Supporting Information

Variable Metal Chelation Modes and Activation Sequence in Pd-Catalyzed B−H Poly-arylation of Carboranes

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1. General Considerations

Carboranyl aldehydes **1a-c**[S1] were synthesized according to literature methods. Unless otherwise noted, all the solvents and commercially available reagents were purchased from commercial sources and used directly. Hexanes, THF and Et_2O were refluxed and distilled over sodium/benzophenone under nitrogen. CH_2Cl_2 and toluene were refluxed and distilled over GaH_2 under nitrogen. Glass-backed Silica Gel 60 thin-layer chromatography (TLC) plates were used as received. Column chromatography was performed on Silica Gel 60 (200–300 or 300–400 Mesh). TLC samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6 M HCl and were developed with heating using a heat gun. Melting points (m. p.) were measured on an X-4 digital melting-point apparatus. Elemental analyses were performed on a Perkin-Elmer 240 analyzer.

Spectroscopic Measurements. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers in ambient conditions unless otherwise stated. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. Note that H_2O resonances are often present due to high humidity. ^{11}B chemical shifts were measured utilizing external $BF_3 \cdot Et_2O$ ($\delta^{11}B$ = 0.00 ppm) as reference. ^{19}F NMR spectra were referenced to fluorobenzene (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 Thermo Q Exactive Mass Spectrometer for ESI-MS. Fluorescence spectral measurements were carried out by using a Hitachi F-4600 fluorescence spectrophotometer. Electronic absorption spectra were recorded with Shimadzu UV-3600 spectrophotometers.

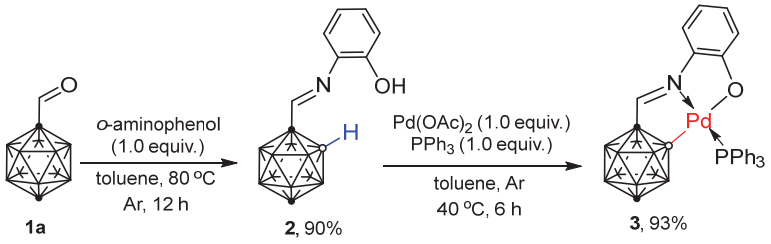
X-ray Crystallography. X-ray diffraction data of **3, 5, 6, 7'**, **8**, **9**, **11, 13a**, **13c**, **13k**, **15b**, **15d**, **16, 17, 18** and **25** (CCDC No. 2045712-2045723, 2056888, 2063807, 2112043, 2063808) were collected on a Bruker Apex-II CCD diffractometer or Bruker

D8 Quest diffractometer by means of graphitemonochromated Mo Kα radiation. During the collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption by using the SADABS program.[S2] The structures were solved by intrinsic phasing or direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL or Olex2 crystallographic software package.[S3] All non-hydrogen atom positions were determined utilizing the difference Fourier synthesis. The hydrogen atoms were placed at geometrically calculated positions, which were refined using a riding model. All calculations were performed by applying the Bruker SMART program. X-ray data can be obtained from the Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures/.

2. Experimental Section

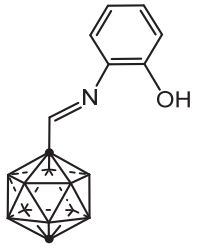
2.1 Mechanistic studies

2.1.1 Pd-mediated B−H activation of *p*-carboranyl aldehyde



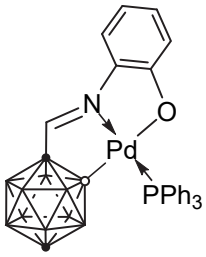
Scheme S1. Synthesis of bicyclic palladium complex **3**.

Procedure for the preparation of *p*-carboranyl imine 2: A reaction tube (50 mL) with a magnetic stir bar was charged with *p*-carboranyl aldehyde **1a** (3.0 mmol, 516.0 mg), *o*-aminophenol (1.0 equiv., 3.0 mmol, 328.0 mg) and toluene (30.0 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 100 °C for 12 hours to form a yellow solution. The reaction mixture was cooled to room temperature and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (gradient of petroleum ether/ethyl acetate = 40/1) to afford **2**, 742 mg.



2: Yield 90%. Light yellow solid. m. p. 143.5 – 143.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H, C**H**=N), 7.19 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 6.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.80 (ddd, *J* = 7.9, 7.3, 1.3 Hz, 1H) (phenyl−**H**), 2.84 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −13.2 (5B), −14.8 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6 (**C**H=N), 151.9, 132.5, 130.5, 120.0, 115.8, 115.6 (phenyl−**C**), 61.4 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_9B_{10}NOH_{16}$ $[M-H]^-$: 262.2241. Found: 262.2241. Elemental analysis (%) calcd for $C_9B_{10}NOH_{17}$: C, 41.05; H, 6.51; N, 5.32. Found: C, 41.25; H, 6.41; N, 5.46.

Synthesis of *p*-carboranyl imine bicyclic palladium complex 3: A reaction tube (10 mL) with a magnetic stir bar was charged with **2** (0.2 mmol, 53 .0mg), $Pd(OAc)_2$ (1.0 equiv., 0.2 mmol, 45.0 mg), PPh_3 (1.0 equiv. 0.2 mmol, 52.0 mg) and toluene (2.0 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 40 ºC for 6 hours. The reaction solution turned from yellow to red. The red reaction mixture was concentrated in *vacuo* and purified by flash chromatography using CH_2Cl_2 as the eluent to obtain **3**.



3: Yield 93%. Yellow solid. m. p. 250.3 – 250.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 − 7.78 (m, 6H), 7.47 − 7.39 (m, 9H) (PPh_3−**H**), 7.34 (d, J = 7.4 Hz, 1H, C**H**=N), 7.02 (ddd, *J* = 8.5, 6.9, 1.6 Hz, 1H), 6.91 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.69 (dd, *J* = 8.5, 1.3 Hz,

1H), 6.28 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H) (N−**Ph**−O), 2.30 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −8.3 (3B), −15.3 (7B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1 (d, J = 2.2 Hz, **C**H=N), 150.3 (d, J = 3.6 Hz), 135.0 (d, J = 12.7 Hz), 133.7, 132.8, 132.2, 131.7, 130.7 (d, J = 2.5 Hz), 128.4 (d, J = 10.9 Hz), 123.5, 116.2 (d, J = 2.3 Hz), 113.0 (phenyl−**C**), 93.0, 61.0 (cage−**C**); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.5. HRMS (ESI, positive mode): *m/z* calcd for $C_{27}B_{10}NOPdPH_{31}$ $[M+H]^+$: 630.2176. Found: 630.2177. Elemental analysis (%) calcd for $C_{27}B_{10}NOPdPH_{30}$: C, 51.47; H, 4.80; N, 2.22. Found: C, 51.32; H, 4.94; N, 2.17.

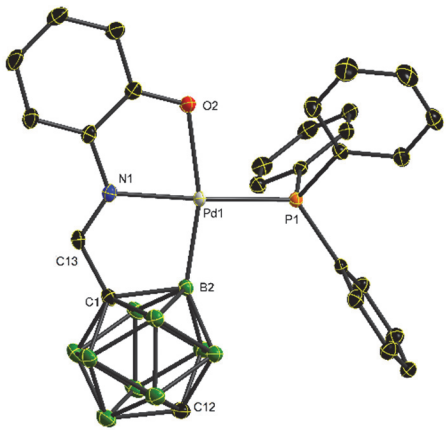
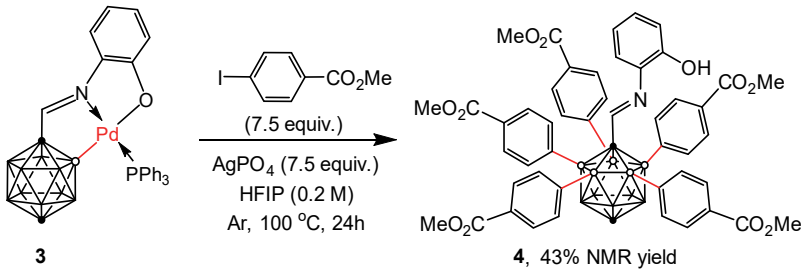


Figure S1. X-Ray structure of **3** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å] and angels [°]: C1−C13 1.480(3), C13−N1 1.276(3), C1−B2 1.771(3), N1−Pd1 2.0723(17), O2−Pd1 2.1448(14), B2−Pd1 2.030(2), P1−Pd1 2.2492(5), ∠O2−Pd1−B2 163.95(8), ∠N1−Pd1−P1 175.01(5).

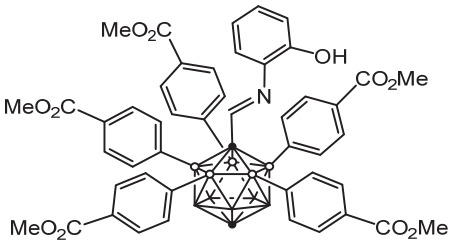
2.1.2 Subsequent penta-arylation of 3 with 4-iodobenzoate



Scheme S2. Arylation of **3** to afford **4**.

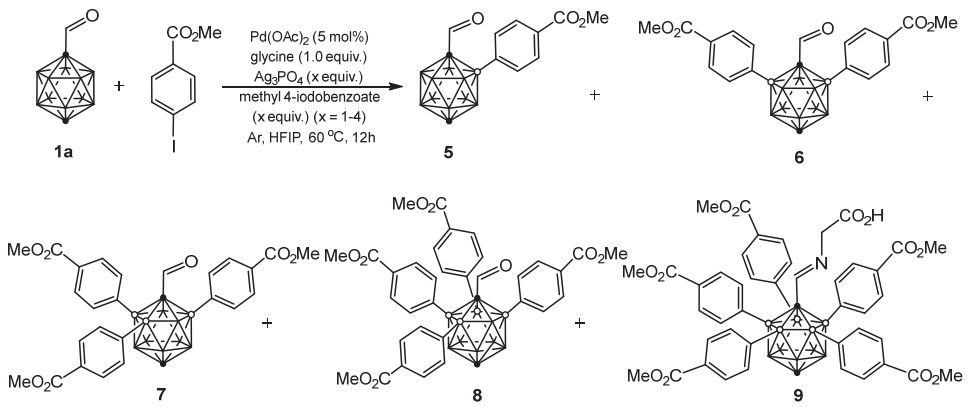
Subsequent Arylation of bicyclic palladium complex 3: A reaction tube (10 mL) with

a magnetic stir bar was charged with **3** (0.1 mmol, 63.0 mg), methyl 4-iodobenzoate (7.5 equiv., 0.75 mmol, 196.5 mg), Ag_3PO_4 (7.5 equiv., 0.75 mmol, 314.0 mg), and HFIP (0.5 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 100 ºC for 24 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2. The organic phase was quenched with CH_2Cl_2 and concentrated in *vacuo*. The crude reaction mixture was purified by PTLC using petroleum ether/ethyl acetate (3/1) as the eluent to obtain **4**.



4: Yield 39%. White solid. m. p. 302.6 – 302.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H, C**H**=N), 7.71 (d, *J* = 8.4 Hz, 10H), 7.18 (ddd, *J* = 8.4, 7.3, 1.5 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 10H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.77 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 6.65 (dd, *J* = 8.1, 1.5 Hz, 1H) (phenyl−**H**), 5.50 (s, 1H, O**H**), 3.87 (s, 15H, C**H**$_3$), 3.59 (s, 1H, cage−C**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.9 (5B), −15.6 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9 (**C**=O), 153.1 (**C**H=N), 148.7, 135.4, 132.6, 131.5, 130.5, 128.7, 120.9, 116.7, 115.4 (phenyl−**C**), 81.2, 60.4 (cage−**C**), 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{49}B_{10}NO_{11}H_{47}$ $[M+H]^+$: 933.4152. Found: 933.4143. Elemental analysis (%) calcd for $C_{49}B_{10}NO_{11}H_{46}$: C, 63.08; H, 4.97; N, 1.50. Found: C, 63.27; H, 5.22; N, 1.38.

2.1.3 Stoichiometric control on the reaction of *p*-carboranyl aldehyde with methyl 4-iosobenzoate

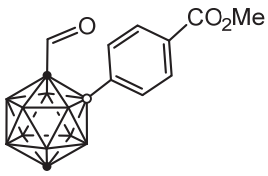


Scheme S3. Reaction of *p*-carboranyl aldehyde (**1a**) and methyl 4-iodobenzoate.

Table S1. Reaction of *p*-carboranyl aldehyde (**1a**) and methyl 4-iodobenzoate.[a]

entry	x	Yield[b]				
		5 (%)	**6** (%)	**7** (%)	**8** (%)	**9** (%)
1	1	33	16	3	0	0
2	2	17	51	26	1	0
3	3	1	21	38	3	10
4	4	0	22	35	4	17

[a] Reaction procedure: A reaction tube (10 mL) with a magnetic stir bar was charged with *p*-carboranyl aldehyde **1a** (0.1 mmol, 17 mg), methyl 4-iodobenzoate (x equiv., x = 1 to 4), $Pd(OAc)_2$ (5 mol%), glycine (1.0 equiv.), Ag_3PO_4 (x equiv., x = 1 to 4) and HFIP (0.5 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 60 ºC for 12 hours. The reaction mixture was cooled to room temperature and concentrated in *vacuo*. The crude reaction mixture was purified by preparative TLC (PTLC) using petroleum ether/ethyl acetate (5/1) as the eluent to obtain **5**-**9**. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.



5: White solid. m. p. 103.1 – 103.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (s, 1H, C**H**O), 7.96 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H) (phenyl−**H**), 3.91 (s, 3H,

OC**H**$_3$), 3.11 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −3.6 (2B), −13.8 (5B), −15.3 (2B), −16.4 (1B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.7 (**C**HO), 167.1 (**C**=O), 135.0, 130.9, 129.0 (phenyl−**C**), 86.0, 64.9 (cage−**C**), 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{11}B_{10}O_3H_{17}$ $[M-H]^-$: 305.2186. Found: 305.2189. Elemental analysis (%) calcd for $C_{11}B_{10}O_3H_{18}$: C, 43.13; H, 5.92. Found: C, 43.08; H, 5.76.

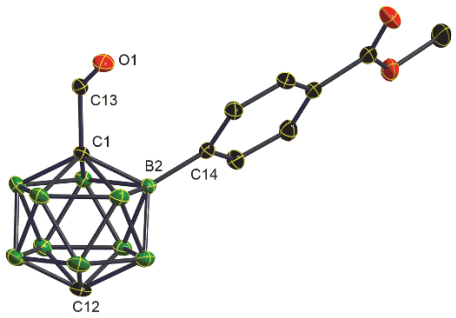
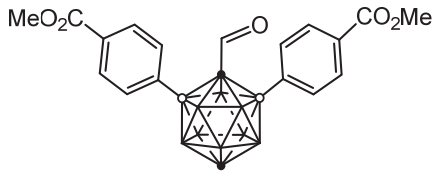


Figure S2. X-Ray structure of **5** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.512(2), C13−O1 1.183(2), C1−B2 1.728(2), B2−C14 1.577(2).



6: White solid. m. p. 163.9 – 164.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (s, 1H, C**H**O), 7.96 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 7.9 Hz, 4H) (phenyl−**H**), 3.90 (s, 6H, O**C**H$_3$), 3.33 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −3.0 (3B), −13.4 (2B), −15.2 (2B), −16.2(3B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.5 (**C**HO), 167.0 (**C**=O), 135.0, 134.8, 130.9, 129.0, 128.8, 128.8 (phenyl−**C**), 87.4, 66.3 (cage−**C**), 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{19}B_{10}O_5H_{23}$ $[M-H]^-$: 439.2554. Found: 439.2560. Elemental analysis (%) calcd for $C_{19}B_{10}O_5H_{24}$: C, 51.81; H, 5.49. Found: C, 51.46; H, 5.61.

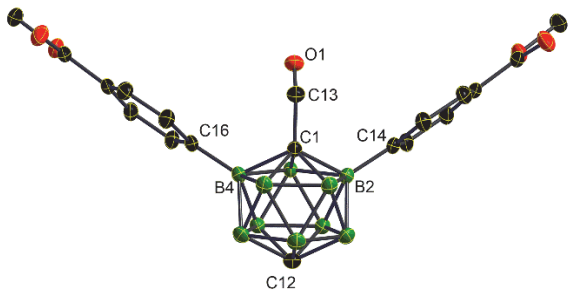
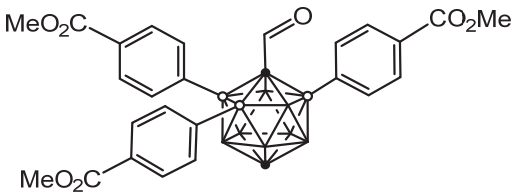
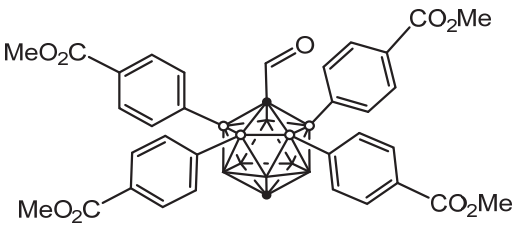


Figure S3. X-Ray structure of **6** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.510(9), C13−O1 1.174(8), C1−B2 1.745(5), C1−B4 1.745(5), B2−C14 1.568(6), B4−C16 1.568(6).



7: Colorless solid. m. p. 195.3 – 195.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (s, 1H, C**H**O), 7.97 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 4H) (phenyl−**H**), 3.91 (s, 3H), 3.89 (s, 6H) (OC**H**$_3$), 3.44 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −3.6 (5B), −12.4 (2B), −15.7 (3B); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.5 (**C**HO), 167.0, 167.0 (**C**=O), 135.3, 135.0, 131.1, 130.7, 129.1, 128.8 (phenyl−**C**), 86.7, 65.2 (cage−**C**), 52.3, 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{27}B_{10}O_7H_{29}$ $[M-H]^-$: 573.2922. Found: 573.2925. Elemental analysis (%) calcd for $C_{27}B_{10}O_7H_{30}$: C, 56.44; H, 5.26. Found: C, 56.05; H, 5.37.



8: White solid. m. p. 219.4 – 219.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.12 (s, 1H, C**H**O), 7.88 (d, *J* = 8.2 Hz, 4H), 7.68 (d, *J* = 8.3 Hz, 4H), 7.47 (d, *J* = 8.2 Hz, 4H), 7.00 (d, *J* = 8.3 Hz, 4H) (phenyl−**H**), 3.91 (s, 6H), 3.84 (s, 6H) (OC**H**$_3$), 3.48 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −3.1 (5B), −15.4 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.2 (**C**HO), 167.1, 166.8 (**C**=O), 135.5, 134.9, 130.9, 130.4, 128.8, 128.7 (phenyl−**C**), 84.9, 63.0 (cage−**C**), 52.4, 52.3. (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{35}B_{10}O_9H_{35}$ $[M-H]^-$: 707.3290. Found: 707.3294. Elemental analysis (%) calcd for $C_{35}B_{10}O_9H_{36}$: C, 59.31; H, 5.12. Found: C, 59.22; H, 4.97.

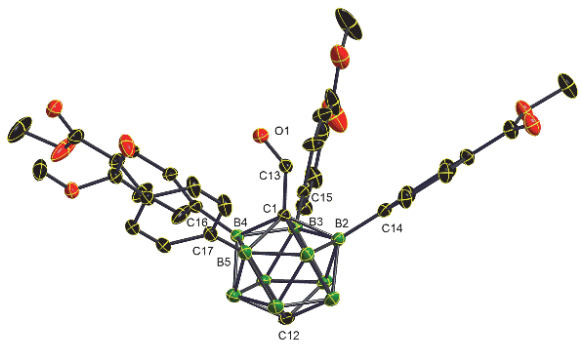
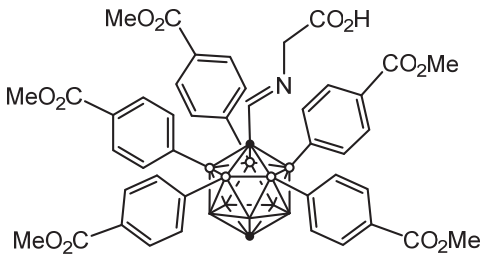


Figure S4. X-Ray structure of **8** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.512(5), C13−O1 1.175(5), C1−B2 1.742(6), C1−B3 1.723(5), C1−B4 1.742(5), C1−B5 1.747(6), B2−C14 1.576(6), B3−C15 1.569(6), B4−C16 1.576(6), B5−C17 1.579(7).



9: White solid. m. p. 318.5 – 318.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (t, *J* = 1.4 Hz, 1H, C**H**=N), 7.67 (d, *J* = 8.4 Hz, 10H), 7.02 (d, *J* = 8.4 Hz, 10H) (phenyl−**H**), 4.00

(s, 2H, C**H**$_2$), 3.85 (s, 15H, OC**H**$_3$), 3.53 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −3.2 (5B), −15.6 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 167.2 (**C**=O), 157.1 (**C**H=N), 136.5, 135.8, 130.2, 128.3 (phenyl−**C**), 80.4 (cage−**C**), 60.6 (**C**H$_2$), 60.3 (cage−**C**), 52.3 (O**C**H$_3$). HRMS (ESI, positive mode): *m/z* calcd for $C_{45}B_{10}NO_{12}H_{46}$ $[M+H]^+$: 900.4018. Found: 900.4020. Elemental analysis (%) calcd for $C_{45}B_{10}NO_{12}H_{45}$: C, 60.06; H, 5.04; N, 1.56. Found: C, 60.18; H, 1.49.

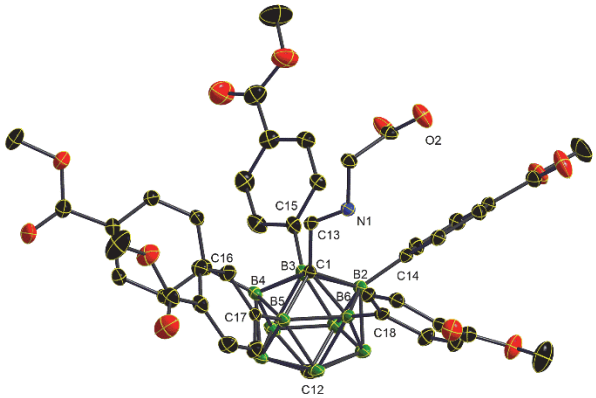
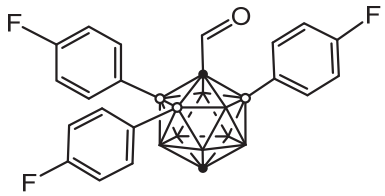


Figure S5. X-Ray structure of **9** (ellipsoids at 30% probability, solvent and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.505(3), C13−N1 1.246(4), C1−B2 1.750(4), C1−B3 1.762(4), C1−B4 1.745(4), C1−B5 1.751(4), C1−B6 1.754(4), B2−C14 1.585(4), B3−C15 1.585(4), B4−C16 1.617(4), B5−C17 1.592(4), B6−C18 1.588(4).

2.1.4 Synthes of B(2,3,5)-(*p*-F-Ph)$_3$-*p*-carboranyl aldehyde 7'.

7' were prepared by a similar procedure to **7** using 3.0 equiv. of 4-fluoroiodobenzene, 3.0 equiv. of Ag_3PO_4 at 60 ºC for 12h.



7': Yield 33%. White solid. m. p. 295.8 – 296.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H, C**H**O), 7.60 − 7.56 (m, 2H), 7.30 − 7.25 (m, 4H), 7.04 – 6.98 (m, 2H), 6.95 – 6.89 (m, 4H) (phenyl−**H**), 3.38 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −3.5 (3B), −12.4 (2B), −16.2 (5B); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2 (**C**HO), 164.1 (d, *J* = 249.3 Hz), 163.7 (d, *J* = 249.3 Hz), 137.2 (d, *J* = 7.9 Hz), 137.0 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 20.2 Hz), 115.1 (d, *J* = 20.3 Hz) (phenyl−**C**), 86.7, 65.0 (cage−**C**). ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.9, −112.1. HRMS (ESI, negative mode): *m/z* calcd for $C_{21}B_{10}F_3H_{22}$ $[M+O-H]^-$: 470.2388. Found: 470.2385. Elemental analysis (%) calcd for $C_{21}B_{10}OF_3H_{21}$: C, 55.50; H, 4.66. Found: C, 55.35; H, 4.78.

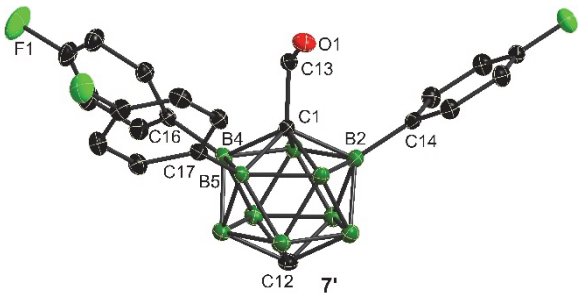
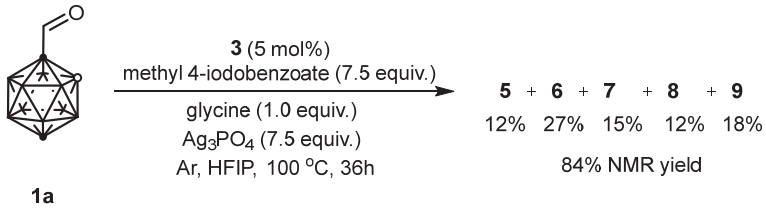


Figure S6. X-Ray structure of **7'** (ellipsoids at 30% probability, H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.551(3), C13−O1 1.185(2), B2−C14 1.558(3), B4−C16 1.588(3), B5−C17 1.578(3).

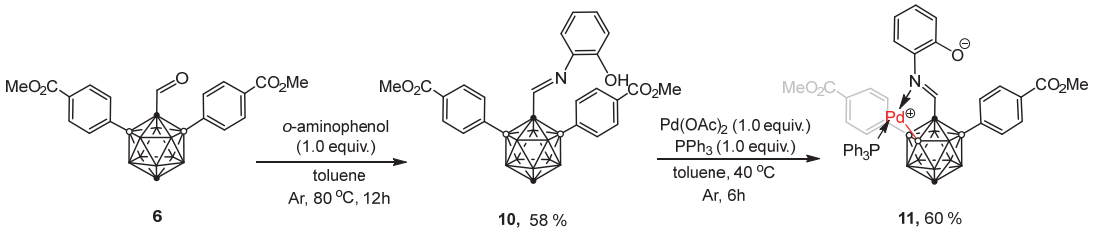
2.1.5 Catalytic performance of 3 in the polyarylation reaction of 1a with methyl 4-iodobenzoate



Scheme S4. Catalytic performance of **3**.

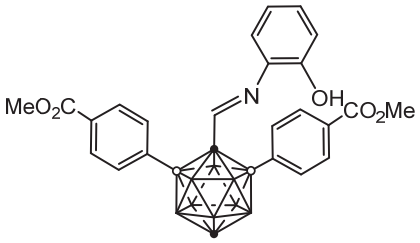
Catalytic performance of 3: A reaction tube (10 mL) with a magnetic stir bar was charged with **1a** (0.1 mmol, 17.2 mg), **3** (0.005 mmol, 3.2 mg), methyl 4-iodobenzoate (7.5 equiv., 0.75 mmol, 197 mg), glycine (1.0 equiv., 0.1 mmol, 7.5 mg), Ag_3PO_4 (7.5 equiv., 0.75 mmol, 314 mg), and HFIP (1.0 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 100 °C for 36 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered through a celite pad. The celite was washed by ethyl acetate (2 × 10 mL). The combined solvent was removed in *vacuo*. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

2.1.6 Stoichiometric reaction of di-aryalted intermediate with $Pd(OAc)_2$

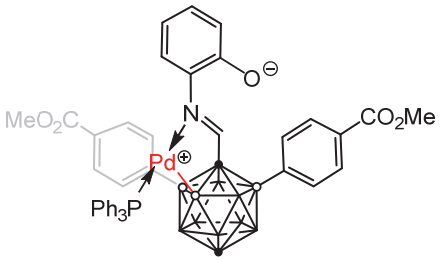


Scheme S5. Synthesis of bicyclic palladium complexe **11**.

Synthesis of di-arylated *p*-carboranyl-imines 10 and corresponding bicyclic palladium complexes 11. 10 were prepared by similar procedure to **2** and the corresponding bicyclic palladium complex, **11** was synthesized by similar procedure to **3**.



10: Yield 58%. Light yellow solid. m. p. 157.5 – 158.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.72 (d, *J* = 7.8 Hz, 4H) (phenyl−**H**), 7.13 (s, 1H, C**H**=N), 7.04 (dd, *J* = 7.5 Hz, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 7.6 Hz, *J* = 7.7 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 1H) (phenyl−**H**), 5.57 (s, 1H, O**H**), 3.91 (s, 6H, OC**H**$_3$), 3.31 (s, 1H, cage−C**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.7 (4B), −12.5 (2B), −15.9 (4B); 13C NMR (101 MHz, $CDCl_3$): δ 167.1 (**C**=O), 151.9 (**C**H=N), 151.2, 135.0, 134.7, 133.3, 130.7, 130.3, 129.1, 128.9, 120.0, 115.9, 115.5 (phenyl−**C**), 85.4, 64.9 (cage−**C**), 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{25}B_{10}NO_5H_{28}$ $[M-H]^-$: 531.2940. Found: 531.2941. Elemental analysis (%) calcd for $C_{25}B_{10}NO_5H_{29}$: C, 56.48; H, 5.50; N, 2.63. Found: C, 56.37; H, 5.41; N, 2.46.



11: Yield 60%. Red solid. m. p. 198.7 – 199.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 − 8.03 (m, 2H), 7.89 − 7.82 (m, 8H), 7.80 − 7.78 (m, 4H), 7.48 − 7.41 (m, 9H) (phenyl−**H**), 7.11 (d, *J* = 7.5 Hz, 1H, C**H**=N), 6.95 (ddd, *J* = 8.5, 6.9, 1.6 Hz, 1H), 6.65 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.59 (dd, *J* = 8.6, 1.2 Hz, 1H), 6.15 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H) (phenyl−**H**), 3.95 (s, 3H), 3.88 (s, 3H) (OC**H**$_3$), 2.79 (s, 1H, cage−C**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 6.6 (2B), −1.0 (4B), −11.0 (4B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.75, 172.73 (**C**=O), 167.2 (d, *J* = 10.5 Hz, **C**H=N), 147.1 (d, *J* = 10.5 Hz), 135.4, 135.0 (d, *J* = 10.5 Hz), 134.6, 133.7 (d, *J* = 1.5 Hz), 133.0, 132.1, 131.7, 130.9 (d, *J* = 2.5 Hz), 130.8, 129.8, 129.1, 128.8, 128.6, 128.5, 123.4, 116.1, 116.1, 112.9 (phenyl−**C**), 95.8, 64.4 (cage−**C**), 52.4, 52.2 (O**C**H$_3$); ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.67. HRMS (ESI, positive mode): *m/z* calcd $C_{43}B_{10}NO_5PPdH_{43}$ $[M+H]^+$: 898.2911. Found: 898.2910. Elemental analysis (%) calcd for $C_{43}B_{10}NO_5PPdH_{42}$: C, 57.49; H, 4.71; N, 1.56. Found: C, 57.25; H, 4.38; N, 1.49.

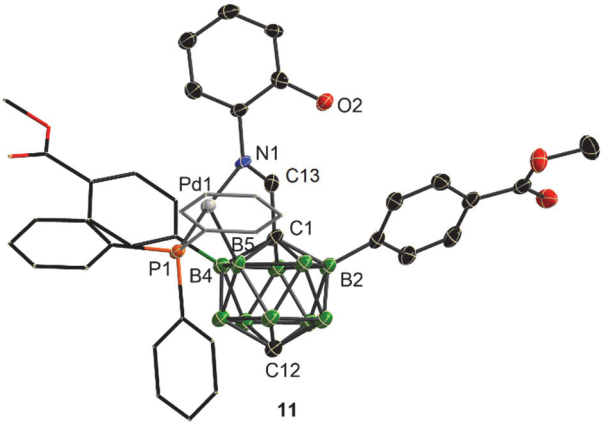
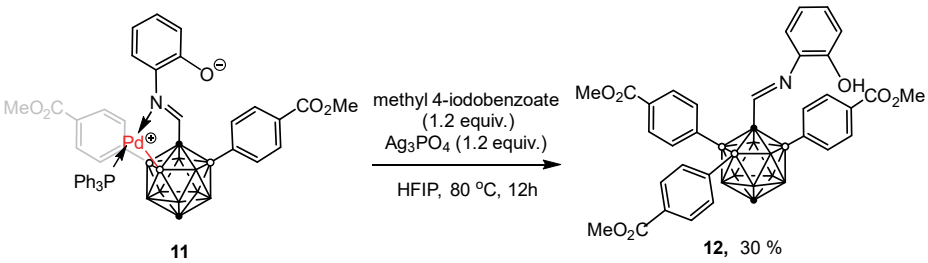


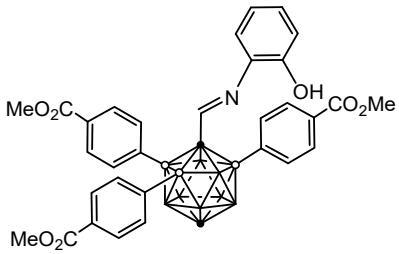
Figure S7. X-Ray structure of **11** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å] and angels [º]: C1−C13 1.489(9), C13−N1 1.267(7), C1−B2 1.690(9), C1−B4 1.721(10), C1−B5 1.746(10), N1−Pd1 2.160(5), B5−Pd1 2.097(8), 2.2492(18), N1−Pd1−P1 175.72(14).

2.1.7 Subsequent arylation of 11 with methyl 4-iodobenzoate



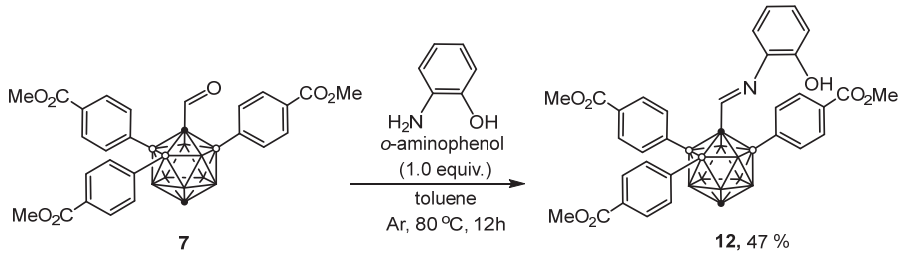
Scheme S6. Arylation of **11** with methyl 4-iodobenzoate.

12 were prepared by a similar procedure to **4** using 1.2 equiv. of methyl 4-iosobenzoate, 1.2 equiv. of Ag_3PO_4 at 80 ºC for 12h.



12: Yield 30%. Yellow solid. m. p. 225.8 – 226.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 4H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 4H) (phenyl−**H**), 7.38 (s, 1H, C**H**=N), 7.05 (ddd, *J* = 8.7, 7.5, 1.5 Hz, 1H), 6.73 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.60 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H), 6.31 (dd, *J* = 8.0, 1.5 Hz, 1H) (phenyl−**H**), 5.28 (s, 1H, O**H**), 3.92 (s, 3H), 3.89 (s, 6H) (OC**H**$_3$), 3.43 (s, 1H, cage−C**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −3.6 (4B), −11.2 (2B), −16.0 (4B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.02, 166.97 (**C**=O), 152.0 (**C**H=N), 150.6, 137.4, 135.1, 134.9, 133.4, 130.9, 130.6, 130.5, 129.2, 128.9, 128.8, 120.2, 115.9, 115.8 (phenyl−**C**), 84.6, 64.1 (cage−**C**), 52.3, 52.3 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{33}B_{10}NO_7H_{34}$ $[M-H]^-$: 664.3344. Found: 664.3349. Elemental analysis (%) calcd for $C_{33}B_{10}NO_7H_{35}$: C, 59.54; H, 5.30; N, 2.10. Found: C, 59.25; H, 4.98; N, 2.27.

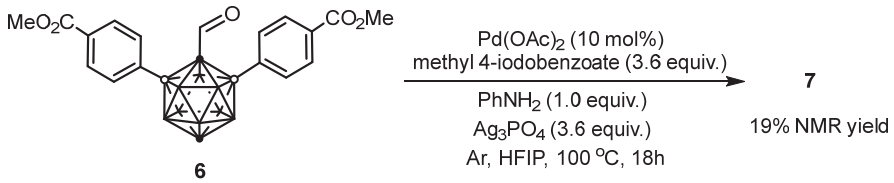
2.1.8 Alternative synthesis of 12 from 7



Scheme S7. Condensation of **7** with *o*-aminophenol to afford **12**.

Alternative synthesis of **12** was prepared by similar procedure to **2**.

2.1.9 Using aniline as transient directing reagent in the polyarylation reaction of 6 with methyl 4-iodobenzoate



Scheme S8. Reaction of **6** with methyl 4-iodobenzoate using aniline as a transient directing reagent.

Procedure: A reaction tube (10 mL) with a magnetic stir bar was charged with **6** (0.1 mmol, 44.0 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol% 2.4 mg), methyl 4-iodobenzoate (3.6 equiv., 0.36 mmol, 94.3 mg), $PhNH_2$ (1.0 equiv., 0.1 mmol, 9.3 mg), Ag_3PO_4 (3.6 equiv., 0.36 mmol, 150.7 mg), and HFIP (1.0 mL). The reaction tube was sealed under Ar atmosphere and allowed to stir at 100 °C for 18 hours. Then, the reaction mixture was cooled to room temperature, and charged with toluene (0.3 mL), HOAc (0.2 mL) and stir at 100 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad. The celite was washed by ethyl acetate (2 × 10 mL). The combined solvent was removed in *vacuo*. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

2.2 Condition screening

2.2.1 Screening of transient direct group, silver salt and solvent.

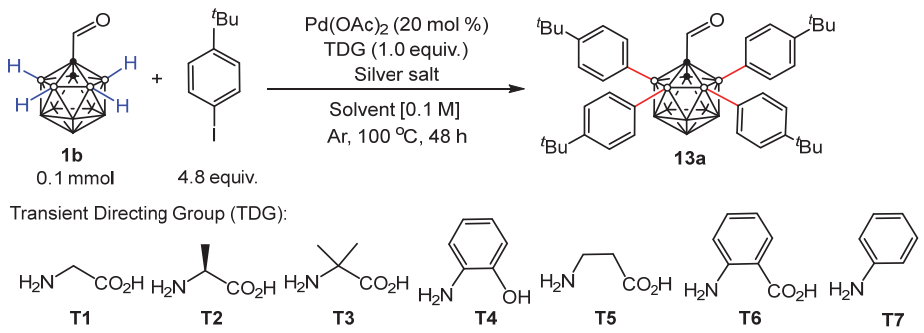


Table S2. Optimization of Pd(II)-catalyzed B(3,4,5,6)–H tetra-arylation of *o*-carboranyl aldehyde (**1b**).[a]

Entry	TDG	Silver salt	Solvent	Yield (**13a**, %)[b]
1	**T1**	AgOAc	HFIP[c]	16
2	**T1**	AgTFA	HFIP	14
3	**T1**	Ag_2CO_3	HFIP	6
4	**T1**	**Ag_3PO_4**	**HFIP**	**58**

5	**T1**	$AgBF_4$	HFIP	0
6	**T1**	$AgSbF_6$	HFIP	0
7	**T1**	AgNTf	HFIP	0
8	**T1**	AgOTf	HFIP	0
9	**T1**	AgO_2CPh	HFIP	12
10	**T1**	Ag_2O	HFIP	8
11	**T2**	Ag_3PO_4	HFIP	38
12	**T3**	Ag_3PO_4	HFIP	0
13	**T4**	Ag_3PO_4	HFIP	16
14	**T5**	Ag_3PO_4	HFIP	36
15	**T6**	Ag_3PO_4	HFIP	12
16	**T7**	Ag_3PO_4	HFIP	0
17	**T1**	Ag_3PO_4	Toluene	0
18	**T1**	Ag_3PO_4	DCE[d]	0
19	**T1**	Ag_3PO_4	THF	0
20	**T1**	Ag_3PO_4	1,4-Dioxane	0
21	**T1**	Ag_3PO_4	CH_3CN	0
22	**T1**	Ag_3PO_4	MeOH	0
23	**T1**	Ag_3PO_4	TFE	27
24	**T1**	Ag_3PO_4	CF_3CO_2H	trace
25[c]	**T1**	Ag_3PO_4	HFIP	62

[a] Conditions: **1b** (0.1 mmol), 4.8 equiv. of 4-tert-butyl-iodobenzene, 20 mol% of $Pd(OAc)_2$, 1.0 equiv. of transient directing group, 4.8 equiv. of silver salt, 1.0 mL of solvent, 100 ^oC, sealed under Ar atmosphere, 48 h. [b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c] 6.0 equiv. of Ag_3PO_4. [d] DCE: 1,2-dichloroethane.

2.2.2 Further optimization on the reaction conditions

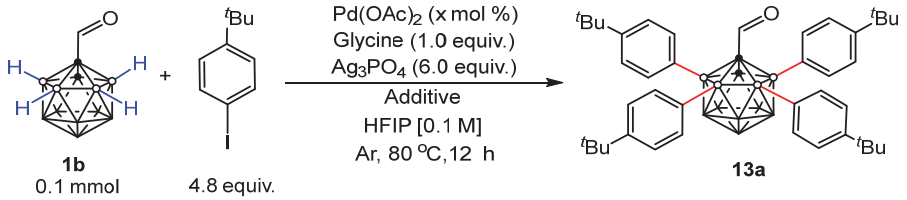


Table S3. Further optimization on the Pd(II)-catalyzed B(3,4,5,6)–H tretraarylation of *o*-carboranyl aldehyde (**1b**).[a]

Entry	$Pd(OAc)_2$ (x mol%)	Additive	Yield (**13a**, %)[b]
1	20 mol%	/	54
2	20 mol%	Na_2CO_3 (0.5 equiv.)	67
3	20 mol%	H_3PO_4 (0.2 equiv.)	30
4	20 mol%	Na_2CO_3 (1.0 equiv.)	89
5	20 mol%	Na_2CO_3 (4.8 equiv.)	n.d.[c]
6	20 mol%	Na_3PO_4 (1.0 equiv.)	87
7	20 mol%	Na_3PO_4 (4.8 equiv.)	n.d.[c]
8	20 mol%	$NaHCO_3$ (1.0 equiv.)	90
9	20 mol%	Na_2HPO_4 (1.0 equiv.)	76
10	10 mol%	$NaHCO_3$ (1.0 equiv.)	92 (90)[f]
11[d]	**10 mol%**	**$NaHCO_3$ (1.0 equiv.)**	**92 (90)**[f]
12	/	$NaHCO_3$ (1.0 equiv.)	0
13[e]	10 mol%	$NaHCO_3$ (1.0 equiv.)	62

[a] Conditions: **1b** (0.1 mmol), 4-tert-butyl-iodobenzene (0.48 mmol), $Pd(OAc)_2$ (10-20 mol%), glycine (0.1 mmol), Ag_3PO_4 (0.48 mmol), Additive, HFIP (1.0 mL), 80 °C, sealed under Ar atmosphere, 12 h. [b] Yield was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. [c] **1b** was decomposed. [d] Optimal condition: **1b** (0.1 mmol), glycine (0.1 mmol), HFIP (1.0 mL), 40 °C, sealed under Ar atmosphere, 1 h; then, 4-tert-butyl-iodobenzene (4.8 equiv.), $Pd(OAc)_2$ (10 mol%), glycine (1.0 equiv.), Ag_3PO_4 (6.0 equiv.), $NaHCO_3$ (1.0 equiv.), HFIP (1.0 mL), 80 °C, sealed under Ar atmosphere, 24 h. [e] Sealed under air atmosphere. n.d.: desired product was not detected. [f] Isolated yield.

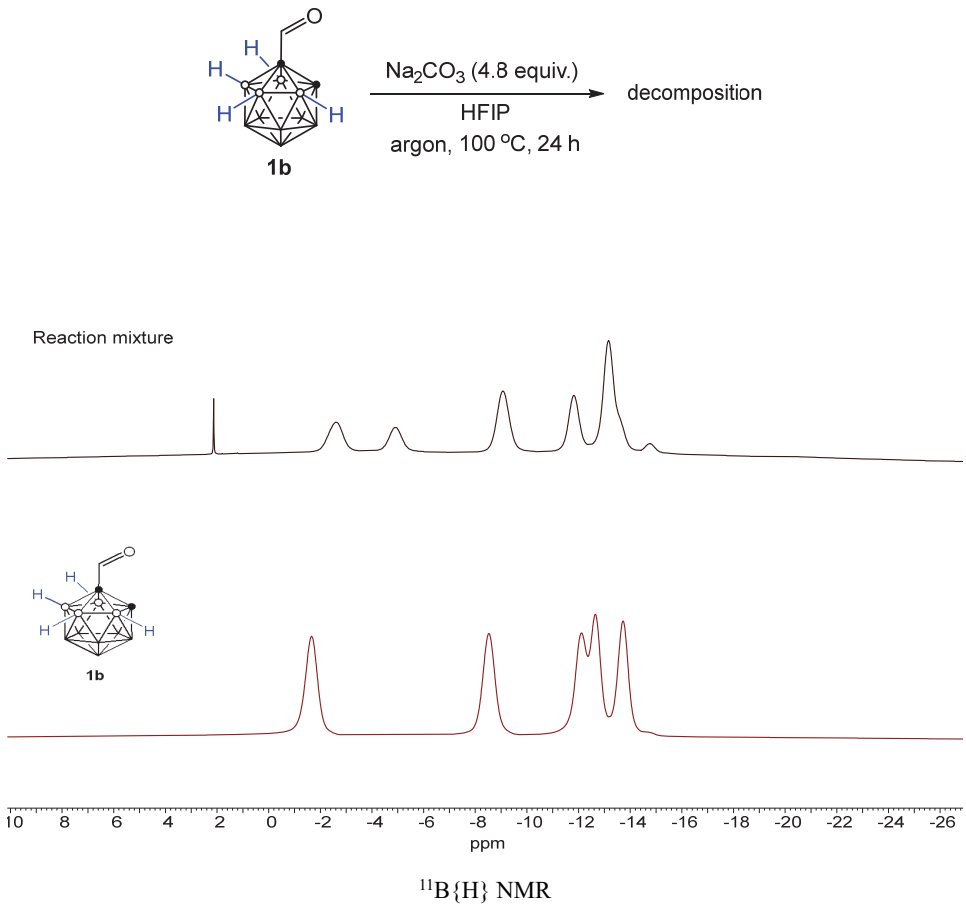


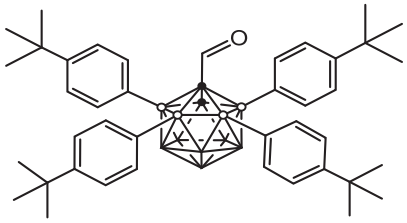
Figure S8. Decomposition of **1b** in the presence of 4.8 equiv. of Na_2CO_3.

2.3 Substrate scope for Pd-catalyzed B(3,4,5,6)-tetra-arylation of *o*-carboranyl aldehyde

General procedure A: A reaction tube (10 mL) with a magnetic stir bar was charged with *o*-carboranyl aldehyde (0.1 mmol), glycine (1.0 equiv. 0.1 mmol, 7.5 mg), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 °C for 1h. Then, aryl iodide (4.8 equiv. 0.48 mmol), silver phosphate (6.0 equiv. 0.60 mmol, 251.0 mg), palladium acetate (10 mol %, 0.01 mmol, 2.2 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) were added and heated at 80 °C for 24 hours. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum ether/CH_2Cl_2 or petroleum ether/ethyl acetate as the eluent to afford the product.

General procedure B: A reaction tube (10 mL) with a magnetic stir bar was charged with *o*-carboranyl aldehyde (0.1 mmol), 2-aminophenol (1.0 equiv.), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 ºC for 1h. Then, aryl iodide (8.0 equiv. 0.80 mmol), silver phosphate (8.0 equiv. 0.8 mmol, 334.9 mg), palladium acetate (20 mol %, 0.01 mmol, 4.5 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) and heated at 80 ºC for 48 hours. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum ether/CH_2Cl_2 or petroleum ether/ethyl acetate as the eluent to afford the product.

Compound data:



13a: Yield 90%. White solid. m. p. 331.2 – 331.5°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H, C**H**O), 7.29 (dd, *J* = 8.3 Hz, 8.3 Hz, 8H), 7.09 (d, *J* = 8.0 Hz, 4H), 6.95 (d, *J* = 8.0 Hz, 4H) (phenyl−**H**), 4.81 (s, 1H, cage C−**H**), 1.32 (s, 18H), 1.25 (s, 18H) (^{t}Bu−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.0 (4B), −3.5 (2B), −9.6 (2B), −14.2 (2B); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1 (**C**HO), 152.7, 151.1, 134.8, 134.7, 124.8, 124.4 (phenyl−**C**), 73.0, 53.0 (cage−**C**), 34.7, 34.4 (^{t}Bu−**C**Me_3), 31.2, 31.2 (^{t}Bu−**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{43}B_{10}OH_{59}$ $[M-H]^-$: 698.5611. Found: 698.5617. Elemental analysis (%) calcd for $C_{43}B_{10}OH_{60}$: C, 73.67; H, 8.63. Found: C, 73.52; H, 8.75.

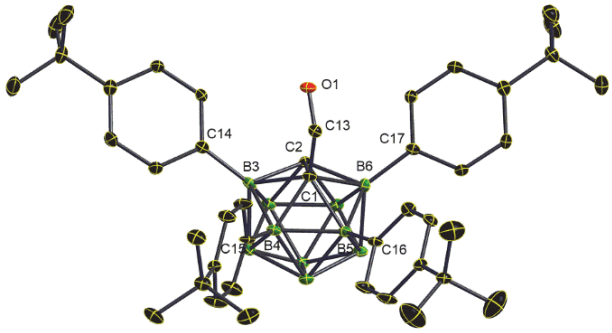
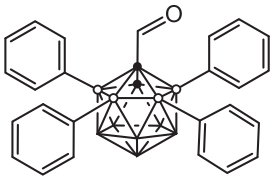
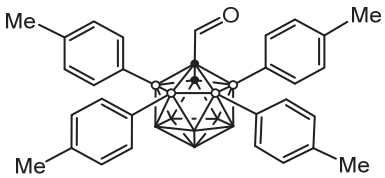


Figure S9. X-Ray structure of **13a** (ellipsoids at 30% probability, H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.519(5), C13−O1 1.191(4), C1−B3 1.772(6), C1−B4 1.725(6), C1−B5 1.731(6), C1−B6 1.773(6), B3−C14 1.558(6), B4−C15 1.591(6), B5−C16 1.587(6), B6−C17 1.573(6).



13b: Yield 60%. White solid. m. p. 199.4 – 199.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.53 (s, 1H, C**H**O), 7.39 − 7.36 (m, 6H), 7.28 − 7.25 (m, 4H), 7.20 − 7.16 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 4H), 7.01 (d, *J* = 7.2 Hz, 4H) (phenyl−**H**), 4.88 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 3.5 (4B), 1.4 (2B), −3.9 (2B), −8.5 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.7 (**C**HO), 135.1, 134.9, 130.0, 128.5, 128.0, 127.7 (phenyl−**C**), 73.1, 52.5 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{27}B_{10}OH_{27}$ $[M-H]^-$: 475.3071. Found: 475.3075. Elemental analysis (%) calcd for $C_{27}B_{10}OH_{28}$: C, 68.04; H, 5.92. Found: C, 67.84; H, 6.11.



13c: Yield 93%. White solid. m. p. 145.2 – 145.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H, C**H**O), 7.26 (d, *J* = 7.8 Hz, 4H), 7.08 (d, *J* = 7.7 Hz, 4H), 6.90 (dd, *J* = 8.2

Hz, 8.2 Hz 8H) (phenyl−**H**), 4.80 (s, 1H, cage C−**H**), 2.33 (s, 6H), 2.23 (s, 6H) (OC**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 3.1 (4B), 1.2 (2B), −4.2 (2B), −8.8 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.1 (**C**HO), 139.9, 138.1, 135.5, 135.1, 134.9, 128.8, 128.5, 128.3 (phenyl−**C**), 73.0, 52.4 (cage−**C**), 21.5, 21.4 (**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{31}B_{10}OH_{35}$ $[M-H]^-$: 531.3697. Found: 534.3705. Elemental analysis (%) calcd for $C_{31}B_{10}OH_{36}$: C, 69.89; H, 6.81. Found: C, 69.76; H, 6.97.

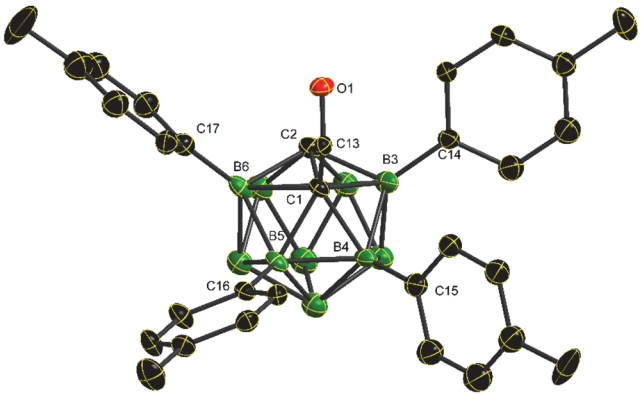
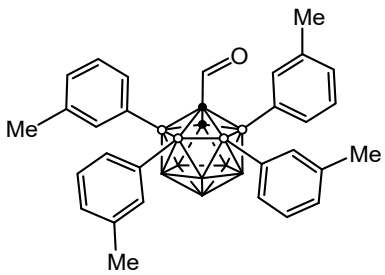
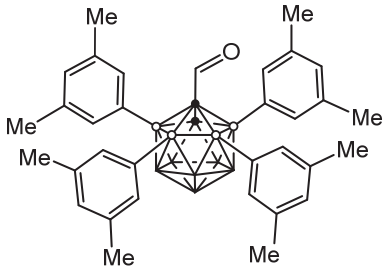


Figure S10. X-Ray structure of **13c** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.507(5), C13−O1 1.195(4), C1−B3 1.776(5), C1−B4 1.721(5), C1−B5 1.730(5), C1−B6 1.764(6), B3−C14 1.565(6), B4−C15 1.568(6), B5−C16 1.572(5), B6−C17 1.557(6).

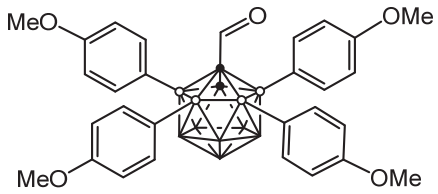


13d: Yield 70%. White solid. m. p. 99.7 – 100.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.50 (s, 1H, C**H**O), 7.22 − 7.11 (m, 8H), 7.00 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 7.5 Hz, 2H), 6.91 (s, 2H), 6.75 (d, J = 6.9 Hz, 2H) (phenyl−**H**), 4.84 (s, 1H, cage C−**H**), 2.27 (s, 6H), 2.12 (s, 6H) (C**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.1 (4B), −3.7 (2B), −9.3 (2B), −13.8 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.9 (**C**HO), 150.8, 137.3,

136.9, 136.6, 136.5, 136.3, 136.3, 136.1, 135.8, 135.6, 132.8, 132.3, 132.2, 132.0, 131.7, 131.2, 131.0, 130.6, 129.9, 128.7, 127.8, 127.4, 127.2, 127.0 (phenyl−**C**), 73.1, 52.7 (cage−**C**), 21.55, 21.50 (**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{31}B_{10}OH_{35}$ $[M-H]^-$: 531.3697. Found: 534.3645. Elemental analysis (%) calcd for $C_{31}B_{10}OH_{36}$: C, 69.89; H, 6.81. Found: C, 69.56; H, 6.95.

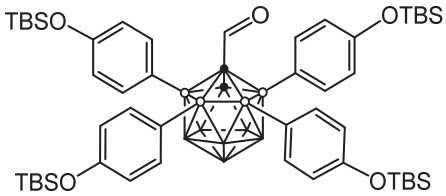


13e: Yield 58%. White solid. m. p. 230.7 – 231.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.42 (s, 1H, C**H**O), 6.99 (s, 2H), 6.96 (s, 4H), 6.82 (s, 2H), 6.64 (s, 4H) (phenyl−**H**), 4.78 (s, 1H, cage C−**H**), 2.22 (s, 12H), 2.06 (s, 12H) (C**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.0 (4B), −3.7 (2B), −9.3 (2B), −13.9 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.1 (**C**HO), 137.1, 136.6, 133.3, 133.1, 131.5, 129.9 (phenyl−**C**), 73.1, 52.8 (cage−**C**), 21.4, 21.3 (**C**H_3). HRMS (ESI, negative mod): *m/z* calcd for $C_{35}B_{10}NOH_{43}$ $[M-H]^-$: 601.4353. Found: 601.4355. Elemental analysis (%) calcd for $C_{35}B_{10}NOH_{44}$: C, 69.73; H, 7.36. Found: C, 69.99; H, 7.12.

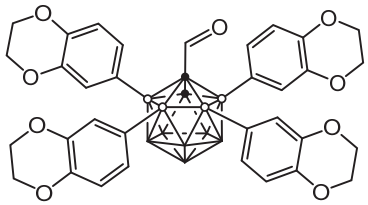


13f: Yield 61%. White solid. m. p. 214.6 – 214.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.44 (s, 1H, C**H**O), 7.28 (d, *J* = 8.7 Hz , 4H), 6.93 (d, *J* = 8.7 Hz, 4H), 6.79 (d, *J* = 8.7 Hz, 4H), 6.63 (d, *J* = 8.7 Hz, 4H) (phenyl−**H**), 4.72 (s, 1H, cage C−**H**), 3.79 (s, 6H), 3.72 (s, 6H) (OC**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 2.9 (4B), 1.1 (2B), −4.4 (2B), −8.9 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.3 (**C**HO), 161.0, 159.8, 137.0, 136.6, 136.3, 113.7, 113.4, 113.1 (phenyl−**C**), 72.8 (cage−**C**), 55.2, 55.1 (**C**H_3), 52.3

(cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{31}B_{10}O_5H_{35}$ $[M-H]^-$: 595.3493. Found: 595.3496. Elemental analysis (%) calcd for $C_{31}B_{10}O_5H_{36}$: C, 62.40; H, 6.08. Found: C, 62.13; H, 6.04.

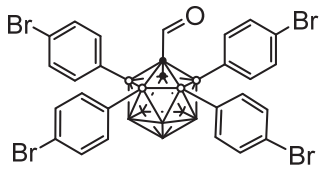


13g: Yield 62%. Colorless solid. m. p. 95.1 – 95.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.44 (s, 1H, C**H**O), 7.20 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 6.71 (d, *J* = 8.5 Hz, 4H), 6.56 (d, *J* = 8.5 Hz, 4H) (phenyl−**H**), 4.68 (s, 1H, cage C−**H**), 0.97 (s, 18H), 0.94 (s, 18H) (^{t}Bu−**H**), 0.20 (s, 12H), 0.14 (s, 12H) (C**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.6 (6B), −9.7 (2B), −14.4 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.2 (**C**HO), 157.3, 156.1, 136.3, 119.6 (phenyl−**C**), 72.8, 52.7 (cage−**C**), 25.80, 25.77, 18.38, 18.35 (^{t}Bu−**C**), −4.22, −4.26 (**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{51}B_{10}OSi_4H_{83}$ $[M-H]^-$: 931.6530. Found: 931.6536. Elemental analysis (%) calcd for $C_{51}B_{10}OSi_4H_{84}$: C, 65.61; H, 9.07. Found: C, 65.33; H, 9.32.

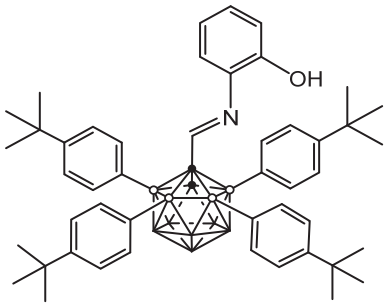


13h: Yield 64%. White solid. m. p. 280.2 – 280.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H, C**H**O), 6.87 (d, *J* = 1.8 Hz, 2H), 6.78 (dd, *J* = 8.3, 1.8 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 1.8 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.41 (dd, *J* = 8.2, 1.8 Hz, 2H) (phenyl−**H**), 4.62 (s, 1H, cage C−**H**), 4.25 − 4.22 (m, 4H), 4.22 − 4.18 (m, 8H), 4.16 − 4.14 (m, 4H) (C**H**$_2$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.2 (6B), −9.7 (2B), −14.1 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.9 (**C**HO), 145.2, 144.0, 143.2, 143.2, 128.7, 128.2, 124.1, 123.7, 117.1, 116.7 (phenyl−**C**), 72.7 (cage−**C**), 64.6, 64.5, 64.3, 64.2 (**C**H$_2$), 52.7 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{35}B_{10}O_9H_{35}$

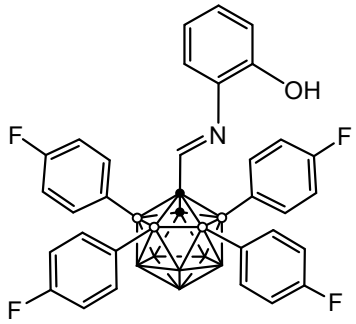
[M−H]⁻: 707.3290. Found: 707.3300. Elemental analysis (%) calcd for $C_{35}B_{10}O_9H_{36}$: C, 59.31; H, 5.12. Found: C, 59.06; H, 5.08.



13i (purity: 88%, based on ^{1}H NMR): Yield 63%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H, C**H**O), 7.47 – 7.41 (m, 4H), 7.26 – 7.22 (m, 4H), 7.21 – 7.16 (m, 4H) (phenyl−**H**), 6.85 – 6.72 (m, 4H), 4.78 (s, 1H, cage C−**H**); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -1.5 (6B), -8.8 (2B), -13.1 (2B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 183.0 (**C**HO), 136.4, 136.1, 131.6, 131.4, 125.7, 124.0 (phenyl−**C**), 72.6, 51.5 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{27}B_{10}OBr_4H_{23}$ [M−H]⁻: 790.9450. Found: 790.9461.



13j: Yield 48%. White solid. m. p. 214.8 – 215.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H, C**H**=N), 7.21 − 7.15 (m, 8H), 7.05 − 6.98 (m, 5H), 6.89 (d, *J* = 8.4, 4H), 6.67 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.60 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 6.19 (dd, *J* = 7.9, 1.5 Hz, 1H) (phenyl−**H**), 4.89 (s, 1H, cage C−**H**), 1.21 (s, 18H), 1.16 (s, 18H) (C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.6 (6B), −9.5 (2B), −13.7 (2B); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 151.1, 151.1 (phenyl−**C**), 150.4 (**C**H=N), 134.7, 134.7, 130.0, 125.2, 124.6, 120.2, 117.6, 115.9 (phenyl−**C**), 70.5, 57.4 (cage−**C**), 34.8, 34.6 (**C**Me$_3$), 31.3, 31.2 (**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{49}B_{10}NOH_{64}$ [M−H]⁻: 790.6009. Found: 790.5997. Elemental analysis (%) calcd for $C_{49}B_{10}NOH_{65}$: C, 74.30; H, 8.27; N, 1.77. Found: C, 74.22; H, 8.18; N, 1.71.



13k: Yield 30%. White solid. m. p. 243.8 – 244.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H, C**H**=N), 7.32 (dd, *J* = 5.8, 5.8 Hz, 4H), 7.20 (ddd, *J* = 7.6, 7.6 Hz, 1.5 Hz, 1H), 7.01 − 6.94 (m, 8H), 6.88 − 6.81 (m, 5H), 6.77 (ddd, *J* = 7.6, 7.6 Hz, 1.2 Hz, 1H), 6.44 (dd, *J* = 7.9, 1.5 Hz, 1H) (phenyl−**H**), 5.02 (br. 2H) (O−**H** + cage C−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.2 (6B), −9.2 (2B), −13.4 (2B); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (d, *J* = 78.5 Hz), 162.4 (d, *J* = 76.2 Hz) (phenyl−**C**), 151.4 (**C**H=N), 148.2, 136.8 (d, *J* = 7.8 Hz), 136.5 (d, *J* = 7.6 Hz), 133.5, 131.2, 120.9, 116.8 (d, *J* = 73.6 Hz), 115.7 (d, *J* = 20.4 Hz), 115.3 (d, *J* = 20.3 Hz) (phenyl−**C**), 70.3, 56.3 (cage−**C**); ^{19}F NMR (471 MHz, $CDCl_3$): δ −109.71, −112.26. HRMS (ESI, negative mode): *m/z* calcd for $C_{33}B_{10}NOF_4H_{28}$ $[M-H]^-$: 642.3110. Found: 642.3113. Elemental analysis (%) calcd for $C_{33}B_{10}NOF_4H_{29}$: C, 61.96; H, 4.57; N, 2.19. Found: C, 61.78; H, 4.49; N, 2.27.

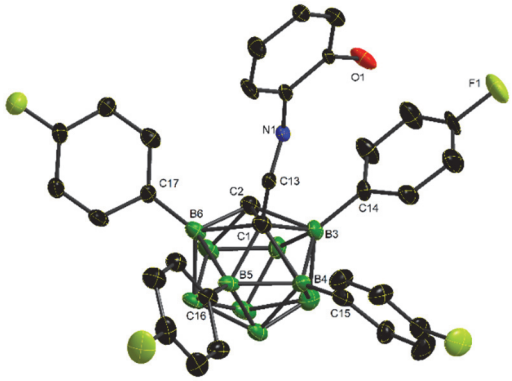
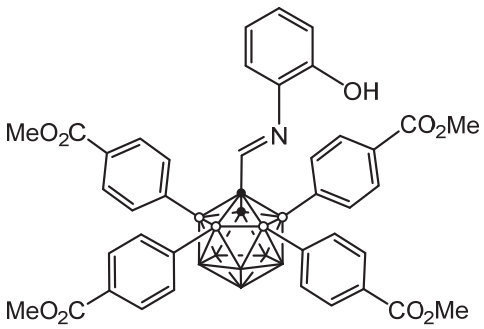


Figure S11. X-Ray structure of **13k** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.462(13), C13−N1 1.266(11), C1−B3 1.794(16), C1−B4 1.753(14), C1−B5 1.712(13), C1−B6 1.767(14), B3−C14 1.555(13), B4−C15 1.551(14), B5−C16 1.565(15), B6−C17 1.549(15).

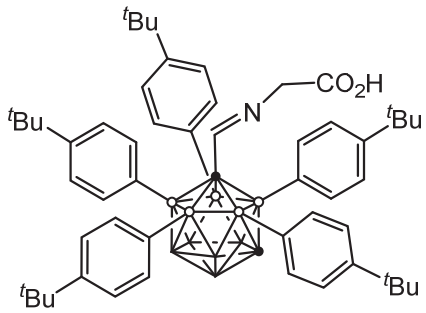


13l: Yield 32%. White solid. m. p. 214.6 – 214.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H, C**H**=N), 7.88 (d, *J* = 8.2 Hz, 4H), 7.73 (d, *J* = 8.3 Hz, 4H), 7.43 (d, *J* = 8.2 Hz, 4H), 7.18 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 4H), 6.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.75 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 6.48 (dd, *J* = 8.0, 1.5 Hz, 1H) (phenyl−**H**), 5.26 (br. 2H) (O−**H** + cage C−**H**), 3.89 (s, 6H), 3.85 (s, 6H) (OMe); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.4 (5B), −8.8 (3B), −13.3 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 166.7 (**C**=O), 151.5 (**C**H=N), 147.1, 134.9, 134.6, 133.0, 131.5, 131.4, 130.3, 129.2, 128.9, 121.1, 117.6, 116.7 (phenyl−**C**), 70.8, 56.0 (cage−**C**), 52.5, 52.3 (O**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{41}B_{10}NO_9H_{41}$ $[M-H]^-$: 798.3826. Found: 798.3823. Elemental analysis (%) calcd for $C_{41}B_{10}NO_9H_{42}$: C, 61.49; H, 5.29; N, 1.75. Found: C, 61.71; H, 5.06; N, 1.63.

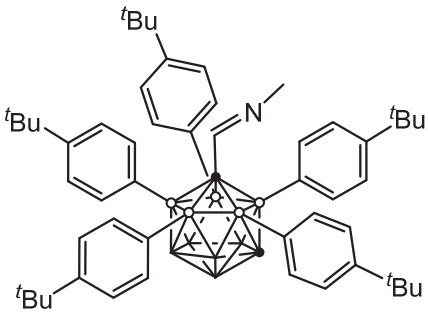
2.4 Substrate scope for Pd-catalyzed B(2,3,4,5,6)-penta-arylation of *m*-carboranyl aldehydes

General procedure: A reaction tube (10 mL) with a magnetic stir bar was charged with *m*-carboranyl aldehyde (0.1 mmol, 17.2 mg), glycine (1.0 equiv. 0.1 mmol, 7.5 mg), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 °C for 1h. Then, aryl iodide (6.0 equiv. 0.6 mmol), silver phosphate (6.0 equiv. 0.75 mmol, 313.9 mg), palladium acetate (10 mol %, 0.01 mmol, 2.3 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) were added and heated at 80 °C for 36 hours. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum ether/CH_2Cl_2

or petroleum ether/ethyl acetate as the eluent to afford the desired product.



14a: Yield 66%. White solid. m. p. 298.8 – 299.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (br. 1H, COOH), 8.09 (t, *J* = 1.8 Hz, 1H, C**H**=N), 7.06 − 7.03 (m, 10H), 6.85 (d, *J* = 8.4 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.4 Hz, 2H) (phenyl−**H**), 4.10 (d, *J* = 1.8 Hz, 2H, C**H**$_2$), 3.67 (s, 1H, cage C−**H**), 1.263 (s, 9H) 1.258 (s, 18H), 1.254 (s, 18H）(^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 5.7 (1B), −1.1 (2B), −6.8 (2B), −11.1 (2B), −13.3 (3B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.2 (**C**O_2H), 159.1 (**C**H=N), 152.3, 151.4, 151.1, 135.4, 135.1, 134.9, 124.6, 124.4, 124.3 (phenyl−**C**), 70.0, 59.1 (cage−**C**), 53.4 (**C**H_2), 34.68, 34.60, 34.58 (^{t}Bu−**C**Me_3), 31.34, 31.30, 31.24 (**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{54}B_{10}NH_{74}$ $[M-CO_2-H]^-$: 846.6827. Found: 846.6823. Elemental analysis (%) calcd for $C_{55}B_{10}NO_2H_{75}$: C, 74.20; H, 8.49; N, 1.57. Found: C, 74.08; H, 8.43; N, 1.51.



Byproduct **16** was isolated from the same crude reaction mixture. **16**: Yield 21%. White solid. m. p. 332.7 – 333.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (q, *J* = 1.6 Hz, 1H, C**H**=N), 7.01 − 6.99 (m, 10H), 6.91 − 6.88 (m, 8H), 6.82 − 6.79 (m, 2H) (phenyl−**H**), 3.59 (s, 1H, cage−C**H**), 3.20 (d, *J* = 1.6 Hz, 3H) (N−C**H**$_3$), 1.25 (s, 36H), 1.24 (s, 9H)

(^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 4.6 (1B), −1.6 (2B), −6.7 (3B), −11.6 (4B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.8 (**C**H=N), 151.3, 150.5, 150.3, 135.64, 135.58, 135.0, 123.83, 123.80, 123.78 (phenyl−**C**), 71.5, 53.5 (cage−**C**), 47.2 (N−**C**H$_3$), 34.6, 34.52, 34.50 (^{t}Bu−**C**Me$_3$), 31.40, 31.33 31.26 (^{t}Bu−**C**H$_3$). HRMS (ESI, positive mode): *m/z* calcd for $C_{54}B_{10}NH_{76}$ $[M+H]^+$: 846.6975. Found: 846.6970. Elemental analysis (%) calcd for $C_{54}B_{10}NH_{75}$: C, 76.64; H, 8.93; N, 1.66. Found: C, 76.58; H, 8.85; N, 1.69.

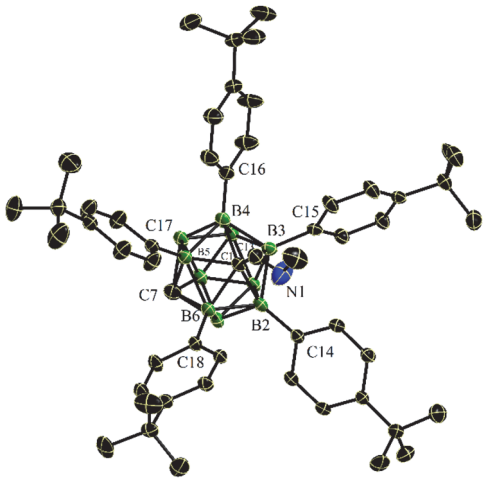
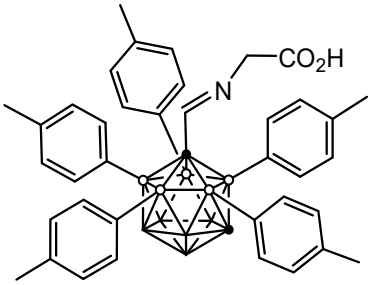
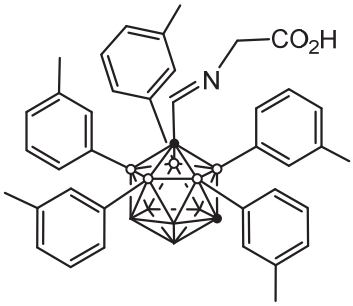


Figure S12. X-Ray structure of **16** (ellipsoids at 30% probability, H atoms were omitted for clarity). Selected bond distances [Å] for **16**: C1−C13 1.516(5), C13−N1 1.139(5), C1−B2 1.781(5), C1−B3 1.762(5), C1−B4 1.758(5), C1−B5 1.758(5), C1−B6 1.774(5), B2−C14 1.593(5), B3−C15 1.584(5), B4−C16 1.599(5), B5−C17 1.592(5), B6−C18 1.575(5).

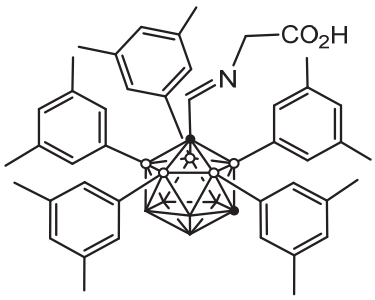


14b: Yield 83%. White solid. m. p. 268.4 – 268.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (br. 1H, COOH), 8.07 (t, *J* = 1.6 Hz, 1H, C**H**=N), 6.91 − 6.79 (m, 18H), 6.71 (d, *J* = 7.9 Hz, 2H) (phenyl−**H**), 4.04 (d, *J* = 1.8 Hz, 2H, C**H**$_2$), 3.68 (s, 1H, cage C−**H**),

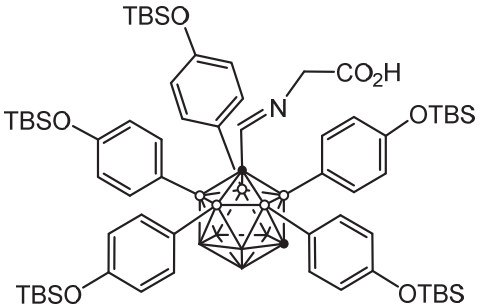
2.28 (s, 6H), 2.26(s, 6H), 2.25(s, 3H) (CH_3); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ 5.2 (1B), −1.1 (2B), −6.3 (3B), −10.7 (2B), −13.1 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.0 (**C**O_2H), 159.1 (**C**H=N), 139.3, 138.3, 138.0, 135.6, 135.5, 135.1, 128.6, 128.4, 128.3 (phenyl−**C**), 69.9, 59.3 (cage−**C**), 53.4 (**C**H_2), 21.42, 21.38, 21.36 (**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{39}B_{10}NH_{44}$ $[M-CO_2-H]^-$: 636.4480. Found: 636.4479. Elemental analysis (%) calcd for $C_{40}B_{10}NO_2H_{45}$: C, 70.66; H, 6.67; N, 2.06. Found: C, 70.33; H, 6.42; N, 2.21.



14c: Yield 58%. White solid. m. p. 153.7 – 153.9 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.08 (t, *J* = 1.5 Hz, 1H, C**H**=N), 7.10 (d, *J* = 7.6 Hz, 2H), 7.07 − 6.91 (m, 8H), 6.77 − 6.69 (m, 9H), 6.63 (d, *J* = 7.6 Hz, 1H) (phenyl−**H**), 4.03 (d, *J* = 1.6 Hz, 2H, C**H**$_2$), 3.74 (s, 1H, cage C−**H**), 2.054 (s, 6H), 2.046 (s, 3H), 2.04 (s, 6H) (C**H**$_3$); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ 5.5 (1B), −1.1 (2B), −6.4 (3B), −10.7 (2B), −13.0 (2B); $^{11}B\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −3.2 (5B), −16.2 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9 (**C**O_2H), 158.9 (**C**H=N), 136.9, 136.6, 136.6, 136.4, 136.4, 136.2, 136.1, 132.6, 132.1, 129.9, 129.1, 128.8, 127.4, 127.2, 127.1 (phenyl−**C**), 70.1, 59.1 (cage−**C**), 53.6 (**C**H_2), 21.41, 21.38, 21.36 (**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{37}B_{10}H_{41}$ $[M-CHNCH_2CO_2H]^-$: 593.4217. Found: 593.4216. Elemental analysis (%) calcd for $C_{40}B_{10}NO_2H_{45}$: C, 70.66; H, 6.67; N, 2.06. Found: C, 70.31; H, 6.39; N, 2.28.

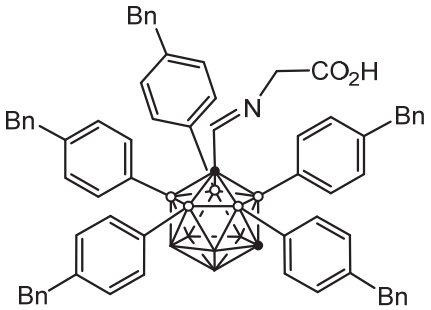


14d: Yield 53%. White solid. m. p. 263.7 – 264.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H, CO_2**H**), 8.00 (t, *J* = 1.8 Hz, 1H, C**H**=N), 6.92 (s, 2H), 6.87 (s, 2H), 6.84 (s, 1H), 6.57 (s, 8H), 6.48 (s, 2H) (phenyl−**H**), 3.97 (d, *J* = 1.7 Hz, 2H, C**H**$_2$), 3.69 (s, 1H, cage C−**H**), 2.03 (s, 12H), 2.02 (s, 18H) (C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 5.2 (2B), −1.5 (2B), −6.8 (2B), −11.1 (2B), −13.6 (2B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8 (**C**O_2H), 159.3 (**C**H=N), 136.7, 136.4, 136.2, 133.9, 133.7, 133.4, 130.6, 129.9, 129.6 (phenyl−**C**), 58.7 (cage−**C**), 53.6 (**C**H_2), 21.38,21.36, 21.34 (**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{45}B_{10}NO_2H_{54}$ $[M-H]^-$: 748.5163. Found: 748.5172. Elemental analysis (%) calcd for $C_{45}B_{10}NO_2H_{55}$: C, 72.06; H, 7.39; N, 1.87. Found: C, 72.36; H, 7.84; N, 2.31.

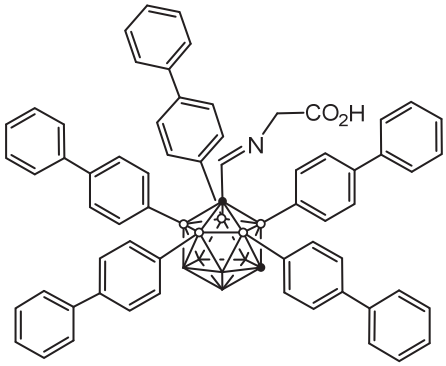


14e: Yield 55%. White solid. m. p. 124.7 – 125.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (t, *J* = 1.7 Hz, 1H, C**H**=N), 6.80 (d, *J* = 8.6 Hz, 4H), 6.76 (d, *J* = 8.6 Hz, 4H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 6.52 (d, *J* = 8.5 Hz, 2H) (phenyl−**H**), 3.99 (d, *J* = 1.7 Hz, 2H, C**H**$_2$), 3.62 (s, 1H, cage C−**H**), 0.962 (s, 18H), 0.956 (s, 27H) (OTBS−^{t}Bu), 0.174 (s, 12H), 0.166 (s, 12H), 0.161 (s, 6H) (OTBS−CH_3); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 4.7 (2B), −2.3 (2B), −6.6 (3B), −11.7 (3B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9 (**C**O_2H), 159.3 (**C**H=N), 156.9, 156.2, 156.0, 137.0, 137.0, 136.5, 119.6, 119.4, 119.3 (phenyl−**C**), 69.6, 59.4 (cage−**C**),

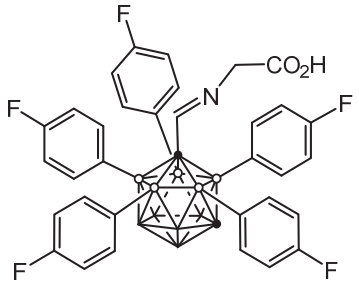
53.0 (**C**H_2), 25.83, 25.81, 25.79, 18.41, 18.39, 18.37 (OTBS−^{t}Bu), −4.26(OTBS−**C**H_3). HRMS (ESI, negative mode): *m/z* calcd for $C_{65}B_{10}NO_7Si_5H_{104}$ $[M-H]^-$: 1258.7688. Found: 1258.7688. $C_{64}B_{10}NO_5Si_5H_{104}$ $[M-CO_2-H]^-$: 1216.7767. Found: 1216.7776. Elemental analysis (%) calcd for $C_{65}B_{10}NO_7Si_5H_{105}$: C, 61.91; H, 8.39; N, 1.11. Found: C, 62.16; H, 8.18; N, 1.27.



14f: Yield 44%. White solid. m. p. 96.2 – 96.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (t, *J* = 1.5 Hz, 1H, C**H**=N), 7.38 − 7.13 (m, 25H), 7.01 − 6.76 (m, 20H) (phenyl−**H**), 4.08 (s, 2H, C**H**$_2$), 3.96 (d, *J* = 3.1 Hz, 10H, Bn−C**H**$_2$), 3.72 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 5.4 (1B), −1.1 (2B), −6.5 (2B), −10.9 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.3 (**C**O_2H), 158.7 (**C**H=N), 142.3, 142.3, 141.4, 141.1, 141.0, 140.9, 140.7, 135.7, 135.7, 135.6, 135.2, 133.1, 129.1, 129.0, 128.6, 128.5, 128.5, 128.3, 128.1, 126.3, 126.2, 126.1 (phenyl−**C**), 70.0, 59.4 (cage−**C**), 53.5 (**C**H_2), 41.69, 41.66 (Bn−**C**H_2). HRMS (ESI, negative mode): *m/z* calcd for $C_{69}B_{10}NH_{64}$ $[M-CO_2-H]^-$: 1016.6045. Found: 1016.6041. Elemental analysis (%) calcd for $C_{70}B_{10}NO_2H_{65}$: C, 79.29; H, 6.18; N, 1.32. Found: C, 78.96; H, 6.23; N, 1.27.



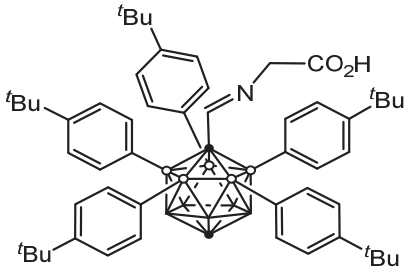
14g: Yield 42%. White solid. m. p. 140.2 – 140.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H, C**H**=N), 7.55 (m, 10H), 7.42 − 7.28 (m, 25H), 7.14 (d, *J* = 8.5 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 7.03 (d, *J* = 8.1 Hz, 2H) (phenyl−**H**), 4.71 (s, 2H, C**H**$_2$), 4.88 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ 5.7 (1B), −0.9 (2B), −6.4 (3B), −11.0 (4B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7 (**C**O_2H), 158.7 (**C**H=N), 141.8, 141.0, 140.8, 140.5, 140.5, 140.1, 136.2, 135.7, 128.9, 128.9, 127.8, 127.6, 127.5, 127.1, 126.8, 126.2, 126.1 (phenyl−**C**), 70.4, 59.9 (cage−**C**), 53.80 (**C**H$_2$). HRMS (ESI, positive mode): *m/z* calcd for $C_{64}B_{10}NH_{54}$ [M−CO_2−H]$^-$: 944.5265. Found: 944.5257. Elemental analysis (%) calcd for $C_{65}B_{10}NO_2H_{55}$: C, 78.84; H, 5.60; N, 1.41. Found: C, 78.48; H, 5.79; N, 1.32.



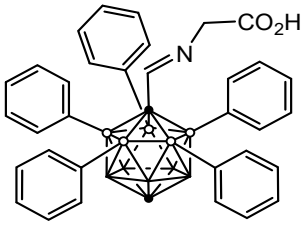
14h: Yield 55%. White solid. m. p. 331.8 – 332.6 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.19 (t, *J* = 1.2 Hz, 1H, C**H**=N), 7.24 (dd, *J* = 8.4, 5.9 Hz, 4H), 7.06 (dd, *J* = 8.4, 6.0 Hz, 4H), 6.98 (dd, *J* = 8.5, 6.0 Hz, 2H), 6.86 − 6.80 (m, 10H) (phenyl−**H**), 4.70 (s, 1H, cage C−**H**), 4.25 (s, 2H, C**H**$_2$); ^{19}F NMR {471 MHz, $(CD_3)_2CO$)}: δ −112.43, −113.64, −113.93; ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 5.2 (1B), −1.5 (3B), −6.7 (3B), −10.9 (2B), −13.1 (1B); ^{13}C NMR {126 MHz, $(CD_3)_2CO$)}: δ 169.4 (**C**O_2H), 164.5 (d, *J* = 41.1 Hz), 164.2, 162.6 (d, *J* = 40.0 Hz) 162.3 (phenyl−**C**), 157.6 (**C**H=N), 138.5 (d, *J* = 7.9 Hz), 138.0 (d, *J* = 7.7 Hz), 137.4 (d, *J* = 7.6 Hz), 114.5 (d, *J* = 7.2 Hz), 114.3 (d, *J* = 6.9 Hz) (phenyl−**C**), 71.3, 60.4 (cage−**C**), 54.8 (**C**H$_2$). HRMS (ESI, positive mode): *m/z* calcd for $C_{34}B_{10}NF_5H_{29}$ [M−CO_2−H]$^-$: 654.3329. Found: 654.3330. Elemental analysis (%) calcd for $C_{35}B_{10}NO_2F_5H_{30}$: C, 60.08; H, 4.32; N, 2.00. Found: C, 60.39; H, 4.04; N, 1.89.

2.5 Substrate scope for Pd-catalyzed B(2,3,4,5,6)-penta-arylation of *p*-carboranyl aldehydes

General procedure: A reaction tube (10 mL) with a magnetic stir bar was charged with *p*-carboranyl aldehyde (0.1 mmol, 17.2 mg), glycine (1.0 equiv. 0.1 mmol, 7.5 mg), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 ºC for 1h. Then, aryl iodide (6.0 equiv. 0.6 mmol), silver phosphate (6.0 equiv. 0.75 mmol, 313.9 mg), palladium acetate (10 mol %, 0.01 mmol, 2.3 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) were added and heated at 80 ºC for 36 hours. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum ether/CH_2Cl_2 or petroleum ether/ethyl acetate as the eluent to afford the product.



15a: Yield 64%. White solid. m. p. 305.2 – 305.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (br, 1H, COOH), 7.90 (t, *J* = 1.7 Hz, 1H, C**H**=N), 7.05 (d, *J* = 7.9 Hz, 10H), 6.83 (d, *J* = 8.0 Hz, 10H) (phenyl−**H**), 3.98 (d, *J* = 1.7 Hz, 2H, C**H**$_2$), 3.39 (s, 1H, cage C−**H**), 1.27 (s, 45H, ^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −2.9 (5B), −16.2 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.2 (**C**O$_2$H), 159.2 (**C**H=N), 169.2, 159.2, 151.3, 135.4, 128.7, 124.2 (phenyl−**C**), 79.1, 59.5, (cage−**C**), 58.8 (**C**H$_2$), 34.5 (**C**Me$_3$), 31.2 (^{t}Bu−**C**H$_3$). HRMS (ESI, positive mode): *m/z* calcd for $C_{54}B_{10}NH_{74}$ $[M-CO_2-H]^-$: 845.6794. Found: 845.6782. Elemental analysis (%) calcd for $C_{55}B_{10}NO_2H_{75}$: C, 74.20; H, 8.49; N, 1.57. Found: C, 74.29; H, 8.41; N, 1.64.



15b: Yield 56%. White solid. m. p. 301.5 – 301.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (br. 1H, COOH), 7.97 (t, *J* = 1.7 Hz, 1H, C**H**=N), 7.24 (tt, *J* = 7.6, 1.2 Hz, 5H), 7.05 (dd, *J* = 7.7, 7.7, Hz, 10H), 6.92 (d, *J* = 8.4 Hz, 10H) (phenyl−**H**), 3.96 (d, *J* = 1.7 Hz, 2H, C**H**$_2$), 3.46 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −3.0 (5B), −16.0 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9 (**C**O$_2$H), 158.9 (**C**H=N), 135.7, 131.5, 128.7, 127.6 (phenyl−**C**), 79.4, 60.1 (cage−**C**), 59.3 (**C**H$_2$). HRMS (ESI, negative mode): *m/z* calcd for $C_{35}B_{10}NO_2H_{34}$ $[M-H]^-$: 608.3598. Found: 608.3605. Elemental analysis (%) calcd for $C_{35}B_{10}NO_2H_{35}$: C, 68.94; H, 5.79; N, 2.30. Found: C, 68.87; H, 5.68; N, 2.23.

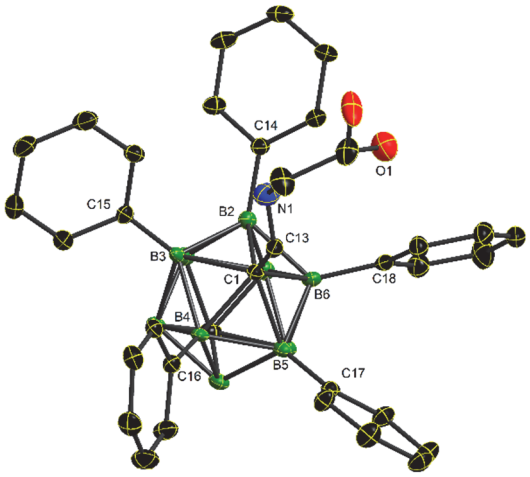
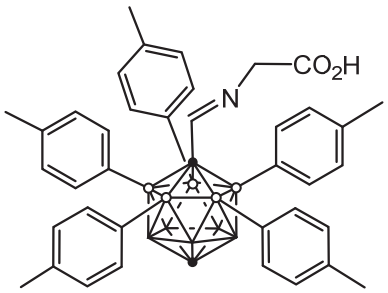
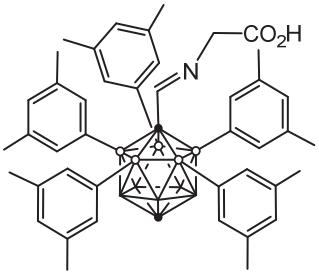


Figure S13. X-Ray structure of **15b** (ellipsoids at 30% probability, solvent and H atoms were omitted for clarity). Selected bond distances [Å]: C1−C13 1.512(6), C13−N1 1.197(5), C1−B2 1.753(6), C1−B3 1.762(6), C1−B4 1.755(6), C1−B5 1.761(6), C1−B6 1.755(6), B2−C14 1.570(6), B3−C15 1.581(6), B4−C16 1.580(7), B5−C17 1.577(6), B6−C18 1.576(6).



15c: Yield 72%. White solid. m. p. 280.1 – 280.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H, C**H**=N), 6.98 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 3H), 6.79 (d, *J* = 7.2 Hz, 5H), 6.71 (dd, *J* = 8.4, 2.0 Hz, 5H), 6.56 (d, *J* = 1.6 Hz, 5H) (phenyl−**H**), 3.89 (s, 2H, C**H**$_2$), 3.40 (s, 1H, cage C−**H**), 3.28 (s, 15H, C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.9 (5B), −15.7 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7 (**C**O$_2$H), 158.2 (**C**H=N), 157.4, 133.5, 129.0, 128.3, 120.9, 115.1 (phenyl−**C**), 80.2, 62.4 (cage−**C**), 59.5 (**C**H$_2$), 55.0 (**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{40}B_{10}NO_2H_{44}$ $[M-H]^-$: 678.4381. Found: 678.4385. Elemental analysis (%) calcd for $C_{40}B_{10}NO_2H_{45}$: C, 70.66; H, 6.67; N, 2.06. Found: C, 70.43; H, 6.76; N, 2.11.



15d: Yield 65%. White solid. m. p. 252.1 – 252.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (br. 1H, COOH), 7.82 (t, *J* = 2.0 Hz, 1H, C**H**=N), 6.89 (s, 5H), 6.58 (s, 10H) (phenyl−**H**), 3.87 (d, *J* = 1.8 Hz, 2H, C**H**$_2$), 3.40 (s, 1H, cage C−**H**), 2.04 (s, 30H, C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −3.2 (5B), −16.2 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0 (**C**O$_2$H), 159.5 (**C**H=N), 136.3, 134, 131.6, 129.8 (phenyl−**C**), 79.6, 60.0 (cage−**C**), 58.5 (**C**H$_2$), 21.3 (**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{45}B_{10}NO_2H_{54}$ $[M-H]^-$: 748.5163. Found: 748.5166. Elemental analysis (%) calcd for $C_{45}B_{10}NO_2H_{55}$: C, 72.06; H, 7.39; N, 1.87. Found: C, 72.32; H, 7.57; N, 2.11.

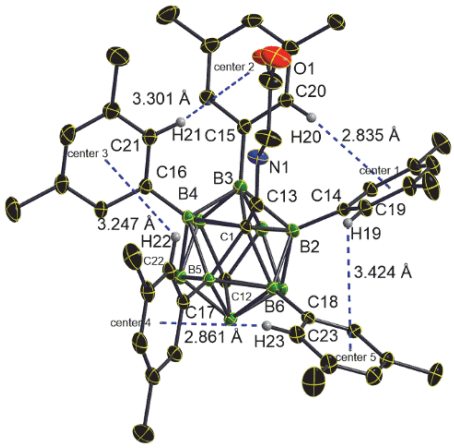
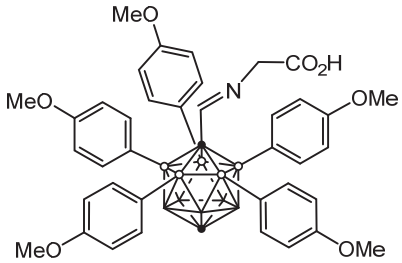
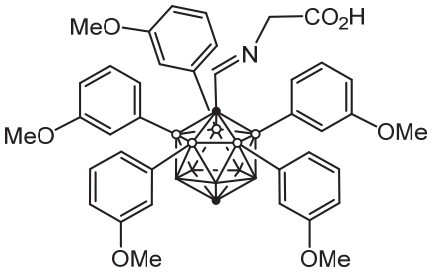


Figure S14. X-Ray structure of **15d** (ellipsoids at 30% probability and H atoms were omitted for clarity). Selected bond and C−H···π hydrogen bond (blue dotted line) distances [Å]: C1−C13 1.531(6), C13−N1 1.307(6), C1−B2 1.730(6), C1−B3 1.752(6), C1−B4 1.749(6), C1−B5 1.836(6), C1−B6 1.657(6), B2−C14 1.637(7), B3−C15 1.579(6), B4−C16 1.495(6), B5−C17 1.584(7), B6−C18 1.553(6), C19−H19···center 5 3.424, C20−H20···center 1 2.835, C21−H21···center 2 3.301, C22−H22···center 3 3.247, C23−H23···center 4 2.861.

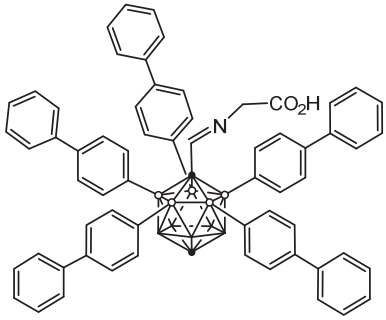


15e: Yield 80%. White solid. m. p. 298.8 – 299.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (s, 1H, C**H**=N), 6.99 (d, *J* = 8.3 Hz, 10H), 6.55 (d, *J* = 8.4 Hz, 10H) (phenyl−**H**), 3.75 (s, 2H, C**H**$_2$), 3.69 (s, 1H, cage C−**H**), 3.53 (s, 15H, OC**H**$_3$); ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ −4.2 (5B), −17.4 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.3 (**C**O$_2$H), 160.0 (**C**H=N), 159.9, 159.4, 156.7, 137.2, 136.9, 136.5, 130.6, 123.9, 113.5, 113.3, 113.2, 113.1, 112.9 (phenyl−**C**), 79.5, 65.2 (cage−**C**), 58.5 (**C**H$_2$), 54.9 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{40}B_{10}NO_7H_{44}$ [M−H]$^-$: 758.4126. Found:

758.4137. Elemental analysis (%) calcd for $C_{40}B_{10}NO_7H_{45}$: C, 63.22; H, 5.97; N, 1.84. Found: C, 63.58; H, 5.69; N, 1.75.

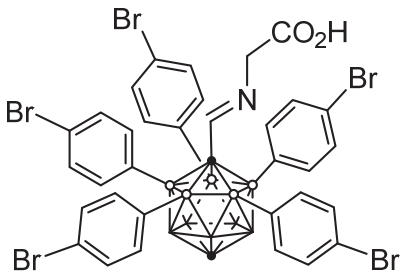


15f: Yield 68%. White solid. m. p. 271.5 – 272.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H, C**H**=N), 6.98 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 3H), 6.79 (d, *J* = 7.6 Hz, 5H), 6.71 (dd, *J* = 8.0, 2.0 Hz, 5H), 6.56 (d, *J* = 1.6 Hz, 5H) (phenyl−**H**), 3.89 (s, 2H, C**H**$_2$), 3.40 (s, 1H, cage C−**H**), 3.28 (s, 15H, OC**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.9 (5B), −15.7 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7 (**C**O$_2$H), 158.2 (**C**H=N), 157.4, 133.5, 129.0, 128.3, 120.9, 115.1 (phenyl−**C**), 80.2, 62.4, (cage−**C**), 59.5 (**C**H$_2$), 55.0 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{40}B_{10}NO_7H_{44}$ $[M-H]^-$: 758.4126. Found: 758.4133. Elemental analysis (%) calcd for $C_{40}B_{10}NO_7H_{45}$: C, 63.22; H, 5.97; N, 1.84. Found: C, 63.47; H, 6.32; N, 1.93.



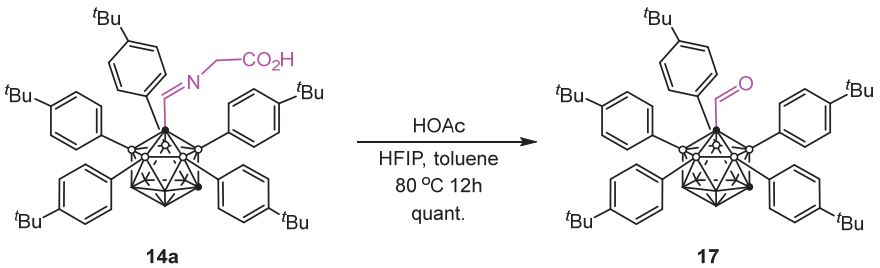
15g: Yield 30%. White solid. m. p. 145.9 – 146.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (t, *J* = 1.8 Hz, 1H, C**H**=N), 7.56 (d, *J* = 7.6, 10H), 7.41 − 7.29 (m, 25H), 7.10 (d, *J* = 8.4, 10H) (phenyl−**H**), 4.02 (d, *J* = 1.6 Hz, 2H, C**H**$_2$), 3.55 (s, 1H, cage C−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.4 (5B), −15.7 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.3 (**C**O$_2$H), 158.8 (**C**H=N), 141.2, 141.1, 140.7, 140.5, 140.4, 138.7, 136.3, 130.0, 129.9, 128.94, 128.87, 128.7, 128.0, 127.6, 127.2, 127.1, 126.9, 126.3, 126.1

(phenyl−**C**), 79.6, 60.8, (cage−**C**), 59.9 (d, J = 31.8 Hz, **C**H_2). HRMS (ESI, negative mode): *m/z* calcd for $C_{65}B_{10}O_2NH_{54}$ $[M-H]^-$: 988.5163. Found: 988.5167. Elemental analysis (%) calcd for $C_{65}B_{10}NO_2H_{55}$: C, 78.84; H, 5.60; N, 1.41. Found: C, 78.39; H, 5.34; N, 1.62.



15h: Yield 51%. White solid. m. p. 159.6 – 161.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H, C**H**=N), 7.17 (d, J = 8.1 Hz, 10H), 6.83 (d, J = 8.1 Hz, 10H) (phenyl−**H**), 3.91 (s, 2H, C**H**$_2$), 3.40 (s, 1H, cage C−**H**); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.7 (5B), -16.2 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.4 (**C**H=N), 137.3, 136.5, 130.6, 123.6, (phenyl−**C**), 79.8, 62.2 (cage−**C**), 59.4 (**C**H_2). HRMS (ESI, negative mode): *m/z* calcd for $C_{34}B_{10}NBr_5H_{29}$ $[M-CO_2-H]^-$: 959.9164. Found: 959.9163. Elemental analysis (%) calcd for $C_{35}B_{10}NO_2Br_5H_{30}$: C, 41.86; H, 3.01; N, 1.39. Found: C, 41.07; H, 3.36; N, 1.18.

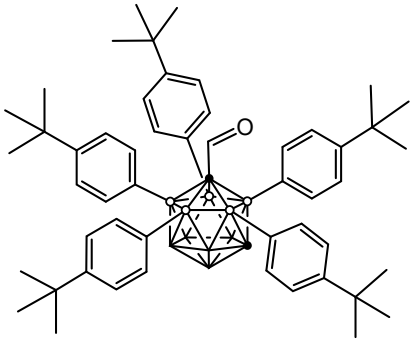
2.6 Synthetic utilities



Scheme S9. Removing glycine.

Removing of glycine: A reaction tube (10 mL) with a magnetic stir bar was charged with **14a** (0.1 mmol, 89.0 mg)), HFIP (0.8 mL), toluene (0.2 mL) and HOAc (0.08 mL). The reaction mixture was allowed to stir at 80 °C for 12h. Upon completion, the reaction mixture was treated with 5 mL of water. The organic layer was extracted with hexanes

for three times (3 × 10 mL). The crude reaction mixture was purified on preparative TLC using petroleum ether/CH_2Cl_2 (v/v = 5/1) as the eluent to afford the desired product **17** (82.5 mg).



17: Yield 99%. White solid. m. p. 302.3 – 302.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H, C**H**O), 7.04 − 7.01 (m, 10H), 6.88 (d, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 6.79 (d, *J* = 8.4 Hz, 2H) (phenyl−**H**), 3.67 (s, 1H, cage C−**H**), 1.24 (s, 45H, ^{t}Bu−C**H**$_3$); ^{11}B NMR (160 MHz, $CDCl_3$): δ 3.5 (1B), −1.4 (1B), −3.9 (2B), −5.3 (2B), −6.1 (2B), −7.5 (2B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.0 (**C**HO), 152.0, 151.1, 150.9, 135.5, 135.3, 135.0, 124.4, 124.3, 124.2 (phenyl−**C**), 73.9, 53.5 (cage−**C**), 34.62, 34.56, 34.54 (^{t}Bu−**C**Me$_3$), 31.33, 31.26 (^{t}Bu−**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{53}B_{10}OH_{71}$ $[M-H]^-$: 833.6511. Found: 833.6513. Elemental analysis (%) calcd for $C_{53}B_{10}OH_{72}$: C, 76.40; H, 8.71. Found: C, 76.33; H, 8.79.

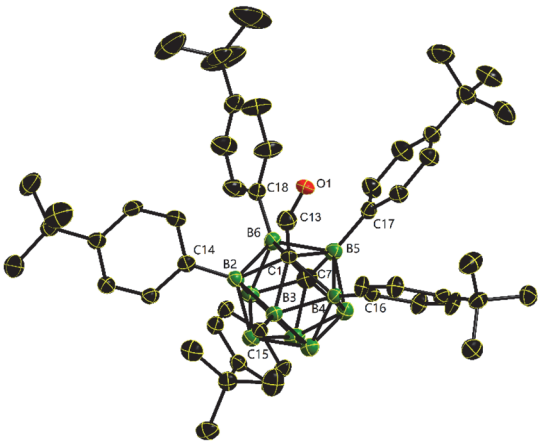
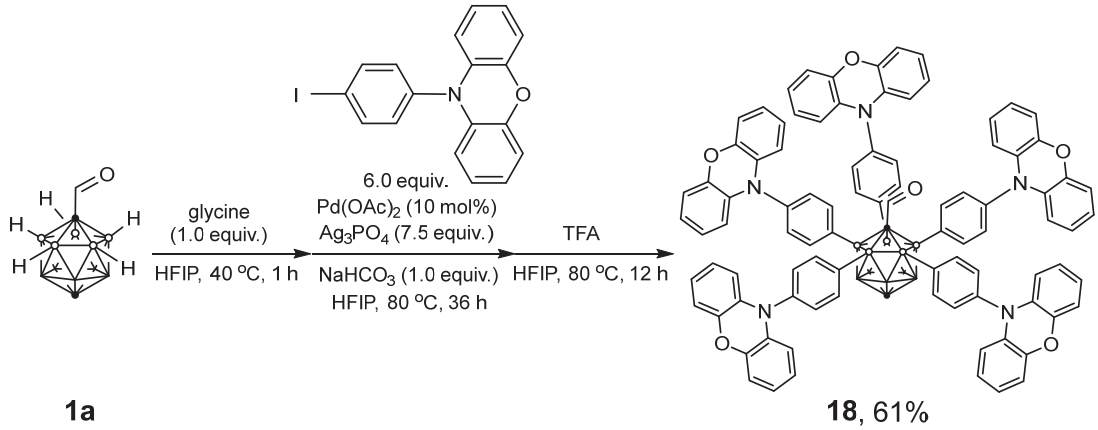


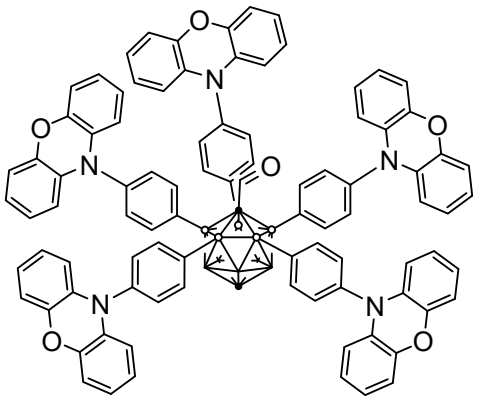
Figure S15. X-Ray structure of **17** (ellipsoids at 30% probability, H atoms and solvent were omitted for clarity). Selected bond distances [Å] for **17**: C1−C13 1.518(4),

C13−O1 1.104(4), C1−B2 1.756(4), C1−B3 1.762(4), C1−B4 1.726(4), C1−B5 1.755(4), C1−B6 1.748(4), B2−C14 1.560(4), B3−C15 1.577(4), B4−C16 1.582(4), B5−C17 1.569(4), B6−C18 1.577(4).



Scheme S10. Synthesis of **18** from **1a**

Synthesis of 18 from 1a: A reaction tube (10 mL) with a magnetic stir bar was charged with *p*-carboranyl aldehyde (0.1 mmol, 17.2 mg), glycine (1.0 equiv. 0.1 mmol, 7.5 mg), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 ºC for 1h. Then, aryl iodide (6.0 equiv. 0.6 mmol), silver phosphate (6.0 equiv. 0.75 mmol, 313.9 mg), palladium acetate (10 mol %, 0.01 mmol, 2.3 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) were added and heated at 80 ºC for 36 hours. Upon completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was transferred to a reaction tube (10 mL) with a magnetic stir bar. Then HFIP (1.2 mL) and TFA (0.8 mL) were added. The reaction mixture was allowed to stir at 80 ºC for 12h. Upon completion, the reaction mixture was treated with 5 mL of water. The organic layer was extracted with ethyl acetate for three times (3 × 10 mL). The crude reaction mixture was purified on preparative TLC using petroleum ether/toluene (v/v = 10/1) as the eluent to afford the desired product **18** (89.0 mg).



18: Yield 61%. Yellow solid. m. p. 404.1 – 405.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H, C**H**O), 7.38 – 7.31 (m, 10H), 7.20 – 7.15 (m, 10H), 6.66 (dd, *J* = 7.9, 1.5 Hz, 10H), 6.58 (td, *J* = 7.6, 1.4 Hz, 10H), 6.46 (td, *J* = 7.7, 1.5 Hz, 10H), 5.85 (dd, *J* = 8.0, 1.5 Hz, 10H) (phenyl−**H**), 3.68 (s, 1H, cage C−**H**); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ -3.3 (7B), -15.2 (3B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.9 (**C**HO), 144.1, 140.1, 138.2, 134.0, 130.8, 130.2, 123.5, 121.7, 115.7, 113.1 (phenyl−**C**), 82.5, 60.5 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{93}B_{10}N_5O_6H_{66}$ $[M-H]^-$: 1456.6022. Found: 1456.6025. Elemental analysis (%) calcd for $C_{93}B_{10}N_5O_6H_{67}$: C, 76.58; H, 4.63; N, 4.80. Found: C, 76.21; H, 4.14; N, 4.38.

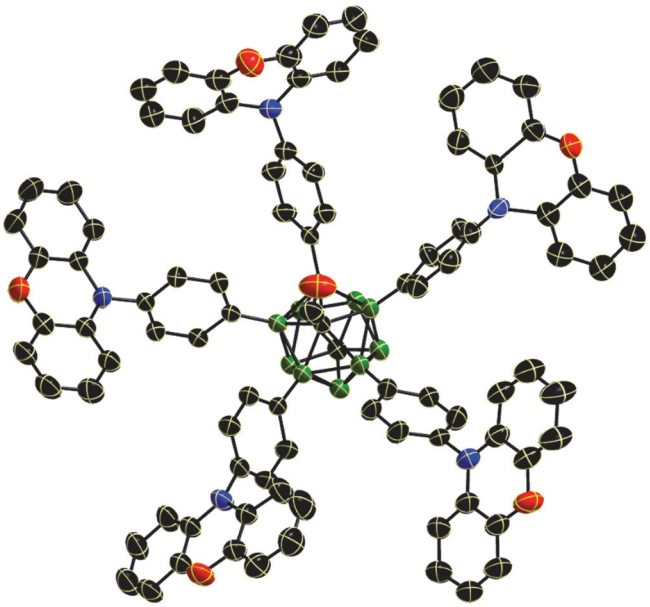


Figure S16. X-Ray structure of **18** (ellipsoids at 30% probability, H atoms and solvent were omitted for clarity).

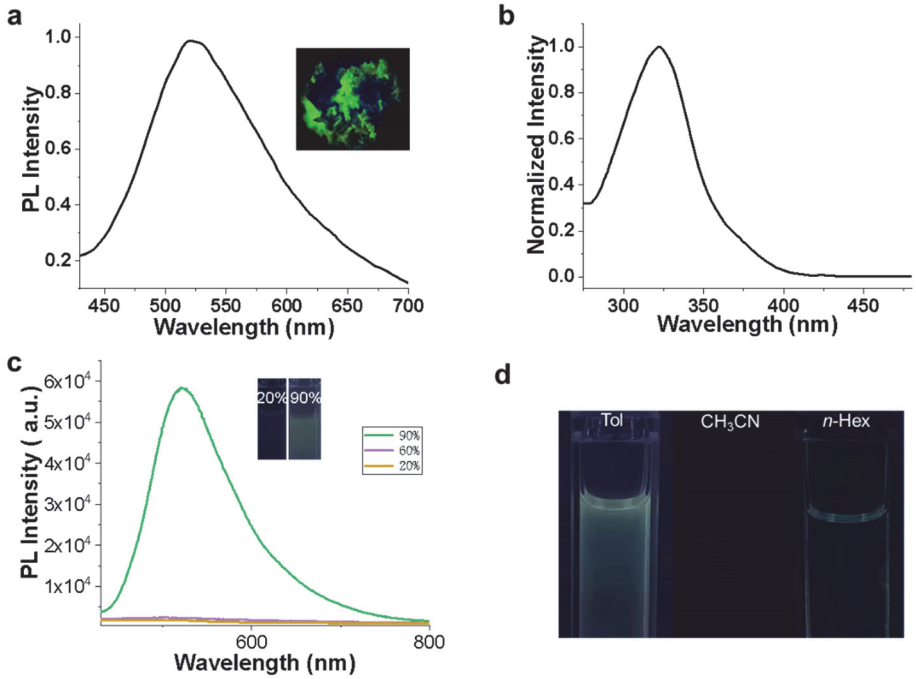
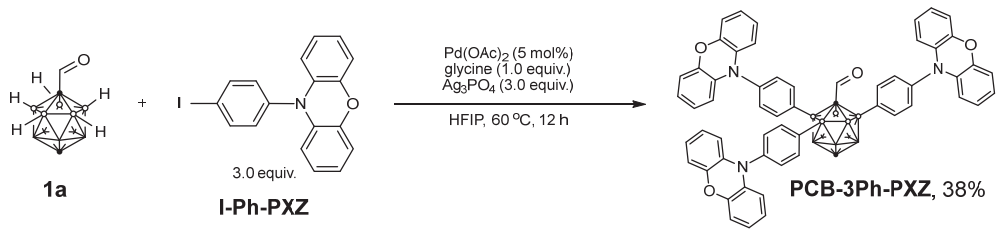


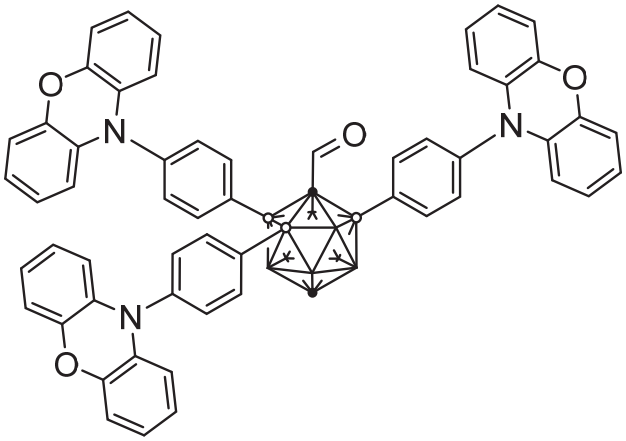
Figure S17. Photophysical properties of **18**. **a**: Luminescent photograph taken under UV light (365 nm), and fluorescence spectrum observed in the solid state under ambient condition (λ_{ex} = 340 nm), the solid-state quantum yield of 12.3%; **b**: Normalized absorption spectrum in THF (1.0×10^{-5} M) under ambient condition; **c**: Luminescent photographs taken under UV light (365 nm) and fluorescence spectra with different water volume fraction (V_{H2O} / V_{THF} %) of **17** (1.0×10^{-5} M, λ_{ex} = 340 nm) under ambient condition; **d**: Luminescence photographs of **17** in different solvents taken under UV light (365 nm).

Note: In order to further study the effect of poly-arylation on lumimescence, we synthesized the tri-arylated compound PCB-3Ph-PXZ (below) for comparison with compound 18.



Scheme S11. Synthesis of **PCB-3Ph-PXZ** from **1a**.

Synthesis of PCB-3Ph-PXZ from 1a: **PCB-3Ph-PXZ** was prepared by a similar procedure to **7** using 3.0 equiv. of **I-Ph-PXZ**, 3.0 equiv. of Ag_3PO_4 at 60 °C for 12h. The crude reaction mixture was purified on preparative TLC using petroleum ether/DCM (v/v = 10/1) as the eluent to afford the desired product **PCB-3Ph-PXZ** (35.9 mg).



PCB-3Ph-PXZ: Yield 38%. Light yellow solid. m. p. 155.8 – 161.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H, C**H**O), 7.93 – 7.84 (m, 2H), 7.67 – 7.56 (m, 4H), 7.38 – 7.31 (m, 2H), 7.26 – 7.21 (m, 4H), 6.76 – 6.57 (m, 14H), 6.54 (td, *J* = 7.6, 1.7 Hz, 4H), 5.93 (dd, *J* = 7.8, 1.6 Hz, 2H), 5.88 (dd, *J* = 7.9, 1.5 Hz, 4H) (phenyl−**H**), 3.52 (s, 1H, cage C−**H**); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.9 (4B), -15.7 (6B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.2 (**C**HO), 144.1, 140.3, 140.0, 138.0, 137.8, 137.6, 134.3, 134.1, 130.4, 130.3, 123.4, 123.4, 121.6, 121.6, 115.6, 113.4, 113.2 (phenyl−**C**), 86.7, 65.2 (cage−**C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{57}B_{10}N_3O_4H_{44}$ $[M-H]^-$: 942.4340. Found: 942.4333. Elemental analysis (%) calcd for $C_{57}B_{10}N_3O_4H_{45}$: C, 72.52; H, 4.80; N, 4.45. Found: C, 71.86; H, 5.04; N, 4.26.

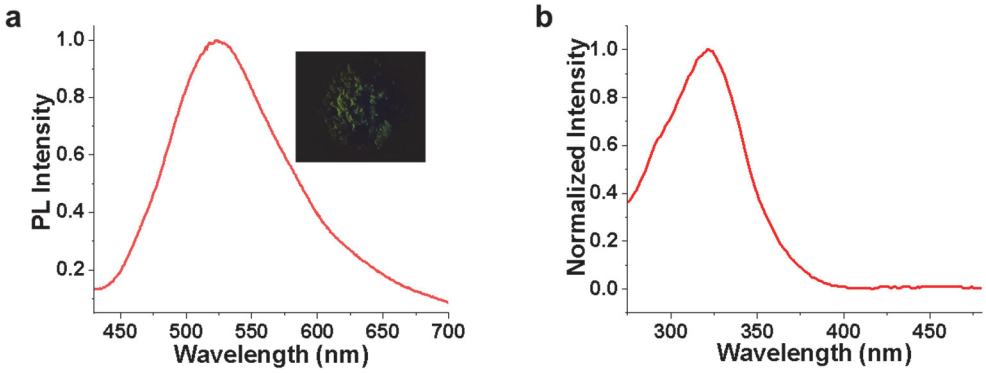
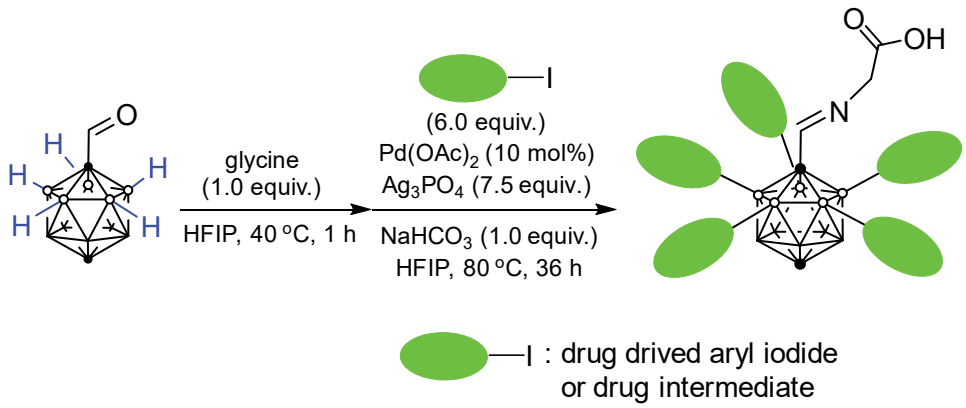


Figure S18. Photophysical properties of **PCB-3Ph-PXZ**. **a**: Luminescent photograph taken under UV light (365 nm), and fluorescence spectrum observed in the solid state under ambient condition (λ_{ex} = 340 nm), the solid-state quantum yield of 0.07%; **b**: Normalized absorption spectrum in THF (1.0×10^{-5} M) under ambient condition.

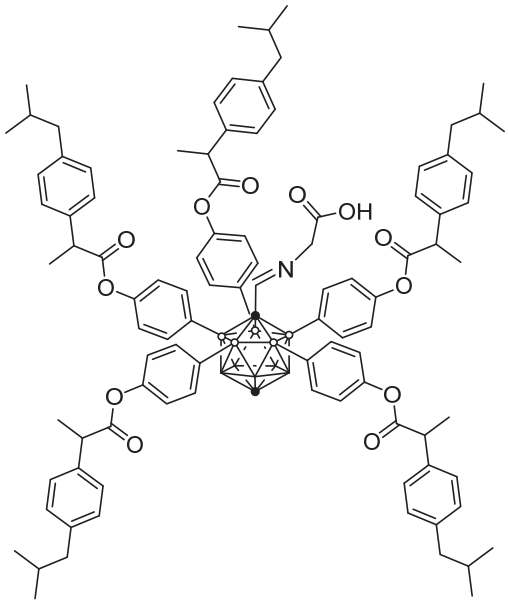
Note: penta-Arylation can enhance luminescence in comparison to tri-arylation.



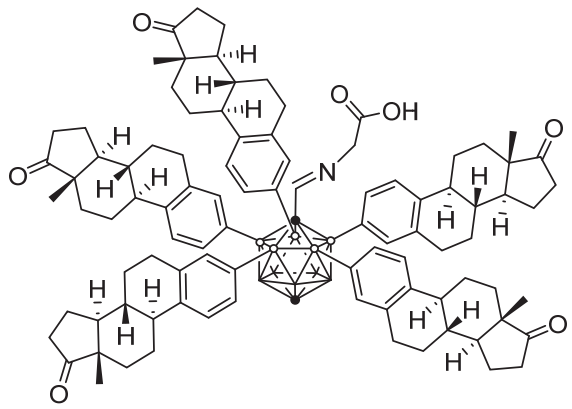
Scheme S12. Late stage modification of drug or drug intermediate

Late stage modification of drug or drug intermediate: A reaction tube (10 mL) with a magnetic stir bar was charged with *p*-carboranyl aldehyde (0.1 mmol, 17.2 mg), glycine (1.0 equiv. 0.1 mmol, 7.5 mg), HFIP (1.0 mL) under Ar atmosphere and allowed to stir at 40 °C for 1h. Then, drug derived or drug intermediated aryl iodide (6.0 equiv. 0.6 mmol), silver phosphate (6.0 equiv. 0.75 mmol, 313.9 mg), palladium acetate (10 mol %, 0.01 mmol, 2.3 mg), sodium bicarbonate (1.0 equiv. 0.1 mmol, 8.4 mg), HFIP (1.0 mL) were added and heated at 80 °C for 36 hours. Upon completion, the reaction

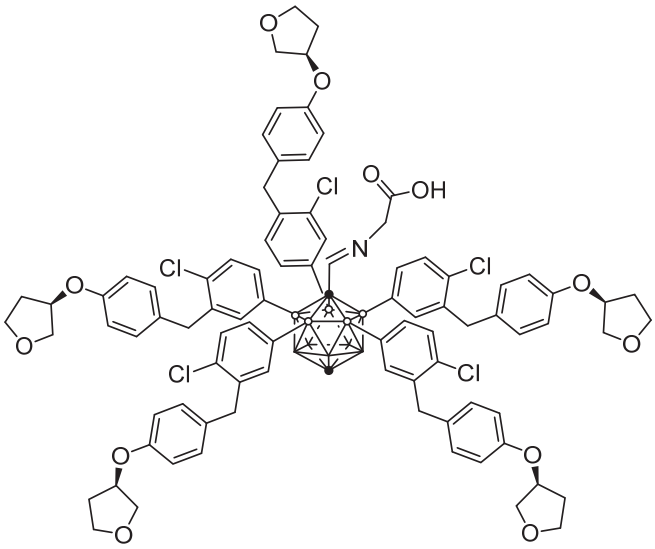
mixture was cooled to room temperature and diluted with 10 mL of EtOAc. The mixture was filtered through a silica gel plug and concentrated in *vacuo*. The crude reaction mixture was purified on PTLC using petroleum ether/ethyl acetate as the eluent to afford the product.



19: Yield 61%. White solid. m. p. 78.5 – 79.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (t, *J* = 1.4 Hz, 1H, C**H**=N), 7.33 – 7.27 (m, 10H), 7.20 – 7.14 (m, 10H), 6.94 – 6.85 (m, 10H), 6.78 – 6.68 (m, 10H) (phenyl−**H**), 3.88 – 3.92 (q, *J* = 7.1 Hz, 5H, OCOC**H**CH_3), 3.85 (d, *J* = 1.4 Hz, 2H, NC**H**$_2$$CO_2$H), 3.39 (s, 1H, cage C−**H**), 2.50 (d, *J* = 7.2 Hz, 10H, PhC**H**$_2$^{i}Pr), 1.91 (hept, *J* = 6.8 Hz, 5H, ^{i}Pr−C**H**), 1.61 (d, *J* = 7.2 Hz, 15H, OCOCHC**H**$_3$), 0.95 (d, *J* = 6.6 Hz, 30H, ^{i}Pr−C**H**$_3$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ -3.3 (5B), -14.9 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2 (O**C**OCHCH_3), 168.4 (NCH$_2$**C**O_2H), 157.0 (**C**H=N), 151.2, 140.8, 137.2, 136.9, 129.6, 128.4, 127.3, 120.3 (phenyl−**C**), 80.1, 61.0 (cage−**C**), 59.6 (N**C**H$_2$$CO_2$H), 45.3, 45.1, 30.2, 22.5, 18.6 (alkyl **C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{100}B_{10}NO_{12}H_{114}$ [M−H]$^{-}$: 1629.9383. Found: 1629.9372. Elemental analysis (%) calcd for $C_{100}B_{10}NO_{12}H_{115}$: C, 73.64; H, 7.11; N, 0.86. Found: C, 73.29; H, 7.69; N, 0.53.

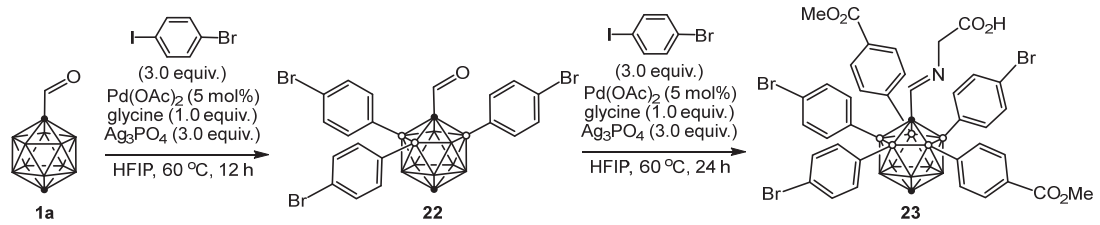


20: Yield 63%. m. p. 248.5 – 251.3 °C. White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (t, *J* = 1.8 Hz, 1H, C**H**=N), 7.01 (d, *J* = 8.1 Hz, 5H), 6.79 (d, *J* = 7.9 Hz, 5H), 6.52 (s, 5H) (phenyl−**H**) 3.87 (d, *J* = 1.8 Hz, 2H, NC**H**$_2$CO$_2$H), 3.39 (s, 1H, cage C−**H**), 2.61 – 2.22 (m, 25H), 2.19 – 2.09 (m, 5H), 2.08 – 2.00 (m, 5H), 1.97 – 1.87 (m, 10H), 1.66 – 1.42 (m, 25H), 1.40 – 1.30 (m, 5H), 0.91 (s, 15H) (estrone alkyl C−**H**); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -4.7 (5B), -16.8 (5B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 220.9 (estrone **C**=O), 169.2 (NCH$_2$**C**O$_2$H), 159.4 (**C**H=N), 140.0, 136.9, 135.0, 133.3, 128.9, 124.4 (phenyl−**C**), 79.3, 59.9 (cage−**C**), 58.7 (N**C**H$_2$CO$_2$H), 50.6, 48.1, 44.5, 38.2, 35.9, 31.7, 29.4, 26.6, 25.7, 21.7, 14.0 (estrone alkyl **C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{95}B_{10}NO_7H_{114}$ $[M-H]^-$: 1489.9638. Found: 1489.9630. Elemental analysis (%) calcd for $C_{95}B_{10}NO_7H_{115}$: C, 76.53; H, 7.77; N, 0.94. Found: C, 76.19; H, 7.34; N, 1.31.



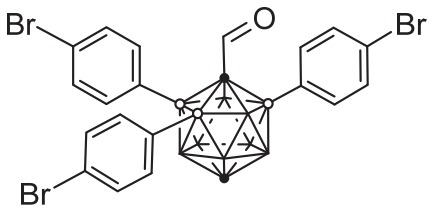
21: Yield 41%. m. p. 113.7 – 114.9 °C. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, *J* = 1.3 Hz, 1H, C**H**=N), 7.07 (d, *J* = 8.2 Hz, 5H), 6.82 (dd, *J* = 8.2, 1.9 Hz, 5H),

6.75 – 6.54 (m, 25H) (phenyl−**H**), 4.83 (ddt, *J* = 6.1, 4.3, 2.2 Hz, 5H, O**C**H), 4.01 – 3.83 (m, 20H), 3.68 (s, 10H) (C**H**$_2$), 3.32 (s, 1H, cage C−**H**), 3.24 (d, *J* = 16.4, 1H), 3.14 – 3.09 (d, *J* = 16.4, 1H) (NC**H**$_2$CO$_2$H), 2.14 (m, 10H, C**H**$_2$); ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -3.0 (5B), -15.9 (5B); ^{13}C NMR (101 MHz, CDCl$_3$): δ 169.2 (**C**=O), 157.8 (**C**H=N), 155.8, 138.4, 137.8, 135.2, 134.9, 131.8, 129.7, 128.8, 115.3 (phenyl−**C**), 79.6 (cage−**C**), 77.2, 73.0, 67.3 (alkyl **C**), 59.3 (cage−**C**), 59.1 (N**C**H$_2$CO$_2$H), 38.4, 33.1, 29.5 (alkyl **C**). HRMS (ESI, negative mode): *m/z* calcd for $C_{90}B_{10}NO_{12}Cl_5H_{89}$ [M−H]$^-$: 1661.5840. Found: 1661.5848. Elemental analysis (%) calcd for $C_{90}B_{10}NO_{12}Cl_5H_{90}$: C, 65.00; H, 5.46; N, 0.84. Found: C, 65.51; H, 5.01; N, 0.73.



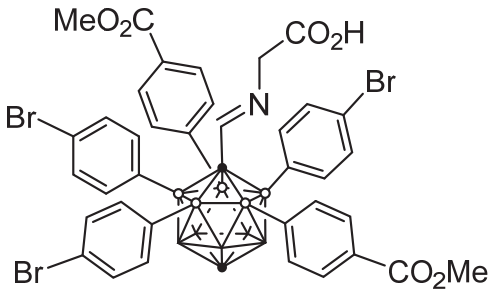
Scheme S13. Stepwise penta-arylation of **1a**.

Stepwise penta-arylation of 1a: **22** were prepared by a similar procedure to **7** using 3.0 equiv. of 1-Bromo-4-iodobenzene, 3.0 equiv. of Ag_3PO_4 at 60 °C for 12h. **23** were also prepared by a similar procedure to **7** using 3.0 equiv. of 1-Bromo-4-iodobenzene, 3.0 equiv. of Ag_3PO_4 at 60 °C for 24h

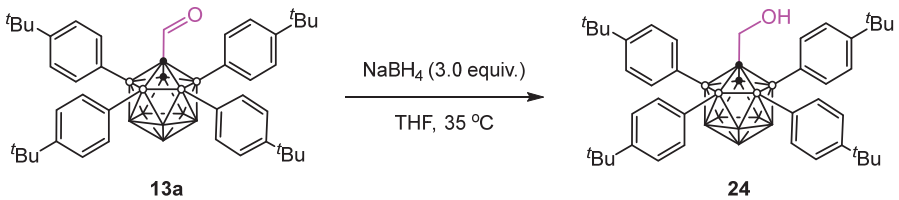


22 (purity: 78%, based on ^{1}H NMR): Yield 41%. White solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.64 (s, 1H, C**H**O), 7.45 (m, *J* = 2.4 Hz, 6H), 7.39 – 7.32 (m, 4H), 7.19 – 7.12 (m, *J* = 8.2 Hz, 4H) (phenyl−**H**), 3.39 (s, 2H, cage C−**H**); ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -3.3 (3B), -15.8 (7B); ^{13}C NMR (101 MHz, CDCl$_3$): δ 185.9 (**C**HO), 136.8, 136.6, 131.4, 131.2, 128.0, 124.6, 124.2 (phenyl−**C**), 85.5, 65.0 (cage−**C**).

HRMS (ESI, negative mode): *m/z* calcd for $C_{21}B_{10}OBr_3H_{21}$ $[M-H]^-$: 635.0052. Found: 635.0056.



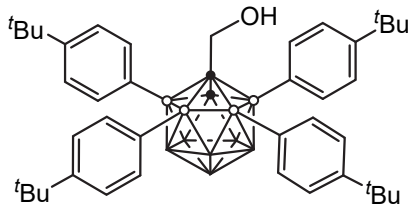
23: Yield 56%. White solid. m. p. 159.6 – 161.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (t, *J* = 1.3 Hz, 1H, C**H**=N), 7.76 – 7.69 (m, 4H), 7.21 – 7.12 (m, 6H), 7.09 – 7.01 (m, 4H), 6.83 – 6.71 (m, 6H) (phenyl−**H**), 4.01 (d, *J* = 1.2 Hz, 2H, C**H**$_2$), 3.87 (s, 6H, OC**H**$_3$), 3.47 (s, 1H, cage C−**H**); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 8.3 (1B), -2.2 (1B), -13.7 (2B), -14.7 (2B), -15.7 (2B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 167.8 (**C**=O), 155.9 (**C**H=N), 137.5, 137.4, 135.9, 130.7, 130.6, 129.9, 128.2, 123.8, 123.7 (phenyl−**C**), 80.4, 62.8 (cage−**C**), 59.7 (**C**H$_2$), 52.4 (O**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{39}B_{10}NO_6Br_3H_{35}$ $[M-H]^-$: 962.0982. Found: 962.0981. Elemental analysis (%) calcd for $C_{39}B_{10}NO_6Br_3H_{36}$: C, 48.67; H, 3.77; N, 1.46. Found: C, 48.18; H, 3.36; N, 1.13.



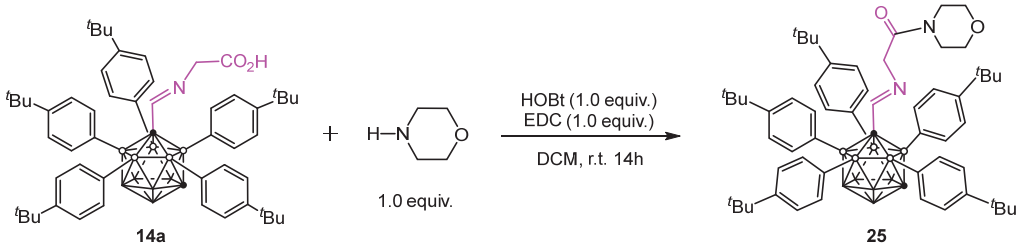
Scheme S14. Reduction of **13a** to **24**.

Reduction of 13a with NaBH$_4$: **13a** (0.1 mmol, 40.0 mg), NaBH$_4$ (3.0 equiv. 0.3 mmol, 11.3 mg) and THF (2.0 mL) were added into a reaction tube (10 mL) and allowed to stir at 35 °C for 4 h. Upon completion as monitored by TLC, the reaction mixture was treated with 5 mL of saturated NaCl solution. The organic layer was extracted with hexanes for three times (3 × 10 mL). The crude reaction mixture was purified on

preparative TLC using hexanes/CH_2Cl_2 (v/v = 5/1) as the eluent to afford the desired product **24** (68.2 mg).

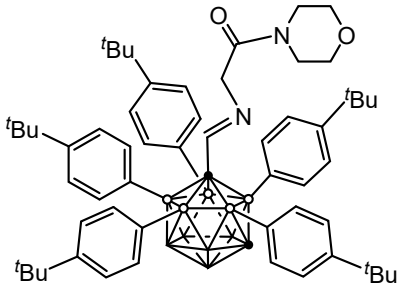


24: Yield 97%. White solid. m. p. 336.0 – 336.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 4H), 6.92 (d, *J* = 8.5 Hz, 4H) (phenyl−**H**), 4.71 (s, 1H, cage C−**H**), 4.47 (d, *J* = 7.9 Hz, 2H, C**H**$_2$), 1.30 (s, 18H), 1.26 (s, 18H) (^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.8 (4B), −5.0 (3B), −10.4 (2B), −14.6 (1B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 150.9, 135.1, 134.1, 125.5, 124.4 (phenyl−**C**), 72.3, 57.9 (**C**H$_2$), 57.7 (cage−**C**), 34.6, 34.4 (^{t}Bu−**C**Me$_3$), 31.22, 31.17 (^{t}Bu−**C**H$_3$). HRMS (ESI, negative mode): *m/z* calcd for $C_{43}B_{10}OH_{61}$ [M−H]$^-$: 702.5695. Found: 702.5692. Elemental analysis (%) calcd for $C_{43}B_{10}OH_{62}$: C, 73.46; H, 8.89. Found: C, 73.40; H, 8.74.



Scheme S15. Amidation of **14a** with morpholine.

Amidation of carboxylic acids: To a solution of morpholine (1.0 equiv., 0.1 mmol, 8.7 mg), hydroxybenzotrizole (HOBt, 1.0 equiv., 0.1 mmol, 13.5 mg) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 1.0 equiv., 0.1 mmol, 19.2 mg) in DCM (0.1 M), **14a** (0.1 mmol, 89.0 mg) was added and the resulting solution was stirred at room temperature for 14 h. After this time, the crude reaction mixture was purified on preparative TLC using petroleum ether/ethyl acetate as the eluent to afford the desired product **25** (93.2 mg).



25: Yield 97%. White solid. m. p. 294.3 – 294.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 1H, C**H**=N), 7.04 − 7.00 (m, 10H), 6.96 − 6.85 (m, 10H) (phenyl−**H**), 4.17 (s, 2H, N−C**H**$_2$−CO), 3.62 (t, J = 4.6 Hz, 2H, N−C$_2$**H**$_4$−O), 3.59 (s, 1H, cage−C**H**), 3.52 (t, J = 4.6 Hz, 2H), 3.32 (t, J = 4.6 Hz, 2H), 3.00 (t, J = 4.6 Hz, 2H, N−C$_2$**H**$_4$−O), 1.27 (s, 9H), 1.26 (s, 36H) (^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 5.6 (1B), −1.1 (2B), −6.6 (2B), −11.2 (2B), −13.3 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0 (**C**=O), 158.2 (**C**H=N), 157.97, 151.7, 150.8, 150.6, 135.6, 135.3, 135.0, 132.9, 124.1, 124.0 (phenyl−**C**), 70.6 (cage−**C**), 66.7, 66.6 (N−**C**$_2$H$_4$−O), 65.5 (N−**C**H$_2$−CO), 53.6 (cage−**C**), 46.6, 42.2 (N−**C**$_2$H$_4$−O), 34.61, 34.55, 34.54 (^{t}Bu−**C**Me$_3$), 31.40, 31.38 31.32 (^{t}Bu−**C**H$_3$). HRMS (ESI, positive mode): *m/z* calcd for $C_{59}B_{10}N_2O_2H_{83}$ $[M+H]^+$: 959.7452. Found: 959.7458. Elemental analysis (%) calcd for $C_{59}B_{10}N_2O_2H_{82}$: C, 73.86; H, 8.62; N, 2.92 Found: C, 73.92; H, 8.71; N, 2.86

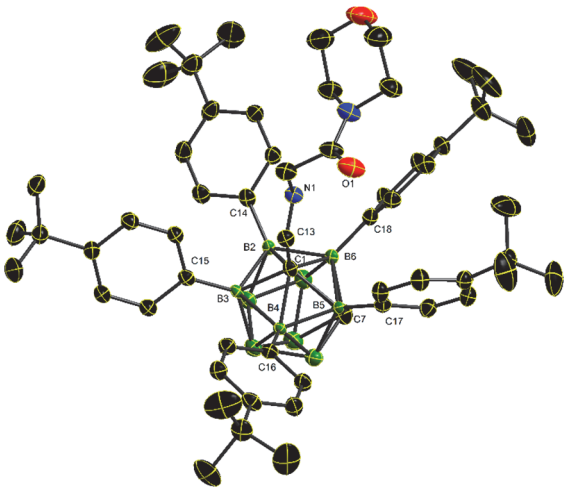
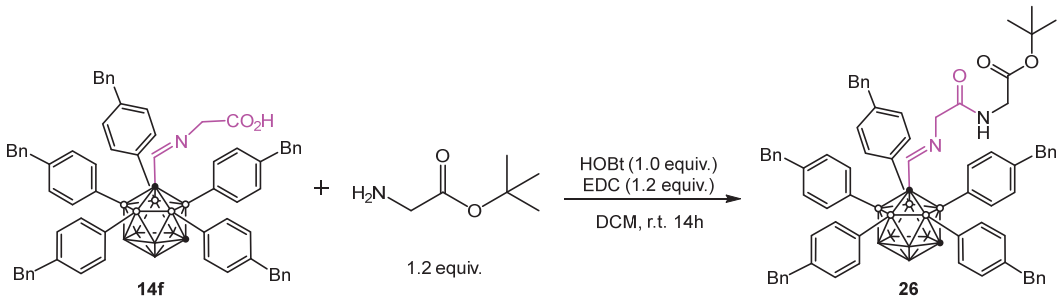


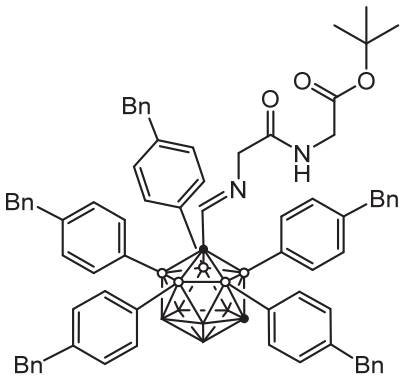
Figure S19. X-Ray structure of **25** (ellipsoids at 30% probability, solvent and H atoms were omitted for clarity). Selected bond distances [Å] for **25**: C1−C13 1.499(4), C13−N1 1.250(4), C1−B2 1.753(4), C1−B3 1.738(4), C1−B4 1.761(4), C1−B5

1.758(4), C1−B6 1.751(5), B2−C14 1.565(4), B3−C15 1.575(5), B4−C16 1.583(5), B5−C17 1.576(4), B6−C18 1.569(4).



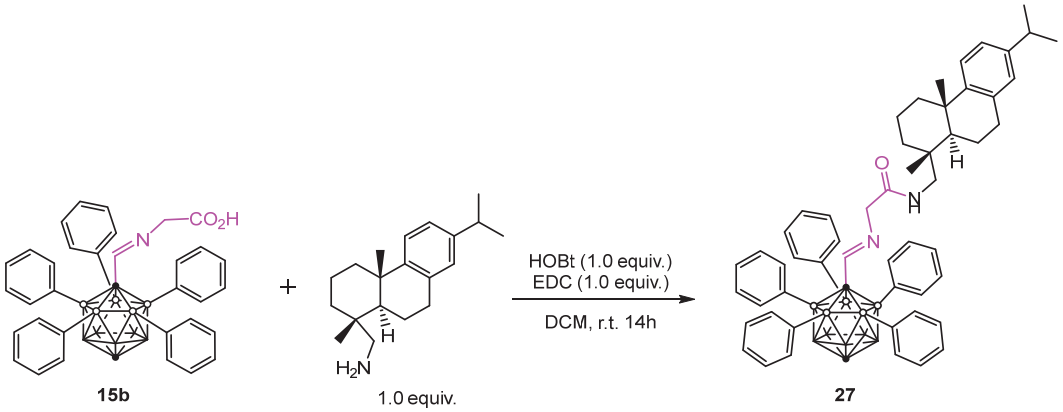
Scheme S16. Peptide synthesis from **14f** with glycine tert-butyl ester

Synthesis of dipeptide: To a solution of glycine tert-butyl ester (1.2 equiv., 0.1 mmol, 15.7 mg), HOBt (1.0 equiv., 0.12 mmol, 16.2 mg) and EDC (1.2 equiv., 0.12 mmol, 18.7 mg) in DCM (0.1 M), **14f** (0.1 mmol, 106.0 mg) was added and the resulting solution was stirred at room temperature 14 h. After this time, the crude reaction mixture was purified on preparative TLC using petroleum ether/ethyl acetate as the eluent to afford the desired product **26** (110.7 mg).



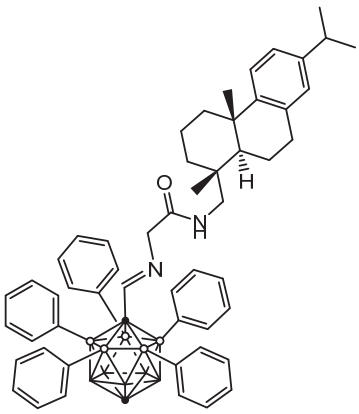
26: Yield 94%. Colorless solid. m. p. 89.7 – 89.0 °C. ^{1}H NMR (400 MHz , $CDCl_3$) δ: 8.02 (t, *J* = 1.7 Hz, 1H, C**H**=N), 7.35 − 7.11 (m, 25H), 7.00 − 6.71 (m, 20H) (phenyl−**H**), 6.01 (t, *J* = 6.5 Hz, 1H, N**H**), 4.00 (d, *J* = 1.7 Hz, 2H, C**H**$_2$−CO), 3.90 (s, 4H), 3.89 (s, 6H, Bn−C**H**$_2$), 3.63 (s, 1H, cage−C**H**), 3.31 (d, *J* = 6.4 Hz, 2H, C**H**$_2$−CO), 1.47 (s, 9H, ^{t}Bu−C**H**$_3$); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 5.6 (1B), −1.3 (2B), −6.1 (2B), −10.9 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 168.0 (**C**=O), 157.2 (**C**H=N), 142.1, 141.2,

141.1, 140.9, 140.7, 135.9, 135.6, 135.3, 133.2, 129.1, 129.0, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 126.3, 126.2, 126.1 (phenyl−**C**), 81.7 (^{t}Bu−**C**Me$_3$), 70.5, 62.0 (cage−**C**), 53.6, 41.75, 41.73, 41.72 (**C**H$_2$), 28.3 (^{t}Bu−**C**H$_3$). HRMS (ESI, negative mode): m/z calcd for $C_{76}B_{10}N_2O_3H_{75}$ $[M-H]^-$: 1173.6784. Found: 1173.6781. Elemental analysis (%) calcd for $C_{76}B_{10}N_2O_3H_{76}$: C, 77.78; H, 6.53; N, 2.39. Found: C, 77.44; H, 6.81; N, 2.51.

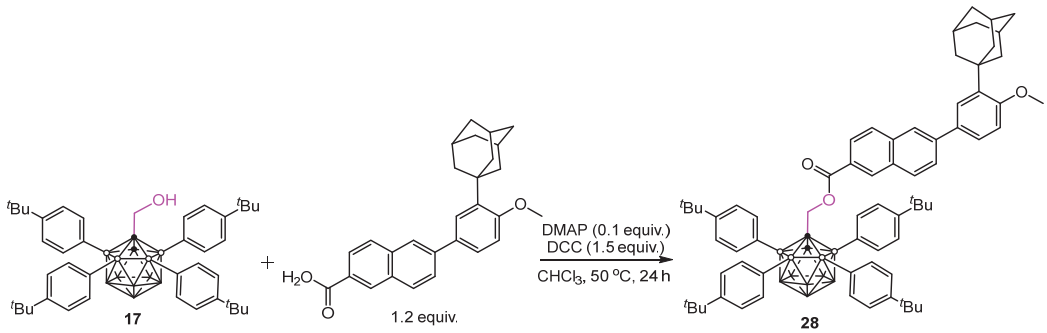


Scheme S17. Late stage modification of dehydrobietylamine with **15b**

Late stage modification of dehydrobietylamine: To a solution of dehydrobietylamine (1.0 equiv., 0.1 mmol, 28.6 mg), HOBt (1.0 equiv., 0.1 mmol, 13.5 mg) and EDC (1.0 equiv., 0.1 mmol, 15.6 mg) in DCM (0.1 M), 1**5b** (0.1 mmol, 61.0 mg) was added and the resulting solution was stirred at room temperature 14 h. After this time, the crude reaction mixture was purified on preparative TLC using petroleum ether/ethyl acetate as the eluent to afford the desired product **27** (79.6 mg).

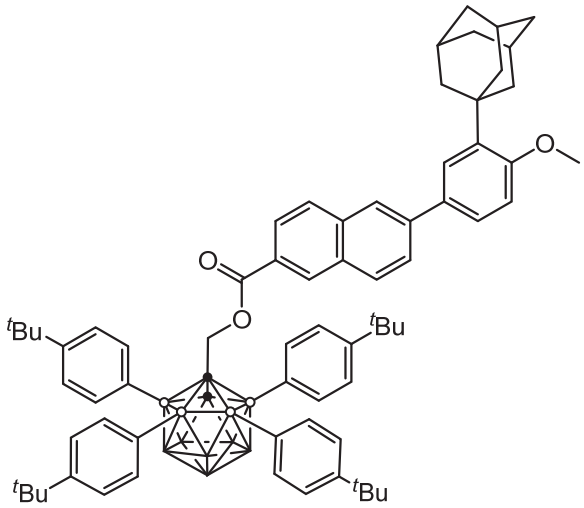


27: Yield 90%. Colorless solid. m. p. 146.7 – 147.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 1H, C**H**=N), 7.21 (t, *J* = 7.4 Hz, 5H, phenyl−**H**), 7.16 (d, *J* = 8.2 Hz, 1H, dehydrobietylamine−**H**), 7.03 (dd, *J* = 7.6 Hz, 7.6 Hz, 10H, phenyl−**H**), 6.99 (d, *J* = 8.5 Hz, 1H, dehydrobietylamine−**H**), 6.95 (d, *J* = 8.5 Hz, 10H, phenyl−**H**), 6.88 (s, 1H, dehydrobietylamine−**H**), 6.02 (t, *J* = 6.9 Hz, 1H, N**H**), 3.93 (d, *J* = 18.5 Hz, 1H), 3.81 (d, *J* = 18.5 Hz, 1H) (NHC$\mathbf{H}_2$), 3.42 (s, 1H, cage C**H**), 2.95 (d, *J* = 6.9 Hz, 2H), 2.90 − 2.73 (m, 4H), 2.26 (d, *J* = 7.5 Hz, 1H), 1.91 − 1.87 (m, 1H), 1.71 – 1.60 (m, 4H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.17 (s, 3H), 1.00 (d, *J* = 13.0 Hz, 1H), 0.74 (s, 3H) (dehydrobietylamine−**H**); ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.7 (5B), −16.0 (5B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9 (**C**=O), 157.5 (**C**H=N), 147.3, 145.7, 135.8, 135.1, 131.9, 128.5, 127.4, 127.1, 124.2, 123.9 (phenyl−**C**), 79.9 (cage−**C**), 62.4 (N−**C**H_2−CO), 59.8 (cage−**C**), 50.1, 46.3, 38.3, 37.9, 37.5, 35.8, 33.6, 30.4, 25.6, 24.1, 19.3, 18.5, 18.1 (dehydrobietylamine−**C**). HRMS (ESI, negative mode): m/z calcd for $C_{55}B_{10}N_2OH_{63}$ $[M-H]^-$: 875.5949. Found: 875.5954. Elemental analysis (%) calcd for $C_{55}B_{10}N_2OH_{64}$: C, 75.31; H, 7.35; N, 3.19. Found: C, 75.70; H, 7.18; N, 3.06.



Scheme S18. Late stage modification of adapalene

Late stage modification of adapalene: To a solution of adapalene (1.2 equiv., 0.12 mmol, 49.5 mg), DMAP (4-dimethylaminopyridine, 0.1 equiv., 0.01 mmol, 1.2 mg) and DCC (N,N'-dicyclohexylcarbodiimide, 1.5 equiv., 0.15 mmol, 31.0 mg) in $CHCl_3$ (0.05 M), **17** (0.1 mmol, 70.3 mg) was added and the resulting solution was stirred at 50 °C for 24 h. After this time, the crude reaction mixture was purified on preparative TLC using petroleum ether/DCM as the eluent to afford the desired product **28** (73.4 mg).



28: Yield 67%. Colorless solid. m. p. 208.7 – 209.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.84 − 7.81 (m, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.50 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 4H), 7.17 − 7.13 (m, 4H), 7.09 − 7.06 (m, 8H), 7.02 (d, *J* = 8.5 Hz, 1H) (phenyl−**H**), 5.24 (s, 2H, $CO_2C\mathbf{H}_2$), 4.86 (s, 1H, cage C**H**), 3.92 (s, 3H, OC$\mathbf{H}_3$), 2.20 (d, *J* = 2.9 Hz, 6H), 2.12 (s, 3H), 1.83 (d, *J* = 3.1 Hz, 6H) (adamantyl−**H**), 1.28 (s, 18H), 1.03 (s, 18H) (^{t}Bu−C$\mathbf{H}_3$). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ −2.9 (5B), −9.7 (3B), −14.3 (2B); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.0 (**C**=O), 159.1, 141.5, 139.2, 136.1, 132.8, 131.4, 130.9, 129.8, 128.3, 127.4, 126.6, 126.1, 125.9, 125.8, 124.9, 112.3 (phenyl−**C**), 61.2 ($CO_2\mathbf{C}H_2$), 60.1 (cage−**C**), 55.3 (O**C**H_3), 40.8 (adamantyl−**C**), 37.4 (^{t}Bu−**C**$(CH_3)_3$), 37.3 (adamantyl−**C**), 29.3 (^{t}Bu−**C**H_3 and adamantyl−**C**). HRMS (ESI, negative mode): m/z calcd for $C_{71}B_{10}O_3H_{87}$ $[M-H]^-$: 1097.7661. Found: 1097.7654. Elemental analysis (%) calcd for $C_{71}B_{10}O_3H_{88}$: C, 77.70; H, 8.08. Found: C, 77.31; H, 7.73.

3. References

(S1) Dozzo, P.; Kasar, R. A.; Kahl, S. B. Simple, High-Yield Methods for the Synthesis of Aldehydes Directly from *o*-, *m*-, and *p*-Carborane and Their Further Conversions. *Inorg. Chem.* **2005**, *44*, 8053-8057.

(S2) Sheldrick, G. M. SADABS, *A Program for Empirical Absorption Correction*; University of Göttingen; Göttingen, Germany, **1998**.

(S3) Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structures*; University of Göttingen; Göttingen, Germany, **1997**.

4. Crystallographic data

Table S4. Crystallographic data of compounds **3**, **5**, **6**, **7'**, **8**, **9**, **11**, **13a**, **13c**, **13k**, **15b**, **15d**, **16, 17, 18** and **25**.

	3	**5**	**6**	**7'**	**8**
Empirical formula	$C_{27}H_{30}B_{10}NOPPd$	$C_{11}H_{18}B_{10}O_3$	$C_{19}H_{24}B_{10}O_5$	$C_{21}H_{21}B_{10}F_3O$	$C_{35}H_{36}B_{10}O_9$
Formula wt	629.99	306.35	440.48	454.48	708.74
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	Pbcm	$P2_1/c$	$P2_1/c$
a/Å	9.0642(12)	22.9926(11)	6.8374(6)	14.2655(18)	22.445(12)
b/Å	13.1695(18)	6.5798(3)	18.2868(15)	19.450(3)	8.524(5)
c/Å	24.860(3)	24.1534(12)	18.8324(16)	8.3140(11)	20.897(11)
α/deg	90	90	90	90	90
β/deg	94.902(2)	115.752(2)	90	102.863(5)	116.232(8)
γ/deg	90	90	90	90	90
V/Å^3	2956.7(7)	3291.2(3)	2354.7(3)	2249.0(5)	3586(3)
Z	4	8	4	4	4
ρ_{calc} [g/cm^3]	1.415	1.237	1.243	1.342	1.313
μ [mm^{-1}]	0.706	0.073	0.400	0.090	0.087
F(000)	1272.0	1264.0	912.0	928.0	1024
2θ range (deg)	3.288/54.852	4.928/55.018	8.168/122.258	4.188/50.728	2.202/54.964
no. of rflns collected	26299	13588	29201	61856	30784
no. of indep rflns	6684	7466	2682	4095	8077
GOF on F^2	1.035	1.035	1.202	1.068	1.021
R1/wR2 [I> 2σ(I)]	0.0272/0.0654	0.0528/ 0.1334	0.1123/0.2766	0.0464/0.1106	0.0882/0.2678
R1/wR2 (all data)	0.0328/0.0686	0.0828/ 0.1492	0.1419/0.2961	0.0687/0.1199	0.1724/0.3467
largest peak/hole (e Å^{-1})	1.34/−0.53	0.31/−0.25	0.26/−0.21	0.18/-0.23	0.44/−0.31
van der Waals volume (Å^3) (calculated by Olex2)	493.54	290.66	395.79	393.42	607.71

	9·CH_2Cl_2	**11**	**13a**	**13c**	**13k**
Empirical formula	$C_{46}H_{48}B_{10}Cl_2NO_{12}$	$C_{43}H_{42}B_{10}NO_5PPd$	$C_{43}H_{60}B_{10}O$	$C_{31}H_{36}B_{10}O$	$C_{66}H_{58}B_{20}F_8N_2O_2$
Formula wt	985.85	898.24	701.01	532.70	1279.34
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/c$	C2/c	C2/c	P-1
a/Å	12.9702(13)	15.4750(11)	30.248(6)	24.4616(12)	10.804(5)
b/Å	13.4980(13)	25.5038(19)	12.321(2)	13.4493(6)	11.906(5)
c/Å	16.6031(16)	16.9662(12)	25.333(5)	18.7508(8)	25.209(11)
α/deg	70.165(2)	90	90	90	90.090(9)
β/deg	71.761(2)	102.143(2)	116.221(4)	100.232(2)	87.216(10)
γ/deg	64.698(2)	90	90	90	88.784(11)
V/Å^3	2423.3(4)	6546.3(8)	8470(3)	6070.7(5)	3238(2)
Z	2	4	8	8	2

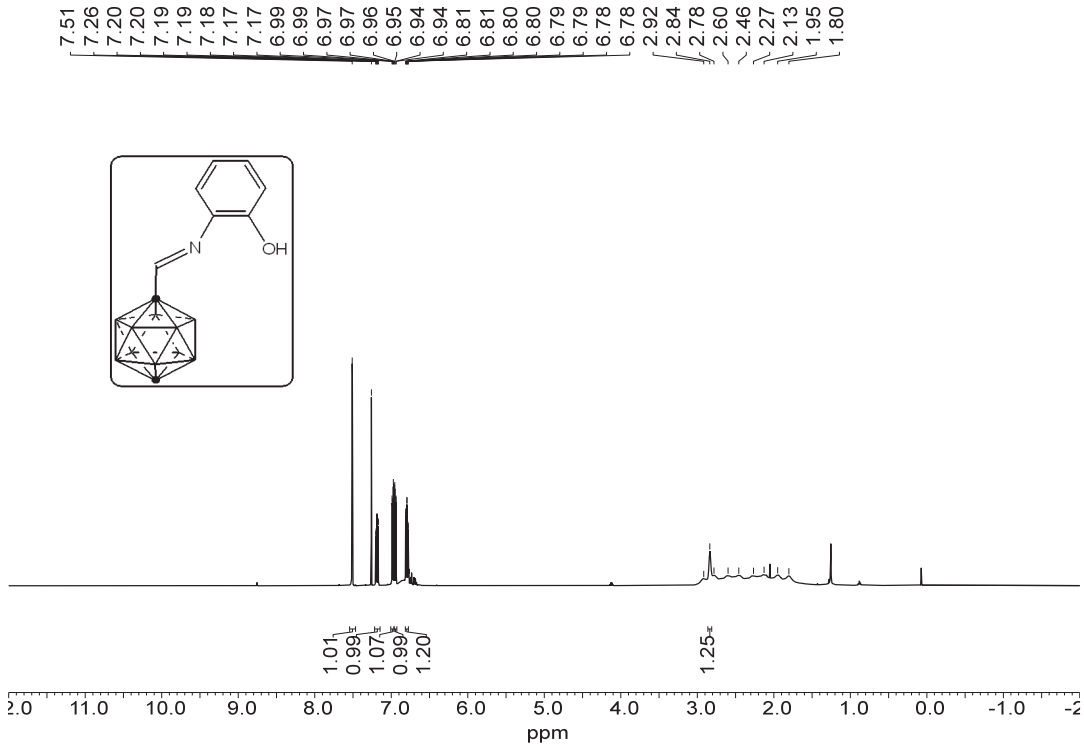
ρ_{calc} [g/cm^3]	1.351	0.911	1.099	1.166	1.312
μ [mm^{-1}]	0.197	0.338	0.060	0.063	0.089
F(000)	1022.0	1832.0	3008.0	2240	1312.0
2θ range (deg)	2.66/55.02	4.028/55.02	4.332/50	4.27/55.096	4.704/48.398
no. of rflns collected	22062	58879	23535	27023	15319
no. of indep rflns	10811	14999	7455	6987	10141
GOF on F^2	1.069	0.979	1.023	1.055	1.071
R1/wR2 [I> 2σ(I)]	0.0834/0.2444	0.0747/0.1846	0.0888/0.1818	0.1041/0.2454	0.1538/0.3544
R1/wR2 (all data)	0.1134/0.2836	0.1714/0.2321	0.1938/0.2224	0.1700/0.2852	0.2215/0.3904
largest peak/hole (e Å^{-1})	1.61/−1.30	1.06/−0.93	0.50/−0.30	0.71/−0.46	0.48/−0.45
van der Waals volume (Å^3) (calculated by Olex2)	758.14 (exclude CH_2Cl_2)	705.16	666.54	496.69	538.73

	15b·DMSO	**15d**	**16**	**17**·*n*-hexane	**18**	**25**·$CHCl_3$
Empirical formula	$C_{37}H_{39}B_{10}NO_3S$	$C_{45}H_{56}B_{10}NO_2$	$C_{54}H_{73}B_{10}N$	$C_{59}H_{86}B_{10}O$	$C_{93}H_{67}B_{10}N_5O_6$	$C_{60}H_{83}B_{10}Cl_3N_2O_2$
Formula wt	685.85	751.01	844.23	919.37	1458.61	1067.92
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P222	$P2_1/n$	P-1	P-1	P-1
a/Å	23.4028(15)	20.541(3)	12.427(12)	11.646(2)	10.8160(18)	14.9214(9)
b/Å	10.4909(7)	21.748(3)	37.88(4)	11.847(2)	16.257(3)	15.0111(10)
c/Å	17.9732(13)	21.850(3)	13.129(13)	22.420(4)	21.721(4)	17.2386(13)
α/deg	90	90	90	91.159(3)	100.657(10)	108.538(2)
β/deg	111.455(2)	90	103.168(19)	103.259(3)	92.975(11)	106.645(2)
γ/deg	90	90	90	105.903(3)	92.071(11)	102.932(2)
V/Å^3	4106.9(5)	9761(2)	6018(10)	2884.2(9)	3744.3(12)	3290.0(4)
Z	4	4	4	2	2	2
ρ_{calc} [g/cm^3]	1.109	1.021	0.932	1.059	1.294	1.078
μ [mm^{-1}]	0.113	0.058	0.050	0.058	0.391	0.179
F(000)	1432.0	3184.0	1816.0	996.0	1516.0	1138.0
2θ range (deg)	4.31/55.12	3.304/58.872	3.362/49.998	3.75/55.124	3.608/102.498	4.362/54.996
no. of rflns collected	33051	91128	44669	26724	41699	30658
no. of indep rflns	9417	22548	10558	113177	11880	14961
GOF on F^2	1.043	0.957	1.050	1.013	1.074	1.001
R1/wR2 [I> 2σ(I)]	0.1042/0.2526	0.0683/0.1512	0.0940/0.2610	0.0775/0.1790	0.1008/0.2114	0.0837/0.2288
R1/wR2 (all data)	0.2007/0.2973	0.1428/0.1897	0.1470/0.3200	0.1550/0.2200	0.2533/0.2683	0.1456/0.2717
largest peak/hole (e Å^{-1})	1.03/−0.93	0.24/−0.29	0.69/−0.42	0.49/−0.35	0.25/-0.23	1.62/−0.60
van der Waals volume (Å^3) (calculated by Olex2)	545.74 (exclude DMSO)	689.88	824.58	880.58 (exclude *n*-hexane)	1340.05	888.59 (exclude $CHCl_3$)

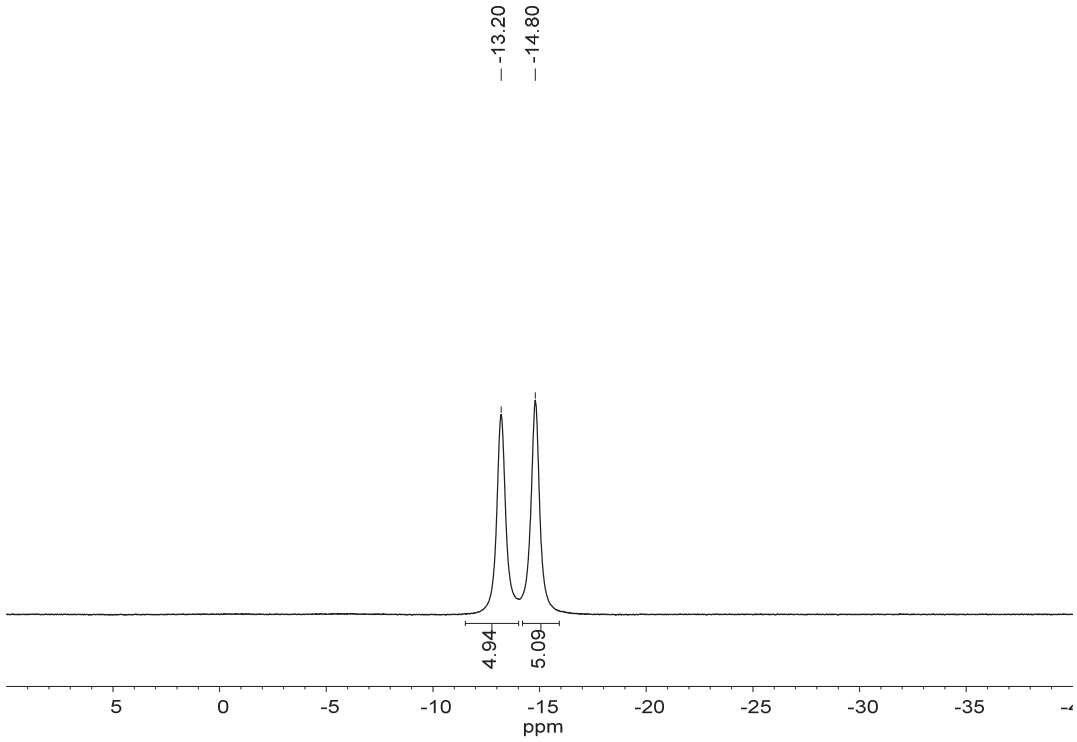
5. NMR Spectra

5.1 Mechanistic Study

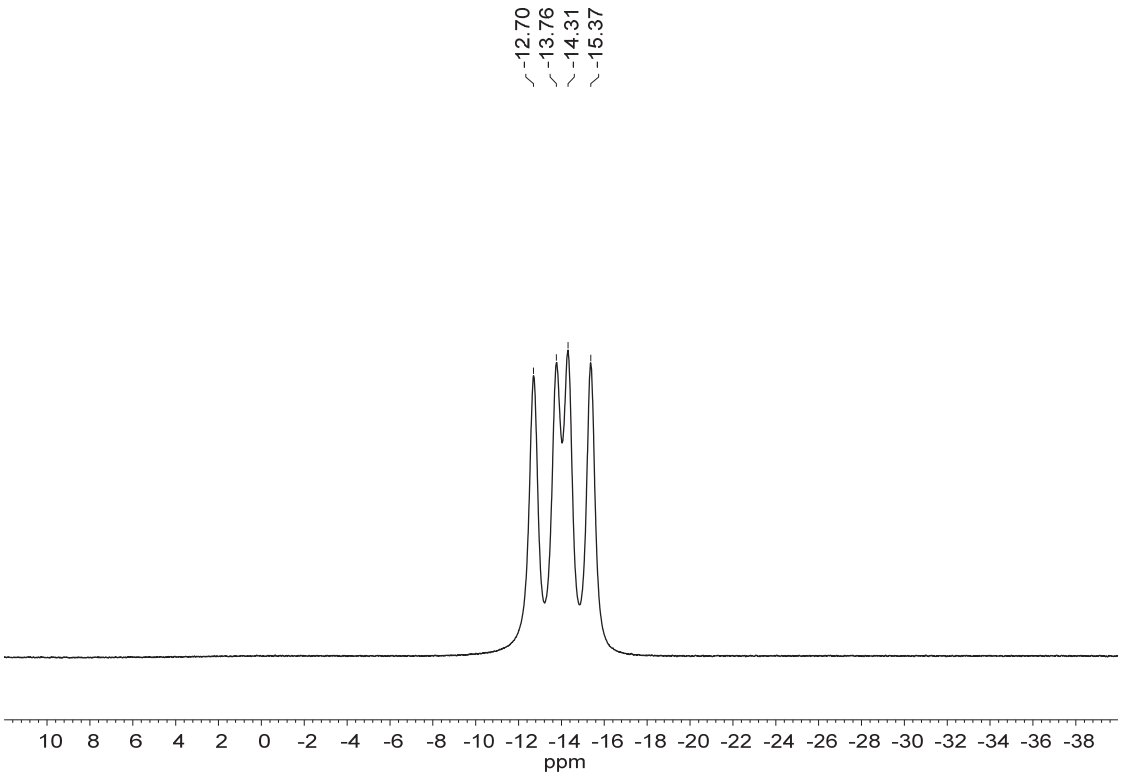
^{1}H NMR of 2, 500 M, $CDCl_3$



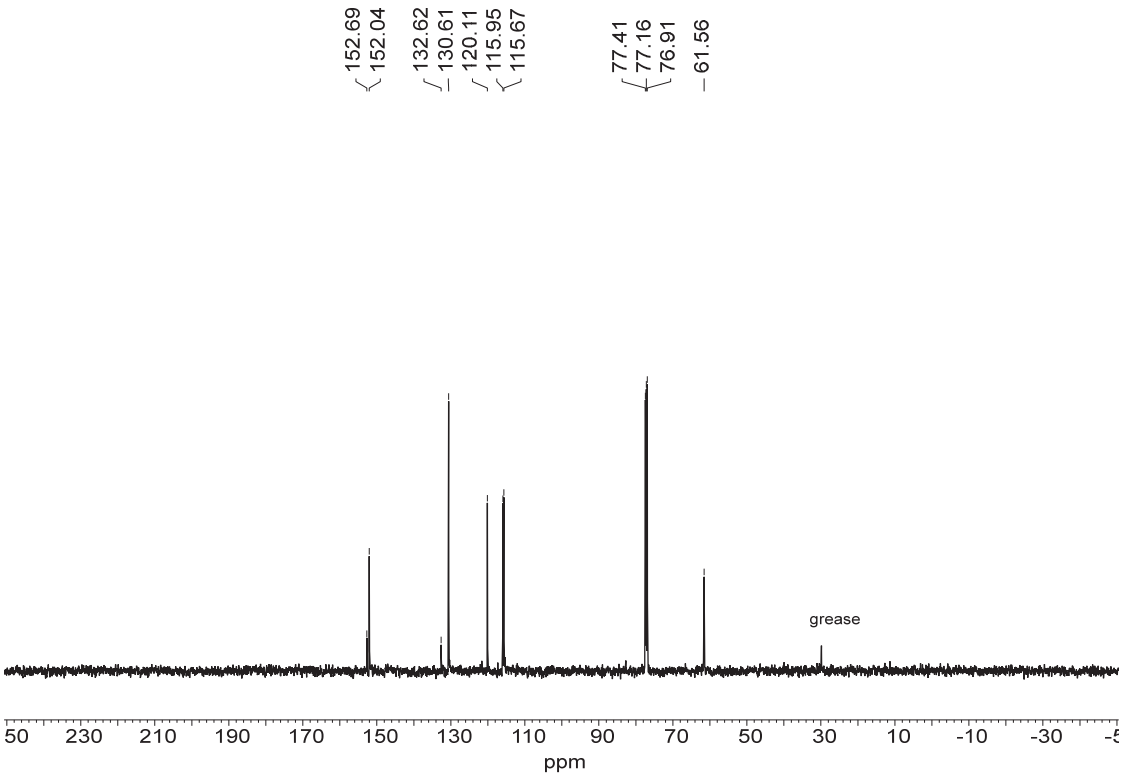
^{11}B {^{1}H} NMR of 2, 160 M, $CDCl_3$



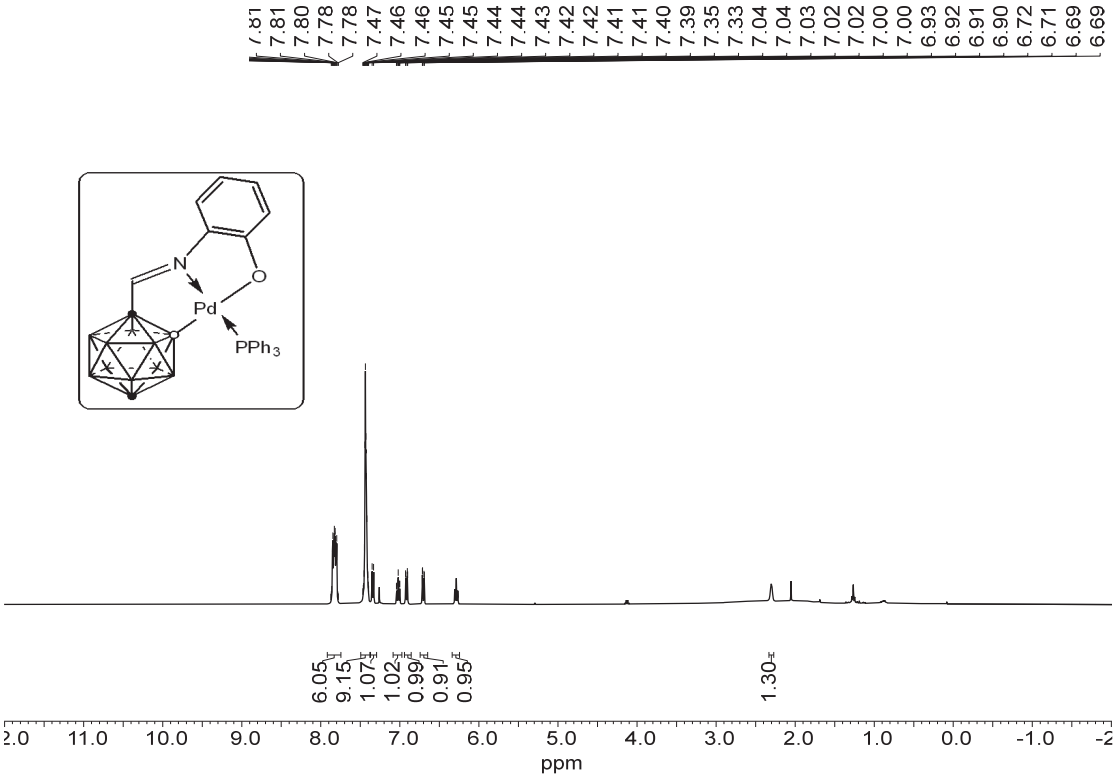
^{11}B NMR of 2, 160 M, $CDCl_3$



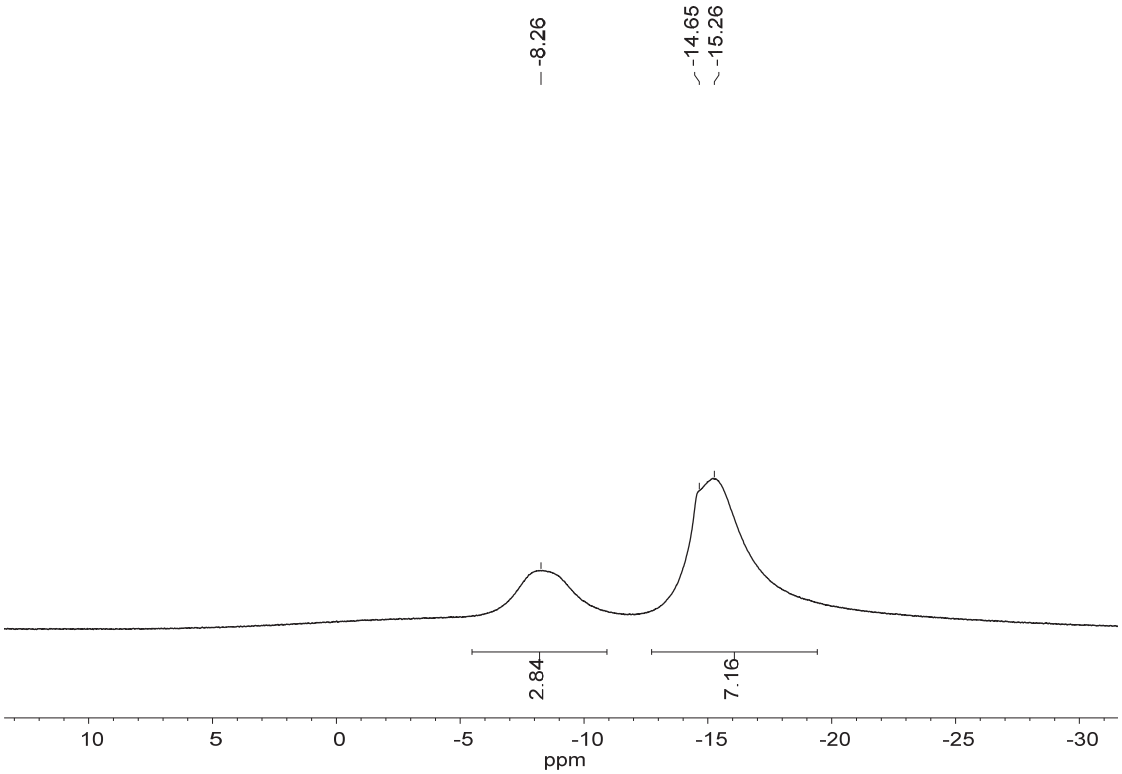
^{13}C NMR of 2, 126 M, $CDCl_3$



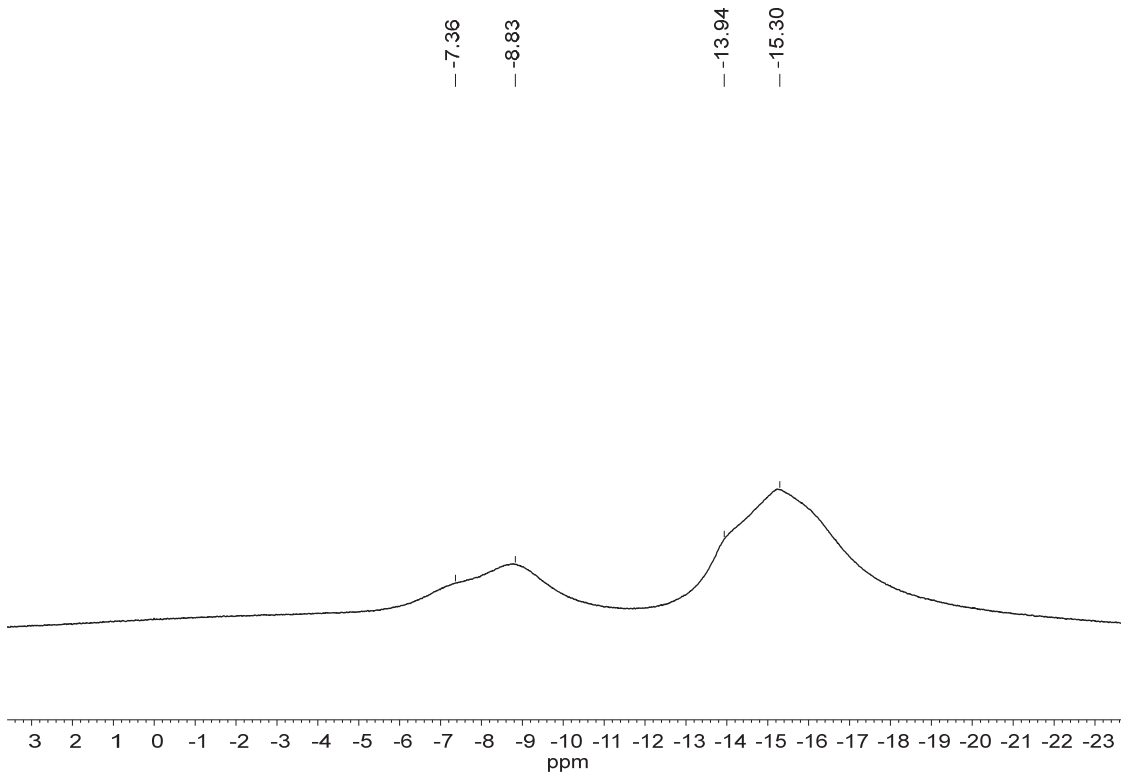
^{1}H NMR of 3, 500 M, $CDCl_3$



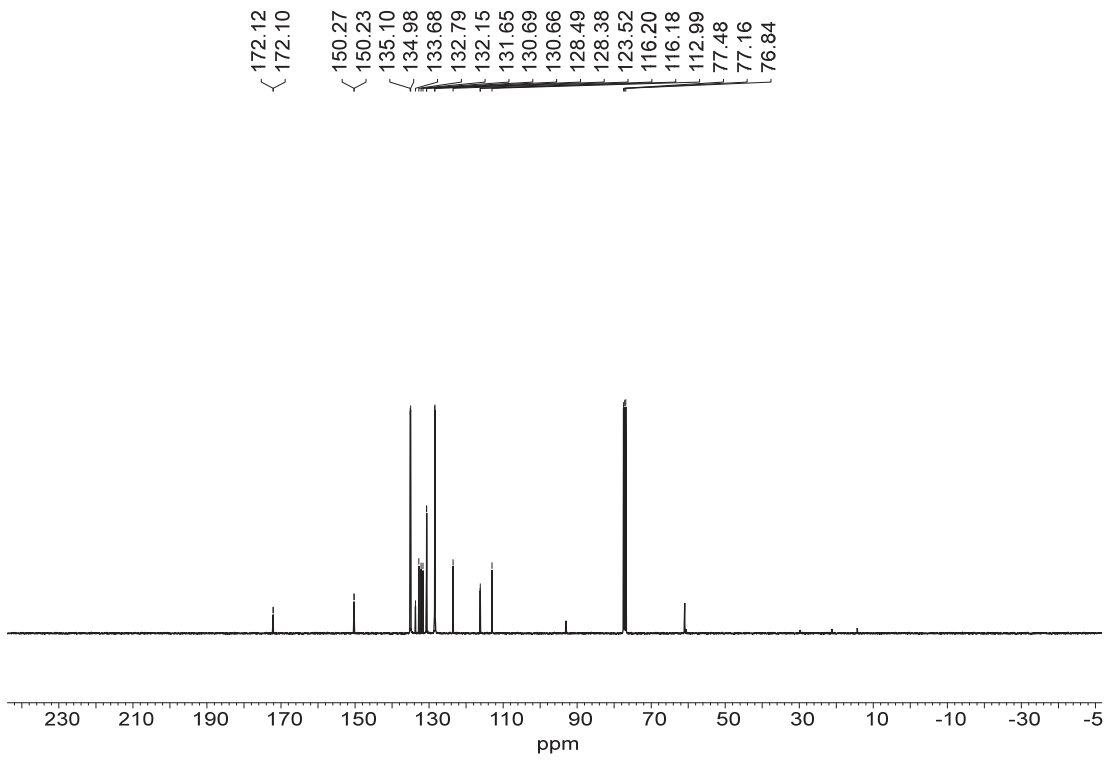
^{11}B {^{1}H} NMR of 3, 160 M, $CDCl_3$



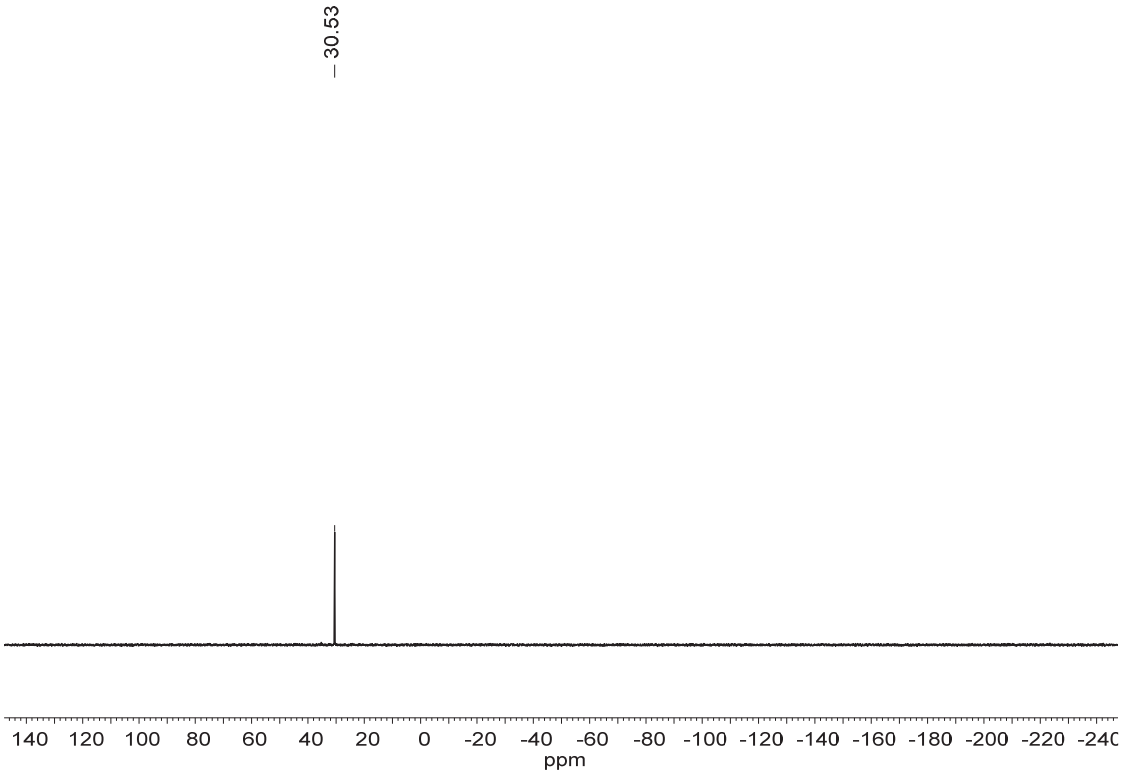
^{11}B NMR of 3, 160 M, $CDCl_3$



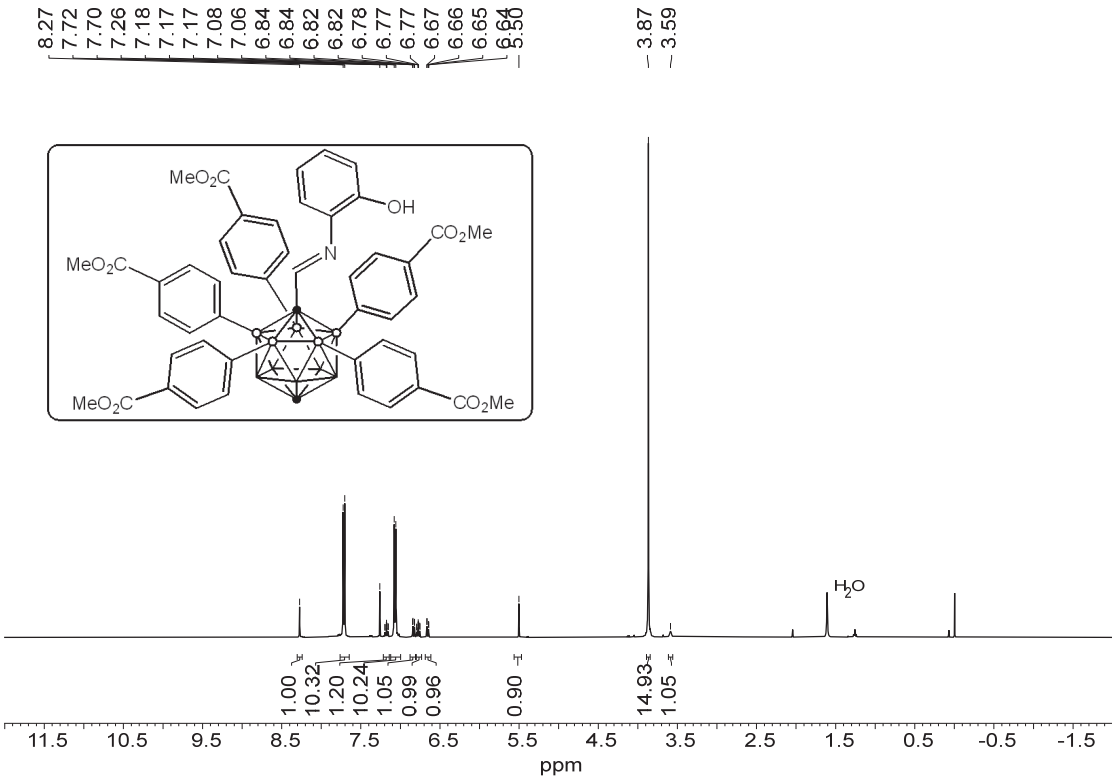
^{13}C NMR of 3, 101 M, $CDCl_3$



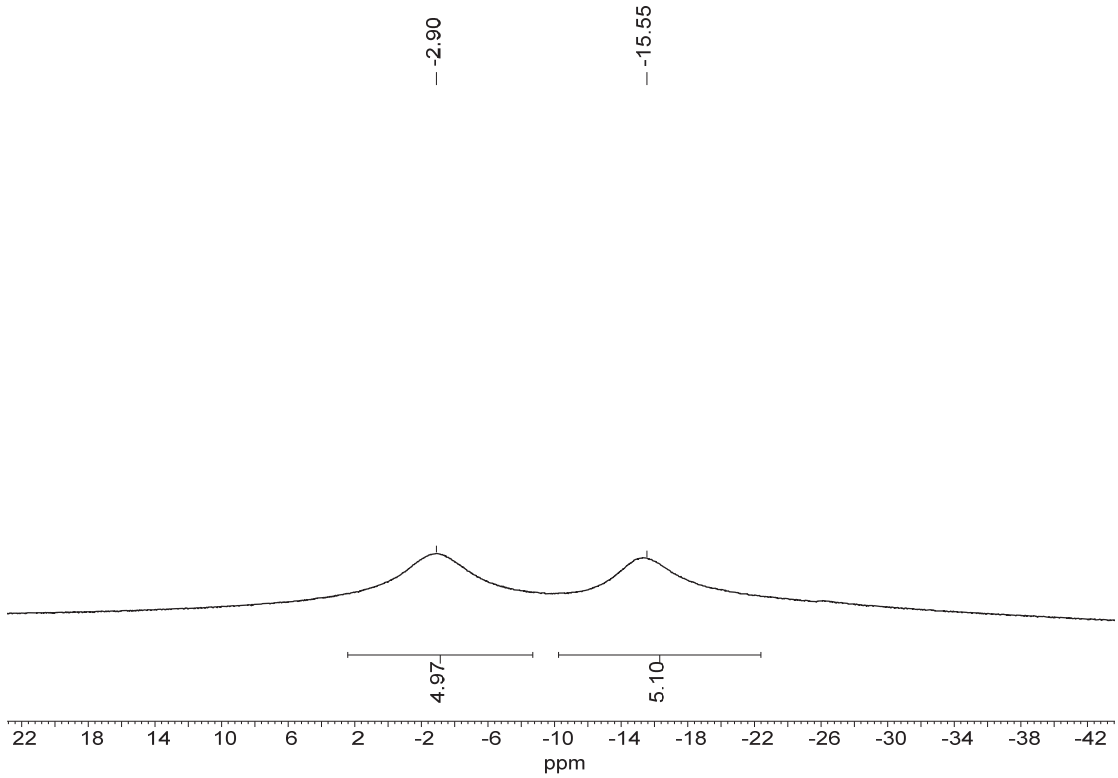
^{31}P NMR of 3, 162 M, $CDCl_3$



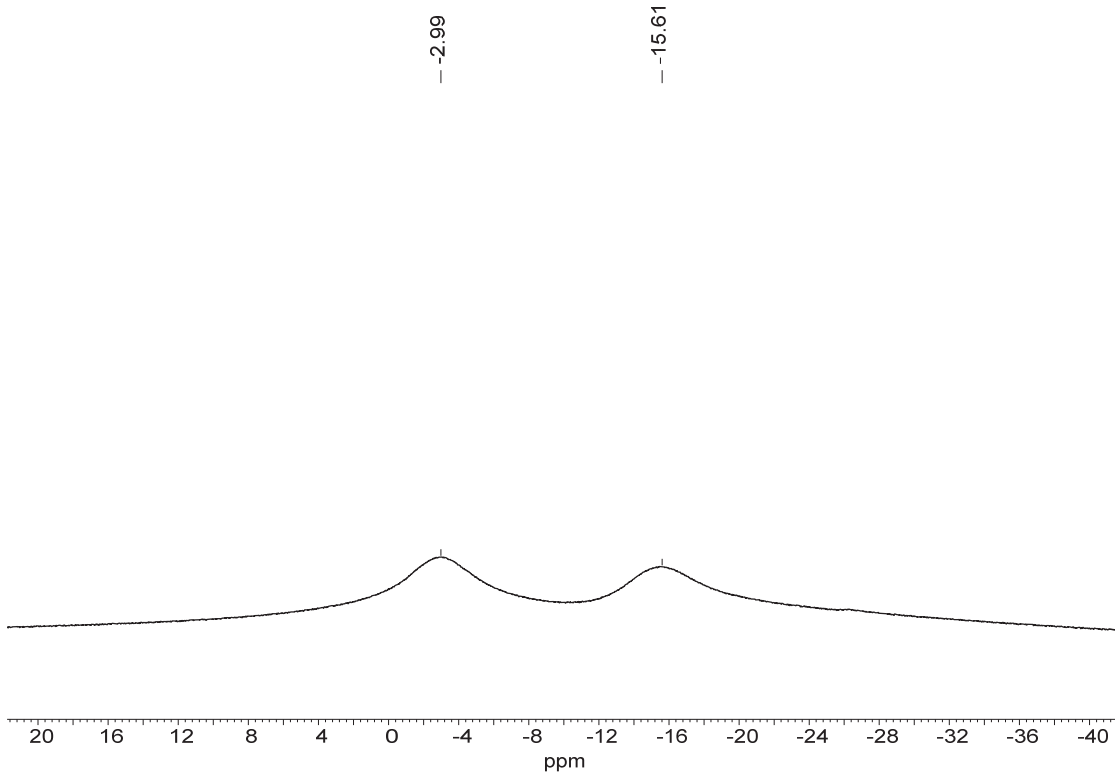
^{1}H NMR of 4, 500 M, $CDCl_3$



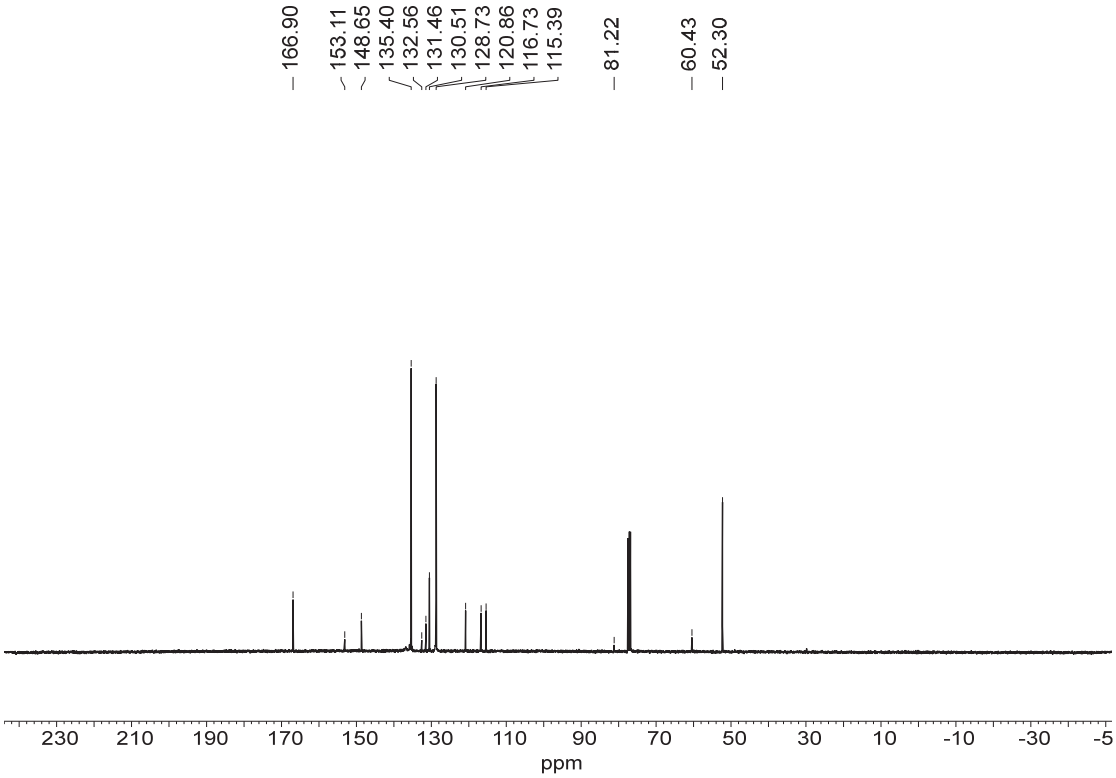
$^{11}B\ \{^{1}H\}$ NMR of 4, 160 M, $CDCl_3$



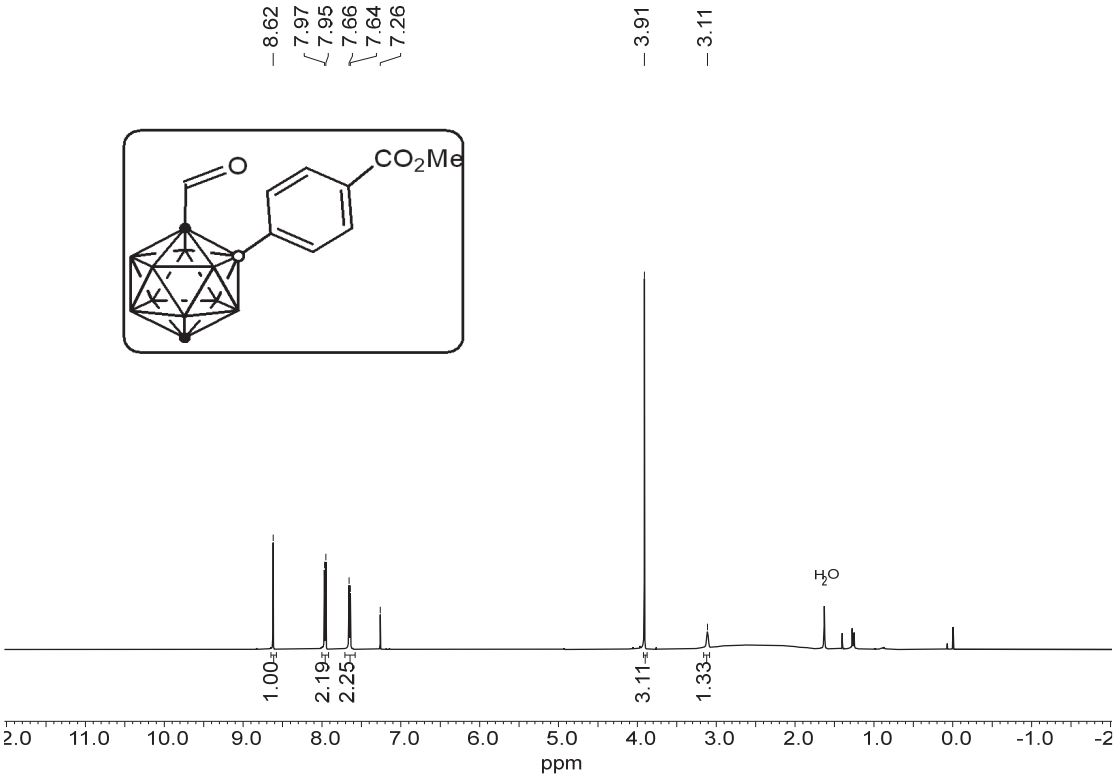
^{11}B NMR of 4, 160 M, $CDCl_3$



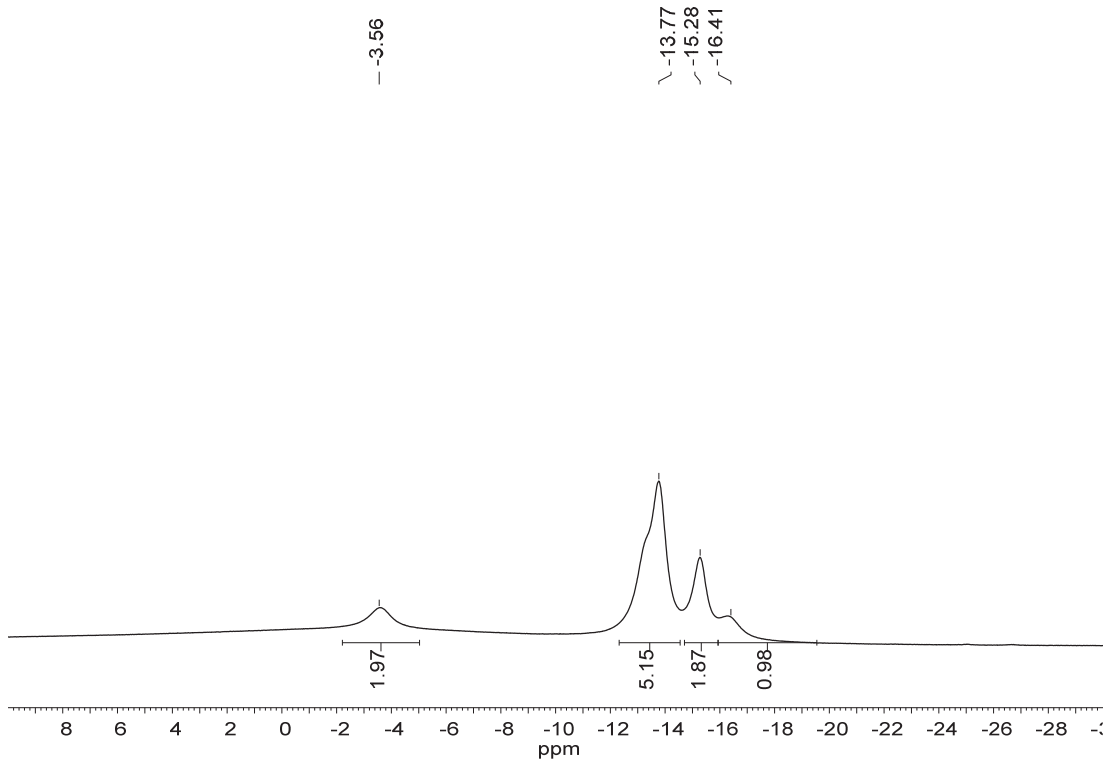
^{13}C NMR of 4, 126 M, $CDCl_3$



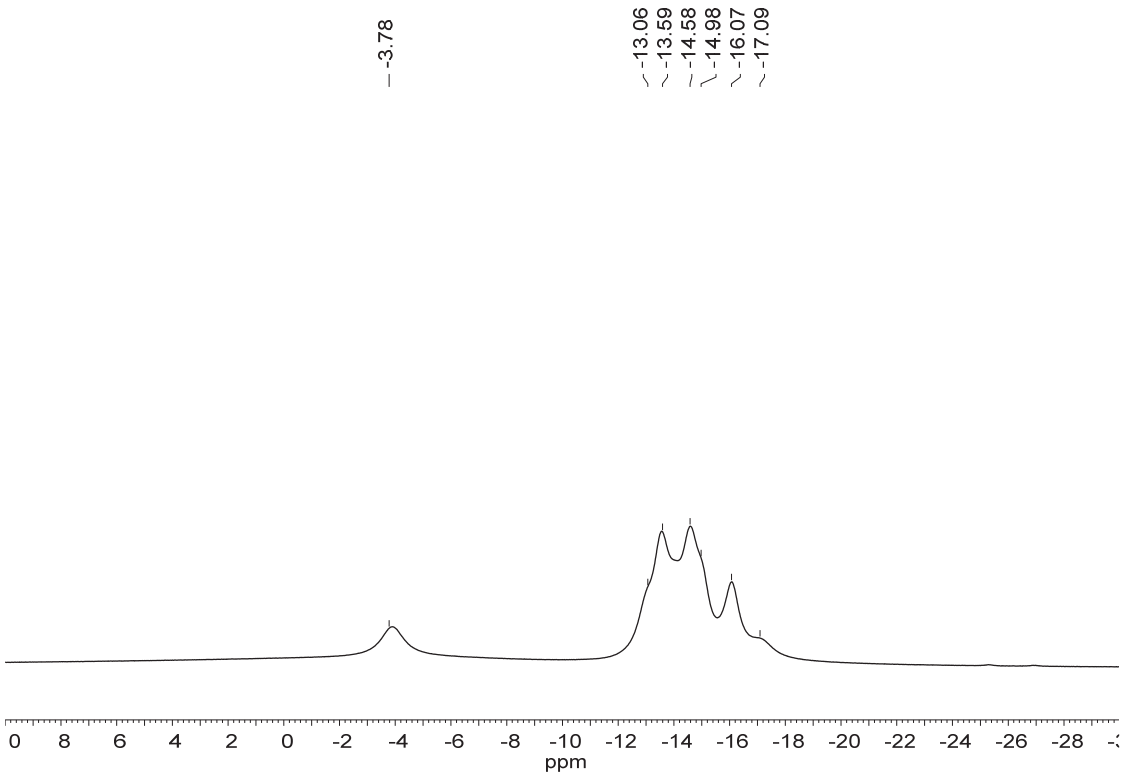
^{1}H NMR of 5, 500 M, $CDCl_3$



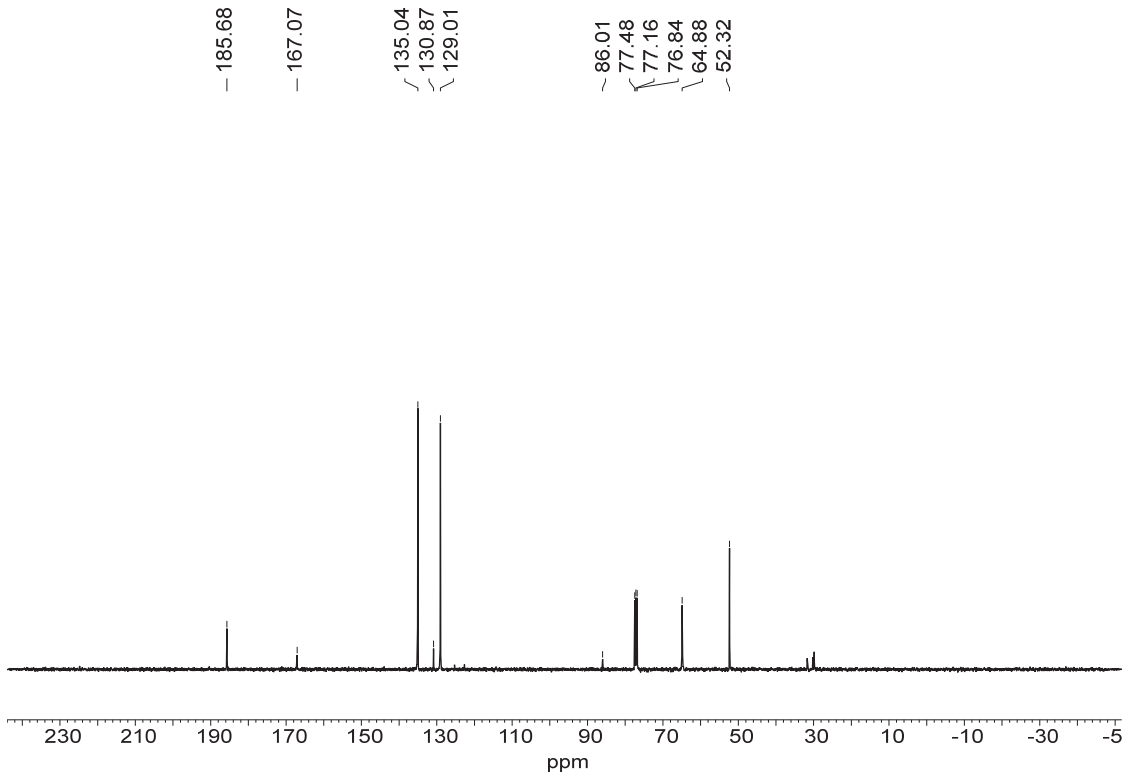
$^{11}B\ \{^{1}H\}$ NMR of 5, 160 M, $CDCl_3$



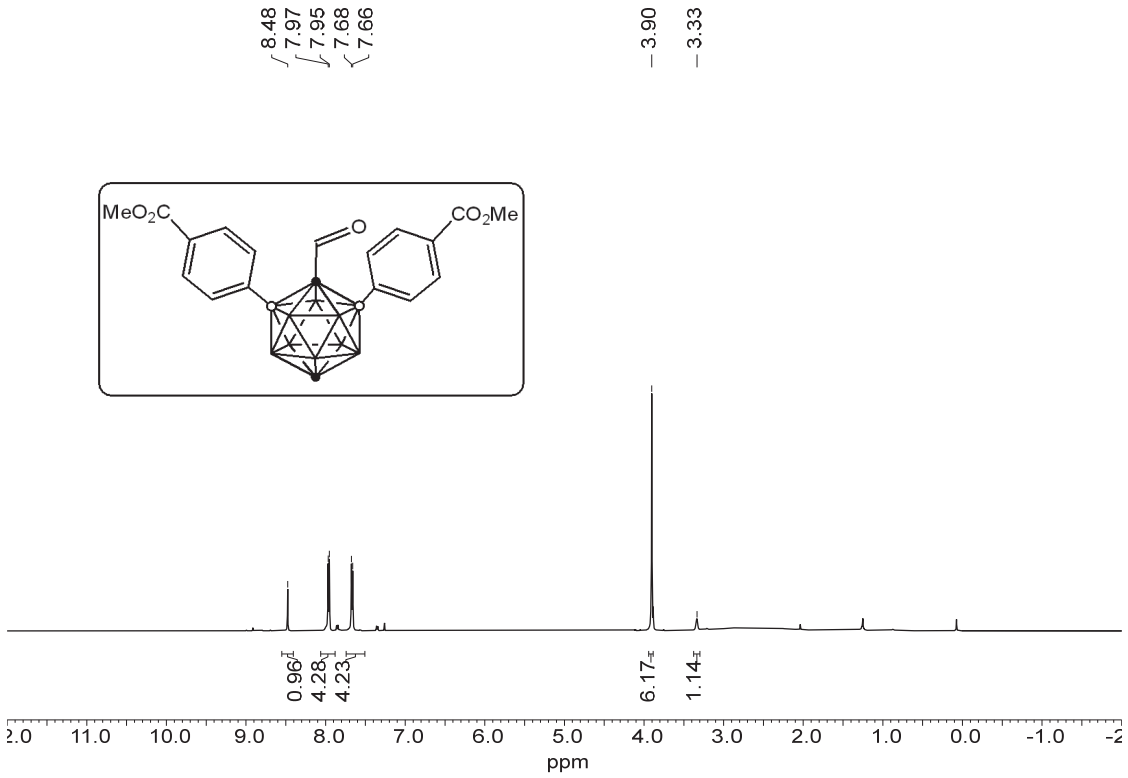
^{11}B NMR of 5, 160 M, $CDCl_3$



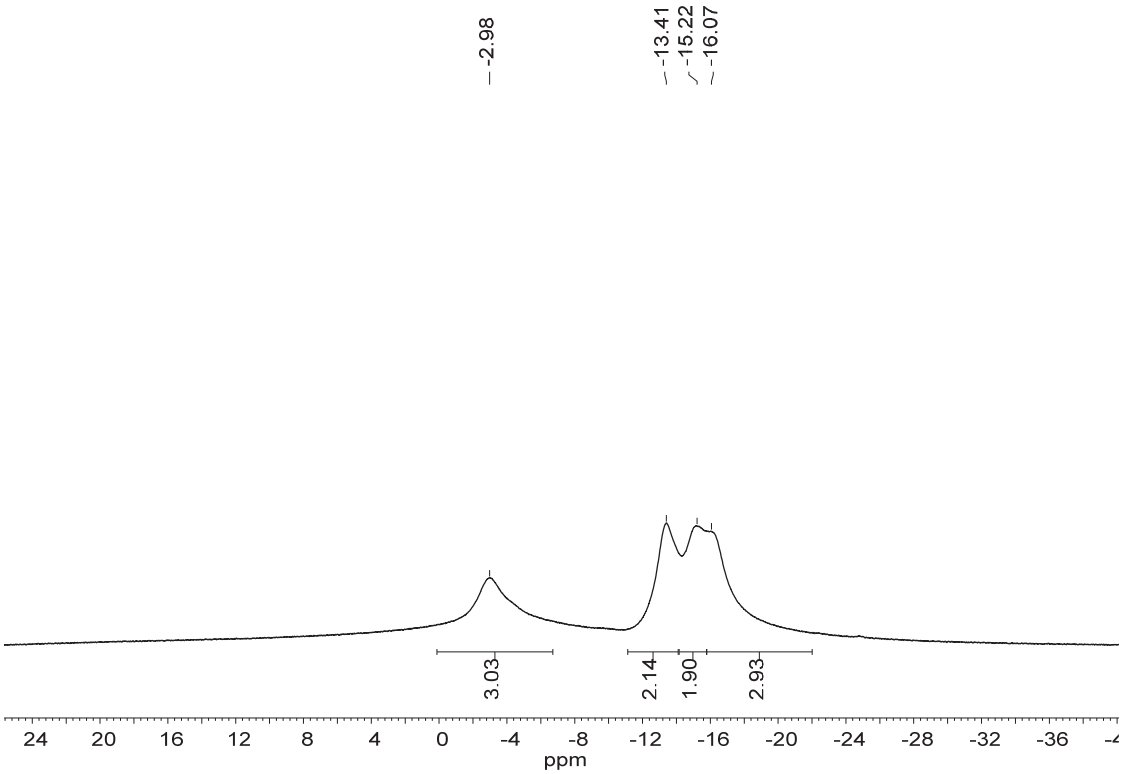
^{13}C NMR of 5, 126 M, $CDCl_3$



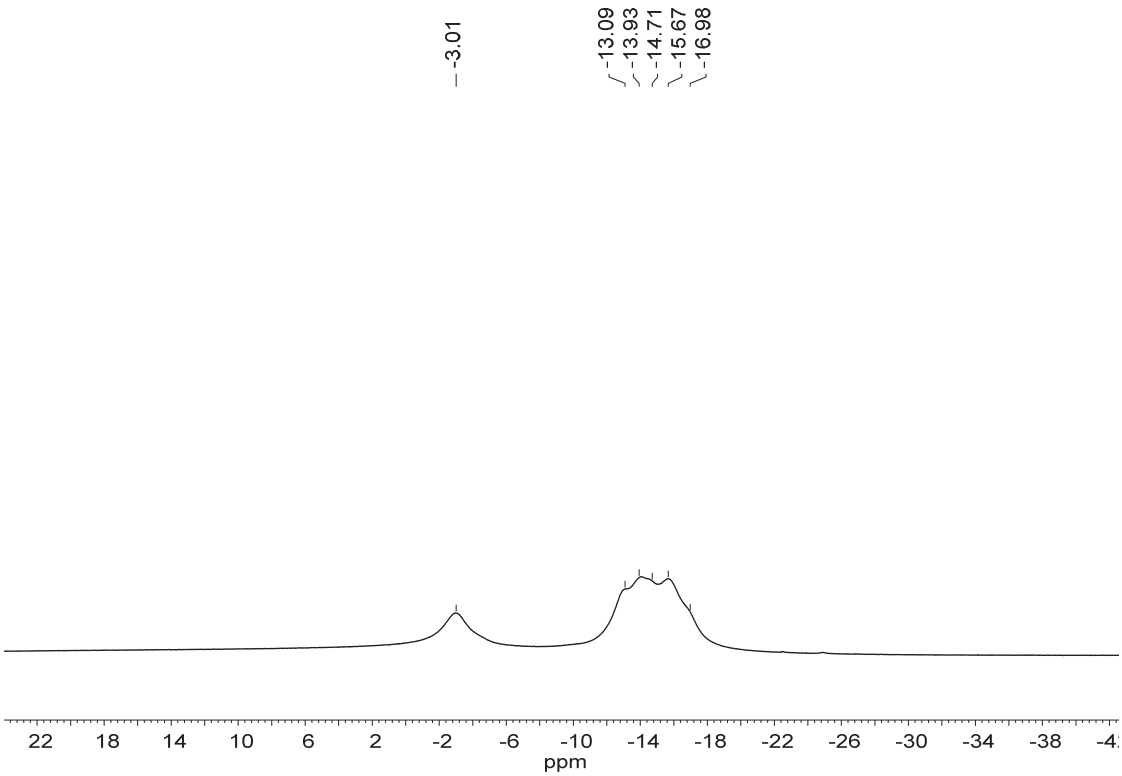
^{1}H NMR of 6, 500 M, $CDCl_3$



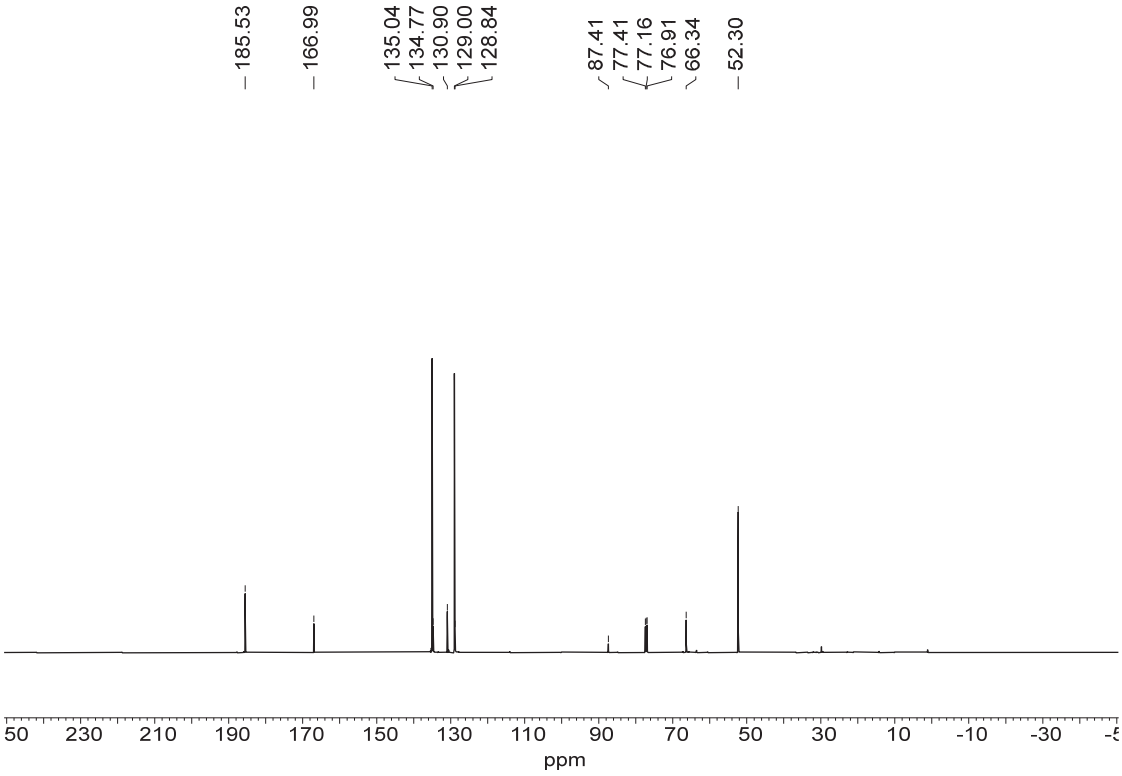
$^{11}B\ \{^{1}H\}$ NMR of 6, 160 M, $CDCl_3$



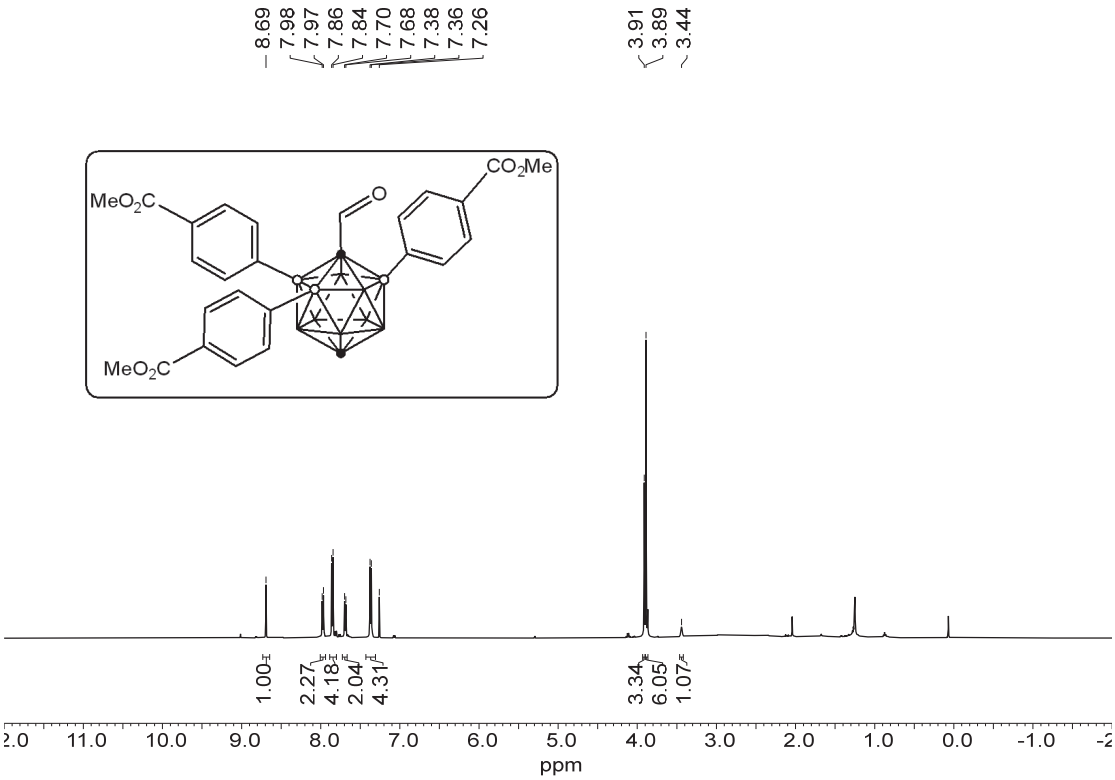
^{11}B NMR of 6, 160 M, $CDCl_3$



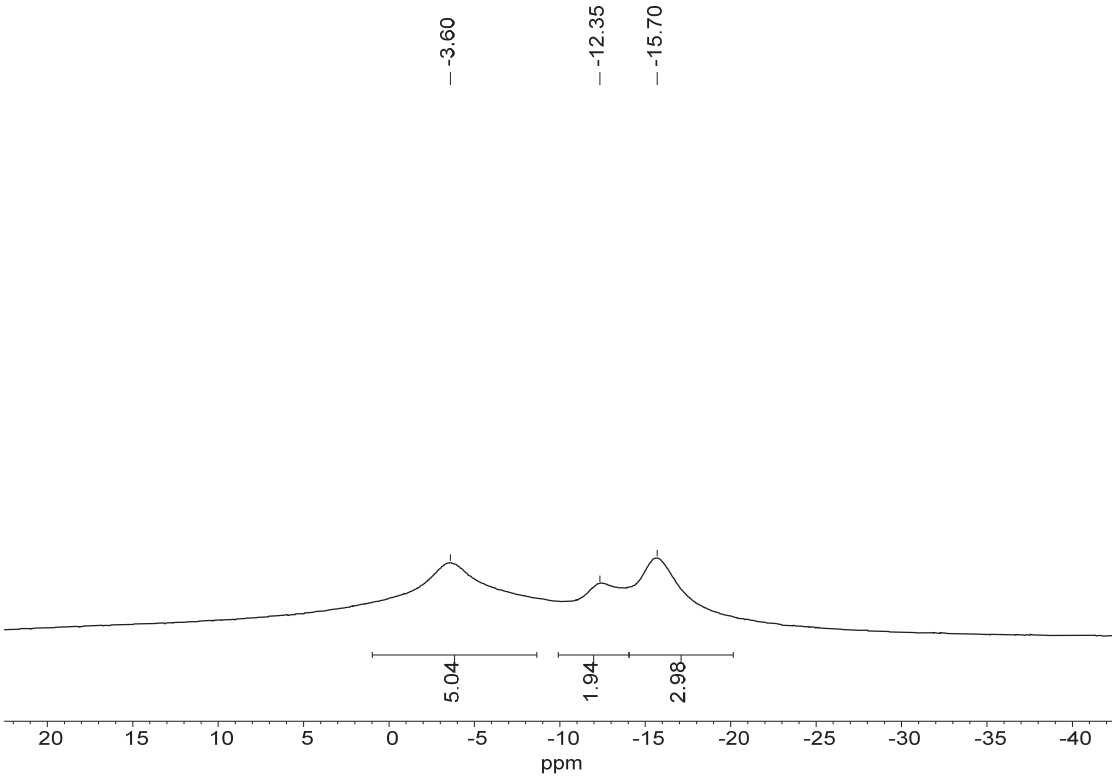
^{13}C (^{1}H) NMR of 6, 126 M, $CDCl_3$



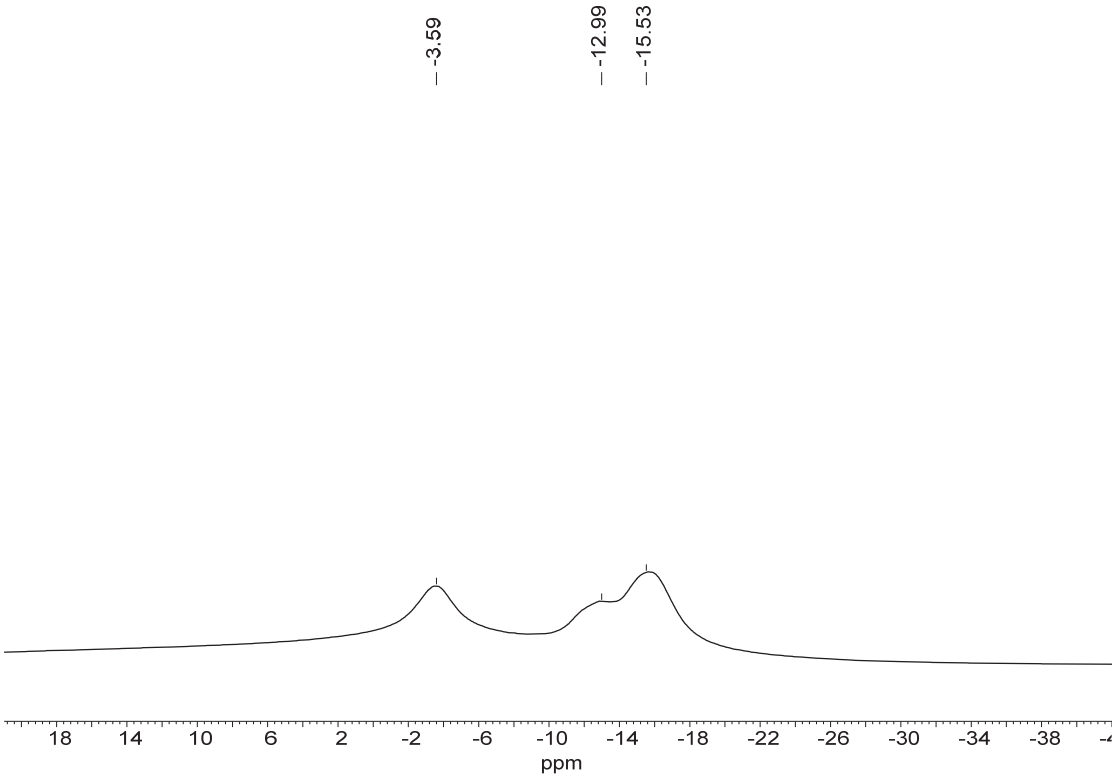
^{1}H NMR of 7, 500 M, $CDCl_3$



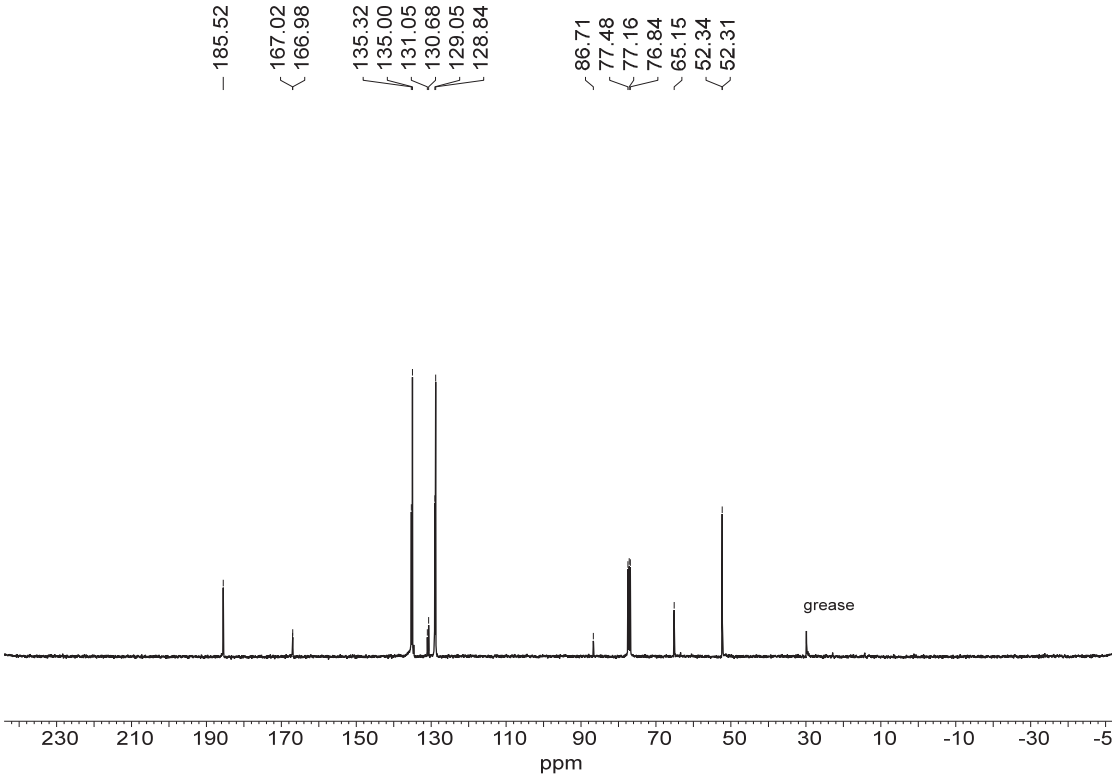
^{11}B (^{1}H) NMR of 7, 160 M, $CDCl_3$



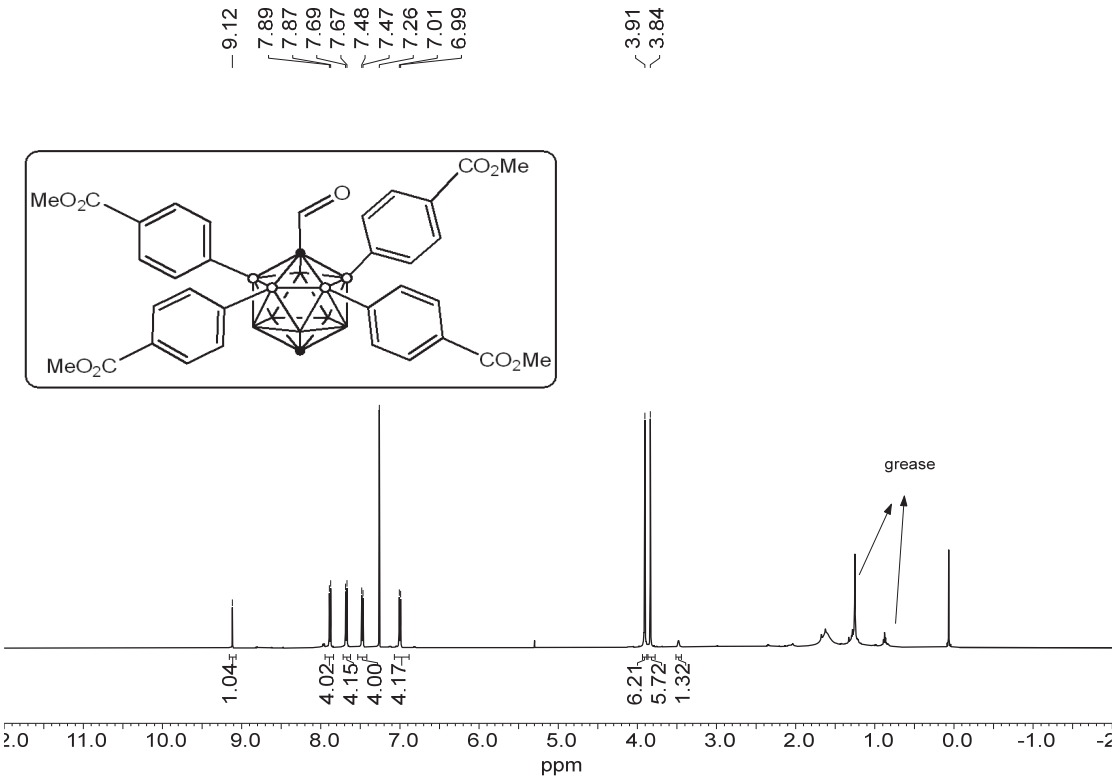
^{11}B NMR of 7, 160 M, $CDCl_3$



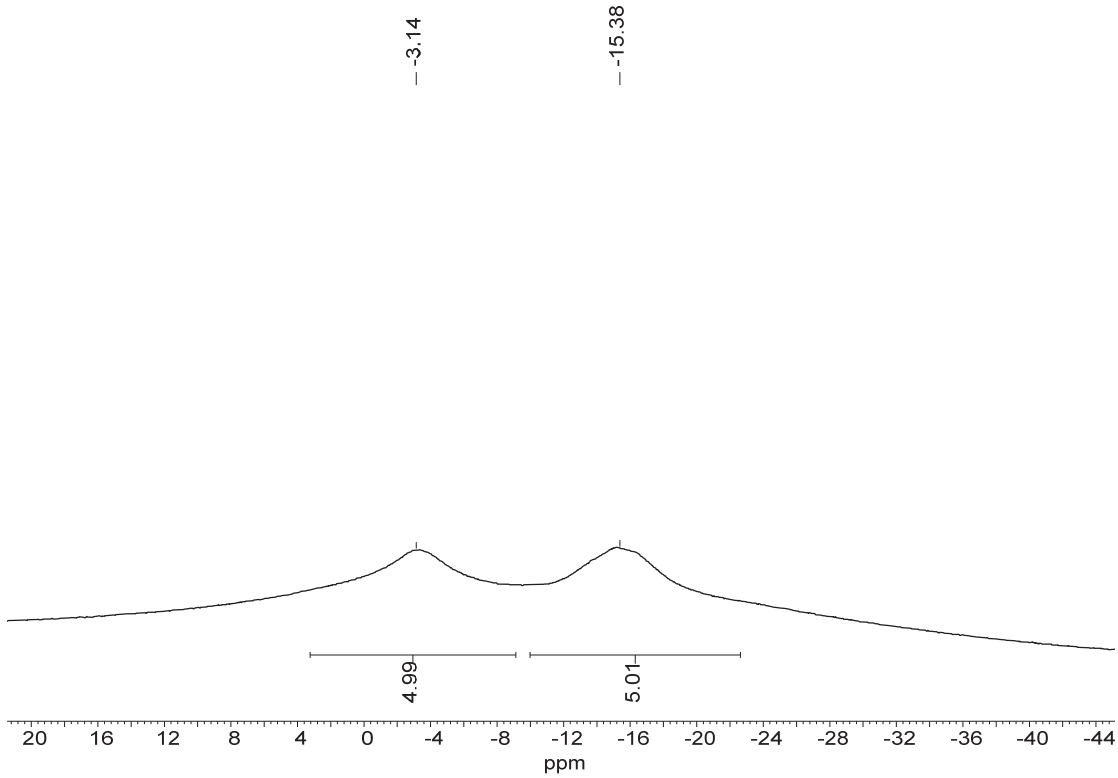
^{13}C NMR of 7, 101 M, $CDCl_3$



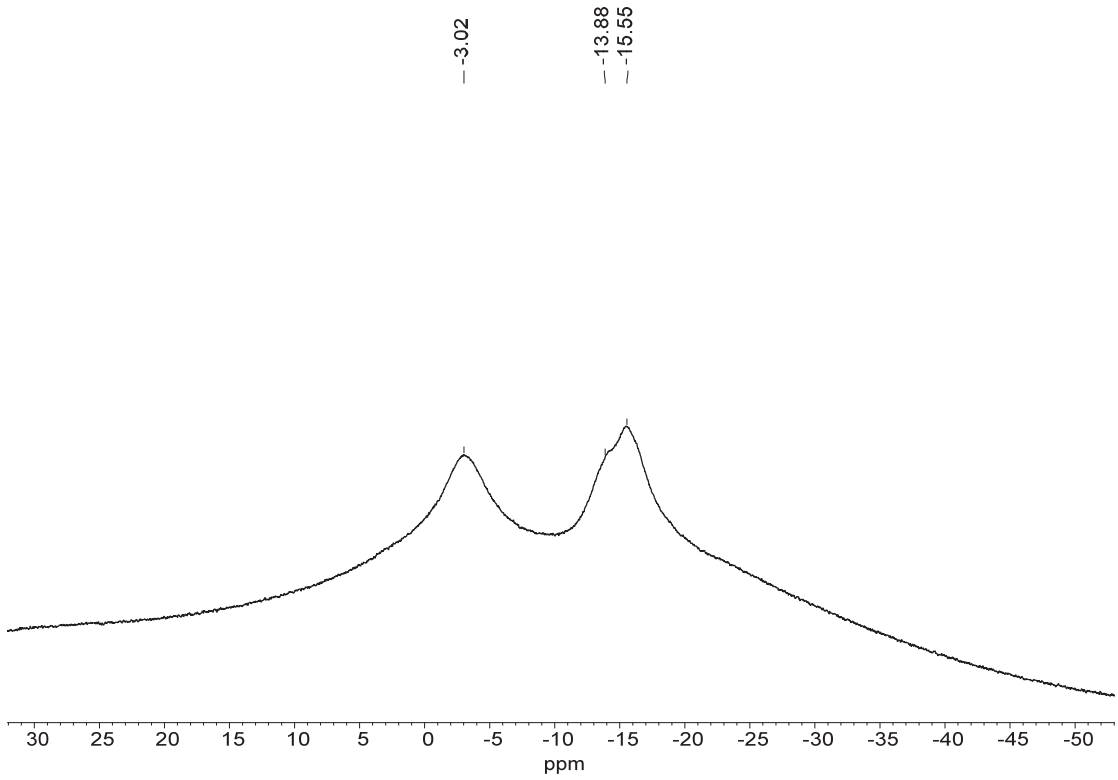
^{1}H NMR of 8, 500 M, $CDCl_3$



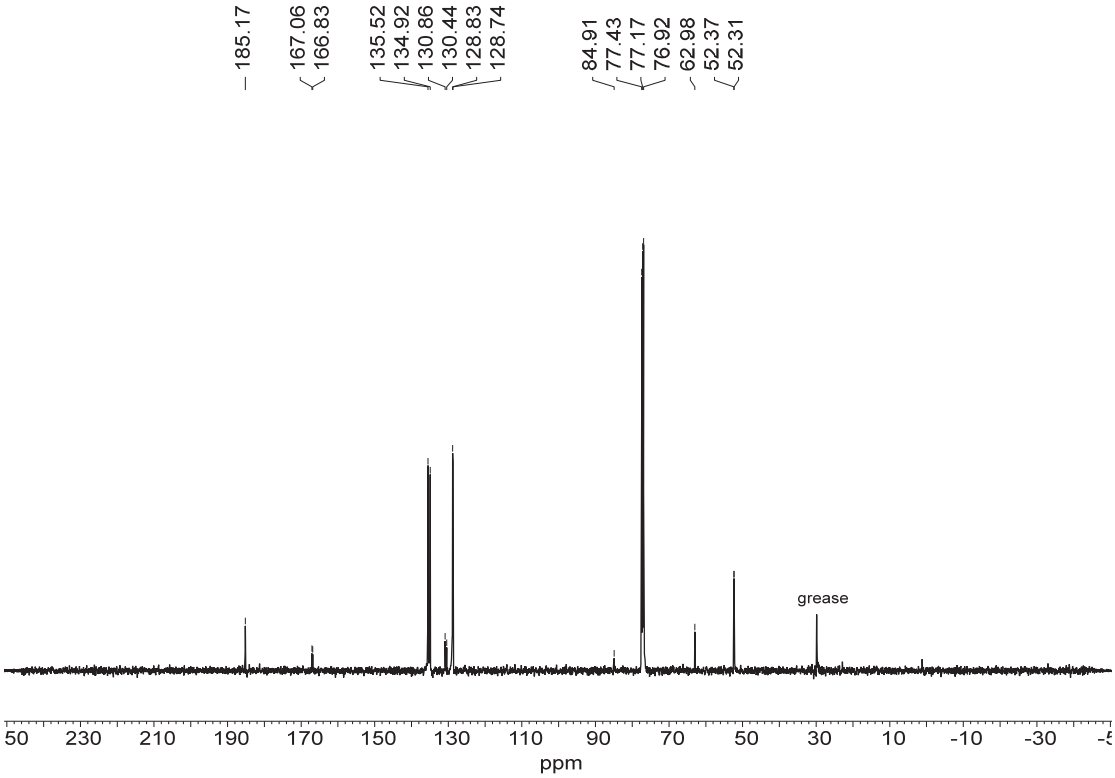
^{11}B {H} NMR of 8, 128 M, $CDCl_3$



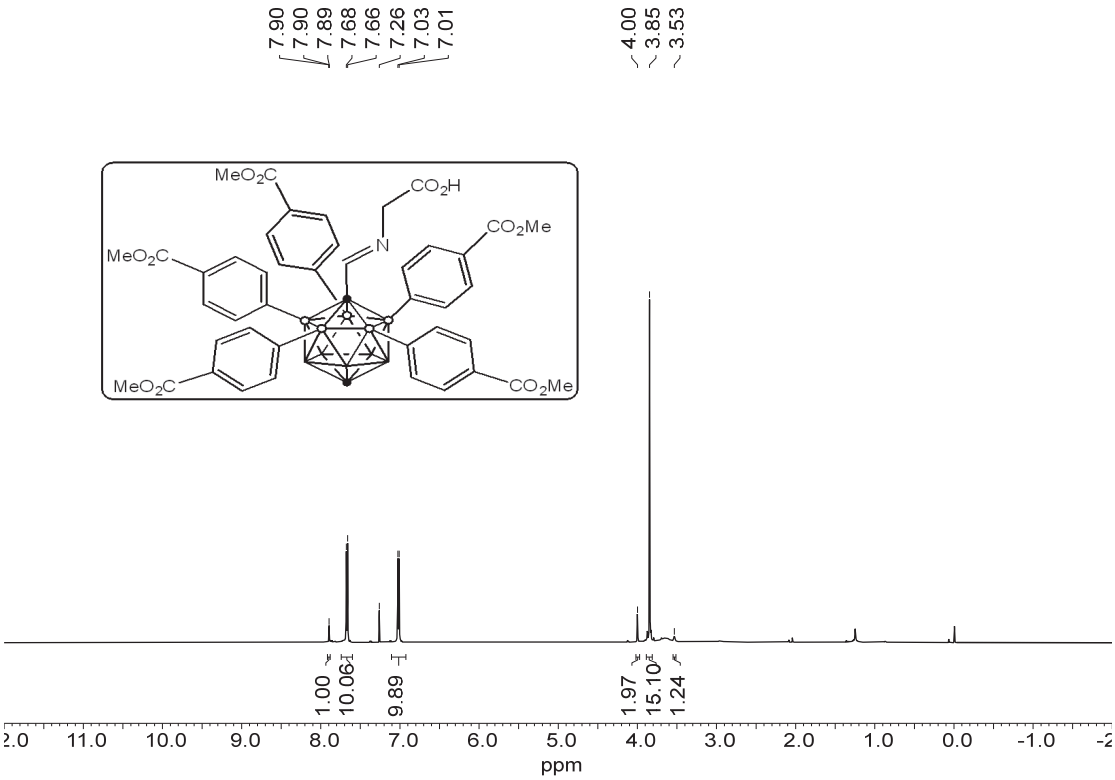
^{11}B NMR of 8, 128 M, $CDCl_3$



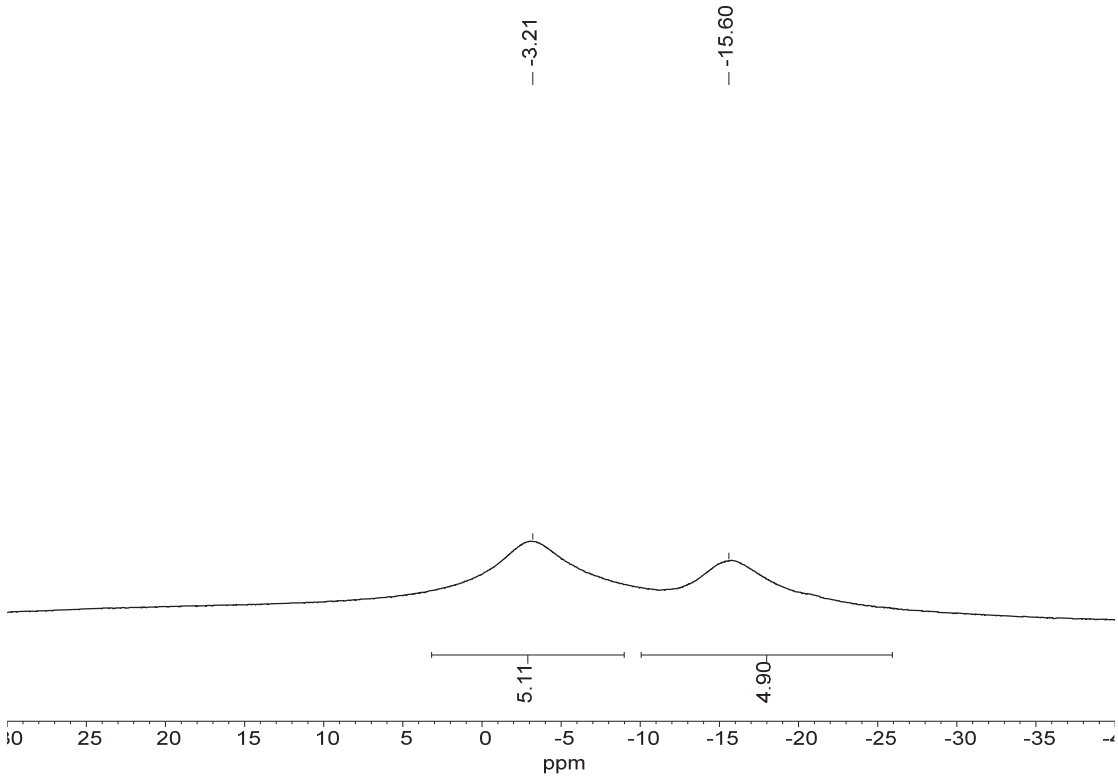
$^{13}C\ \{^1H\}$ NMR of 8, 126 M, $CDCl_3$



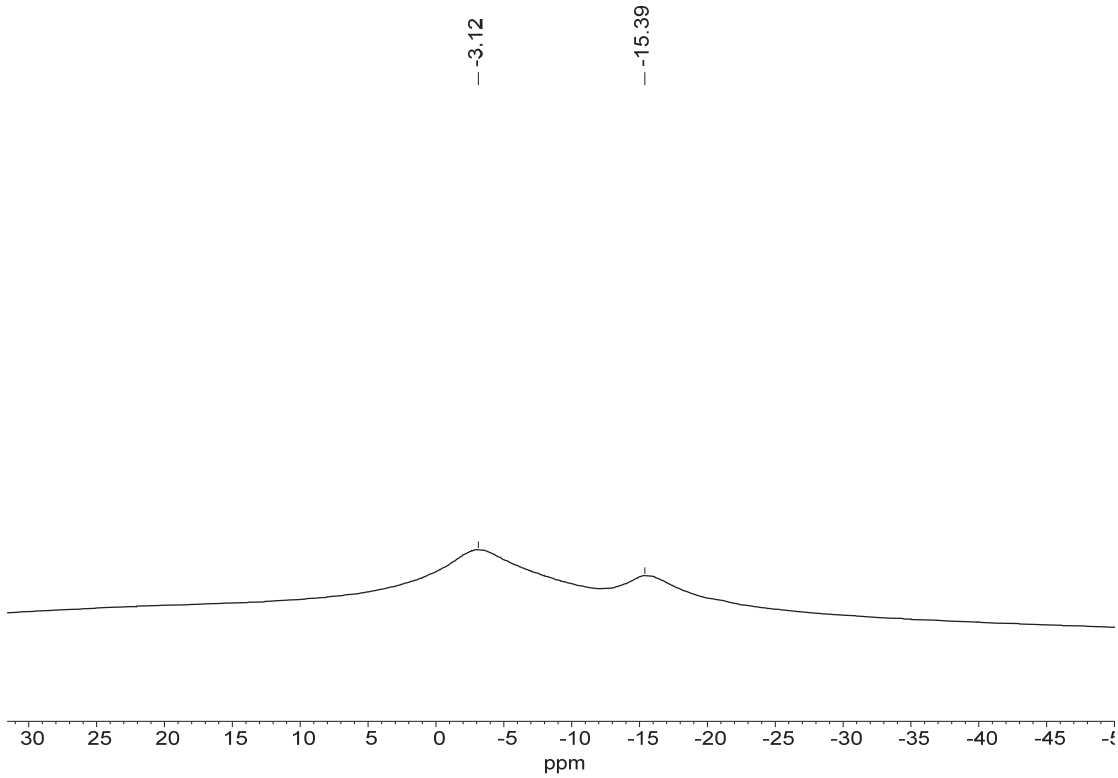
^1H NMR of 9, 400 M, $CDCl_3$



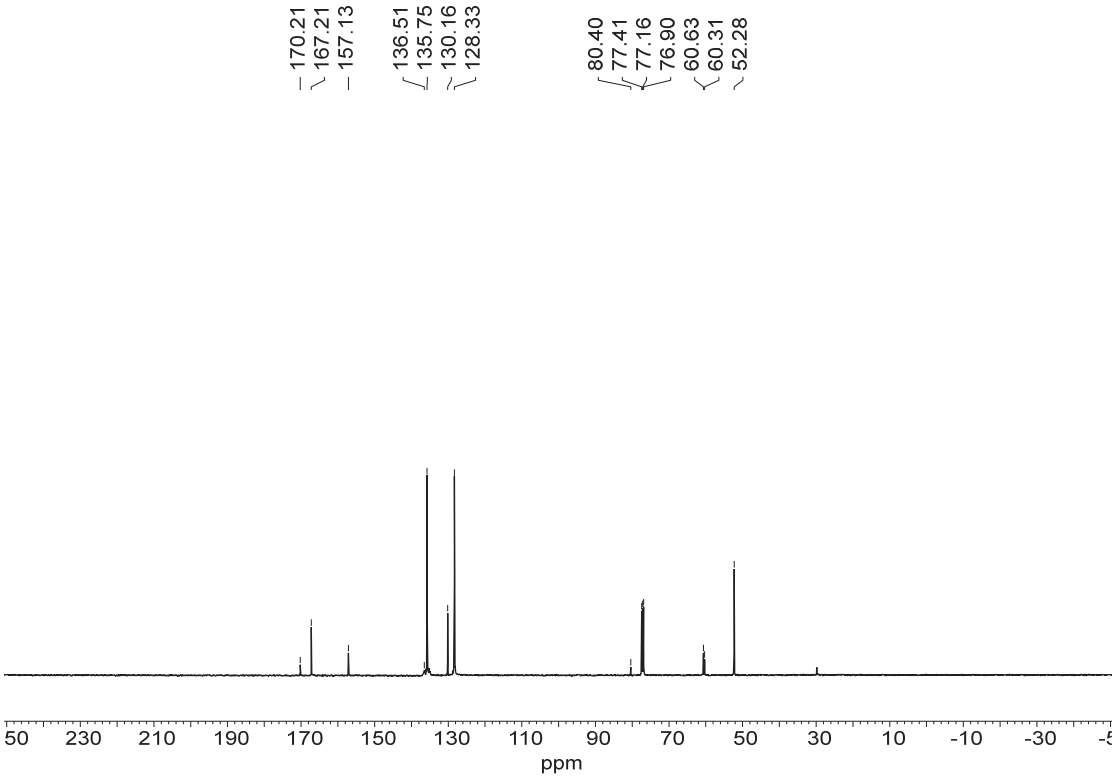
$^{11}B\ \{^{1}H\}$ NMR of 9, 128 M, $CDCl_3$



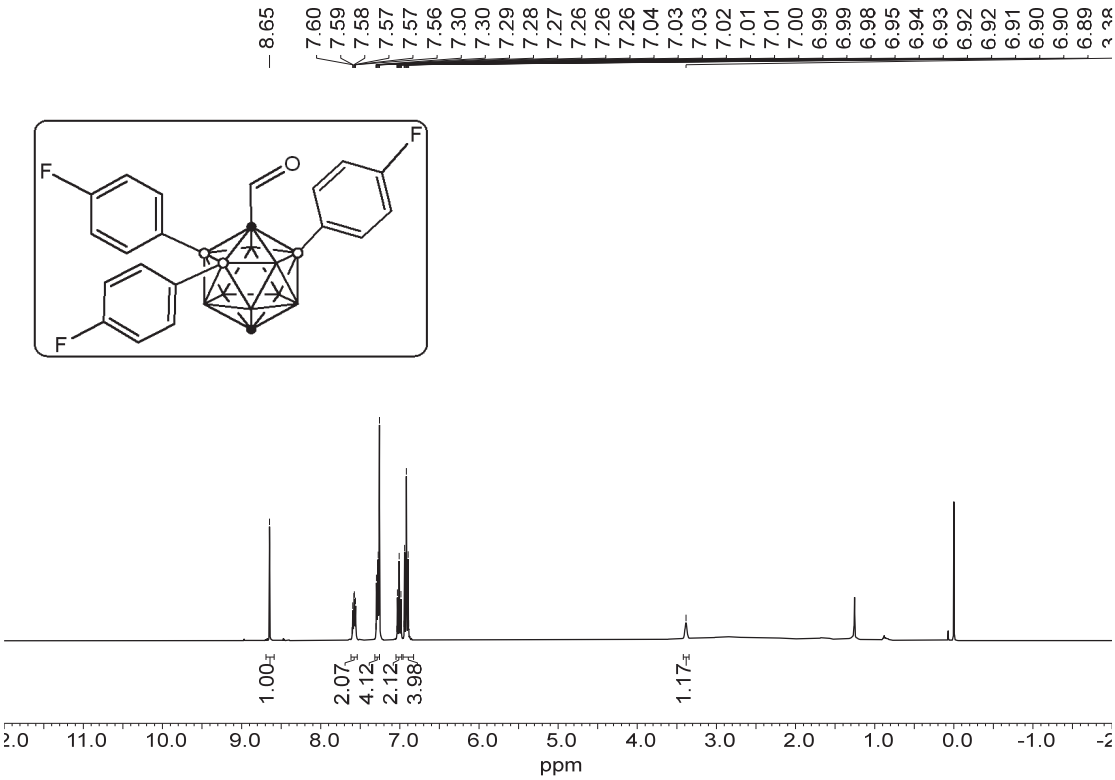
^{11}B NMR of 9, 128 M, $CDCl_3$



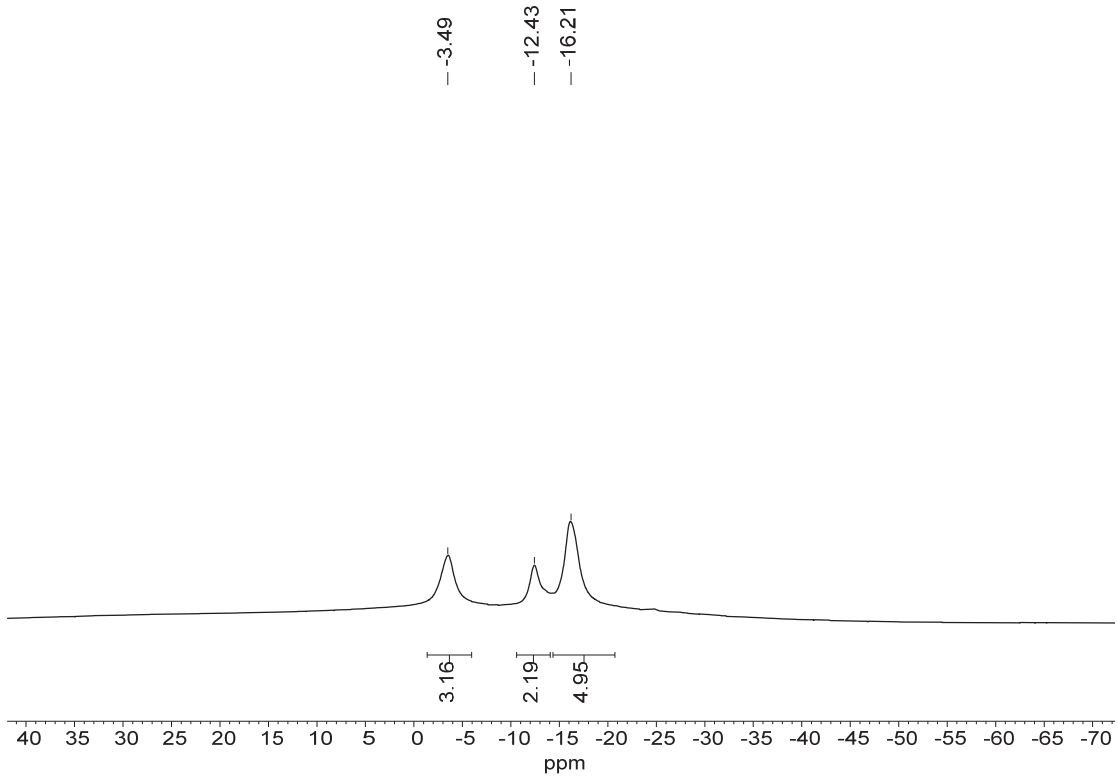
^{13}C NMR of 9, 101 M, $CDCl_3$



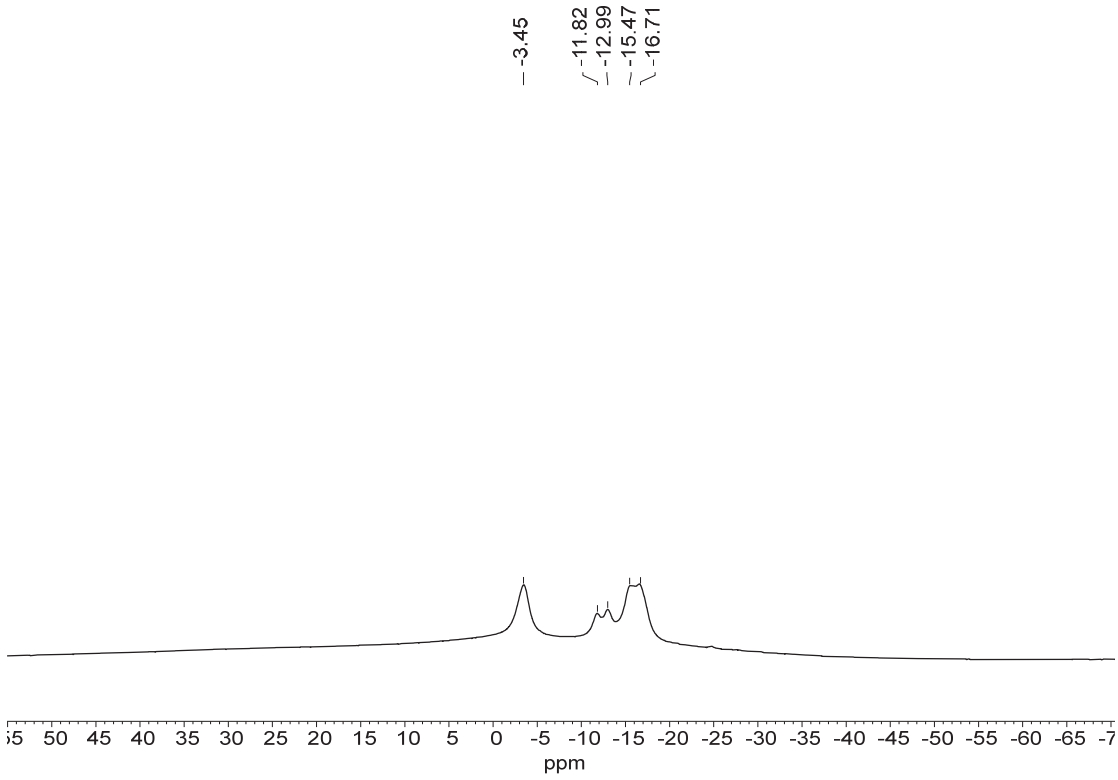
^{1}H NMR of 7', 400 M, $CDCl_3$



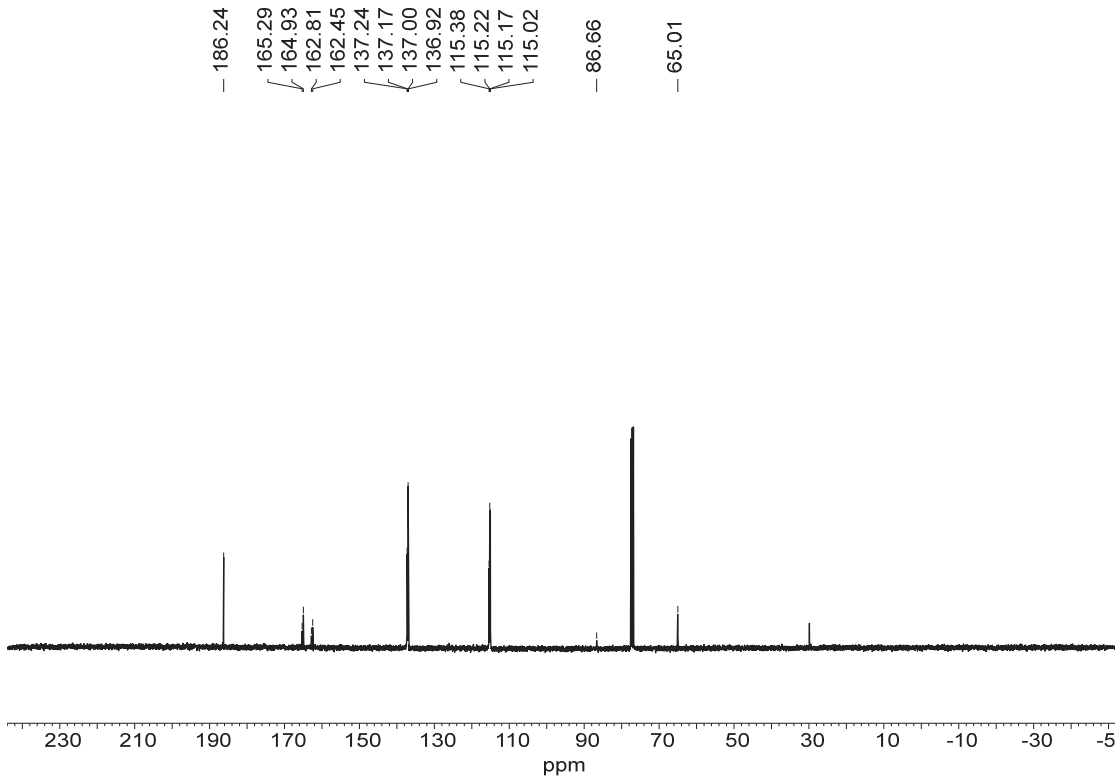
$^{11}B\ \{^{1}H\}$ NMR of 7', 128 M, $CDCl_3$



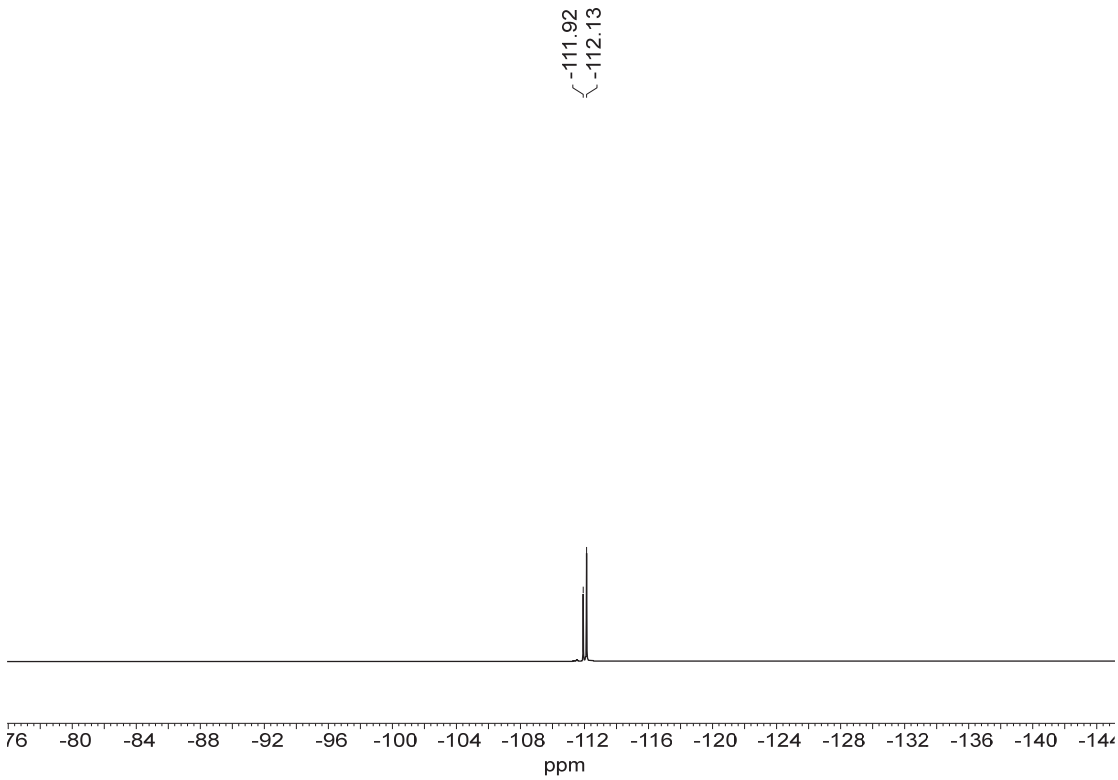
$^{11}B\ \{^{1}H\}$ NMR of 7', 128 M, $CDCl_3$



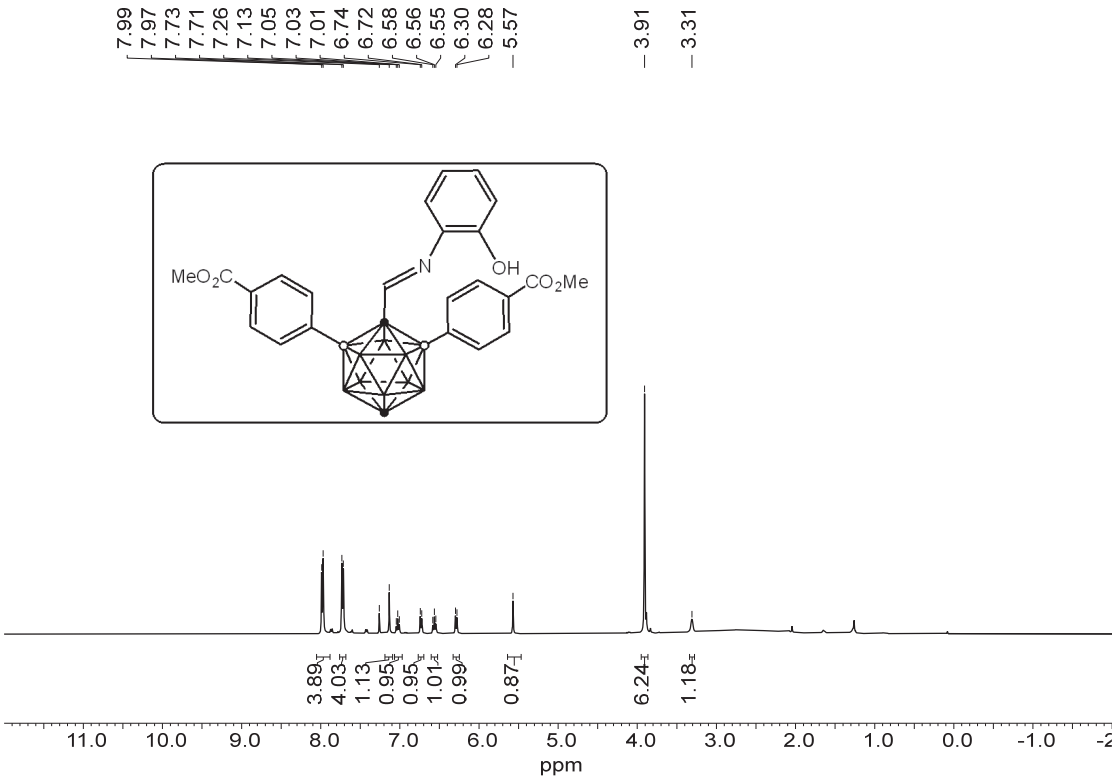
$^{13}C\ \{^{1}H\}$ NMR of 7', 101 M, $CDCl_3$



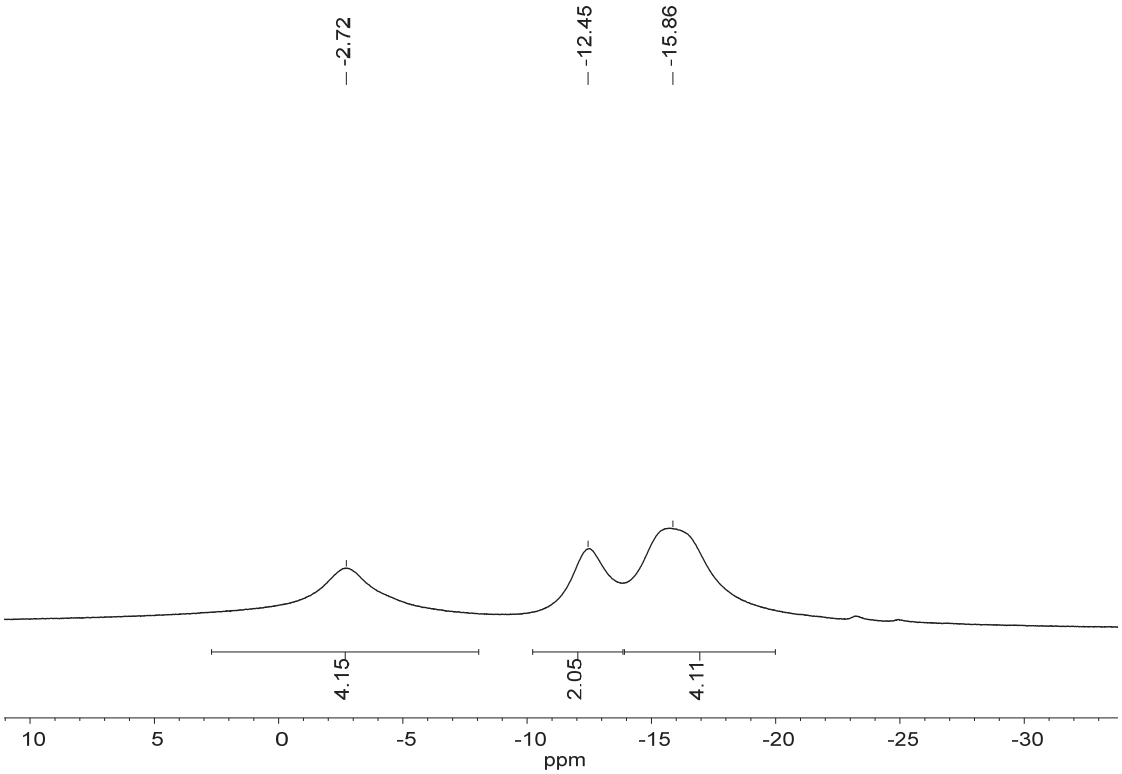
^{19}F NMR of 7', 376 M, $CDCl_3$



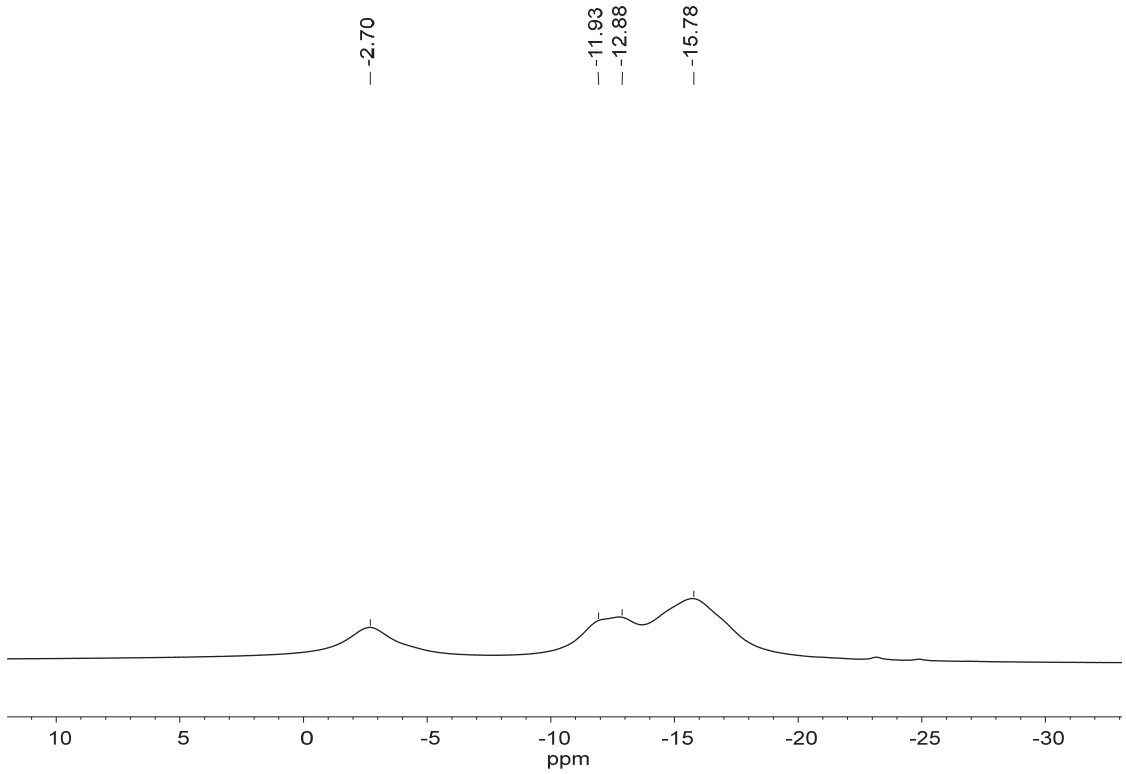
^{1}H NMR of 10, 400 M, $CDCl_3$



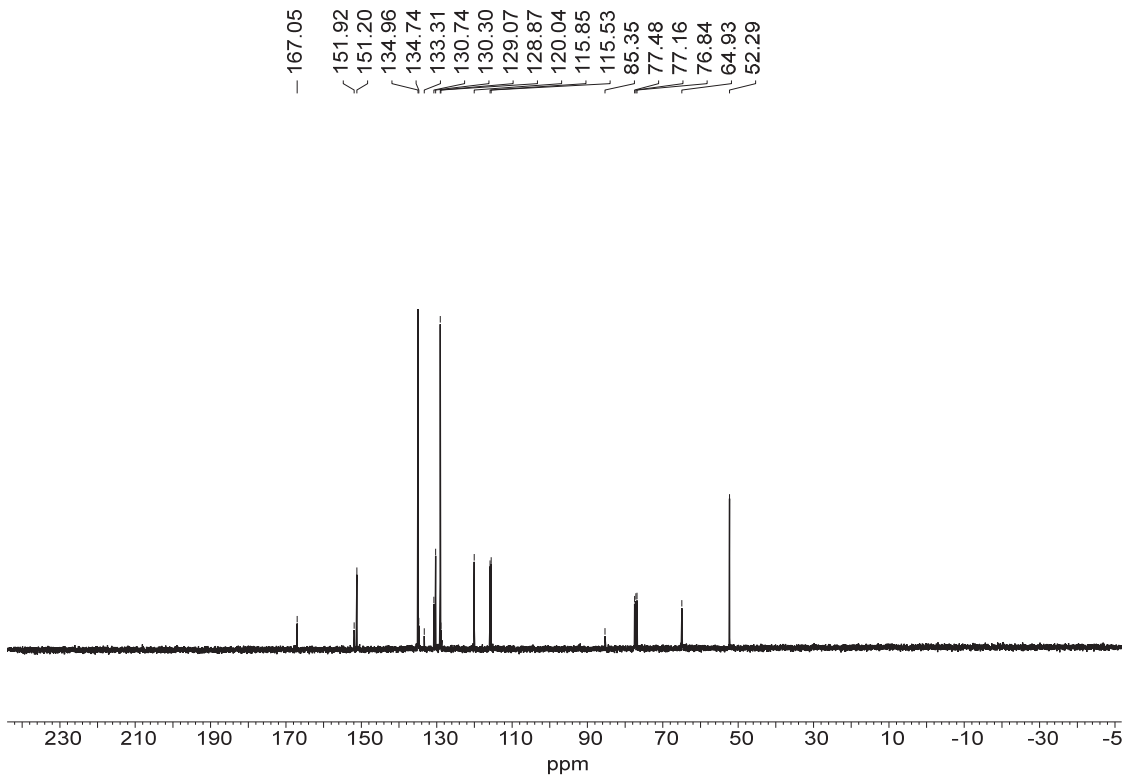
^{11}B {^{1}H} NMR of 10, 160 M, $CDCl_3$



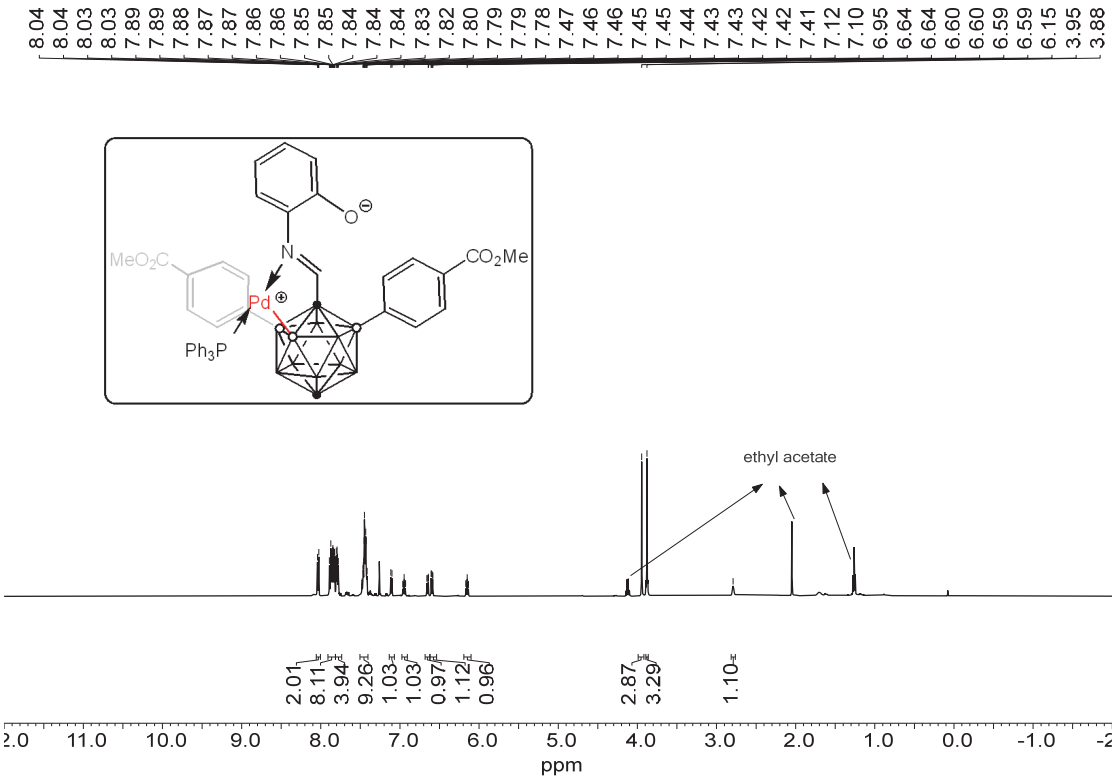
^{11}B NMR of 10, 160 M, $CDCl_3$



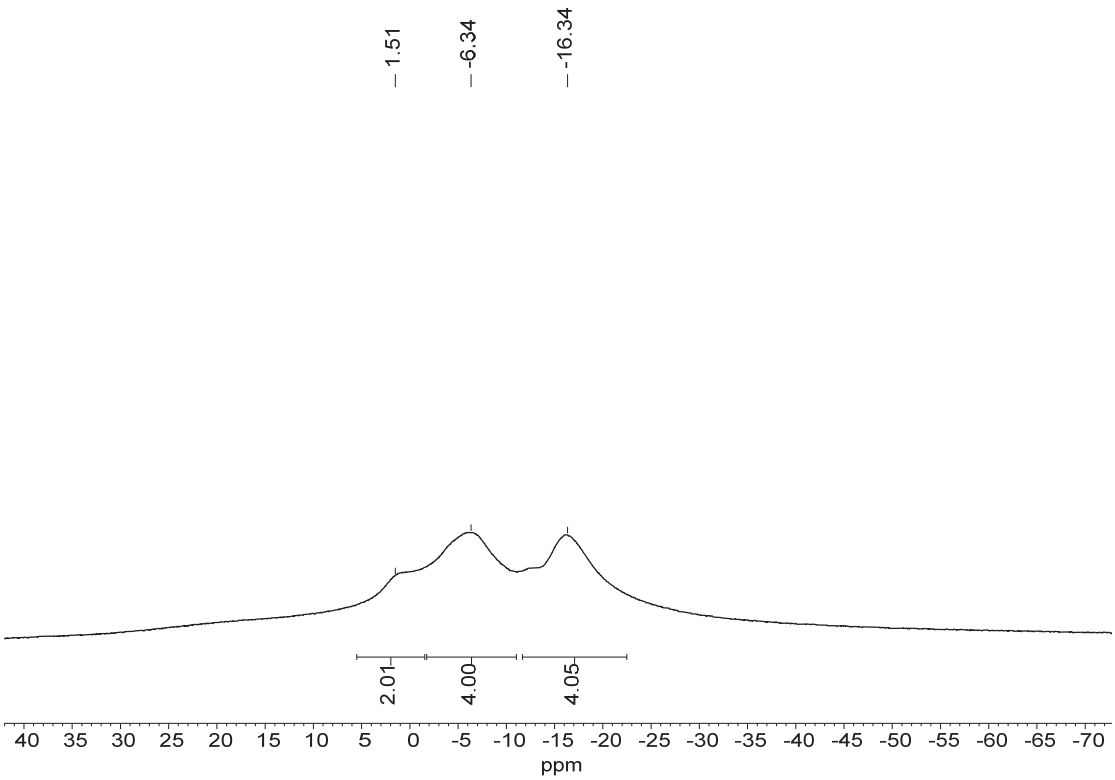
^{13}C {^{1}H} NMR of 10, 101 M, $CDCl_3$



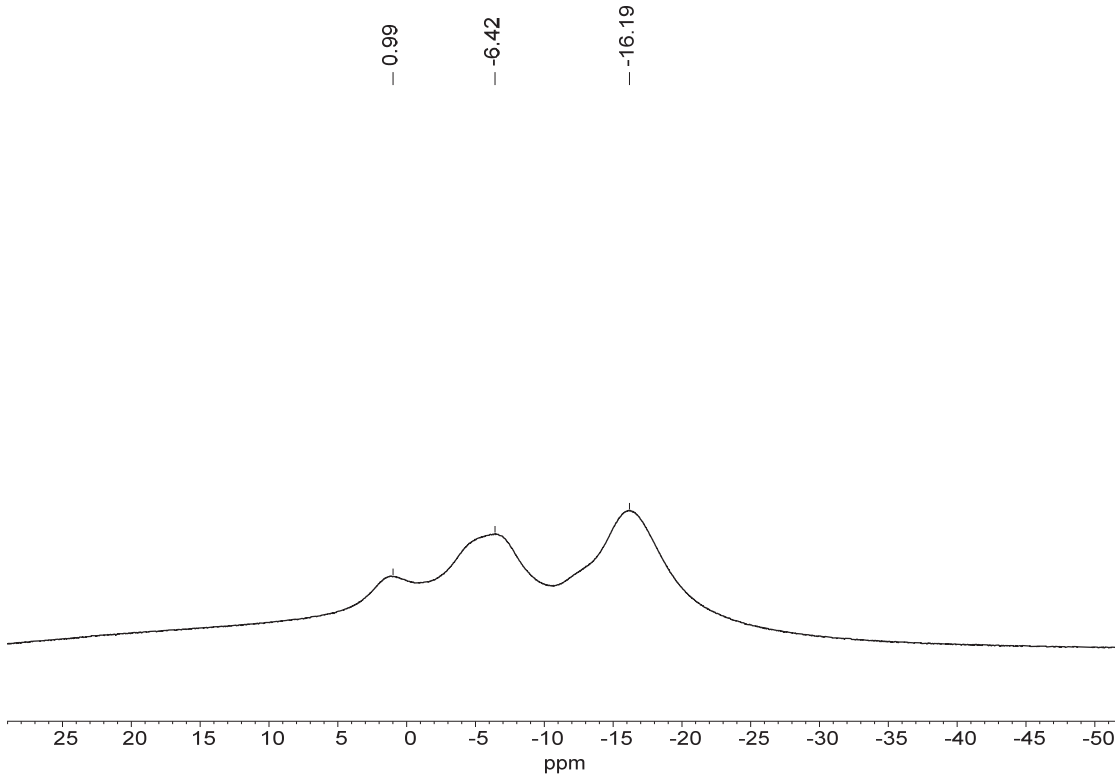
^{1}H NMR of 11, 500 M, $CDCl_3$



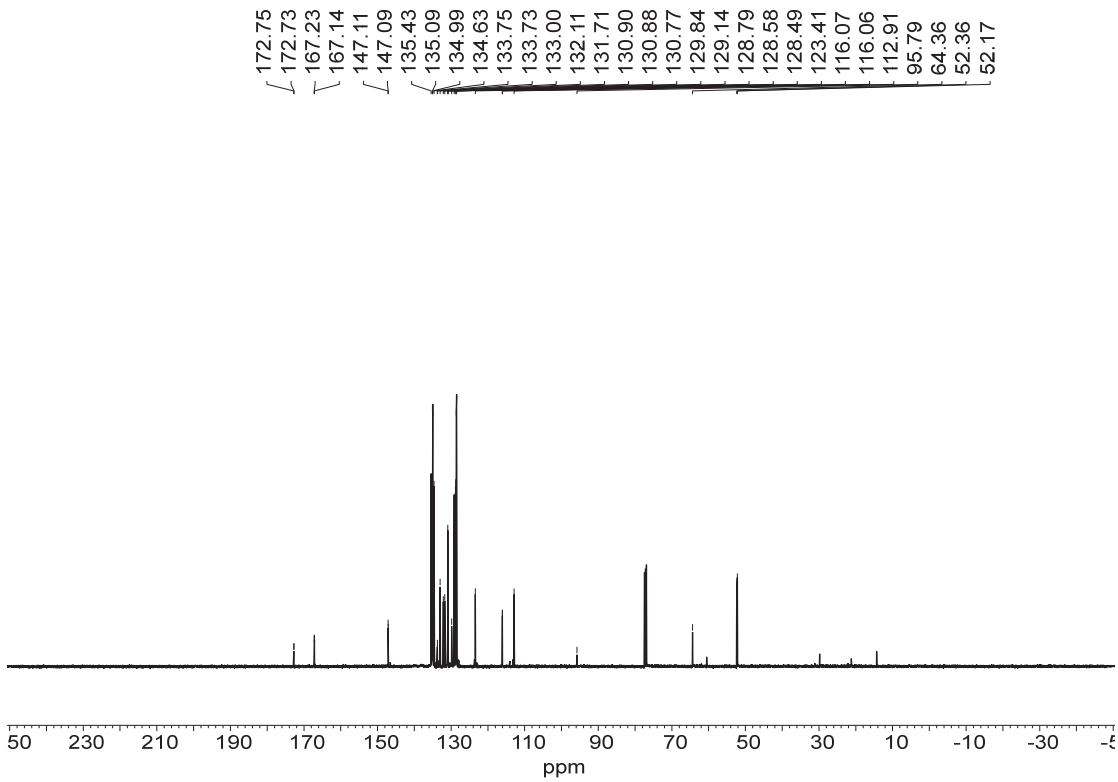
^{11}B {^{1}H} NMR of 11, 160 M, $CDCl_3$



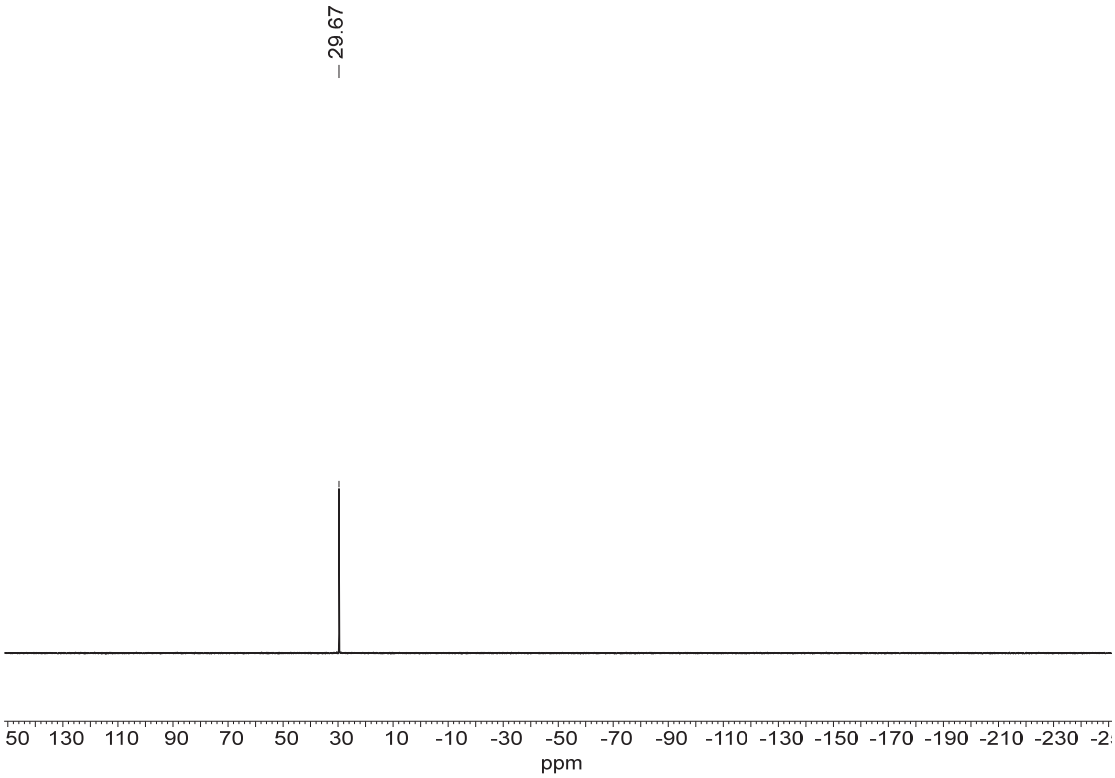
^{11}B NMR of 11, 160 M, $CDCl_3$



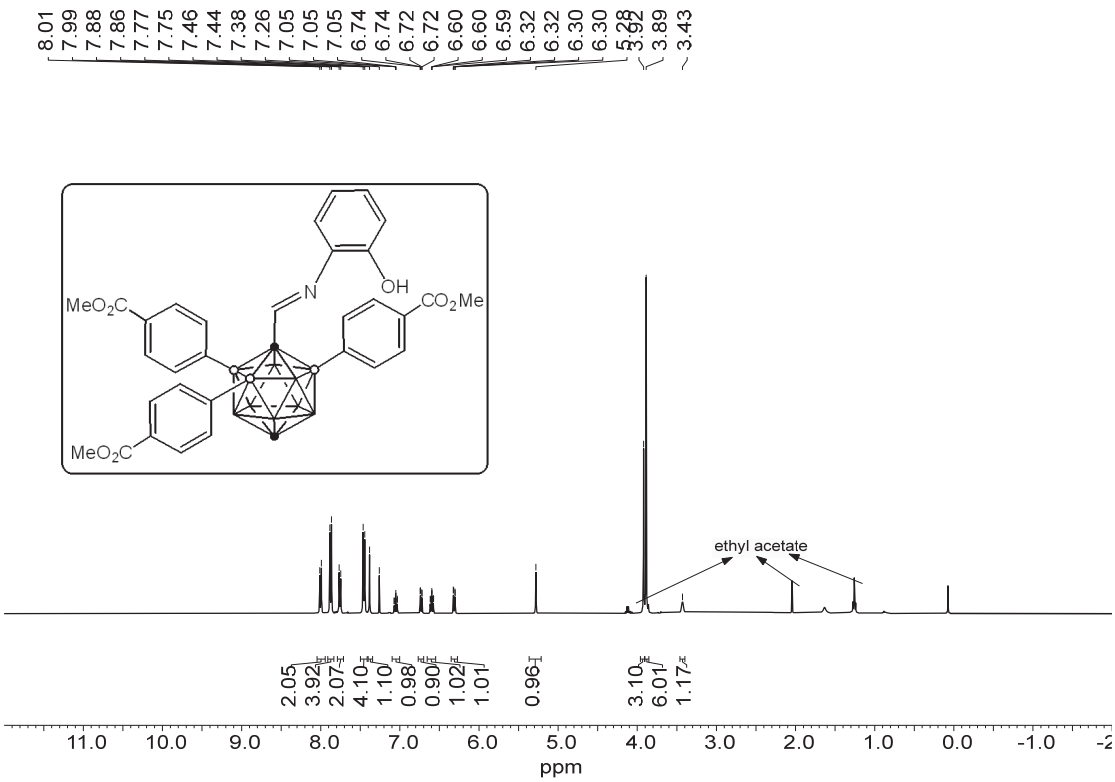
^{13}C NMR of 11, 126 M, $CDCl_3$



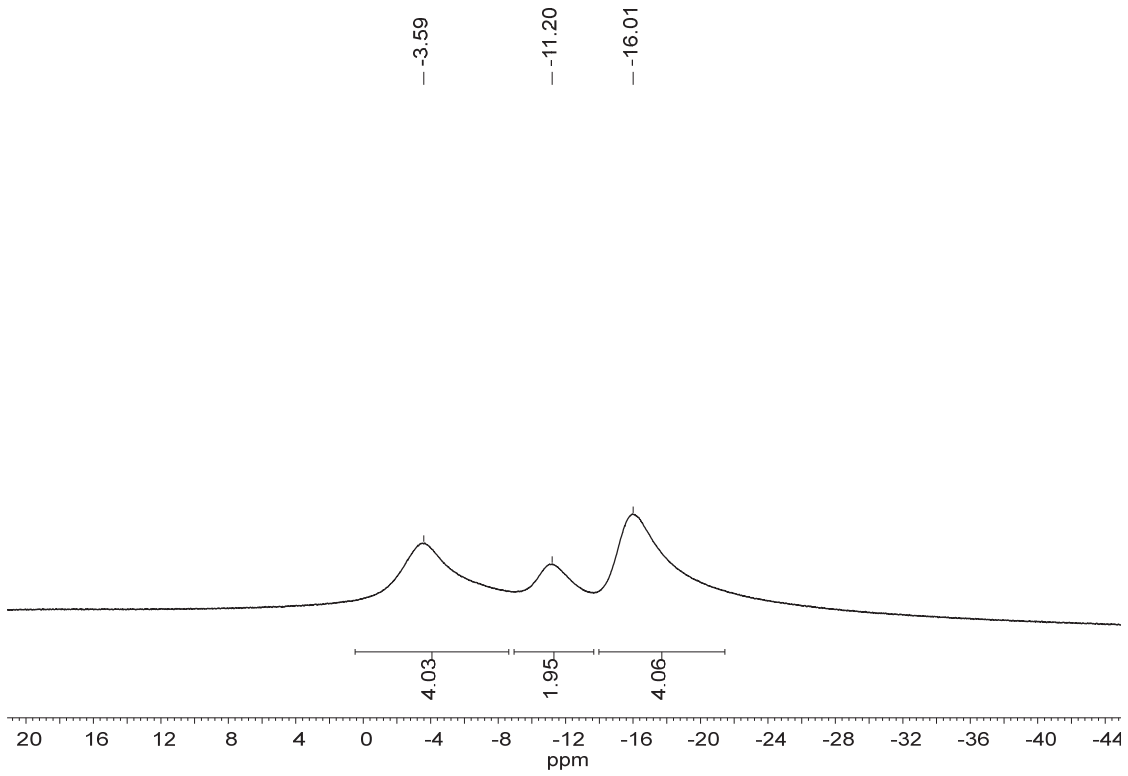
^{31}P NMR of 11, 202 M, $CDCl_3$



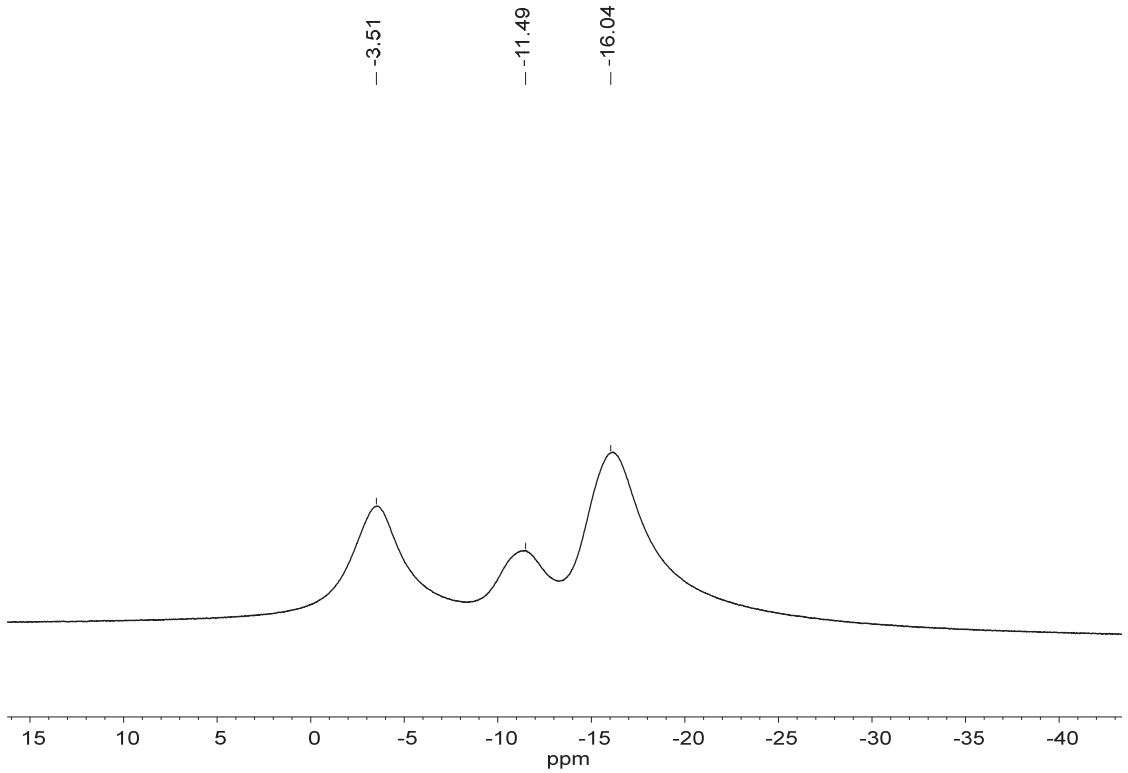
^{1}H NMR of 12, 400 M, $CDCl_3$



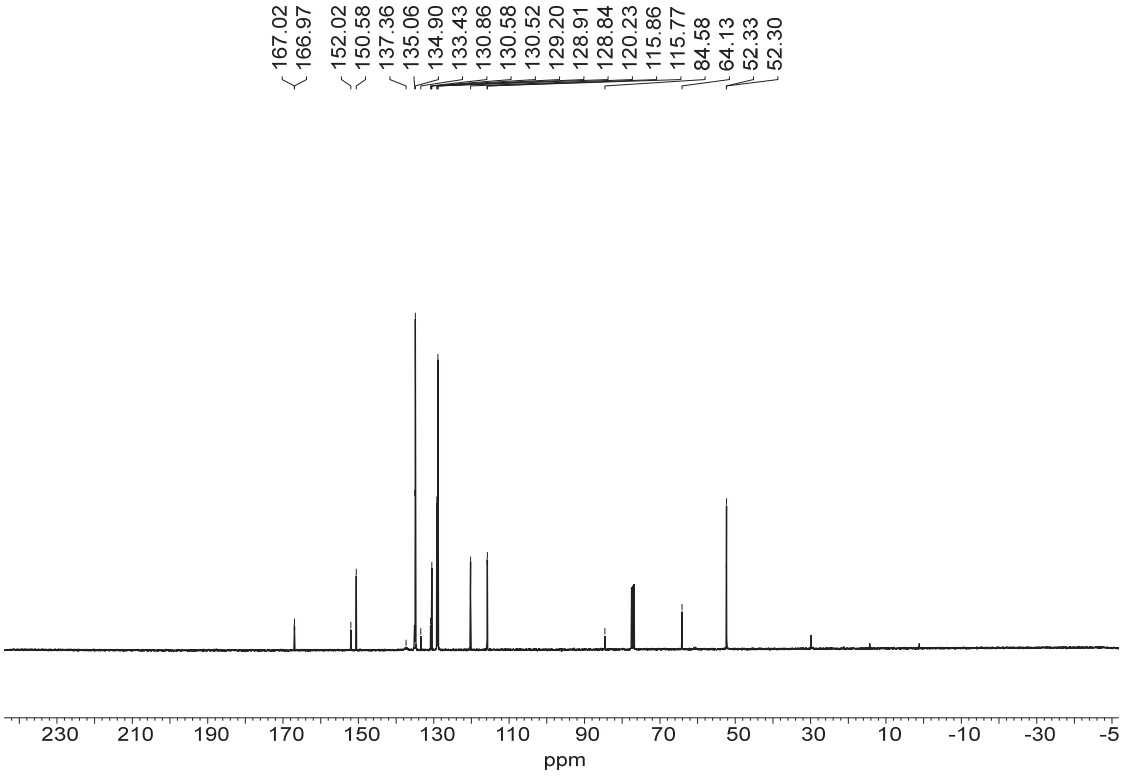
$^{11}B\ \{^{1}H\}$ NMR of 12, 160 M, $CDCl_3$



^{11}B NMR of 12, 160 M, $CDCl_3$

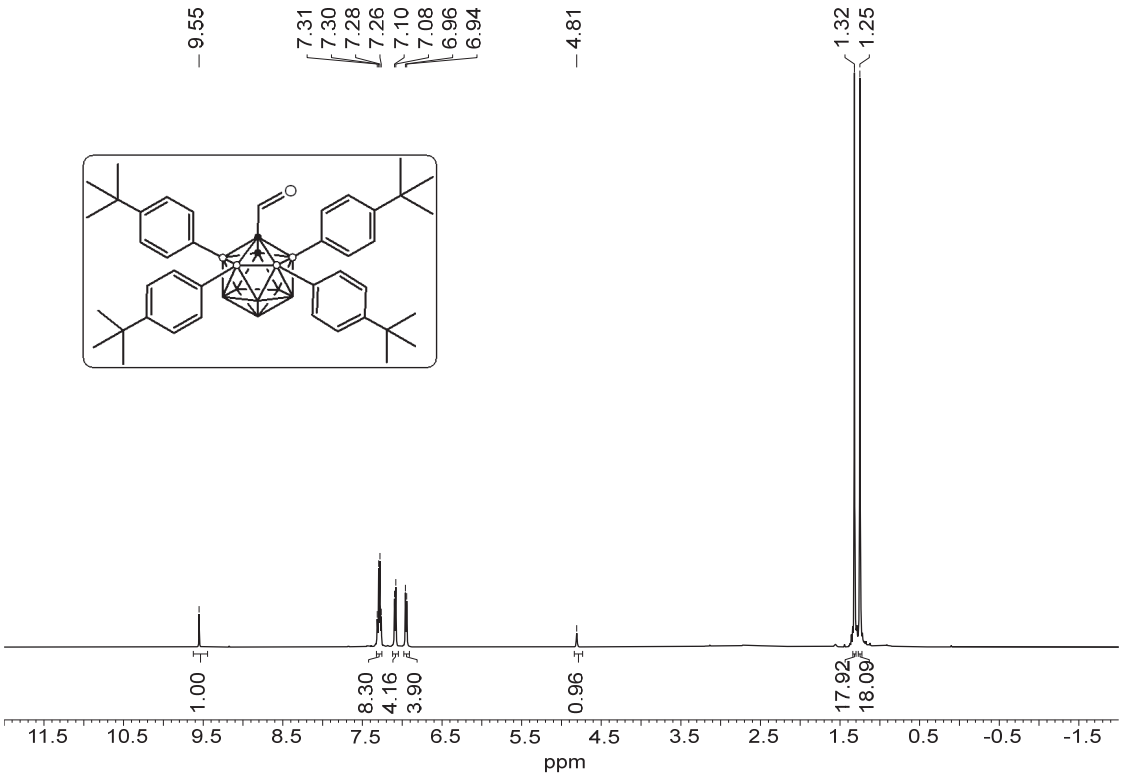


^{13}C NMR of 12, 101 M, $CDCl_3$

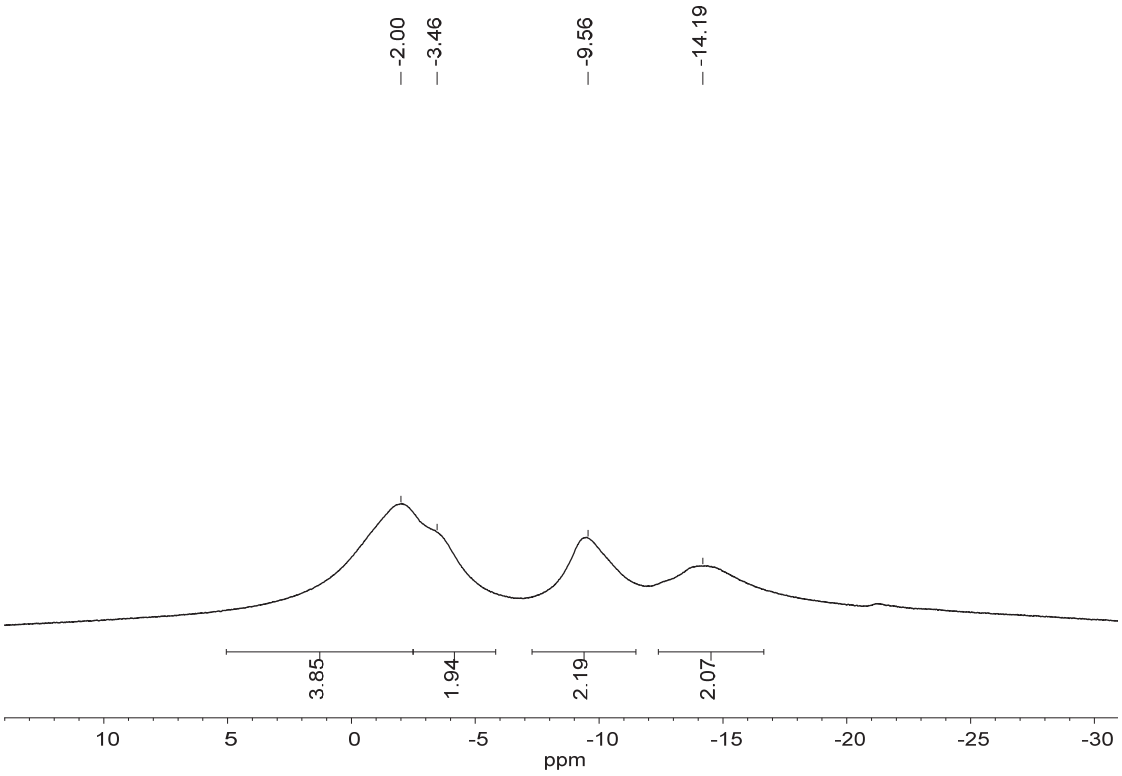


B(3,4,5,6)-tetra-arylated-*o*-carborane

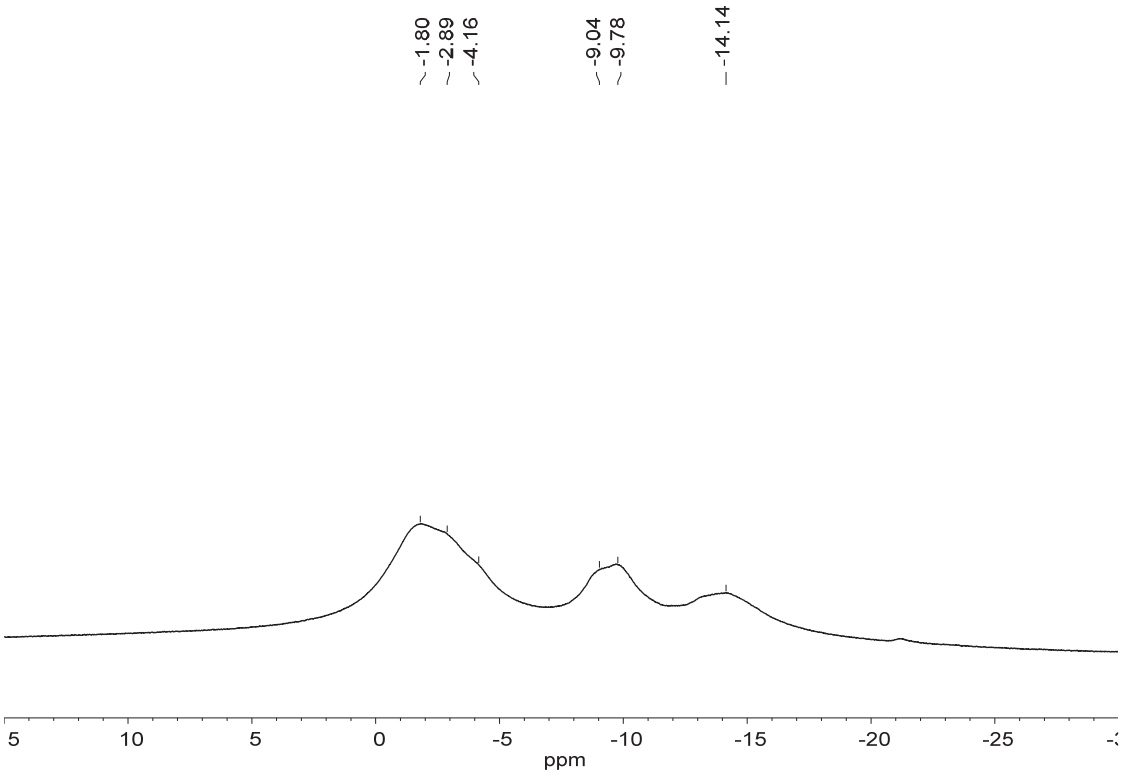
^{1}H NMR of 13a, 500 M, $CDCl_3$



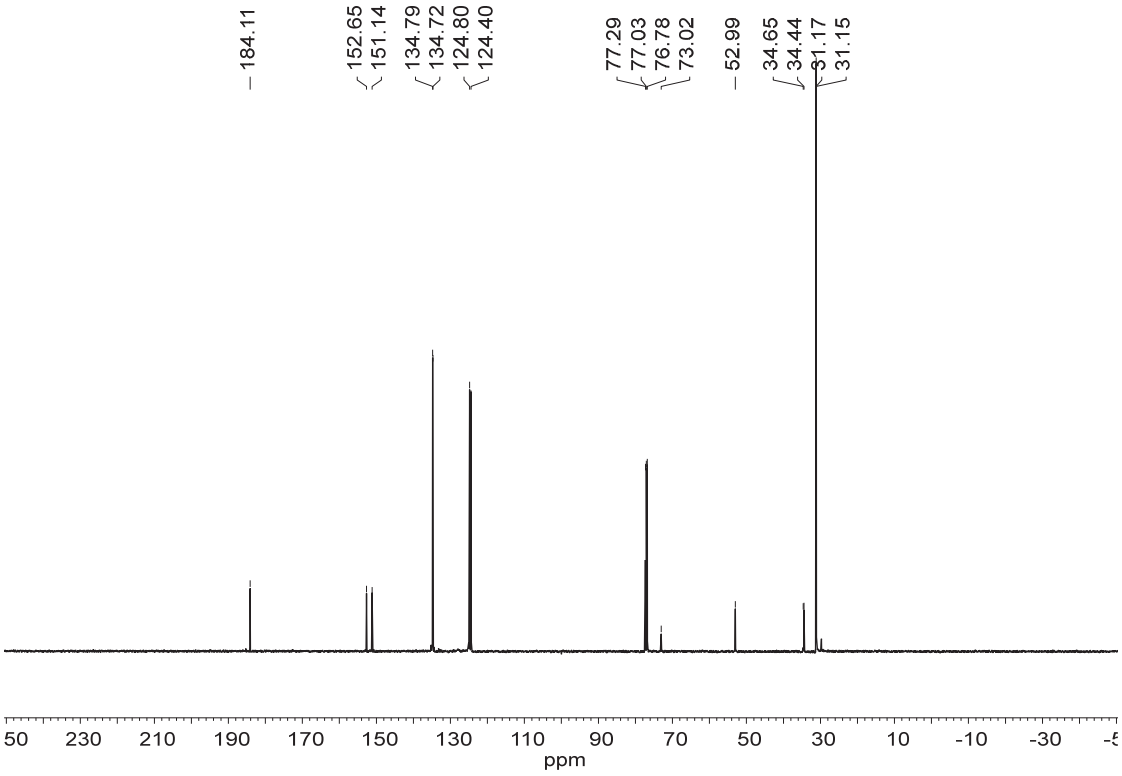
$^{11}B\ \{^{1}H\}$ NMR of 13a, 128 M, $CDCl_3$



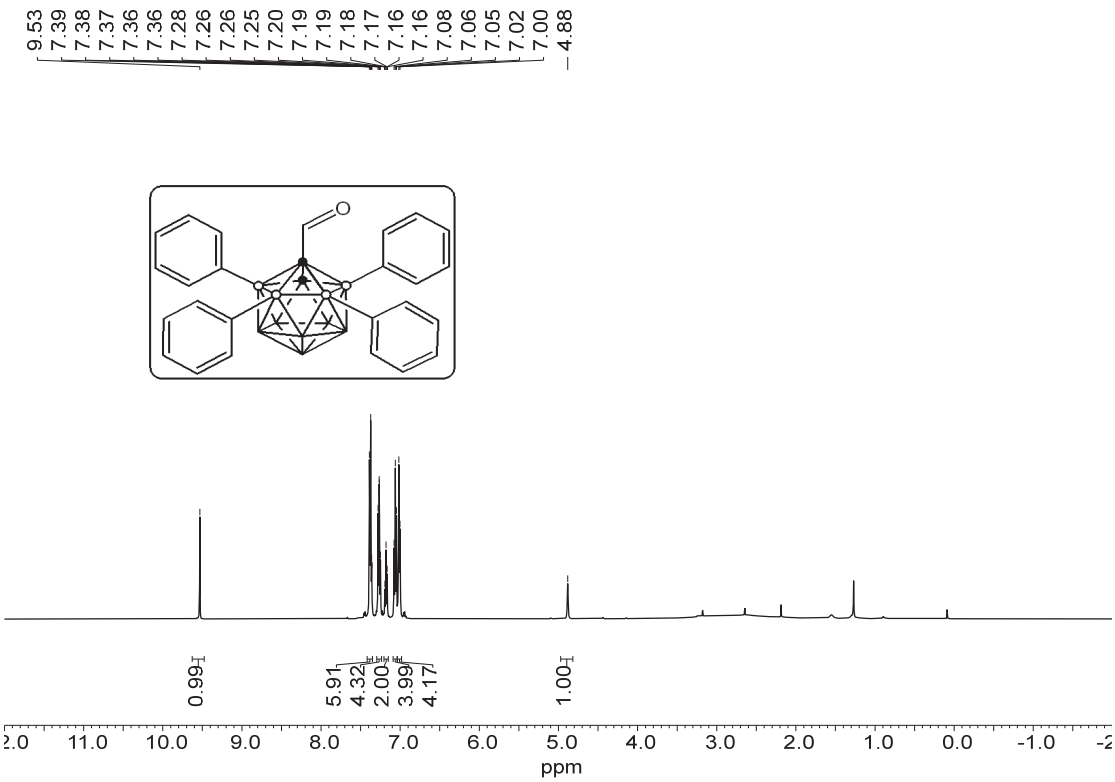
^{11}B NMR of 13a, 128 M, $CDCl_3$



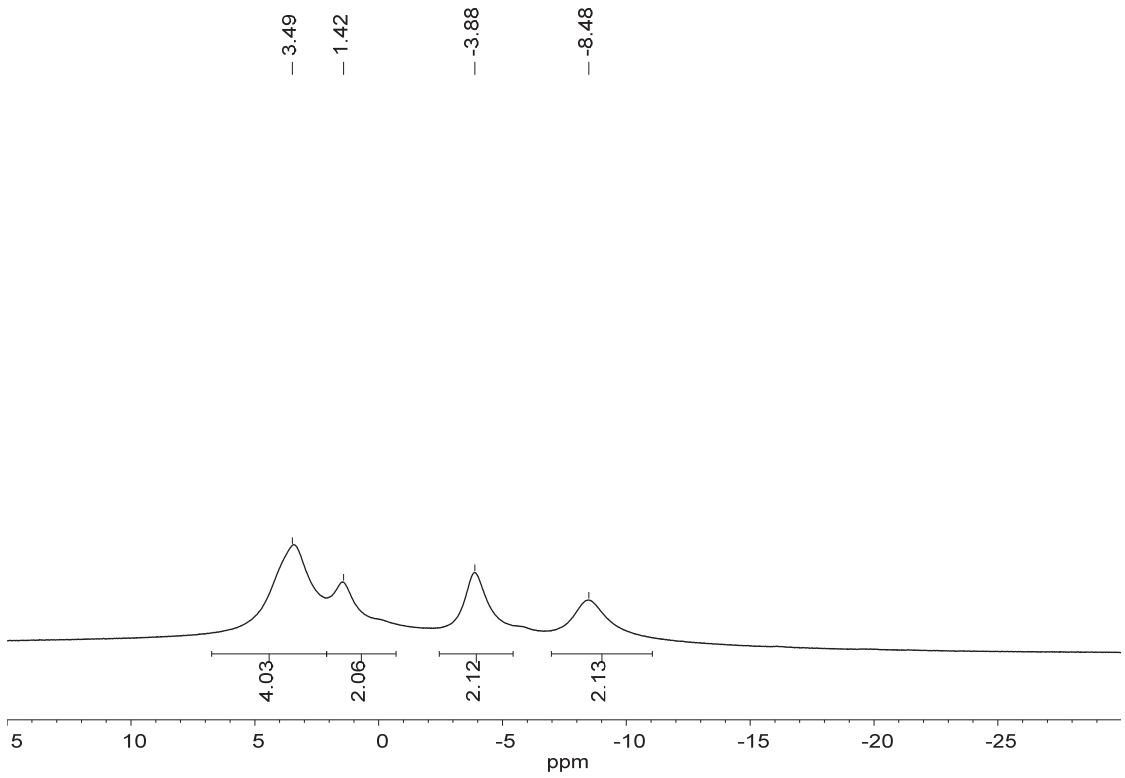
^{13}C NMR of 13a, 100 M, $CDCl_3$



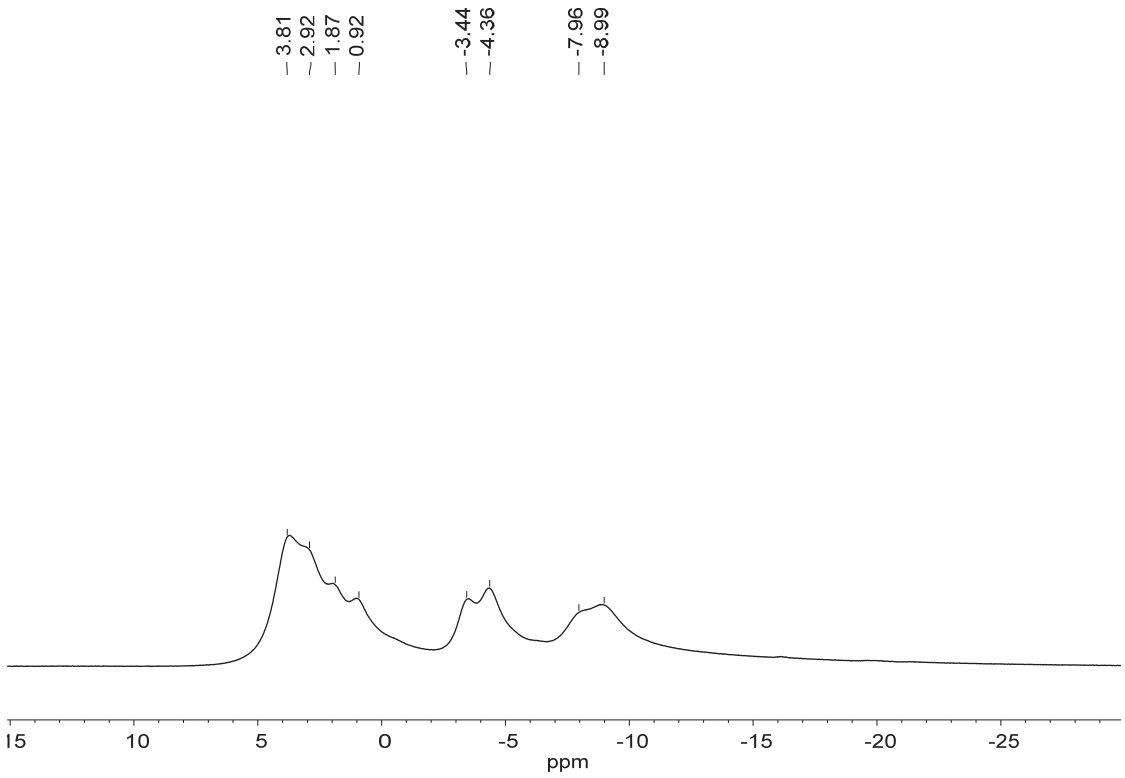
^{1}H NMR of 13b, 500 M, $CDCl_3$



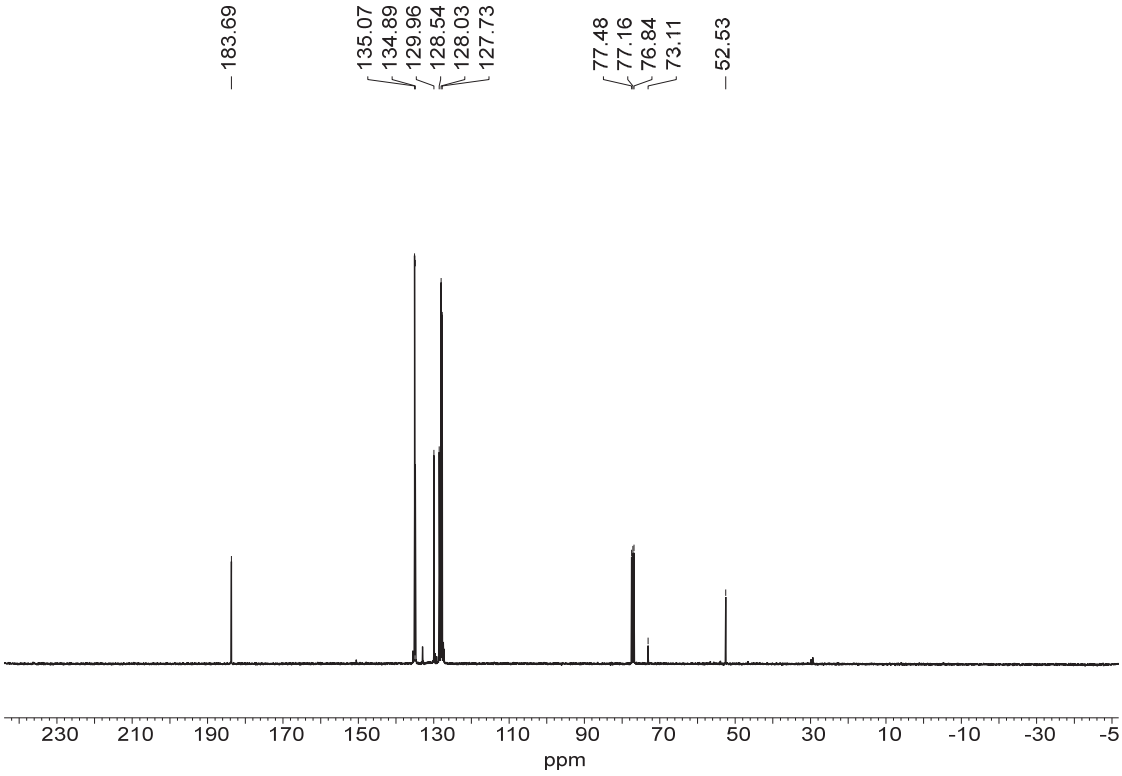
$^{11}B\ \{^{1}H\}$ NMR of 13b, 160 M, $CDCl_3$



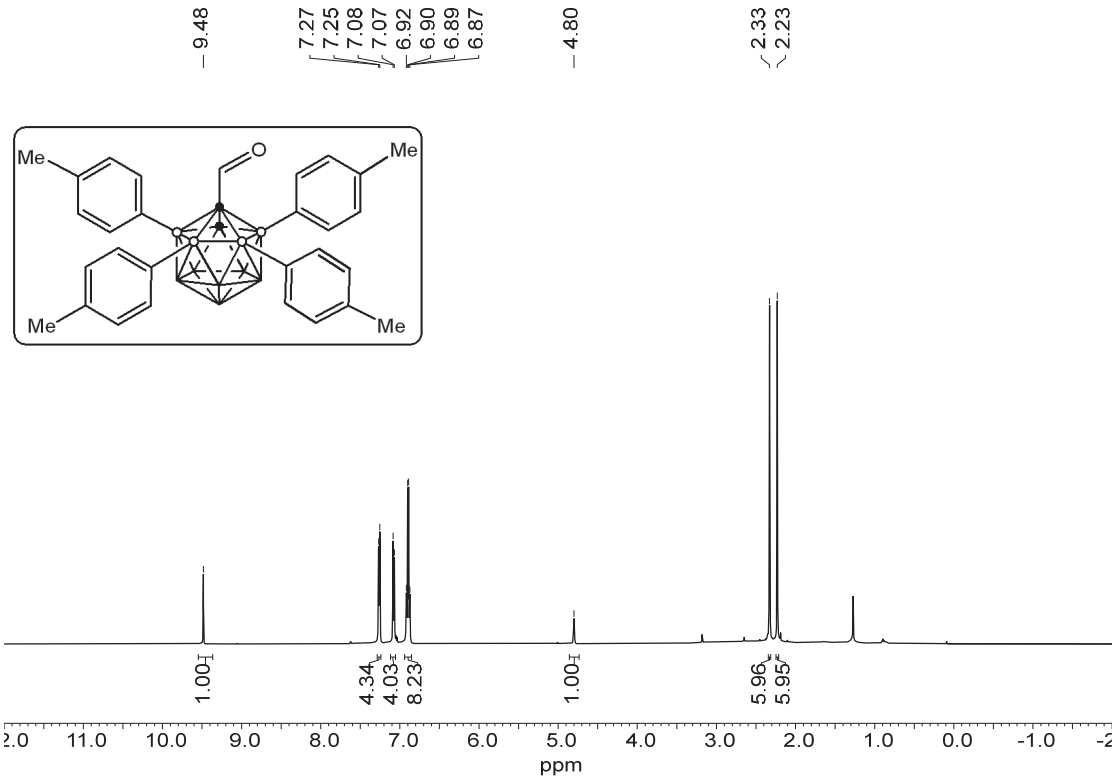
^{11}B NMR of 13b, 160 M, $CDCl_3$



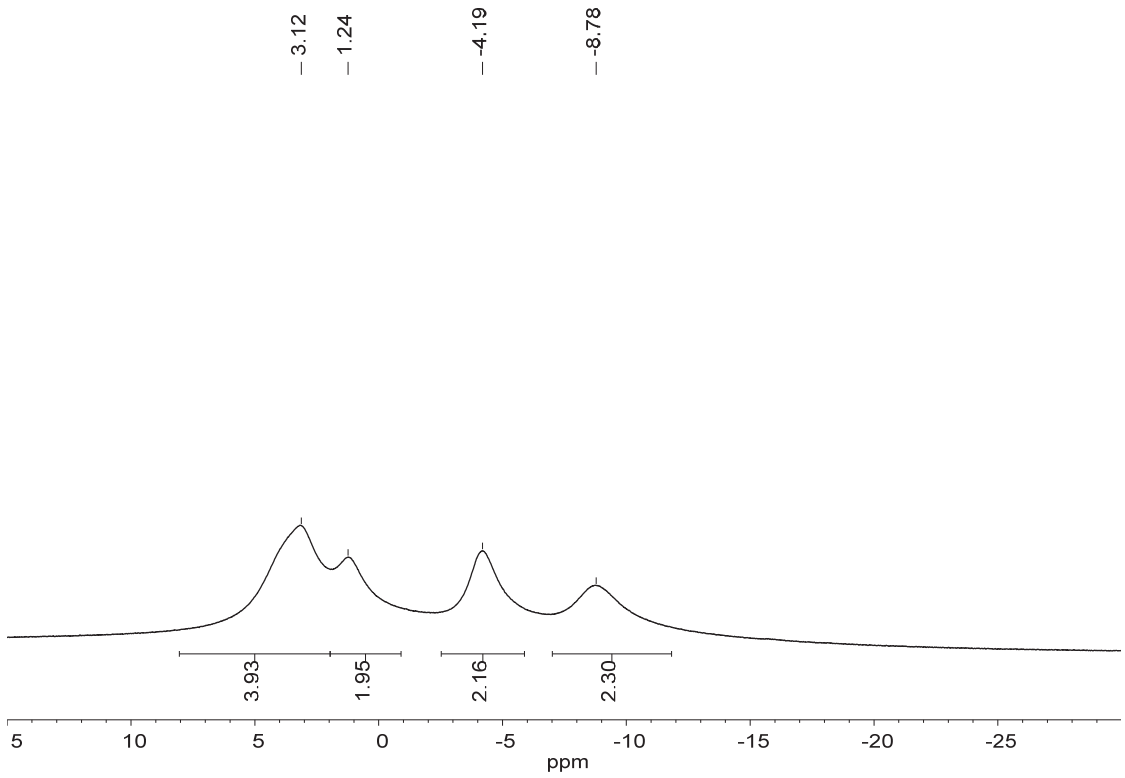
^{13}C NMR of 13b, 126 M, $CDCl_3$



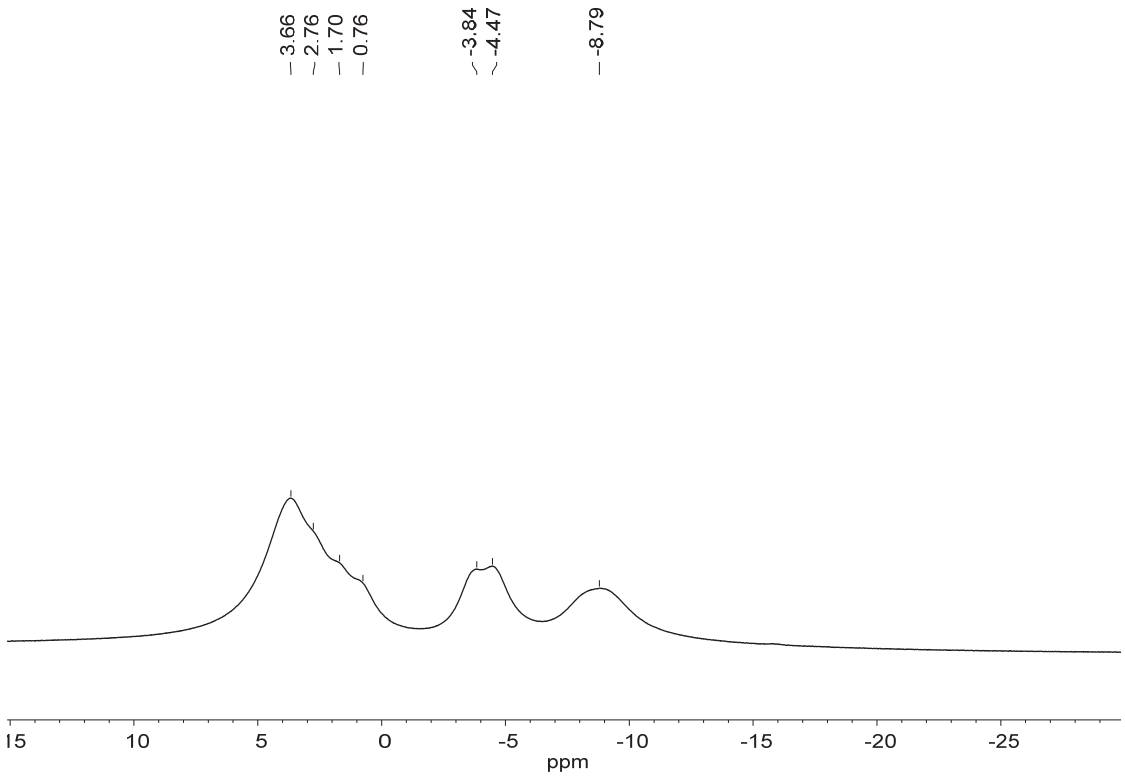
^{1}H NMR of 13c, 500 M, $CDCl_3$



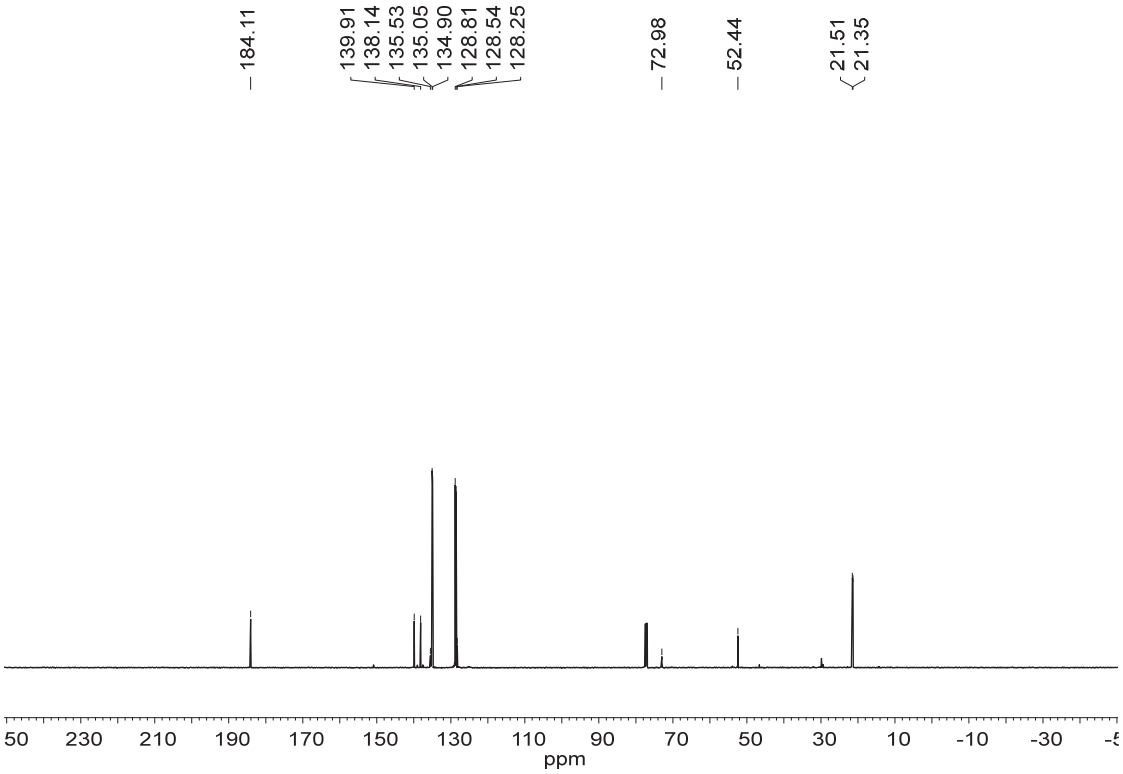
$^{11}B\ \{^{1}H\}$ NMR of 13c, 160 M, $CDCl_3$



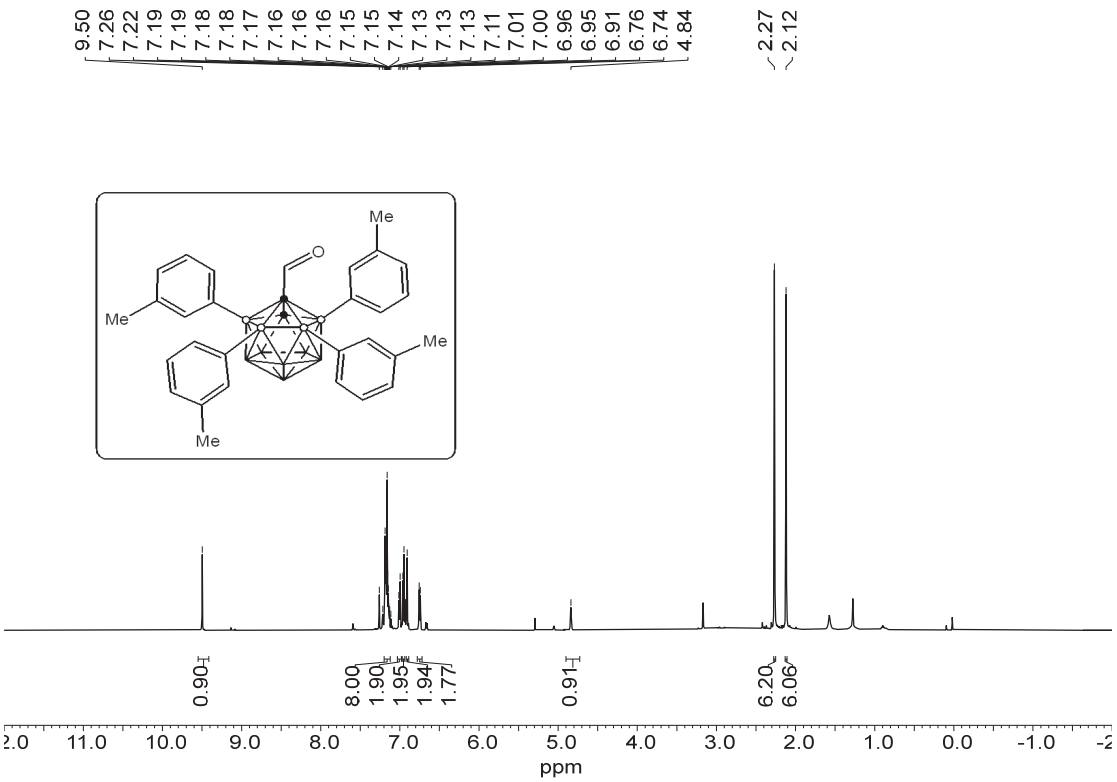
^{11}B NMR of 13c, 160 M, $CDCl_3$



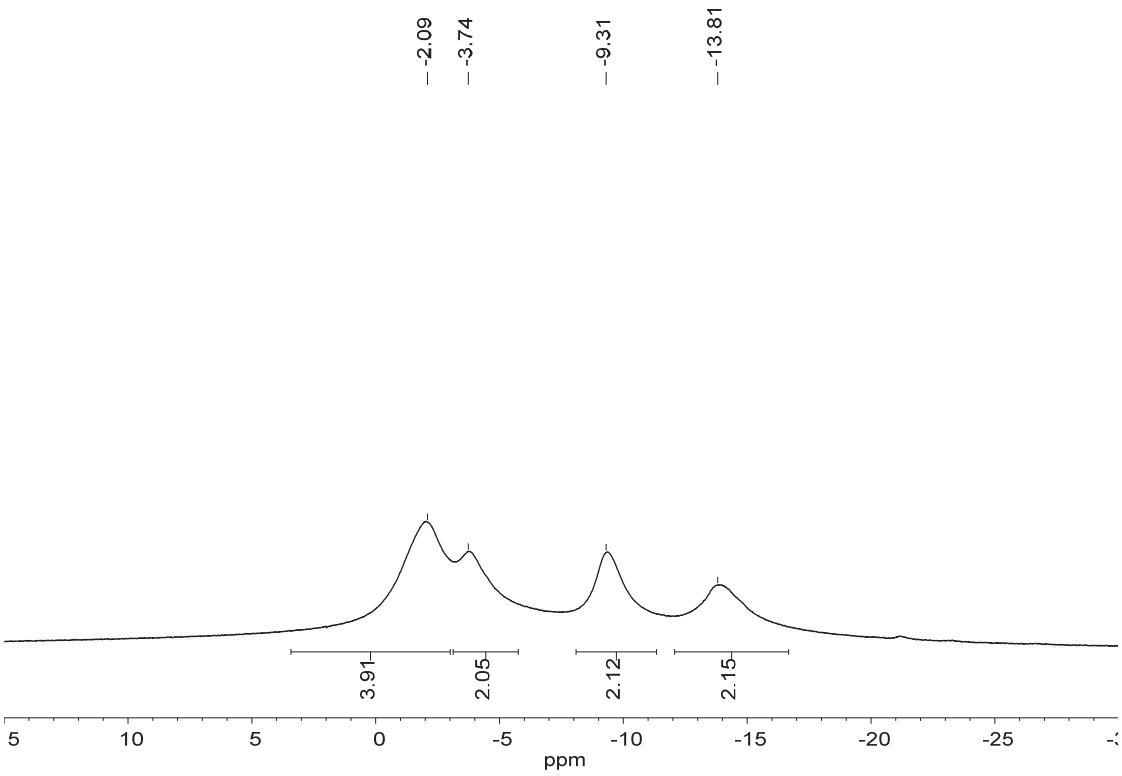
^{13}C NMR of 13c, 126 M, $CDCl_3$



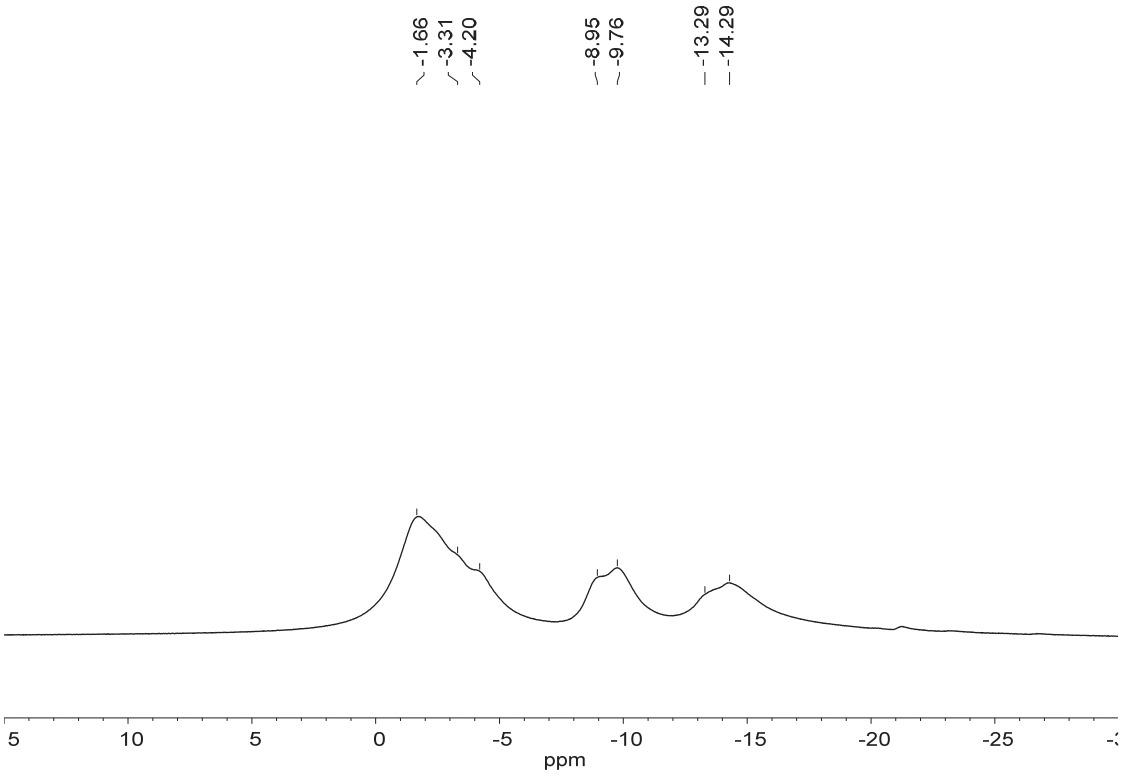
^{1}H NMR of 13d, 500 M, $CDCl_3$



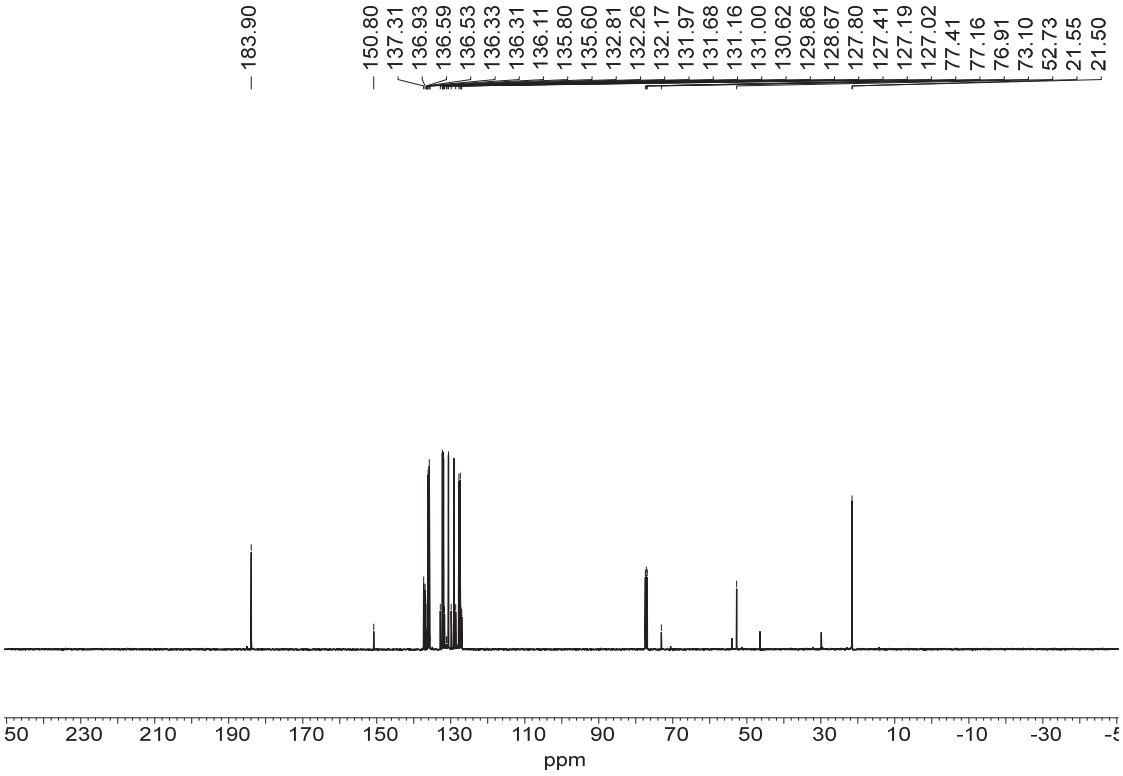
$^{11}B\ \{^{1}H\}$ NMR of 13d, 160 M, $CDCl_3$



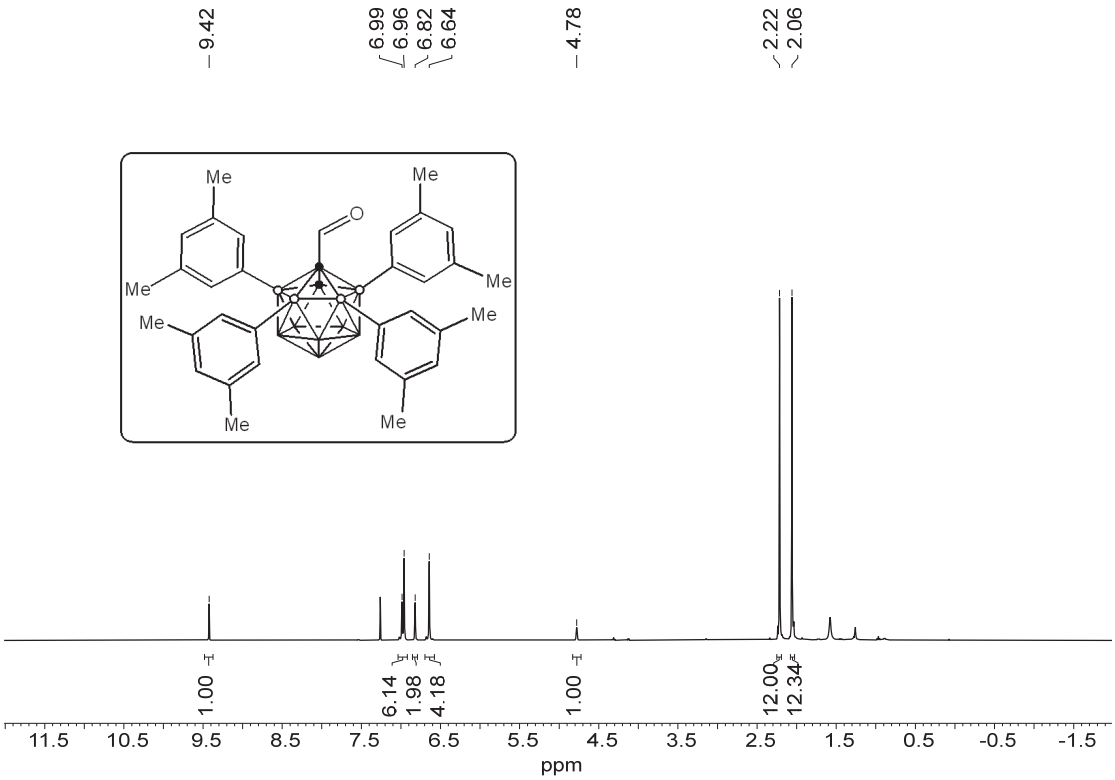
^{11}B NMR of 13d, 160 M, $CDCl_3$



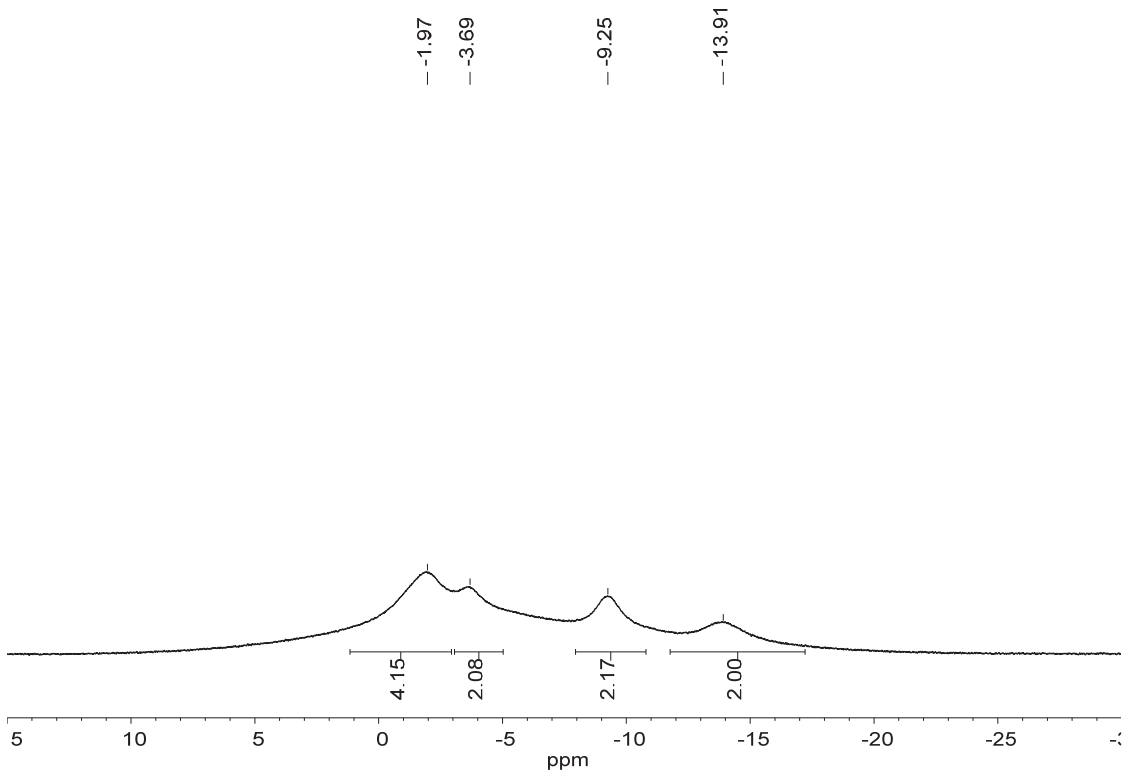
^{13}C NMR of 13d, 126 M, $CDCl_3$



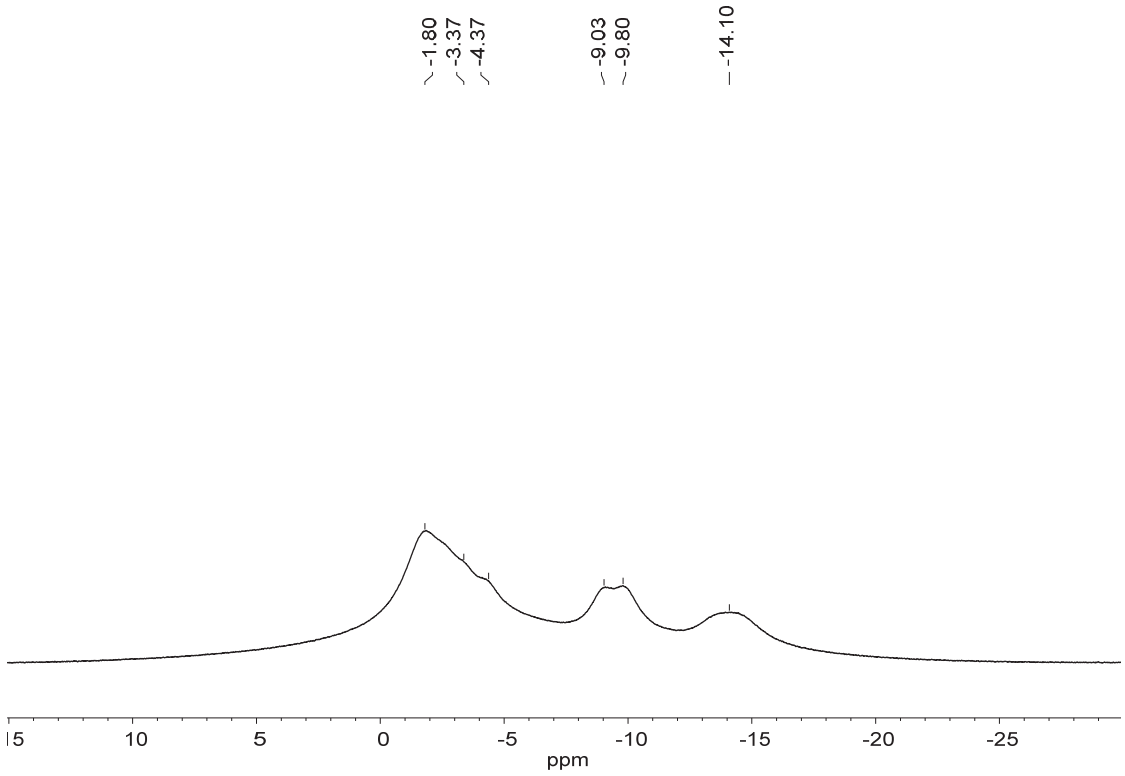
^{1}H NMR of 13e, 500 M, $CDCl_3$



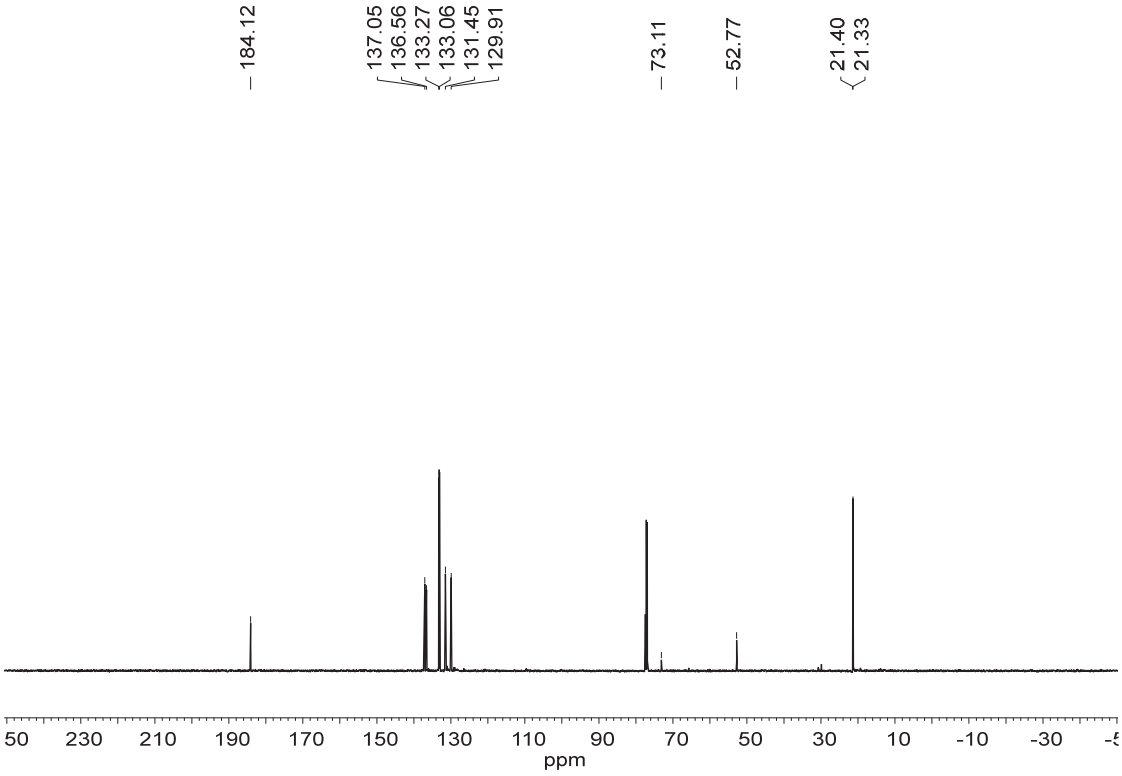
$^{11}B\ \{^{1}H\}$ NMR of 13e, 160 M, $CDCl_3$



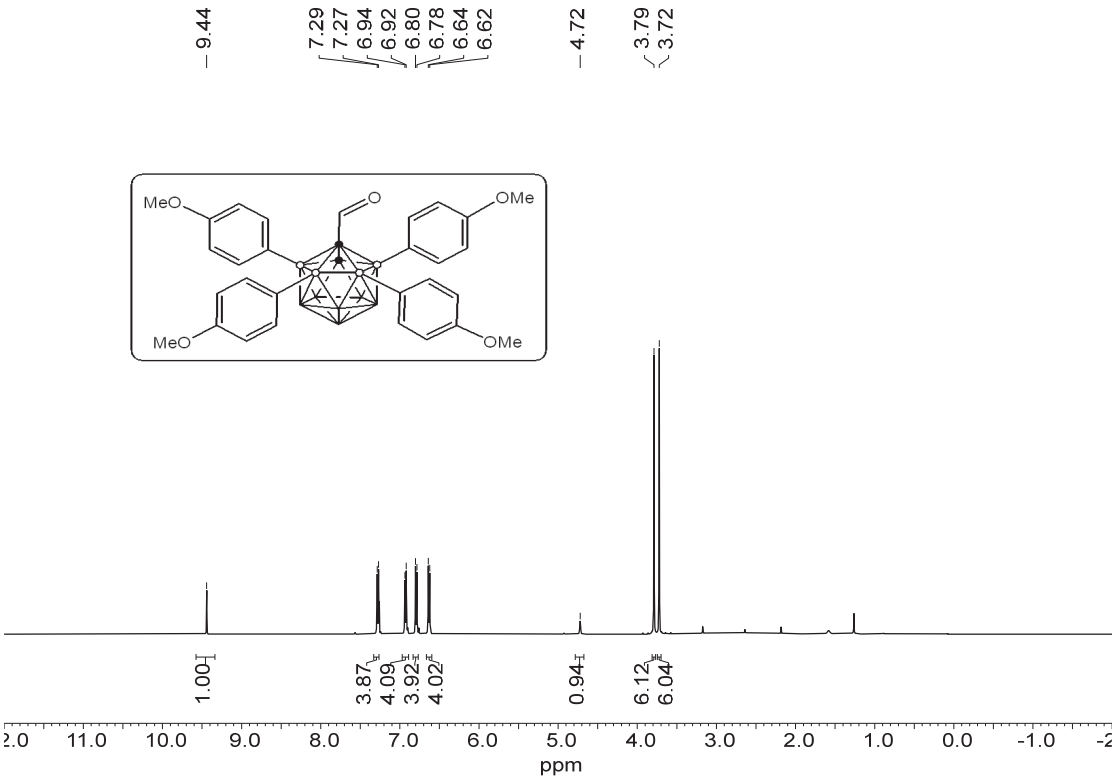
^{11}B NMR of 13e, 160 M, $CDCl_3$



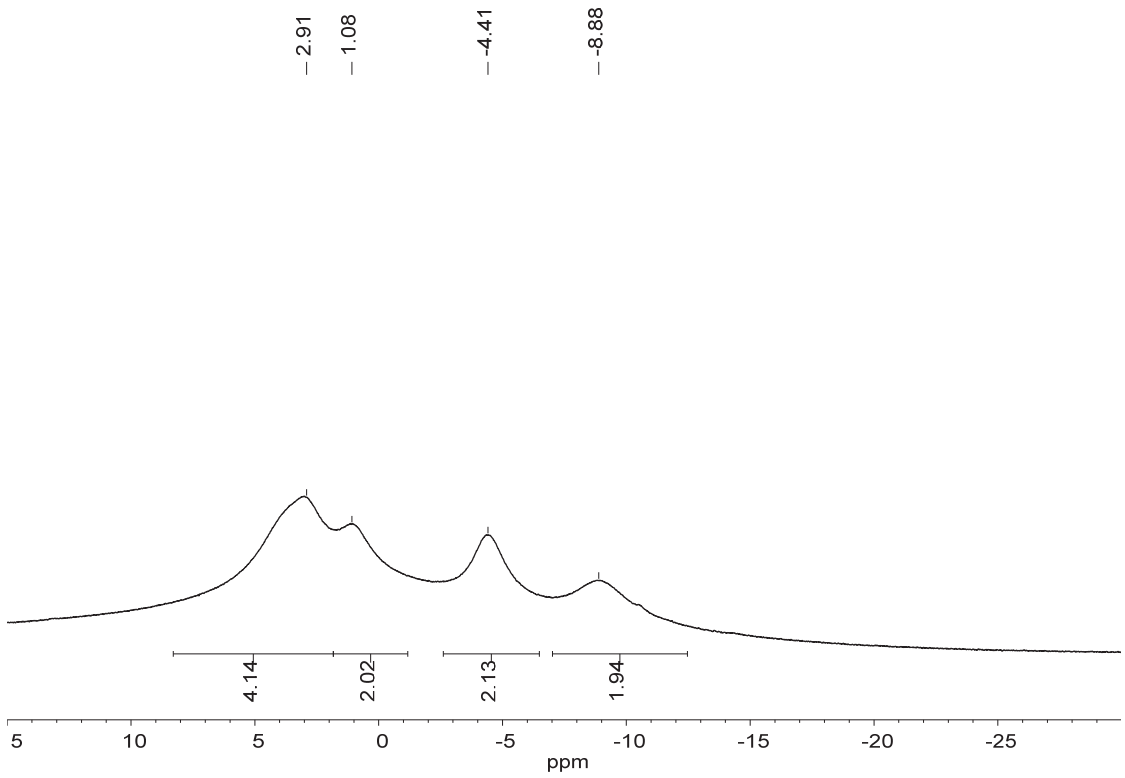
$^{13}C\ \{^1H\}$ NMR of 13e, 126 M, $CDCl_3$



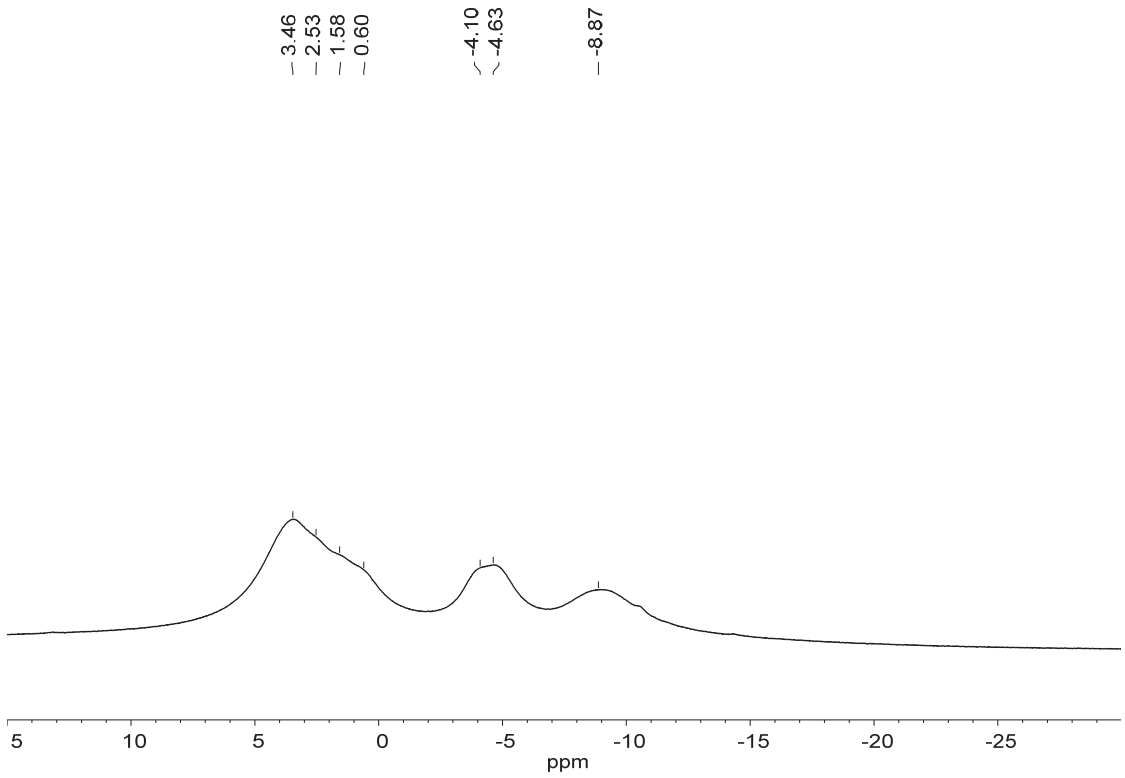
^1H NMR of 13f, 500 M, $CDCl_3$



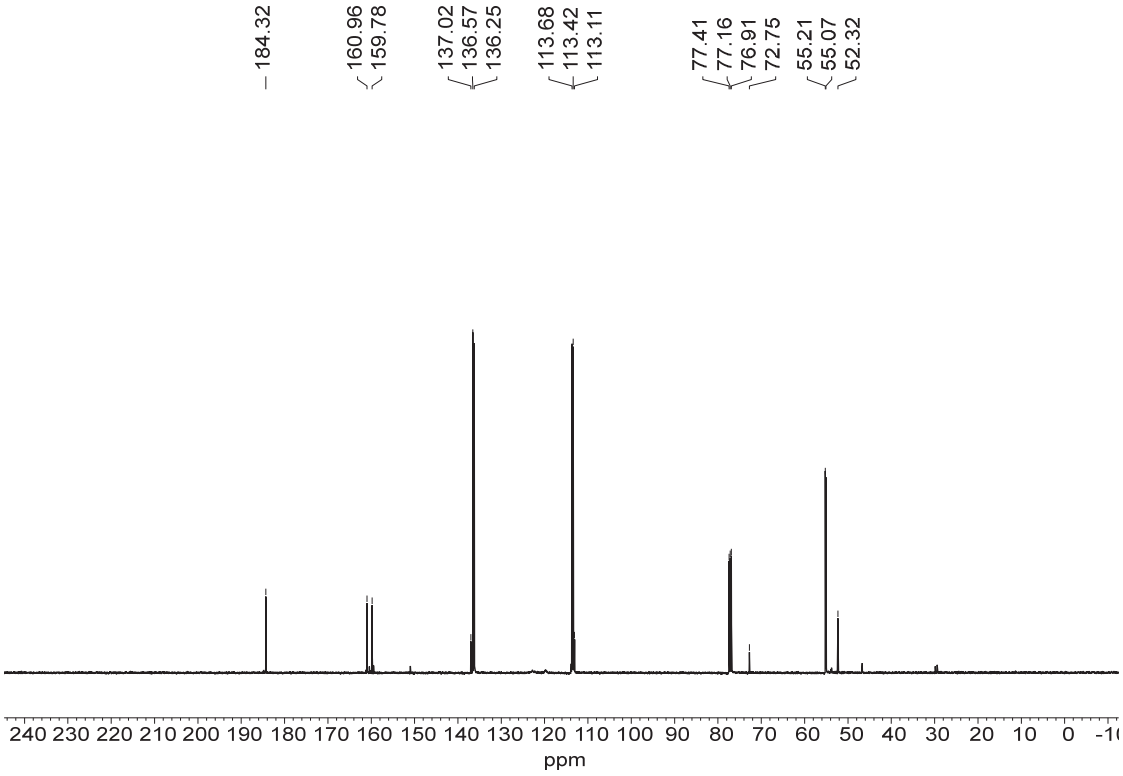
$^{11}B\ \{^{1}H\}$ NMR of 13f, 160 M, $CDCl_3$



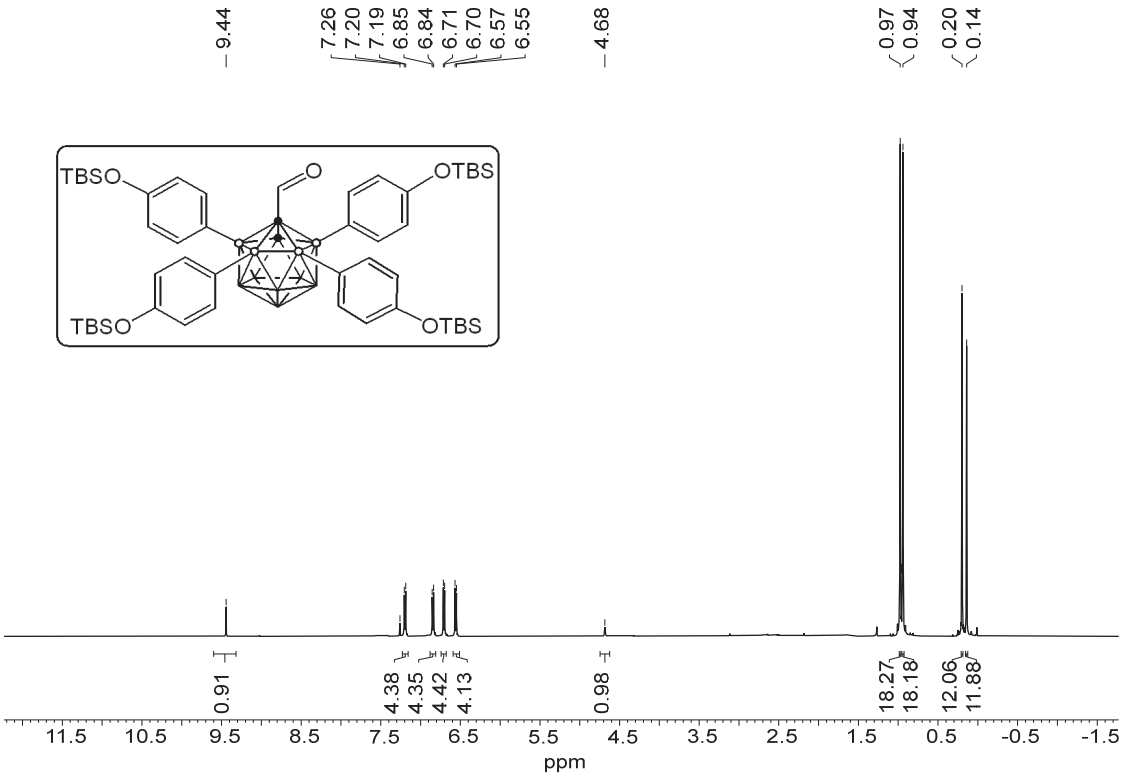
^{11}B NMR of 13f, 160 M, $CDCl_3$



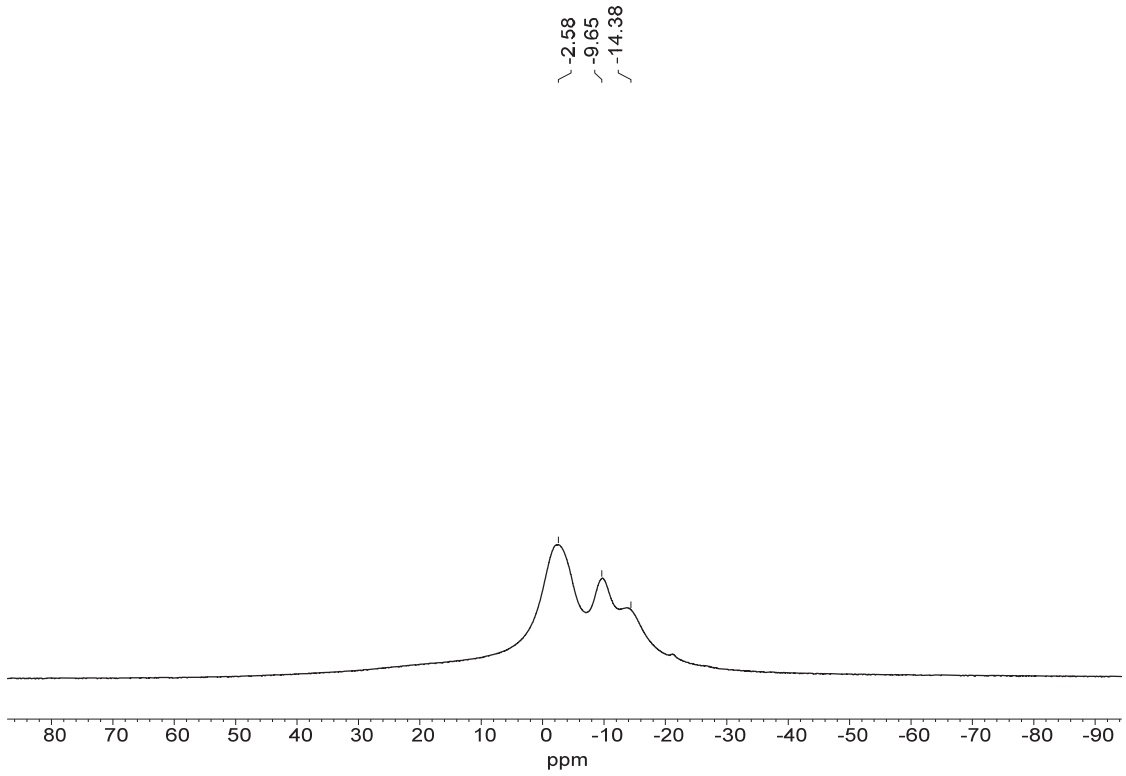
^{13}C NMR of 13f, 126 M, $CDCl_3$



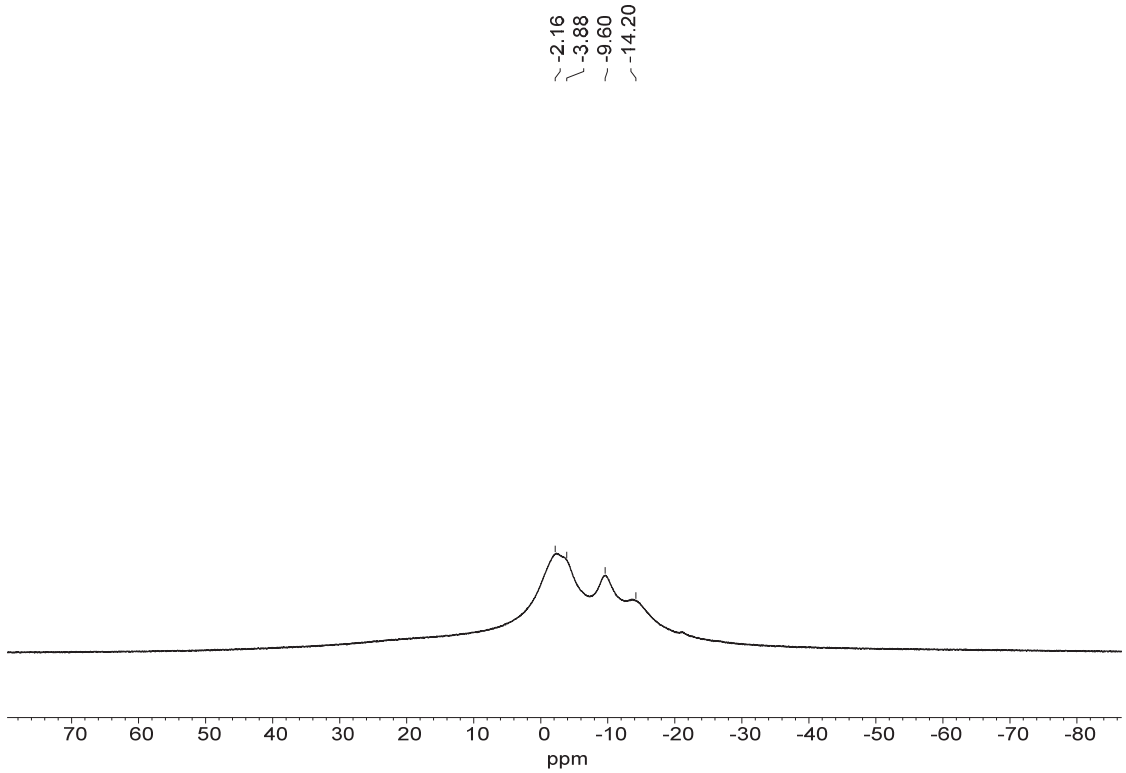
^{1}H NMR of 13g, 500 M, $CDCl_3$



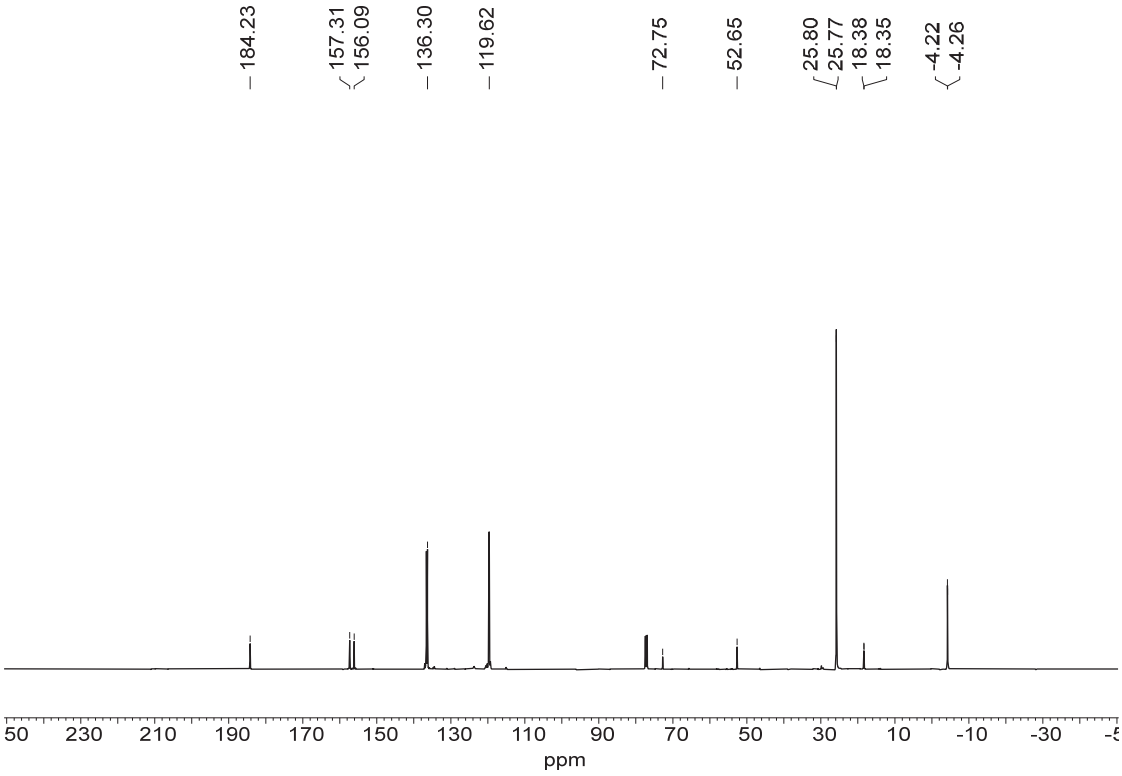
$^{11}B\ \{^{1}H\}$ NMR of 13g, 160 M, $CDCl_3$



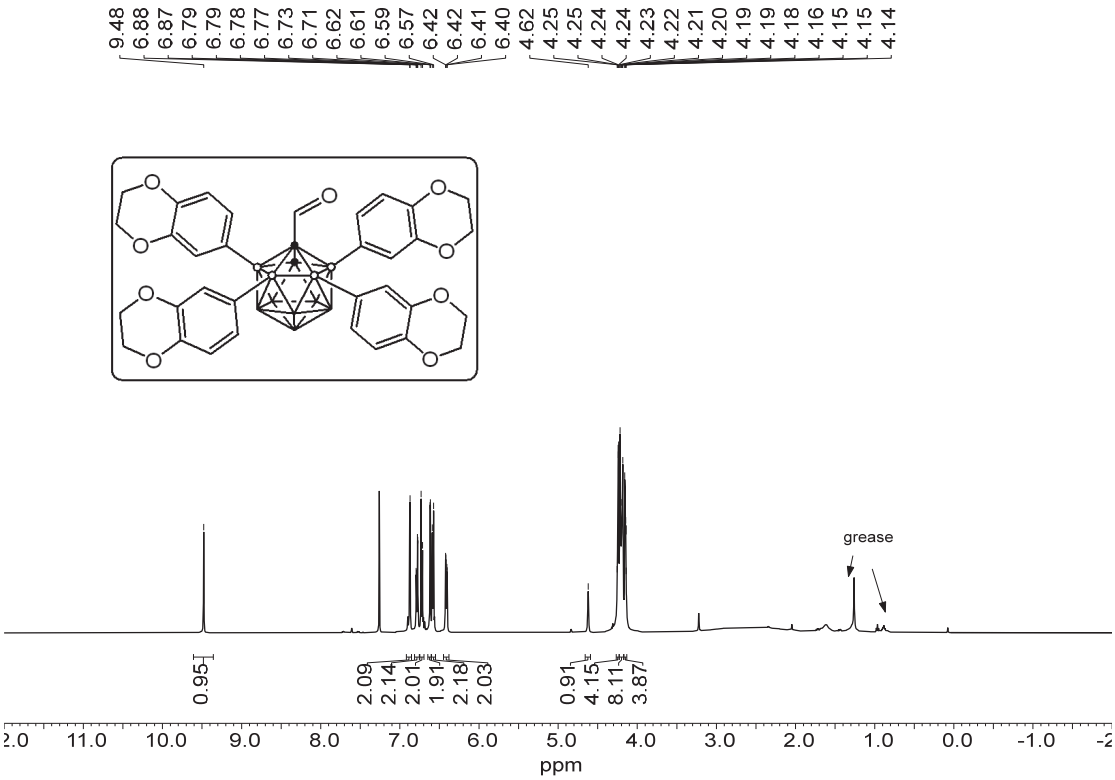
^{11}B NMR of 13g, 160 M, $CDCl_3$



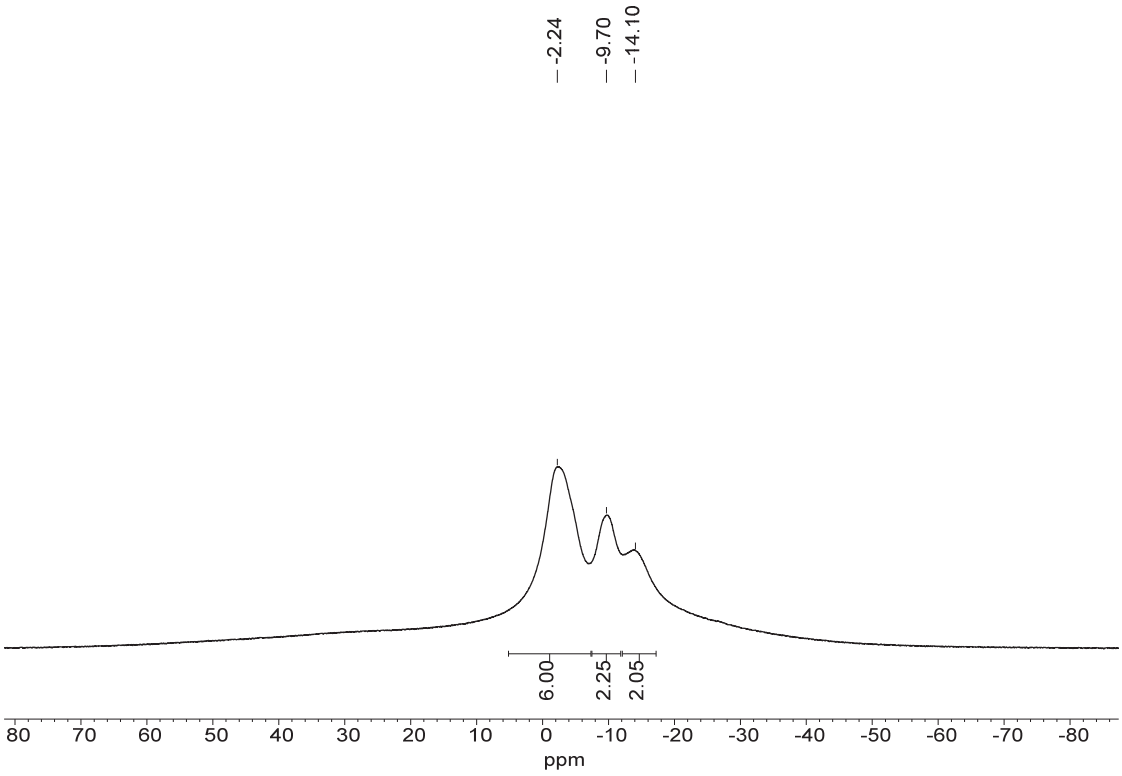
^{13}C NMR of 13g, 126 M, $CDCl_3$



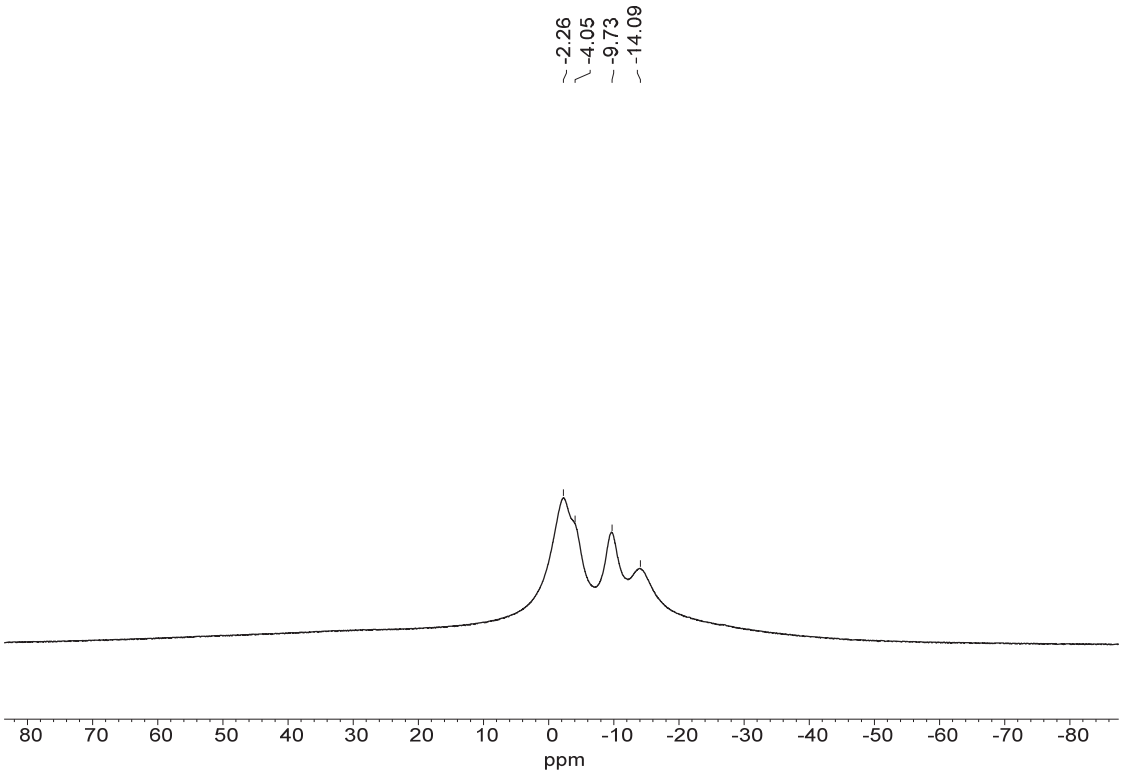
^{1}H NMR of 13h, 500 M, $CDCl_3$



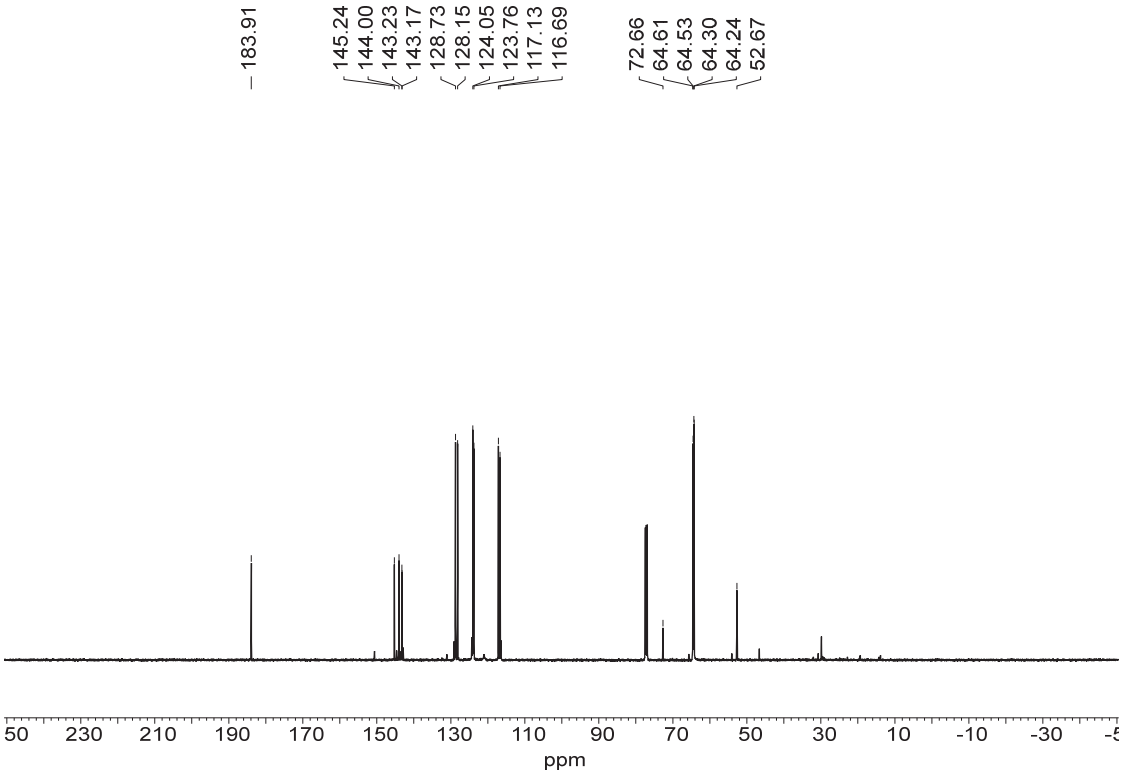
$^{11}B\ \{^{1}H\}$ NMR of 13h, 128 M, $CDCl_3$



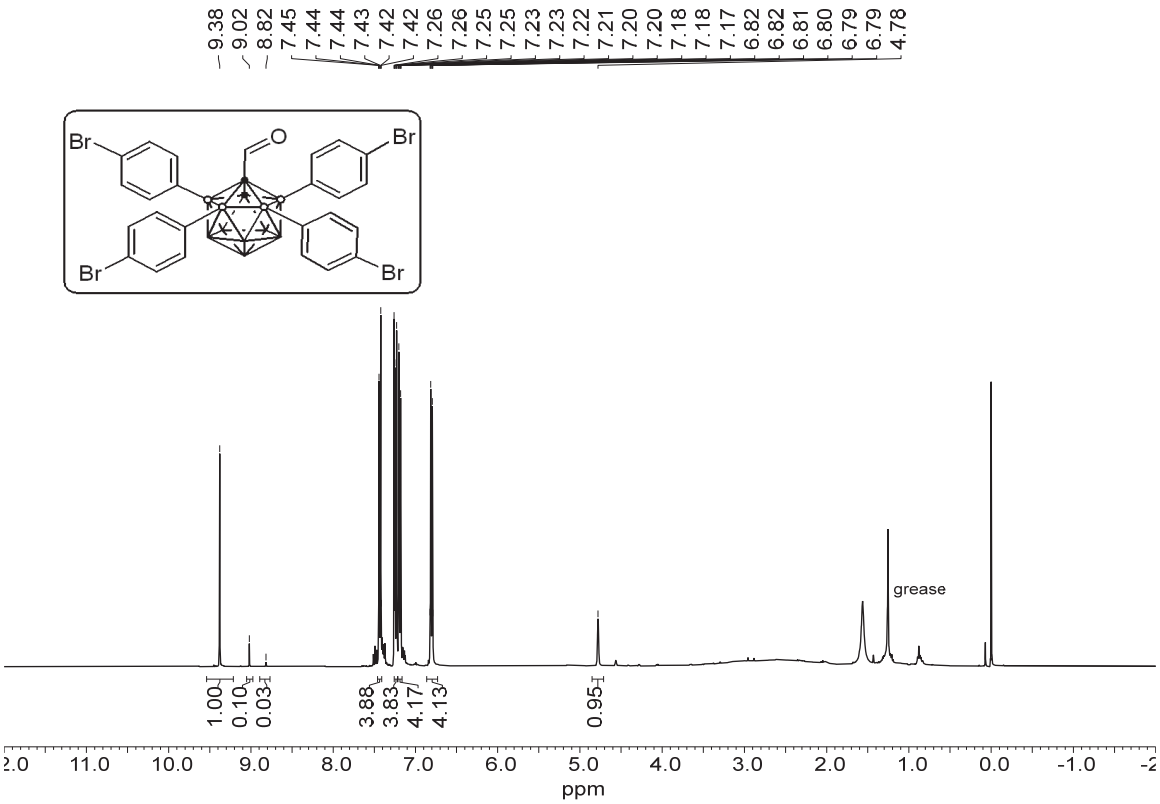
^{11}B NMR of 13h, 128 M, $CDCl_3$



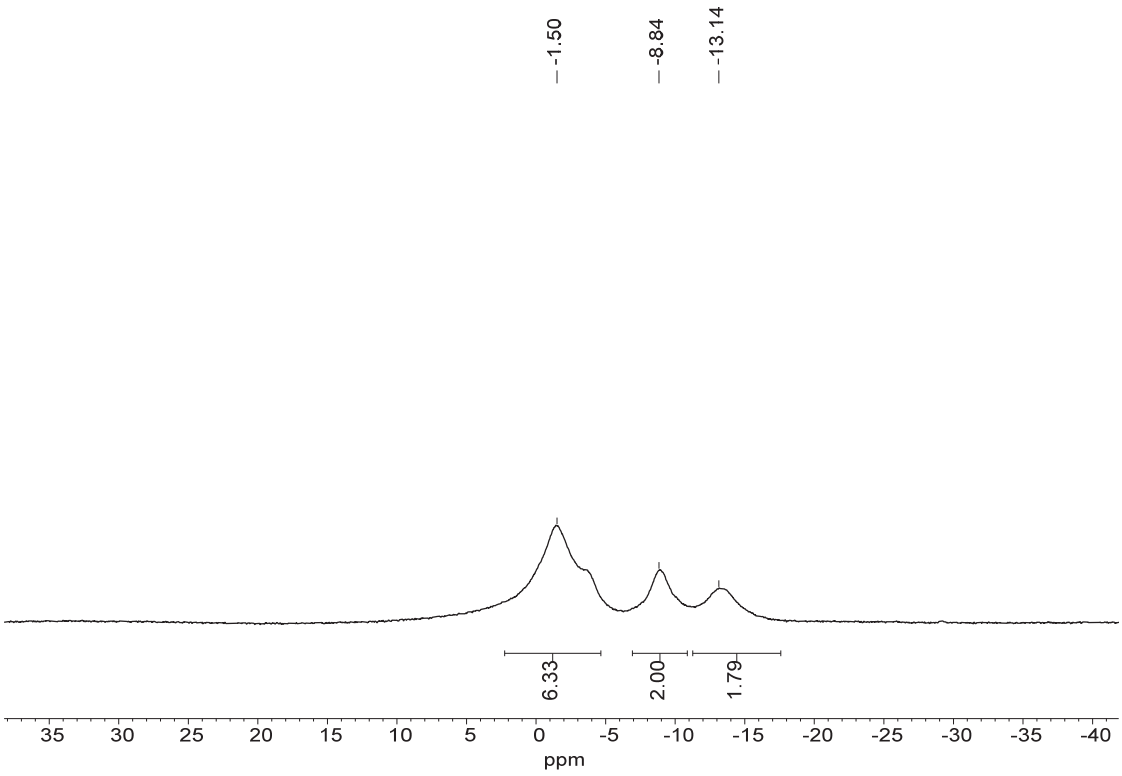
^{13}C {H} NMR of 13h, 126 M, $CDCl_3$



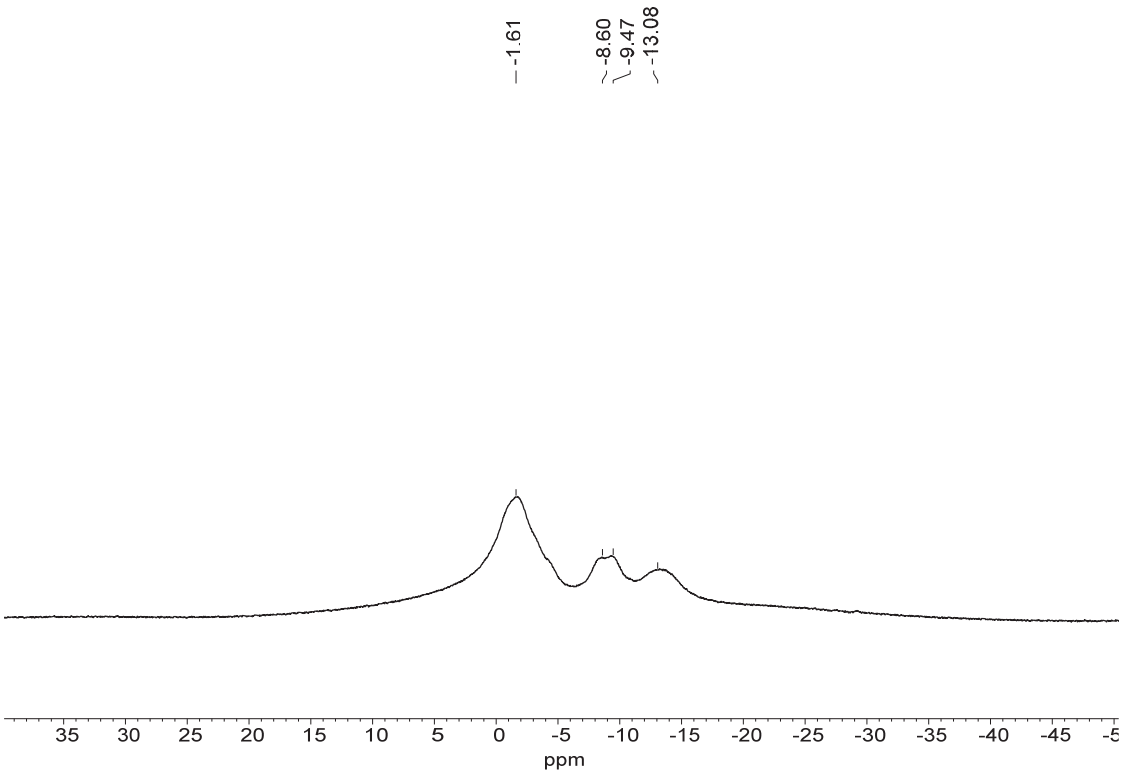
^{1}H NMR of 13i, 400 M, $CDCl_3$



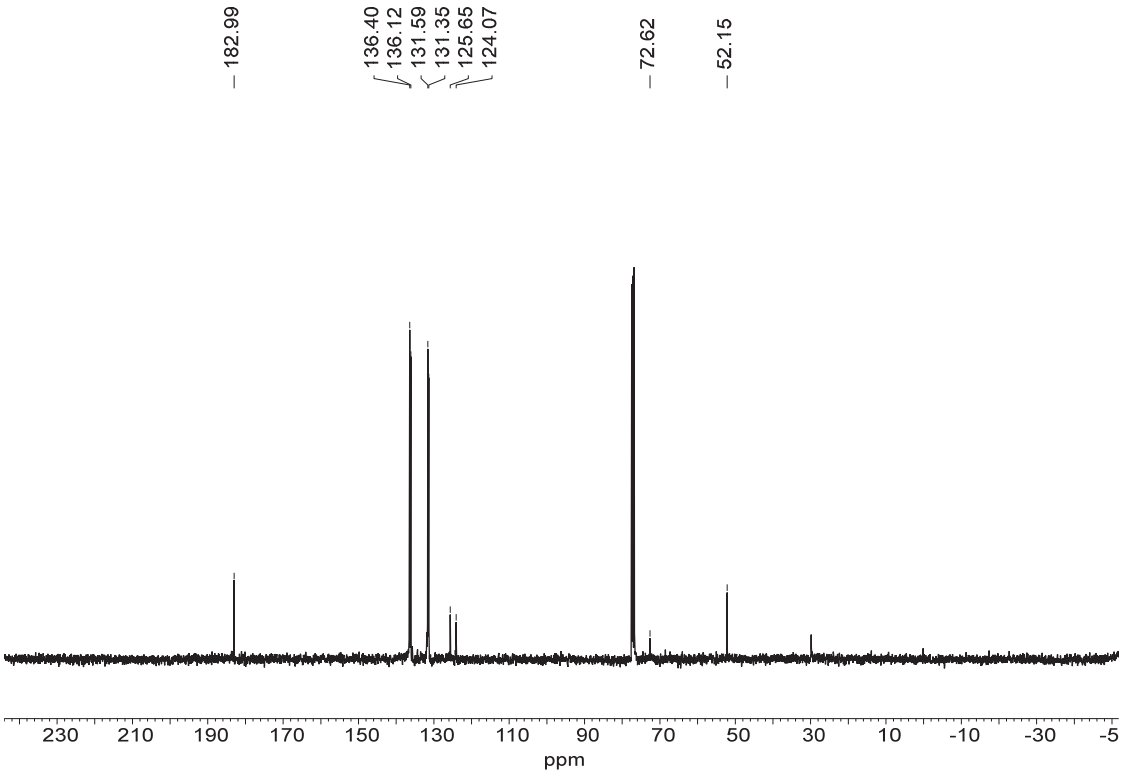
$^{11}B\ \{^{1}H\}$ NMR of 13i, 128 M, $CDCl_3$



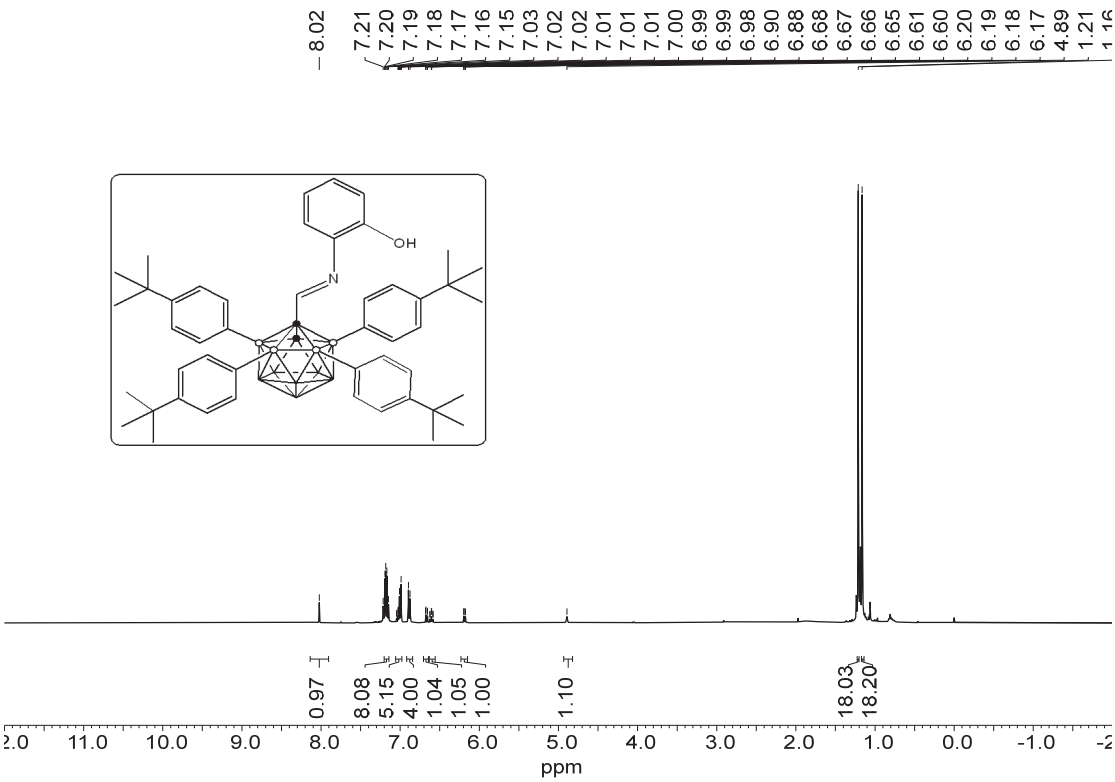
^{11}B NMR of 13i, 128 M, $CDCl_3$



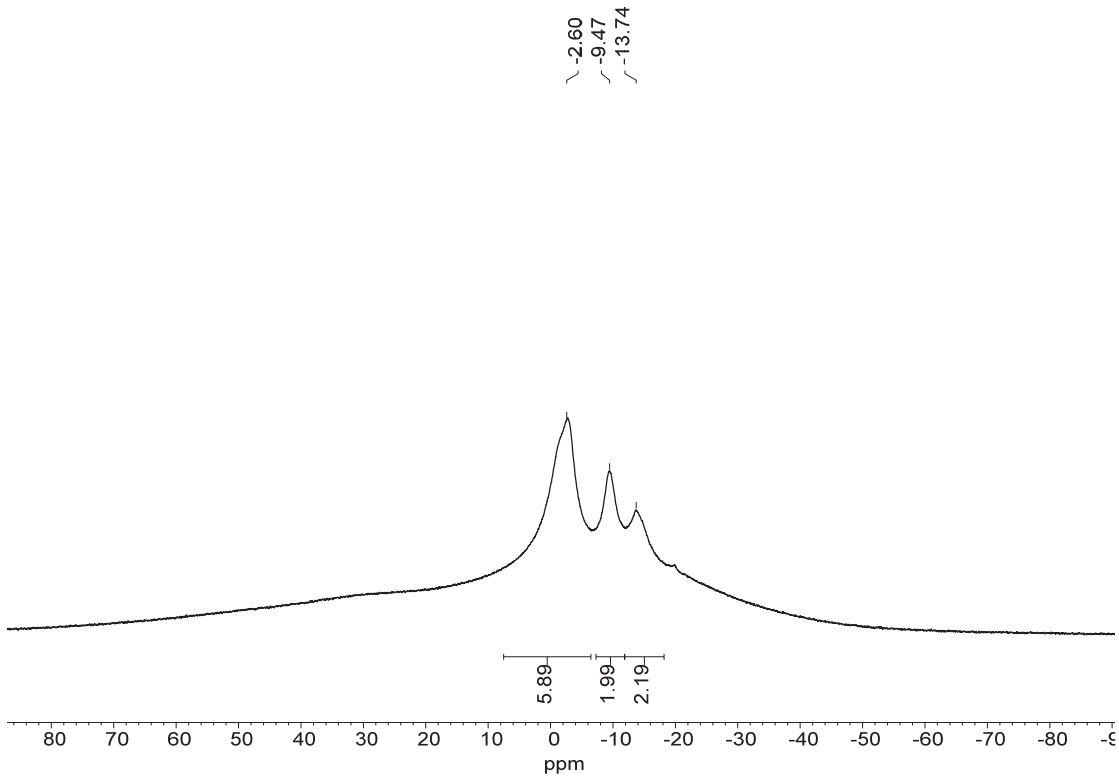
^{13}C NMR of 13i, 101 M, $CDCl_3$



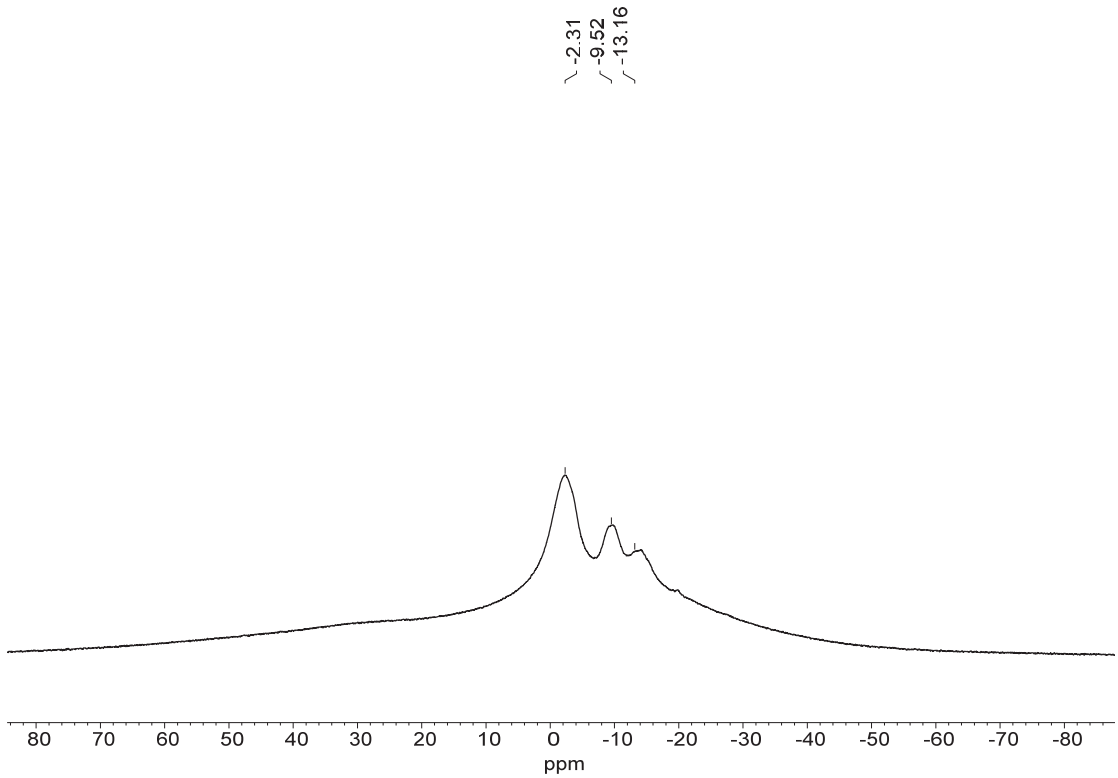
^{1}H NMR of 13j, 400 M, $CDCl_3$



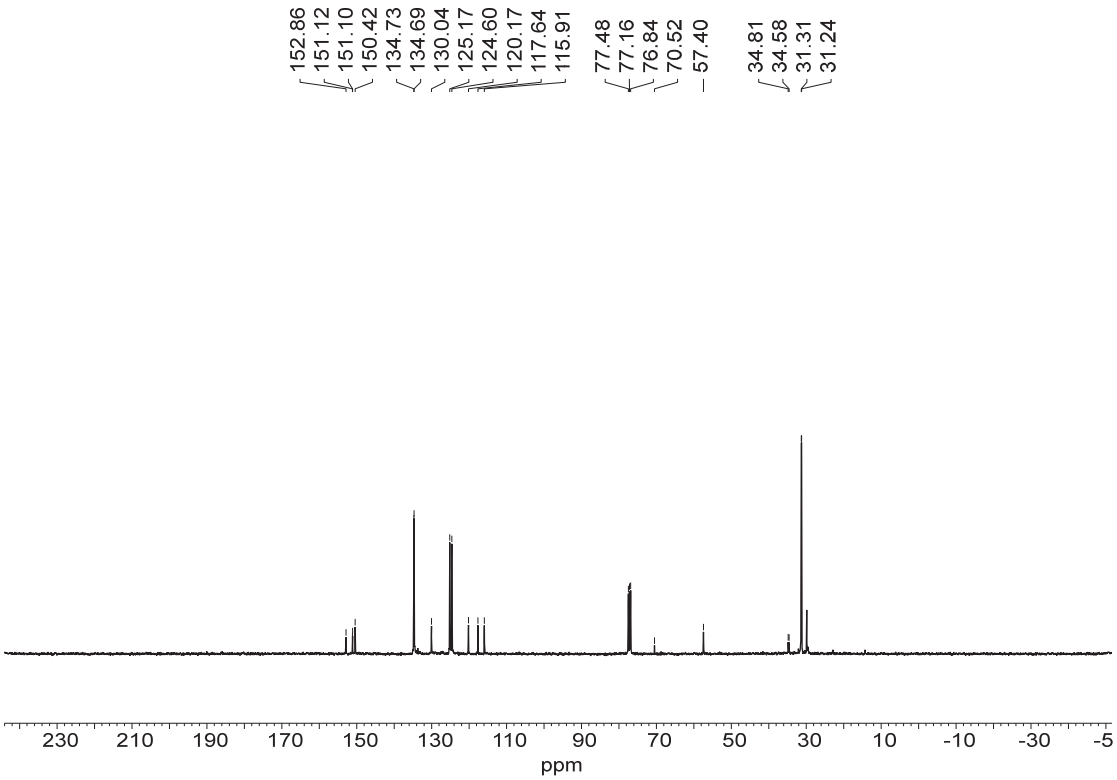
$^{11}B\ \{^{1}H\}$ NMR of 13j, 128 M, $CDCl_3$



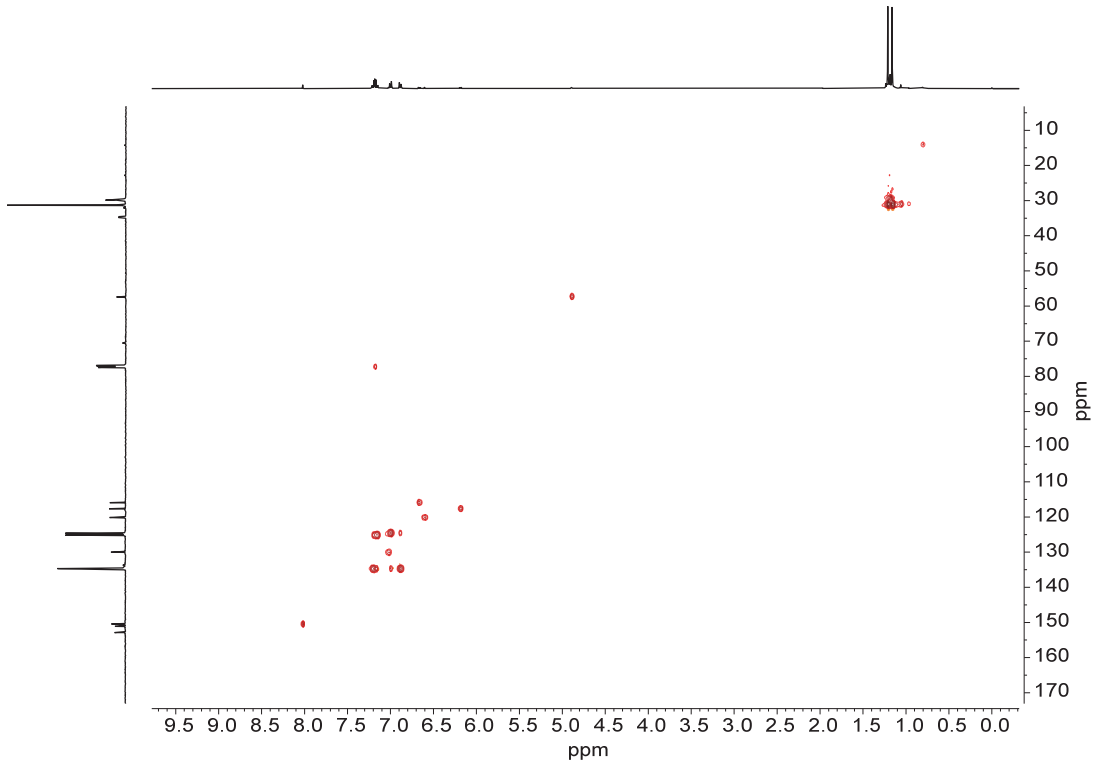
$^{11}B\ \{^{1}H\}$ NMR of 13j, 128 M, $CDCl_3$



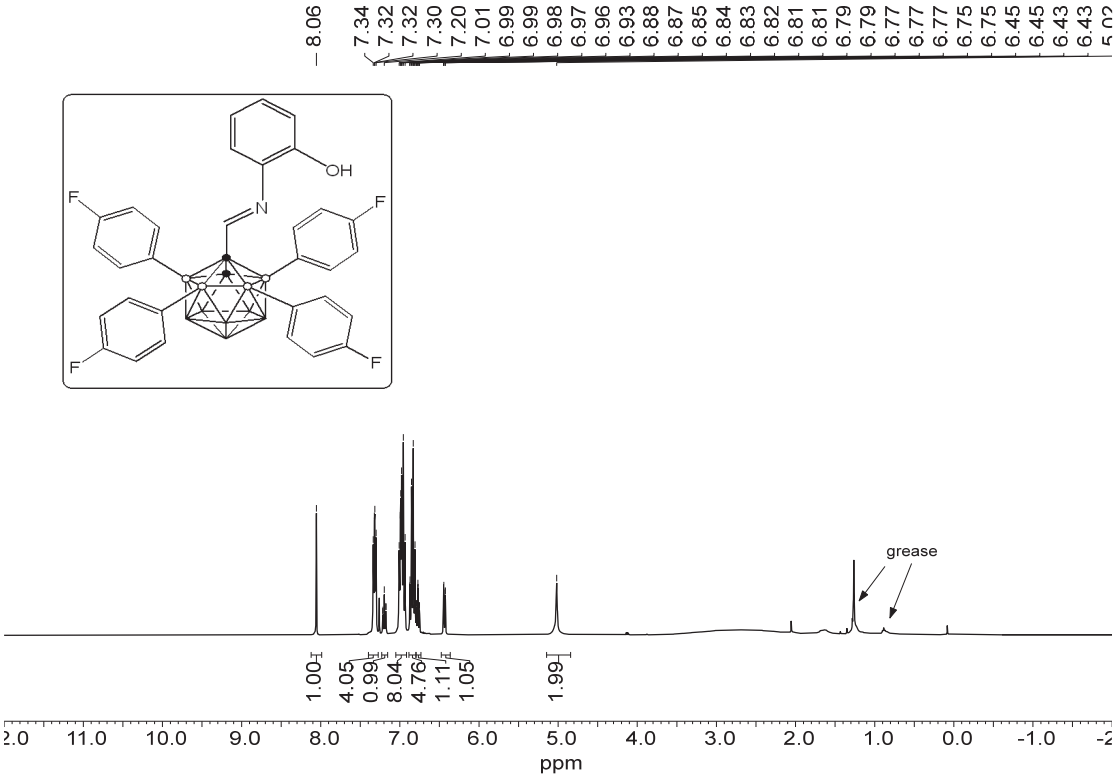
^{13}C NMR, 100 M of 13j, $CDCl_3$



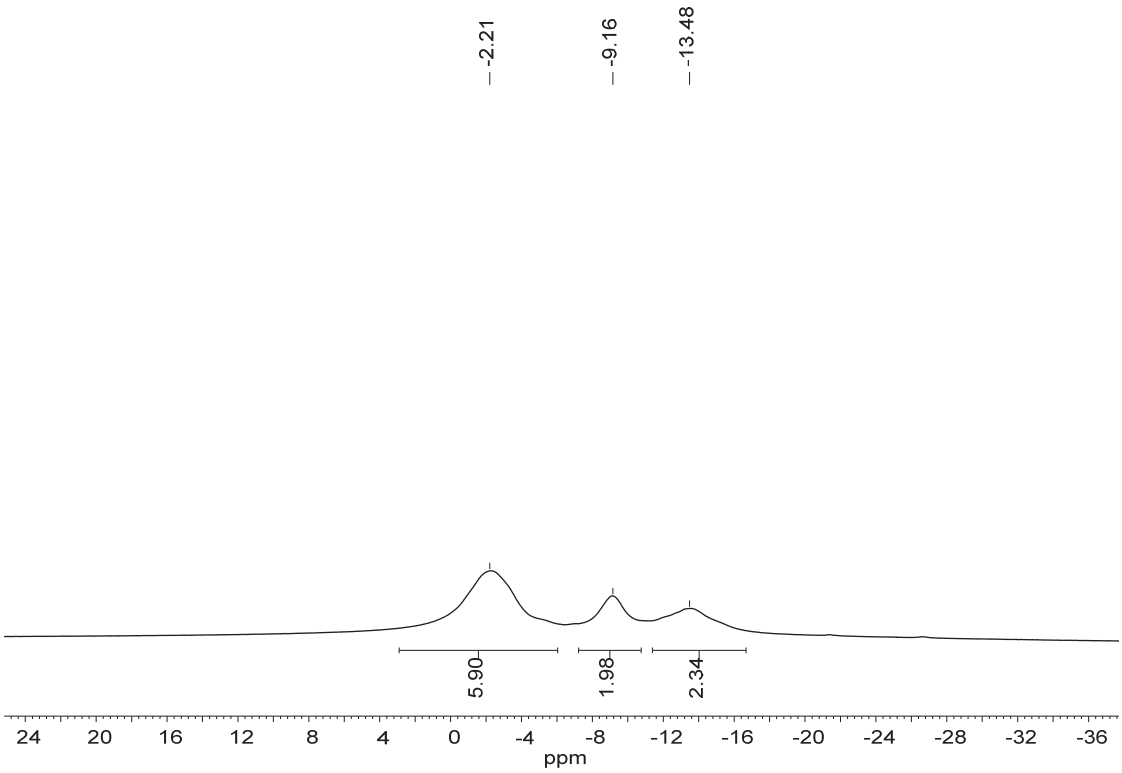
^{1}H-^{13}C HSQC of 13j, 400 M, $CDCl_3$



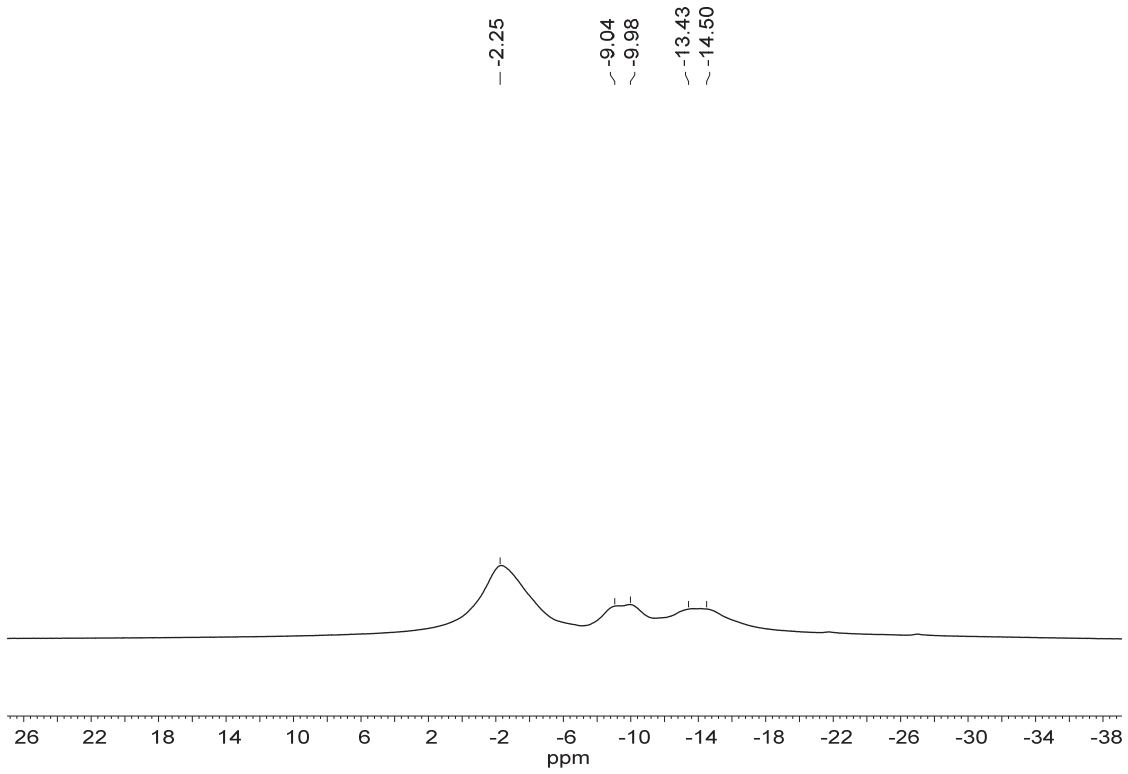
^{1}H NMR of 13k, 400 M, $CDCl_3$



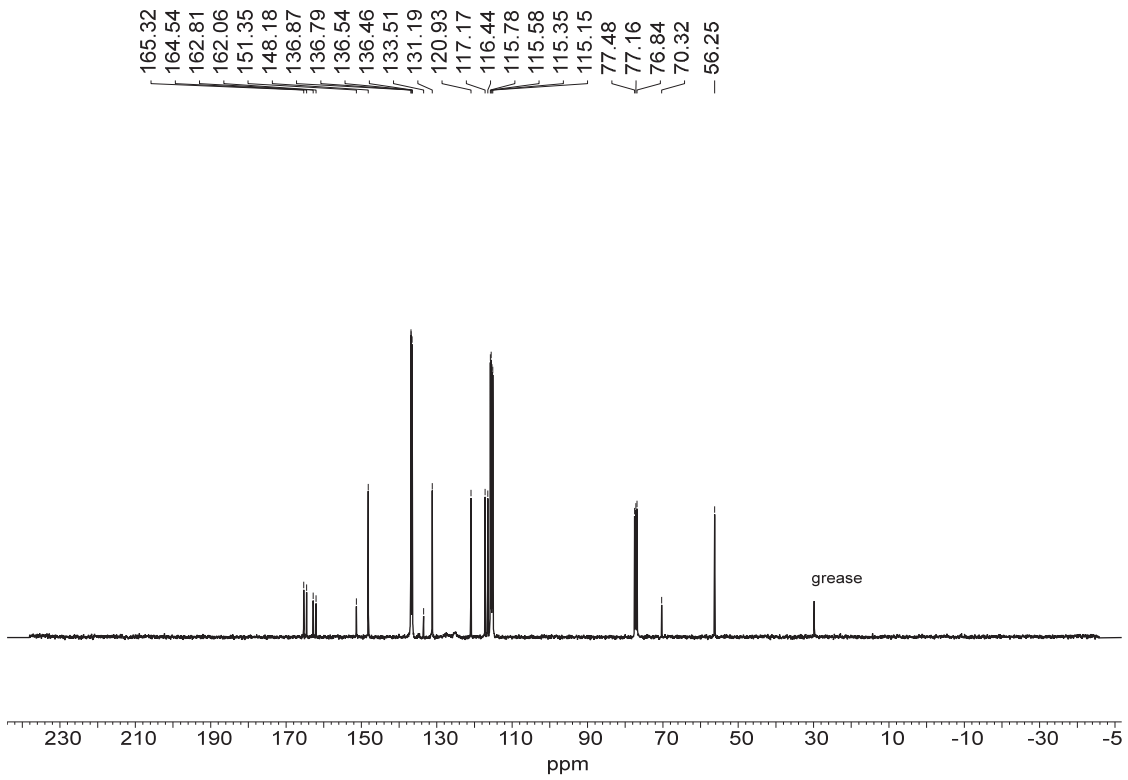
^{11}B {^{1}H} NMR of 13k, 128 M, $CDCl_3$



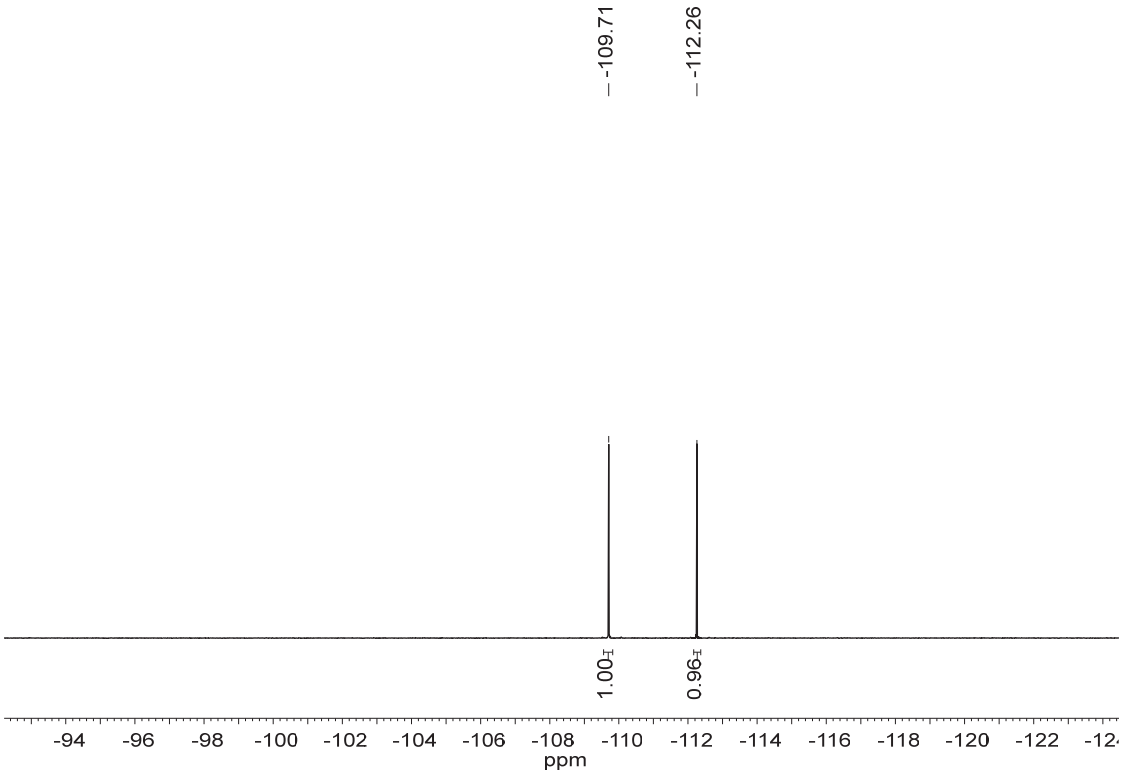
$^{11}B\ \{^{1}H\}$ NMR of 13k, 128 M, $CDCl_3$



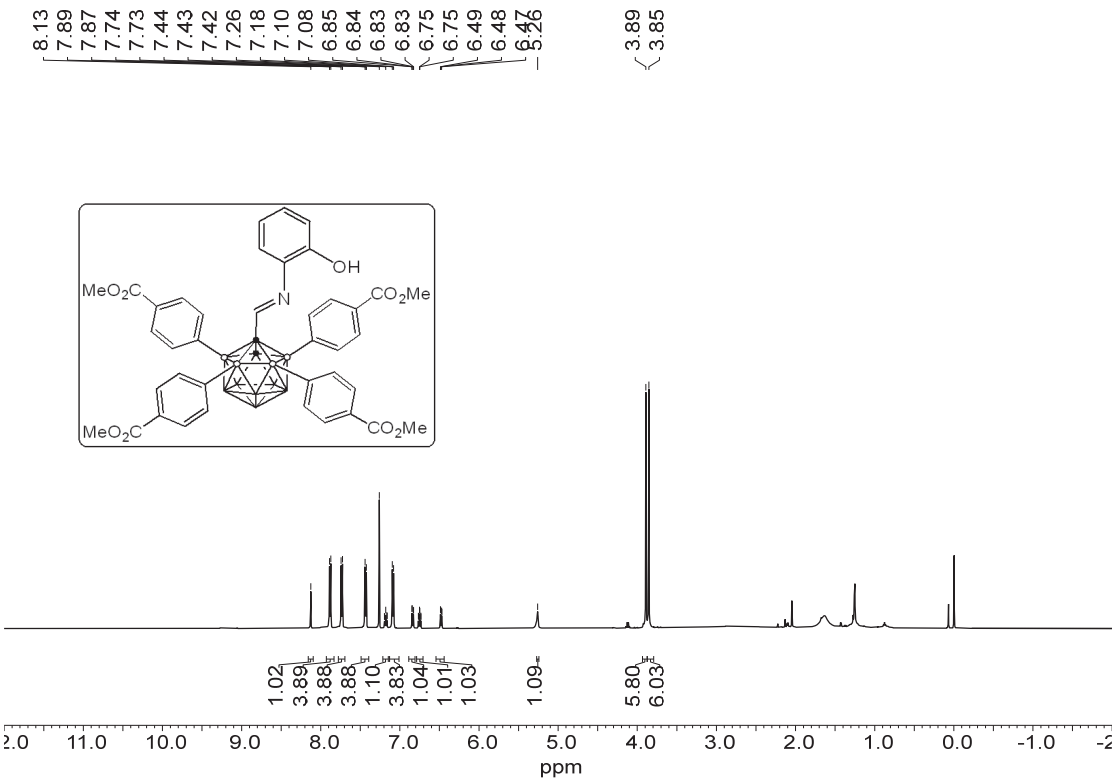
^{13}C NMR of 13k, 100 M, $CDCl_3$



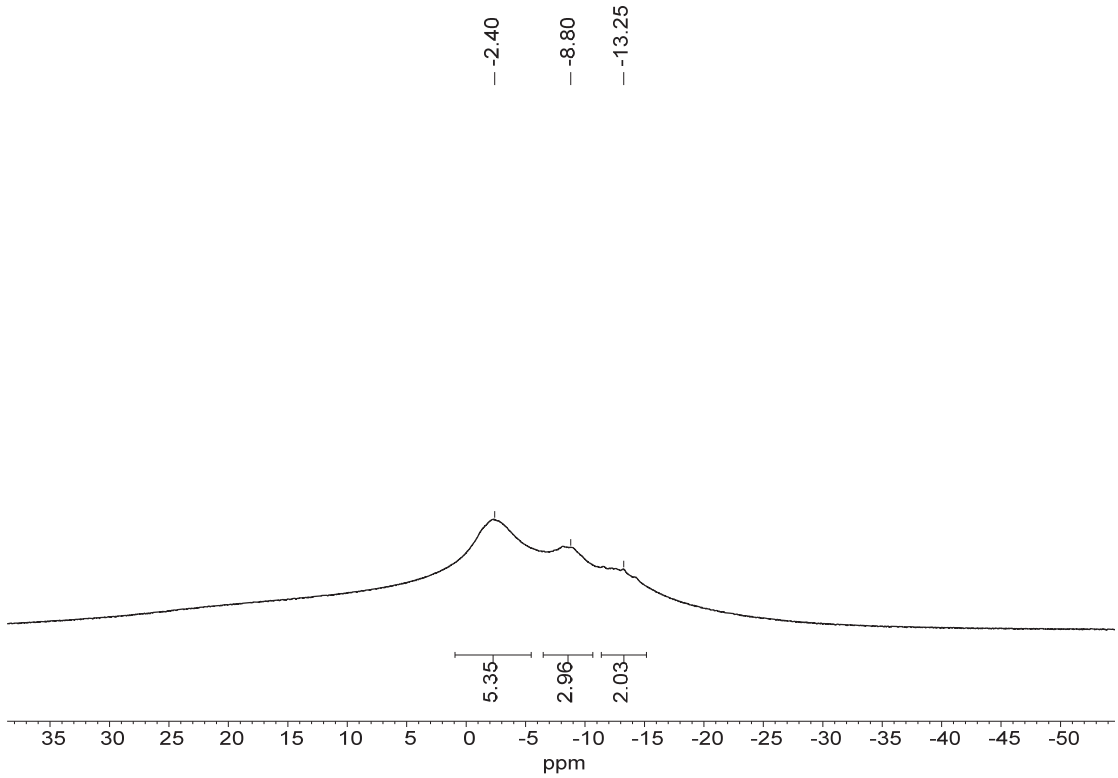
^{19}F NMR of 13k, 471 MHz, $CDCl_3$



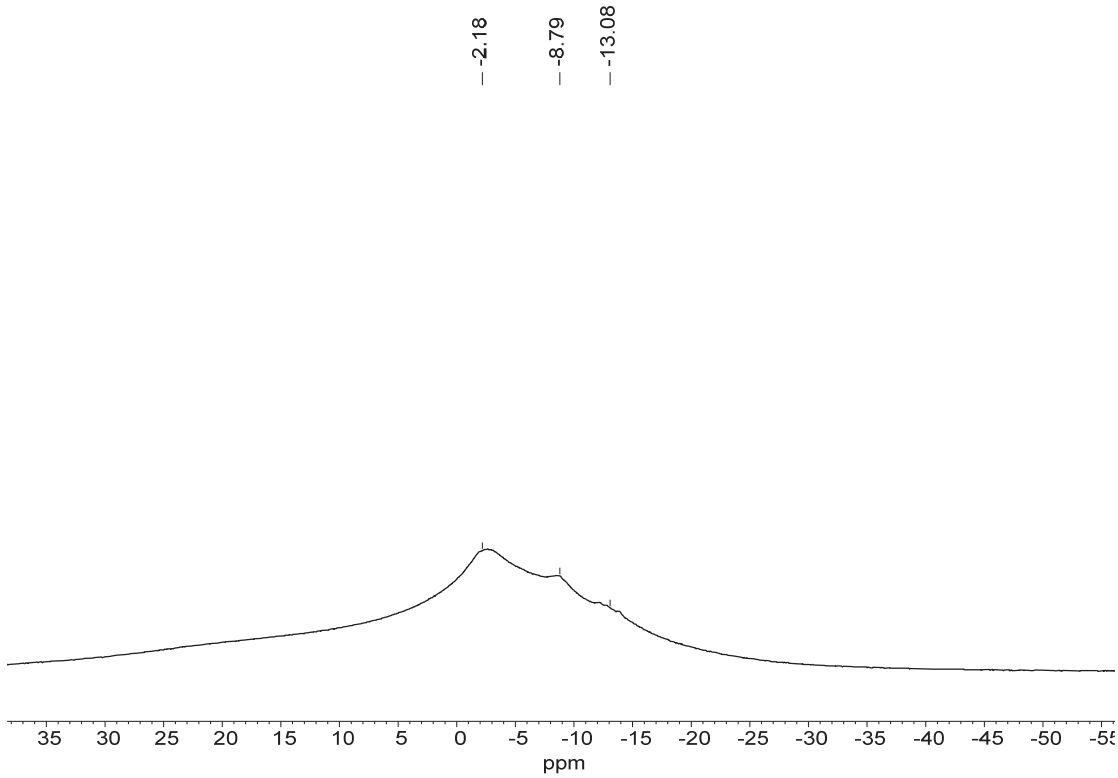
^{1}H NMR of 13l, 500 M, $CDCl_3$



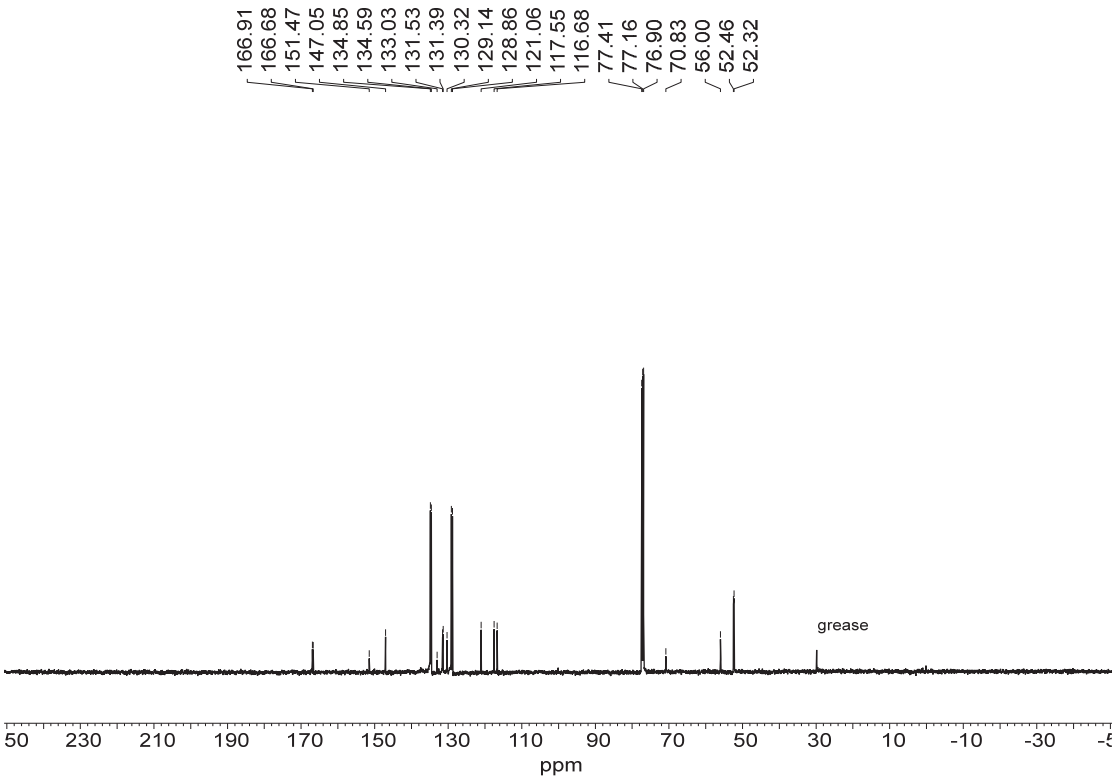
$^{11}B\ \{^{1}H\}$ NMR of 13l, 160 M, $CDCl_3$



^{11}B NMR of 13l, 160 M, $CDCl_3$

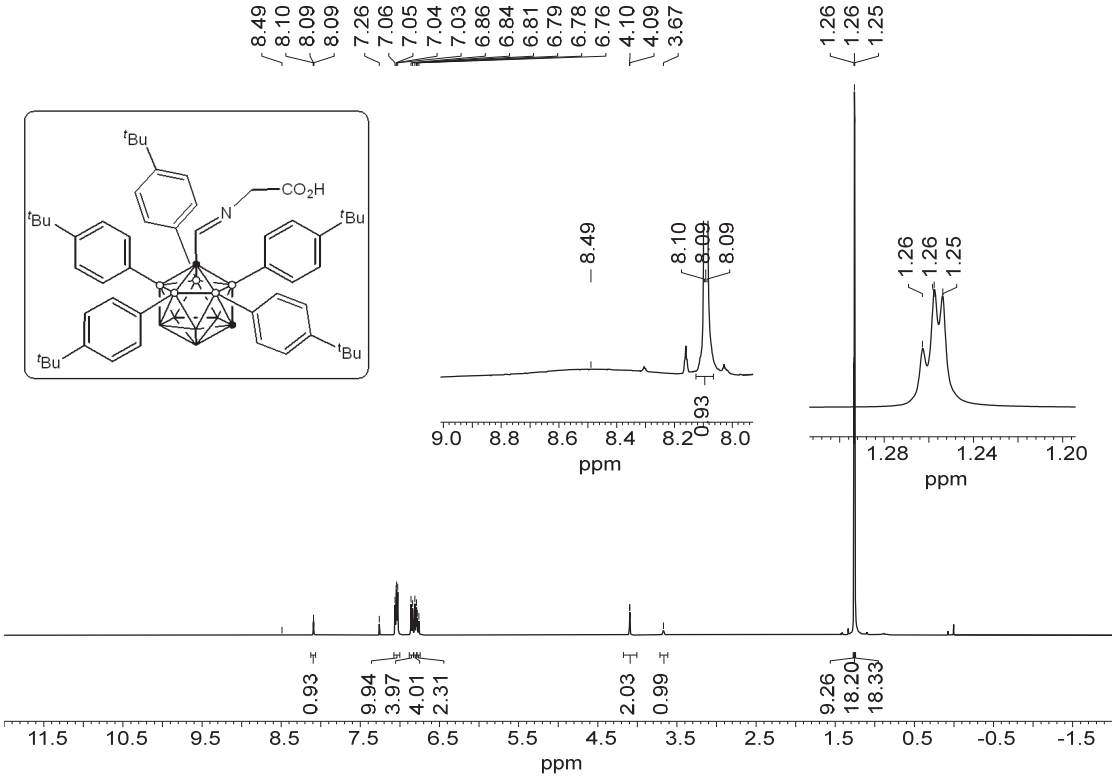


$^{13}C\ \{^1H\}$ NMR of 13l, 126 M, $CDCl_3$

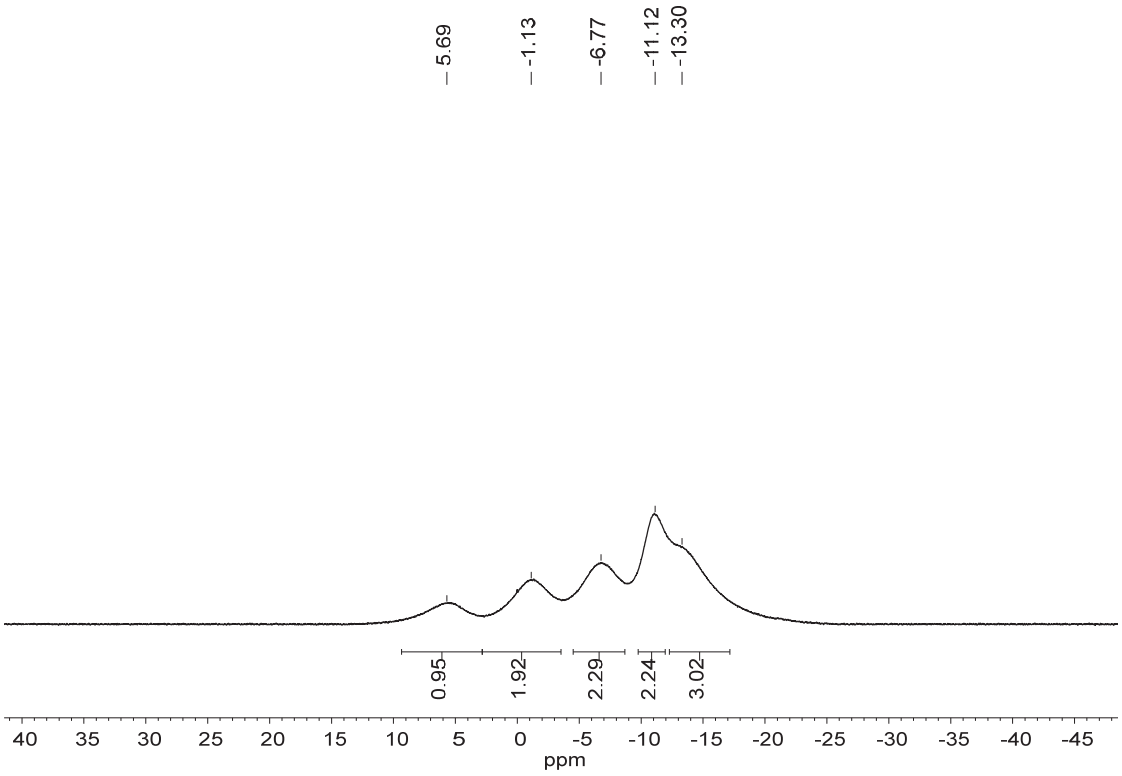


B(2,3,4,5,6)-penta-arylated-*m*-carborane

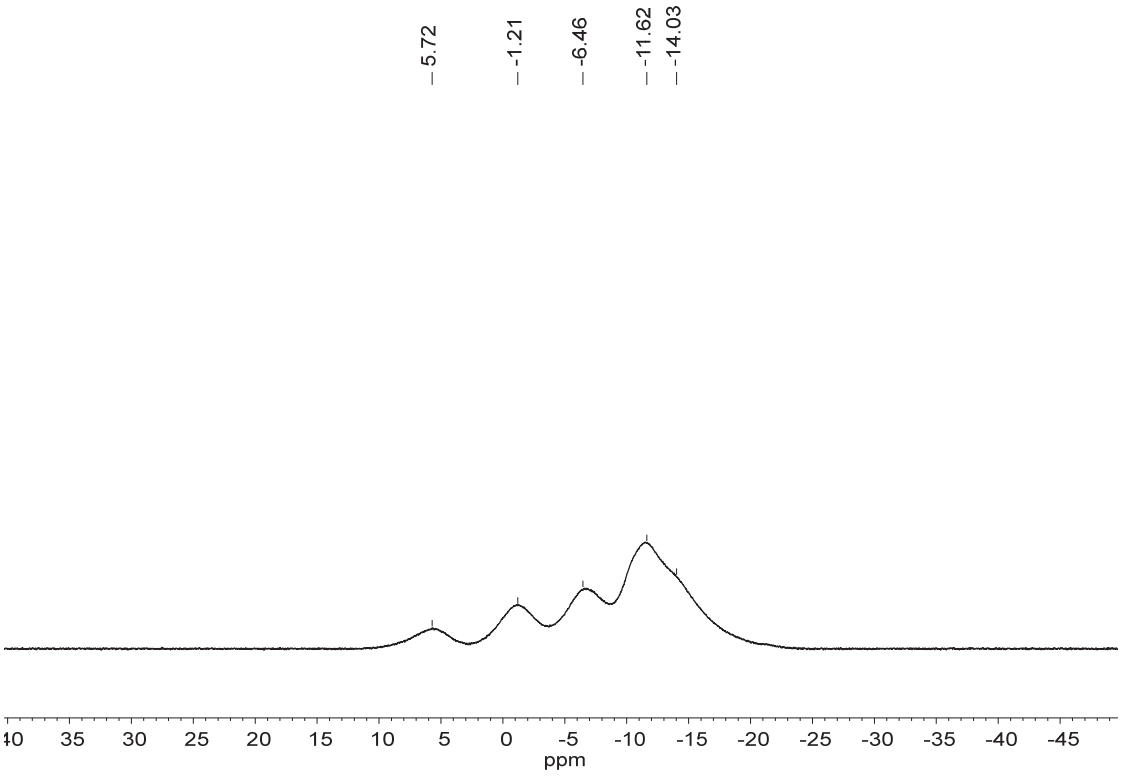
^1H NMR of 14a, 400 M, $CDCl_3$



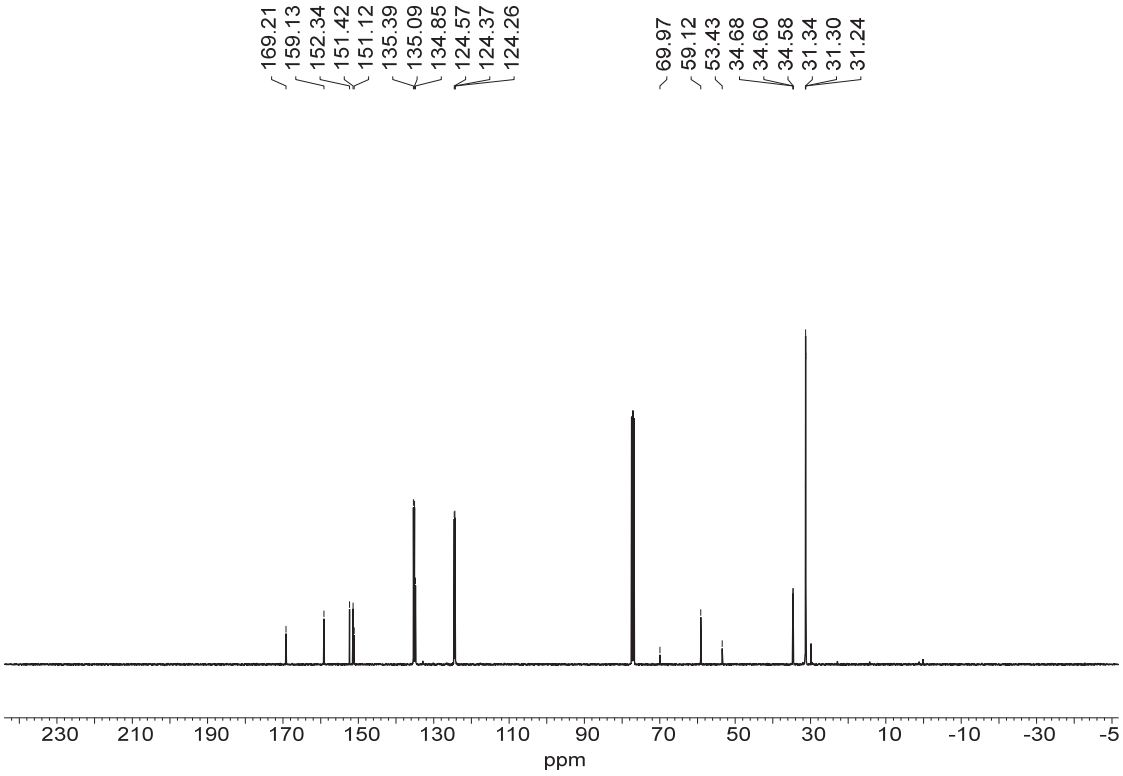
$^{11}B\ \{^{1}H\}$ NMR of 14a, 128 M, $CDCl_3$



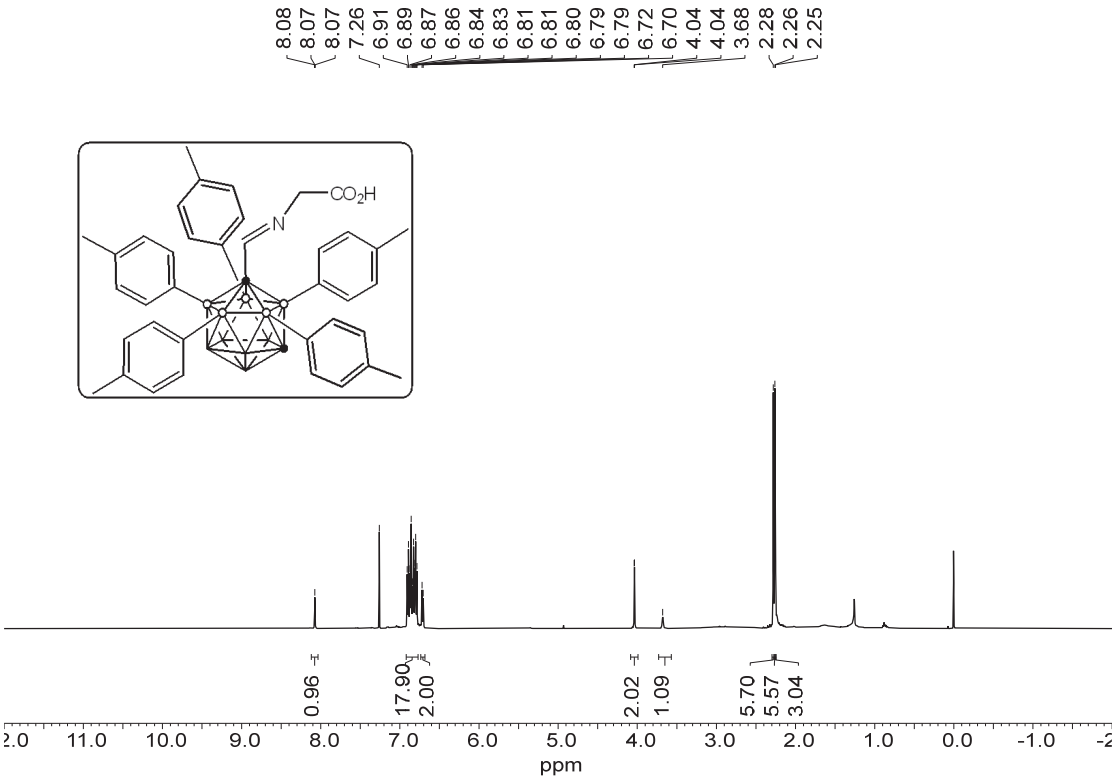
^{11}B NMR of 14a, 128 M, $CDCl_3$



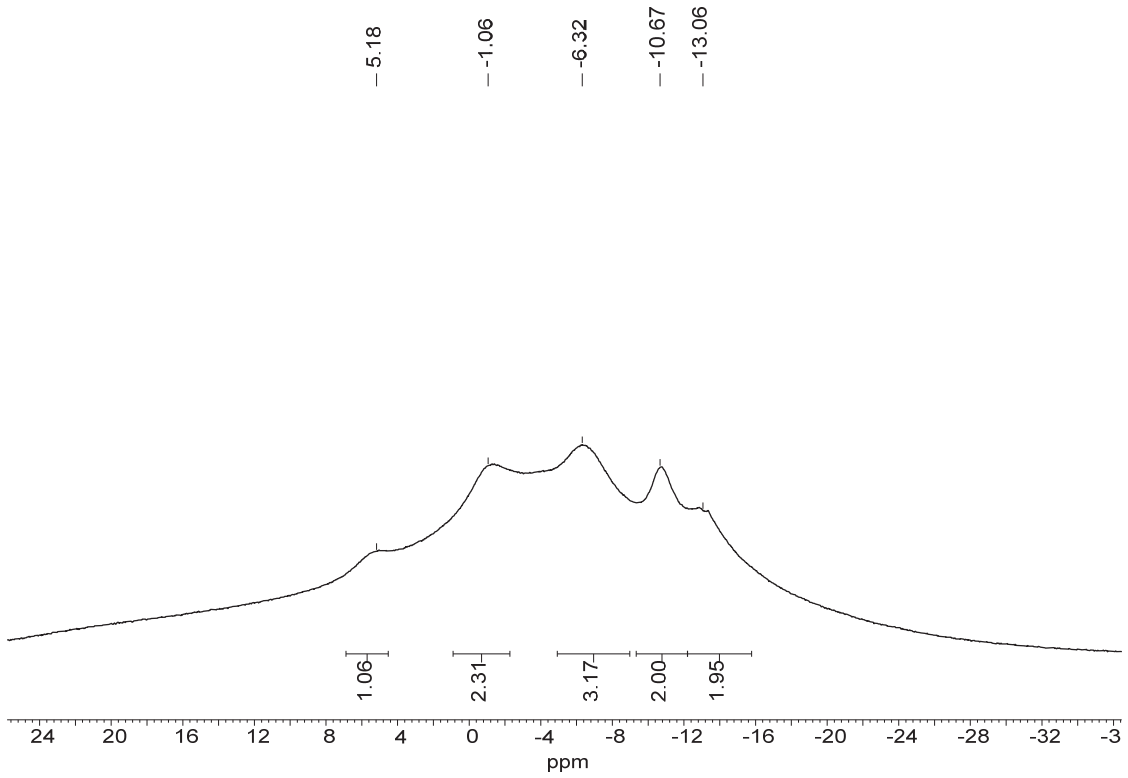
^{13}C NMR of 14a, 101 M, $CDCl_3$



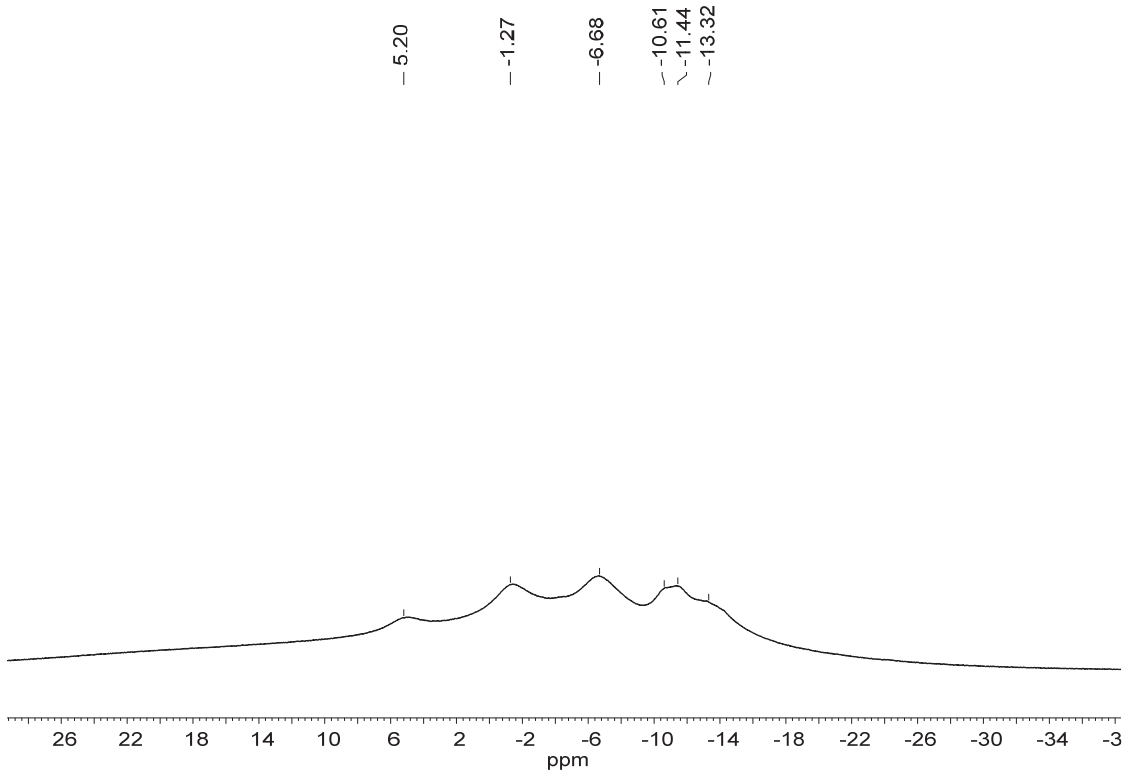
^{1}H NMR of 14b, 500 M, $CDCl_3$



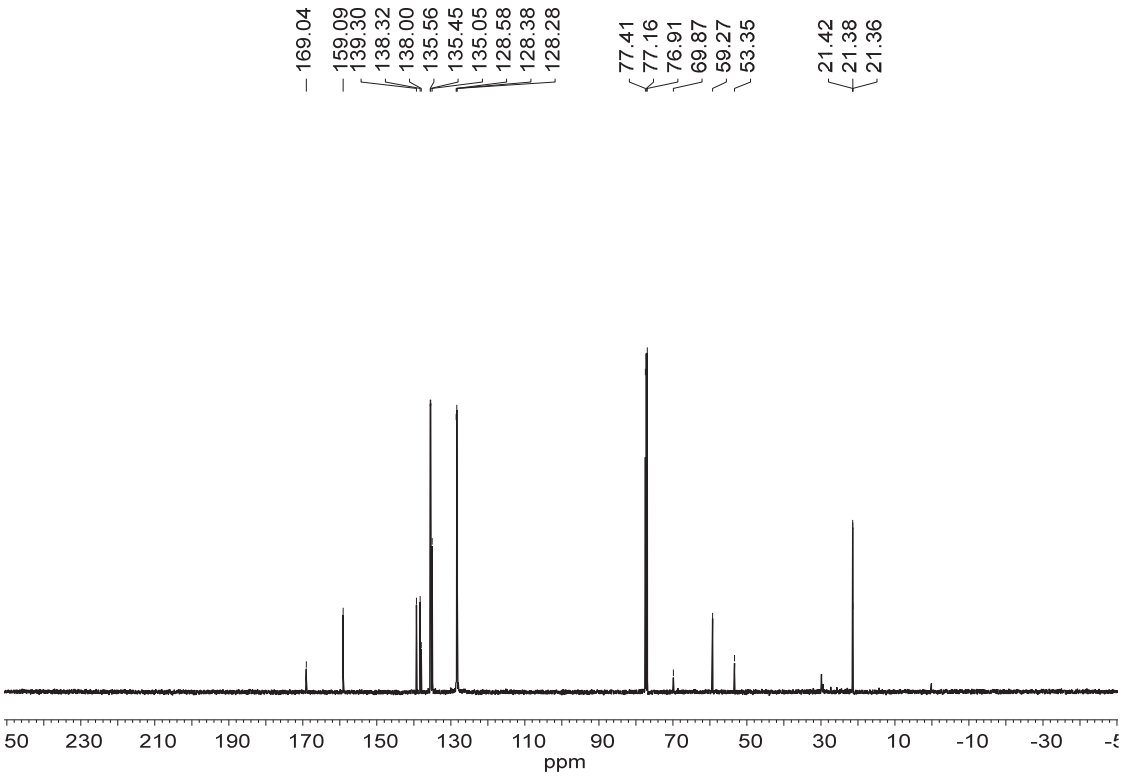
^{11}B {H} NMR of 14b, 160 M, $CDCl_3$



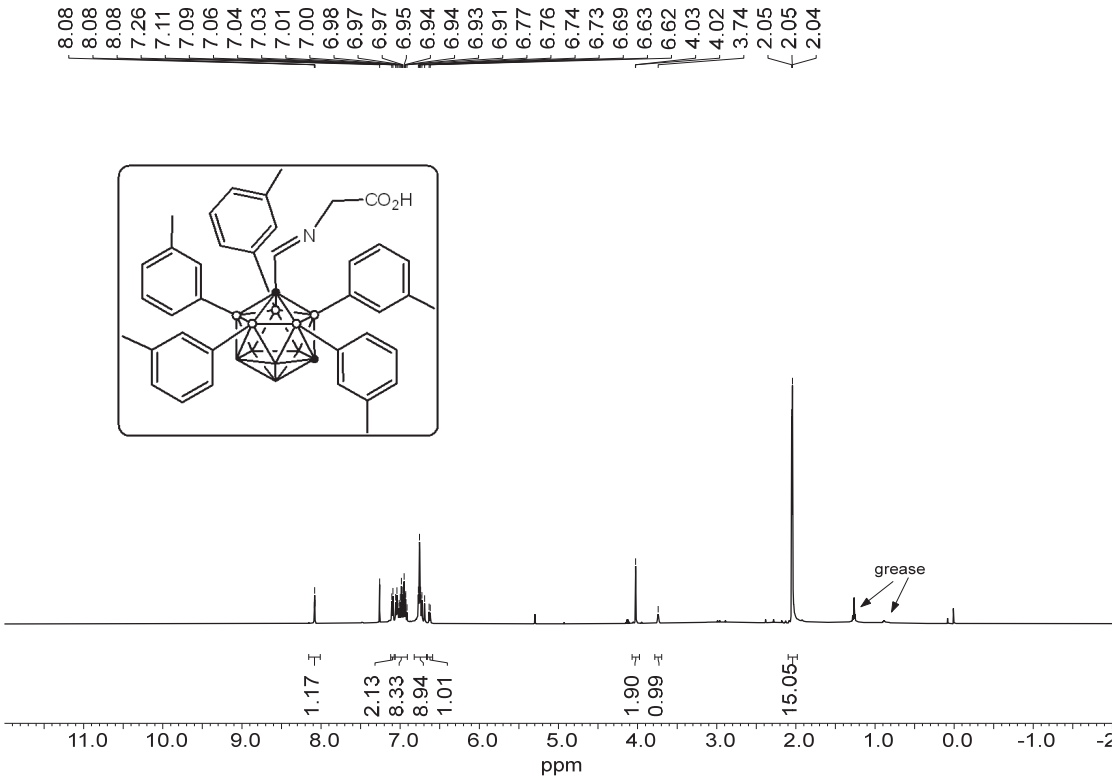
^{11}B {H} NMR of 14b, 160 M, $CDCl_3$



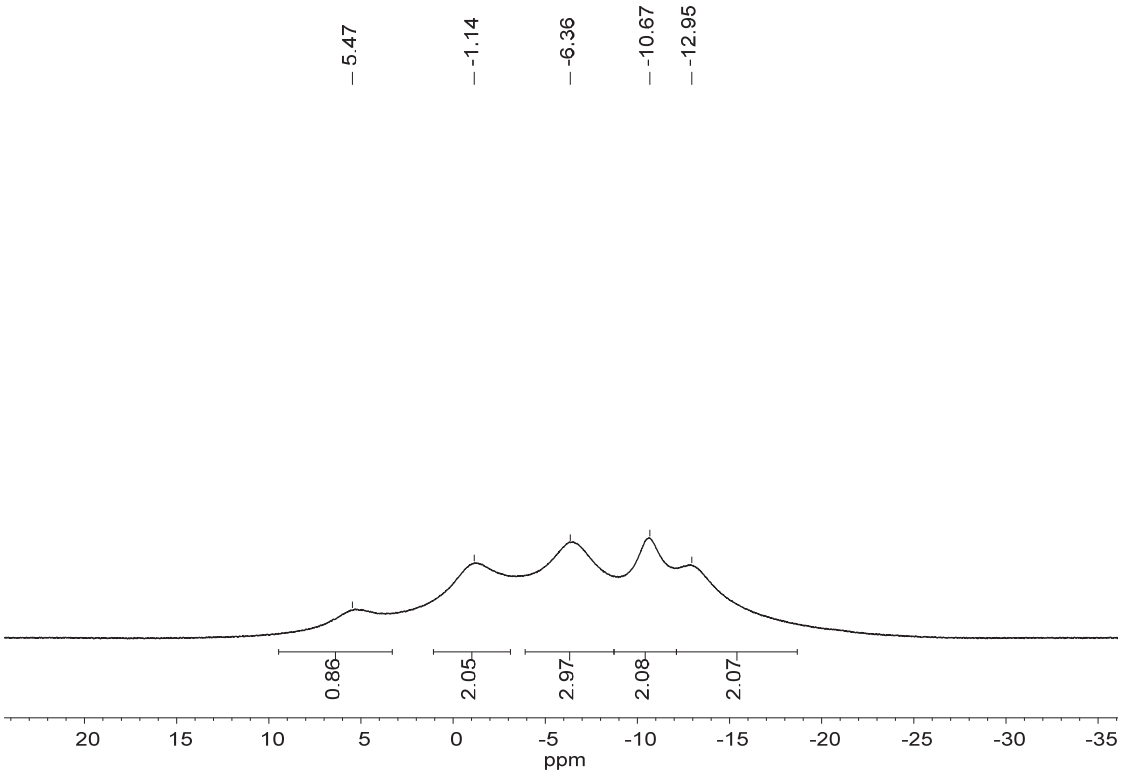
^{13}C NMR of 14b, 126 M, $CDCl_3$



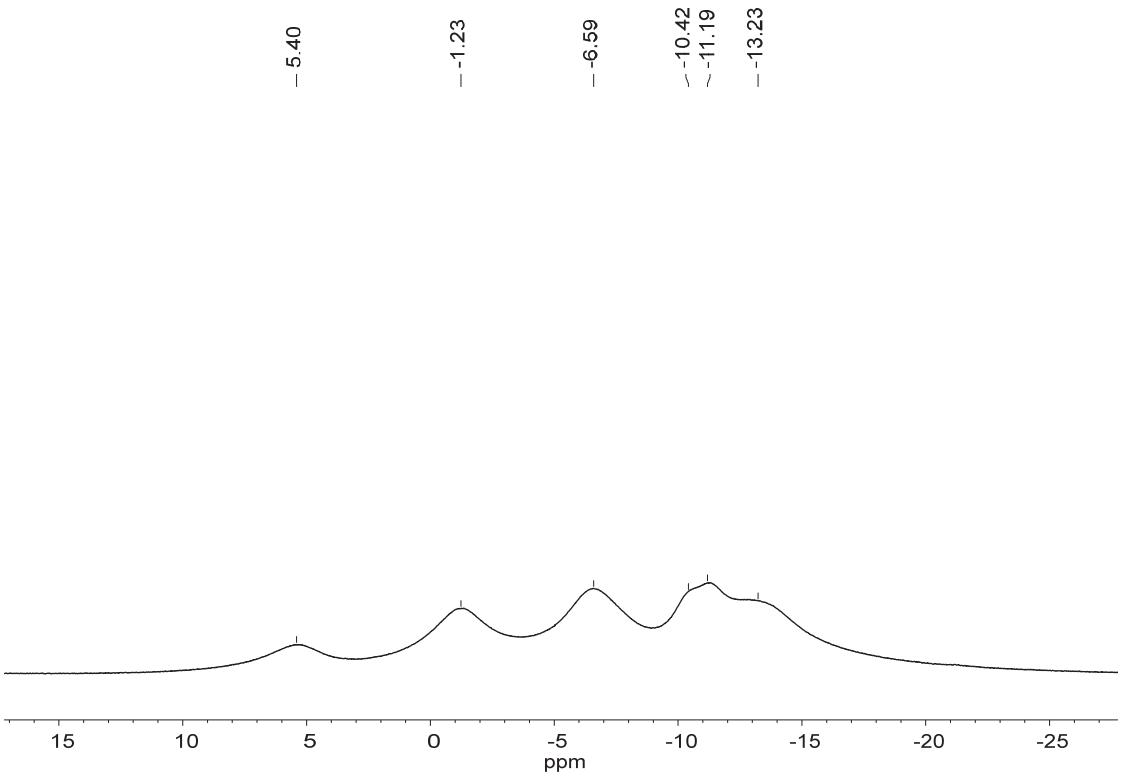
^{1}H NMR of 14c, 500 M, $CDCl_3$



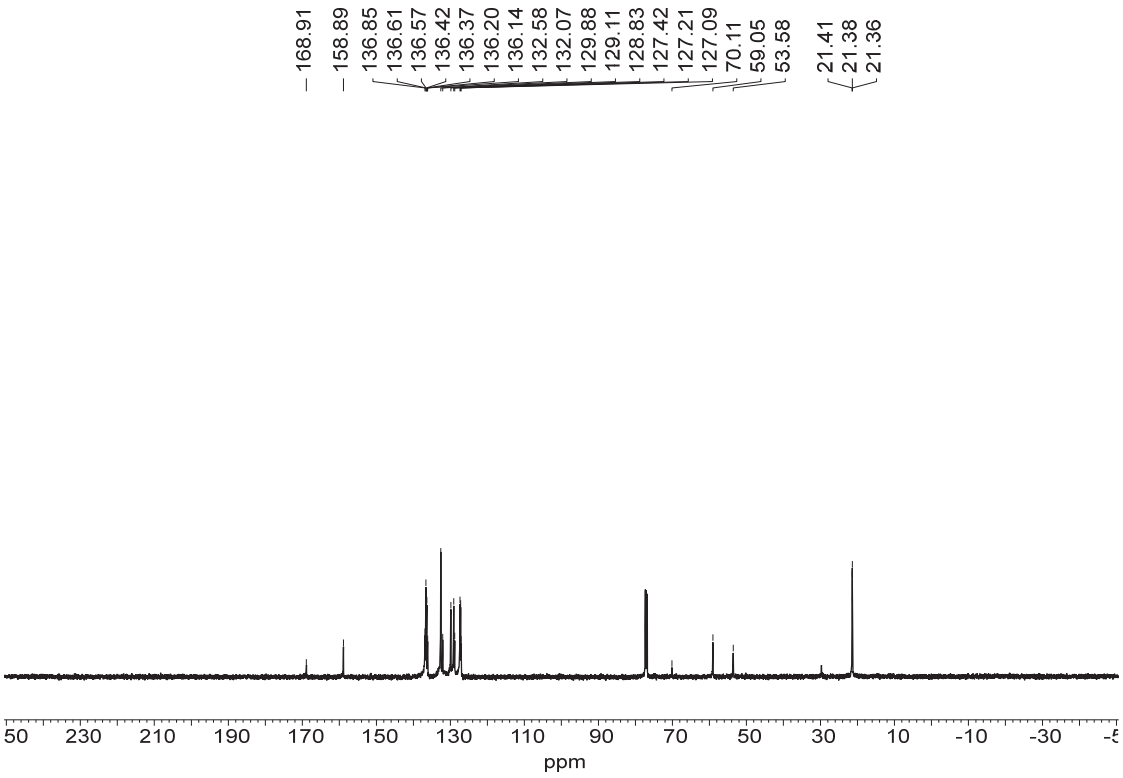
$^{11}B\ \{^{1}H\}$ NMR of 14c, 160 M, $CDCl_3$



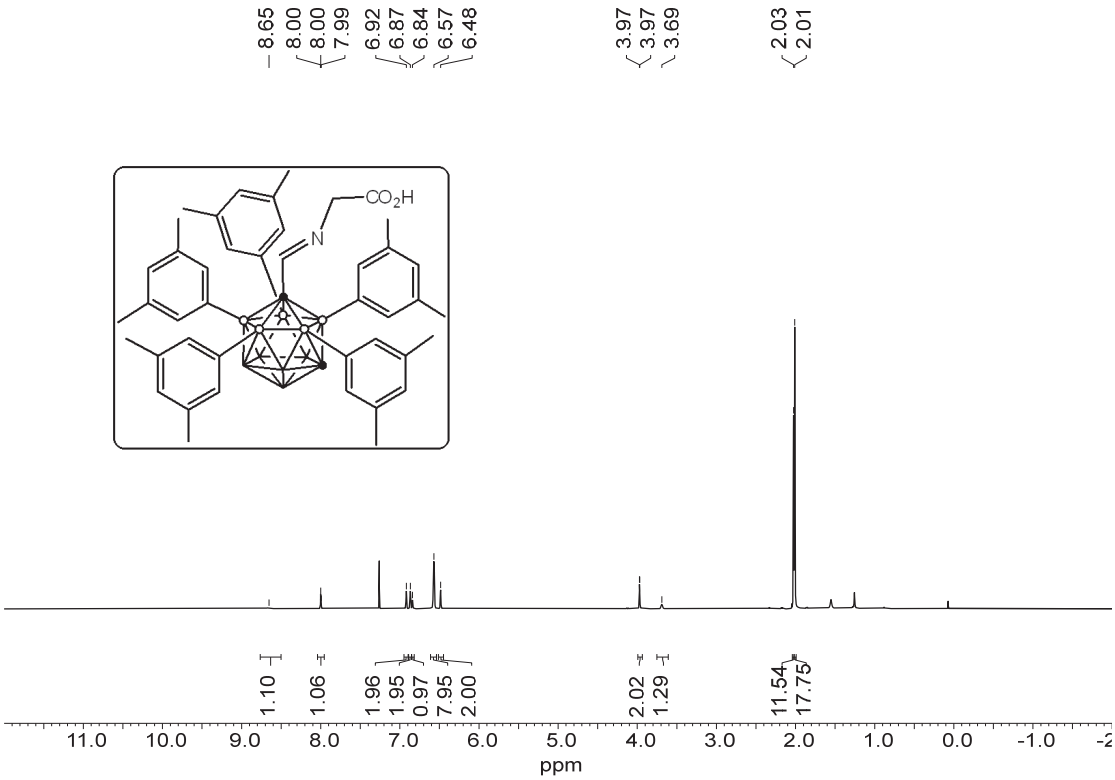
^{11}B NMR of 14c, 160 M, $CDCl_3$



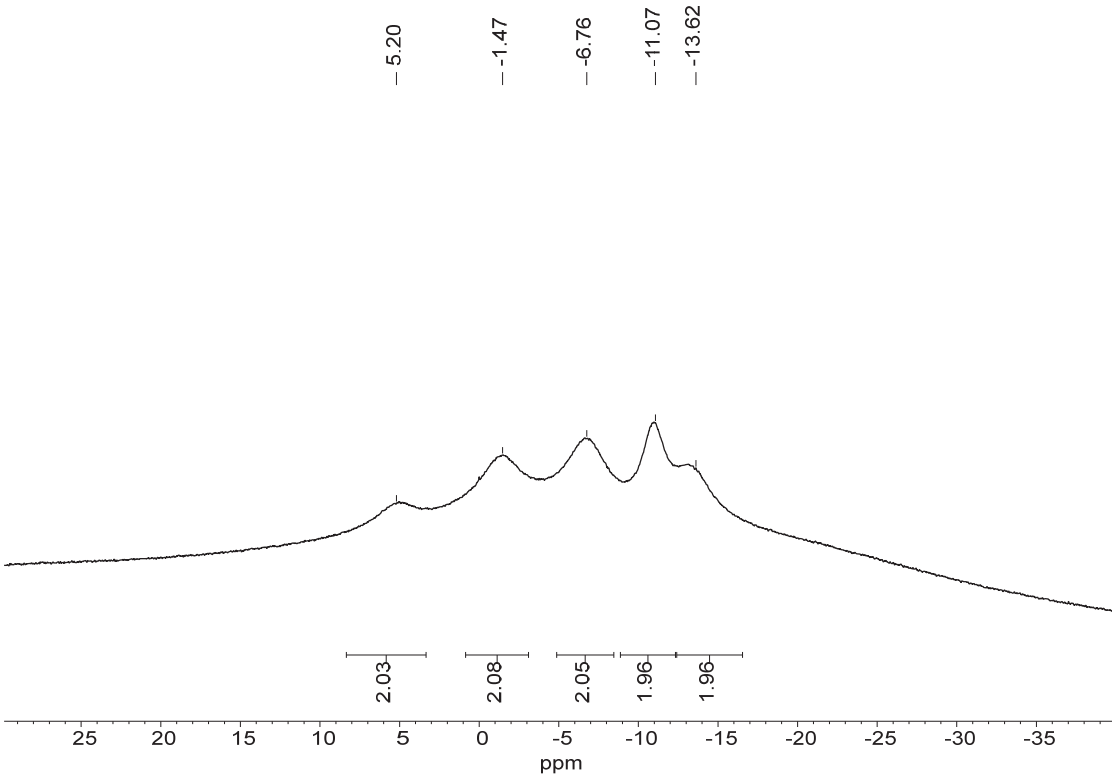
^{13}C NMR of 14c, 126 M, $CDCl_3$



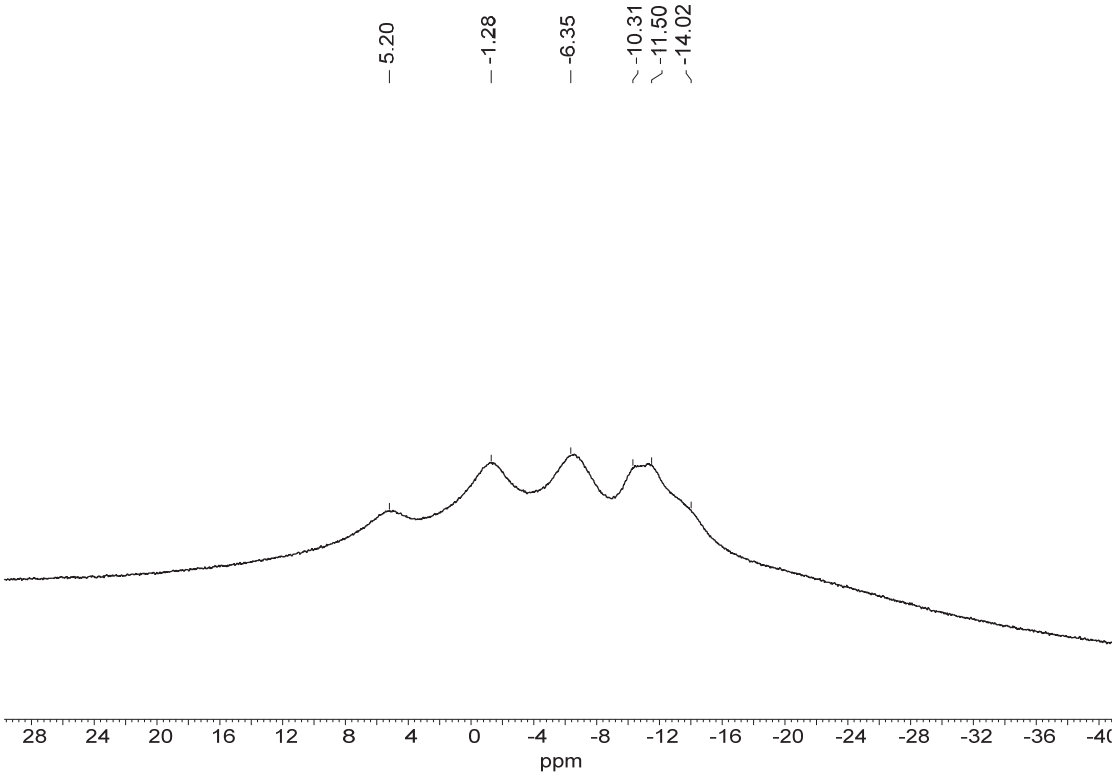
^{1}H NMR of 14d, 400 M, $CDCl_3$



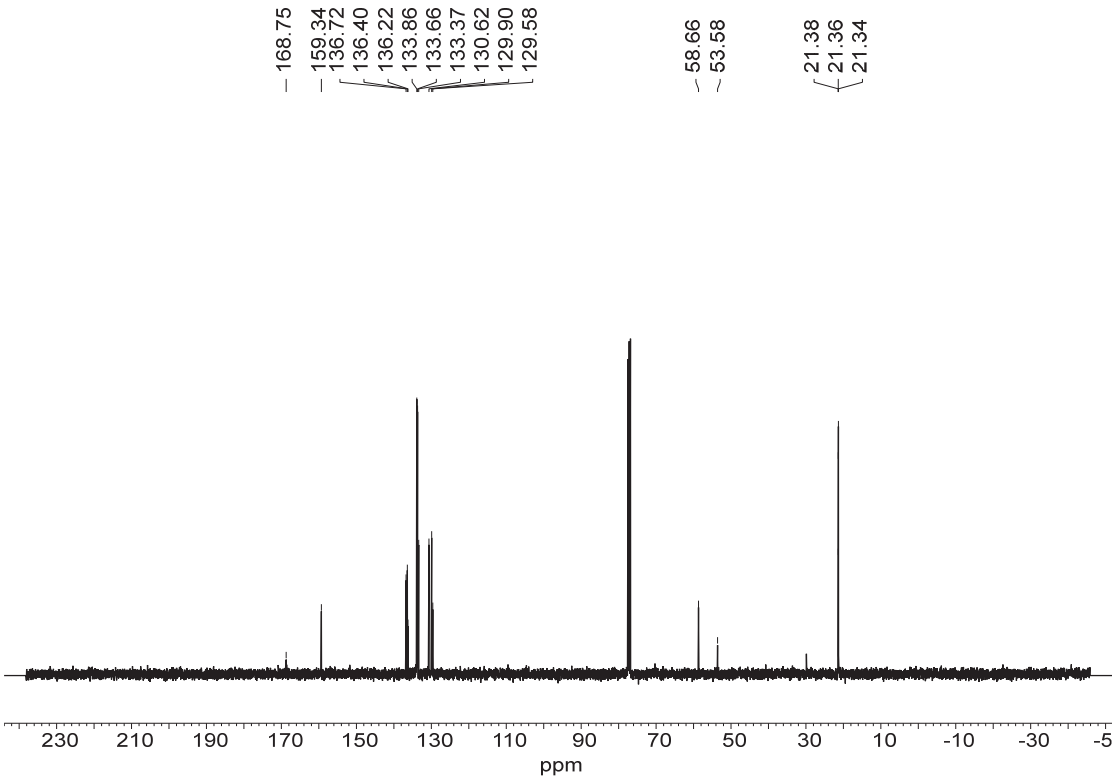
$^{11}B\ \{^{1}H\}$ NMR of 14d, 128 M, $CDCl_3$



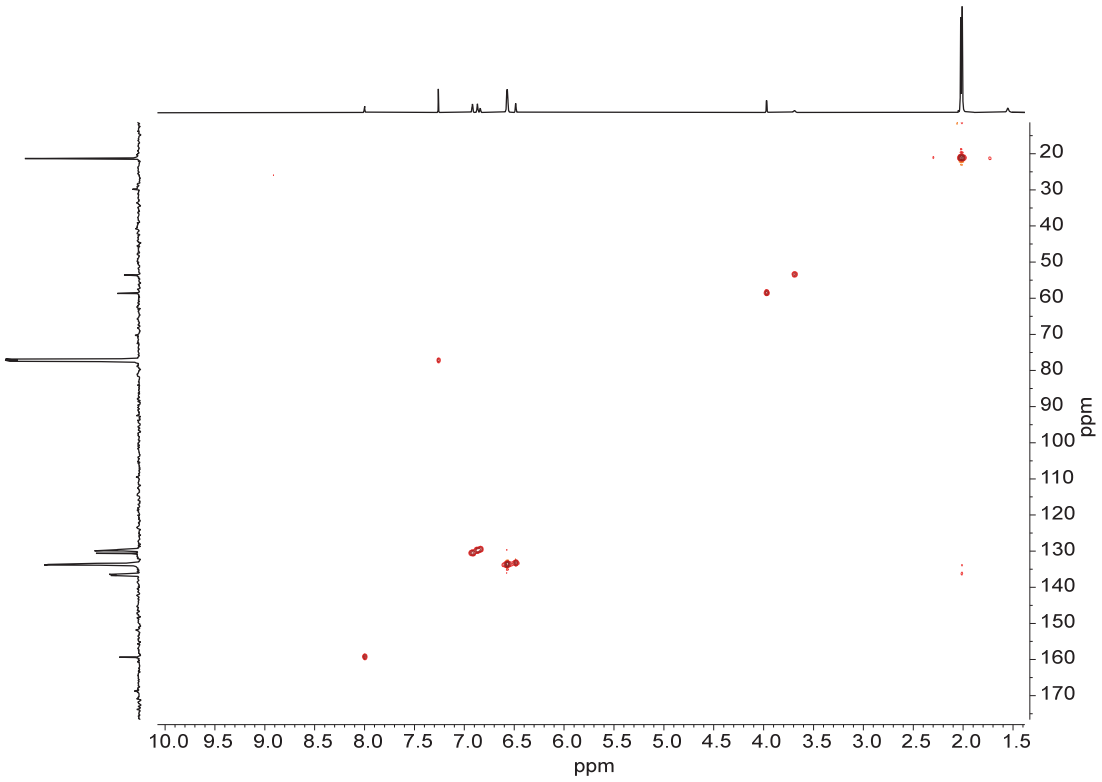
$^{11}B\ \{^{1}H\}$ NMR of 14d, 128 M, $CDCl_3$



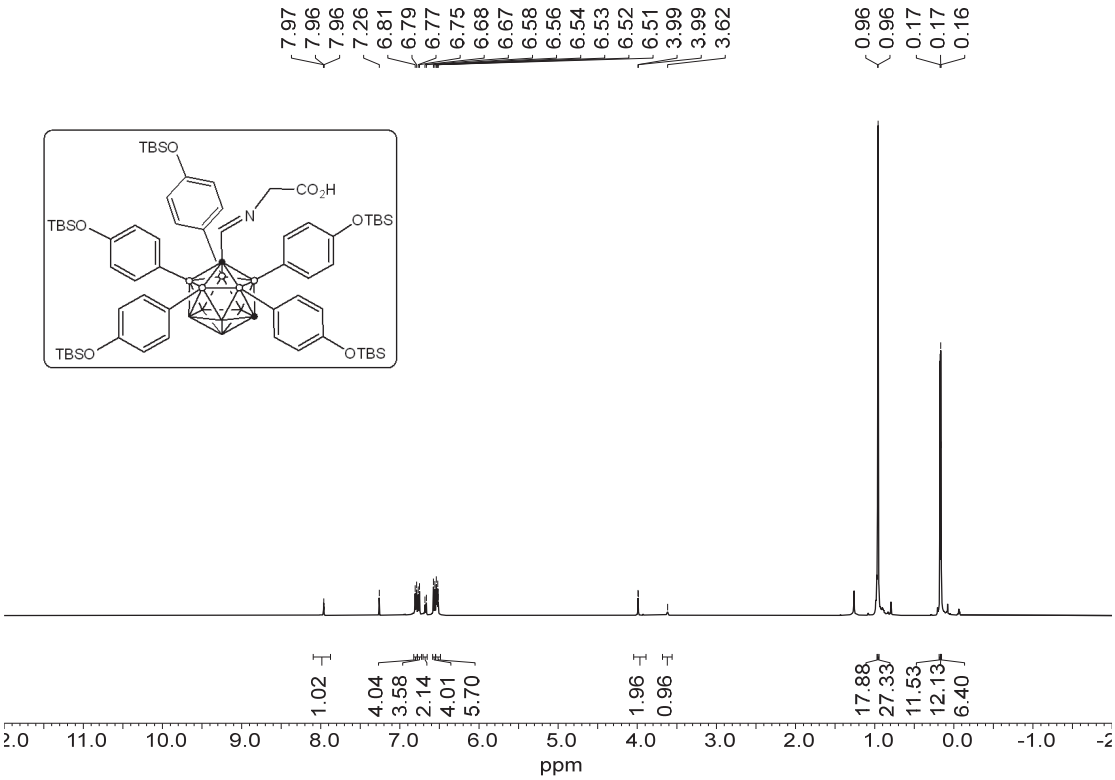
$^{13}C\ \{^{1}H\}$ NMR of 14d, 101 M, $CDCl_3$



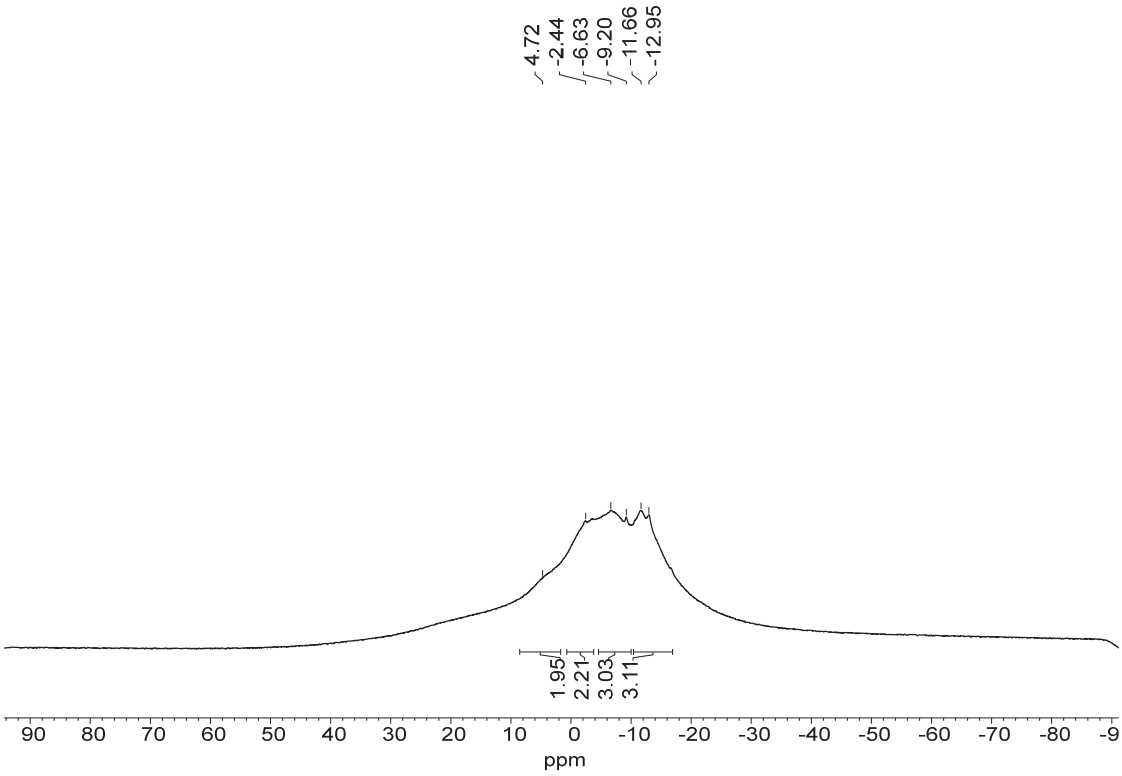
^{1}H-^{13}C HSQC of 14d, 400 M, $CDCl_3$



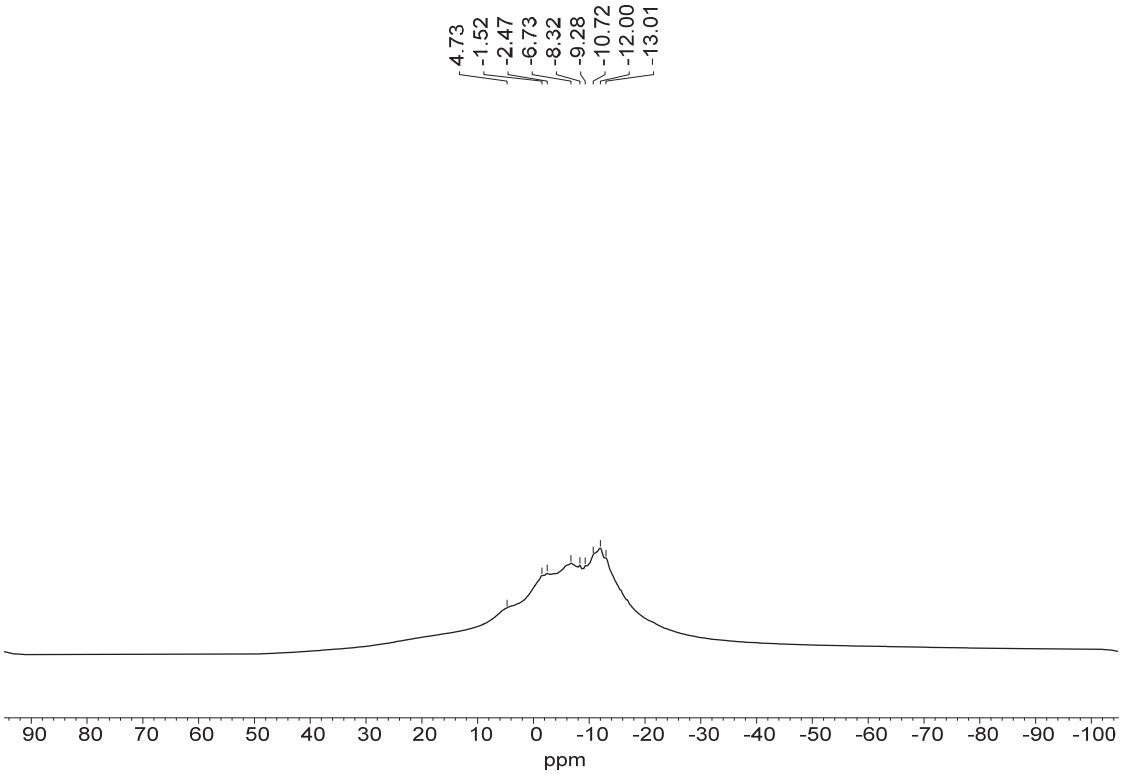
^{1}H NMR of 14e, 500 M, $CDCl_3$



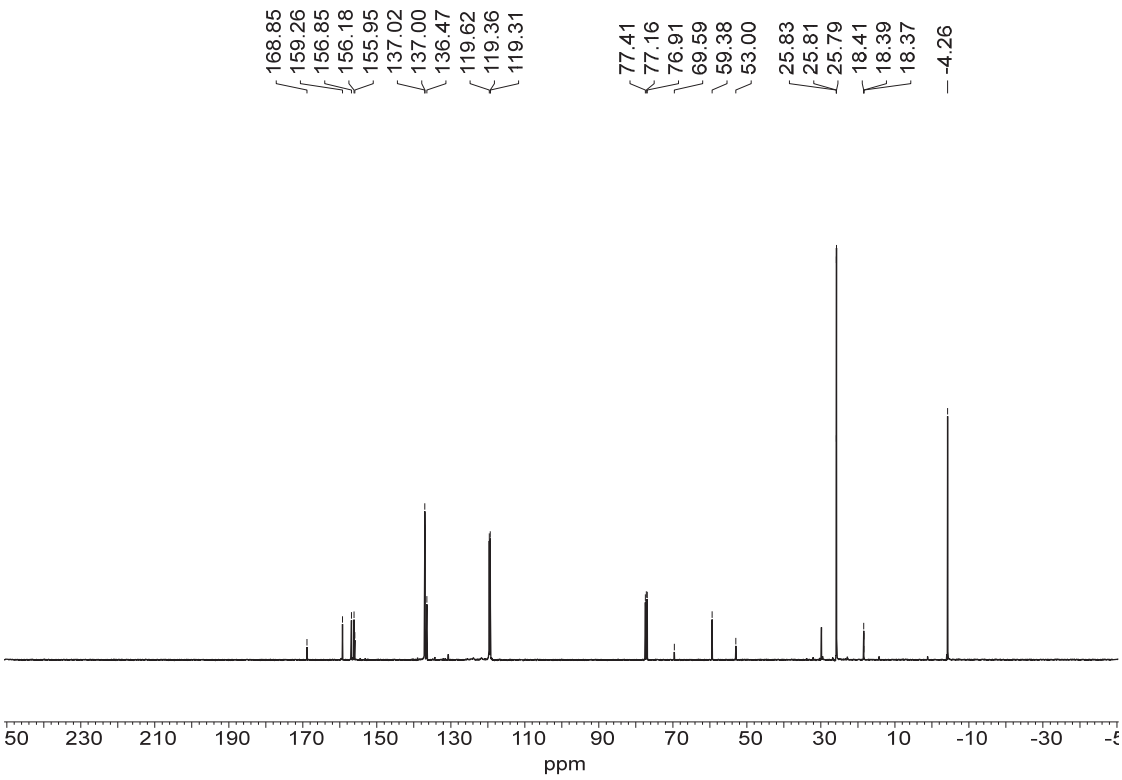
^{11}B {^{1}H} NMR of 14e, 160 M, $CDCl_3$



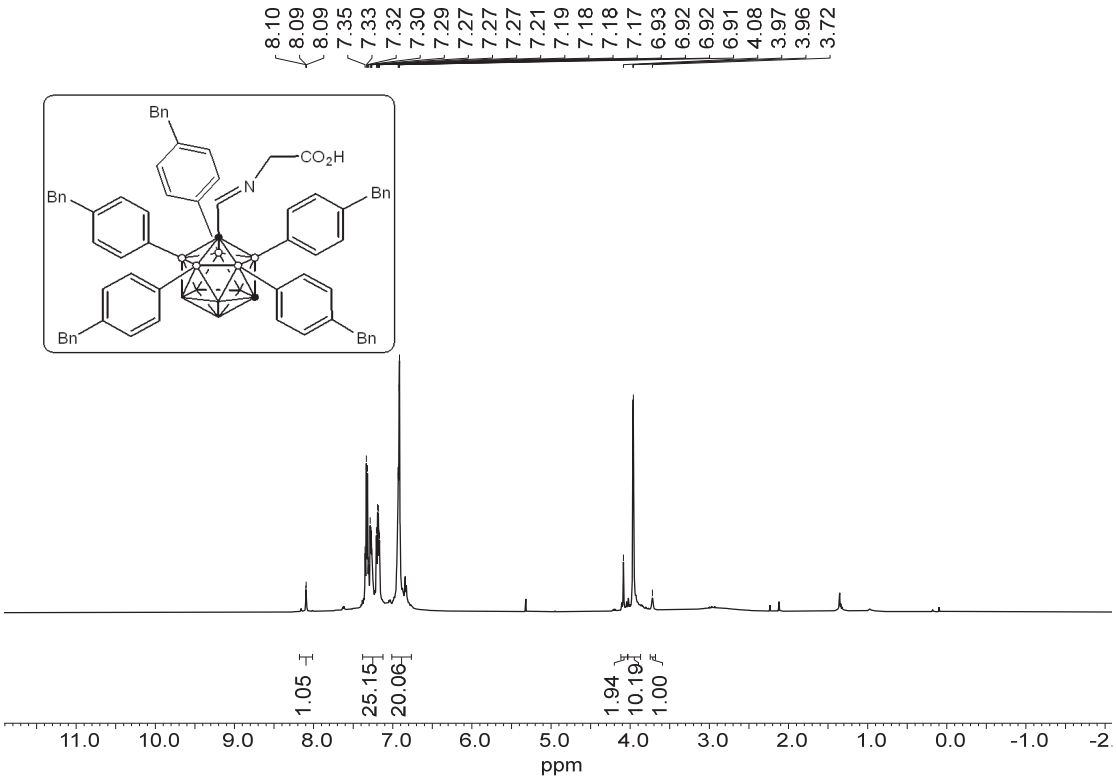
^{11}B NMR of 14e, 160 M, $CDCl_3$



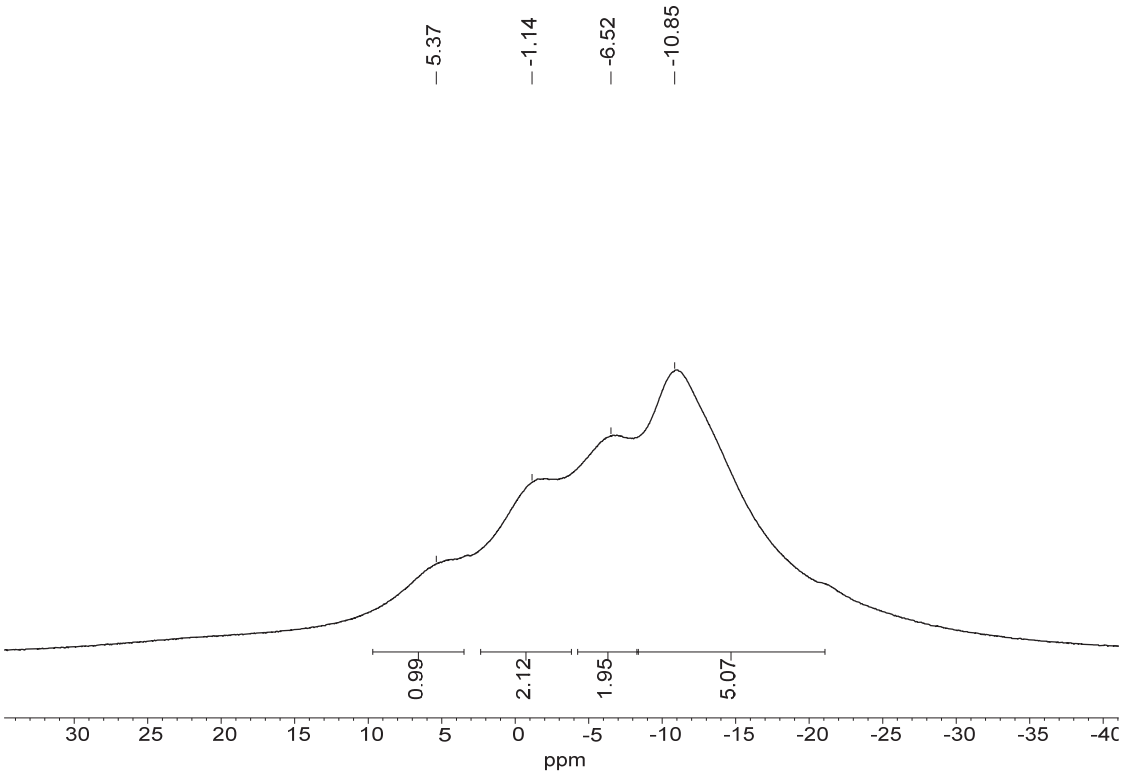
^{13}C NMR of 14e, 126 M, $CDCl_3$



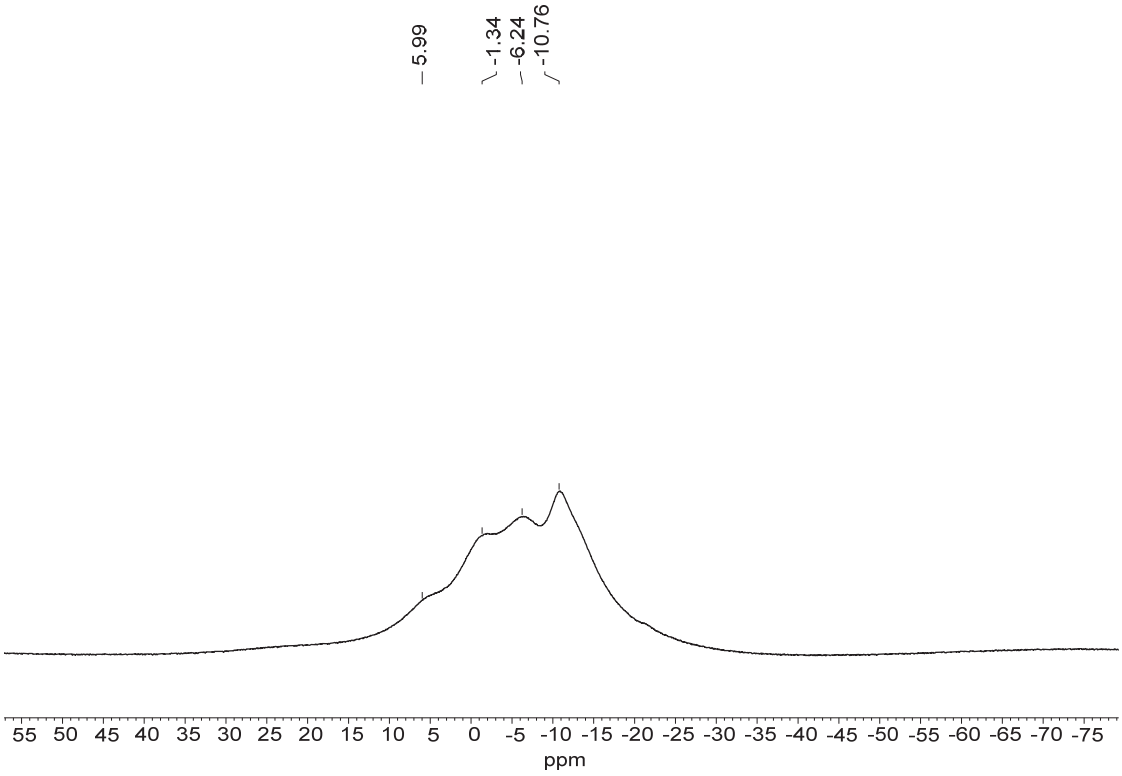
^{1}H NMR of 14f, 500 M, $CDCl_3$



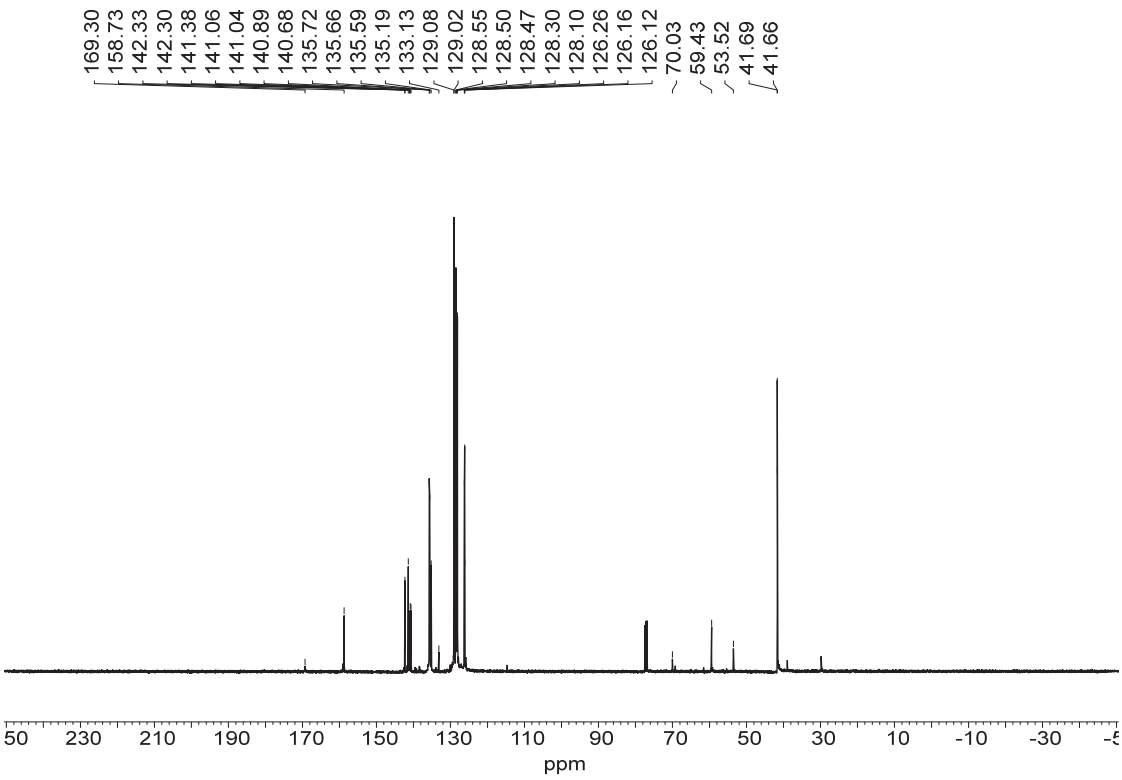
^{11}B {^{1}H} NMR of 14f, 160 M, $CDCl_3$



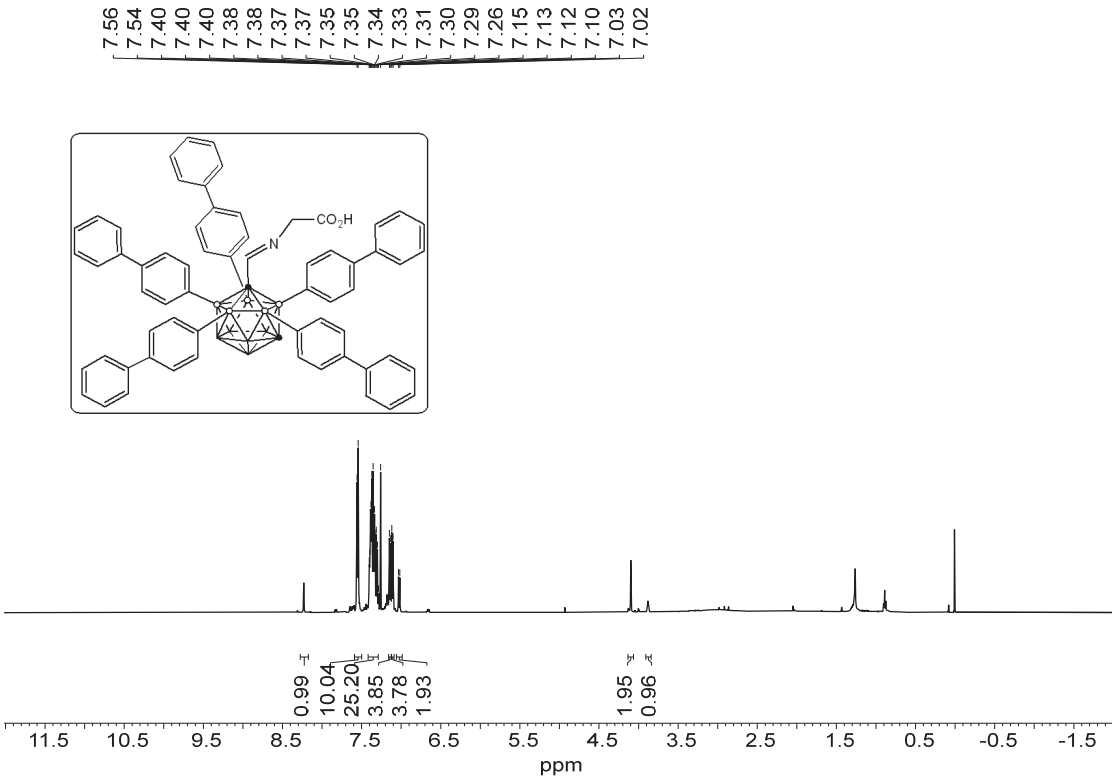
^{11}B NMR of 14f, 160 M, $CDCl_3$



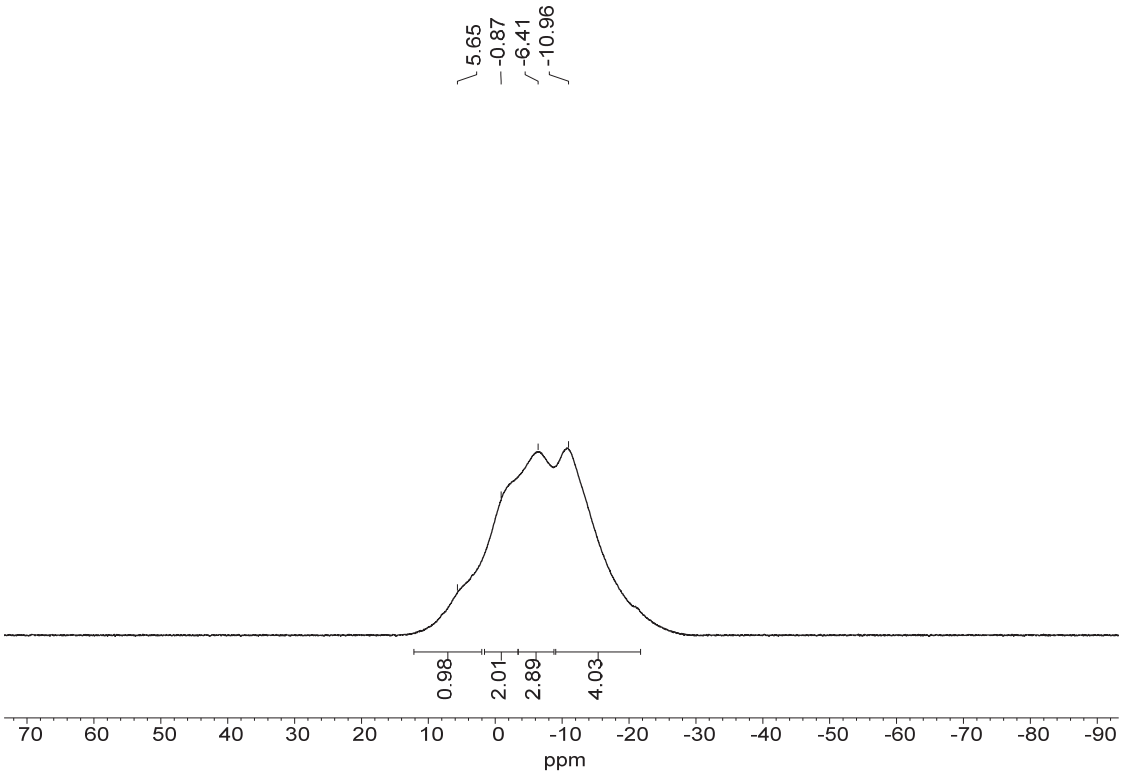
^{13}C NMR of 14f, 126 M, $CDCl_3$



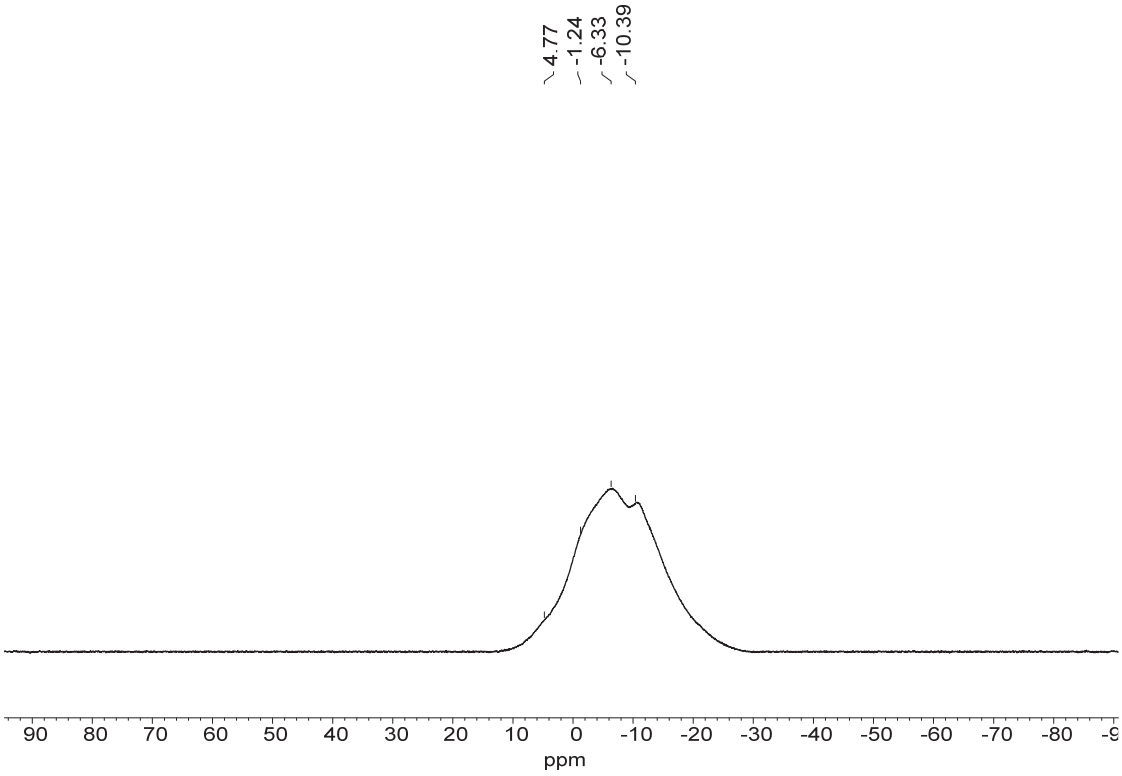
^{1}H NMR, 500 M of 14g, $CDCl_3$



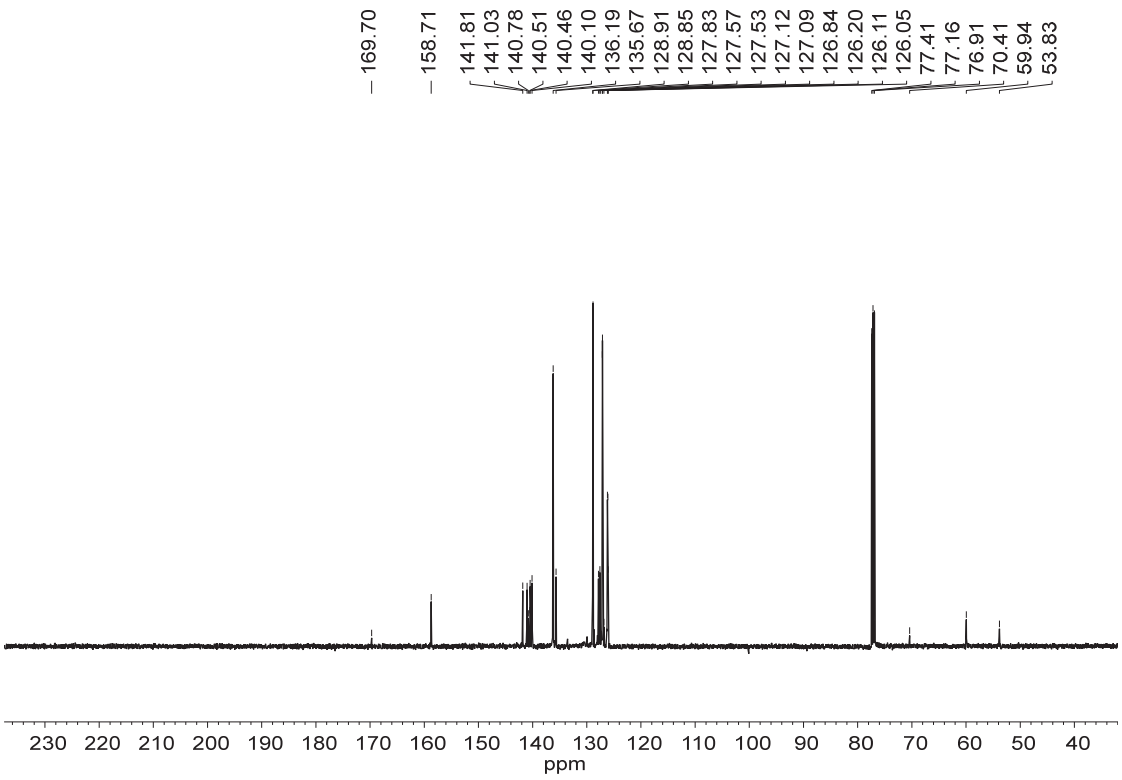
^{11}B {^{1}H} NMR of 14g, 160 M, $CDCl_3$



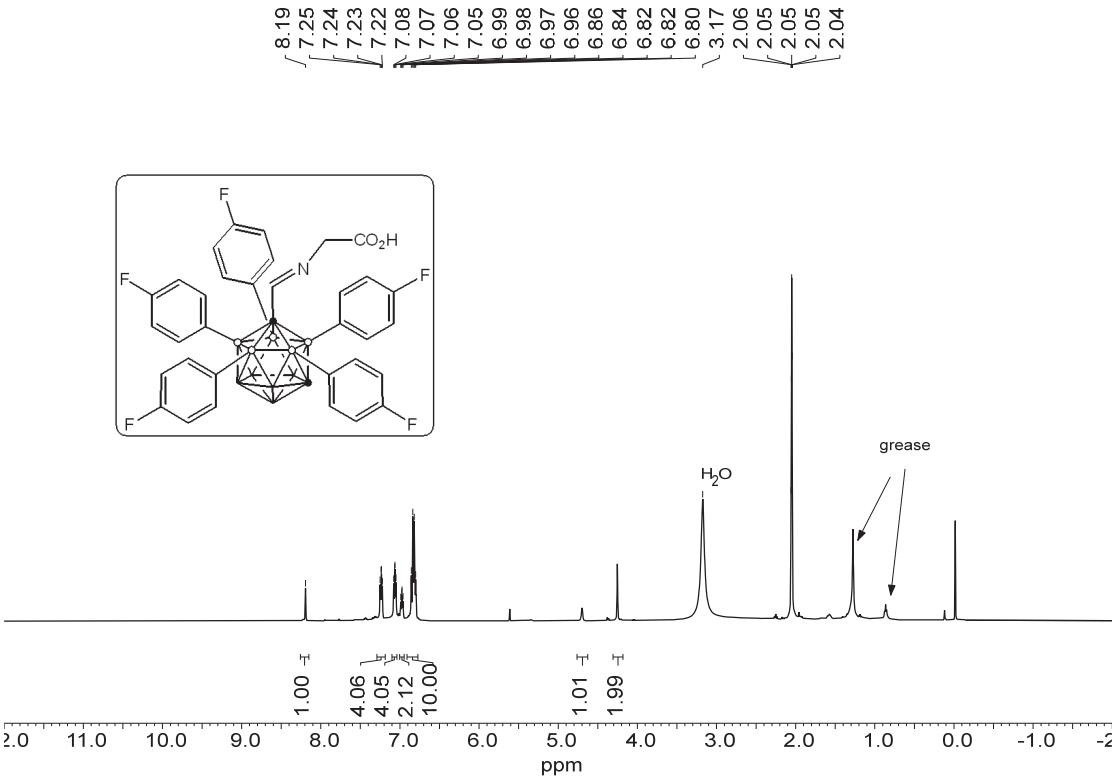
^{11}B NMR of 14g, 160 M, $CDCl_3$



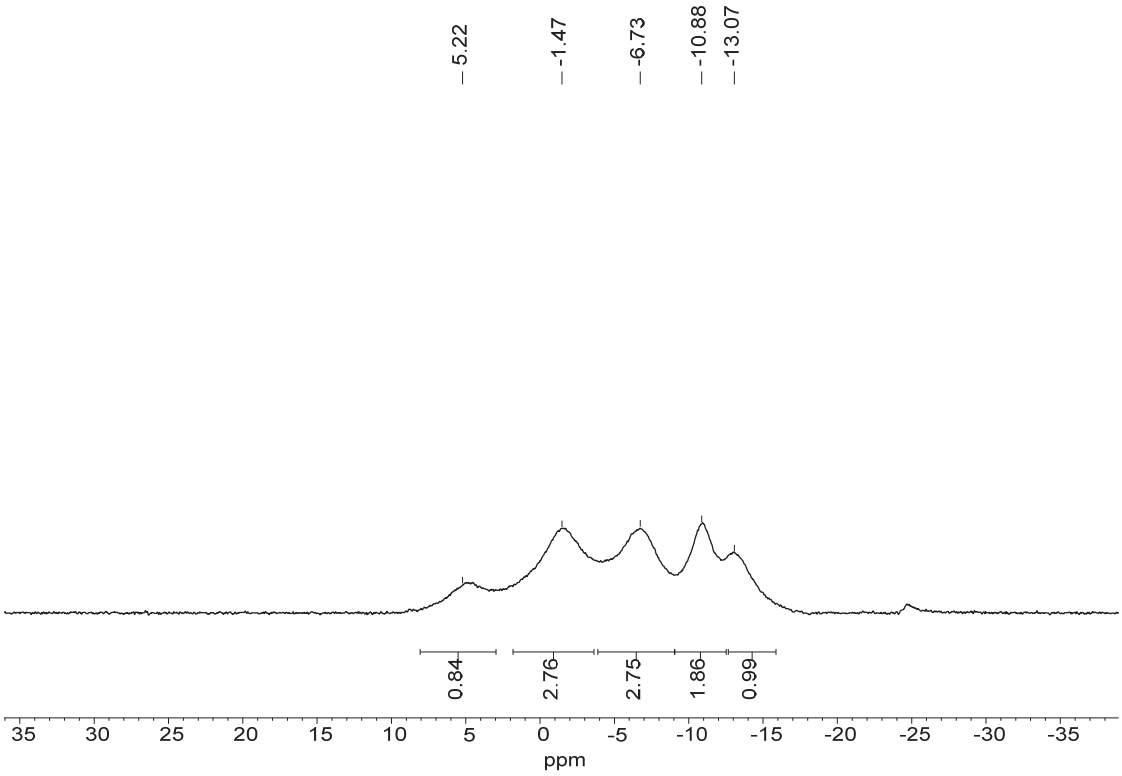
^{13}C NMR of 14g, 126 M, $CDCl_3$



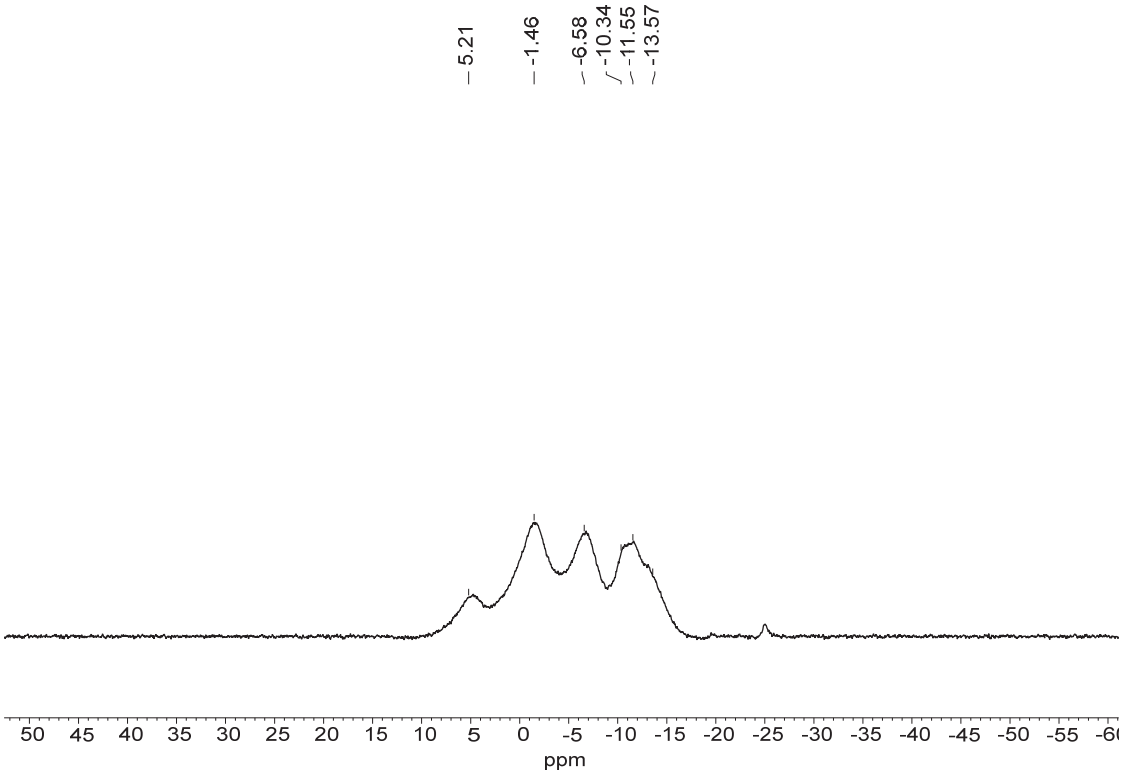
^{1}H NMR of 14h, 500 M, acetone-d$_6$



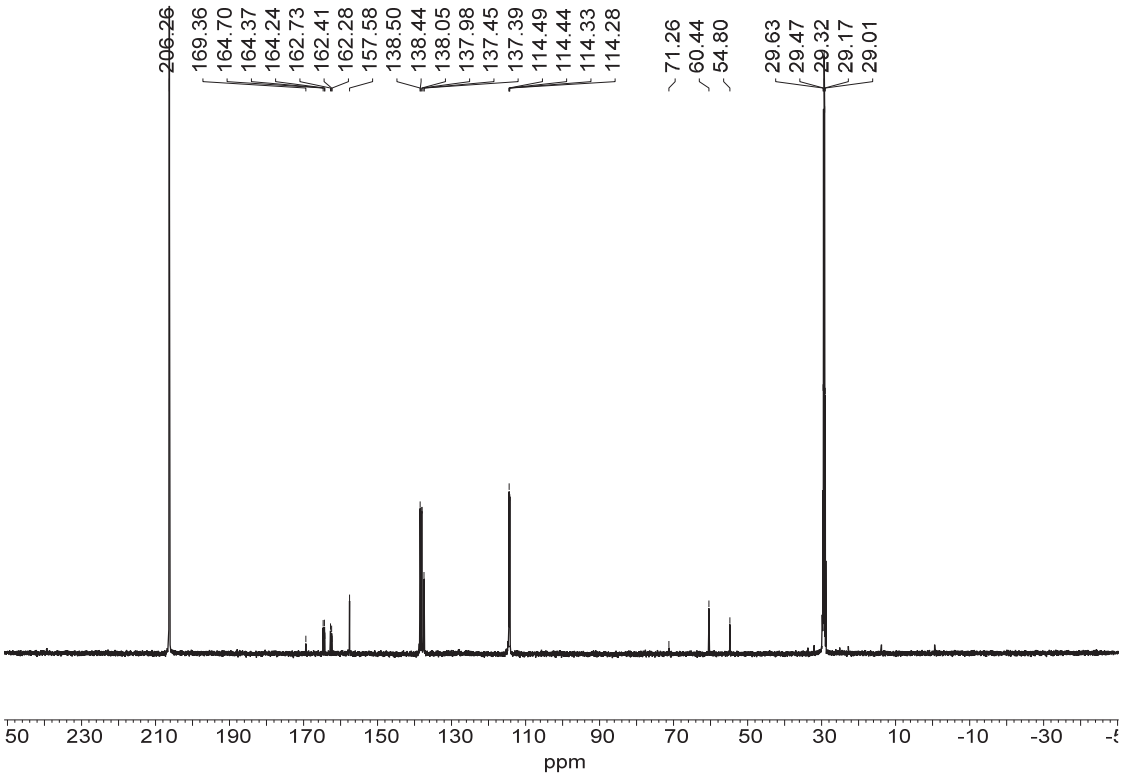
^{11}B {^{1}H} NMR of 14h, 160 M, $CDCl_3$



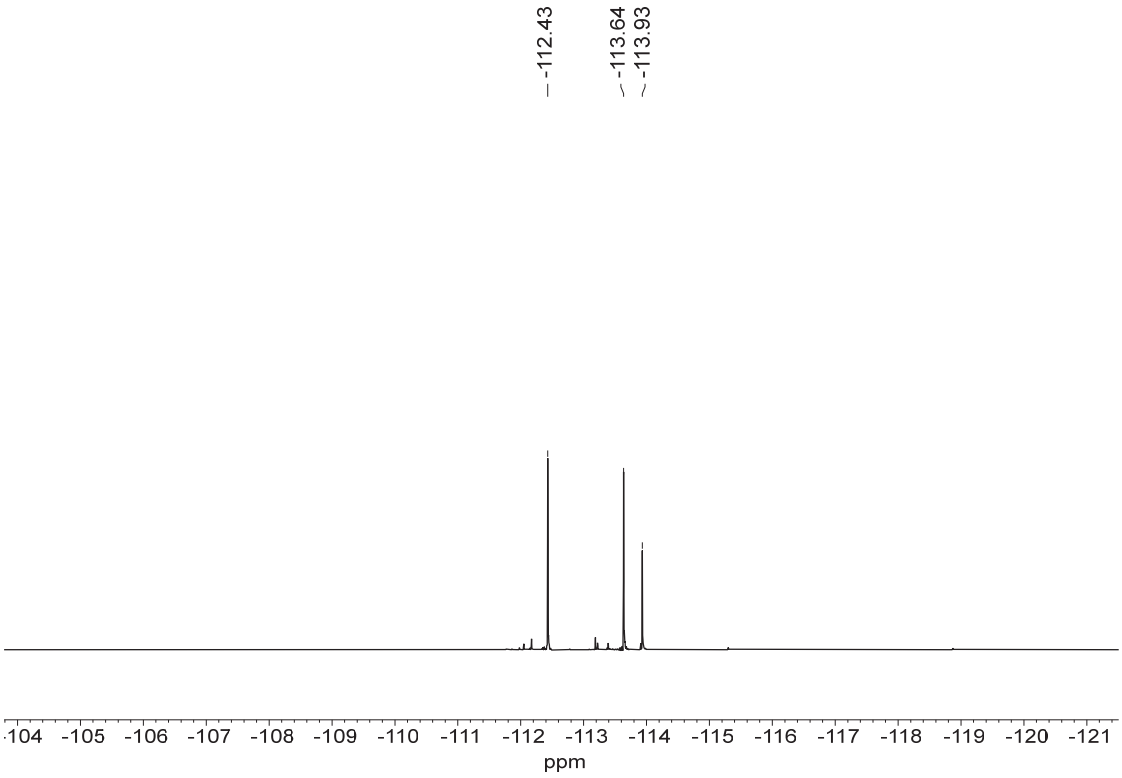
^{11}B NMR of 14h, 160 M, $CDCl_3$



^{13}C NMR of 14h, 126 M, acetone-d_6

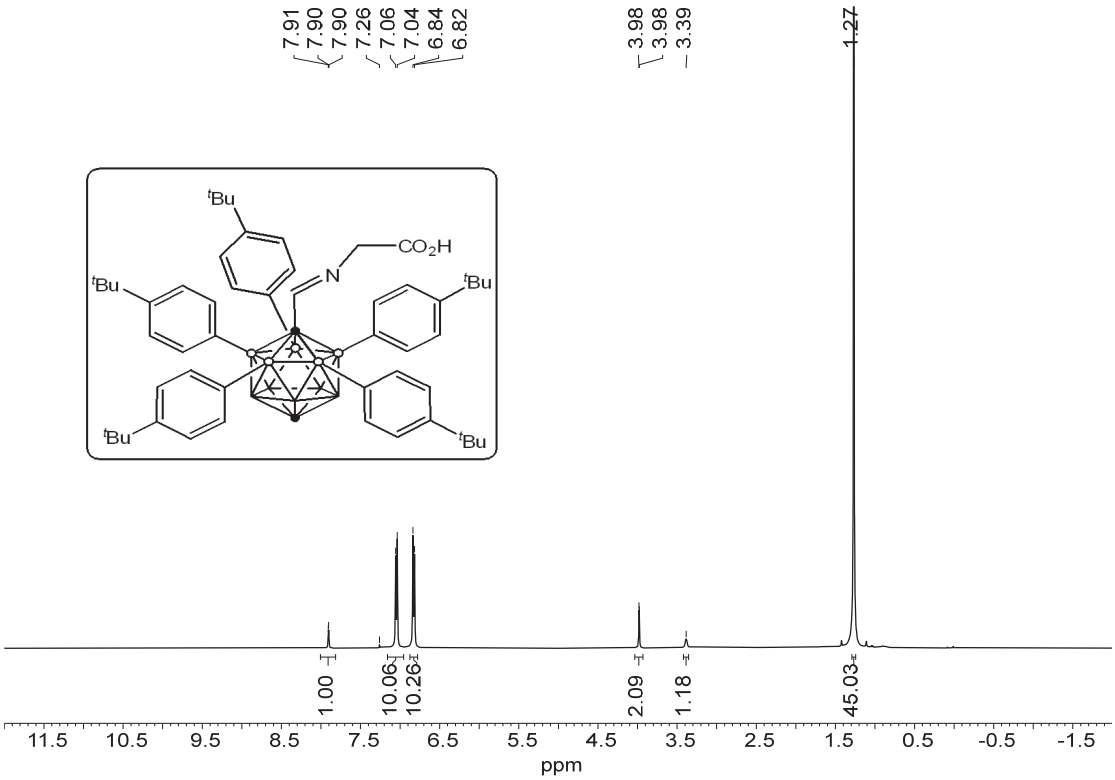


^{19}F NMR of 14h, 471 M, acetone-d$_6$

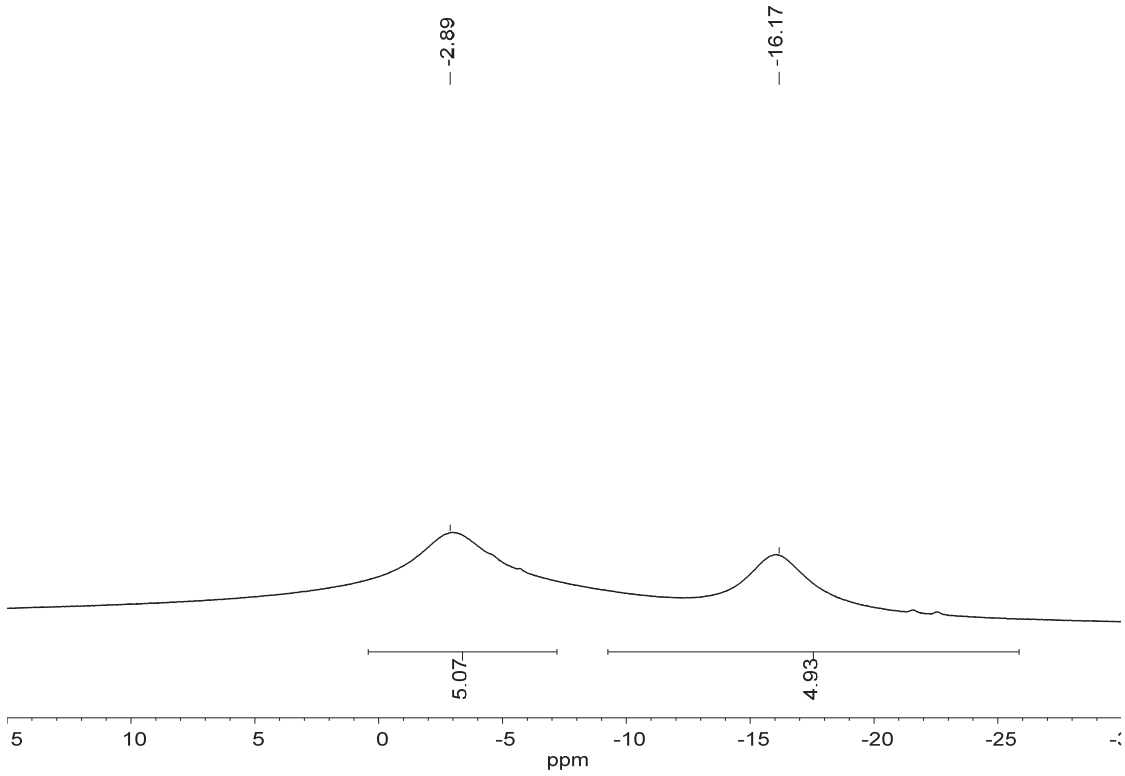


B(2,3,4,5,6)-penta-arylated-*p*-carborane

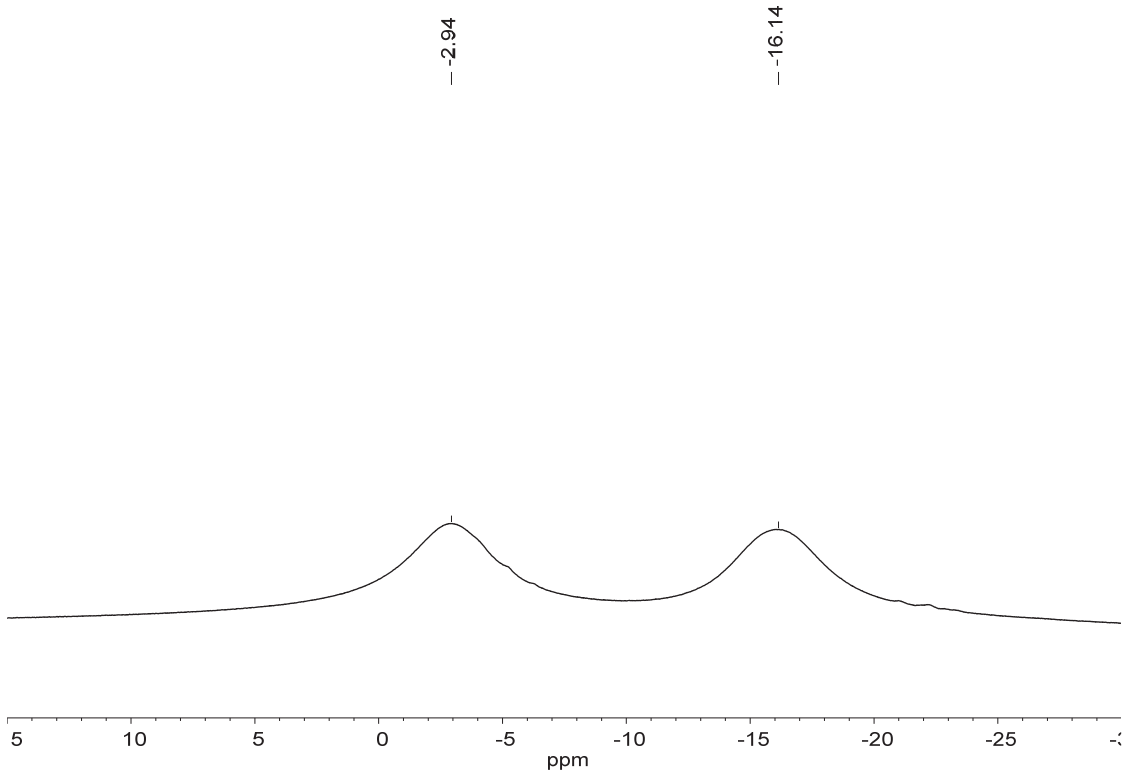
^{1}H NMR of 15a, 400 M, CDCl$_3$



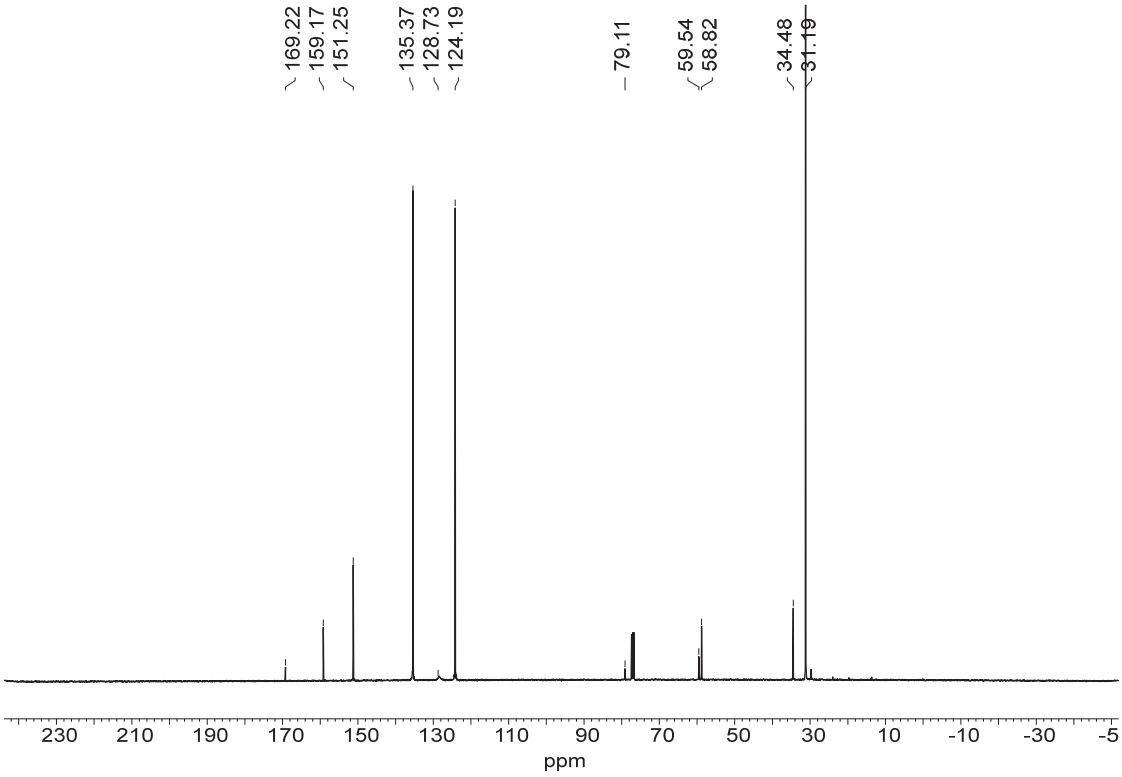
$^{11}B\ \{^{1}H\}$ NMR of 15a, 160 M, $CDCl_3$



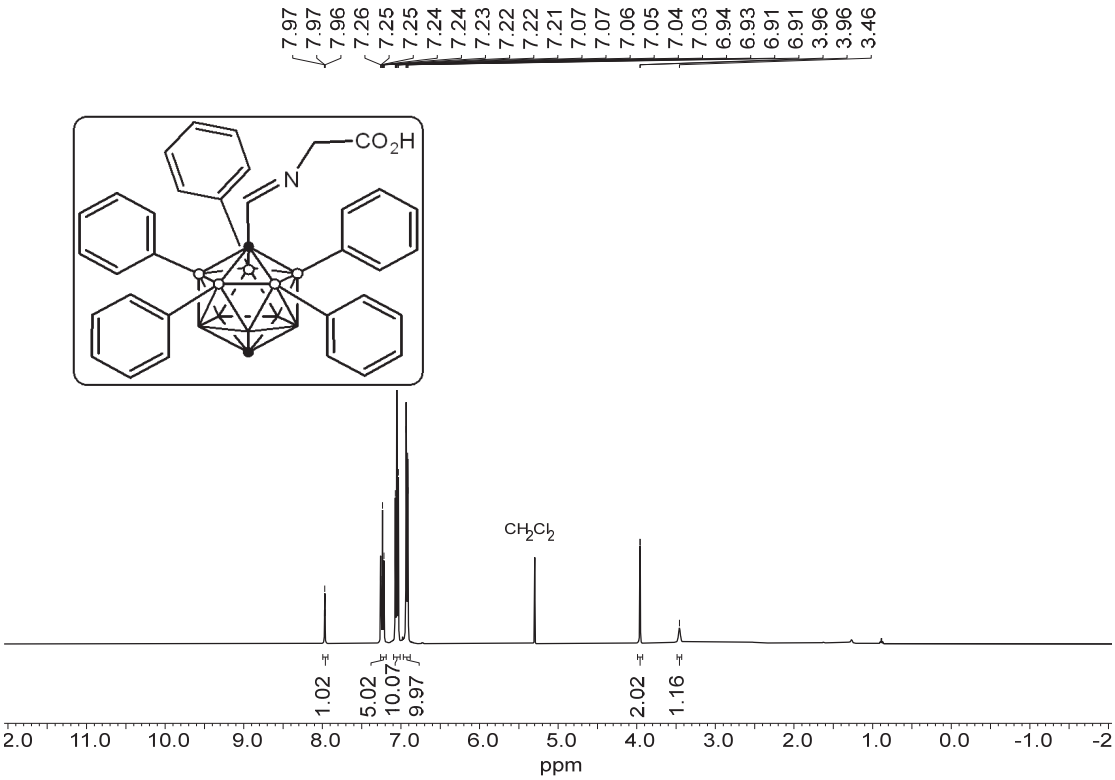
^{11}B NMR of 15a, 160 M, $CDCl_3$



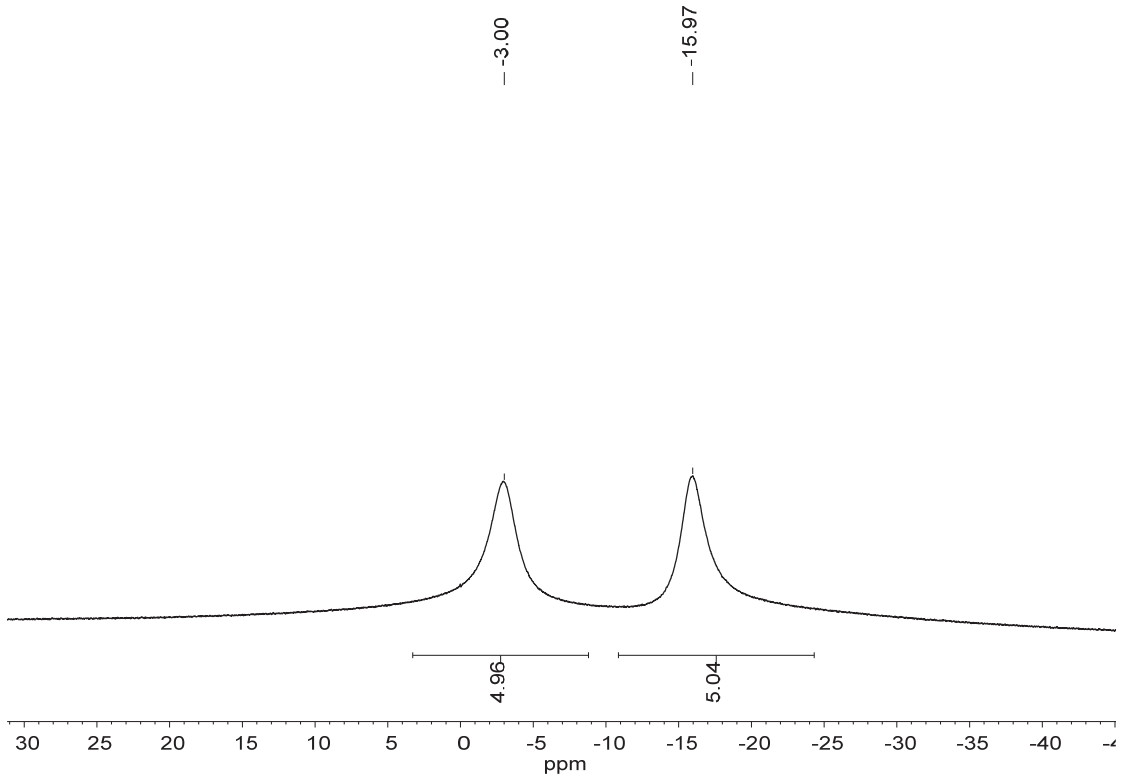
^{13}C NMR of 15a, 101 M, $CDCl_3$



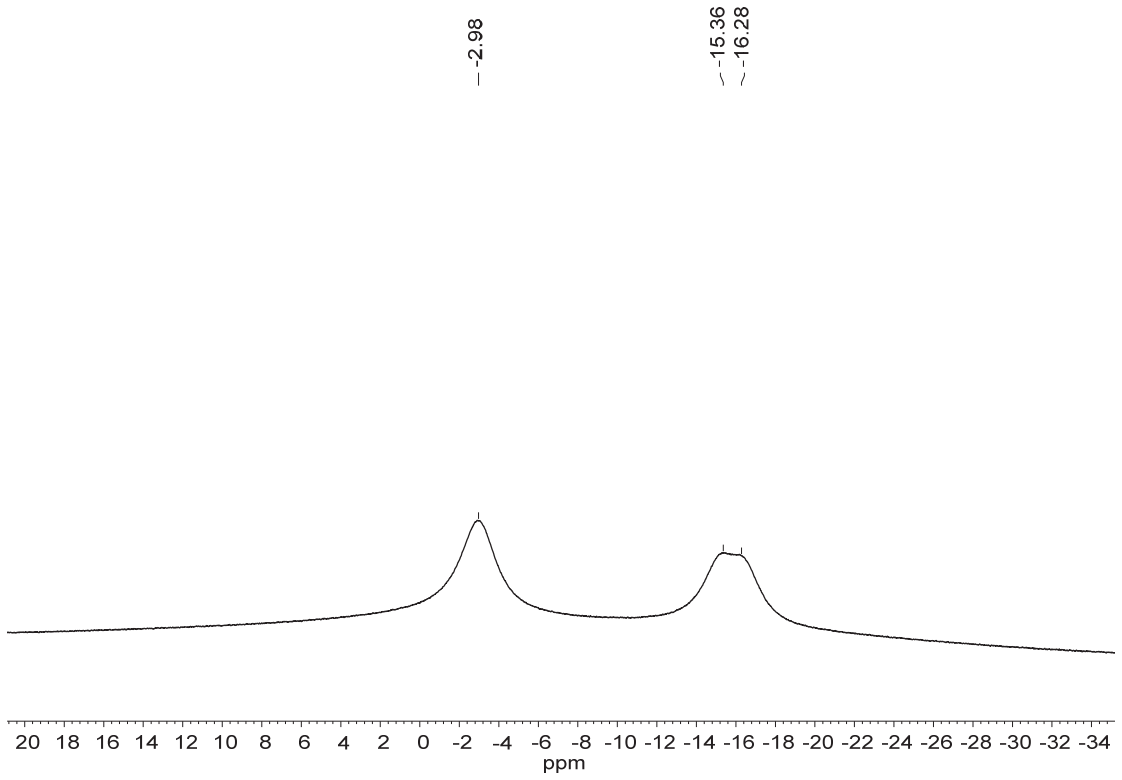
^{1}H NMR of 15b, 400 M, $CDCl_3$



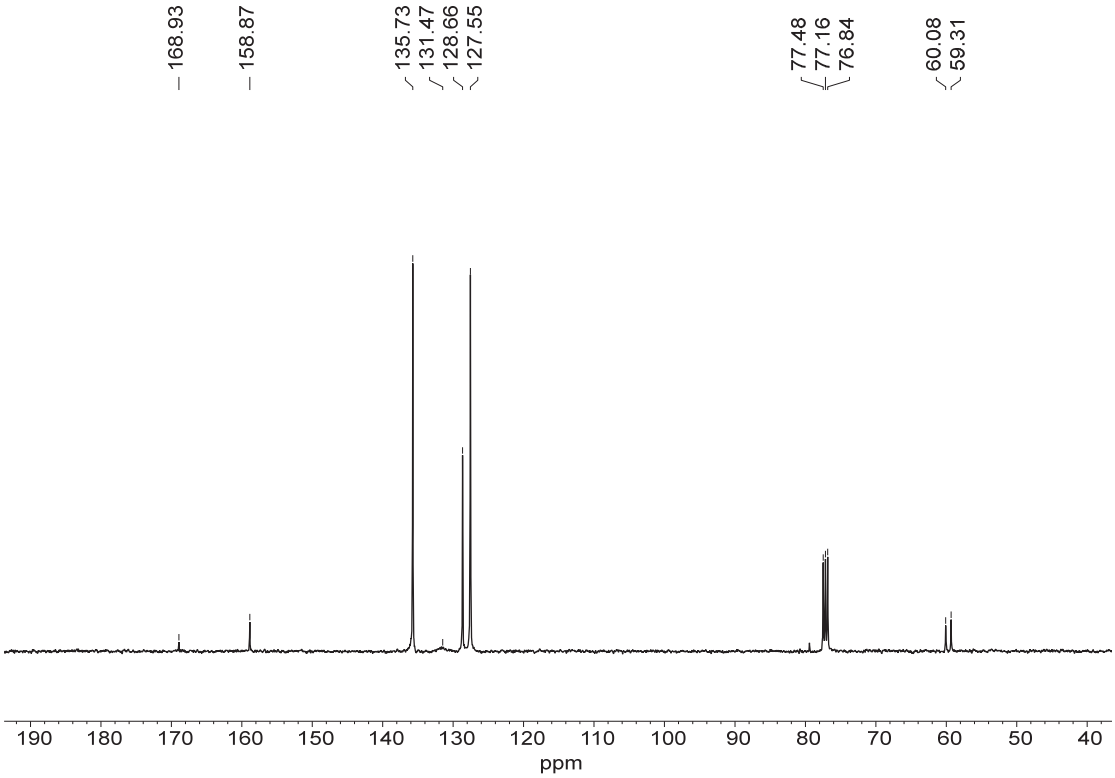
$^{11}B\ \{^{1}H\}$ NMR of 15b, 128 M, $CDCl_3$



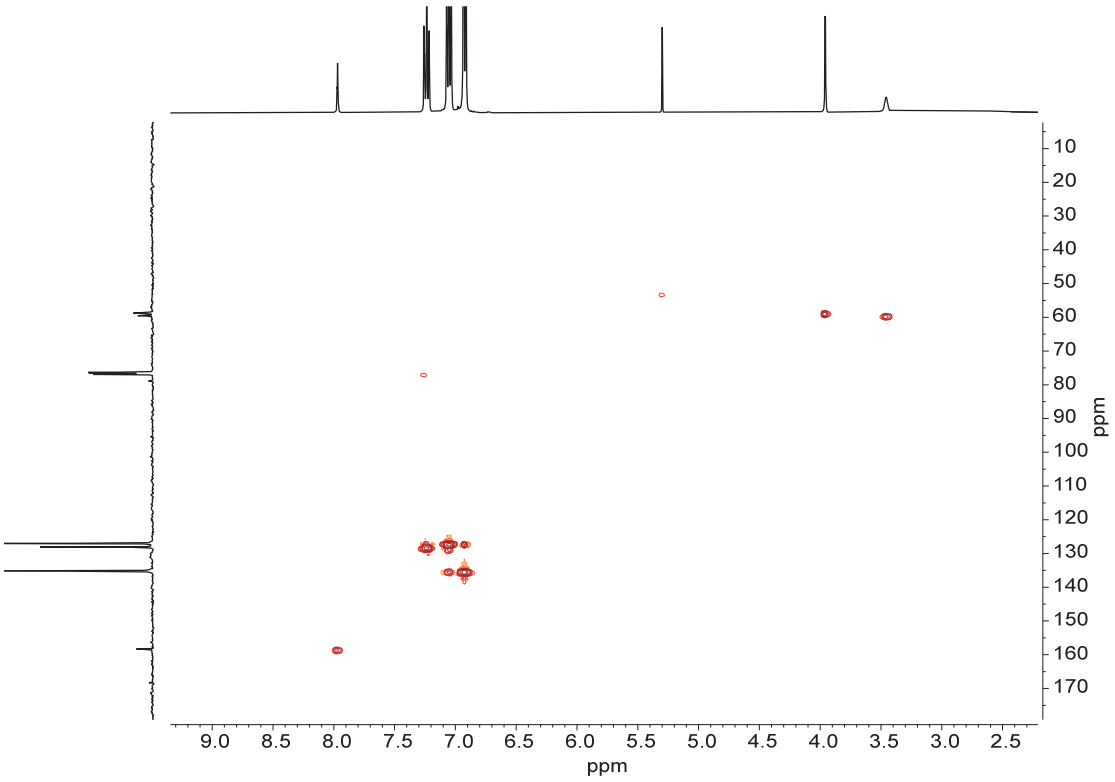
^{11}B NMR of 15b, 128 M, $CDCl_3$



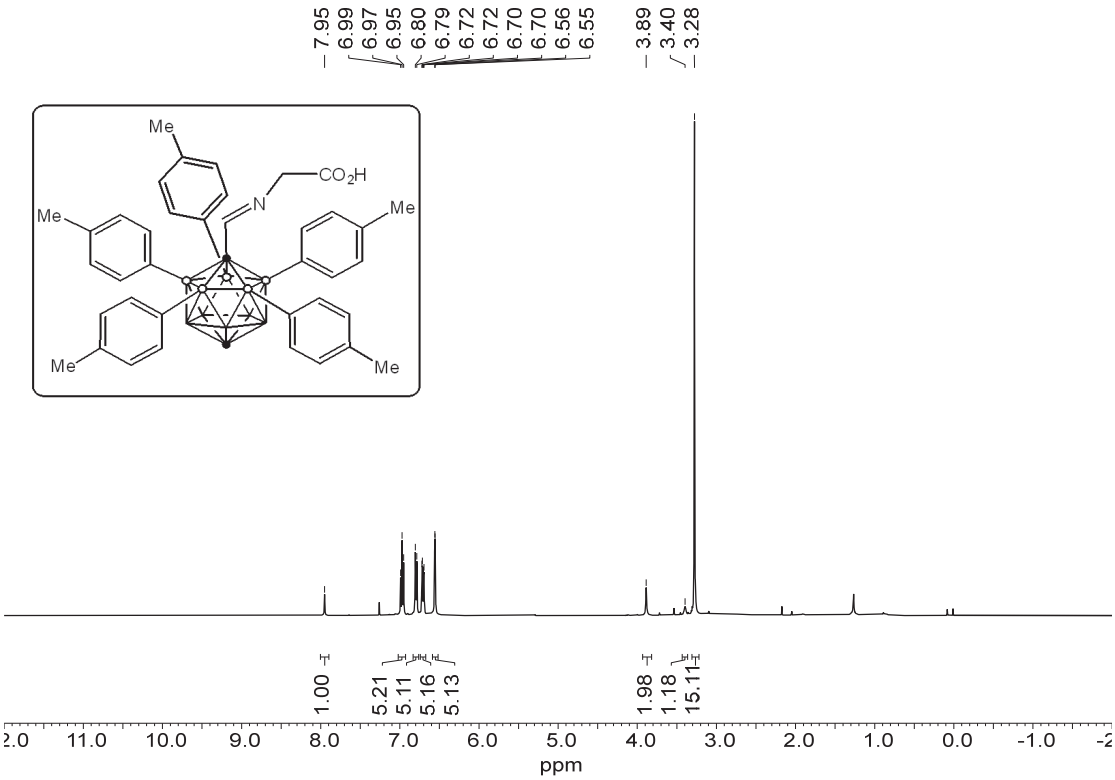
^{13}C NMR of 15b, 101 M, $CDCl_3$



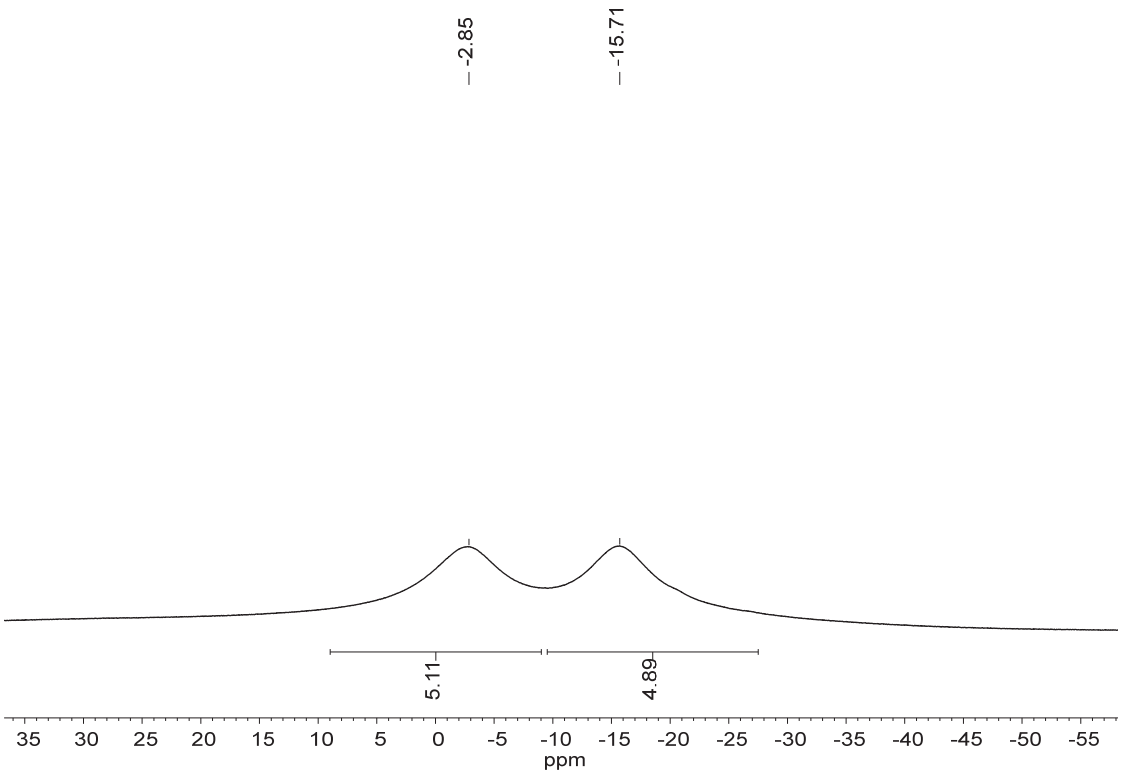
^{13}C-^{1}H HSQC of 15b, 400 M, $CDCl_3$



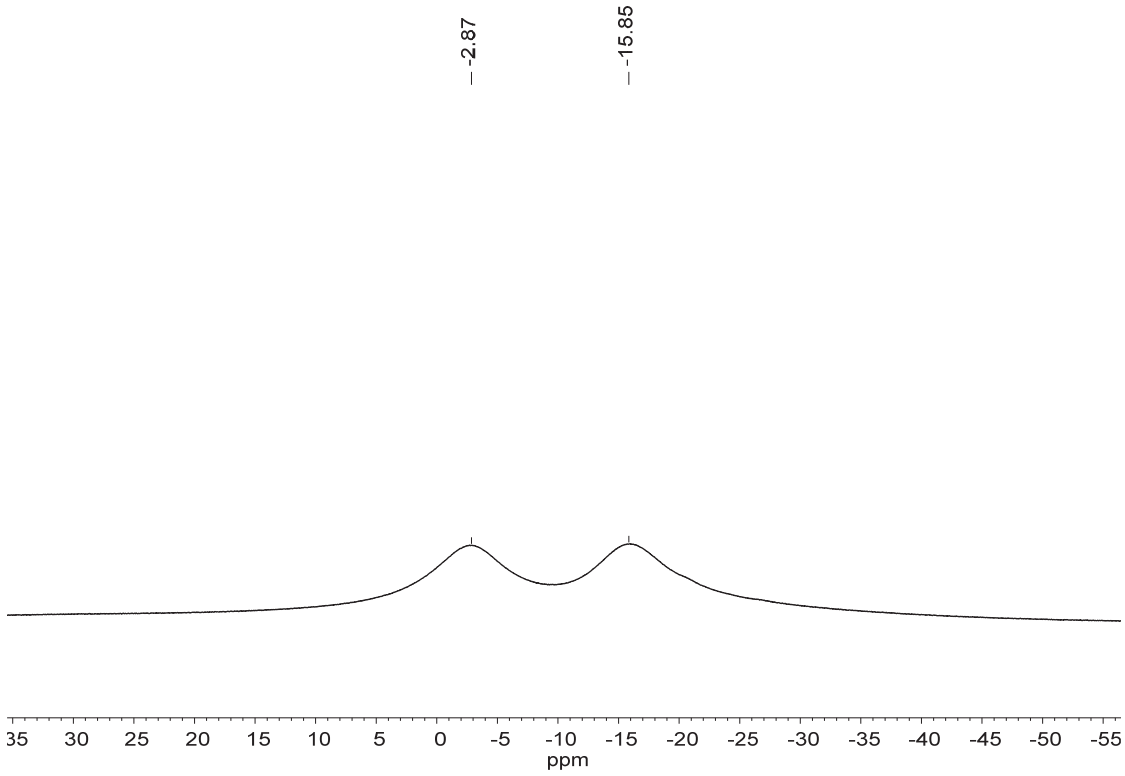
^{1}H NMR of 15c, 400 M, $CDCl_3$



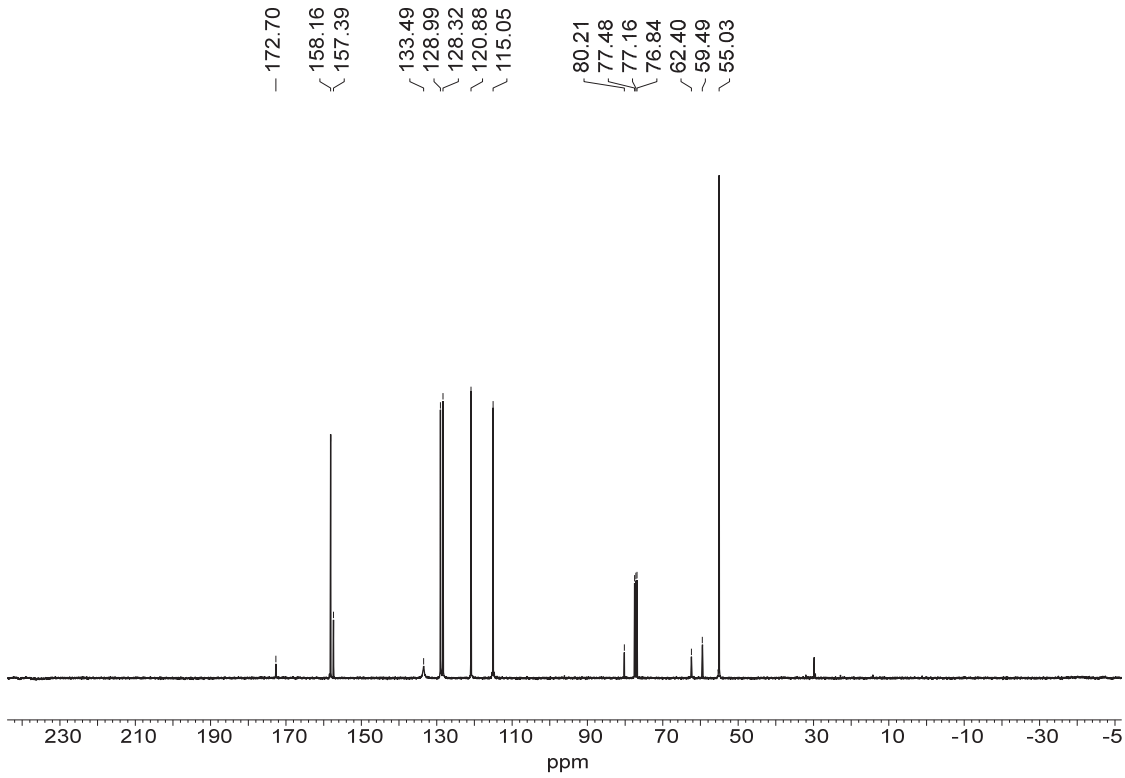
^{11}B {^{1}H} NMR of 15c, 128 M, $CDCl_3$



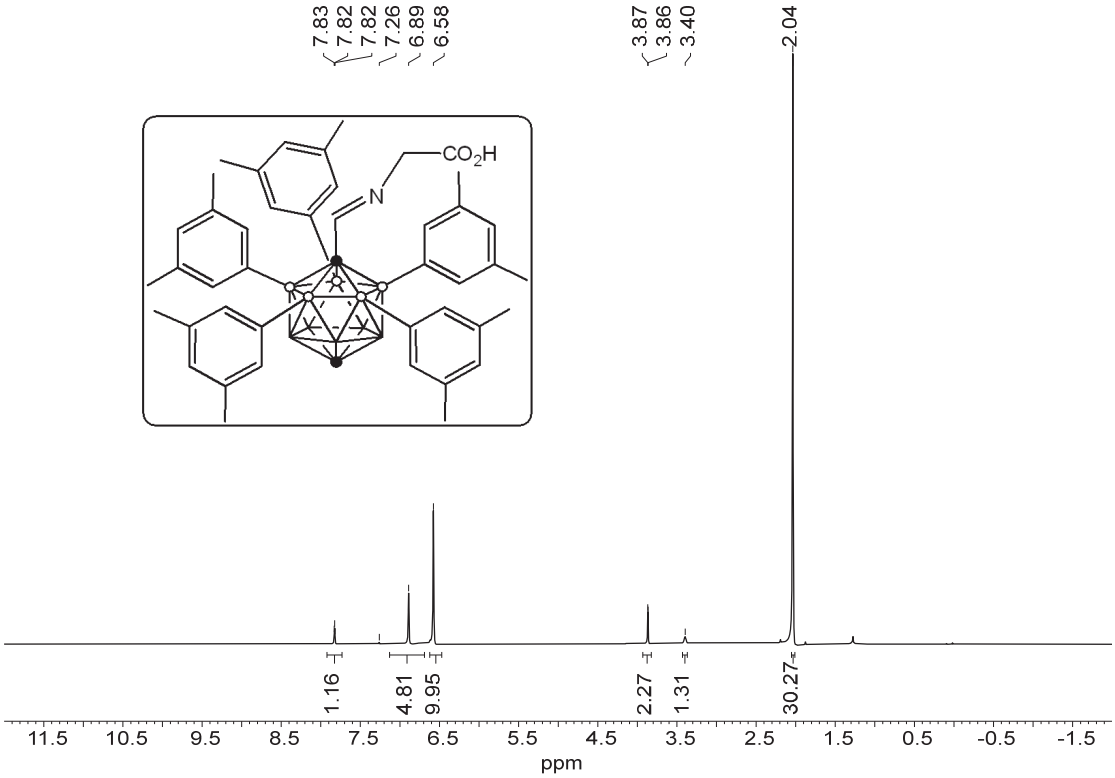
^{11}B NMR of 15c, 128 M, $CDCl_3$



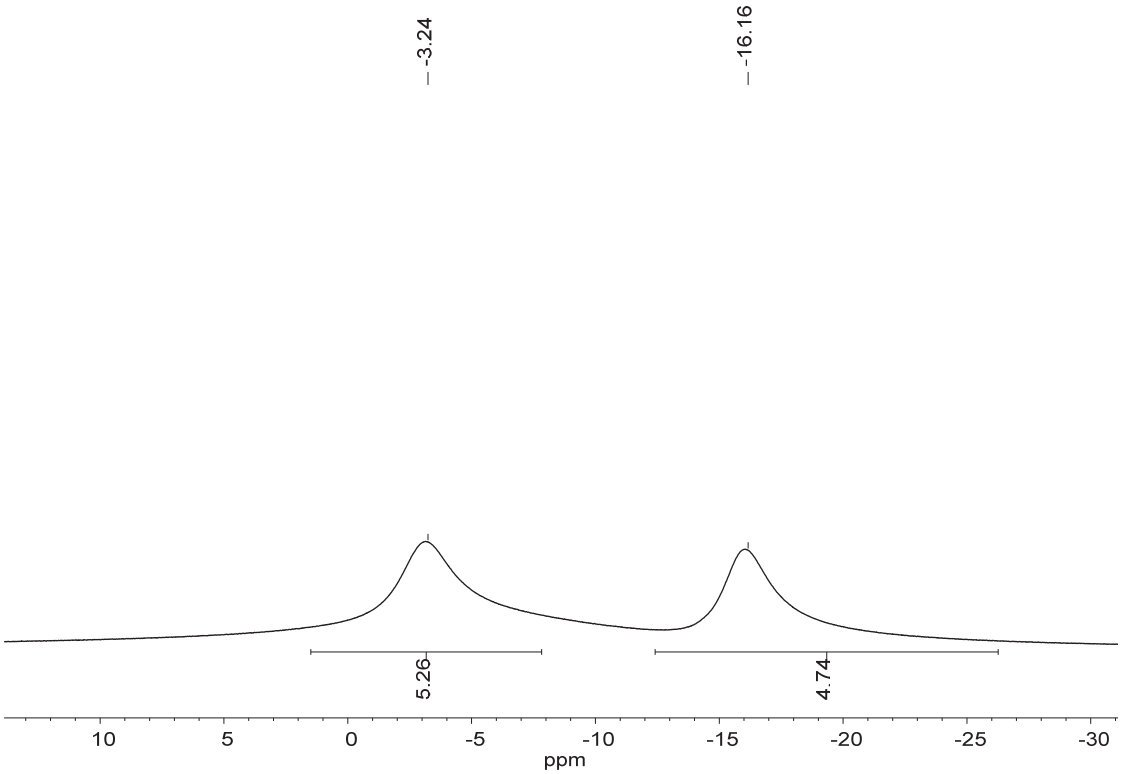
^{13}C {^{1}H} NMR of 15c, 101 M, $CDCl_3$



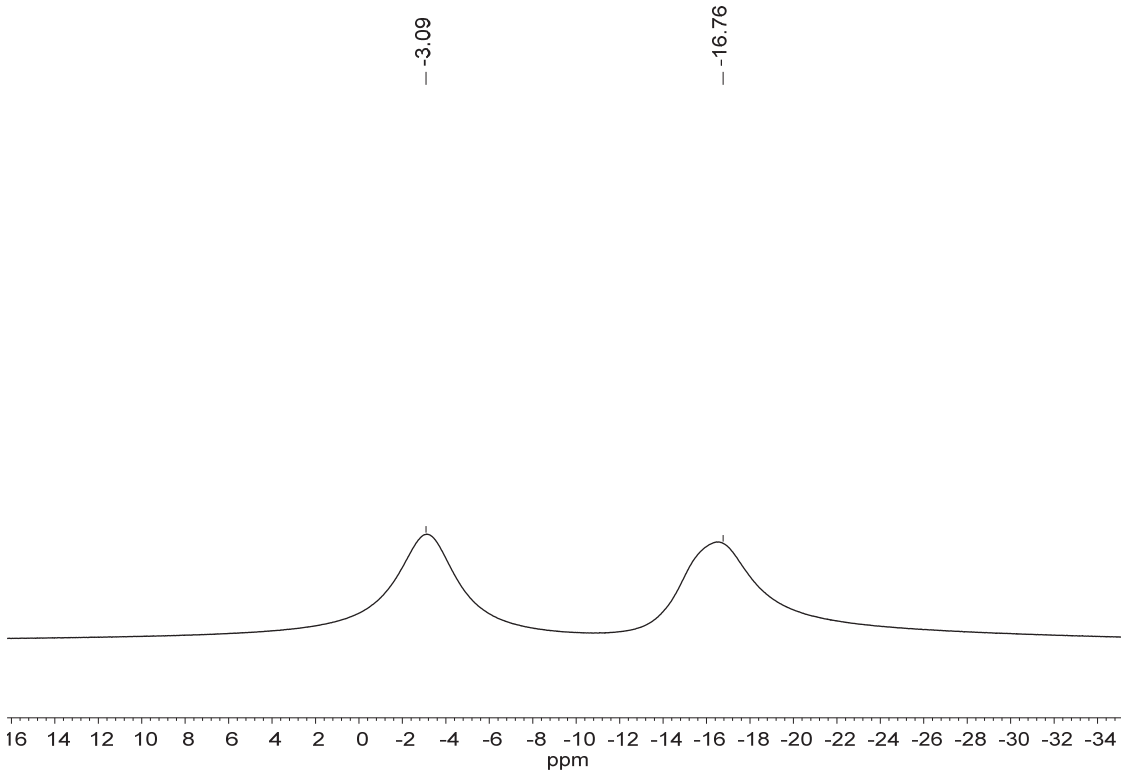
^{1}H NMR of 15d, 400 M, $CDCl_3$



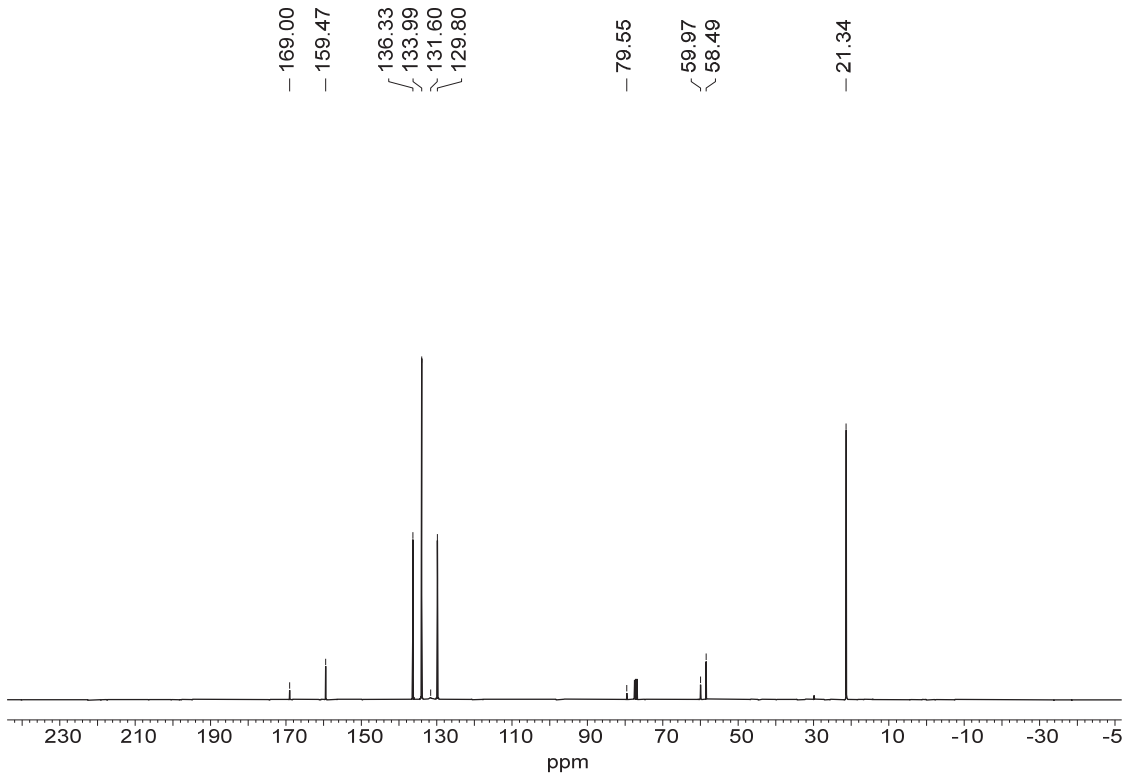
^{11}B NMR of 15d, 128 M, $CDCl_3$



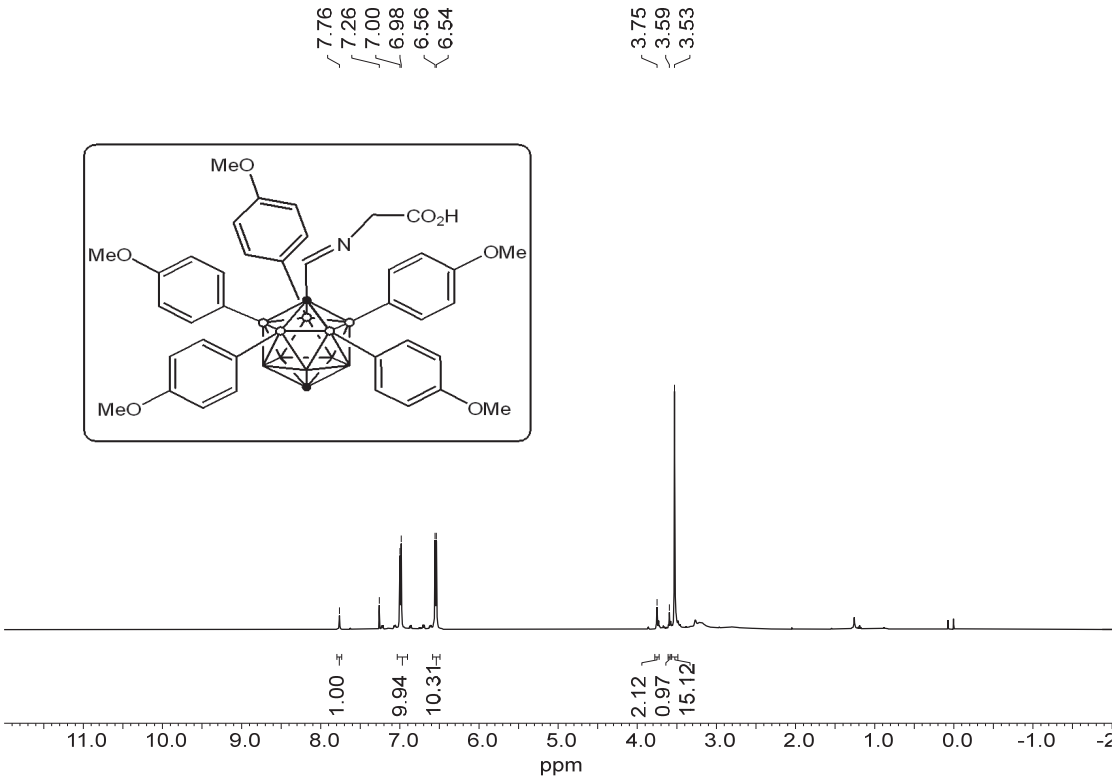
^{11}B NMR of 15d, 128 M, $CDCl_3$



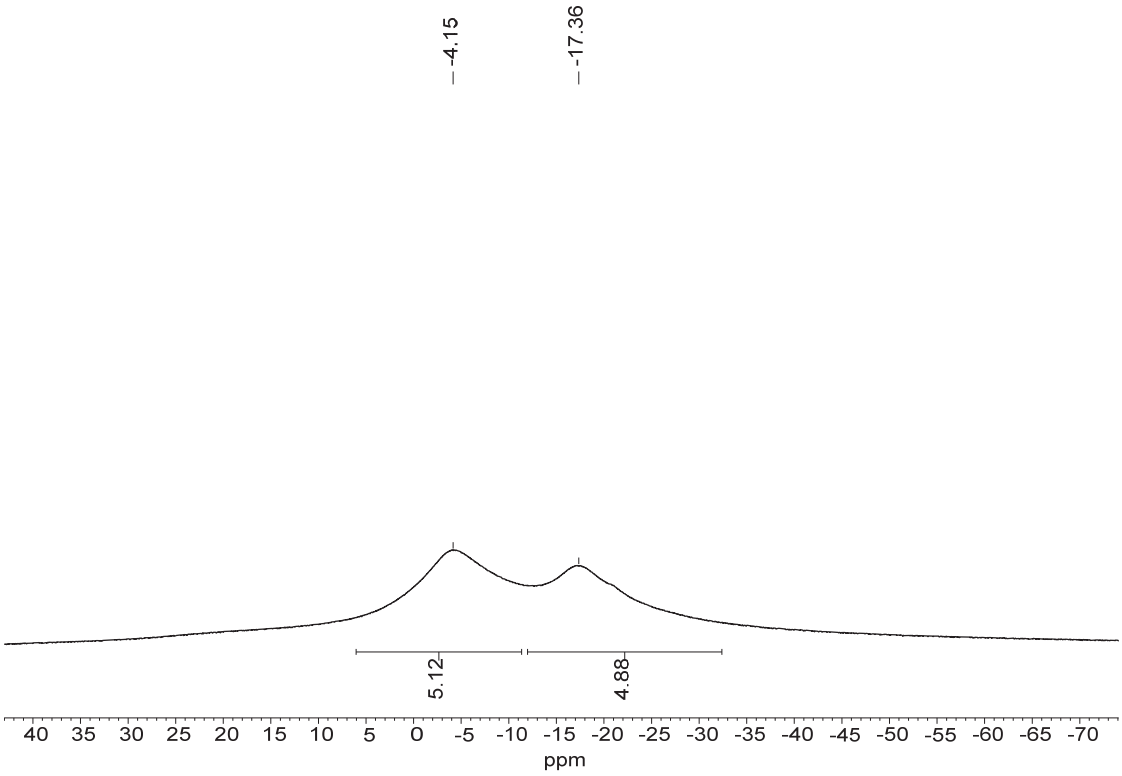
^{13}C NMR of 15d, 101 M, $CDCl_3$



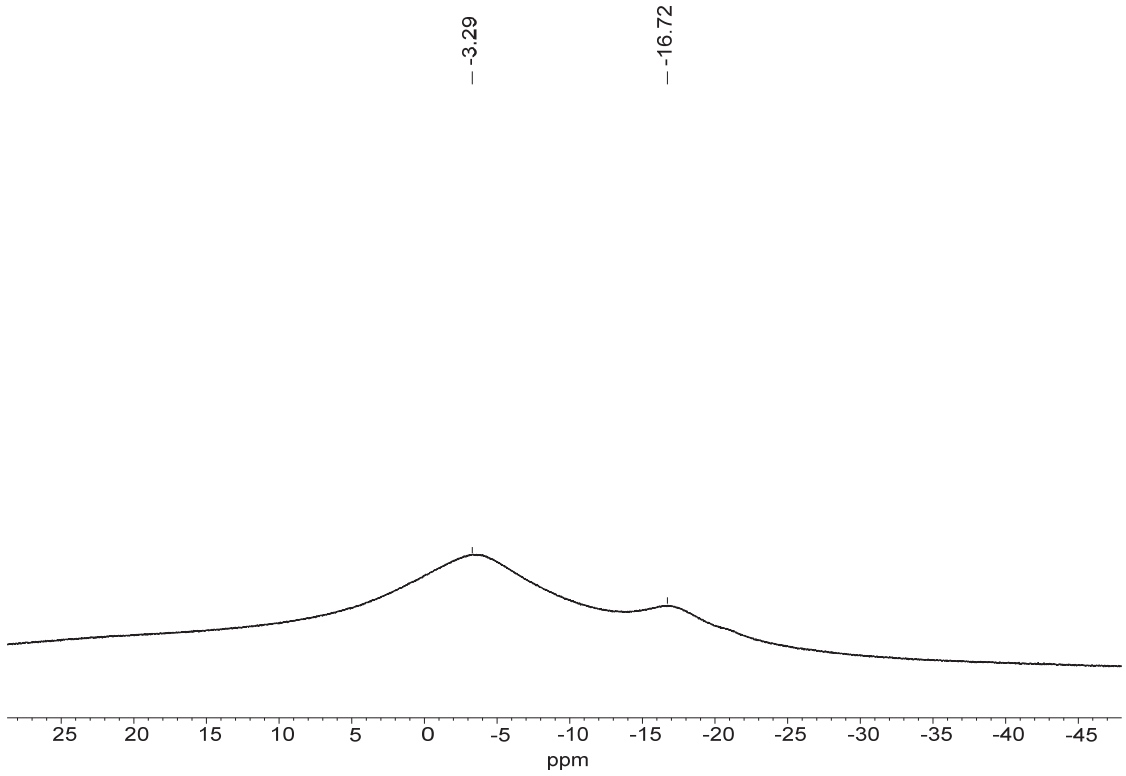
^{1}H NMR of 15e, 500 M, $CDCl_3$



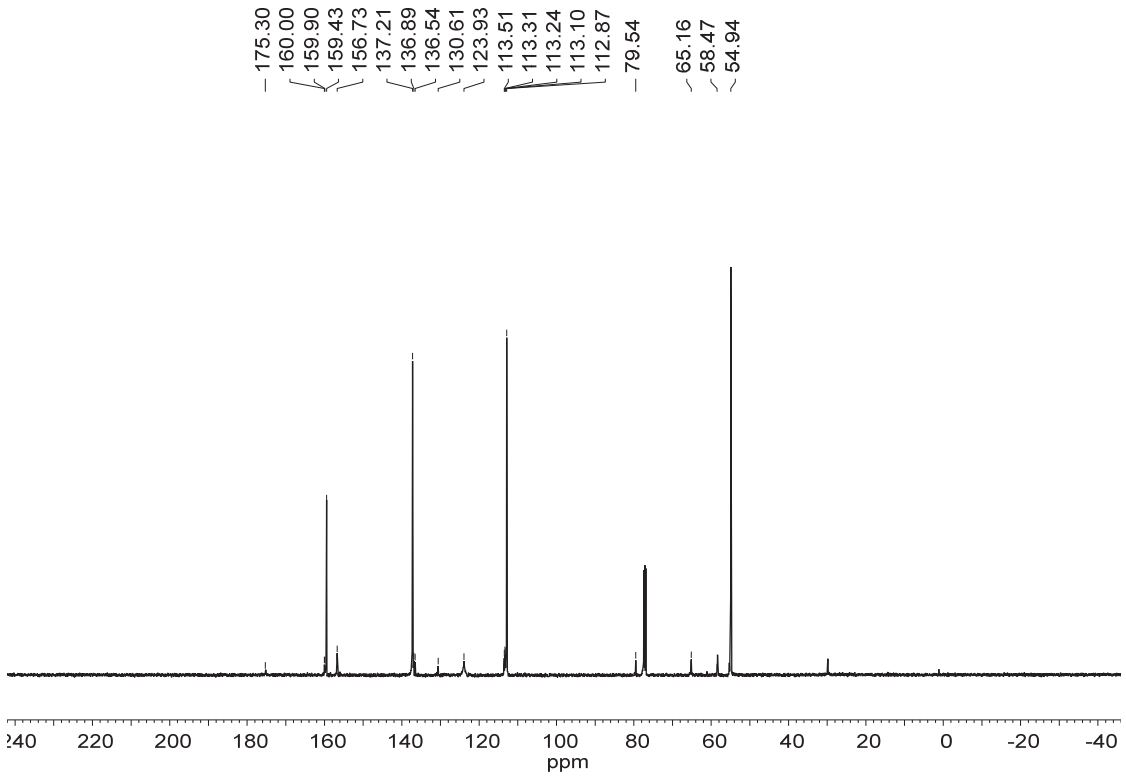
^{11}B {^{1}H} NMR of 15e, 160 M, $CDCl_3$



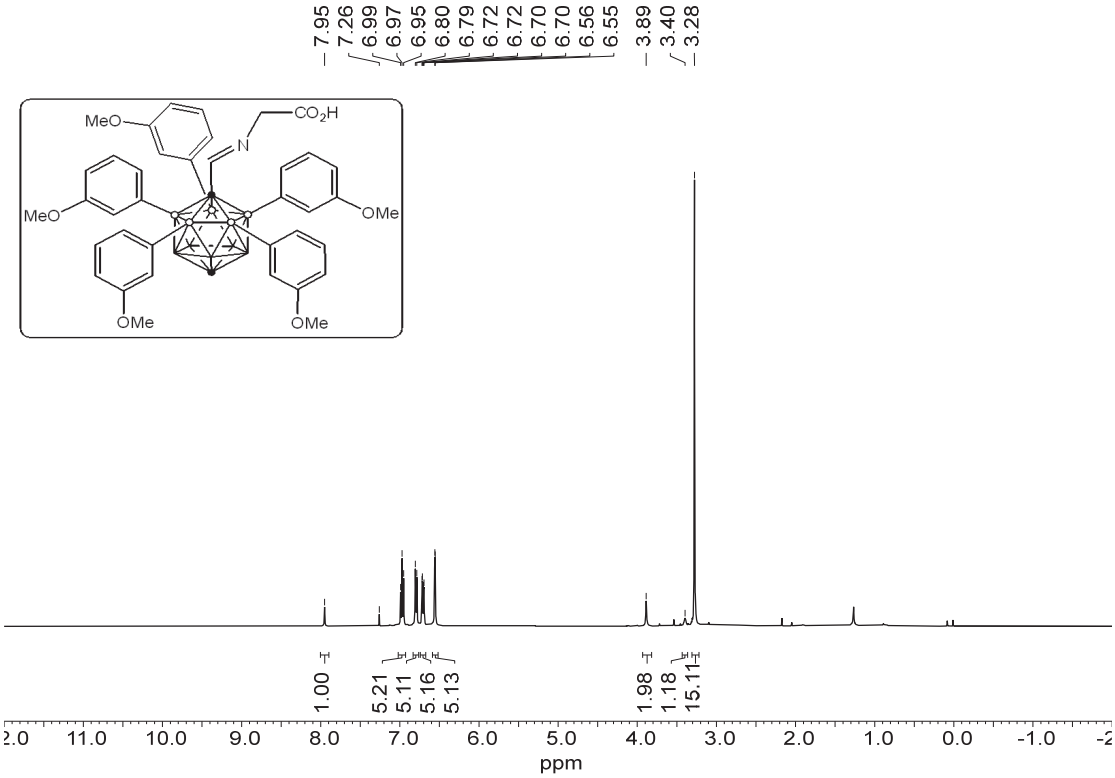
^{11}B NMR of 15e, 160 M, $CDCl_3$



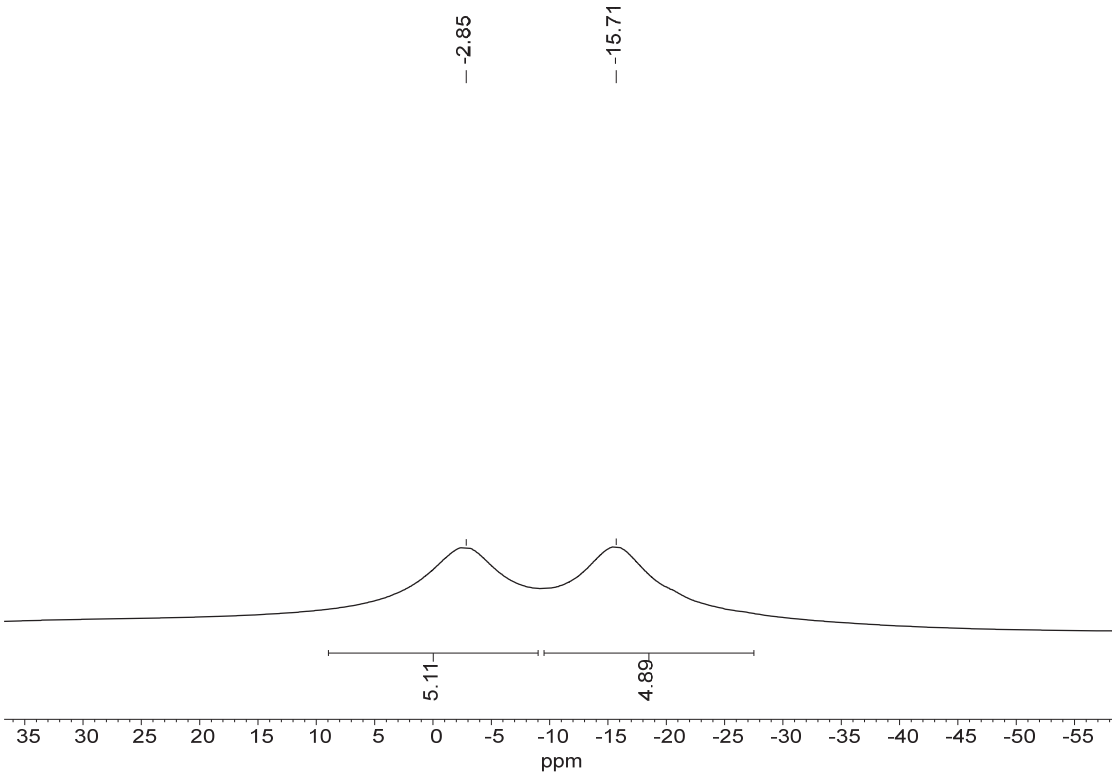
^{13}C NMR of 15e, 126 M, $CDCl_3$



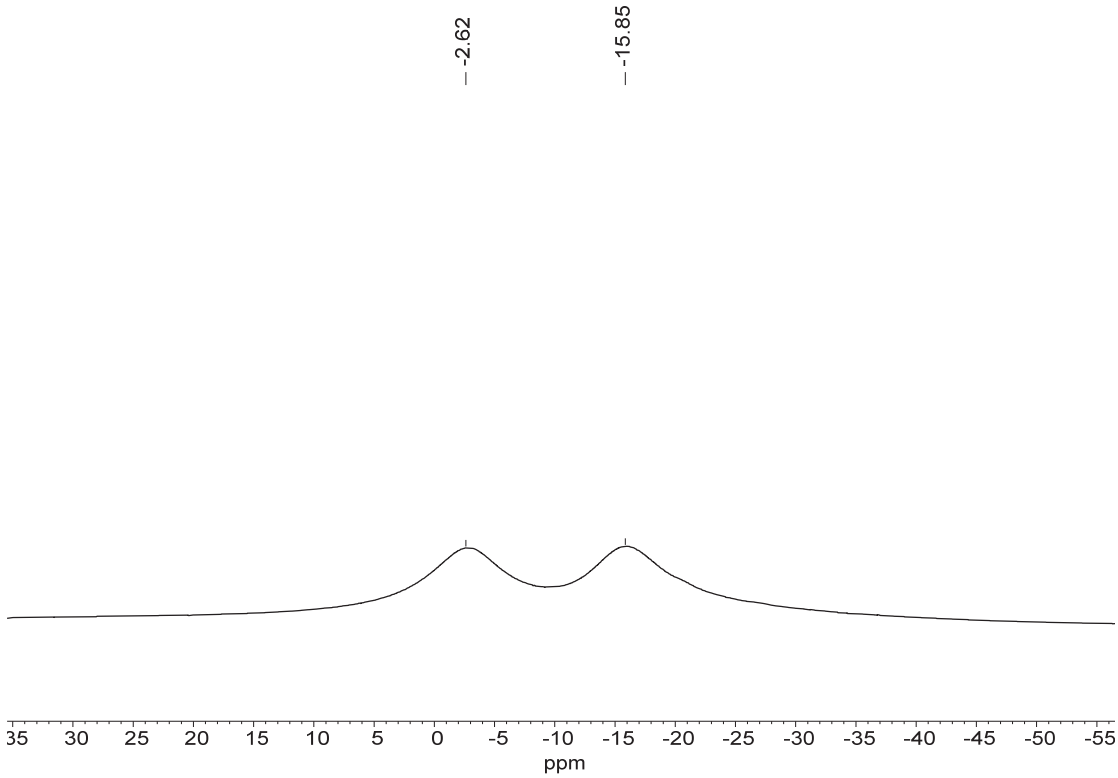
^{1}H NMR of 15f, 400 M, $CDCl_3$



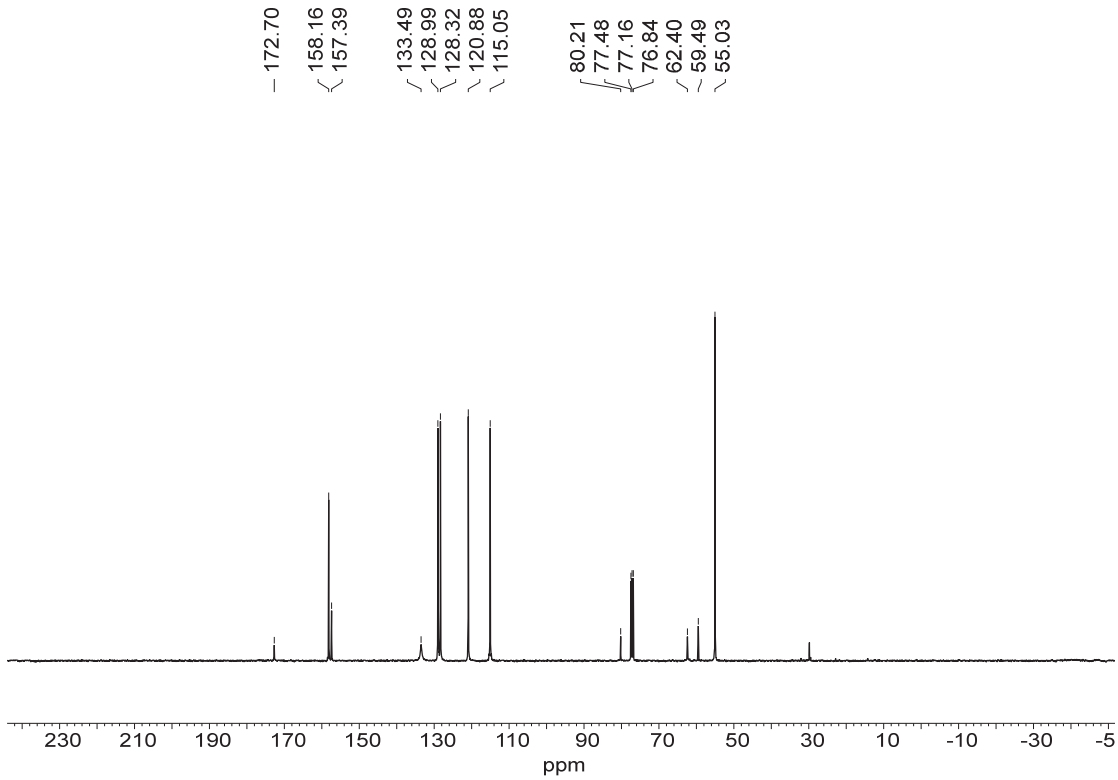
^{11}B {H} NMR of 15f, 128 M, $CDCl_3$



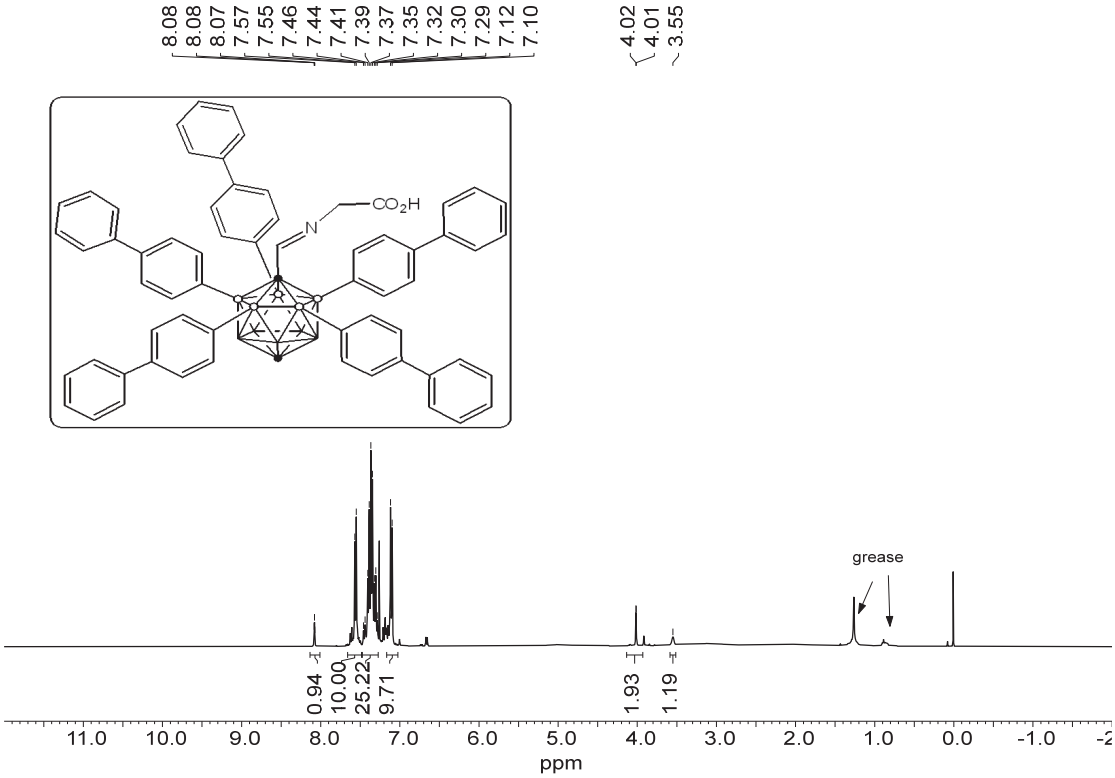
^{11}B NMR of 15f, 128 M, $CDCl_3$



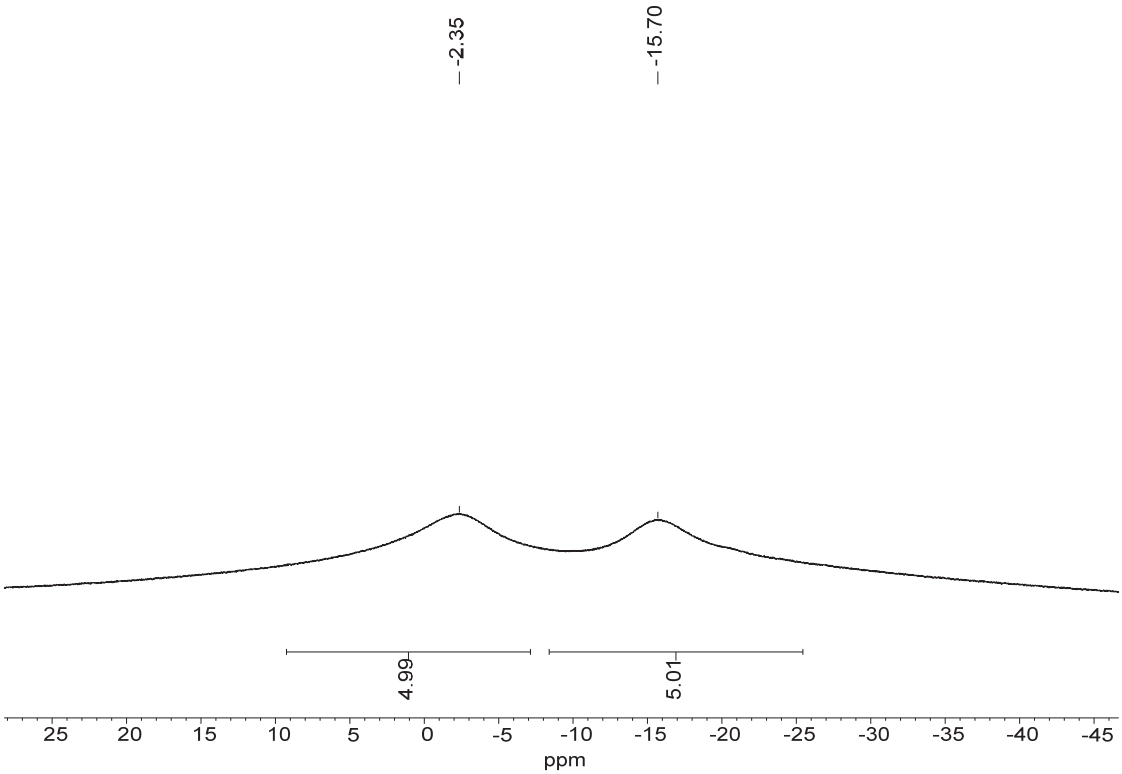
^{13}C NMR of 15f, 101 M, $CDCl_3$



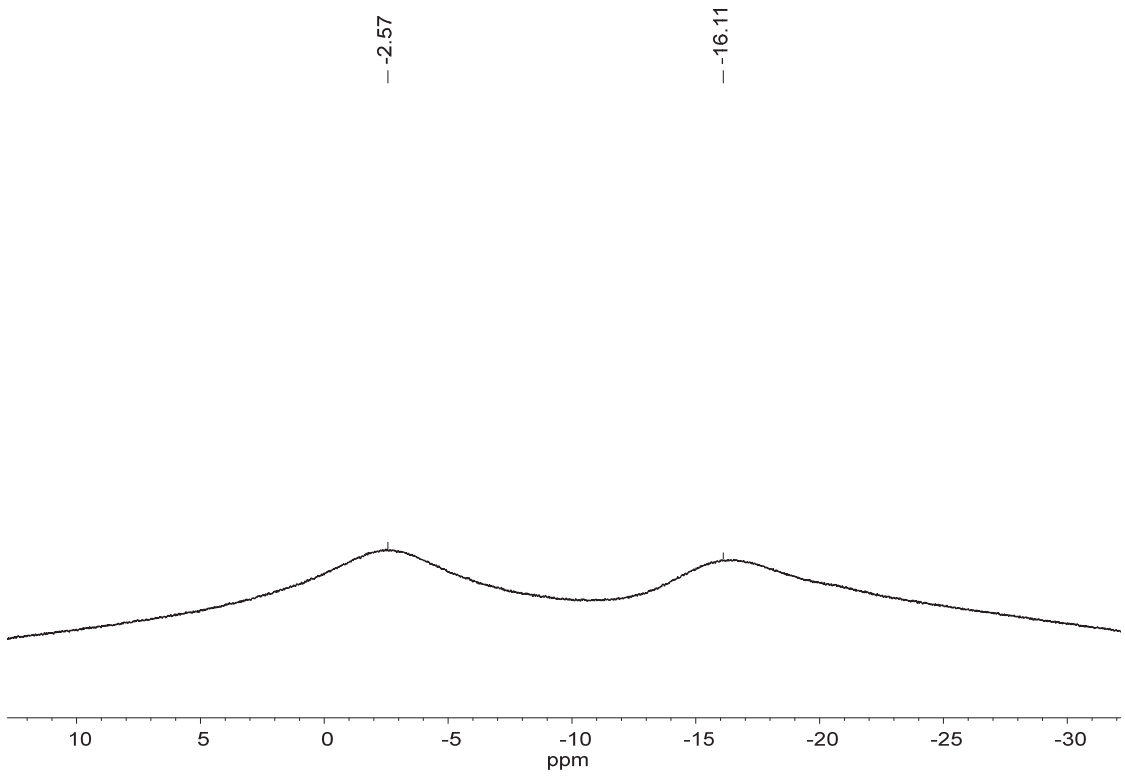
^{1}H NMR of 15g, 400 M, $CDCl_3$



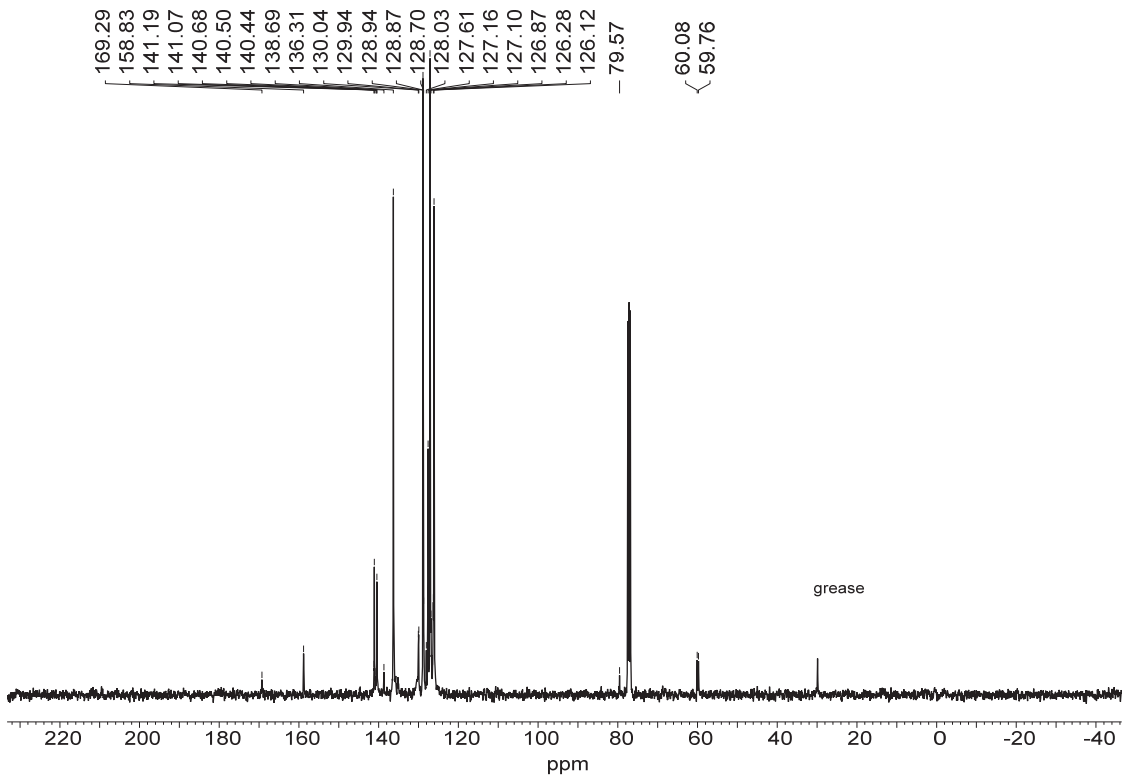
^{11}B {H} NMR of 15g, 128 M, $CDCl_3$



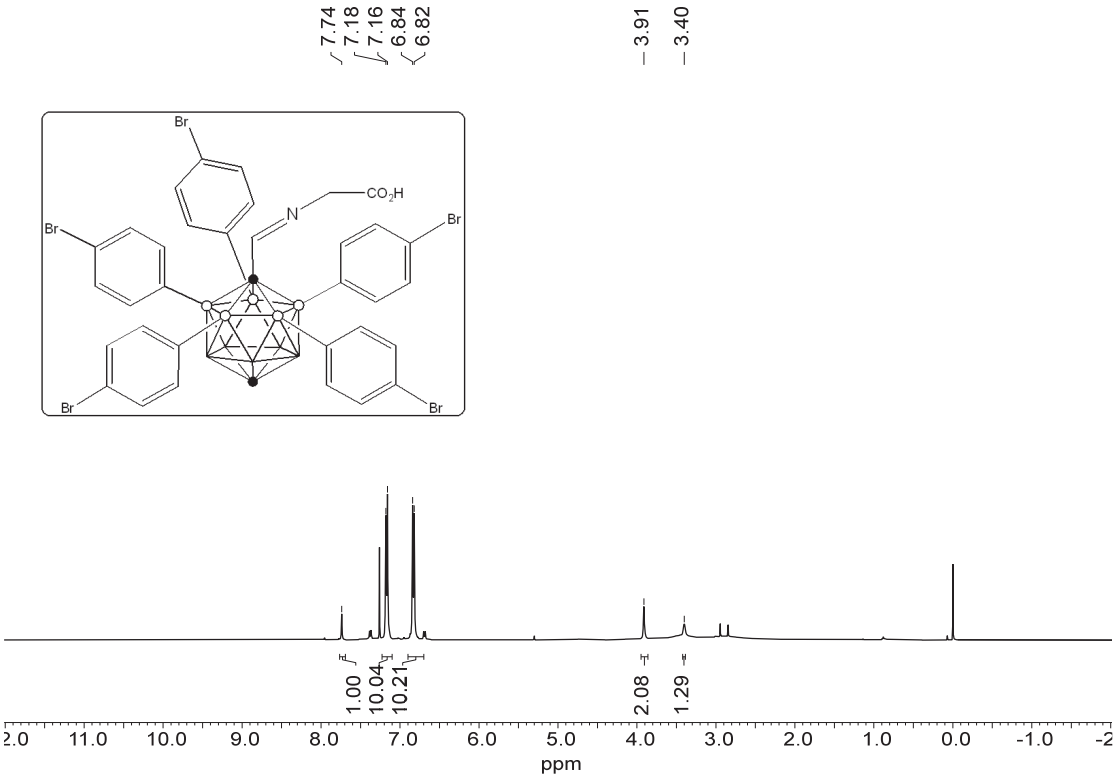
^{11}B NMR of 15g, 128 M, $CDCl_3$



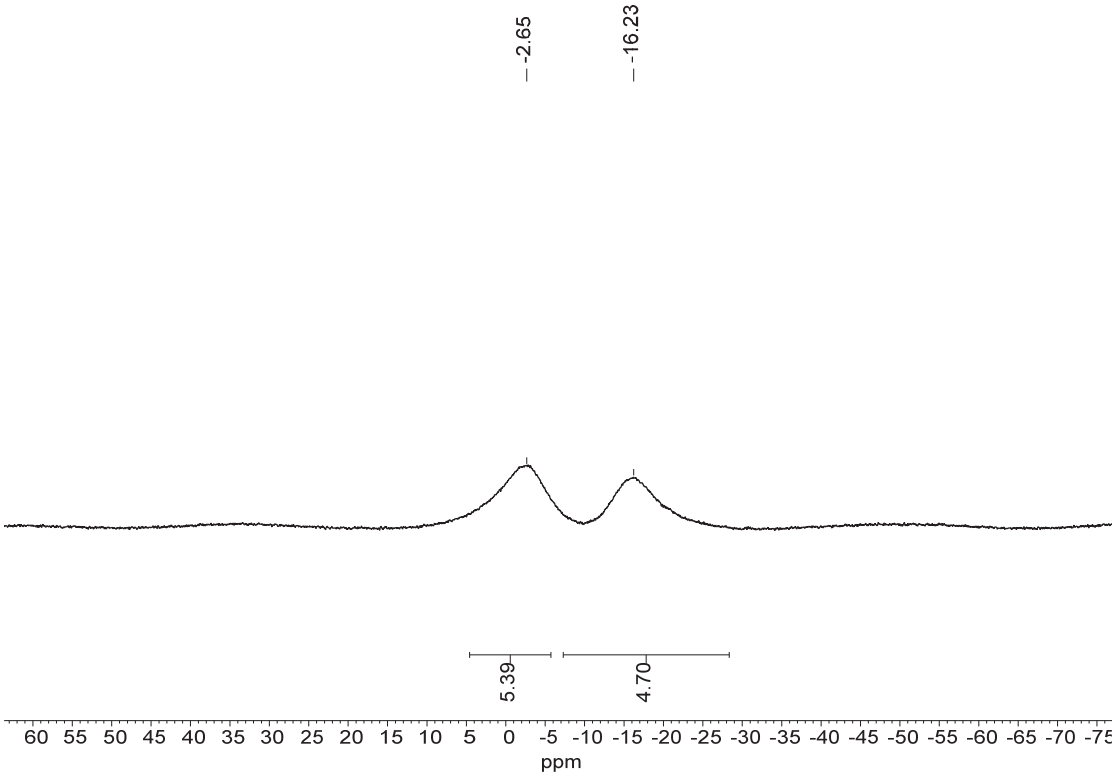
^{13}C NMR of 15g, 101 M, $CDCl_3$



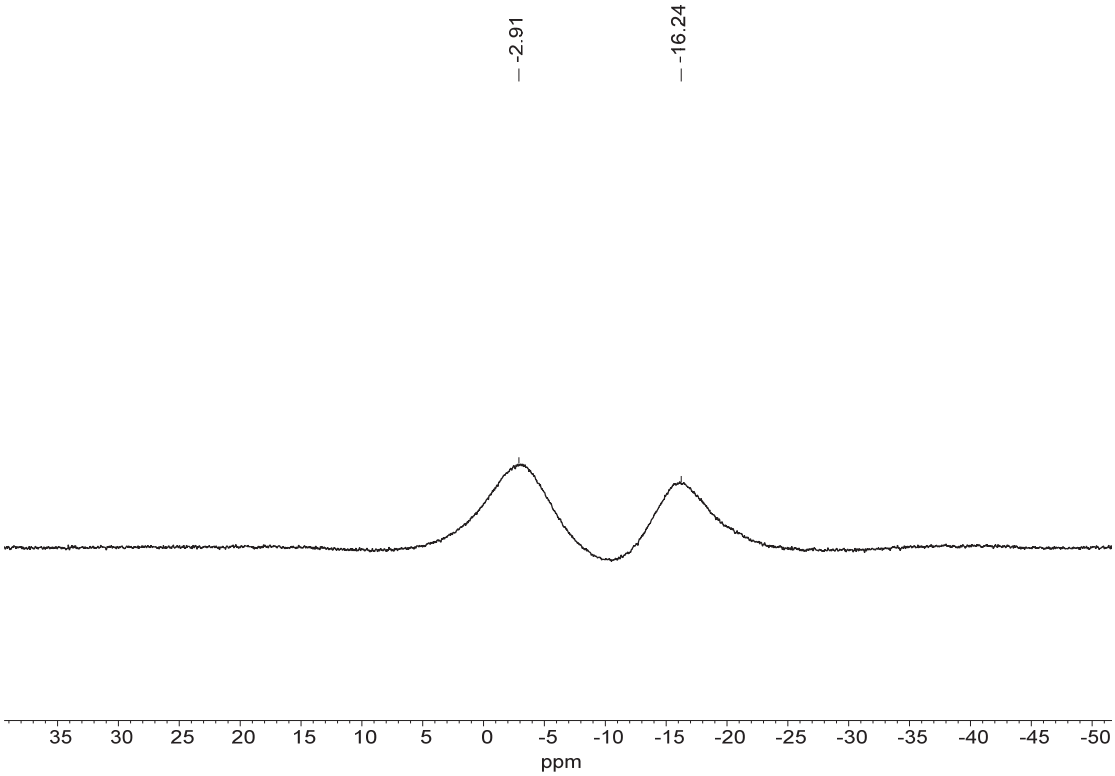
^{1}H NMR of 15h, 400 M, $CDCl_3$



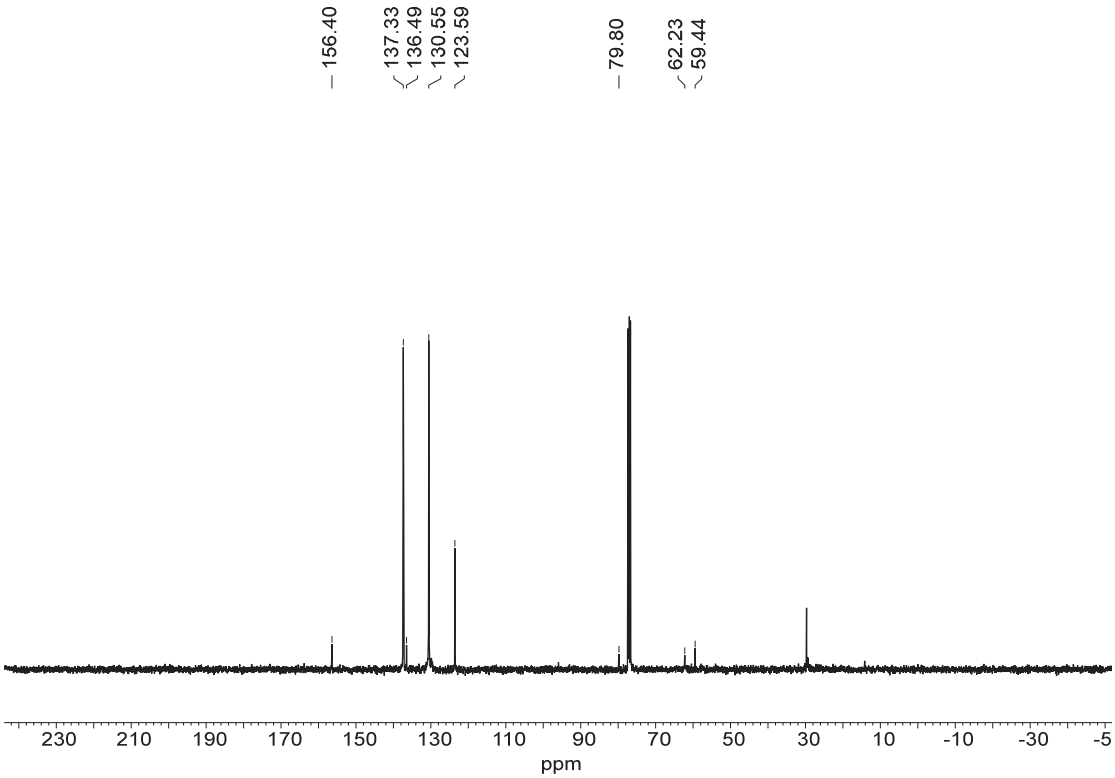
^{11}B {^{1}H} NMR of 15h, 128 M, $CDCl_3$



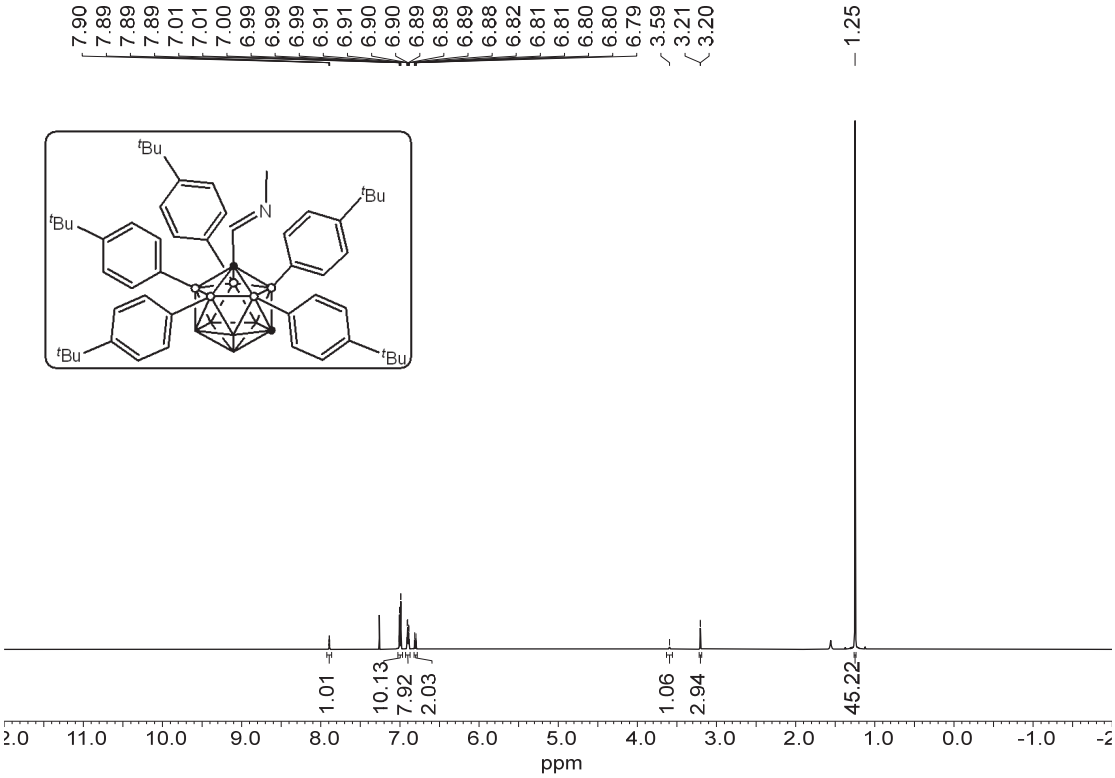
^{11}B NMR of 15h, 128 M, $CDCl_3$



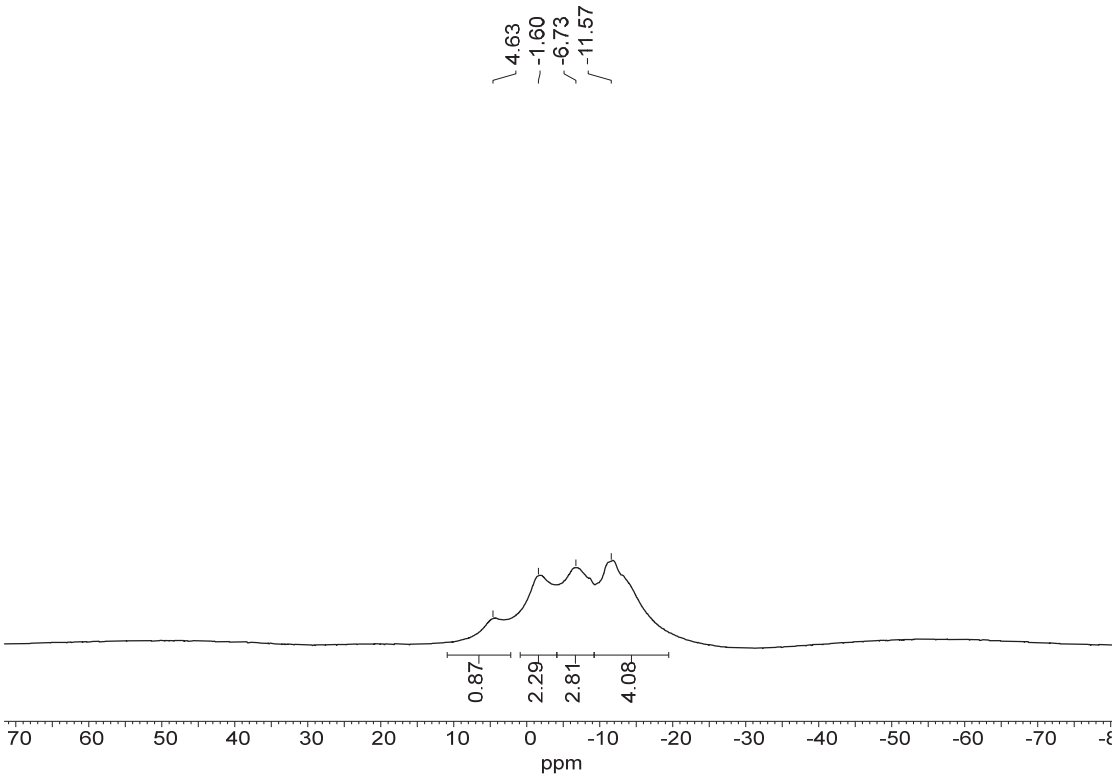
^{13}C NMR of 15h, 101 M, $CDCl_3$



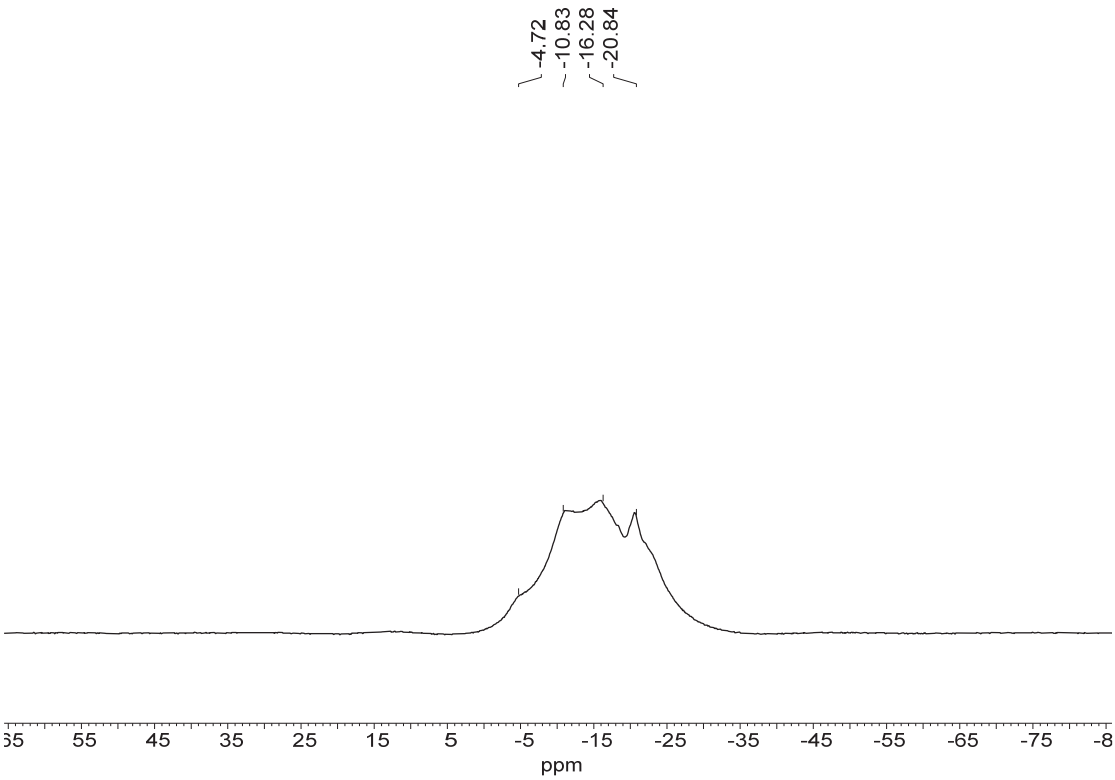
^{1}H NMR of 16, 500 M, $CDCl_3$



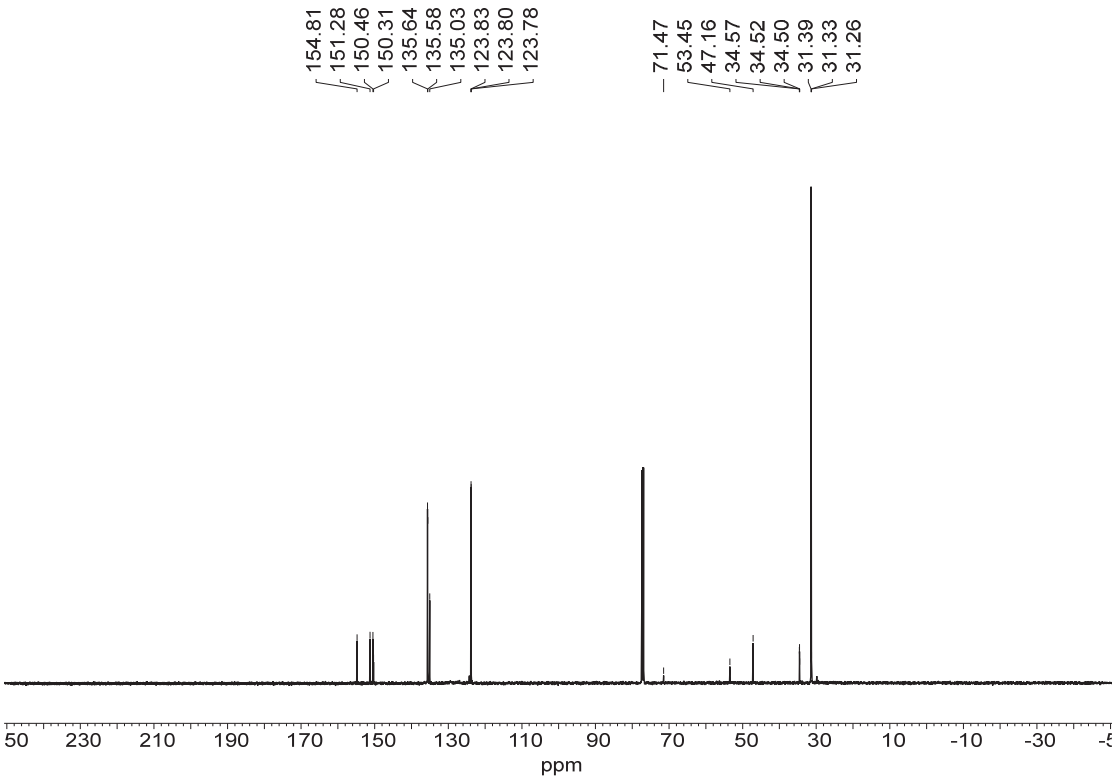
^{11}B {^{1}H} NMR of 16, 160 M, $CDCl_3$



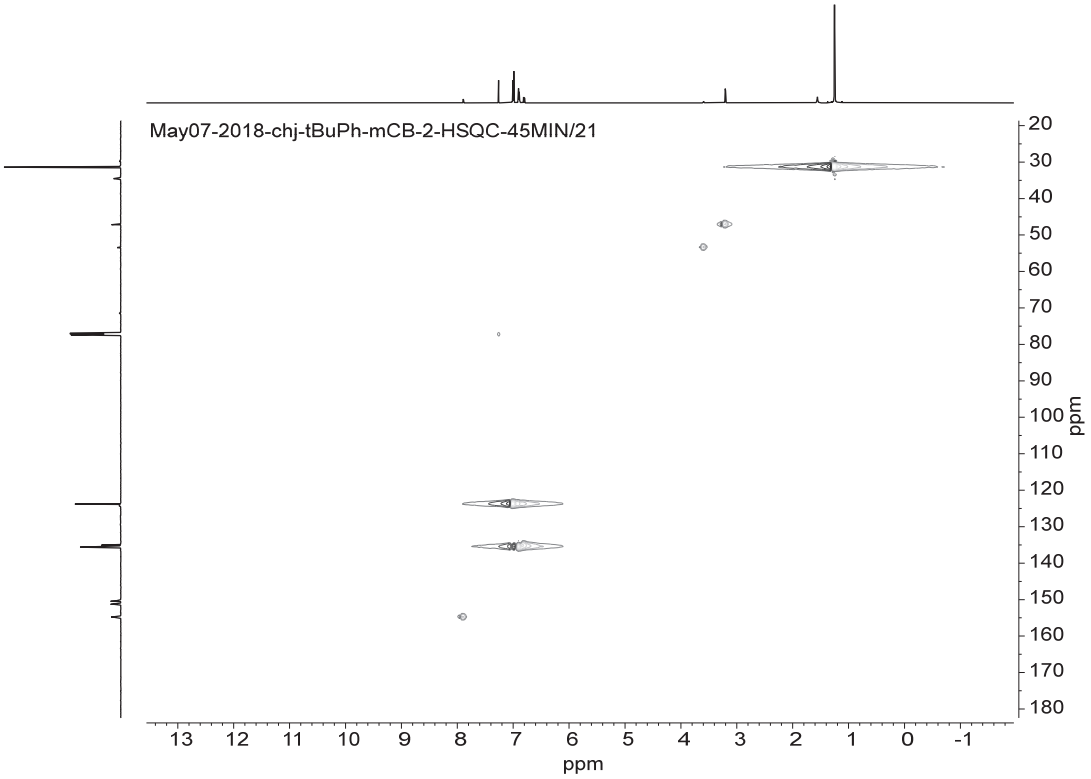
^{11}B NMR of 16, 160 M, $CDCl_3$



^{13}C NMR of 16, 126 M, $CDCl_3$

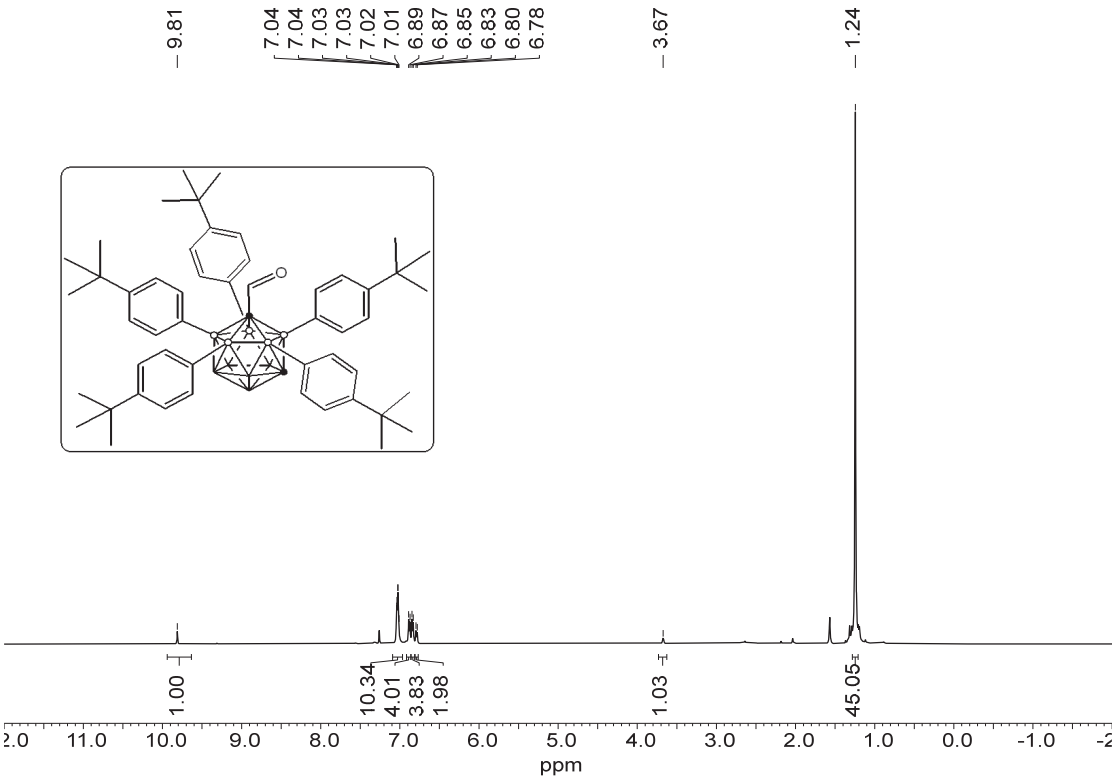


^{13}C-^{1}H HSQC of 16, 500 M, $CDCl_3$

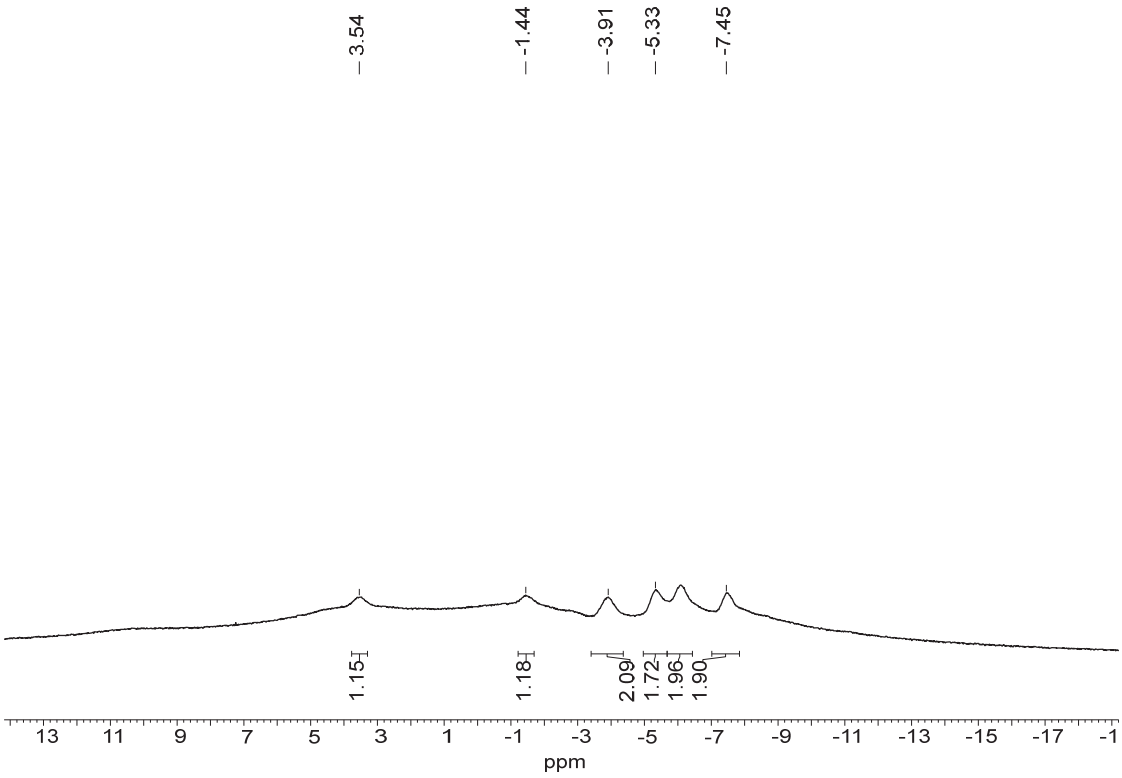


Synthetic utilities

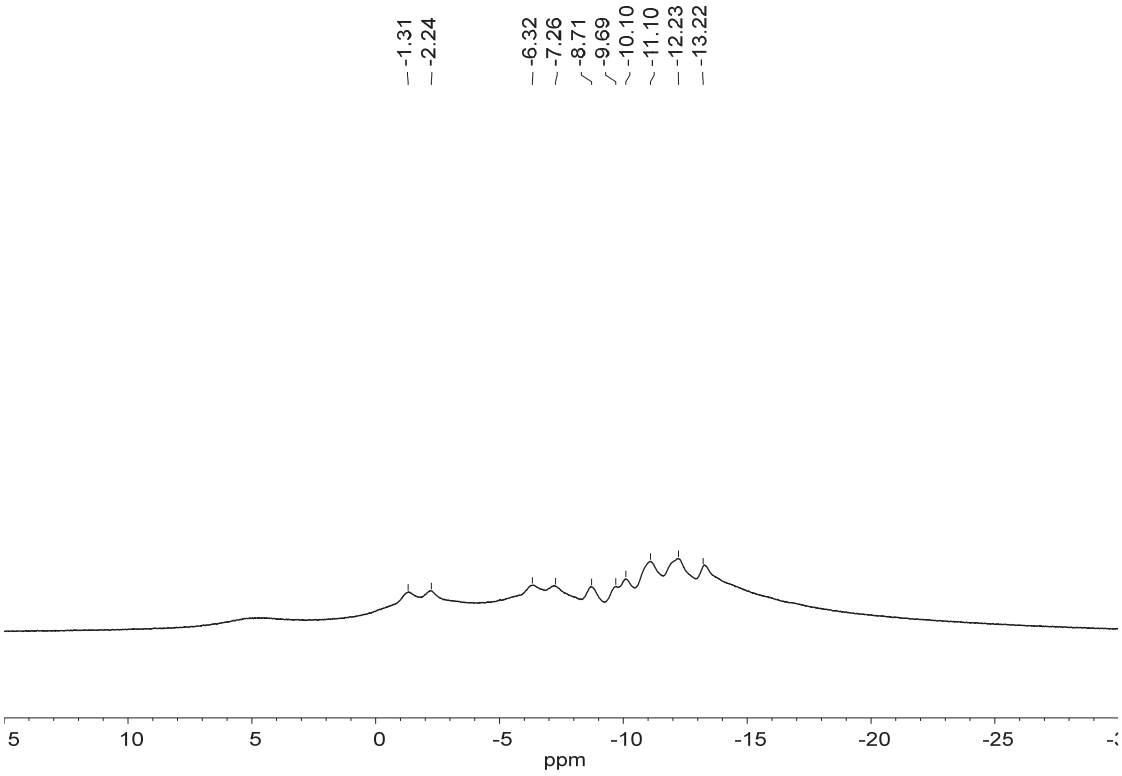
^{1}H NMR of 17, 500 M, $CDCl_3$



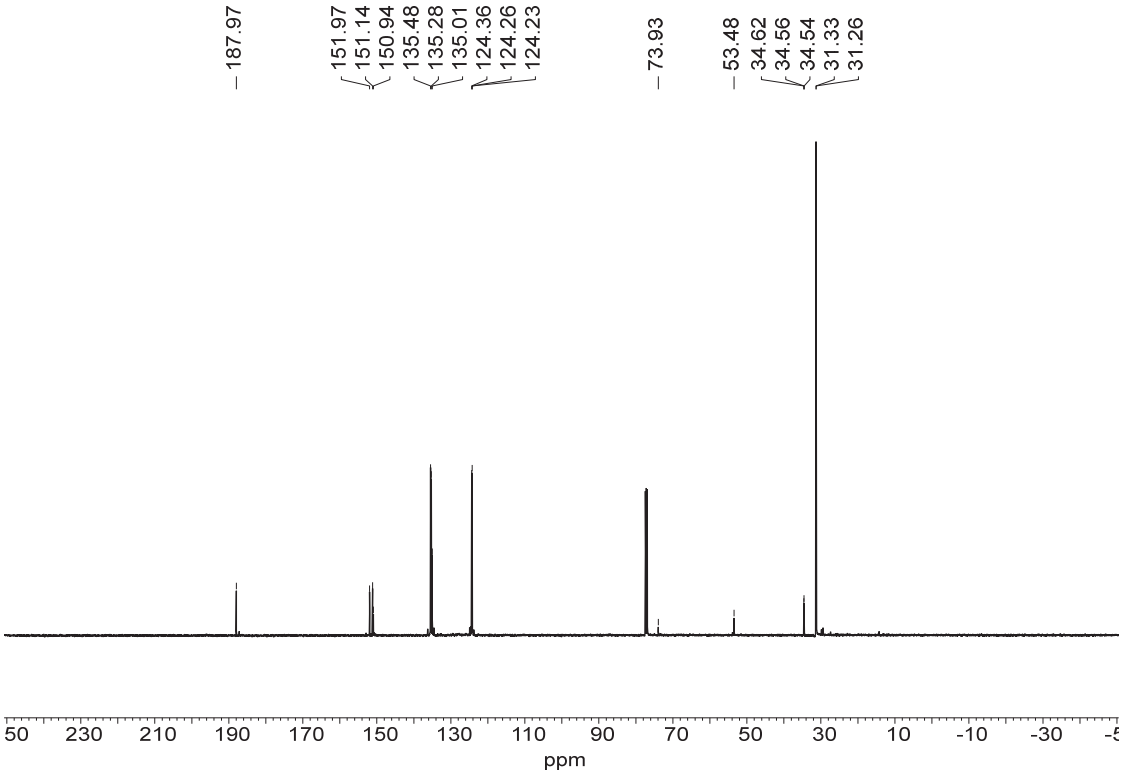
$^{11}B\ \{^{1}H\}$ NMR of 17, 160 M, $CDCl_3$



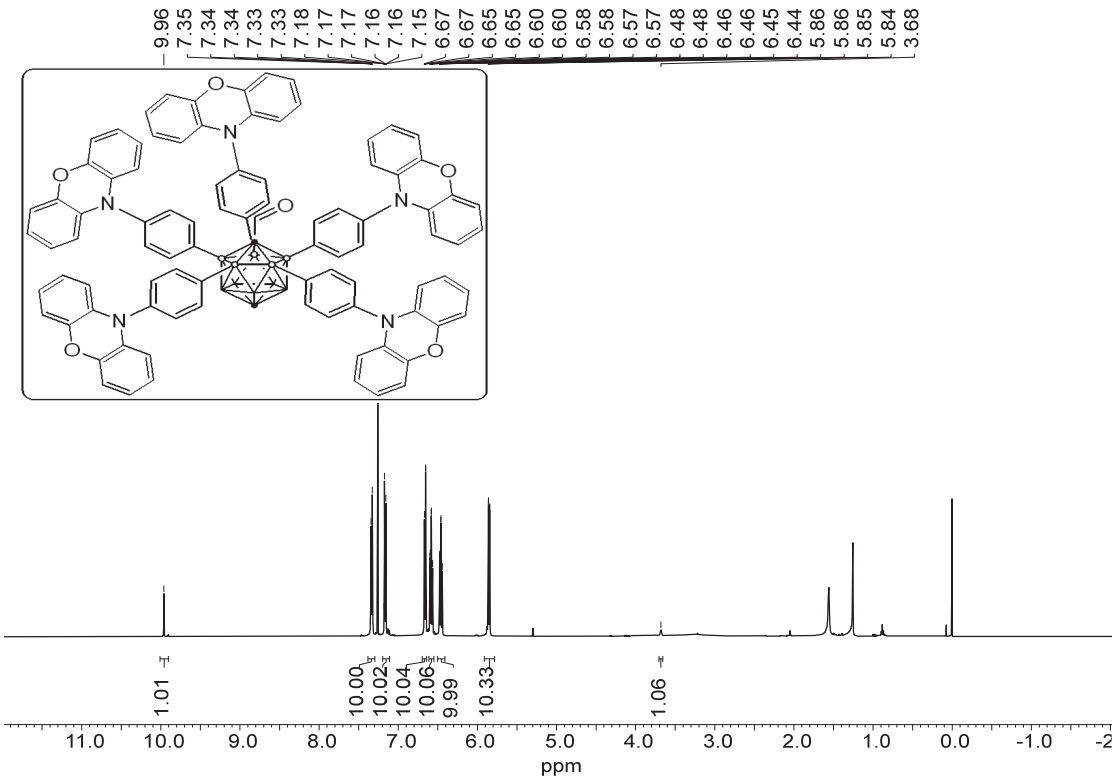
^{11}B NMR of 17, 160 M, $CDCl_3$



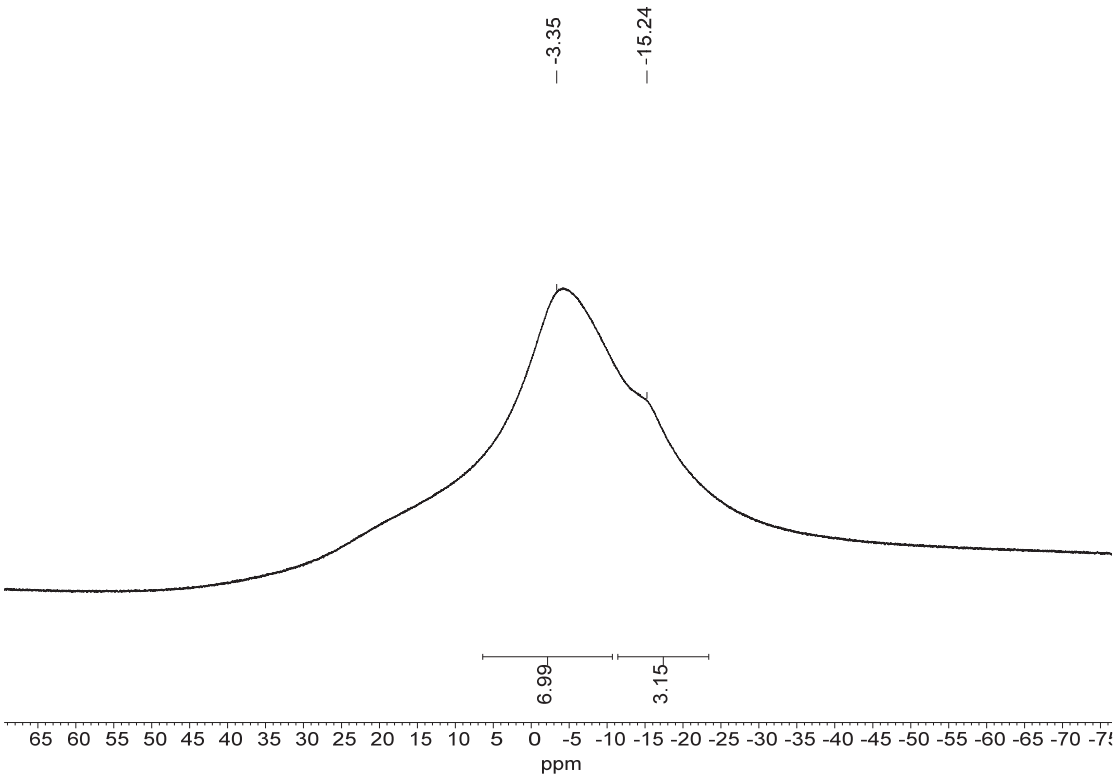
^{13}C NMR of 17, 126 M, $CDCl_3$



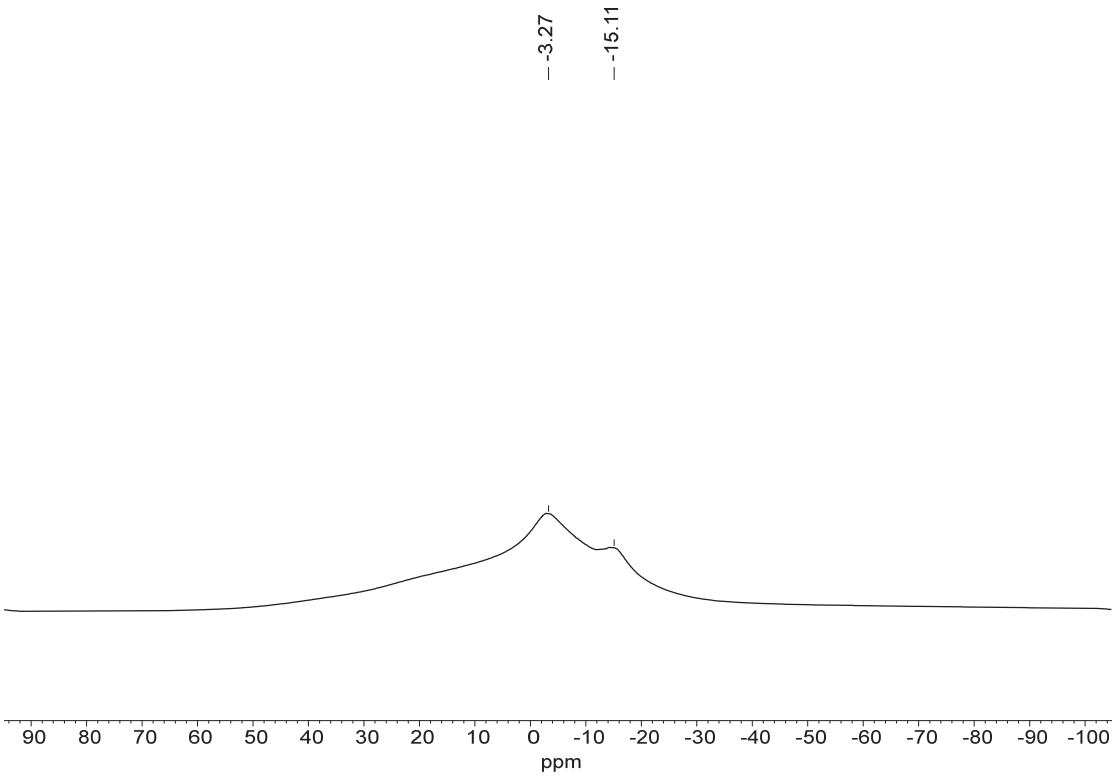
^{1}H NMR of 18, 400 M, $CDCl_3$



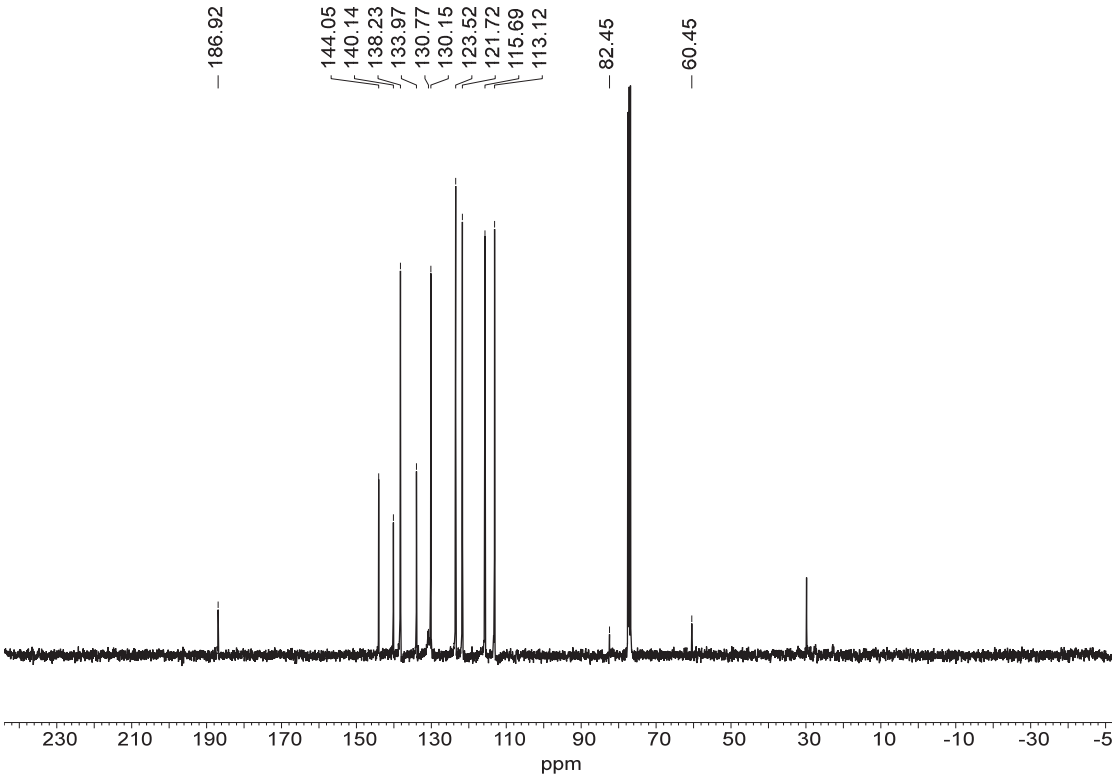
$^{11}B\ \{^{1}H\}$ NMR of 18, 128 M, $CDCl_3$



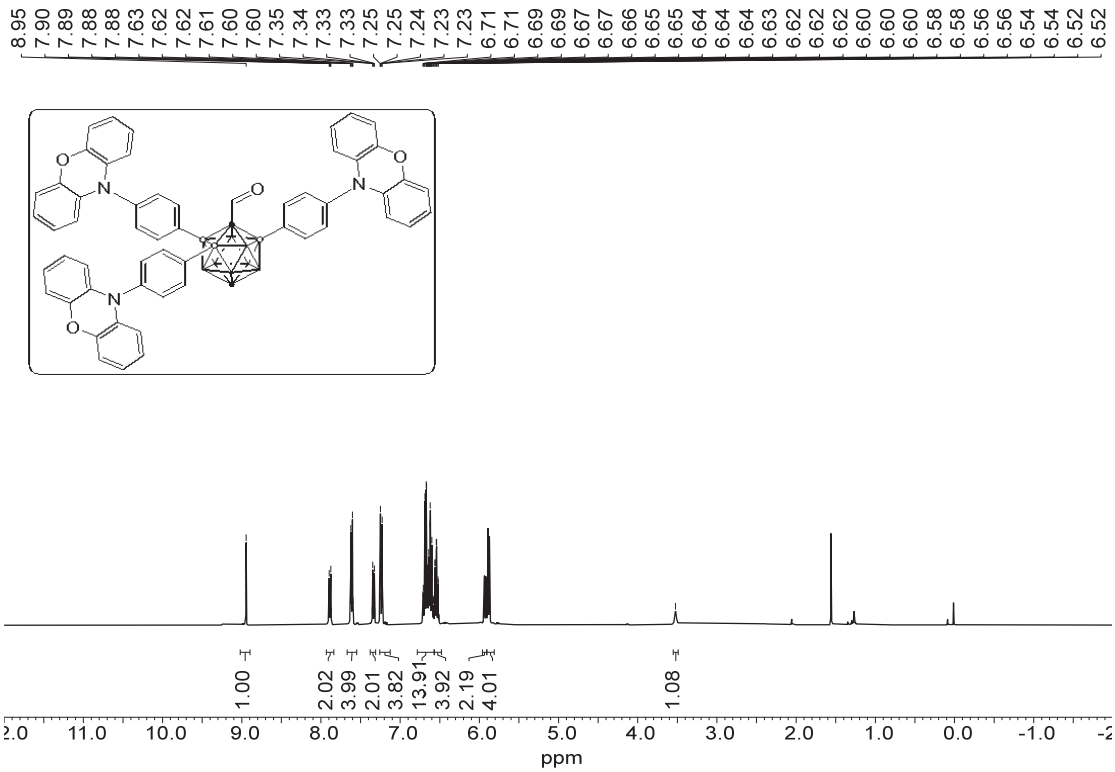
^{11}B NMR of 18, 128 M, $CDCl_3$



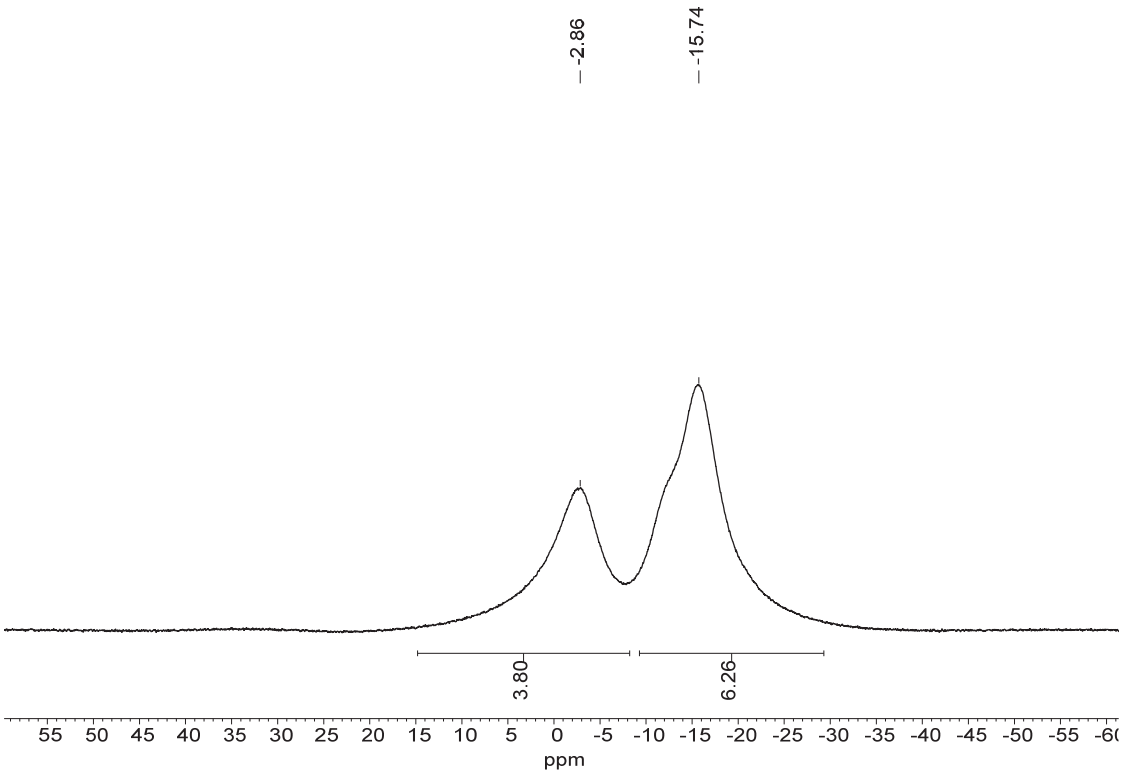
^{13}C NMR of 18, 101 M, $CDCl_3$



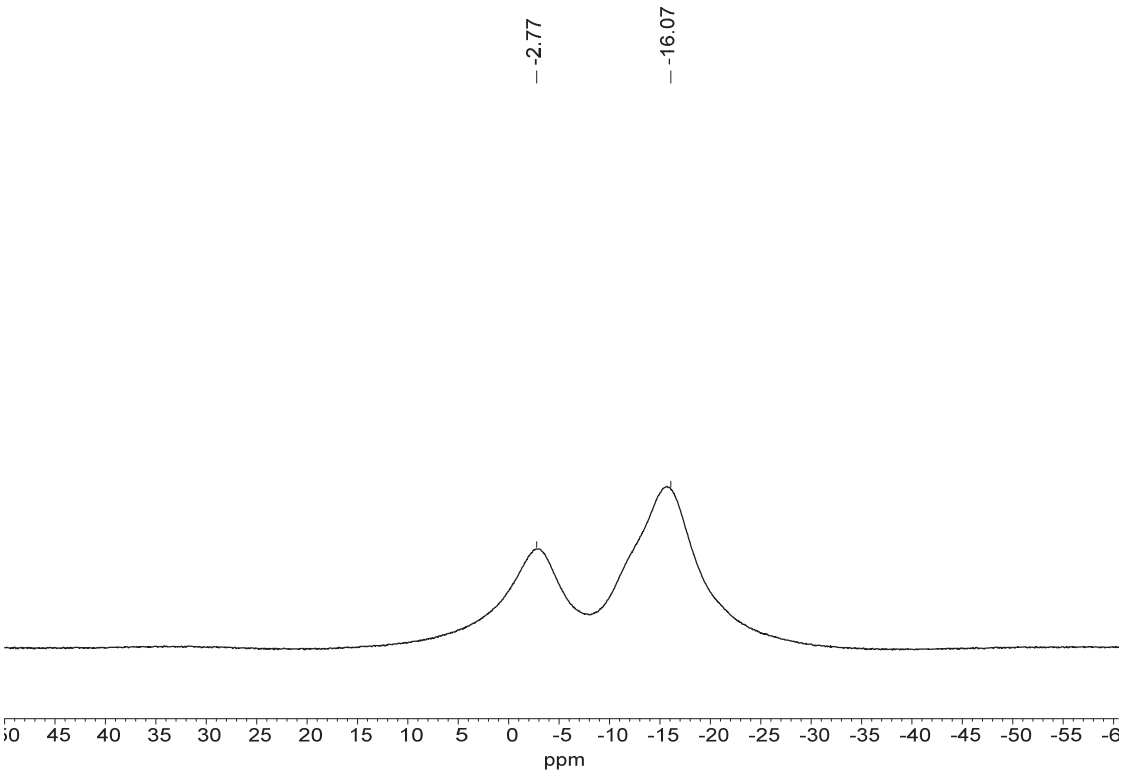
^{1}H NMR of PCB-3Ph-PXZ, 400 M, $CDCl_3$



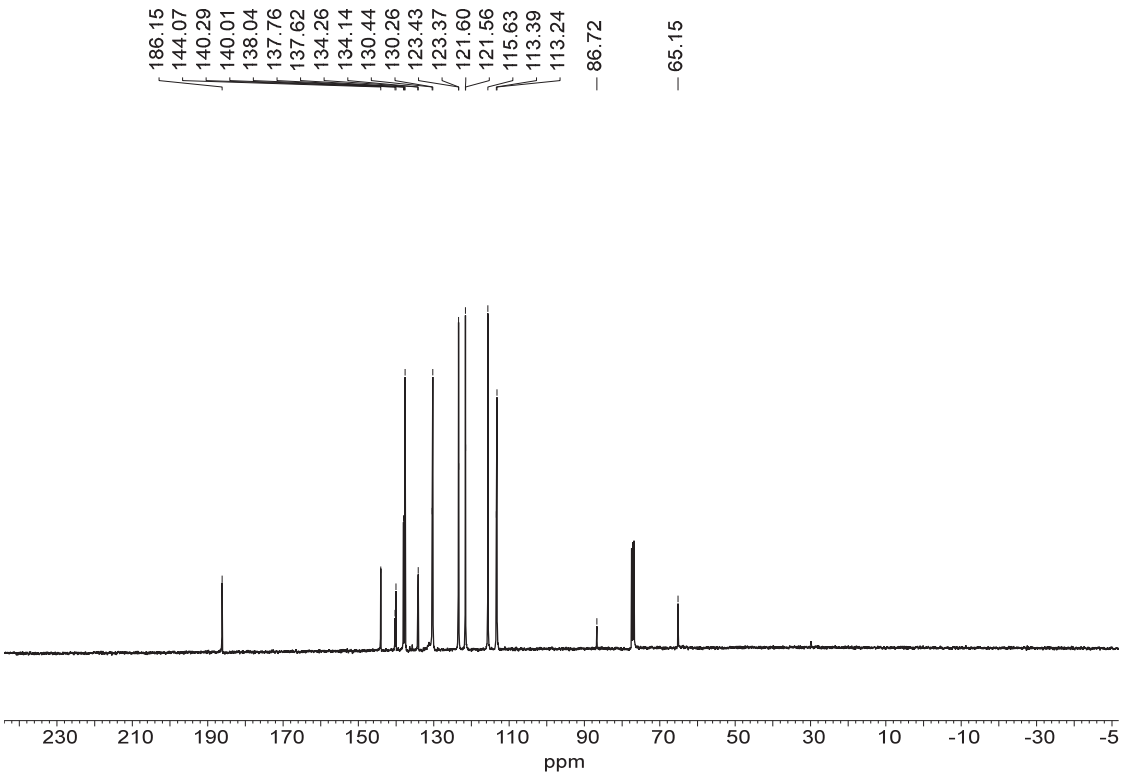
$^{11}B\ \{^{1}H\}$ NMR of PCB-3Ph-PXZ, 128 M, $CDCl_3$



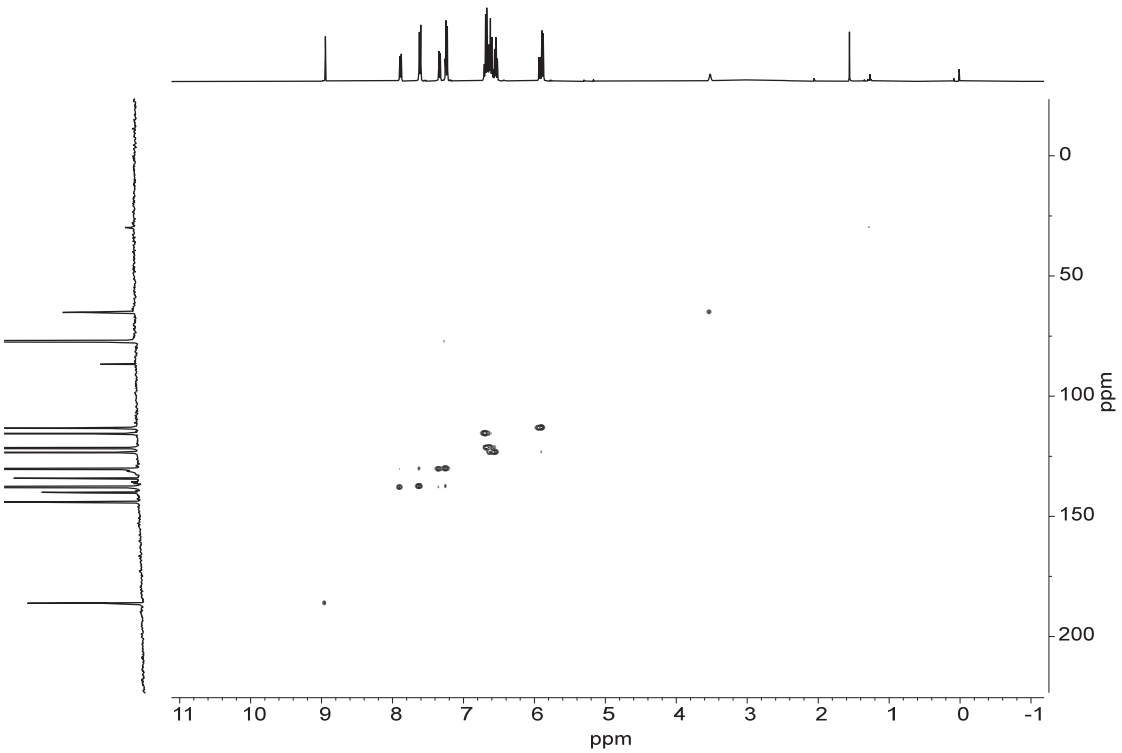
^{11}B NMR of PCB-3Ph-PXZ, 128 M, $CDCl_3$



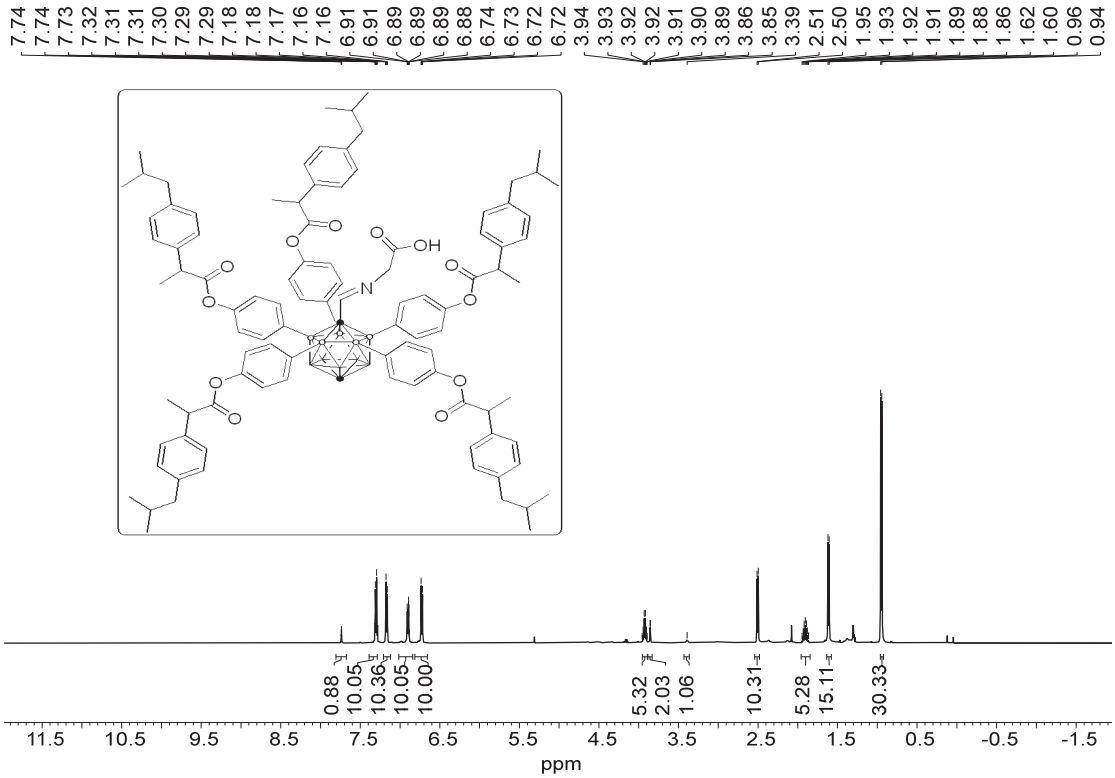
^{13}C NMR of PCB-3Ph-PXZ, 101 M, $CDCl_3$



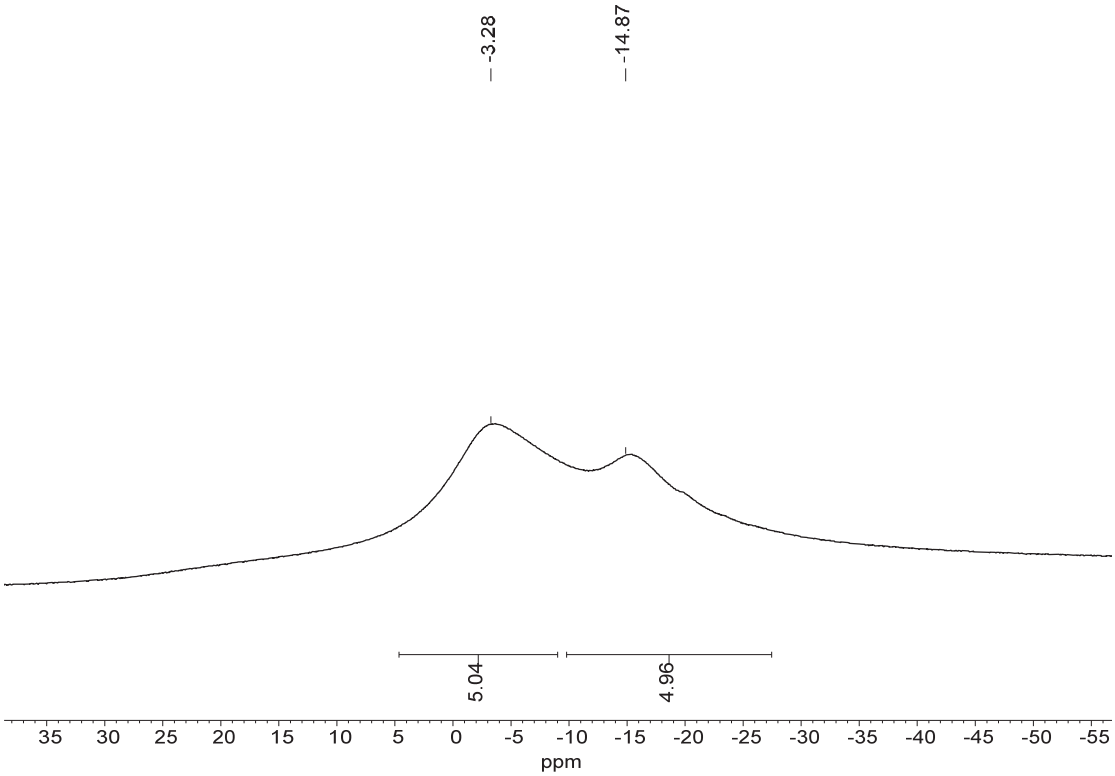
^{13}C-^{1}H HSQC of PCB-3Ph-PXZ, 400 M, $CDCl_3$



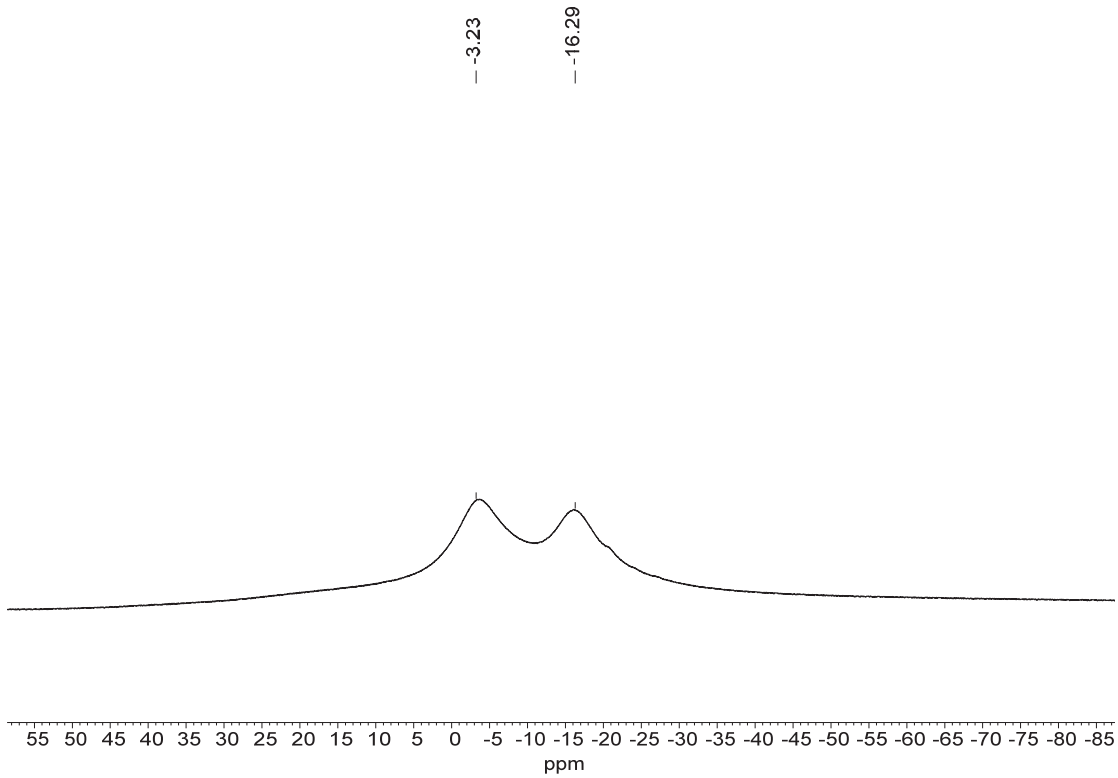
^{1}H NMR of 19, 400 M, $CDCl_3$



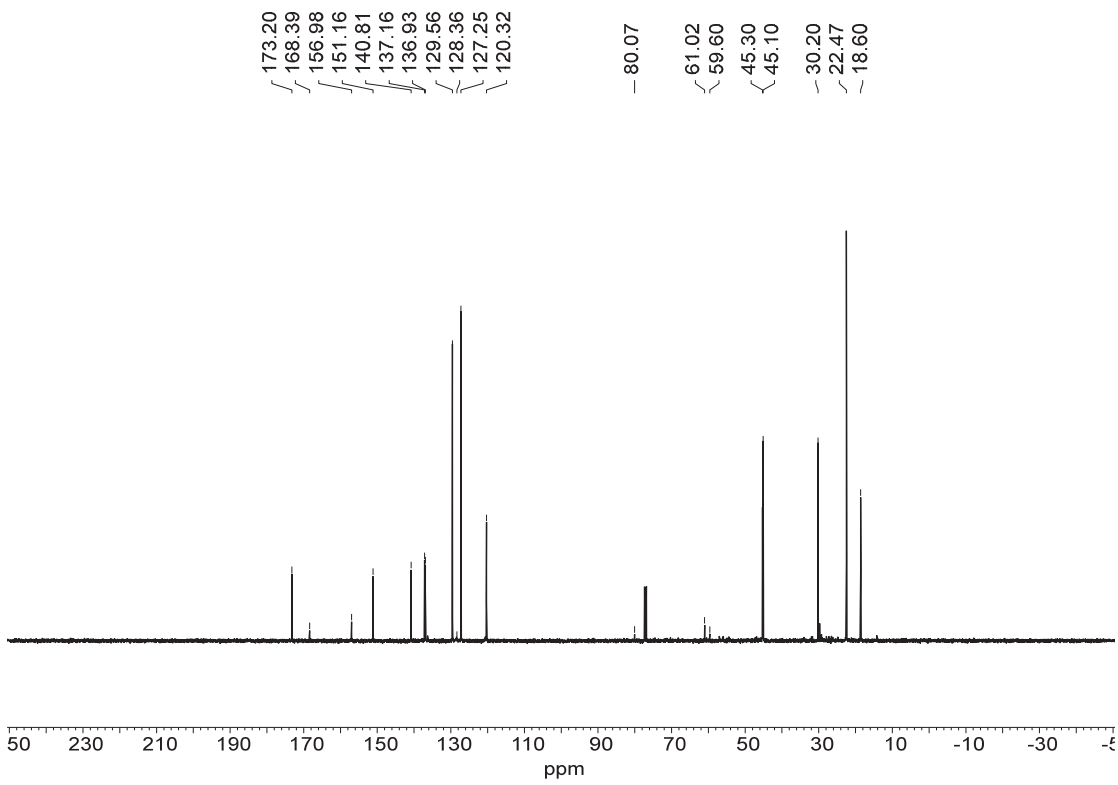
^{11}B {^{1}H} NMR of 19, 128 M, $CDCl_3$



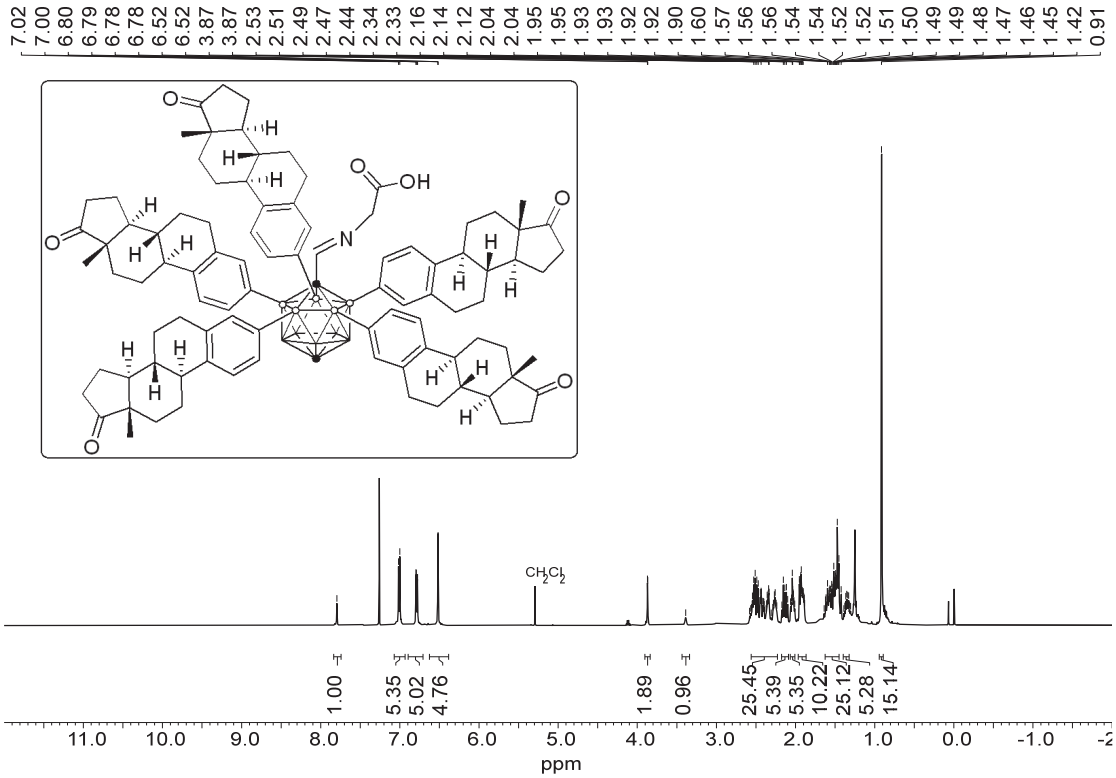
^{11}B NMR of 19, 128 M, $CDCl_3$



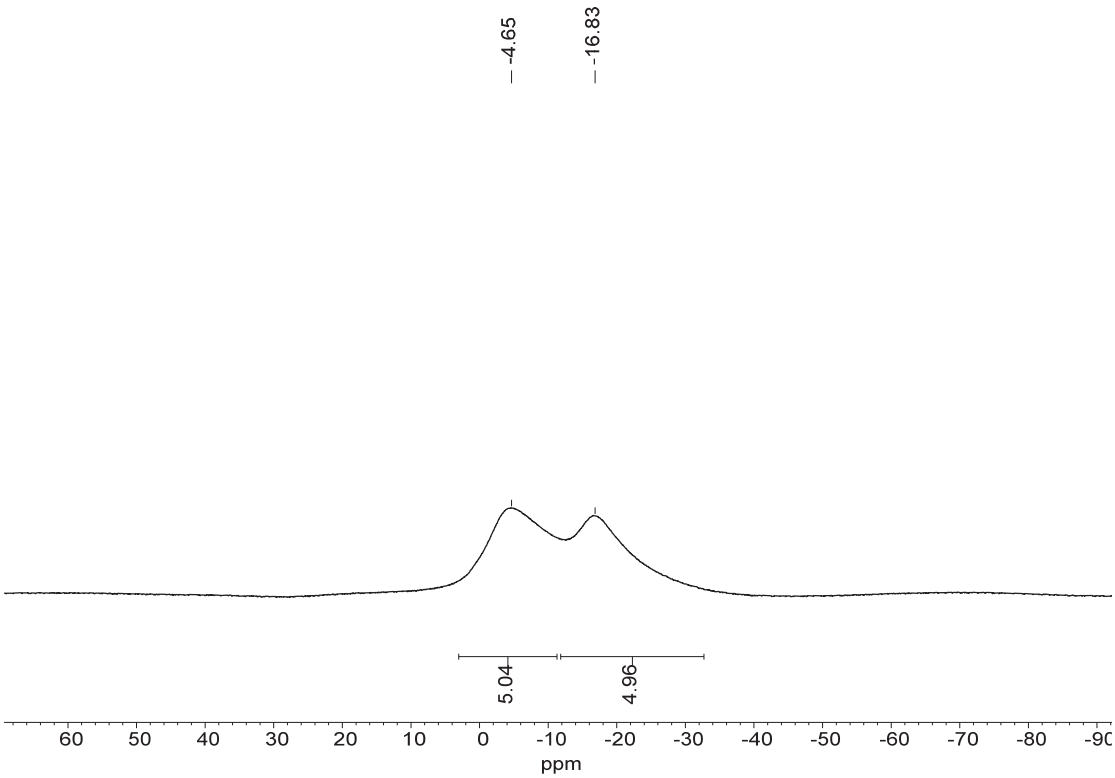
^{13}C NMR of 19, 101 M, $CDCl_3$



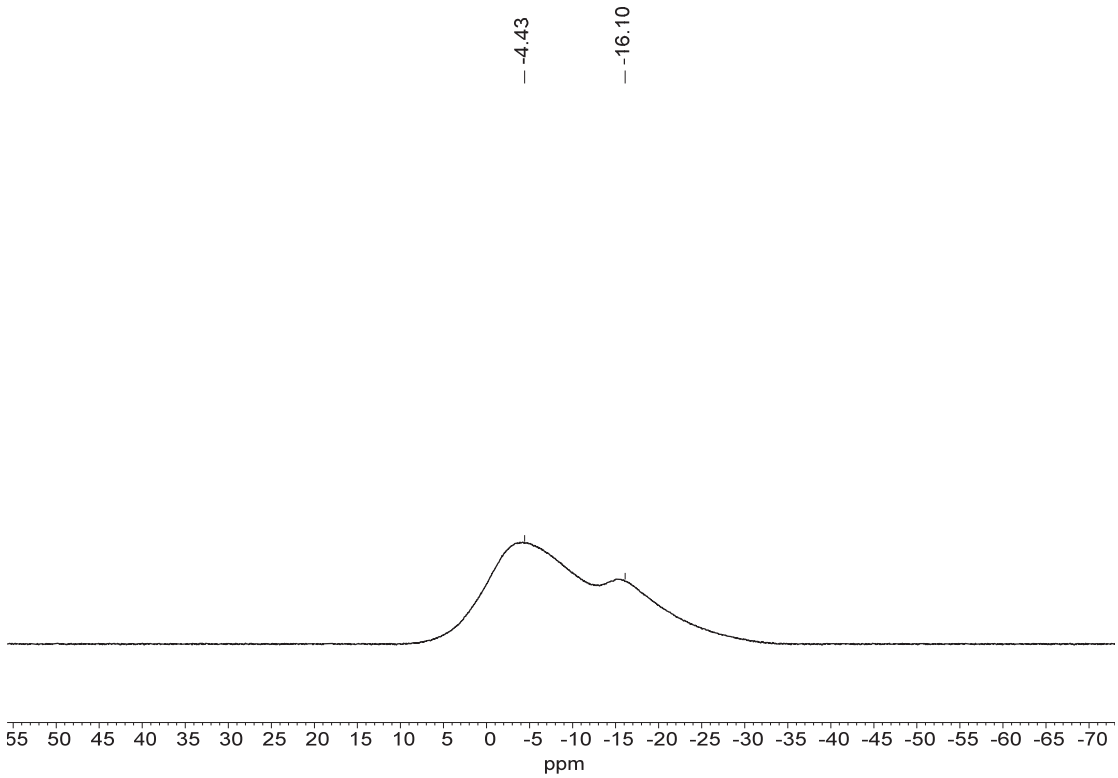
^{1}H NMR of 20, 400 M, $CDCl_3$



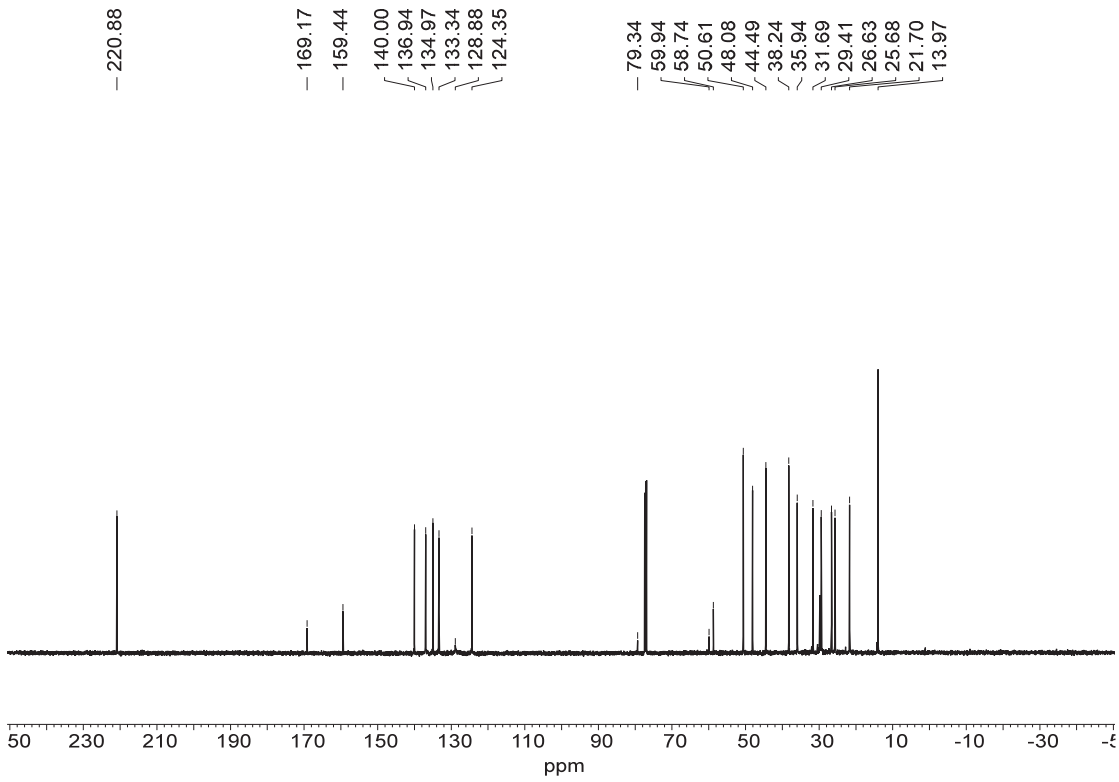
^{11}B {^{1}H} NMR of 20, 128 M, $CDCl_3$



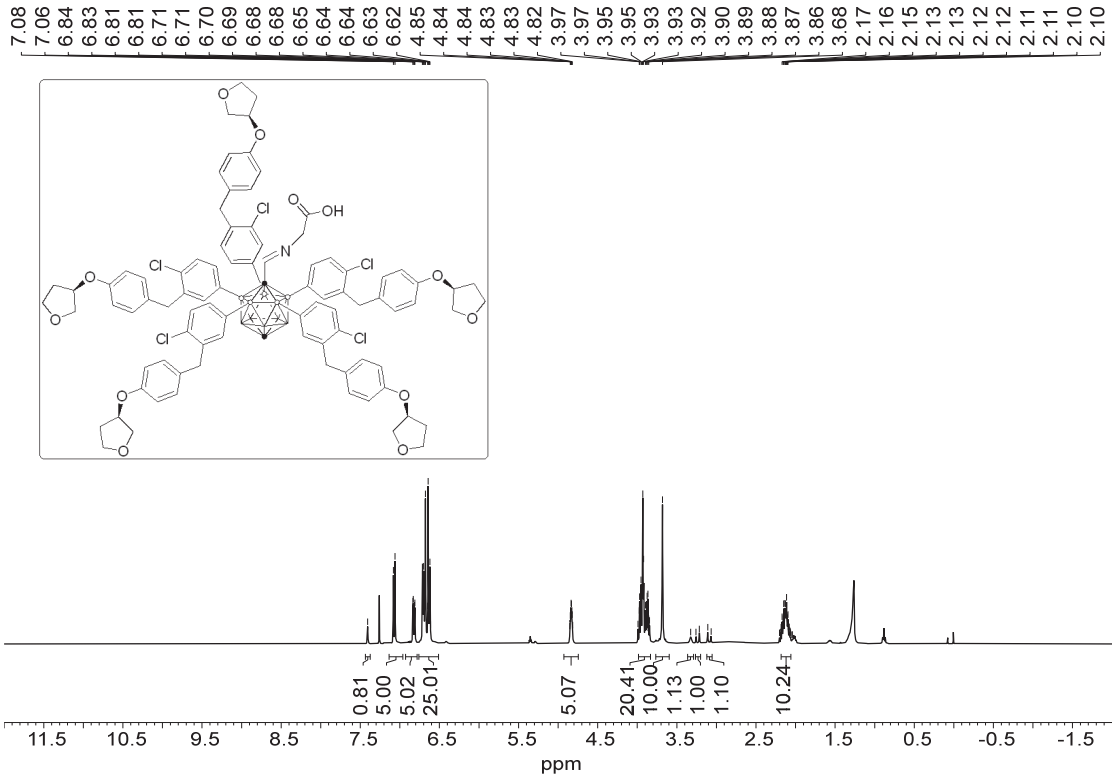
^{11}B NMR of 20, 128 M, $CDCl_3$



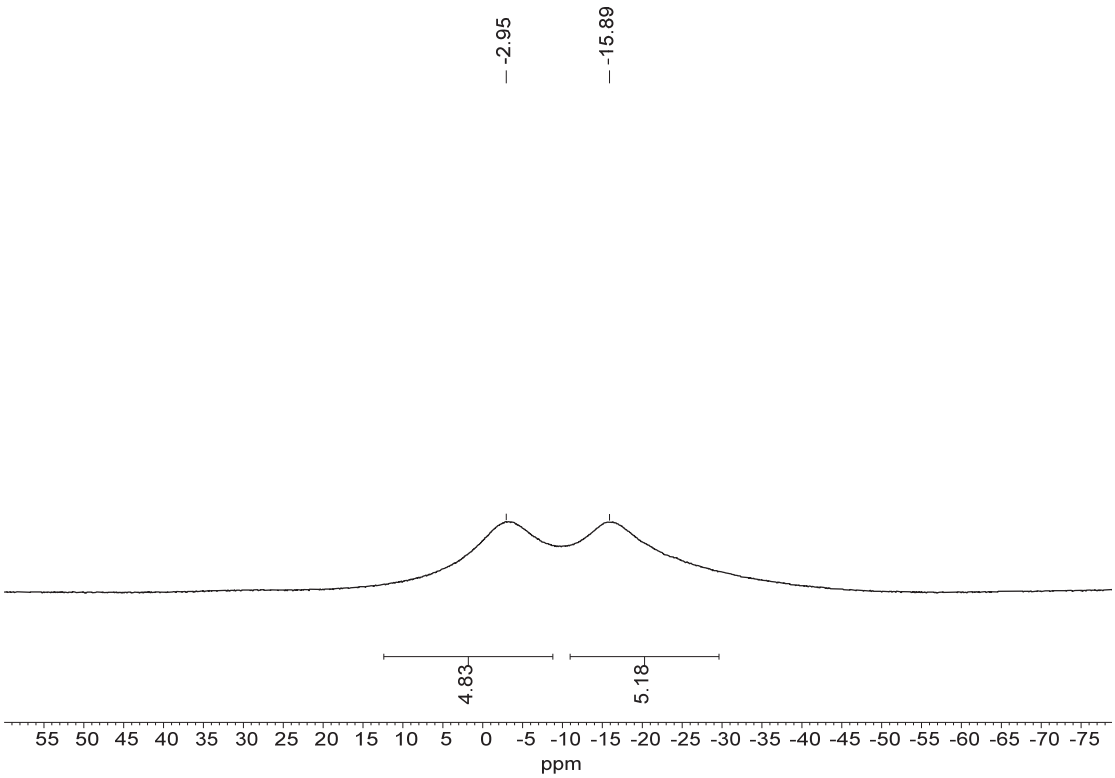
^{13}C NMR of 20, 101 M, $CDCl_3$



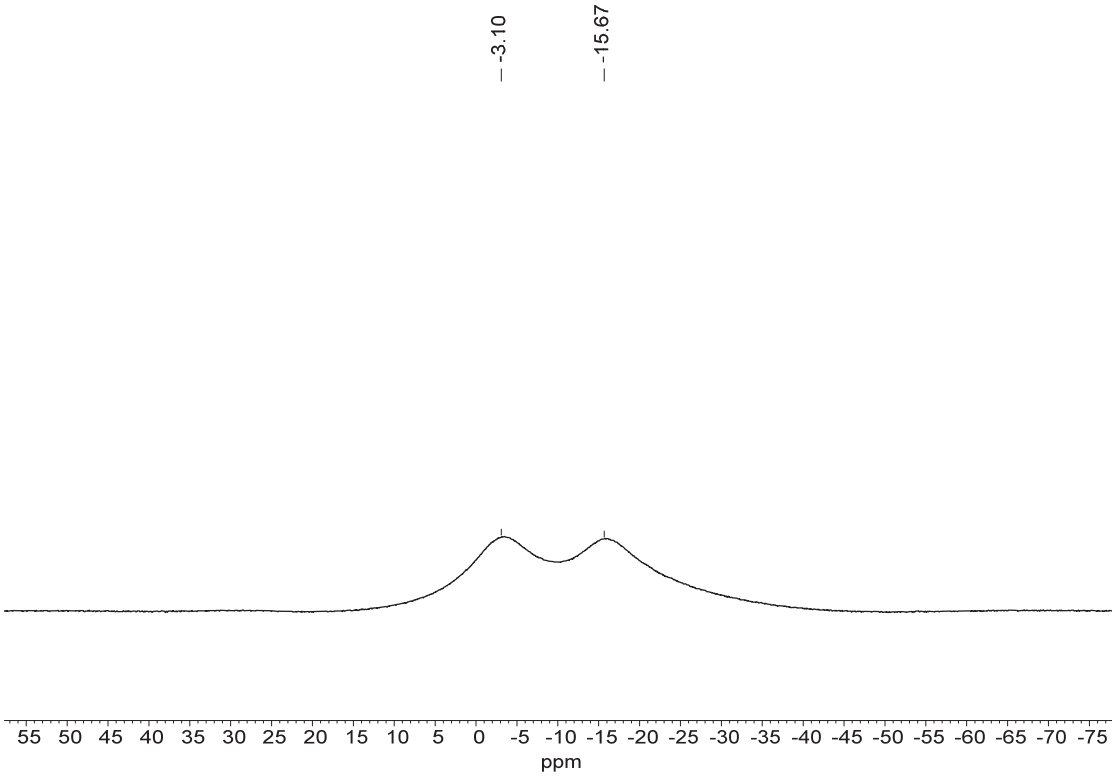
^{1}H NMR of 21, 400 M, $CDCl_3$



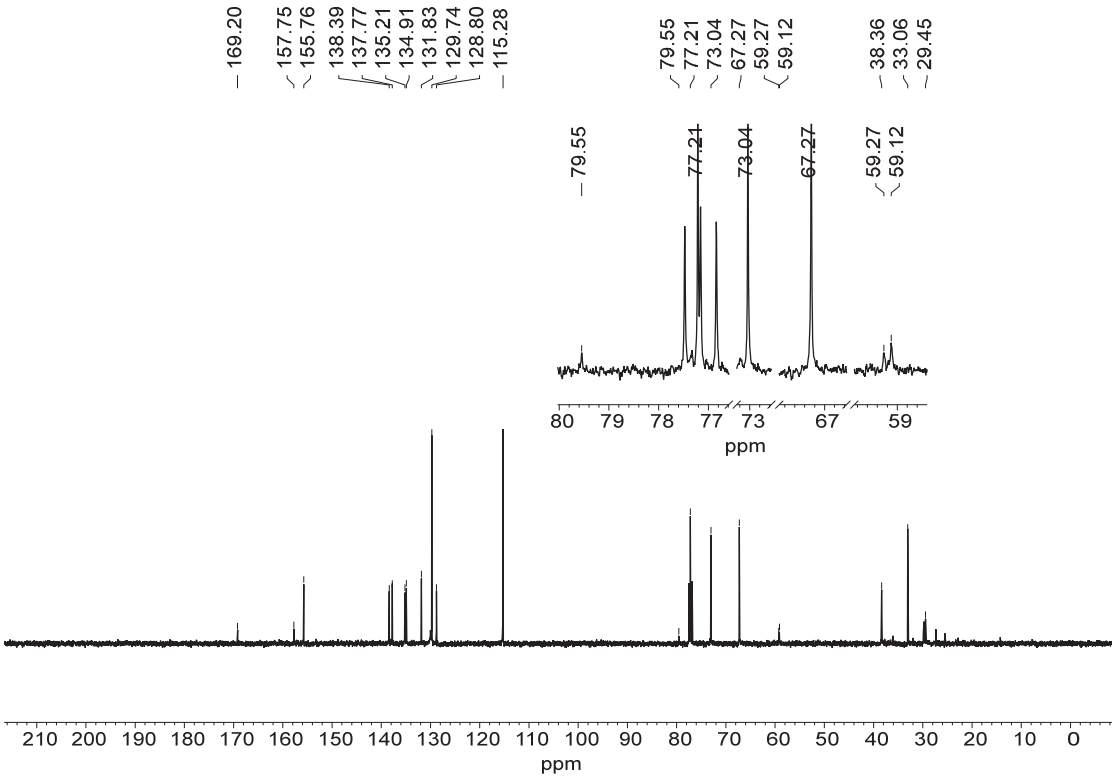
^{11}B {^{1}H} NMR of 21, 128 M, $CDCl_3$



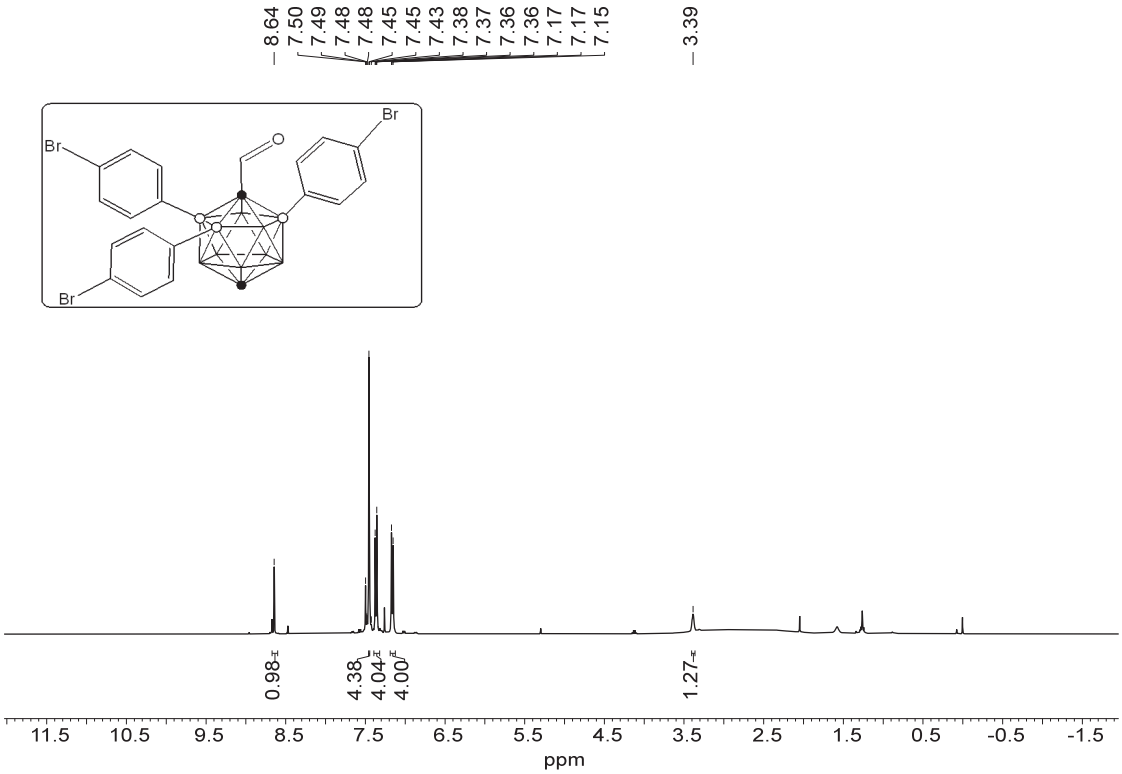
^{11}B NMR of 21, 128 M, $CDCl_3$



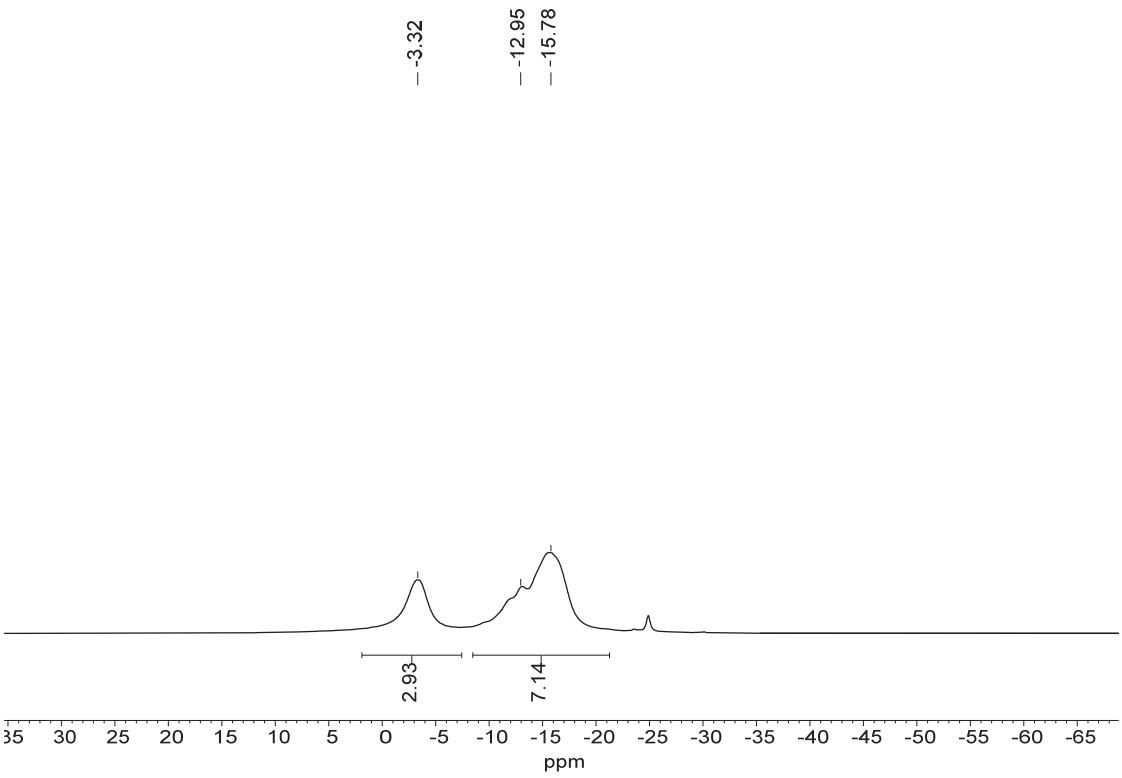
^{13}C NMR of 21, 101 M, $CDCl_3$



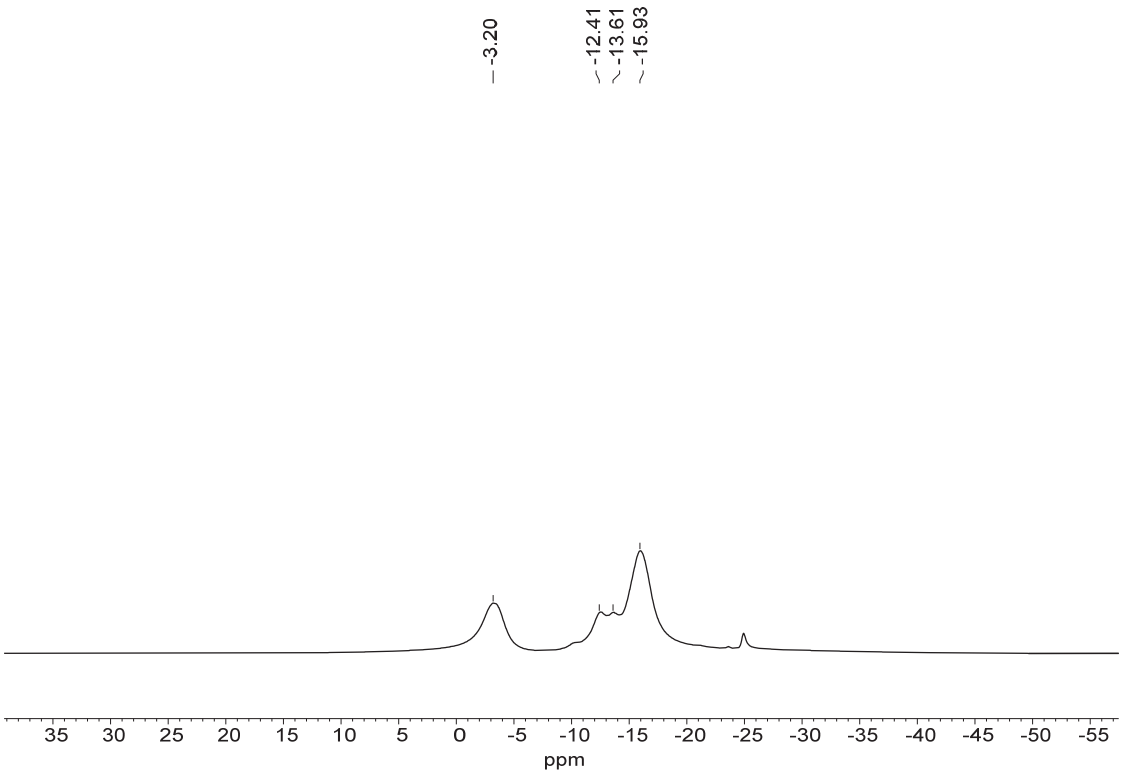
^{1}H NMR of 22, 400 M, $CDCl_3$



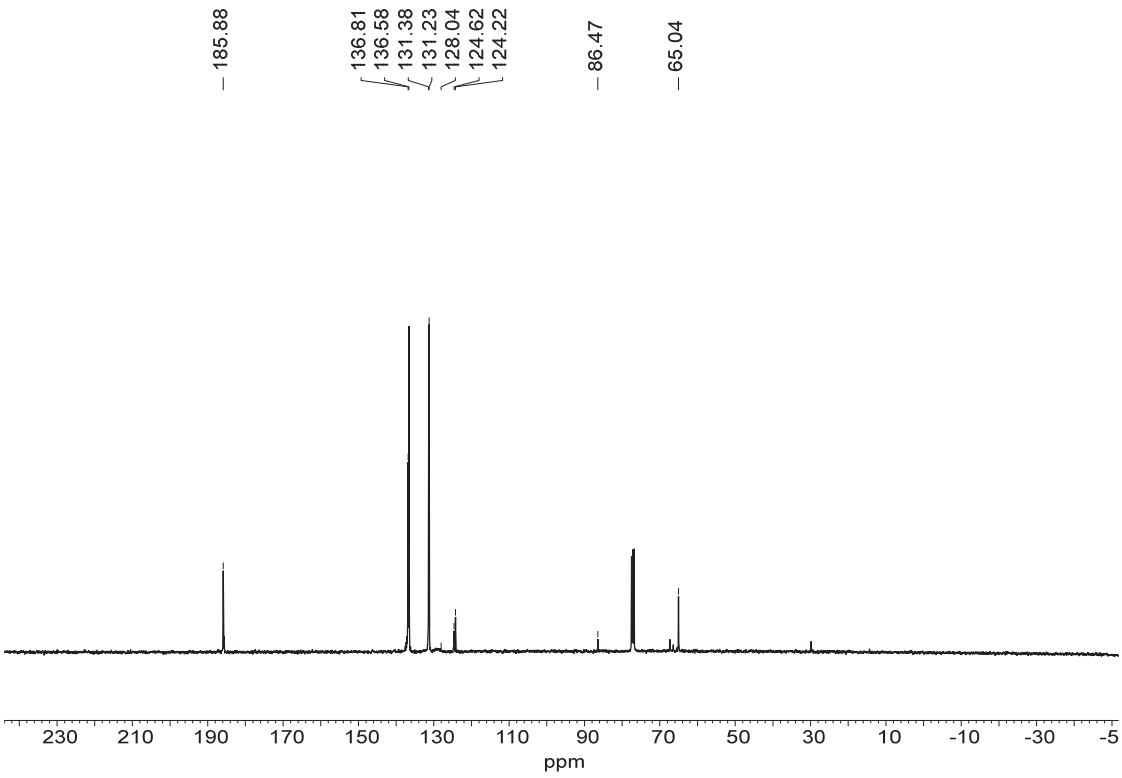
^{11}B {^{1}H} NMR of 22, 128 M, $CDCl_3$



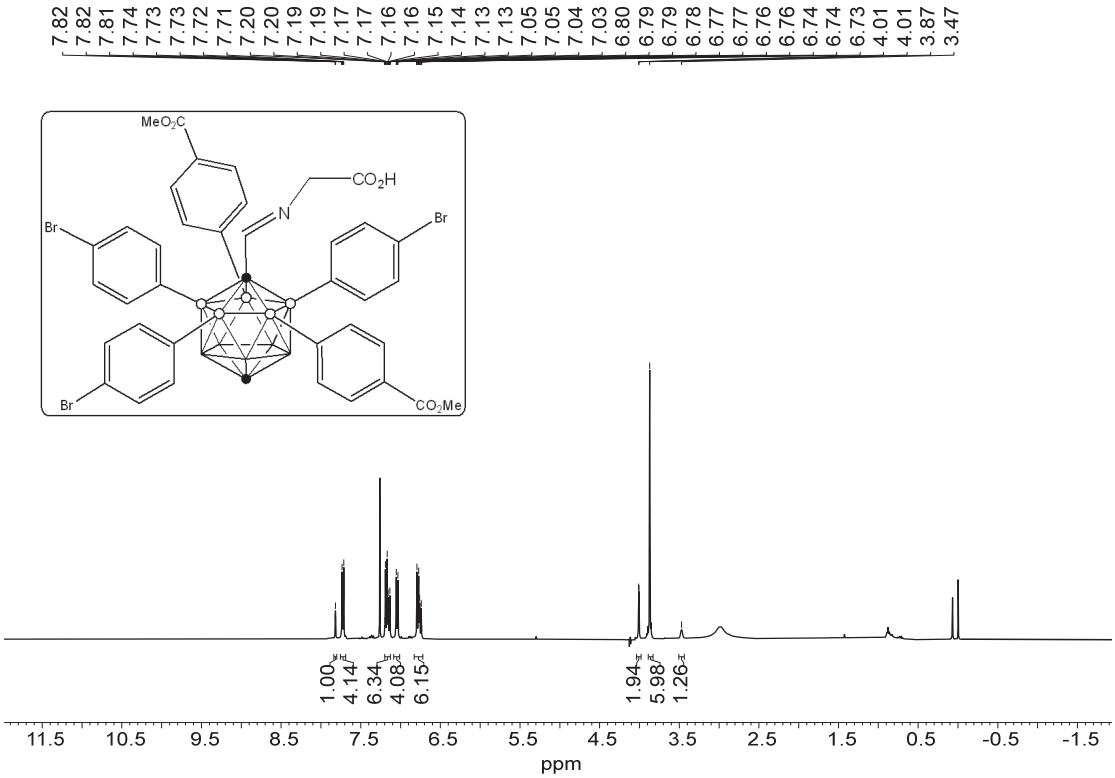
^{11}B NMR of 22, 128 M, $CDCl_3$



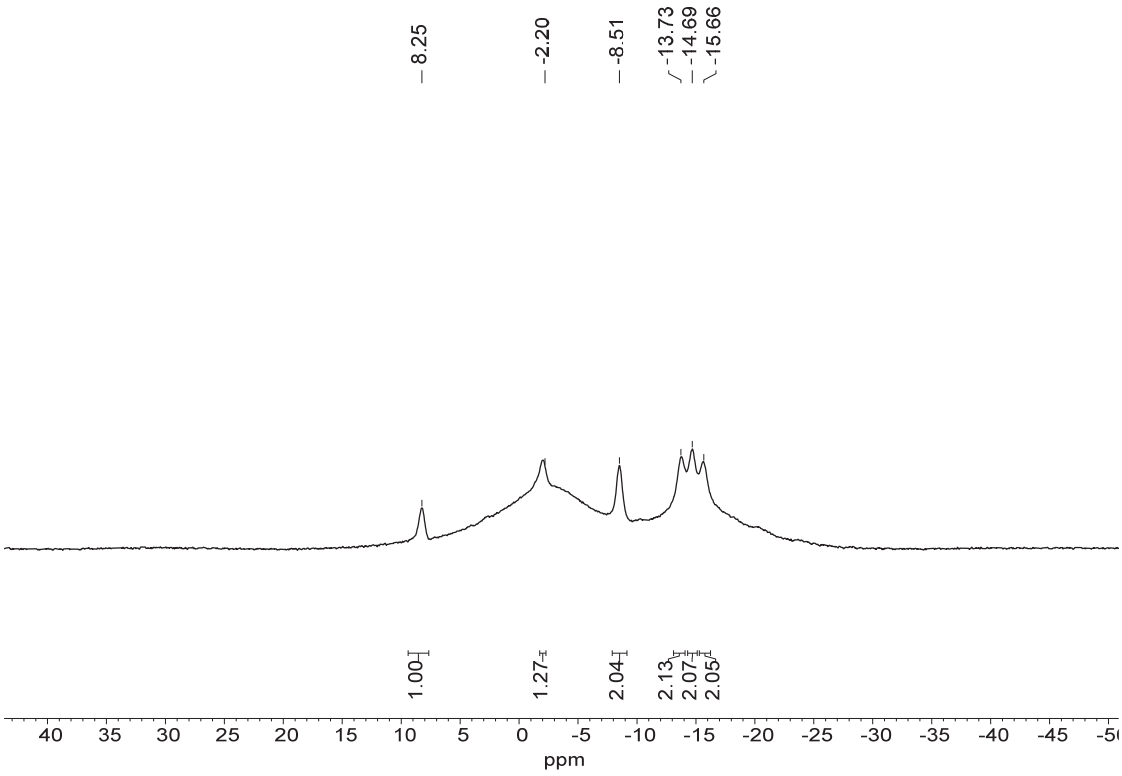
^{13}C NMR of 22, 101 M, $CDCl_3$



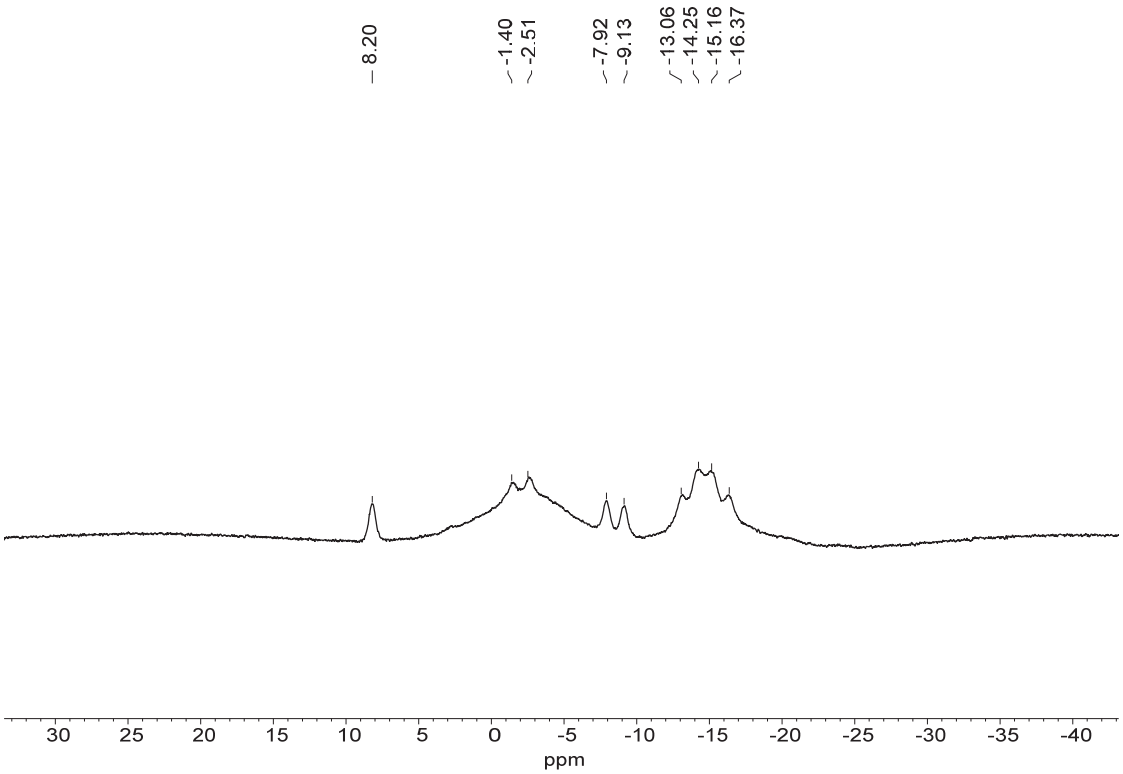
^{1}H NMR of 23, 400 M, $CDCl_3$



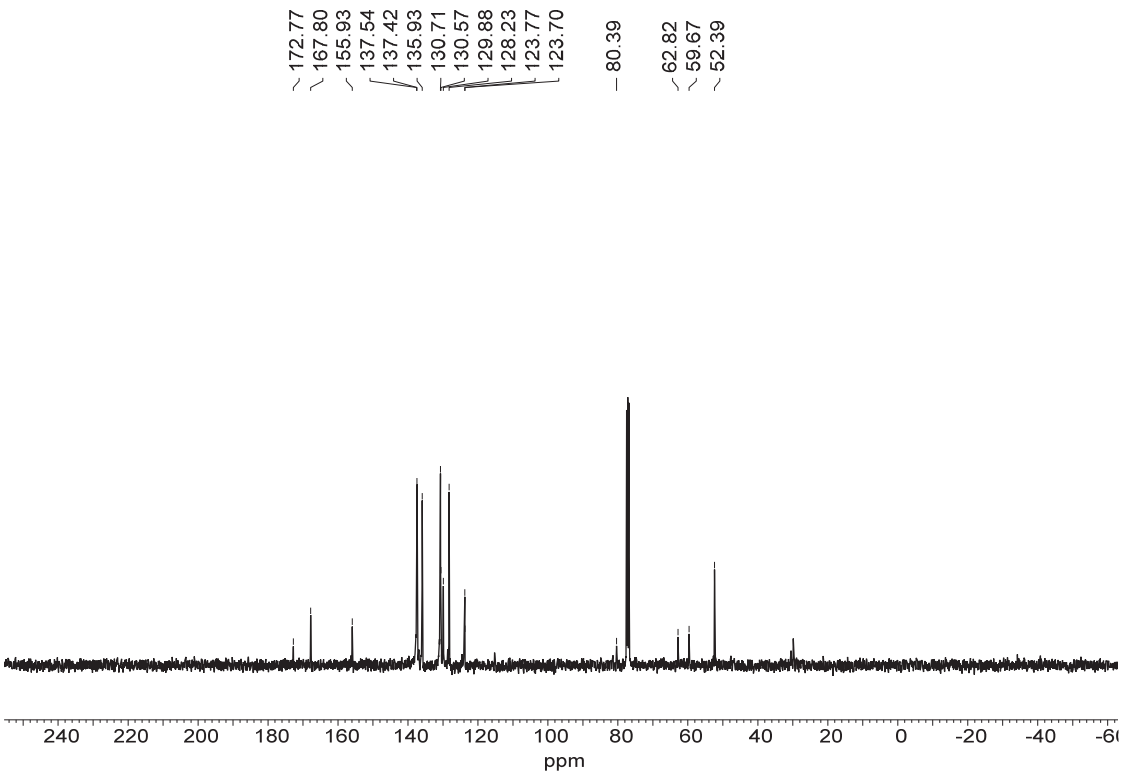
^{11}B {^{1}H} NMR of 23, 128 M, $CDCl_3$



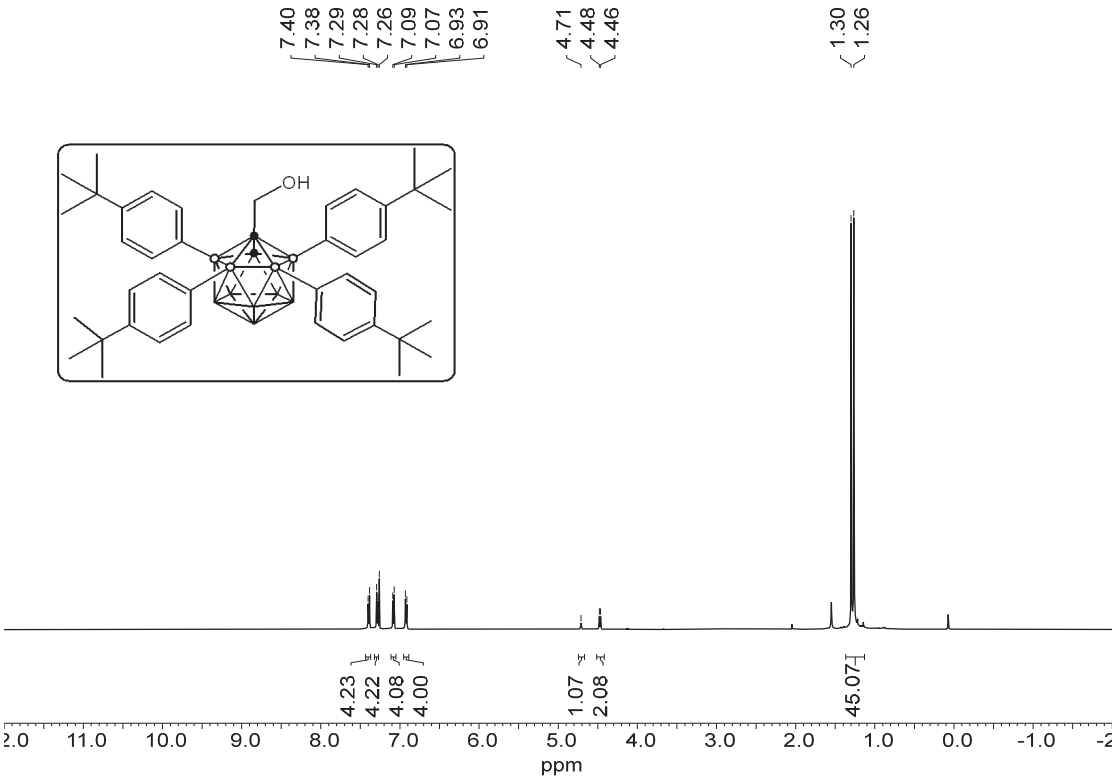
^{11}B NMR of 23, 128 M, $CDCl_3$



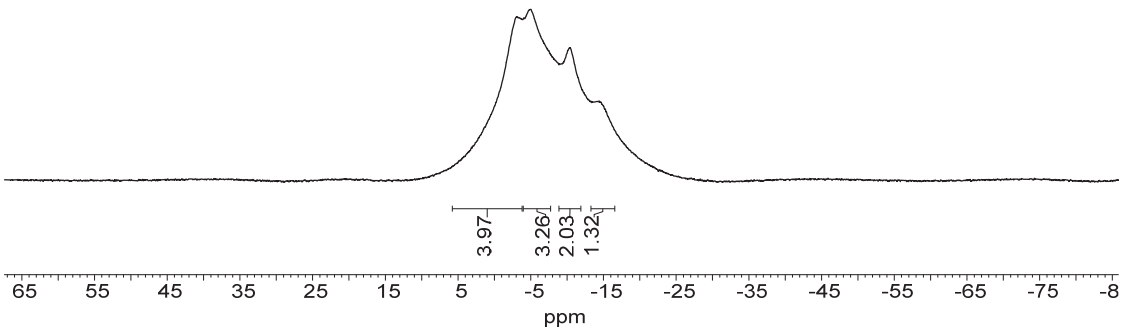
^{13}C NMR of 23, 101 M, $CDCl_3$



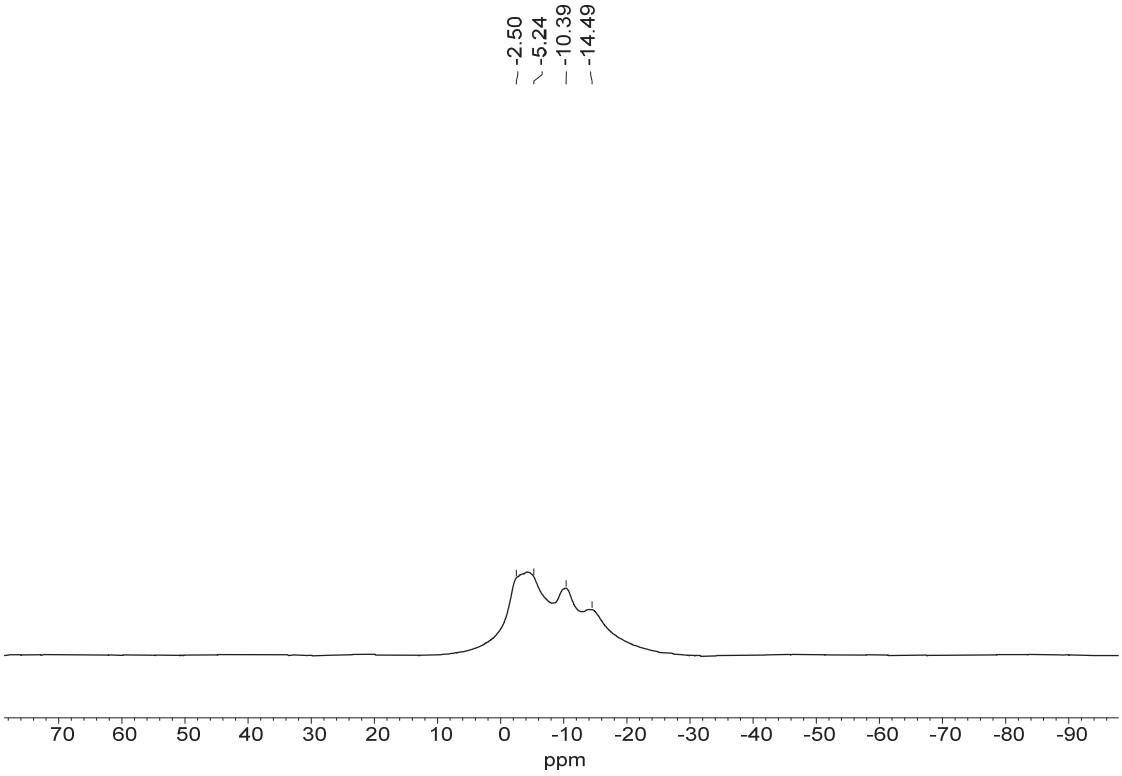
^{1}H NMR of 24, 500 M, $CDCl_3$



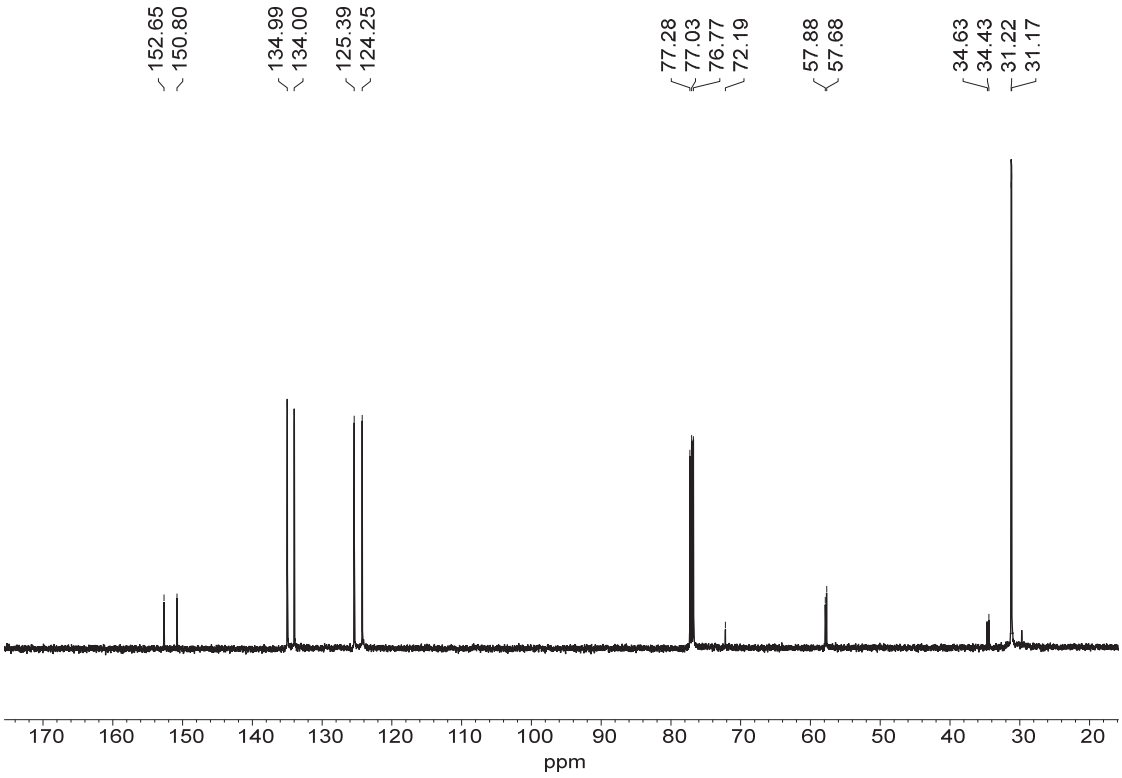
^{11}B {^{1}H} NMR of 24, 128 M, $CDCl_3$



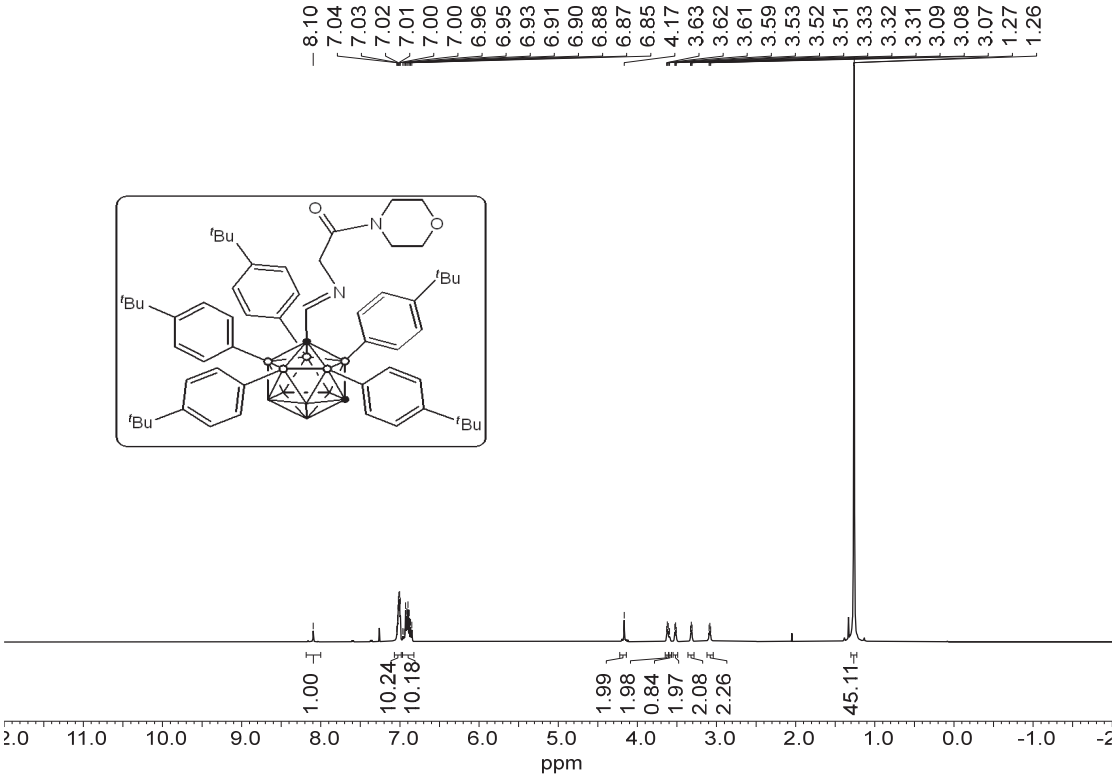
^{11}B NMR of 24, 128 M, $CDCl_3$



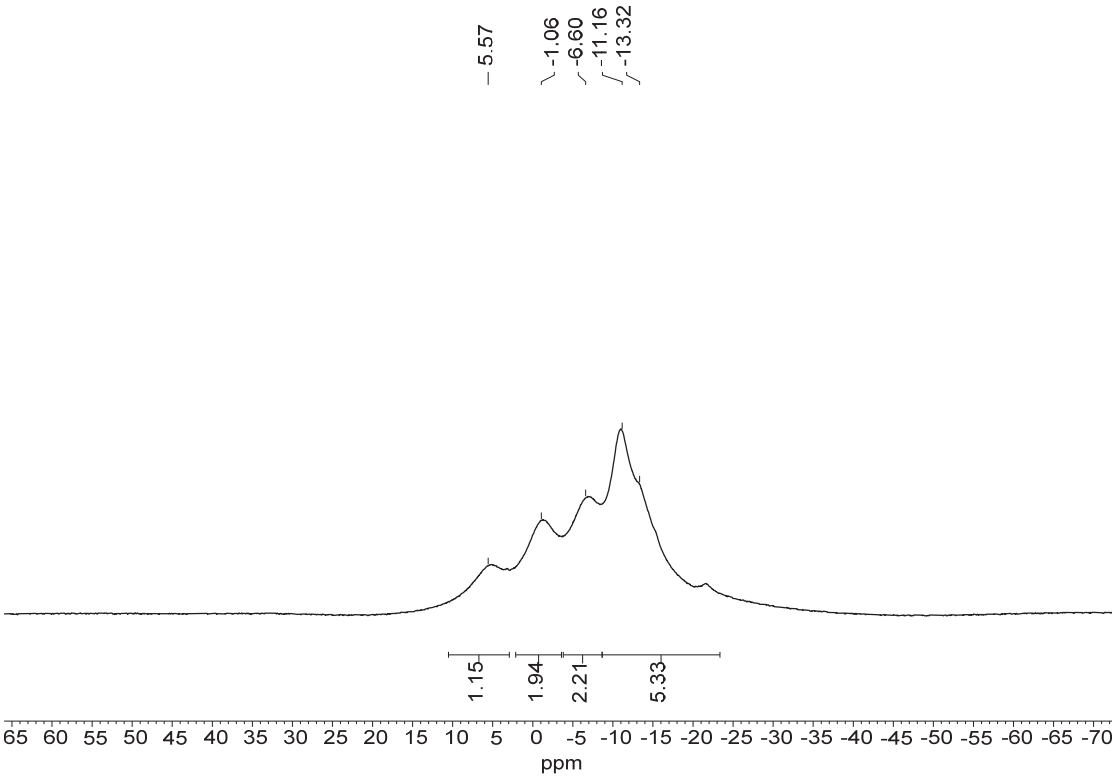
^{13}C NMR of 24, 126 M, $CDCl_3$



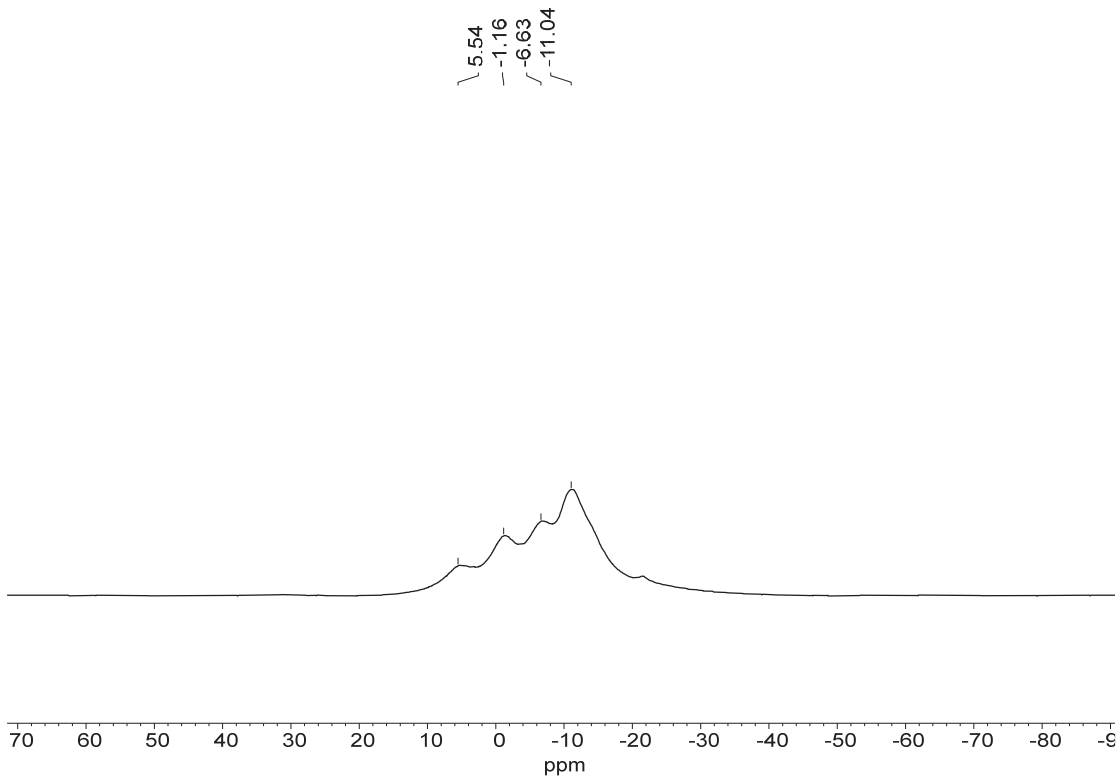
^{1}H NMR of 25, 500 M, $CDCl_3$



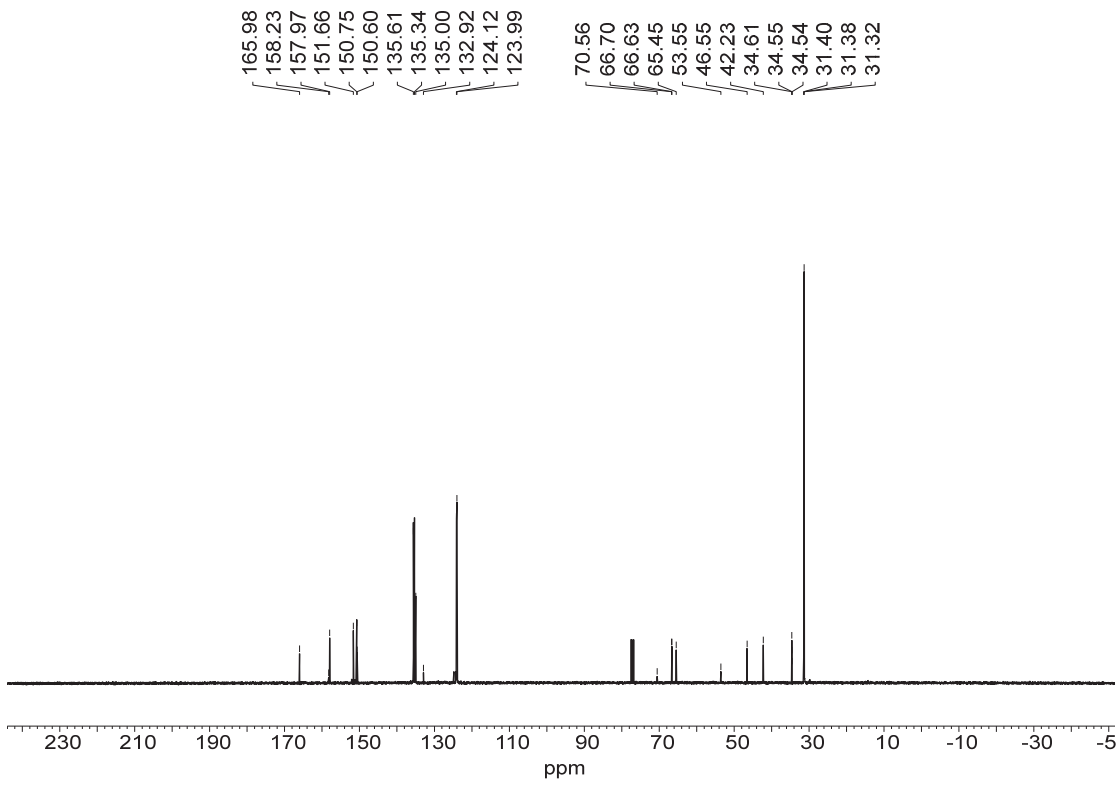
^{11}B {^{1}H} NMR of 25, 128 M, $CDCl_3$



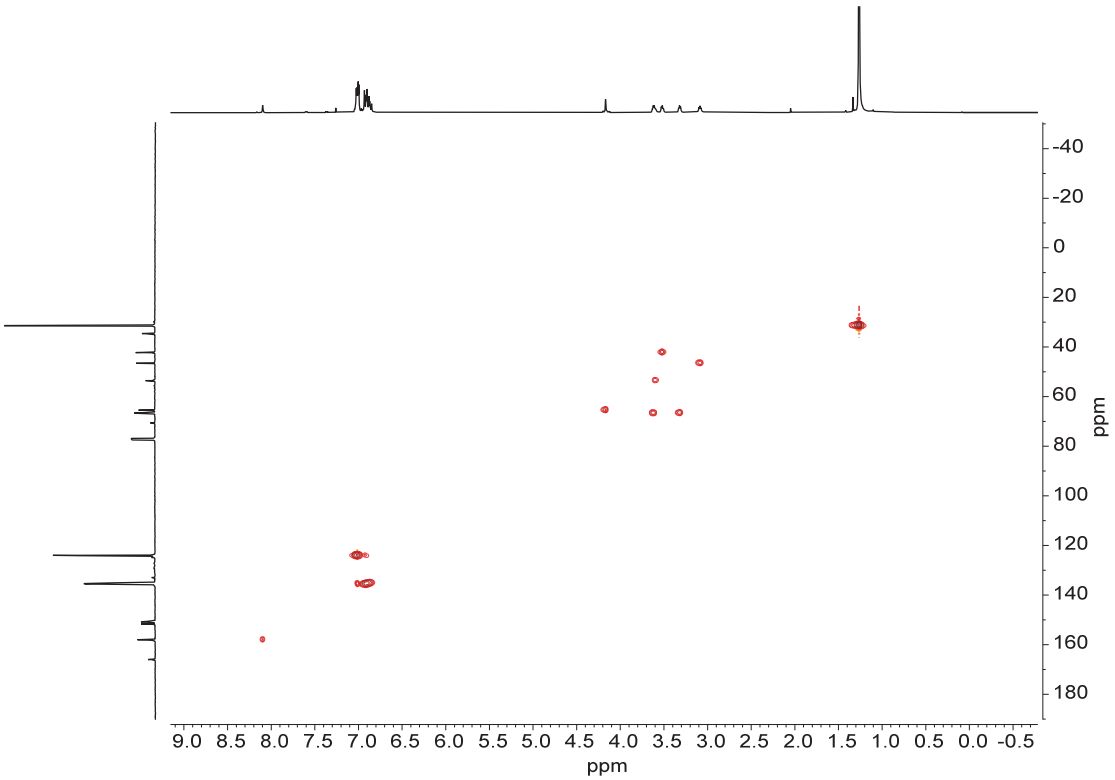
^{11}B NMR of 25, 128 M, $CDCl_3$



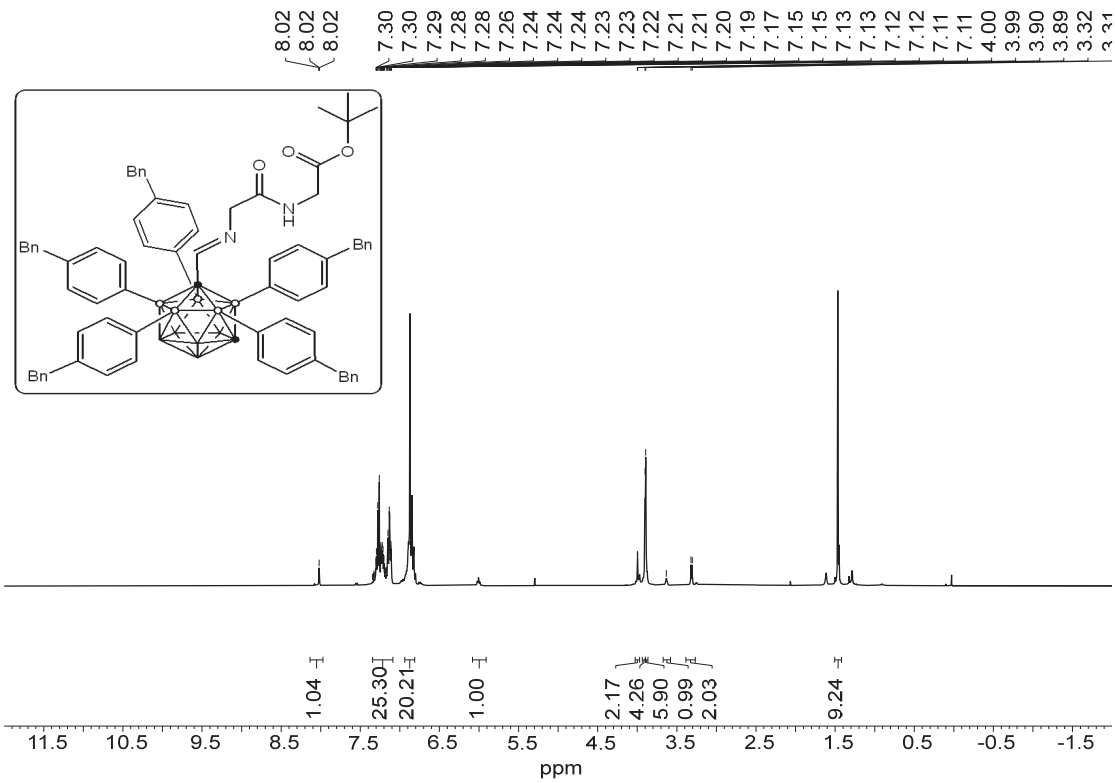
^{13}C NMR of 25, 101 M, $CDCl_3$



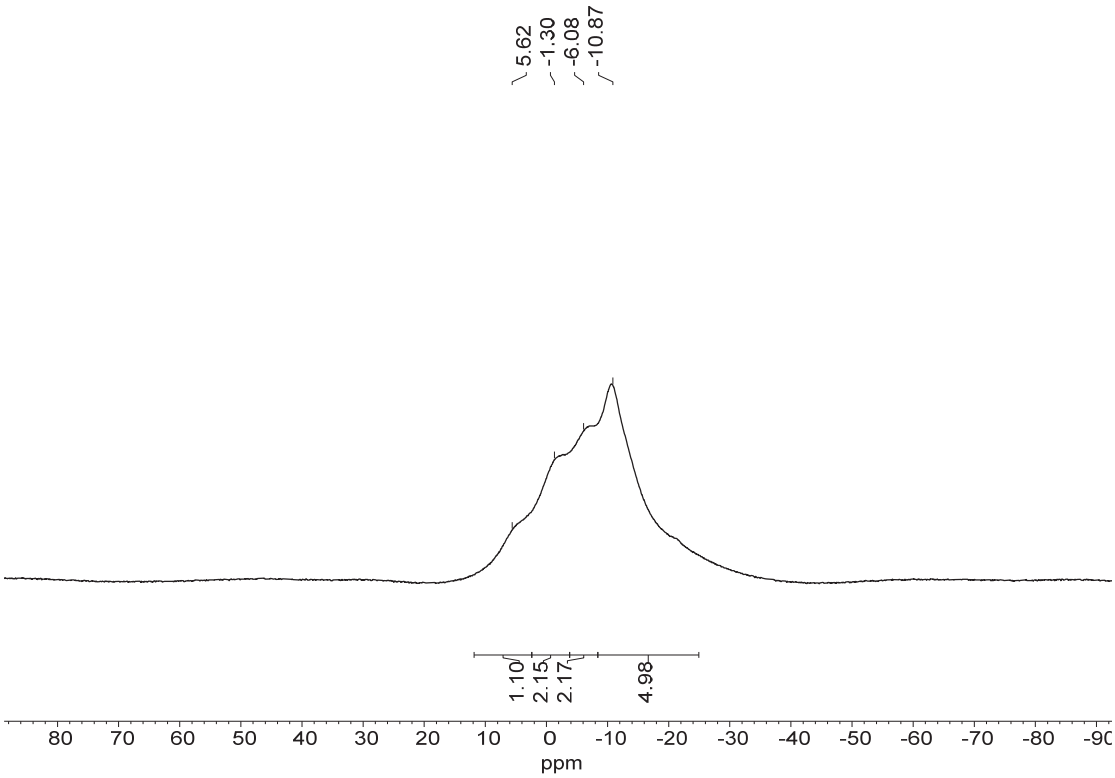
^{13}C-^{1}H HSQC of 25, 400 M, $CDCl_3$



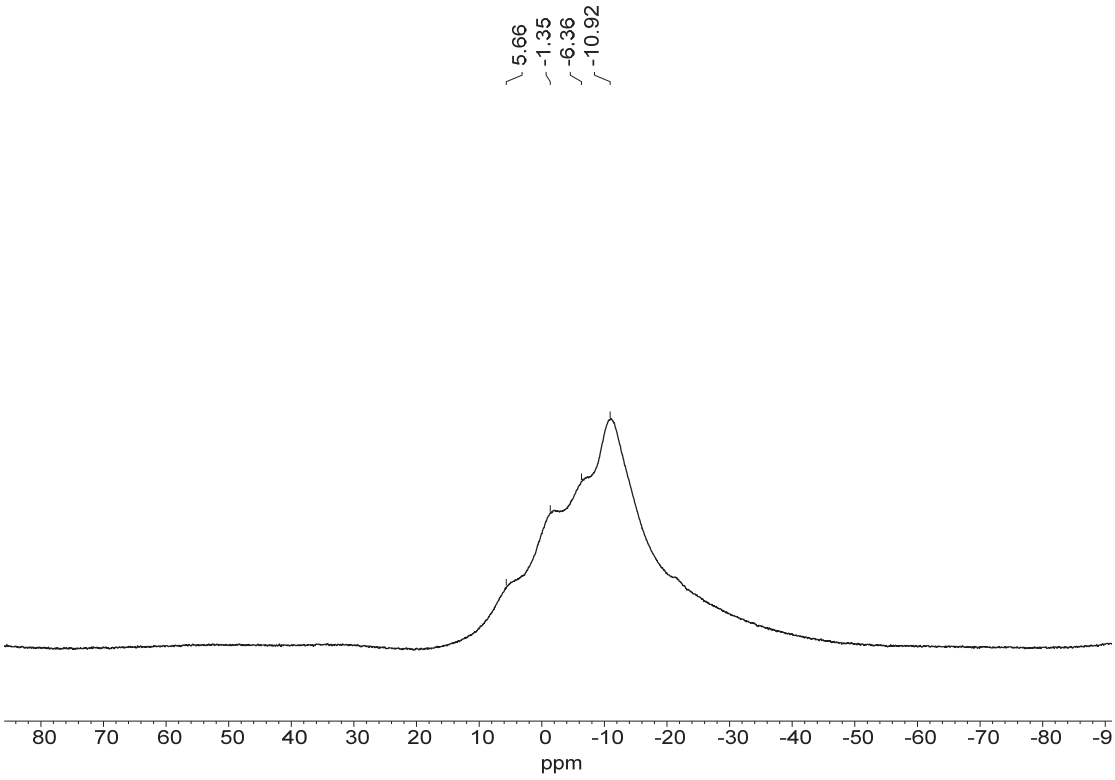
^{1}H NMR of 26, 400 M, $CDCl_3$



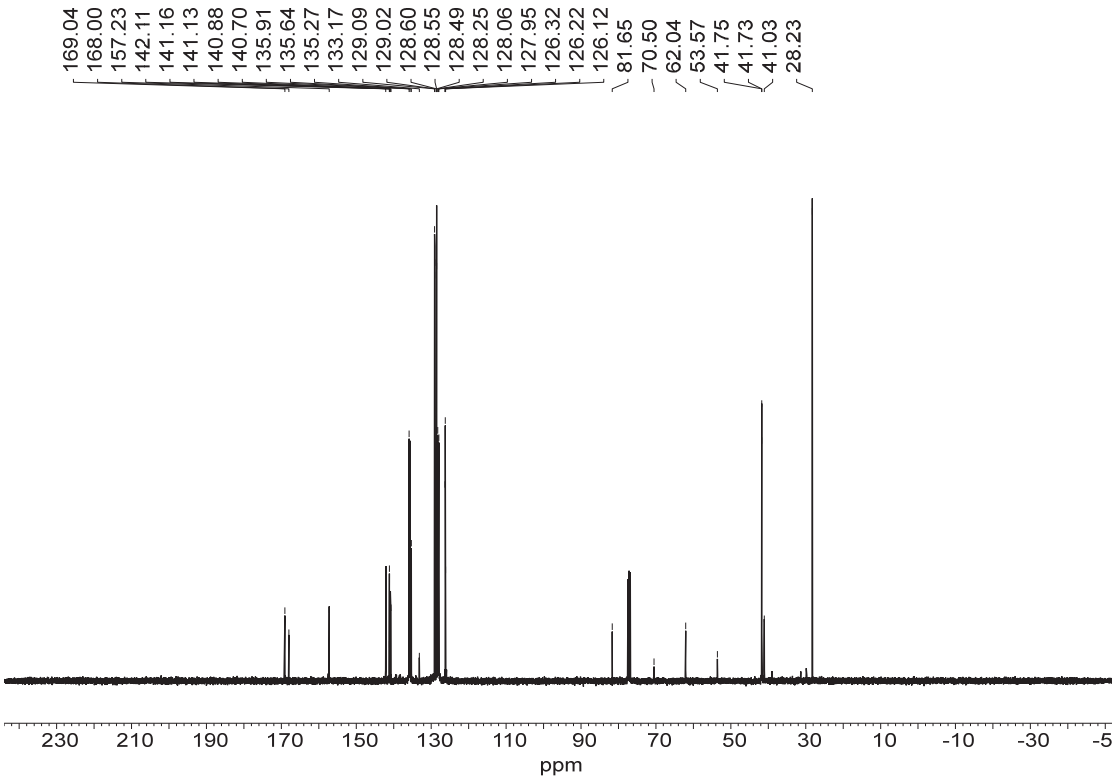
$^{11}B\ \{^{1}H\}$ NMR of 26, 128 M, $CDCl_3$



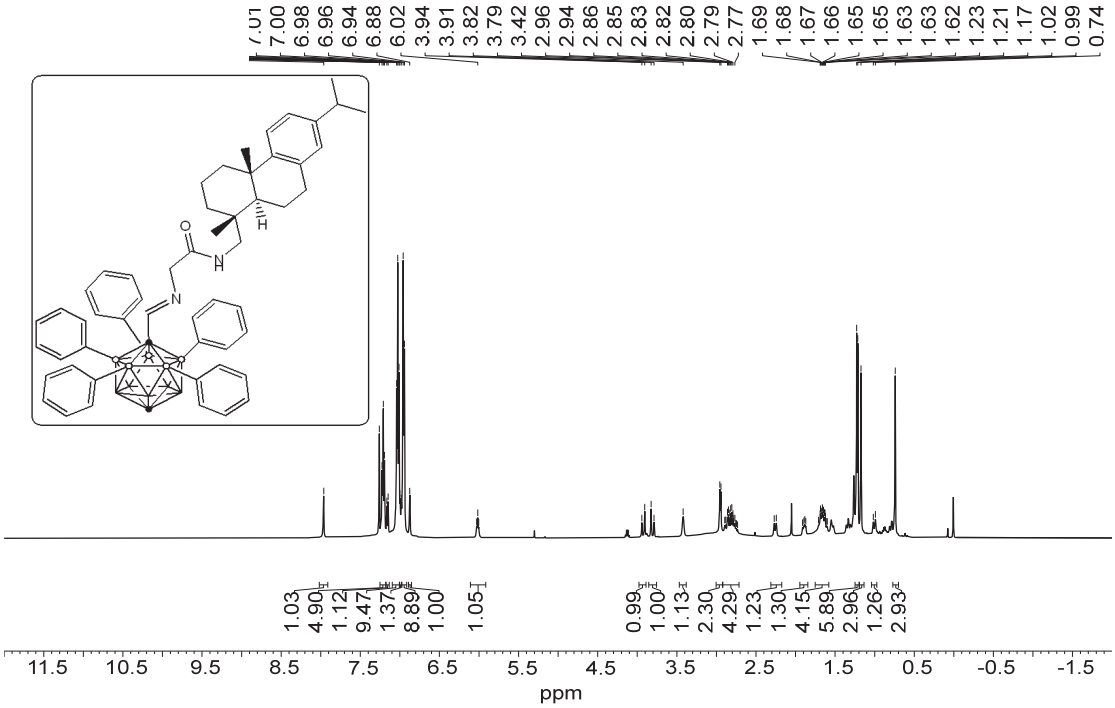
^{11}B NMR of 26, 128 M, $CDCl_3$



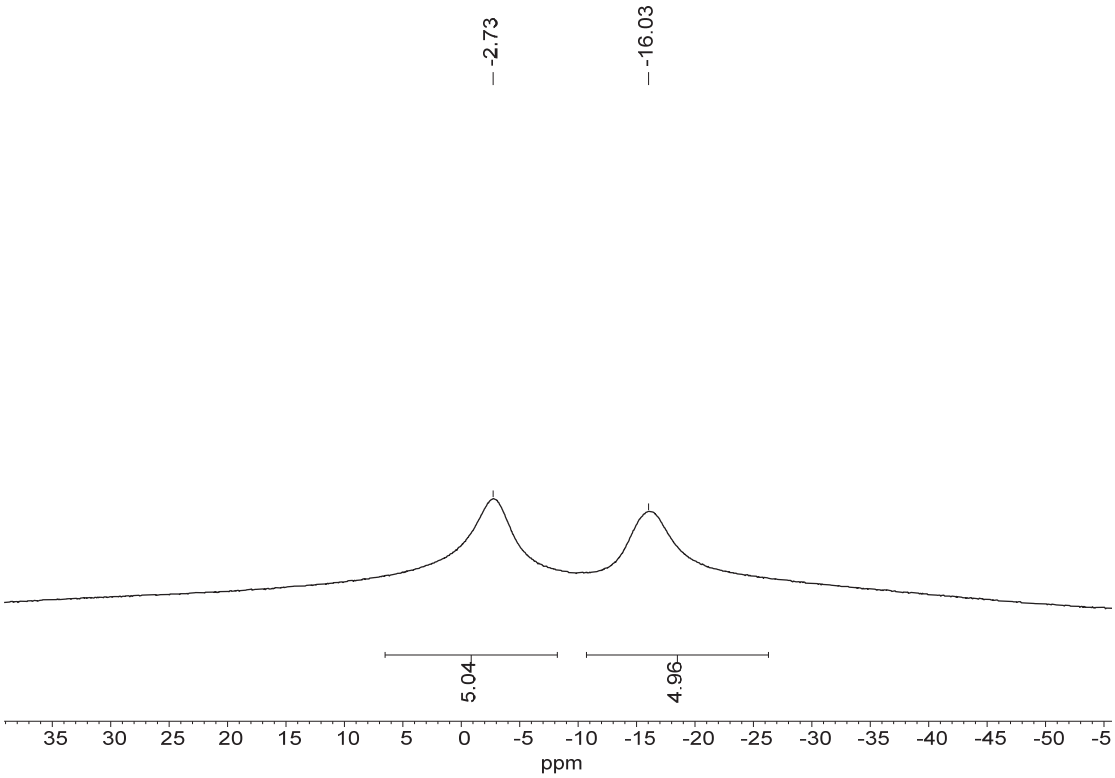
^{13}C NMR of 26, 101 M, $CDCl_3$



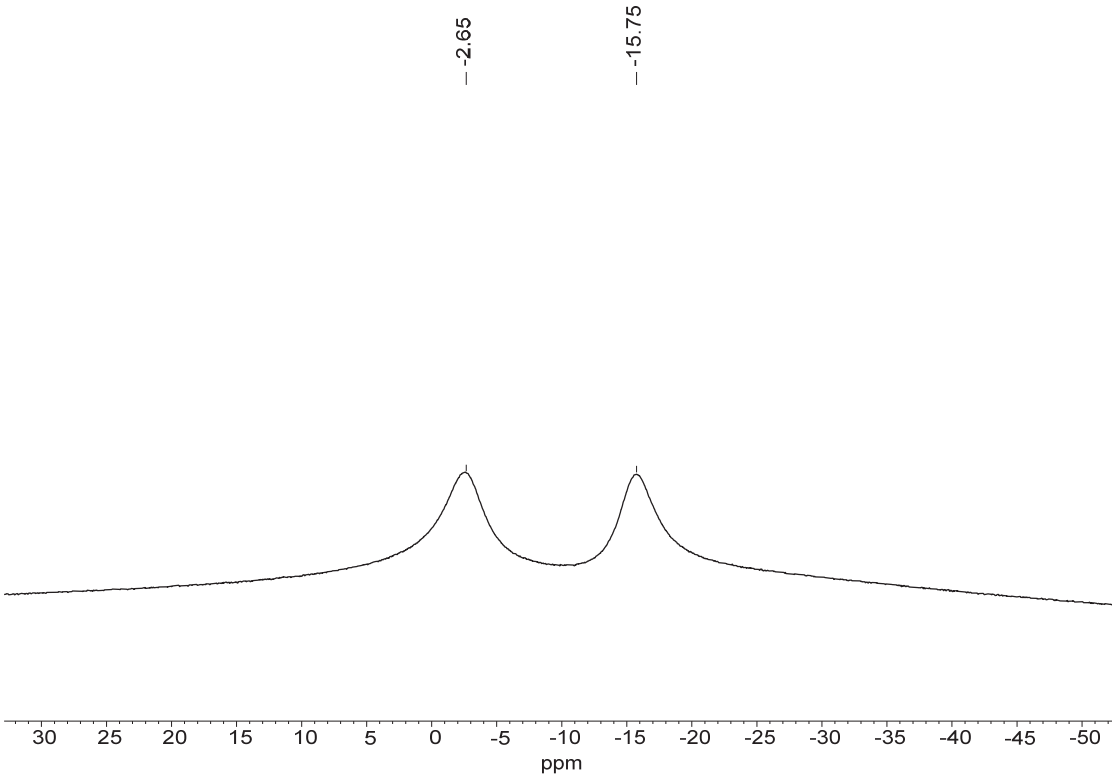
^{1}H NMR of 27, 500 M, $CDCl_3$



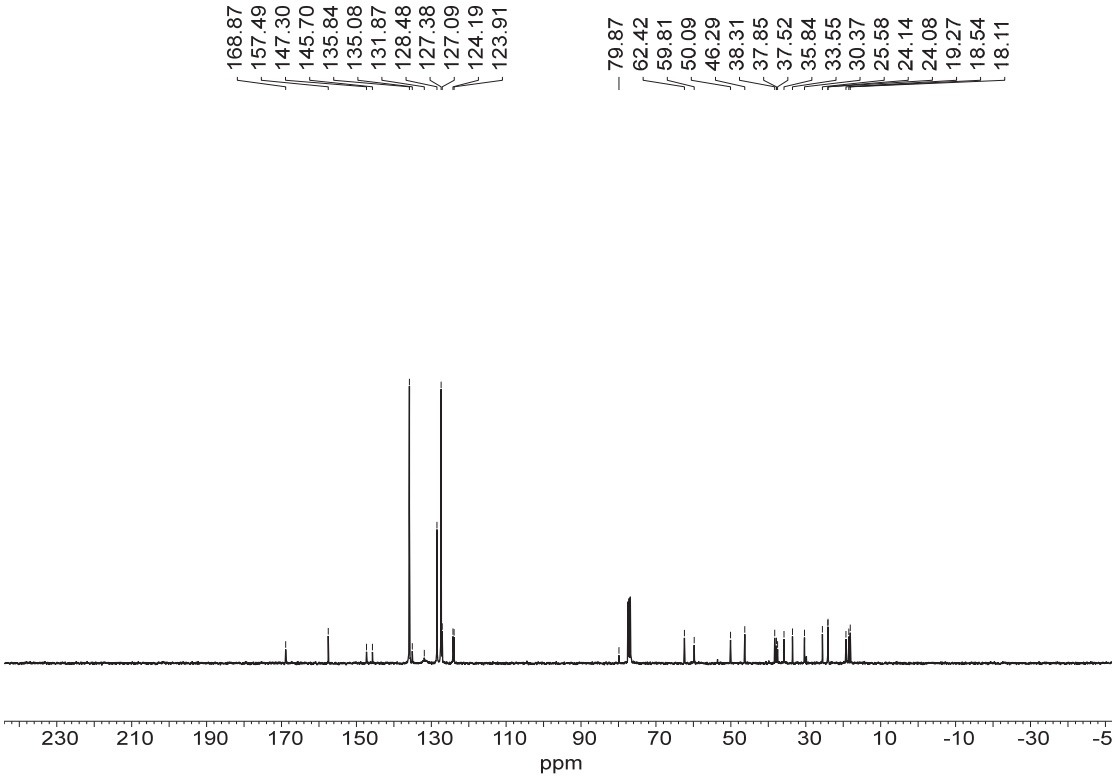
$^{11}B\ \{^{1}H\}$ NMR of 27, 128 M, $CDCl_3$



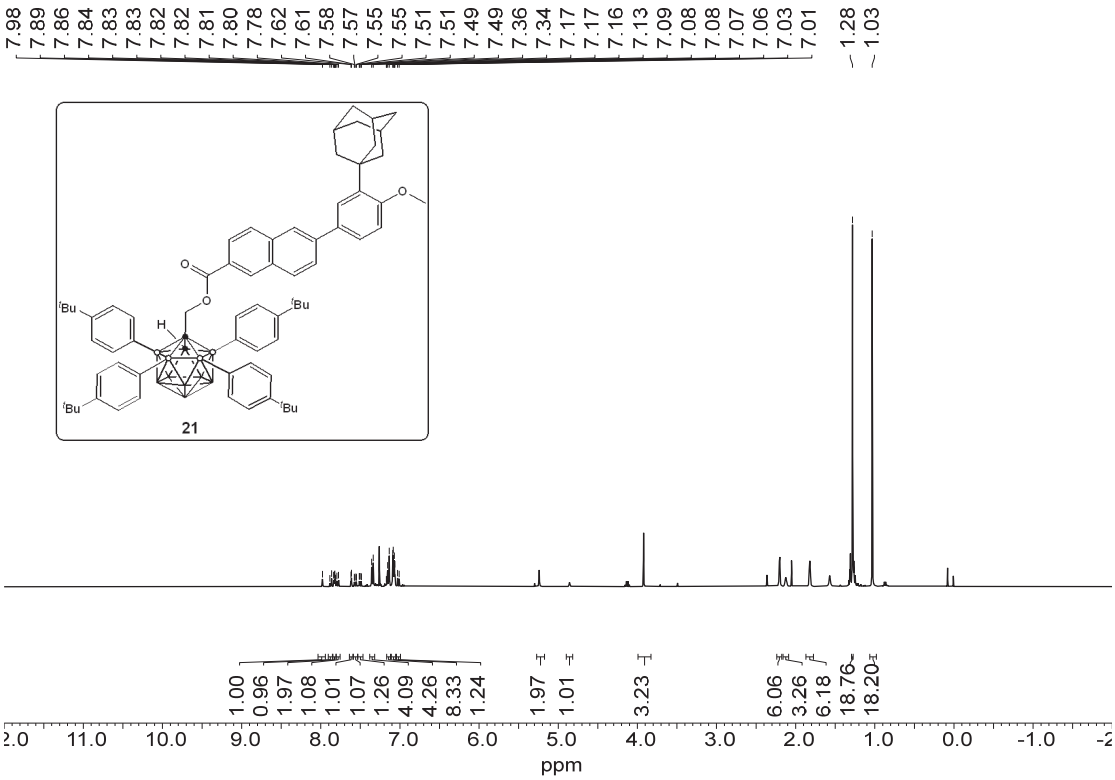
^{11}B NMR of 27, 128 M, $CDCl_3$



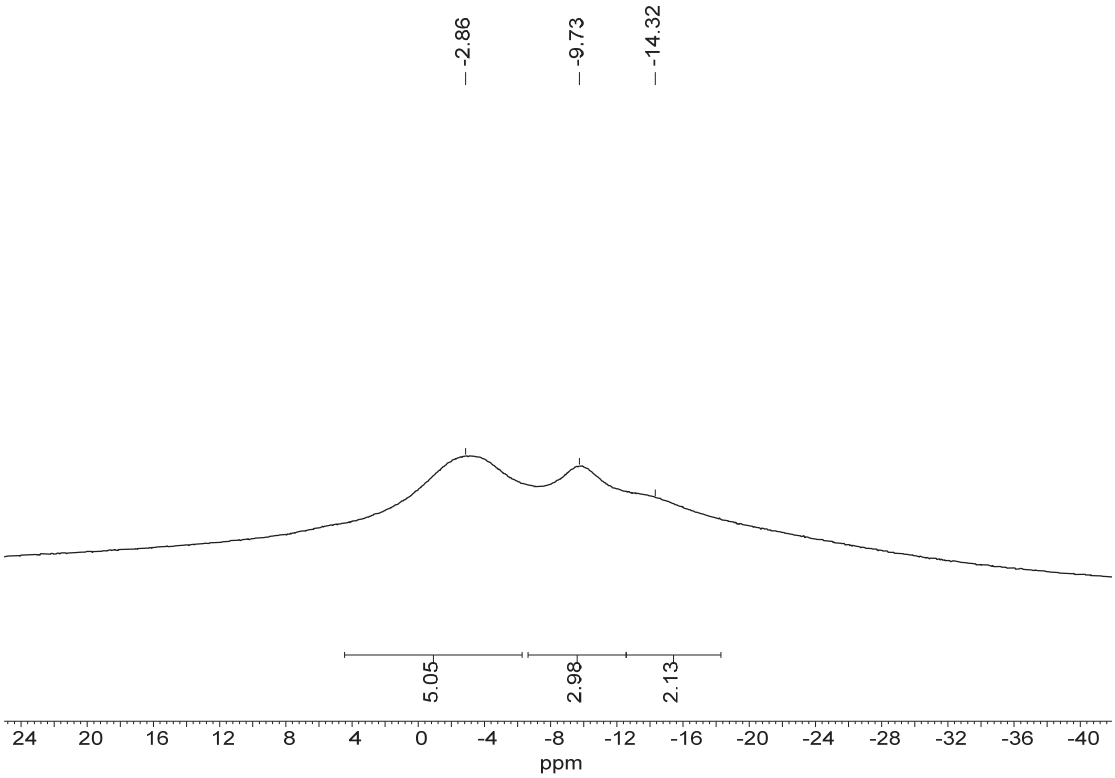
^{13}C NMR of 27, 101 M, $CDCl_3$



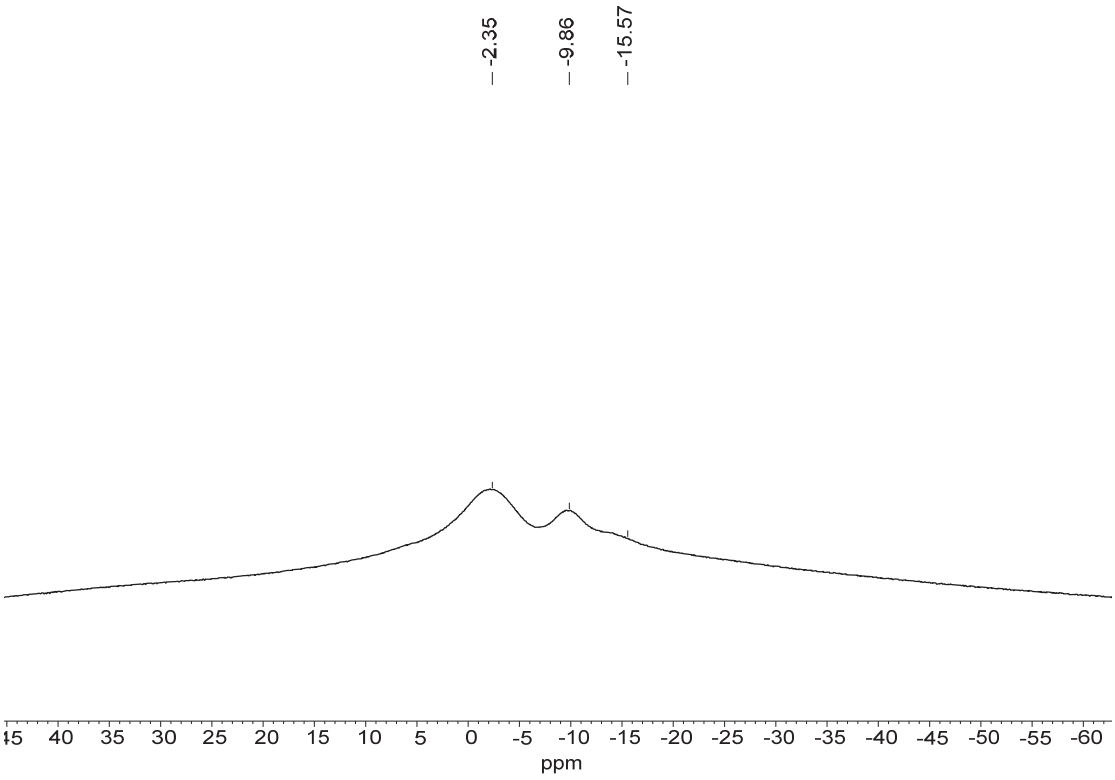
^{1}H NMR of 28, 400 M, $CDCl_3$



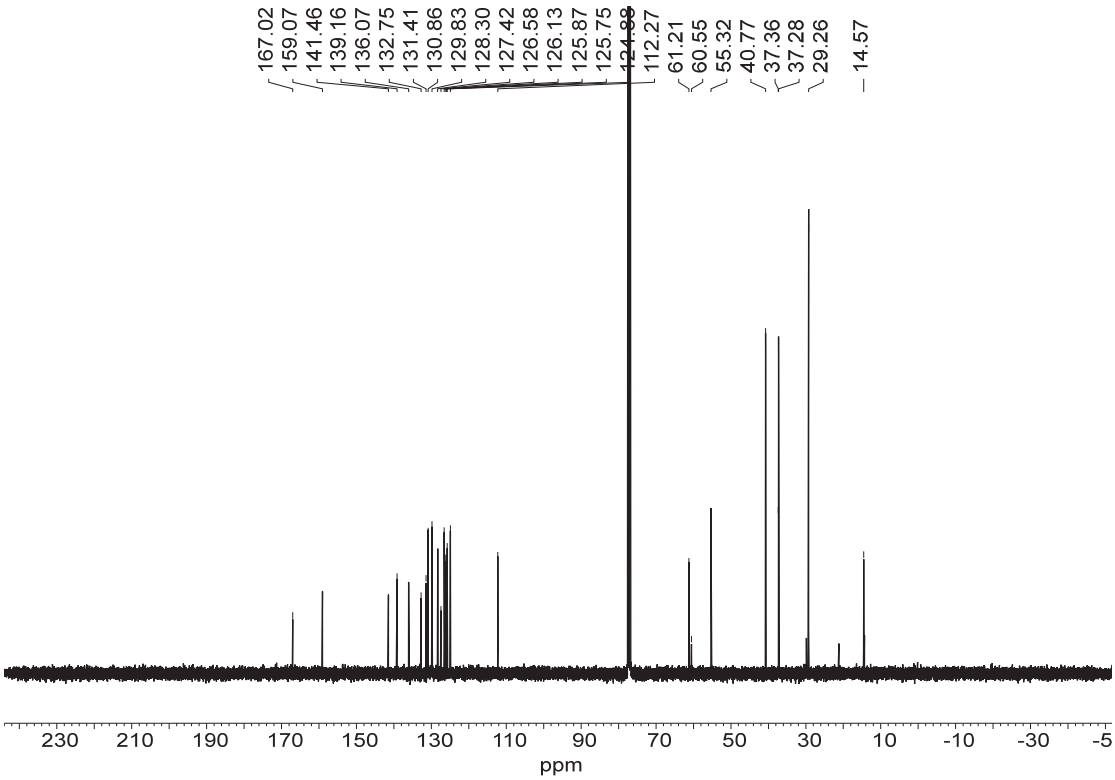
$^{11}B\ \{^{1}H\}$ NMR of 28, 128 M, $CDCl_3$



^{11}B NMR of 28, 128 M, $CDCl_3$



^{13}C NMR of 28, 101 M, $CDCl_3$



^{13}C-^{1}H HSQC of 28, 400 M, $CDCl_3$