Supporting Information

Post-coordination of Ru(II) Controlled Regioselective B(4)–H Acylmethylation of *o*-Carboranes with Sulfoxonium Ylides

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1. General Information

Solvents

Unless otherwise noted, all the solvents were purchased from commercial sources and used directly. Toluene, tetrahydrofuran (THF), and Et_2O were refluxed and distilled over sodium/benzophenone under nitrogen. Dry 1,2-dichloroethane (DCE), anisole, and CH_3CN were purchased from J&K Chemicals and Energy Chemical. CH_2Cl_2 (DCM), petroleum ether (PE), ethyl acetate (EA), 2,2,2-Trifluoroethanol (TFE), and hexafluoroisopropanol (HFIP) were purchased from Energy Chemical.

Chromatography

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). The plates were visualized using a 254 nm ultraviolet lamp.

Spectroscopy and Instruments

^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 or 600 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 (δ = –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 Bruker Mass spectrometer using ESI-TOF (electrospray ionization time of flight).

Starting materials

Commercially available chemicals, including catalysts and salts, were purchased from Energy Chemica, and J&K Chemicals, and used without additional purification. *o*-carborane containing starting materials **1**[1] and sulfoxonium ylides **2**[2] were synthesized according to reported procedures. **1a-d10** (90% deuterium incorporation, DI) was prepared from 1-Ph-$C_2B_{10}D_{10}$ (90% DI) in almost quantitative yield.

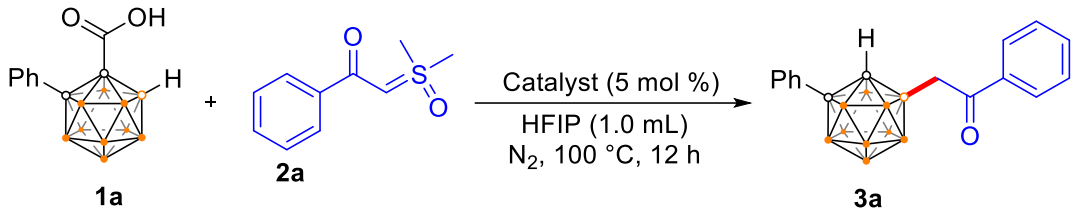
X-ray Crystallography.

X-ray diffraction data of **3b, 3l, 7** and **A_2** (CCDC No. 2426834-2426837) were collected on a Rigaku SuperNova, Dual, Cu at home/near, EosS2 diffractometer with hi-flux X-ray microfocus sources, upon irradiation of Cu Kα radiation (λ = 1.54184 Å). The data collection, processing, and analysis were performed using CrysAlis^{Pro} software (Rigaku Oxford Diffraction, 2019). An EosS2 CCD detector was used for the collection of frames and were processed with the CrysAlis^{Pro} software[3]. CrysAlis^{Pro} was used for empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm[4]. Using Olex2[5], the structure was solved with the SHELXT[6] structure solution program using Intrinsic Phasing and refined with the SHELXL[7] refinement package using Least Squares minimization. The non-hydrogen atoms were refined with anisotropic parameters, and the hydrogen atoms were added with appropriate AFIX recommendations. 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 Condition Optimization

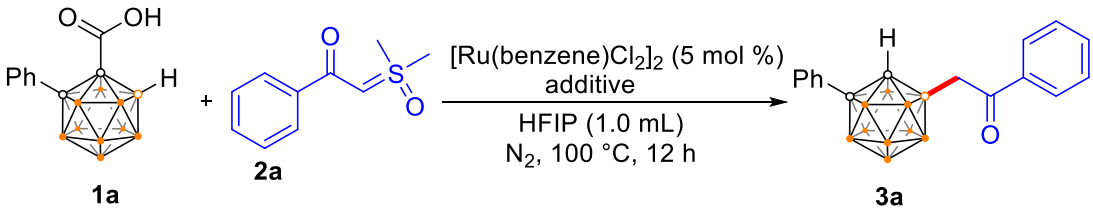
Table S1. Effect of Catalyst[a]



Entry	Catalyst	Yield [%][b] of **3a**
1	[Ru(*p*-cymene)Cl_2]$_2$	73
2	[Cp*$RhCl_2$]$_2$	0
3	[Cp*$IrCl_2$]$_2$	64
4	Cp*Co(CO)I_2	0
5	$Cu(CH_3CN)_4PF_6$	0
6	Cp*Ru(COD)Cl	0
7	**[Ru(benzene)Cl_2]$_2$**	**93**
8	[Cp*$RuCl_2$]$_2$	0
9	Ru(COD)Cl_2	0

[a]Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (0.005 mmol), HFIP (1.0 mL), 100 °C, 12 h, N_2 atmosphere.
[b]Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

Table S2. Effect of Additives[a]

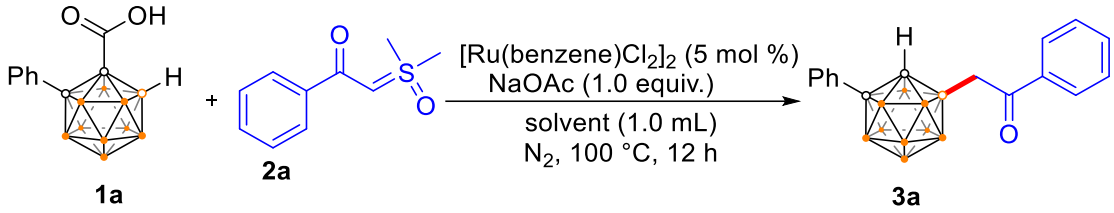


Entry	Additive (equiv.)	Yield [%][b] of **3a**
1	**NaOAc (1.0)**	**quant.**
2	PivOH (1.0)	78

3	AgOAc (0.2)	91
4	AgOAc (1.0)	35
5	NaOTf (1.0)	52
6	Na_2CO_3 (1.0)	15
7	Na_2HPO_4 (1.0)	84
8	**KOAc (1.0)**	**quant.**

[a]Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[Ru(benzene)Cl_2]_2$ (0.005 mmol), additive (0.1 mmol), HFIP (1.0 mL), 100 °C, 12 h, N_2 atmosphere. [b]Yield was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

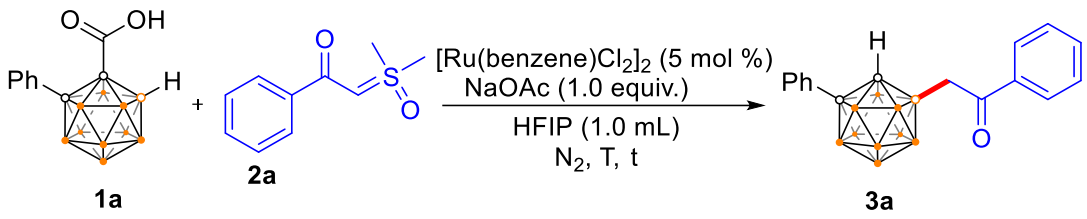
Table S3. Effect of Solvents[a]



Entry	Solvent	Yield [%][b] of **3a**
1	**HFIP**	**quant**
2	toluene	0
3	CH_3CN	0
4	THF	89
5	DCE	0
6	Anisole	0
7	TFE	75

[a]Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[Ru(benzene)Cl_2]_2$ (0.005 mmol), NaOAc (0.1 mmol), solvent (1.0 mL), 100 °C, 12 h, N_2 atmosphere. [b]Yield was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

Table S4. Effect of Temperature and Time[a]

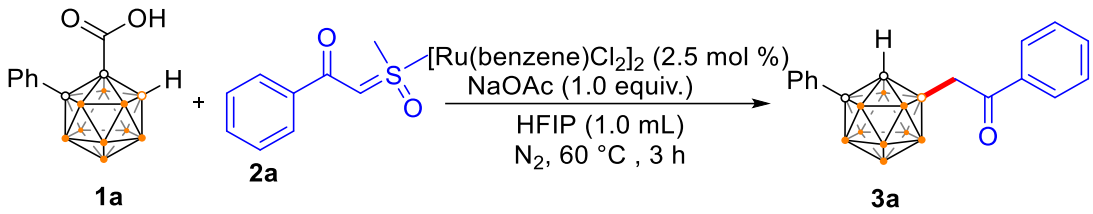


1a 2a 3a

Entry	T/ °C	t/h	Yield [%][b] of **3a**
1	60	12	quant.
2	40	12	82
3	**60**	**3**	**quant.**
4	60	1	90

[a]Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[Ru(benzene)Cl_2]_2$ (0.005 mmol), NaOAc (0.1 mmol), HFIP (1.0 mL), N_2 atmosphere. [b]Yield was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

Table S5. Effect of the Amount of 2a and $[Ru(benzene)Cl_2]_2$[a]



1a 2a 3a

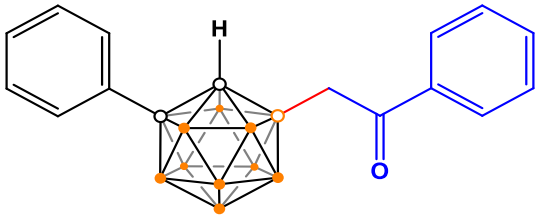
Entry	2a/equiv.	$[Ru(benzene)Cl_2]_2$/[x mol%]	Yield [%][b] of **3a**
1	1.2	5	93
2	**1.5**	**2.5**	**quant. (99%)**[c]
3	1.5	0	0
4	under air	2.5	78

[a]Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[Ru(benzene)Cl_2]_2$ (0.005 mmol), NaOAc (0.1 mmol), HFIP (1.0 mL), 100 °C, 3 h, N_2 atmosphere. [b]Yield was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. [c]Isolated yield.

2.2 General procedure for the preparation of B(4)-acylmethylated carboranes.

General procedure for the preparation of 3 or 4. *o*-Carboranyl acid **1** (0.1 mmol), sulfoxonium ylide **2** (0.15 mmol), NaOAc (0.1 mmol, 8.2 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under N_2 atmosphere. The resulting mixture was stirred at 60 °C for 3 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The filtrate was concentrated in *vacuo*. The crude reaction mixture was purified using preparative thin-layer chromatography (PTLC) with PE/DCM or PE/EA as the eluent to obtain the desired products **3** or **4**.

Compound data:



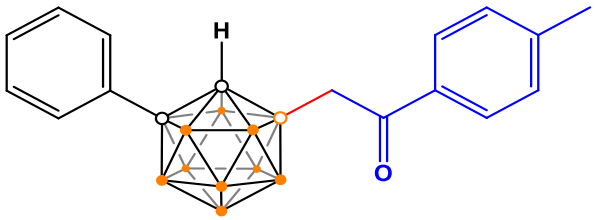
3a: Yield 99%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H) (aryl C−***H***), 4.39 (s, 1H, cage C−***H***), 2.98 (d, *J* = 13.6 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 1H) (B−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 (2B), -11.0 (3B), -13.4 (1B).

^{13}C{^{1}H} 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 (aryl−***C***), 77.3, 61.2 (cage ***C***), 28.2 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{23}$ $[M+H^+]$: 339.2754. Found: 339.2781.



3b: Yield 91%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.24 (m, 4H) (aryl C−***H***), 4.38 (s, 1H, cage C−***H***), 2.94 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$), 2.42 (s, 3H, C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.7 (1B), -5.0 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.7 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.3 (***C***=O), 144.2, 135.0, 133.4, 130.0, 129.5, 129.0, 128.9, 127.6 (aryl−***C***), 77.3, 61.3 (cage ***C***), 28.5 (B−***C***H$_2$), 21.8 (***C***H$_3$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{25}$ $[M+H]^-$: 369.2860. Found: 369.2860.

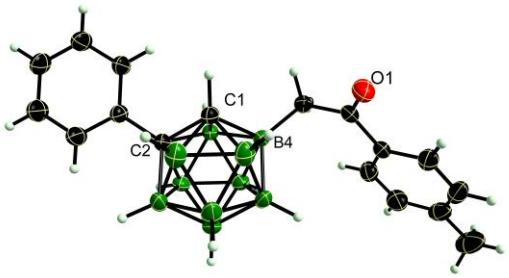
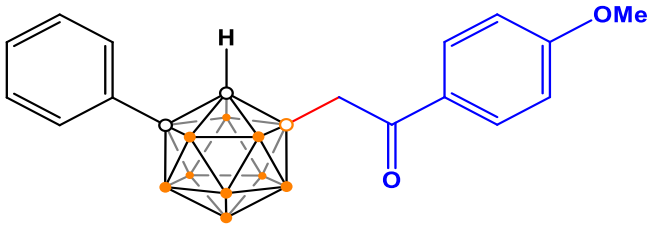


Figure S1. Molecular structure of compound **3b** (ellipsoids at 30% probability)**.**



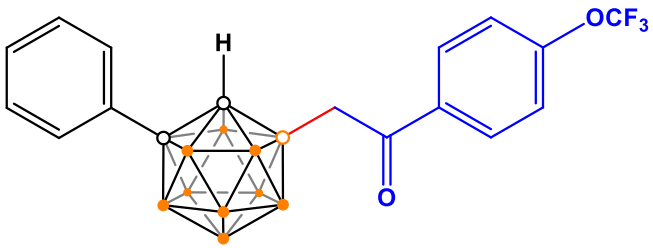
3c: Yield 95%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (m 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.34 – 7.27 (m, 2H), 7.01 – 6.87 (m, 2H) (aryl C−***H***), 4.38 (s, 1H, cage C−***H***), 3.88 (s, 3H, C***H***$_3$), 2.92 (d, *J* = 13.4 Hz, 1H), 2.86 (d, *J* = 13.4 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -4.9 (1B), -8.5 (1B), -9.3 (1B), -10.5 (1B), -11.2 (2B), -11.7 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.1 (***C***=O), 163.8, 133.4, 131.15, 130.5, 130.0, 128.9, 127.6, 113.9 (aryl−***C***), 77.3, 61.3 (cage ***C***), 55.6 (***C***H$_3$), 28.2 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{25}$ $[M+H]^-$: 369.2860. Found: 369.2860.



3d: Yield 80%. White solid.

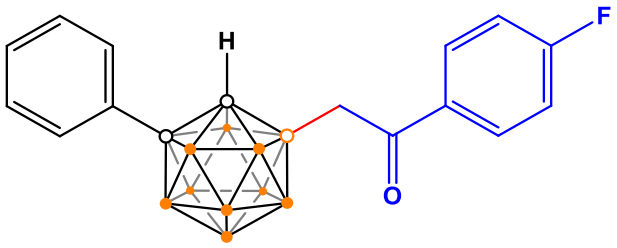
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.98 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.27 (m, 4H) (aryl C−***H***), 4.36 (s, 1H, cage C−***H***), 2.96 (d, *J* = 13.5 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.2 (1B), -10.6 (1B), -11.1 (2B), -11.8 (1B), -13.3 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 200.0 (***C***=O), 152.9, 135.6, 133.3, 130.9, 130.1, 129.0, 127.6, 120.46 (aryl−***C***), 120.44 (q, $J_{C\text{-}F}$ = 258.8 Hz, ***C***F$_3$), 77.4, 61.3 (cage ***C***), 28.0 (B−***C***H$_2$).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -57.6.

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2F_3H_{22}$ $[M+H^+]$: 423.2578. Found: 423.2579.



3e: Yield 93%. White solid.

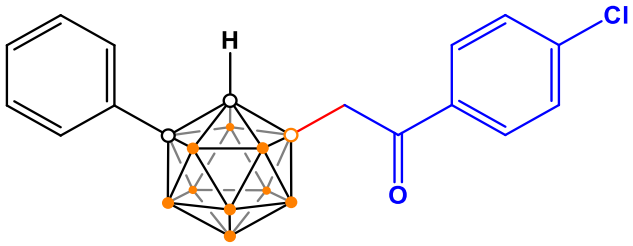
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.93 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 7.17 – 7.12 (m, 2H) (aryl C−***H***), 4.36 (s, 1H, cage C−***H***), 2.94 (d, *J* = 13.6 Hz, 1H), 2.89 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.2 (1B), 8.5 (1B), -9.3 (1B), -10.7 (1B), -11.1 (2B), -11.8 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.0 (***C***=O), 166.0 (d, $J_{C\text{-}F}$ = 254.9 Hz), 133.8 (d, *J* = 3.2 Hz), 133.3, 131.5 (d, $J_{C\text{-}F}$ = 9.4 Hz), 130.1, 129.0, 127.7, 115.9 (d, $J_{C\text{-}F}$ = 21.9 Hz) (aryl−**C**), 77.4, 61.3 (cage−***C***), 28.6 (B−**C**H$_2$).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -105.1.

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}FOH_{22}$ [M+H$^+$]: 357.2660. Found: 357.2660.



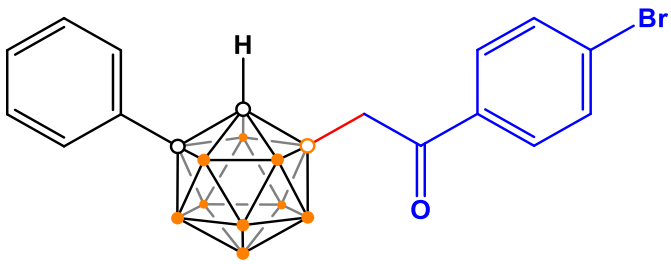
3f: Yield 99%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 4H), 7.41 – 7.36 (m, 1H), 7.36 – 7.28 (m, 2H) (aryl C−***H***), 4.35 (s, 1H, cage C−***H***), 2.94 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.8 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 200.3 (***C***=O), 139.9, 135.7, 133.3, 130.3, 130.1, 129.1, 129.0, 127.7 (aryl−**C**), 61.3 (cage−***C***), 28.7 (B−***C***H$_2$).

HRMS (ESI, positive mode): m/z calcd for $C_{16}B_{10}ClOH_{22}$ [M+H$^+$]: 374.2339. Found: 374.2348.



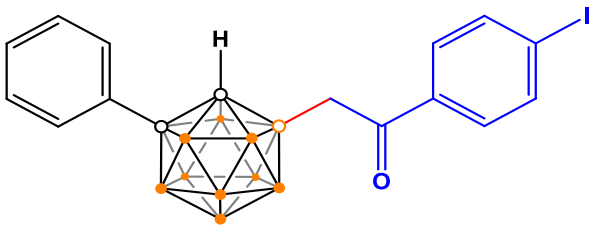
3g: Yield 99%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.78 (m, 2H), 7.65 – 7.58 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.28 (m, 2H) (aryl C−***H***), 4.35 (s, 1H, cage C−***H***), 2.94 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.0 (2B), -11.7 (1B), -13.3 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) 200.4 (***C***=O), 136.1, 133.3, 132.1, 130.1, 129.0, 128.6, 127.6 (aryl−***C***), 77.4, 61.3 (cage−***C***), 28.2 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}BrOH_{22}$ [M+H$^+$]: 418.1845. Found: 418.1845.



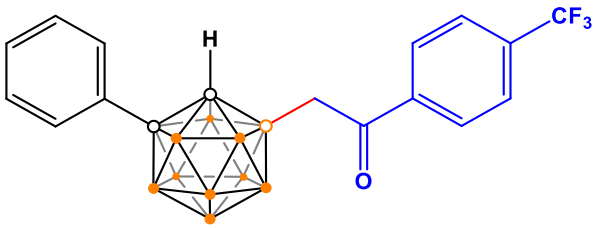
3h: Yield 99%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 2H), 7.72 – 7.65 (m, 2H), 7.50 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.35 – 7.29 (m, 2H) (aryl C−***H***), 4.34 (s, 1H, cage C−***H***), 2.92 (d, *J* = 13.5 Hz, 1H), 2.87 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{1H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.8 (1B), -13.3 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 200.8 (***C***=O), 138.1, 136.6, 133.3, 130.2, 130.1, 129.0, 127.6, 101.5 (aryl−***C***), 61.2 (cage−***C***), 28.6 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}IOH_{22}$ [M+H^+]: 465.1720. Found: 465.1720.



3i: Yield 99%. White solid.

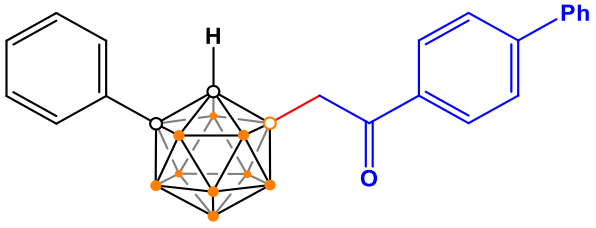
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.36 – 7.29 (m, 2H) (aryl C−***H***), 4.35 (s, 1H, cage C−***H***), 3.00 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.0 (1B), -3.8 (1B), -5.4 (1B), -8.5 (1B), -9.2 (1B), -11.0 (3B), -11.7 (1B), -13.0 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 200.5 (***C***=O), 140.0, 134.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 133.2, 130.2, 129.1, 129.0, 127.6, 125.9 (q, $J_{C\text{-}F}$ = 3.7 Hz) (aryl−***C***), 123.8 (q, $J_{C\text{-}F}$ = 273.3 Hz, ***C***F_3) 61.3 (s, 1H, cage−***C***), 29.0 (B−***C***H_2);

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.07.

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OF_3H_{22}$ [M+H^+]: 407.2628. Found: 407.2626.



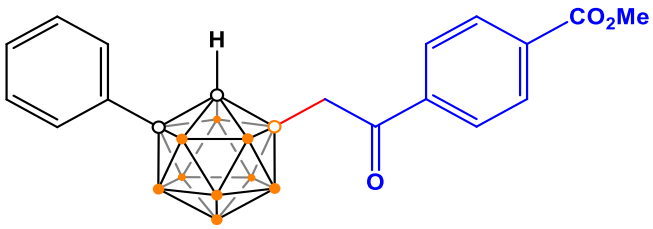
3j: Yield 99%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 – 8.03 (m, 2H), 7.73 – 7.69 (m, 2H), 7.68 – 7.62 (m, 2H), 7.51 – 7.45 (m, 4H), 7.43 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H) (aryl C−***H***), 4.42 (s, 1H, cage C−***H***), 3.02 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.7 (1B), -5.1 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.2 (2B) -11.7 (1B), -13.4 (1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.2 (***C***=O), 146.0, 139.9, 136.1, 133.4, 130.0, 129.4, 129.1, 128.9, 128.4, 127.6, 127.4 (aryl−***C***), 77.3, 61.3 (cage−***C***), 28.3 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{22}B_{10}OH_{27}$ [M+H$^+$]: 415.3070. Found: 415.3070.



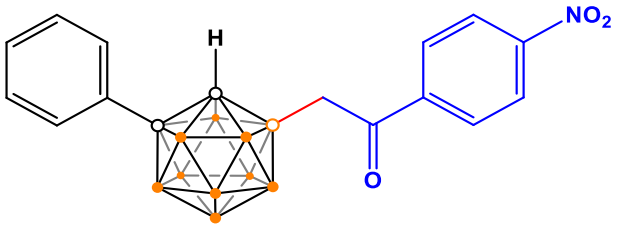
3k: Yield 99%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.10 (m, 2H), 8.07 – 7.96 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.28 (m, 2H) (aryl C−***H***), 4.35 (s, 1H, cage C−***H***), 3.95 (s, 3H, CO$_2$C***H***$_3$), 3.00 (d, *J* = 13.6 Hz, 1H), 2.94 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.2 (1B), -11.1 (3B), -11.9 (1B), -13.3 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 201.0 (***C***=O), 166.4 (***C***O$_2$Me), 140.6, 134.1, 133.3, 130.1, 130.0, 129.0, 128.7, 127.6 (aryl−***C***), 61.2 (cage−***C***), 52.6 (CO$_2$***C***H$_3$), 29.2 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}O_3H_{25}$ [M+H$^+$]: 397.2810. Found: 397.2810.



3l: Yield 99%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.39 – 8.29 (m, 2H), 8.16 – 8.09 (m, 2H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 (dd, *J* = 8.5, 7.0 Hz, 2H) (aryl C−***H***), 4.34 (s, 1H, cage C−***H***), 3.02 (d, *J* = 13.6 Hz, 1H), 2.97 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -1.9 (1B), -3.9 (1B), -5.5 (1B), -8.6 (1B), -9.1 (1B), -11.0 (3B), -11.9 (1B), -13.1 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 199.8 (***C***=O), 150.5, 141.8, 133.1, 130.2, 129.8, 129.0, 127.6, 124.0 (aryl−***C***), 77.6, 61.3 (cage−***C***), 29.3 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}NO_3H_{22}$ [M+H$^+$]: 384.2605. Found: 384.2605.

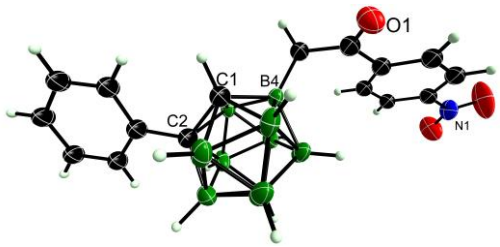
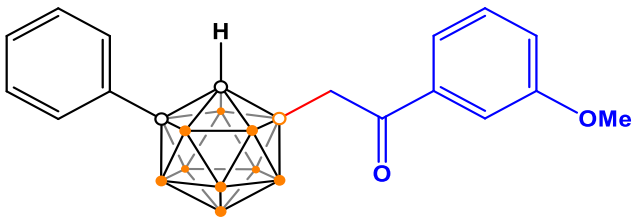


Figure S2. Molecular structure of compound **3l** (ellipsoids at 30% probability)**.**



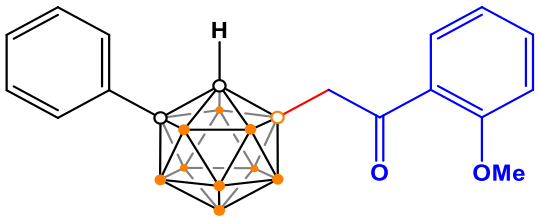
3m: Yield 87%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (m, 1H), 7.50 (m, 1H), 7.45 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.13 (m, 1H) (aryl C−***H***), 4.37 (s, 1H, cage C−***H***), 3.86 (s, 3H, C***H***$_3$), 2.96 (d, *J* = 13.5 Hz, 1H), 2.91 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -5.1 (1B), -8.4 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.8 (2B), -13.4 (1B).

$^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 201.4 (***C***=O), 160.0, 138.8, 133.4, 130.0, 129.8, 129.0, 127.6, 121.6, 120.0, 112.8 (aryl−***C***), 77.3, 61.2 (cage ***C***), 55.6 (***C***H_3), 28.9 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{25}$ $[M+H]^-$: 369.2860. Found: 369.2859.



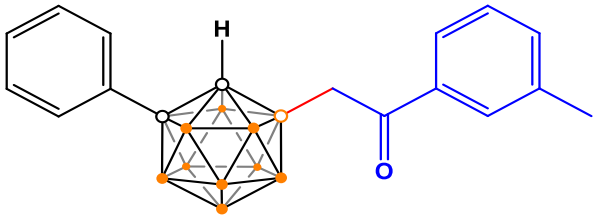
3n: Yield 68%. White solid.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.40 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.04 – 6.94 (m, 2H) (aryl C−***H***), 4.47 (s, 1H, cage C−***H***), 3.91 (s, 3H, C***H***$_3$), 3.05 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.5 (1B), -3.7 (1B), -4.9 (1B), -8.3 (1B), -9.4 (1B), -10.4 (1B), -11.3 (2B), -11.6 (1B), -13.6 (1B).

$^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 203.6 (***C***=O), 158.7, 133.8, 133.7, 130.6, 129.9, 129.1, 128.9, 127.6, 120.7, 111.8 (aryl−***C***), 77.4, 61.3 (cage ***C***), 55.6 (***C***H_3), 32.7 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{25}$ $[M+H^+]$: 369.2860. Found: 369.2861.



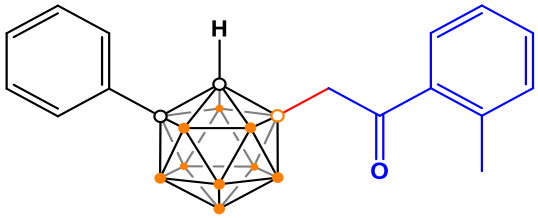
3o: Yield 89%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H) (aryl C−***H***), 4.38 (s, 1H, cage C−***H***), 2.96 (d, *J* = 13.6 Hz, 1H), 2.91 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$), 2.42 (s, 3H, C***H***$_3$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.3 (1B), -3.8 (1B), -5.1 (1B), -8.4 (1B), -9.3 (1B), -11.2 (4B), -13.5 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 201.9 (**C**=O), 138.6, 137.5, 134.2, 133.4, 130.0, 129.3, 128.9, 128.6, 127.6, 126.1 (aryl−**C**), 77.3, 61.2 (cage−**C**), 21.5 (**C**H$_3$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{25}$ [M+H$^+$]: 353.2911. Found: 353.2911.



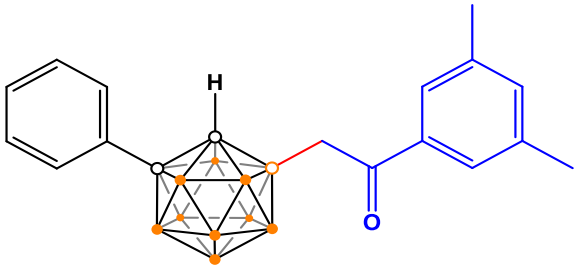
3p: Yield 70%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (m, 1H), 7.50 – 7.43 (m, 2H), 7.42 – 7.21 (m, 6H) (aryl C−***H***), 4.48 (s, 1H, cage C−***H***), 2.93 (d, *J* = 14.0 Hz, 1H), 2.87 (d, *J* = 14.0 Hz, 1H) (B−C***H***$_2$), 2.52 (s, 3H, C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -3.7 (1B), -5.0 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.7 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 205.3 (***C***=O), 138.5, 138.4, 133.5, 132.2, 131.7, 130.0, 129.7, 129.0, 127.6, 125.9 (aryl−***C***), 77.2, 61.2 (cage ***C***), 30.6 (B−***C***H_2), 21.6 (***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{25}$ [M+H^+]: 353.2911. Found: 353.2910.



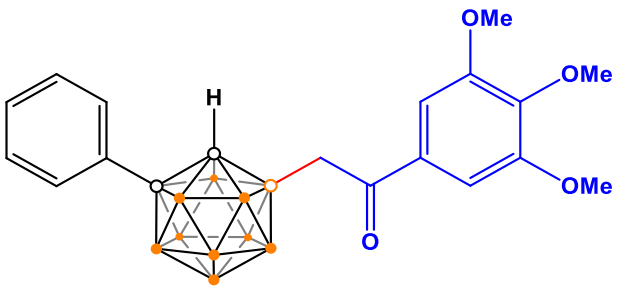
3q: Yield 87%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 7.50 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 7.22 (s, 1H) (aryl C−***H***), 4.39 (s, 1H, cage C−***H***), 2.95 (d, *J* = 13.6 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$), 2.38 (s, 6H, C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.7 (1B), -5.0 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.2 (2B), -11.7 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 202.1 (***C***=O), 138.4, 137.5, 133.4, 130.0, 128.9, 129.0, 127.6, 126.6 (aryl−***C***), 77.2, 61.2 (cage ***C***), 28.6 (B−***C***H_2), 21.4 (***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}OH_{27}$ [M+H^+]: 367.3068. Found: 367.3068.



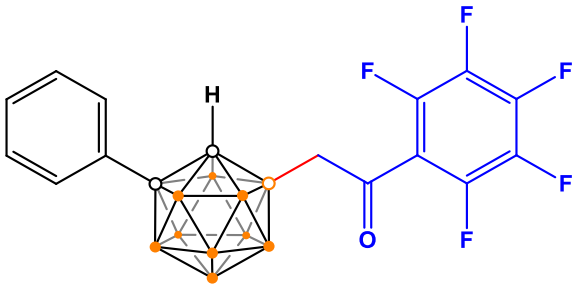
3r: Yield 98%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 7.35 – 7.29 (m, 2H), 7.24 (s, 2H) (aryl C−***H***), 4.35 (s, 1H, cage C−***H***), 3.93 (s, 3H), 3.92 (s, 6H) (C***H***$_3$), 2.93 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.1 (1B), -3.8 (1B), -5.1 (1B), -8.5 (1B), -9.2 (1B), -11.2 (4B), -13.6 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.3, 153.1, 142.7, 133.3, 132.5, 130.1, 128.9, 127.6, 106.2 (aryl−***C***), 77.4 (cage ***C***), 61.3 (cage ***C***), 61.1 (***C***H$_3$), 56.4 (***C***H$_3$), 28.8 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}NO_4H_{29}$ [M+H$^+$]: 429.3073. Found: 429.3073.



3s: Yield 98%. White solid.

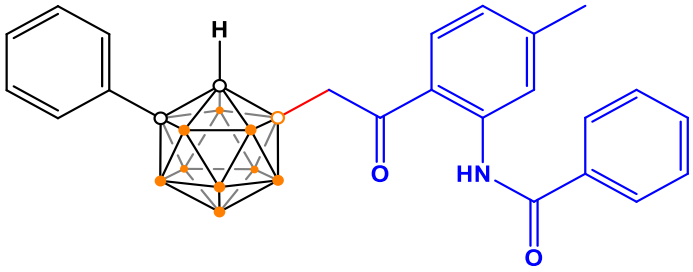
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.31 (m, 1H) (aryl C−***H***), 4.39 (s, 1H, cage C−***H***), 2.91 (s, 2H, B−C***H***$_2$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.0 (1B), -3.8 (1B), -6.1 (1B), -8.5 (1B), -9.1 (1B), -10.9 (3B), -11.9 (1B), -13.6 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 194.7 (***C***=O), 145.8 – 145.3 (m), 144.5 – 144.2 (m), 142.5 – 142.0 (m), 137.8 (dtd, *J* = 255.1 Hz, 15.9 Hz, 5.8 Hz), 137.0, 133.2, 130.2, 129.1, 127.6, 115.8 (t, *J* = 16.5 Hz), H (aryl−***C***), 77.5, 61.2 (cage *C*), 34.9 (B−***C***H$_2$).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -140.18 – -140.38 (m, 2F), -148.73 (m, 1F), -159.82 – -160.00 (m, 2F).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OF_5H_{18}$ [M+H$^+$]: 451.2102. Found: 451.2106.



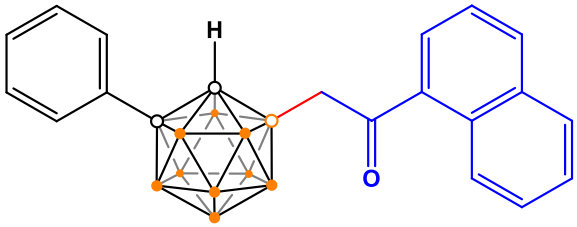
3t: Yield 41%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.77 (s, 1H), 8.84 (s, 1H), 8.06 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 1H), 7.32 – 7.23 (m, 2H), 7.06 – 6.95 (m, 1H) (aryl C−***H***), 4.21 (s, 1H, cage C−***H***), 3.01 (d, *J* = 13.2 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H) (B−C***H***$_2$), 2.46 (s, 3H, C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -1.9 (1B), -3.9 (1B), -5.1 (1B), -8.5 (1B), -9.2 (1B), -11.1 (3B), -11.1 (1B), -13.3 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 206.1 (CH$_2$***C***=O), 166.2 (***C***=O NH), 147.2, 141.8, 135.2, 133.2, 132.6, 132.0, 130.1, 129.0, 128.9, 127.7, 127.6, 123.8, 121.3, 119.9 (aryl−***C***), 77.6, 61.3 (cage ***C***), 22.4 (***C***H$_3$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{24}B_{10}NO_2H_{30}$ [M+H$^+$]: 472.3285. Found: 472.3285.



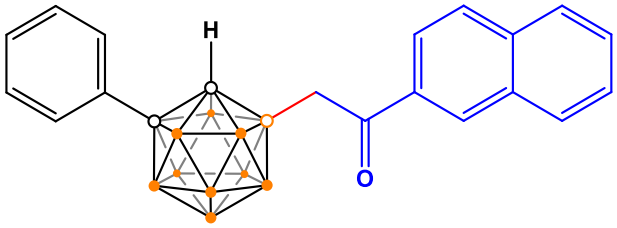
3u: Yield 65%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 8.6 Hz, 1H), 8.01 (m, 2H), 7.90 (d, *J* = 8.1, Hz, 1H), 7.60 (m, 1H), 7.57 – 7.52 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.35 (m, 1H), 7.34 – 7.28 (M, 2H) (aryl C−***H***), 4.51 (s, 1H, cage C−***H***), 3.11 (d, *J* = 13.9 Hz, 1H), 3.07 (d, *J* = 13.9 Hz, 1H) (B−C***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -3.7 (1B), -5.0 (1B), -8.3 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.6 (1B), -13.5 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 205.2 (***C***=O), 136.19, 134.2, 133.4, 133.3, 130.3, 130.0, 129.1, 128.9, 128.7, 128.2, 127.6, 126.6, 126.0, 124.6 (aryl−***C***), 77.3, 61.1 (cage ***C***), 32.5 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}OH_{25}$ [M+H^+]: 289.2912. Found: 289.2912.



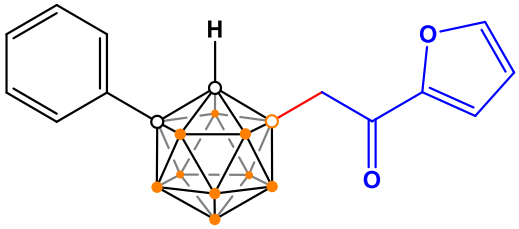
3v: Yield 99%. White solid.

^1H NMR (600 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.65 – 7.54 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H) (aryl C−***H***), 4.42 (s, 1H, cage C−***H***), 3.11 (d, *J* = 13.9 Hz, 1H), 3.06 (d, *J* = 13.9 Hz, 1H) (B−C***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.7 (1B), -5.0 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.7 (1B), -13.4 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 201.5 (***C***=O), 135.8, 134.7, 133.4, 132.7, 130.9, 130.0, 129.9, 128.9, 128.7, 128.7, 127.9, 127.6, 126.9, 124.3 (aryl−***C***), 77.3, 61.3 (cage ***C***), 28.7 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{20}B_{10}OH_{25}$ [M+H^+]: 289.2912. Found: 289.2910.



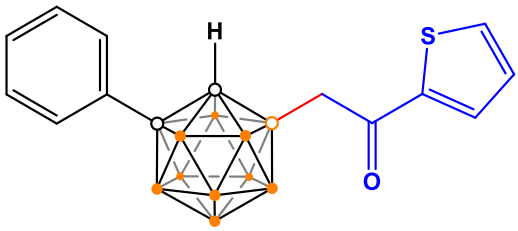
3w Yield 94%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62–7.61 (d, *J* = 1.6 Hz, 1H), 7.47 –7.46 (m, 2H), 7.40 –7.37 (m, 1H), 7.33 – 7.31 (m, 2H), 7.22 (d, *J* = 3.5 Hz, 1H) (aryl C−***H***), 6.56 – 7.22 (dd, *J* = 5.1 Hz, 1.8 Hz, 1H), 4.39 (s, 1H, cage C−***H***), 2.81 (d, *J* = 12 Hz, 1H), 2.79 (d, *J* = 12 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.1(1B), -4.8 (1B), -8.4 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.8 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 189.9 (**C**=O), 152.9, 147.0, 133.4, 130.0, 129.0, 127.6, 127.4, 118.2, 112.6 (Ph−**C**), 77.3, 61.2 (cage−**C**), 28.5 (**C**H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}O_2H_{30}$ [M+H$^+$]: 328.2568. Found: 328.2561.



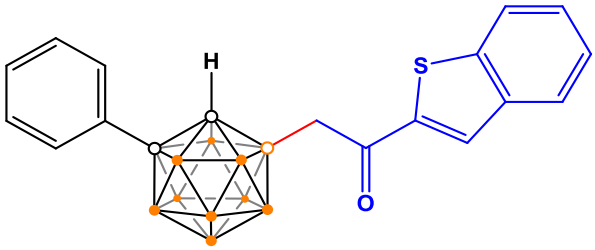
3x Yield 93%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.47 (s, 1H), 7.45 (s, 1H), 7.42 – 7.28 (m, 3H), 7.15 (t, *J* = 4.4 Hz, 1H) (aryl C−***H***), 4.42 (s, 1H, cage C−***H***), 2.89 (d, *J* = 13.5 Hz, 2H), 2.85 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.7 (1B), -5.2 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.8 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 194.1 (***C***=O), 145.1, 134.5, 133.4, 133.1, 130.0, 129.0, 128.5, 127.6 (aryl−***C***), 77.3, 61.2 (cage ***C***), 29.8 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}OSH_{21}$ [M+H$^+$]: 345.2318. Found: 345.2315.



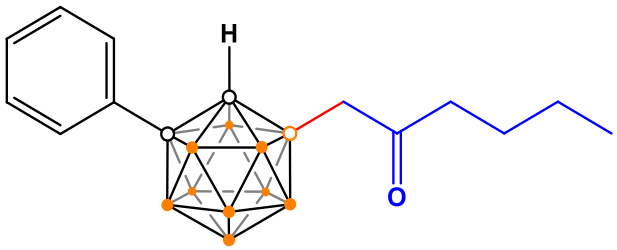
3y: Yield 46%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.28 (m, 7H) (aryl C−***H***), 4.41 (s, 1H, cage C−***H***), 3.00 (d, *J* = 13.7 Hz, 1H), 2.95 (d, *J* = 13.4 Hz, 1H) (B−C***H***$_2$);

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.7 (1B), -5.3 (1B), -8.4 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.7 (1B), -13.4 (1B);

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 195.7 (***C***=O), 144.4, 143.1, 139.4, 133.3, 130.3, 130.1, 129.0, 127.68, 127.65, 126.3, 125.2, 123.2 (aryl−***C***), 77.4, 61.2 (cage ***C***), 29.4 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{18}B_{10}OSH_{23}$ [M+H$^+$]: 395.2476. Found: 395.2476.



3z: 52%. White solid.

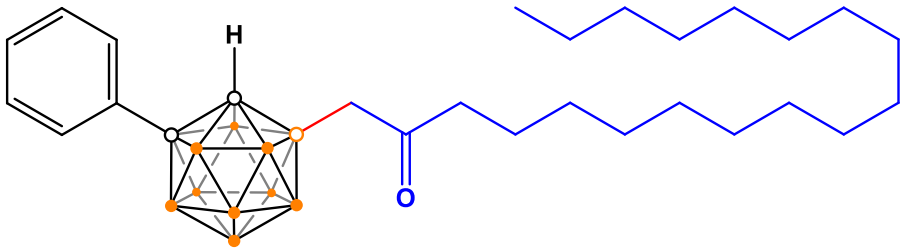
^{1}H NMR (600 MHz, Chloroform-*d*) 7.47 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H) (aryl C−***H***), 4.36 (s, 1H, cage C−***H***), 2.51 (t, *J* = 7.5 Hz, 2H, alkyl chain−C***H***$_2$), 2.41 (d, *J* = 13.3 Hz, 1H), 2.39 (d, *J* = 13.3 Hz, 1H) (B−C***H***$_2$), 1.57 – 1.52

(m, 2H), 1.36 – 1.25 (m, 2H) (alkyl chain−C***H***$_2$), 0.91 (t, *J* = 7.2 Hz, 3H, alkyl chain−C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.2 (2B), -11.9 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 212.4 (***C***=O), 133.4, 130.0, 129.0, 127.6, (aryl−***C***), 77.3, 61.2 (s, 1H, cage−***C***), 44.5 (CO***C***H$_2$CH$_2$), 32.6 (B−***C***H$_2$), 25.9, 22.5 (alkyl chain−***C***H$_2$), 14.0 (alkyl chain−***C***H$_3$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}OH_{27}$ [M+H$^+$]: 319.3060. Found: 319.3052.



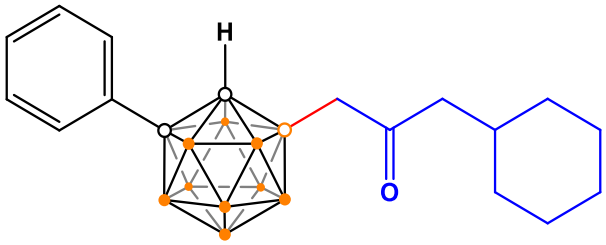
3A: 63%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H) (aryl C−***H***), 4.36 (s, 1H, cage C−***H***), 2.50 (t, *J* = 7.5 Hz, 1H) (alkyl chain−C***H***$_2$), 2.41 (d, *J* = 13.8 Hz, 1H), 2.38 (d, *J* = 13.2 Hz, 1H) (B−C***H***$_2$), 1.56 (p, *J* = 7.2 Hz, 2H), 1.30 – 1.28 (m, 27H) (alkyl chain−C***H***$_2$), 0.88 (t, *J* = 7.8 Hz, 3H) ((alkyl chain−C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.9 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 212.3 (***C***=O), 133.4, 130.0, 128.9, 127.6 (aryl−***C***), 77.3, 61.2 (s, 1H, cage−***C***), 44.8 (CO***C***H$_2$CH$_2$), 32.4 (B−***C***H$_2$), 32.1, 29.84, 29.82, 29.80, 29.76, 29.63, 29.58, 29.51, 29.4, 23.8, 22.8 (alkyl chain−***C***H$_2$), 14.3 (alkyl chain−***C***H$_3$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{27}B_{10}OH_{53}$[M+H$^+$]:502.5078. Found: 502.5084.



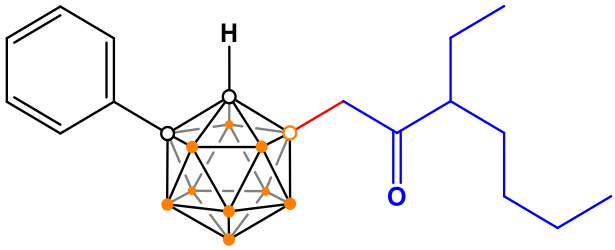
3B: 90%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H) (Ph−**H**), 4.39 (s, 1H) (cage−C**H**), 2.41-2.34 (m, 4H, B−C***H***$_2$ and COC***H***$_2$CH), 1.86 – 1.76 (m, 1H), 1.73 – 1.58 (m, 5H), 1.34 – 1.22 (m, 2H), 1.19 – 1.08 (m, 1H), 1.00 – 0.89 (m, 2H) (cyclohexyl C***H***).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -3.8 (1B), -5.4 (1B), -8.5 (1B), -9.3 (1B), -10.5 (1B), -11.2 (2B), -12.0 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 211.9 (**C**=O), 133.5, 130.0, 128.9, 127.6, (aryl−***C***),77.2, 61.2 (cage−***C***), 52.3 (CO***C***H$_2$CH), 33.8 (cyclohexyl ***C***H), 33.45 (cyclohexyl ***C***H$_2$), 32.7 (B−***C***H$_2$), 26.4, 26.3 (cyclohexyl ***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{31}[M+H^+]$:359.3381. Found: 359.3381.



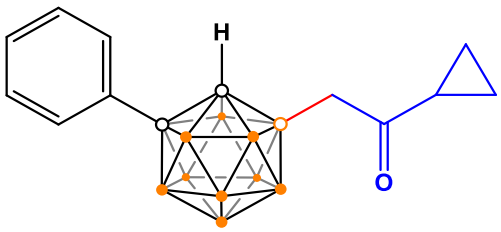
3C: 66%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) 7.50 – 7.47 (m, 2H), 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H) (aryl C−***H***), 4.67 (s, 1H, cage C−***H***), 2.44 – 2.37 (m, 3H) (B−C***H***$_2$ and COC***H***), 1.69 – 1.57 (m, 2H), 1.53 – 1.38(m, 2H), 1.35 – 1.26 (m, 2H), 1.26 – 1.19 (m, 2H) (alkyl chain−C***H***$_2$), 0.92-0.84 (m, 6H) (alkyl chain−C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.6 (1B), -3.7 (1B), -5.3 (1B), -8.4 (1B), -9.4 (1B), -10.5 (1B), -11.2 (2B), -11.8 (1B), -13.5 (1B).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 215.7 (***C***=O), 133.7, 129.9, 128.9, 128.8, 127.6, (aryl−***C***), 61.2 (cage−***C***), 55.6 (CO***C***H), 30.7 (B−***C***H_2), 30.3, 30.2, 23.97, 23.94, 23.87, 23.0, 14.1 (alkyl chain−***C***H_2), 11.95, 11.88 (alkyl chain−***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{33}$ $[M+H^+]$:361.3537. Found: 361.3537.



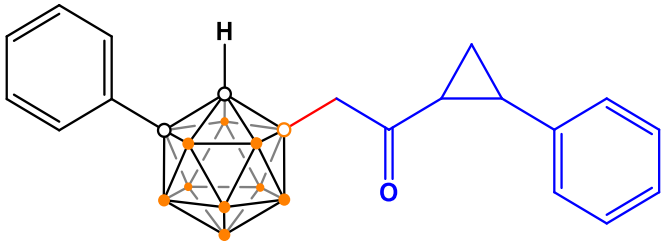
3D: 98%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) 7.47 – 7.45 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H) (aryl C−***H***), 4.30 (s, 1H, cage C−***H***), 2.52 (d, *J* = 13.8 Hz, 1H), 2.49 (d, *J* = 13.8 Hz, 1H) (B−C***H***$_2$), 2.01 – 1.95 (m, 1H, cyclopropyl−C***H***), 1.04 (m, 2H), 0.93 (m, 2H, cyclopropyl−C***H***$_2$).

$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), -11.8 (1B), -13.5 (1B).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 211.9 (***C***=O), 133.4, 130.0, 129.0, 127.6, (aryl−***C***), 77.3, 61.2 (cage−***C***), 33.4 (B−***C***H_2), 22.2 (cyclopropyl−***C***H), 11.30, 11.25 (cyclopropyl−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{13}B_{10}OH_{23}$ $[M+H^+]$:303.2753. Found: 303.2751.



3E: 95%. White solid.

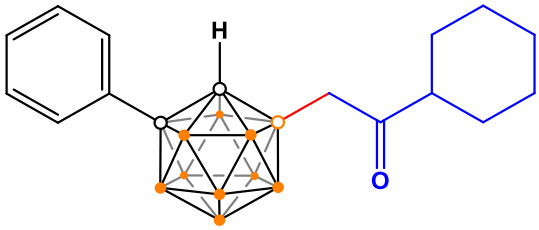
Conformer I : **Conformer II** = 58 : 42.

^{1}H NMR (600 MHz, Chloroform-*d*), **Conformer I**: δ 7.50 – 7.44 (m, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.26 (m, 4H), 7.21 (m, 1H), 7.14 – 7.08 (m, 2H) (aryl C−***H***), 4.29 (s, 1H, cage C−***H***), 2.64 – 2.51 (m, 3H B−C***H***$_2$ and cyclopropyl−C***H***), 2.28 – 2.21 (m, 1H), 1.68 (m, 1H), 1.43 (m, 1H) (cyclopropyl−C***H***); **Conformer II**: δ 7.50 – 7.44 (m, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.26 (m, 4H), 7.21 (m, 1H), 7.14 – 7.08 (m, 2H) (aryl C−***H***), 4.26 (s, 1H, cage C−***H***), 2.64 – 2.51 (m, 3H, B−C***H***$_2$ and cyclopropyl−C***H***), 2.28 – 2.21 (m, 1H), 1.68 (m, 1H), 1.43 (m, 1H) (cyclopropyl−C***H***).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -3.7 (1B), -5.3 (1B), -8.5 (1B), -9.3 (1B), -10.5 (1B), -11.1 (2B), 11.9 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*), **Conformer I**: δ 209.6, 209.5 (***C***=O), 140.30, 133.35, 130.02, 128.97, 128.67, 127.56, 126.70, 126.20, 126.12 (aryl−***C***), 77.3, 61.1 (cage−***C***), 34.7 (B−***C***H$_2$), 33.8 (CO***C***H), 29.6 (Ph***C***H), 19.36 (cyclopropyl−***C***H$_2$). **Conformer II**: 209.6, 209.5(***C***=O), 140.26, 133.37, 130.05, 128.97, 128.64, 127.62, 126.68, 126.28 (aryl−***C***), 77.3, 61.2 (cage−***C***), 34.7 (B−***C***H$_2$), 33.7 (CO***C***H), 29.5 (Ph***C***H), 19.40 (cyclopropyl−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{19}B_{10}OH_{27}[M+H^+]$:379.3069. Found: 379.3070.



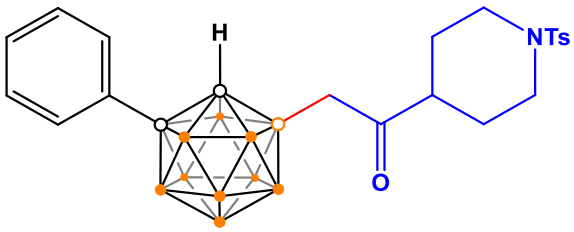
3F: 96%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) 7.48 – 7.45 (m, 2H), 7.39 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H) (aryl C−***H***), 4.46 (s, 1H, cage C−***H***), 2.45 (d, *J* = 13.8 Hz, 1H), 2.40 (d, *J* = 13.8 Hz, 1H) (B−C***H***$_2$), 1.93 – 1.84 (m, 2H), 1.83 – 1.75 (m, 1H), 1.63 (s, 1H), 1.36 – 1.14 (m, 4H).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.4 (1B), -3.8 (1B), -5.3 (1B), -8.5 (1B), -9.4 (1B), 10.5(1B) -11.1 (2B), 11.8(1B), -13.4 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 215.3 (***C***=O), 133.5, 130.0, 128.9, 127.6, (aryl−***C***), 77.2, 61.1 (s, 1H, cage−***C***), 52.3 (CO***C***H), 30.7 (B−***C***H_2), 28.5, 28.3, 26.1, 25.9, 25.8 (cyclohexyl ***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{29}[M+H^+]$:345.3324. Found:345.3320.



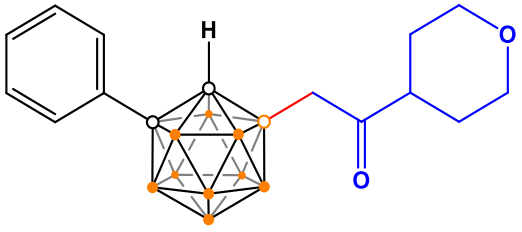
3G: 99%. White solid.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.63 (m, 2H), 7.45 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 4H) (aryl C−***H***), 4.34 (s, 1H, cage C−***H***), 3.76 (dt, *J* = 11.8, 3.9 Hz, 2H, NC***H***$_2$), 2.43 (s, 3H, Ts−C***H***$_3$), 2.42-2.28 (m, 5H) (B−C***H***$_2$ and (COC***H***C***H***$_2$)), 1.97 – 1.86 (m, 2H, NC***H***$_2$), 1.75 – 1.65 (m, 2H), 1.65 – 1.56 (m, 2H) (CHC***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -4.0 (1B), -5.6 (1B), -8.7(1B), -9.4 (1B), -11.2 (3B), 12.1 (1B), -13.3 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 212.4 (***C***=O), 143.8, 133.2, 133.2, 130.1, 129.9, 129.8, 129.0, 127.8, 127.8, 127.6 (aryl−***C***), 77.4, 61.1 (cage ***C***), 48.6 (CO***C***H), 45.8, 45.8 (N***C***H_2), 30.4 (B−***C***H_2), 27.0, 26.8 (CH***C***H_2), 21.7 (Ts−***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{22}B_{10}O_3SNH_{34}$ $[M+H^+]$: 501.3238. Found: 501.3236.



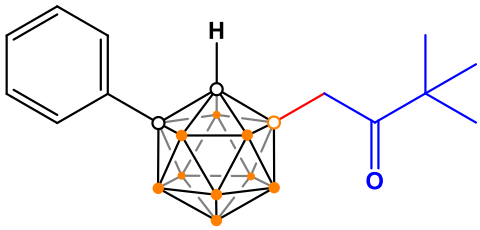
3G: 70%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.46 (m, 2H), 7.40 – 7.38 (m, 1H), 7.34 – 7.32 (m, 2H) (aryl C−***H***), 4.43 (s, 1H, cage C−***H***), 4.02 (m, 2H), 3.44 (m, 2H) (OC***H***$_2$), 2.66-2.58 (m, 1H), 2.47 (d, *J* = 13.8 Hz, 1H), 2.42 (d, *J* = 13.9 Hz, 1H) (B−C***H***$_2$), δ 1.79 (m, 2H), 1.73-1.60 (m, 2H) (CHC***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8 (1B), -5.4 (1B), -8.5 (1B), -9.3 (1B), -10.6 (1B), -11.1 (2B), -11.9 (1B), -13.4 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 213.1 (***C***=O), 133.4, 130.1, 129.0, 127.6 (aryl−***C***), 67.43, 67.40 (O***C***H$_2$), 61.1 (cage ***C***), 48.9 (CO***C***H), 30.3 (B−***C***H$_2$), 28.2, 28.0 (CH***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{15}B_{10}O_2H_{27}$ [M+Na$^+$]:369.2835. Found: 369.2834.



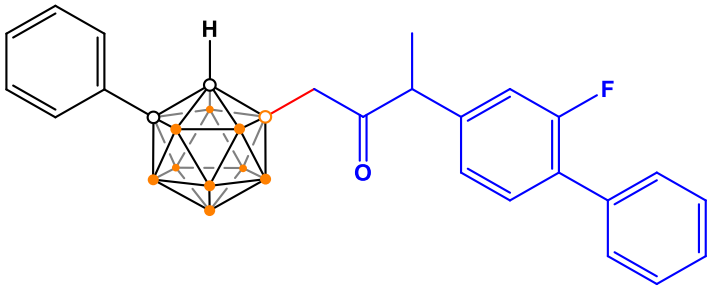
3I: 48%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.48 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H) (aryl C−***H***), 4.69 (s, 1H, cage C−***H***), 2.51 (d, *J* = 12 Hz, 1H), 2.39 (d, *J* = 12 Hz, 1H) (B−C***H***$_2$), 1.16 (s, 9H).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.6 (1B), -3.7 (1B), -5.0 (1B), -8.4 (1B), -9.5 (1B), -10.3 (1B), -11.3 (2B), -11.9 (1B), -13.6 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 217.5 (**C**=O), 133.7, 129.9, 128.9, 127.6 (aryl−***C***), 77.1, 61.1 (cage ***C***), 45.2 (**C**(CH$_3$)$_3$), 26.2 (C(**C**H$_3$)$_3$), 25.6 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{14}B_{10}OH_{27}$ [M+H$^+$]: 319.3066. Found: 319.3063.



3J: 73%. White solid.

Conformer I : **Conformer II** = 54 : 46

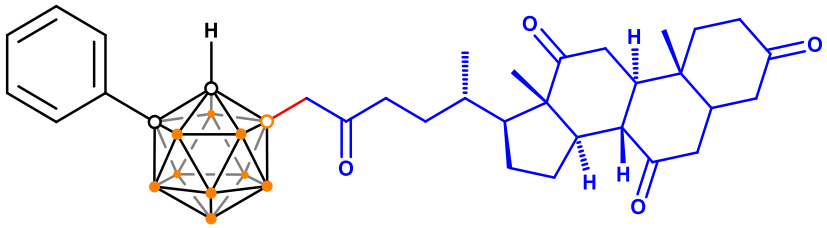
^{1}H NMR (600 MHz, Chloroform-*d*), **Conformer I**: δ 7.57 – 7.29 (m, 11H), 7.09 (d, *J* = 7.9 Hz, 1H) (aryl C−***H***), 4.32 (s, 1H, cage C−***H***), 3.89 (q, *J* = 7.0 Hz, 1H, COC***H***CH_3), 2.53 (d, *J* = 13.8 Hz, 1H) , 2.50 (d, *J* = 13.8 Hz, 1H) (B−C***H***$_2$), 1.43 (d, *J* = 6.8 Hz, 3H, COCHC***H***$_3$); **Conformer II**: δ 7.57 – 7.29 (m, 11H), 7.04 (d, *J* = 7.9 Hz, 1H) (aryl C−***H***), 4.30 (s, 1H, cage C−***H***), 3.92 (q, *J* = 7.0 Hz, 1H, COC***H***CH_3), 2.32 (d, *J* = 14.6 Hz, 1H), 2.29 (d, *J* = 14.6 Hz, 1H) (B−C***H***$_2$), 1.45 (d, *J* = 6.8 Hz, 3H, COCHC***H***$_3$);

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -3.8, -5.4 (1B), -8.5 (1B), -9.3 (1B), -11.1 (3B), -12.2 (1B), 13.3 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*), **Conformer I**: δ 210.8 (***C***=O), 160.03 (d, $J_{C\text{-}F}$ = 249.0 Hz), 141.7 (d, *J* = 7.5 Hz), 135.5, 133.34, 131.27 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.1, 129.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.6, 128.1, 127.9, 127.61, 124.34 (d, $J_{C\text{-}F}$ = 3.7 Hz), 115.86 (d$_{C\text{-}F}$, *J* = 23.2 Hz) (aryl−***C***), 77.3, 61.1 (cage−***C***), 53.7 (CO***C***HCH$_3$), 31.5 (B−***C***H$_2$), 17.26 (COCH***C***H$_3$); **Conformer II**: δ 210.6 (***C***=O), 160.00 (d, $J_{C\text{-}F}$ = 249.0 Hz), 141.6 (d, $J_{C\text{-}F}$ = 7.3 Hz), 135.5, 133.37, 131.31 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.1, 129.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.6, 128.2, 127.9, 127.62, 124.32 (d, $J_{C\text{-}F}$ = 3.7 Hz), 115.87 (d, $J_{C\text{-}F}$ = 23.2 Hz) (aryl−***C***), 77.3, 61.3 (cage−***C***), 53.6 (CO***C***HCH$_3$), 31.5 (B−***C***H$_2$), 17.31 (COCH***C***H$_3$).

^{19}F NMR (565 MHz, Chloroform-*d*), **Conformer I**: δ -117.08; **Conformer II**: δ -117.12;

HRMS (ESI, positive mode): *m/z* calcd for $C_{24}B_{10}FOH_{30}$ [M+H$^+$]: 461.3289. Found: 461.3291.



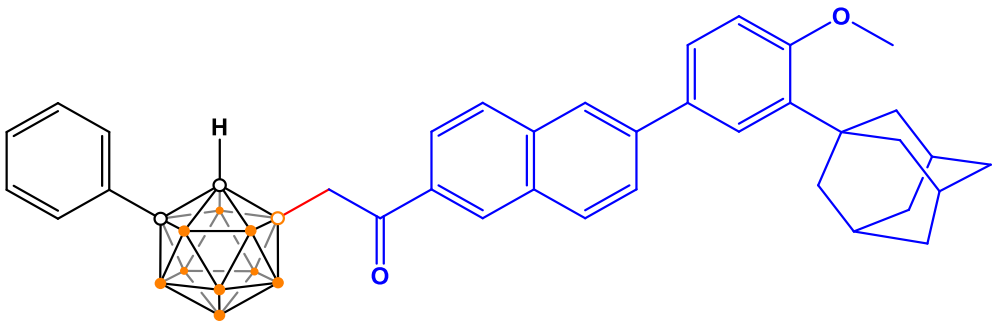
3K: 51%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) 7.46 – 7.45 (m, 2H), 7.39 – 7.36(m, 1H), 7.33 – 7.30 (m, 2H) (aryl C−***H***), 4.34 (cage C−***H***), 2.92 (dd, *J* = 13.1, 6.1 Hz, 1H), 2.84 (t, *J* = 11.6 Hz, 1H), 2.76 (t, *J* = 12.6 Hz, 1H), 2.66 – 2.51 (m, 3H), 2.48 – 2.34 (m, 2H), 2.32 – 2.23 (m, 3H), 2.19 (td, *J* = 12.6, 5.0 Hz, 2H), 2.11 – 1.55 (m, 12H), 1.39 – 1.18 (m, 5H), 1.03 (d, *J* = 4.5 Hz, 4H) (alkyl C−***H***), 0.83 (d, *J* = 6.5 Hz, 3H, C***H***$_3$)).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -3.9 (1B), -5.4 (1B), -8.6 (1B), -9.4 (1B), -11.3 (3B), -12.0(1B), -13.7 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 212.85, 212.83, 212.5, 209.9 (***C***=O), 133.36, 133.34, 130.0, 128.9, 127.6 (aryl−***C***), 77.3, 61.2 (cage−***C***), 58.0, 57.0, 53.5, 52.0, 49.2, 45.7, 45.7, 45.7, 45.4, 45.2, 44.2, 41.8, 41.7, 38.8, 36.0, 35.6, 35.5, 34.8, 33.1, 32.5, 29.1, 27.8, 27.6, 25.3, 22.7, 19.0, 11.9 (alkyl ***C***).

HRMS (ESI, positive mode): *m/z* calcd for $C_{33}B_{10}O_4H_{51}$ [M+H$^+$]: 620.4773. Found: 620.4779.



3L: 53%. White solid.

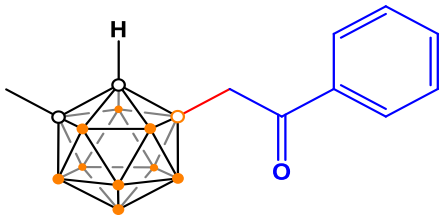
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.11 – 8.00 (m, 3H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.45 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.7 Hz,

2H), 7.01 (d, *J* = 8.4 Hz, 1H) (aryl C−***H***), 4.42 (s, 1H, cage C−***H***), 3.91 (s, 3H, OC$\boldsymbol{H}_3$)), 3.11 (d, *J* = 13.5 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H) (B−C$\boldsymbol{H}_2$), 2.19 (d, *J* = 3.0 Hz, 6H), 2.11 (s, 3H), 1.81 (s, 6H) (adamantly C−***H***).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.2 (2B), -3.7 (1B), -5.0 (1B)，-8.4 (1B), -9.3 (1B), -11.4 (4B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.4 (***C***=O), 159.1, 141.9, 139.2, 136.3, 134.3, 133.4, 132.7, 131.4, 130.7, 130.2, 130.0, 129.0, 128.7, 127.6, 126.8, 126.1, 125.9, 124.9, 124.7, 112.3 (aryl ***C***), 77.4, 61.3 (cage−***C***), 55.3 (O***C***H_3), 40.8, 37.4, 37.3, 29.3 (adamantly ***C***), 28.6 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{38}B_{10}O_2H_{49}$ [M+H^+]: 630.4775. Found: 630.4772.



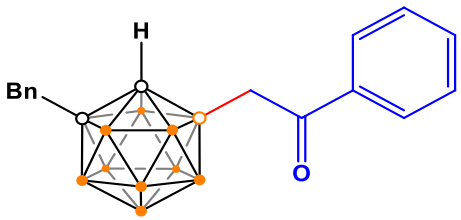
4b: 86%. White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H) (aryl C−***H***), 3.95 (s, 1H, cage C−***H***), 2.91 (d, *J* = 15.6 Hz, 1H), 2.87 (s d, *J* = 15.6 Hz, 1H) (B−C$\boldsymbol{H}_2$), 2.01 (s, 3H, C$\boldsymbol{H}_3$).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.8 (1B), -5.0 (1B), -6.0 (1B), -8.6 (1B), -9.5 (1B), -10.8 (3B), -11.6 (1B), -13.2 (1B).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 201.7 (***C***=O), 137.4, 133.3, 128.81, 128.76 (aryl−***C***), 71.2, 62.7 (cage ***C***), 28.5 (B−***C***H_2), 26.0 (***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{11}B_{10}OH_{21}$ [M+H^+]: 277.2595. Found: 277.2594.



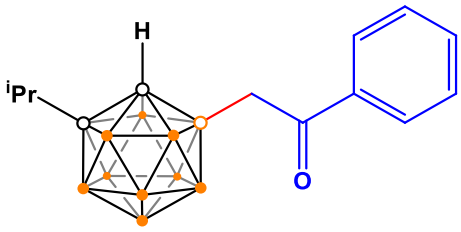
4c: 87%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 – 7.87 (m, 2H), 7.9 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.30 (m, 3H), 7.12 – 7.04 (m, 2H) (aryl C−***H***), 3.61 (s, 1H, cage C−***H***), 3.47 (s, 2H, Bn−C***H***$_2$), 2.83 (d, *J* = 13.5 Hz, 1H), 2.80 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.4 (1B), -4.9 (1B), -5.4 (1B), -8.5 (1B), -9.4 (1B), -11.2 (1B), -12.0 (2B), -12.6 (1B), -13.5 (1B).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.2 (***C***=O), 137.4, 134.4, 133.2, 129.9, 129.2, 129.0, 128.8, 128.7, 128.6 (aryl−***C***), 75.5, 60.8 (cage ***C***), 43.8 (Bn−***C***H$_2$), 28.8 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{25}$ [M+H$^+$]: 375.2730. Found: 375.2721.



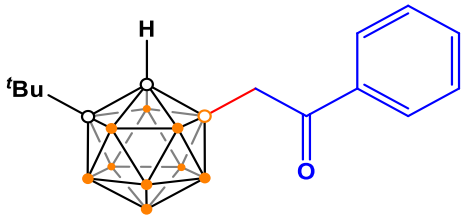
4d: 86%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.63 – 7.51 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H) (aryl C−***H***), 4.00 (s, 1H, cage C−***H***), 2.90 (d, *J* = 13.5 Hz, 1H), 2.86 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$), 2.48 (hept, *J* = 6.9 Hz, 1H, ^{i}Pr−C***H***), 1.10 (d, *J* = 6.9 Hz, 6H, ^{i}Pr−C***H***$_3$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) -3.1 (1B), -4.5 (1B), -5.9 (1B), -8.9 (1B), -9.7 (1B), 11.9 (1B), -12.5 (2B), 13.2 (1B), -14.1 (1B).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 201.7 (***C***=O), 137.5, 133.3, 128.80, 128.75 (aryl−***C***), 82.1, 61.3 (cage−***C***), 34.9 (^{i}Pr−***C***H), 29.0 (B−***C***H_2), 23.02, 22.99 (^{i}Pr−***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{13}B_{10}OH_{25}$ [M+H^+]: 305.2909. Found: 305.2910.



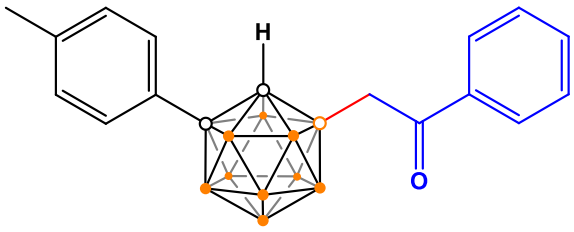
4e: 88%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.61 – 7.54 (m, 1H), 7.47 (m, 2H) (aryl C−***H***), 4.10 (s, 1H, cage C−***H***), 2.90 (d, *J* = 13.3 Hz, 1H), 2.85 (d, *J* = 13.3 Hz, 1H) (B−C***H***$_2$), 1.19 (s, 9H, ^{t}Bu−C***H***$_3$).

$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*) δ -3.8 (2B), -6.1 (1B), 8.5 (1B), -9.3 (1B), -11.5 (1B), -12.8 (2B), -13.8 (2B).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 201.9 (***C***=O), 137.5, 133.3, 128.81, 128.77 (aryl−***C***), 86.6, 62.9 (cage ***C***), 36.6 (^{t}Bu−***C***Me_3), 32.0 (***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for calcd for $C_{14}B_{10}OH_{27}$ [M+H^+]: 319.3066. Found: 319.3063.



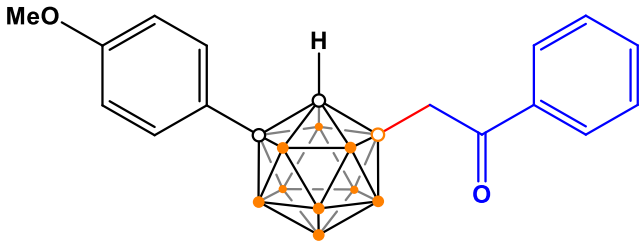
4f: 86%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.43 (m, 2H), 7.33 (m, *J* = 8.2 Hz, 2H), 7.13 – 7.07 (m, 2H) (aryl C−***H***), 4.33 (s, 1H, cage C−***H***), 2.97 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$), 2.33 (s, 3H, C***H***$_3$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.2 (1B), -4.0 (1B), -5.2 (1B), -8.5 (1B), -9.4 (1B), -10.5 (1B), -11.1 (1B), -11.8 (2B), -13.5 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 201.7 (***C***=O), 140.3, 137.5, 133.3, 130.6, 129.6, 128.82, 128.78, 127.6 (aryl−***C***), 77.5, 61.5 (cage ***C***), 29.1 (B−***C***H_2), 21.1 (***C***H_3).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}OH_{25}$ [M+Na^+]: 375.2730. Found: 375.2721.



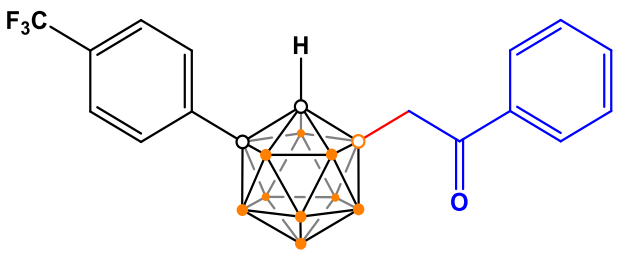
4g: 87%. White solid.

^1H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 2H), 7.63 – 7.53 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.34 (m, 2H), 6.84 – 6.77 (m, 2H) (aryl C−***H***), 4.28 (s, 1H, cage C−***H***), 3.80 (s, 3H, C***H***$_3$), 2.96 (d, *J* = 13.5 Hz, 1H), 2.91 (d, *J* = 13.5 Hz, 1H) (B−C***H***$_2$).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.1 (1B), -4.2 (1B), -5.1 (1B), -8.7 (1B), -9.5 (1B), -11.0 (3B), 11.8(1B), -13.5 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 201.7 (***C***=O), 160.9, 137.5, 133.3, 129.4, 128.83, 128.78, 125.5, 114.1 (aryl−***C***), 77.7, 62.1 (cage ***C***),55.6 (***C***H_3), 28.5 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}O_2H_{25}$ [M+H^+]: 369.2860. Found: 369.2869.



4h: 76%. White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (m, 2H), 7.64 – 7.56 (m, 5H), 7.52 – 7.45 (m, 2H) (aryl C−***H***), 4.48 (s, 1H), 2.98 (d, *J* = 13.8 Hz, 1H), 2.94 (d, *J* = 13.8 Hz, 1H) (B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.0 (1B), -3.2 (1B), -4.9 (1B), -8.2 (1B), -9.1 (1B), -10.6 (1B), -11.3 (2B), -11.5 (1B), -13.6 (1B).

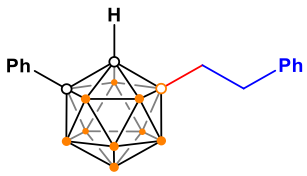
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.7 (**C**=O), 137.4, 137.1, 133.5, 132.3 (q, *J* = 99.1, 32.8 Hz), 128.8 (d, *J* = 8.4 Hz), 128.1, 126.0 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.5 Hz) (aryl−***C***), 75.8, 60.1 (cage−**C**), 28.4 (B−***C***H$_2$).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -63.07.

HRMS (ESI, positive mode): *m/z* calcd for $C_{17}B_{10}F_3OH_{22}$ [M+H$^+$]: 407.2628. Found: 407.2626.

3 Transformations and Synthetic Applications

Transformation of 3a to 5. A solution of THF·BH$_3$ (1.0 M, 0.5 mL, 5.0 equiv., 0.5 mmol) was added via syringe to a solution of **3a** (1.0 equiv., 33.8 mg, 0.1 mmol) in THF (1 mL). The reaction mixture was refluxed for 12 h under N$_2$ atmosphere. After refluxing, the mixture was cooled to 0 °C, and the reaction was quenched by adding MeOH (0.25 mL). Next, the solvent was evaporated, and an aqueous of HCl (2N, 1.0 mL) was added to the residue, which was then refluxed for 1 h. The reaction mixture was made basic by adding K_2CO_3 and extracted with $CHCl_3$ (5 mL x 3). The organic layer was dried over $MgSO_4$, filtered, and concentrated. Finally, the residue was purified using PTLC using PE/DCM as an eluent to give the product **5**.



5: Yield 78%. White solid.

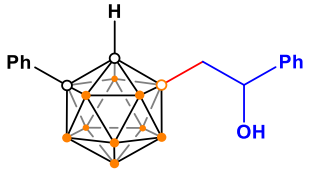
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.27 (m, 4H), 7.24 – 7.21 (m, 2H), 7.21 – 7.17 (m, 1H)， 3.82 (s, 1H, cage C−***H***), 2.80 – 2.70 (m, 2H)， 1.40 – 1.34 (m, 2H).

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.9 (1B), -2.3 (1B), -3.8 (1B), -8.5 (1B), -9.4 (1B), -11.3 (3B), -12.0 (1B), -14.1 (1B).

^{13}C NMR (128 MHz, Chloroform-*d*) δ 144.2 (***C***=O), 133.8, 129.9, 128.9, 128.5, 128.1, 127.6, 125.9 (aryl−***C***), 76.8, 61.4 (cage ***C***), 34.9 (B−CH_2***C***H_2), 17.6 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}H_{25}$ [M+Na^+]: 347.2781. Found: 347.2789.

Transformation of 3a to 9. To a solution of **3a** (33.8 mg, 0.1 mmol) in MeOH (1 mL) was added $NaBH_4$ (3 equiv., 11.4 mg, 0.3 mmol) carefully at 0 ℃. The mixture was stirred at 0 ℃ for 15 min, then warmed to 25 ℃ and stirred for 20 min before being quenched with water. Subsequently, the mixture was extracted with ethyl acetate (5 mL x 3). The combined organic extracts were washed with water and brine and then dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by PTLC using PE/EA as an eluent to give the product **6**.



6: Yield 90%. White solid.

Conformer I: **Conformer II** = 46 : 54

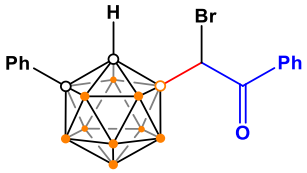
^{1}H NMR (600 MHz, Chloroform-*d*), **Conformer I**: δ 7.44 – 7.41 (m, 2H), 7.41 – 7.27 (m, 8H) (aryl C−***H***), 4.92 (dd, *J* = 9.6, 4.4 Hz, 1H, C***H***OH), 4.15 (s, 1H, cage C−***H***), 1.70 – 1.46 (m, 2H, B−CH_2); **Conformer II**: δ 7.45 – 7.44 (m, 11H), 7.41 – 7.27 (m, 8H) (aryl C−***H***), 4.88 (dd, *J* = 10.1, 3.8 Hz, 1H, C***H***OH), 4.31 (s, 1H, cage C−***H***), 1.70 – 1.46 (m, 2H, B−CH_2).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.4 (1B), -3.4 (2B), -8.3 (1B), -9.6 (1B), -11.4 (3B), 12.4 (1B), -13.7 (1B).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*), **Conformer I**: δ 146.1 (***C***=O), 134.0, 129.9, 128.89, 128.79, 127.9, 127.5, 126.0(aryl−***C***), 76.8, 74.6, 61.5 (cage−***C***), 26.4 (B−***C***H_2); **Conformer II**: δ 146.3 (***C***=O), 133.9, 129.9, 128.9, 128.87, 127.77, 127.8, 127.6, 125.9 (aryl−***C***), 76.8, 74.7, 61.6, 61.4 (cage−***C***), 26.4 (B−***C***H_2).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{25}$ $[M+H^+]$: 341.2911. Found: 341.2908.

Transformation of 3a to 7. Compound **3a** (33.8 mg，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 ℃ for 18 h under N_2 atmosphere. After diluting with CH_2Cl_2 (2 mL), the solvent was evaporated under reduced pressure, and the residue was purified by PTLC using PE/CH_2Cl_2 as an eluent to give the product.



7: Yield 90%. White solid.

Conformer I : **Conformer II** = 48 : 52

^1H NMR (600 MHz, Chloroform-*d*), **Conformer I**: δ 7.99 (m, 2H), 7.65 – 7.59 (m, 1H), 7.54 – 7.45 (m, 4H), 7.44 – 7.30 (m, 3H) (aryl C−***H***), 5.25 (s, 1H, B−C***H***Br), 4.66 (s, 1H, cage C−***H***); **Conformer II**: δ 7.99 (m, 2H), 7.65 – 7.59 (m, 1H), 7.54 – 7.45 (m, 4H), 7.44 – 7.30 (m, 3H) (aryl C−***H***), 5.22 (s, 1H, B−C***H***Br), 4.74 (s, 1H, cage C−***H***).

$^{11}B\{^1H\}$ NMR (193 MHz, Chloroform-*d*) δ -2.3 (1B), -3.6 (1B), -4.9 (1B), -8.4 (1B), -9.2 (1B), -11.1 (3B), 12.6 (2B).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*), Conformer I: δ 195.8 (***C***=O), 135.7, 134.0, 133.1, 130.3, 129.15, 129.05, 128.99, 127.71 (aryl−***C***), 76.6, 63.1 (cage ***C***), 35.3 (B−***C***HBr); **Conformer II**: δ 196.2 (***C***=O), 135.6, 134.1, 133.2, 130.2, 129.11, 129.07, 129.02, 127.67 (aryl−***C***), 77.5, 62.2 (cage ***C***), 34.9 (B−***C***HBr).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}H_{22}BrO$ $[M+H^+]$: 418.1845. Found: 418.1845.

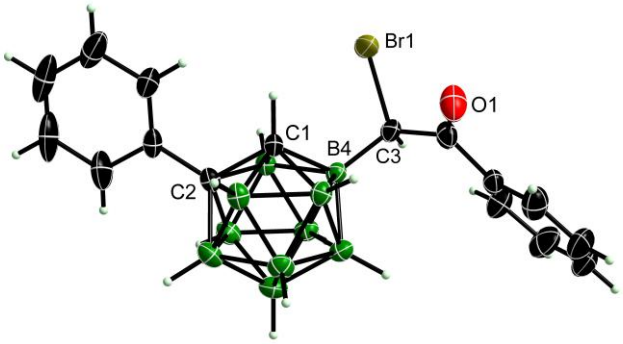
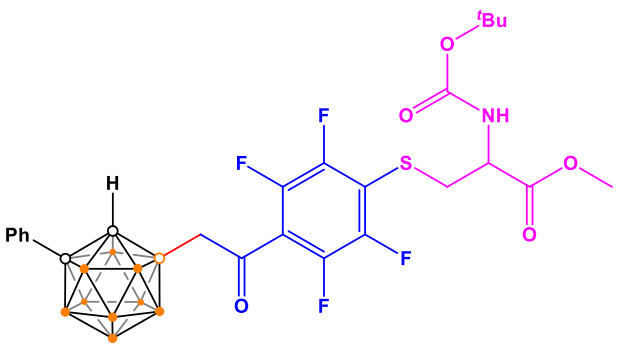


Figure S3. Molecular structure of compound **7** (ellipsoids at 30% probability)**.**

General procedure for the nucleophilic substitution reaction of 3t. K_3PO_4 (0.2 mmol, 42.5 mg), **3t** (0.1 mmol, 43 mg), and nucleophile (0.2 mmol) were combined in DMF (1 ml). The resultant mixture was then stirred at room temperature for 12 h under N_2 atmosphere. Afterward, the mixture was extracted with water/CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel chromatography with PE/DCM as an eluent to give the product.



8: Yield 51%. White solid.

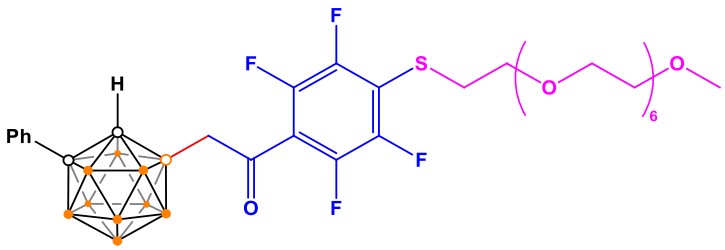
^{1}H NMR (600 MHz, Chloroform-d) δ 7.52 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H) (aryl C−***H***), 5.33 (d, *J* = 7.8 Hz, 1H, N***H***), 4.58 (q, *J* = 5.6 Hz, 1H, C***H***NH), 4.44 (s, 1H, cage C−***H***), 3.69 (s, 3H, OC***H***$_3$), 3.55 (dd, *J* = 14.2, 4.7 Hz, 1H), 3.39 (dd, *J* = 14.2, 5.0 Hz, 1H, SC***H***$_2$), 2.91 (s, 2H, B−C***H***$_2$), 1.40 (s, 9H, ^{t}Bu−C***H***$_3$).

^{11}B NMR (193 MHz, CDCl$_3$) δ -2.1 (1B), -3.8(1B), -6.1 (1B), -8.5 (1B), -9.1 (1B), -10.9 (3B), -11.9 (2B), -13.0 (1B).

^{13}C NMR (151 MHz, CDCl$_3$) δ 195.3 (B−CH$_2$***C***=O), 170.4 (***C***O$_2$Me), 154.9 (***C***O$_2$^{t}Bu), 147.8, 146.1, 144.8, 143.1 (Ph−***C***F), 133.2, 130.2, 129.0, 127.6 (Ph−***C***H), 120.2 (CH$_2$S***C***), 117.5 (B−CH$_2$CO***C***), 80.7 (***C***Me$_3$), 77.5, 61.2 (cage ***C***), 53.8 (***C***HNH), 52.9 (O***C***H$_3$), 36.5 (S***C***H$_2$), 34.3 (B−***C***H$_2$), 28.3 (^{t}Bu−***C***H$_3$).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -131.75 (dd, *J* = 23.7, 12.4 Hz, 2F), -140.80 (dd, *J* = 23.8, 12.4 Hz, 2F).

HRMS (ESI, positive mode): m/z calcd for $C_{25}B_{10}H_{37}F_4NO_5S$ [M+H$^+$]: 645.3075. Found: 645.3079.



9: Yield 38%. White solid.

^{1}H NMR (600 MHz, Chloroform-d): 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.31 (m, 2H) (aryl C−***H***), 4.43 (s, 1H, cage C−***H***), 3.68 (t, *J* = 6.3 Hz, 2H, SCH$_2$C***H***$_2$), 3.66 – 3.61 (m, 18H), 3.57 (s, 4H), 3.56 – 3.52 (m, 2H) (OC***H***$_2$C***H***$_2$), 3.37 (s, 3H, OC***H***$_3$), 3.19 (t, *J* = 6.3 Hz, 2H, SC***H***$_2$CH$_2$), 2.91 (s, 2H, B−C***H***$_2$).

^{11}B{^{1}H} NMR (193 MHz, Chloroform-d) δ -2.2 (1B), -3.8 (1B), -6.1 (1B), -8.5 (1B), -9.1 (1B), -11.0 (3B), -12.0 (1B), -13.2 (1B).

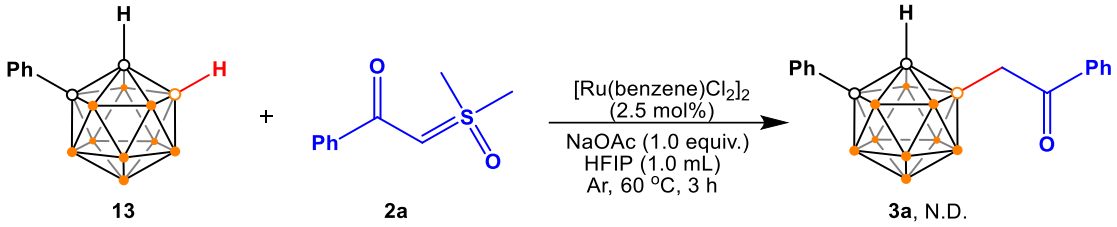
^{13}C NMR (151 MHz, $CDCl_3$) δ 195.4 (***C***=O), 147.3, 145.9, 144.7, 142.6 (Ph−***C***F), 133.2, 130.1, 129.3, 127.6 (Ph−***C***H), 119.6 (CH_2S***C***), 118.7 (B−CH_2CO***C***), 77.4 (cage ***C***Ph), 72.0, 70.7, 70.63, 70.60, 70.55, 70.48 (O***C***H_2***C***H_2O), 61.2 (cage ***C***H), 59.1 (O***C***H_3), 35.0 (B−***C***H_2), 34.1 (S***C***H_2).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -132.72 (q, *J* = 11.2 Hz, 2F), -141.15 (q, *J* = 11.0 Hz, 2F).

HRMS (ESI, positive mode): m/z calcd for $C_{31}B_{10}H_{49}F_4O_8S$ [M+Na^+]: 788.3889. Found: 788.3891.

4 Mechanistic study

4.1 Reaction with 1-Ph-*o*-carborane without directing group

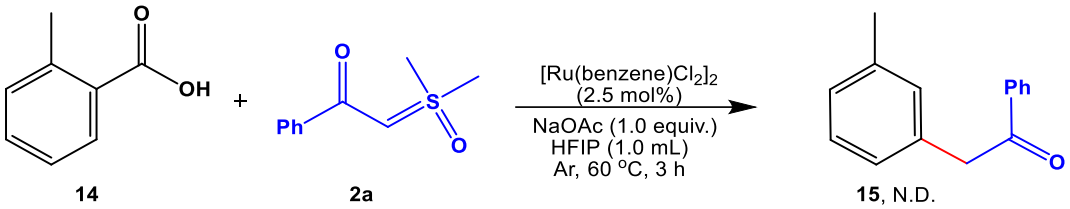


Scheme S1. Attempts without directing group.

Note: The reaction of 13 and 2a does not proceed, implying that the directing group is essential.

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 1-Ph-*o*-carborane **13** (0.1 mmol, 13.6 mg), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), and HFIP (1.0 mL) under N_2 atmosphere. After being stirred at 60 °C for 3 h, the reaction mixture was cooled to room temperature, and filtered through a pad of Celite. Removal of the solvent gave a white solid subjected to TLC, GC-MS, and ^{1}H NMR analyses. No target product was identified.

4.2 Reaction with *2-methyl-benzoic acid*

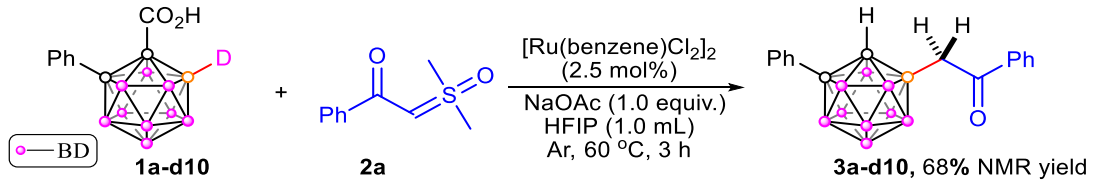


Scheme S2. Reaction with 2-methyl-benzoic acid.

Note: 2-methyl-benzoic acid did not react with sulfoxonium ylide 2a under the optimal reaction conditions. This indicated a significant difference in reactivity between the 3D delocalization σ aromatic carborane and the 2D π aromatic benzene.

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-methyl-benzoic acid **14** (0.1 mmol, 13.6 mg), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), and HFIP (1.0 mL) under N_2 atmosphere. After being stirred at 60 °C for 3 h, the reaction mixture was cooled to room temperature, and filtered through a pad of Celite. Removal of the solvent gave a white solid subjected to TLC, GC-MS, and ^1H NMR analyses. No target product **15** was identified.

4.3 Deuterium labeling experiments



Scheme S3. Reaction with **1a-d10**

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a-d10** (27.4 mg, 0.1 mmol), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), and HFIP (1.0 mL)

under N_2 atmosphere. The reaction mixture was stirred at 60 °C for 3 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The filtrate was concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum/ethyl acetate as an eluent to afford compound **3l-d10** as a white solid (27 mg, 62 %). The reaction of **1a-D10** with **2a** proceeded smoothly, yielding **3a-D10** in 68% yield with 78% DI.

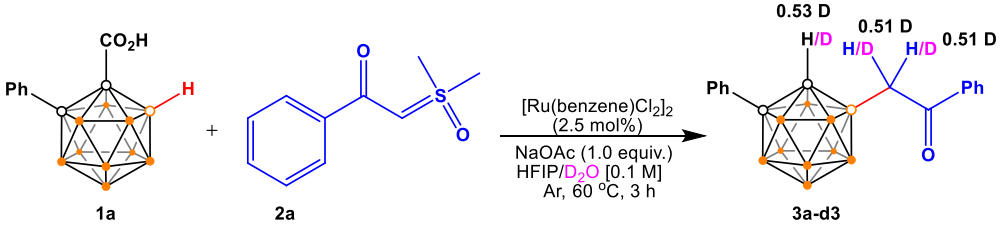
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H) (aryl C−***H***), 4.39 (s, 1H, cage C−***H***), 2.98 (d, *J* = 13.6 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$).

^{1}H {^{11}B} NMR (600 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H) (aryl C−***H***), 4.37 (s, 1H, cage C−***H***), 2.98 (d, *J* = 13.6 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 1H) (B−C***H***$_2$), 2.57 (s, 0.48H), 2.44 (s, 0.12H), 2.42 (s, 0.17H), 2.40 (s, 0.25H), 2.34 (s, 0.22H), 2.26 (s, 0.17H), 2.15 (s, 0.67H).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -2.4 (1B), -3.9 (1B), -5.2 (1B), -8.7 (1B), -9.5 (1B), -11.4 (3B), -13.6 (1B).

^{13}C {^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.6 (***C***=O), 137.5, 133.3, 130.0, 128.9, 128.82, 128.79, 127.7, 127.7 (aryl−***C***), 61.1 (cage ***C***), 28.1 (B−***C***H$_2$).

HRMS (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{20}D_9$ [M+H$^+$]: 370.3138. Found: 370.3138.



Scheme S4 Deuterium labeling experiments

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (26.5 mg, 0.1 mmol), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), HFIP (0.8 mL) and D_2O (0.2 mL) under N_2 atmosphere. After being stirred at 60 °C for 3 h, 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 PTLC using petroleum/ethyl acetate as an eluent to afford compound **3a-d3** as a white solid (23.1 mg, 73%).

^{1}H {^{11}B} NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H) (aryl C−***H***), 4.39 (s, 0.47H, cage C−***H***), 2.99 – 2.88 (m, 0.98H) (B−C***H***$_2$), 2.56 (s, 2H), 2.45 (s, 1H), 2.41 (s, 3H), 2.34 (s, 1H), 2.26 (s, 1H), 2.14 (s, 1H) (B−***H***). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}OH_{20}D_3$ $[M+H^+]$: 343.2911. Found: 343.2911.

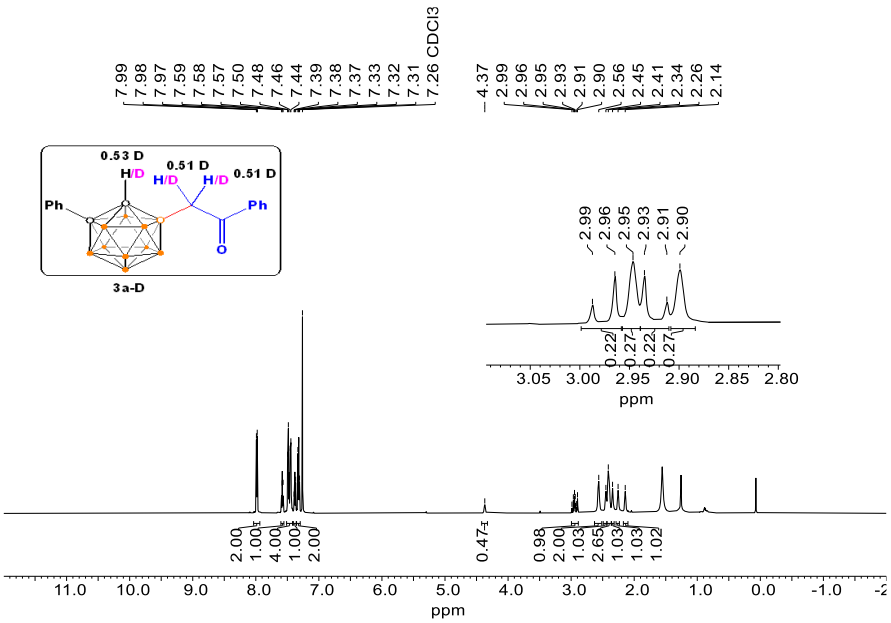


Figure S4. ^{1}H{^{11}B} NMR of **3a-d3**.

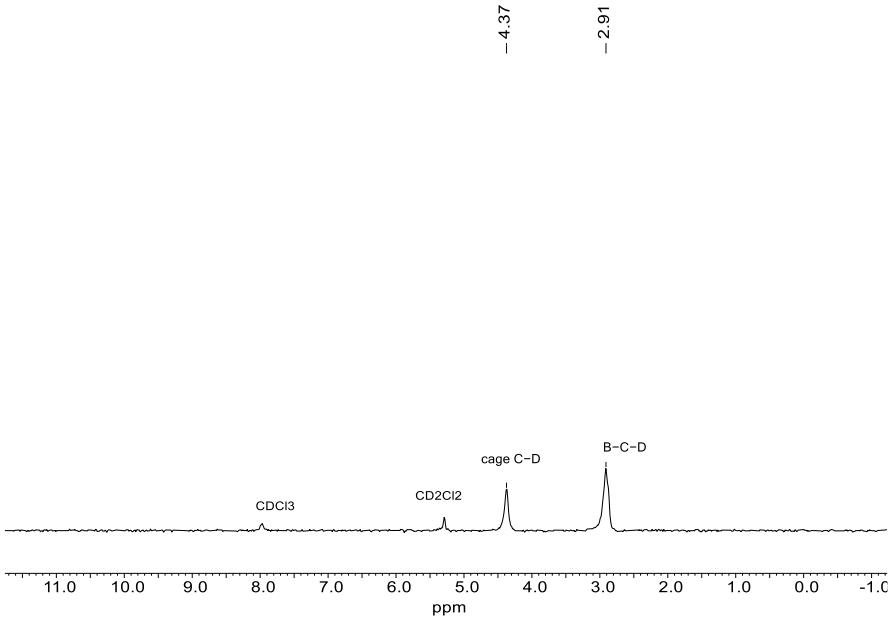
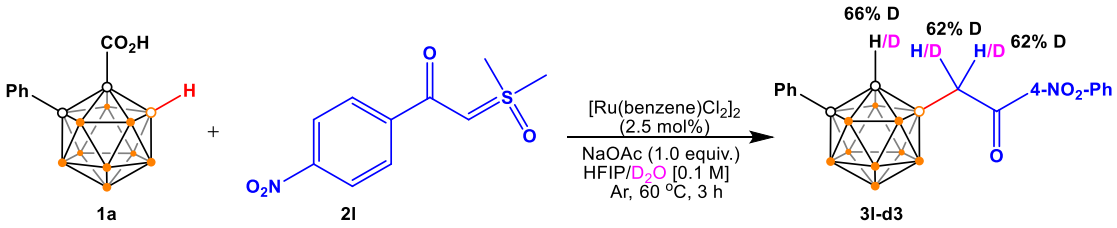


Figure S5. ^{2}H NMR (92 MHz, DCM) of **3a-d3**.



Scheme S5. Deuterium labeling experiments

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (26.5 mg, 0.1 mmol), sulfoxonium ylide **2l** (1.5 equiv., 36.2 mg, 0.15 mmol), [Ru(benzene)Cl_2]$_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), HFIP (0.8 mL) and D_2O (0.2 mL) under N_2 atmosphere. After being stirred at 60 °C for 3 h, 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 PTLC using petroleum/ethyl acetate as an eluent to afford compound **3l-d3** as a white solid (31.2 mg, 81 %).

^{1}H {^{11}B} NMR (600 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.37 – 7.30 (m, 2H) (aryl C−***H***), 4.31 (s, 0.34H, cage C−***H***), 3.04 – 2.92 (m, 0.76H) (B−C***H***$_2$), 2.61 (s, 1H), 2.57 (s, 1H), 2.47 (s, 1H), 2.43 (s, 2H), 2.35 (s, 1H), 2.30 (s, 1H), 2.27 (s, 1H), 2.12 (s, 1H) (B−***H***). **HRMS** (ESI, positive mode): *m/z* calcd for $C_{16}B_{10}O_3H_{21}D_3$ [M+H$^+$]: 389.2738. Found: 389.2744.

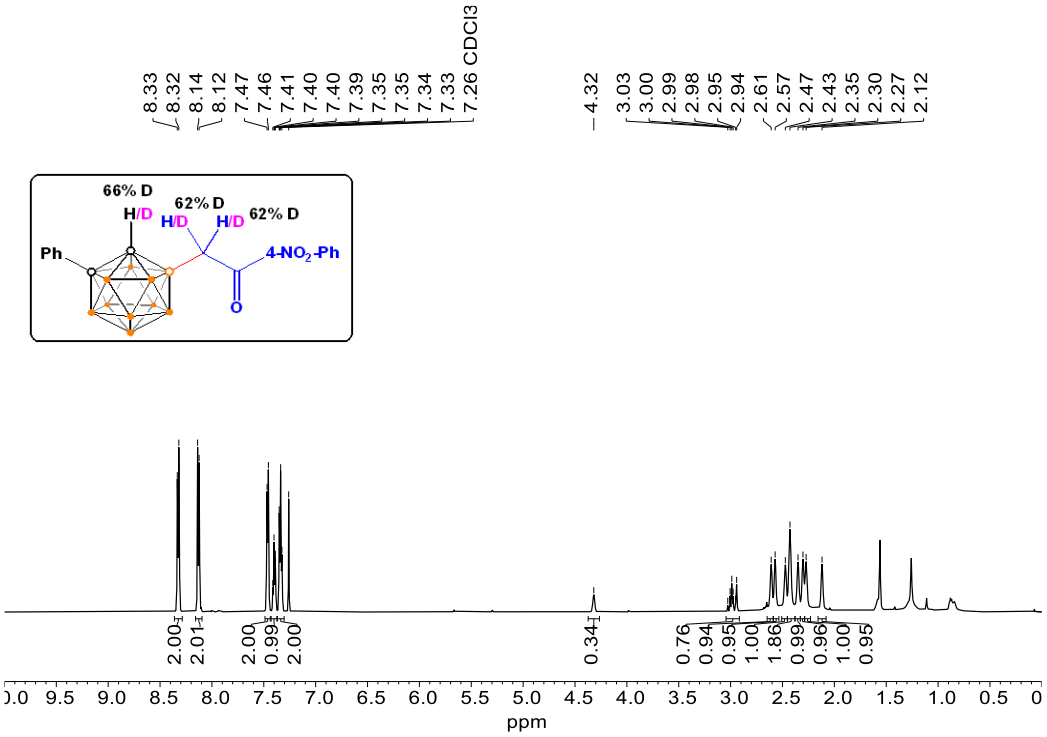


Figure S6. ^{1}H{^{11}B} NMR of **3l-d3**.

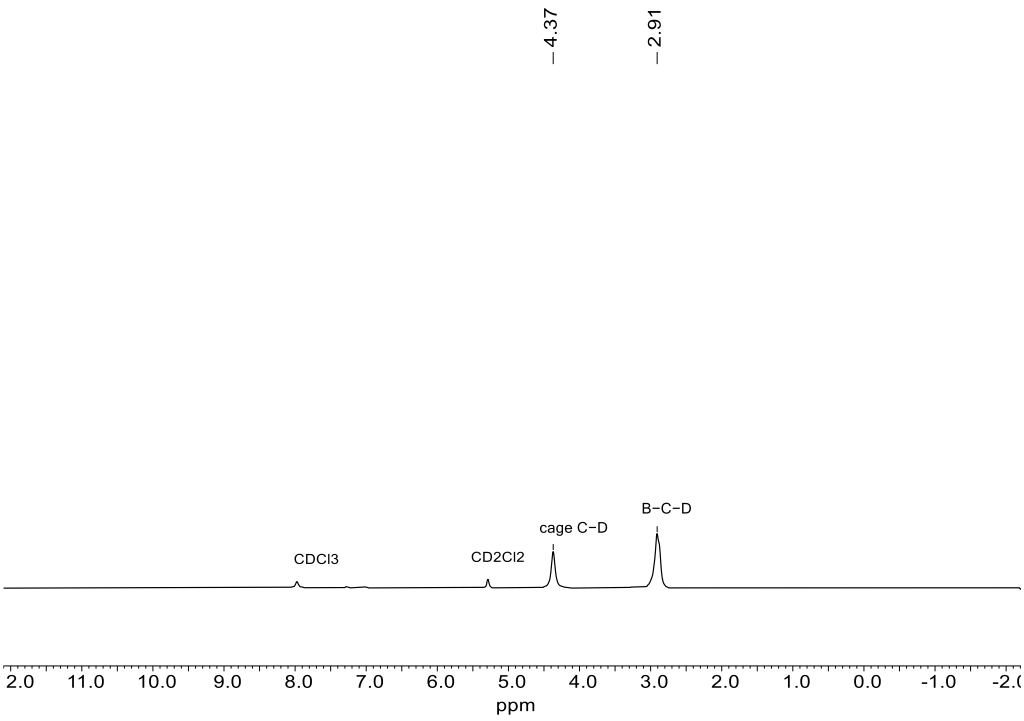
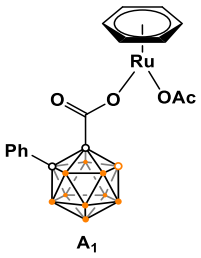


Figure S7. ^{2}H NMR (92 MHz, DCM) of **3l-d3**.

4.4 *In situ* HRMS studies on the reaction of 1a and 2a

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (26.5 mg, 0.1 mmol), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), [Ru(benzene)Cl_2]$_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), and HFIP (1.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 60 °C under N_2 atmosphere. ESI-HRMS directly analyzed the reaction system at different times. The mass spectrum indicated the formation of ruthenium intermediates **A$_1$**, **B**, and **D**.



A_1

M = $C_{17}H_{24}O_4RuB_{10}$
[M+H$^+$]
Calcd. : 504.1743
Found : 504.1758

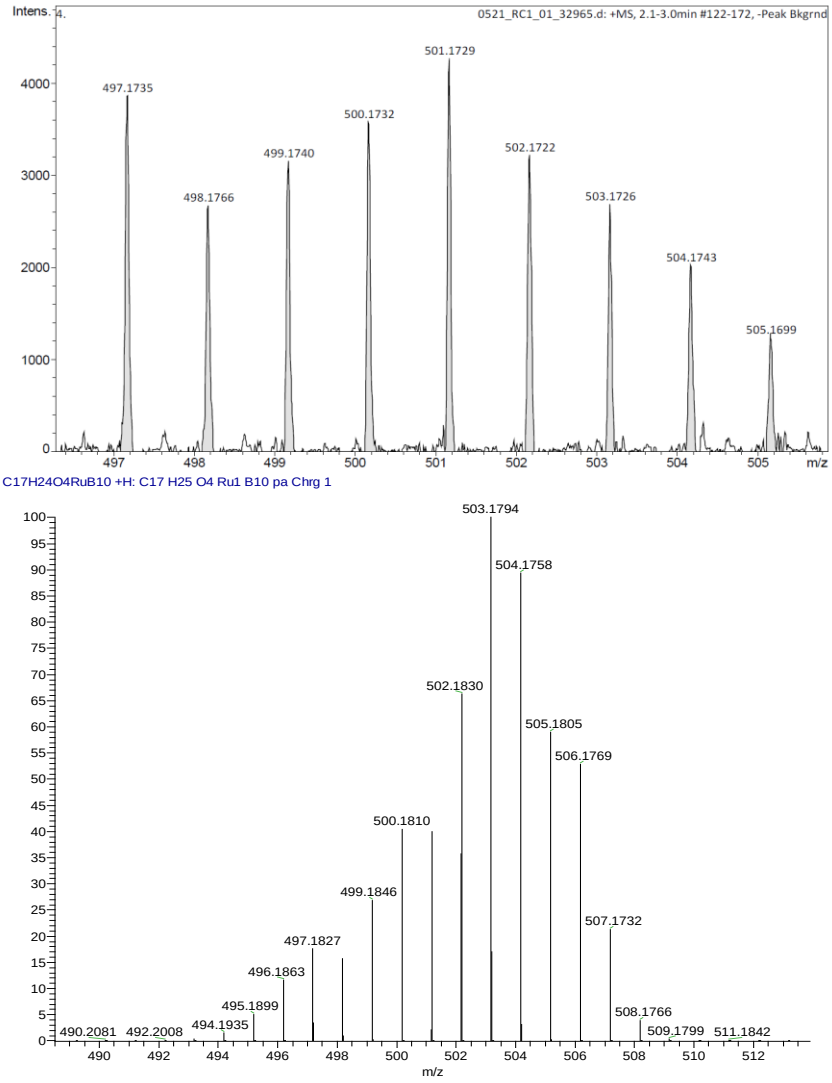


Figure S8. HRMS of **A**$_1$. Up: experimental MS. Down: calculated MS.

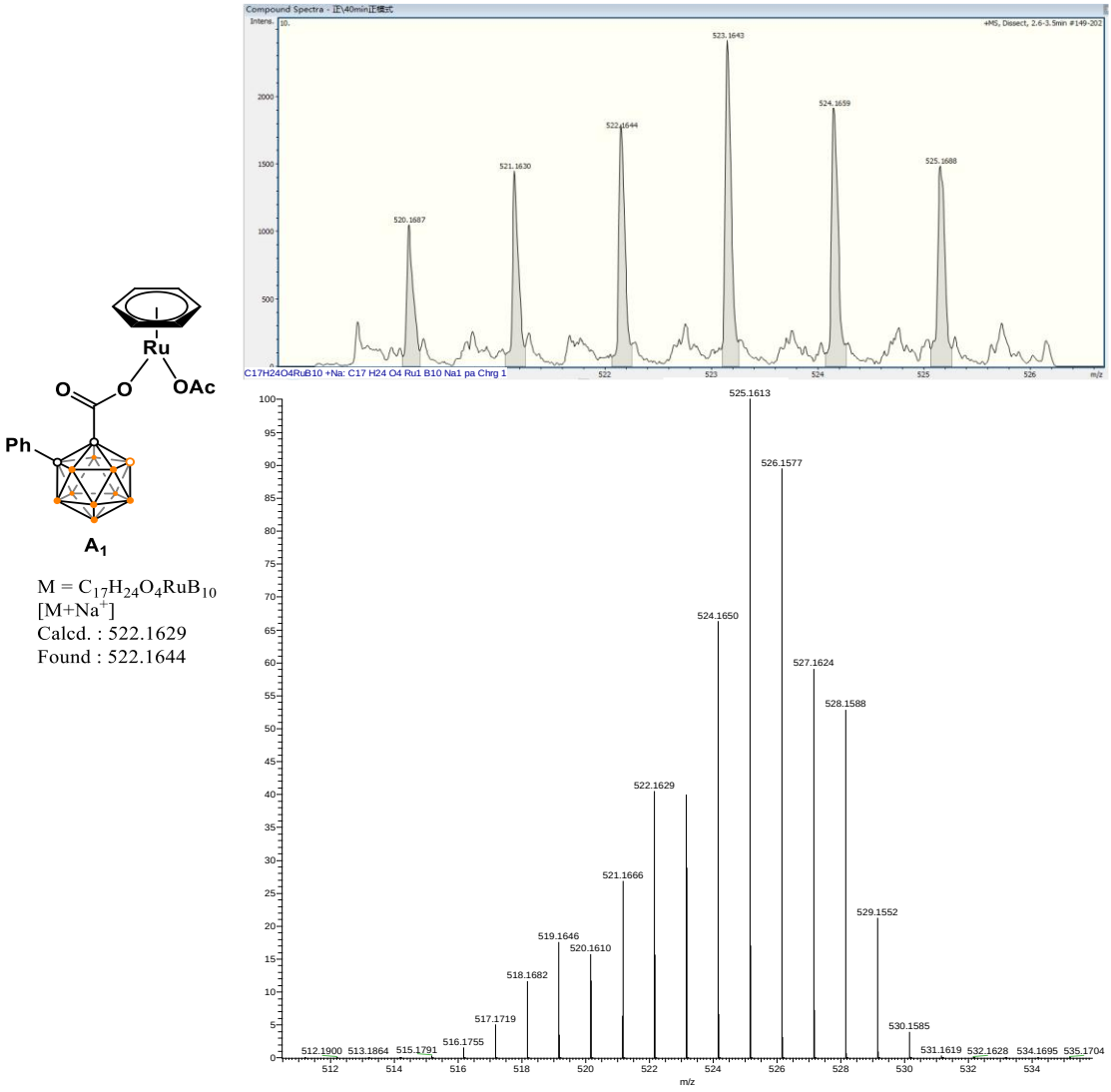


Figure S9. HRMS of **A1**. Up: experimental MS. Down: calculated MS.

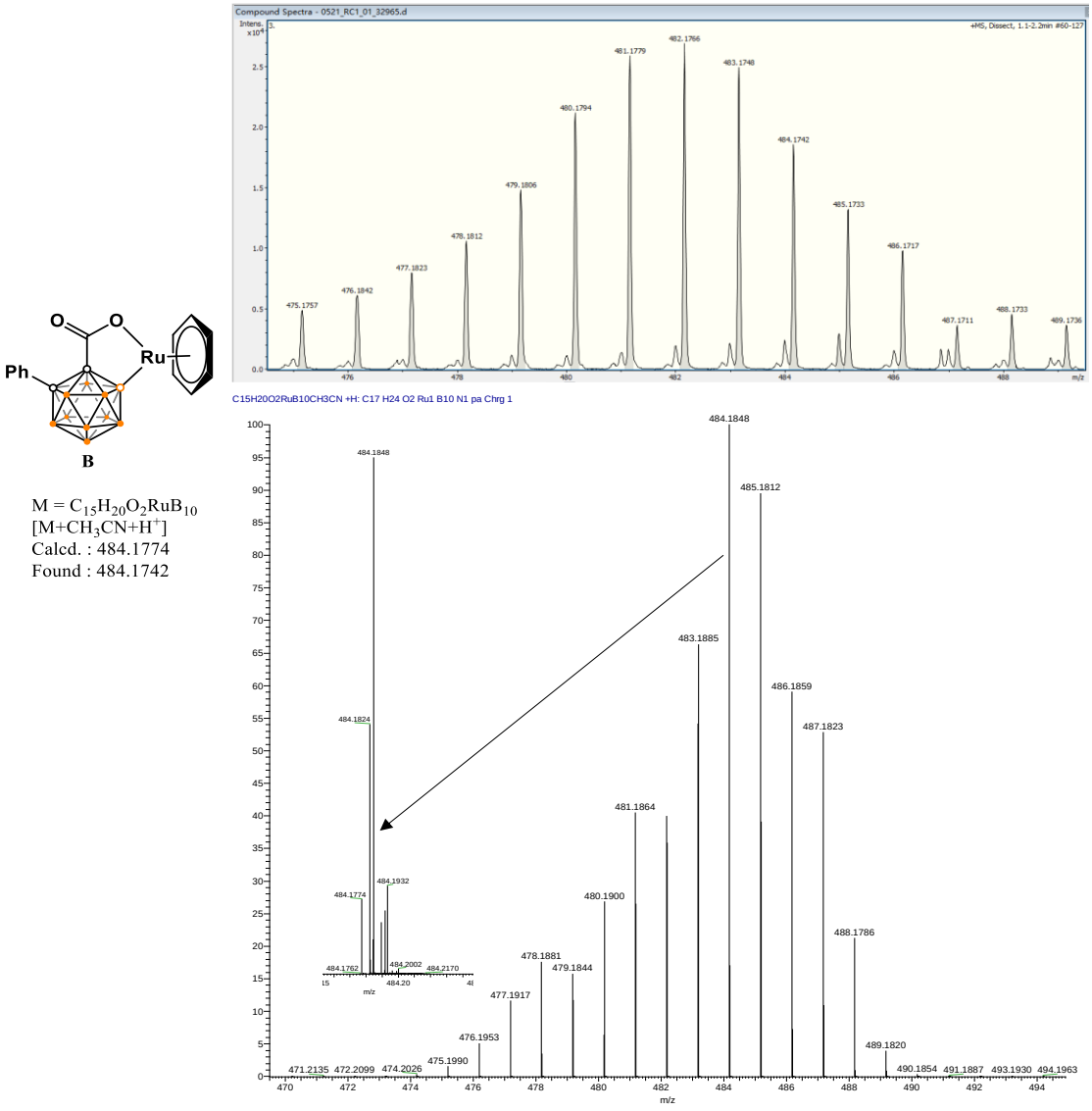
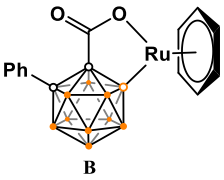


Figure S10. HRMS of **B**. Up: experimental MS. Down: calculated MS.



B

M = $C_{15}H_{20}O_2RuB_{10}$
[M+CH_3CN+Na^+]
Calcd. : 502.1720
Found : 502.1701

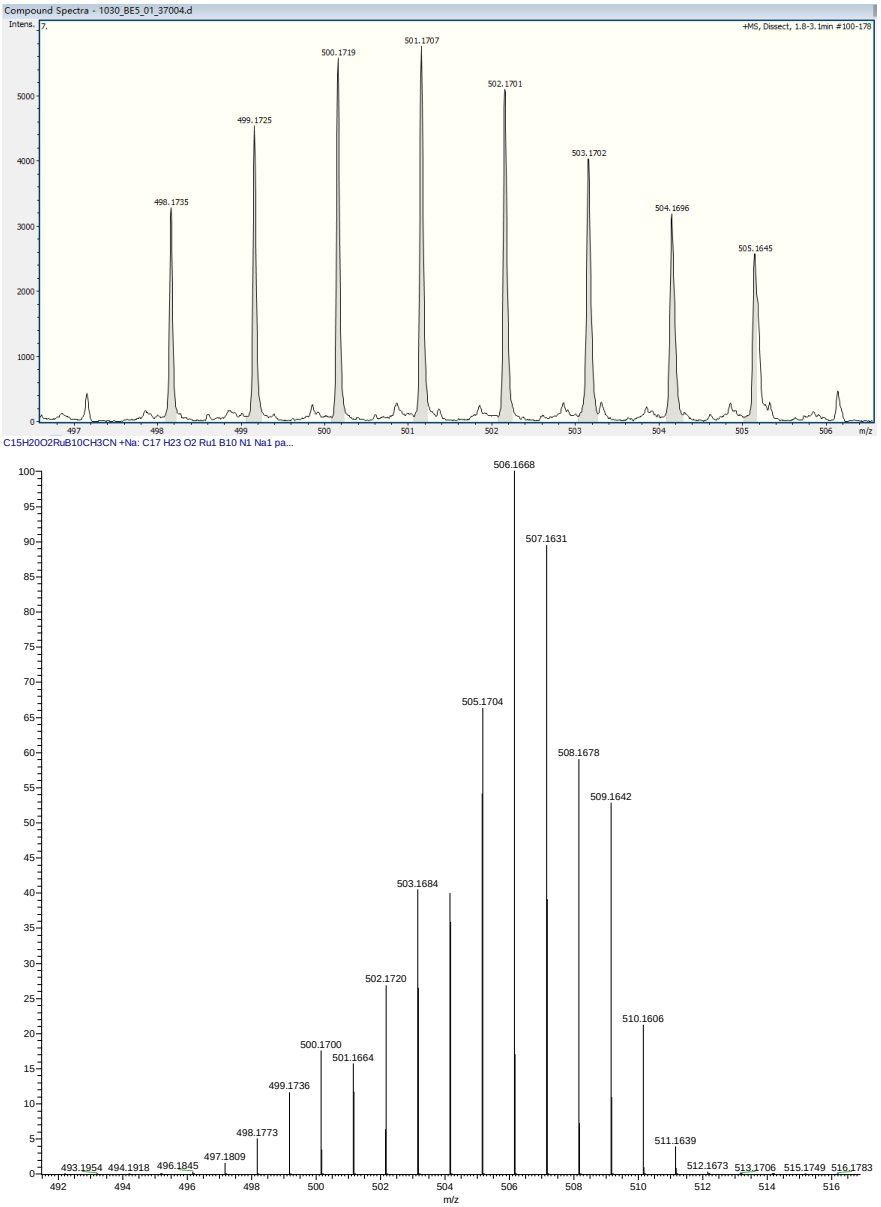
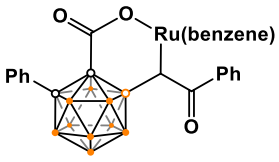


Figure S11. HRMS of **B**. Up: experimental MS. Down: calculated MS.



M = $C_{23}H_{26}B_{10}O_3Ru$
$[M+H^+]$
Calcd. : 561.2085
Found : 561.2075

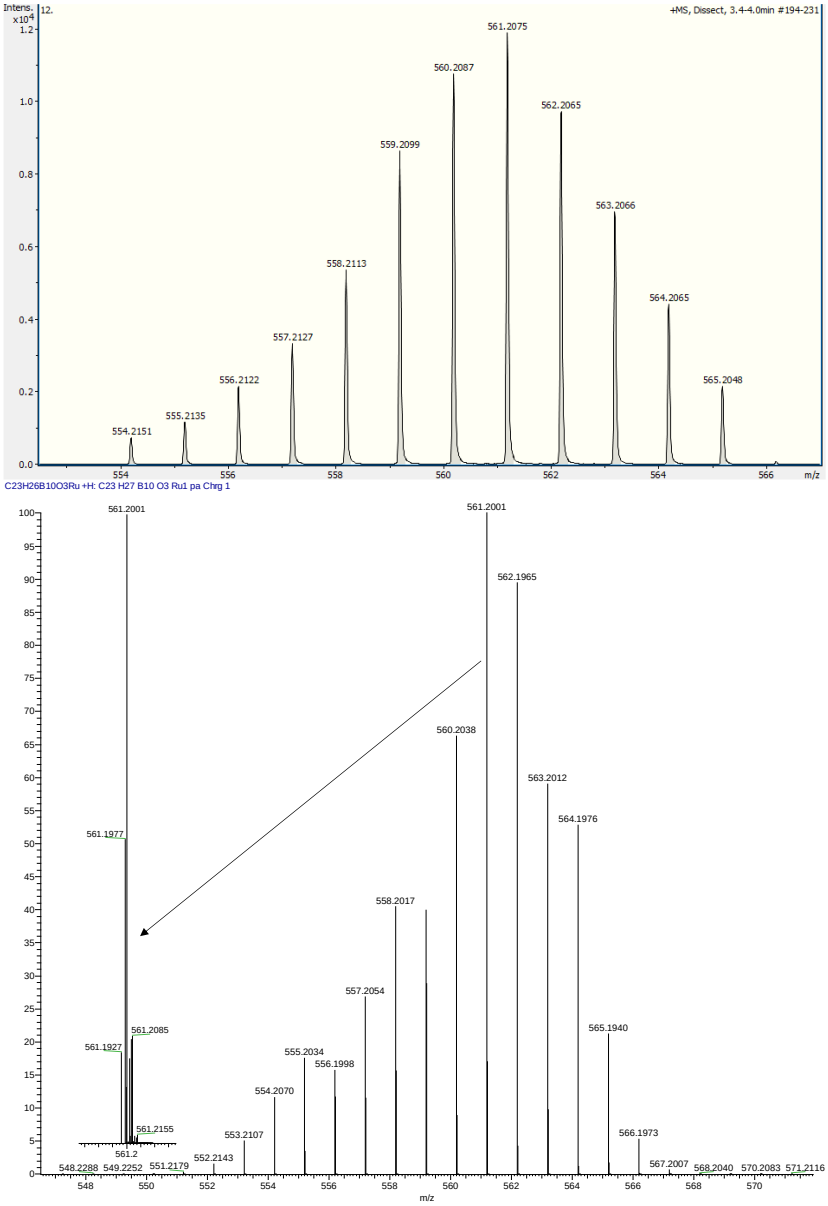
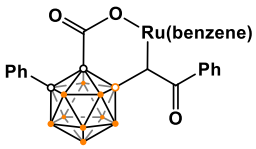


Figure S12. HRMS of **D**. Up: experimental MS. Down: calculated MS.



M = $C_{23}H_{26}B_{10}O_3Ru$
[M+Na^+]
Calcd. : 583.1910
Found : 583.1904

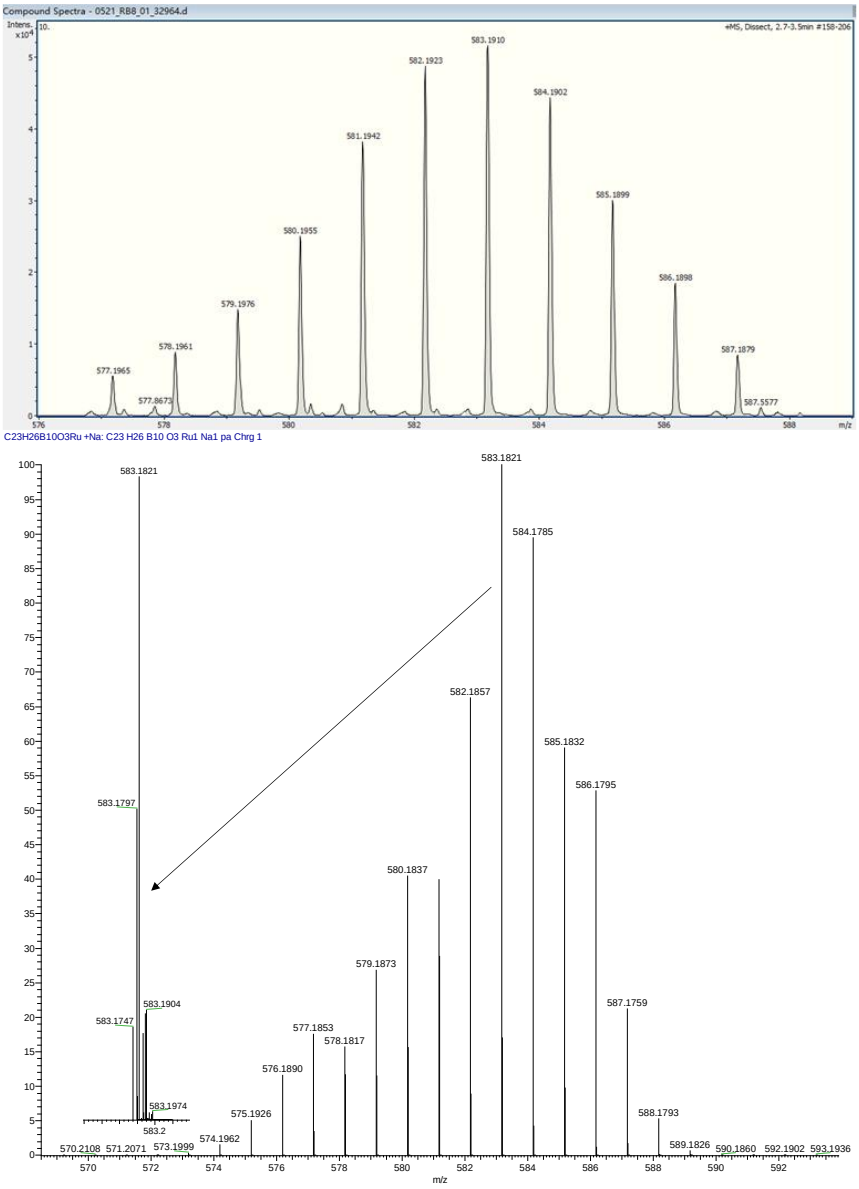


Figure S13. HRMS of **D**. Up: experimental MS. Down: calculated MS.

4.5 X-ray study A_2

o-Carboranyl acid **1a** (0.05 mmol, 13.3 mg), NaOAc (0.1 mmol, 8.2 mg), $[Ru(benzene)Cl_2]_2$ (0.05 mol, 25 mg) and HFIP (1 mL) were mixed in a 10 mL Schlenk tube under N_2 atmosphere. The resulting mixture was stirred at 60 °C for 3 h. Subsequently, the reaction mixture was allowed to cool to room temperature and left to stand for several days, leading the formation of a small brown crystal suitable for single-crystal X-ray analysis. The endeavor to adequately isolate this Ru intermediate for additional characterization was unsuccessful.

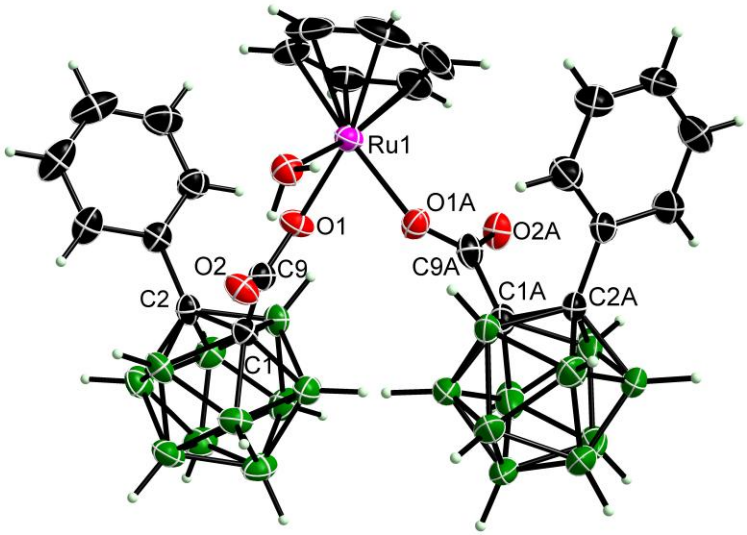
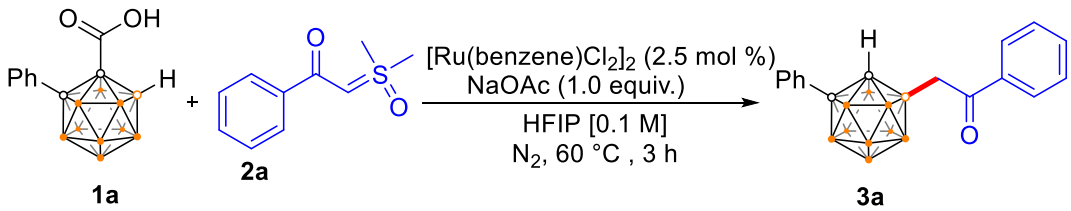


Figure S14. Molecular structure of compound $\mathbf{A_2}\cdot H_2O$ (ellipsoids at 30% probability).

4.6 Detection of DMSO lost from sulfoxonium ylide



Scheme S6. Reaction of **1a** and **2a**.

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (26.5 mg, 0.1 mmol), sulfoxonium ylide **2a** (0.15 mmol, 29.5 mg), $[Ru(benzene)Cl_2]_2$ (2.5 mol%, 1.3 mg, 0.0025 mmol), NaOAc (0.1 mmol, 8.2 mg), and HFIP (1.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 60 °C for 3 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The filtrate was concentrated in *vacuo*.

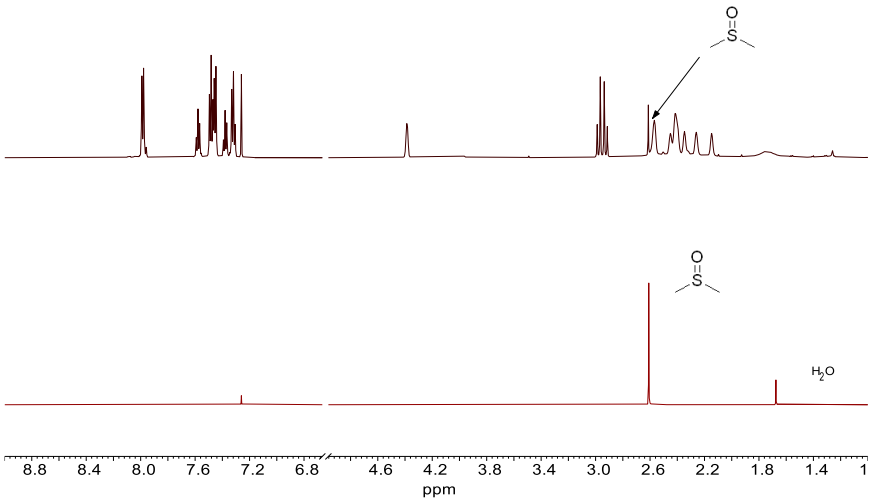


Figure S15. Up: $^1H\{^{11}B\}$ NMR ($CDCl_3$) spectrum for the reaction mixture of **1a** with **2**; down: ^1H NMR ($CDCl_3$) for pure DMSO for comparison.

Note: The reaction of 1a with 2a confirms the formation of DMSO.

5. References

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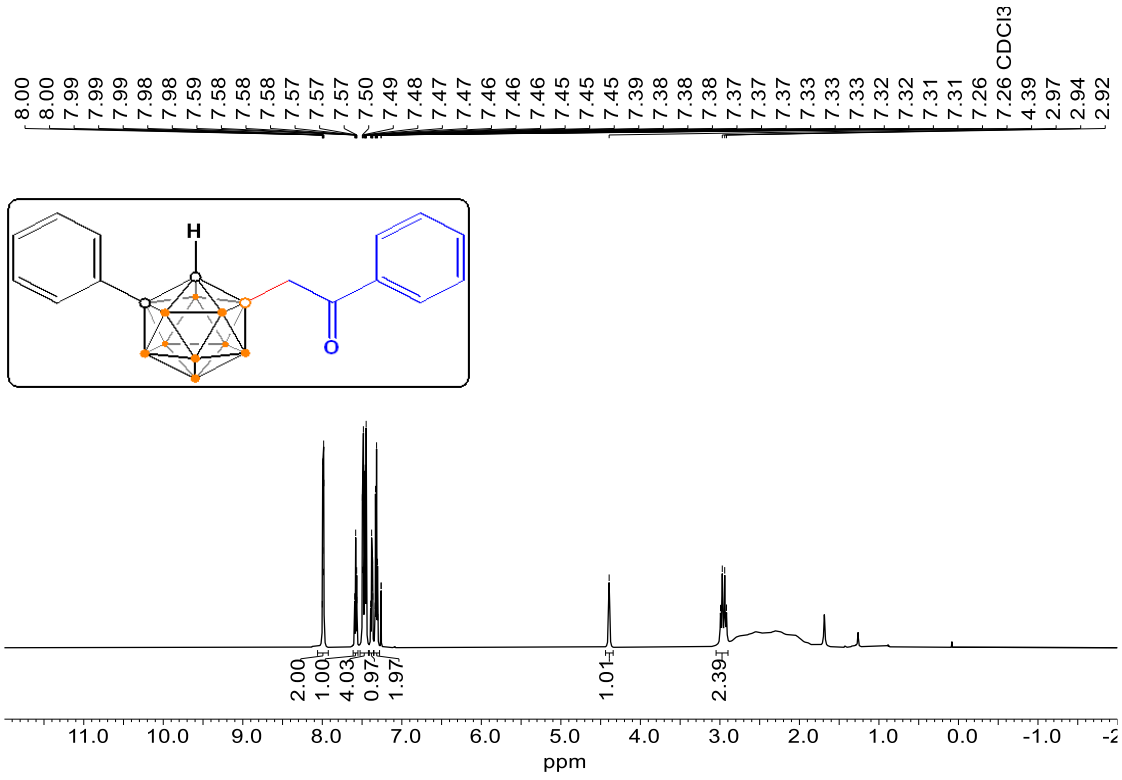
6. Crystallographic data

Table S3. Crystallographic data of compounds **3b**, **3l, 7 and A2·H_2O**.

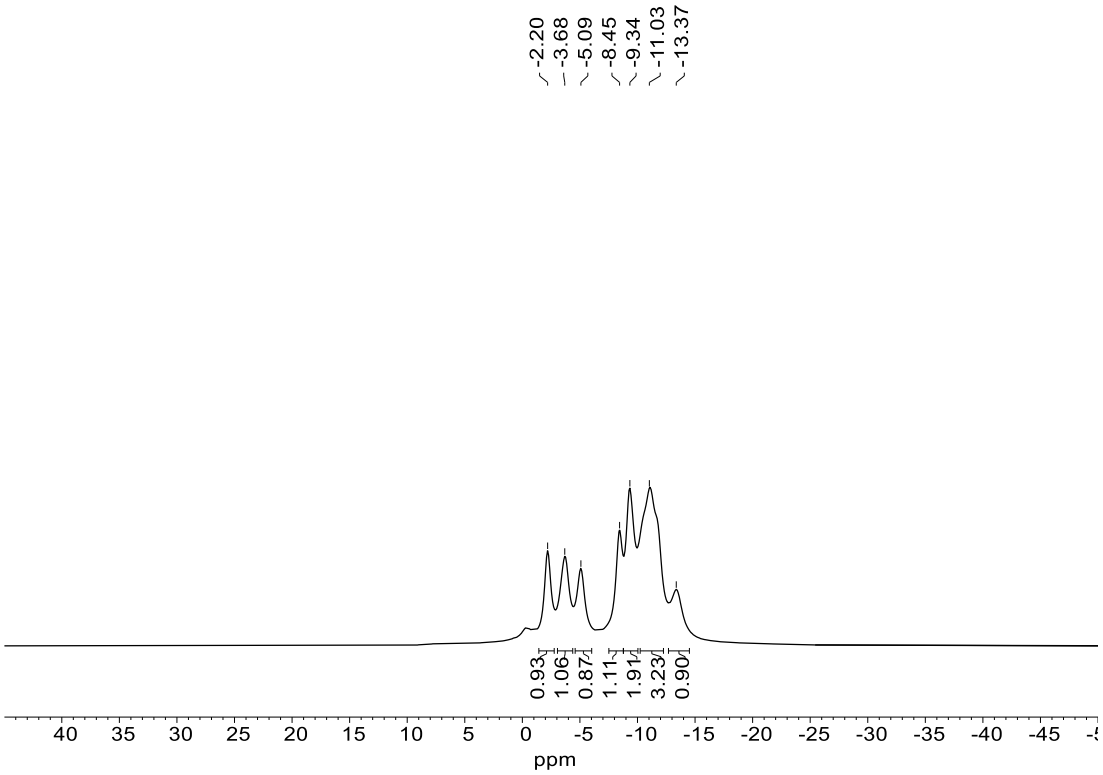
	3b	**3l**	**7**	**A2·H_2O**
Empirical formula	$C_{17}H_{24}B_{10}O$	$C_{16}H_{21}B_{10}NO_3$	$C_{16}H_{21}B_{10}BrO$	$C_{24}H_{38}B_{20}O_5Ru$
Formula weight	352.46	383.44	417.34	723.81
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	P-1	$P2_1/n$	Pbca
a/Å	10.2082(11)	10.0973(4)	10.5191(2)	20.4669(2)
b/Å	10.3206(9)	10.5194(3)	10.8321(3)	12.00586(15)
c/Å	10.8736(9)	10.8504(5)	18.0396(4)	28.6857(3)
α/deg	95.963(7)	103.664(3)	90	90
β/deg	114.424(10)	111.893(4)	98.262(2)	90
γ/deg	96.569(8)	96.953(3)	90	90
V/$Å^3$	1021.64(18)	1010.78(7)	2034.17(8)	7048.75(14)
Z	2	2	4	8
ρ_{calcd}(g cm^{-3})	1.146	1.260	1.363	1.364
μ/mm^{-1}	0.443	0.584	2.747	3.863
F(000)	368.0	396.0	840.0	2928.0
2θ range (deg)	8.748/144.004	8.894/142.996	9.198/142.69	7.526/140.89
no. of rflns collected	8499	8588	8822	22139
no. of indep rflns	3893	3849	3881	6568
GoF on F^2	1.104	1.074	1.032	1.027
R1/wR2 (I> 2σ(I))	0.0701/0.2045	0.0629/0.1732	0.0465/0.1255	0.0527/0.1459
R1/wR2 (all data)	0.0952/0.2243	0.0709/0.1813	0.0529/0.1326	0.0683/0.1612
largest peak/hole (e $Å^{-1}$)	0.37/−0.22	0.34/−0.33	0.79/−0.77	1.40/−0.39

7. NMR Spectra

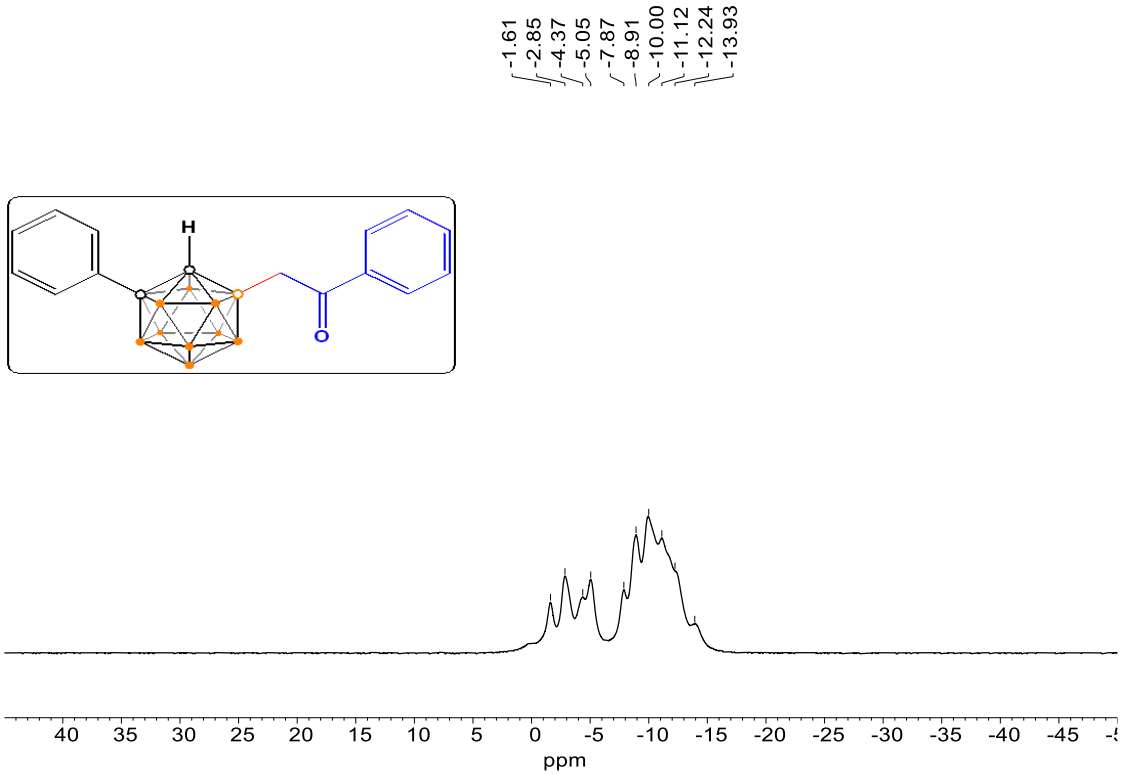
^{1}H NMR (600 MHz, Chloroform-*d*)



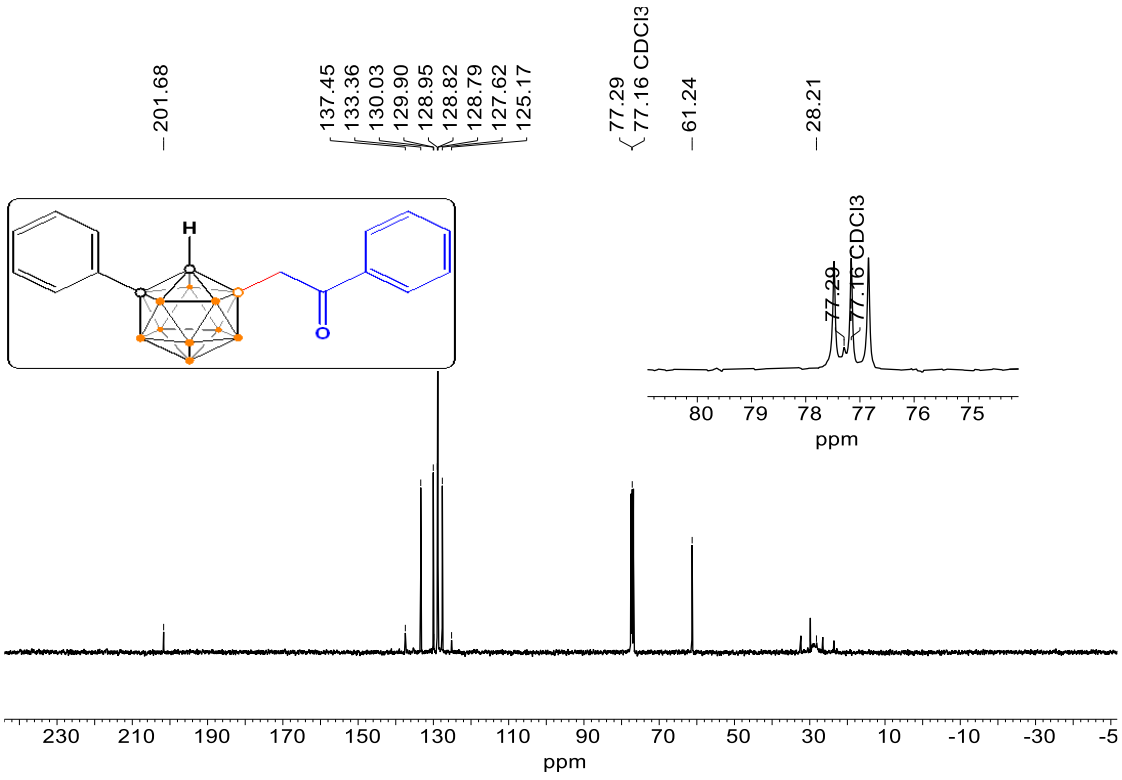
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)



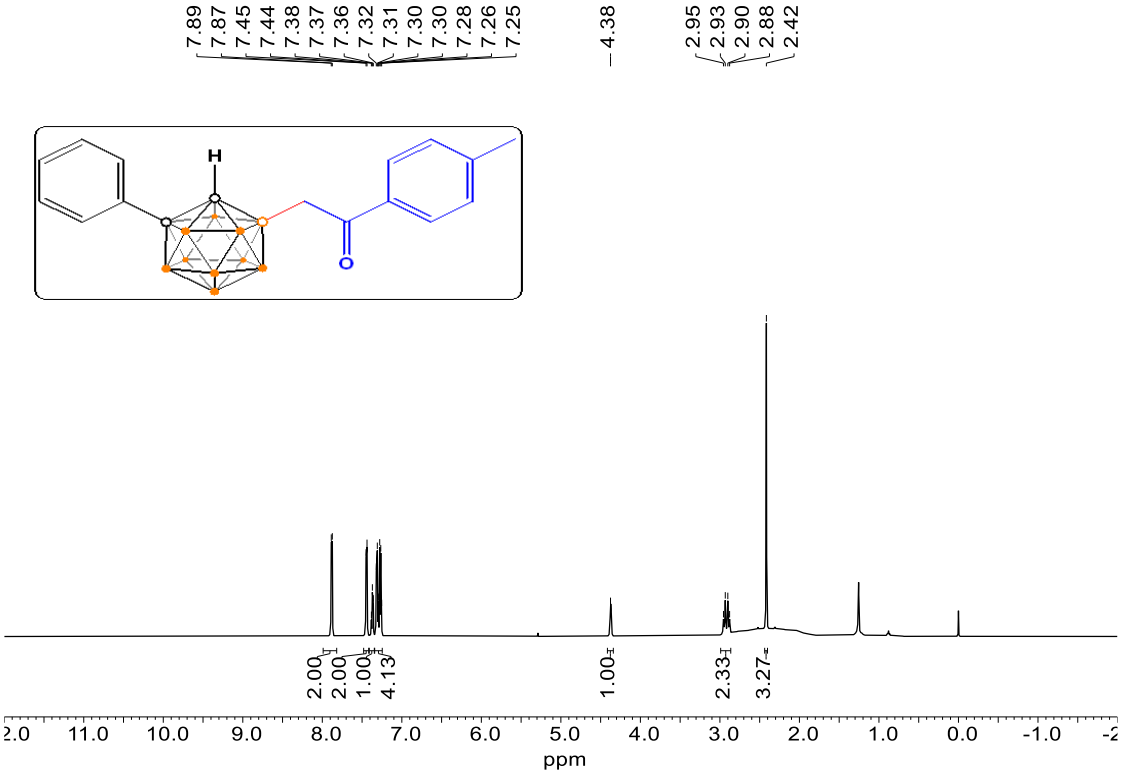
^{11}B NMR (128 MHz, Chloroform-*d*)



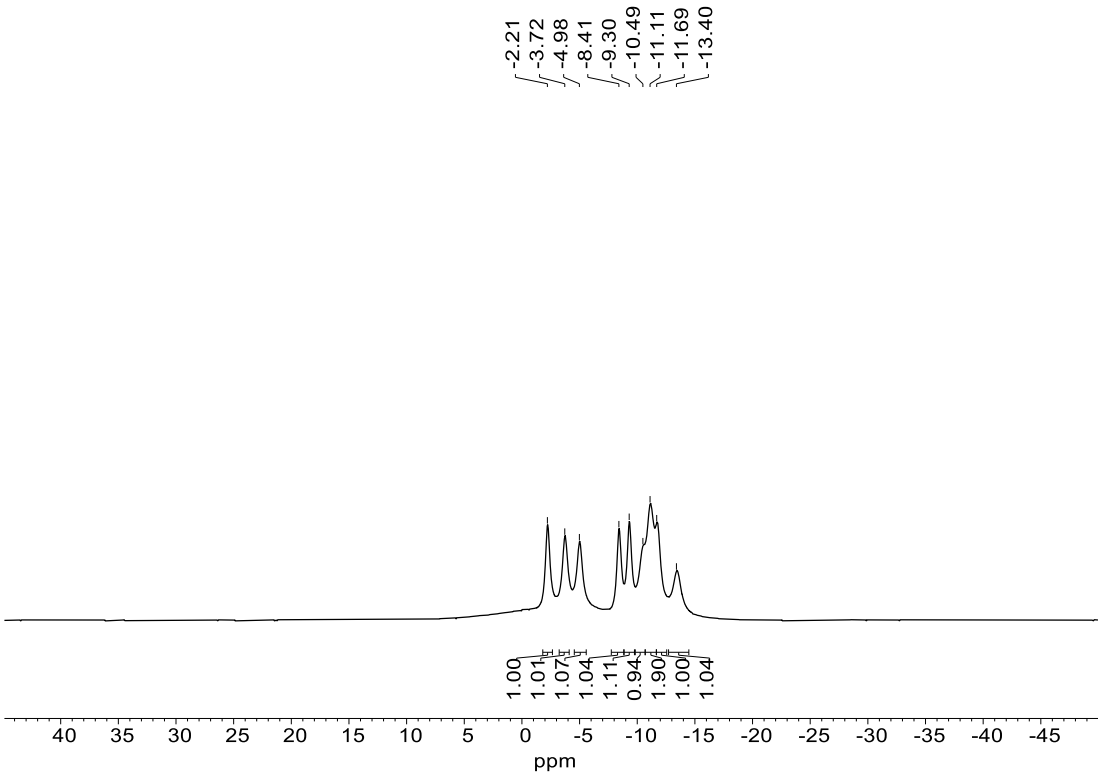
^{13}C NMR (101 MHz, Chloroform-*d*)



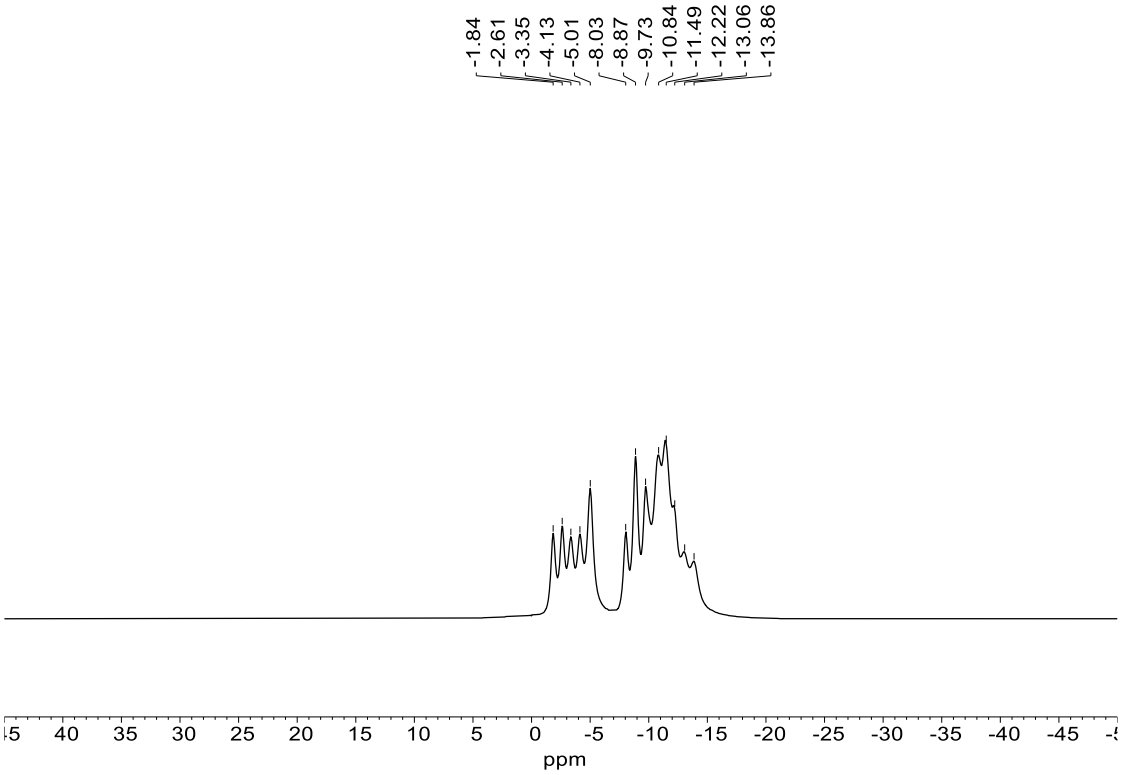
^{1}H NMR (600 MHz, Chloroform-*d*)



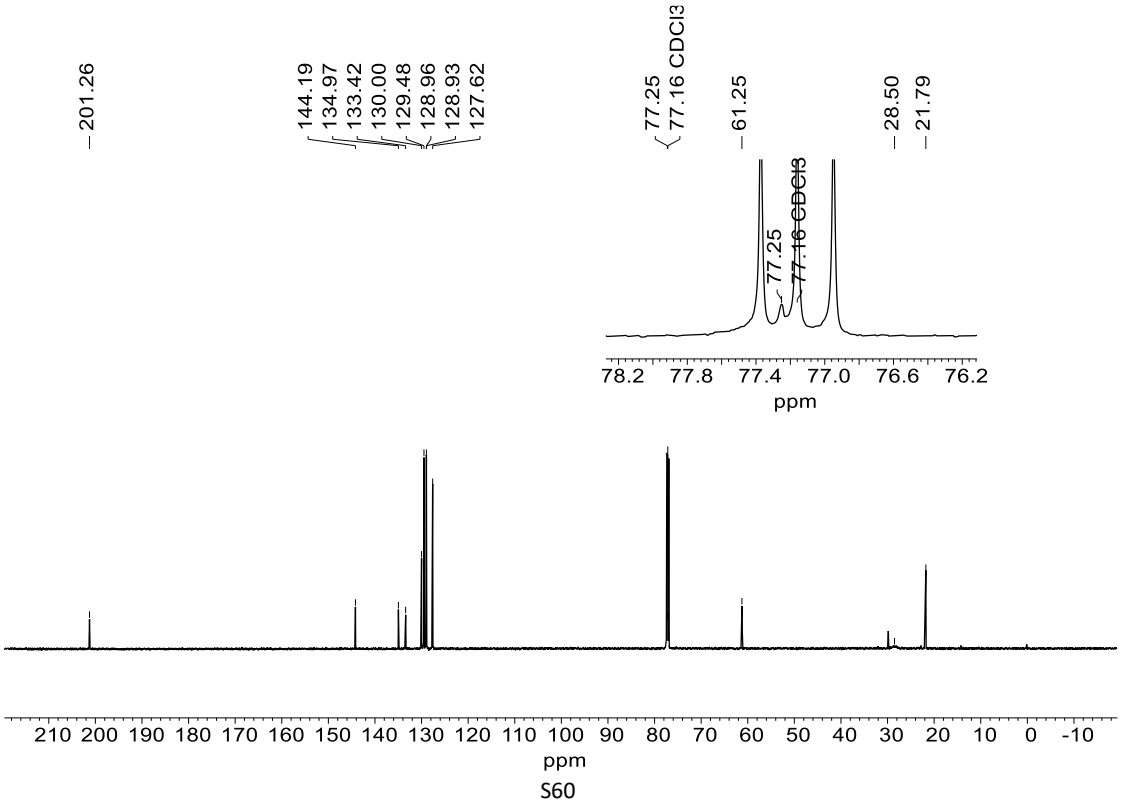
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



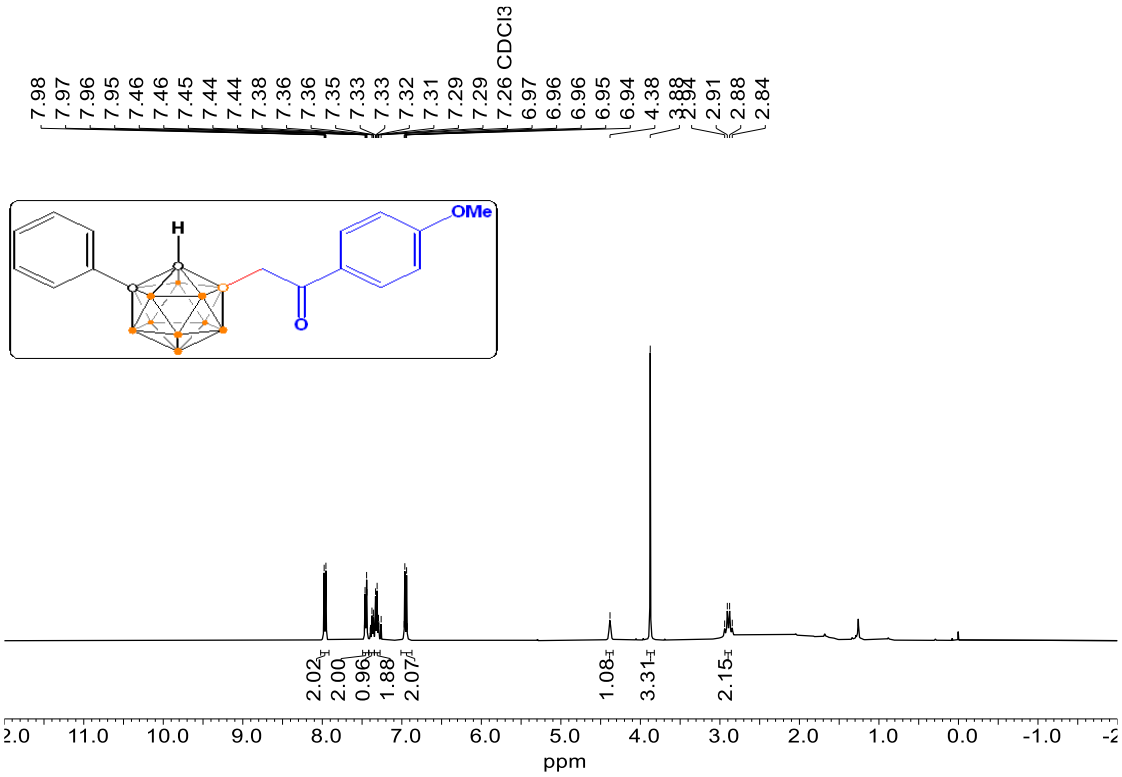
^{11}B NMR (193 MHz, Chloroform-*d*)



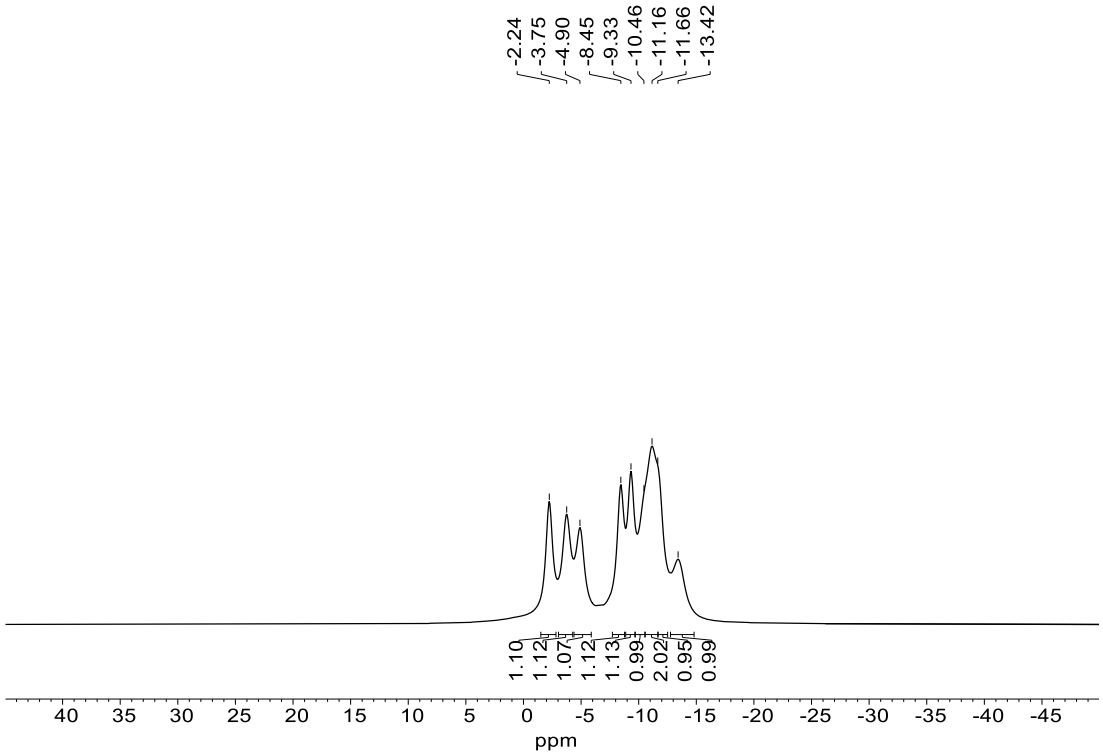
^{13}C NMR (151 MHz, Chloroform-*d*)



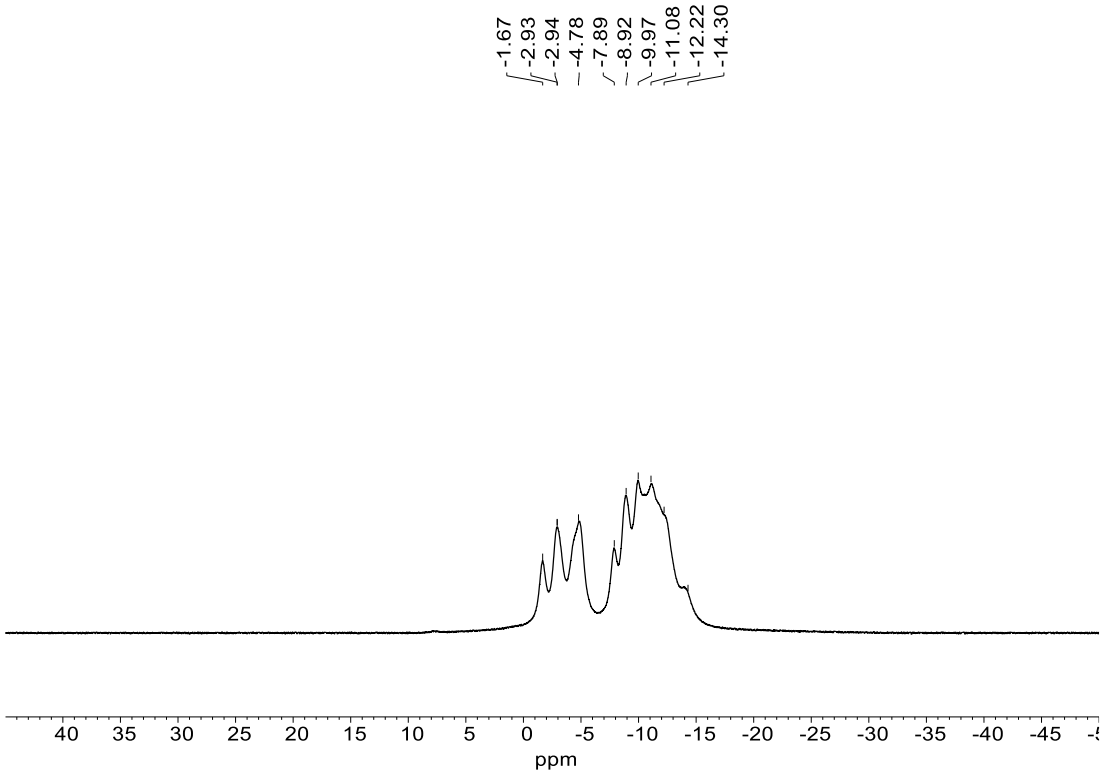
^{1}H NMR (400 MHz, Chloroform-*d*)



^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)



^{11}B NMR (128 MHz, Chloroform-*d*)



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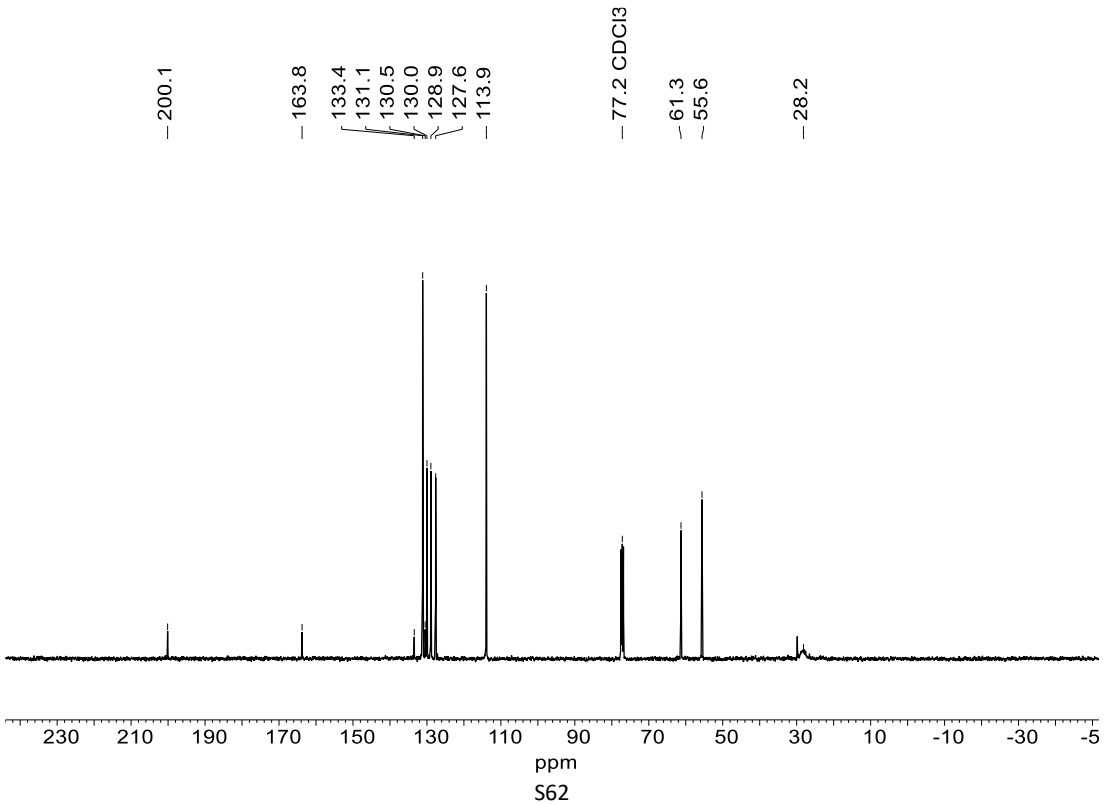
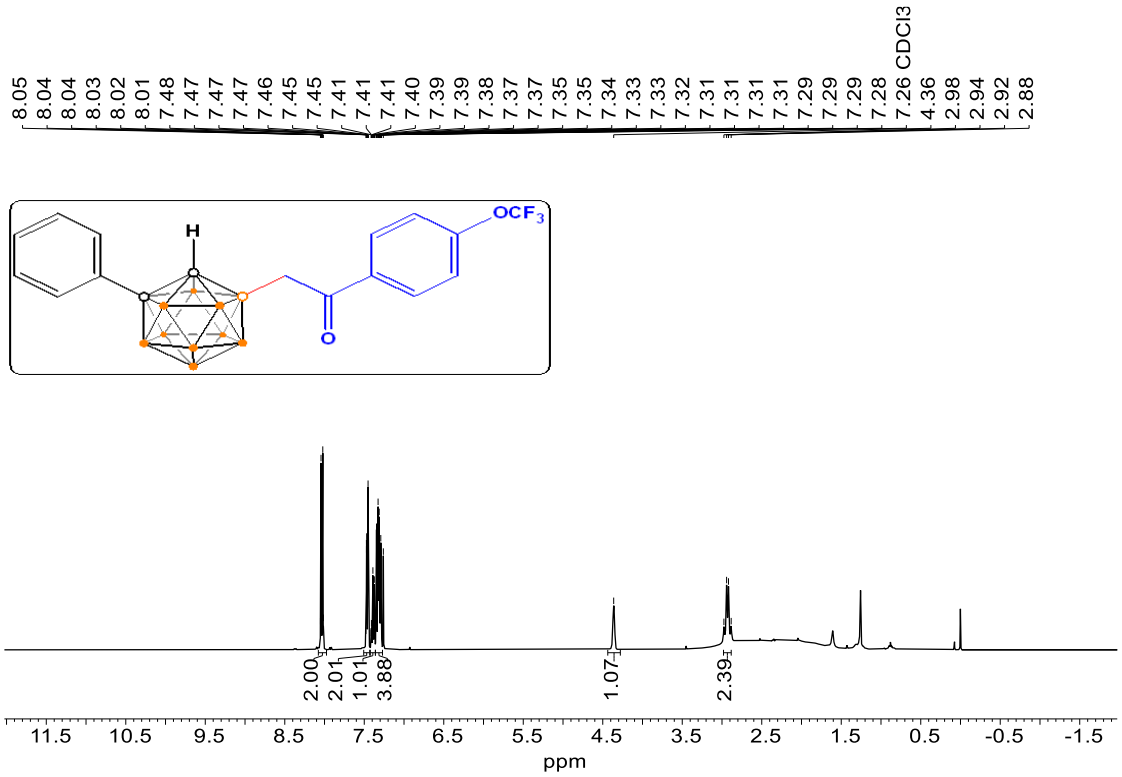
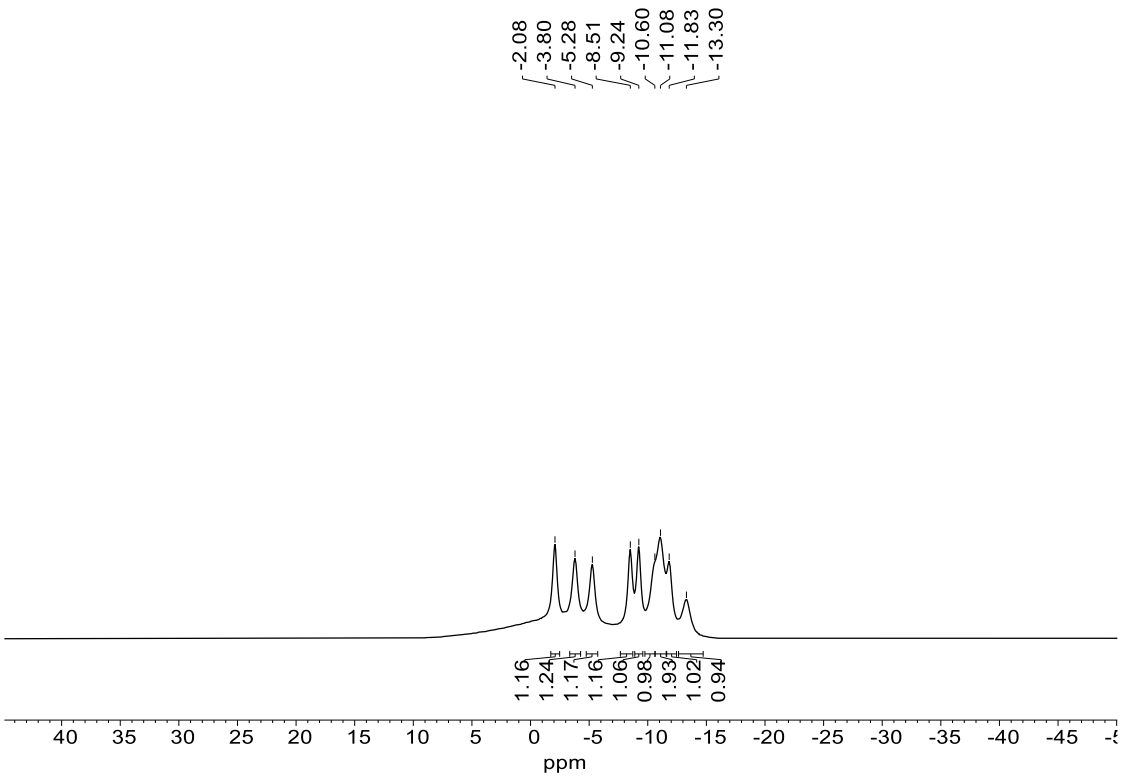


^{1}H NMR (400 MHz, Chloroform-*d*)



^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



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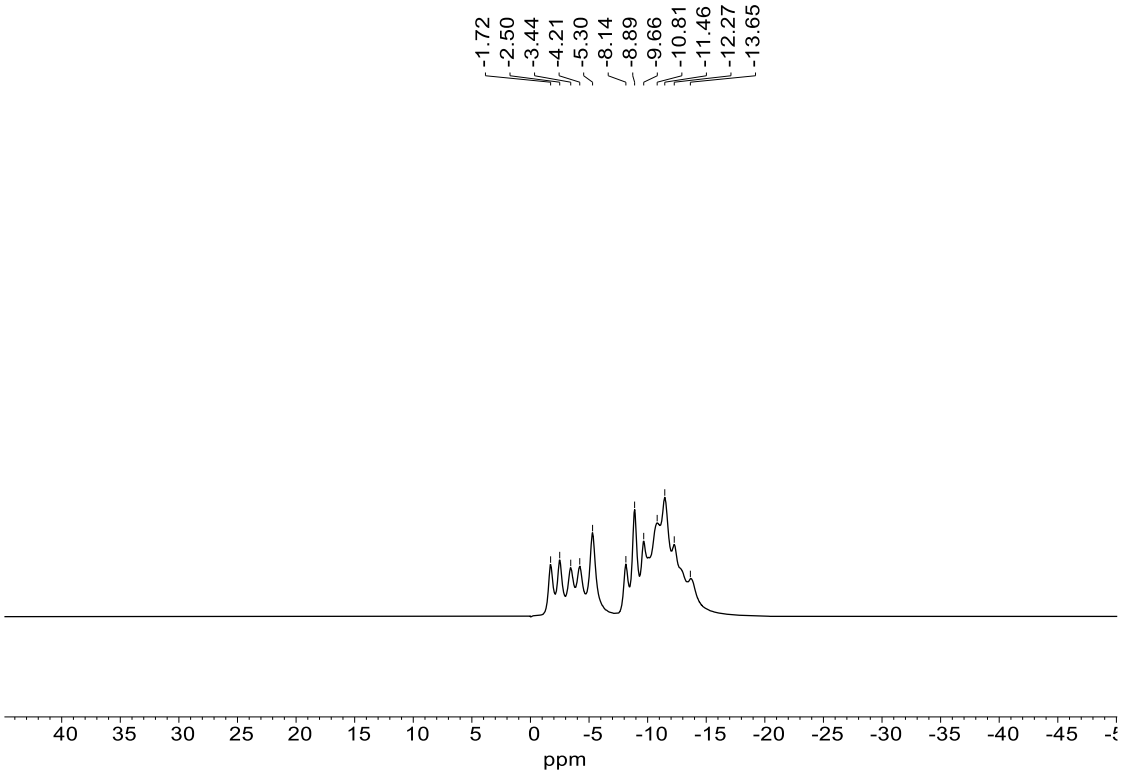
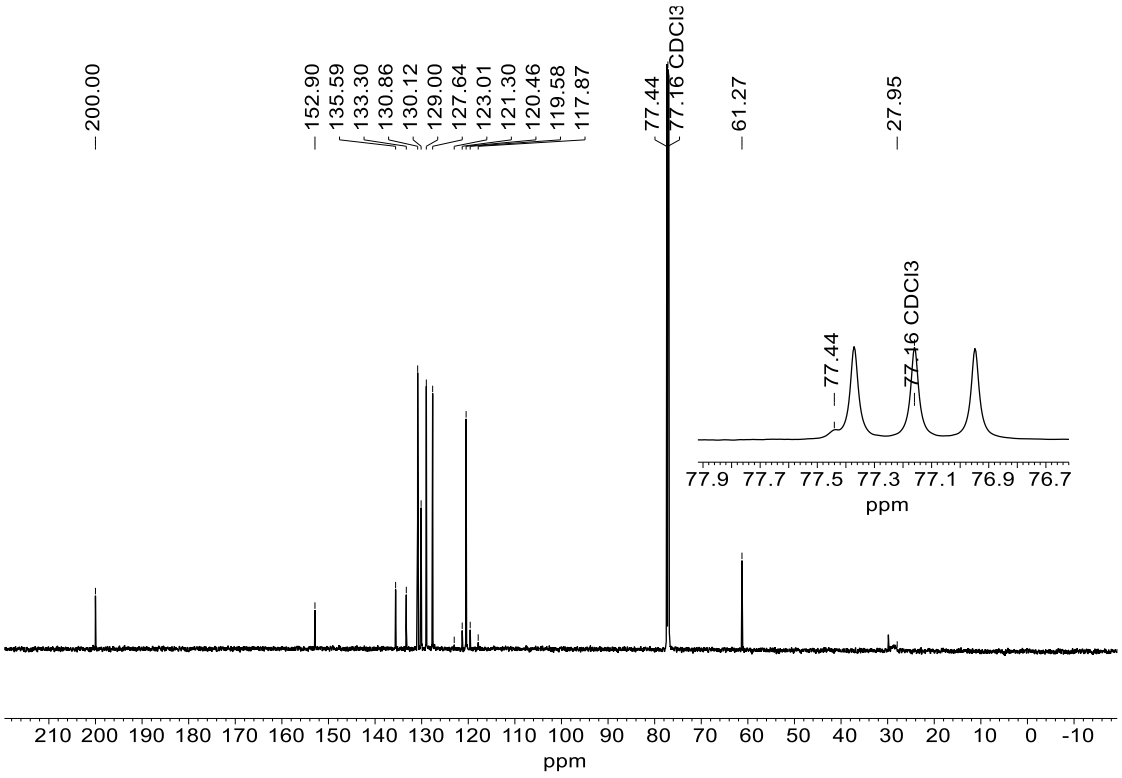
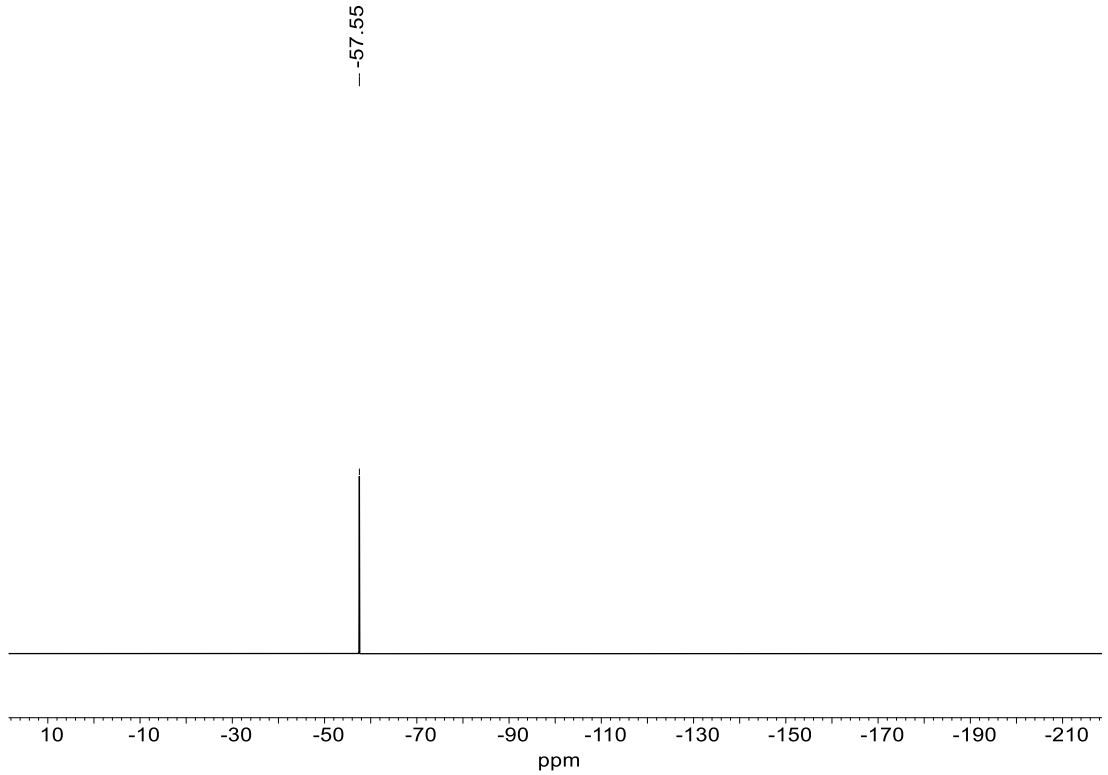


^{13}C NMR (151 MHz, Chloroform-*d*)



^{19}F NMR (565 MHz, Chloroform-*d*)



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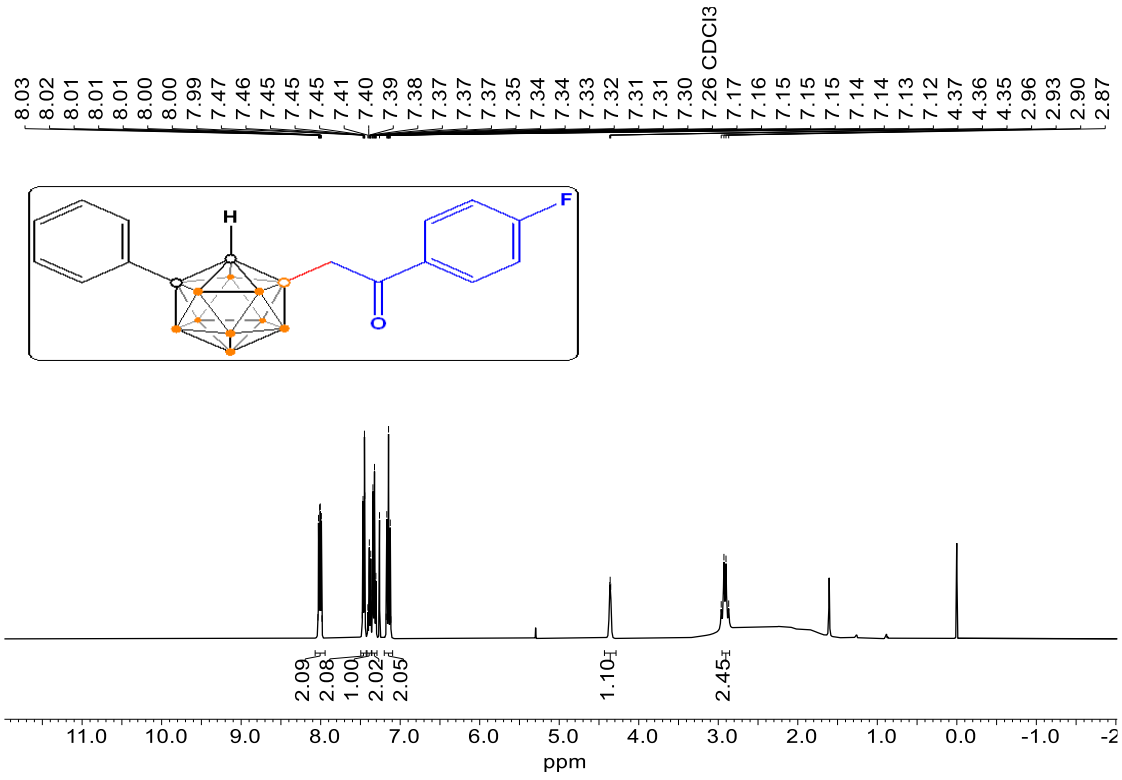
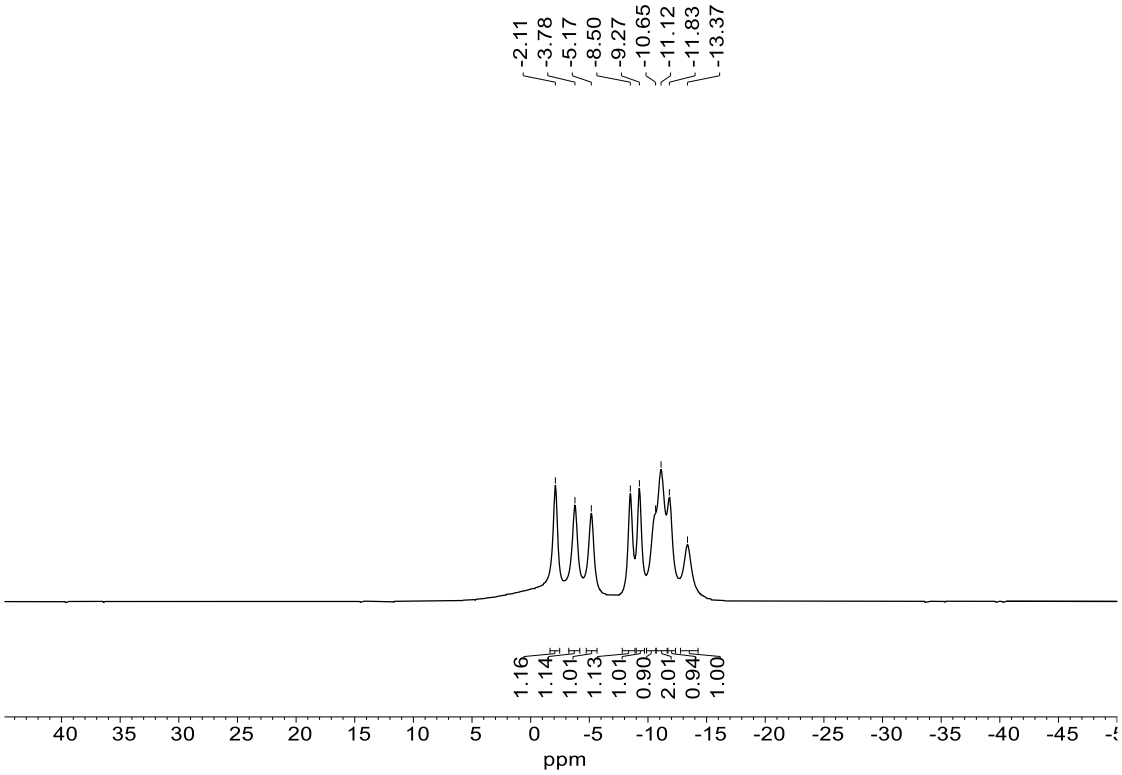
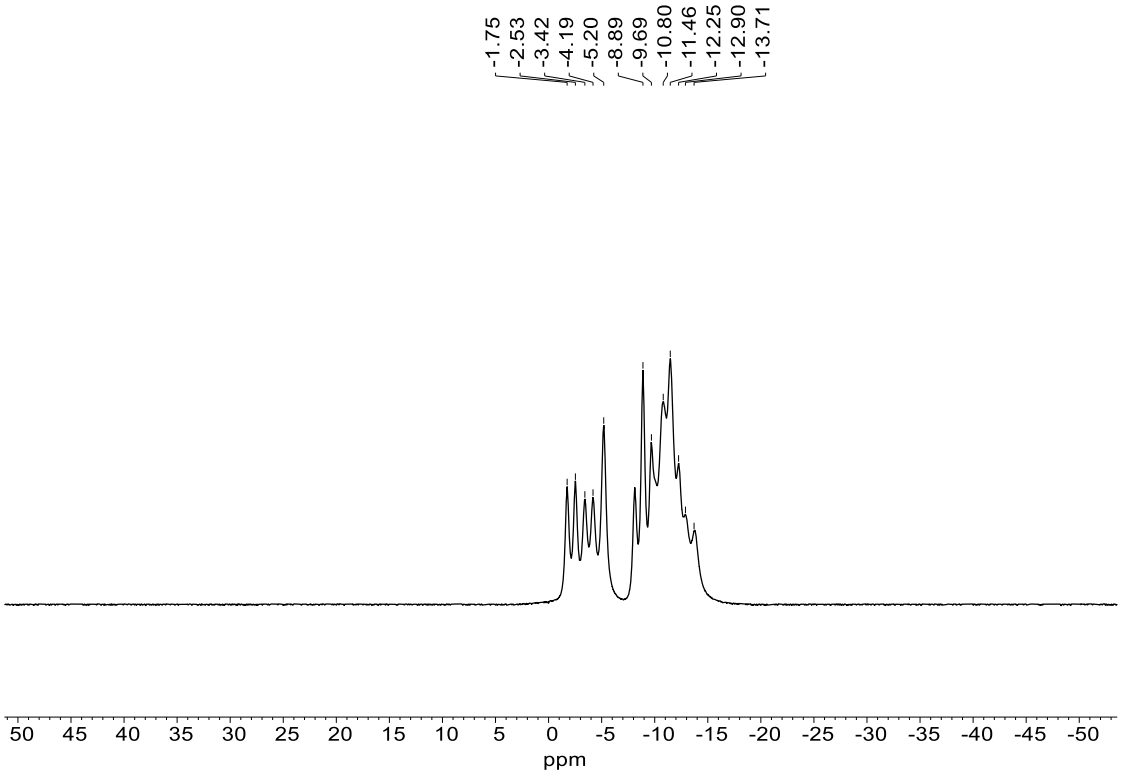


$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



^{11}B NMR (193 MHz, Chloroform-*d*)



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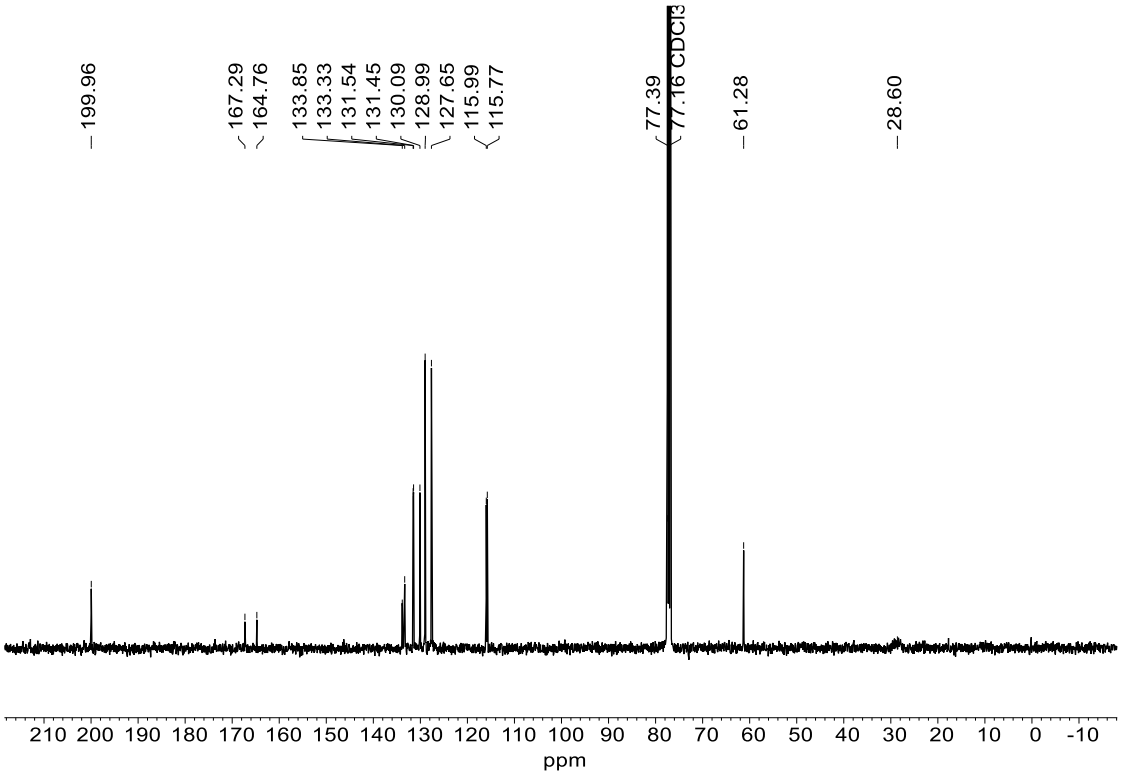
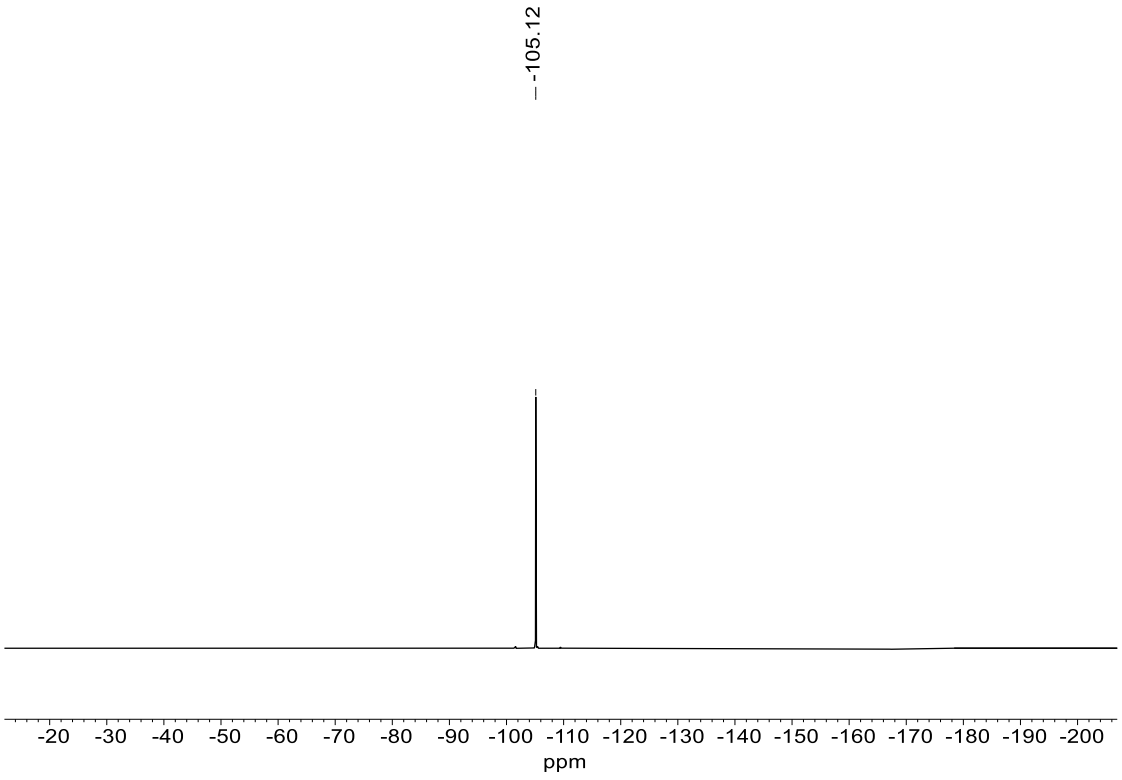


^{19}F NMR (565 MHz, Chloroform-*d*)



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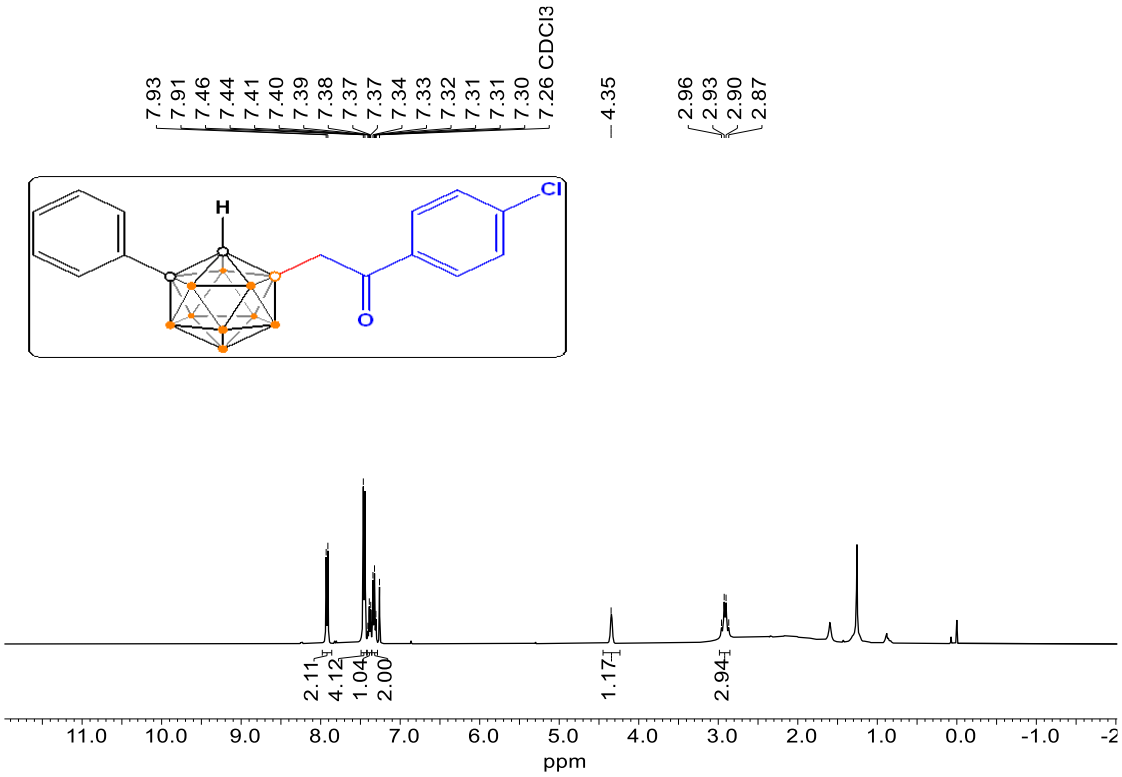

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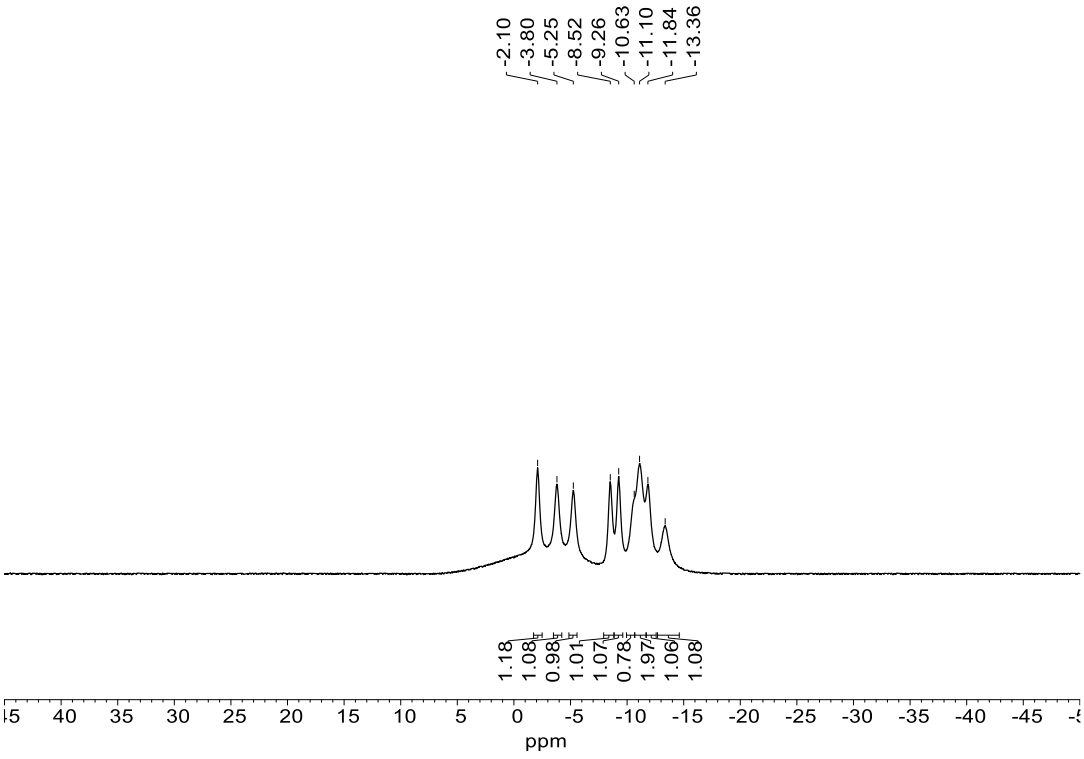

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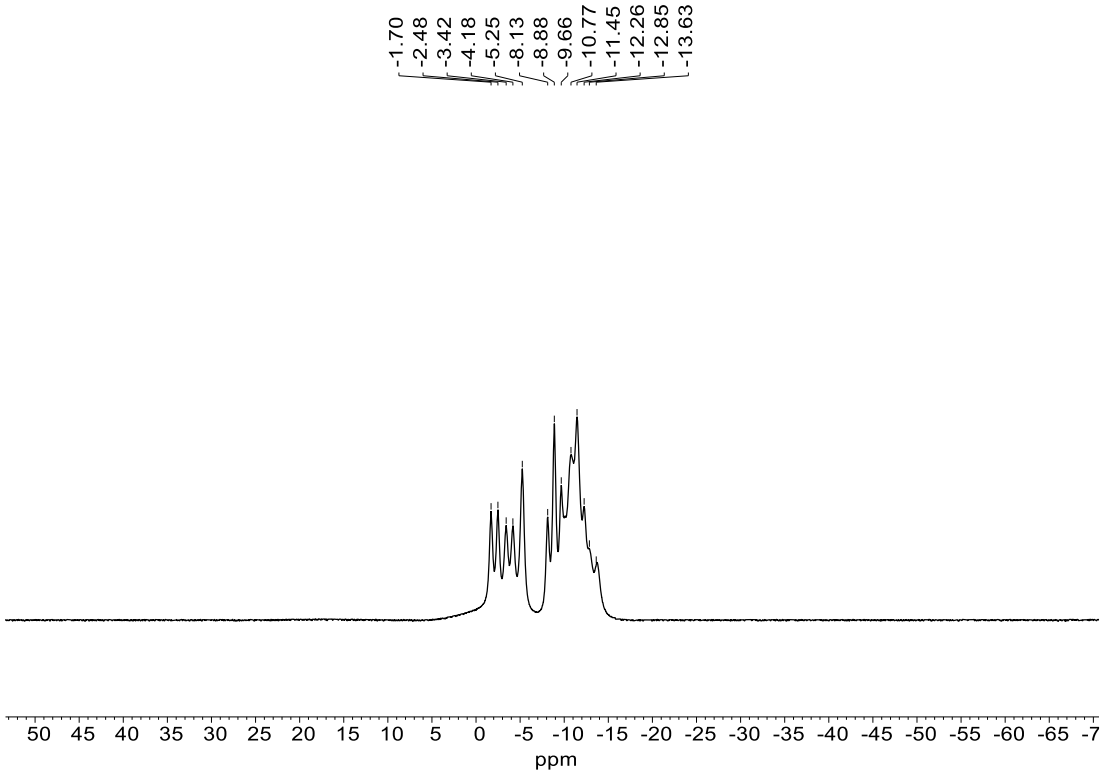

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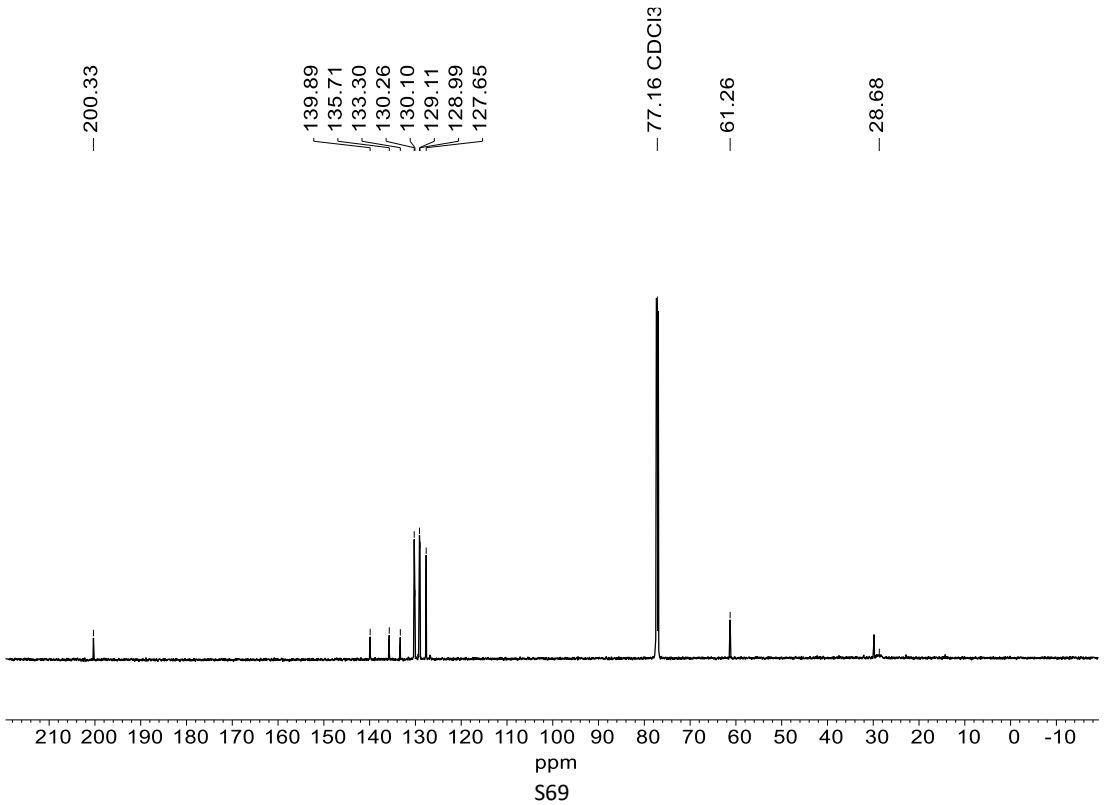

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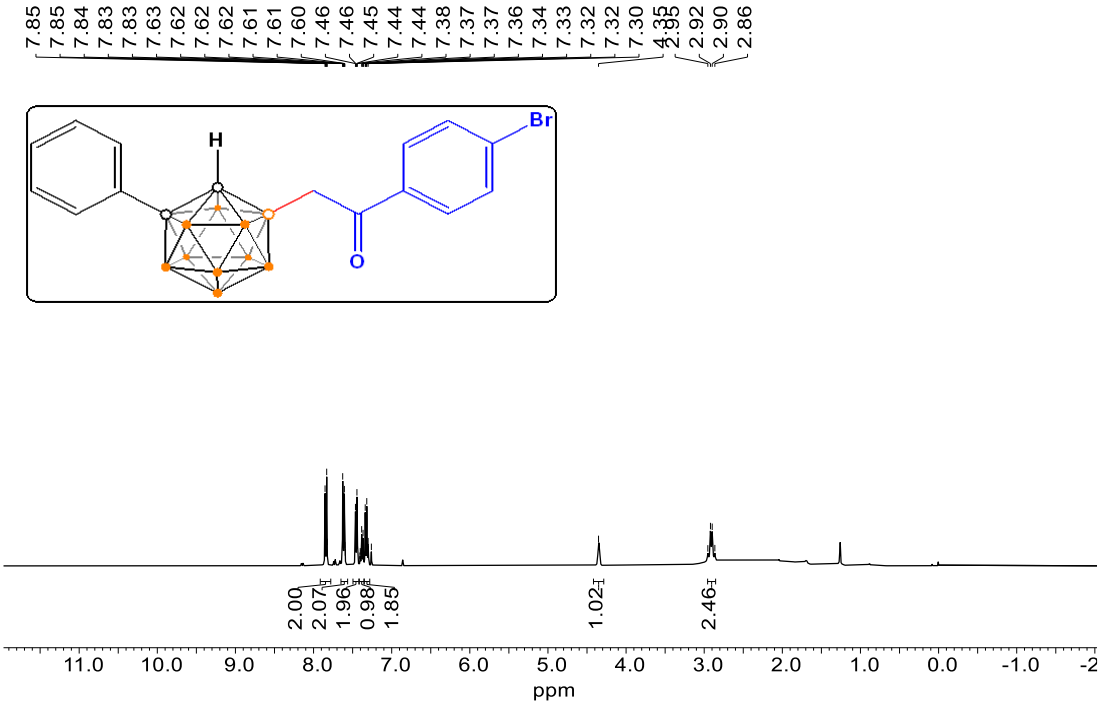

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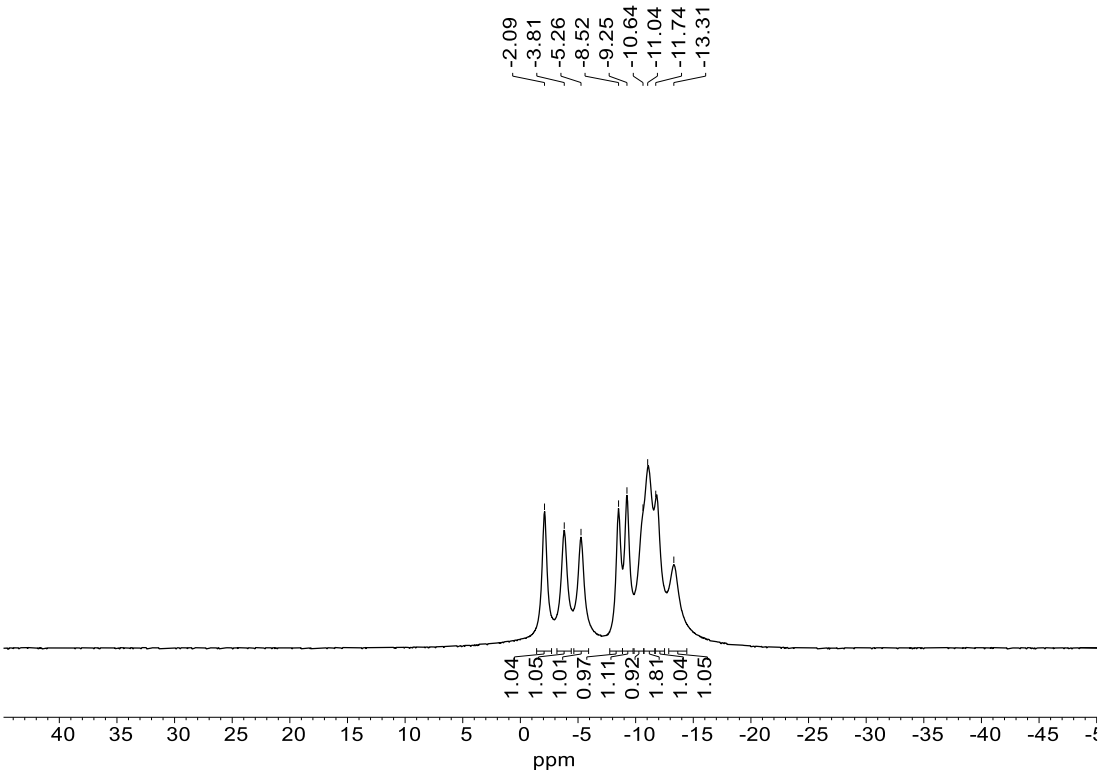

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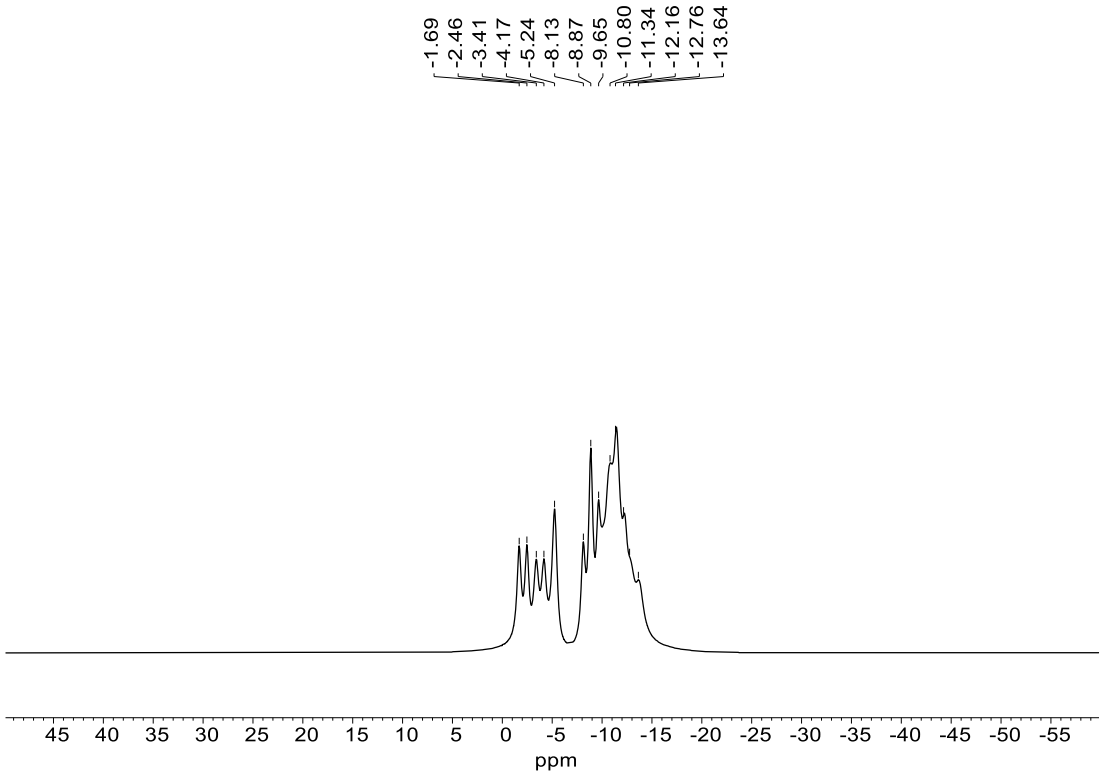

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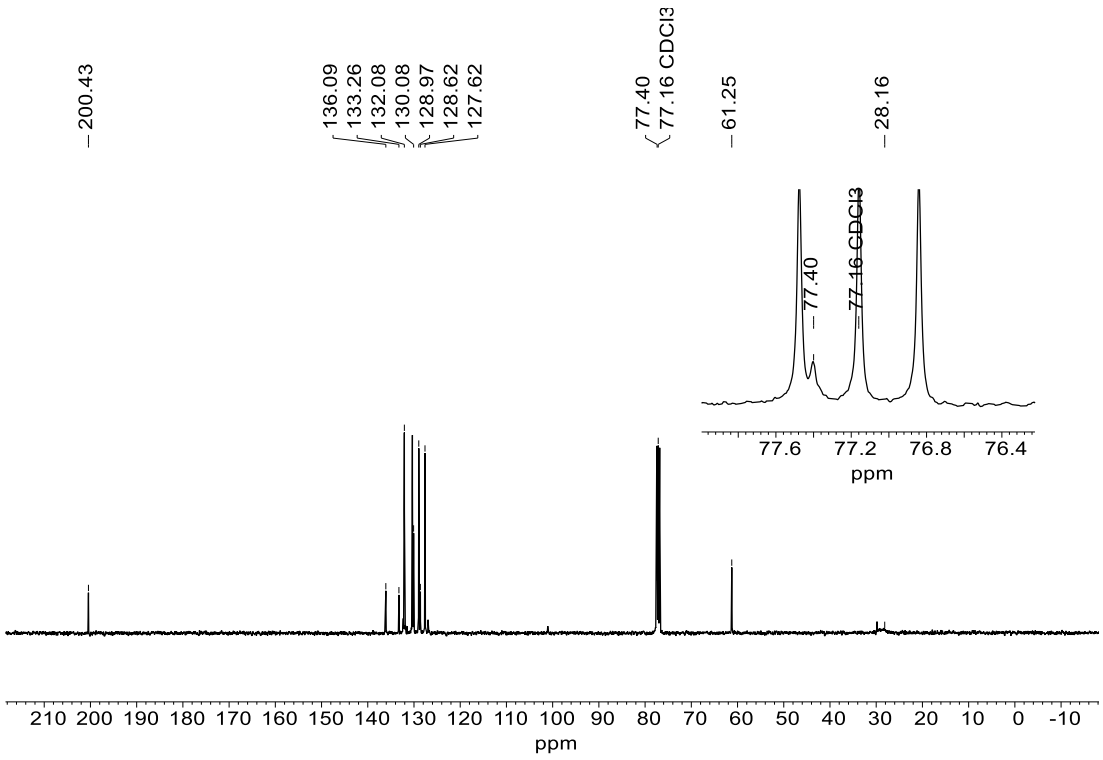

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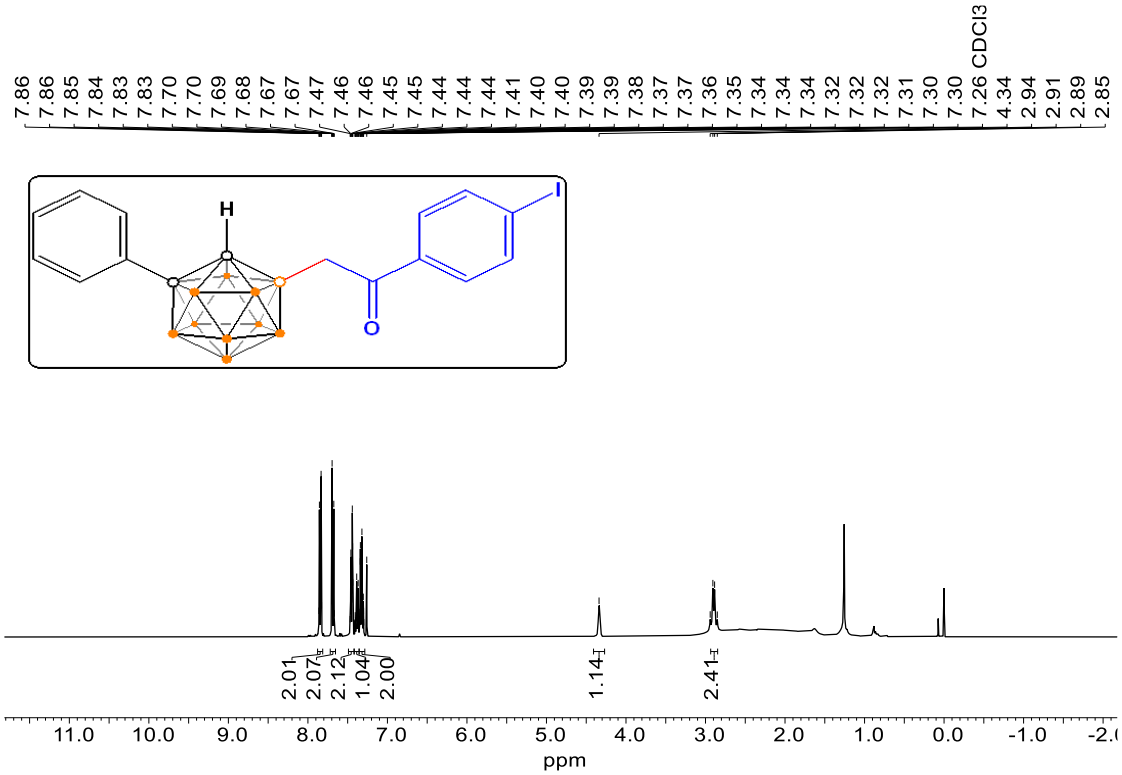

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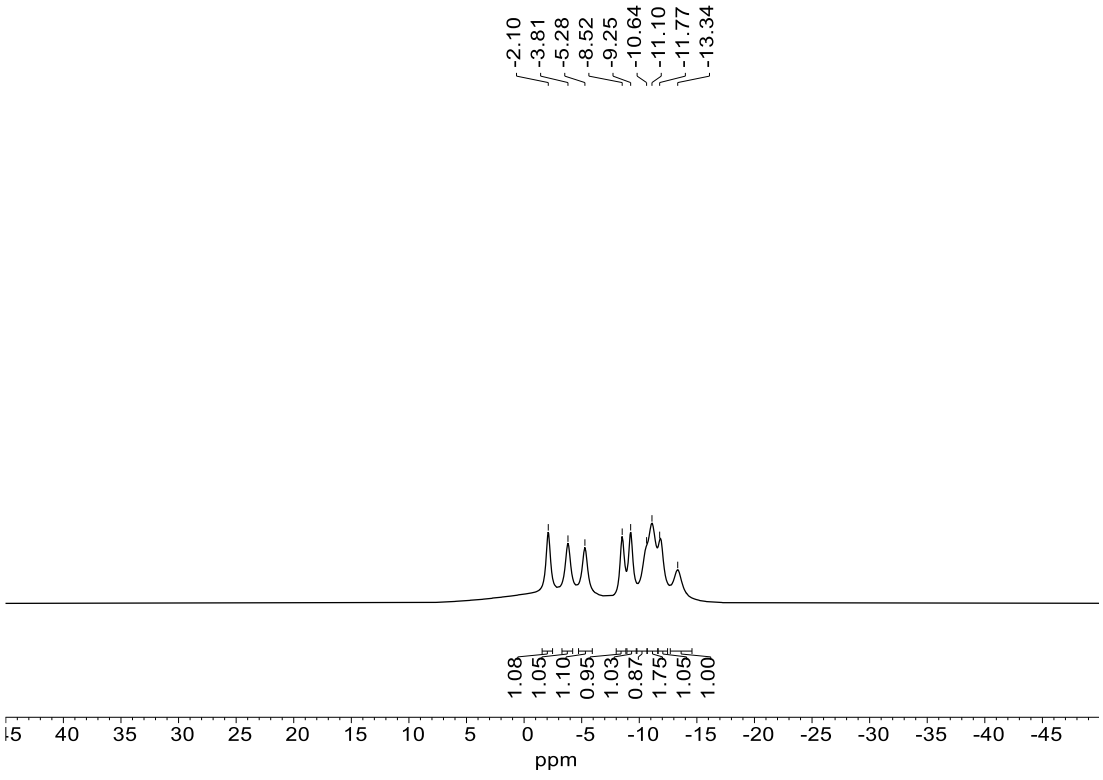

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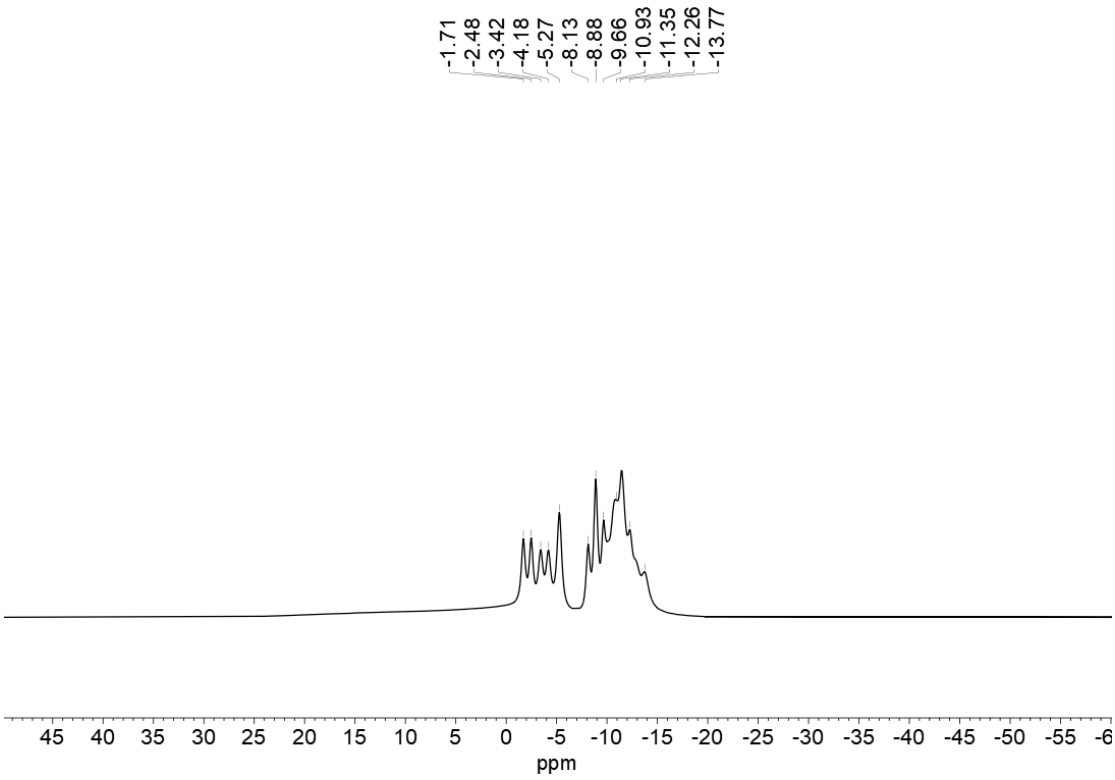

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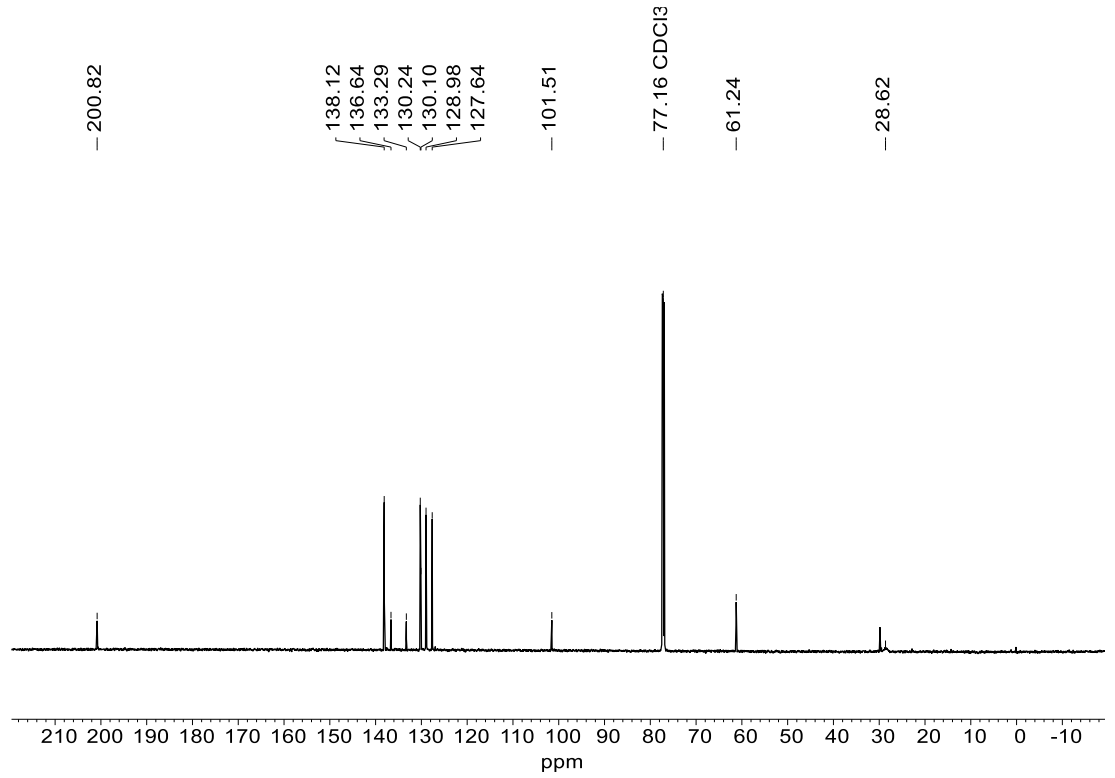
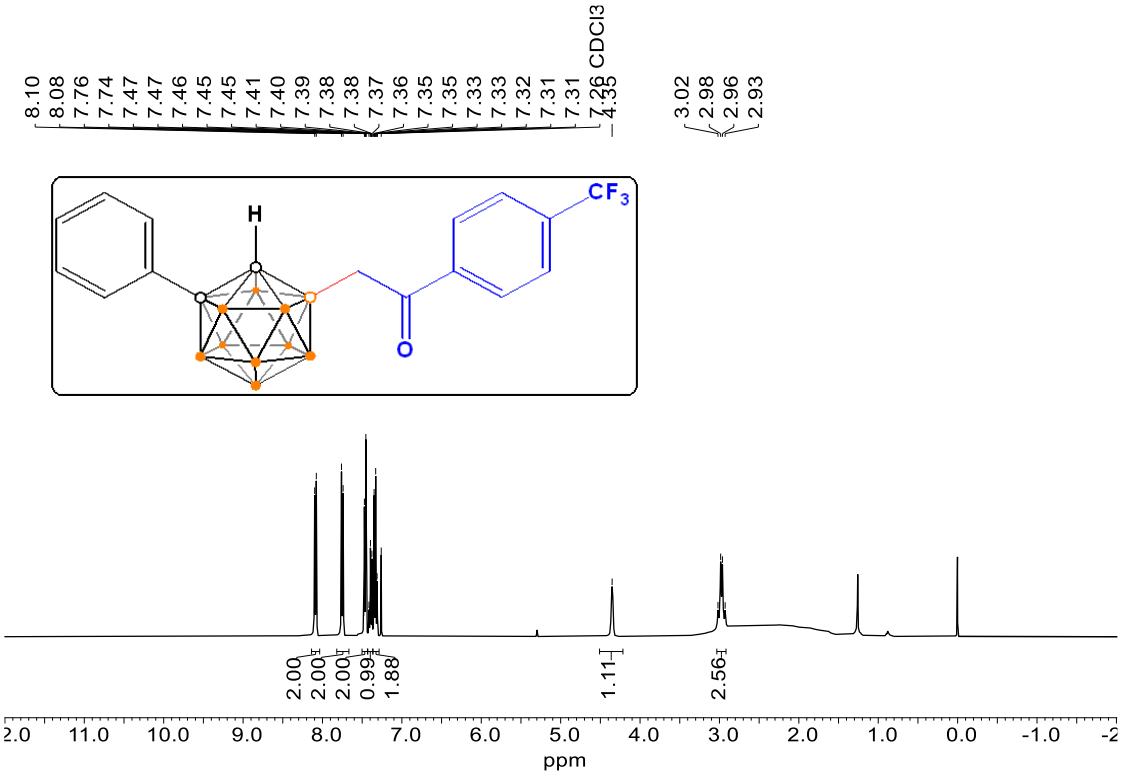
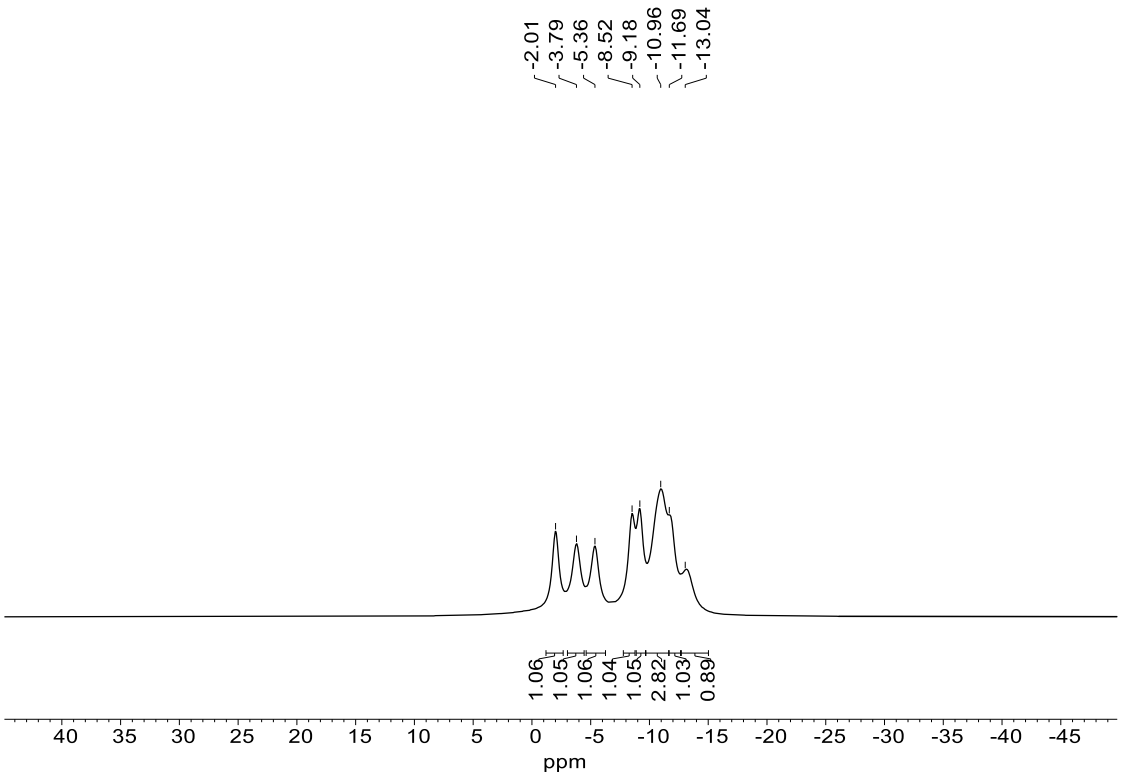


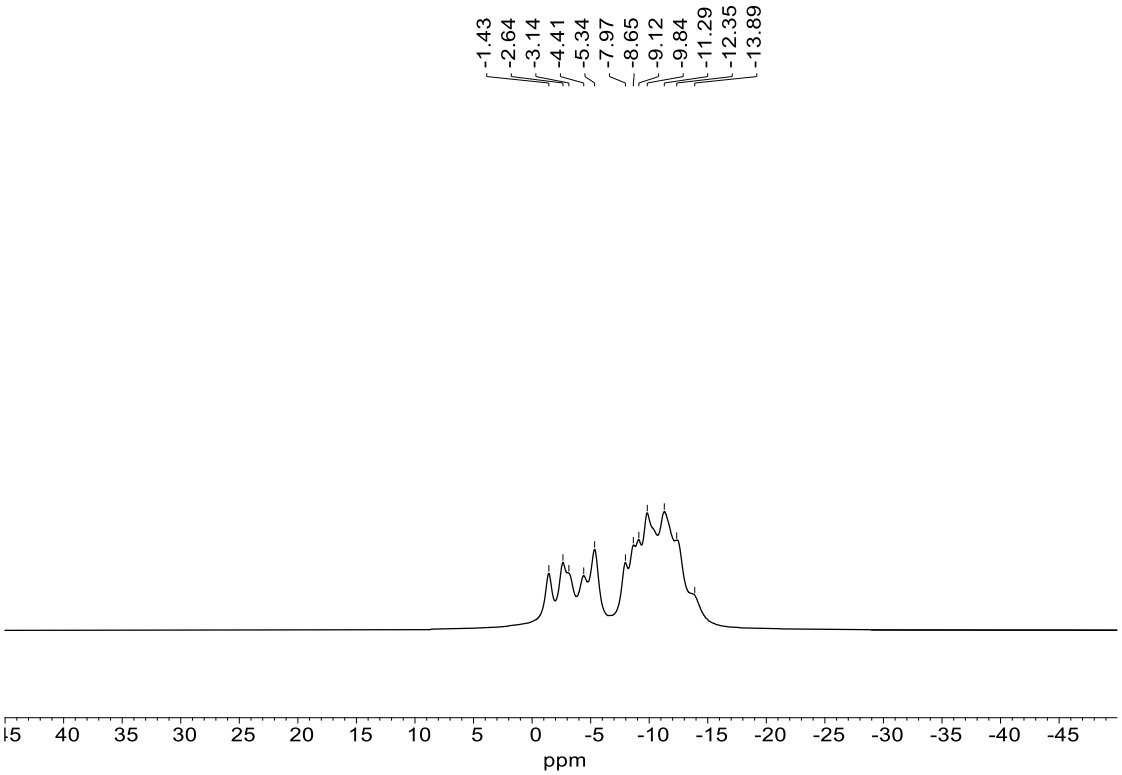
^{1}H NMR (400 MHz, Chloroform-*d*)



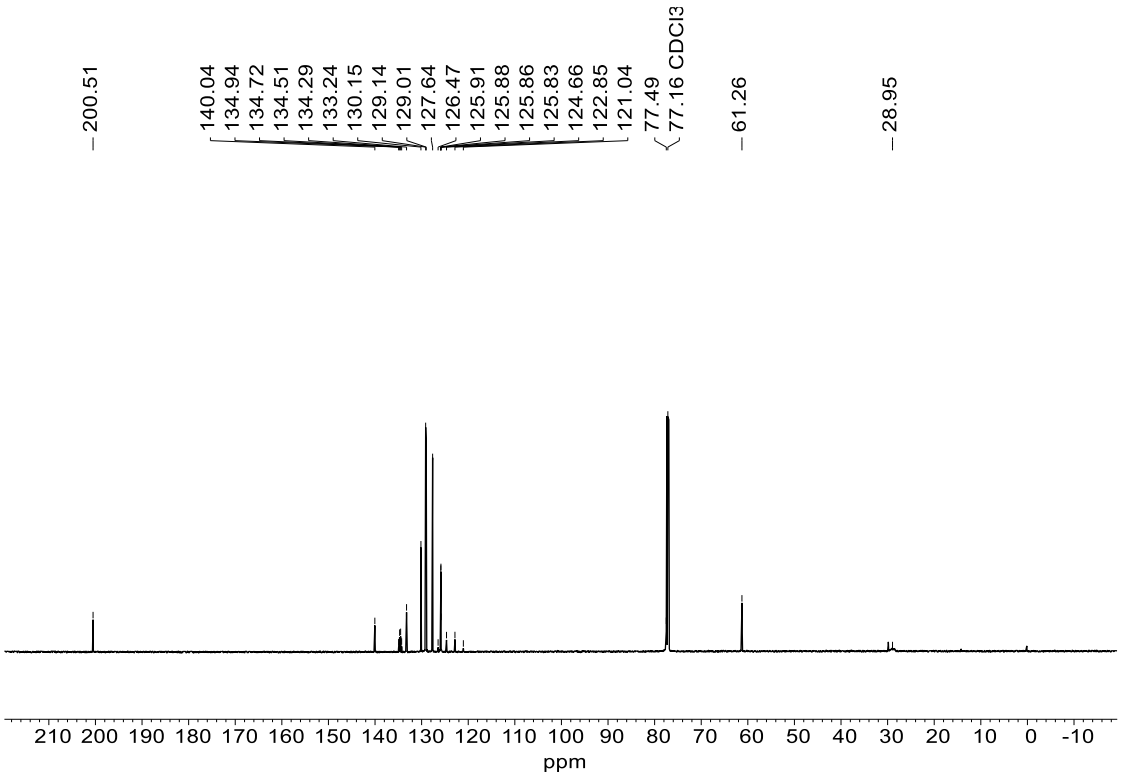
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*)



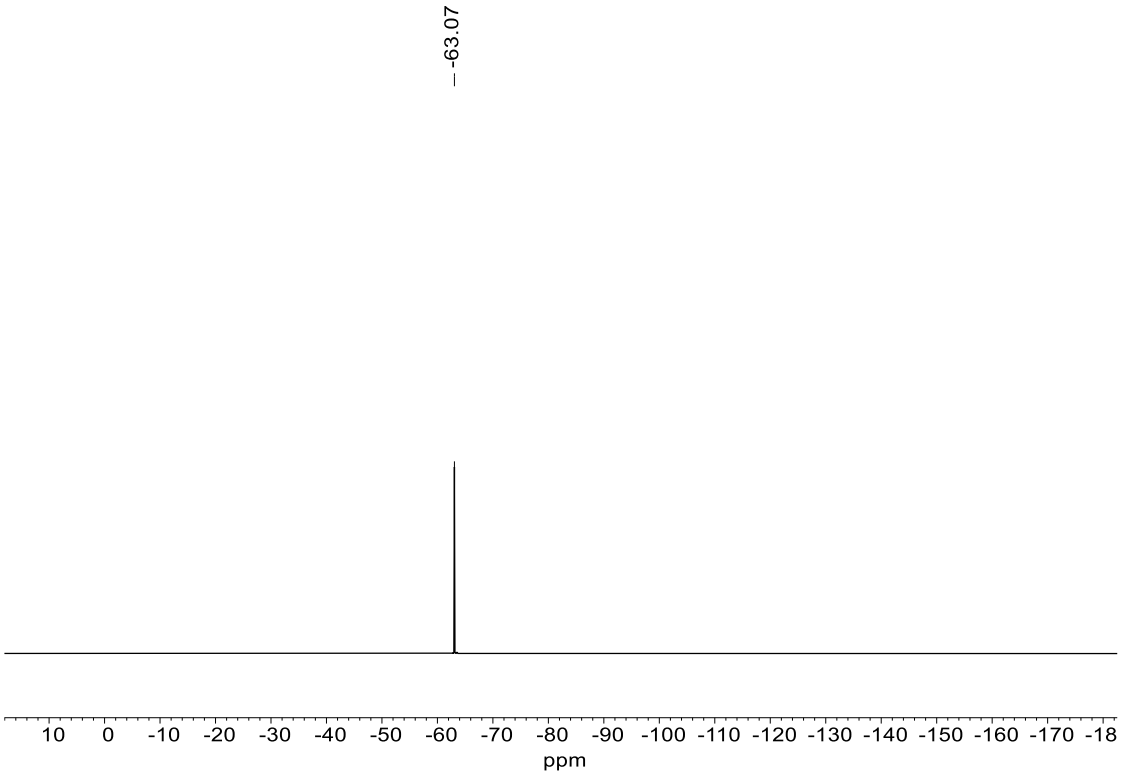
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*)



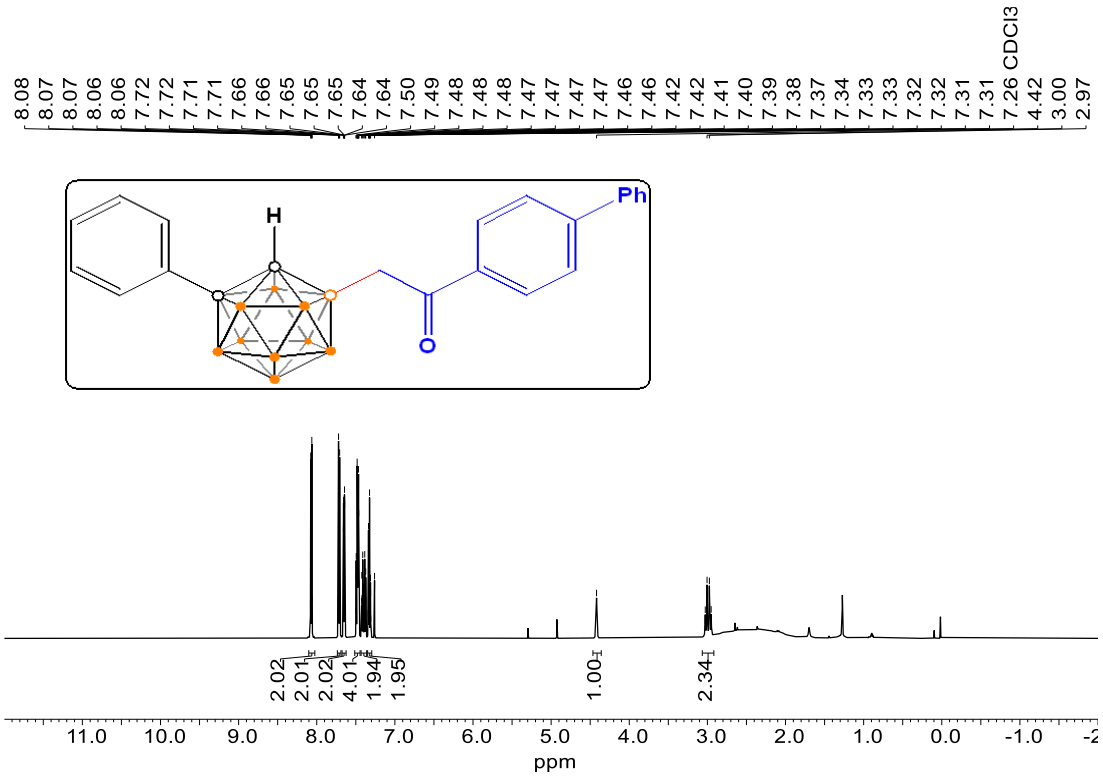
^{13}C NMR (151 MHz, Chloroform-*d*)



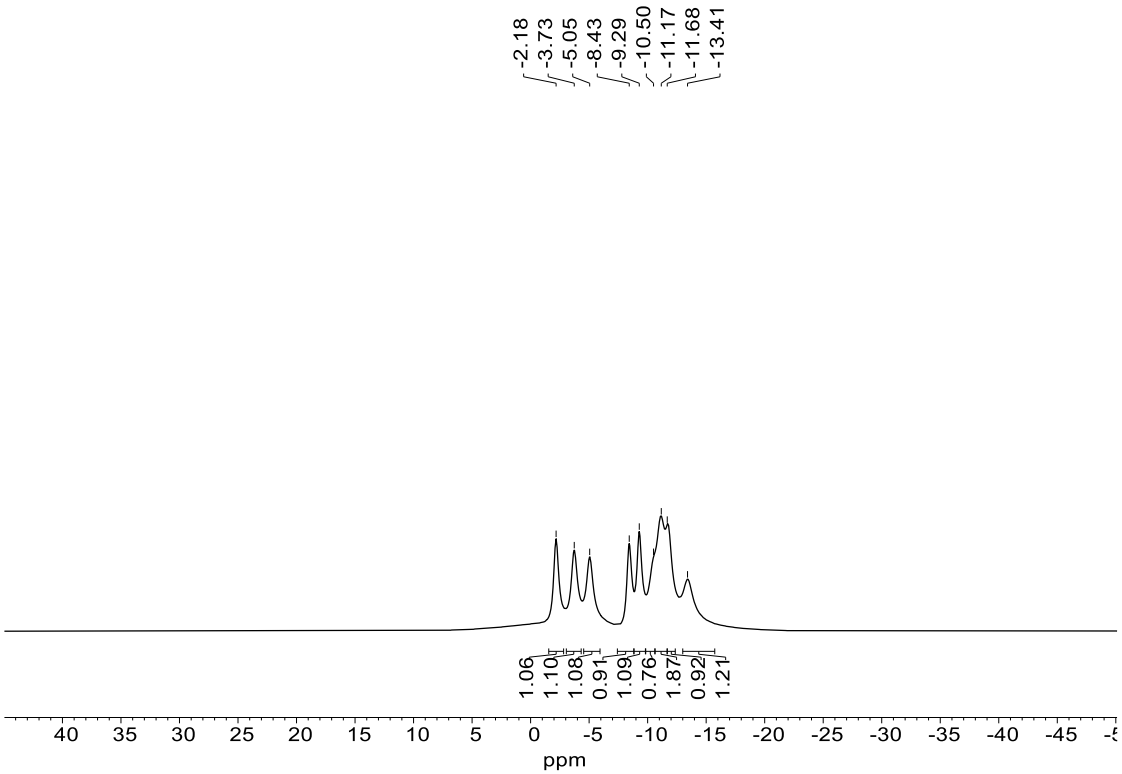
^{19}F NMR (376 MHz, Chloroform-*d*)



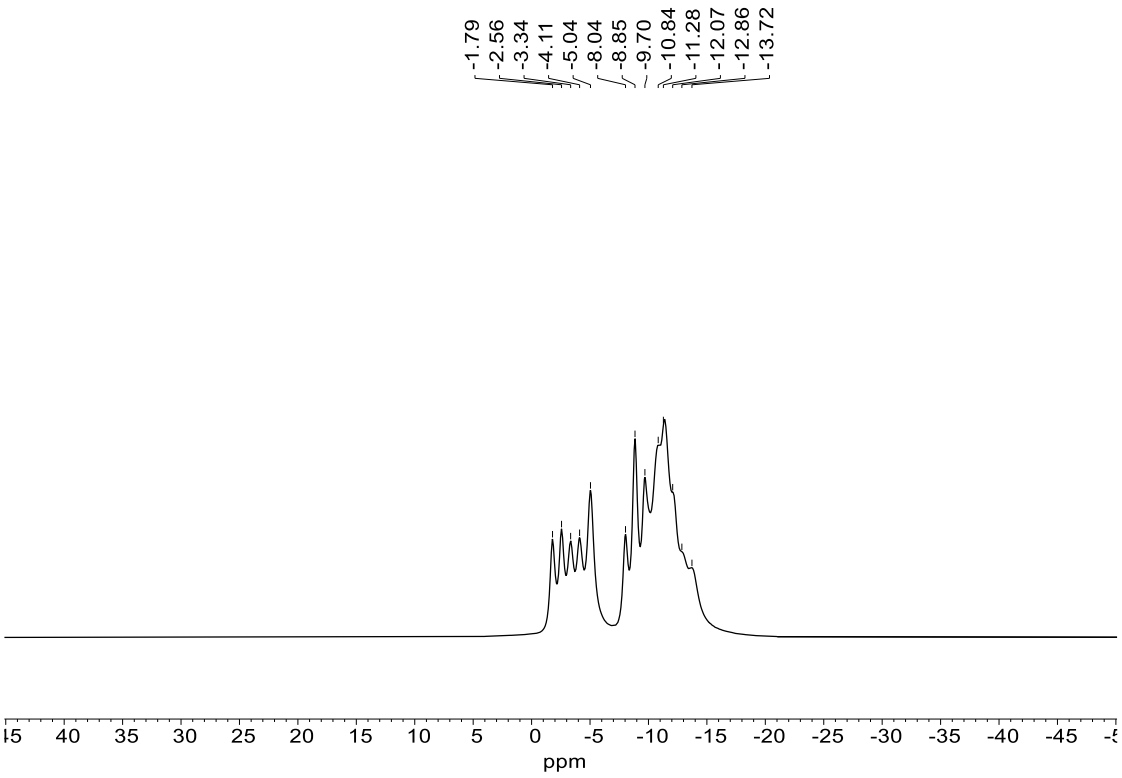
^{1}H NMR (600 MHz, Chloroform-*d*)



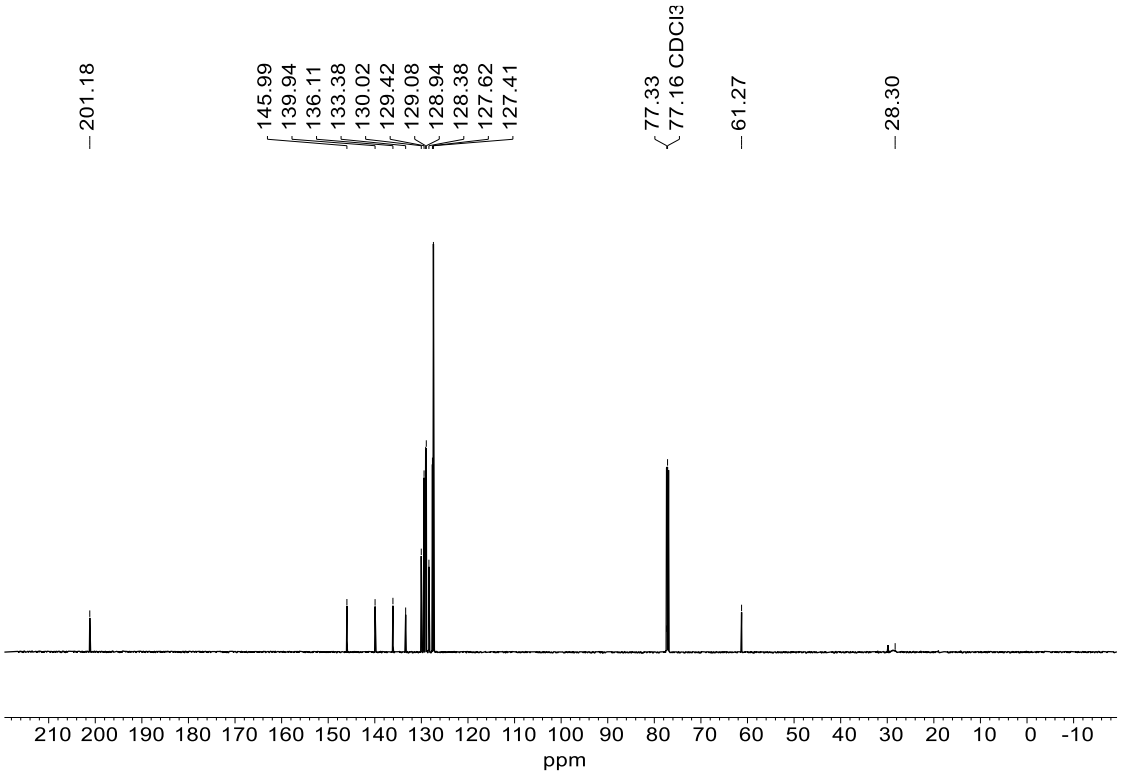
^{11}B{1H} NMR (193 MHz, Chloroform-*d*)



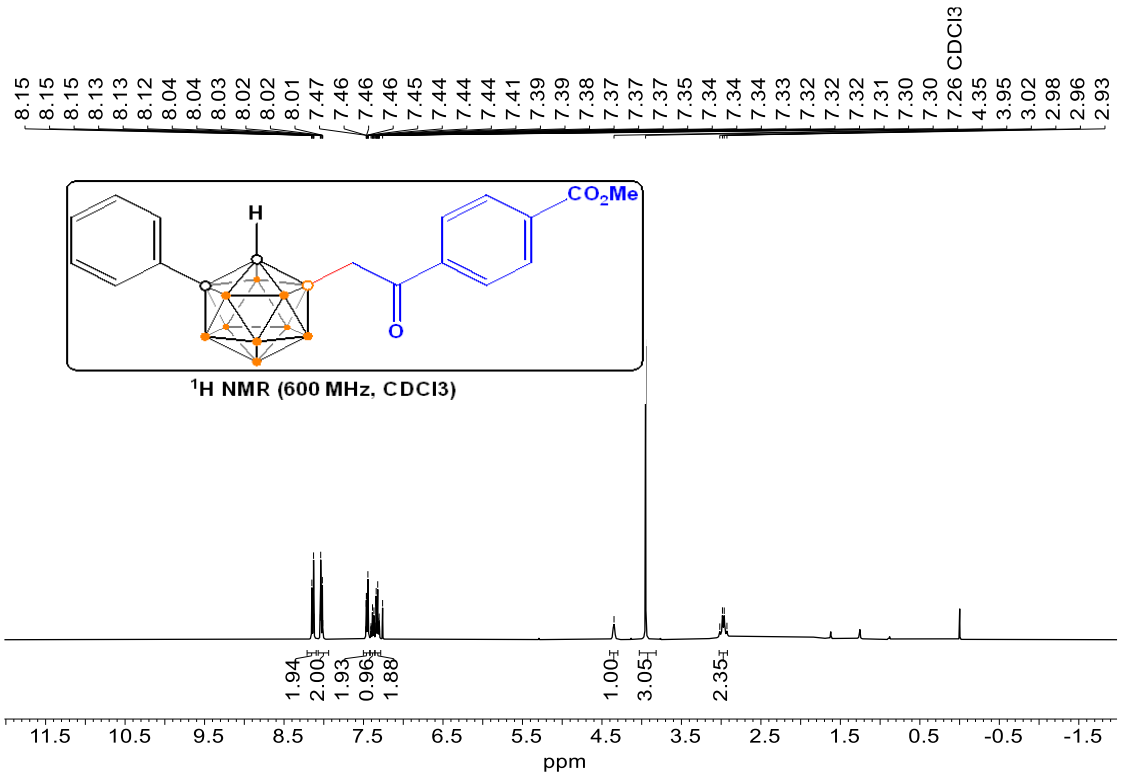
^{11}B NMR (193 MHz, Chloroform-*d*)



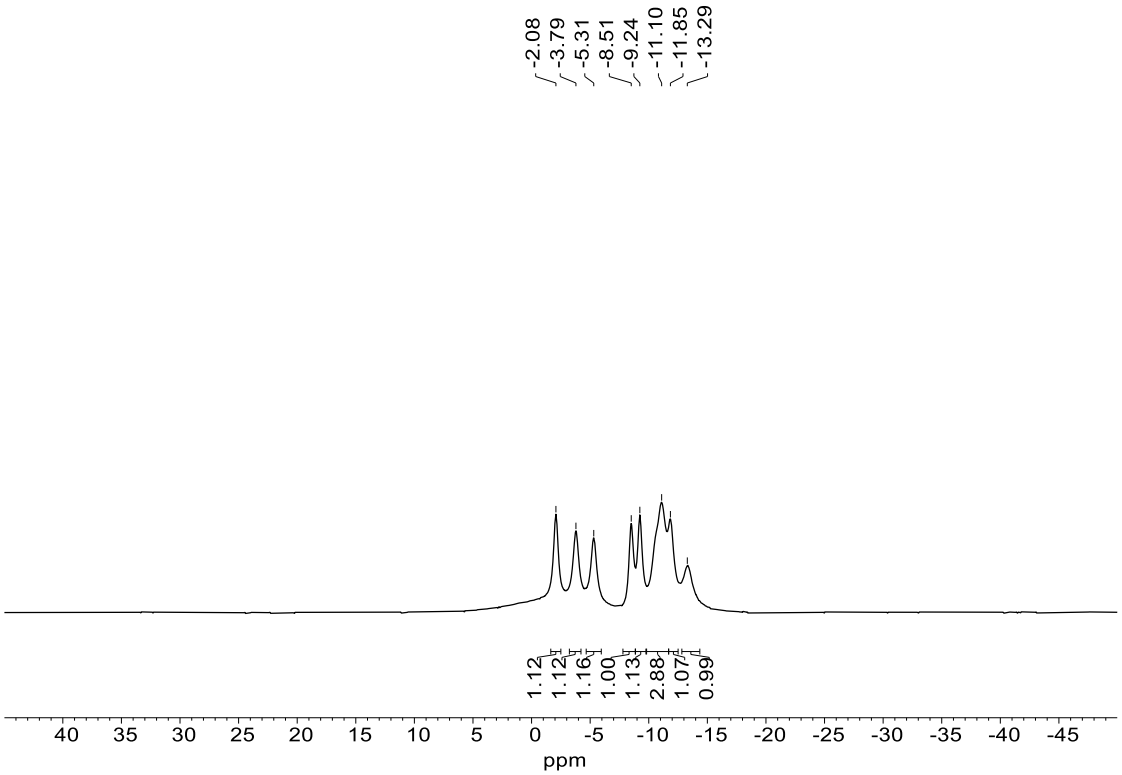
^{13}C NMR (151 MHz, Chloroform-*d*)



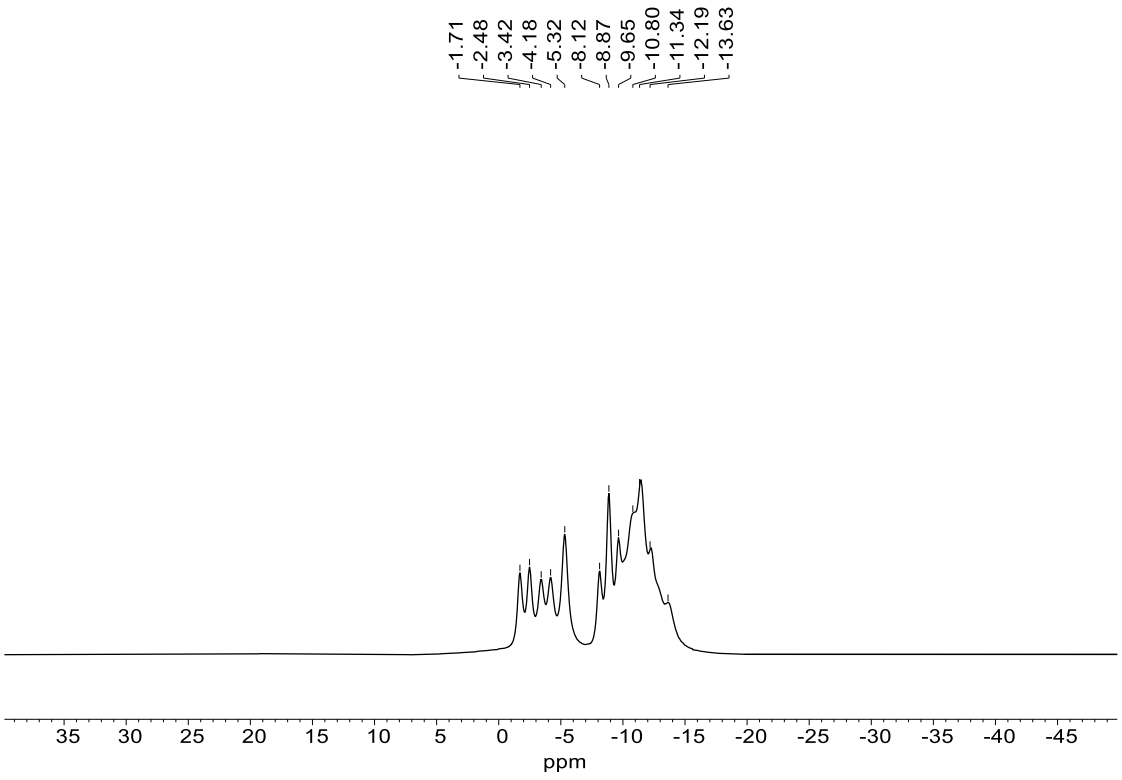
^{1}H NMR (400 MHz, Chloroform-*d*)



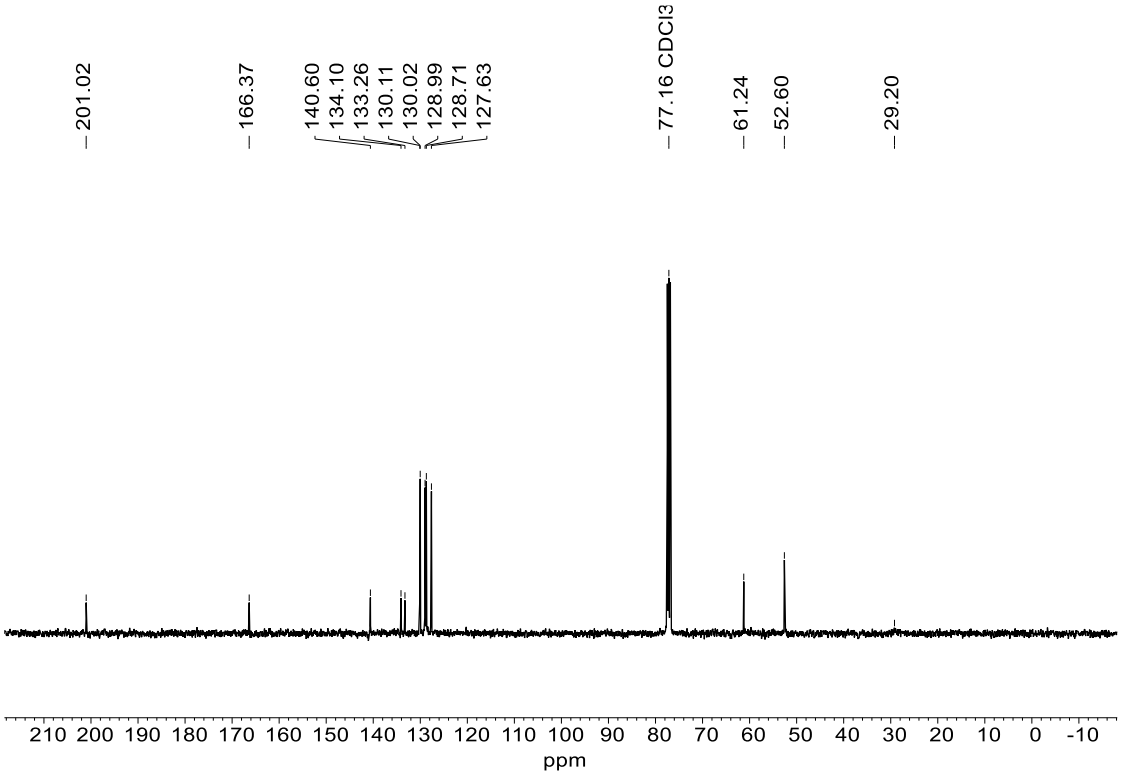
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



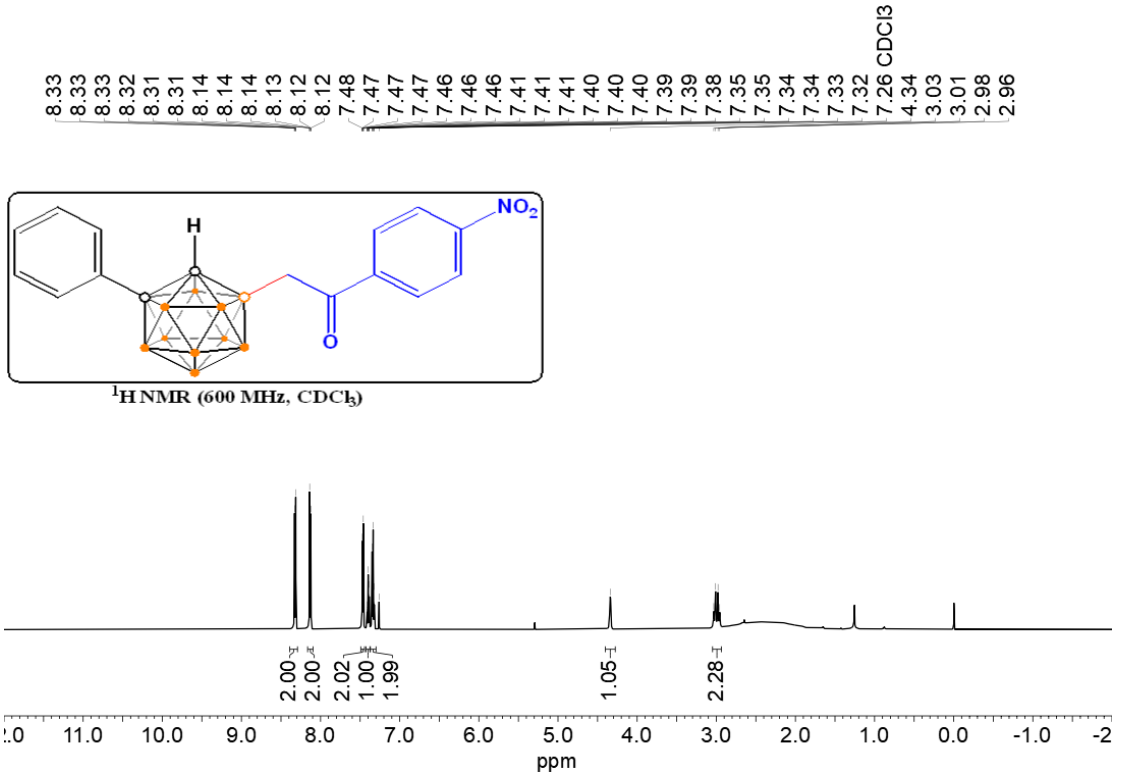
^{11}B NMR (193 MHz, Chloroform-*d*)



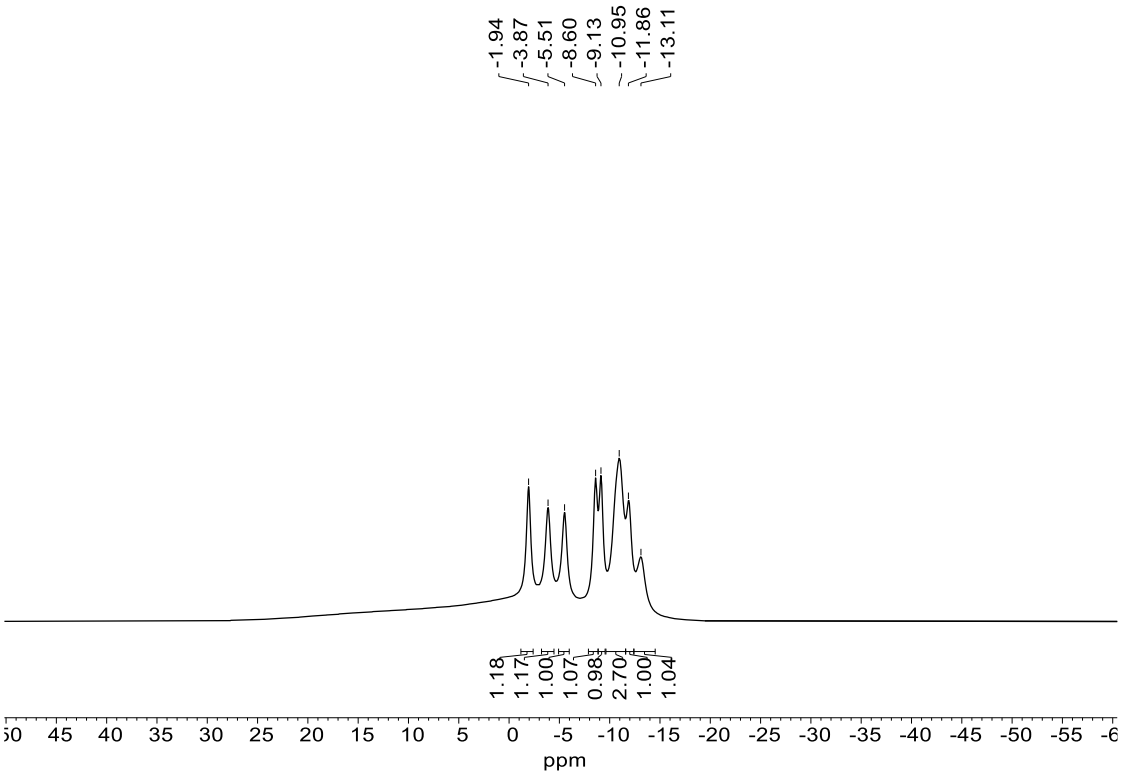
^{13}C NMR (101 MHz, Chloroform-*d*)



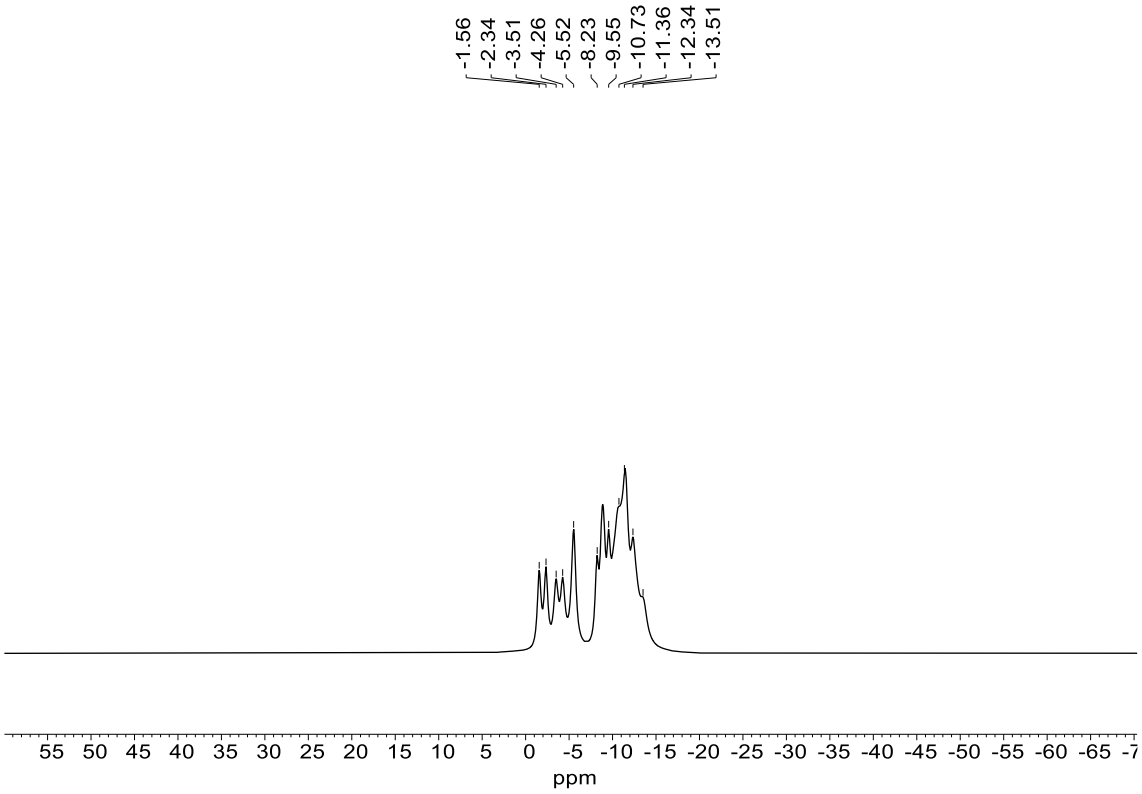
^{1}H NMR (600 MHz, Chloroform-*d*)



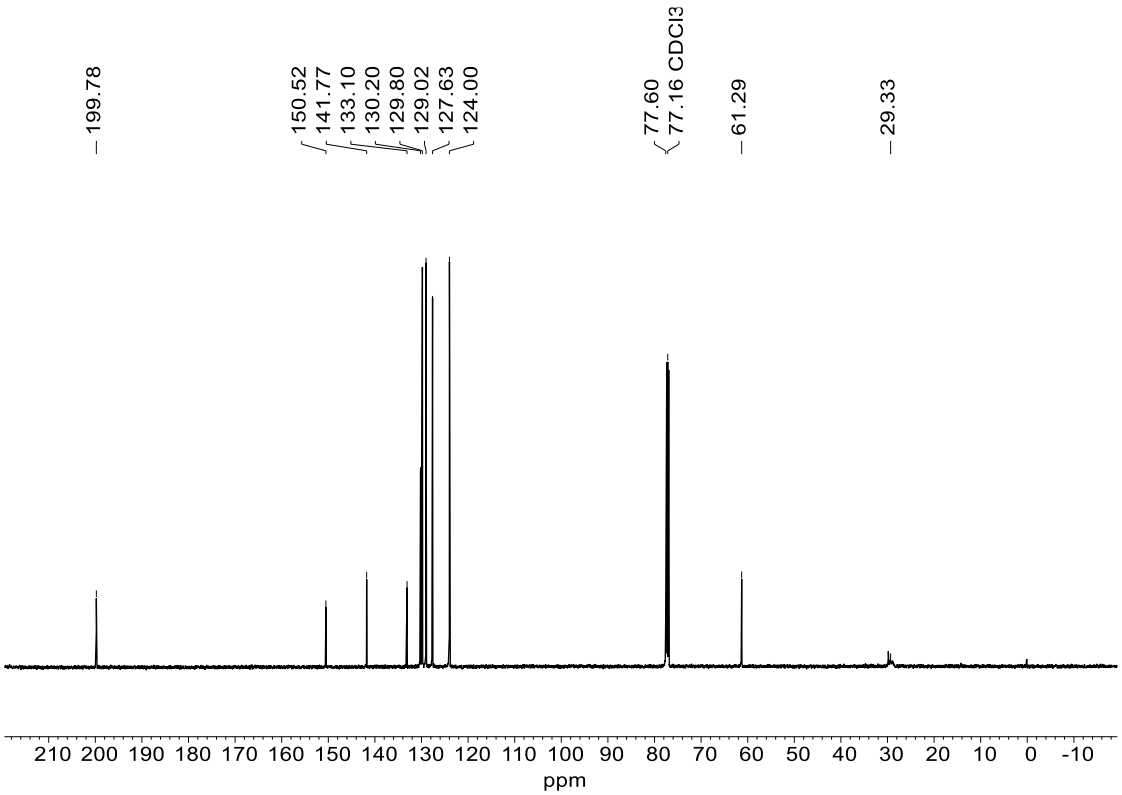
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



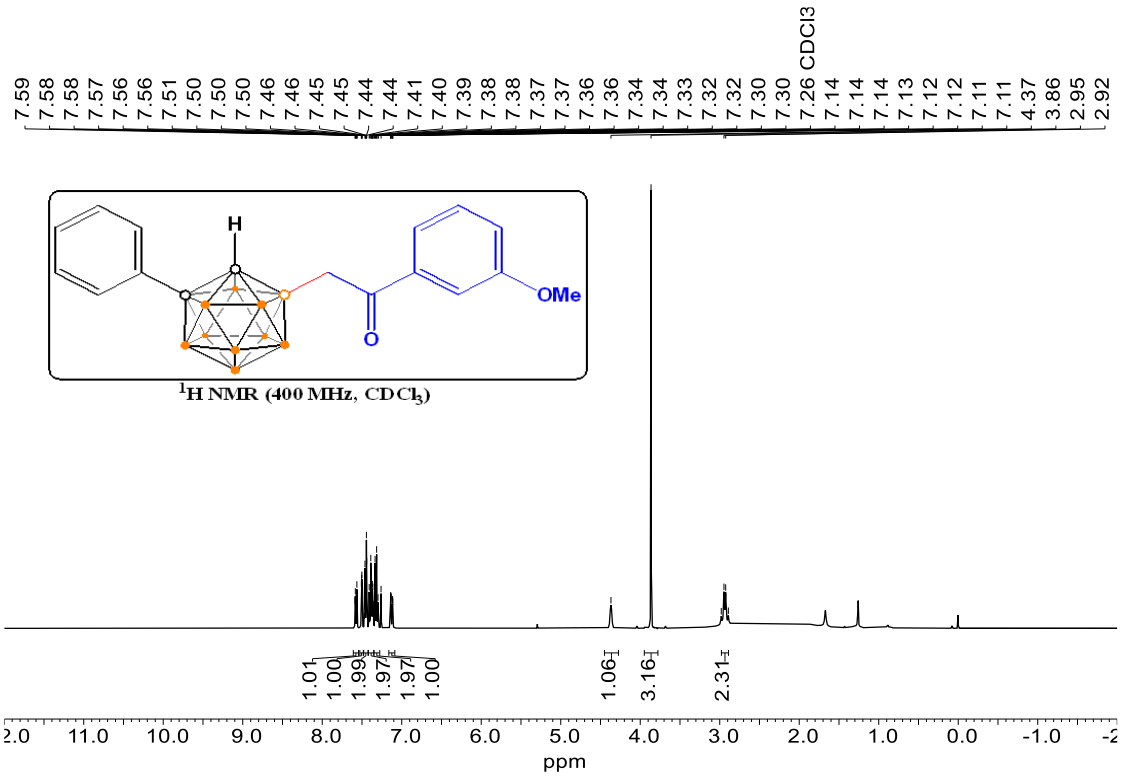
^{11}B NMR (193 MHz, Chloroform-*d*)



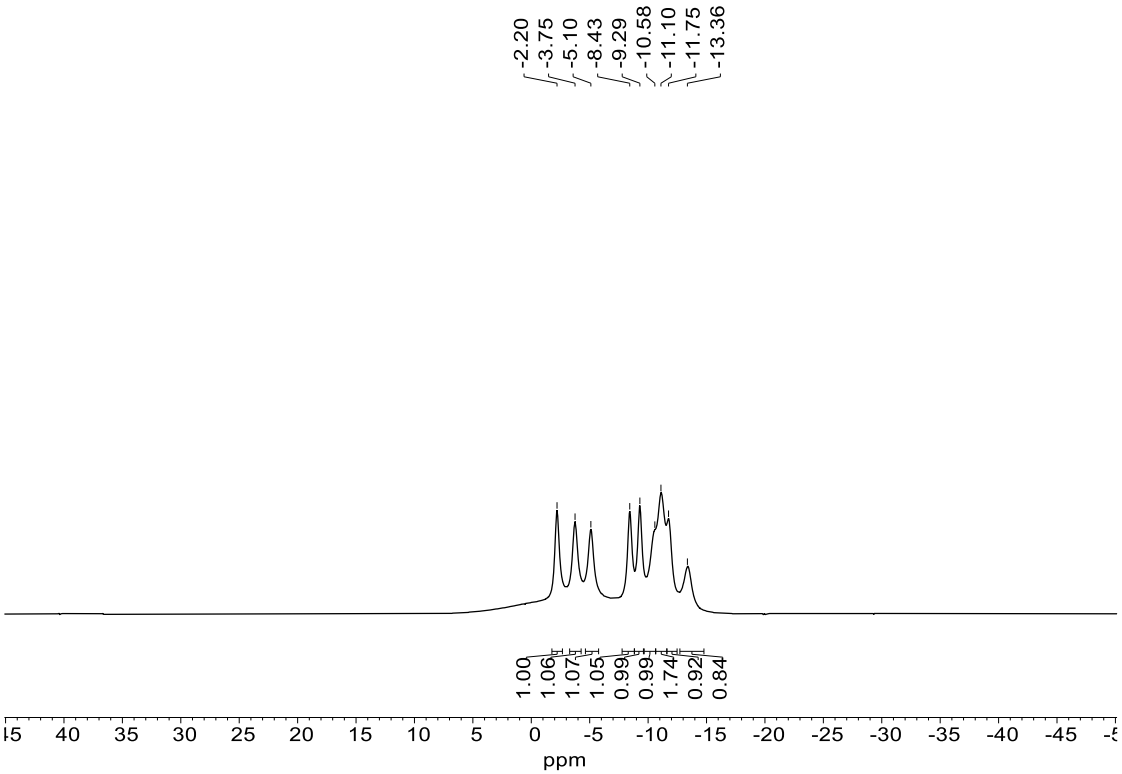
^{13}C NMR (151 MHz, Chloroform-*d*)



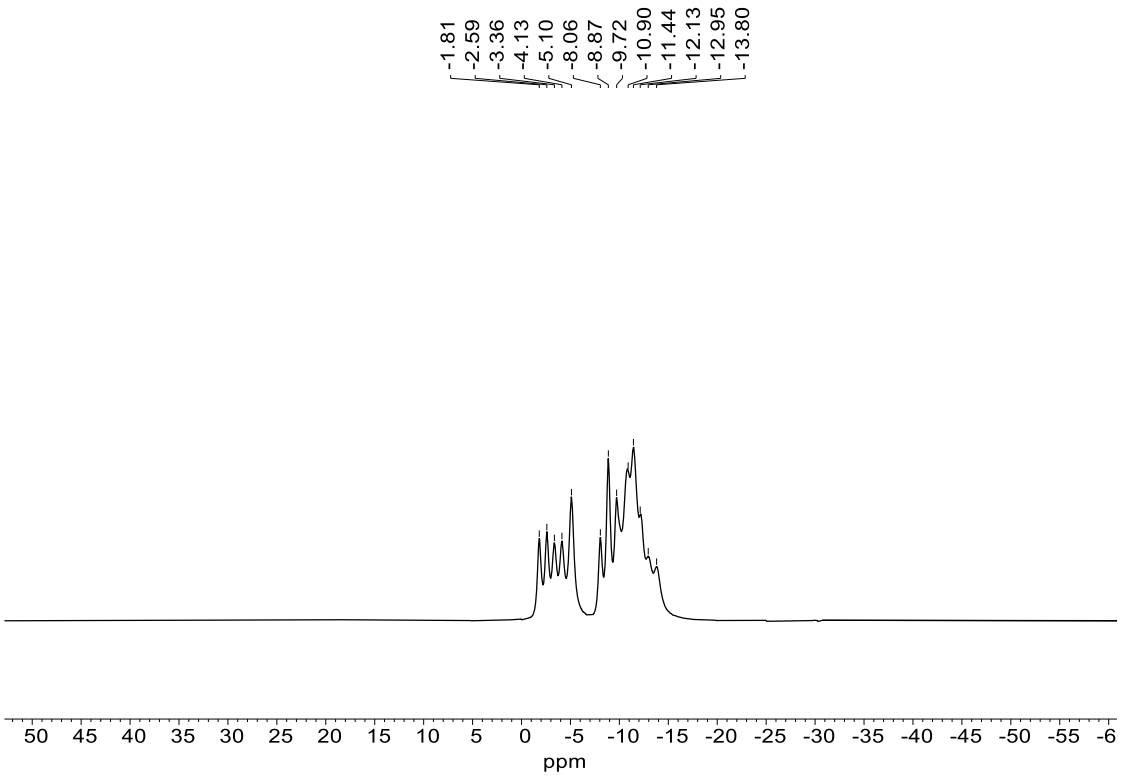
^{1}H NMR (400 MHz, Chloroform-*d*)



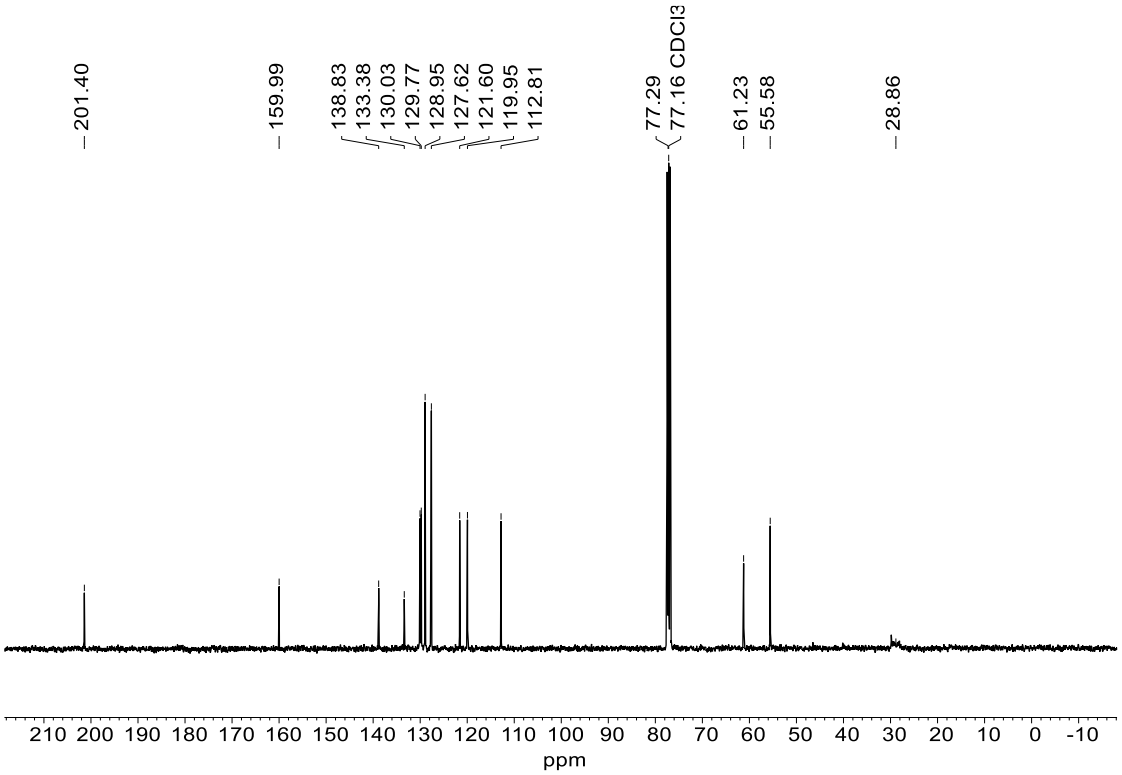
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



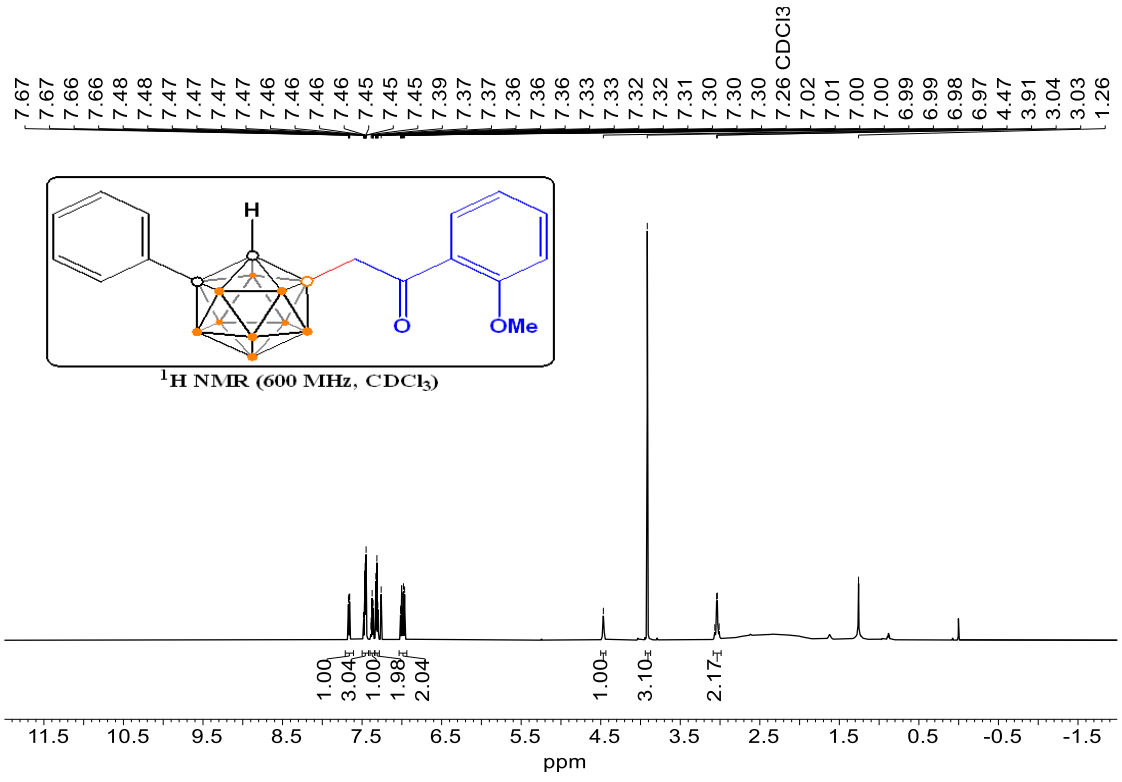
^{11}B NMR (193 MHz, Chloroform-*d*)



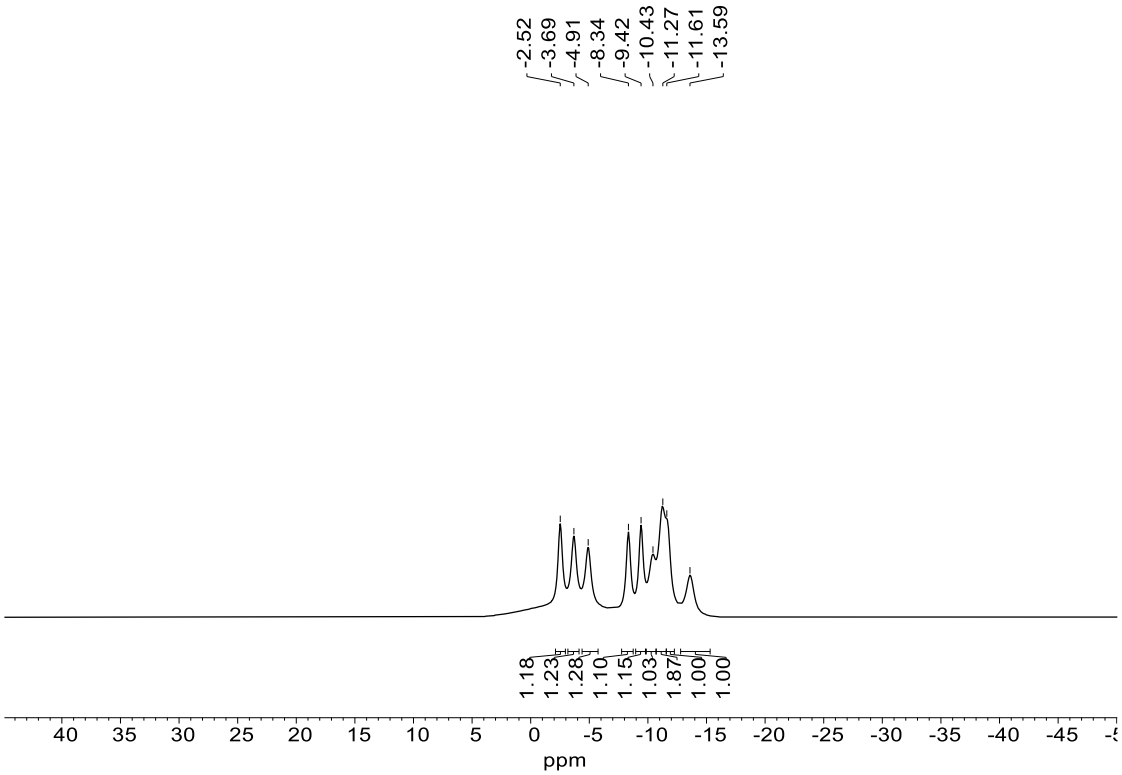
^{13}C NMR (101 MHz, Chloroform-*d*)



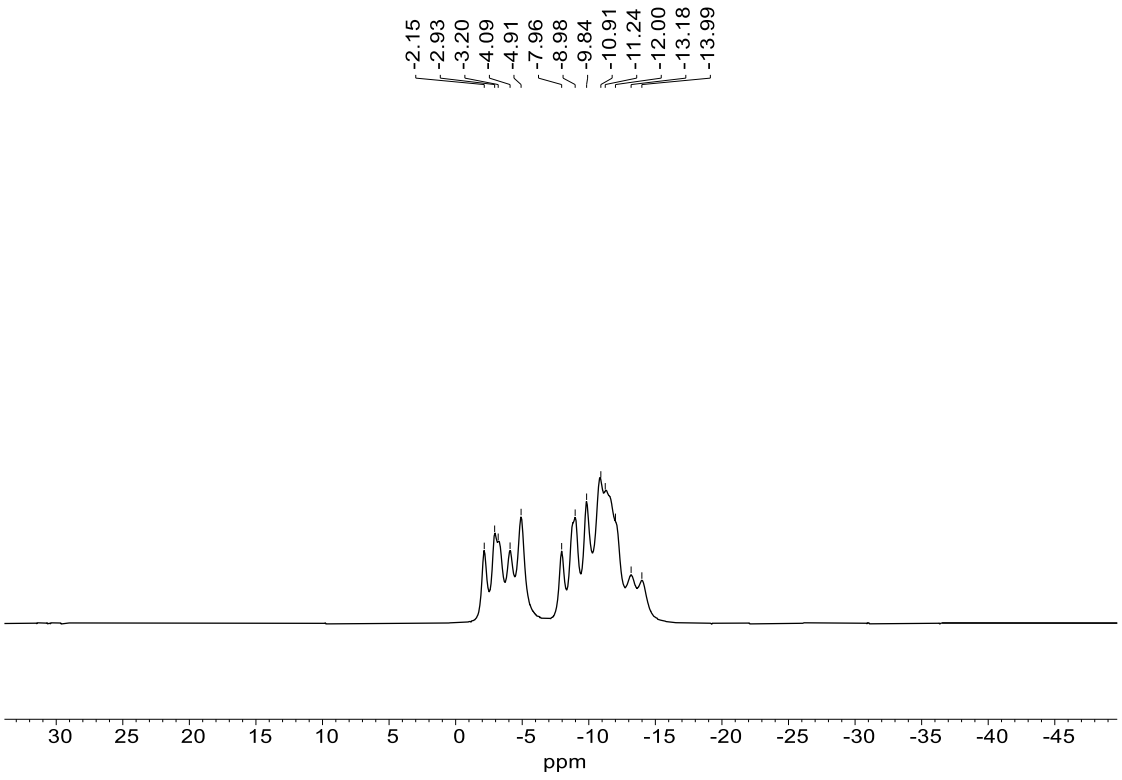
^{1}H NMR (600 MHz, Chloroform-*d*)



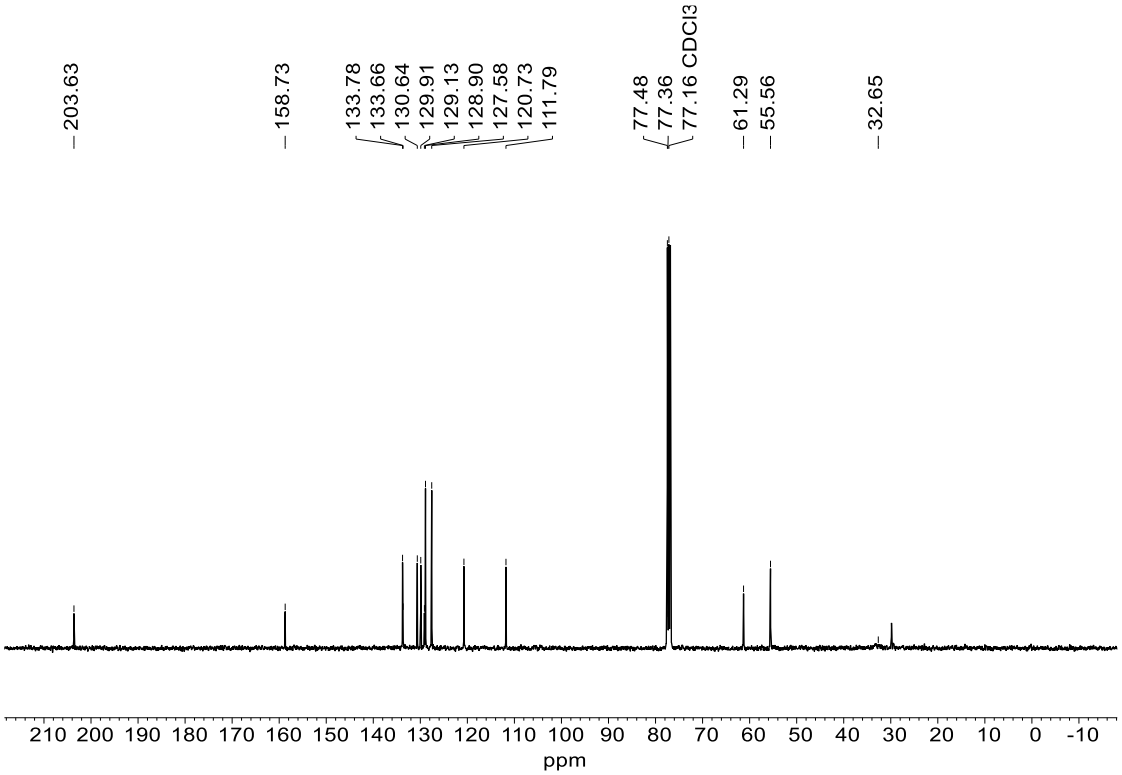
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



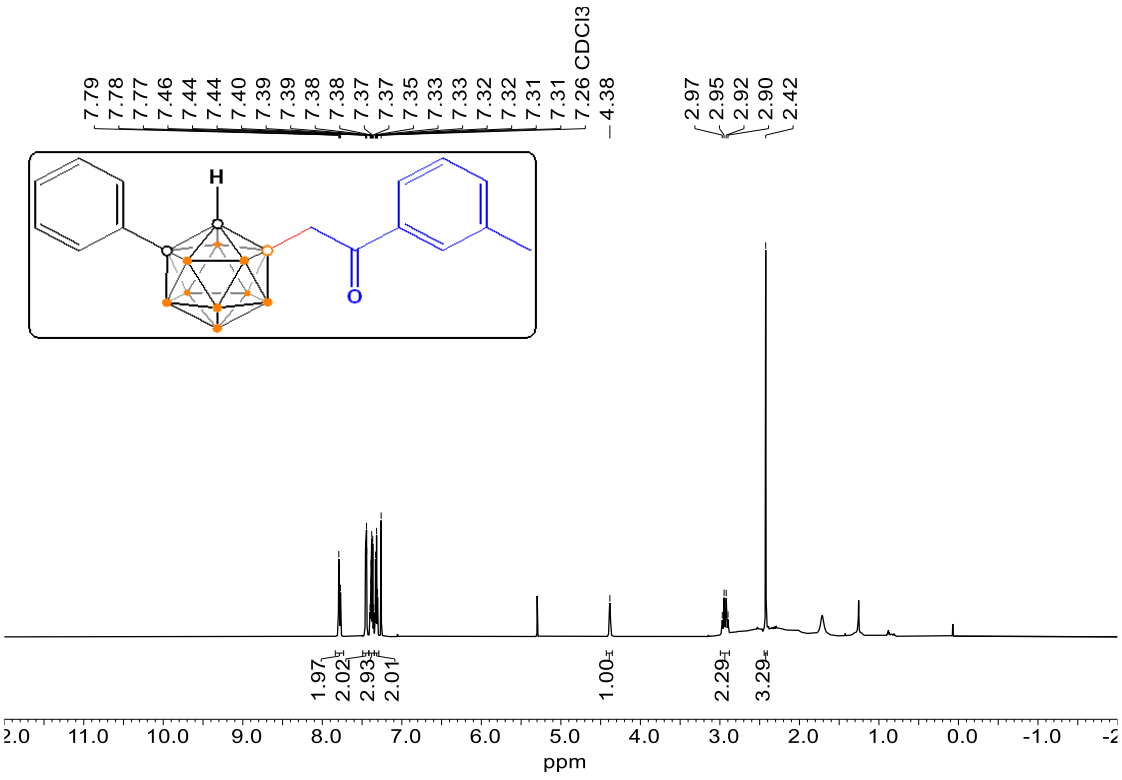
^{11}B NMR (193 MHz, Chloroform-*d*)



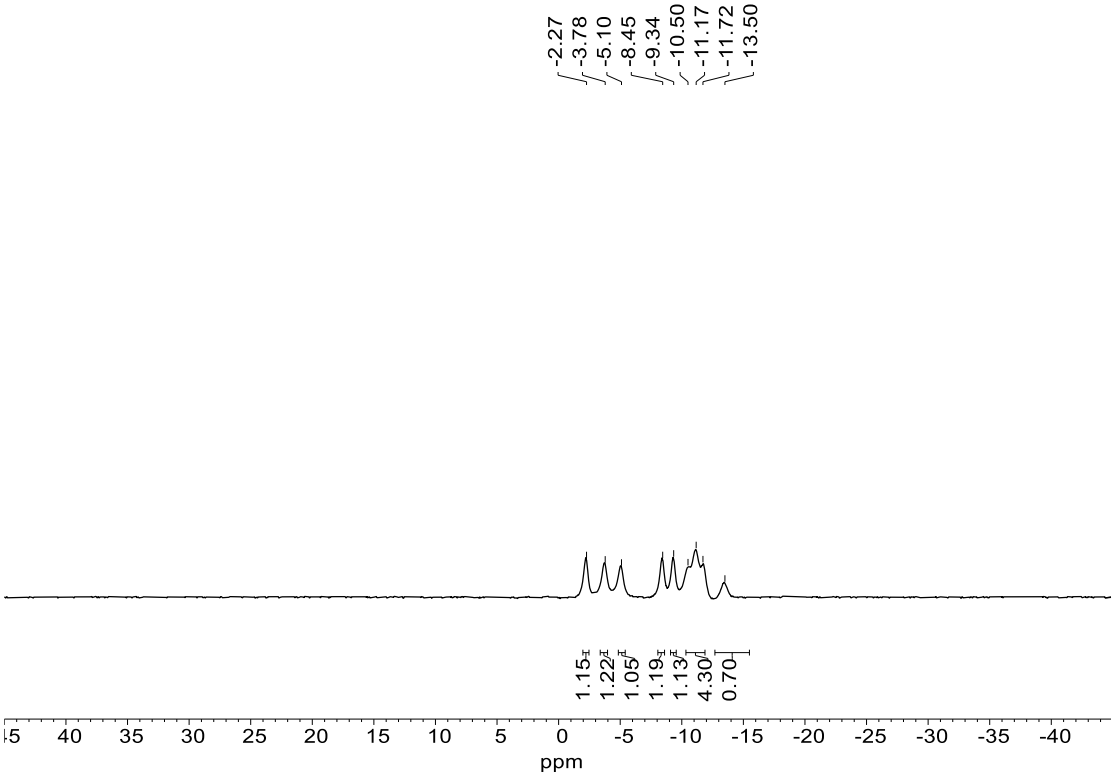
^{13}C NMR (101 MHz, Chloroform-*d*)



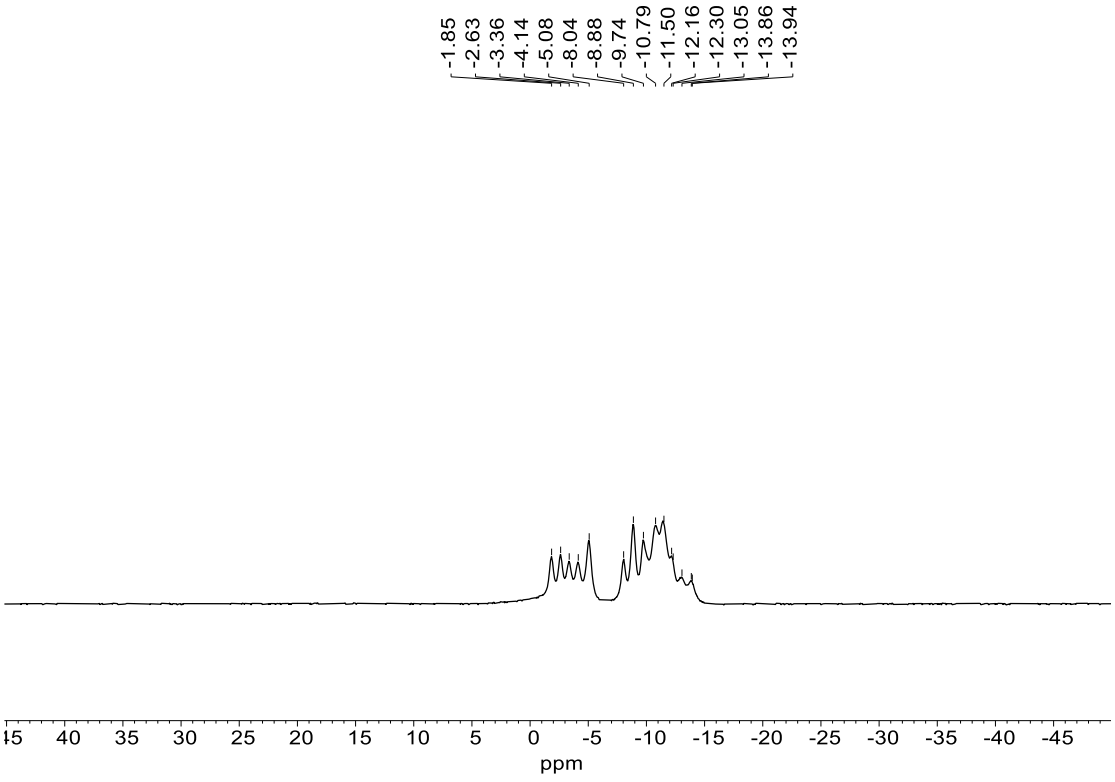
^{1}H NMR (600 MHz, Chloroform-*d*)



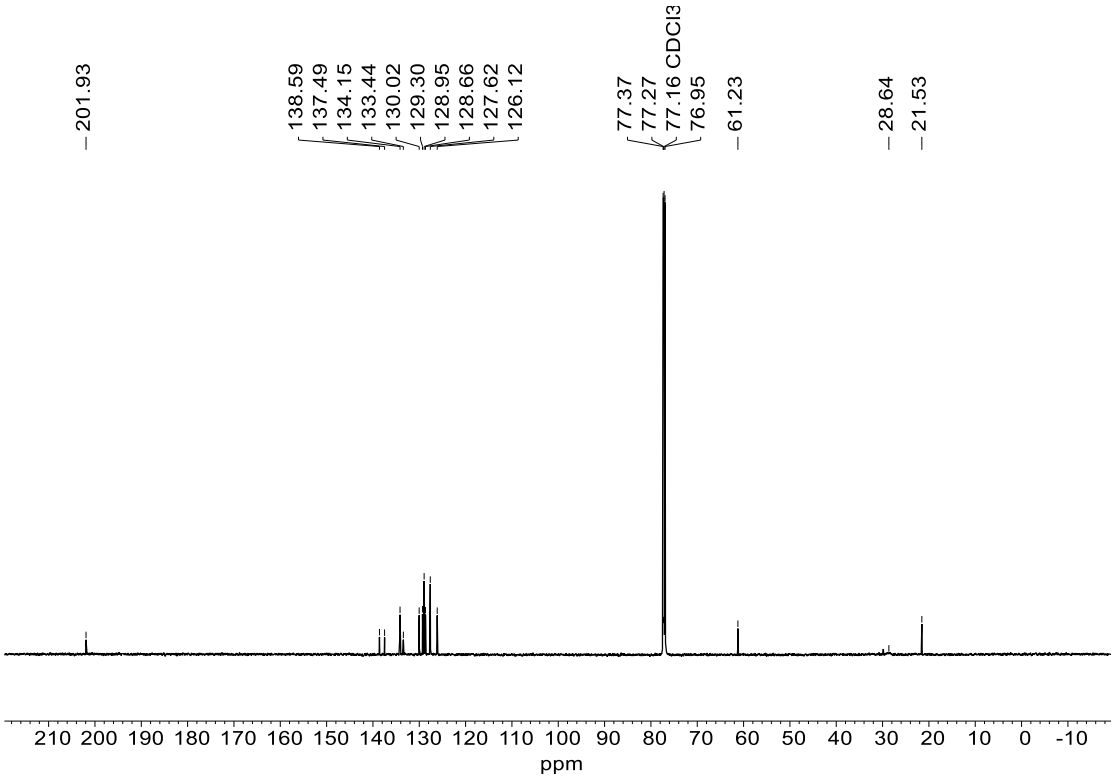
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



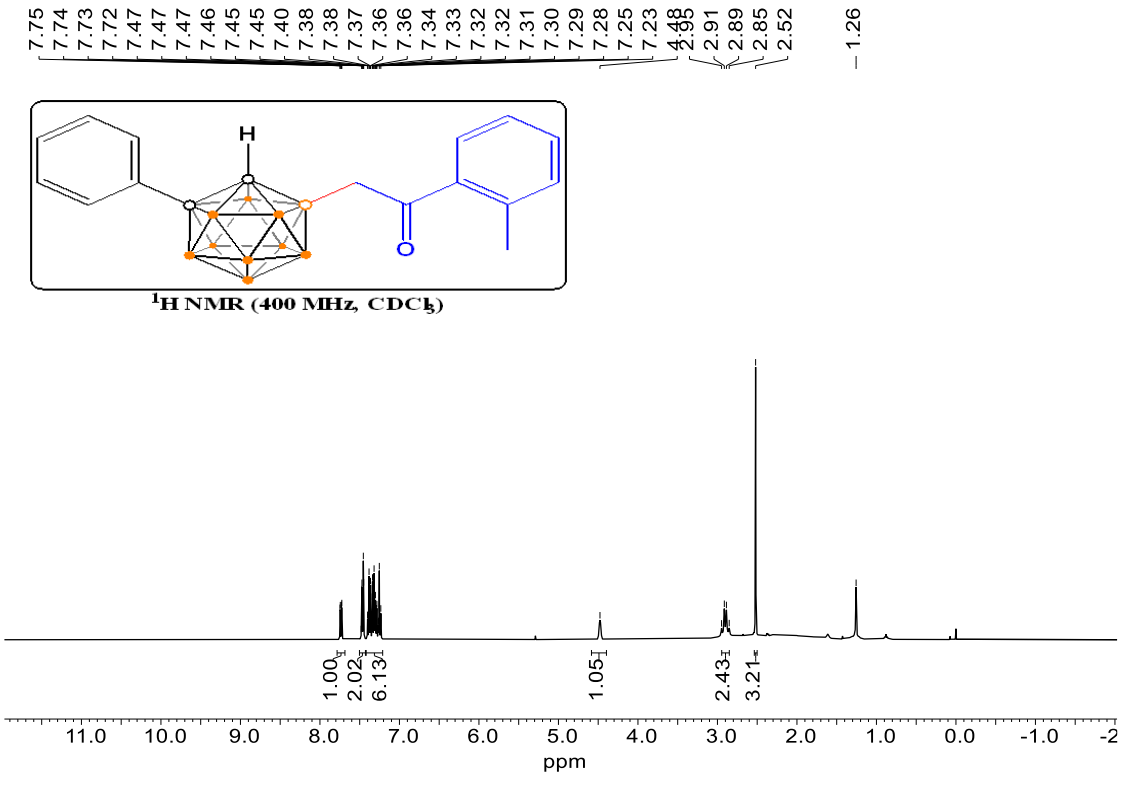
^{11}B NMR (193 MHz, Chloroform-*d*)



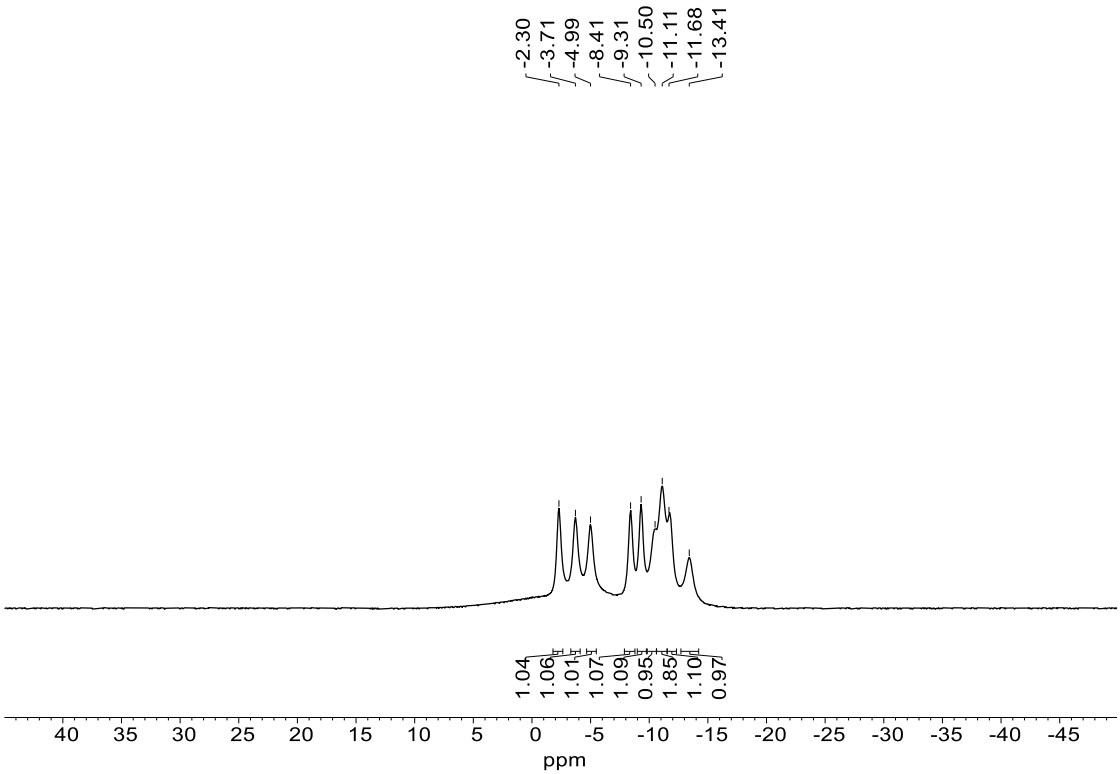
^{13}C NMR (151 MHz, Chloroform-*d*)



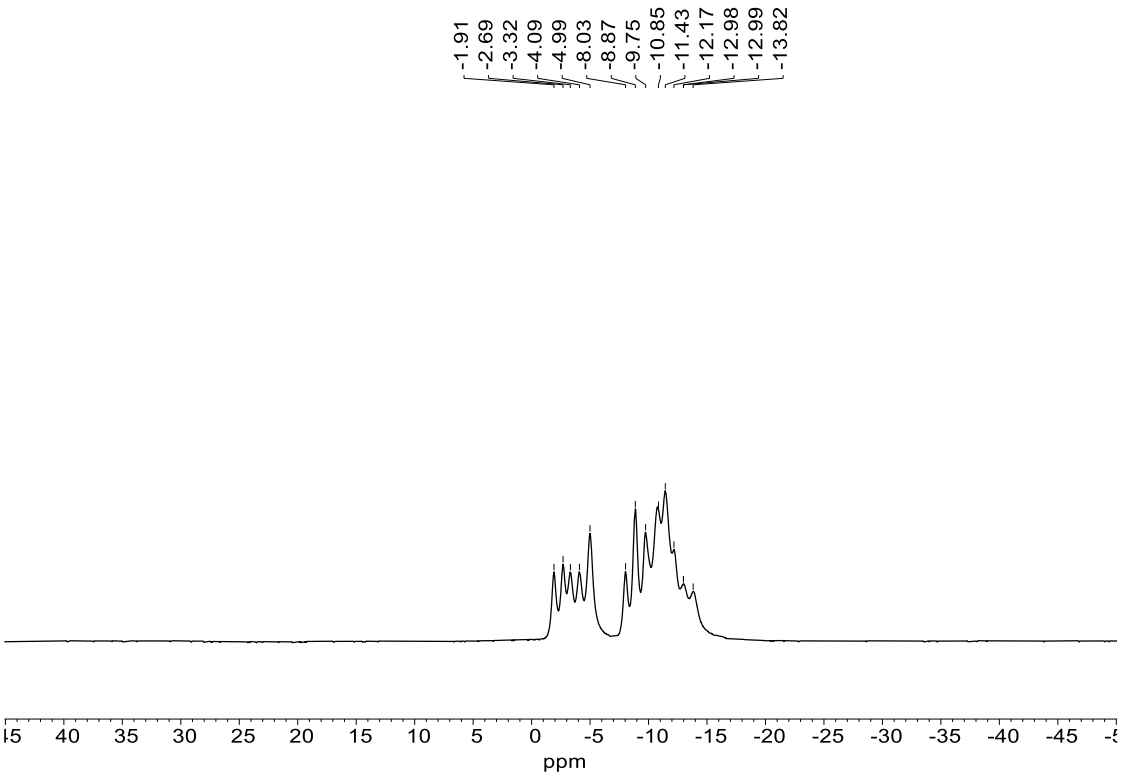
^{1}H NMR (400 MHz, Chloroform-*d*)



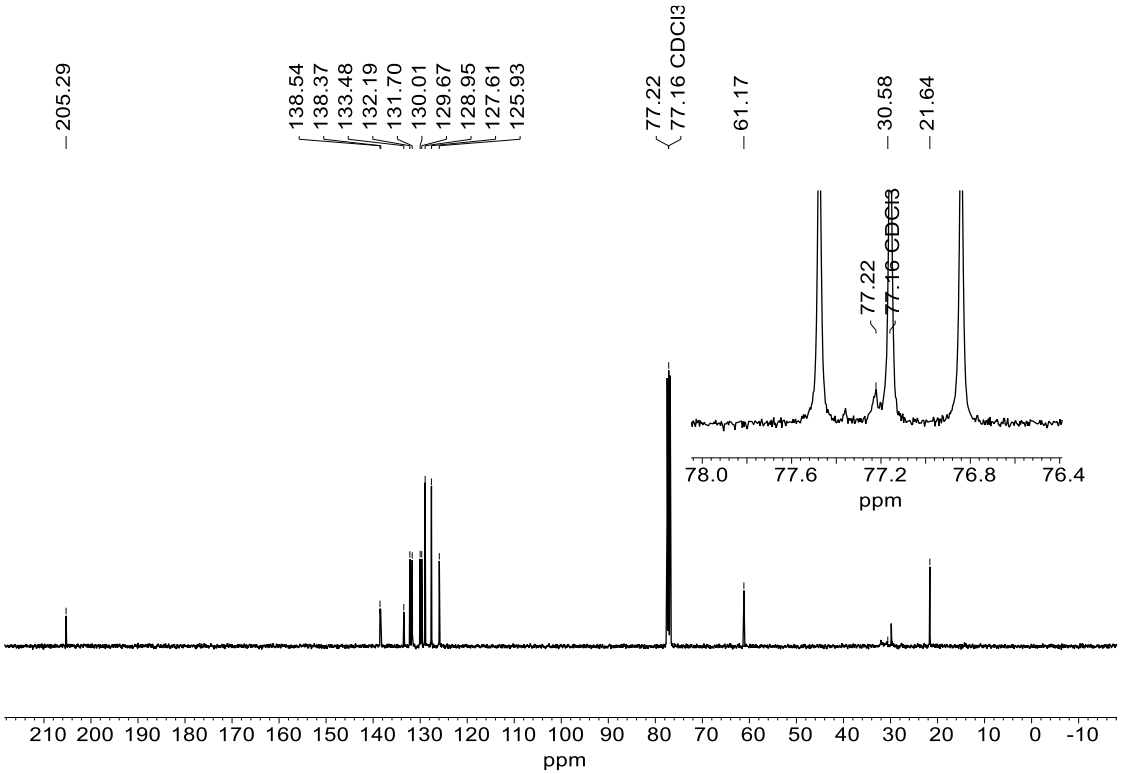
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



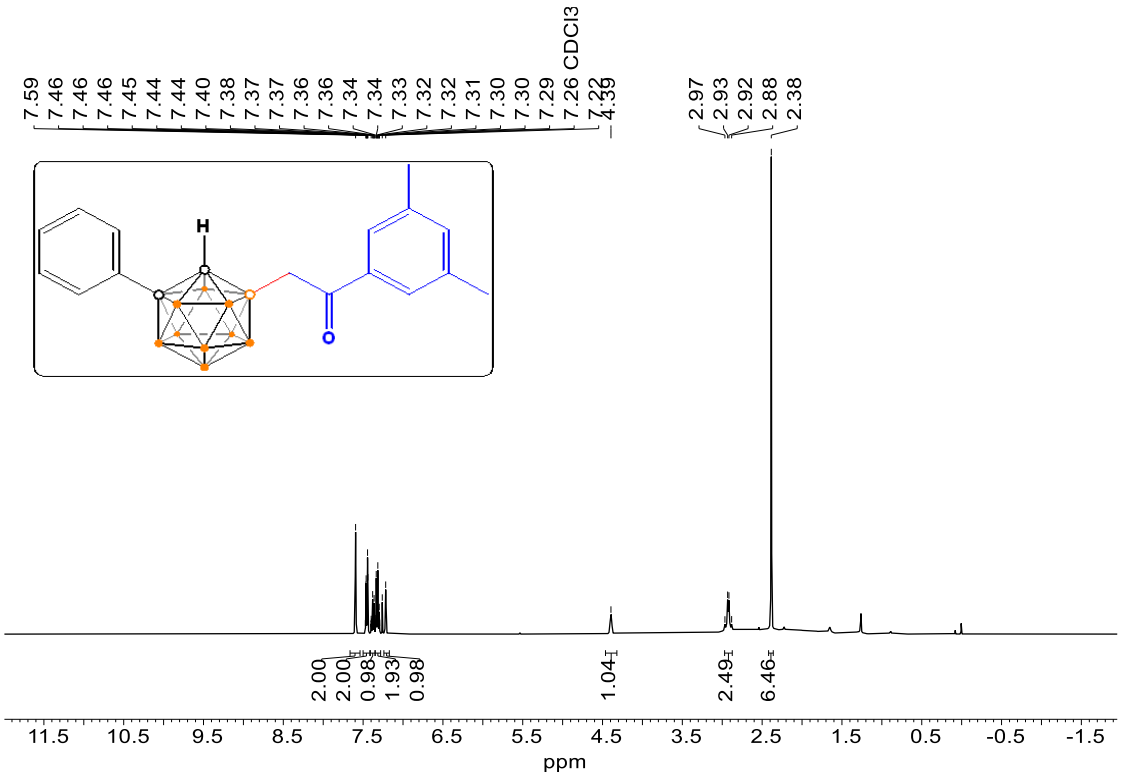
^{11}B NMR (193 MHz, Chloroform-*d*)



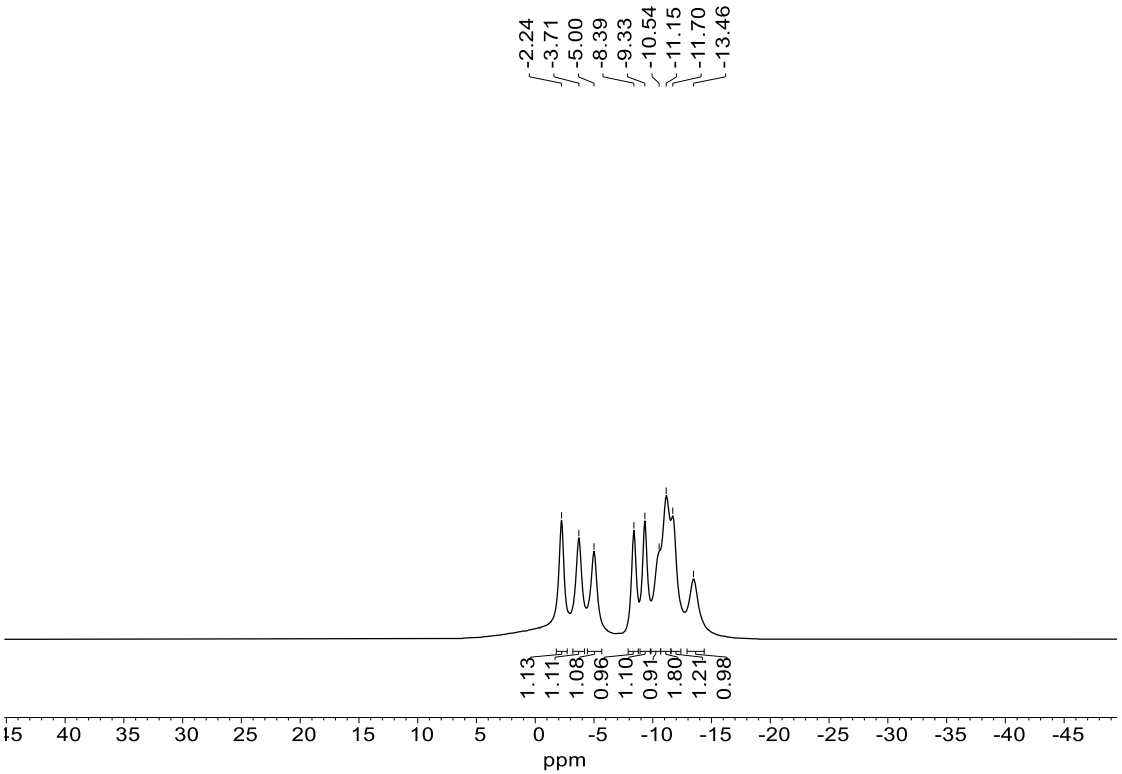
^{13}C NMR (101 MHz, Chloroform-*d*)



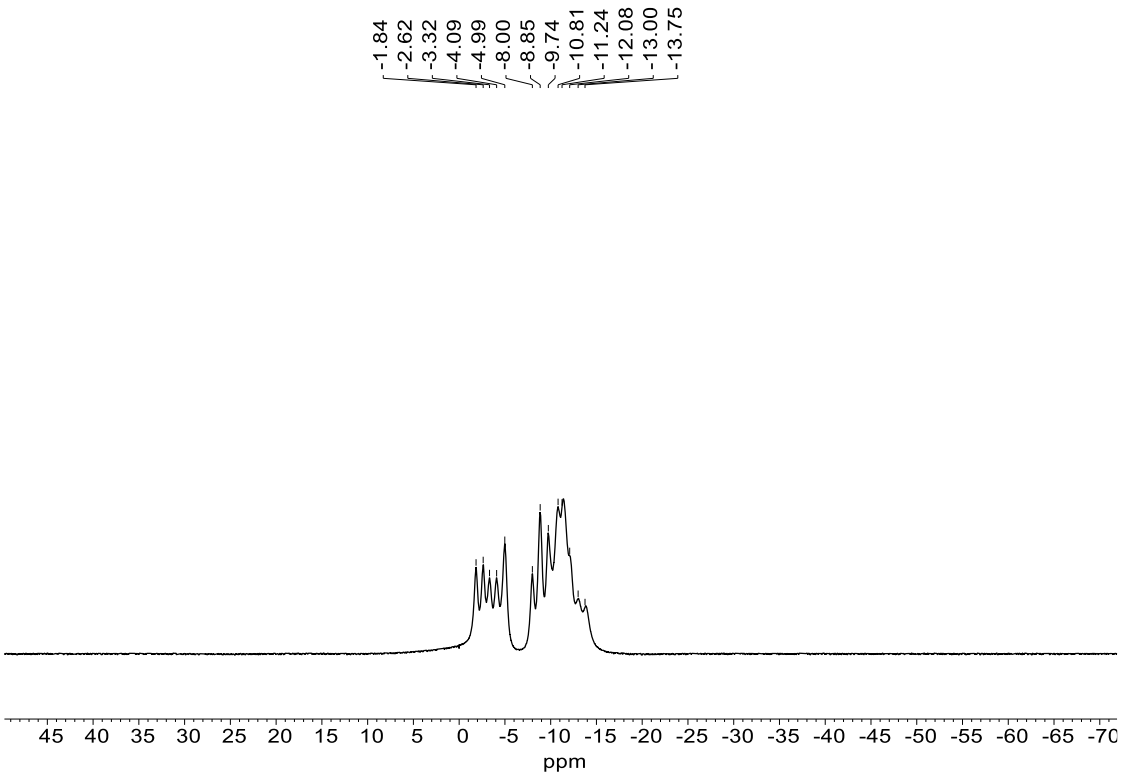
^{1}H NMR (400 MHz, Chloroform-*d*)



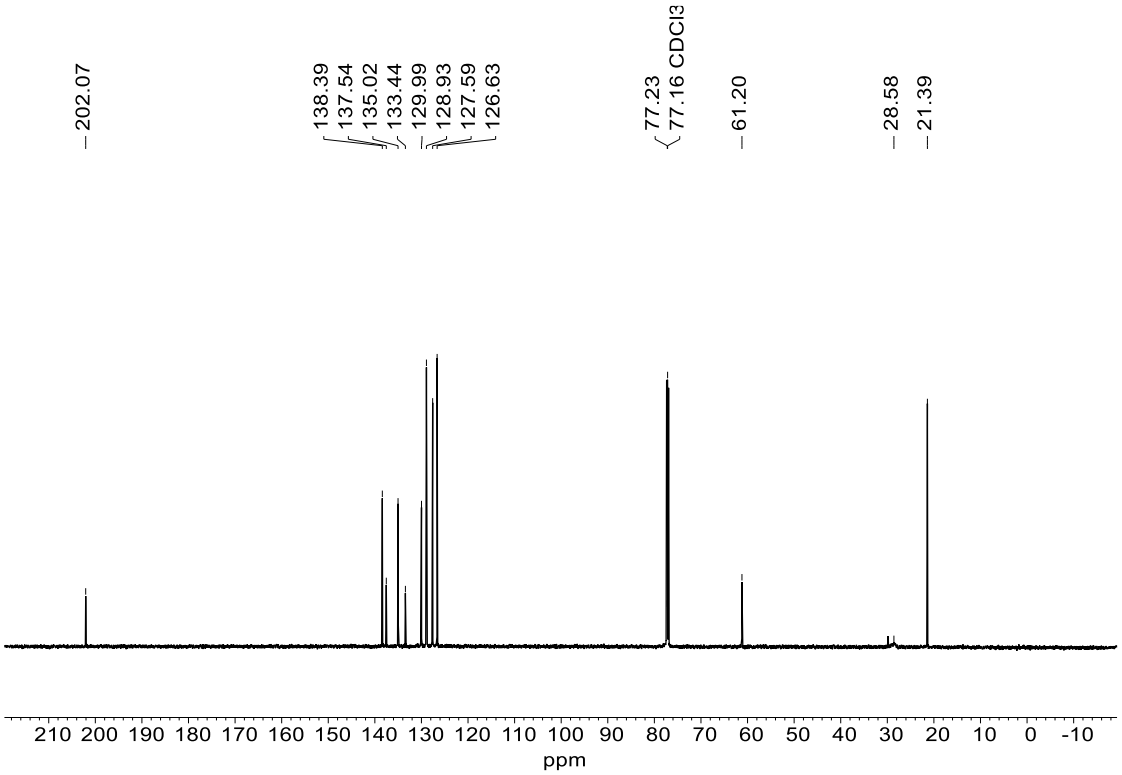
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



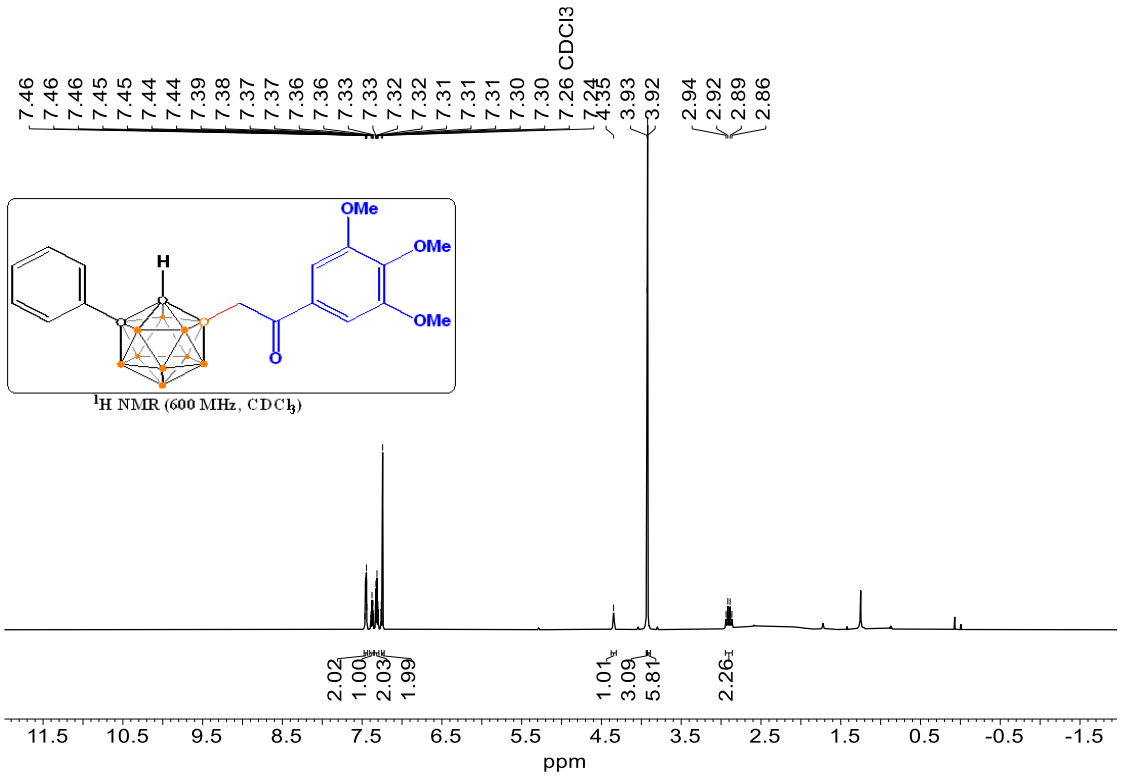
^{11}B NMR (193 MHz, Chloroform-*d*)



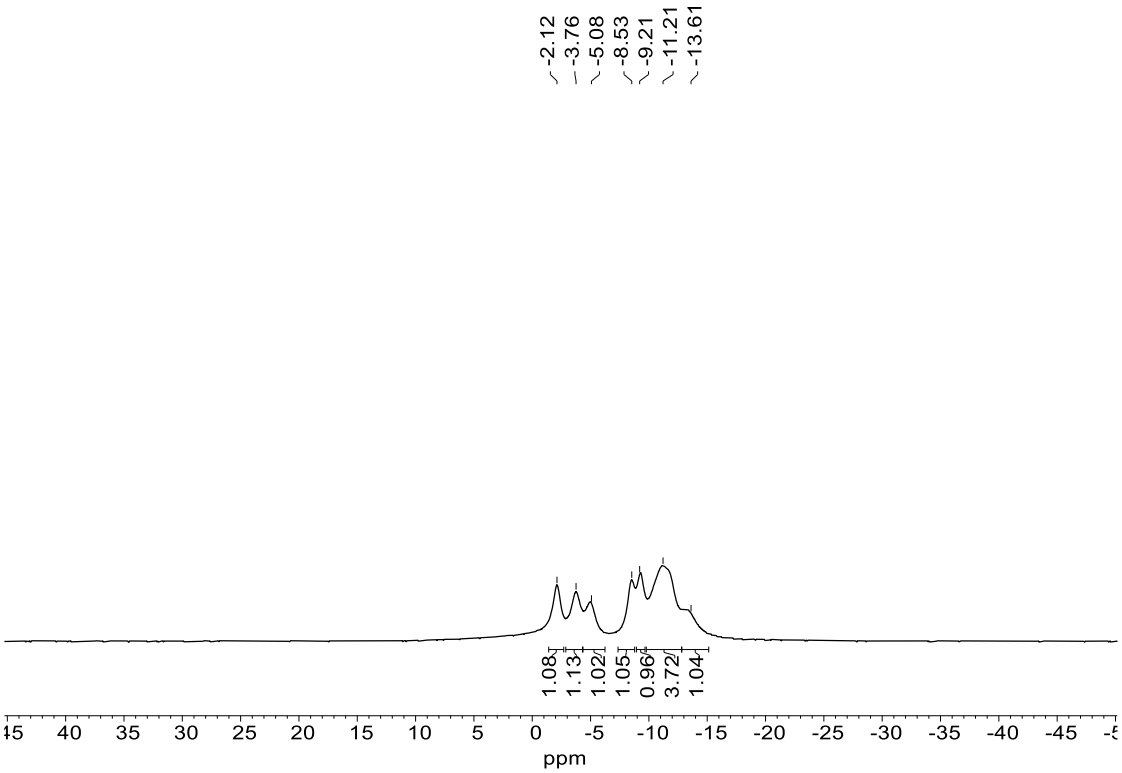
^{13}C NMR (151 MHz, Chloroform-*d*)



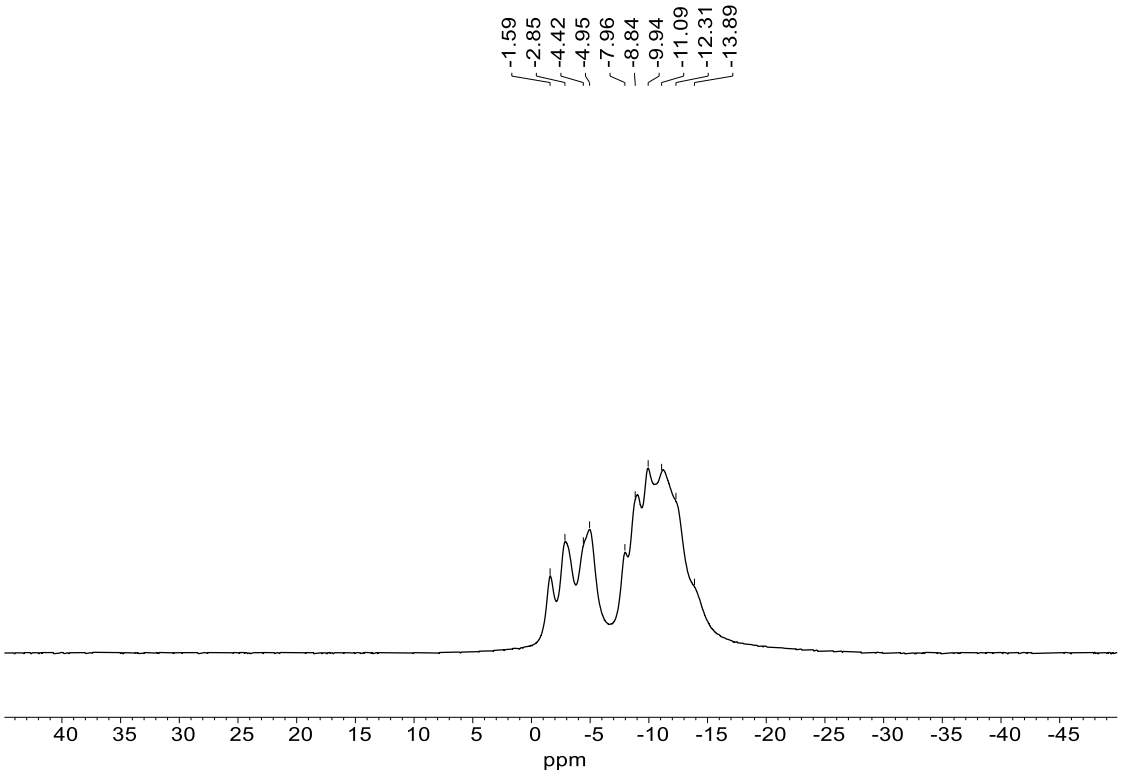
^{1}H NMR (600 MHz, Chloroform-*d*)



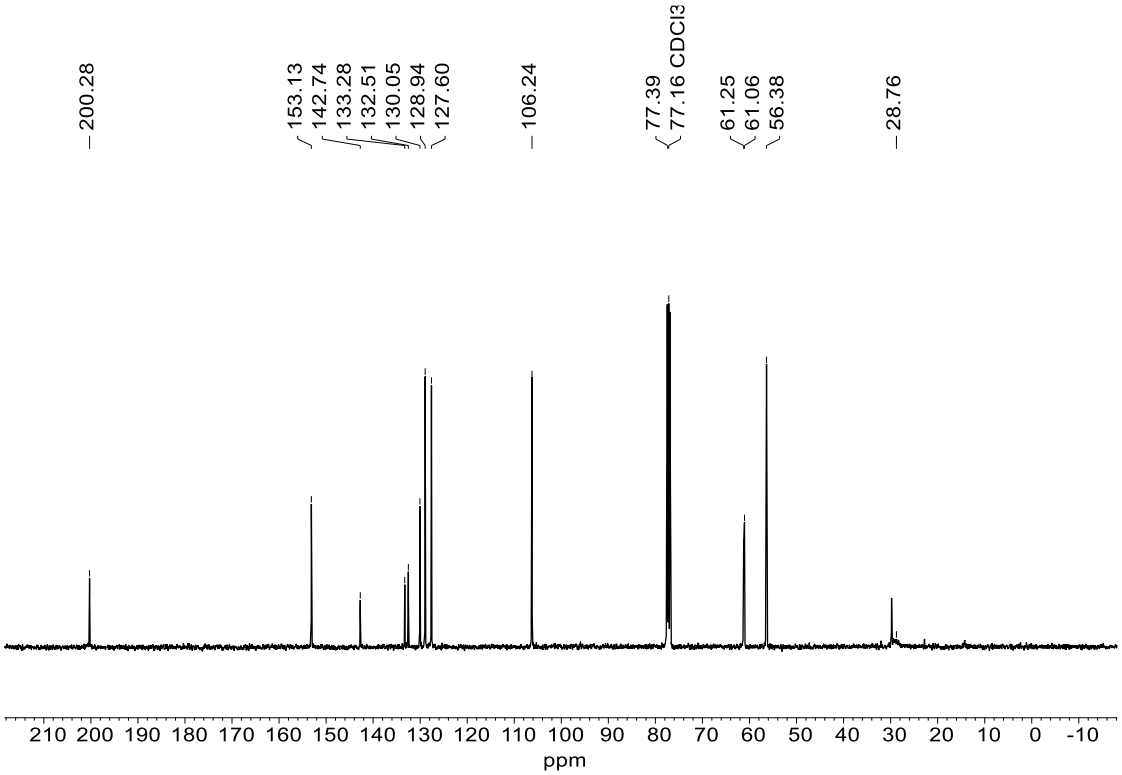
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*)



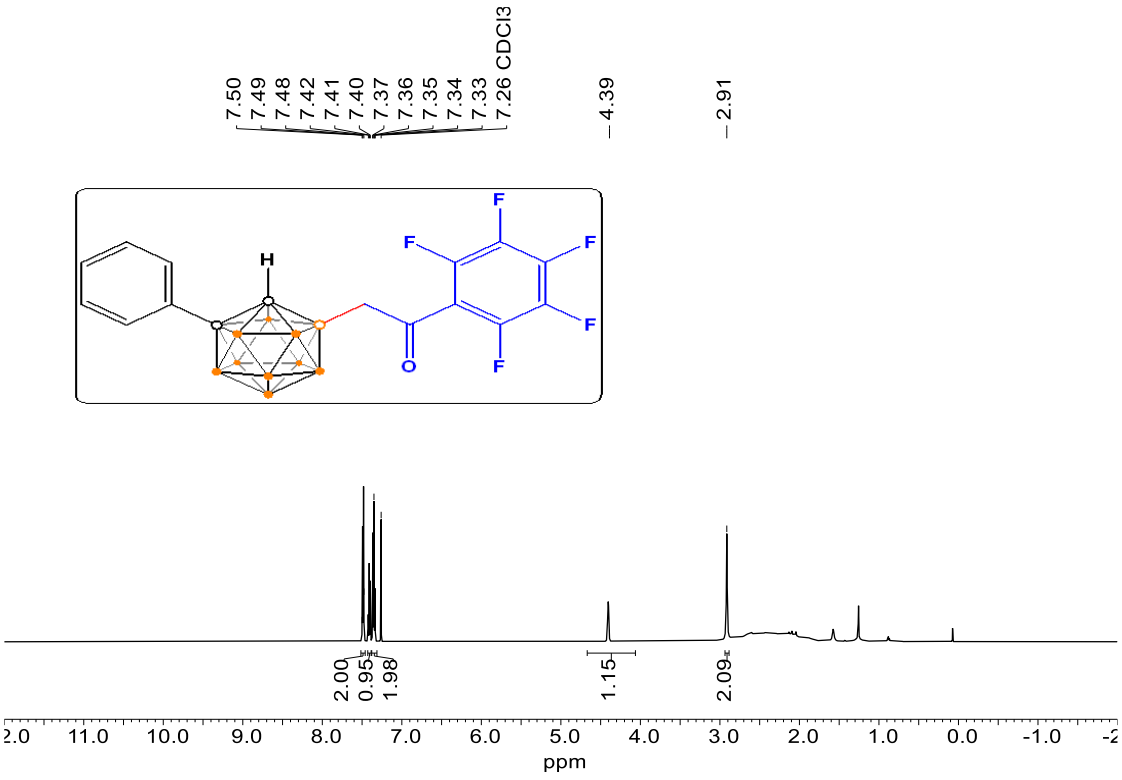
^{11}B NMR (128 MHz, Chloroform-*d*)



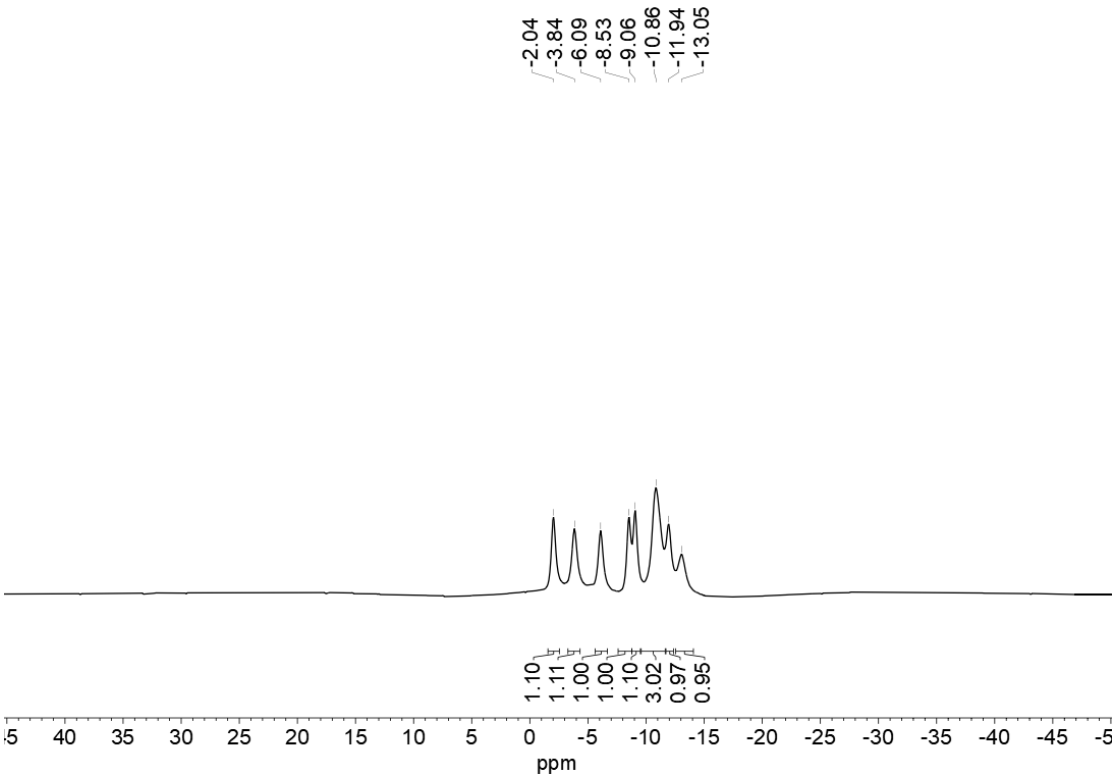
^{13}C NMR (101 MHz, Chloroform-*d*)



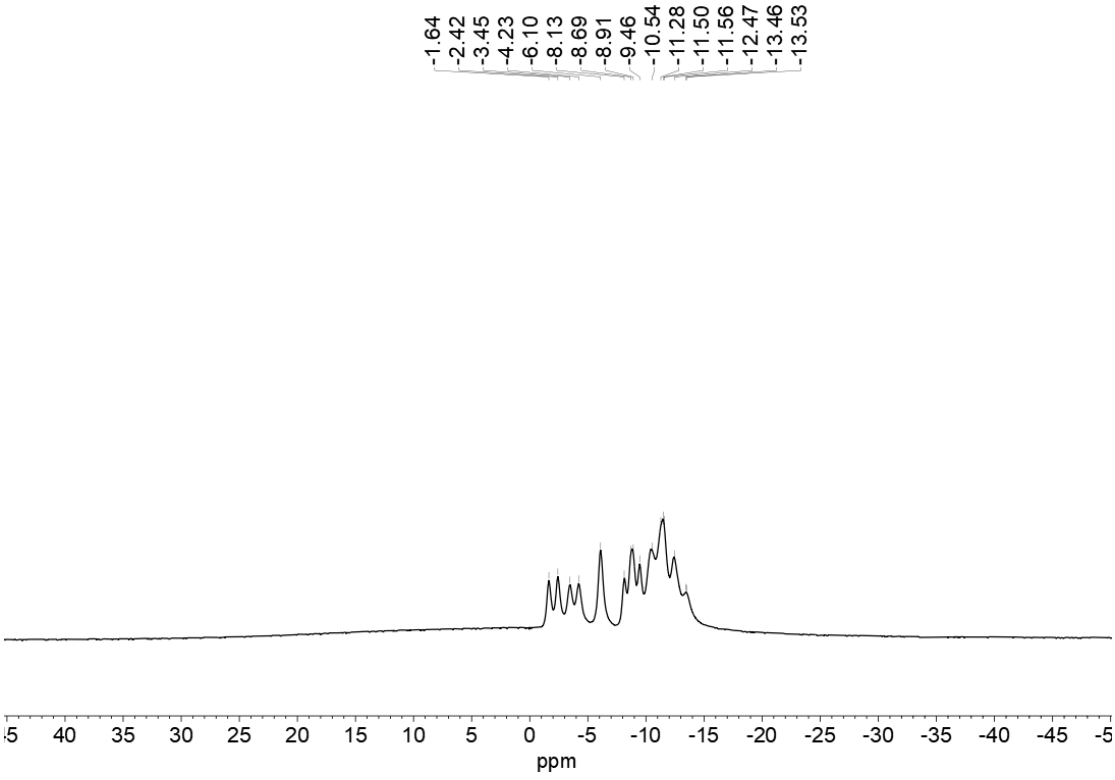
^{1}H NMR (600 MHz, Chloroform-*d*)



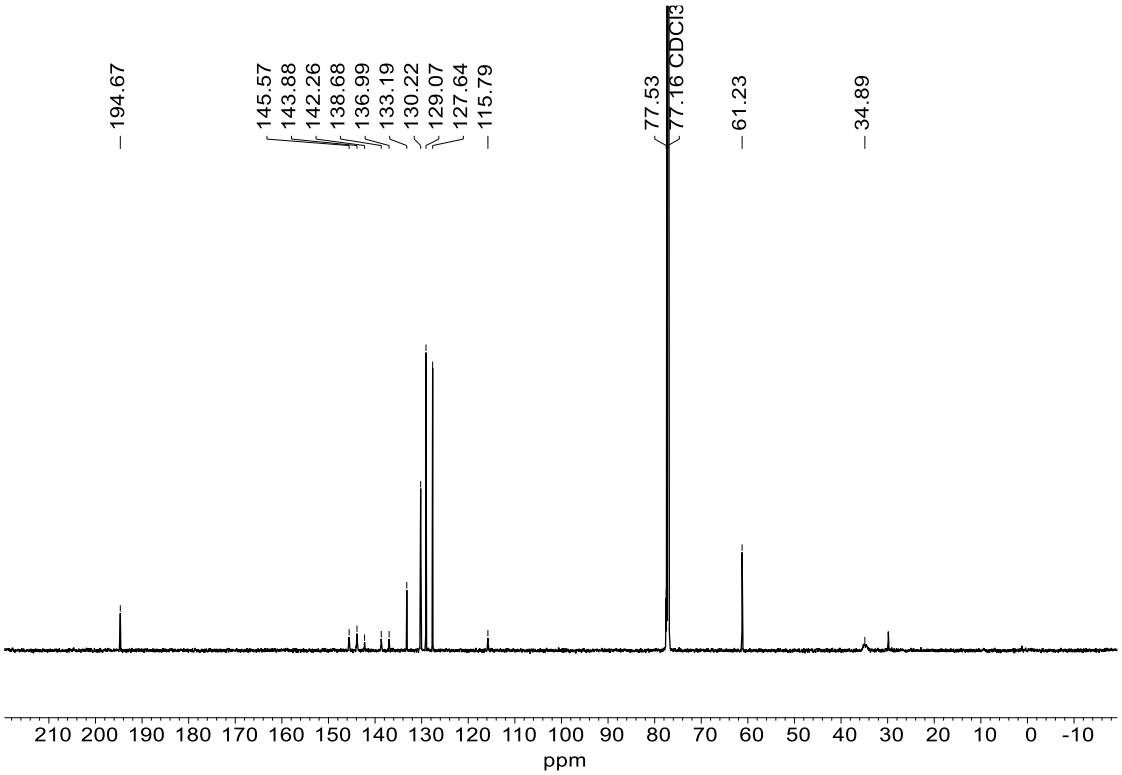
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*)



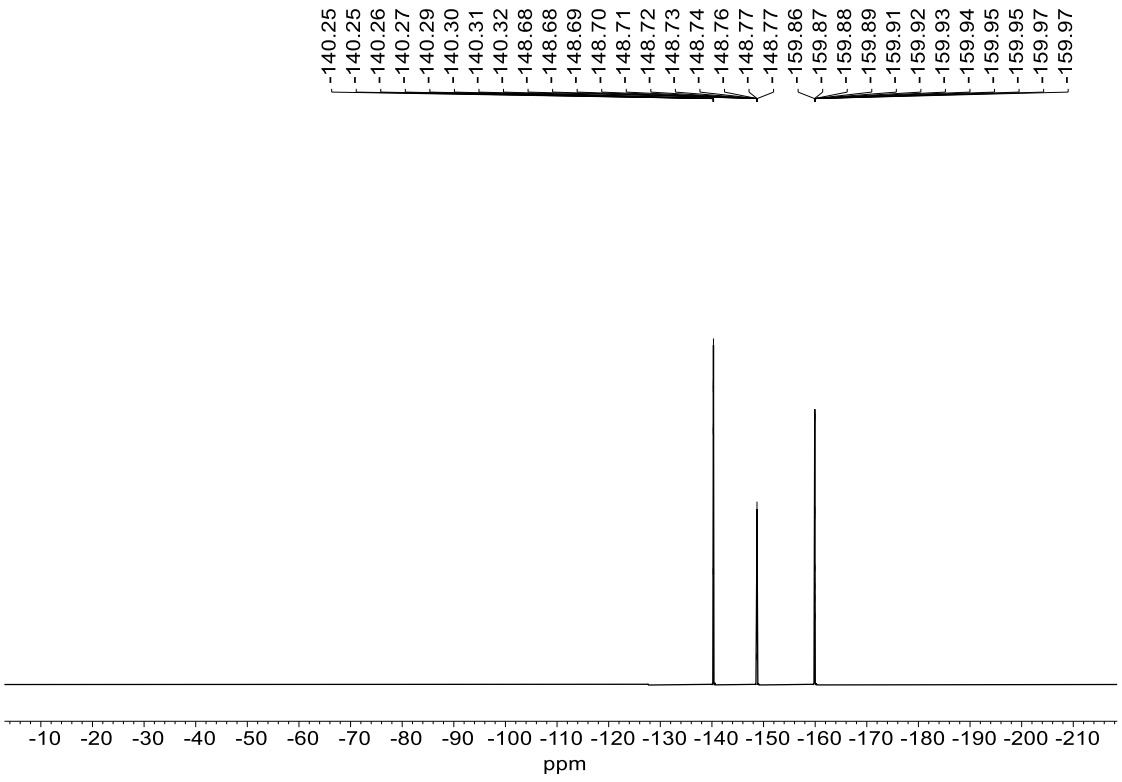
^{11}B NMR (128 MHz, Chloroform-*d*)



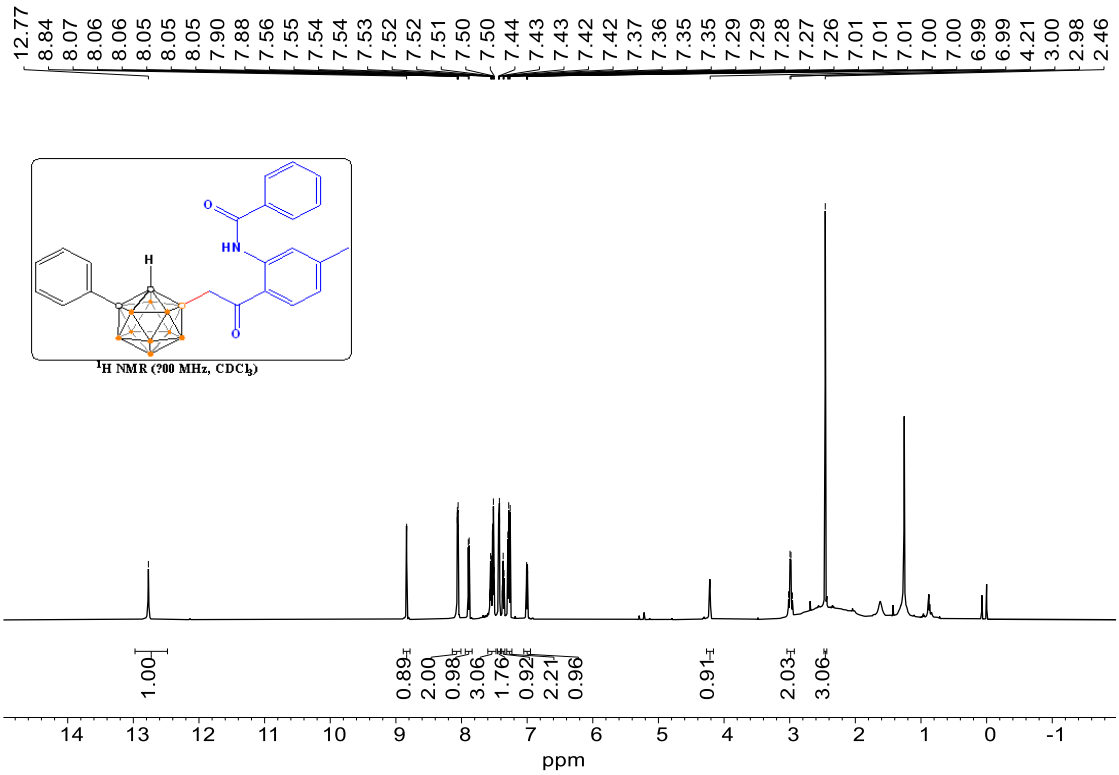
^{13}C NMR (151 MHz, Chloroform-*d*)



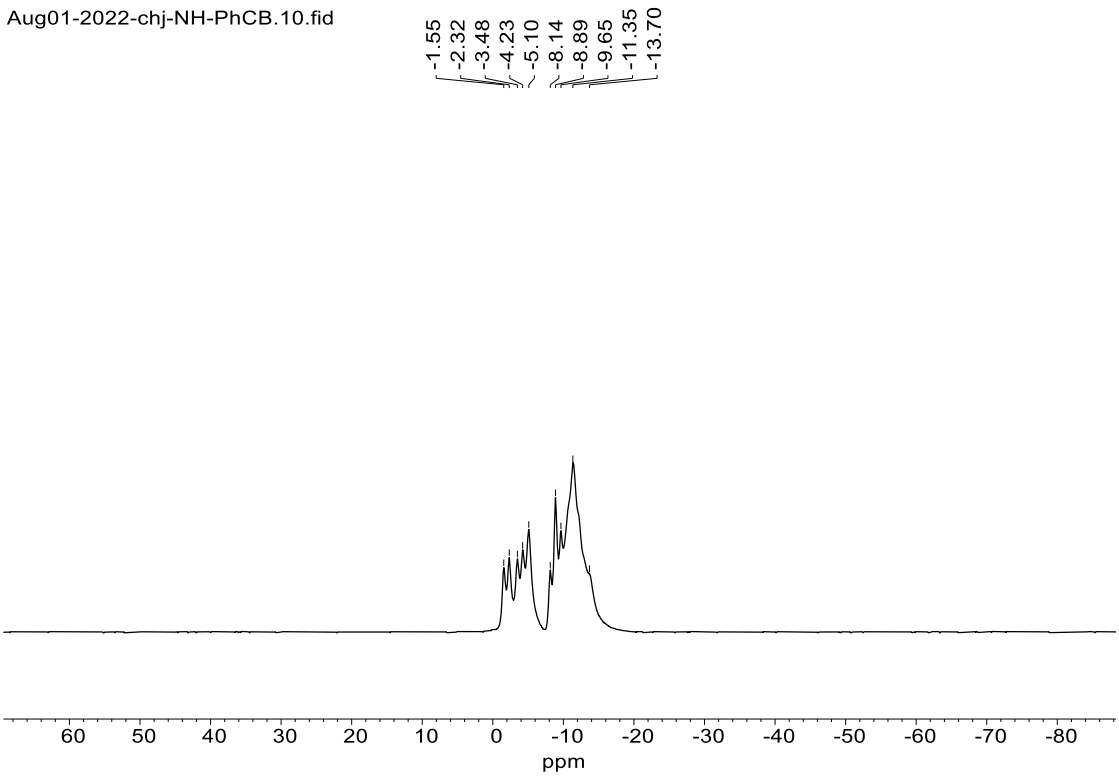
^{19}F NMR (565 MHz, Chloroform-*d*)



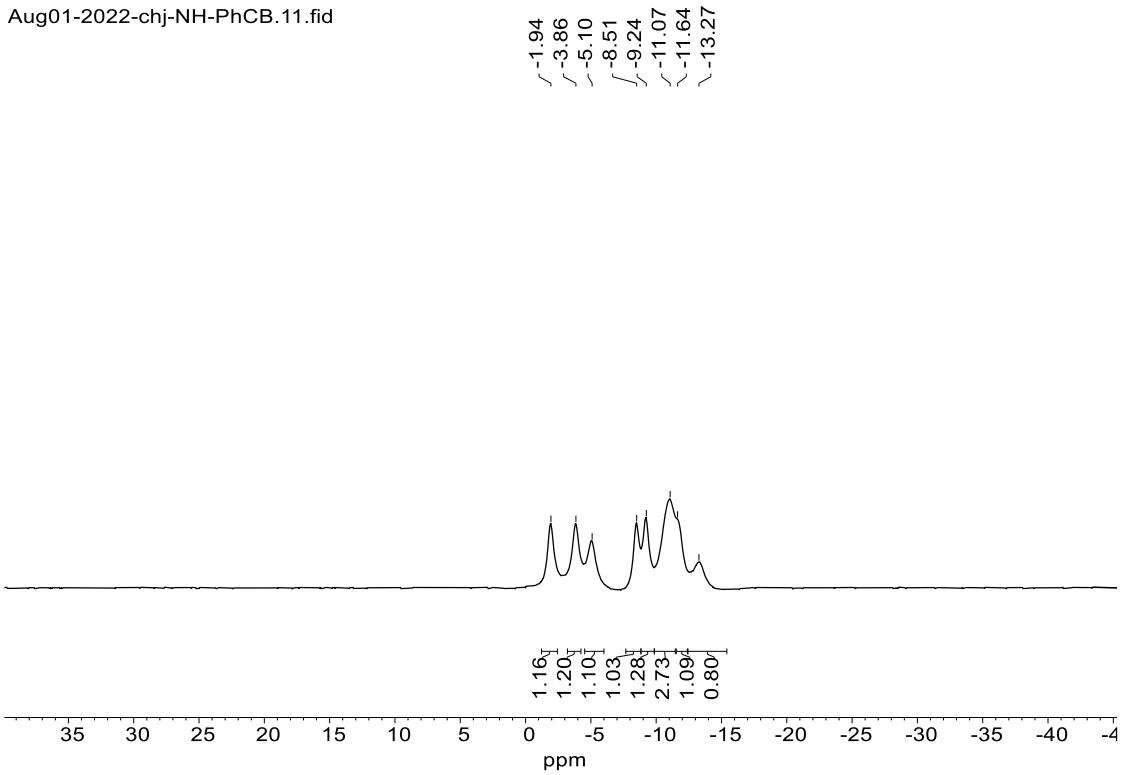
^{1}H NMR (600 MHz, Chloroform-*d*)



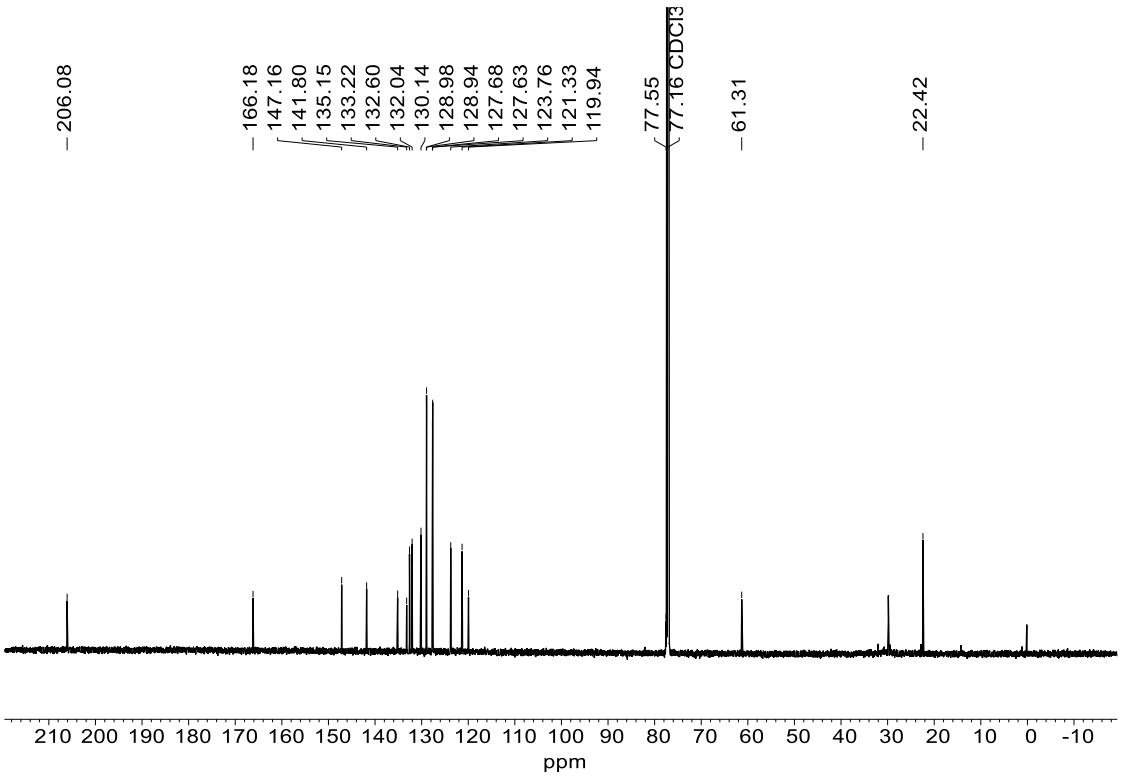
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



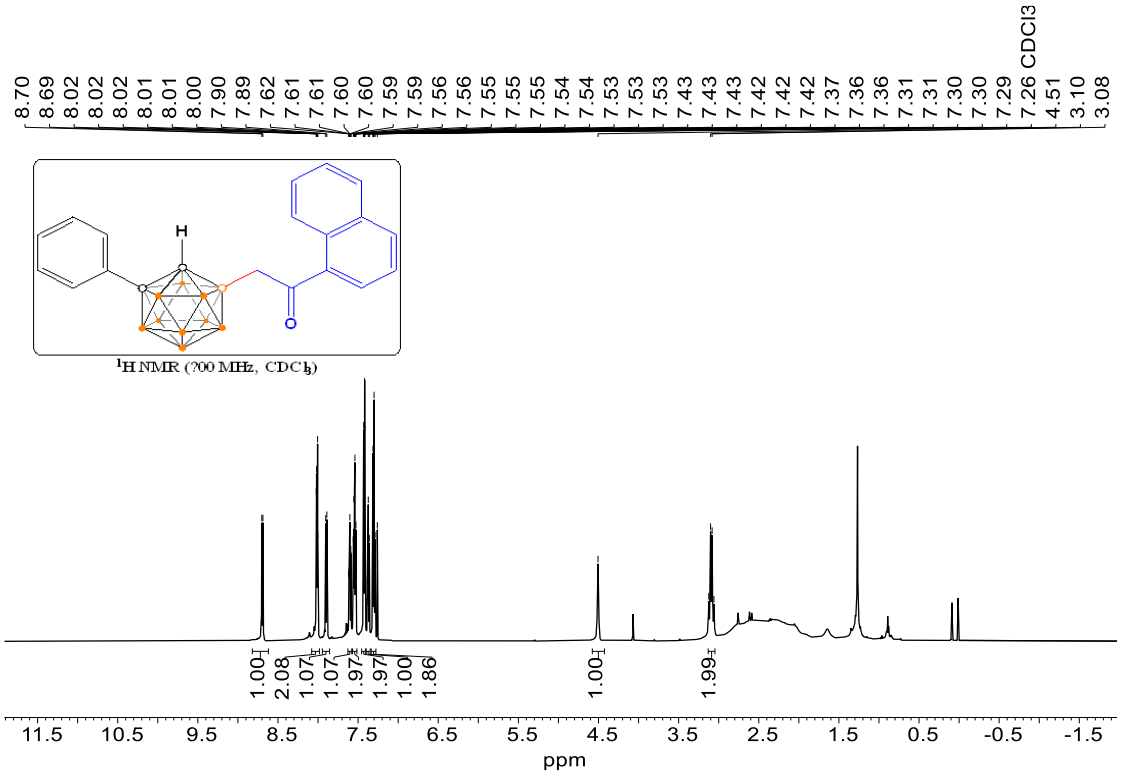
^{11}B NMR (193 MHz, Chloroform-*d*)



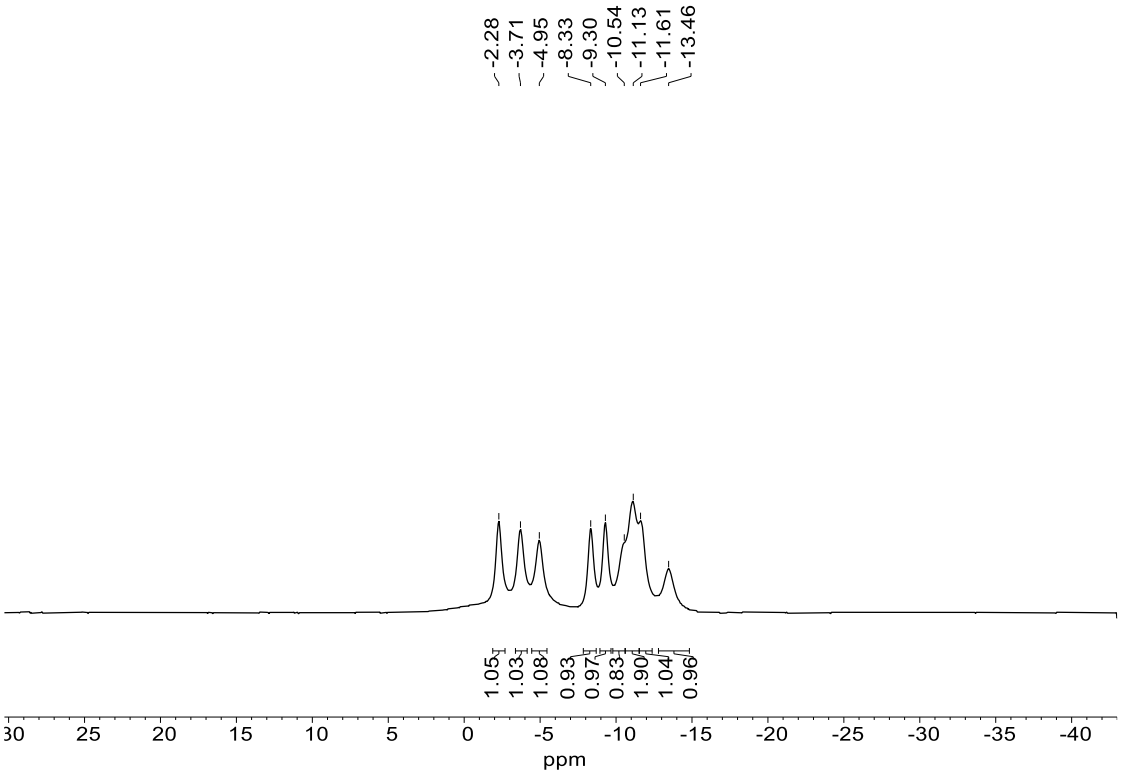
^{13}C NMR (151 MHz, Chloroform-*d*)



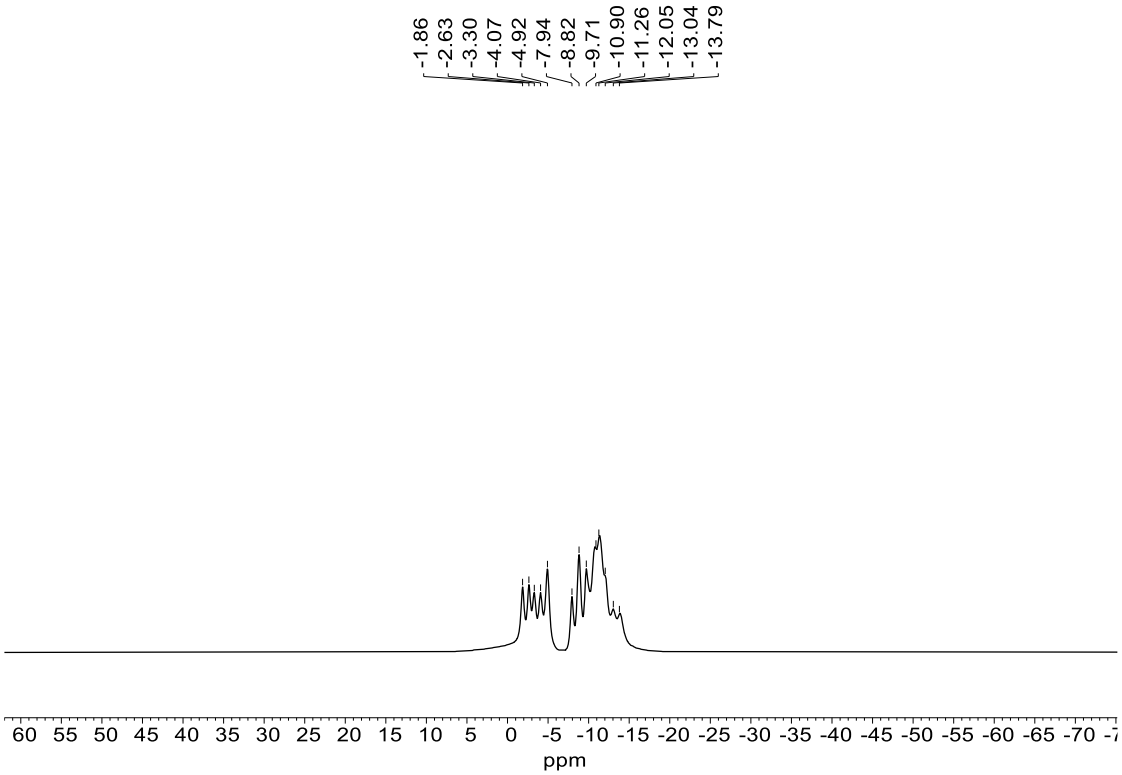
^{1}H NMR (600 MHz, Chloroform-*d*)



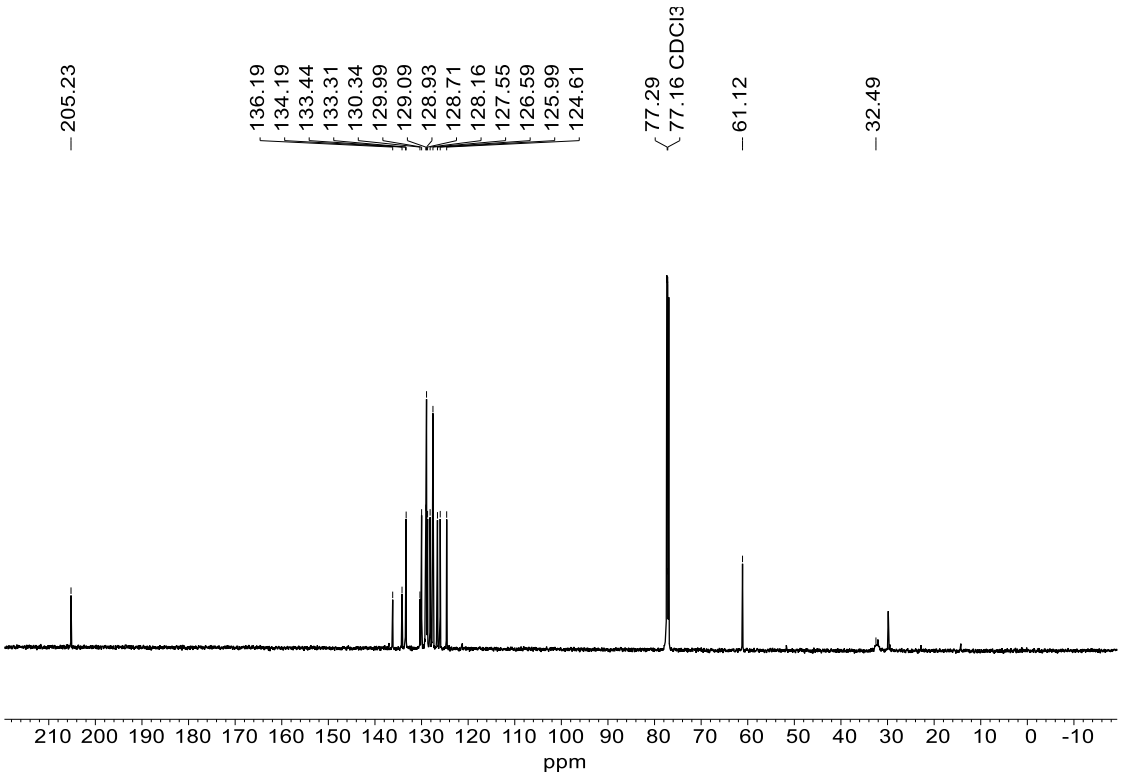
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



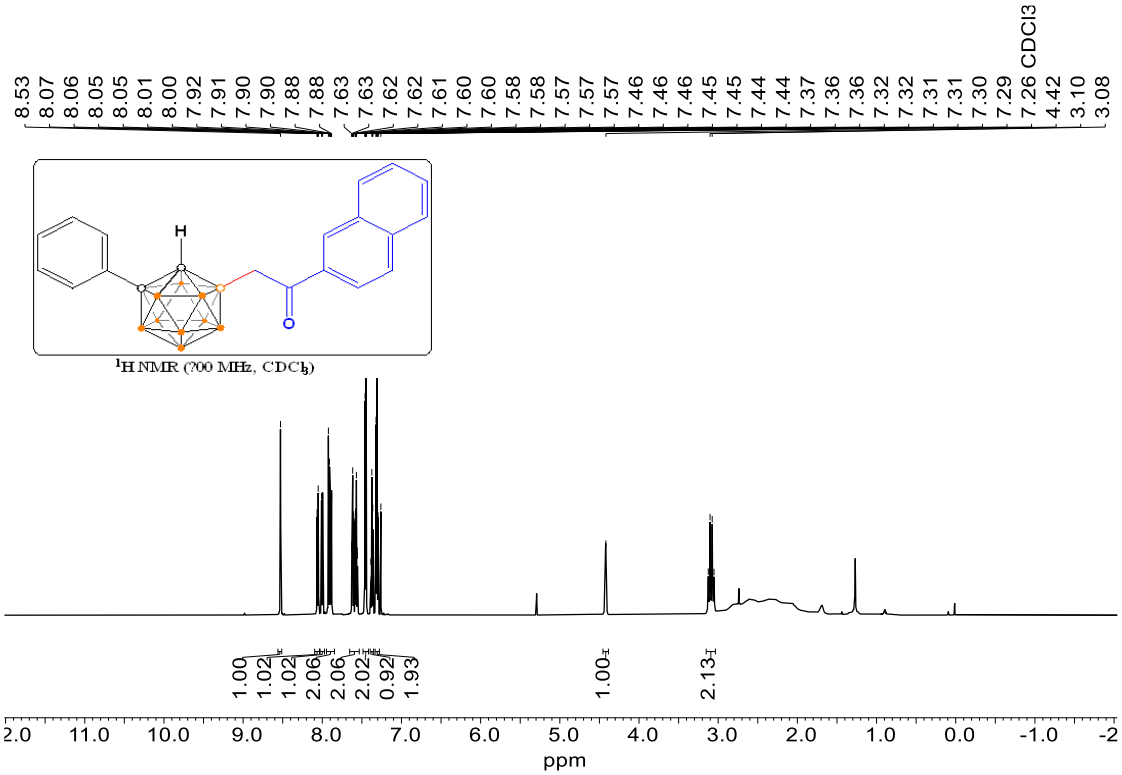
^{11}B NMR (193 MHz, Chloroform-*d*)



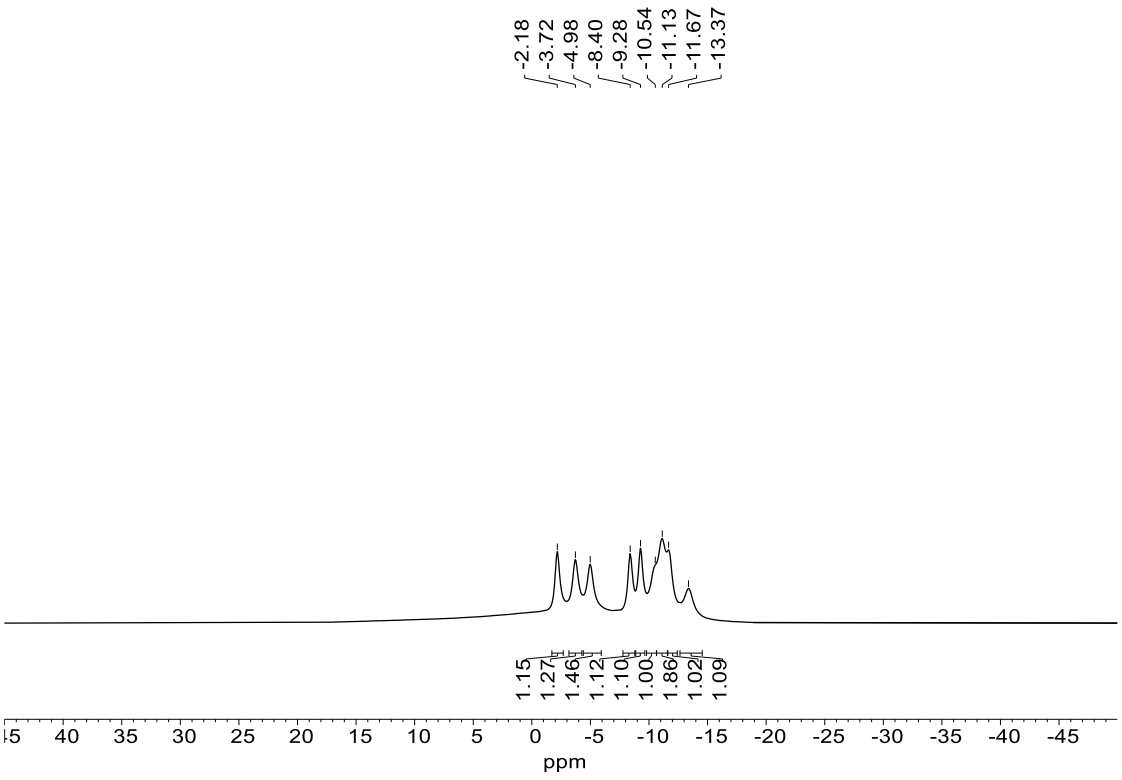
^{13}C NMR (151 MHz, Chloroform-*d*)



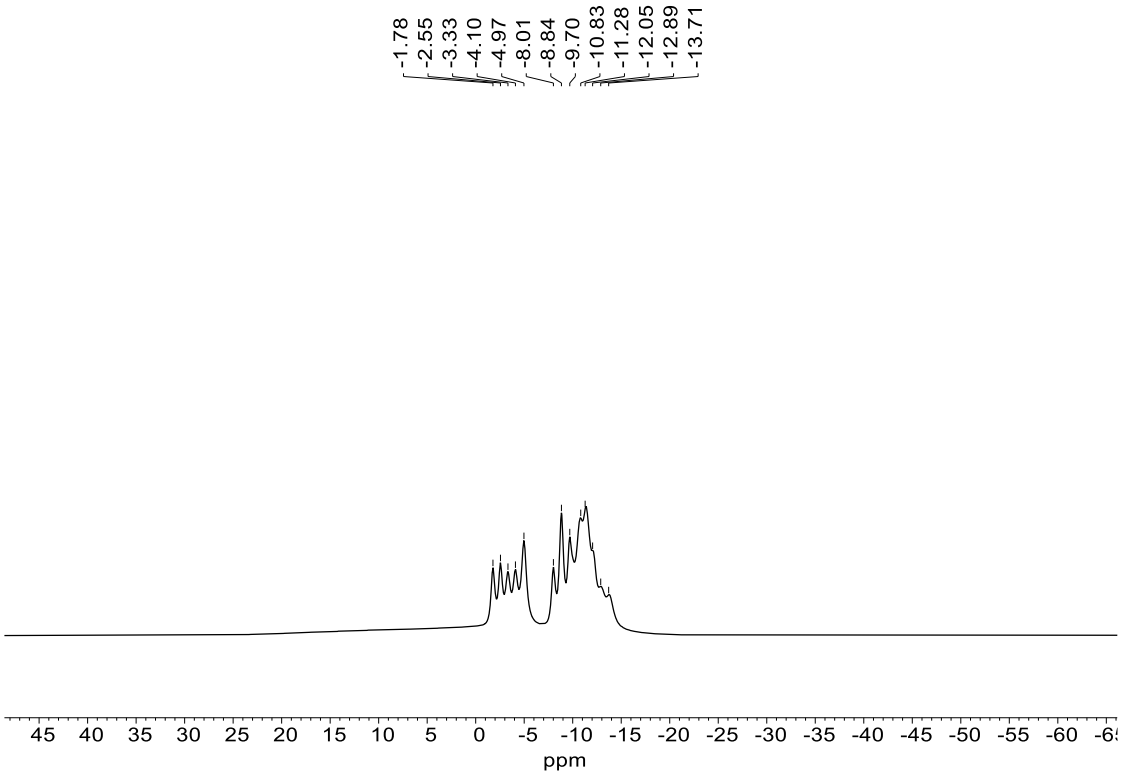
^{1}H NMR (600 MHz, Chloroform-*d*)



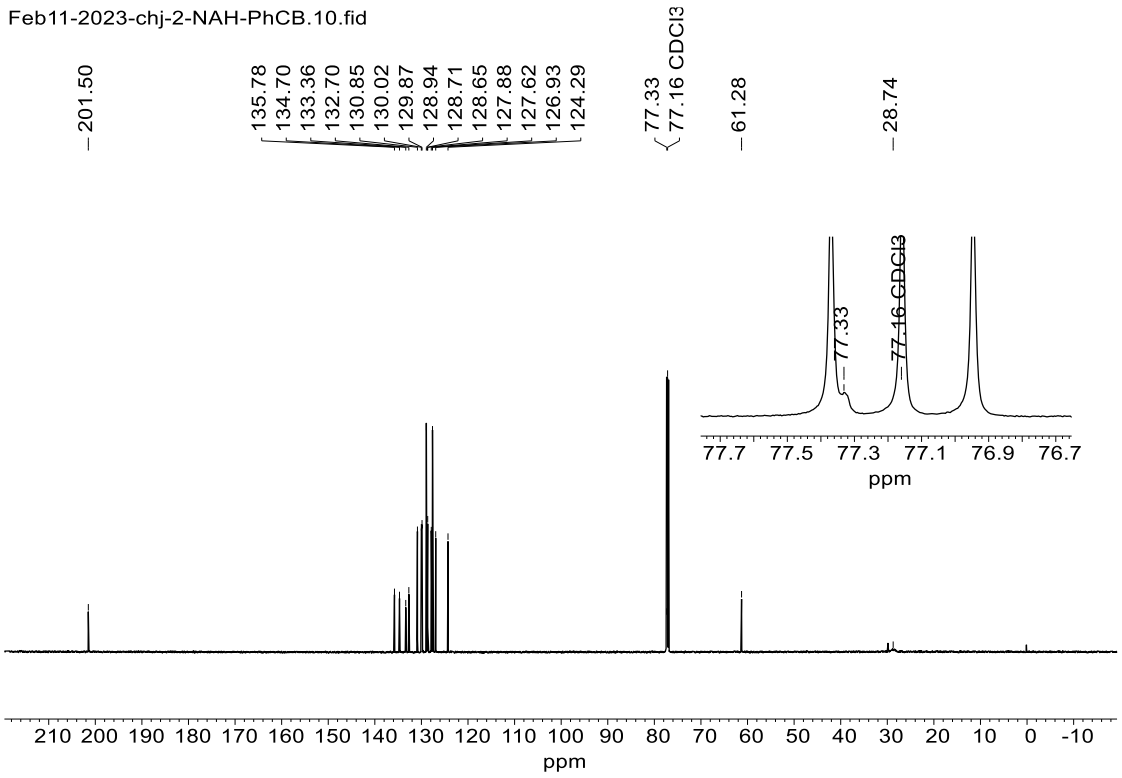
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



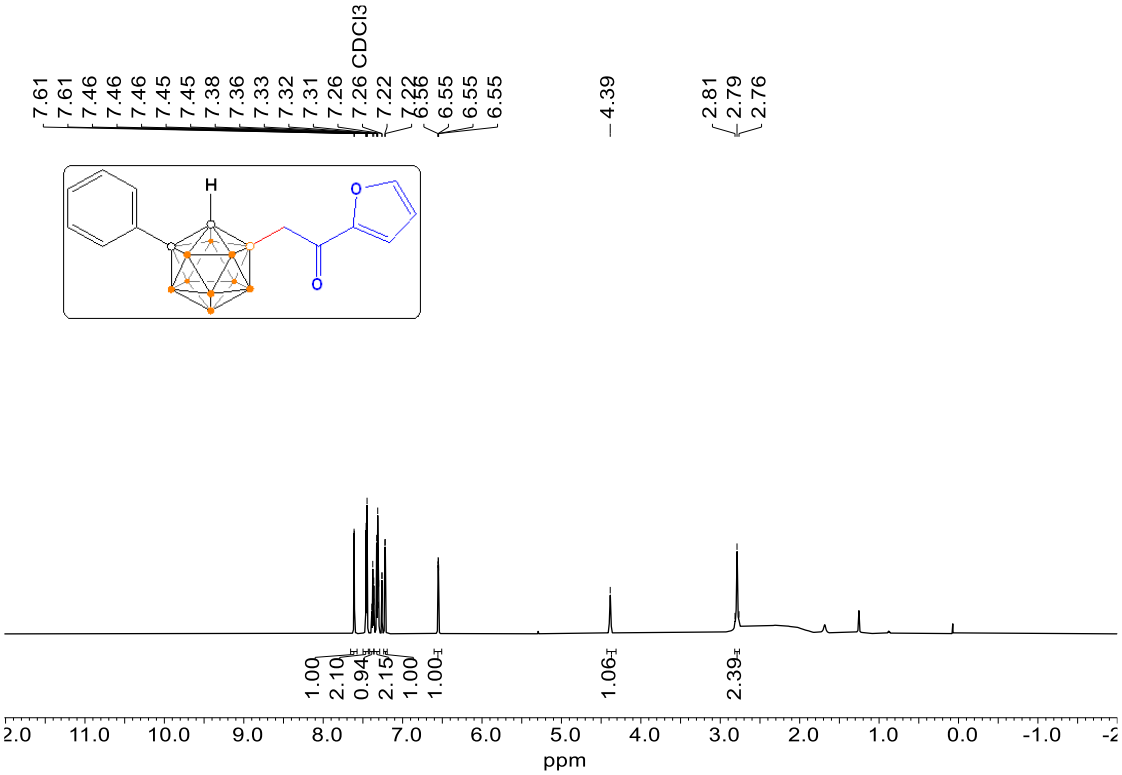
^{11}B NMR (193 MHz, Chloroform-*d*)



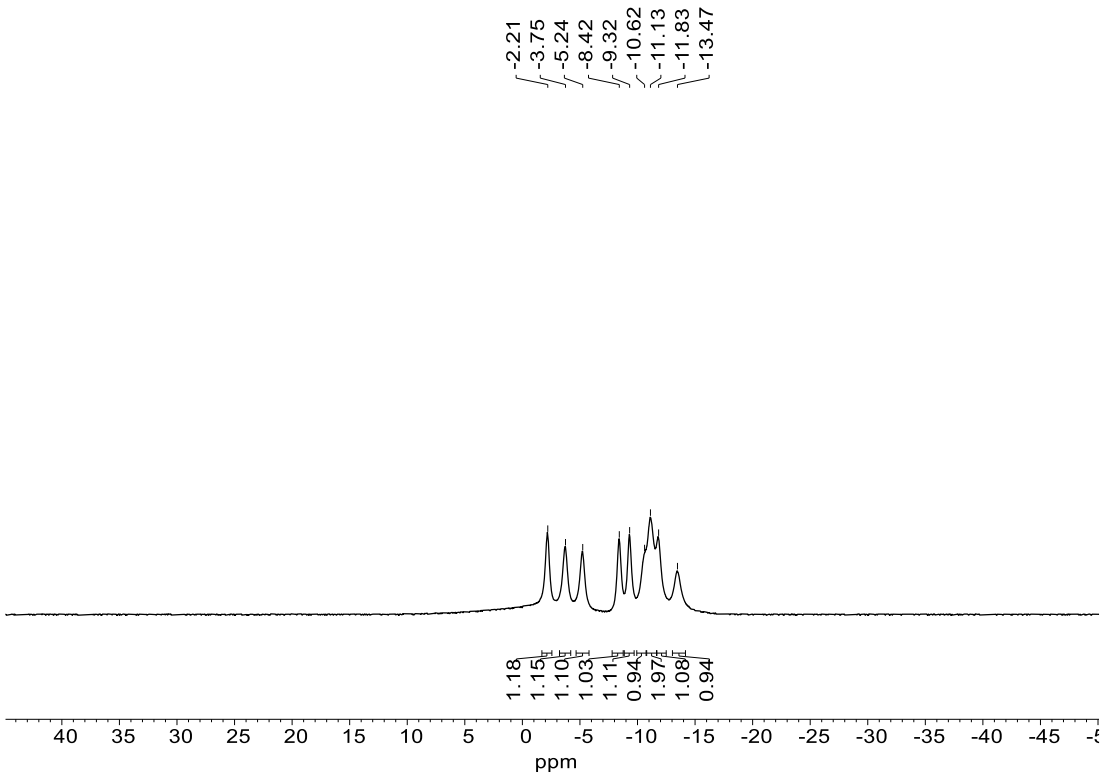
^{13}C NMR (151 MHz, Chloroform-*d*)



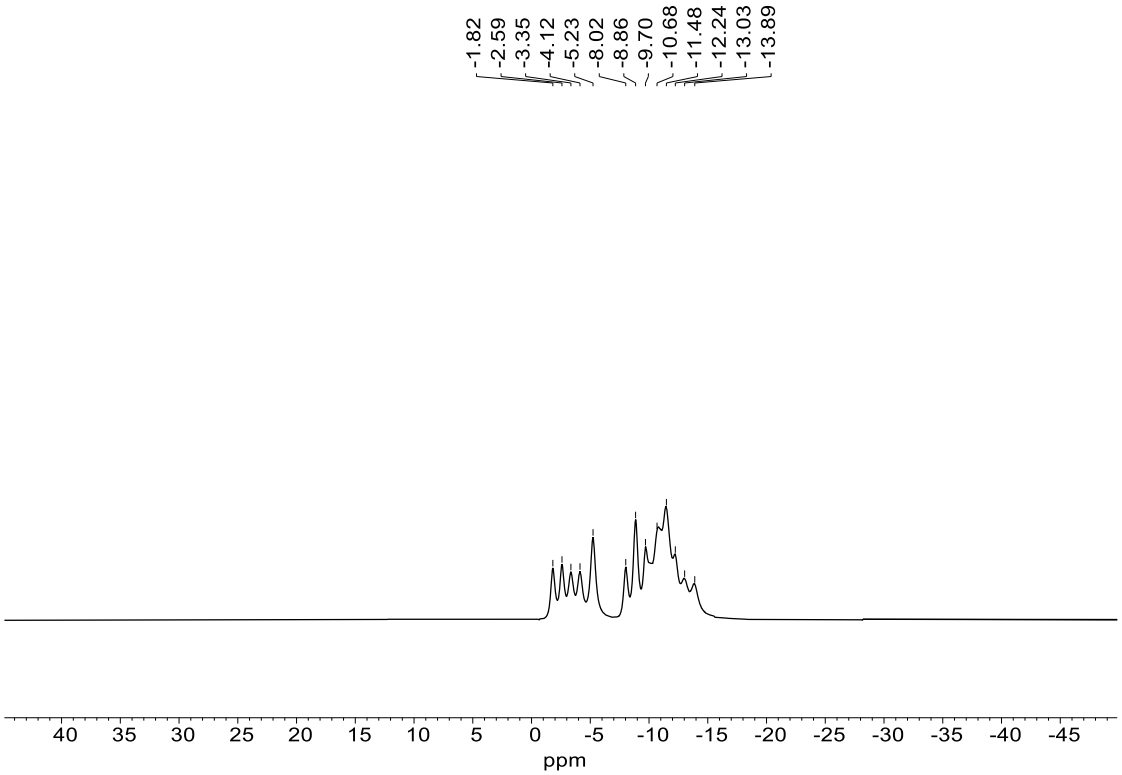
^{1}H NMR (600 MHz, Chloroform-*d*)



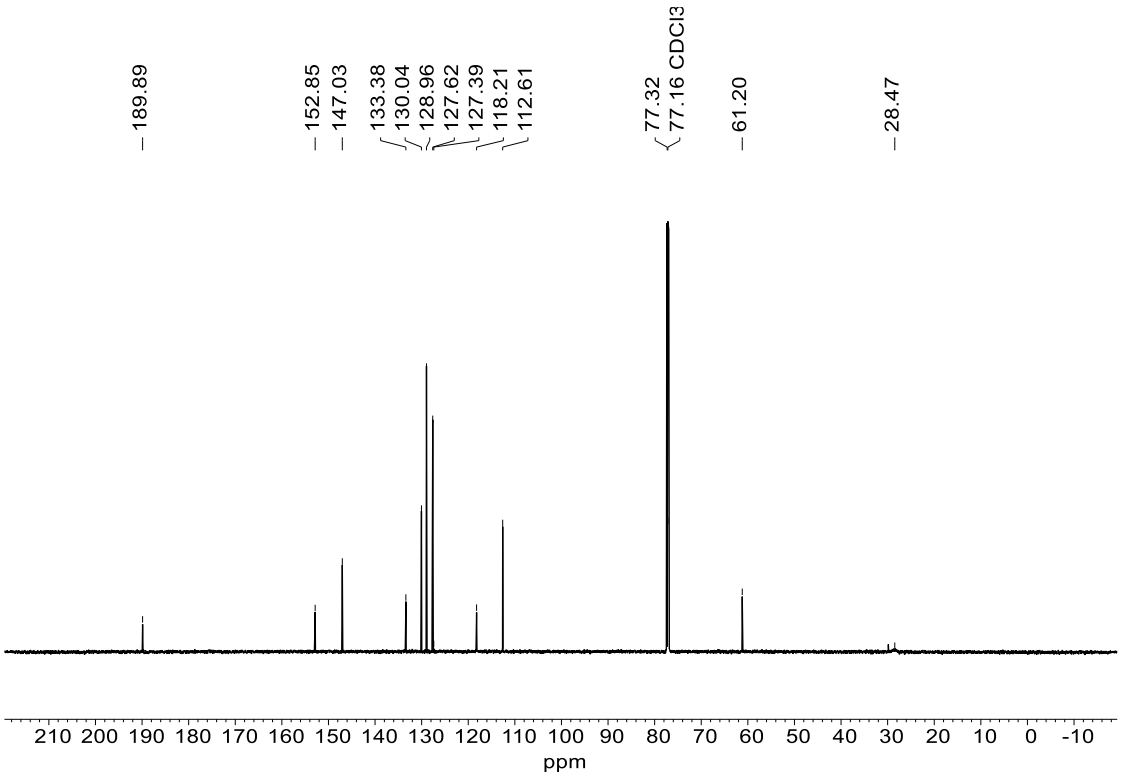
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



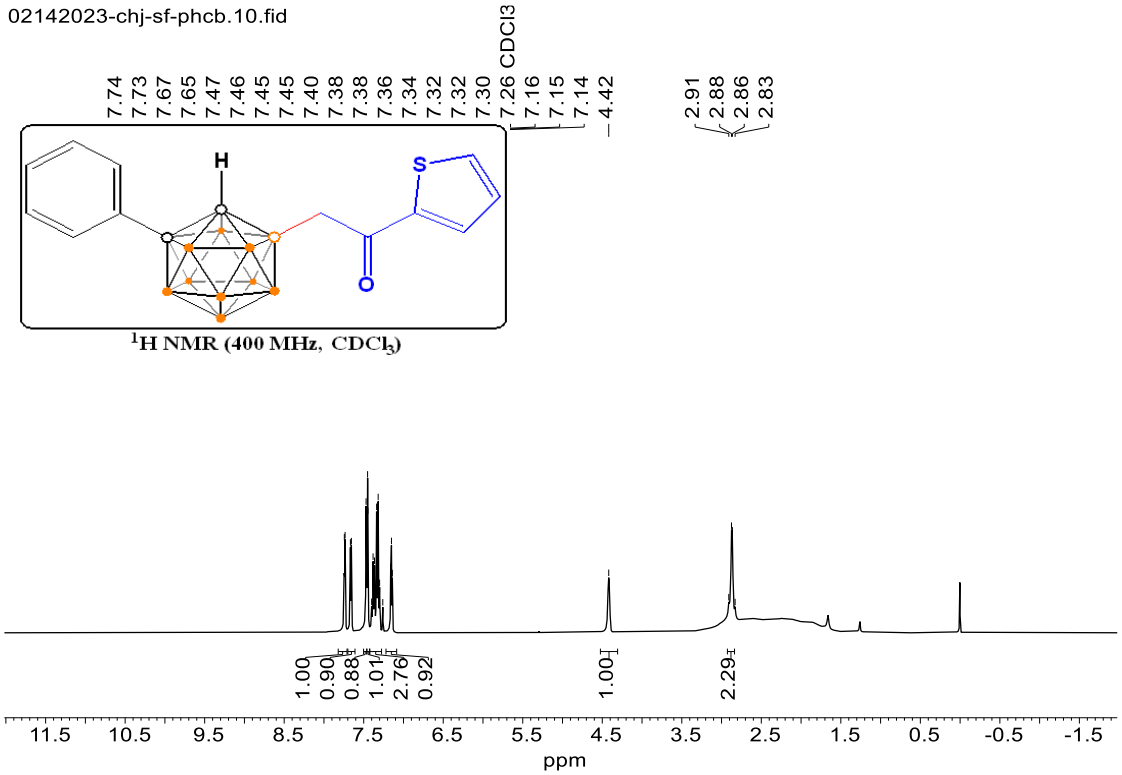
^{11}B NMR (193 MHz, Chloroform-*d*)



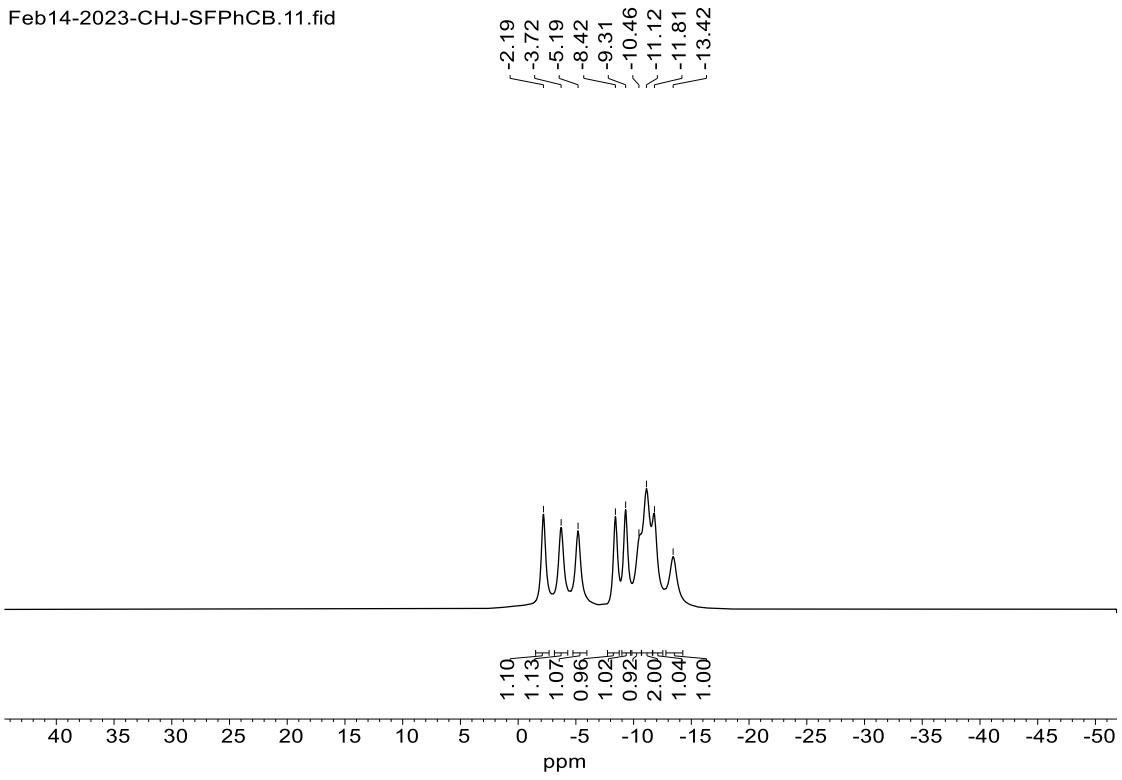
^{13}C NMR (151 MHz, Chloroform-*d*)



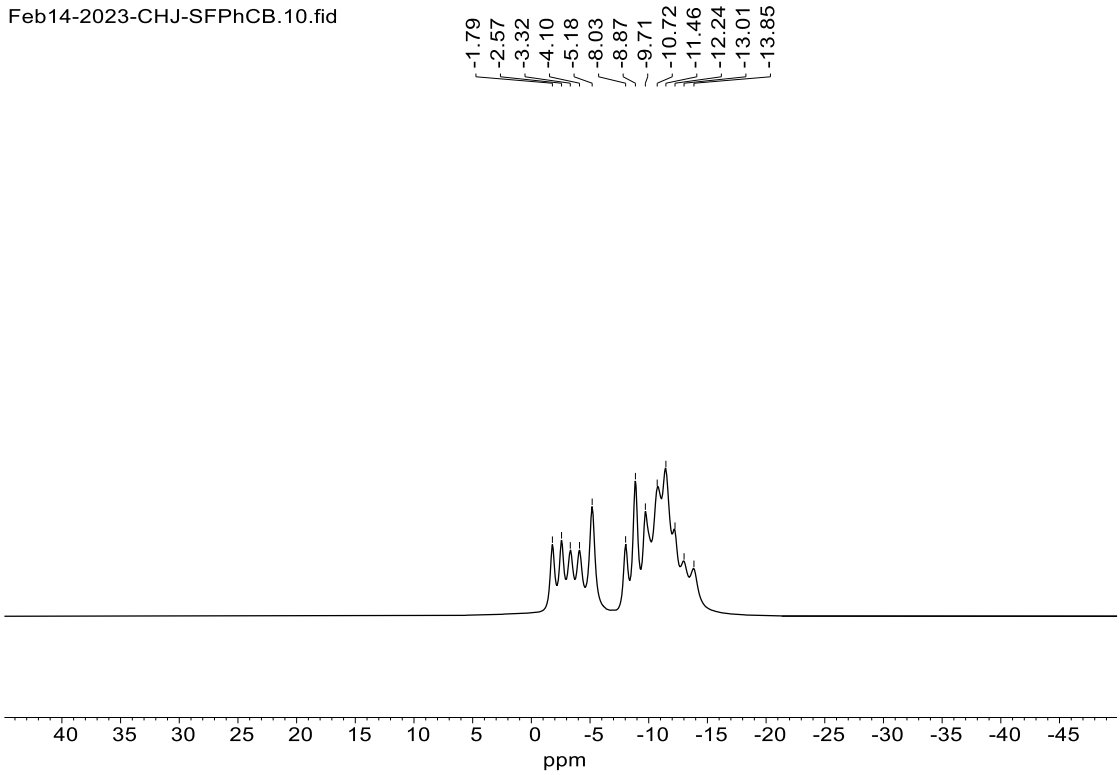
^{1}H NMR (400 MHz, Chloroform-*d*)



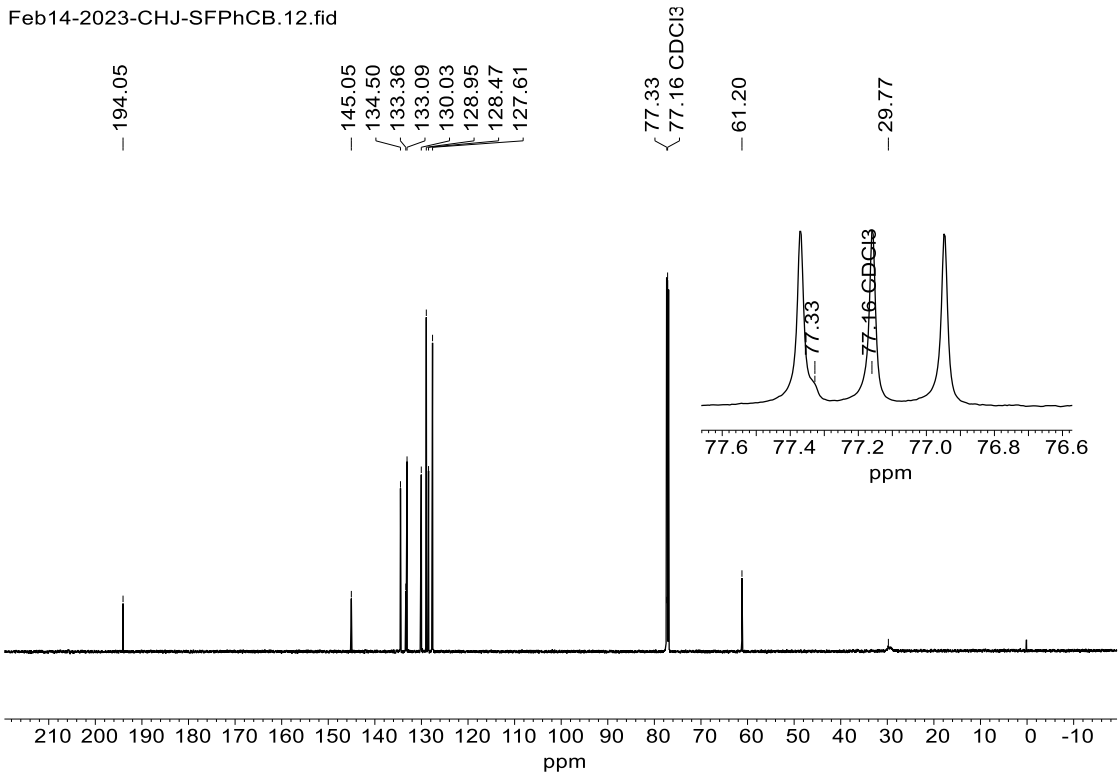
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



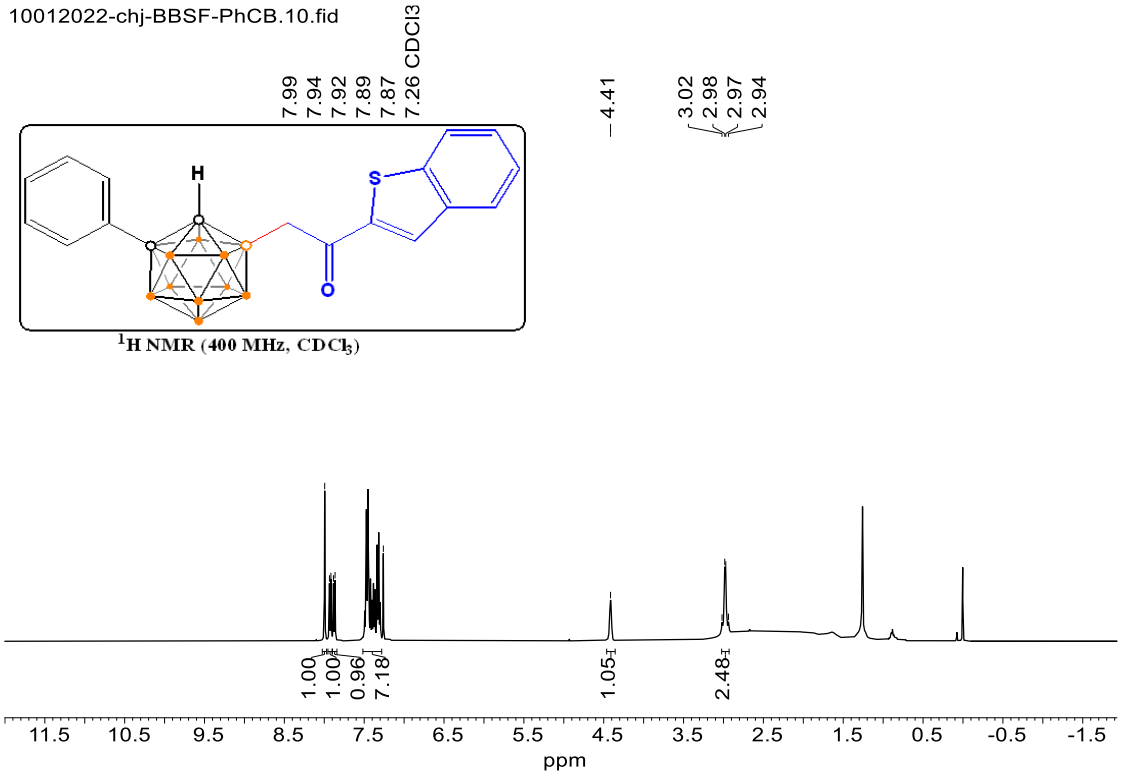
^{11}B NMR (193 MHz, Chloroform-*d*)



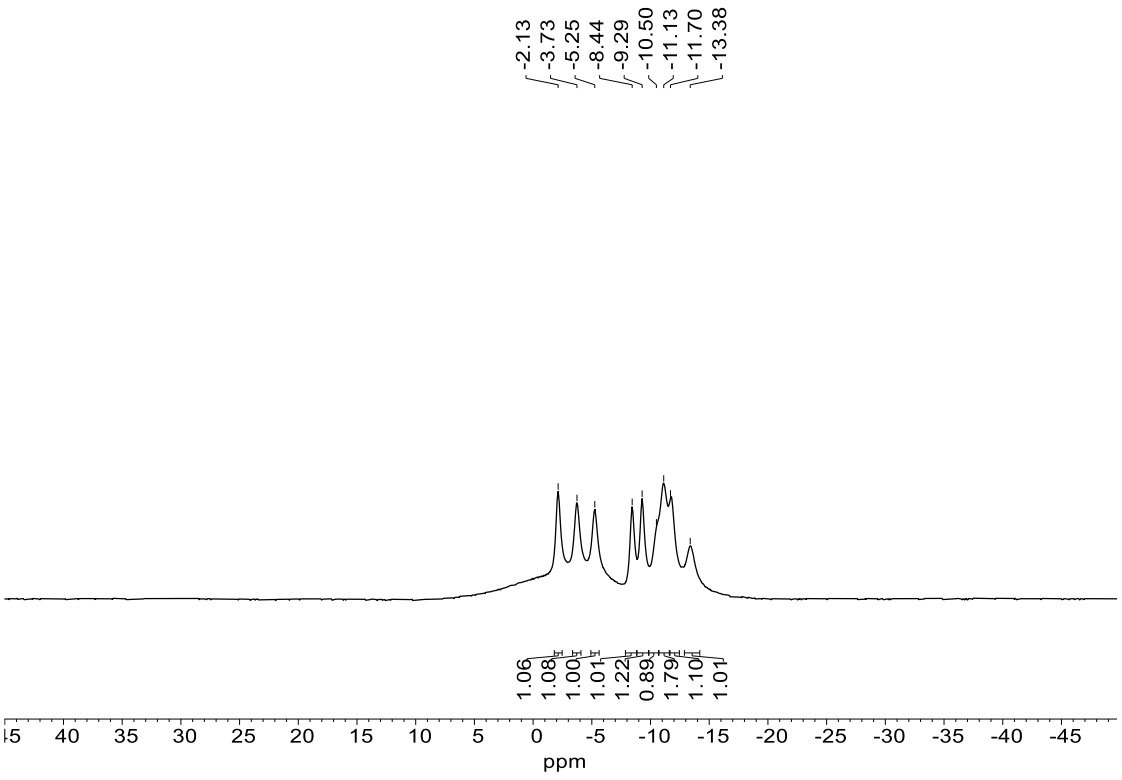
^{13}C NMR (151 MHz, Chloroform-*d*)



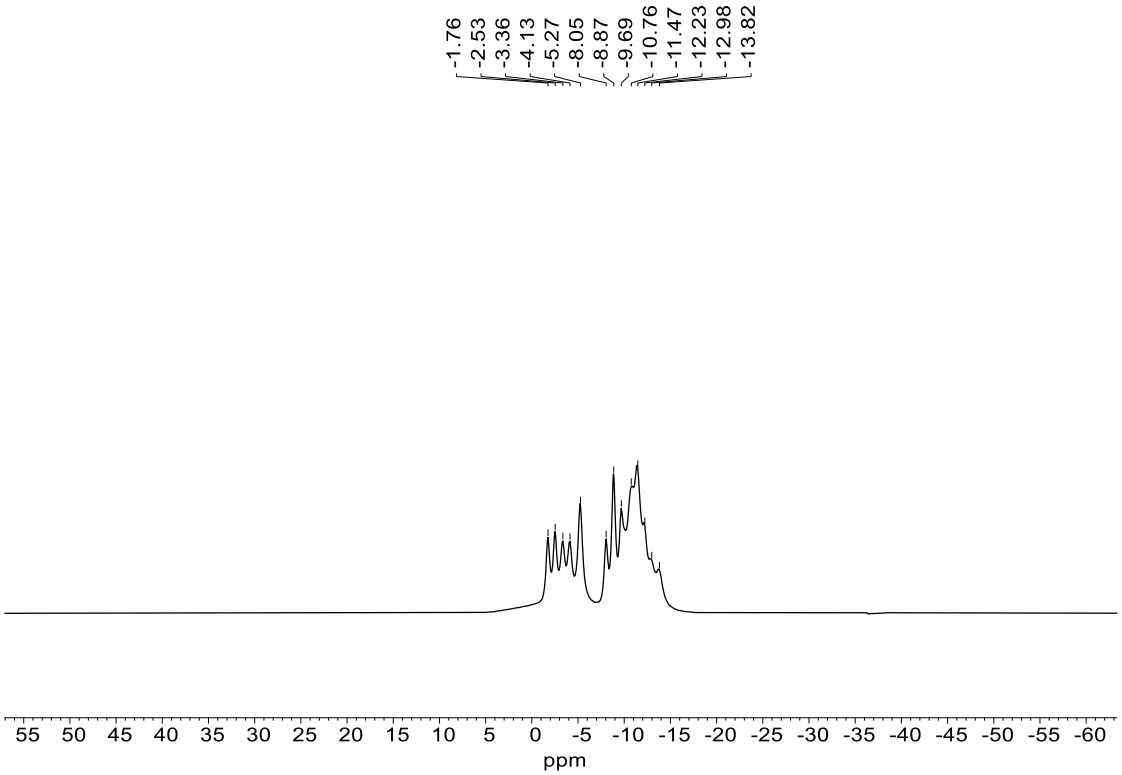
^{1}H NMR (400 MHz, Chloroform-*d*)



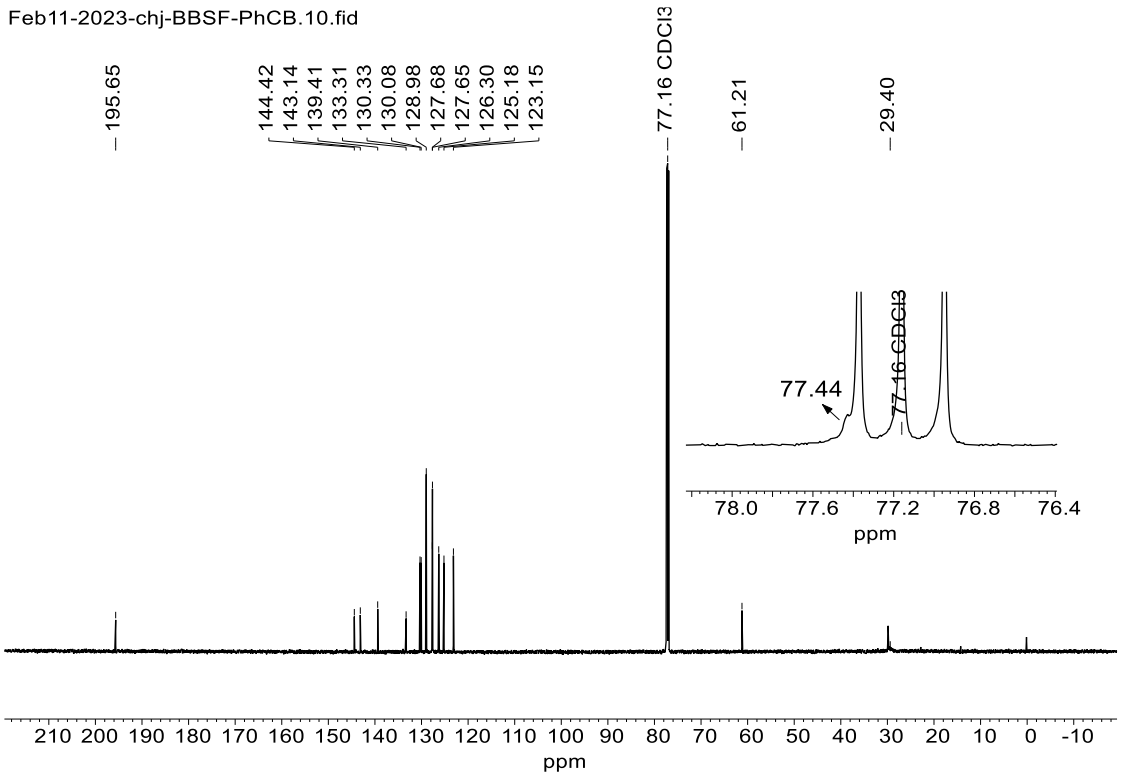
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



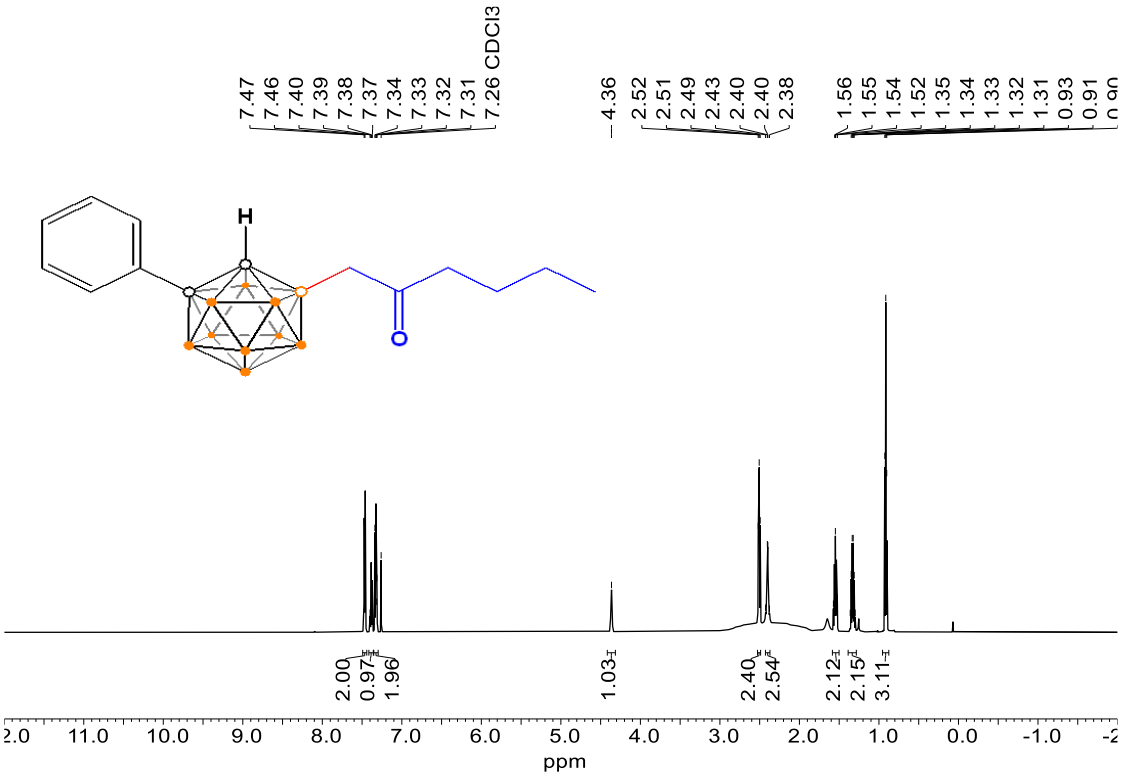
^{11}B NMR (193 MHz, Chloroform-*d*)



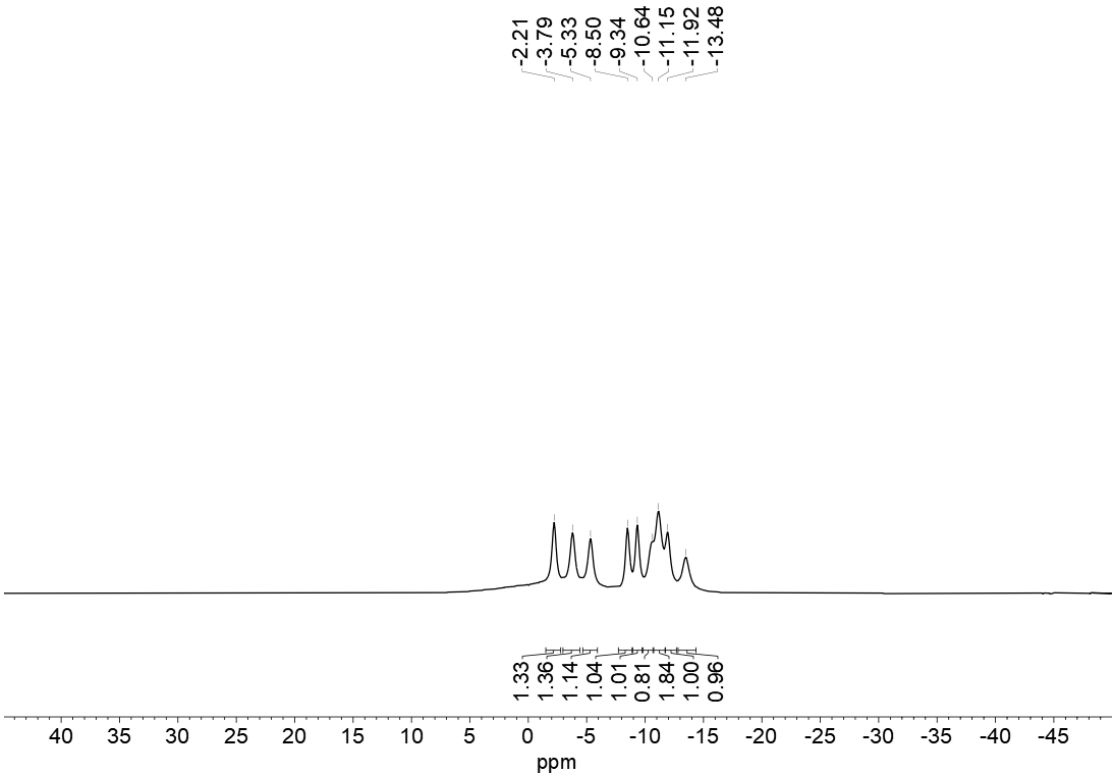
^{13}C NMR (151 MHz, Chloroform-*d*)



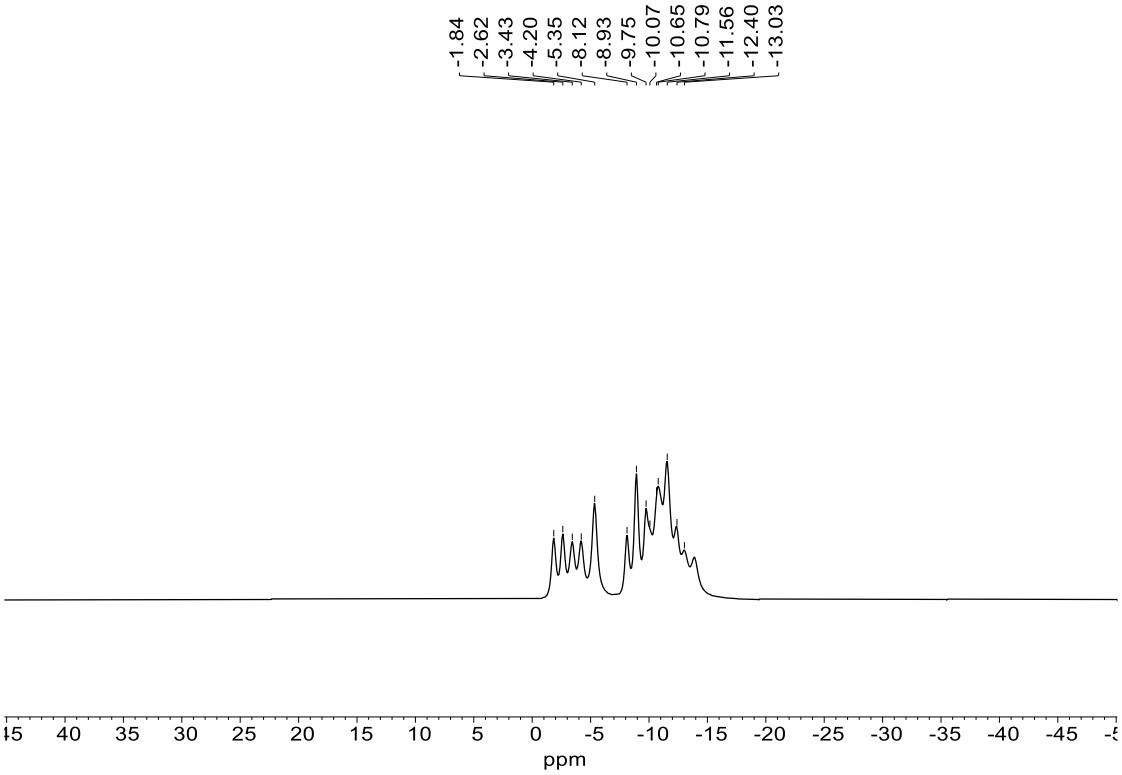
^{1}H NMR (600 MHz, Chloroform-*d*)



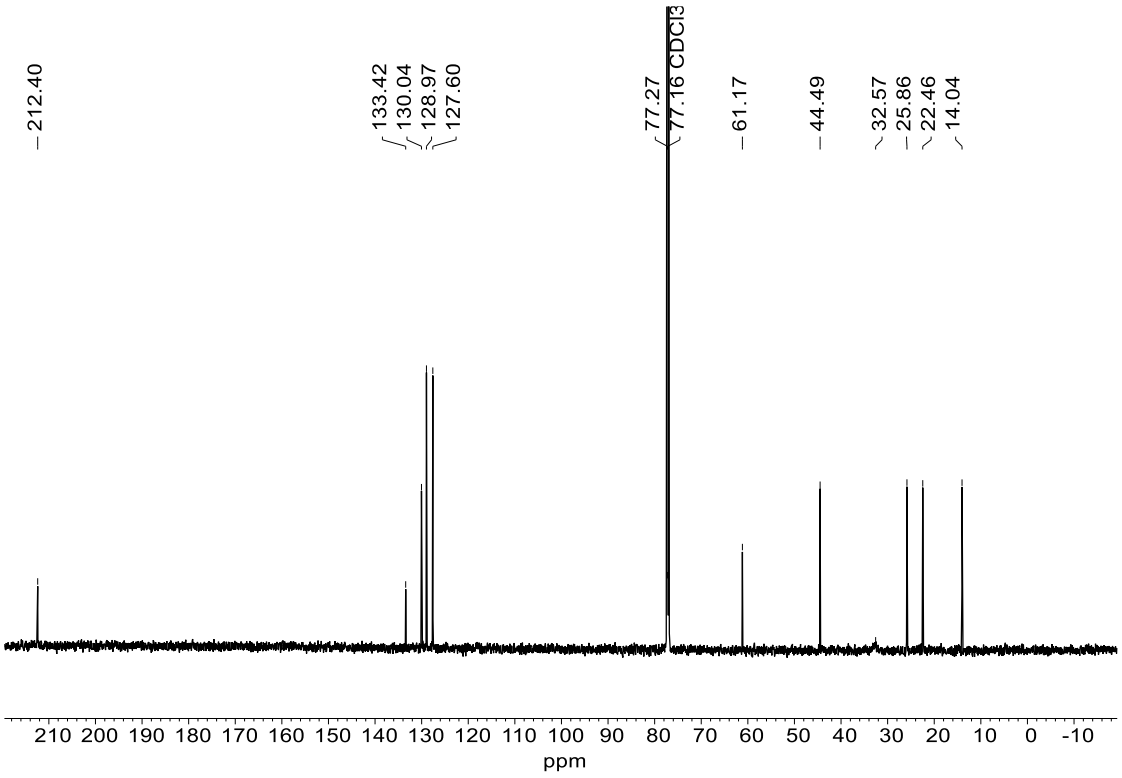
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



^{11}B NMR (193 MHz, Chloroform-*d*)



^{13}C NMR (151 MHz, Chloroform-*d*)



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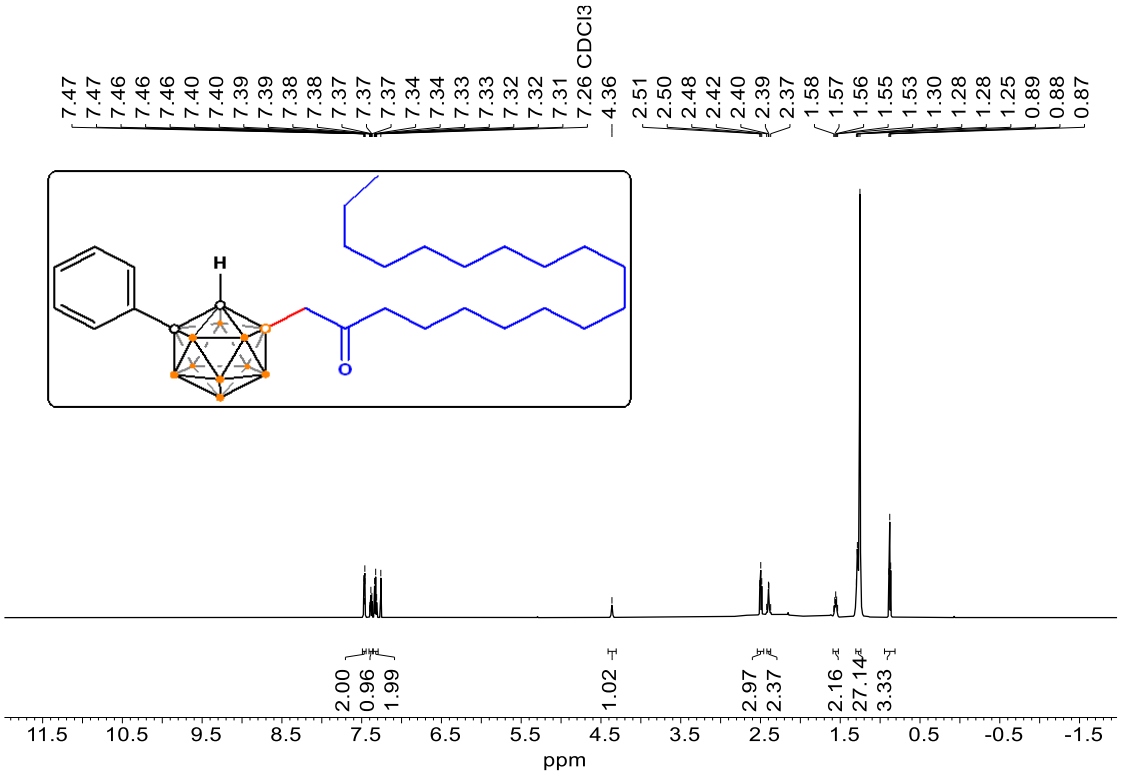

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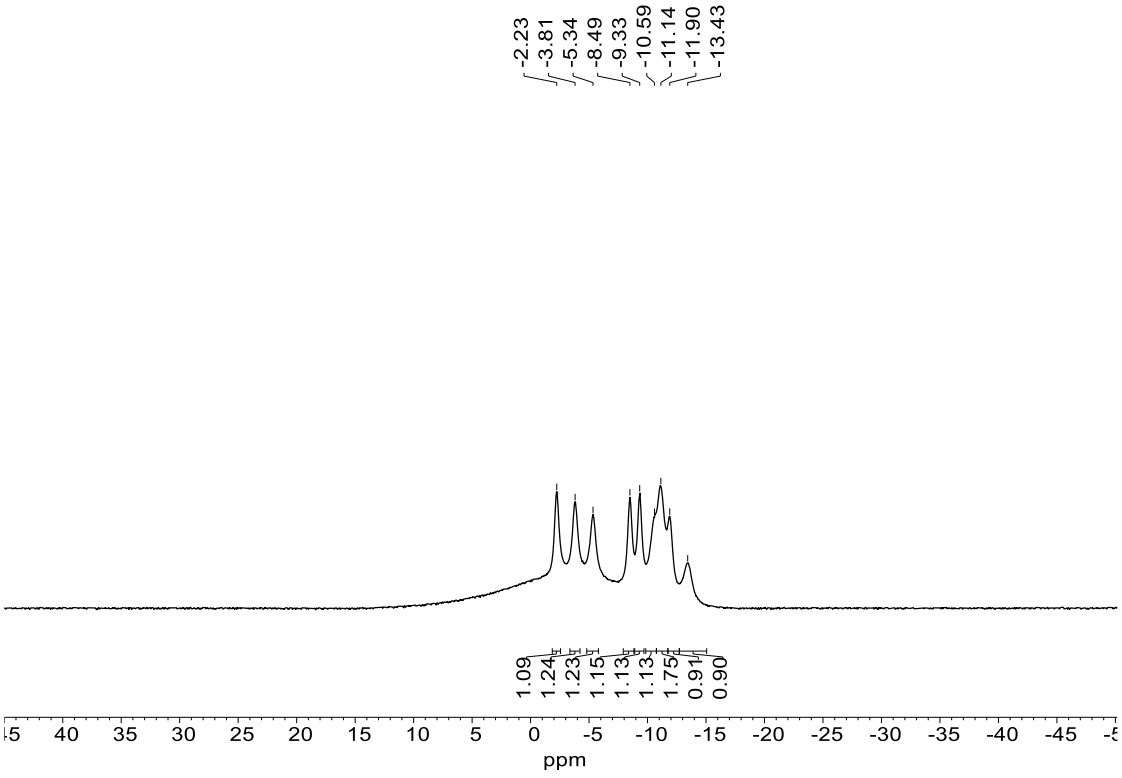

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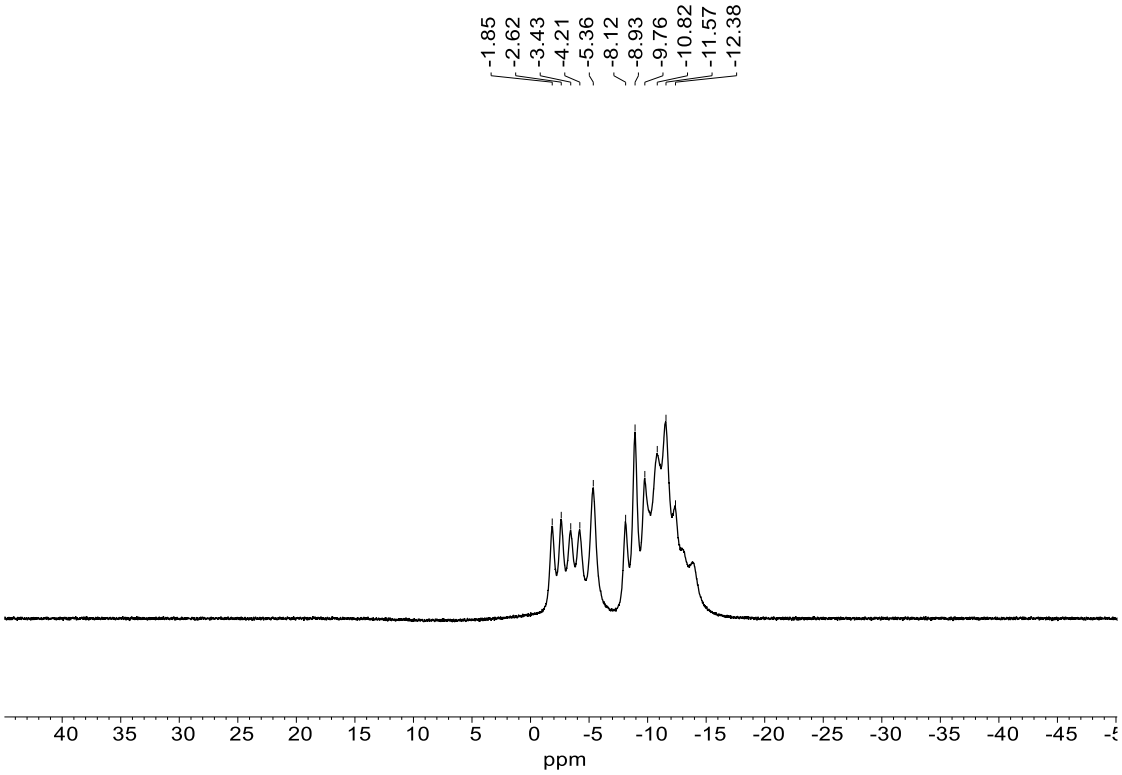

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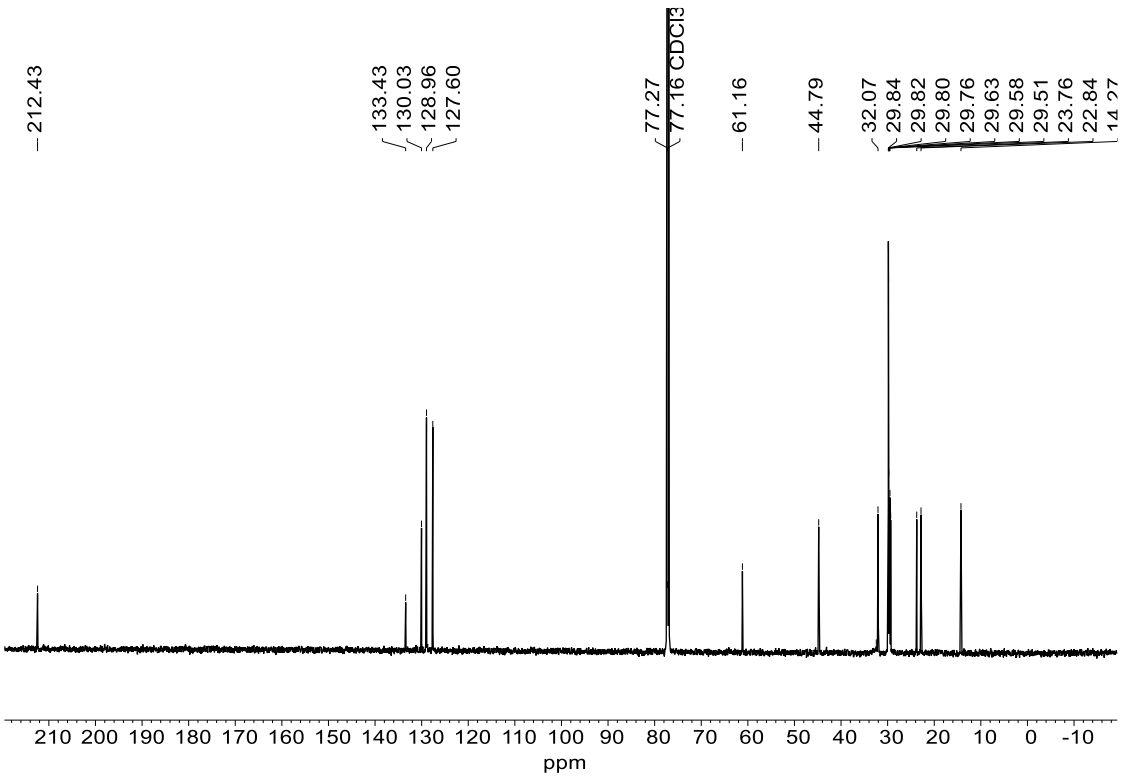

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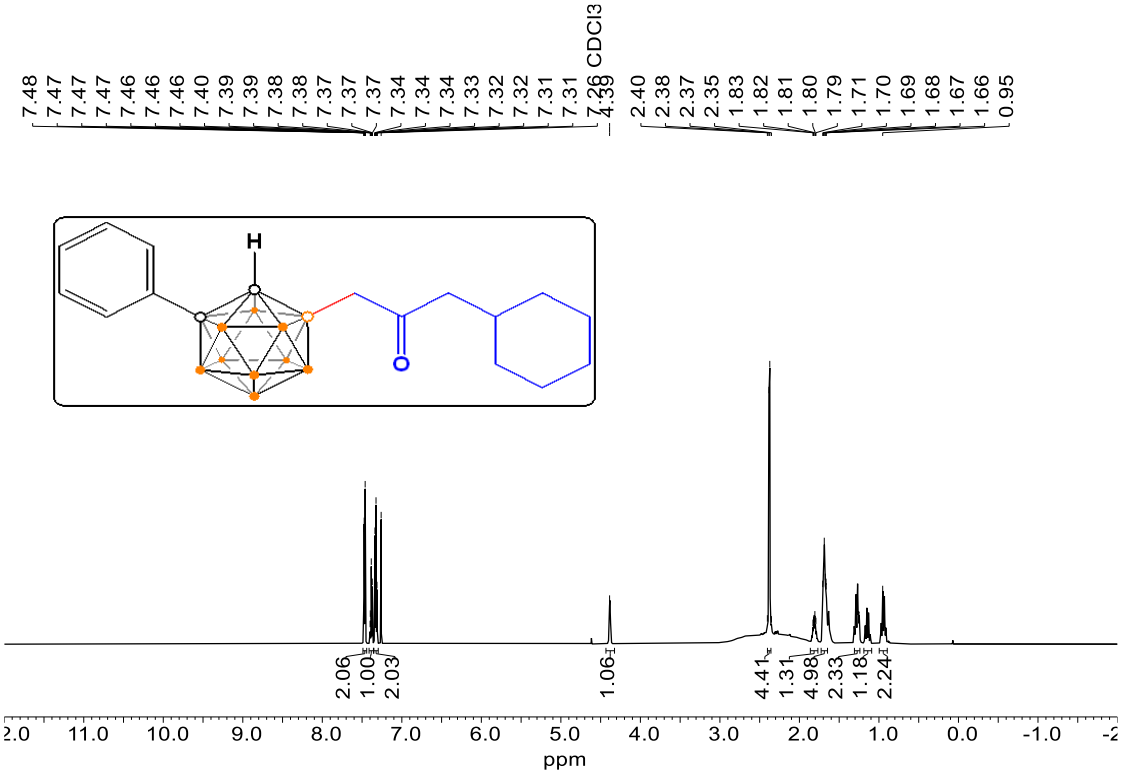

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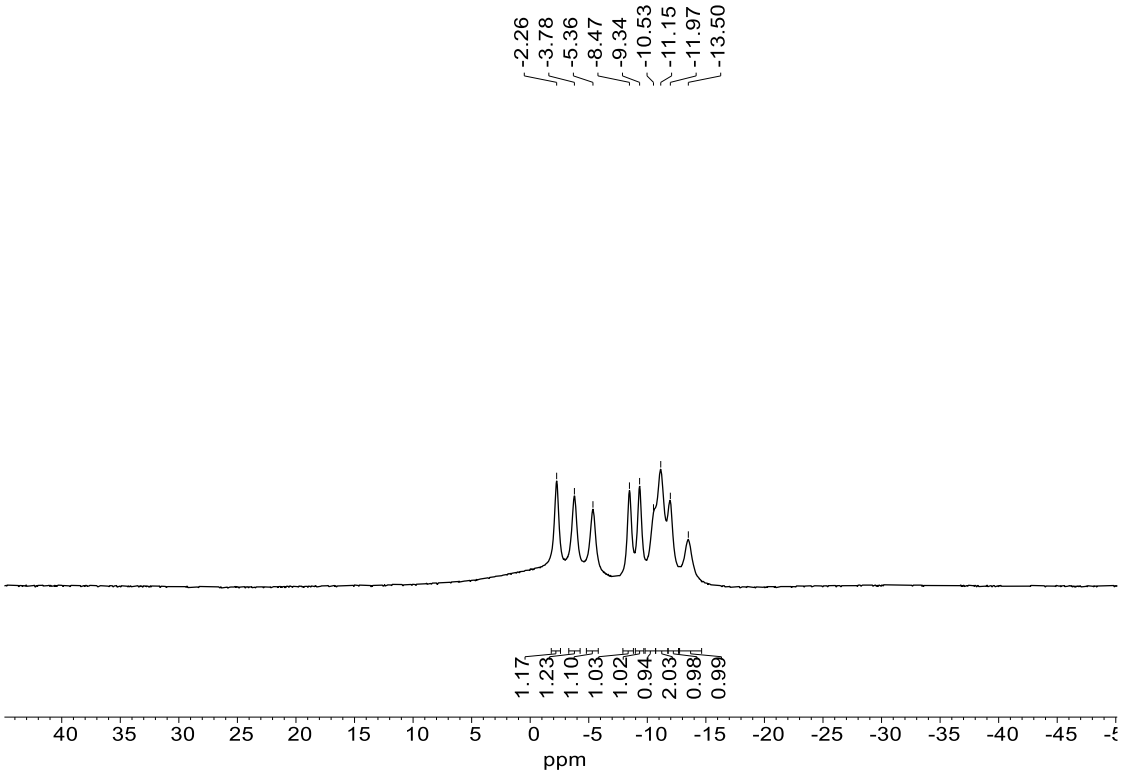

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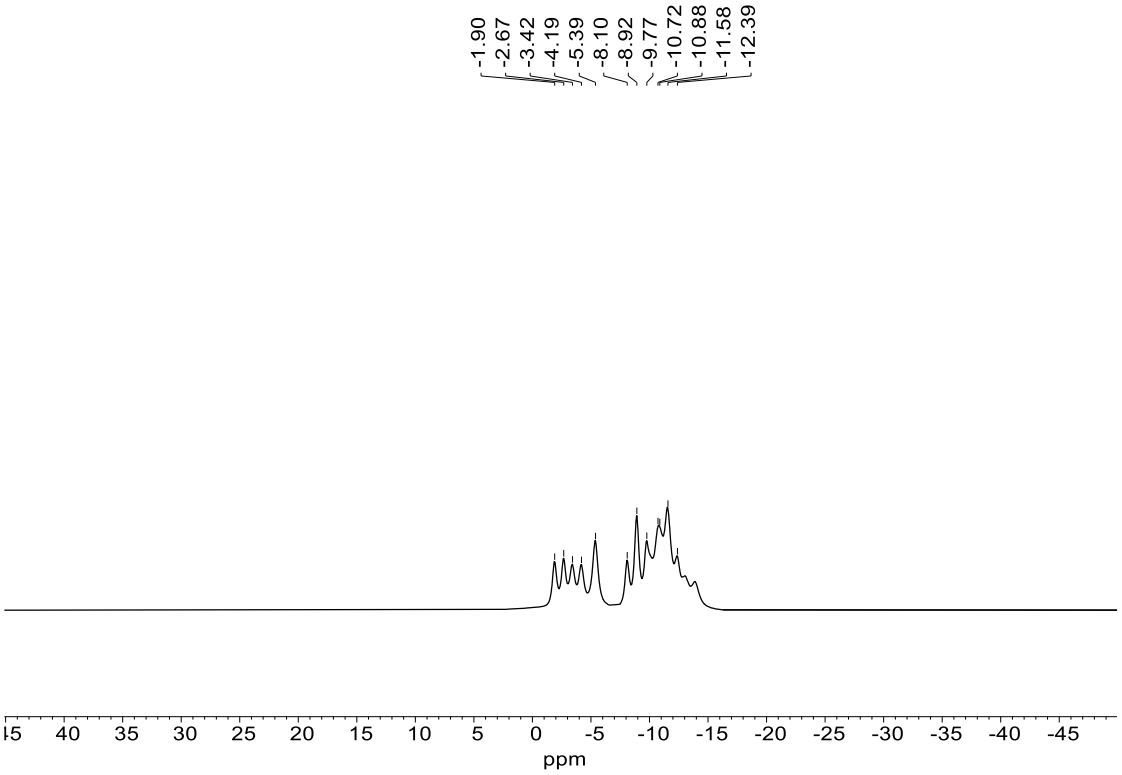

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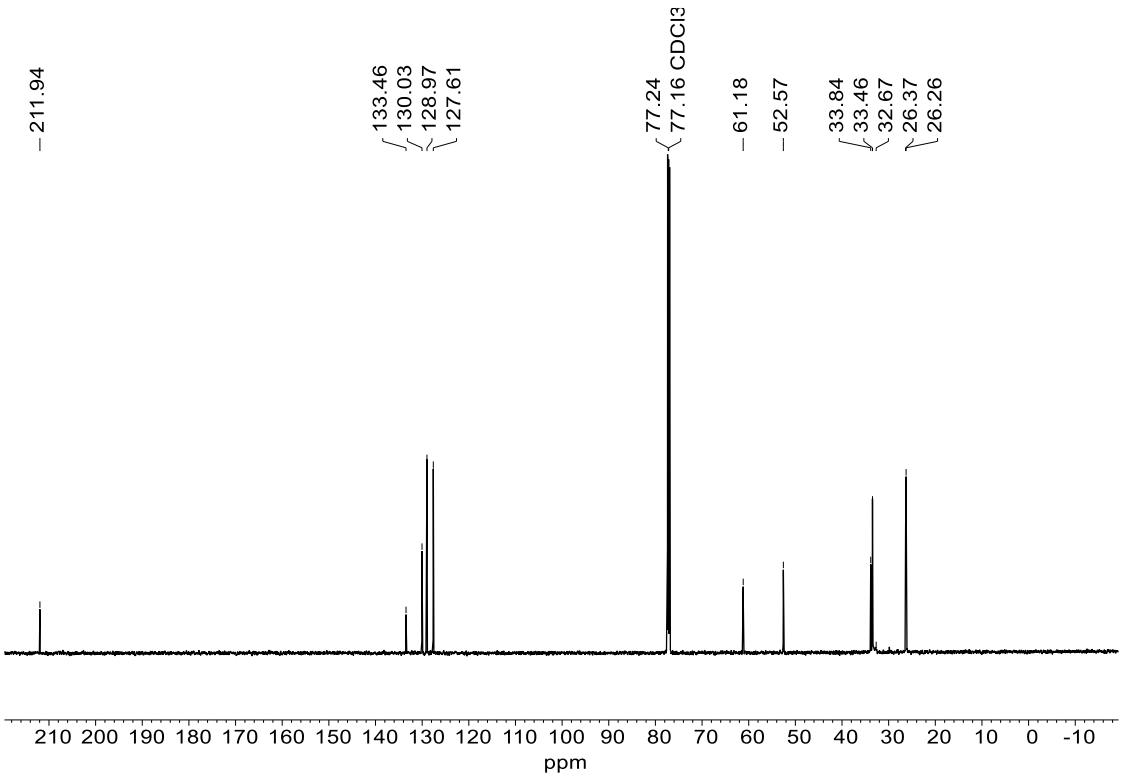

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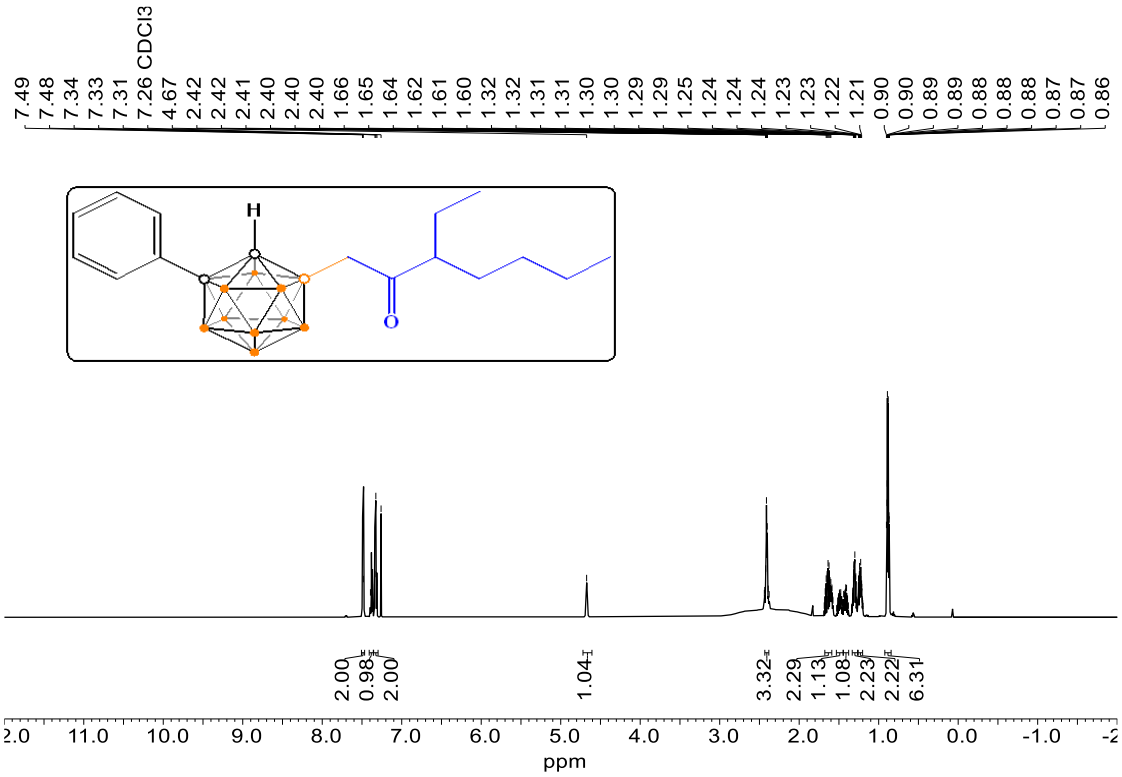

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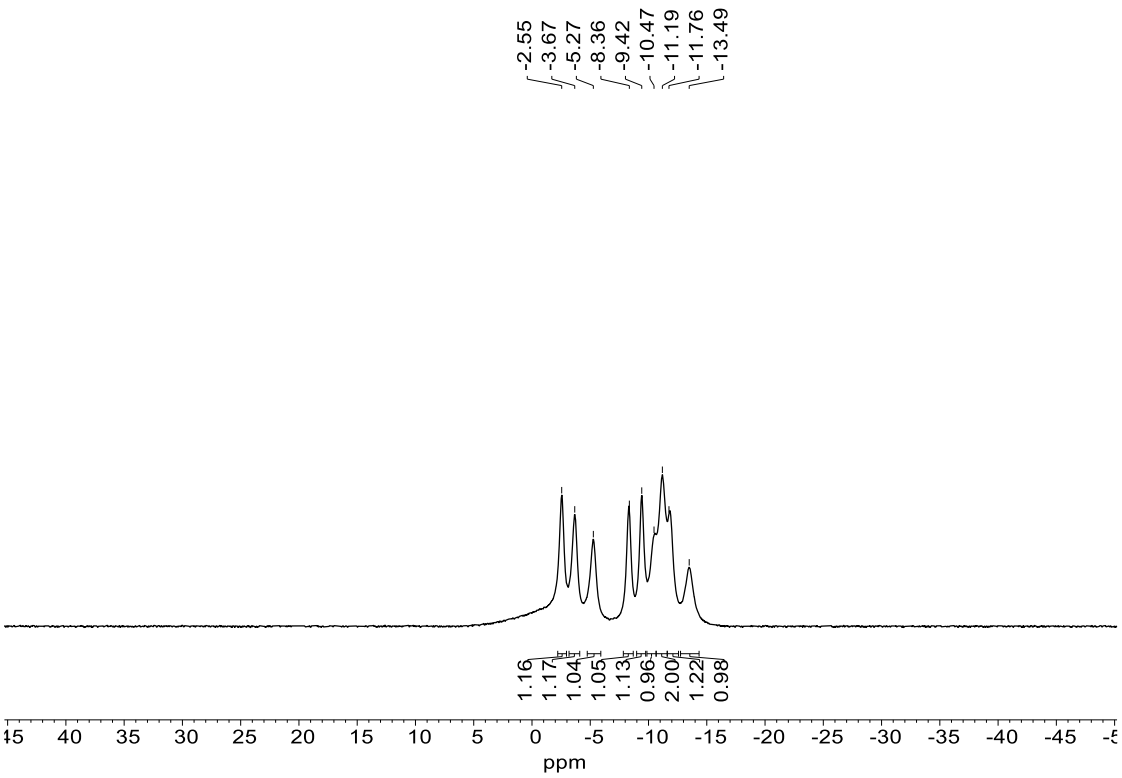

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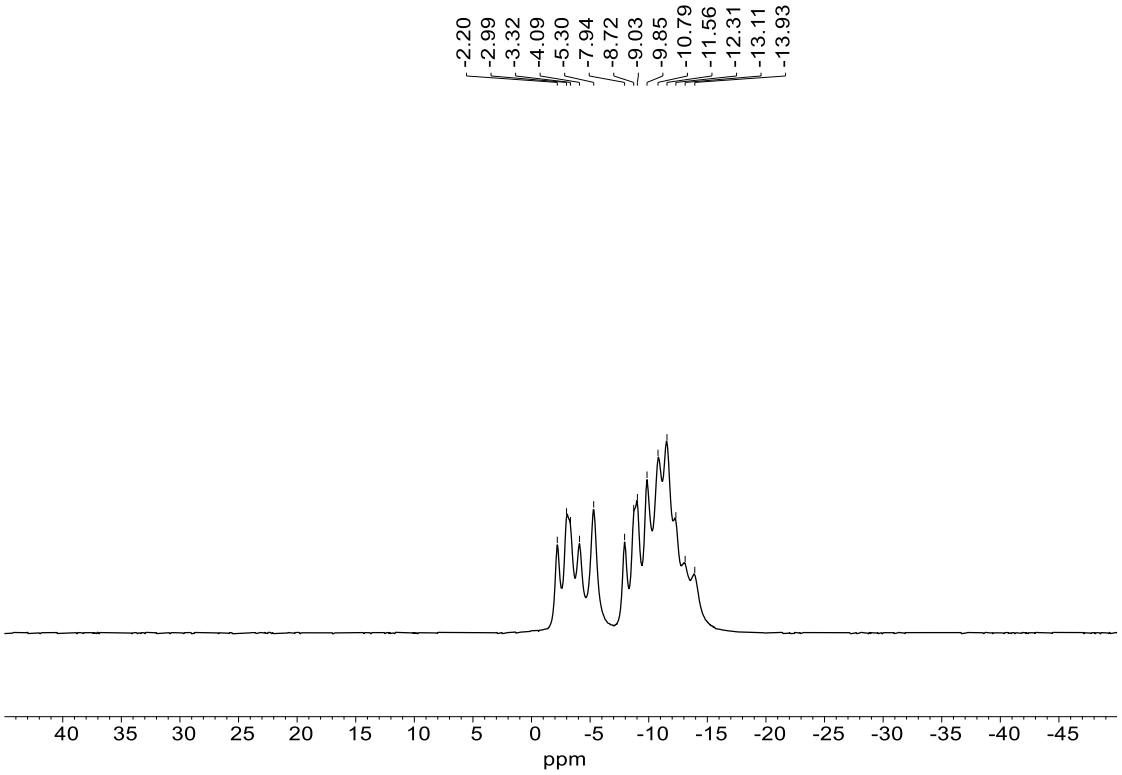

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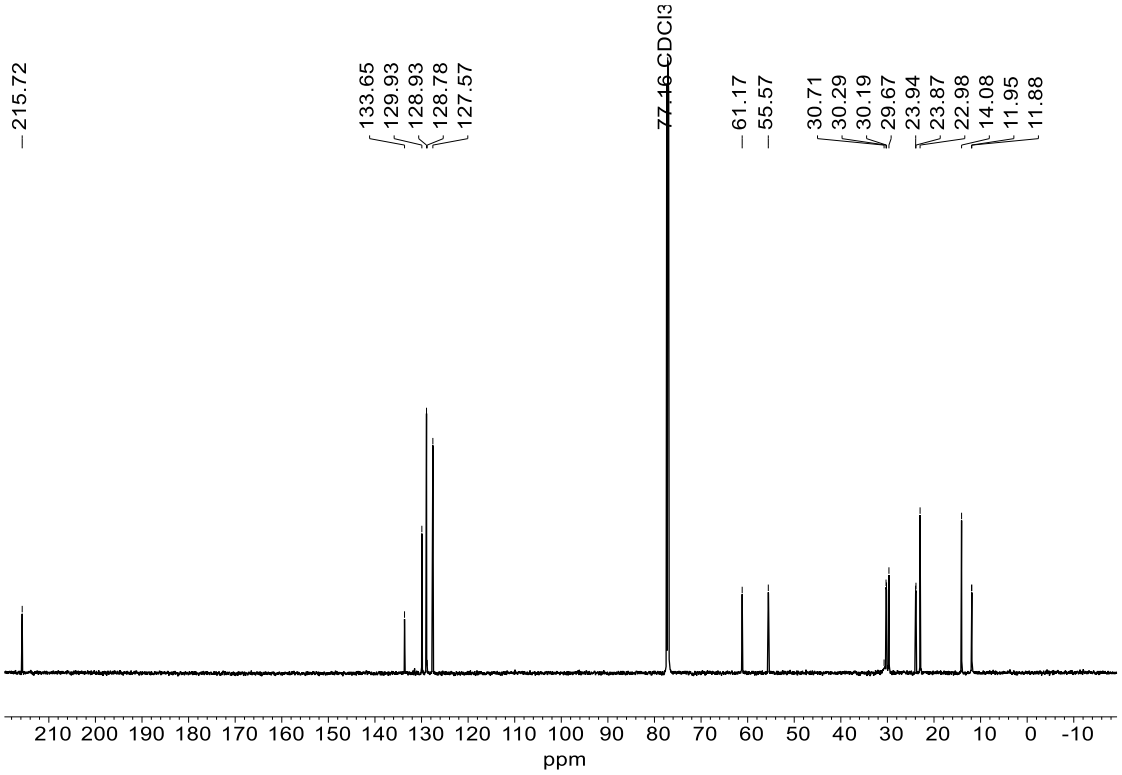

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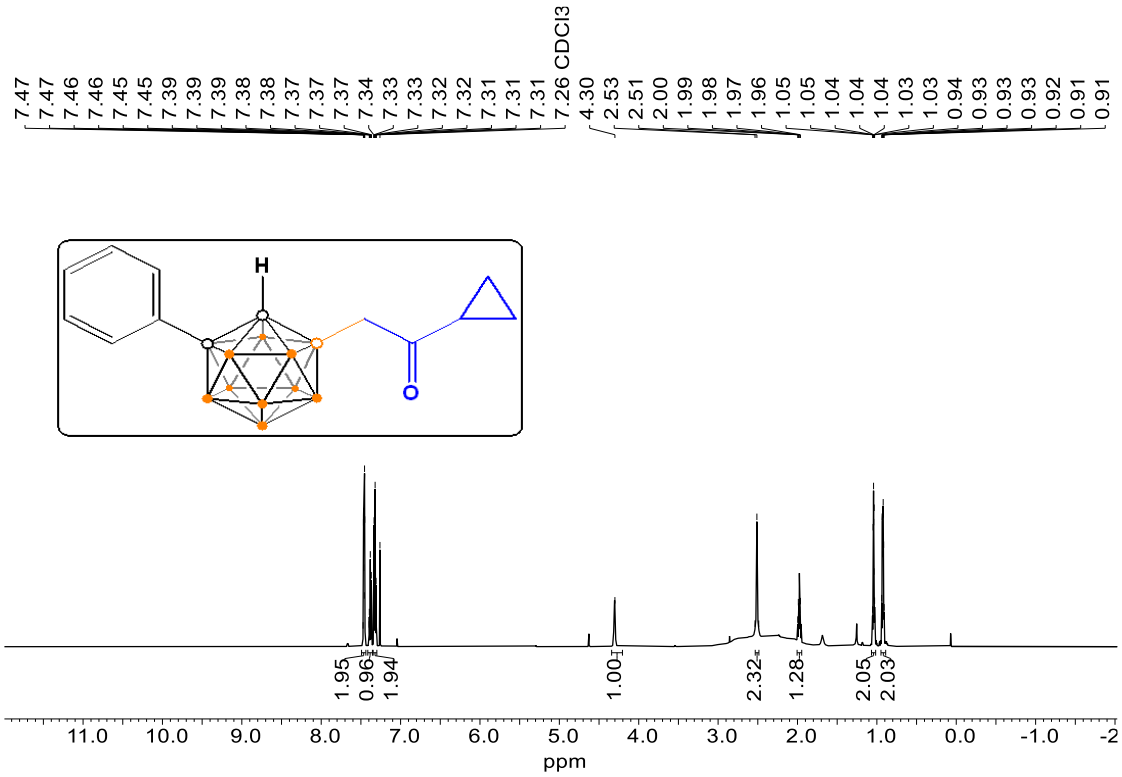
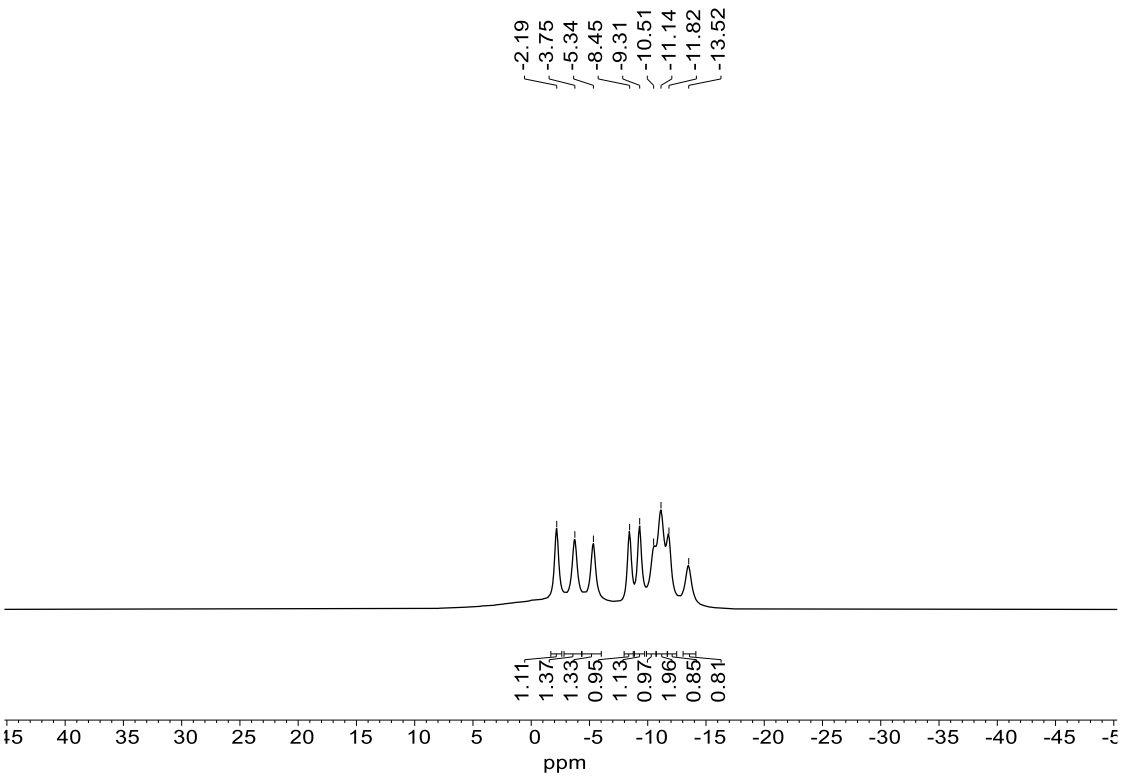


^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



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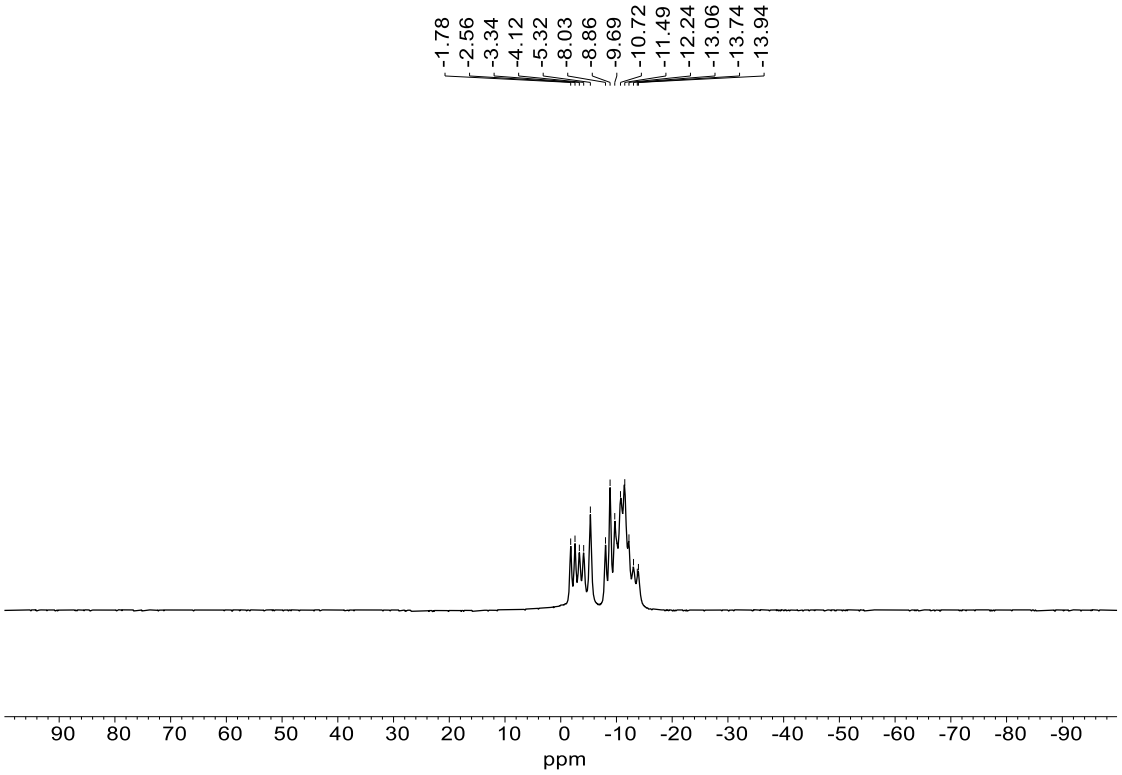

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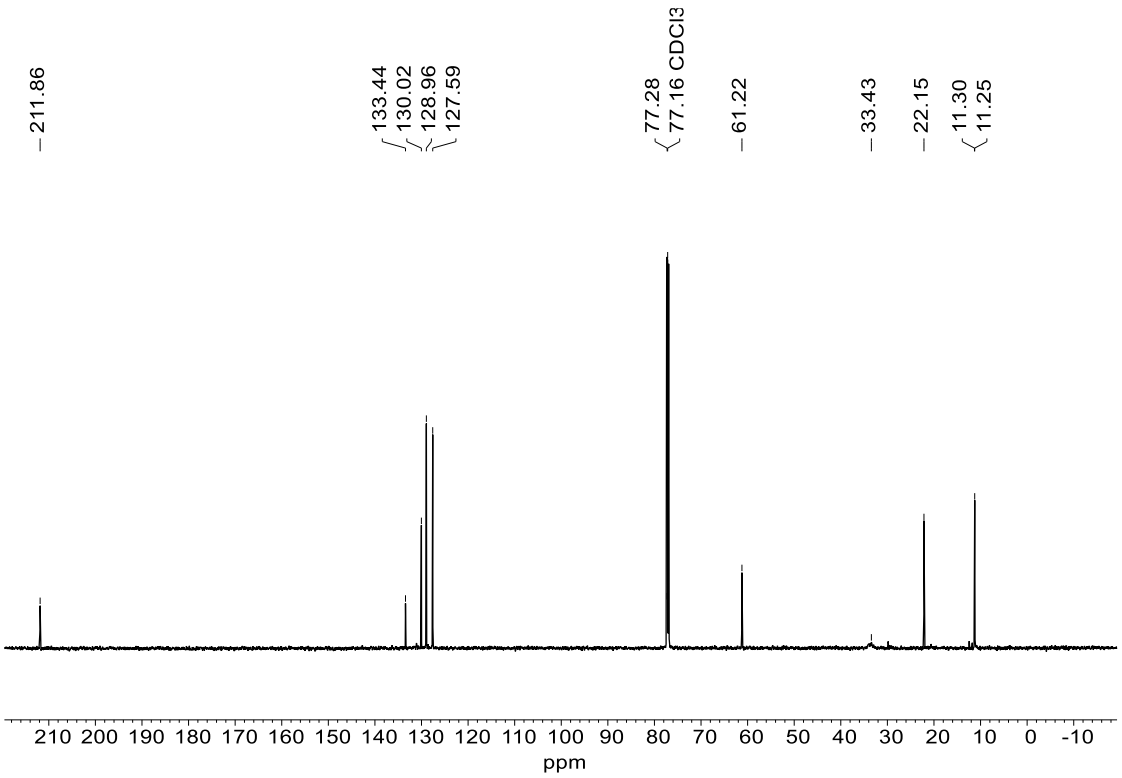

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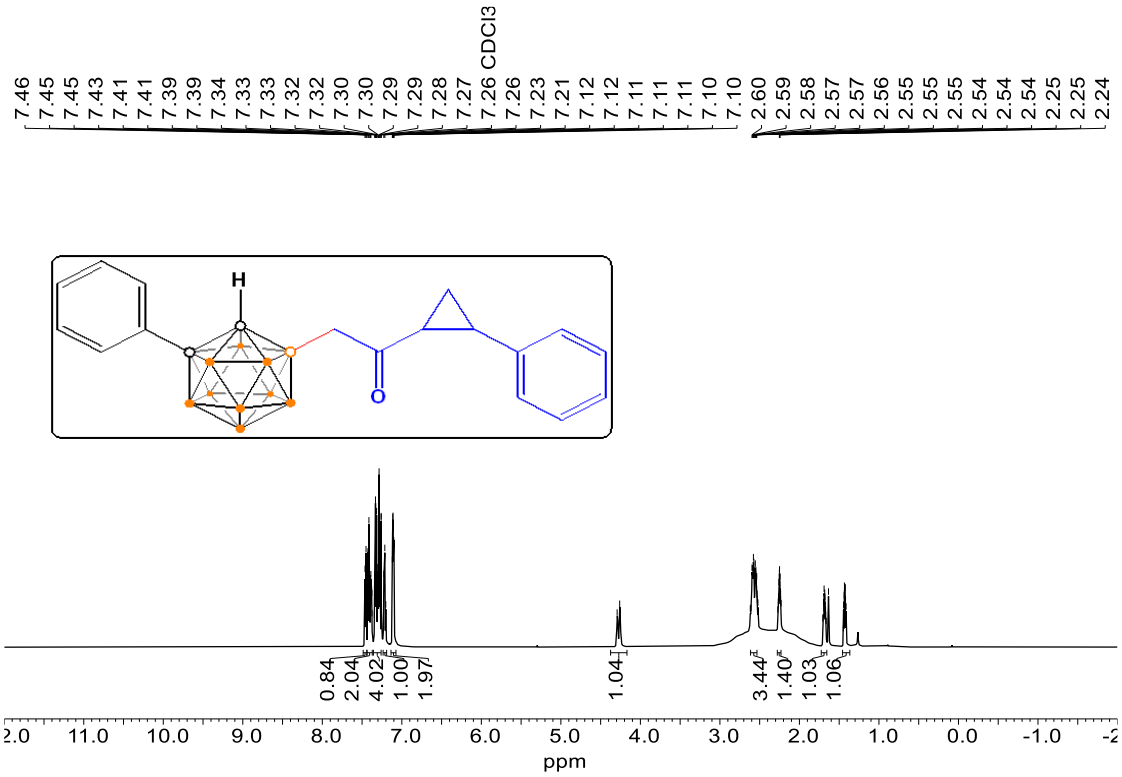
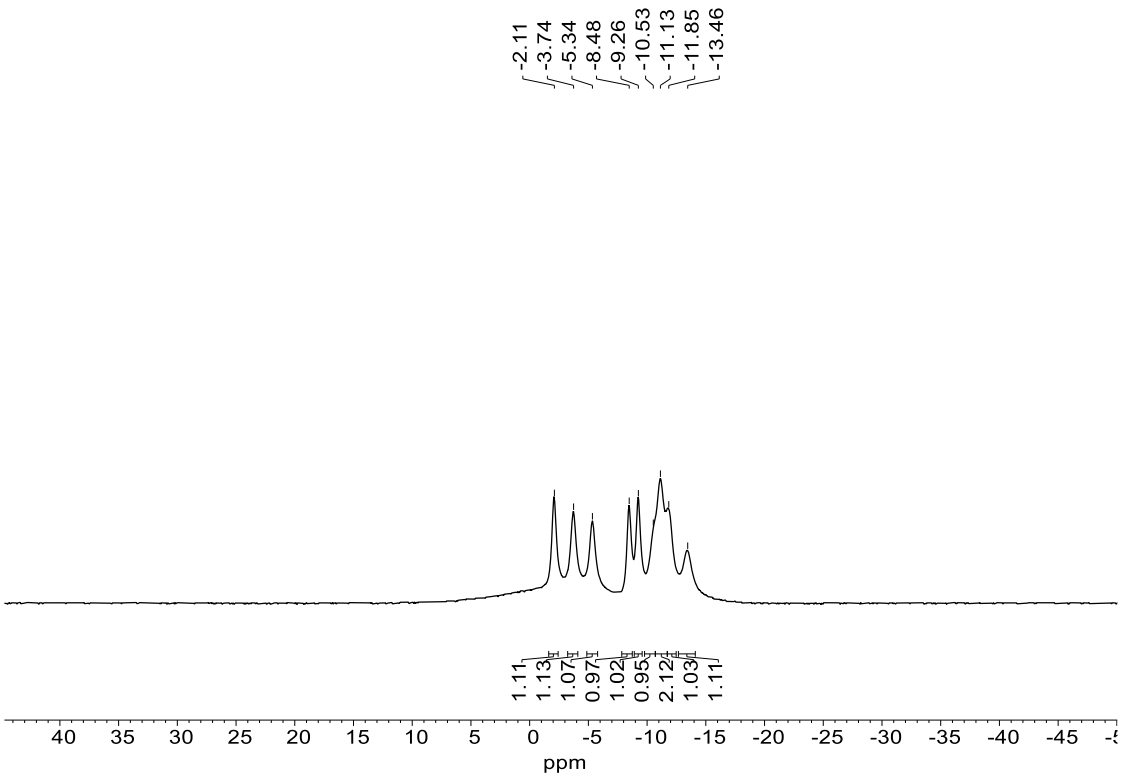
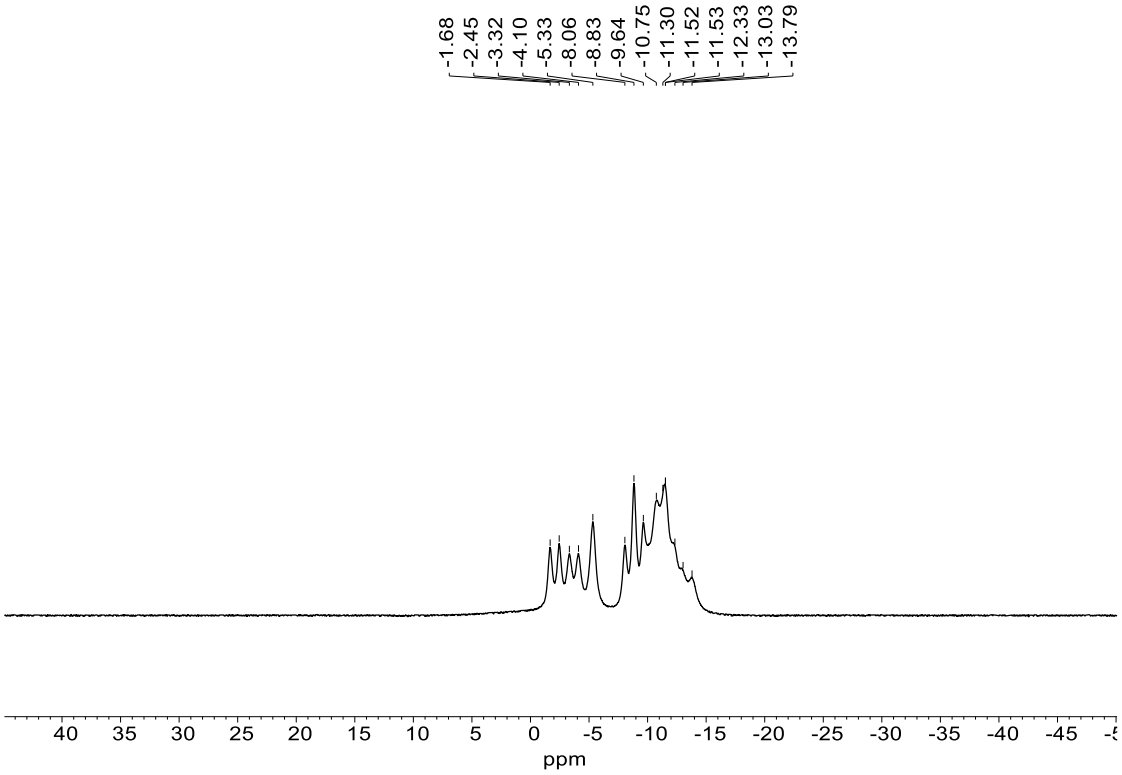


^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



^{11}B NMR (193 MHz, Chloroform-*d*)



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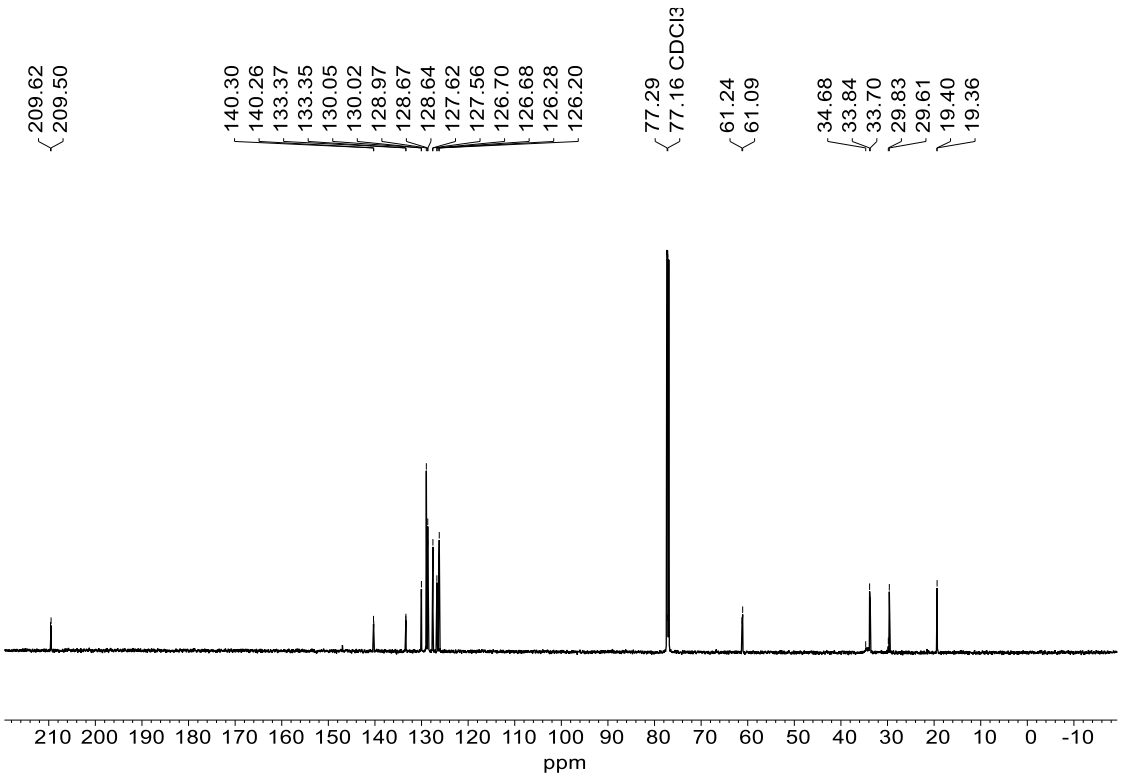
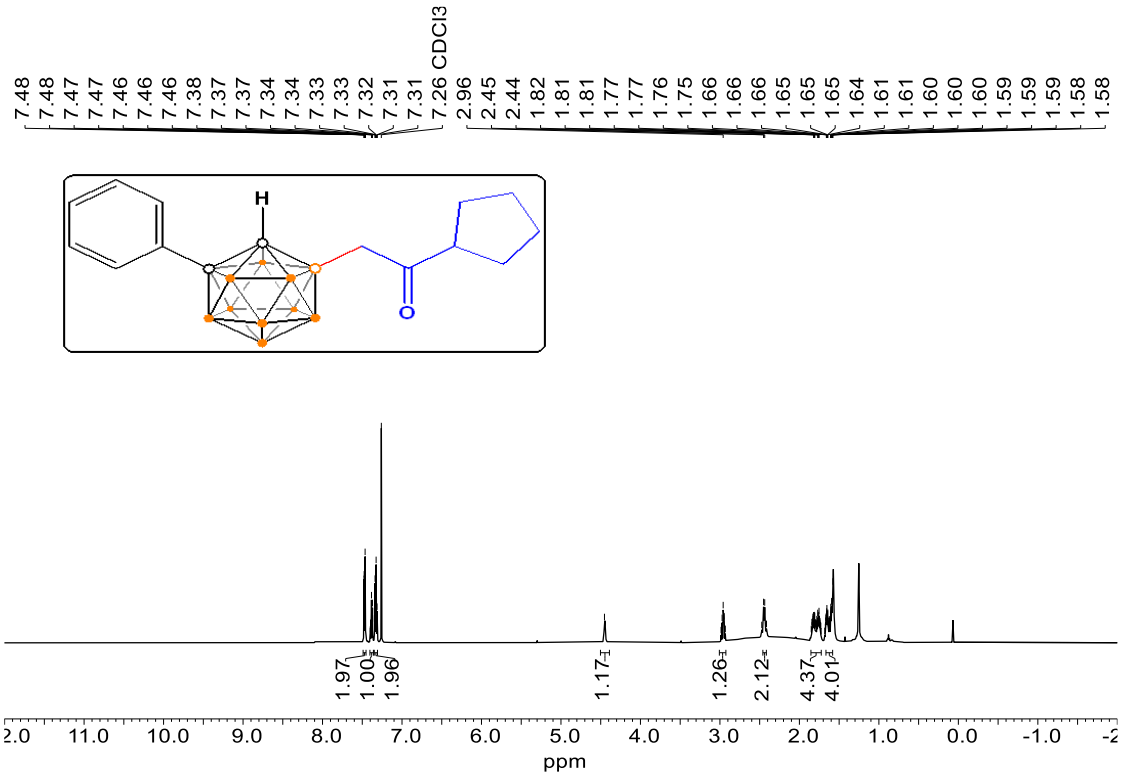
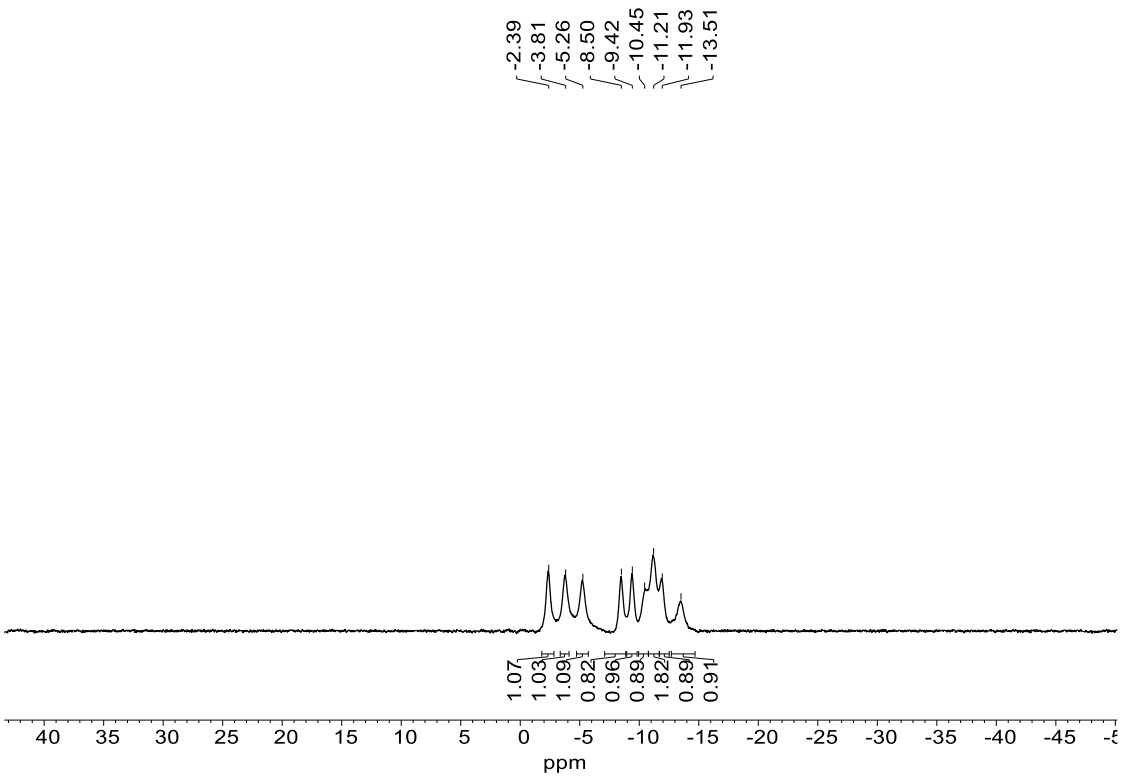


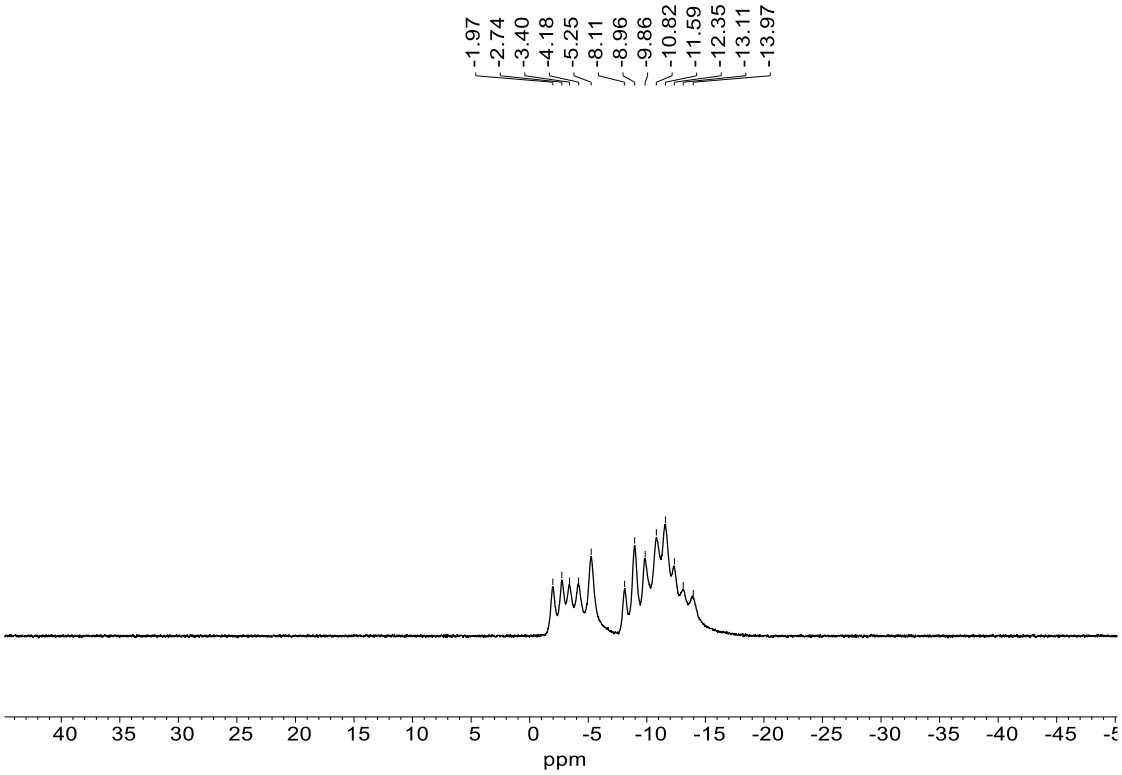
^{1}H NMR (600 MHz, Chloroform-*d*)



^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



^{11}B NMR (193 MHz, Chloroform-*d*)



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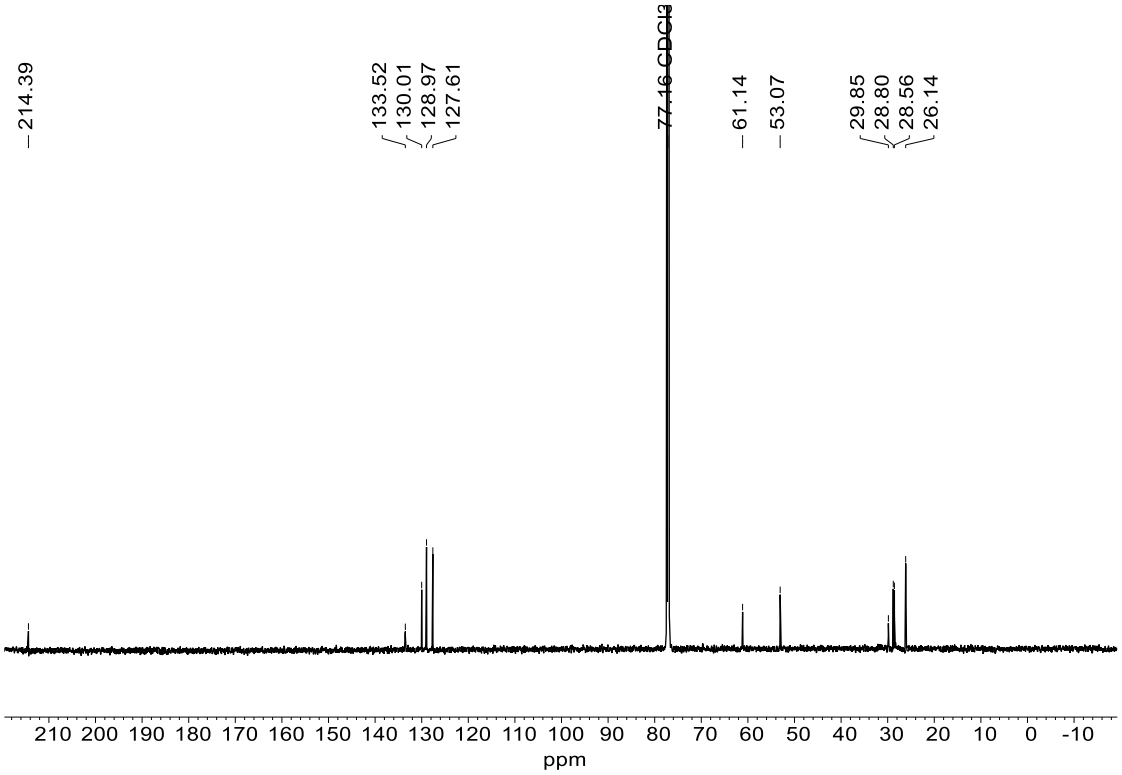
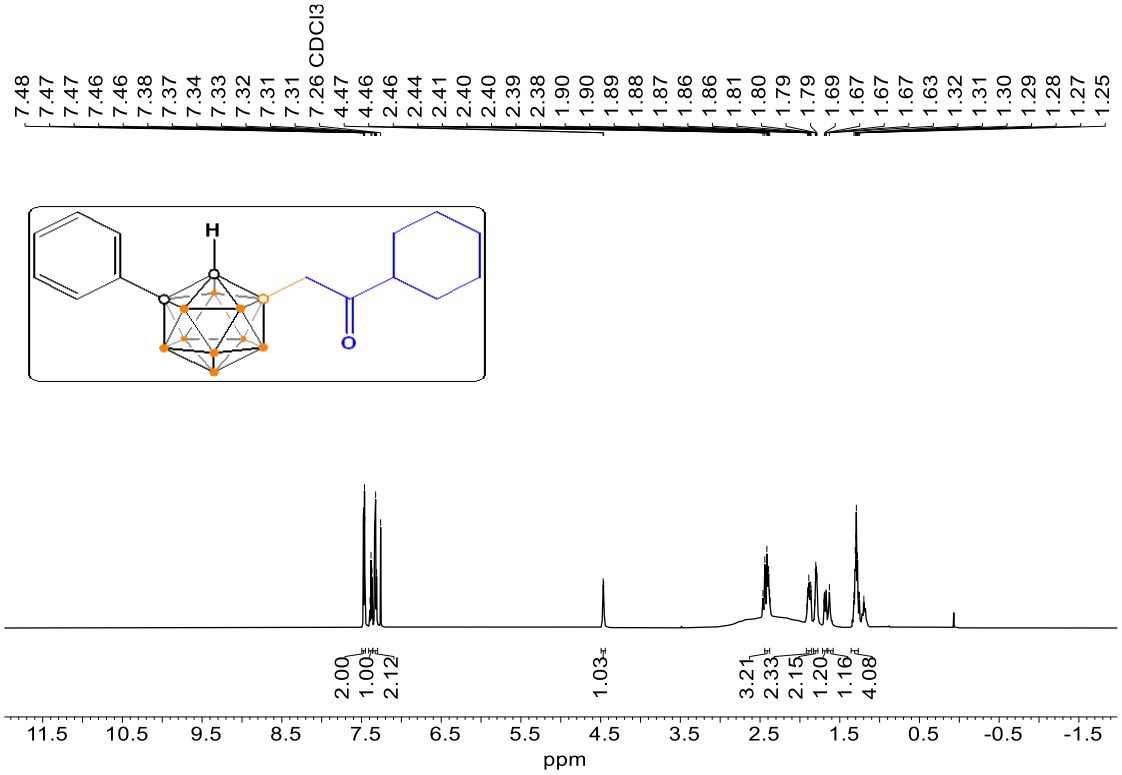


^{1}H NMR (600 MHz, Chloroform-*d*)



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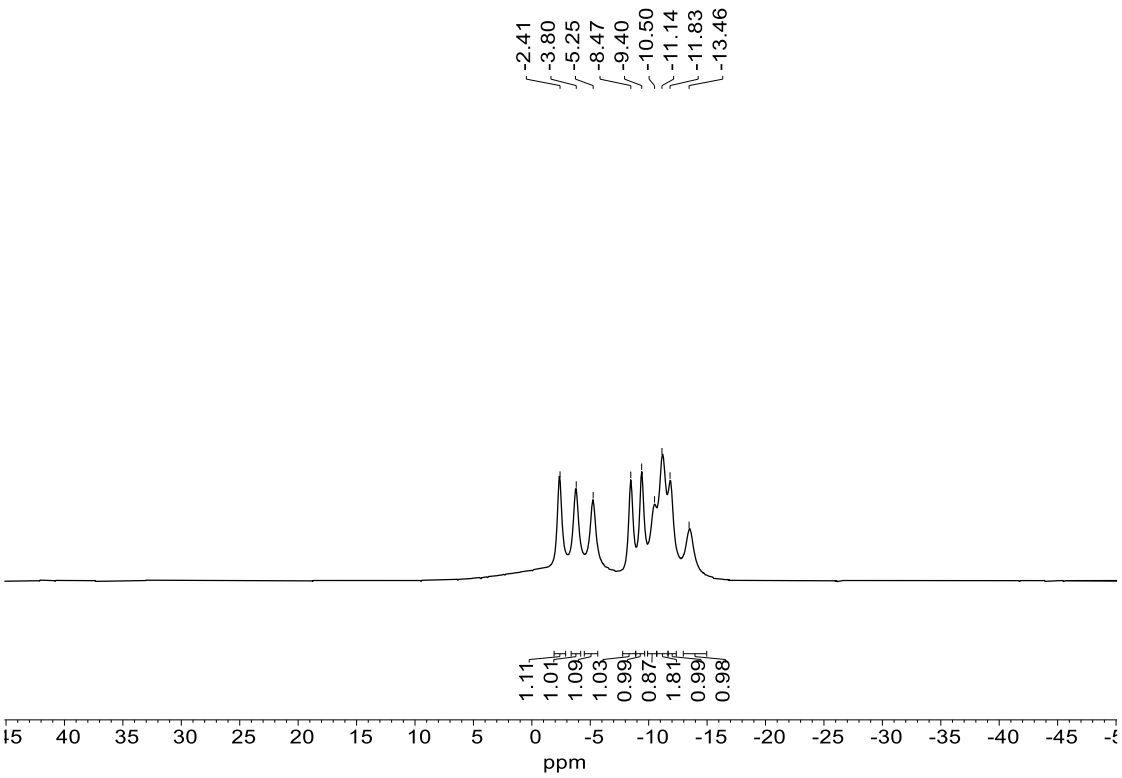
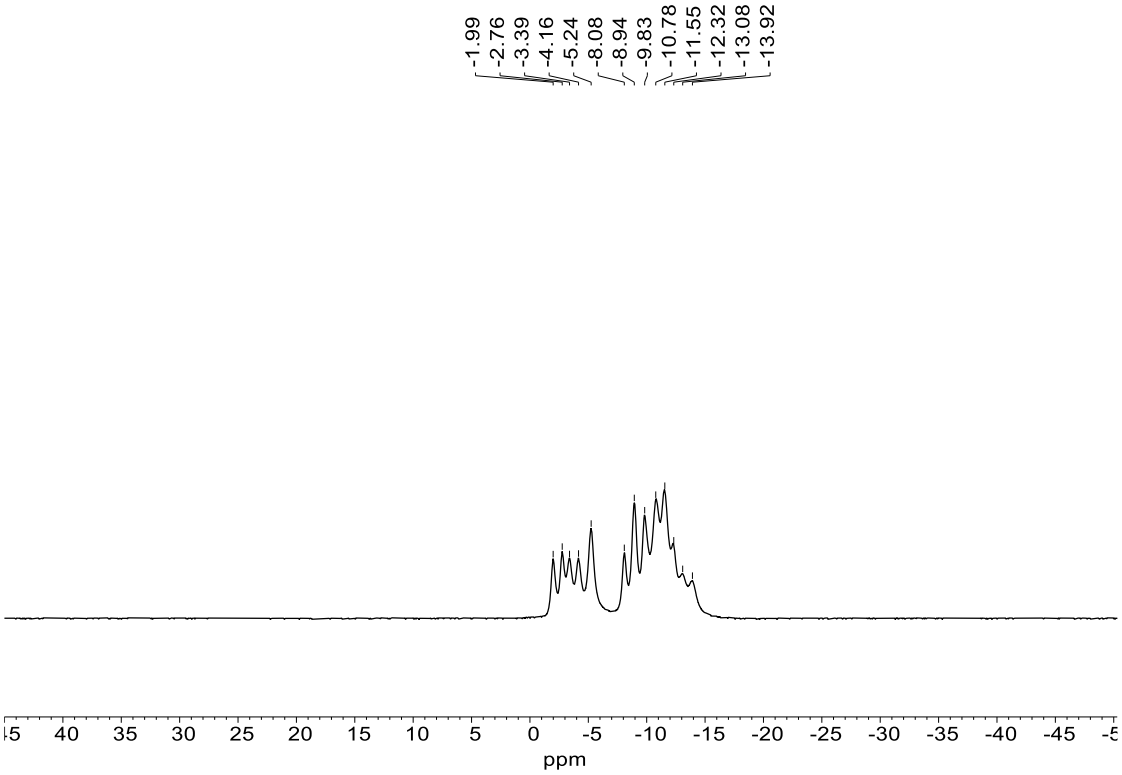


^{11}B NMR (193 MHz, Chloroform-*d*)



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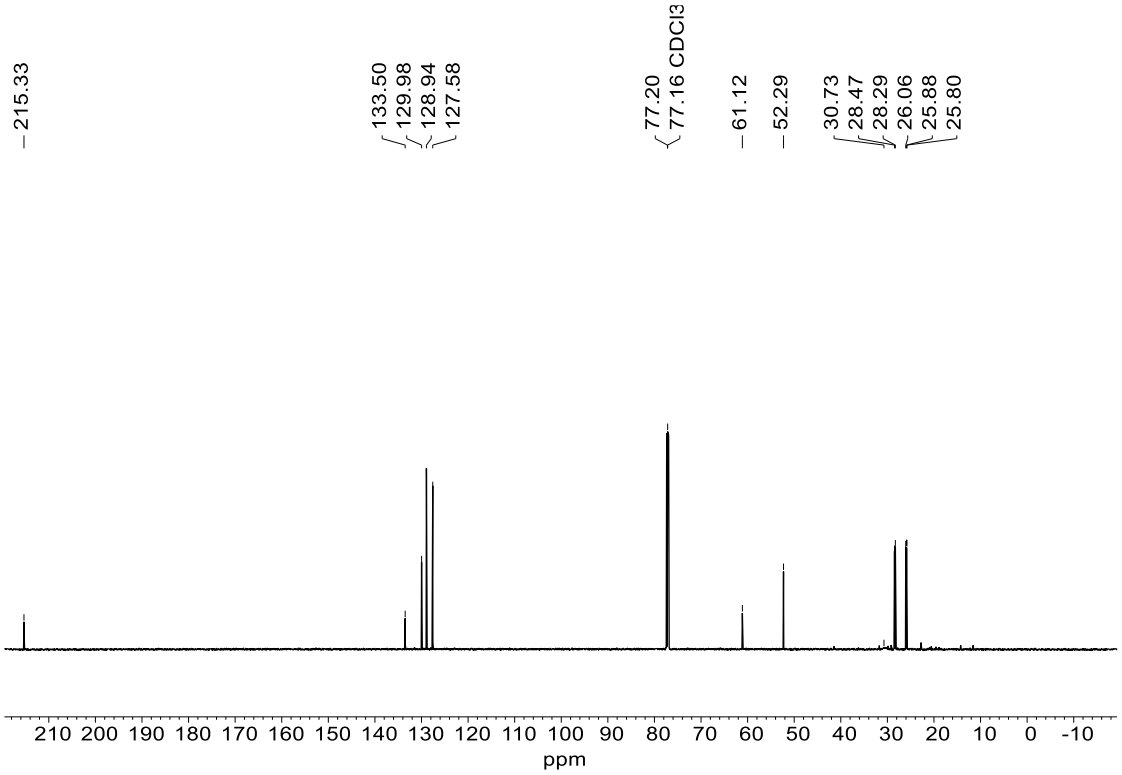

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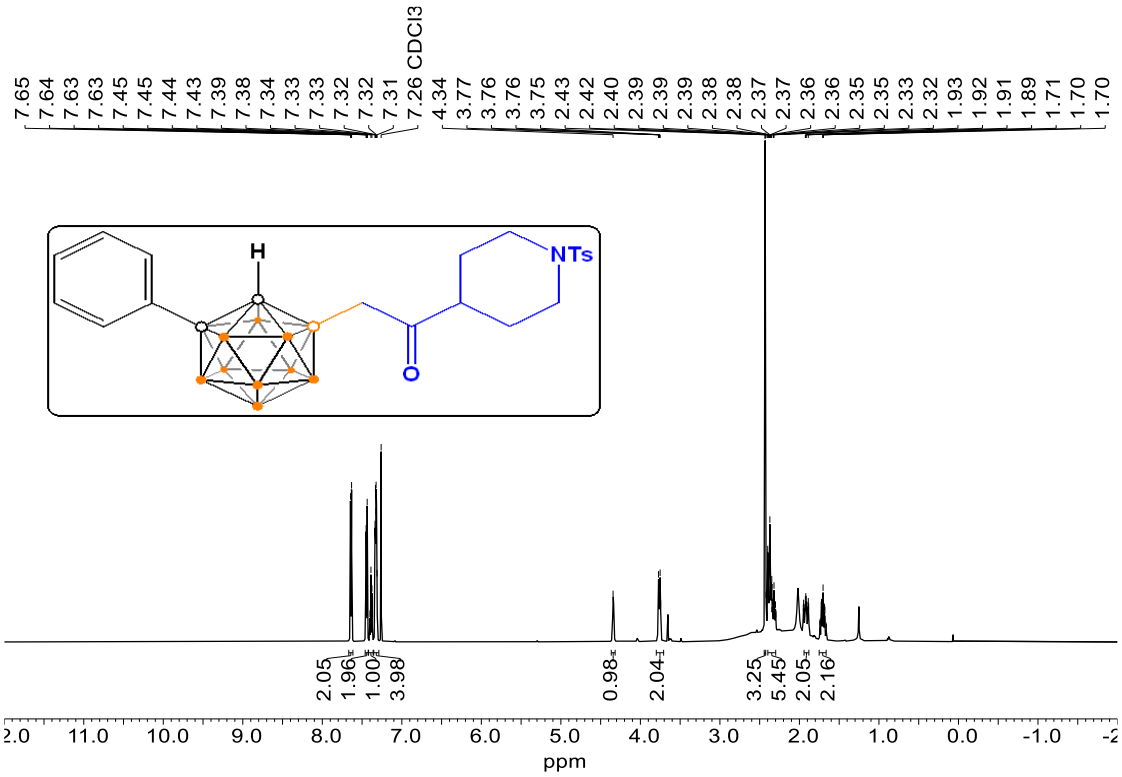
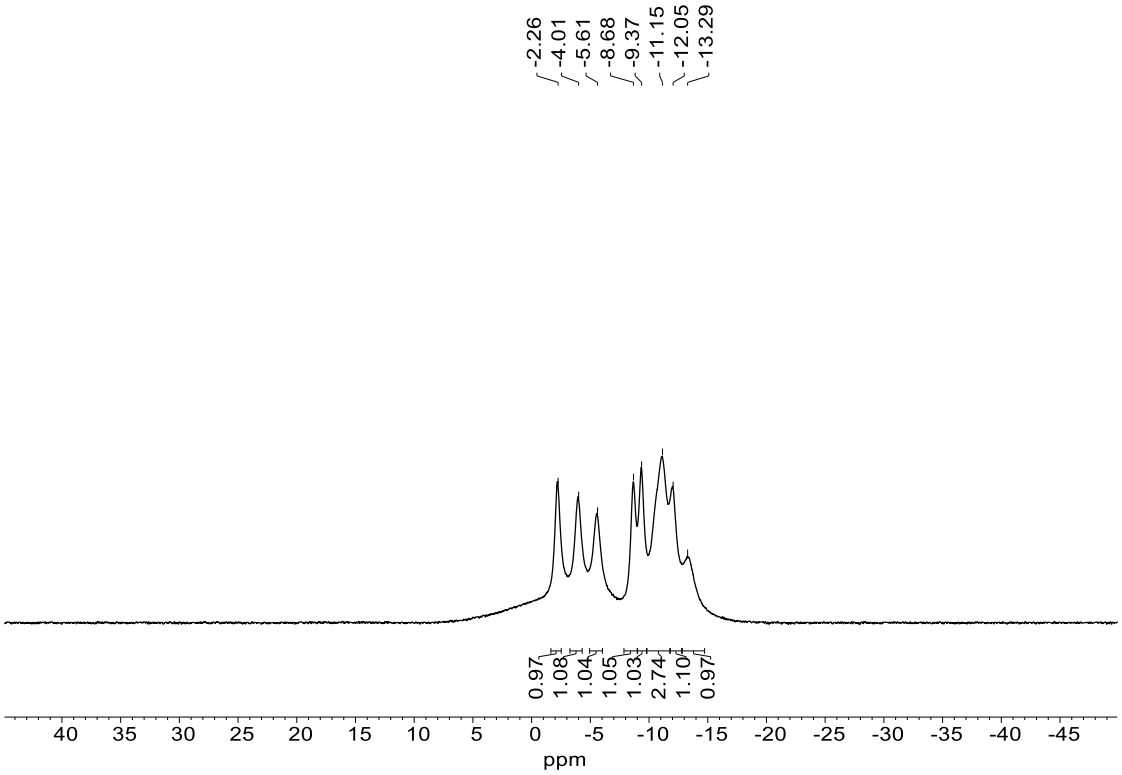


^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



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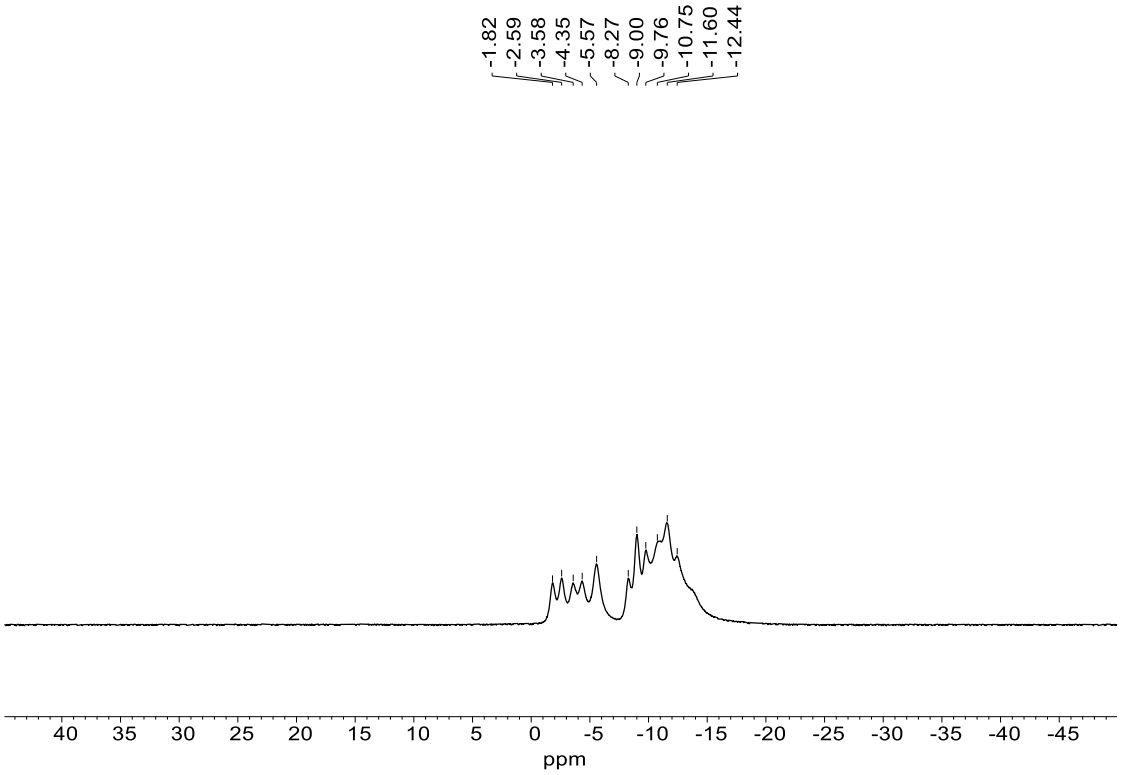
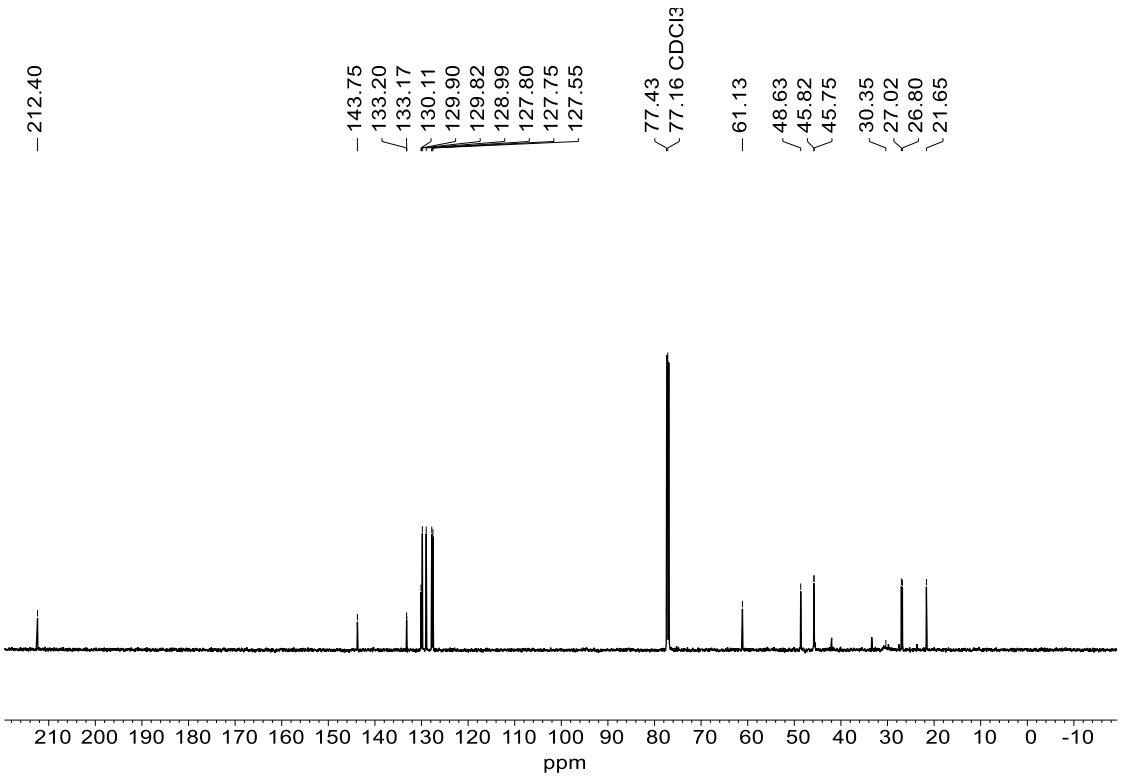
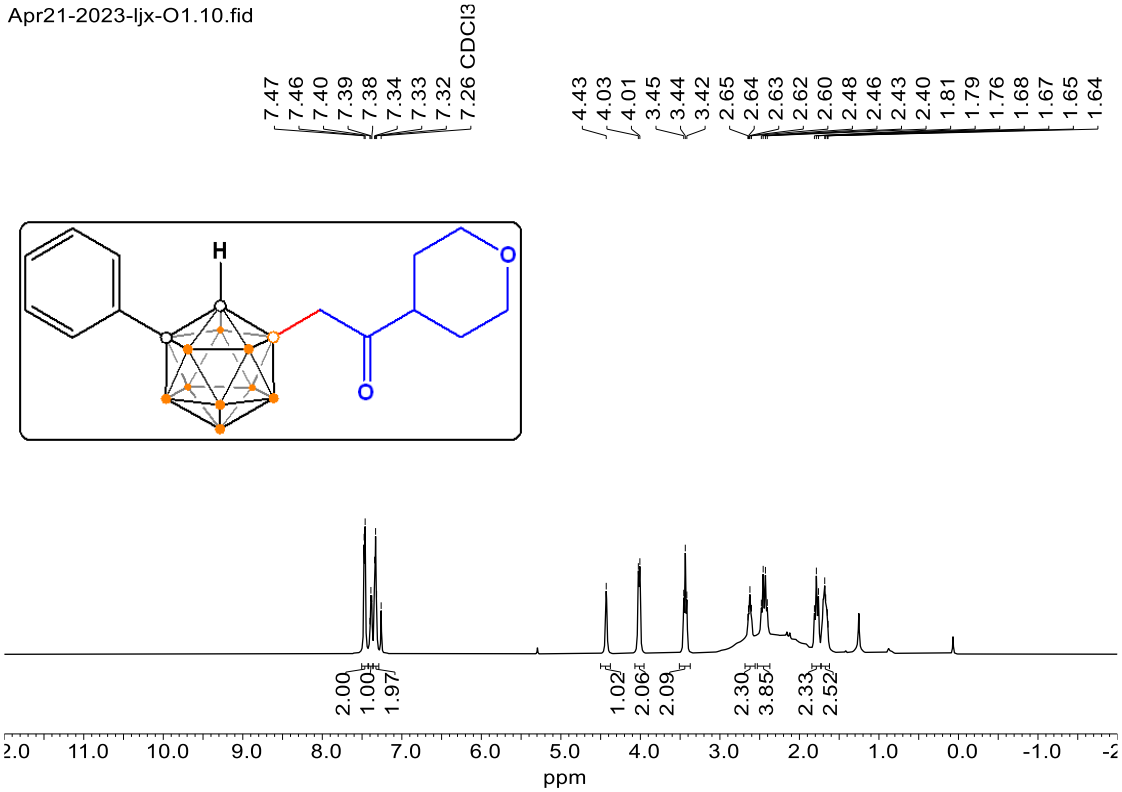


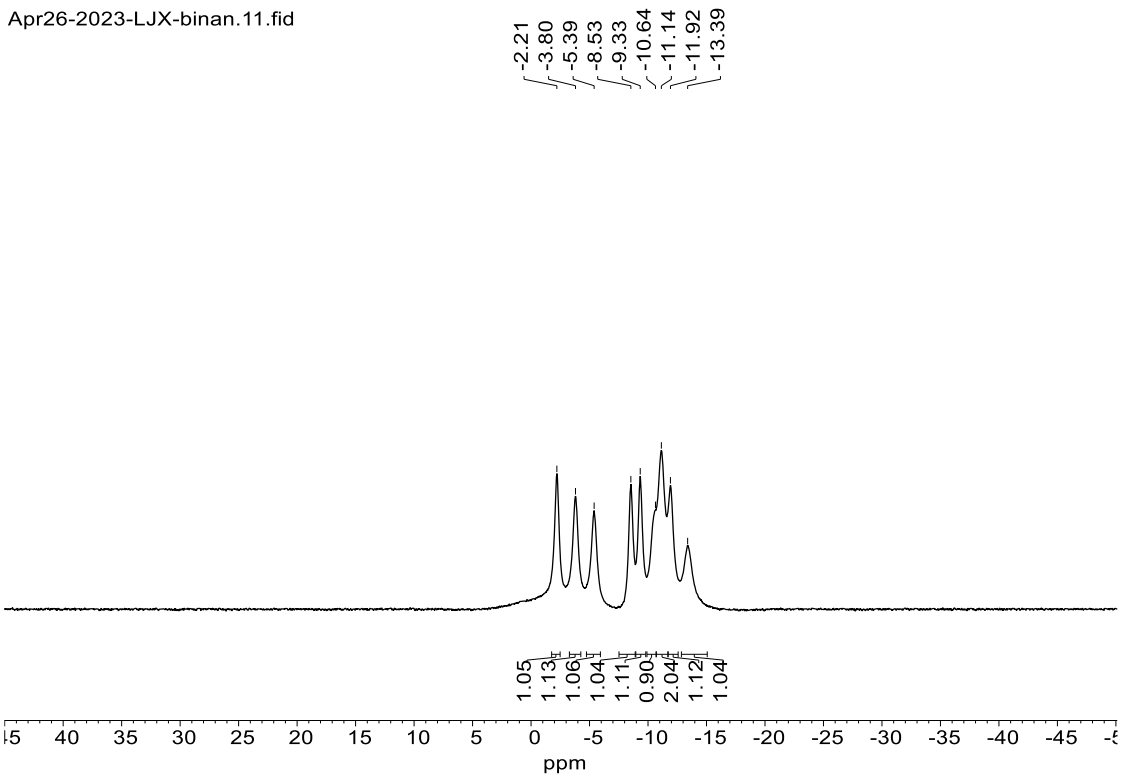
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



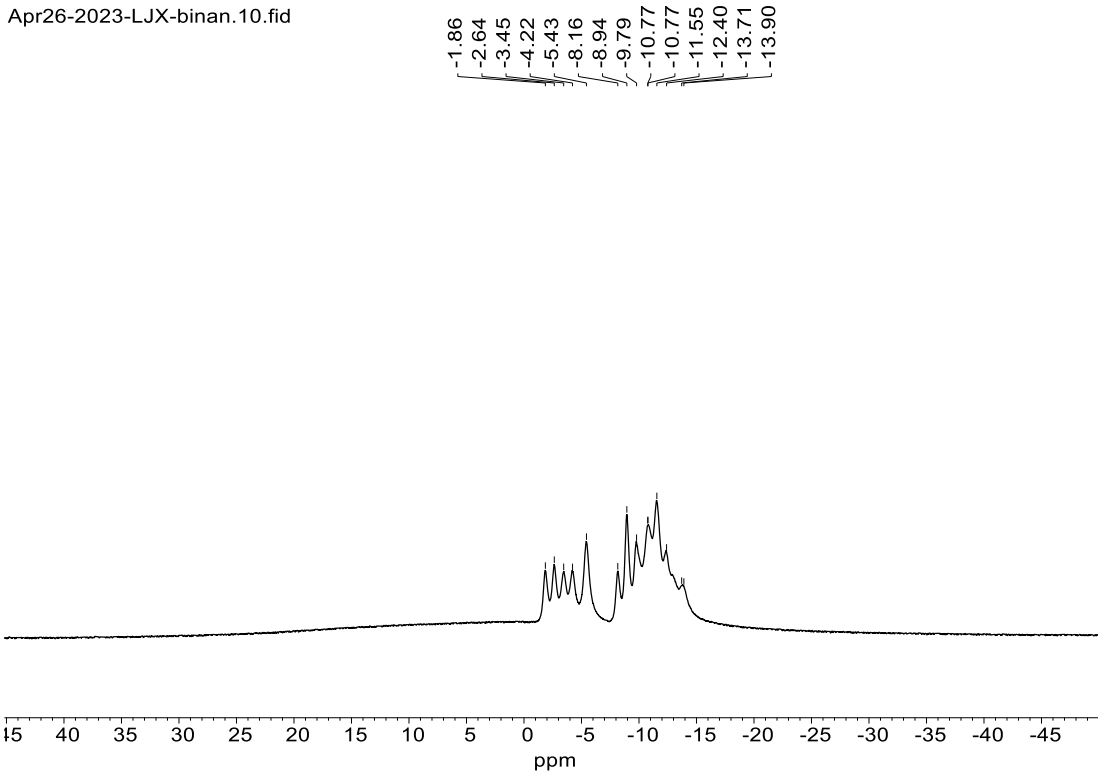
^{1}H NMR (600 MHz, Chloroform-*d*)



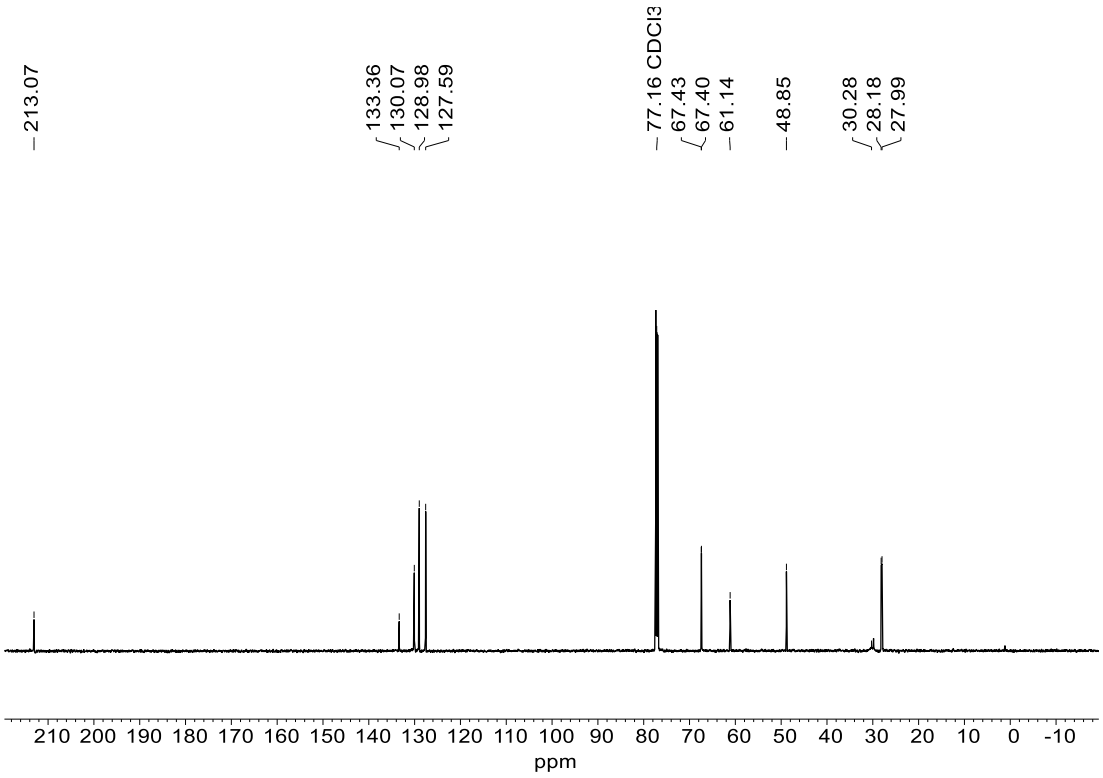
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



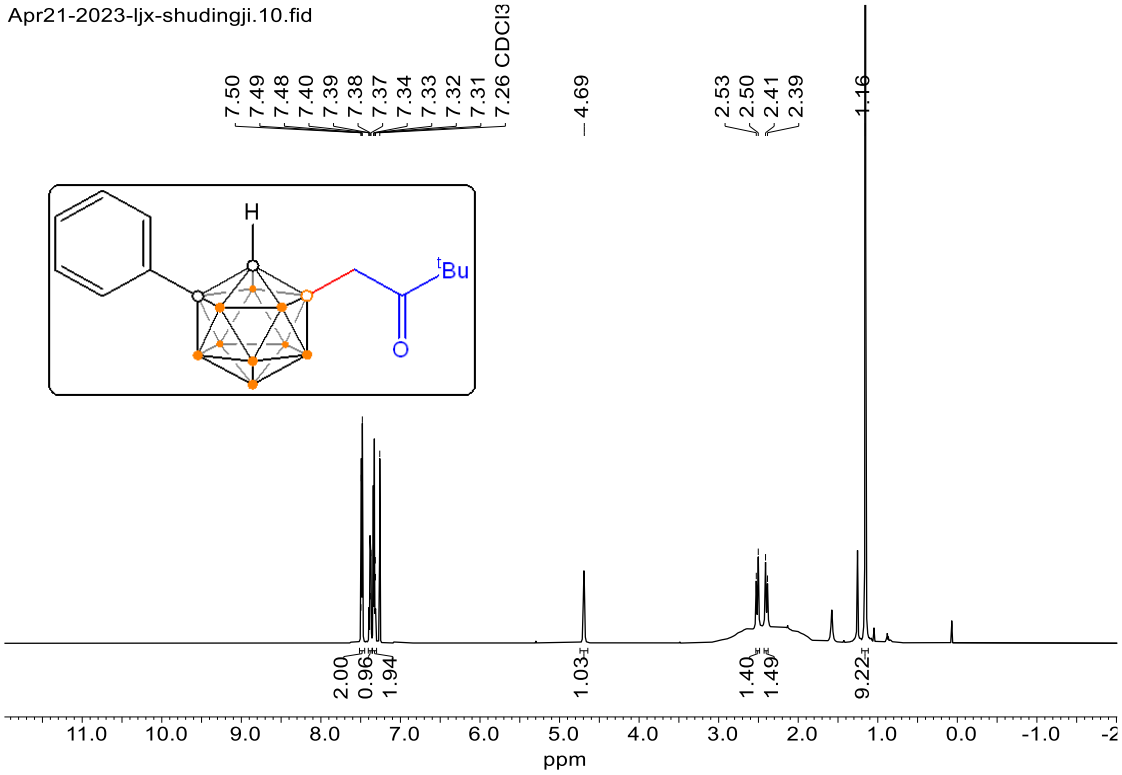
^{11}B NMR (193 MHz, Chloroform-*d*)



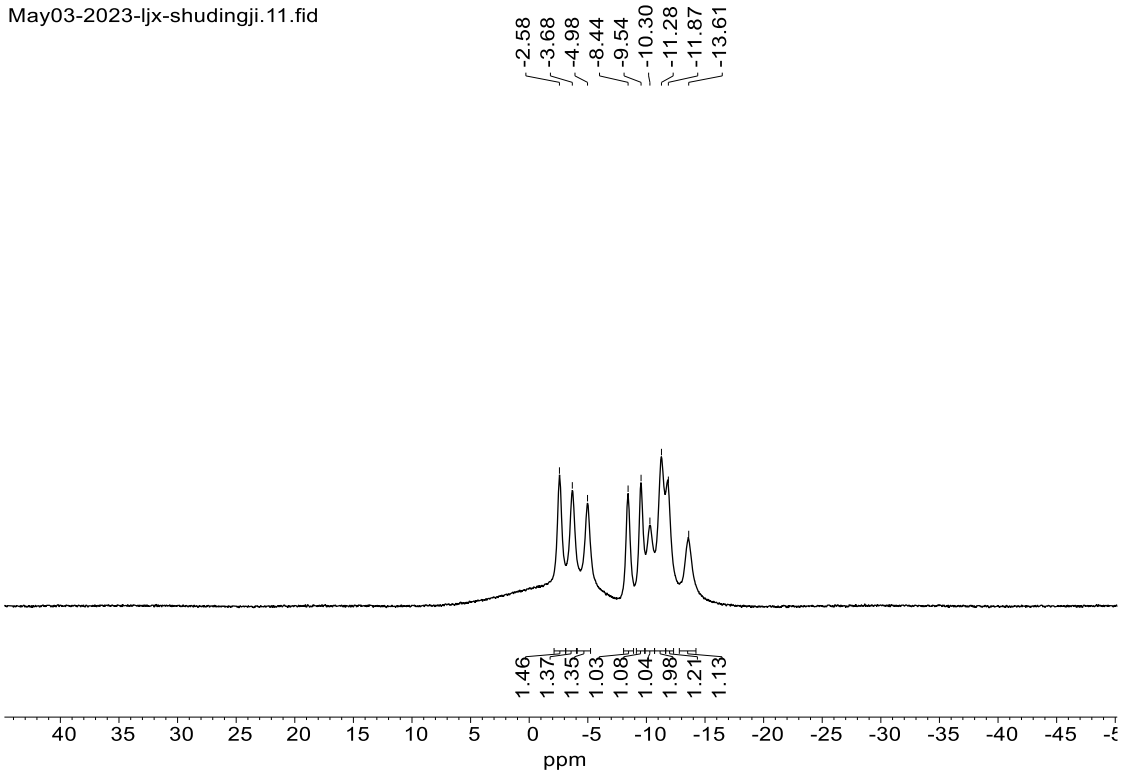
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



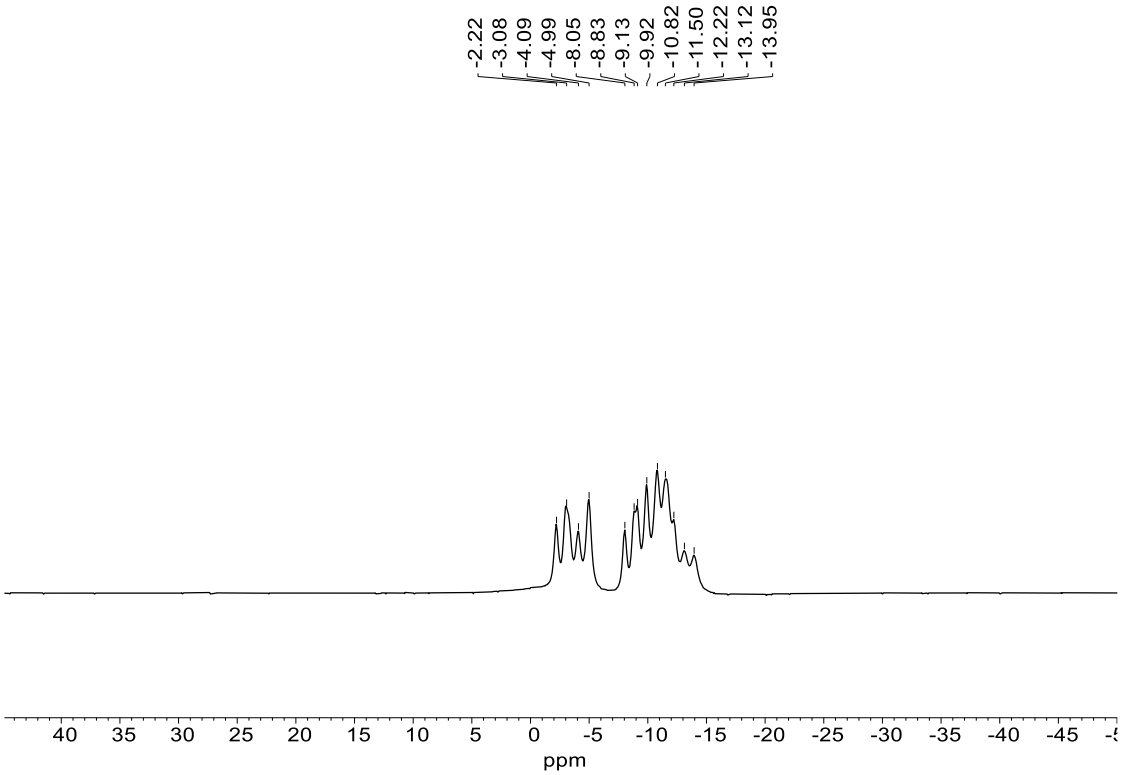
^{1}H NMR (600 MHz, Chloroform-*d*)



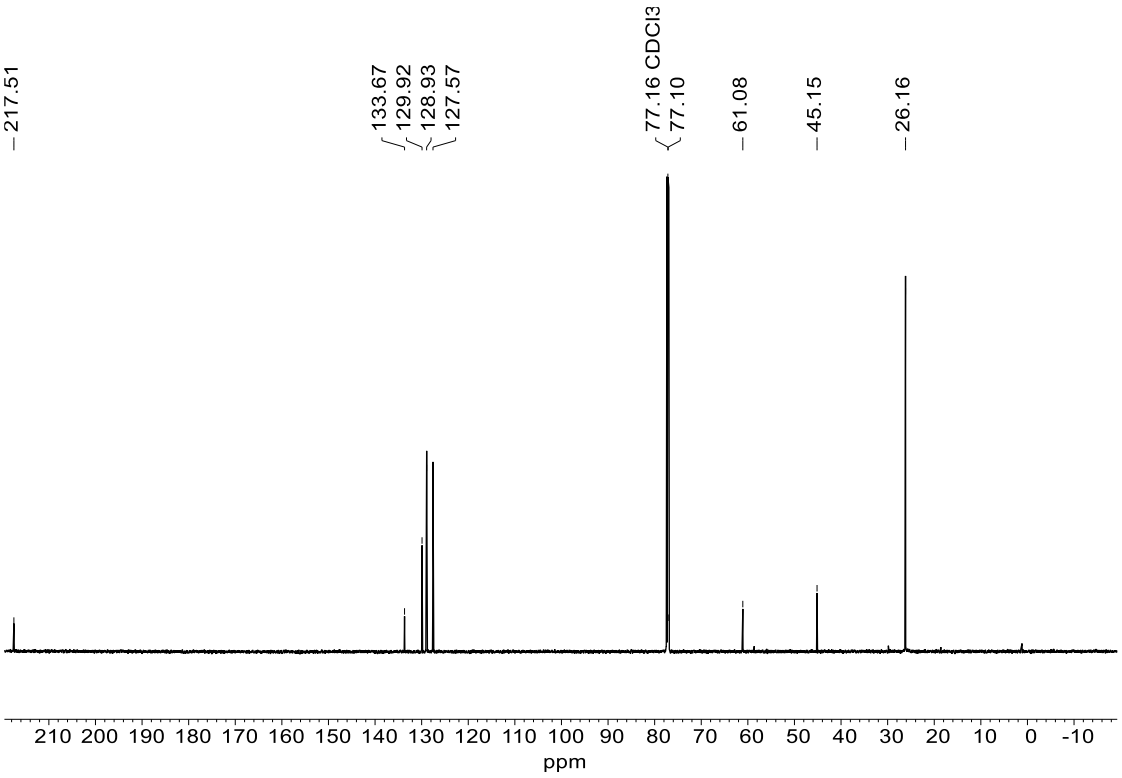
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



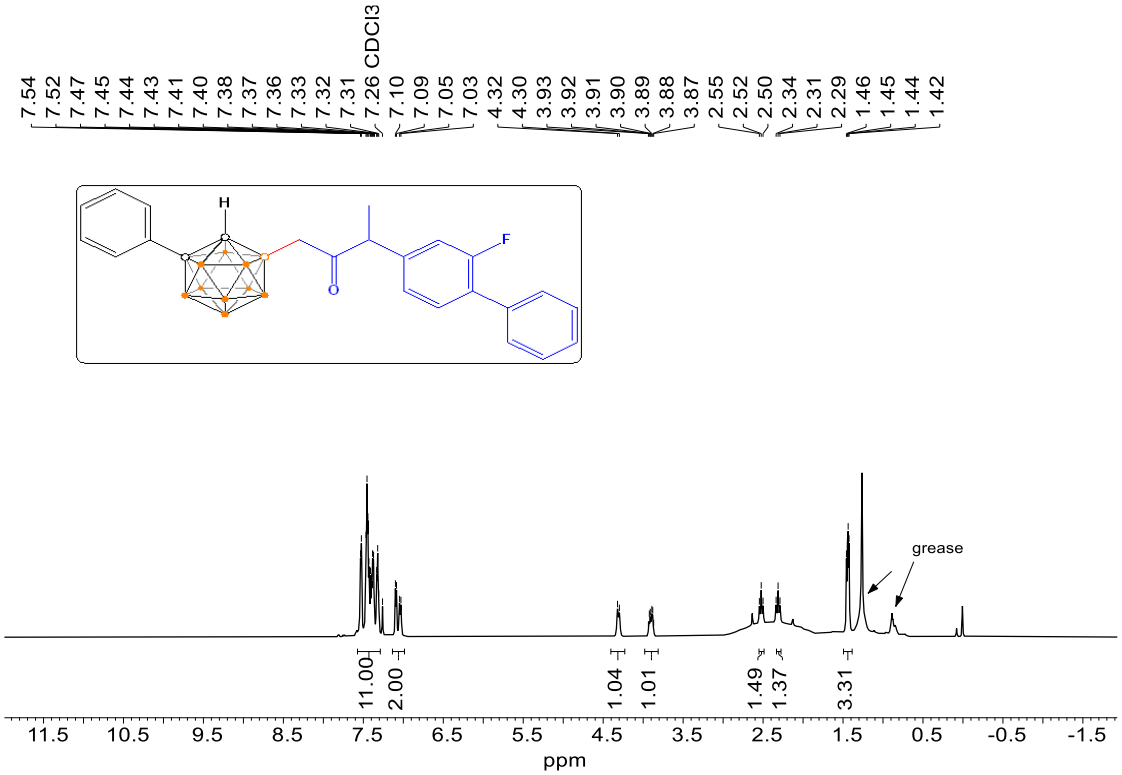
^{11}B NMR (193 MHz, Chloroform-*d*)



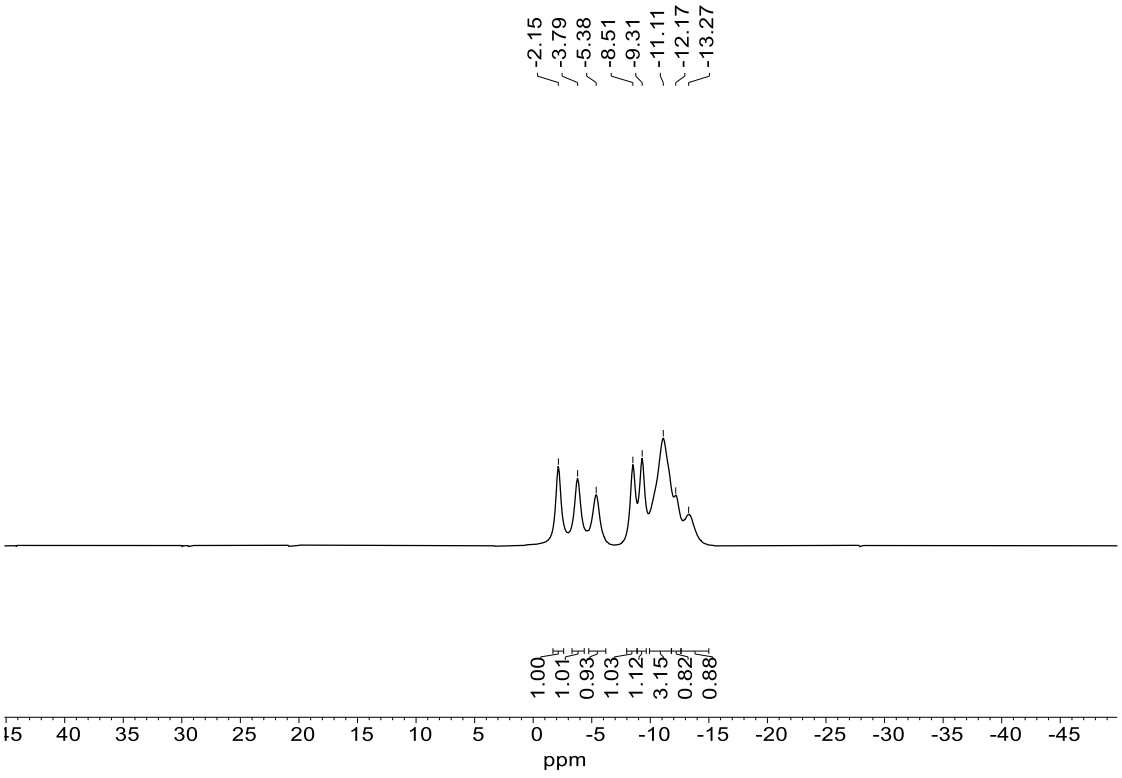
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



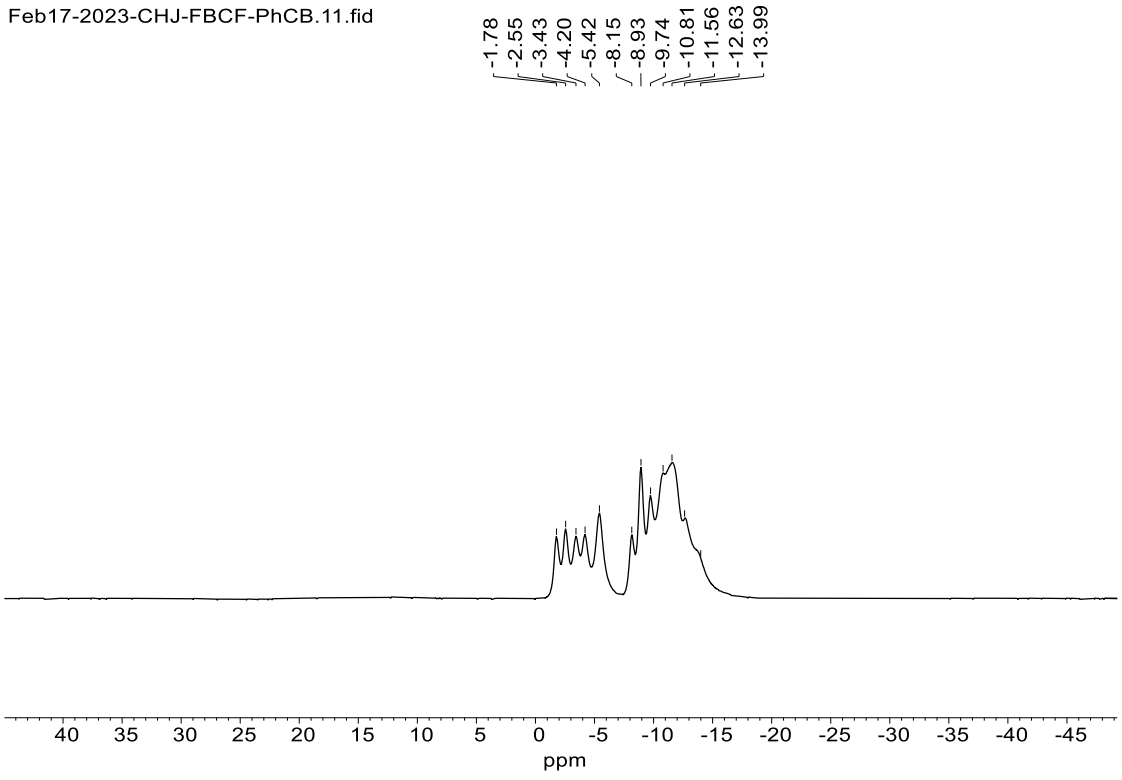
^{1}H NMR (600 MHz, Chloroform-*d*)



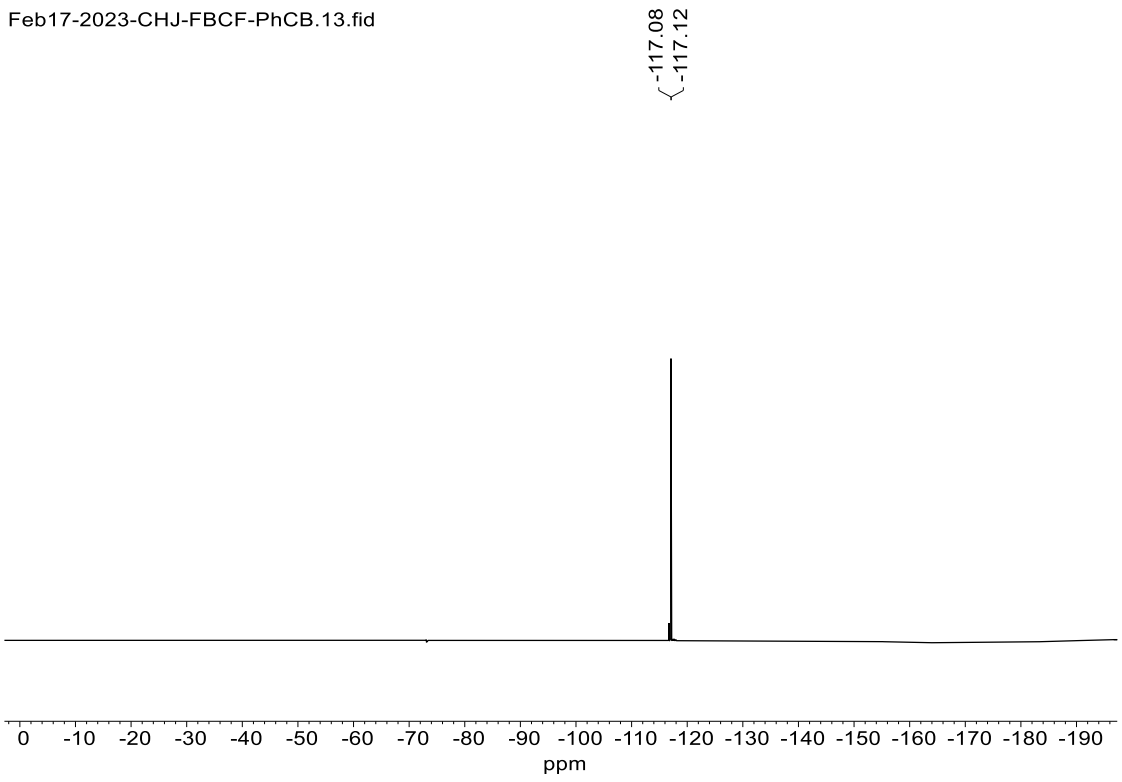
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



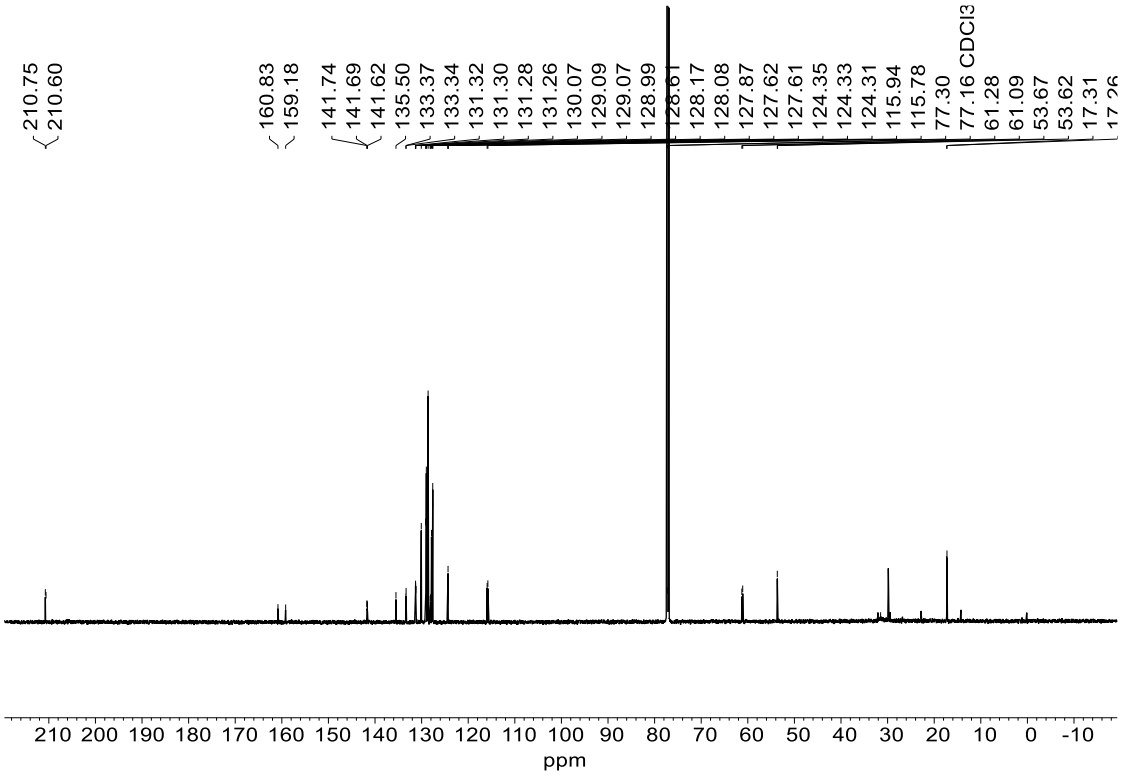
^{11}B NMR (193 MHz, Chloroform-*d*)



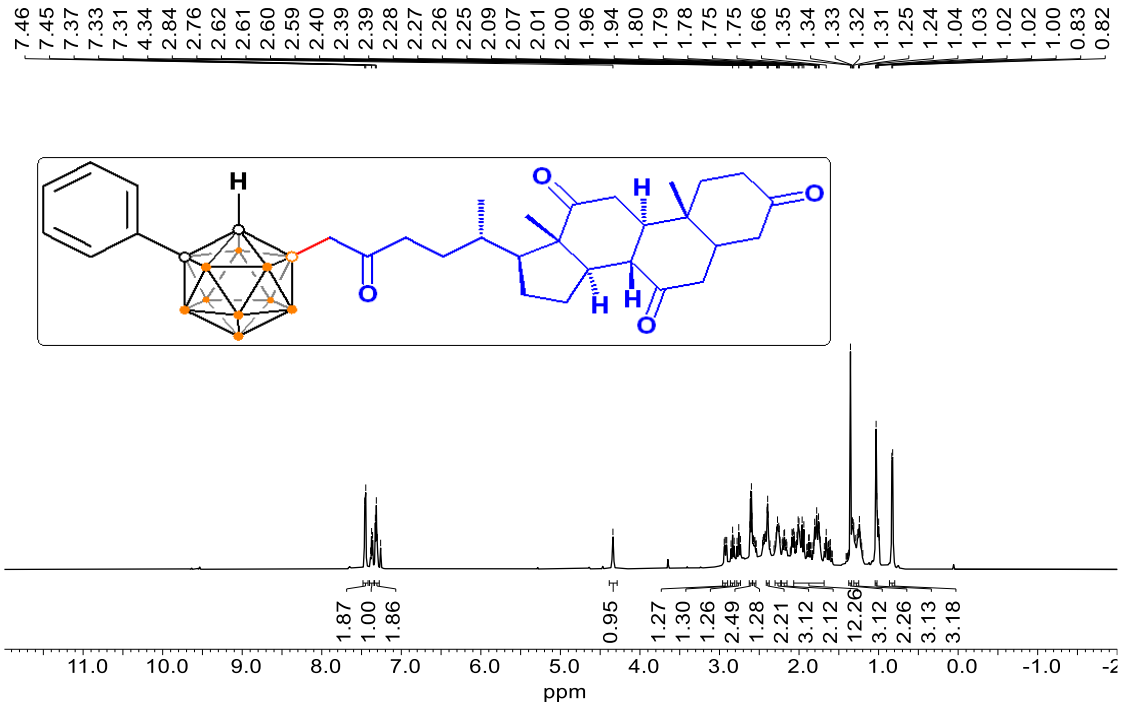
^{19}F NMR (565 MHz, Chloroform-*d*)



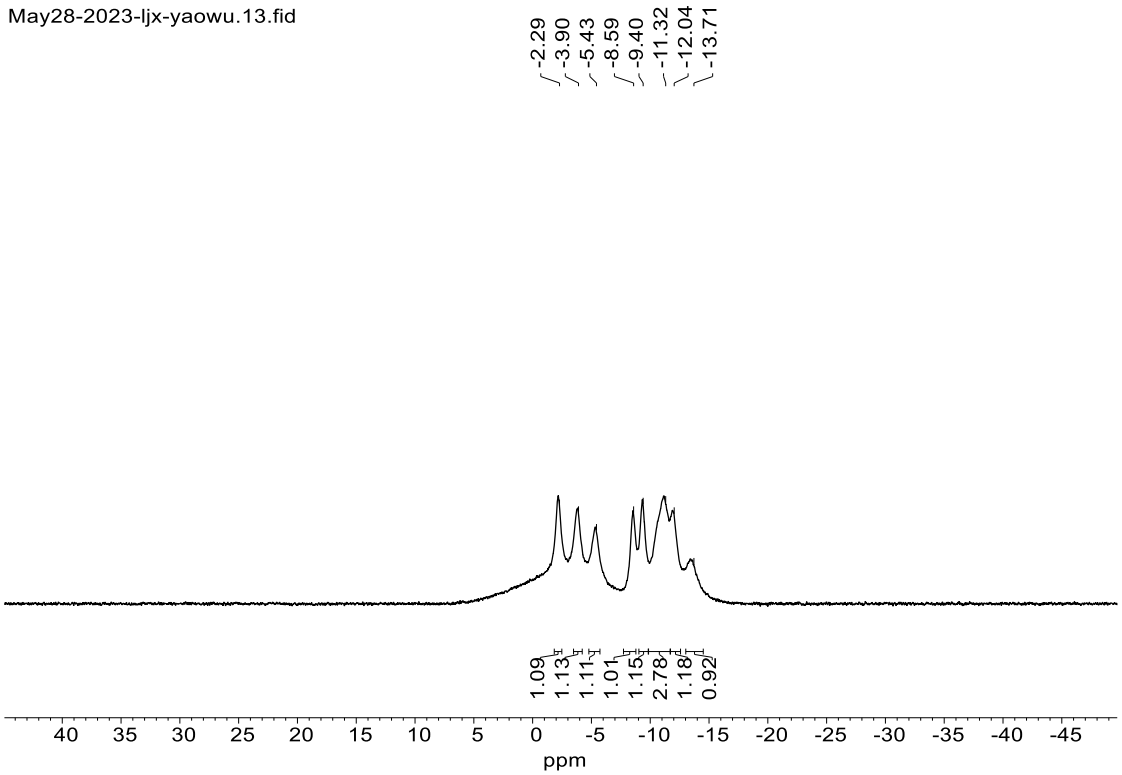
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



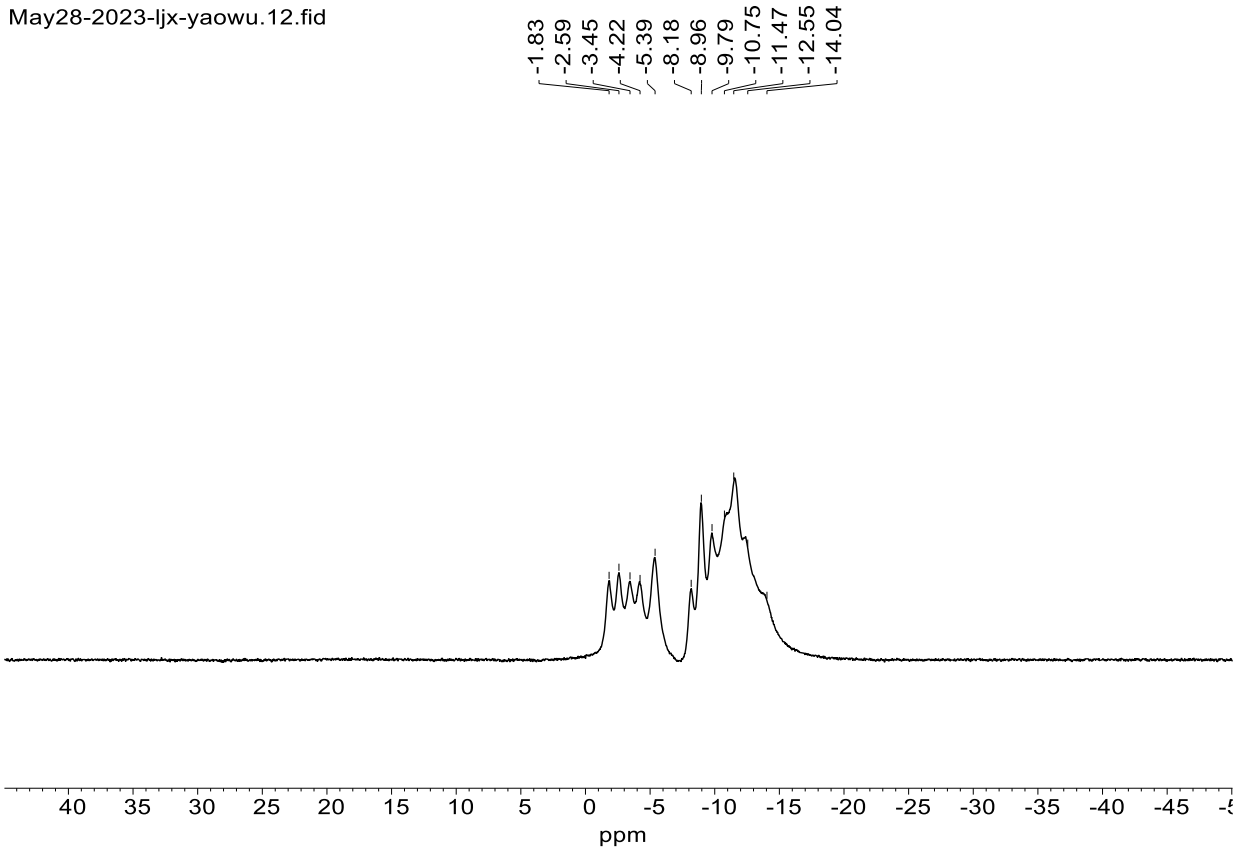
^{1}H NMR (600 MHz, Chloroform-*d*)



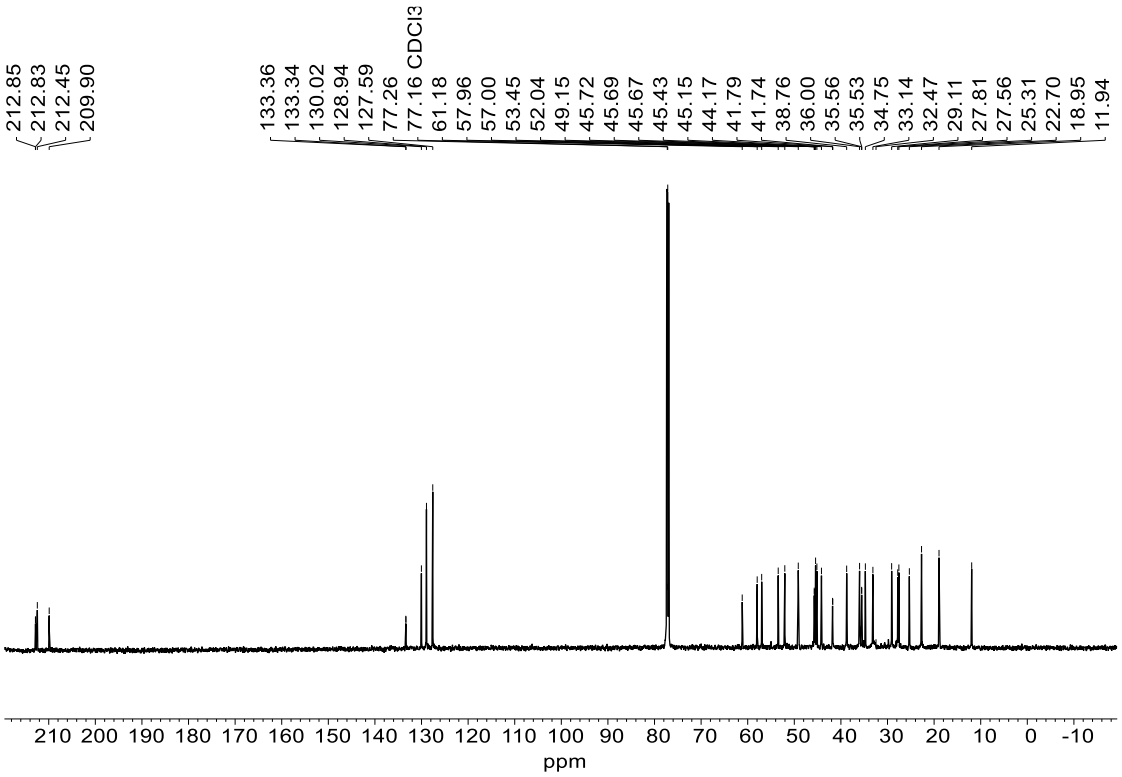
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



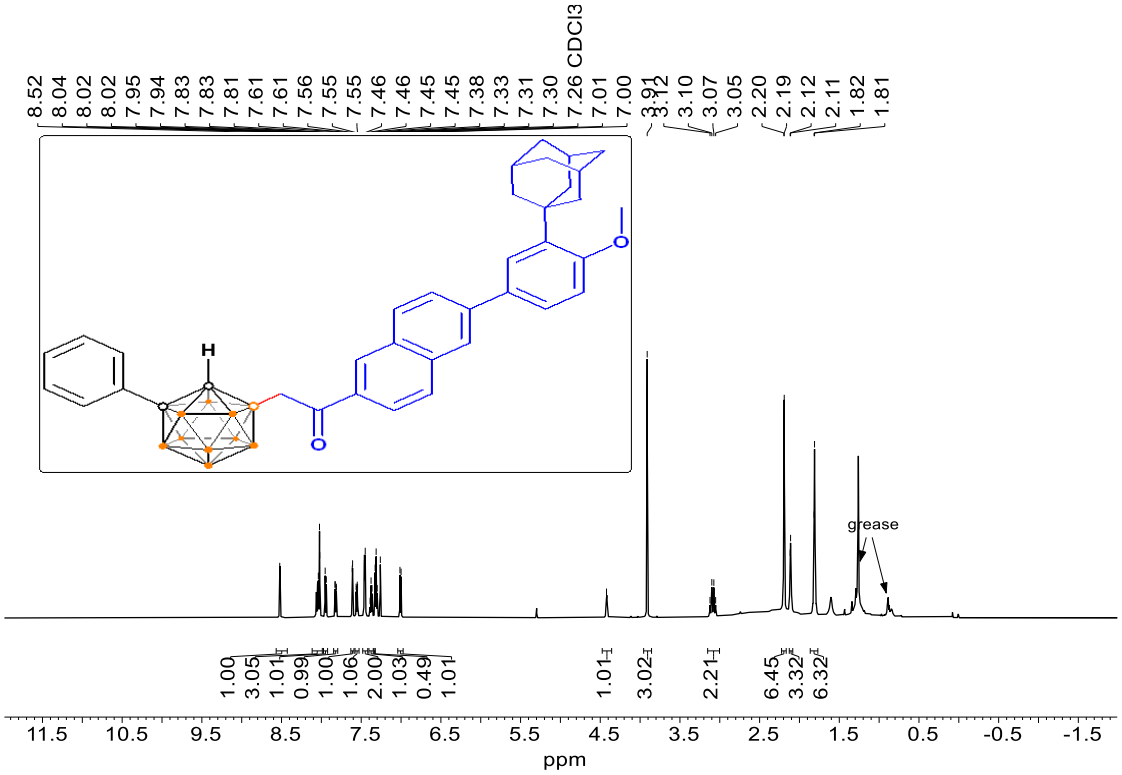
^{11}B NMR (193 MHz, Chloroform-*d*)



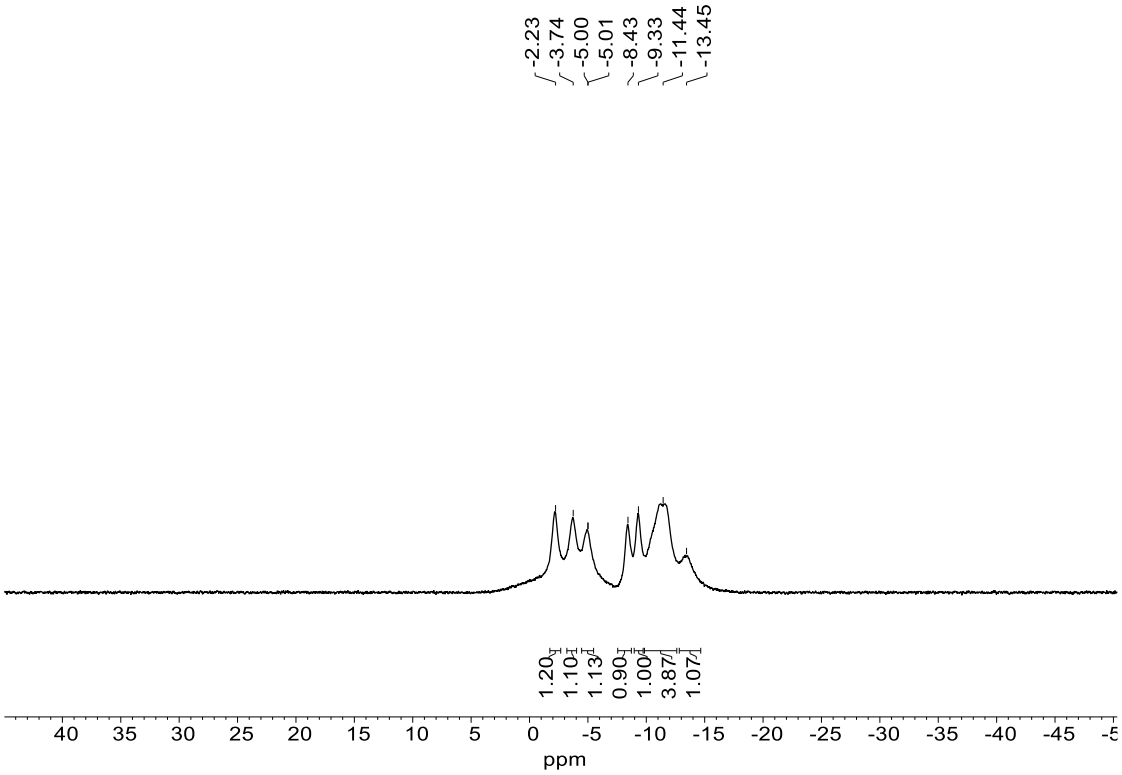
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



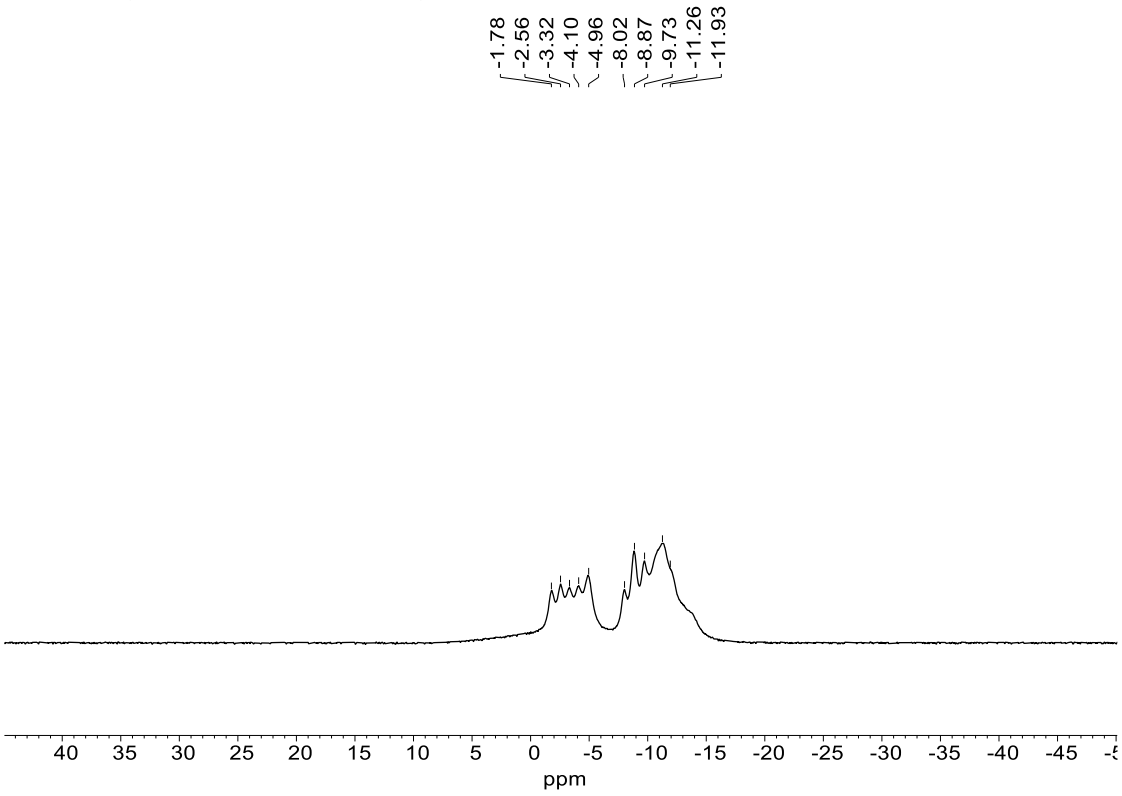
^{1}H NMR (600 MHz, Chloroform-*d*)



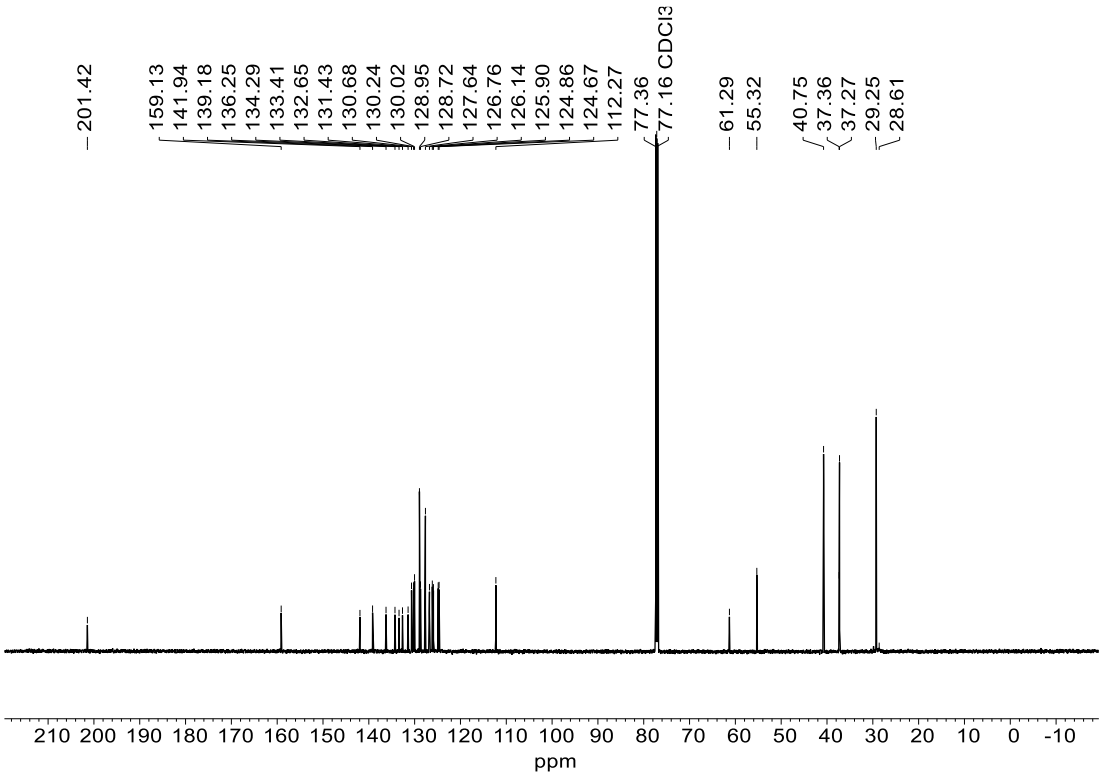
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



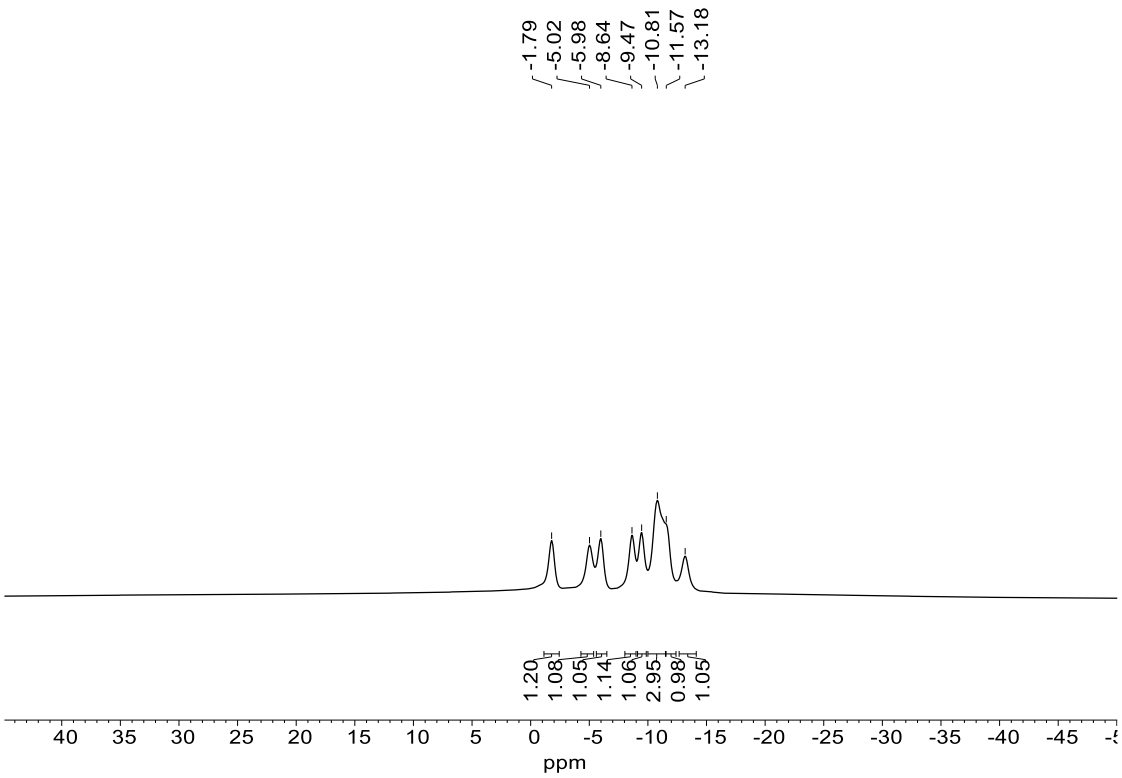
^{11}B NMR (193 MHz, Chloroform-*d*)



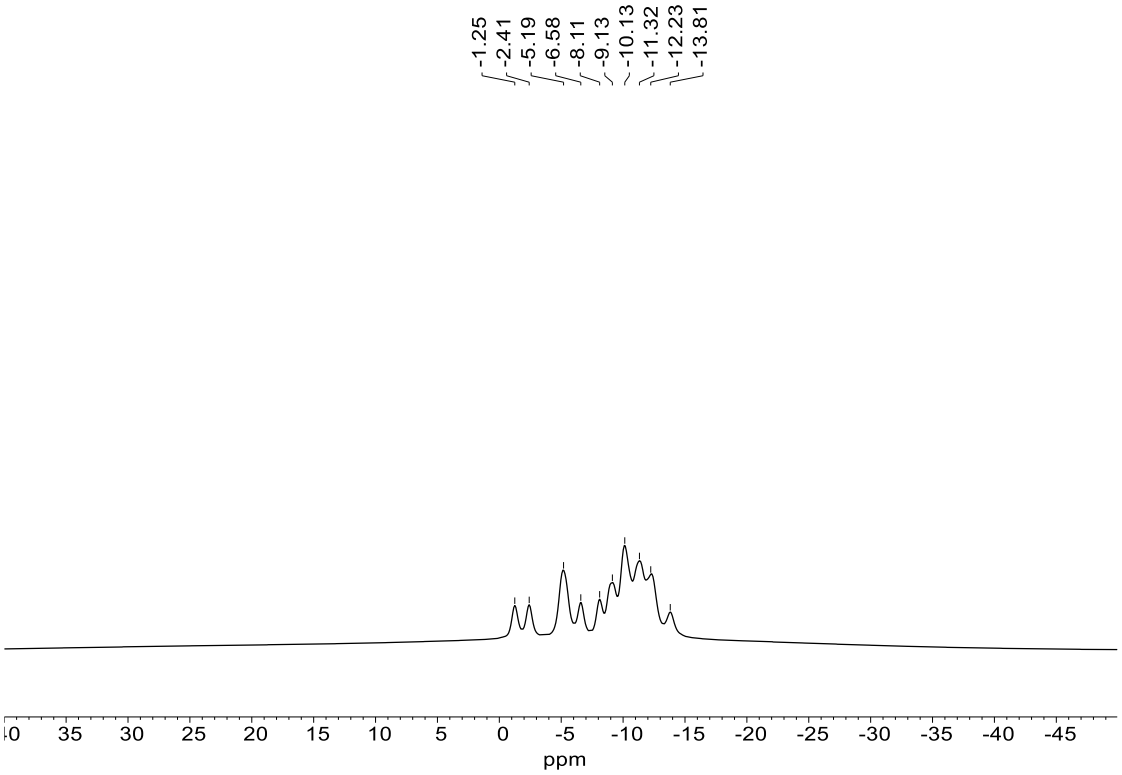
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



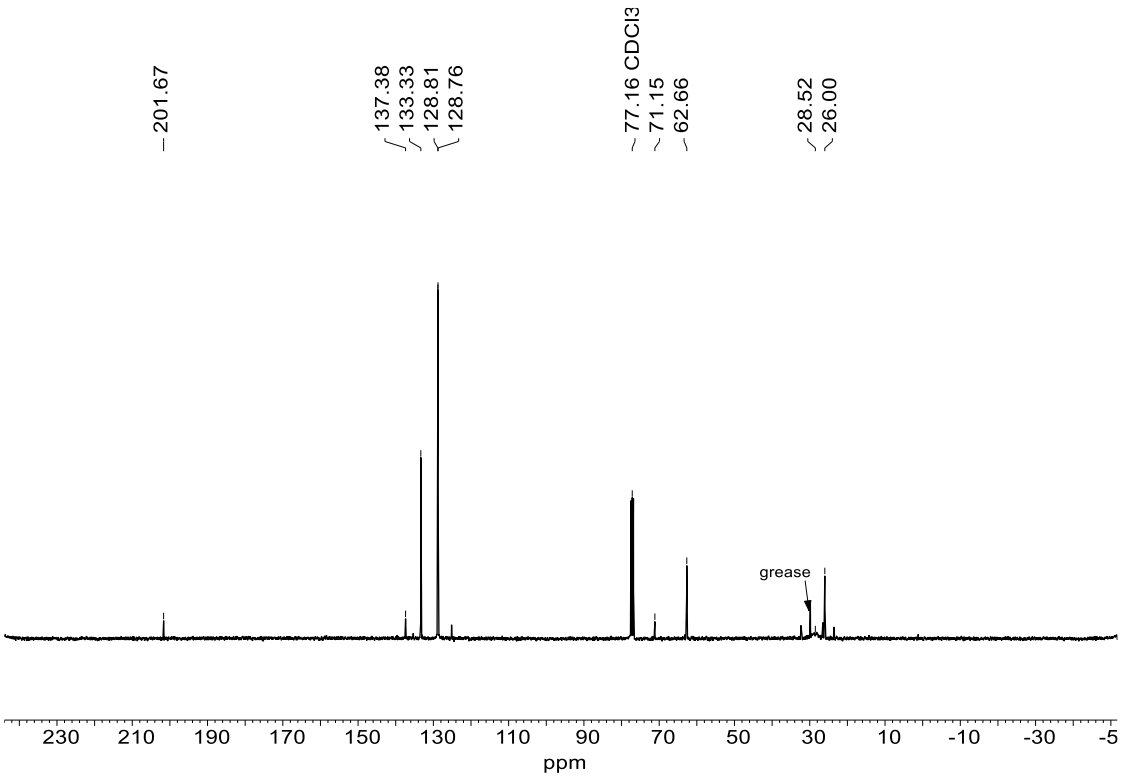
^{1}H NMR (400 MHz, Chloroform-*d*)



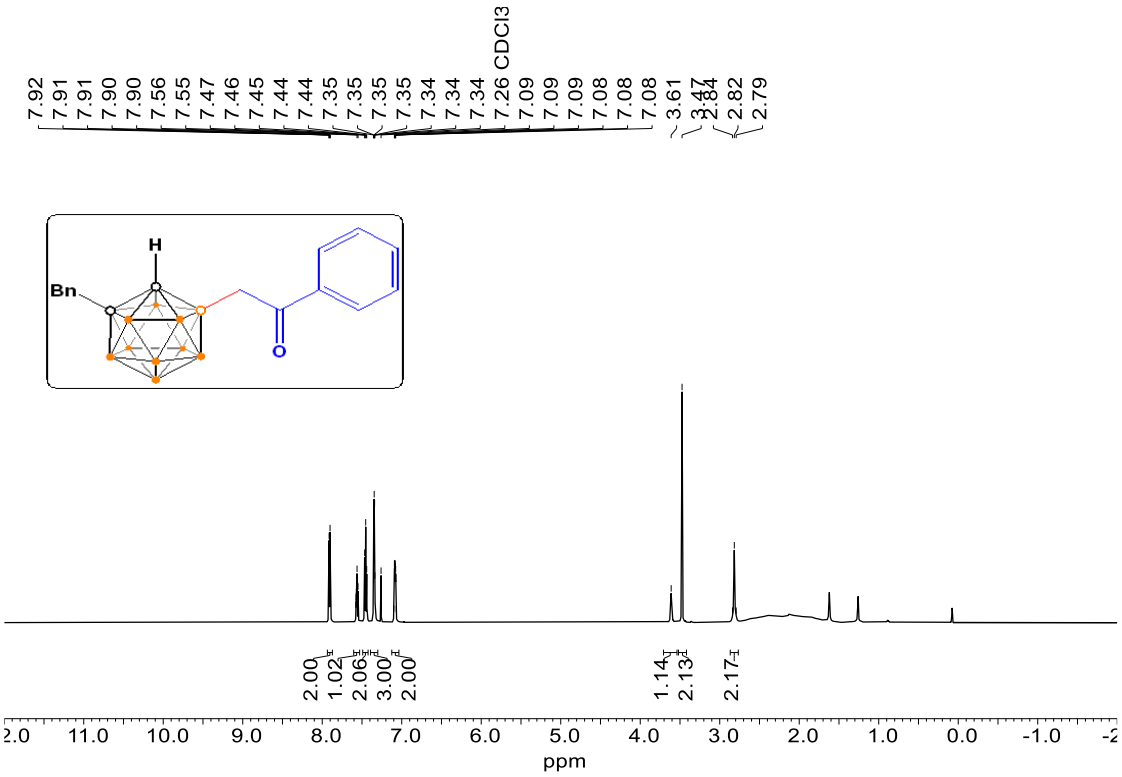
^{11}B NMR (128 MHz, Chloroform-*d*)



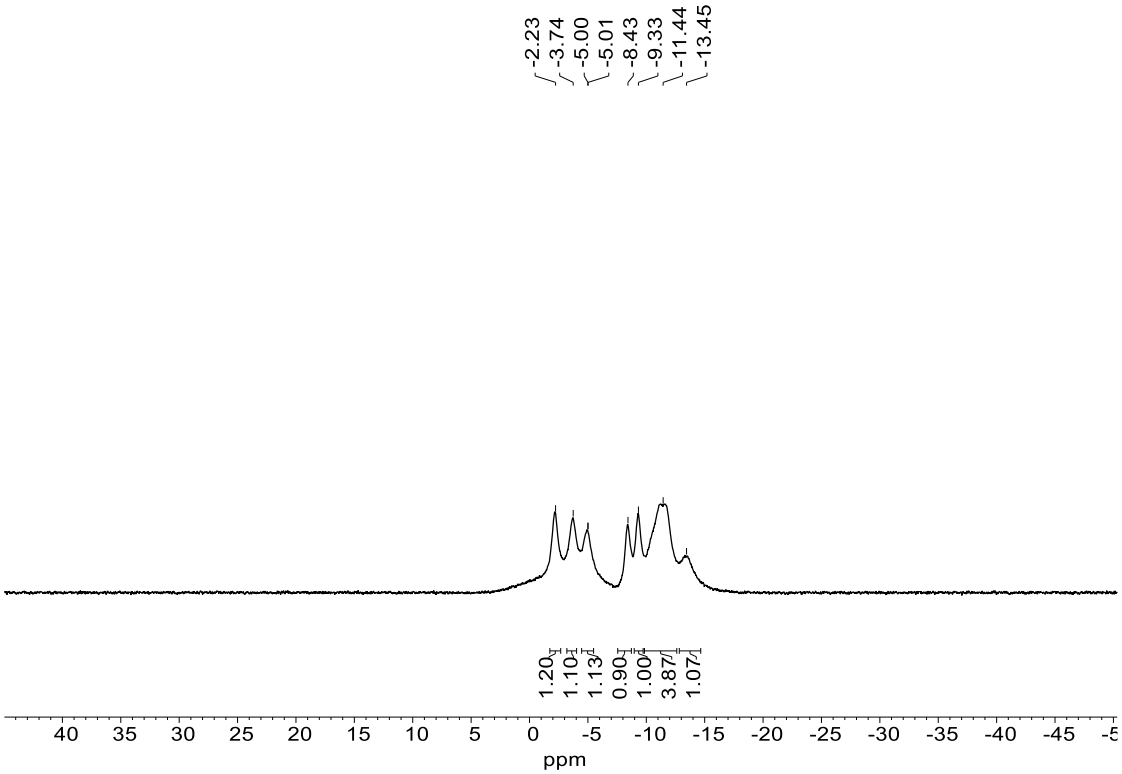
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



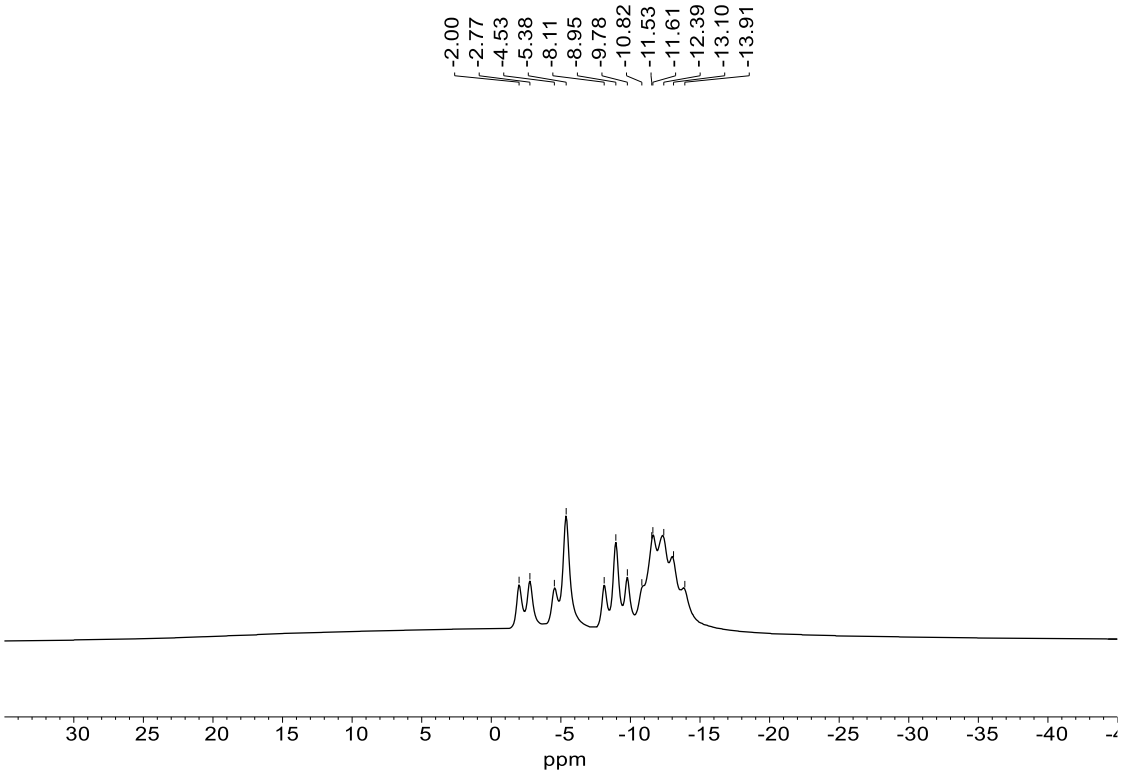
^{1}H NMR (600 MHz, Chloroform-*d*)



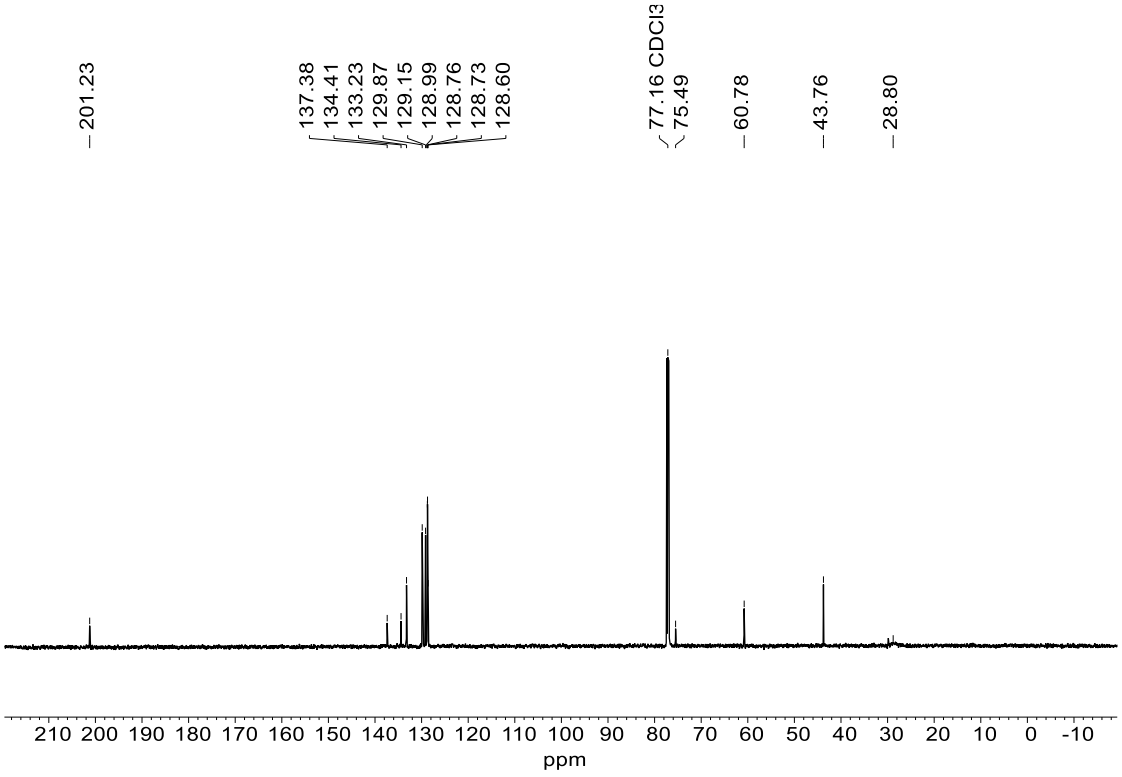
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



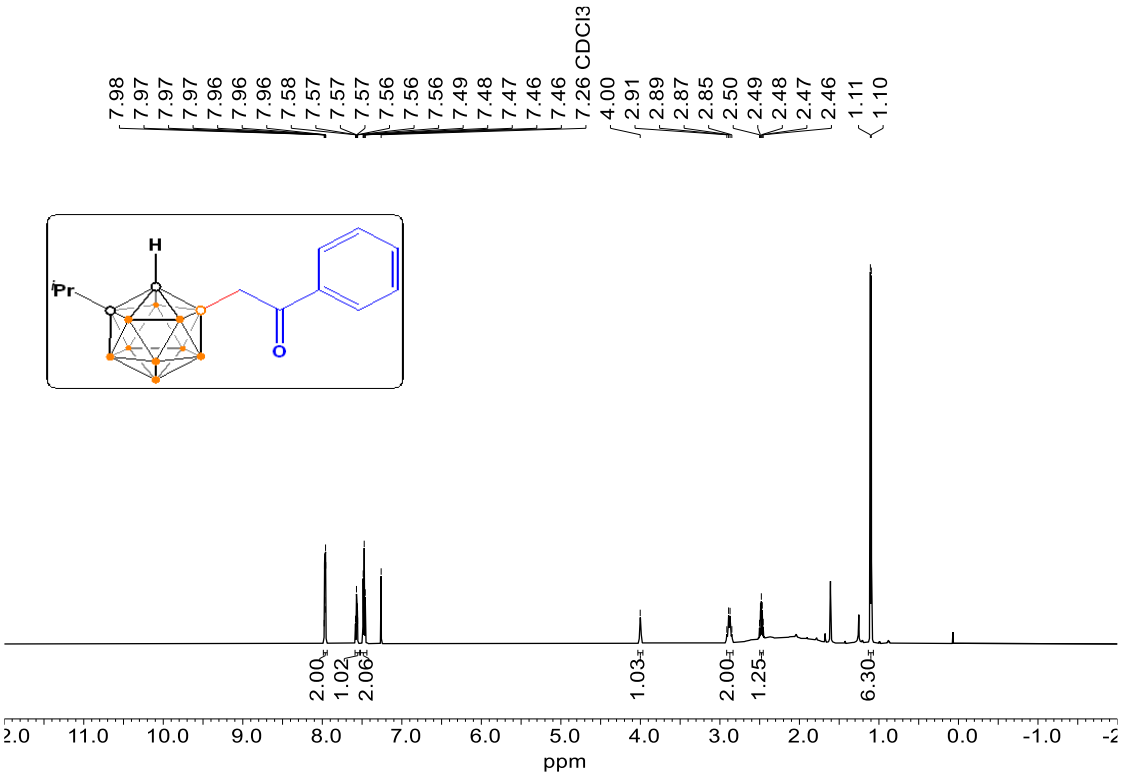
^{11}B NMR (193 MHz, Chloroform-*d*)



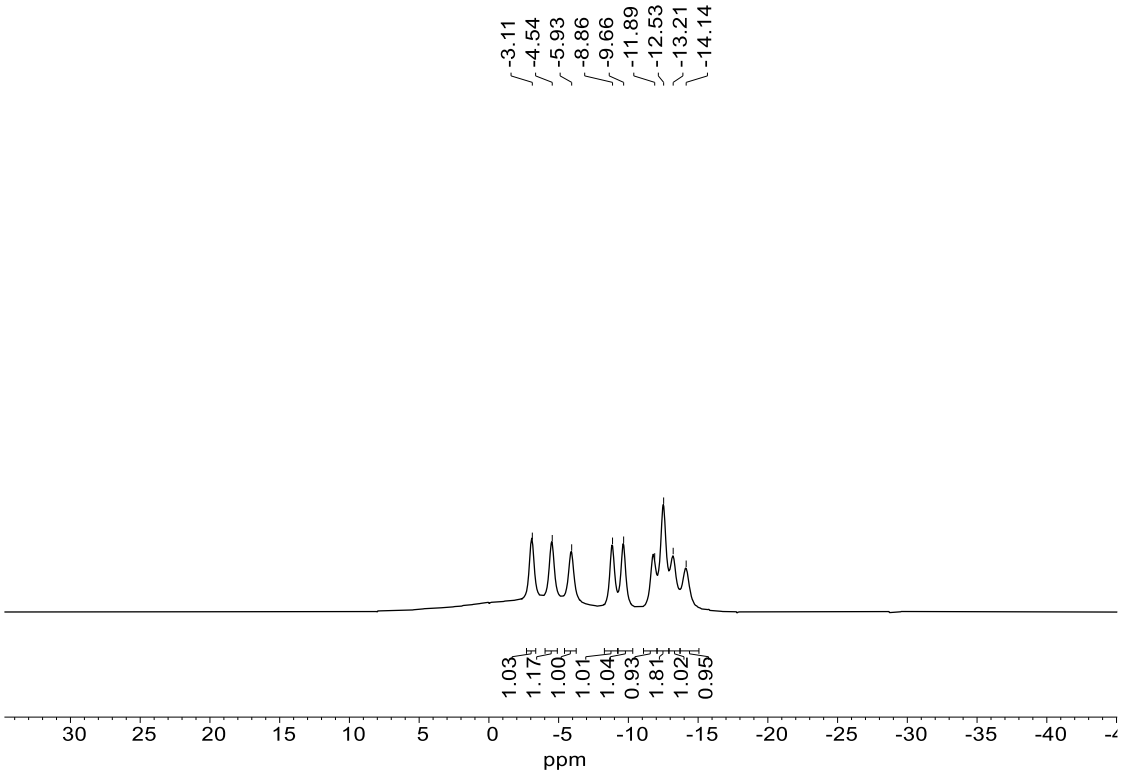
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



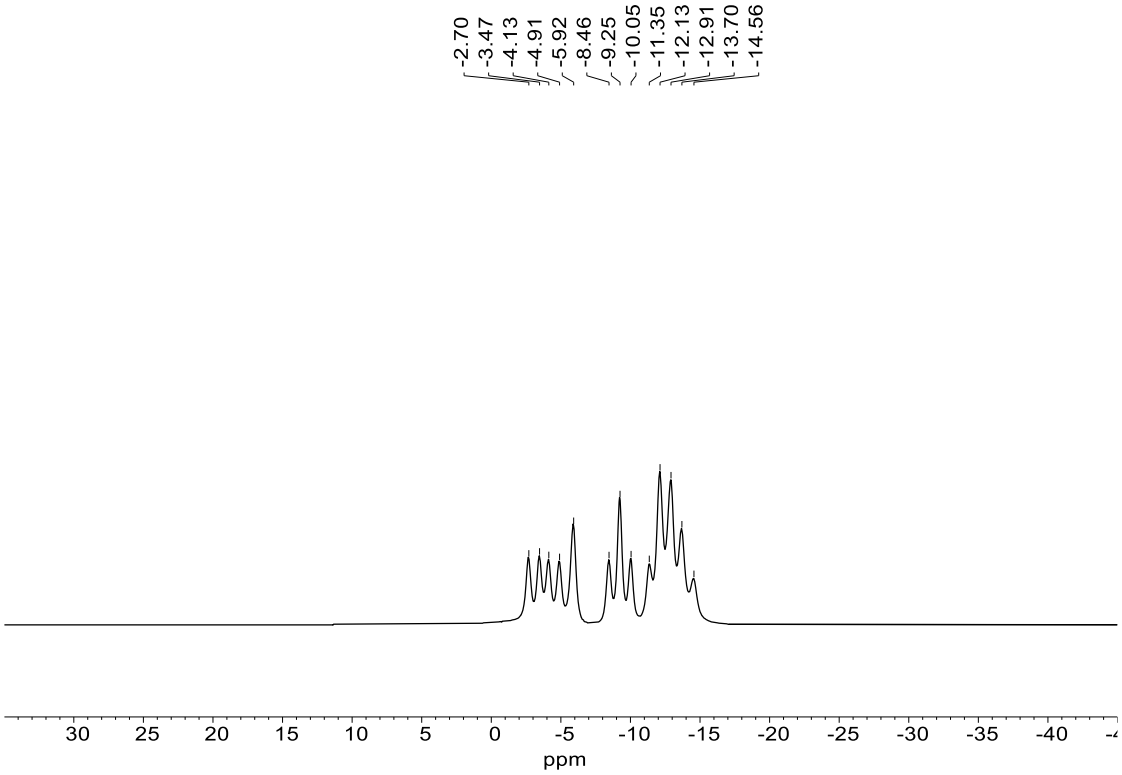
^{1}H NMR (600 MHz, Chloroform-*d*)



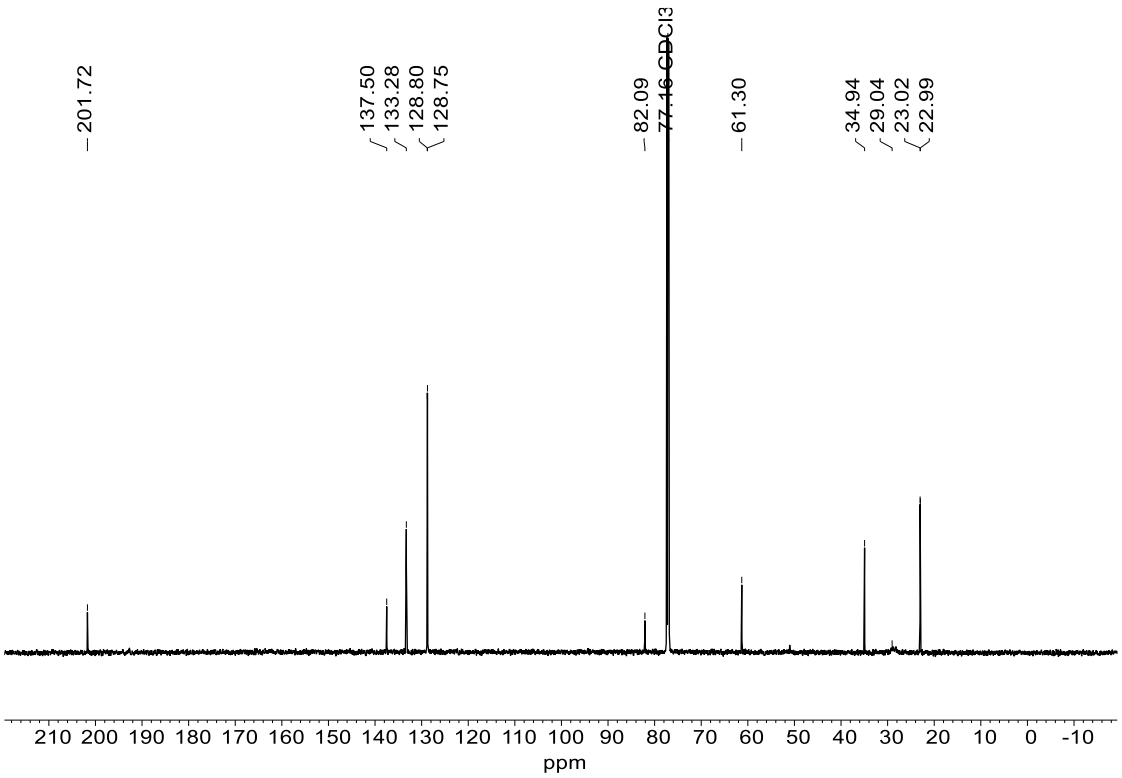
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



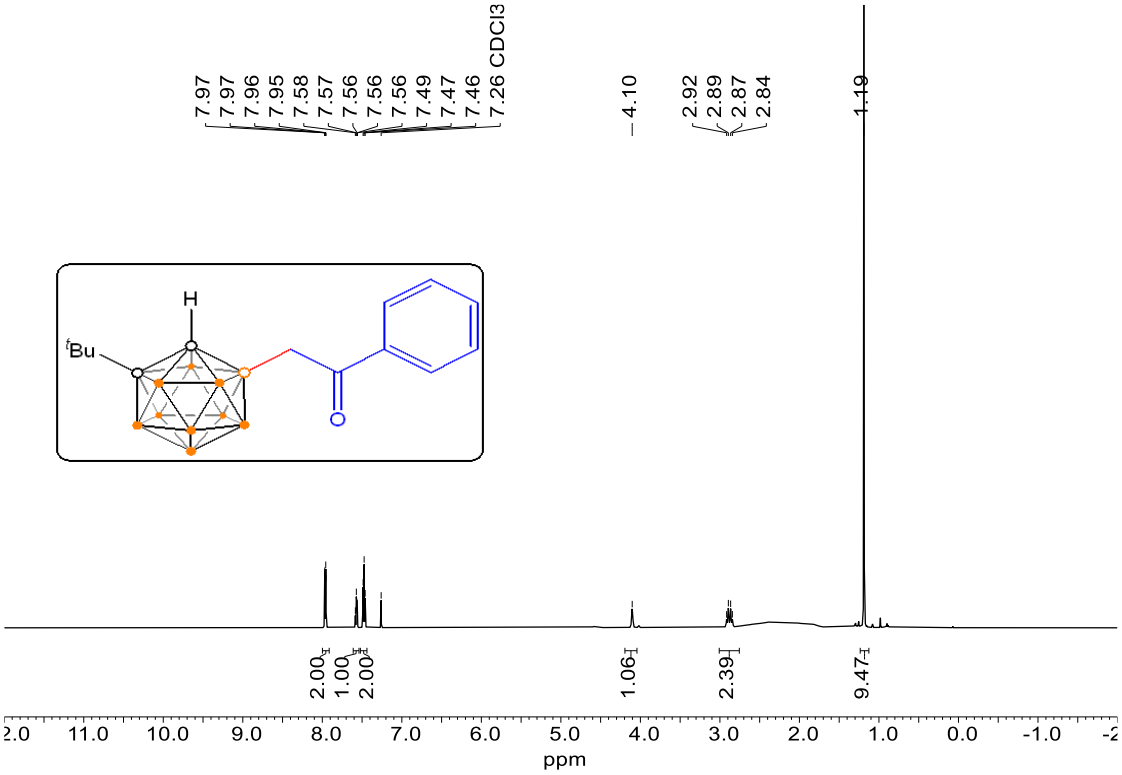
^{11}B NMR (193 MHz, Chloroform-*d*)



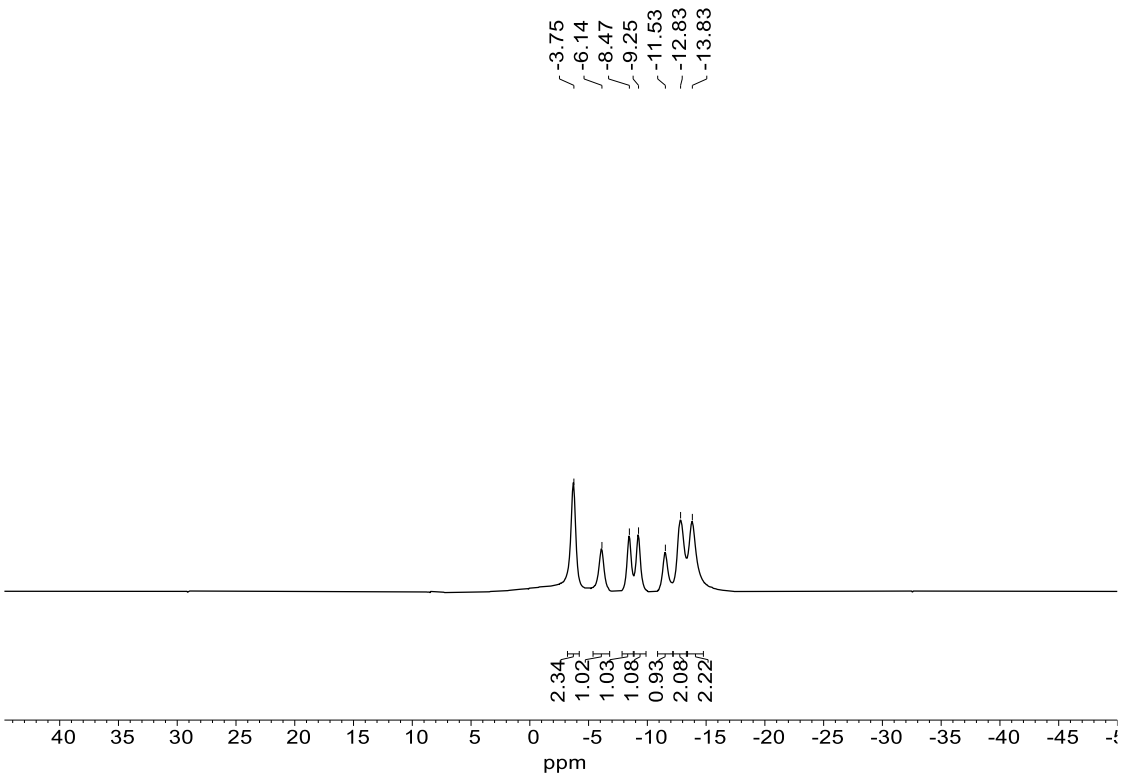
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



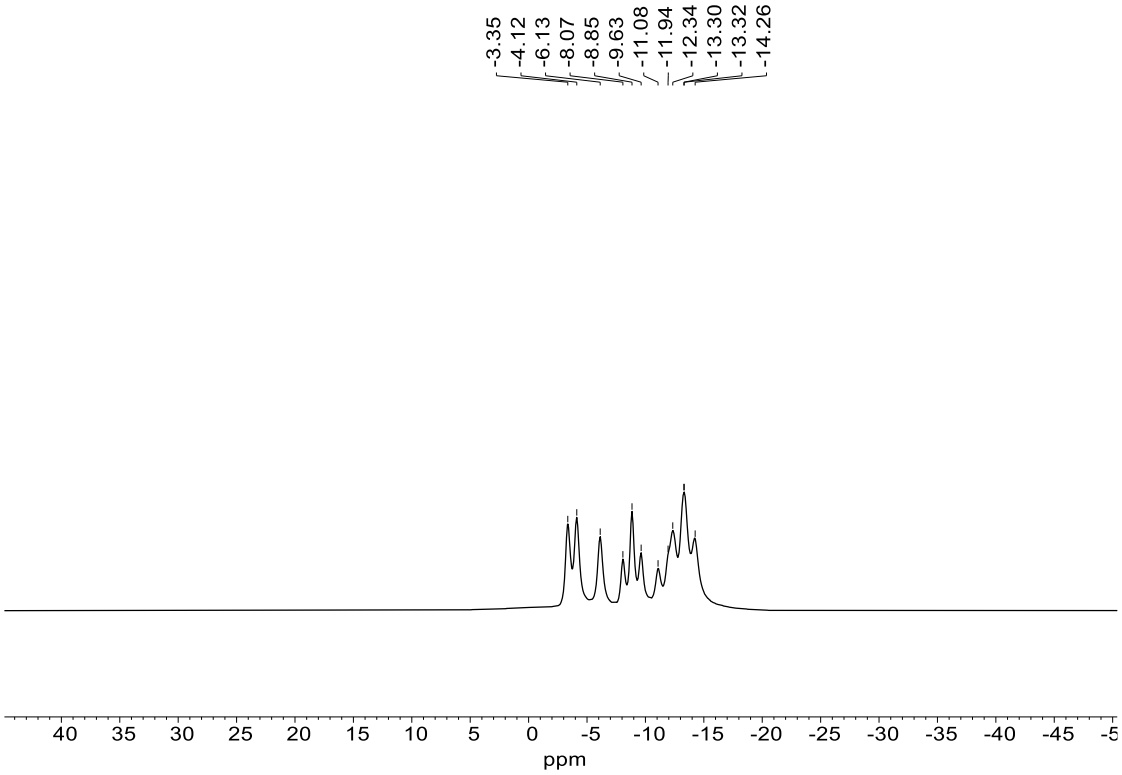
^{1}H NMR (600 MHz, Chloroform-*d*)



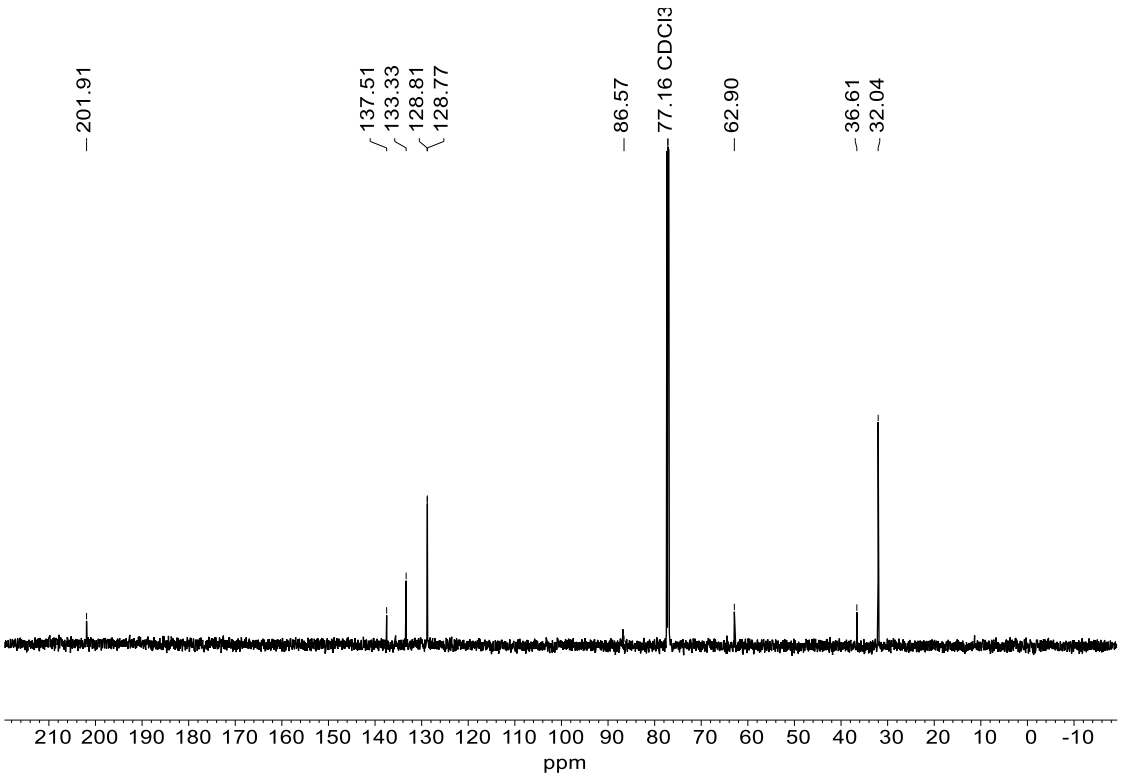
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



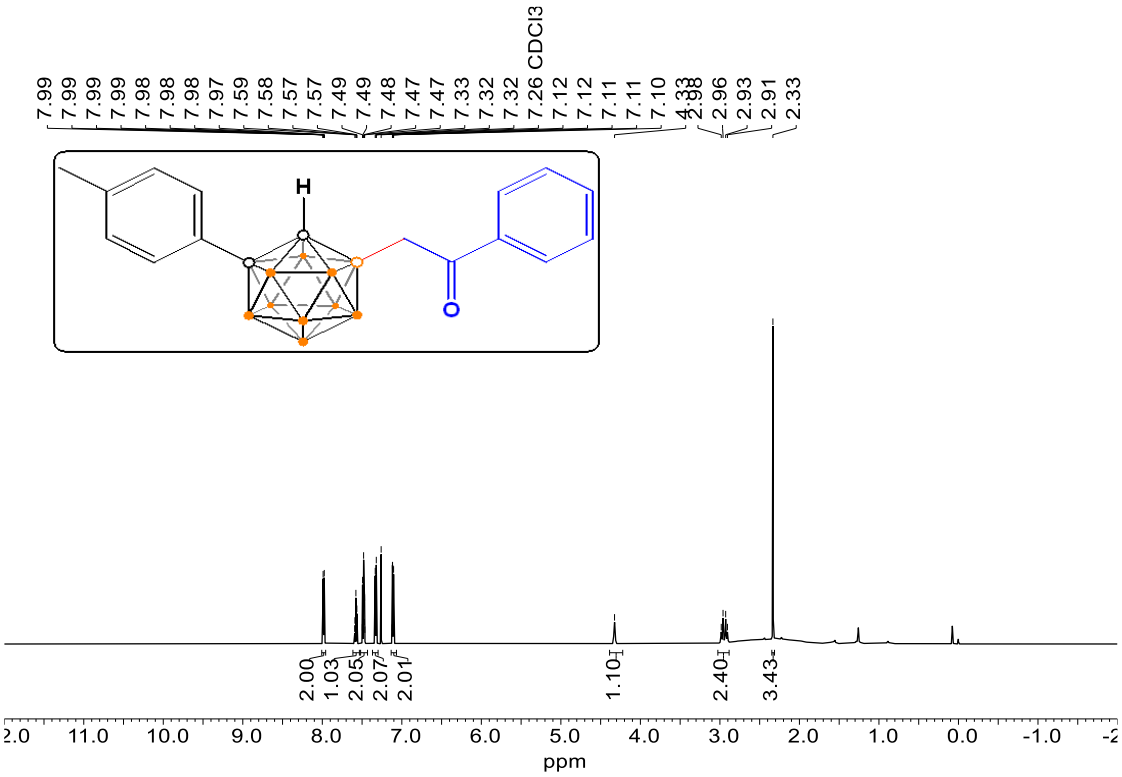
^{11}B NMR (193 MHz, Chloroform-*d*)



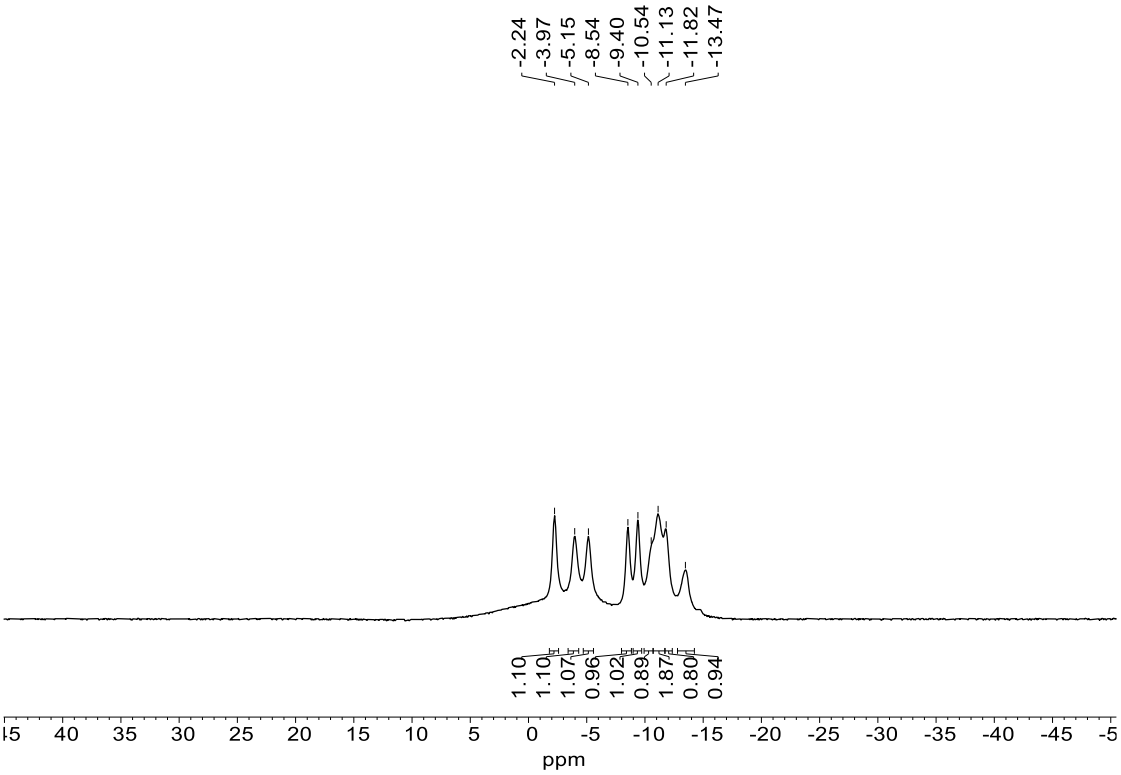
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



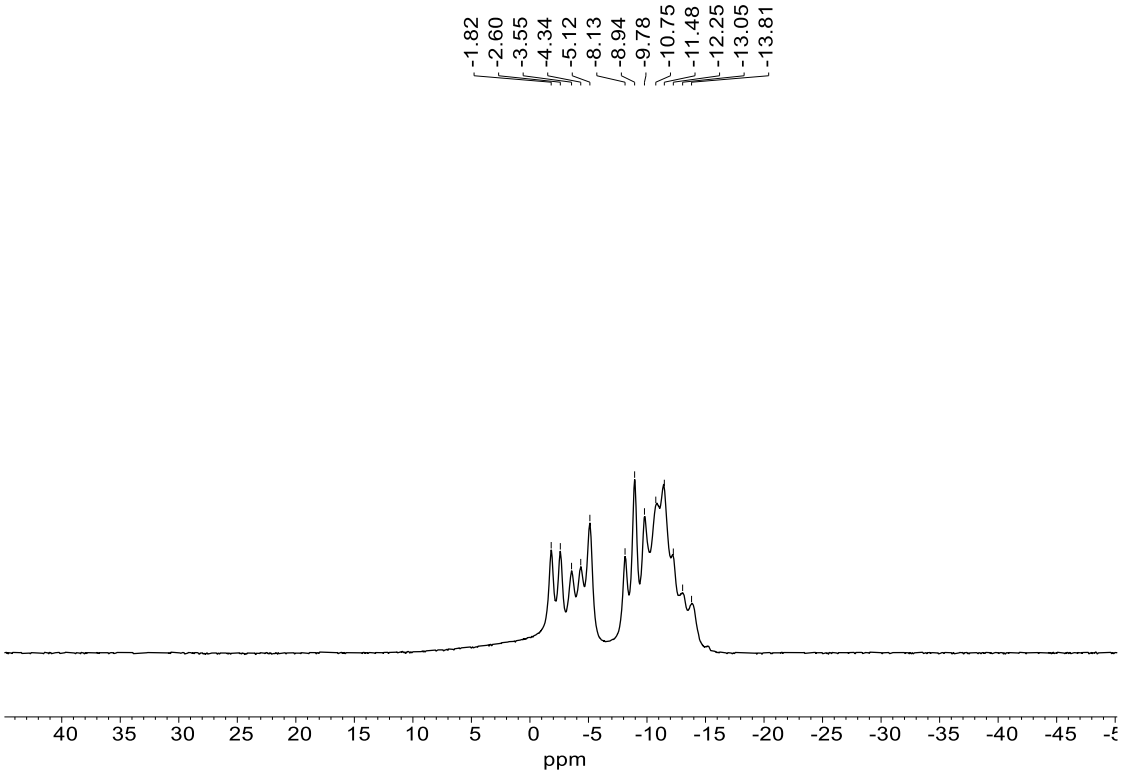
^{1}H NMR (600 MHz, Chloroform-*d*)



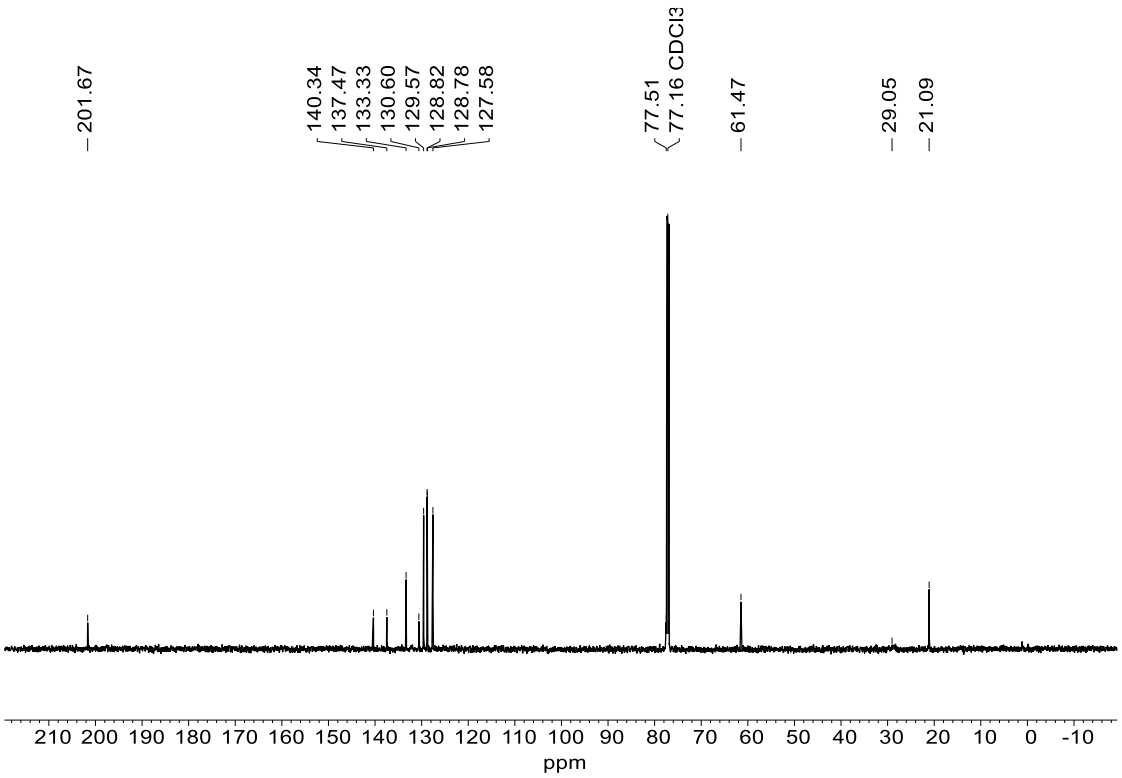
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



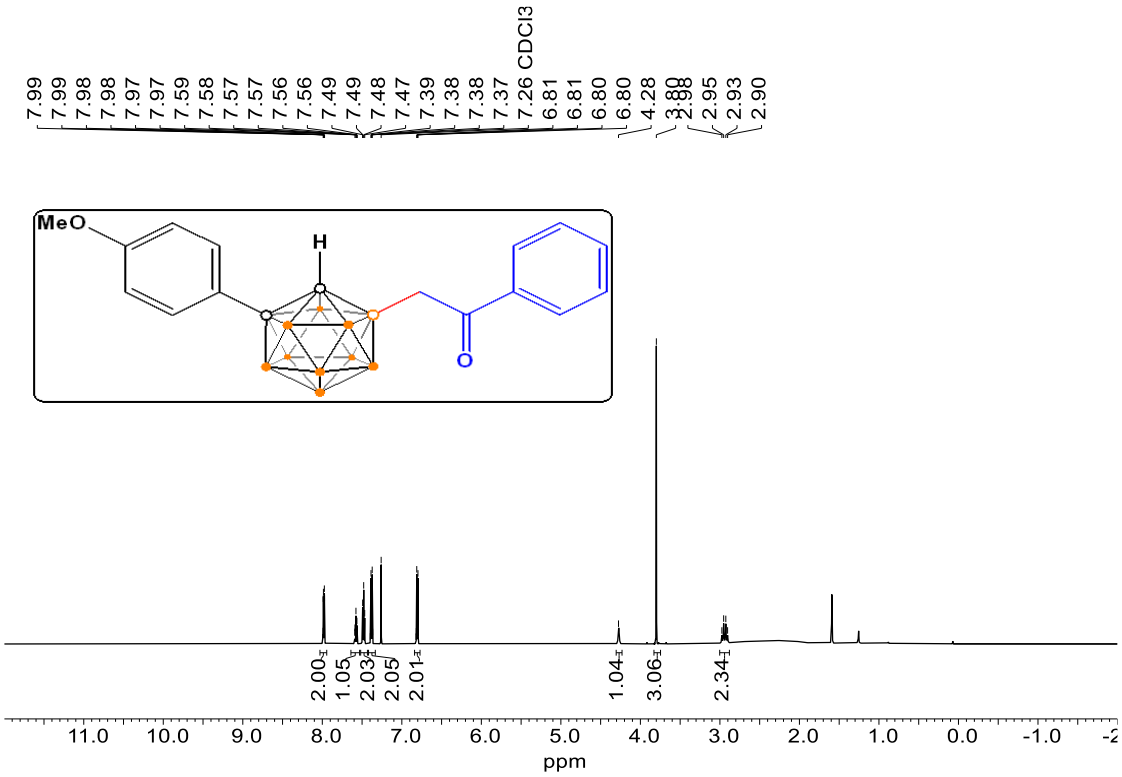
^{11}B NMR (193 MHz, Chloroform-*d*)



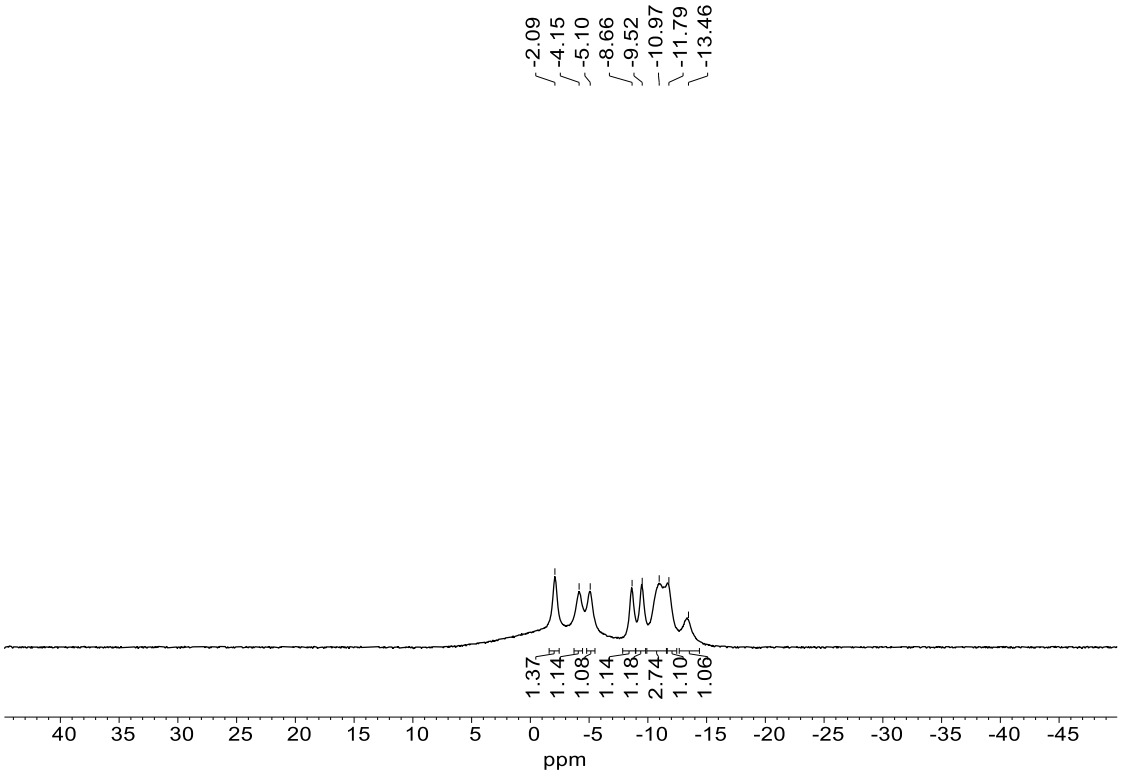
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



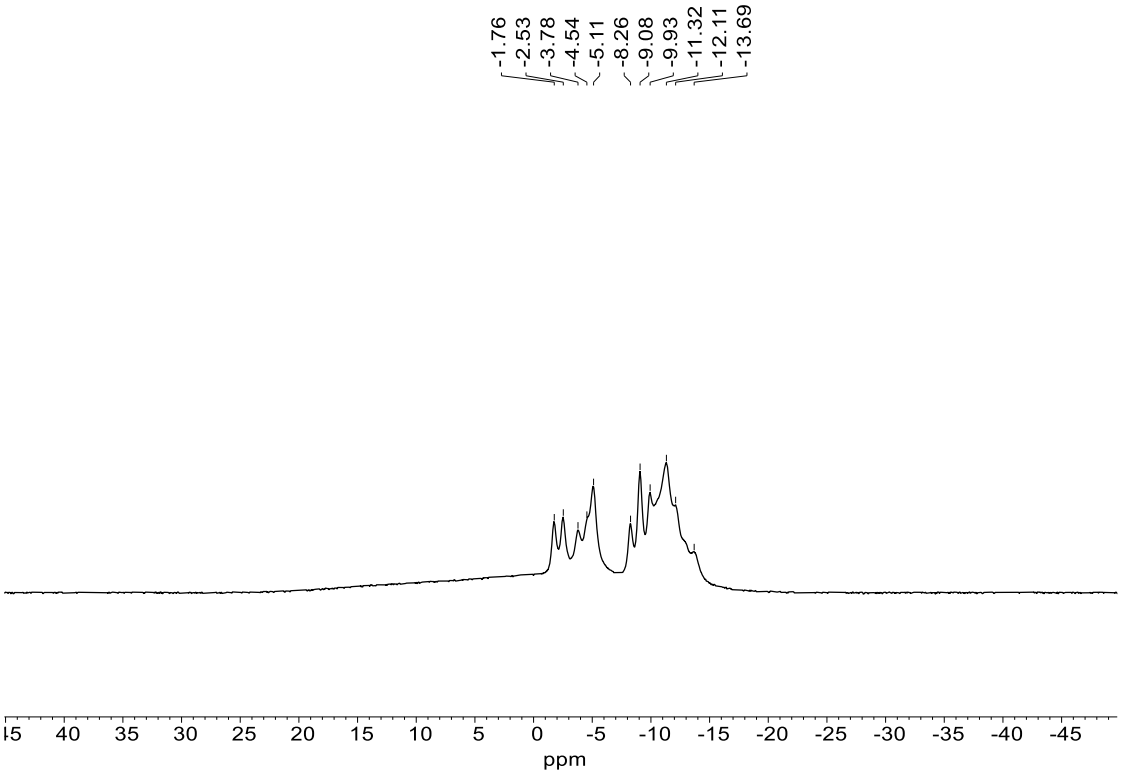
^{1}H NMR (600 MHz, Chloroform-*d*)



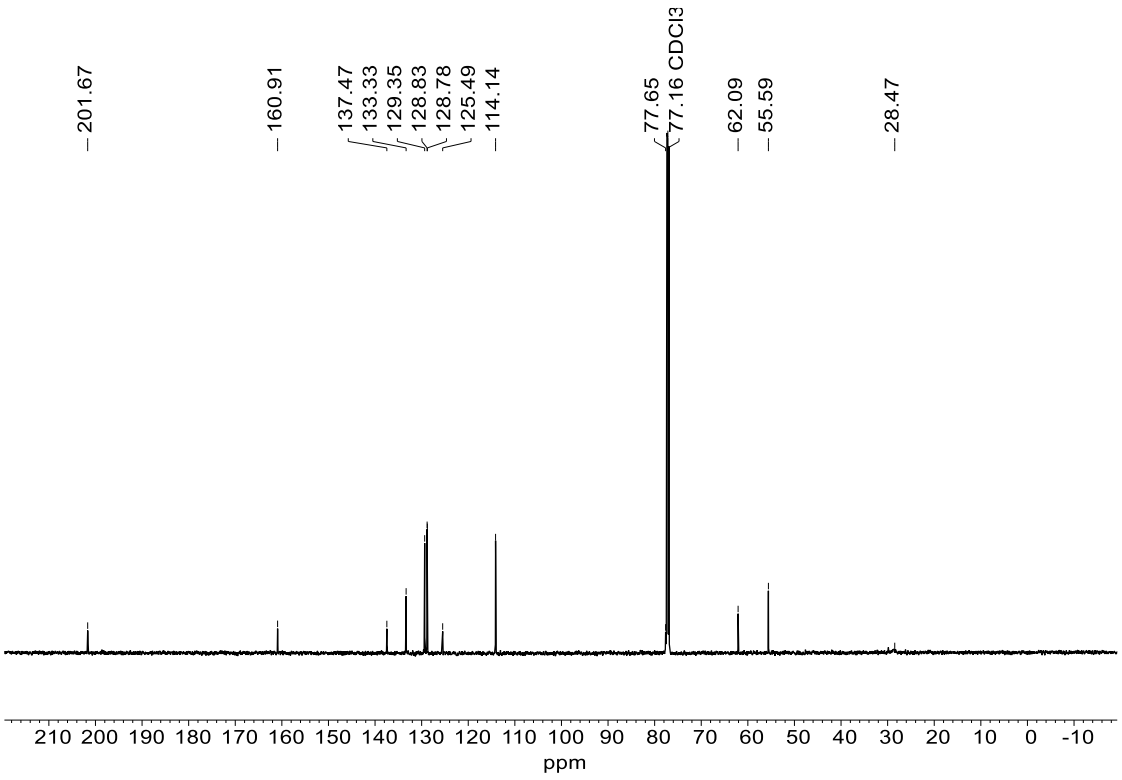
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



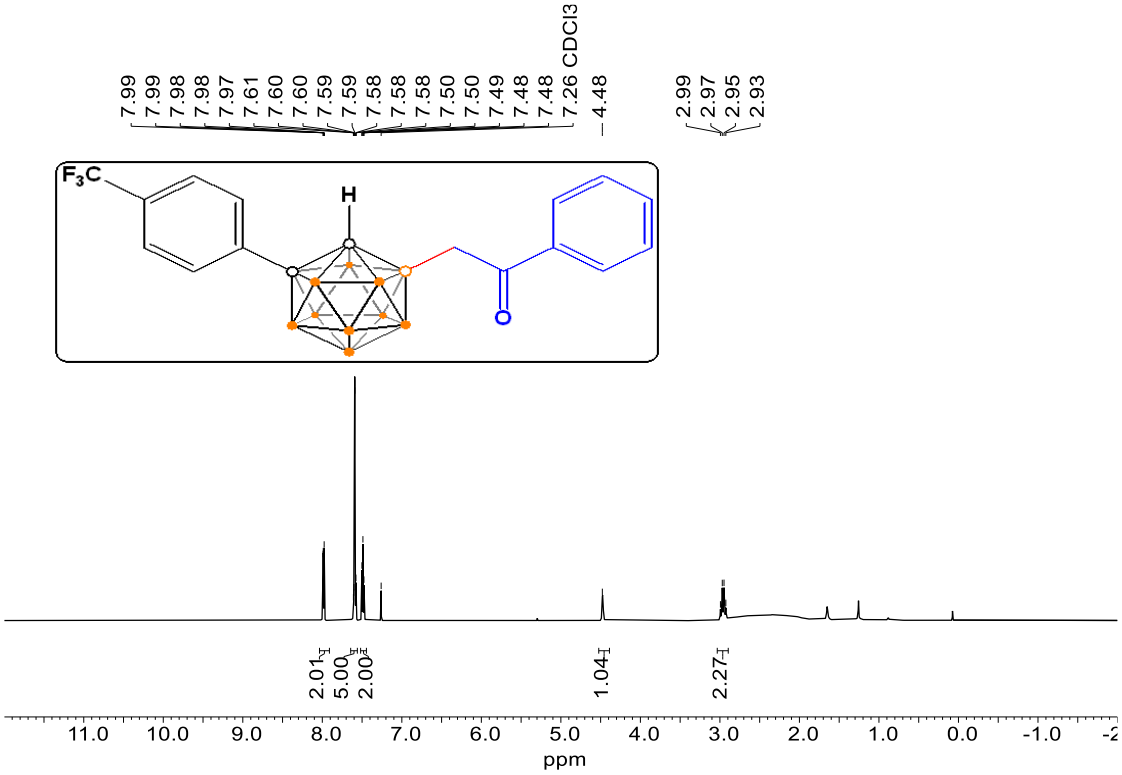
^{11}B NMR (193 MHz, Chloroform-*d*)



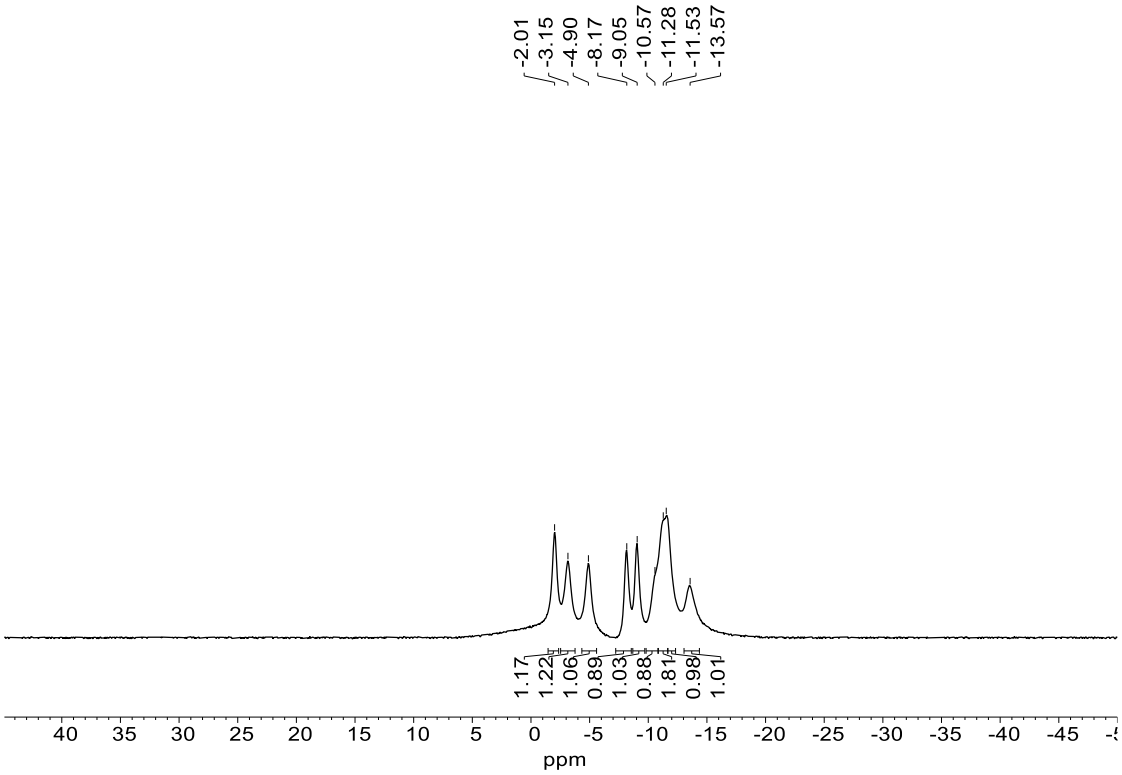
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



^{1}H NMR (600 MHz, Chloroform-*d*)



^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



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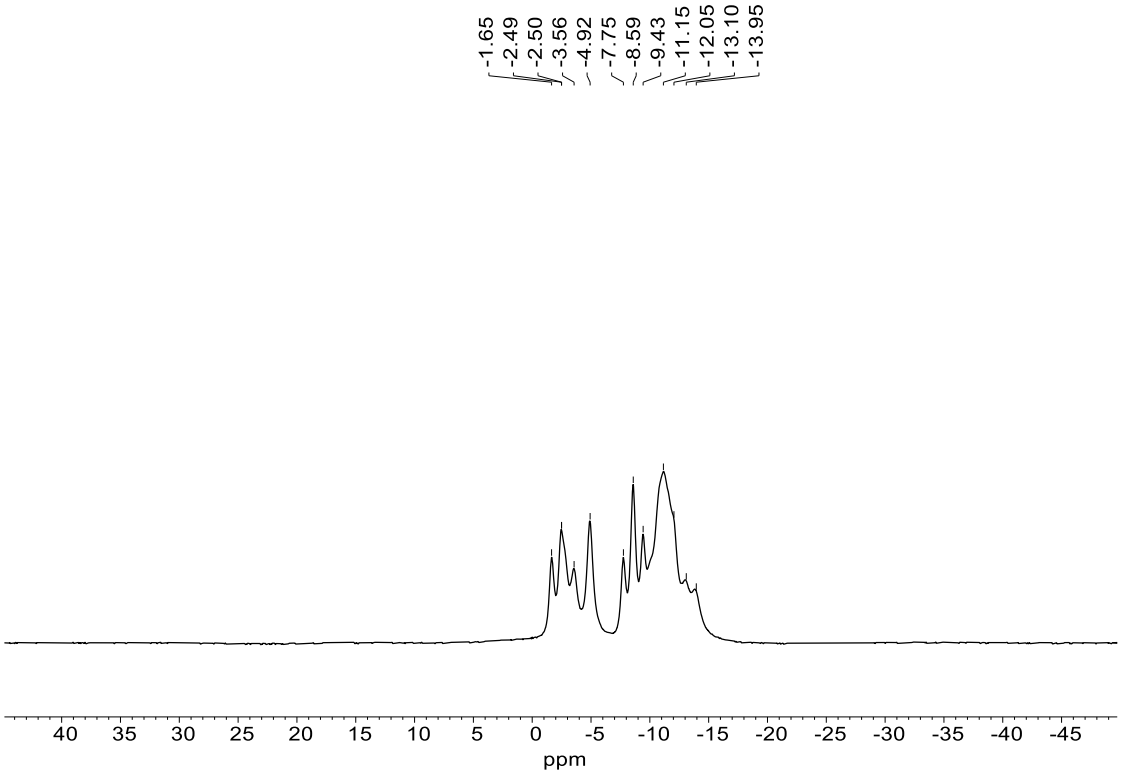
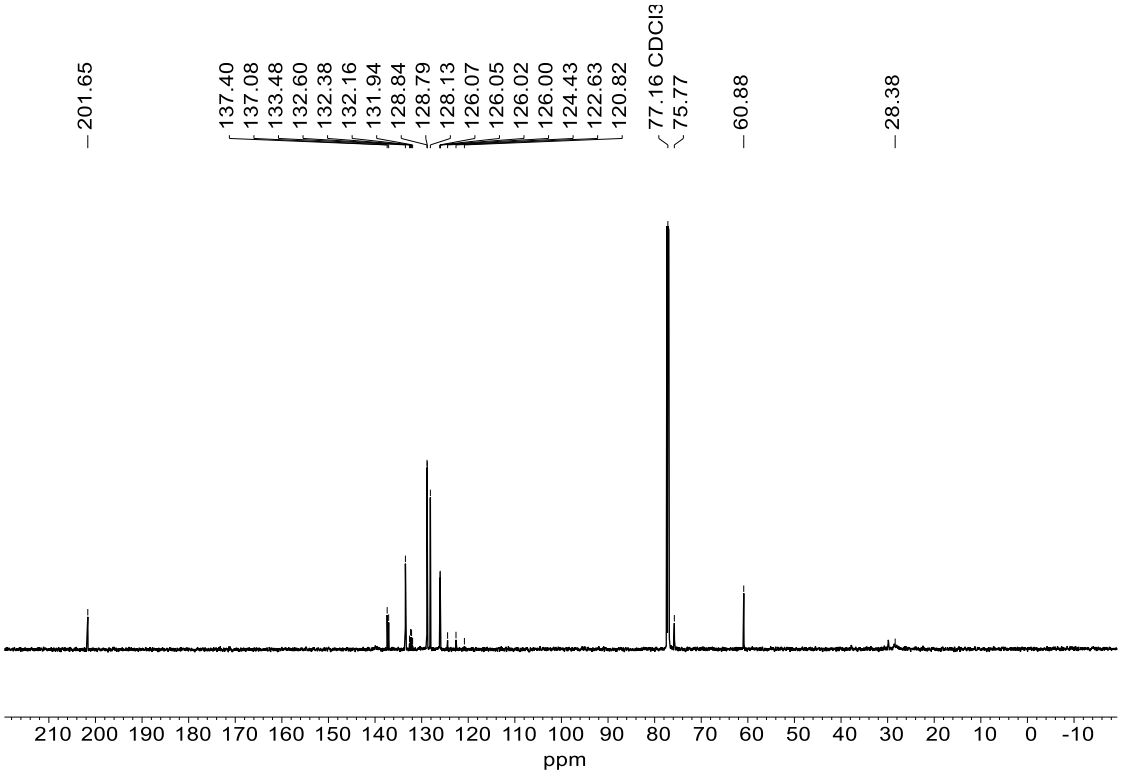
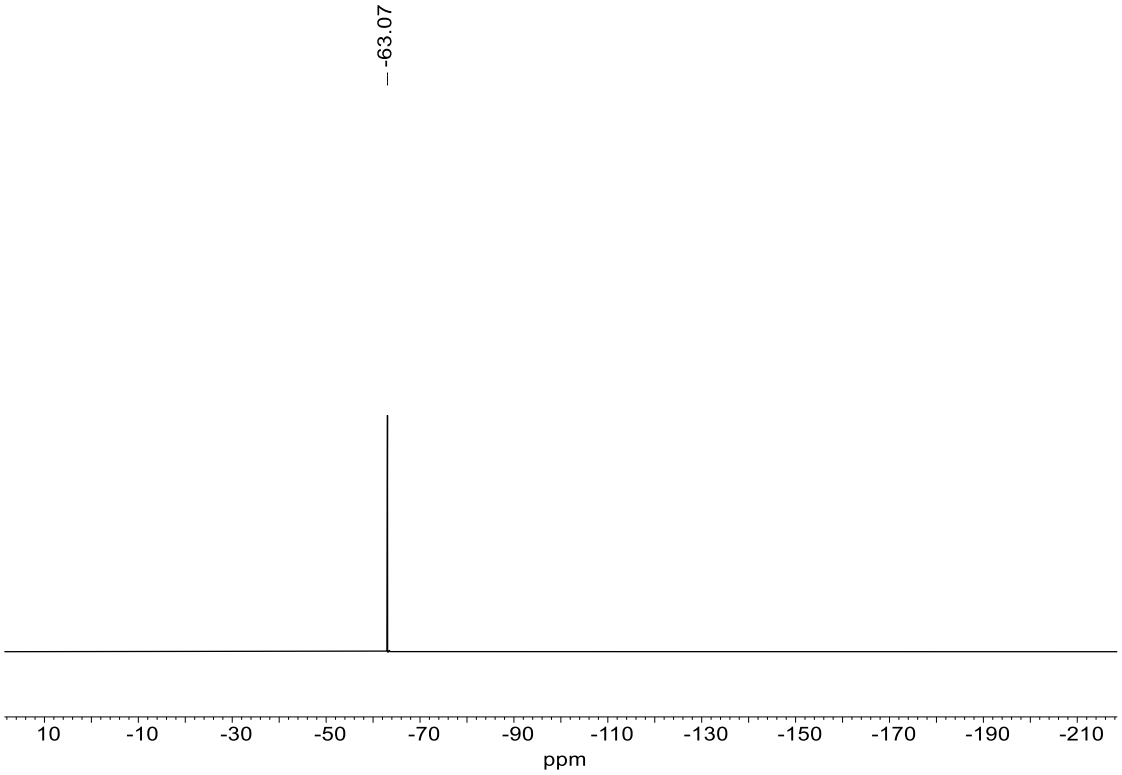


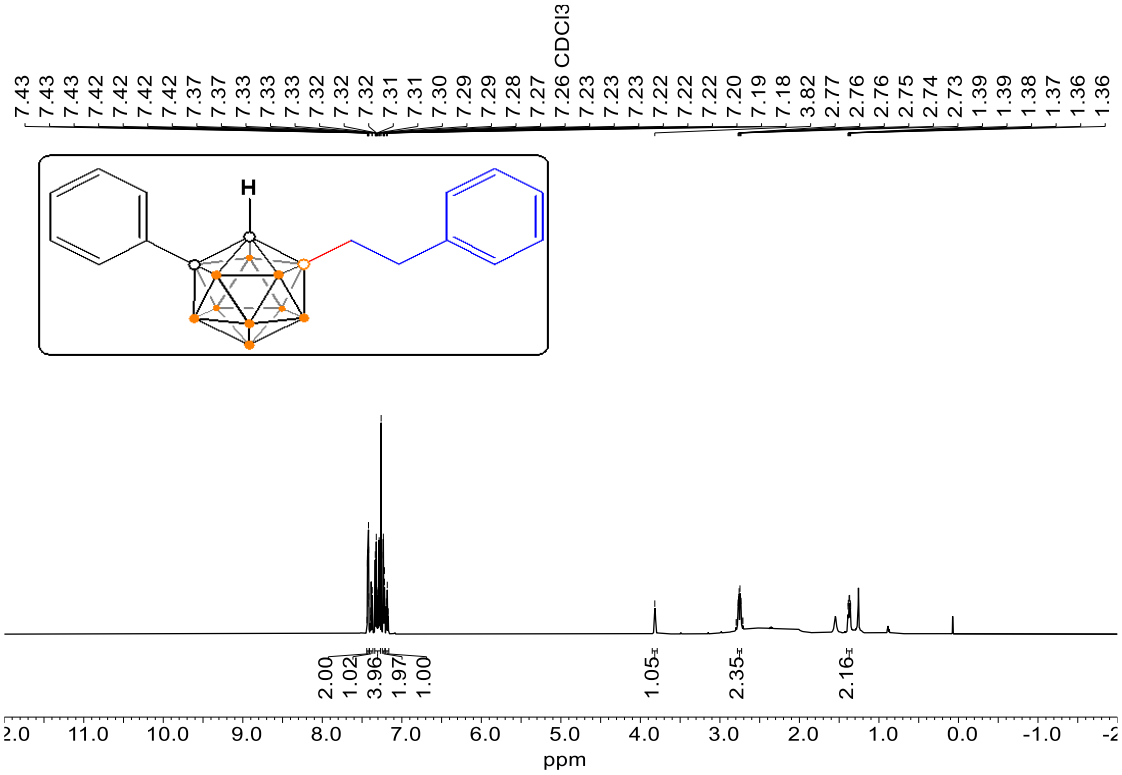
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



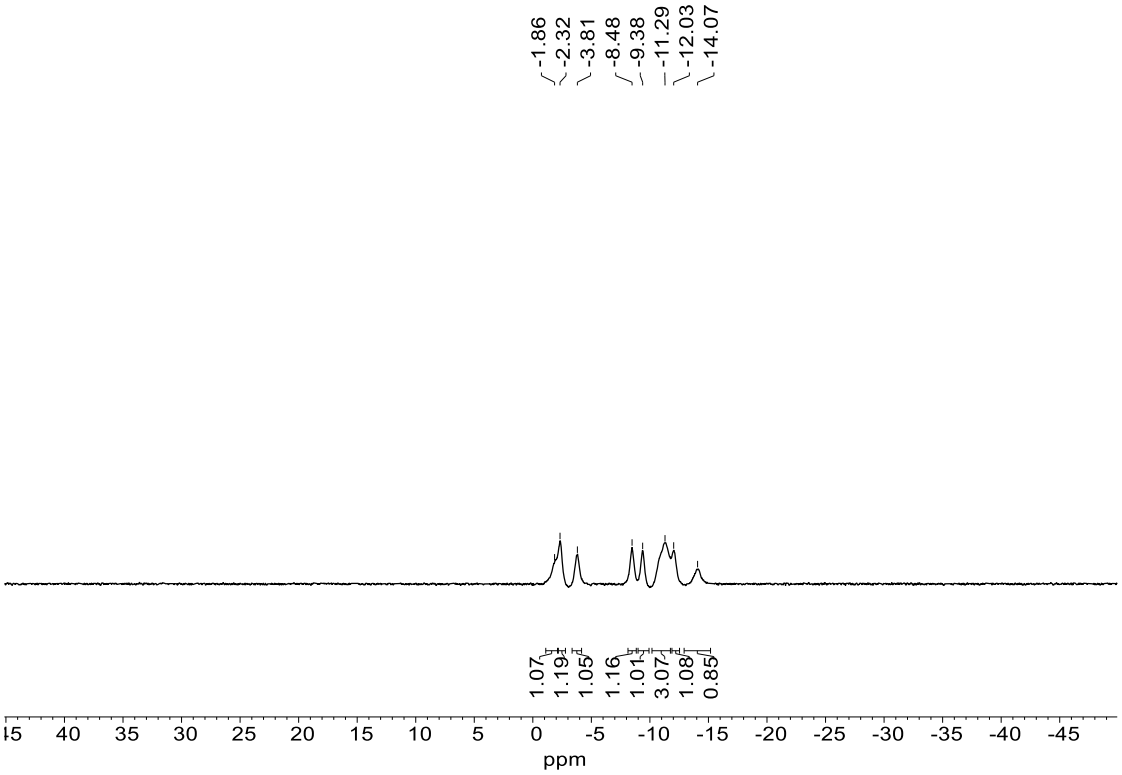
^{19}F NMR (565 MHz, Chloroform-*d*)



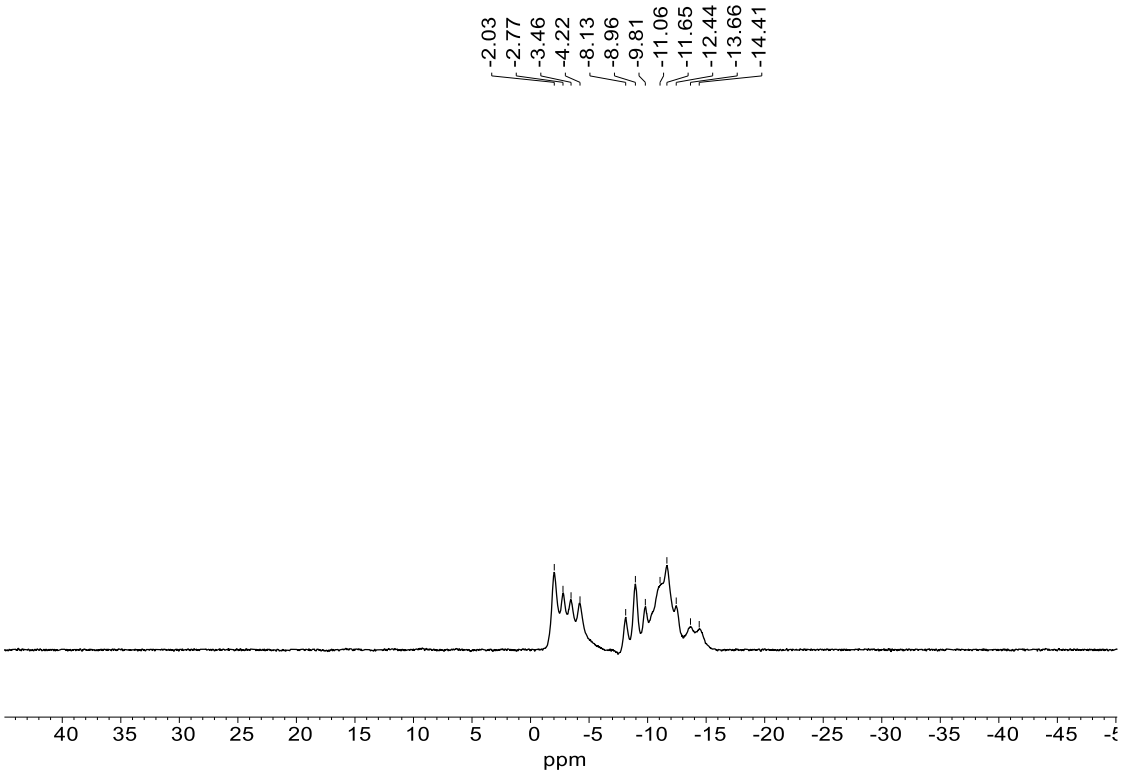
^{1}H NMR (600 MHz, Chloroform-*d*)



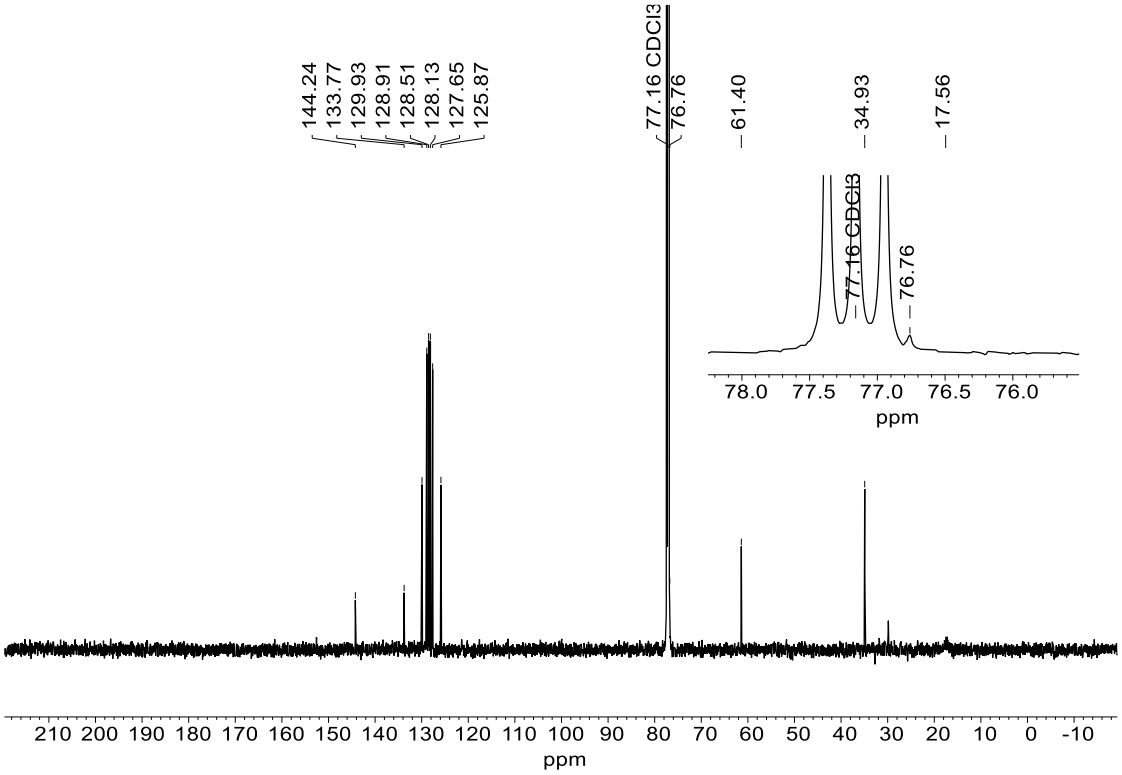
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



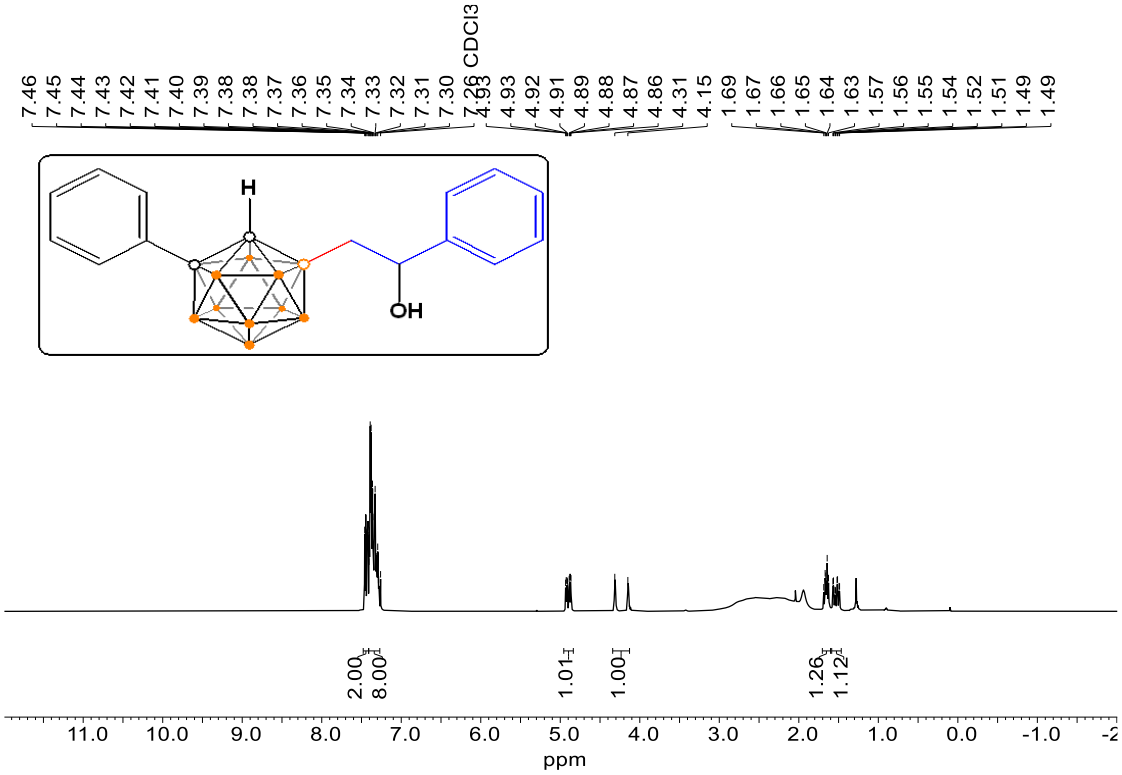
^{11}B NMR (193 MHz, Chloroform-*d*)



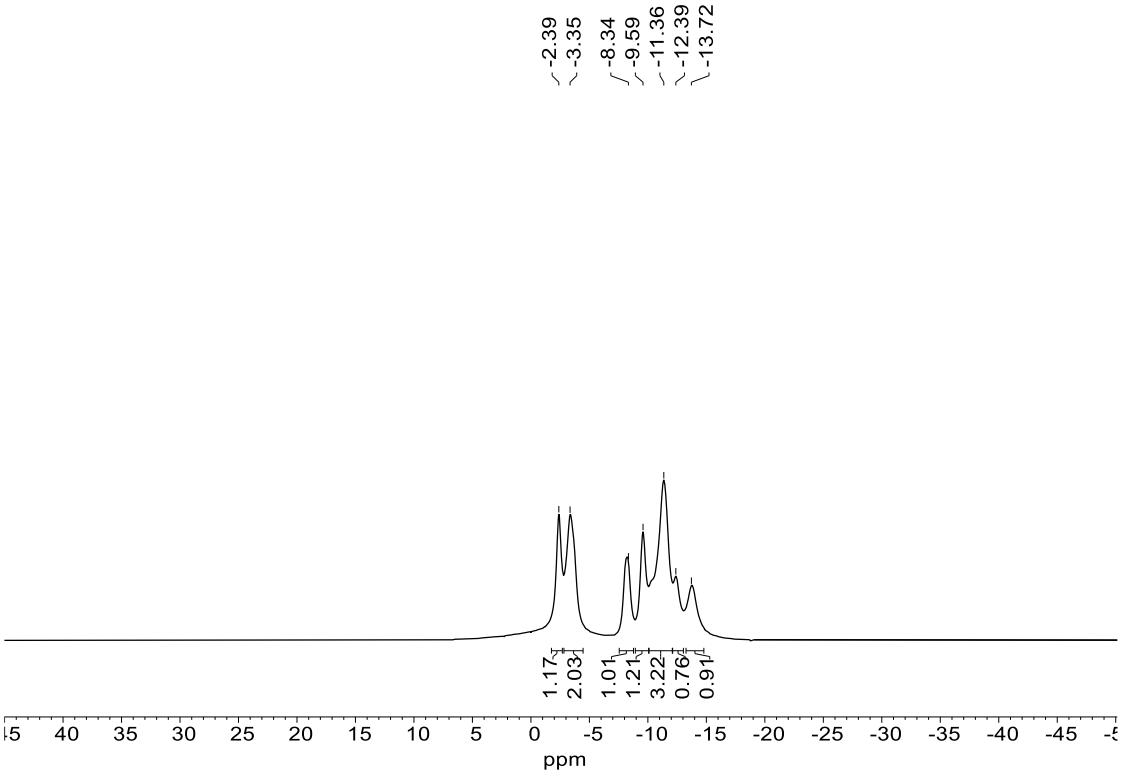
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



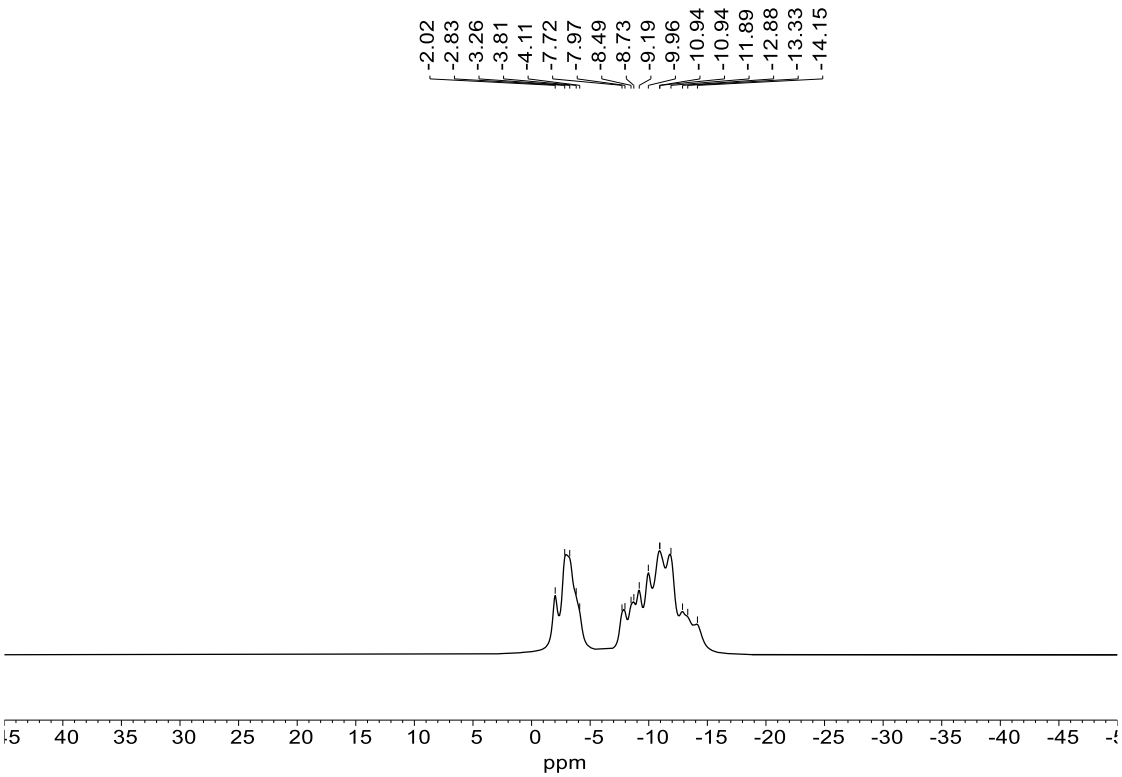
^{1}H NMR (600 MHz, Chloroform-*d*)



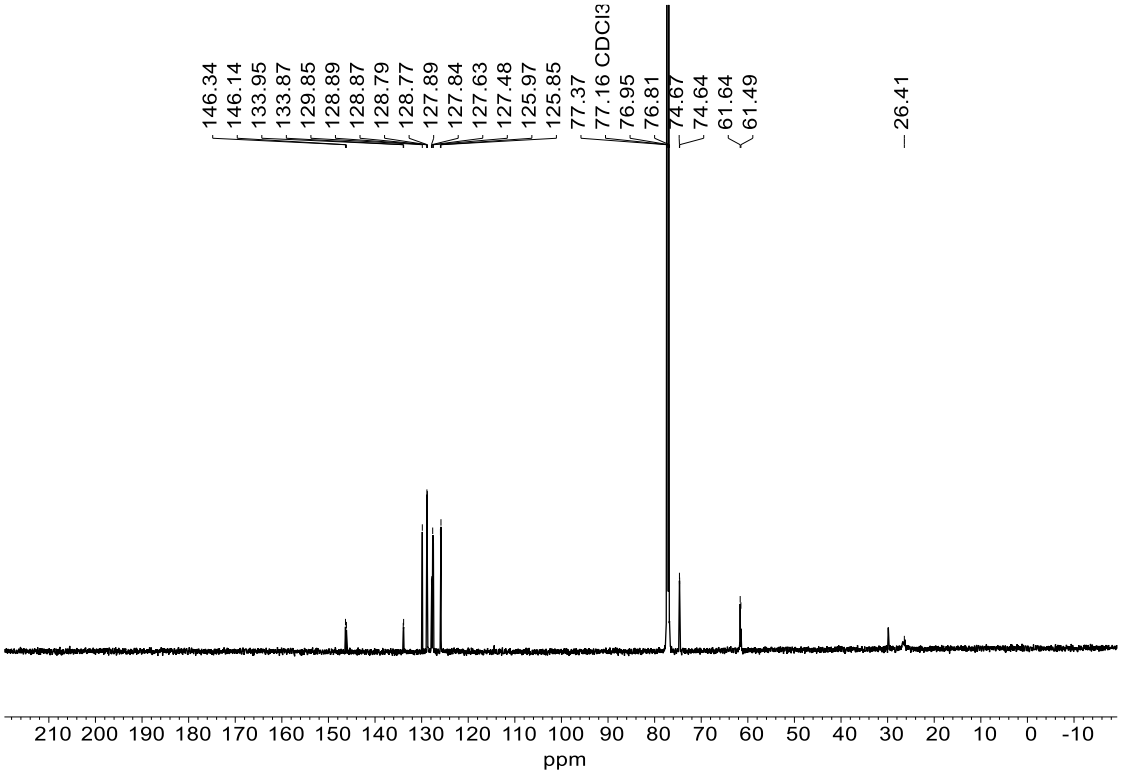
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



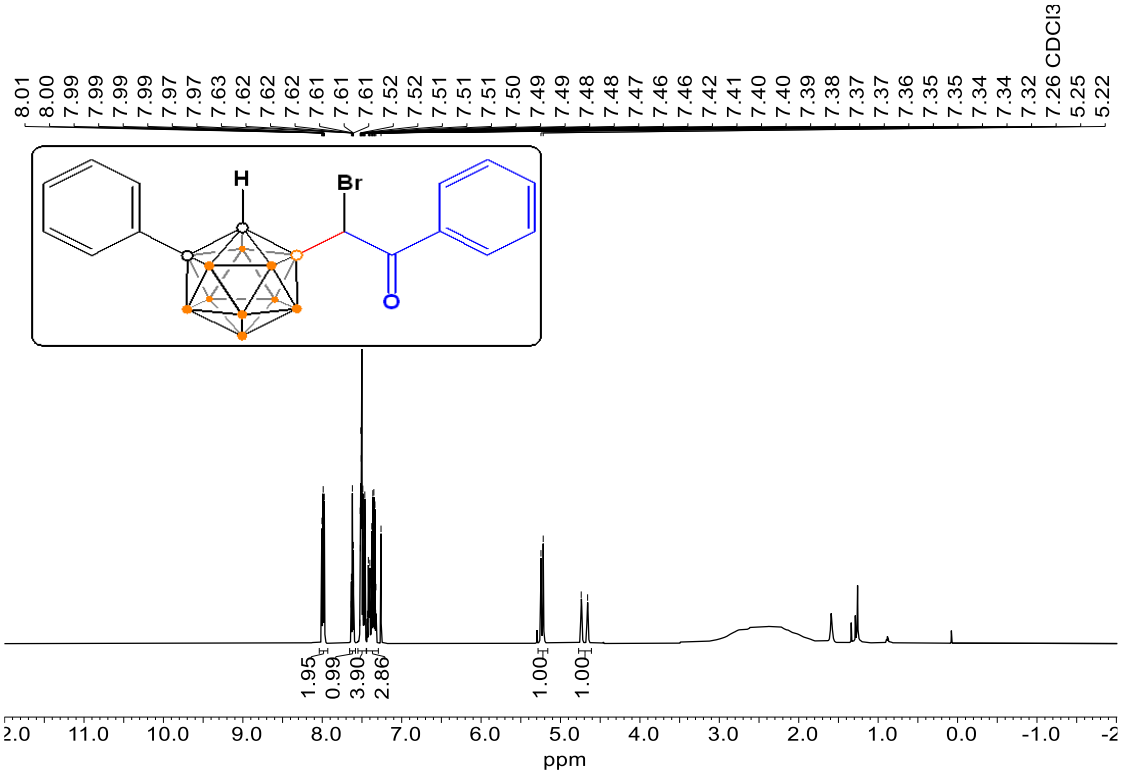
^{11}B NMR (193 MHz, Chloroform-*d*)



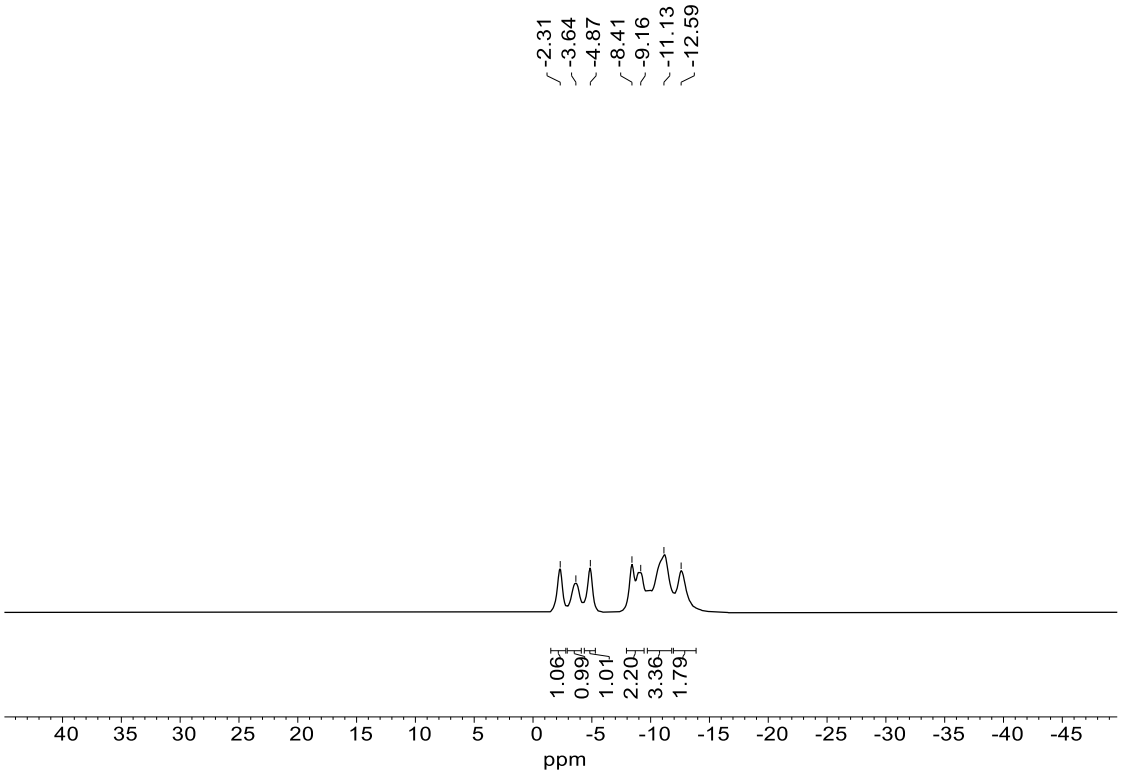
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



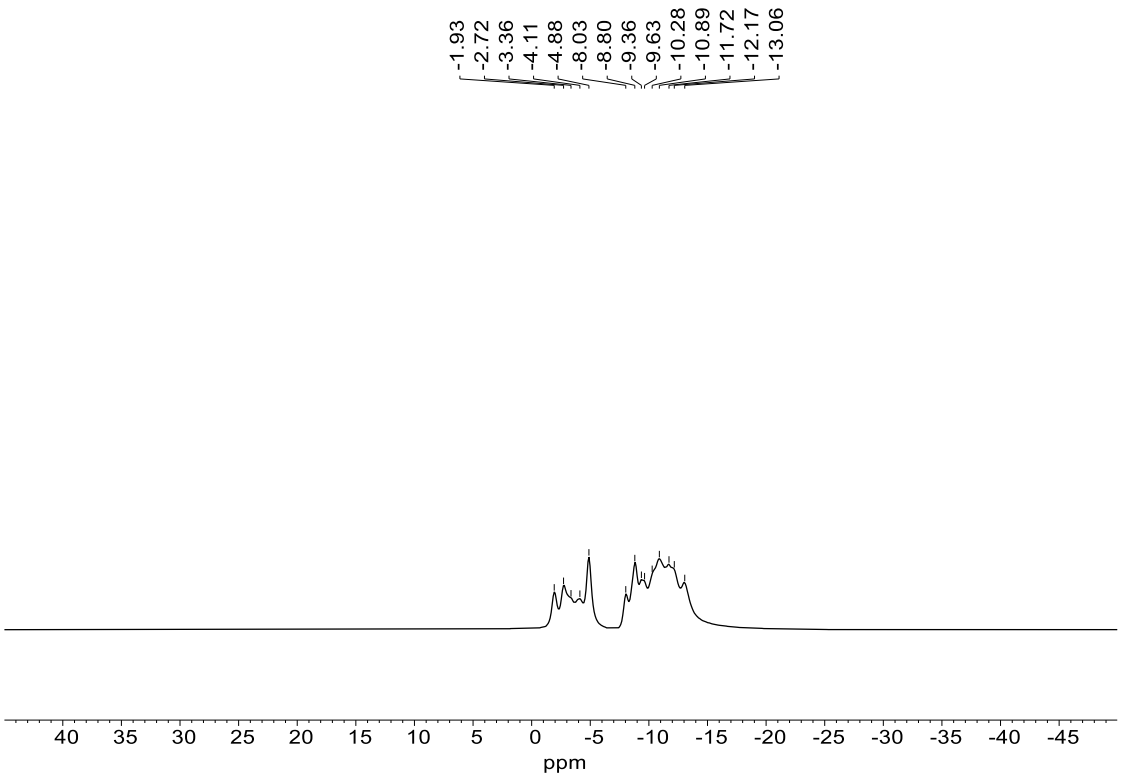
^{1}H NMR (600 MHz, Chloroform-*d*)



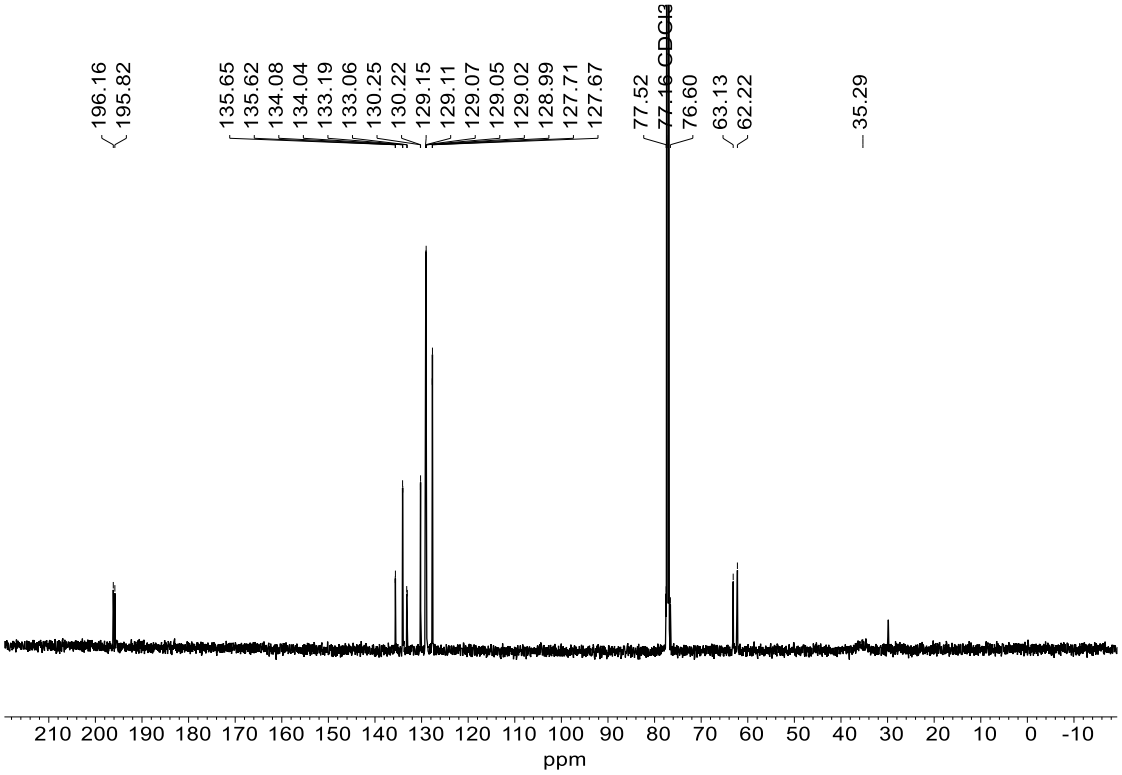
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



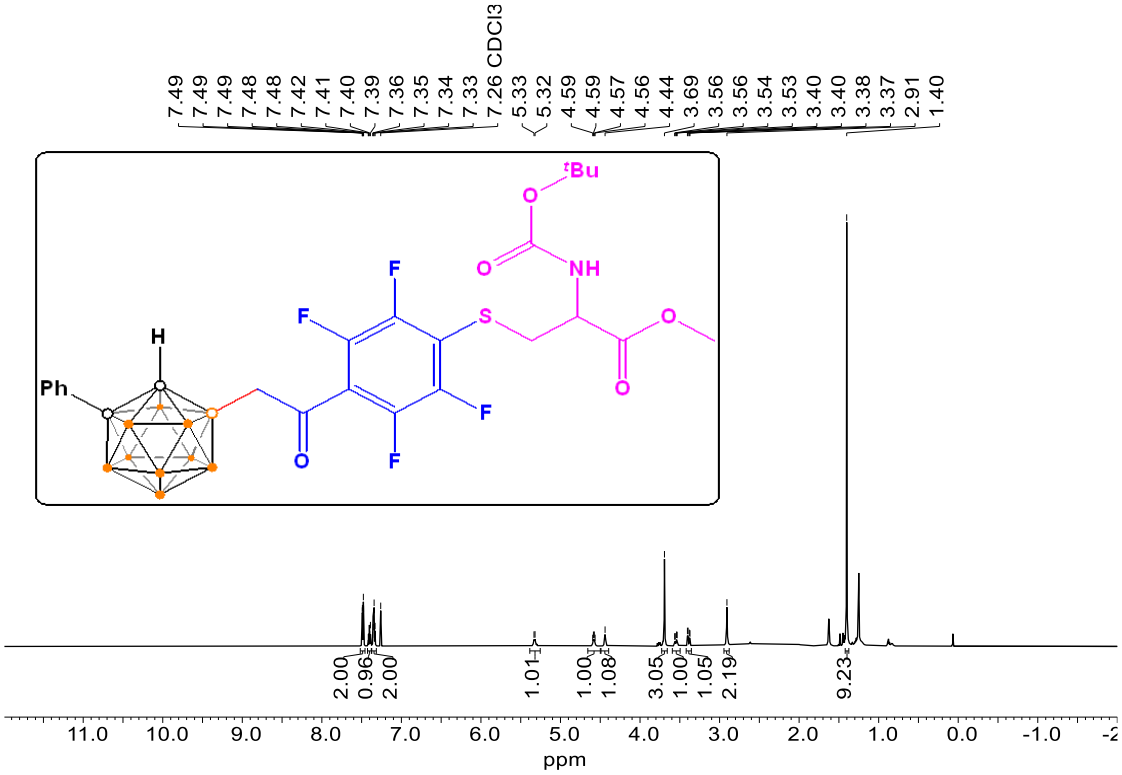
^{11}B NMR (193 MHz, Chloroform-*d*)



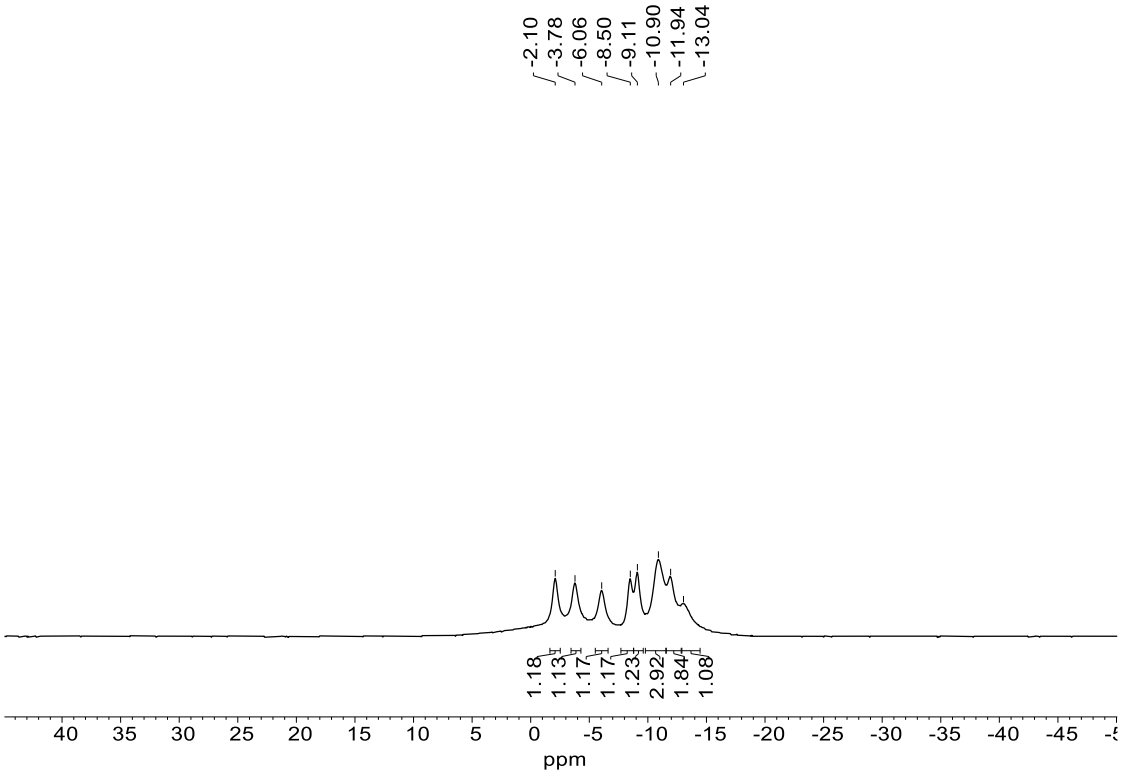
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



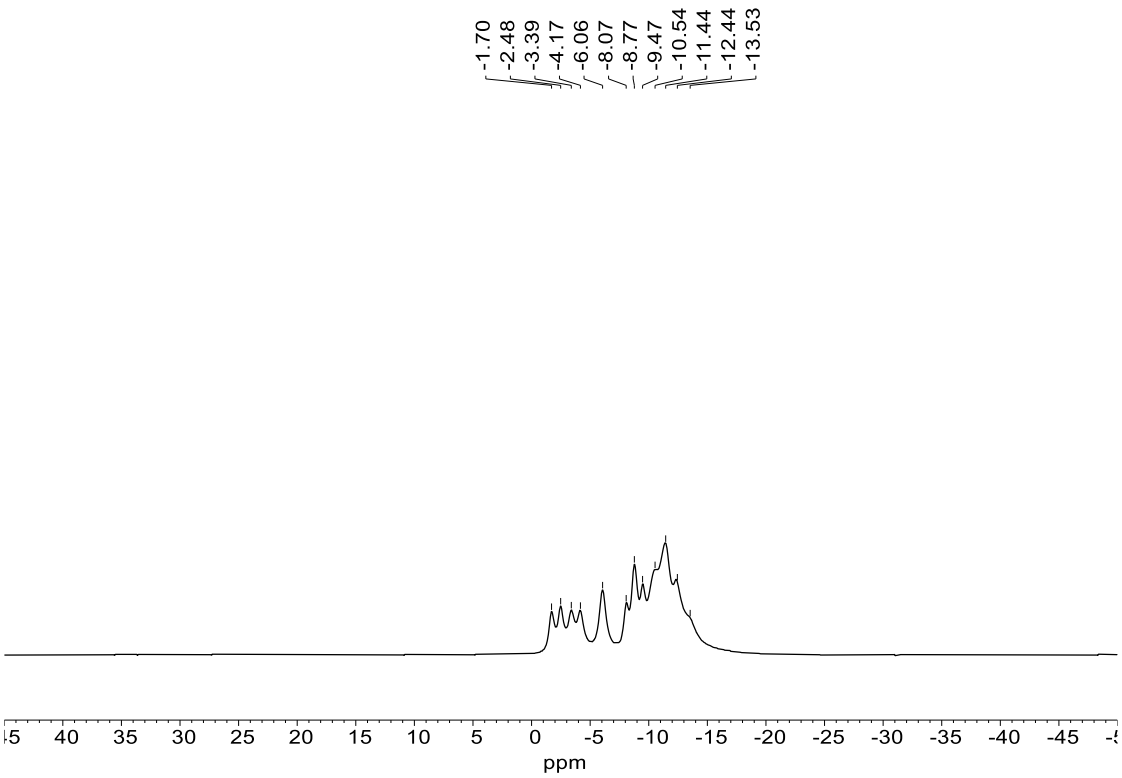
^{1}H NMR (600 MHz, Chloroform-*d*)



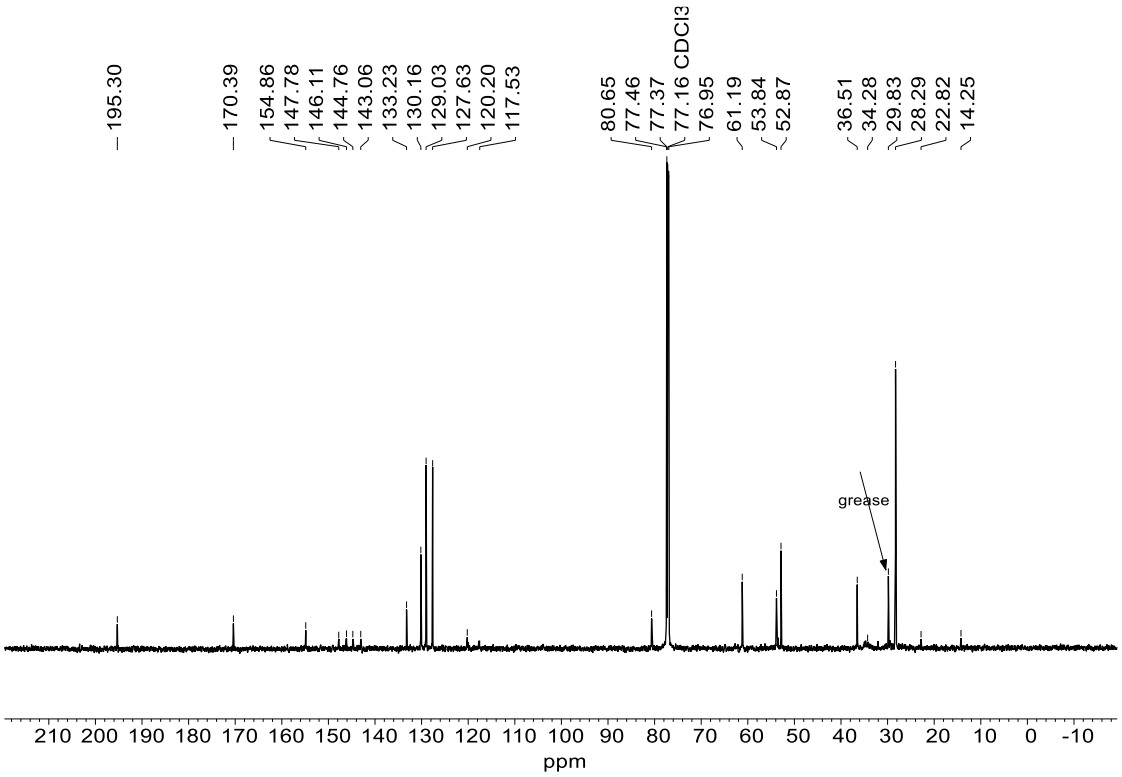
$^{11}B\{^{1}H\}$ NMR (193 MHz, Chloroform-*d*)



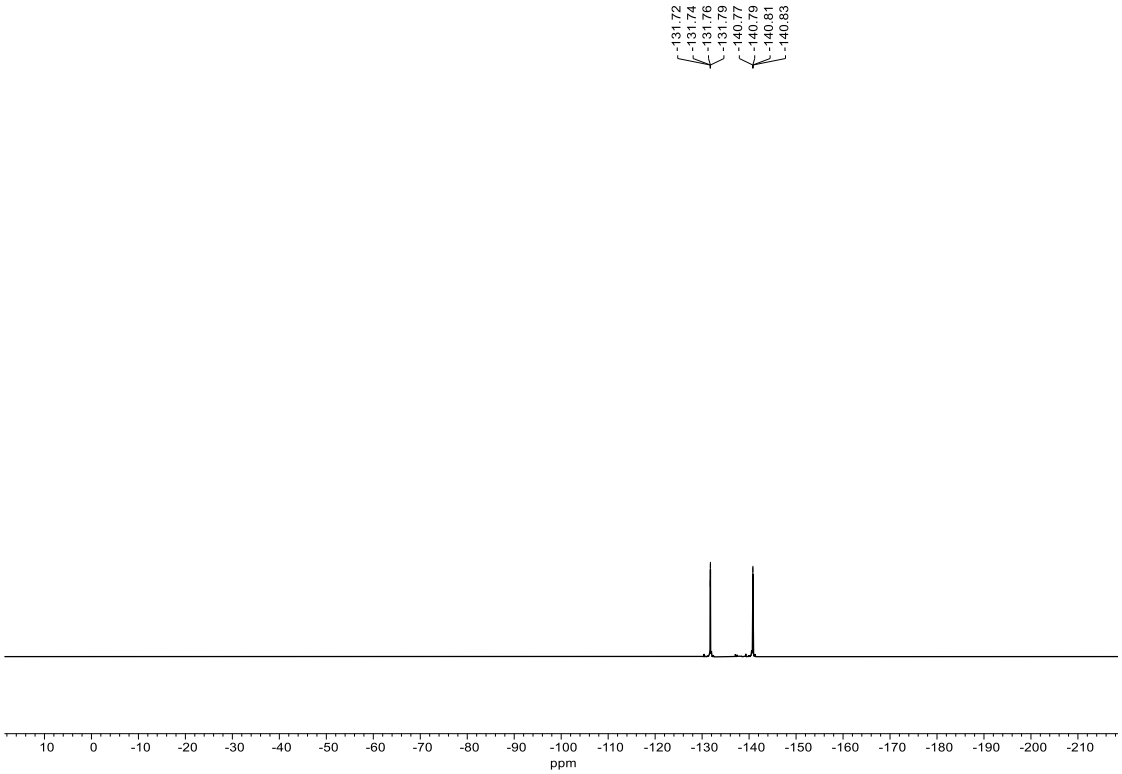
^{11}B NMR (193 MHz, Chloroform-*d*)



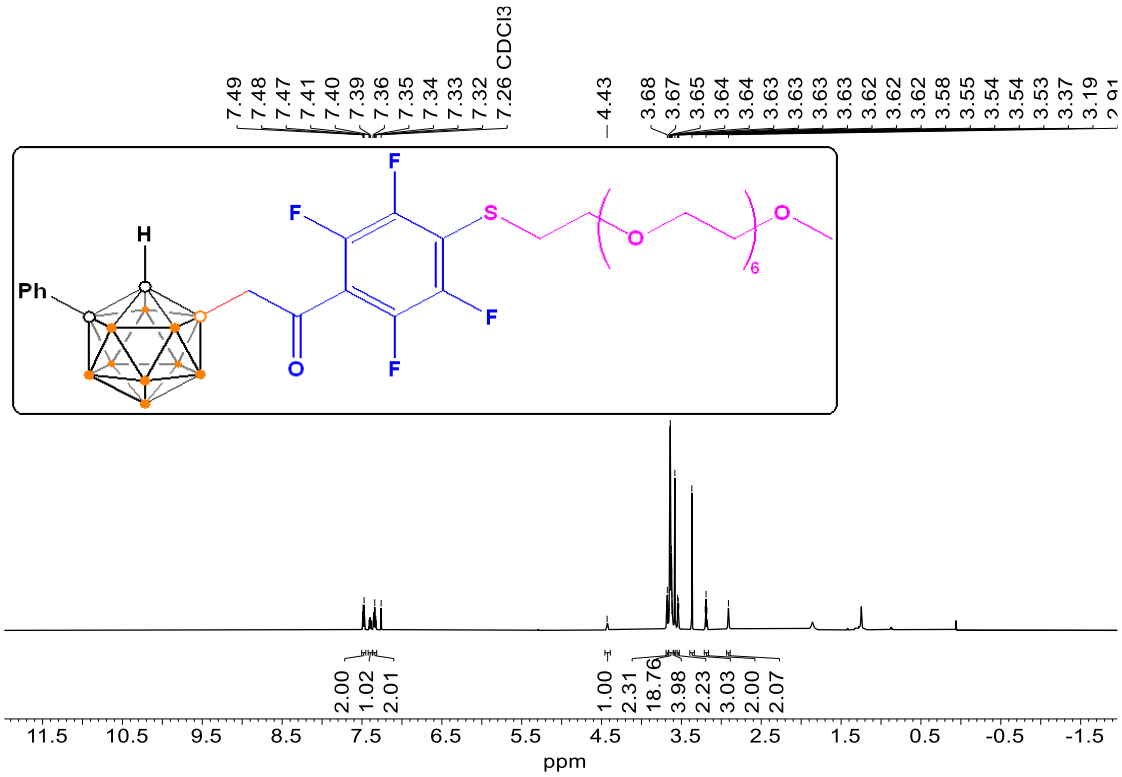
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*)



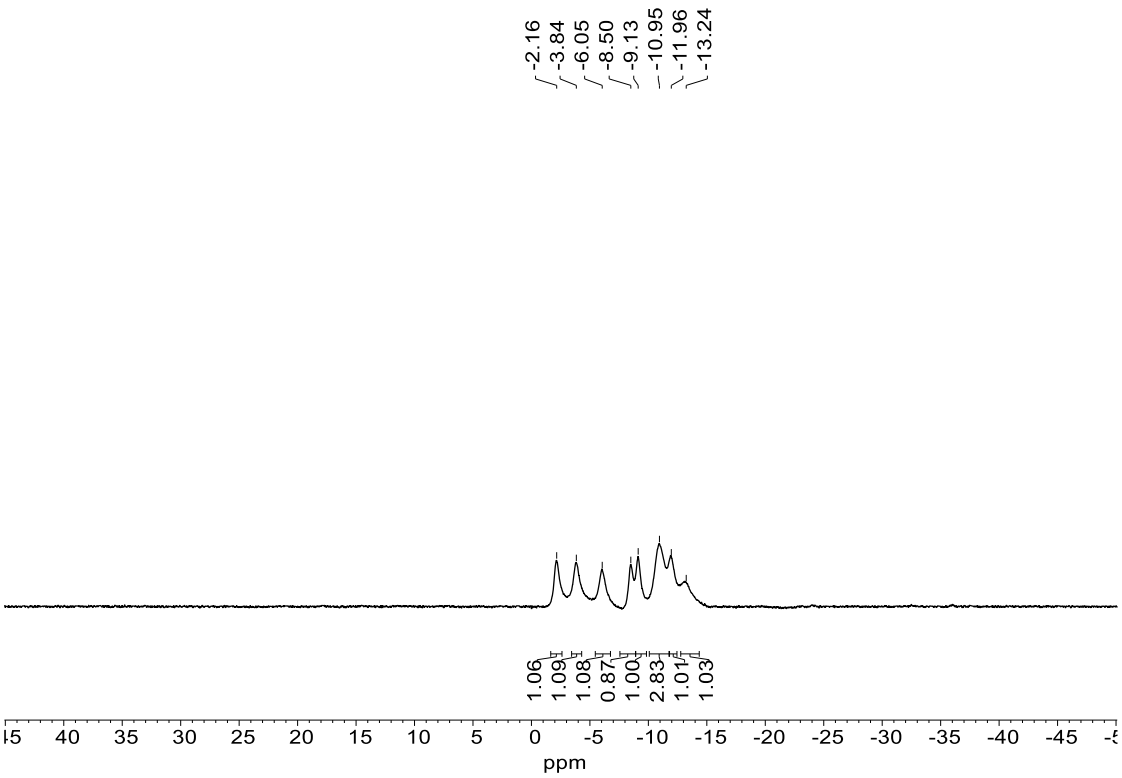
^{10}F NMR (600 MHz, Chloroform-*d*)



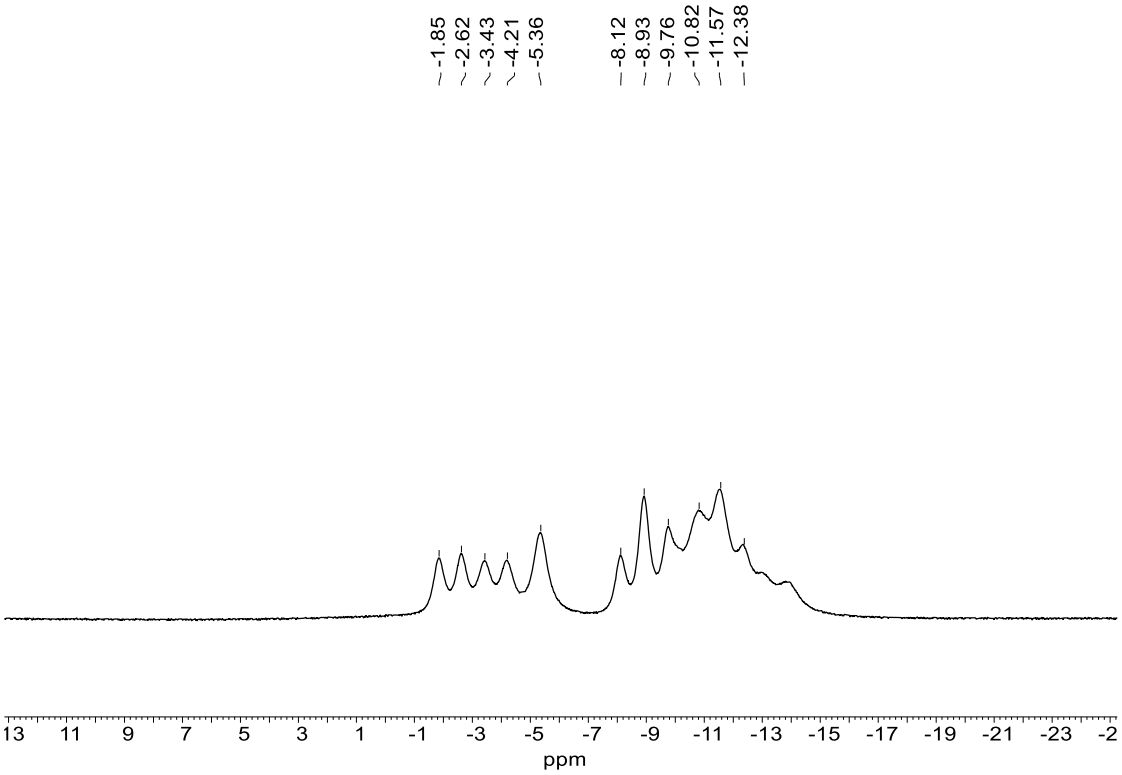
^{1}H NMR (600 MHz, Chloroform-*d*)



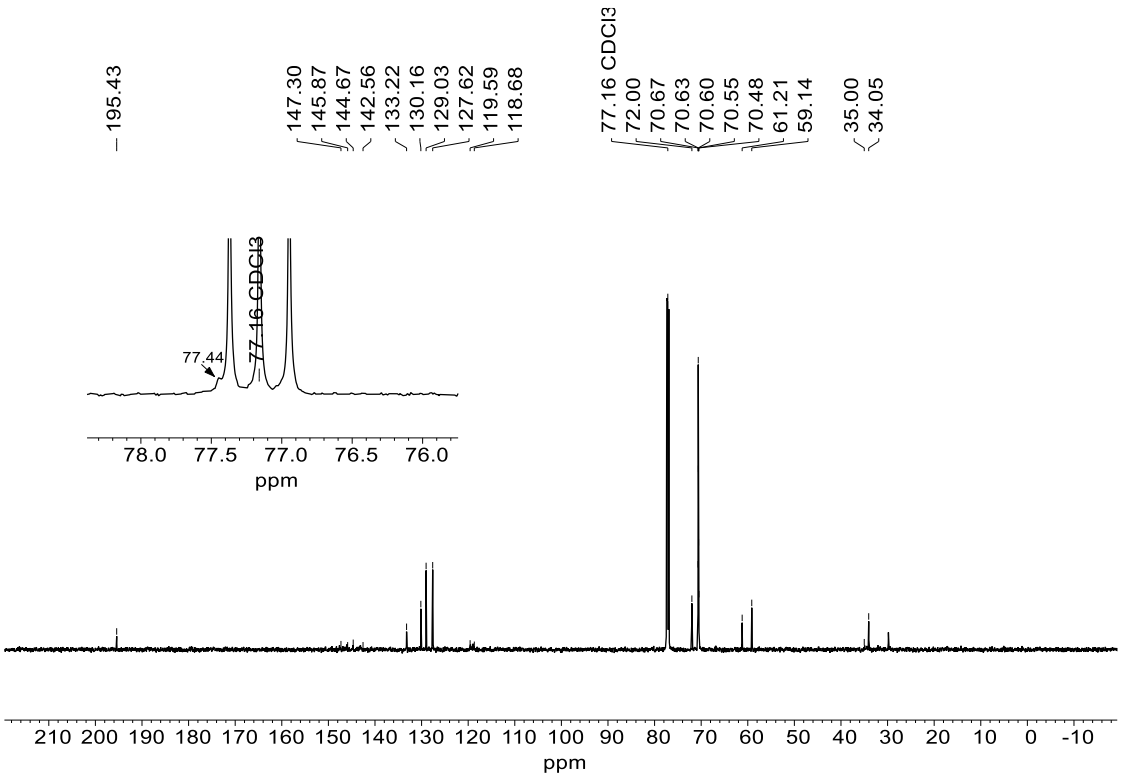
^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



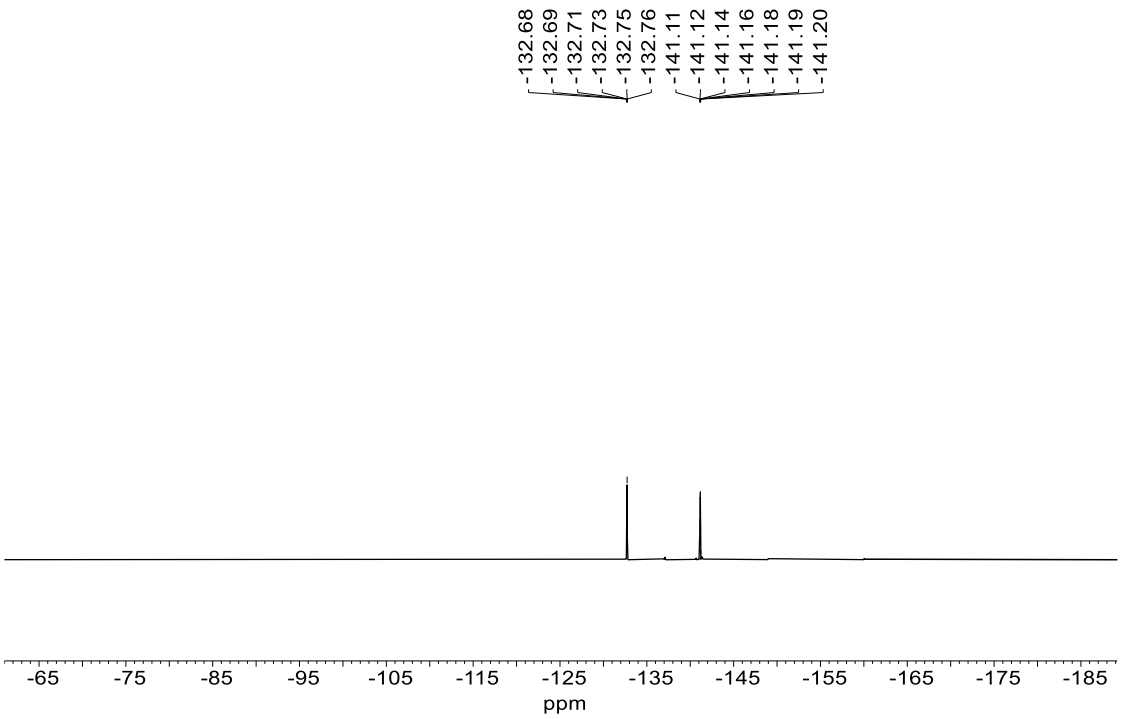
^{11}B NMR (193 MHz, Chloroform-*d*)



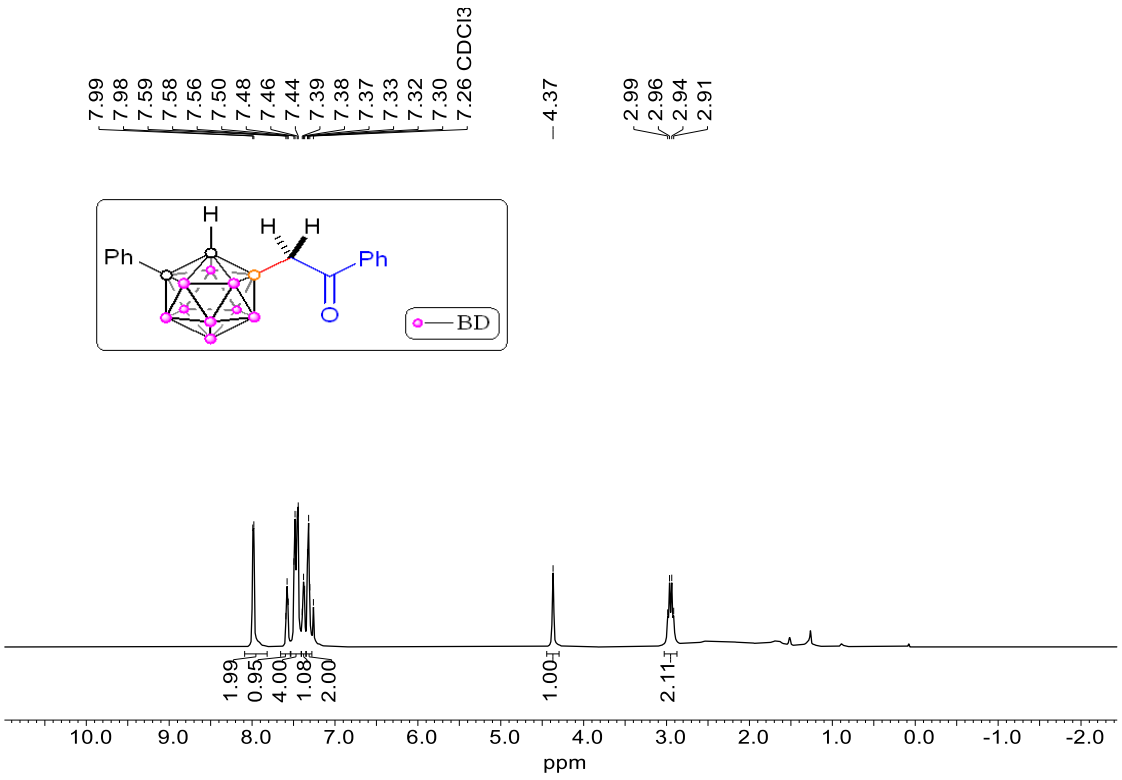
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)



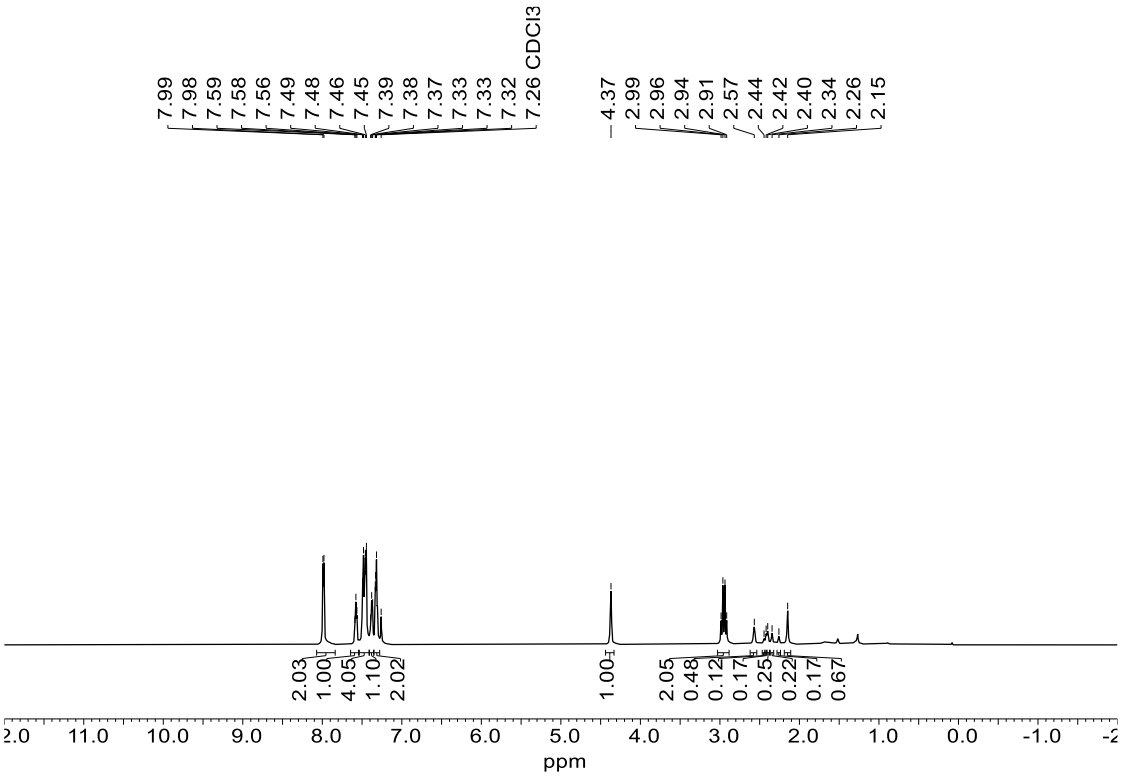
^{10}F NMR (600 MHz, Chloroform-*d*)



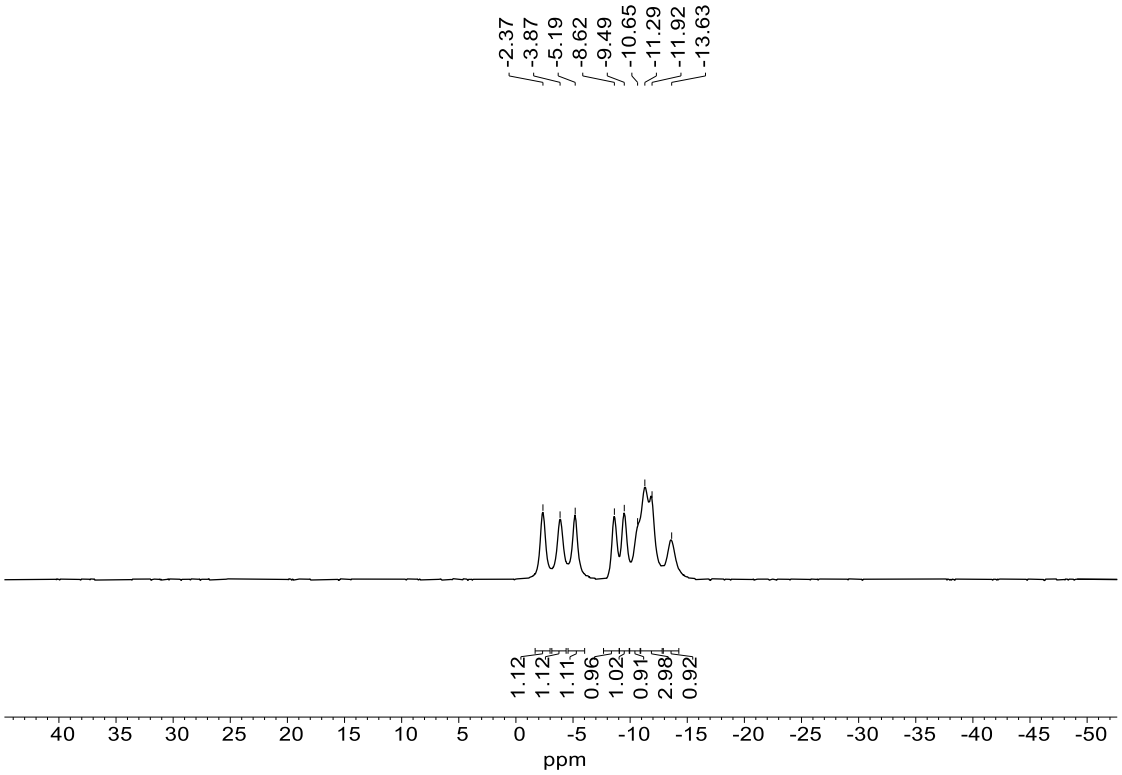
^{1}H NMR (600 MHz, Chloroform-*d*)



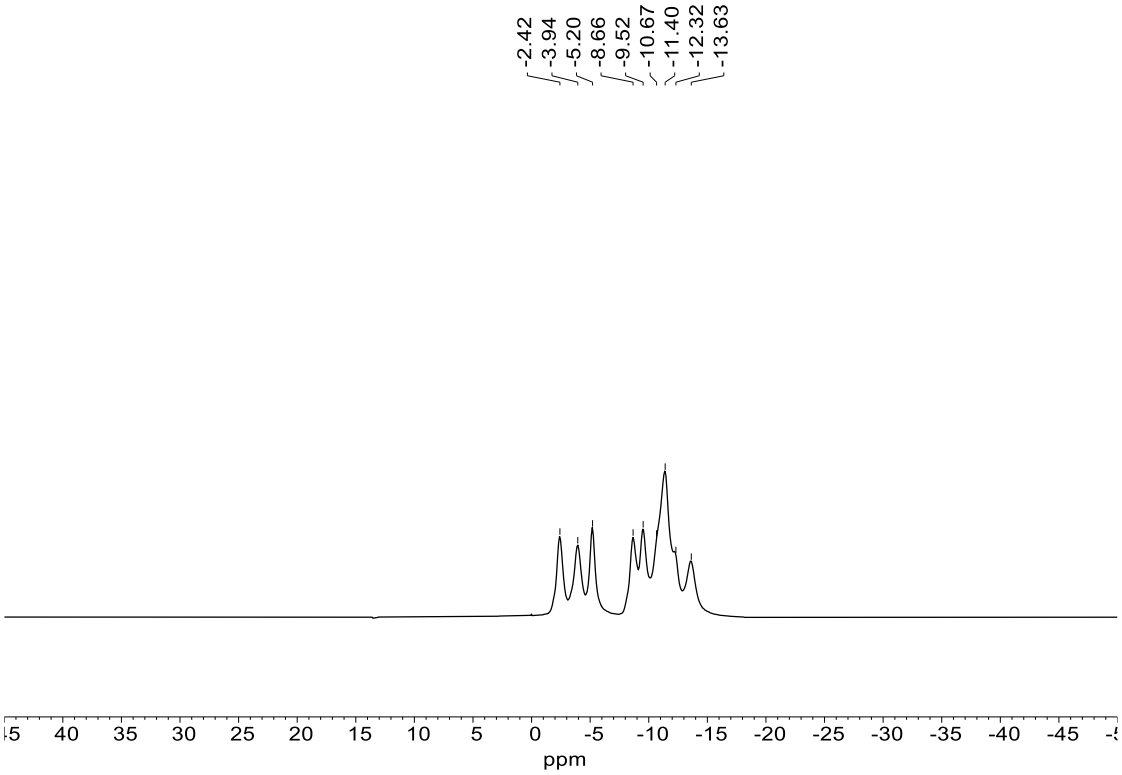
^{1}H {^{11}B} NMR (600 MHz, Chloroform-d)



^{11}B{^{1}H} NMR (193 MHz, Chloroform-*d*)



^{11}B NMR (193 MHz, Chloroform-*d*)



^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*)