Supporting Information

Electrooxidative *o*-Carborane Chalcogenations Without Directing Groups: Cage Activation by Copper Catalysis at Room Temperature

*Long Yang,[+] Becky Bongsuiru Jei,[+] Alexej Scheremetjew, Binbin Yuan, A. Claudia Stückl and Lutz Ackermann**

Institut für Organische und Biomolekulare Chemie and
Wöhler Research Institute for Sustainable Chemistry

Georg-August-Universität Göttingen

Tammannstraße 2, 37077 Göttingen, Germany

Lutz.Ackermann@chemie.uni-goettingen.de

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General remarks

Catalytic reactions were carried out in undivided electrochemical cells (10 mL) using pre-dried glassware, unless otherwise stated. The following starting materials were synthesized according to previously described methods: **1a**–**1g**.[1-3] Other chemicals were obtained from commercial sources and used without further purification. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and graphite felt (GF) electrodes (10 mm × 15 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode. IR spectra were recorded on a Bruker FT-IR alpha-P device. EI-MS was recorded on Jeol *AccuTOF* at 70 eV. Melting points (M.p.) were measured on Stuart™ melting point apparatus SMP3, and the values are uncorrected. NMR spectra were recorded on Inova 500 or Bruker Avance III 300, Avance III 400 and Avance III HD 500 in the solvent indicated. Chemical shifts (δ) are provided in ppm and spectra refer to non-deuterated solvent signal. Yields refer to isolated compounds estimated to be >95% pure as determined by ^{1}H NMR. Recycling preparative HPLC (GPC) was performed on a system from JAI (LC-92XX II Series, Injection-and Control-Valve, UV and RI Detector) connected to JAIGEL HH series columns. $CHCl_3$ of HPLC grade was employed. X-ray structures were measured on Bruker APEX-II CCD diffractometer. CV studies were performed using a Metrohm Autolab PGSTAT204 workstation and Nova 2.1 software.

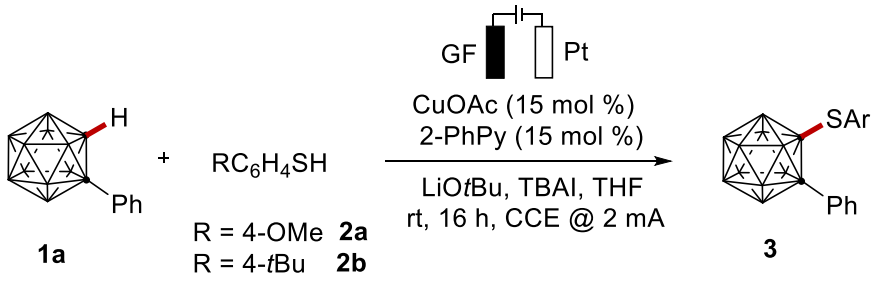
General procedure for electrochemical cage C–H chalcogenation

Procedure A: The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). *o*-Carborane **1** (0.10 mmol, 1.0 equiv), thiol **2** (0.30 mmol, 3.0 equiv), CuOAc (15 mol %), 2-PhPy (15 mol %), LiO*t*Bu (0.2 mmol, 2.0 equiv) and TBAI (0.2 mmol, 2.0 equiv) were dissolved in THF (3.0 mL). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 16 h. The GF anode was washed with ethyl acetate (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with *n*-hexane (500 mL) or gel permeation chromatography (GPC) afford the corresponding products **3**.

Procedure B: The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Thiol **2** (0.30 mmol, 3.0 equiv), LiO*t*Bu (0.2 mmol, 2.0 equiv) and TBAI (0.2 mmol, 2.0 equiv) were dissolved in THF (3.0 mL). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 3 h. Then, *o*-carborane **1** (0.10 mmol, 1.0 equiv), CuOAc (15 mol %) and 2-PhPy (15 mol %) were added to the reaction mixture and electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for another 16 h. The GF anode was washed with ethyl acetate (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with *n*-hexane (500 mL) or gel permeation chromatography (GPC) afford the corresponding products **3**.

Optimization studies

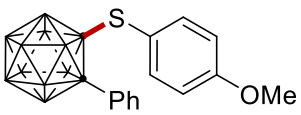
Table S1. Optimization of reaction conditions.[a]



Entry	Variation from standard conditions	Yield [%][b]
1	**none**	**90% (85%)[c]**
2	$Cu(OAc)_2$ instead of CuOAc	51%
3	CuI instead of CuOAc	43%
4	2,6-Lutidine instead of 2-PhPy	71%
5	1,10-Phen instead of 2-PhPy	16%
6	$TBAPF_6$ instead of TBAI	---
7	TBAI (1 equiv) and $TBAPF_6$ (1 equiv)	57%
8	TBAI (3 equiv)	49%
9	KI (1 equiv) as additive	67%
10	KI (0.5 equiv) as additive	23%
11	DCE instead of THF	---
12	CH_3CN instead of THF	49%
13	No electricity	14%[d]
14	In the dark	89%
15	Under N_2	19%
16	No [Cu]	---
17	Procedure B (**2b**)	66% (62%)[e,d]
18	Procedure B: second step without electricity (**2b**)	---[f]
19	Procedure B (**2a**)	92%[e]

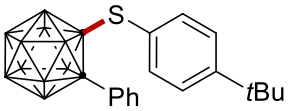
[a] Reaction conditions: Procedure A: **1a** (0.10 mmol), **2a** (0.30 mmol), CuOAc (15 mol %), 2-PhPy (15 mol %), LiO*t*Bu (0.2 mmol), TBAI (2.0 equiv), THF (3.0 mL), platinum (Pt) cathode (10 mm × 15 mm × 0.25 mm), graphite felt (GF) anode (10 mm × 15 mm × 6 mm), 2 mA, under air, 25 °C, 16 h. [b] Yield was determined by ^1H NMR with CH_2Br_2 as the standard. [c] Isolated yields in parenthesis. [d] KI (1.0 equiv) as additive. [e] Procedure B: **2** (0.3 mmol), LiO*t*Bu (0.2 mmol), TBAI (2.0 equiv), THF (3.0 mL), 2 mA, 25 °C, 3 h, then **1a** (0.10 mmol), 2-PhPy (15 mol %), CuOAc (15 mol %), 2 mA, 25 °C, 16 h. [f] **2b** (0.30 mmol), LiO*t*Bu (0.2 mmol), KI (1.0 equiv), TBAI (2.0 equiv), solvent (3.0 mL), 2 mA, 25 °C, 3 h, then adding **1a** (0.10 mmol), 2-PhPy (15 mol %), CuOAc (15 mol %), 25 °C, 16 h. TBAI = Tetrabutylammonium iodide, $TBAPF_6$ = Tetrabutylammonium hexafluorophosphate. DCE = 1,2-Dichloroethane, THF = Tetrahydrofuran.

Analytical data for products



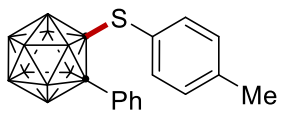
3aa

3aa. The representative procedure A was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-methoxybenzenethiol **2a** (36.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3aa** (30.5 mg, 85%) as a colorless solid. **M.p.** = 141 – 143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.8 (C_q), 138.5 (CH), 132.2 (CH), 131.0 (C_q), 130.8 (CH), 128.5 (CH), 120.8 (C_q), 114.5 (CH), 87.9 (Cage C), 86.9 (Cage C), 55.4 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.78 (2B), -9.14 (3B), -10.46 (3B), -11.59 (2B). **IR** (ATR): 2924, 2853, 2601, 2574, 2561, 1588, 1253, 1170, 1027 cm^{-1}. **MS** (EI) *m*/*z*: 358 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8OS$ $[M]^+$: 358.2397, found: 358.2386.



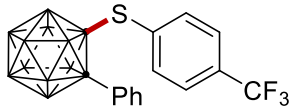
3ab

3ab. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-(*tert*-butyl)benzenethiol **2b** (49.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ab** (24.0 mg, 62%) as a colorless solid. **M.p.** = 177 – 179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 – 7.64 (m, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.46 (m, 2H), 7.30 – 7.26 (m, 2H), 6.92 – 6.85 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.7 (C_q), 136.5 (CH), 132.2 (CH), 131.0 (C_q), 130.8 (CH), 128.5 (CH), 126.4 (C_q), 126.1 (CH), 88.1 (Cage C), 86.6 (Cage C), 34.9 (C_q), 31.1 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -3.00 (2B), -9.24 (3B), -10.43 (2B), -11.65 (3B). **IR** (ATR): 2966, 2924, 2866, 2577, 2564, 1446, 1073, 687 cm^{-1}. **MS** (EI) *m*/*z*: 384 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{18}H_{28}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 384.2919, found: 384.2904.



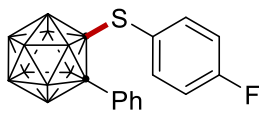
3ac

3ac. The representative procedure A with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-methylbenzenethiol **2c** (37.2 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ac** (18.9 mg, 55%) as a colorless solid. **M.p.** = 146 – 148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.58 (m, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.39 (m, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.6 (C_q), 136.7 (CH), 132.2 (CH), 130.9 (C_q), 130.8 (CH), 129.8 (CH), 128.5 (C_q), 126.5 (CH), 88.0 (Cage C), 86.5 (Cage C), 21.37 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.59 (1B), -3.22 (1B), -8.51 (2B), -9.22 (2B), -10.42 (2B), -11.56 (2B). **IR** (ATR): 2954, 2598, 2568, 1973, 1492, 1446, 1179, 1073, 885 cm^{-1}. **MS** (EI) *m*/*z*: 342 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 342.2448, found: 342.2435.



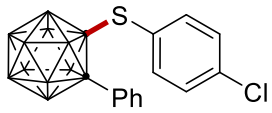
3ad

3ad. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-(trifluoromethyl)benzenethiol **2d** (41.1 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ad** (30.6 mg, 77%) as a colorless solid. **M.p.** = 84 – 86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.51 – 7.47 (m, 2H), 7.47 – 7.42 (m, 2H), 7.05 – 7.00 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.0 (CH), 133.8 (C_q), 133.0 (q, $^{2}J_{C\text{-}F}$ = 33 Hz, C_q), 132.1 (CH), 131.0 (CH), 130.7 (C_q), 128.6 (CH), 125.9 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, CH), 123.4 (q, $^{1}J_{C\text{-}F}$ = 273 Hz, C_q), 88.0 (Cage C), 84.7 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.47 (2B), -9.09 (4B), -10.22 (2B), -11.48 (2B). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -63.07. **IR** (ATR): 2925, 2572, 1495, 1447, 1322, 1172, 1135, 1062, 842 cm^{-1}. **MS** (EI) *m*/*z*: 396 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{19}{}^{10}B_2{}^{11}B_8F_3S$ $[M]^+$: 396.2165, found: 396.2158.



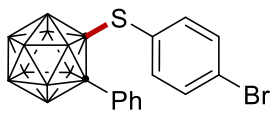
3ae

3ae. The representative procedure A with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-fluorobenzenethiol **2e** (32.0 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ae** (21.0 mg, 61%) as a colorless solid. **M.p.** = 103 – 105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 – 7.61 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.01 – 6.87 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.4 (d, $^{1}J_{C\text{-}F}$ = 254 Hz, C_q), 139.0 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz, CH), 132.1 (CH), 130.9 (CH), 130.8 (C_q), 128.6 (CH), 125.3 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz, C_q), 116.4 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, CH), 87.8 (Cage C), 85.8 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.67 (2B), -8.91 (4B), -10.32 (2B), -11.54 (2B). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = -107.68. **IR** (ATR): 2609, 2572, 2561, 1585, 1486, 1233, 1155, 835, 687 cm^{-1}. **MS** (EI) *m*/*z*: 346 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8FS$ $[M]^+$: 346.2197, found: 346.2185.



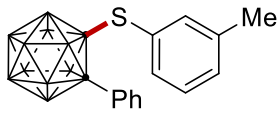
3af

3af. The representative procedure A was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-chlorobenzenethiol **2f** (43.0 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3af** (26.0 mg, 71%) as a colorless solid. **M.p.** = 108 – 110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 – 7.62 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.28 – 7.22 (m, 2H), 6.90 – 6.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 138.0 (CH), 137.9 (C_q), 132.1 (CH), 131.0 (CH), 130.8 (C_q), 129.4 (CH), 128.6 (CH), 128.1 (C_q), 87.9 (Cage C), 85.4 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.60 (2B), -8.90 (4B), -10.31 (2B), -11.54 (2B). **IR** (ATR): 2610, 2567, 1572, 1473, 1445, 1092, 1073, 746 cm^{-1}. **MS** (EI) *m*/*z*: 362 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8{}^{35}ClS$ $[M]^+$: 362.1904, found: 362.1893.



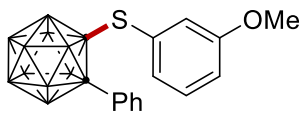
3ag

3ag. The representative procedure B with KI (16.6 mg, 0.10 mmol) and CuI (2.9 mg, 15 mol %) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 4-bromobenzenethiol **2g** (56.1 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ag** (29.0 mg, 71 %) as a colorless solid. **M.p.** = 126 – 128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 – 7.58 (m, 2H), 7.56 – 7.50 (m, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 6.78 – 6.70 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 138.1 (CH), 132.4 (CH), 132.1 (CH), 130.9 (CH), 130.7 (C_q), 128.6 (C_q), 128.5 (CH), 126.3 (C_q), 87.9 (Cage C), 85.2 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.46 (2B), -9.13 (4B), -10.31 (2B), -11.52 (2B). **IR** (ATR): 2622, 2596, 1564, 1471, 1446, 1386, 1070, 1010, 810 cm^{-1}. **MS** (EI) *m*/*z*: 408 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{11}B_{10}S^{79}Br$ $[M]^+$: 408.1363, found: 408.1358.



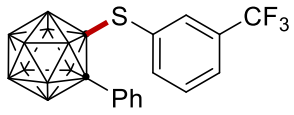
3ah

3ah. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 3-methylbenzenethiol **2h** (35.6 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ah** (30.3 mg, 88%) as a colorless solid. **M.p.** = 58 – 60 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 – 7.59 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.41 (m, 2H), 7.20 – 7.16 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.55 (s, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 138.9 (C_q), 137.3 (CH), 133.6 (CH), 132.2 (CH), 131.8 (CH), 130.8 (C_q), 130.7 (CH), 129.4 (C_q), 128.8 (CH), 128.4 (CH), 87.8 (Cage C), 86.2 (Cage C), 21.1 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.43 (1B), -3.16 (1B), -8.42 (1B), -9.16 (2B), -10.45 (3B), -11.42 (2B). **IR** (ATR): 2922, 2564, 1591, 1494, 1474, 1446, 1377, 885, 780 cm^{-1}. **MS** (EI) *m*/*z*: 342 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 342.2448, found: 342.2434.



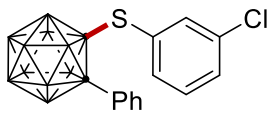
3ai

3ai. The representative procedure B was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 3-methoxylbenzenethiol **2i** (37.2 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ai** (22.2 mg, 62%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 6.97 (dd, J = 8.4, 2.5 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 6.50 (s, 1H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.5 (C_q), 132.2 (CH), 131.0 (C_q), 130.8 (CH), 130.6 (C_q), 129.8 (CH), 129.0 (CH), 128.5 (CH), 121.5 (CH), 117.4 (CH), 88.1 (Cage C), 86.1 (Cage C), 55.4 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.69 (2B), -9.12 (4B), -10.34 (2B), -11.44 (2B). **IR** (ATR): 2961, 2934, 2597, 2564, 1589, 1479, 1249, 1231, 1040, 688 cm^{-1}. **MS** (EI) *m*/*z*: 358 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8OS$ $[M]^+$: 358.2397, found: 358.2385.



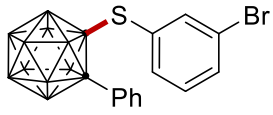
3aj

3aj. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 3-(trifluoromethyl)benzenethiol **2j** (40.8 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3aj** (29.5 mg, 74%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.8 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.47 – 7.40 (m, 3H), 7.34 – 7.30 (m, 1H), 6.93 – 6.87 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 139.9 (CH), 133.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH), 132.0 (CH), 131.5 (q, $^{2}J_{C\text{-}F}$ = 33 Hz, C_q), 131.1 (CH), 130.8 (C_q), 130.5 (C_q), 129 (CH), 128.7 (CH), 127.9 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, CH), 123.2 (q, $^{1}J_{C\text{-}F}$ = 273 Hz, C_q), 88.0 (Cage C), 84.9 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.31 (2B), -9.02 (4B), -10.25 (2B), -11.46 (2B). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.78. **IR** (ATR): 2755, 1580, 1420, 1320, 1272, 1165, 1122, 1071, 792 cm^{-1}. **MS** (EI) *m*/*z*: 396 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{19}{}^{10}B_2{}^{11}B_8F_3S$ $[M]^+$: 396.2165, found: 396.2154.



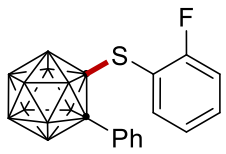
3ak

3ak. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 3-chlorobenzenethiol **2k** (34.5 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ak** (21.4 mg, 59%) as a colorless solid. **M.p.** = 60 – 62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 – 7.52 (m, 3H), 7.49 – 7.42 (m, 2H), 7.37 (ddd, *J* = 8.1, 2.1, 1.0 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.95 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 6.62 (ddd, *J* = 2.1, 1.7, 0.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 136.4 (CH), 134.7 (CH), 134.4 (C_q), 132.1 (CH), 131.3 (CH), 131.1 (C_q), 131.0 (CH), 130.6 (C_q), 130.1 (CH), 128.6 (CH), 87.8 (Cage C), 85.1 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.37 (1B), -2.90 (1B), -9.11 (4B), -10.37 (2B), -11.46 (2B). **IR** (ATR): 2922, 2565, 1573, 1459, 1398, 1116, 1071, 864, 771 cm^{-1}. **MS** (EI) *m*/*z*: 362 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8S^{35}Cl$ $[M]^+$: 362.1904, found: 362.1893.



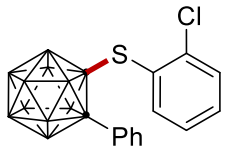
3al

3al. The representative procedure B with KI (16.6 mg, 0.10 mmol) and CuI (2.9 mg, 15 mol %) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 3-bromobenzenethiol **2l** (31.0 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3al** (24.1 mg, 59%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 – 7.57 (m, 2H), 7.57 – 7.50 (m, 2H), 7.49 – 7.42 (m, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.02 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 6.75 (t, *J* = 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 139.2 (CH), 135.1 (CH), 134.2 (CH), 132.1 (CH), 131.4 (C_q), 131.0 (CH), 130.5 (C_q), 130.4 (CH), 128.7 (CH), 122.4 (C_q), 87.8 (Cage C), 85.1 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.35 (2B), -9.11 (4B), -10.37 (2B), -11.44 (2B). **IR** (ATR): 2918, 2589, 1559, 1455, 1394, 1066, 866, 770, 672 cm^{-1}. **MS** (EI) *m*/*z*: 408 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{11}B_{10}S^{79}Br$ $[M]^+$: 408.1363, found: 408.1360.



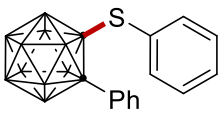
3am

3am. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 2-florobenzenethiol **2m** (32.0 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3am** (18.5 mg, 53%) as a colorless solid. **M.p.** = 116 – 118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.73 – 7.66 (m, 2H), 7.61 – 7.54 (m, 1H), 7.53 – 7.44 (m, 3H), 7.17 – 7.03 (m, 2H), 6.94 – 6.84 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.3 (d, $^{1}J_{C\text{-}F}$ = 253 Hz, C_q), 139.4 (CH), 134.1 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz, CH), 132.1 (CH), 130.9 (C_q), 130.9 (CH), 128.5 (CH), 124.5 (d, $^{3}J_{C\text{-}F}$ = 4.0 Hz, CH), 117.0 (d, $^{2}J_{C\text{-}F}$ = 18.2 Hz, C_q), 116.5 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz, CH), 88.7 (Cage C), 85.2 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.87 (2B), -8.30 (2B), -9.21 (1B), -9.90 (3B), -11.53 (2B). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = -102.48. **IR** (ATR): 2598, 2557, 1470, 1261, 1223, 1067, 755, 689 cm^{-1}. **MS** (EI) *m*/*z*: 346 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8FS$ $[M]^+$: 346.2197, found: 346.2183.



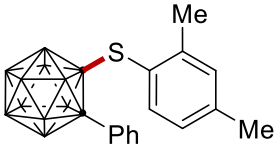
3an

3an. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 2-chlorobenzenethiol **2n** (33.6 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3an** (27.5 mg, 76%) as a colorless solid. **M.p.** = 146 – 148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.72 – 7.64 (m, 2H), 7.56 – 7.47 (m, 1H), 7.49 – 7.40 (m, 3H), 7.40 – 7.31 (m, 1H), 7.21 – 7.12 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.1 (C_q), 140.0 (CH), 132.7 (CH), 132.1 (CH), 131.1 (C_q), 130.9 (CH), 130.6 (CH), 128.9 (C_q), 128.6 (CH), 127.1 (CH), 89.5 (Cage C), 85.7 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.90 (2B), -8.40 (2B), -9.57 (4B), -11.70 (2B). **IR** (ATR): 2500, 1945, 1447, 1321, 1259, 1166, 1134, 1070, 749 cm^{-1}. **MS** (EI) *m*/*z*: 362 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8S^{35}Cl$ $[M]^+$: 362.1904, found: 362.1893.



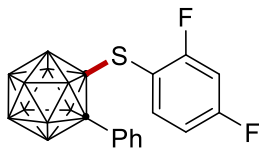
3ao

3ao. The representative procedure B was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and benzenethiol **2o** (31.0 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ao** (20.0 mg, 61%) as a colorless solid. **M.p.** = 112 – 114 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.6 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.40 (m, 3H), 7.32 – 7.25 (m, 2H), 6.96 (d, J = 7.7 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 136.8 (CH), 132.2 (CH), 131.1 (CH), 130.9 (C_q), 130.9 (CH), 129.8 (C_q), 129.1 (CH), 128.5 (CH), 88.1 (Cage C), 86.1 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.78 (2B), -9.14 (3B), -10.35 (3B), -11.50 (2B). **IR** (ATR): 2612, 2589, 2560, 1585, 1486, 1232, 1077, 686 cm^{-1}. **MS** (EI) *m*/*z*: 328 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{20}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 328.2291, found: 328.2279.



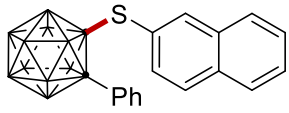
3ap

3ap. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 2,4-dimethylbenzenethiol **2p** (40.3 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ap** (23.1 mg, 65%) as a colorless solid. **M.p.** = 97 – 99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 – 7.64 (m, 2H), 7.55 – 7.47 (m, 1H), 7.49 – 7.40 (m, 2H), 7.05 – 6.99 (m, 1H), 6.91 – 6.84 (m, 1H), 6.75 (d, J = 7.9 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.9 (C_q), 141.9 (C_q), 138.6 (CH), 132.1 (CH), 131.7 (CH), 131.3 (C_q), 130.7 (CH), 128.6 (CH), 127.3 (CH), 126.1 (C_q), 89.5 (Cage C), 87.4 (Cage C), 21.3 (CH_3), 20.7 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -3.05 (2B), -8.58 (2B), -9.80 (4B), -11.72 (2B). **IR** (ATR): 2919, 2851, 2586, 2569, 1600, 1446, 1232, 1074, 886 cm^{-1}. **MS** (EI) *m*/*z*: 356 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{16}H_{24}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 356.2605, found: 356.2593.



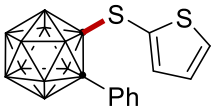
3aq

3aq. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 2,4-difluorobenzenethiol **2q** (33.1 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3aq** (32.8 mg, 65%) as a colorless solid. **M.p.** = 109 – 111 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 – 7.60 (m, 2H), 7.56 – 7.48 (m, 1H), 7.48 – 7.39 (m, 2H), 6.88 – 6.71 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 165.4 (dd, $^{1}J_{C\text{-}F}$ = 257 Hz, $^{3}J_{C\text{-}F}$ = 10.8 Hz, C_q), 163.9 (dd, $^{1}J_{C\text{-}F}$ = 256 Hz, $^{3}J_{C\text{-}F}$ = 13.4 Hz, C_q), 140.6 (dd, $^{3}J_{C\text{-}F}$ = 10.2, 10.2 Hz, CH), 132.1 (CH), 131.0 (CH), 130.9 (C_q), 128.6 (CH), 112.9 (dd, $^{2}J_{C\text{-}F}$ = 18.5 Hz, $^{4}J_{C\text{-}F}$ = 3.9 Hz, C_q), 112.2 (dd, $^{2}J_{C\text{-}F}$ = 22.0 Hz, $^{4}J_{C\text{-}F}$ = 3.9 Hz, CH), 105.1 (dd, $^{2}J_{C\text{-}F}$ = 25.8, 25.9 Hz, CH), 88.5 (Cage C), 84.9 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.20 (1B), -3.38 (1B), -7.71 (2B), -9.26 (2B), -10.50 (2B), -12.38 (2B). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = -97.08 (d, J = 11.5 Hz), -101.85 (d, J = 11.5 Hz). **IR** (ATR): 3059, 1487, 1443, 1201, 1155, 1056, 907, 734 cm^{-1}. **MS** (EI) *m*/*z*: 364 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{18}{}^{10}B_2{}^{11}B_8SF_2$ $[M]^+$: 364.2102, found: 364.2098.



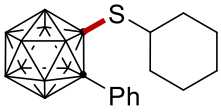
3ar

3ar. The representative procedure B was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and naphthalene-2-thiol **2r** (43.2 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3ar** (35.2 mg, 93%) as a colorless solid. **M.p.** = 129 – 131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.83 – 7.79 (m, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.64 – 7.44 (m, 8H), 7.18 – 7.15 (m, 1H), 7.08 (dd, J = 8.5, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.6 (CH), 133.9 (C_q), 132.8 (C_q), 132.3 (CH), 132.1 (CH), 130.9 (C_q), 130.8 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 126.8 (CH), 126.8 (C_q) 87.8 (Cage C), 85.9 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.37 (1B), -3.12 (1B), -8.44 (2B), -9.14 (2B), -10.49 (3B), -11.39 (1B). **IR** (ATR): 3057, 2594, 1581, 1494, 1446, 1072, 901, 859, 808, 743 cm^{-1}. **MS** (EI) *m*/*z*: 378 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{18}H_{22}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 378.2449, found: 378.2436.



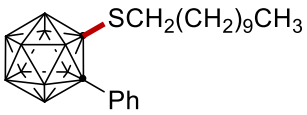
3as

3as. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and benzenethiol **2s** (27.8 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3as** (18.0 mg, 54%) as a colorless solid. **M.p.** = 83 – 85 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.6 Hz, 2H), 7.59 – 7.45 (m, 4H), 6.97 (dd, J = 5.3, 3.6 Hz, 1H), 6.64 (d, J = 3.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.3 (CH), 134.1 (CH), 132.1 (CH), 130.9 (CH), 130.6 (C_q), 128.6 (CH), 127.7 (CH), 127.6 (C_q), 87.4 (Cage C), 85.6 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.70 (2B), -9.16 (3B), -10.37 (3B), -11.72 (2B). **IR** (ATR): 2922, 2852, 2605, 2589, 2559, 1399, 1218, 852, 710 cm^{-1}. **MS** (EI) *m*/*z*: 334 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{12}H_{18}{}^{10}B_2{}^{11}B_8S_2$ $[M]^+$: 334.1854, found: 334.1845.



3at

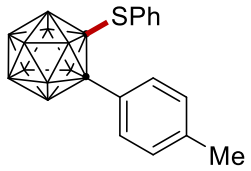
3at. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and cyclohexanethiol **2t** (35.5 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **3at** (20.0 mg, 60%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.58 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 2.76 – 2.68 (m, 1H), 1.69 – 1.60 (m, 2H), 1.51 – 1.40 (m, 2H), 1.33 – 0.98 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 131.8 (CH), 131.0 (C_q), 130.6 (CH), 128.3 (CH), 88.6 (Cage C), 87.0 (Cage C), 50.5 (CH), 33.9 (CH_2), 25.7 (CH_2), 25.0 (CH_2). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.81 (2B), -8.18 (2B), -9.37 (2B), -10.21 (2B), -11.07 (2B). **IR** (ATR): 2932, 2852, 2557, 1494, 1447, 1321, 1261, 1075, 884 cm^{-1}. **MS** (EI) *m*/*z*: 334 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{26}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 334.2760, found: 334.2748.



3au

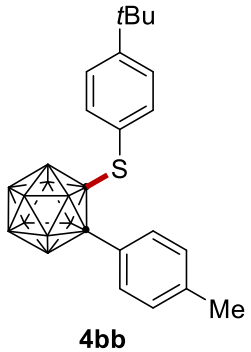
3au. The representative procedure B was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and 1-undecanethiol **2u** (67.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane)

yielded **3au** (22.0 mg, 54%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.6 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.37 (m, 2H), 2.65 (t, J = 7.2 Hz, 2H), 1.37 – 1.12 (m, 18H), 0.95 – 0.88 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 131.6 (CH), 131.1 (C_q), 130.7 (CH), 128.5 (CH), 88.7 (Cage C), 86.7 (Cage C), 36.9 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 ($2CH_2$), 28.8 (CH_2), 28.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.96 (2B), -8.35 (2B), -10.02 (5B), -11.34 (1B). **IR** (ATR): 2957, 2923, 2853, 2593, 1447, 1276, 766, 750 cm^{-1}. **MS** (EI) m/z: 406 $[M]^+$. **HR-MS** (EI): m/z calcd. for $C_{19}H_{38}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 406.3702, found: 406.3694.



4bo

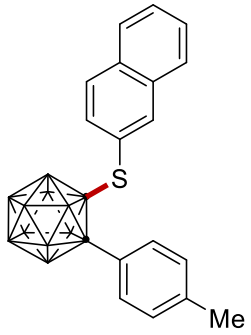
4bo. The representative procedure B was followed using *o*-carborane **1b** (23.4 mg, 0.10 mmol) and benzenethiol **2o** (30.8 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4bo** (32.2 mg, 94%) as a colorless solid. **M.p.** = 114 – 116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 – 7.46 (m, 2H), 7.42 – 7.37 (m, 1H), 7.28 – 7.21 (m, 4H), 7.01 – 6.96 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.3 (C_q), 137.0 (CH), 132.1 (CH), 131.1 (CH), 129.9 (C_q), 129.2 (CH), 129.1 (CH), 128.2 (C_q), 88.6 (Cage C), 86.3 (Cage C), 21.2 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.90 (2B), -9.10 (3B), -10.40 (3B), -11.55 (2B). **IR** (ATR): 2922, 2564, 1612, 1509, 1471, 1439, 1260, 1193, 888 cm^{-1}. **MS** (EI) m/z: 342 $[M]^+$. **HR-MS** (EI): m/z calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 342.2448, found: 342.2436.



4bb

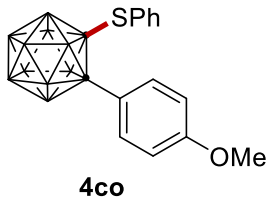
4bb. The representative procedure B was followed using *o*-carborane **1b** (23.0 mg, 0.10 mmol) and 4-(*tert*-butyl)benzenethiol **2b** (49.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4bb** (24.7 mg, 62%) as a colorless solid. **M.p.** = 106 – 108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 6.0 Hz, 2H), 7.25 (d,

J = 6.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.6 (C_q), 141.2 (C_q), 136.6 (CH), 132.1 (CH), 129.2 (CH), 128.3 (C_q), 126.5 (C_q), 126.1 (CH), 88.6 (Cage C), 86.7 (Cage C), 34.9 (C_q), 31.1 (CH_3), 21.2 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -3.14 (2B), -9.15 (3B), -10.52 (3B), -11.76 (2B). **IR** (ATR): 2962, 2924, 2852, 2594, 2572, 1460, 1259, 765 cm^{-1}. **MS** (EI) *m*/*z*: 398 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{19}H_{30}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 398.3076, found: 398.3064.



4br

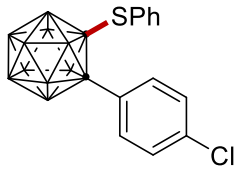
4br. The representative procedure B was followed using *o*-carborane **1b** (23.4 mg, 0.10 mmol) and naphthalene-2-thiol **2r** (43.2 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4br** (39.2 mg, 62%) as a colorless solid. **M.p.** = 165 – 166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 – 7.79 (m, 1H), 7.72 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.53 (m, 1H), 7.53 – 7.47 (m, 3H), 7.27 – 7.24 (m, 2H), 7.22 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.3 (C_q), 137.6 (CH), 133.9 (C_q), 132.9 (C_q), 132.2 (CH), 132.2 (CH), 129.2 (CH), 128.8 (CH), 128.2 (CH), 128.2 (C_q), 128.0 (CH), 127.7 (CH), 126.9 (C_q), 126.8 (CH), 88.1 (Cage C), 86.0 (Cage C), 21.3 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.63 (2B), -9.08 (4B), -10.53 (2B), -11.48 (2B). **IR** (ATR): 2591, 1276, 1259, 816, 766, 748 cm^{-1}. **MS** (EI) *m*/*z*: 392 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{19}H_{24}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 392.2606, found: 392.2600.



4co

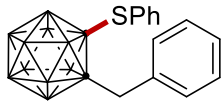
4co. The representative procedure B was followed using *o*-carborane **1c** (25.1 mg, 0.10 mmol) and benzenethiol **2o** (30.8 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4co** (25.1 mg, 70%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 9.0 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.28 – 7.22 (m, 2H), 6.99 (dd, *J* = 8.3, 1.3 Hz, 2H), 6.92 (d, *J*

= 9.0 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.6 (C_q), 136.9 (CH), 133.7 (CH), 131.1 (CH), 129.9 (C_q), 129.1 (CH), 123.3 (C_q), 113.7 (CH), 88.9 (Cage C), 86.7 (Cage C), 55.5 (CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -3.01 (2B), -9.06 (4B), -10.52 (2B), -11.55 (2B). **IR** (ATR): 2588, 1971, 1607, 1511, 1302, 1261, 1184, 835, 748 cm^{-1}. **MS** (EI) *m*/*z*: 358 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8SO$ $[M]^+$: 358.2395, found: 358.2391.



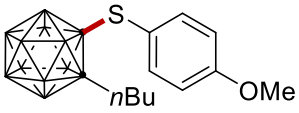
4do

4do. The representative procedure B with KI (16.6 mg, 0.10 mmol) was followed using *o*-carborane **1d** (25.4 mg, 0.10 mmol) and benzenethiol **2o** (30.8 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4do** (28.2 mg, 78%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.5 (C_q), 136.8 (CH), 133.4 (CH), 131.3 (CH), 129.7 (C_q), 129.6 (C_q), 129.2 (CH), 128.7 (CH), 87.1 (Cage C), 86.2 (Cage C). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = -2.39 (1B), -3.00 (1B), -8.40 (2B), -9.20 (1B), -10.19 (3B), -11.56 (2B). **IR** (ATR): 2924, 2593, 1593, 1492, 1401, 1100, 1070, 1016, 887 cm^{-1}. **MS** (EI) *m*/*z*: 362 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{19}{}^{10}B_2{}^{11}B_8S^{35}Cl$ $[M]^+$: 362.1904, found: 362.1894.



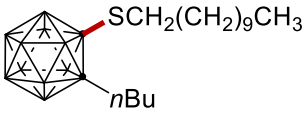
4eo

4eo. The representative procedure B was followed using *o*-carborane **1e** (23.4 mg, 0.10 mmol) and benzenethiol **2o** (31.0 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4eo** (22.0 mg, 64%) as a colorless solid. **M.p.** = 119 – 121 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.70 – 7.66 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.33 (m, 3H), 7.29 – 7.25 (m, 2H), 3.80 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 137.2 (CH), 135.6 (C_q), 131.5 (CH), 130.4 (CH), 130.0 (C_q), 129.6 (CH), 128.6 (CH), 128.0 (CH), 84.3 (Cage C), 84.2 (Cage C), 40.9 (CH_2). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -3.85 (2B), -9.37 (4B), -10.84 (4B). **IR** (ATR): 2923, 2852, 2577, 2560, 1493, 1470, 1439, 1419, 745 cm^{-1}. **MS** (EI) *m*/*z*: 342 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 342.2448, found: 342.2432.



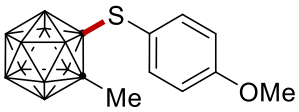
4fa

4fa. The representative procedure A was followed using *o*-carborane **1f** (20.0 mg, 0.10 mmol) and 4-methoxybenzenethiol **2a** (36.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4fa** (18.0 mg, 53%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 2.52 – 2.47 (m, 2H), 1.59 – 1.53 (m, 2H), 1.49 – 1.41 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.0 (C_q), 138.8 (CH), 120.9 (C_q), 114.9 (CH), 84.7 (Cage C), 84.6 (Cage C), 55.5 (CH_3), 35.0 (CH_2), 31.8 (CH_2), 22.5 (CH_2), 13.8 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -4.27 (2B), -9.91 (4B), -10.94 (4B). **IR** (ATR): 2959, 2930, 2564, 1591, 1493, 1254, 1172, 830 cm^{-1}. **MS** (EI) *m*/*z*: 338 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{13}H_{26}{}^{10}B_2{}^{11}B_8OS$ $[M]^+$: 338.2709, found: 338.2703.



4fu

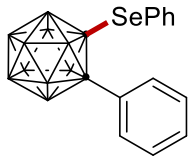
4fu. The representative procedure B was followed using *o*-carborane **1f** (20.0 mg, 0.10 mmol) and 1-undecanethiol **2u** (67.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4fu** (20.7 mg, 54%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 2.86 (t, J = 7.2 Hz, 2H), 2.35 – 2.26 (m, 2H), 1.67 – 1.59 (m, 2H), 1.57 – 1.47 (m, 2H), 1.45 – 1.21 (m, 18H), 1.01 – 0.85 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 85.0 (Cage C), 83.9 (Cage C), 37.2 (CH_2), 34.6 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 28.2 (CH_2), 22.7 (CH_2), 22.4 (CH_2), 14.1 (CH_3), 13.7 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -4.29 (2B), -9.85 (4B), -10.95 (4B). **IR** (ATR): 2958, 2924, 2853, 2606, 2569, 1466, 1259, 748 cm^{-1}. **MS** (EI) *m*/*z*: 386 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{17}H_{42}{}^{10}B_2{}^{11}B_8S$ $[M]^+$: 386.4014, found: 386.4008.



4ga

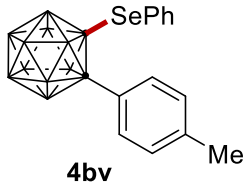
4ga. The representative procedure B was followed using *o*-carborane **1g** (15.8 mg, 0.10 mmol) and 4-methoxybenzenethiol **2a** (36.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-

hexane) yielded **4ga** (20.0 mg, 68%) as a colorless solid. **M.p.** = 81 – 83 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.0 (C_q), 138.9 (CH), 121.0 (C_q), 114.9 (CH), 82.7 (Cage C), 79.3 (Cage C), 55.5 (CH_3), 23.6 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -3.86 (1B), -4.97 (1B), -8.82 (2B), -9.90 (6B). **IR** (ATR): 2838, 2600, 2571, 2557, 1590, 1493, 1254, 828 cm^{-1}. **MS** (EI) *m*/*z*: 296 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{10}H_{20}{}^{10}B_2{}^{11}B_8OS$ $[M]^+$: 296.2238, found: 296.2230.



4av

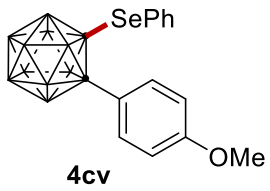
4av. The representative procedure B was followed using *o*-carborane **1a** (22.0 mg, 0.10 mmol) and benzeneselenol **2v** (31.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4av** (22.0 mg, 59%) as a colorless solid. **M.p.** = 112 – 114 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.63 – 7.52 (m, 3H), 7.45 (t, J = 7.5 Hz, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 7.3 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 137.6 (CH), 132.0 (CH), 131.7 (C_q), 130.8 (CH), 130.7 (CH), 129.2 (CH), 128.5 (CH), 127.1 (C_q), 86.3 (Cage C), 72.7 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.44 (2B), -8.29 (1B), -9.00 (1B), -9.78 (3B), -11.45 (3B). **IR** (ATR): 2630, 2609, 2572, 2561, 1585, 1486, 1233, 754 cm^{-1}. **MS** (EI) *m*/*z*: 376 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{14}H_{20}{}^{10}B_2{}^{11}B_8Se$ $[M]^+$: 376.1729, found: 376.1726.



4bv

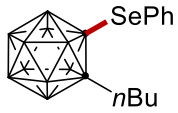
4bv. The representative procedure B was followed using *o*-carborane **1b** (23.0 mg, 0.10 mmol) and benzeneselenol **2v** (31.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4bv** (30.0 mg, 77%) as a colorless solid. **M.p.** = 100 – 101 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.53 – 7.42 (m, 3H), 7.35 – 7.19 (m, 6H), 2.47 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 141.1 (C_q), 137.7 (CH), 131.8 (CH), 130.8 (CH), 129.2 (CH), 129.1 (CH), 129.1 (C_q), 127.1 (C_q), 86.7 (Cage C), 73.0 (Cage C), 21.2 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.5 (3B), -9.0 (3B), -9.8 (3B), -11.4 (1B). **IR** (ATR): 2918, 2848, 2598, 2555, 1473, 1436, 1066, 820, 738

cm^{-1}. **MS** (EI) *m*/*z*: 390 [M]$^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8Se$ [M]$^+$: 390.1885, found: 390.1887.



4cv

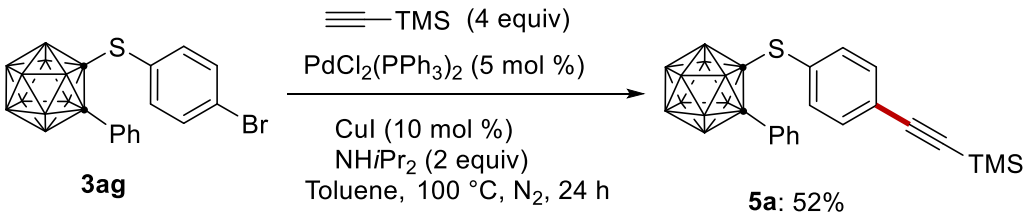
4cv. The representative procedure B was followed using *o*-carborane **1c** (25.0 mg, 0.10 mmol) and benzeneselenol **2v** (31.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4cv** (21.0 mg, 52%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.54 – 7.43 (m, 3H), 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 2H), 7.00 – 6.90 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.4 (C_q), 137.7 (CH), 137.7 (CH), 133.4 (CH), 130.8 (CH), 129.2 (CH), 127.2 (C_q), 124.2 (C_q), 113.6 (CH), 87.0 (Cage C), 73.7 (Cage C), 55.5 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.5 (3B), -9.0 (3B), -9.9 (3B), -11.4 (1B). **IR** (ATR): 2959, 2837, 2567, 1734, 1605, 1510, 1258, 1183, 739 cm^{-1}. **MS** (EI) *m*/*z*: 406 [M]$^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{15}H_{22}{}^{10}B_2{}^{11}B_8OSe$ [M]$^+$: 406.1834, found: 406.1833.



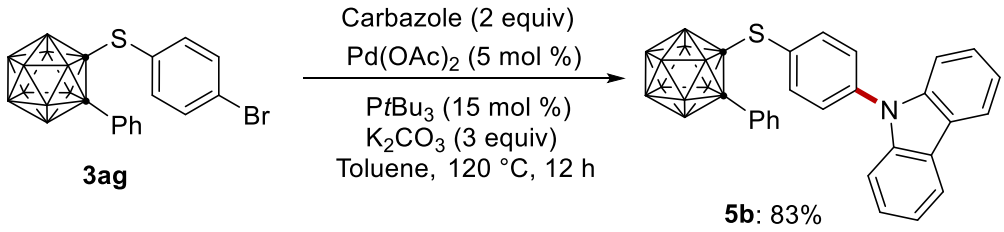
4fv

4fv. The representative procedure B was followed using *o*-carborane **1f** (20.0 mg, 0.10 mmol) and benzeneselenol **2v** (31.9 µL, 0.30 mmol). Isolation by column chromatography (*n*-hexane) yielded **4fv** (23.0 mg, 65%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.73 – 7.65 (m, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 2.47 – 2.38 (m, 2H), 1.56 – 1.37 (m, 4H), 1.00 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 137.8 (CH), 131.0 (CH), 129.6 (CH), 127.3 (C_q), 82.6 (Cage C), 71.3 (Cage C), 36.6 (CH_2), 31.8 (CH_2), 22.5 (CH_2), 13.8 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -3.7 (3B), -9.3 (4B), -10.7 (3B). **IR** (ATR): 2960, 2934, 2873, 2573, 1736, 1372, 1237, 1045, 741 cm^{-1}. **MS** (EI) *m*/*z*: 356 [M]$^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{12}H_{24}{}^{10}B_2{}^{11}B_8Se$ [M]$^+$: 356.2041, found: 356.2043.

Late-stage diversification.



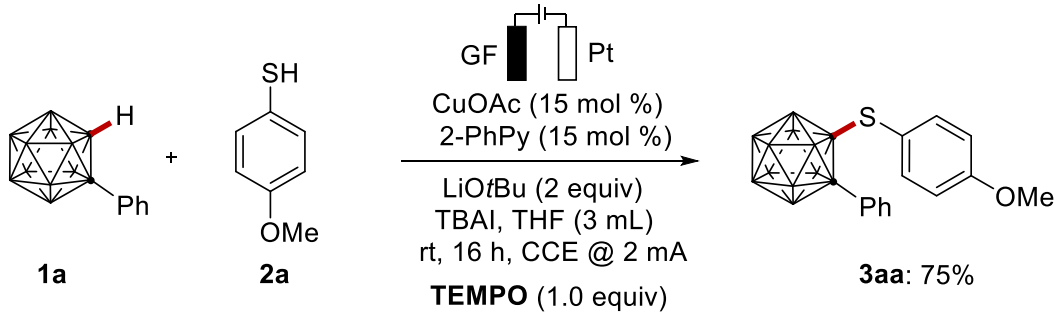
Compound **3ag** (40.7 mg, 0.10 mmol), trimethylsilylacetylene (56.5 µL, 0.40 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol) and $NHiPr_2$ (28.2 µL, 0.20 mmol) were combined together in toluene (2.5 mL). The resulting mixture was heated at 100 °C for 24 h under N_2. Then, the reaction was quenched with with water (10 mL) and extracted with diethyl ether (10 mL x 3). The organic layers were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel using *n*-hexane as eluent to give the product **5a** as a colorless oil (52%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.66 – 7.60 (m, 2H), 7.60 – 7.53 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 0.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 136.6 (CH), 132.5 (CH), 132.3 (CH), 131.0 (CH), 130.9 (C_q), 129.9 (C_q), 128.7 (CH), 126.3 (C_q), 103.6 (C_q), 98.0 (C_q), 88.1 (Cage C), 85.8 (Cage C), 0.0 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.65 (2B), -8.99 (3B), -10.46 (5B). **IR** (ATR): 2958, 2923, 2594, 2575, 2158, 1480, 1250, 862, 841 cm^{-1}. **MS** (EI) *m*/*z*: 424 $[M]^+$. **HR-MS** (EI): *m*/*z* calcd. for $C_{19}H_{28}{}^{10}B_2{}^{11}B_8SSi$ $[M]^+$: 424.2690, found: 424.2678.



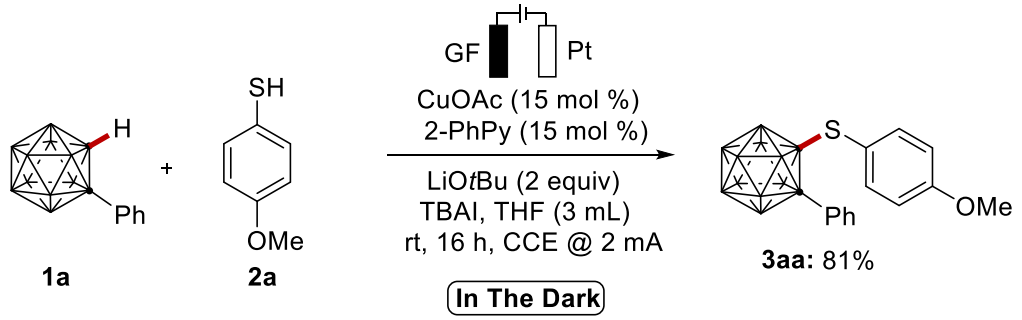
Compound **3ag** (40.7 mg, 0.10 mmol), carbazole (33.4 mg, 0.20 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), P*t*Bu$_3$ (3.0 mg, 0.015 mmol), and K_2CO_3 (41.4 mg, 0.30 mmol) were combined together in toluene (2.5 mL). The resulting mixture was heated at 120 °C for 12 h. Then, the reaction was quenched with with water (10 mL) and extracted with diethyl ether (10 mL x 3). The organic layers were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel using *n*-hexane and ethyl acetate (20/1) as eluent to give the product **5b** as a colorless solid (83%). **M.p.** = 214 – 216 °C. **^{1}H NMR** (300

MHz, $CDCl_3$): δ = 8.14 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.49 (d, J = 8.5 Hz, 4H), 7.45 – 7.39 (m, 4H), 7.32 (ddd, J = 8.0, 6.1, 2.1 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.5 (C_q), 140.1 (C_q), 138.4 (CH), 132.2 (CH), 131.0 (CH), 130.9 (C_q), 128.6 (CH), 128.0 (C_q), 127.0 (CH), 126.2 (CH), 123.8 (C_q), 120.7 (CH), 120.5 (CH), 109.6 (CH), 87.9 (Cage C), 85.7 (Cage C). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = -2.51 (2B), -9.09 (4B), -10.13 (4B). **IR** (ATR): 2921, 2851, 2595, 2565, 2555, 1586, 1446, 1223, 720 cm^{-1}. **MS** (EI) m/z: 493 $[M]^+$. **HR-MS** (EI): m/z calcd. for $C_{26}H_{27}{}^{10}B_2{}^{11}B_8NS$ $[M]^+$: 493.2875, found: 493.2861.

Mechanistic studies



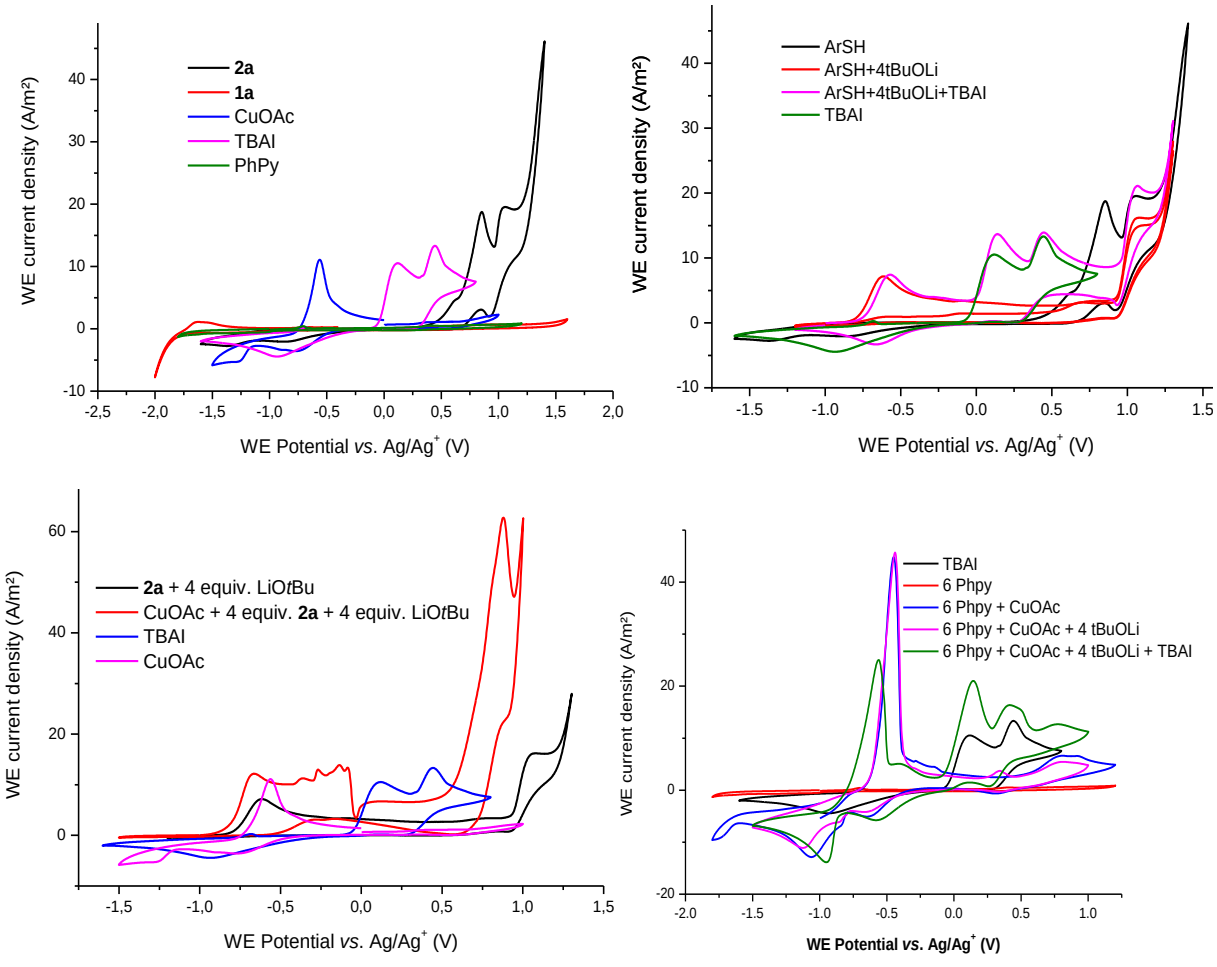
The general procedure A was followed using *o*-carborane **1a** (0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol **2a** (36.9 μL, 0.30 mmol) and TEMPO (0.1 mmol, 1.0 equiv). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 16 h. The GF anode was washed with ethyl acetate (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with *n*-hexane afforded the corresponding product **3aa** (75%).

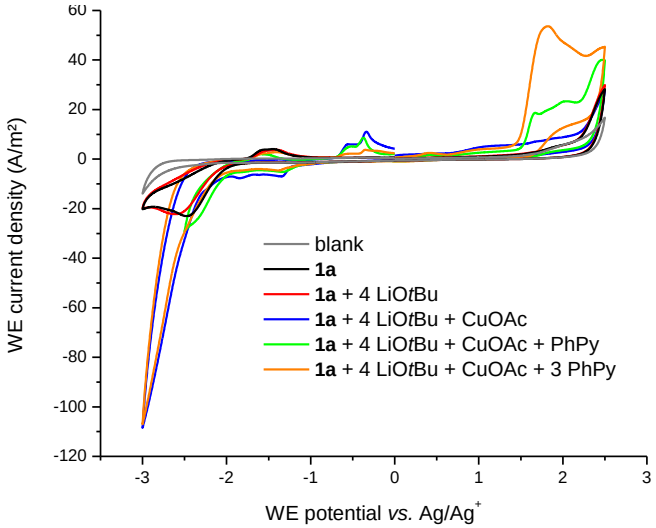


The general procedure A was followed using *o*-carborane **1a** (0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol **2a** (36.9 μL, 0.30 mmol). Electrocatalysis was performed in the dark at room temperature with a constant current of 2.0 mA maintained for 16 h. The GF anode was washed with ethyl acetate (3×10 mL). Evaporation of the solvent and subsequent purification by column chromatography on silica gel with *n*-hexane afforded the corresponding product **3aa** (81%).

Cyclic voltammetry

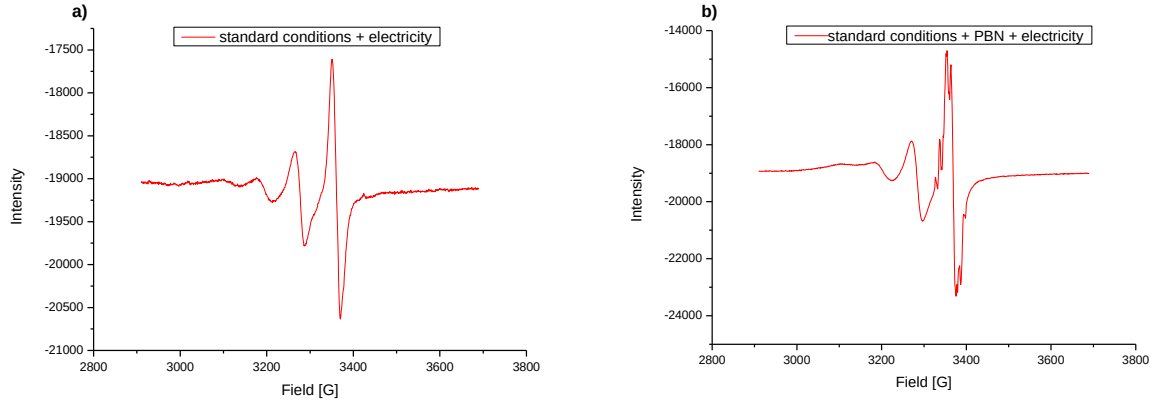
CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon working electrode (disk, diameter: 3mm), a coiled platinum wire counter electrode and a non-aqueous Ag/Ag^+ reference electrode (ALS Japan, 10 mmol/L $AgNO_3$ and 100 mmol/L *n*-Bu_4NPF_6 in acetonitrile) were employed. The voltammograms were recorded at room temperature in dry acetonitrile at a substrate concentration of 5 mmol/L and with 100 mmol/L *n*-Bu_4NPF_6 as supporting electrolyte. Prior to each measurement, the working electrode was thoroughly polished with 0.05 µm alumina polishing powder and rinsed with water and methanol. All measured solutions were saturated with nitrogen gas and an overpressure of protective gas was maintained throughout the experiment. The nitrogen gas was previously saturated with solvent vapour by passing it through a gas washing bottle with acetonitrile. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures.



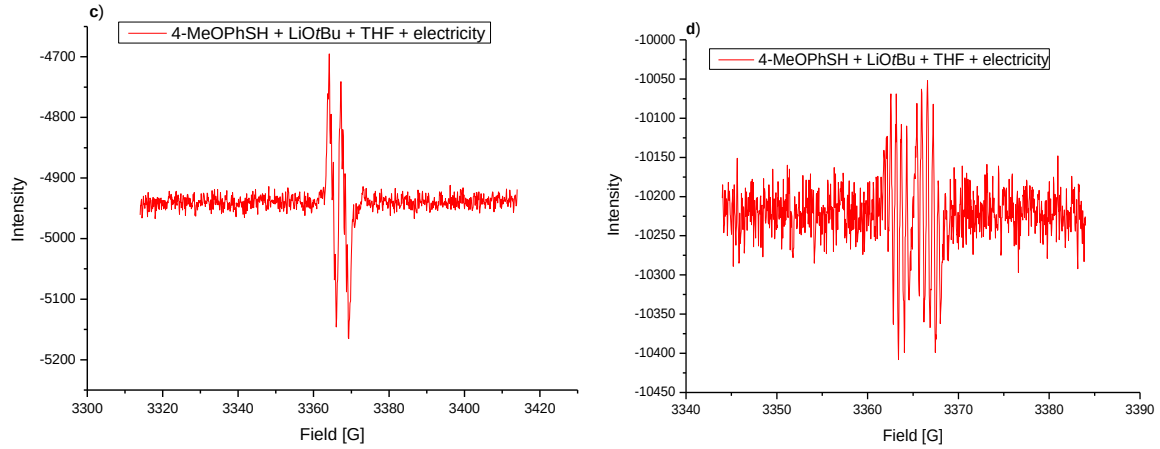

WE current density (A/m²)
WE potential *vs.* Ag/Ag⁺
blank
1a
1a + 4 LiO*t*Bu
1a + 4 LiO*t*Bu + CuOAc
1a + 4 LiO*t*Bu + CuOAc + PhPy
1a + 4 LiO*t*Bu + CuOAc + 3 PhPy

EPR studies

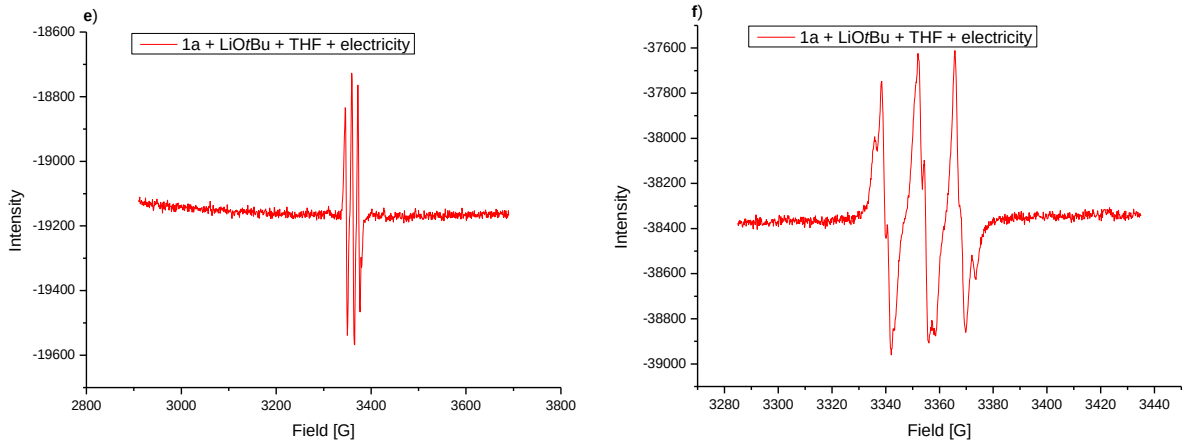
The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). *o*-Carborane **1a** (0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol **2a** (0.30 mmol, 3.0 equiv), CuOAc (15 mol %), 2-PhPy (15 mol %), LiO*t*Bu (0.2 mmol, 2.0 equiv) and TBAI (0.2 mmol, 2.0 equiv) were dissolved in THF (3.0 mL). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 2 h. Then PBN (N-tert-butyl-alpha-Phenylnitrone) (5 equiv.) (if noted) was added into the reaction system. After stirring 2 minutes, the mixture was immediately transferred into the EPR tube for EPR measurement.



The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). 4-methoxybenzenethiol **2a** (0.30 mmol) and LiO*t*Bu (0.2 mmol) were dissolved in THF (3.0 mL). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 2 h. Then PBN (N-tert-butyl-alpha-Phenylnitrone) (5 equiv.) was added into the reaction system. After stirring 2 minutes, the mixture was immediately transferred into the EPR tube for EPR measurement.

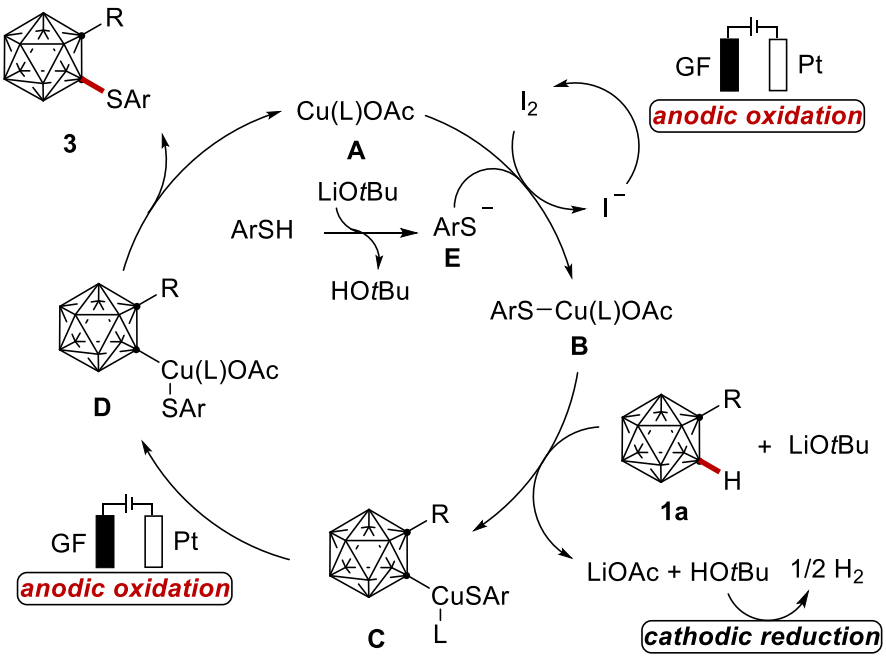


The electrocatalysis was carried out in an undivided cell under air, with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). o-carborane **1a** (0.10 mmol) and LiO*t*Bu (0.2 mmol) were dissolved in THF (3.0 mL). Electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 2 h. Then PBN (N-tert-butyl-alpha-Phenylnitrone) (5 equiv.) was added into the reaction system. After stirring 2 minutes, the mixture was immediately transferred into the EPR tube for EPR measurement.



Possible catalytic cycle

Another plausible reaction mechanism is proposed as shown in below. An anodically generated redox mediator I_2 oxidize copper(I) **A** to deliver copper(II) **B**, which next reacts with *o*-carborane **1** in the presence of LiO*t*Bu to generate a copper(II)-*o*-carborane complex **C**. Thereafter, the complex **C** is oxidized by the electricity to furnish the copper(III) species **D**, which subsequently undergoes reductive elimination, affording the final product and regenerating the catalytically active complex **A**.



Computational studies

All DFT calculations were performed with Gaussian 16, Revision A.03 package.[4] All structures were optimized at the TPSS[5] level of theory in combination with D3 dispersion corrections with the Becke-Johnson damping scheme (D3BJ).[6] All atoms were described with a def2-SVP basis set.[7] Analytical frequency calculations were carried out at the same level of theory in order to identify each stationary point as either an intermediate (no imaginary frequencies) or as a transition state (only one imaginary frequency) and to provide thermal and non-thermal corrections to the Gibbs free energy at 298.15 K and 1 atm. The electronic energy was then improved through PW6B95[8] single-point calculations on the optimized geometries in combination with a standalone version of Grimme's D4 dispersion corrections,[9] with a def2-TZVP basis set.[7] Solvent effects were taken into consideration in the single-point calculations through the use of the SMD model[10] with dielectric constant of ε = 35.688, which corresponds to acetonitrile. All reported energies are based on gas-phase Gibbs free energies with def2-SVP basis set for which the electronic energies were corrected with PW6B95-D4 in combination with def2-TZVP basis set and solvent effects. Non-covalent interactions were calculated using the Multiwfn program[11] and visualized with the help of the VMD program.[12] Oxidation potentials were calculated using the following equation:[13]

$$E_{1/2}^{\mathrm{o,calc}} = -\frac{\Delta G_{\frac{1}{2}}^{o}}{n_e F} - E_{\frac{1}{2}}^{\mathrm{o,SHE}} - E^{\mathrm{o,SCE}} \qquad (1)$$

with

$$\Delta G_{1/2}^{o} = G_{298.15}(reduced) - G_{298.15}(oxidized) \qquad (2)$$

In equation 1, n_e is the number of electrons transferred during the oxidation process, *F* is the Faraday constant with a value of 23.061 kcal mol^{-1} V^{-1}, $E_{1/2}^{\mathrm{o,SHE}}$ is the absolute value of the standard hydrogen electrode (4.281 V),[14] $E^{\mathrm{o,SCE}}$ is the potential of the saturated calomel electrode relative to SHE in acetonitrile (-0.141 V). [13]

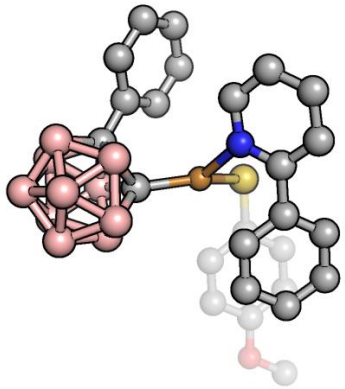


Figure S1. Computed structure for the most stable doublet copper(II)-*o*-carborane complex **C**. Nonrelevant hydrogens were omitted for clarity.

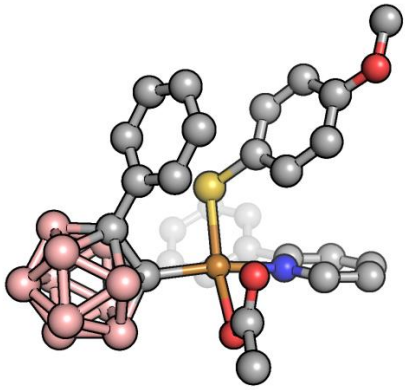


Figure S2. Computed structure for the most stable triplet copper(III) species **D**. Nonrelevant hydrogens were omitted for clarity.

Table S2. Calculated electronic energies at the PW6B95-D4/def2-TZVP+SMD(MeCN) level of theory and Gibbs free energies with dispersion corrections (all in Hartree).[a]

Structure	Electronic Energy	Gibbs Free Energy
C^{2}	-3430.556888	-3430.088733
C^{4}	-3430.458955	-3429.994465
C^{6}	-3430.330544	-3429.875170
D^{1}	-3659.397710	-3658.881099
D^{3}	-3659.398685	-3658.883936
D^{5}	-3659.276166	-3658.767648
Acetate	-228.974116	-228.954875

[a] Superscripts correspond to the respective spin state.

Cartesian coordinates of the optimized structure

C^2
Lowest frequency = 16.6867 cm^{-1}
Charge = 0, Multiplicity = 2

71

S	-1.041295	-0.953734	-1.739619
C	-2.512577	-0.058739	-1.415133
B	2.846156	1.028495	1.428656
B	1.640440	2.551790	-0.655909
B	1.481263	1.903998	2.116830
B	0.733856	2.841766	0.827039
C	-3.772094	-0.642481	-1.689789
C	-2.482294	1.262581	-0.893955
C	2.927079	1.518307	-0.209628
H	3.151118	-0.096704	1.695049
B	4.043819	2.230285	0.872597
B	3.135102	2.508180	2.371118
B	3.296545	3.178018	-0.435186
H	1.140055	2.436904	-1.734629
B	1.906481	4.054403	0.250918
B	1.811028	3.651185	1.992989
H	0.817100	1.353850	2.949579
H	-0.457828	2.949822	0.758474
H	-3.807715	-1.656491	-2.099662
C	-4.959966	0.044811	-1.428883
C	-3.657523	1.954427	-0.634199
H	-1.514689	1.735182	-0.696950
C	3.333558	0.425597	-1.168921
H	5.194886	1.914400	0.801074
B	3.400551	3.848330	1.212019
H	3.671615	2.444427	3.442322
H	3.930413	3.470144	-1.406957
H	1.547654	5.103170	-0.207934
H	1.379362	4.423562	2.803996
H	-5.916662	-0.438628	-1.641940
C	-4.909214	1.347794	-0.887188
H	-3.639623	2.971409	-0.231948
C	2.443442	-0.021011	-2.164618
C	4.576383	-0.220302	-1.030304
H	4.141545	4.761254	1.452808
O	-6.002978	2.094496	-0.581579
H	1.483608	0.484175	-2.303440
C	2.776215	-1.108476	-2.984460
C	4.915496	-1.295799	-1.863312
H	5.272493	0.116813	-0.258846
C	-7.294375	1.553055	-0.838619
H	2.060247	-1.447252	-3.740062
C	4.012969	-1.751420	-2.836331

H	5.887723	-1.785027	-1.742141
H	-7.432154	1.336055	-1.914671
H	-7.466462	0.628572	-0.254944
H	-8.012875	2.323626	-0.524410
H	4.274827	-2.599270	-3.477911
C	1.424966	1.309837	0.511604
Cu	0.358647	-0.229611	-0.154940
C	-0.033368	-2.735706	1.279823
C	2.139687	-2.588707	0.412696
C	0.176576	-4.079686	1.635819
C	-1.301216	-2.014795	1.530121
C	2.413929	-3.919081	0.741334
H	2.881799	-1.955846	-0.083192
C	1.411069	-4.677357	1.360655
H	-0.619025	-4.633256	2.141903
C	-1.255889	-0.662673	1.941897
C	-2.551448	-2.629802	1.325109
H	3.394135	-4.344231	0.509133
H	1.591549	-5.721593	1.635577
C	-2.441259	0.058124	2.134138
H	-0.292988	-0.192384	2.172601
C	-3.732161	-1.900859	1.511887
H	-2.595525	-3.666179	0.975039
C	-3.680866	-0.557907	1.915801
H	-2.388630	1.102844	2.454807
H	-4.699121	-2.378494	1.323901
H	-4.606292	0.010701	2.049921
N	0.947759	-2.018527	0.670660

C[4]
Lowest frequency = 20.4062 cm^{-1}
Charge = 0, Multiplicity = 4

71

S	-1.278054	1.330720	1.198630
C	-2.618272	0.231224	1.094701
B	3.076910	-1.094679	-1.308420
B	1.285107	-2.518607	0.400488
B	1.759396	-1.723358	-2.306138
B	0.650417	-2.602316	-1.246986
C	-3.918245	0.687332	1.438016
C	-2.471973	-1.117335	0.662879
C	2.764230	-1.666673	0.285834
H	3.577128	-0.018508	-1.426391
B	3.959041	-2.485741	-0.616363
B	3.331947	-2.558954	-2.280192
B	2.847223	-3.373206	0.454346
H	0.597796	-2.372240	1.368408
B	1.506750	-3.999482	-0.546233
B	1.814211	-3.507865	-2.243945
H	1.343320	-1.033206	-3.190976
H	-0.534911	-2.517885	-1.401331

H	-4.045496	1.726439	1.755691
C	-5.022196	-0.162262	1.372547
C	-3.562135	-1.970417	0.601656
H	-1.481683	-1.488940	0.378846
C	3.096491	-0.672158	1.371361
H	5.105405	-2.348524	-0.307869
B	3.174349	-3.971214	-1.189419
H	4.075136	-2.533097	-3.220206
H	3.226112	-3.801174	1.504586
H	0.919771	-4.998086	-0.236628
H	1.448468	-4.170676	-3.173978
H	-6.009636	0.221262	1.640151
C	-4.851518	-1.501052	0.953125
H	-3.452673	-3.008944	0.277355
C	2.082221	-0.135938	2.188903
C	4.408636	-0.184549	1.510248
H	3.809668	-4.975922	-1.352557
O	-5.854350	-2.405052	0.851015
H	1.062625	-0.531442	2.131680
C	2.364920	0.892152	3.097884
C	4.694372	0.827946	2.435748
H	5.201682	-0.589475	0.877227
C	-7.182792	-2.003395	1.180239
H	1.555296	1.308693	3.705040
C	3.672341	1.379987	3.222096
H	5.720424	1.198352	2.528520
H	-7.252639	-1.683529	2.236506
H	-7.525735	-1.182794	0.522877
H	-7.812176	-2.890297	1.021318
H	3.894909	2.185205	3.929458
C	1.492368	-1.221053	-0.700537
Cu	0.367080	0.259158	-0.056615
C	0.217716	2.849563	-1.159813
C	2.407503	2.403551	-0.299144
C	0.527978	4.238664	-1.165809
C	-1.040180	2.276202	-1.546547
C	2.754490	3.747014	-0.329365
H	3.106941	1.642289	0.060407
C	1.774977	4.689864	-0.769113
H	-0.231787	4.939443	-1.525457
C	-1.102292	0.894844	-2.000093
C	-2.297341	2.980328	-1.425235
H	3.754542	4.056071	-0.015490
H	2.011282	5.758105	-0.801260
C	-2.325829	0.264506	-2.205386
H	-0.177445	0.399776	-2.322067
C	-3.500950	2.326096	-1.626700
H	-2.291883	4.025549	-1.100938
C	-3.541742	0.951034	-1.987049
H	-2.340147	-0.770204	-2.564197
H	-4.439062	2.873297	-1.482480
H	-4.499675	0.440180	-2.119738
N	1.194194	1.959693	-0.689892

C^6
Lowest frequency = 16.4769 cm^{-1}
Charge = 0, Multiplicity = 6

71

S	-1.232597	1.313642	1.229589
C	-2.559601	0.212071	1.169407
B	3.121862	-1.041943	-1.314130
B	1.407097	-2.473685	0.467258
B	1.819995	-1.761134	-2.272157
B	0.758225	-2.642736	-1.167547
C	-3.867019	0.673974	1.502869
C	-2.405093	-1.150553	0.771680
C	2.850283	-1.568675	0.304209
H	3.571049	0.051309	-1.475044
B	4.066147	-2.371958	-0.582971
B	3.424652	-2.531327	-2.234940
B	3.002459	-3.263454	0.532715
H	0.722813	-2.321340	1.436383
B	1.677525	-3.978475	-0.427760
B	1.946266	-3.538000	-2.145586
H	1.366961	-1.121665	-3.176388
H	-0.432116	-2.609698	-1.307074
H	-3.995378	1.719265	1.798036
C	-4.967033	-0.176808	1.442416
C	-3.489356	-2.006750	0.729383
H	-1.411303	-1.521223	0.499494
C	3.157558	-0.526296	1.351543
H	5.209208	-2.179449	-0.292172
B	3.335467	-3.907916	-1.092199
H	4.155406	-2.511641	-3.184795
H	3.409504	-3.637563	1.593005
H	1.134215	-4.987577	-0.074686
H	1.597215	-4.248924	-3.046196
H	-5.958955	0.208370	1.689924
C	-4.786801	-1.526256	1.056121
H	-3.378560	-3.053260	0.433080
C	2.142891	-0.029098	2.192003
C	4.442625	0.039830	1.431479
H	4.008765	-4.892074	-1.226044
O	-5.782224	-2.432396	0.964071
H	1.145353	-0.479005	2.171364
C	2.397969	1.031206	3.071449
C	4.701238	1.087708	2.324653
H	5.235125	-0.331815	0.777727
C	-7.121648	-2.033235	1.262506
H	1.588174	1.414865	3.699744
C	3.678397	1.594874	3.139587
H	5.706160	1.519706	2.370775
H	-7.208305	-1.691408	2.309925
H	-7.456160	-1.230737	0.580037
H	-7.739813	-2.929106	1.112588

H	3.879036	2.425823	3.823399
C	1.551336	-1.211725	-0.683038
Cu	0.397250	0.266131	-0.099381
C	0.035371	2.739597	-1.300518
C	2.246305	2.474803	-0.386421
C	0.175592	4.203496	-1.190924
C	-1.158467	2.110672	-1.713441
C	2.402412	3.915078	-0.270997
H	3.017184	1.780574	-0.048865
C	1.385266	4.770443	-0.652166
H	-0.607062	4.832319	-1.620821
C	-1.158701	0.680206	-2.048507
C	-2.448160	2.786223	-1.688628
H	3.353415	4.290634	0.120396
H	1.491972	5.855284	-0.567244
C	-2.355566	-0.009340	-2.186505
H	-0.216230	0.213330	-2.358973
C	-3.618614	2.063438	-1.798230
H	-2.483337	3.861658	-1.496333
C	-3.598740	0.650261	-2.017562
H	-2.335604	-1.069148	-2.461869
H	-4.581392	2.580248	-1.720380
H	-4.536378	0.093838	-2.109043
N	1.087854	1.924820	-0.920212

D[1]

Lowest frequency = 11.6905 cm^{-1}

Charge = 0, Multiplicity = 1

78

S	-0.368640	-0.141127	-1.523468
C	-2.013333	-0.634008	-1.162846
B	3.224145	-0.802237	1.023607
B	2.680551	-0.499765	-1.746856
B	3.559785	0.886036	0.589671
B	3.208272	1.068665	-1.135758
C	-3.111815	0.138846	-1.600599
C	-2.266114	-1.842441	-0.461658
C	2.761546	-1.592677	-0.428764
H	2.734860	-1.144221	2.049096
B	4.362103	-1.846322	0.140975
B	4.899401	-0.272938	0.774595
B	4.023753	-1.654333	-1.591638
H	1.828383	-0.637817	-2.565056
B	4.341554	0.033952	-2.044425
B	4.897889	0.895790	-0.581560
H	3.286180	1.741199	1.375287
H	2.671282	2.040719	-1.571414
H	-2.920458	1.071313	-2.140254
C	-4.425620	-0.271376	-1.356719
C	-3.569127	-2.245122	-0.193612
H	-1.419659	-2.444397	-0.120805

C	1.732708	-2.695438	-0.379459
H	4.606174	-2.923739	0.599328
B	5.390860	-0.792279	-0.858950
H	5.644148	-0.206702	1.712376
H	4.046617	-2.600975	-2.321625
H	4.681167	0.319068	-3.158683
H	5.657094	1.824298	-0.627291
H	-5.255894	0.342216	-1.714898
C	-4.660349	-1.462998	-0.636798
H	-3.777807	-3.167837	0.355653
C	1.261930	-3.260619	-1.580728
C	1.260411	-3.203280	0.842385
H	6.518371	-1.111069	-1.119899
O	-5.894838	-1.934432	-0.320098
H	1.618452	-2.869965	-2.536258
C	0.345403	-4.317116	-1.559166
C	0.336595	-4.257419	0.862165
H	1.592380	-2.763194	1.782098
C	-7.037615	-1.203139	-0.752143
H	-0.008908	-4.743723	-2.503129
C	-0.119792	-4.823127	-0.335850
H	-0.024651	-4.633075	1.824946
H	-7.052962	-0.186150	-0.315615
H	-7.072794	-1.126830	-1.855219
H	-7.910549	-1.768153	-0.395105
H	-0.838166	-5.649769	-0.318661
C	2.295649	0.009701	-0.156140
C	-1.681355	2.484905	0.431528
C	-2.237522	0.535252	1.623698
C	-2.997709	2.961244	0.578379
C	-0.638047	3.274402	-0.258341
C	-3.551406	0.966712	1.814701
H	-1.863095	-0.415362	2.011913
C	-3.940129	2.197072	1.270730
H	-3.253426	3.940790	0.165923
C	0.637359	3.415731	0.328990
C	-0.912490	3.908241	-1.486868
H	-4.250597	0.335885	2.369242
H	-4.964858	2.563138	1.392702
C	1.619592	4.181780	-0.310352
H	0.846961	2.948493	1.296736
C	0.078464	4.662018	-2.125130
H	-1.894043	3.781265	-1.955738
C	1.344884	4.802489	-1.536613
H	2.606211	4.282821	0.151323
H	-0.134010	5.133660	-3.090068
H	2.120164	5.389472	-2.039478
N	-1.335063	1.275048	0.943932
Cu	0.462758	0.494485	0.483872
O	1.103565	1.028513	2.277903
C	0.742674	0.027201	3.021131
C	1.167897	0.099365	4.474570
H	2.207992	-0.267043	4.544099
H	1.152158	1.137878	4.840119

H	0.523283	-0.545160	5.090679
O	0.122021	-0.953388	2.556707

D^3
Lowest frequency = 19.2771 cm^{-1}
Charge = 0, Multiplicity = 3

78

S	-0.483642	-0.013362	-1.246960
C	-1.990996	-0.665256	-0.708878
B	3.038588	-1.390378	1.216560
B	2.805728	-0.306113	-1.399888
B	3.846387	0.173627	1.215876
B	3.694204	0.847741	-0.401952
C	-2.981419	-0.984317	-1.677136
C	-2.272819	-0.911504	0.667252
C	2.505770	-1.651295	-0.388757
H	2.400101	-1.804352	2.130598
B	3.922716	-2.477834	0.107452
B	4.811792	-1.317948	1.115093
B	3.782925	-1.791128	-1.527747
H	1.988241	-0.011638	-2.220505
B	4.571329	-0.202479	-1.544410
B	5.227969	0.087578	0.093382
H	3.759887	0.869596	2.180473
H	3.507969	2.020053	-0.549375
H	-2.759302	-0.812100	-2.734771
C	-4.217997	-1.500646	-1.297095
C	-3.505599	-1.417739	1.047791
H	-1.494670	-0.722036	1.416284
C	1.223179	-2.416388	-0.604010
H	3.826901	-3.659151	0.272668
B	5.271479	-1.551756	-0.596487
H	5.479187	-1.689358	2.040587
H	3.617892	-2.513566	-2.466963
H	5.064223	0.233671	-2.548511
H	6.210980	0.750615	0.280205
H	-4.962847	-1.733295	-2.061947
C	-4.490431	-1.717158	0.074927
H	-3.736651	-1.614058	2.098785
C	0.805948	-2.723583	-1.920187
C	0.441133	-2.862593	0.478029
H	6.286363	-2.104709	-0.921460
O	-5.657054	-2.212369	0.550438
H	1.405240	-2.376665	-2.764933
C	-0.358508	-3.467894	-2.145502
C	-0.724737	-3.600789	0.245800
H	0.723539	-2.598400	1.498296
C	-6.690922	-2.557018	-0.370510
H	-0.664194	-3.693876	-3.172160
C	-1.129153	-3.909843	-1.063038
H	-1.328155	-3.929447	1.097469

H	-7.024680	-1.673084	-0.945004
H	-6.355733	-3.345958	-1.069038
H	-7.522670	-2.935045	0.240440
H	-2.044624	-4.485466	-1.234401
C	2.436611	-0.100222	0.264184
C	-1.382770	2.995148	0.075786
C	-1.684716	1.966735	2.152032
C	-2.507762	3.812774	0.301444
C	-0.604484	3.088293	-1.178532
C	-2.812031	2.740570	2.434723
H	-1.330707	1.194442	2.840590
C	-3.230988	3.684773	1.489055
H	-2.784929	4.557142	-0.449743
C	0.803945	2.987894	-1.158657
C	-1.267226	3.244511	-2.414573
H	-3.345166	2.597850	3.378715
H	-4.103663	4.318613	1.677259
C	1.527629	3.018382	-2.356163
H	1.332345	2.910532	-0.199981
C	-0.539262	3.272410	-3.608426
H	-2.360693	3.296314	-2.438266
C	0.858433	3.153949	-3.581059
H	2.616641	2.931452	-2.328922
H	-1.064545	3.370758	-4.564071
H	1.428915	3.167370	-4.515365
N	-0.988147	2.084012	1.003355
Cu	0.629152	0.745812	0.704767
O	1.327042	1.335460	2.532739
C	0.918155	0.329269	3.220712
C	1.474853	0.177506	4.622541
H	2.464529	-0.306898	4.540573
H	1.622072	1.161052	5.095601
H	0.818080	-0.460317	5.232908
O	0.111439	-0.521247	2.748534

D[5]

Lowest frequency = 10.2928 cm^{-1}

Charge = 0, Multiplicity = 5

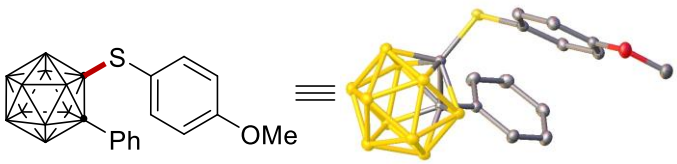
78

S	-0.488583	0.721627	-1.431249
C	-2.059081	0.125622	-1.049421
B	2.773545	-1.820560	0.886653
B	2.104155	-1.184407	-1.783310
B	3.772477	-0.444670	0.400394
B	3.343202	-0.051712	-1.267847
C	-3.125853	0.377283	-1.959306
C	-2.329227	-0.619865	0.136402
C	1.848665	-2.254947	-0.485597
H	2.308773	-1.962509	1.971906
B	3.218203	-3.222074	-0.118516
B	4.469611	-2.084816	0.427685

B	2.799931	-2.822383	-1.798178
H	1.184933	-0.876913	-2.481725
B	3.781157	-1.434426	-2.303795
B	4.831141	-0.977873	-0.930562
H	3.995429	0.405604	1.210449
H	3.259998	1.071636	-1.661202
H	-2.919246	0.945484	-2.871260
C	-4.412796	-0.079041	-1.697083
C	-3.609652	-1.074117	0.398202
H	-1.512646	-0.848656	0.826997
C	0.462149	-2.822708	-0.305933
H	3.004040	-4.316997	0.314654
B	4.485148	-2.695418	-1.252015
H	5.272735	-2.406102	1.259018
H	2.301673	-3.646843	-2.507954
H	4.081814	-1.273385	-3.454025
H	5.913842	-0.483717	-1.087777
H	-5.215005	0.132965	-2.407804
C	-4.664762	-0.809259	-0.508817
H	-3.827924	-1.657651	1.296207
C	-0.398031	-2.945323	-1.415164
C	0.041743	-3.333029	0.935454
H	5.311589	-3.472224	-1.645454
O	-5.874700	-1.298817	-0.160539
H	-0.076927	-2.569772	-2.389205
C	-1.648640	-3.559564	-1.284708
C	-1.212030	-3.943335	1.065753
H	0.700753	-3.252941	1.800602
C	-6.990005	-1.087452	-1.027893
H	-2.301994	-3.644198	-2.159264
C	-2.061075	-4.062451	-0.043048
H	-1.521114	-4.333393	2.041145
H	-7.196288	-0.008771	-1.153360
H	-6.816586	-1.549862	-2.016746
H	-7.845368	-1.572775	-0.537665
H	-3.039363	-4.543959	0.059818
C	2.171044	-0.616767	-0.162448
C	-0.689651	3.175502	0.327986
C	-1.778142	1.773016	1.898233
C	-1.934116	3.847087	0.074339
C	0.556632	3.523234	-0.255879
C	-2.991329	2.463816	1.754041
H	-1.698385	0.912859	2.571129
C	-3.070696	3.504912	0.777411
H	-1.958782	4.655741	-0.661221
C	1.794532	2.979484	0.313194
C	0.679675	4.359333	-1.425228
H	-3.855212	2.176463	2.358808
H	-4.015178	4.027729	0.598237
C	3.025865	3.225073	-0.297802
H	1.772473	2.558739	1.323636
C	1.908060	4.565149	-2.013694
H	-0.218098	4.786327	-1.881089
C	3.106736	3.994700	-1.465291

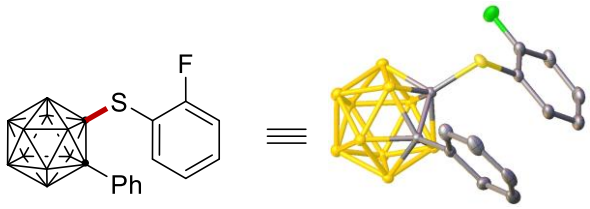
H	3.934653	2.827743	0.163310
H	1.974225	5.168715	-2.925520
H	4.070840	4.181086	-1.946918
N	-0.669433	2.072328	1.214157
Cu	0.749266	0.637161	0.640293
O	1.685547	0.726337	2.527944
C	0.907238	-0.148334	3.031977
C	1.116166	-0.596836	4.457774
H	1.909667	-1.365474	4.461564
H	1.456075	0.245333	5.080244
H	0.193644	-1.038281	4.864123
O	-0.011817	-0.662197	2.317030

X-Ray crystallographic analysis



CCDC 2049567
3aa

Identification code	mo_1224_CG_0m
Empirical formula	$C_{15}H_{22}B_{10}OS$
Formula weight	358.48
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.0280(5)
b/Å	18.2663(11)
c/Å	15.1077(11)
α/°	90
β/°	99.556(2)
γ/°	90
Volume/Å^3	1912.5(2)
Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.171
F(000)	744.0
Crystal size/mm^3	0.529 × 0.459 × 0.168
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.46 to 63.05
Index ranges	$-10 \le h \le 10$, $-26 \le k \le 26$, $-22 \le l \le 22$
Reflections collected	103018
Independent reflections	6368 [R_{int} = 0.0250, R_{sigma} = 0.0120]
Data/restraints/parameters	6368/0/285
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0282, wR_2 = 0.0777
Final R indexes [all data]	R_1 = 0.0304, wR_2 = 0.0798
Largest diff. peak/hole / e Å^{-3}	0.46/-0.21



CCDC 2049566

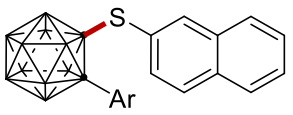
3am

Identification code	mo_1222_CG_0m
Empirical formula	$C_{14}H_{19}B_{10}FS$
Formula weight	346.45
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.5577(11)
b/Å	27.778(5)
c/Å	10.1198(10)
α/°	90
β/°	100.877(5)
γ/°	90
Volume/Å^3	1810.3(5)
Z	4
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	0.182
F(000)	712.0
Crystal size/mm^3	0.358 × 0.268 × 0.263
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.352 to 63.066
Index ranges	$-9 \le h \le 9$, $-40 \le k \le 40$, $-14 \le l \le 14$
Reflections collected	63225
Independent reflections	6029 [R_{int} = 0.0240, R_{sigma} = 0.0130]
Data/restraints/parameters	6029/0/275
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0289, wR_2 = 0.0773
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0802
Largest diff. peak/hole / e Å^{-3}	0.38/-0.22

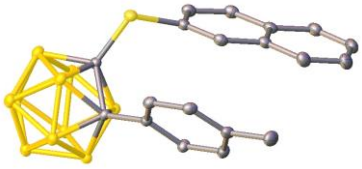
CCDC 2049564

3ao

Identification code	mo_1203_CG_0m
Empirical formula	$C_{14}H_{20}B_{10}S$
Formula weight	328.46
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4152(7)
b/Å	28.237(4)
c/Å	8.6124(9)
α/°	90
β/°	102.204(4)
γ/°	90
Volume/Å^3	1762.6(3)
Z	4
ρ_{calc}g/cm^3	1.238
μ/mm^{-1}	0.175
F(000)	680.0
Crystal size/mm^3	0.25 × 0.208 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.05 to 61.098
Index ranges	$-9 \leq h \leq 10$, $-39 \leq k \leq 40$, $-12 \leq l \leq 12$
Reflections collected	44747
Independent reflections	5398 [R_{int} = 0.0208, R_{sigma} = 0.0131]
Data/restraints/parameters	5398/0/266
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0298, wR_2 = 0.0780
Final R indexes [all data]	R_1 = 0.0337, wR_2 = 0.0813
Largest diff. peak/hole / e Å^{-3}	0.41/-0.26



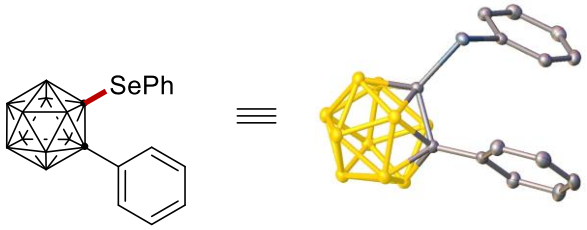
Ar = 4-MePh



CCDC 2065339

4br

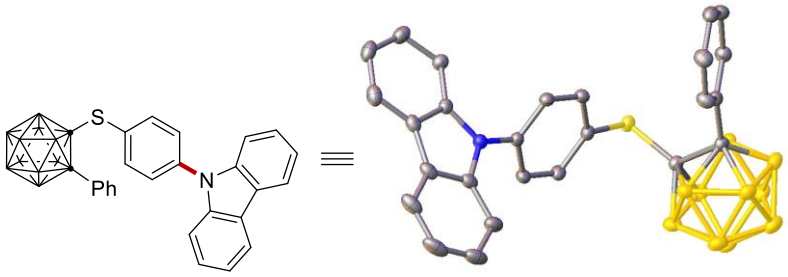
Identification code	1284_Pna21
Empirical formula	$C_{19}H_{24}B_{10}S$
Formula weight	392.54
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	23.8557(17)
b/Å	12.6391(11)
c/Å	6.8918(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2078.0(3)
Z	4
ρ_{calc}g/cm^3	1.255
μ/mm^{-1}	0.160
F(000)	816.0
Crystal size/mm^3	0.454 × 0.198 × 0.066
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.696 to 61.138
Index ranges	$-34 \le h \le 34$, $-18 \le k \le 18$, $-9 \le l \le 9$
Reflections collected	136112
Independent reflections	6375 [R_{int} = 0.0363, R_{sigma} = 0.0124]
Data/restraints/parameters	6375/1/302
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0254, wR_2 = 0.0696
Final R indexes [all data]	R_1 = 0.0262, wR_2 = 0.0703
Largest diff. peak/hole / e Å^{-3}	0.32/-0.18
Flack parameter	0.009(9)



CCDC 2049565

4av

Identification code	mo_1218_CG_0m
Empirical formula	$C_{14}H_{20}B_{10}Se$
Formula weight	375.36
Temperature/K	110
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.6595(9)
b/Å	28.316(4)
c/Å	8.5737(12)
α/°	90
β/°	103.115(3)
γ/°	90
Volume/Å^3	1811.0(4)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	2.065
F(000)	752.0
Crystal size/mm^3	0.221 × 0.162 × 0.058
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.086 to 61.016
Index ranges	$-10 \leq h \leq 10$, $-40 \leq k \leq 40$, $-12 \leq l \leq 11$
Reflections collected	40969
Independent reflections	5465 [R_{int} = 0.0296, R_{sigma} = 0.0194]
Data/restraints/parameters	5465/0/306
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0229, wR_2 = 0.0502
Final R indexes [all data]	R_1 = 0.0291, wR_2 = 0.0528
Largest diff. peak/hole / e Å^{-3}	0.38/-0.43



CCDC 2063919
5b

Identification code	mo_1274_CG_0m
Empirical formula	$C_{26}H_{27}B_{10}NS$
Formula weight	493.64
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.2524(16)
b/Å	12.5432(12)
c/Å	14.6594(17)
α/°	90
β/°	95.765(4)
γ/°	90
Volume/Å^3	2607.4(5)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	0.143
F(000)	1024.0
Crystal size/mm^3	0.563 × 0.352 × 0.202
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.202 to 59.248
Index ranges	$-19 \le h \le 19$, $-17 \le k \le 17$, $-20 \le l \le 20$
Reflections collected	64184
Independent reflections	7308 [R_{int} = 0.0311, R_{sigma} = 0.0193]
Data/restraints/parameters	7308/0/373
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1143
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	0.56/-0.32

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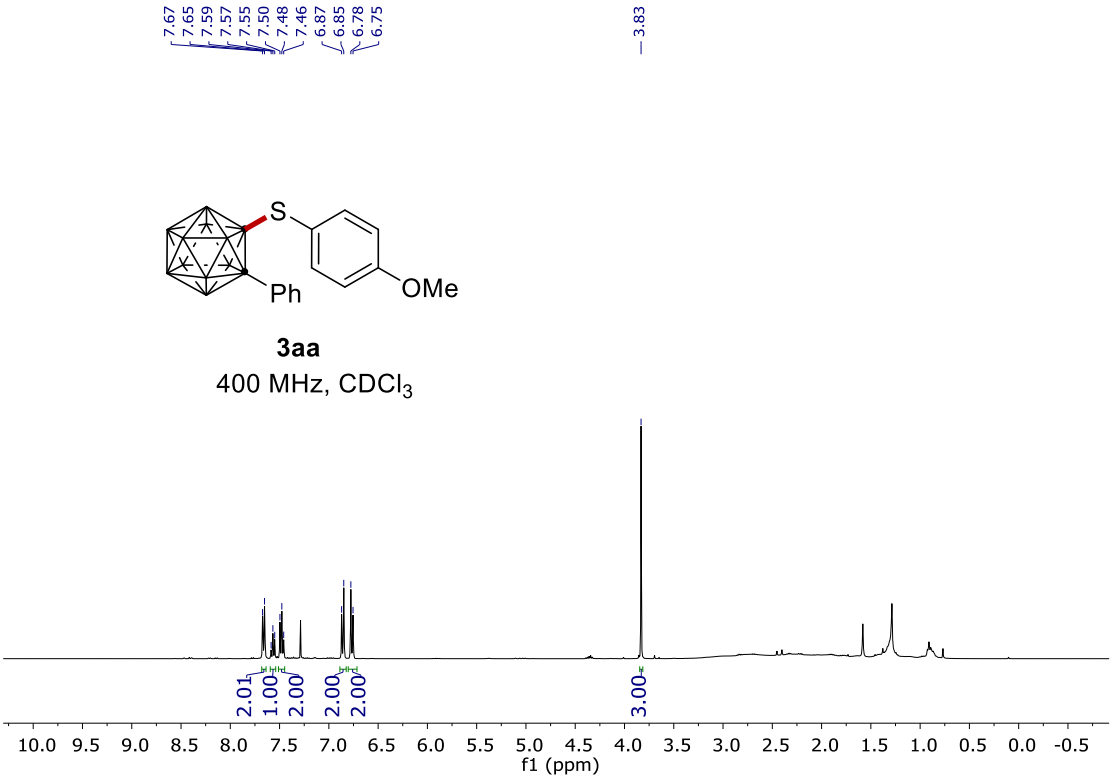
^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra



3aa

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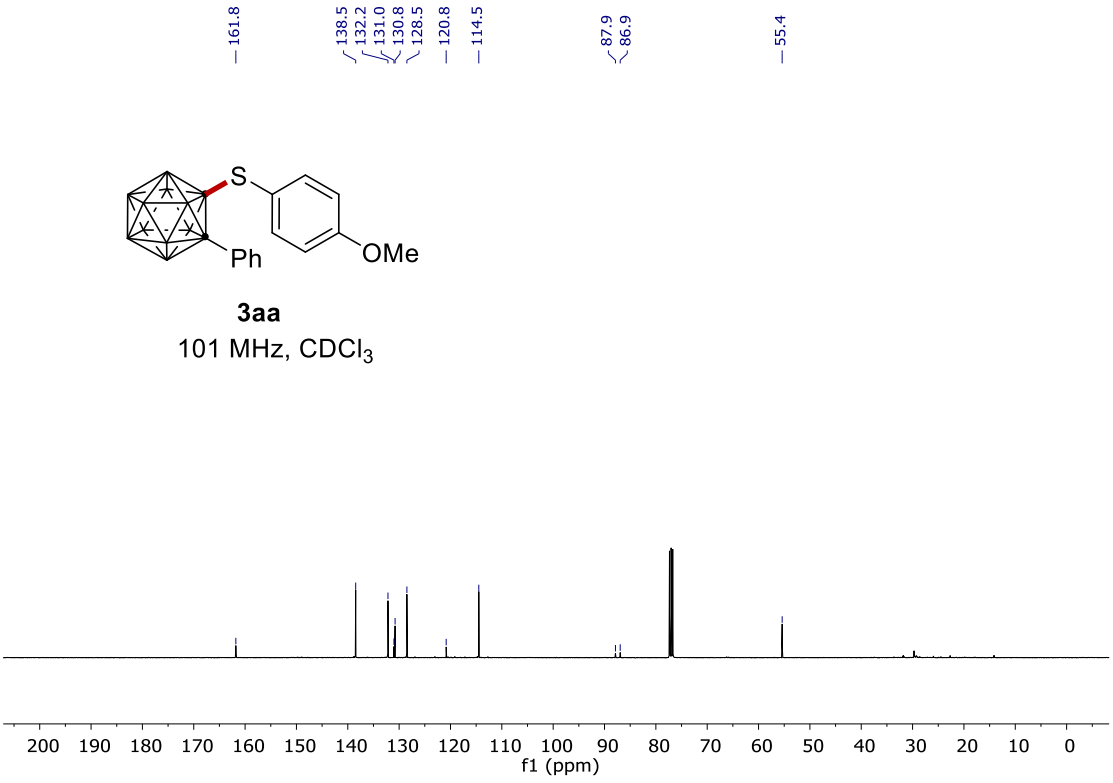

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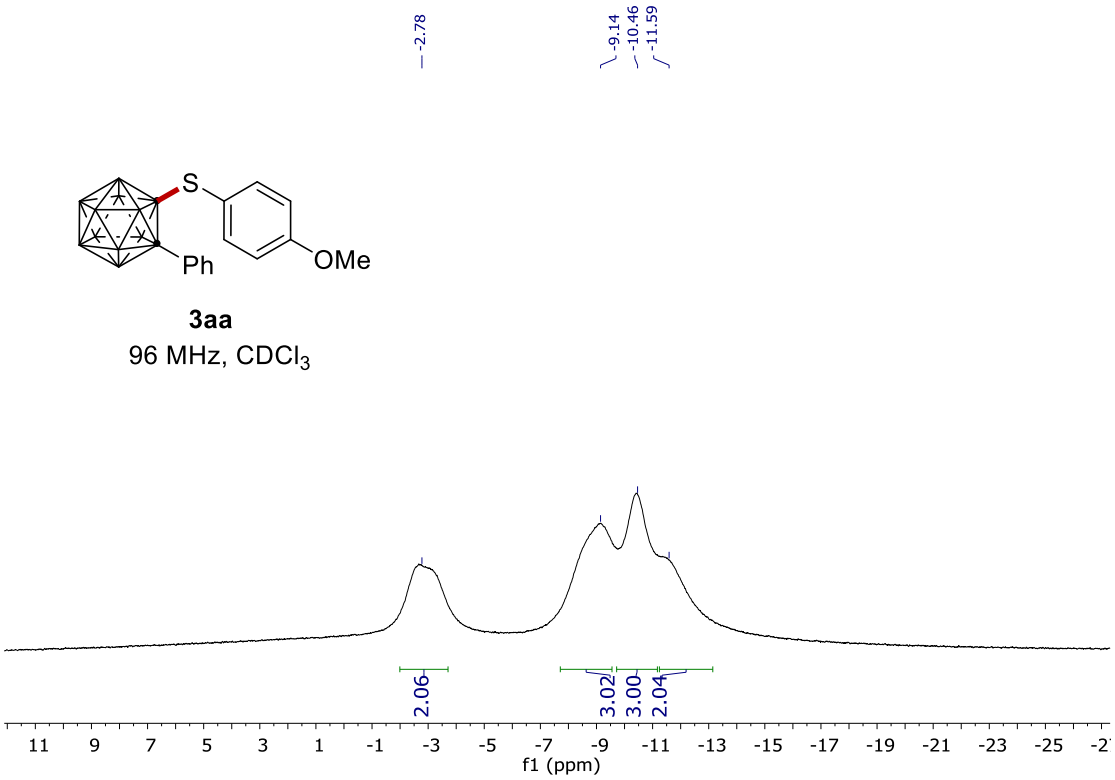

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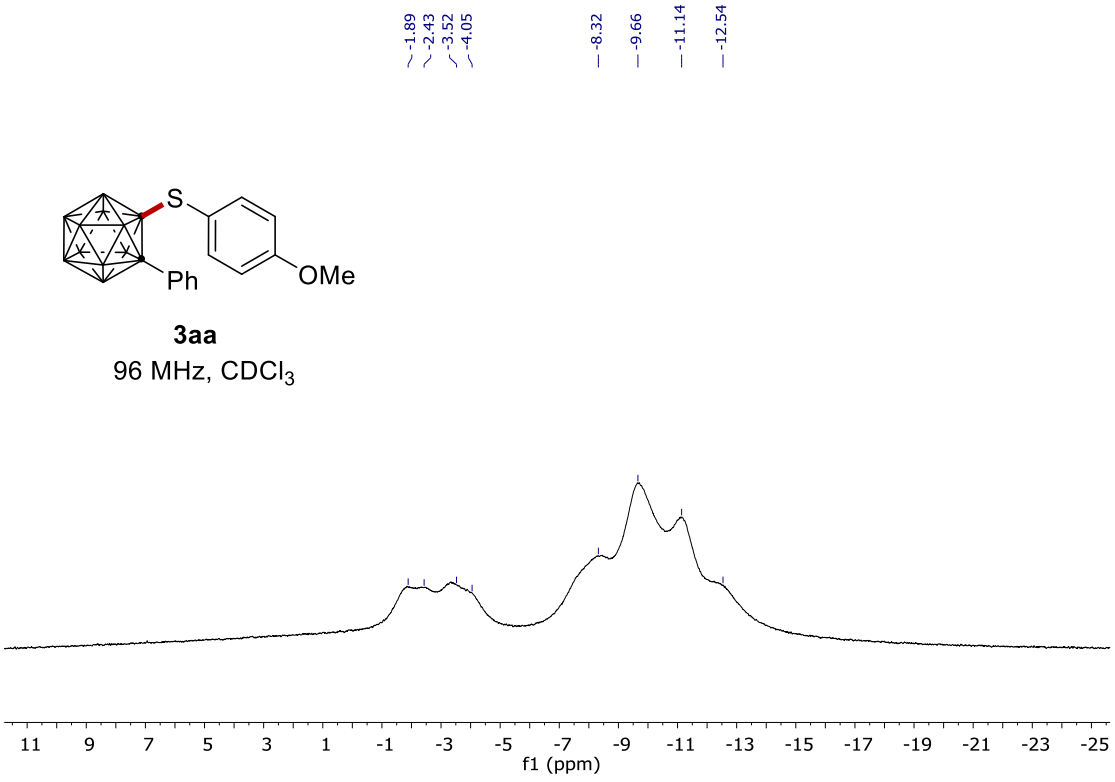

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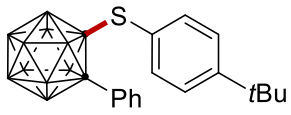

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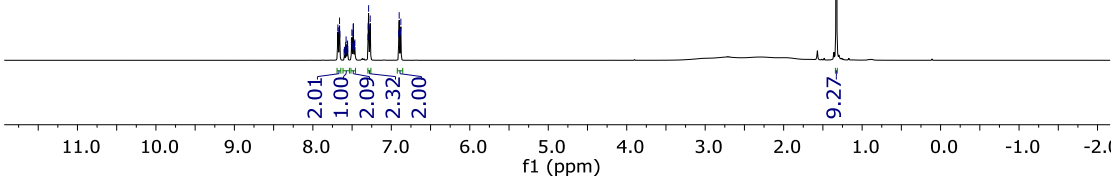

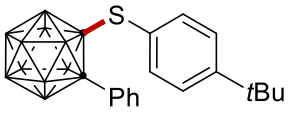

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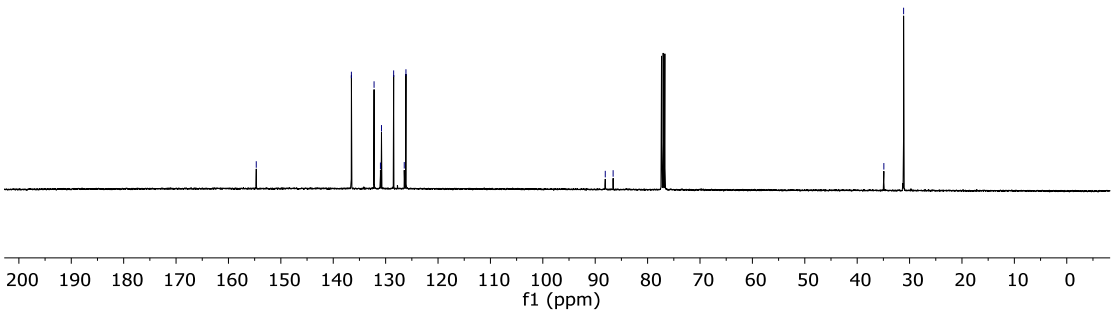

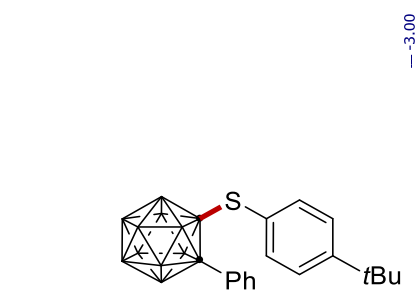

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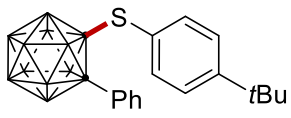

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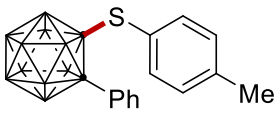

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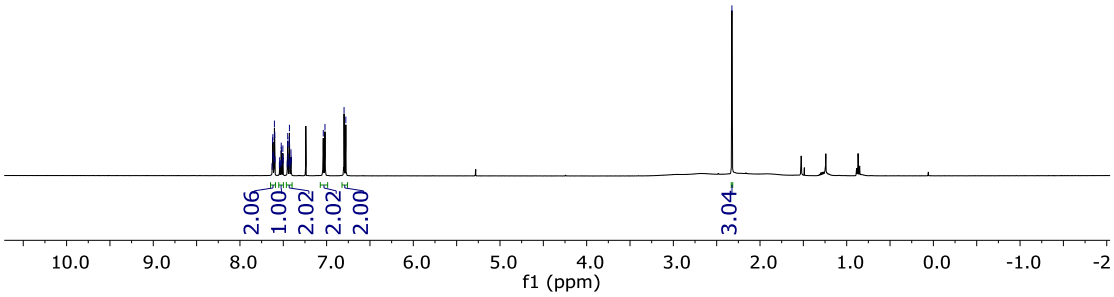

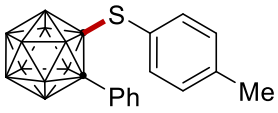

3ac

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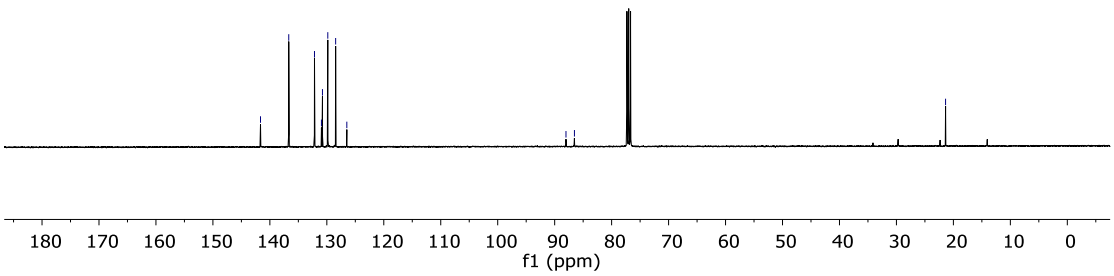
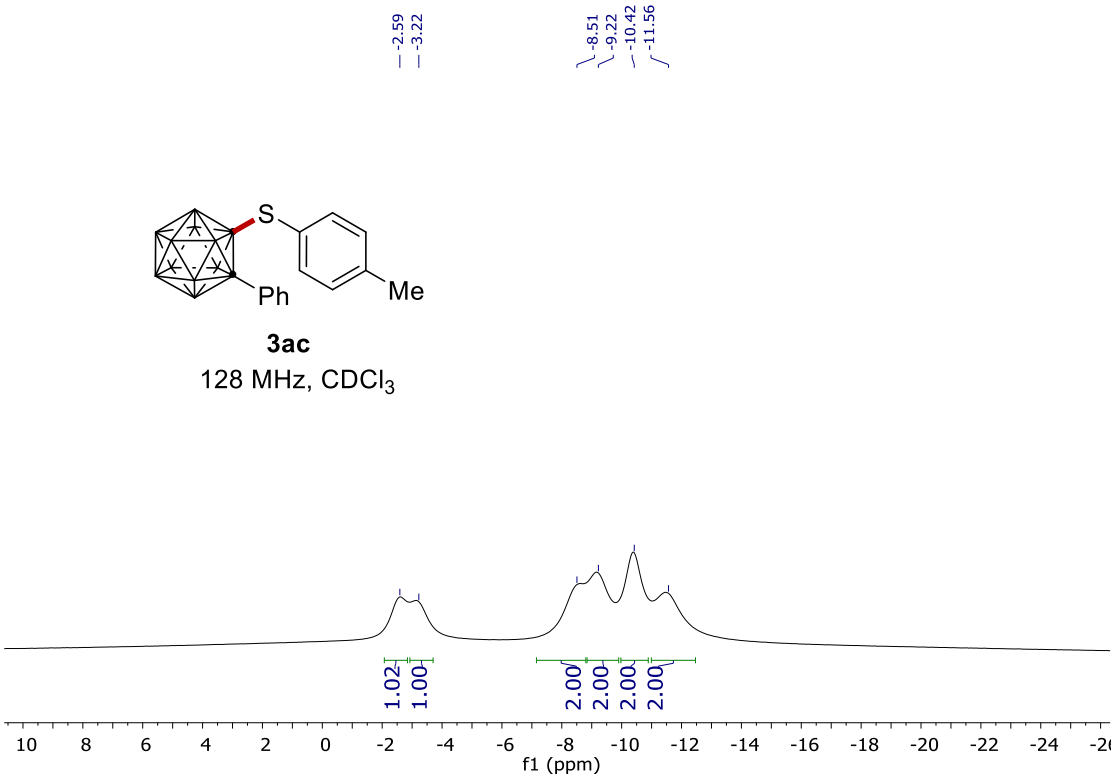
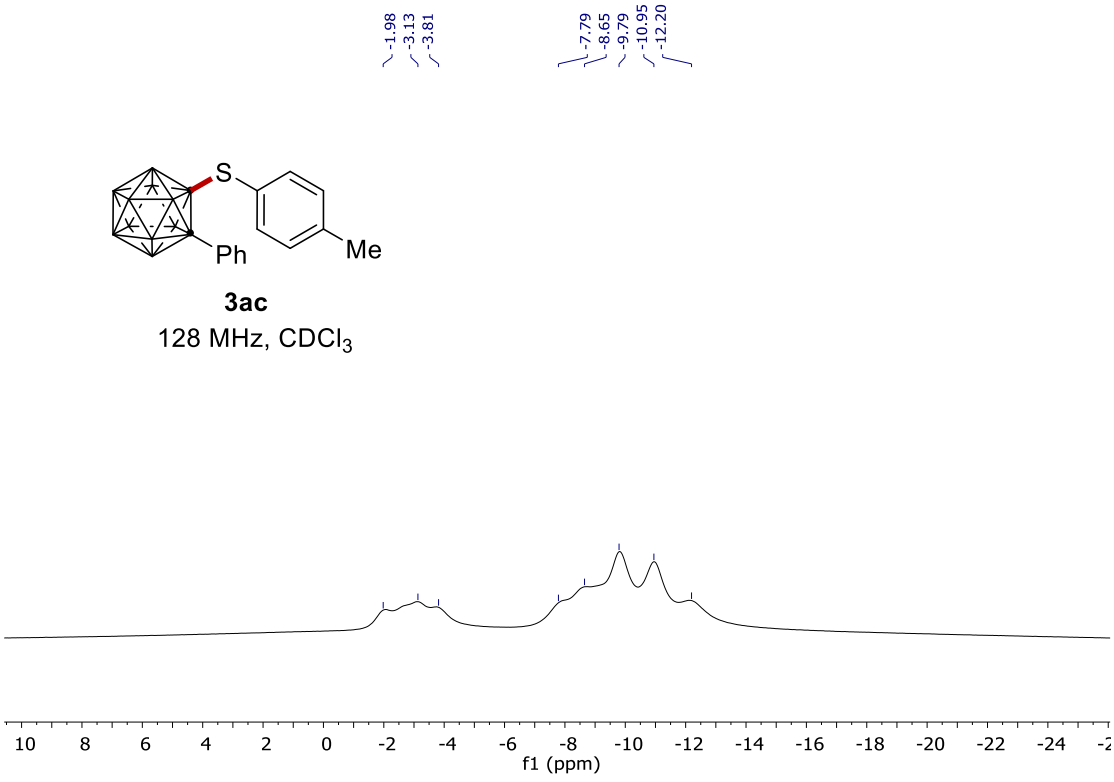




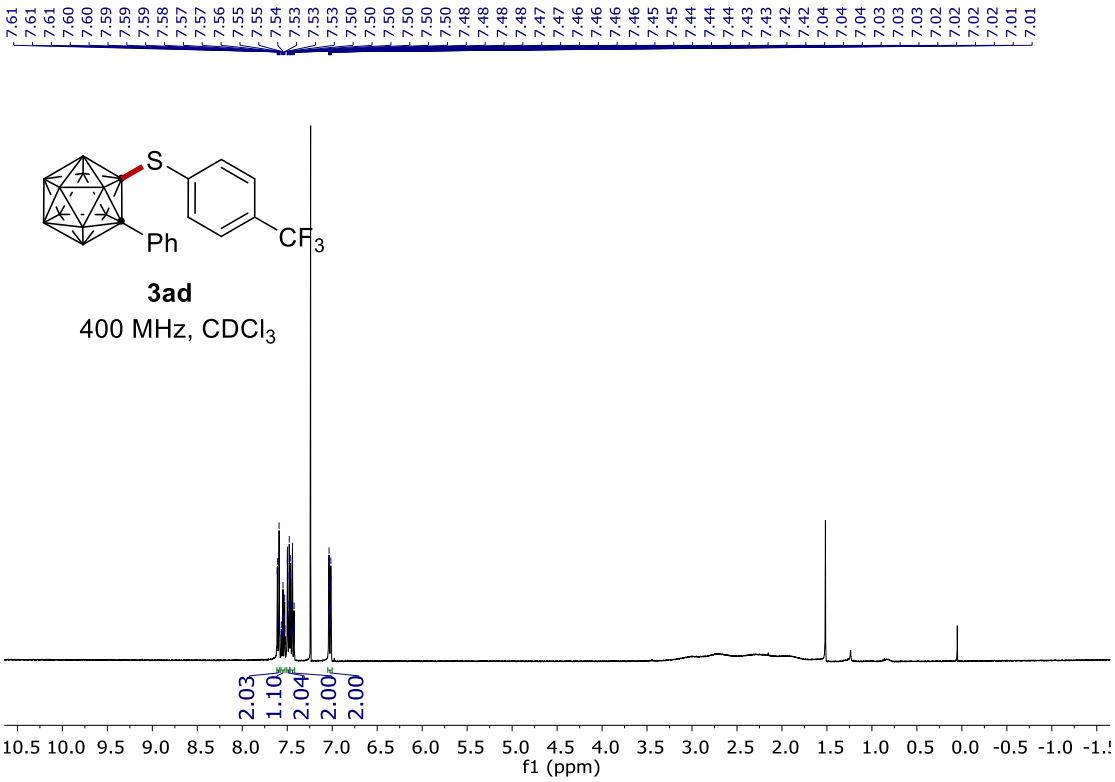
3ac

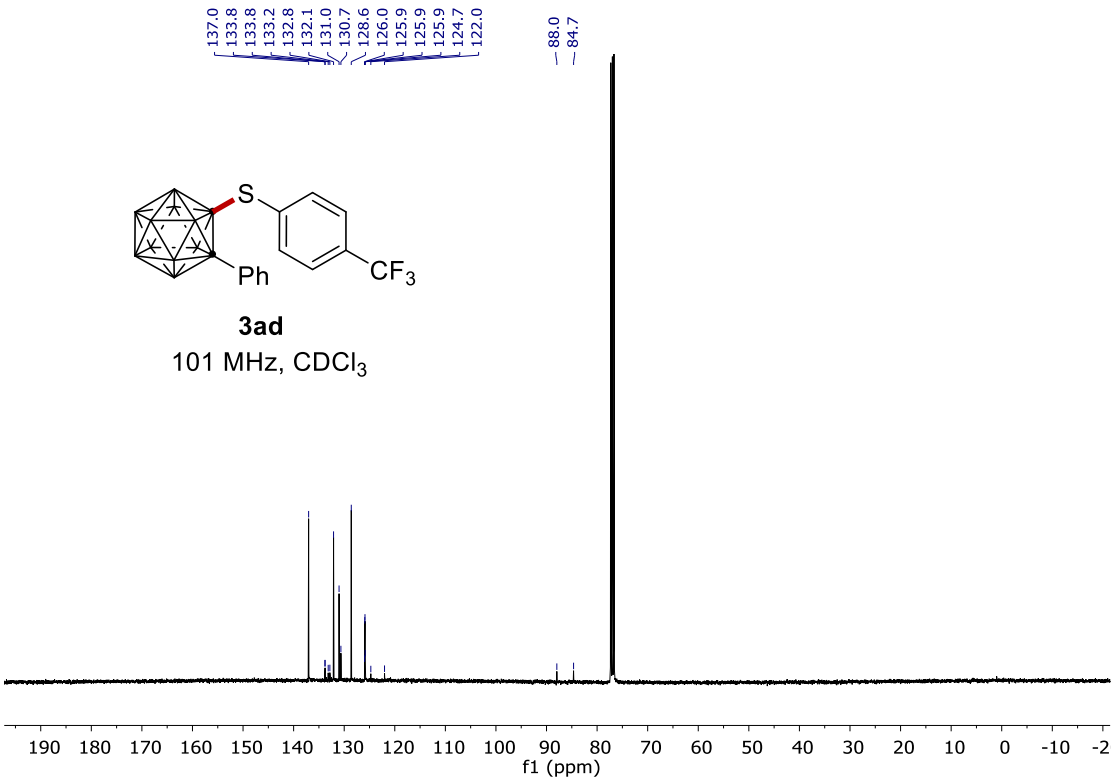
128 MHz, $CDCl_3$

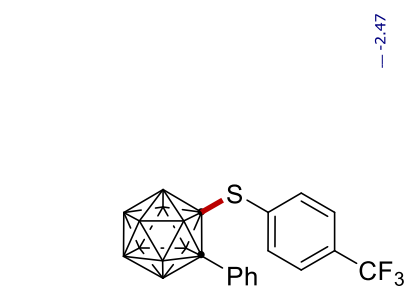


3ac

128 MHz, $CDCl_3$

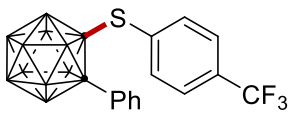

7.61 7.61 7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.50 7.50 7.50 7.50 7.50 7.50 7.48 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.04 7.04 7.03 7.03 7.03 7.02 7.02 7.02 7.02 7.01 7.01
S
Ph
CF3
3ad
400 MHz, CDCl3
2.03 1.10 2.04 2.00 2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


137.0 133.8 133.8 133.2 132.8 132.1 131.0 130.7 128.6 126.0 125.9 125.9 125.9 124.7 122.0
88.0 84.7
S
Ph
CF3
3ad
101 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



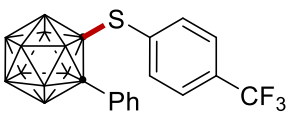
3ad

128 MHz, $CDCl_3$



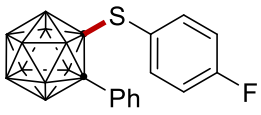
3ad

128 MHz, $CDCl_3$



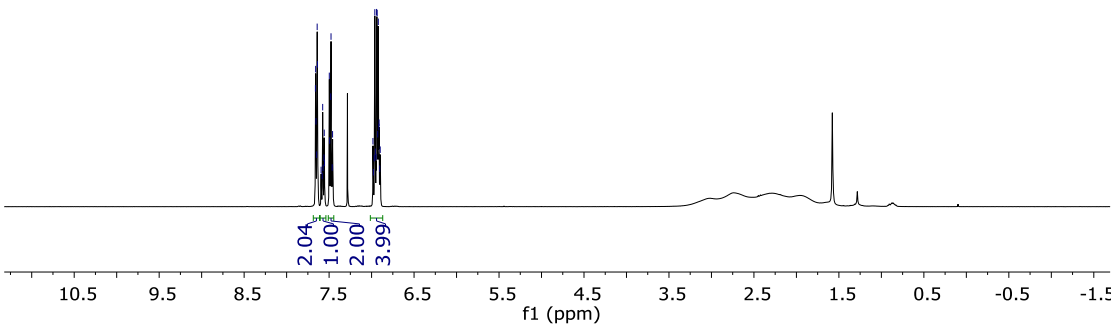
3ad

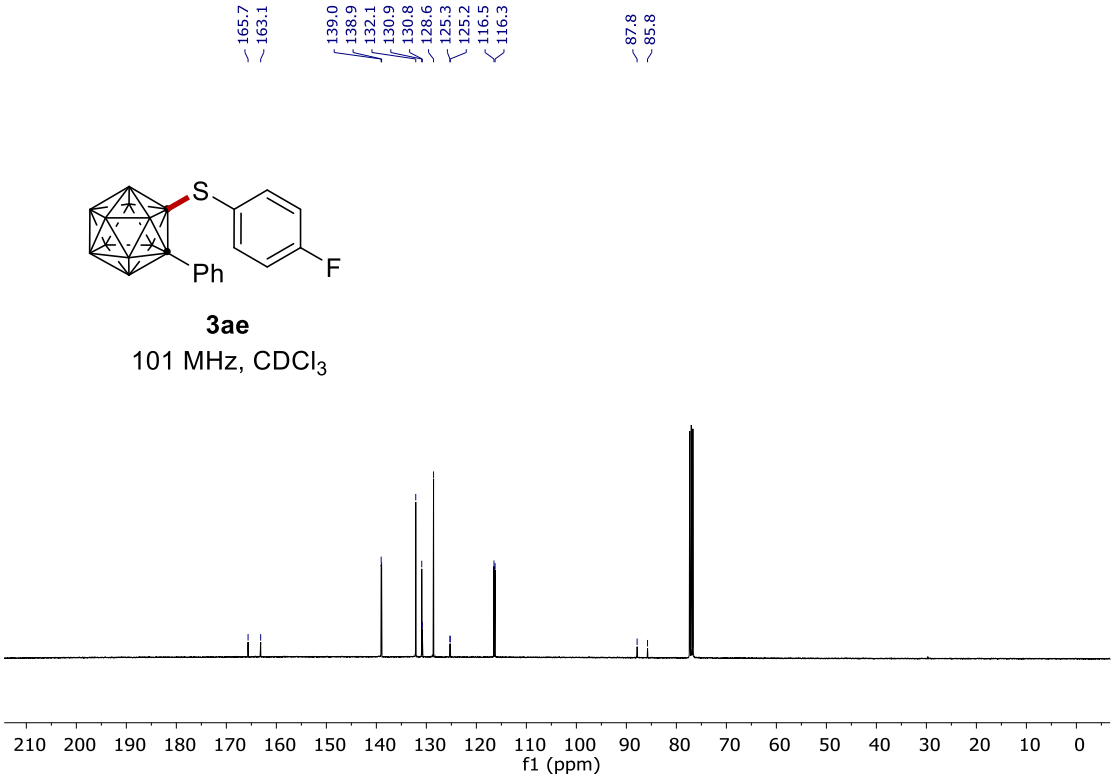
376 MHz, $CDCl_3$



3ae

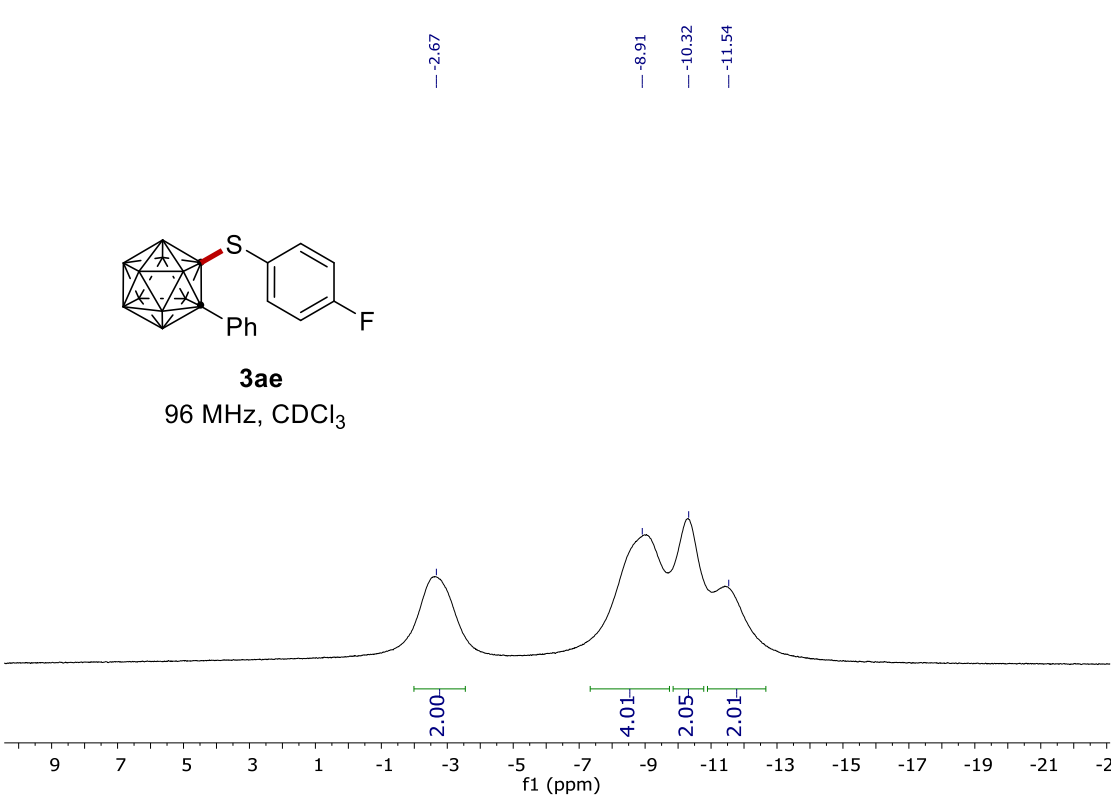
400 MHz, $CDCl_3$





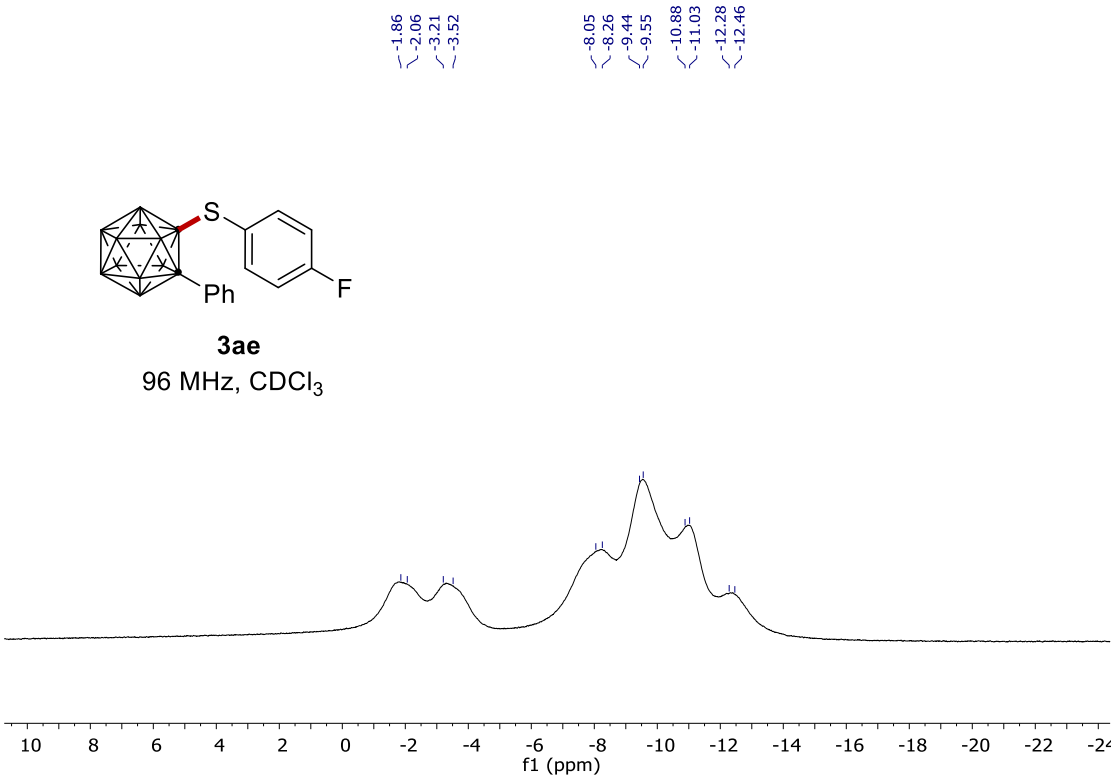
3ae

101 MHz, $CDCl_3$



3ae

96 MHz, $CDCl_3$



3ae

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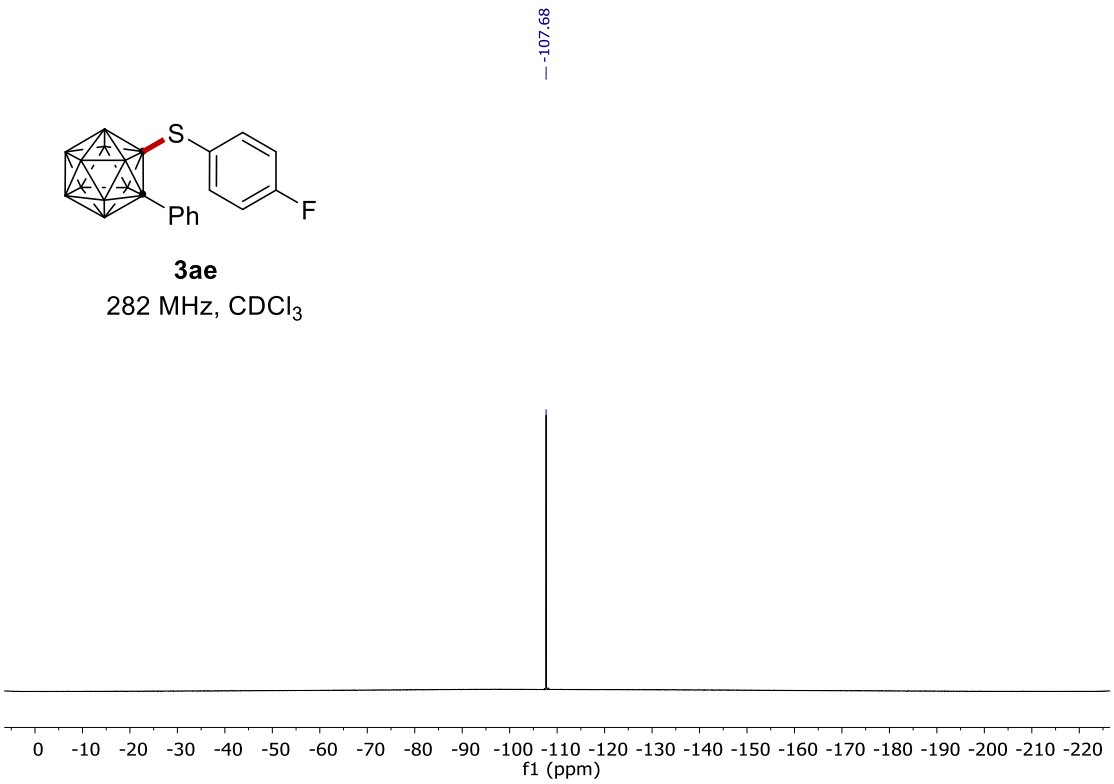

3ae

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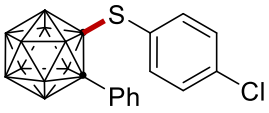

3af

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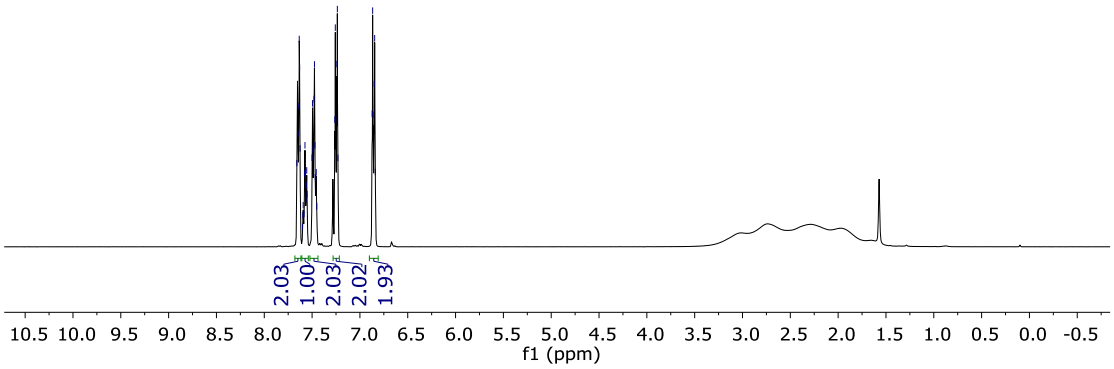

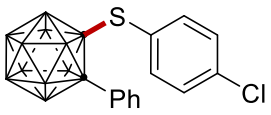

3af

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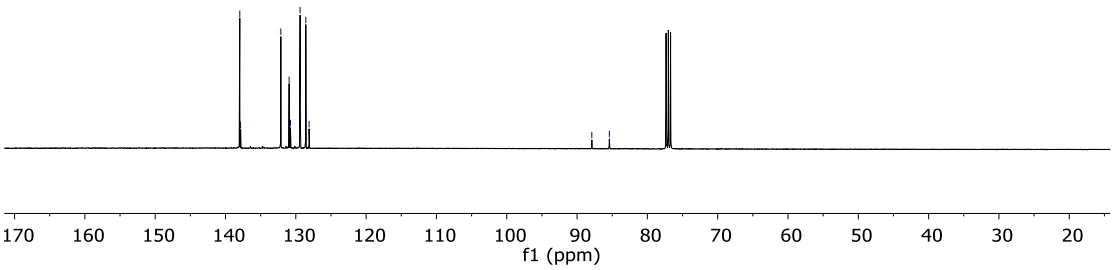
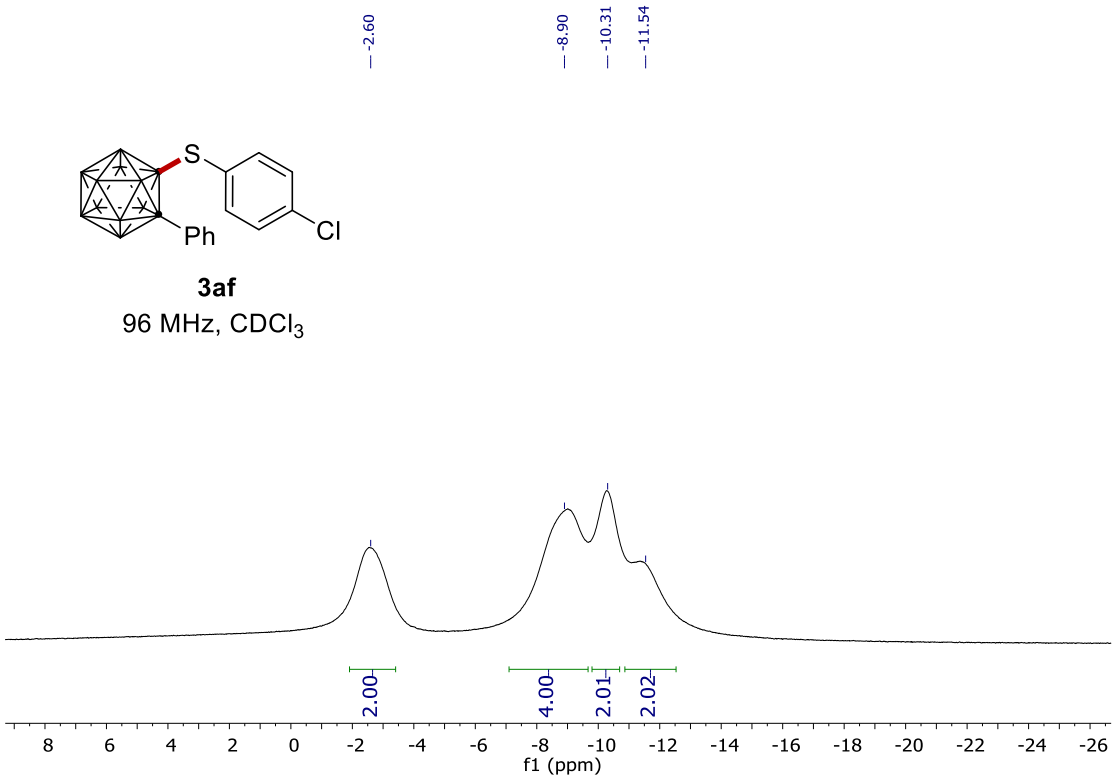
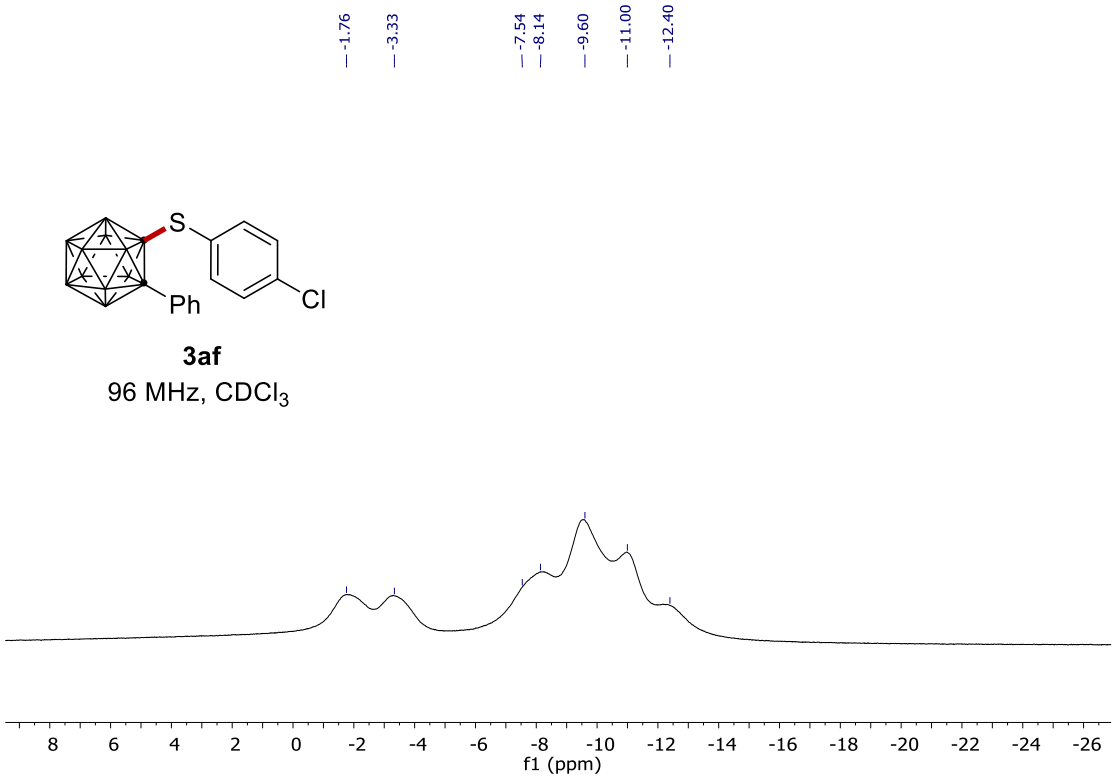




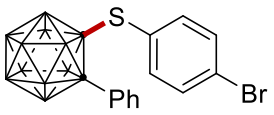
3af

96 MHz, $CDCl_3$



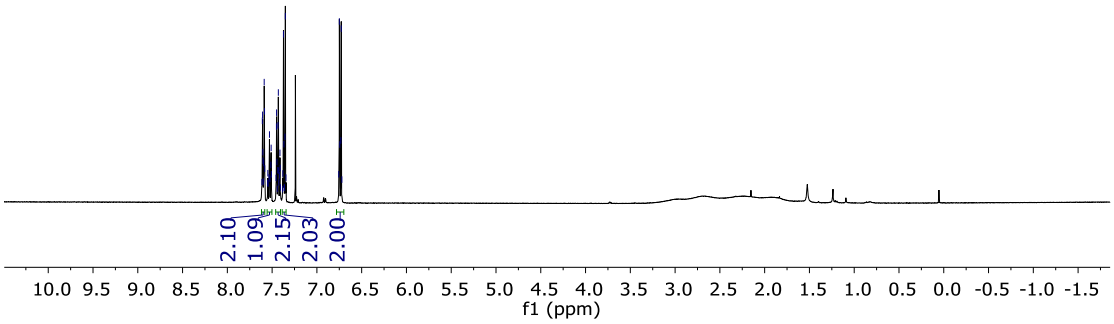
3af

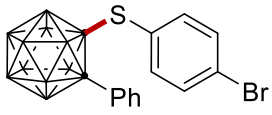
96 MHz, $CDCl_3$



3ag

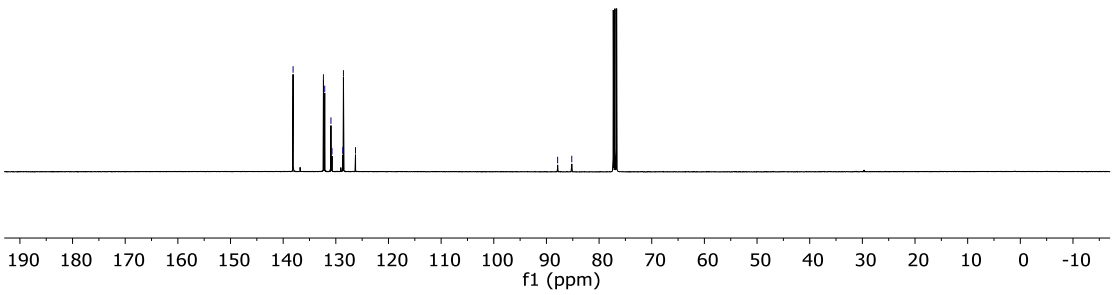
400 MHz, $CDCl_3$

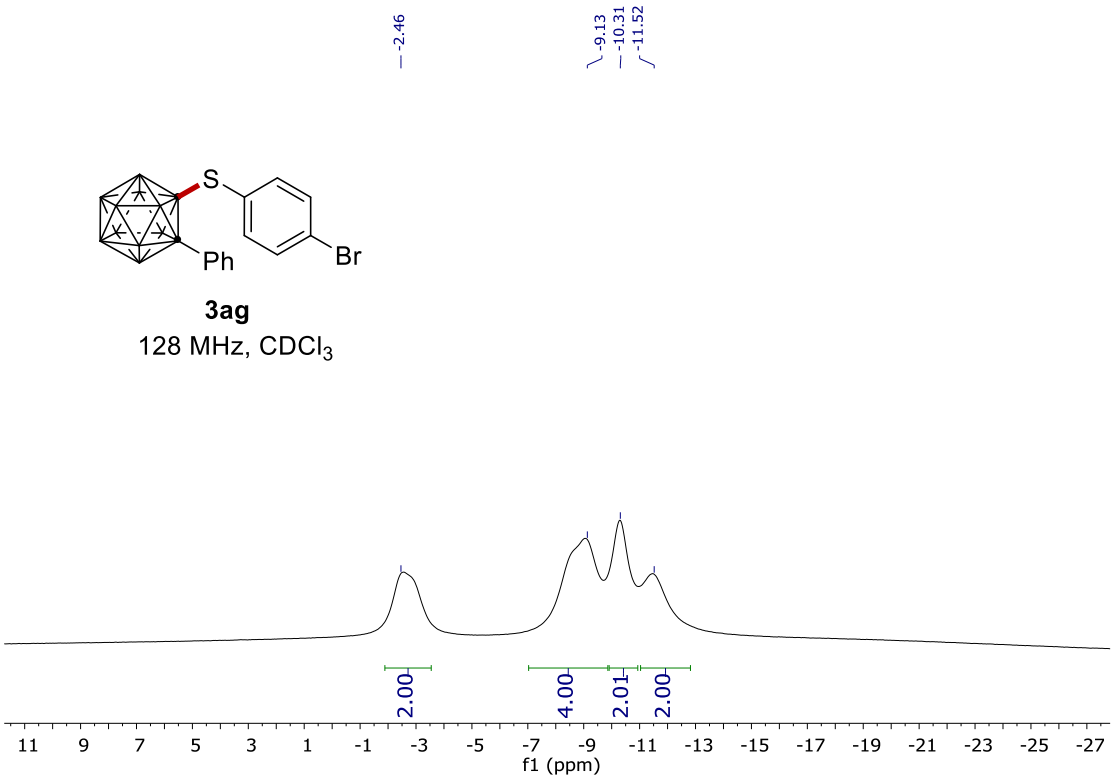




3ag

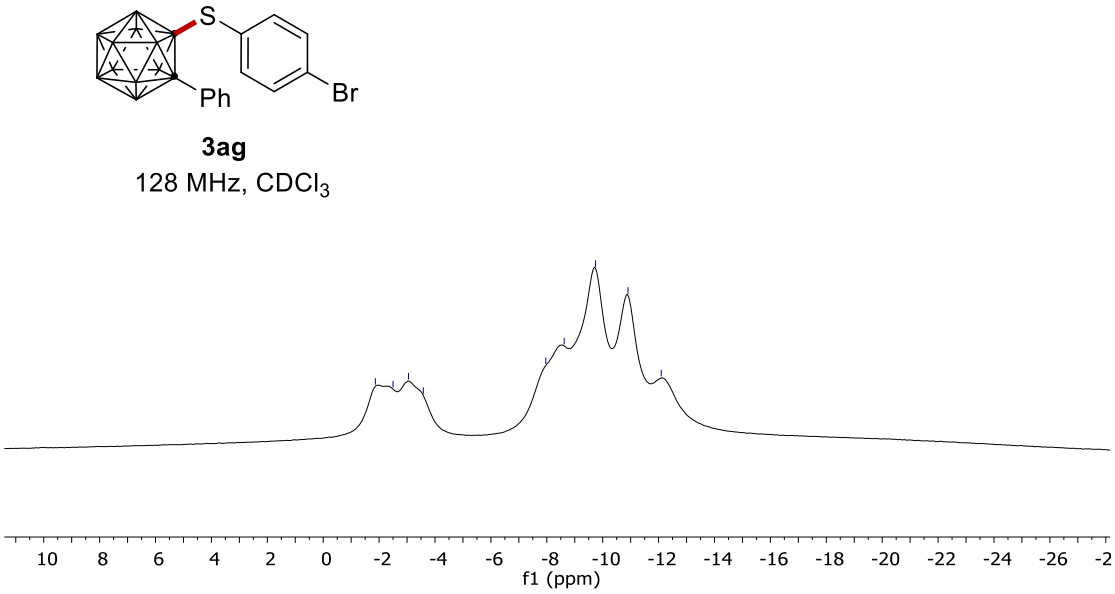
101 MHz, $CDCl_3$





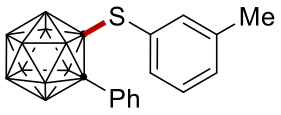
3ag

128 MHz, $CDCl_3$



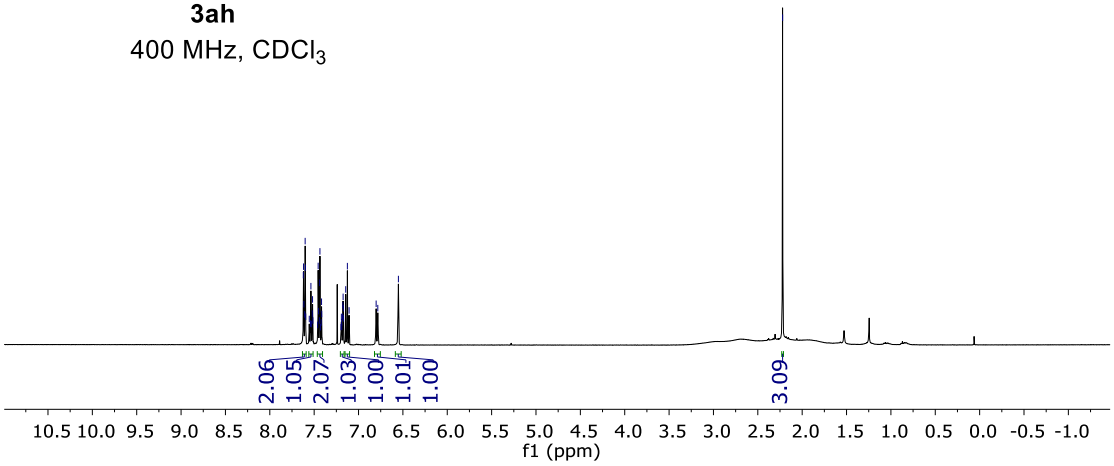
3ag

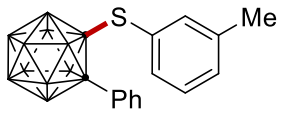
128 MHz, $CDCl_3$



3ah

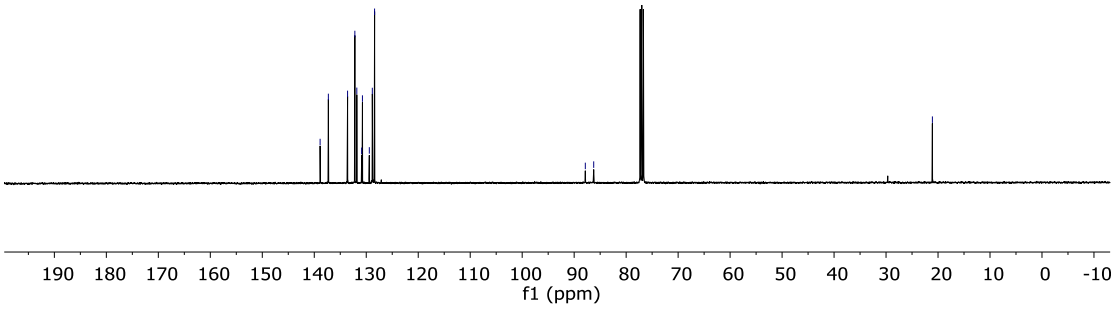
400 MHz, $CDCl_3$

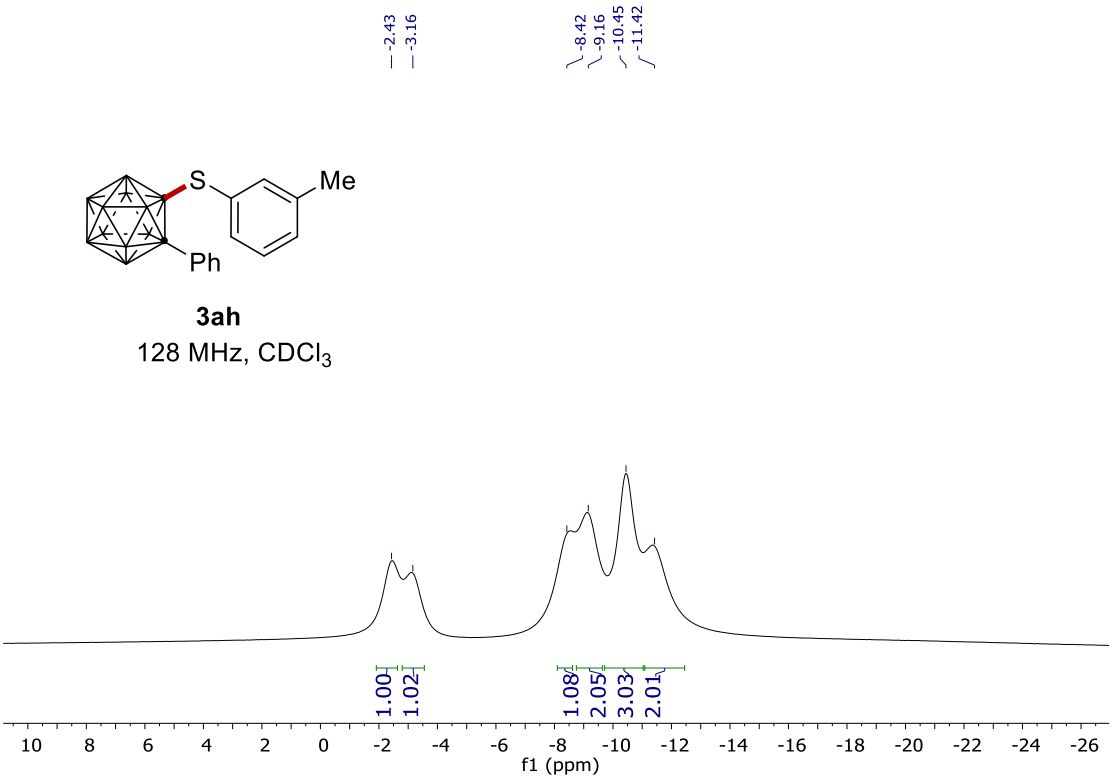




3ah

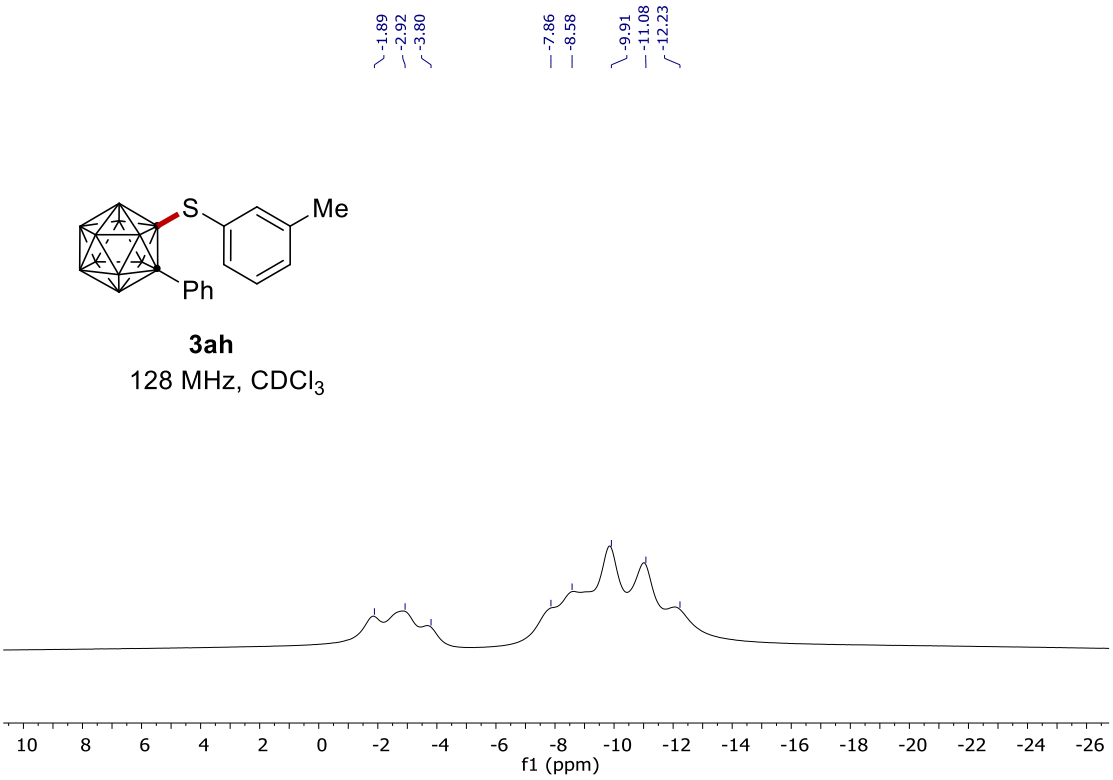
101 MHz, $CDCl_3$





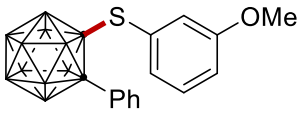
3ah

128 MHz, $CDCl_3$



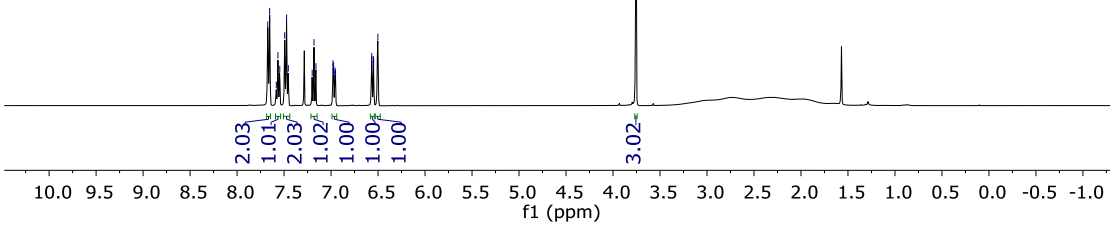
3ah

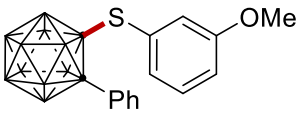
128 MHz, $CDCl_3$



3ai

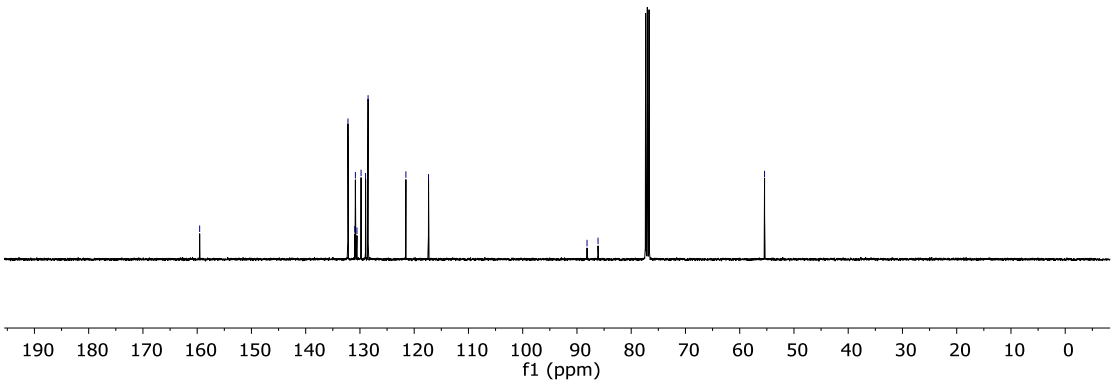
400 MHz, $CDCl_3$

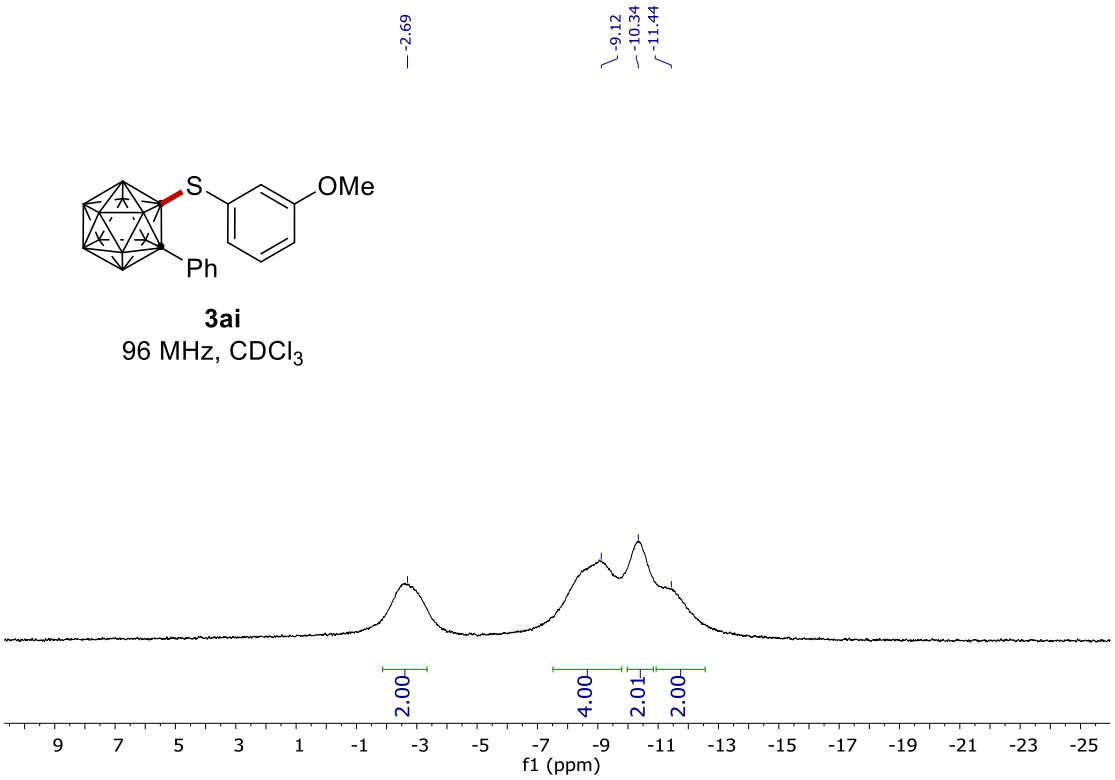




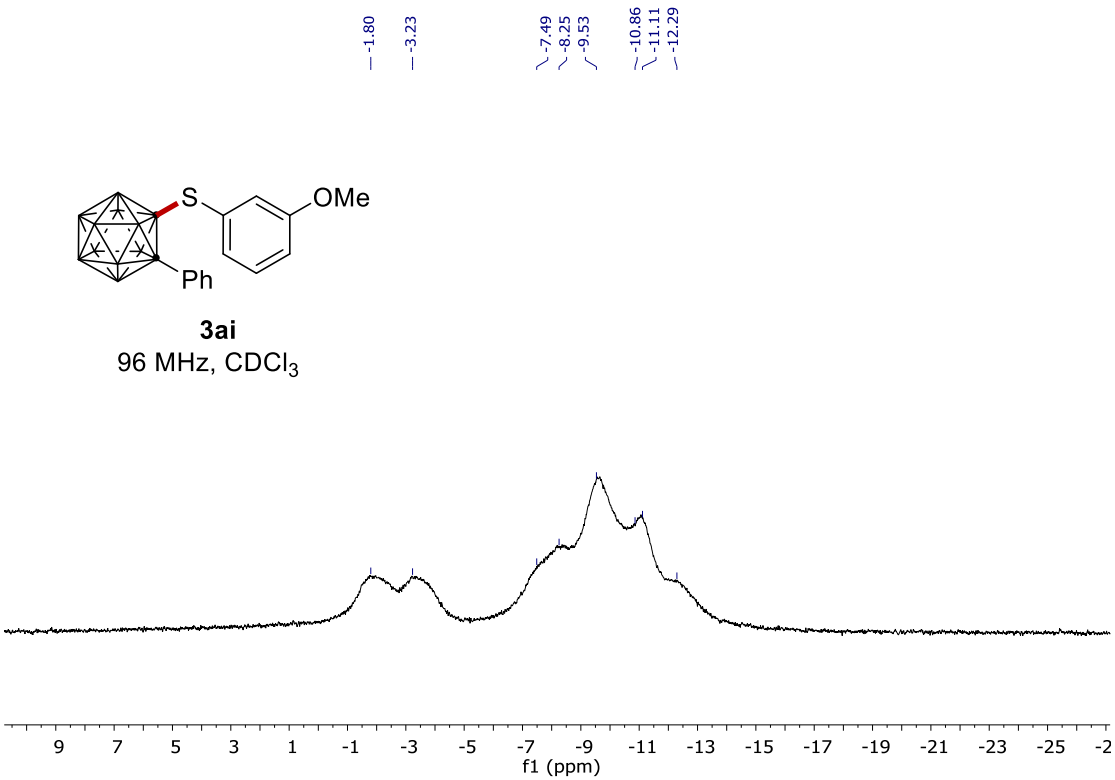
3ai

101 MHz, $CDCl_3$

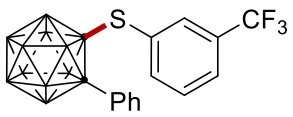




3ai
96 MHz, $CDCl_3$

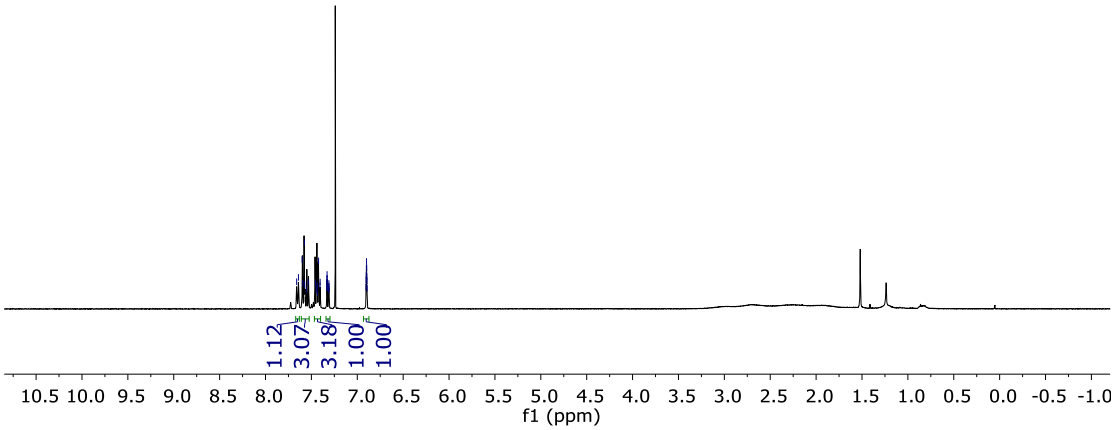


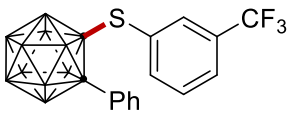
3ai
96 MHz, $CDCl_3$



3aj

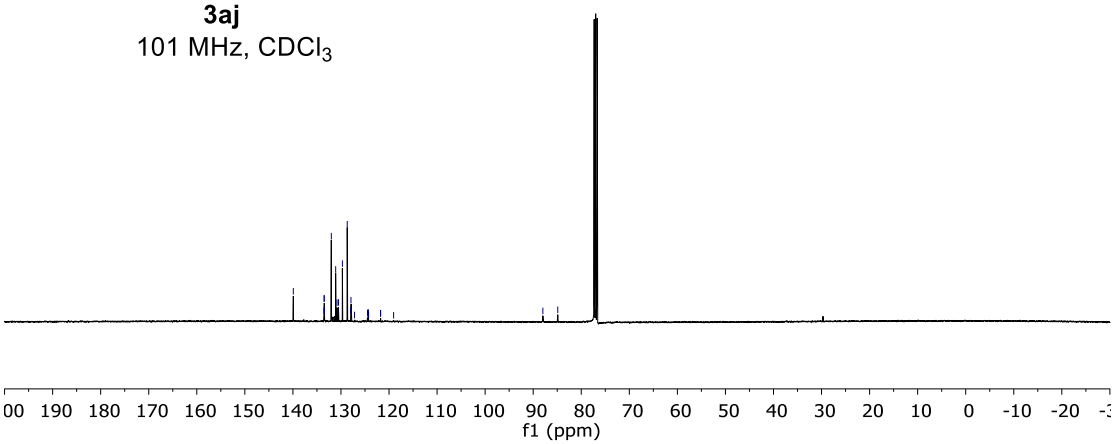
400 MHz, $CDCl_3$

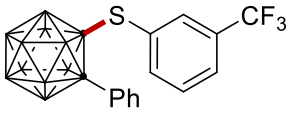




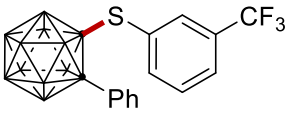
3aj

101 MHz, $CDCl_3$

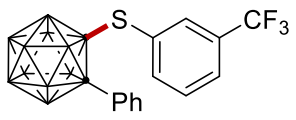




3aj
128 MHz, $CDCl_3$

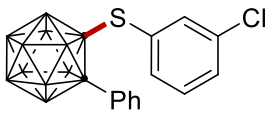


3aj
128 MHz, $CDCl_3$



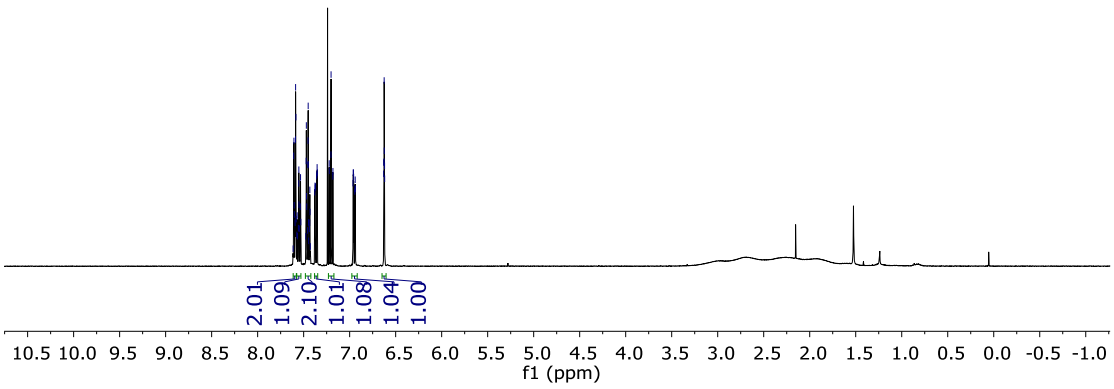
3aj

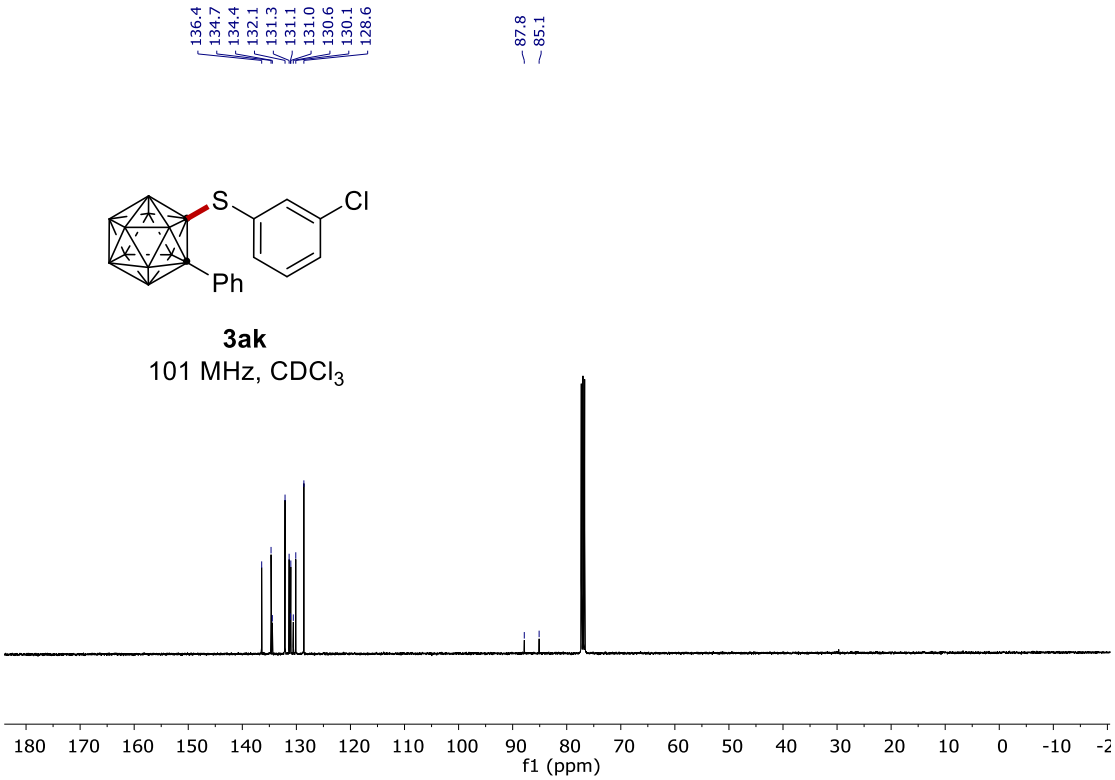
376 MHz, $CDCl_3$



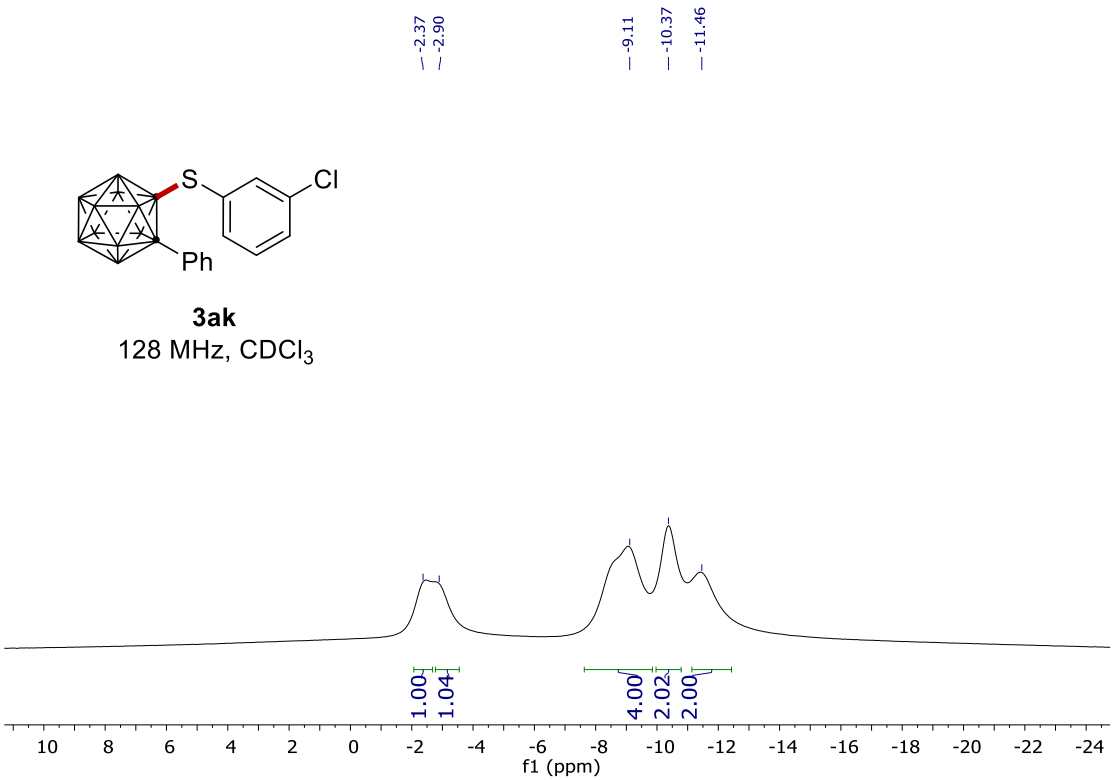
3ak

400 MHz, $CDCl_3$



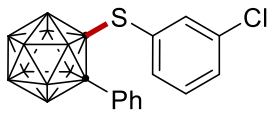


3ak
101 MHz, $CDCl_3$

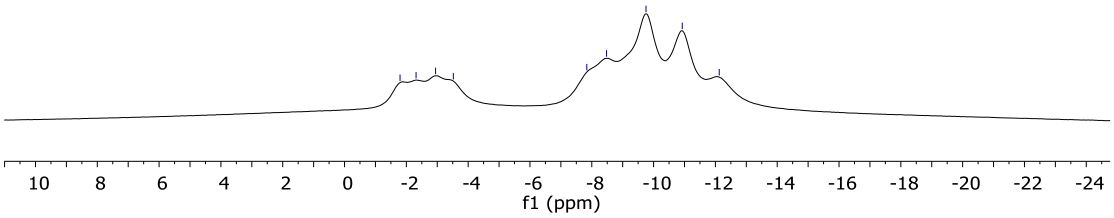


3ak
128 MHz, $CDCl_3$

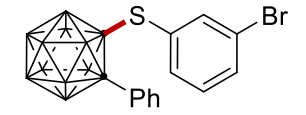
-1.80
-2.31
-2.95
-3.52
-7.84
-8.48
-9.75
-10.93
-12.12



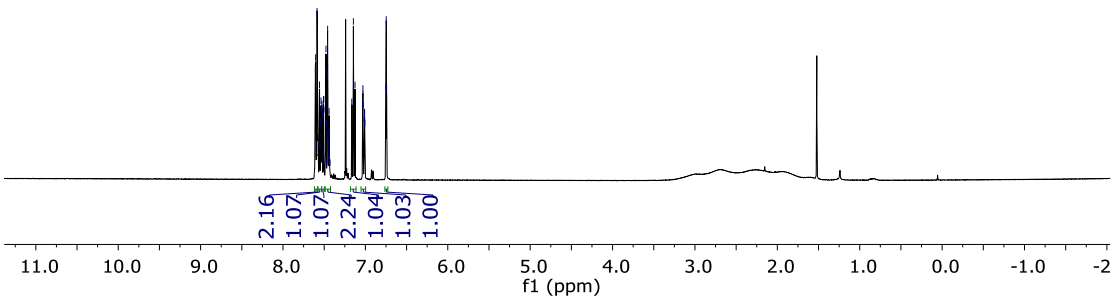
3ak
128 MHz, $CDCl_3$

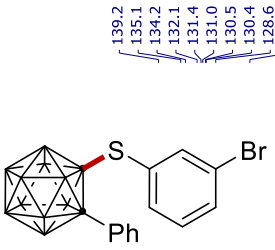


7.61 7.60 7.59 7.58 7.56 7.56 7.55 7.54 7.54 7.54 7.53 7.53 7.53 7.52 7.51 7.51 7.51 7.51 7.51 7.50 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.44 7.43 7.43 7.17 7.15 7.13 7.03 7.03 7.03 7.03 7.02 7.01 7.01 7.01 7.01 6.75 6.75 6.74

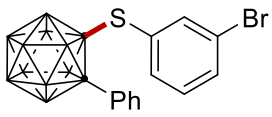


3al
400 MHz, $CDCl_3$

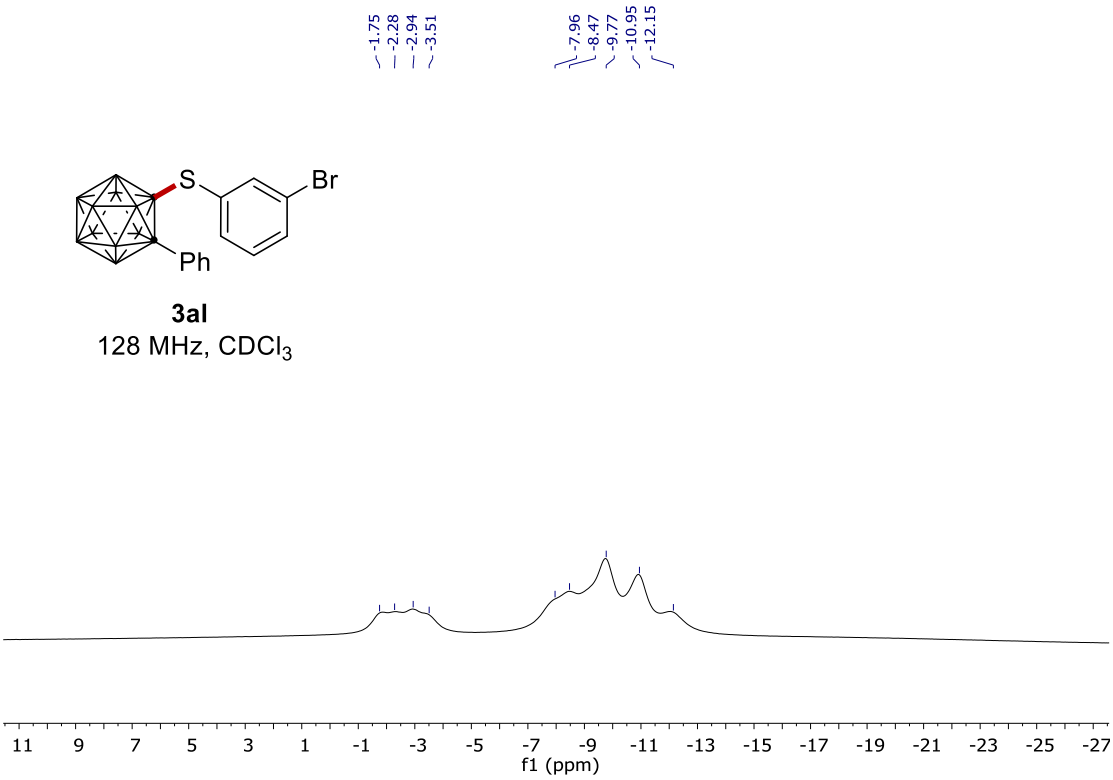




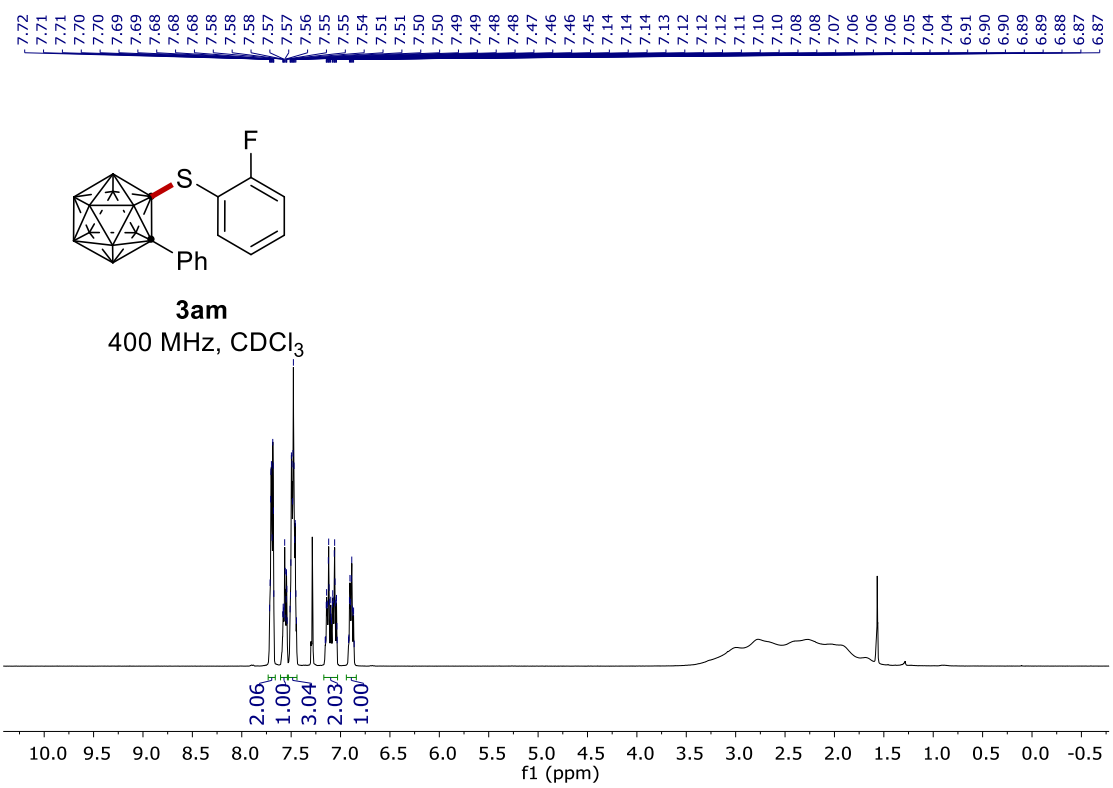
3al
101 MHz, $CDCl_3$



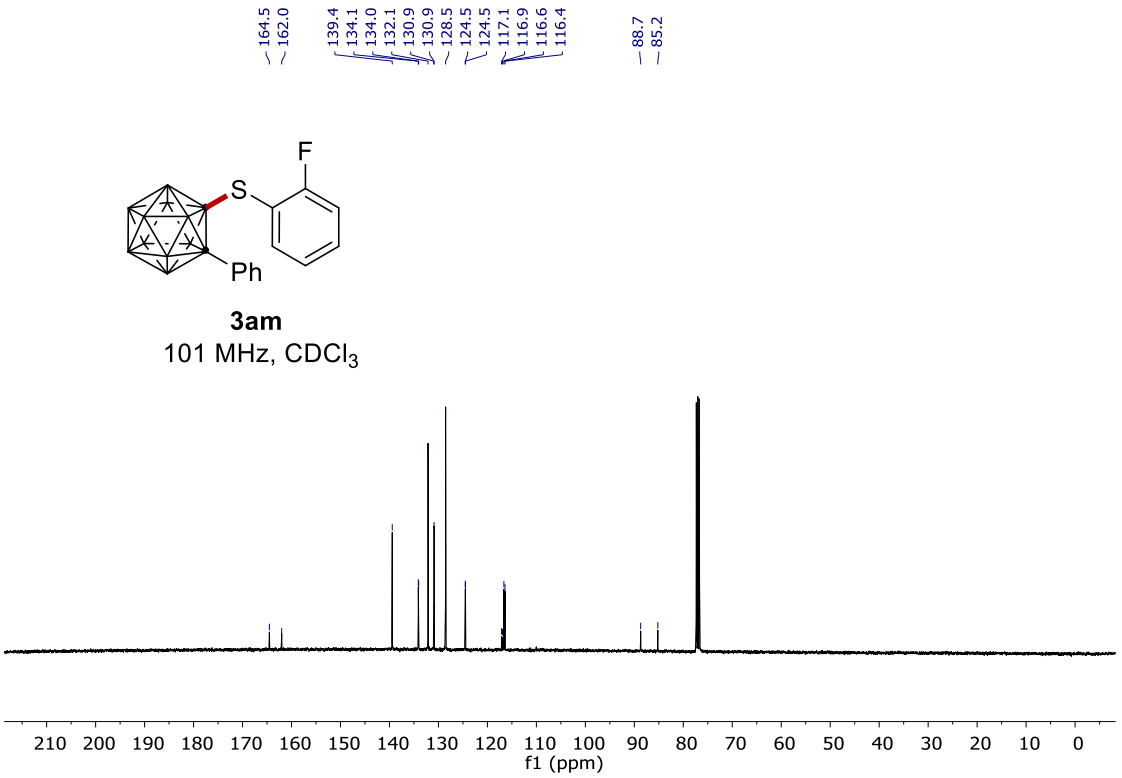
3al
128 MHz, $CDCl_3$



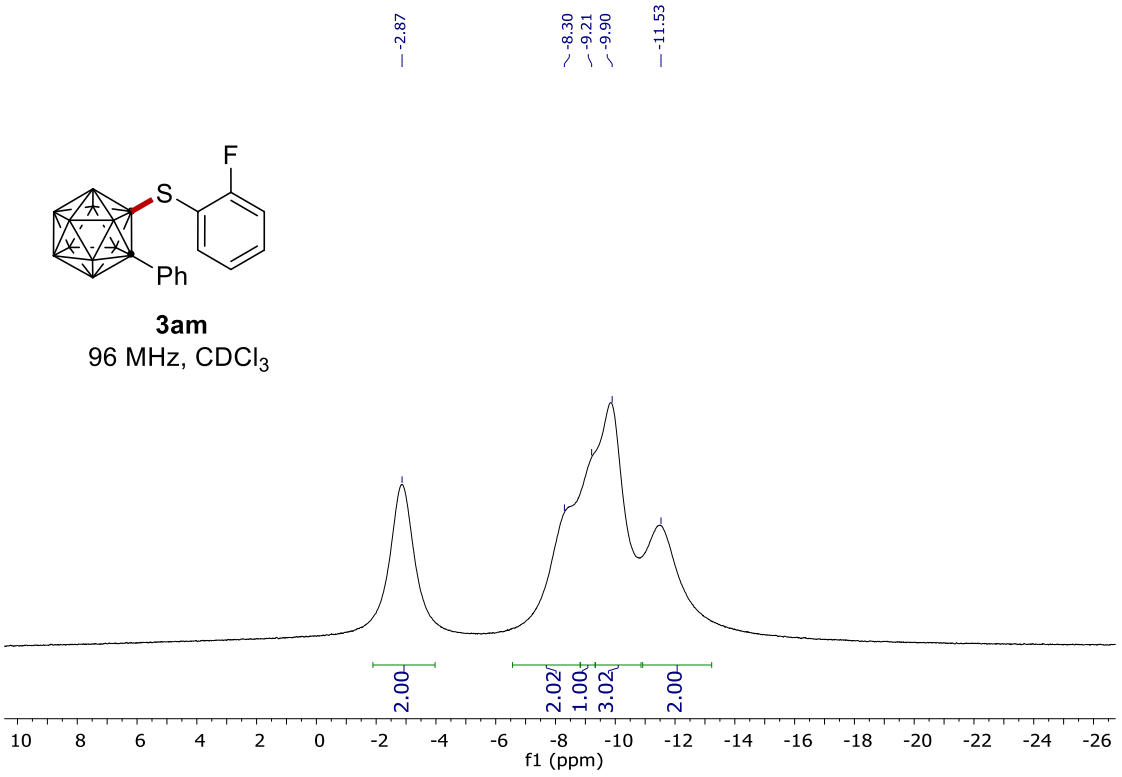
3al
128 MHz, $CDCl_3$



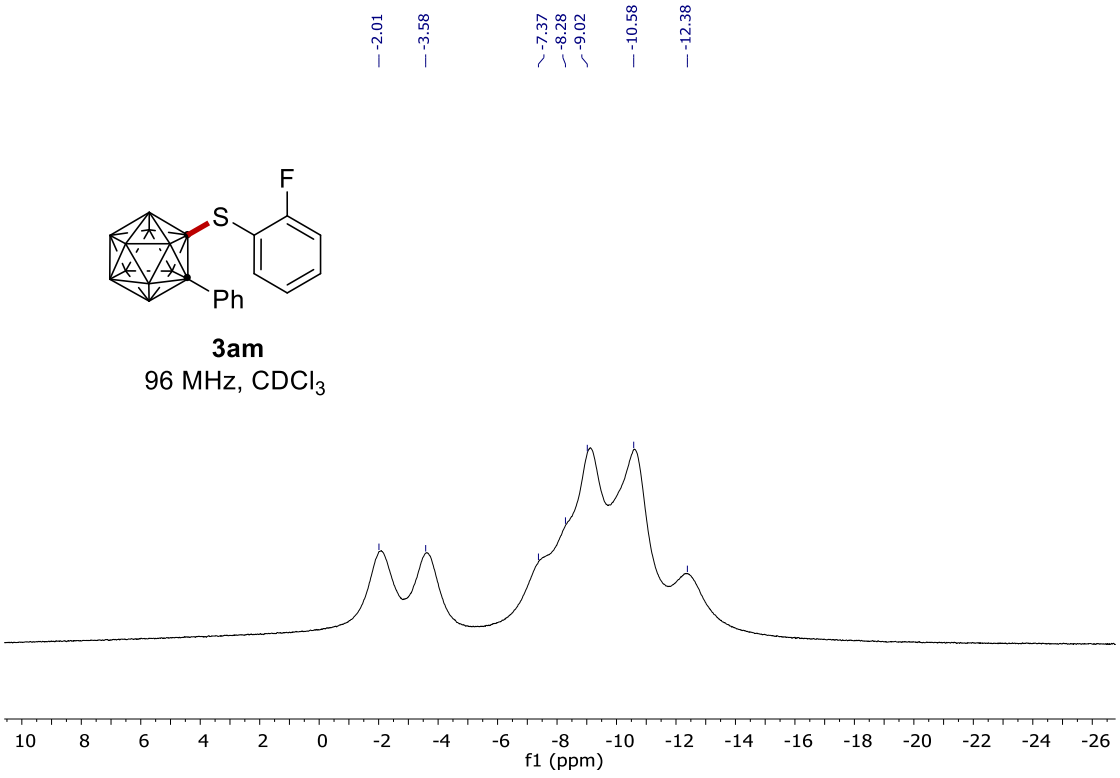
3am
400 MHz, $CDCl_3$



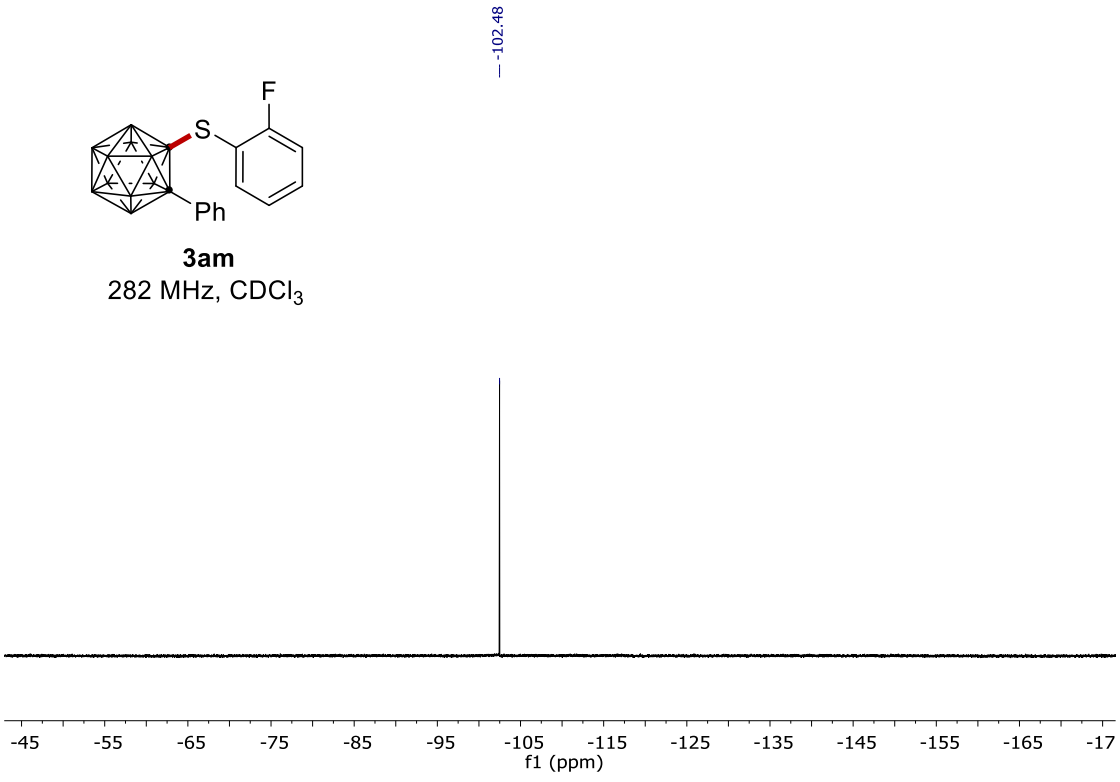
3am
101 MHz, $CDCl_3$



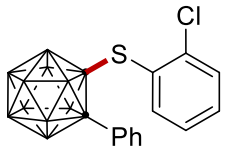
3am
96 MHz, $CDCl_3$



3am
96 MHz, $CDCl_3$

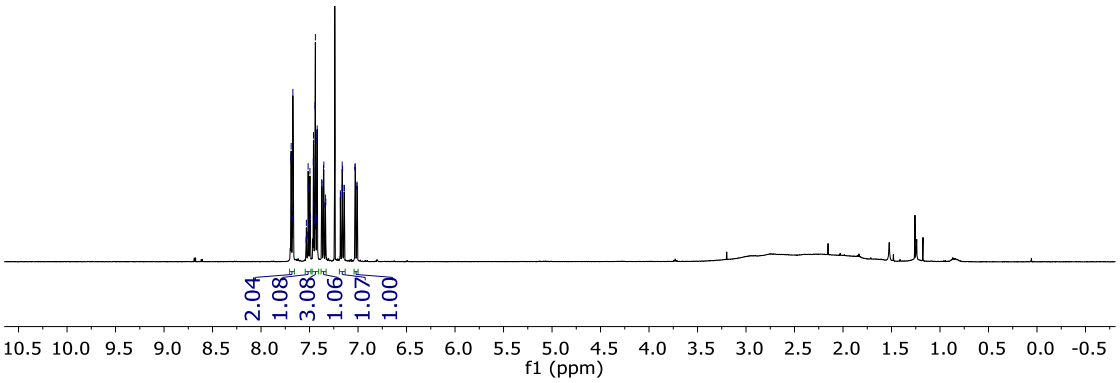


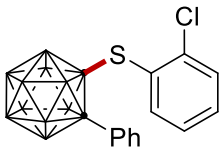
3am
282 MHz, $CDCl_3$



3an

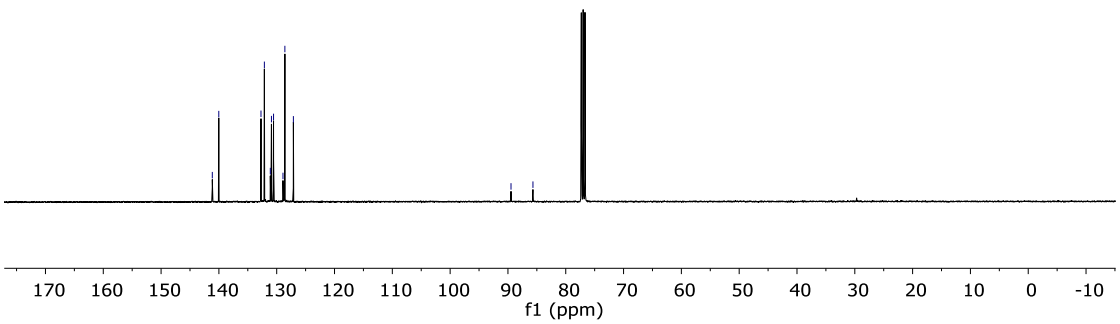
400 MHz, $CDCl_3$

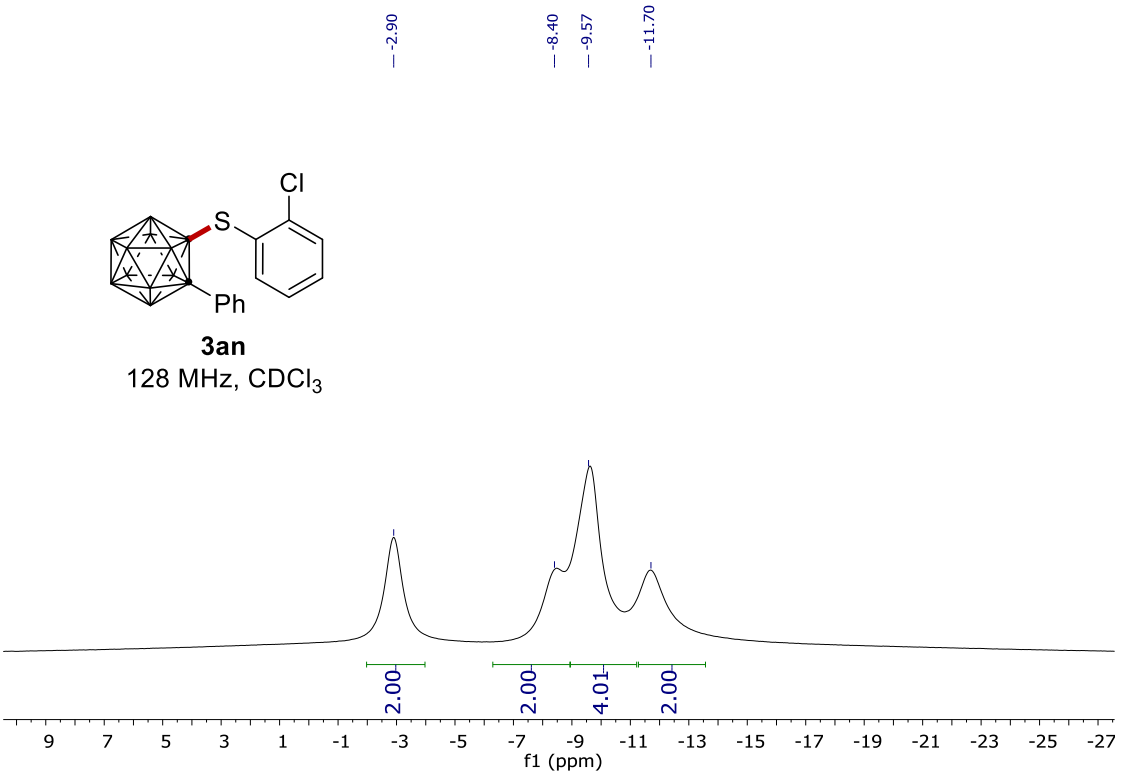




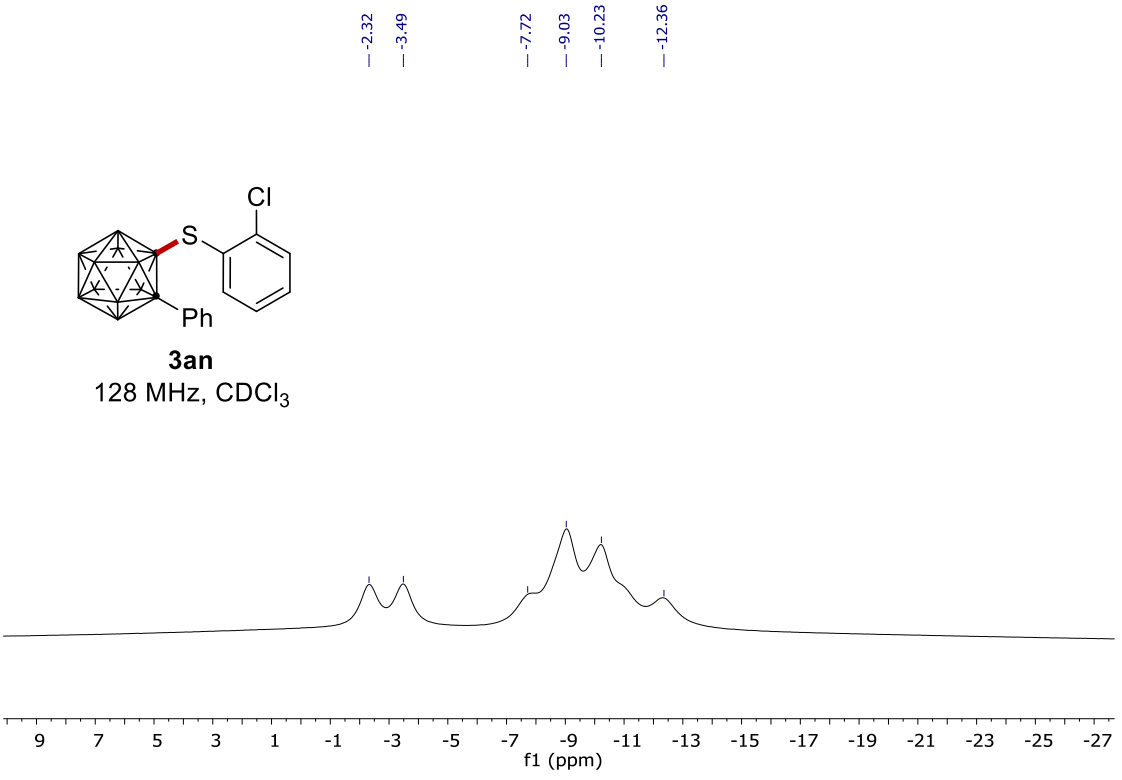
3an

101 MHz, $CDCl_3$

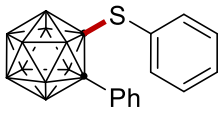




3an
128 MHz, $CDCl_3$

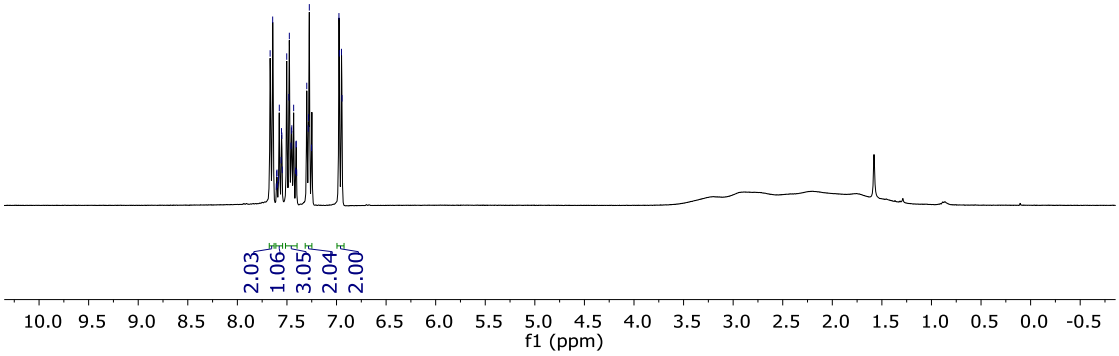


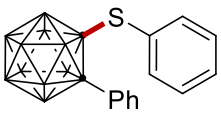
3an
128 MHz, $CDCl_3$



3ao

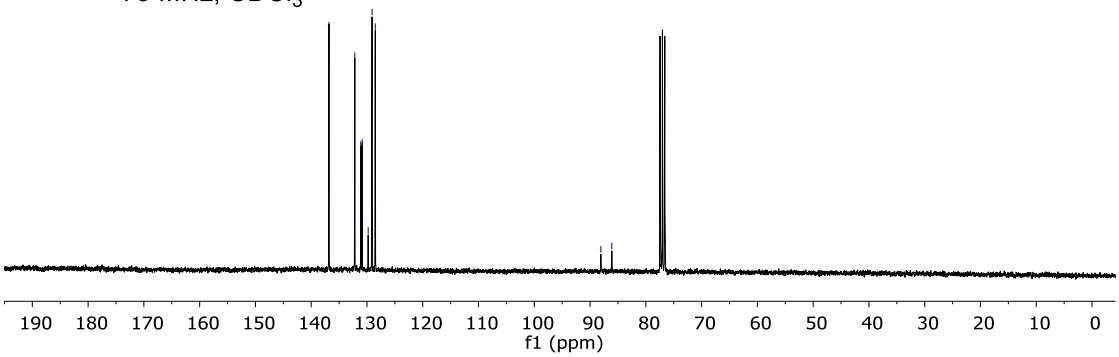
300 MHz, $CDCl_3$

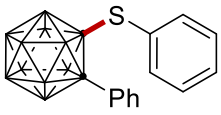




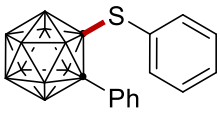
3ao

75 MHz, $CDCl_3$

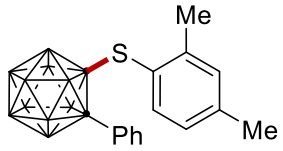




3ao
96 MHz, $CDCl_3$

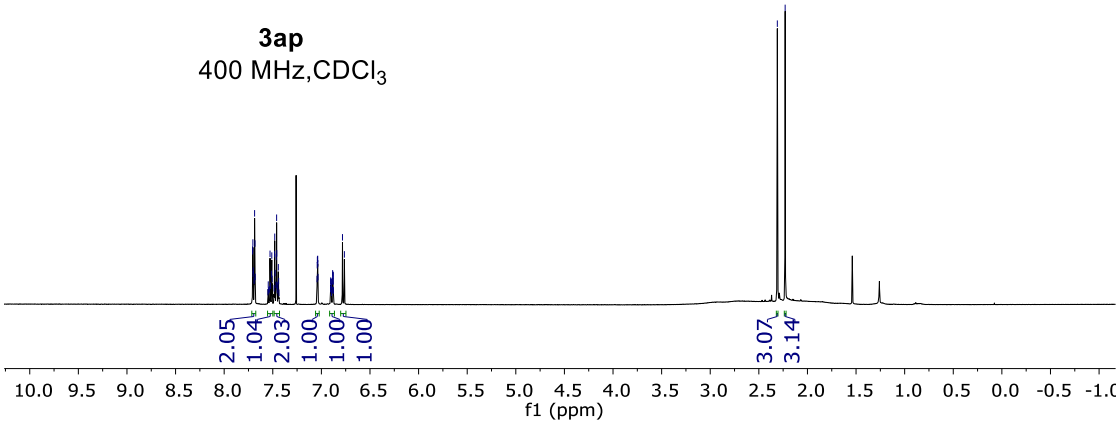


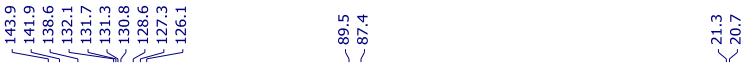
3ao
96 MHz, $CDCl_3$

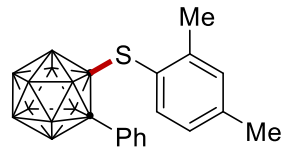


3ap

400 MHz,$CDCl_3$

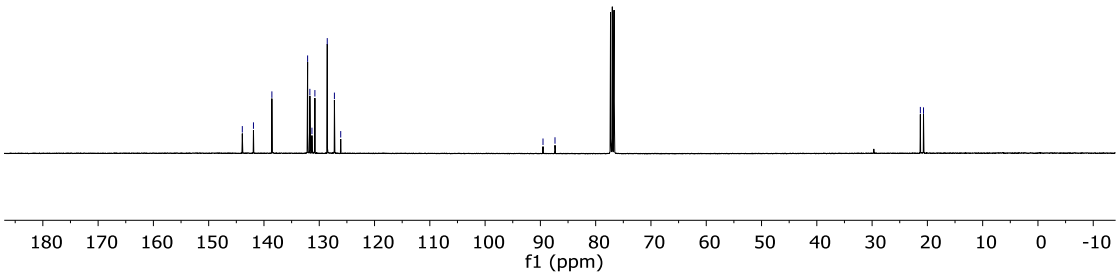


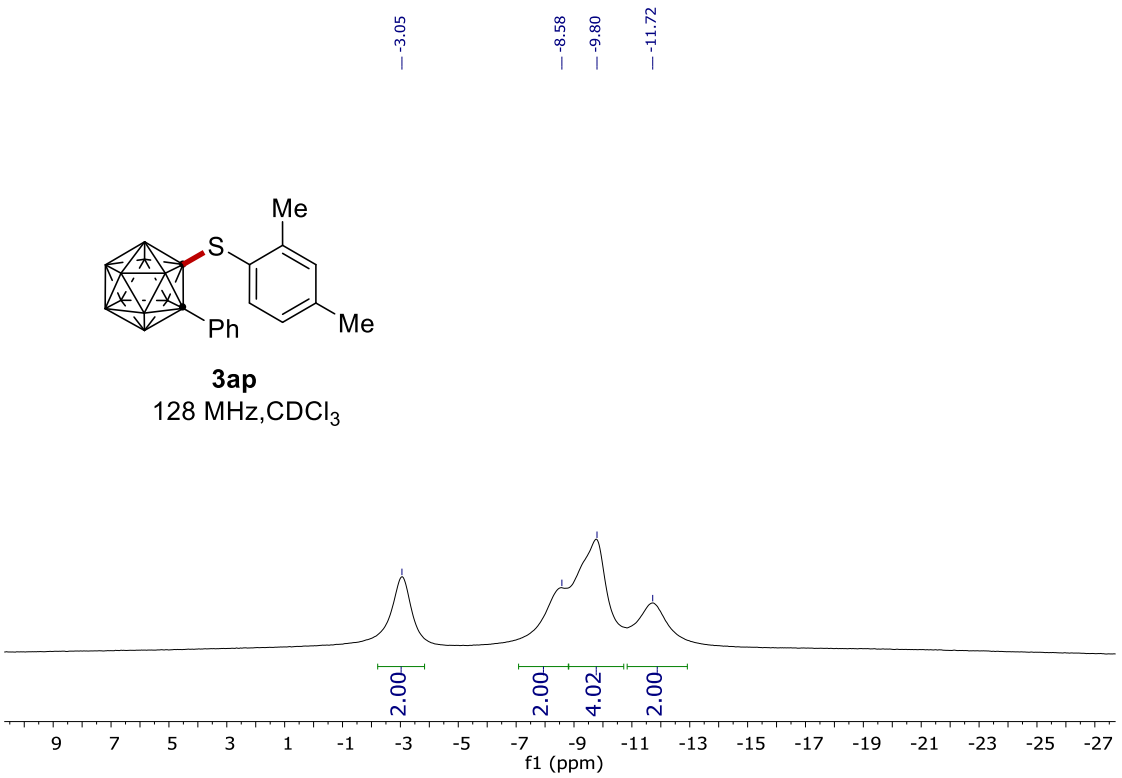




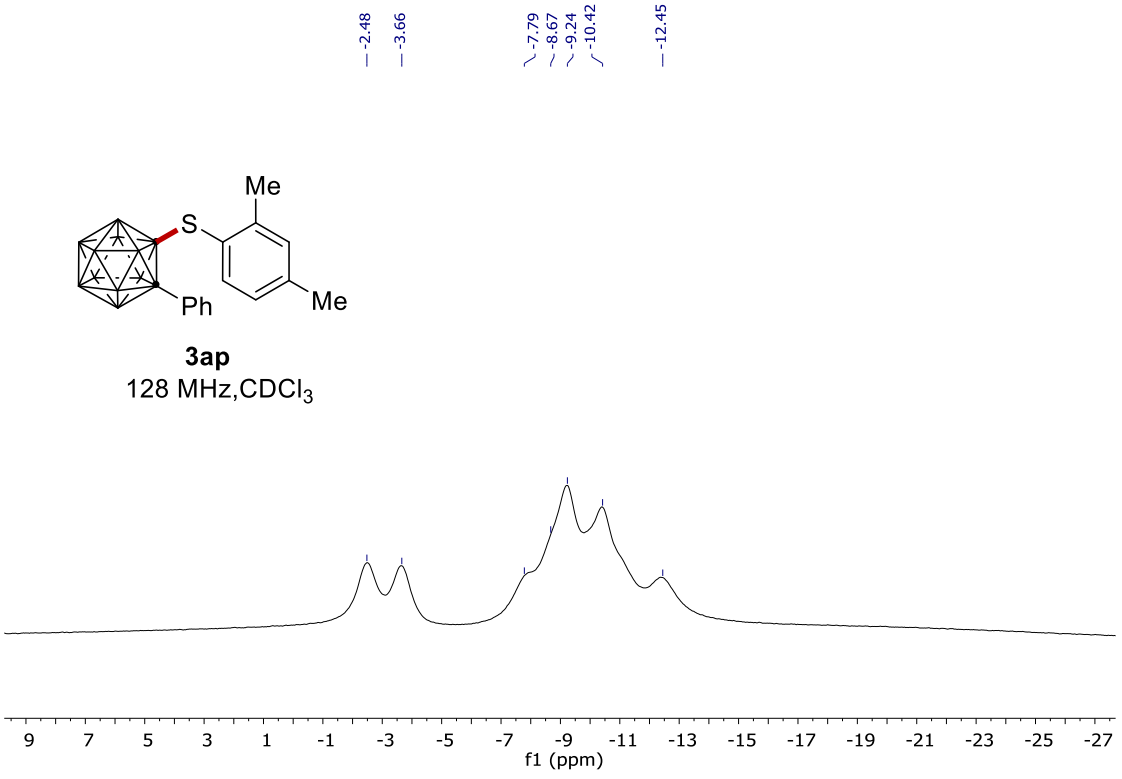
3ap

101 MHz,$CDCl_3$

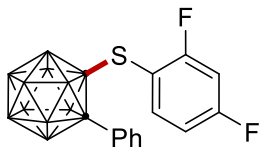




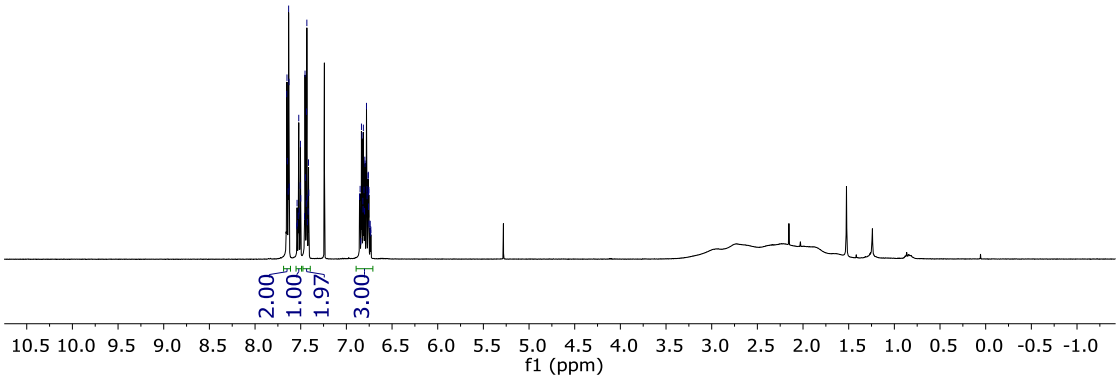
3ap
128 MHz,$CDCl_3$

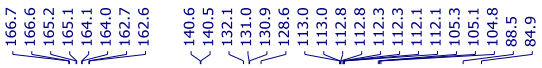


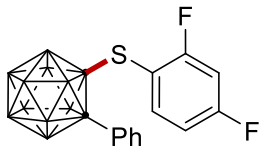
3ap
128 MHz,$CDCl_3$



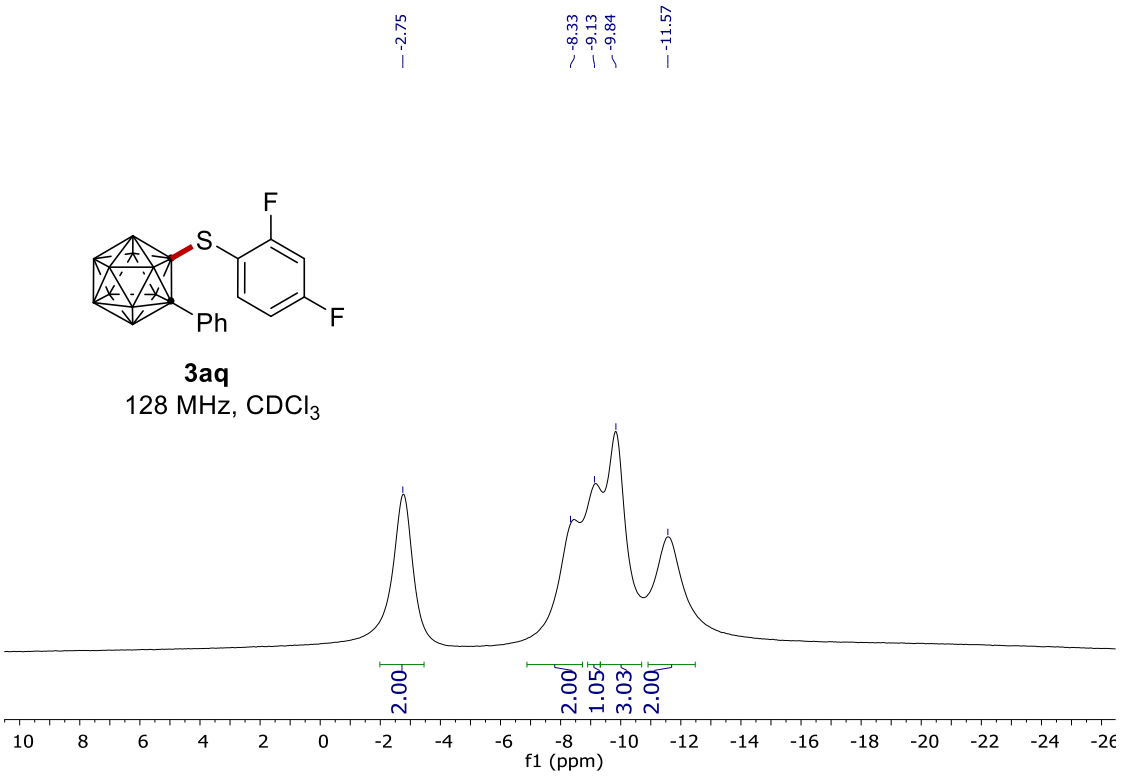
3aq
400 MHz, $CDCl_3$



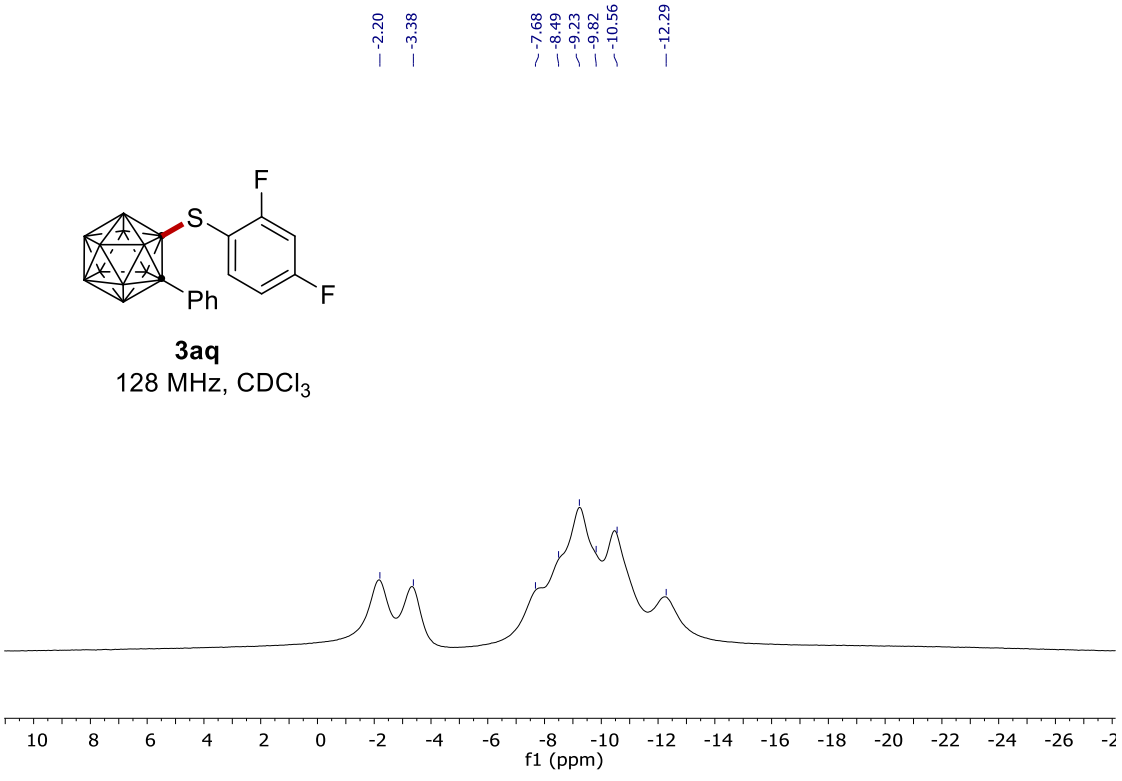




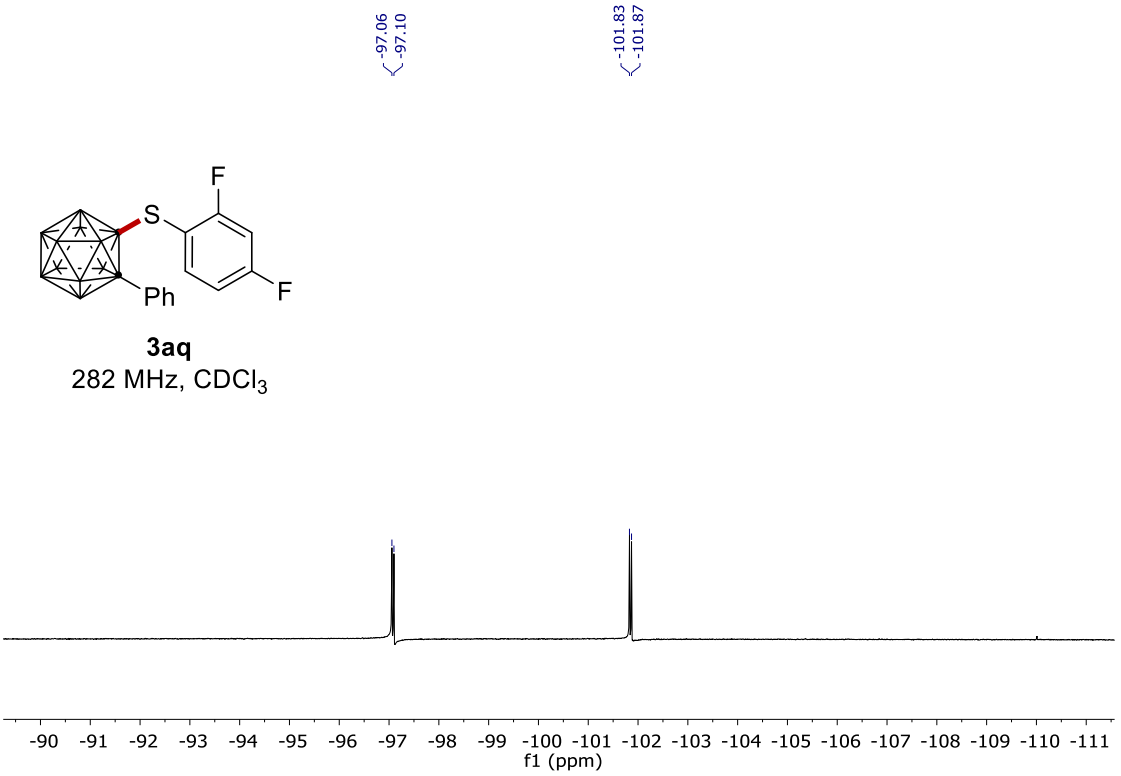
3aq
101 MHz, $CDCl_3$



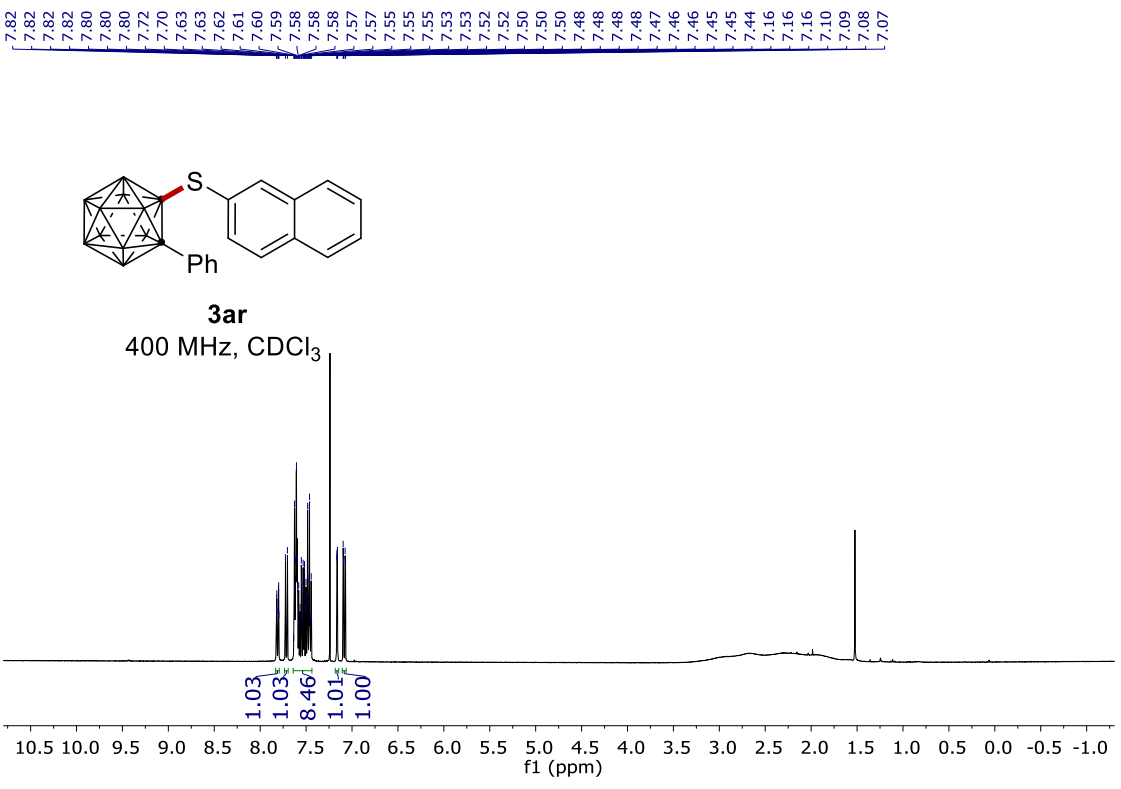
3aq
128 MHz, $CDCl_3$



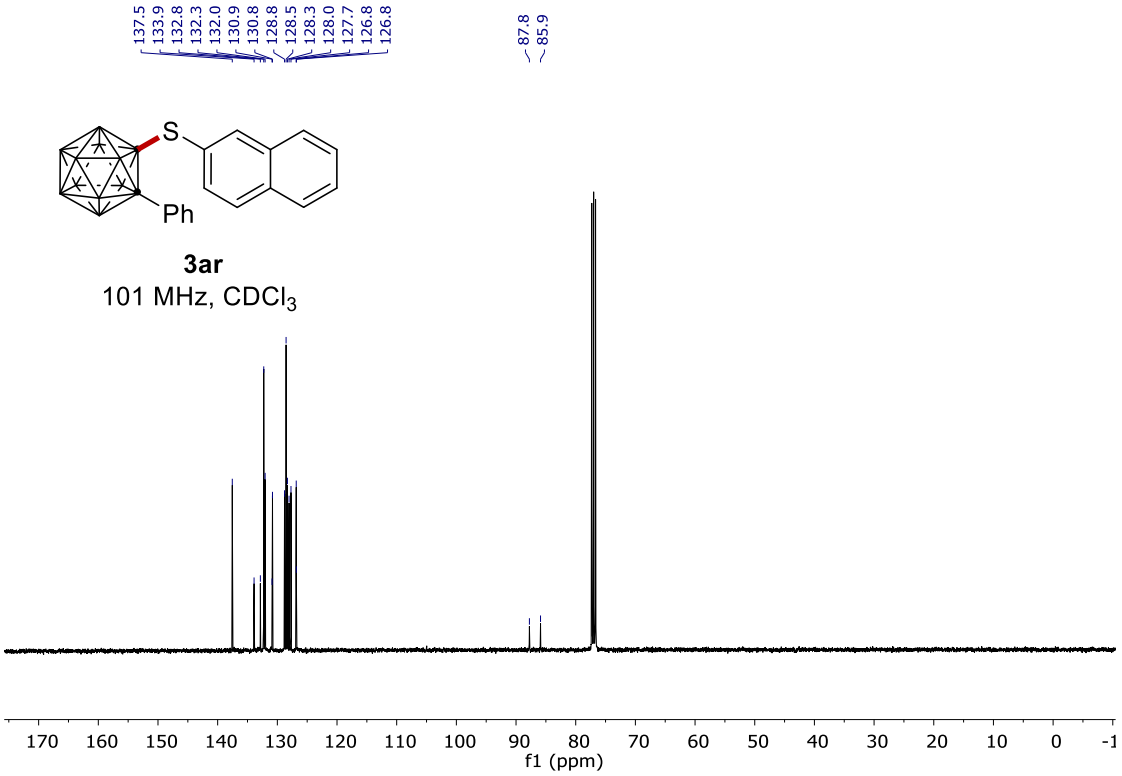
3aq
128 MHz, $CDCl_3$



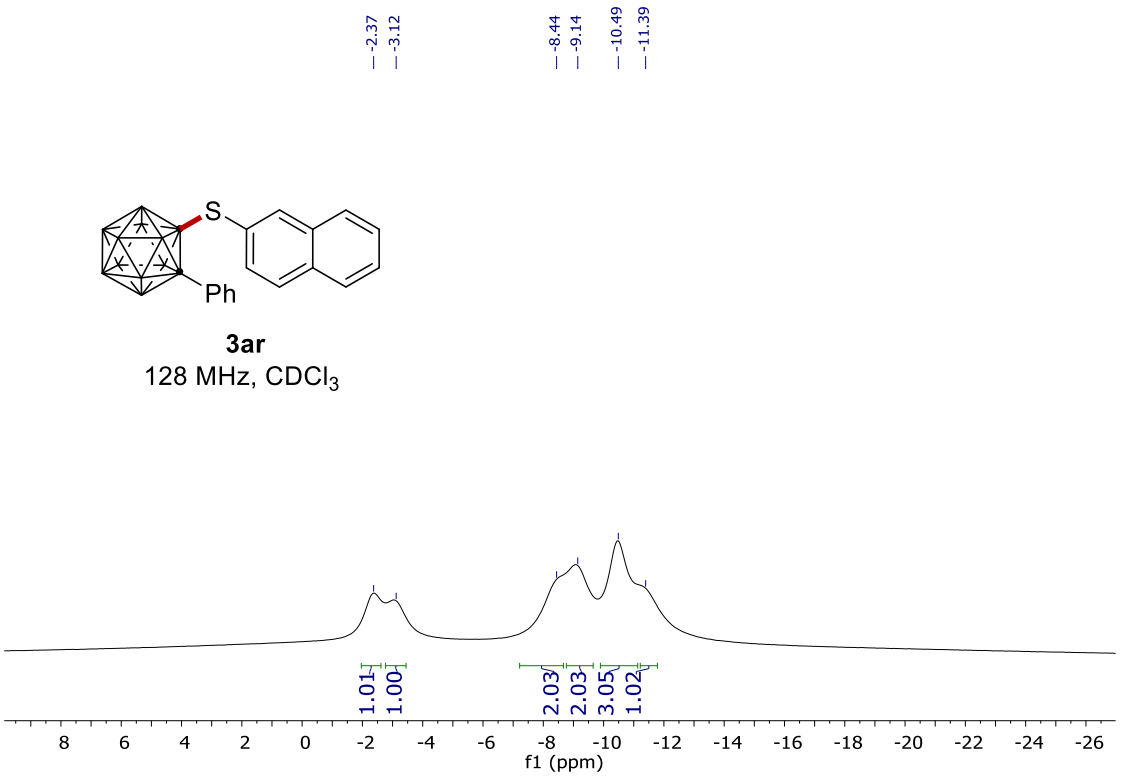
3aq
282 MHz, $CDCl_3$



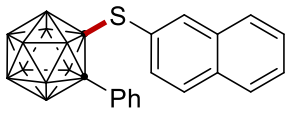
3ar
400 MHz, $CDCl_3$



3ar
101 MHz, $CDCl_3$

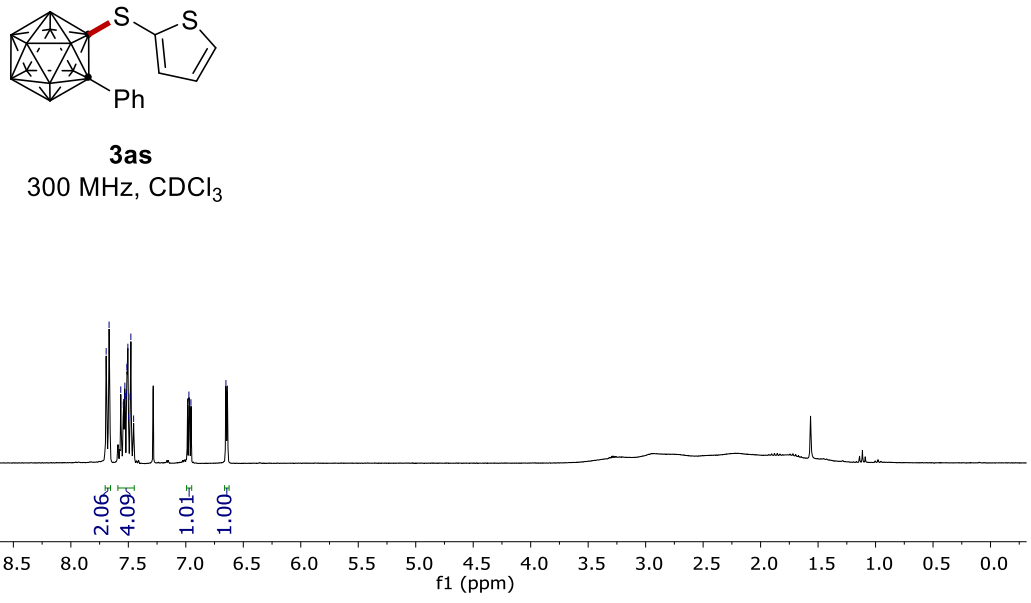


3ar
128 MHz, $CDCl_3$



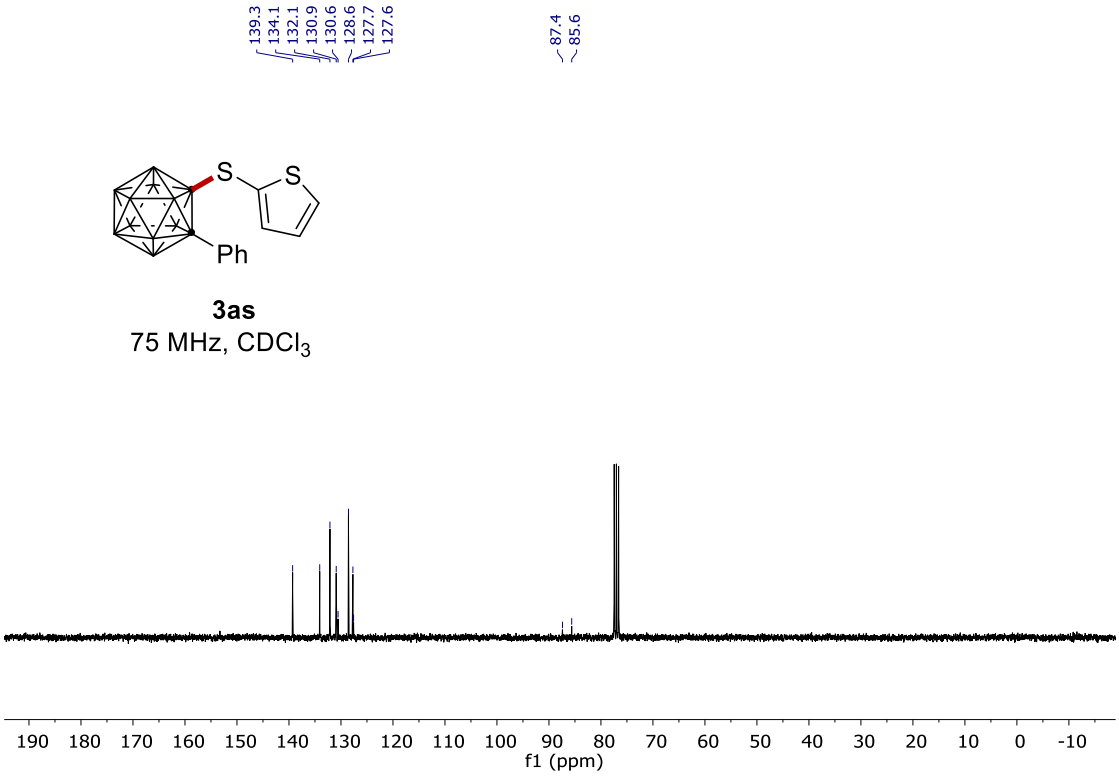
3ar

128 MHz, $CDCl_3$

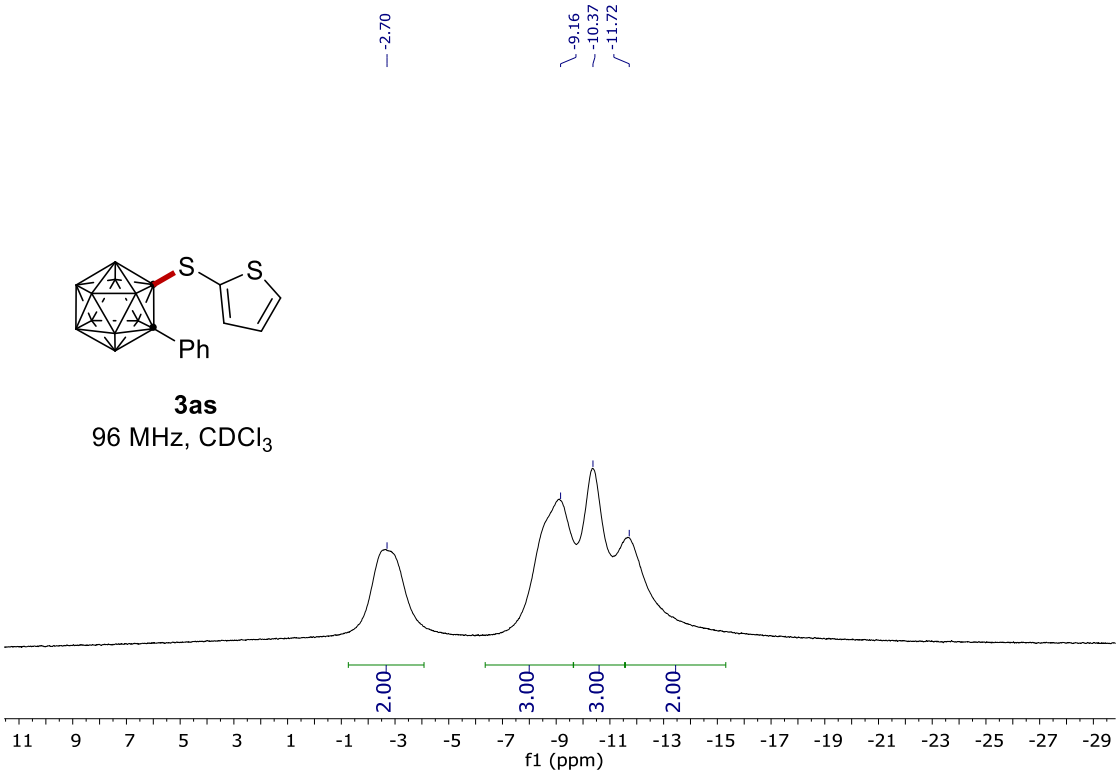


3as

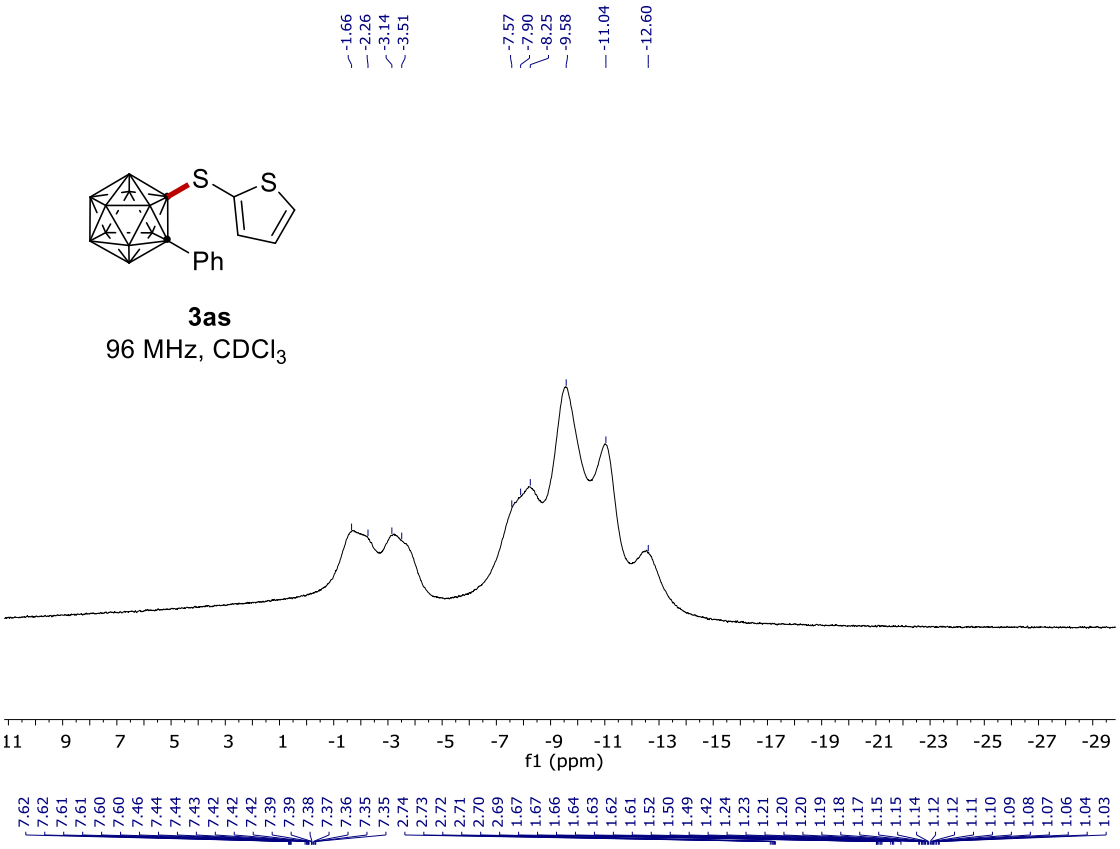
300 MHz, $CDCl_3$

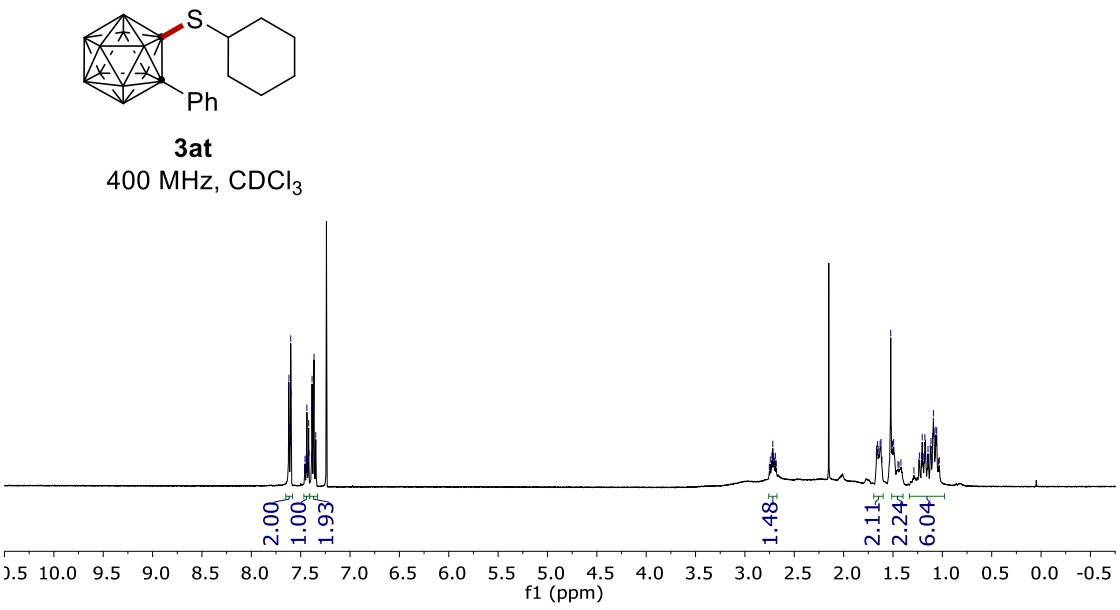


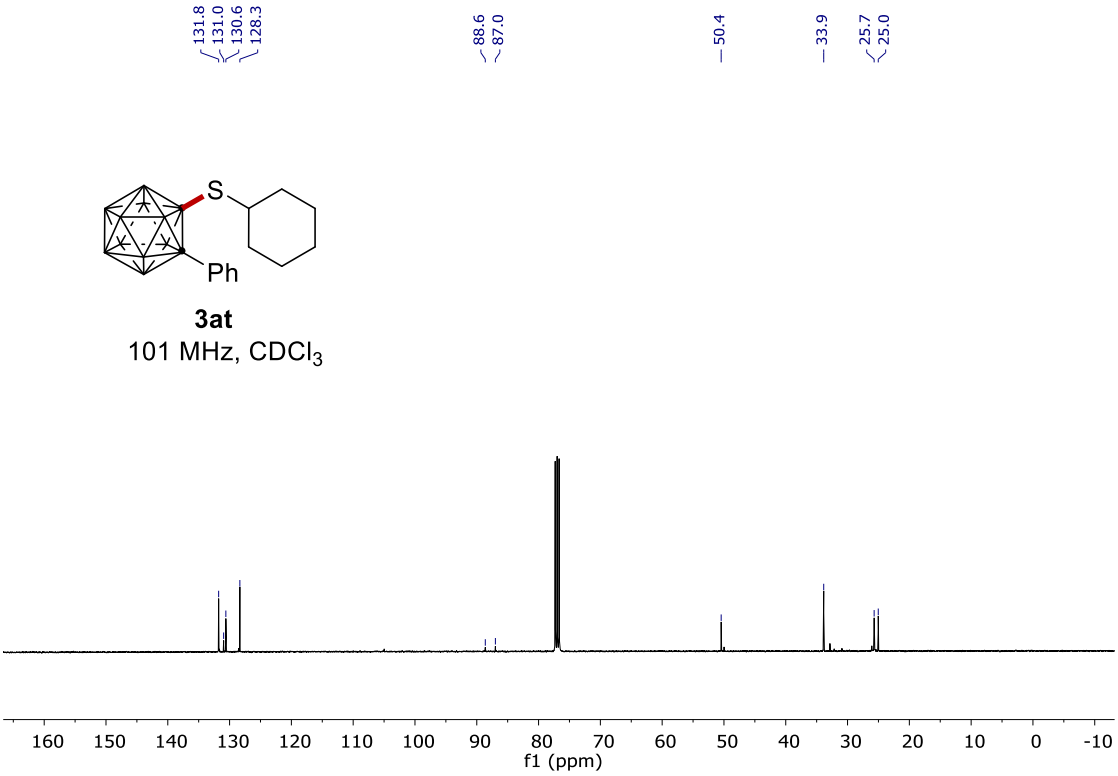
3as
75 MHz, $CDCl_3$



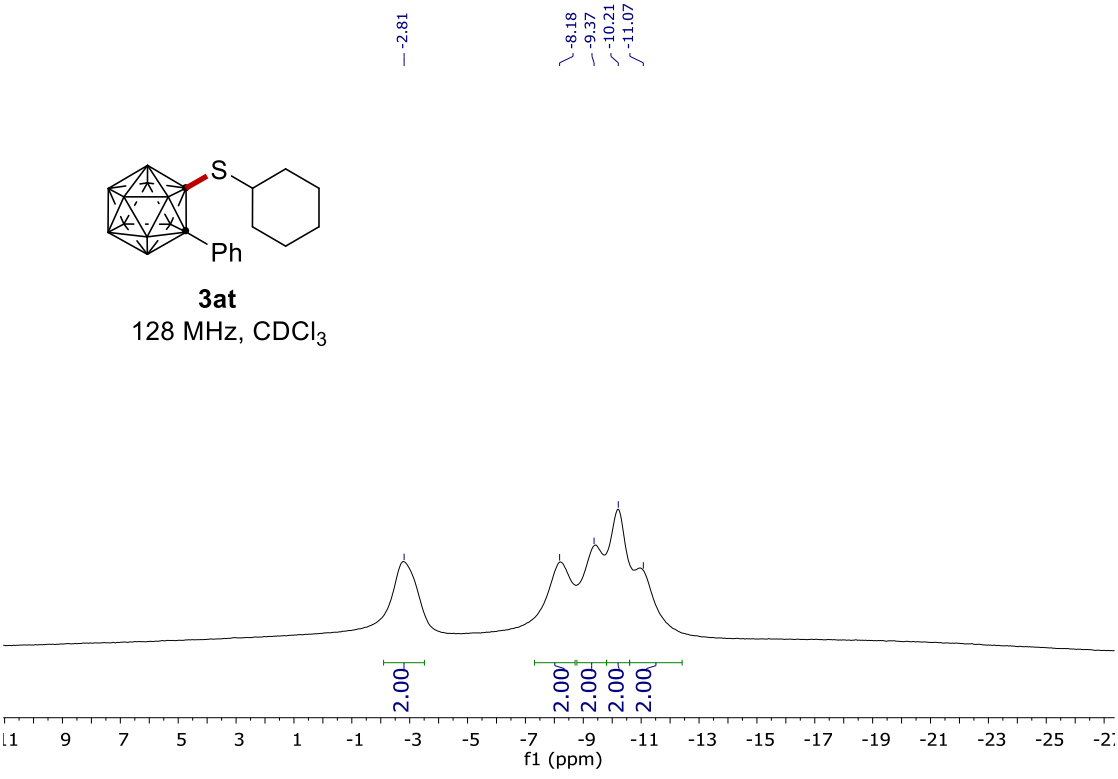
3as
96 MHz, $CDCl_3$


-1.66
-2.26
-3.14
-3.51
-7.57
-7.90
-8.25
-9.58
-11.04
-12.60
S
S
Ph
3as
96 MHz, CDCl3
11 9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27 -29
f1 (ppm)
7.62 7.62 7.61 7.61 7.60 7.60 7.46 7.44 7.44 7.43 7.42 7.42 7.42 7.39 7.39 7.38 7.37 7.36 7.35 7.35
2.74 2.73 2.72 2.71 2.70 2.69 1.67 1.67 1.66 1.64 1.63 1.62 1.61 1.52 1.50 1.49 1.42 1.24 1.23 1.21 1.20 1.20 1.19 1.18 1.17 1.15 1.15 1.14 1.12 1.12 1.11 1.10 1.09 1.08 1.07 1.06 1.04 1.03

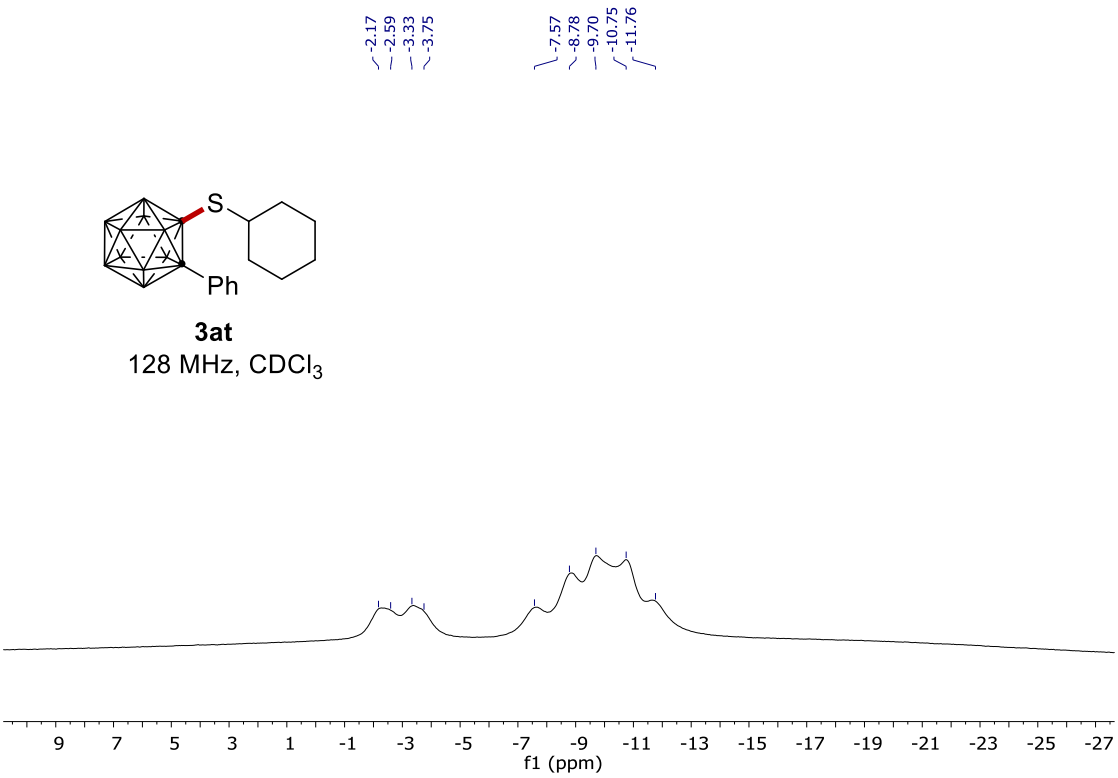

S
Ph
3at
400 MHz, CDCl3
2.00
1.00
1.93
1.48
2.11
2.24
6.04
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

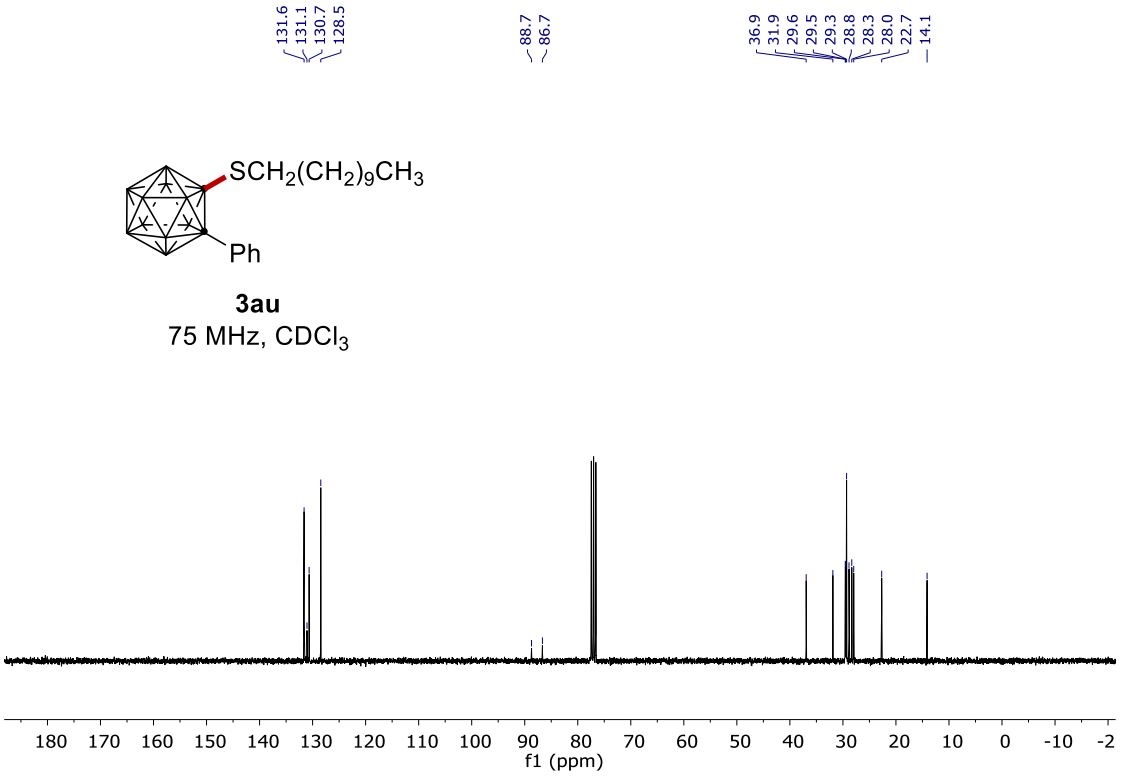


3at
101 MHz, $CDCl_3$

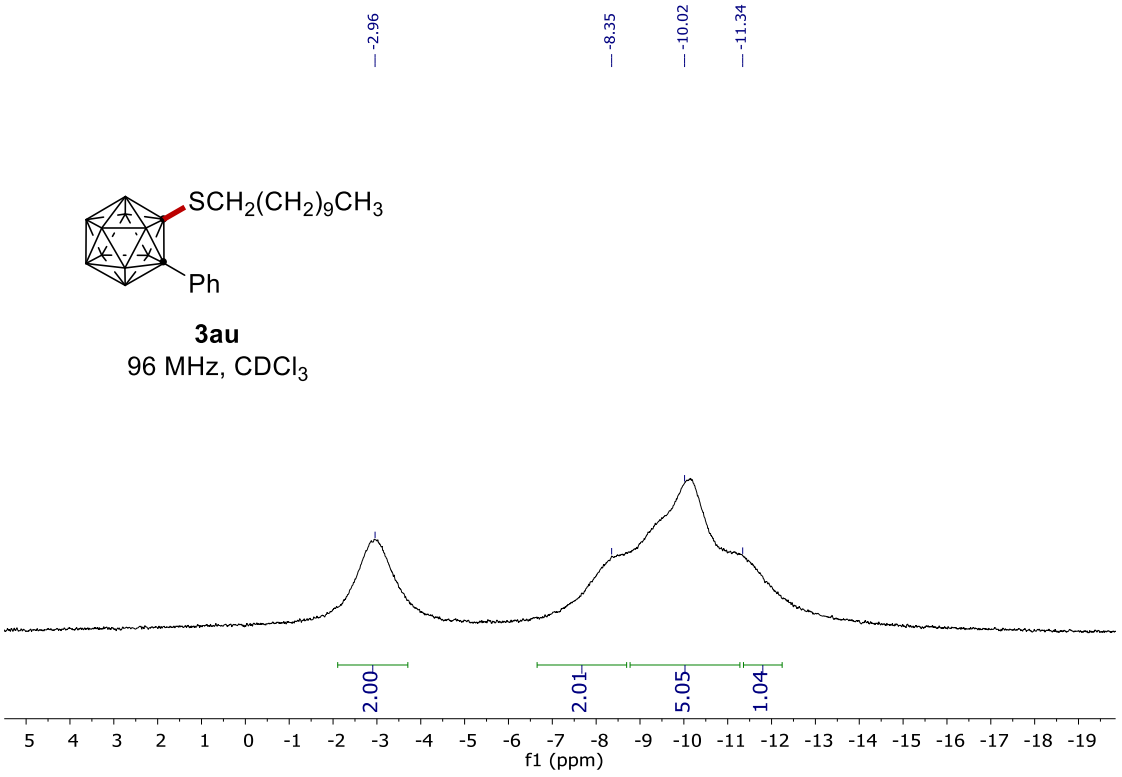


3at
128 MHz, $CDCl_3$

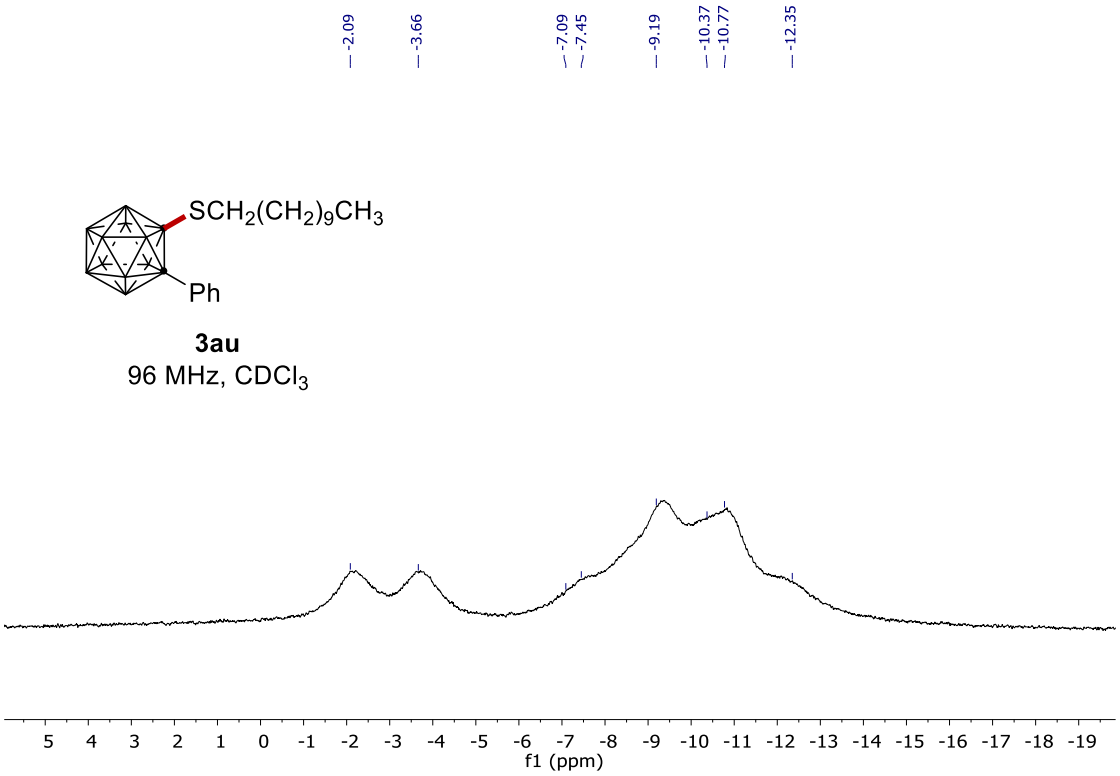

-2.17
-2.59
-3.33
-3.75
-7.57
-8.78
-9.70
-10.75
-11.76
S
Ph
3at
128 MHz, CDCl3
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)
7.66
7.64
7.51
7.49
7.48
7.47
7.47
7.46
7.44
7.43
7.42
7.41
7.39
7.39
7.38
2.68
2.65
2.63
1.34
1.33
1.32
1.28
1.27
1.22
1.19
1.15
1.14
1.13
0.93
0.91
0.89
SCH2(CH2)9CH3
Ph
3au
300 MHz, CDCl3
2.01
1.03
2.00
2.26
18.65
3.21
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

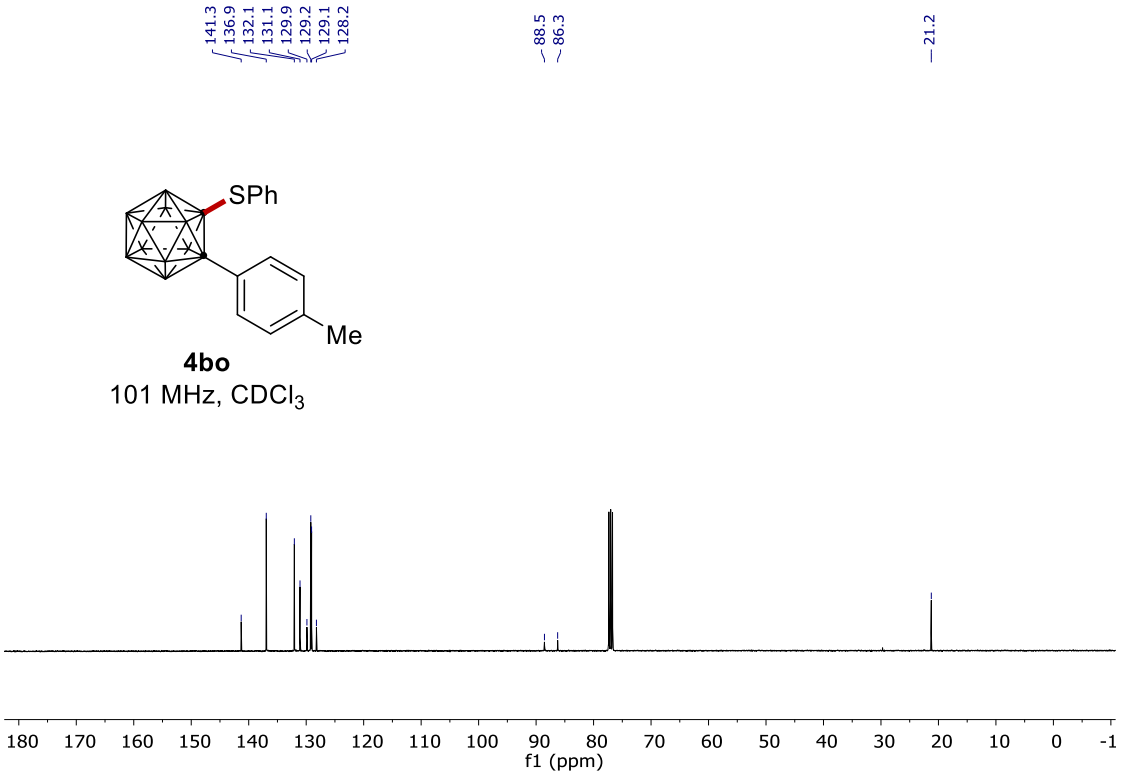


3au
75 MHz, $CDCl_3$



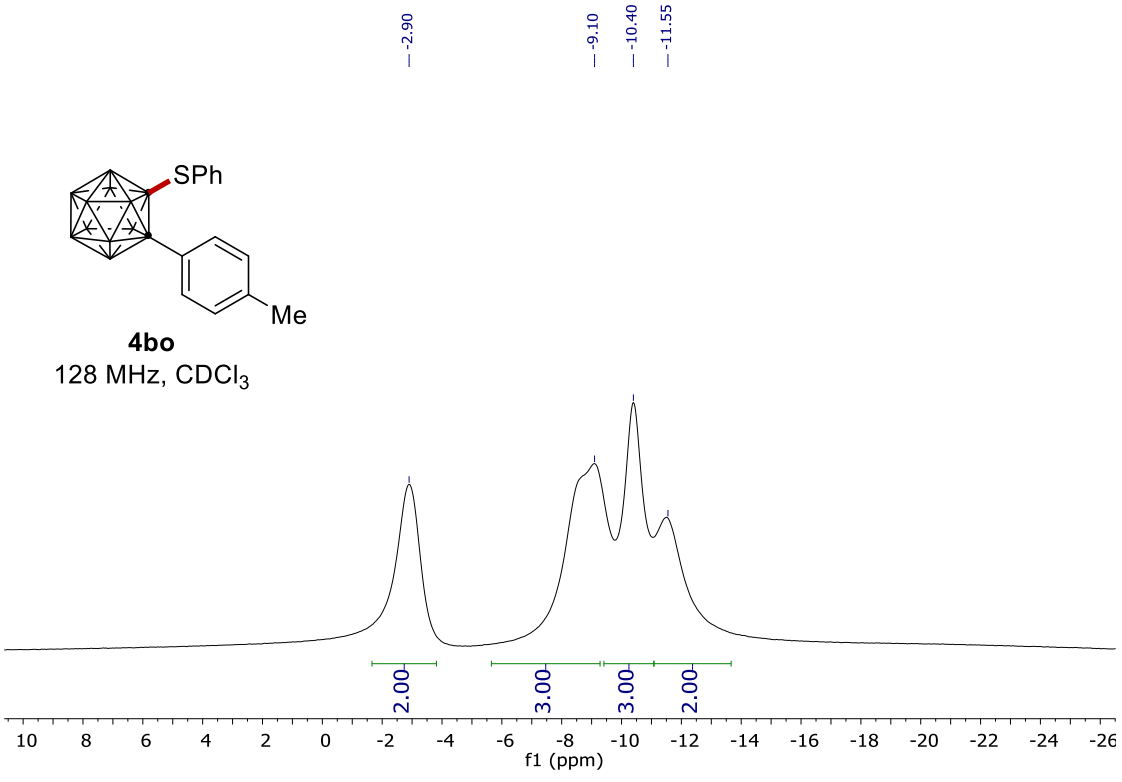
3au
96 MHz, $CDCl_3$


-2.09
-3.66
-7.09
-7.45
-9.19
-10.37
-10.77
-12.35
SCH2(CH2)9CH3
Ph
3au
96 MHz, CDCl3
f1 (ppm)
7.50
7.49
7.48
7.47
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.27
7.26
7.25
7.25
7.24
7.24
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.22
6.99
6.99
6.99
6.99
6.98
6.98
6.97
6.97
2.43
SPh
Me
4bo
400 MHz, CDCl3
2.08
1.02
4.34
2.00
3.11
f1 (ppm)



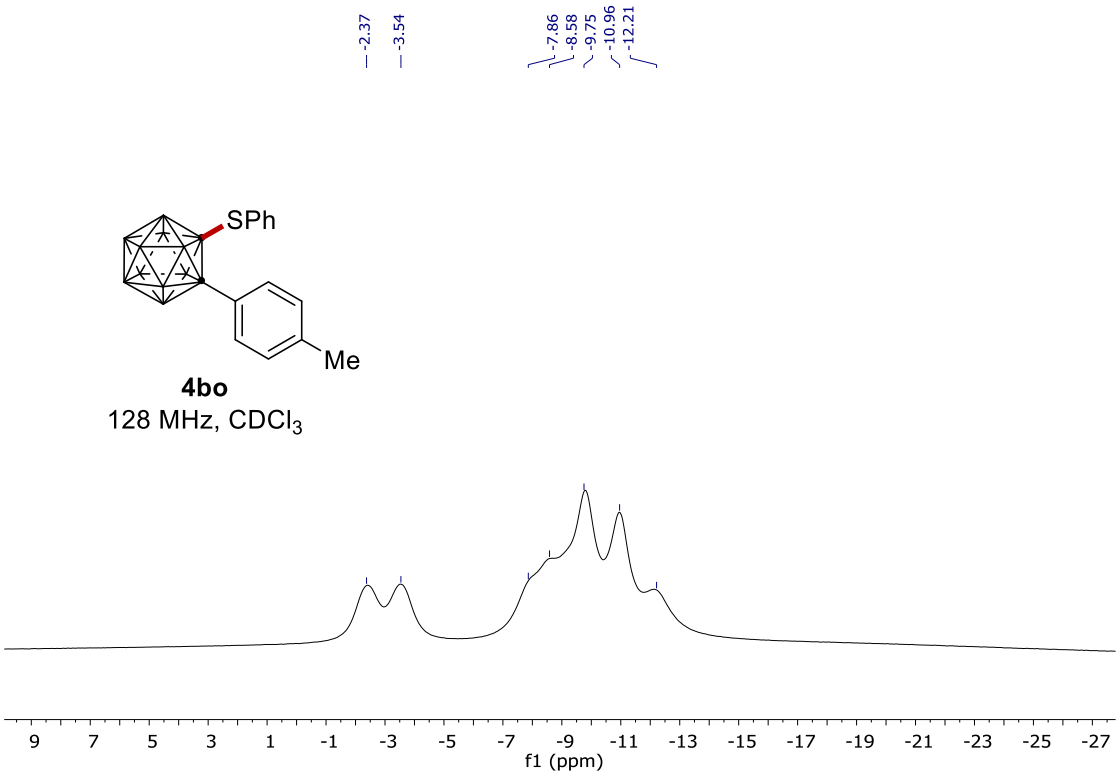
4bo

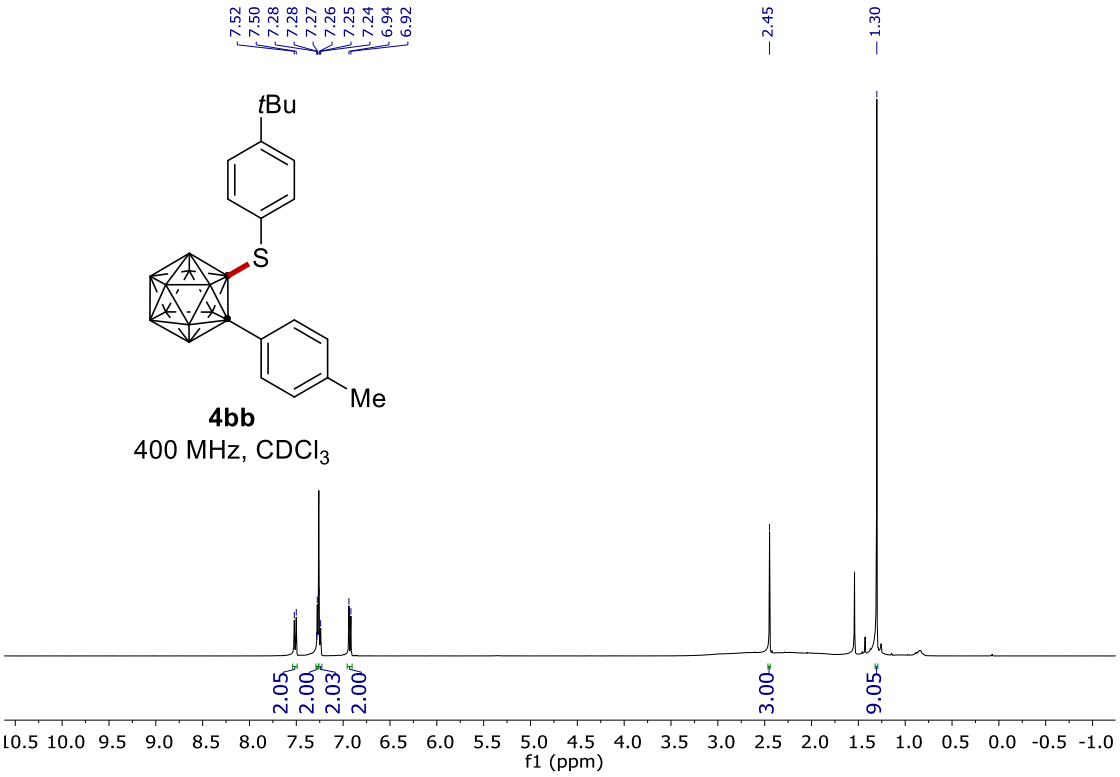
101 MHz, $CDCl_3$

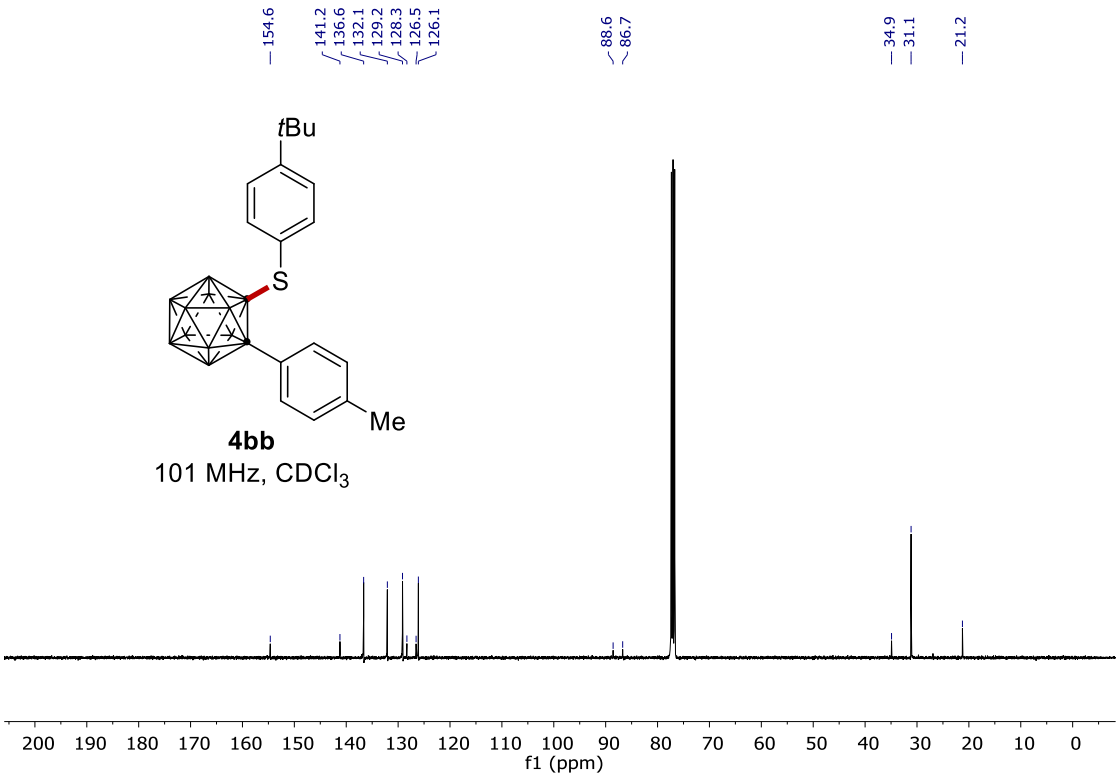


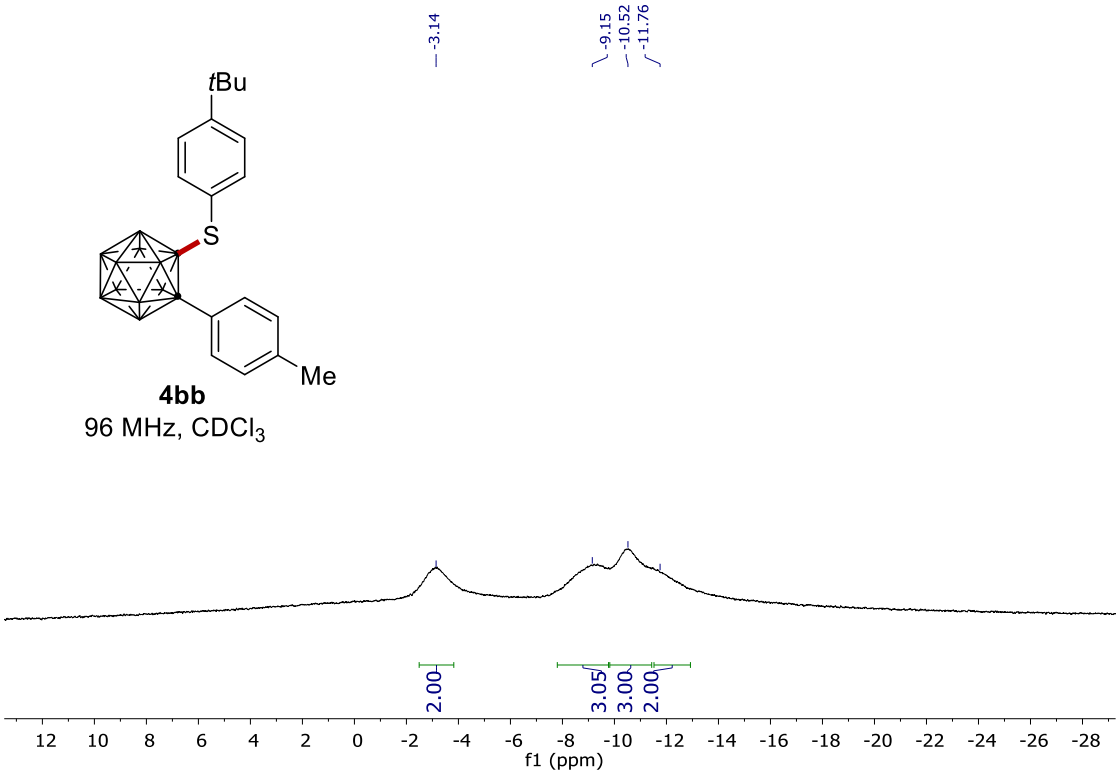
4bo

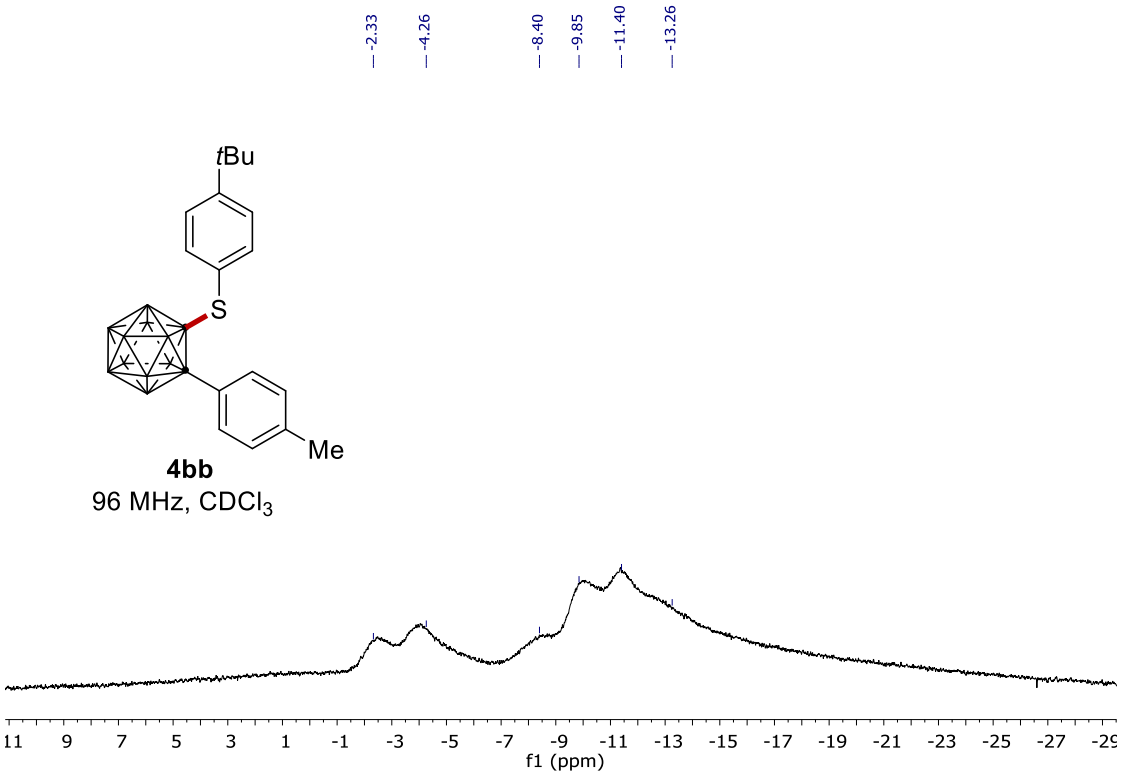
128 MHz, $CDCl_3$

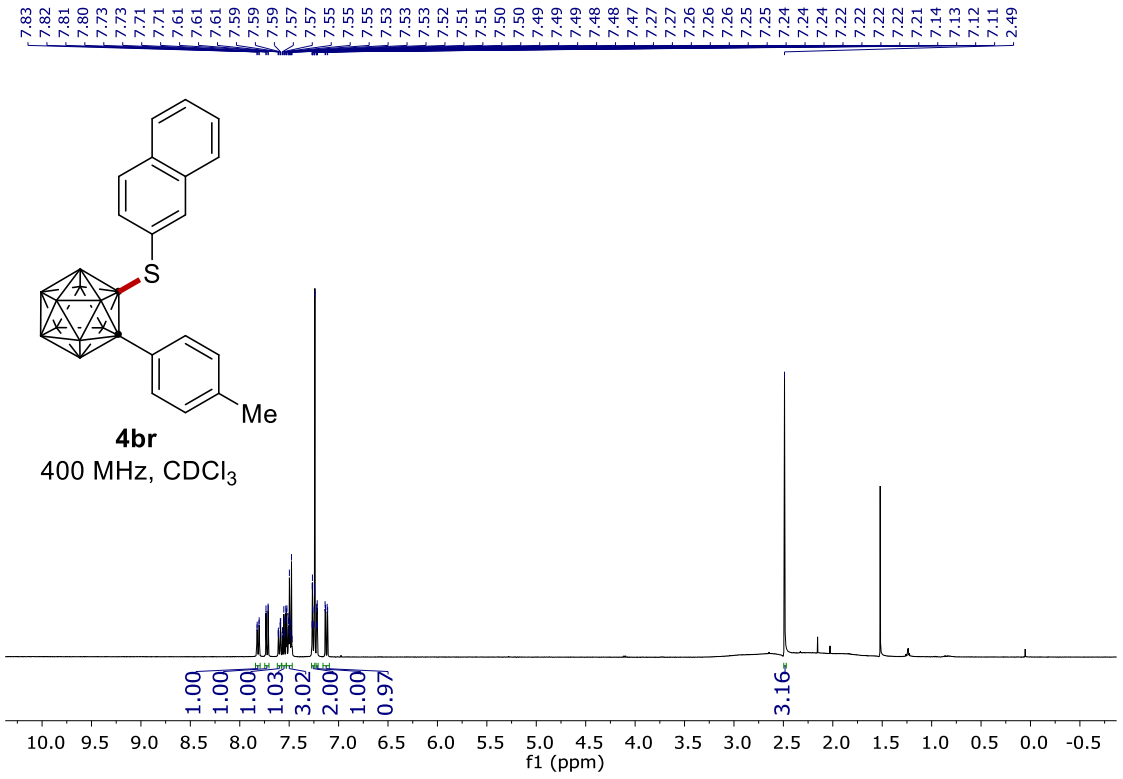

-2.37
-3.54
-7.86
-8.58
-9.75
-10.96
-12.21
SPh
Me
4bo
128 MHz, CDCl3
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)

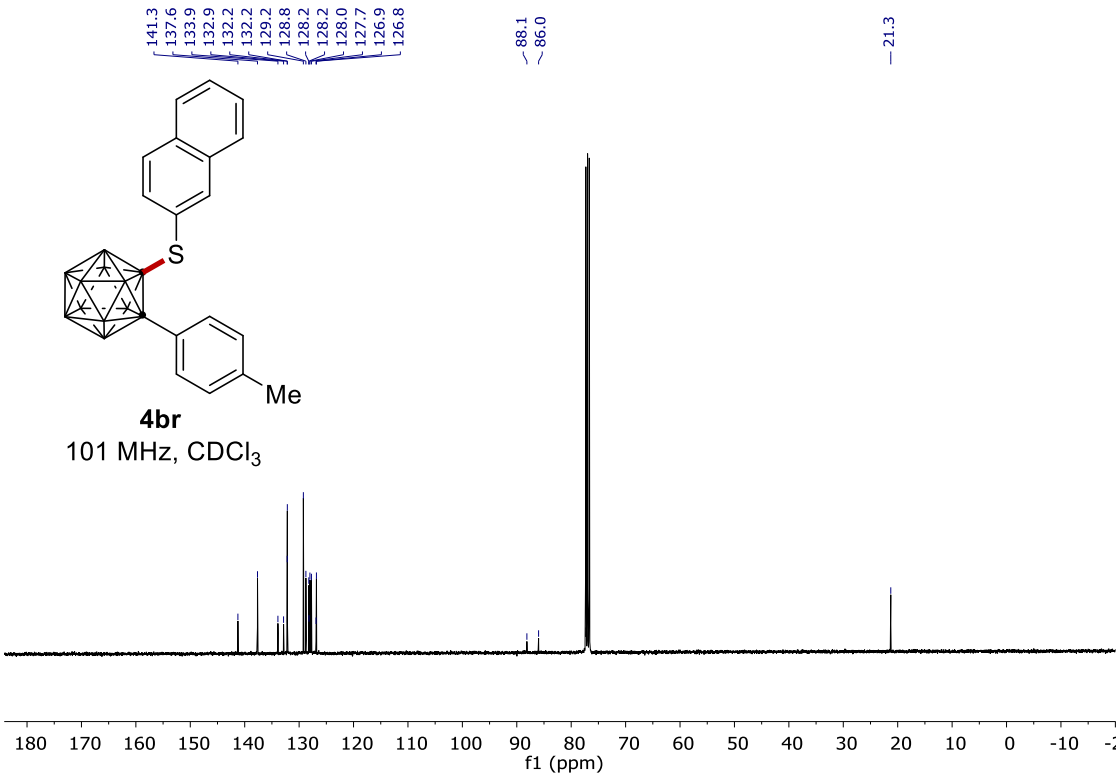

7.52
7.50
7.28
7.28
7.28
7.27
7.26
7.25
7.24
6.94
6.92
2.45
1.30
tBu
S
Me
4bb
400 MHz, CDCl3
2.05
2.00
2.03
2.00
3.00
9.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

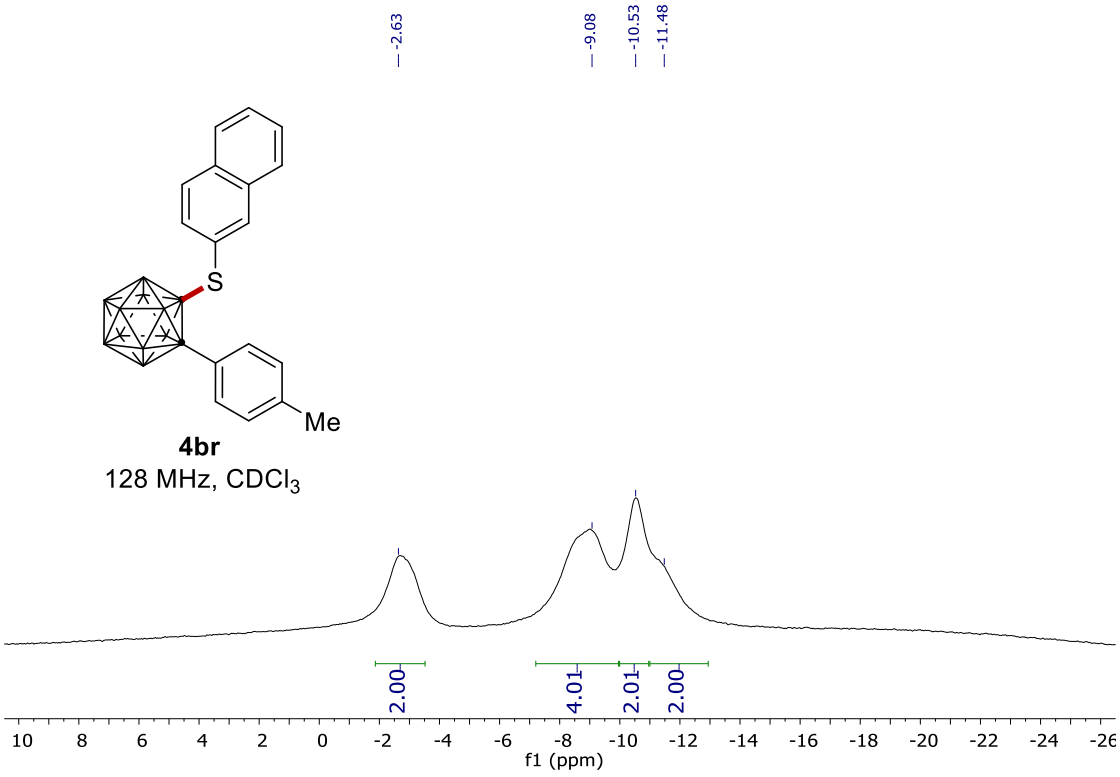

154.6
141.2
136.6
132.1
129.2
128.3
126.5
126.1
88.6
86.7
34.9
31.1
21.2
tBu
S
Me
4bb
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

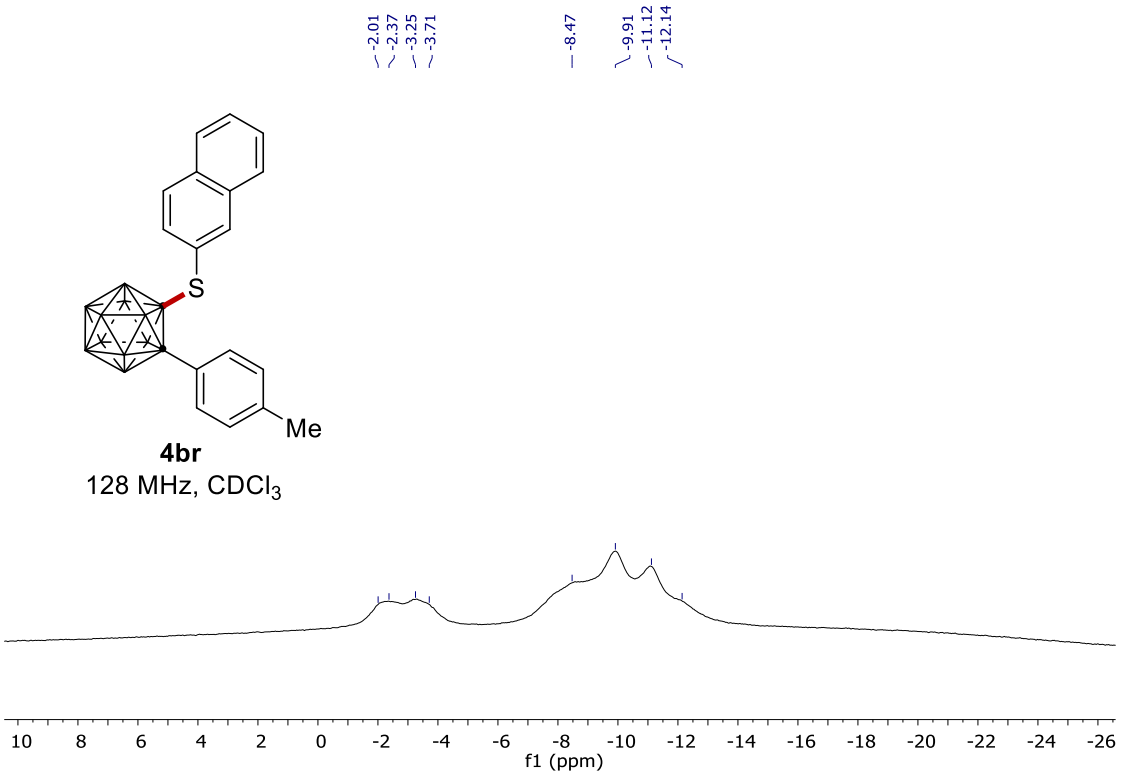

-3.14
-9.15
-10.52
-11.76
tBu
S
Me
4bb
96 MHz, CDCl3
2.00
3.05
3.00
2.00
12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28
f1 (ppm)

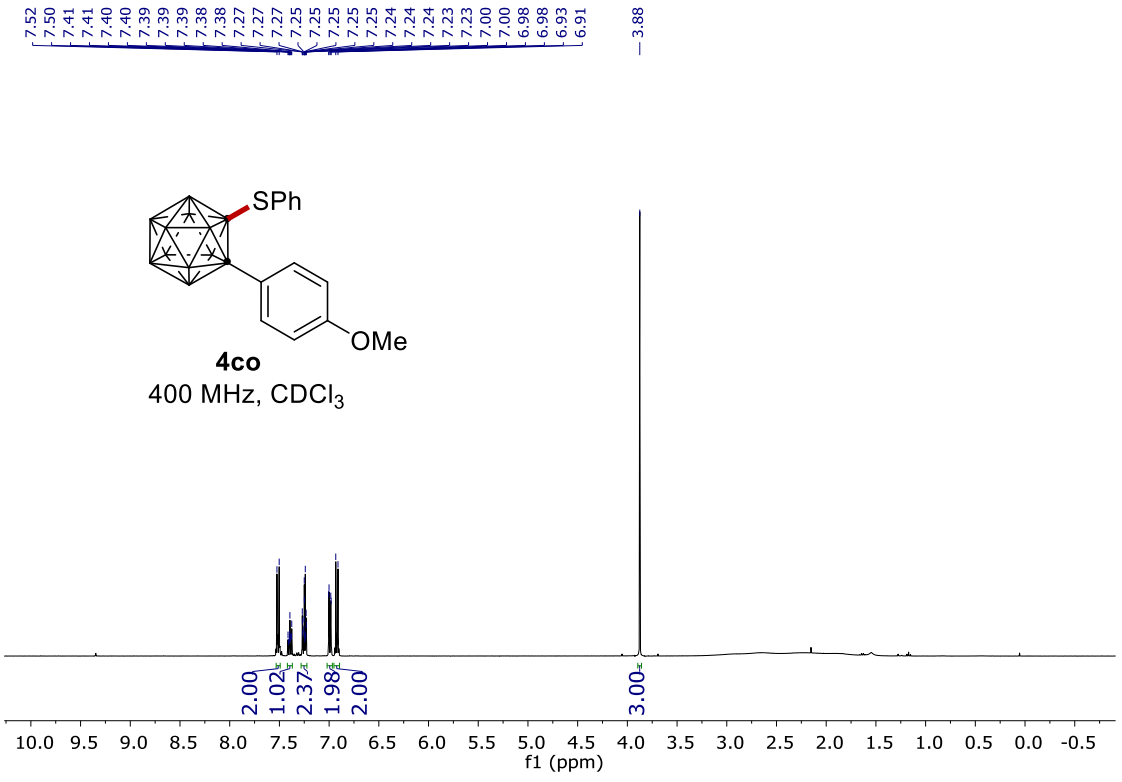

-2.33
-4.26
-8.40
-9.85
-11.40
-13.26
tBu
S
Me
4bb
96 MHz, CDCl3
f1 (ppm)

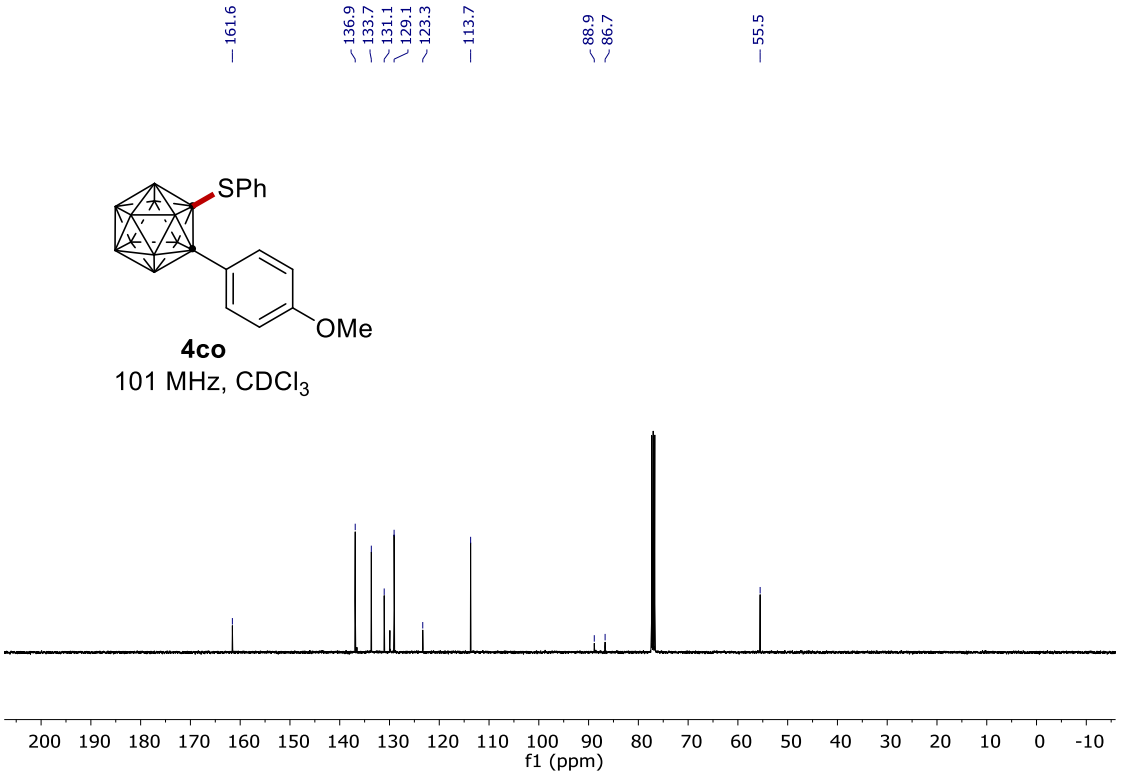

7.83
7.82
7.81
7.80
7.73
7.73
7.71
7.71
7.61
7.61
7.61
7.59
7.59
7.59
7.57
7.57
7.57
7.55
7.55
7.55
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.22
7.22
7.22
7.22
7.21
7.14
7.13
7.12
7.11
2.49
S
Me
4br
400 MHz, CDCl3
1.00
1.00
1.00
1.03
3.02
2.00
1.00
0.97
3.16
f1 (ppm)

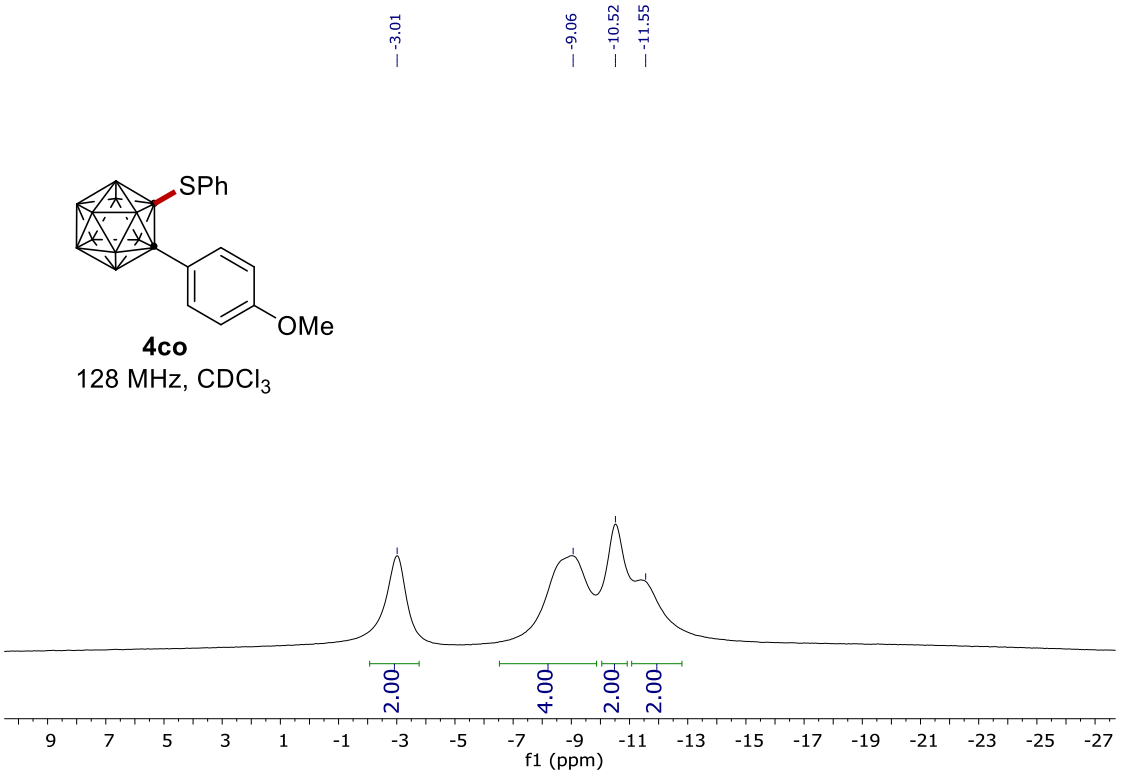

141.3
137.6
133.9
132.9
132.2
132.2
129.2
128.8
128.2
128.2
128.0
127.7
126.9
126.8
88.1
86.0
21.3
S
Me
4br
101 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

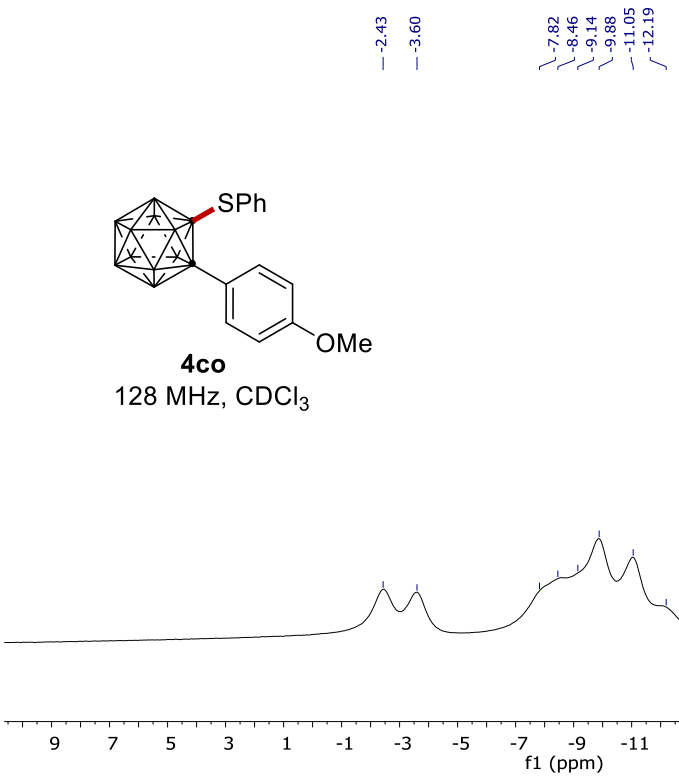

-2.63
-9.08
-10.53
-11.48
S
Me
4br
128 MHz, CDCl3
2.00
4.01
2.01
2.00
10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26
f1 (ppm)

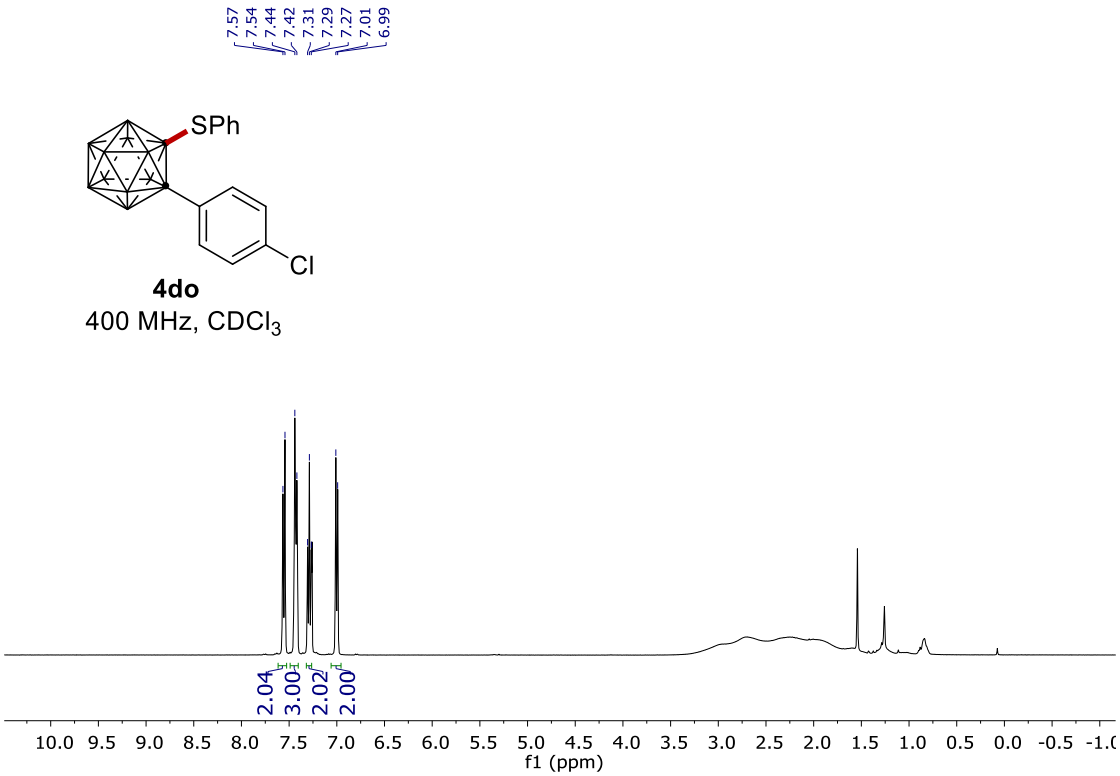

-2.01
-2.37
-3.25
-3.71
-8.47
-9.91
-11.12
-12.14
S
Me
4br
128 MHz, CDCl3
10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26
f1 (ppm)

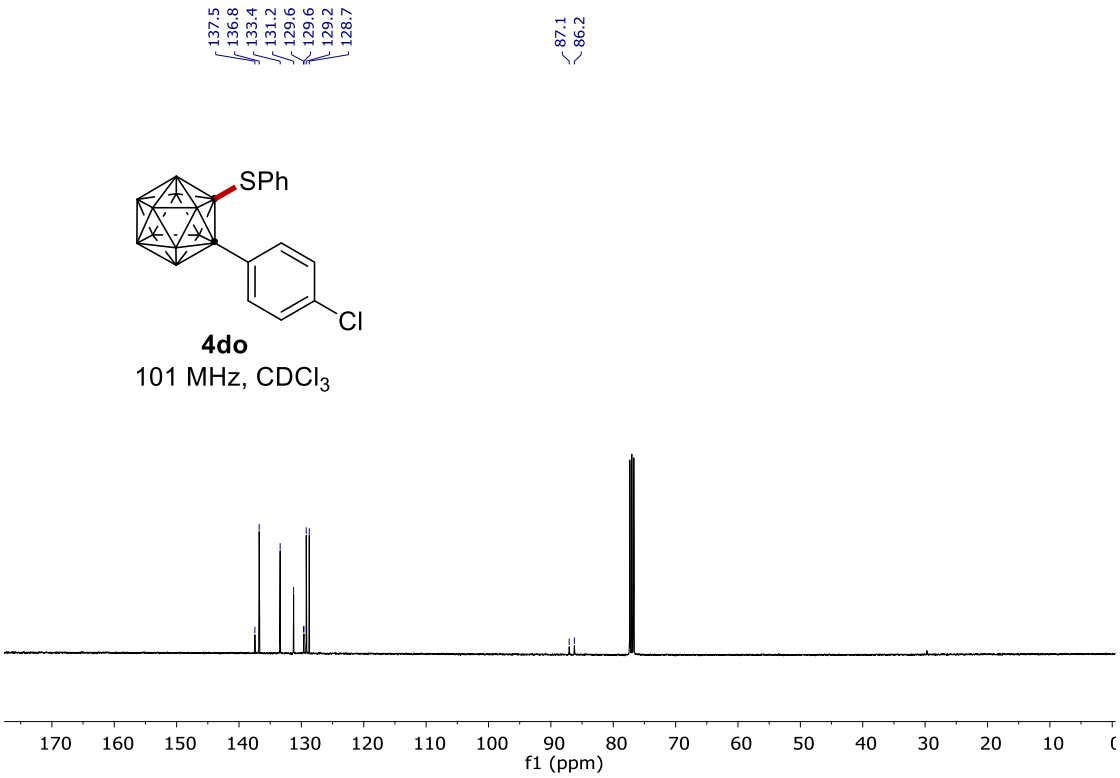

7.52
7.50
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.27
7.27
7.27
7.25
7.25
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.00
7.00
6.98
6.98
6.93
6.91
3.88
SPh
OMe
4co
400 MHz, CDCl3
2.00
1.02
2.37
1.98
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

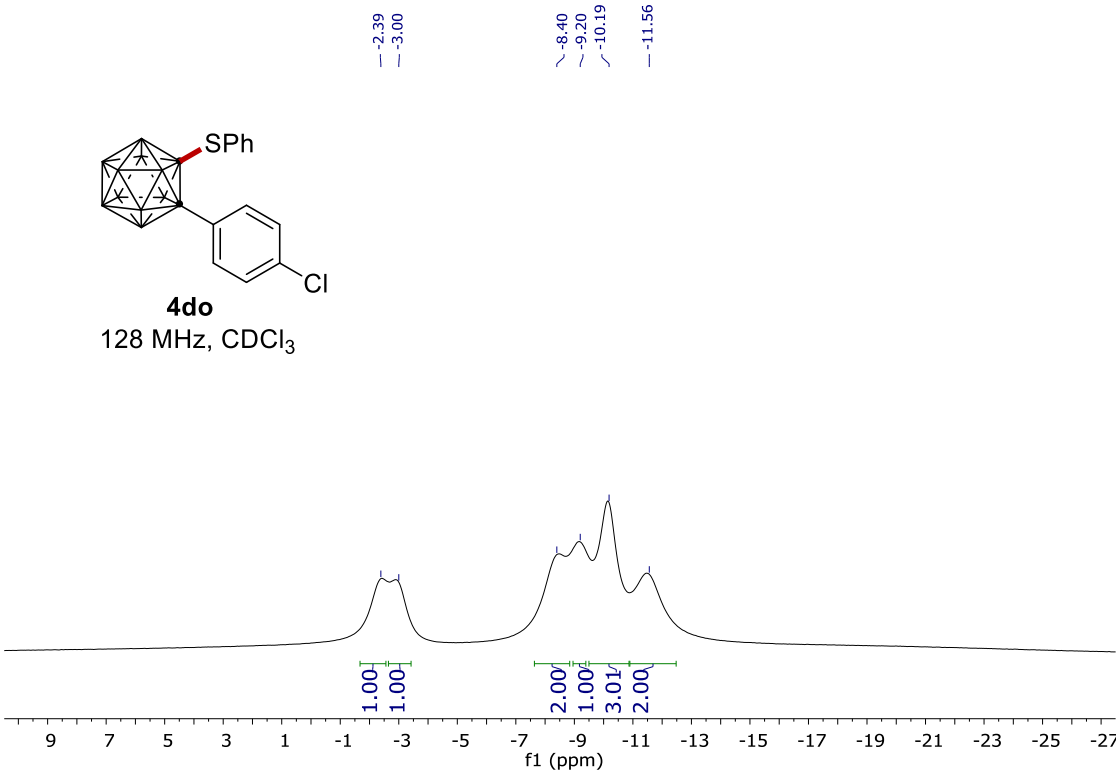

161.6
136.9
133.7
131.1
129.1
123.3
113.7
88.9
86.7
55.5
SPh
OMe
4co
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

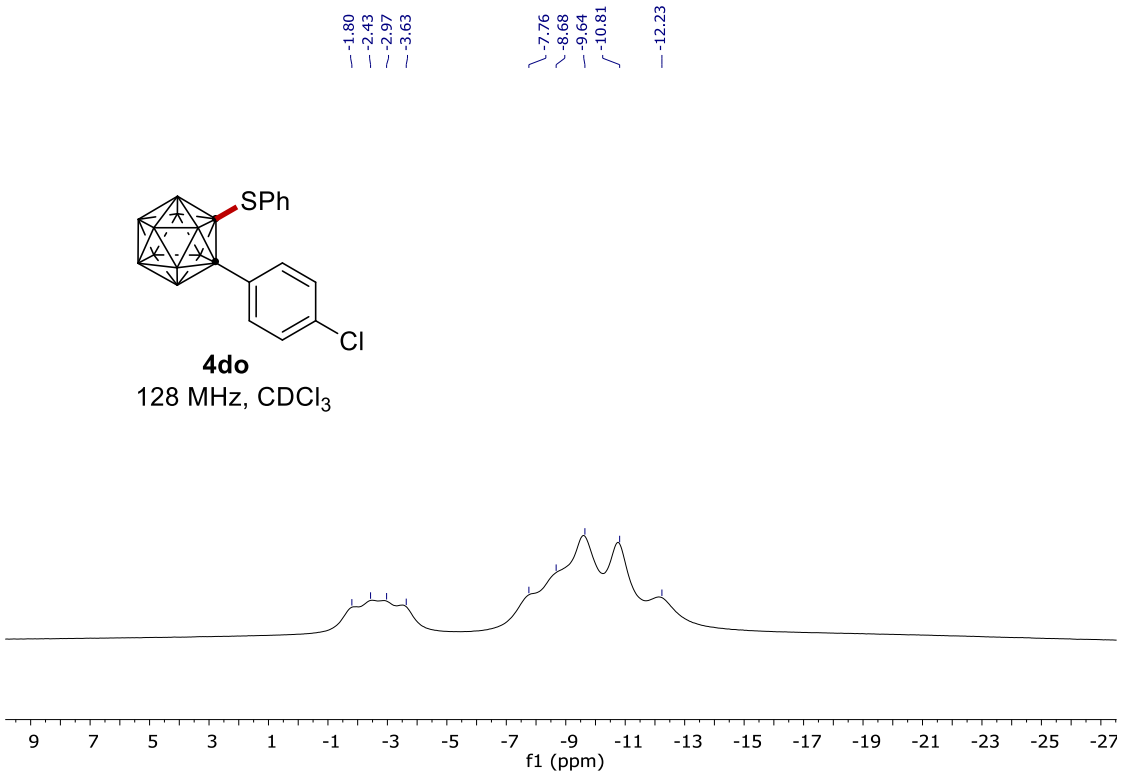

-3.01
-9.06
-10.52
-11.55
SPh
OMe
4co
128 MHz, CDCl3
2.00
4.00
2.00
2.00
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)

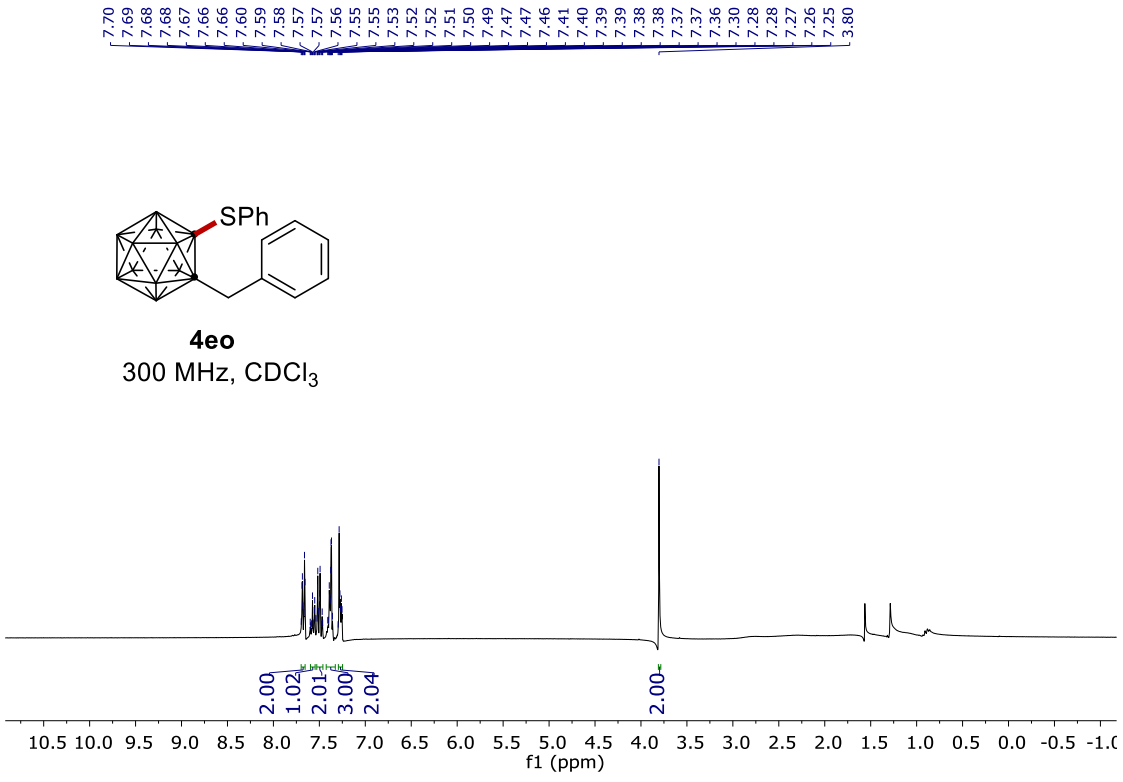

-2.43
-3.60
-7.82
-8.46
-9.14
-9.88
-11.05
-12.19
SPh
OMe
4co
128 MHz, CDCl3
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)

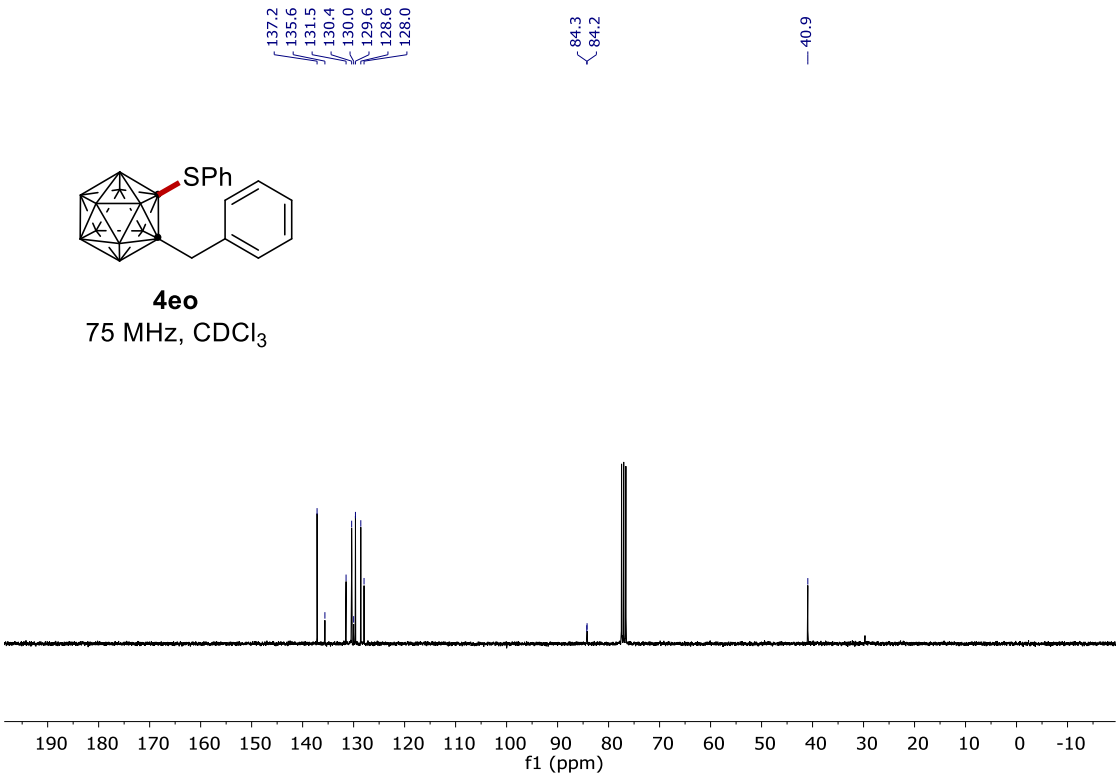

7.57
7.54
7.44
7.42
7.31
7.29
7.27
7.01
6.99
SPh
Cl
4do
400 MHz, CDCl3
2.04
3.00
2.02
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

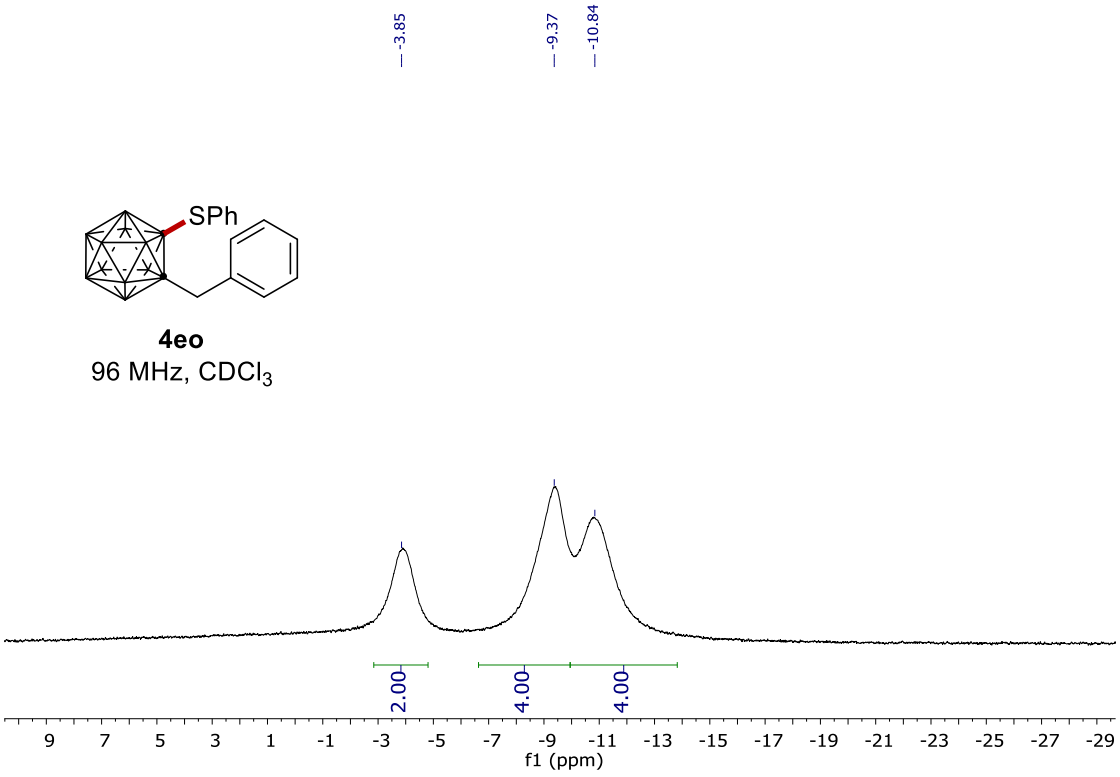

137.5
136.8
133.4
131.2
129.6
129.6
129.2
128.7
87.1
86.2
SPh
Cl
4do
101 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

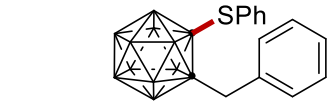

-2.39
-3.00
-8.40
-9.20
-10.19
-11.56
SPh
Cl
4do
128 MHz, CDCl3
1.00
1.00
2.00
1.00
3.01
2.00
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)


-1.80
-2.43
-2.97
-3.63
-7.76
-8.68
-9.64
-10.81
-12.23
SPh
Cl
4do
128 MHz, CDCl3
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)


7.70 7.69 7.68 7.68 7.67 7.66 7.66 7.60 7.59 7.58 7.57 7.57 7.56 7.55 7.55 7.53 7.52 7.52 7.51 7.50 7.49 7.47 7.47 7.46 7.41 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.30 7.28 7.28 7.27 7.26 7.25 3.80
SPh
4eo
300 MHz, CDCl3
2.00 1.02 2.01 3.00 2.04
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

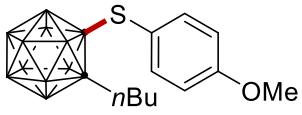

137.2
135.6
131.5
130.4
130.0
129.6
128.6
128.0
84.3
84.2
40.9
SPh
4eo
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-3.85
-9.37
-10.84
SPh
4eo
96 MHz, CDCl3
2.00
4.00
4.00
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27 -29
f1 (ppm)



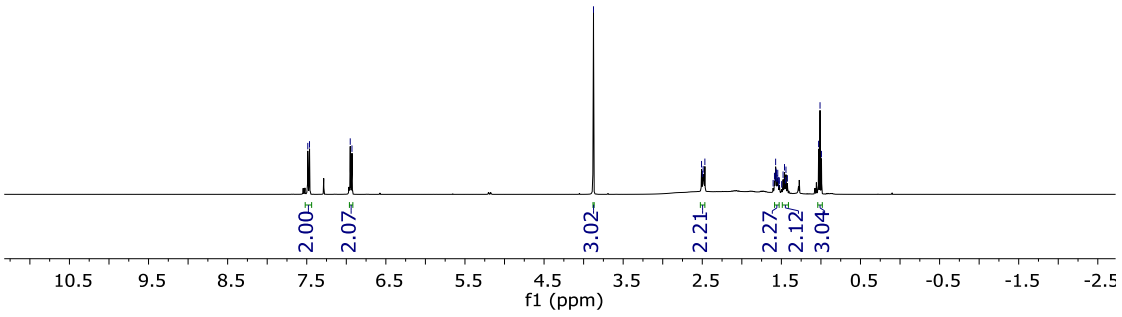
4eo

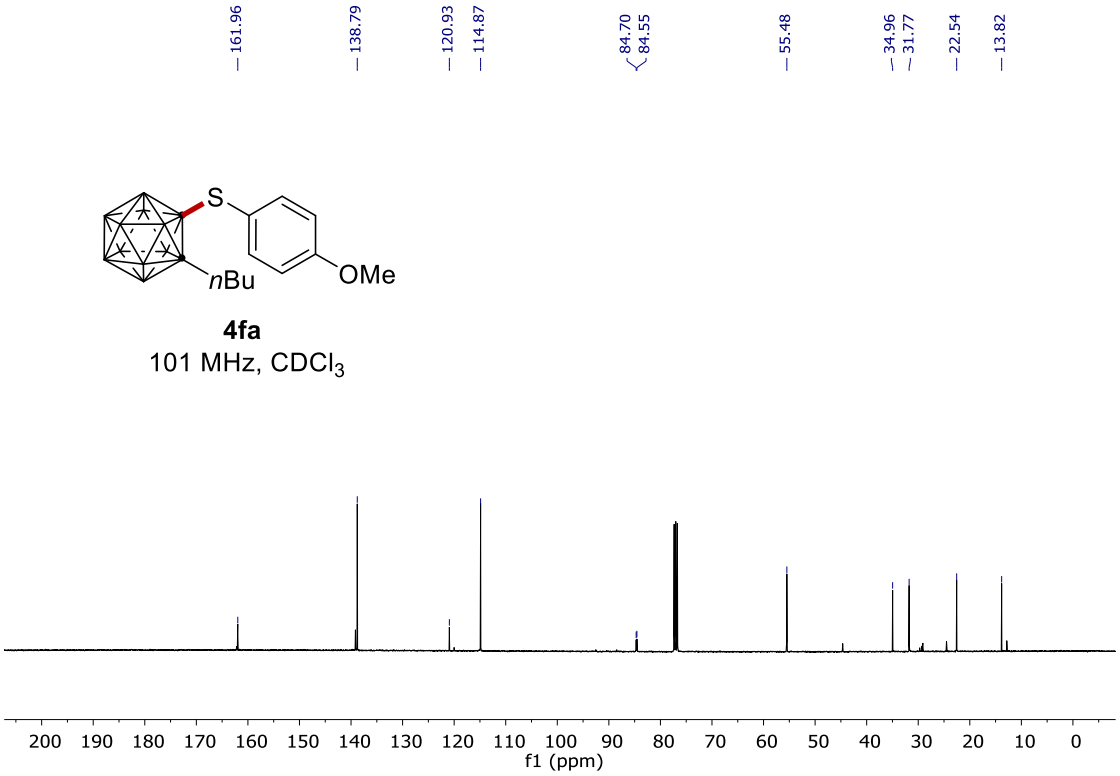
96 MHz, $CDCl_3$



4fa

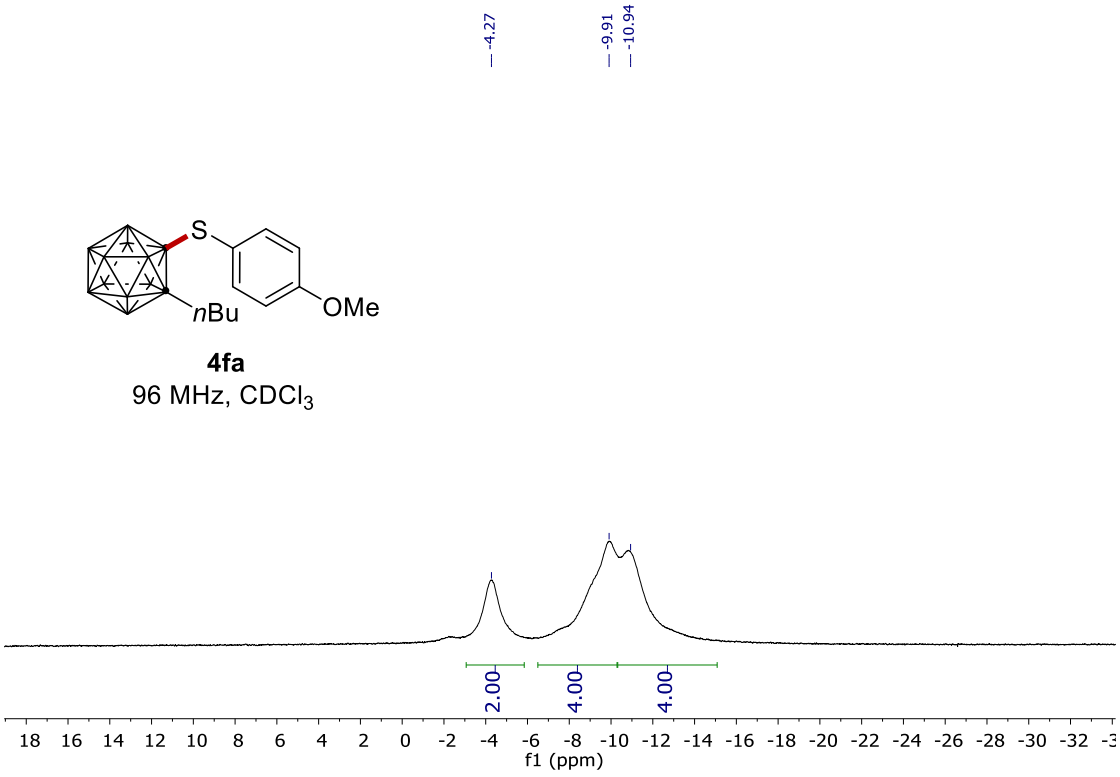
400MHz, $CDCl_3$





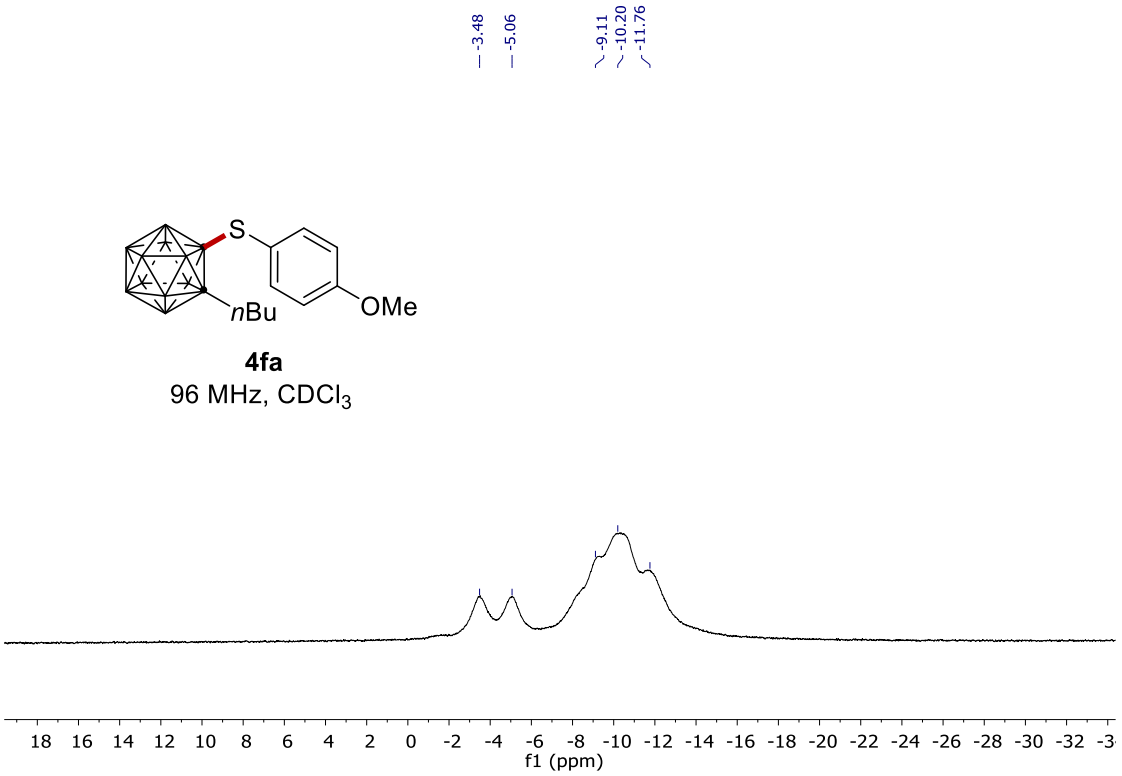
4fa

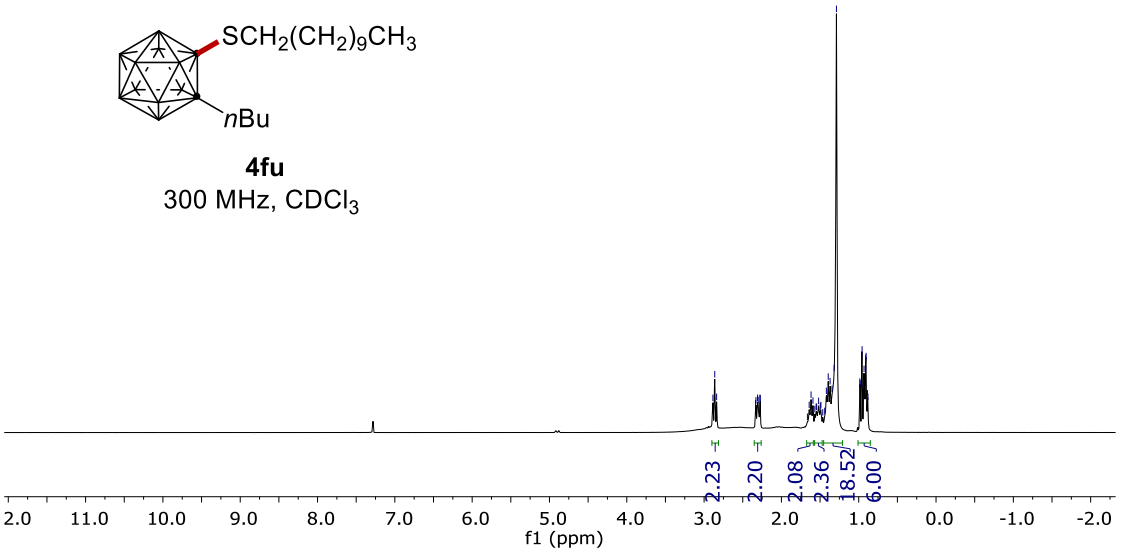
101 MHz, $CDCl_3$

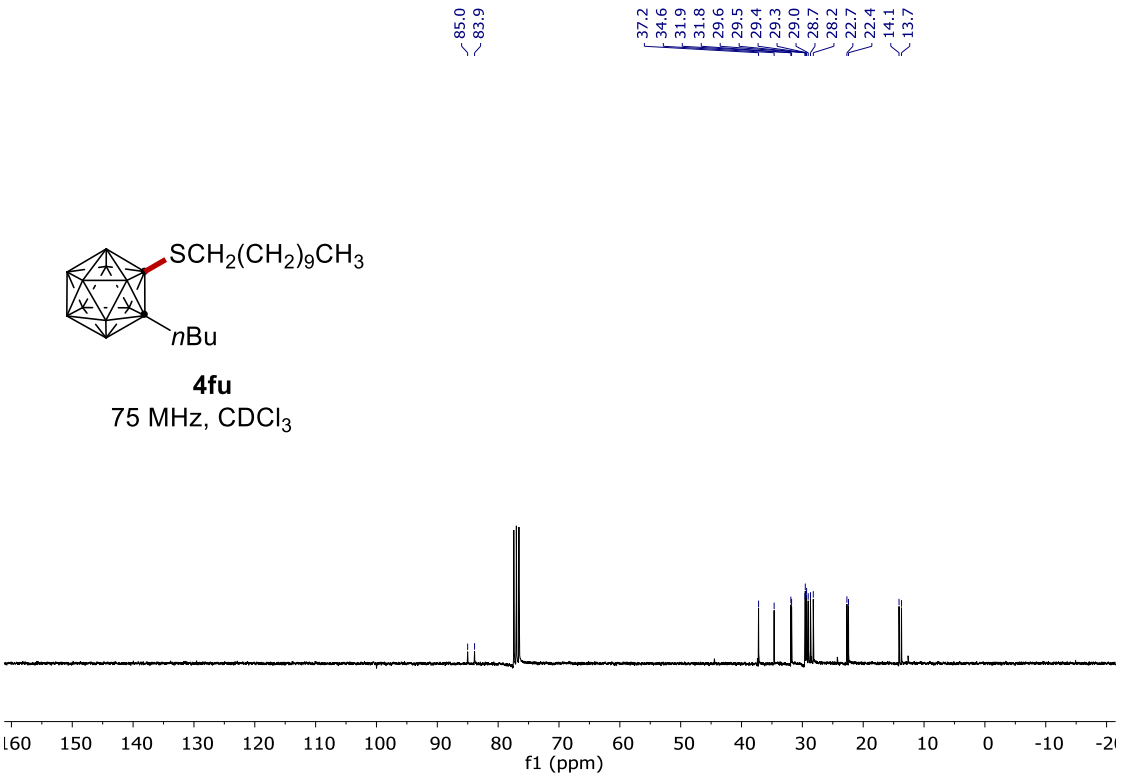


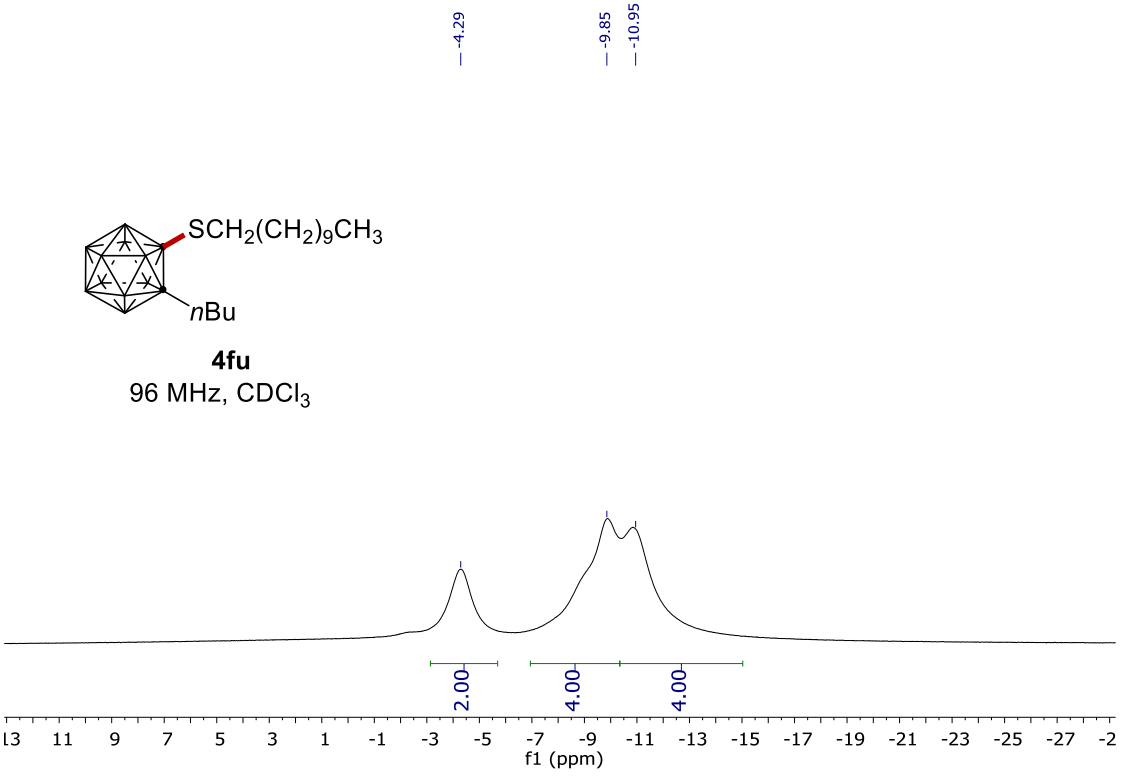
4fa

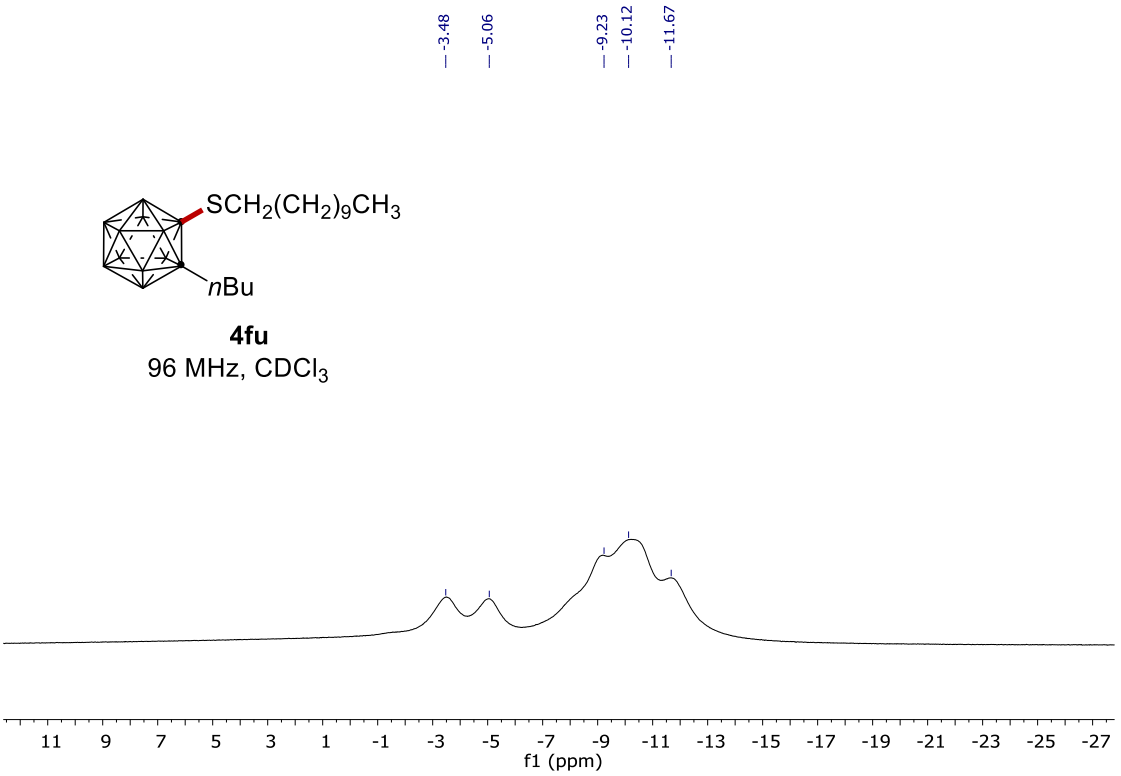
96 MHz, $CDCl_3$


-3.48
-5.06
-9.11
-10.20
-11.76
S
nBu
OMe
4fa
96 MHz, CDCl3
18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -3
f1 (ppm)
2.89
2.86
2.84
2.33
2.31
2.30
2.28
2.27
1.62
1.42
1.39
1.37
1.35
1.32
1.29
0.99
0.98
0.96
0.96
0.94
0.93
0.91
0.90
0.89

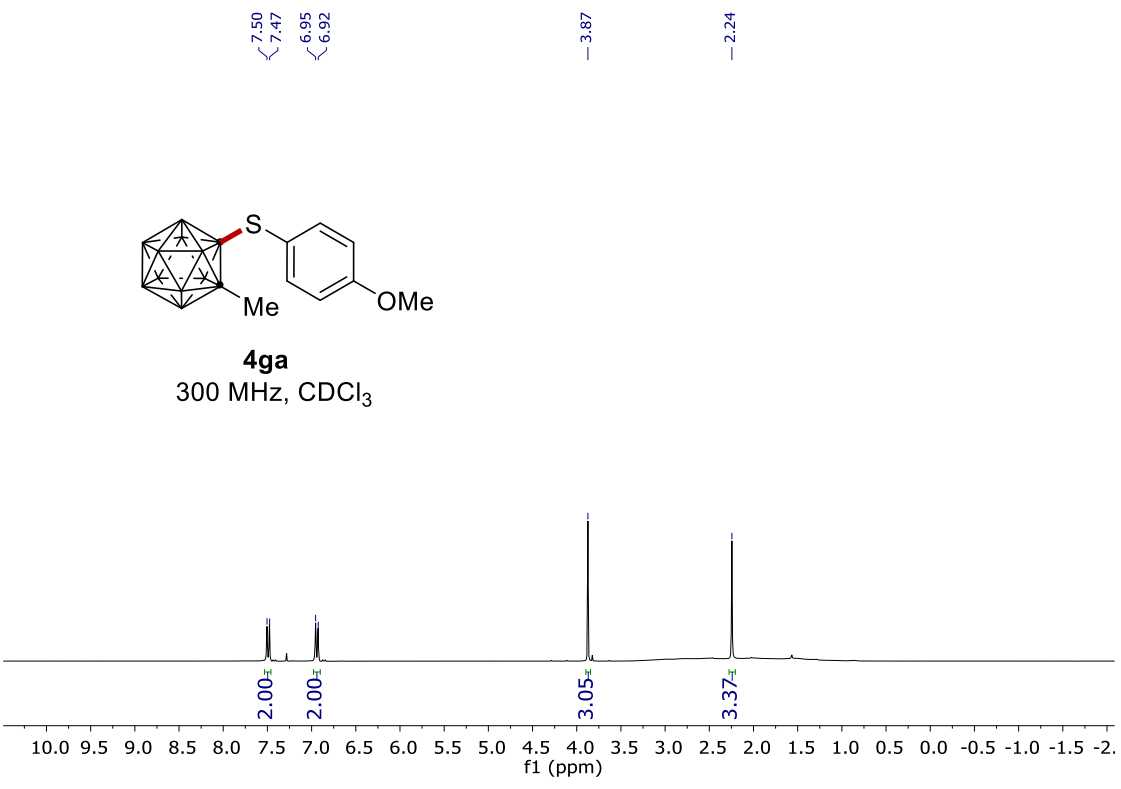

SCH2(CH2)9CH3
nBu
4fu
300 MHz, CDCl3
2.23
2.20
2.08
2.36
18.52
6.00
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


85.0
83.9
37.2
34.6
31.9
31.8
29.6
29.5
29.4
29.3
29.0
28.7
28.2
22.7
22.4
14.1
13.7
SCH2(CH2)9CH3
nBu
4fu
75 MHz, CDCl3
f1 (ppm)

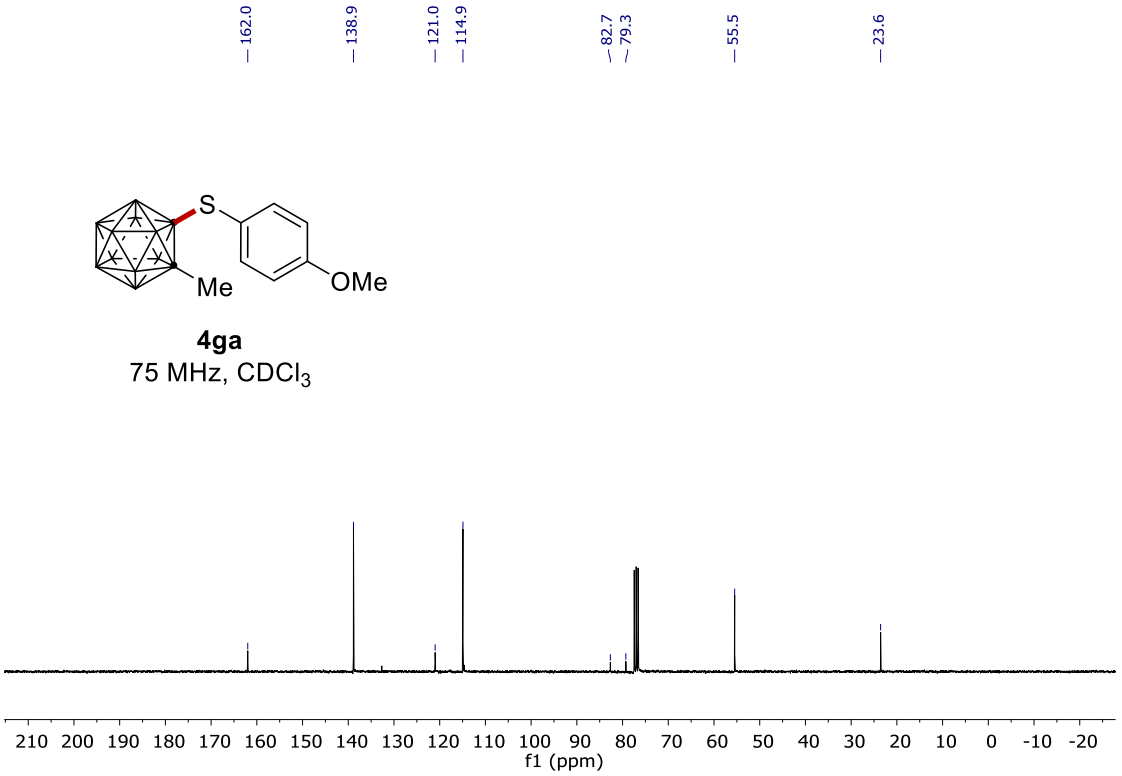

-4.29
-9.85
-10.95
SCH2(CH2)9CH3
nBu
4fu
96 MHz, CDCl3
2.00
4.00
4.00
f1 (ppm)



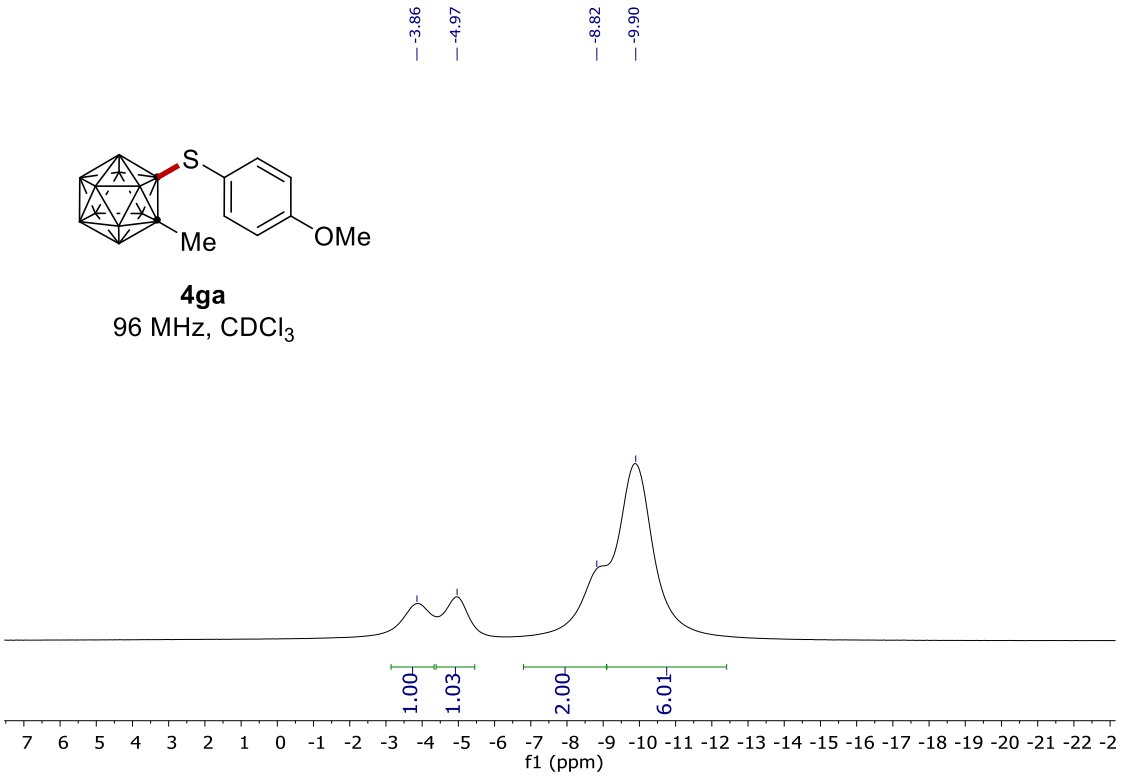
4fu
96 MHz, $CDCl_3$



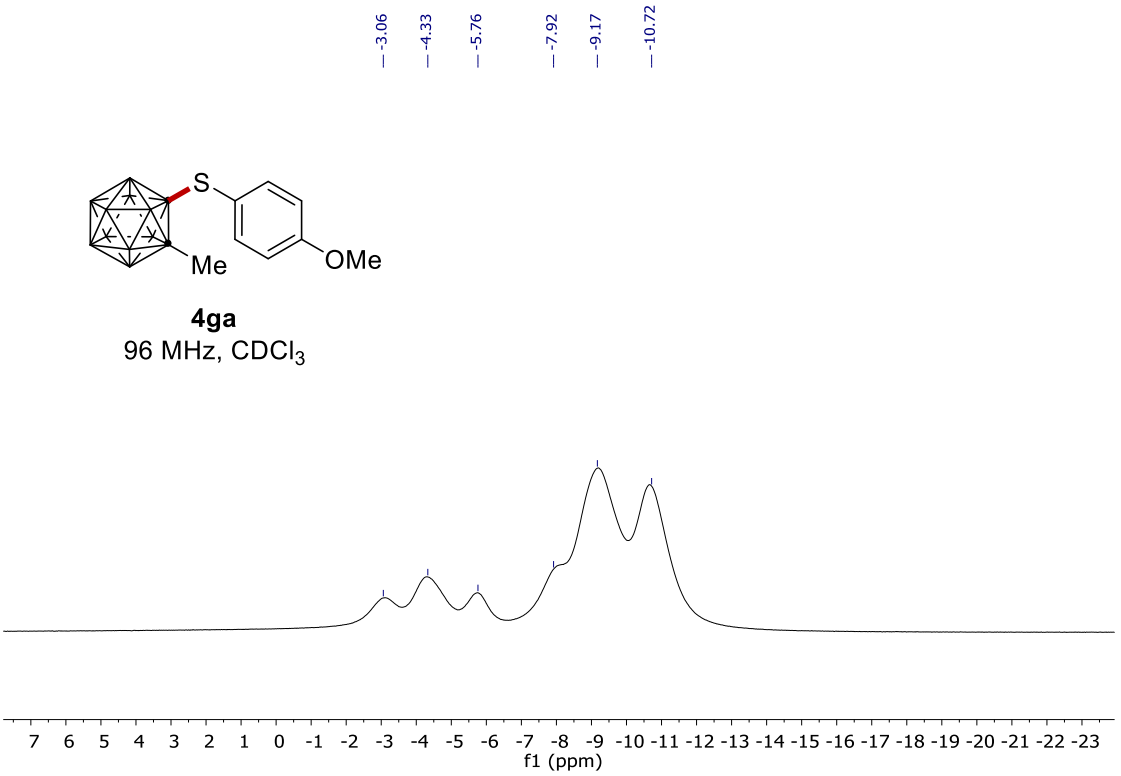
4ga
300 MHz, $CDCl_3$



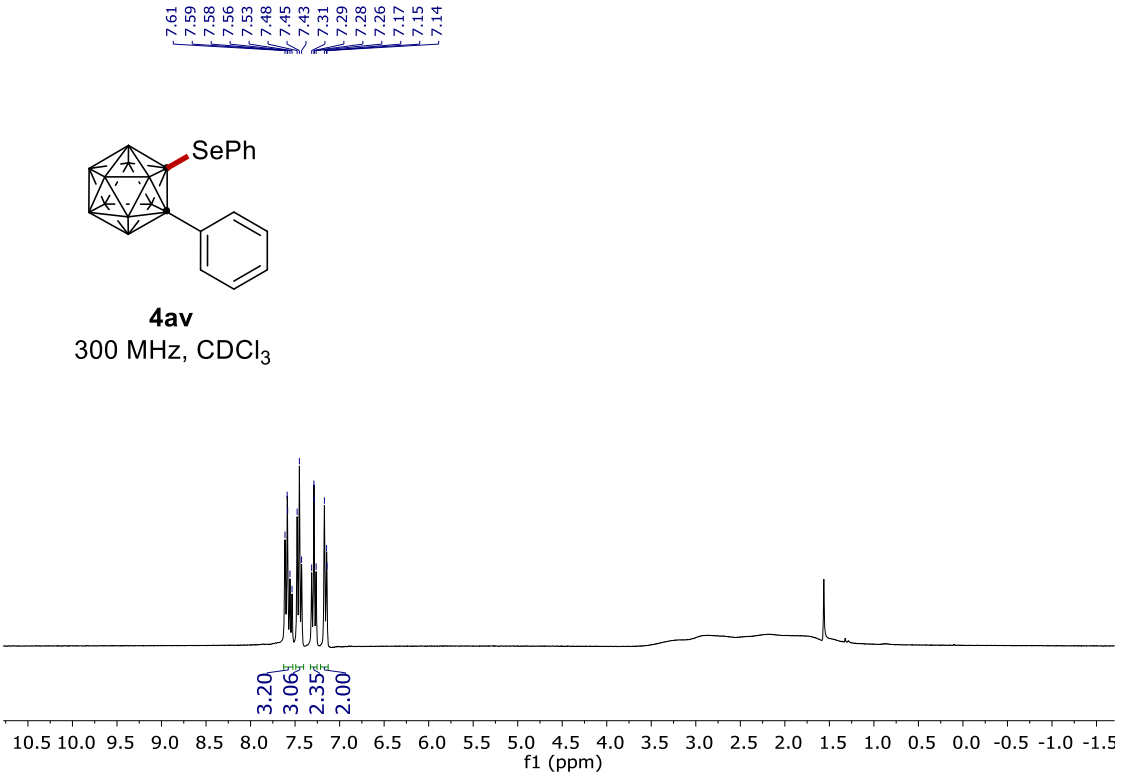
4ga
75 MHz, $CDCl_3$



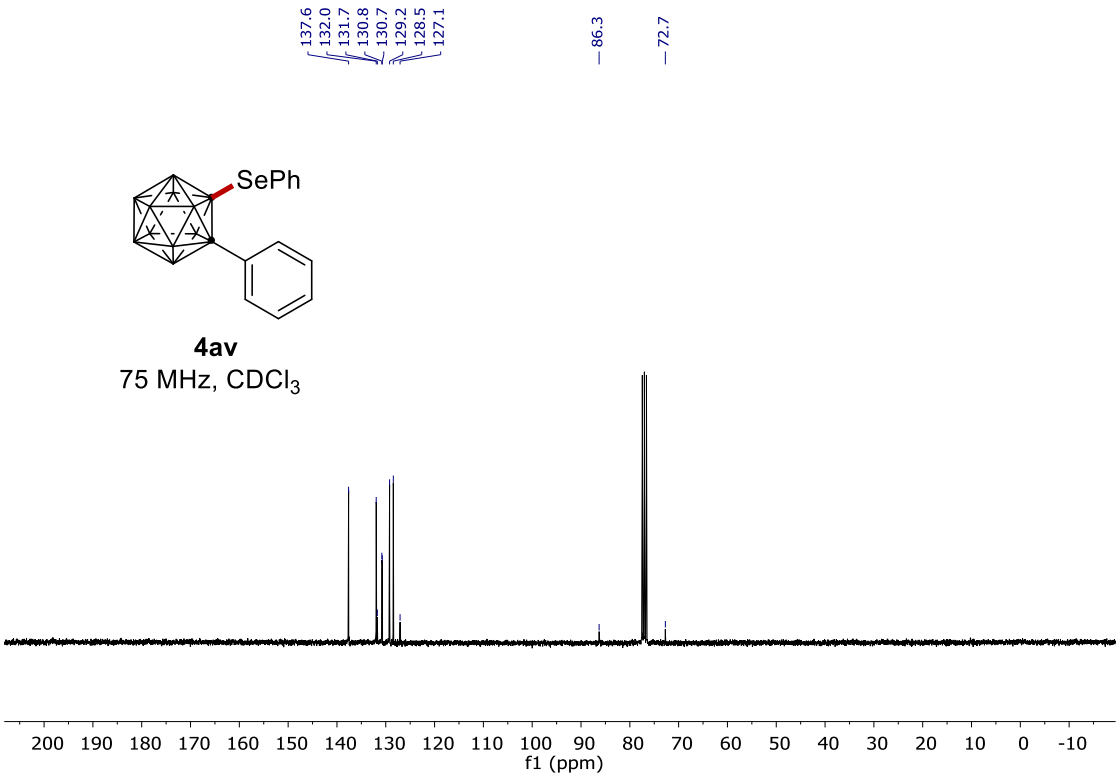
4ga
96 MHz, $CDCl_3$

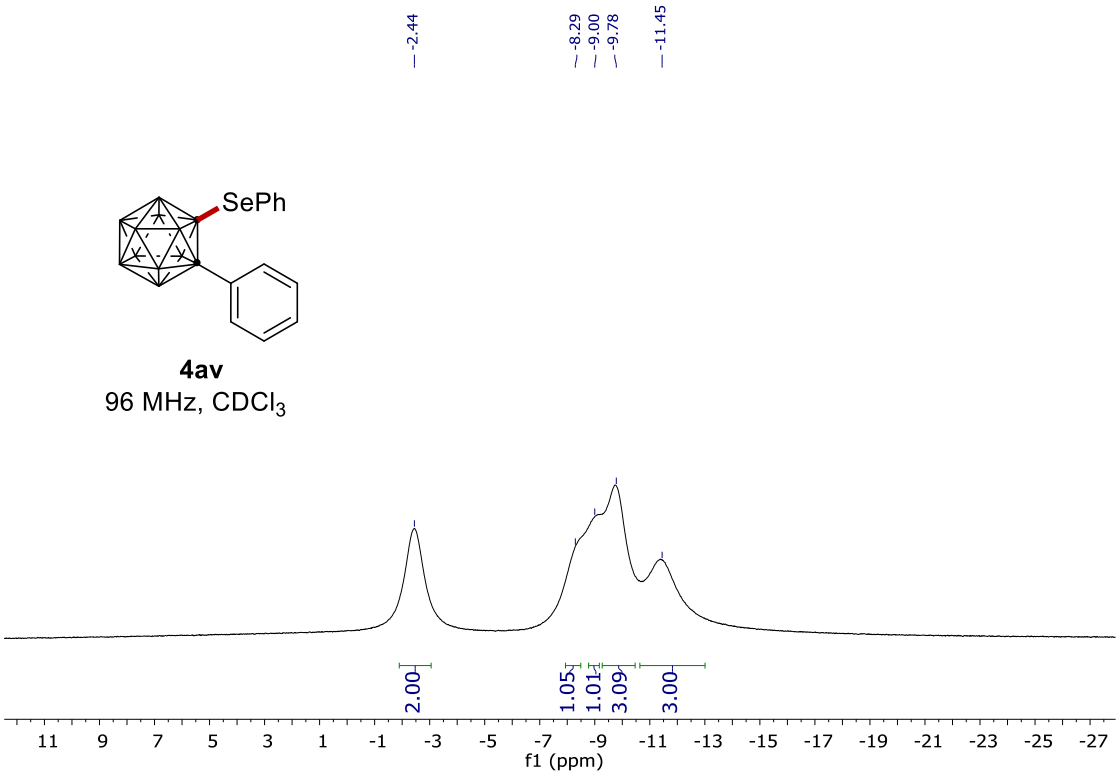


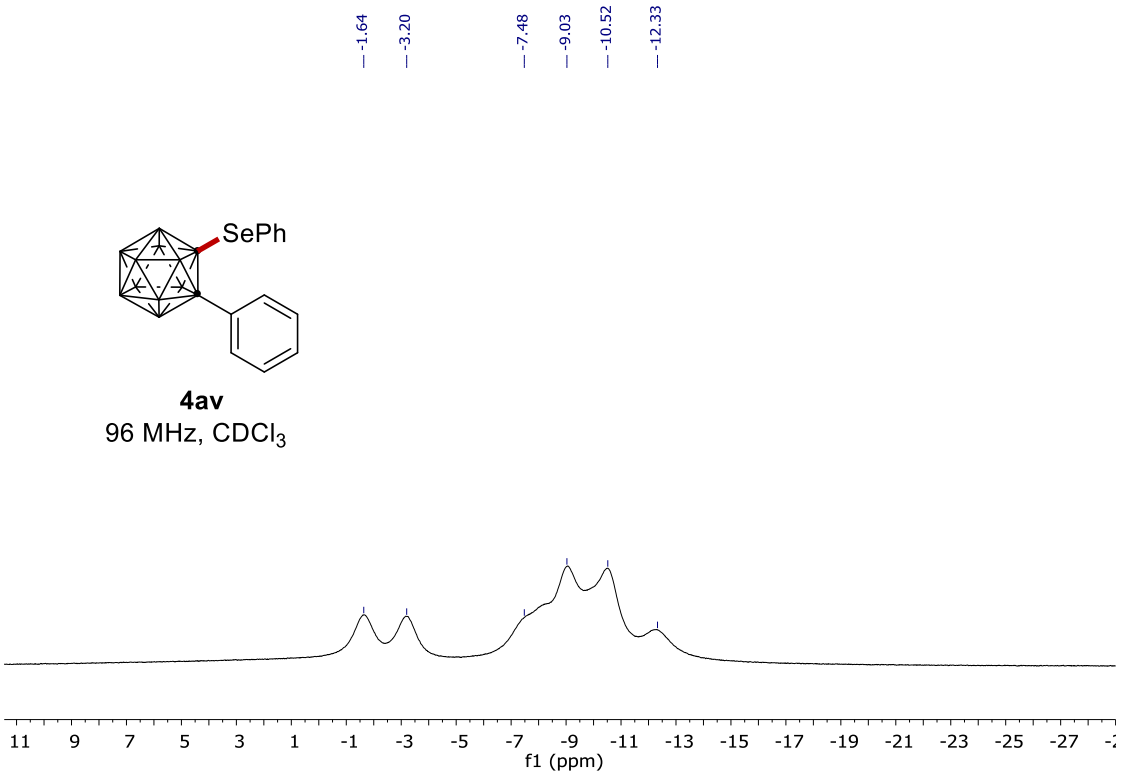
4ga
96 MHz, $CDCl_3$

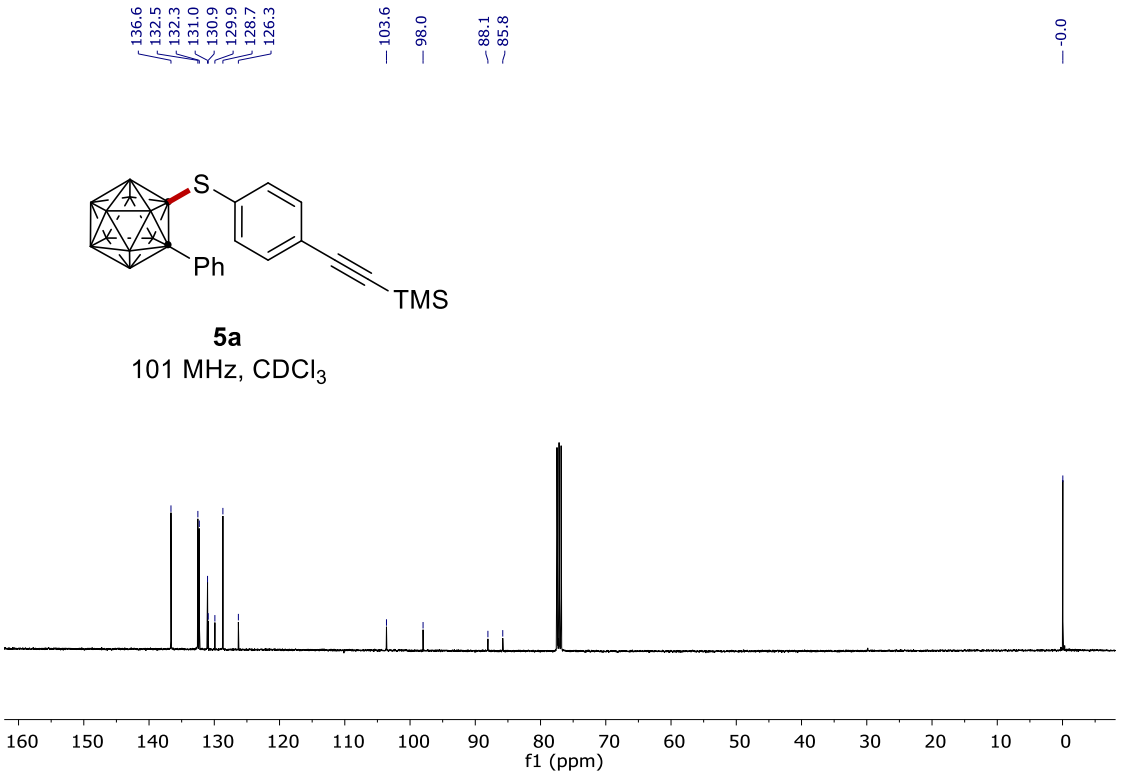


4av
300 MHz, $CDCl_3$

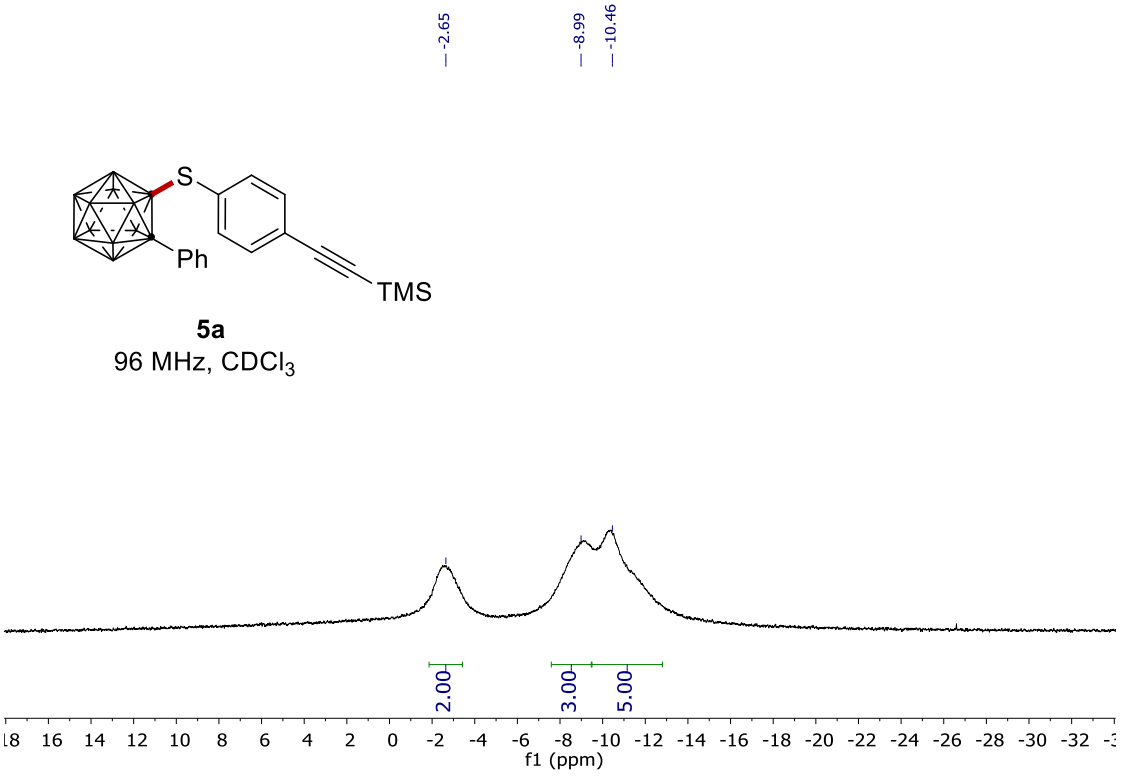

137.6
132.0
131.7
130.8
130.7
129.2
128.5
127.1
86.3
72.7
SePh
4av
75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-2.44
-8.29
-9.00
-9.78
-11.45
SePh
4av
96 MHz, CDCl3
2.00
1.05
1.01
3.09
3.00
11 9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23 -25 -27
f1 (ppm)

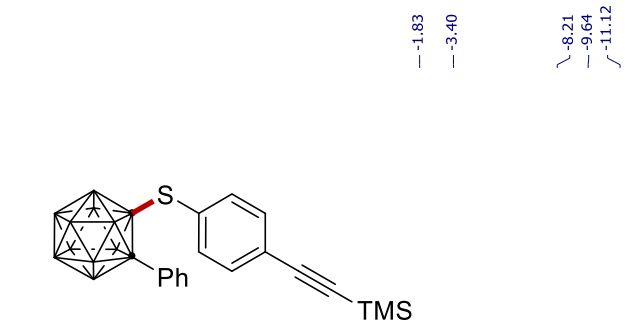

-1.64
-3.20
-7.48
-9.03
-10.52
-12.33
SePh
4av
96 MHz, CDCl3
f1 (ppm)
7.64
7.64
7.63
7.62
7.61
7.59
7.57
7.55
7.54
7.49
7.46
7.44
7.35
7.33
6.87
6.84
0.28
S
Ph
TMS
5a
300 MHz, CDCl3
2.00
1.00
2.00
2.00
2.00
9.02
f1 (ppm)



5a
101 MHz, $CDCl_3$

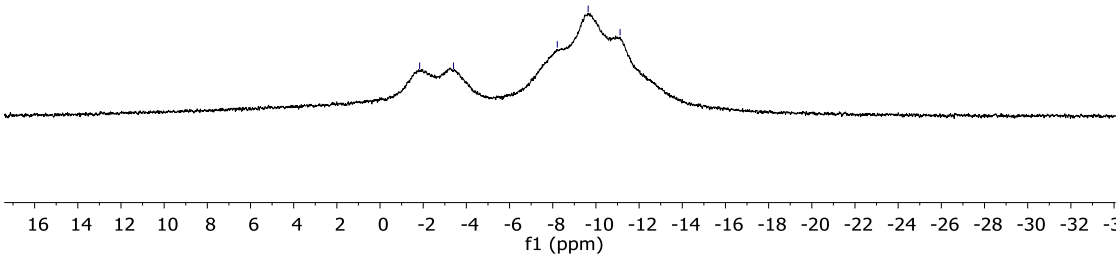


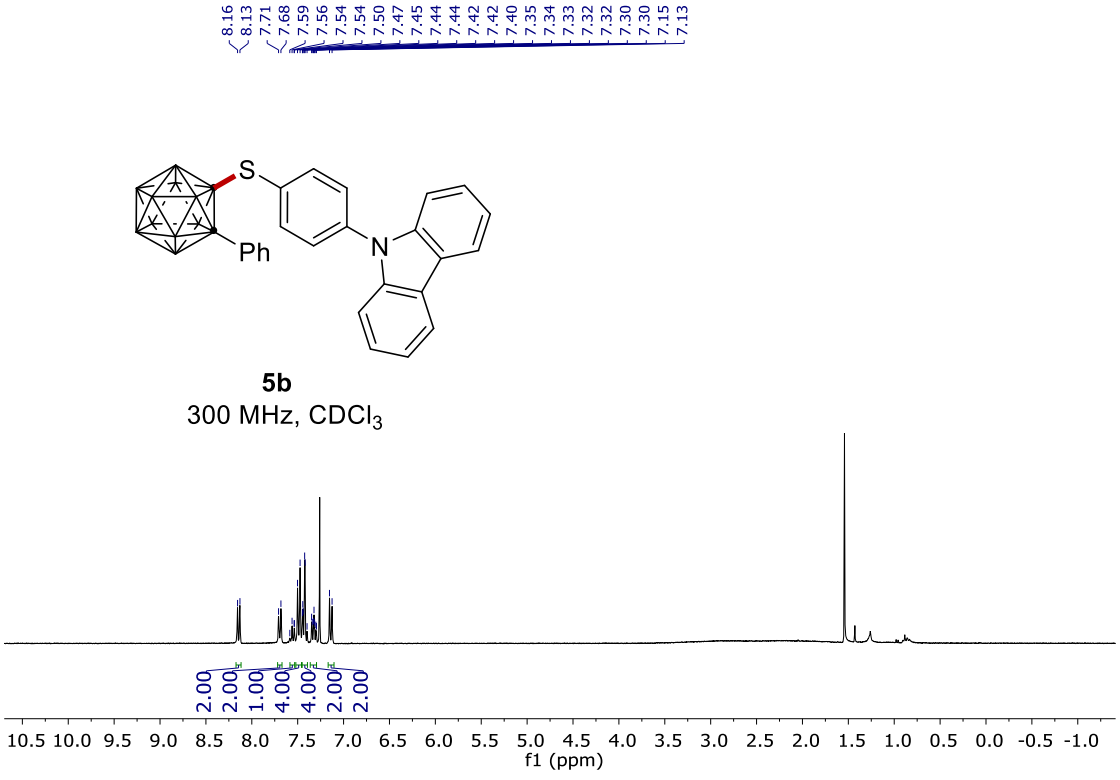
5a
96 MHz, $CDCl_3$



5a

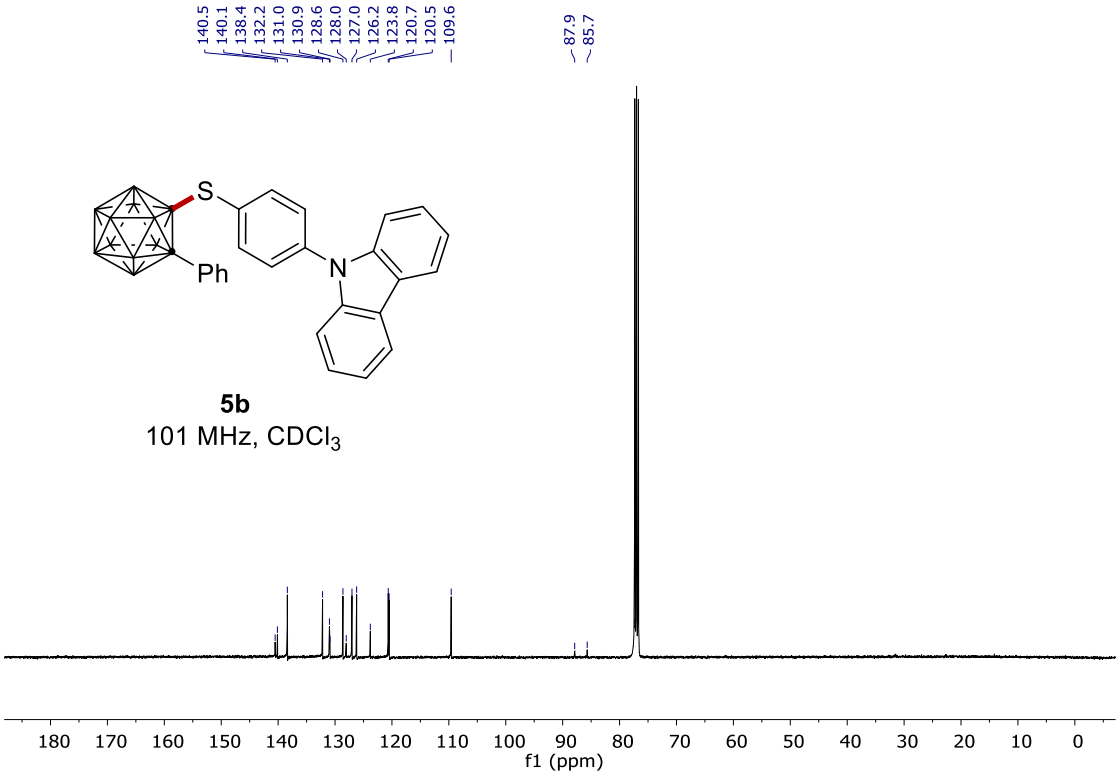
96 MHz, $CDCl_3$



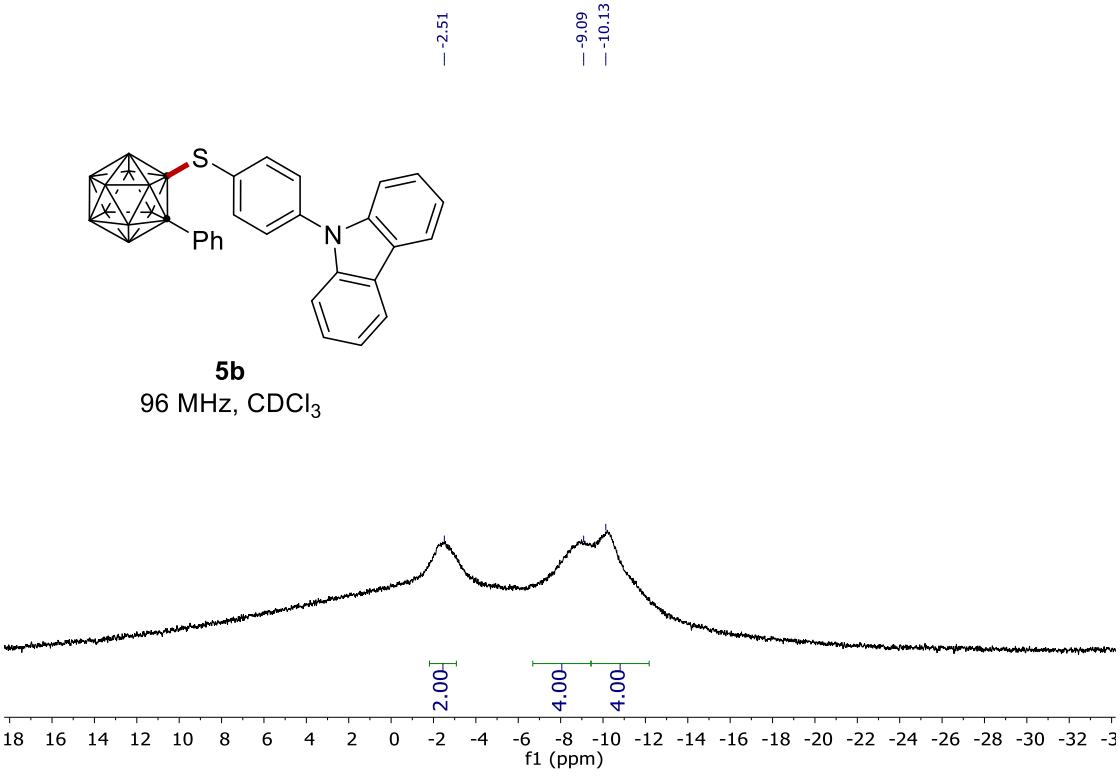


5b

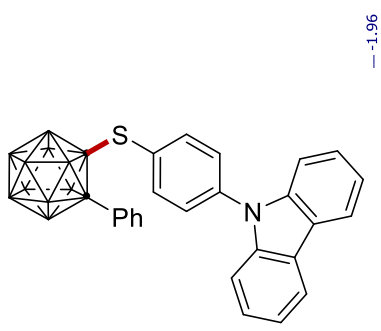
300 MHz, $CDCl_3$



5b
101 MHz, $CDCl_3$

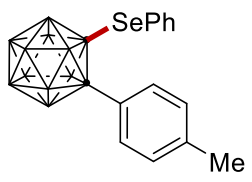


5b
96 MHz, $CDCl_3$



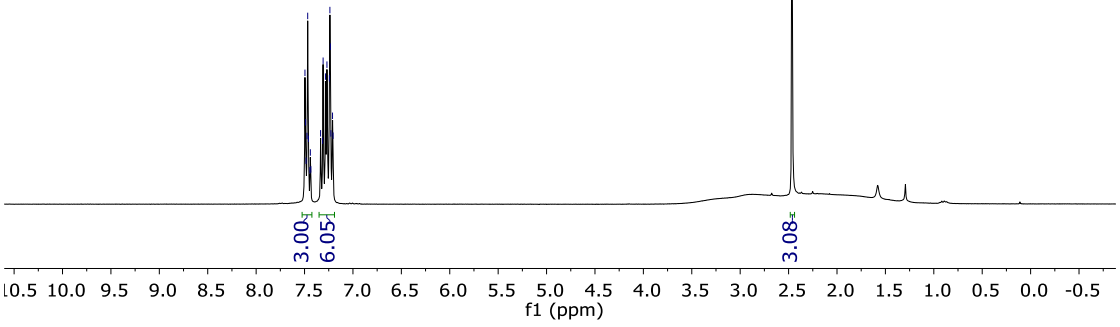
5b

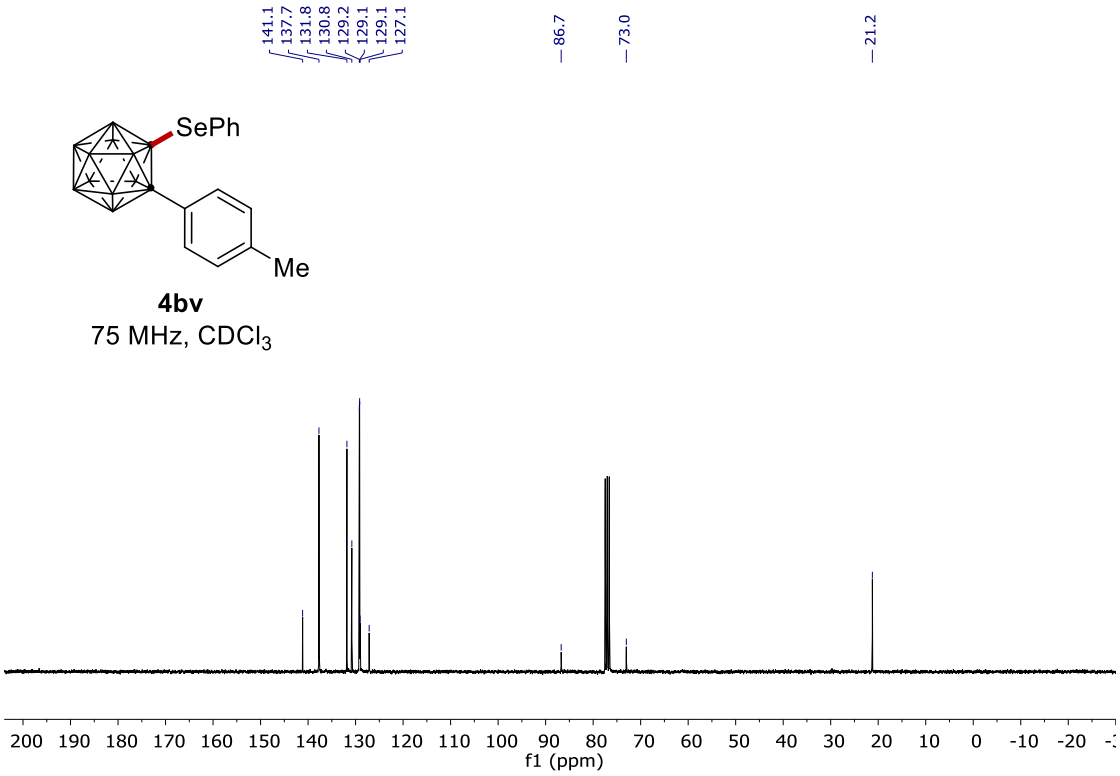
96 MHz, $CDCl_3$

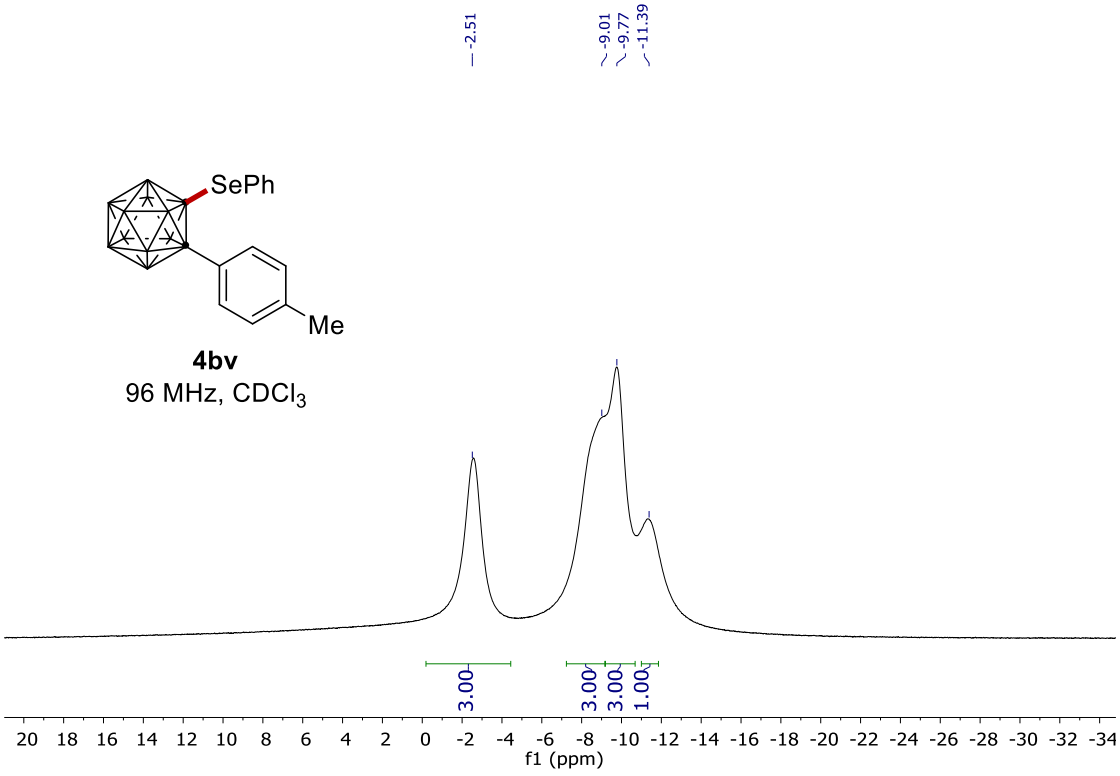


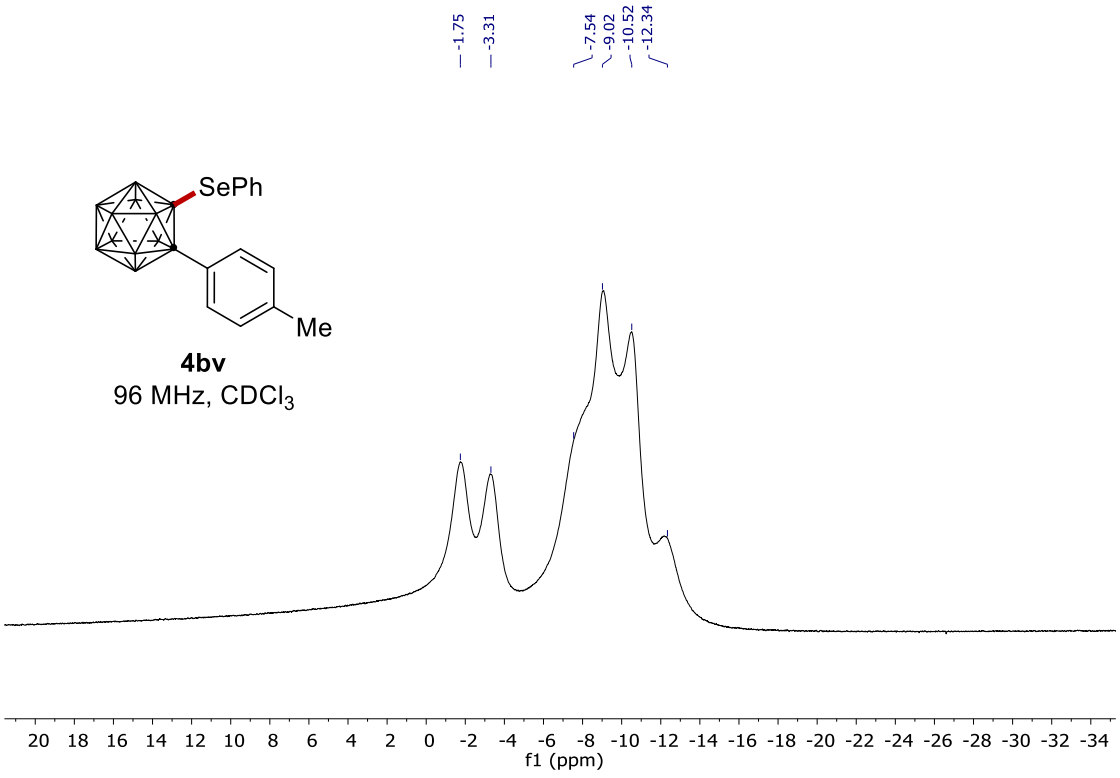
4bv

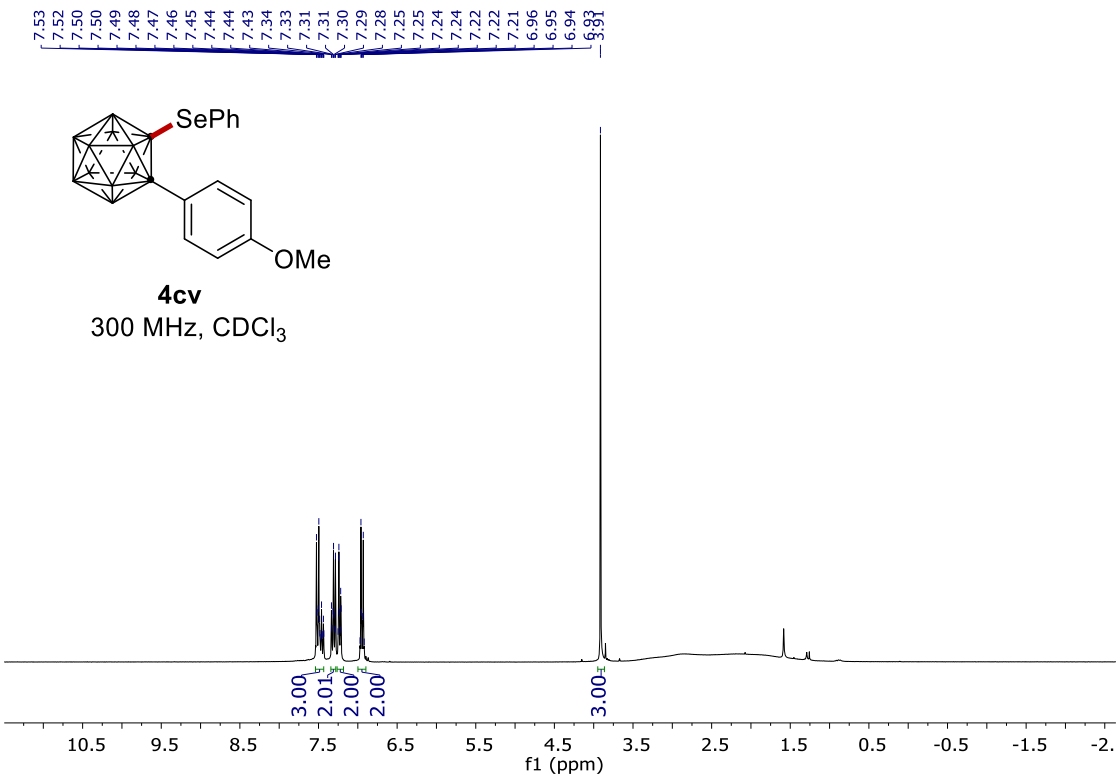
300 MHz, $CDCl_3$

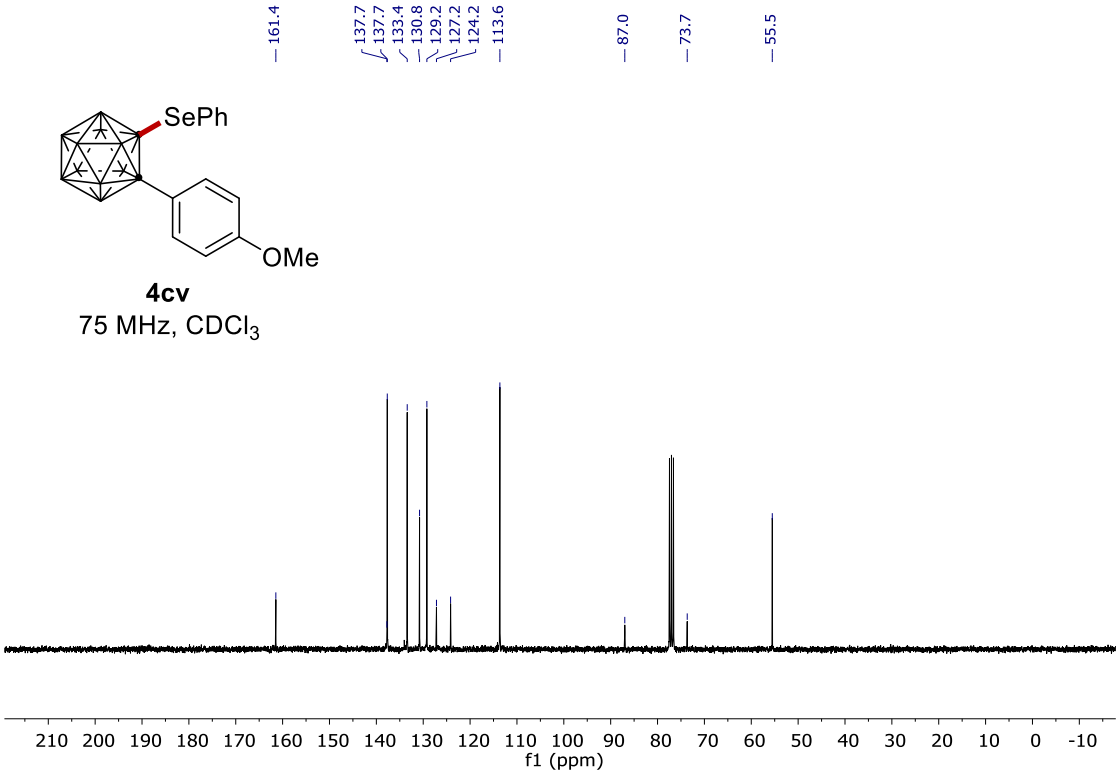


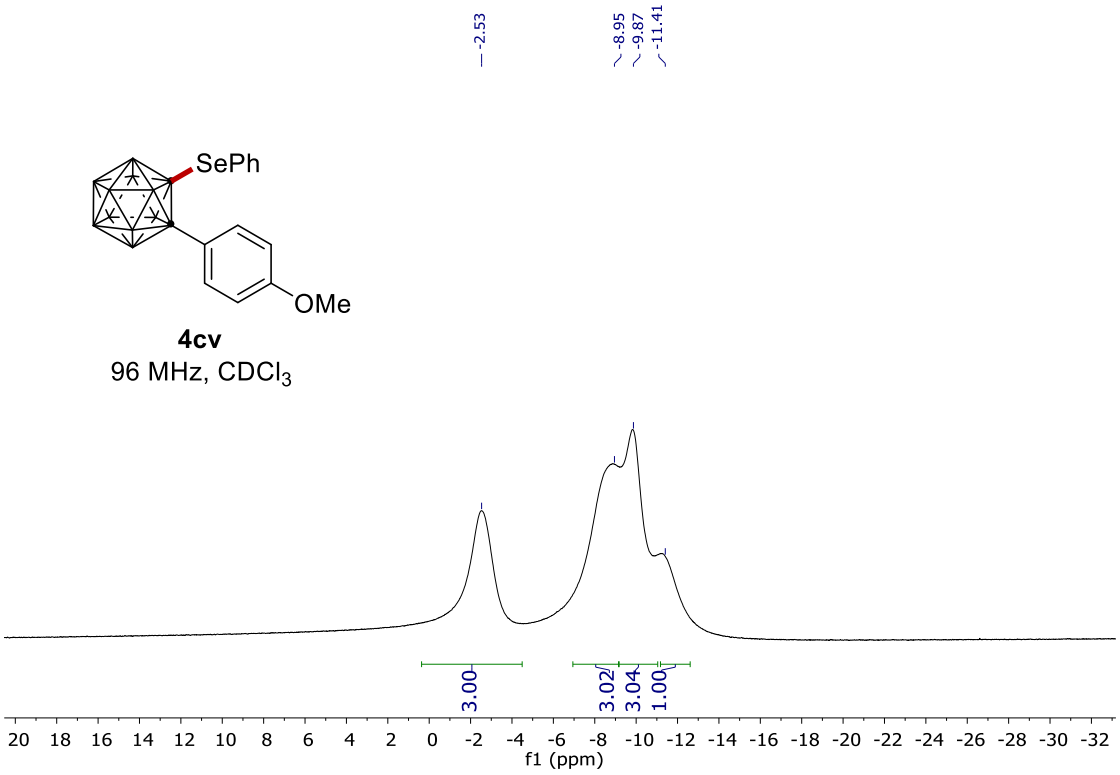

141.1
137.7
131.8
130.8
129.2
129.1
129.1
127.1
86.7
73.0
21.2
SePh
Me
4bv
75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

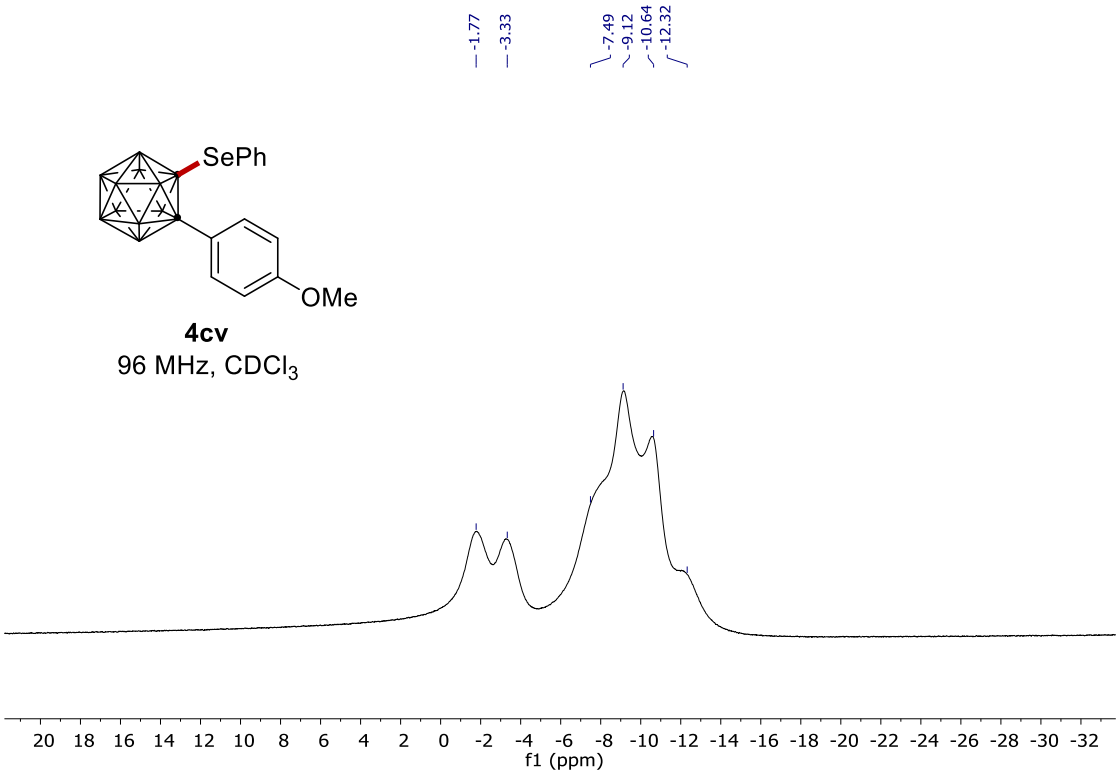

-2.51
-9.01
-9.77
-11.39
SePh
Me
4bv
96 MHz, CDCl3
3.00
3.00
3.00
1.00
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34
f1 (ppm)

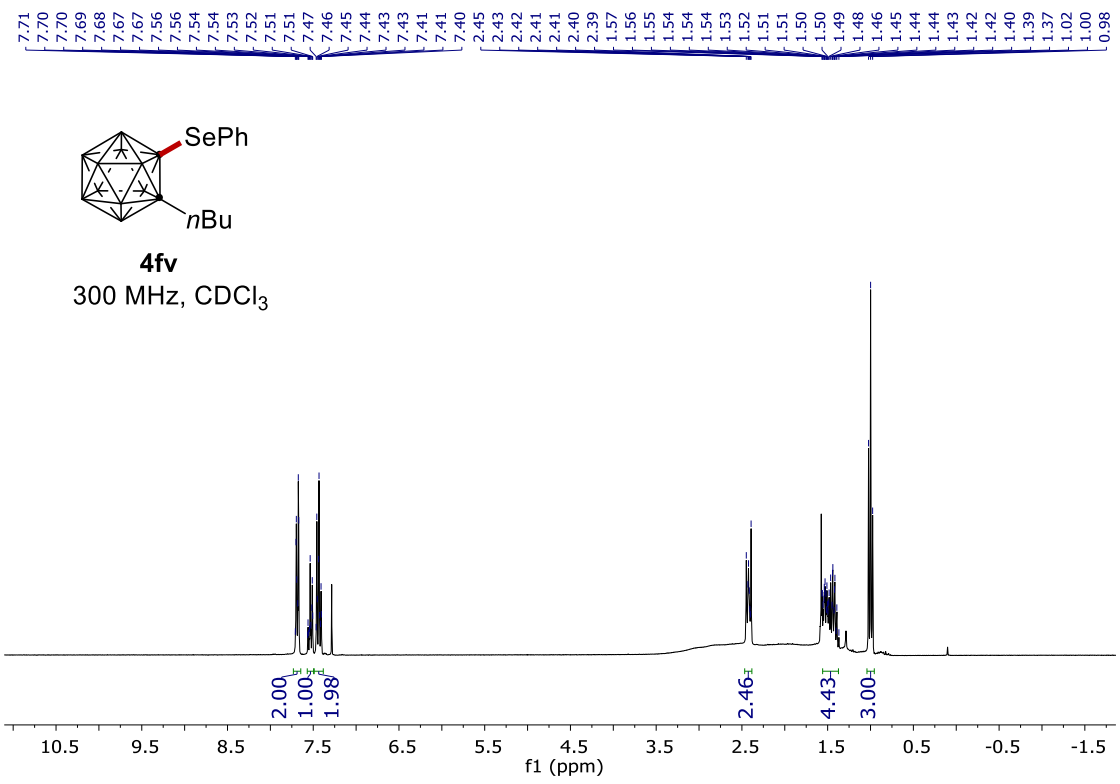

-1.75
-3.31
-7.54
-9.02
-10.52
-12.34
SePh
Me
4bv
96 MHz, CDCl3
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34
f1 (ppm)

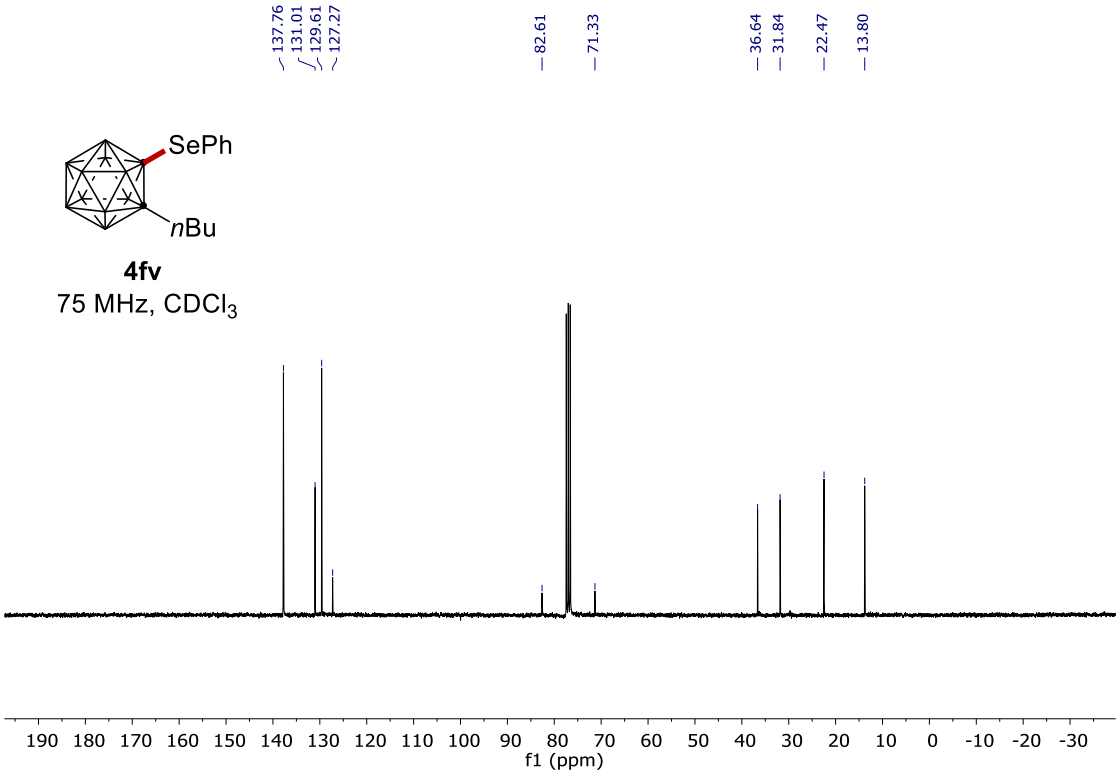

7.53
7.52
7.50
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.44
7.43
7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.25
7.25
7.24
7.24
7.22
7.22
7.21
6.96
6.95
6.94
6.93
3.91
SePh
OMe
4cv
300 MHz, CDCl3
3.00
2.01
2.00
2.00
3.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2.
f1 (ppm)

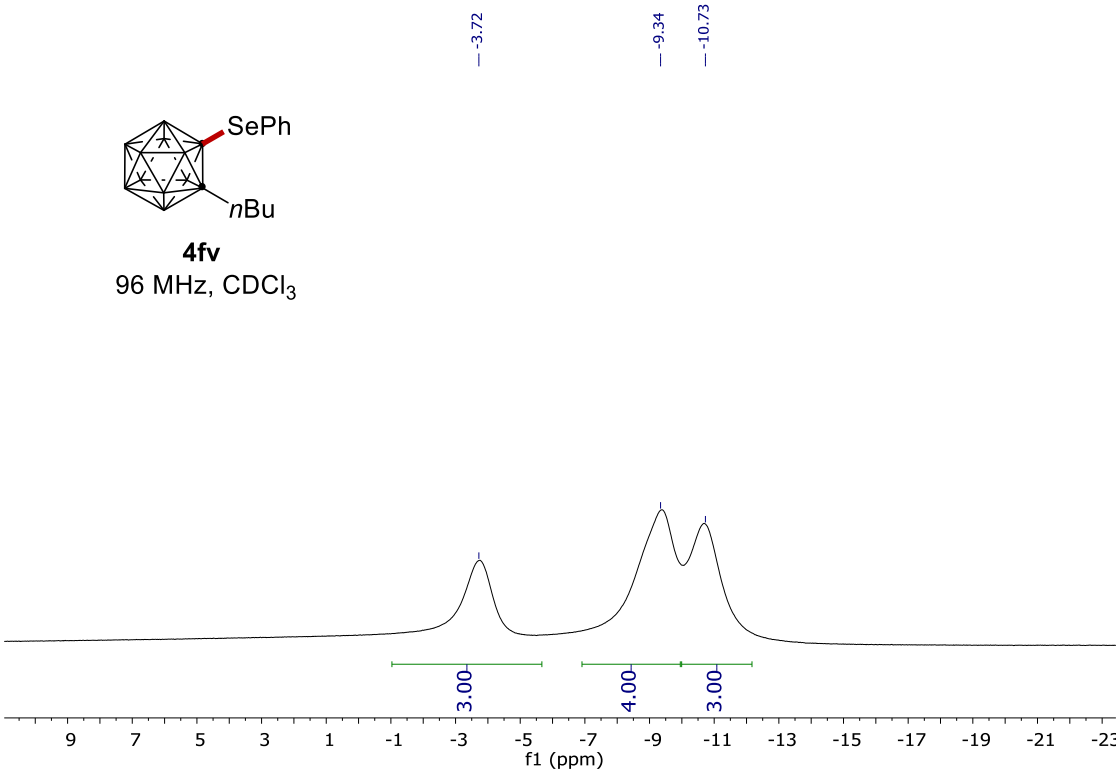

161.4
137.7
137.7
133.4
130.8
129.2
127.2
124.2
113.6
87.0
73.7
55.5
SePh
OMe
4cv
75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

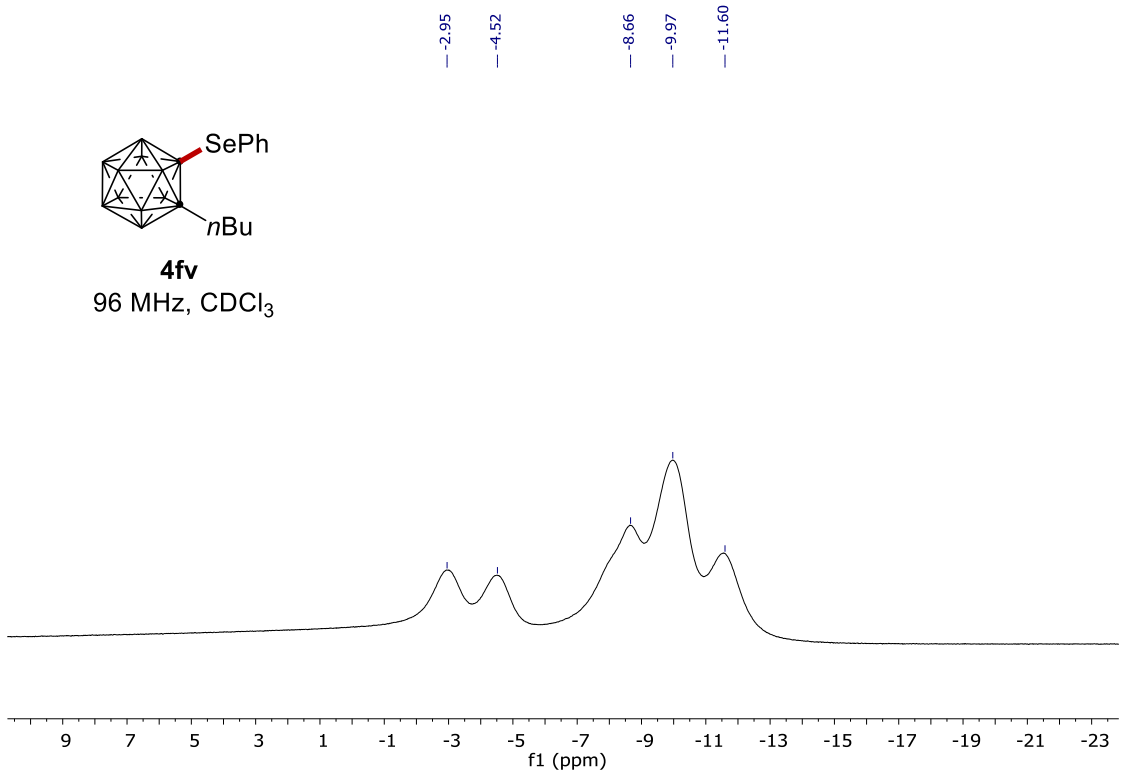

-2.53
-8.95
-9.87
-11.41
SePh
OMe
4cv
96 MHz, CDCl3
3.00
3.02
3.04
1.00
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32
f1 (ppm)


-1.77
-3.33
-7.49
-9.12
-10.64
-12.32
SePh
OMe
4cv
96 MHz, CDCl3
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32
f1 (ppm)


7.71 7.70 7.70 7.69 7.68 7.67 7.67 7.56 7.56 7.54 7.54 7.53 7.52 7.51 7.51 7.47 7.46 7.45 7.44 7.43 7.43 7.41 7.41 7.40
2.45 2.43 2.42 2.41 2.41 2.40 2.39 1.57 1.56 1.55 1.54 1.54 1.54 1.53 1.52 1.51 1.51 1.50 1.50 1.49 1.48 1.46 1.45 1.44 1.44 1.43 1.42 1.42 1.40 1.39 1.37 1.02 1.00 0.98
SePh
nBu
4fv
300 MHz, CDCl3
2.00
1.00
1.98
2.46
4.43
3.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)


137.76
131.01
129.61
127.27
82.61
71.33
36.64
31.84
22.47
13.80
SePh
nBu
4fv
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


-3.72
-9.34
-10.73
SePh
nBu
4fv
96 MHz, CDCl3
3.00
4.00
3.00
9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19 -21 -23
f1 (ppm)


-2.95
-4.52
-8.66
-9.97
-11.60
SePh
nBu
4fv
96 MHz, CDCl3
9
7
5
3
1
-1
-3
-5
-7
-9
-11
-13
-15
-17
-19
-21
-23
f1 (ppm)