

Supplementary Information

Pd-catalysed synthesis of carborane sulfides from carborane thiols

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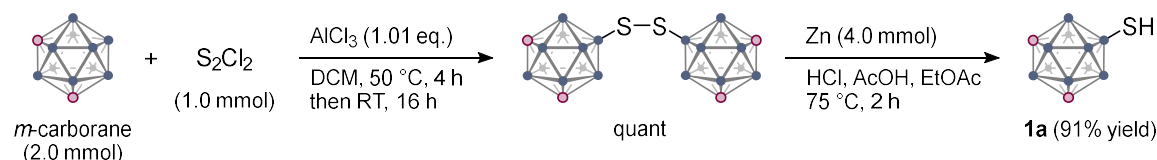
1. General Information

All manipulations were performed under N₂ 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 CaH₂ and stored with MS 4A. 1,4-Dioxane was dried and deoxygenated by a Glass Counter Solvent Dispensing System (Nikko Hansen & Co., Ltd.). Toluene, diethylether (Et₂O), 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 (¹H NMR), at 100 MHz (¹³C{¹H} NMR), and at 128 MHz (¹¹B NMR) in 5 mm NMR tubes (quartz glass tubes were used for ¹¹B NMR). ¹H NMR chemical shifts were reported in ppm relative to the resonance of the residual solvent signals at δ 7.26 for CDCl₃. ¹³C NMR chemical shifts were reported in ppm relative to the residual solvent signals at δ 77.2 for CDCl₃. Melting points were measured with Mettler Toledo MP90. High resolution mass spectra (HRMS) were recorded by APCI-TOF or EI-EB.

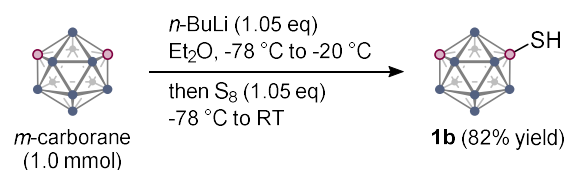
2. Preparation of Carborane Derivatives

m-Carborane-9-thiol (1a)



Prepared according to the literature procedure.¹ To a two-necked flask equipped with an N₂ balloon were added *m*-carborane (288 mg, 2.0 mmol), AlCl₃ (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 CHCl₃ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/CHCl₃ = 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. HCl aq (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 KOH aq and washed with Et₂O. The aqueous layer was acidified with HCl aq and extracted with Et₂O three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/CHCl₃ = 4/1) to give the title compound as white solid (215 mg, 61% yield).

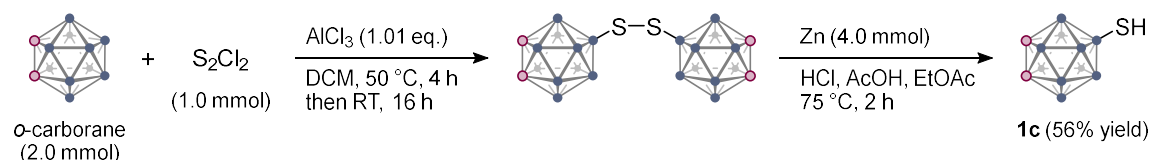
m-Carborane-1-thiol (1b)



To a two-necked flask equipped with an N₂ balloon were added *m*-carborane (144 mg, 1.0 mmol) and Et₂O (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 S₈ (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 NH₄Cl aq and extracted with CHCl₃ three times. The

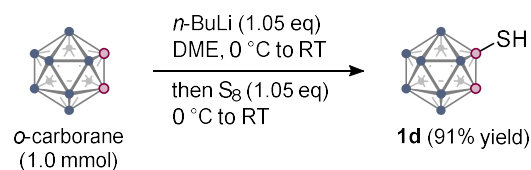
combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to give the title compound as white solid (144 mg, 82% yield).

[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 (CHCl₃).

[o-Carborane-1-thiol \(1d\)](#)



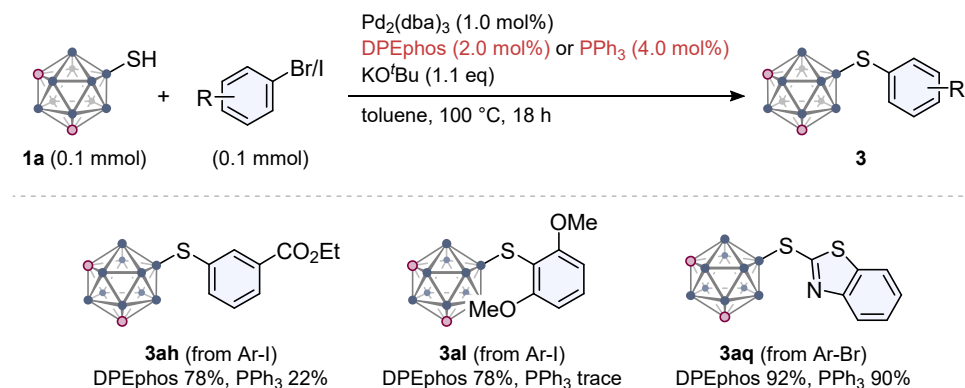
Prepared according to the literature procedure.² To a two-necked flask equipped with an N₂ balloon were added *o*-carborane (144 mg, 1.0 mmol) and DME (4.0 mL). The solution was cooled to 0 °C with ice bath, and *n*-BuLi (1.51 mol/L in hexane, 0.70 mL, 1.05 mmol) was added dropwise. After stirring at 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 S₈ (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 NH₄Cl aq and extracted with CHCl₃ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by silica gel column chromatography (CHCl₃) to give the title compound as white solid (161 mg, 91% yield).

[9-Iodo-*m*-carborane \(4\)](#)

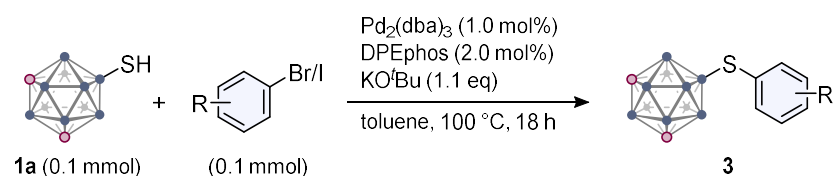
Prepared according to the literature procedure.³

3. Experimental Procedures and Product Identification Data

[Additional Data for the Optimization Study \(Table 1\)](#)

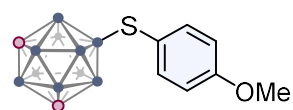


[General Procedure for the Pd-Catalyzed Coupling Reaction \(Scheme 2\)](#)



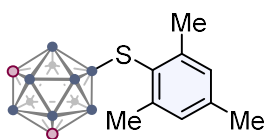
To an oven-dried Schlenk tube were added $\text{Pd}_2(\text{dba})_3$ (0.9 mg, 1.0 mol%) and DPEphos (1.1 mg, 2.0 mol%). The tube was filled with dry N_2 , and toluene (1.0 mL) was added via syringe. *m*-Carborane-9-thiol (17.6 mg, 0.1 mmol), aryl halide (0.1 mmol), and KO^tBu (12.3 mg, 0.11 mmol) were 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**)



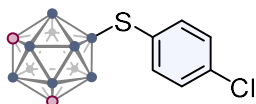
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 19.2 mg (68% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.38~1.43 (cage BH), 2.90 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 136.3, 126.3, 114.2, 55.3, 53.9; ^{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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_{18}\text{B}_{10}\text{OS}$ 283.2159; Found 283.2131.

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



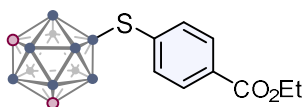
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 20.5 mg (70% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.90 (s, 2H), 3.39~1.36 (cage BH), 2.87 (s, 2H), 2.50 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 136.9, 131.5, 128.6, 53.8, 22.5, 21.0; ^{11}B NMR (128 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{22}\text{B}_{10}\text{S}$ 295.2524; Found 295.2531.

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



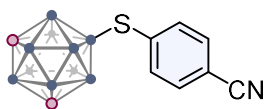
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.3 mg (81% yield), white solid, m.p. 128.0~130.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 3.40~1.44 (cage BH), 2.92 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.3, 134.1, 133.3, 128.8, 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_8\text{H}_9\text{B}_{10}\text{SCl}$ 287.1666; Found 287.1637.

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



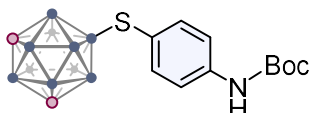
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 25.3 mg (78% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.39~1.36 (cage BH), 2.94 (s, 2H), 1.39 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 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 : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_{20}\text{B}_{10}\text{O}_2\text{S}$ 324.2193; Found 324.2191.

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



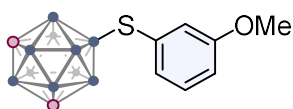
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 22.6 mg (81% yield), white solid, m.p. 112.0~114.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 3.39~1.43 (cage BH), 2.97 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 135.0, 132.1, 118.8, 110.5, 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_{15}\text{B}_{10}\text{NS}$ 278.2006; Found 278.1979.

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



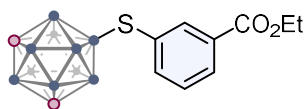
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 20.0 mg (54% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 8.6 Hz, 2H), 7.32~7.24 (m, 2H), 6.46 (s, 1H), 3.40~1.32 (cage BH), 2.90 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 137.6, 135.8, 129.1, 118.6, 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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{25}\text{B}_{10}\text{NO}_2\text{S}$ 367.2616; Found 367.2613.

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



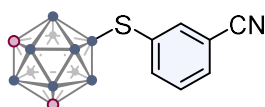
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 22.7 mg (80% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, J = 7.8 Hz, 1H), 7.12~7.08 (m, 2H), 6.80 (dd, J = 8.1, 2.4 Hz, 1H), 3.80 (s, 3H), 3.41~1.41 (cage BH), 2.91 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 136.5, 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 : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_{18}\text{B}_{10}\text{OS}$ 282.2087; Found 282.2078.

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



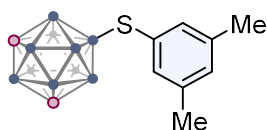
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 25.3 mg (78% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 3.42~1.43 (cage BH), 2.93 (s, 2H), 1.40 (t, $J = 7.1$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{20}\text{B}_{10}\text{O}_2\text{S}$ 325.2266; Found 325.2256.

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



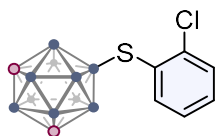
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.6 mg (85% yield), pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 3.43~1.39 (cage BH), 2.96 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_{15}\text{B}_{10}\text{NS}$ 279.1967; Found 279.1975.

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



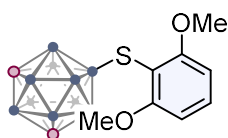
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 21.4 mg (76% yield), white solid, 108.5~110.5 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.07 (s, 2H), 6.80 (s, 1H), 3.37~1.32 (cage BH), 2.83 (s, 2H), 2.71 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 134.7, 132.6, 128.8, 53.9, 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_{20}\text{B}_{10}\text{S}$ 282.2328; Found 282.2313.

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



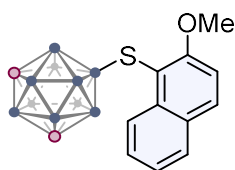
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 23.7 mg (82% yield), white solid, 61.0~62.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J = 7.7 Hz, 1H), 7.42 (dd, J = 7.5, 2.0 Hz, 1H), 7.22~7.15 (m, 2H), 3.36~1.38 (cage BH), 2.92 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 138.0, 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_8\text{H}_{15}\text{B}_{10}\text{SCl}$ 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; ^1H 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_{20}\text{B}_{10}\text{O}_2\text{S}$ 313.2266; Found 313.2278.

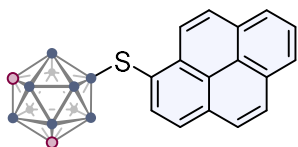
9-(2-methoxy-1-naphthalenylthio)-*m*-carborane (**3am**)



Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 26.6 mg (80% yield), white solid, m.p. 179.2~181.2 °C; ^1H 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);

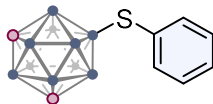
HRMS (EI) m/z : $[M]^+$ Calcd for $C_{13}H_{20}B_{10}OS$ 332.2245; Found 332.2245.

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



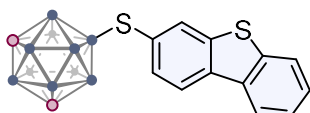
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 33.1 mg (88% yield), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 9.2 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.16~8.12 (m, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.05~7.96 (m, 3H), 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; 1H 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; Found 253.2036.

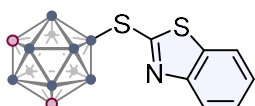
9-(dibenzo[*b,d*]thiophene-3-thio)-*m*-carborane (**3ap**)



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; 1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.15~8.13 (m, 1H), 7.84~7.82 (m, 1H),

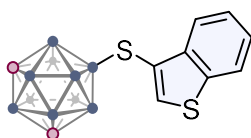
7.74 (d, $J = 8.2$ Hz, 1H), 7.60 (dd, $J = 8.3, 1.6$ Hz, 1H), 7.46~7.44 (m, 2H), 3.35~1.40 (cage BH), 2.89 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.8, 138.5, 136.2, 135.2, 133.6, 131.5, 128.1, 126.9, 124.5, 122.9, 121.7, 54.0 (1 peak overlapped); ^{11}B NMR (128 MHz, CDCl_3) δ 0.91 (s, 1B), -6.44 (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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{B}_{10}\text{OS}$ 358.1861; Found 358.1849.

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



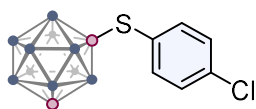
Conducted with 2-bromobenzothiazole (0.15 mmol), $\text{Pd}_2(\text{dba})_3$ (2.0 mol%), and DPEphos (4.0 mol%). Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 28.5 mg (92% yield), white solid, m.p. 127.5~128.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 8.1, 0.4$ Hz, 1H), 7.77 (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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{B}_{10}\text{OS}$ 309.1655; Found 309.1669.

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



Conducted with 3-bromobenzo[*b*]thiophene (0.15 mmol), $\text{Pd}_2(\text{dba})_3$ (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; ^1H 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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{B}_{10}\text{OS}$ 308.1703; Found 308.1704.

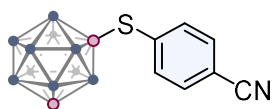
1-(4-chlorophenylthio)-*m*-carborane (**3bc**)



Conducted with *m*-carborane-1-thiol (**1b**, 0.1 mmol), 1-chloro-4-iodobenzene (0.15 mmol), Pd₂(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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 137.6, 129.6, 73.8, 55.6 (1 peak overlapped); ¹¹B NMR (128 MHz, CDCl₃) 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 C₁₃H₂₀B₁₀OS 287.1564; Found 287.1567.

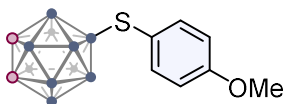
1-(4-cyanophenylthio)-*m*-carborane (**3be**)



Conducted with *m*-carborane-1-thiol (**1b**, 0.1 mmol), 1-cyano-4-iodobenzene (0.15 mmol), Pd₂(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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 136.6, 132.8, 117.8, 114.7, 72.6, 55.7; ¹¹B NMR (128 MHz, CDCl₃) δ -3.47 (d, *J* = 167.9 Hz, 1B), -8.71~-15.5 (m, 9B); HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₃H₂₀B₁₀OS 277.1933; Found 277.1932.

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

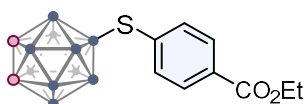


Conducted with *o*-carborane-9-thiol (**1c**, 0.1 mmol), 1-iodo-4-methoxybenzene (0.15 mmol), Pd₂(dba)₃ (2.0 mol%), and DPEphos (4.0 mol%).

Purified by silica gel column chromatography (hexane/EtOAc = 2/1), 25.2 mg (89% yield), white solid, m.p. 140.2~140.7 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{B}_{10}\text{OS}$ 282.2087; Found 282.2083.

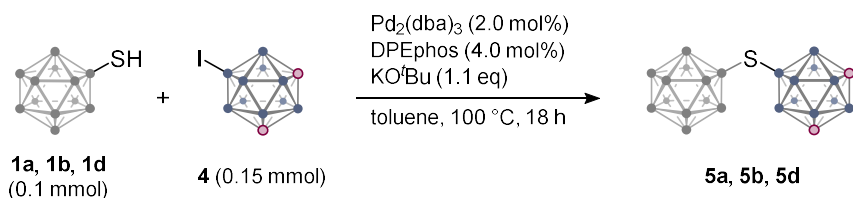
9-(4-ethoxycarbonylphenylthio)-*o*-carborane (**3ca**)



Conducted with *o*-carborane-9-thiol (**1c**, 0.1 mmol), ethyl 4-iodobenzoate (0.15 mmol), $\text{Pd}_2(\text{dba})_3$ (2.0 mol%), and DPEphos (4.0 mol%).

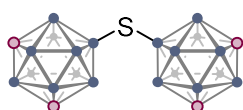
Purified by silica gel column chromatography (hexane/EtOAc = 2/1), 24.2 mg (75% yield), white solid, m.p. 140.5~141.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 4.35 (q, $J = 7.2$ Hz, 2H), 3.55 (s, 1H), 3.46 (s, 1H), 3.15~1.16 (cage BH), 1.38 (t, $J = 7.1$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{B}_{10}\text{OS}$ 324.2193; Found 324.2190.

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



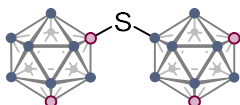
To an oven-dried Schlenk tube were added $\text{Pd}_2(\text{dba})_3$ (1.8 mg, 2.0 mol%) and DPEphos (2.2 mg, 4.0 mol%). The tube was filled with dry N_2 , and toluene (1.0 mL) was added via syringe. Carborane thiol (17.6 mg, 0.1 mmol), 9-iodo-*m*-carborane (40.5 mg, 0.15 mmol), and KO^tBu (12.3 mg, 0.11 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**)



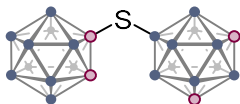
Purified by silica gel column chromatography (hexane/EtOAc = 10/1), 142.2 mg (89% yield), white solid (single crystals suitable for X-ray analysis were obtained by slow evaporation from the CHCl₃ solution), m.p. 174.5~176.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36~1.46 (cage BH), 2.91 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 53.7; ¹¹B NMR (128 MHz, CDCl₃) 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 C₄H₂₂B₂₀S 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; ¹H NMR (CDCl₃, 400 MHz) δ 3.86~1.38 (cage BH), 2.97 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 71.3, 55.4, 54.0; ¹¹B NMR (128 MHz, CDCl₃) δ -1.80~-19.8 (m, 20B); HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₄H₂₂B₂₀S 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 CHCl₃ solution), m.p. 167.6~169.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (s, 1H), 3.67~1.02 (cage BH), 2.65 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 73.3, 67.9, 54.2; ¹¹B NMR (128 MHz, CDCl₃) δ -1.24~-19.3 (m, 20B); HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₄H₂₂B₂₀S 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 AgSbF₆. 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 NaHCO₃/Na₂S₂O₃ solution (if the substrate has acid functionality, NaHCO₃ was not used), and extracted with CHCl₃ three times. The combined organic layer was dried over Na₂SO₄ 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 AgSbF₆ (5.0 mol%) in MeNO₂ (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 AgSbF₆ (5.0 mol%) in MeNO₂ (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 AgSbF₆ (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 AgSbF₆ (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 AgSbF₆ (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 AgSbF₆ (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 AgSbF₆ (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>.

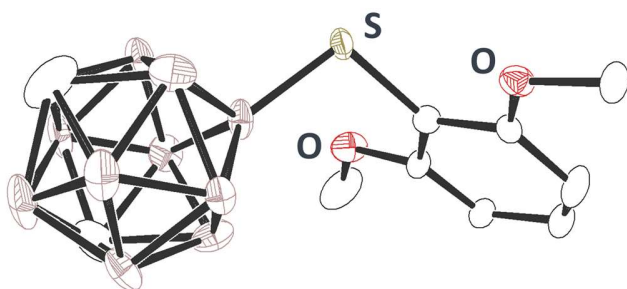


Figure S1. ORTEP drawing for **3al** with 40% thermal ellipsoid.

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

CCDC No.	2369107
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)
<i>Z</i>	4
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0880$, $wR2 = 0.2467$
R factor (all data)	$R1 = 0.0996$, $wR2 = 0.2553$
<i>R</i> _{int}	0.0940
Goodness of fit	1.762

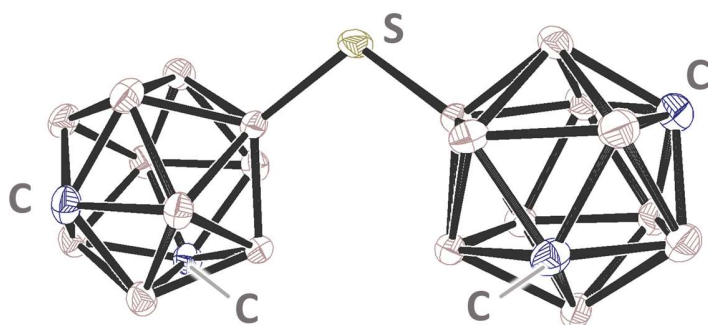


Figure S2. ORTEP drawing for **5a** with 40% thermal ellipsoid.

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

CCDC No.	2369108
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)
<i>Z</i>	4
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0408$, $wR2 = 0.1072$
R factor (all data)	$R1 = 0.0430$, $wR2 = 0.1092$
<i>R</i> _{int}	0.0464
Goodness of fit	1.076

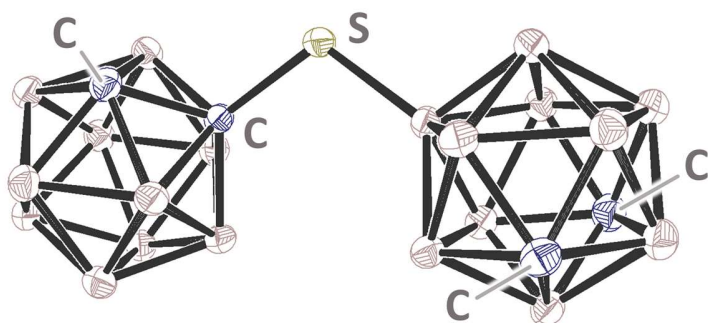


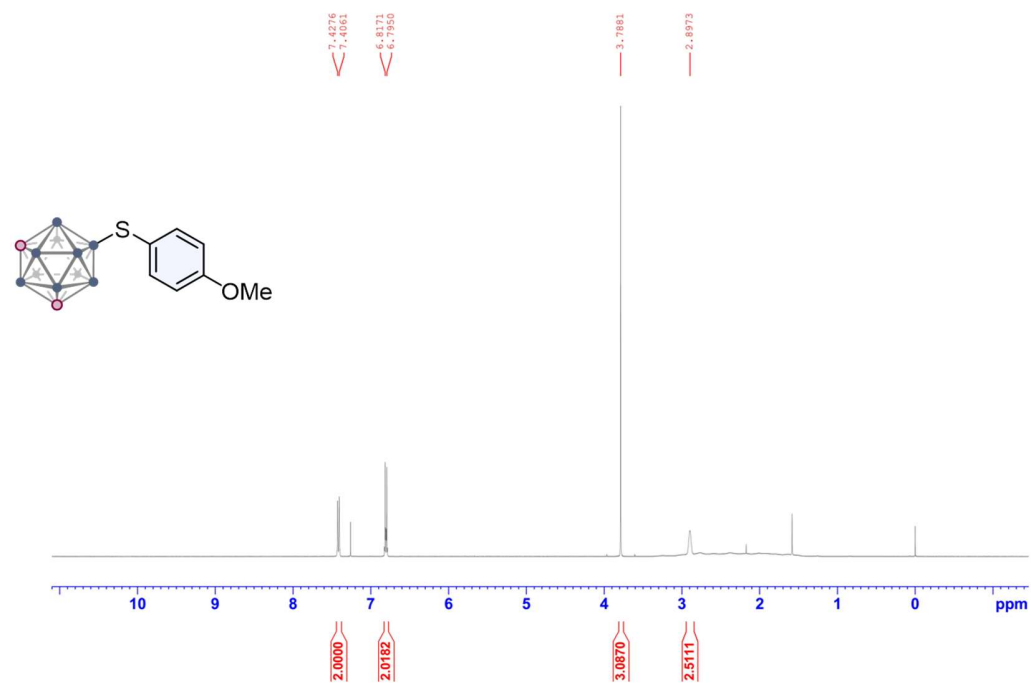
Figure S2. ORTEP drawing for **5d** with 40% thermal ellipsoid.

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

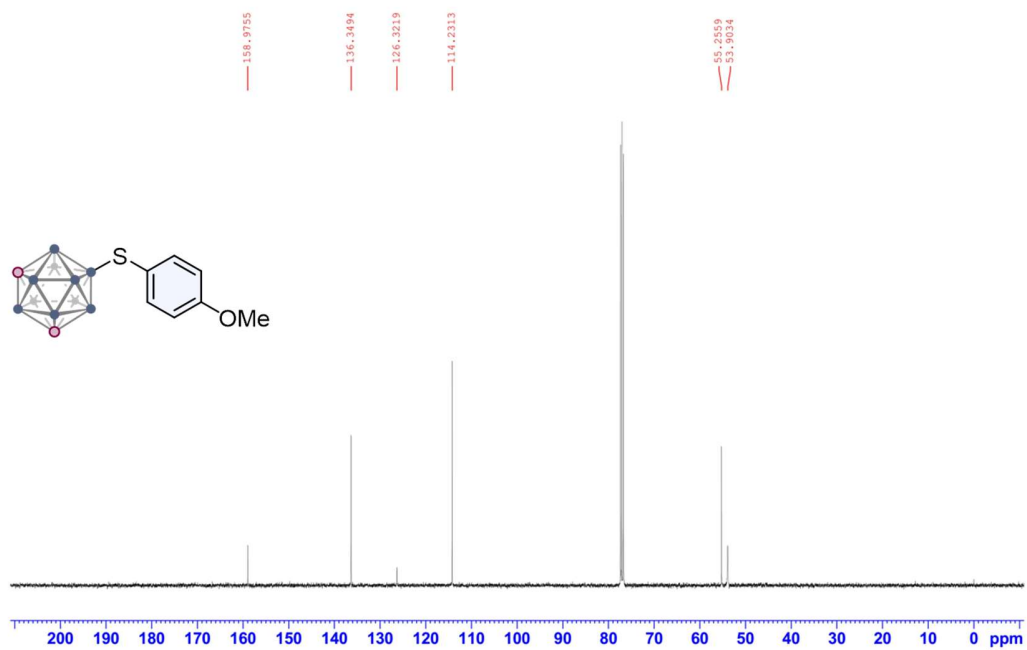
CCDC No.	2369109
Crystal system	triclinic
Space group	<i>P</i> -1 (No. 2)
Unit cell parameter [Å, deg]	$a = 7.0096(3)$, $\alpha = 94.038(3)$ $b = 11.3433(5)$, $\beta = 92.610(3)$ $c = 11.4466(3)$, $\gamma = 98.639(3)$
Cell volume [Å ³]	896.13(6)
<i>Z</i>	2
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0497$,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

5. Copy of NMR Spectra

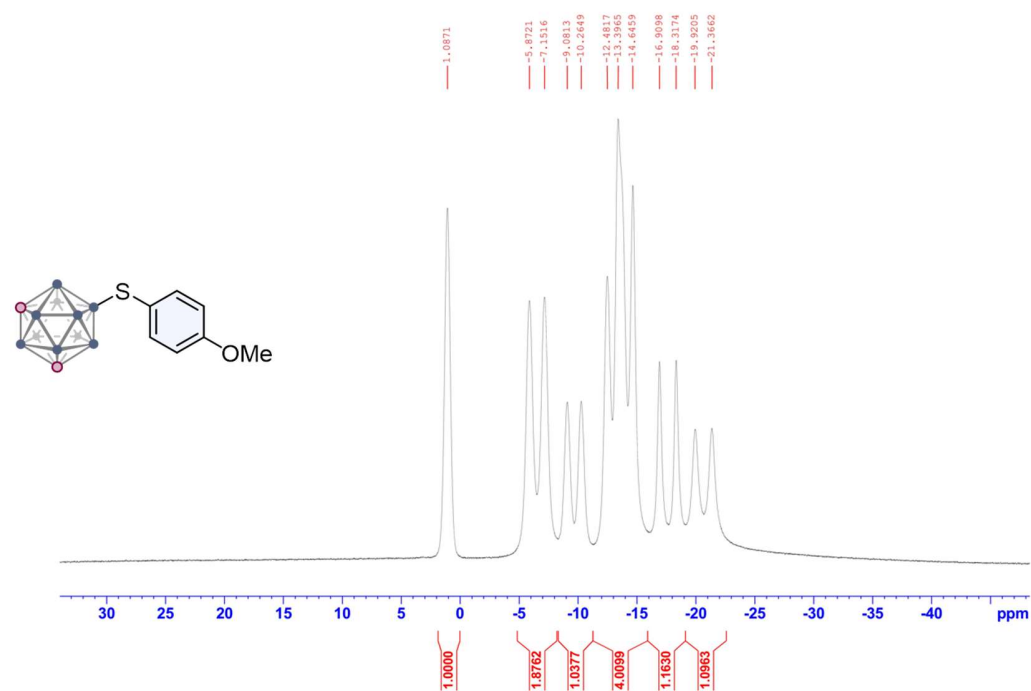
^1H NMR of **3aa** (CDCl_3 , 400 MHz)



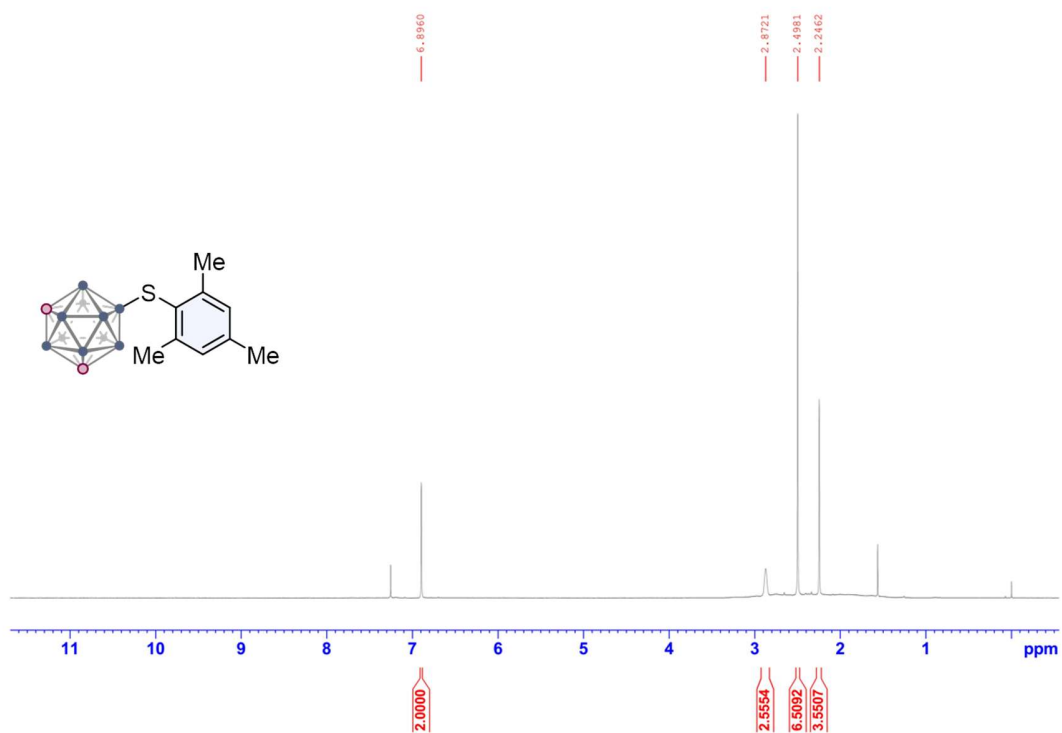
^{13}C NMR of **3aa** (CDCl_3 , 100 MHz)



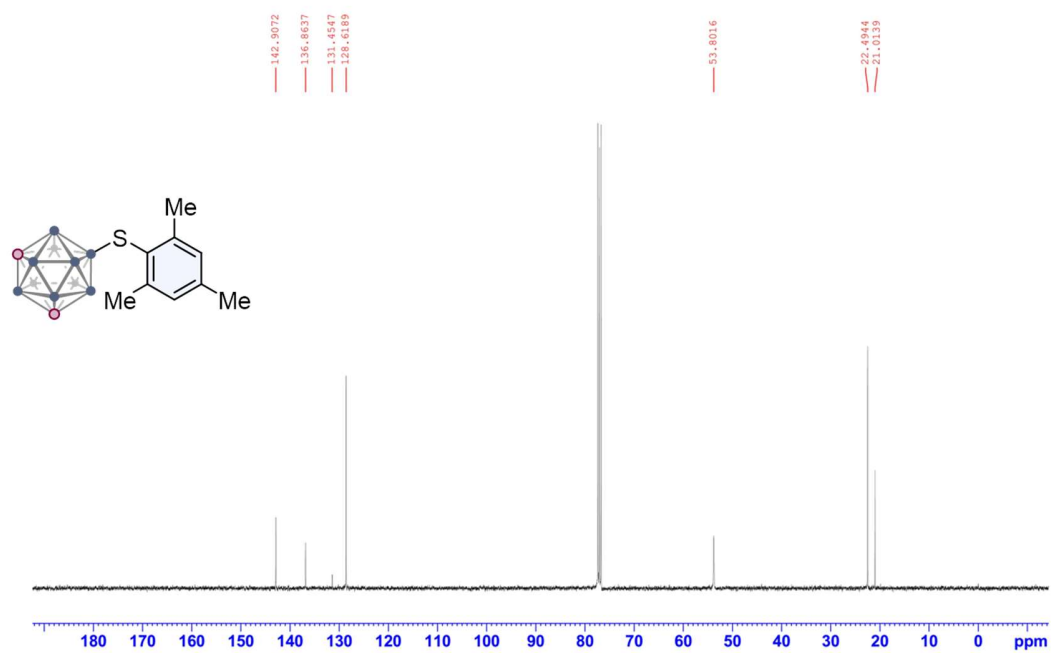
^{11}B NMR of **3aa** (CDCl_3 , 128 MHz)



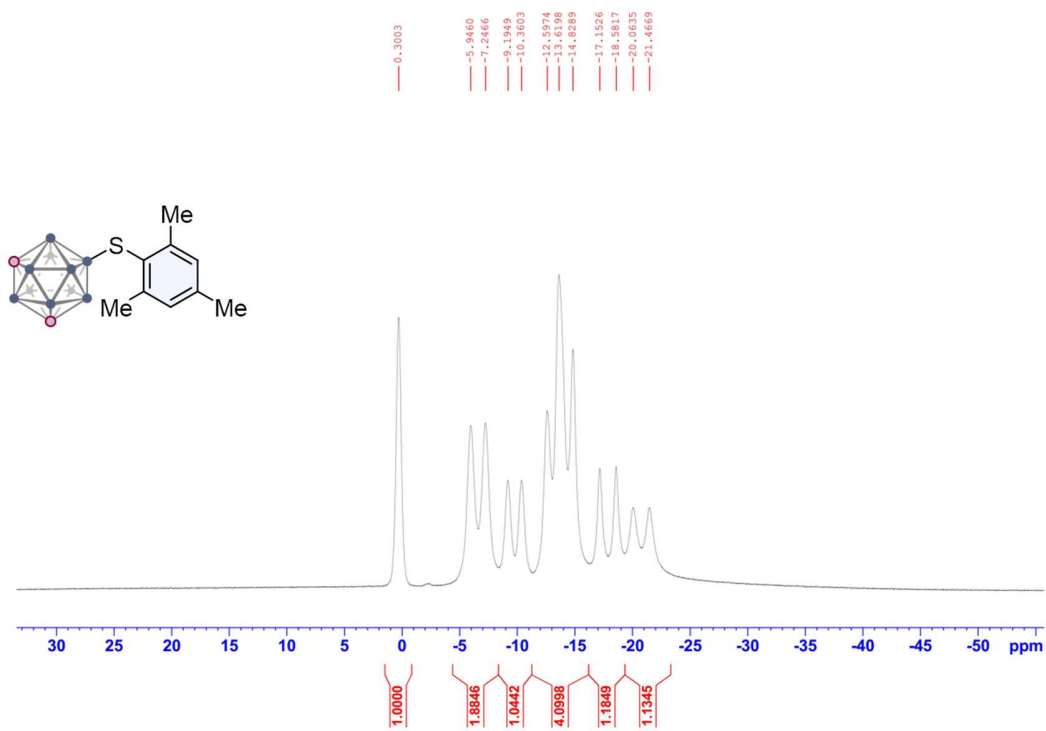
^1H NMR of **3ab** (CDCl_3 , 400 MHz)



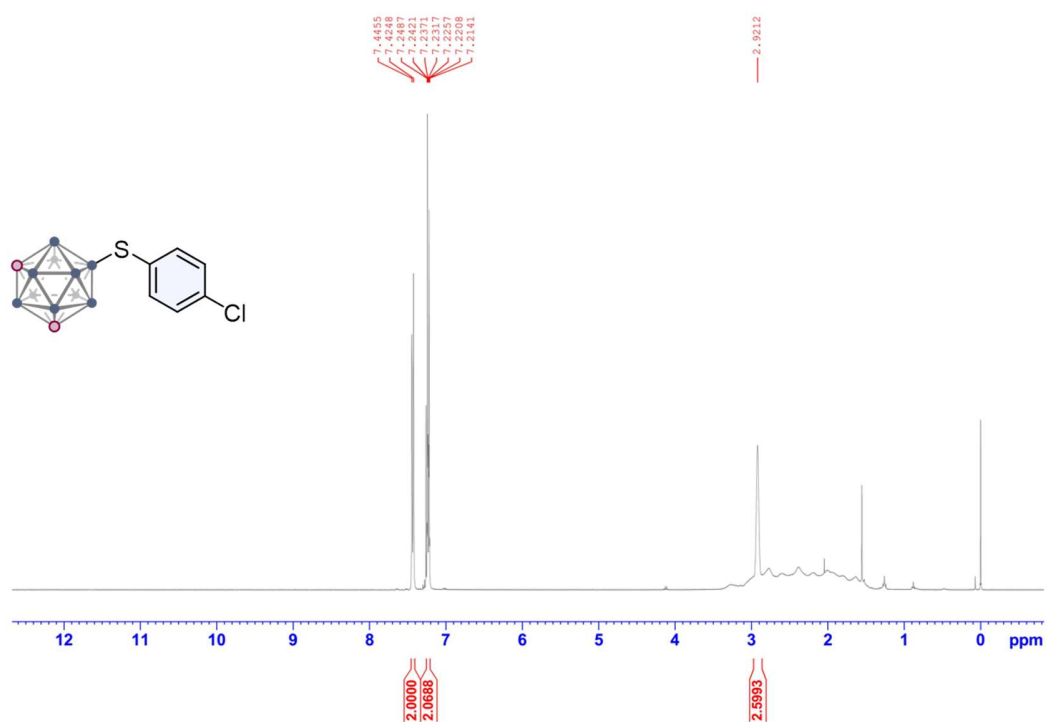
^{13}C NMR of **3ab** (CDCl_3 , 100 MHz)



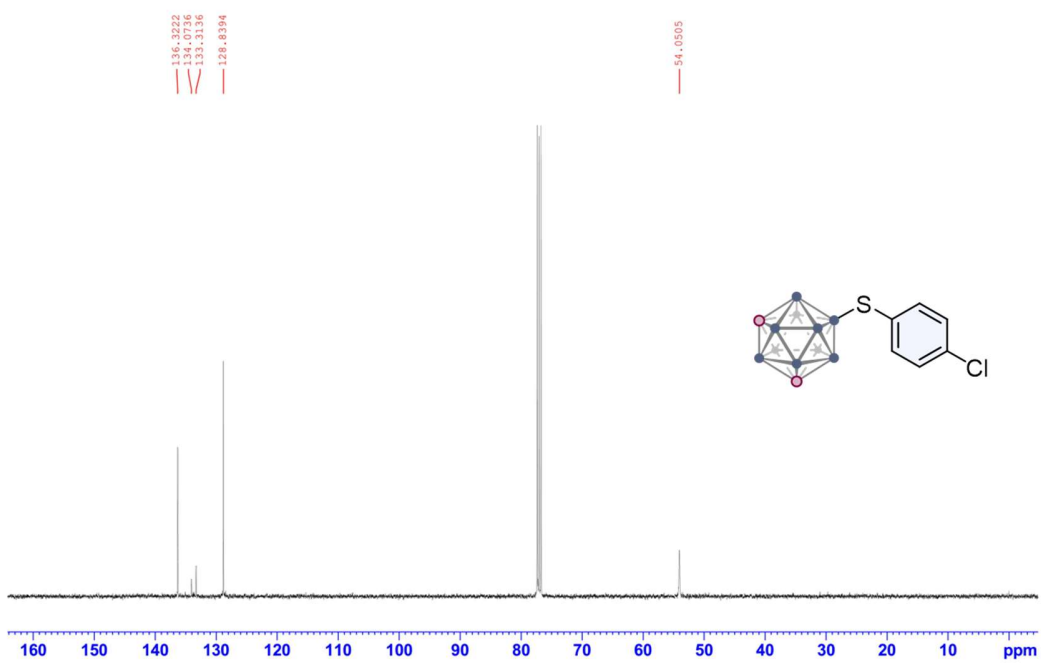
^{11}B NMR of **3ab** (CDCl_3 , 128 MHz)



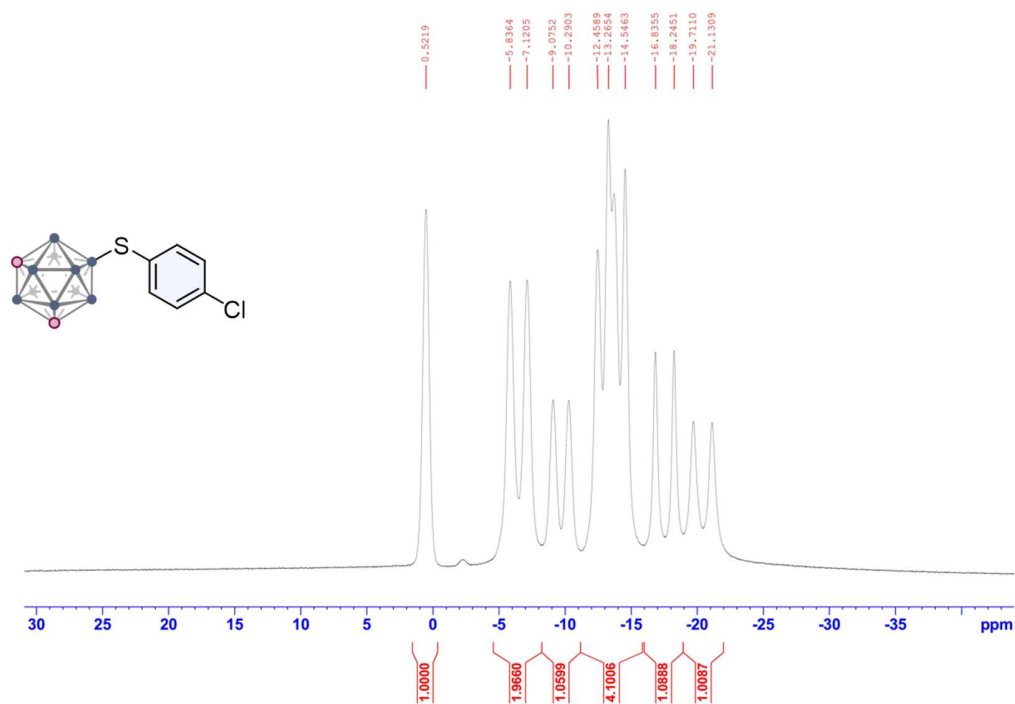
^1H NMR of **3ac** (CDCl_3 , 400 MHz)



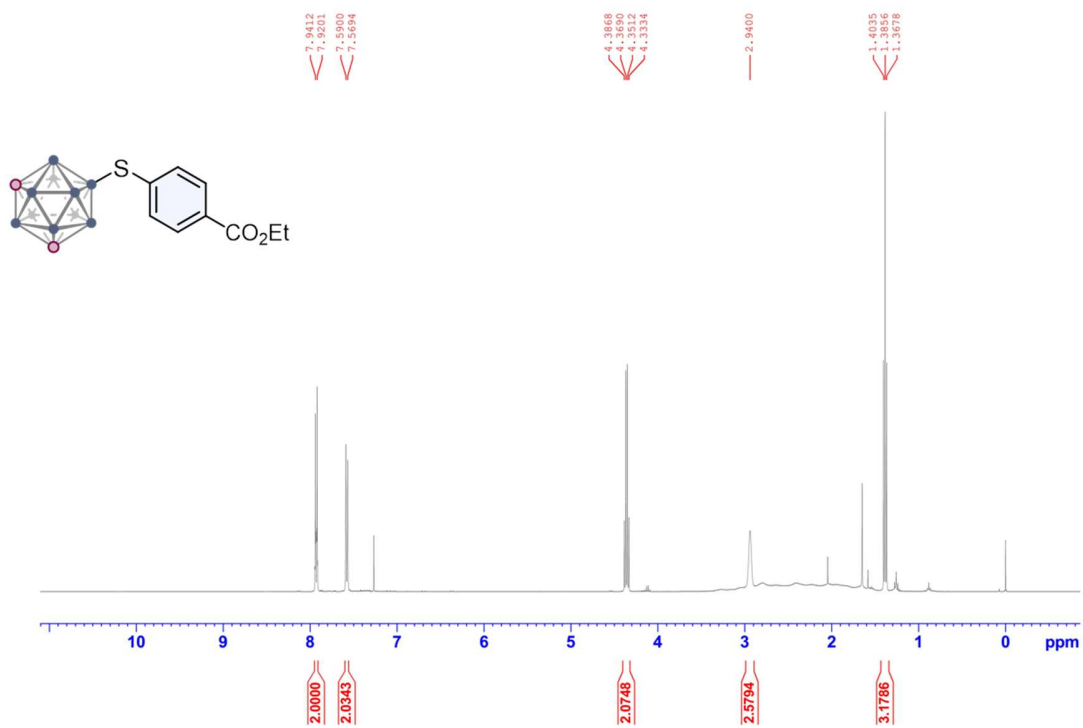
^{13}C NMR of **3ac** (CDCl_3 , 100 MHz)



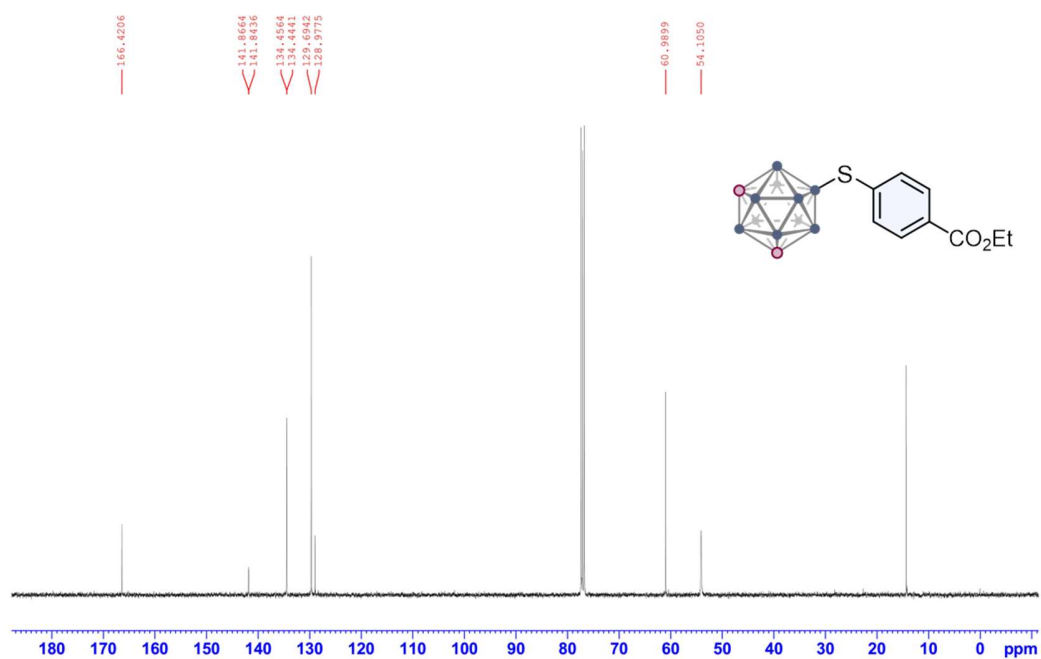
^{11}B NMR of **3ad** (CDCl_3 , 128 MHz)



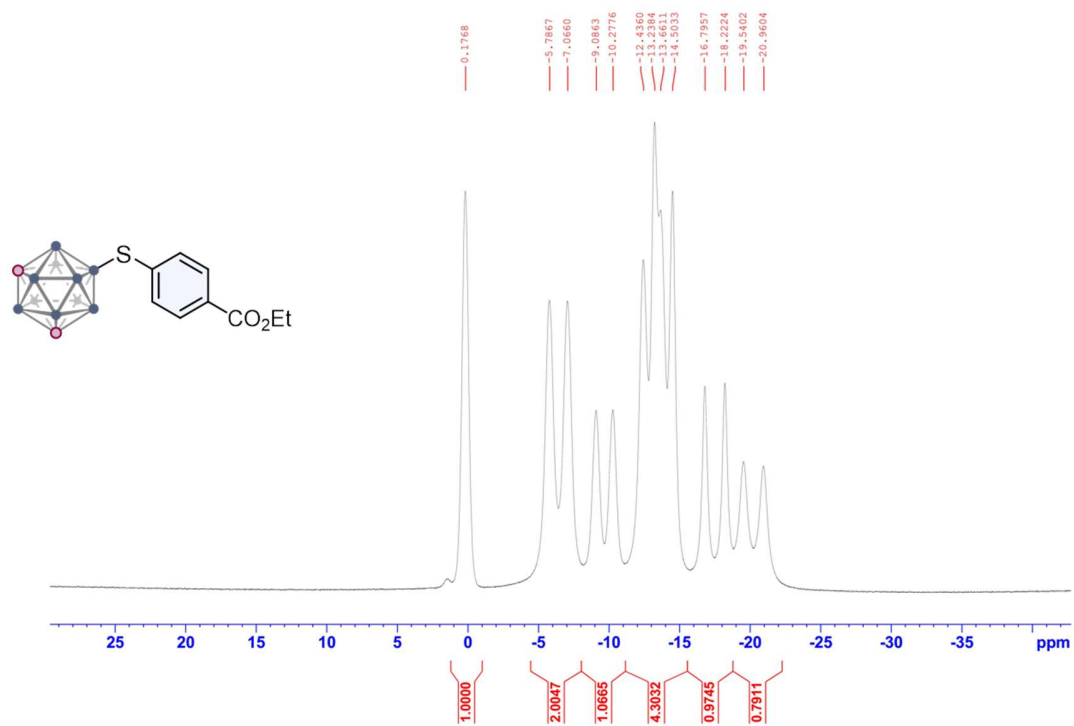
^1H NMR of **3ad** (CDCl_3 , 400 MHz)



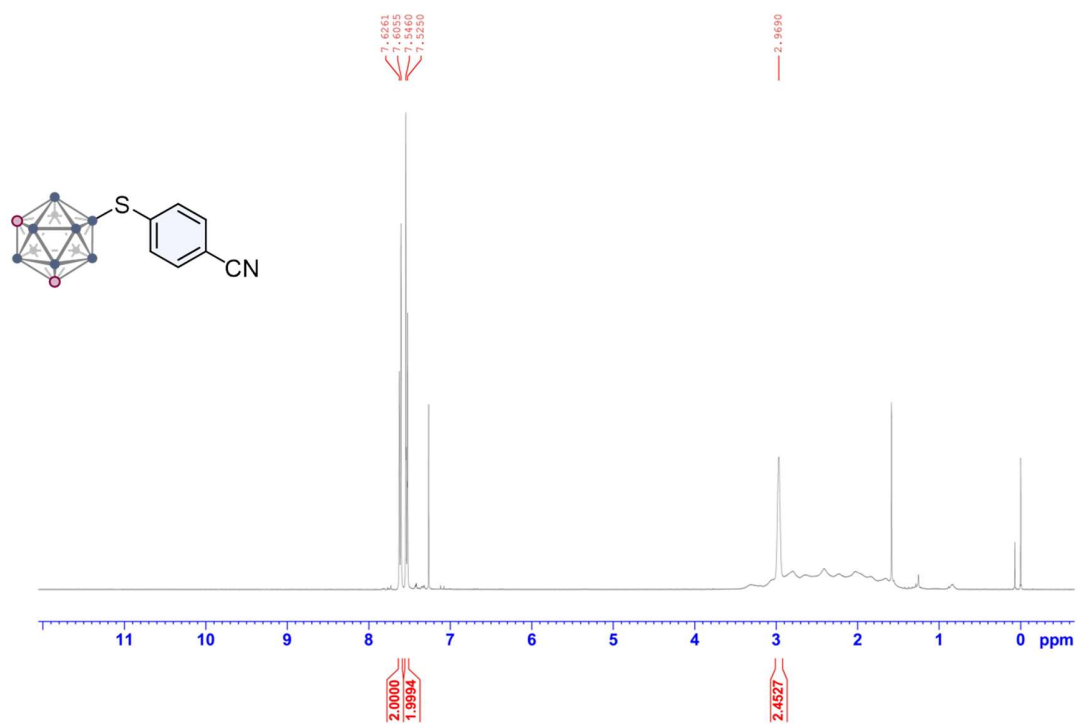
^{13}C NMR of **3ad** (CDCl_3 , 100 MHz)



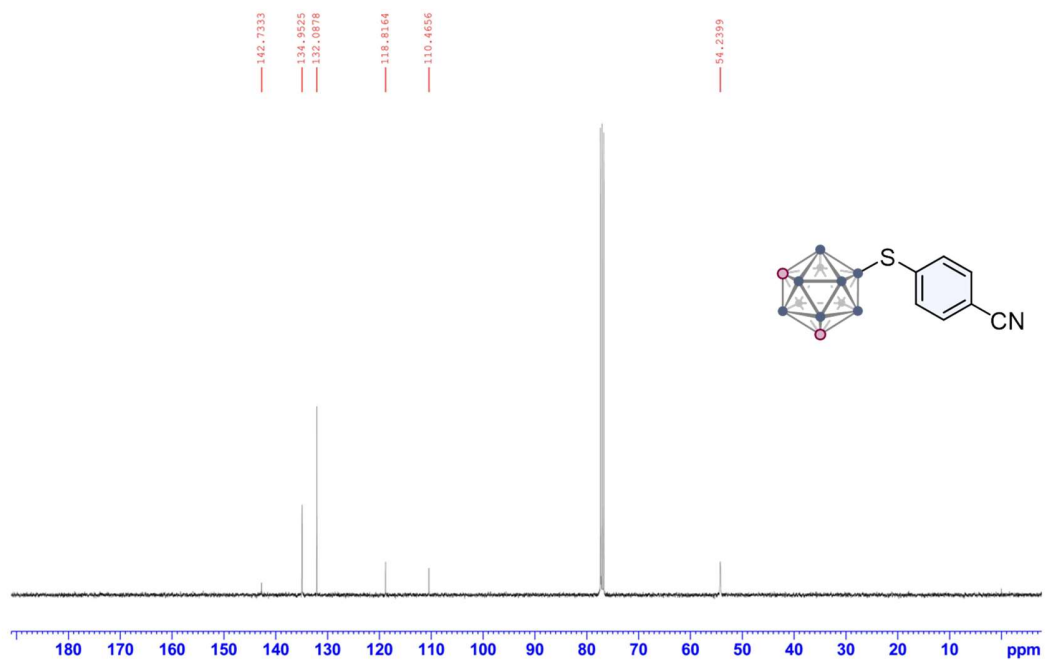
^{11}B NMR of **3ad** (CDCl_3 , 128 MHz)



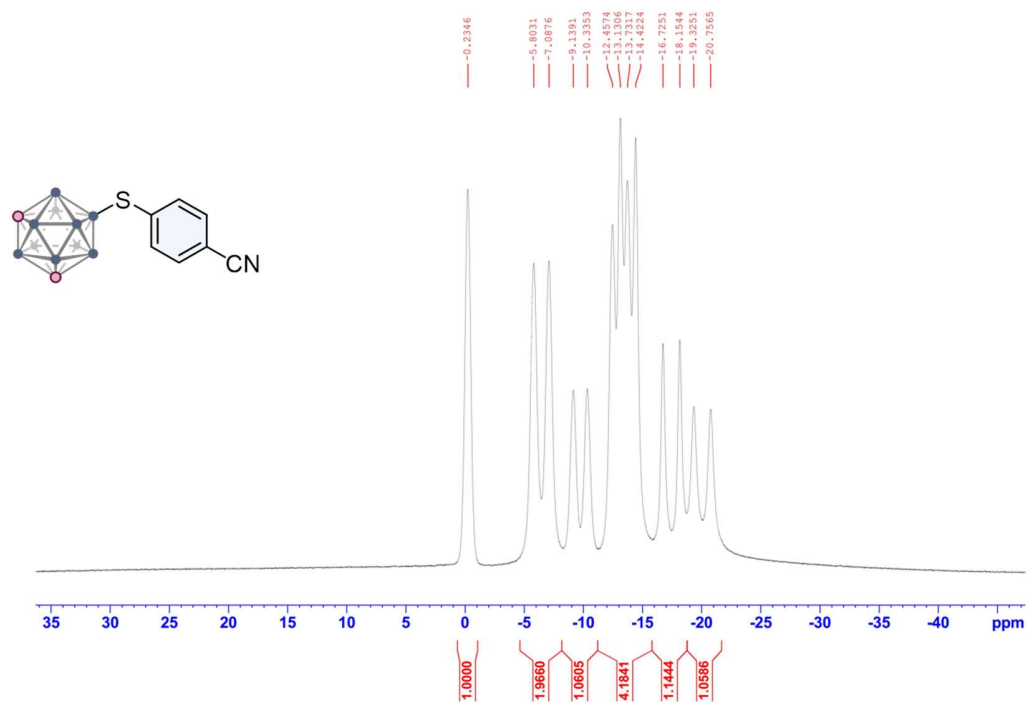
^1H NMR of **3ae** (CDCl_3 , 400 MHz)



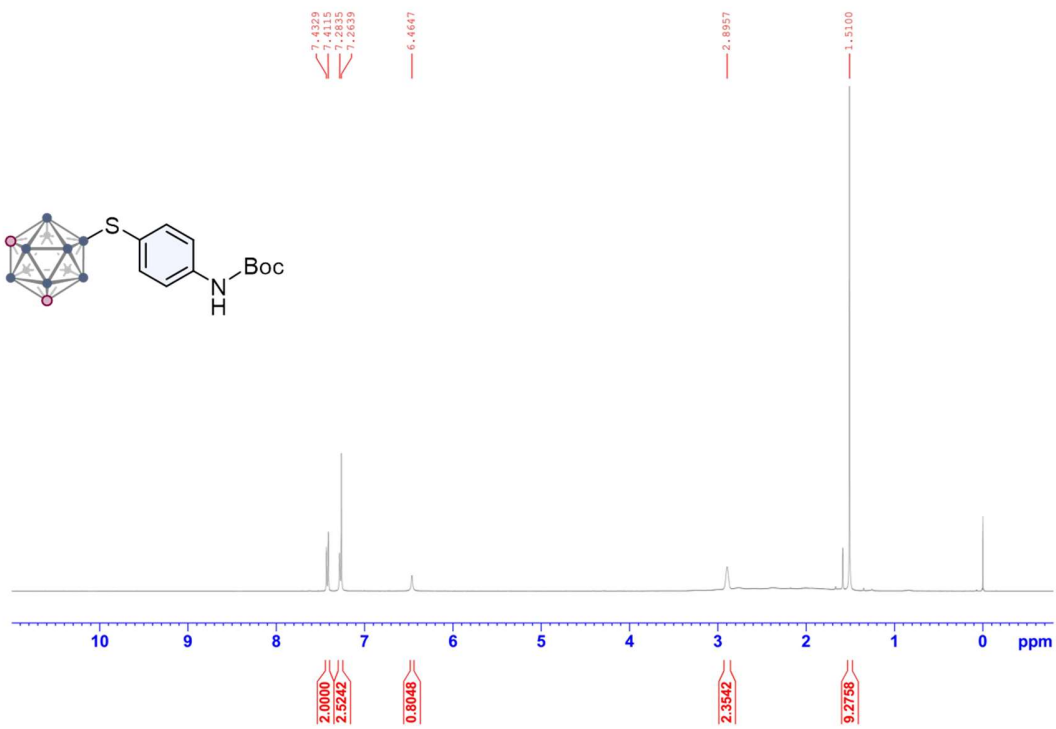
^{13}C NMR of **3ae** (CDCl_3 , 100 MHz)



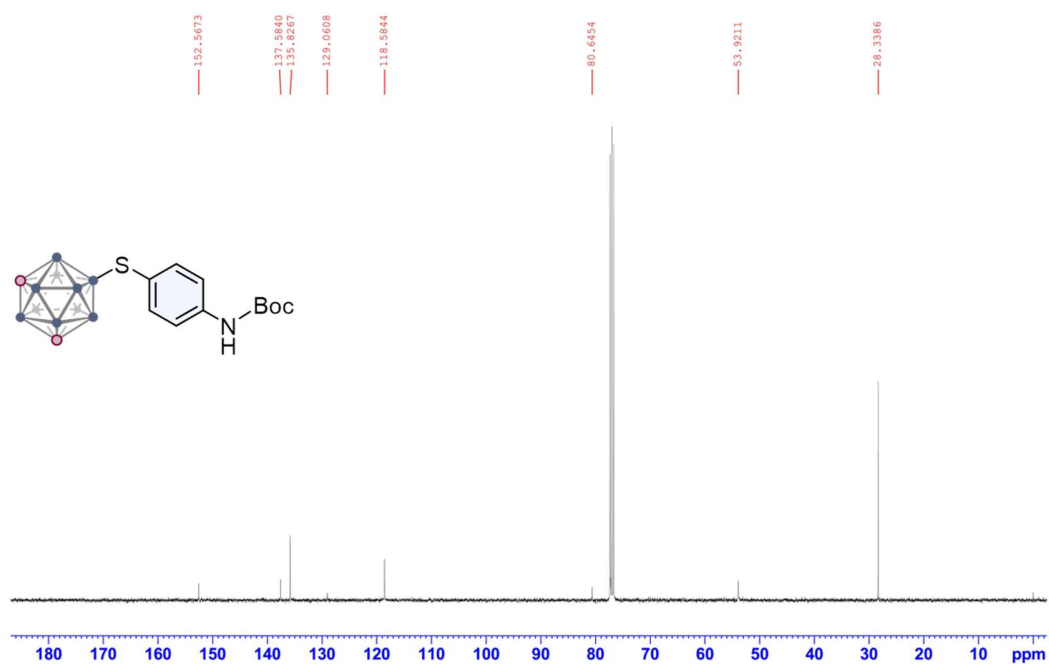
^{11}B NMR of **3ae** (CDCl_3 , 128 MHz)



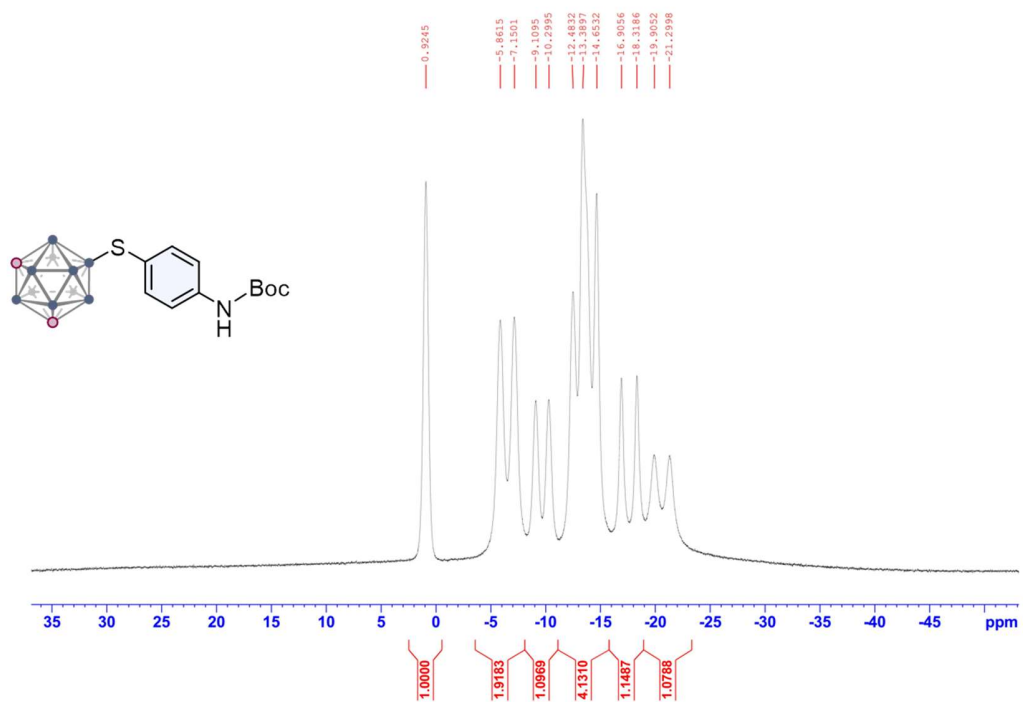
^1H NMR of **3af** (CDCl_3 , 400 MHz)



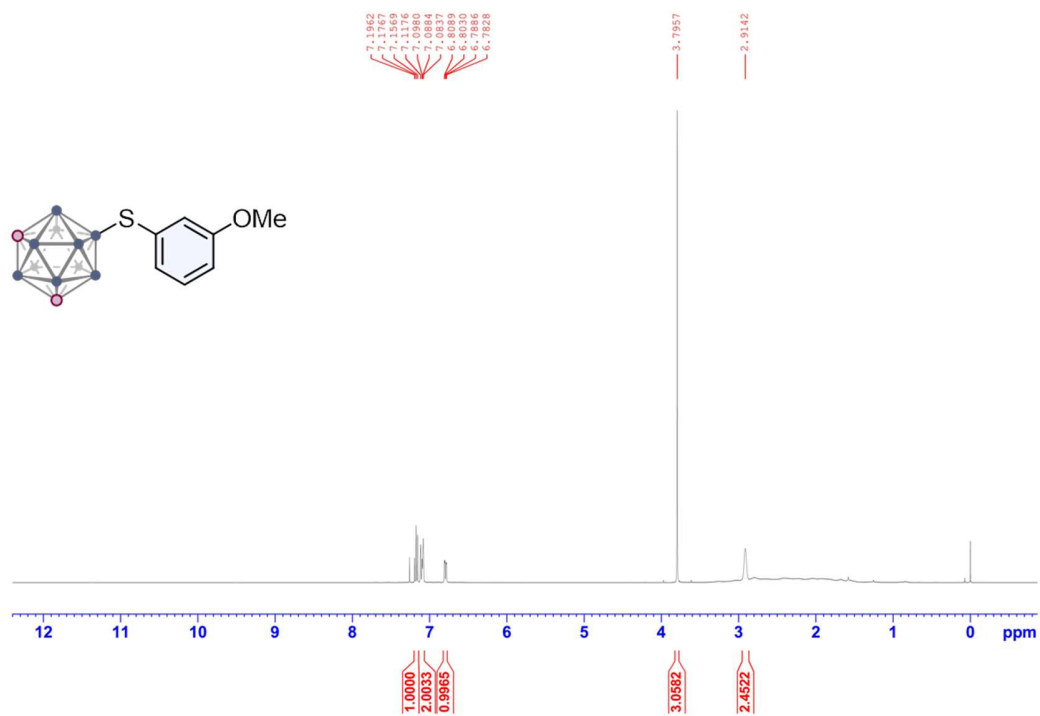
^{13}C NMR of **3af** (CDCl_3 , 100 MHz)



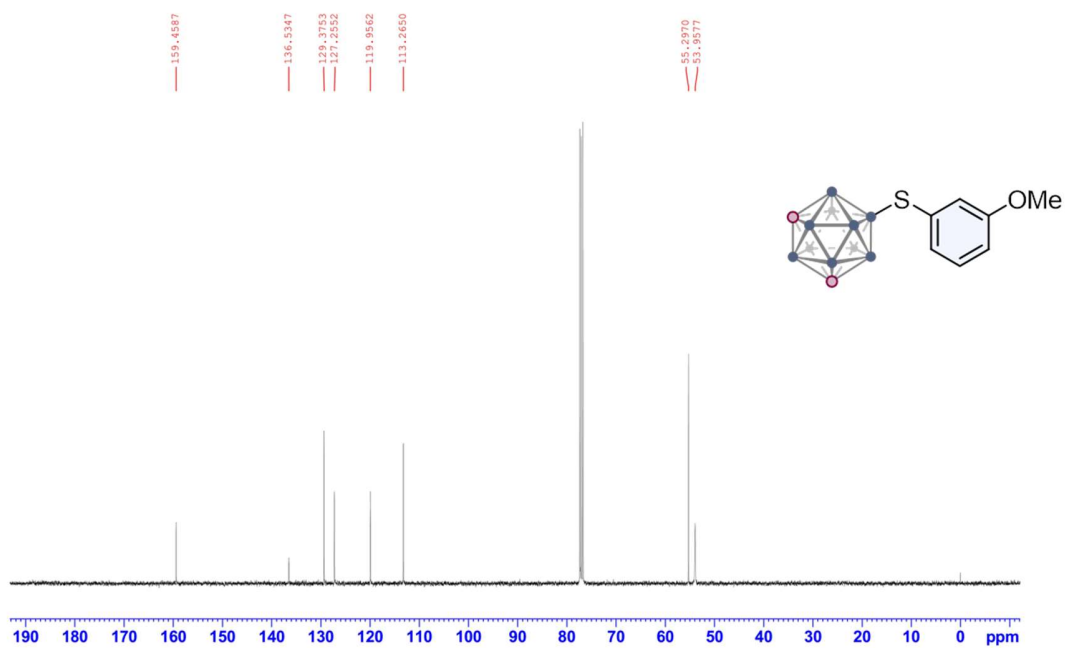
^{11}B NMR of **3af** (CDCl_3 , 128 MHz)



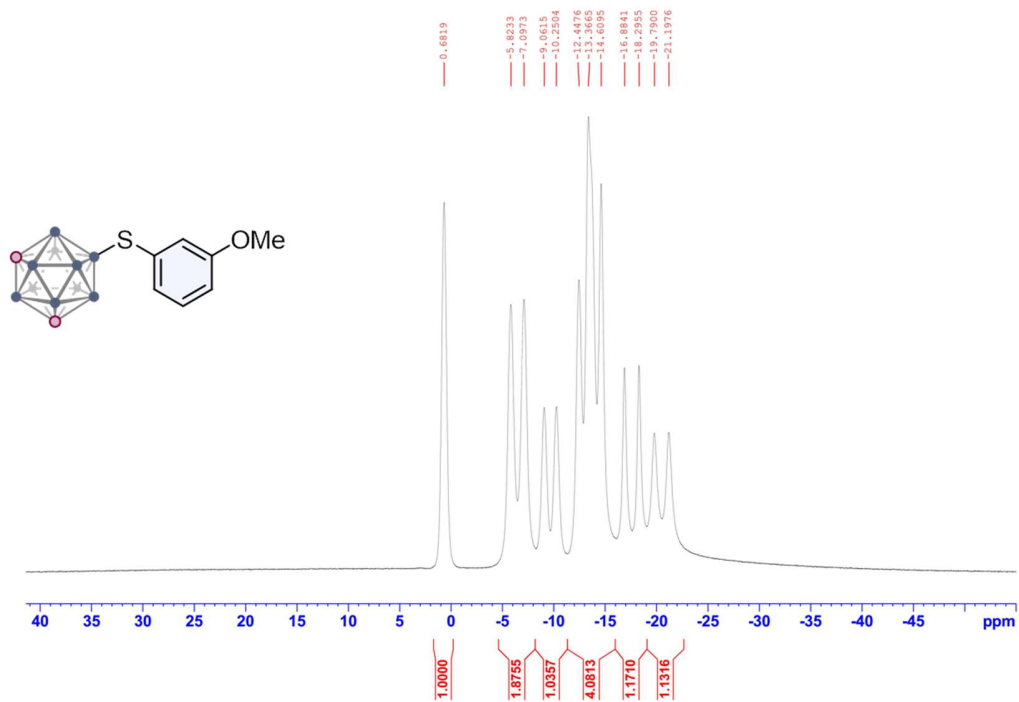
^1H NMR of **3ag** (CDCl_3 , 400 MHz)



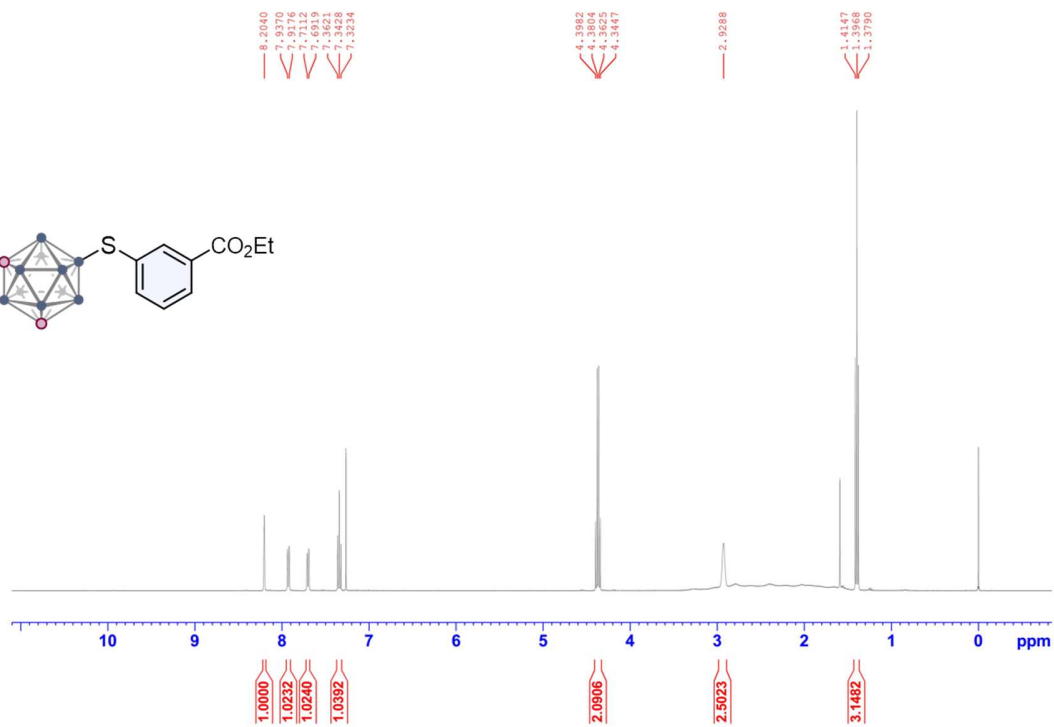
^{13}C NMR of **3ag** (CDCl_3 , 100 MHz)



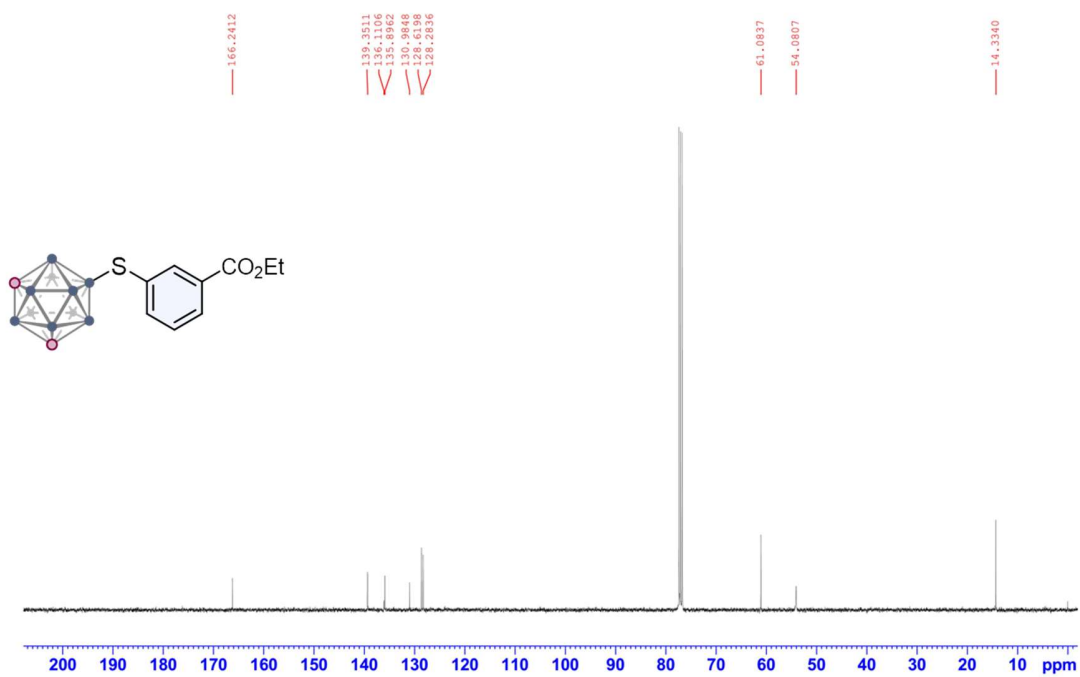
^{11}B NMR of **3ag** (CDCl_3 , 128 MHz)



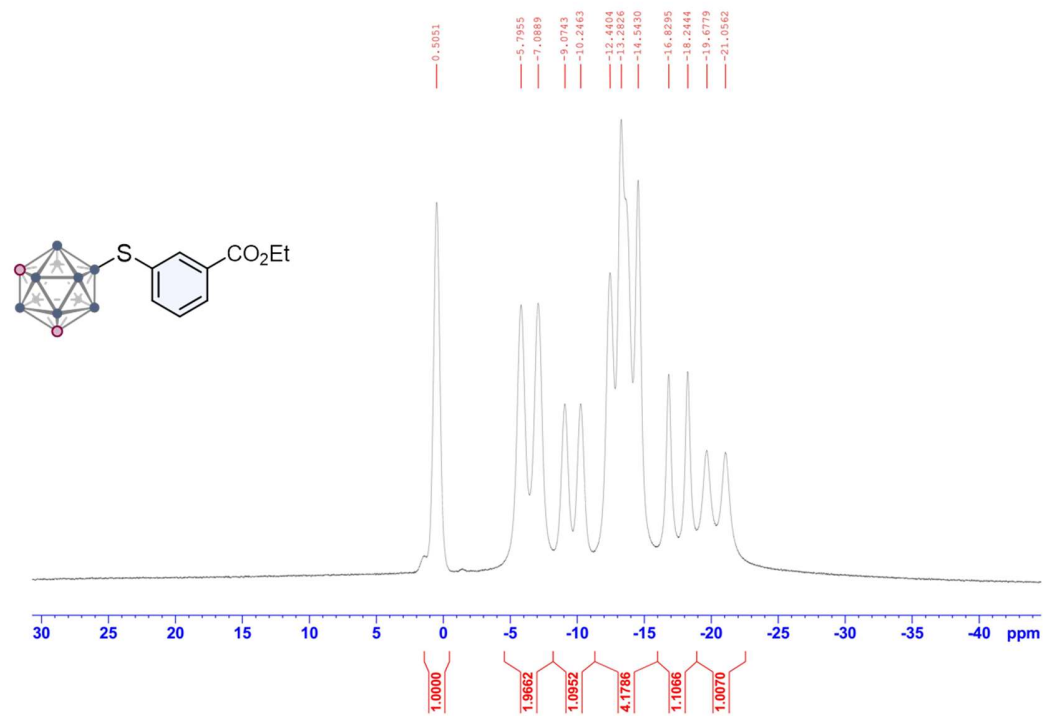
^1H NMR of **3ah** (CDCl_3 , 400 MHz)



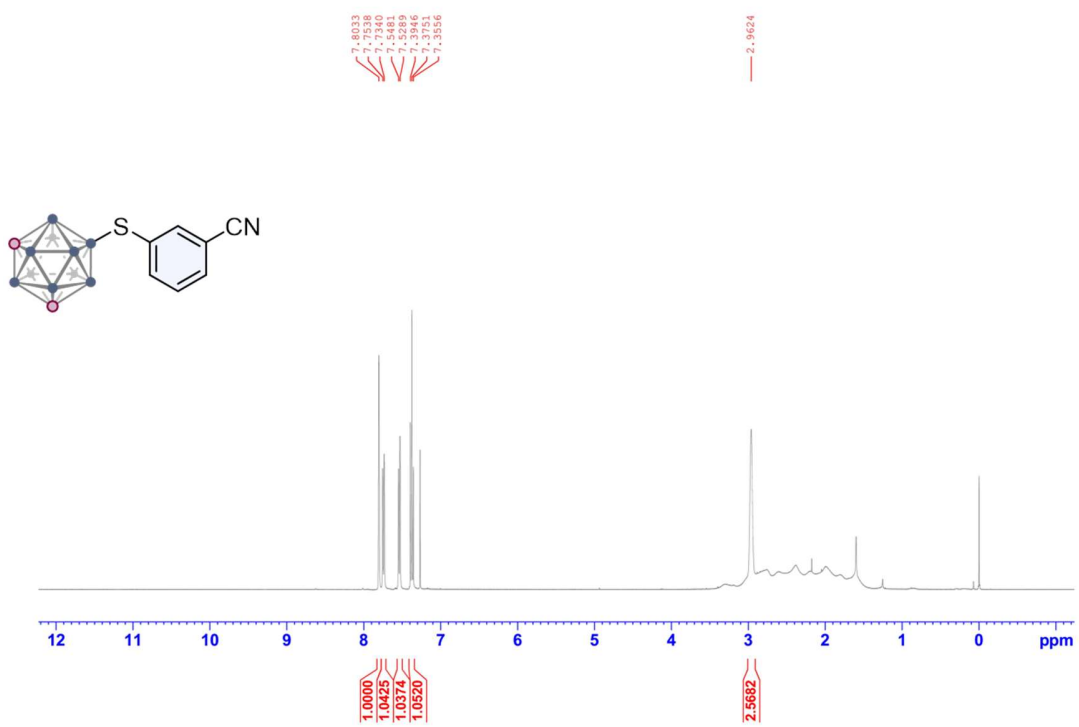
^{13}C NMR of **3ah** (CDCl_3 , 100 MHz)



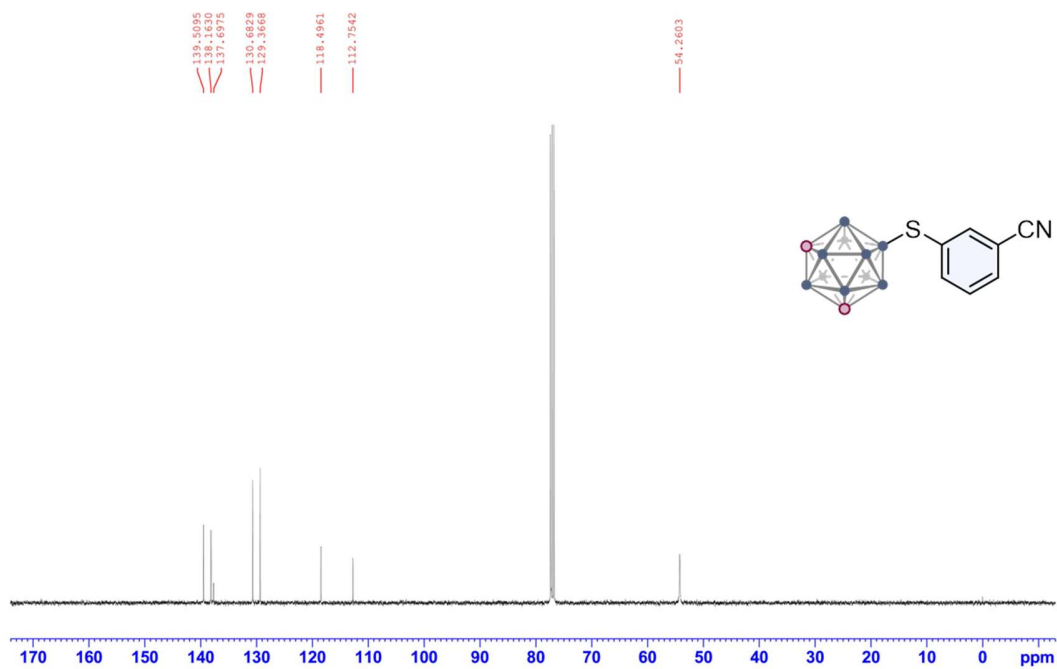
^{11}B NMR of **3ah** (CDCl_3 , 128 MHz)



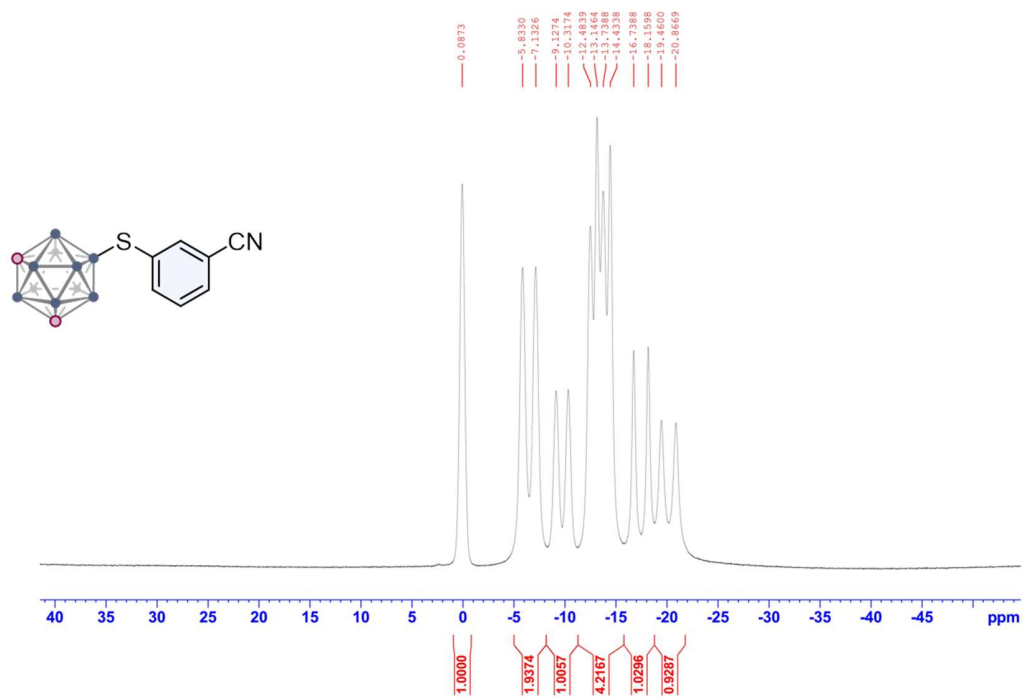
¹H NMR of **3ai** (CDCl₃, 400 MHz)



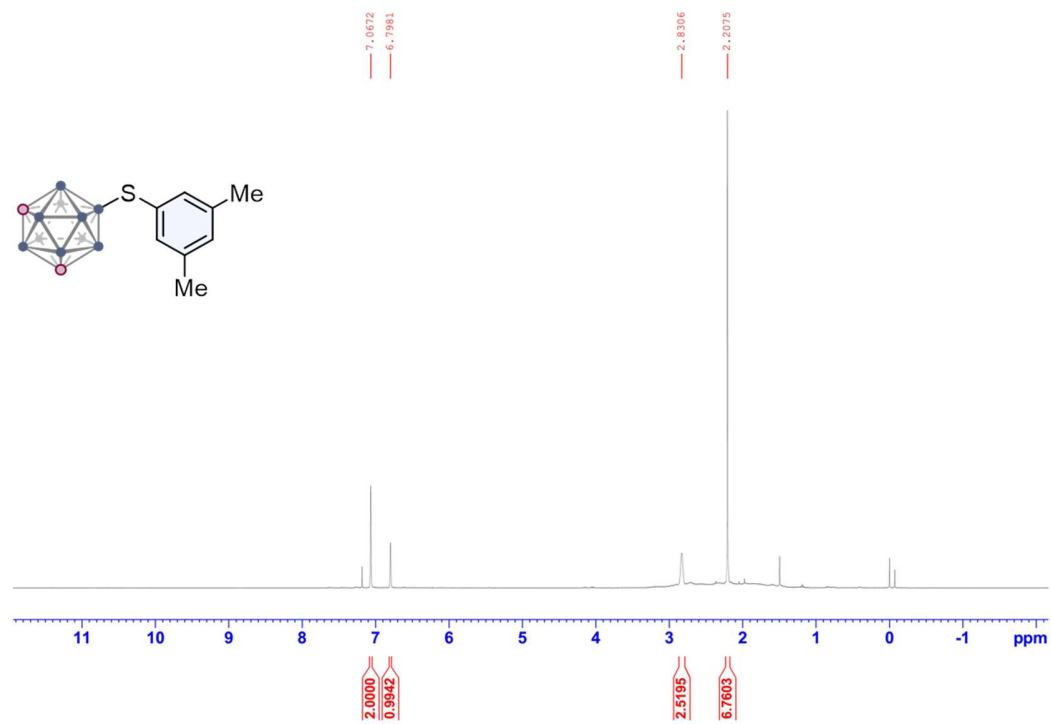
¹³C NMR of **3ai** (CDCl₃, 100 MHz)



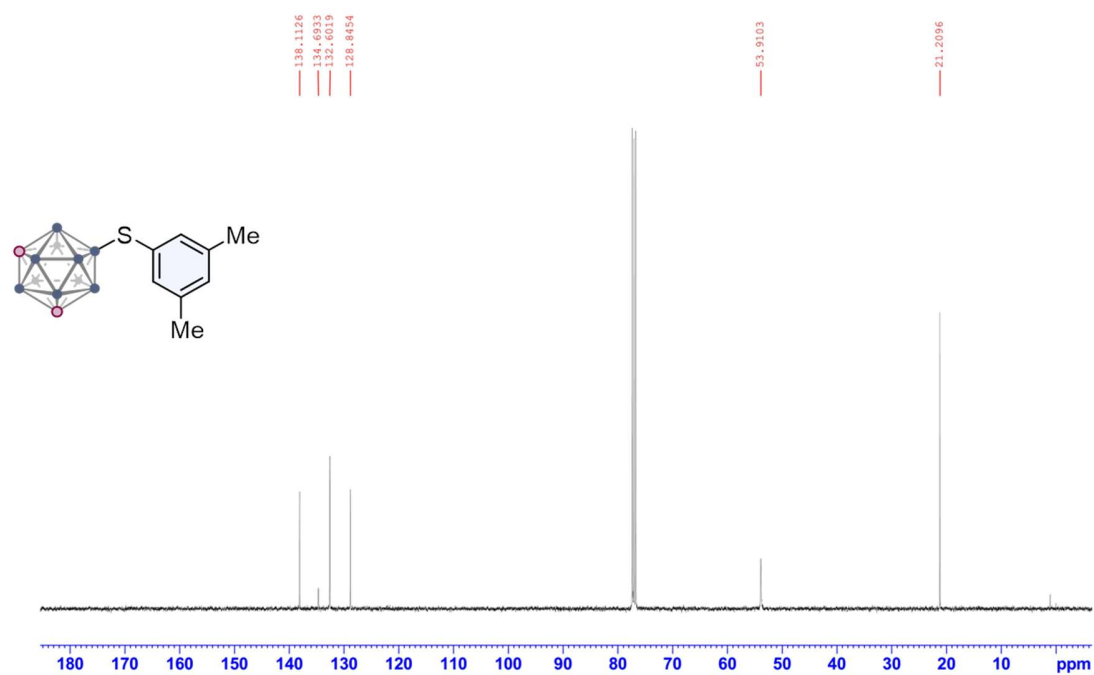
^{11}B NMR of **3ai** (CDCl_3 , 128 MHz)



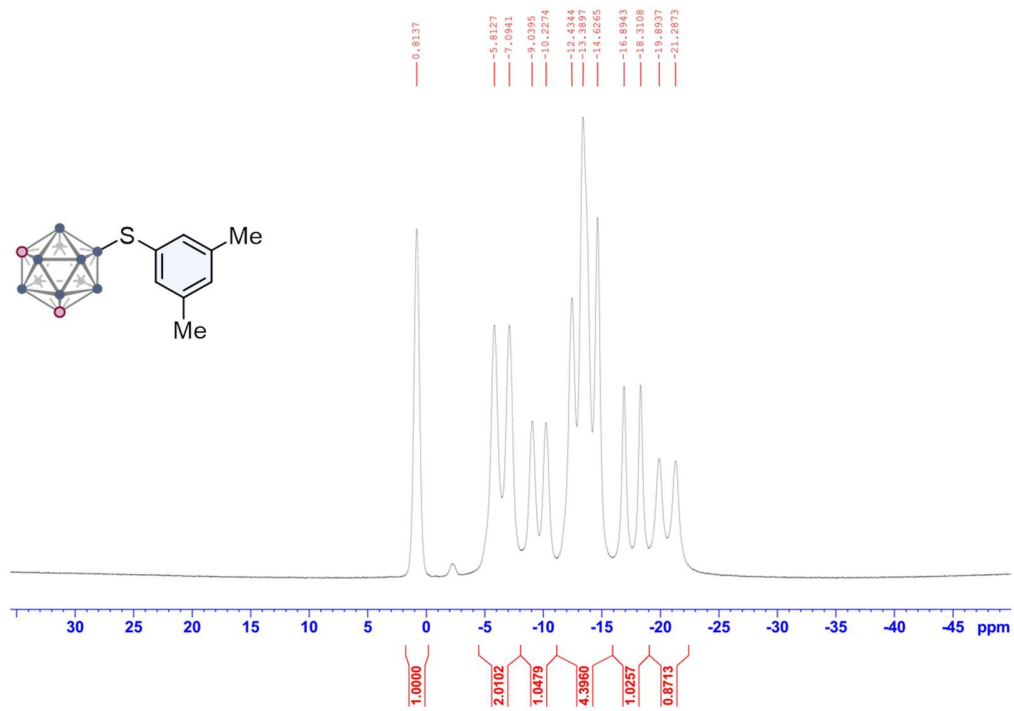
^1H NMR of **3aj** (CDCl_3 , 400 MHz)



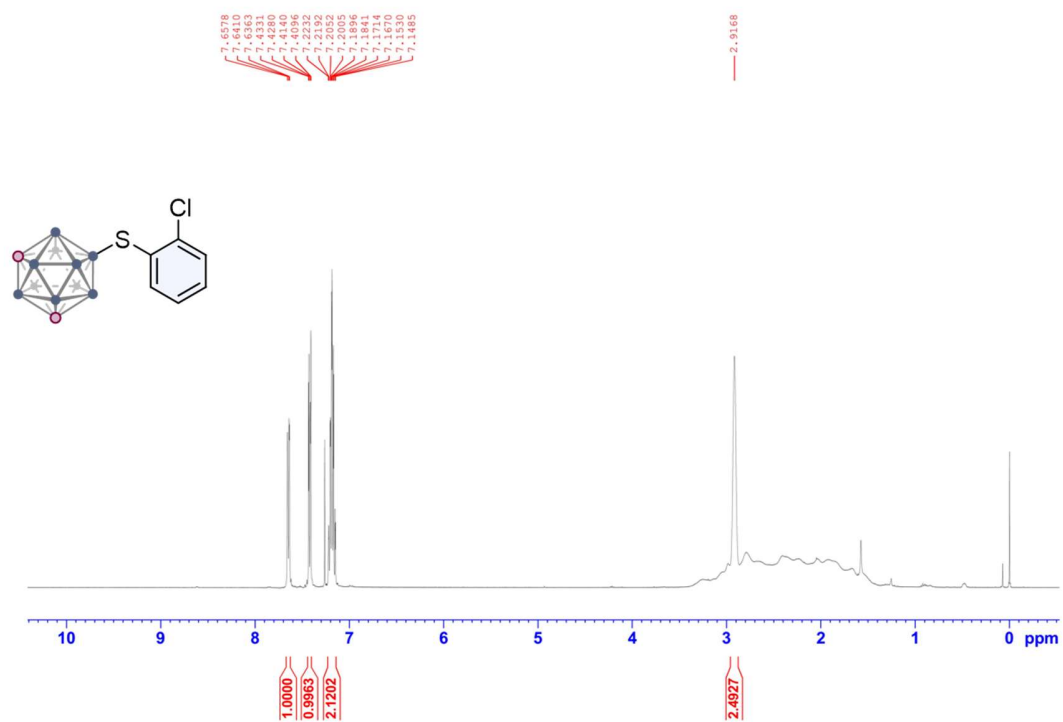
^{13}C NMR of **3aj** (CDCl_3 , 100 MHz)



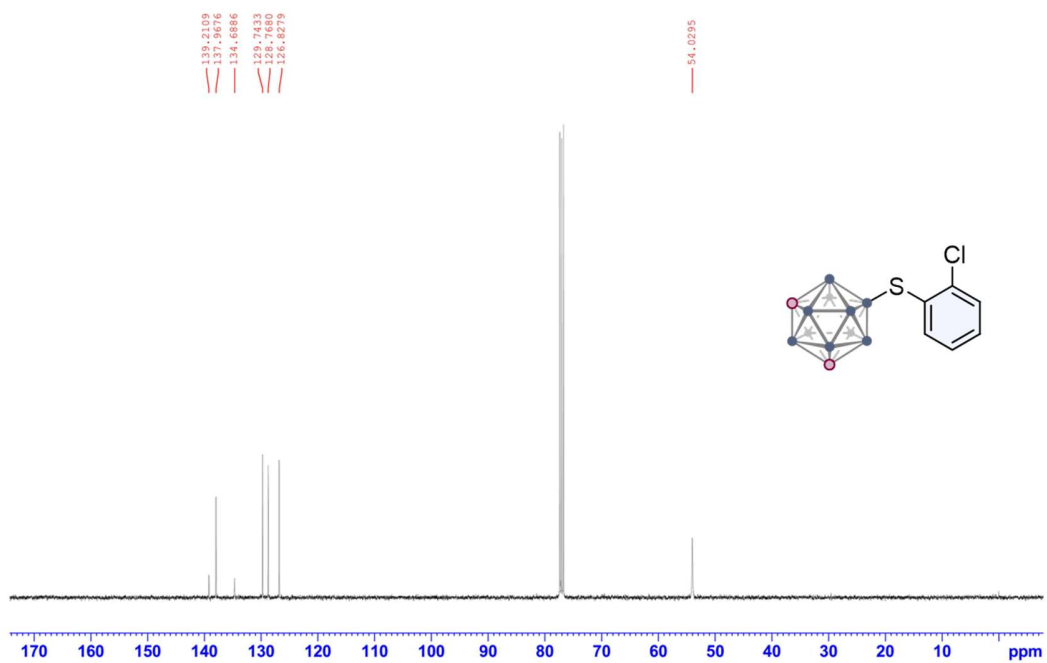
^{11}B NMR of **3aj** (CDCl_3 , 128 MHz)



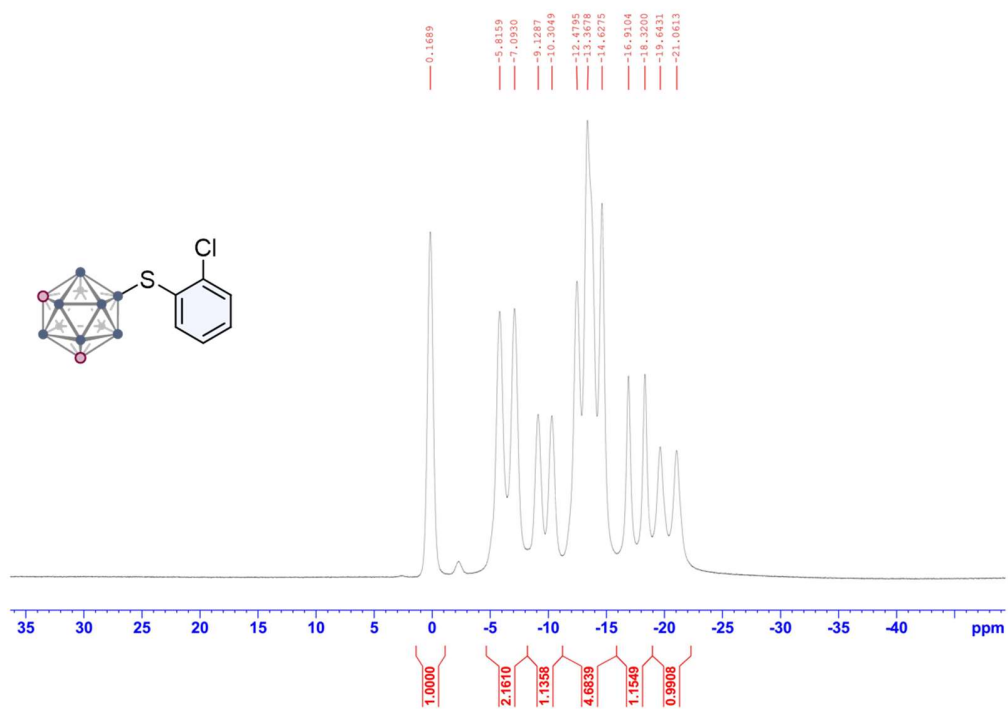
^1H NMR of **3ak** (CDCl_3 , 400 MHz)



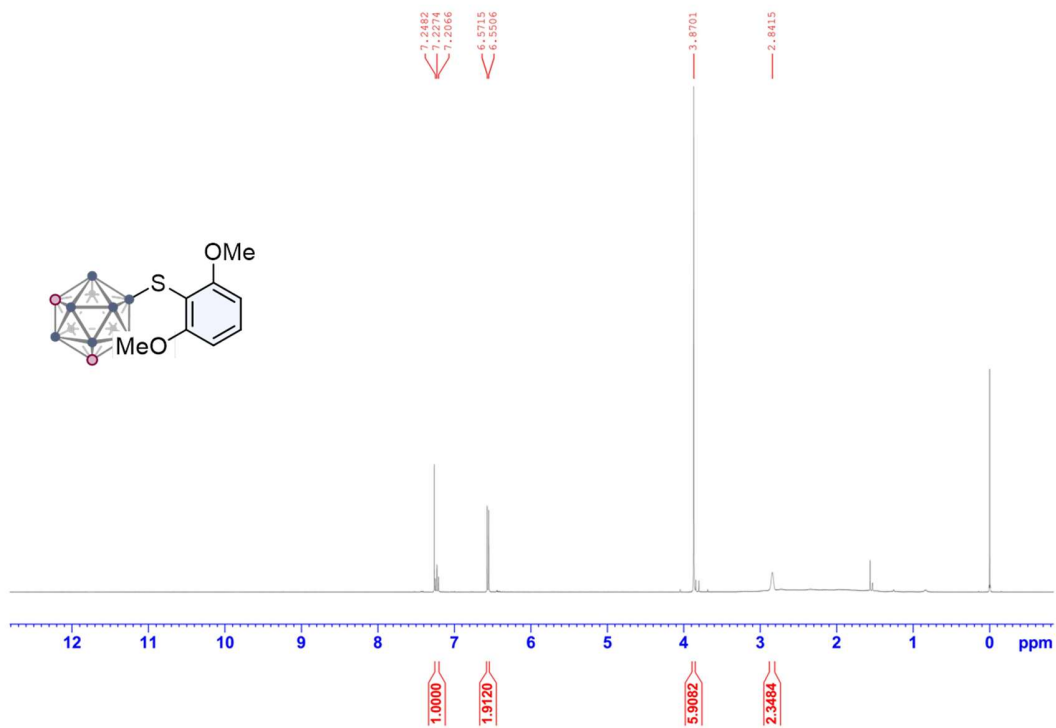
^{13}C NMR of **3ak** (CDCl_3 , 100 MHz)



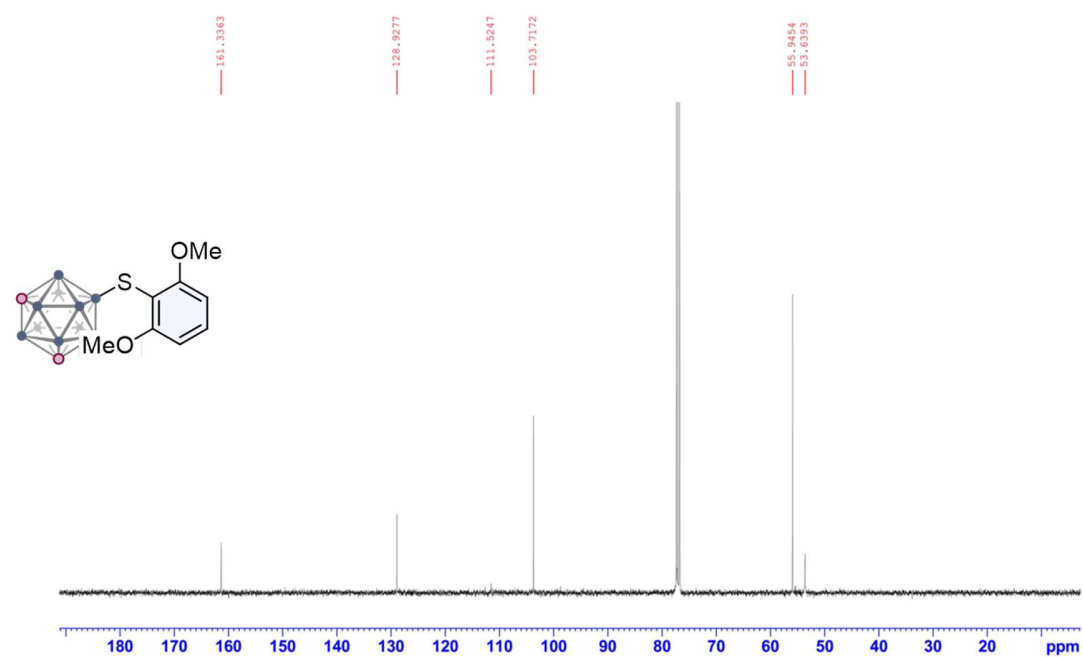
^{11}B NMR of **3ak** (CDCl_3 , 128 MHz)



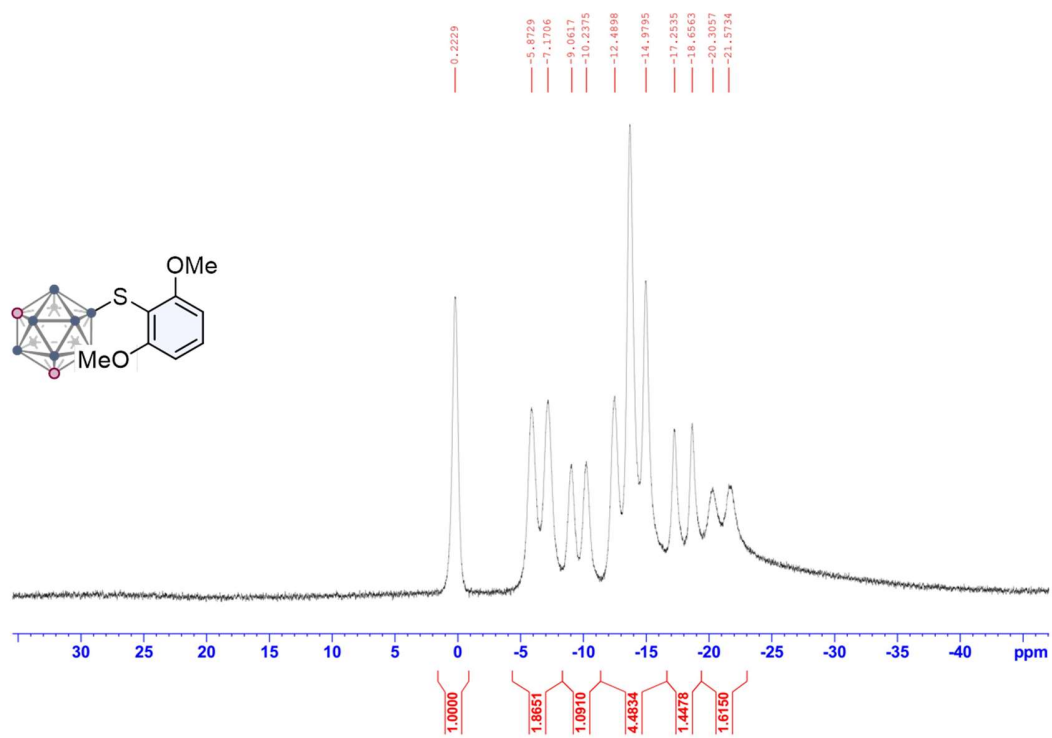
^1H NMR of **3al** (CDCl_3 , 400 MHz)



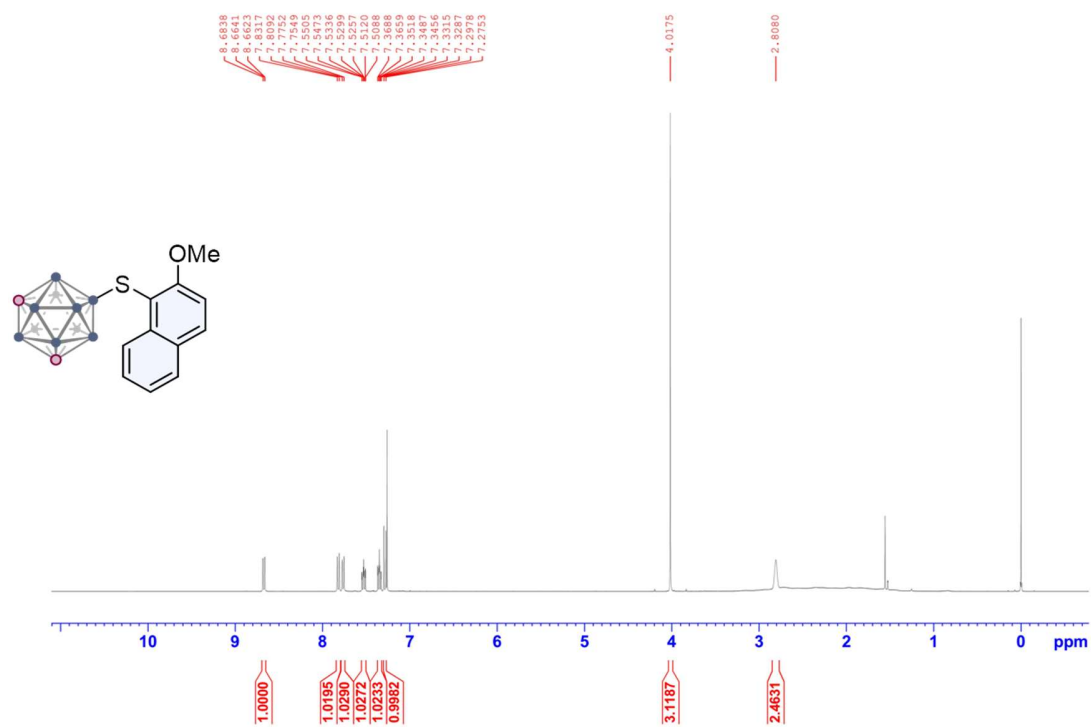
^{13}C NMR of **3al** (CDCl_3 , 100 MHz)



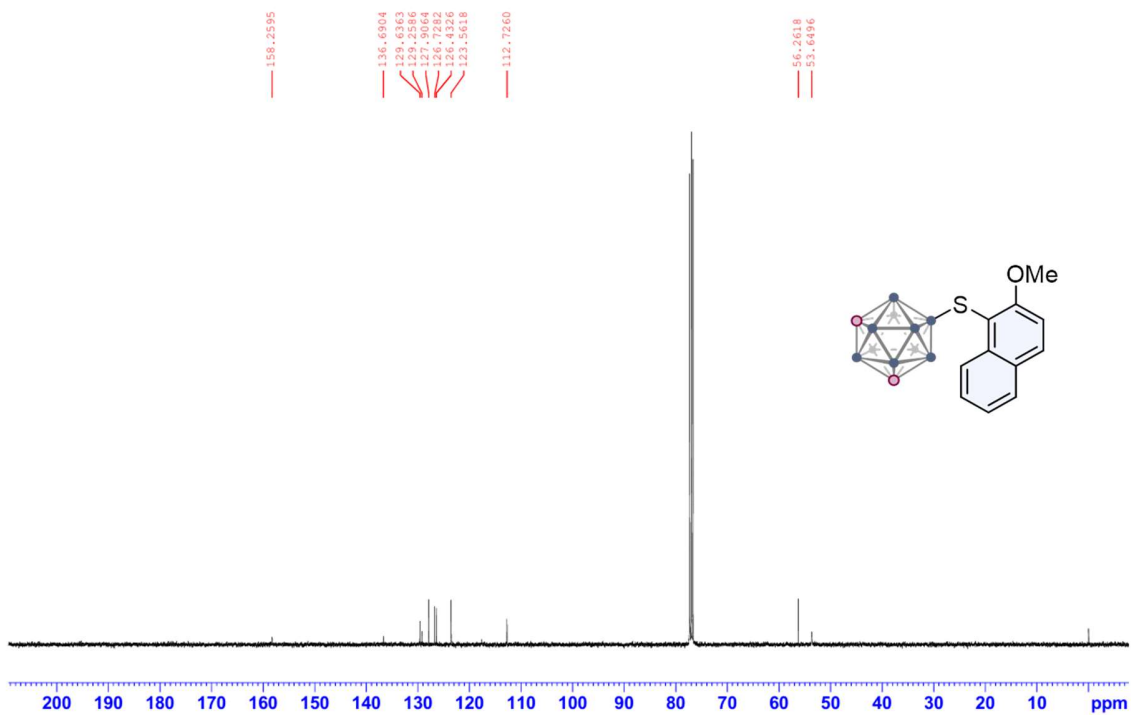
^{11}B NMR of **3al** (CDCl_3 , 128 MHz)



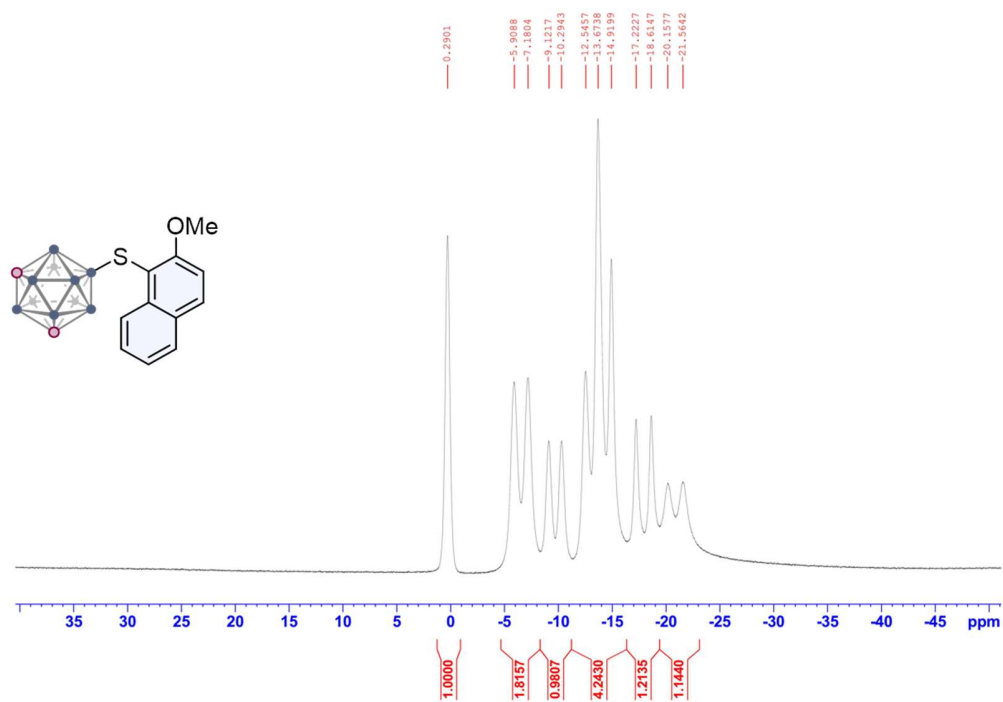
^1H NMR of **3am** (CDCl_3 , 400 MHz)



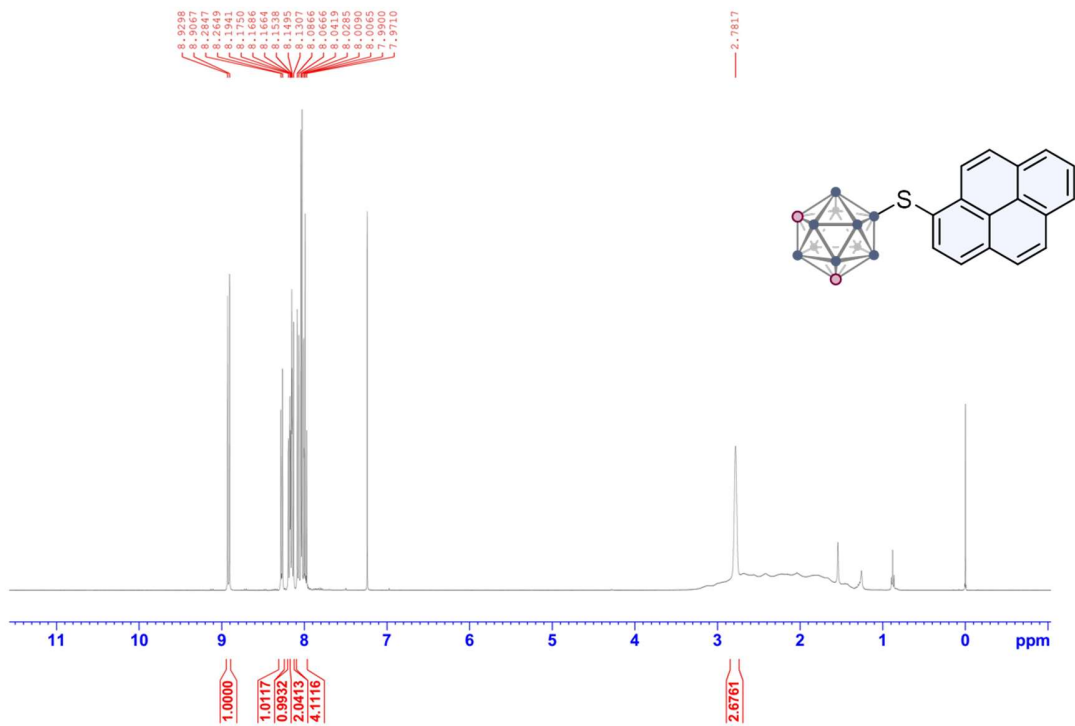
^{13}C NMR of **3am** (CDCl_3 , 100 MHz)



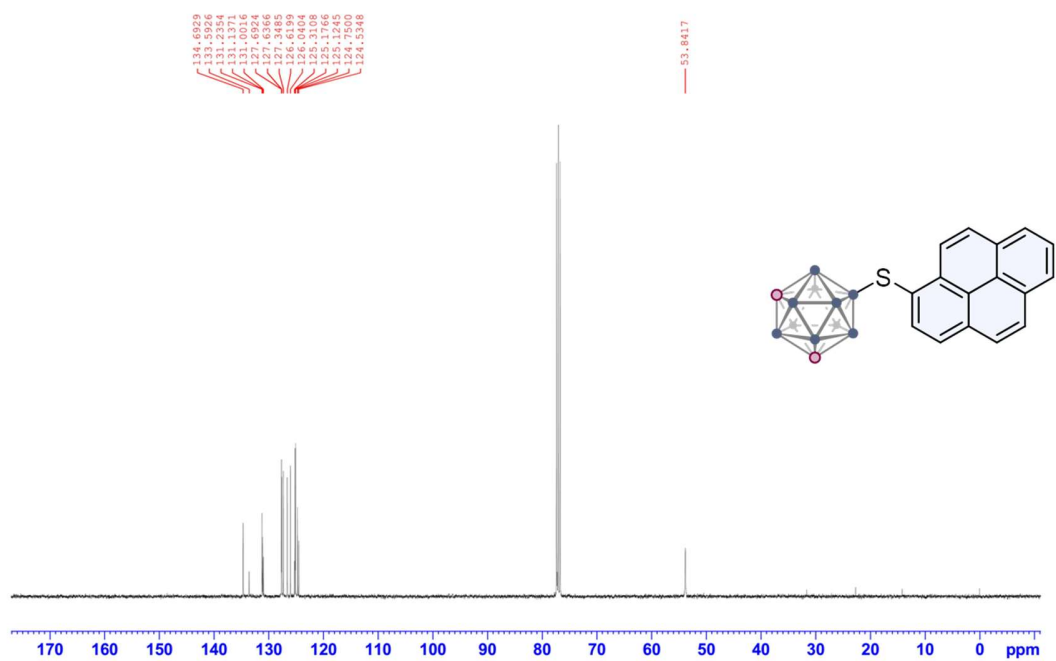
^{11}B NMR of **3am** (CDCl_3 , 128 MHz)



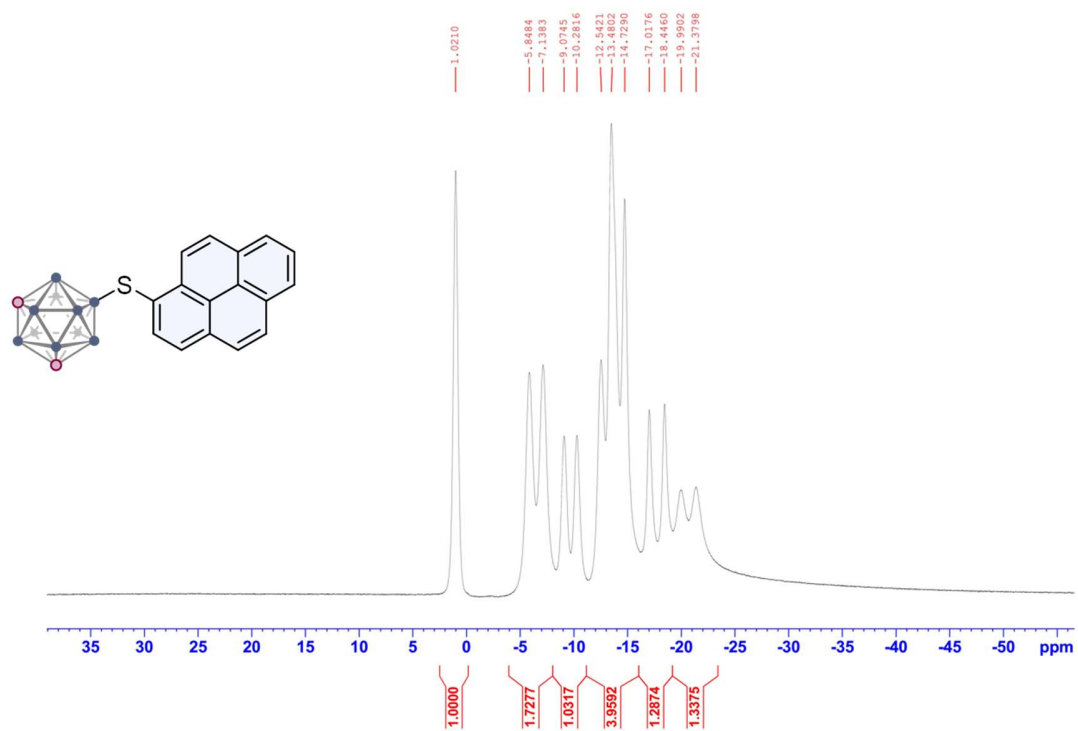
^1H NMR of **3an** (CDCl_3 , 400 MHz)



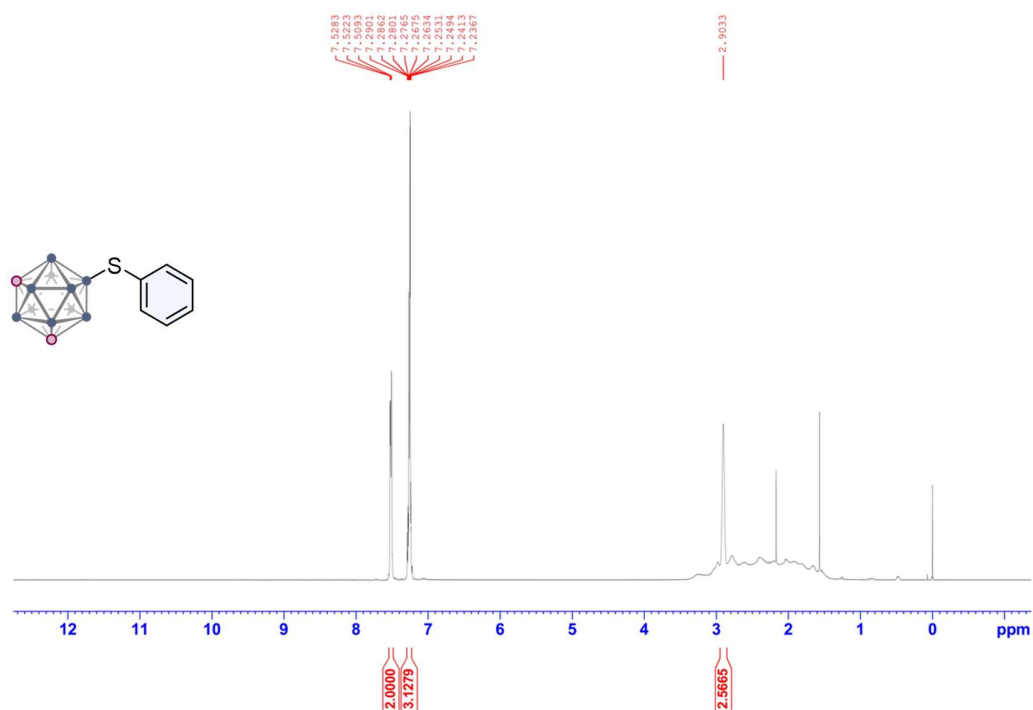
^{13}C NMR of **3an** (CDCl_3 , 100 MHz)



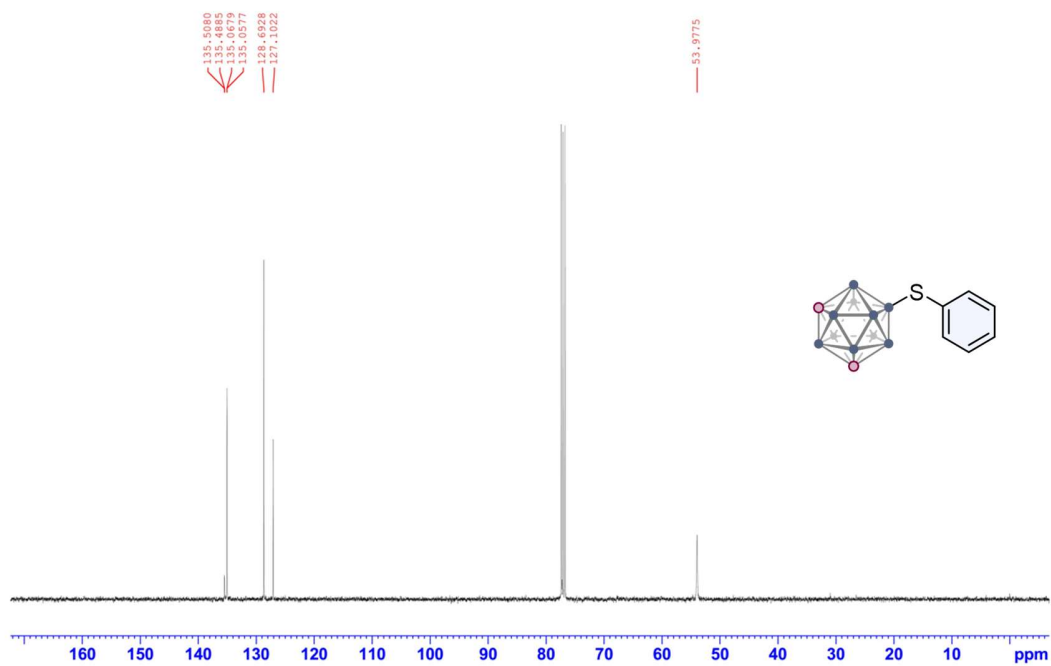
^{11}B NMR of **3an** (CDCl_3 , 128 MHz)



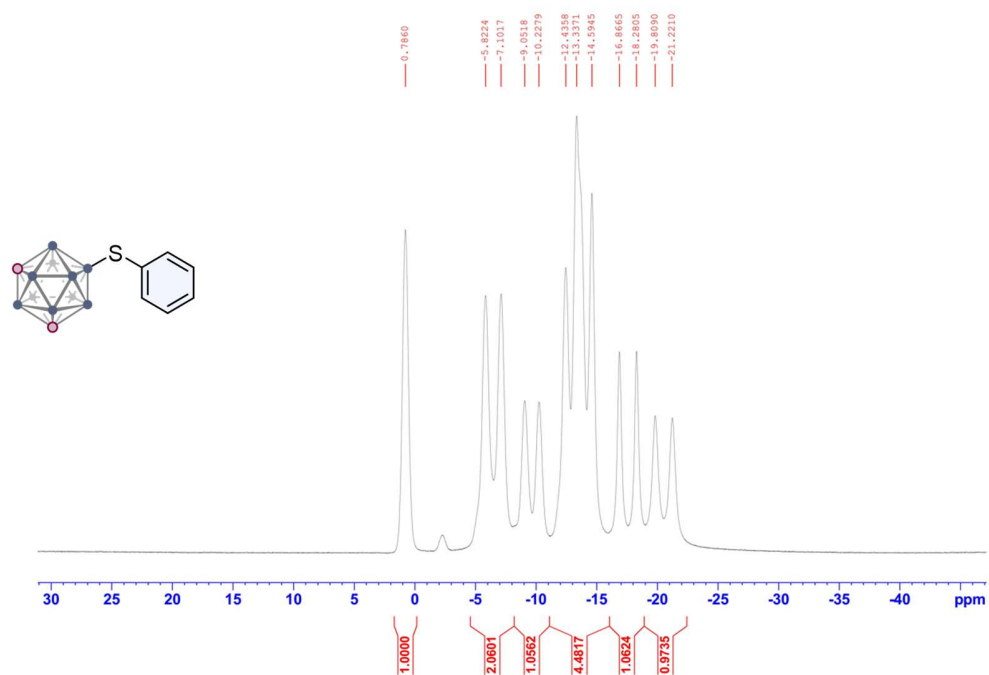
^1H NMR of **3ao** (CDCl_3 , 400 MHz)



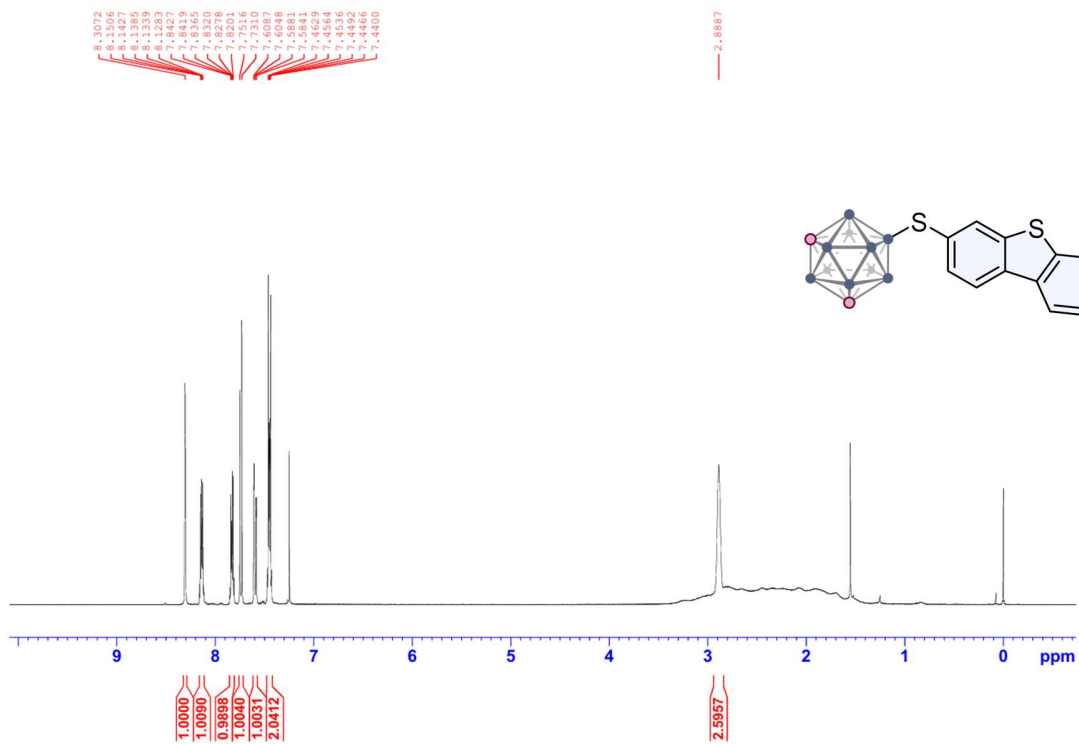
^{13}C NMR of **3ao** (CDCl_3 , 100 MHz)



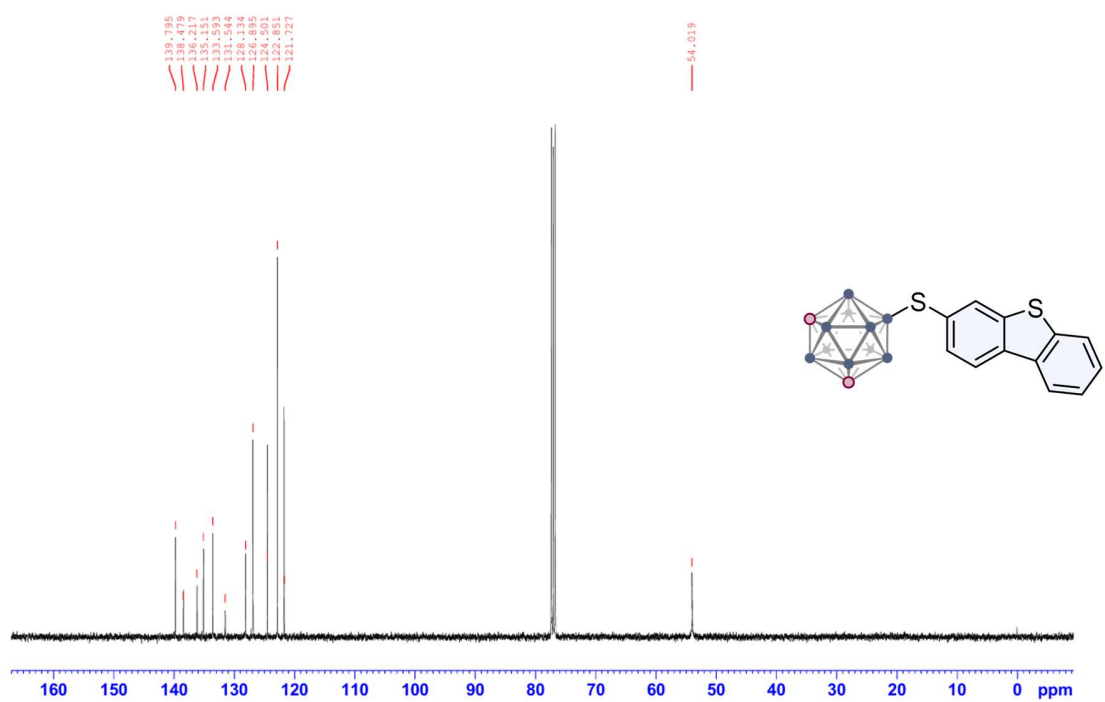
^{11}B NMR of **3ao** (CDCl_3 , 128 MHz)



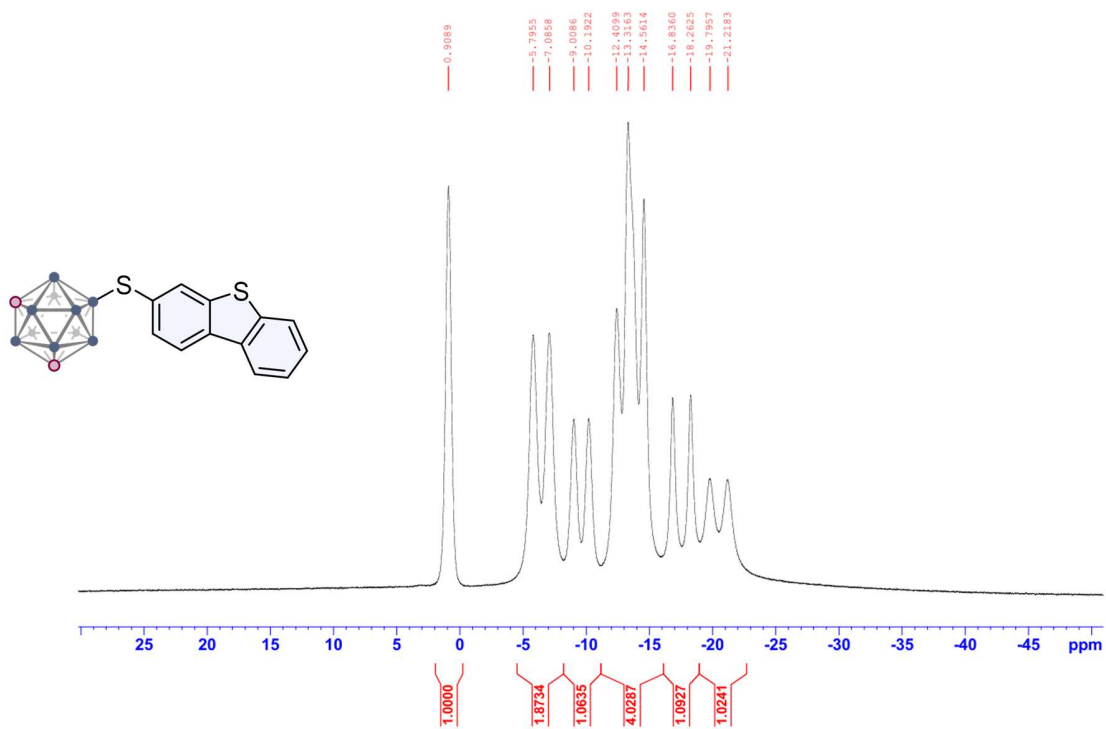
^1H NMR of **3ap** (CDCl_3 , 400 MHz)



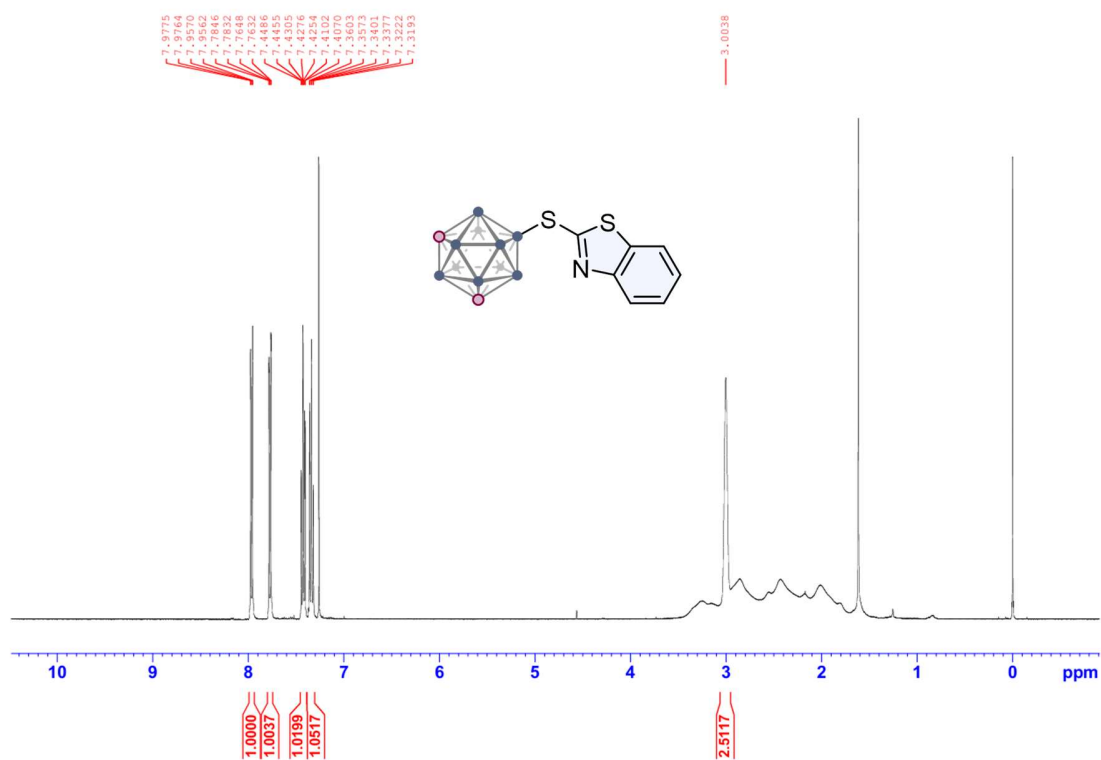
^{13}C NMR of **3ap** (CDCl_3 , 100 MHz)



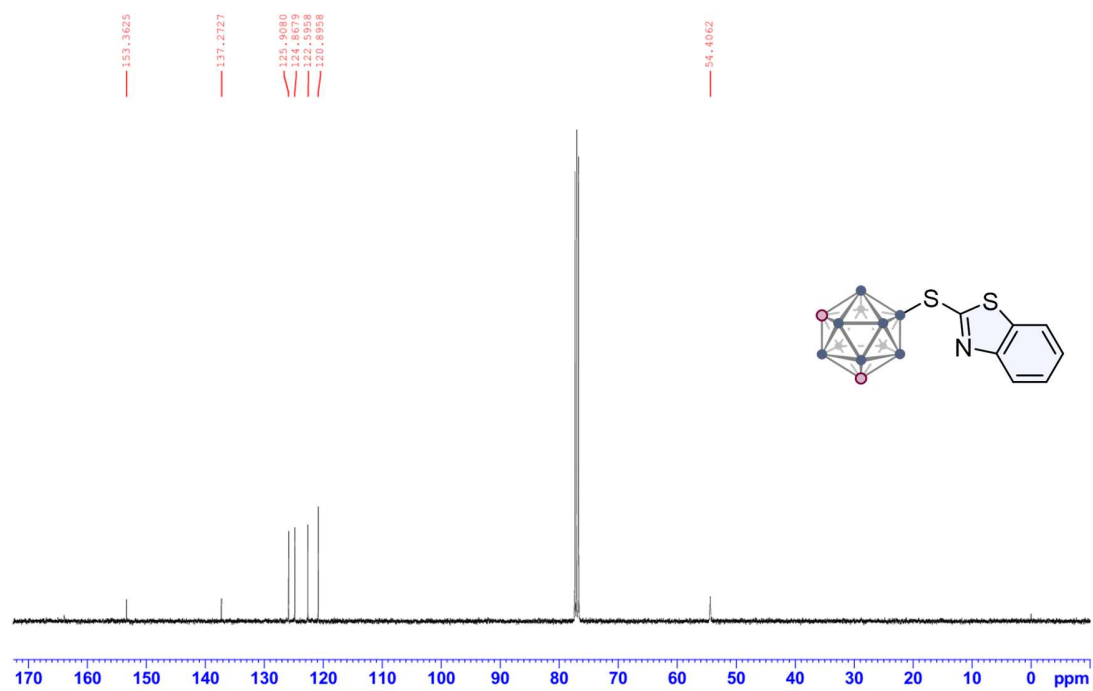
^{11}B NMR of **3ap** (CDCl_3 , 128 MHz)



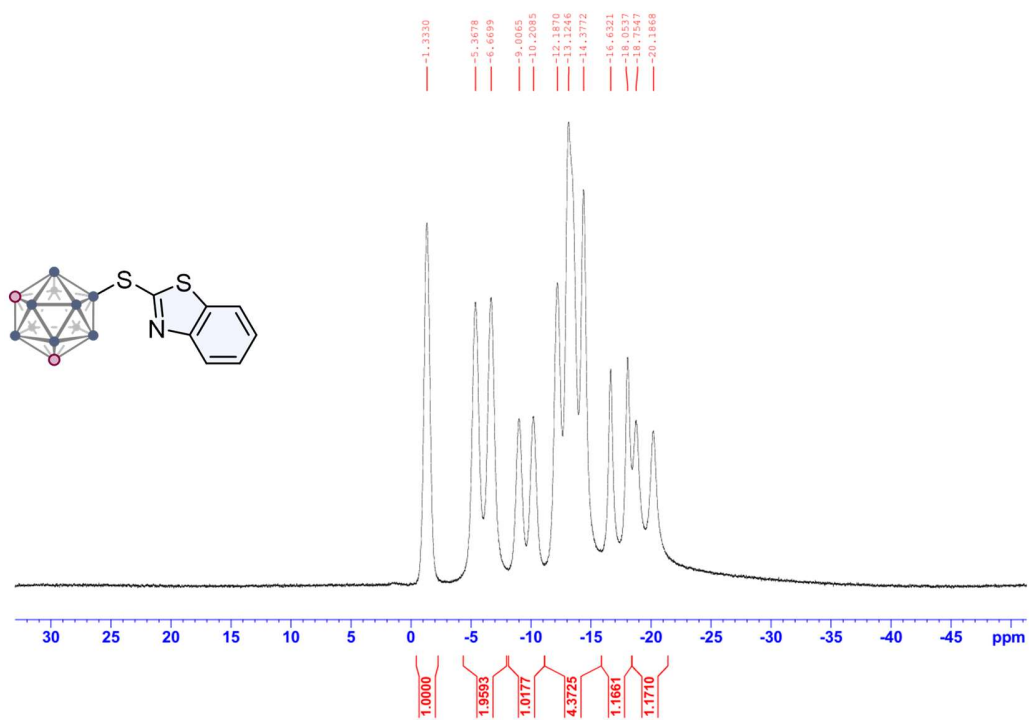
¹H NMR of **3aq** (CDCl₃, 400 MHz)



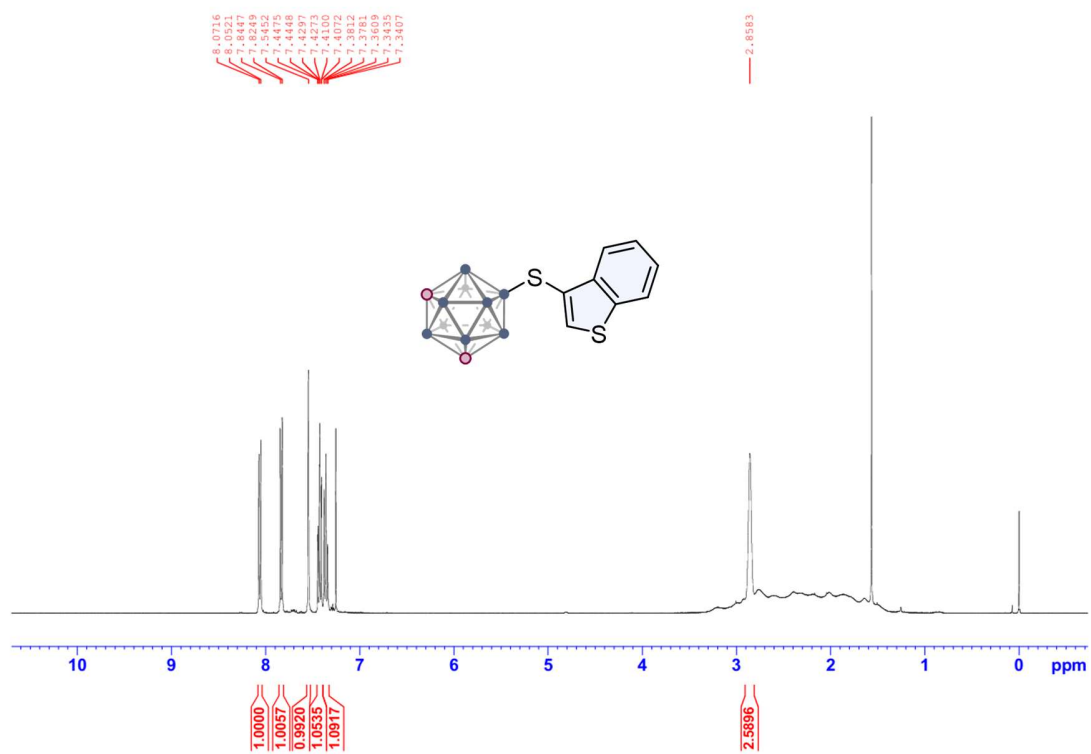
¹³C NMR of **3aq** (CDCl₃, 100 MHz)



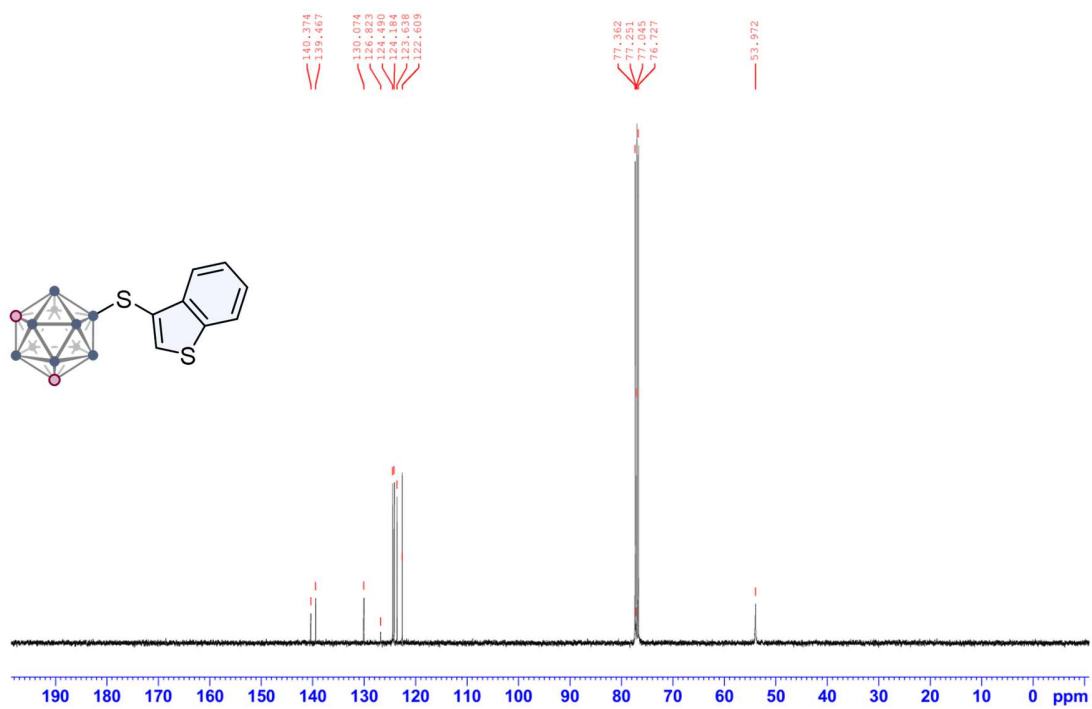
^{11}B NMR of **3aq** (CDCl_3 , 128 MHz)



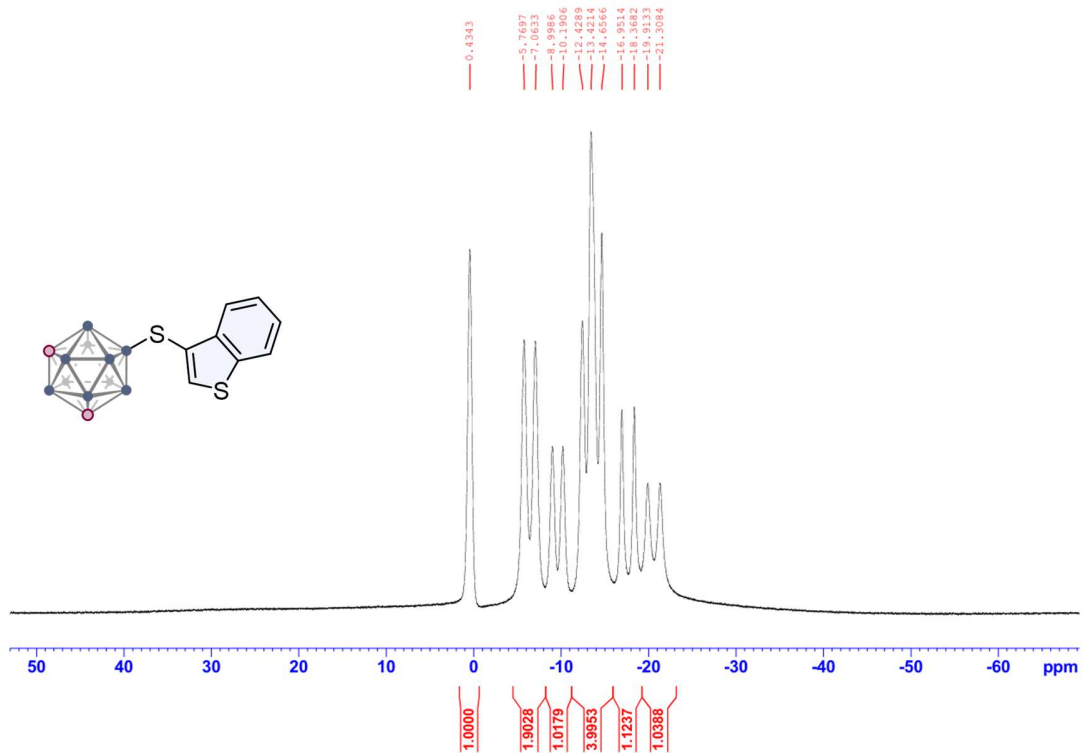
^1H NMR of **3ar** (CDCl_3 , 400 MHz)



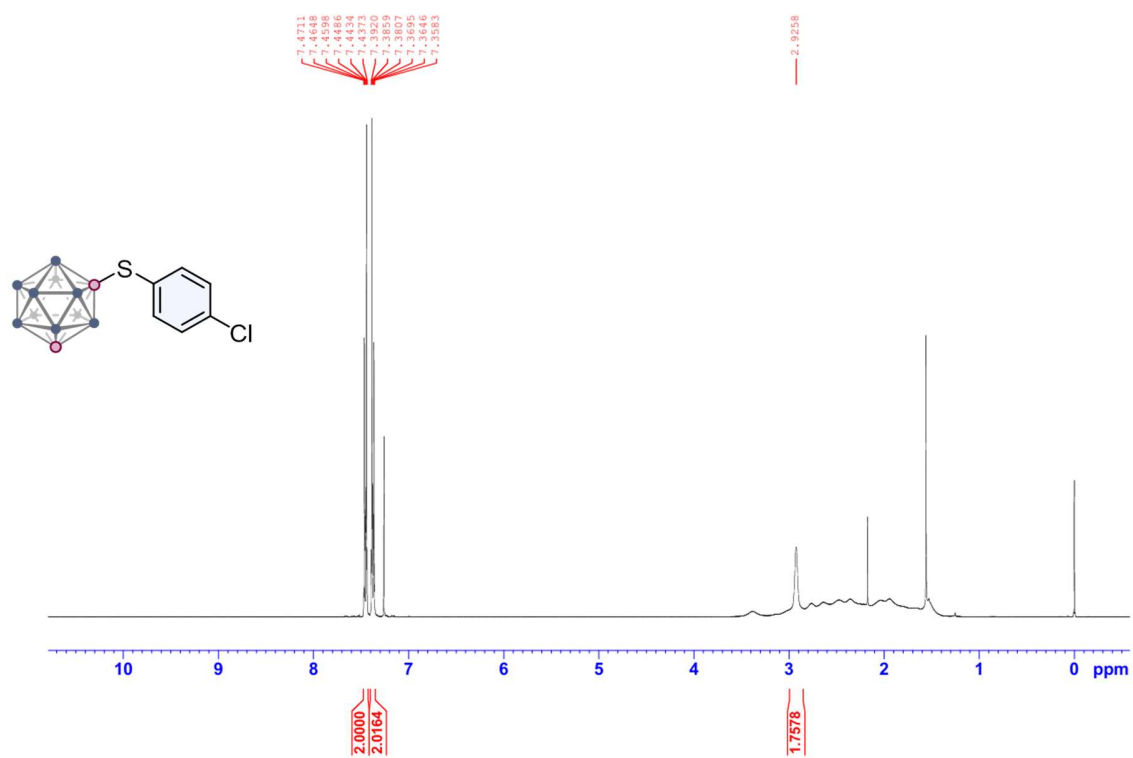
¹³C NMR of **3ar** (CDCl₃, 100 MHz)



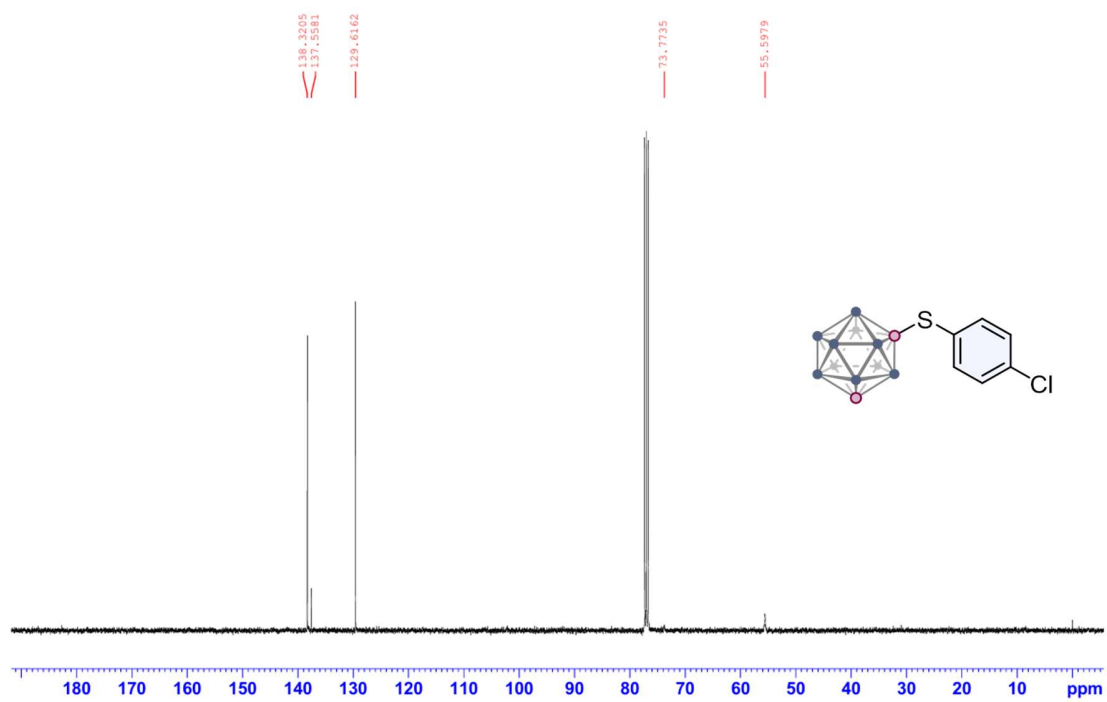
¹¹B NMR of **3ar** (CDCl₃, 128 MHz)



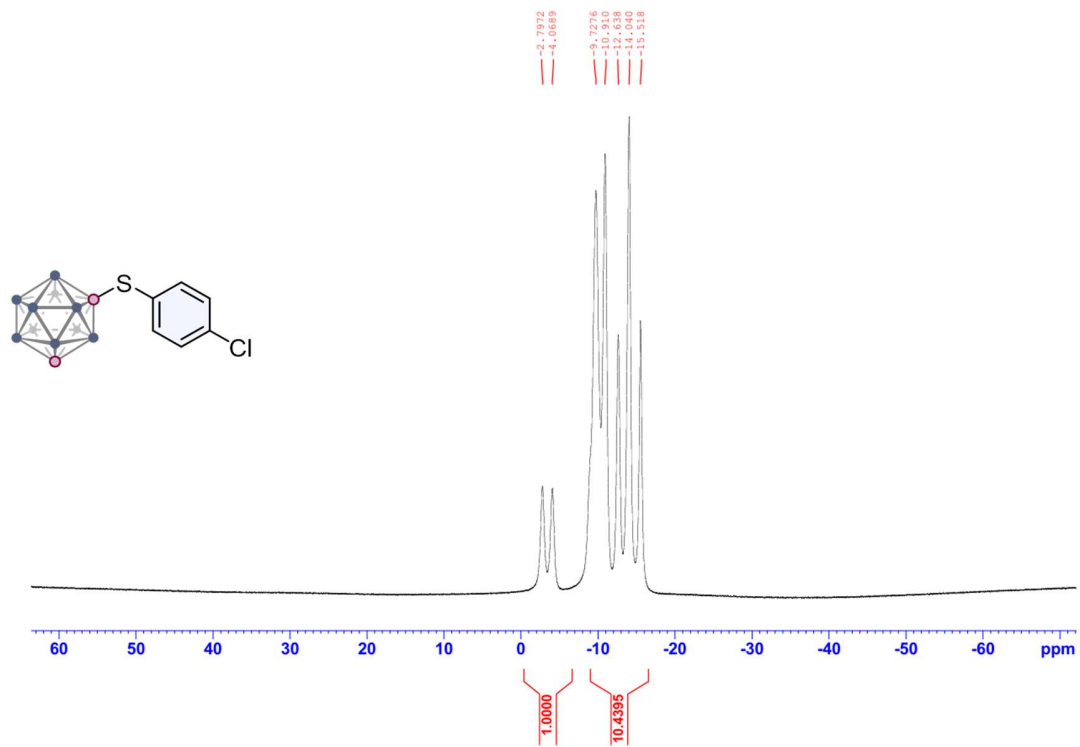
^1H NMR of **3bc** (CDCl_3 , 400 MHz)



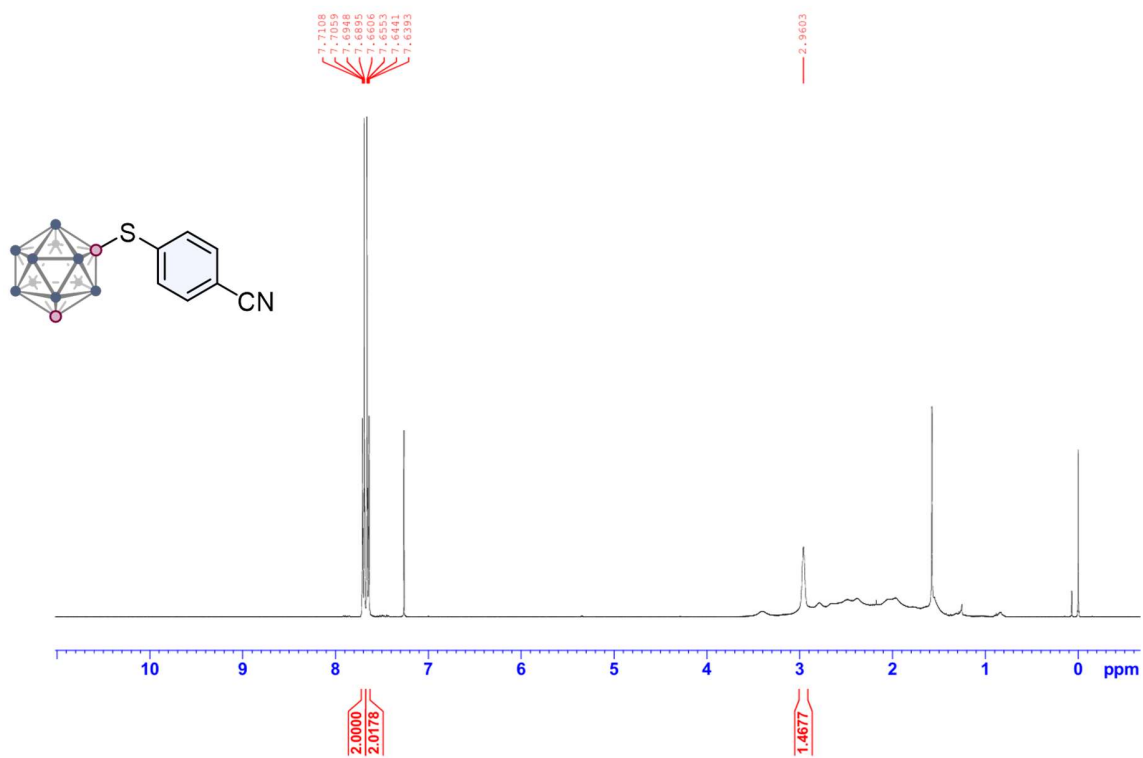
^{13}C NMR of **3bc** (CDCl_3 , 100 MHz)



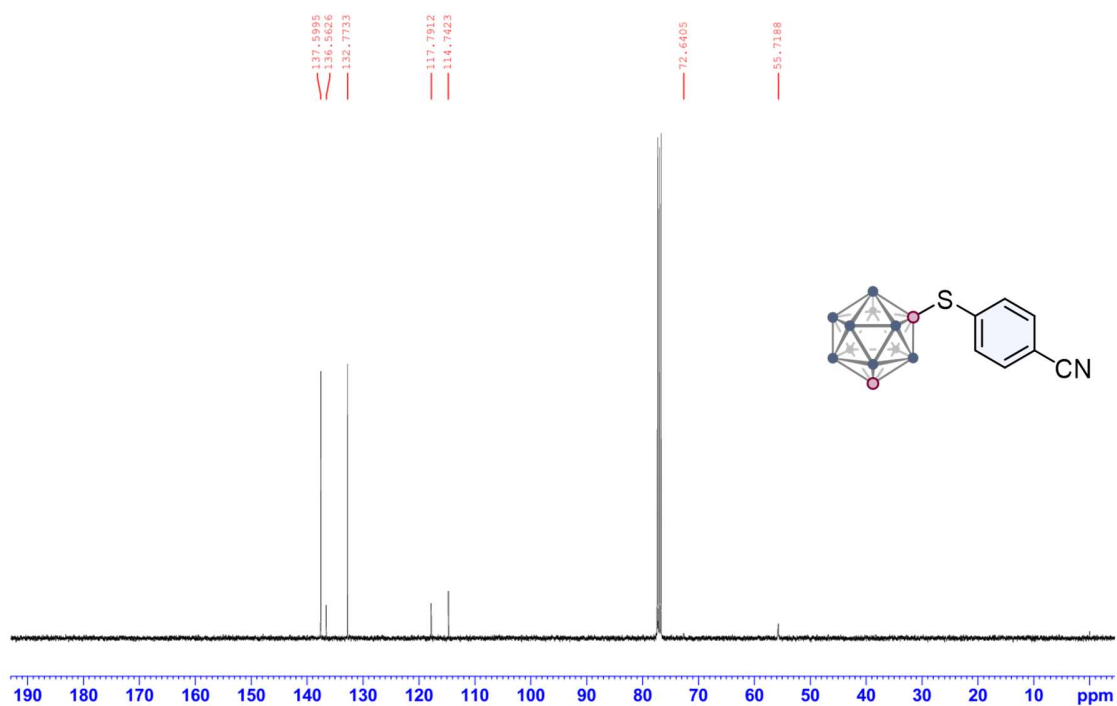
^{11}B NMR of **3bc** (CDCl_3 , 128 MHz)



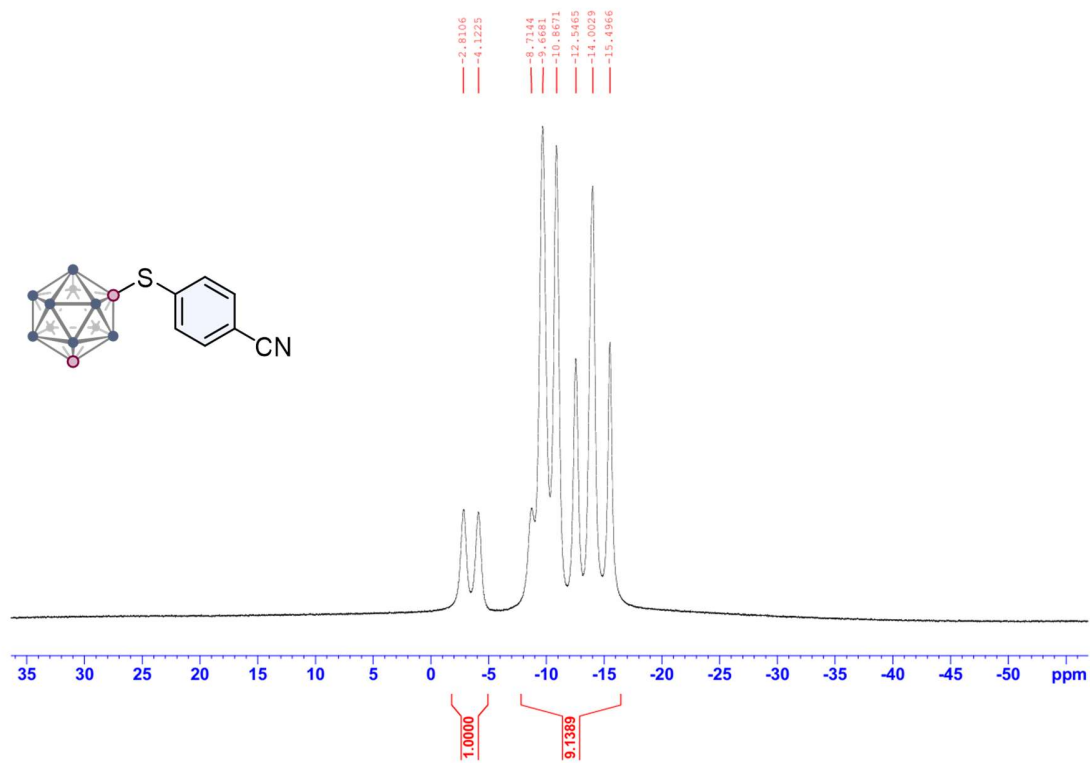
^1H NMR of **3be** (CDCl_3 , 400 MHz)



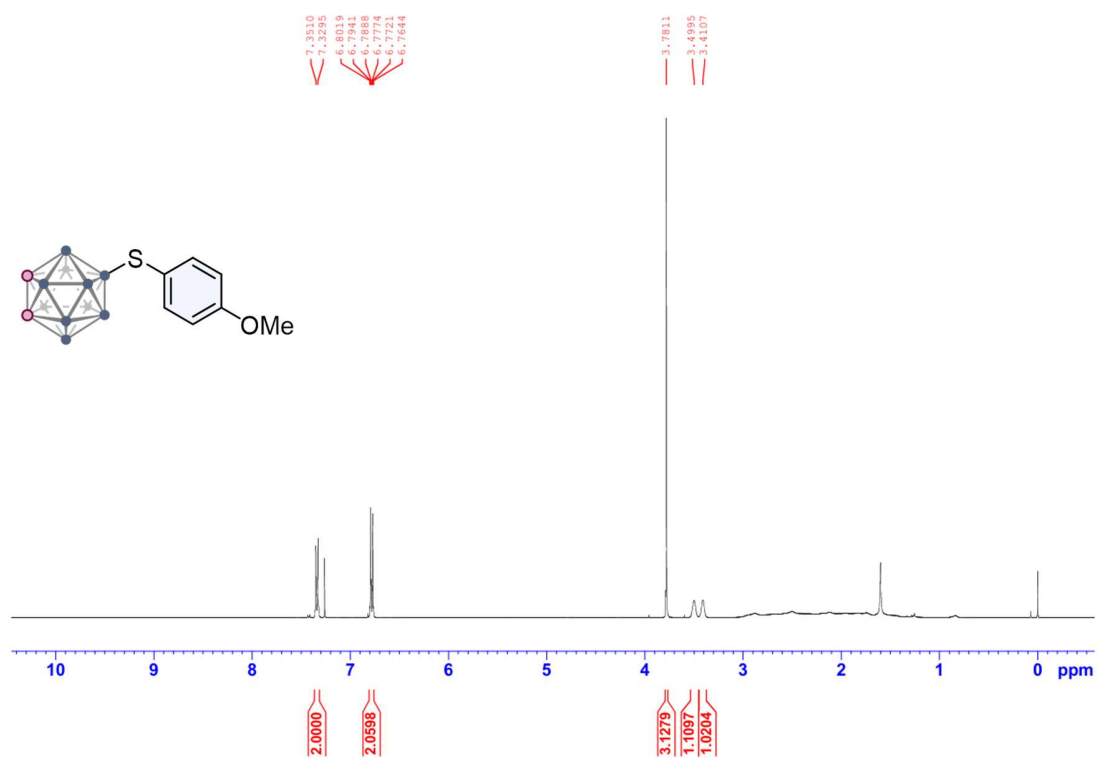
^{13}C NMR of **3be** (CDCl_3 , 100 MHz)



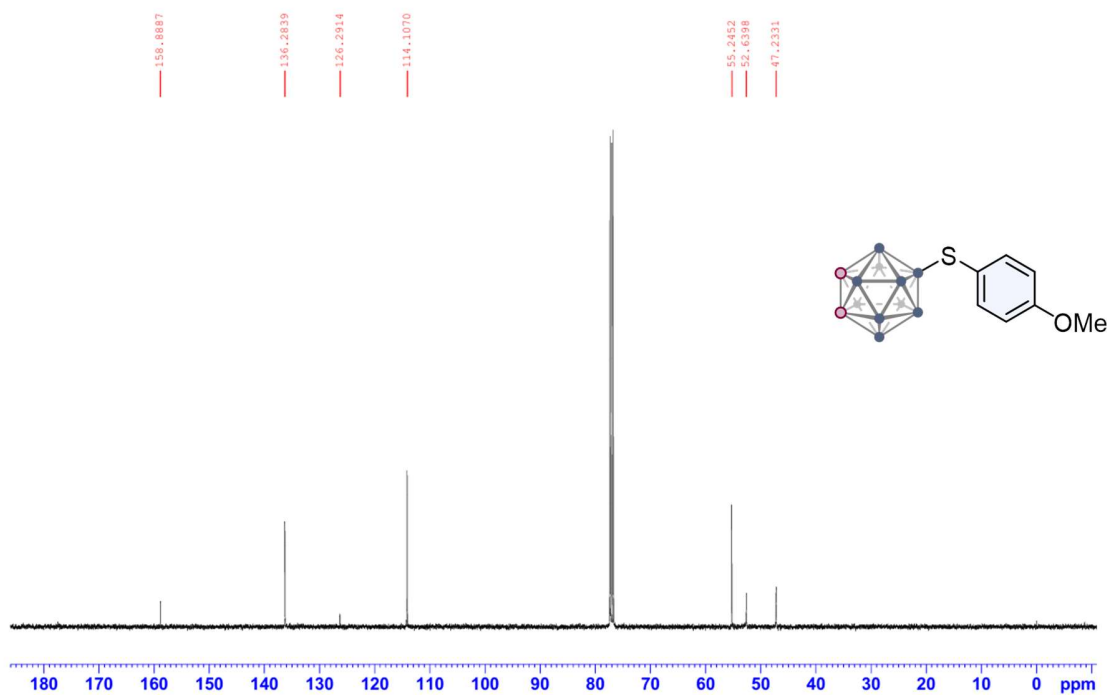
^{11}B NMR of **3be** (CDCl_3 , 128 MHz)



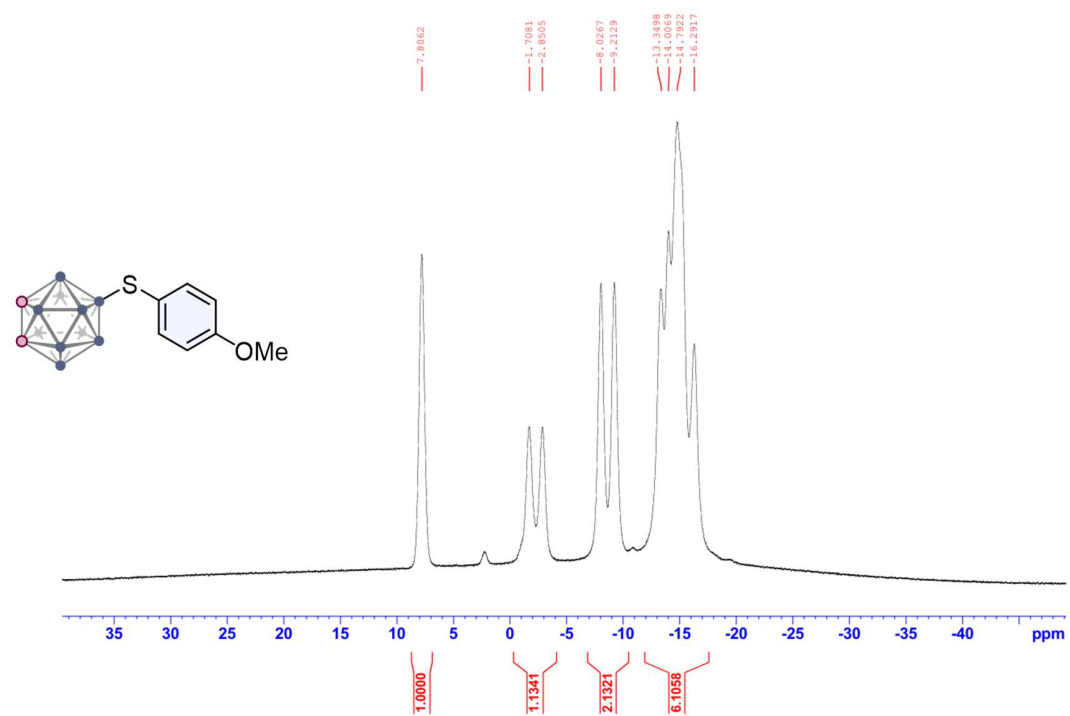
^1H NMR of **3ca** (CDCl_3 , 400 MHz)



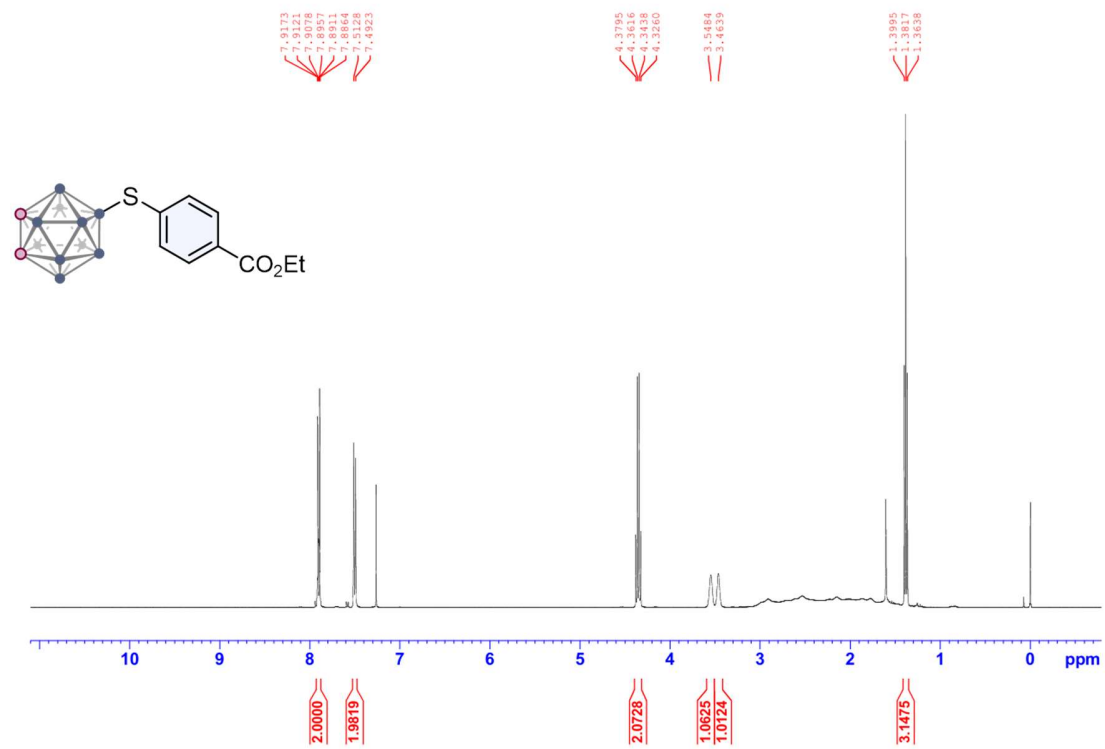
^{13}C NMR of **3ca** (CDCl_3 , 100 MHz)



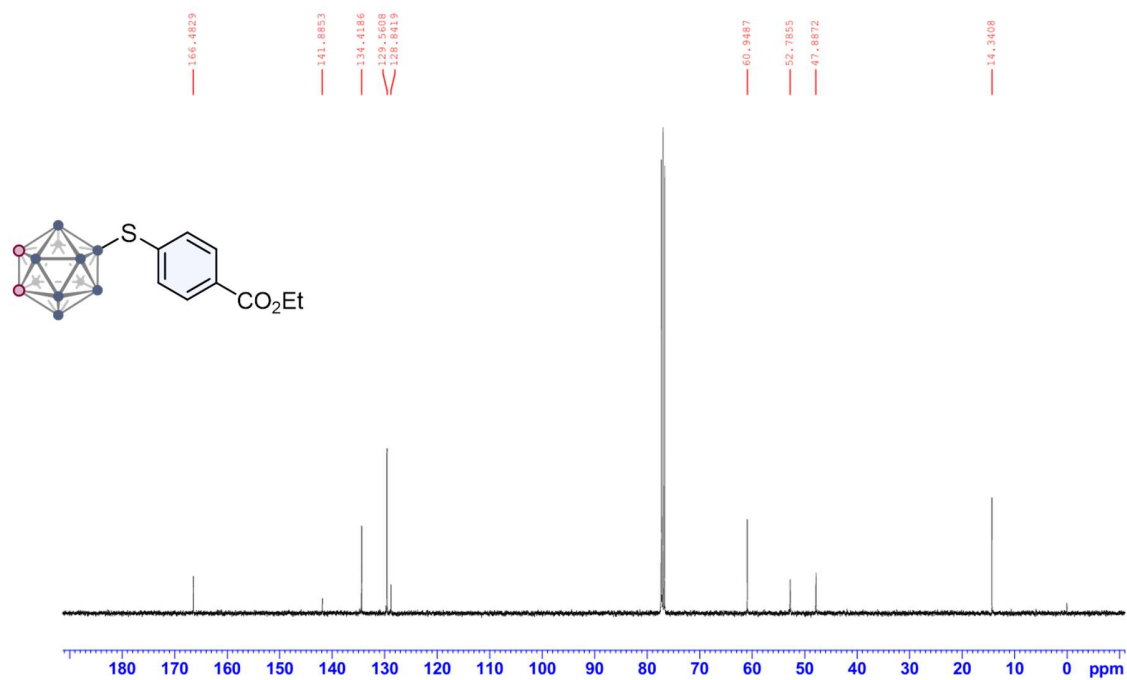
^{11}B NMR of **3ca** (CDCl_3 , 128 MHz)



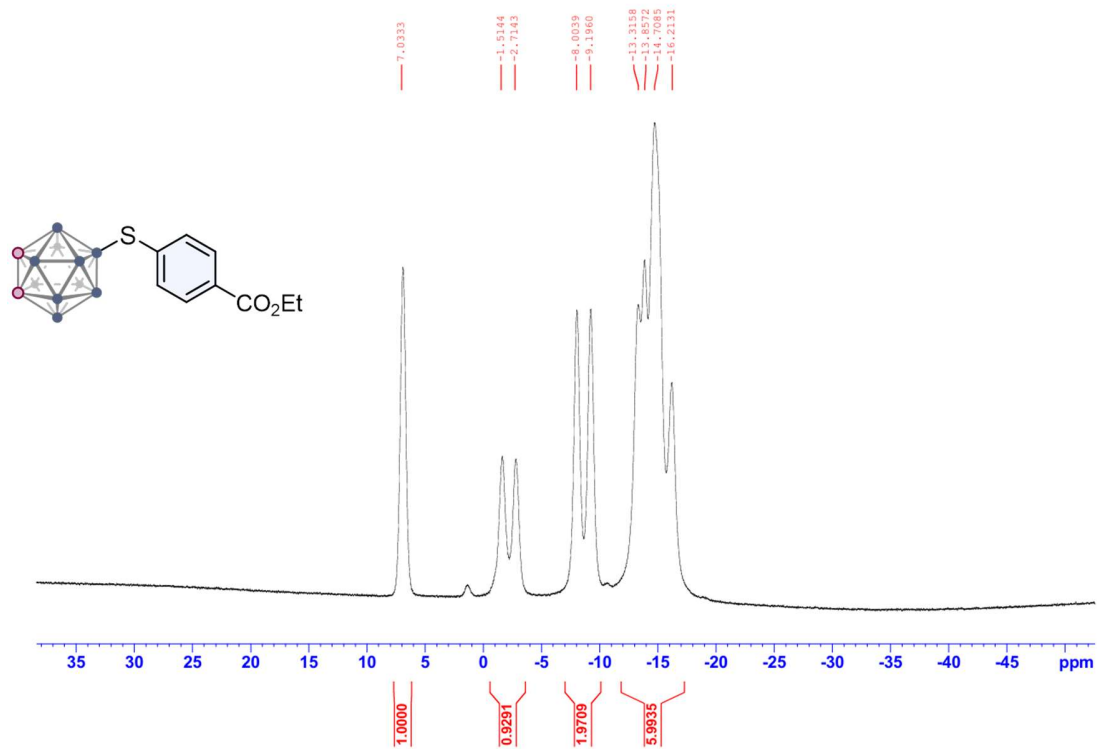
^1H NMR of **3cd** (CDCl_3 , 400 MHz)



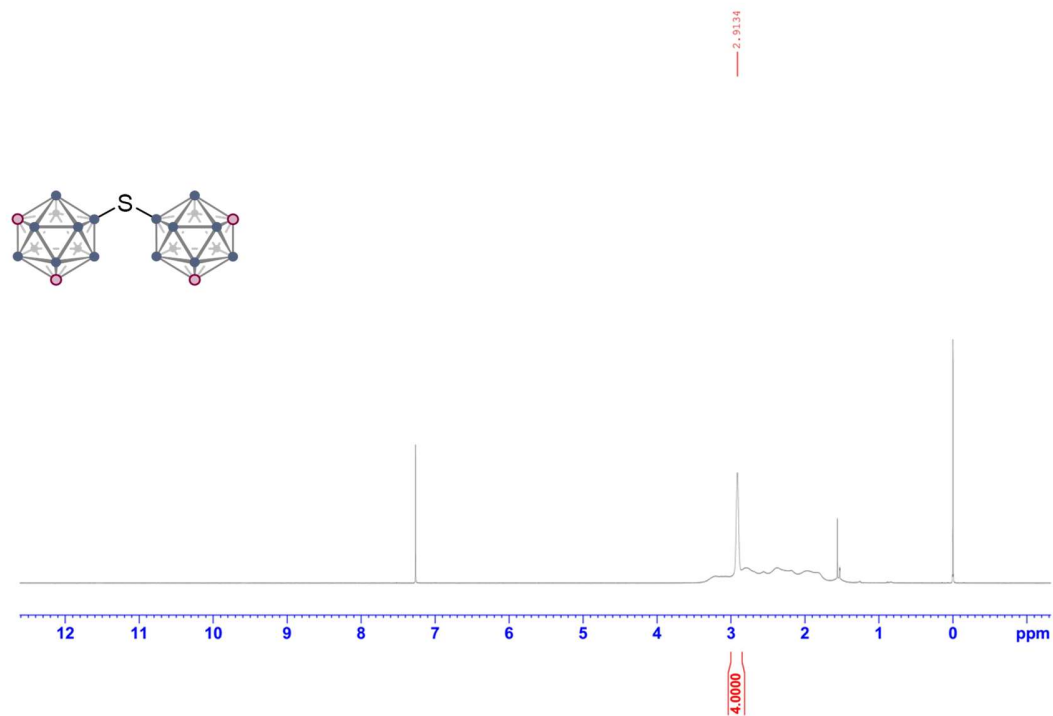
^{13}C NMR of **3cd** (CDCl_3 , 100 MHz)



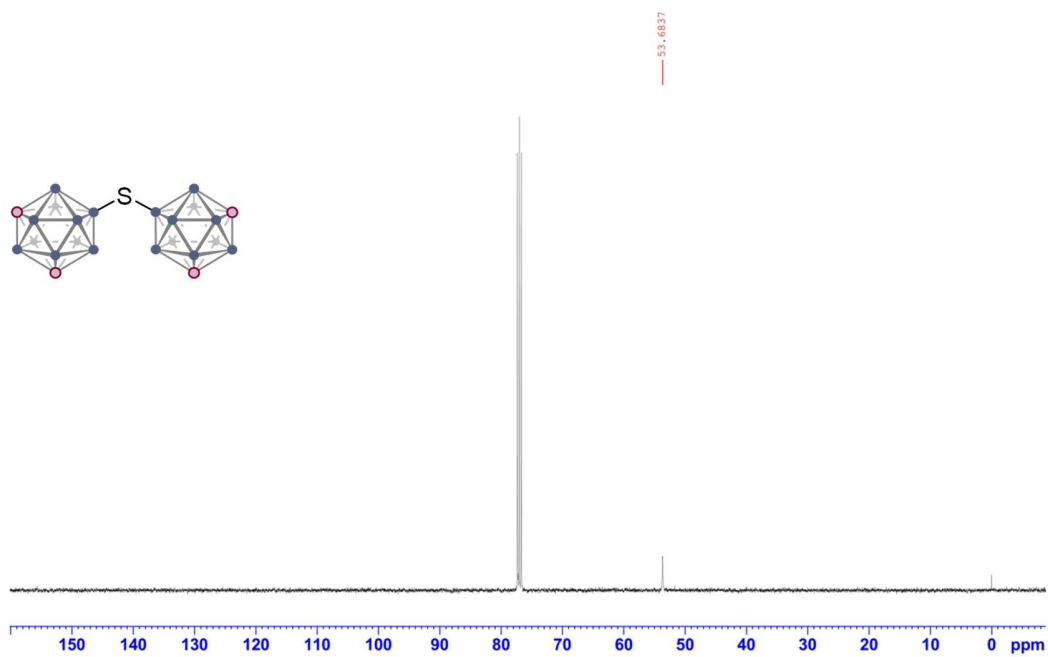
^{11}B NMR of **3cd** (CDCl_3 , 128 MHz)



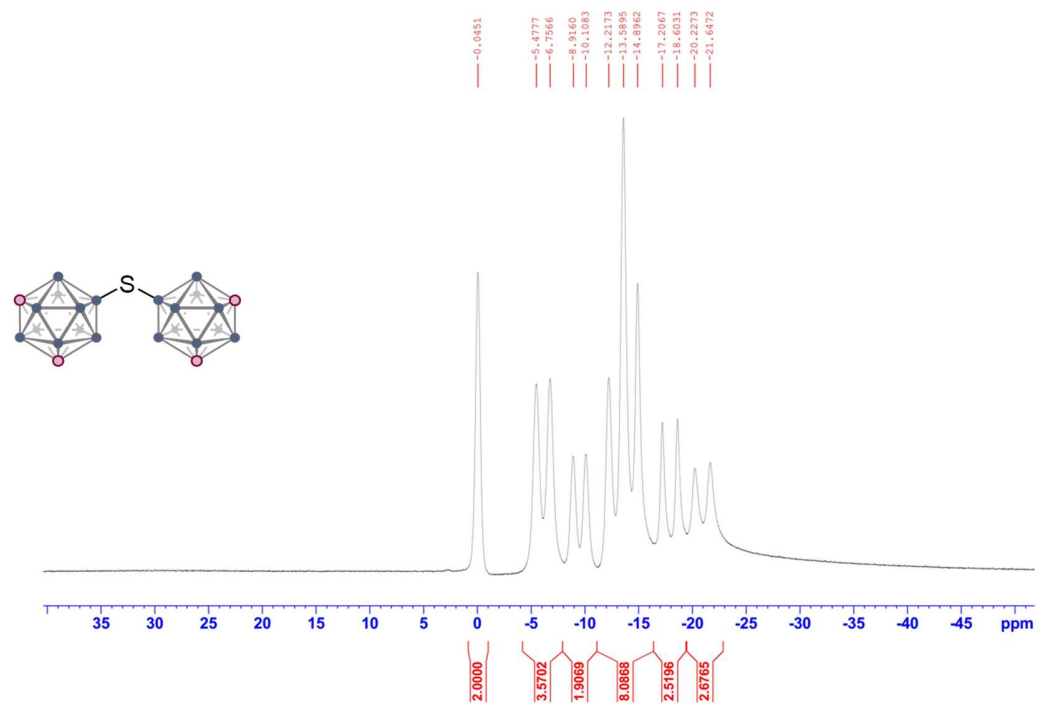
^1H NMR of **5a** (CDCl_3 , 400 MHz)



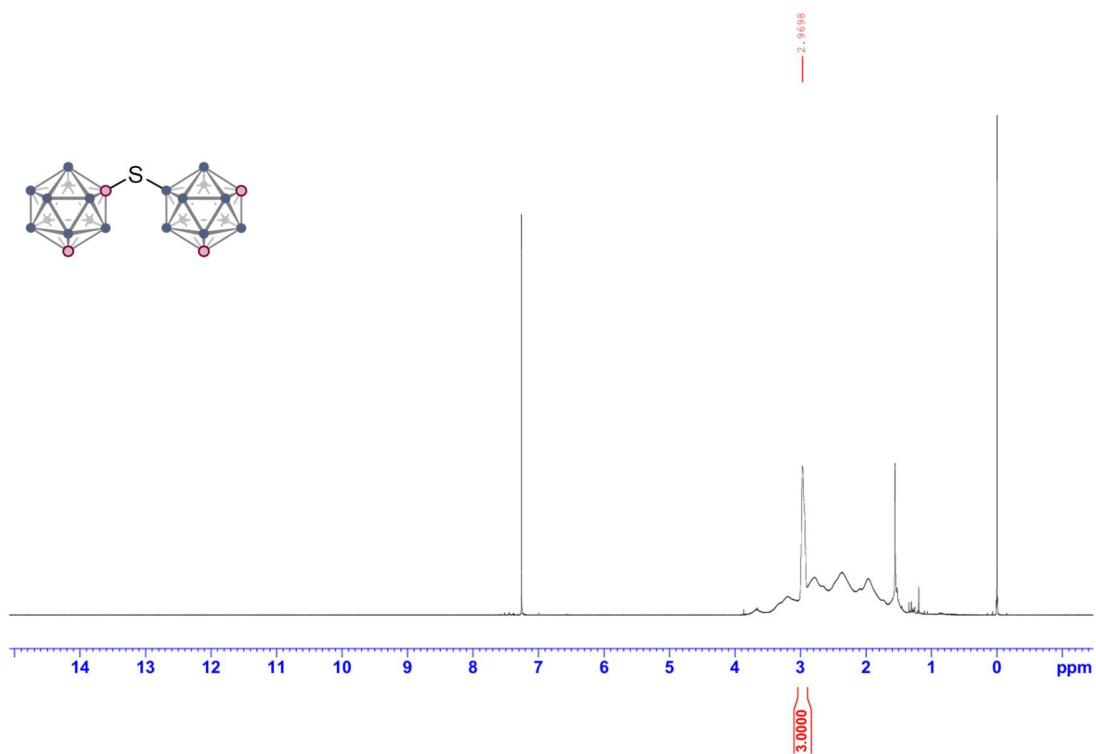
^{13}C NMR of **5a** (CDCl_3 , 100 MHz)



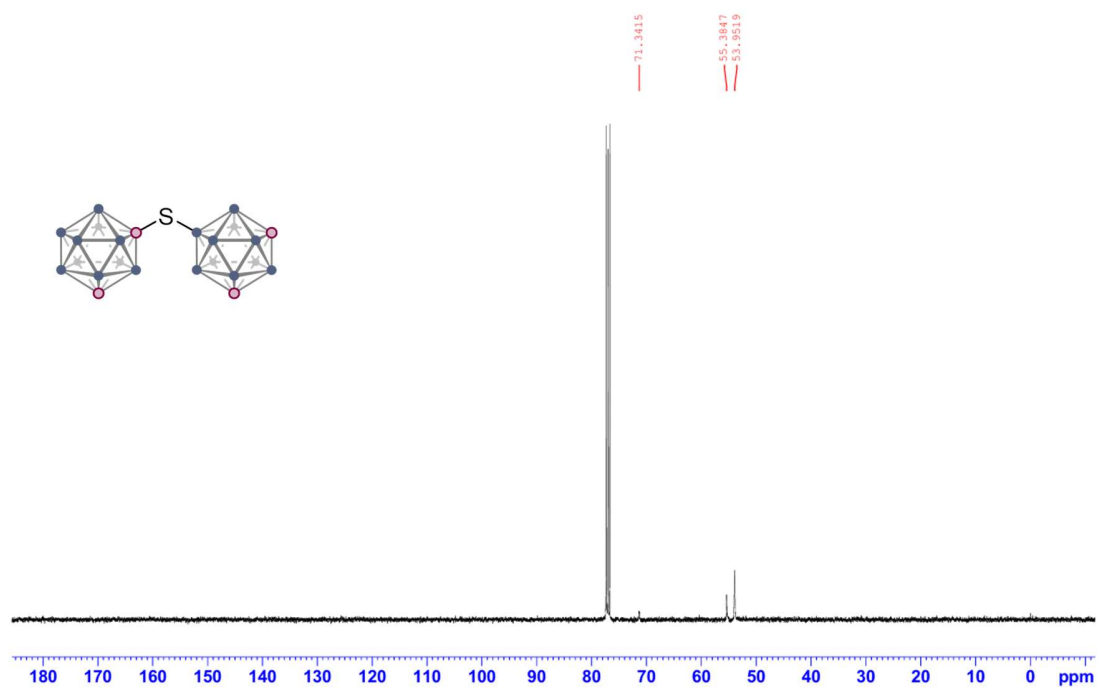
^{11}B NMR of **5a** (CDCl_3 , 128 MHz)



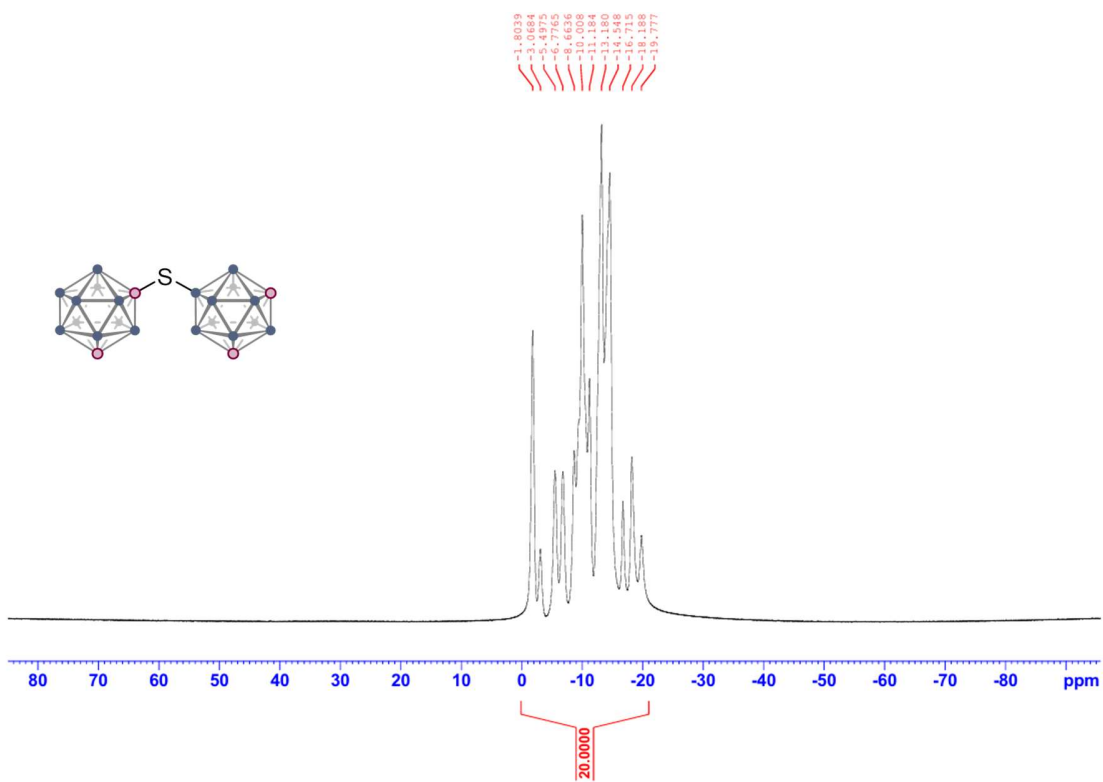
^1H NMR of **5b** (CDCl_3 , 400 MHz)



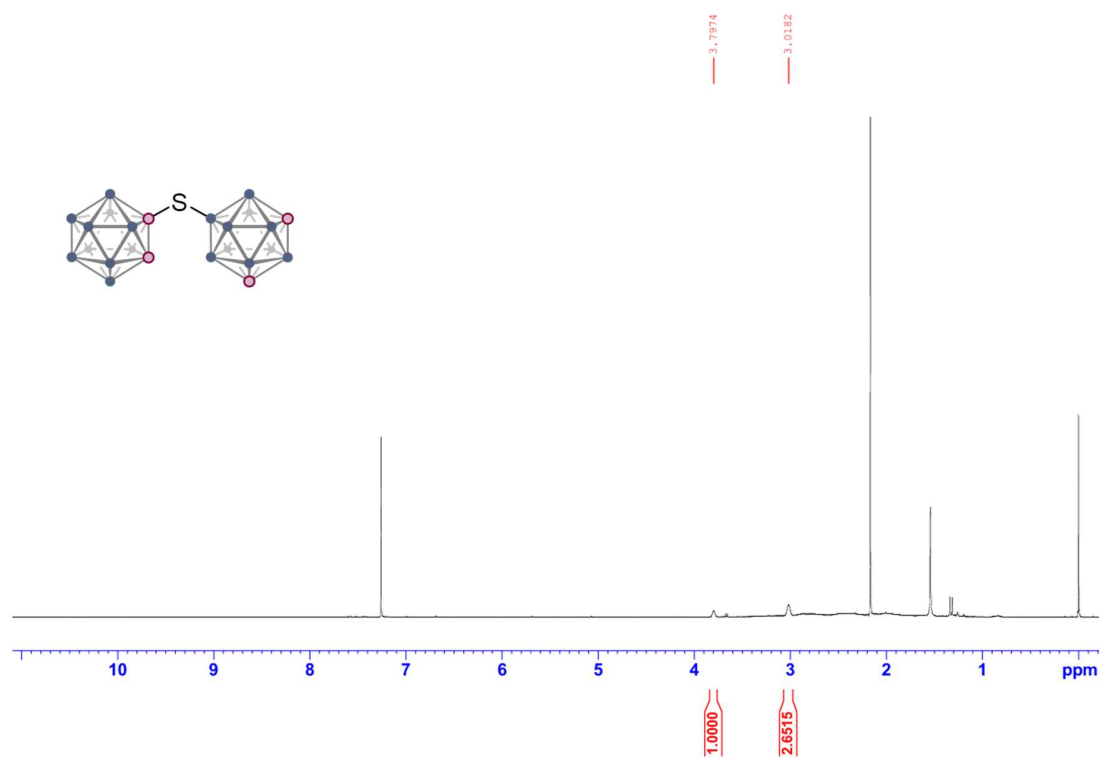
^{13}C NMR of **5b** (CDCl_3 , 100 MHz)



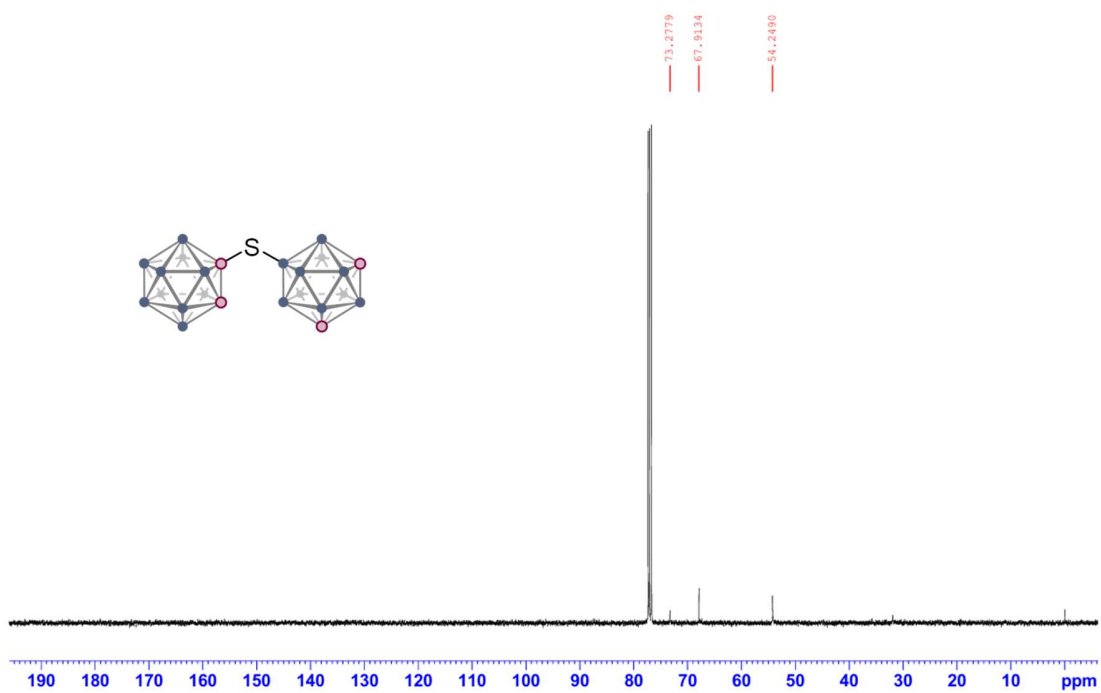
^{11}B NMR of **5b** (CDCl_3 , 128 MHz)



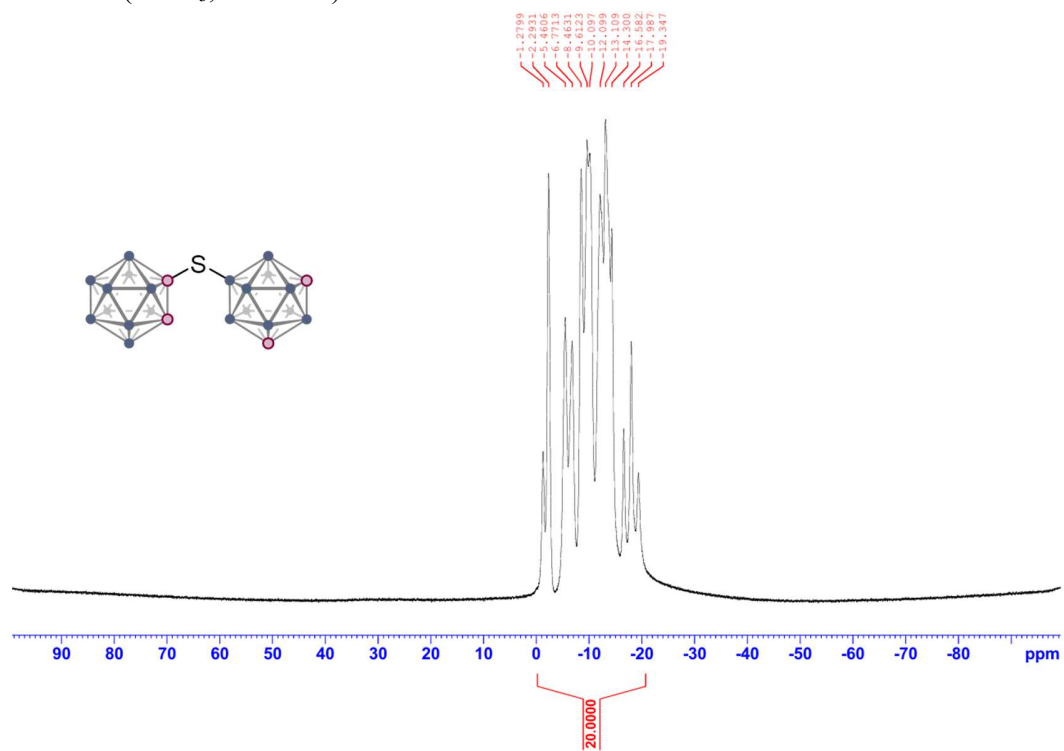
^1H NMR of **3ap** (CDCl_3 , 400 MHz)



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



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



6. References

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