Supplementary Information

Pd-catalysed synthesis of carborane sulfides from carborane thiols

Natsuki Minematsu,[a] Yuji Nishii*[a,b,c] and Koji Hirano*[a,b]

[a.] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

[b.] Center for Future Innovation, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

[c.] Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan.

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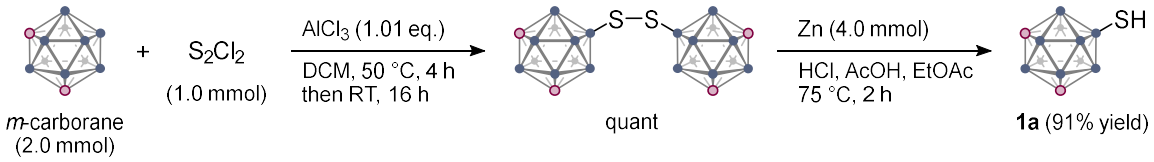
1. General Information

All manipulations were performed under N_2 using standard Schlenk techniques unless otherwise noted. Toluene and diethyl ether were purchased as dehydrated solvent and used as received. 1,2-Dimethoxyethane (DME) was distilled from CaH_2 and stored with MS 4A. 1,4-Dioxane was dried and deoxygenated by a Glass Counter Solvent Dispending System (Nikko Hansen & Co., Ltd.). Toluene, diethylether (Et_2O), dichloromethane (DCM), and 1,2-dichloroethane (DCE) were purchased as dehydrated solvent and used as received. Silica gel column chromatography was performed using Wakosil® C-200 (64~210 μm). Preparative gel permeation chromatography (GPC) was conducted with two in-line YMC-GPC T2000 preparative columns.

Nuclear magnetic resonance (NMR) spectra were measured at 400 MHz (^{1}H NMR), at 100 MHz (^{13}C{^{1}H} NMR), and at 128 MHz (^{11}B NMR) in 5 mm NMR tubes (quartz glass tubes were used for ^{11}B NMR). ^{1}H NMR chemical shifts were reported in ppm relative to the resonance of the residual solvent signals at δ 7.26 for $CDCl_3$. ^{13}C NMR chemical shifts were reported in ppm relative to the residual solvent signals at δ 77.2 for $CDCl_3$. Melting points were measured with Mettler Toledo MP90. High resolution mass spectra (HRMS) were recorded by APCI-TOF or EI-EB.

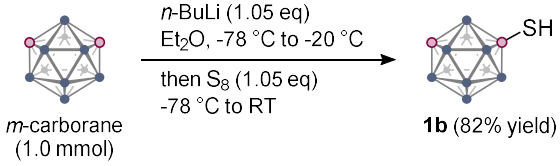
2. Preparation of Carborane Derivatives

m-Carborane-9-thiol (**1a**)



Prepared according to the literature procedure.[1] To a two-necked flask equipped with an N_2 balloon were added *m*-carborane (288 mg, 2.0 mmol), $AlCl_3$ (269 mg, 2.02 mmol), and DCM (5.0 mL). The mixture was cooled with an ice bath, and disulfur dichloride (135 mg, 1.0 mmol) was added dropwise. The yellow suspension was heated at 50 °C with an oil bath for 4 h, and the resulting orange suspension was stirred at room temperature for additional 16 h. The mixture was poured into ice water and extracted with $CHCl_3$ three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/$CHCl_3$ = 1/1) to give the corresponding disulfide (351 mg, quant). The disulfide was placed in a round-bottom flask with EtOAc (4.0 mL), AcOH (2.0 mL), and conc. HClaq (2.0 mL). The mixture was warmed to 75 °C with an oil bath, and Zn powder (262 mg, 4.0 mmol) was added portionwise. After 40 min. the resulting solution was poured into 2.0 mol/L KOHaq and washed with Et_2O. The aqueous layer was acidified with HClaq and extracted with Et_2O three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/$CHCl_3$ = 4/1) to give the title compound as white solid (215 mg, 61% yield).

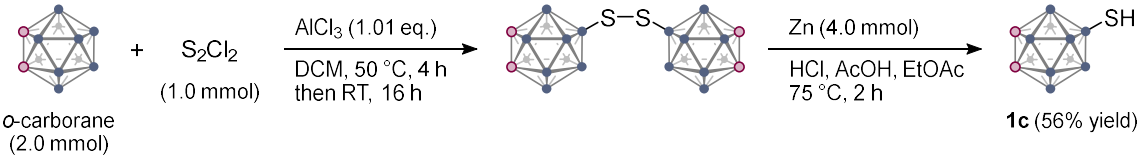
m-Carborane-1-thiol (**1b**)



To a two-necked flask equipped with an N_2 balloon were added *m*-carborane (144 mg, 1.0 mmol) and Et_2O (4.0 mL). The solution was cooled to −78 °C with dry ice bath, and *n*-BuLi (1.51 mol/L in hexane, 0.70 mL, 1.05 mmol) was added dropwise. After stirring at this temperature for 30 min, the resulting suspension was allowed to warm to −20 °C within 20 min. The mixture was again cooled to −78 °C, and S_8 (34 mg, 1.05 mmol as S) was added in one portion. The mixture was allowed to warm to room temperature and stirred for 1 h. The resulting solution was poured into NH_4Claq and extracted with $CHCl_3$ three times. The

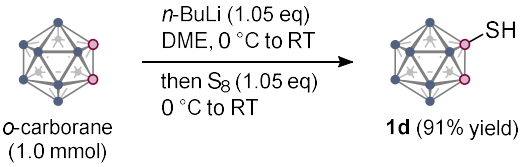
combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to give the title compound as white solid (144 mg, 82% yield).

o-Carborane-9-thiol (**1c**)



The title compound was prepared similarly to *m*-carborane-9-thiol (**1a**). After reduction using Zn powder, *o*-carborane-9-thiol (**1c**) was isolated as white solid (199 mg, 56% yield) by silica gel column chromatography ($CHCl_3$).

o-Carborane-1-thiol (**1d**)



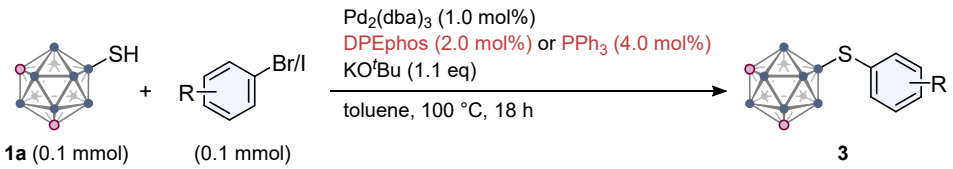
Prepared according to the literature procedure.[2] To a two-necked flask equipped with an N_2 balloon were added *o*-carborane (144 mg, 1.0 mmol) and DME (4.0 mL). The solution was cooled to 0 °C with ice bath, and *n*-BuLi (1.51 mol/L in hexane, 0.70 mL, 1.05 mmol) was added dropwise. After stirring at this temperature for 10 min, the resulting suspension was allowed to warm to room temperature within 30 min. The mixture was again cooled to 0 °C, and S_8 (34 mg, 1.05 mmol as S) was added in one portion. The mixture was allowed to warm to room temperature and stirred for 1 h. The resulting solution was poured into NH_4Claq and extracted with $CHCl_3$ three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by silica gel column chromatography ($CHCl_3$) to give the title compound as white solid (161 mg, 91% yield).

9-Iodo-*m*-carborane (**4**)

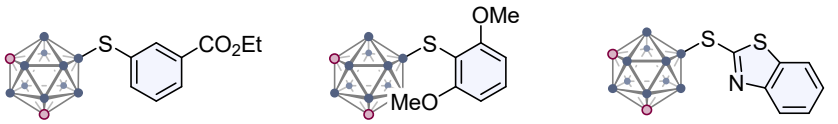
Prepared according to the literature procedure.[3]

3. Experimental Procedures and Product Identification Data

Additional Data for the Optimization Study (Table 1)



1a (0.1 mmol) (0.1 mmol) **3**

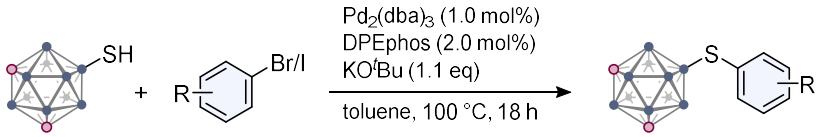


3ah (from Ar-I)
DPEphos 78%, PPh_3 22%

3al (from Ar-I)
DPEphos 78%, PPh_3 trace

3aq (from Ar-Br)
DPEphos 92%, PPh_3 90%

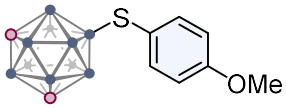
General Procedure for the Pd-Catalyzed Coupling Reaction (Scheme 2)



1a (0.1 mmol) (0.1 mmol) **3**

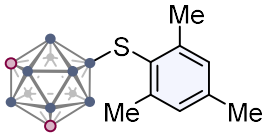
To an oven-dried Schlenk tube were added $Pd_2(dba)_3$ (0.9 mg, 1.0 mol%) and DPEphos (1.1 mg, 2.0 mol%). The tube was filled with dry N_2, and toluene (1.0 mL) was added via syringe. *m*-Carborane-9-thiol (17.6 mg, 0.1 mmol), aryl halide (0.1 mmol), and KO^{t}Bu (12.3 mg, 0.11 mmol) were added to the tube. The mixture was heated at 100 °C with aluminum heating blocks for 18 h. After cooling to room temperature, the resulting suspension was filtered through a pad of silica gel eluting with $CHCl_3$. The obtained crude material was purified by silica gel column chromatography and, if indicated, GPC.

9-(4-methoxyphenylthio)-*m*-carborane (**3aa**)



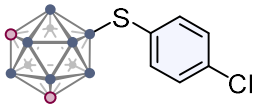
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 19.2 mg (68% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.38~1.43 (cage BH), 2.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.3, 126.3, 114.2, 55.3, 53.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 1.09 (s, 1B), -6.51 (d, J = 163.8 Hz, 2B), -9.67 (d, J = 151.5 Hz, 1B), -12.5~-14.6 (m , 4B), -17.6 (d, J = 180.2 Hz, 1B), -20.6 (d, J = 185.0 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_9H_{18}B_{10}OS$ 283.2159; Found 283.2131.

9-(2,4,6-trimethylphenylthio)-*m*-carborane (**3ab**)



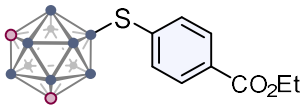
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 20.5 mg (70% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 3.39~1.36 (cage BH), 2.87 (s, 2H), 2.50 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 136.9, 131.5, 128.6, 53.8, 22.5, 21.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.81 (s, 1B), -6.45 (d, J = 164.0 Hz, 2B), -9.63 (d, J = 152.1 Hz, 1B), -12.4~-14.6 (m, 4B), -17.6 (d, J = 181.3 Hz, 1B), -20.6 (d, J = 178.4 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{22}B_{10}S$ 295.2524; Found 295.2531.

9-(4-chlorophenylthio)-*m*-carborane (**3ac**)



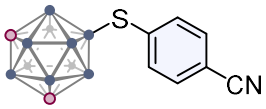
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.3 mg (81% yield), white solid, m.p. 128.0~130.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 3.40~1.44 (cage BH), 2.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.1, 133.3, 128.8, 54.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.52 (s, 1B), -6.48 (d, J = 164.4 Hz, 2B), -9.68 (d, J = 155.5 Hz, 1B), -12.5~-14.5 (m , 4B), -17.5 (d, J = 180.4 Hz, 1B), -20.4 (d, J = 181.7 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_8H_{15}B_{10}SCl$ 287.1666; Found 287.1637.

9-(4-ethoxycarbonylphenylthio)-*m*-carborane (**3ad**)



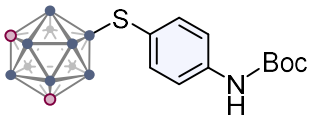
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 25.3 mg (78% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.39~1.36 (cage BH), 2.94 (s, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 141.87, 141.84, 134.46, 134.44, 129.7, 129.0, 61.0, 54.1, 14.3 (with rotamers); ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.18 (s, 1B), -6.43 (d, J = 163.8 Hz, 2B), -9.68 (d, J = 152.5 Hz, 1B), -12.4~-14.5 (m , 4B), -17.5 (d, J = 182.6 Hz, 1B), -20.3 (d, J = 181.8 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{11}H_{20}B_{10}O_2S$ 324.2193; Found 324.2191.

9-(4-cyanophenylthio)-*m*-carborane (**3ae**)



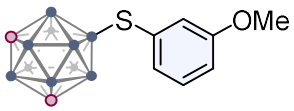
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 22.6 mg (81% yield), white solid, m.p. 112.0~114.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 3.39~1.43 (cage BH), 2.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 135.0, 132.1, 118.8, 110.5, 54.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.23 (s, 1B), -6.45 (d, *J* = 164.4 Hz, 2B), -9.74 (d, *J* = 153.1 Hz, 1B), -12.5~-14.4 (m , 4B), -17.4 (d, *J* = 183.0 Hz, 1B), -20.0 (d, *J* = 183.2 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_9H_{15}B_{10}NS$ 278.2006; Found 278.1979.

9-(4-(*N*-Boc)aminophenylthio)-*m*-carborane (**3af**)



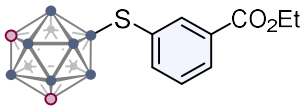
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 20.0 mg (54% yield), colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.32~7.24 (m, 2H), 6.46 (s,1H), 3.40~1.32 (cage BH), 2.90 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 137.6, 135.8, 129.1, 118.6, 80.6, 53.9, 28.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.92 (s, 1B), -6.51 (d, *J* = 164.9 Hz, 2B), -9.70 (d, *J* = 152.3 Hz, 1B), -12.5~-14.7 (m, 4B), -17.6 (d, *J* = 180.9 Hz, 1B), -20.6 (d, *J* = 178.5 Hz, 1B); HRMS (APCI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{25}B_{10}NO_2S$ 367.2616; Found 367.2613.

9-(3-methoxyphenylthio)-*m*-carborane (**3ag**)



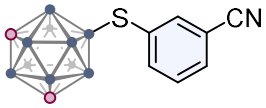
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 22.7 mg (80% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.12~7.08 (m, 2H), 6.80 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.80 (s, 3H), 3.41~1.41 (cage BH), 2.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 136.5, 129.4, 127.3, 120.0, 113.3, 55.3, 54.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.68 (s, 1B), -6.46 (d, *J* = 163.1 Hz, 2B), -9.66 (d, *J* = 152.2 Hz, 1B), -12.4~-14.6 (m , 4B), -17.6 (d, *J* = 180.7 Hz, 1B), -20.5 (d, *J* = 180.2 Hz, 1B); HRMS (APCI) *m/z*: $[M]^+$ Calcd for $C_9H_{18}B_{10}OS$ 282.2087; Found 282.2078.

9-(3-ethoxycarbonylphenylthio)-*m*-carborane (**3ah**)



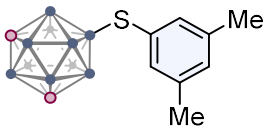
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 25.3 mg (78% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.42~1.43 (cage BH), 2.93 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 139.4, 136.1, 135.9, 131.0, 128.6, 128.3, 61.1, 54.1, 14.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.51 (s, 1B), -6.44 (d, *J* = 165.6 Hz, 2B), -9.66 (d, *J* = 150.0 Hz, 1B), -12.4~-14.5 (m , 4B), -17.5 (d, *J* = 181.1 Hz, 1B), -20.4 (d, *J* = 176.4 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{20}B_{10}O_2S$ 325.2266; Found 325.2256.

9-(3-cyanophenylthio)-*m*-carborane (**3ai**)



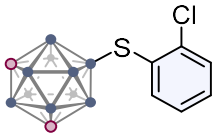
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.6 mg (85% yield), pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 3.43~1.39 (cage BH), 2.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.2, 127.3, 130.7, 129.4, 118.5, 112.8, 54.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.09 (s, 1B), -6.48 (d, *J* = 166.3 Hz, 2B), -9.72 (d, *J* = 152.3 Hz, 1B), -12.5~-14.4 (m, 4B), -17.4 (d, *J* = 181.9 Hz, 1B), -20.2 (d, *J* = 180.1 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_9H_{15}B_{10}NS$ 279.1967; Found 279.1975.

9-(3,5-dimethylphenylthio)-*m*-carborane (**3aj**)



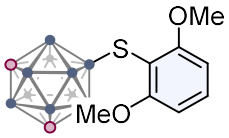
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 21.4 mg (76% yield), white solid, 108.5~110.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 2H), 6.80 (s, 1H), 3.37~1.32 (cage BH), 2.83 (s, 2H), 2.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 134.7, 132.6, 128.8, 53.9, 21.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.81 (s, 1B), -6.45 (d, *J* = 164.0 Hz, 2B), -9.63 (d, *J* = 152.1 Hz, 1B), -12.4~-14.6 (m , 4B), -17.6 (d, *J* = 181.3 Hz, 1B), -20.6 (d, *J* = 178.4 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{20}B_{10}S$ 282.2328; Found 282.2313.

9-(2-chlorophenylthio)-*m*-carborane (**3ak**)



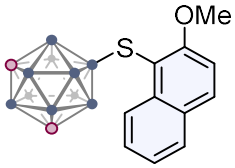
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.7 mg (82% yield), white solid, 61.0~62.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.22~7.15 (m, 2H), 3.36~1.38 (cage BH), 2.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.0, 134.7, 129.7, 128.8, 126.8, 54.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.17 (s, 1B), -6.45 (d, *J* = 163.5 Hz, 2B), -9.72 (d, *J* = 150.6 Hz, 1B), -12.5~-14.6 (m , 4B), -17.6 (d, *J* = 180.4 Hz, 1B), -20.4 (d, *J* = 181.5 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_8H_{15}B_{10}SCl$ 288.1626; Found 288.1610.

9-(2,6-dimethoxyphenylthio)-*m*-carborane (**3al**)



Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 16.6 mg (53% yield), white solid (single crystals suitable for X-ray analysis were obtained by pentane vapor diffusion into the $CHCl_3$ solution), m.p. 162.1~164.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 6H), 3.35~1.38 (cage BH), 2.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 128.9, 111.5, 103.7, 55.9, 53.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.22 (s, 1B), -6.52 (d, *J* = 166.1 Hz, 2B), -9.65 (d, *J* = 150.5 Hz, 1B), -12.5~-15.0 (m, 4B), -18.0 (d, *J* = 180.0 Hz, 1B), -20.9 (d, *J* = 162.3 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{20}B_{10}O_2S$ 313.2266; Found 313.2278.

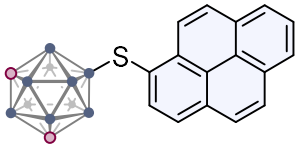
9-(2-methoxy-1-naphthalenylthio)-*m*-carborane (**3am**)



Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 26.6 mg (80% yield), white solid, m.p. 179.2~181.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.76 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.52 (m, 1H), 7.34 (m, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 4.01 (s, 3H), 3.27~1.43 (cage BH), 2.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 136.7, 129.6, 129.3, 127.9, 126.7, 126.4, 123.6, 117.6, 112.7, 56.3, 53.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.29 (s, 1B), -6.54 (d, *J* = 162.8 Hz, 2B), -9.71 (d, *J* = 150.1 Hz, 1B), -12.5~-14.9 (m, 4B), -17.9 (d, *J* = 178.2 Hz, 1B), -20.9 (d, *J* = 180.0 Hz, 1B);

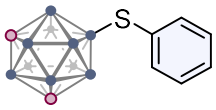
HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 332.2245; Found 332.2245.

9-(1-pyrenylthio)-*m*-carborane (**3an**)



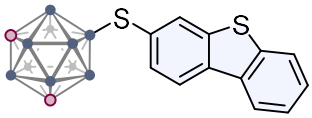
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 33.1 mg (88% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 9.2 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.16~8.12 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.05~7.96 (m, 3H), 3.42-1.43 (cage BH), 2.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7 133.6, 131.2, 131.1, 131.0, 127.7, 127.6, 127.3, 126.6, 126.0, 125.3, 125.2, 125.1, 124.8, 124.5, 53.8 (1 peak overlapped); ^{11}B NMR (128 MHz, $CDCl_3$) δ 1.02 (s, 1B), -6.49 (d, *J* = 165.1 Hz, 2B), -9.68 (d, *J* = 154.5 Hz, 1B), -12.5~-14.7 (m, 4B), -17.7 (d, *J* = 182.8 Hz, 1B), -20.7 (d, *J* = 177.9 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{20}B_{10}S$ 376.2298; Found 376.2297.

9-(phenylthio)-*m*-carborane (**3ao**)



Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 24.6 mg (97% yield), white solid, m.p. 83.0~84.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53~7.51 (m, 2H), 7.91~7.24 (m, 3H), 3.40~1.42 (cage BH), 2.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.51, 135.50, 135.07, 135.06, 128.7, 127.1, 54.0 (with rotamers); ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.79 (s, 1B), -6.46 (d, *J* = 163.8 Hz, 2B), -9.64 (d, *J* = 150.5 Hz, 1B), -12.4~-14.6 (m, 4B), -17.6 (d, *J* = 181.0 Hz, 1B), -20.5 (d, *J* = 180.7 Hz, 1B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_8H_{16}B_{10}S$ 253.2053; Found253.2036.

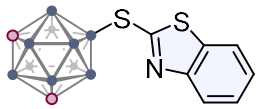
9-(dibenzo[*b,d*]thiophene-3-thio)-*m*-carborane (**3ap**)



Conducted with 3-bromodibenzothiophene (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%). Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 33.8 mg (94% yield), white solid, m.p. 100.2~102.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.15~8.13 (m, 1H), 7.84~7.82 (m, 1H),

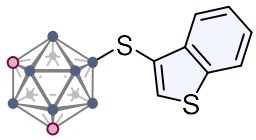
7.74 (d, J = 8.2 Hz, 1H), 7.60 (dd, J = 8.3, 1. 6 Hz, 1H), 7.46~7.44 (m, 2H), 3.35~1.40 (cage BH), 2.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.5, 136.2, 135.2, 133.6, 131.5, 128.1, 126.9, 124.5, 122.9, 121.7, 54.0 (1 peak overlapped); ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.91 (s, 1B), -6.44 (d, J = 165.2 Hz, 2B), -9.60 (d, J = 151.5 Hz, 1B), -12.4~-14.6 (m, 4B), -17.5 (d, J = 182.6 Hz, 1B), -20.5 (d, J = 182.1 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 358.1861; Found 358.1849.

9-(benzo[*d*]thiazole-2-thio)-*m*-carborane (**3aq**)



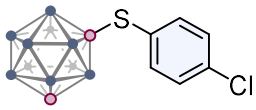
Conducted with 2-bromobenzothiazole (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%). Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 28.5 mg (92% yield), white solid, m.p. 127.5~128.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.1, 0.4 Hz, 1H), 7.77 (dd, J = 8.0, 0.6 Hz, 1H), 7.43 (td, J = 7.8, 1.2 Hz, 1H), 7.34 (td, J = 8.0, 1.2 Hz, 1H), 3.47~1.48 (cage BH), 3.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 137.3, 125.9, 124.9, 122.6, 120.9, 54.4 (1 peak overlapped); ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.33 (s, 1B), -6.02 (d, J = 166.7 Hz, 2B), -9.61 (d, J = 153.9 Hz, 1B), -12.2~-14.4 (m, 4B), -17.3 (d, J = 182.0 Hz, 1B), -19.5 (d, J = 183.3 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 309.1655; Found 309.1669.

9-(benzo[*b*]thiophene-3-thio)-*m*-carborane (**3ar**)



Conducted with 3-bromobenzo[*b*]thiophene (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%). Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 28.1 mg (91% yield), pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.55 (s, 1H), 7.43 (td, J = 7.1, 1.1 Hz, 1H), 7.36 (td, J = 7.5, 1.2 Hz, 1H), 3.31~1.35 (cage BH), 2.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.5, 130.1, 126.8, 124.5, 124.2, 123.6, 122.6, 54.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.43 (s, 1B), -6.42 (d, J = 165.6 Hz, 2B), -9.59 (d, J = 152.6 Hz, 1B), -12.4~-14.7 (m, 4B), -17.7 (d, J = 181.4 Hz, 1B), -20.6 (d, J = 178.6 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 308.1703; Found 308.1704.

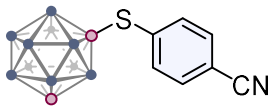
1-(4-chlorophenylthio)-*m*-carborane (**3bc**)



Conducted with *m*-carborane-1-thiol (**1b**, 0.1 mmol), 1-chloro-4-iodobenzene (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%).

Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 28.4 mg (99% yield), white solid, m.p. 144.6~145.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 3.46~1.40 (cage BH), 2.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.6, 129.6, 73.8, 55.6 (1 peak overlapped); ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.33 (s, 1B), -6.02 (d, J = 166.7 Hz, 2B), -9.61 (d, J = 153.9 Hz, 1B), -12.2~-14.4 (m, 4B), -17.3 (d, J = 182.0 Hz, 1B), -19.5 (d, J = 183.3 Hz, 1B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 287.1564; Found 287.1567.

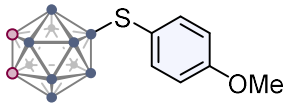
1-(4-cyanophenylthio)-*m*-carborane (**3be**)



Conducted with *m*-carborane-1-thiol (**1b**, 0.1 mmol), 1-cyano-4-iodobenzene (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%).

Purified by GPC (EtOAc), 14.0 mg (50% yield), white solid, m.p. 153.5~154.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 3.49~1.27 (cage BH), 2.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.6, 132.8, 117.8, 114.7, 72.6, 55.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.47 (d, J = 167.9 Hz, 1B), -8.71~-15.5 (m, 9B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 277.1933; Found 277.1932.

9-(4-methoxyphenylthio)-*o*-carborane (**3ca**)

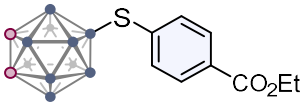


Conducted with *o*-carborane-9-thiol (**1c**, 0.1 mmol), 1-iodo-4-methoxybenzene (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%).

Purified by silica gel column chromatography (hexane/EtOAc = 2/1), 25.2 mg (89% yield), white solid, m.p. 140.2~140.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.50 (s, 1H), 3.41 (s, 1H), 3.10~1.19 (cage BH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 136.3,

126.3, 114.1, 55.2, 52.6, 47.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 7.80 (s, 1B), -2.28 (d, J = 146.2 Hz, 1B), -8.62 (d, J = 151.8 Hz, 2B), -13.3~-16.3 (m, 6B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 282.2087; Found 282.2083.

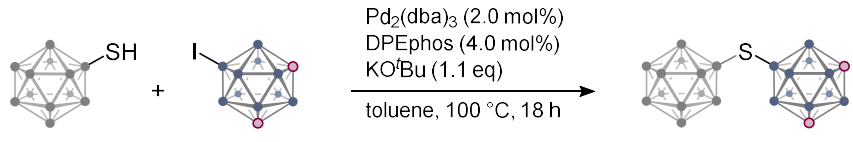
9-(4-ethoxycarbonylphenylthio)-*o*-carborane (**3ca**)



Conducted with *o*-carborane-9-thiol (**1c**, 0.1 mmol), ethyl 4-iodobenzoate (0.15 mmol), $Pd_2(dba)_3$ (2.0 mol%), and DPEphos (4.0 mol%).

Purified by silica gel column chromatography (hexane/EtOAc = 2/1), 24.2 mg (75% yield), white solid, m.p. 140.5~141.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 3.55 (s, 1H), 3.46 (s, 1H), 3.15~1.16 (cage BH), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.9, 134.4, 129.6, 128.8, 60.9, 52.8, 47.9, 14.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 7.03 (s, 1B), -2.21 (d, J = 153.6 Hz, 1B), -8.60 (d, J = 152.6 Hz, 2B), -13.3~-16.2 (m, 6B); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 324.2193; Found 324.2190.

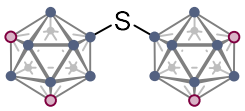
General Procedure for the di(carboranyl) sulfide synthesis (Scheme 3)



1a, 1b, 1d (0.1 mmol) **4** (0.15 mmol) **5a, 5b, 5d**

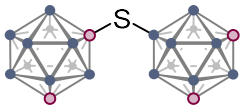
To an oven-dried Schlenk tube were added $Pd_2(dba)_3$ (1.8 mg, 2.0 mol%) and DPEphos (2.2 mg, 4.0 mol%). The tube was filled with dry N_2, and toluene (1.0 mL) was added via syringe. Carborane thiol (17.6 mg, 0.1 mmol), 9-iodo-*m*-carborane (40.5 mg, 0.15 mmol), and KO^{t}Bu (12.3 mg, 0.11 mmol) were added to the tube. The mixture was heated at 100 °C with aluminum heating blocks for 18 h. After cooling to room temperature, the resulting suspension was filtered through a pad of silica gel eluting with $CHCl_3$. The obtained crude material was purified by silica gel column chromatography and, if indicated, GPC.

di(9-*m*-carboranyl) sulfide (**5a**)



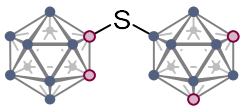
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 142.2 mg (89% yield), white solid (single crystals suitable for X-ray analysis were obtained by slow evaporation from the $CHCl_3$ solution), m.p. 174.5~176.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36~1.46 (cage BH), 2.91 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.06 (s, 2B), -6.12 (d, J = 163.4 Hz, 4B), -9.47 (d, J = 151.4 Hz, 2B), -12.2~-14.9 (m, 8B), -17.9 (d, J = 181.3 Hz, 2B), -20.9 (d, J = 180.0 Hz, 2B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_4H_{22}B_{20}S$ 319.3525; Found 319.3536.

(1-*m*-carboranyl) (9-*m*-carboranyl) sulfide (**5b**)



Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 60.1 mg (94% yield), white solid, m.p. 190.4~191.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86~1.38 (cage BH), 2.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 71.3, 55.4, 54.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.80~-19.8 (m, 20B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_4H_{22}B_{20}S$ 319.3525; Found 319.3548.

(1-*o*-carboranyl) (9-*m*-carboranyl) sulfide (**5d**)



Purified by GPC (EtOAc), 21.7 mg (68% yield), white solid (single crystals suitable for X-ray analysis were obtained by slow evaporation from the $CHCl_3$ solution), m.p. 167.6~169.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 1H), 3.67~1.02 (cage BH), 2.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.3, 67.9, 54.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.24~-19.3 (m, 20B); HRMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_4H_{22}B_{20}S$ 319.3524; Found 319.3510.

General Procedure for the Aromatic Halogenation (Scheme 5b)

To a screw-top glass tube were added substrate (0.2 mmol), **5b**, and $AgSbF_6$. Solvent (1.0 mL) was added via syringe, and *N*-halosuccinimide was added to the mixture in one portion. The tube was sealed with a cap and stirred under the indicated conditions. The resulting mixture was poured into aqueous $NaHCO_3$/$Na_2S_2O_3$ solution (if the substrate has acid functionality, $NaHCO_3$ was not used), and extracted with $CHCl_3$ three times. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by silica-gel column chromatography and/or GPC. Analytical data of the

halogenation products were identical to those of reported in our previous study.[4]

1-Bromo-4-fluoro-2-methyl-5-nitrobenzene (**6b**)

Reaction conditions: substrate (0.2 mmol), NBS (0.4 mmol), **5b** (5.0 mol%), and $AgSbF_6$ (5.0 mol%) in $MeNO_2$ (1.0 mL), 80 °C, 18 h. Purified by silica gel column chromatography (hexane/EtOAc = 20/1), colorless oil (42.3 mg, 80% yield).

2-Bromo-1,3,5-trichlorobenzene (**6c**)

Reaction conditions: substrate (0.2 mmol), NBS (0.4 mmol), **5b** (5.0 mol%), and $AgSbF_6$ (5.0 mol%) in $MeNO_2$ (1.0 mL), 80 °C, 18 h. Purified by silica gel column chromatography (hexane), white solid (44.4 mg, 85% yield).

4-Bromophenyl acrylate (**6d**)

Reaction conditions: substrate (0.2 mmol), NBS (0.24 mmol), **5b** (5.0 mol%), and $AgSbF_6$ (5.0 mol%) in DCE (1.0 mL), 60 °C, 18 h. Purified by silica gel column chromatography (hexane/EtOAc = 10/1), white solid (38.0 mg, 84% yield).

2-((4-bromophenoxy)methyl)oxirane (**6e**)

Reaction conditions: substrate (0.2 mmol), NBS (0.4 mmol), **5b** (5.0 mol%), and $AgSbF_6$ (5.0 mol%) in DCE (1.0 mL), room temp., 18 h. Purified by silica gel column chromatography (hexane/EtOAc = 3/1), colorless oil (42.6 mg, 99% yield).

Ciprofibrate-Cl (**6f**)

Reaction conditions: Ciprofibrate (0.2 mmol), NCS (0.2 mmol), **5b** (2.0 mol%), and $AgSbF_6$ (2.0 mol%) in DCE (1.0 mL), 60 °C, 18 h. Purified by GPC (EtOAc), colorless oil (47.5 mg, 73% yield).

Flurbiprofen-Br (**6g**)

Reaction conditions: Flurbiprofen (0.2 mmol), NBS (0.2 mmol), **5b** (2.0 mol%), and $AgSbF_6$ (2.0 mol%) in DCE (1.0 mL), 60 °C, 18 h. Purified by GPC (EtOAc), white solid (57.3 mg, 89% yield), m.p. = 140.4-141.6 °C.

Clofibrate-I (**6h**)

Reaction conditions: Clofibrate (0.2 mmol), NIS (0.2 mmol), **5b** (2.0 mol%), and $AgSbF_6$ (2.0 mol%) in DCE (1.0 mL), 60 °C, 18 h. Purified by GPC (EtOAc), colorless oil (51.0 mg, 69% yield).

4. X-ray Crystallographic Analysis

Single crystal X-ray diffraction analysis was conducted with RIGAKU XtaLAB Synergy-S system. Crystal structures were refined by full-matrix least-squares method using SHELXL-2016/6.[5] Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. ORTEP-3 program was used to draw the molecule.[6] These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk.

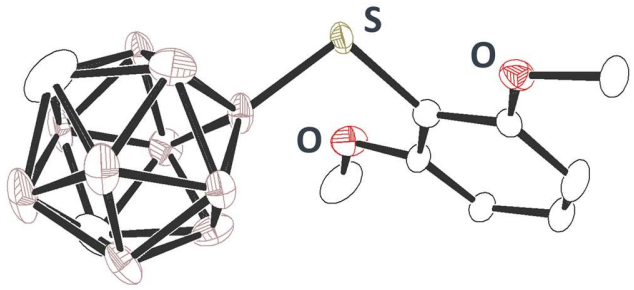


Figure S1. ORTEP drawing for **3al** with 40% thermal ellipsoid.

Table S1. Selected crystal data for **3al**

CCDC No.	2369107 [7]
Crystal system	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$ (No. 19)
Unit cell parameter [Å, deg]	a = 8.7117(2)
	b = 7.2609(2)
	c = 26.2516(7)
Cell volume [Å^3]	1660.54(7)
Z	4
R factor ($I > 2.0\sigma(I)$)	$R1$ = 0.0880, $wR2$ = 0.2467
R factor (all data)	$R1$ = 0.0996, $wR2$ = 0.2553
Rint	0.0940
Goodness of fit	1.762

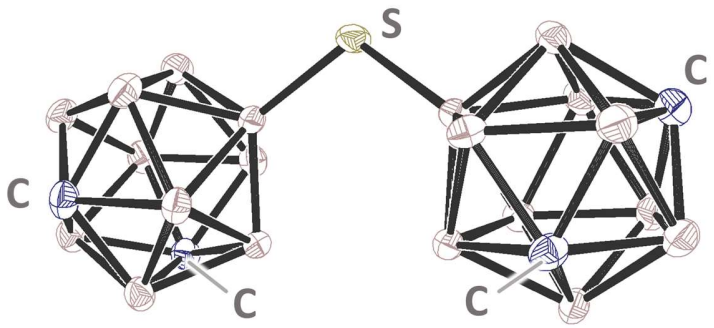


Figure S2. ORTEP drawing for **5a** with 40% thermal ellipsoid.

Table S2. Selected crystal data for **5a**

CCDC No.	2369108 [8]
Crystal system	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$ (No. 19)
Unit cell parameter [Å, deg]	a = 7.33343(14)
	b = 11.54333(19)
	c = 21.4760(4)
Cell volume [Å^3]	1817.99(6)
Z	4
R factor ($I > 2.0\sigma(I)$)	$R1$ = 0.0408, $wR2$ = 0.1072
R factor (all data)	$R1$ = 0.0430, $wR2$ = 0.1092
Rint	0.0464
Goodness of fit	1.076

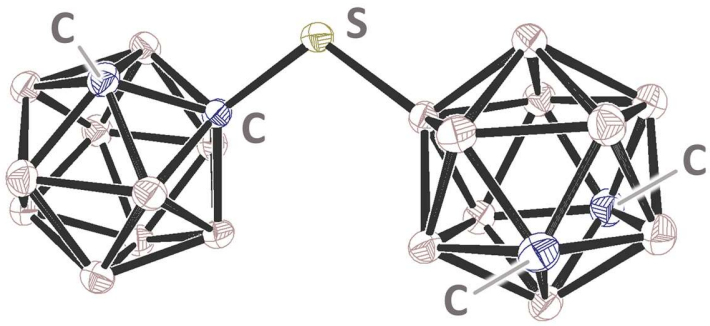


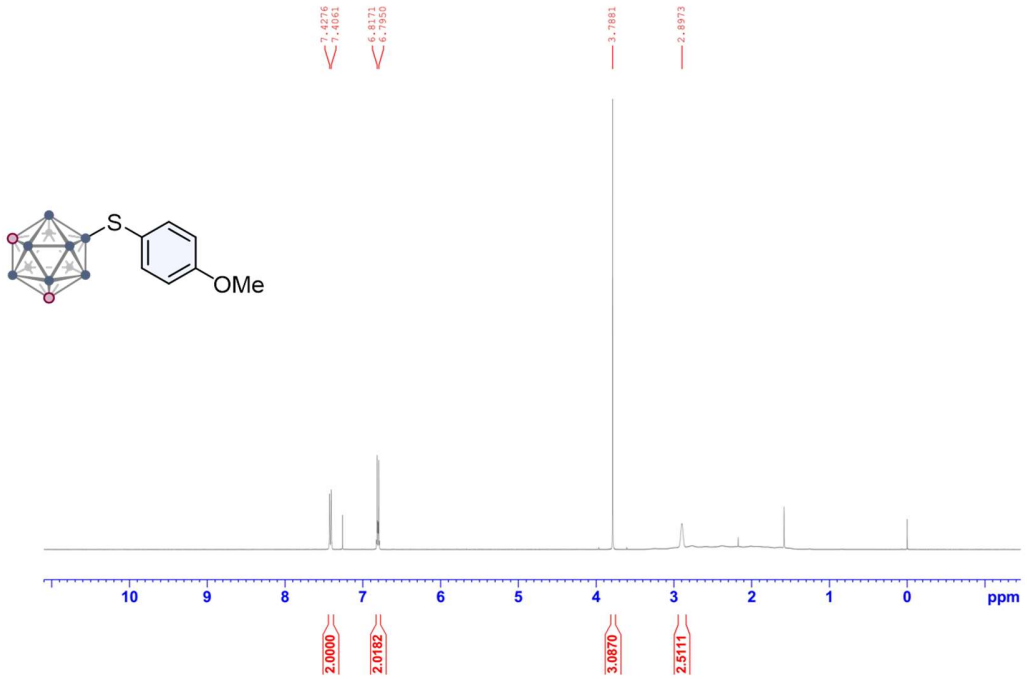
Figure S2. ORTEP drawing for **5d** with 40% thermal ellipsoid.

Table S2. Selected crystal data for **5d**

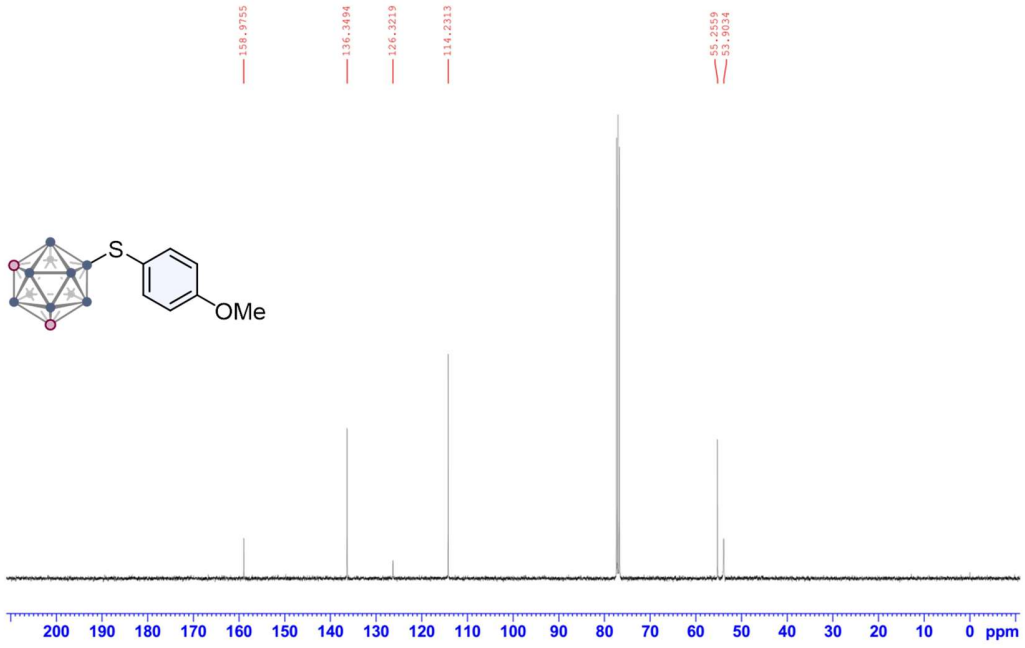
CCDC No.	2369109 [9]
Crystal system	triclinic
Space group	*P* -1 (No. 2)
Unit cell parameter [Å, deg]	a = 7.0096(3), α = 94.038(3)
	b = 11.3433(5), β = 92.610(3)
	c = 11.4466(3), γ = 98.639(3)
Cell volume [Å^3]	896.13(6)
Z	2
R factor ($I > 2.0\sigma(I)$)	$R1$ = 0.0497, $wR2$ = 0.1372
R factor (all data)	$R1$ = 0.0593, $wR2$ = 0.1544
*R*int	0.0454
Goodness of fit	1.068

5. Copy of NMR Spectra

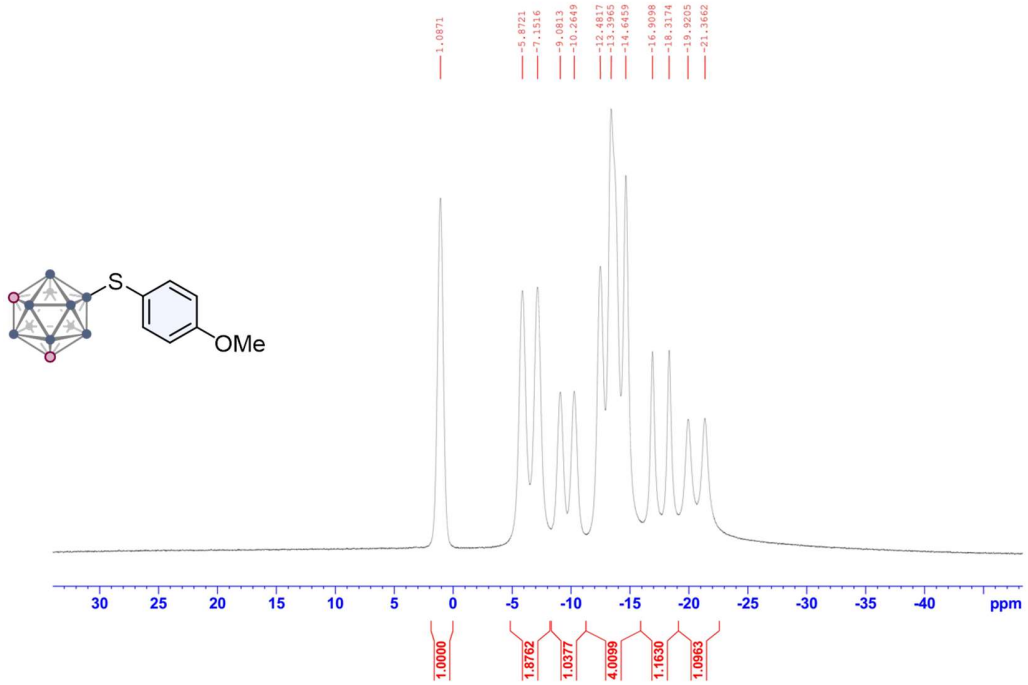
^{1}H NMR of **3aa** ($CDCl_3$, 400 MHz)



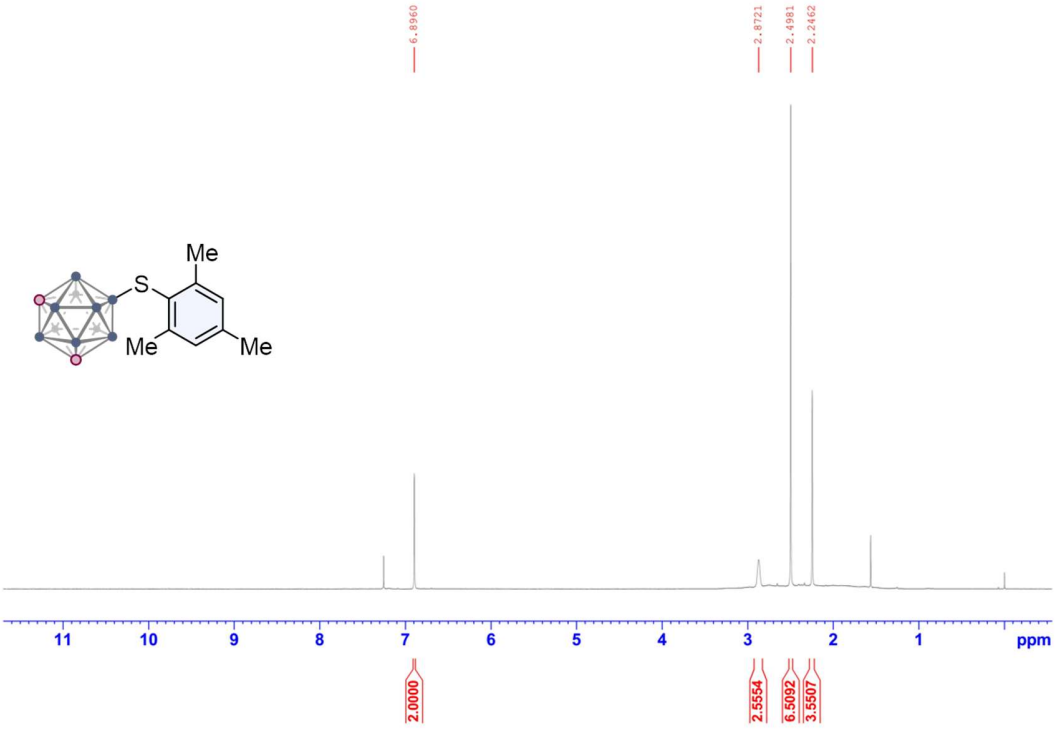
^{13}C NMR of **3aa** ($CDCl_3$, 100 MHz)



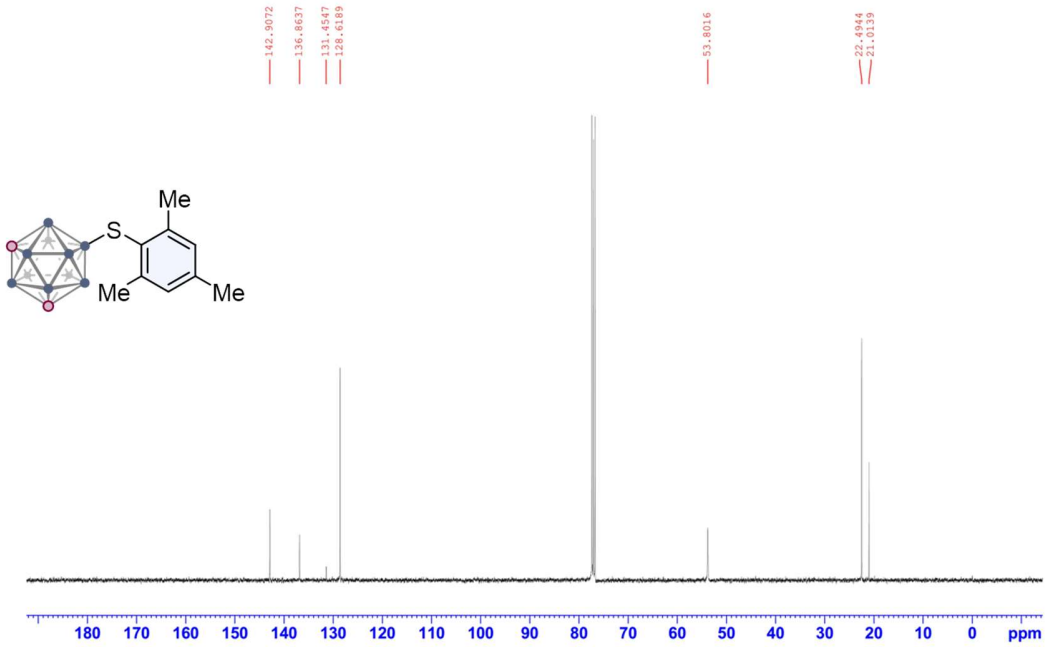
^{11}B NMR of **3aa** ($CDCl_3$, 128 MHz)



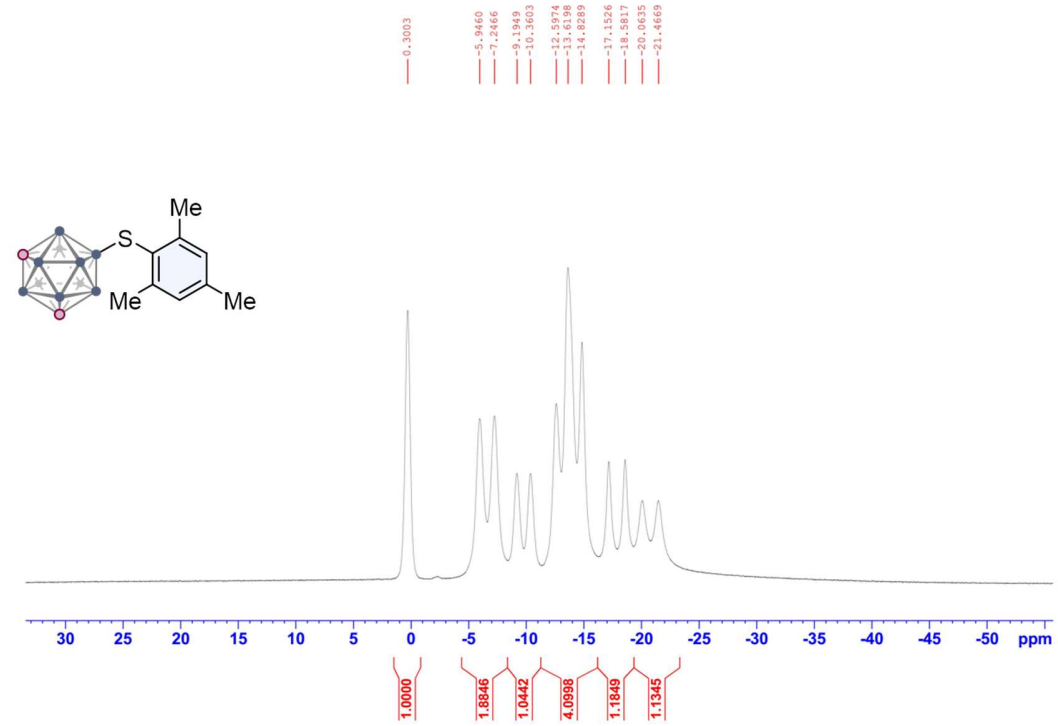
^{1}H NMR of **3ab** ($CDCl_3$, 400 MHz)



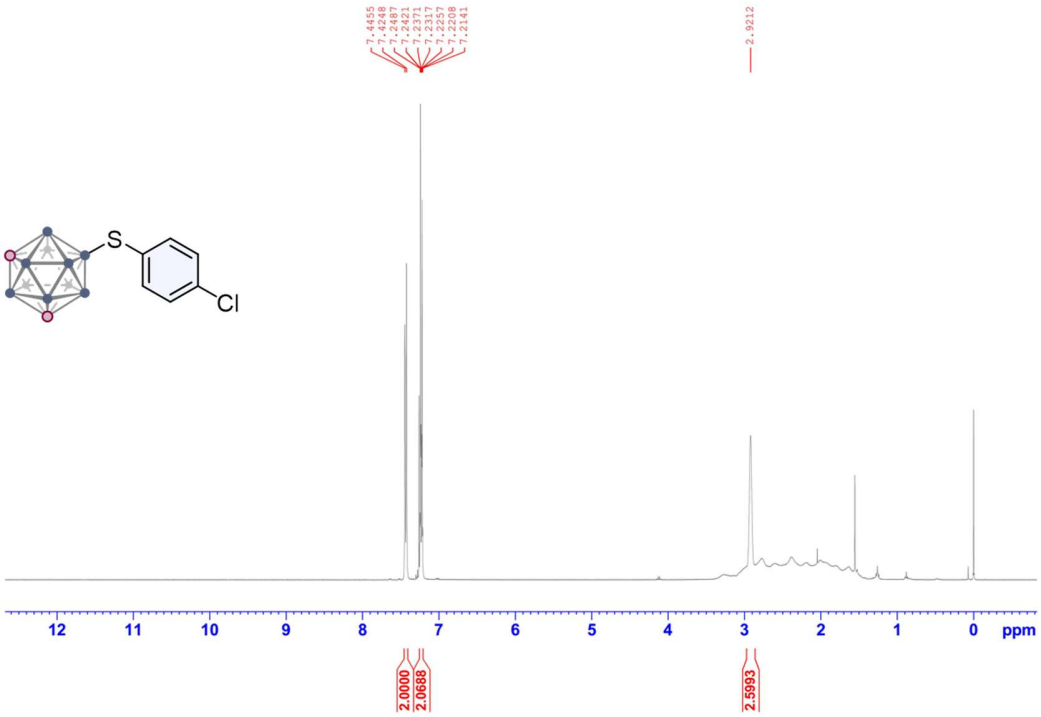
^{13}C NMR of **3ab** ($CDCl_3$, 100 MHz)



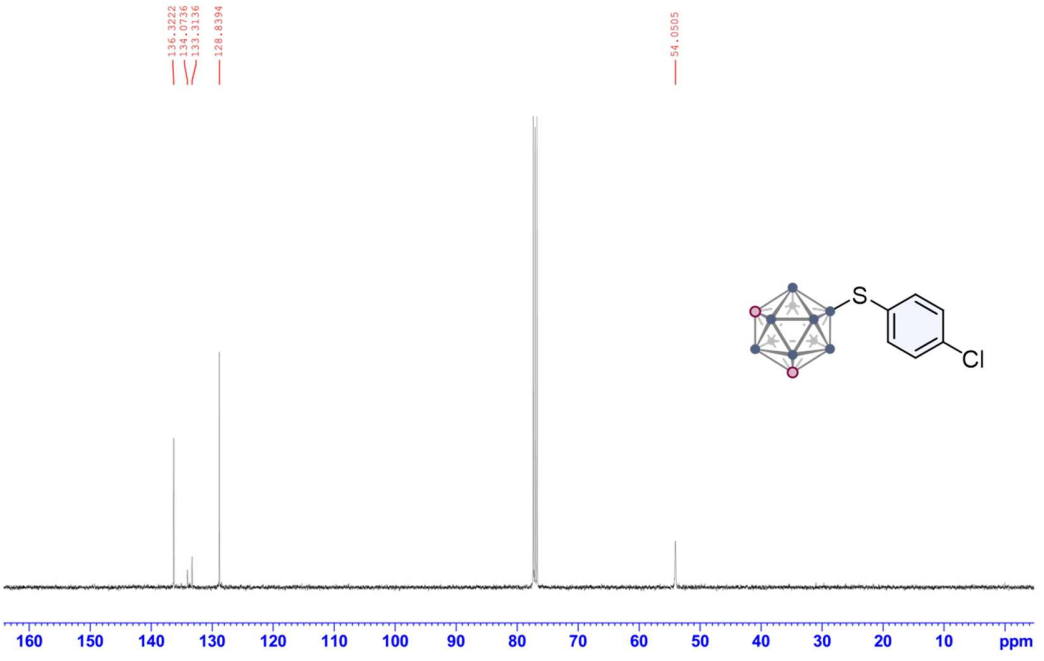
^{11}B NMR of **3ab** ($CDCl_3$, 128 MHz)



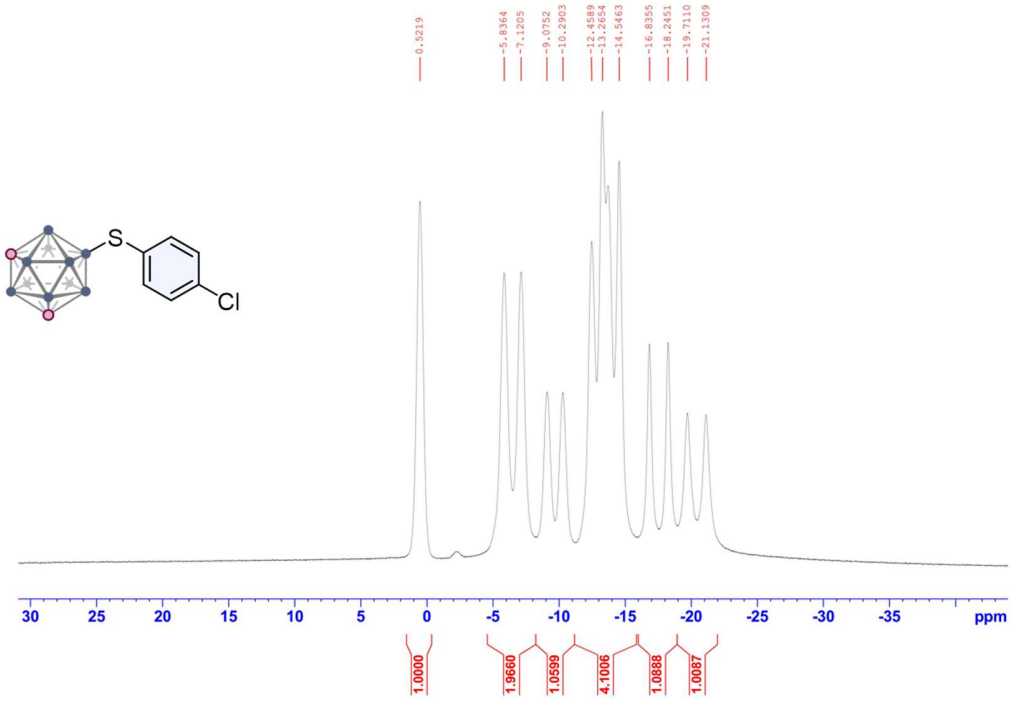
^{1}H NMR of **3ac** ($CDCl_3$, 400 MHz)



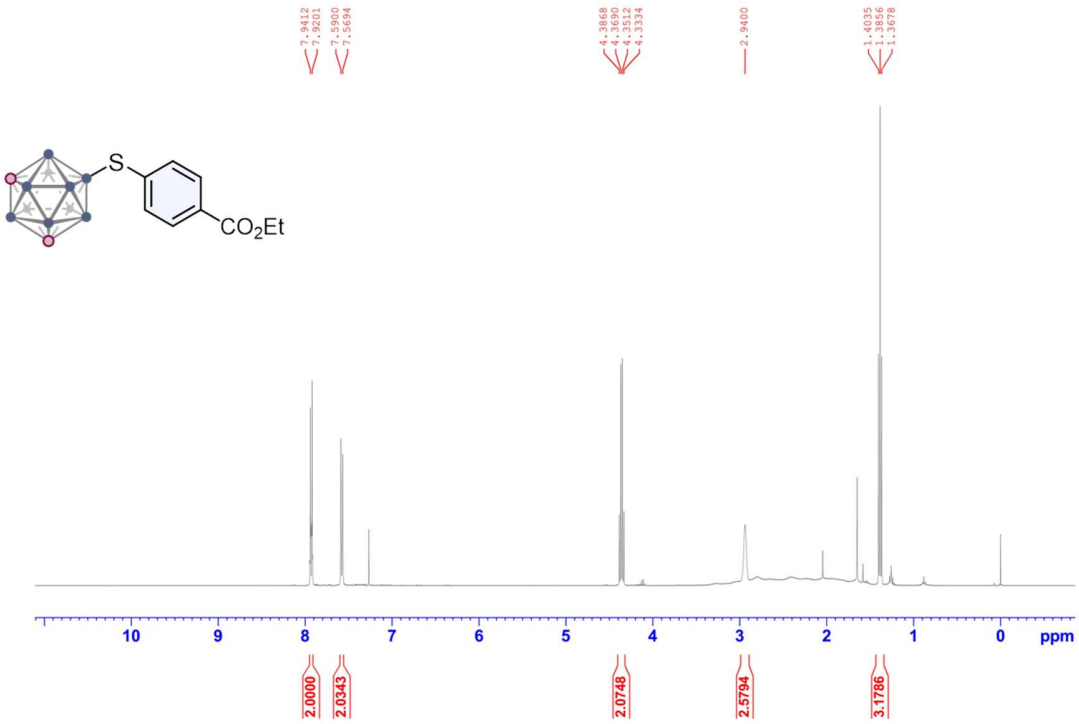
^{13}C NMR of **3ac** ($CDCl_3$, 100 MHz)



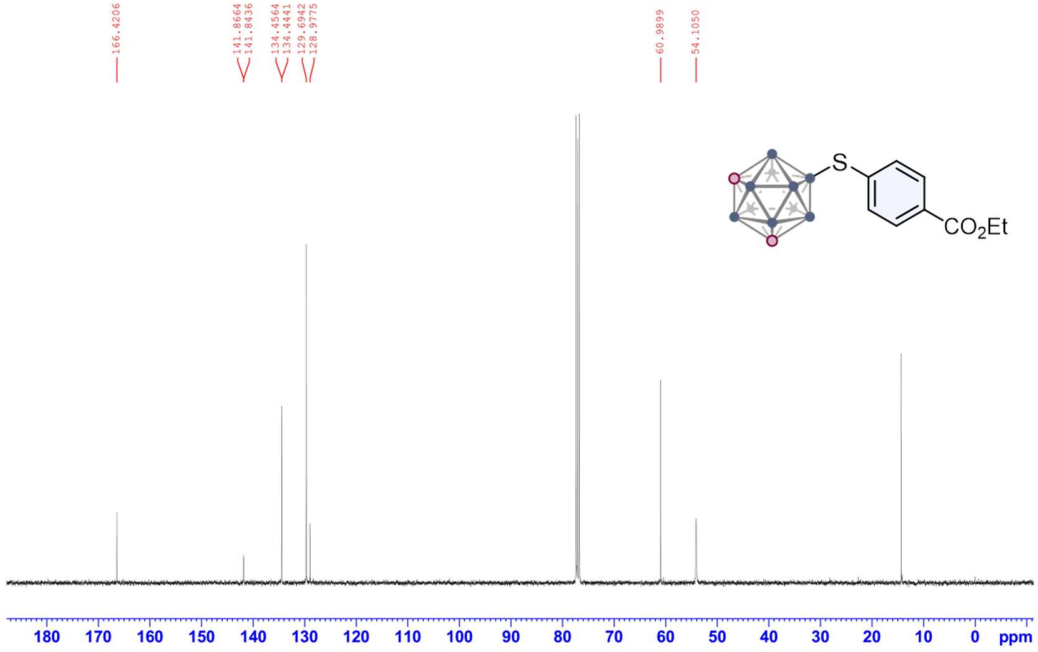
^{11}B NMR of **3ad** ($CDCl_3$, 128 MHz)



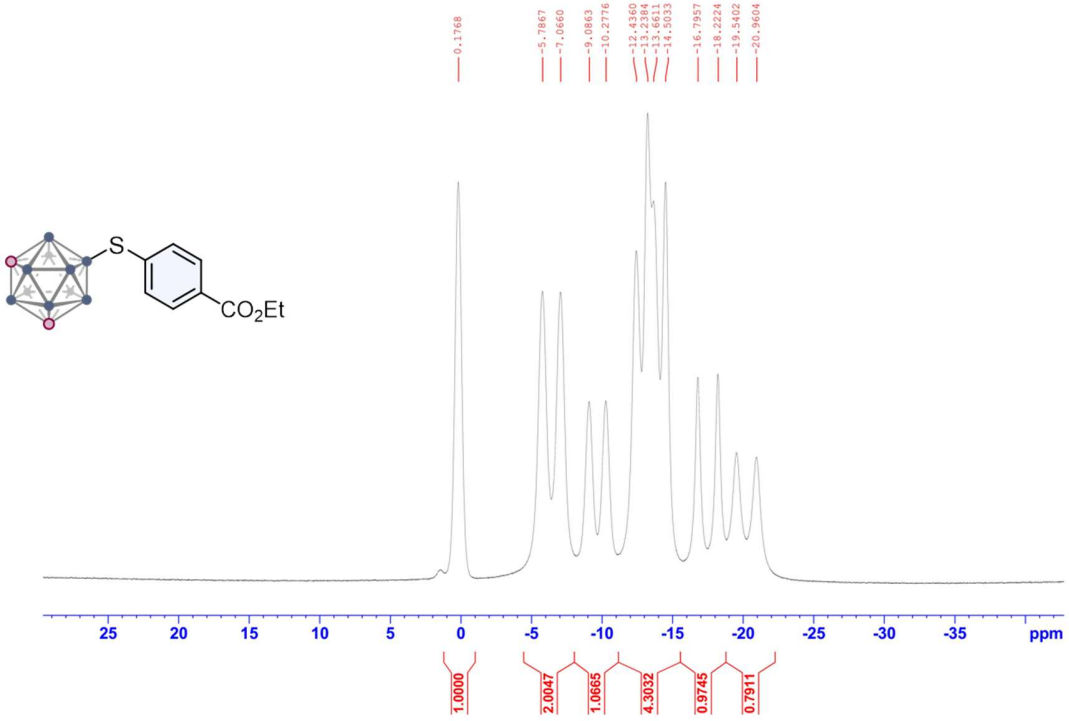
^{1}H NMR of **3ad** ($CDCl_3$, 400 MHz)



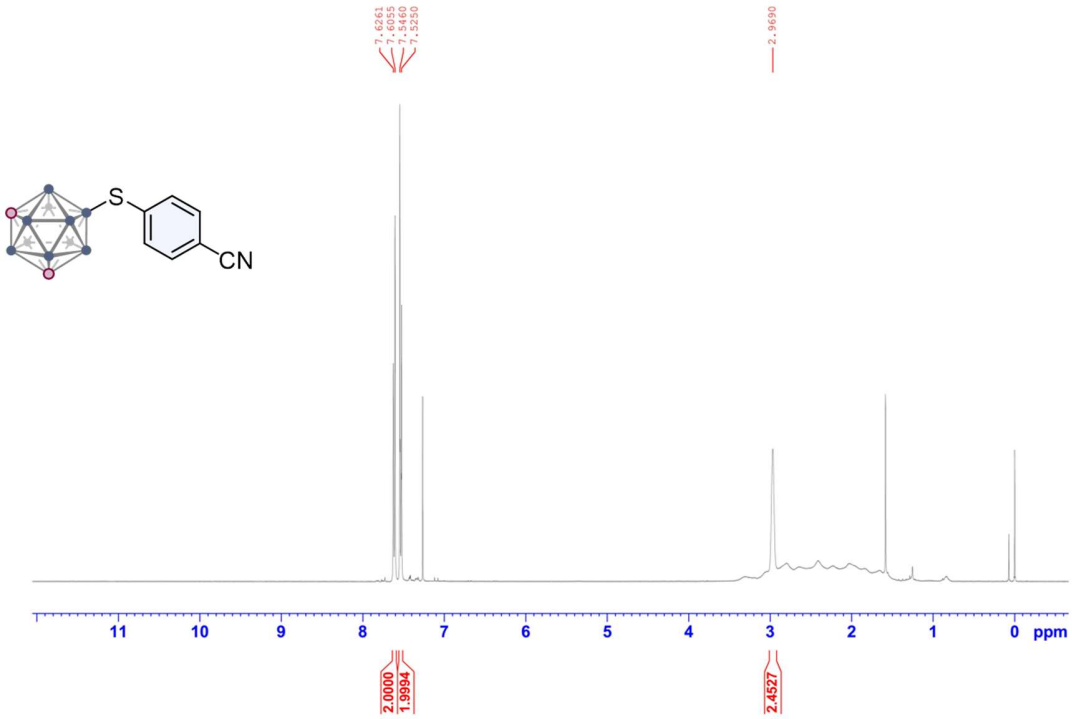
^{13}C NMR of **3ad** ($CDCl_3$, 100 MHz)



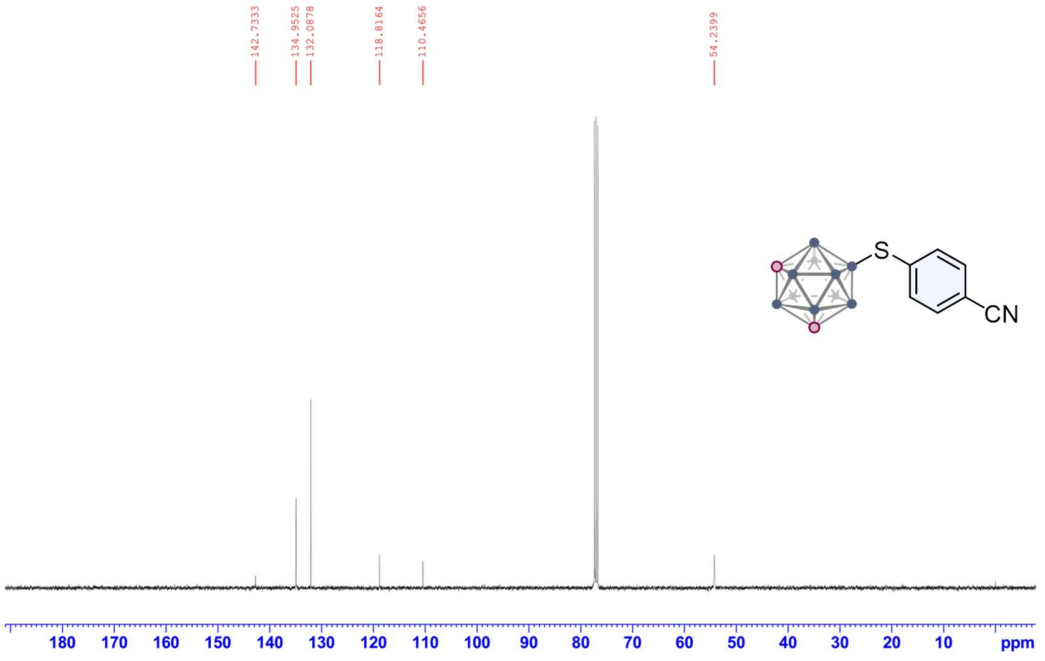
^{11}B NMR of **3ad** ($CDCl_3$, 128 MHz)



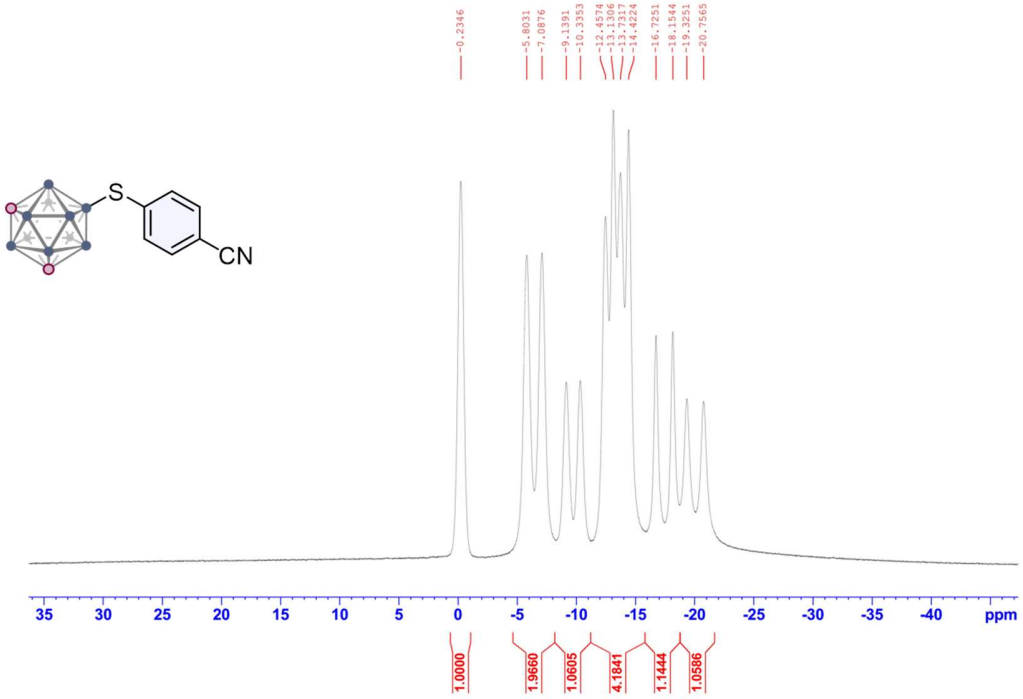
^{1}H NMR of **3ae** ($CDCl_3$, 400 MHz)



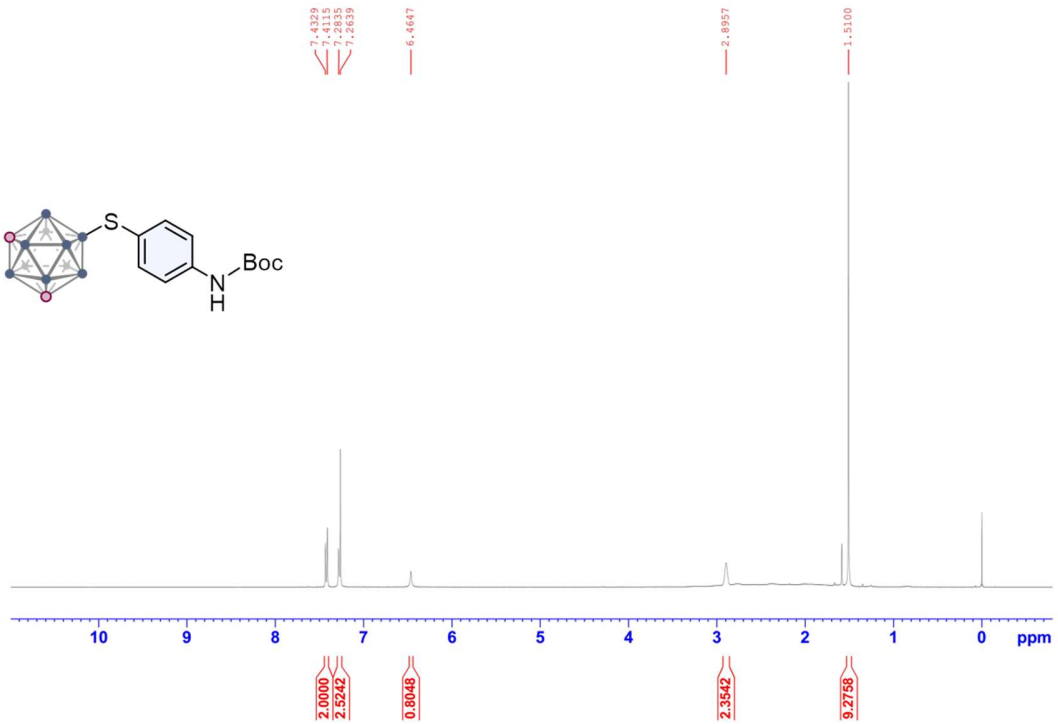
^{13}C NMR of **3ae** ($CDCl_3$, 100 MHz)



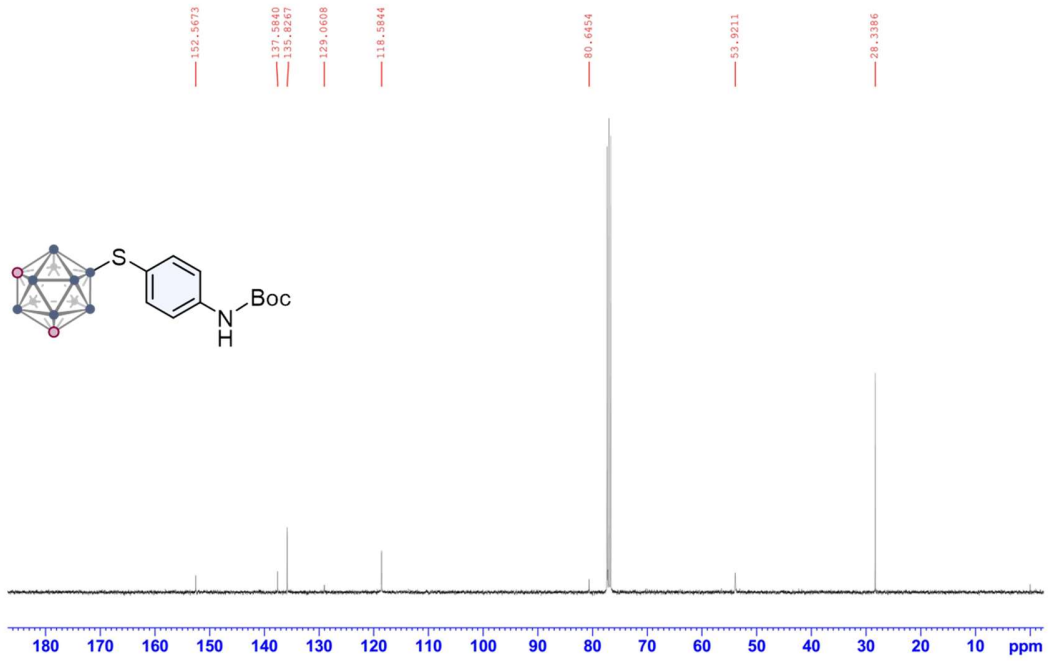
^{11}B NMR of **3ae** ($CDCl_3$, 128 MHz)



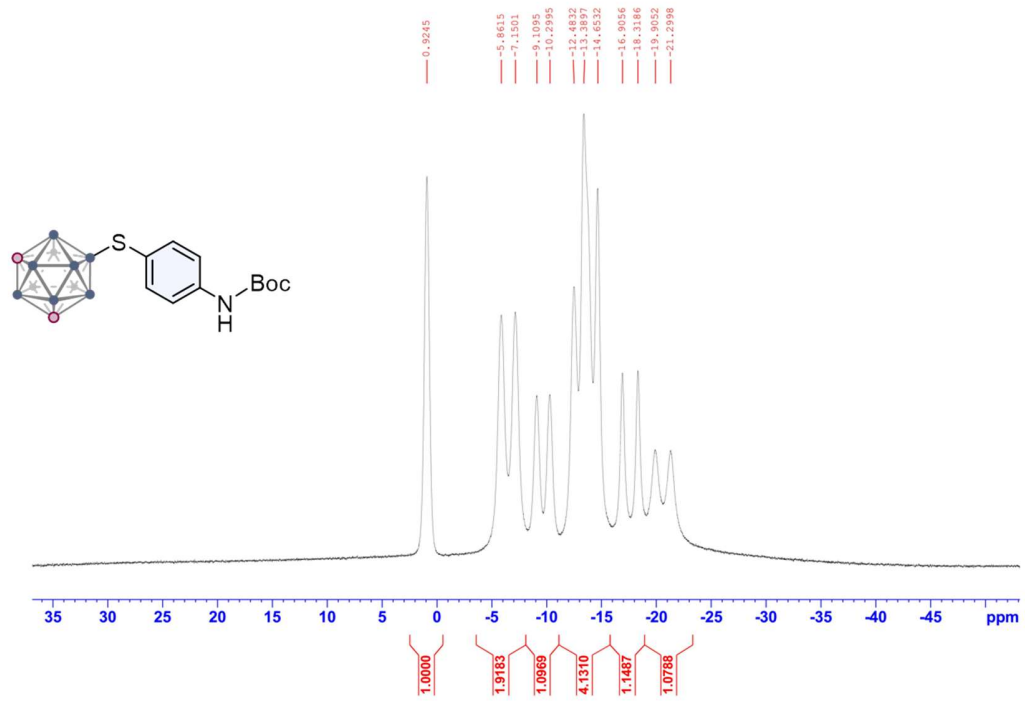
^{1}H NMR of **3af** ($CDCl_3$, 400 MHz)



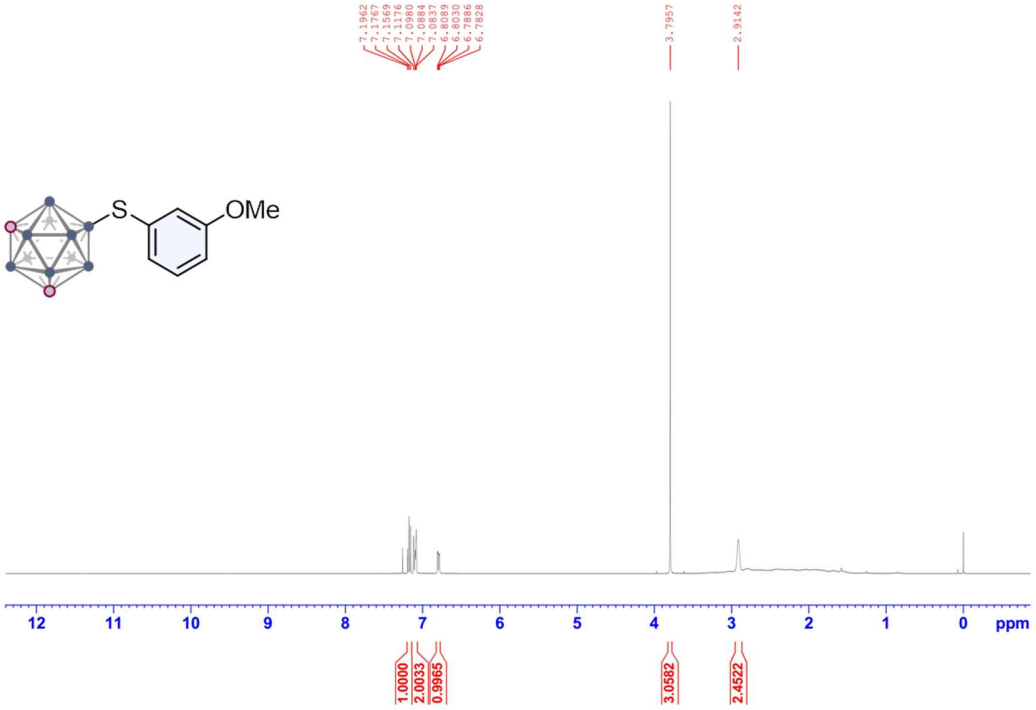
^{13}C NMR of **3af** ($CDCl_3$, 100 MHz)



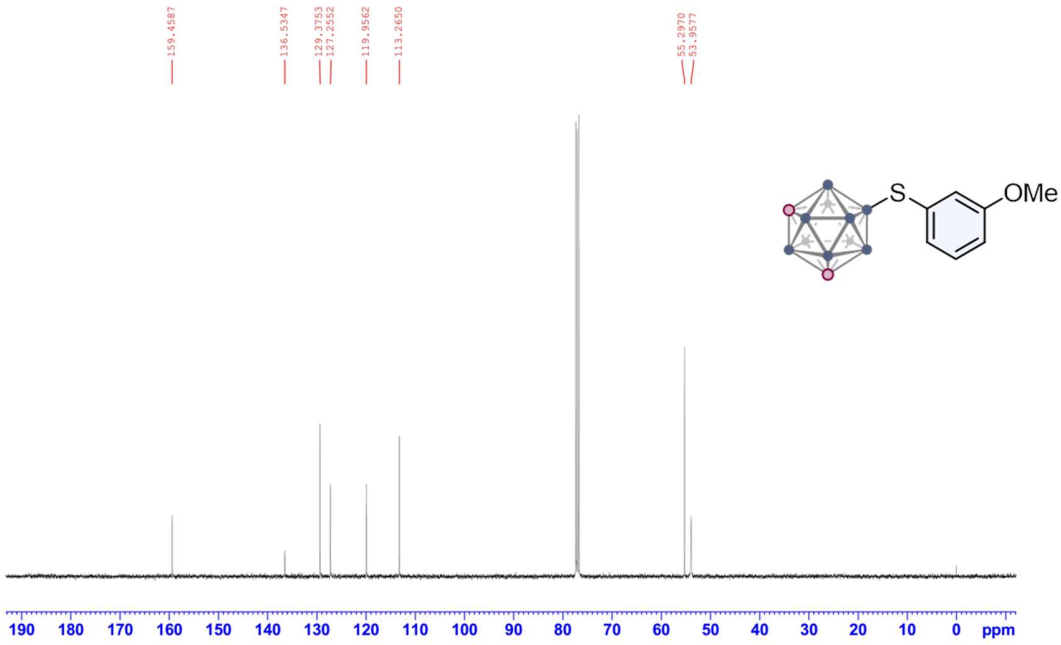
^{11}B NMR of **3af** ($CDCl_3$, 128 MHz)



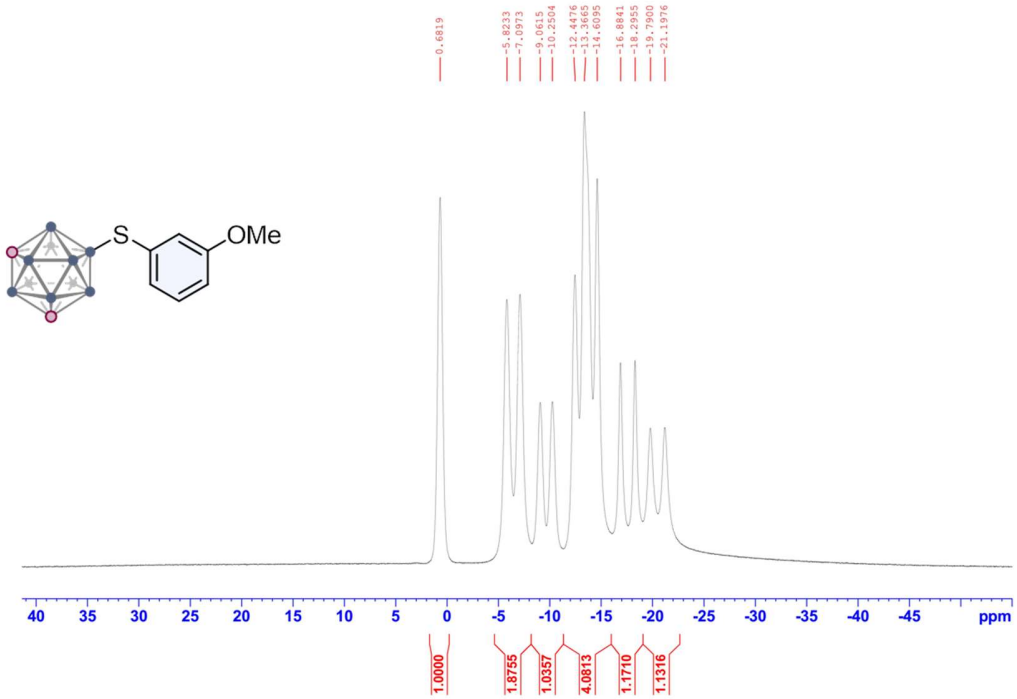
^{1}H NMR of **3ag** ($CDCl_3$, 400 MHz)



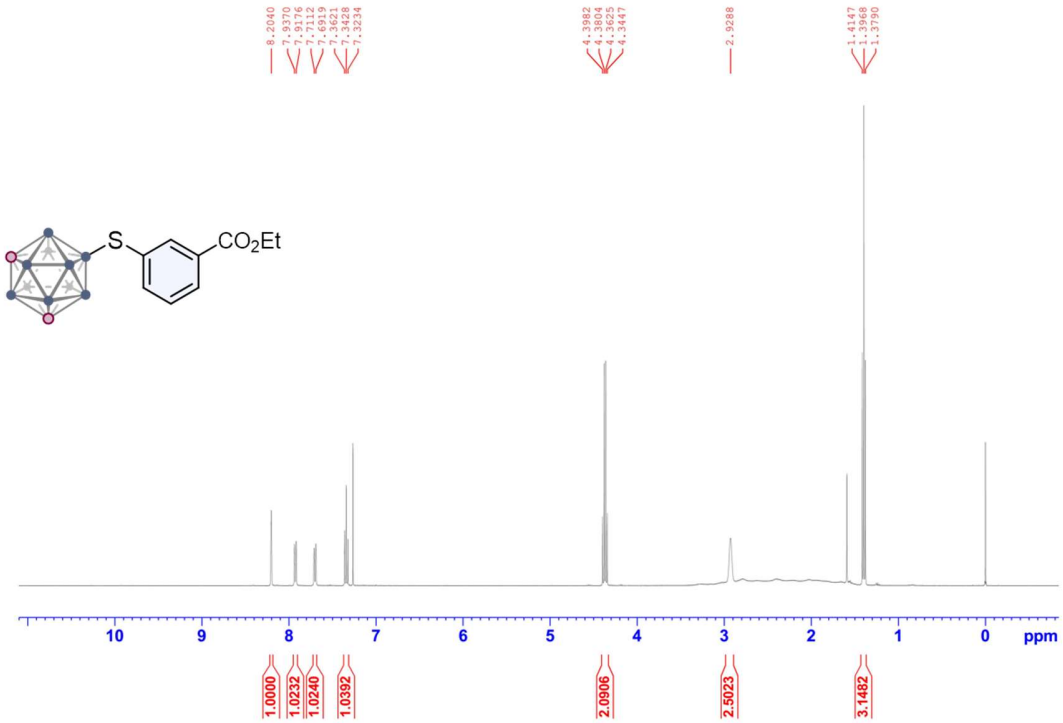
^{13}C NMR of **3ag** ($CDCl_3$, 100 MHz)



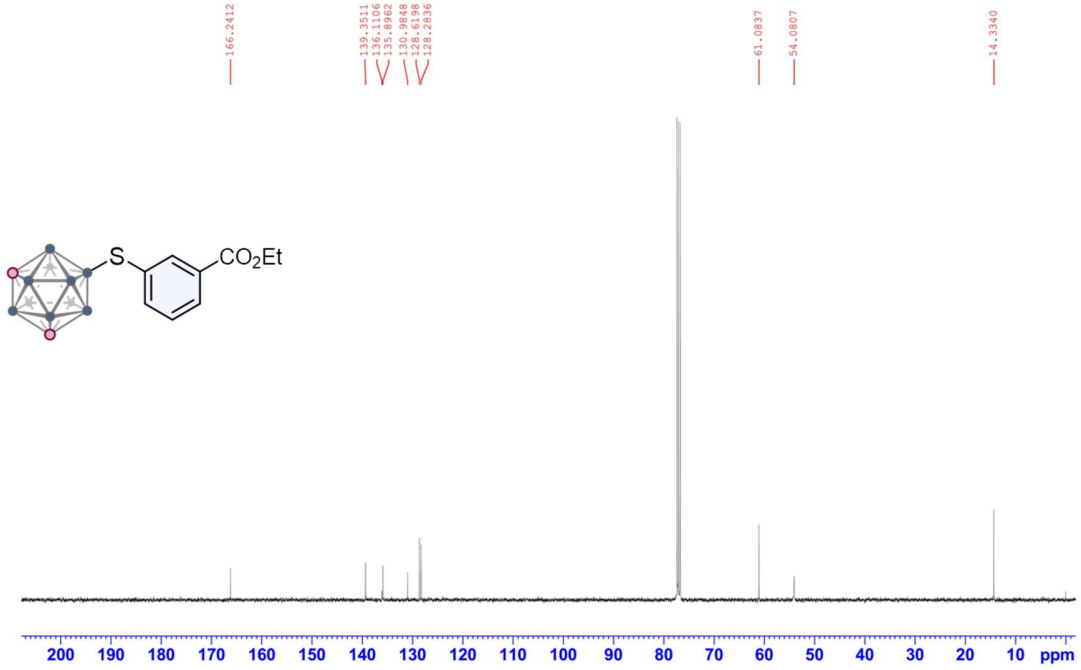
^{11}B NMR of **3ag** ($CDCl_3$, 128 MHz)



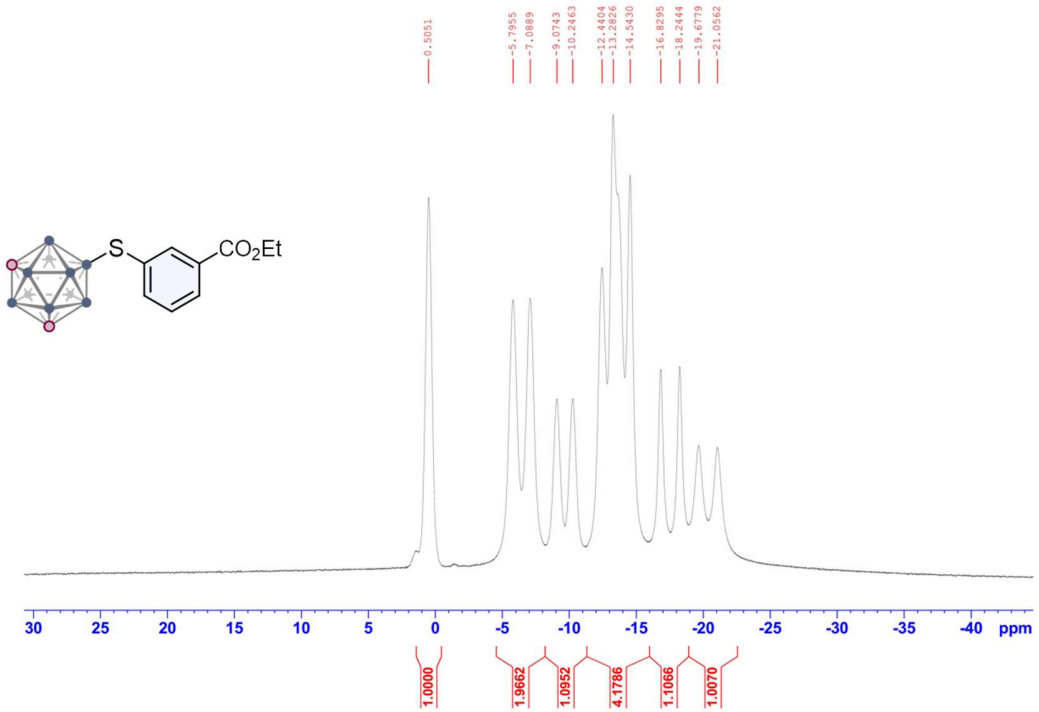
^{1}H NMR of **3ah** ($CDCl_3$, 400 MHz)



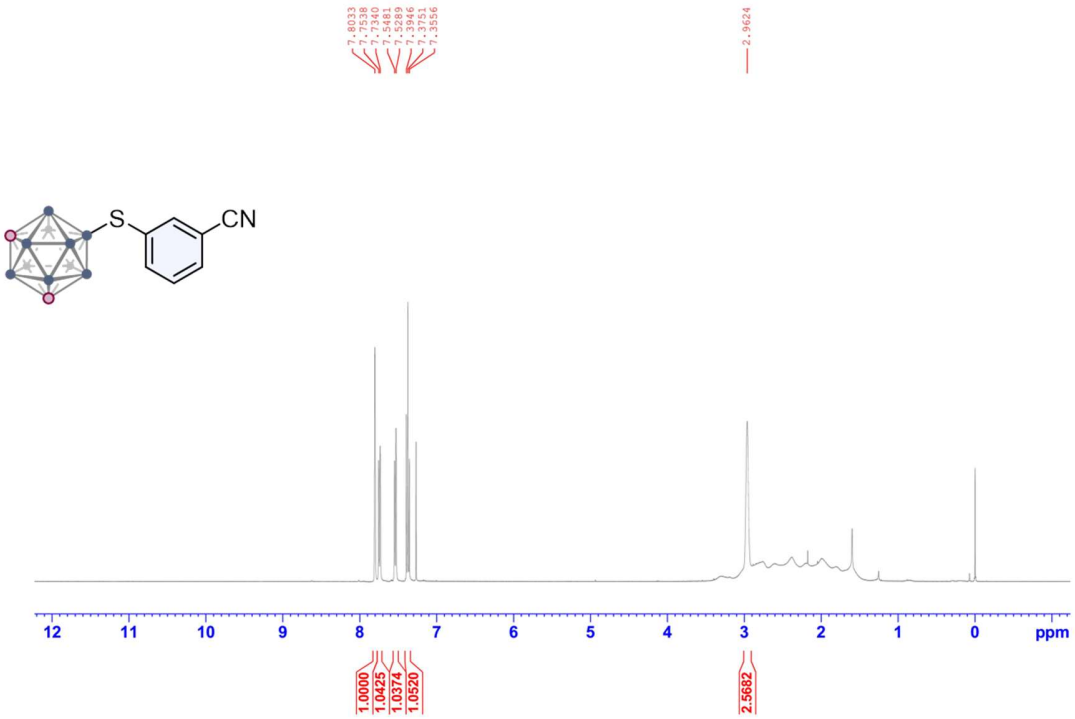
^{13}C NMR of **3ah** ($CDCl_3$, 100 MHz)



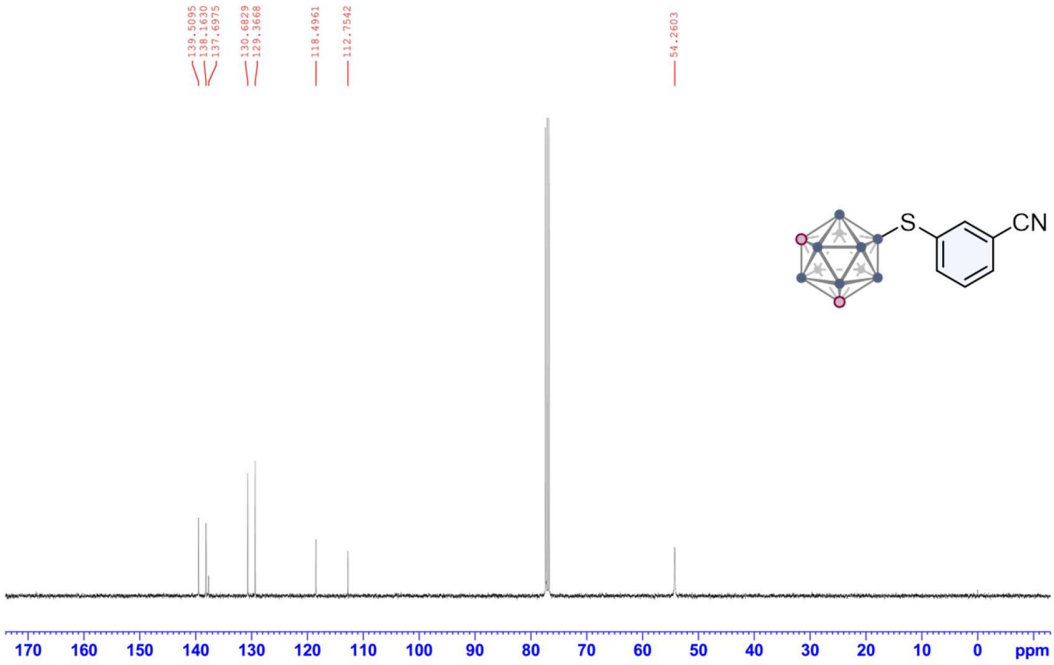
^{11}B NMR of **3ah** ($CDCl_3$, 128 MHz)



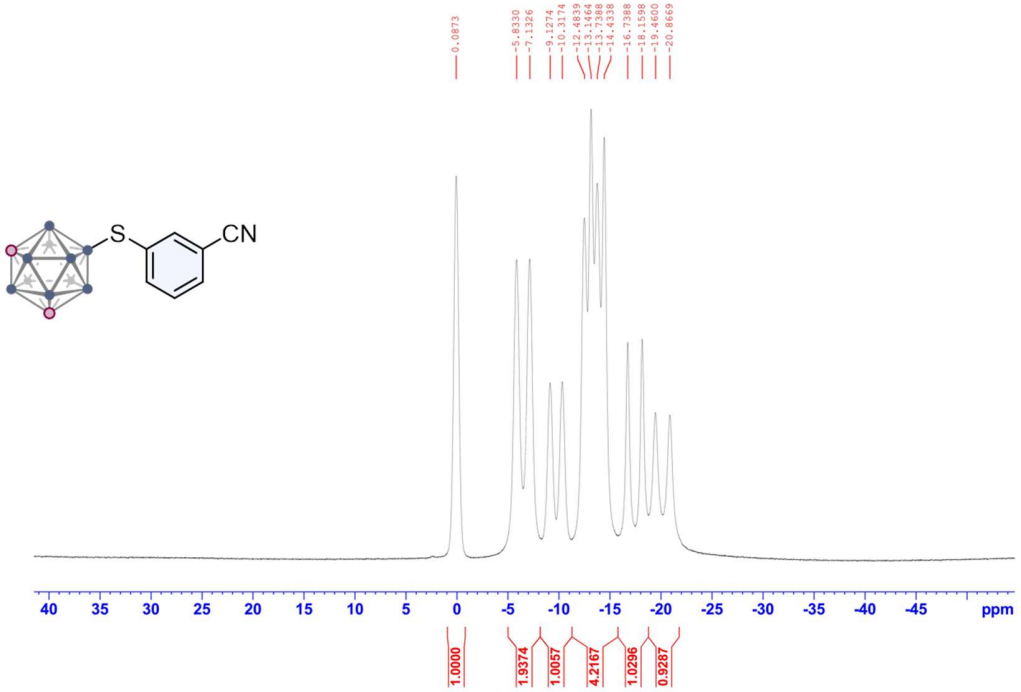
^{1}H NMR of **3ai** ($CDCl_3$, 400 MHz)



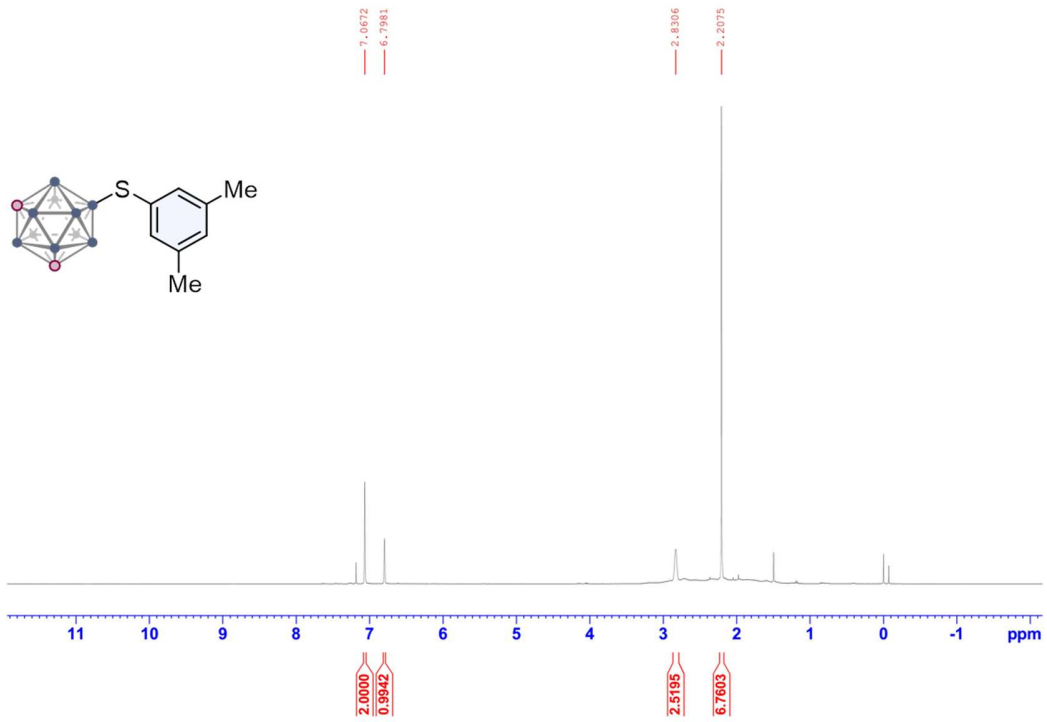
^{13}C NMR of **3ai** ($CDCl_3$, 100 MHz)



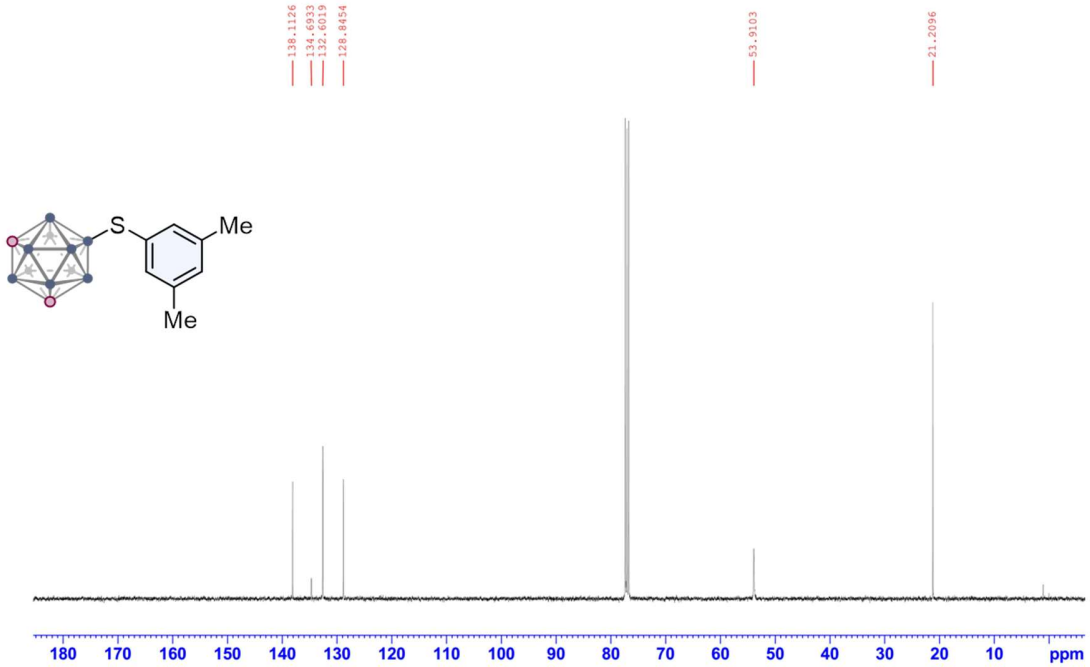
^{11}B NMR of **3ai** ($CDCl_3$, 128 MHz)



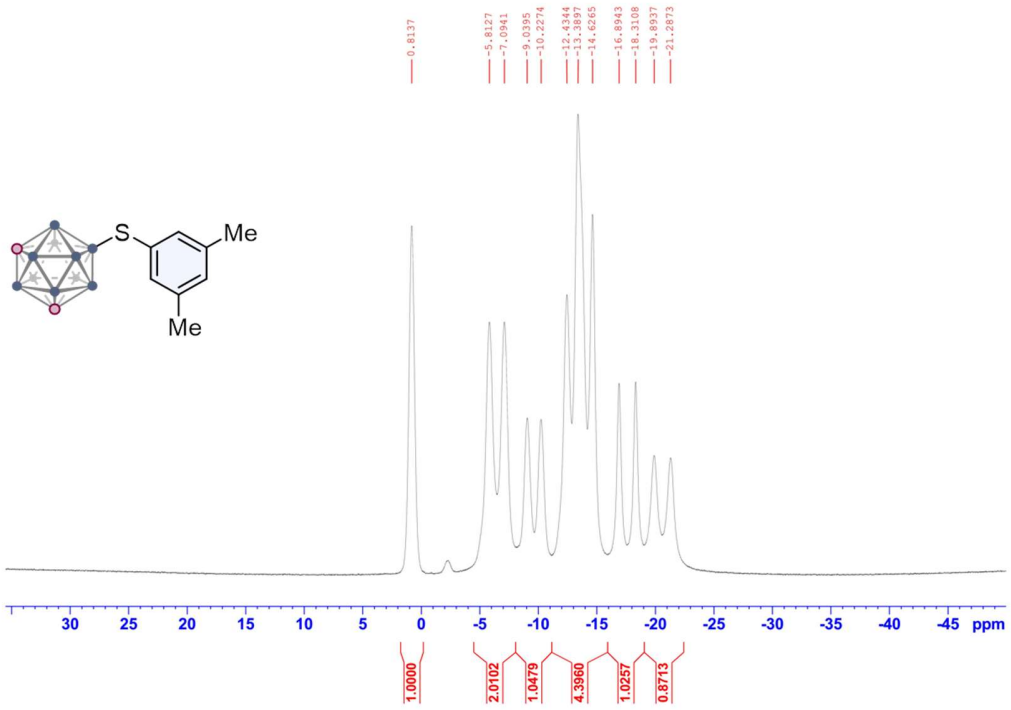
^{1}H NMR of **3aj** ($CDCl_3$, 400 MHz)



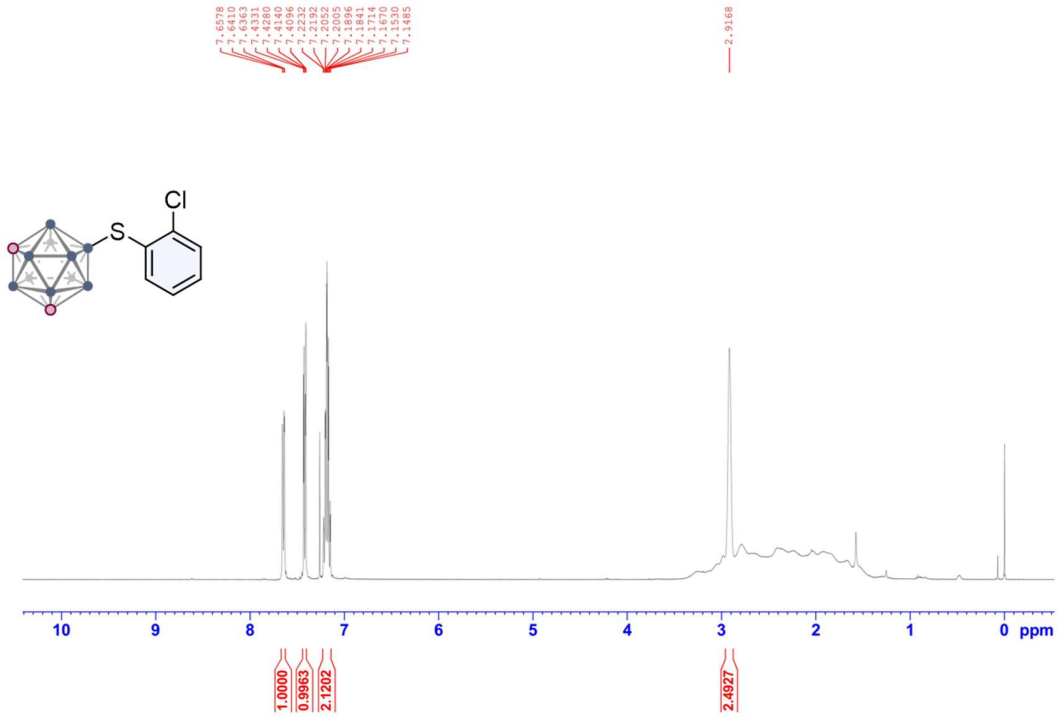
^{13}C NMR of **3aj** ($CDCl_3$, 100 MHz)



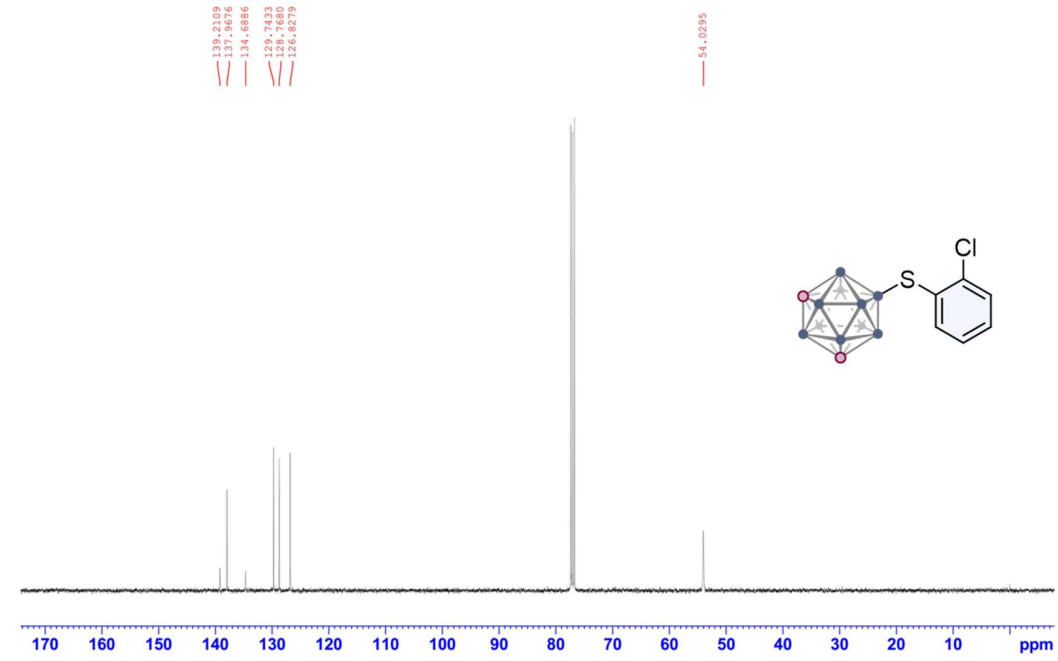
^{11}B NMR of **3aj** ($CDCl_3$, 128 MHz)



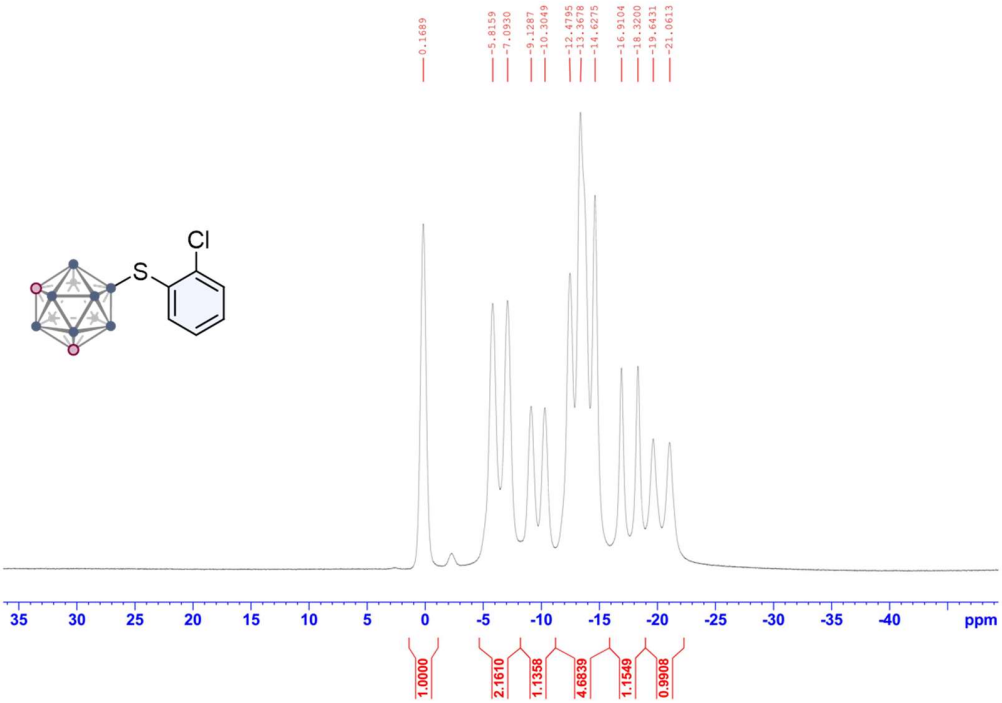
^{1}H NMR of **3ak** ($CDCl_3$, 400 MHz)



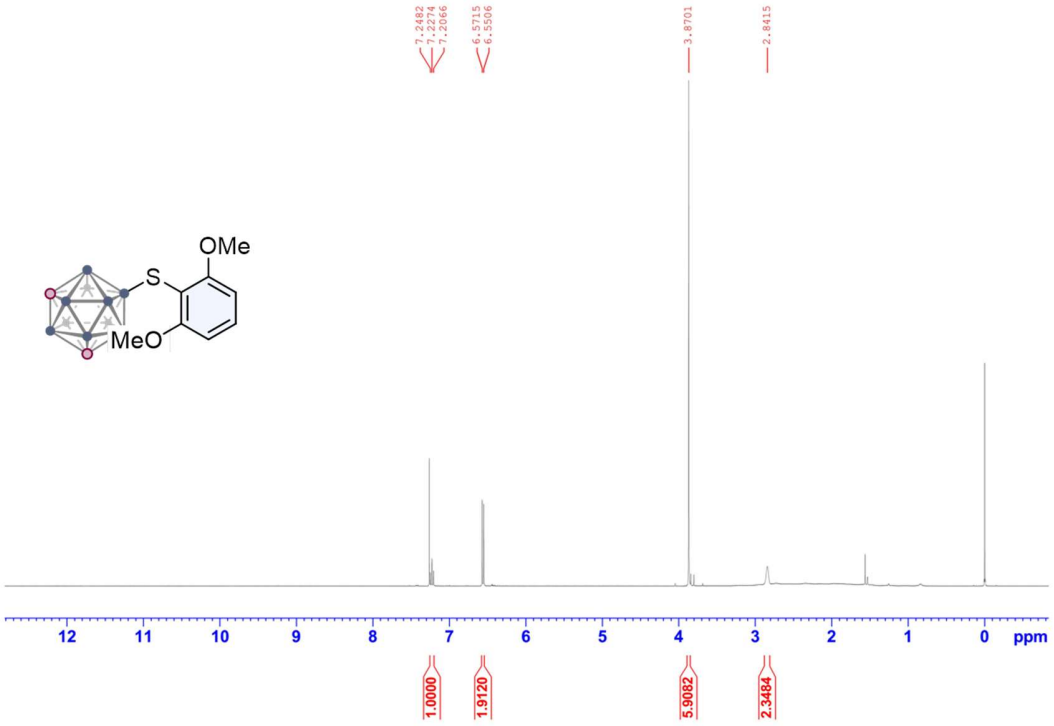
^{13}C NMR of **3ak** ($CDCl_3$, 100 MHz)



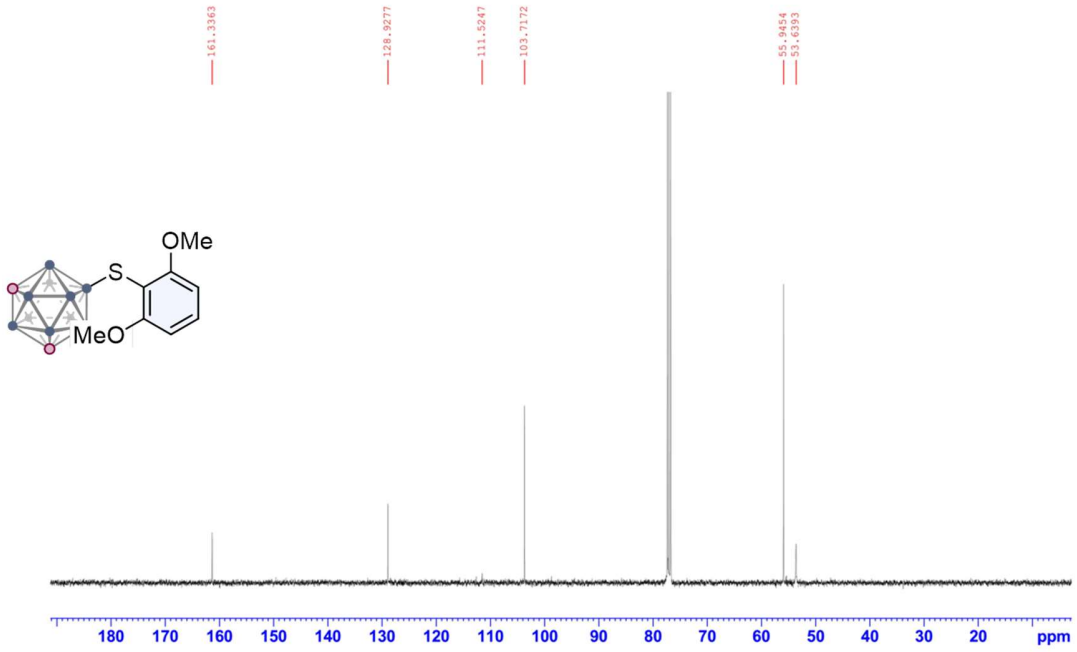
^{11}B NMR of **3ak** ($CDCl_3$, 128 MHz)



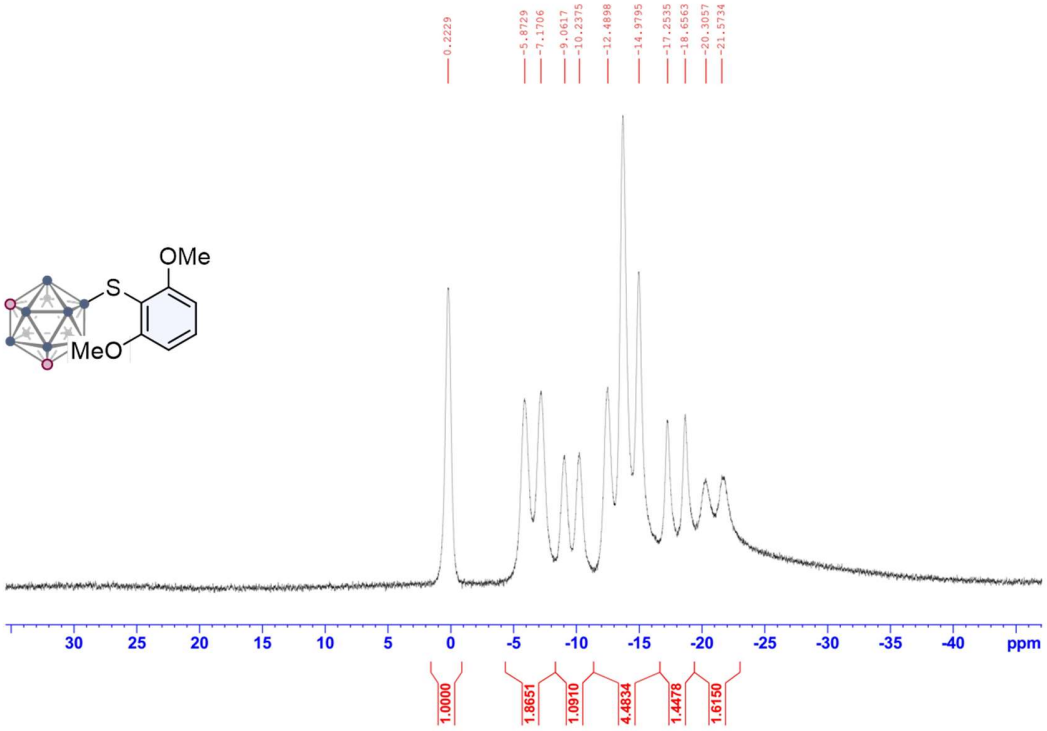
^{1}H NMR of **3al** ($CDCl_3$, 400 MHz)



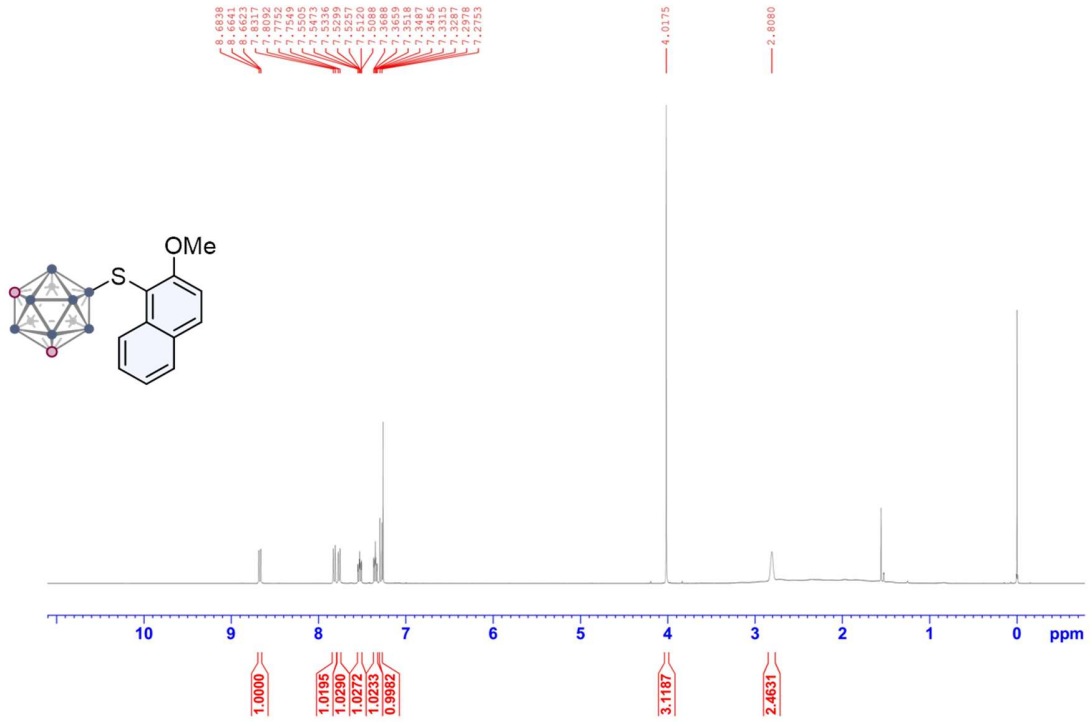
^{13}C NMR of **3al** ($CDCl_3$, 100 MHz)



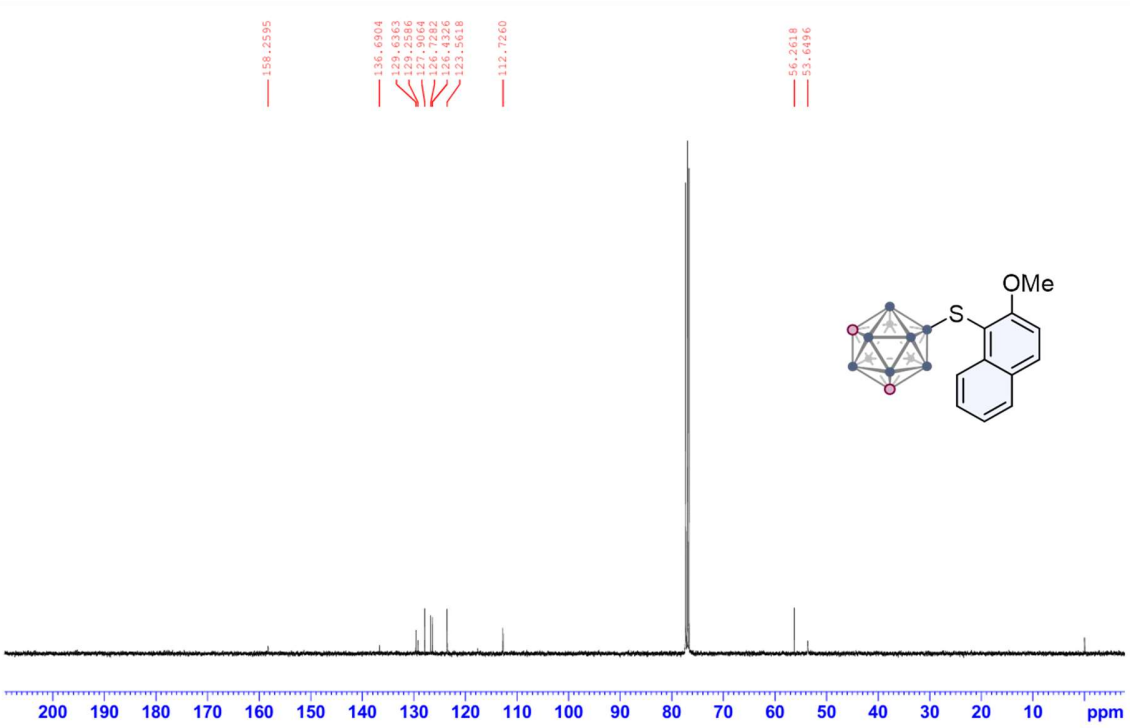
^{11}B NMR of **3al** ($CDCl_3$, 128 MHz)



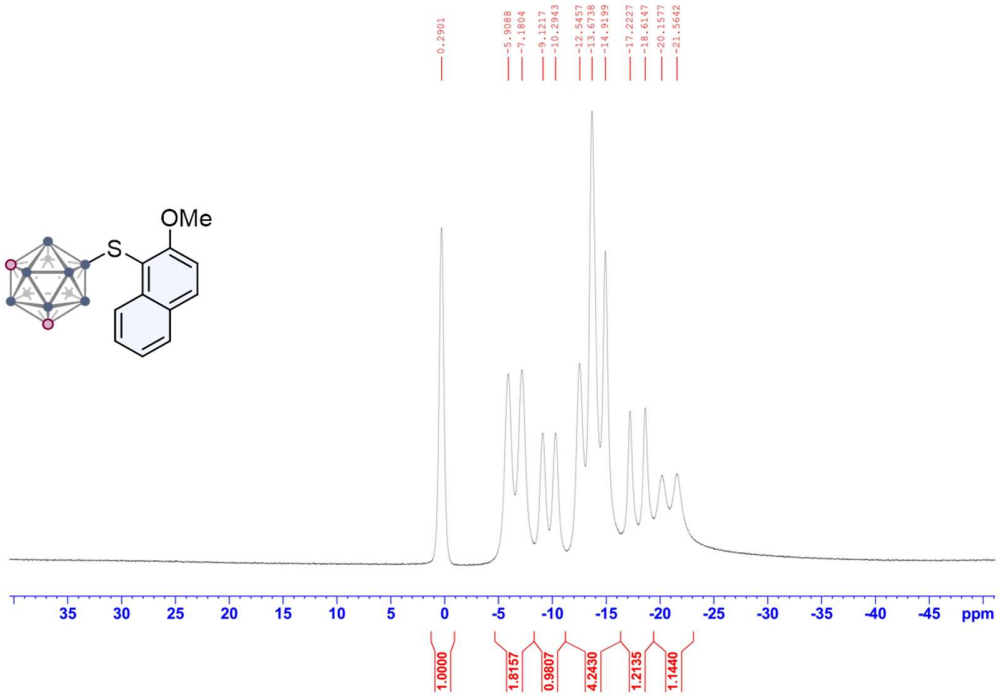
^{1}H NMR of **3am** ($CDCl_3$, 400 MHz)



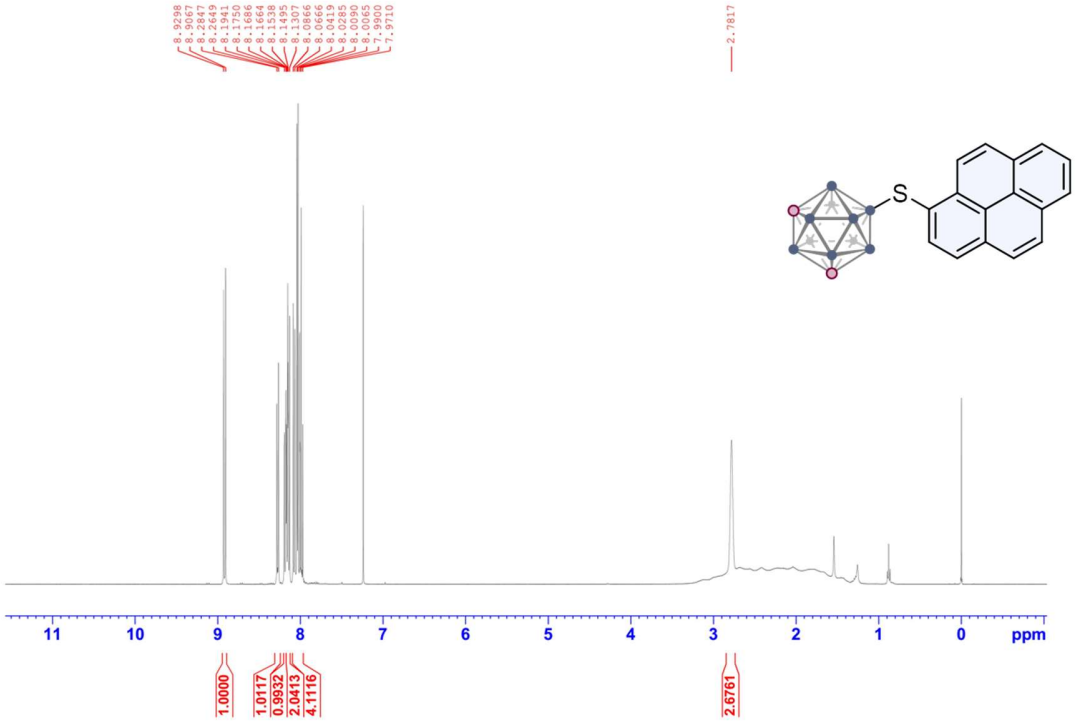
^{13}C NMR of **3am** ($CDCl_3$, 100 MHz)



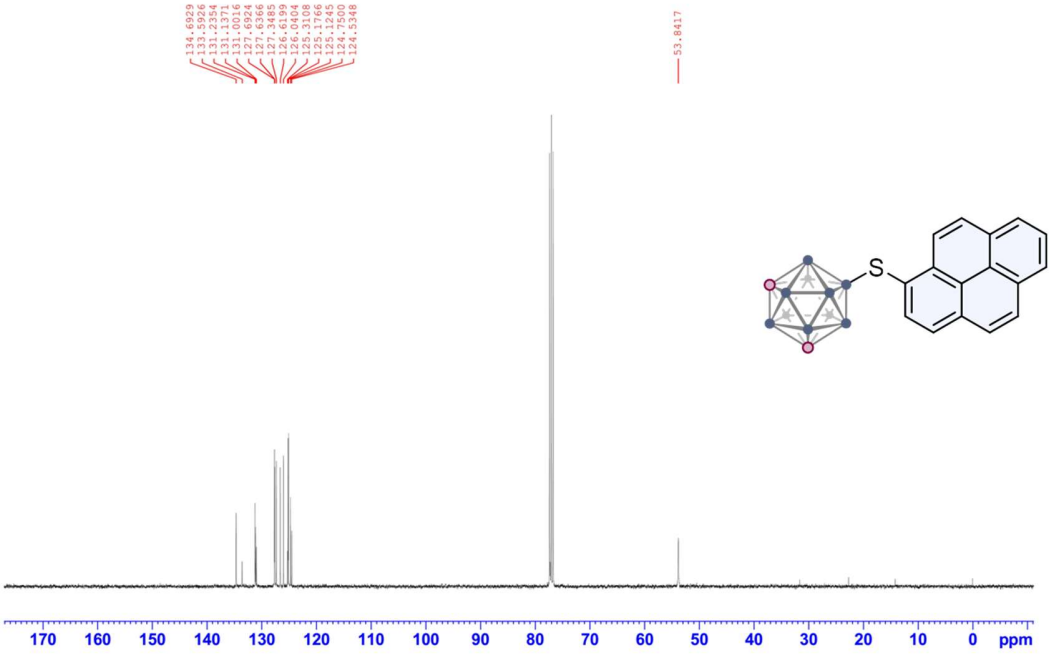
^{11}B NMR of **3am** ($CDCl_3$, 128 MHz)



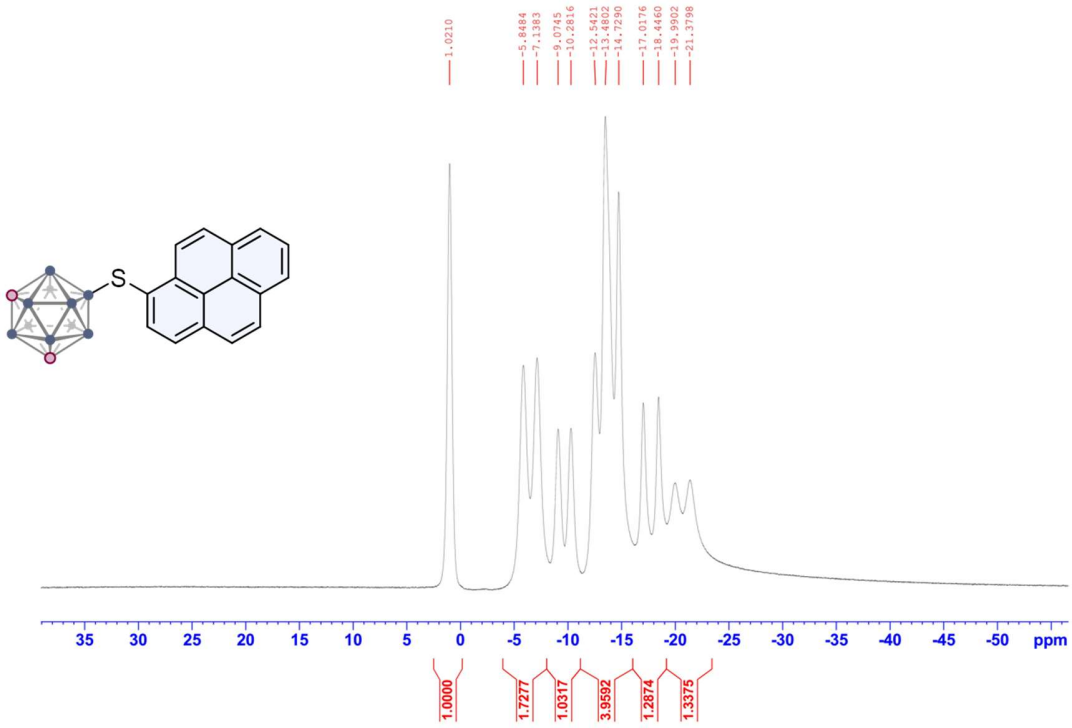
^{1}H NMR of **3an** ($CDCl_3$, 400 MHz)



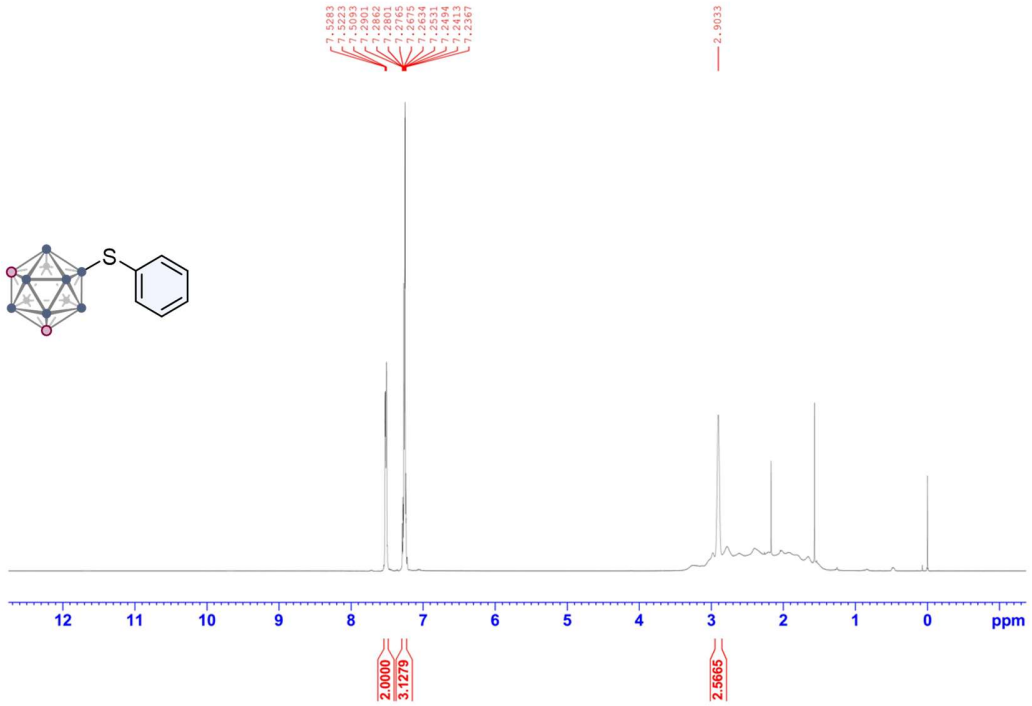
^{13}C NMR of **3an** ($CDCl_3$, 100 MHz)



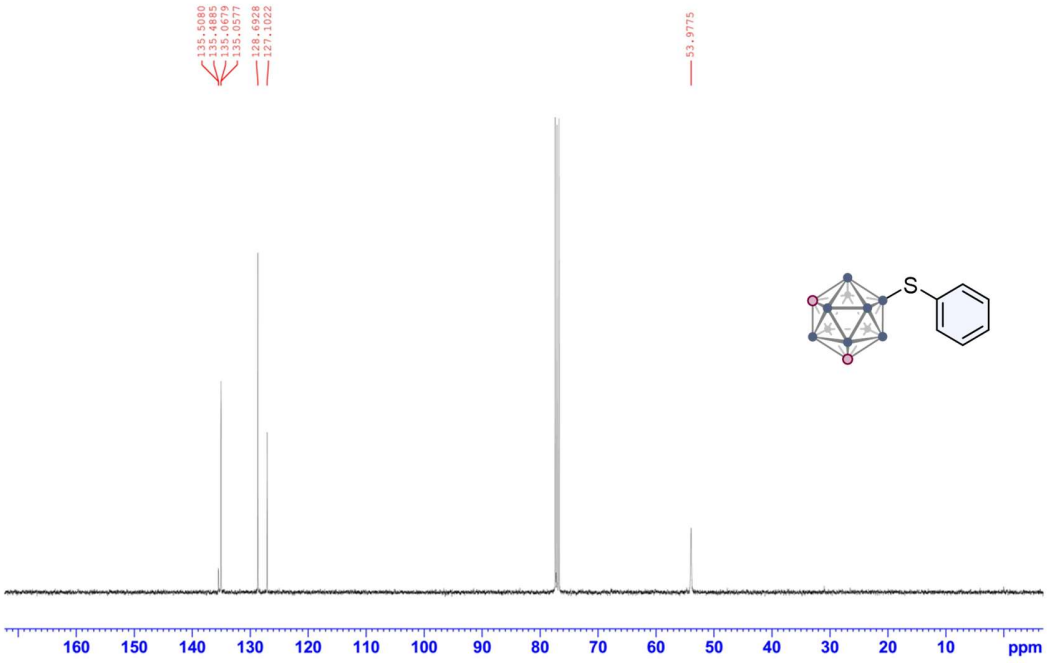
^{11}B NMR of **3an** ($CDCl_3$, 128 MHz)



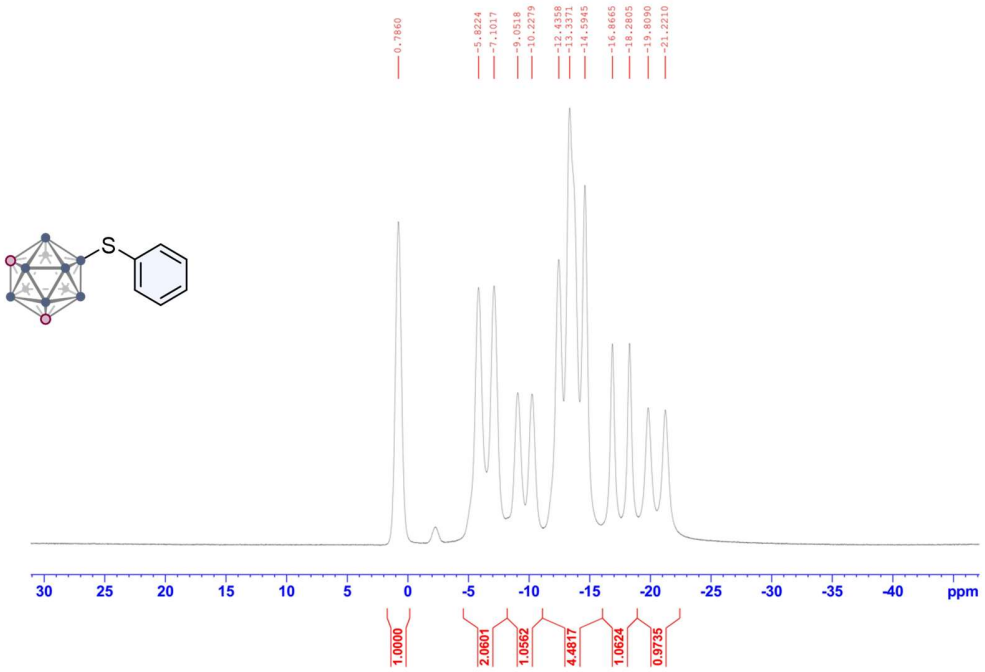
^{1}H NMR of **3ao** ($CDCl_3$, 400 MHz)



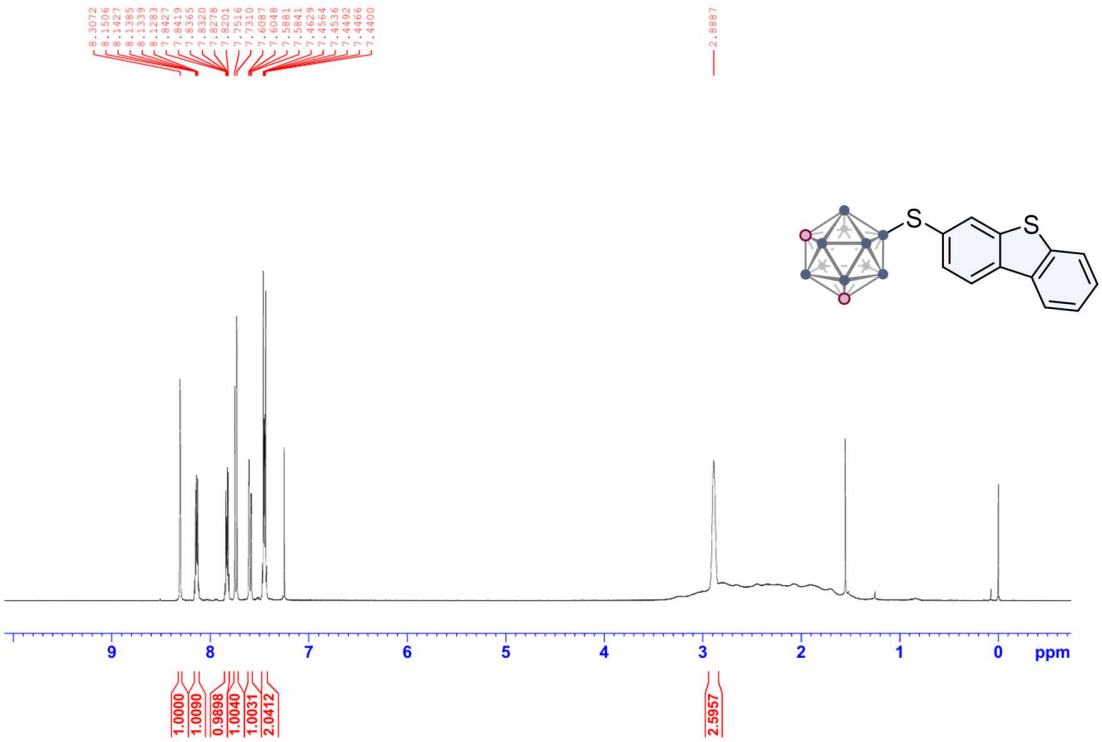
^{13}C NMR of **3ao** ($CDCl_3$, 100 MHz)



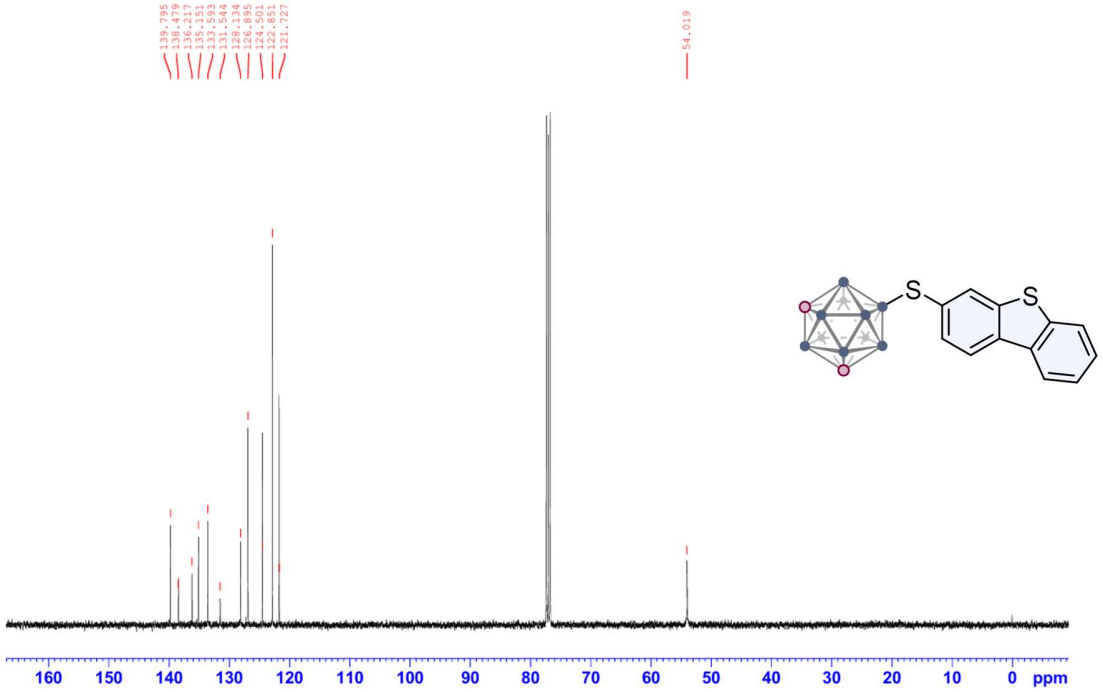
^{11}B NMR of **3ao** ($CDCl_3$, 128 MHz)



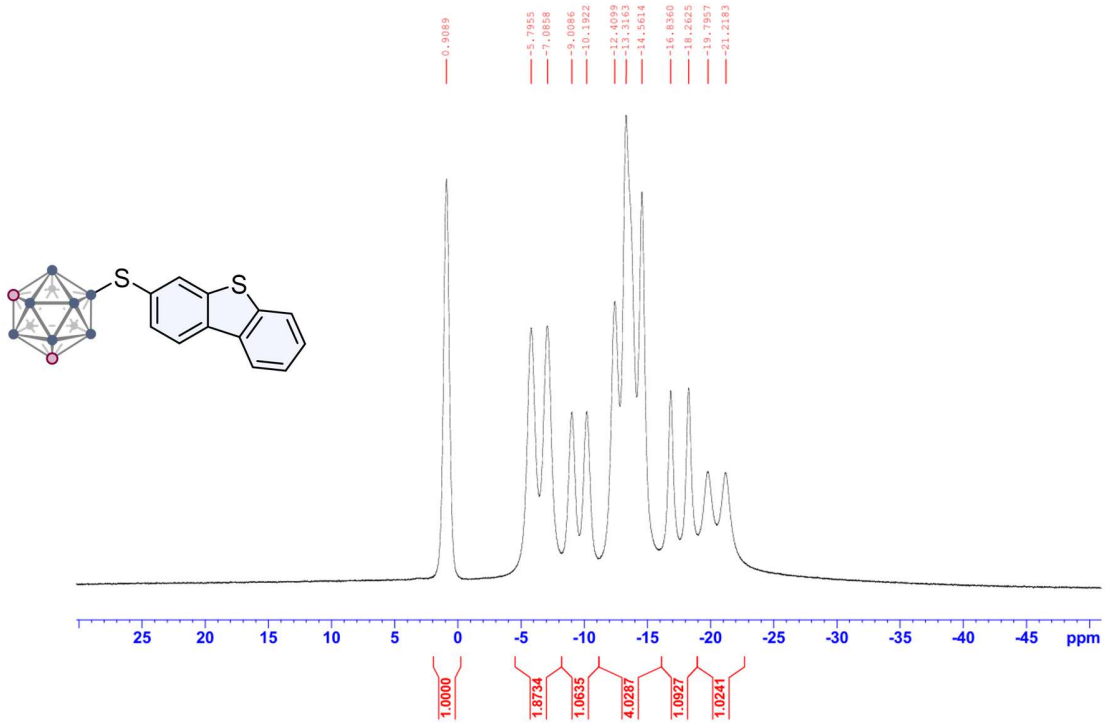
^{1}H NMR of **3ap** ($CDCl_3$, 400 MHz)



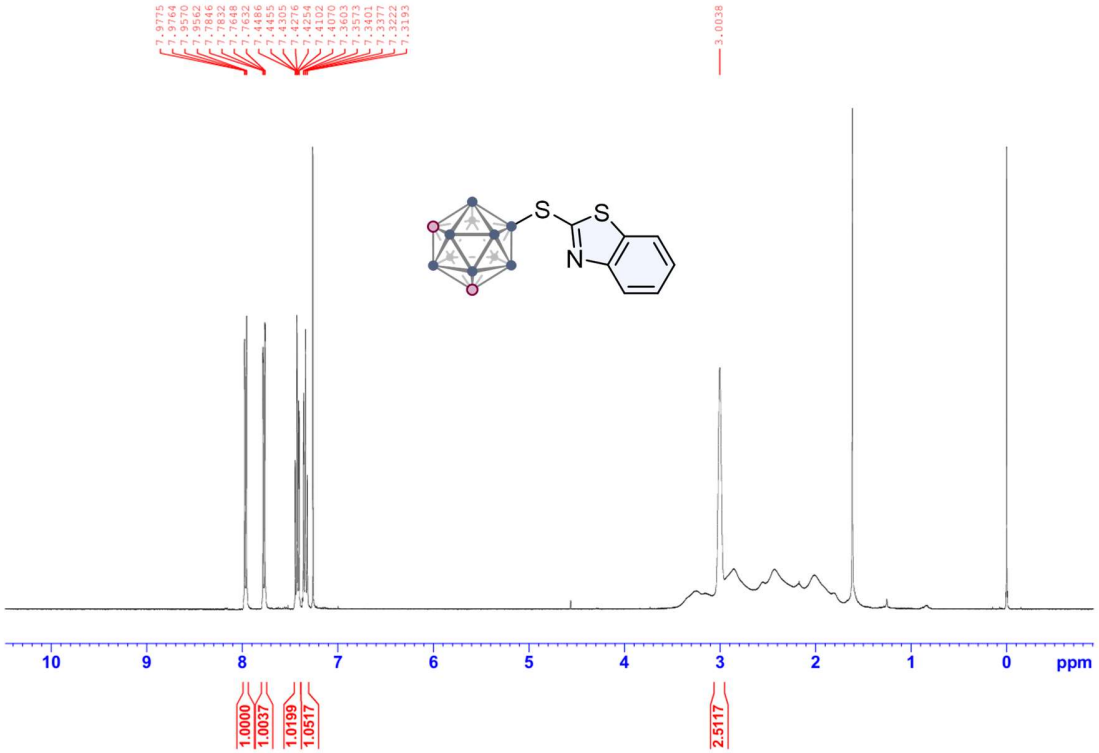
^{13}C NMR of **3ap** ($CDCl_3$, 100 MHz)



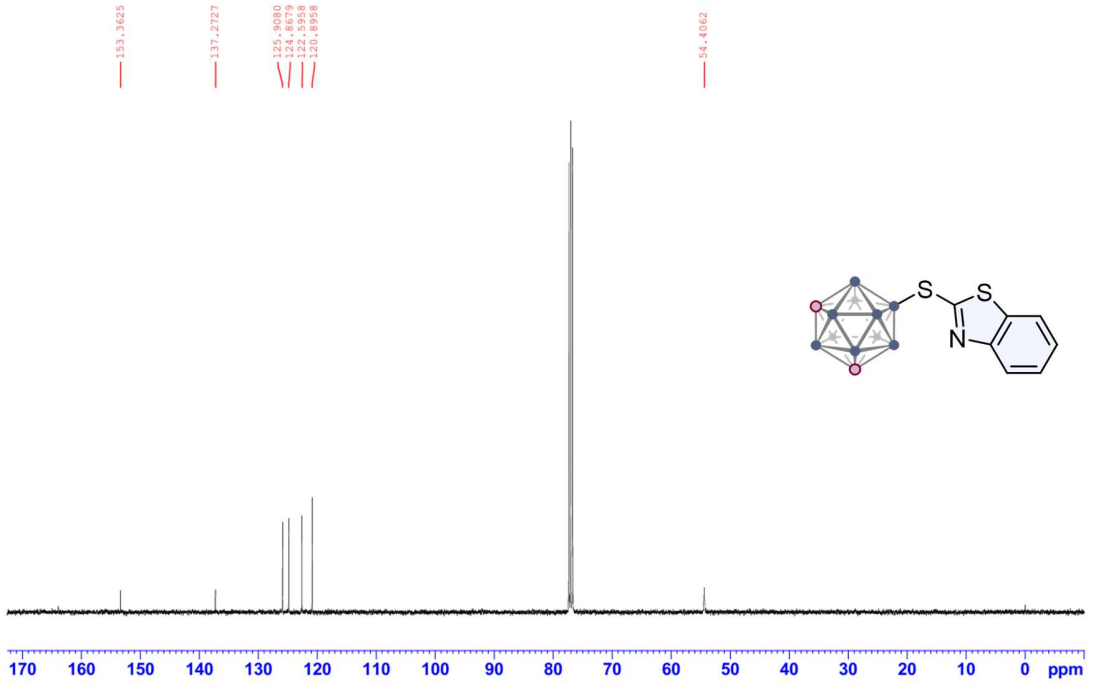
^{11}B NMR of **3ap** ($CDCl_3$, 128 MHz)



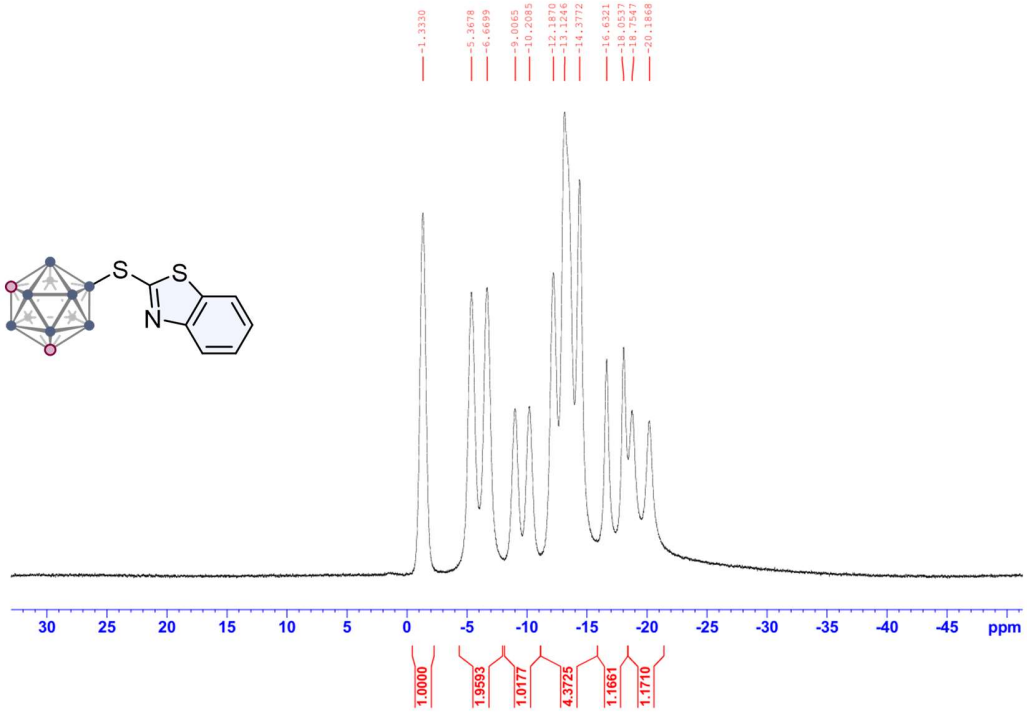
^{1}H NMR of **3aq** ($CDCl_3$, 400 MHz)



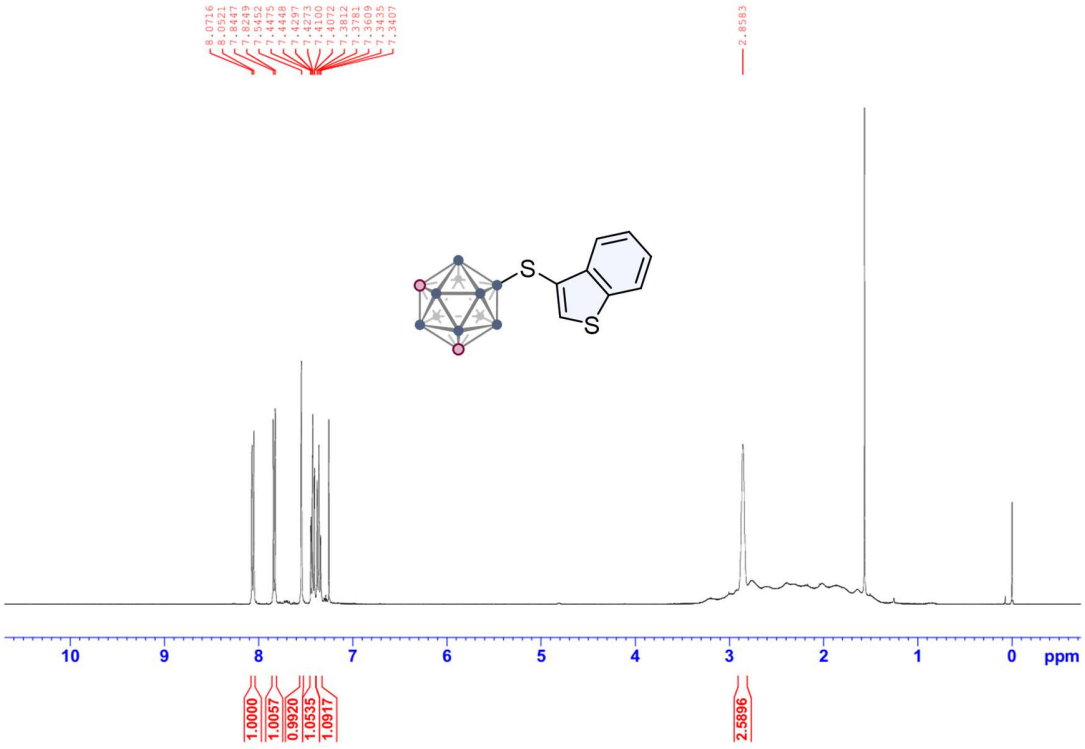
^{13}C NMR of **3aq** ($CDCl_3$, 100 MHz)



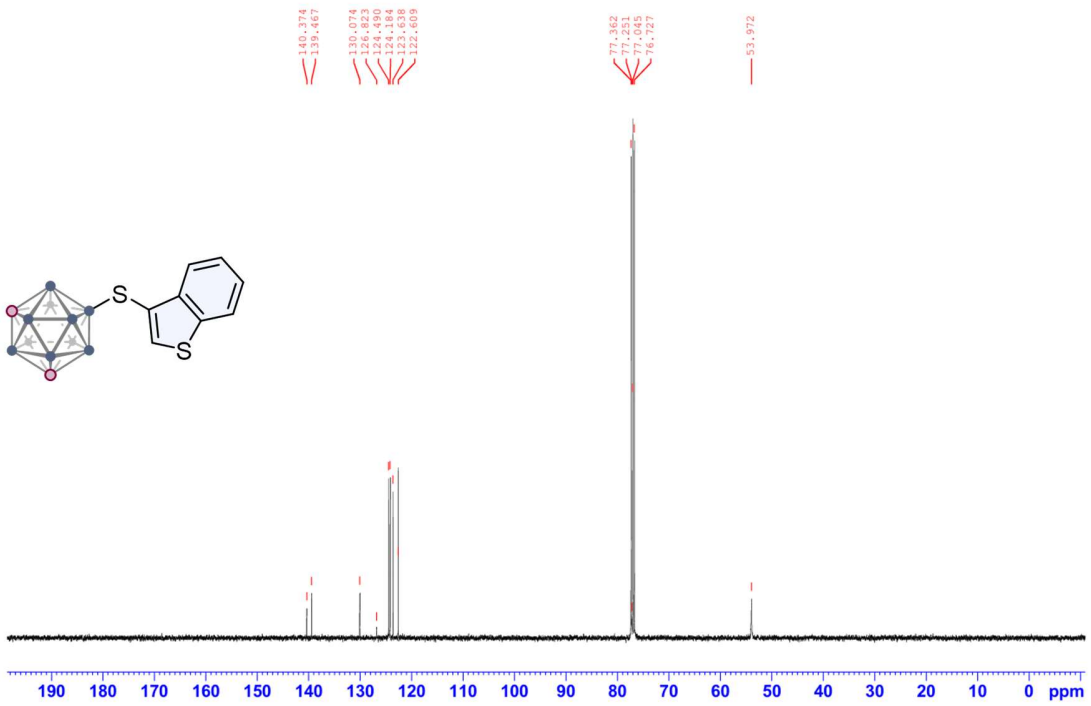
^{11}B NMR of **3aq** ($CDCl_3$, 128 MHz)



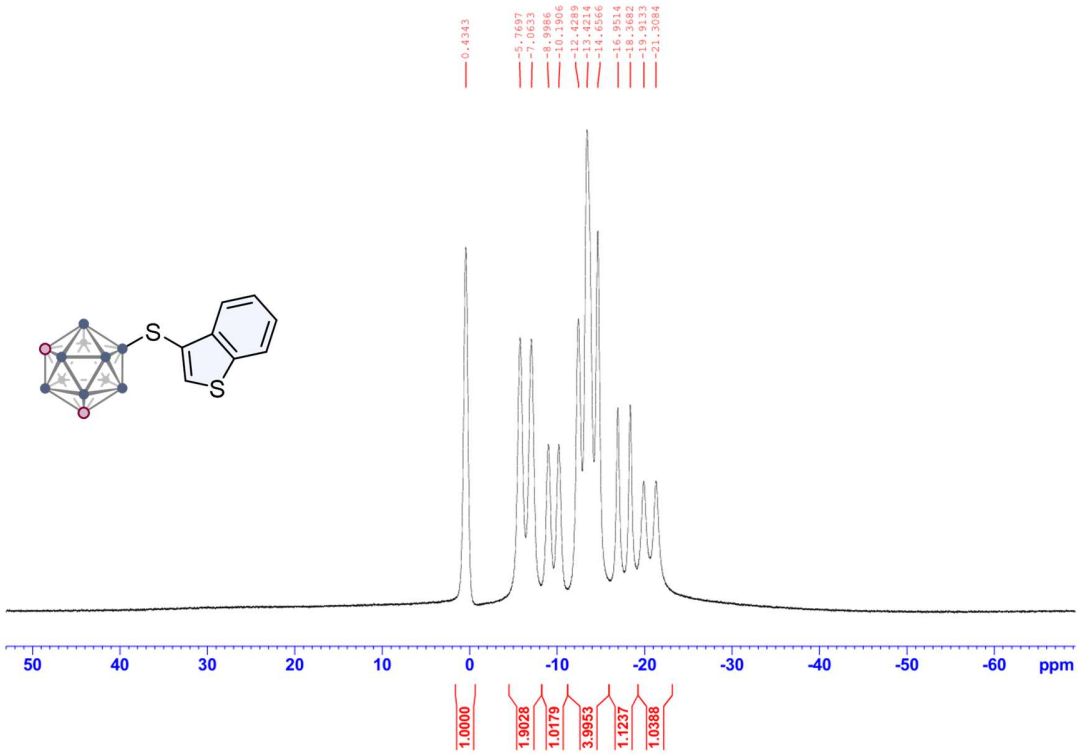
^{1}H NMR of **3ar** ($CDCl_3$, 400 MHz)



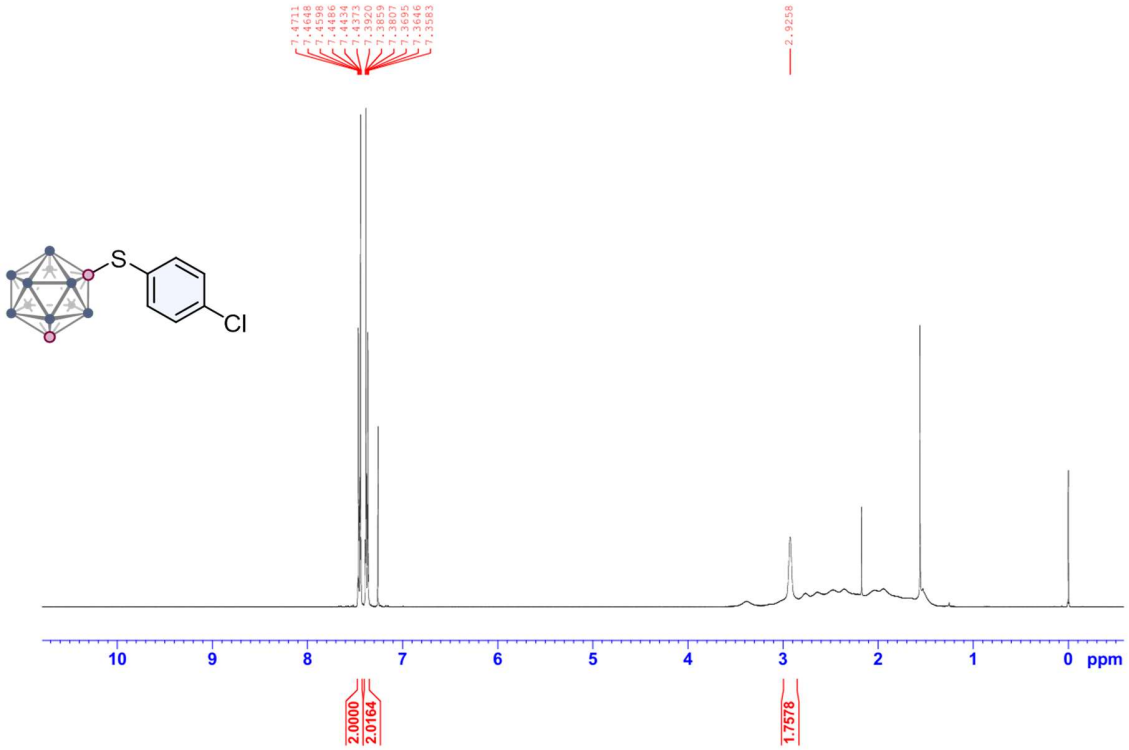
^{13}C NMR of **3ar** ($CDCl_3$, 100 MHz)



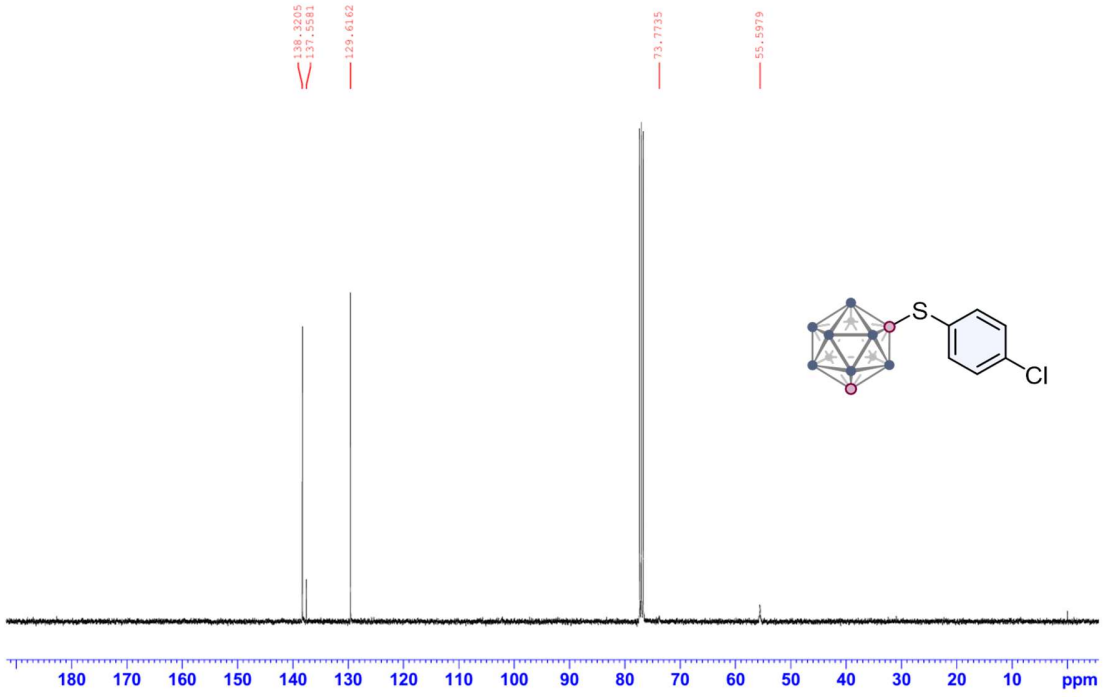
^{11}B NMR of **3ar** ($CDCl_3$, 128 MHz)



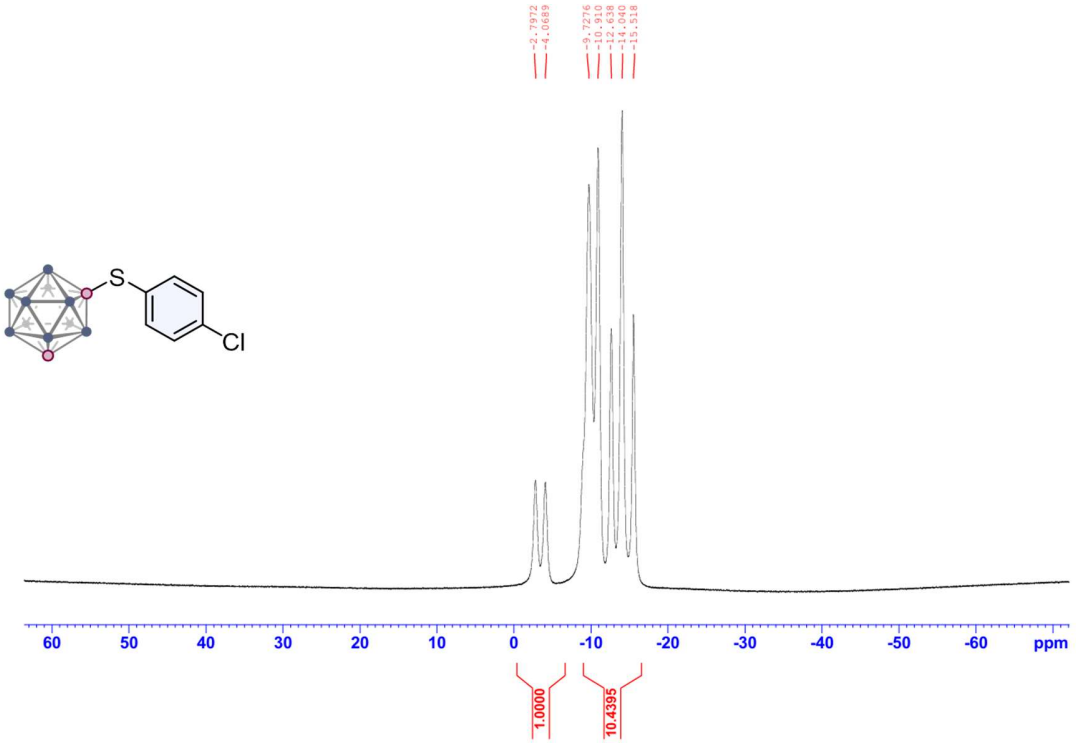
^{1}H NMR of **3bc** ($CDCl_3$, 400 MHz)



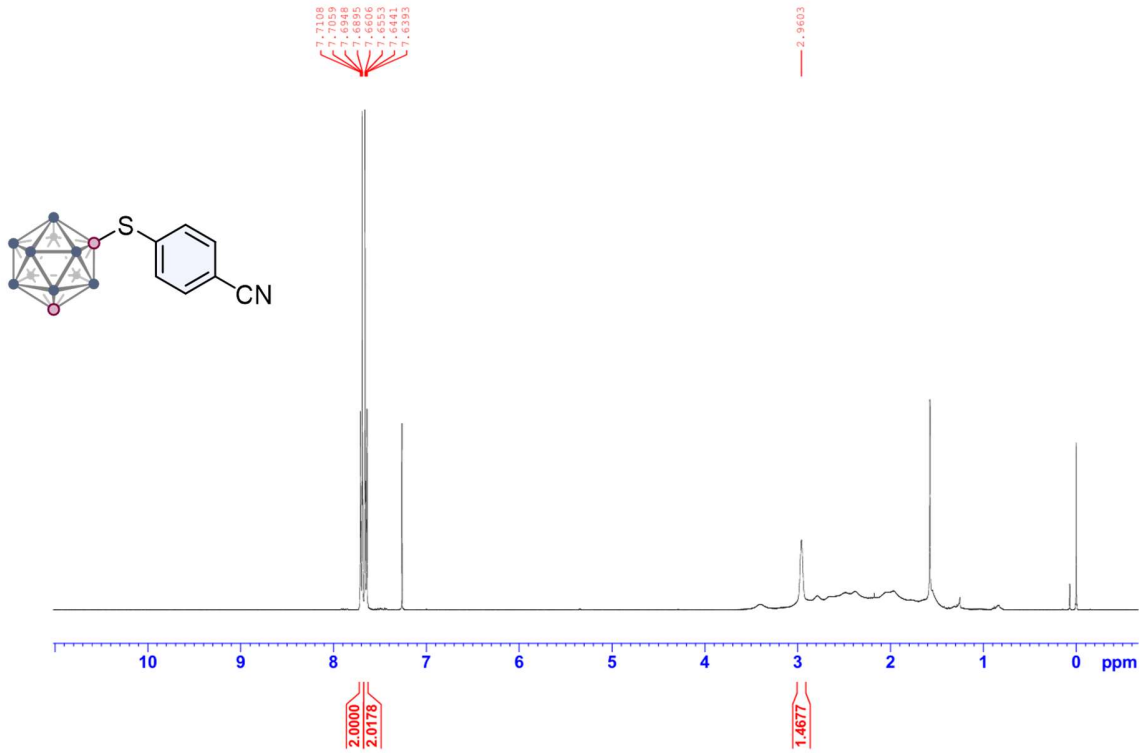
^{13}C NMR of **3bc** ($CDCl_3$, 100 MHz)



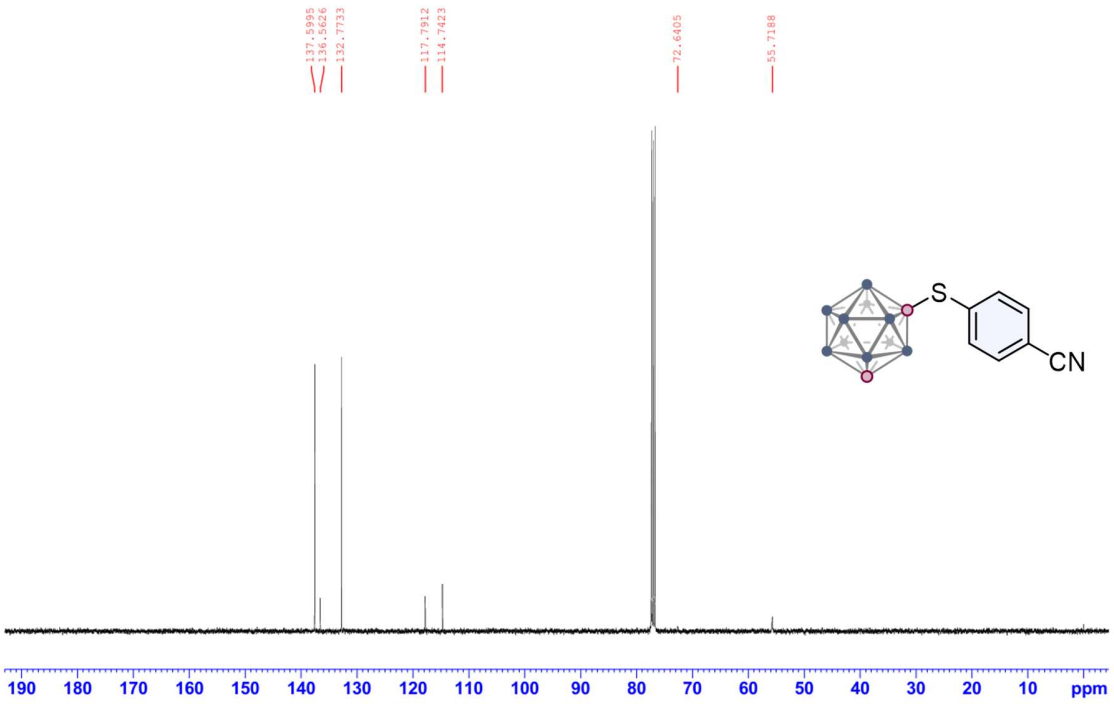
^{11}B NMR of **3bc** ($CDCl_3$, 128 MHz)



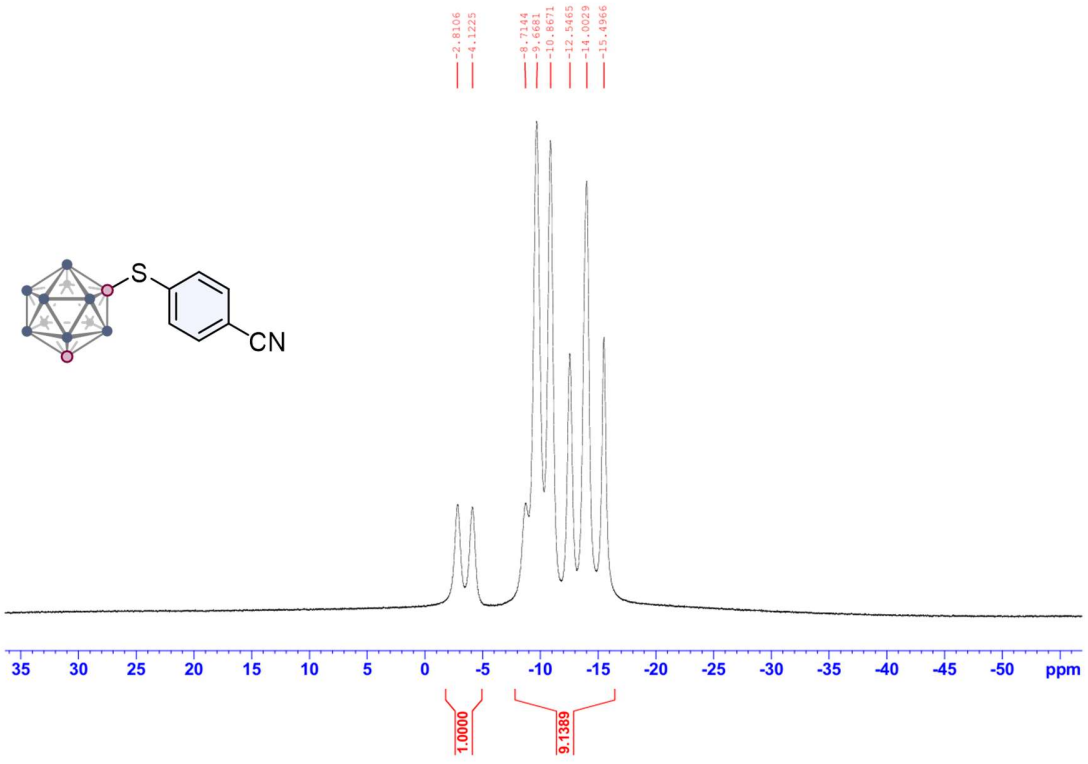
^{1}H NMR of **3be** ($CDCl_3$, 400 MHz)



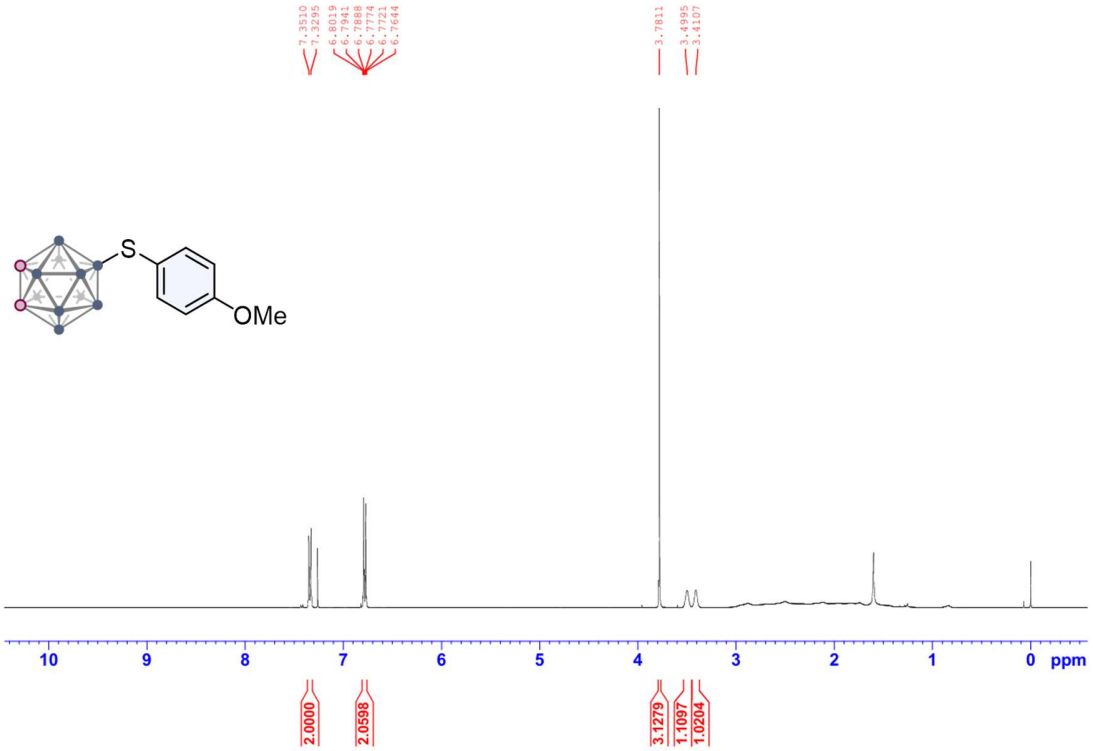
^{13}C NMR of **3be** ($CDCl_3$, 100 MHz)



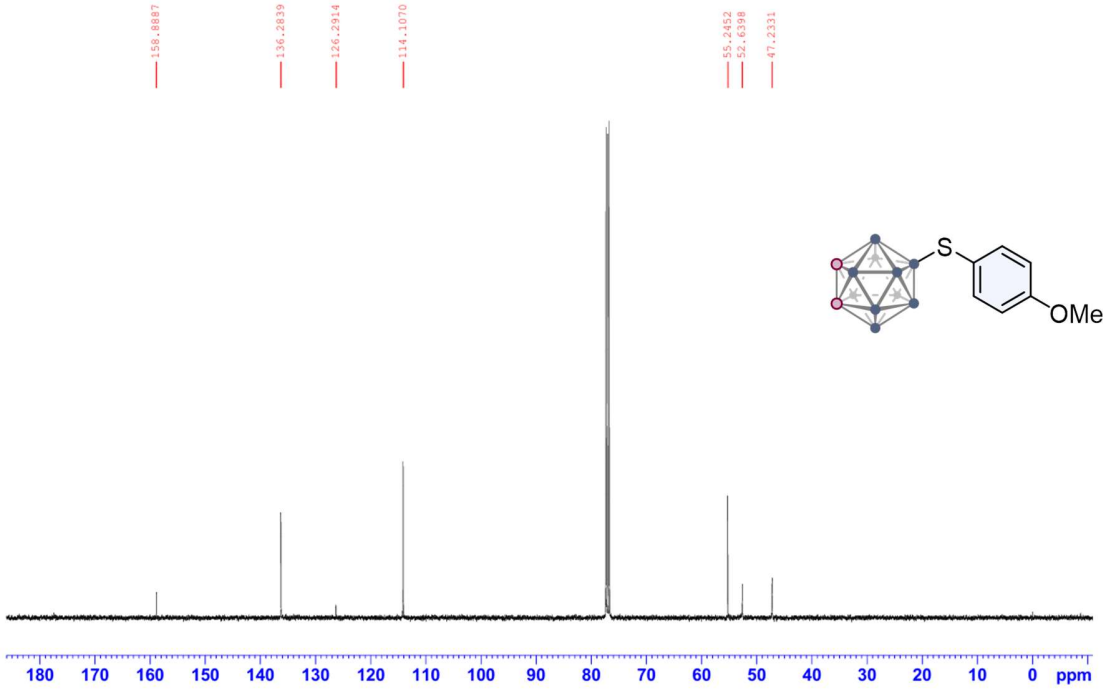
^{11}B NMR of **3be** ($CDCl_3$, 128 MHz)



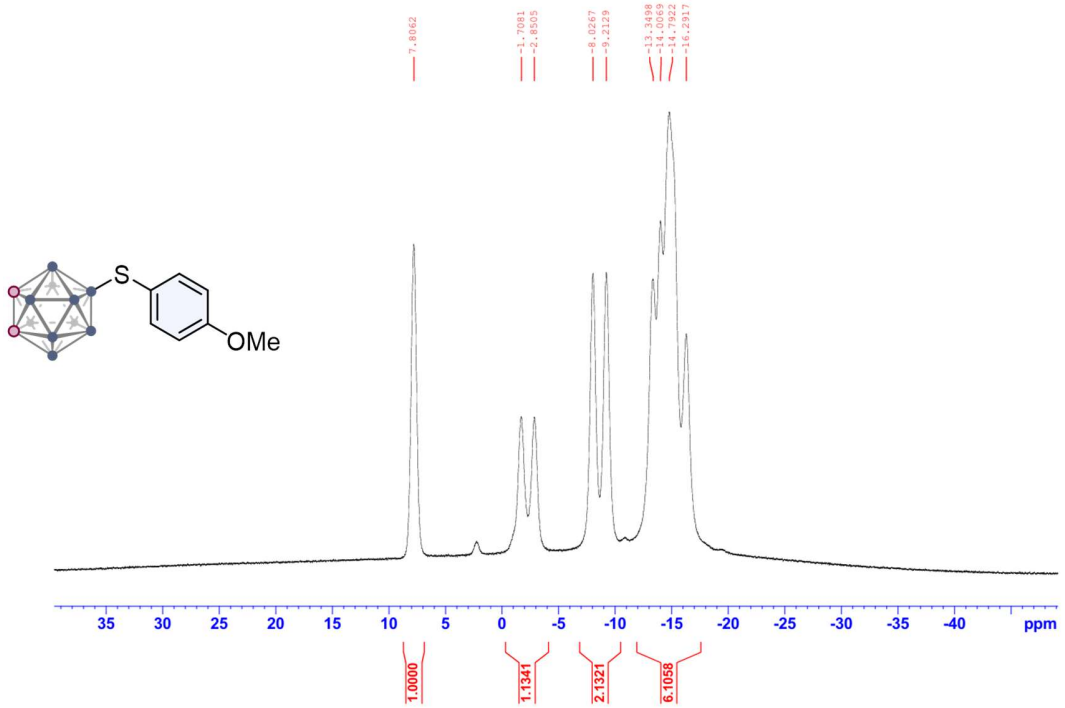
^{1}H NMR of **3ca** ($CDCl_3$, 400 MHz)



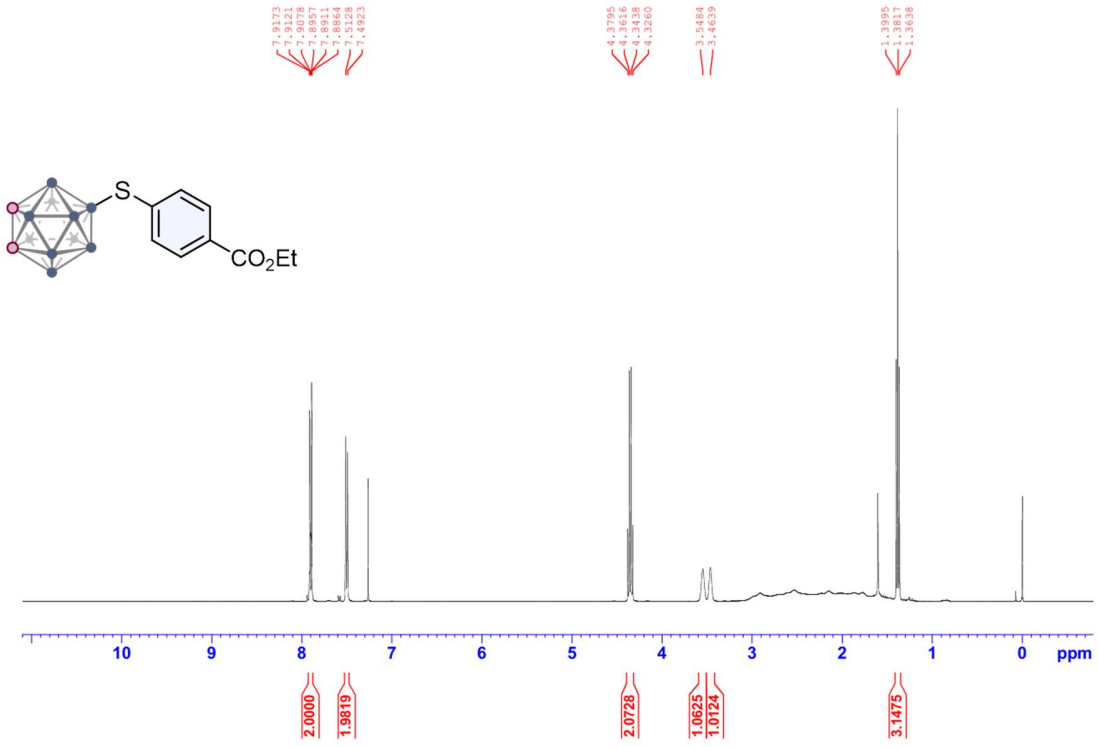
^{13}C NMR of **3ca** ($CDCl_3$, 100 MHz)



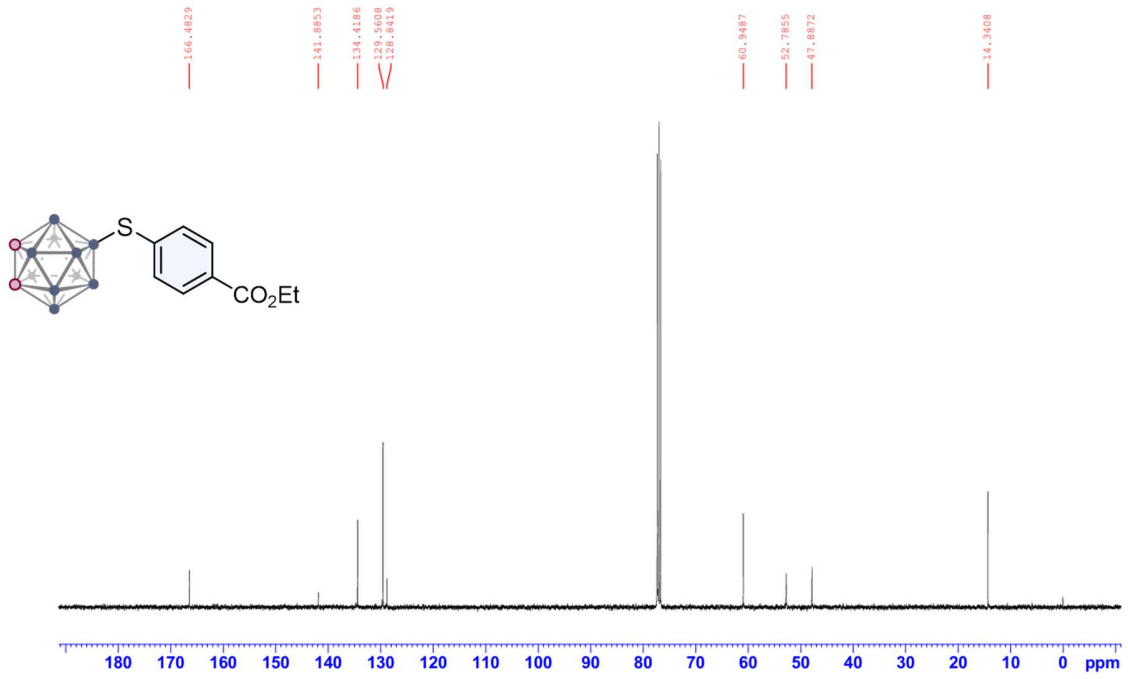
^{11}B NMR of **3ca** ($CDCl_3$, 128 MHz)



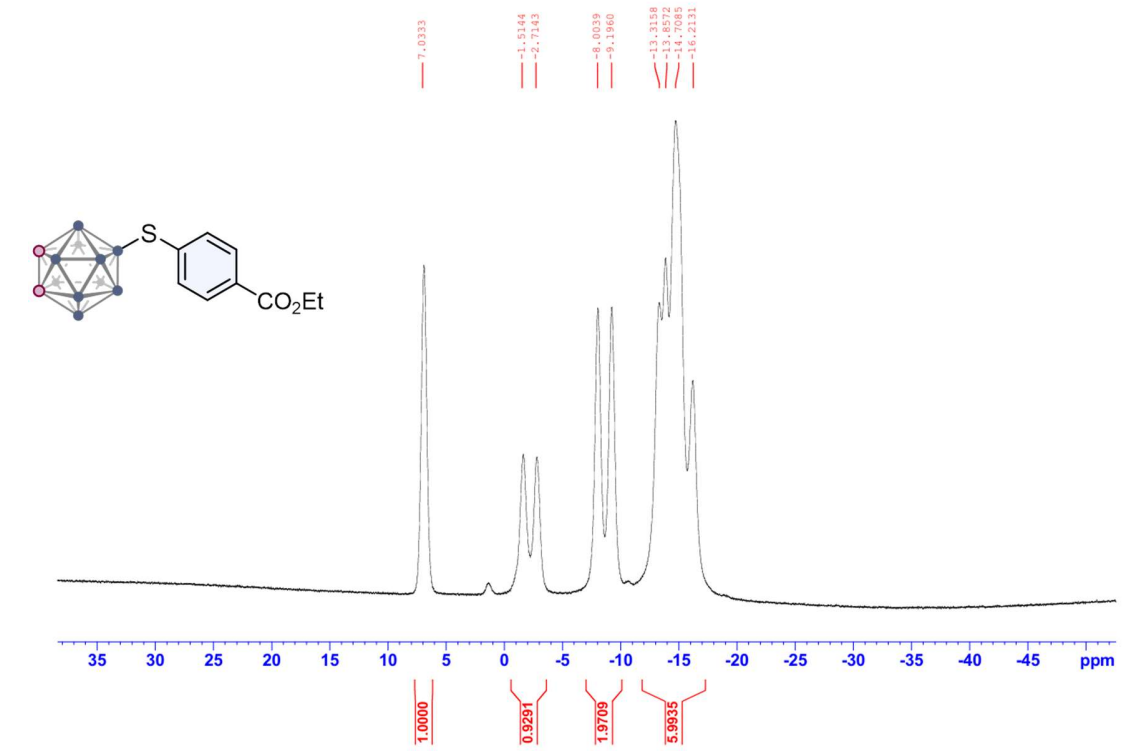
^{1}H NMR of **3cd** ($CDCl_3$, 400 MHz)



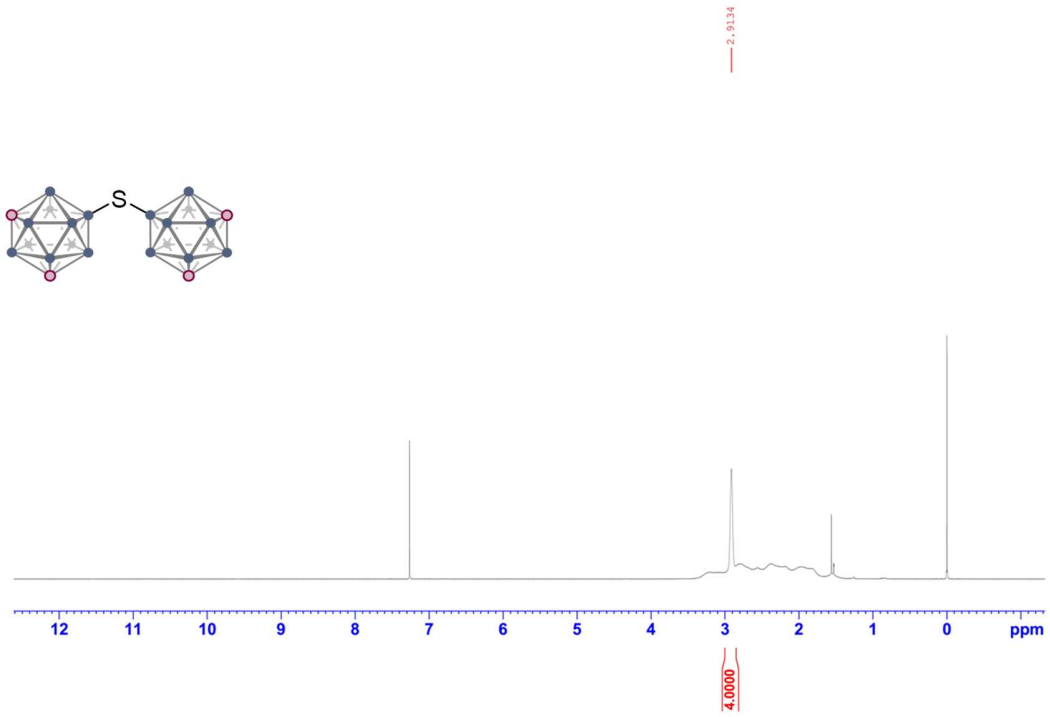
^{13}C NMR of **3cd** ($CDCl_3$, 100 MHz)



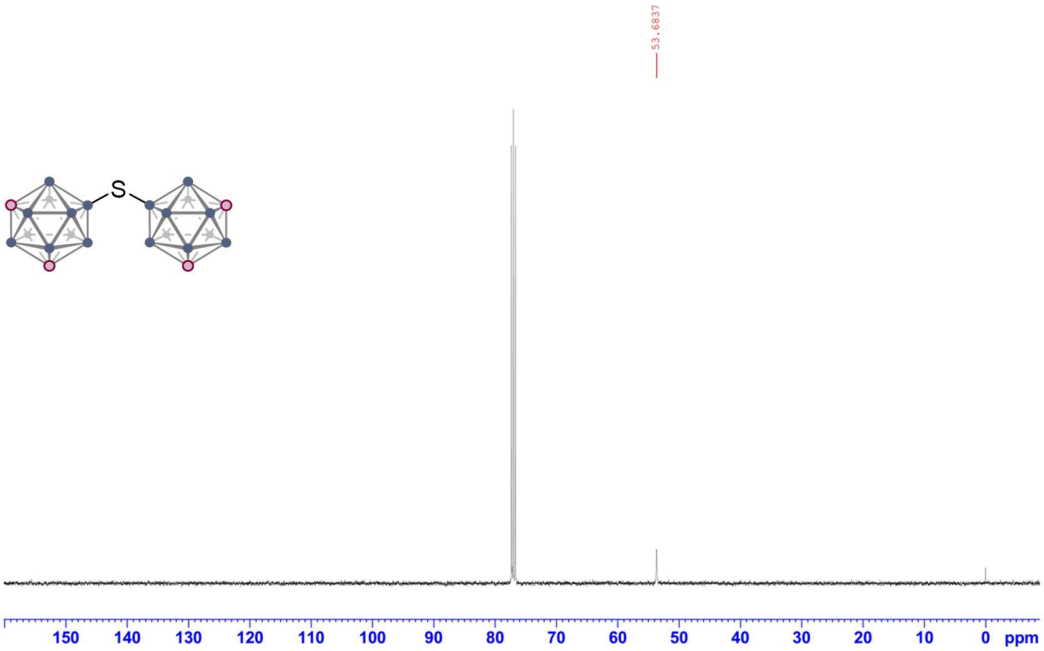
^{11}B NMR of **3cd** ($CDCl_3$, 128 MHz)



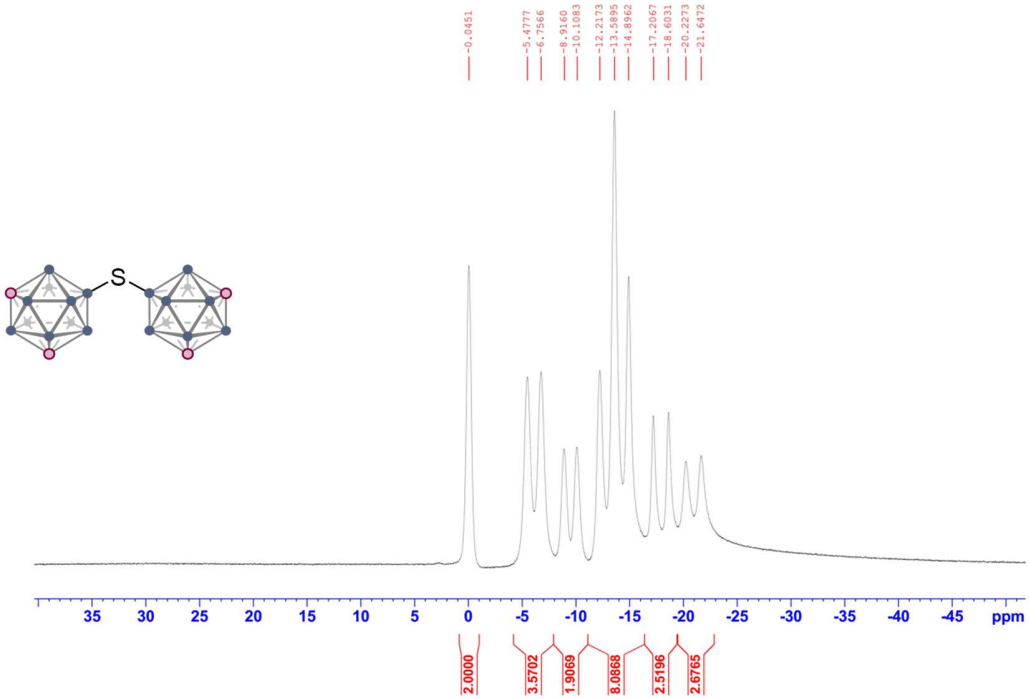
^{1}H NMR of **5a** ($CDCl_3$, 400 MHz)



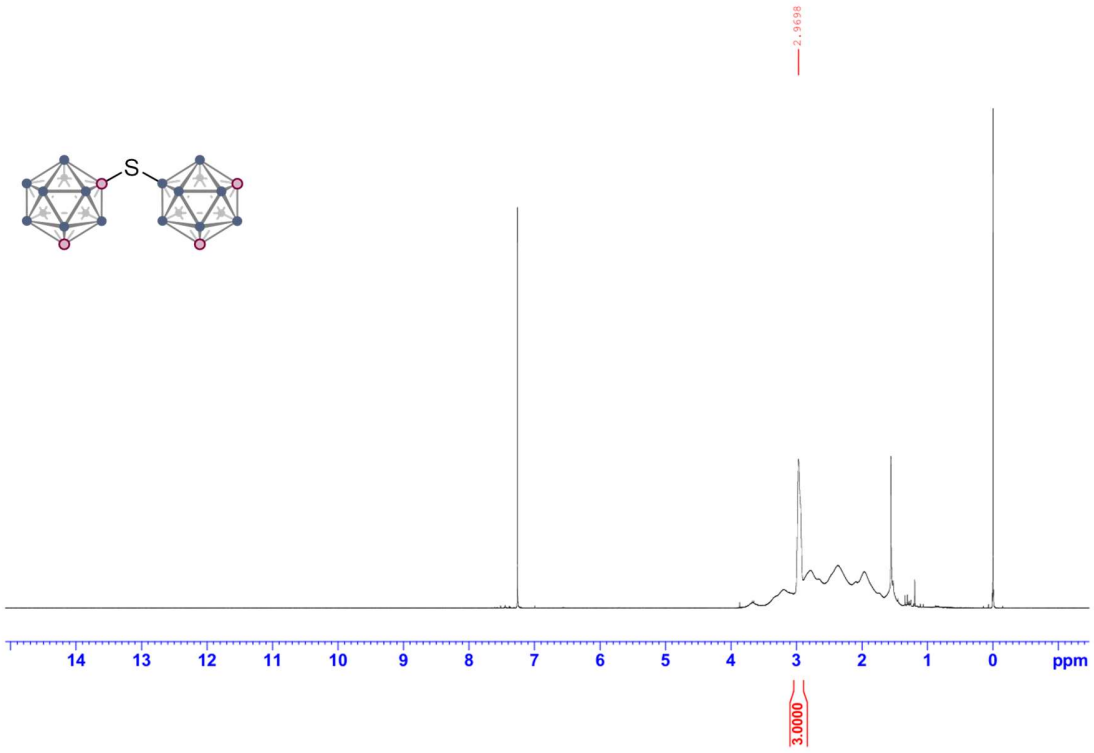
^{13}C NMR of **5a** ($CDCl_3$, 100 MHz)



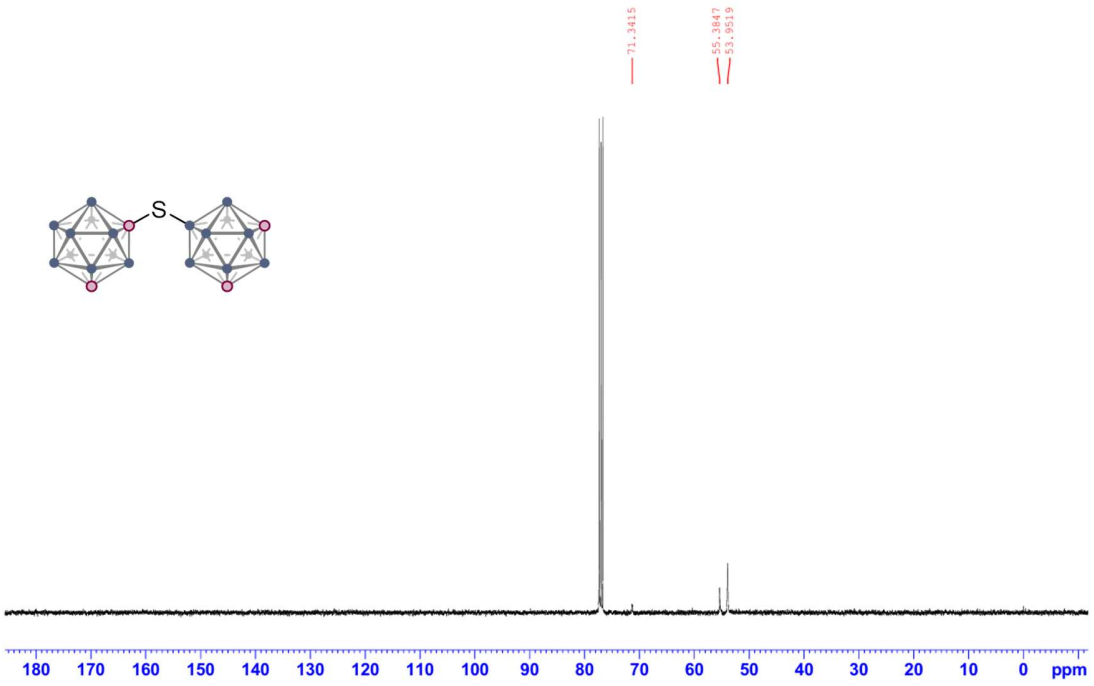
^{11}B NMR of **5a** ($CDCl_3$, 128 MHz)



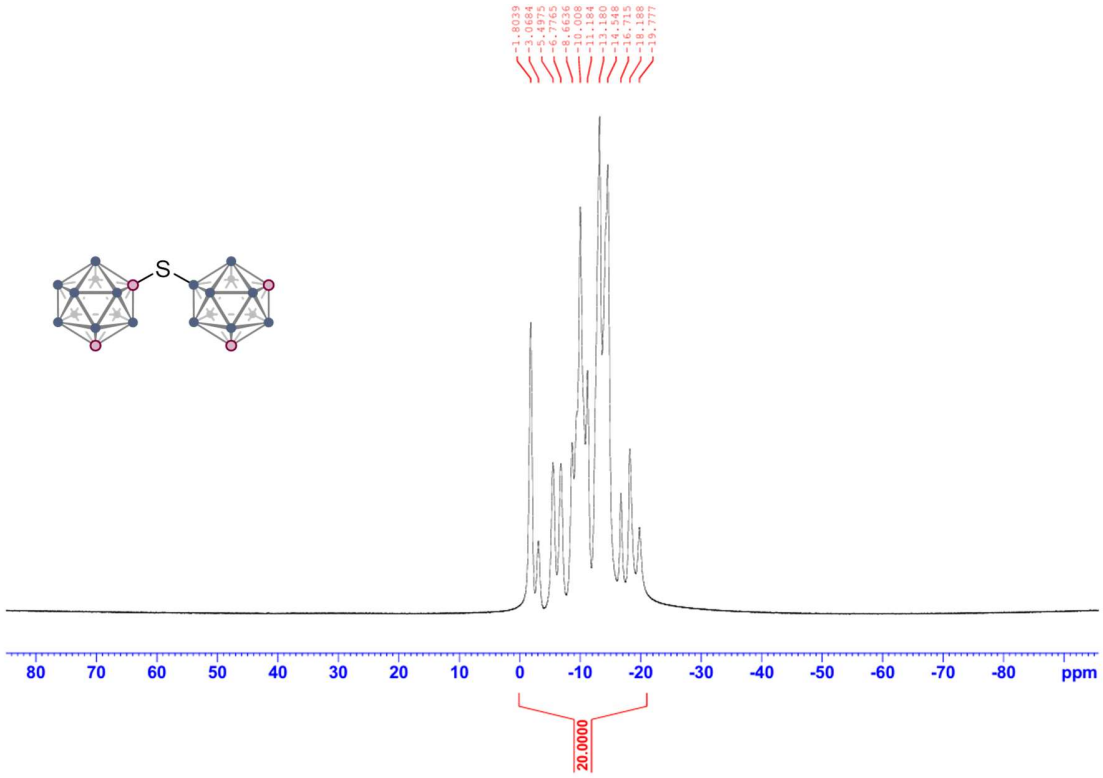
^{1}H NMR of **5b** ($CDCl_3$, 400 MHz)



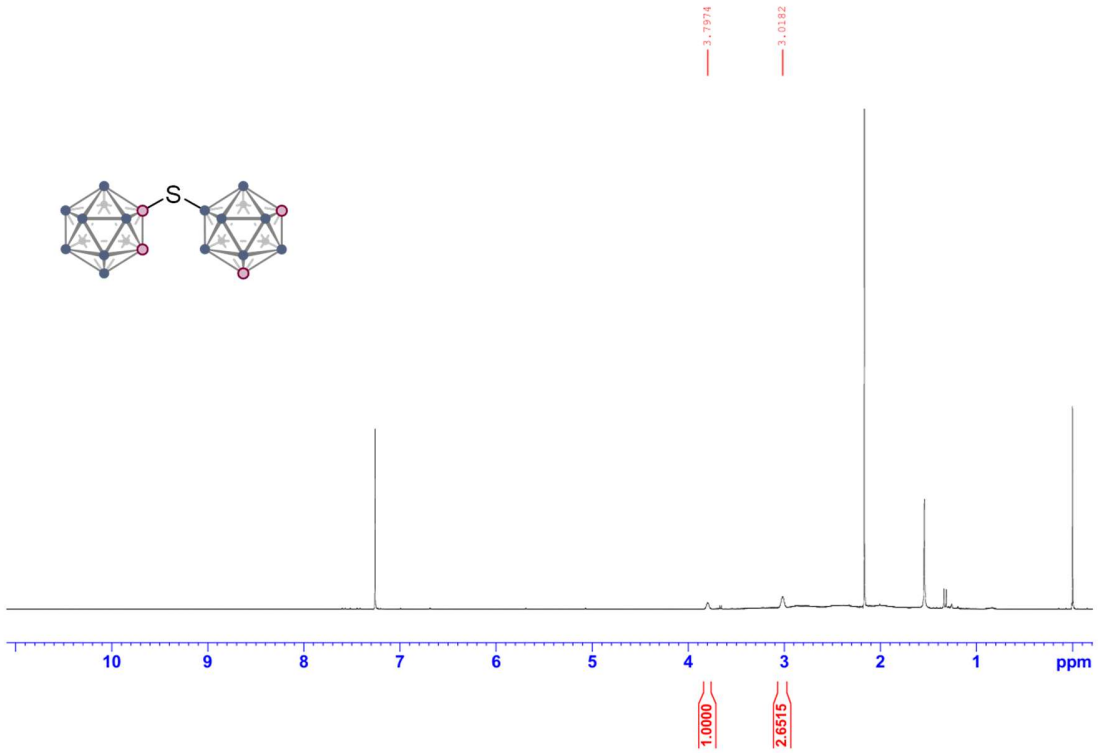
^{13}C NMR of **5b** ($CDCl_3$, 100 MHz)



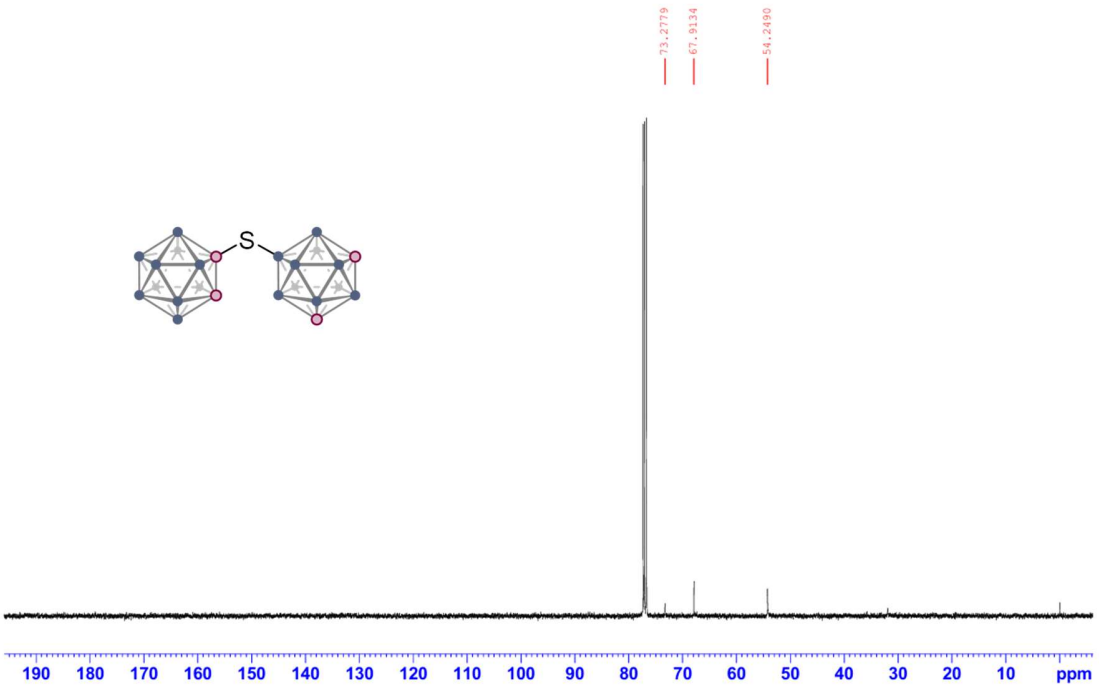
^{11}B NMR of **5b** ($CDCl_3$, 128 MHz)



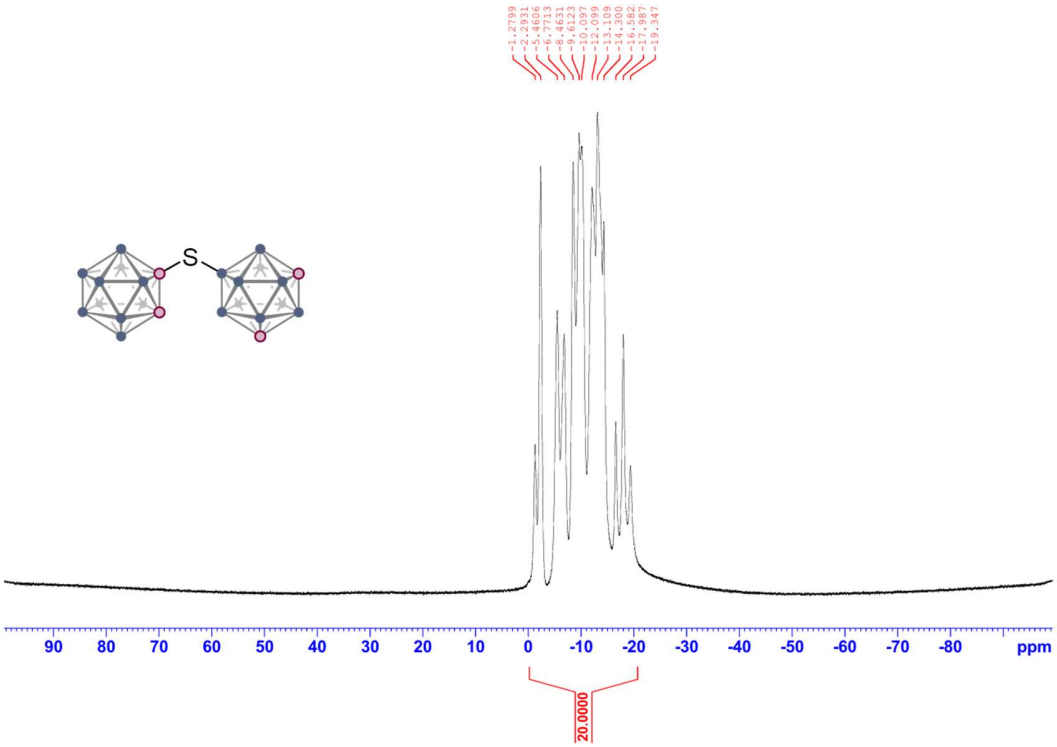
^{1}H NMR of **3ap** ($CDCl_3$, 400 MHz)



^{13}C NMR of **3ao** ($CDCl_3$, 100 MHz)



^{11}B NMR of **3ao** ($CDCl_3$, 128 MHz)



6. References

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