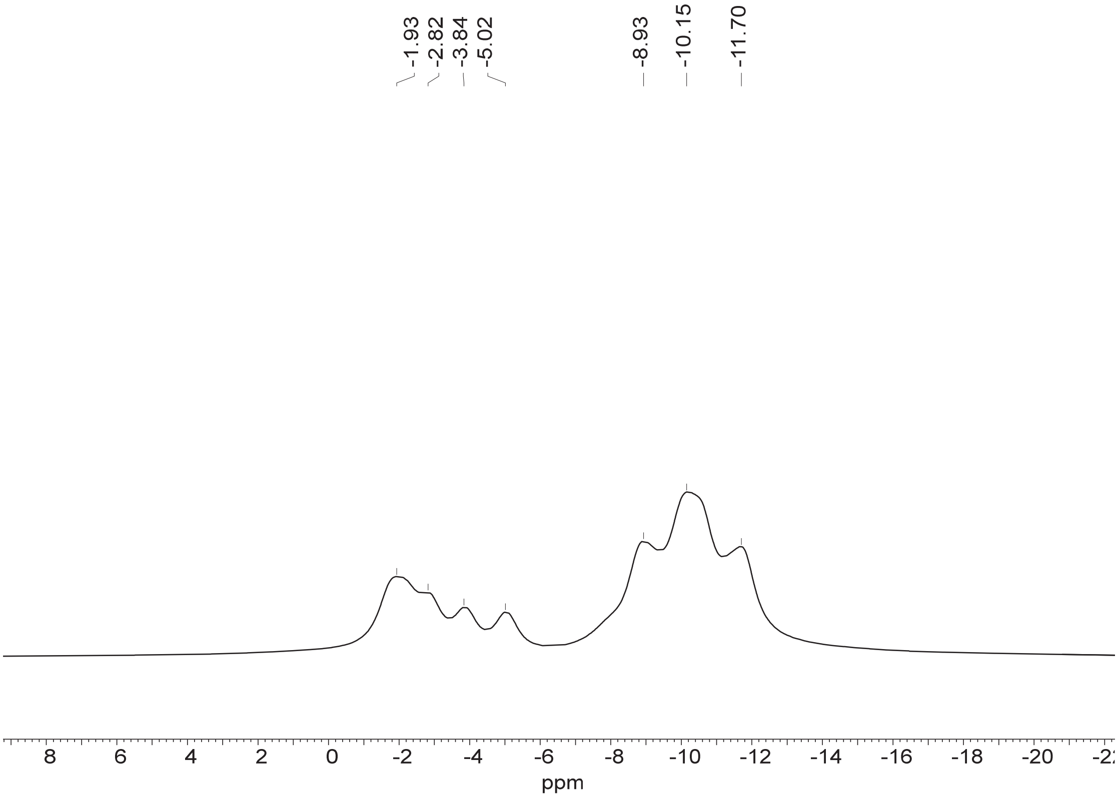

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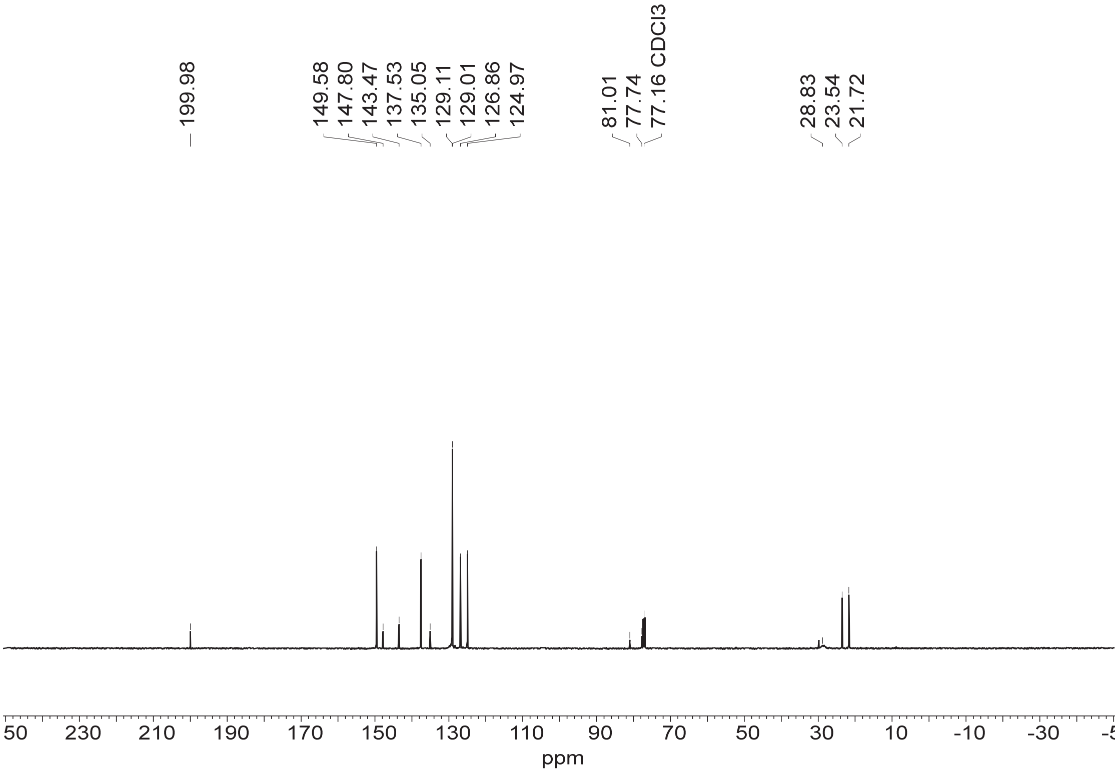

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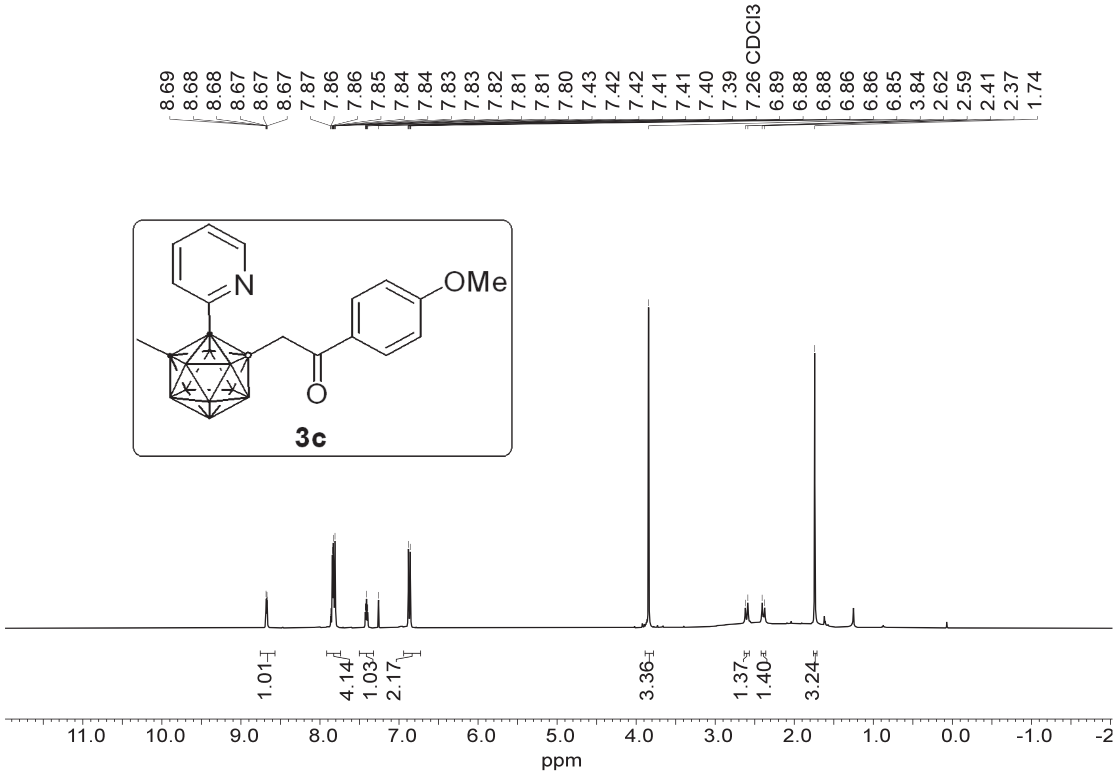

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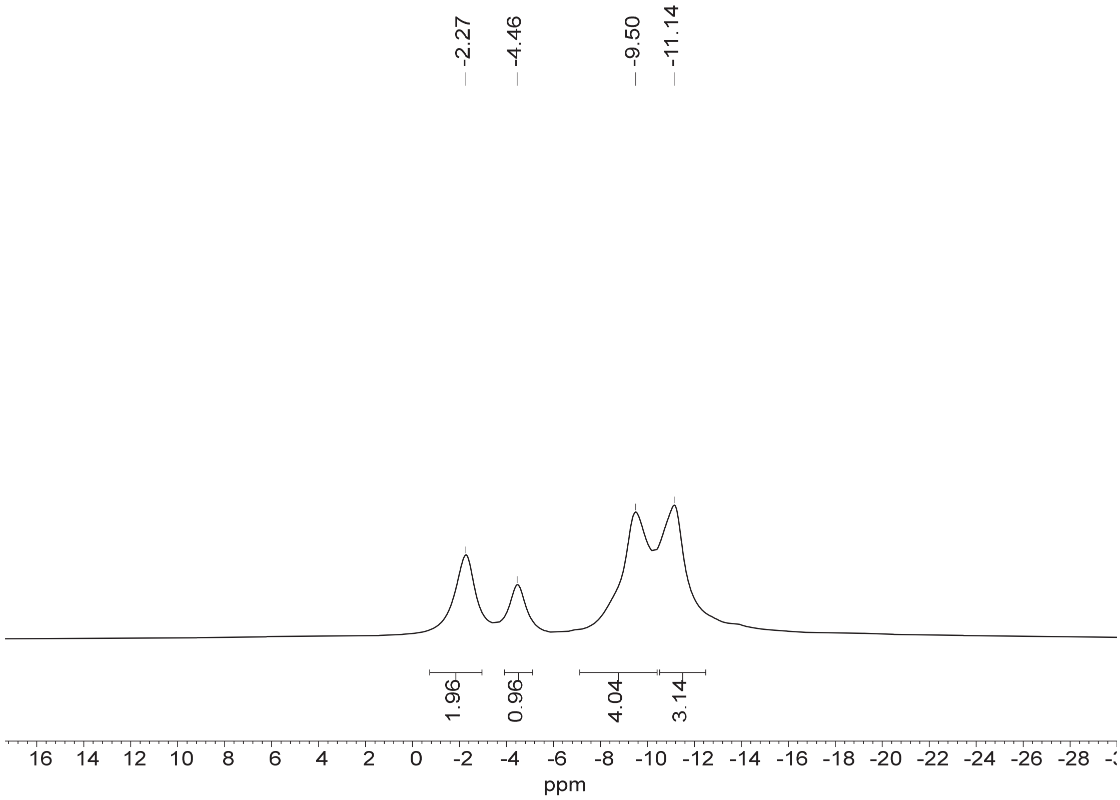

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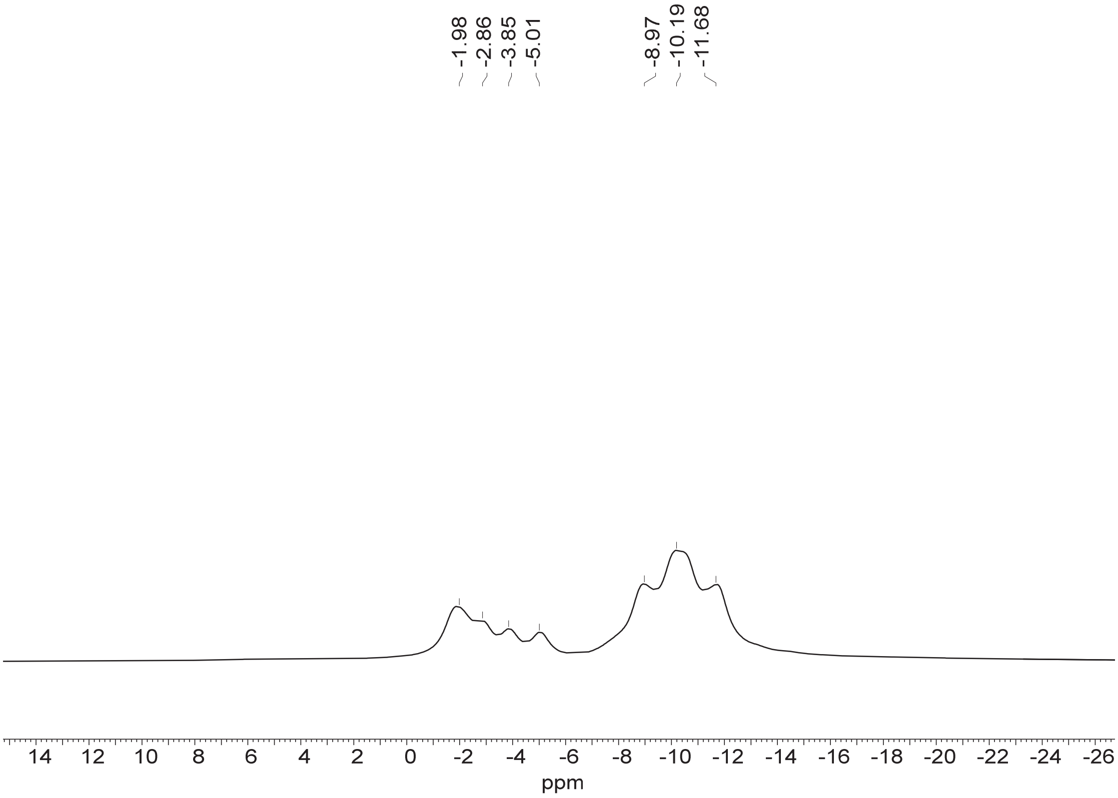

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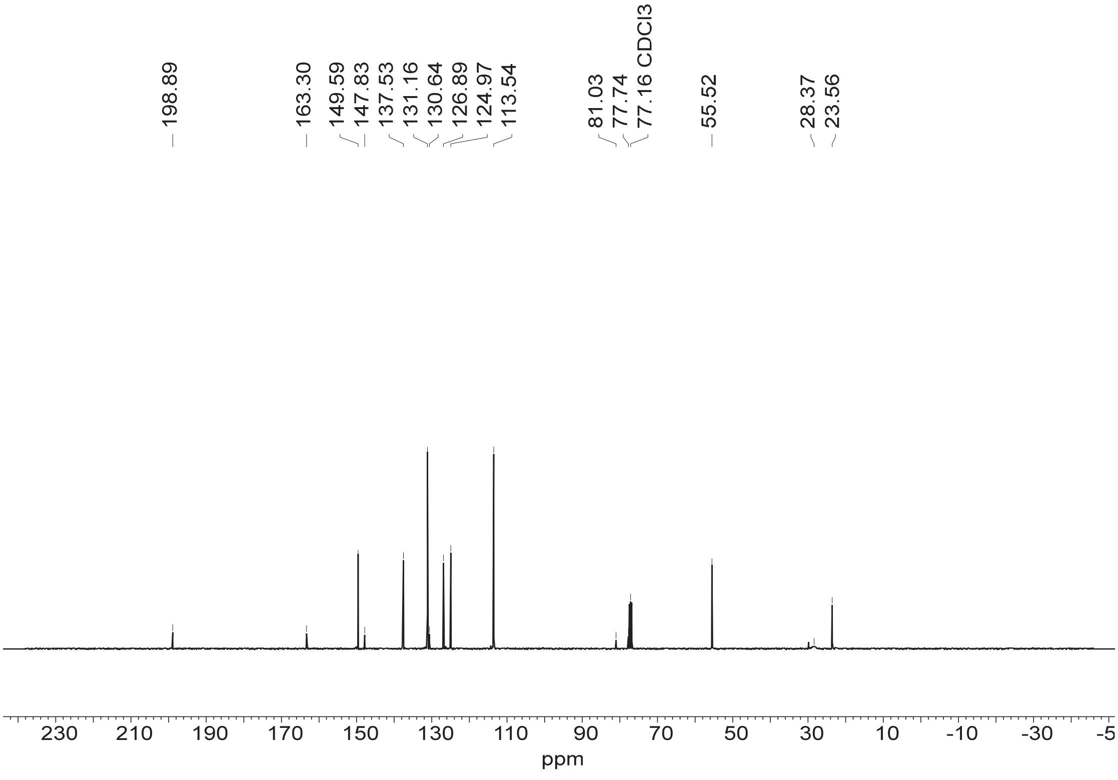

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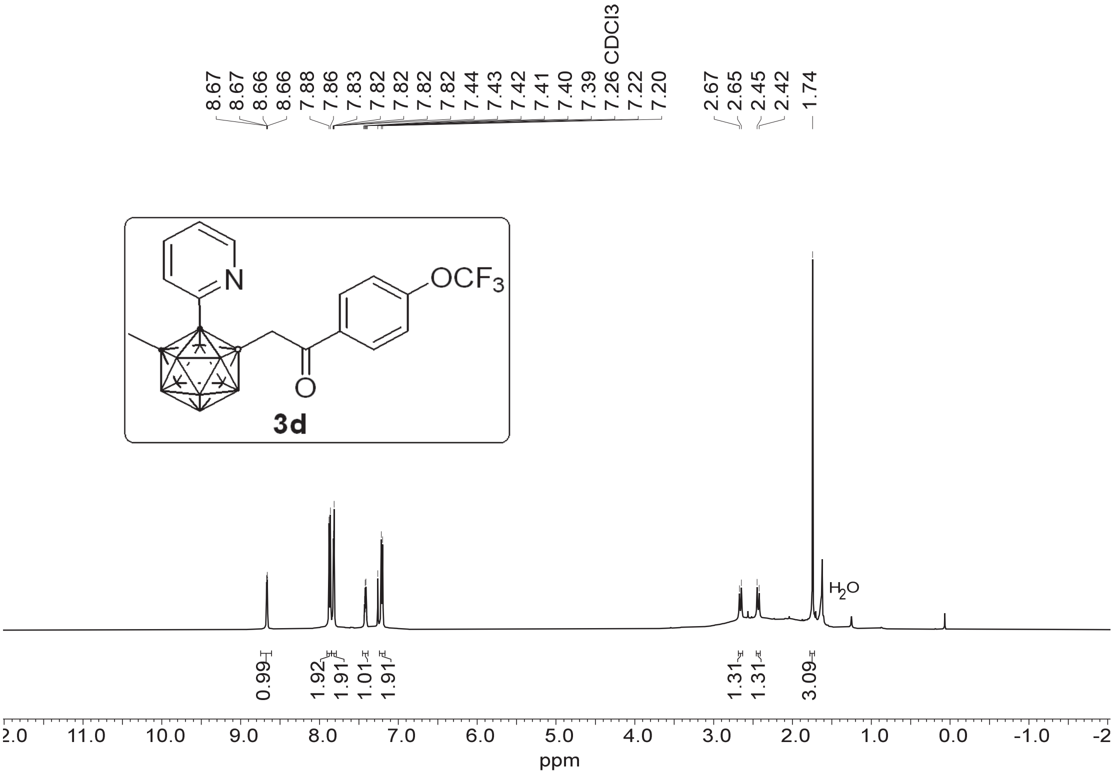

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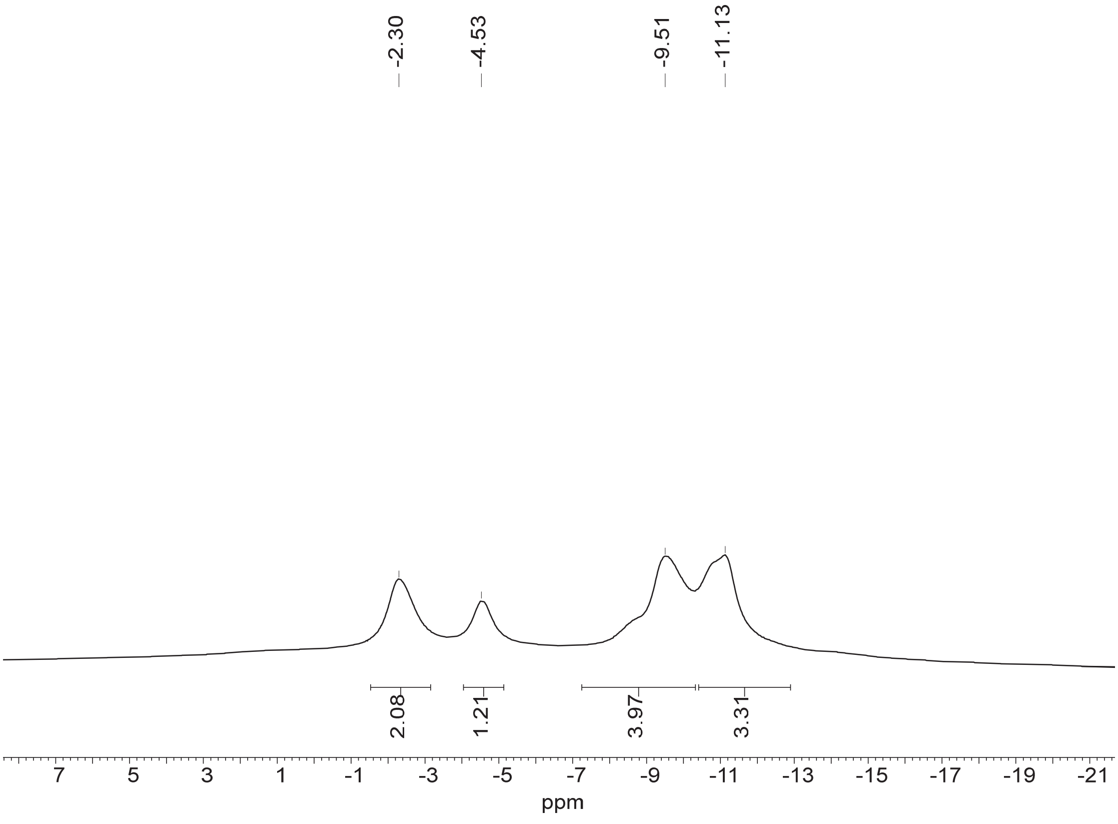

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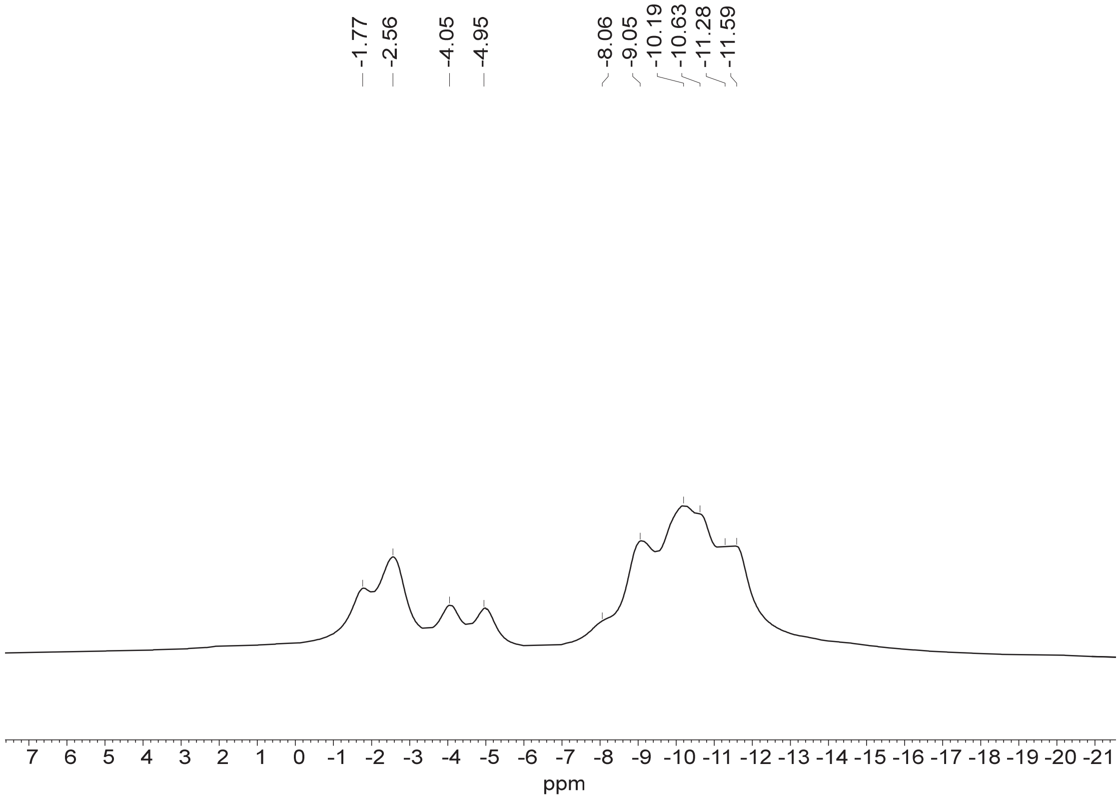

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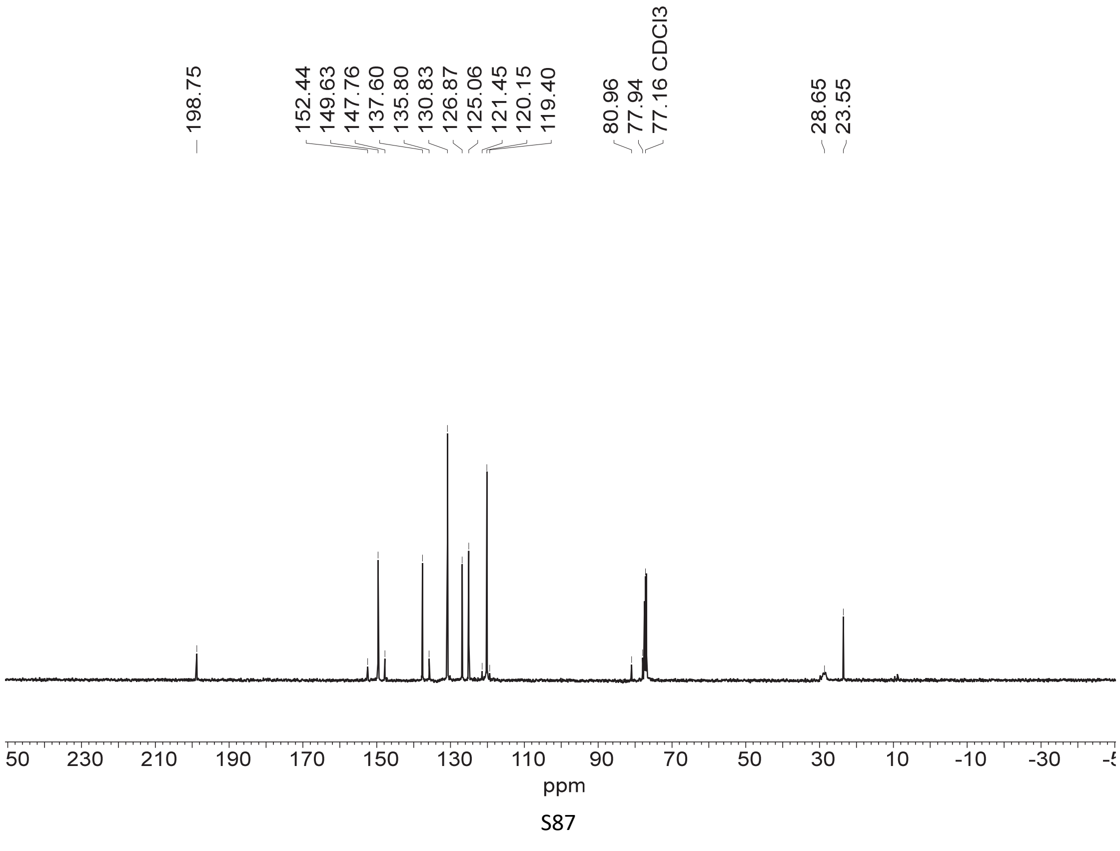
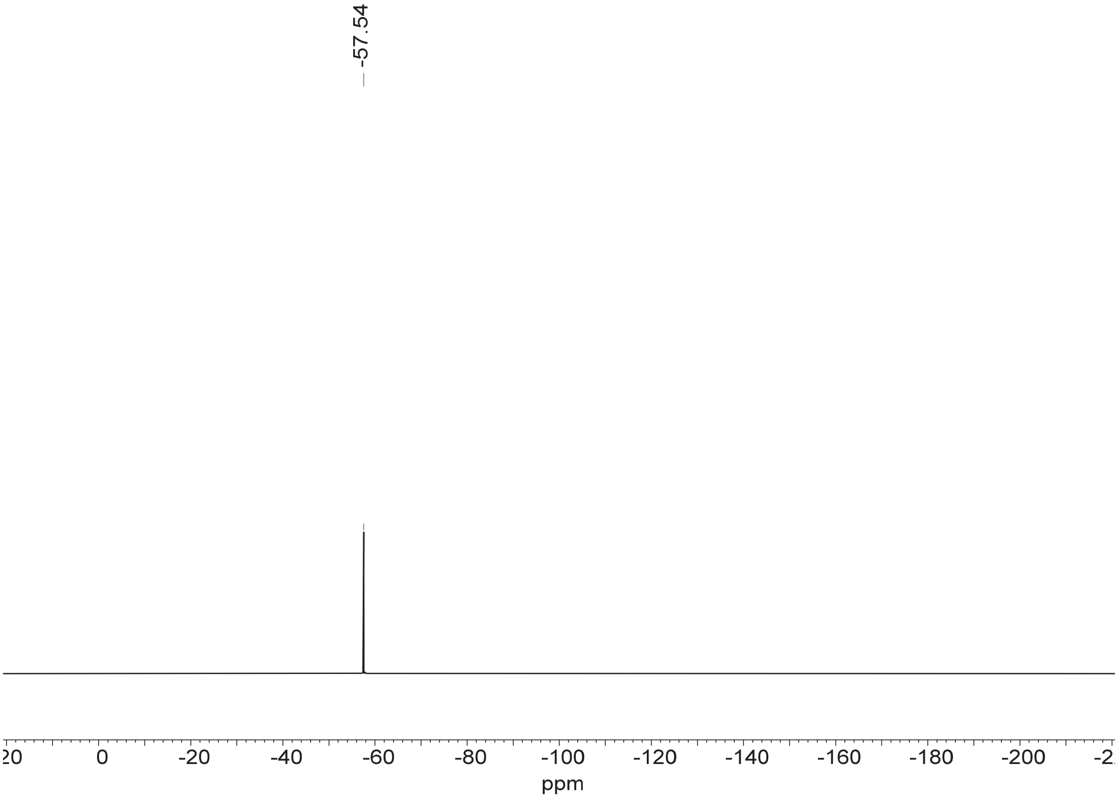


^{19}F NMR (471 MHz, $CDCl_3$)



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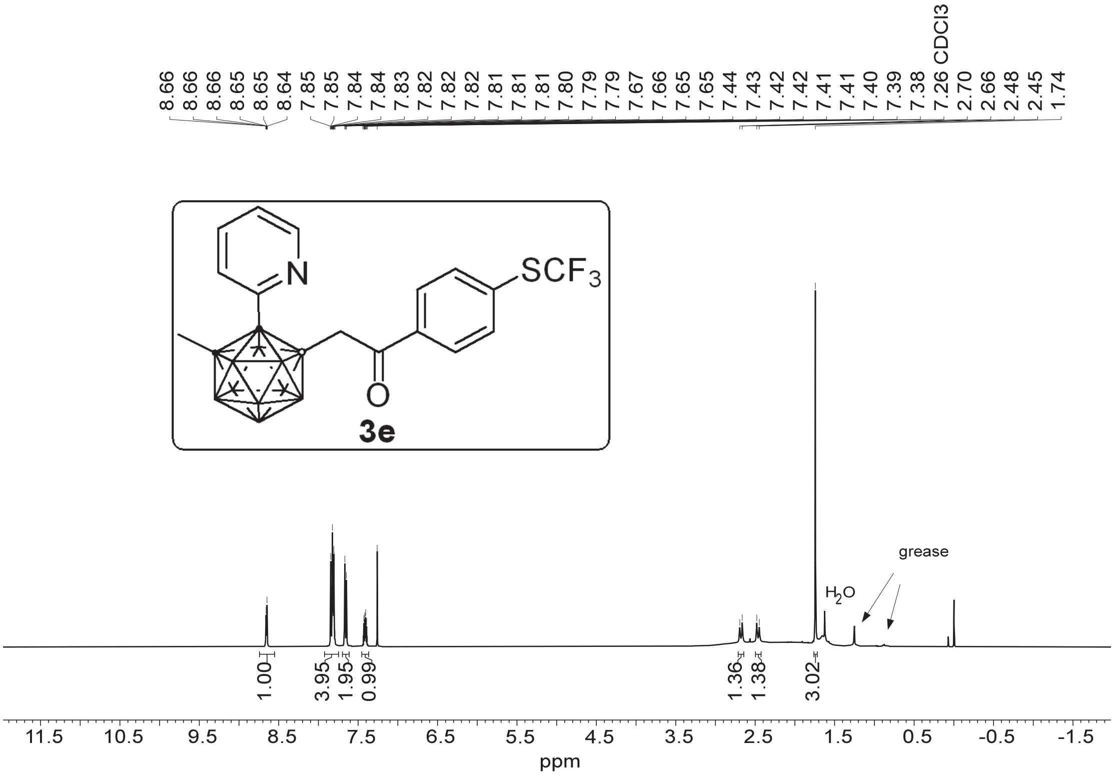

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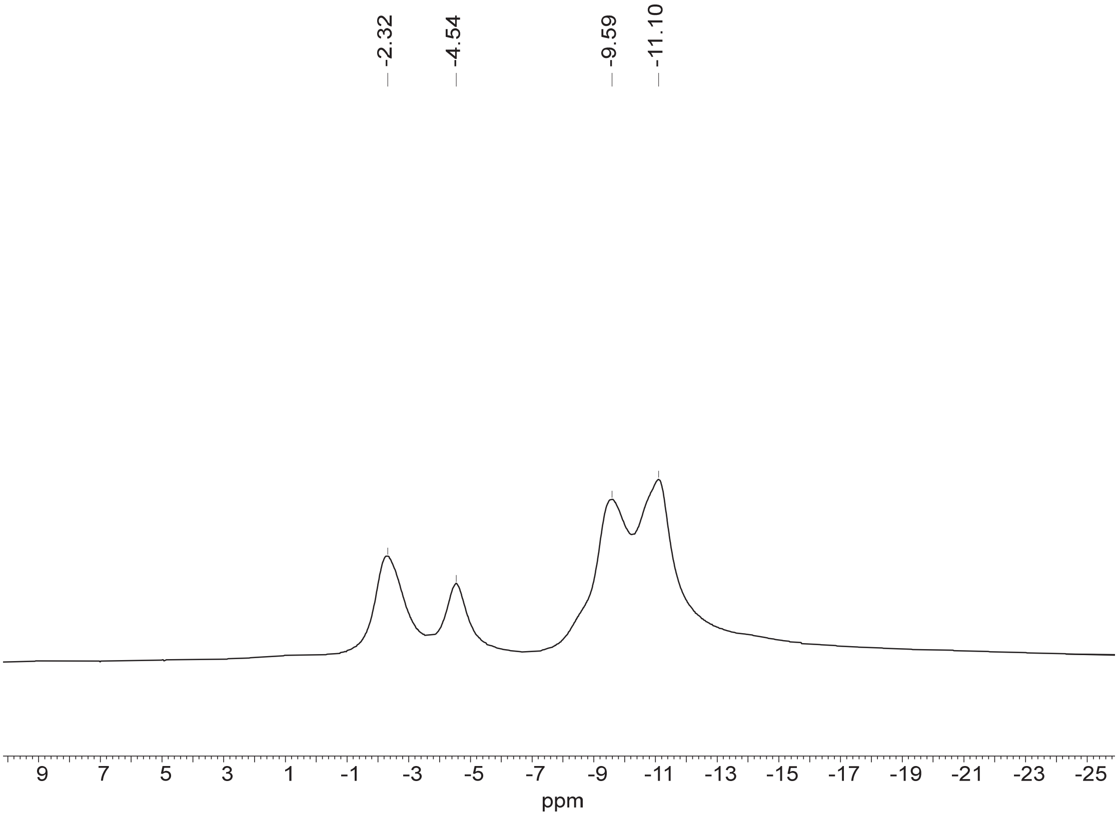

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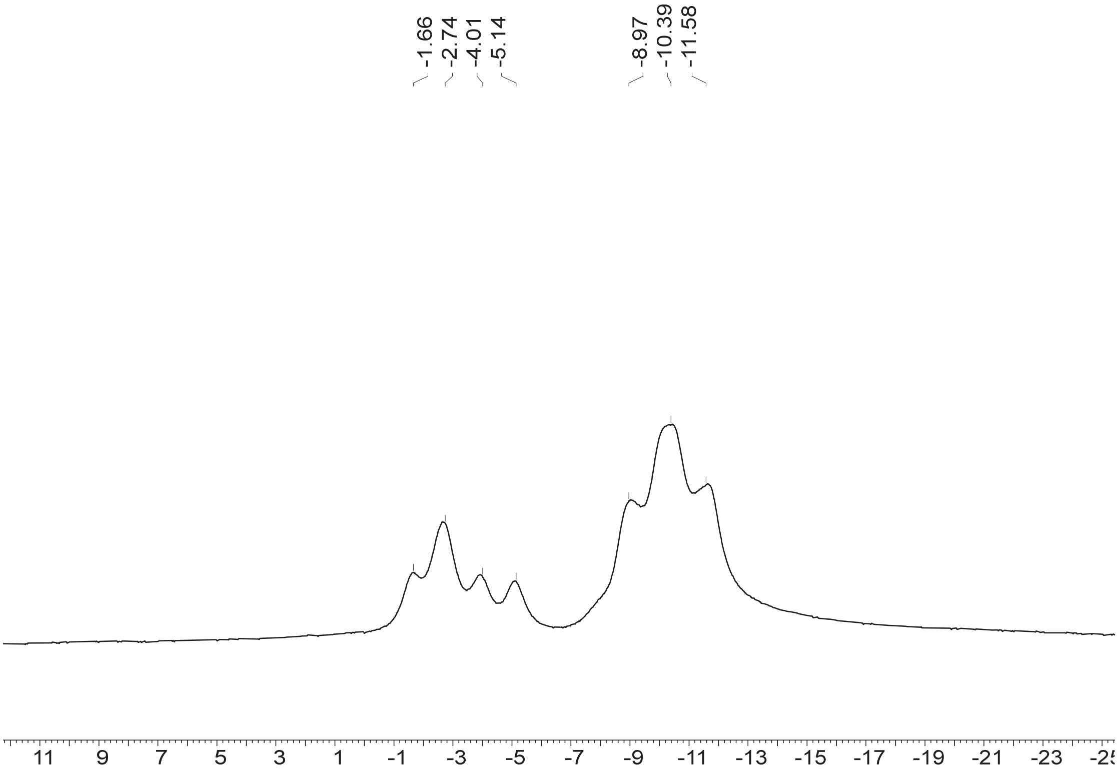

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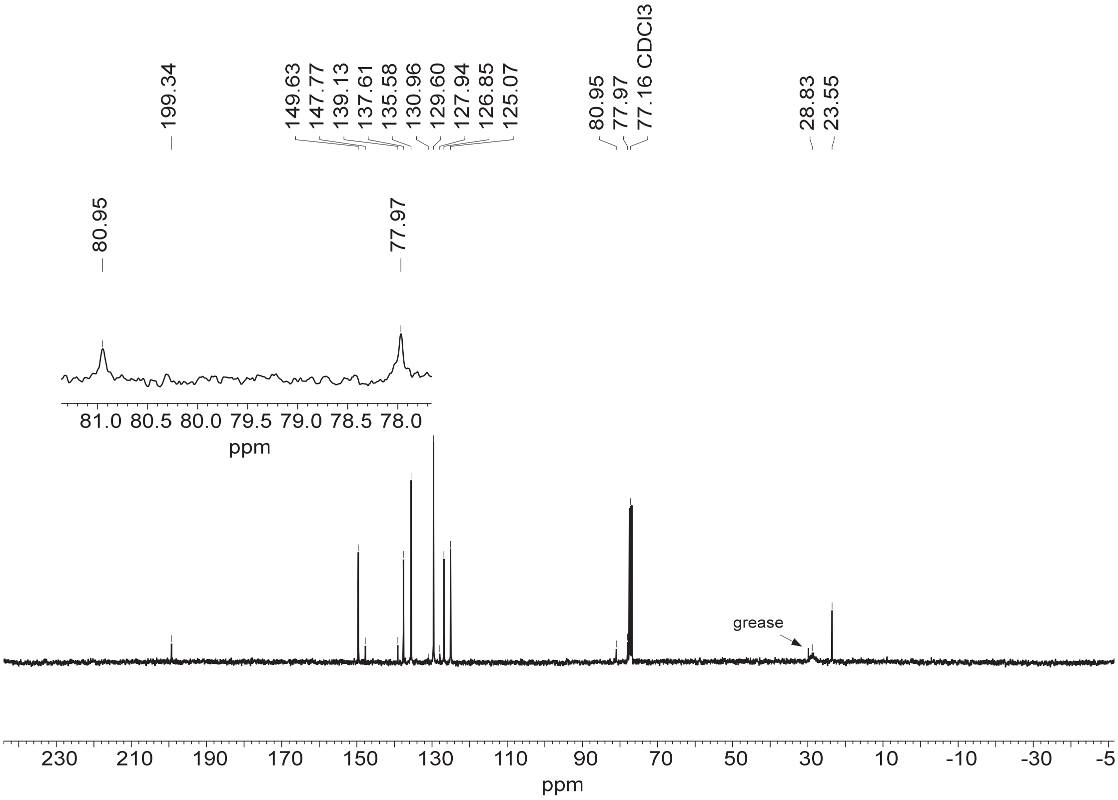

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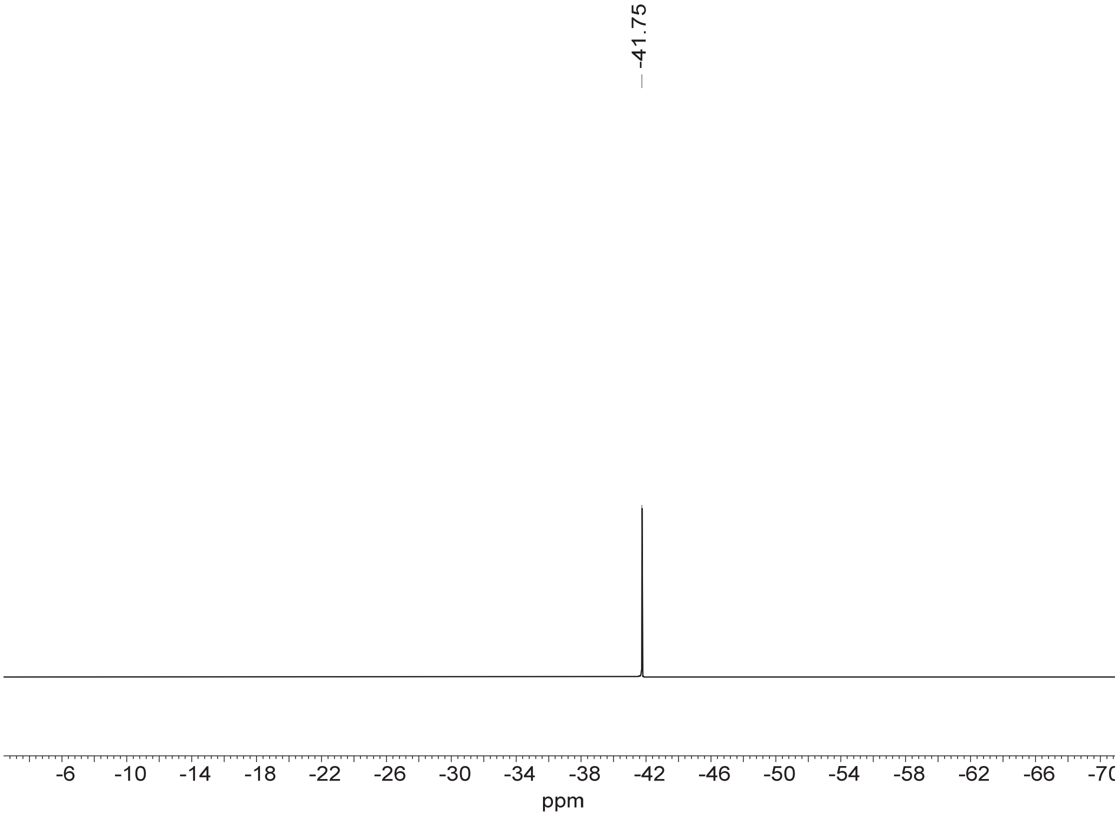

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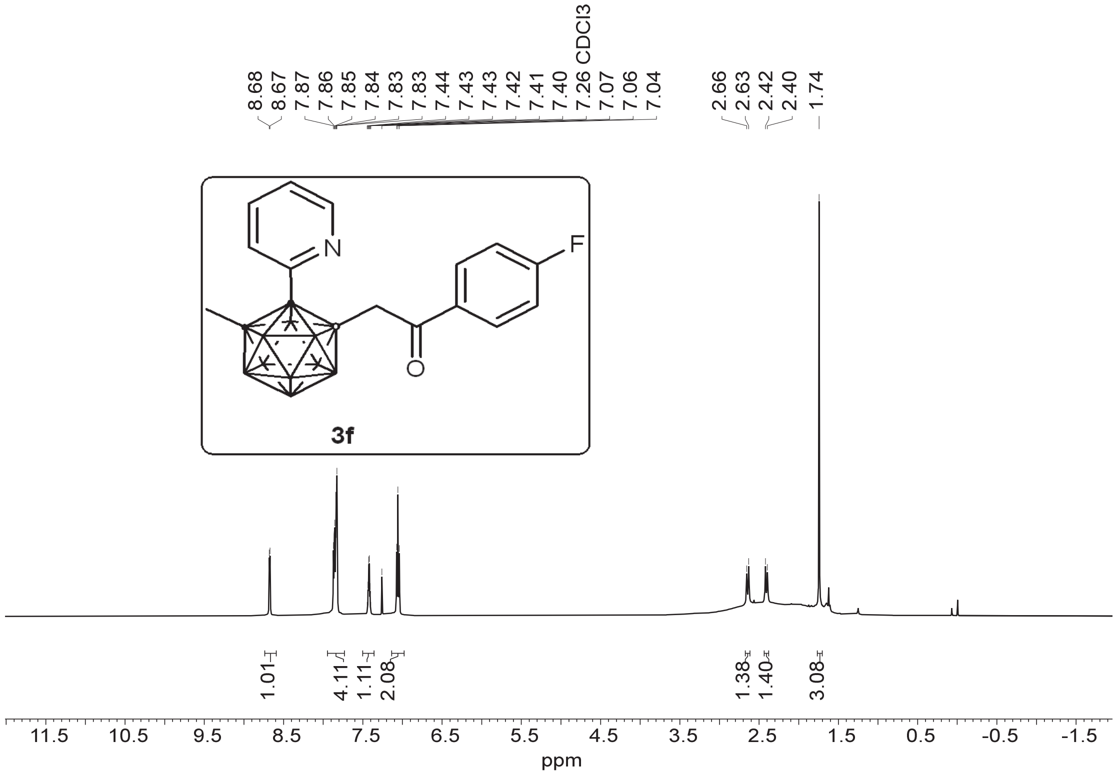

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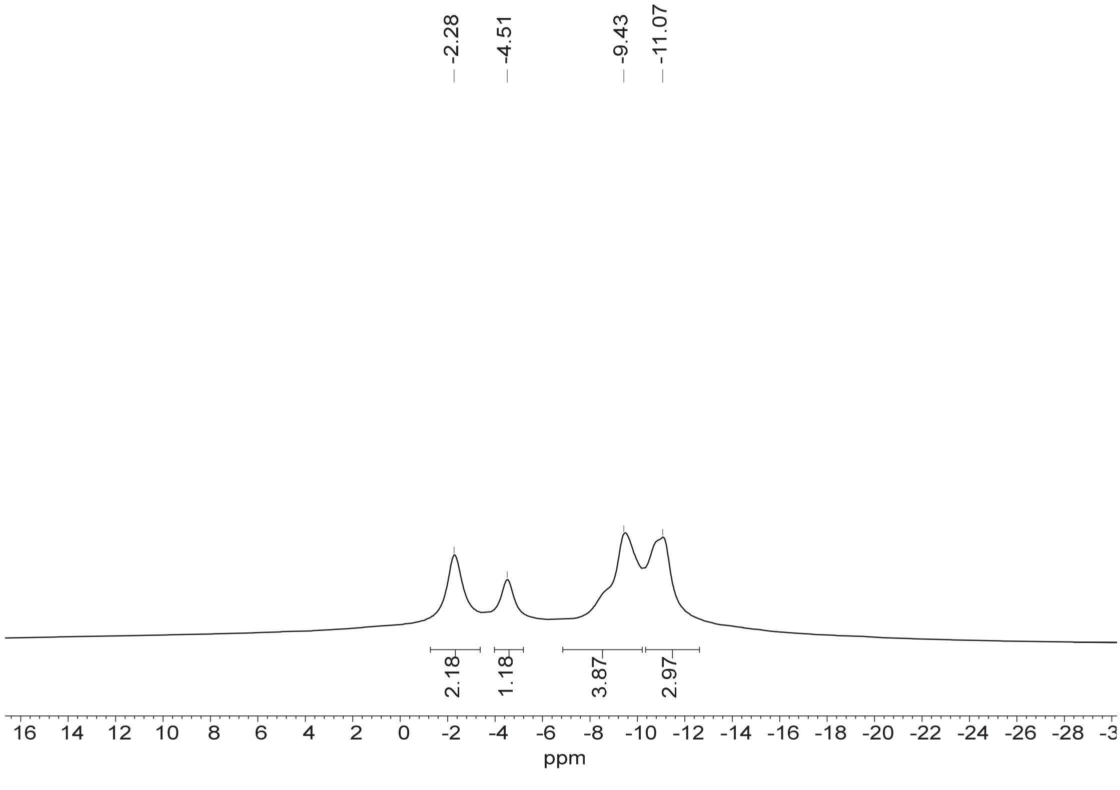

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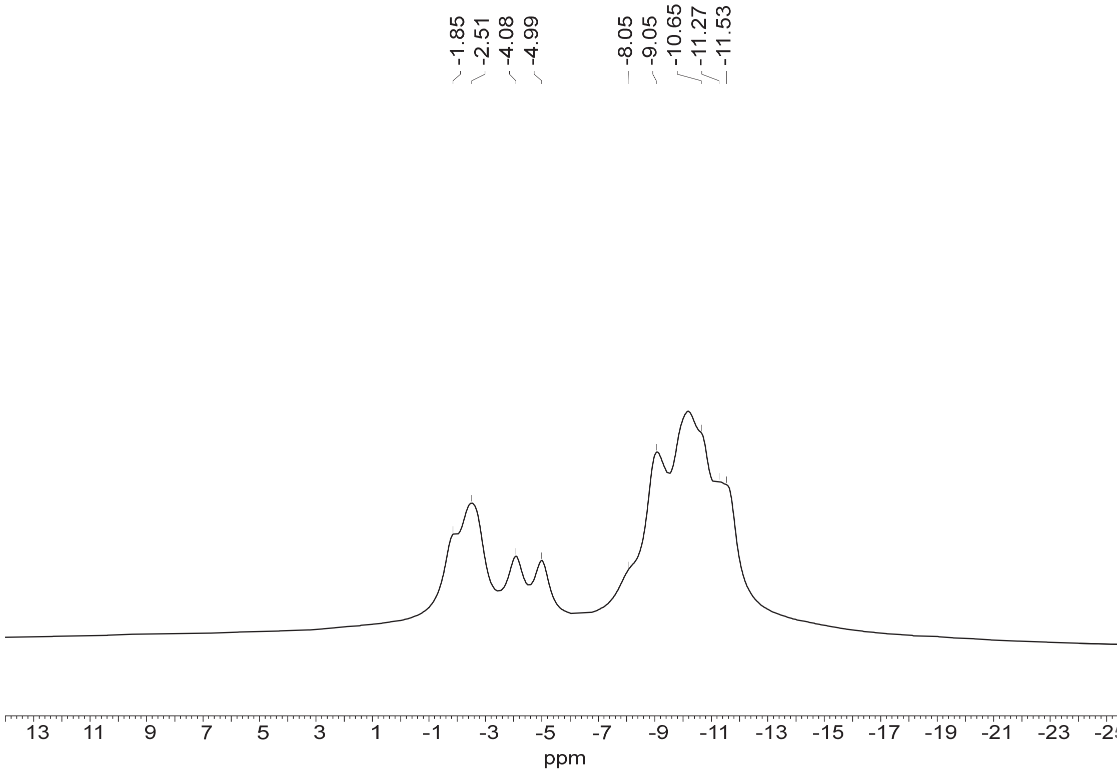

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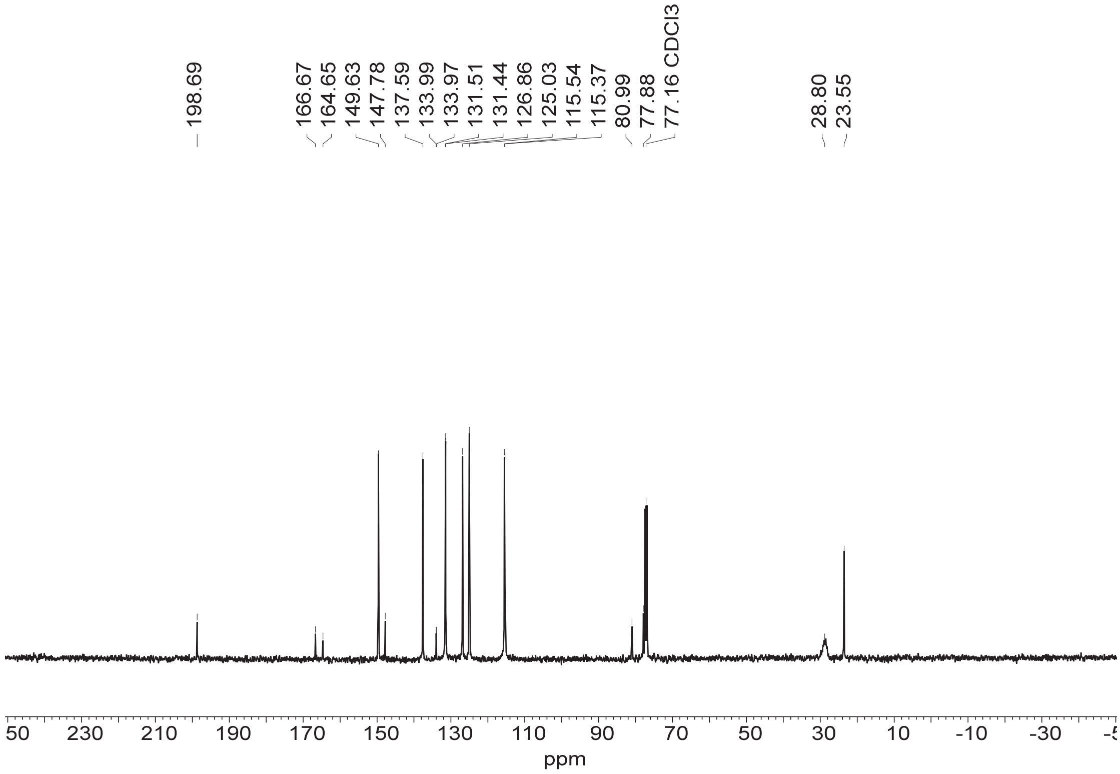

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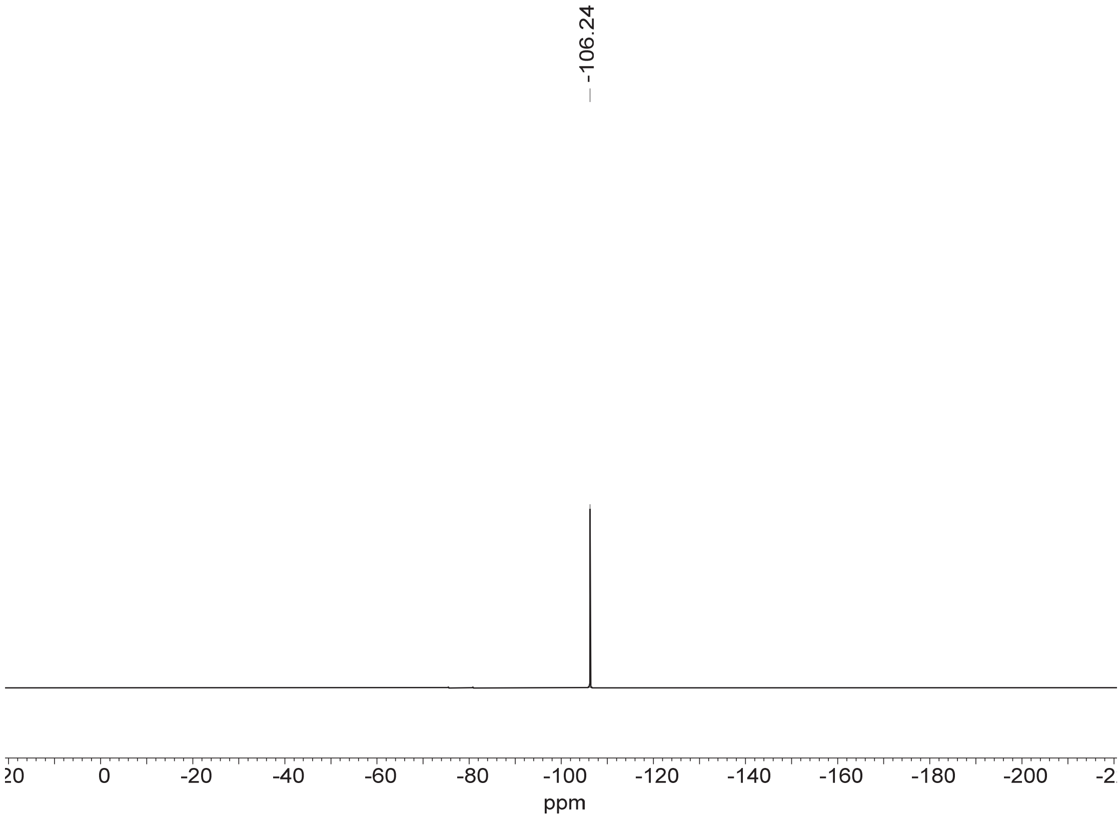

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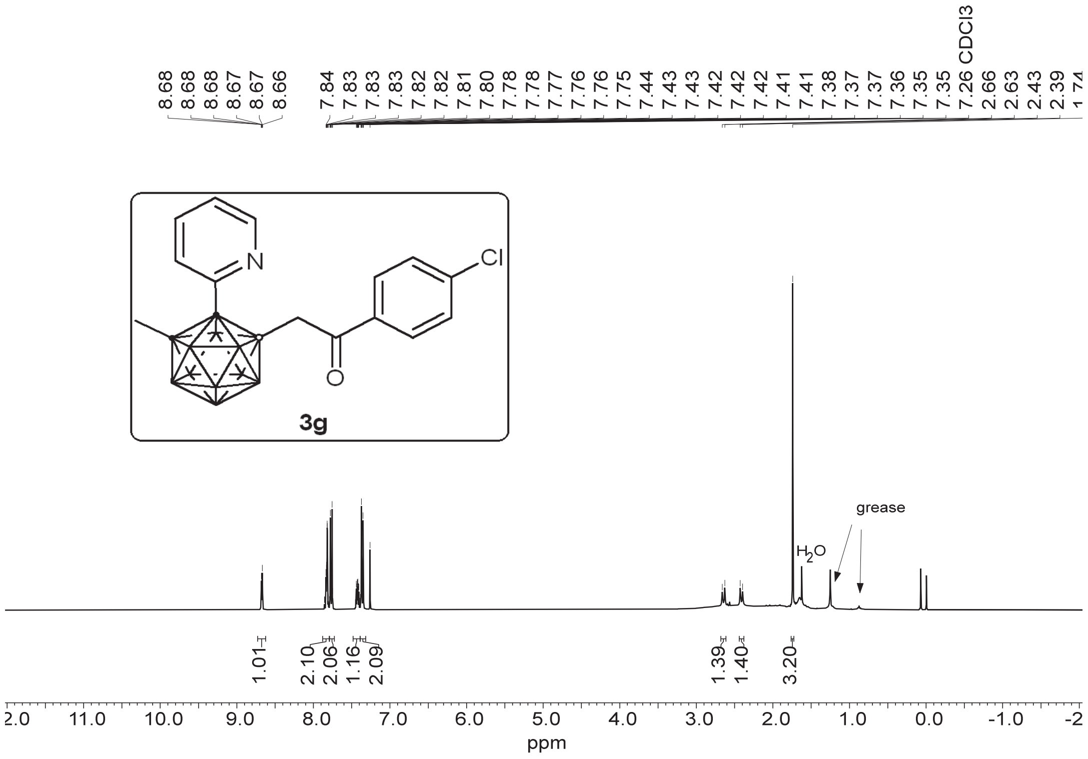

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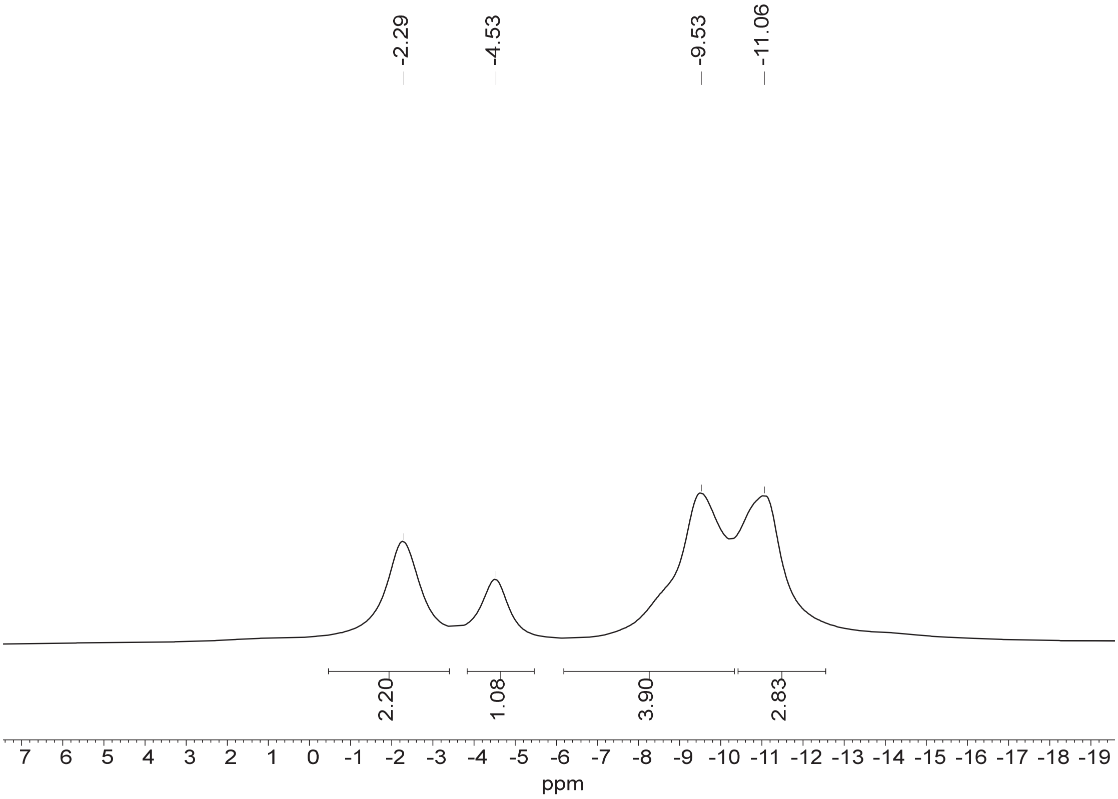

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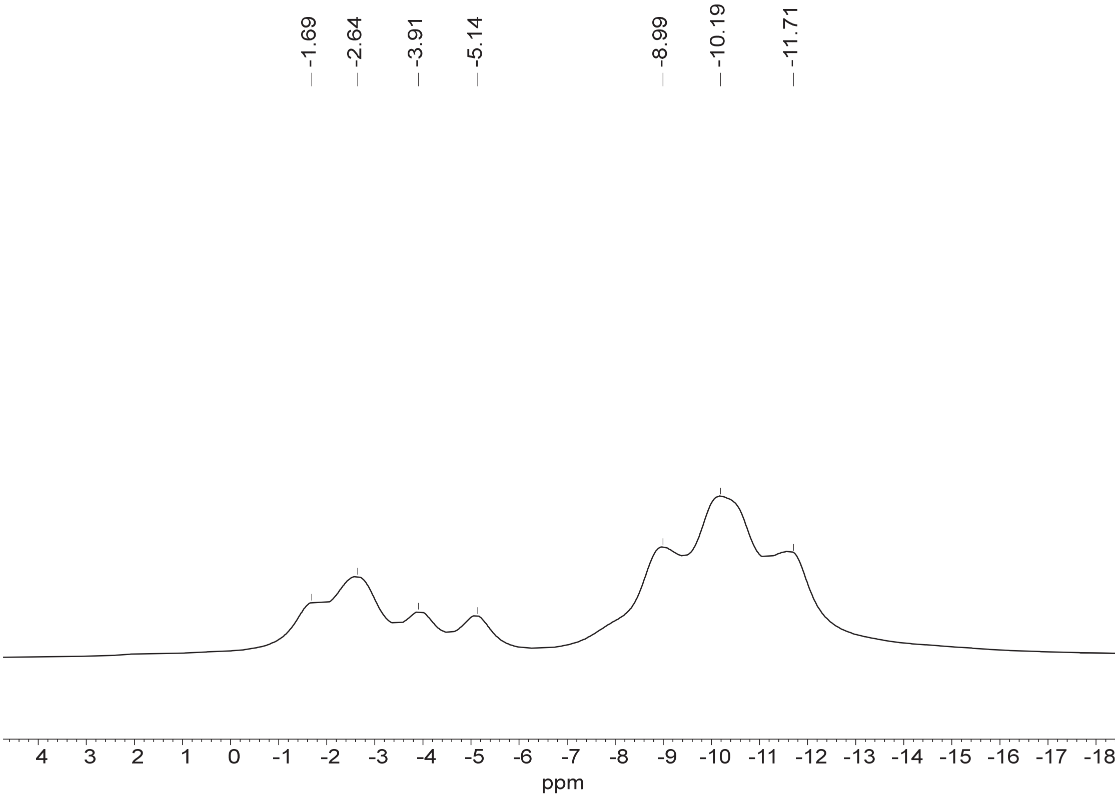

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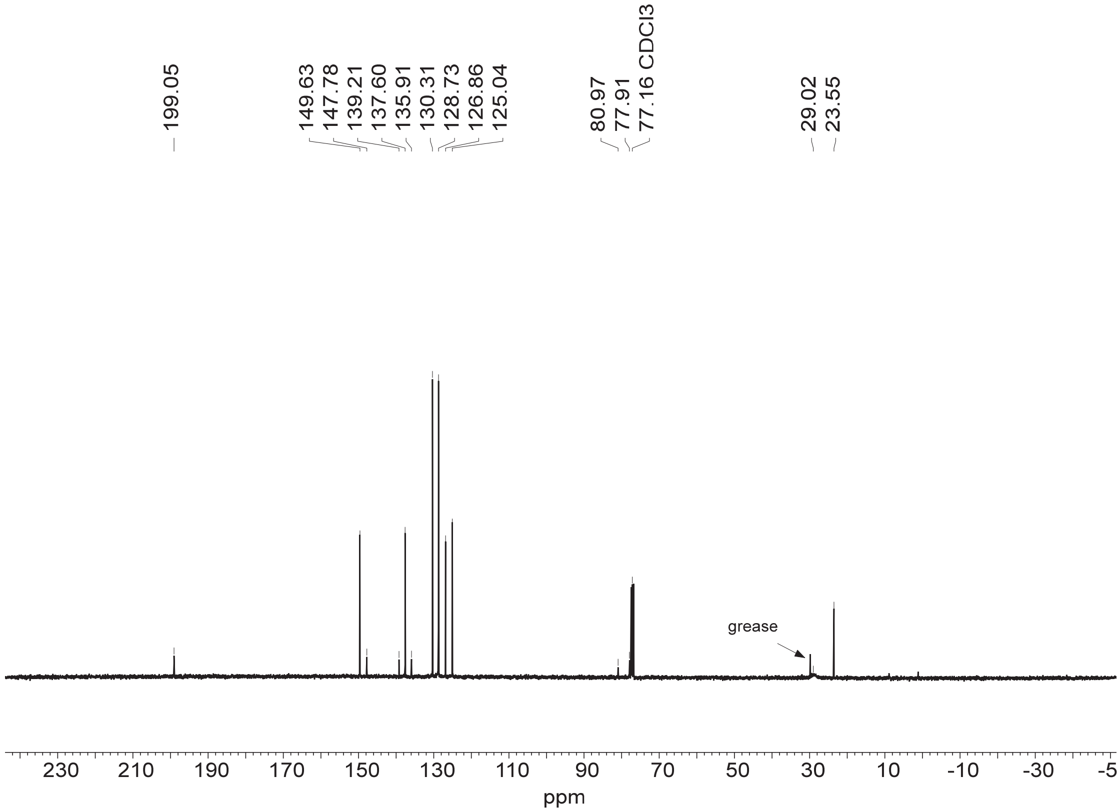

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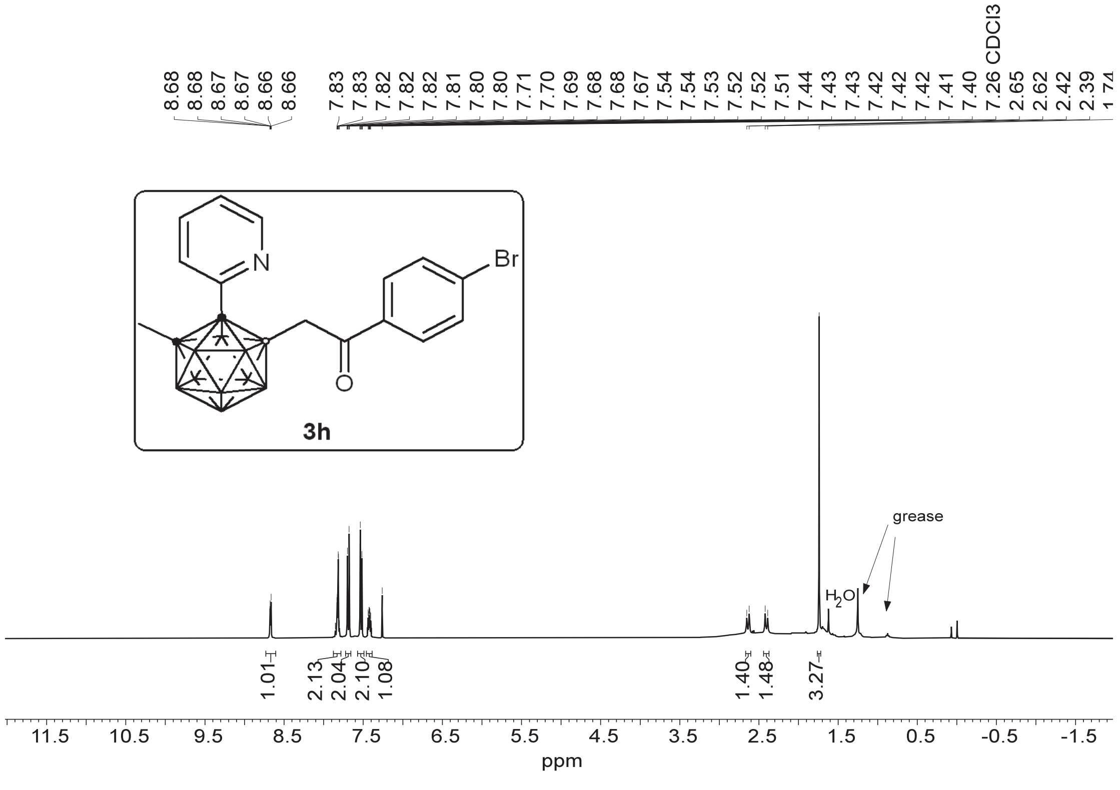

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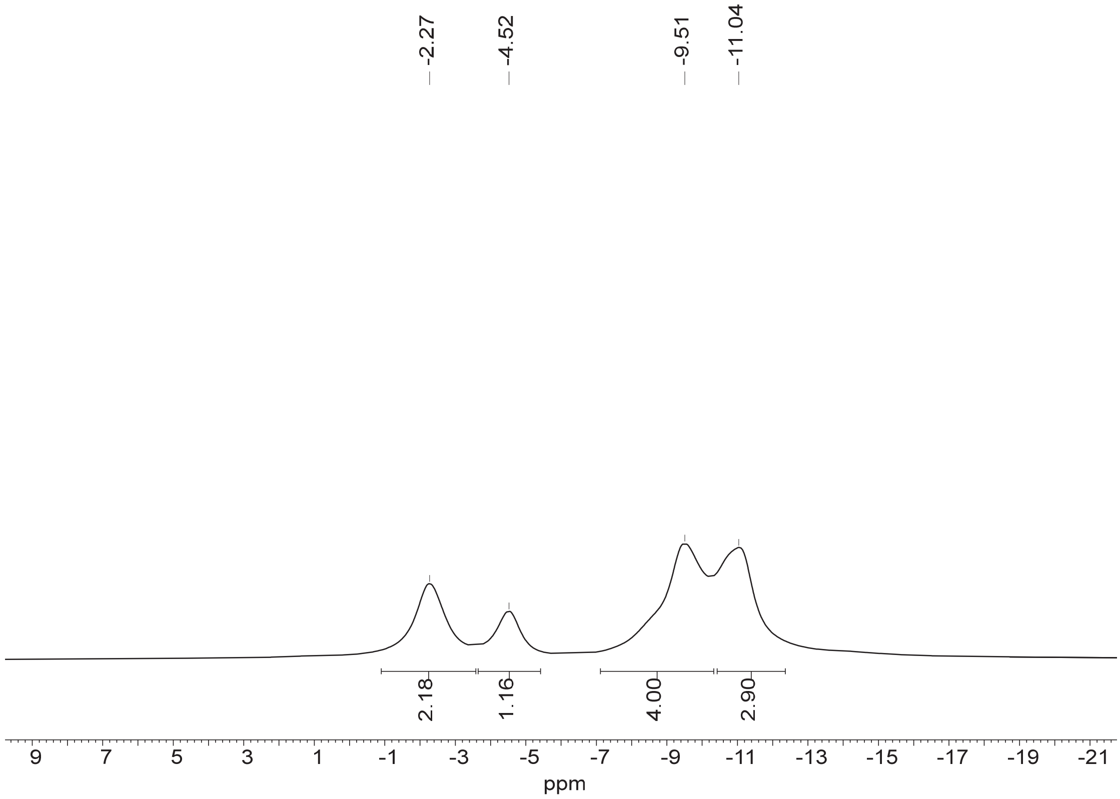

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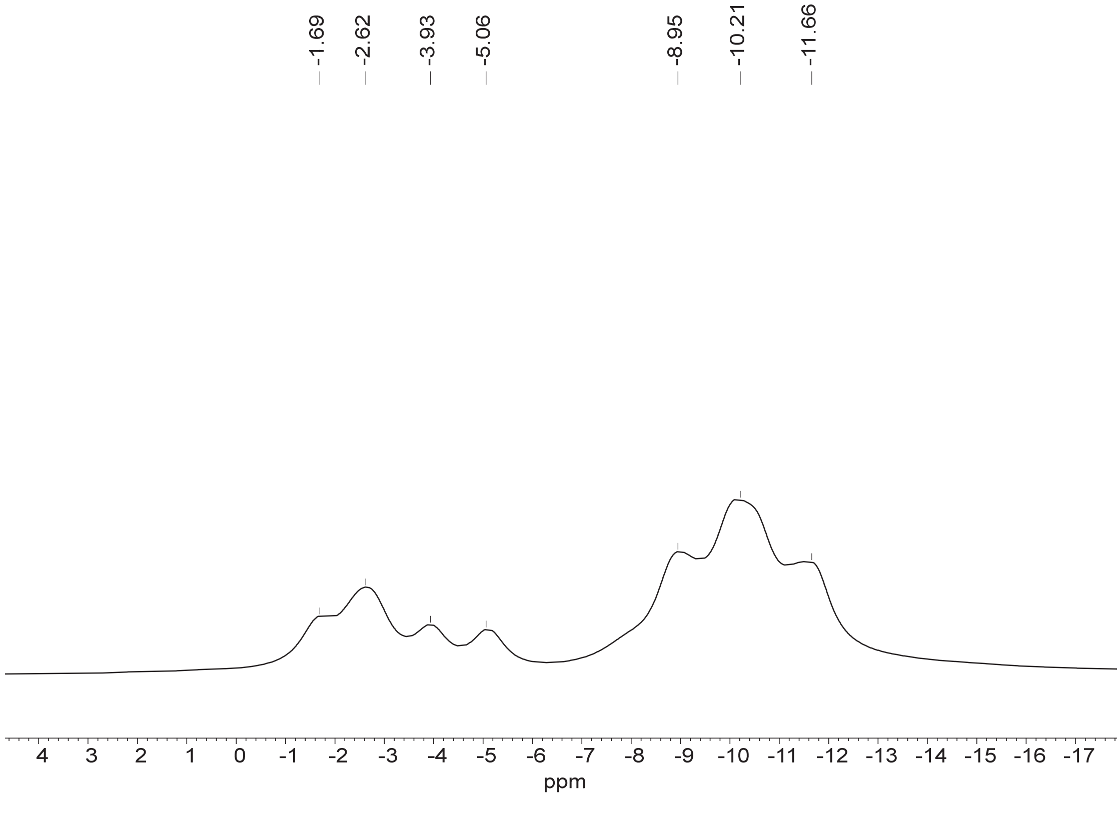

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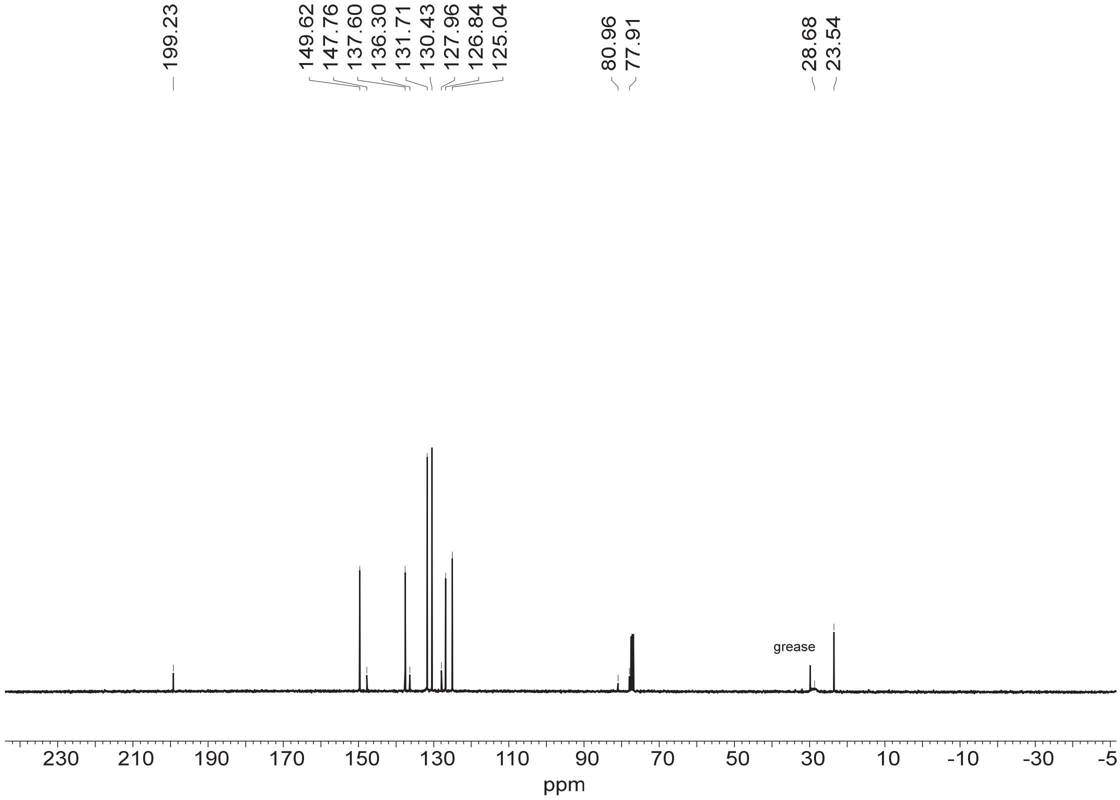

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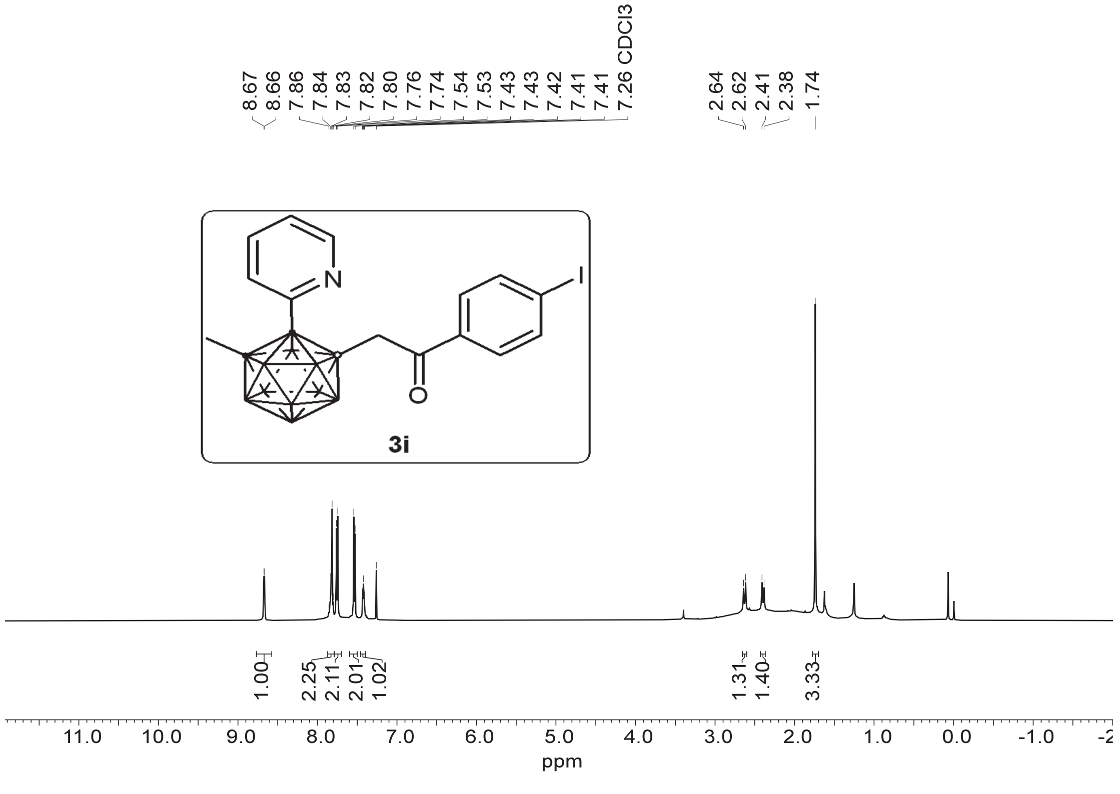

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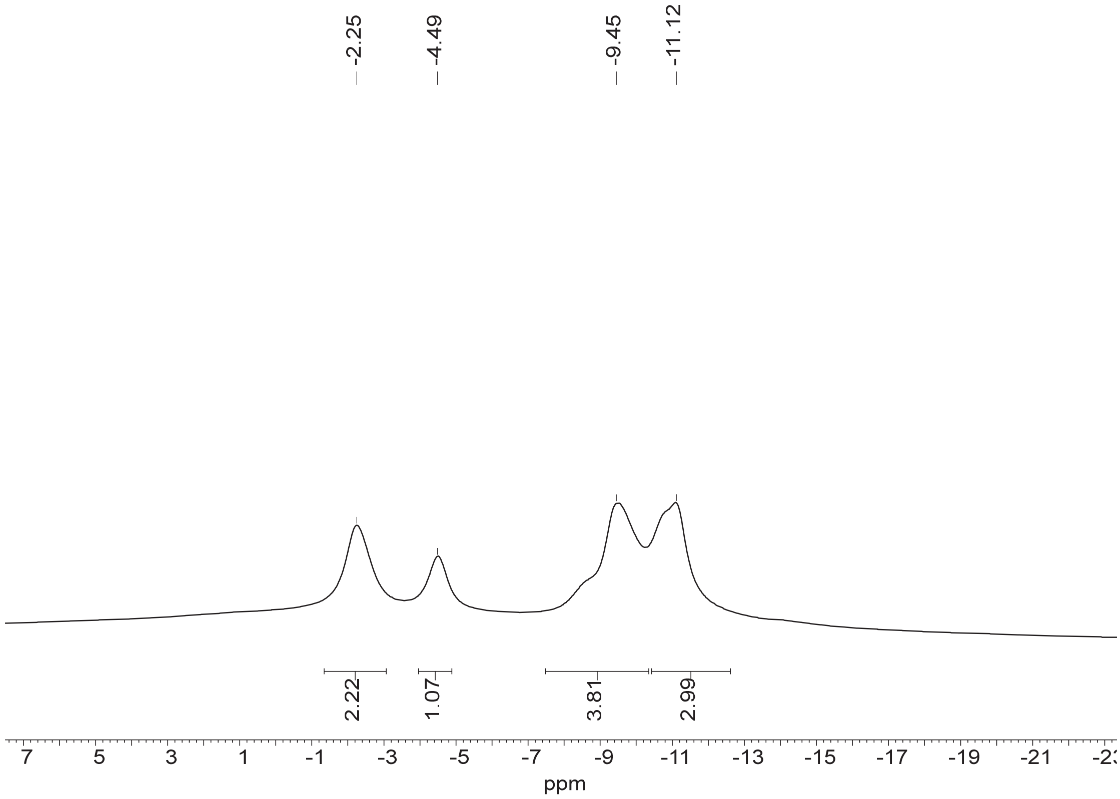

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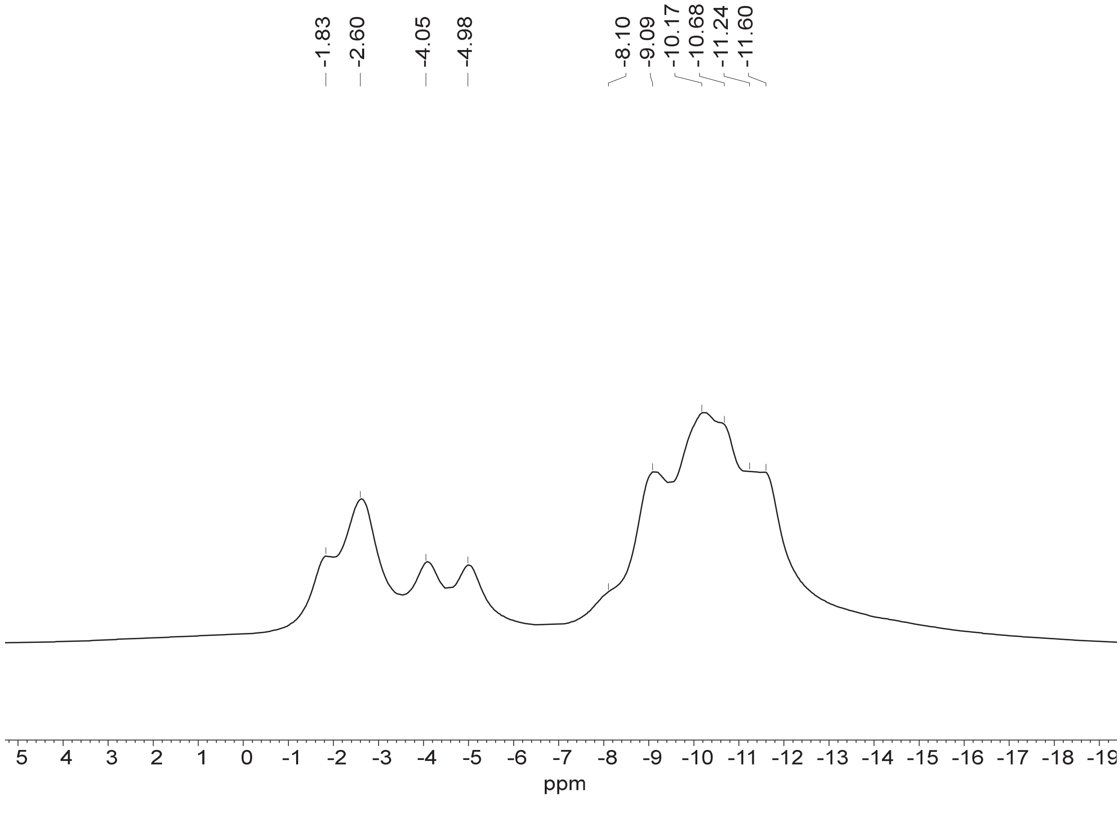
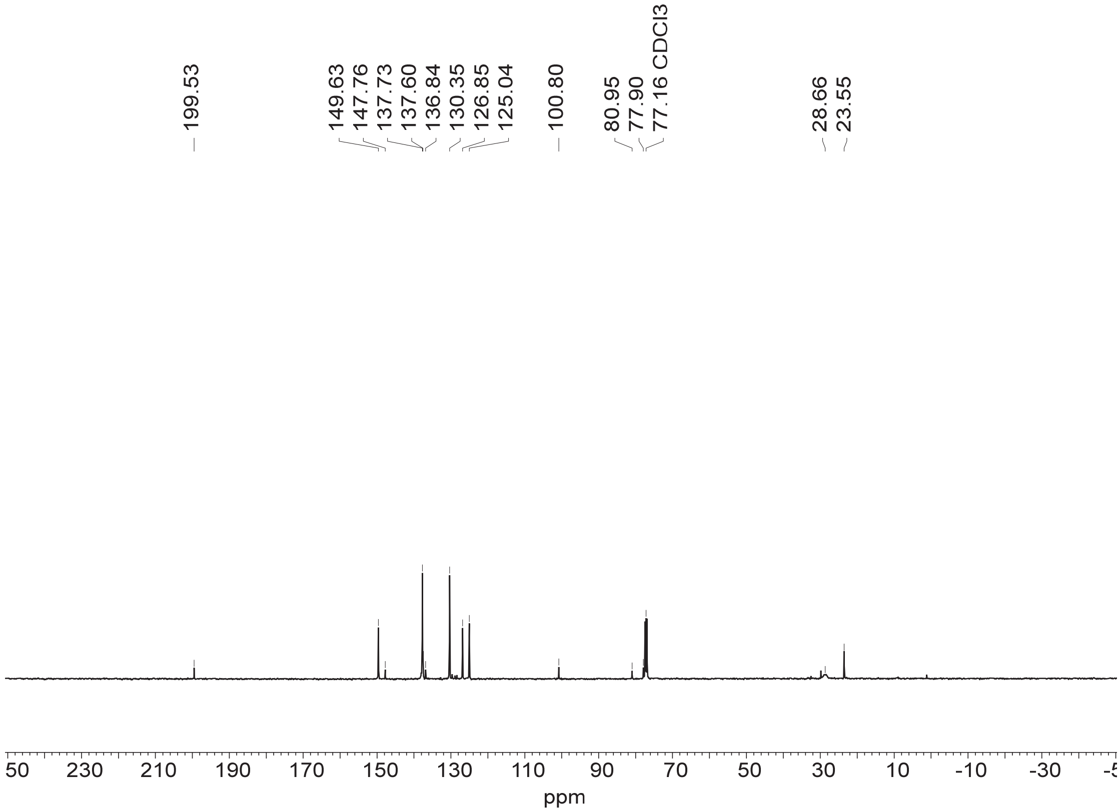


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



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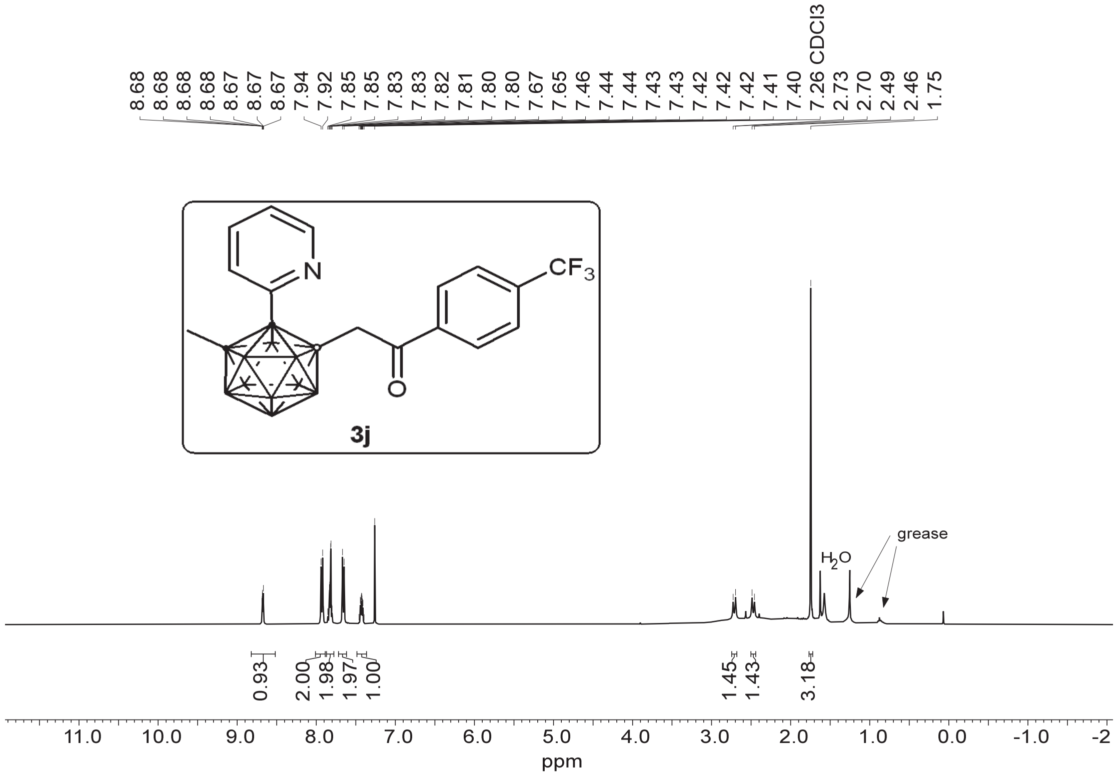

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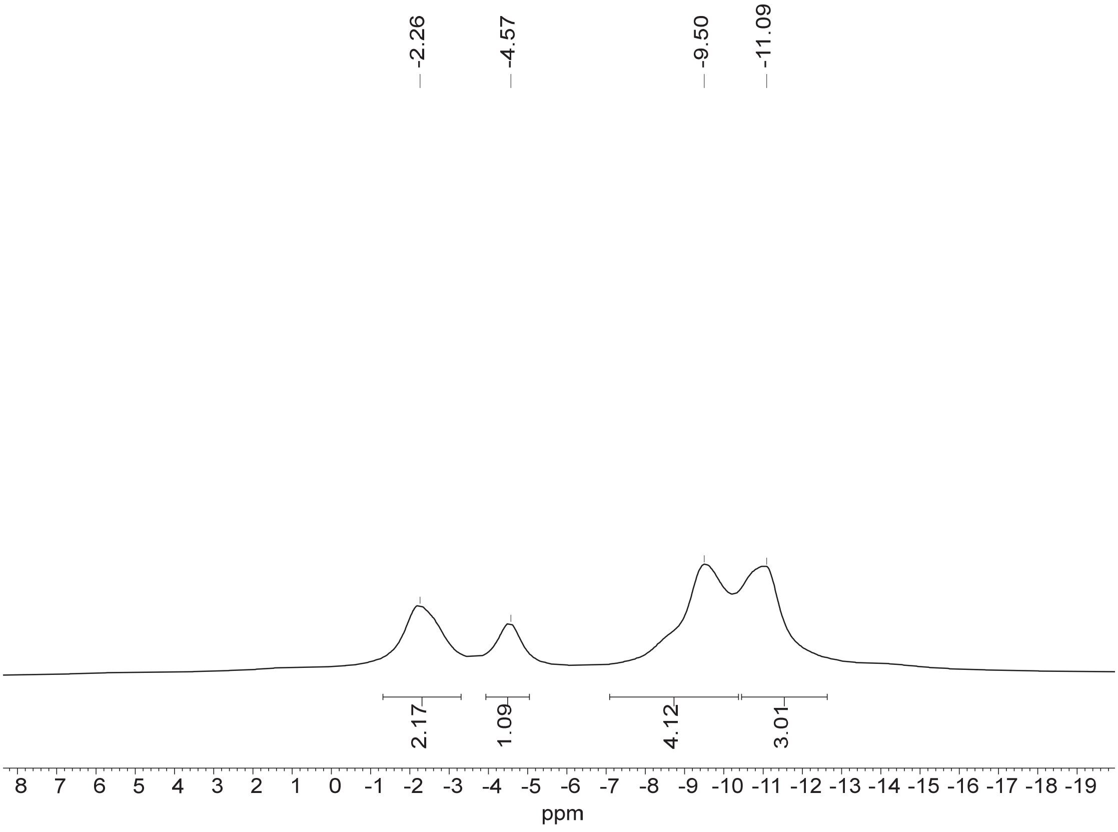

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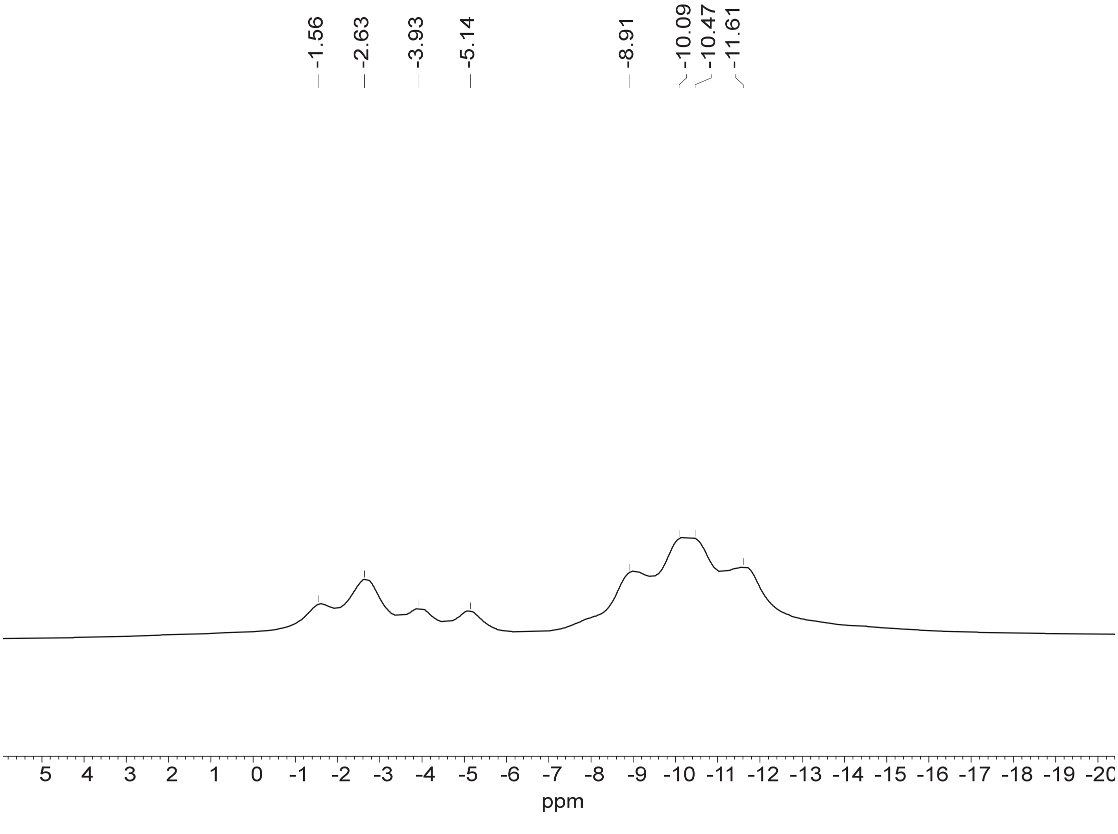

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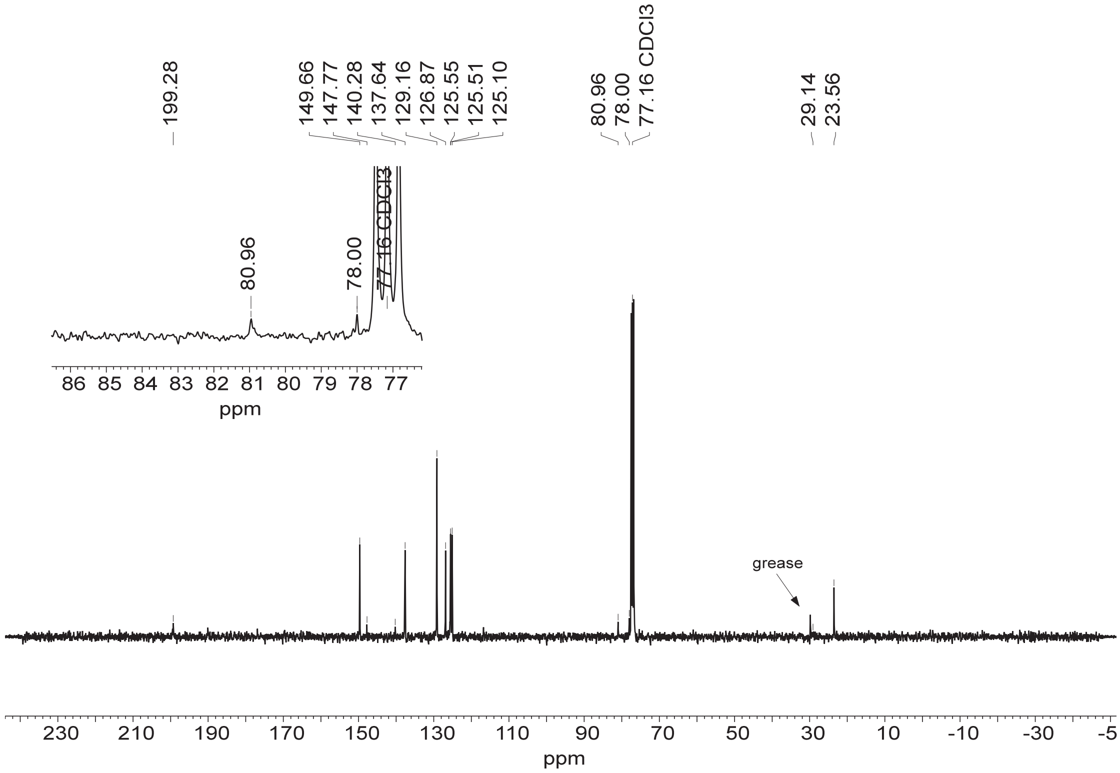

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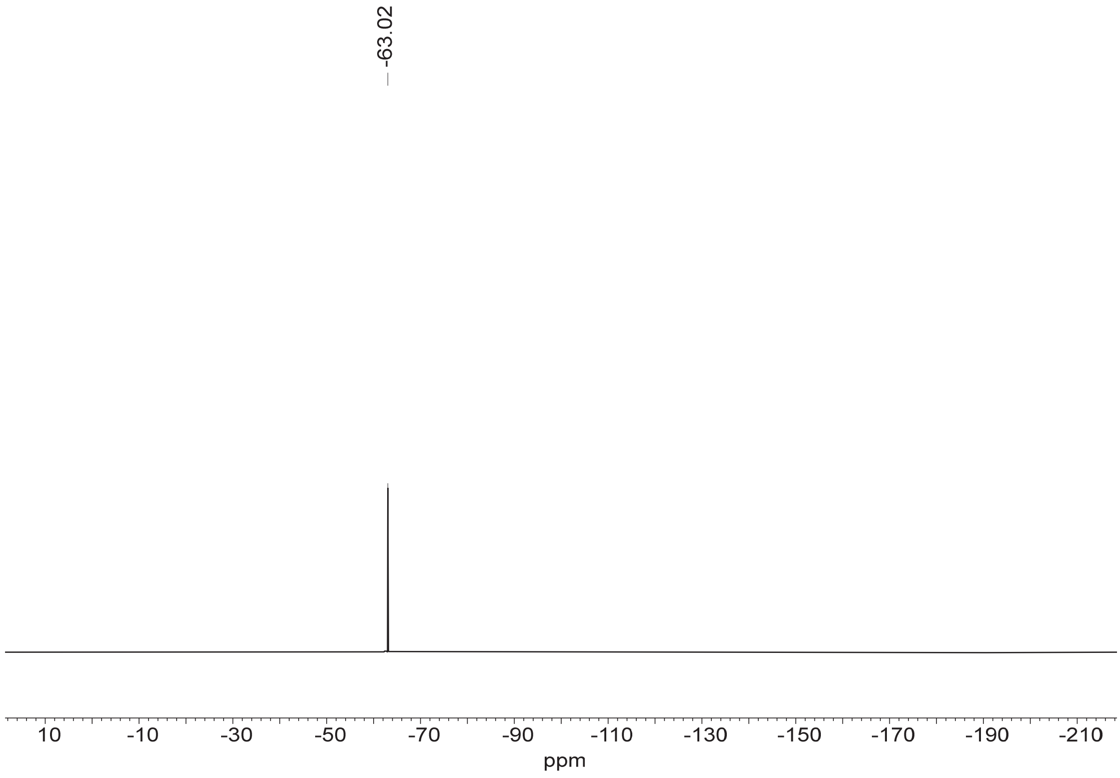

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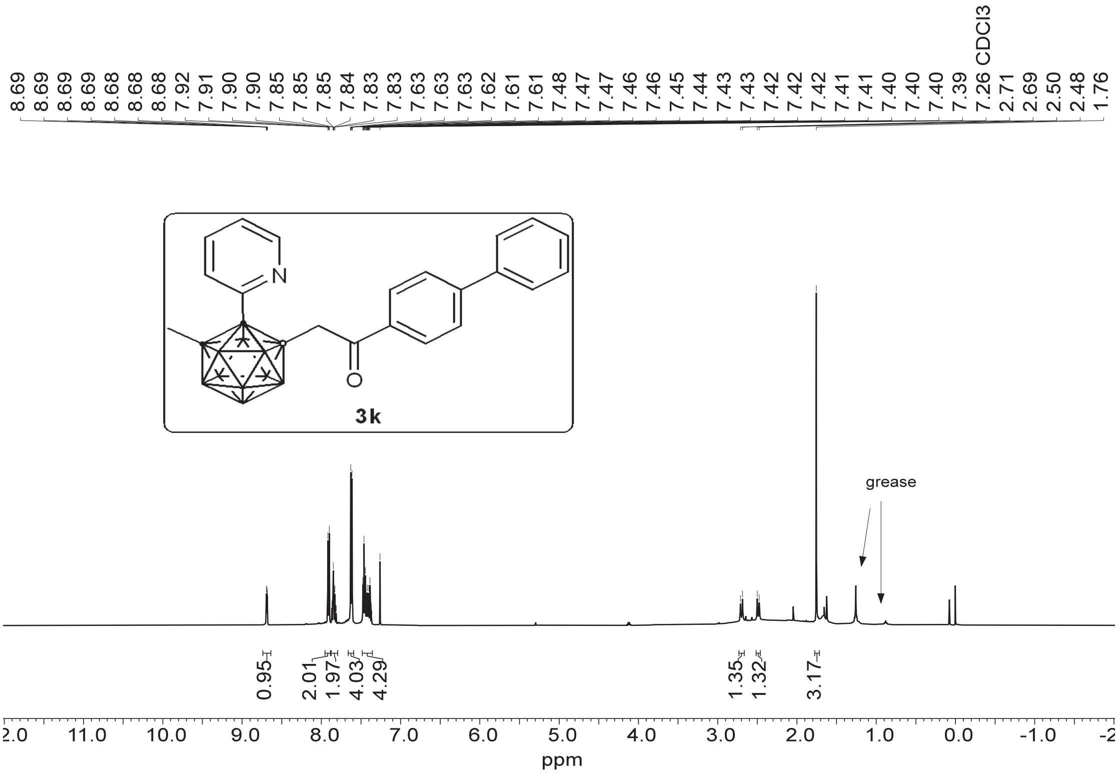

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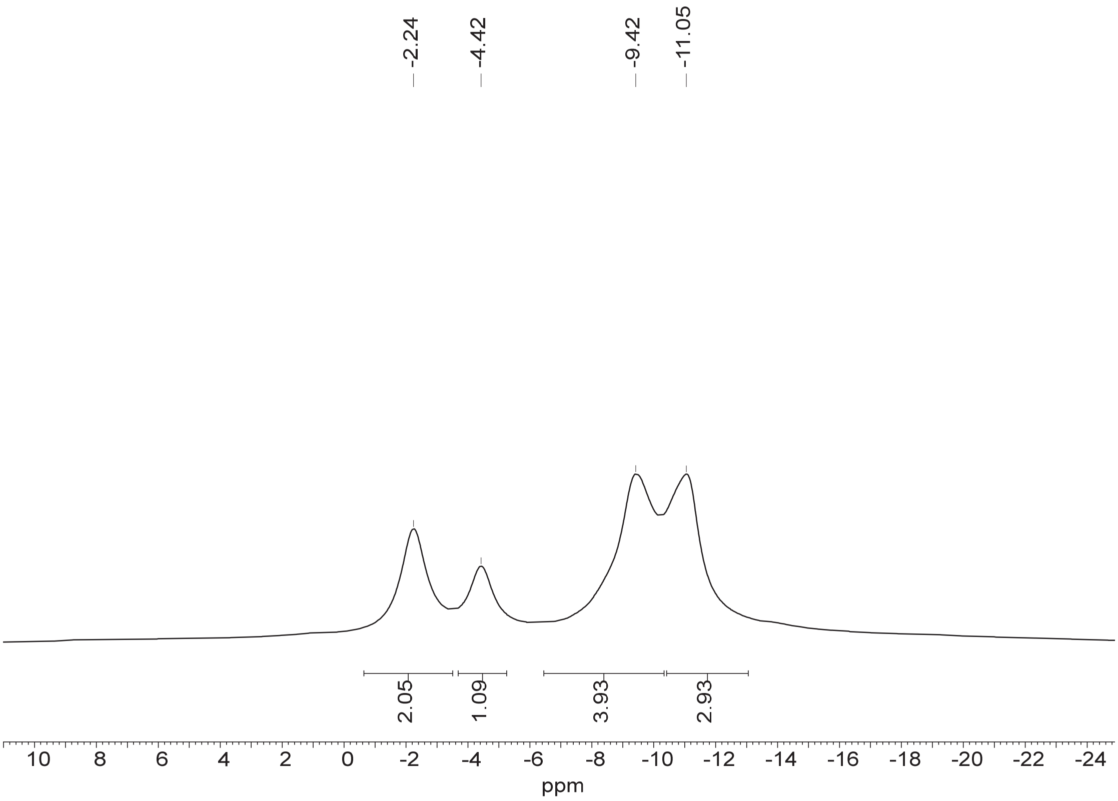
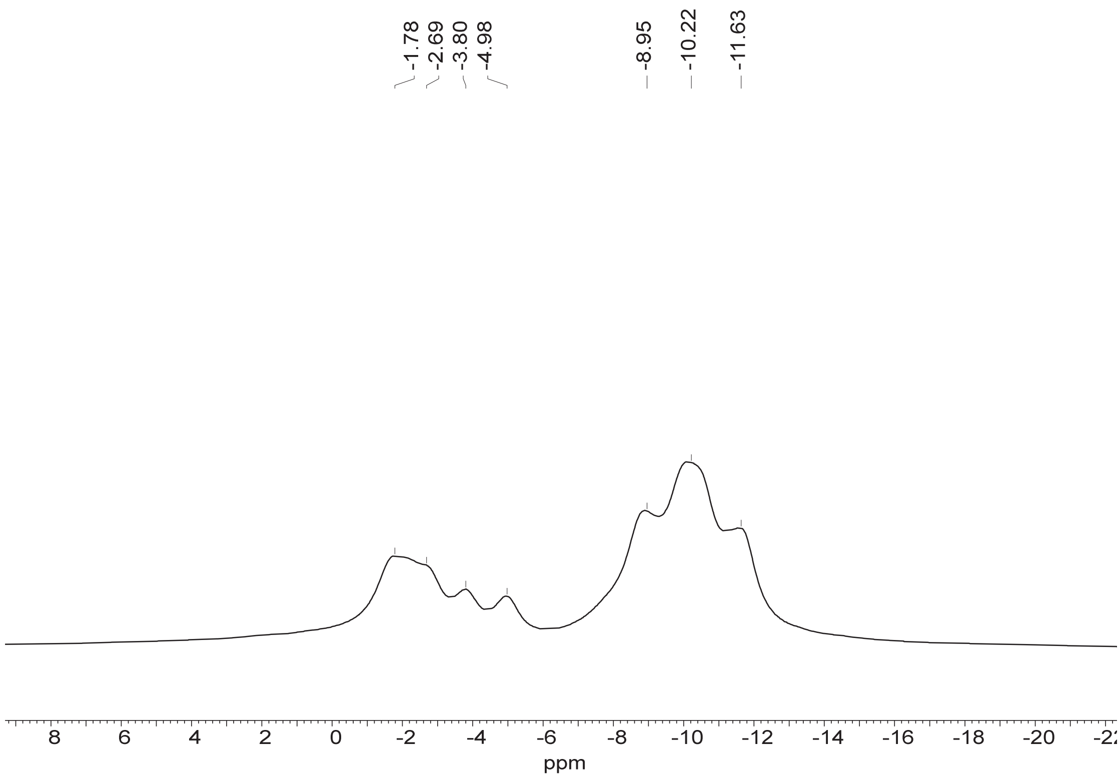
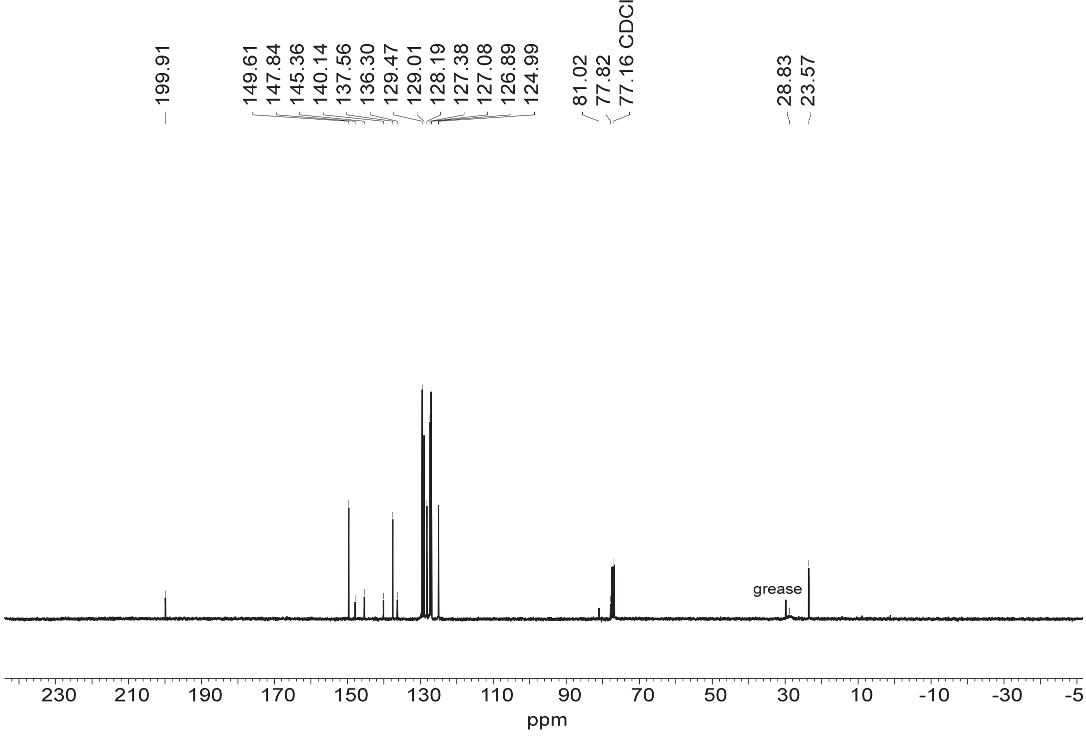


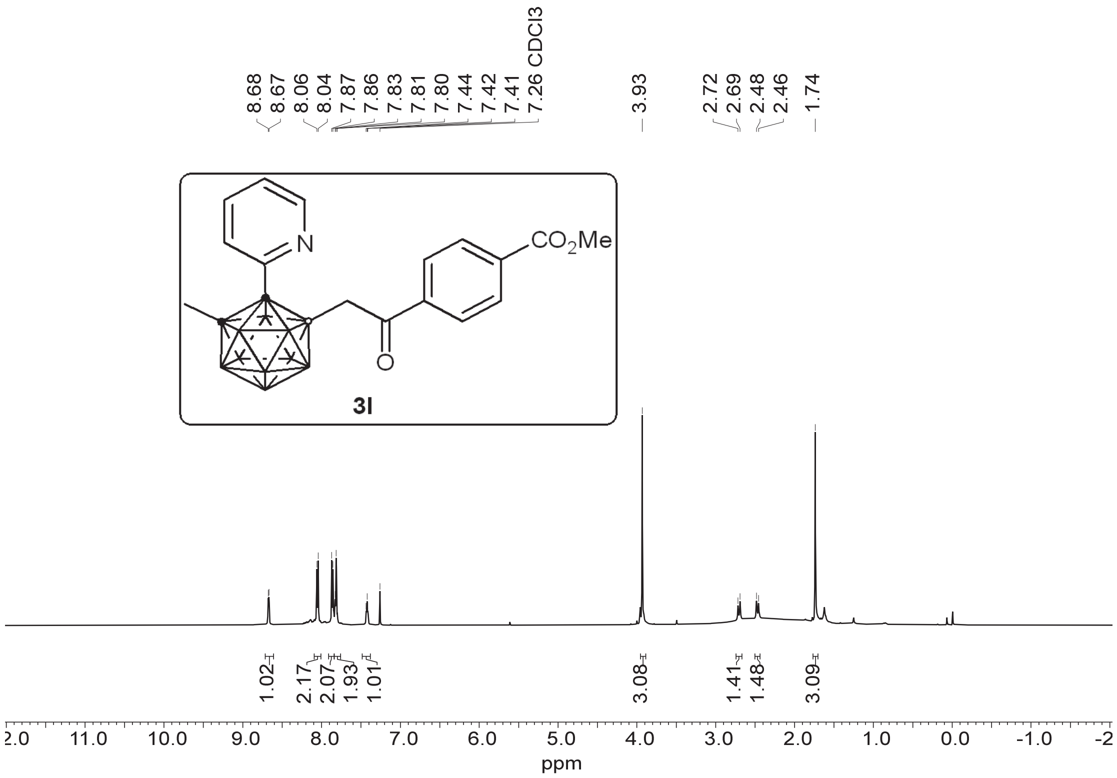
^{11}B NMR (128 MHz, CDCl$_3$)



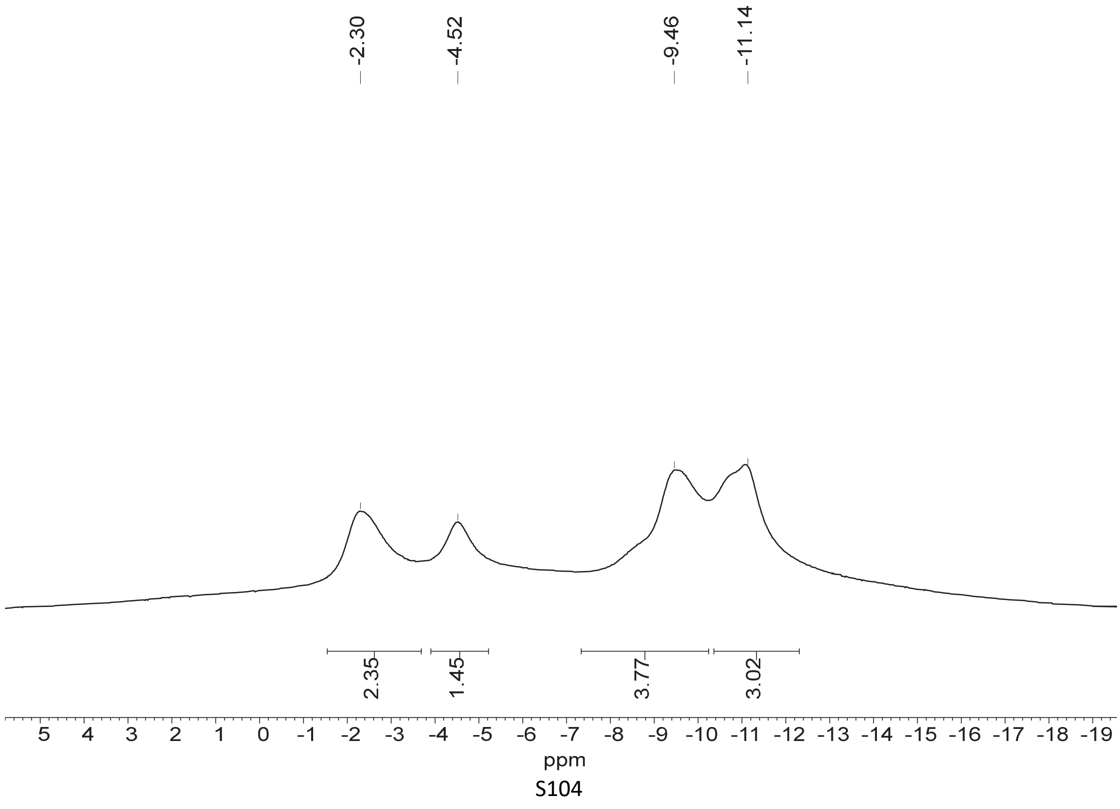
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



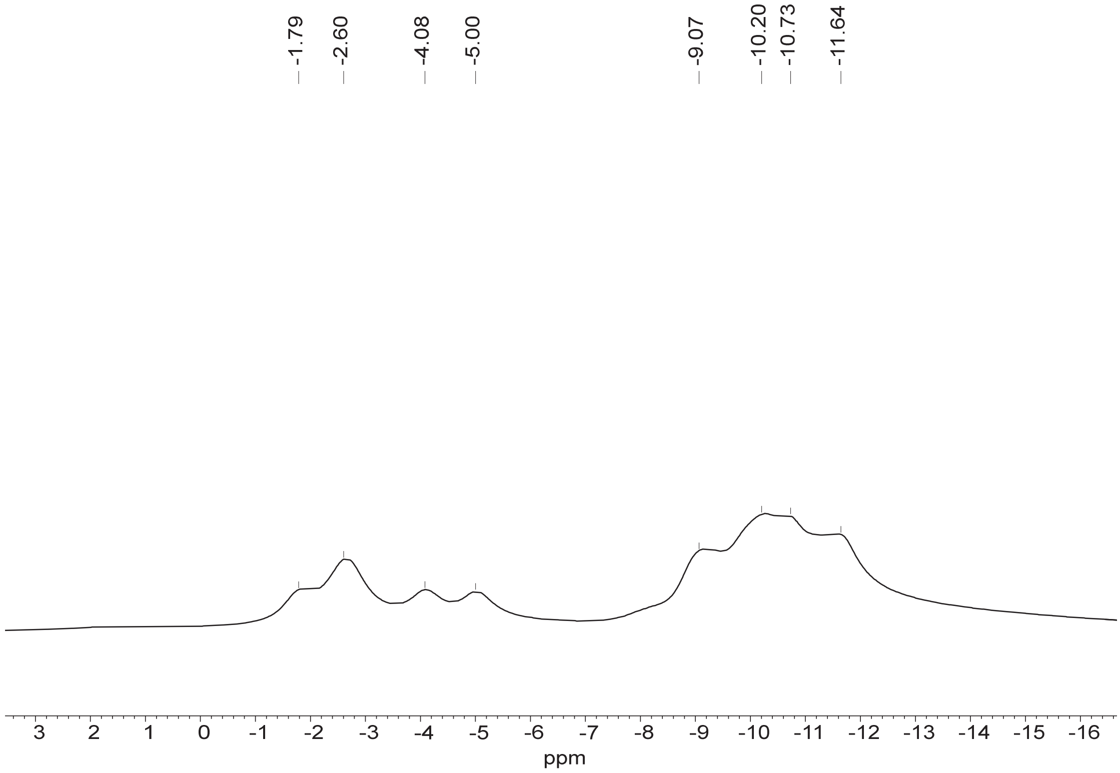
^{1}H NMR (500 MHz, CDCl$_3$)



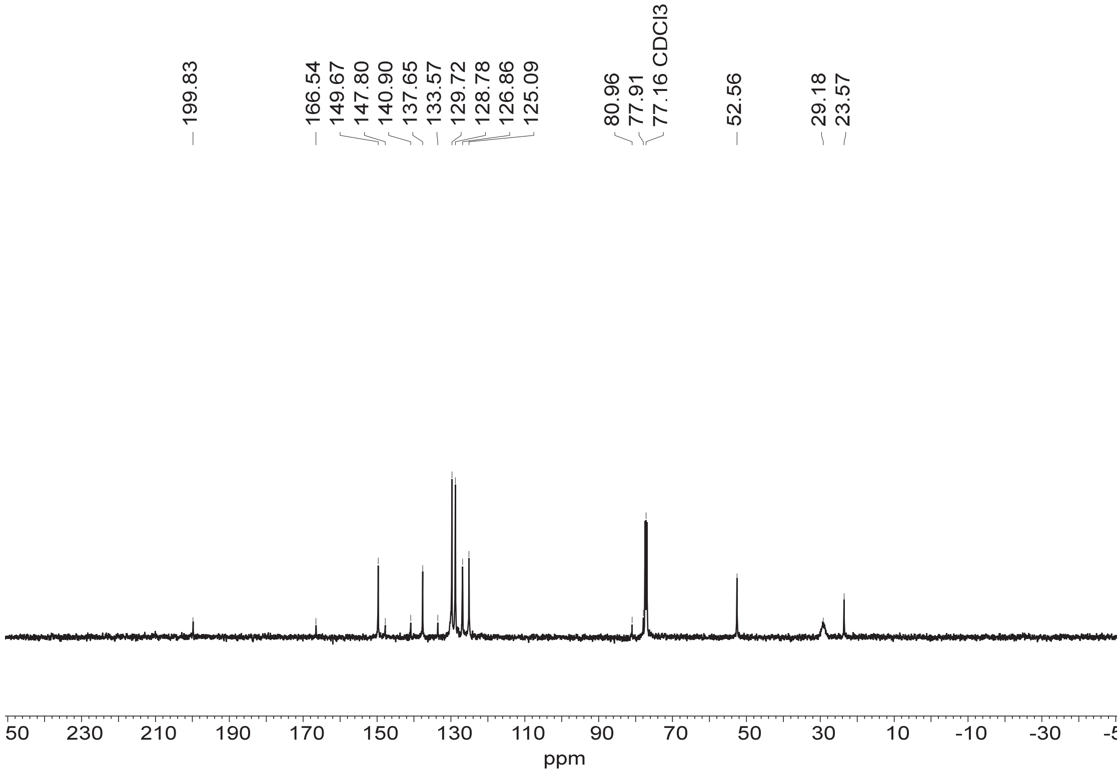
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



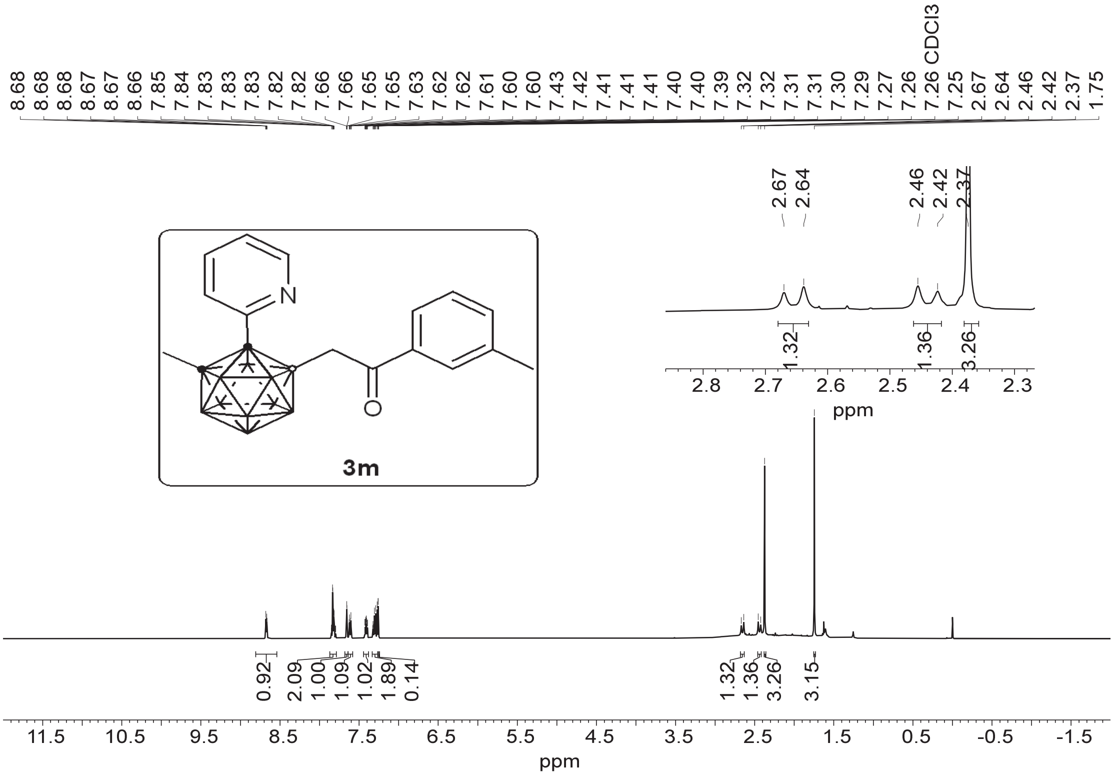
^{11}B NMR (160 MHz, CDCl$_3$)



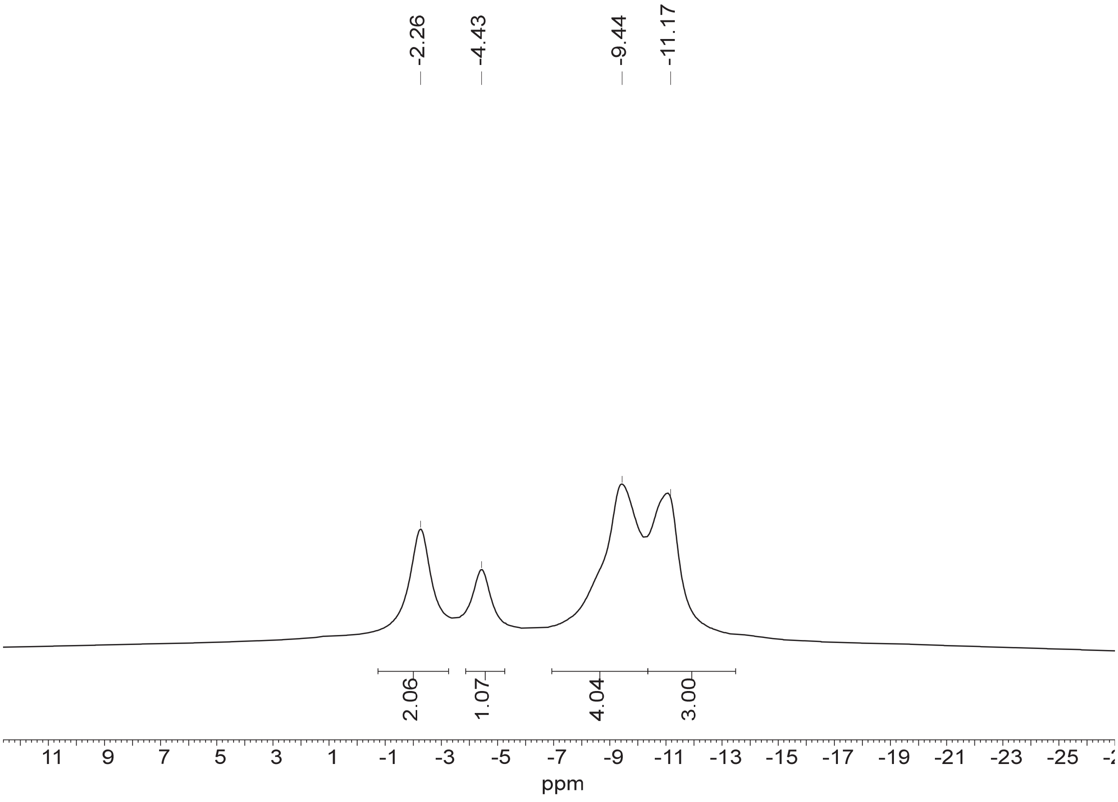
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



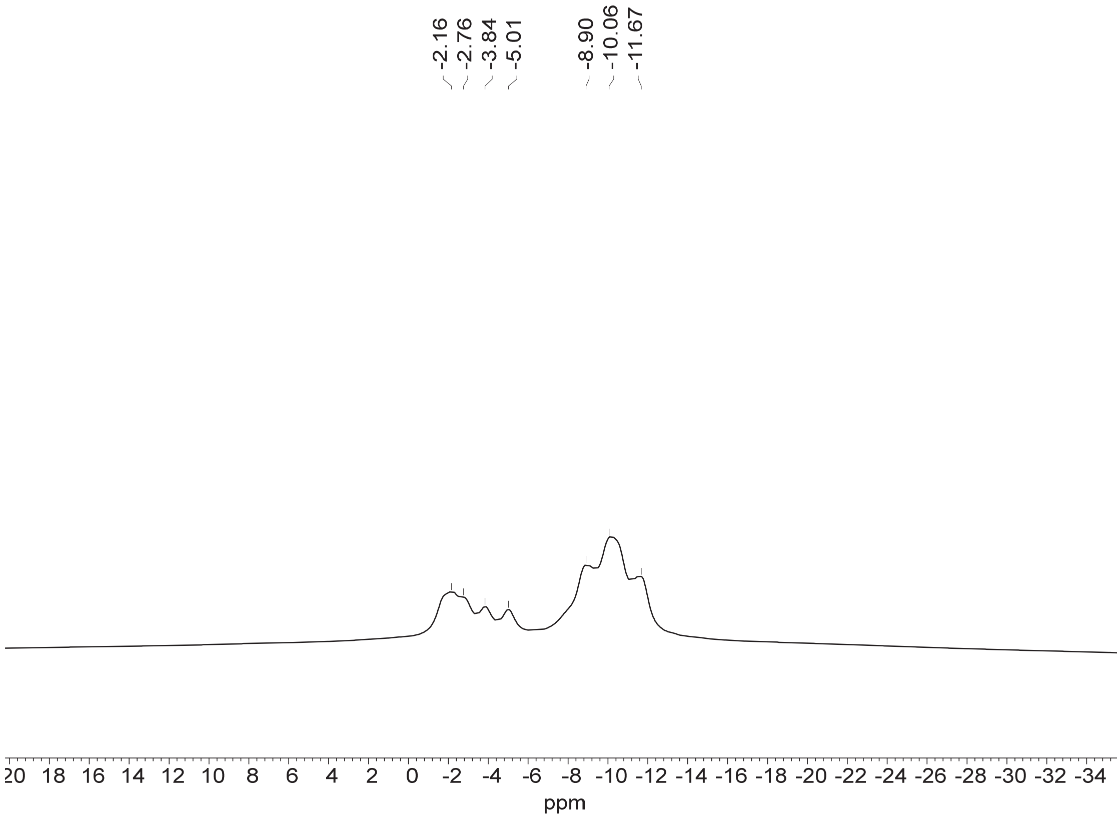
^{1}H NMR (400 MHz, CDCl$_3$)



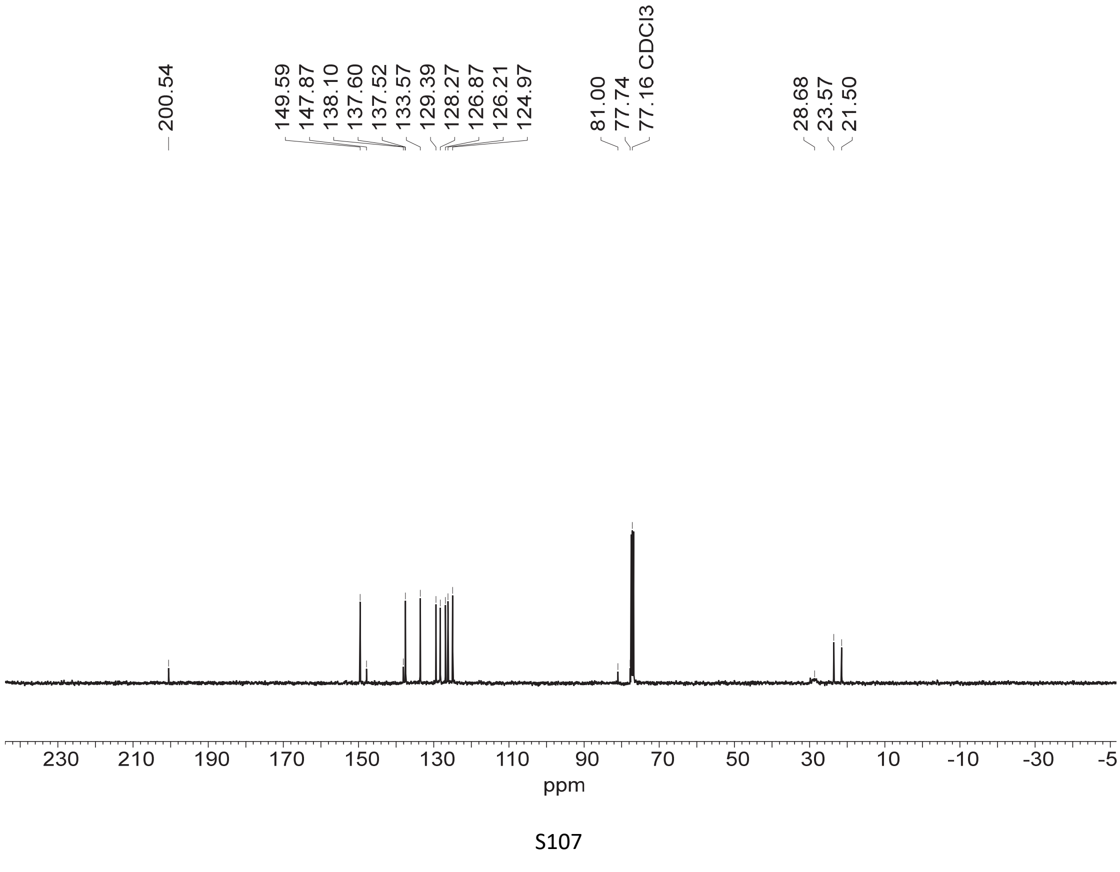
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



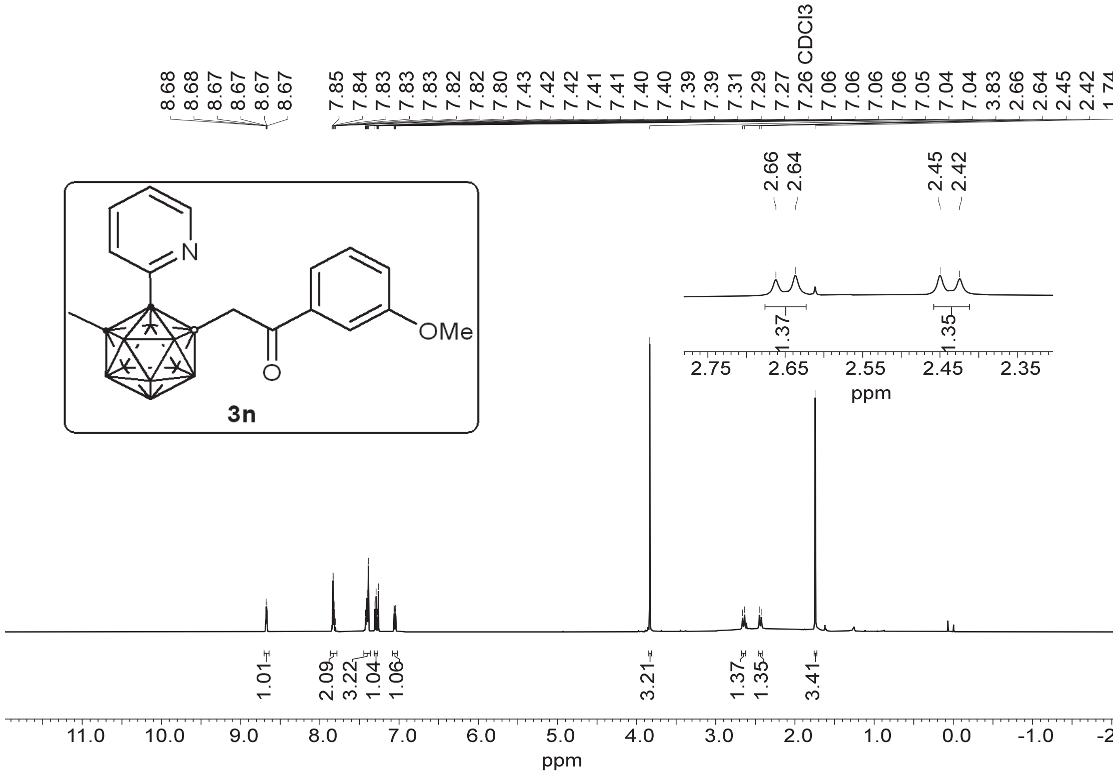
^{11}B NMR (128 MHz, CDCl$_3$)



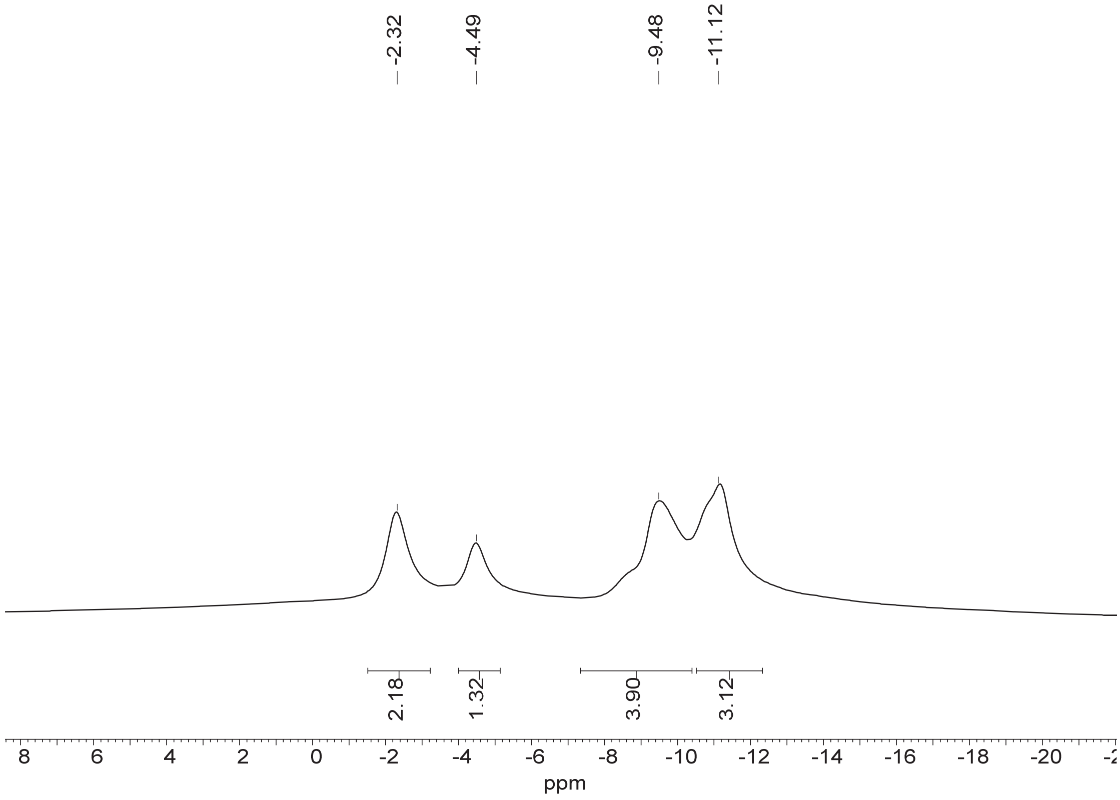
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



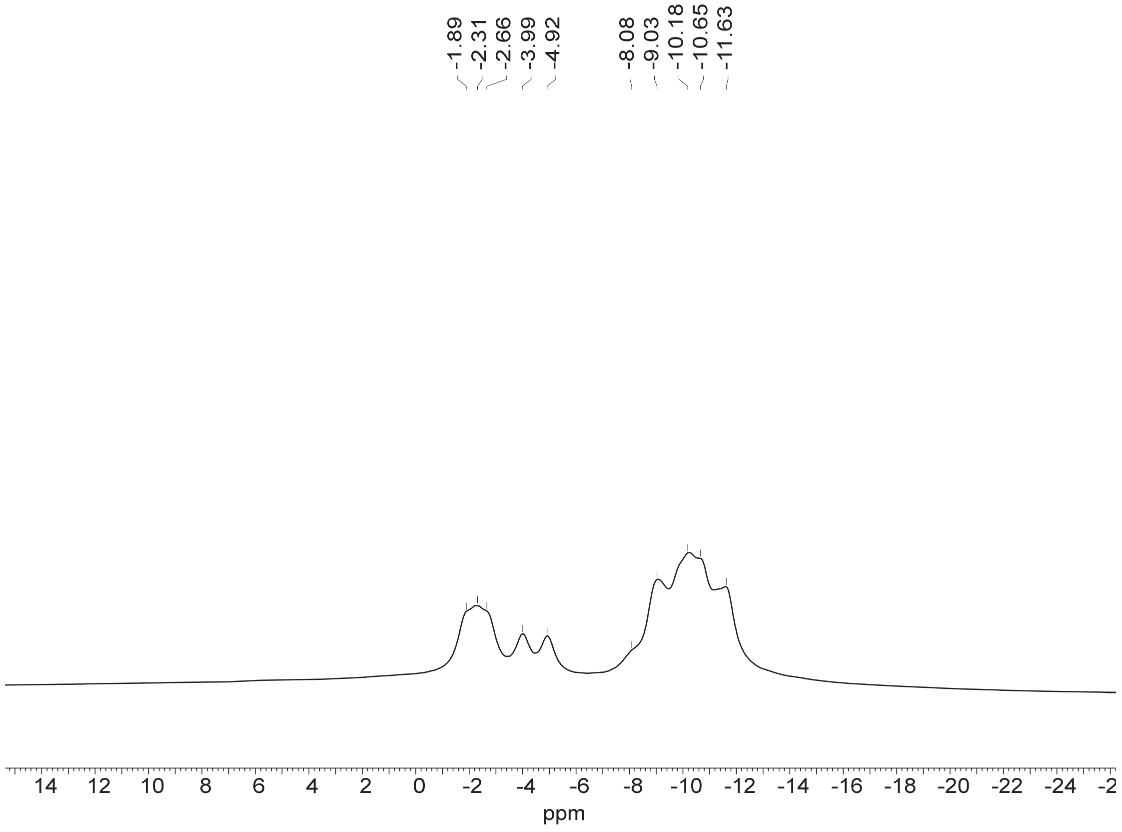
^{1}H NMR (500 MHz, CDCl$_3$)



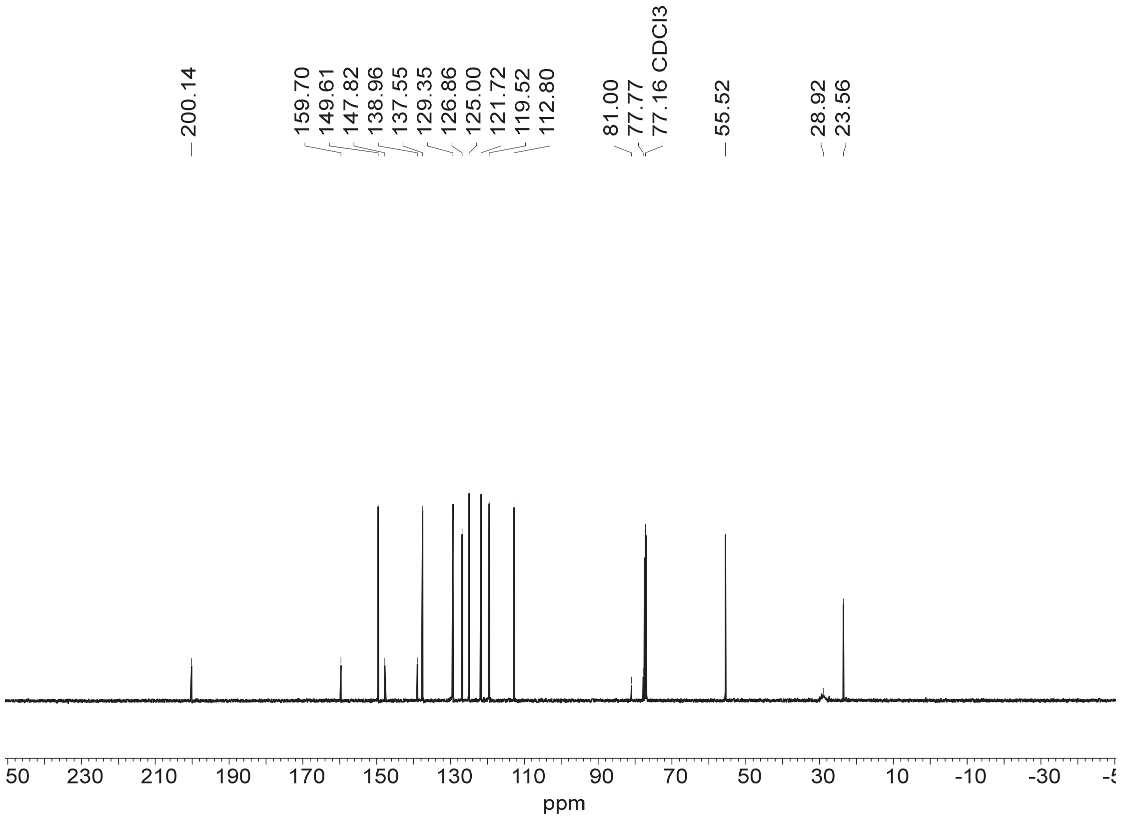
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



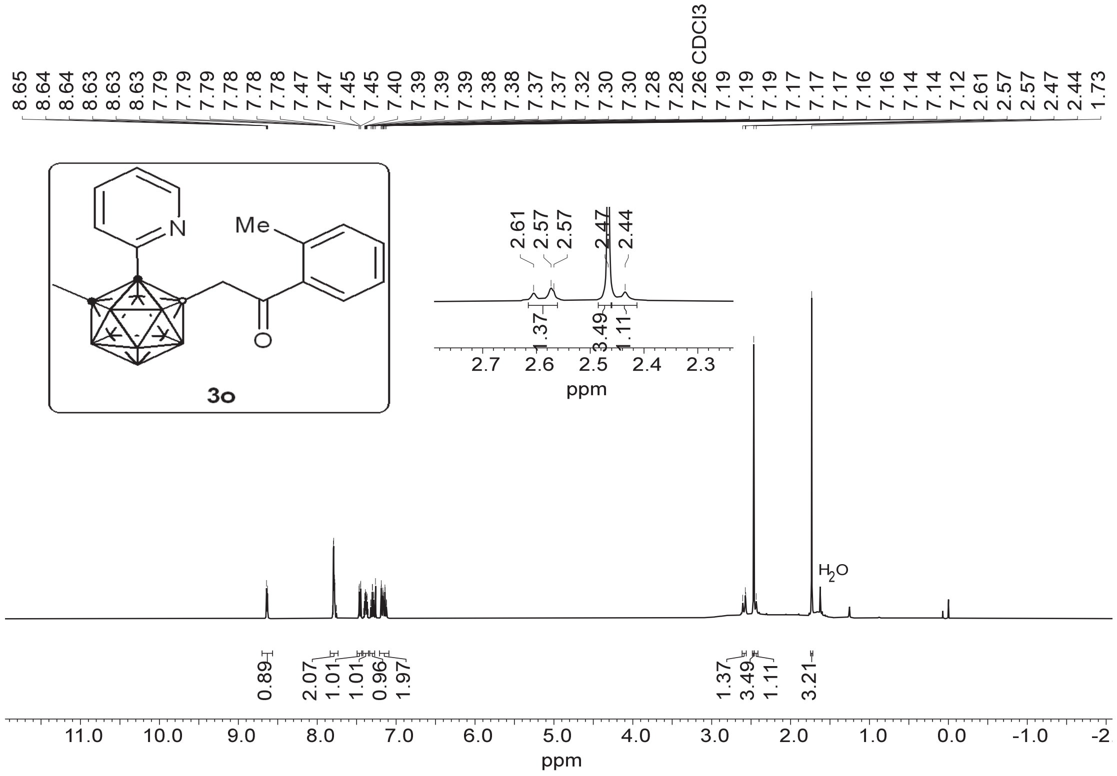
^{11}B NMR (160 MHz, CDCl$_3$)



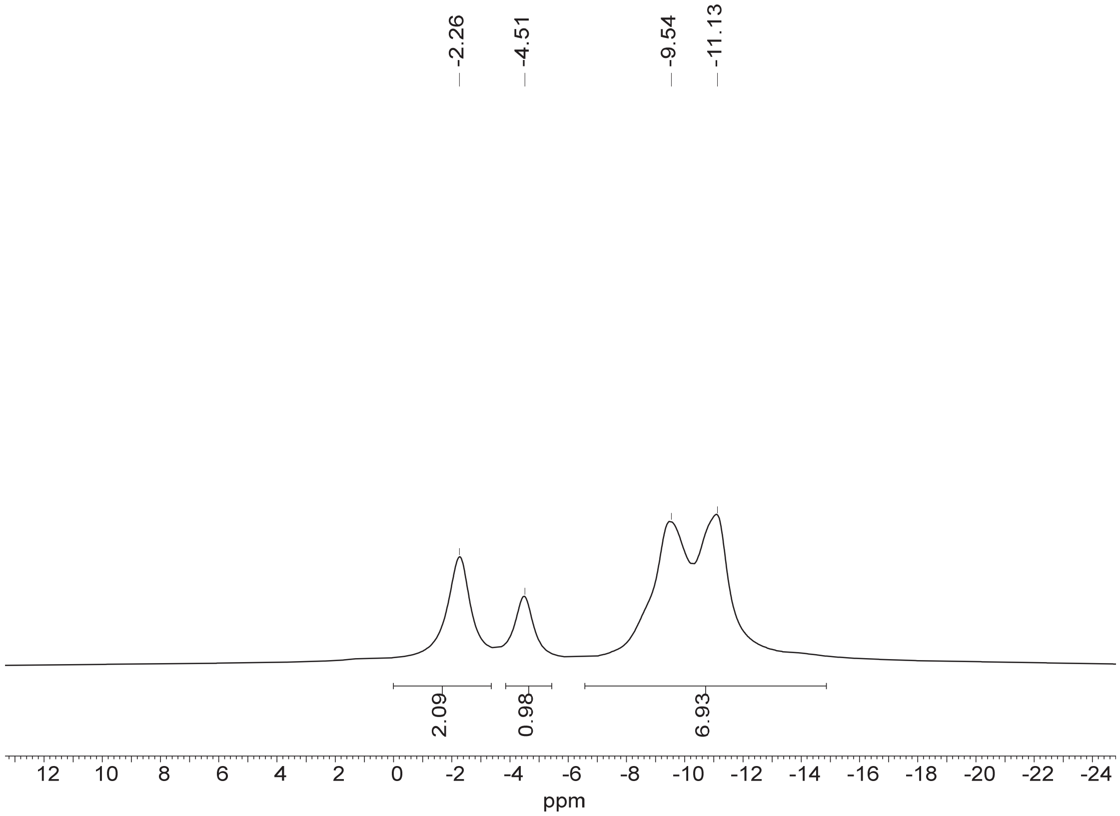
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



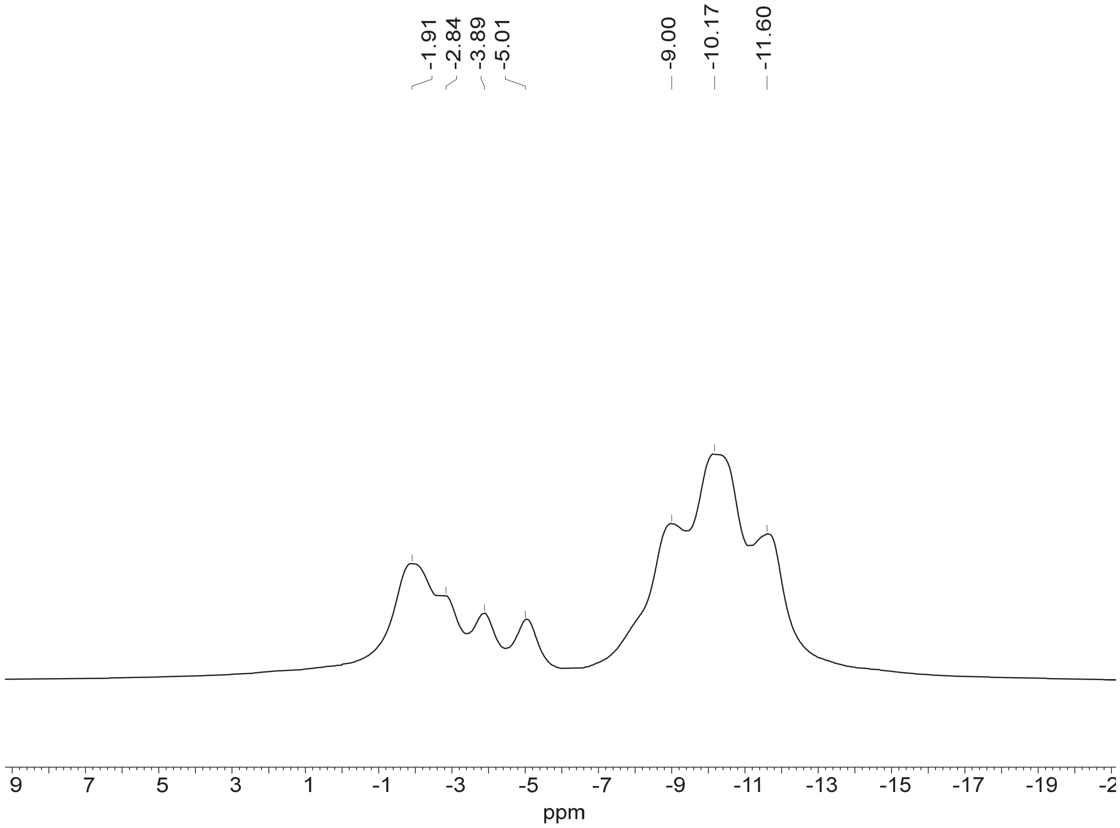
^{1}H NMR (400 MHz, $CDCl_3$)



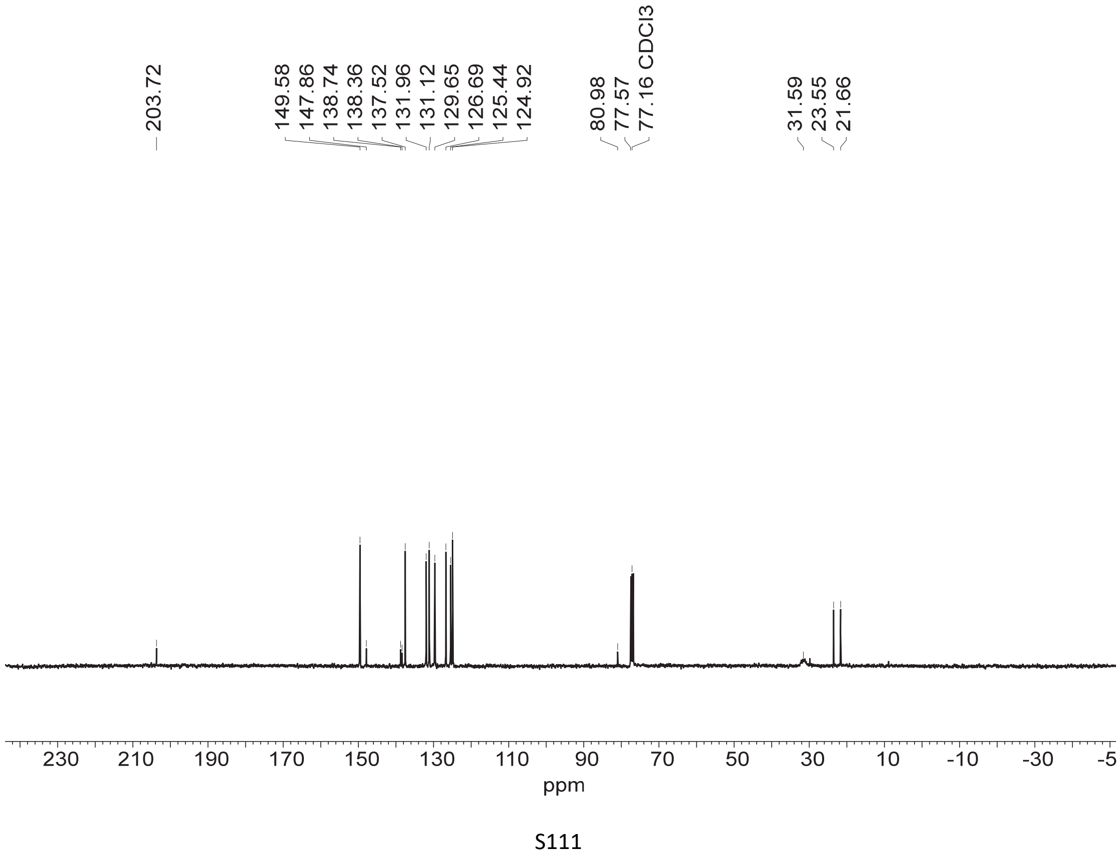
^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)



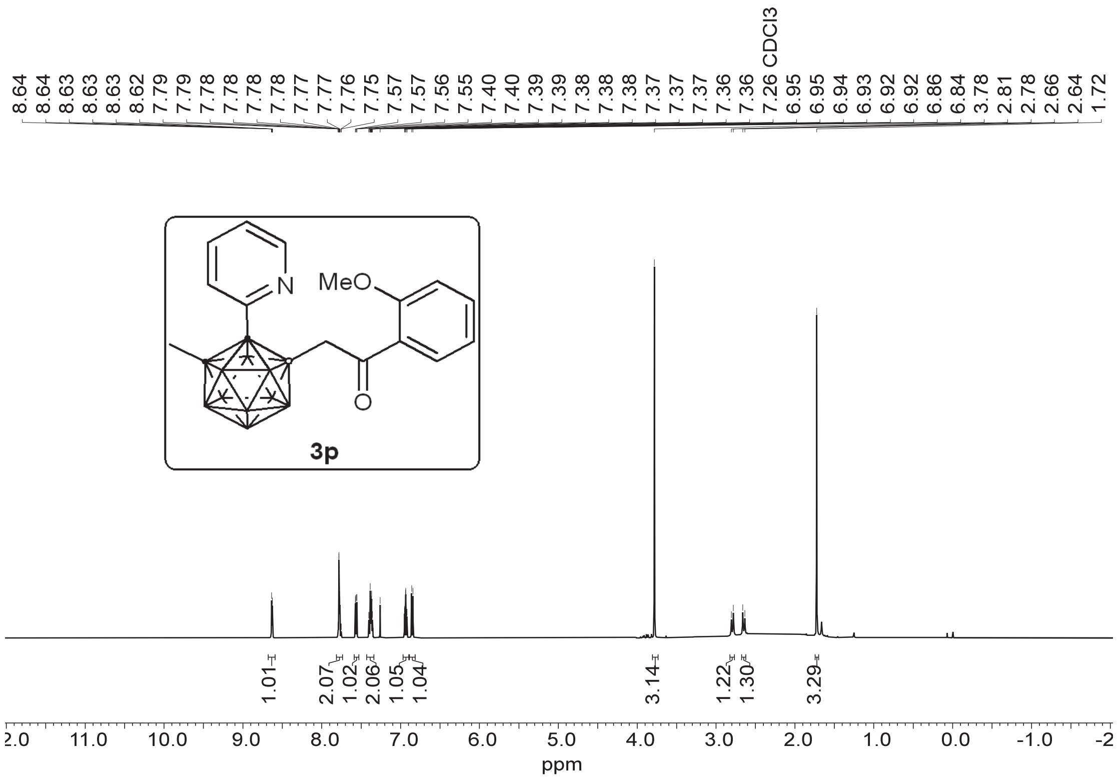
^{11}B NMR (128 MHz, $CDCl_3$)



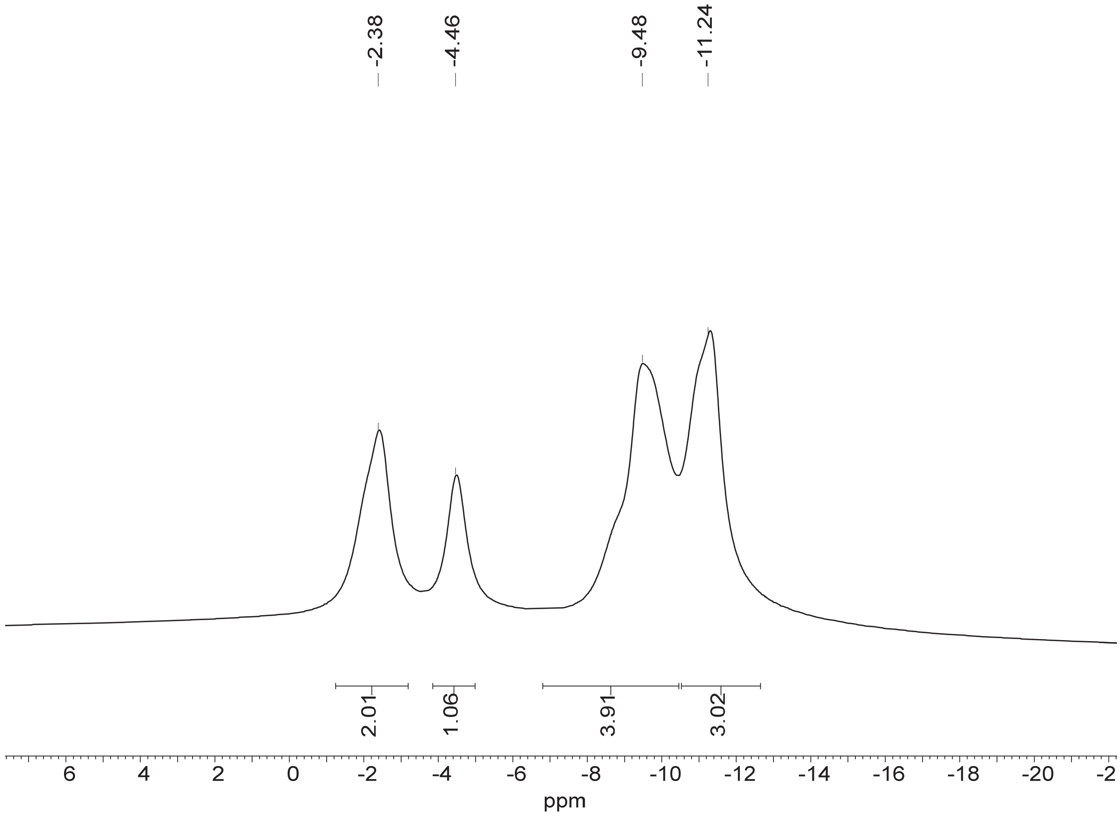
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



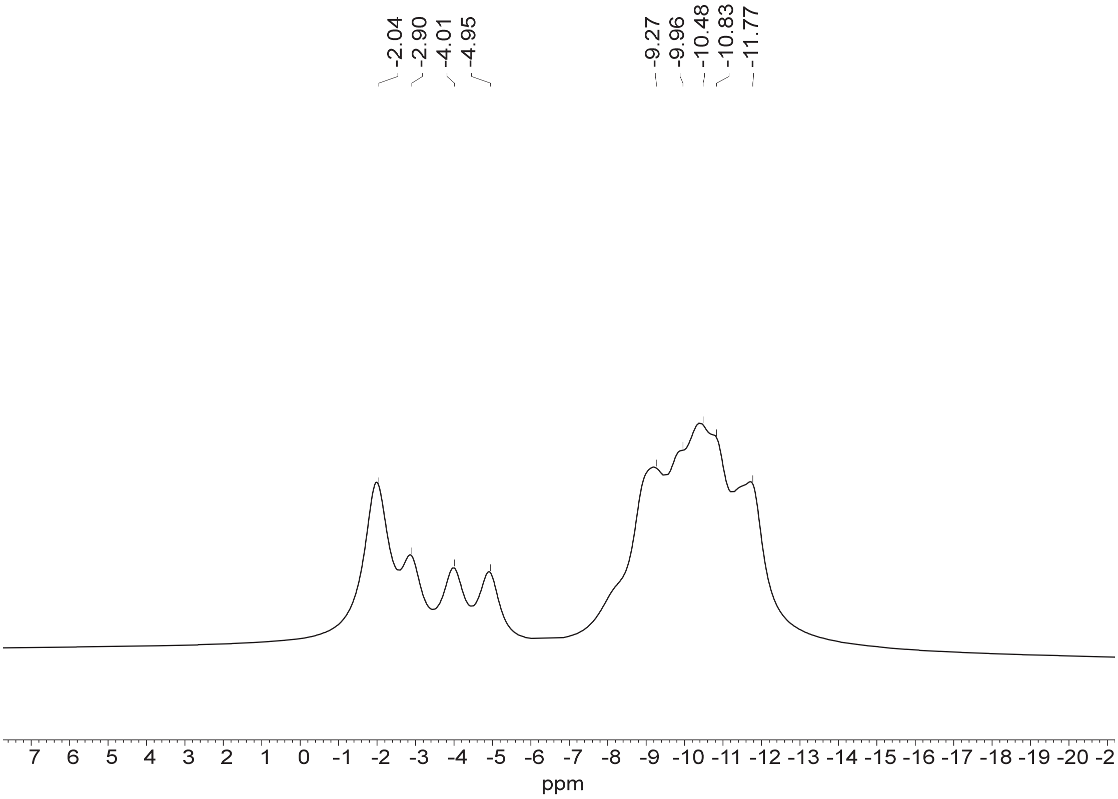
^{1}H NMR (500 MHz, $CDCl_3$)



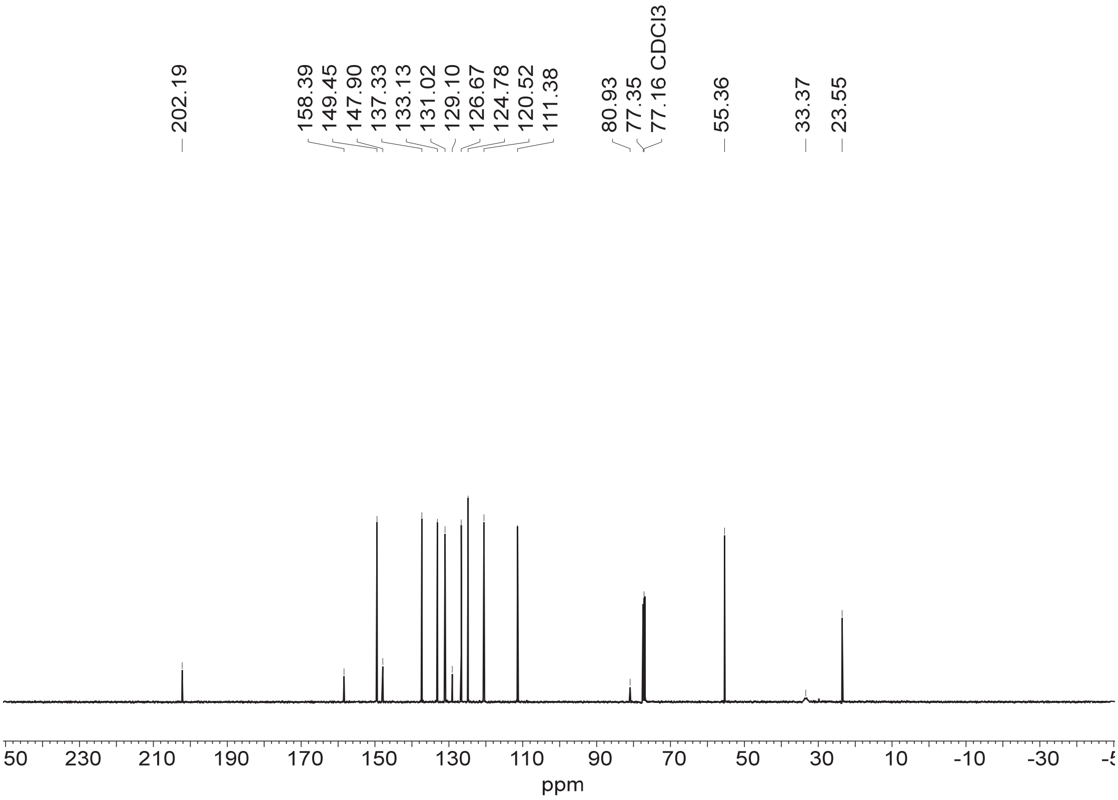
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



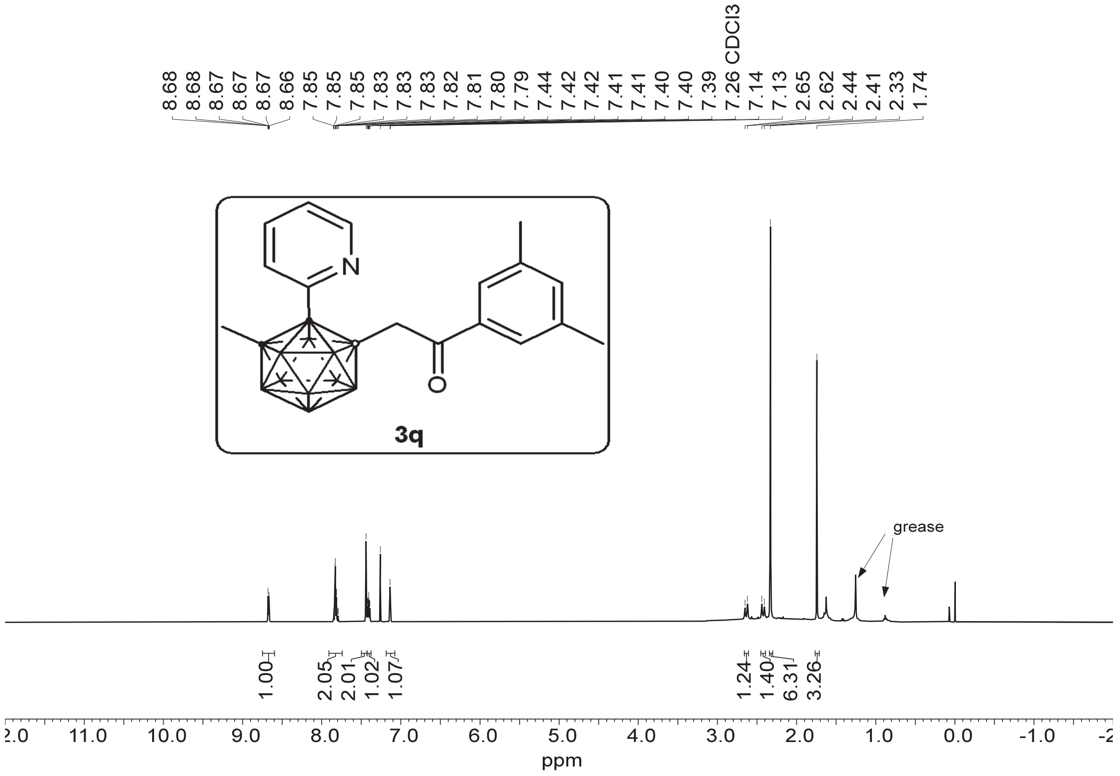
^{11}B NMR (160 MHz, CDCl$_3$)



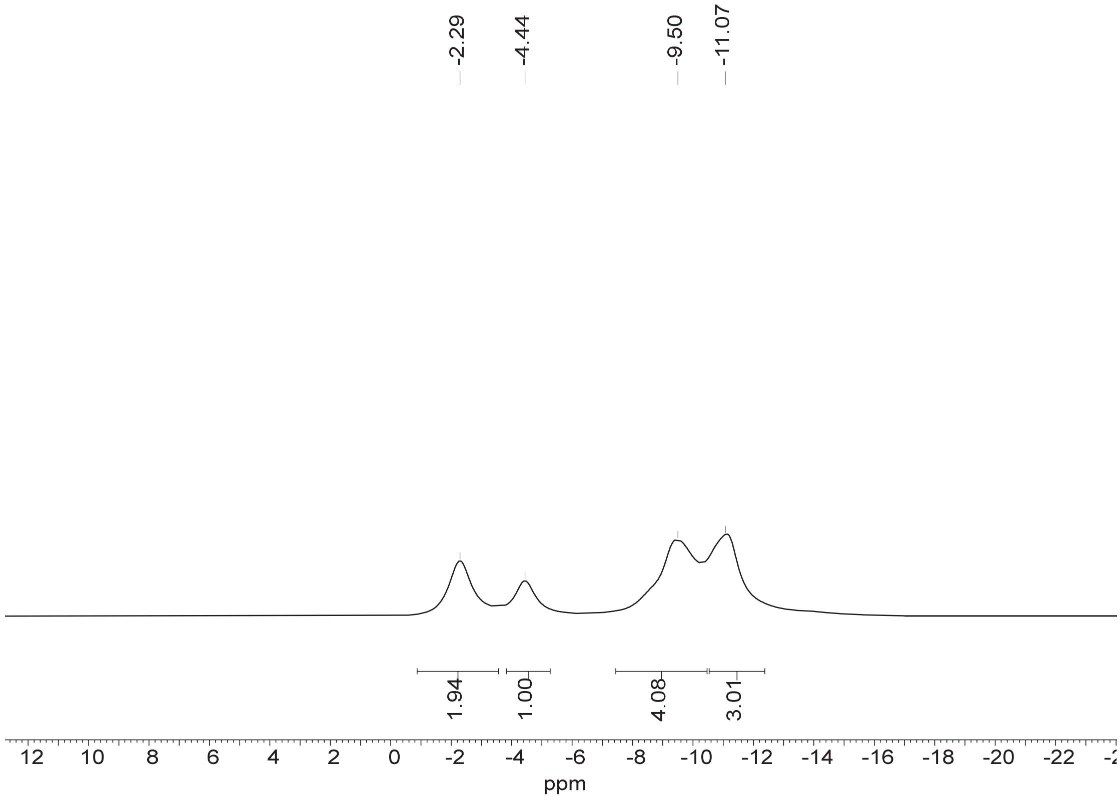
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



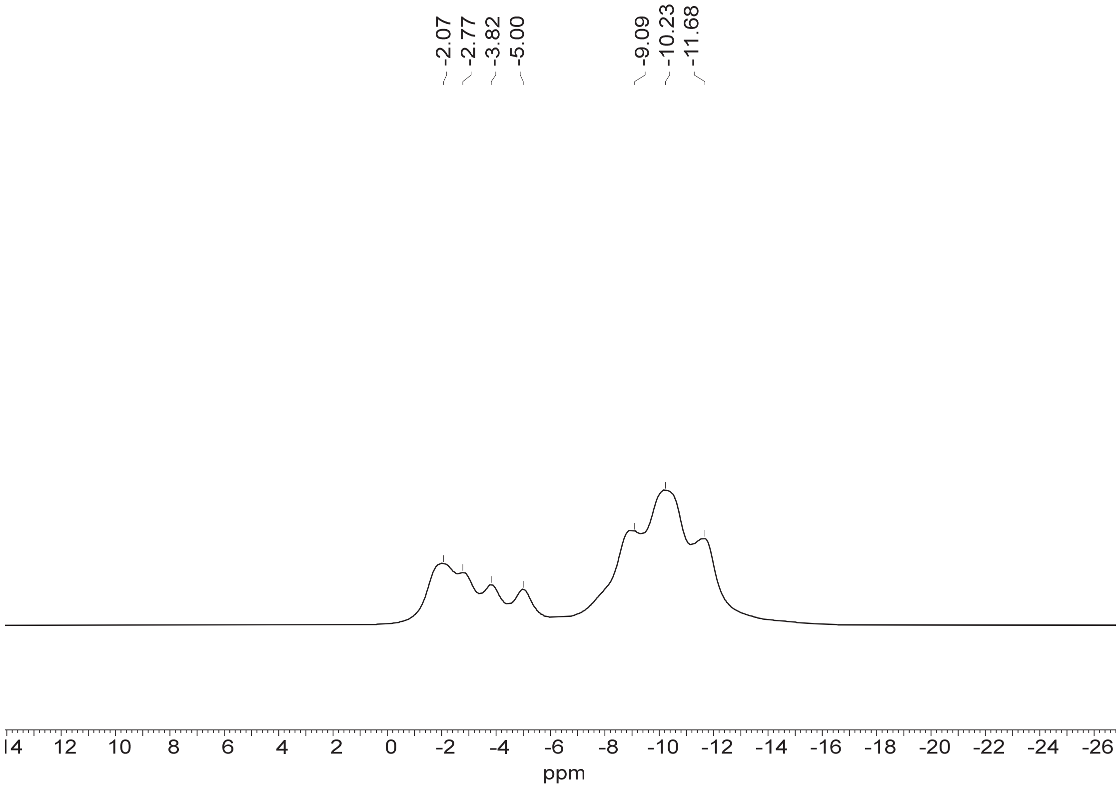
^{1}H NMR (400 MHz, CDCl$_3$)



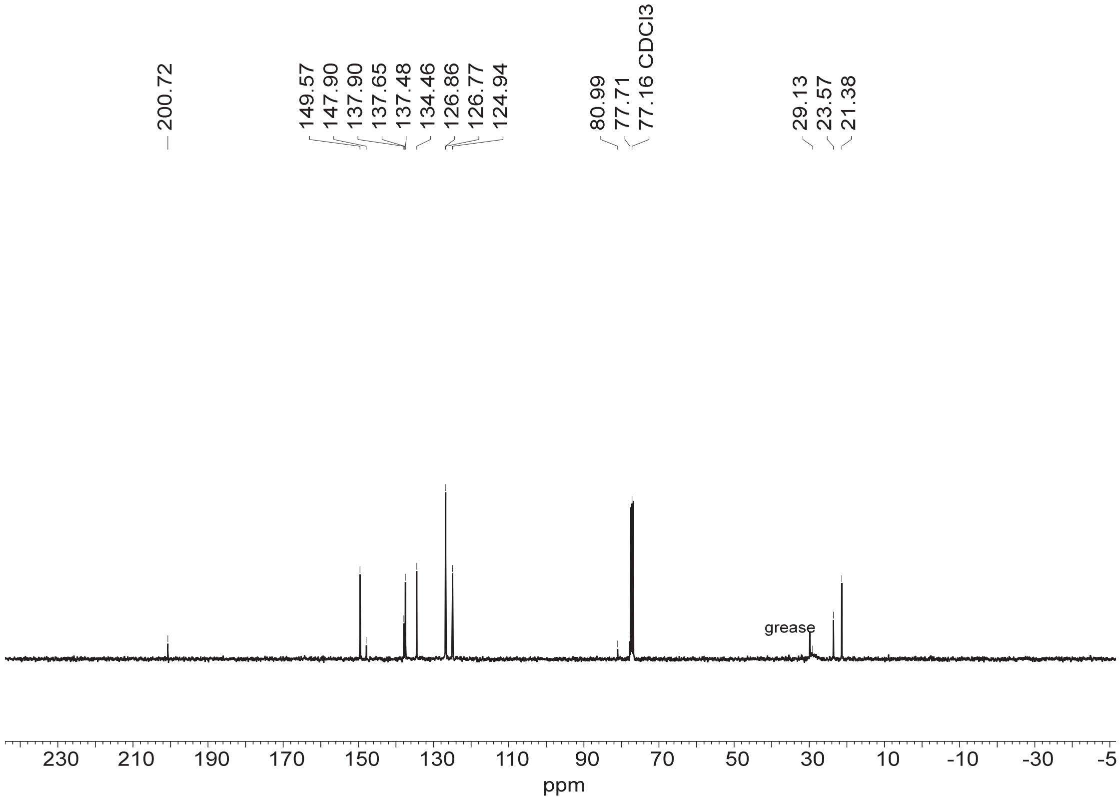
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



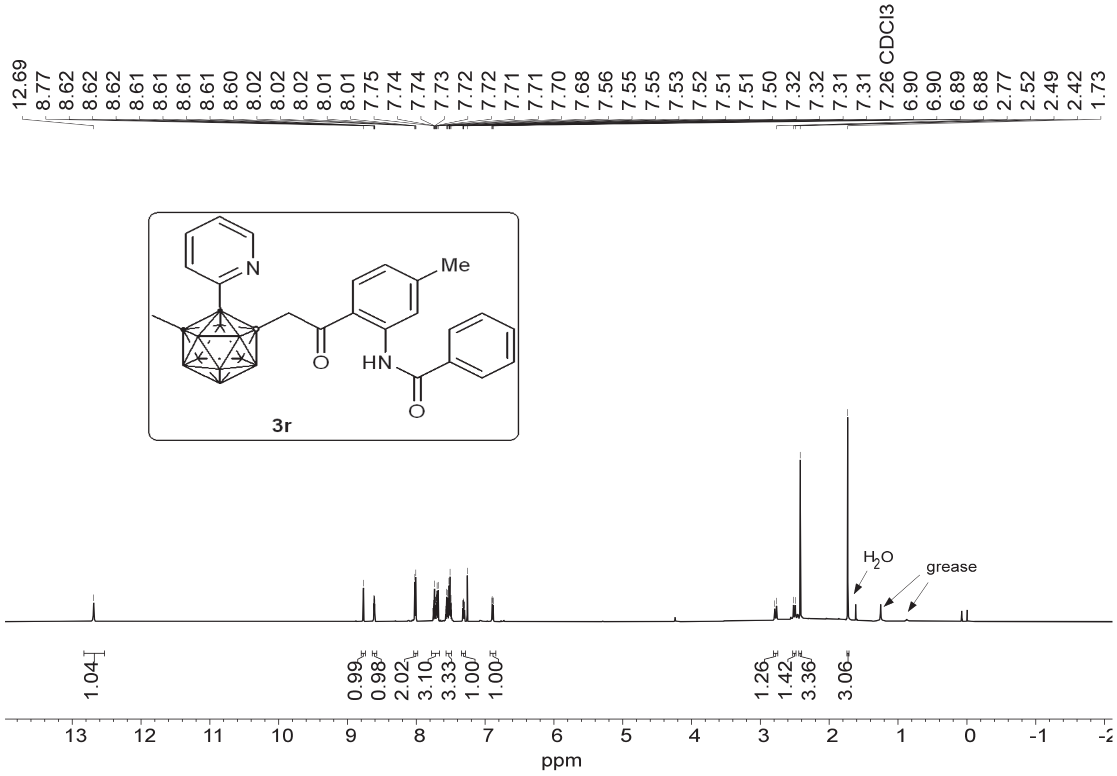
^{11}B NMR (128 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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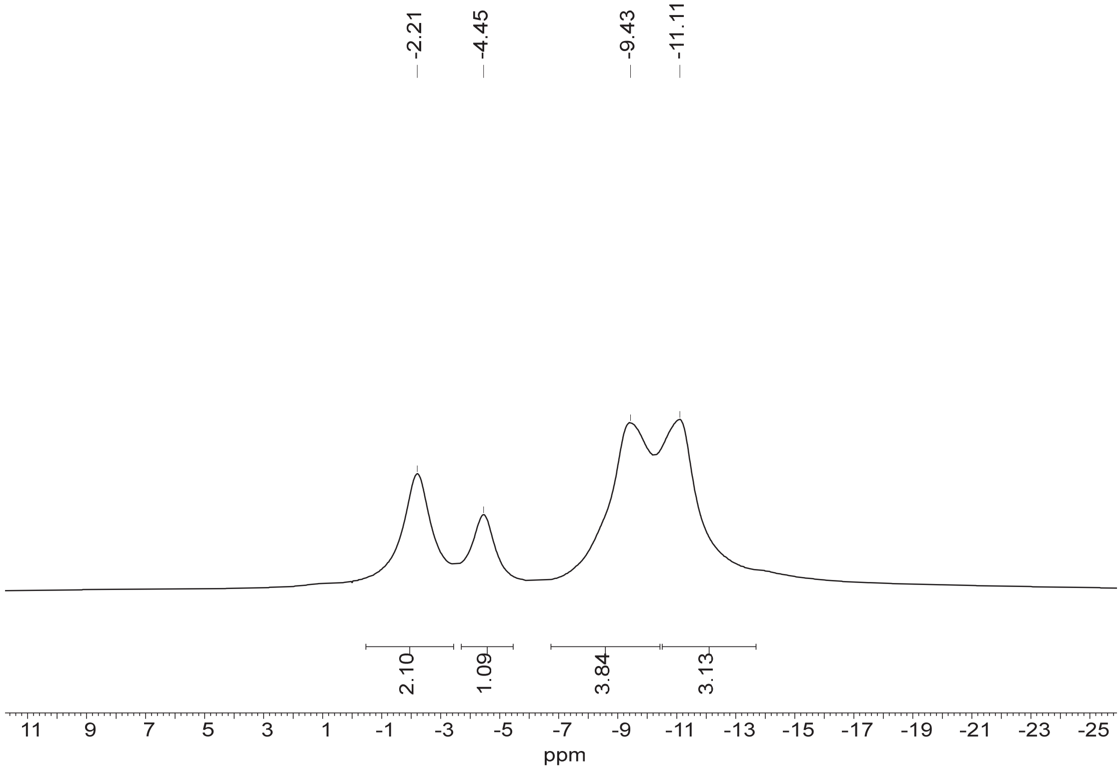
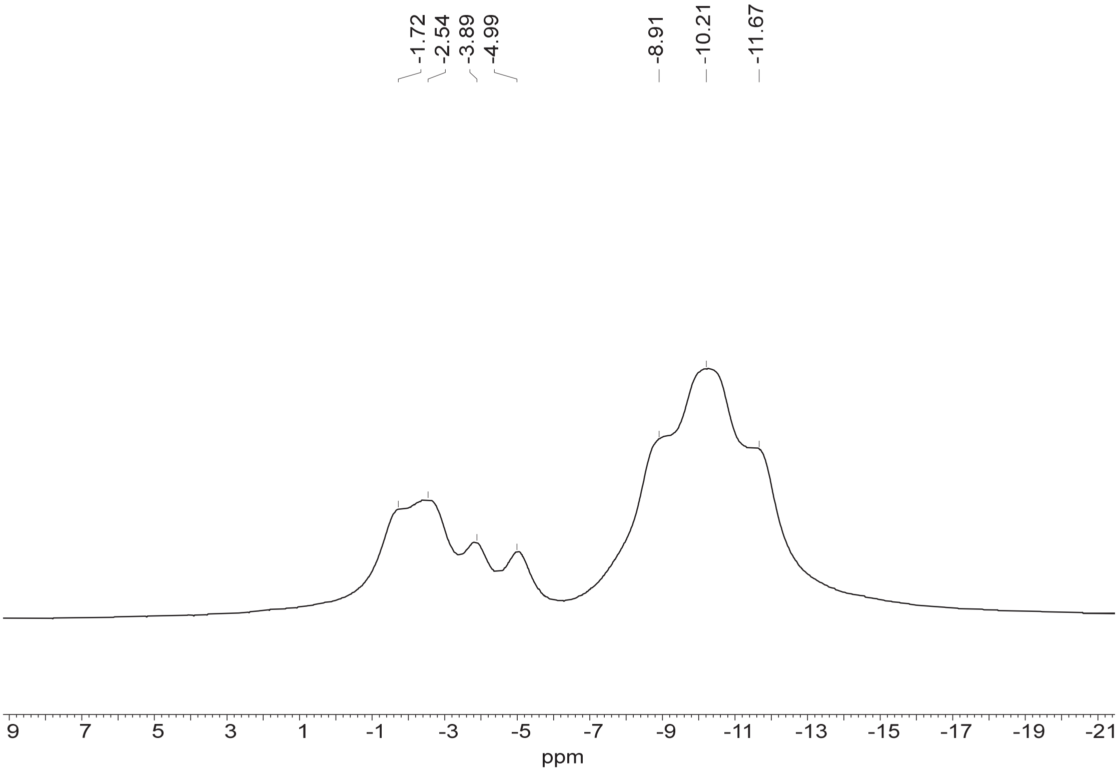
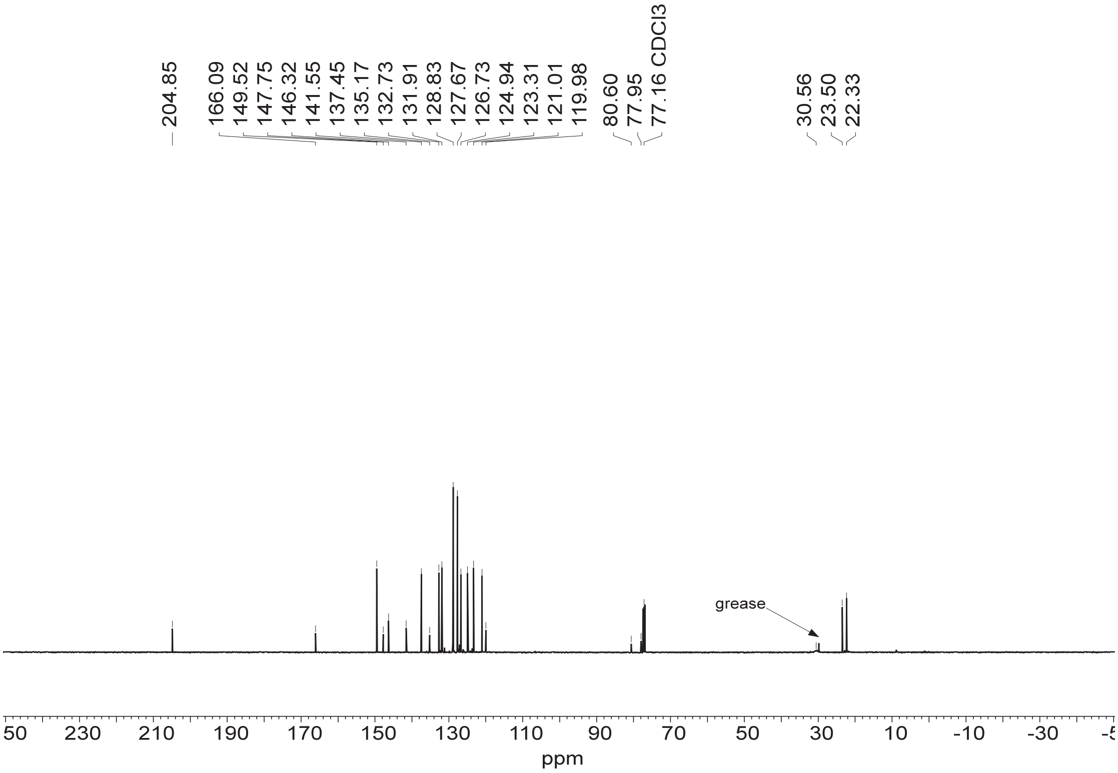
^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$)



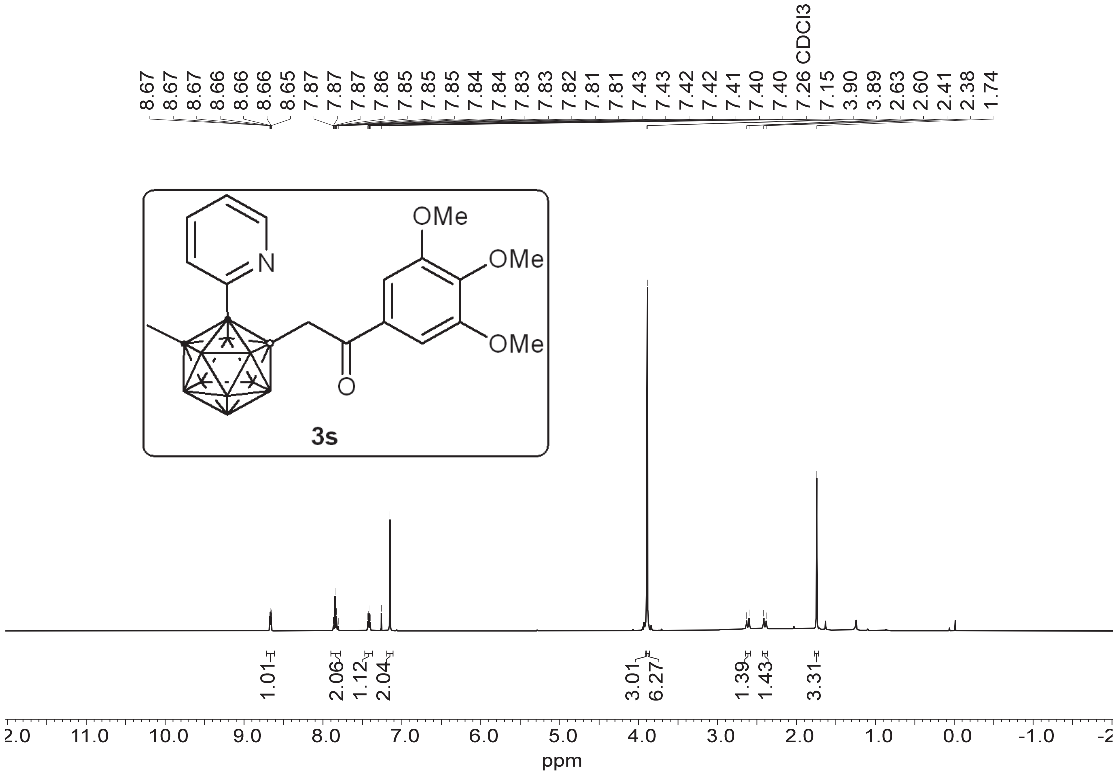
^{11}B NMR (160 MHz, CDCl$_3$)



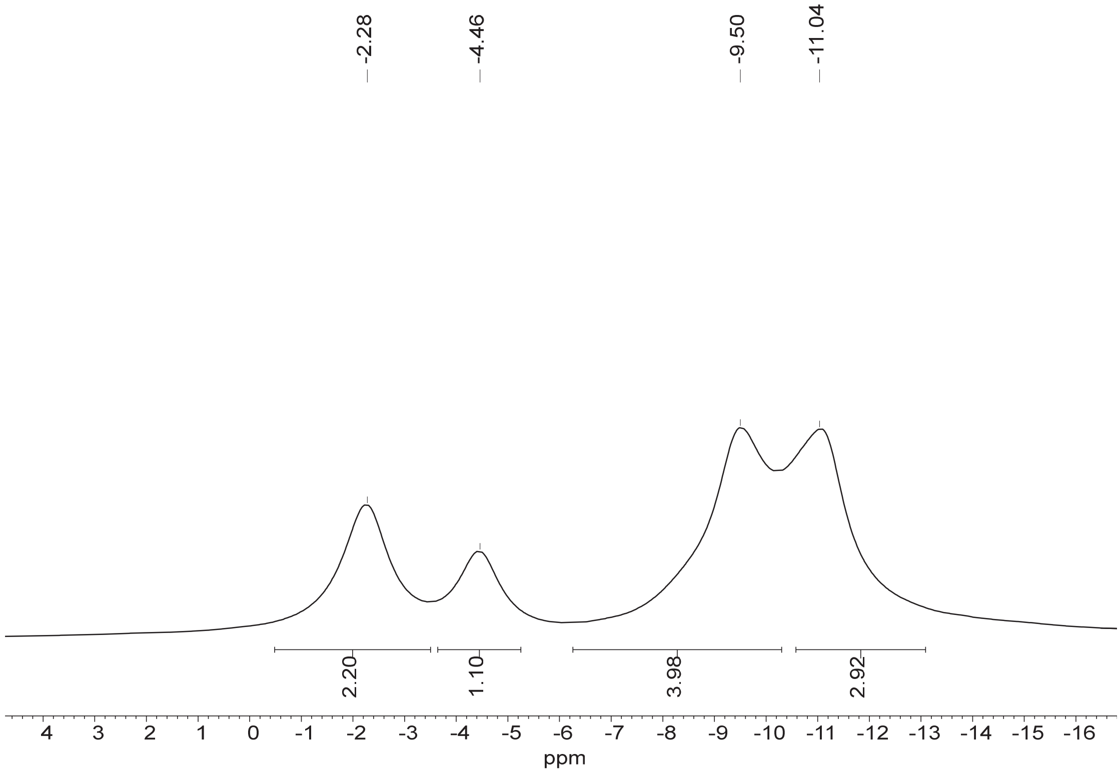
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



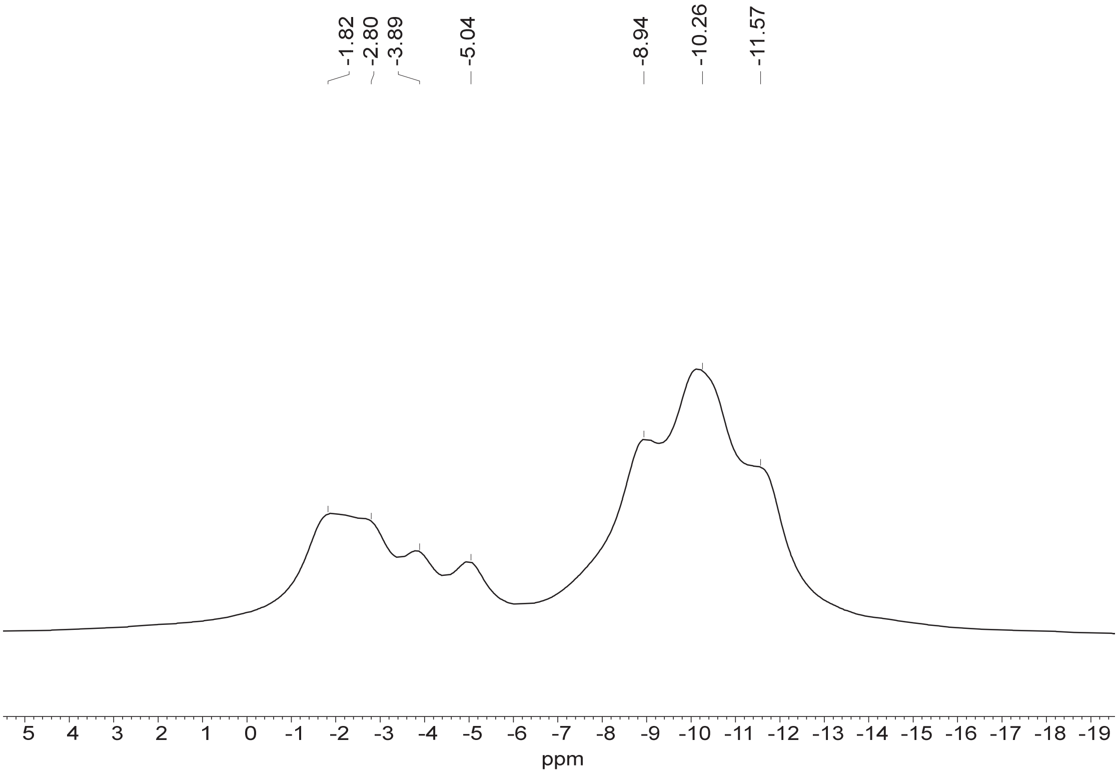
^{1}H NMR (400 MHz, CDCl$_3$)



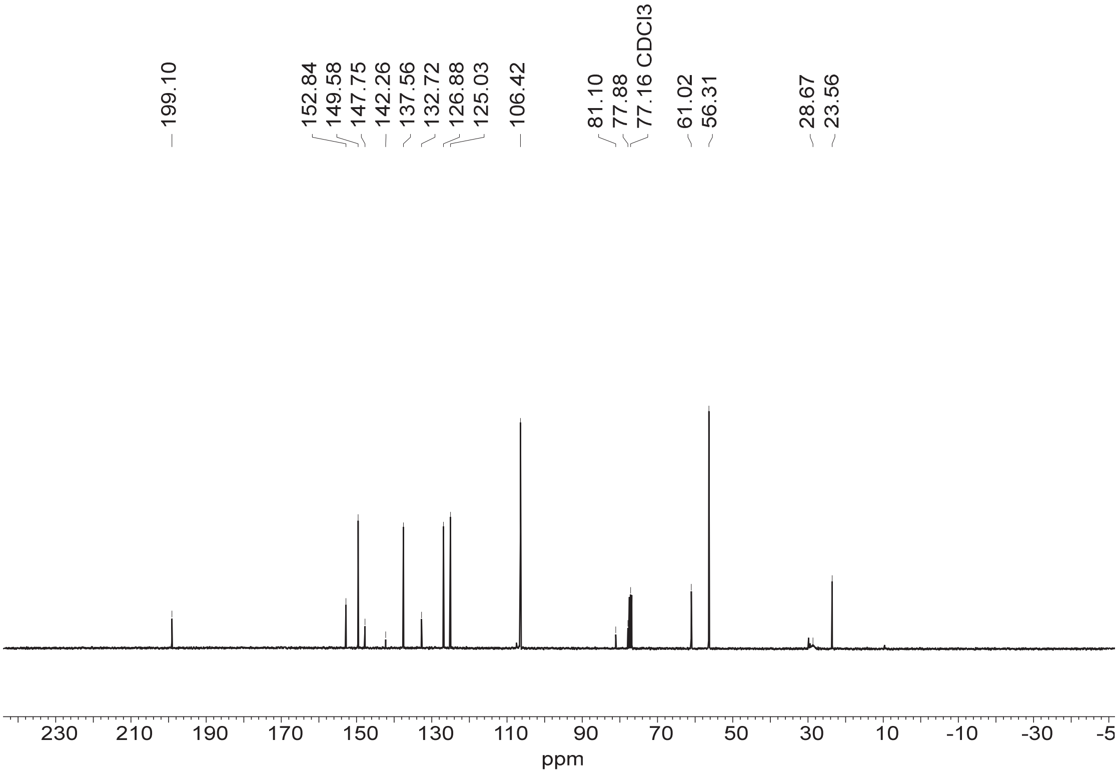
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



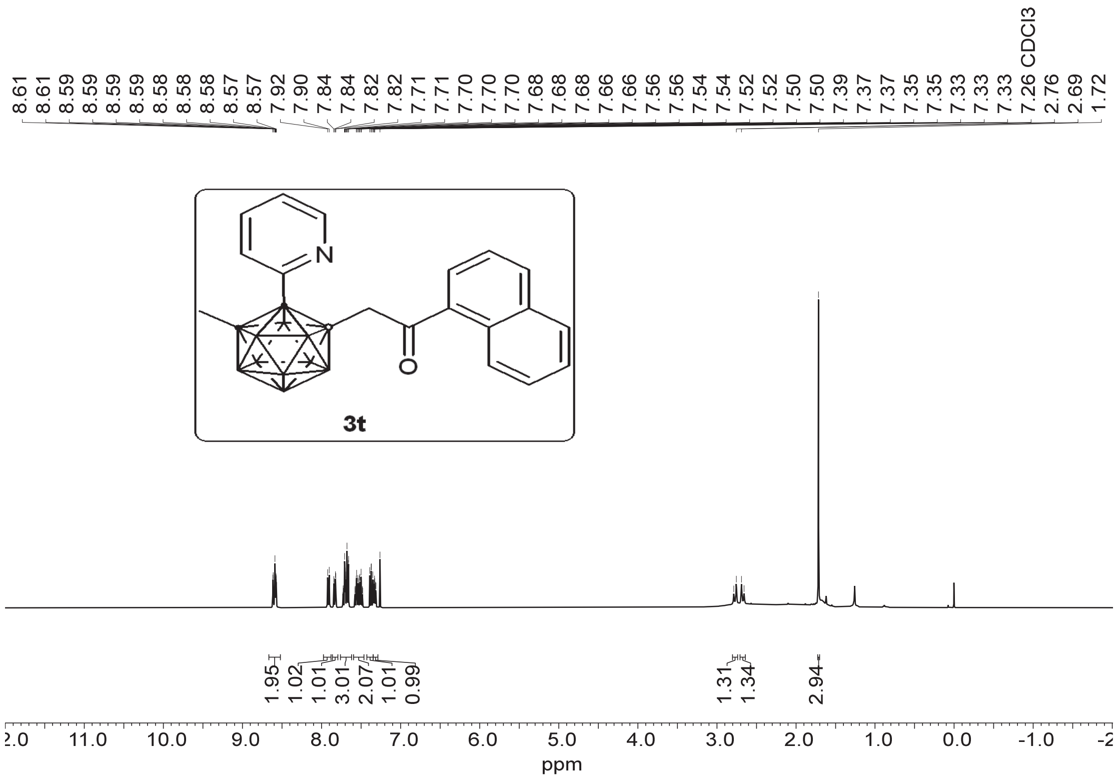
^{11}B NMR (128 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



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



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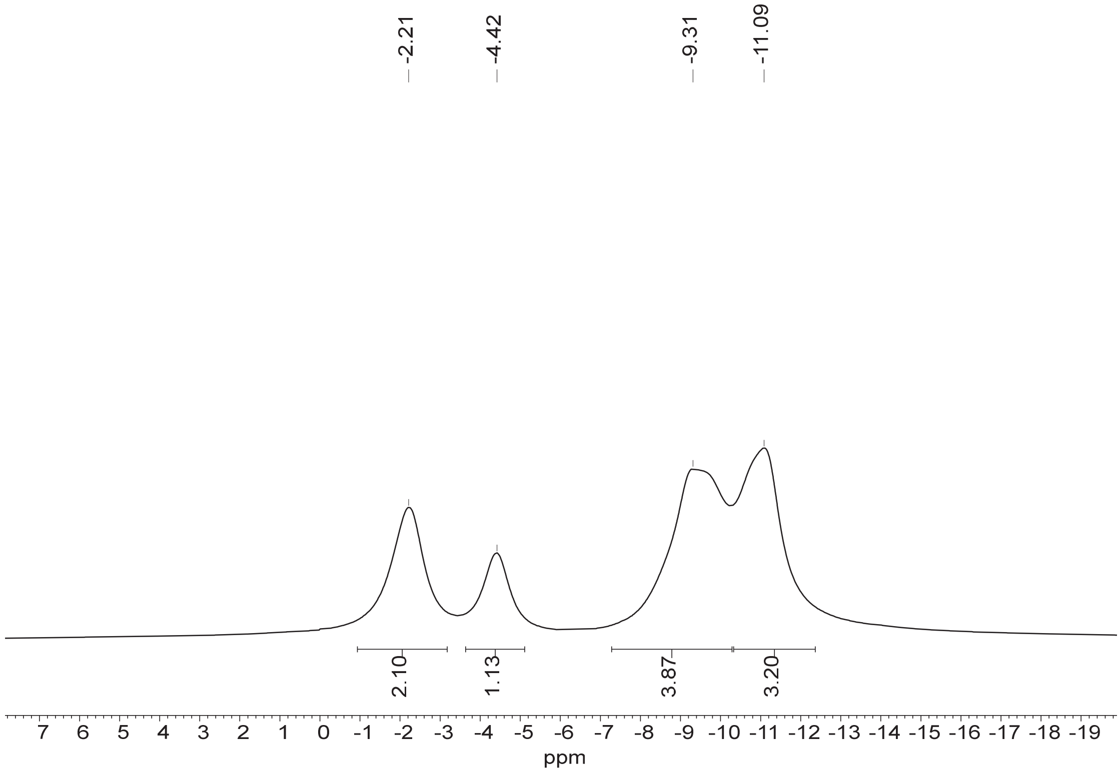
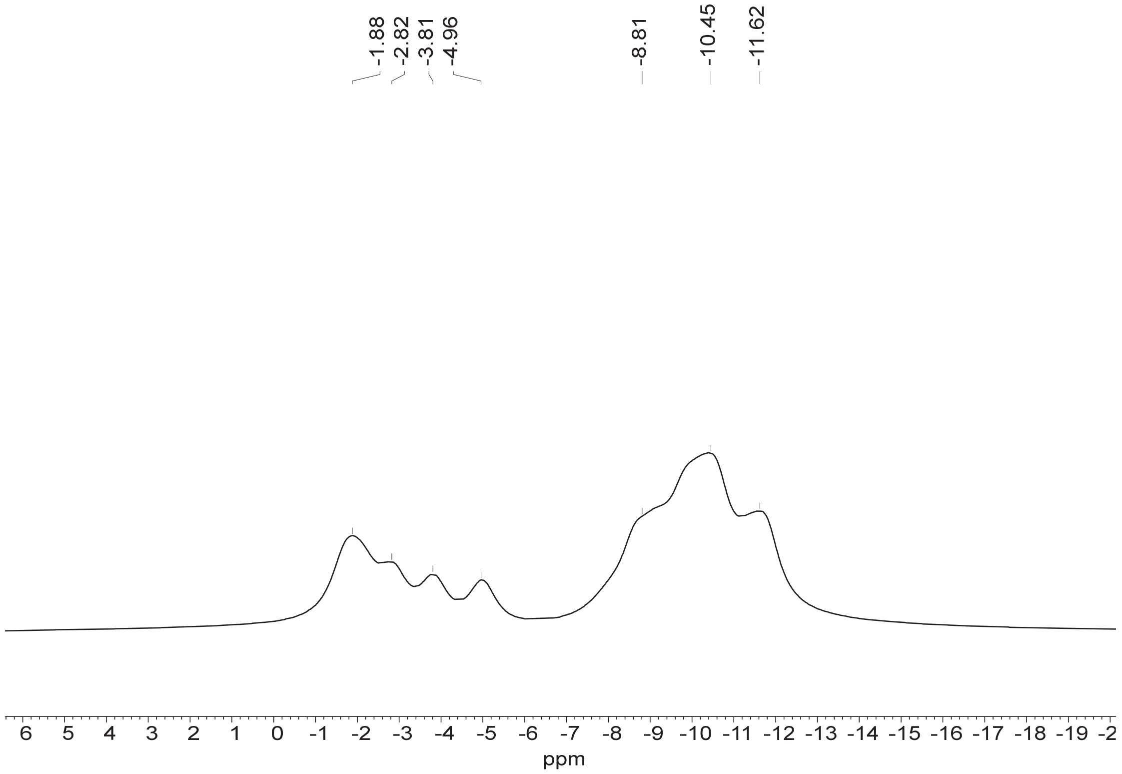
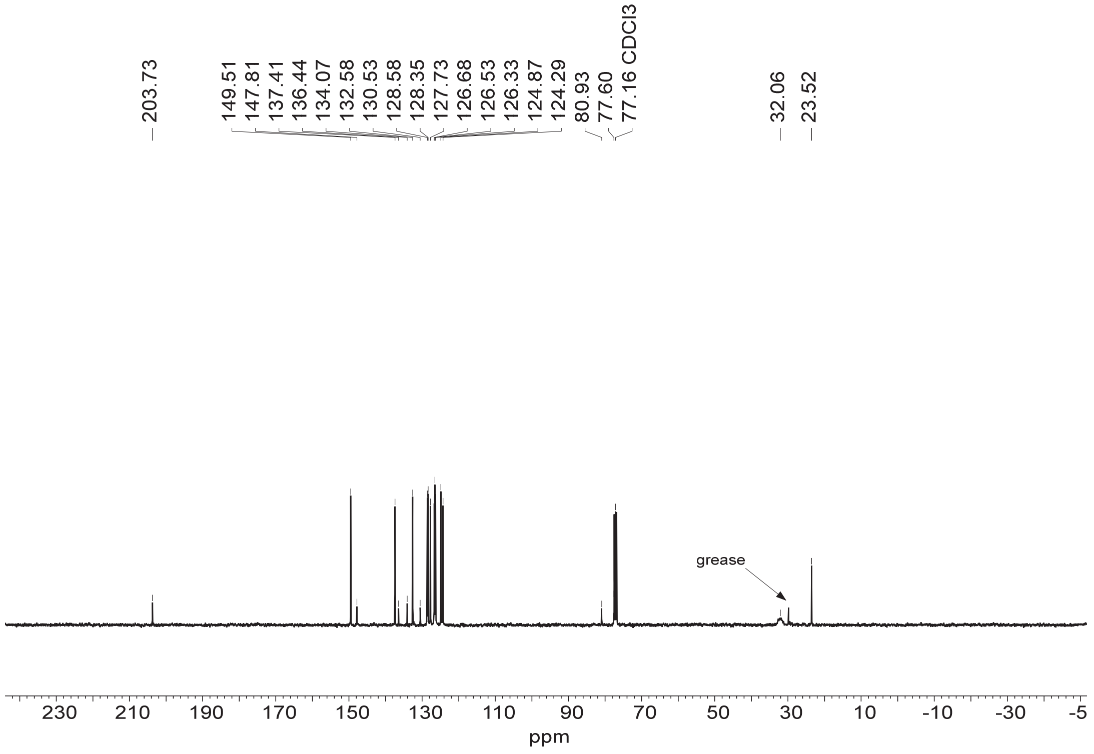


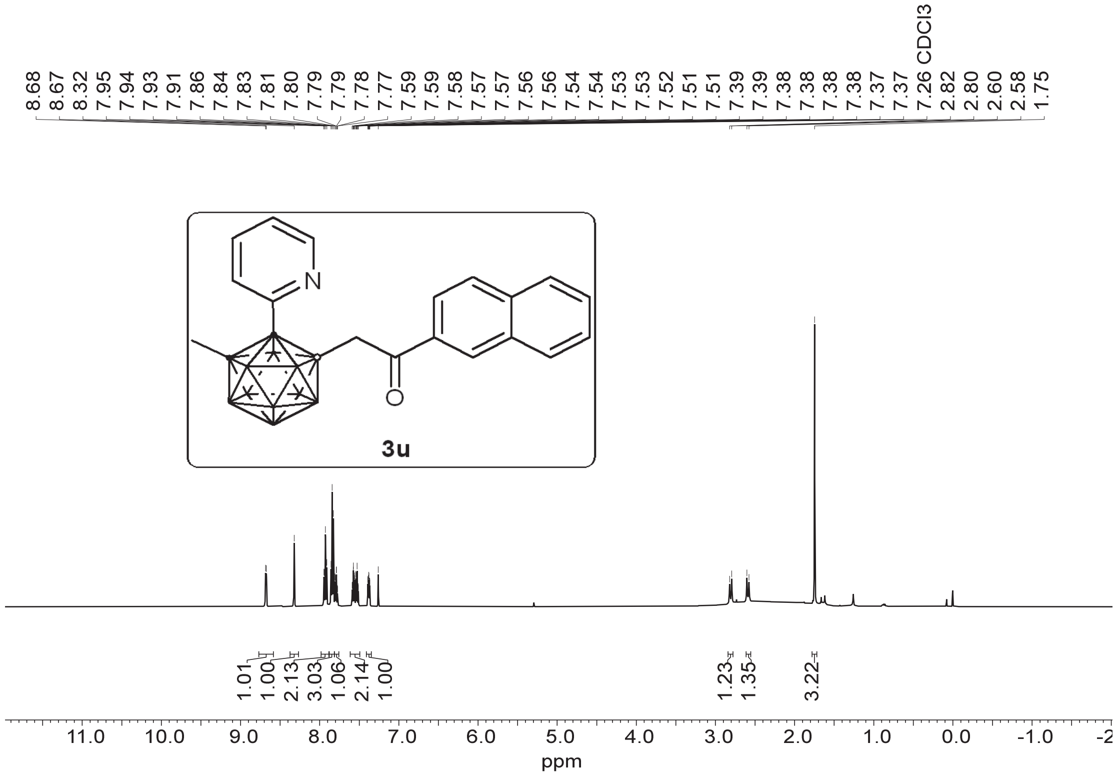
^{11}B NMR (128 MHz, $CDCl_3$)



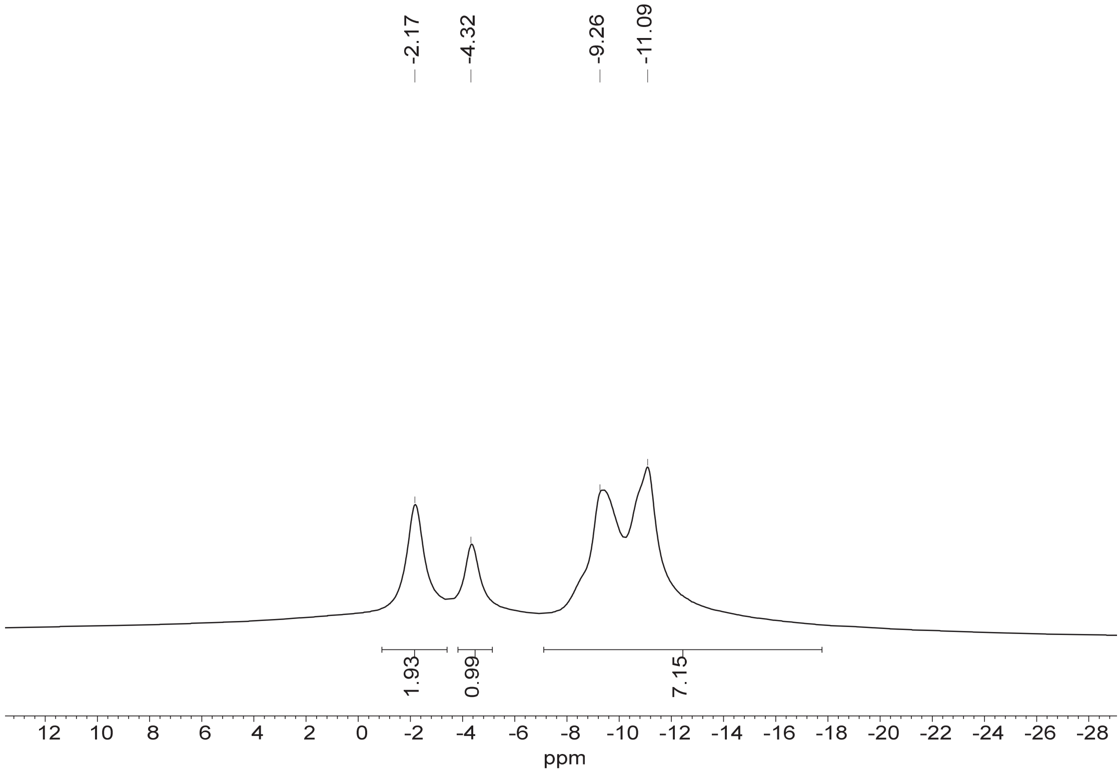
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



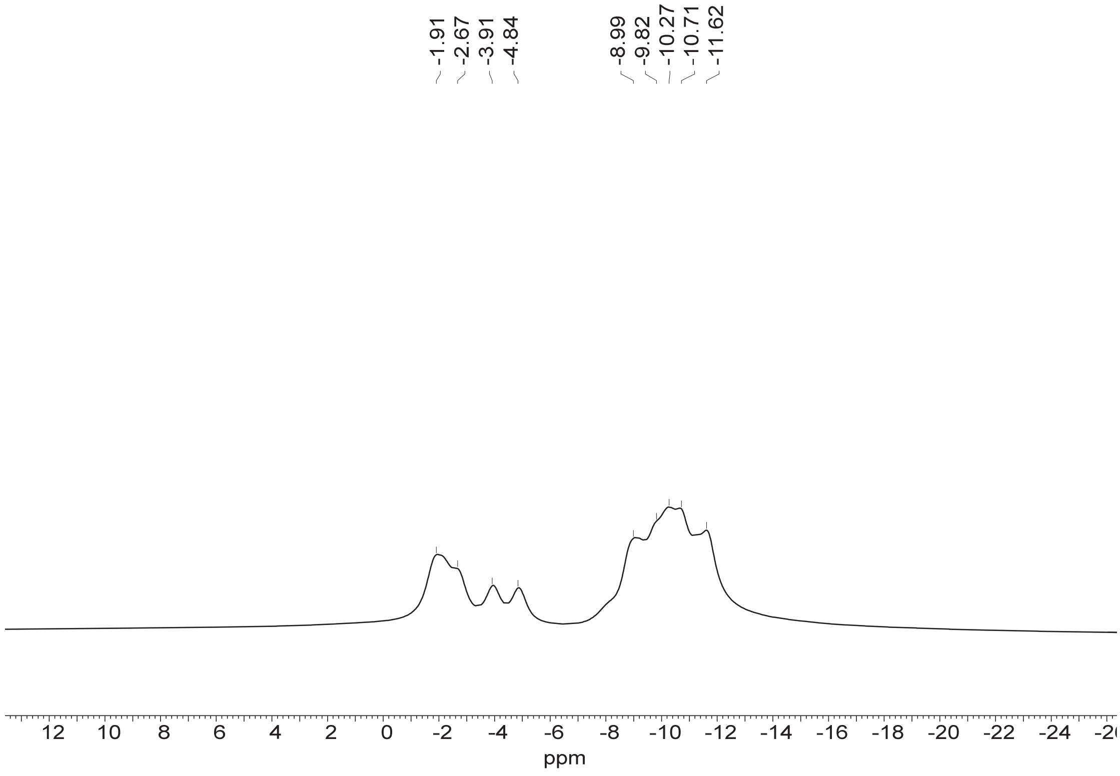
^{1}H NMR (500 MHz, CDCl$_3$)



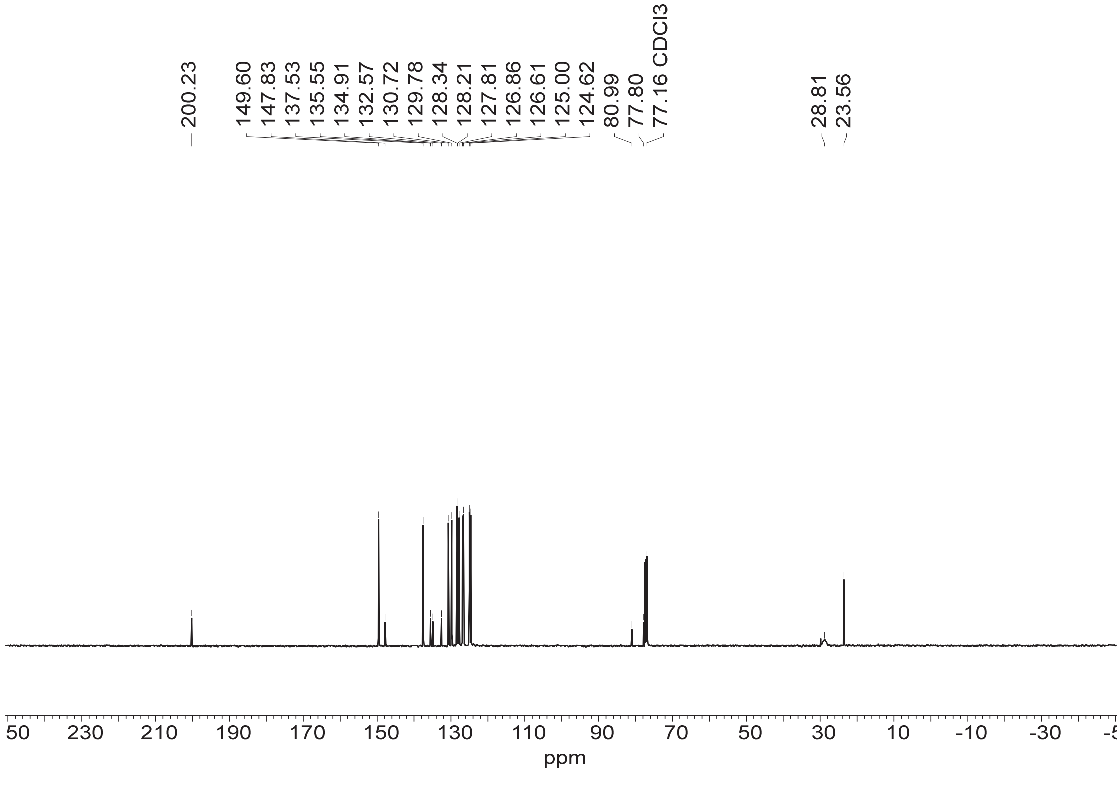
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



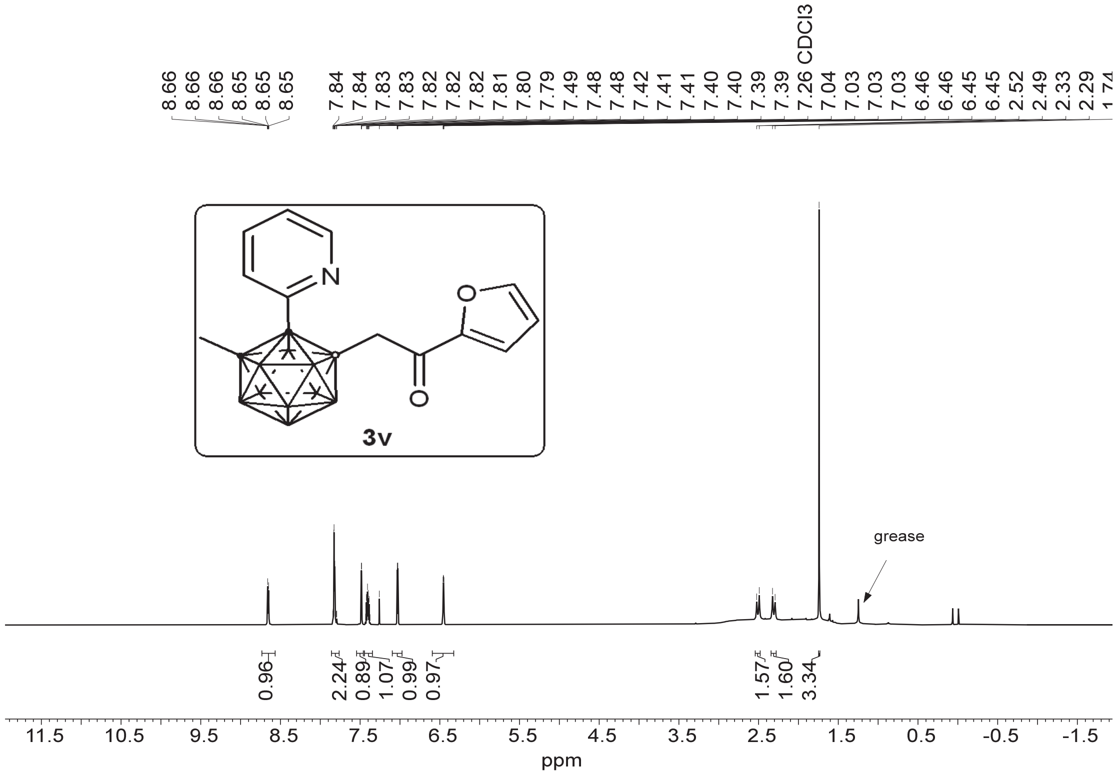
^{11}B NMR (160 MHz, $CDCl_3$)



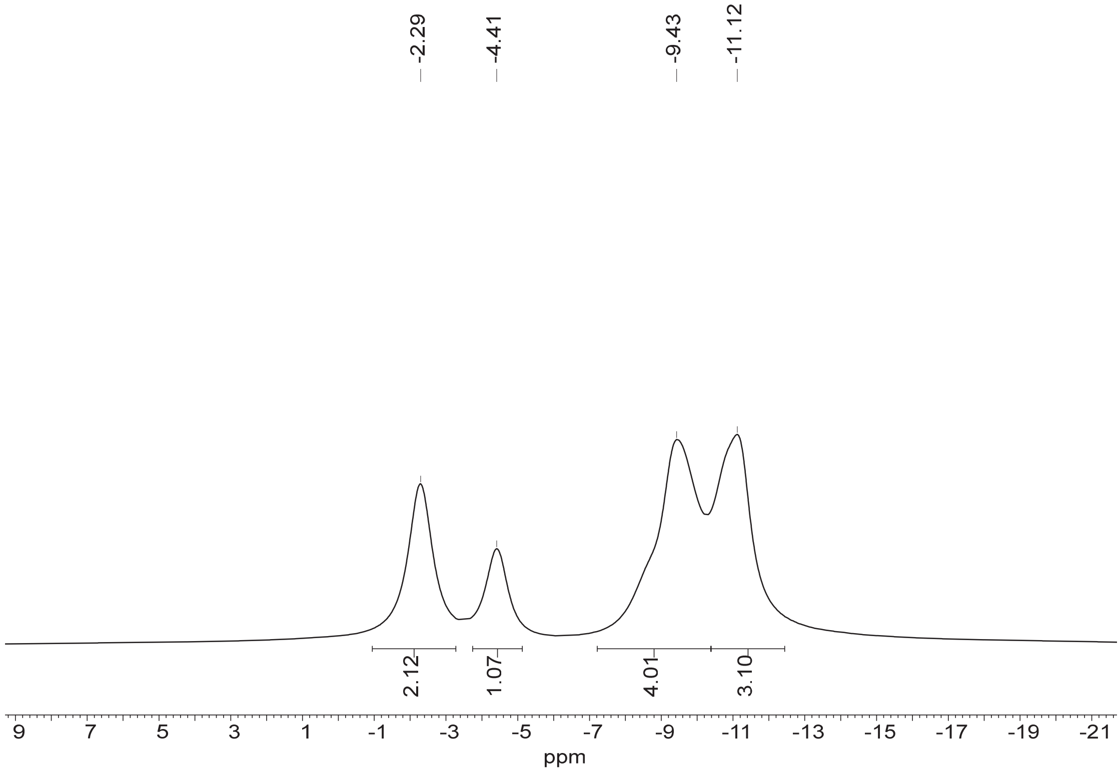
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



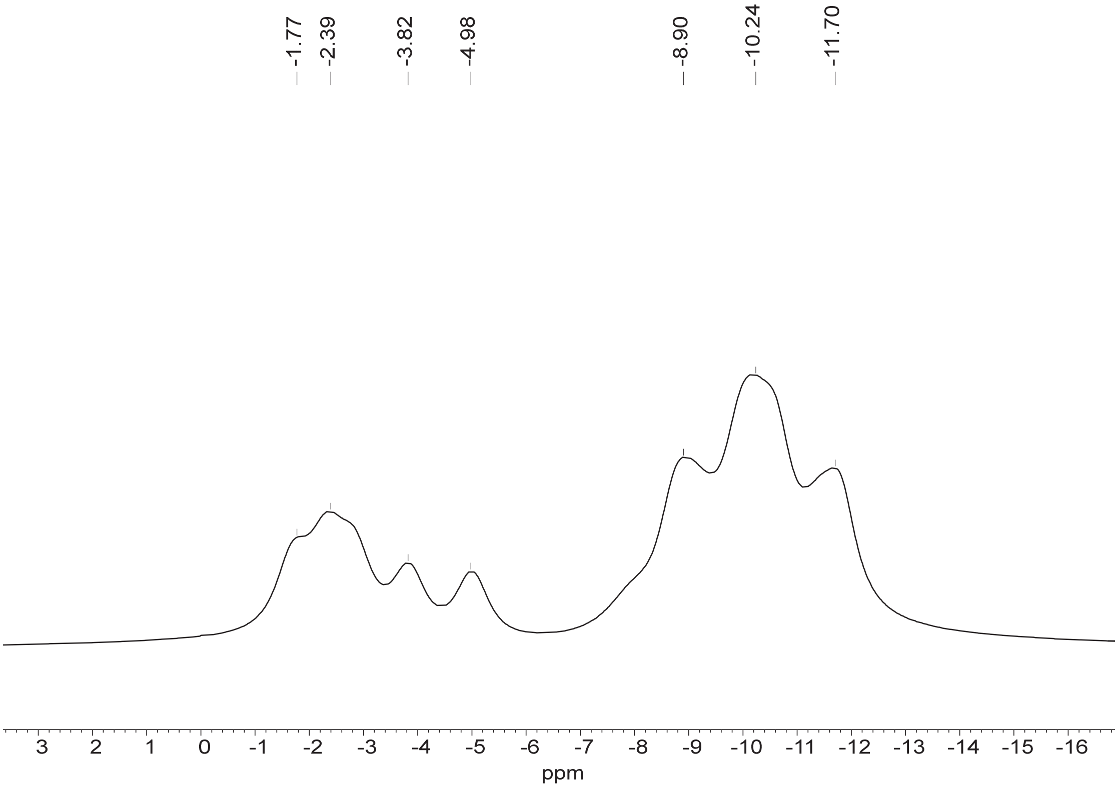
^{1}H NMR (400 MHz, CDCl$_3$)



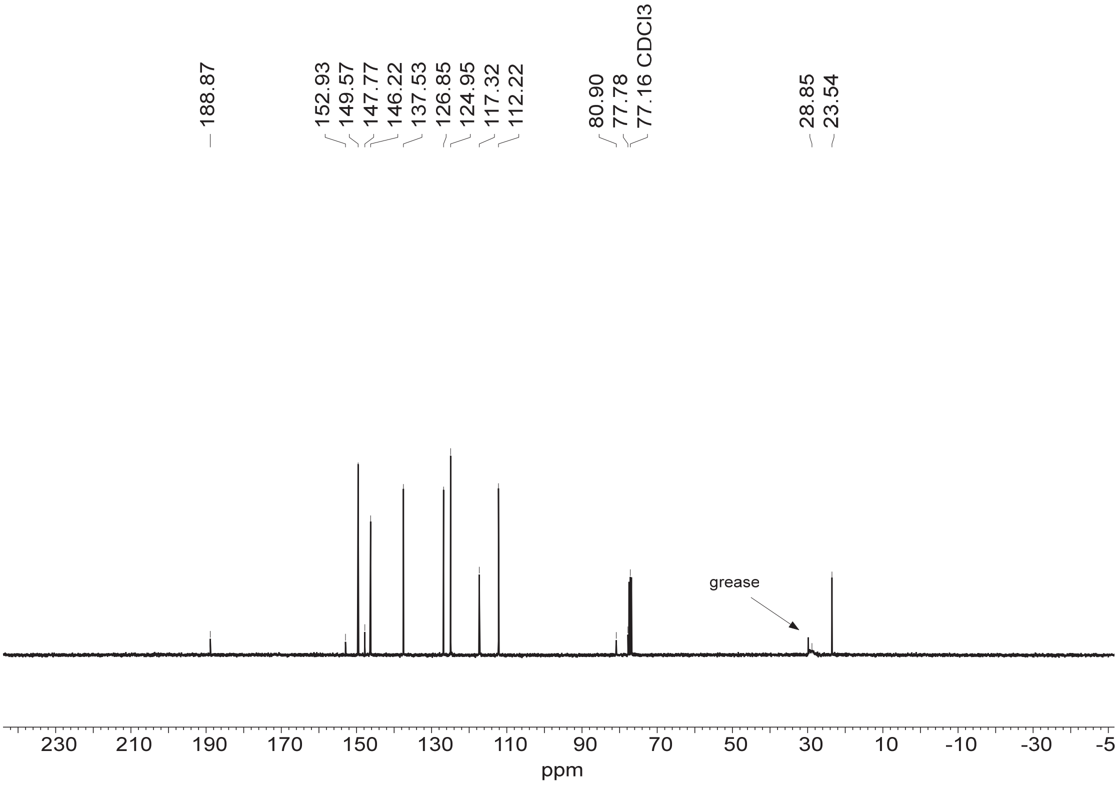
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



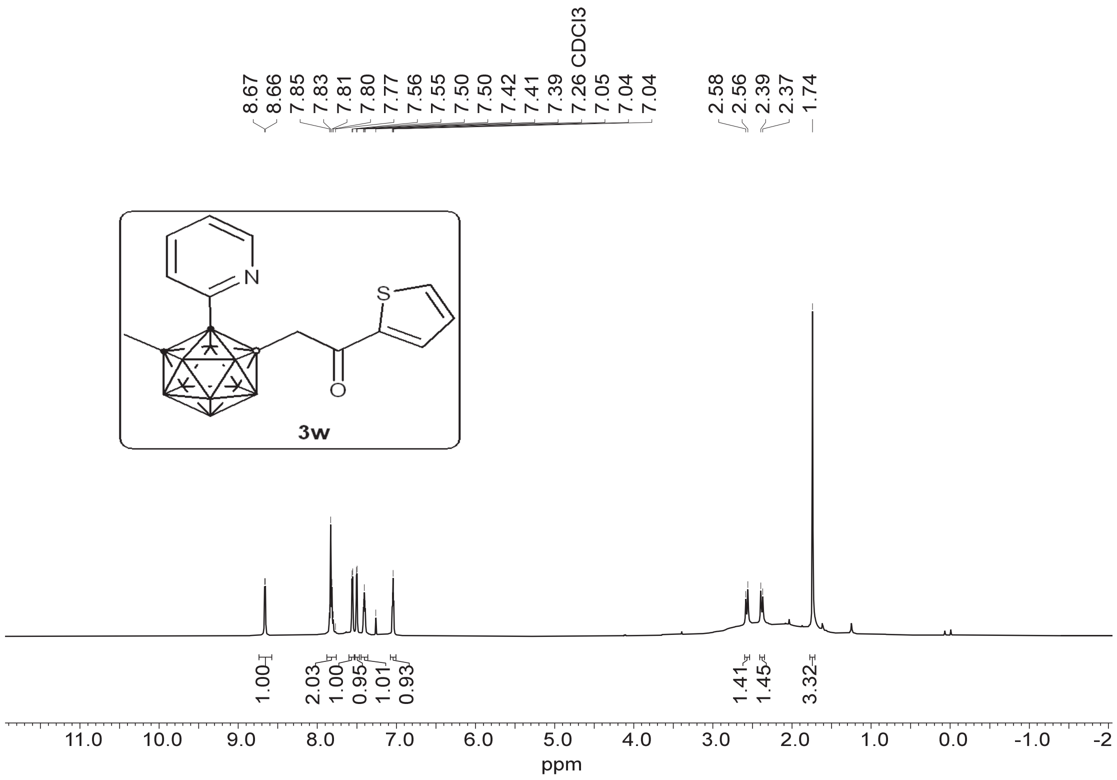
^{11}B NMR (128 MHz, CDCl$_3$)



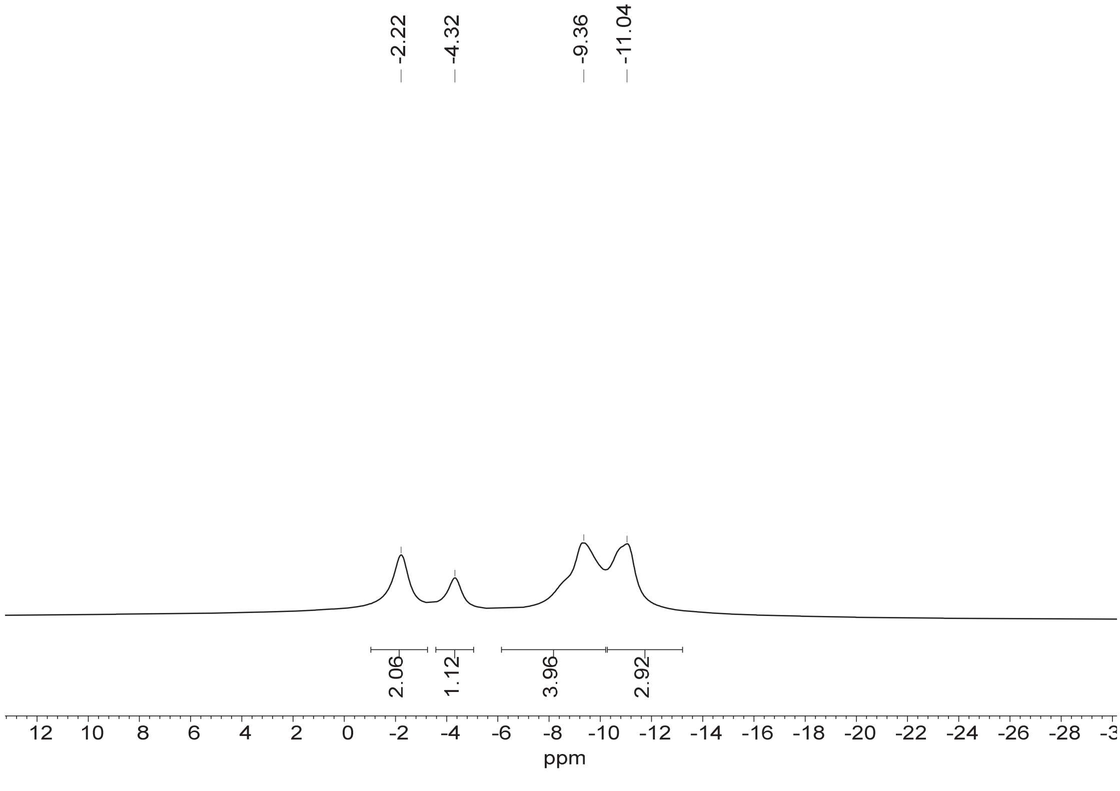
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



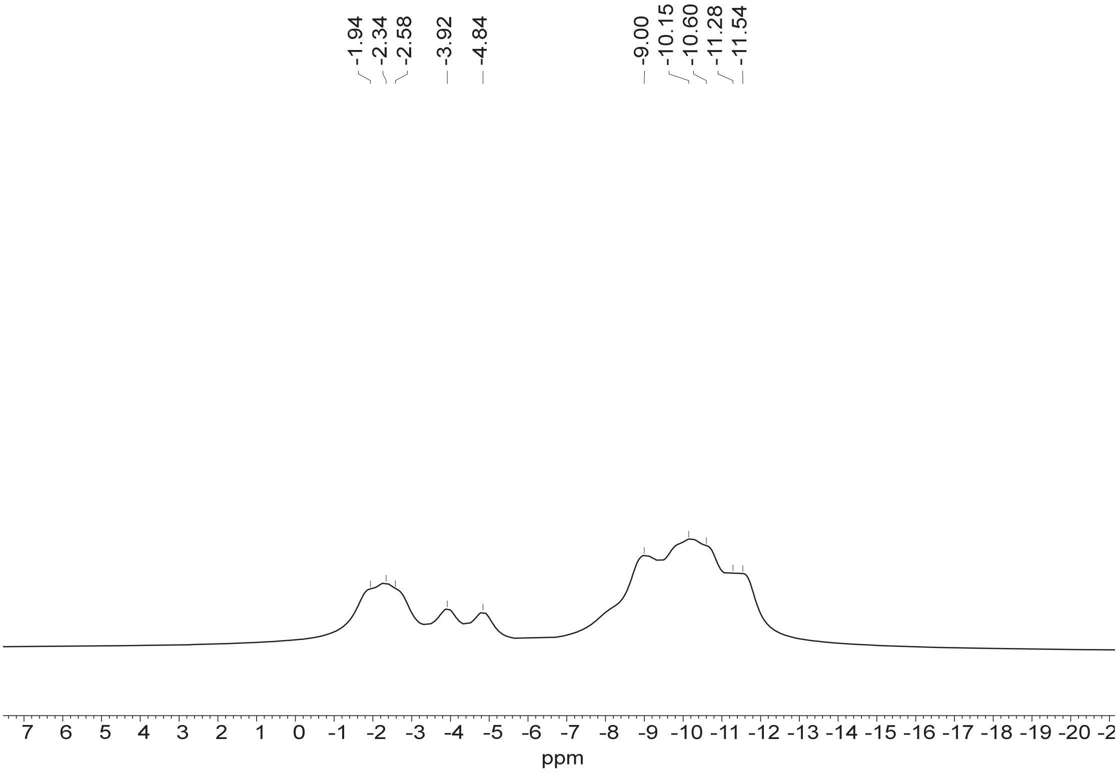
^{1}H NMR (500 MHz, CDCl$_3$)



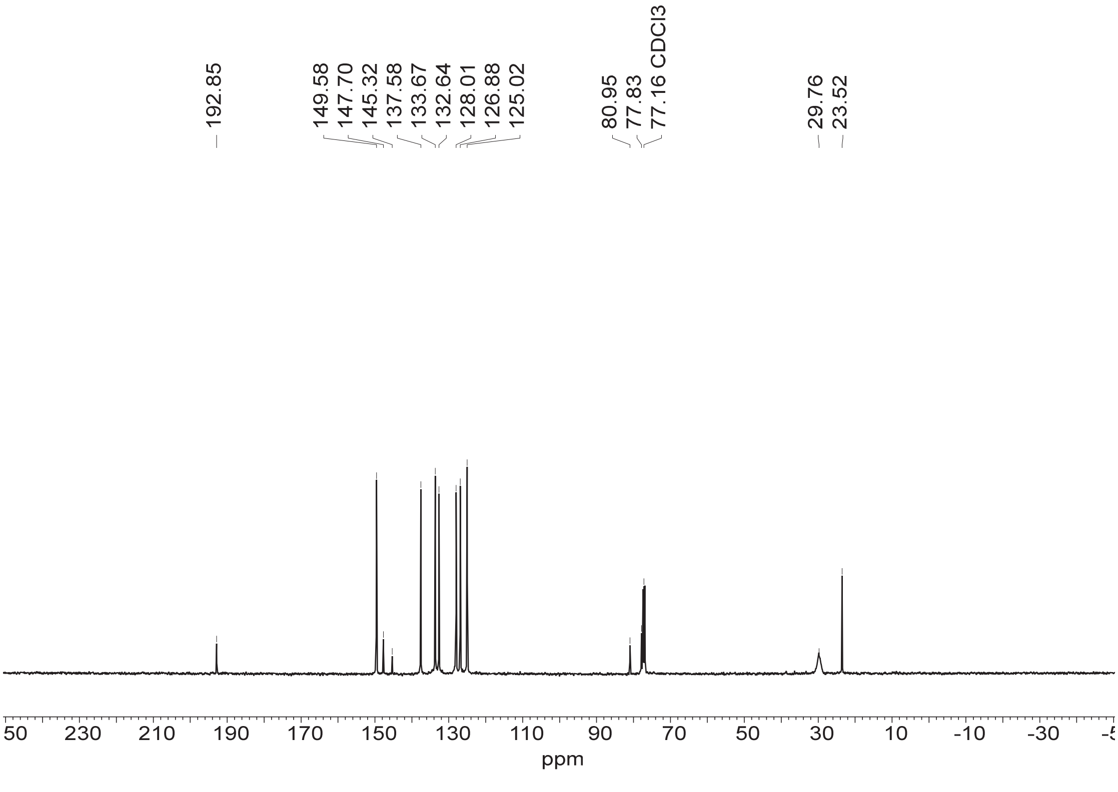
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



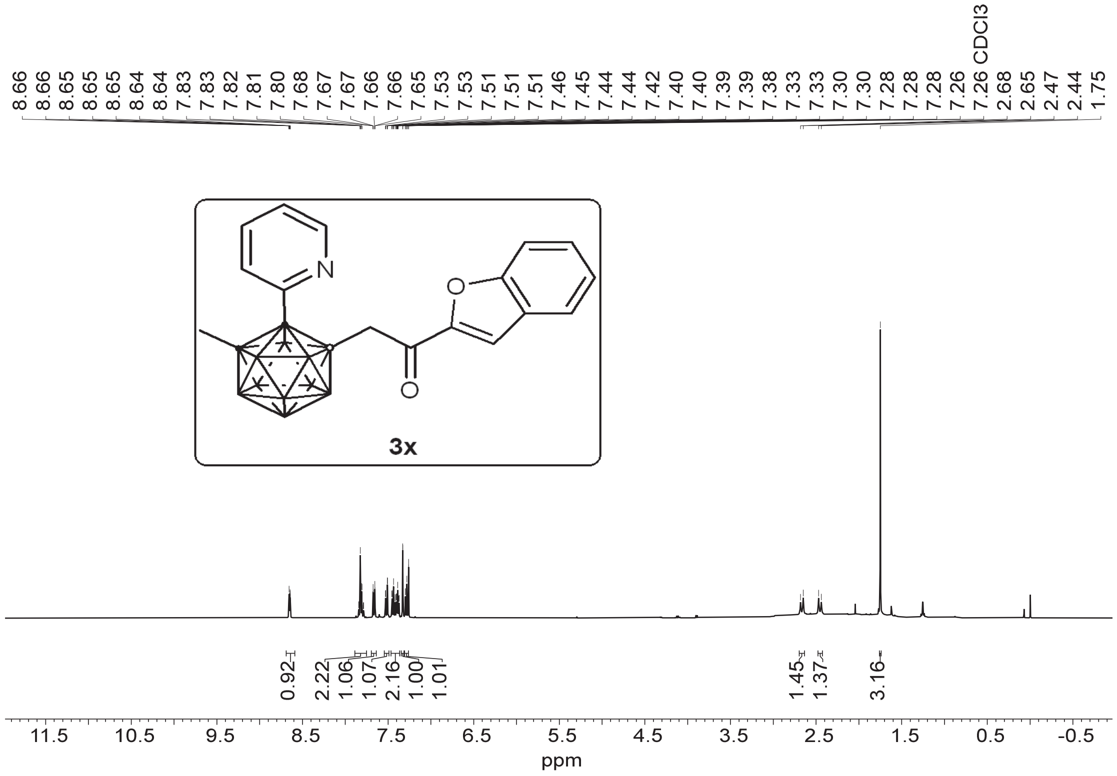
^{11}B NMR (160 MHz, CDCl$_3$)



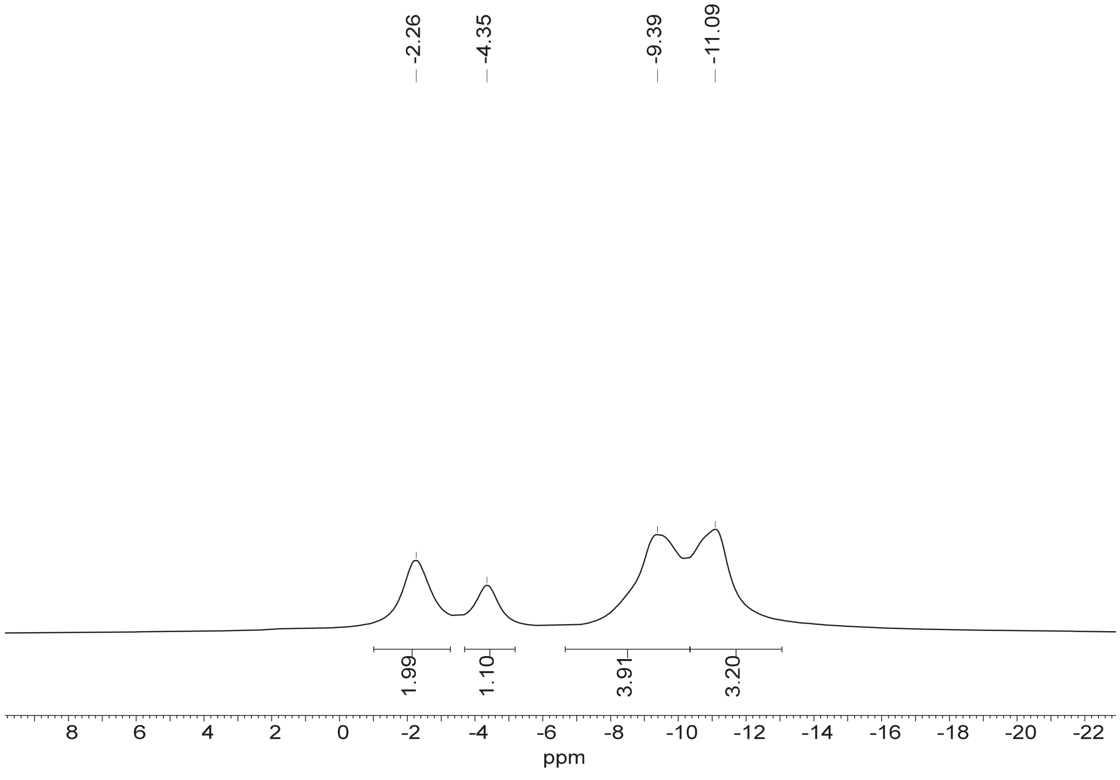
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



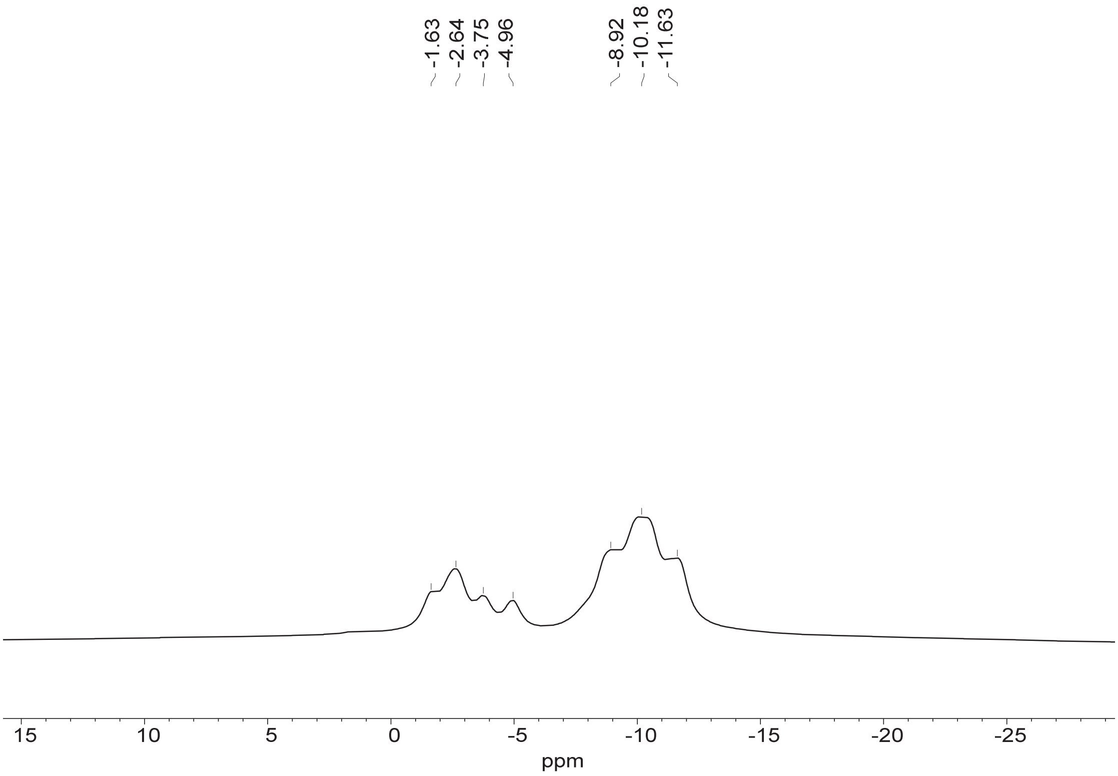
^{1}H NMR (400 MHz, CDCl$_3$)



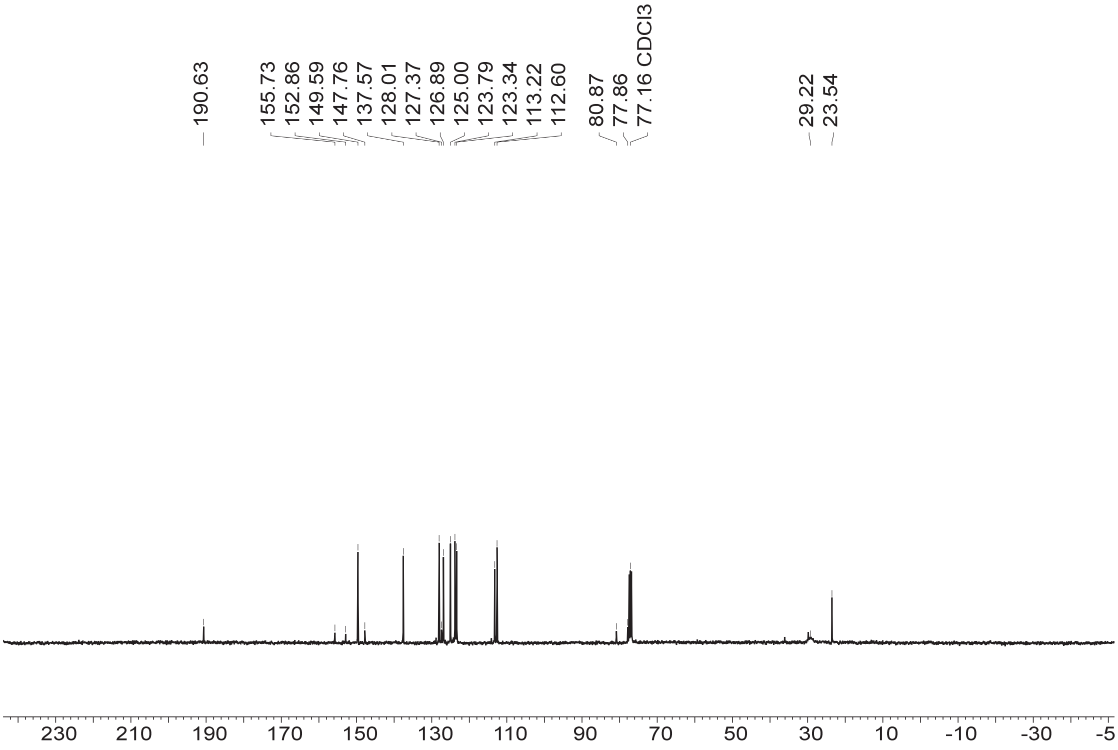
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



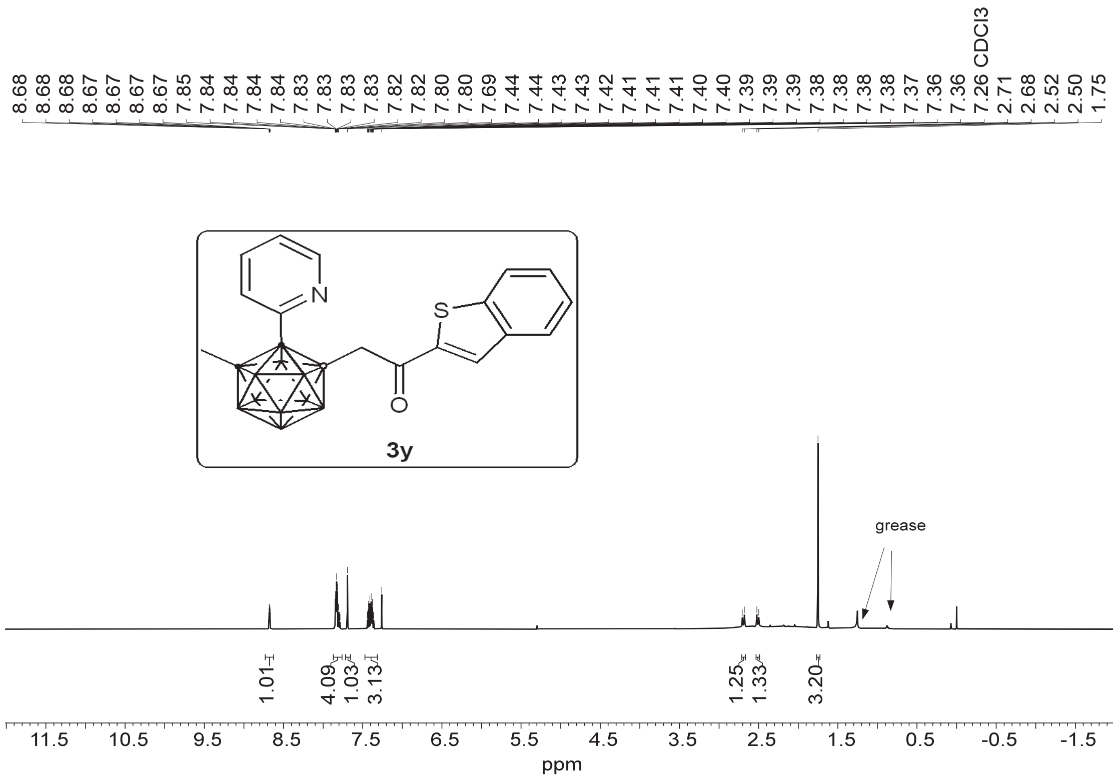
^{11}B NMR (128 MHz, $CDCl_3$)



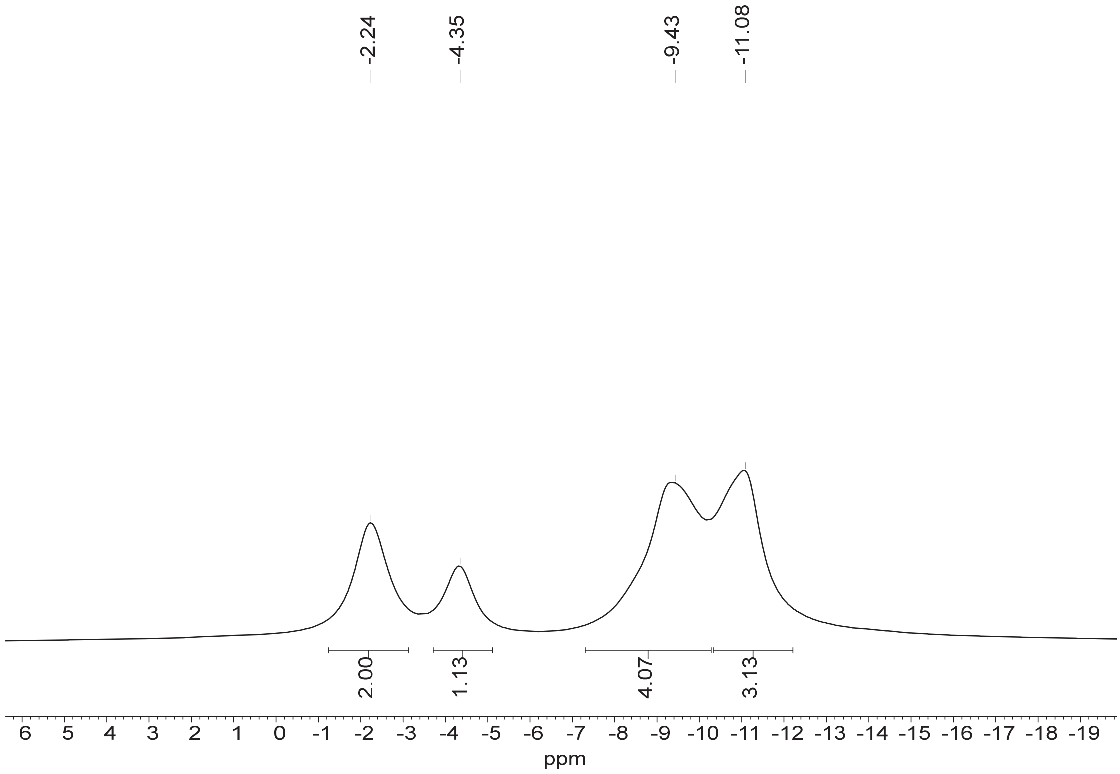
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



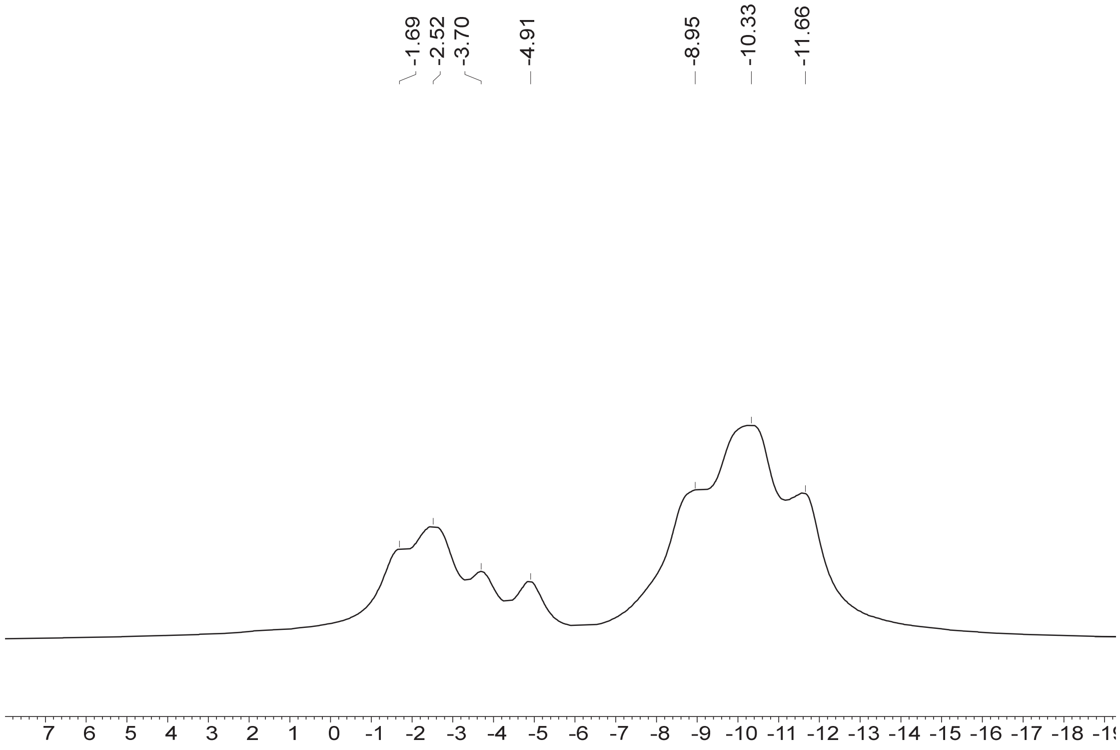
^{1}H NMR (500 MHz, CDCl$_3$)



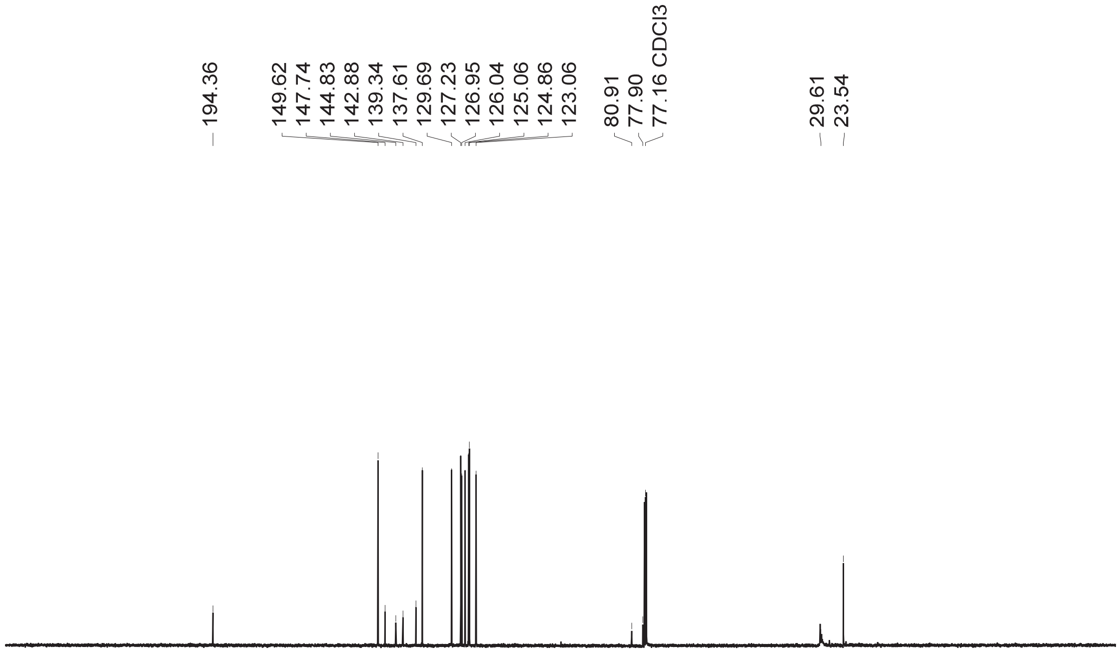
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



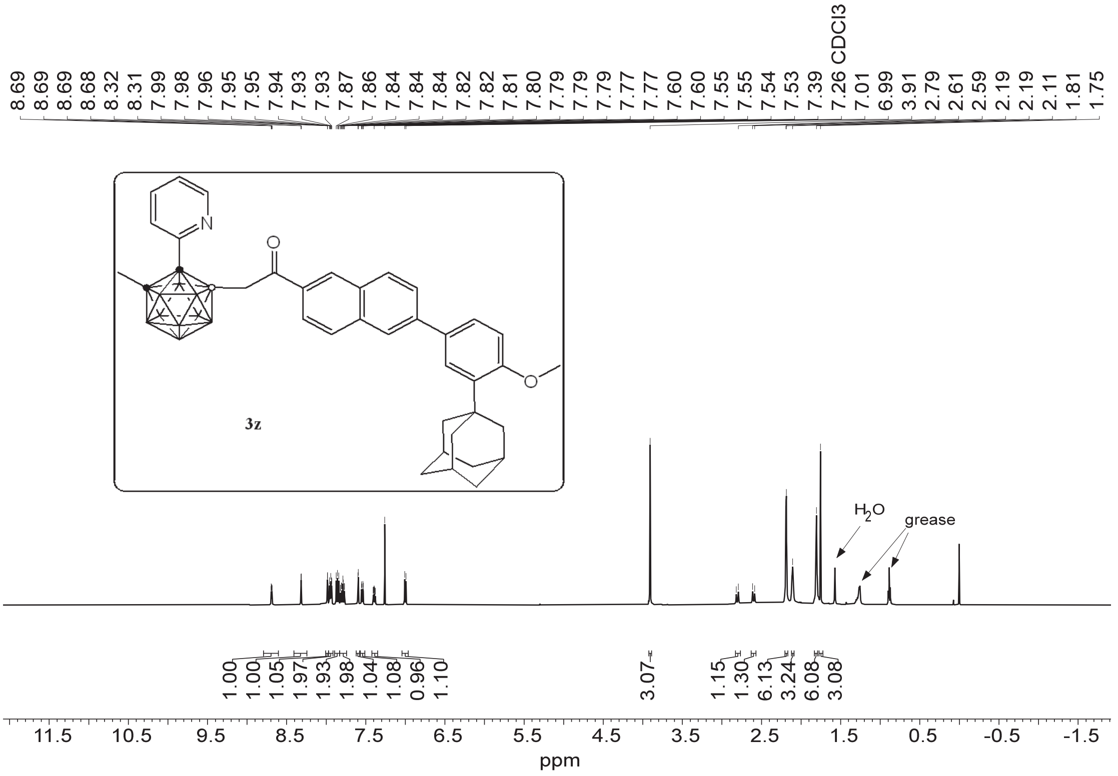
^{11}B NMR (160 MHz, $CDCl_3$)



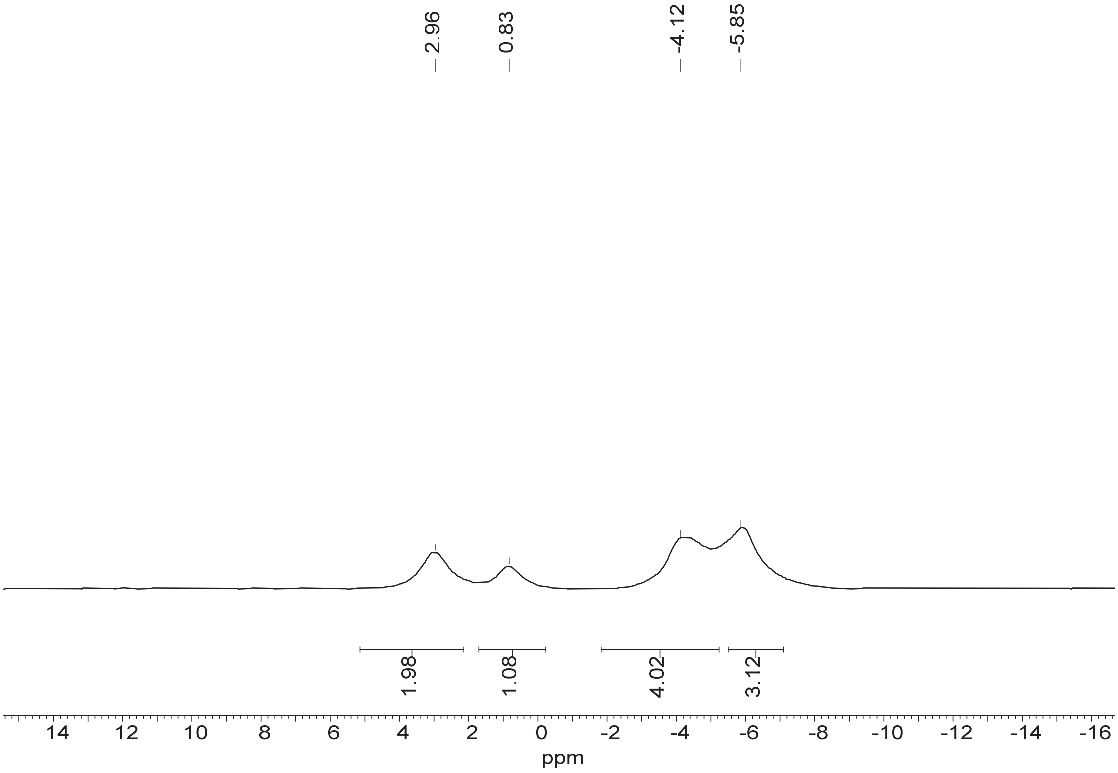
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



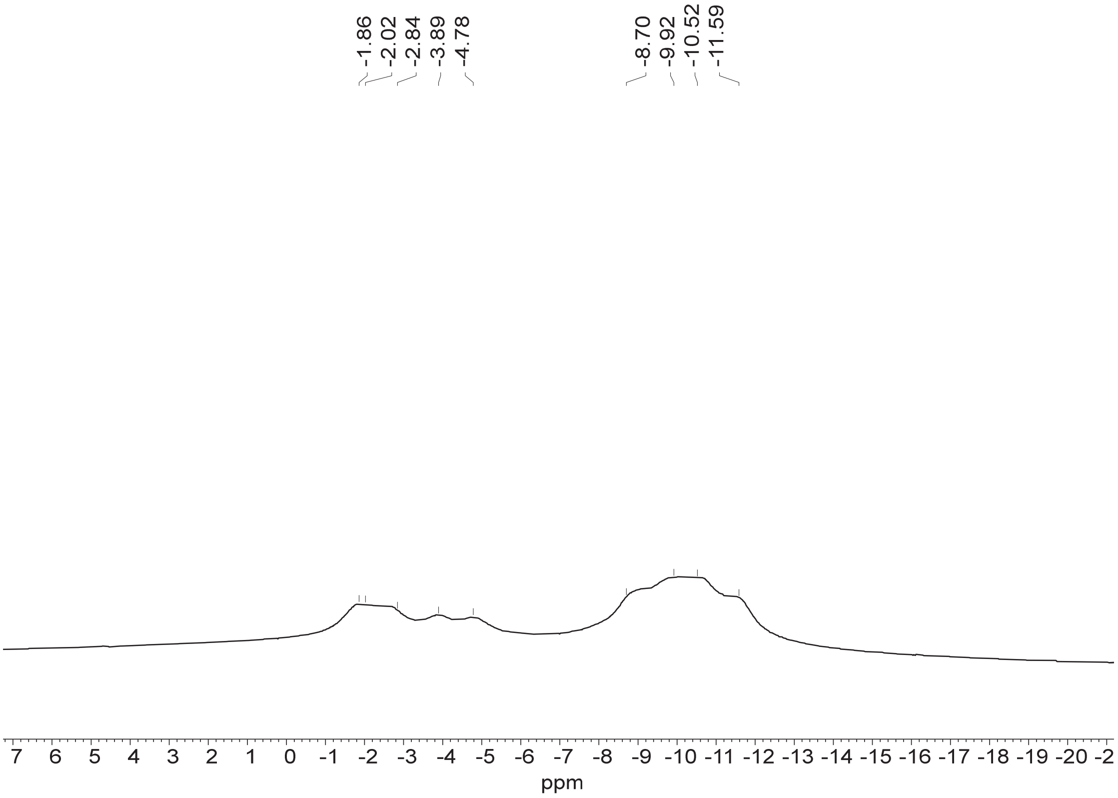
^{1}H NMR (500 MHz, CDCl$_3$)



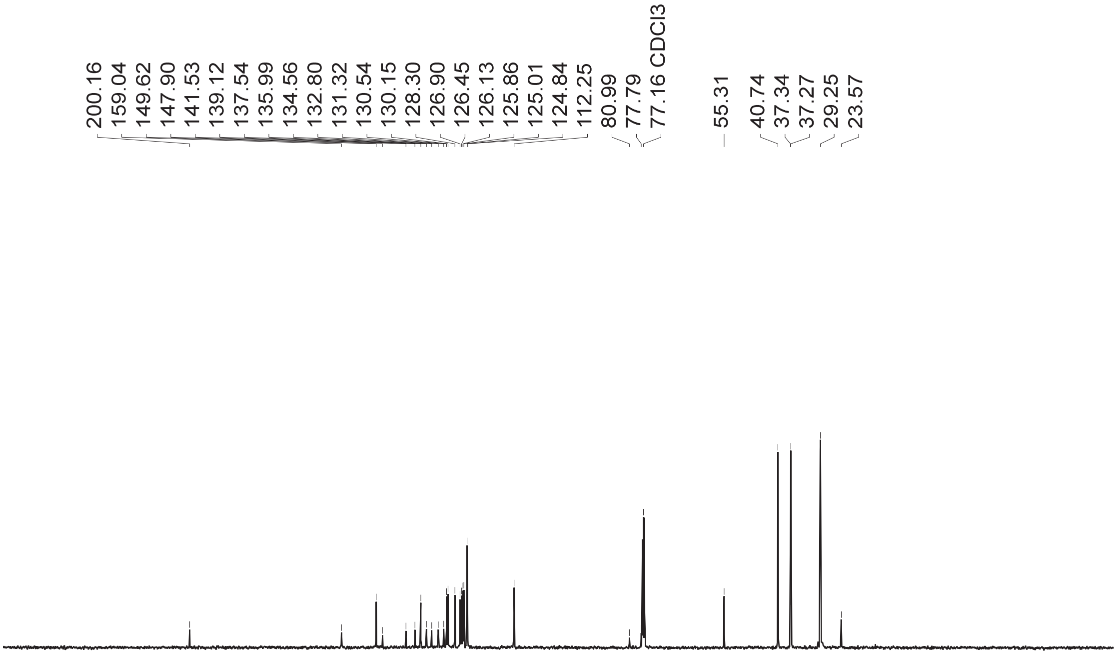
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



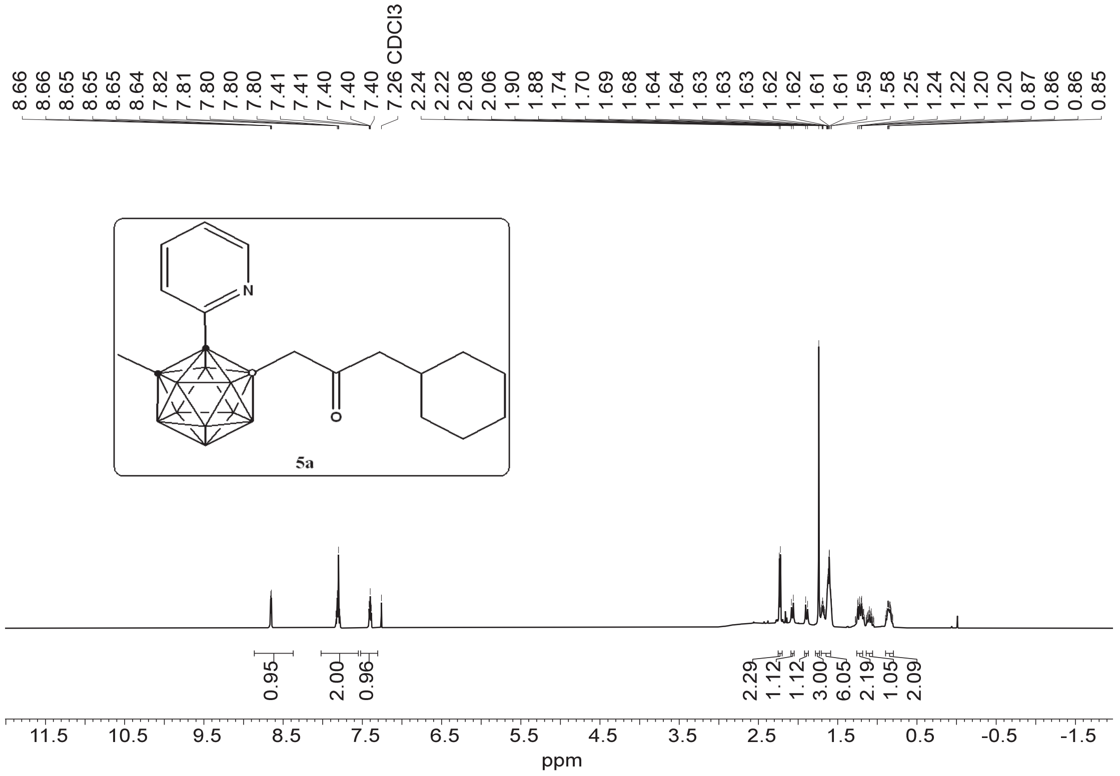
^{11}B NMR (160 MHz, $CDCl_3$)



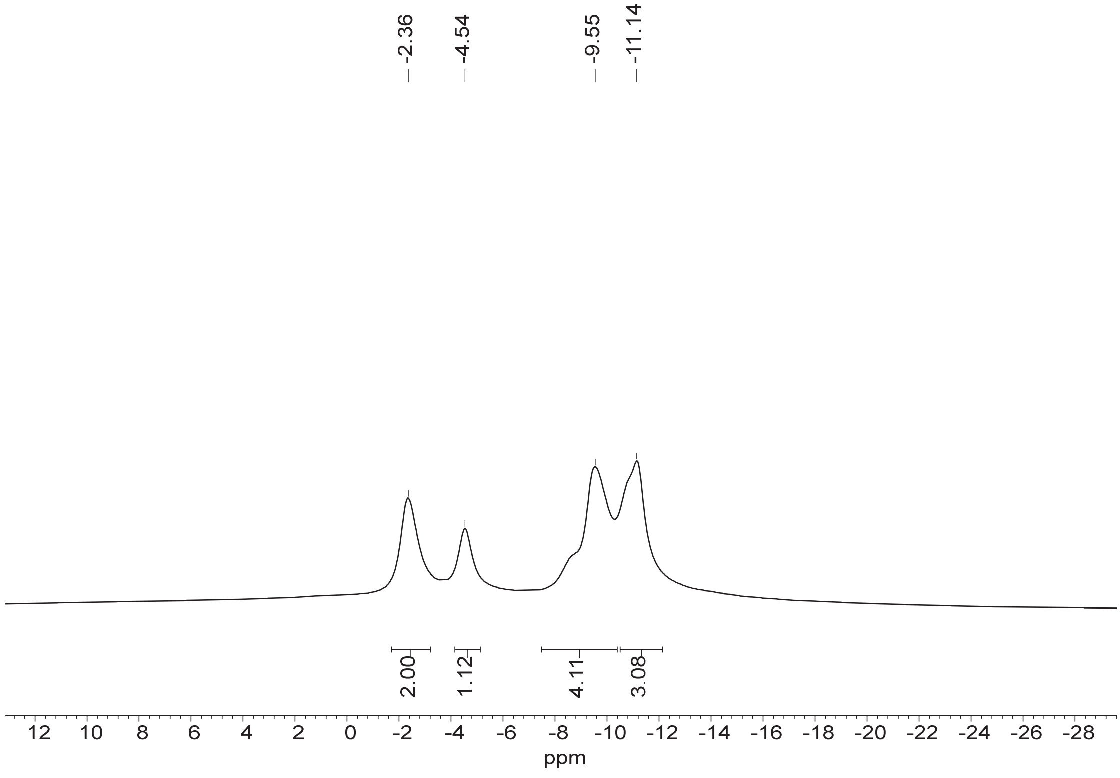
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



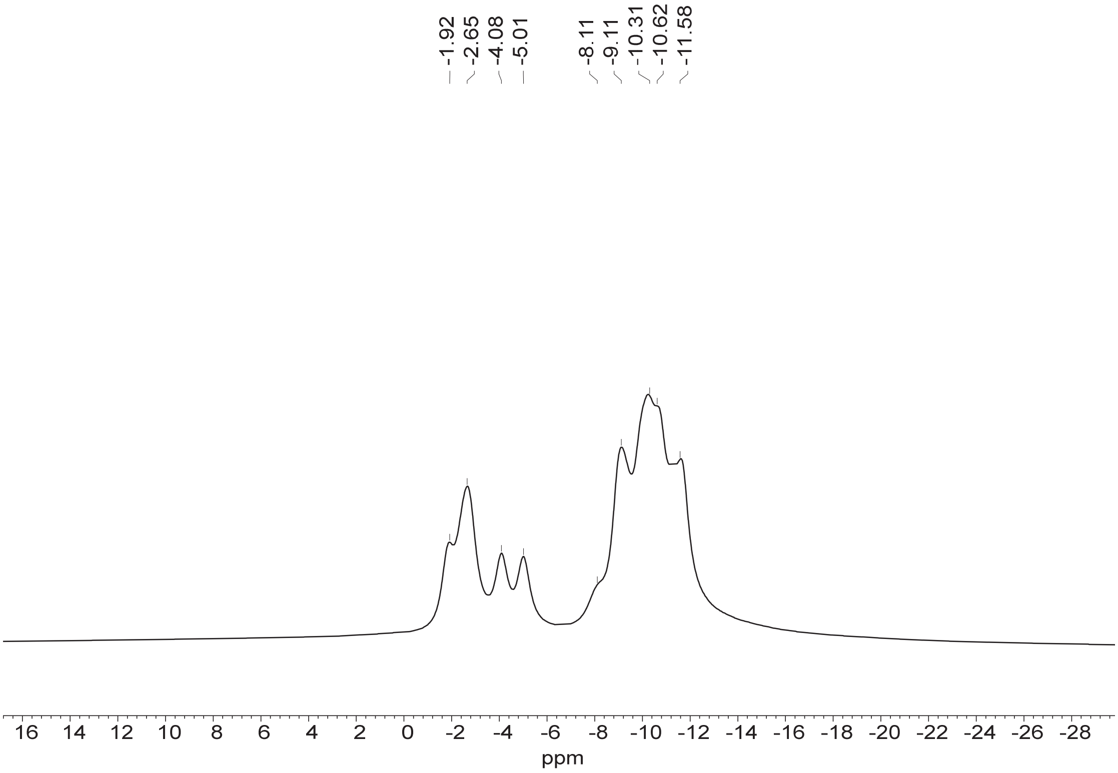
^{1}H NMR (500 MHz, $CDCl_3$)



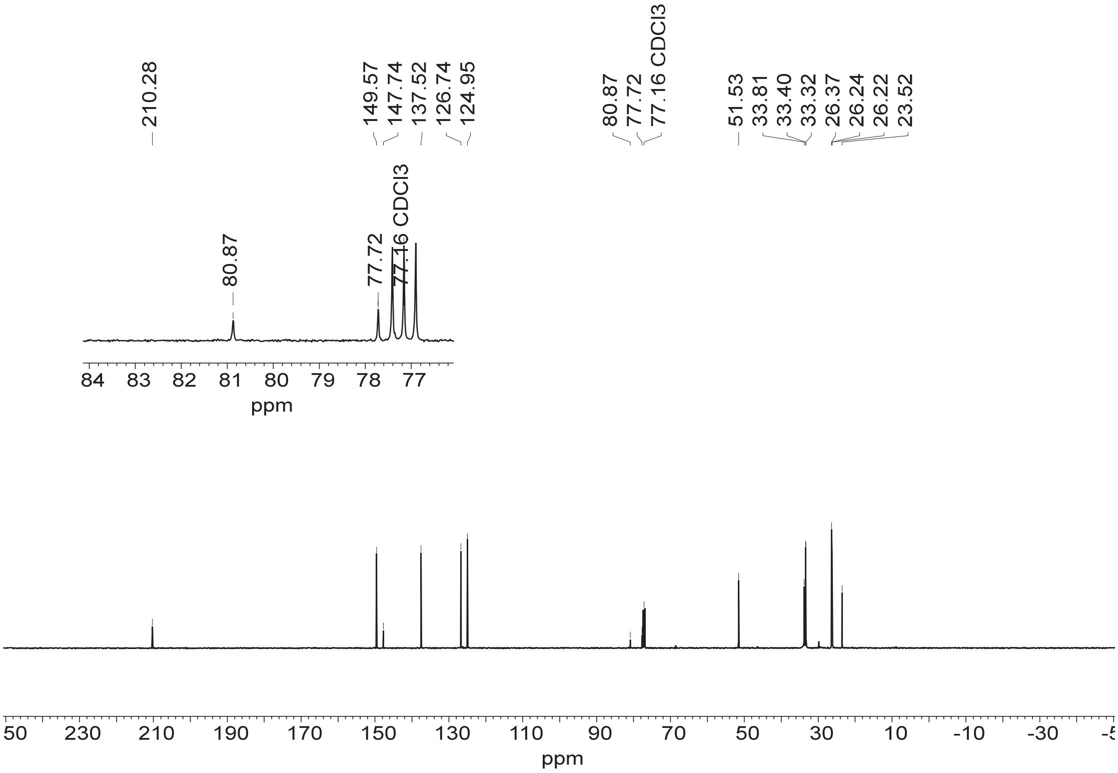
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



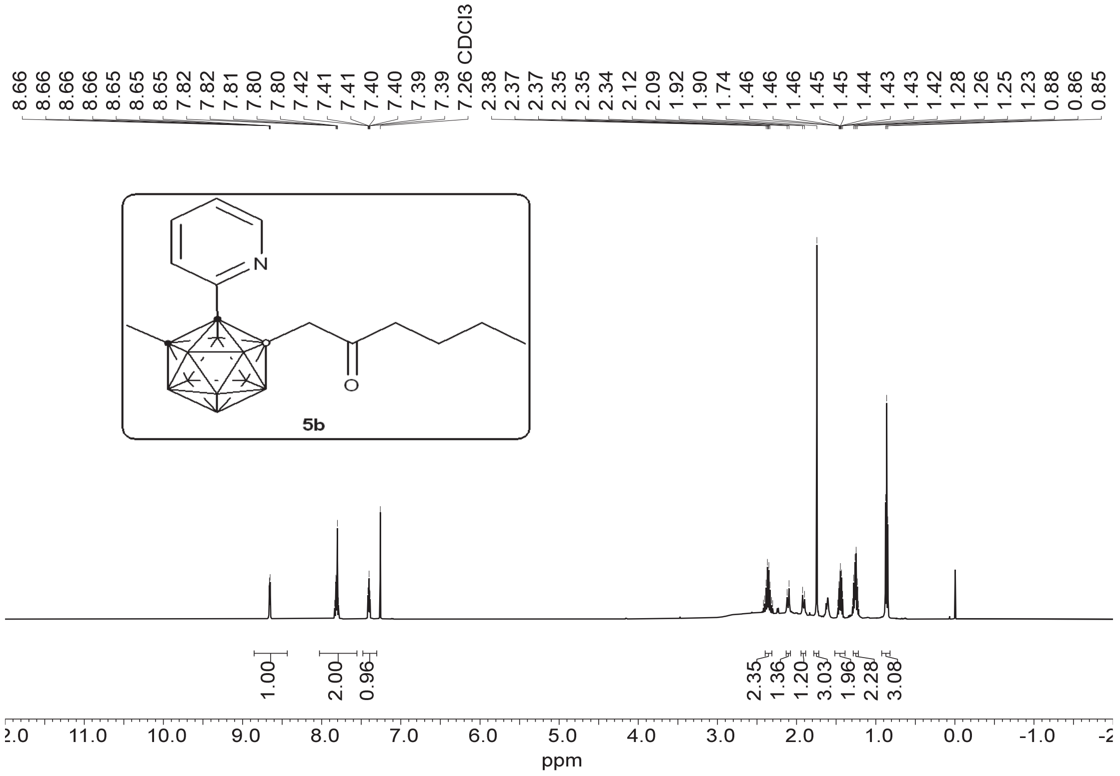
^{11}B NMR (160 MHz, CDCl$_3$)



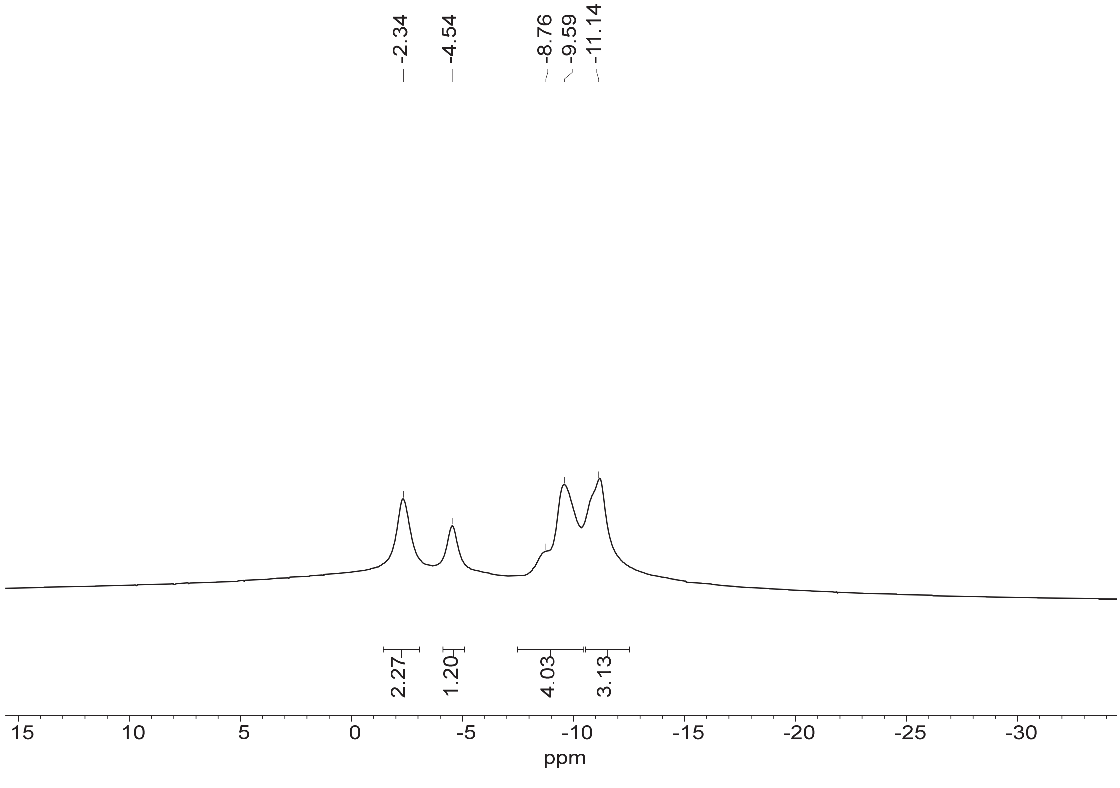
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



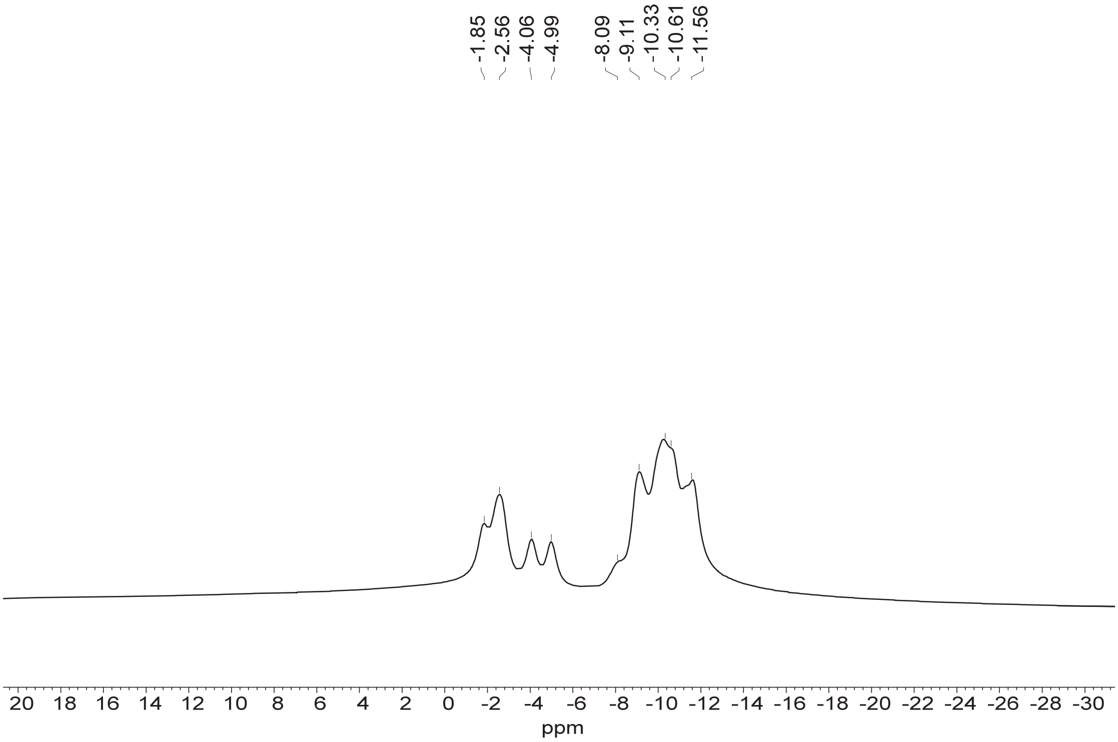
^1H NMR (500 MHz, $CDCl_3$)



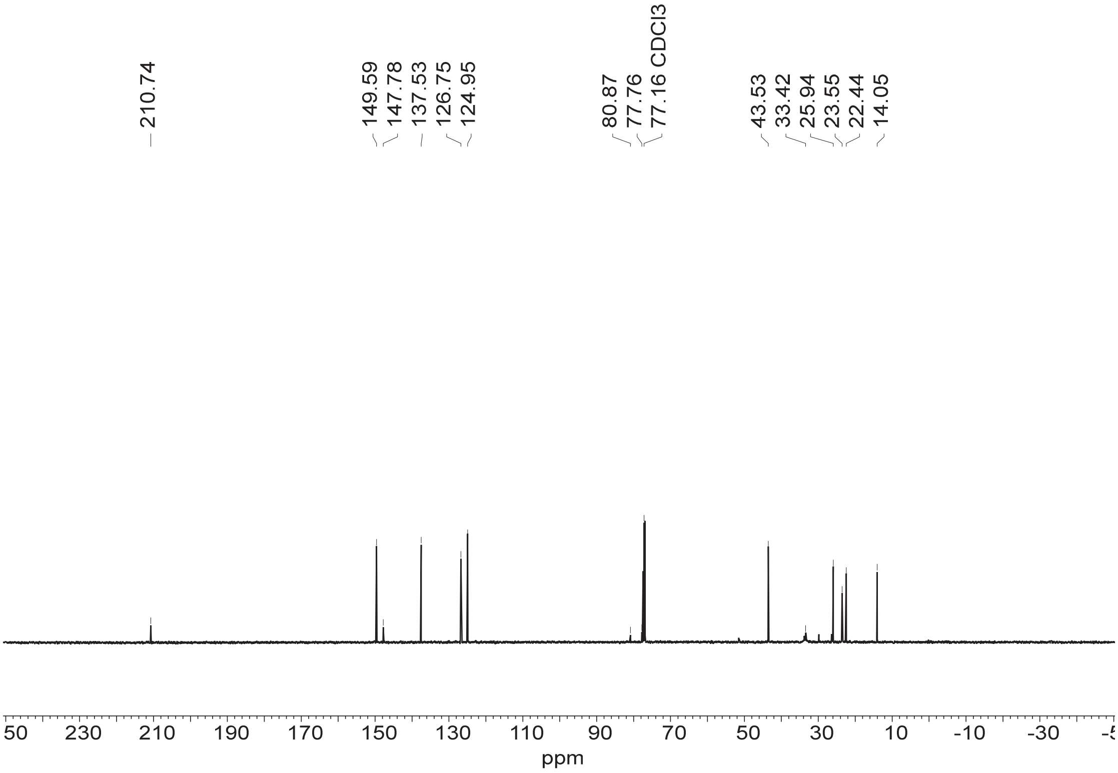
$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$)



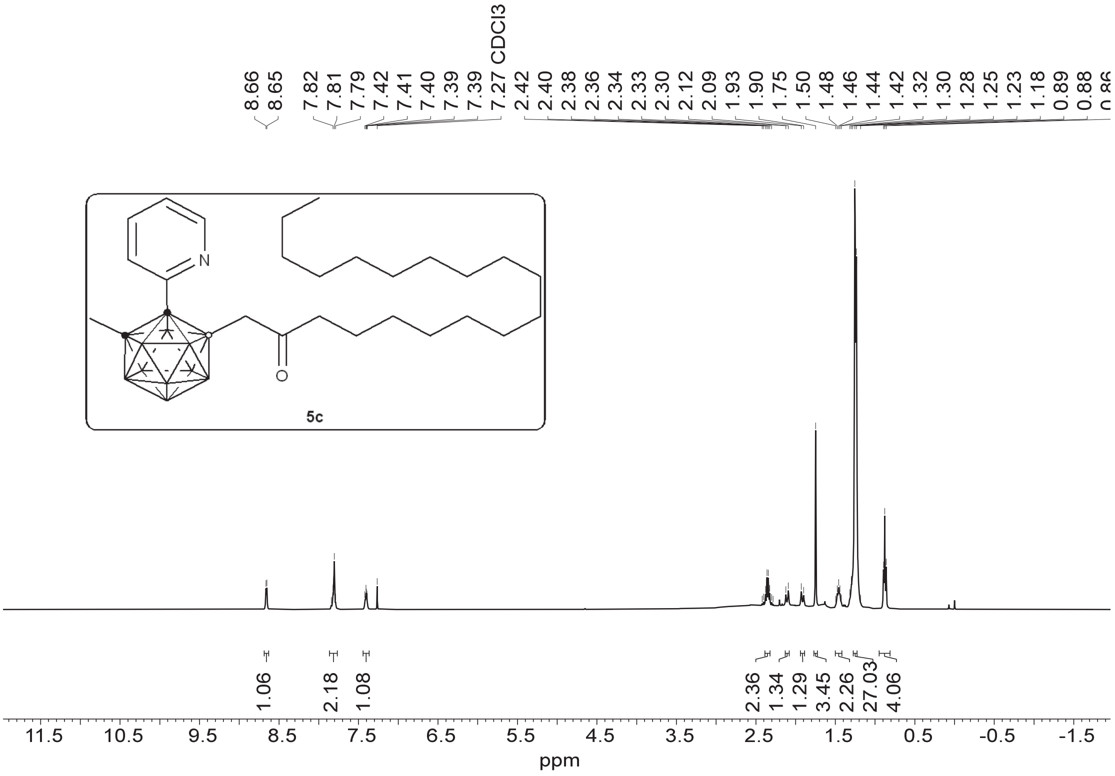
^{11}B NMR (160 MHz, $CDCl_3$)



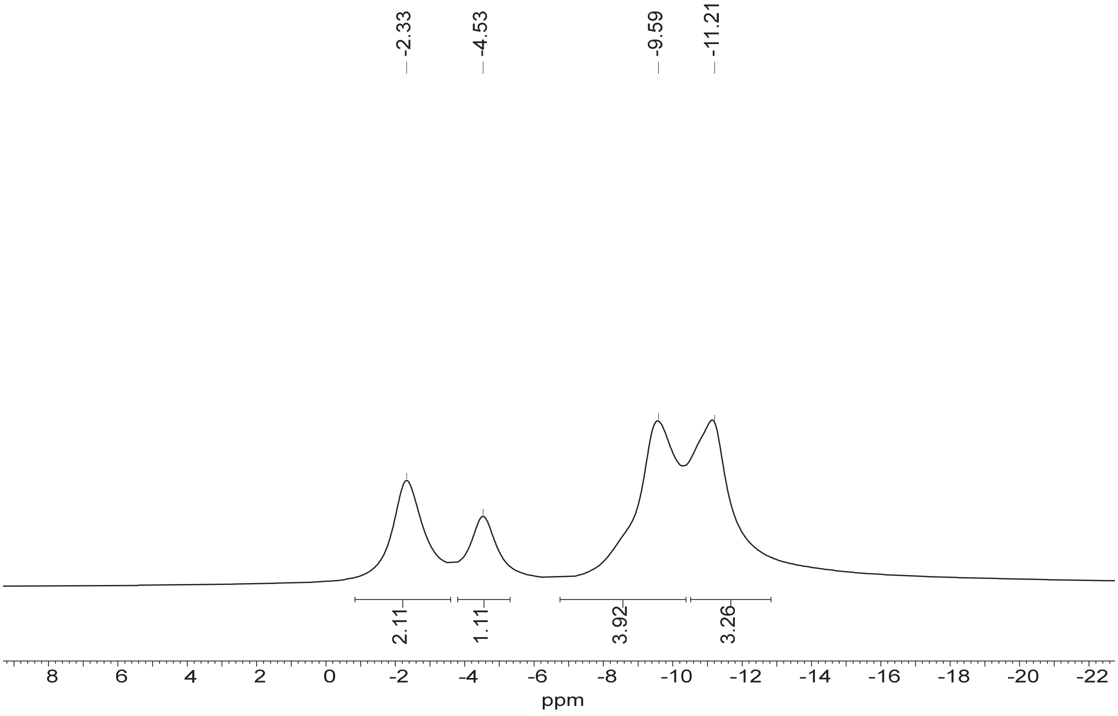
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



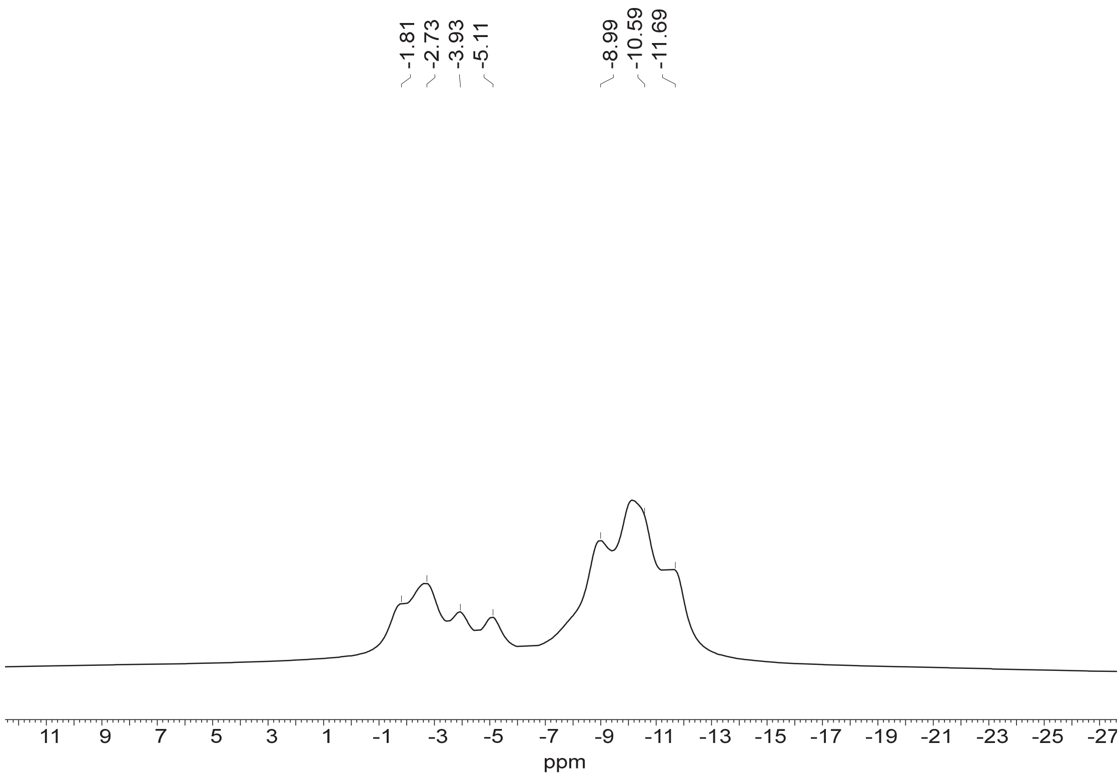
^{1}H NMR (400 MHz, $CDCl_3$)



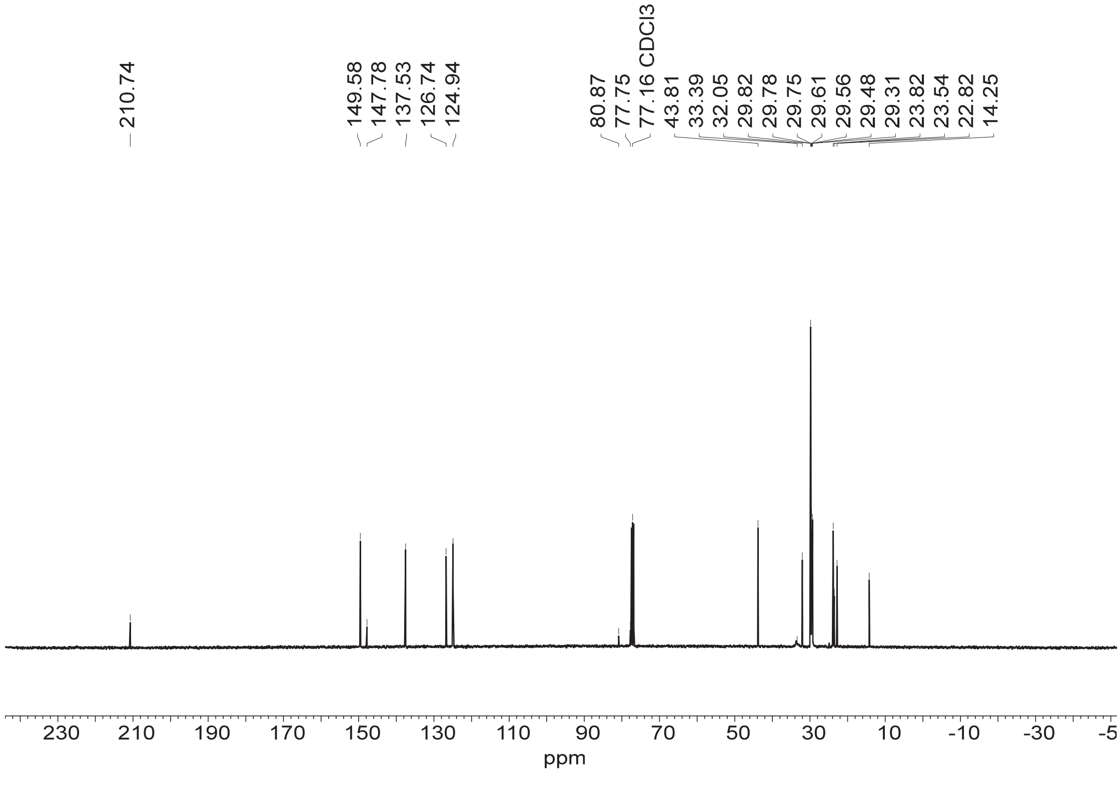
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



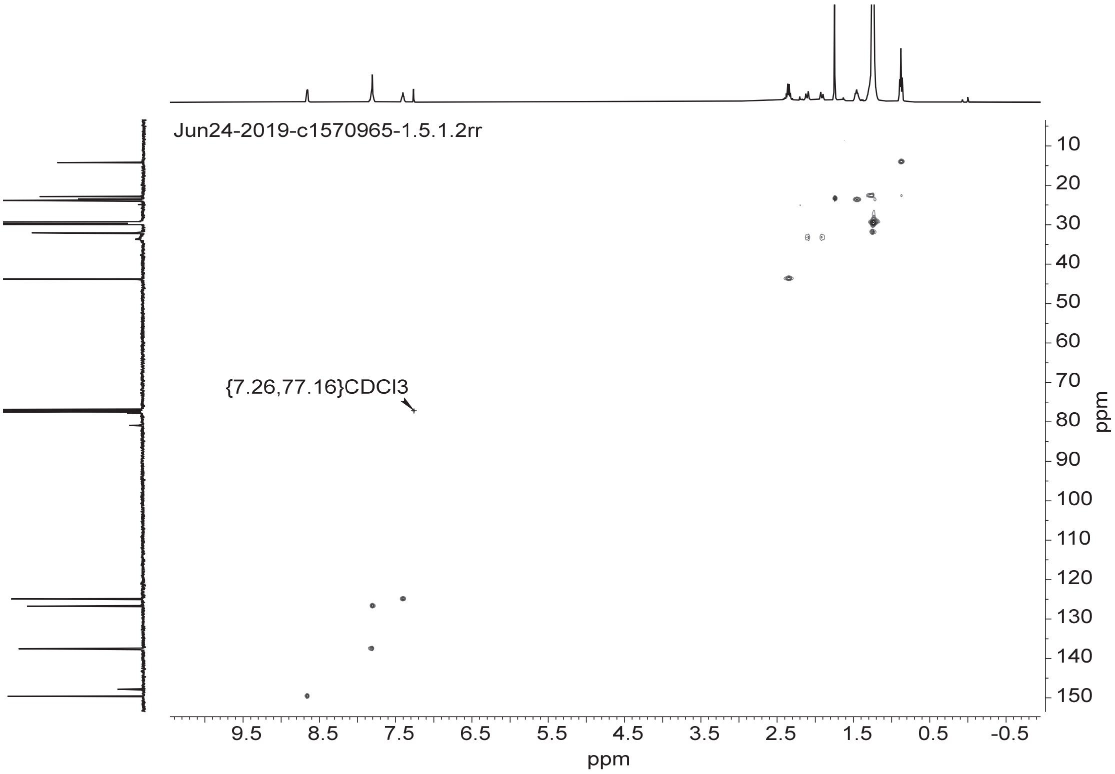
^{11}B NMR (128 MHz, $CDCl_3$)



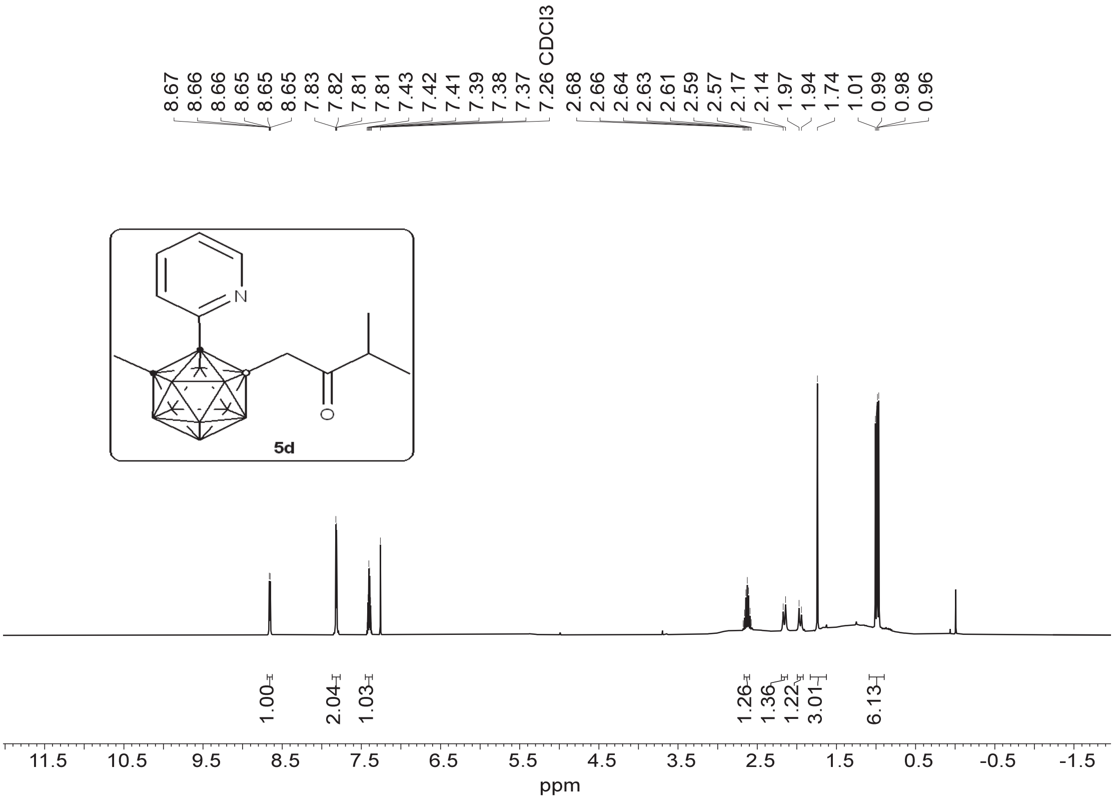
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



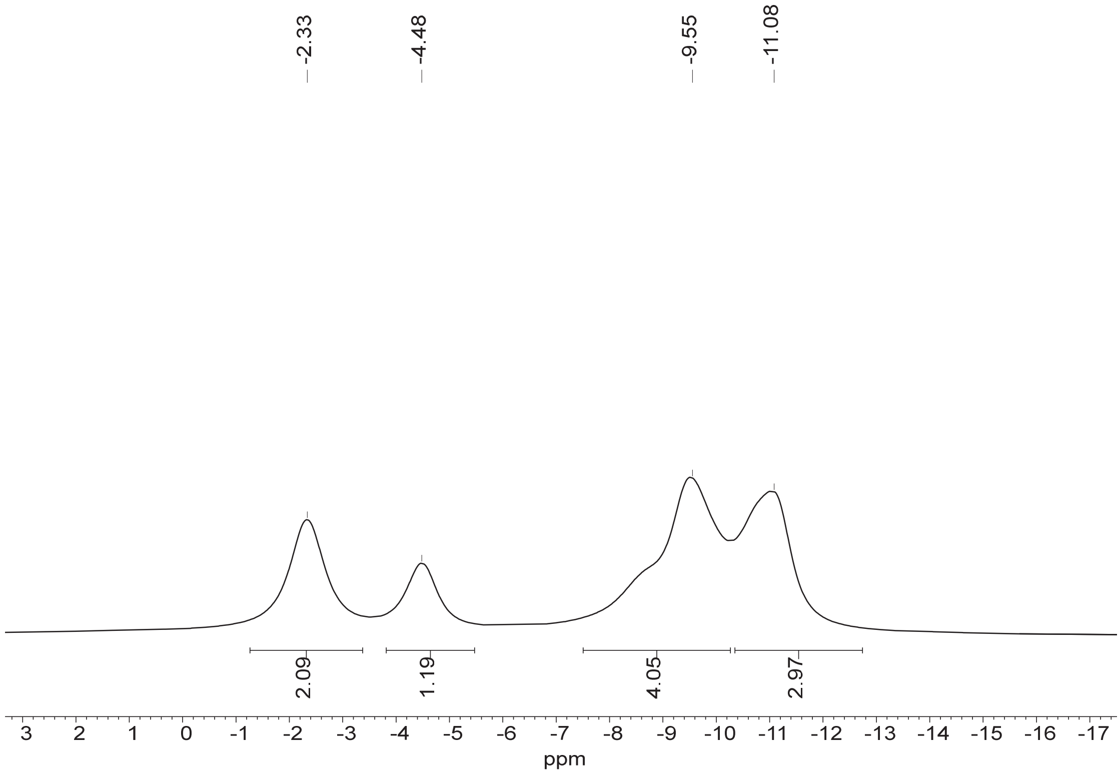
^{1}H-^{13}C HSQC NMR (400 MHz, CDCl$_3$)



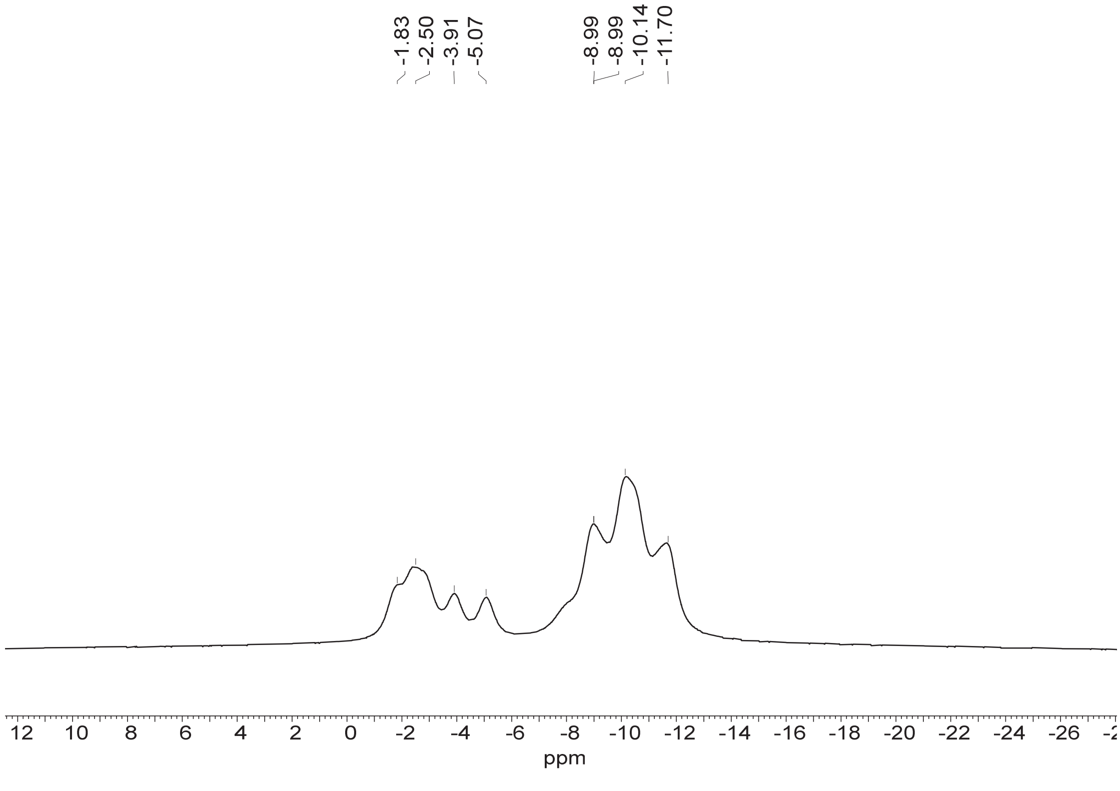
^{1}H NMR (400 MHz, CDCl$_3$)



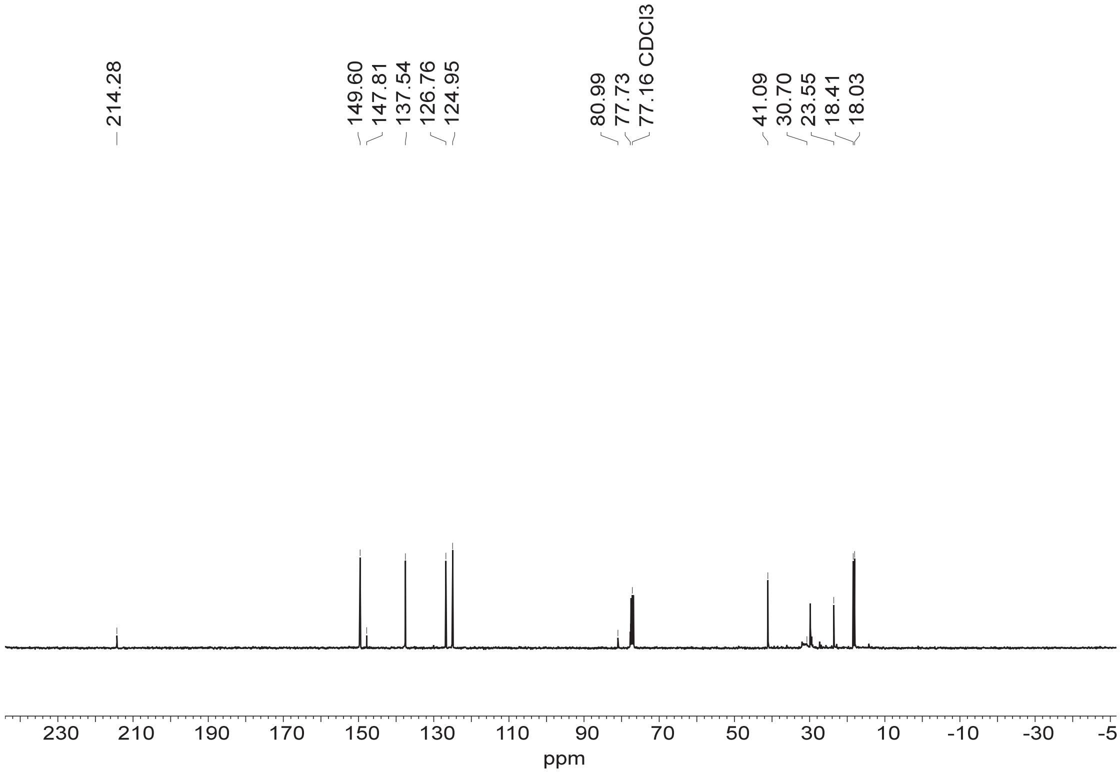
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



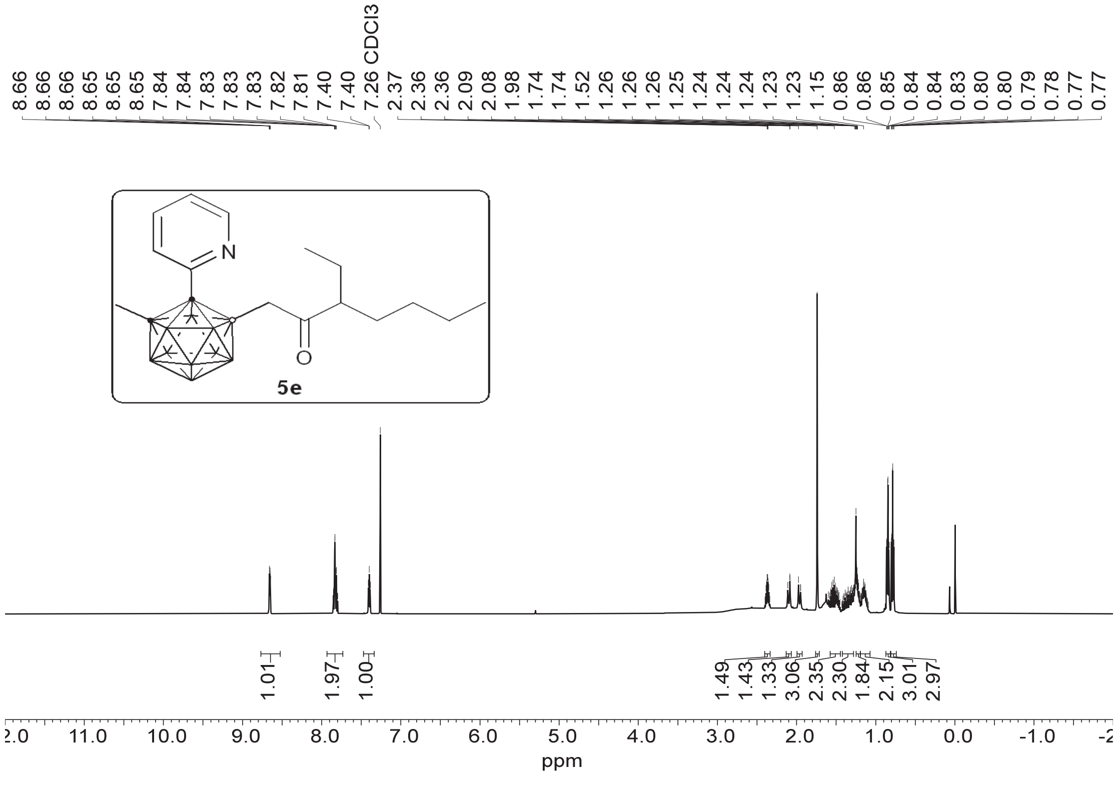
^{11}B NMR (128 MHz, $CDCl_3$)



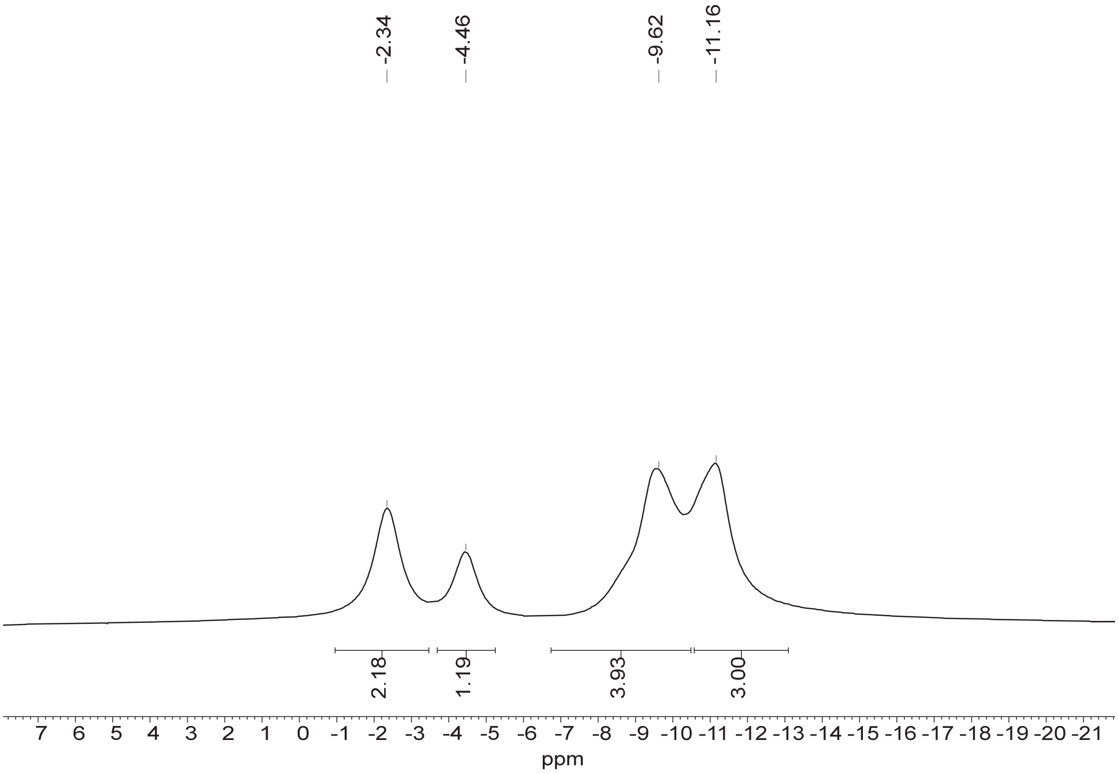
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



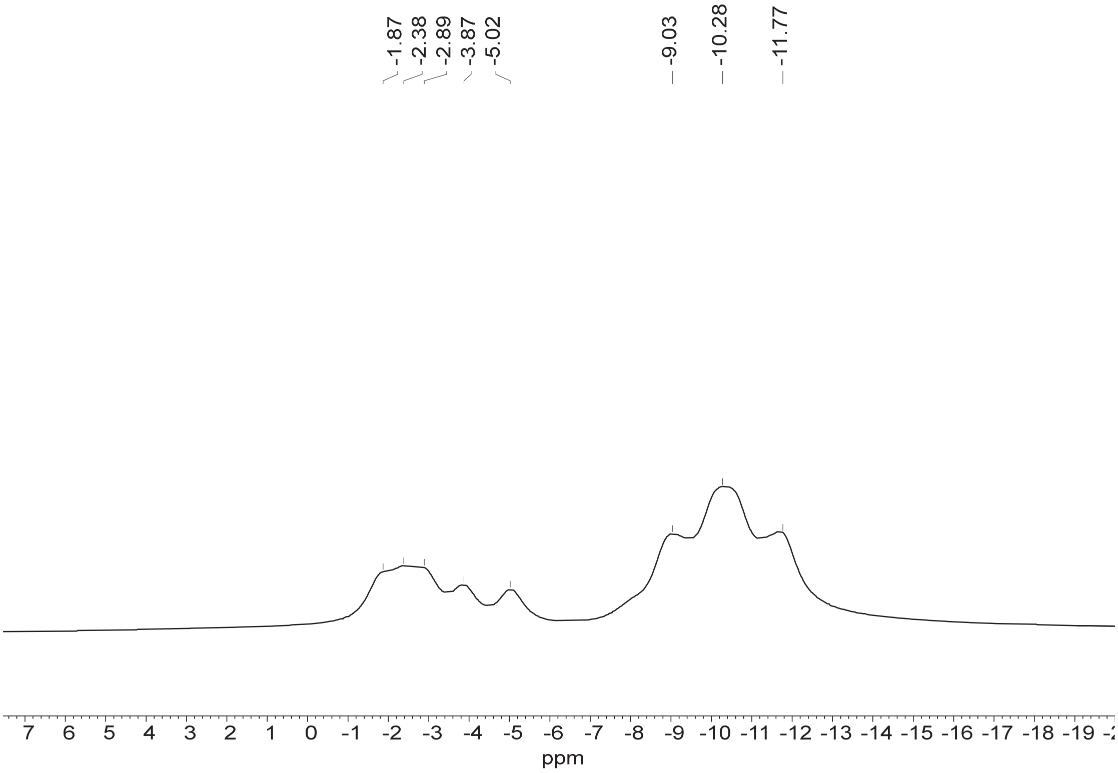
^1H NMR (500 MHz, $CDCl_3$)



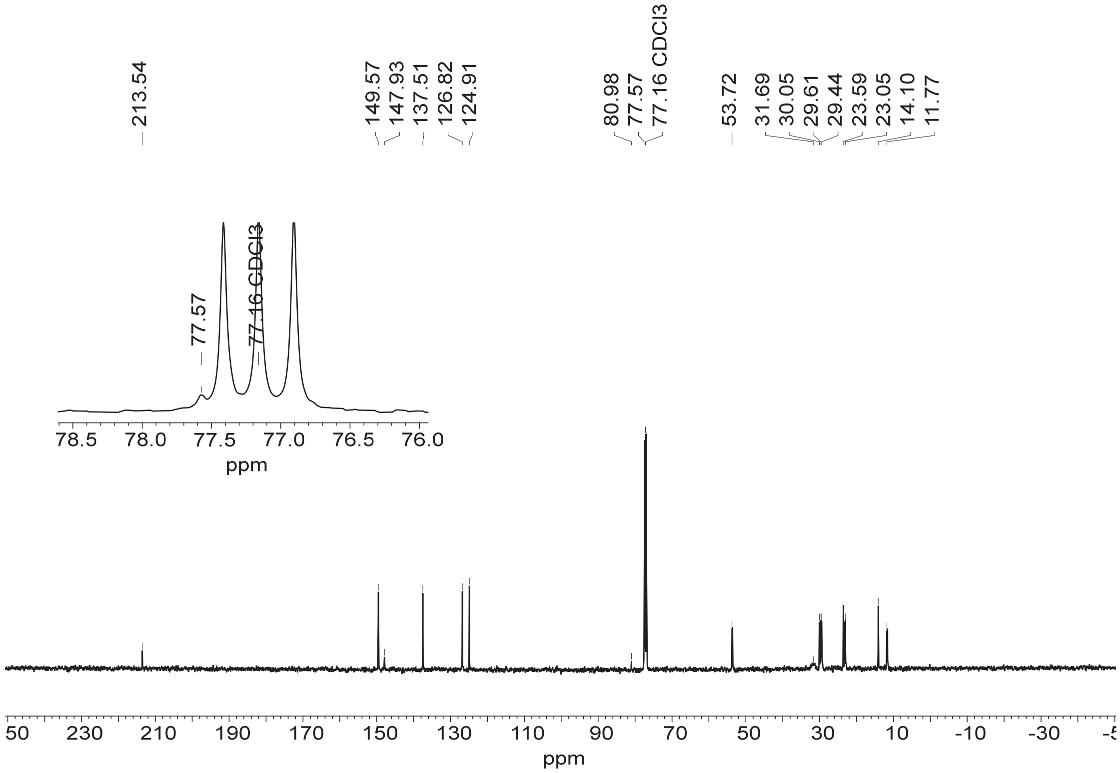
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



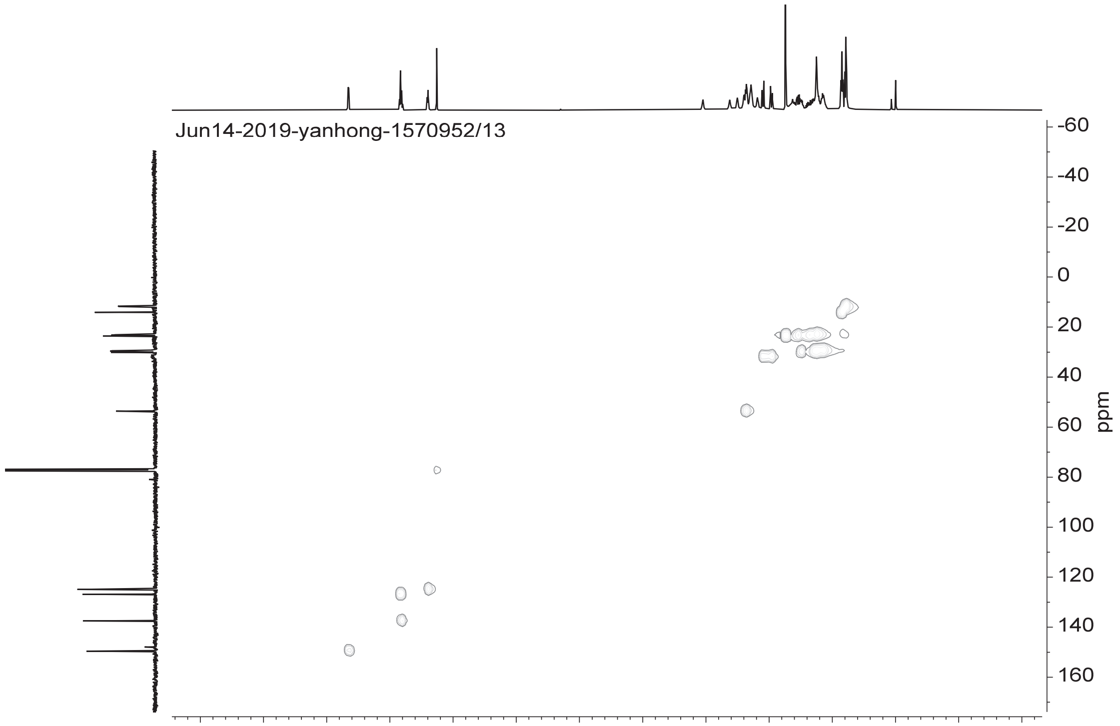
^{11}B NMR (128 MHz, $CDCl_3$)



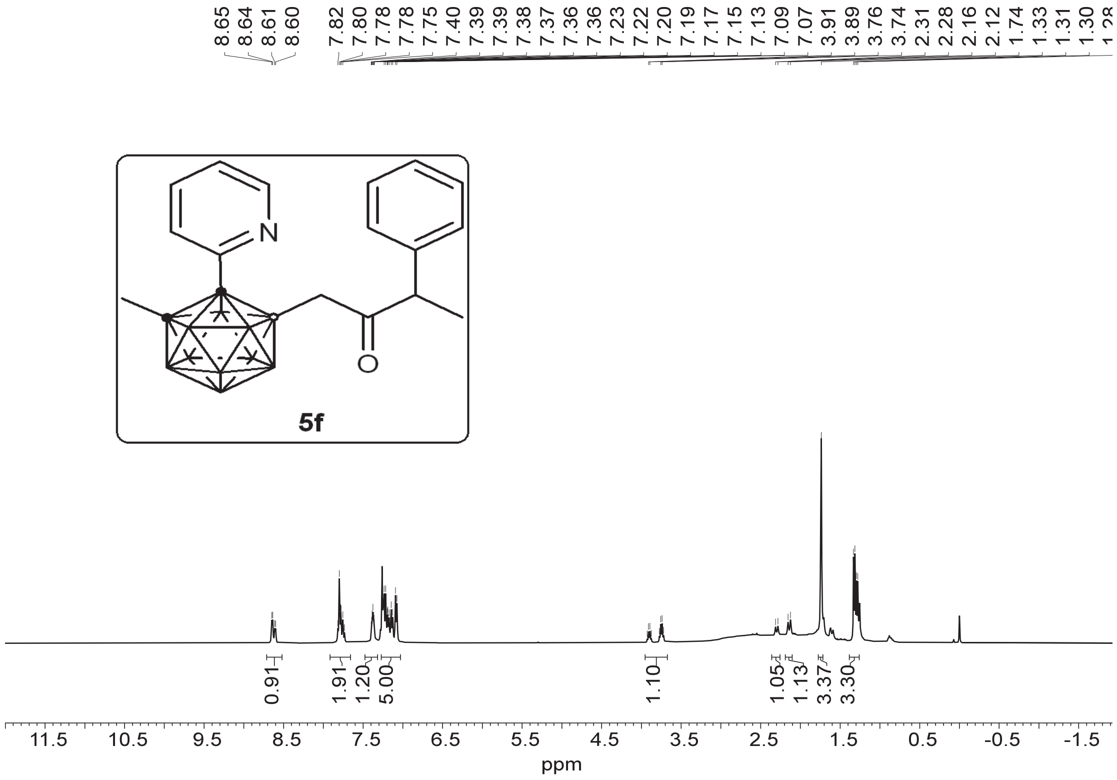
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



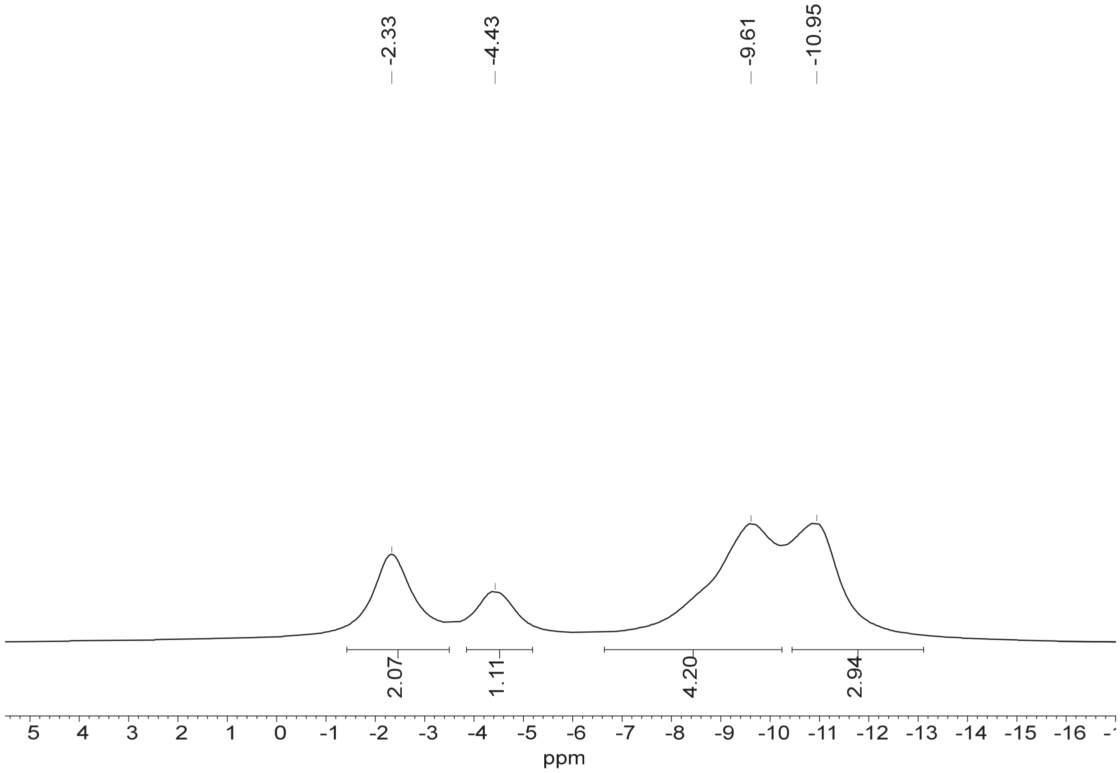
^{1}H-^{13}C HSQC NMR (500 MHz, $CDCl_3$)



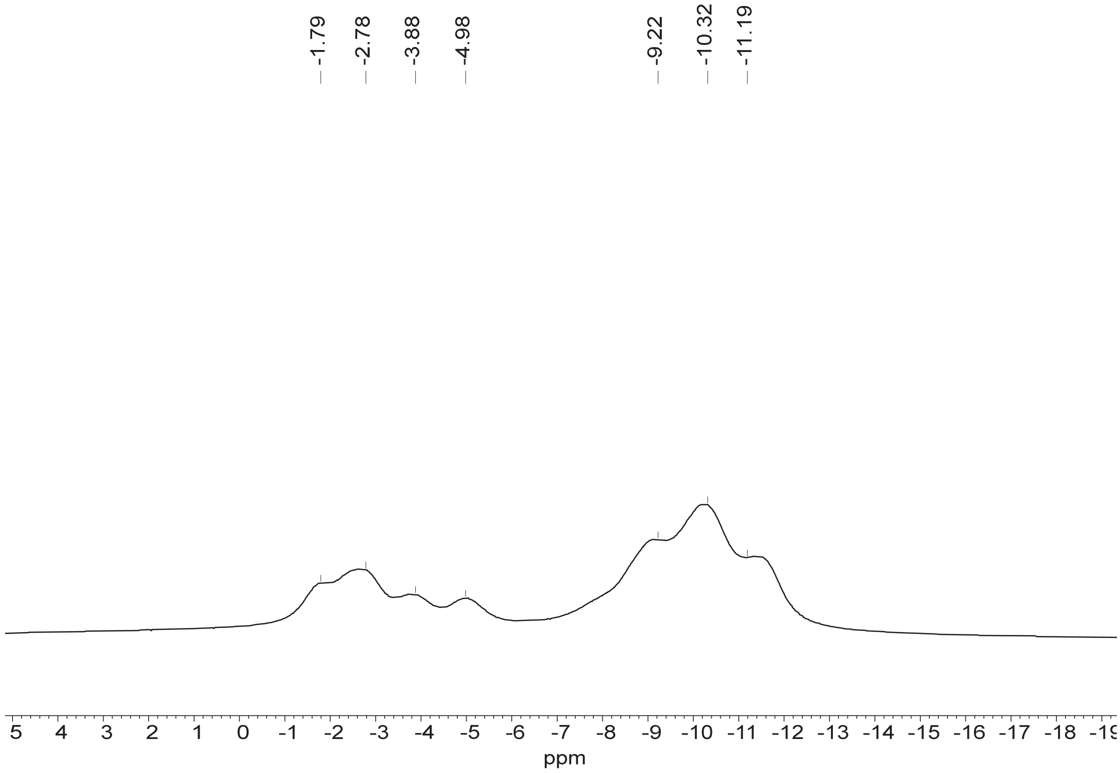
^1H NMR (400 MHz, $CDCl_3$)



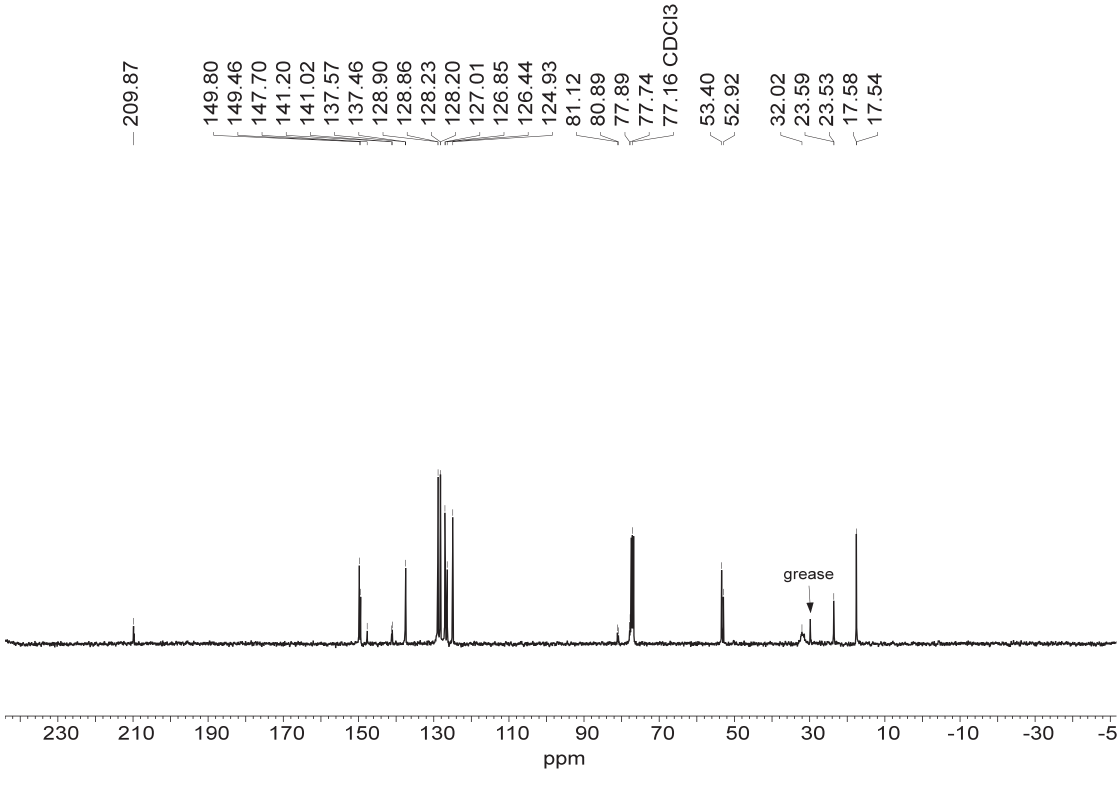
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



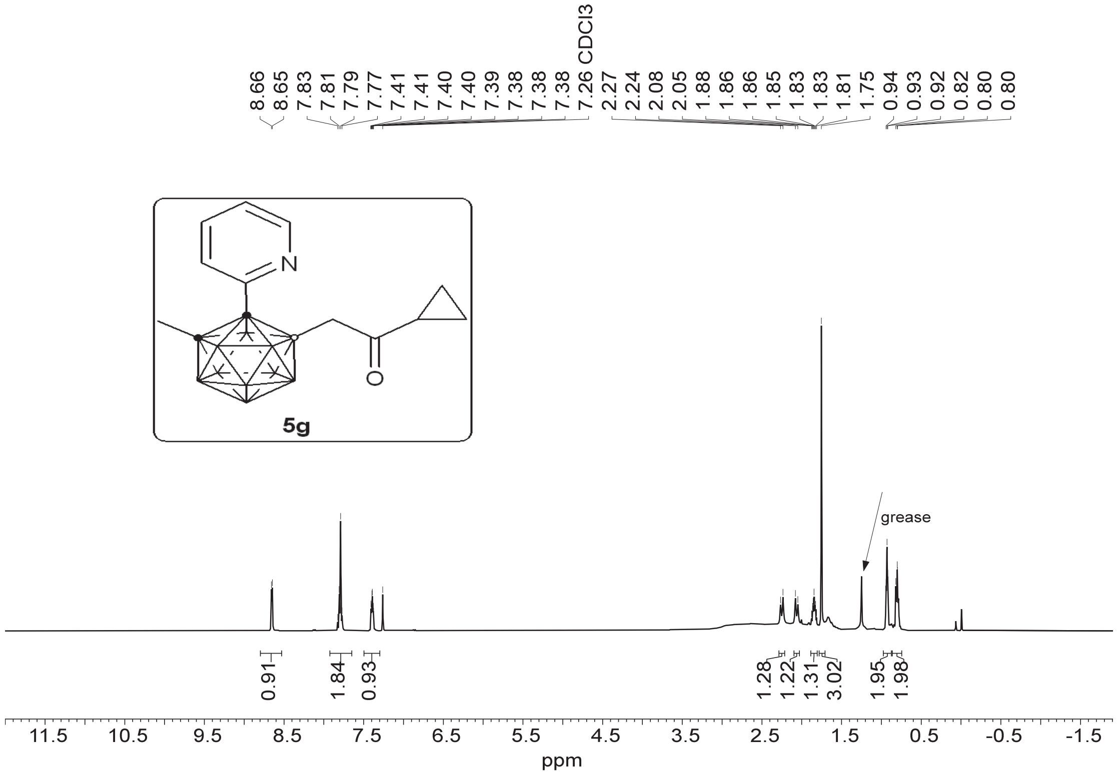
^{11}B NMR (128 MHz, $CDCl_3$)



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



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



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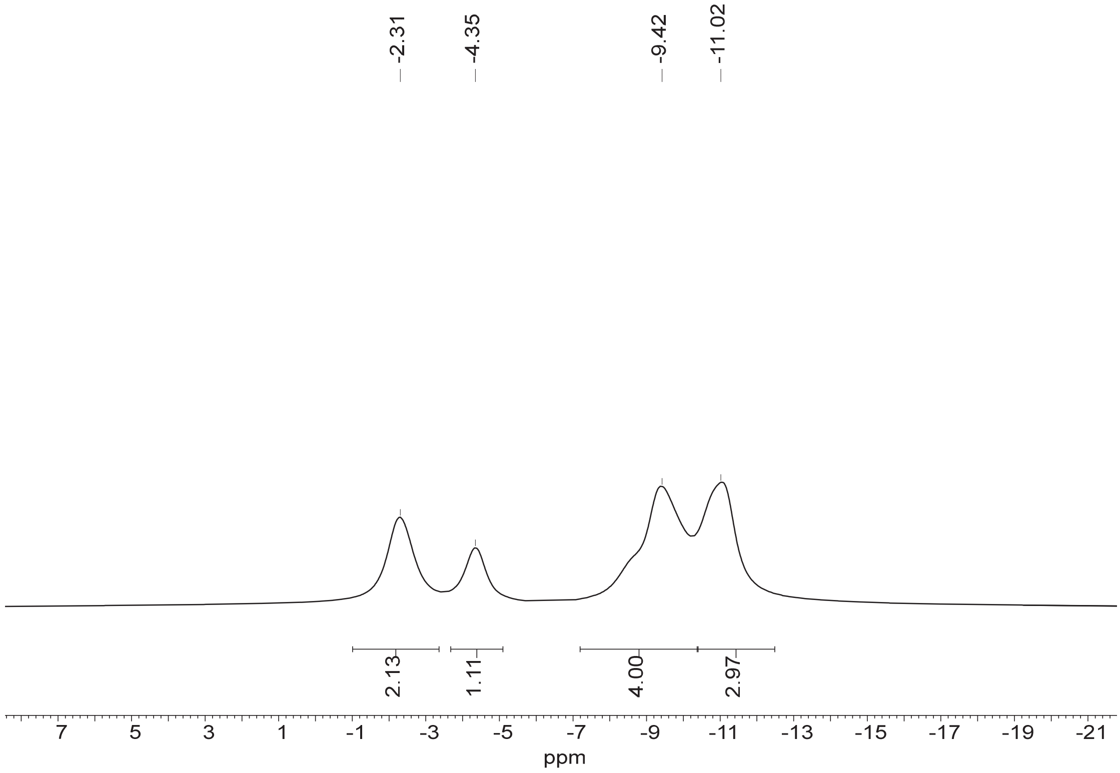

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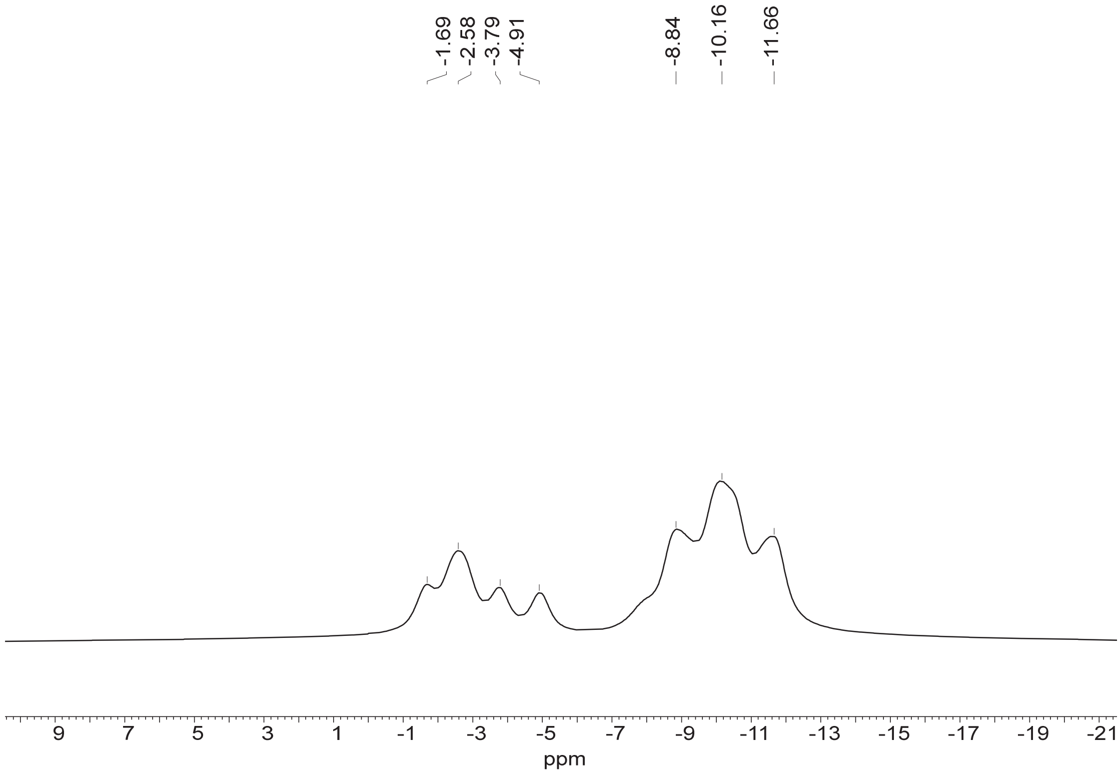

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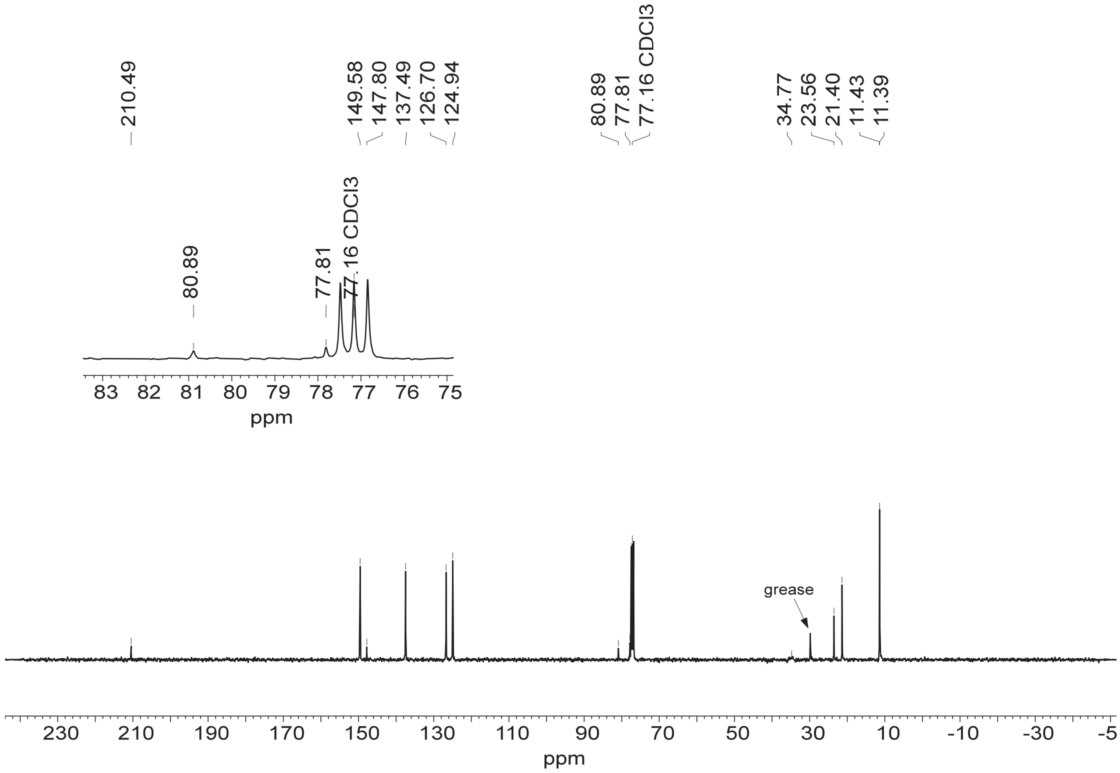

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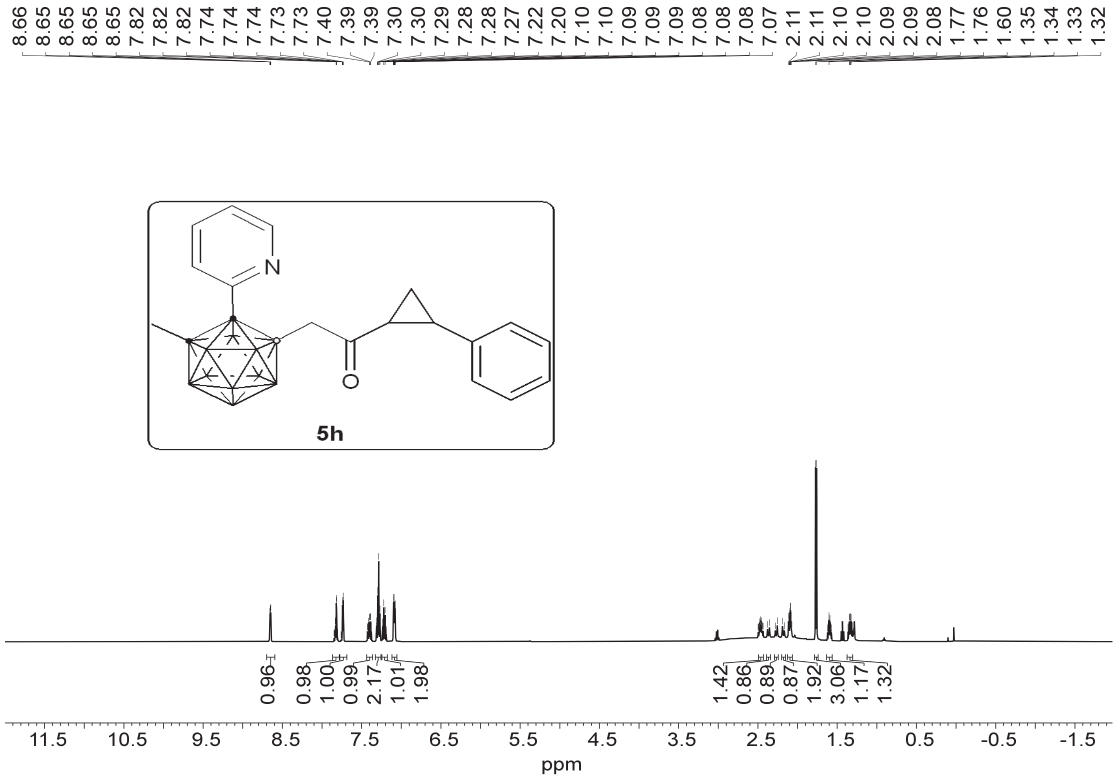
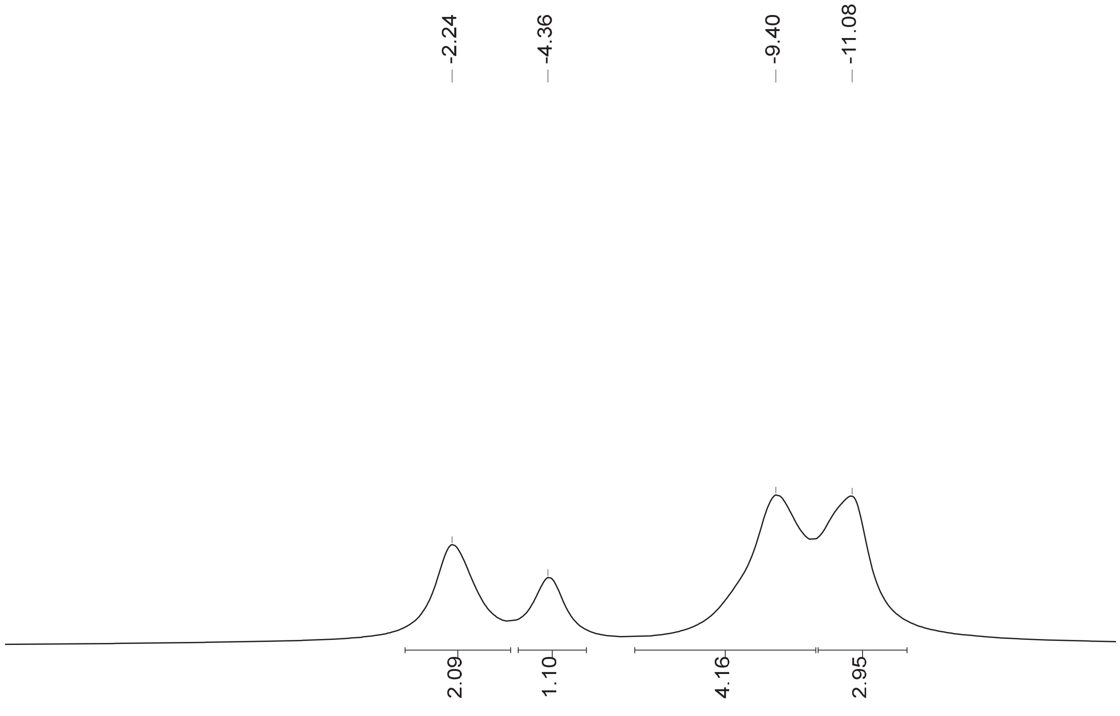
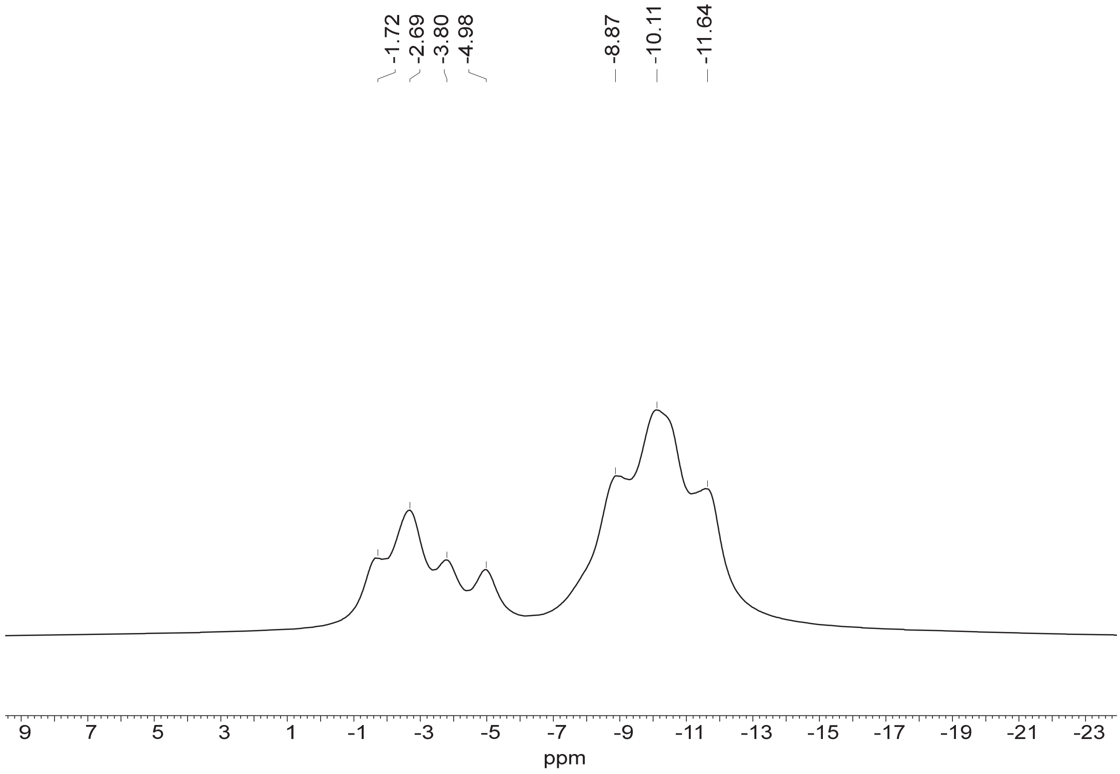


$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, CDCl$_3$)



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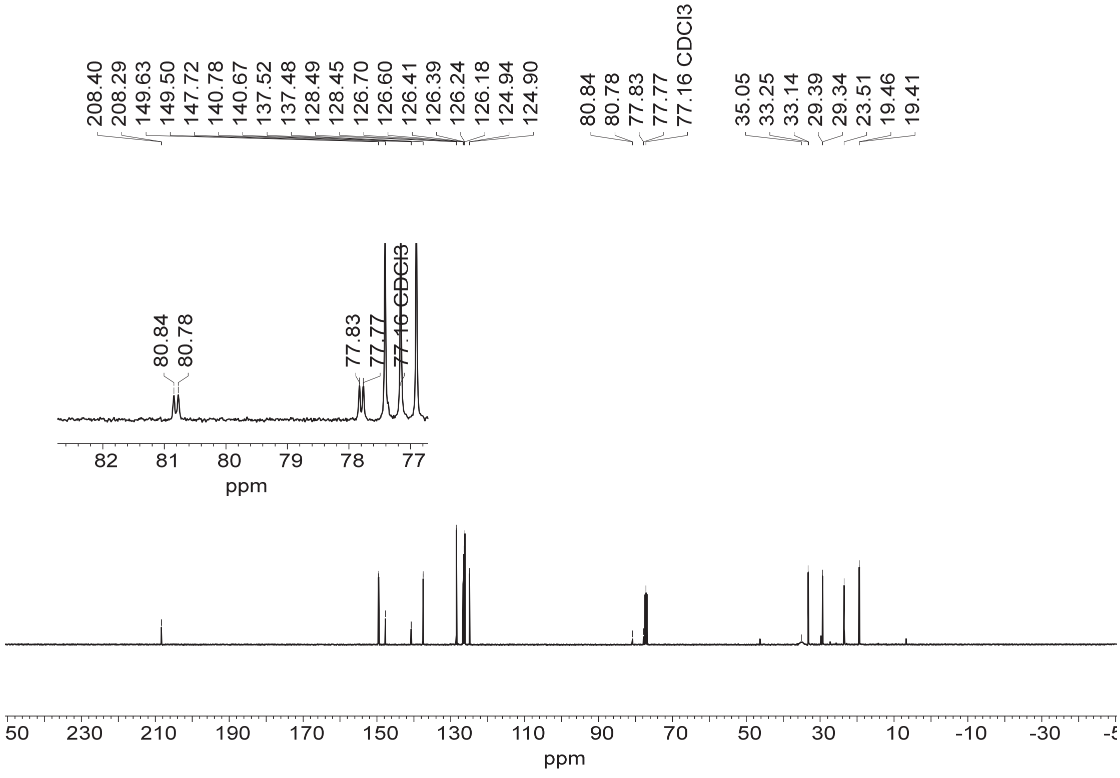

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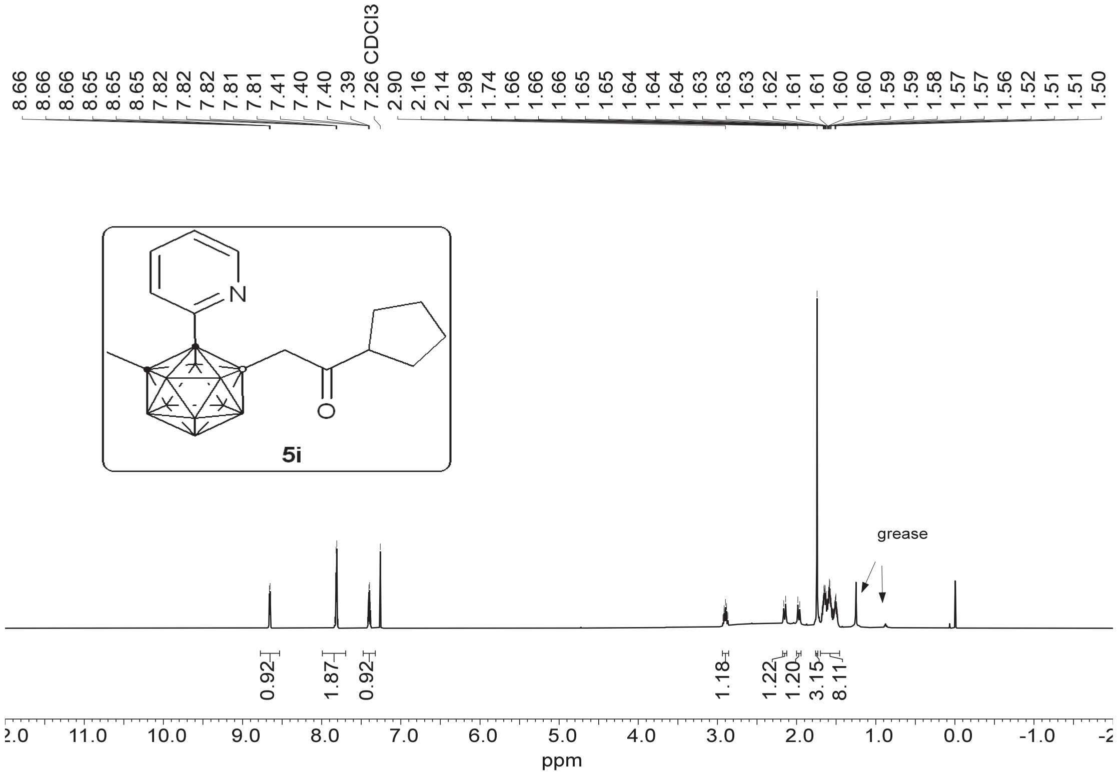
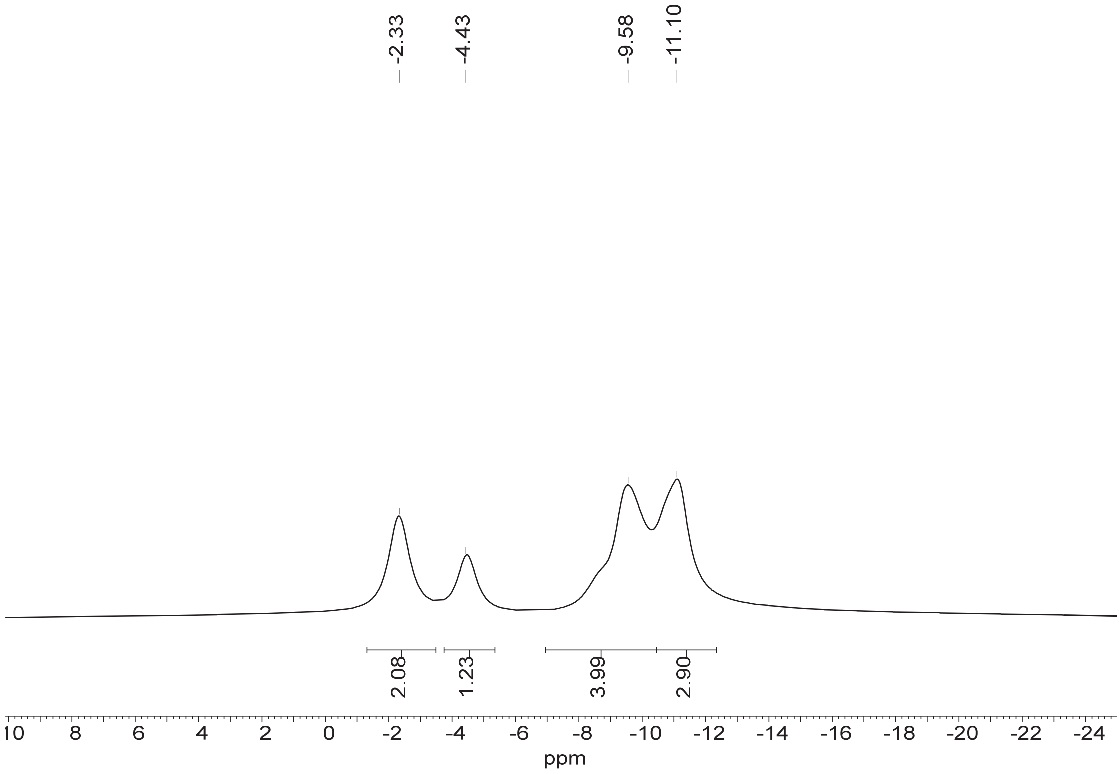
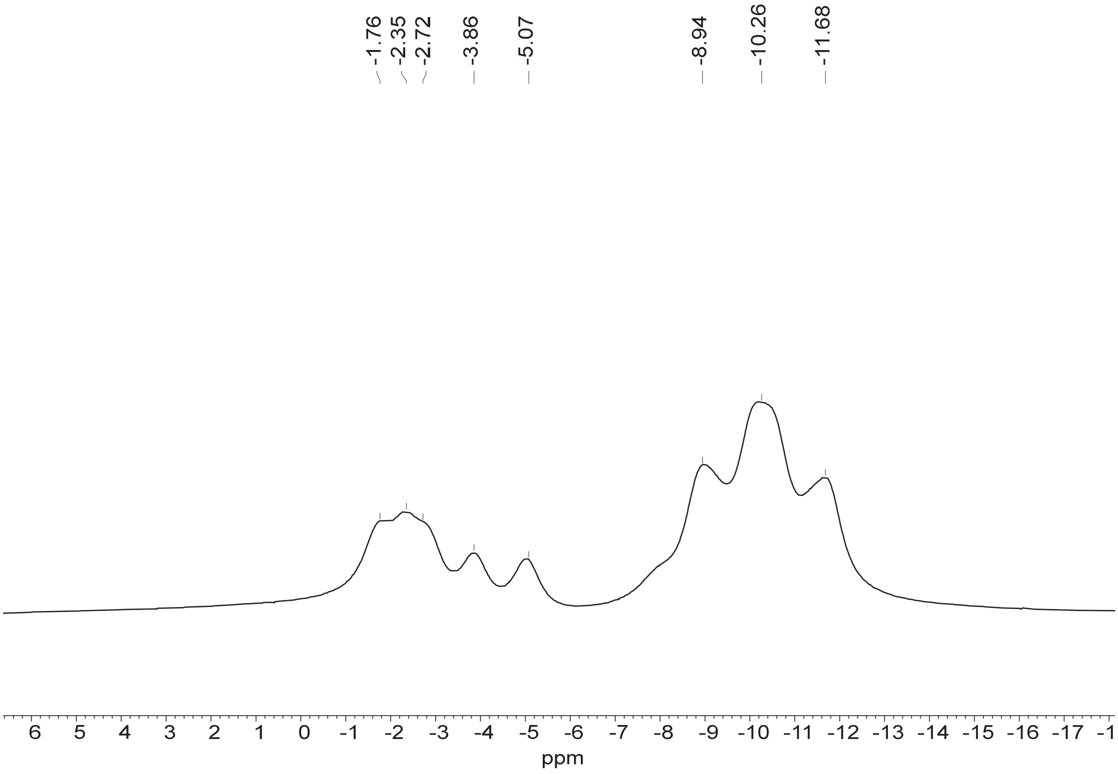


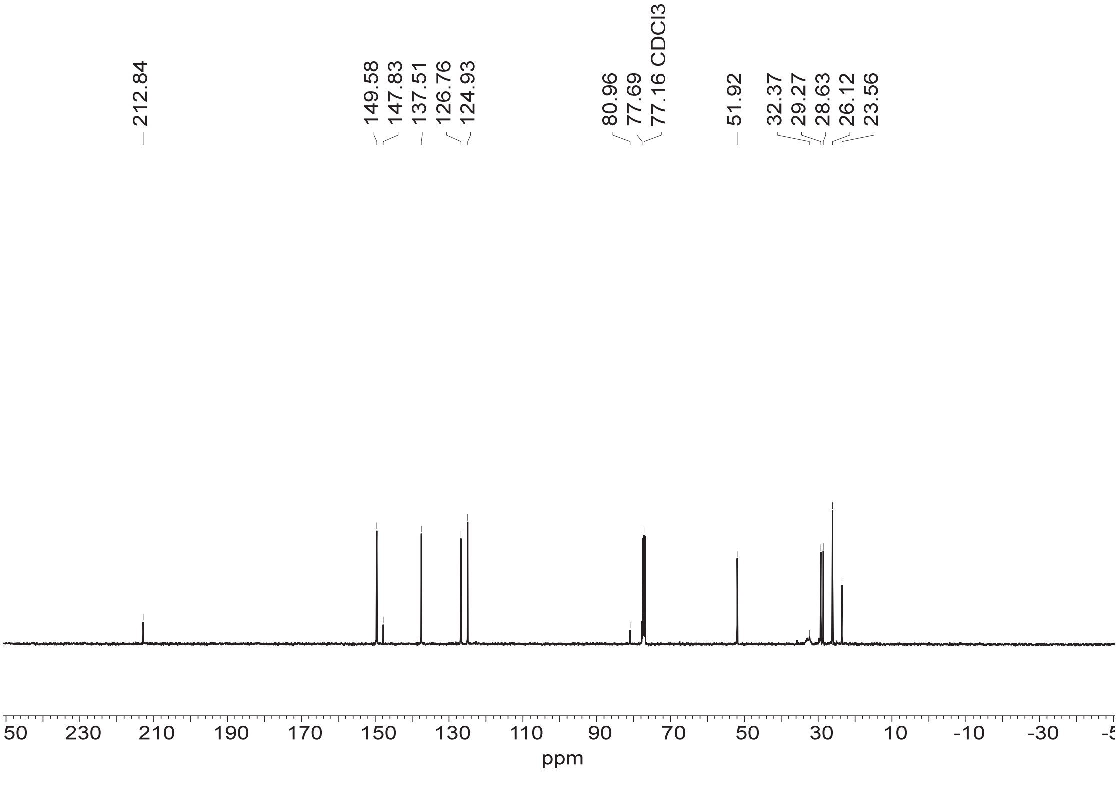
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



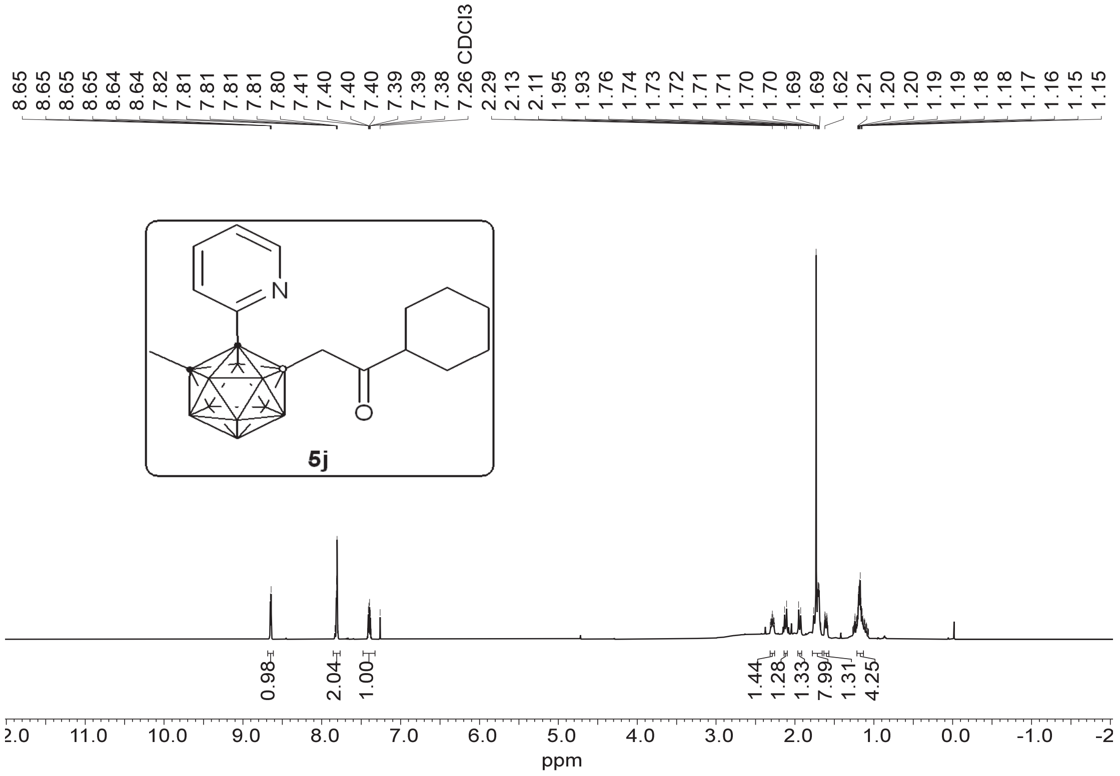
^{11}B NMR (160 MHz, $CDCl_3$)



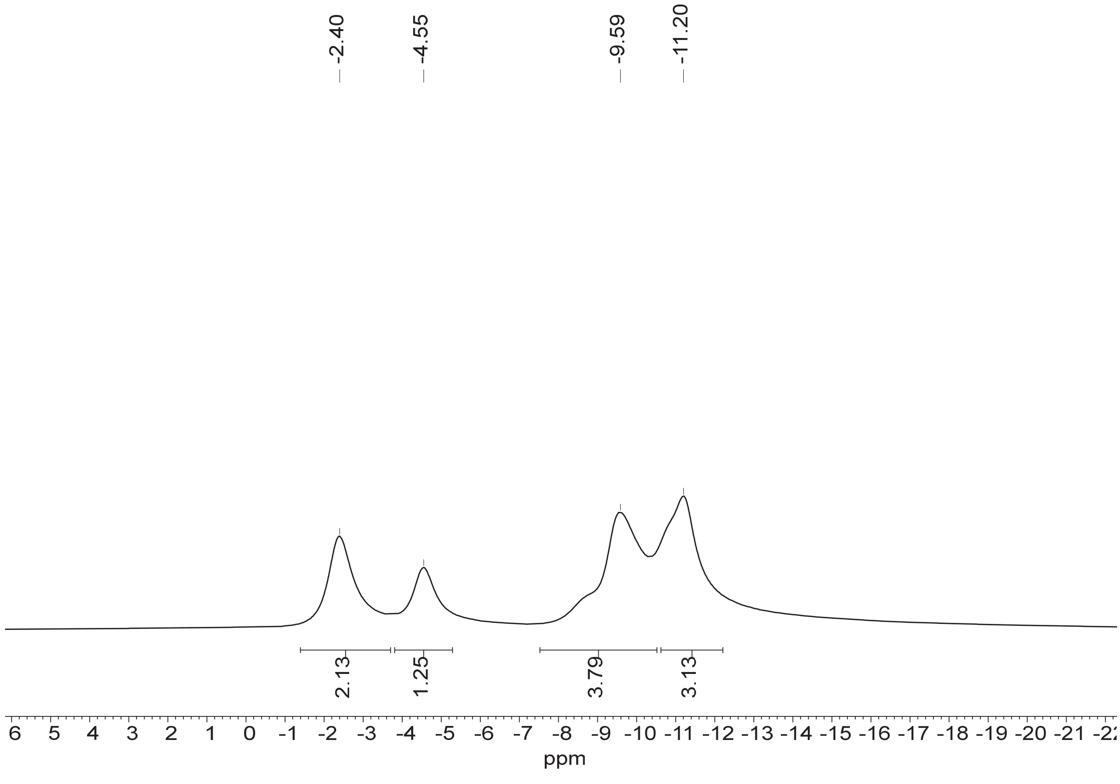
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



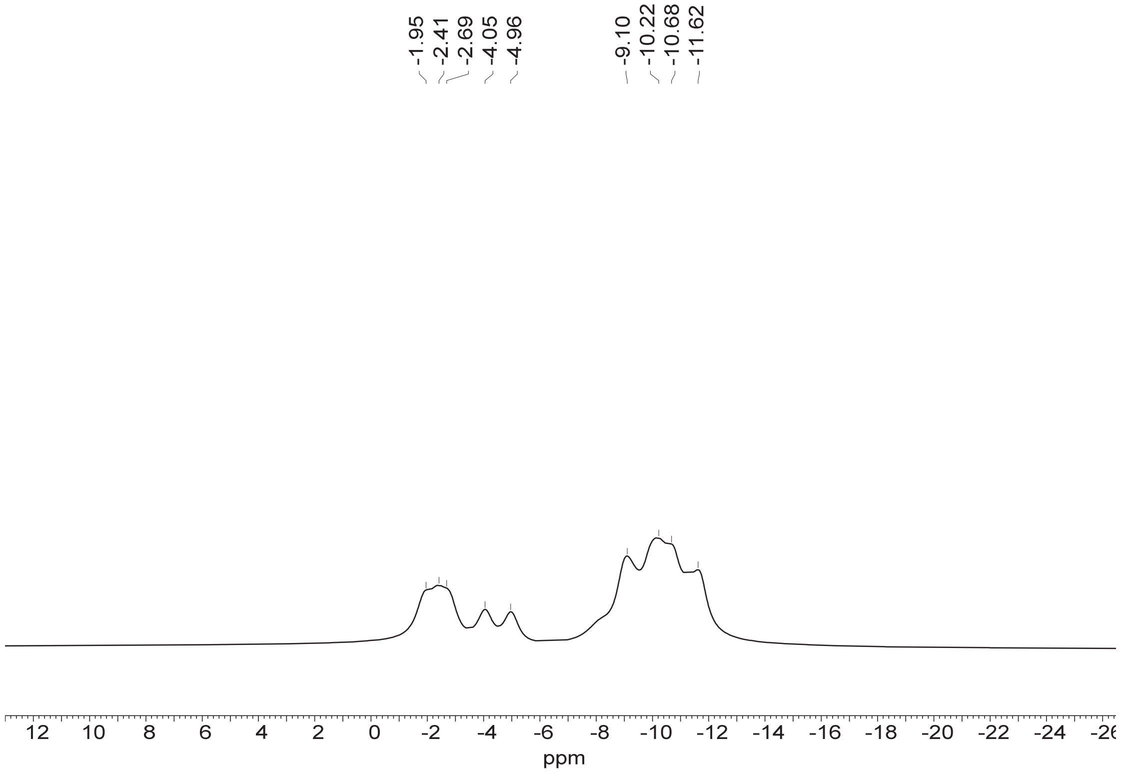
^{1}H NMR (500 MHz, CDCl$_3$)



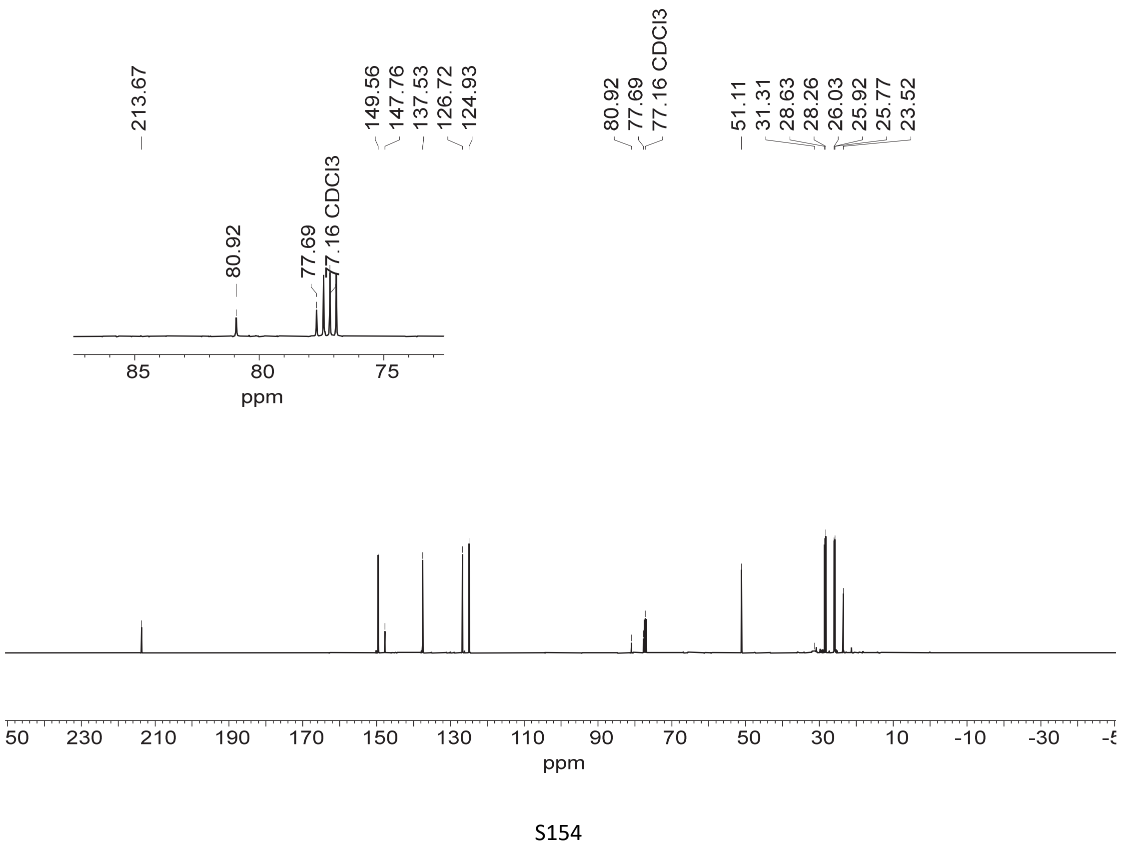
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



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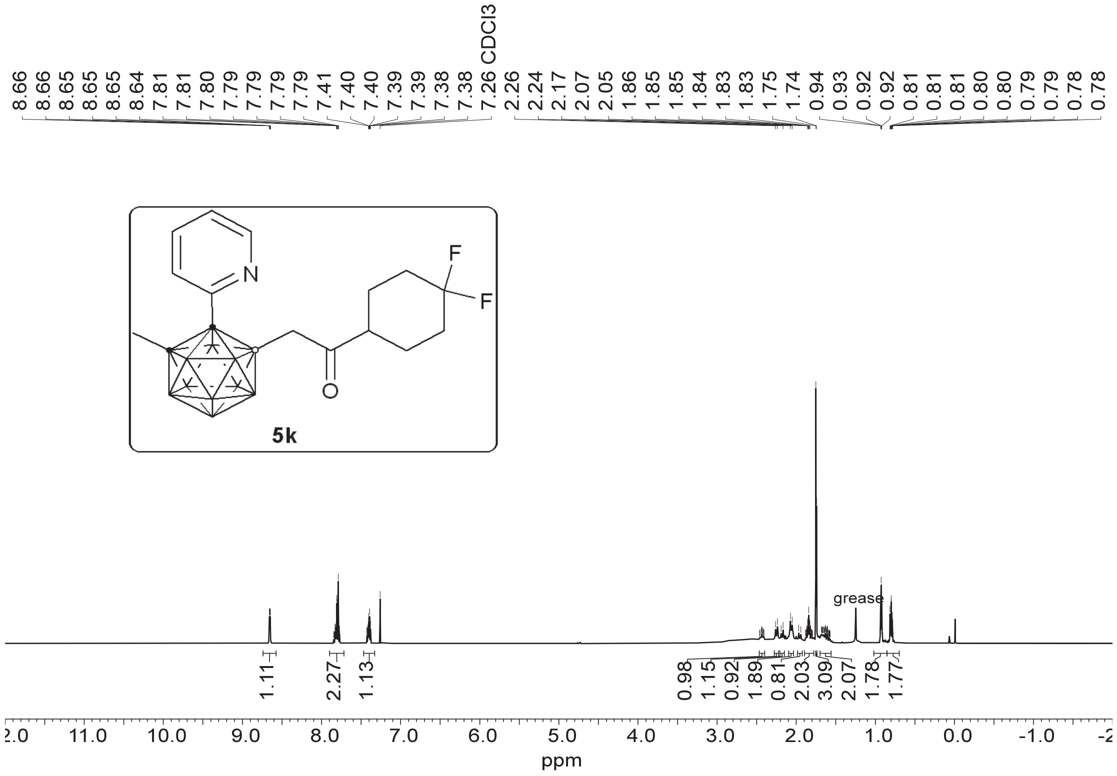
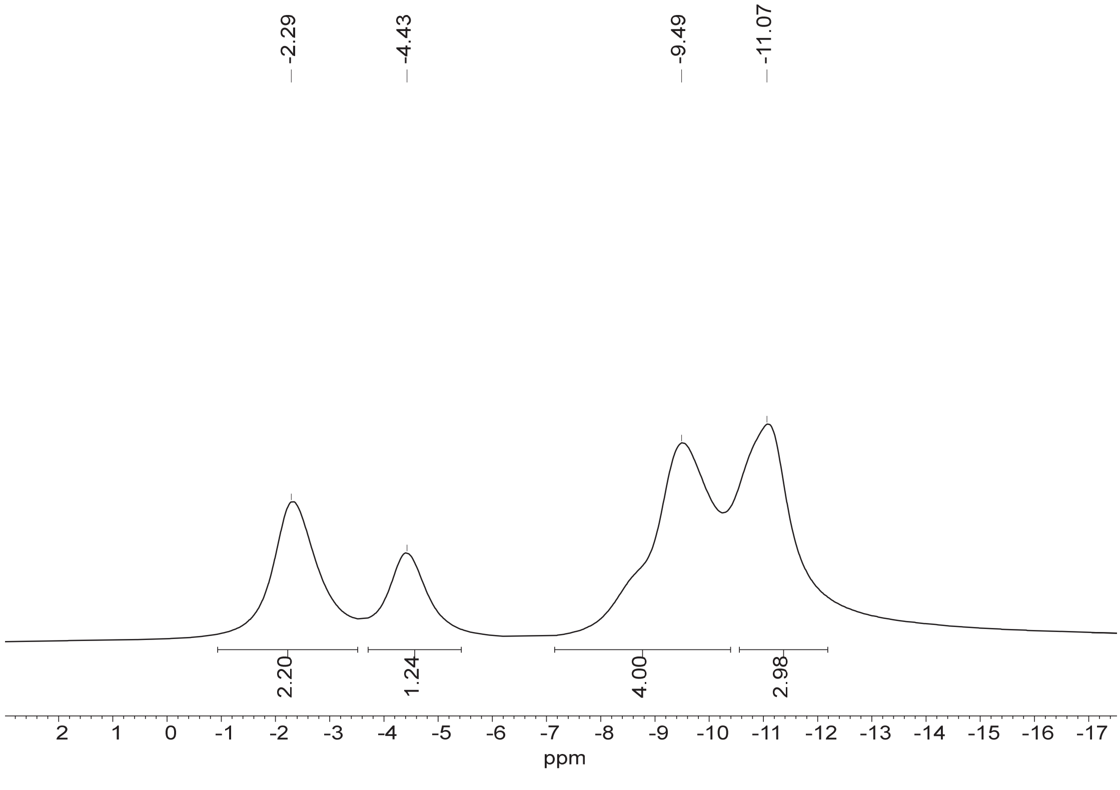
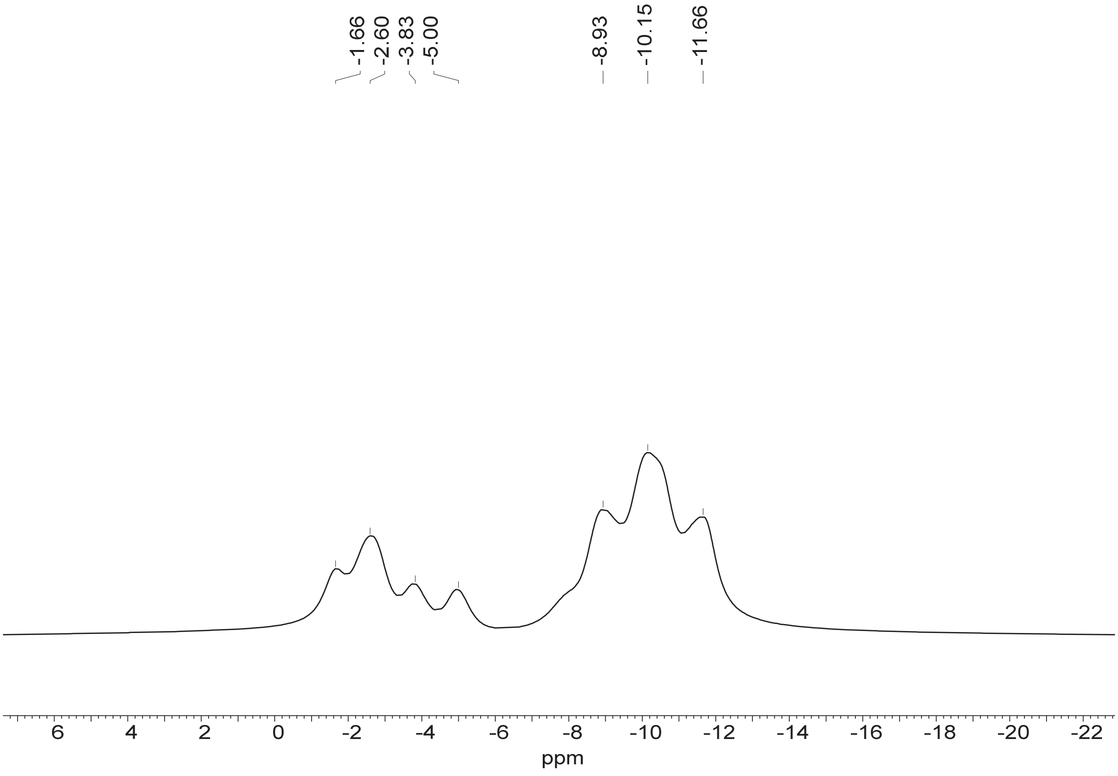


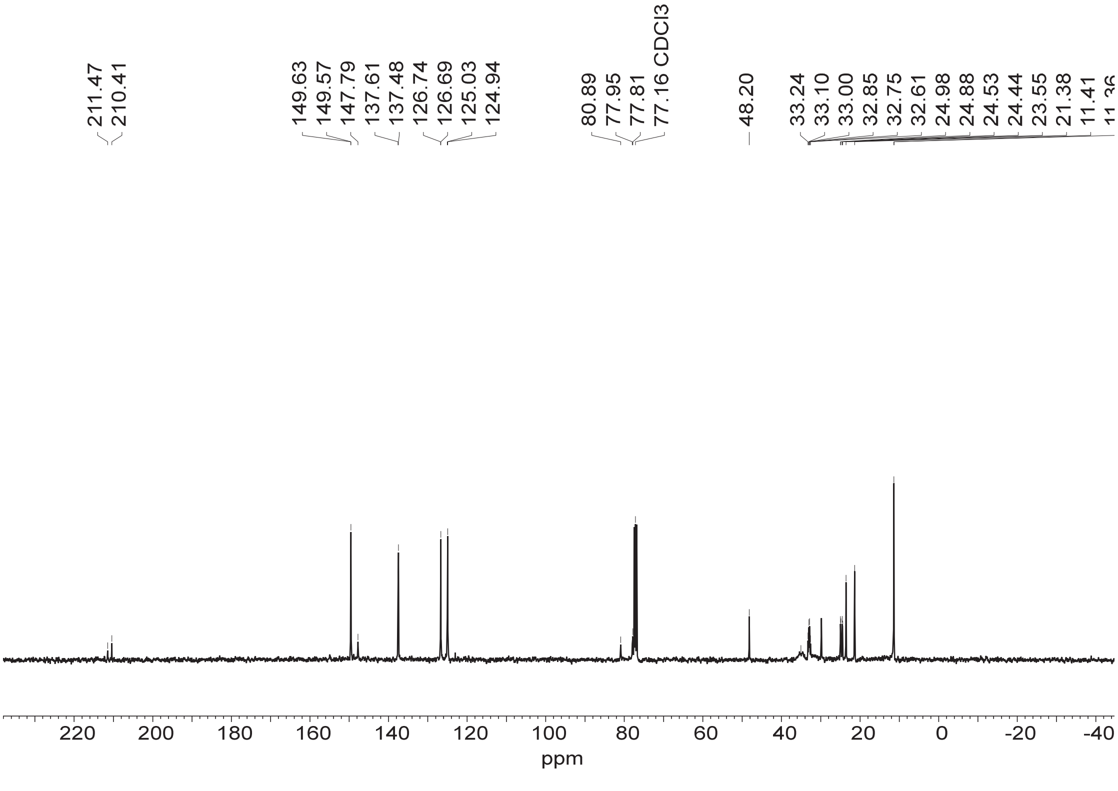
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



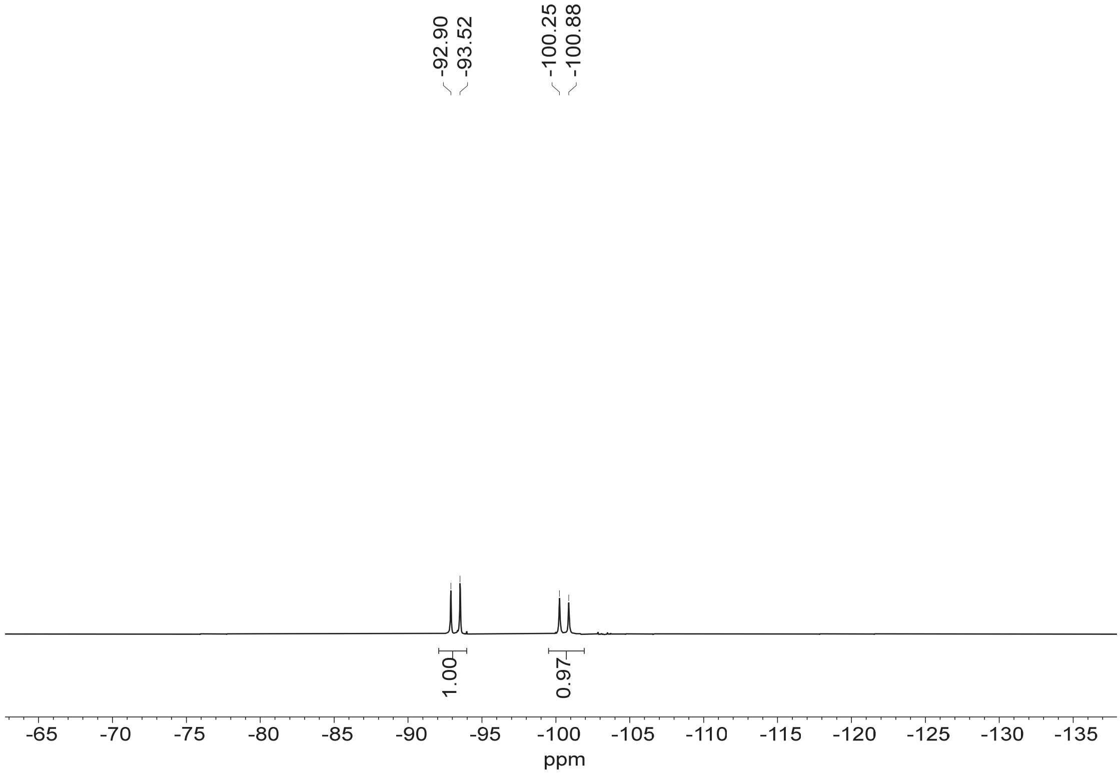
^{11}B NMR (160 MHz, CDCl$_3$)



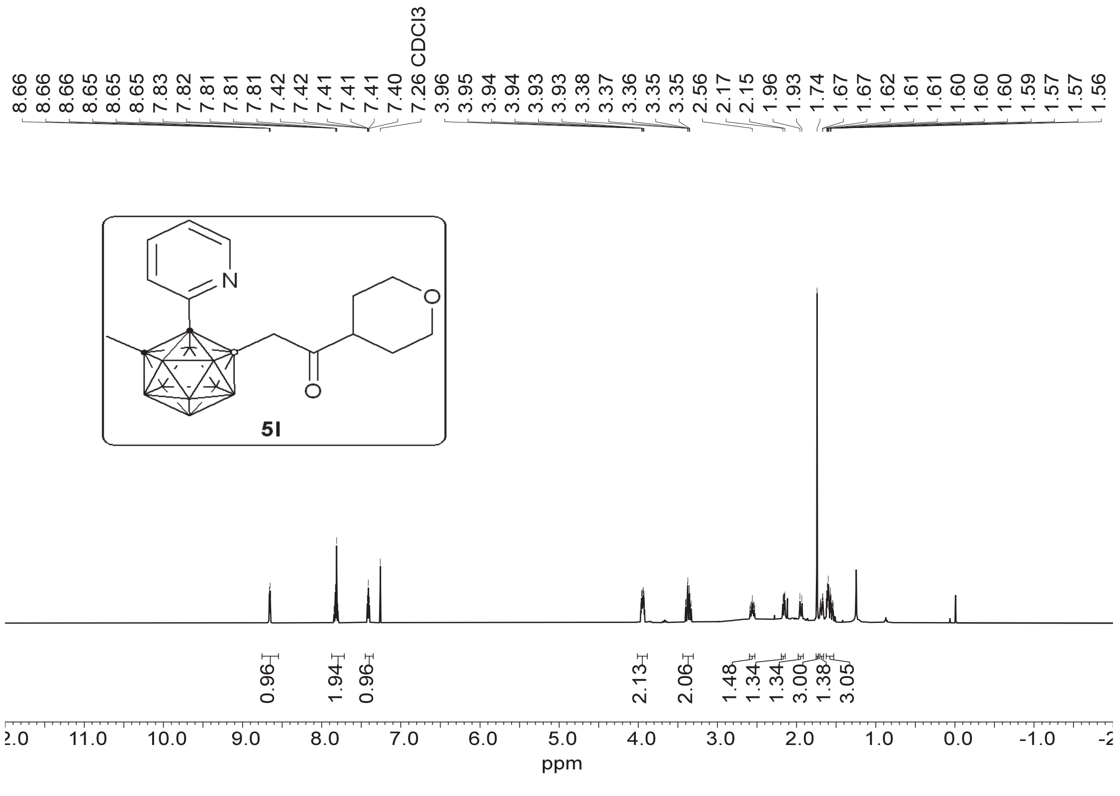
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



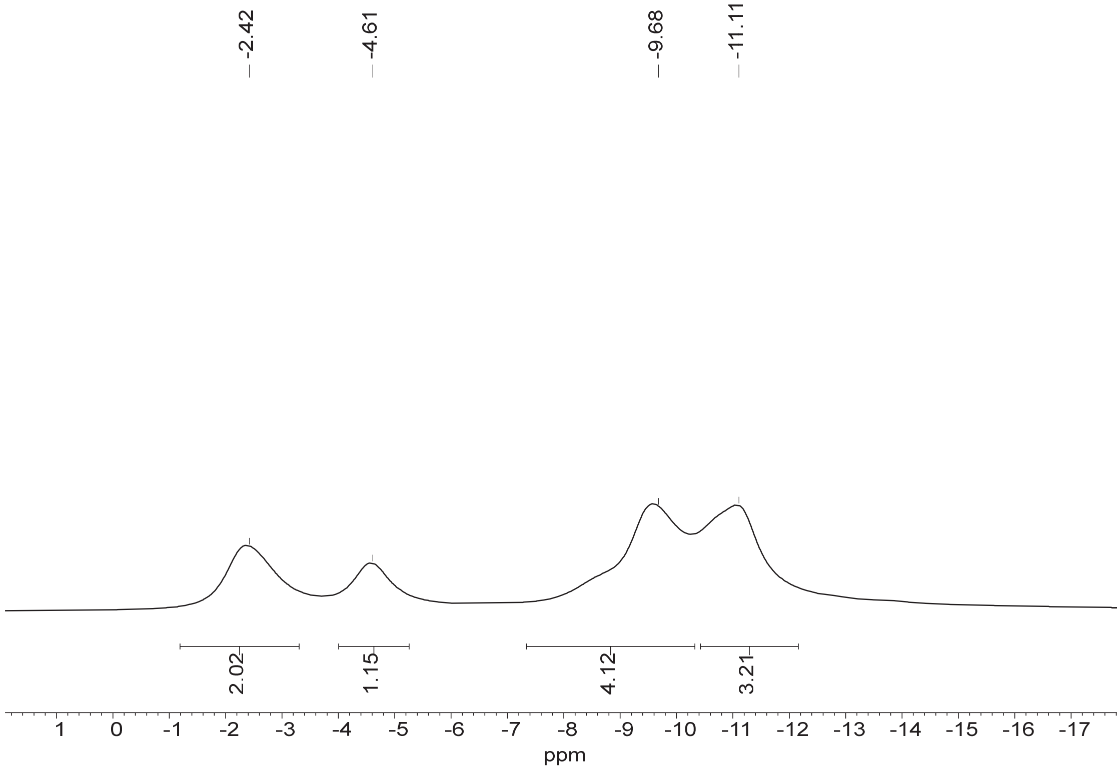
^{19}F NMR (376 MHz, CDCl$_3$)



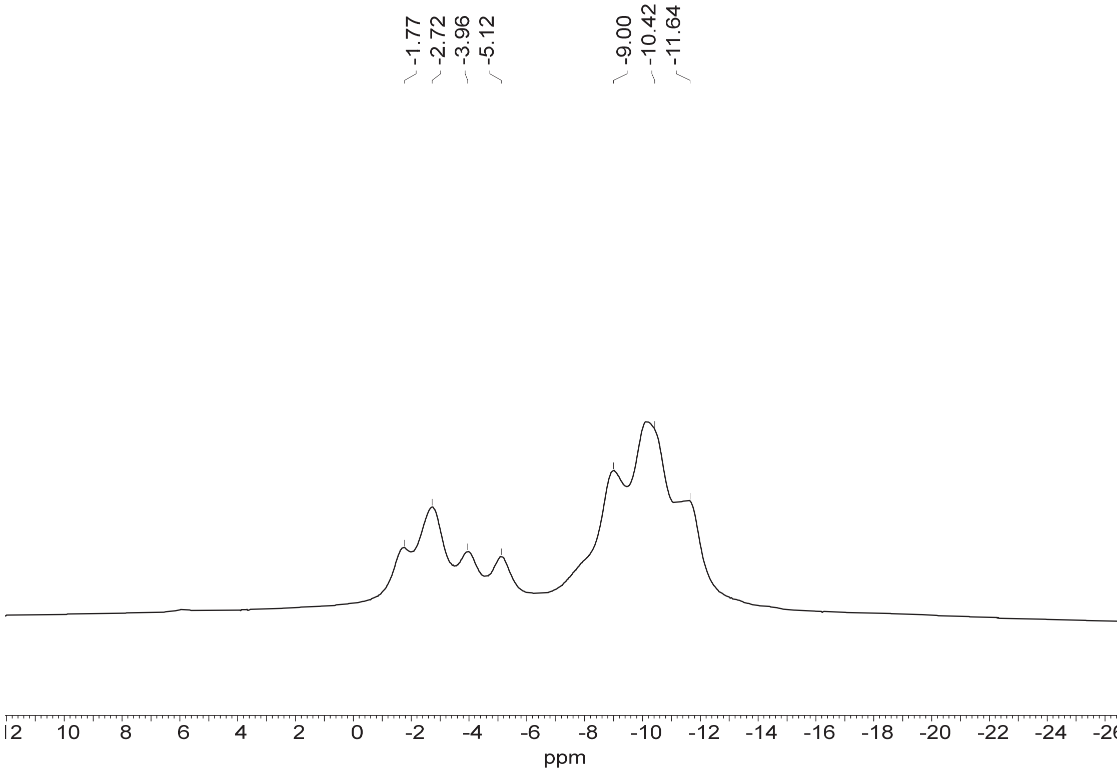
^{1}H NMR (500 MHz, CDCl$_3$)



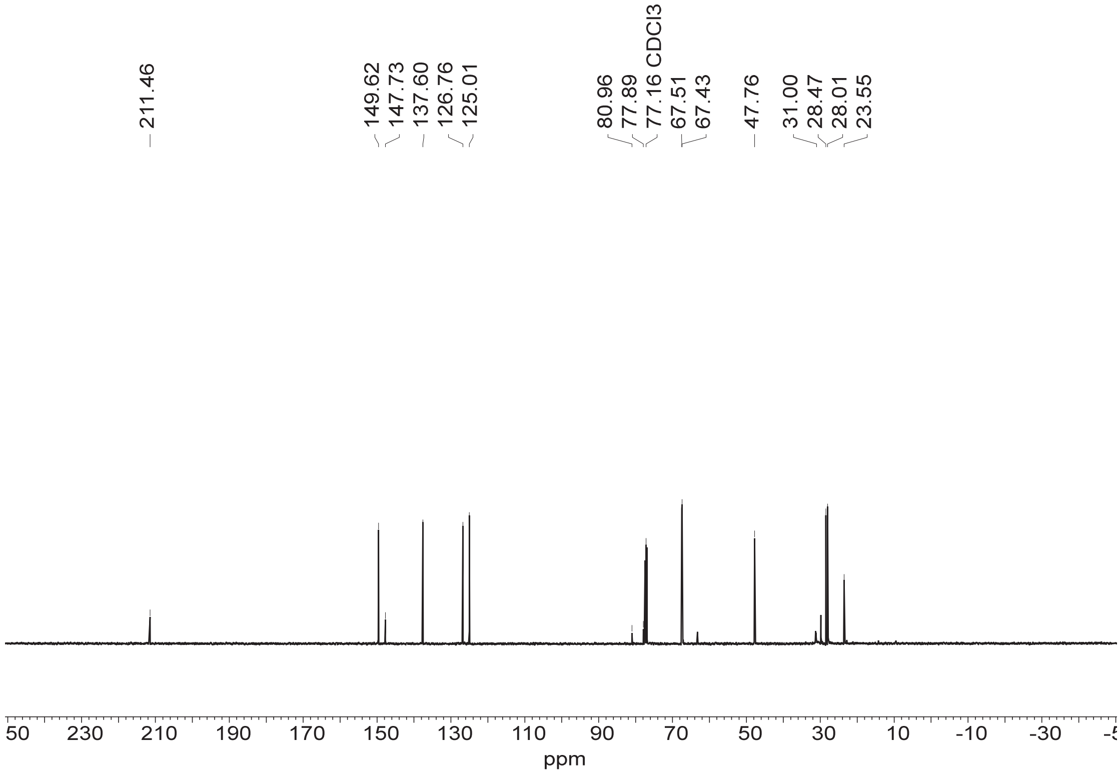
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



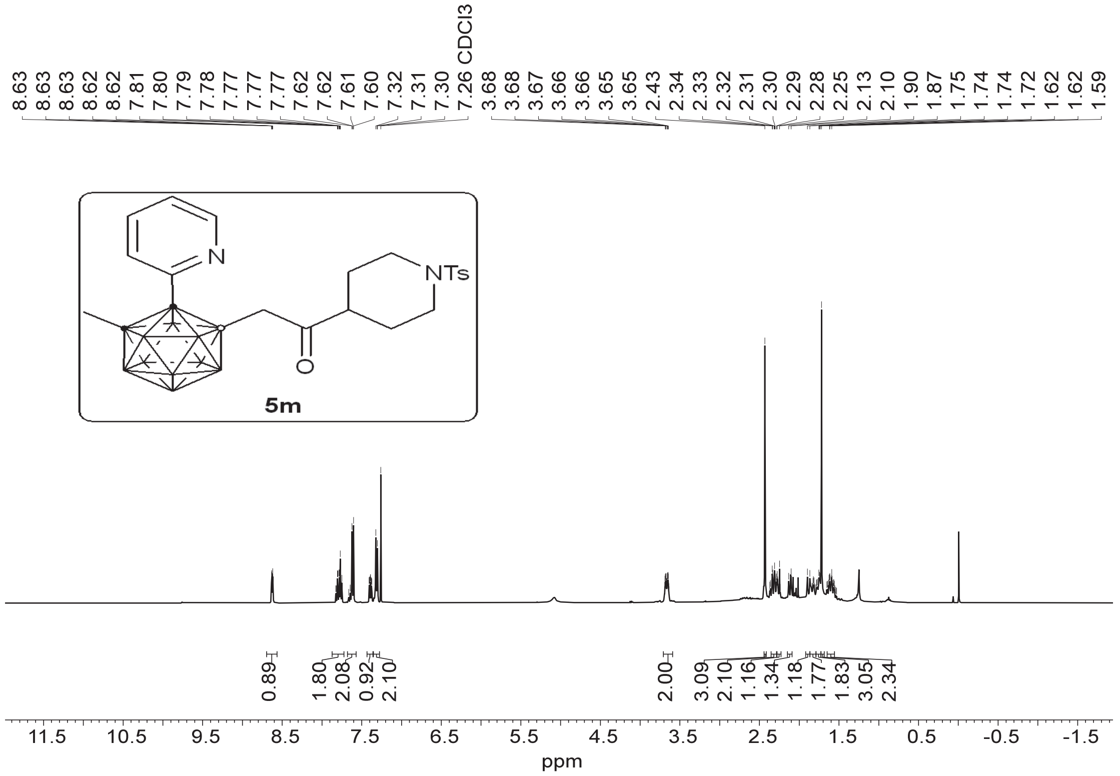
^{11}B NMR (128 MHz, $CDCl_3$)



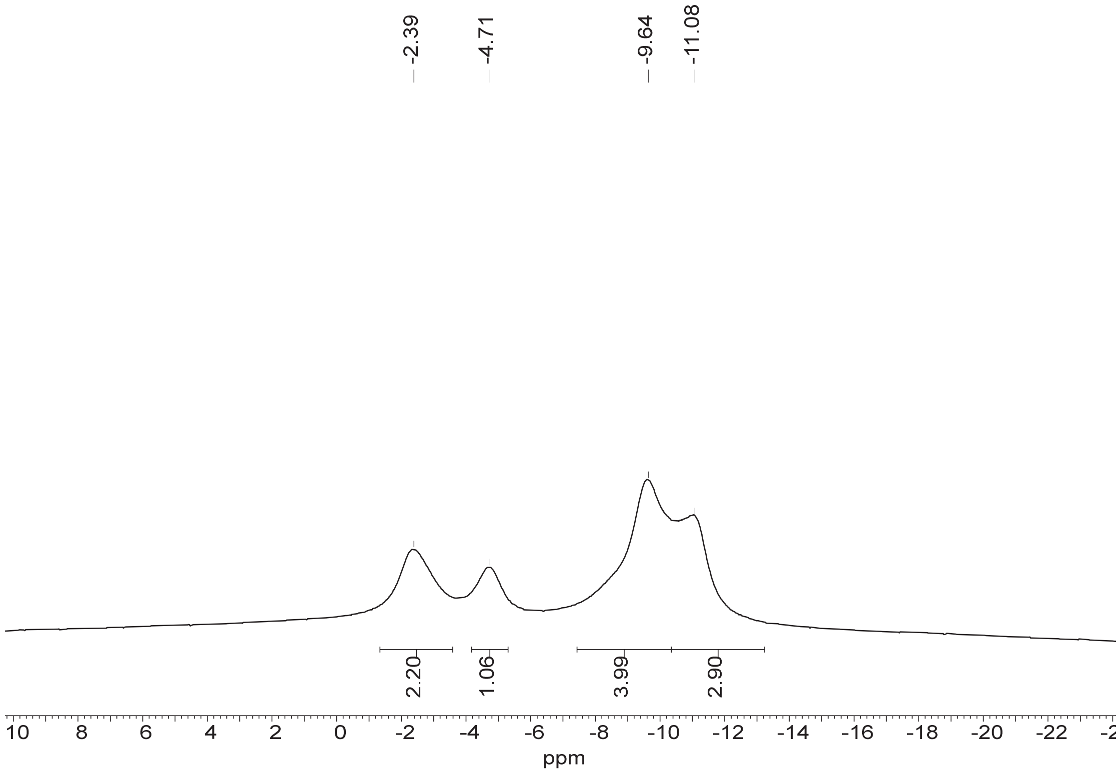
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



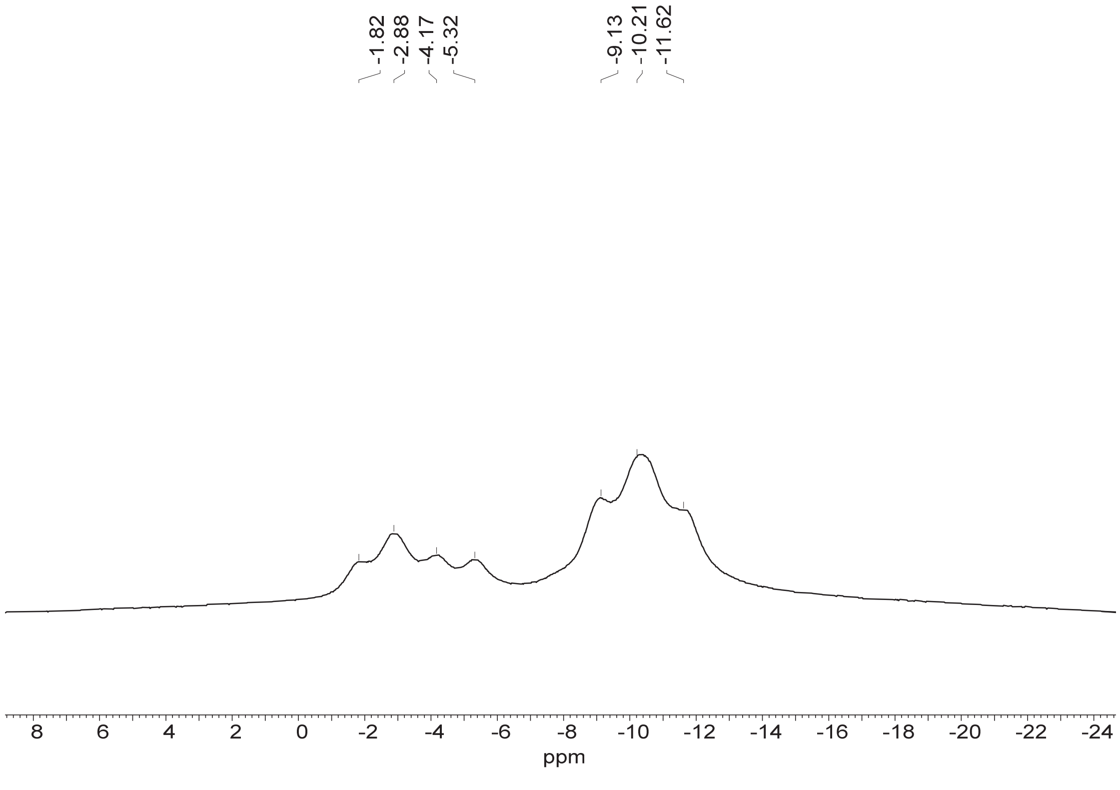
^1H NMR (400 MHz, $CDCl_3$)



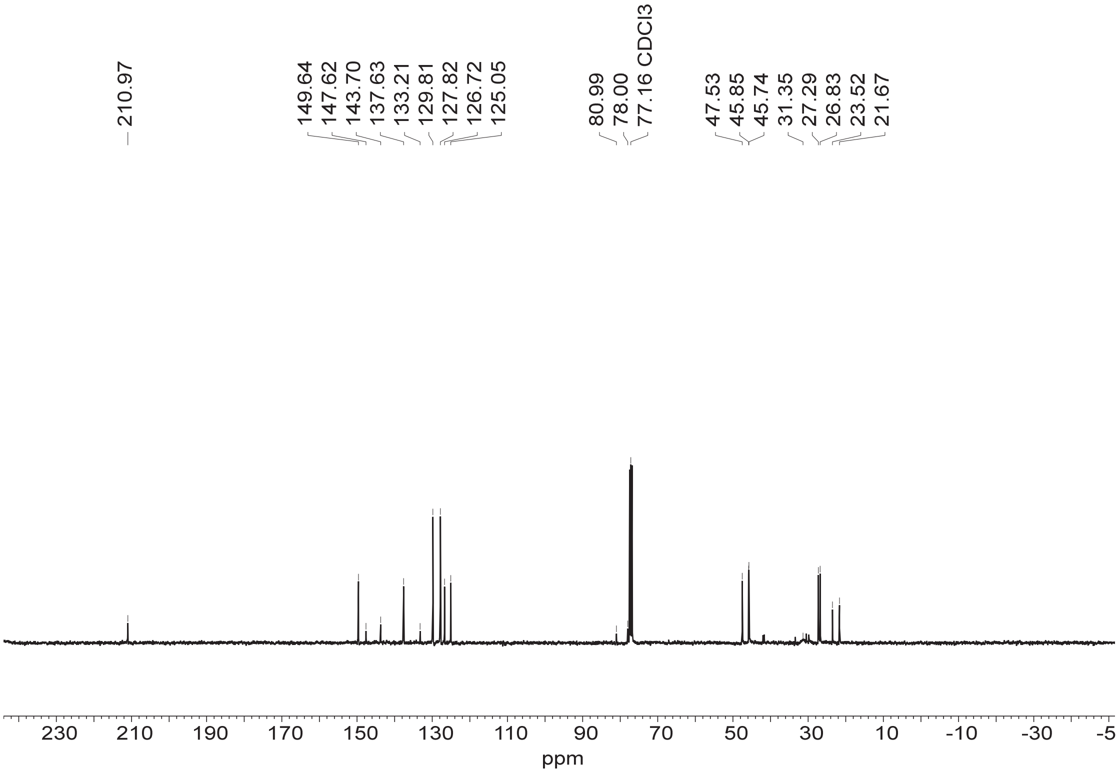
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



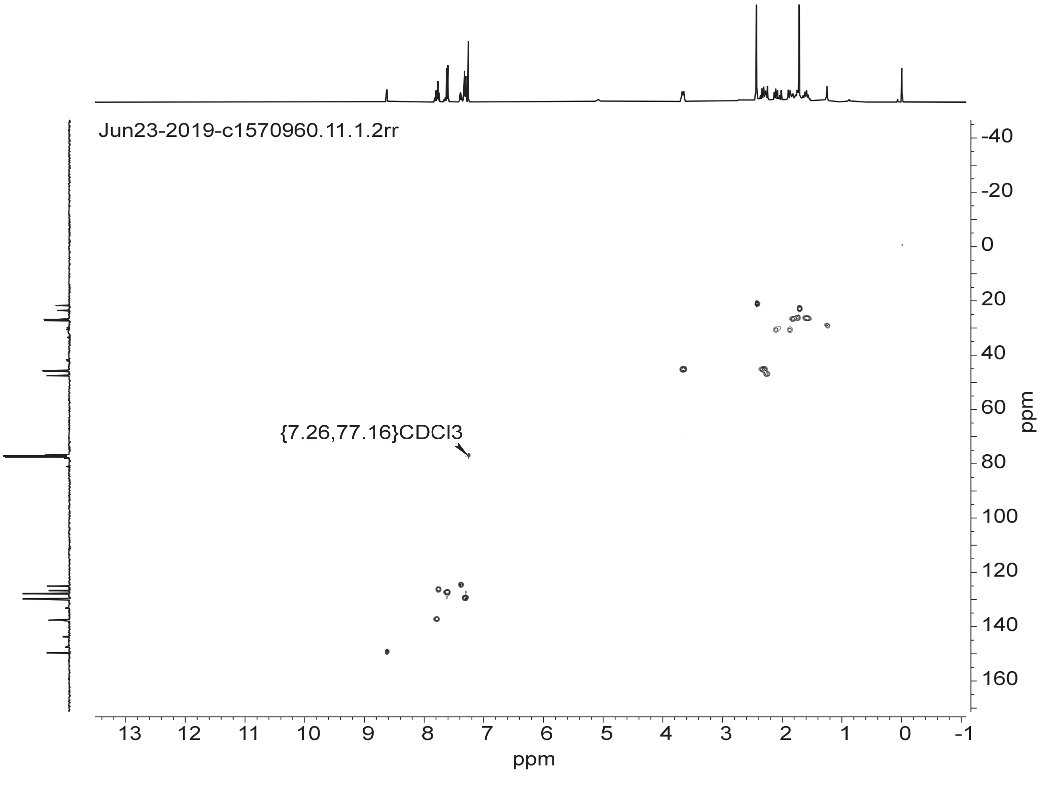
^{11}B NMR (160 MHz, $CDCl_3$)



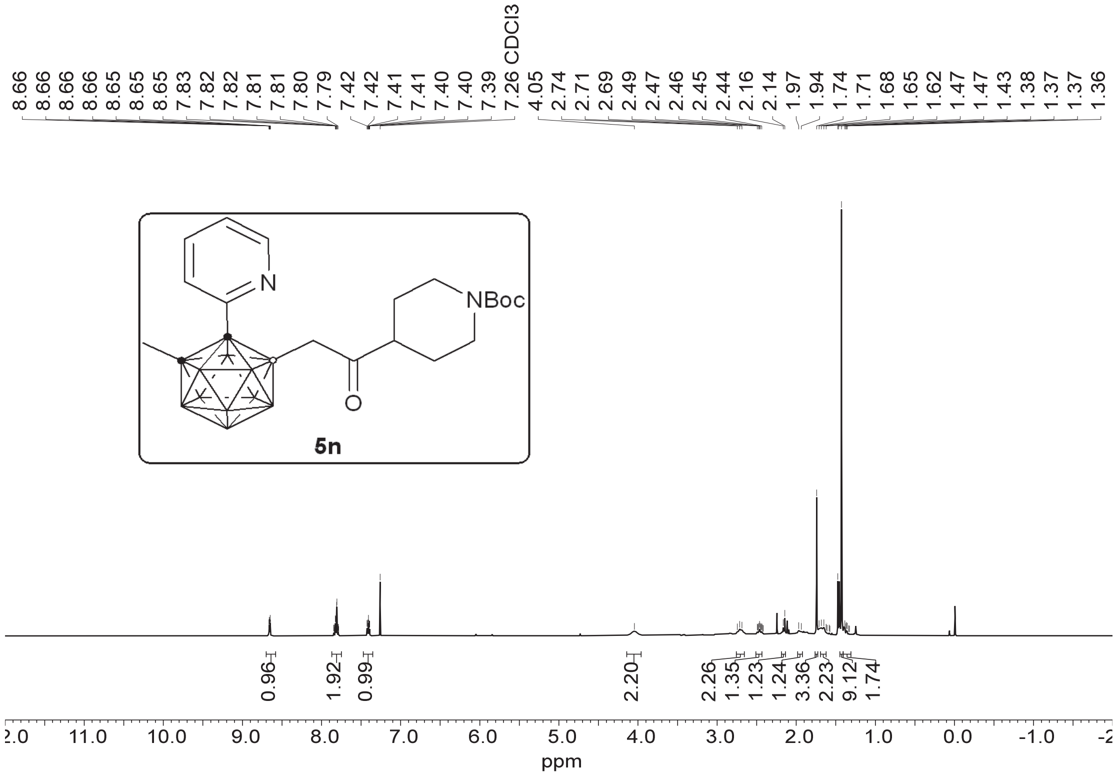
$^{13}C\{^{1}H\}$ NMR (01 MHz, $CDCl_3$)



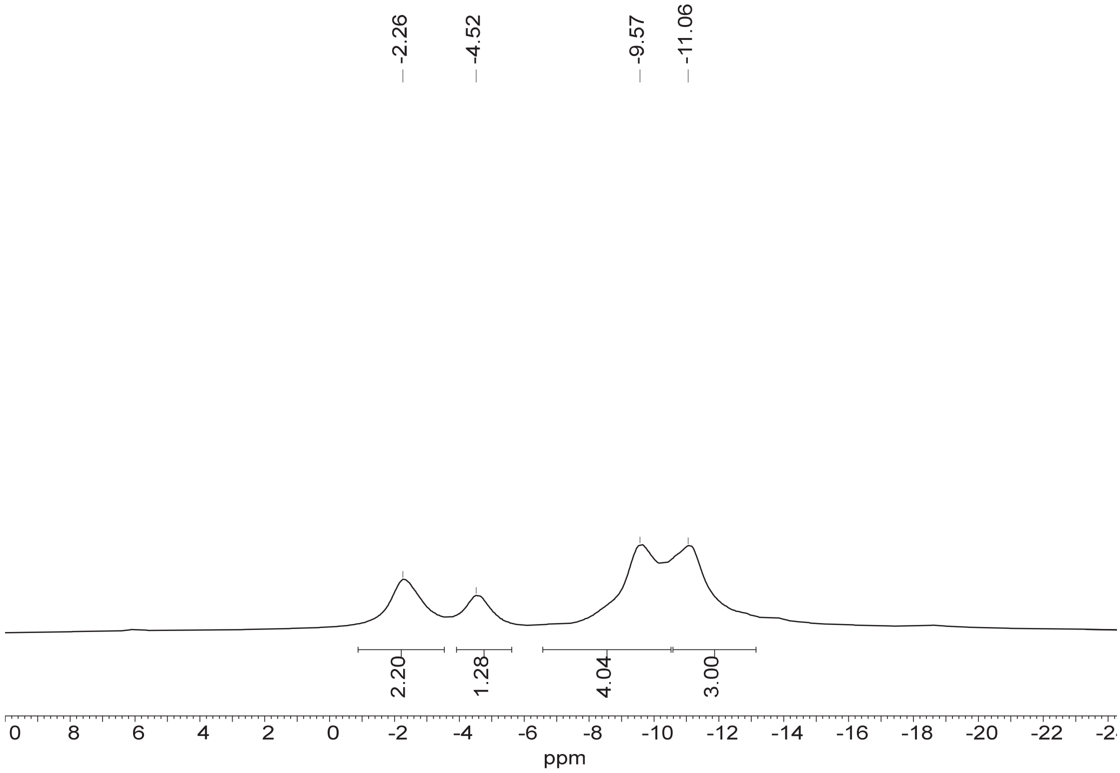
^{1}H-^{13}C HSQC NMR (400 MHz, $CDCl_3$)



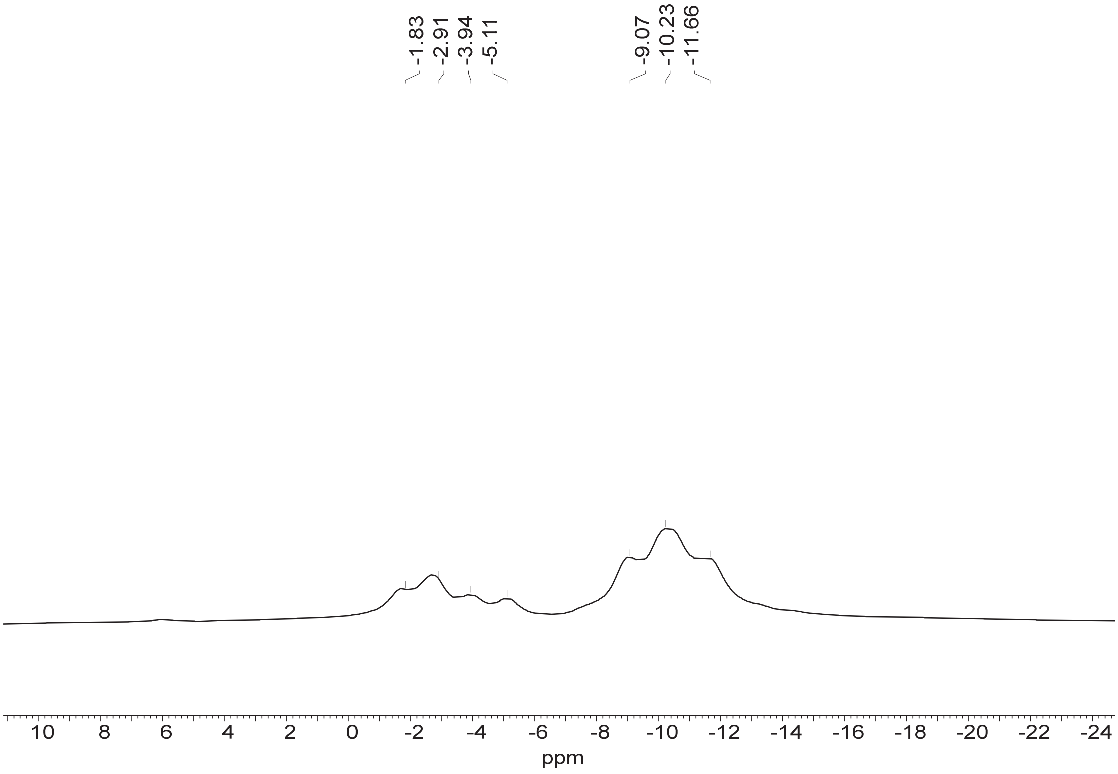
^{1}H NMR (400 MHz, CDCl$_3$)



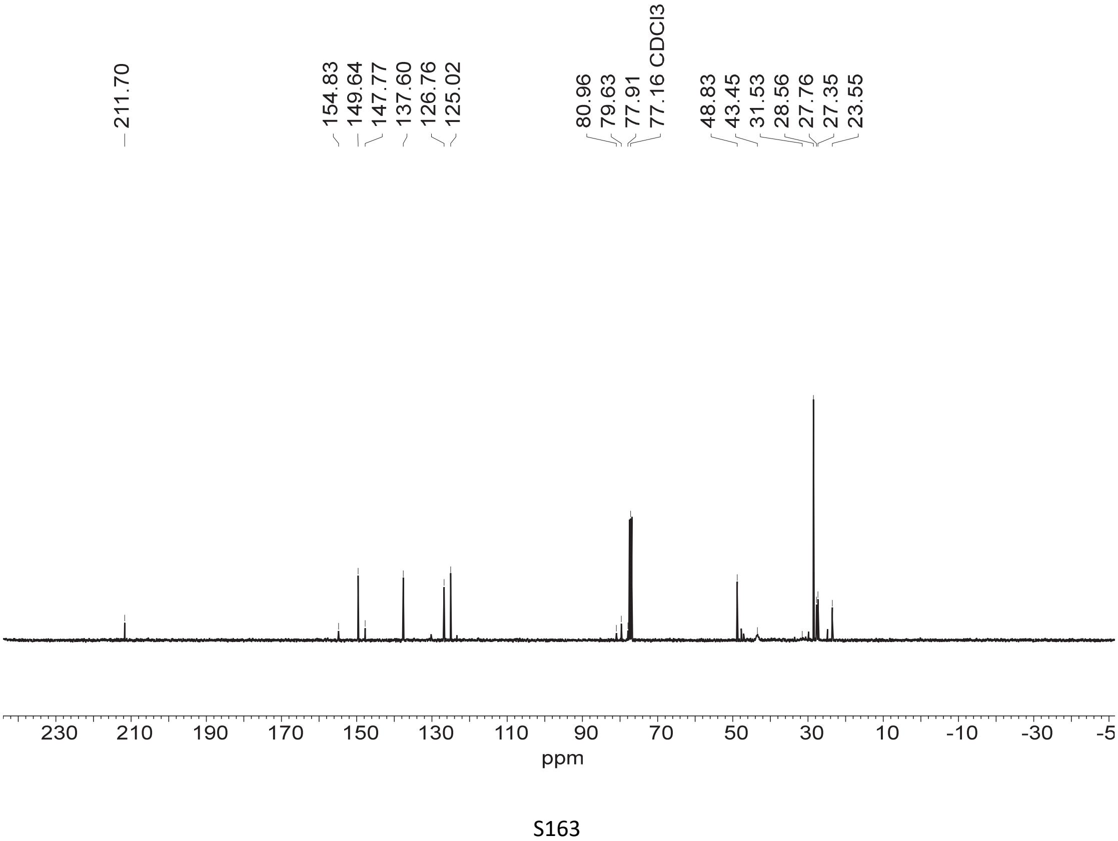
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



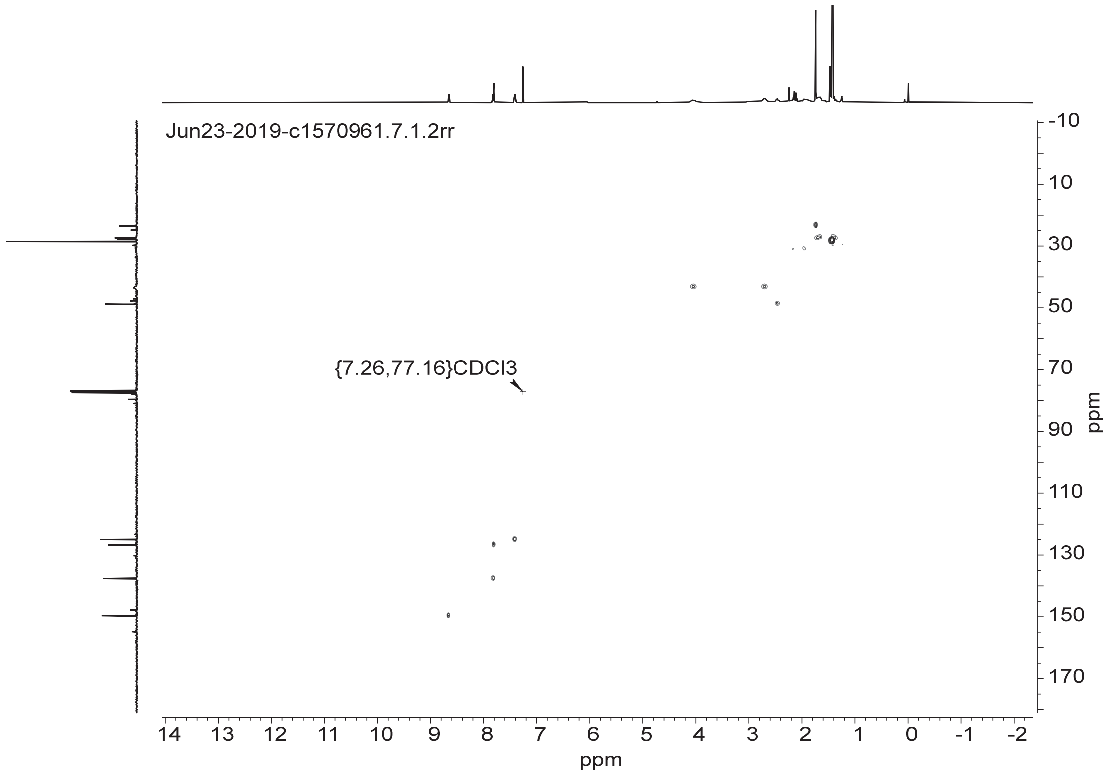
^{11}B NMR (128 MHz, CDCl$_3$)



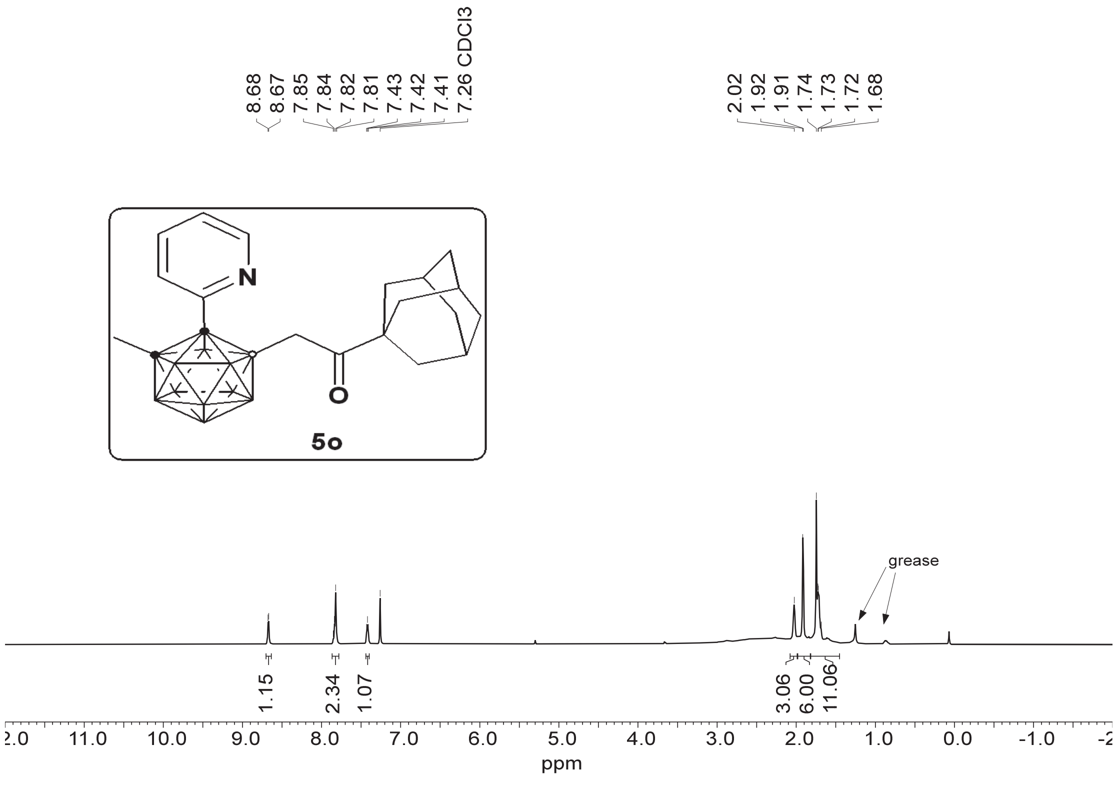
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



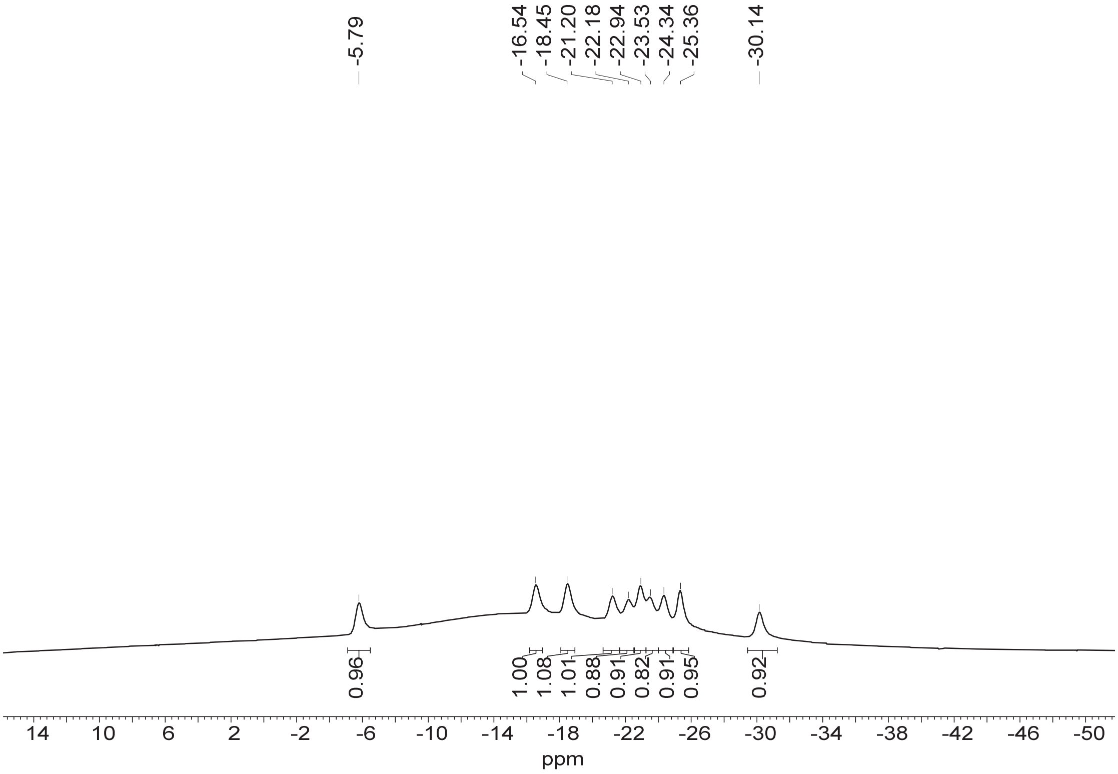
^{1}H-^{13}C HSQC NMR (400 MHz, $CDCl_3$)



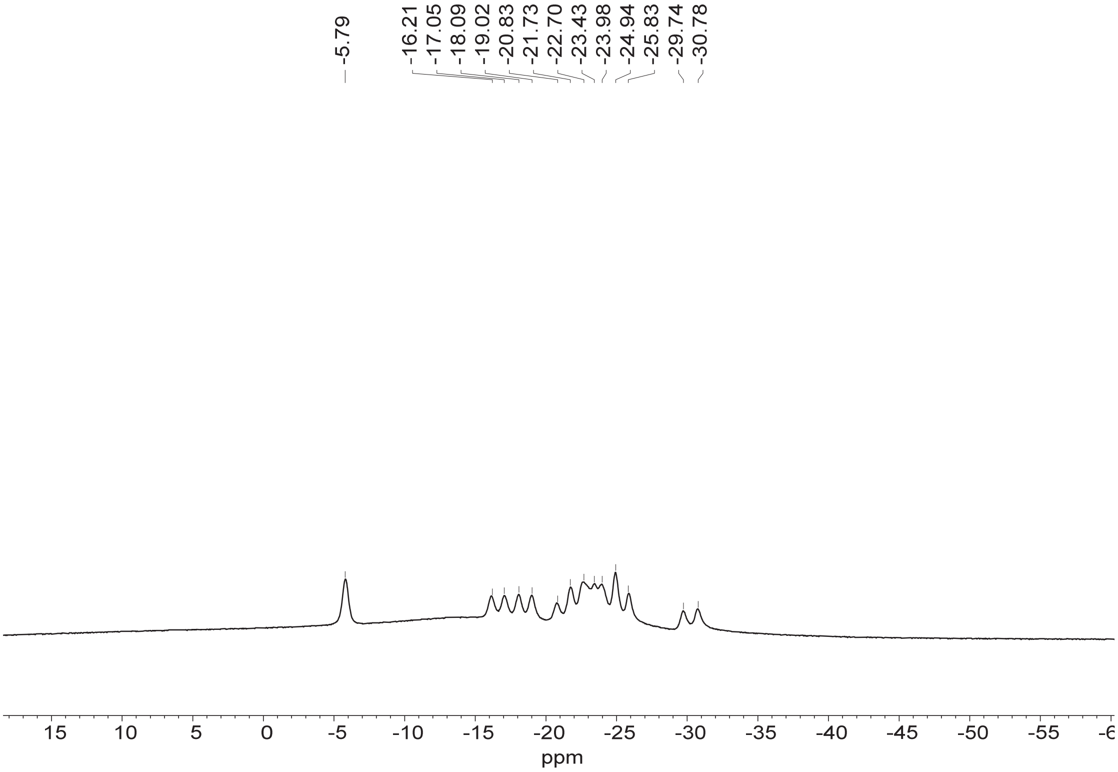
^{1}H NMR (500 MHz, $CDCl_3$)



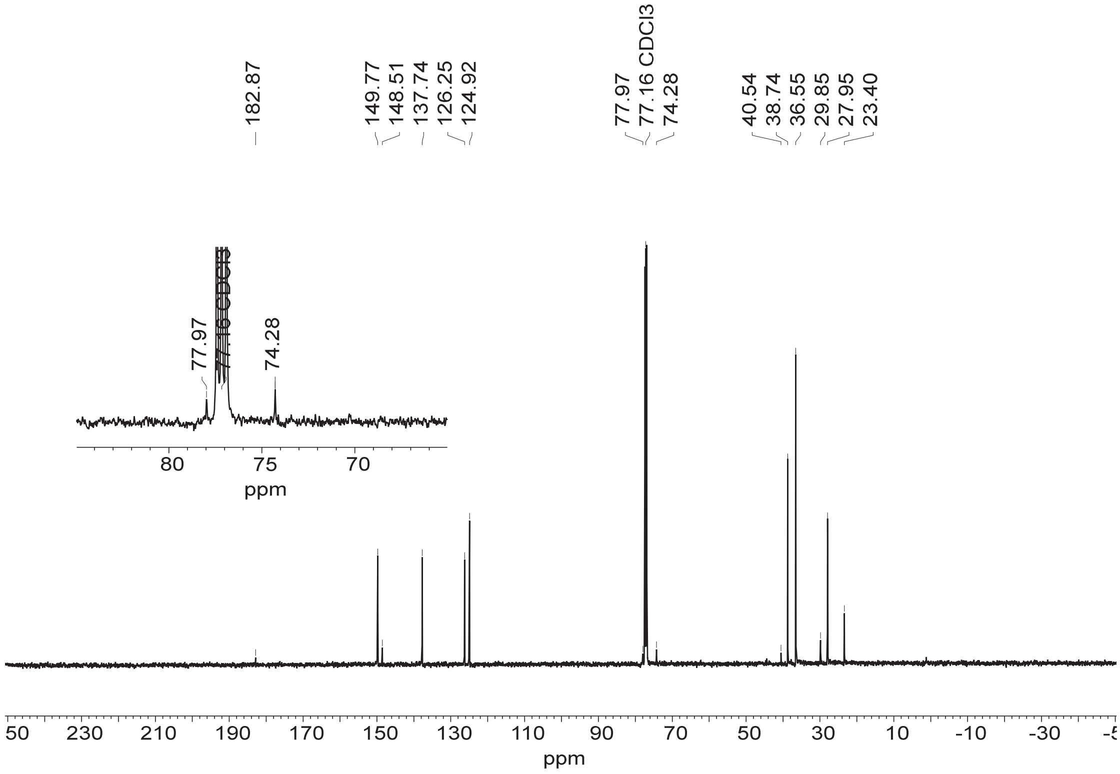
$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$)



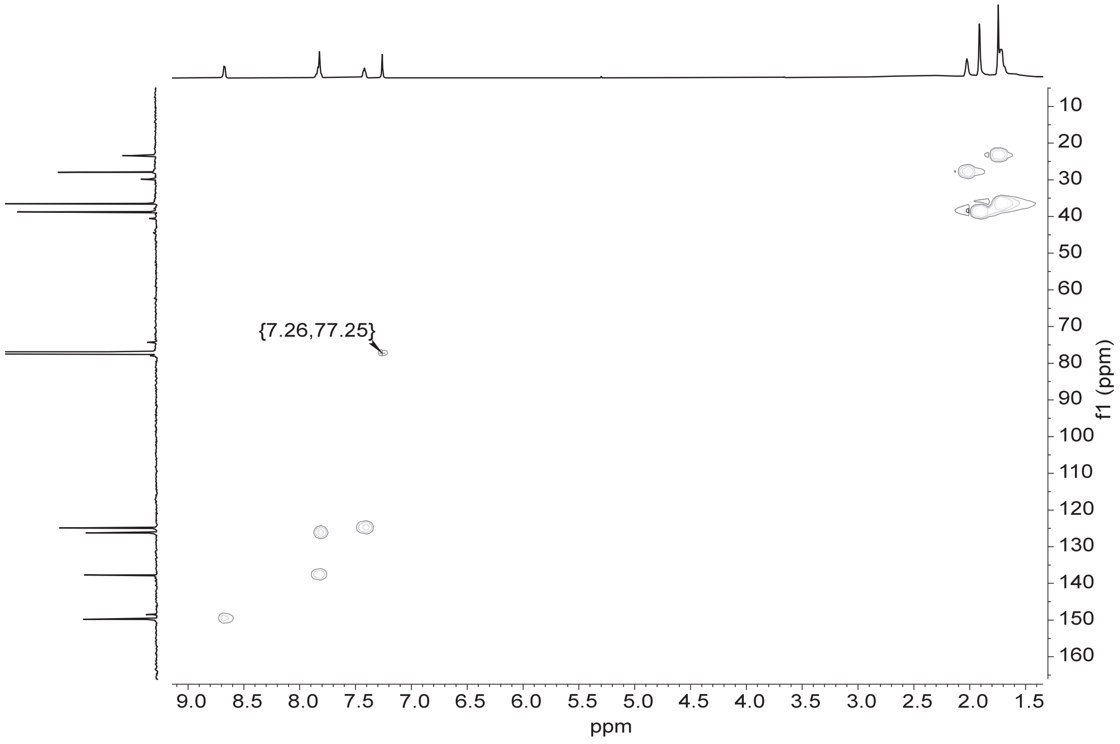
^{11}B NMR (160 MHz, $CDCl_3$)



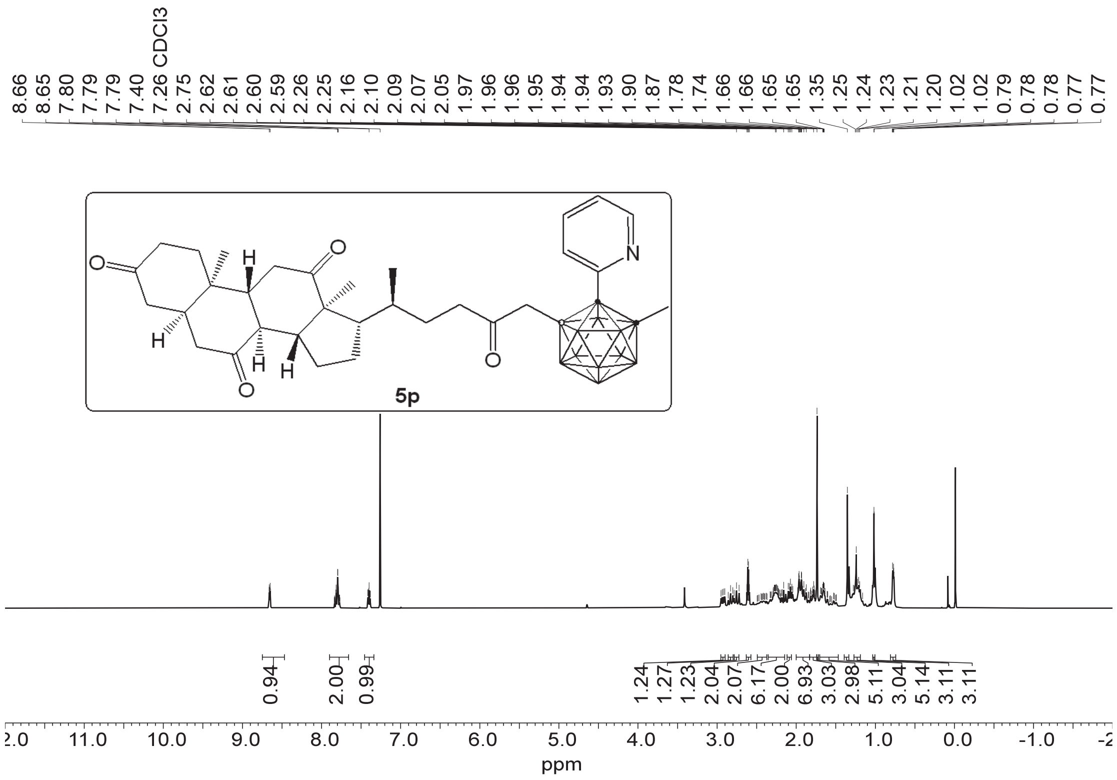
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



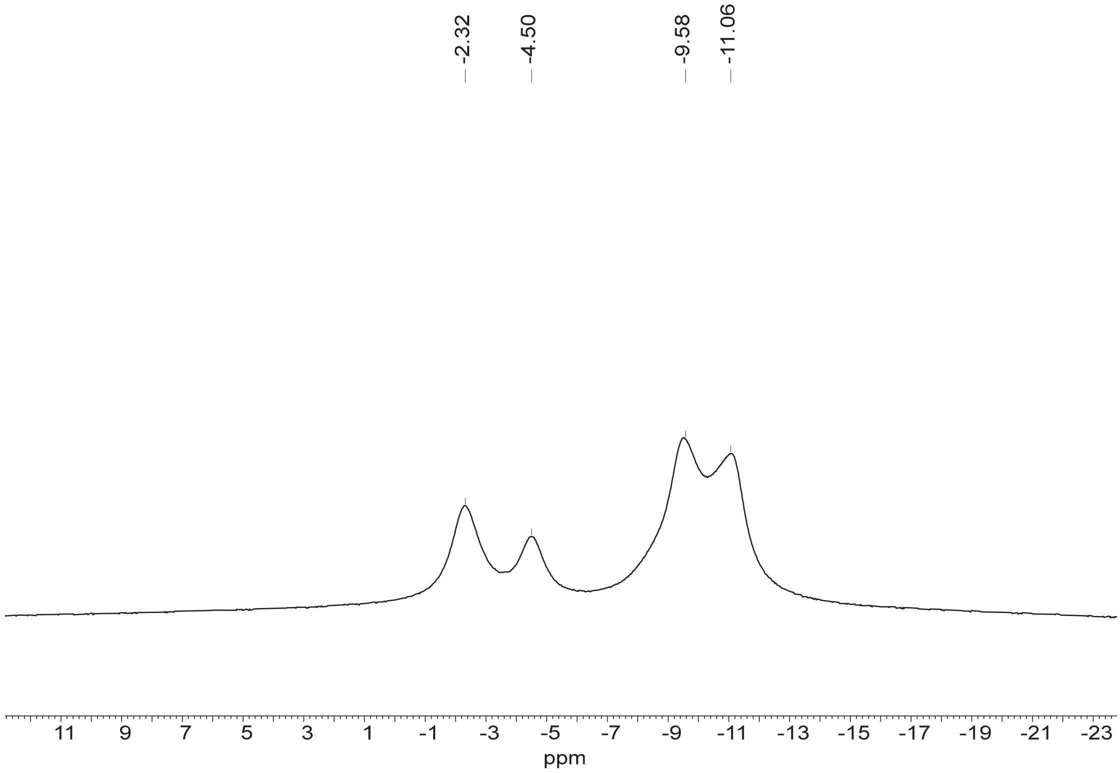
^{1}H-^{13}C HSQC NMR (500 MHz, $CDCl_3$)



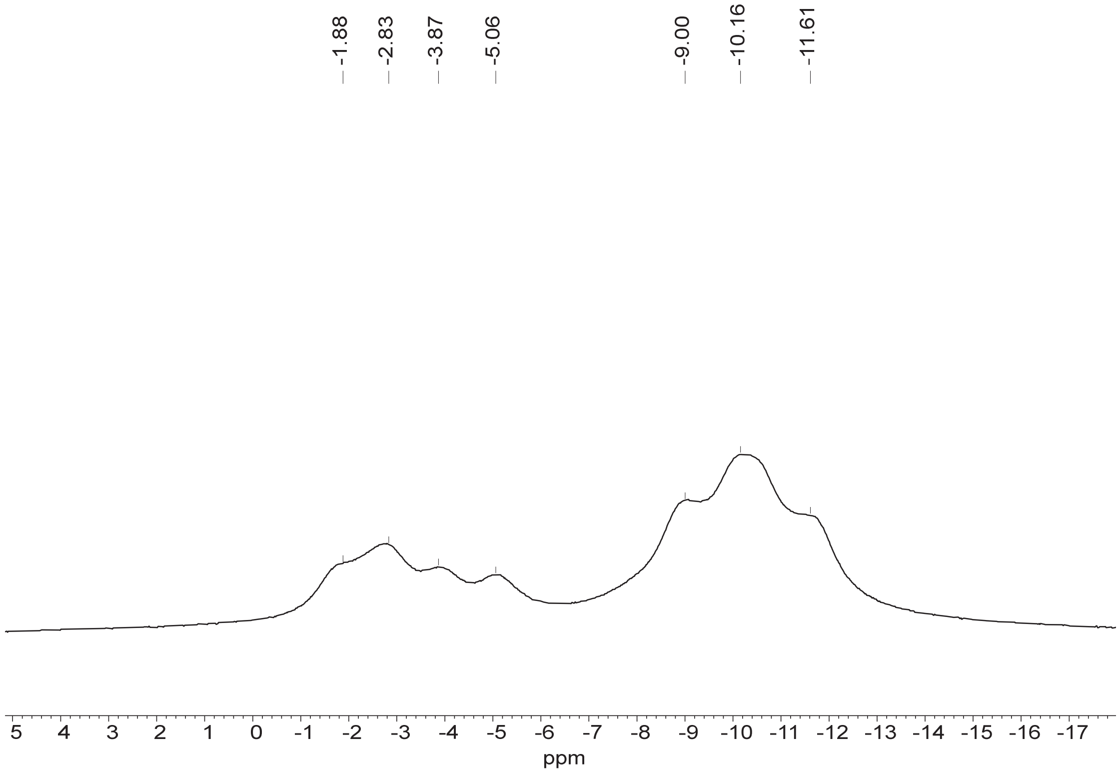
^{1}H NMR (400 MHz, CDCl$_3$)



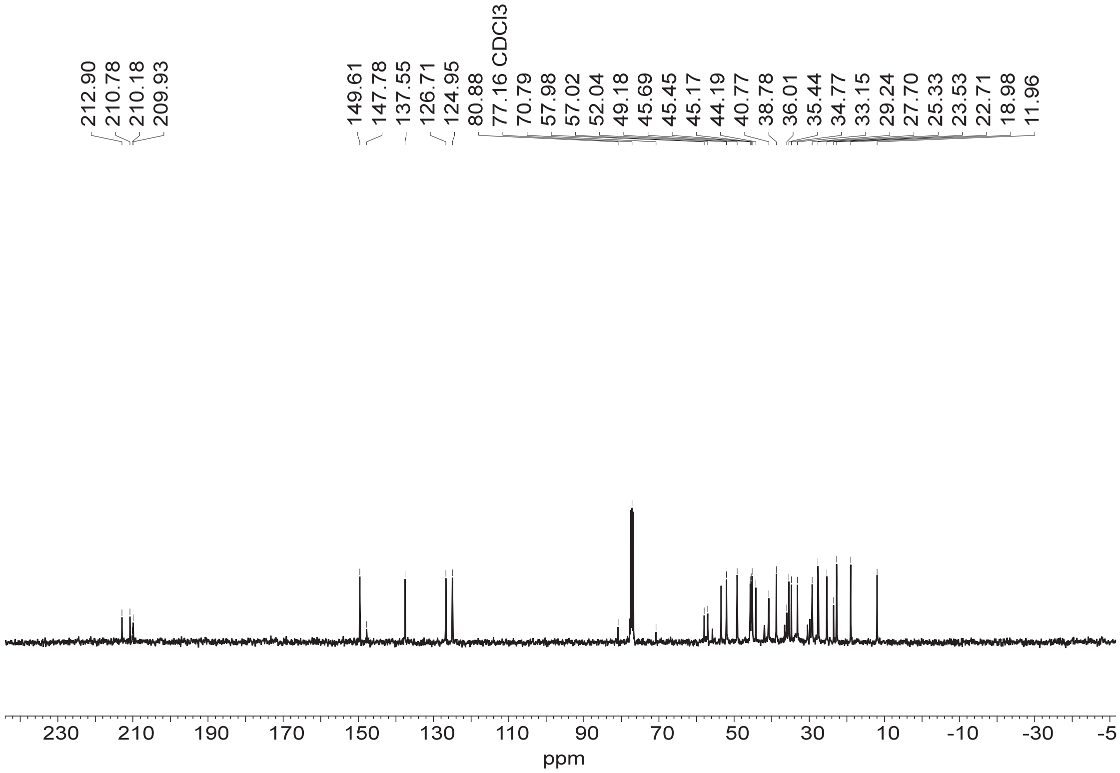
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



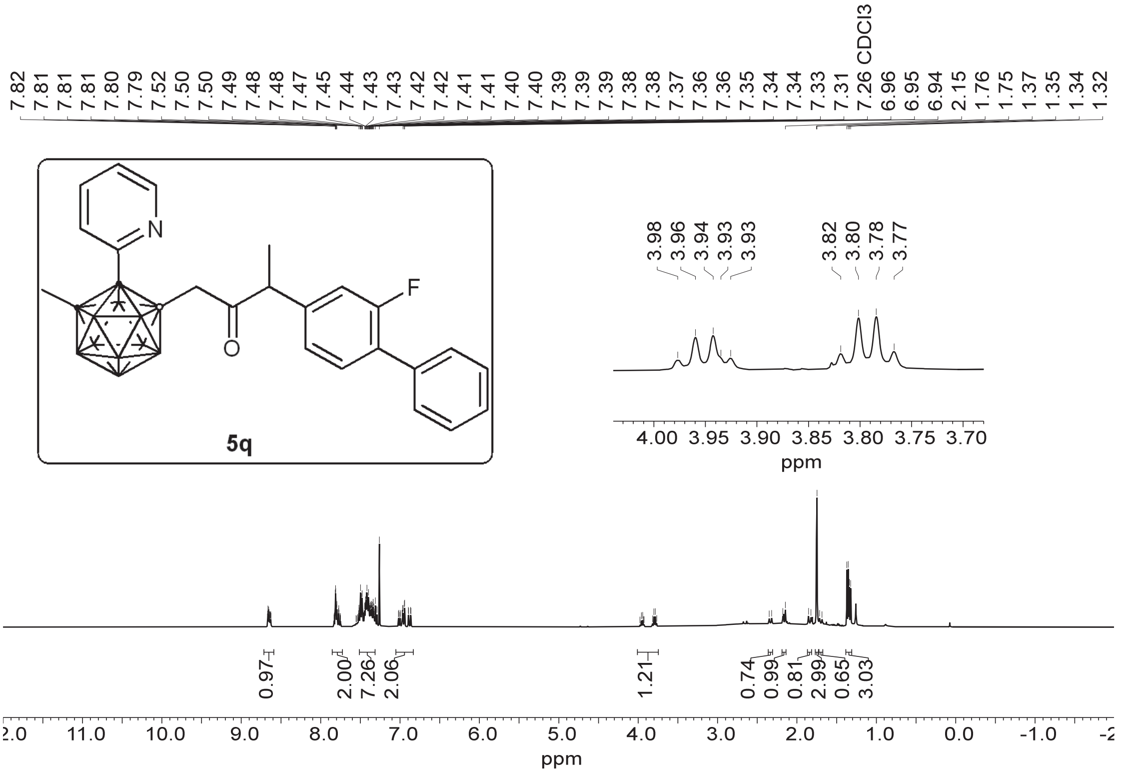
^{11}B NMR (128 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



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



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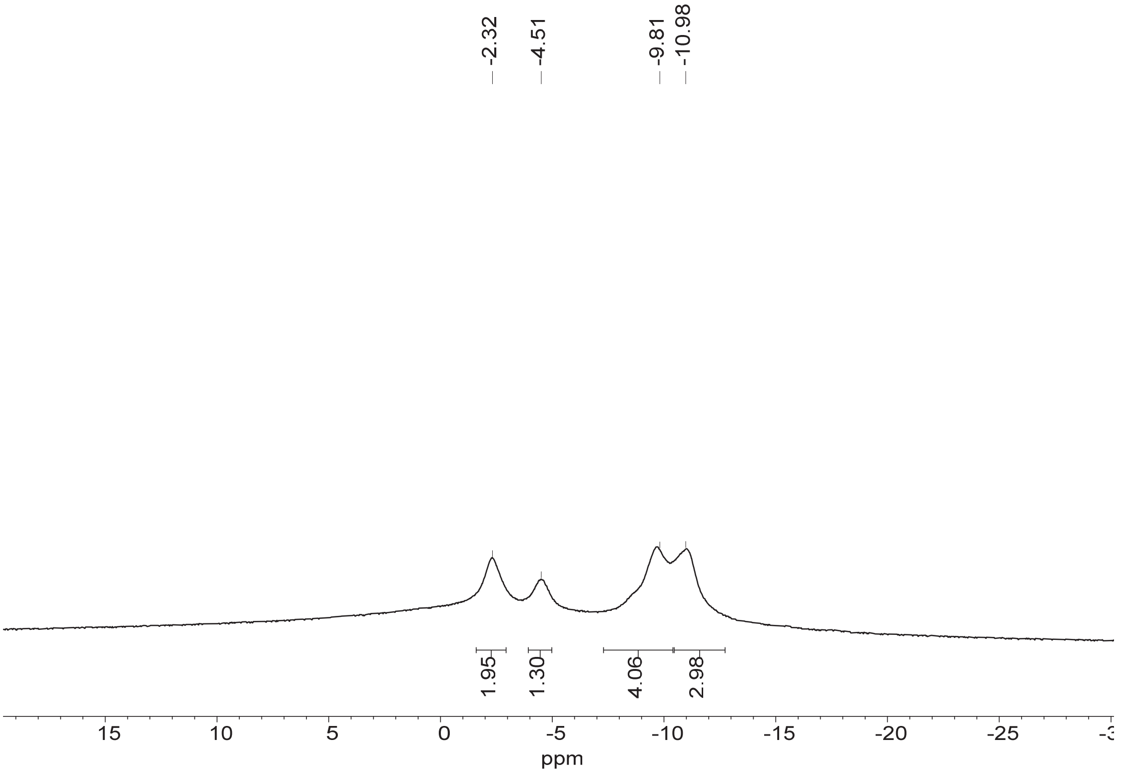
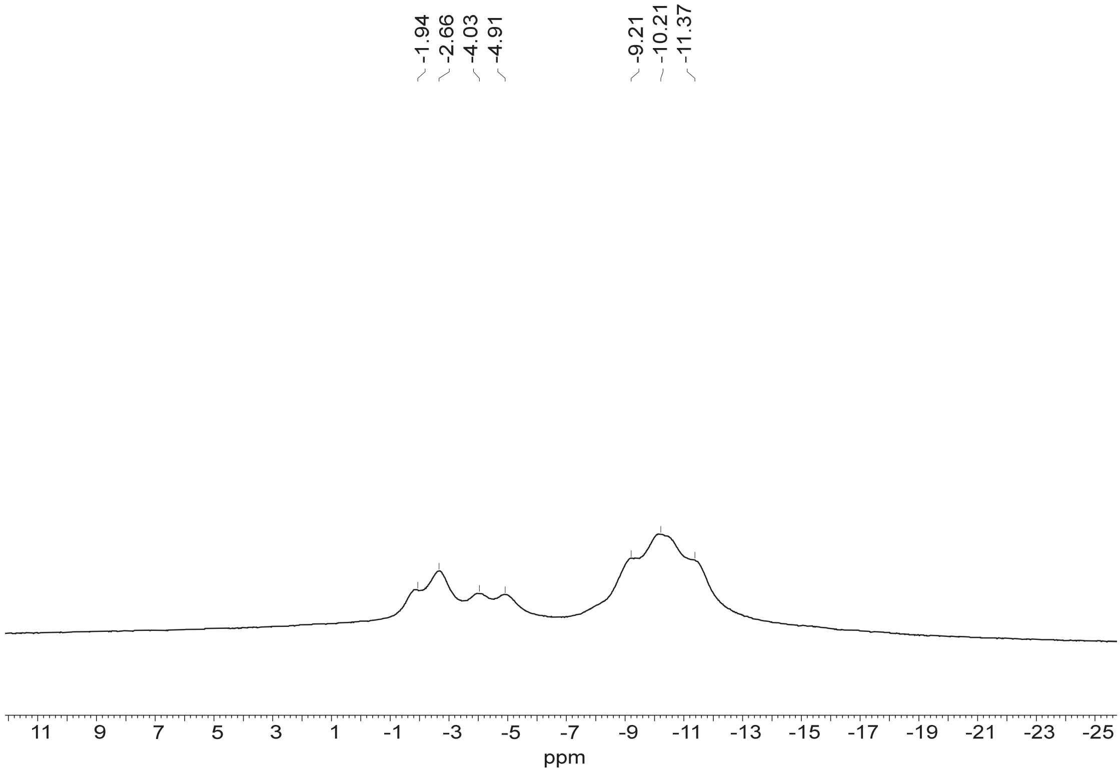
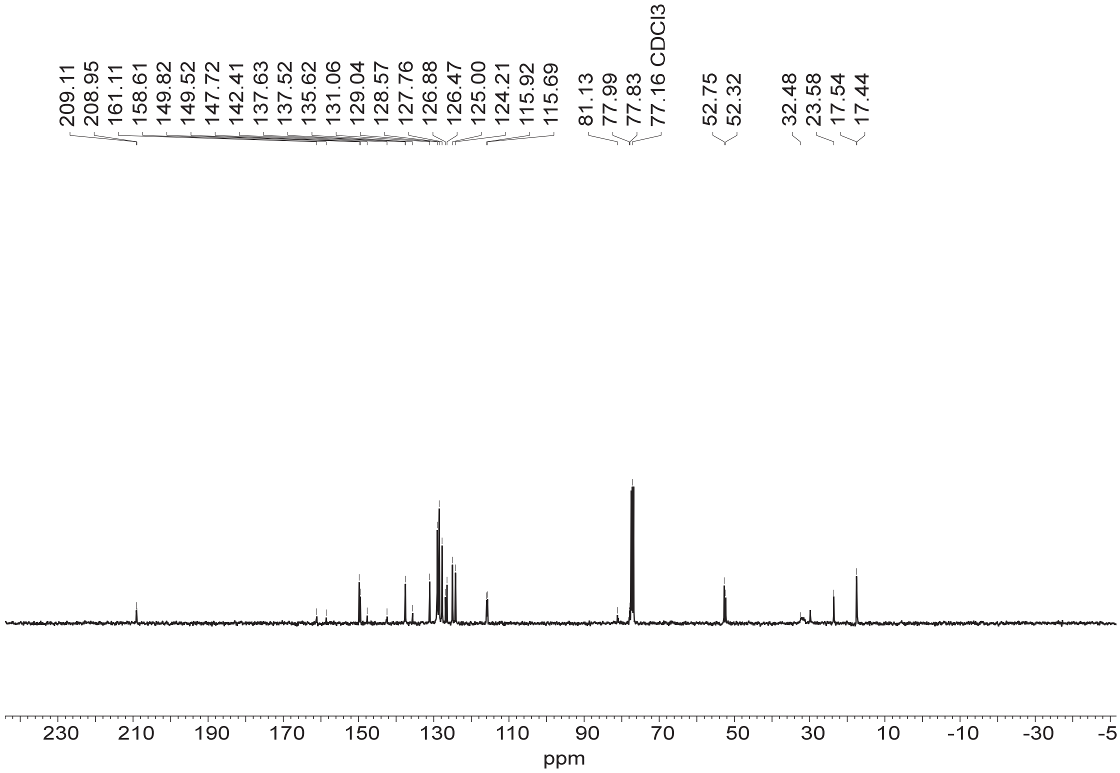
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



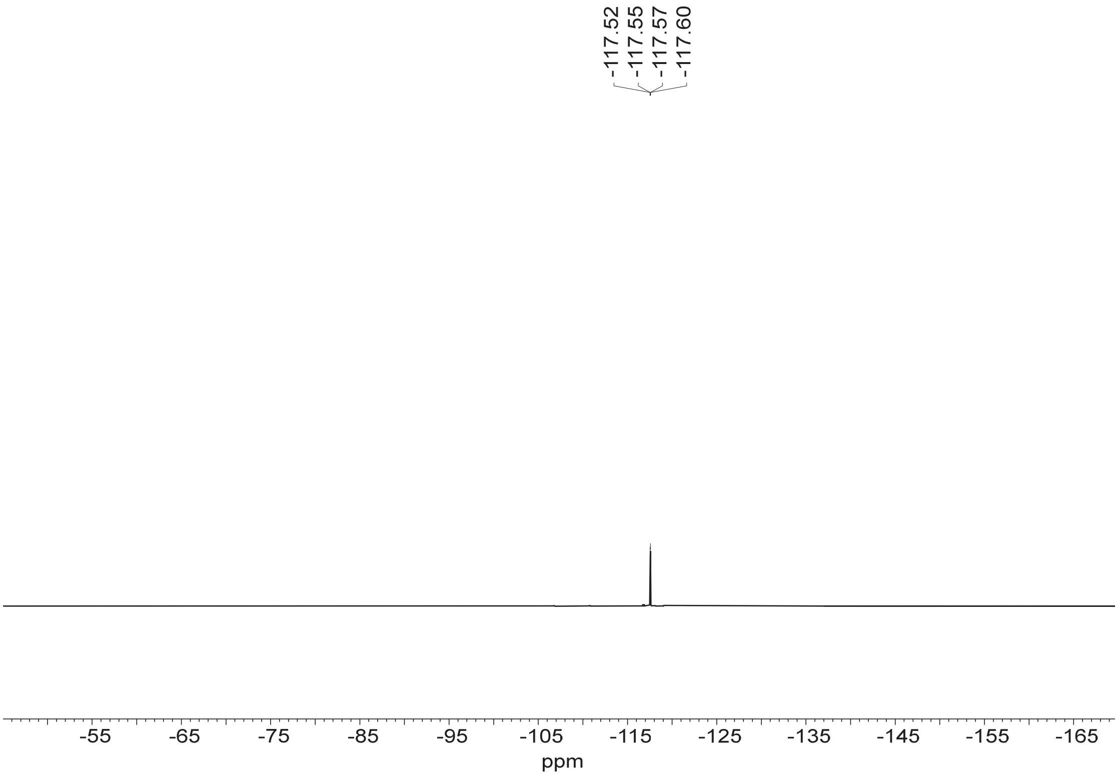
^{11}B NMR (128 MHz, CDCl$_3$)



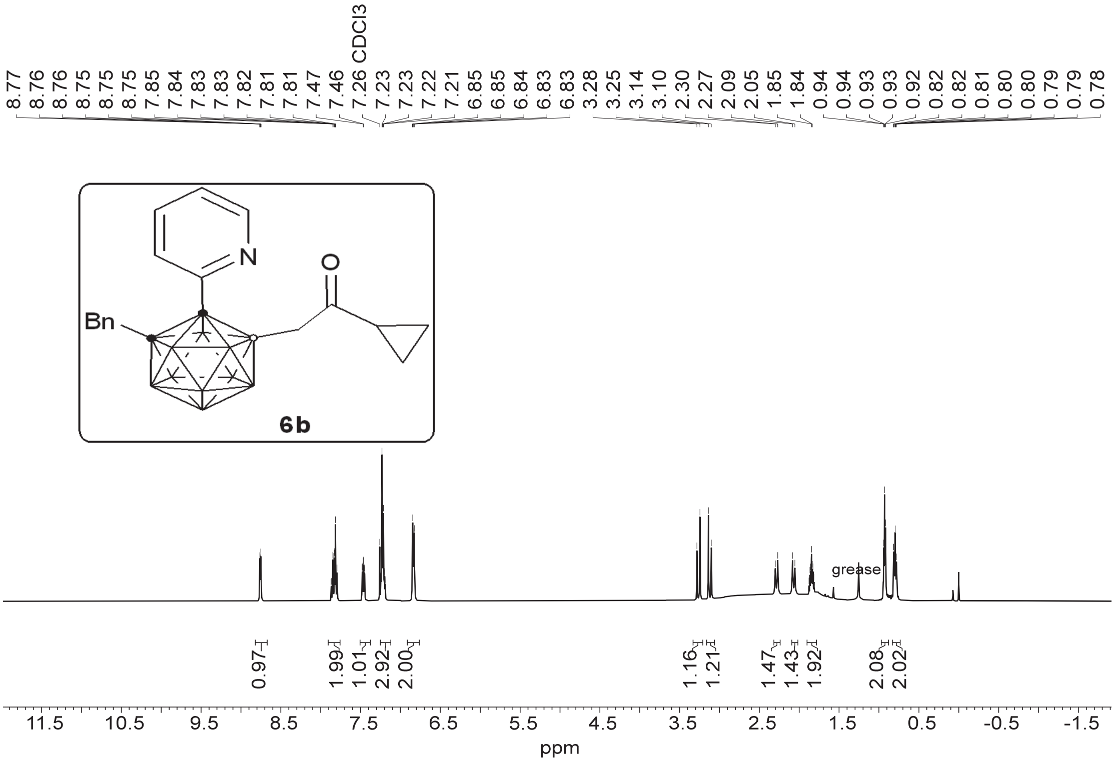
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



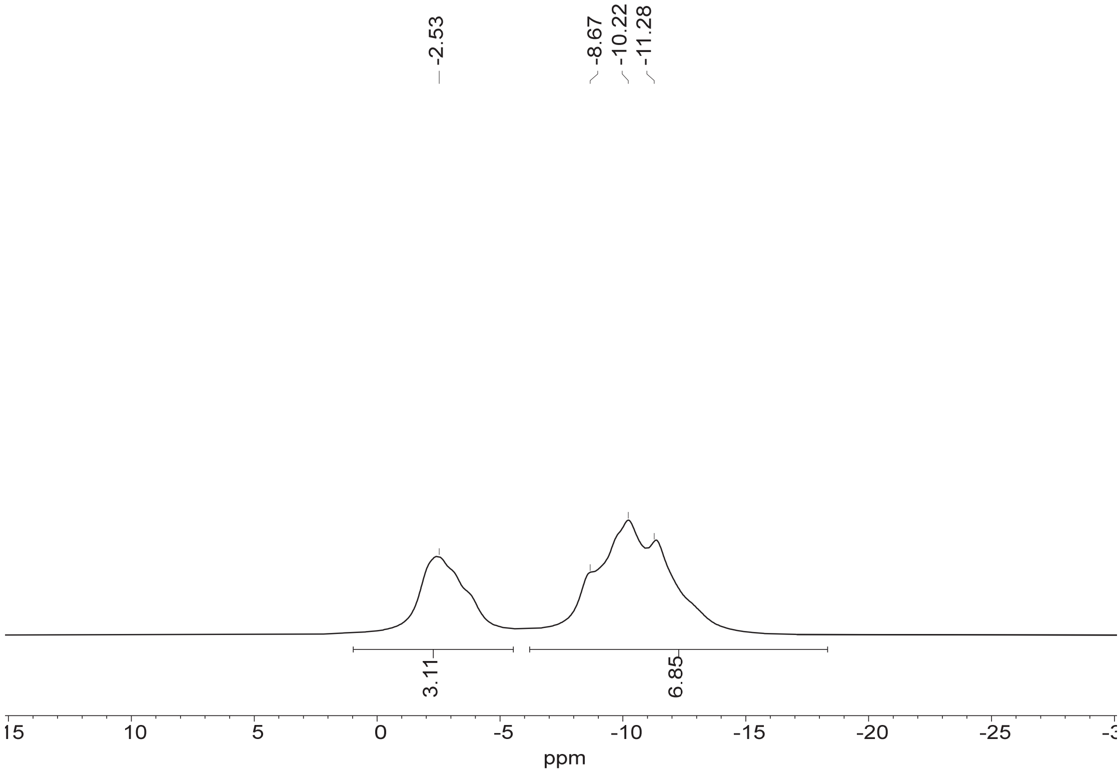
^{19}F NMR (376 MHz, CDCl$_3$)



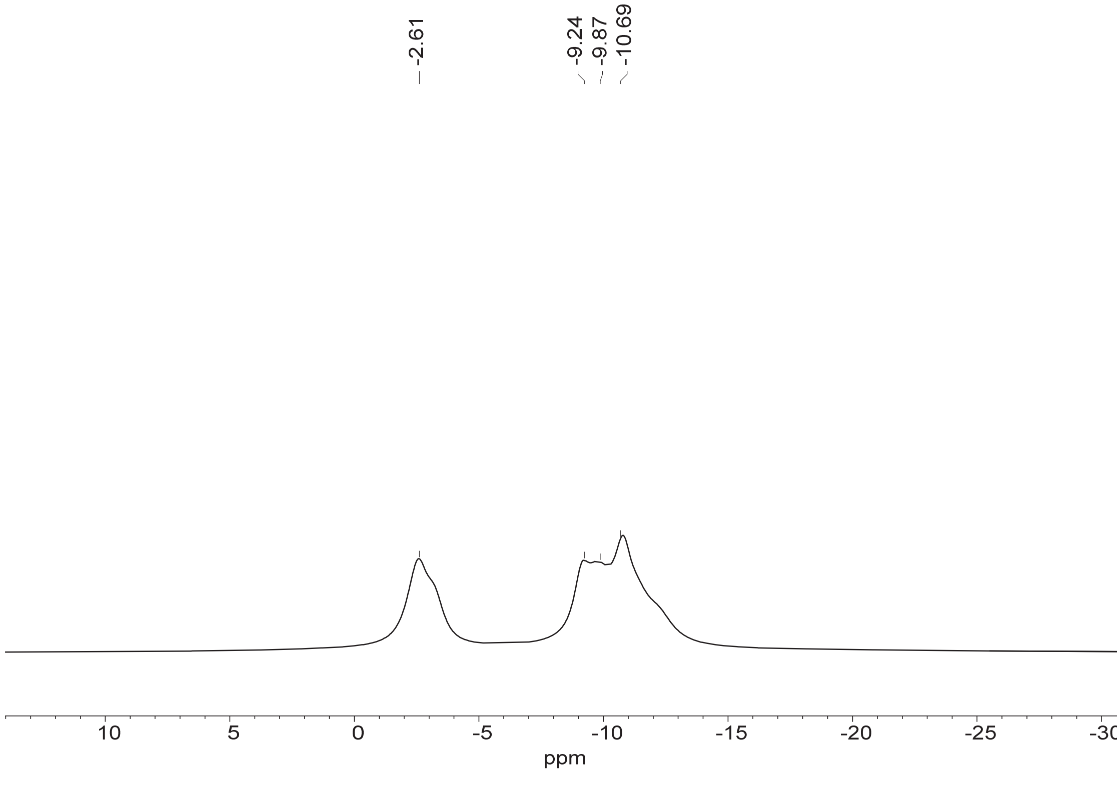
^{1}H NMR (400 MHz, CDCl$_3$)



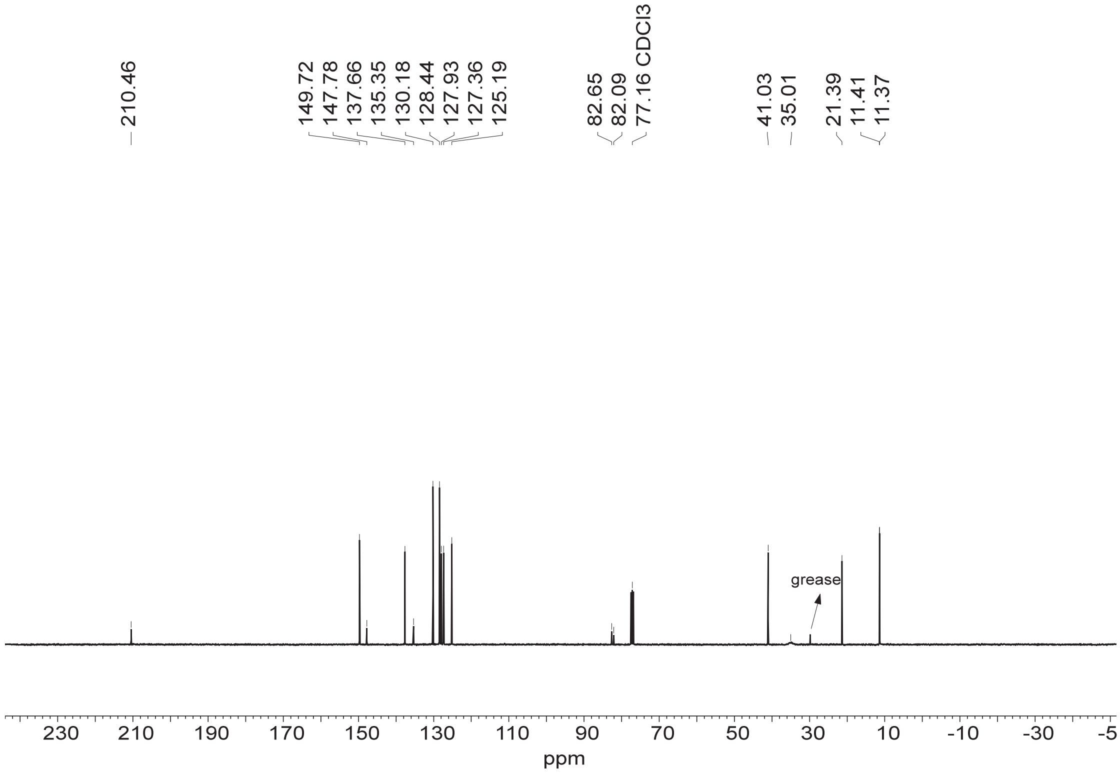
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



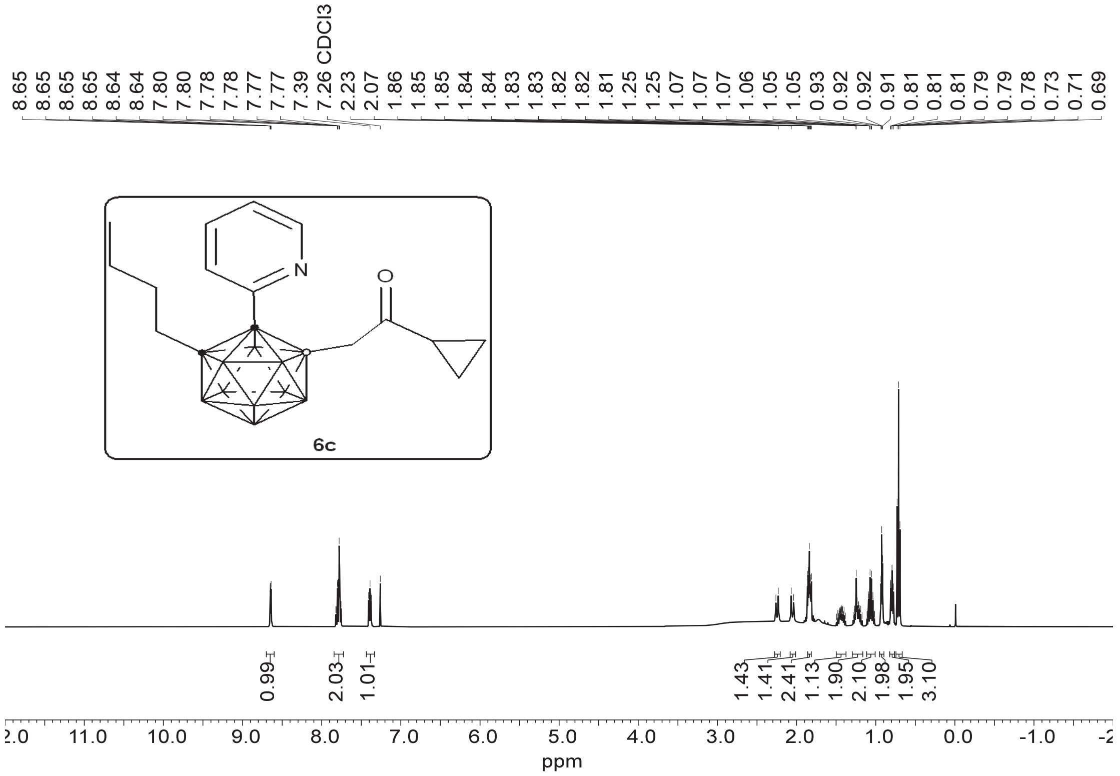
^{11}B NMR (128 MHz, $CDCl_3$)



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



^1H NMR (400 MHz, $CDCl_3$)



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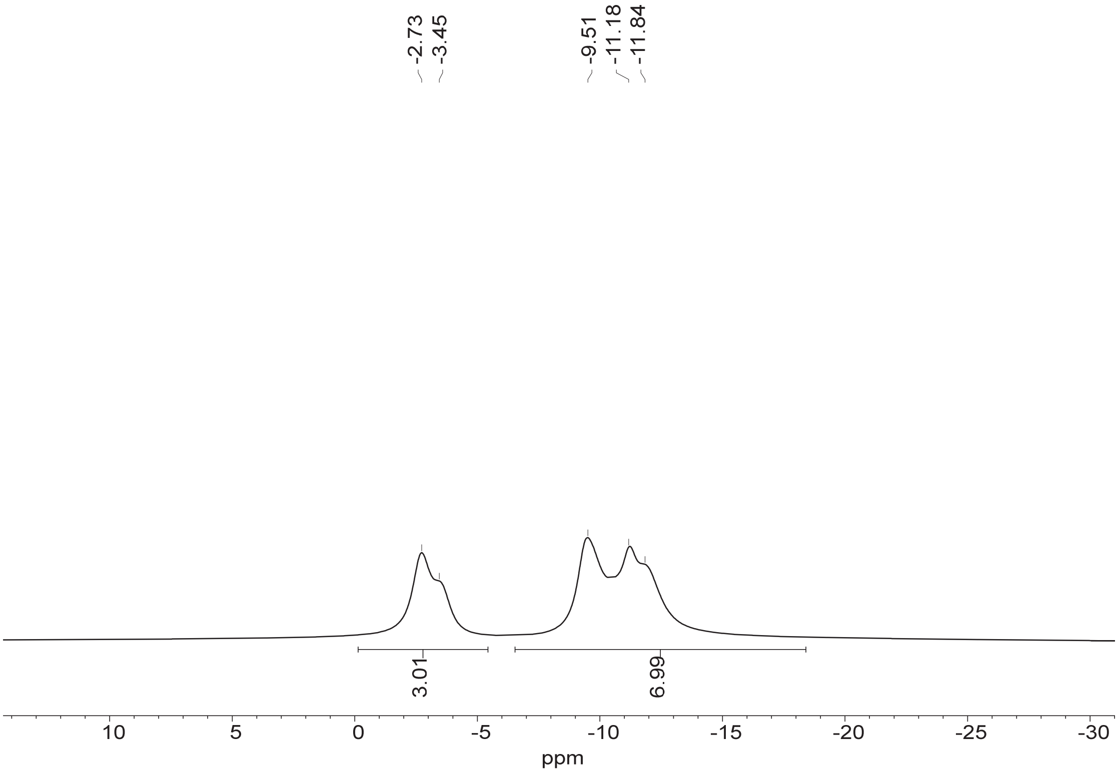
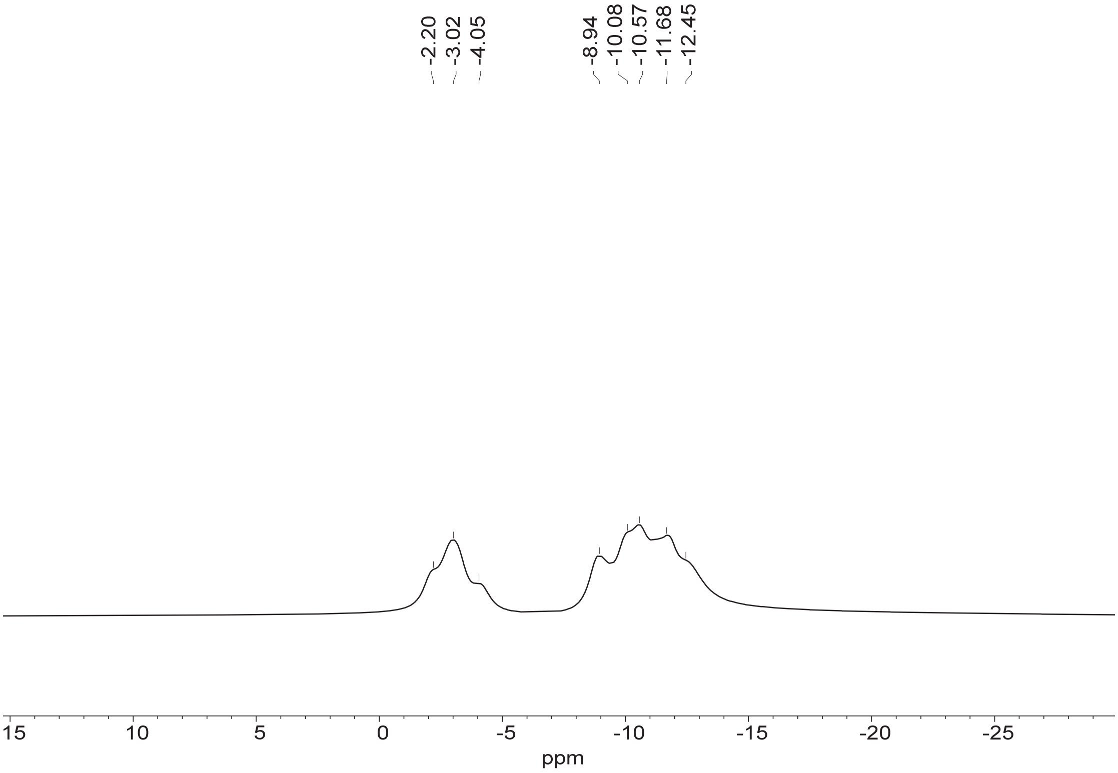
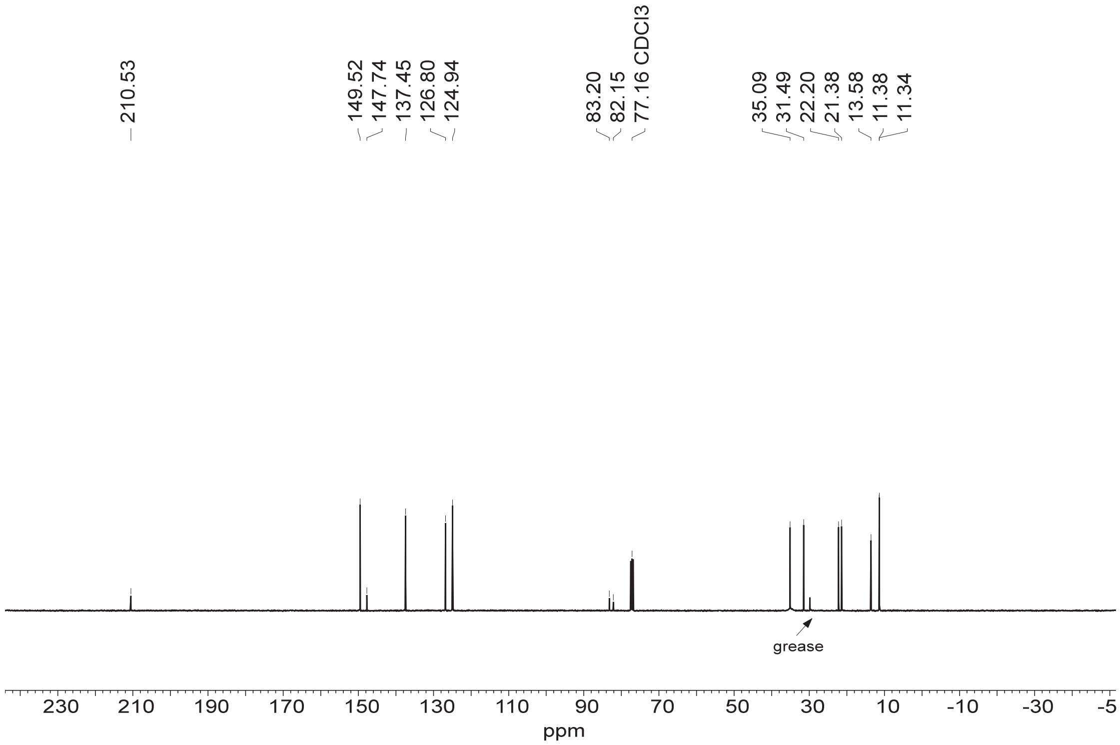


^{11}B NMR (128 MHz, $CDCl_3$)



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



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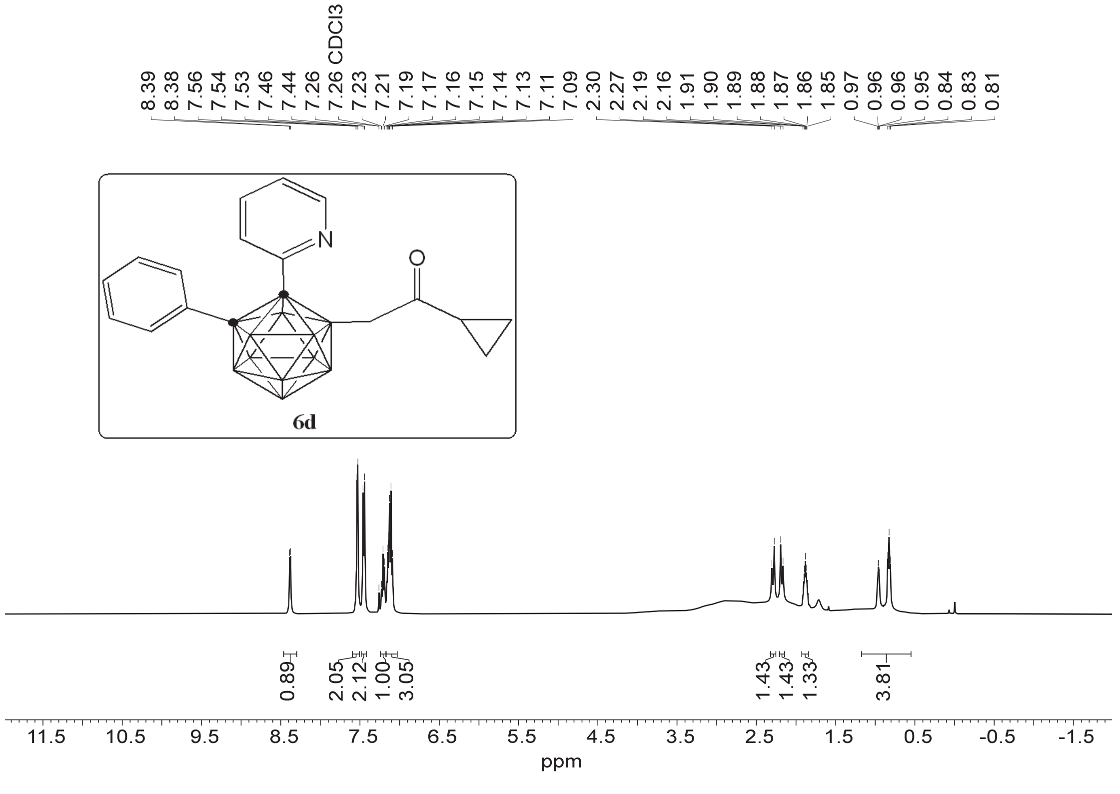
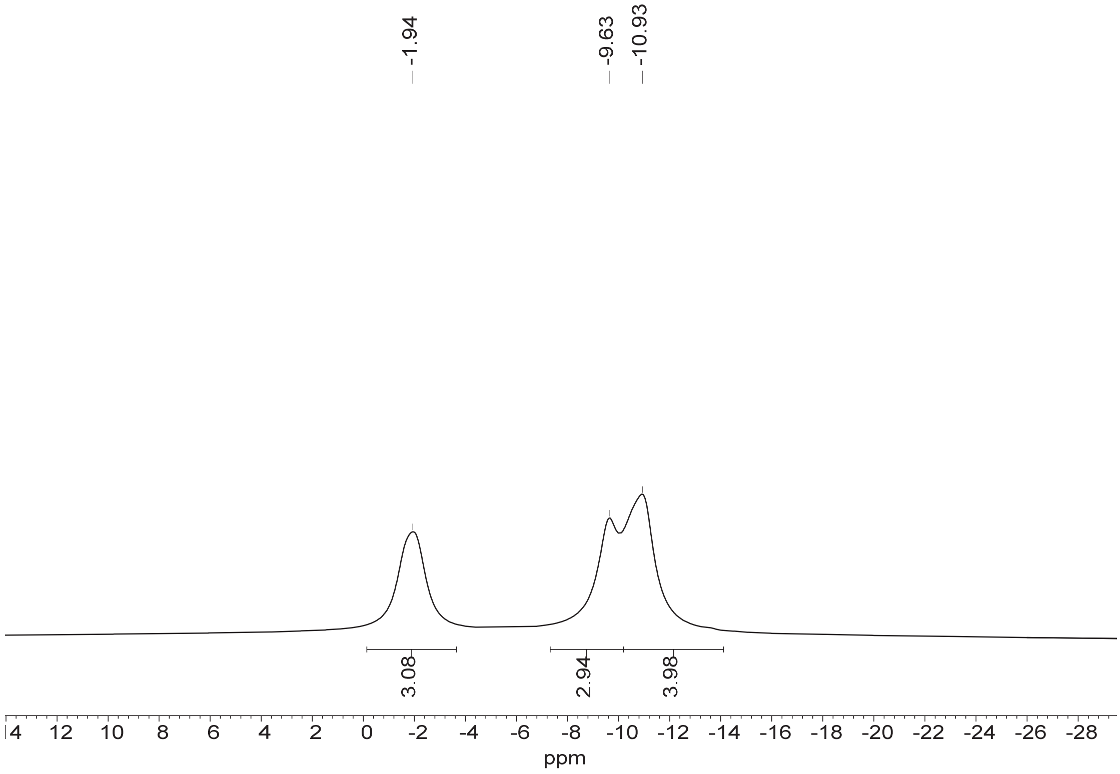
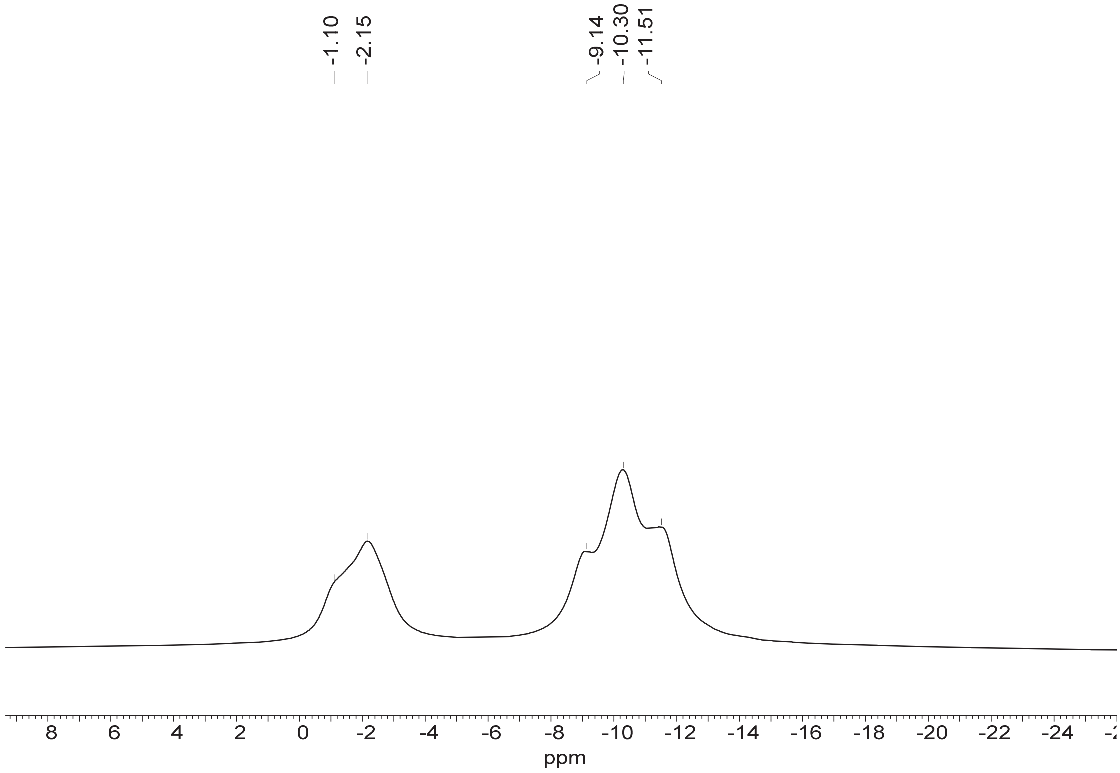


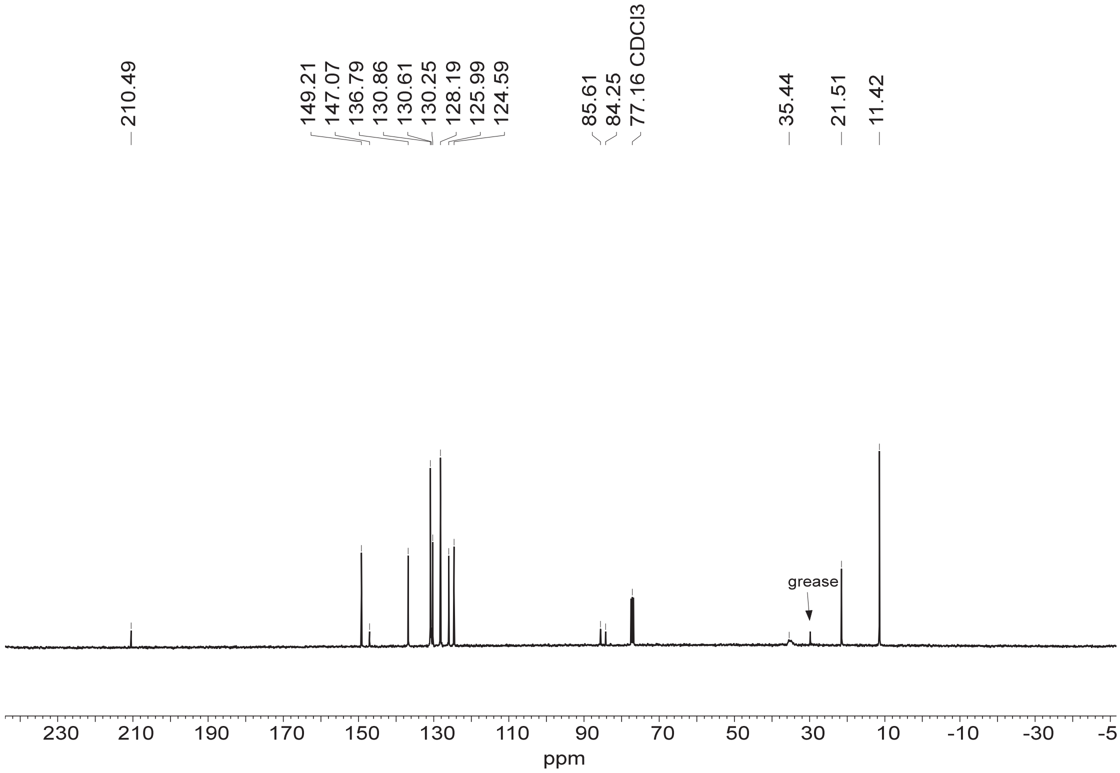
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



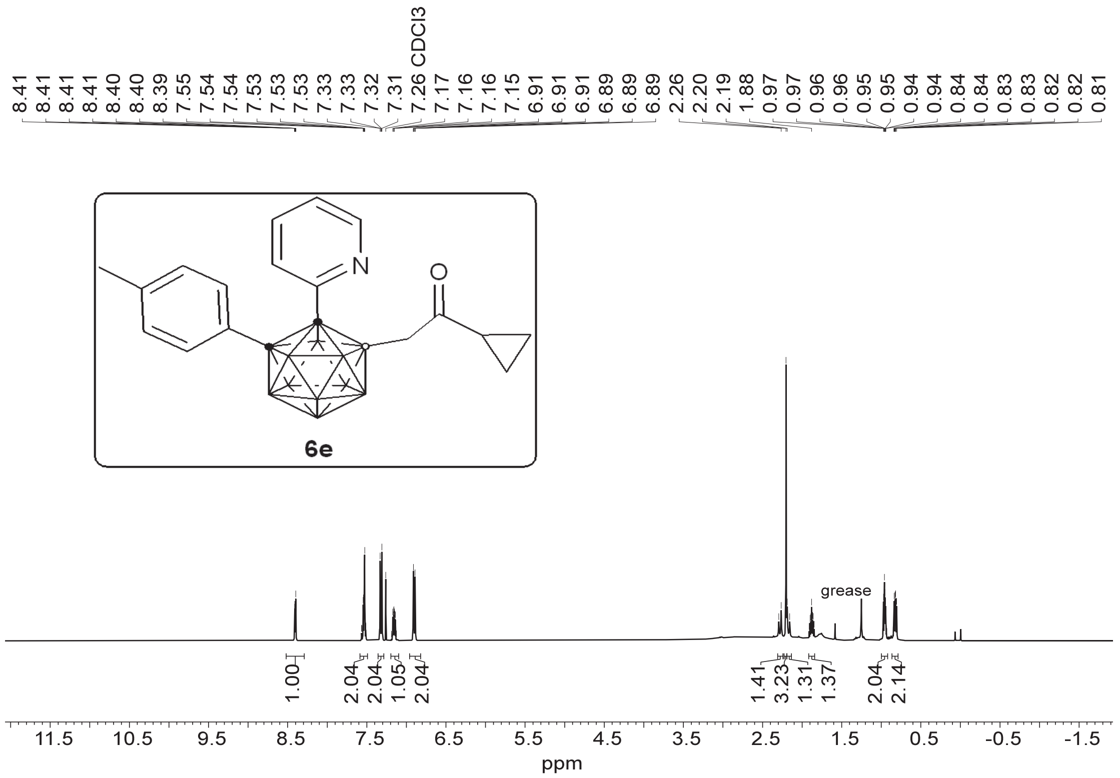
^{11}B NMR (128 MHz, $CDCl_3$)



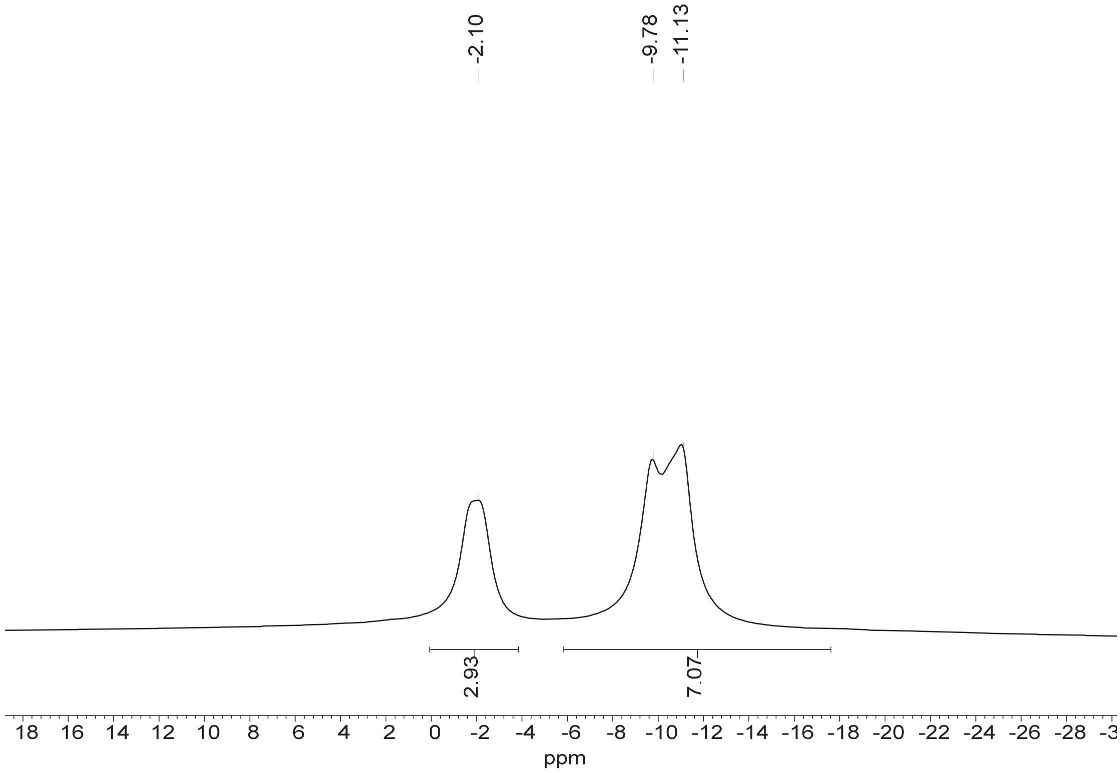
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



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



$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



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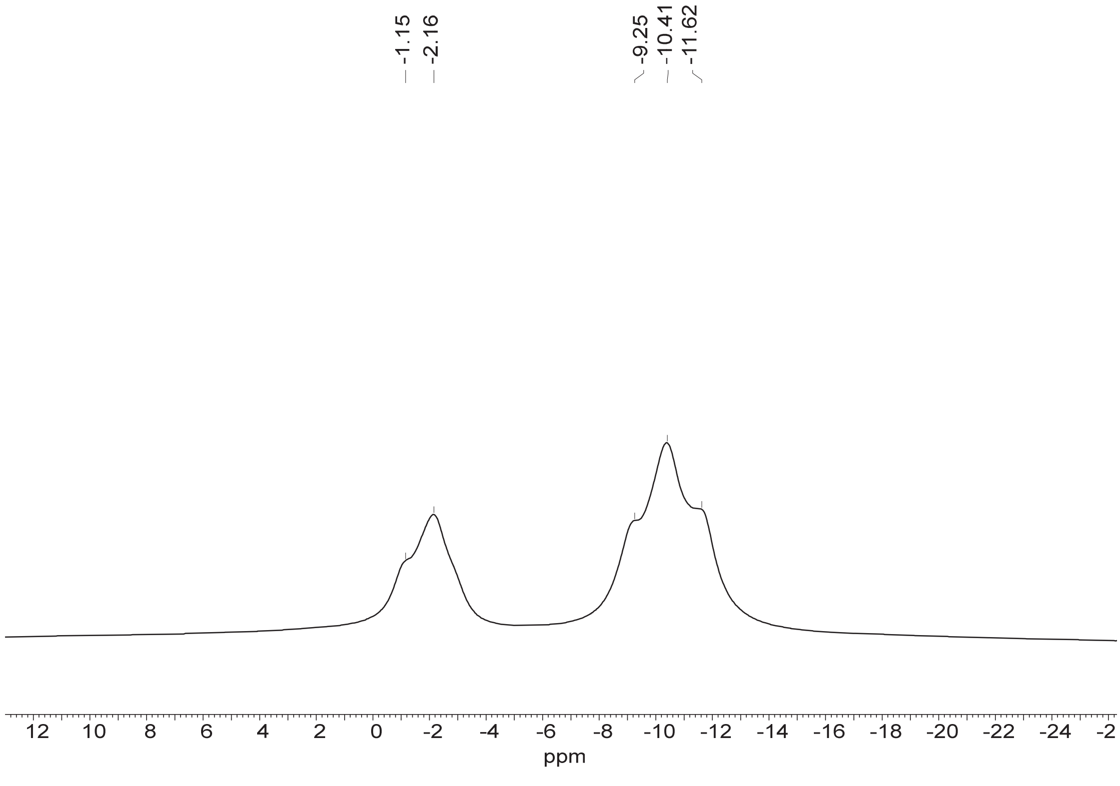
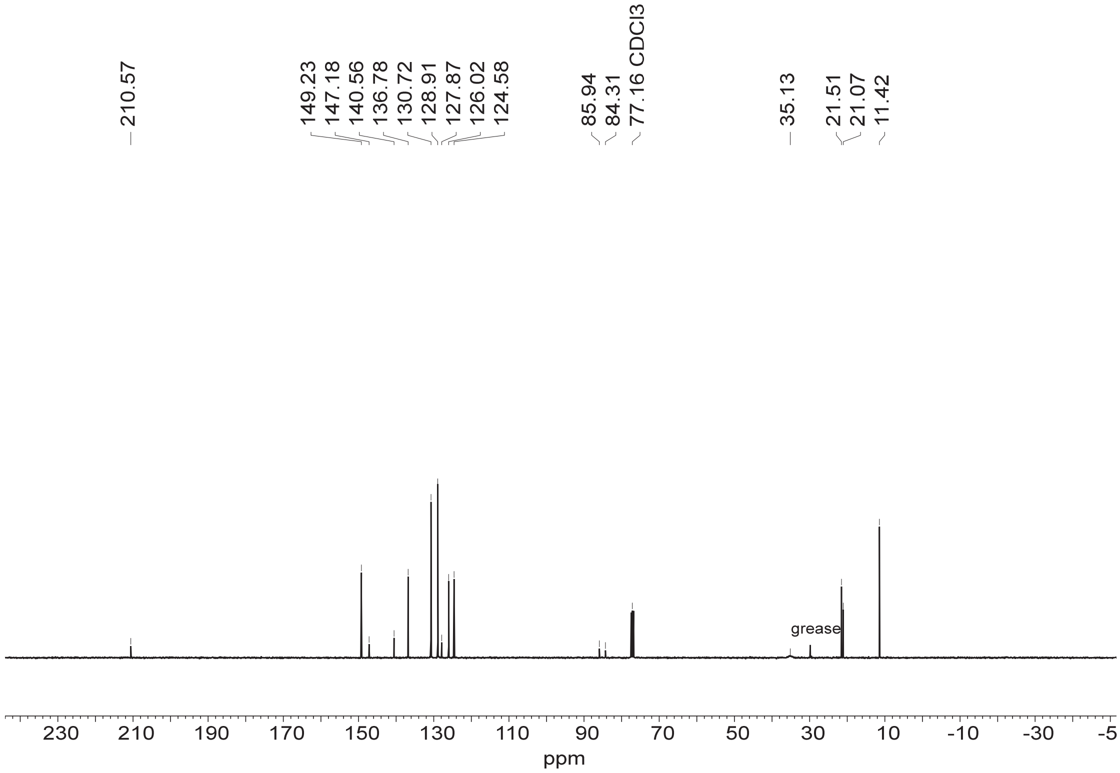
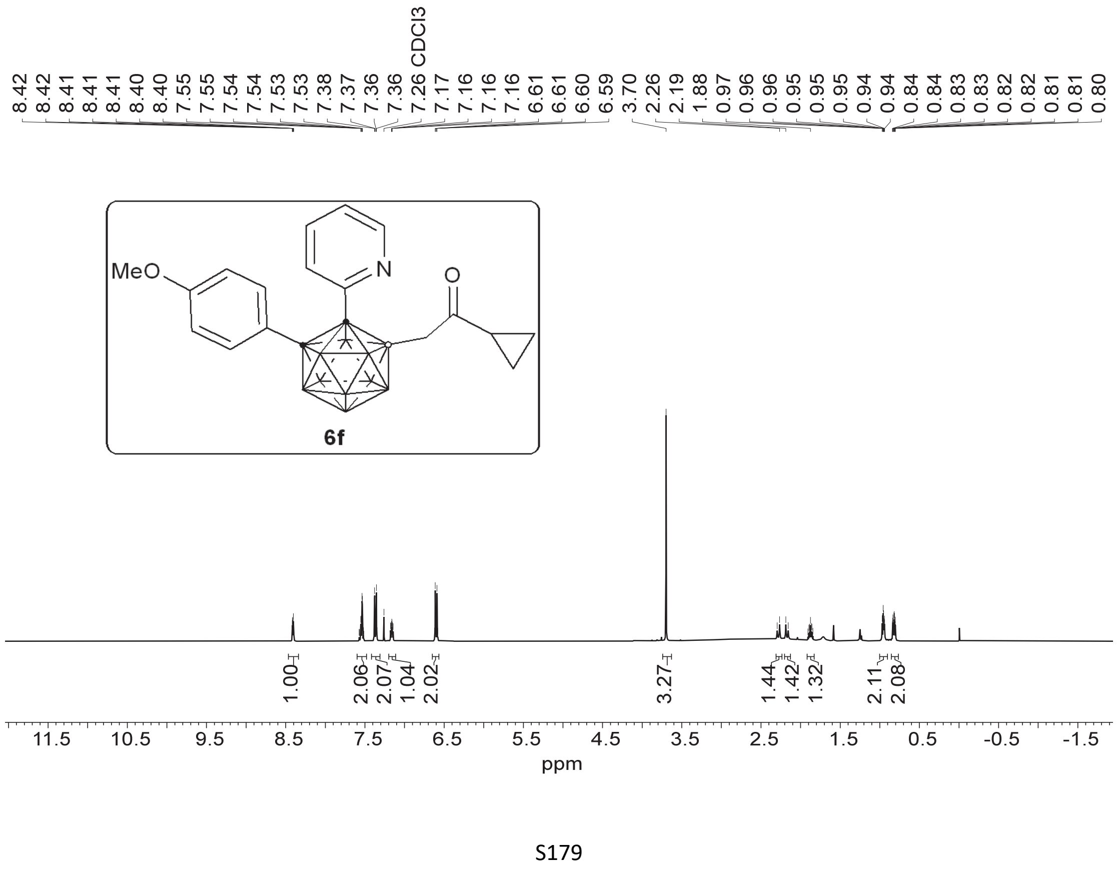


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

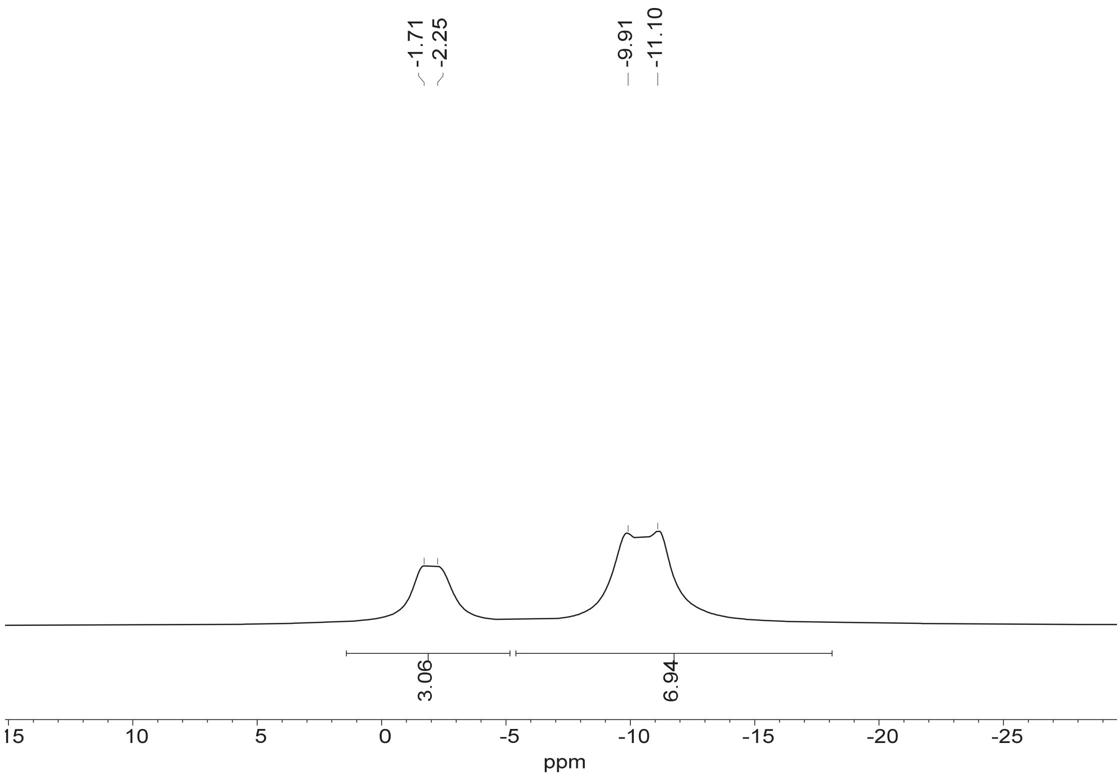


^{1}H NMR (400 MHz, $CDCl_3$)

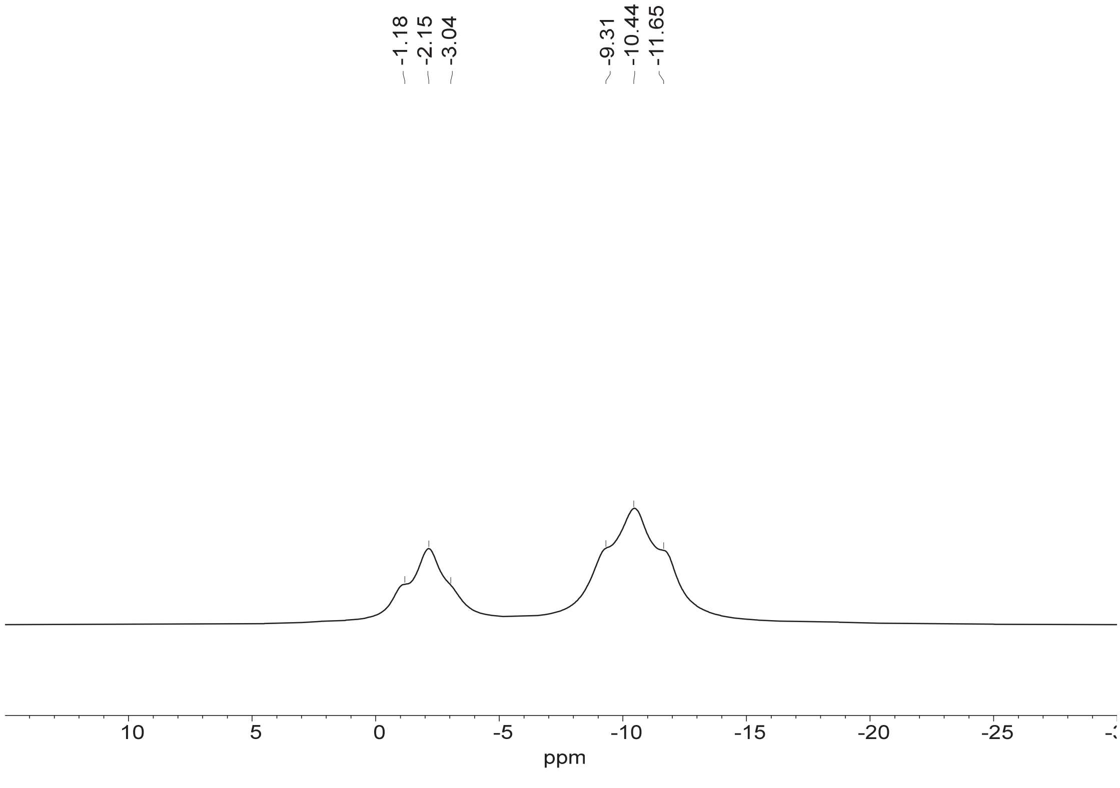


6f

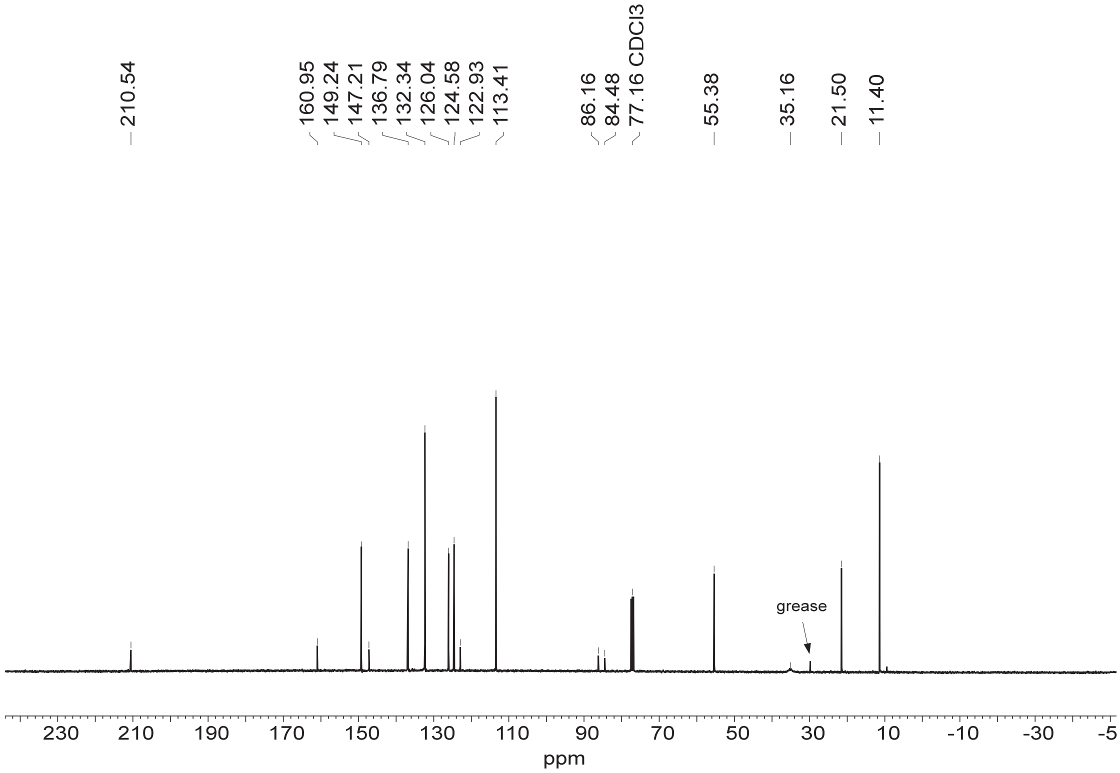
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



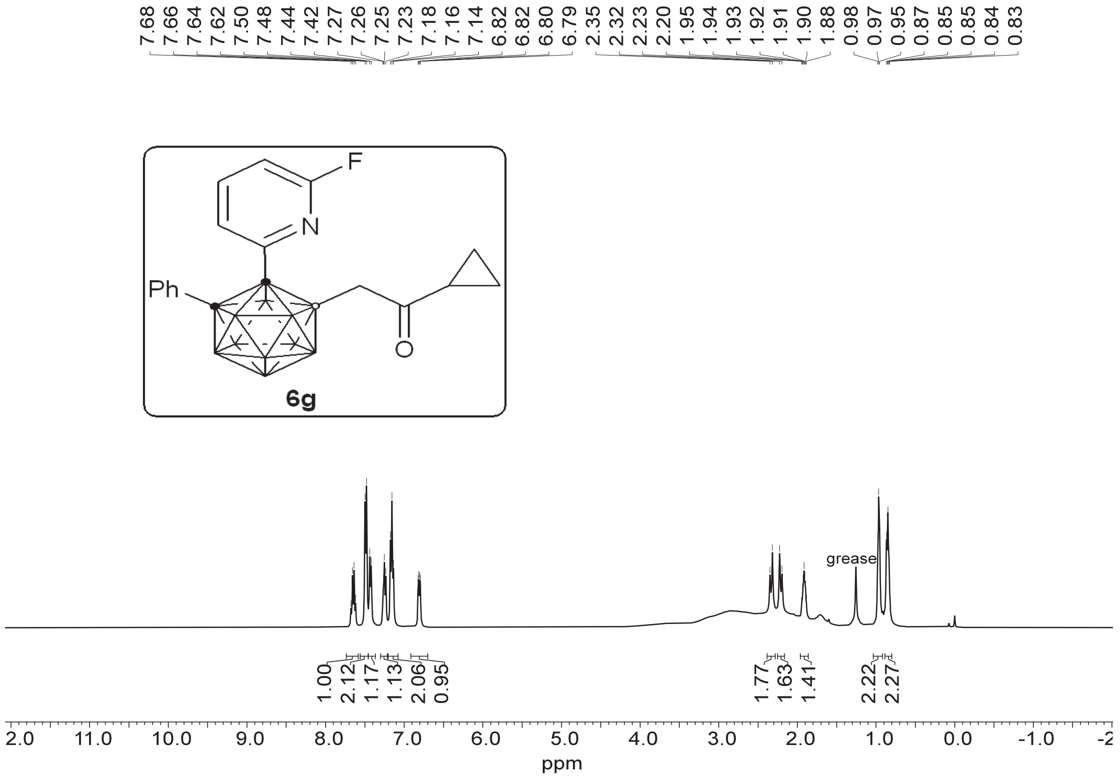
^{11}B NMR (128 MHz, $CDCl_3$)



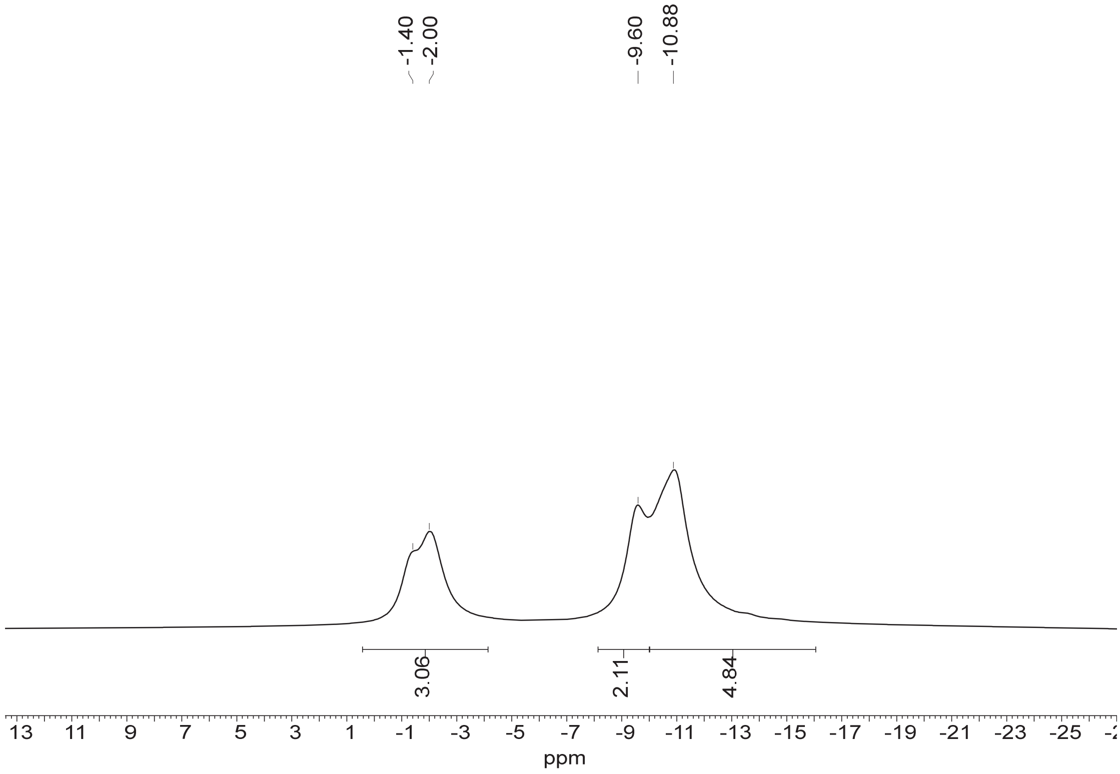
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



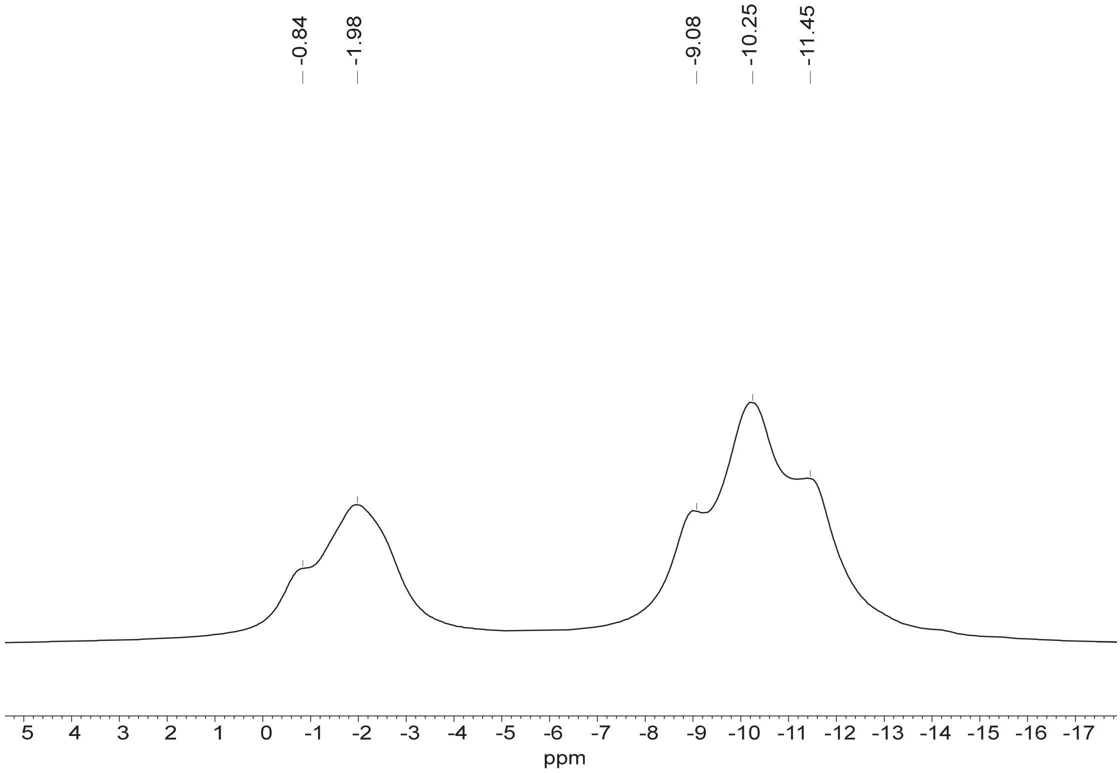
^1H NMR (400 MHz, $CDCl_3$)



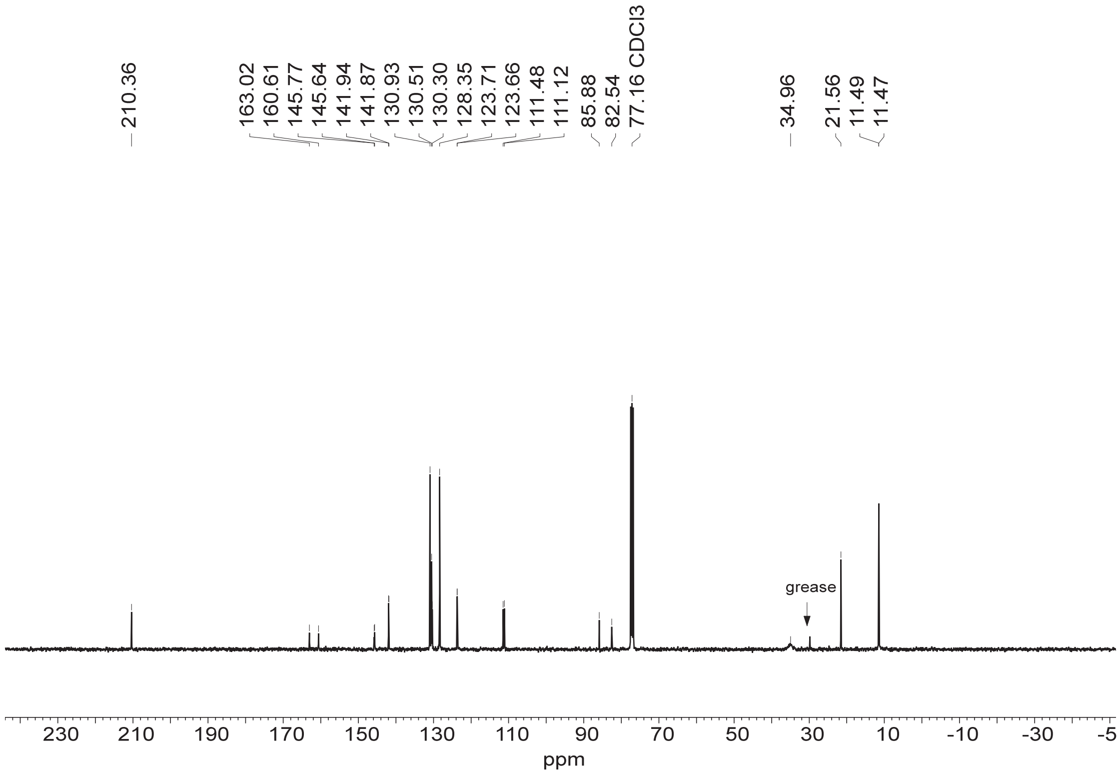
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



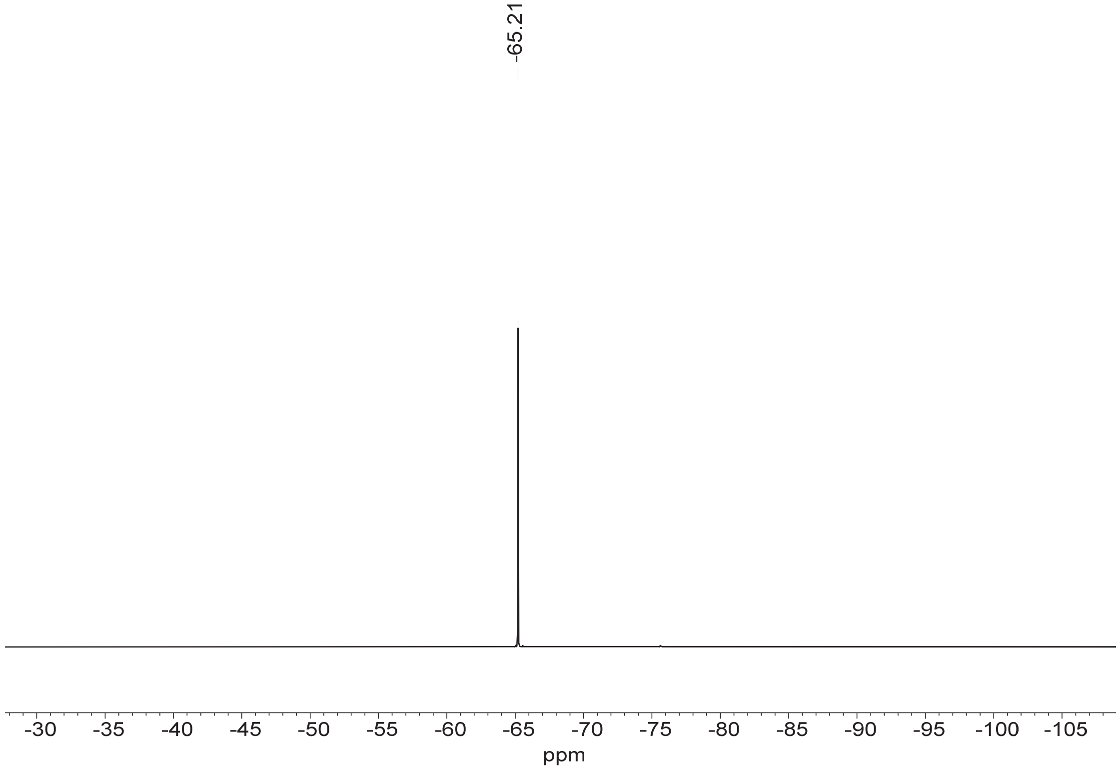
^{11}B NMR (128 MHz, $CDCl_3$)



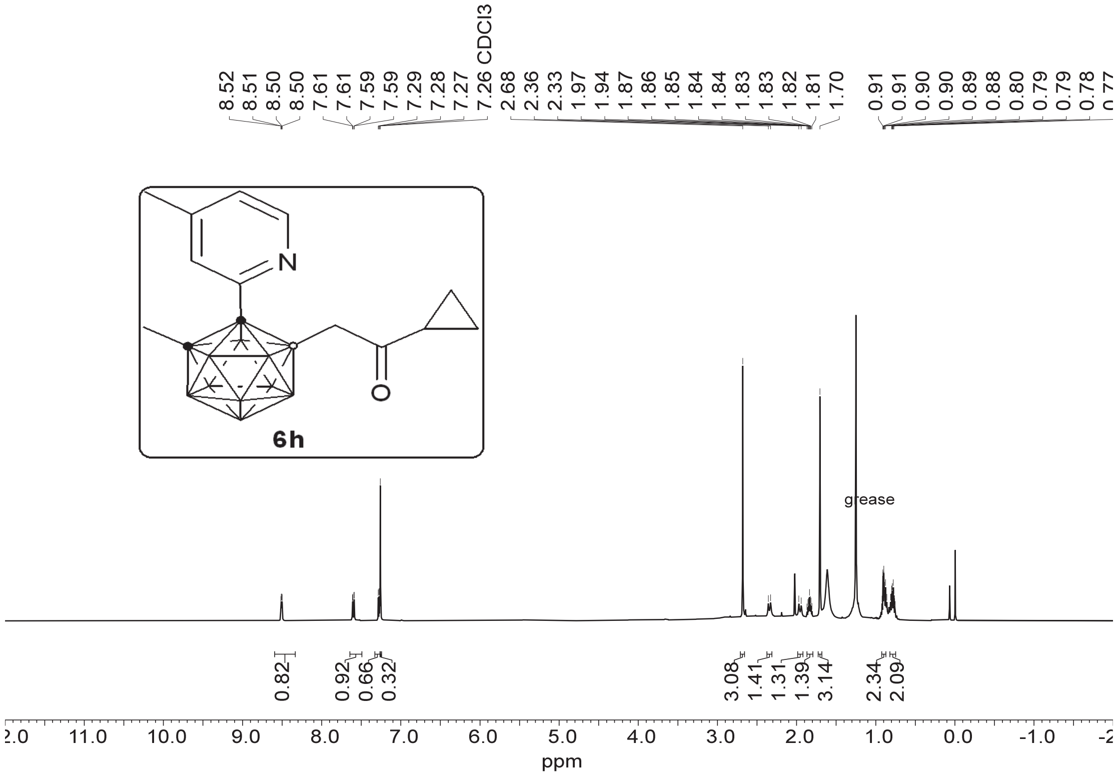
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



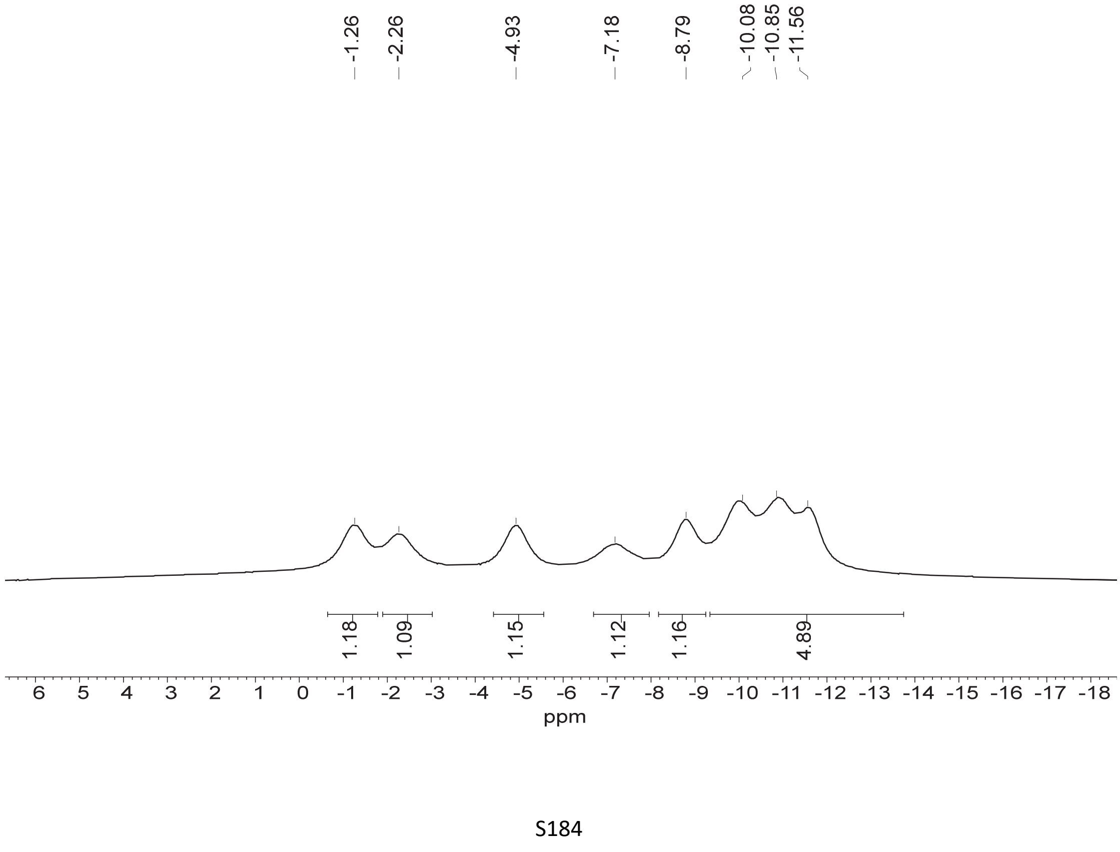
^{19}F NMR (471 MHz, CDCl$_3$)



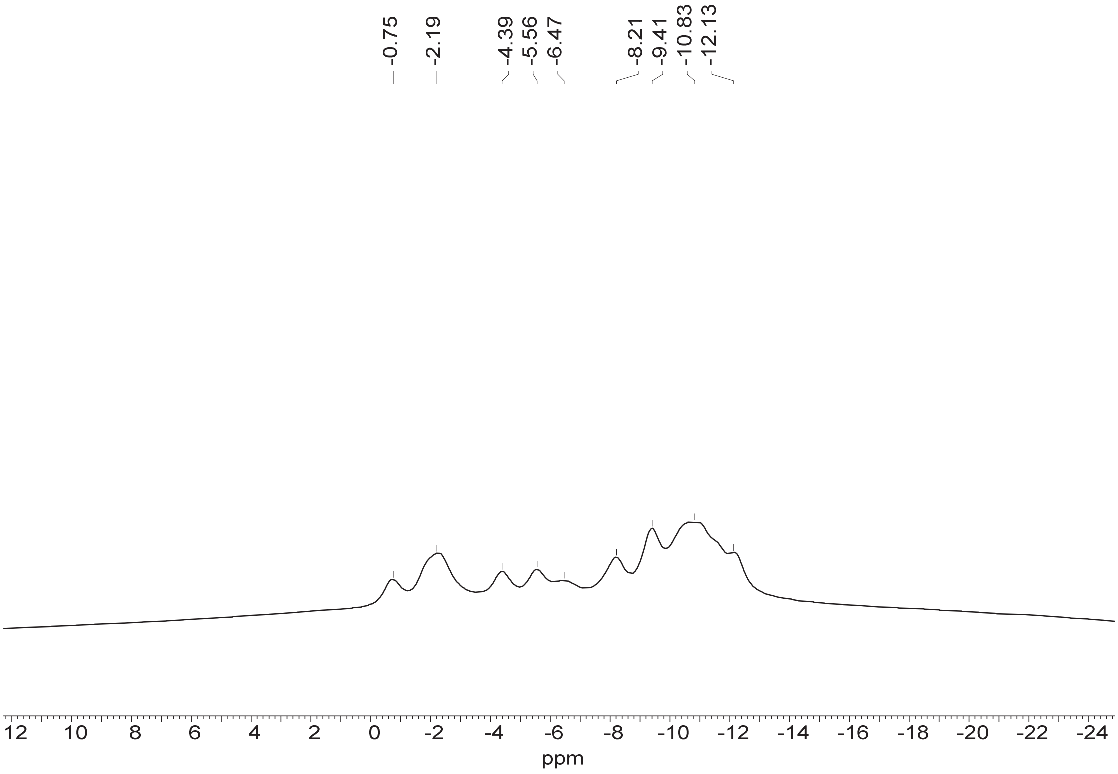
^{1}H NMR (400 MHz, $CDCl_3$)



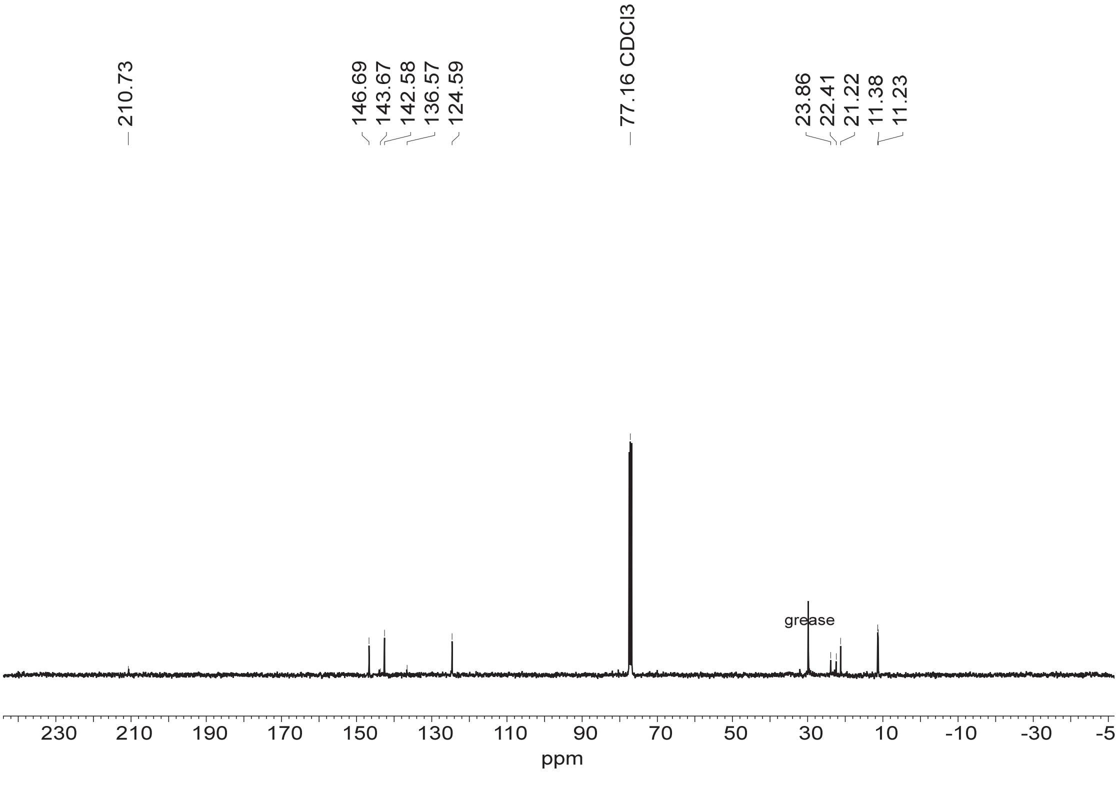
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



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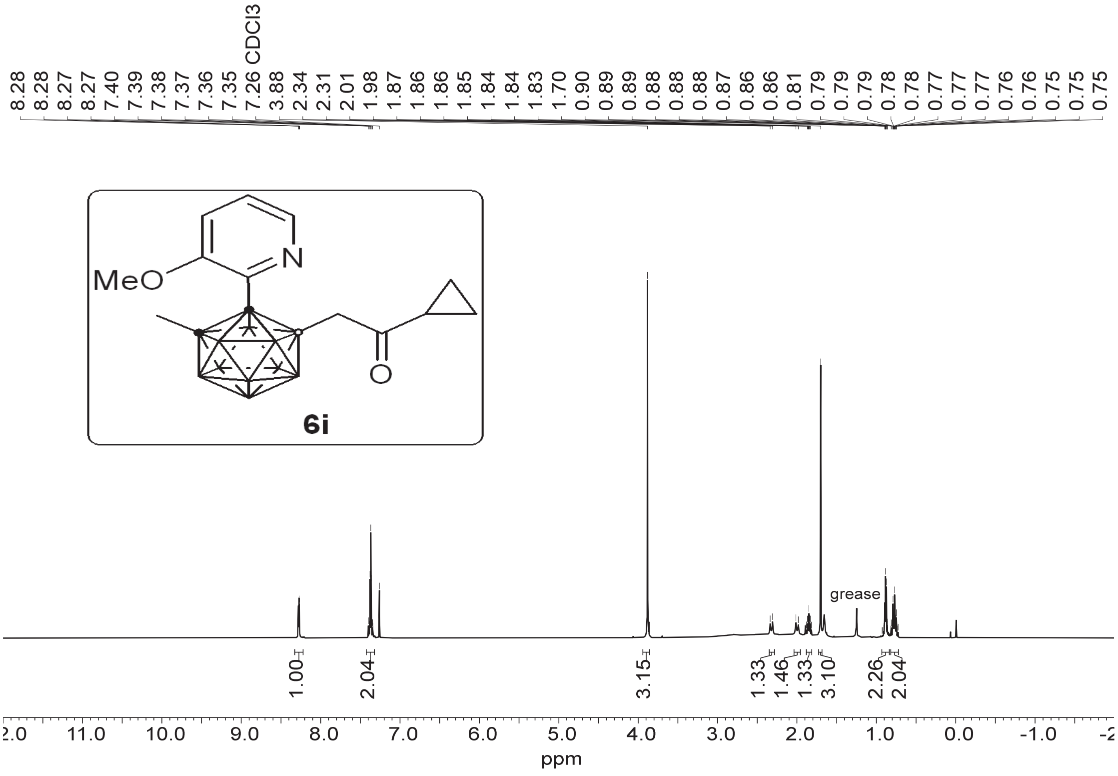

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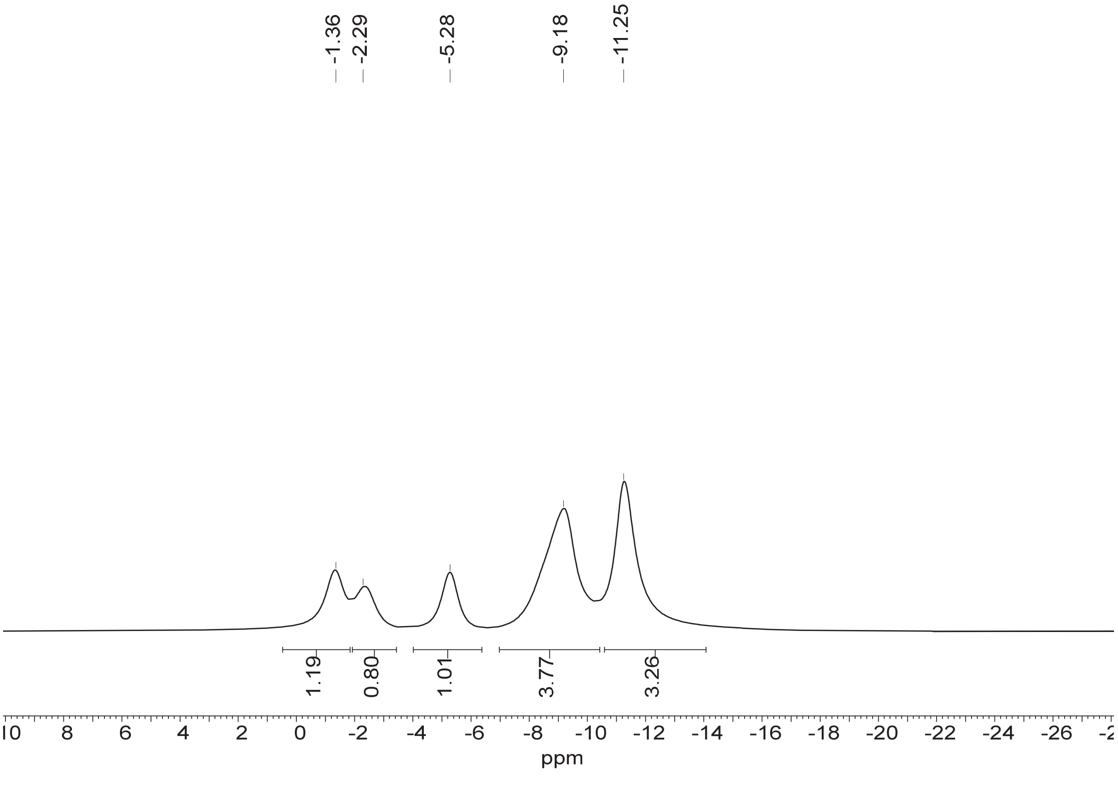

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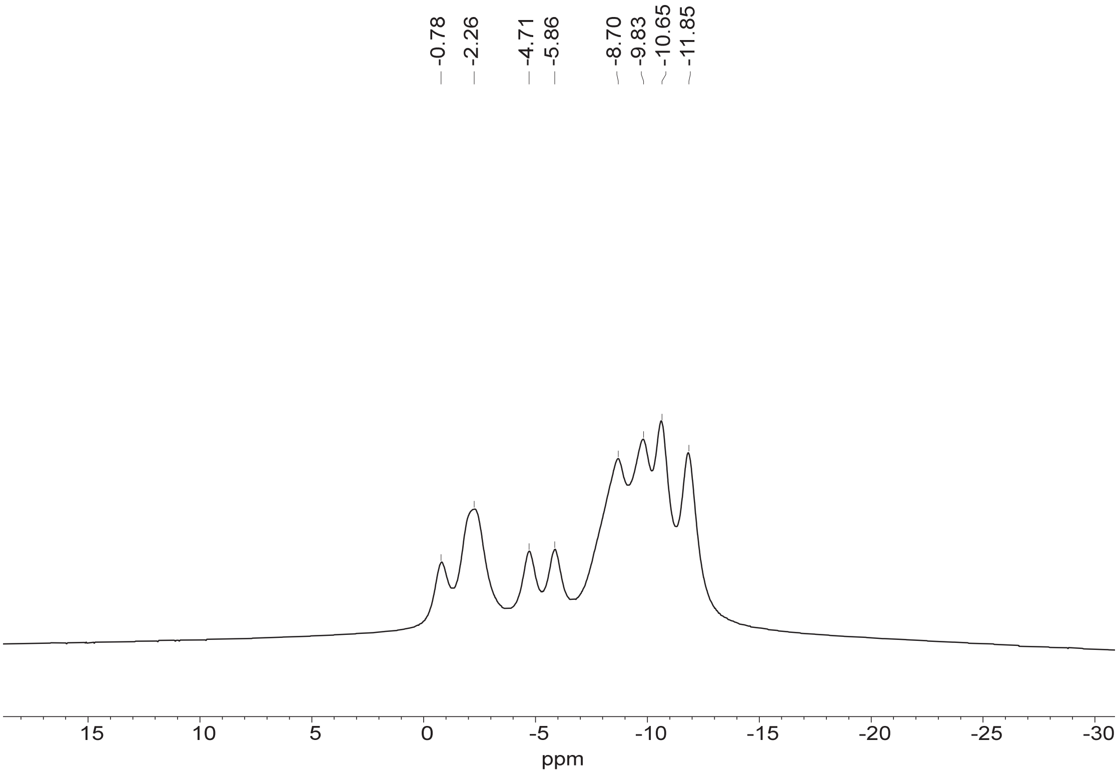

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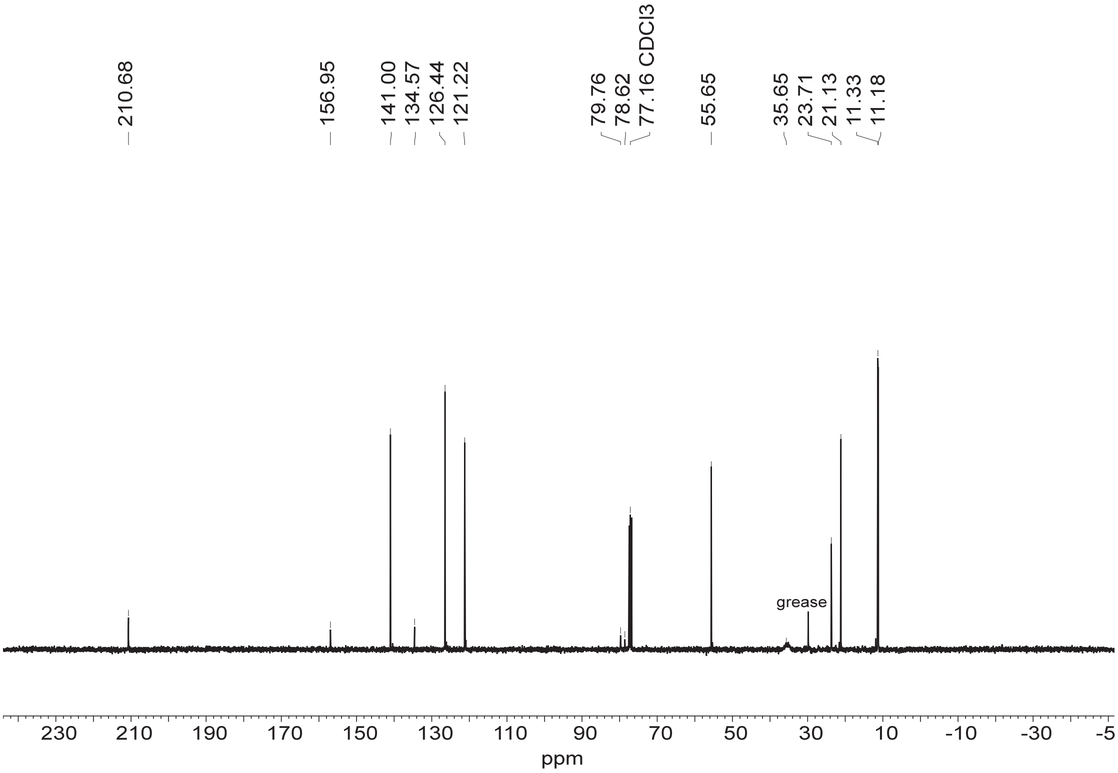
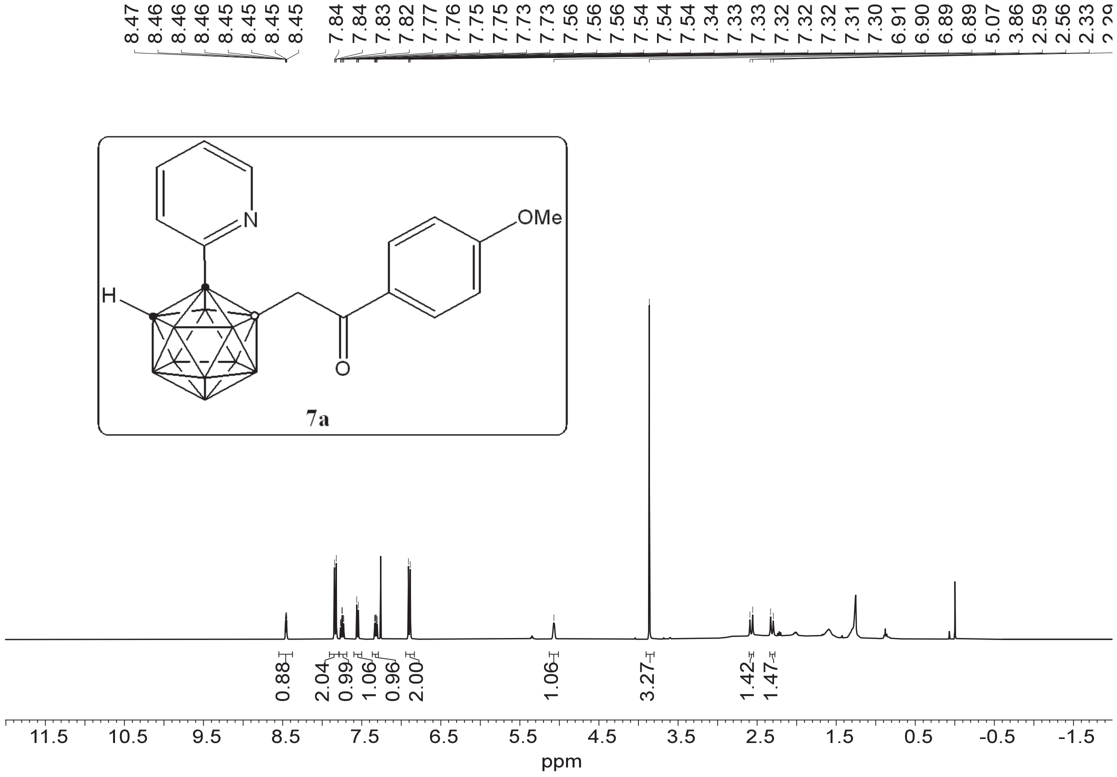
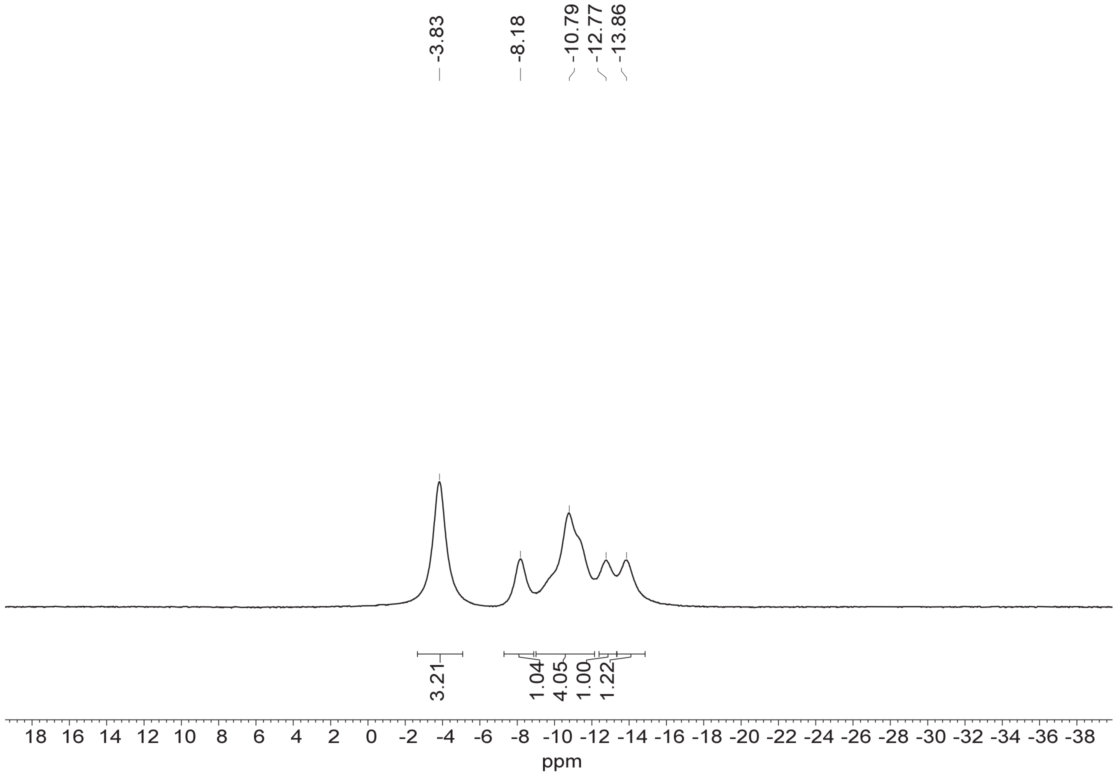


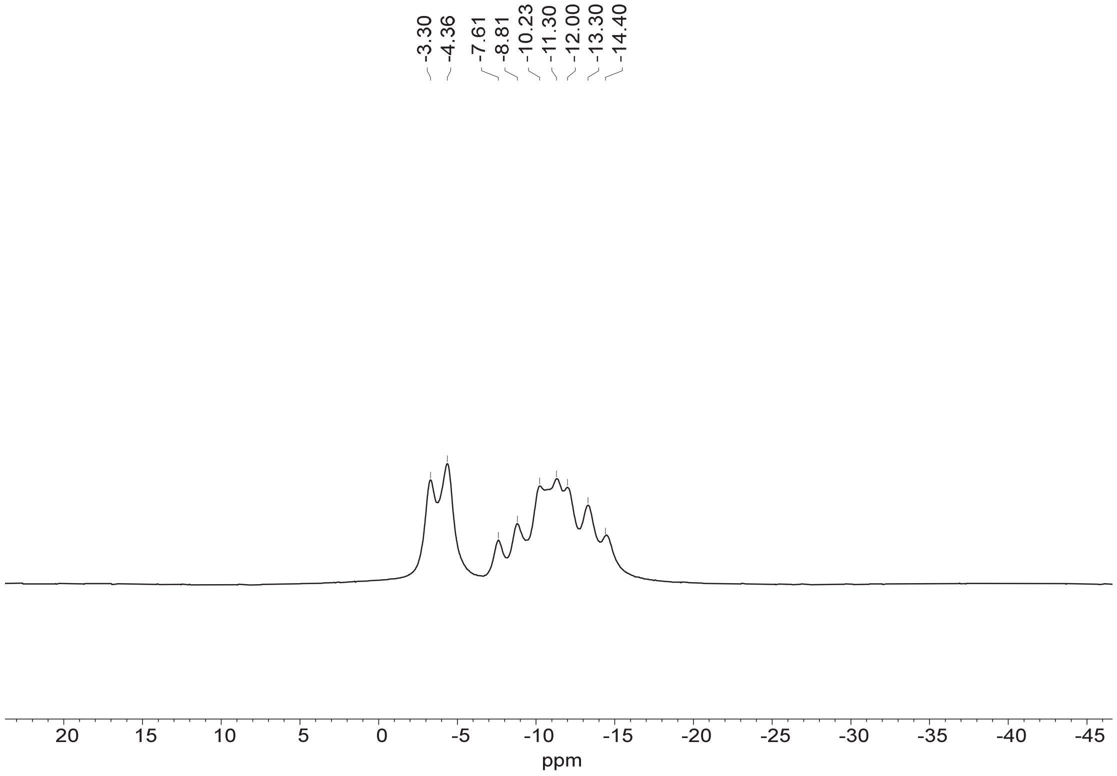
^{1}H NMR (400 MHz, $CDCl_3$)



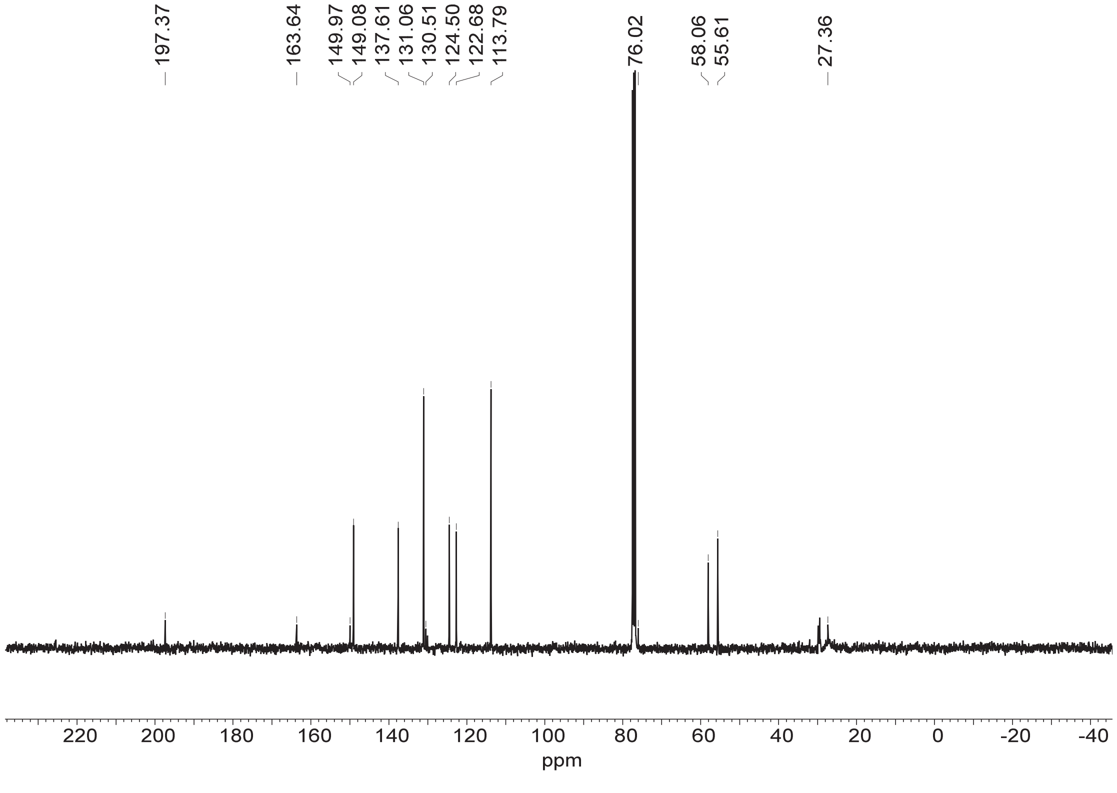
^{11}B NMR (128 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



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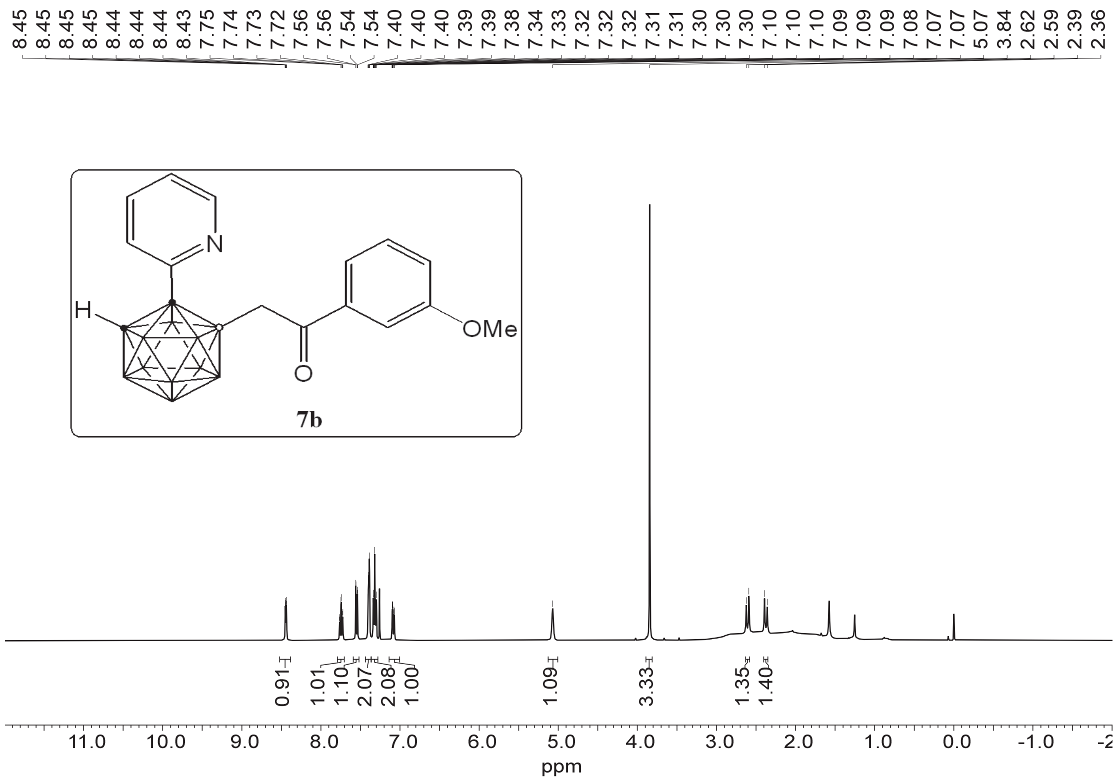
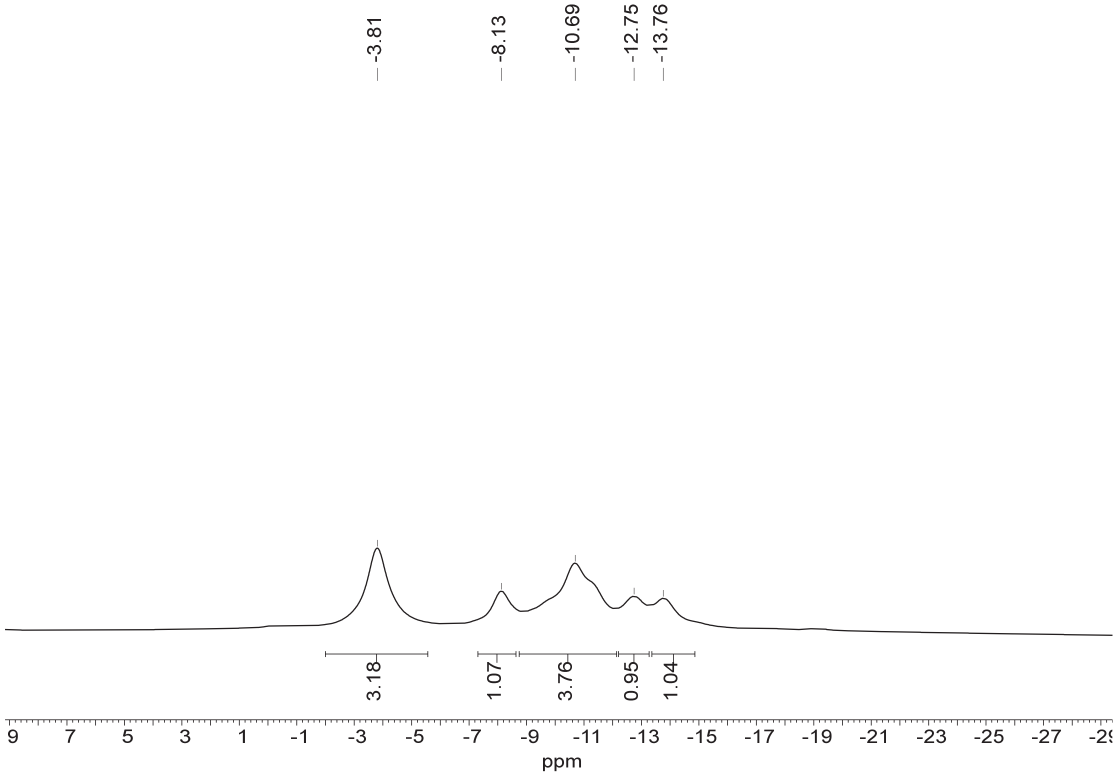
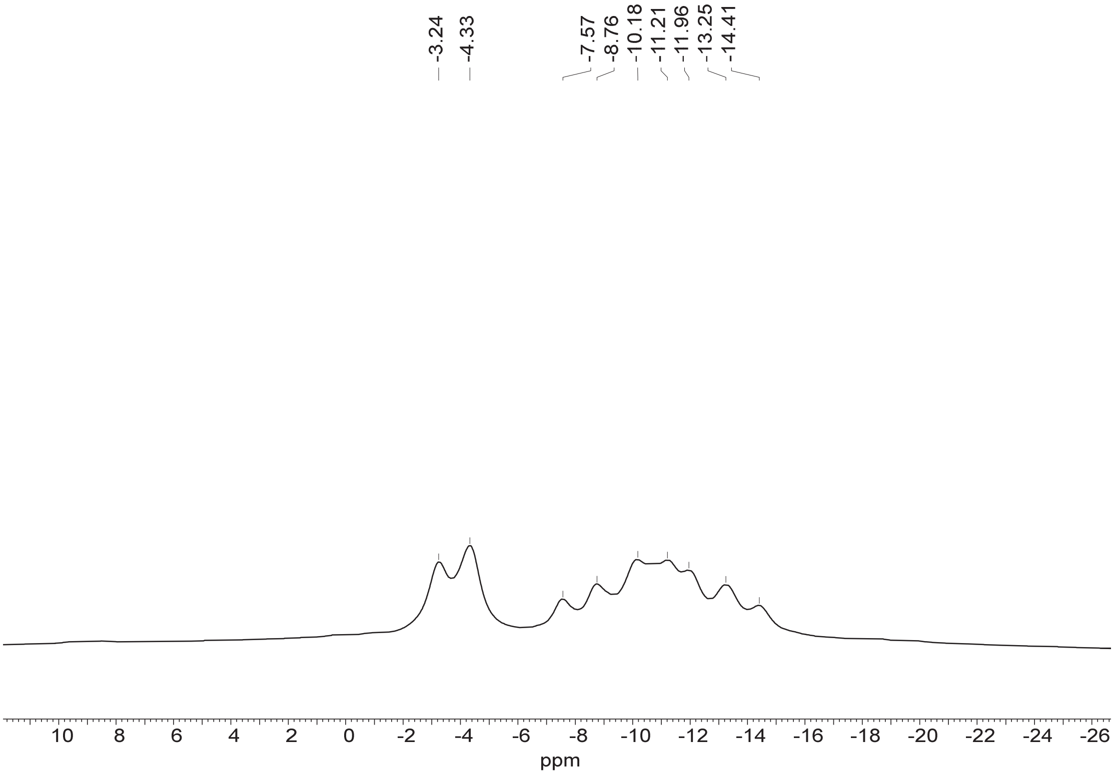


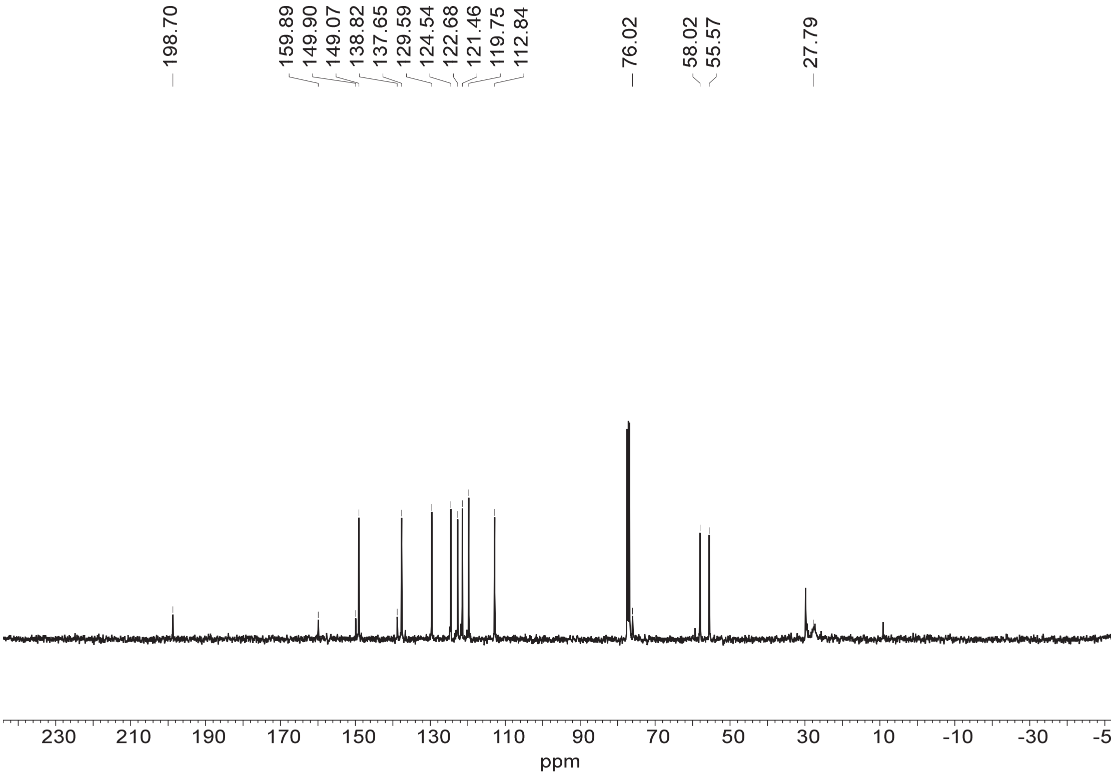
^{11}B NMR (128 MHz, CDCl$_3$)



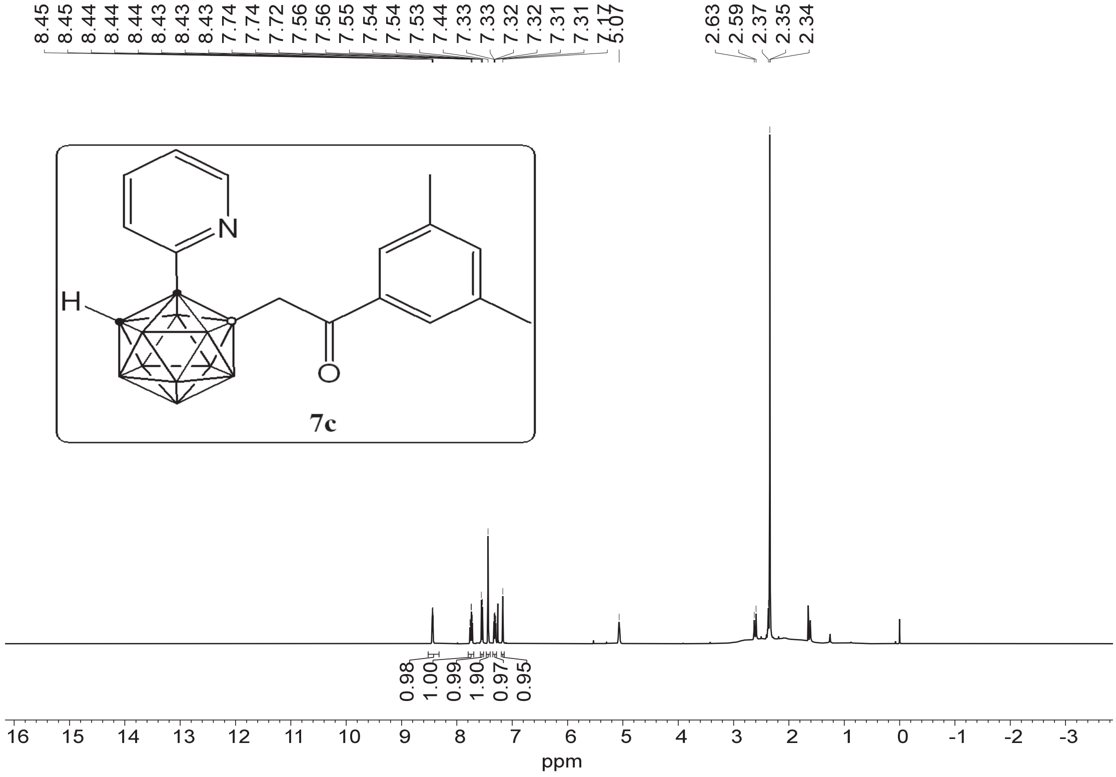
^{11}B NMR (128 MHz, $CDCl_3$)



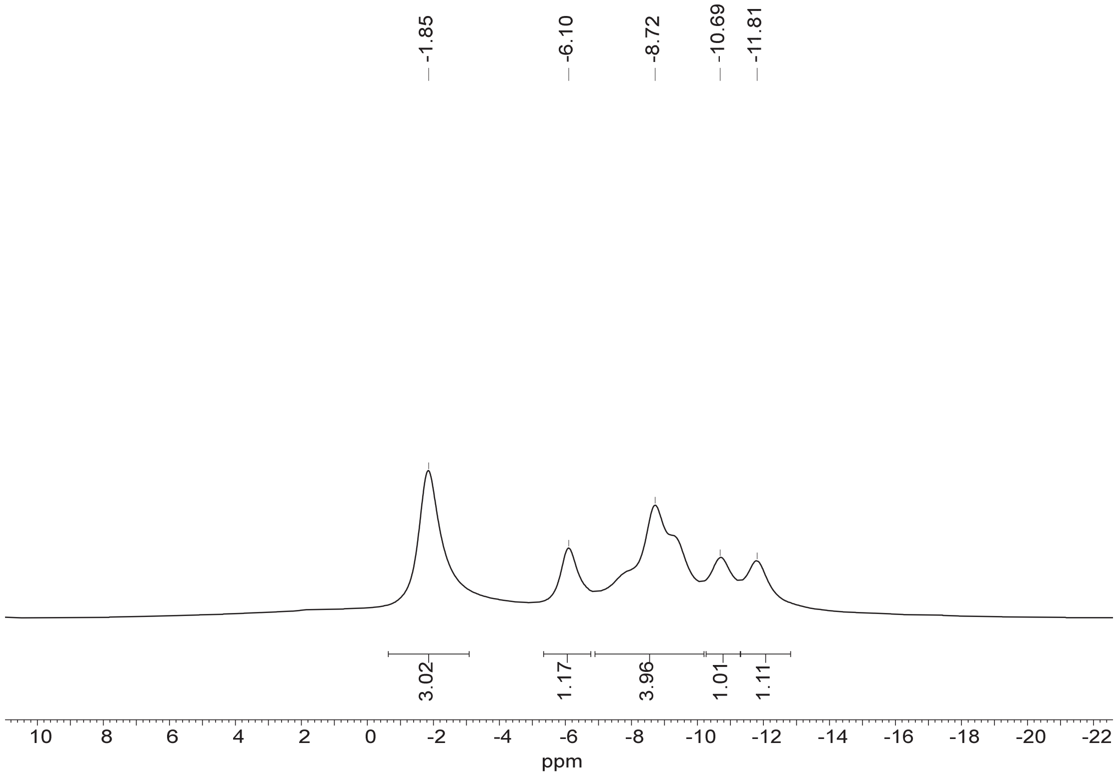
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



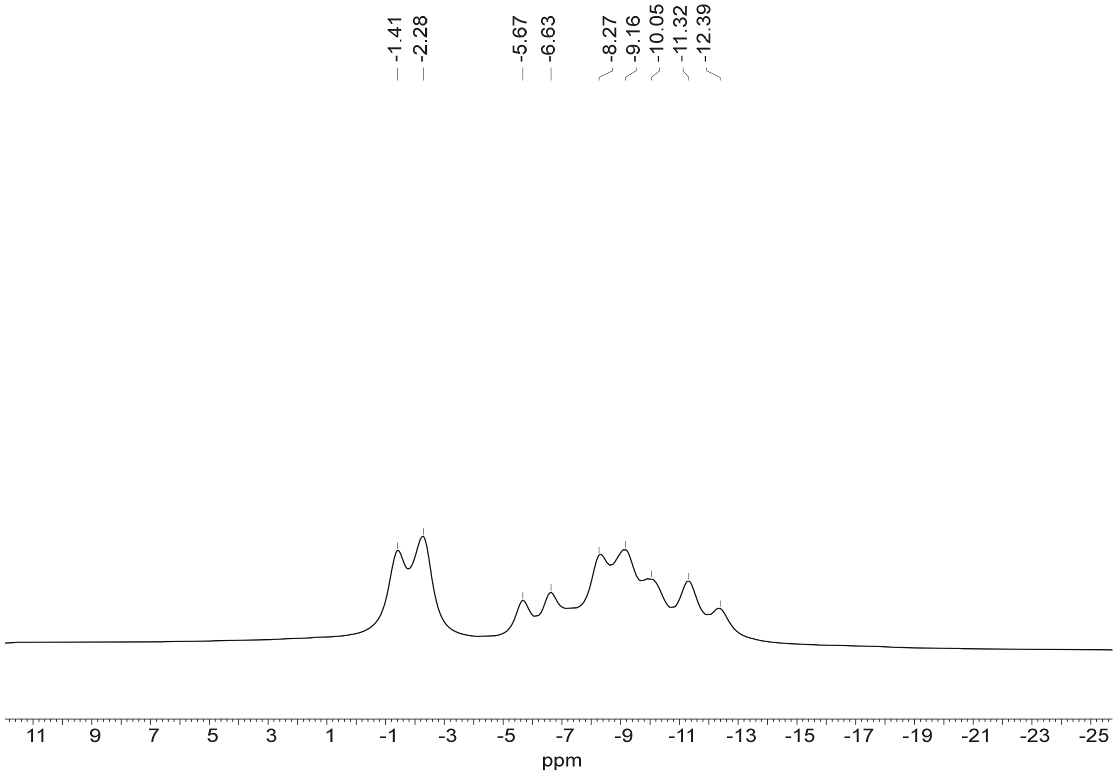
^{1}H NMR (400 MHz, $CDCl_3$)



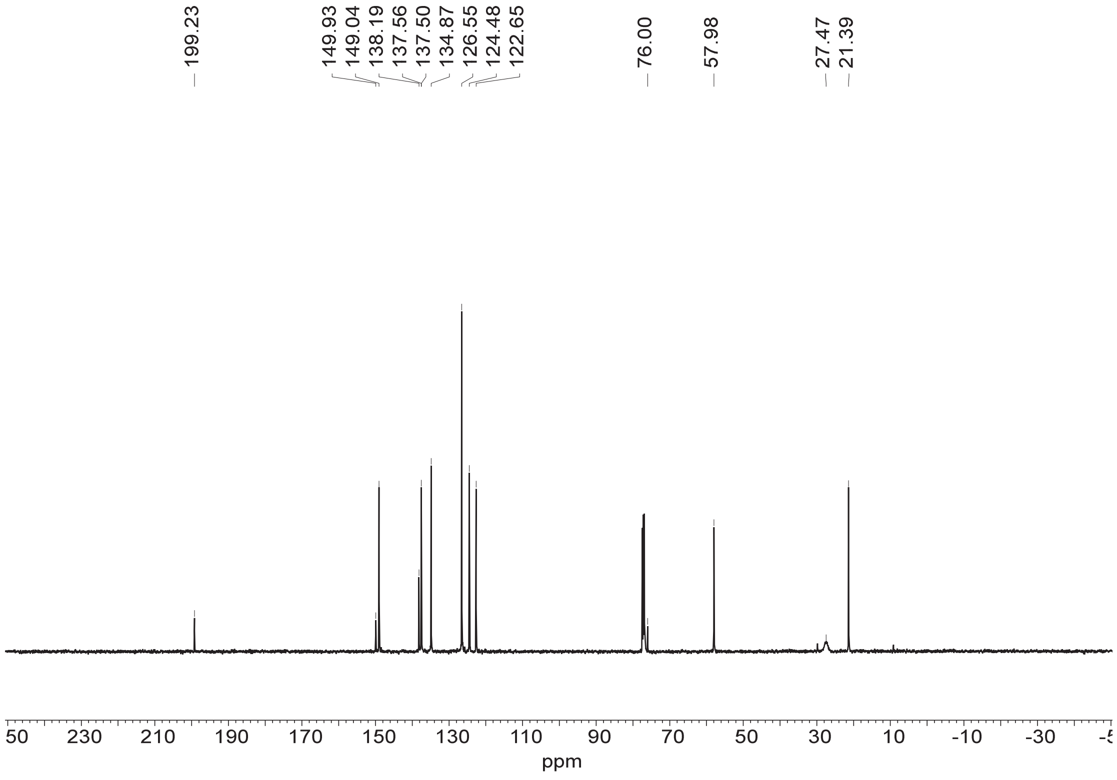
^{11}B NMR (160 MHz, $CDCl_3$)



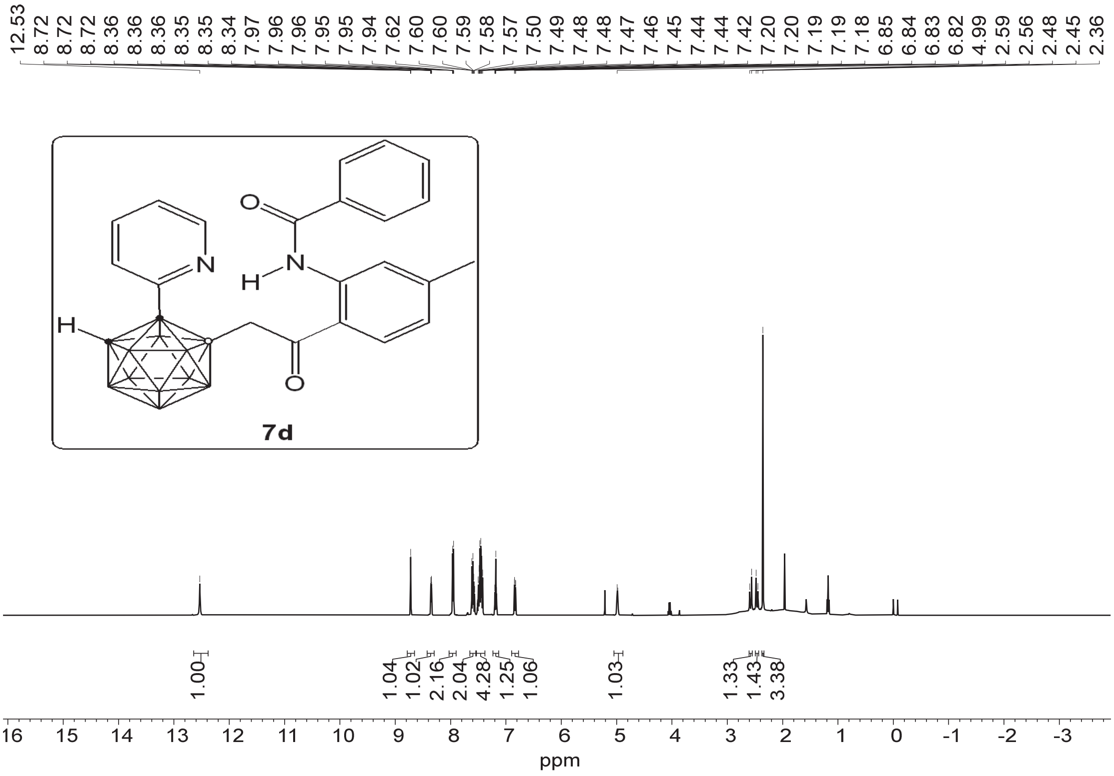
$^{11}B\{^{1}H\}$ NMR (128 MHz, CDCl$_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl$_3$)

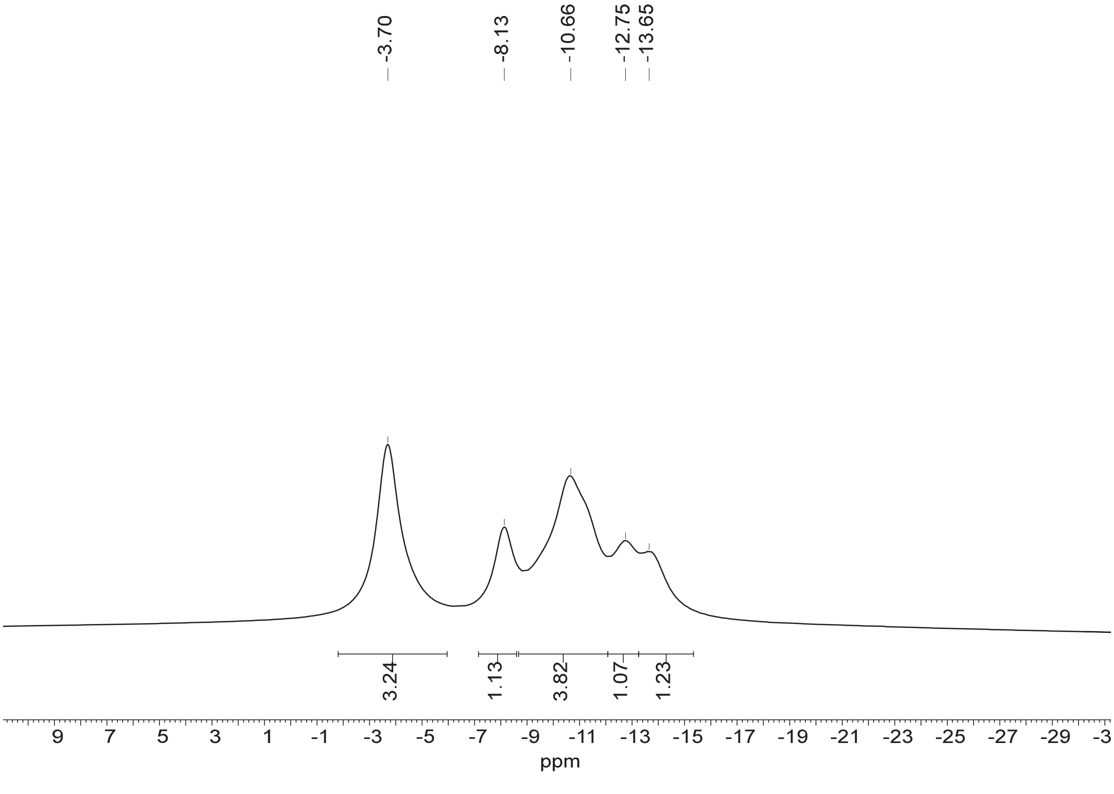


^1H NMR (400 MHz, $CDCl_3$)

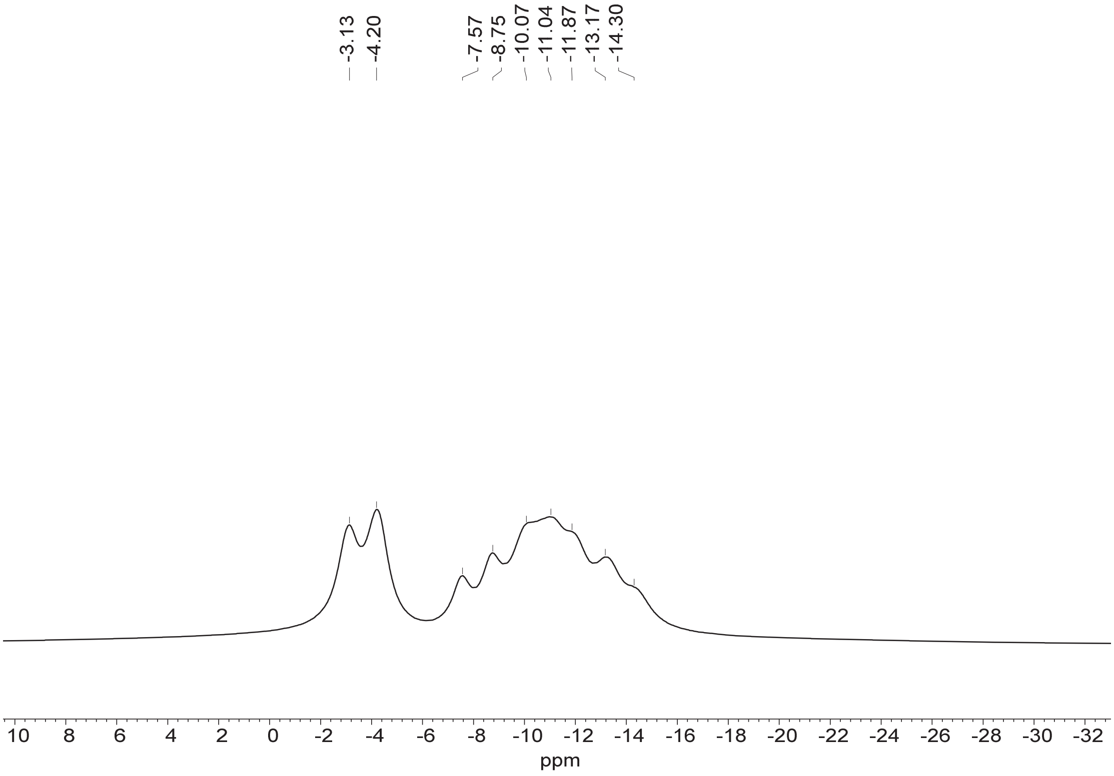


7d

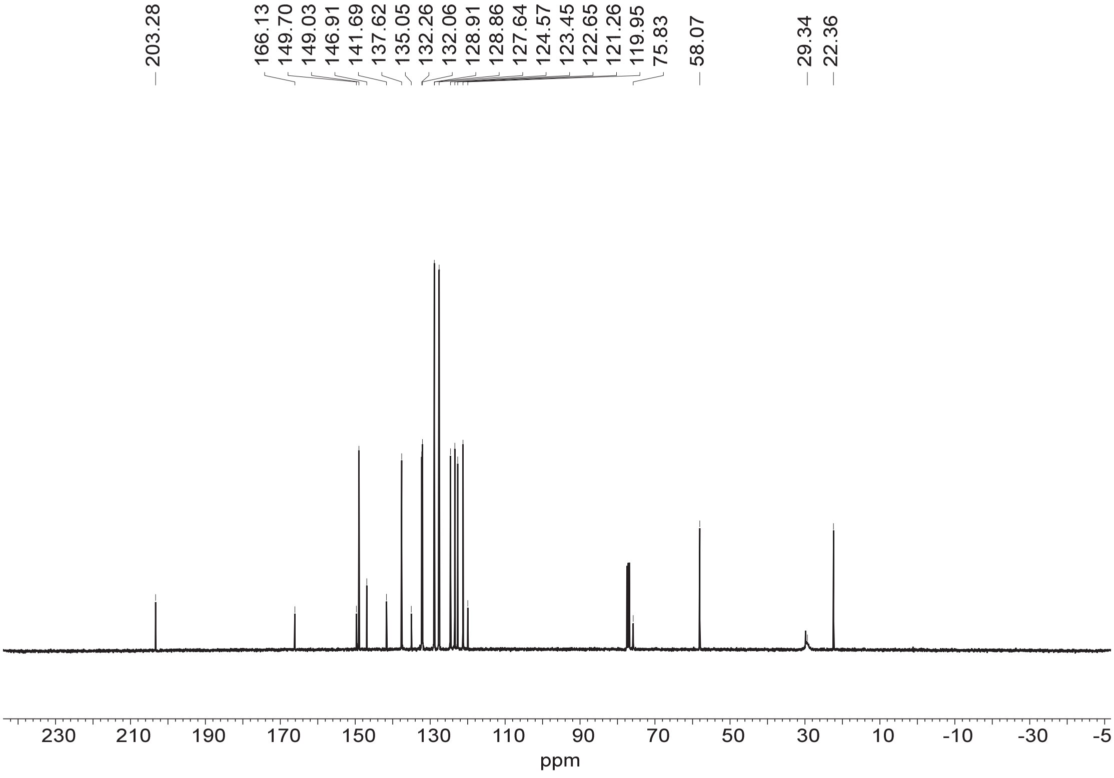
^{11}B NMR (128 MHz, $CDCl_3$)



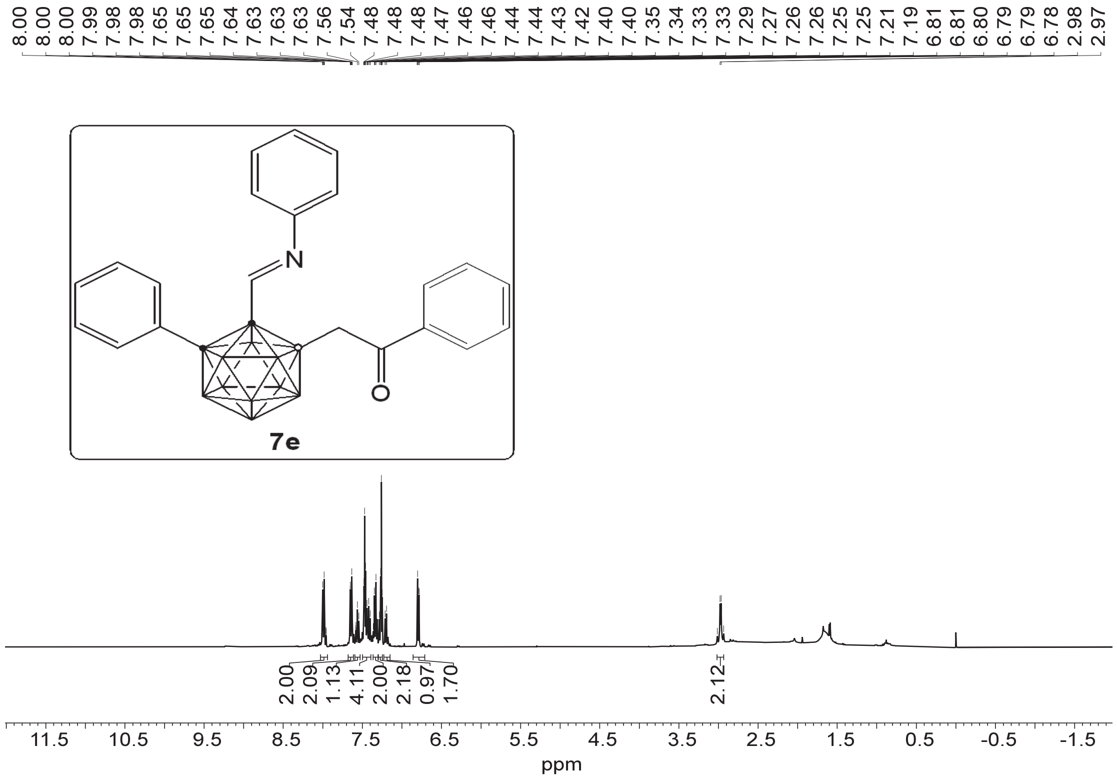
^{11}B NMR (128 MHz, CDCl$_3$)



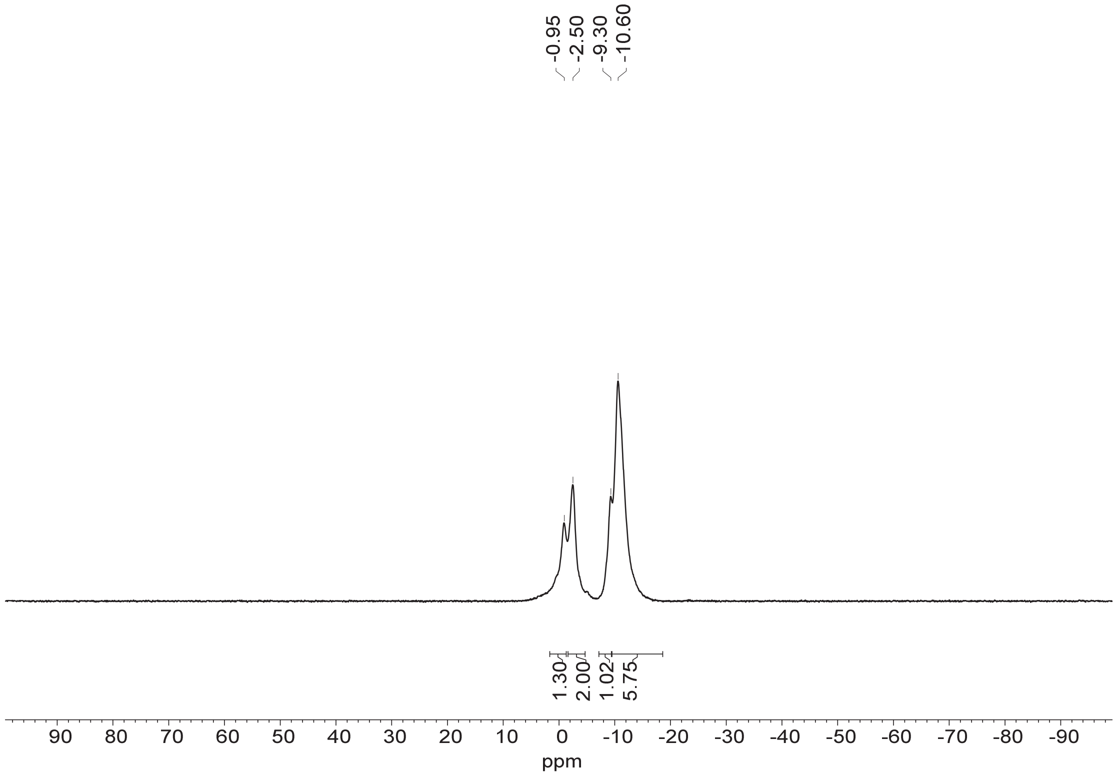
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



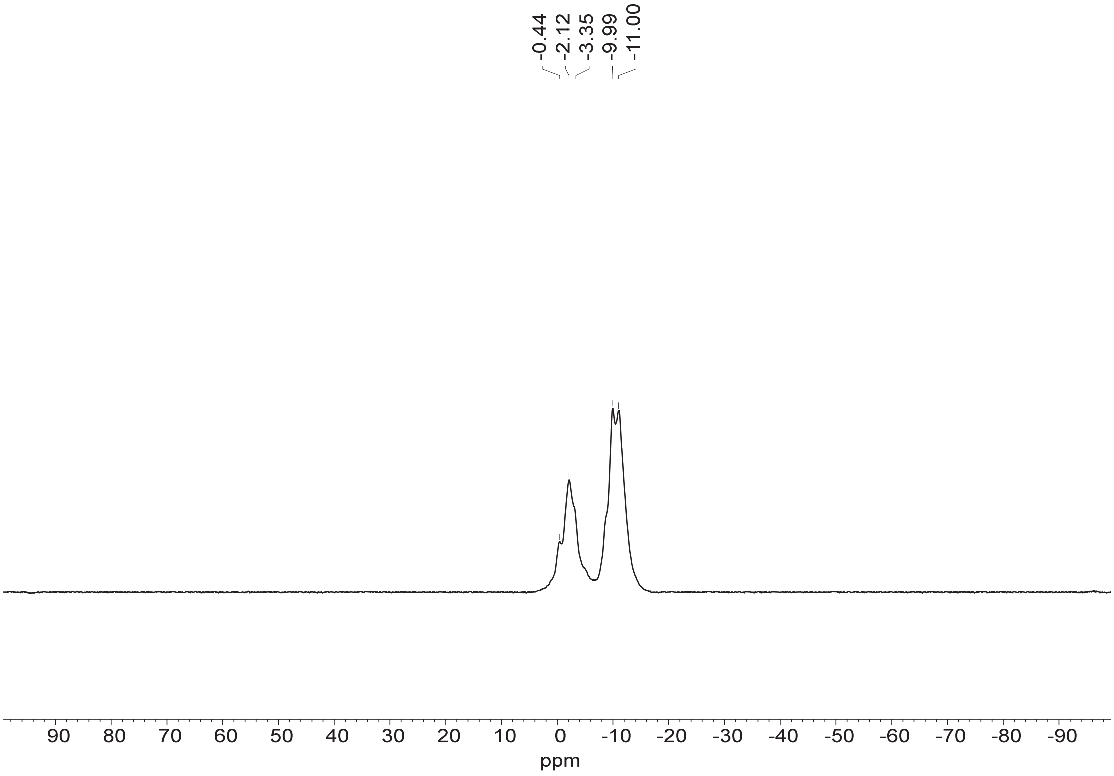
^{1}H NMR (400 MHz, CDCl$_3$)



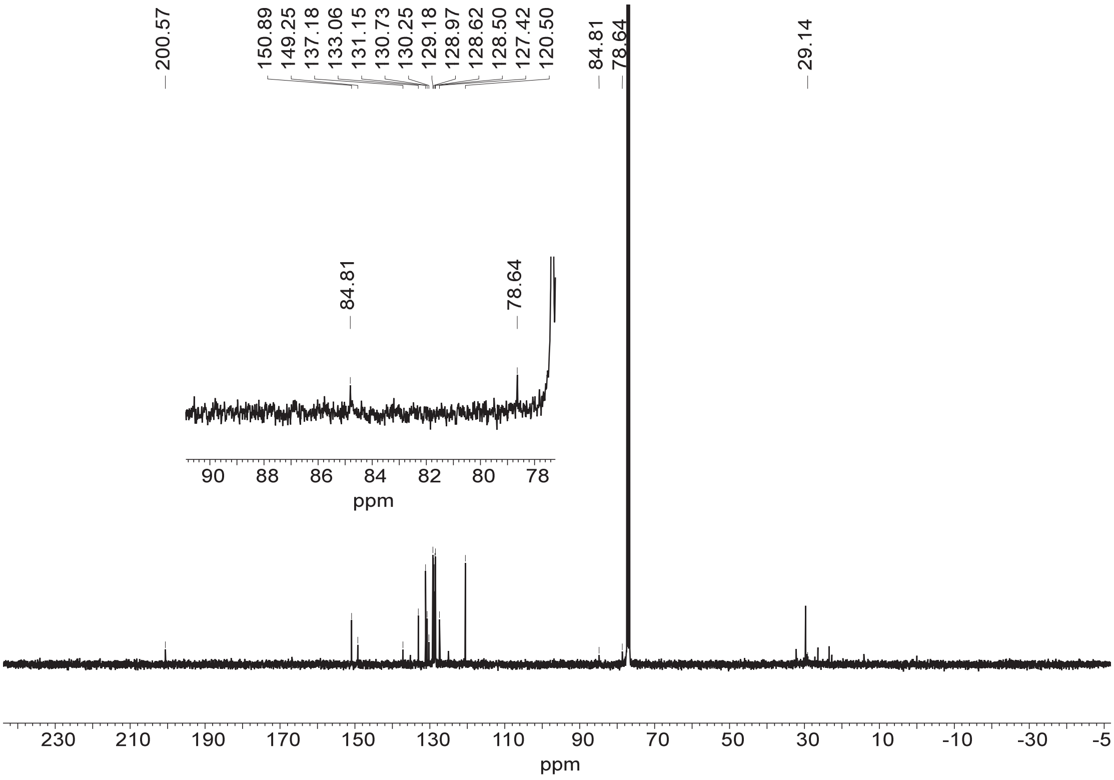
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



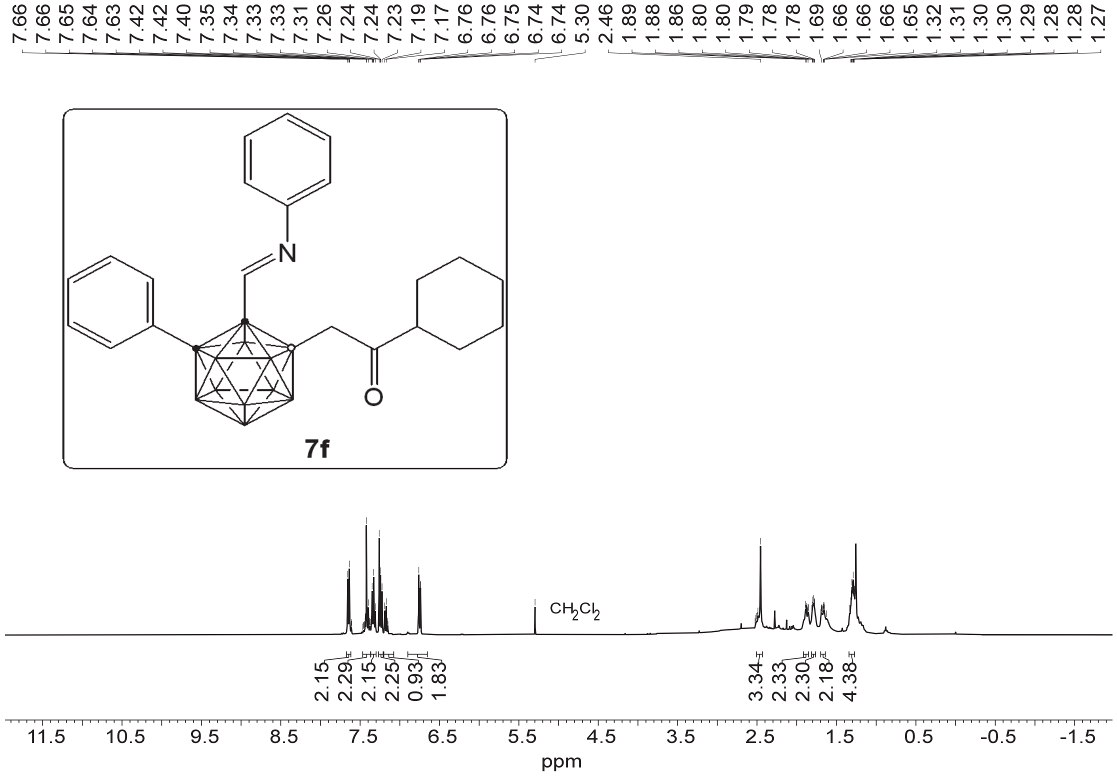
^{11}B NMR (128 MHz, CDCl$_3$)



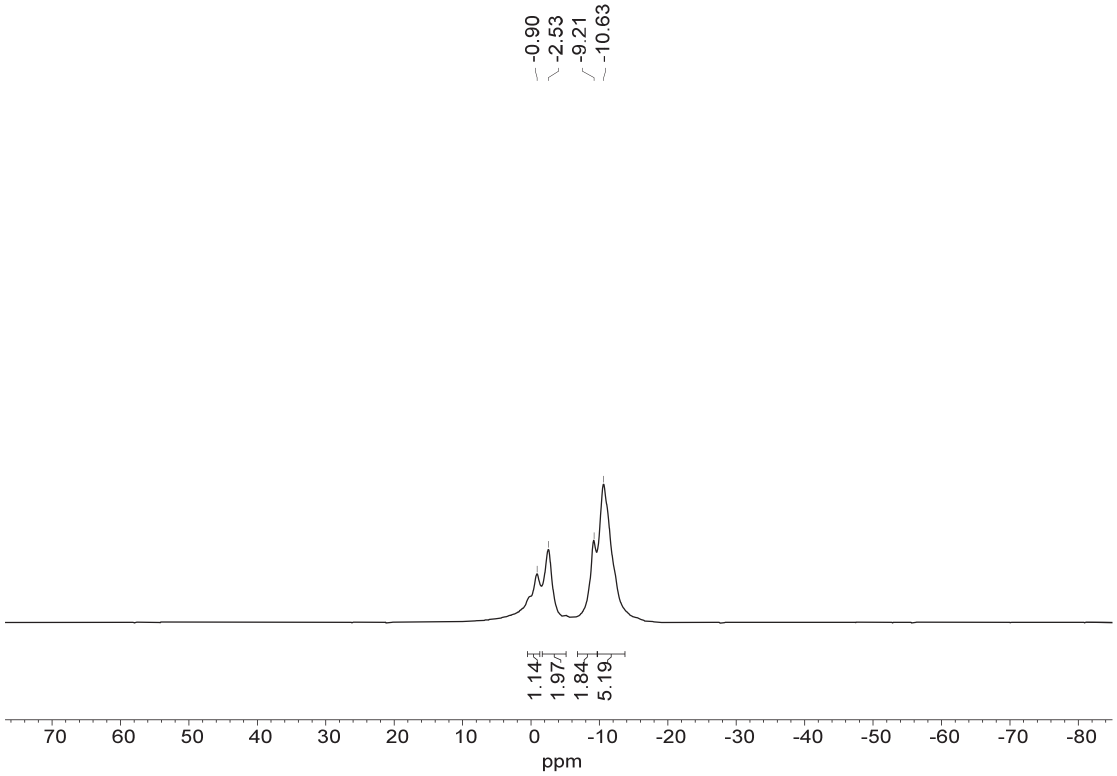
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



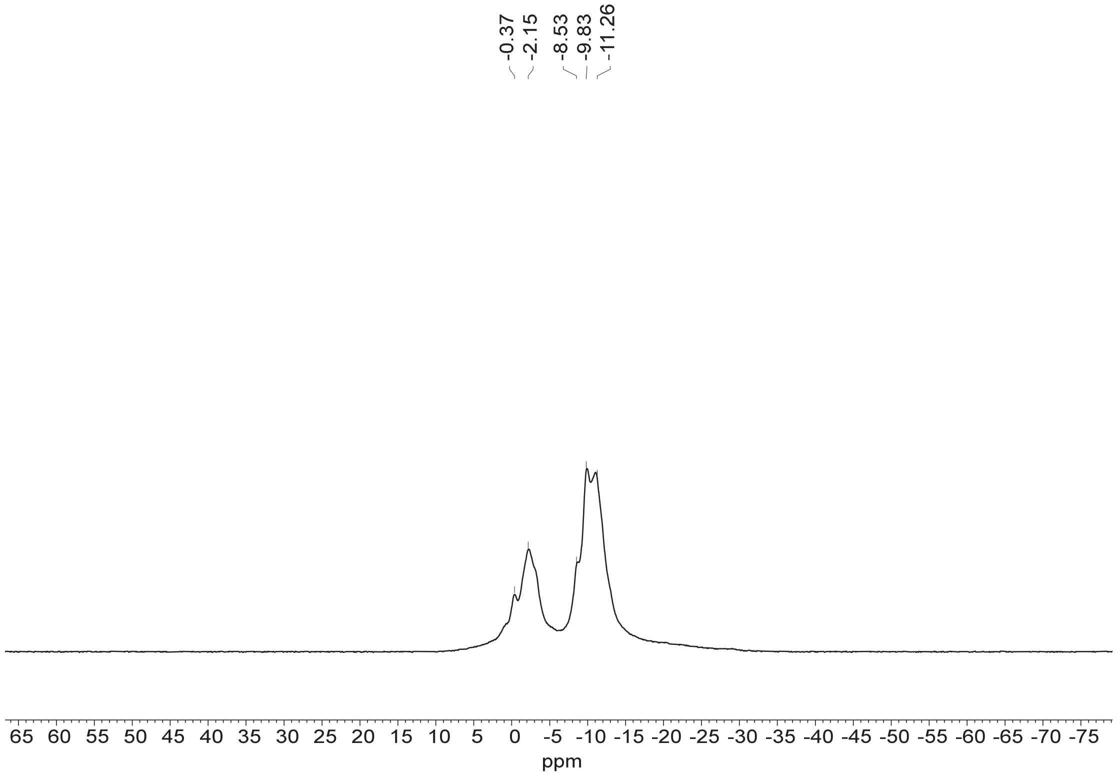
^{1}H NMR (400 MHz, $CDCl_3$)



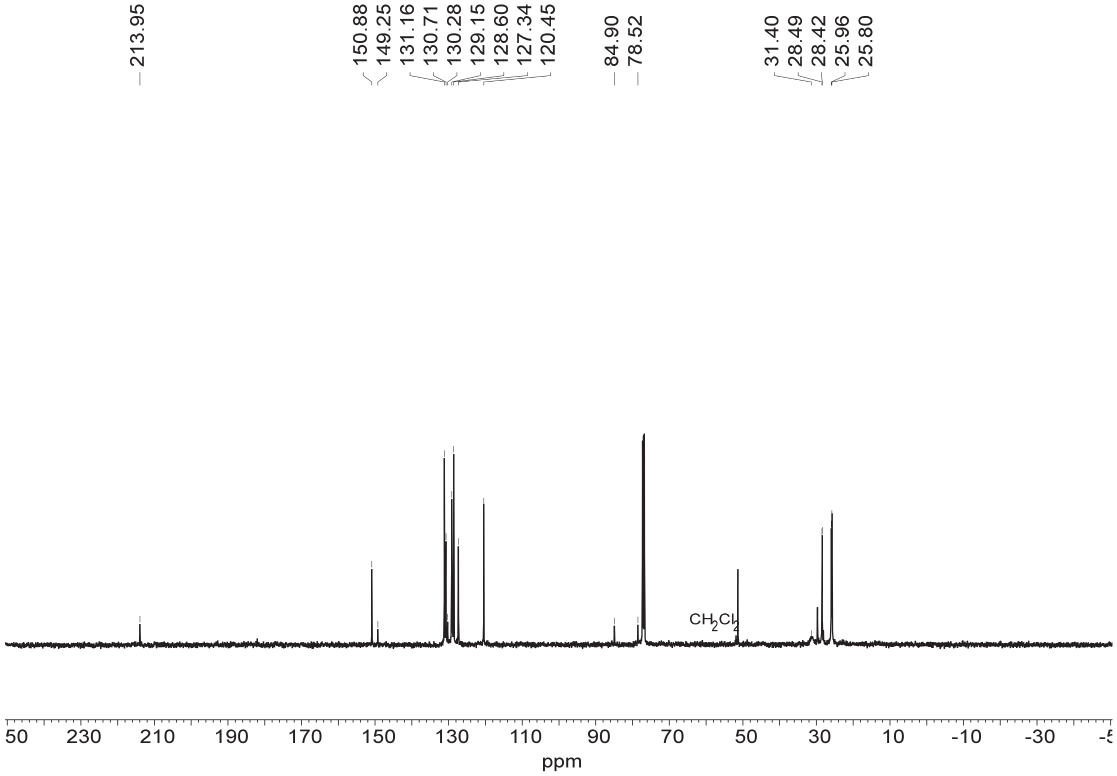
^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)



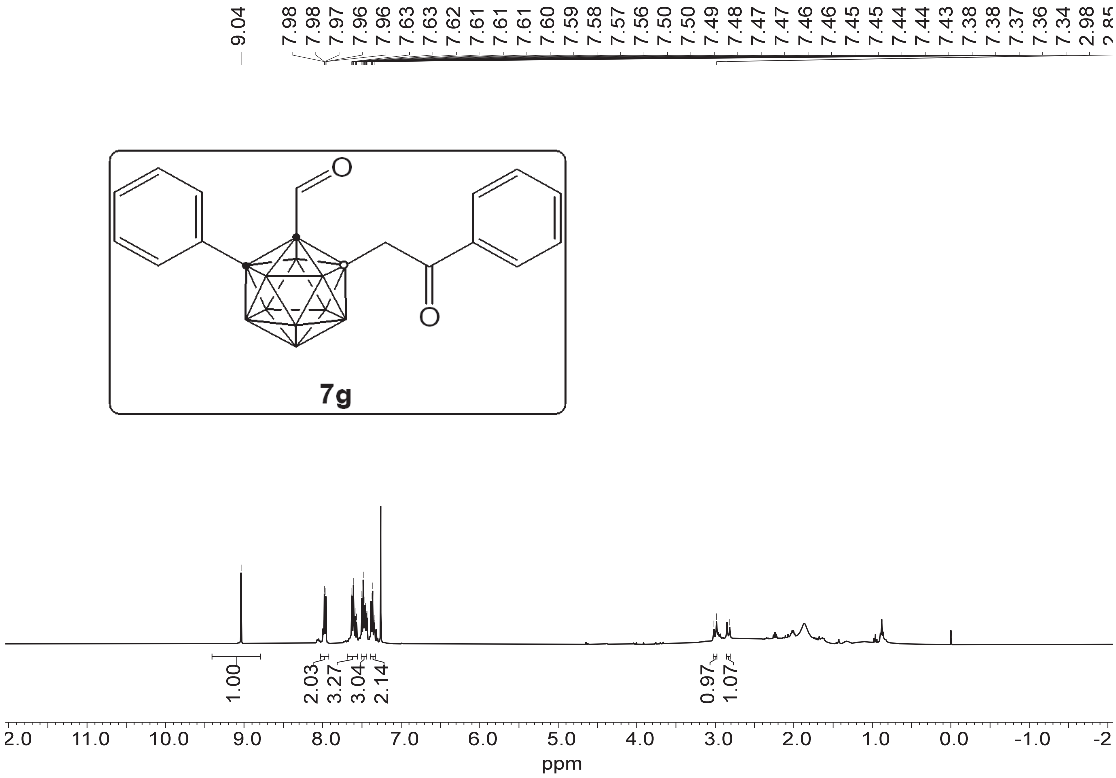
^{11}B NMR (128 MHz, CDCl$_3$)



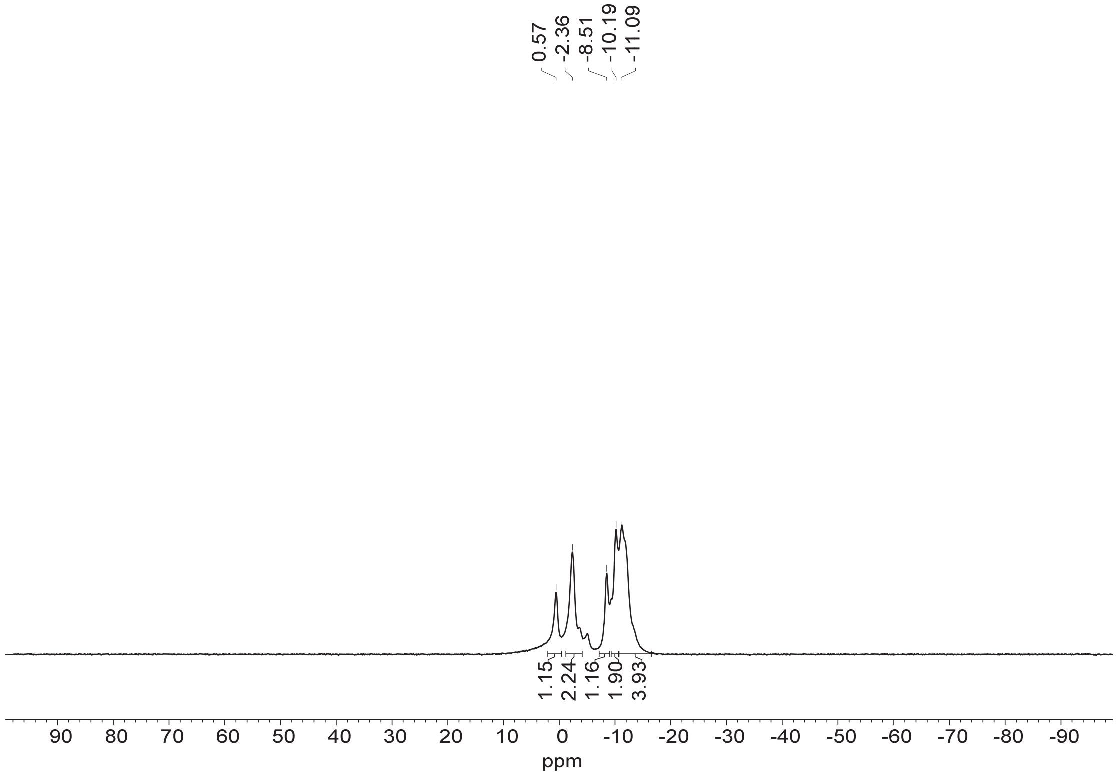
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



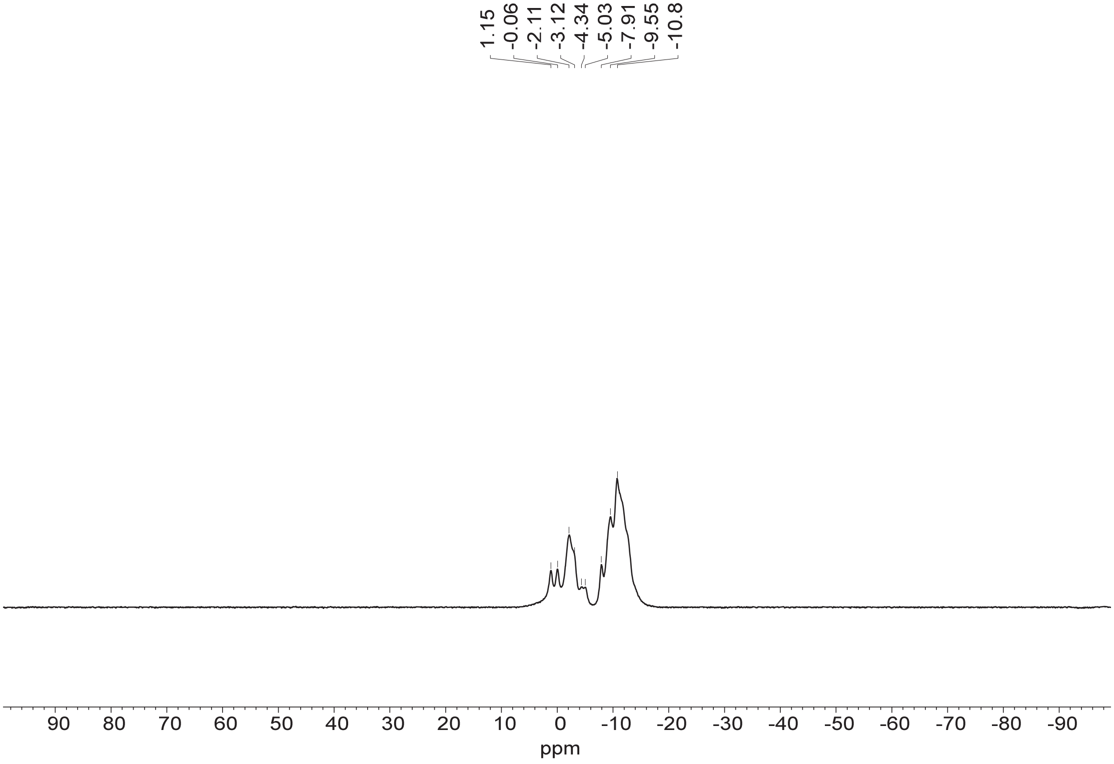
^{1}H NMR (400 MHz, CDCl$_3$)



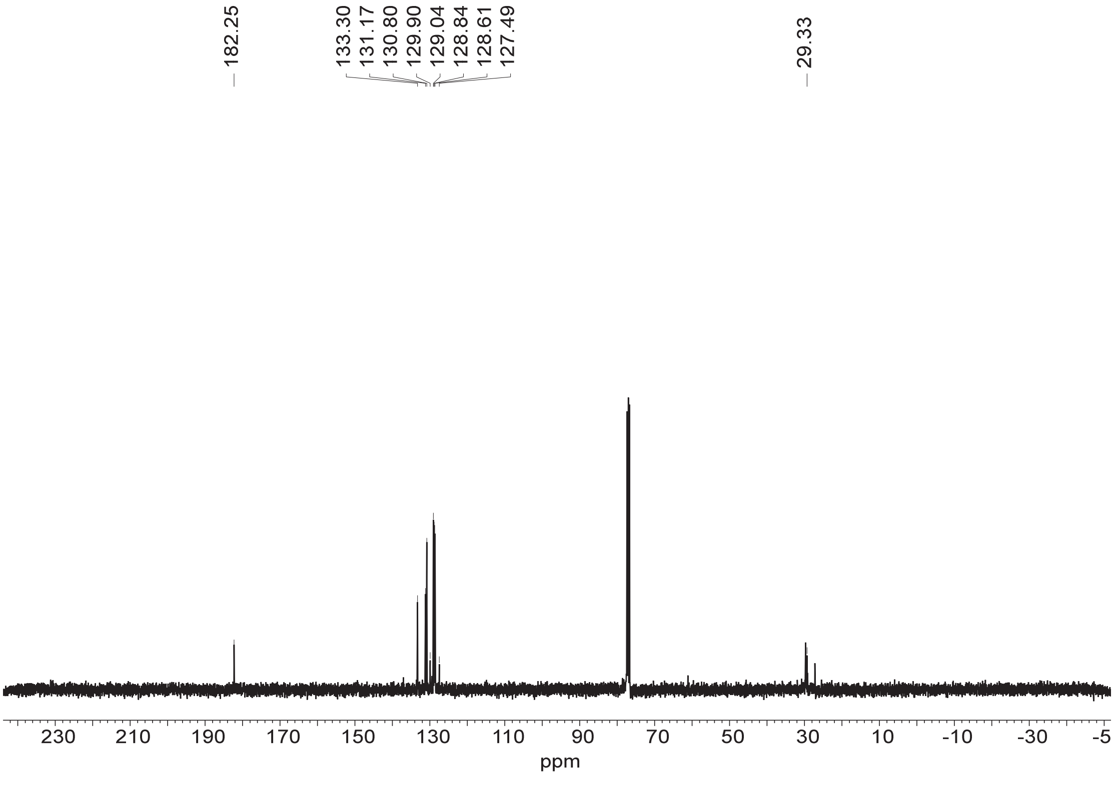
^{1}B{^{1}H} NMR (128 MHz, CDCl$_3$)



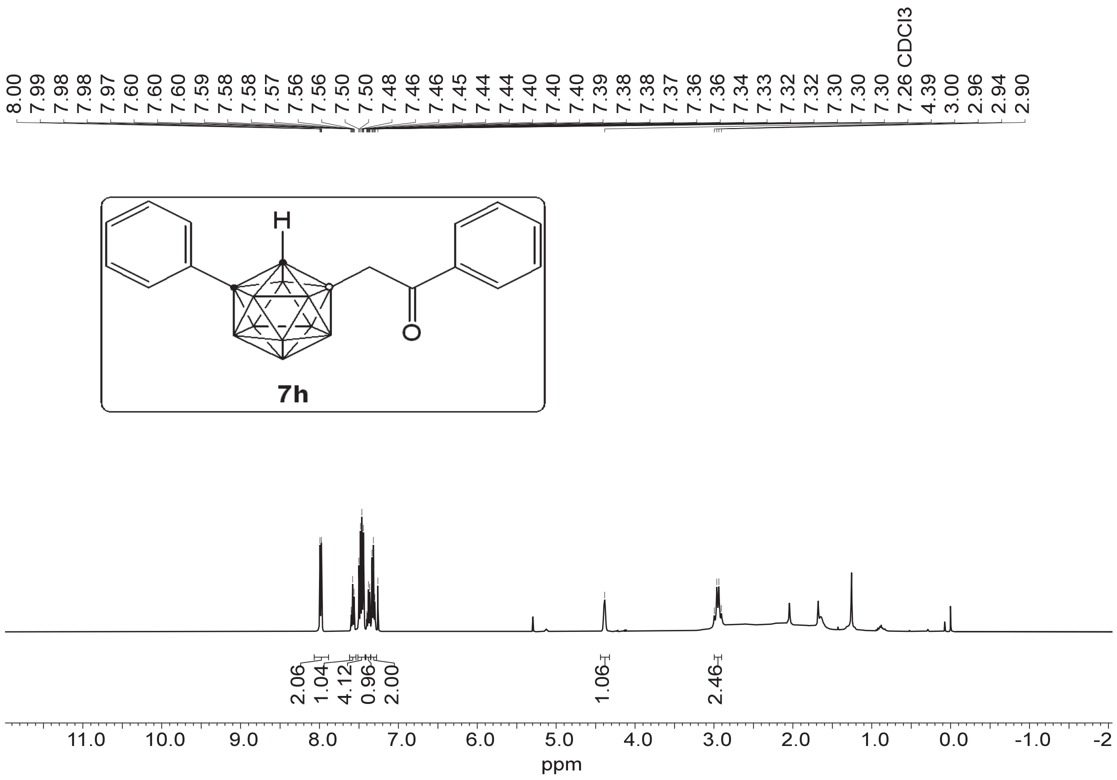
^{11}B NMR (128 MHz, $CDCl_3$)



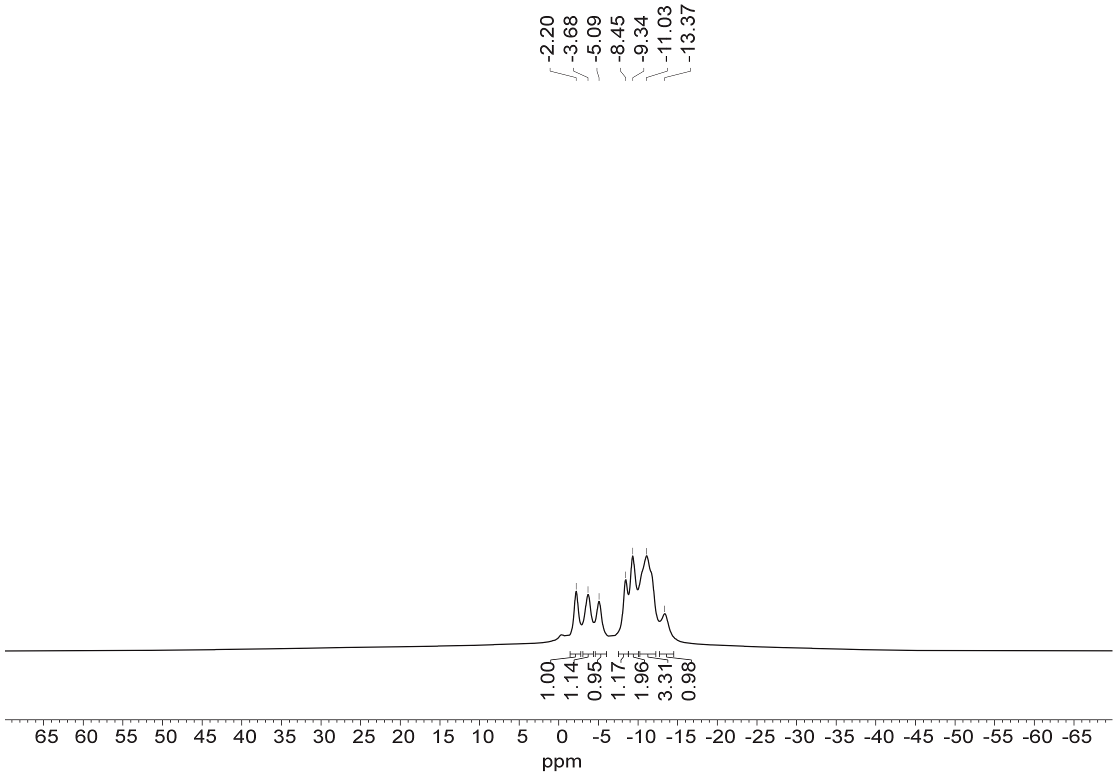
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



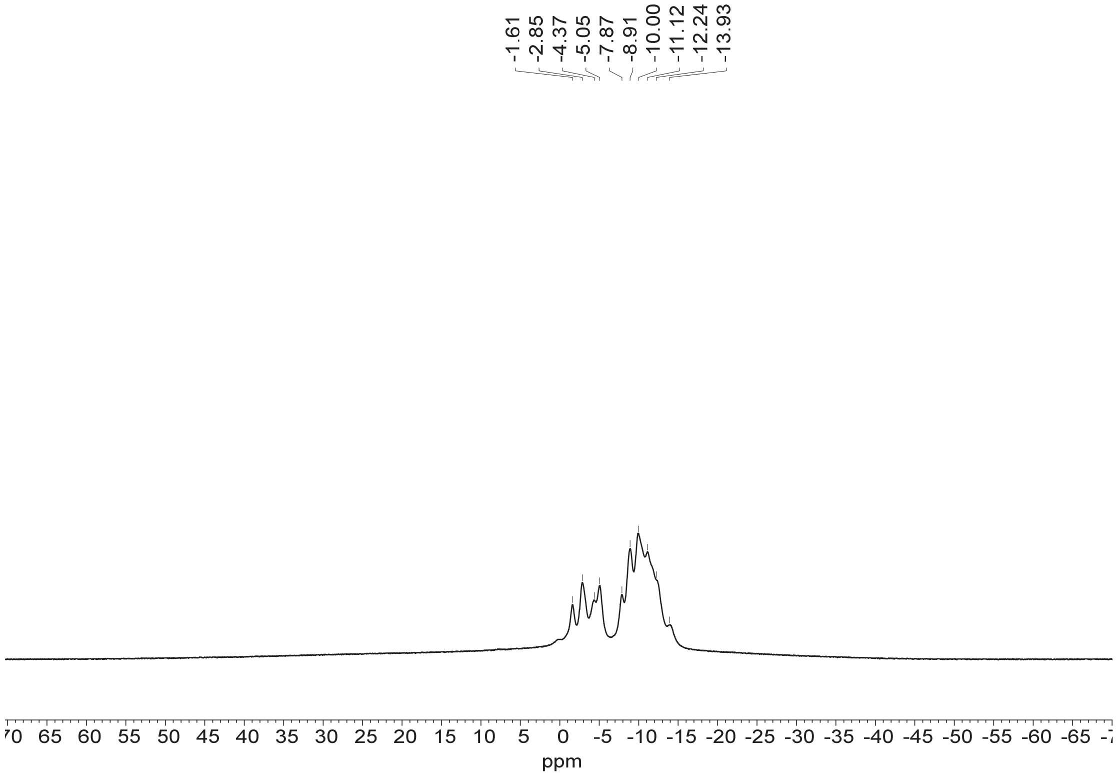
^{1}H NMR (400 MHz, CDCl$_3$)



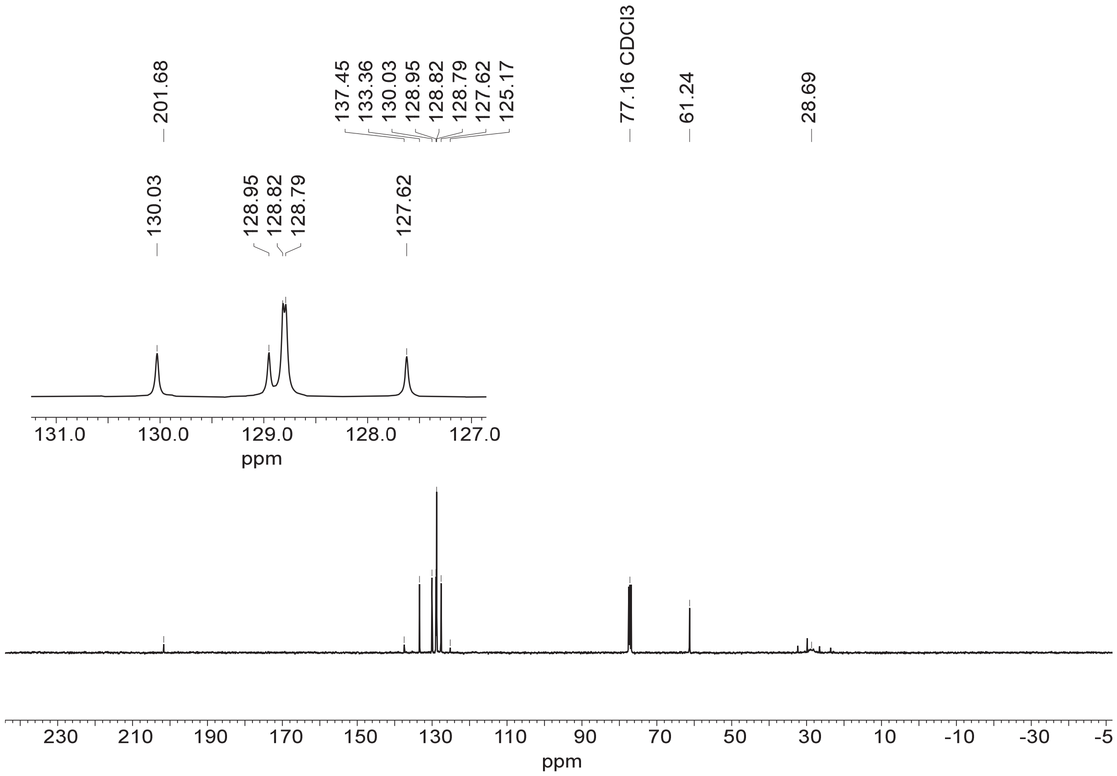
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



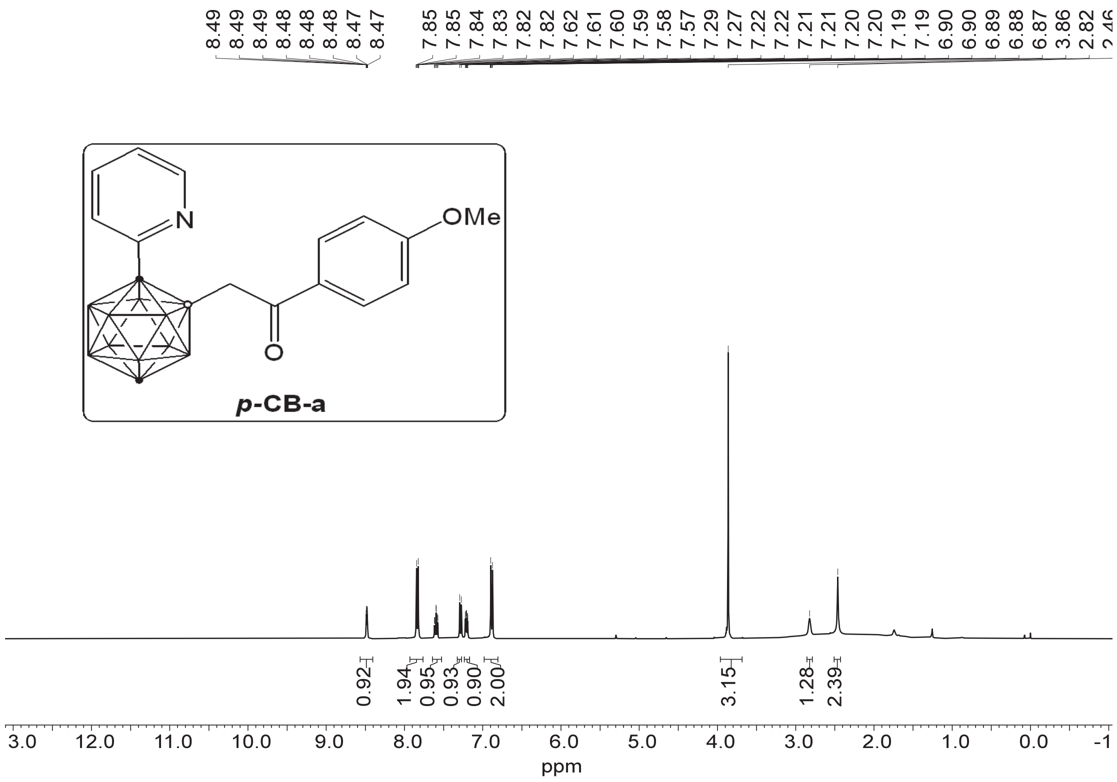
^{11}B NMR (128 MHz, CDCl$_3$)



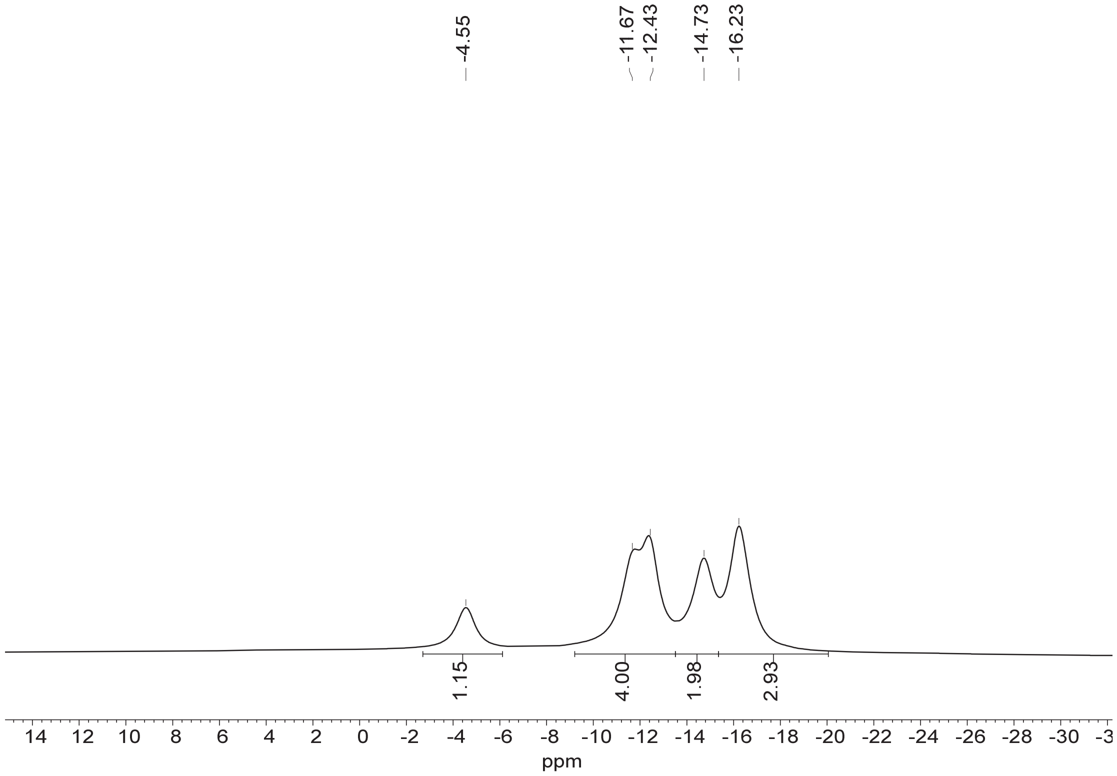
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



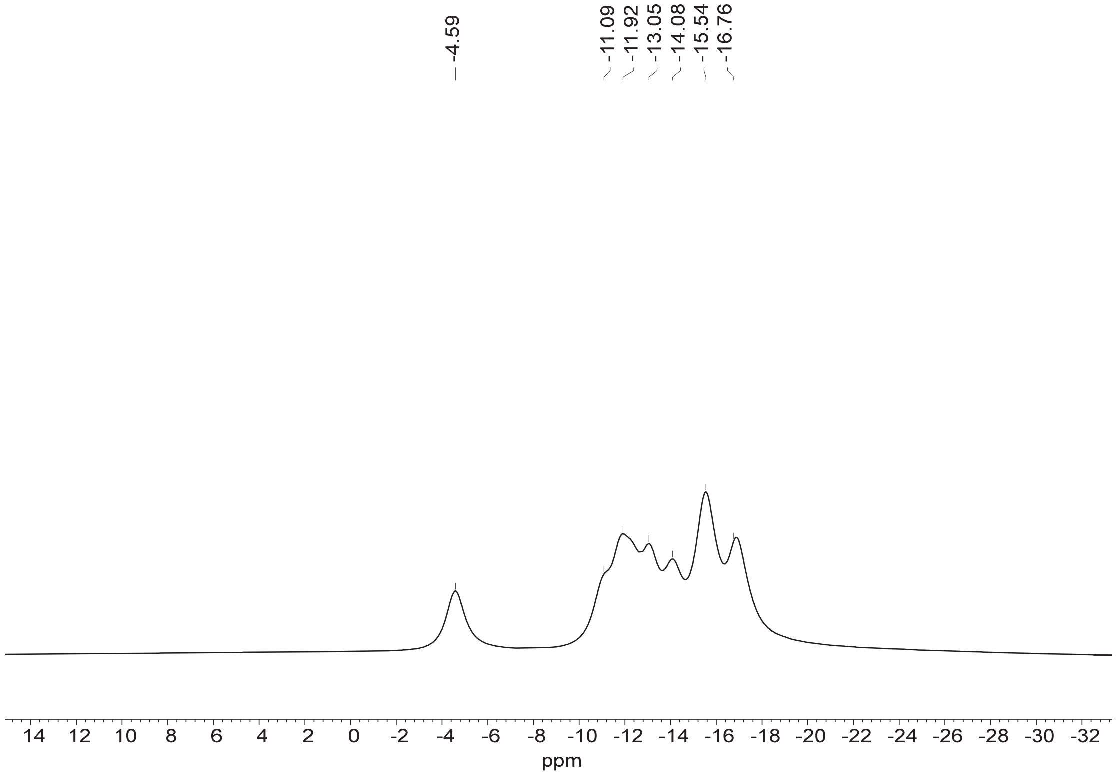
^{1}H NMR (400 MHz, $CDCl_3$)



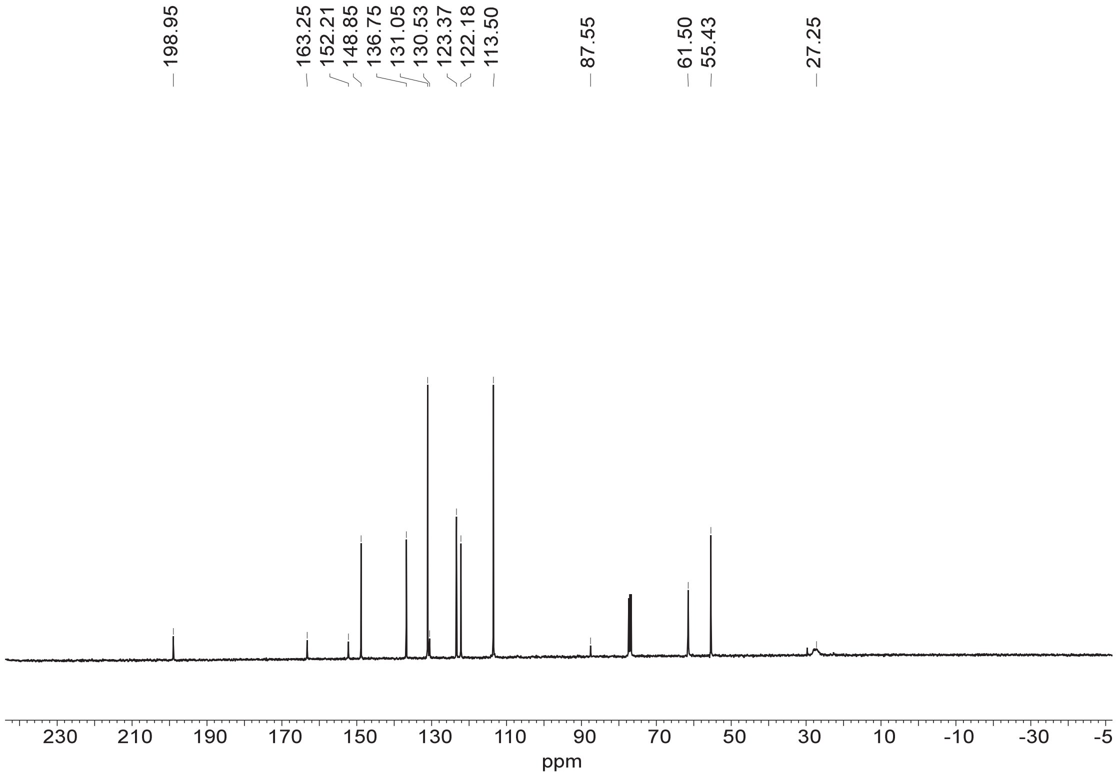
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

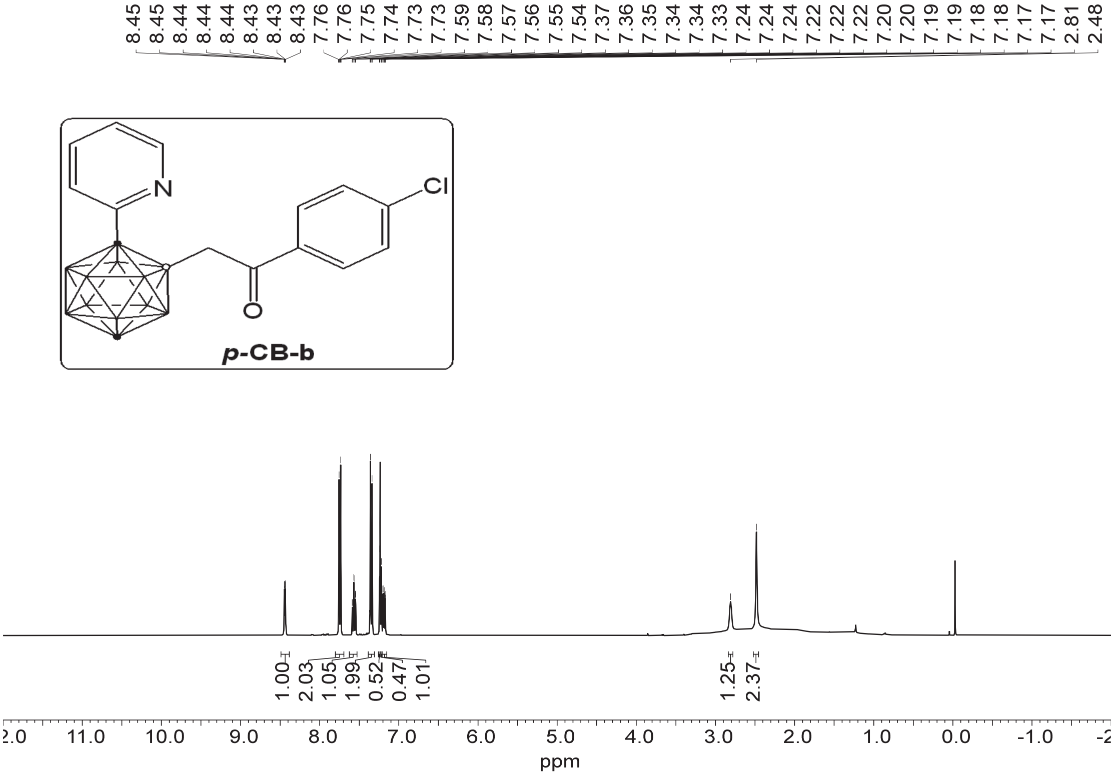


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



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

***p*-CB-b**



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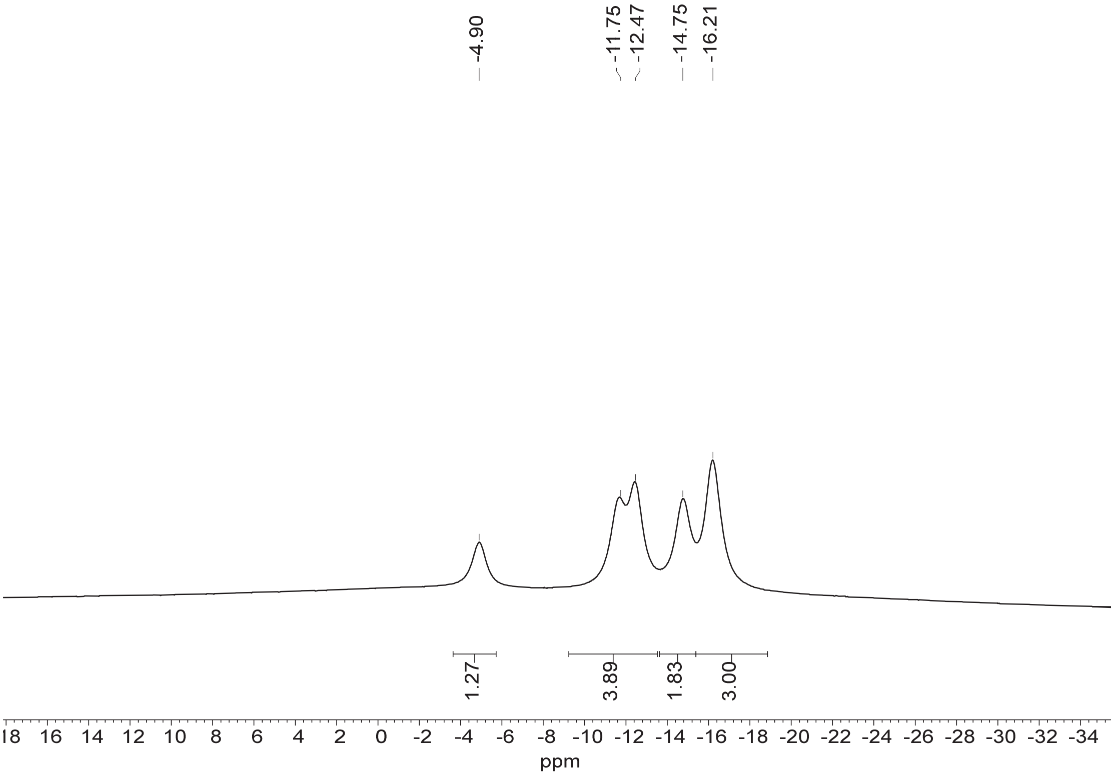

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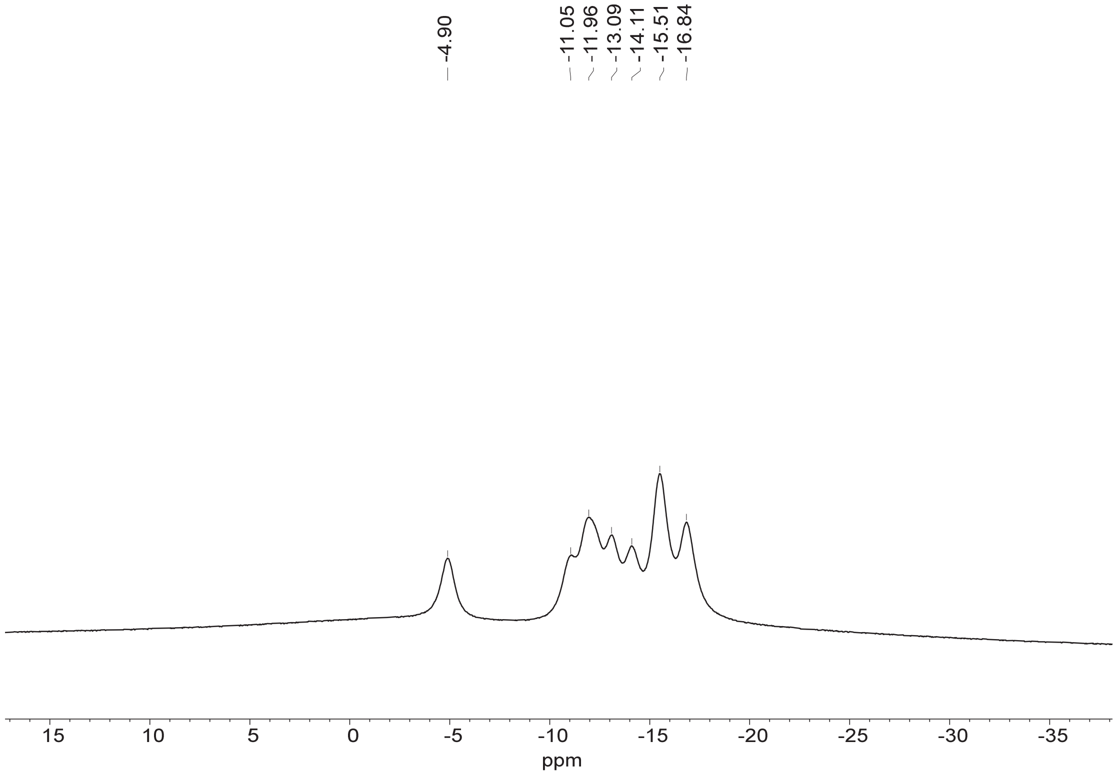
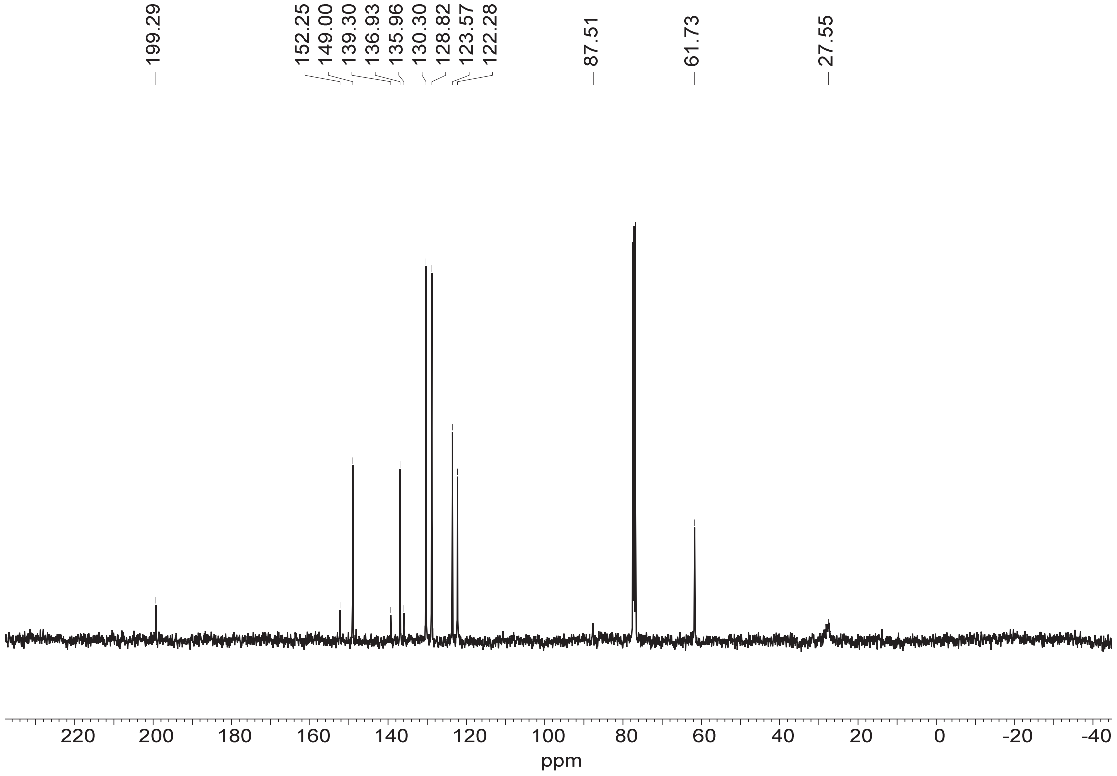
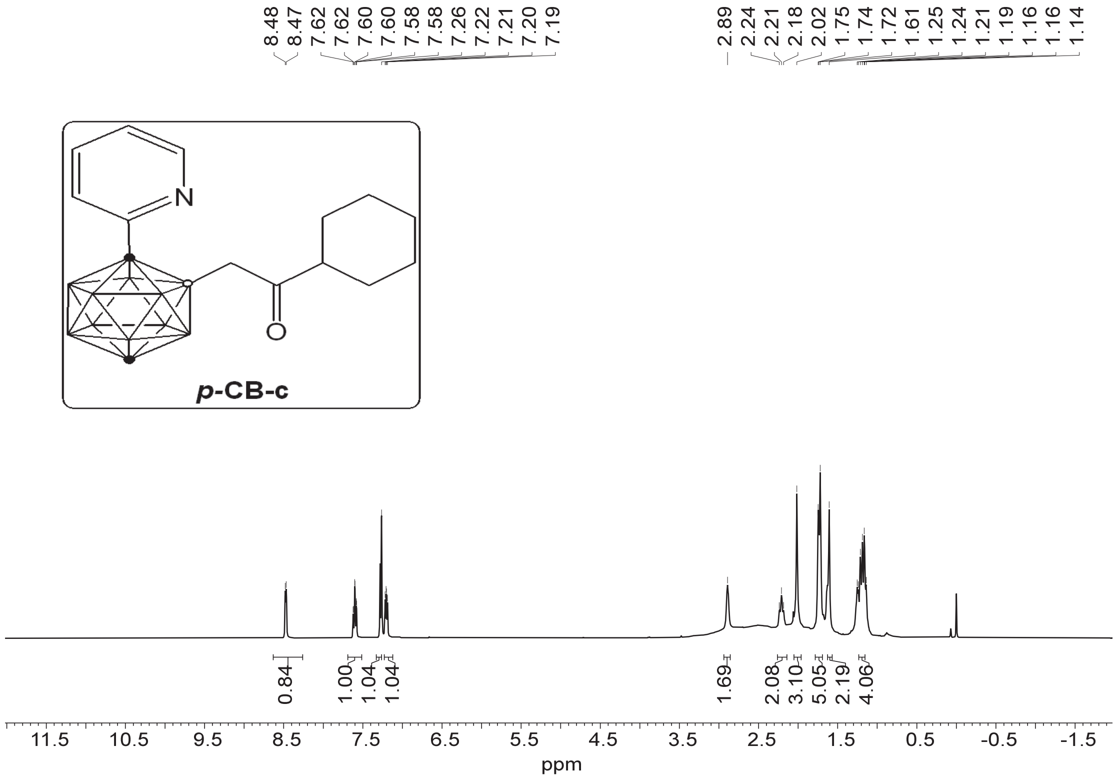


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



^1H NMR (400 MHz, $CDCl_3$)



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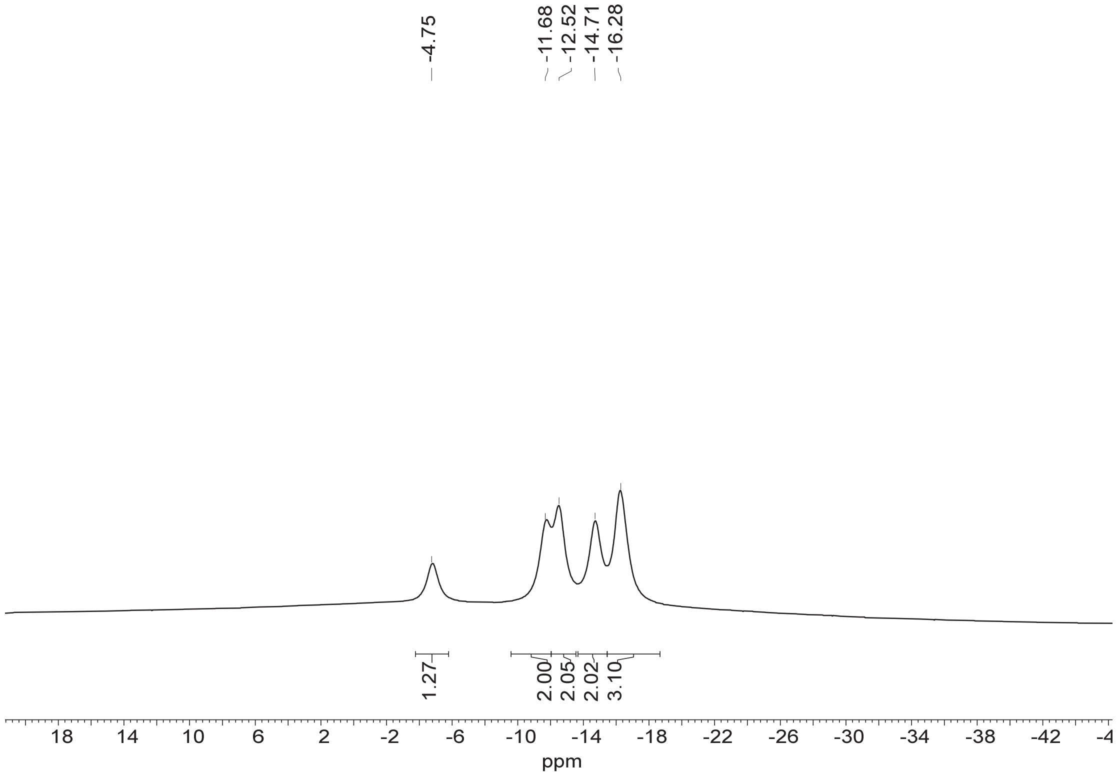
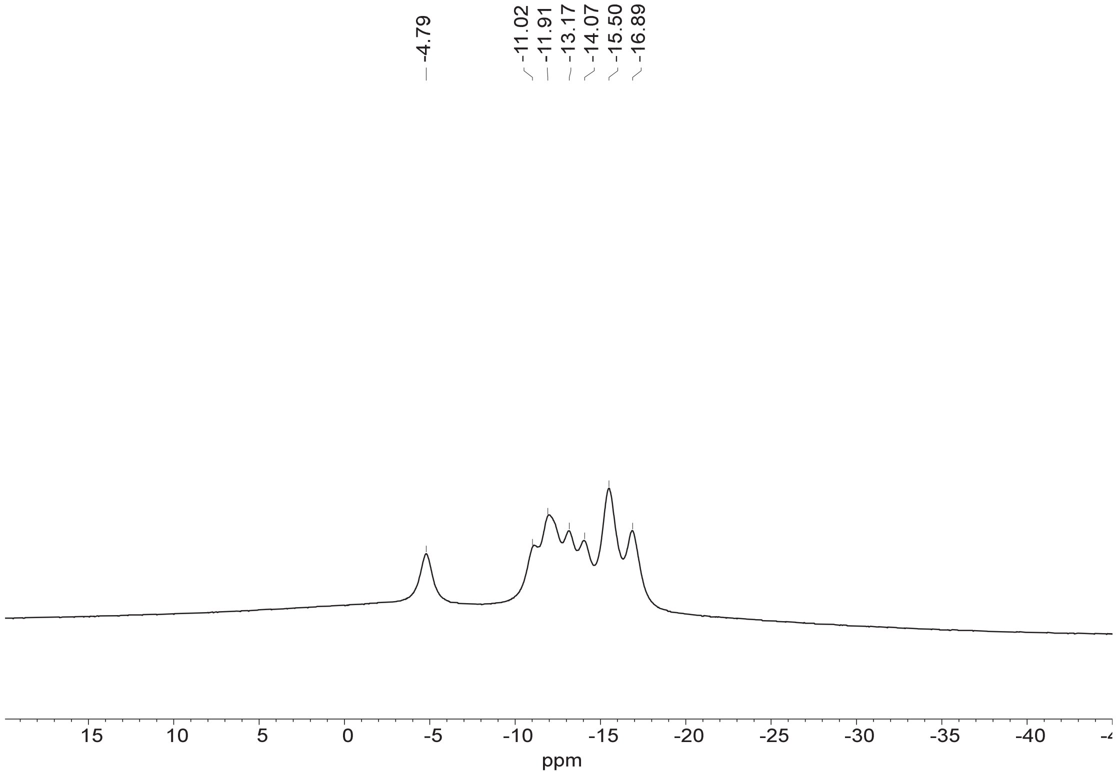
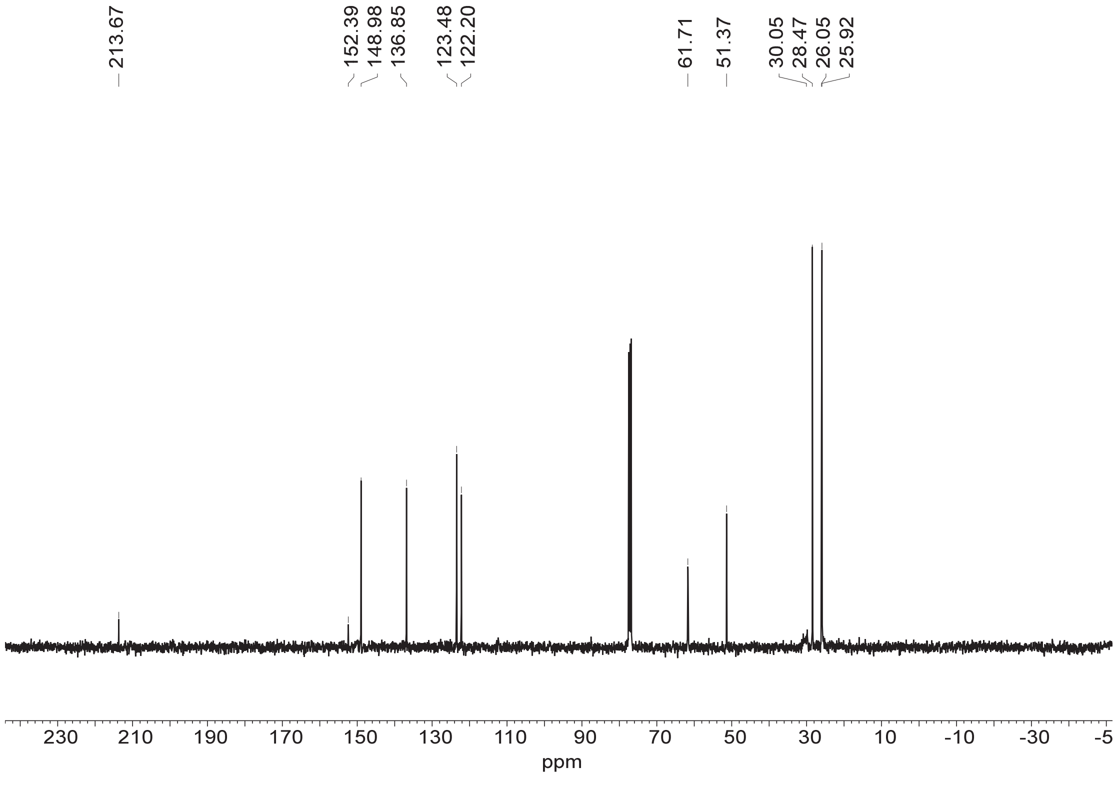


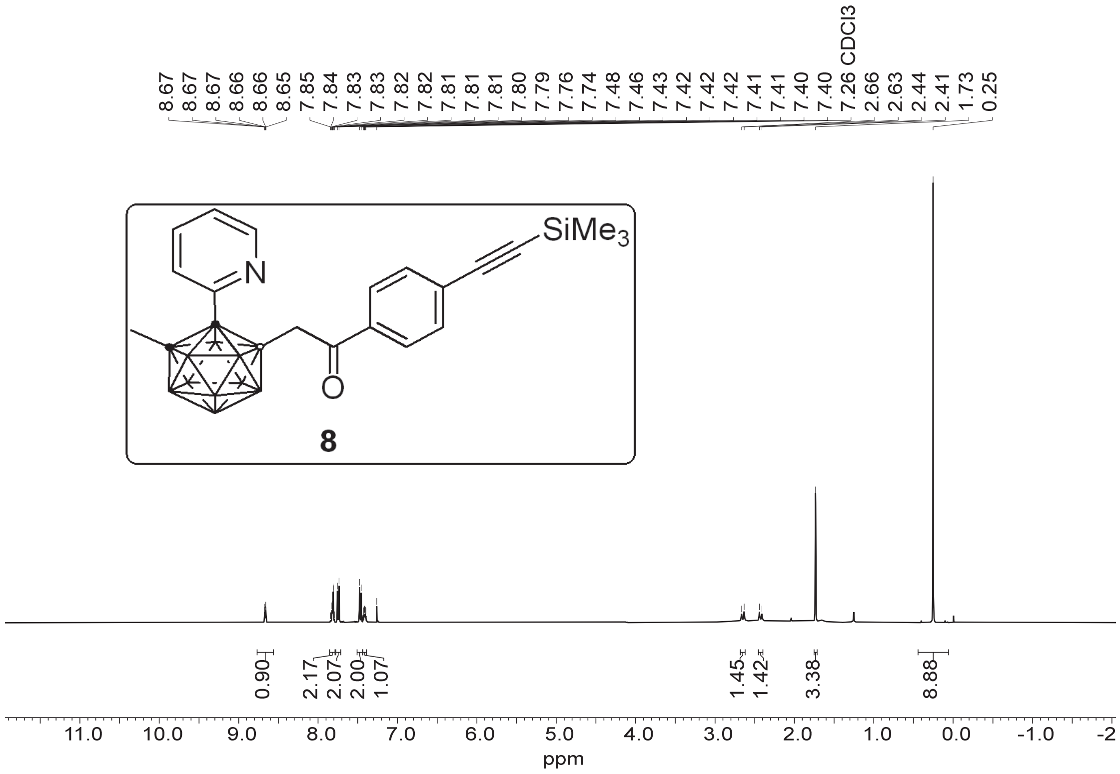
^{11}B NMR (128 MHz, CDCl$_3$)



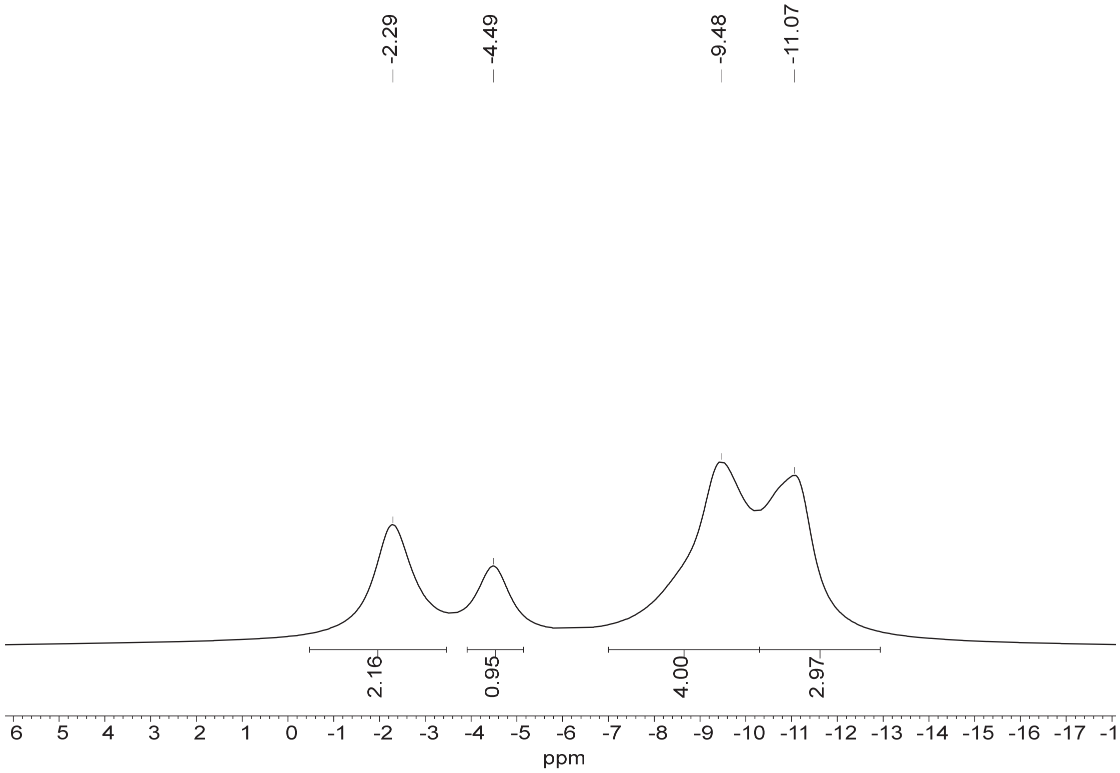
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



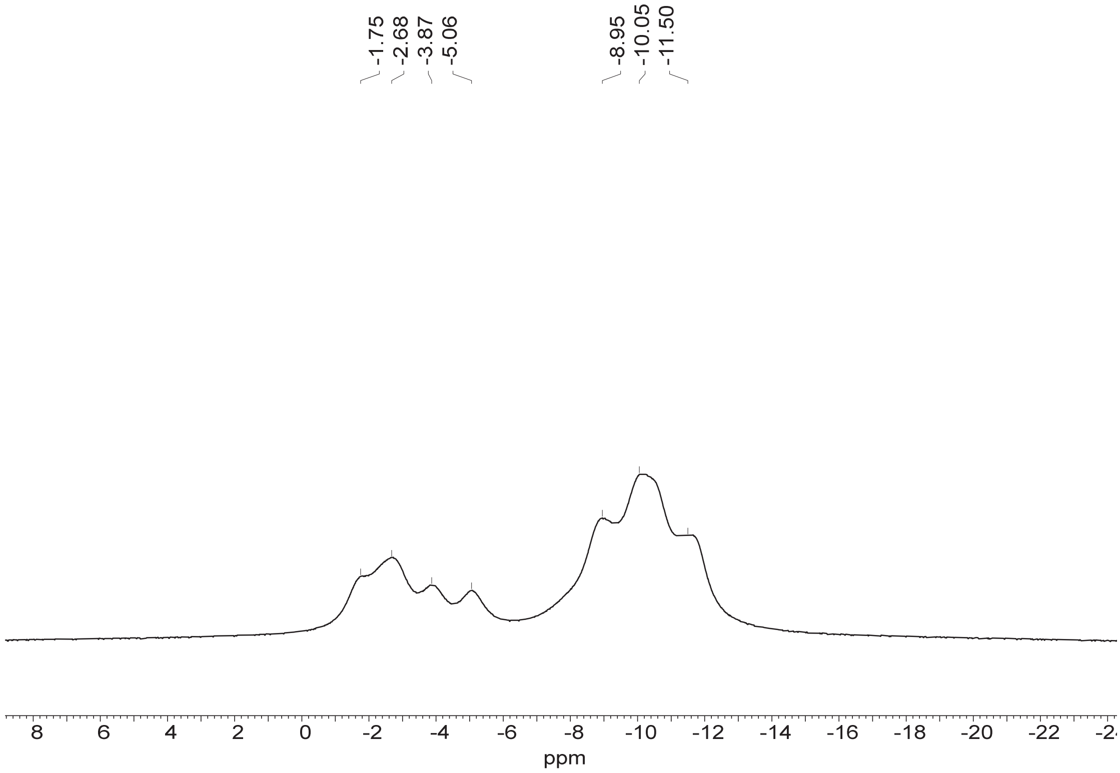
^{1}H NMR (400 MHz, CDCl$_3$)



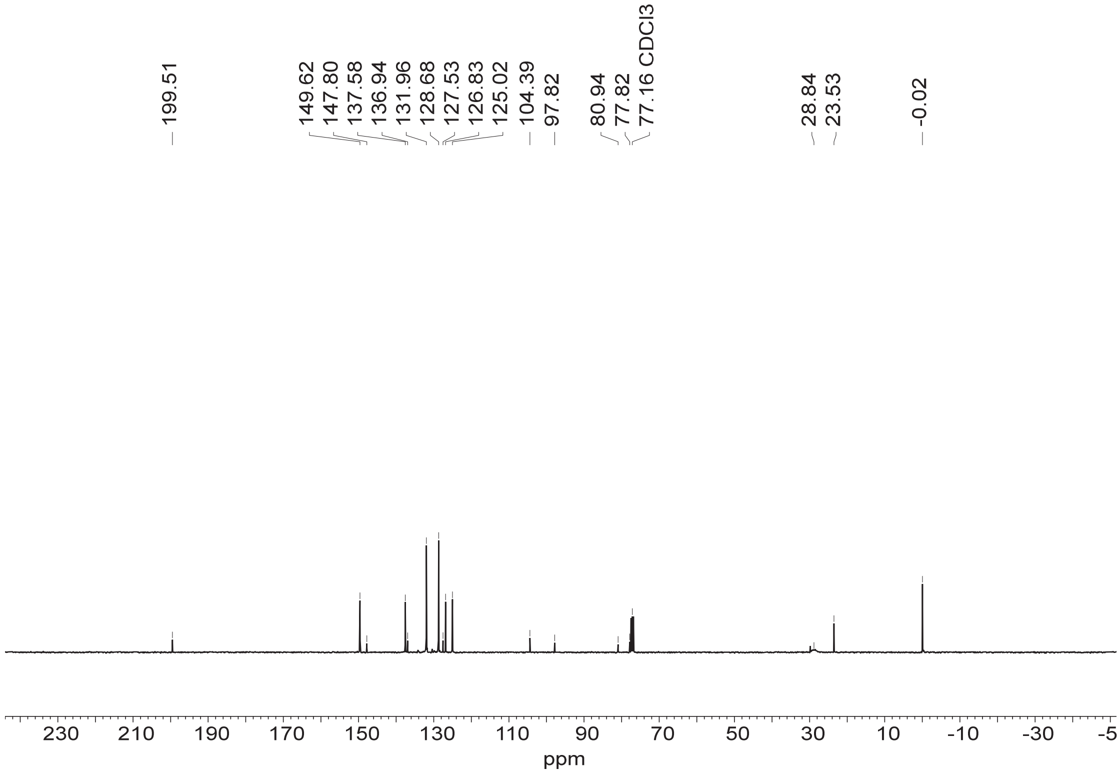
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



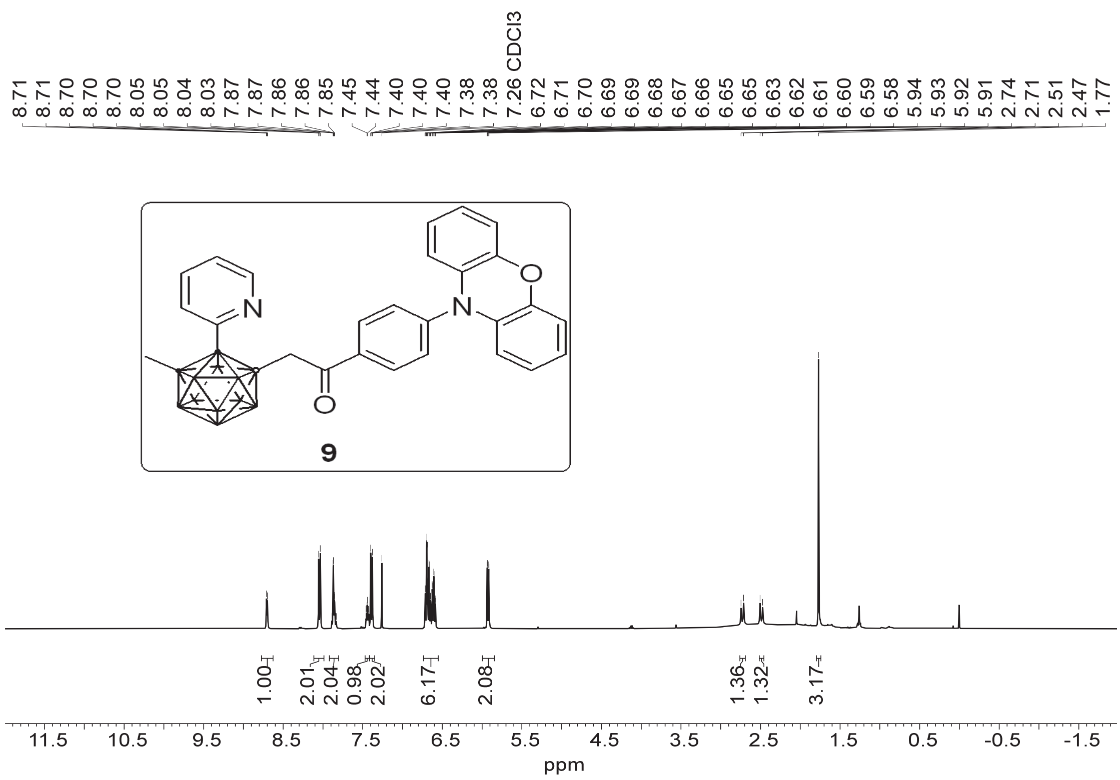
^{11}B NMR (128 MHz, $CDCl_3$)



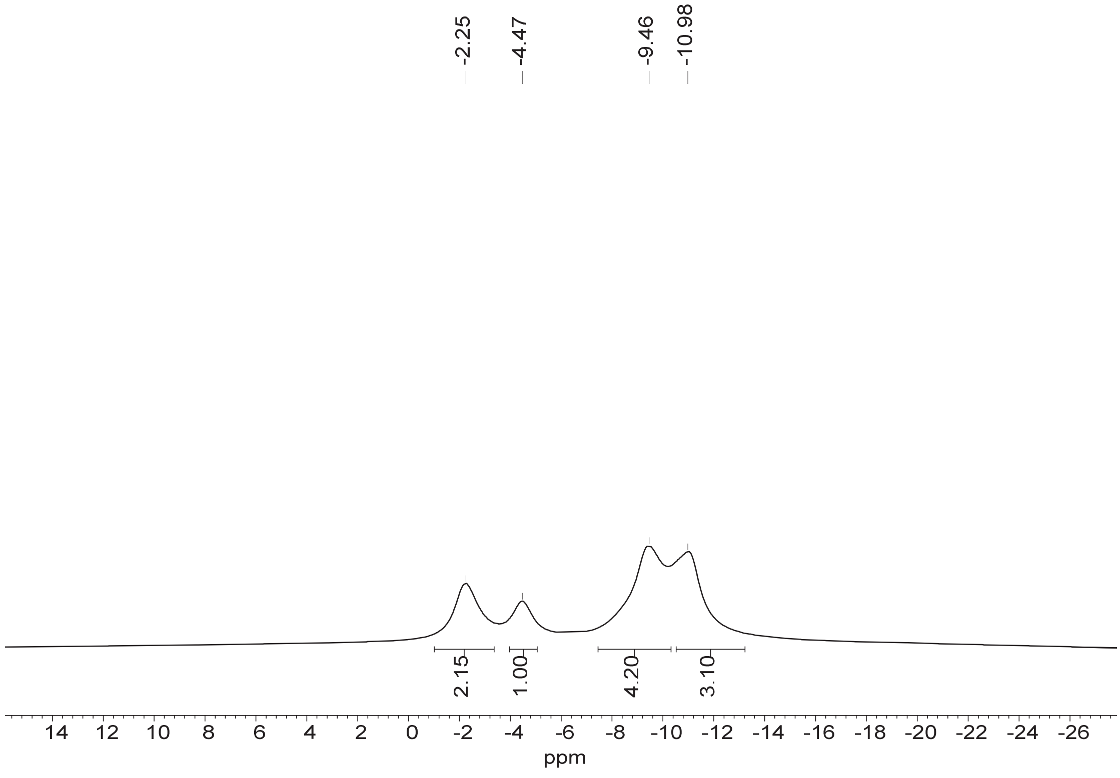
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



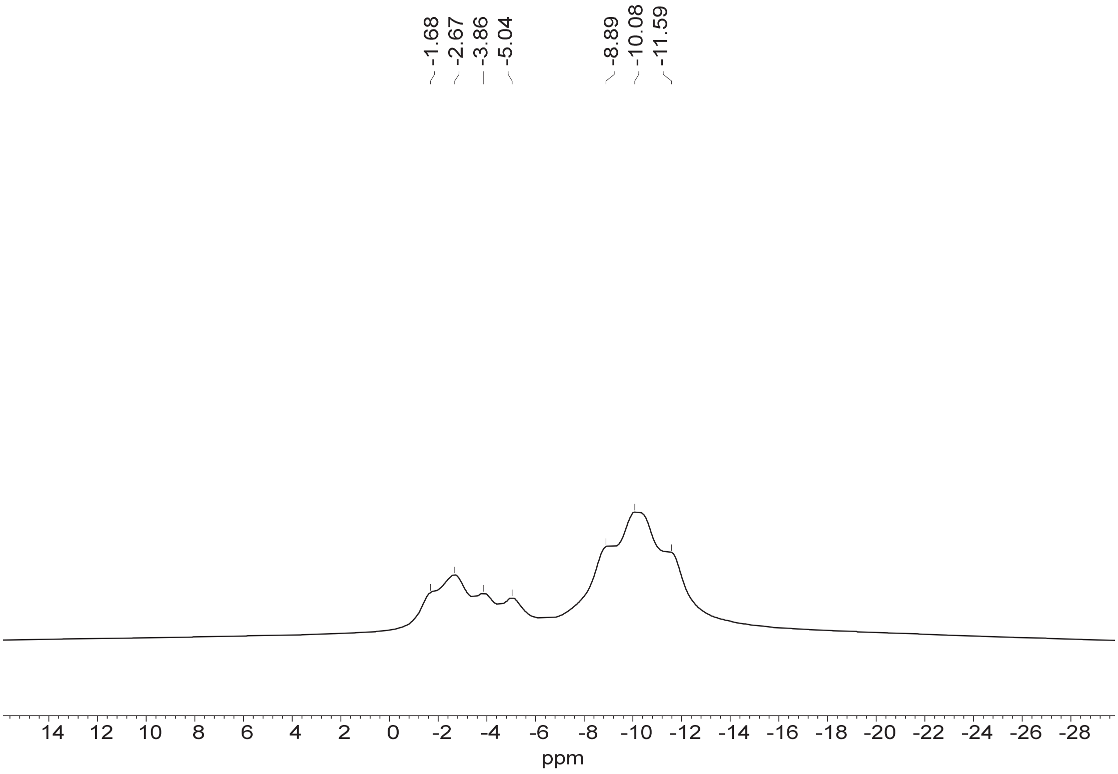
^{1}H NMR (400 MHz, $CDCl_3$)



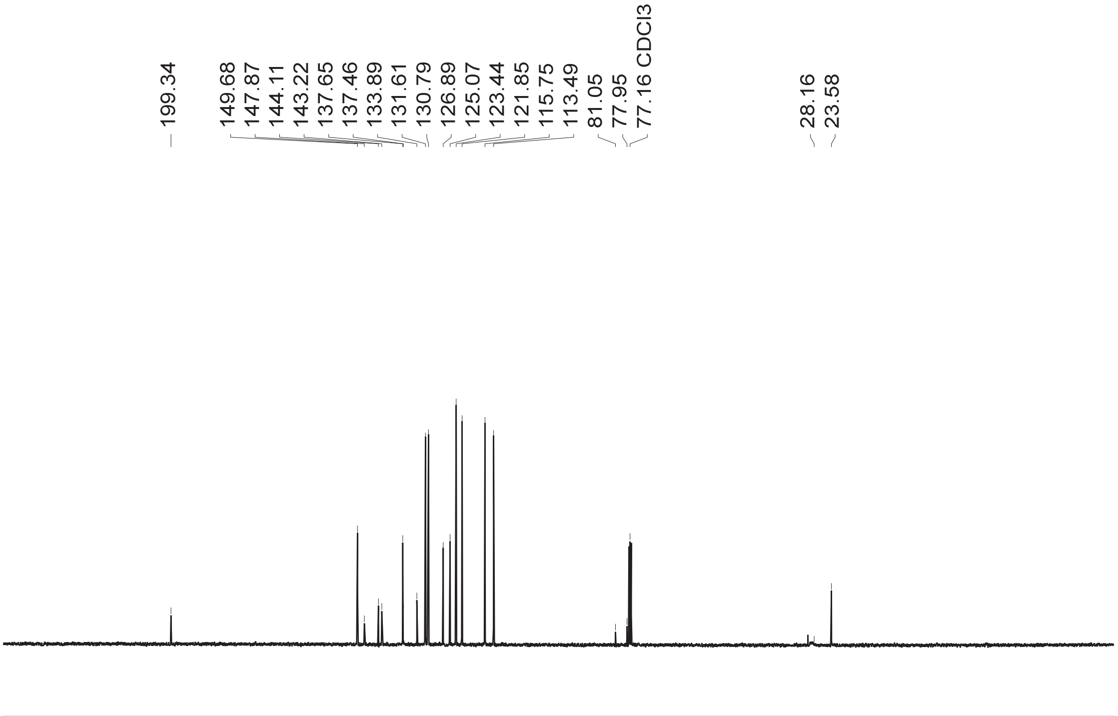
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



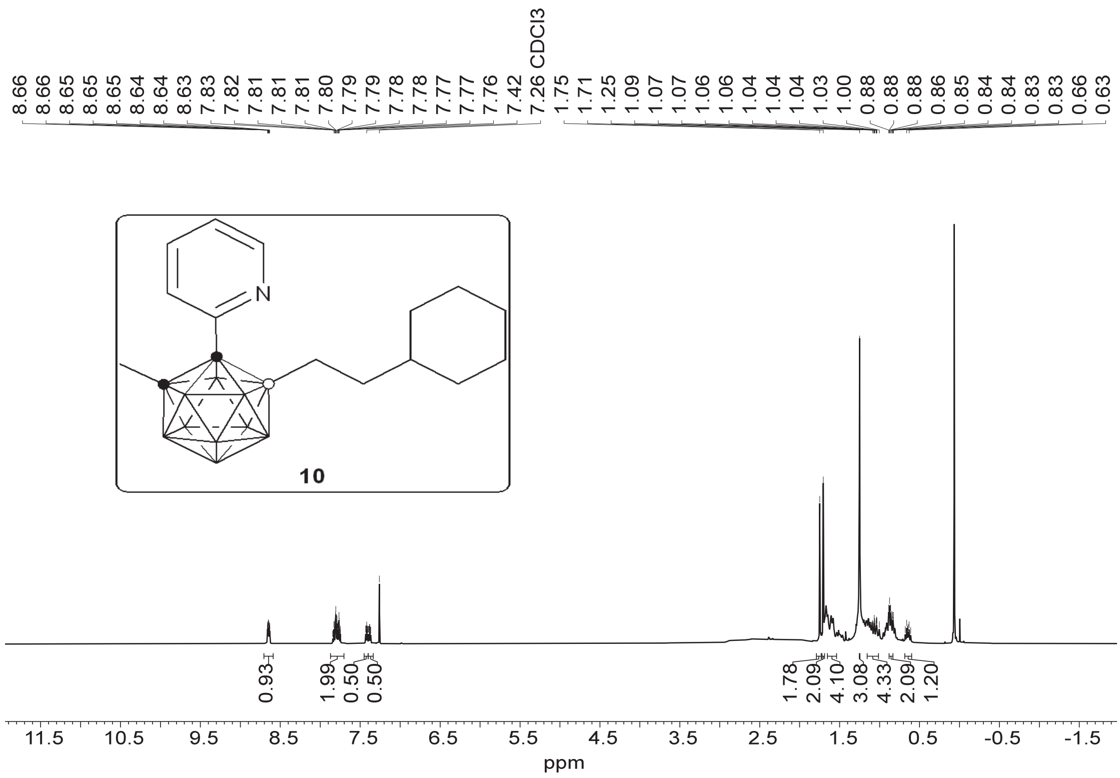
^{11}B NMR (128 MHz, $CDCl_3$)



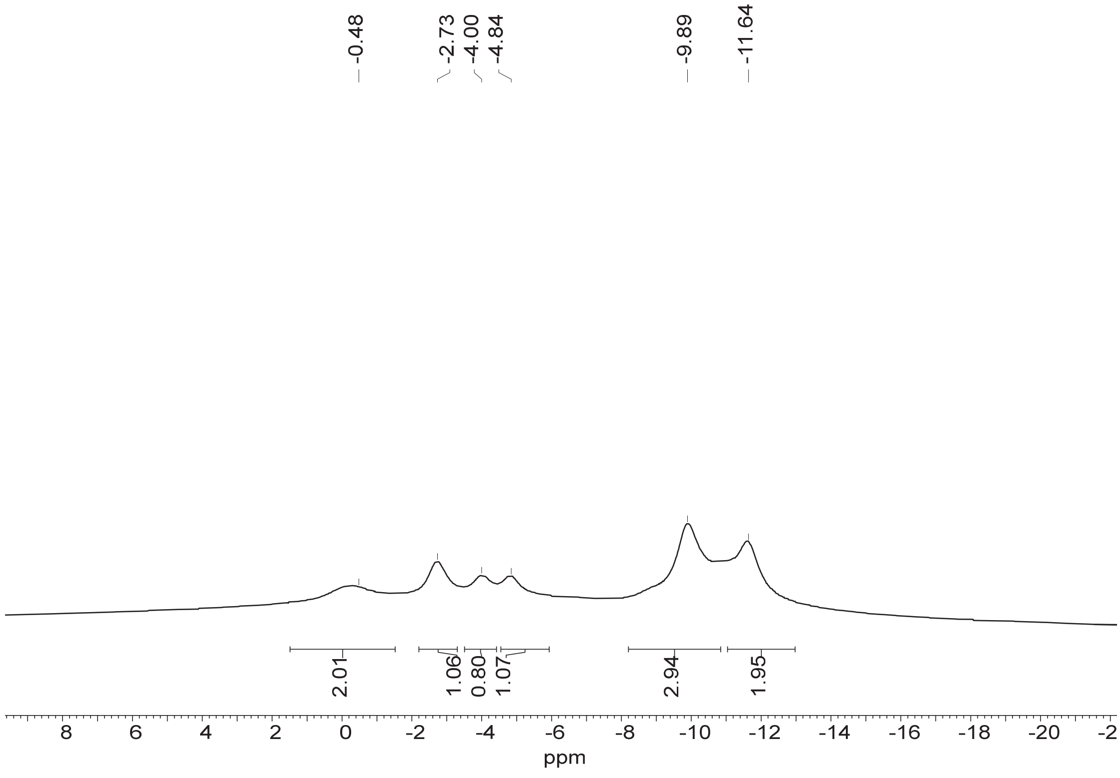
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



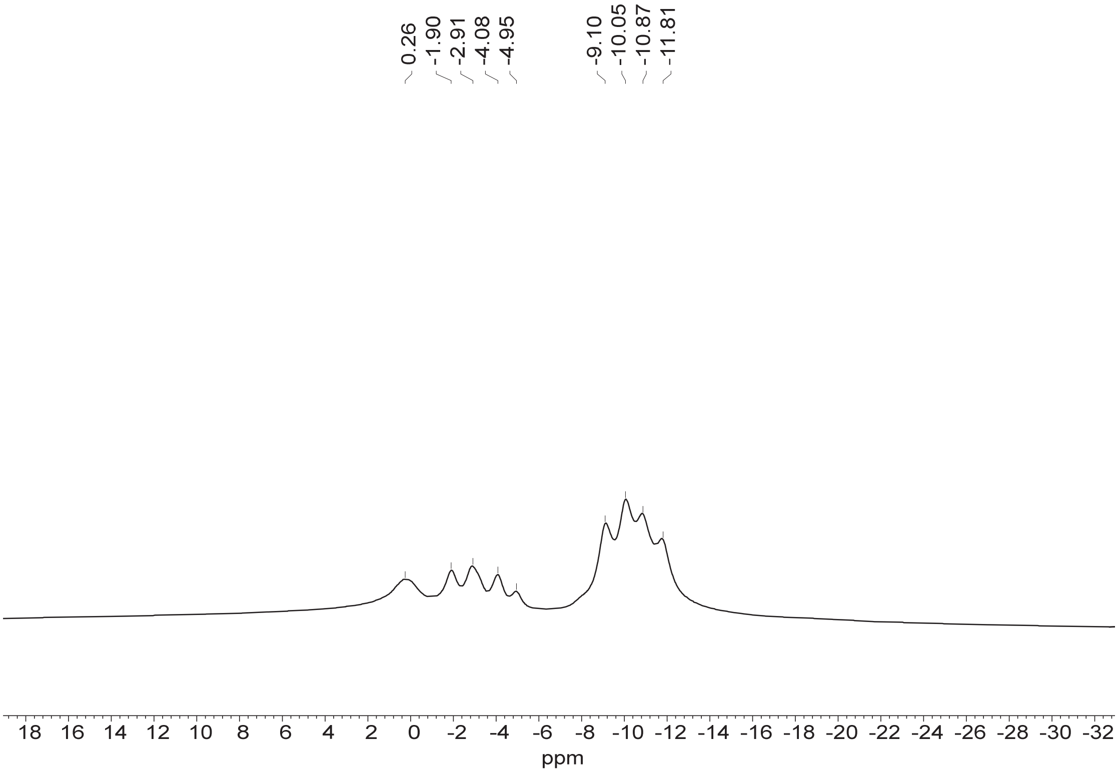
^{1}H NMR (500 MHz, CDCl$_3$)



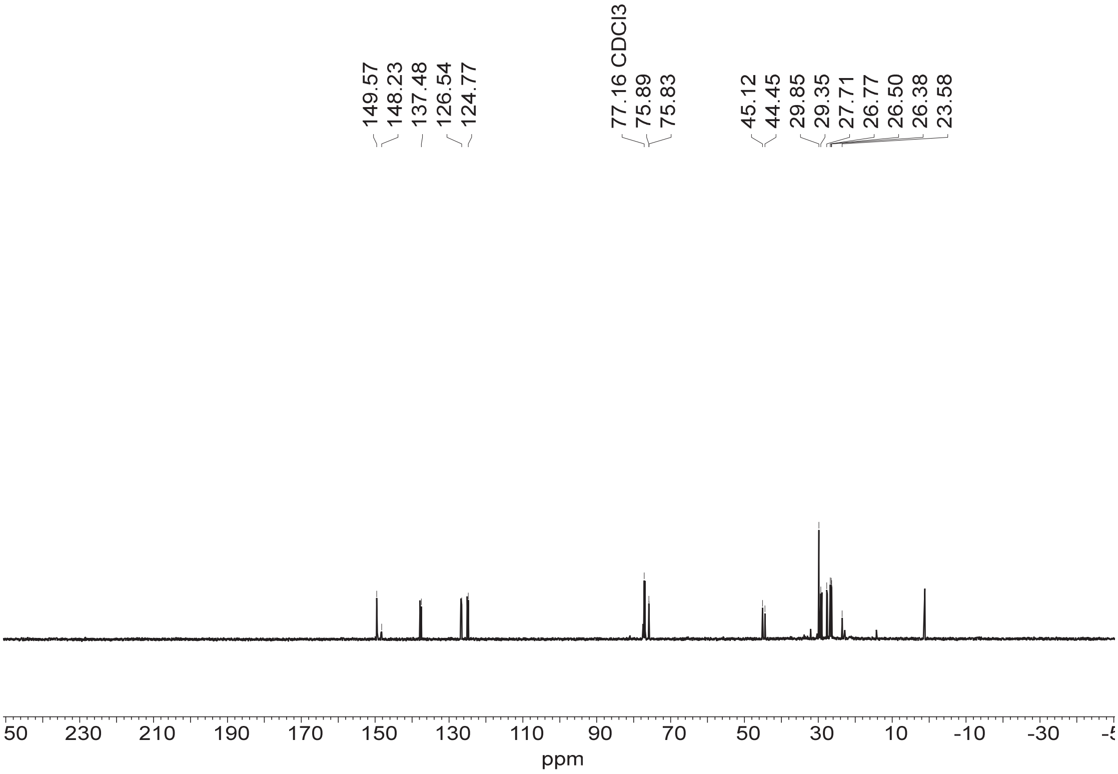
^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)



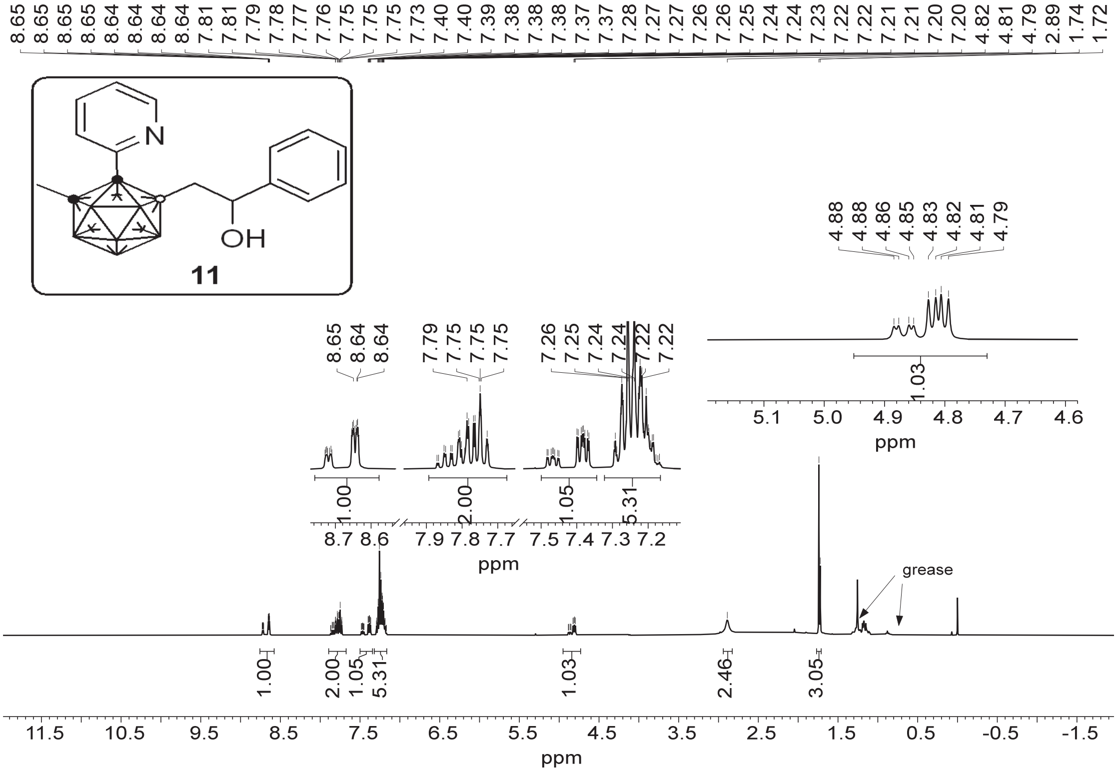
^{11}B NMR (160 MHz, CDCl$_3$)



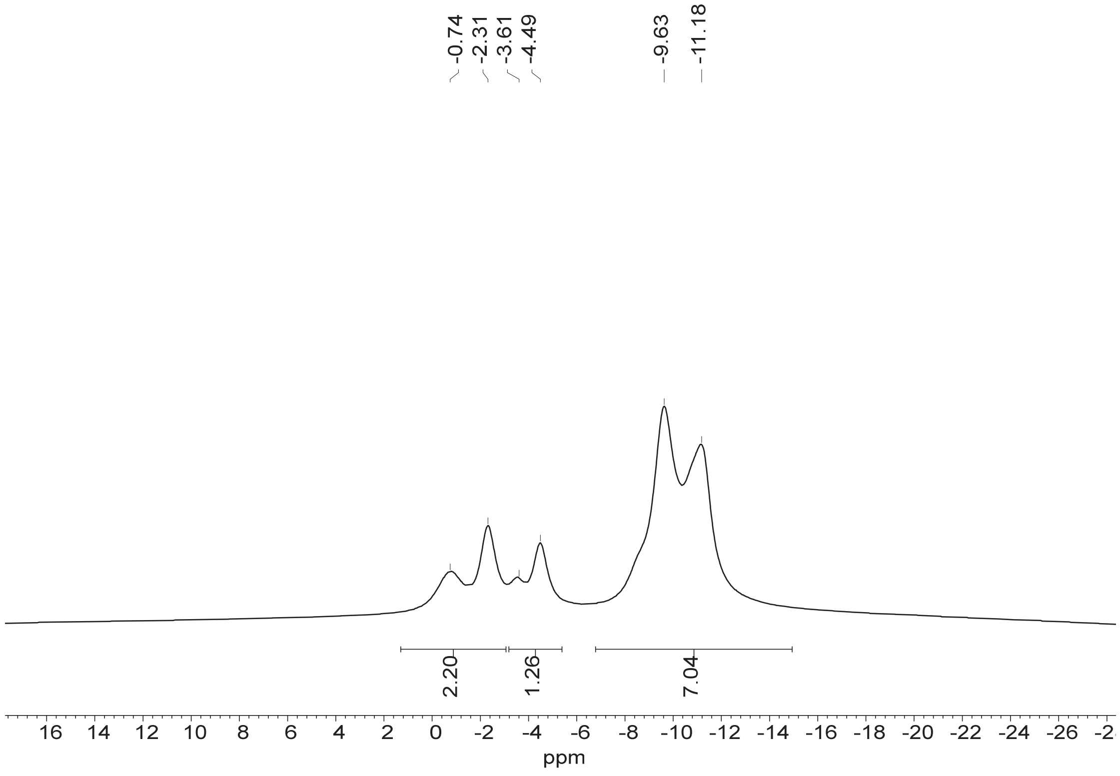
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



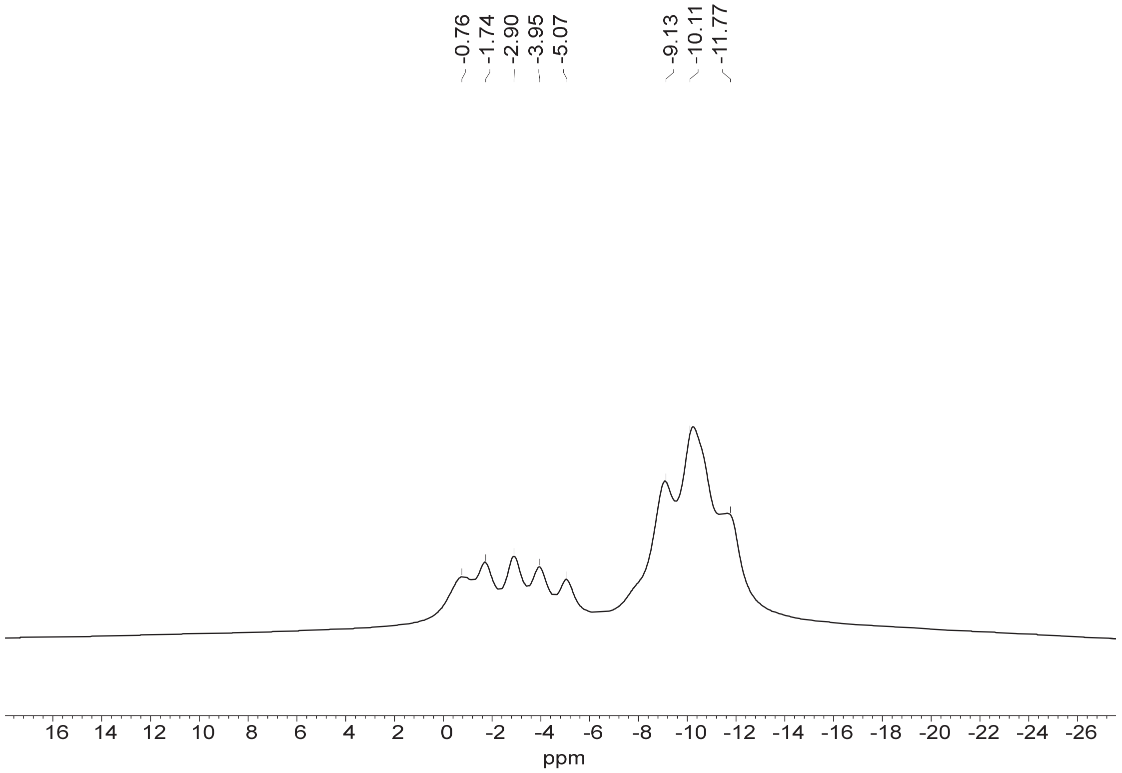
^{1}H NMR (400 MHz, CDCl$_3$)



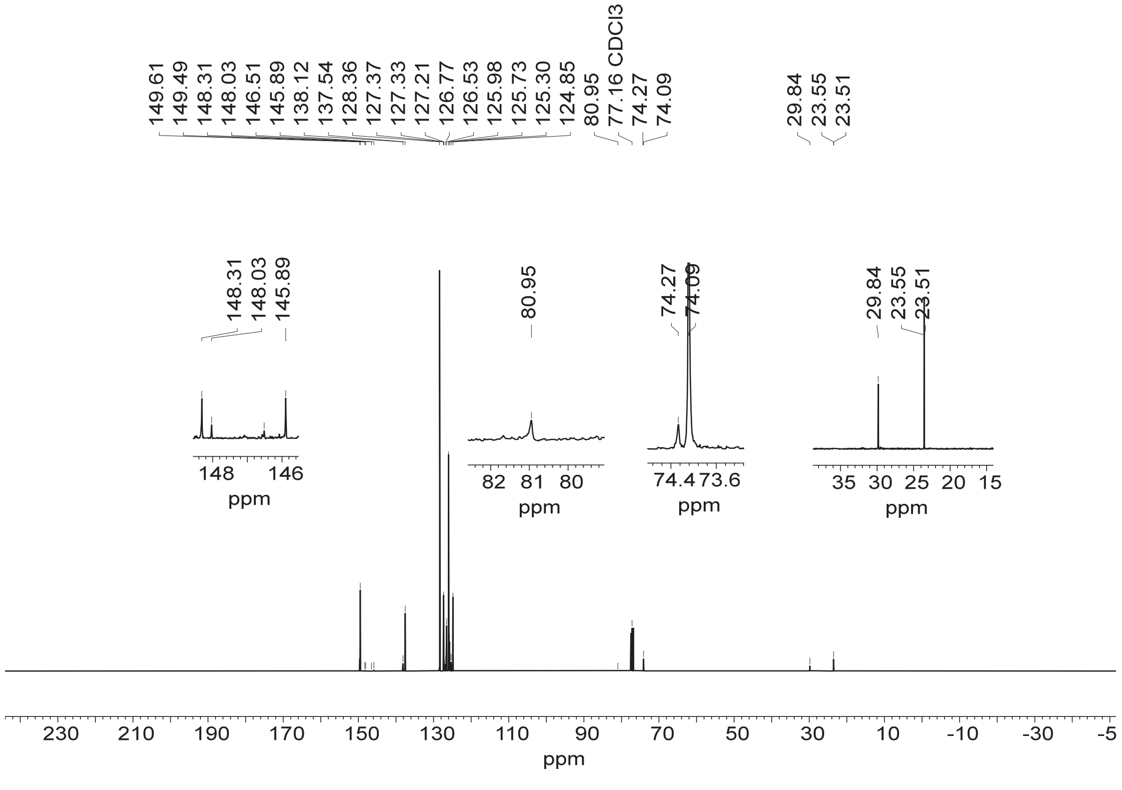
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



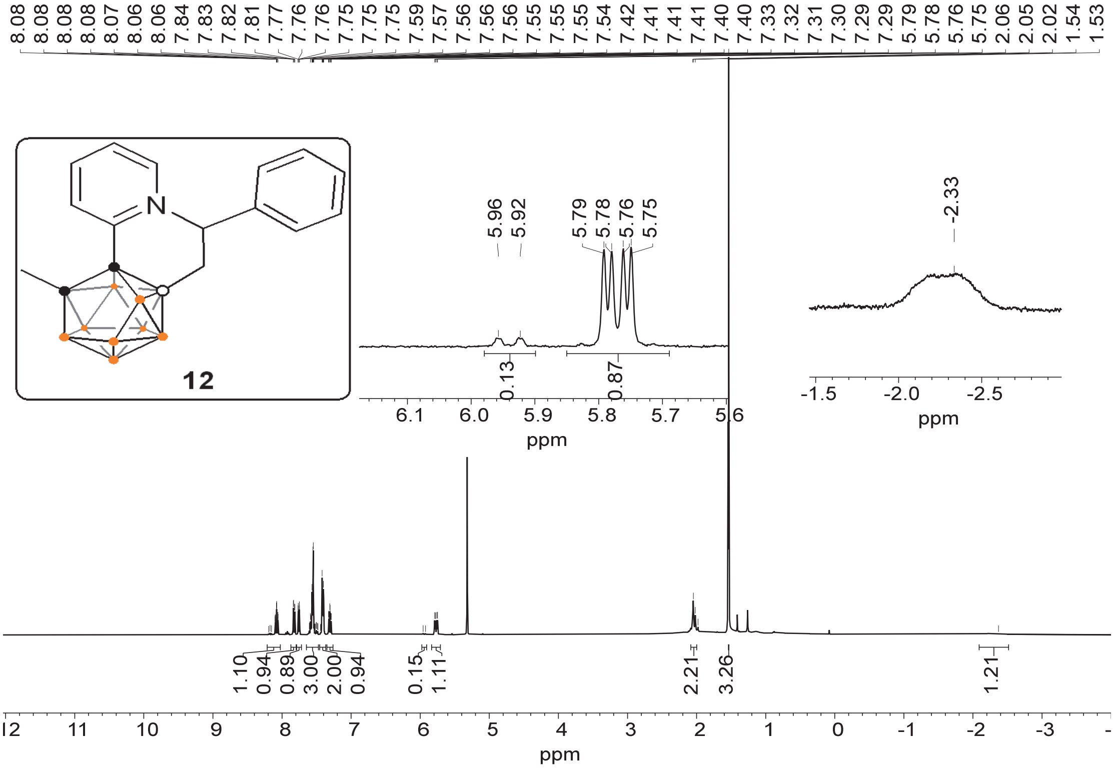
^{11}B NMR (128 MHz, $CDCl_3$)



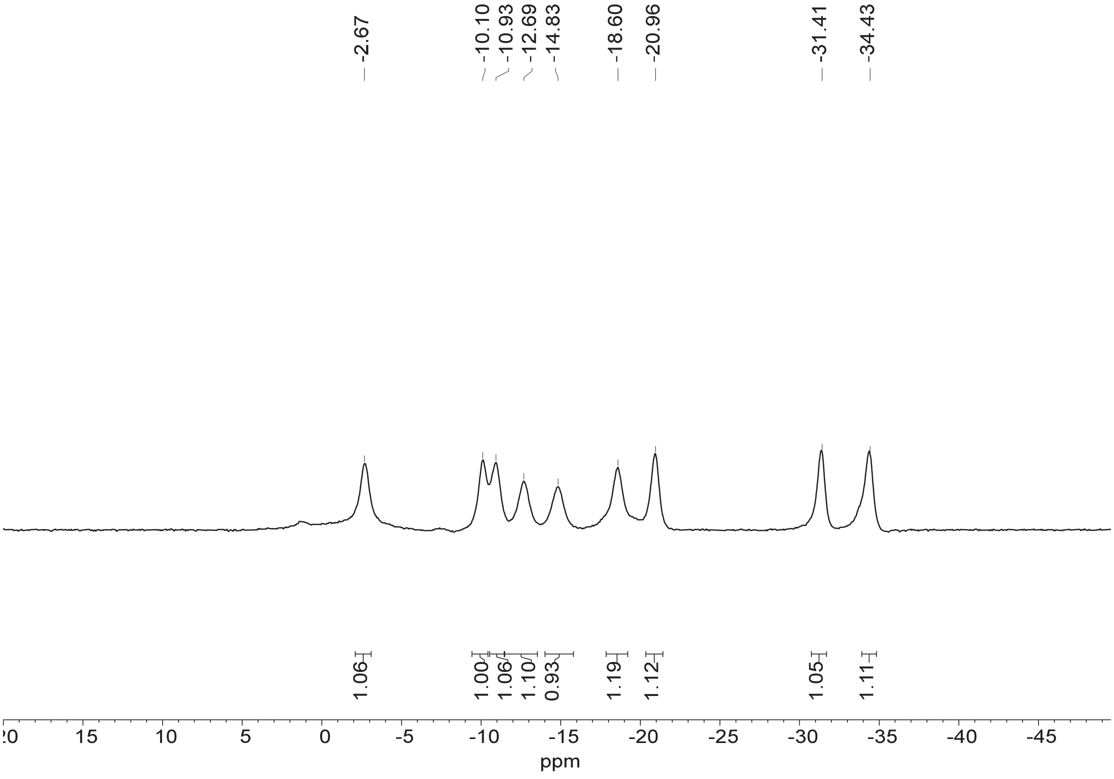
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



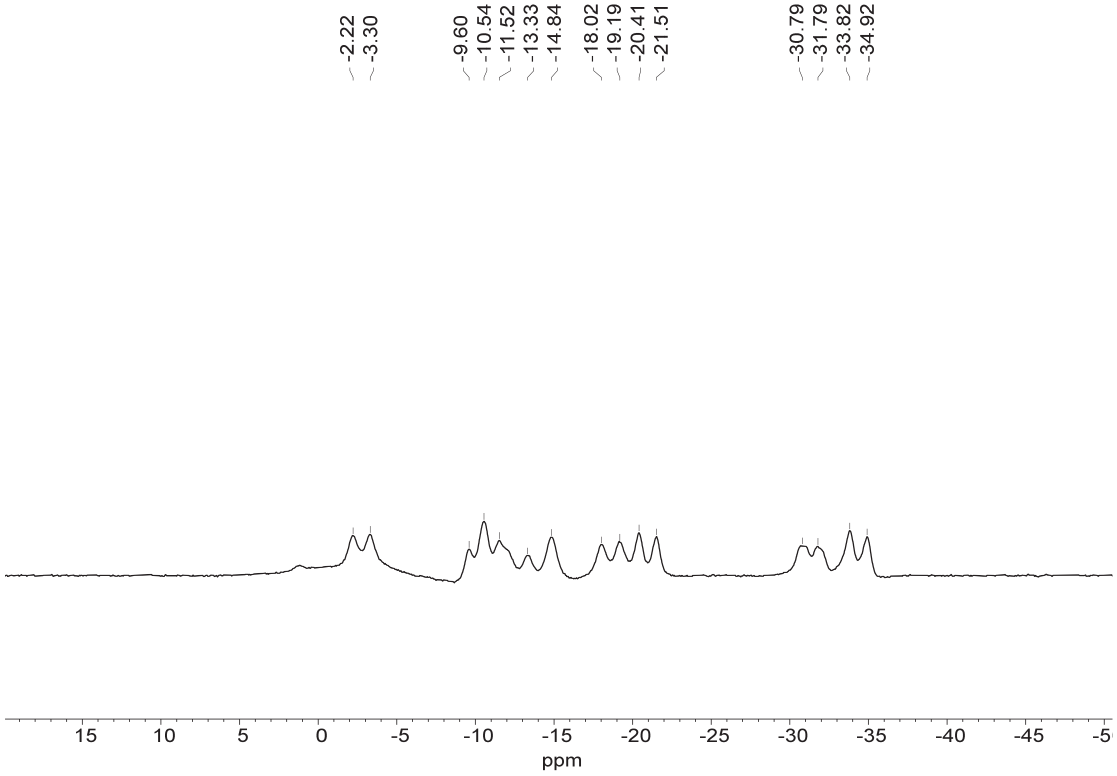
^{1}H NMR (400 MHz, CD$_2$Cl$_2$)



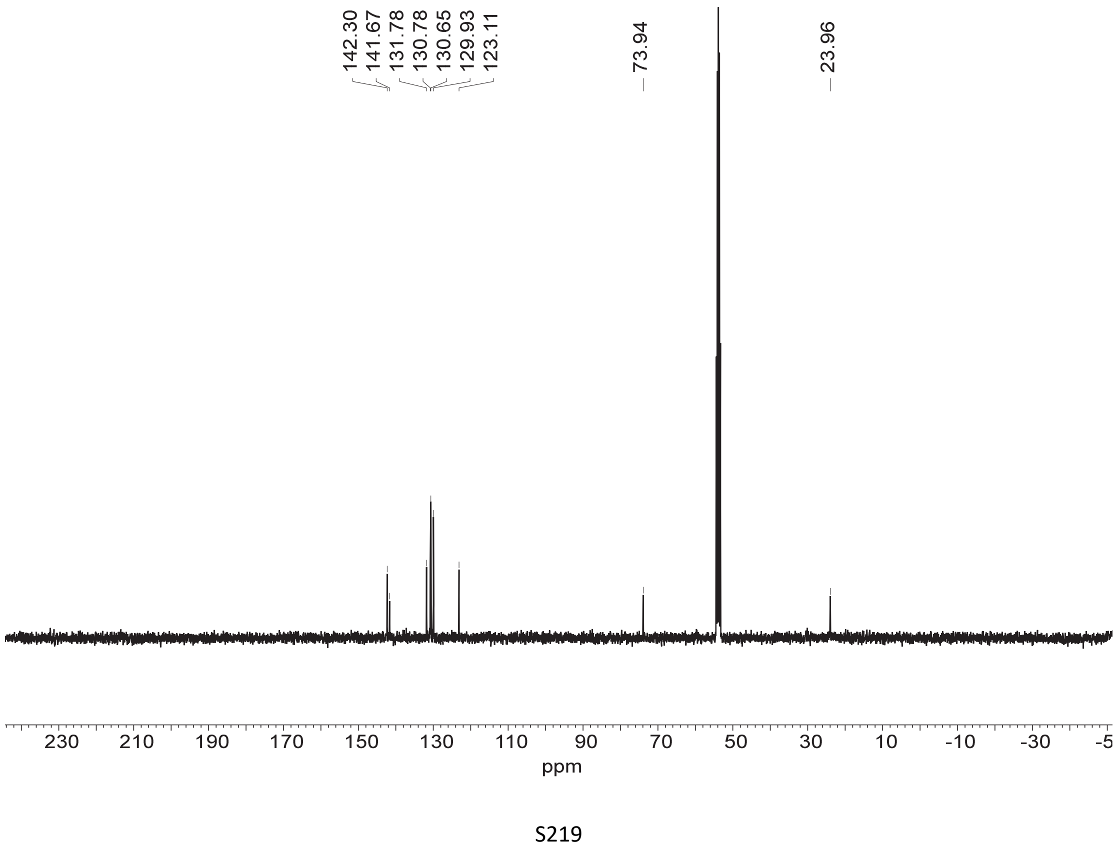
^{11}B{^{1}H} NMR (128 MHz, CD$_2$Cl$_2$)



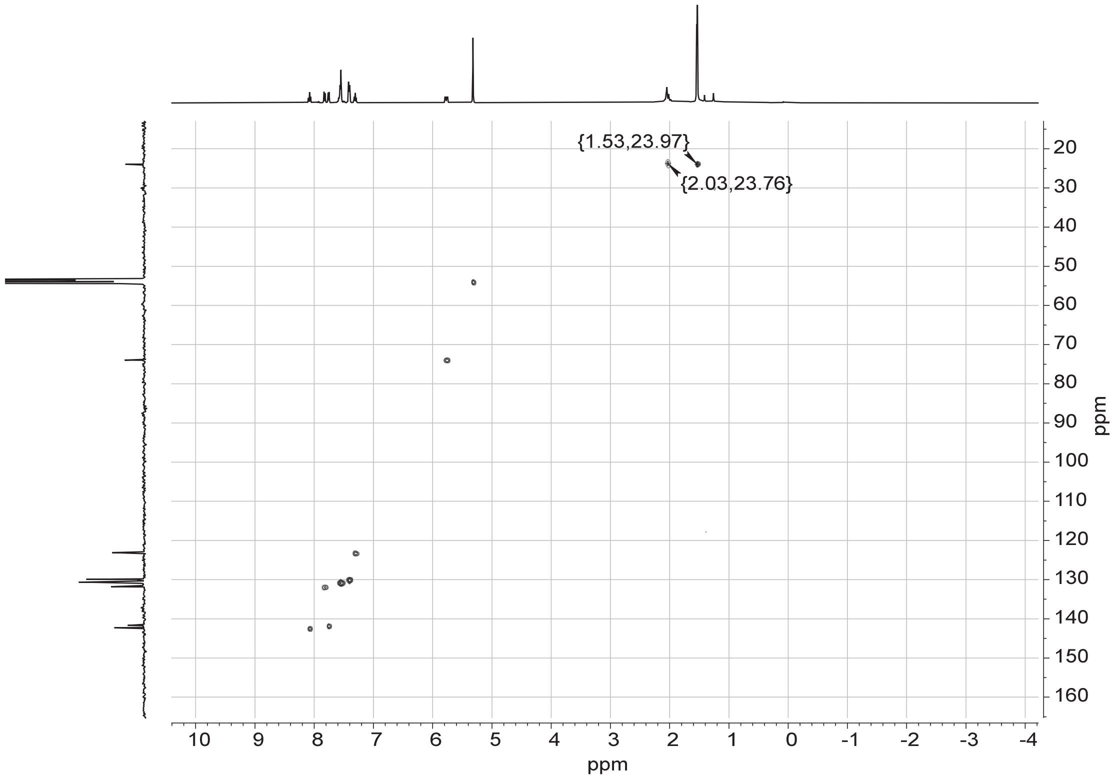
^{11}B NMR (128 MHz, CD$_2$Cl$_2$)



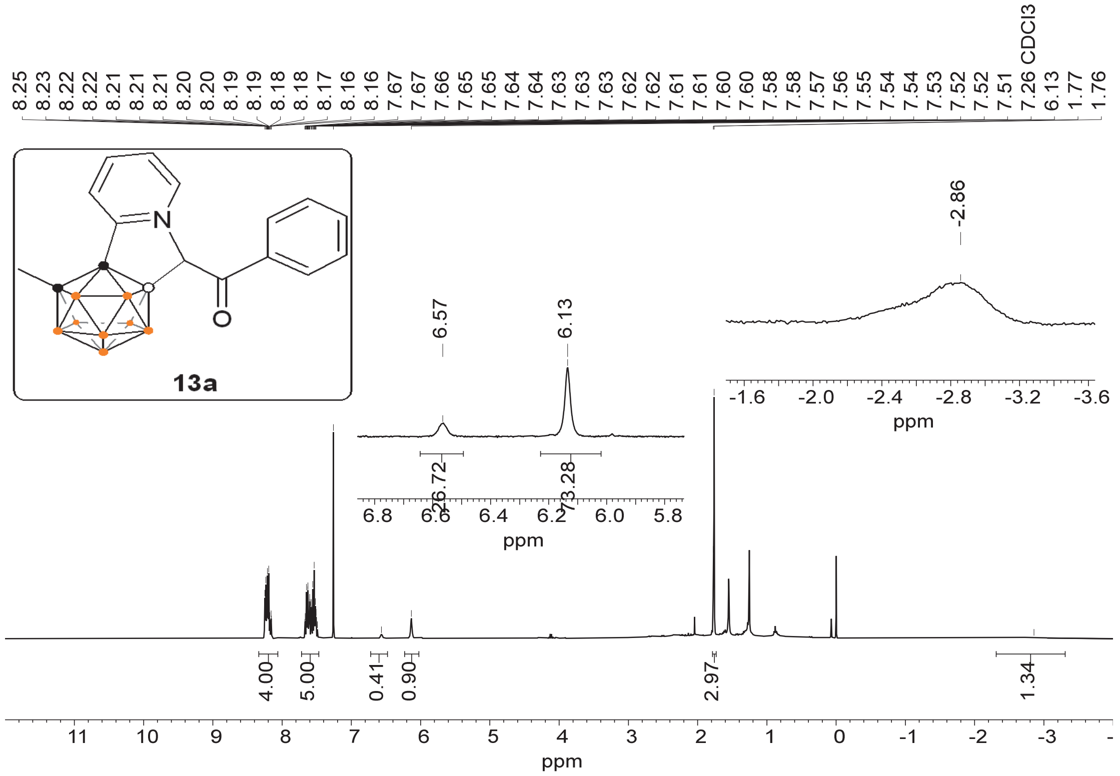
^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$)



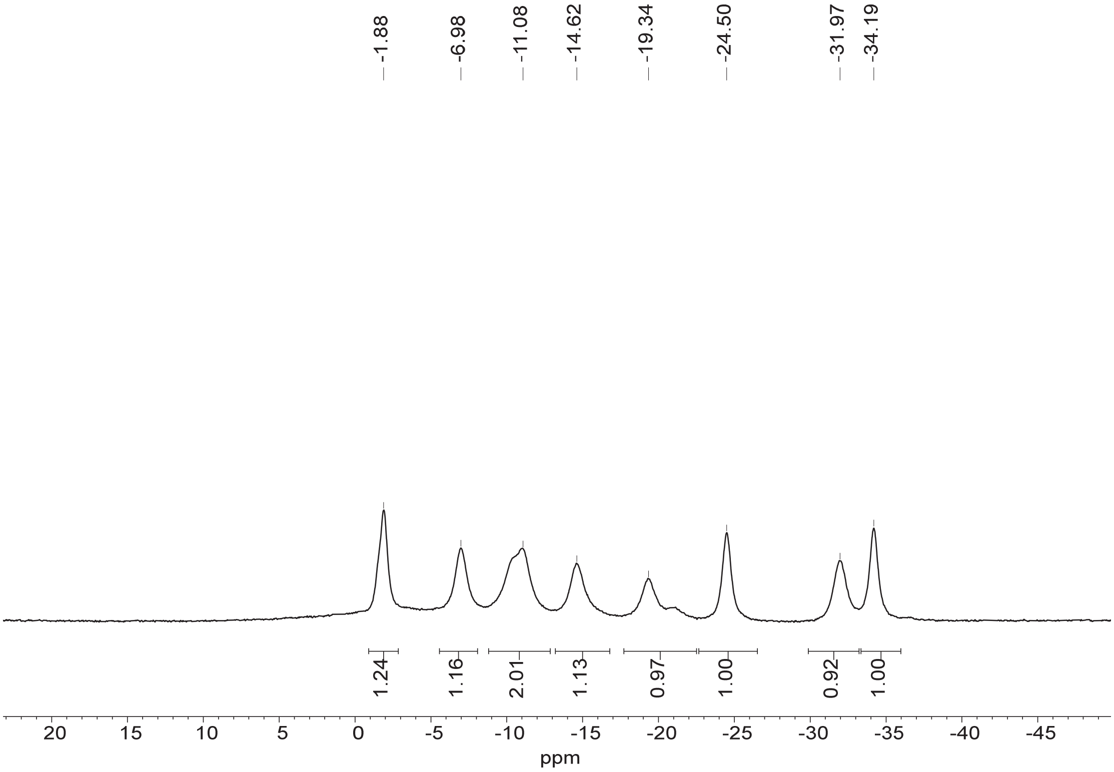
^{13}C–^{1}H HSQC (400 MHz, CDCl$_3$)



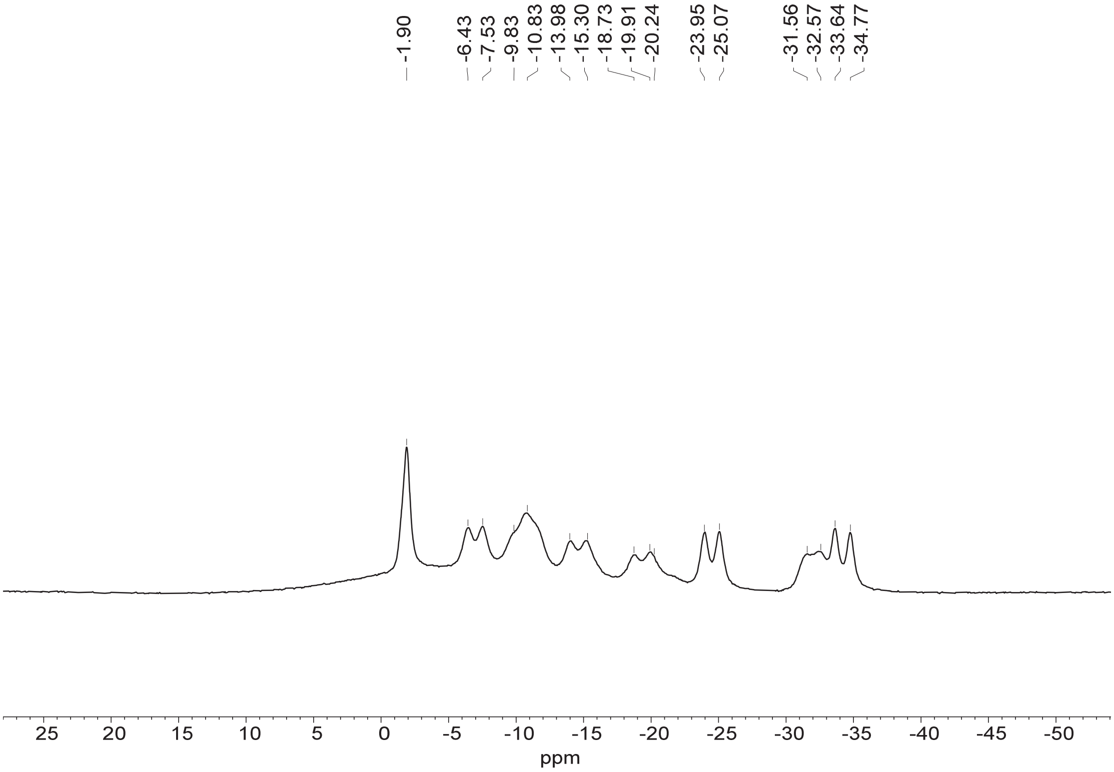
^{1}H NMR (400 MHz, CDCl$_3$)



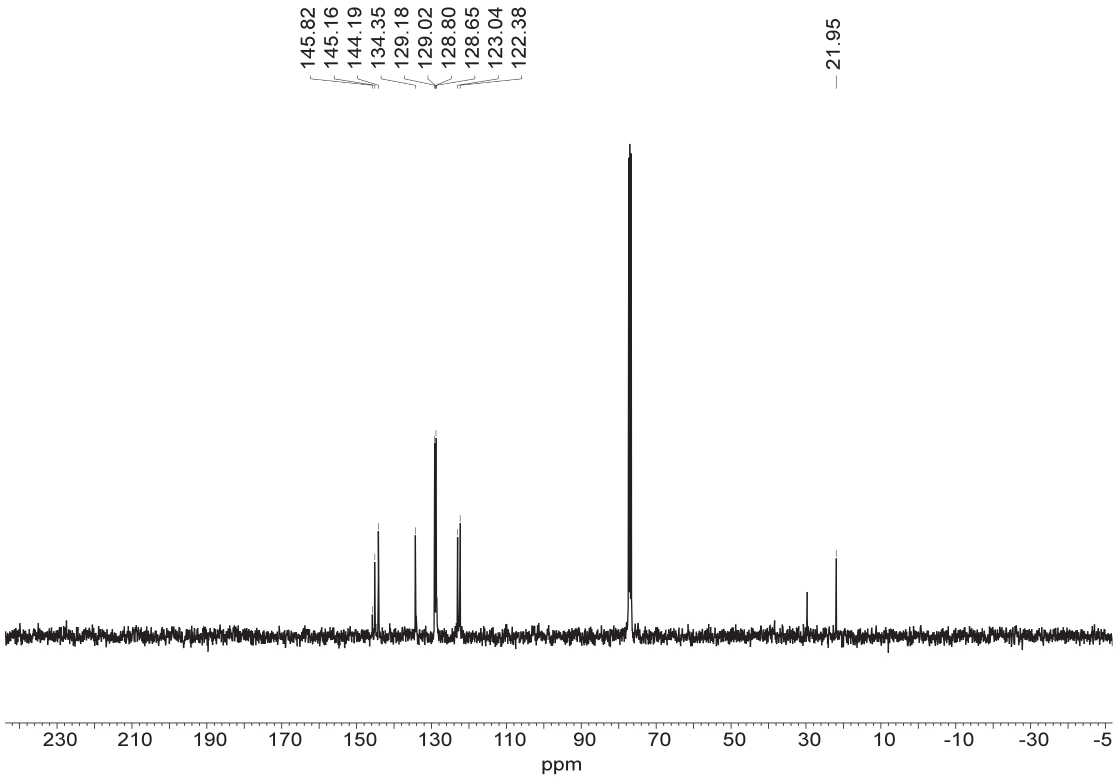
$^{11}B\{^{1}H\}$ NMR (128 MHz, CDCl$_3$)



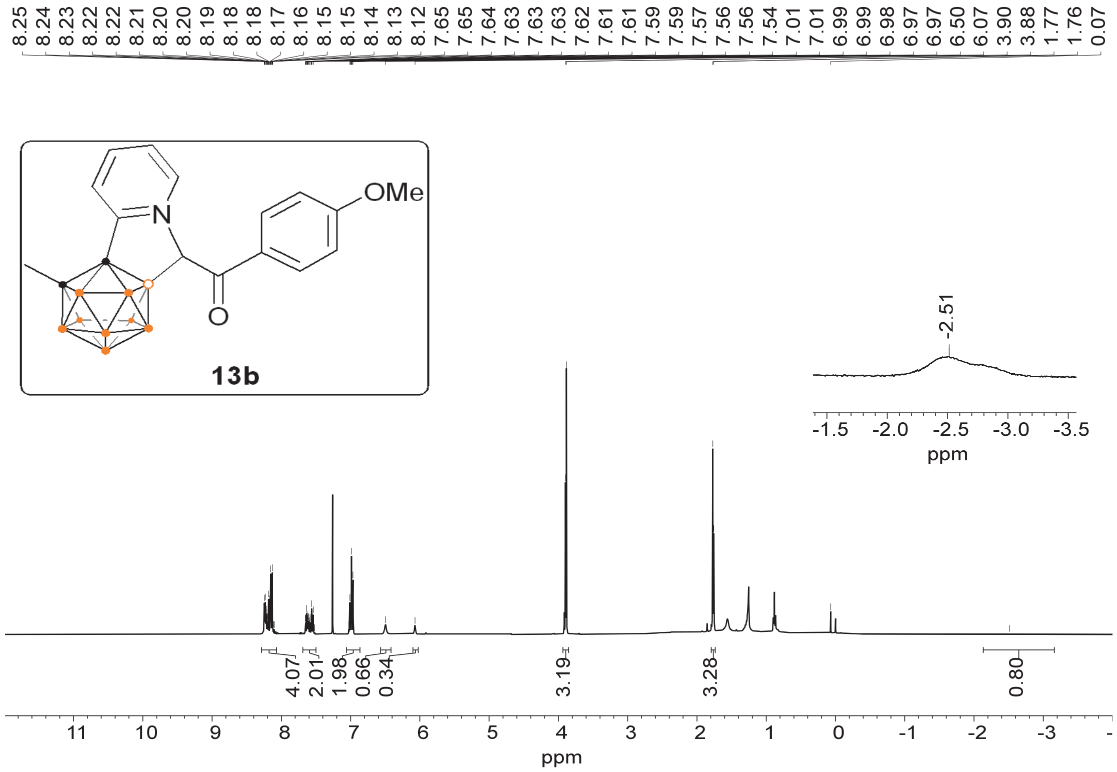
^{11}B NMR (128 MHz, CDCl$_3$)



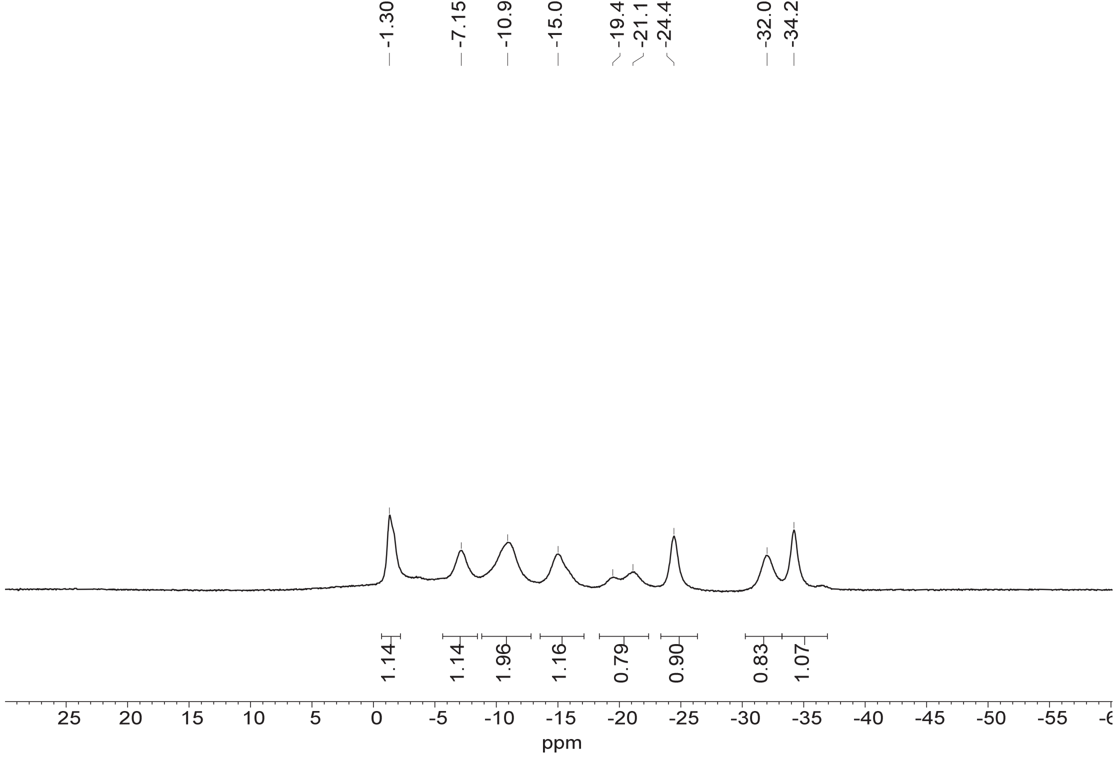
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



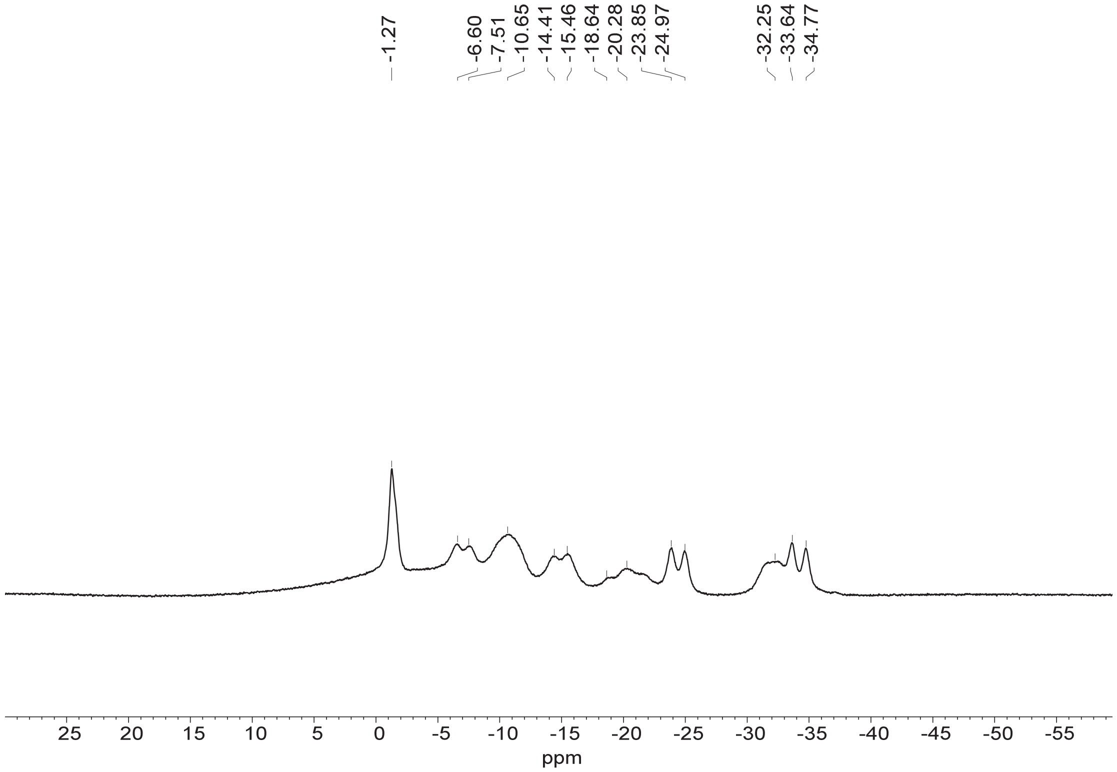
^{1}H NMR (400 MHz, CDCl$_3$)



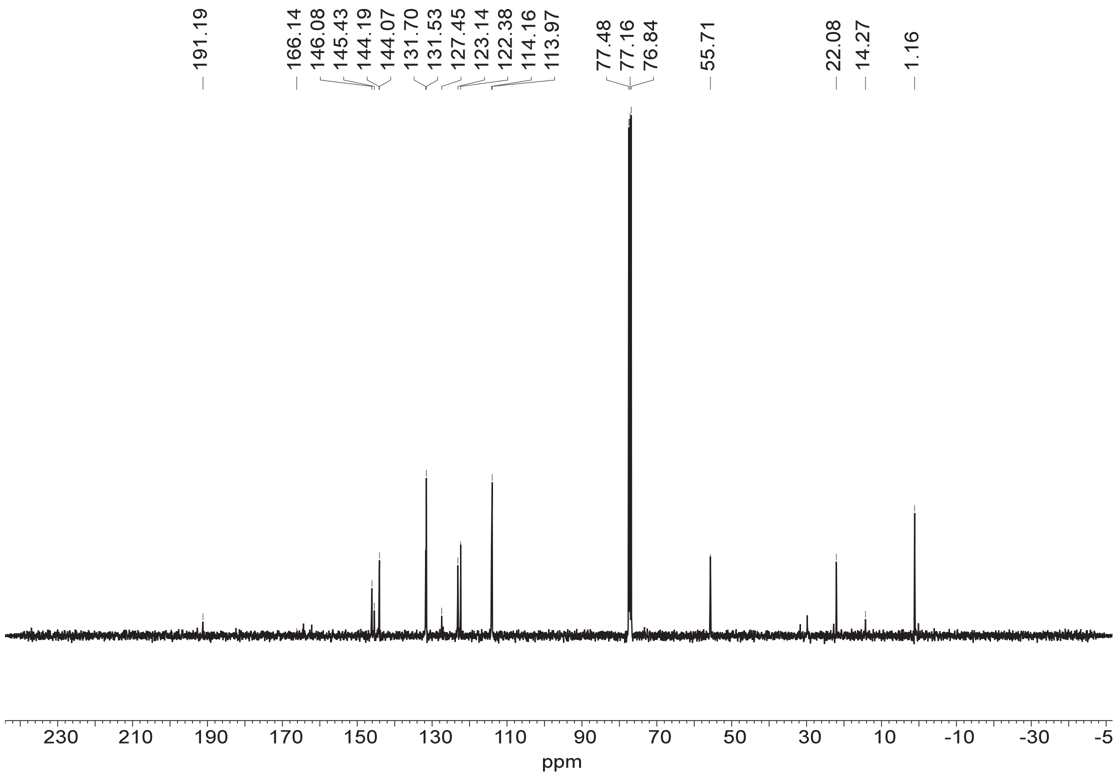
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



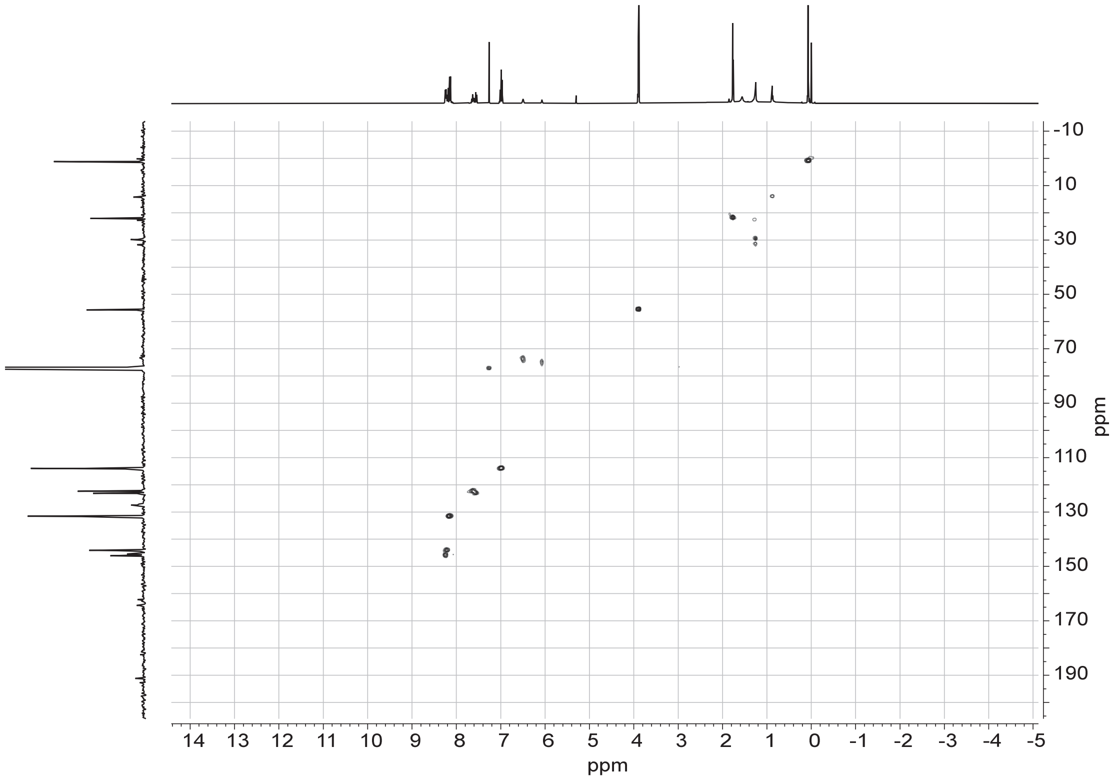
^{11}B NMR (128 MHz, $CDCl_3$)



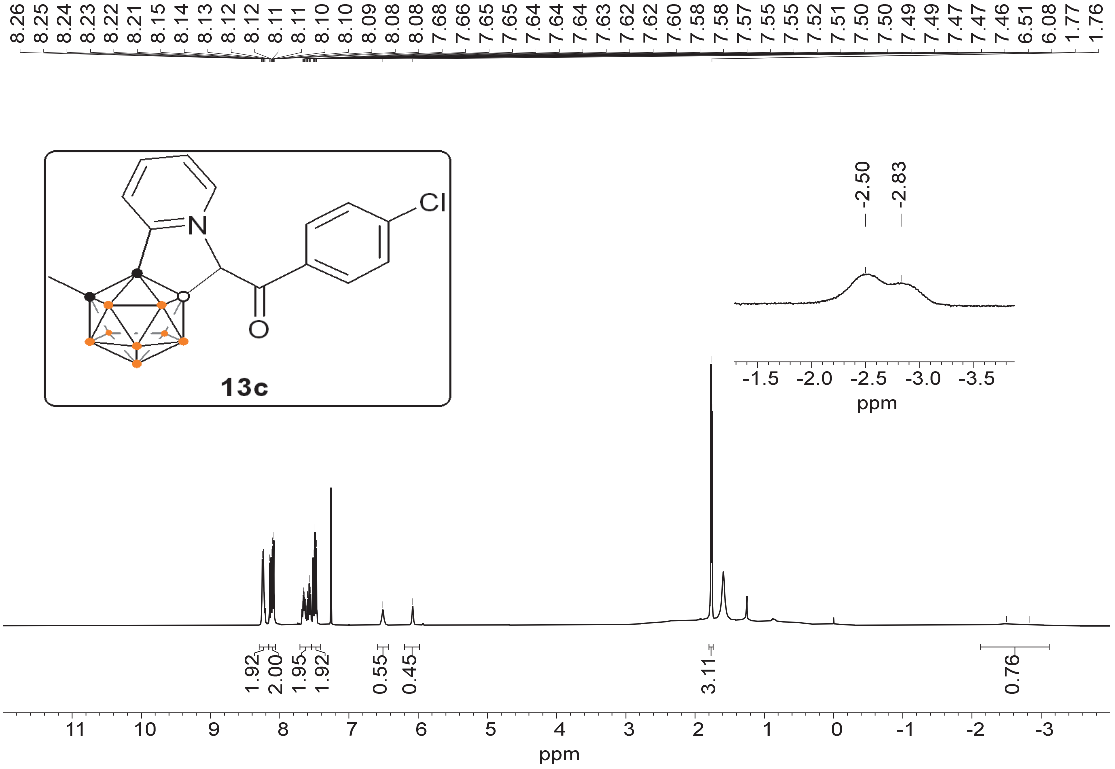
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



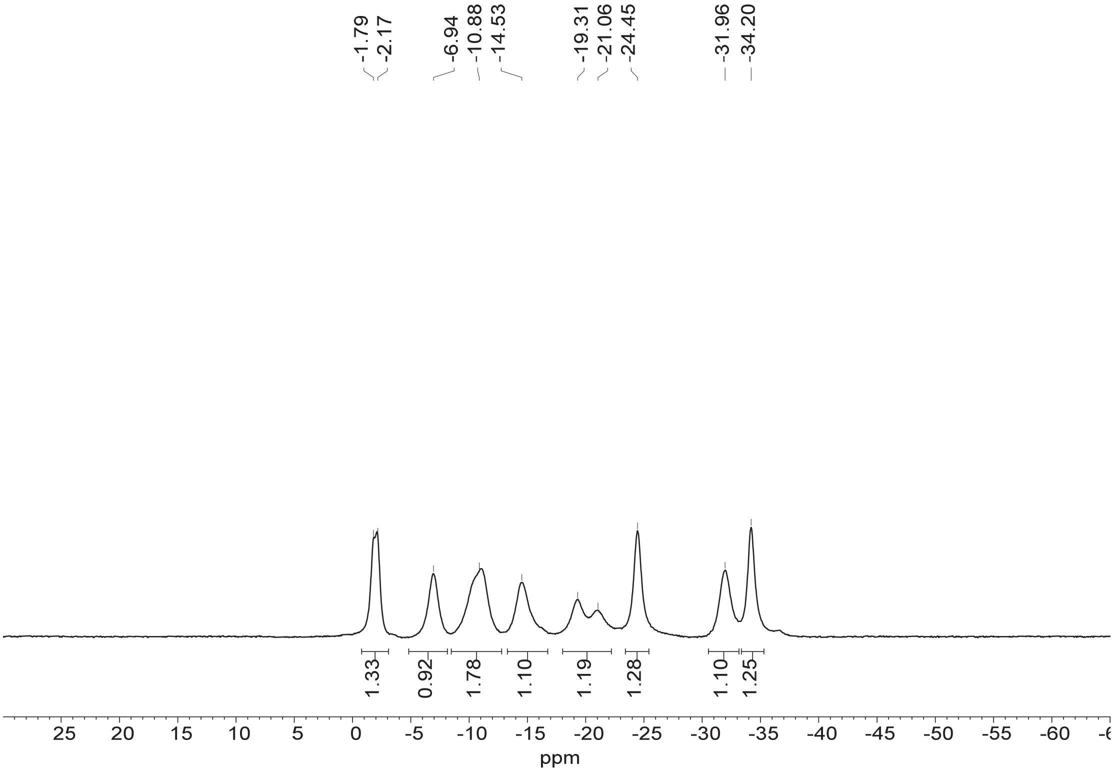
$^{13}C{-}^{1}H$ HSQC (400 MHz, $CDCl_3$)



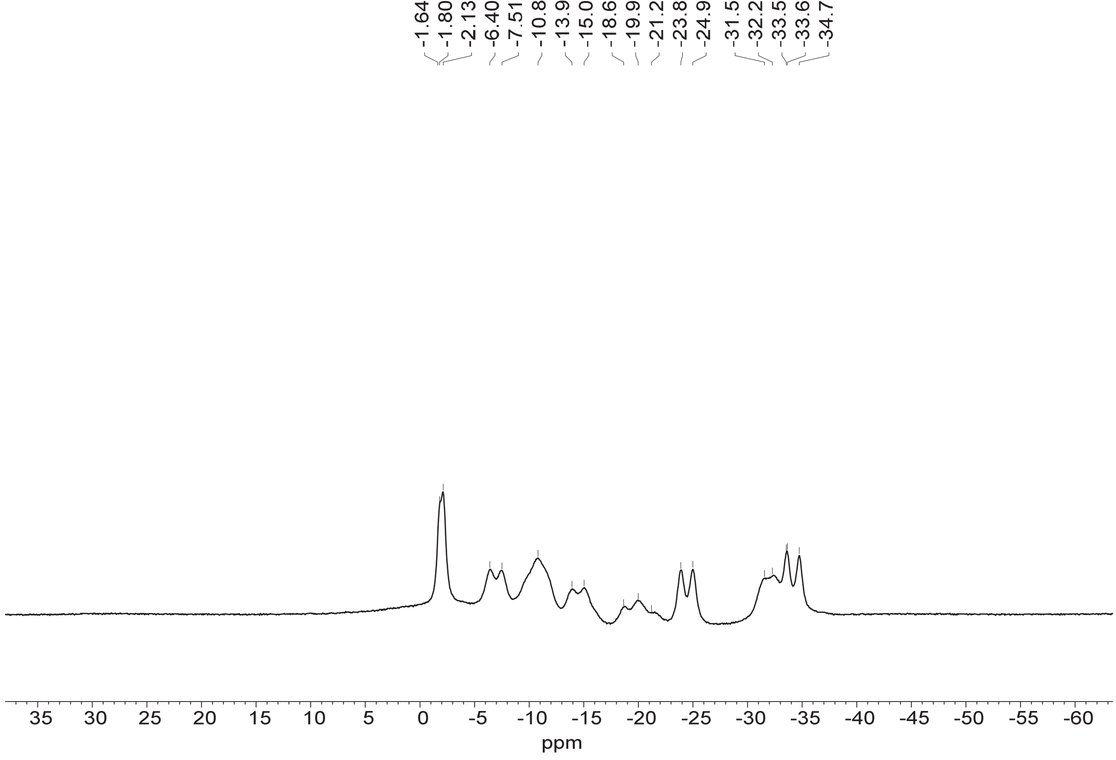
^{1}H NMR (400 MHz, CDCl$_3$)



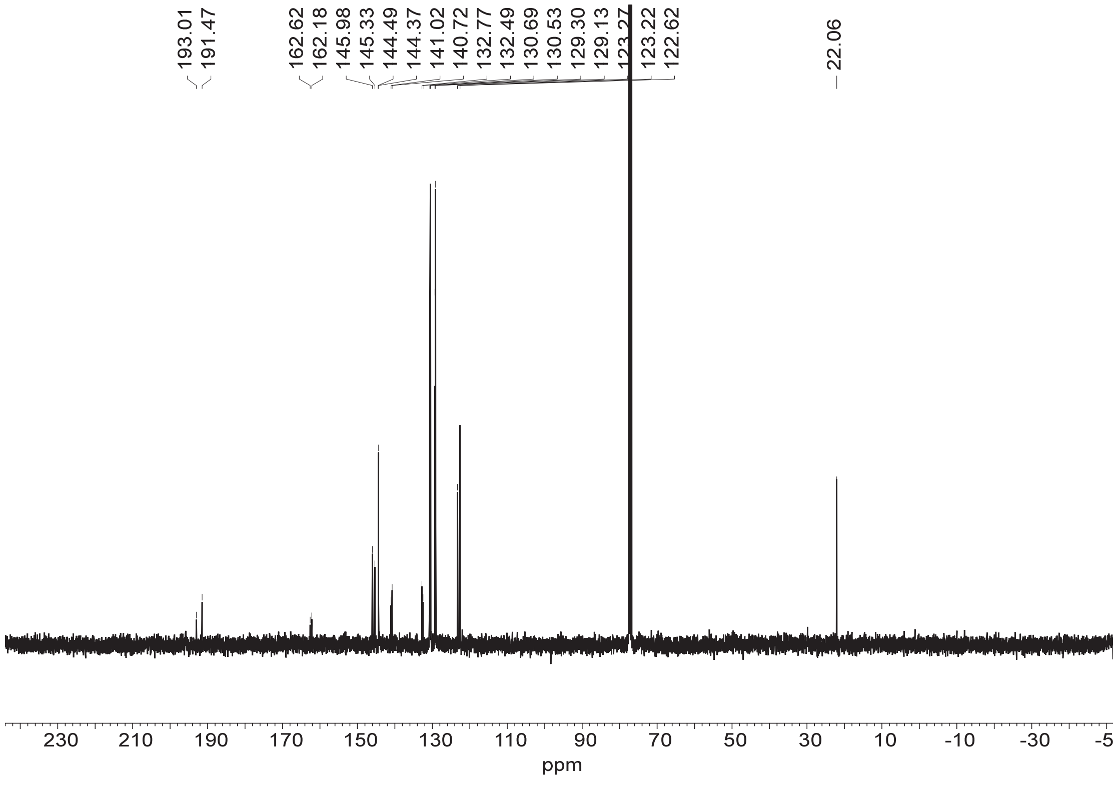
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



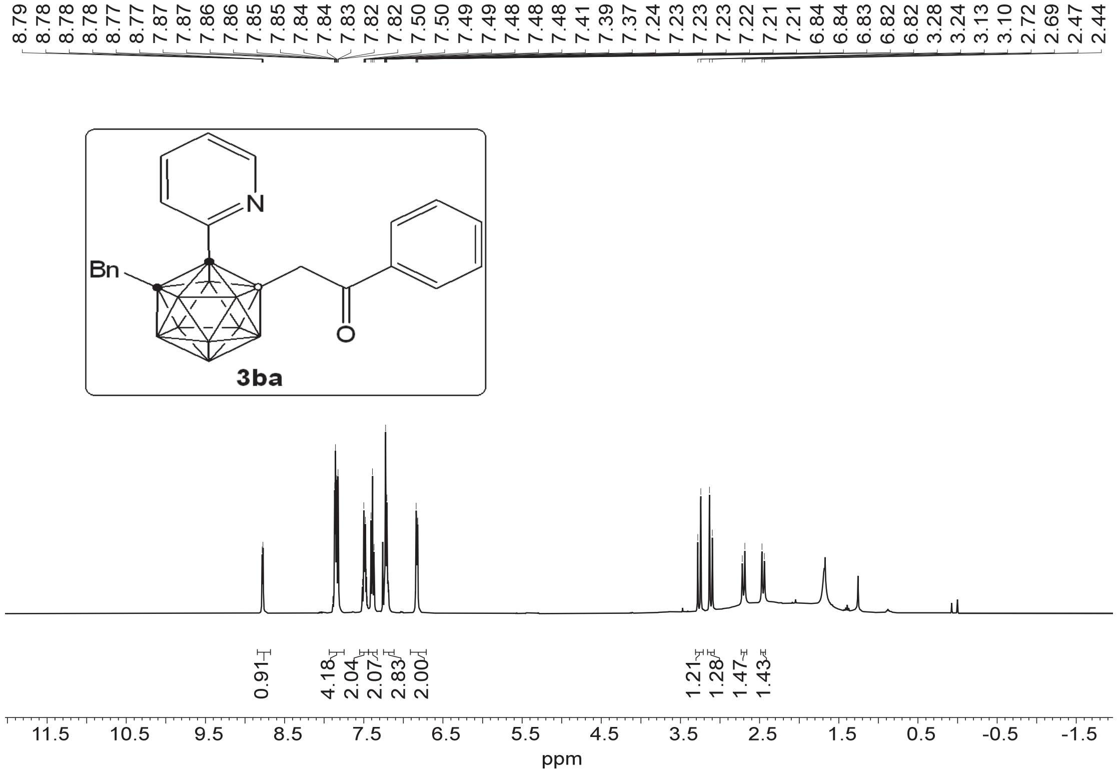
^{11}B NMR (128 MHz, CDCl$_3$)



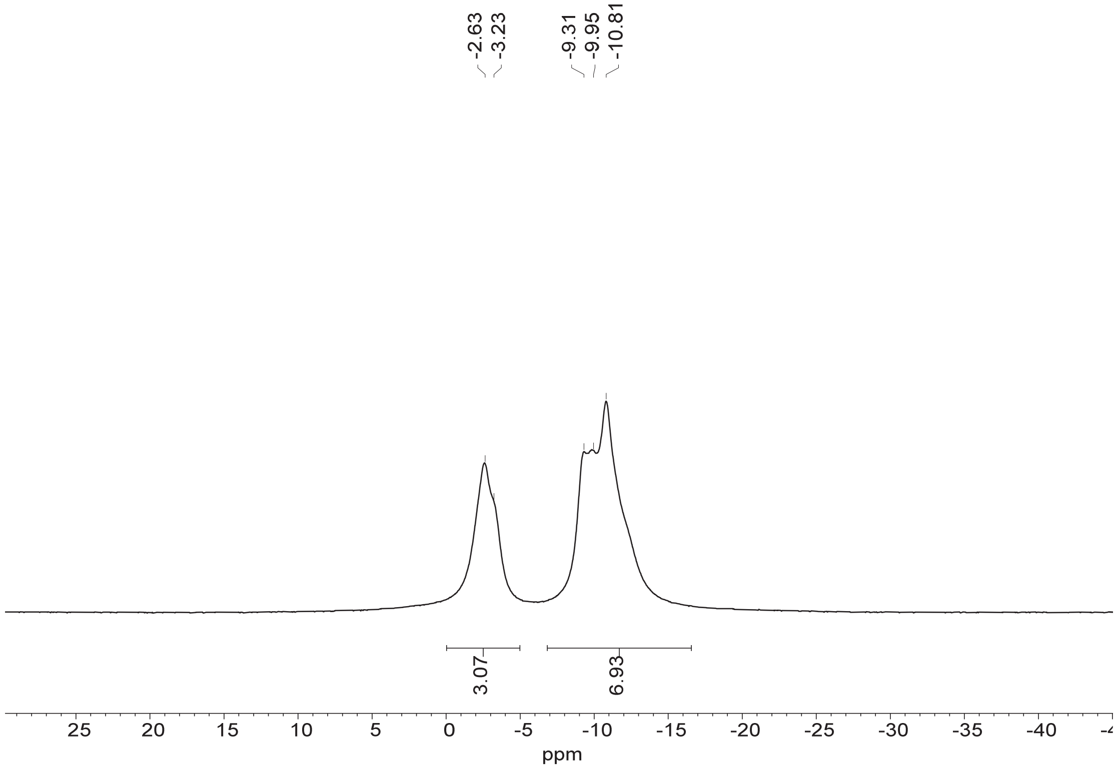
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



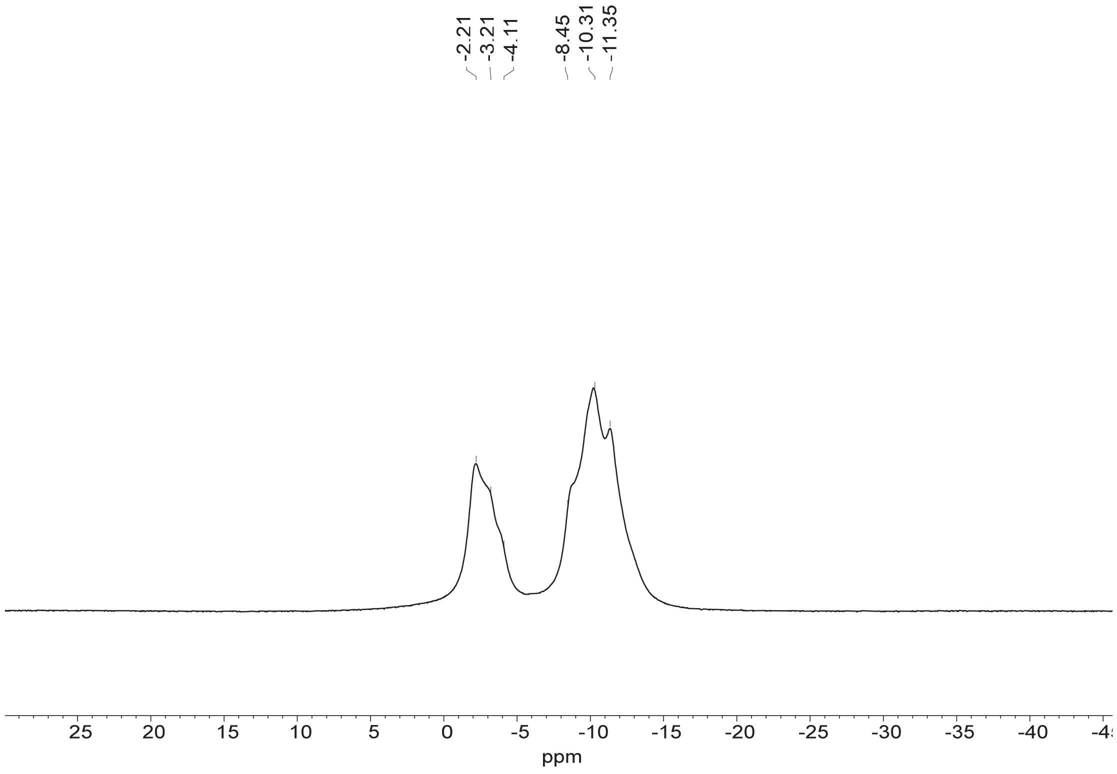
^{1}H NMR (400 MHz, CDCl$_3$)



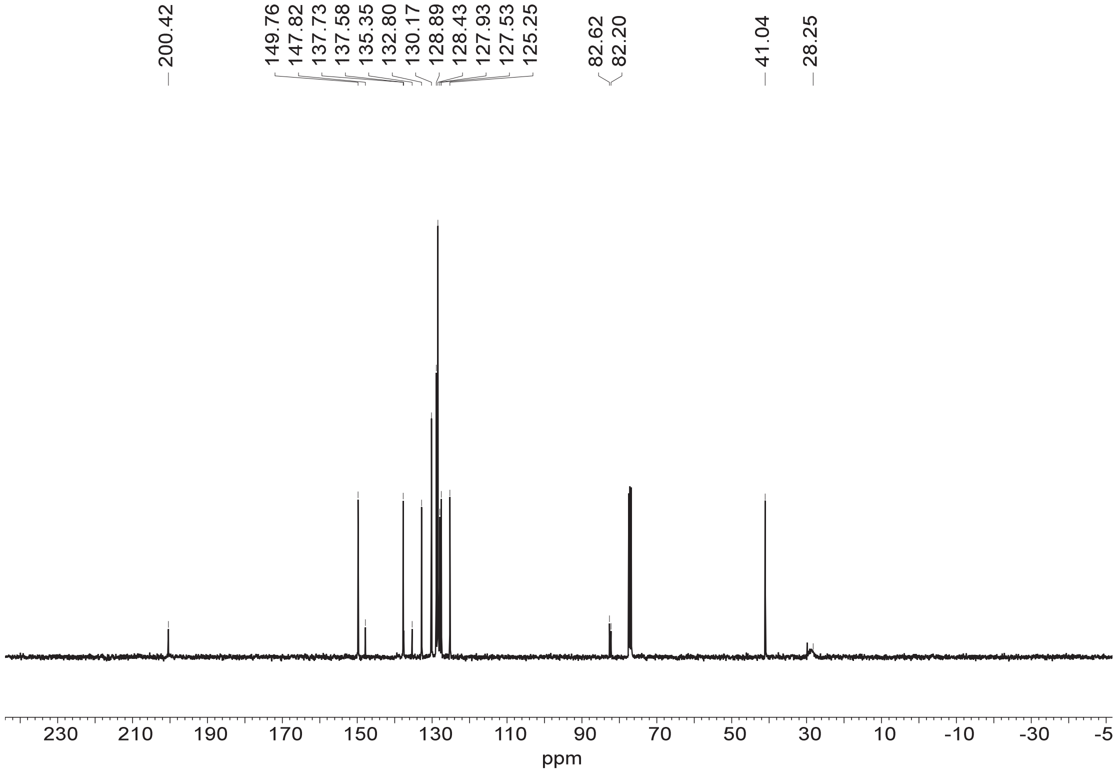
^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$)



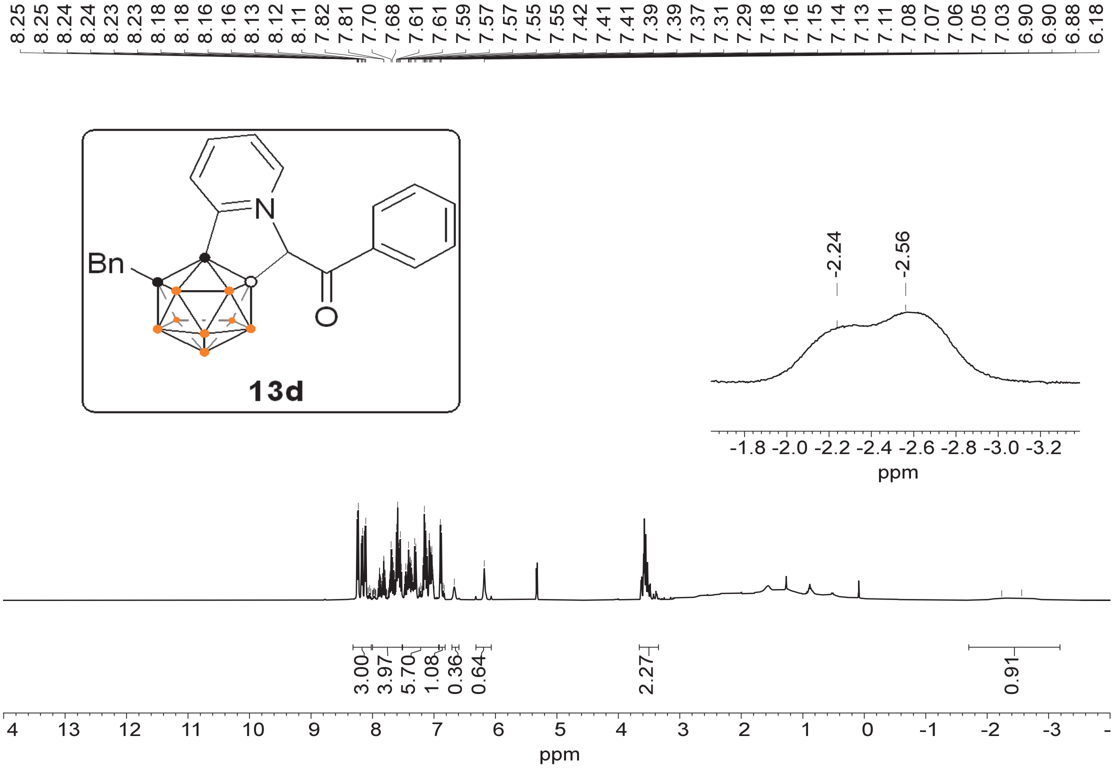
^{11}B NMR (128 MHz, CDCl$_3$)



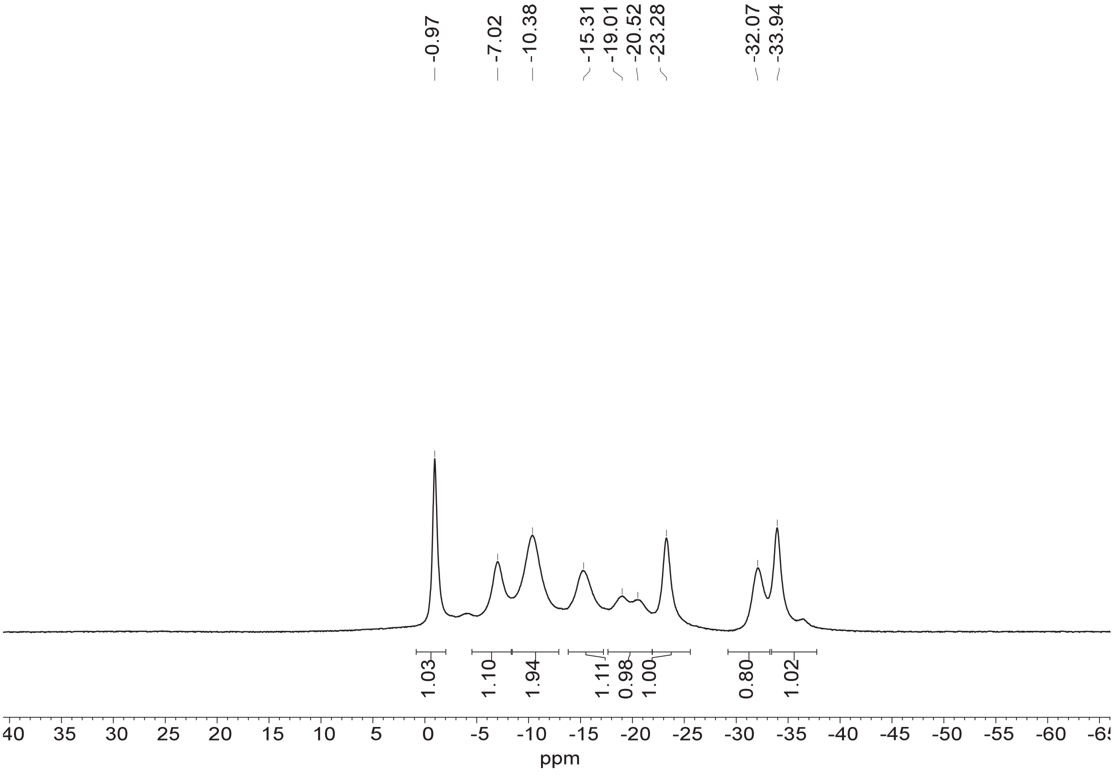
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



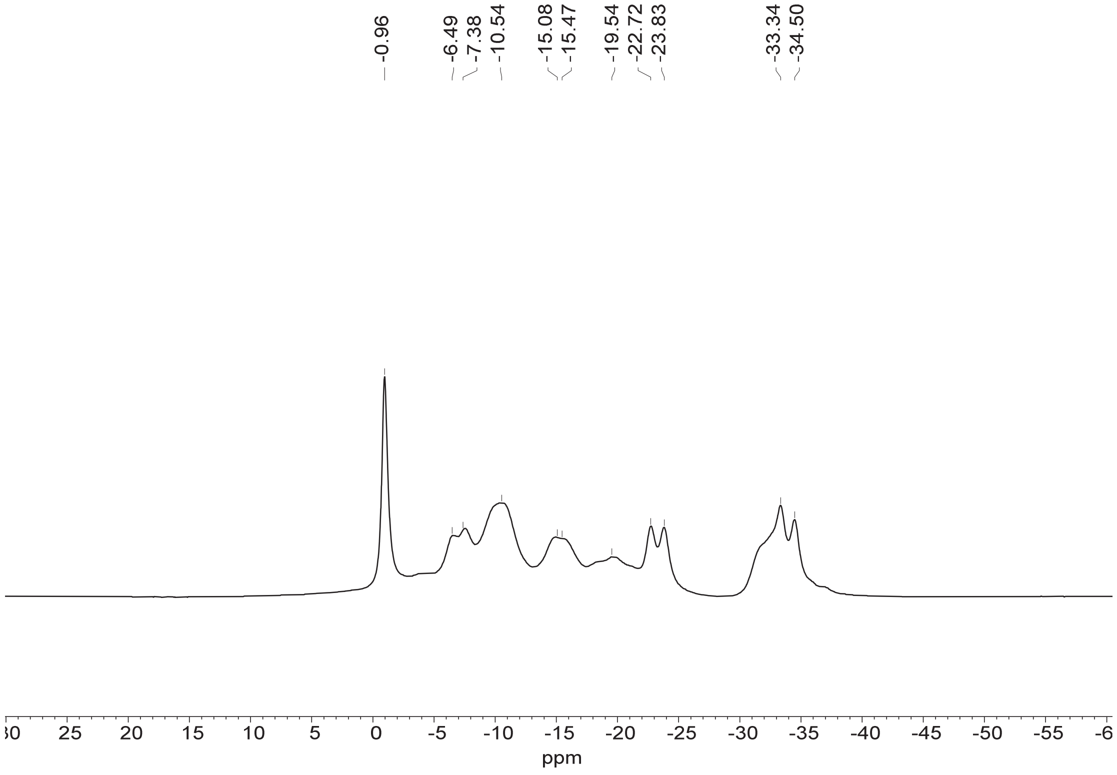
^{1}H NMR (400 MHz, CD_2Cl_2)



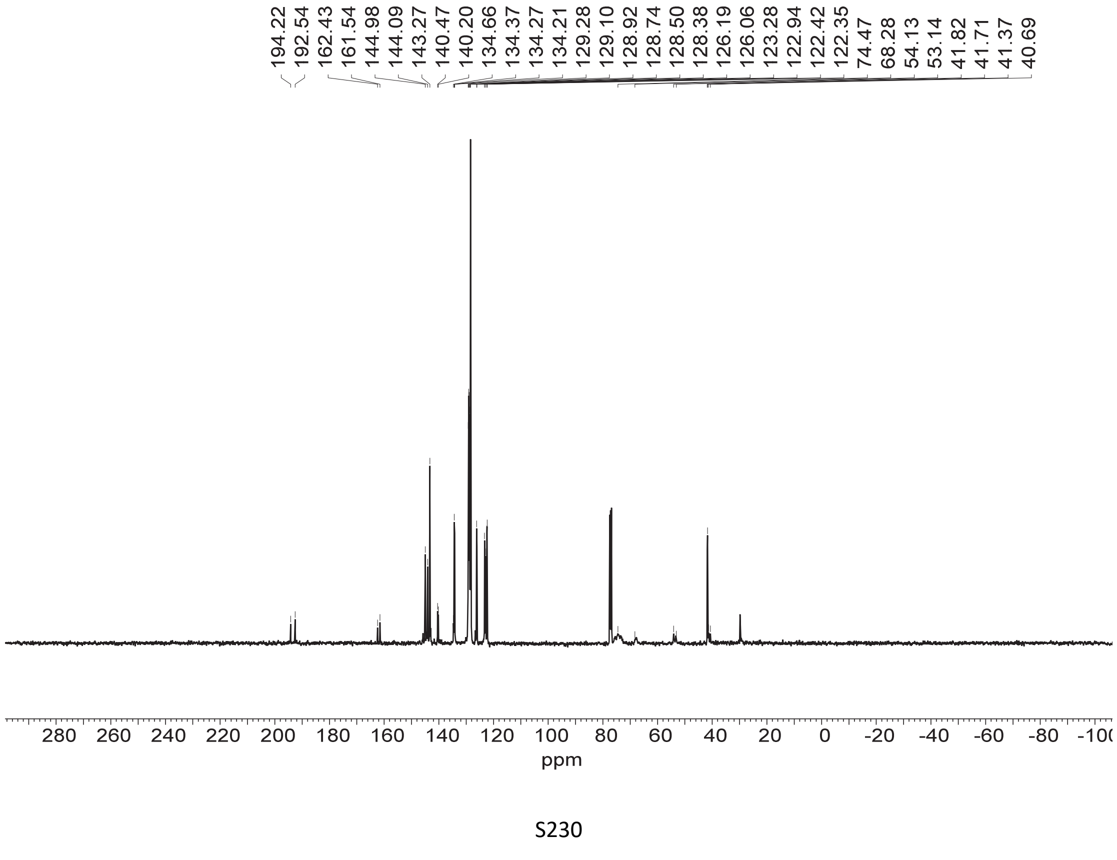
^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)



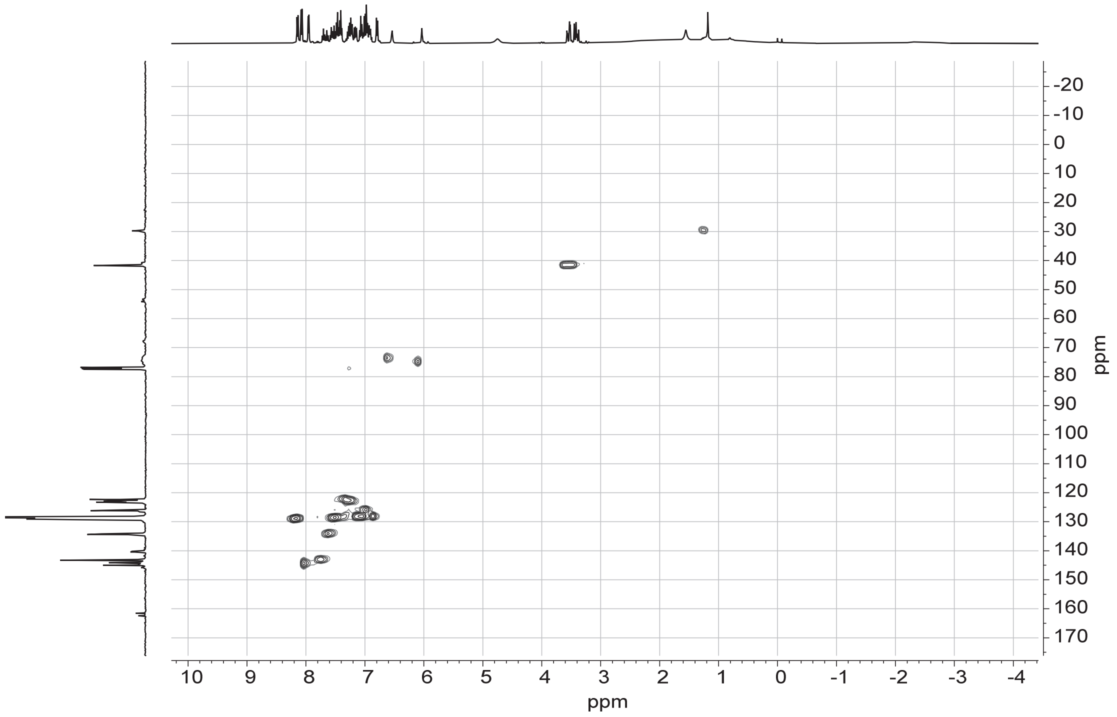
^{11}B NMR (128 MHz, $CDCl_3$)



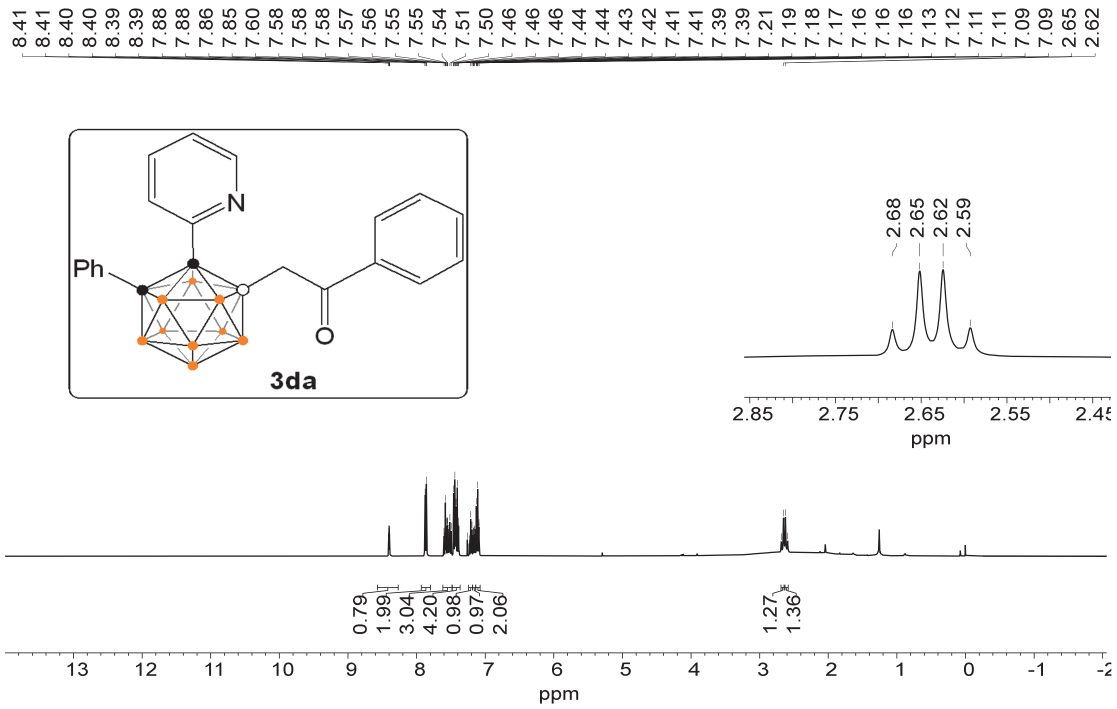
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



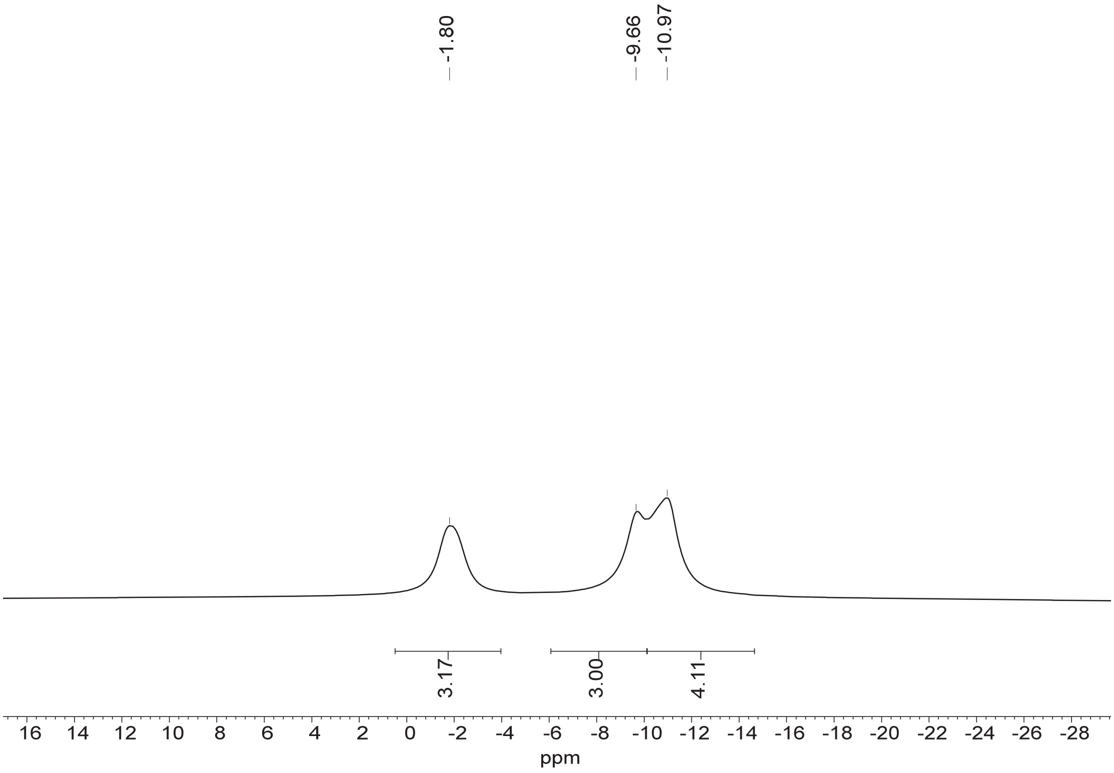
^{13}C–^{1}H HSQC (400 MHz, $CDCl_3$)



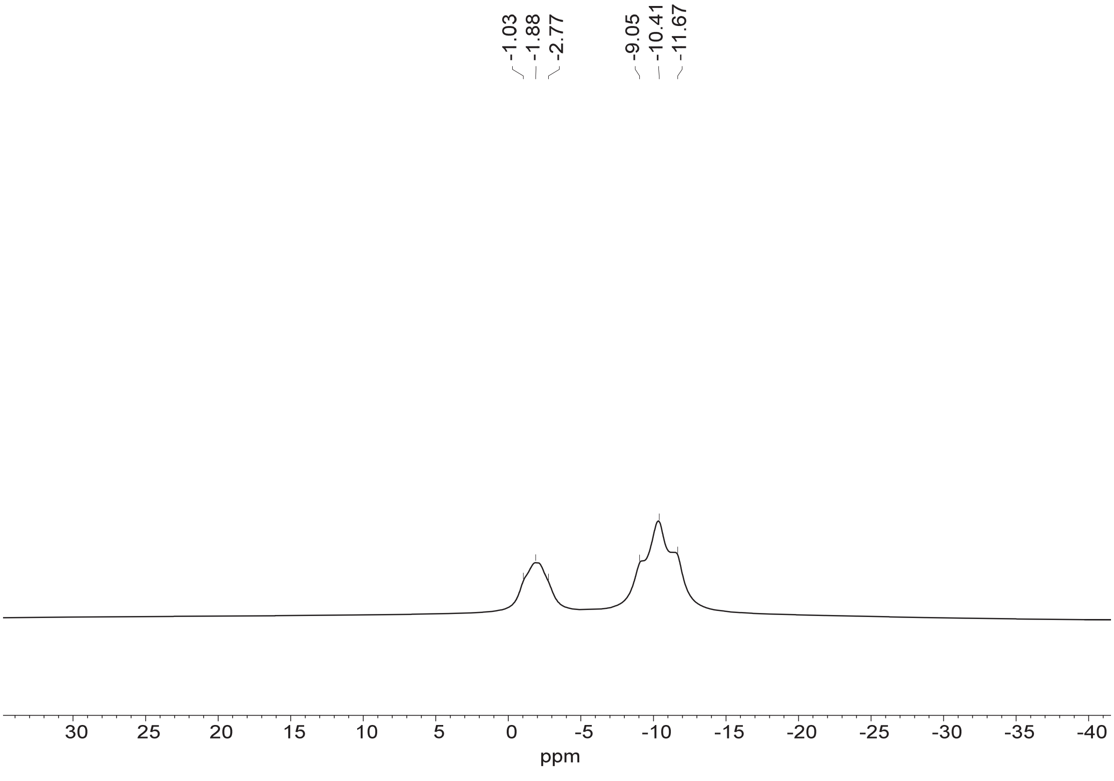
^{1}H NMR (400 MHz, $CDCl_3$)



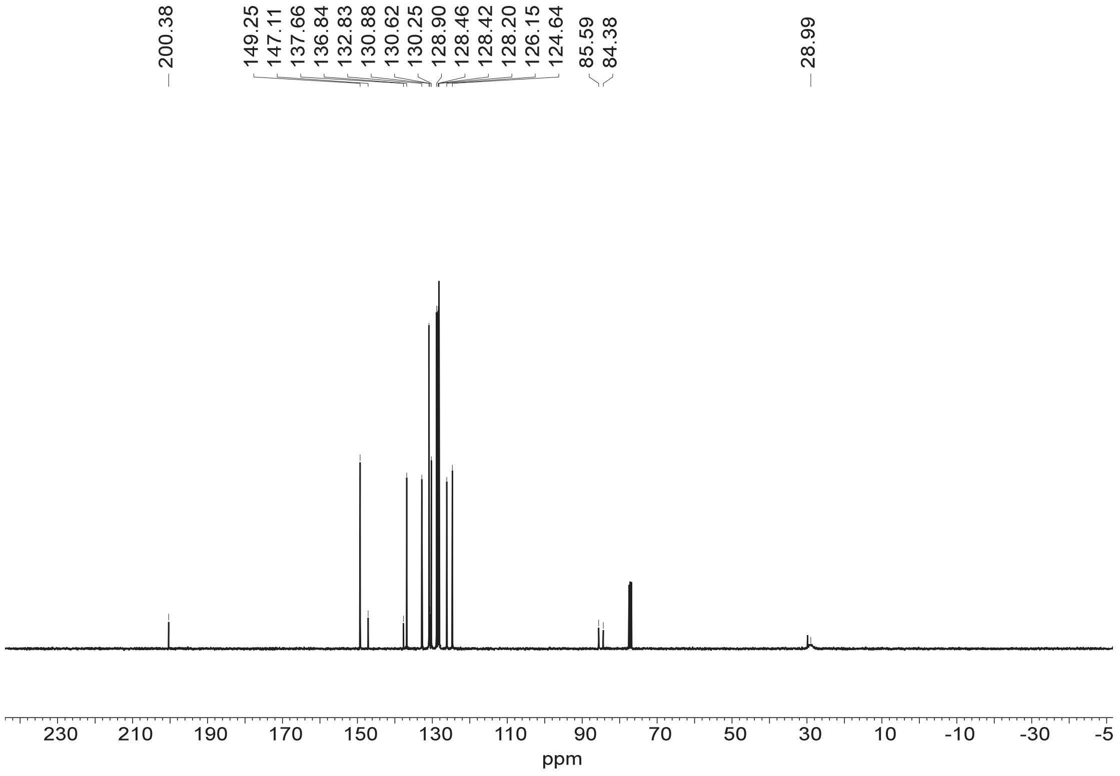
$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)



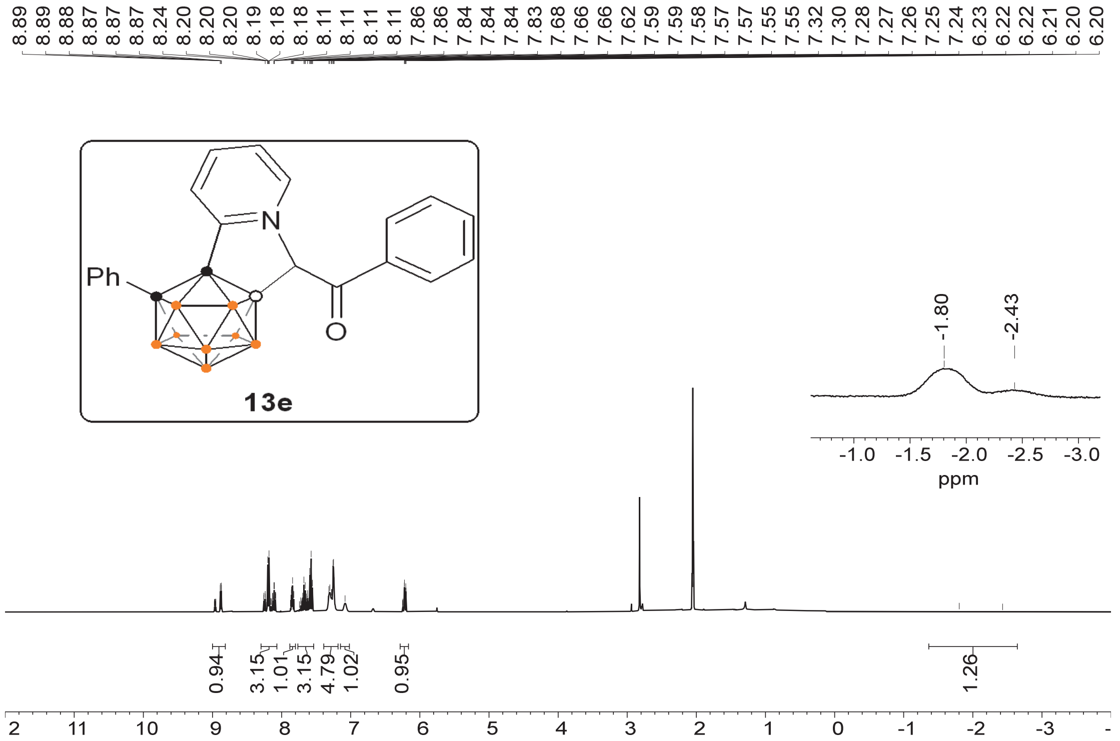
^{11}B NMR (128 MHz, $CDCl_3$)



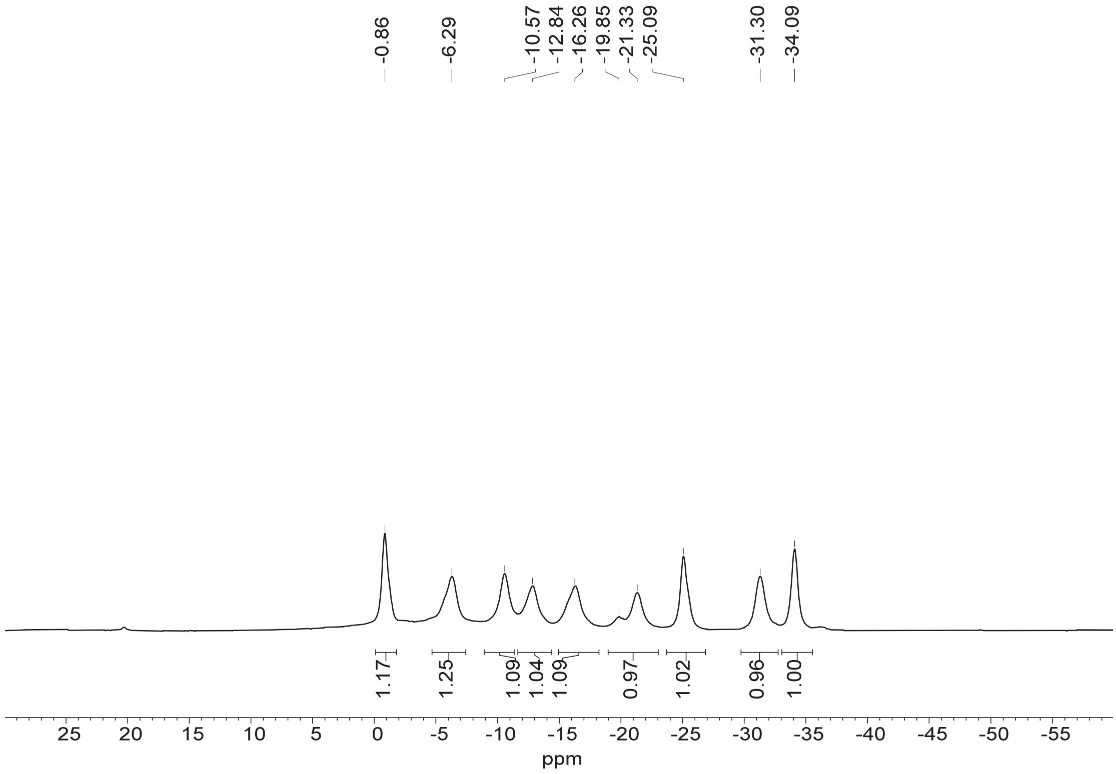
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



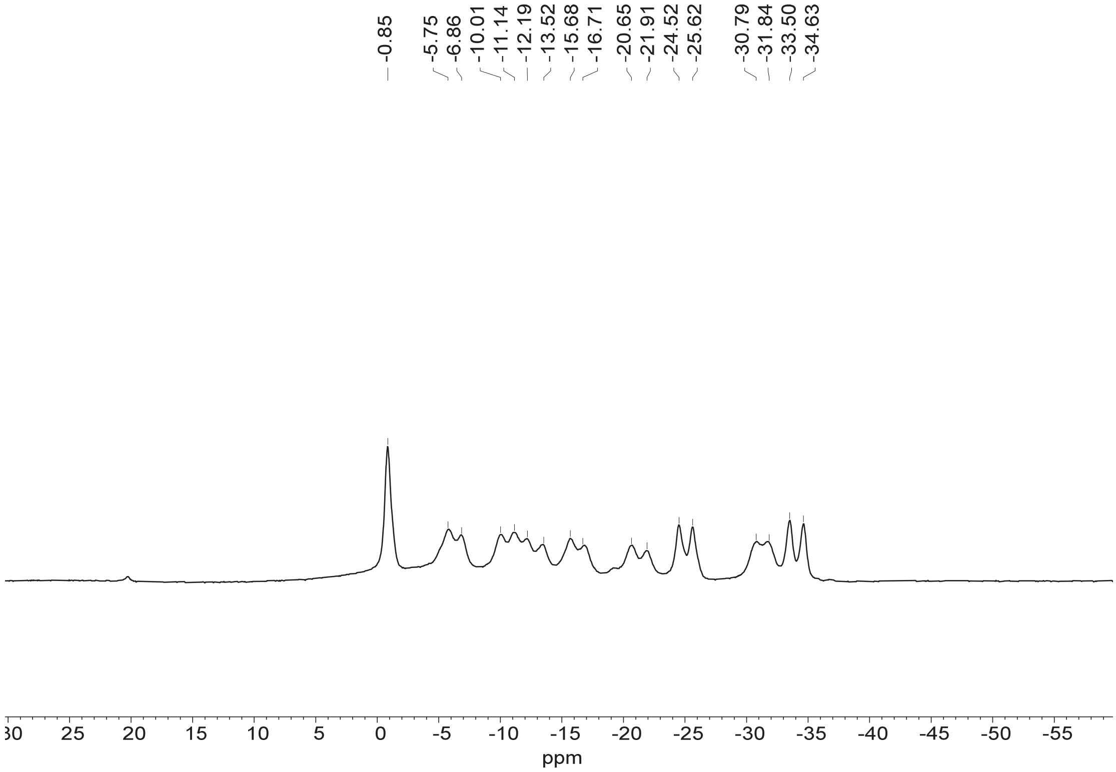
^1H NMR (400 MHz, acetone-D_6)



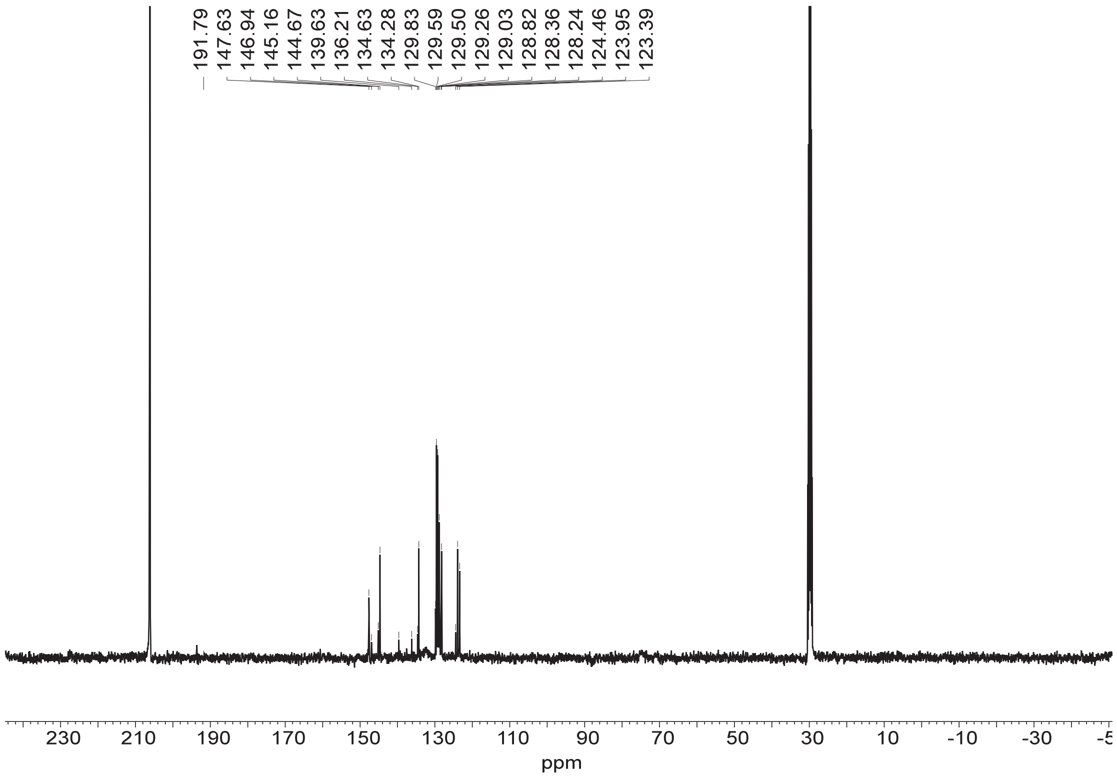
$^{11}B\{^1H\}$ NMR (128 MHz, acetone-D$_6$)



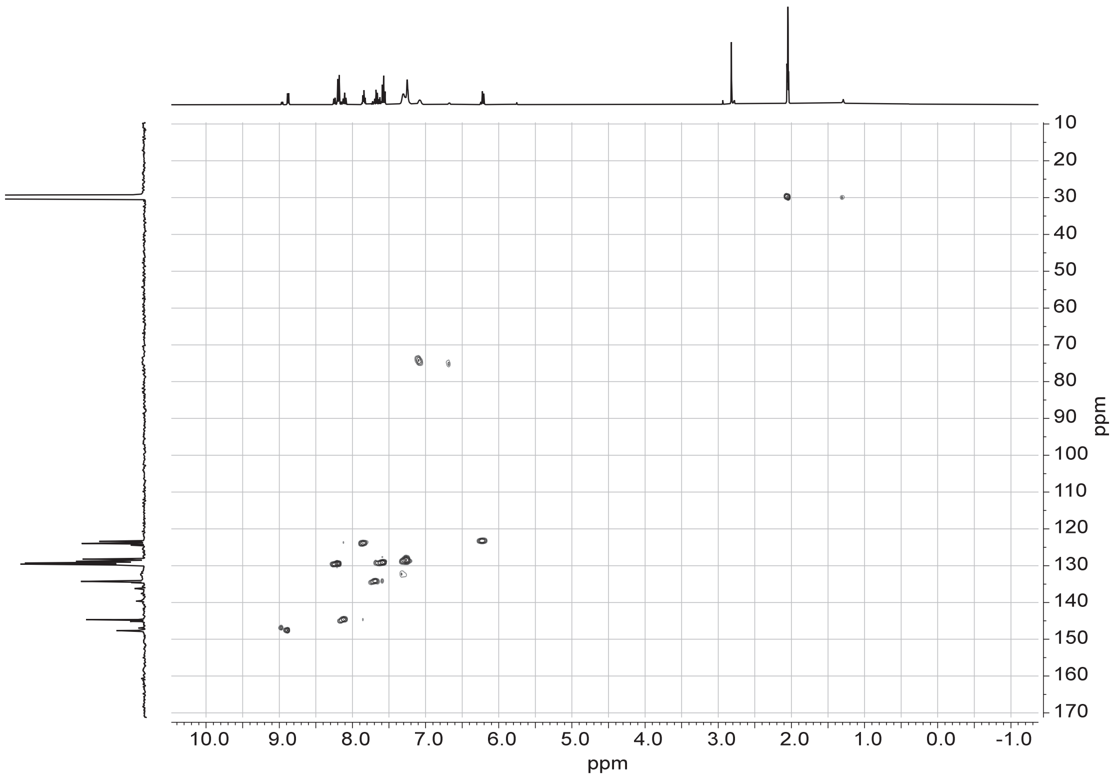
^{11}B NMR (128 MHz, acetone-D$_6$)



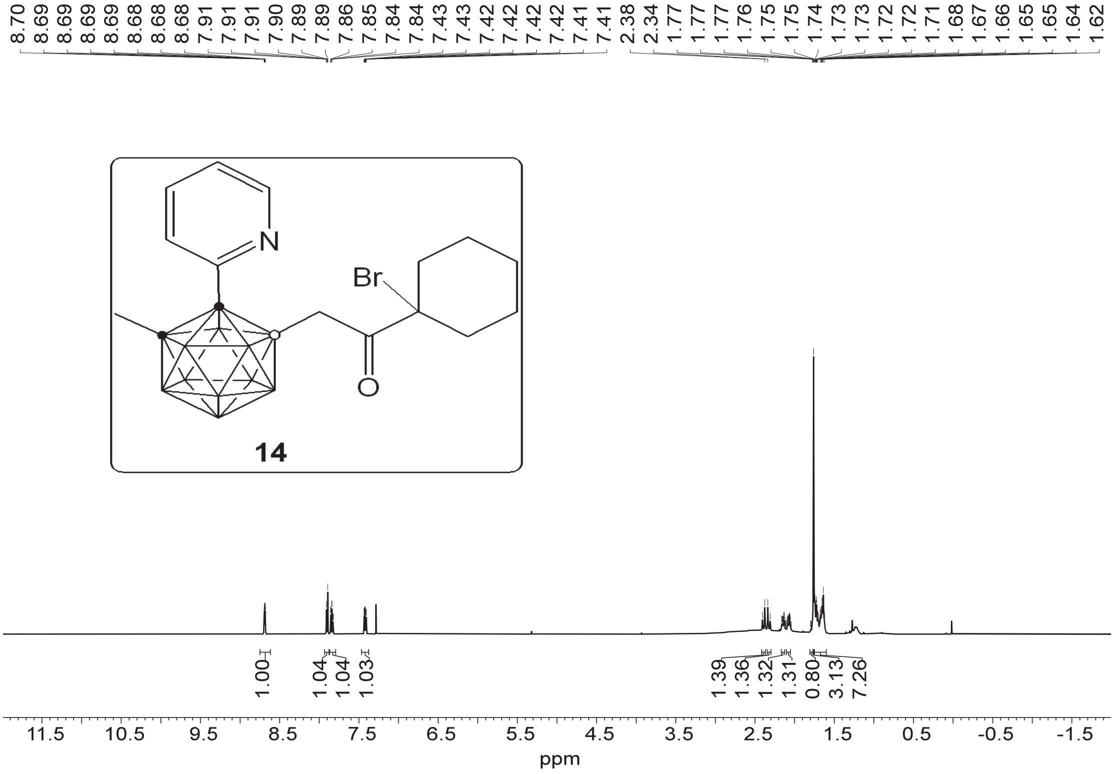
$^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-D_6)



$^{13}C-^{1}H$ HSQC (400 MHz, acetone-D_6)

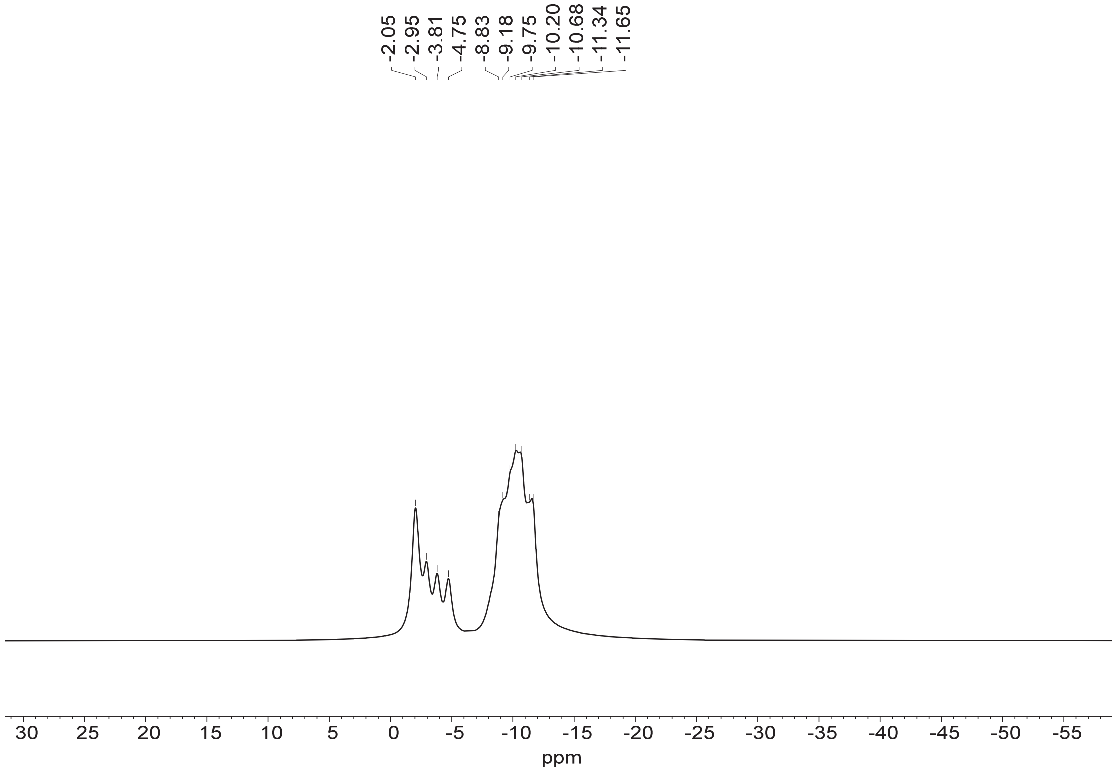


^{1}H NMR (500 MHz, CDCl$_3$)



^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$)

^{11}B NMR (160 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)