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Supporting Information

Photo-Induced Copper-Catalyzed C–H Chalcogenation of Azoles at Room Temperature

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Contents

General Remarks

Photo-induced catalytic reactions were performed under an atmosphere of ambient air in pre-dried quartz tubes using a Luzchem LZC-ICH2 photoreactor with 254 nm irradiation. The temperature was determined to be 25–27 °C in the reaction mixture. The following starting materials were synthesized according to previously described methods: Benzothiazoles (**1b-1c, 1f**),[1] 5-phenylthiazole (**1e**).[2] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.040– 0.063 mm, 70–230 mesh ASTM). Melting points (M. p.): Stuart melting point apparatus SMP3, Barloworld Scientific, the reported values are not corrected. NMR: Spectra were recorded on Varian VX 300, Varian VNMRS 300, Bruker Avance 300, Bruker Avance 400 and 500 or Varian Inova 500 and 600 spectrometers in the solvent indicated; chemical shifts (δ) are given in ppm and referenced to the residual solvent peak. All IR spectra were recorded on a Bruker ATR FT-IR Alpha device. MS: ESI-MS-spectra as well as high resolution mass spectrometry (HRMS) were recorded with a microTOF (ESI-TOF-MS), Bruker Daltonik; EI-spectra were recorded with a AccuTOF (EI-TOF) instrument from Jeol.

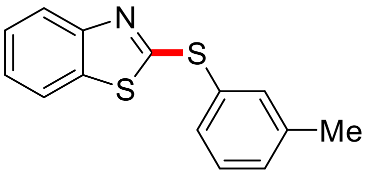
General Procedure for Photo-Induced Copper-Catalyzed C–H Thioarylation:

To a pre-dried 10 mL quartz tube were added heterocycle **1** (0.40 mmol), haloarene **2** or **5** (1.20 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiO*t*Bu (96.0 mg, 1.20 mmol), sulfur powder (26.0 mg, 0.80 mmol), and DMF (2.0 mL) under an ambient air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et_2O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield the desired product **3**.

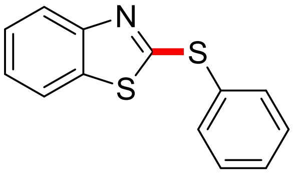
General Procedure for Photo-Induced Copper-Catalyzed C–H Selenoarylation:

To a pre-dried 10 mL quartz tube were added heterocycle **1** (0.40 mmol), haloarene **2** or **5** (1.20 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiO*t*Bu (96.0 mg, 1.20 mmol), selenium powder (63.2 mg, 0.80 mmol), and DMF (2.0 mL) under an ambient air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et_2O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield the desired product **4**.

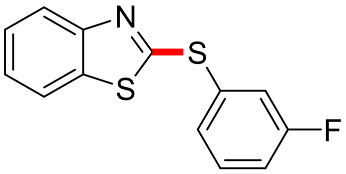
Characterization Data for the Products 3 and 4:



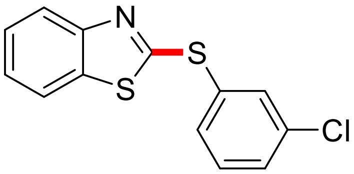
2-(*m*-Tolylthio)benzo[*d*]thiazole (3aa): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-iodo-3-methylbenzene (**2a**) (262 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3aa** (51 mg, 50%) as a pale yellow liquid. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.2, 1.0 Hz, 1H), 7.63 (dd, J = 7.9, 1.1 Hz, 1H), 7.54 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 2.39 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 170.0 (C_q), 153.9 (C_q), 139.9 (C_q), 135.8 (CH), 135.5 (C_q), 132.3 (CH), 131.2 (CH), 129.7 (CH), 129.6 (C_q), 126.1 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH), 21.2 (CH_3). **IR** (ATR): 1455, 1423, 1236, 1019, 1006, 983, 779, 753, 725, 691, 665, 428 cm^{-1}. **MS** (ESI) m/z (relative intensity): 258 $[M+H]^+$ (100), 166 $[M-C_7H_8]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{14}H_{12}NS_2^+$ $[M+H]^+$ 258.0406, found 258.0408. The analytical data are in accordance with those reported in the literature.[3]



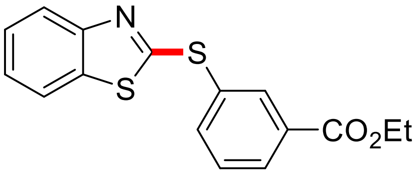
2-(Phenylthio)benzo[*d*]thiazole (3ab): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and iodobenzene (**2b**) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ab** (56 mg, 58%) as a pale yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.87 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.73 (dd, J = 8.0, 1.6 Hz, 2H), 7.63 (ddd, J = 7.9, 1.3, 0.6 Hz, 1H), 7.53–7.43 (m, 3H), 7.39 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.25 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 169.6 (C_q), 153.8 (C_q), 135.5 (C_q), 135.3 (CH), 130.4 (CH), 129.9 (C_q), 129.8 (CH), 126.1 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH). **IR** (ATR): 3057, 1456, 1424, 1006, 982, 752, 726, 703, 689, 496 cm^{-1}. **MS** (ESI) m/z (relative intensity): 266 $[M+Na]^+$ (15), 244 $[M+H]^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{13}H_{10}NS_2^+$ $[M+H]^+$ 244.0249, found 244.0255. The analytical data are in accordance with those reported in the literature.[4]



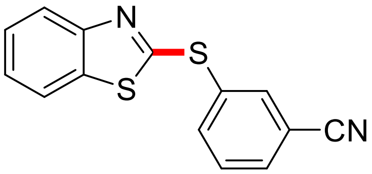
2-{(3-Fluorophenyl)thio}benzo[*d*]thiazole (3ac): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ac** (69.0 mg, 66%) as a pale yellow liquid. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.89 (dt, J = 8.2, 0.9 Hz, 1H), 7.68 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.49 (ddd, J = 7.7, 1.7, 1.0 Hz, 1H), 7.46–7.39 (m, 3H), 7.29 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.18 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.2 (C_q), 162.7 (d, $^1J_{C\text{-}F}$ = 250.3 Hz, C_q), 153.6 (C_q), 135.6 (C_q), 132.0 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, C_q), 131.0 (d, $^3J_{C\text{-}F}$ = 8.3 Hz, CH), 130.3 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, CH), 126.2 (CH), 124.6 (CH), 122.2 (CH), 121.5 (d, $^2J_{C\text{-}F}$ = 22.6 Hz, CH), 120.8 (CH), 117.3 (d, $^2J_{C\text{-}F}$ = 20.9 Hz, CH). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ -110.3 (td, J = 8.4, 5.6 Hz). **IR** (ATR): 1579, 1472, 1457, 1424, 1218, 1007, 879, 783, 726 cm^{-1}. **MS** (ESI) m/z (relative intensity): 262 $[M+H]^+$ (100), 166 $[M\text{-}C_6H_5F]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{13}H_9FNS_2^+$ $[M+H]^+$ 262.0155, found 262.0156.



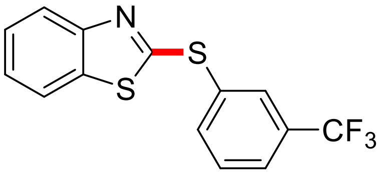
2-{(3-Chlorophenyl)thio}benzo[*d*]thiazole (3ad): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-chloro-3-iodobenzene (**2d**) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ad** (79.0 mg, 71%) as a pale yellow liquid. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.89 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.71 (t, J = 1.9 Hz, 1H), 7.67 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.59 (ddd, J = 7.7, 1.8, 1.1 Hz, 1H), 7.45 (ddd, J = 8.1, 2.0, 1.1 Hz, 1H), 7.41 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.28 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 167.0 (C_q), 153.5 (C_q), 135.5 (C_q), 135.2 (C_q), 134.2 (CH), 132.6 (CH), 131.8 (C_q), 130.6 (CH), 130.2 (CH), 126.2 (CH), 124.5 (CH), 122.1 (CH), 120.7 (CH). **IR** (ATR): 1565, 1456, 1424, 1401, 1019, 1007, 984, 780, 755 cm^{-1}. **MS** (ESI) m/z (relative intensity): 278 $[M+H]^+$ (100), 166 $[M\text{-}C_6H_5Cl]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{13}H_9ClNS_2^+$ $[M+H]^+$ 277.9859, found 277.9860. The analytical data are in accordance with those reported in the literature.[3]



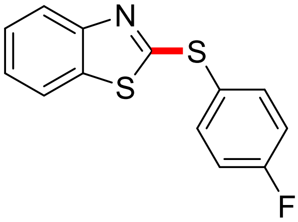
Ethyl 3-(benzo[*d*]thiazol-2-ylthio)benzoate (3ae): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and ethyl 3-iodobenzoate (**2e**) (331.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **3ae** (66.0 mg, 52%) as a colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.16 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.91–7.88 (m, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.40 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.27 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 168.0 (C_q), 165.3 (C_q), 153.7 (C_q), 139.2 (CH), 136.0 (CH), 135.5 (C_q), 132.2 (C_q), 131.3 (CH), 130.6 (C_q), 129.8 (CH), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH), 61.4 (CH_2), 14.2 (CH_3). **IR** (ATR): 1716, 1457, 1424, 1279, 1258, 1124, 1007, 751 cm^{-1}. **MS** (EI) m/z (relative intensity): 315 $[M]^+$ (100), 286 $[M-C_2H_5]^+$ (100), 243 $[M-CO_2Et]^+$ (50). **HR-MS** (ESI) m/z calcd for $C_{16}H_{14}NO_2S_2^+$ $[M+H]^+$ 316.0460, found 316.0460.



3-(Benzo[*d*]thiazol-2-ylthio)benzonitrile (3af): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 3-iodobenzonitrile (**2f**) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **3af** (73.0 mg, 68%) as a colorless solid. M. p.: 77–78 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.93–7.87 (m, 2H), 7.73–7.69 (m, 2H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.43 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 164.9 (C_q), 153.4 (C_q), 138.2 (CH), 137.1 (CH), 135.7 (C_q), 133.1 (CH), 132.5 (C_q), 130.3 (CH), 126.4 (CH), 125.0 (CH), 122.3 (CH), 120.9 (CH), 117.5 (C_q), 114.0 (C_q). **IR** (ATR): 2230, 1456, 1424, 1407, 1007, 986, 765, 757, 726 cm^{-1}. **MS** (ESI) m/z (relative intensity): 291 $[M+Na]^+$ (5), 269 $[M+H]^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{14}H_9N_2S_2^+$ $[M+H]^+$ 269.0202, found 269.0203.

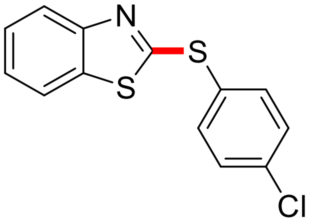


2-{[3-(Trifluoromethyl)phenyl]thio}benzo[*d*]thiazole (3ag): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-iodo-3-(trifluoromethyl)benzene (**2g**) (326.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3af** (90.0 mg, 72%) as a colorless solid. M. p.: 57–59 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.98 (d, J = 0.9 Hz, 1H), 7.91–7.87 (m, 2H), 7.72 (dd, J = 7.9, 0.9 Hz, 1H), 7.68 (dd, J = 8.0, 0.9 Hz, 1H), 7.60–7.55 (m, 1H), 7.41 (ddt, J = 8.3, 7.2, 1.1 Hz, 1H), 7.29 (ddd, J = 8.3, 7.2, 1.1 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 166.4 (C_q), 153.6 (C_q), 137.8 (CH), 135.6 (C_q), 132.2 (q, $^2J_{C\text{-}F}$ = 32.9 Hz, C_q), 131.6 (C_q), 131.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, CH), 130.2 (CH), 126.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, CH), 126.3 (CH), 125.5 (d, $^1J_{C\text{-}F}$ = 273.1 Hz, C_q), 124.8 (CH), 122.2 (CH), 120.9 (CH). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ -62.8 (s). **IR** (ATR): 1458, 1420, 1319, 1273, 1167, 1122, 1067, 1007, 983 cm^{-1}. **MS** (ESI) m/z (relative intensity): 312 $[M+H]^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{14}H_9F_3NS_2^+$ $[M+H]^+$ 312.0123, found 312.0126. The analytical data are in accordance with those reported in the literature.[3]

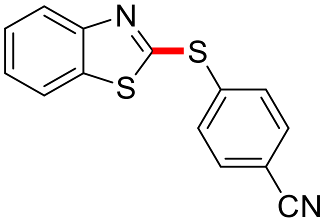


2-{(4-Fluorophenyl)thio}benzo[*d*]thiazole (3ah): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-fluoro-4-iodobenzene (**2h**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ah** (59.0 mg, 56%) as a pale yellow liquid. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.86 (dt, J = 8.2, 0.9 Hz, 1H), 7.72 (dd, J = 8.8, 5.2 Hz, 2H), 7.65 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.39 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.26 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.19–7.14 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 169.4 (C_q), 164.1 (d, $^1J_{C\text{-}F}$ = 252.1 Hz, C_q), 153.9 (C_q), 137.7 (d, $^3J_{C\text{-}F}$ = 8.8 Hz, CH), 135.4 (C_q), 126.2 (CH), 125.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, C_q), 124.3 (CH), 121.9 (CH), 120.7 (CH), 117.2 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, CH). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -108.94 (tt, J = 8.4, 5.2 Hz). **IR** (ATR): 2924, 1588, 1489, 1458, 1425, 1232, 1156, 1020, 1006, 983, 755 cm^{-1}. **MS** (ESI) m/z (relative intensity): 262 $[M+H]^+$ (100), 166 $[M-C_6H_5F]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{13}H_9FNS_2^+$

$[M+H]^+$ 262.0155, found 262.0154. The analytical data are in accordance with those reported in the literature.[3]

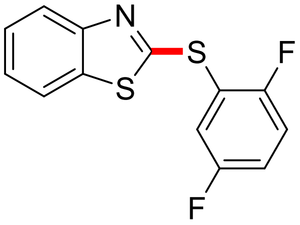


2-{(4-Chlorophenyl)thio}benzo[*d*]thiazole (3ai): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-chloro-4-iodobenzene (**2i**) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ai** (66.0 mg, 59%) as a pale yellow liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.87 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.69–7.61 (m, 3H), 7.45–7.42 (m, 2H), 7.40 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.27 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 168.3 (C_q), 153.7 (C_q), 136.9 (C_q), 136.3 (CH), 135.4 (C_q), 130.1 (CH), 128.3 (C_q), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH). **IR** (ATR): 1571, 1474, 1456, 1425, 1092, 1004, 986, 820, 755, 725, 501 cm^{-1}. **MS** (ESI) m/z (relative intensity): 262 $[M+H]^+$ (100), 244 $[M-Cl]^+$ (10), 166 $[M-C_6H_5Cl]^+$ (10). **HR-MS** (ESI) m/z calcd for $C_{13}H_9ClNS_2^+$ $[M+H]^+$ 277.9859, found 277.9861. The analytical data are in accordance with those reported in the literature.[4]

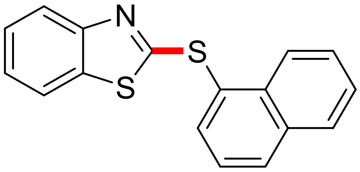


4-(Benzo[*d*]thiazol-2-ylthio)benzonitrile (3aj): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 4-iodobenzonitrile (**2j**) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **3aj** (65.0 mg, 61%) as a colorless solid. M. p.: 110–113 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 7.93 (ddd, *J* = 8.2, 1.2, 0.7 Hz, 1H), 7.76 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.45 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.0, 7.3, 1.3 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 163.3 (C_q), 153.2 (C_q), 137.4 (C_q), 135.9 (C_q), 132.9 (CH), 132.8 (CH), 126.4 (CH), 125.2 (CH), 122.5 (CH), 120.9 (CH), 117.8 (C_q), 112.7 (C_q).

IR (ATR): 2229, 1591, 1455, 1423, 1398, 1273, 1079, 1007, 987, 833, 755, 723, 553 cm^{-1}. **MS** (ESI) m/z (relative intensity): 269 [M+H]$^+$ (100), 291 [M+Na]$^+$ (7). **HR-MS** (ESI) m/z calcd for $C_{14}H_9N_2S_2^+$ [M+H]$^+$ 269.0202, found 269.0202.

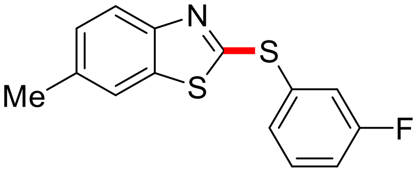


2-{(2,5-Difluorophenyl)thio}benzo[*d*]thiazole (3ak): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1,4-difluoro-2-iodobenzene (**2k**) (289.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **3ak** (57.0 mg, 51%) as a pale yellow solid. M. p.: 86–87 °C. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ 7.86 (dt, J = 8.2, 0.8 Hz, 1H), 7.76–7.69 (m, 1H), 7.66 (dt, J = 8.1, 0.9 Hz, 1H), 7.40 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.27 (ddd, J = 8.2, 7.3, 1.2 Hz, 1H), 7.04–6.97 (m, 2H). **^{13}C-NMR** (126 MHz, CDCl$_3$): δ 167.0 (C$_q$), 165.1 (dd, $J_{C\text{-}F}$ = 214.0, 11.4 Hz, C$_q$), 163.1 (dd, $J_{C\text{-}F}$ = 225.5, 12.7, C$_q$), 153.7 (C$_q$), 138.7 (d, $J_{C\text{-}F}$ = 10.7 Hz, CH), 135.5 (C$_q$), 126.2 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH), 112.9 (dd, $J_{C\text{-}F}$ = 21.8, 3.9 Hz, CH), 112.6 (dd, $J_{C\text{-}F}$ = 18.7, 4.1 Hz, C$_q$), 105.5 (t, $J_{C\text{-}F}$ = 26.1 Hz, CH). **^{19}F NMR** (471 MHz, CDCl$_3$): δ -99.4– -99.5 (m), -103.5 (dt, J = 18.7, 7.7 Hz). **IR** (ATR): 1594, 1484, 1460, 1423, 1266, 1143, 1006, 755, 726 cm^{-1}. **MS** (EI) m/z (relative intensity): 279 [M]$^+$ (60), 260 [M-F]$^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{13}H_8F_2NS_2^+$ [M+H]$^+$ 280.0061, found 280.0060.

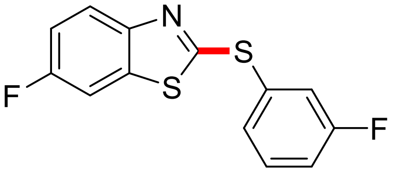


2-(Naphthalen-1-ylthio)benzo[*d*]thiazole (3al): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-iodonaphthalene (**2l**) (305.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3al** (59.0 mg, 50%) as a pale yellow solid. M. p.: 98–99 °C. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ 8.48 (dd, J = 6.3, 3.5 Hz, 1H), 8.06-8.04 (m 2H), 7.93 (dd, J = 6.1, 3.4 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.57–7.54 (m, 3H), 7.50 (dt, J = 7.9, 0.9 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.19 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (126 MHz, CDCl$_3$): δ 170.0 (C$_q$), 153.8

(C_q), 136.3 (CH), 135.5 (C_q), 134.4 (C_q), 134.2 (C_q), 132.1 (CH), 128.7 (CH), 127.8 (CH), 126.9 (CH), 126.7 (C_q), 126.0 (CH), 125.8 (CH), 125.4 (CH), 124.1 (CH), 121.7 (CH), 120.6 (CH). **IR** (ATR): 3054, 1502, 1456, 1424, 1006, 786, 770, 755, 726, 664 cm^{-1}. **MS** (ESI) m/z (relative intensity): 294 $[M+H]^+$ (100), 166 $[M-C_{10}H_8]$ (5). **HR-MS** (ESI) m/z calcd for $C_{17}H_{12}NS_2^+$ $[M+H]^+$ 294.0406, found 294.0405. The analytical data are in accordance with those reported in the literature.[3]

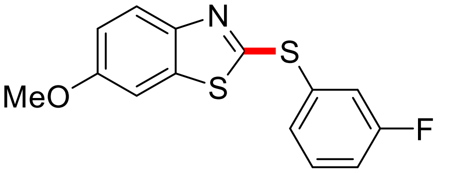


2-{(3-Fluorophenyl)thio}-6-methylbenzo[*d*]thiazole (3bc): The representative procedure was followed using 6-methylbenzo[*d*]thiazole (**1b**) (60.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3bc** (65.0 mg, 58%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 1H), 7.48–7.44 (m, 2H), 7.43–7.36 (m, 2H), 7.22 (ddd, J = 8.3, 1.7, 0.6 Hz, 1H), 7.15 (tdd, J = 8.3, 2.6, 1.1 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 165.4 (C_q), 162.8 (d, $^1J_{C\text{-}F}$ = 250.5 Hz, C_q), 151.8 (C_q), 135.9 (C_q), 134.9 (C_q), 132.4 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, C_q), 130.9 (d, $^3J_{C\text{-}F}$ = 8.3 Hz, CH), 129.9 (d, $^4J_{C\text{-}F}$ = 3.2 Hz, CH), 127.8 (CH), 121.8 (CH), 121.2 (d, $^2J_{C\text{-}F}$ = 22.6 Hz, CH), 120.7 (CH), 117.1 (d, $^2J_{C\text{-}F}$ = 21.1 Hz, CH), 21.4 (CH_3). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -110.4 (dd, J = 8.5, 5.8 Hz). **IR** (ATR): 1595, 1579, 1471, 1440, 1263, 1218, 1012, 990, 879 cm^{-1}. **MS** (ESI) m/z (relative intensity): 298 $[M+Na]^+$ (15), 276 $[M+H]^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{14}H_{11}FNS_2^+$ $[M+H]^+$ 276.0311, found 276.0312.

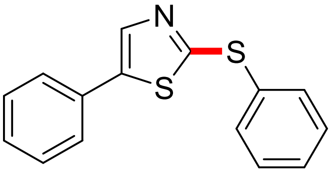


6-Fluoro-2-{(3-fluorophenyl)thio}benzo[*d*]thiazole (3cc): The representative procedure was followed using 6-fluorobenzo[*d*]thiazole (**1c**) (60.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3cc** (60.0 mg, 54%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.82 (ddd, J = 9.0, 4.8, 0.5 Hz, 1H), 7.50–7.39 (m, 3H), 7.36 (ddd, J = 8.0, 2.6, 0.4 Hz, 1H), 7.21–7.10 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.7 (C_q), 162.8 (d, $J_{C\text{-}F}$ = 251.0 Hz, C_q), 160.1 (d, $J_{C\text{-}F}$ = 245.9 Hz, C_q), 150.3 (C_q), 136.6 (d, $J_{C\text{-}F}$ = 11.1 Hz, C_q), 131.7

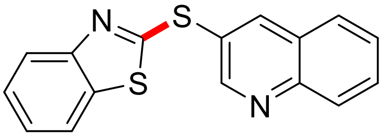
(d, $J_{\text{C-F}}$ = 7.9 Hz, C_q), 131.2 (d, $J_{\text{C-F}}$ = 8.3 Hz, CH), 130.3 (d, $J_{\text{C-F}}$ = 3.3 Hz, CH), 123.1 (d, $J_{\text{C-F}}$ = 9.3 Hz, CH), 121.5 (d, $J_{\text{C-F}}$ = 22.6 Hz, CH), 117.5 (d, $J_{\text{C-F}}$ = 21.0 Hz, CH), 114.8 (d, $J_{\text{C-F}}$ = 24.6 Hz, CH), 107.3 (d, $J_{\text{C-F}}$ = 26.9 Hz, CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -110.1 (td, J = 8.4, 5.6 Hz), -116.2 (td, J = 8.4, 4.7 Hz). **IR** (ATR): 1595, 1579, 1567, 1469, 1443, 1420, 1250, 1217, 1192 cm^{-1}. **MS** (EI) m/z (relative intensity): 278 $[M]^+$ (100), 260 $[M-F]^+$ (5). **HR-MS** (EI) m/z calcd for $C_{13}H_7F_2NS_2$ $[M]^+$ 278.9988, found 278.9985.



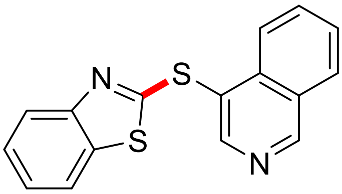
2-{(3-Fluorophenyl)thio}-6-methoxybenzo[*d*]thiazole (3dc): The representative procedure was followed using 6-methoxybenzo[*d*]thiazole (**1d**) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **3dc** (86.0 mg, 74%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.9, 0.4 Hz, 1H), 7.44–7.34 (m, 3H), 7.14 (d, J = 2.4 Hz, 1H), 7.14–7.09 (m, 1H), 7.01 (dd, J = 9.0, 2.4 Hz, 1H), 3.80 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 162.8 (C_q), 162.7 (d, $^1J_{\text{C-F}}$ = 251.3 Hz, C_q), 157.4 (C_q), 148.1 (C_q), 137.3 (C_q), 132.8 (d, $^3J_{\text{C-F}}$ = 7.9 Hz, C_q), 130.9 (^{3}d, $J_{\text{C-F}}$ = 8.3 Hz, CH), 129.4 (d, $^4J_{\text{C-F}}$ = 3.2 Hz, CH), 122.8 (CH), 120.7 (d, $^2J_{\text{C-F}}$ = 22.7 Hz, CH), 116.7 (d, $^2J_{\text{C-F}}$ = 21.0 Hz, CH), 115.3 (CH), 103.8 (CH), 55.7 (CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -110.46 (td, J = 8.5, 5.7 Hz). IR (ATR): 1597, 1473, 1452, 1432, 1260, 1221, 1027, 1011, 878, 782, 520 cm^{-1}. **MS** (ESI) m/z (relative intensity): 314 $[M+Na]^+$ (5), 292 $[M+H]^+$ (100). **HR-MS** (ESI) m/z calcd for $C_{14}H_{11}FNOS_2^+$ $[M+H]^+$ 292.0261, found 292.0261.



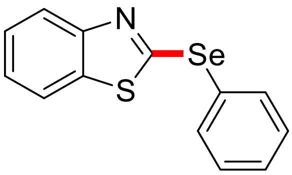
5-Phenyl-2-(phenylthio)thiazole (3eb): The representative procedure was followed using 5-phenylthiazole (**1e**) (64.0 mg, 0.40 mmol) and iodobenzene (**2b**) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3eb** (60.0 mg, 56%) as a yellow liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.65–7.63 (m, 2H), 7.43-7.41 (m, 5H), 7.35–7.31 (m, 2H), 7.29–7.25 (m, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 164.8 (C_q), 140.7 (C_q), 138.6 (CH), 133.7 (CH), 131.8 (C_q), 130.9 (C_q), 129.7 (CH), 129.5 (CH), 129.0 (CH), 128.2 (CH), 126.4 (CH). **IR** (ATR): 1475, 1444, 1389, 1041, 1016, 754, 689 cm^{-1}. **MS** (ESI) m/z (relative intensity): 270 [M+H]$^+$ (100), 192 [M-Ph]$^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{15}H_{12}NS_2^+$ [M+H]$^+$ 270.0406, found 270.0408.



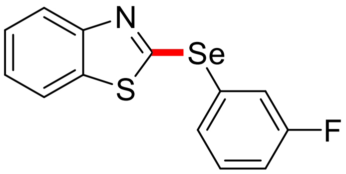
2-(Quinolin-3-ylthio)benzo[*d*]thiazole (3am): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 3-bromoquinoline (**5m**) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/3) yielded **3am** (71.0 mg, 60%) as a colorless solid. M. p.: 138–139 °C. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ 9.08 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 2.3, 0.8 Hz, 1H), 8.15 (dd, J = 8.5, 1.0 Hz, 1H), 7.89–7.76 (m, 3H), 7.67–7.55 (m, 2H), 7.39 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.25 (ddd, J = 8.1, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, CDCl$_3$): δ 167.0 (C$_q$), 154.0 (CH), 153.6 (C$_q$), 147.9 (C$_q$), 142.6 (CH), 135.5 (C$_q$), 131.1 (CH), 129.5 (CH), 128.0 (C$_q$), 127.9 (CH), 127.6 (CH), 126.3 (CH), 124.6 (CH), 123.8 (C$_q$), 122.1 (CH), 120.8 (CH). **IR** (ATR): 3060, 1561, 1488, 1455, 1423, 1354, 1310, 1019, 1005, 955 cm^{-1}. **MS** (ESI) m/z (relative intensity): 295 [M+H]$^+$ (100), 317 [M+Na]$^+$ (10). **HR-MS** (ESI) m/z calcd for $C_{16}H_{11}N_2S_2^+$ [M+H]$^+$ 295.0358, found 295.0364.



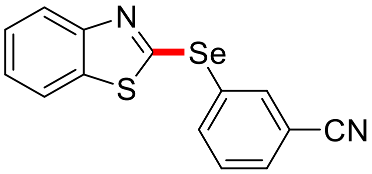
2-(Isoquinolin-4-ylthio)benzo[*d*]thiazole (3an): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 4-bromoisoquinoline (**5n**) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/3) yielded **3an** (61.0 mg, 52%) as a pale yellow solid. M. p.: 136–138 °C. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ 9.39 (s, 1H), 8.97 (s, 1H), 8.35 (dd, J = 8.4, 1.0 Hz, 1H), 8.06 (ddd, J = 8.1, 1.4, 0.8 Hz, 1H), 7.85 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.76 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.68 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.53 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.21 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, CDCl$_3$): δ 167.9 (C$_q$), 155.7 (CH), 153.7 (C$_q$), 150.7 (CH), 136.9 (C$_q$), 135.5 (C$_q$), 132.2 (CH), 129.3 (C$_q$), 128.4 (2 CH), 126.2 (CH), 124.5 (CH), 124.4 (CH), 122.4 (C$_q$), 122.0 (CH), 120.8 (CH). **IR** (ATR): 1616, 1564, 1455, 1423, 1376, 1231, 1018, 1005, 977, 776, 751 cm^{-1}. **MS** (ESI) m/z (relative intensity): 295 [M+H]$^+$ (100), 130 [M-$C_7H_4NS_2$]$^+$ (10). **HR-MS** (ESI) m/z calcd for $C_{16}H_{11}N_2S_2^+$ [M+H]$^+$ 295.0358, found 295.0361.



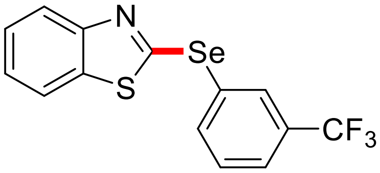
2-(Phenylselanyl)benzo[*d*]thiazole (4ab): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and iodobenzene (**2b**) (245.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **4ab** (63.0 mg, 54%) as a pale yellow liquid. **^{1}H-NMR** (301 MHz, CDCl$_3$): δ 7.91 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.84–7.80 (m, 2H), 7.67 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.53–7.35 (m, 4H), 7.29–7.22 (m, 1H). **^{13}C-NMR** (76 MHz, CDCL$_3$): δ 162.7 (C$_q$), 154.6 (C$_q$), 136.6 (CH), 132.4 (C$_q$), 130.1 (CH), 129.9 (CH), 126.6 (C$_q$), 126.0 (CH), 124.3 (CH), 121.9 (CH), 120.8 (CH). **IR** (ATR): 3055, 1454, 1437, 1421, 1232, 972, 755, 740, 726, 689 cm^{-1}. **MS** (ESI) m/z (relative intensity): 292 [M+H]$^+$ (100), 214 [M-Ph]$^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{13}H_{10}NSSe^+$ [M+H]$^+$ 291.9694, found 291.9694. The analytical data are in accordance with those reported in the literature.[4]



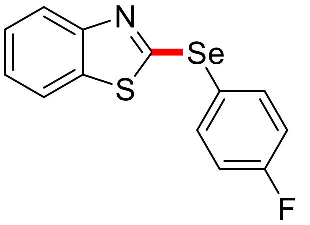
2-{(3-Fluorophenyl)selanyl}benzo[*d*]thiazole (4ac): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4ac** (73.0 mg, 59%) as a yellow liquid. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ 7.93 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.70 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.57 (ddd, J = 7.7, 1.6, 0.9 Hz, 1H), 7.53 (ddd, J = 8.2, 2.6, 1.5 Hz, 1H), 7.43–7.35 (m, 2H), 7.29 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.16 (tdd, J = 8.5, 2.6, 1.0 Hz, 1H). **^{13}C-NMR** (126 MHz, CDCl$_3$): δ 162.6 (d, $^1J_{C\text{-}F}$ = 251.5 Hz, C$_q$), 160.6 (C$_q$), 154.3 (C$_q$), 136.7 (C$_q$), 131.7 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, CH), 131.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, CH), 127.9 (d, $^3J_{C\text{-}F}$ = 7.1 Hz, C$_q$), 126.1 (CH), 124.7 (CH), 122.9 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, CH), 122.2 (CH), 120.8 (CH), 117.0 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, CH). **^{19}F-NMR** (471 MHz, CDCl$_3$): δ -110.2 (td, J = 8.3, 5.8 Hz). **IR** (ATR): 3060, 1586, 1470, 1455, 1422, 1212, 973, 858, 781, 756, 726, 679 cm^{-1}. **MS** (ESI) m/z (relative intensity): 310 [M+H]$^+$ (100), 213 [M-PhF]$^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{13}H_9FNSSe^+$ [M+H]$^+$ 309.9599, found 309.9602.



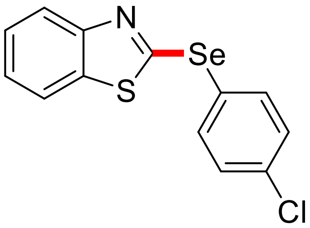
3-(Benzo[*d*]thiazol-2-ylselanyl)benzonitrile (4af): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 3-iodobenzonitrile (**2f**) (275.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4af** (71.0 mg, 56%) as a colorless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 8.08 (dt, J = 1.7, 0.8 Hz, 1H), 8.01 (ddd, J = 7.9, 1.7, 1.2 Hz, 1H), 7.96 (ddd, J = 8.2, 1.3, 0.6 Hz, 1H), 7.77–7.71 (m, 2H), 7.51 (td, J = 7.8, 0.6 Hz, 1H), 7.45 (ddd, J = 8.2, 7.3, 1.3 Hz, 1H), 7.34 (ddd, J = 7.9, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 158.4 (C_q), 154.2 (C_q), 139.7 (CH), 138.6 (CH), 136.7 (C_q), 133.0 (CH), 130.4 (CH), 128.5 (C_q), 126.4 (CH), 125.1 (CH), 122.4 (CH), 120.9 (CH), 117.6 (C_q), 114.0 (C_q). **IR** (ATR): 3057, 2229, 1454, 1421, 1404, 973, 793, 757, 727, 681 cm^{-1}. **MS** (ESI) m/z (relative intensity): 317 $[M+H]^+$ (100), 339 $[M+Na]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{14}H_9N_2SSe^+$ $[M+H]^+$ 316.9646, found 316.9641.



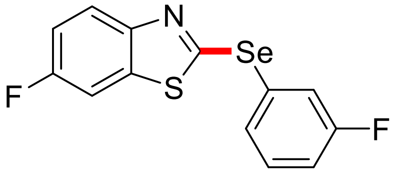
2-{[3-(Trifluoromethyl)phenyl]selanyl}benzo[*d*]thiazole (4ag): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-iodo-3-(trifluoromethyl)benzene (**2g**) (326.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4ag** (86.0 mg, 60%) as a pale yellow solid. M. p.: 64–66 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.08 (dq, J = 1.7, 0.9 Hz, 1H), 7.99 (dddt, J = 7.8, 1.7, 1.2, 0.6 Hz, 1H), 7.94 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.74–7.69 (m, 2H), 7.54 (ddt, J = 8.5, 7.8, 0.7 Hz, 1H), 7.42 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.31 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 159.9 (C_q), 154.3 (C_q), 139.3 (CH), 136.7 (C_q), 132.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH), 132.2 (d, $^{2}J_{C\text{-}F}$ = 32.9 Hz, C_q), 130.2 (CH), 127.7 (C_q), 126.6 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, CH), 126.3 (CH), 124.8 (CH), 122.3 (CH), 123.4 (d, $^{1}J_{C\text{-}F}$ = 274.0 Hz, C_q), 120.9 (CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -62.75 (s). **IR** (ATR): 1455, 1421, 1320, 1272, 1167, 1128, 1080, 1066, 973 cm^{-1}. **MS** (ESI) m/z (relative intensity): 360 $[M+H]^+$ (100), 381 $[M+Na]^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{14}H_9F_3NSSe^+$ $[M+H]^+$ 359.9568, found 359.9565. The analytical data are in accordance with those reported in the literature.[4]



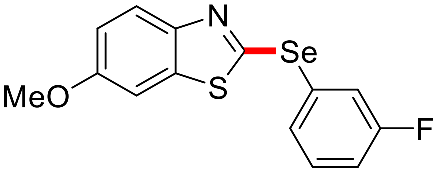
2-{(4-Fluorophenyl)selanyl}benzo[*d*]thiazole (4ah): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-fluoro-4-iodobenzene (**2h**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4ah** (70.0 mg, 57%) as a pale yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.90 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.82–7.78 (m, 2H), 7.68 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.39 (ddd, J = 8.2, 7.3, 1.3 Hz, 1H), 7.26 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.16–7.07 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 164.0 (d, $^1J_{C\text{-}F}$ = 251.4 Hz, C_q), 162.5 (C_q), 154.5 (C_q), 138.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, CH), 136.5 (C_q), 126.1 (CH), 124.4 (CH), 121.9 (CH), 121.2 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, C_q), 120.8 (CH), 117.3 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -109.66 (tt, J = 8.5, 5.2 Hz). **IR** (ATR): 1582, 1485, 1454, 1422, 1396, 1228, 1156, 971, 827, 811 cm^{-1}. **MS** (ESI) m/z (relative intensity): 310 $[M+H]^+$ (100), 213 $[M-C_6H_5F]^+$ (10). **HR-MS** (ESI) m/z calcd for $C_{13}H_9FNSSe^+$ $[M+H]^+$ 309.9599, found 309.9608. The analytical data are in accordance with those reported in the literature.[4]



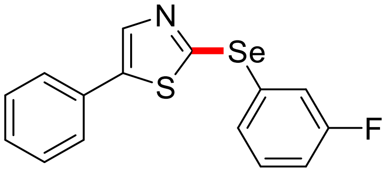
2-{(4-Chlorophenyl)selanyl}benzo[*d*]thiazole (4ai): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 1-chloro-4-iodobenzene (**2i**) (286.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4ai** (70.0 mg, 54%) as a pale yellow solid. M. p.: 55–56 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.91 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.76–7.72 (m, 2H), 7.69 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.43–7.36 (m, 3H), 7.28 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 161.5 (C_q), 154.5 (C_q), 137.7 (CH), 136.6 (C_q), 136.5 (C_q), 130.2 (CH), 126.1 (CH), 124.7 (C_q), 124.6 (CH), 122.1 (CH), 120.8 (CH). **IR** (ATR): 1586, 1470, 1454, 1440, 1422, 1212, 1193, 1088, 1011, 857 cm^{-1}. **MS** (ESI) m/z (relative intensity): 325 $[M+H]^+$ (100), 292 $[M-Cl]^+$ (13), 213 $[M-C_6H_4Cl]$ (10). **HR-MS** (ESI) m/z calcd for $C_{13}H_9ClNSSe^+$ $[M+H]^+$ 325.9304, found 325.9302. The analytical data are in accordance with those reported in the literature.[4]



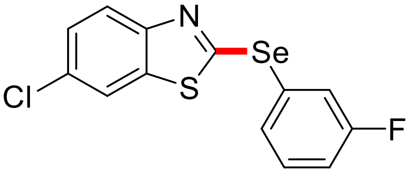
6-Fluoro-2-{(3-fluorophenyl)selanyl}benzo[*d*]thiazole (4cc): The representative procedure was followed using 6-fluorobenzo[*d*]thiazole (**1c**) (61.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4cc** (80.0 mg, 61%) as a yellow oil. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.9, 4.8 Hz, 1H), 7.56 (ddd, J = 7.7, 1.6, 1.0 Hz, 1H), 7.52 (ddd, J = 8.2, 2.6, 1.6 Hz, 1H), 7.41–7.35 (m, 2H), 7.19–7.10 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 162.7 (d, $J_{C\text{-}F}$ = 251.7 Hz, C_q), 160.1 (d, $J_{C\text{-}F}$ = 246.1 Hz, C_q), 159.8 (d, $J_{C\text{-}F}$ = 2.9 Hz, C_q), 151.0 (d, $J_{C\text{-}F}$ = 1.7 Hz, C_q), 137.6 (d, $J_{C\text{-}F}$ = 11.0 Hz, C_q), 131.7 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH), 131.2 (d, $J_{C\text{-}F}$ = 8.0 Hz, CH), 127.7 (d, $J_{C\text{-}F}$ = 7.1 Hz, C_q), 123.1 (d, $J_{C\text{-}F}$ = 4.7 Hz, CH), 122.9 (d, $J_{C\text{-}F}$ = 17.5 Hz, CH), 117.2 (d, $J_{C\text{-}F}$ = 20.9 Hz, CH), 114.7 (d, $J_{C\text{-}F}$ = 24.7 Hz, CH), 107.2 (d, $J_{C\text{-}F}$ = 26.9 Hz, CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -110.05 (td, J = 8.3, 5.8 Hz), -116.22 (td, J = 8.5, 4.8 Hz). **IR** (ATR): 1586, 1564, 1468, 1440, 1407, 1247, 1212, 1193, 898, 856, 813, 781, 679 cm^{-1}. **MS** (ESI) m/z (relative intensity): 327 $[M+H]^+$ (100), 177 $[M-C_7H_4FNS]^+$ (10). **HR-MS** (ESI) m/z calcd for $C_{13}H_8F_2NSSe^+$ $[M+H]^+$ 327.9505, found 327.9511.



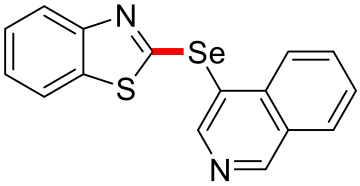
2-{(3-Fluorophenyl)selanyl}-6-methoxybenzo[*d*]thiazole (4dc): The representative procedure was followed using 6-methoxybenzo[*d*]thiazole (**1d**) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **4dc** (92.0 mg, 68%) as a pale yellow liquid. **^{1}H-NMR** (400 MHz,$CDCl_3$): δ 7.82 (dd, J = 8.9, 0.4 Hz, 1H), 7.52 (ddd, J = 7.7, 1.6, 0.9 Hz, 1H), 7.48 (ddd, J = 8.3, 2.5, 1.5 Hz, 1H), 7.37–7.31 (m, 1H), 7.17 (dd, J = 2.5, 0.4 Hz, 1H), 7.11 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H), 7.01 (dd, J = 9.0, 2.6 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{C\text{-}F}$ = 251.3 Hz, C_q), 157.4 (C_q), 155.8 (C_q), 148.9 (C_q), 138.3 (C_q), 131.0 (d, $^4J_{C\text{-}F}$ = 2.1 Hz, CH), 130.9 (d, $^3J_{C\text{-}F}$ = 6.9 Hz, CH), 128.6 (d, $^3J_{C\text{-}F}$ = 7.1 Hz, C_q), 122.8 (CH), 122.3 (d, $^2J_{C\text{-}F}$ = 22.3 Hz, CH), 116.6 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, CH), 115.3 (CH), 103.6 (CH), 55.7 (CH_3). **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -110.42 (td, J = 8.3, 5.8 Hz). IR (ATR): 1587, 1470, 1449, 1429, 1408, 1256, 1219, 1060, 1025, 974 cm^{-1}. **MS** (ESI) m/z (relative intensity): 340 [M+H]$^+$ (100), 362 [M+Na]$^+$ (15). **HR-MS** (ESI) m/z calcd for $C_{14}H_{11}FNOSSe^+$ [M+H]$^+$ 339.9705, found 339.9703.



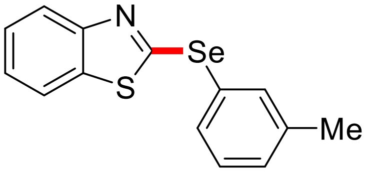
2-{(3-Fluorophenyl)selanyl}-5-phenylthiazole (4ec): The representative procedure was followed using 5-phenylthiazole (**1e**) (65.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **4ec** (82.0 mg, 61%) as a pale yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.49–7.40 (m, 4H), 7.38–7.26 (m, 4H), 7.07 (tdd, J = 8.4, 2.5, 1.0 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 162.7 (d, ^1J = 251.0 Hz, C_q), 154.05 (C_q), 143.2 (C_q), 139.6 (CH), 130.9 (d, ^3J = 8.0 Hz, CH), 130.7 (C_q), 130.0 (d, ^3J = 7.1 Hz, C_q), 129.8 (d, ^4J = 3.2 Hz, CH), 129.1 (CH), 128.5 (CH), 126.7 (CH), 121.2 (d, ^2J = 22.4 Hz, CH), 116.1 (d, ^2J = 21.1 Hz, CH). **^{19}F-NMR** (376 MHz, $CDCl_3$): δ -110.56 (td, J = 8.4, 5.8 Hz). **IR** (ATR): 3059, 1586, 1470, 1445, 1424, 1384, 1262, 1211, 988, 856, 780, 757, 689, 678 cm^{-1}. MS (ESI) m/z (relative intensity): 336 [M+H]$^+$ (100), 358 [M+Na]$^+$ (60). HR-MS (ESI) m/z calcd for $C_{15}H_{11}FNSSe^+$ [M+H]$^+$ 335.9756, found 335.9765.



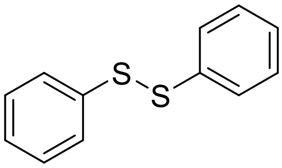
6-Chloro-2-((3-fluorophenyl)selanyl)benzo[*d*]thiazole (4fc): The representative procedure was followed using 6-chlorobenzo[*d*]thiazole (**1f**) (66.0 mg, 0.40 mmol) and 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/2) yielded **4fc** (70.0 mg, 51%) as a pale yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.81 (dd, J = 8.7, 0.5 Hz, 1H), 7.67 (dd, J = 2.1, 0.5 Hz, 1H), 7.57 (ddd, J = 7.7, 1.6, 1.0 Hz, 1H), 7.53 (ddd, J = 8.2, 2.6, 1.5 Hz, 1H), 7.43–7.39 (m, 1H), 7.36 (dd, J = 8.7, 2.1 Hz, 1H), 7.18 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{C\text{-}F}$ = 251.9 Hz, C_q), 161.6 (C_q), 152.9 (C_q), 137.7 (C_q), 131.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, CH), 131.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, CH), 130.7 (C_q), 127.4 (d, $^3J_{C\text{-}F}$ = 7.1 Hz, C_q), 126.9 (CH), 123.2 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, CH), 122.8 (CH), 120.5 (CH), 117.3 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, CH). **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -109.97 (td, J = 8.3, 5.9 Hz). IR (ATR): 1586, 1470, 1457, 1426, 1393, 1262, 1212, 1102, 975, 857, 815, 781, 757, 679 cm^{-1}. **MS** (ESI) m/z (relative intensity): 343 [M+H]$^+$ (100), 310 [M-Cl]$^+$ (20). **HR-MS** (ESI) m/z calcd for $C_{13}H_8ClFNSSe^+$ [M+H]$^+$ 343.9210, found 343.9192.



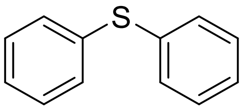
2-(Isoquinolin-4-ylselanyl)benzo[*d*]thiazole (4an): The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol) and 4-bromoisoquinoline (**5n**) (250.0 mg, 1.20 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/3) yielded **4an** (72.0 mg, 53%) as a pale yellow solid. M. p.: 84–86 °C. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ 9.39 (s, 1H), 9.08 (s, 1H), 8.36 (dd, J = 8.4, 1.2 Hz, 1H), 8.04 (ddd, J = 8.0, 1.4, 0.8 Hz, 1H), 7.90 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.69 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.56 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.38 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.22 (ddd, J = 7.9, 7.2, 1.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 160.9 (C_q), 155.5 (CH), 154.3 (C_q), 151.5 (CH), 137.3 (C_q), 136.5 (C_q), 132.1 (CH), 129.5 (C_q), 128.3 (CH), 128.3 (CH), 126.8 (CH), 126.0 (CH), 124.4 (CH), 121.9 (CH), 121.2 (C_q), 120.7 (CH). **IR** (ATR): 1615, 1561, 1487, 1454, 1422, 1375, 1309, 752 cm^{-1}. **MS** (EI) m/z (relative intensity): 341 [M]$^+$ (100), 262 (95), 235 (20), 181 (25). **HR-MS** (ESI) m/z calcd for $C_{16}H_{11}N_2SSe^+$ [M+H]$^+$ 342.9803, found 342.9800.



2-(*m*-Tolylselanyl)benzo[*d*]thiazole (4aa): Yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.91 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 7.69–7.60 (m, 3H), 7.39 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.34–7.22 (m, 3H), 2.38 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 163.0 (C_q), 154.6 (C_q), 139.9 (C_q), 137.1 (CH), 136.6 (C_q), 133.5 (CH), 130.8 (CH), 129.6 (CH), 126.2 (C_q), 125.9 (CH), 124.2 (CH), 121.9 (CH), 120.7 (CH), 21.2 (CH_3). **IR** (ATR): 3054, 1454, 1421, 1232, 972, 775, 755, 726, 687, 428 cm^{-1}. **MS** (ESI) m/z (relative intensity): 306 [M+H]$^+$ (100), 214 [M-C_7H_8]$^+$ (5). **HR-MS** (ESI) m/z calcd for $C_{14}H_{12}NSSe^+$ [M+H]$^+$ 305.9850, found 305.9859. The analytical data are in accordance with those reported in the literature.[6]

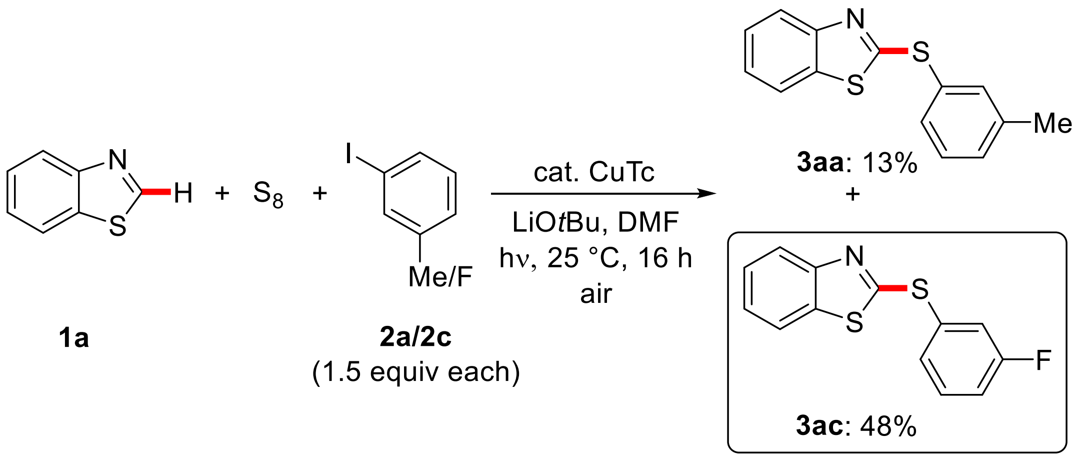


Phenyl disulfide (7a): Colorless solid. M. p.: 59–60 °C. **^{1}H-NMR** (400 MHz, CDCl$_3$): *δ* 7.49 (dd, *J* = 7.0, 1.3 Hz, 4H), 7.29 (td, *J* = 8.0, 2.4 Hz, 4H), 7.21 (ddd, *J* = 7.6, 2.5, 1.3 Hz, 2H). **^{13}C-NMR** (101 MHz, CDCl$_3$): *δ* 137.0 (C$_q$), 129.0 (CH), 127.5 (CH), 127.1 (CH). **IR** (ATR): 3056, 1575, 1473, 1436, 1020, 735, 685, 464 cm^{-1}. **MS** (EI) m/z (relative intensity): 218 [M]$^+$ (100), 185 (30), 154 (35), 109 (90). **HR-MS** (EI) m/z calcd for $C_{12}H_{10}S_2$ [M]$^+$ 218.0224, found 218.0232.[7]

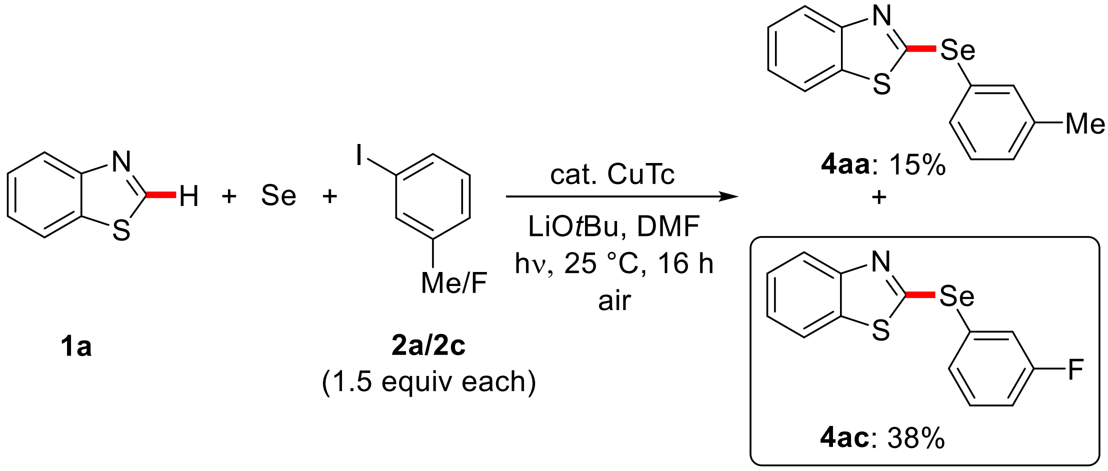


Diphenyl sulfide (8a): Colorless liquid. **^{1}H-NMR** (400 MHz, CDCl$_3$): *δ* 7.36 (dd, *J* = 7.0, 1.7 Hz, 4H), 7.31 (dt, *J* = 7.0, 1.4 Hz, 4H), 7.28–7.23 (m, 2H).. ^{13}C-NMR (101 MHz, CDCl$_3$): δ 135.7 (C$_q$), 130.9 (CH), 129.1 (CH), 126.9 (CH). **IR** (ATR): 3057, 1578, 1474, 1438, 1023, 736, 688, 516, 463 cm^{-1}. **MS** (EI) m/z (relative intensity): 186 [M]$^+$ (100), 152 (15), 109 (10). **HR-MS** (EI) m/z calcd for $C_{12}H_{10}S$ [M]$^+$ 186.0503, found 186.0498.[8]

Competition Experiment:

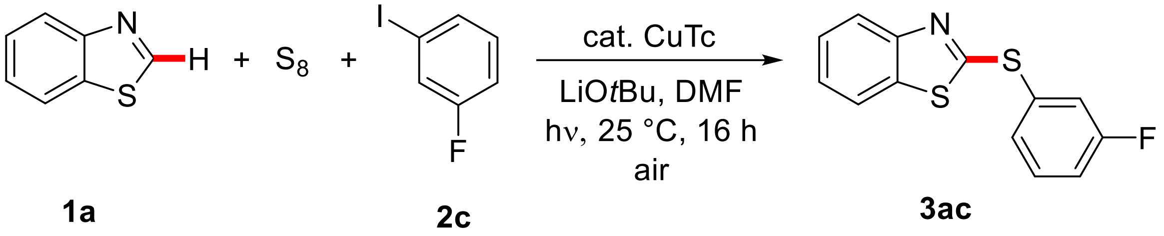


The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol), 1-iodo-3-methylbenzene (**2a**) (131.0 mg, 0.6 mmol) and 1-fluoro-3-iodobenzene (**2c**) (133.0 mg, 0.6 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3aa** (13.0 mg, 13%) and **3ac** (50.0 mg, 48%).



The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol), 1-iodo-3-methylbenzene (**2a**) (131.0 mg, 0.6 mmol) and 1-fluoro-3-iodobenzene (**2c**) (133.0 mg, 0.6 mmol). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **4aa** (18.0 mg, 15%) and **4ac** (47.0 mg, 38%).

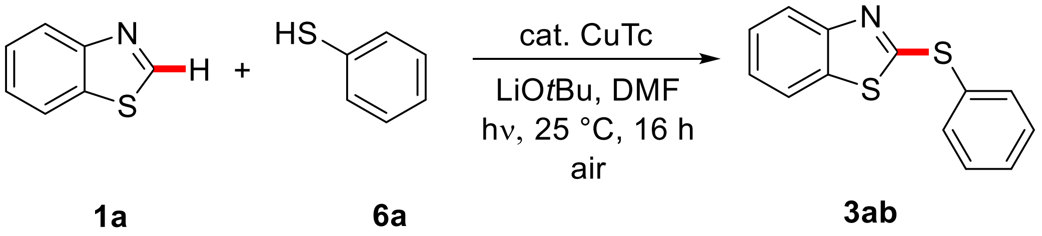
Probing SET-Type Mechanism:



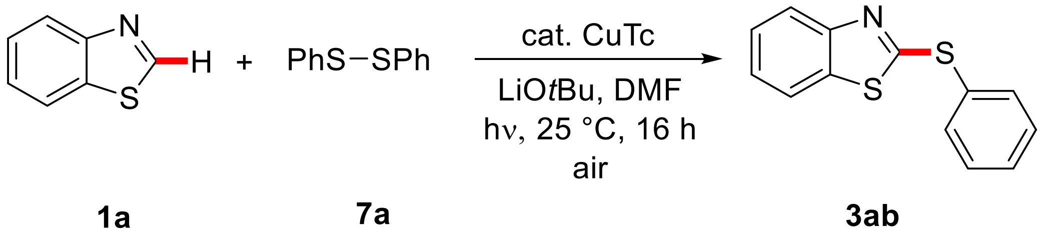
standard conditions: 66%
galvinoxyl (1.0 equiv): 36%
galvinoxyl (3.0 equiv): 0%

The representative procedure was followed using benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol), 1-fluoro-3-iodobenzene (**2c**) (266.0 mg, 1.2 mmol) and galvinoxyl (169 mg, 100 mol %; or 506 mg, 300 mol %, respectively). After stirring at room temperature under irradiation for 16 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **3ac** (38.0 mg, 36% or 0 mg, 0%, respectively).

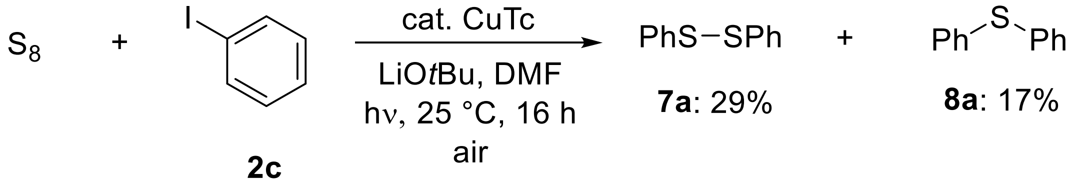
Probing a Reaction Intermediate:



To a pre-dried 10 mL quartz tube were added benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol), thiophenol (**6a**) (88.0 mg, 0.8 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiO*t*Bu (96.0 mg, 1.20 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et_2O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The NMR and GC analysis of the crude mixture showed only a trace amount of the desired product **3ab**.



To a pre-dried 10 mL quartz tube were added benzo[*d*]thiazole (**1a**) (54.0 mg, 0.40 mmol), diphenyl disulfide **7a** (87.0 mg, 0.40 mmol), copper(I) thiophene-2-carboxylate (15.3 mg, 20 mol %), LiO*t*Bu (96.0 mg, 1.20 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et_2O (100 mL) and washed with water (4 × 50 mL). The combined organic extracts were dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield the product **3ab** (76.0 mg, 78%).



To a pre-dried 10 mL quartz tube were added sulfur powder (15.0 mg, 0.46 mmol), iodobenzene (**2b**) (282.0 mg, 1.38 mmol), copper(I) thiophene-2-carboxylate (18.0 mg, 20 mol %), LiO*t*Bu (110.0 mg, 1.38 mmol), and DMF (2.0 mL) under an air atmosphere. The tube was sealed tightly and stirred under 254 nm irradiation in a Luzchem LZC-ICH2 photoreactor for 16 h at ambient temperature. The temperature was determined to be 25–27 °C in the reaction mixture. Afterwards the reaction mixture was diluted with Et_2O (100 mL) and washed four times with water. The combined organic extracts were dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield the product **7a** (29.0 mg, 29%) and **8a** (15.0 mg, 17%).

References:

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[4] A. R. Rosario, K. K. Casola, C. E. S. Oliveira, G. Zeni, *Adv. Synth. Catal.* **2013**, *355*, 2960–2966.

[5] M. Arisawa, T. Tazawa, S. Tanii, K. Horiuchi, M. Yamaguchi, *J. Org. Chem.* **2017**, *82*, 804–810.

[6] C. Gao, G. Wu, L. Min, M. Liu, W. Gao, J. Ding, J. Chen, X. Huang, H. Wu, *J. Org. Chem.* **2017**, *82*, 250–255.

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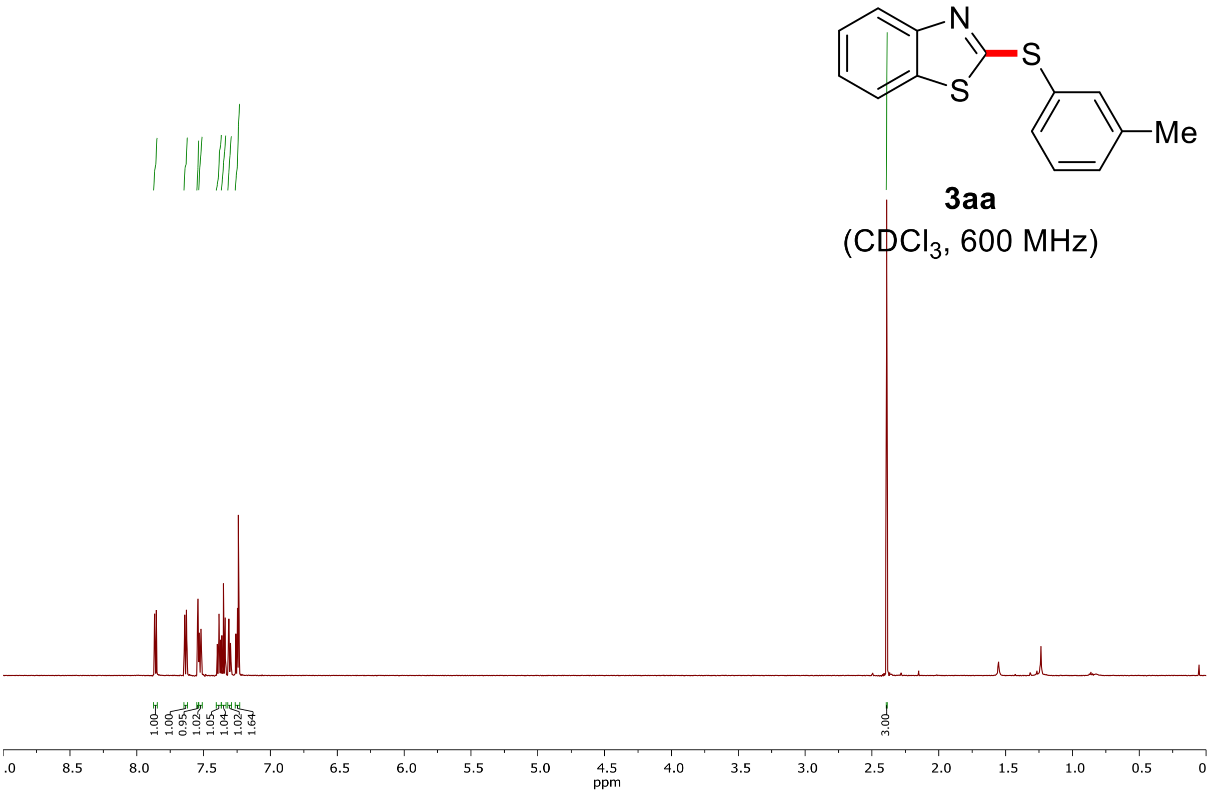
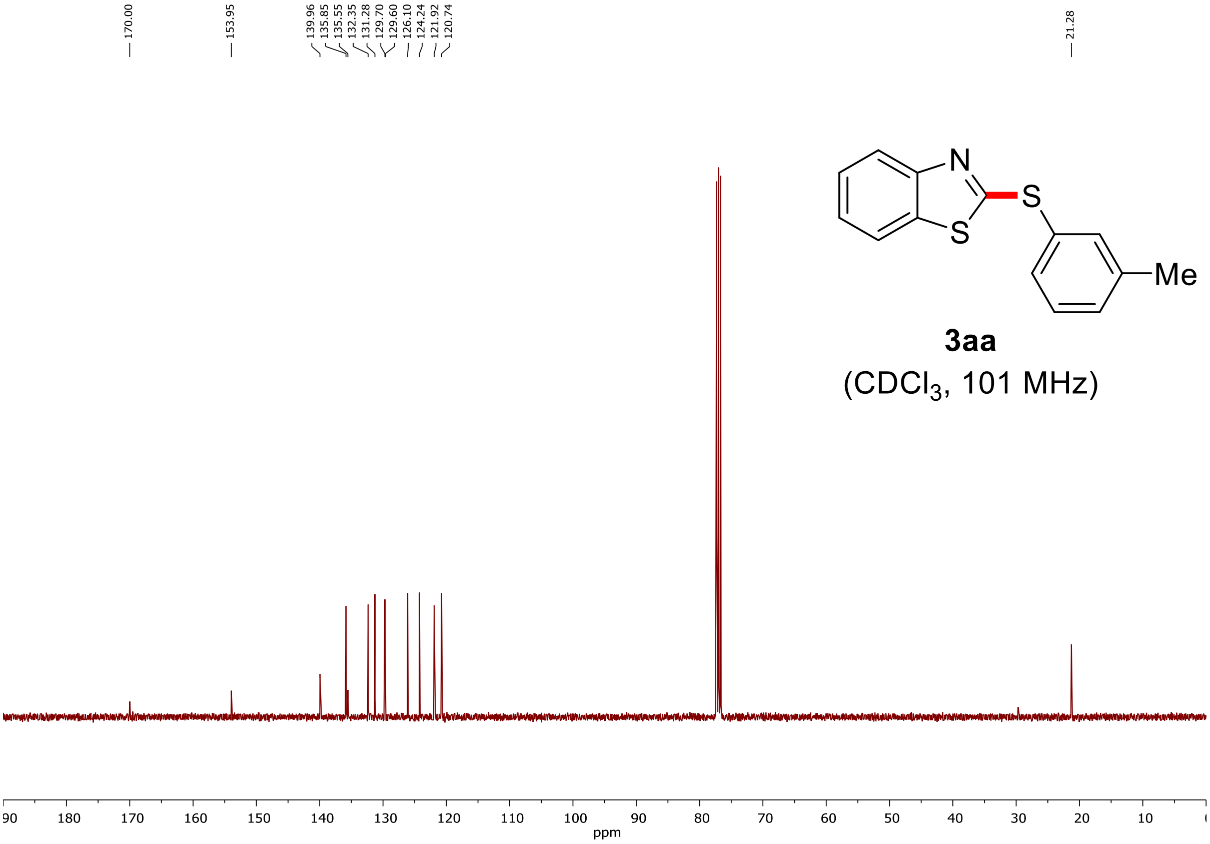
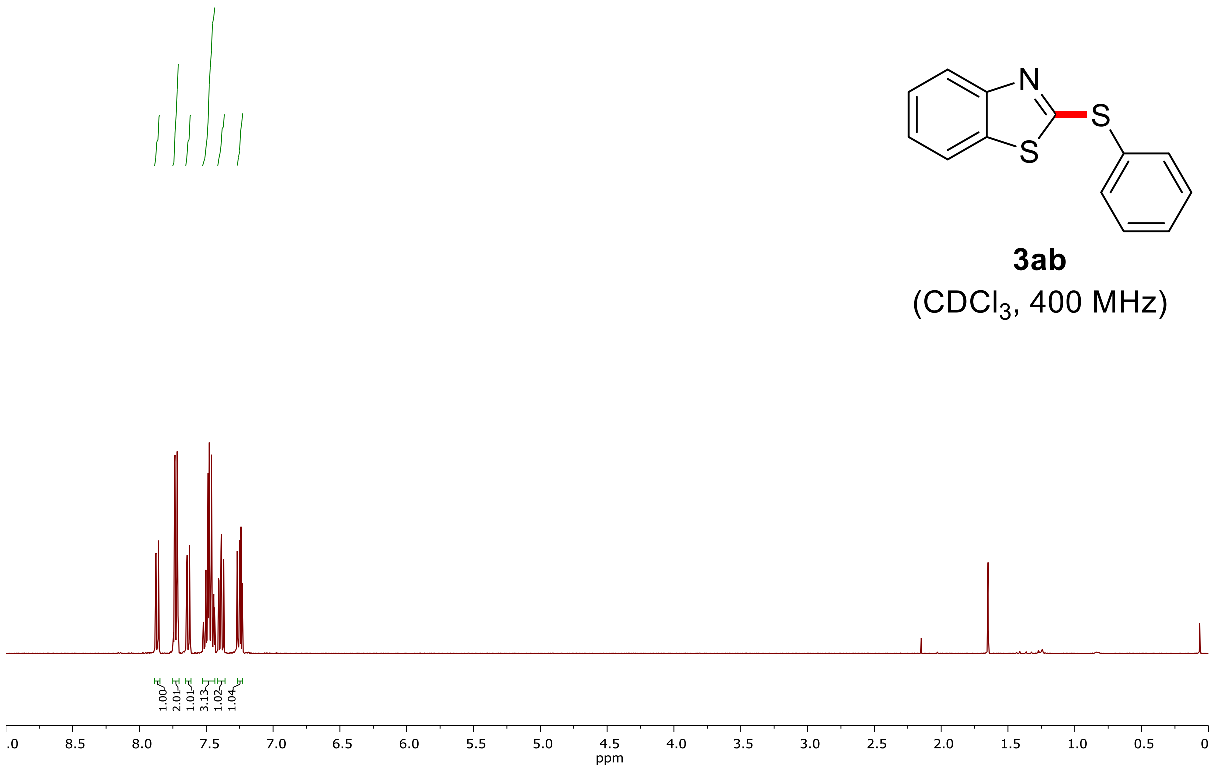
^{1}H-, ^{13}C-, and ^{19}F-NMR Spectra

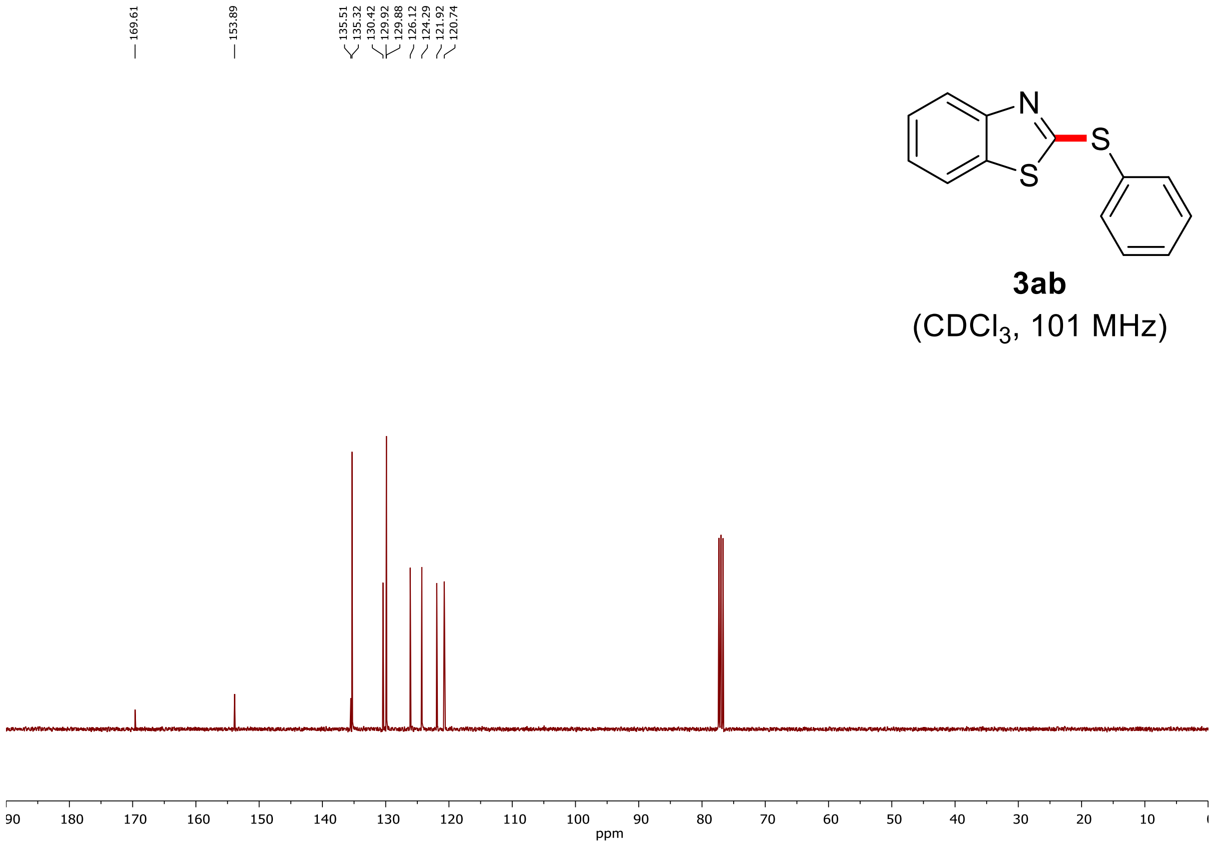






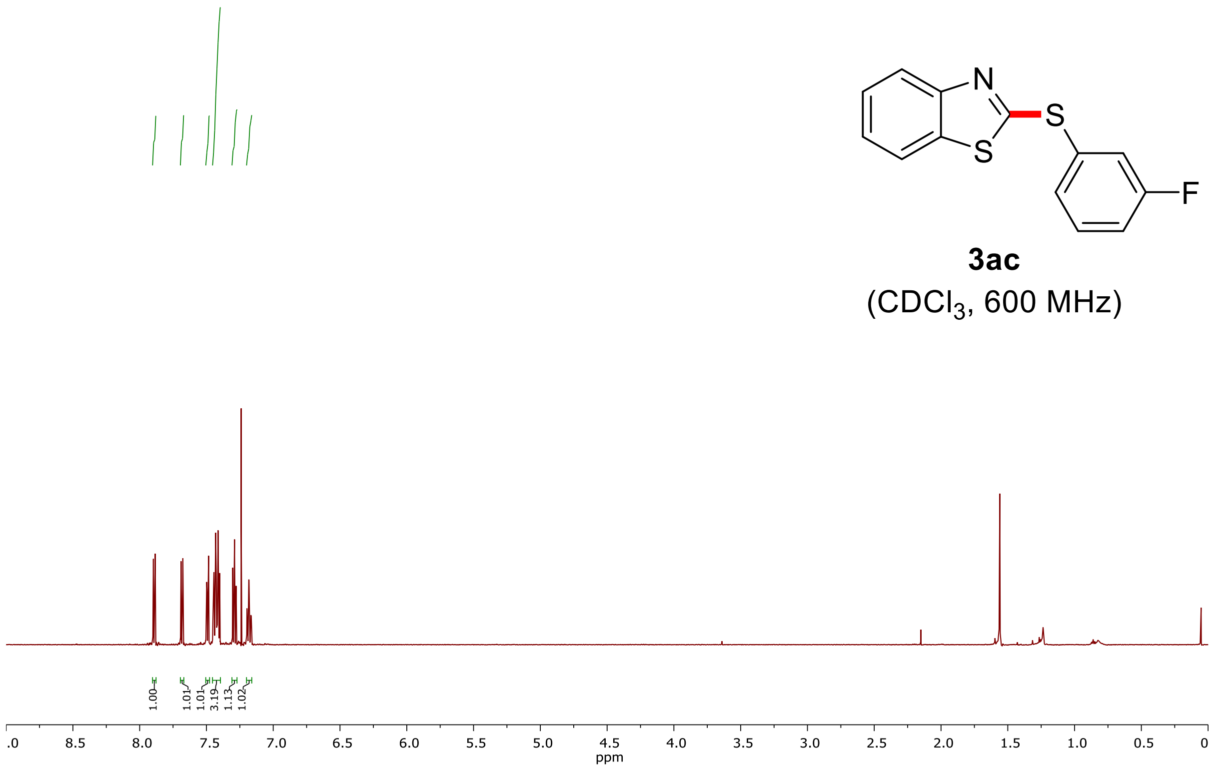
3ab

(CDCl$_3$, 400 MHz)

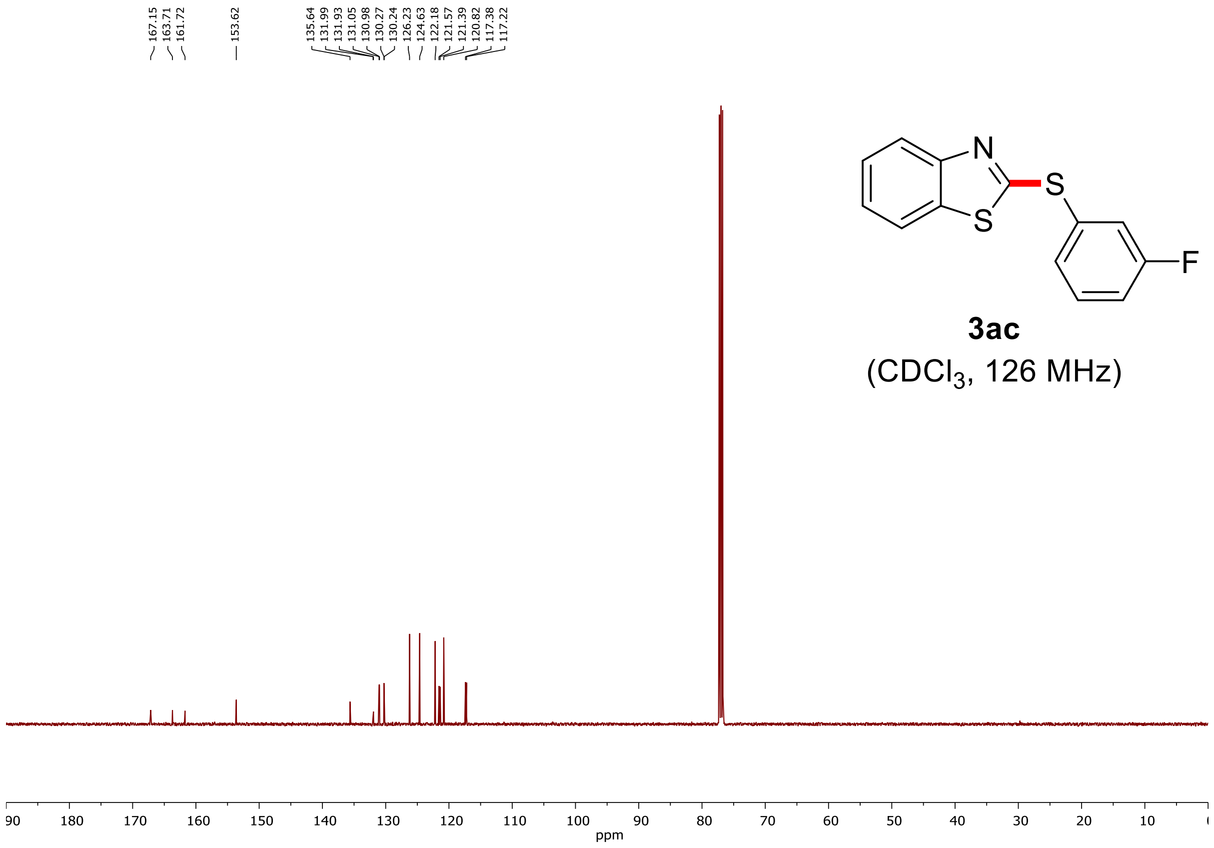


3ab

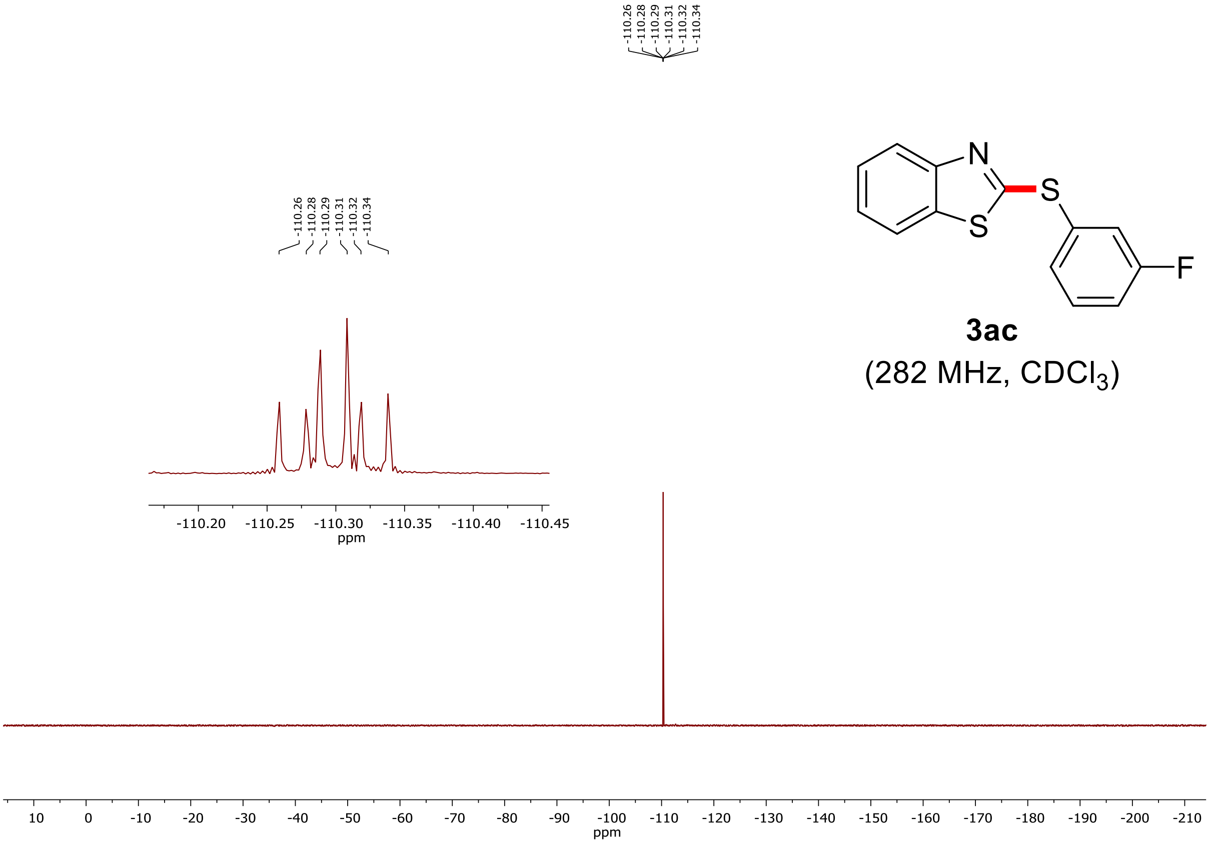
(CDCl$_3$, 101 MHz)



3ac
($CDCl_3$, 600 MHz)

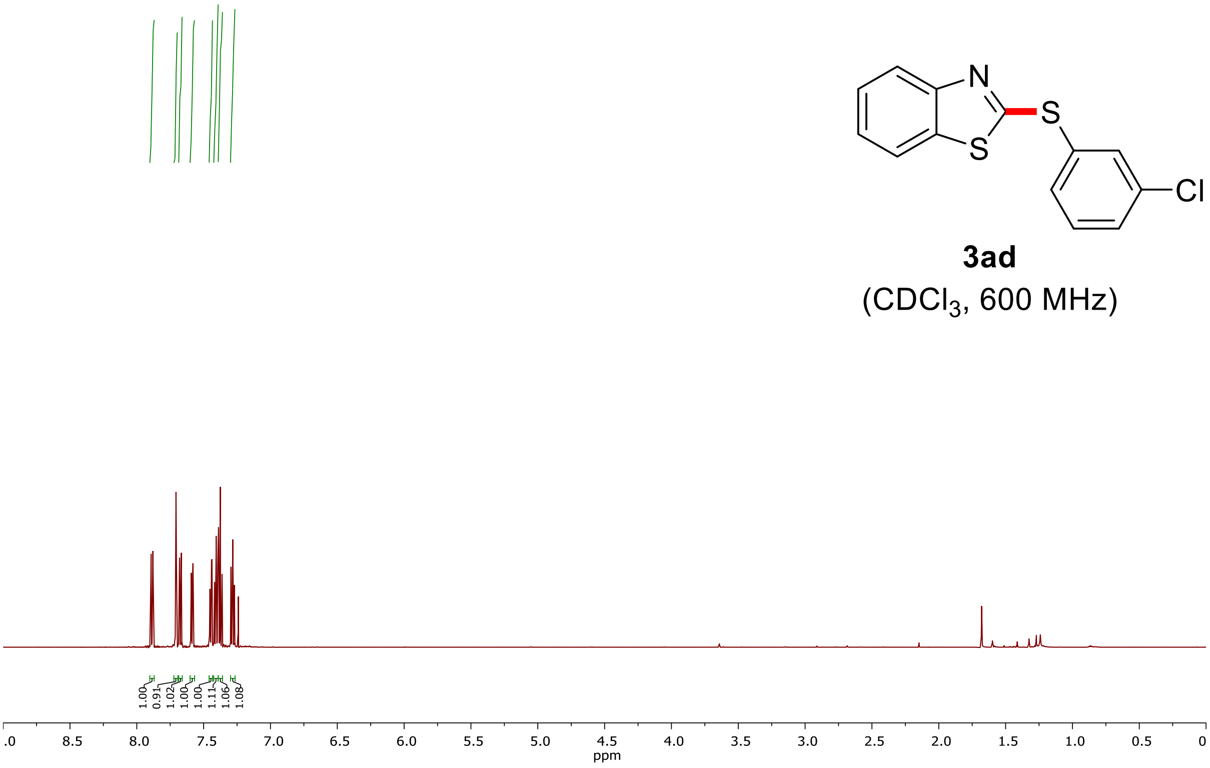


3ac
($CDCl_3$, 126 MHz)



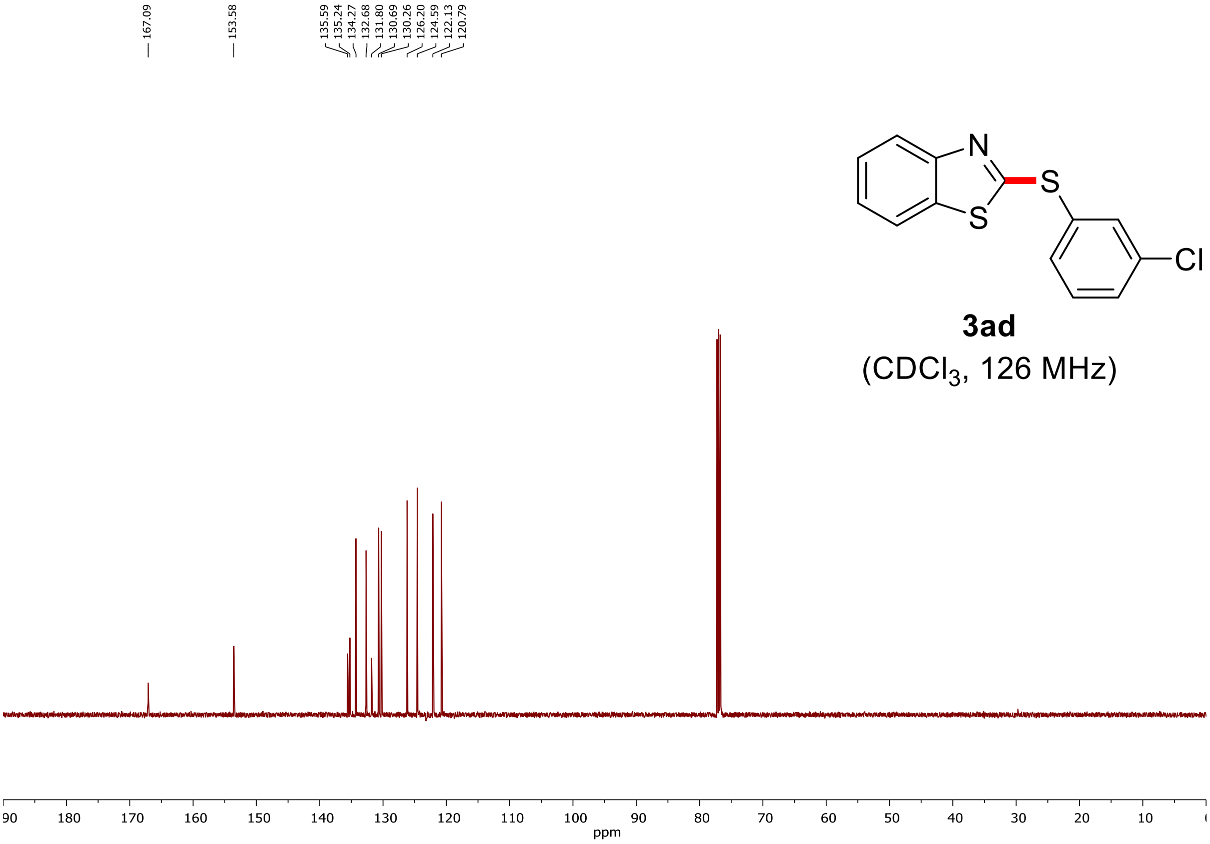
3ac

(282 MHz, $CDCl_3$)



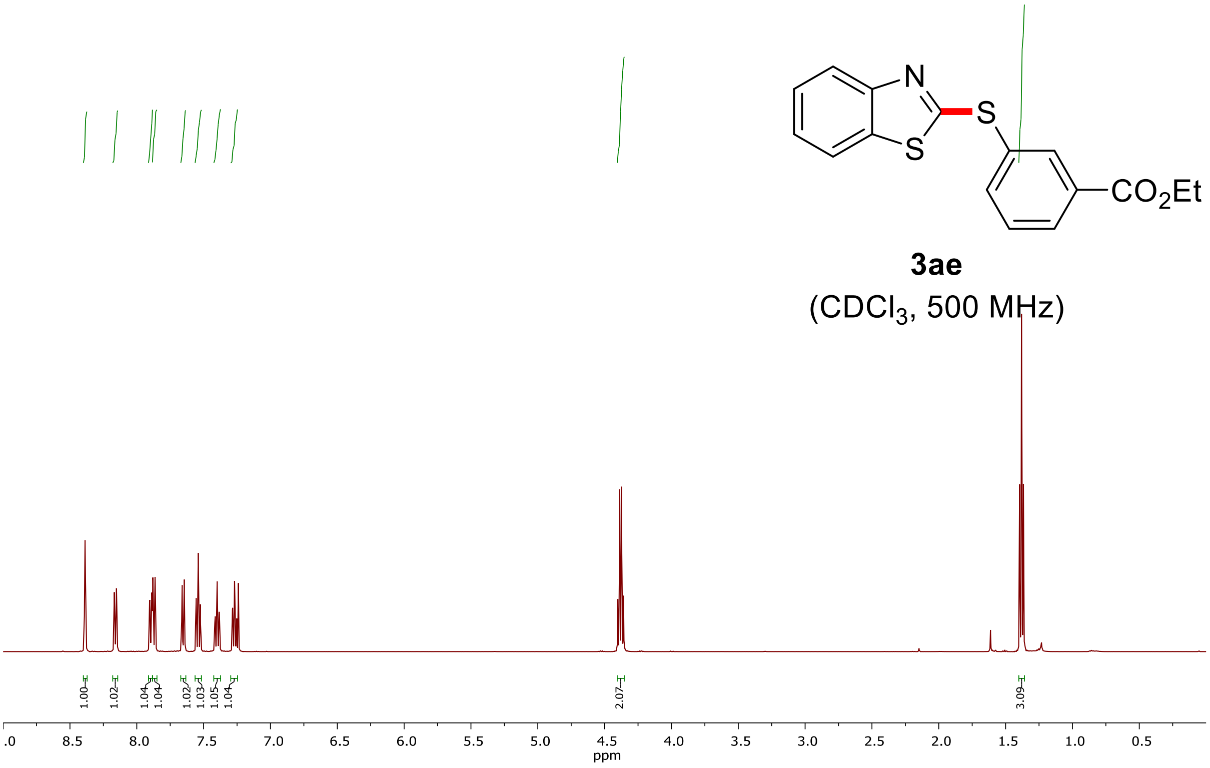
3ad

($CDCl_3$, 600 MHz)



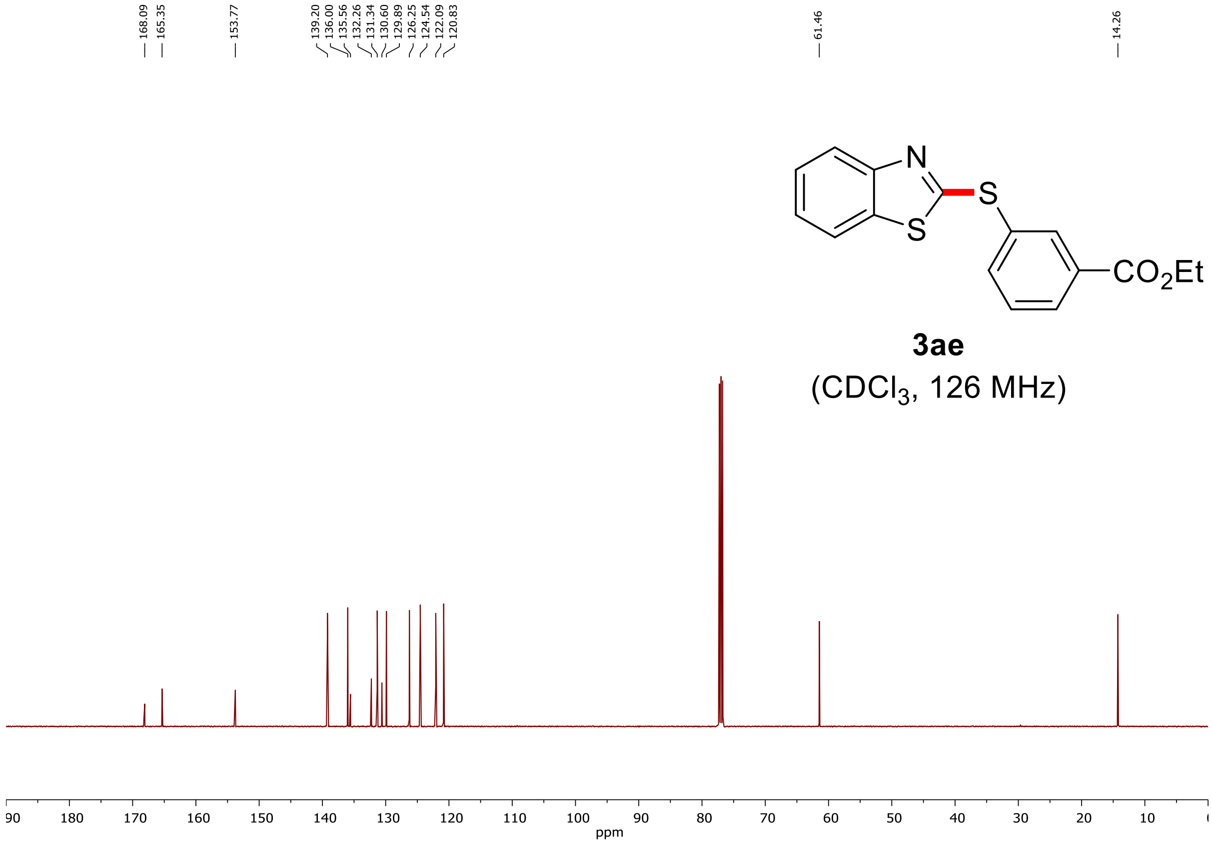
3ad

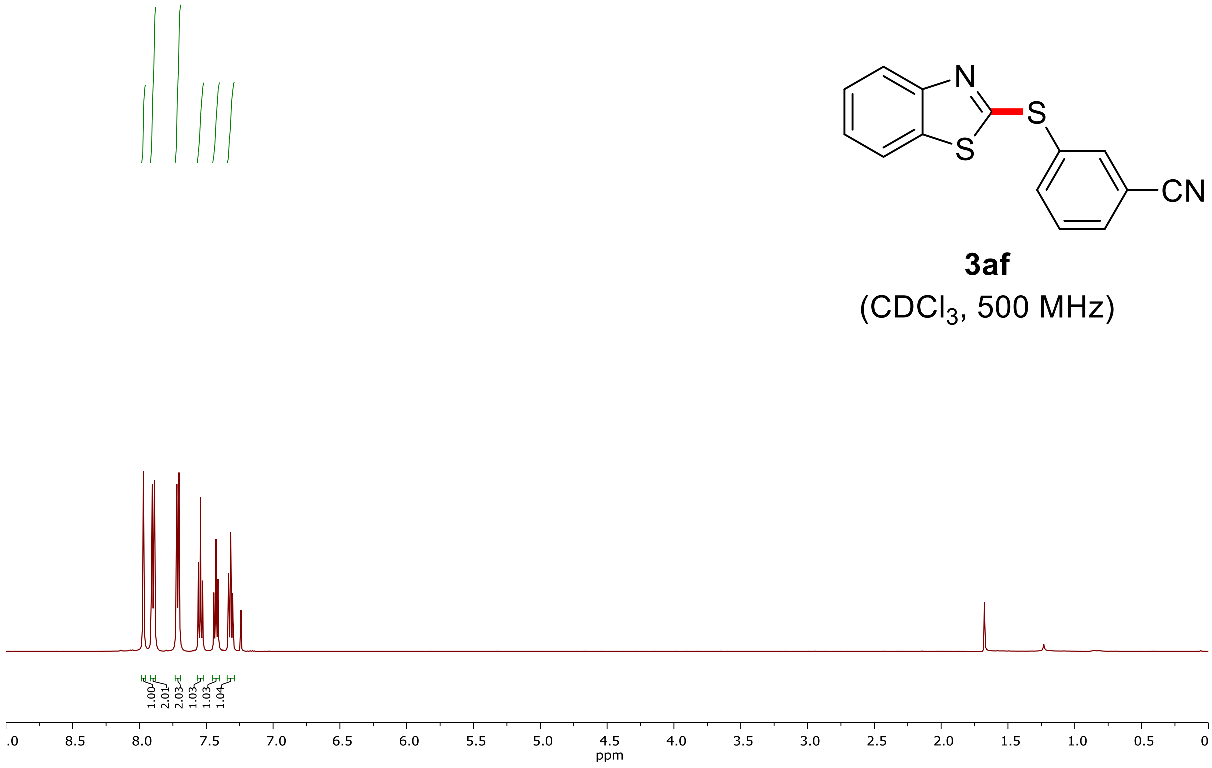
(CDCl$_3$, 126 MHz)



3ae

(CDCl$_3$, 500 MHz)


168.09
165.35
153.77
139.20
136.00
135.56
132.26
131.34
130.60
129.89
126.25
124.54
122.09
120.83
61.46
14.26
N
S
S
CO2Et
3ae
(CDCl3, 126 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


N
S
S
CN
3af
(CDCl3, 500 MHz)
1.00
2.01
2.03
1.03
1.03
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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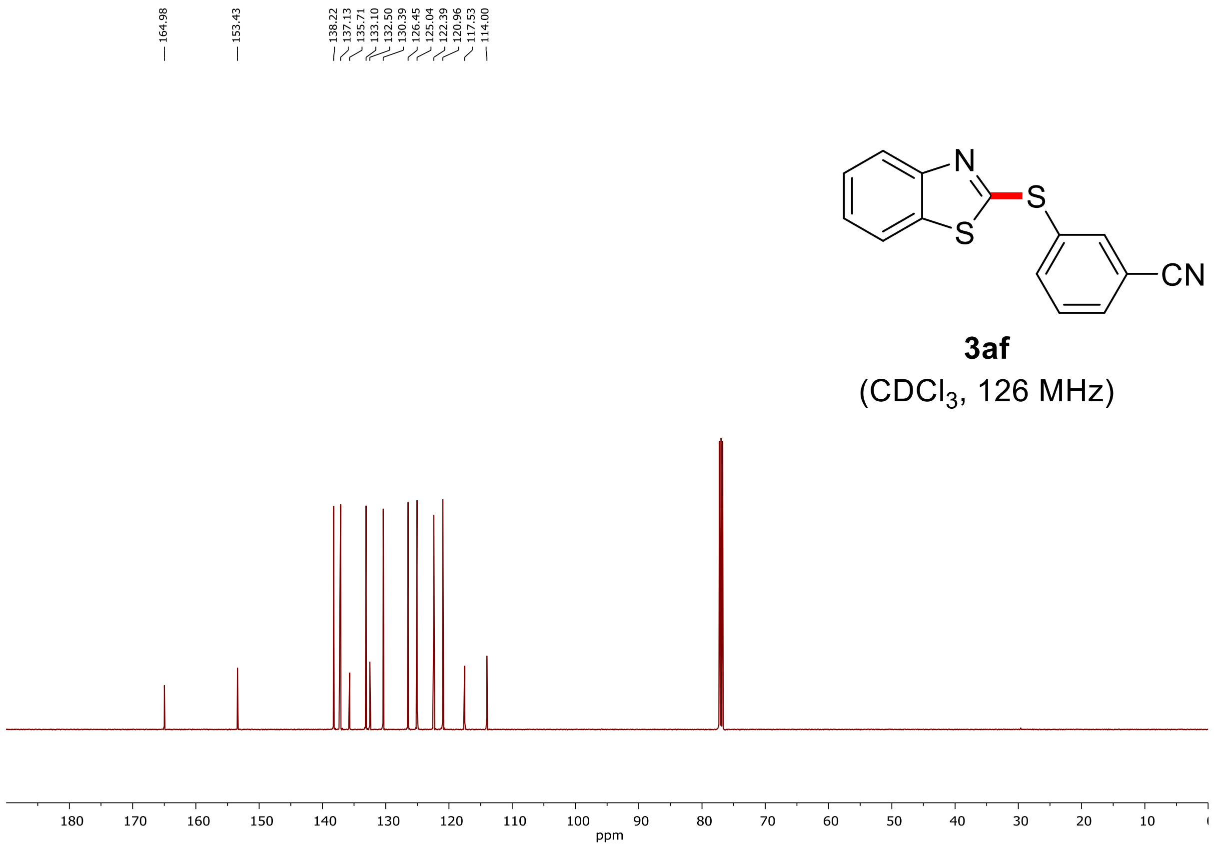
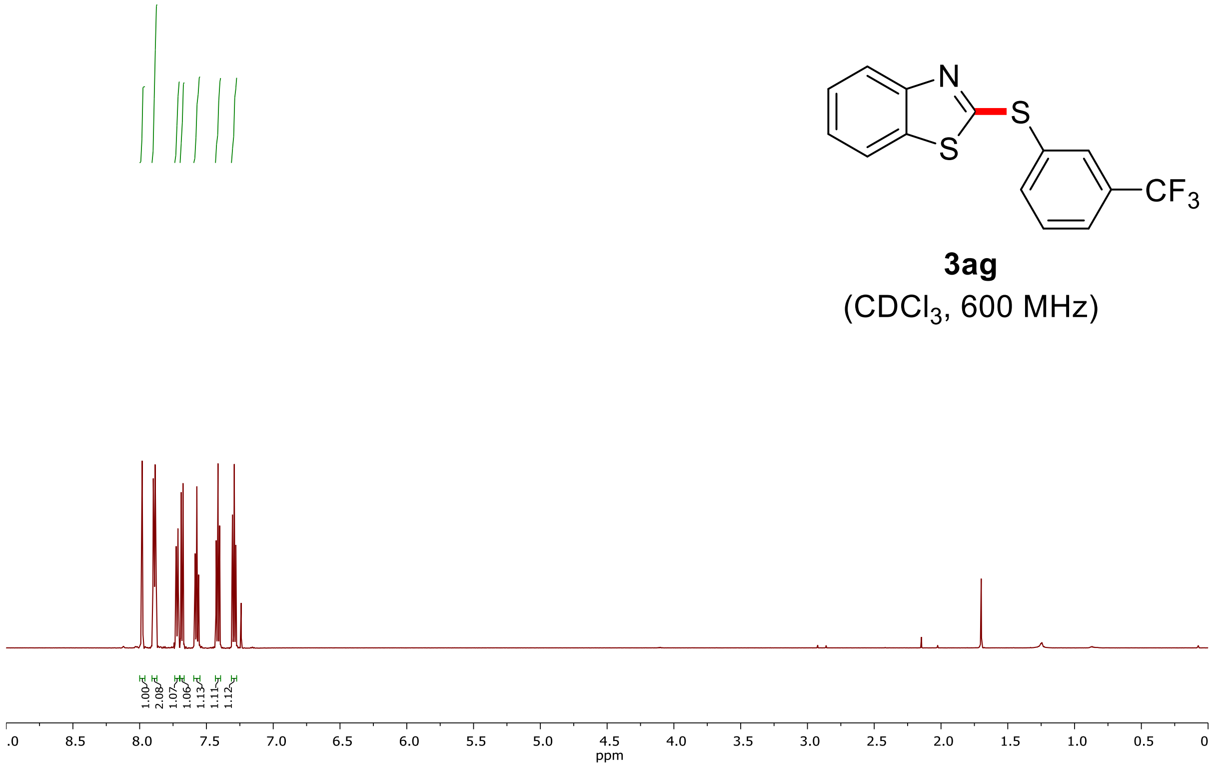
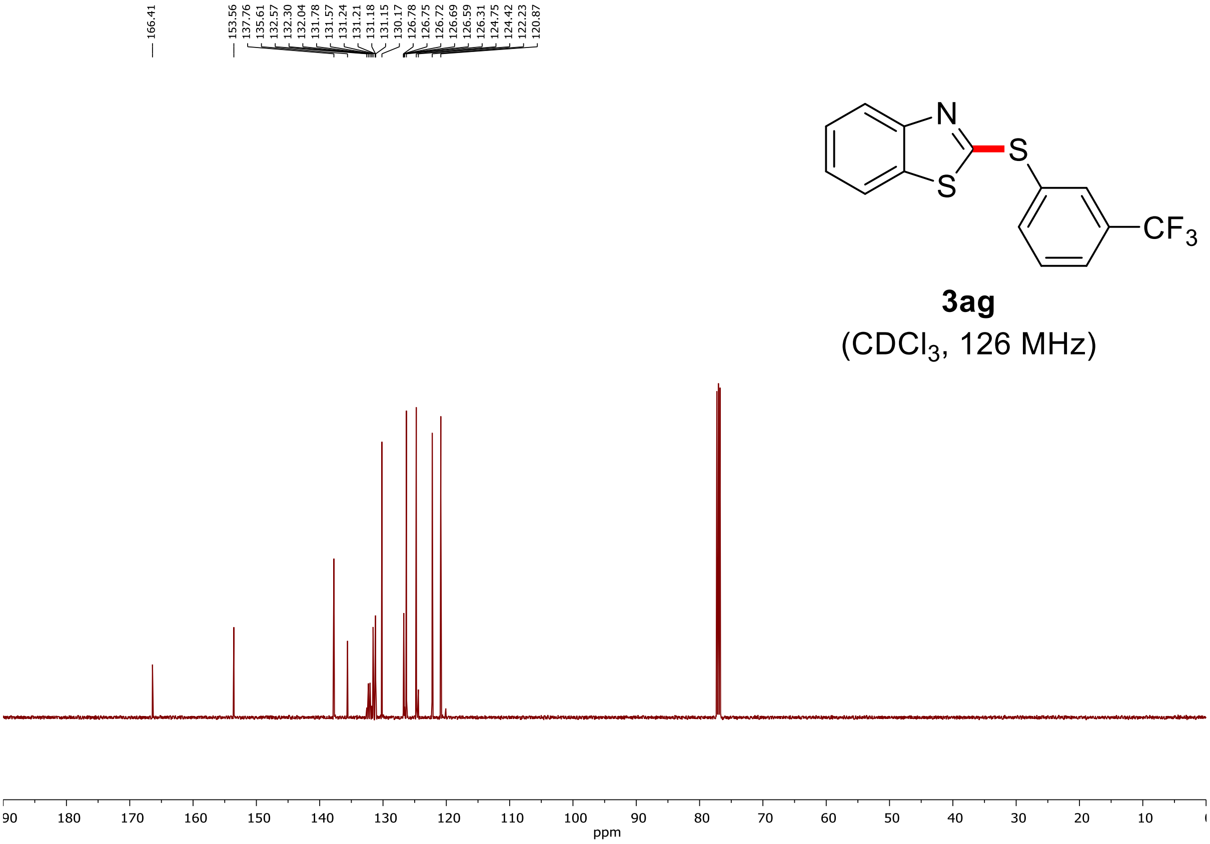
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
ppm



3af
($CDCl_3$, 126 MHz)

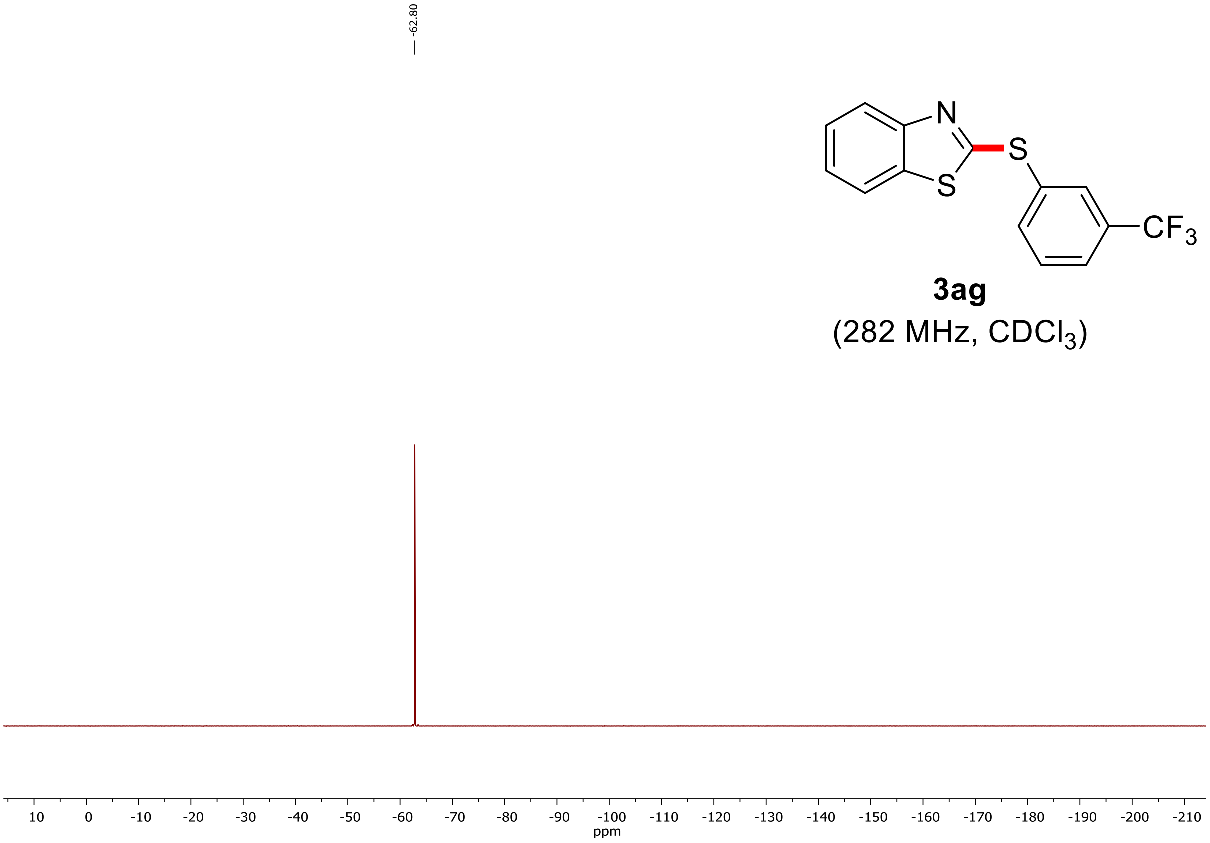


3ag
($CDCl_3$, 600 MHz)



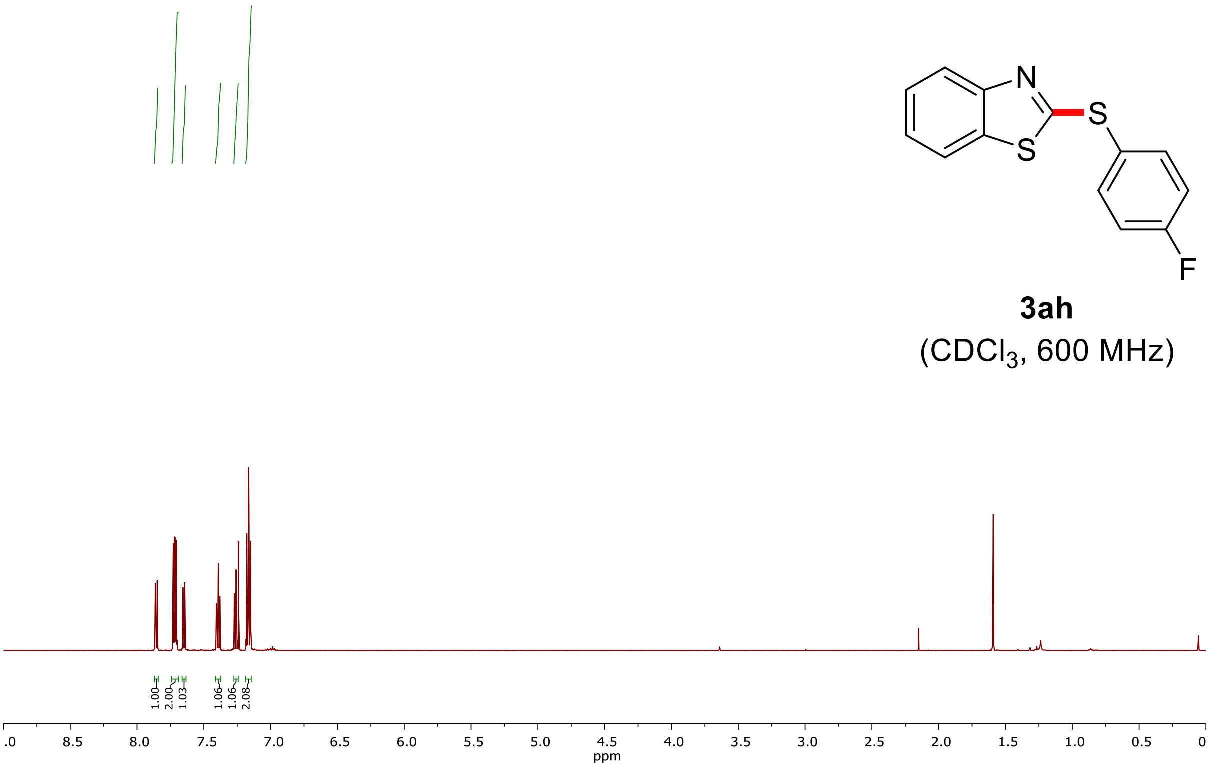
3ag

($CDCl_3$, 126 MHz)



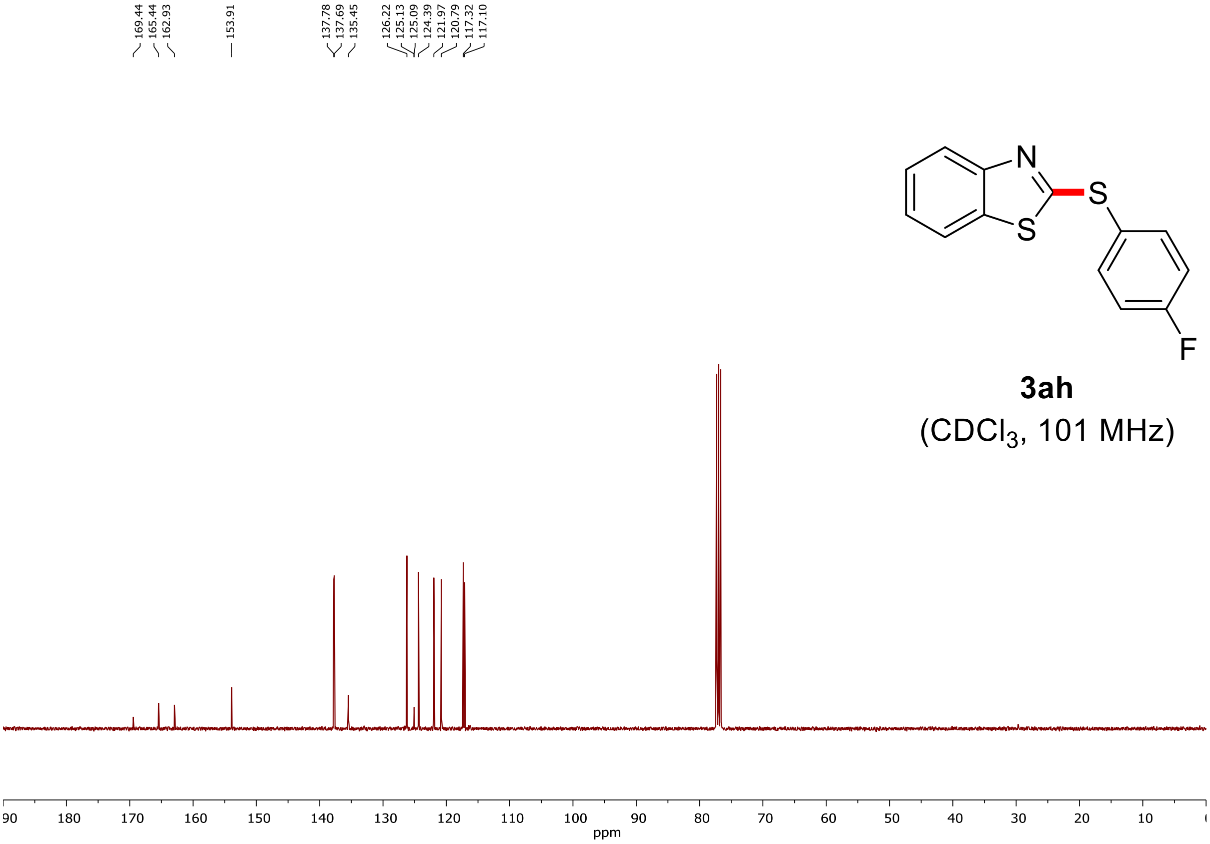
3ag

(282 MHz, $CDCl_3$)



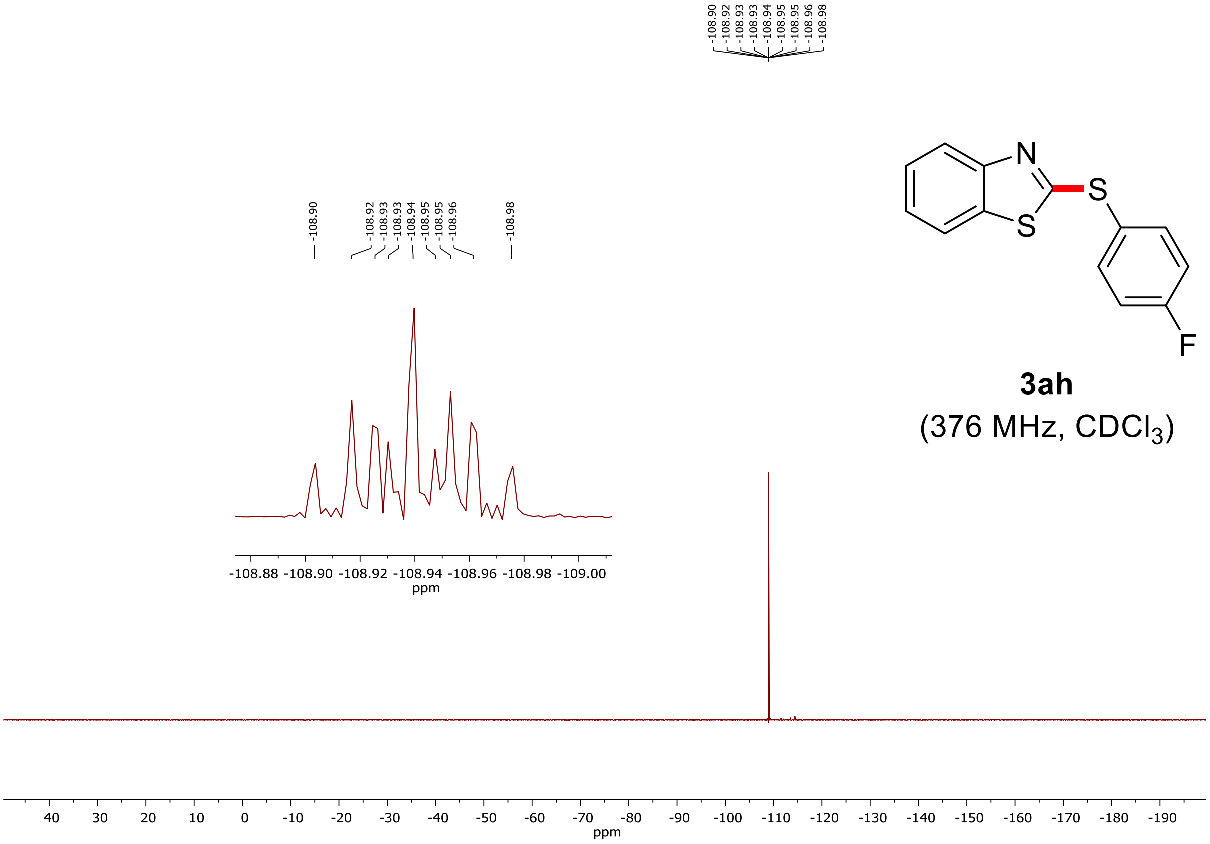
3ah

(CDCl$_3$, 600 MHz)

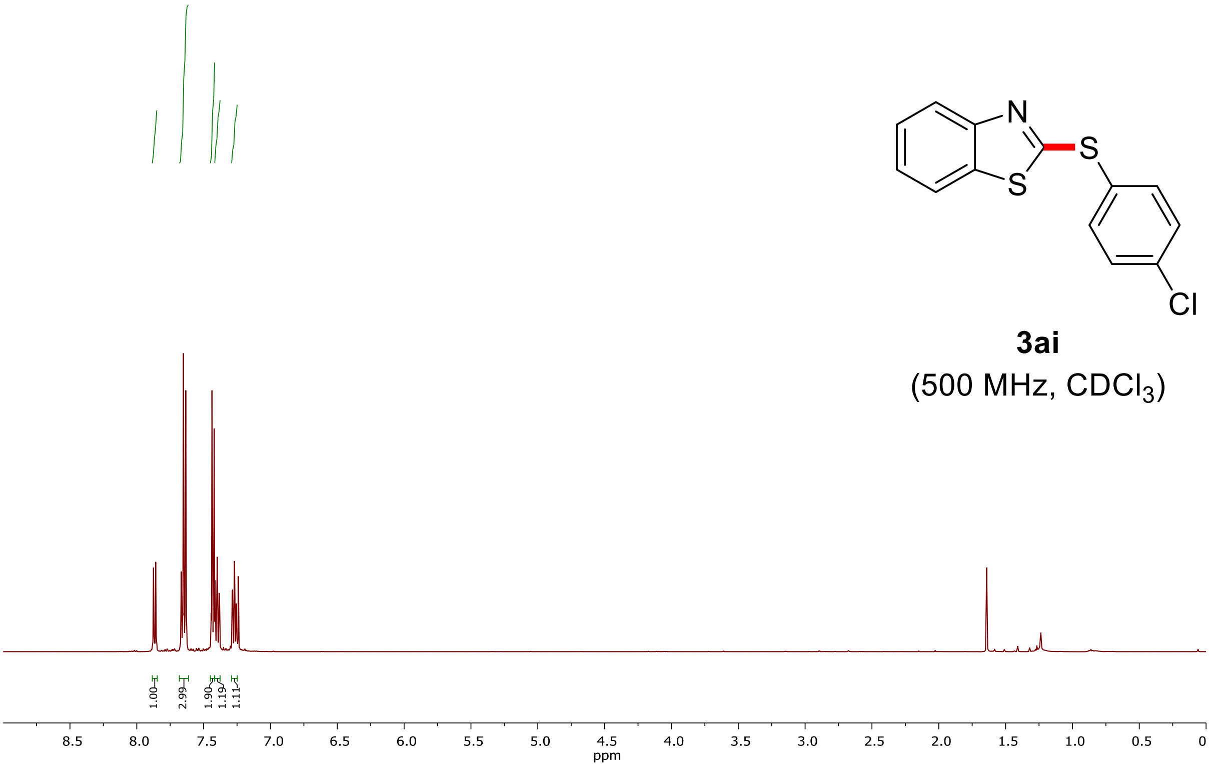


3ah

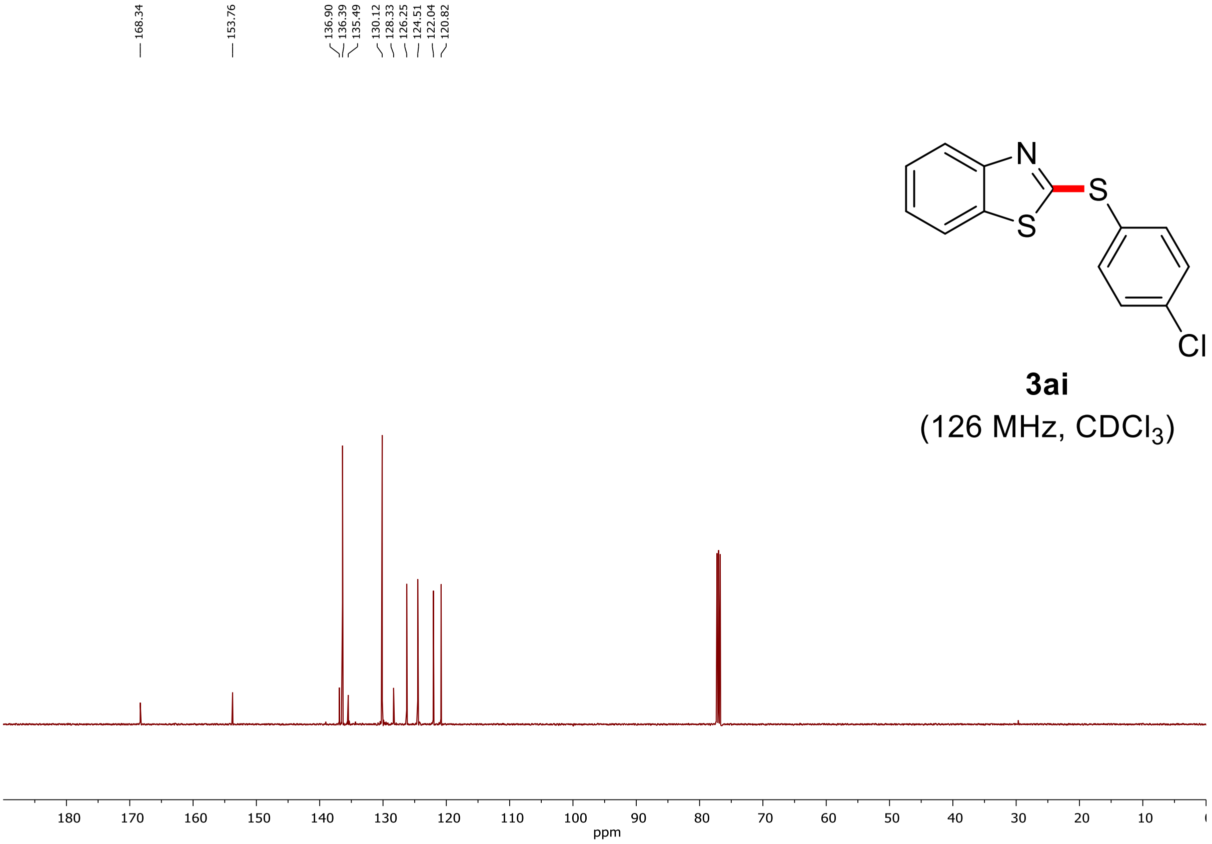
(CDCl$_3$, 101 MHz)



3ah
(376 MHz, $CDCl_3$)

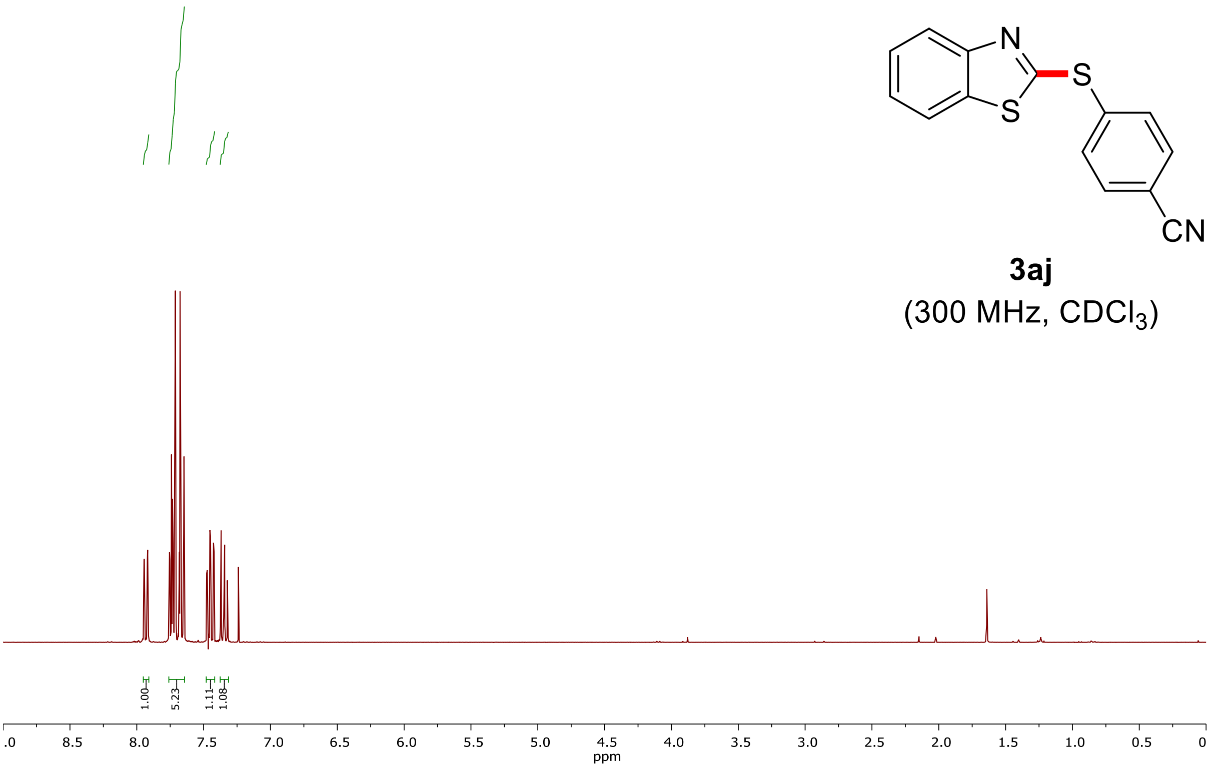


3ai
(500 MHz, $CDCl_3$)



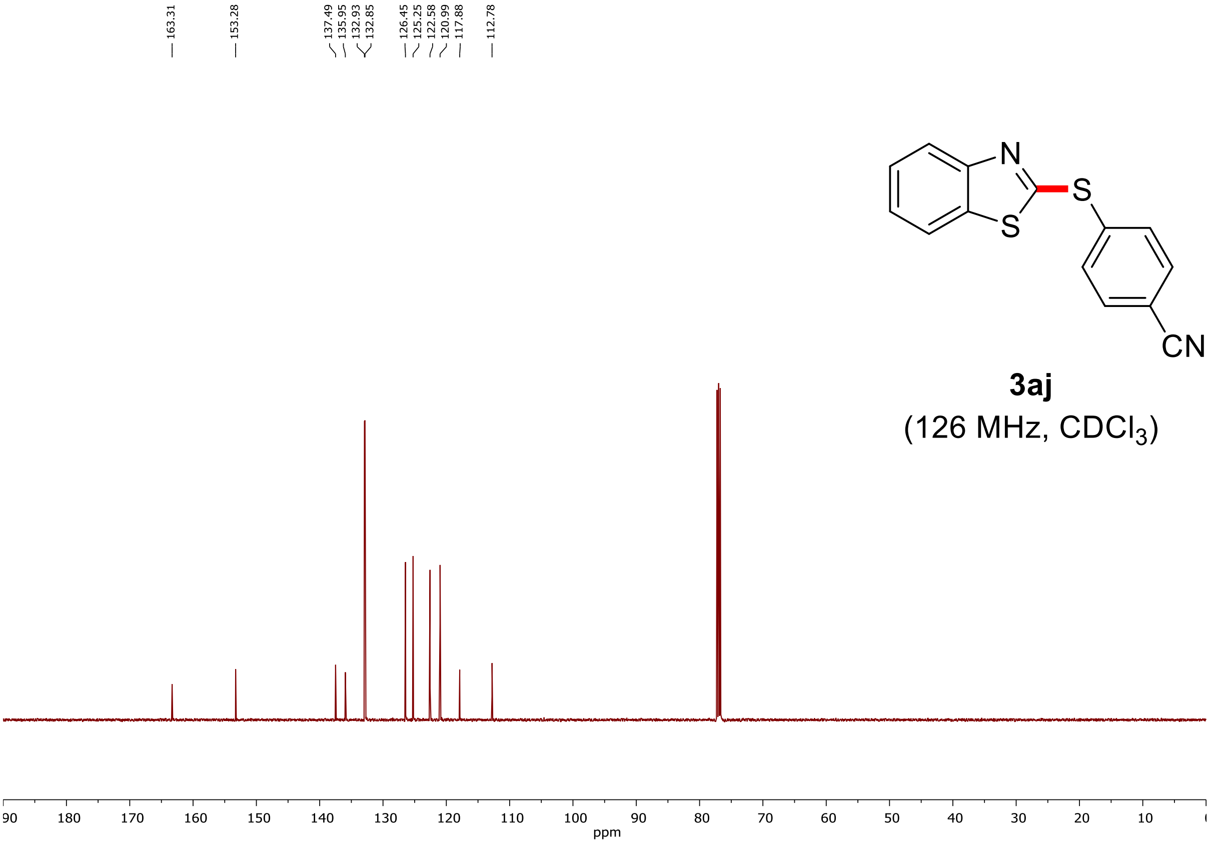
3ai

(126 MHz, CDCl$_3$)



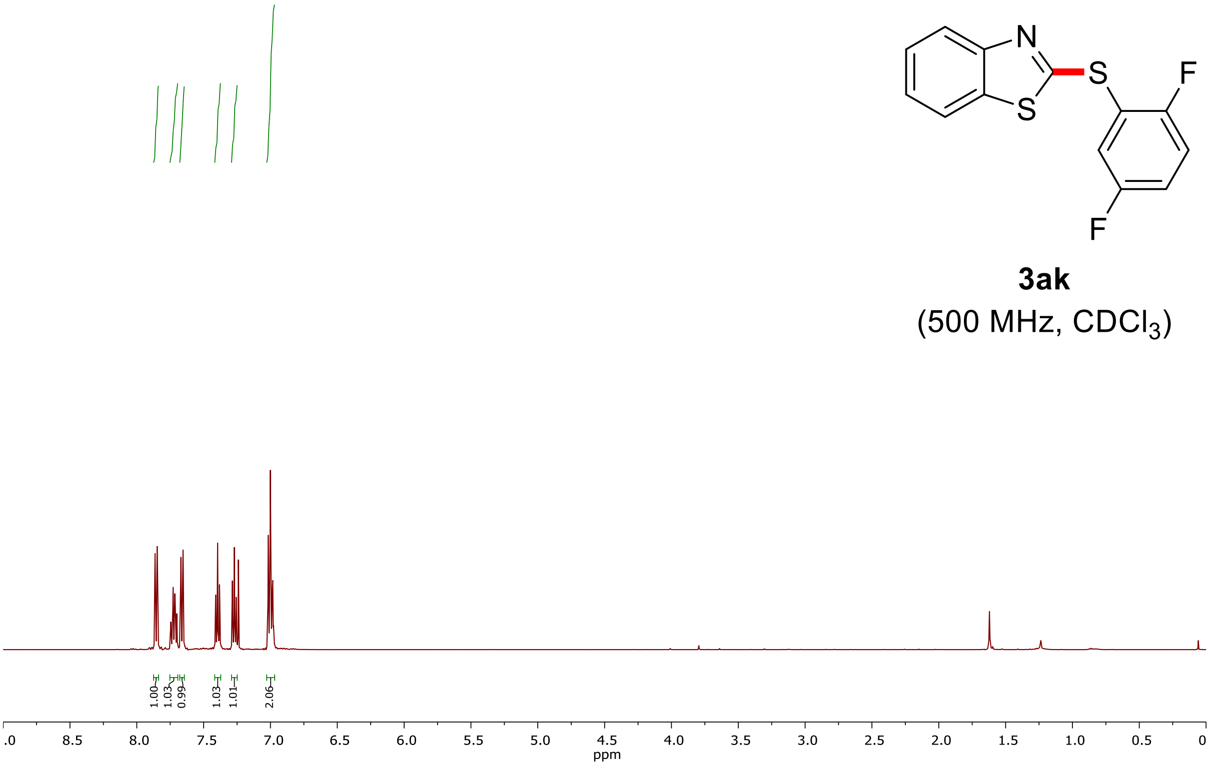
3aj

(300 MHz, CDCl$_3$)



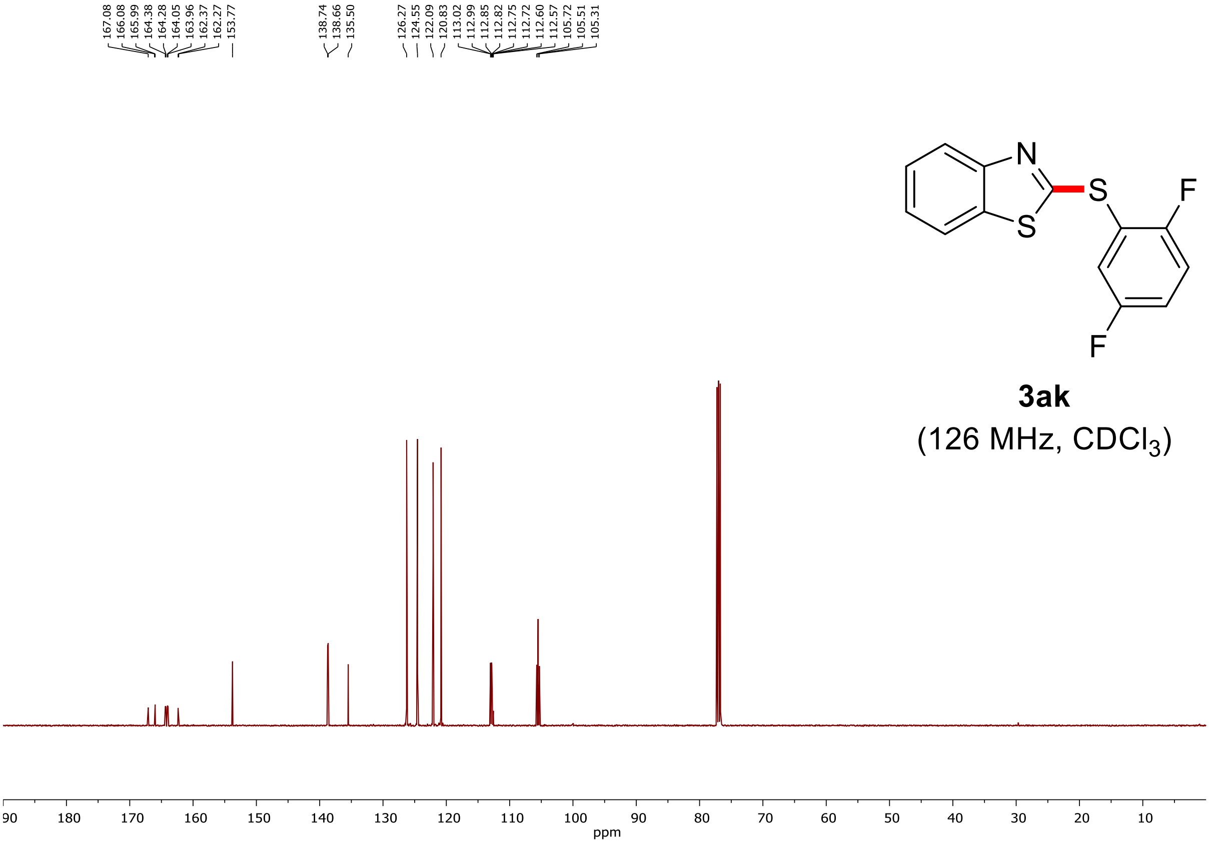
3aj

(126 MHz, CDCl$_3$)



3ak

(500 MHz, CDCl$_3$)



3ak

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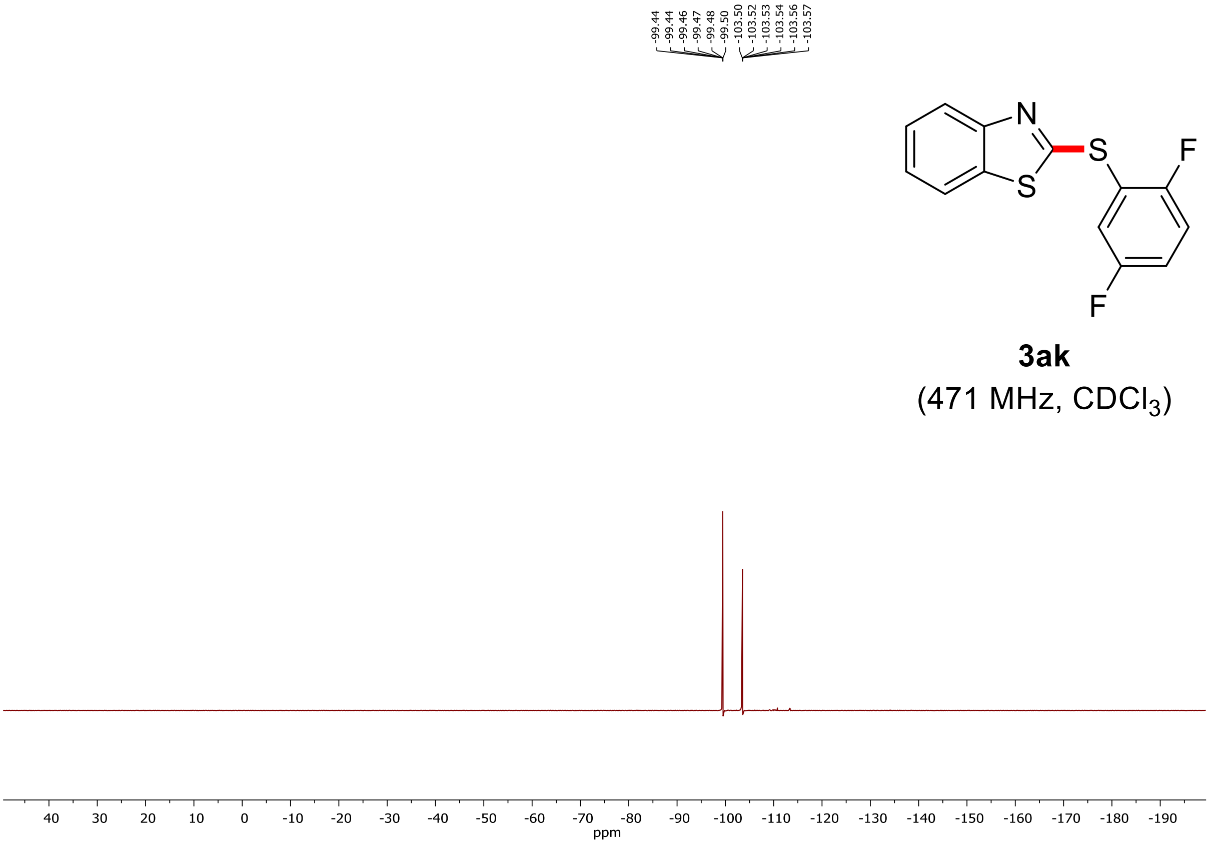
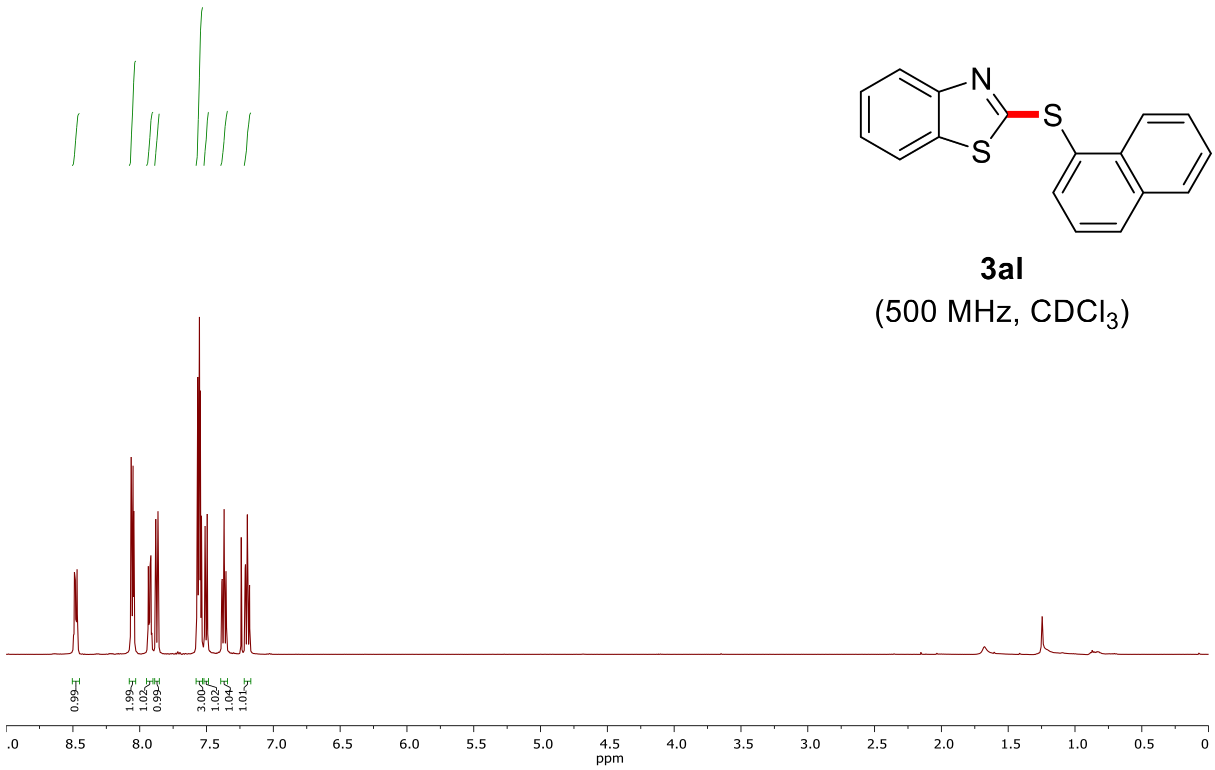
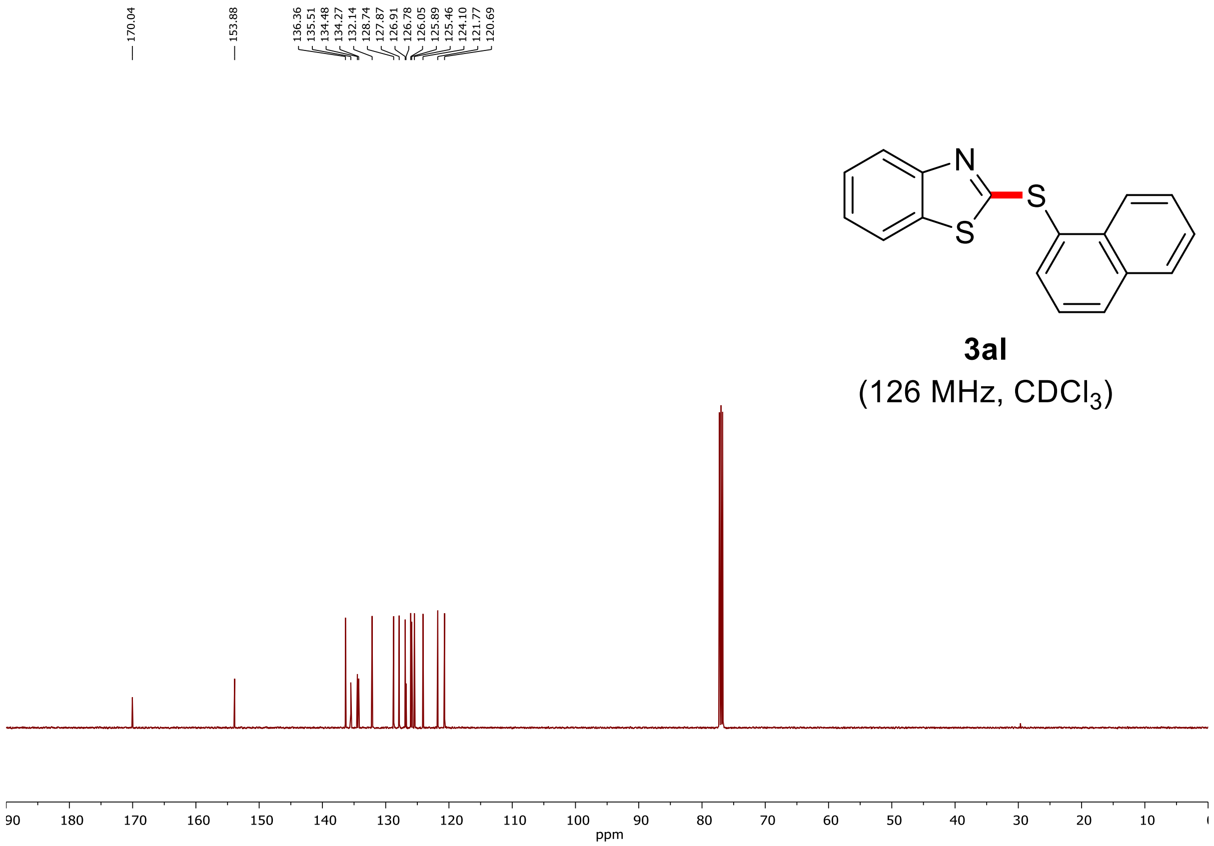


3ak

(471 MHz, $CDCl_3$)



3al
(500 MHz, $CDCl_3$)



3al
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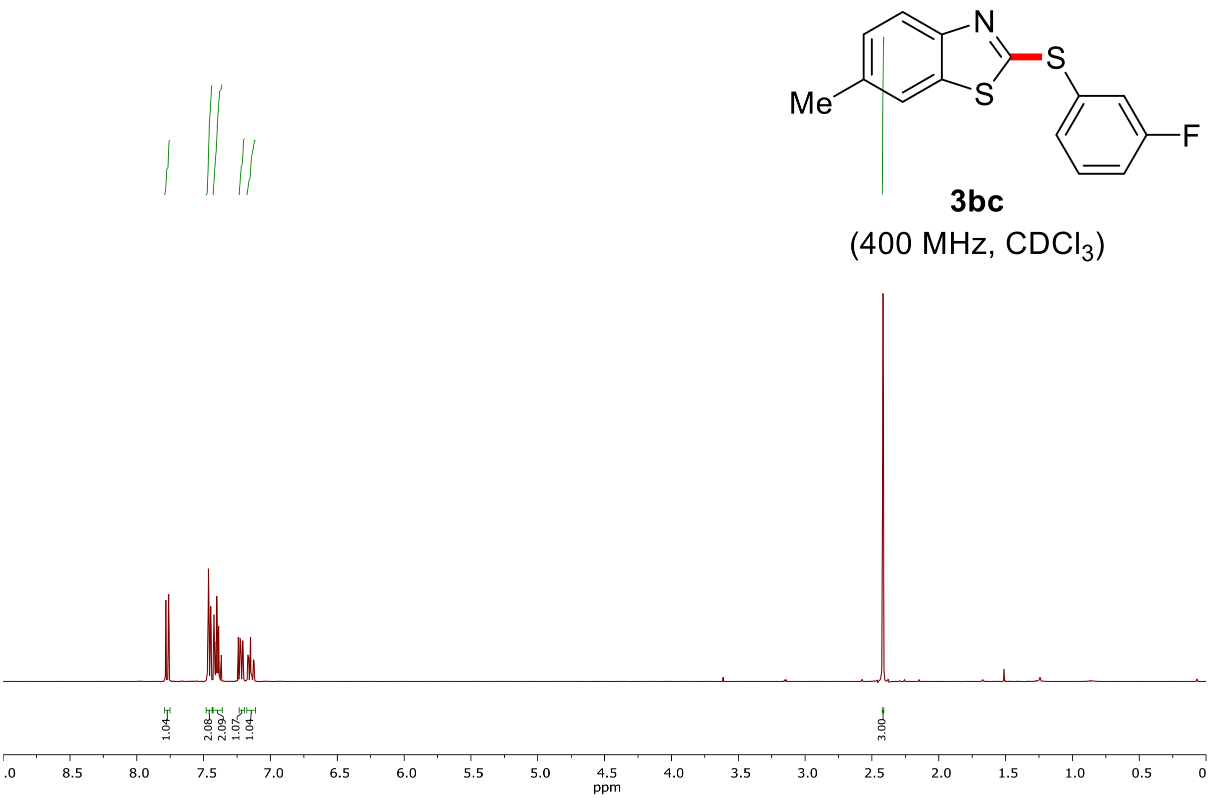
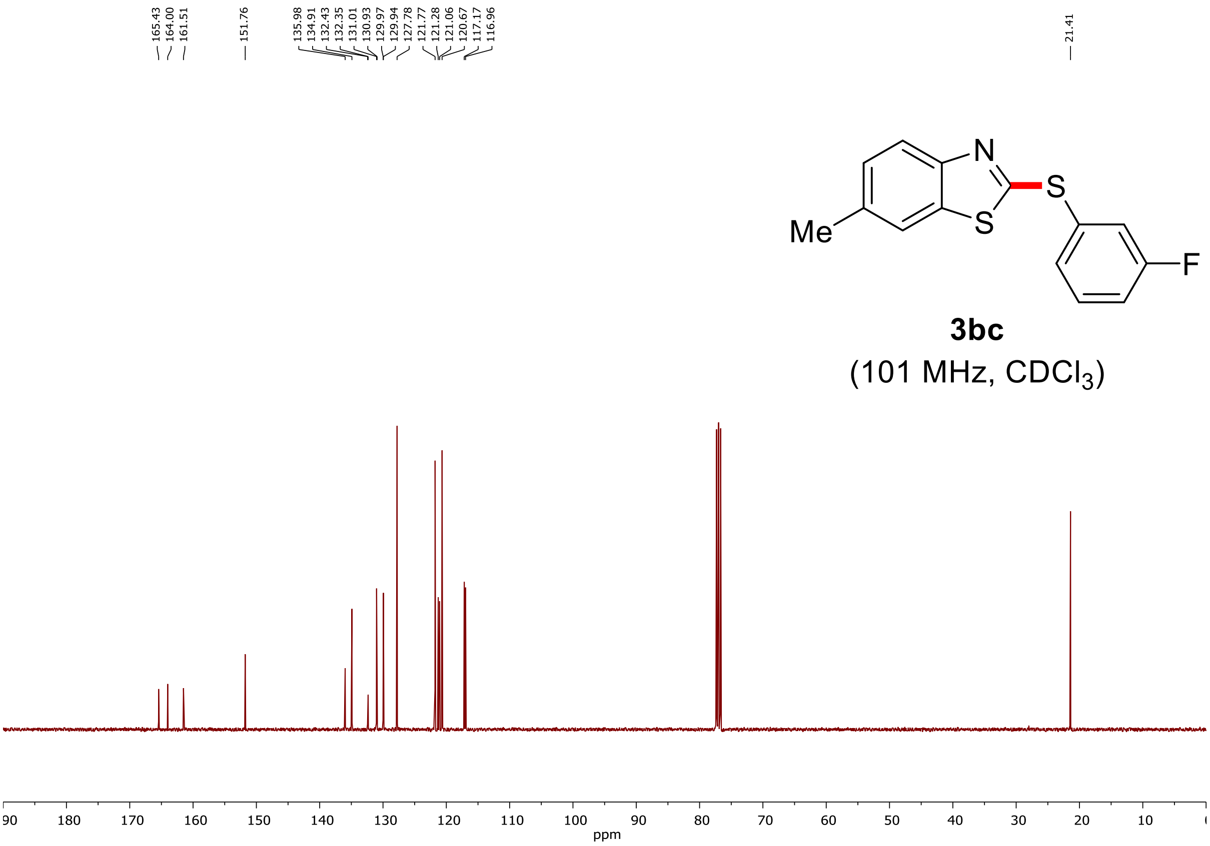


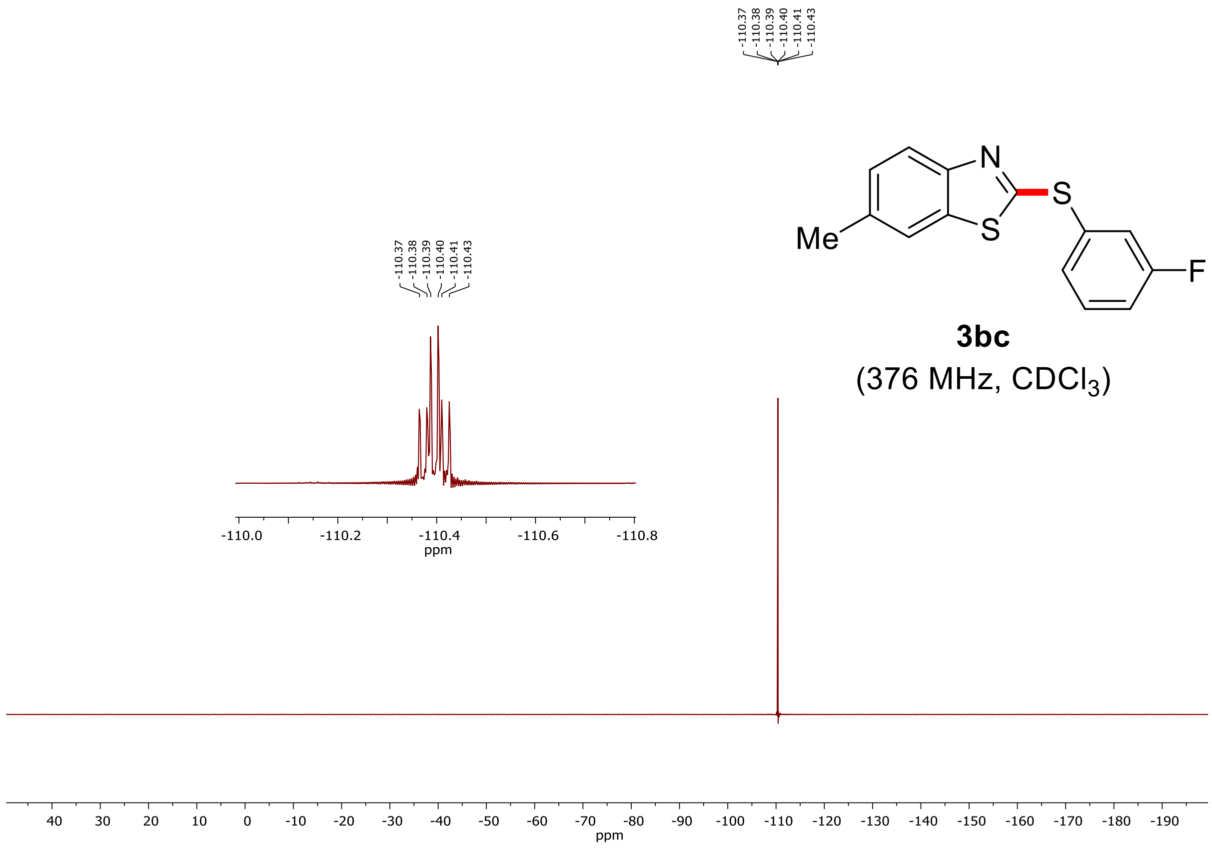
3bc

(400 MHz, $CDCl_3$)

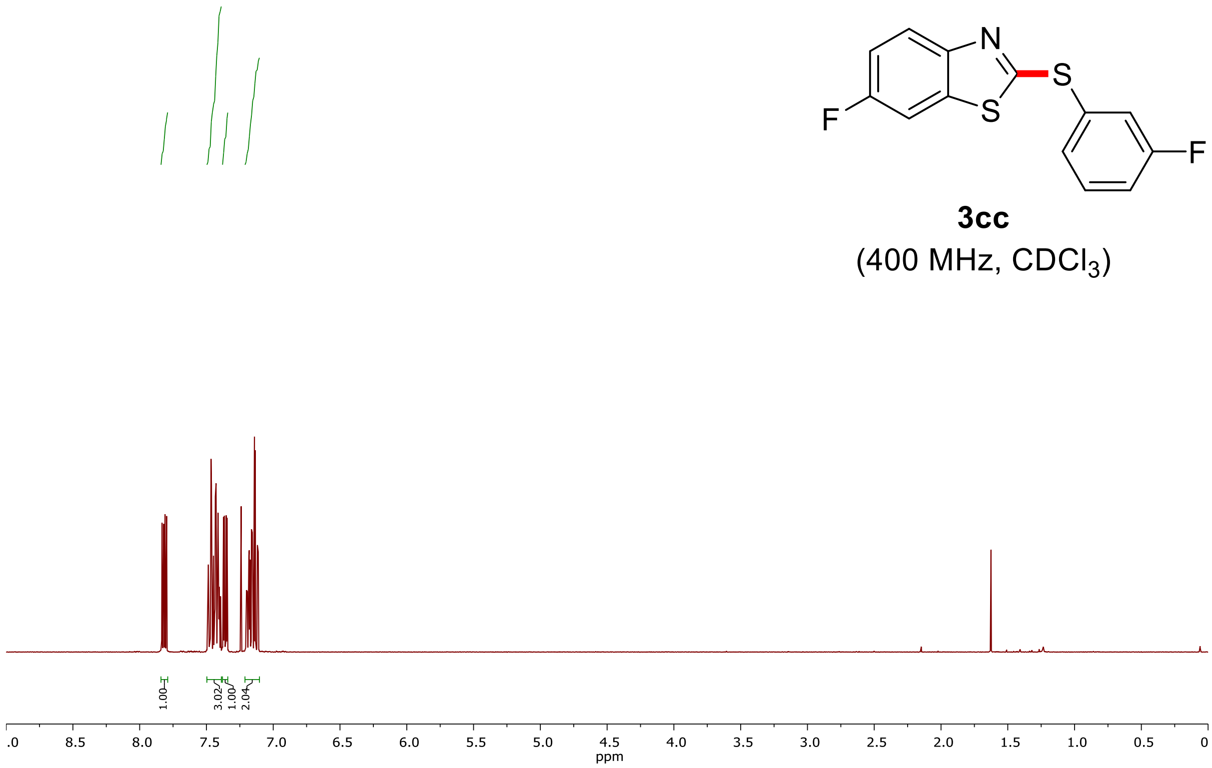


3bc

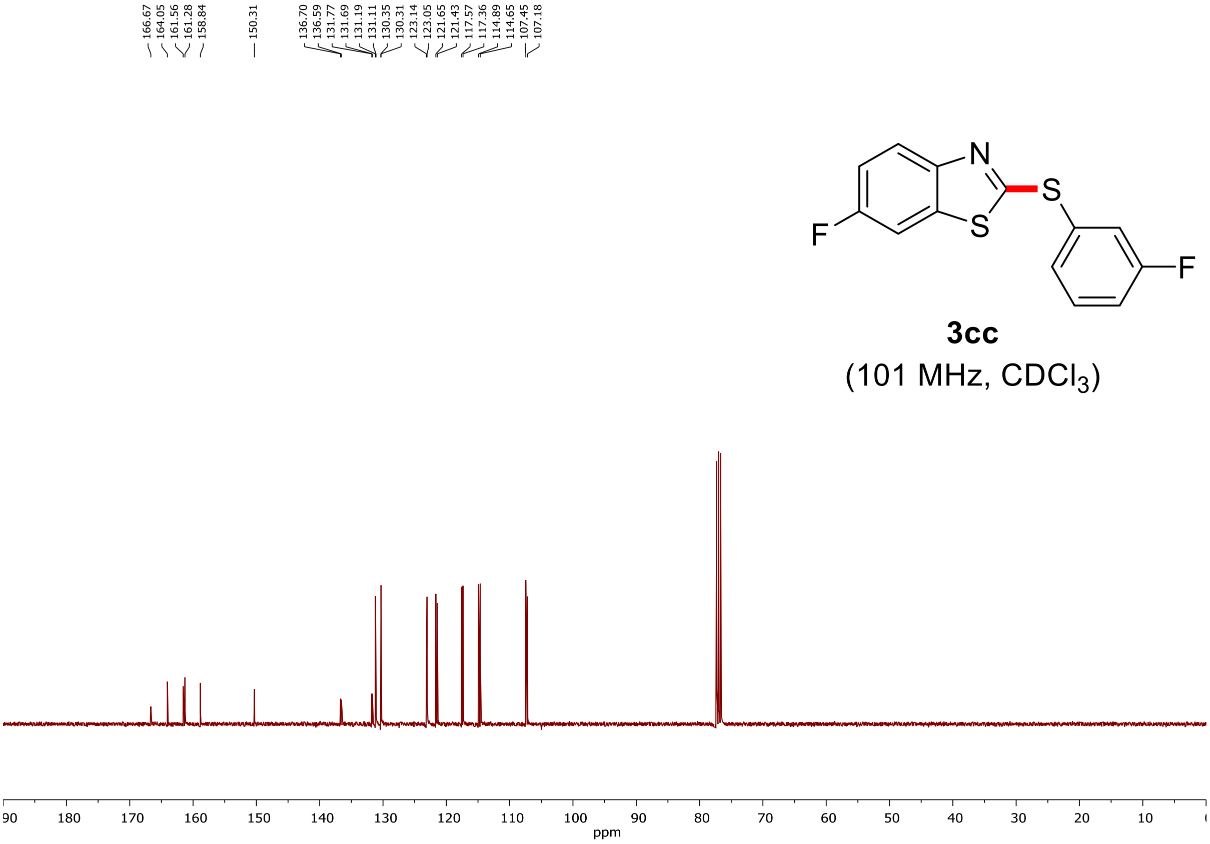
(101 MHz, $CDCl_3$)



3bc
(376 MHz, $CDCl_3$)



3cc
(400 MHz, $CDCl_3$)



3cc

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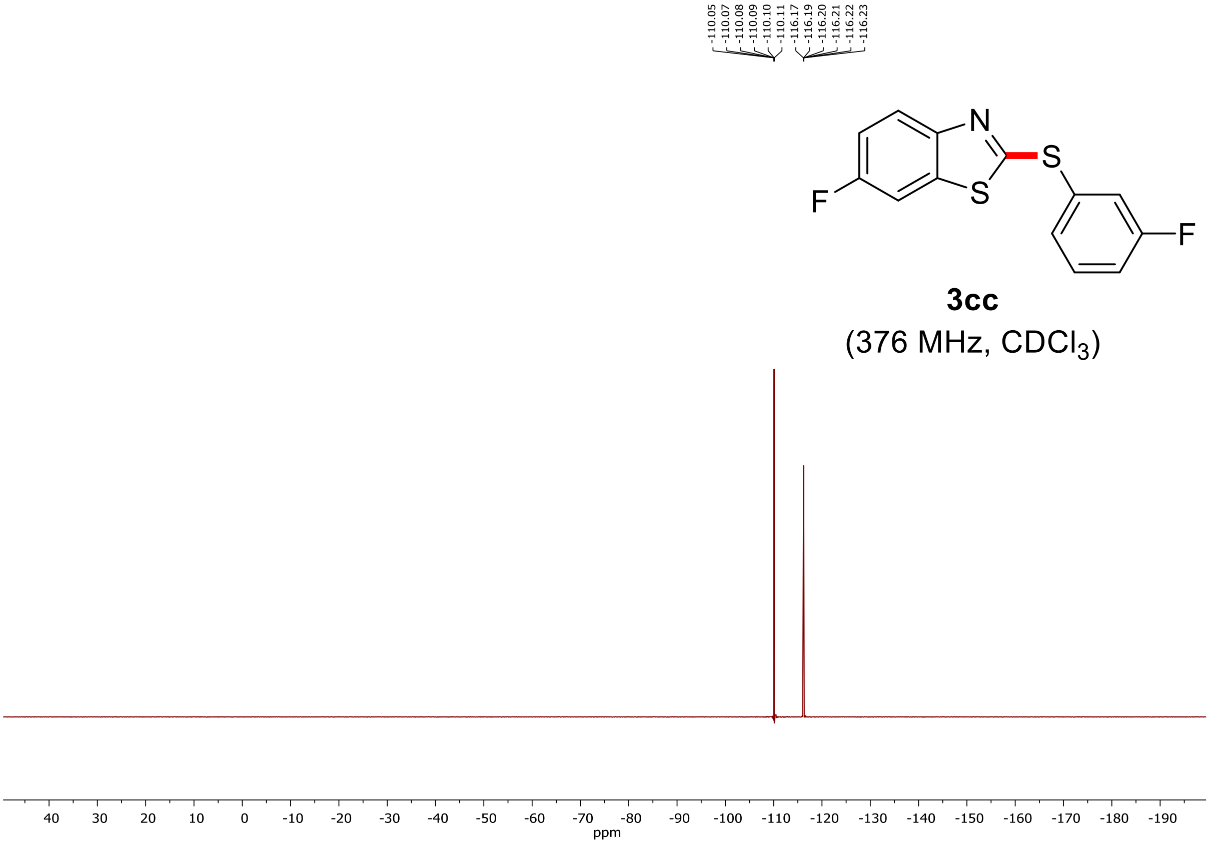

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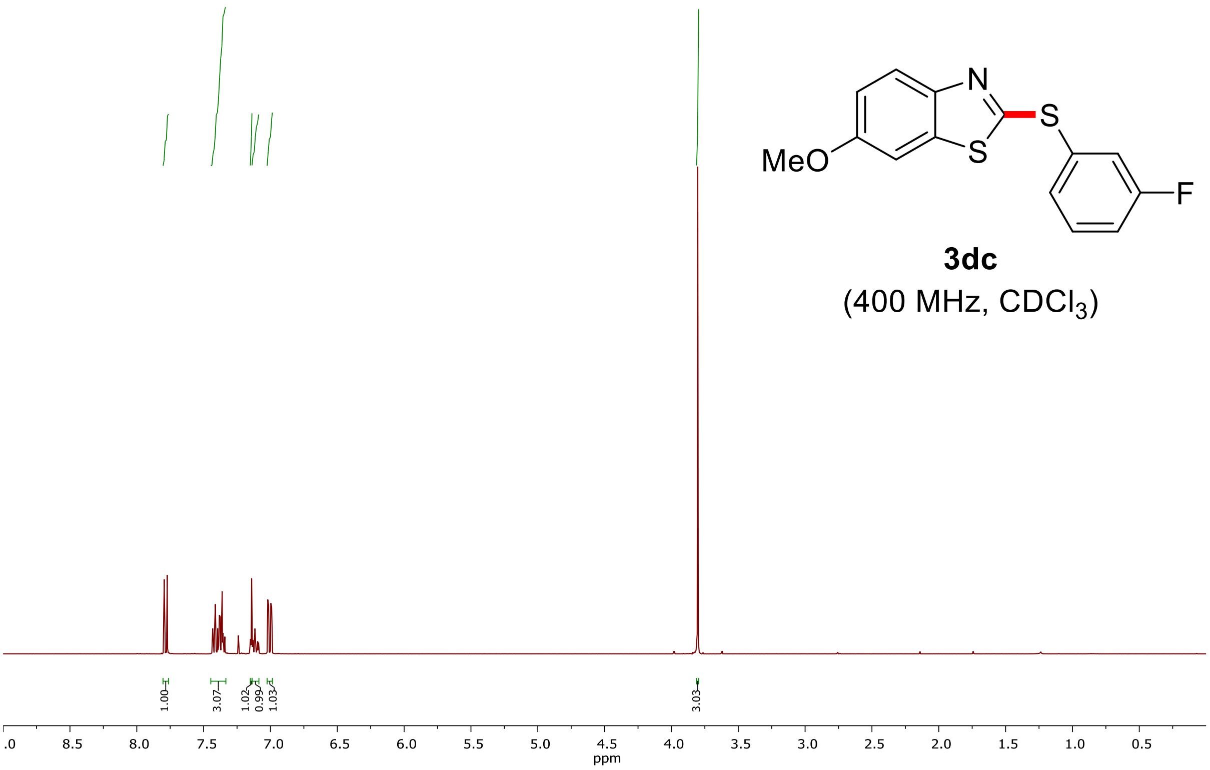
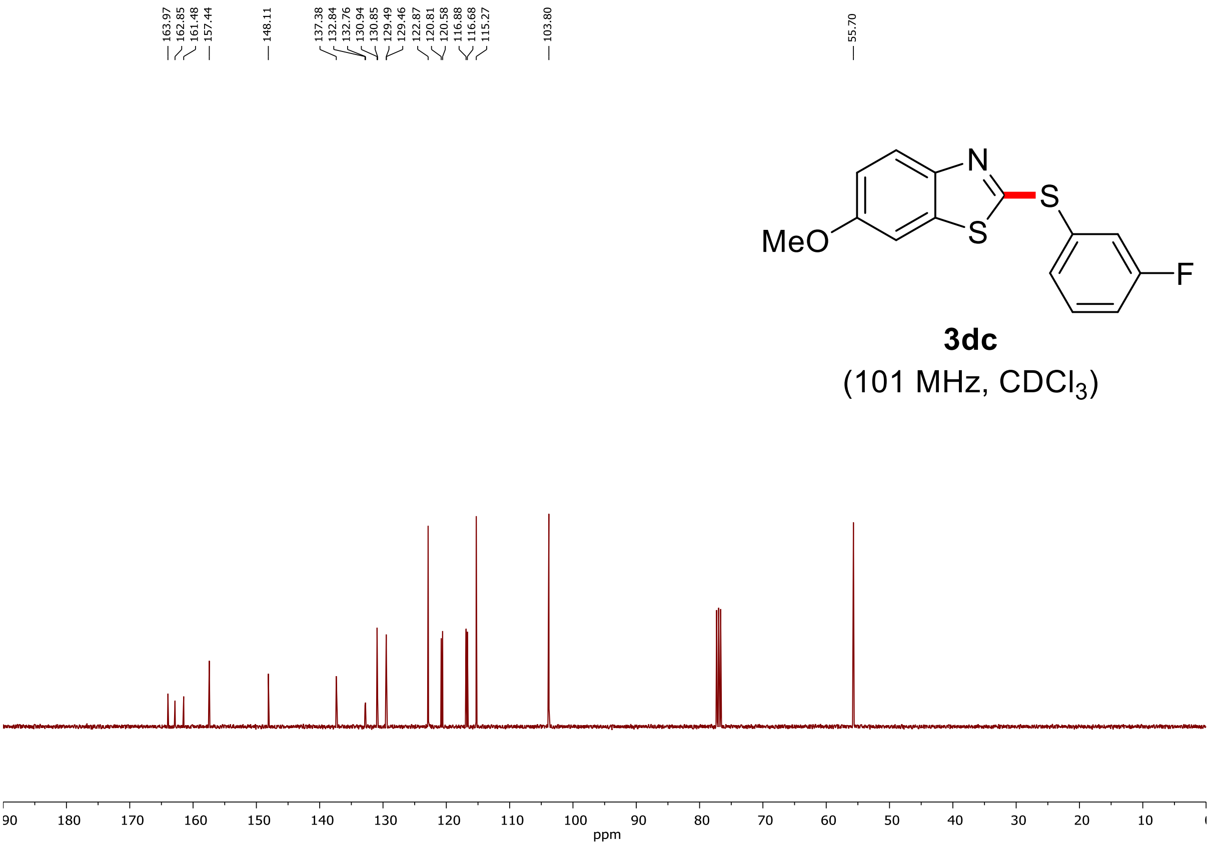
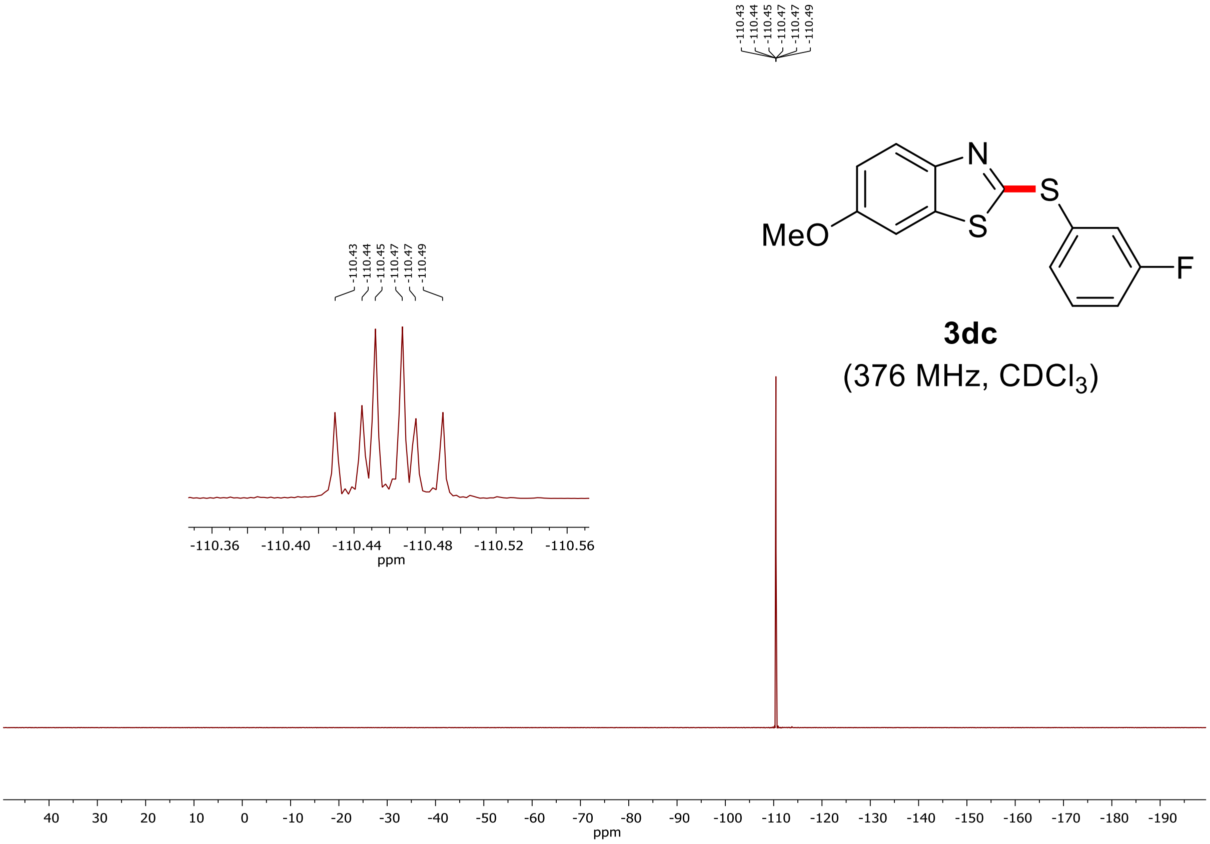


3dc
(400 MHz, $CDCl_3$)

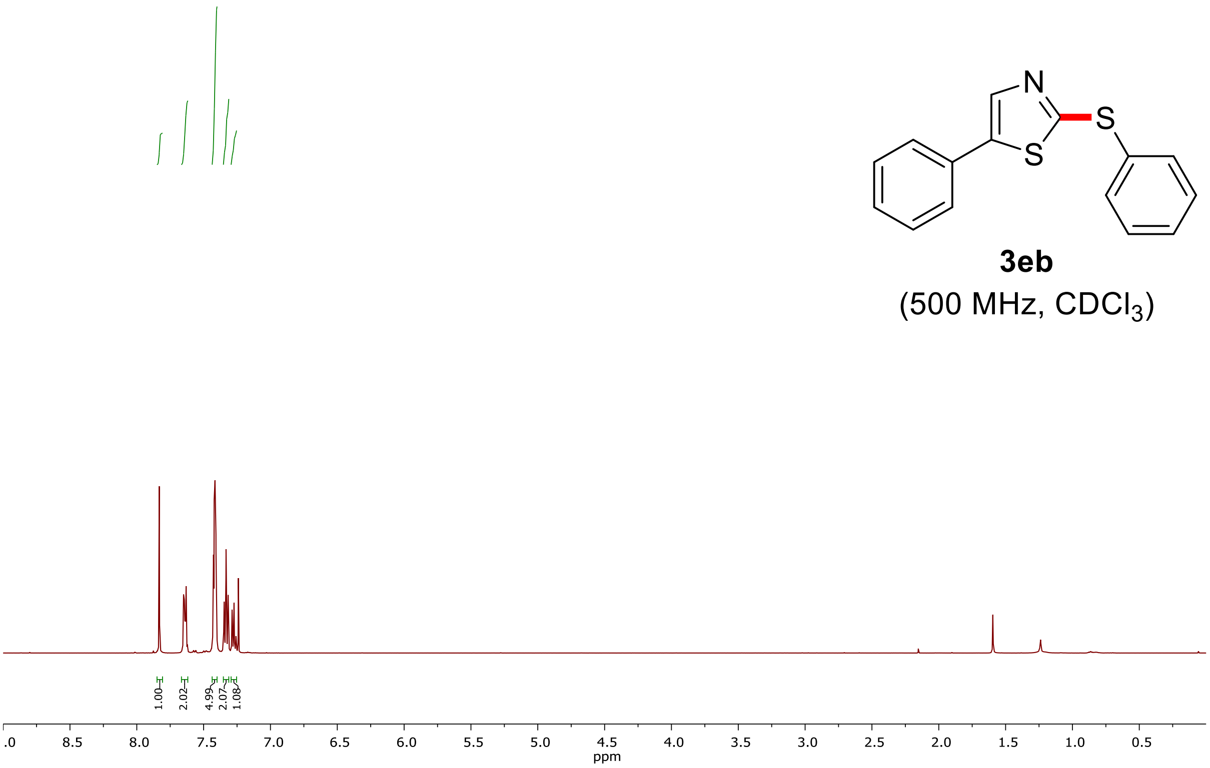


3dc
(101 MHz, $CDCl_3$)



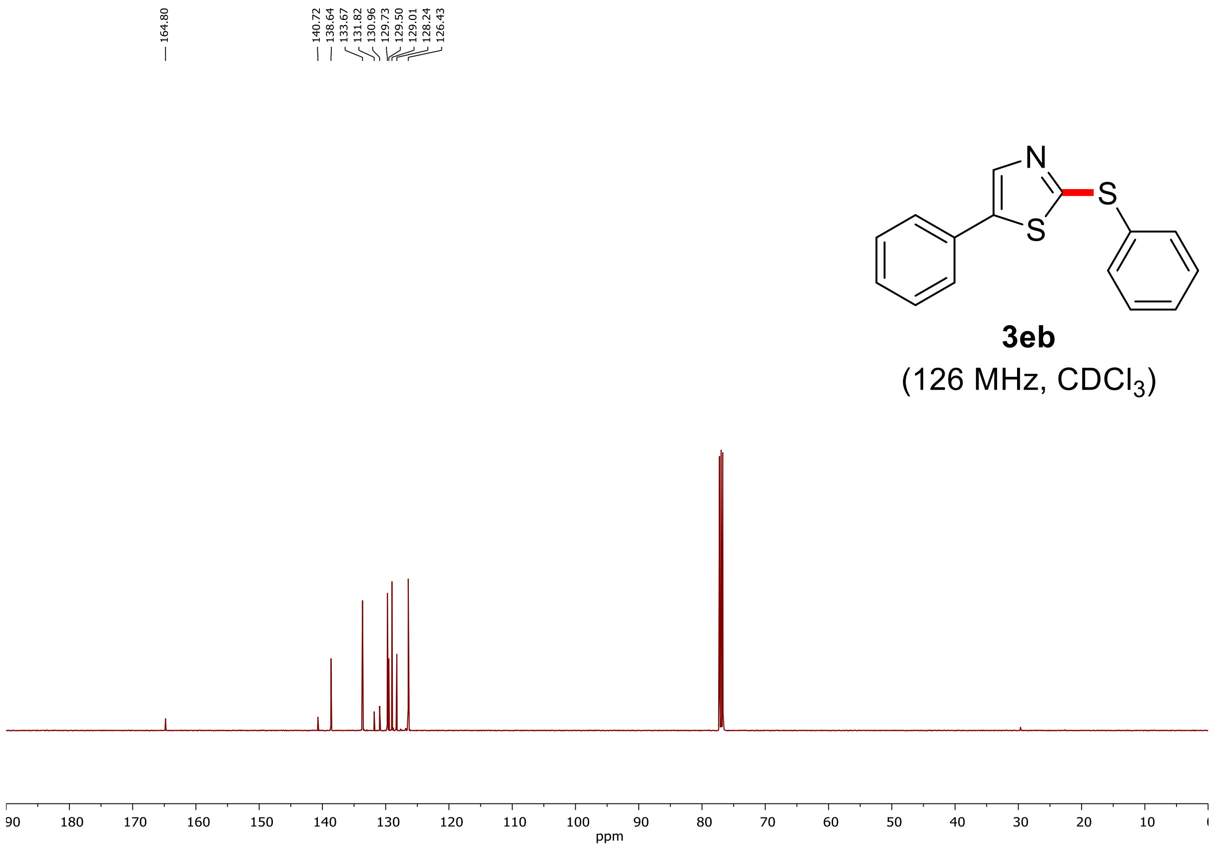
3dc

(376 MHz, CDCl$_3$)



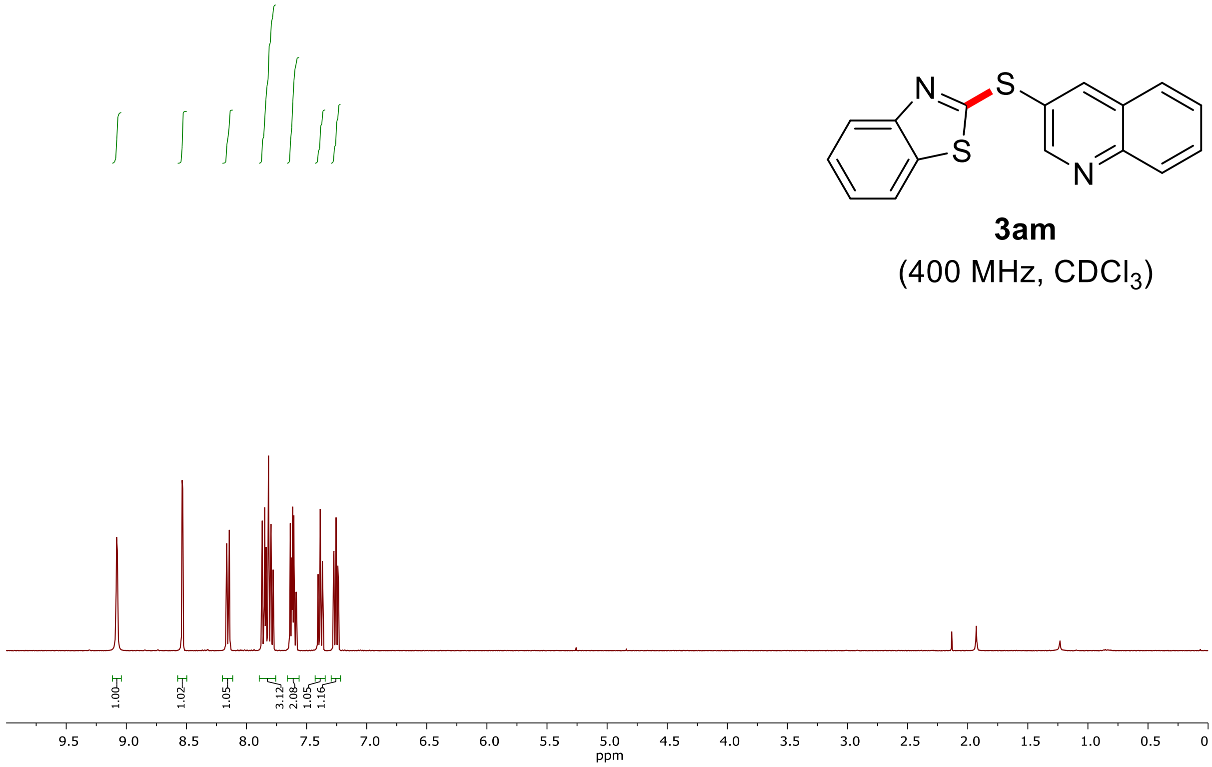
3eb

(500 MHz, CDCl$_3$)



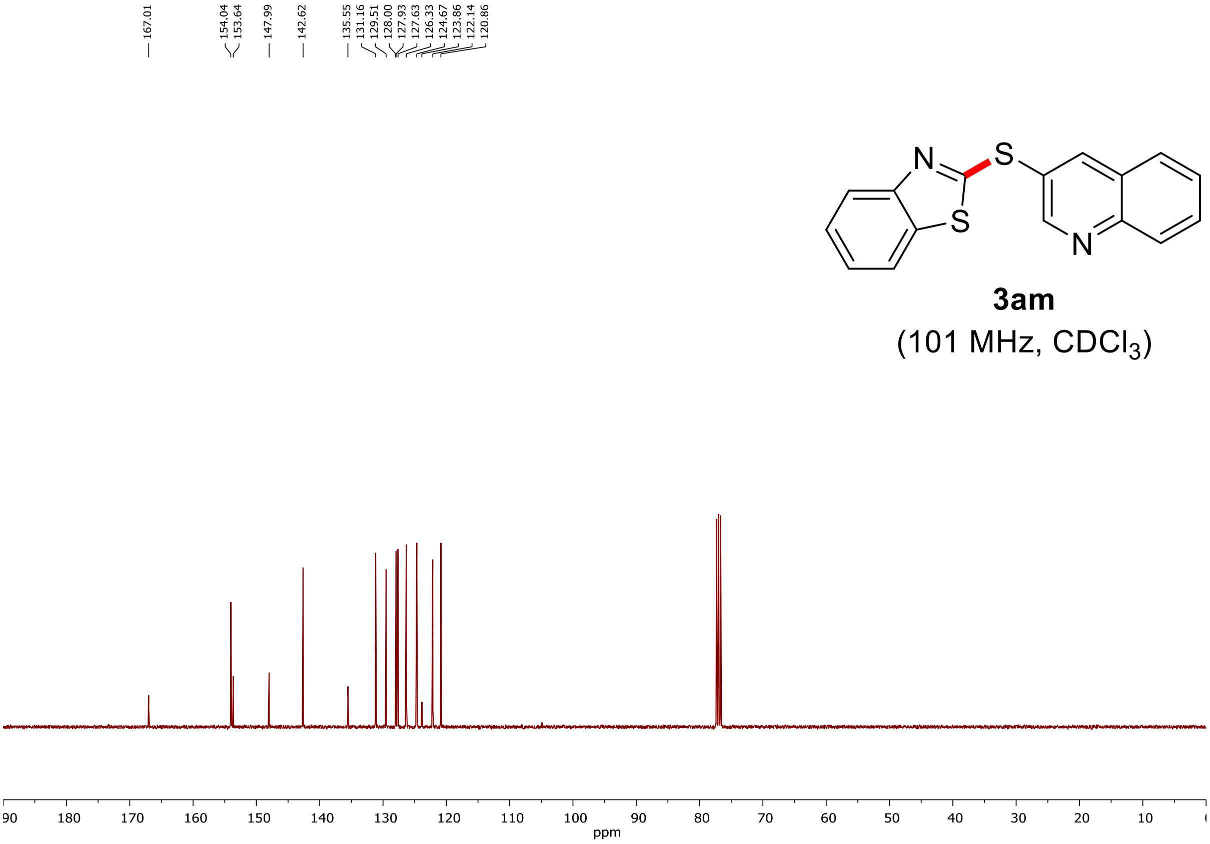
3eb

(126 MHz, $CDCl_3$)



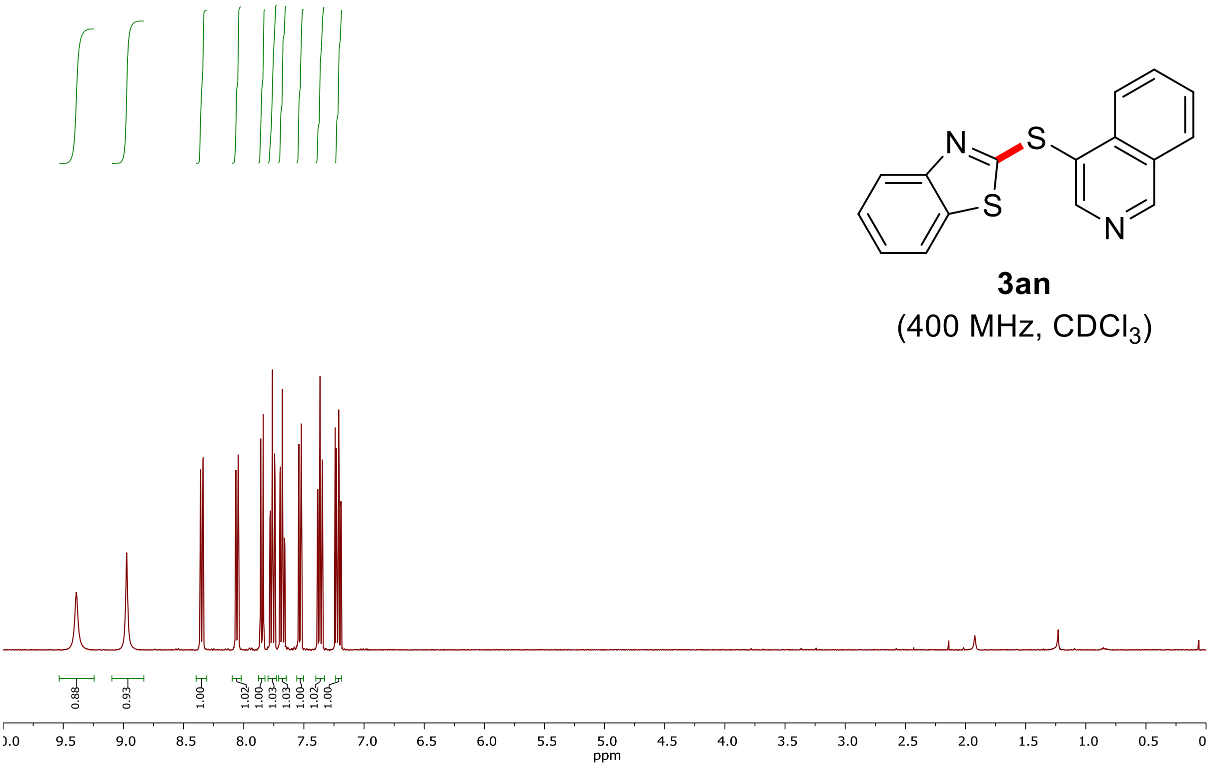
3am

(400 MHz, $CDCl_3$)



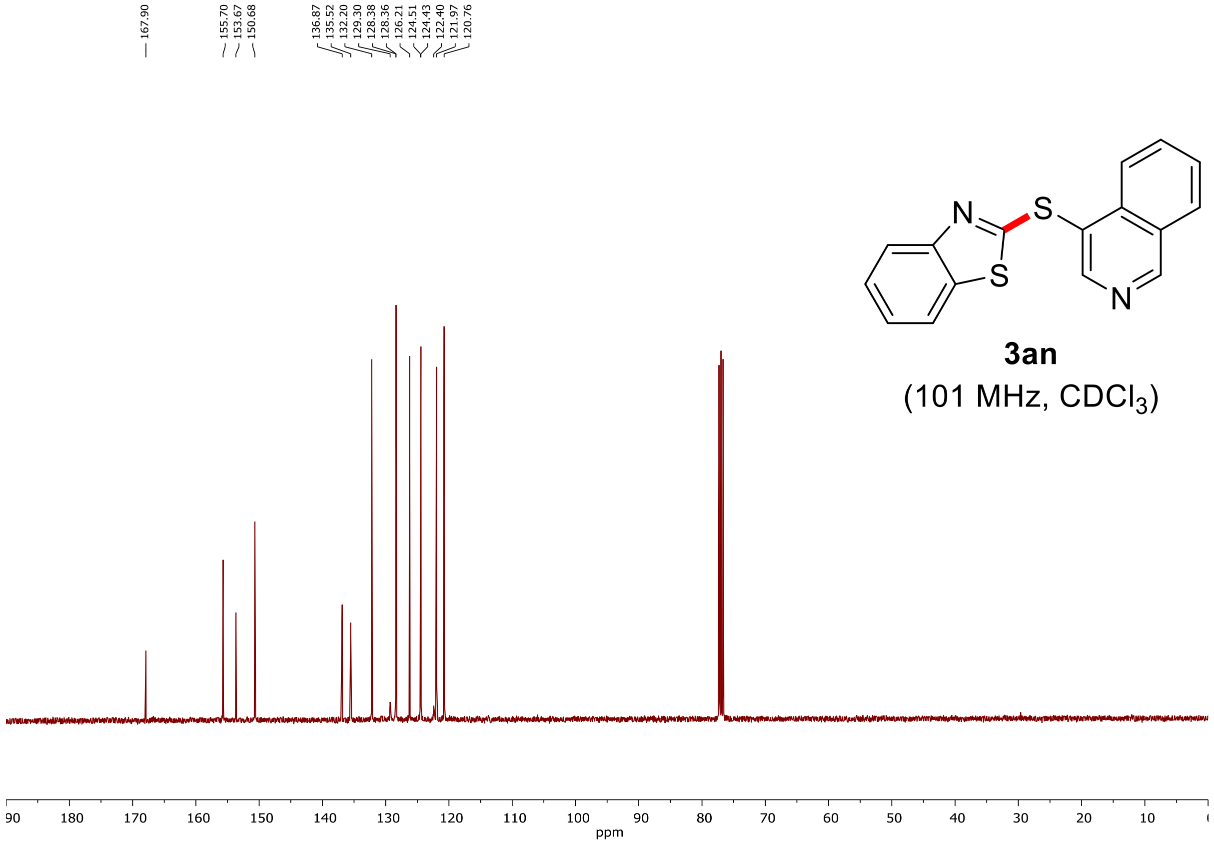
3am

(101 MHz, $CDCl_3$)



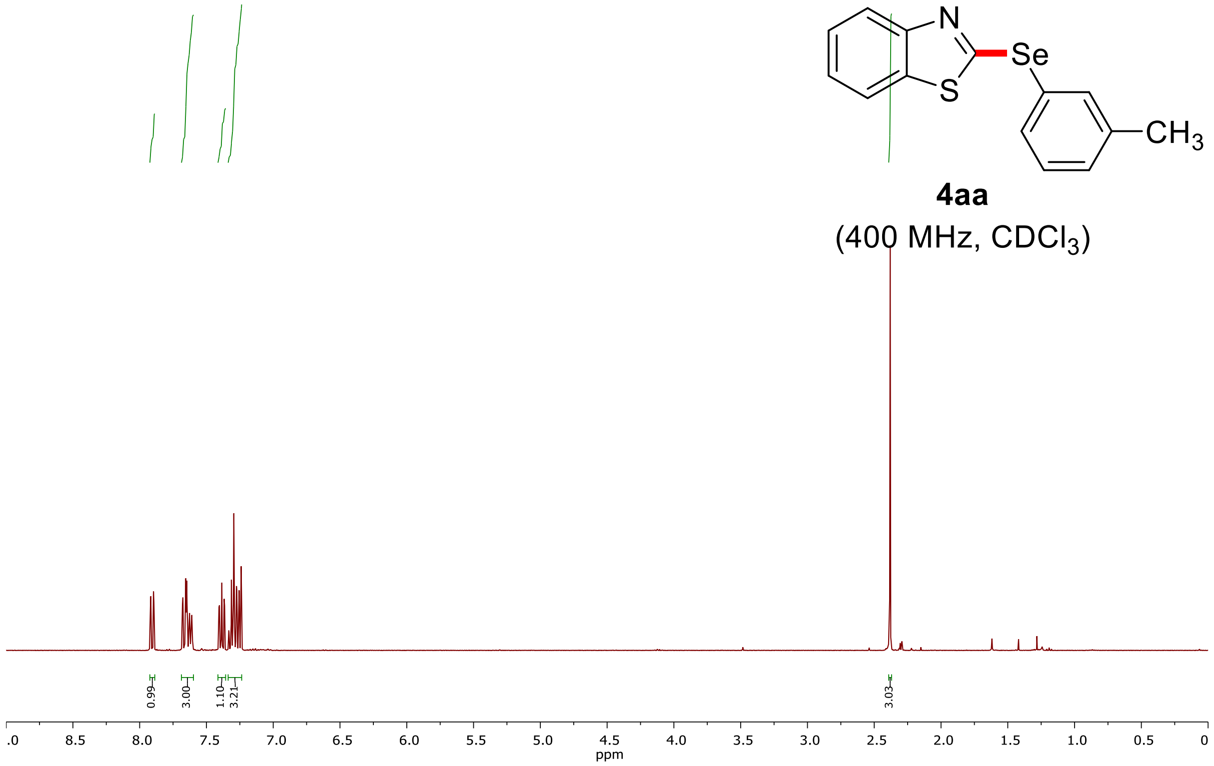
3an

(400 MHz, $CDCl_3$)



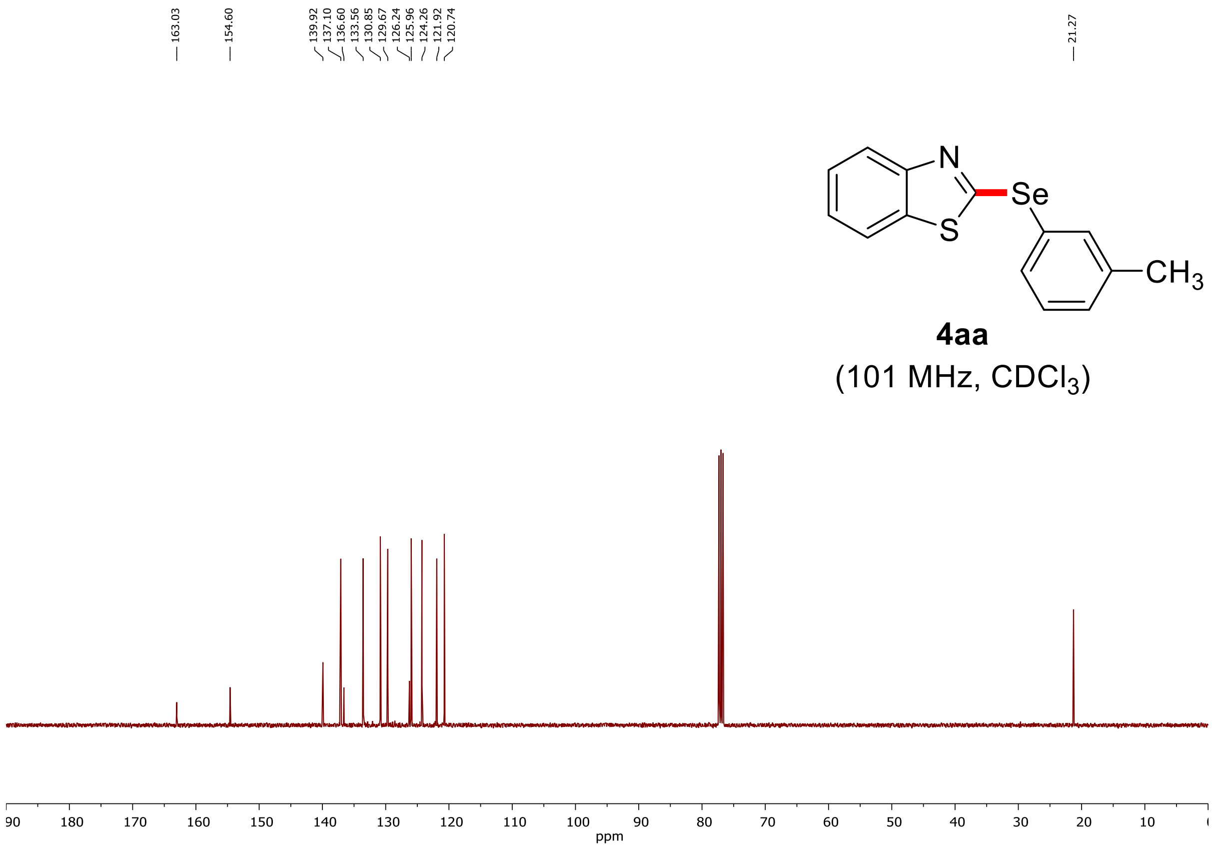
3an

(101 MHz, $CDCl_3$)



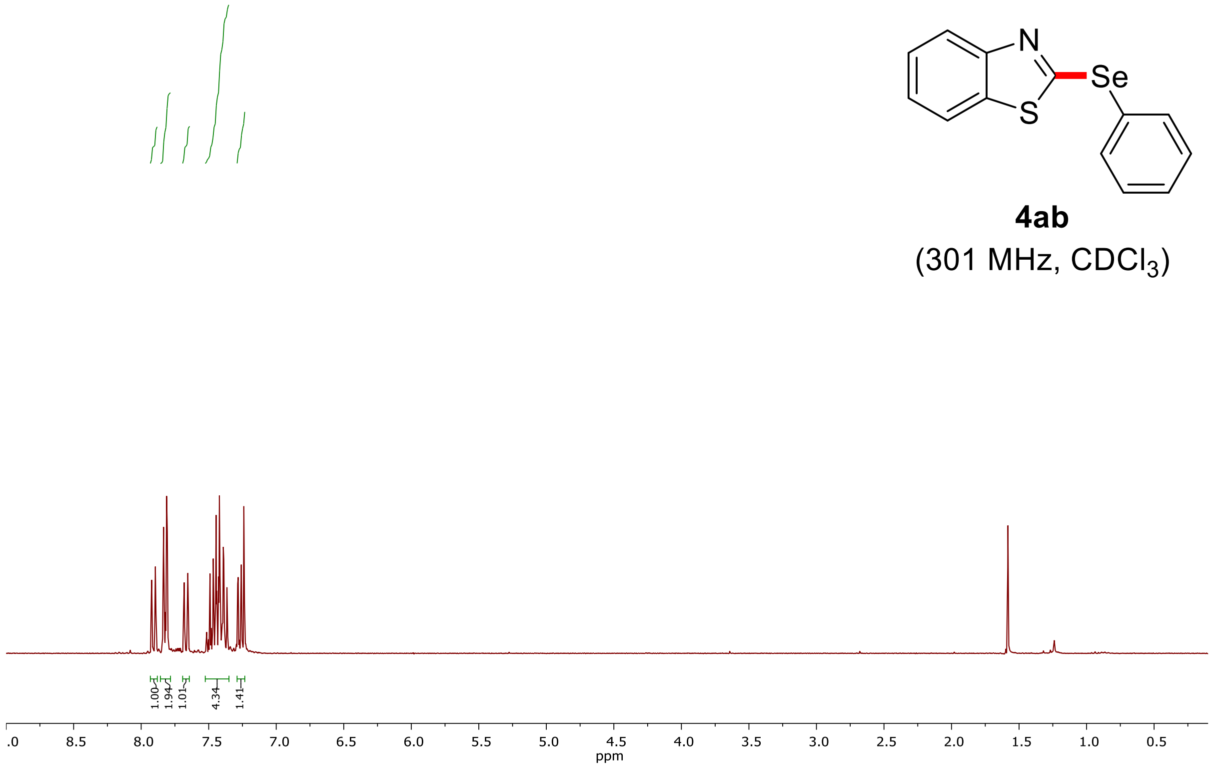
4aa

(400 MHz, $CDCl_3$)



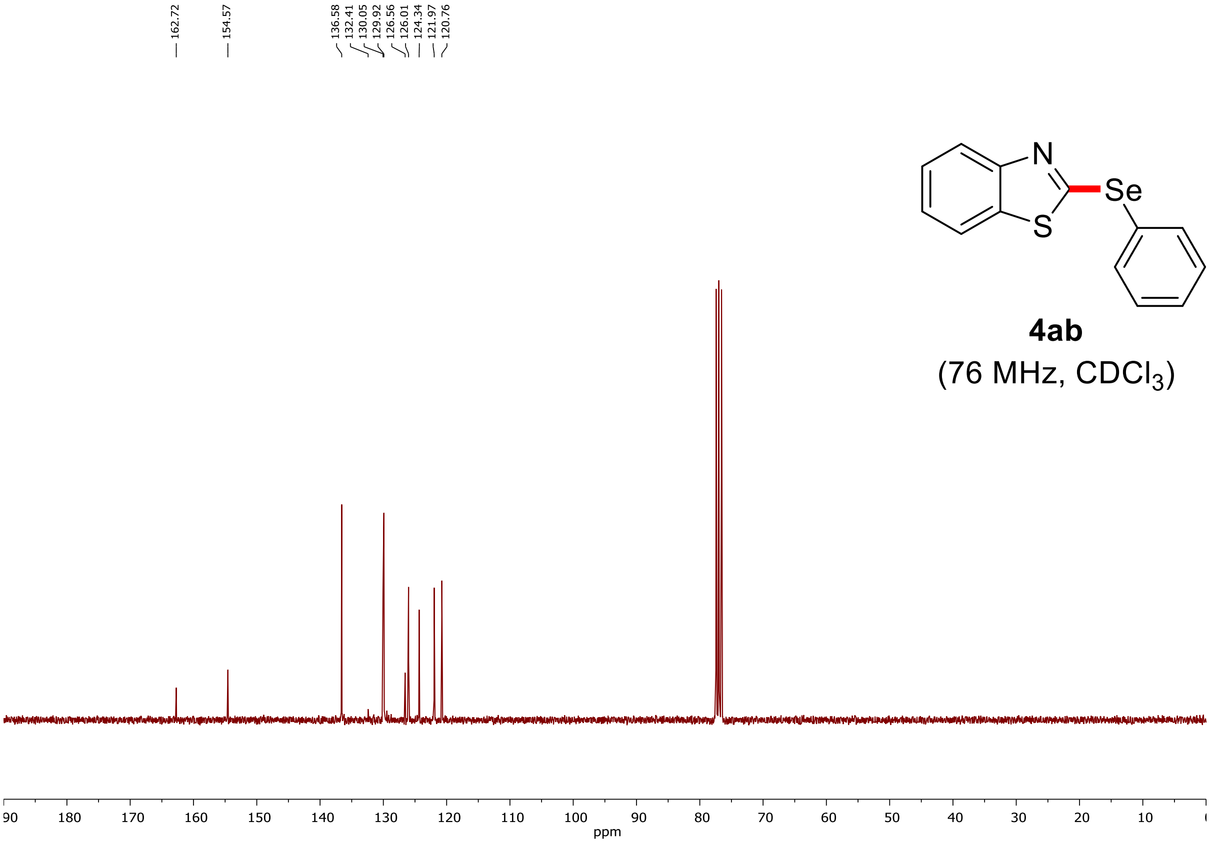
4aa

(101 MHz, $CDCl_3$)



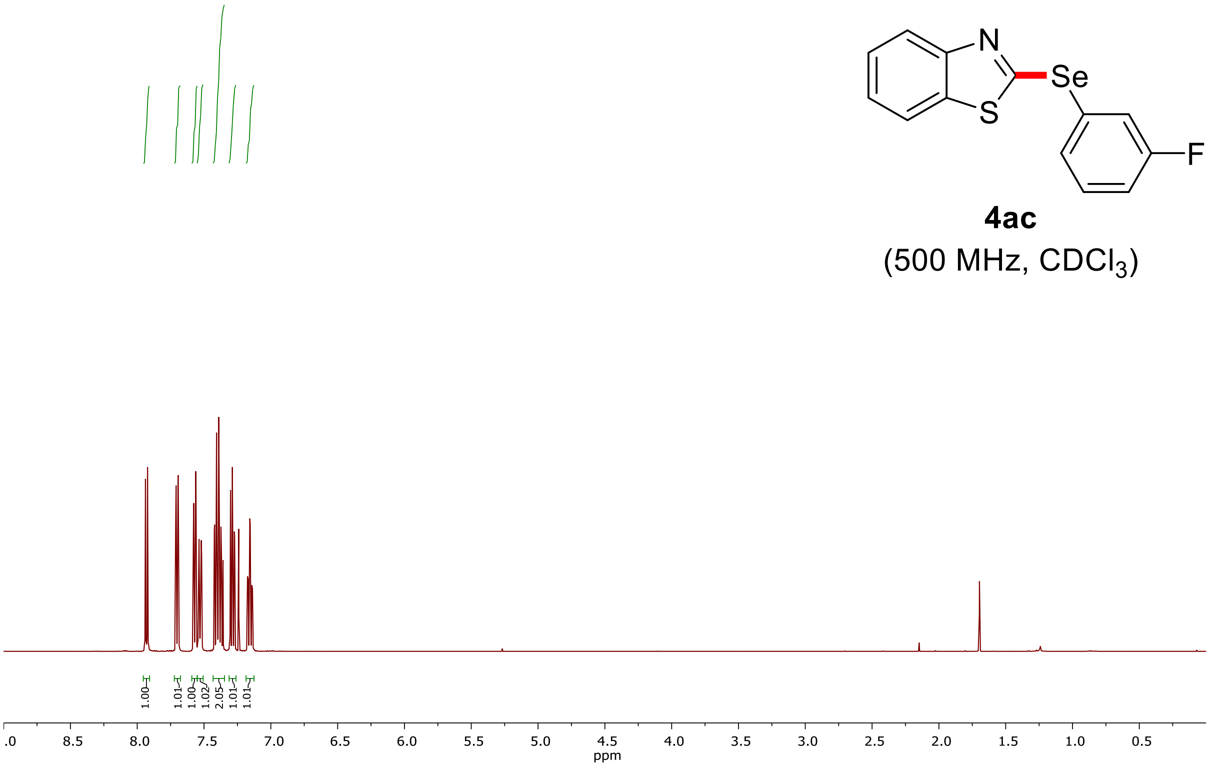
4ab

(301 MHz, $CDCl_3$)



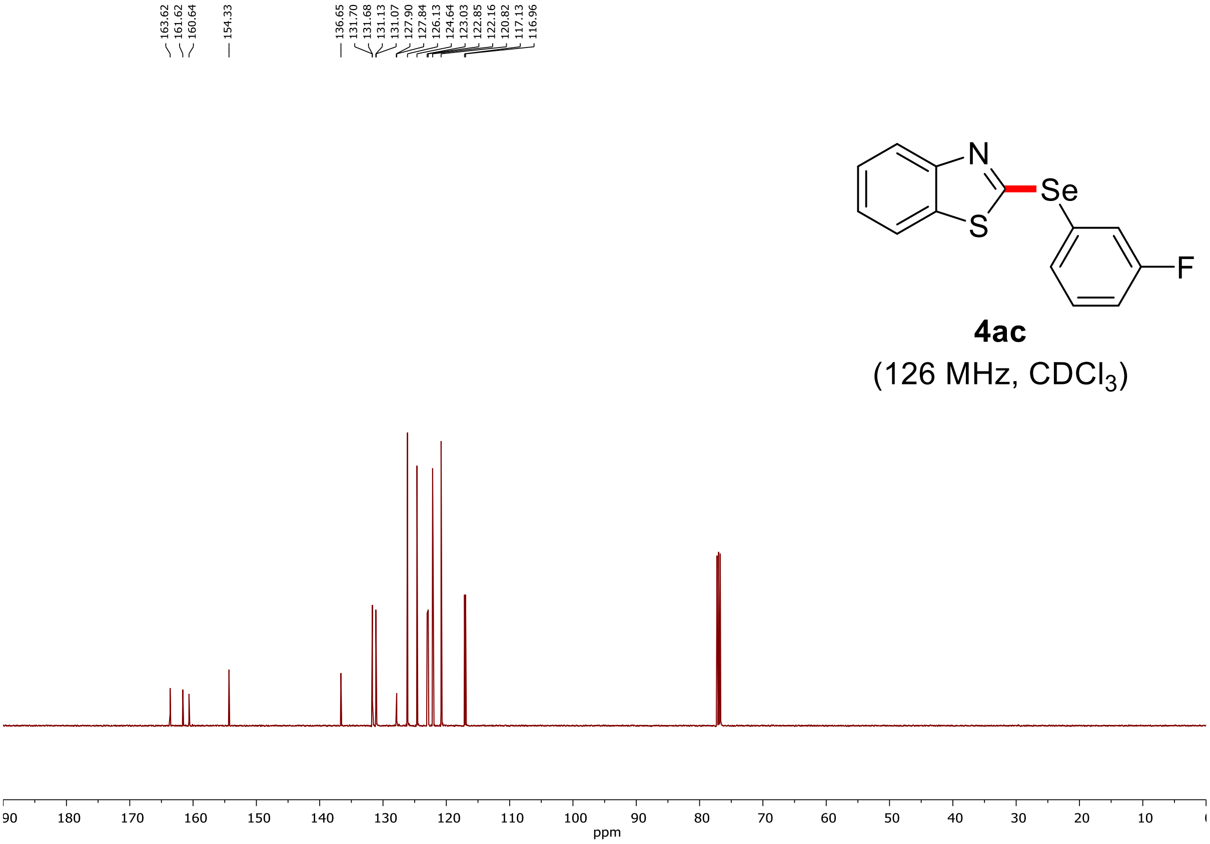
4ab

(76 MHz, $CDCl_3$)



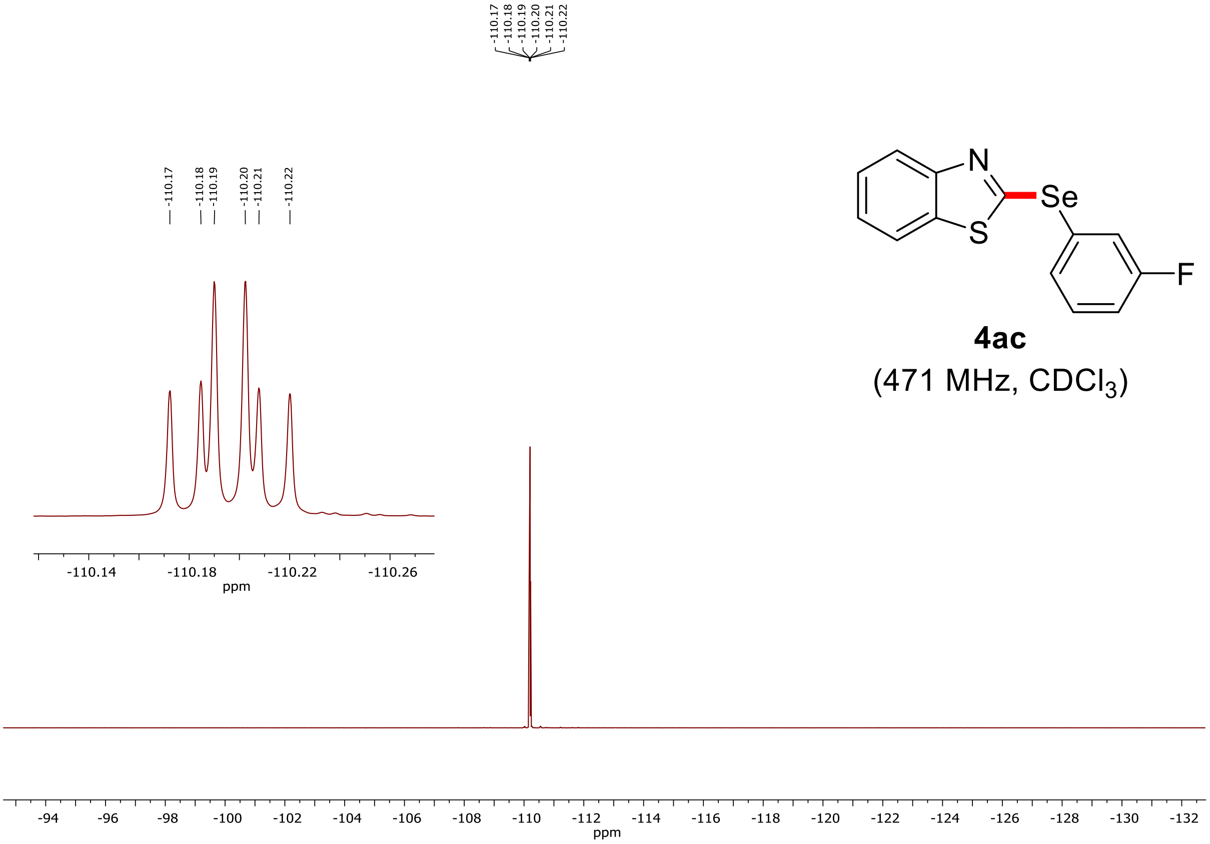
4ac

(500 MHz, $CDCl_3$)



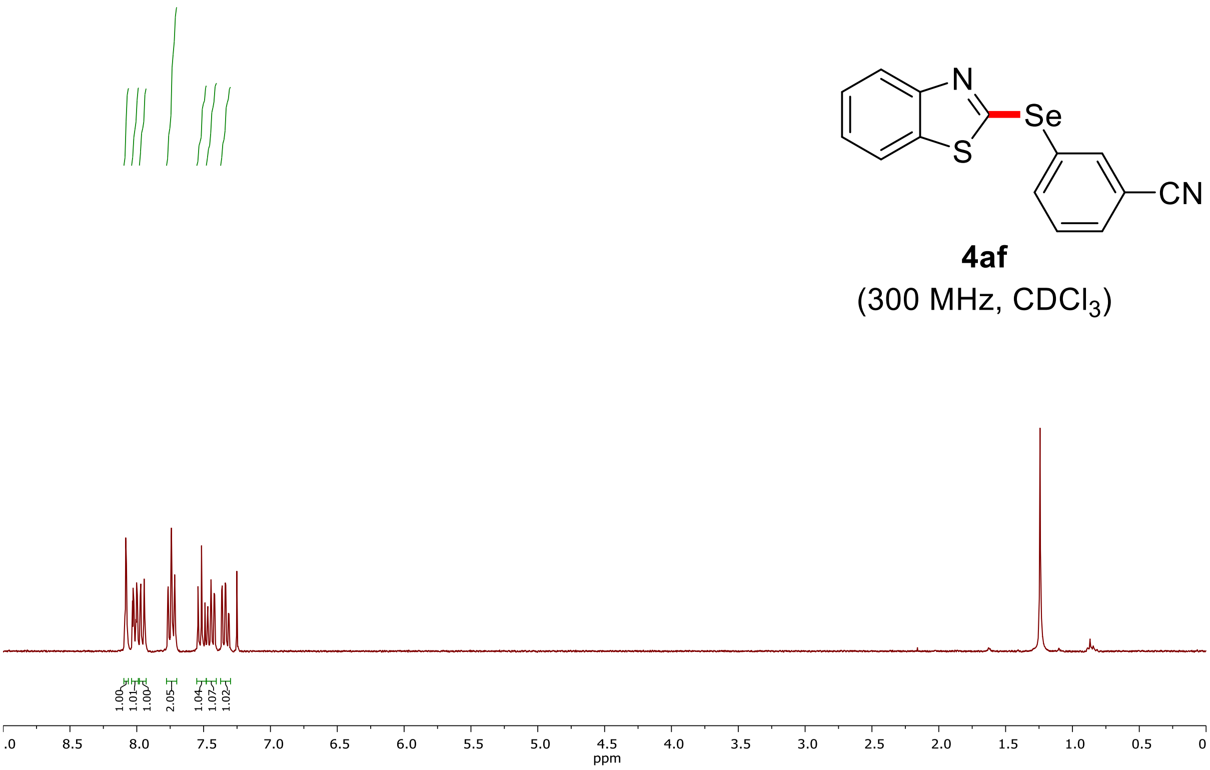
4ac

(126 MHz, $CDCl_3$)

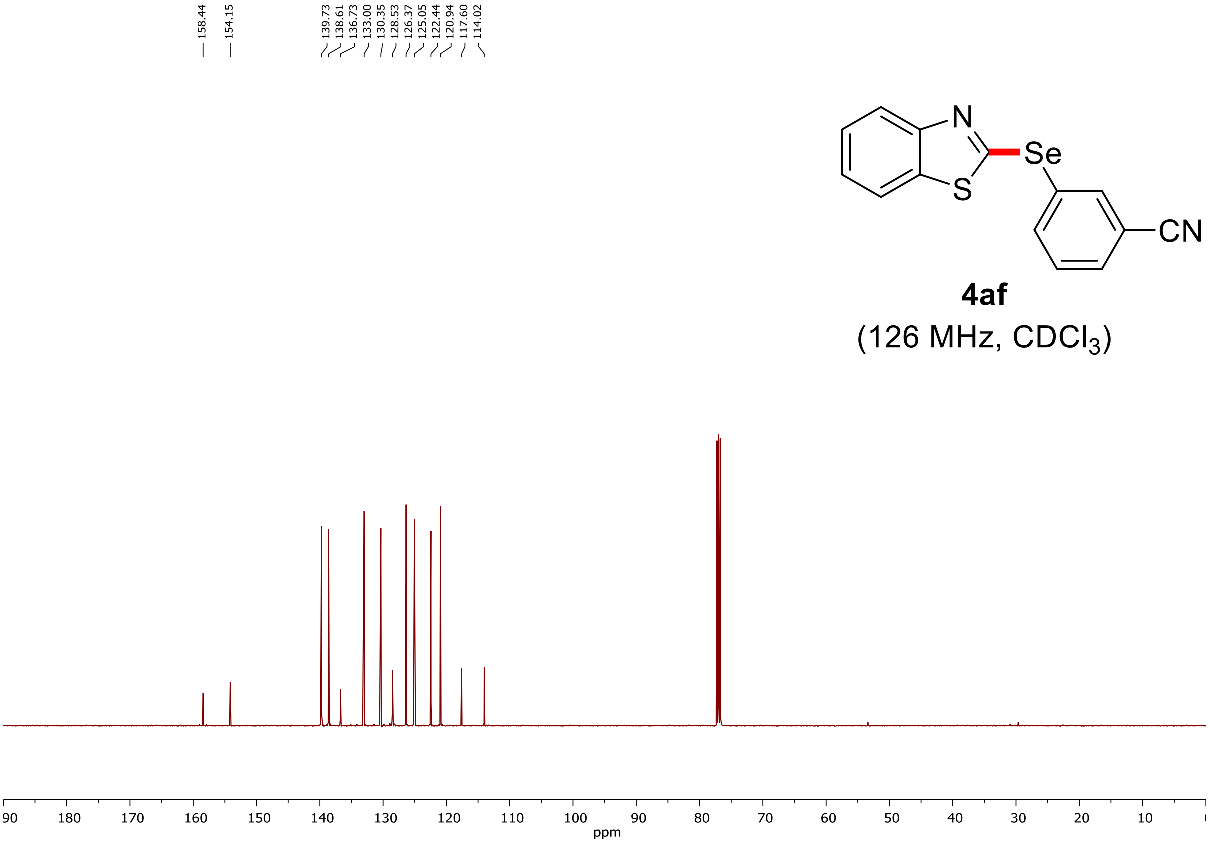


4ac

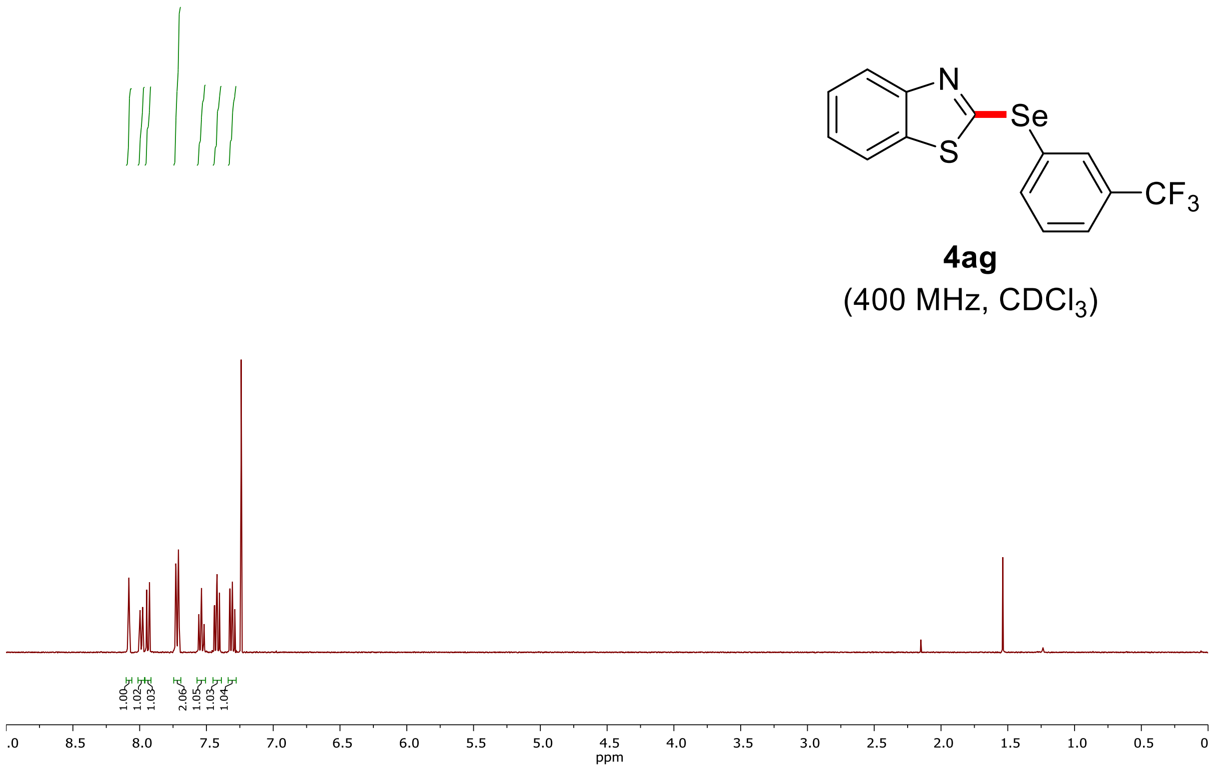
(471 MHz, $CDCl_3$)



4af
(300 MHz, $CDCl_3$)

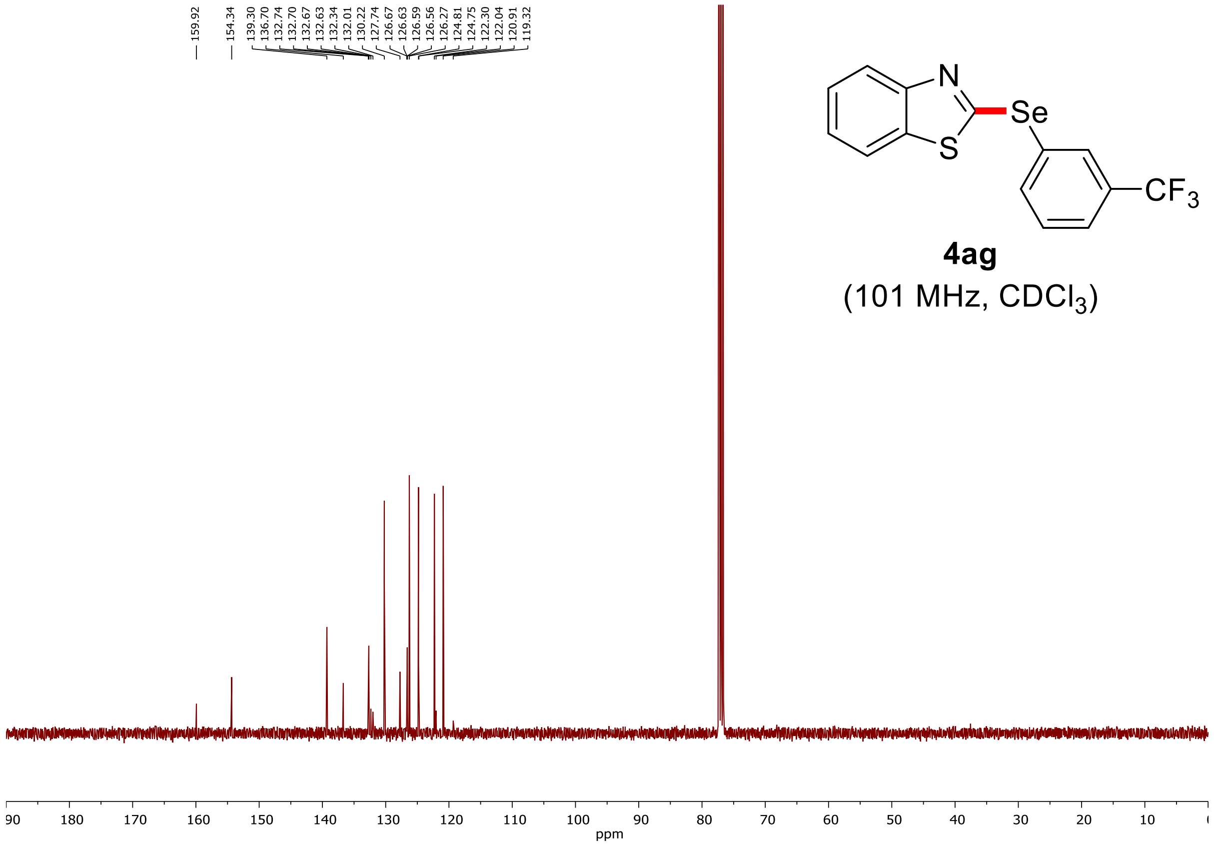


4af
(126 MHz, $CDCl_3$)



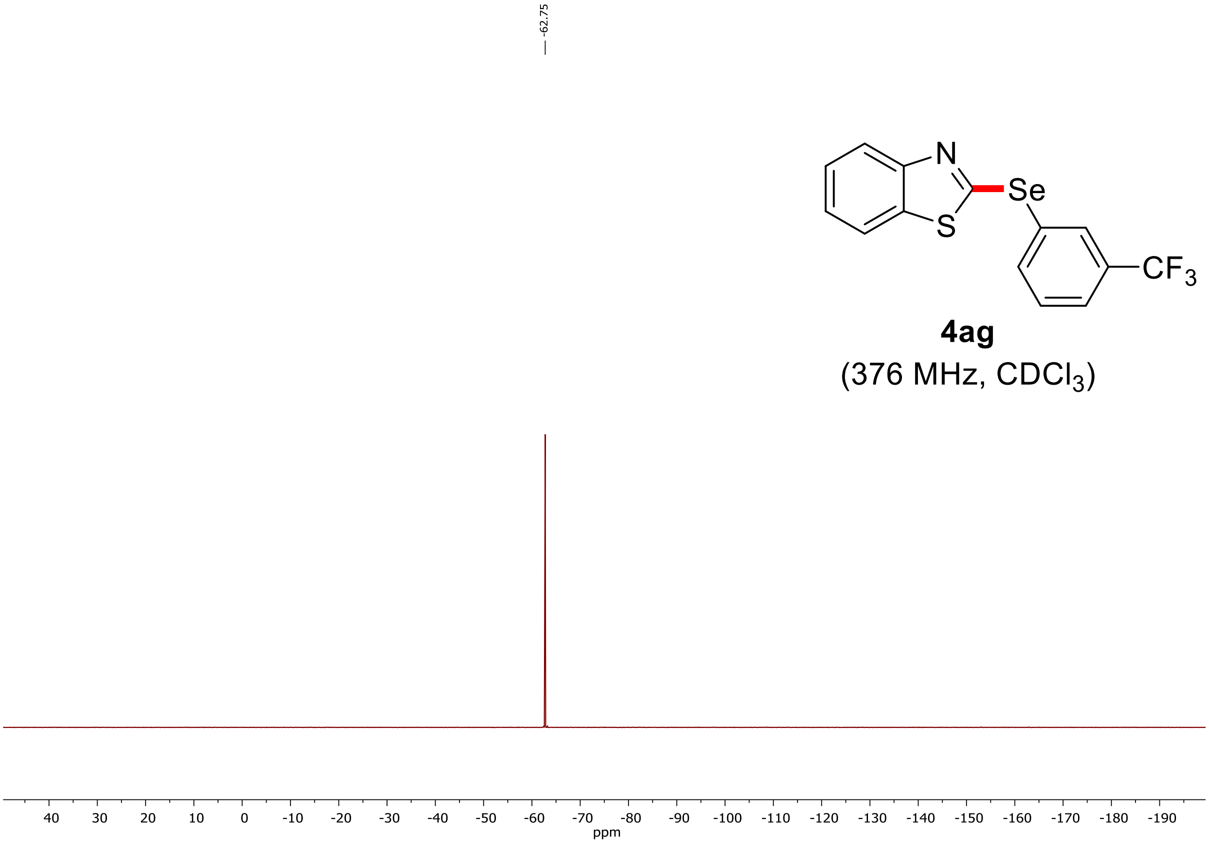
4ag

(400 MHz, CDCl$_3$)



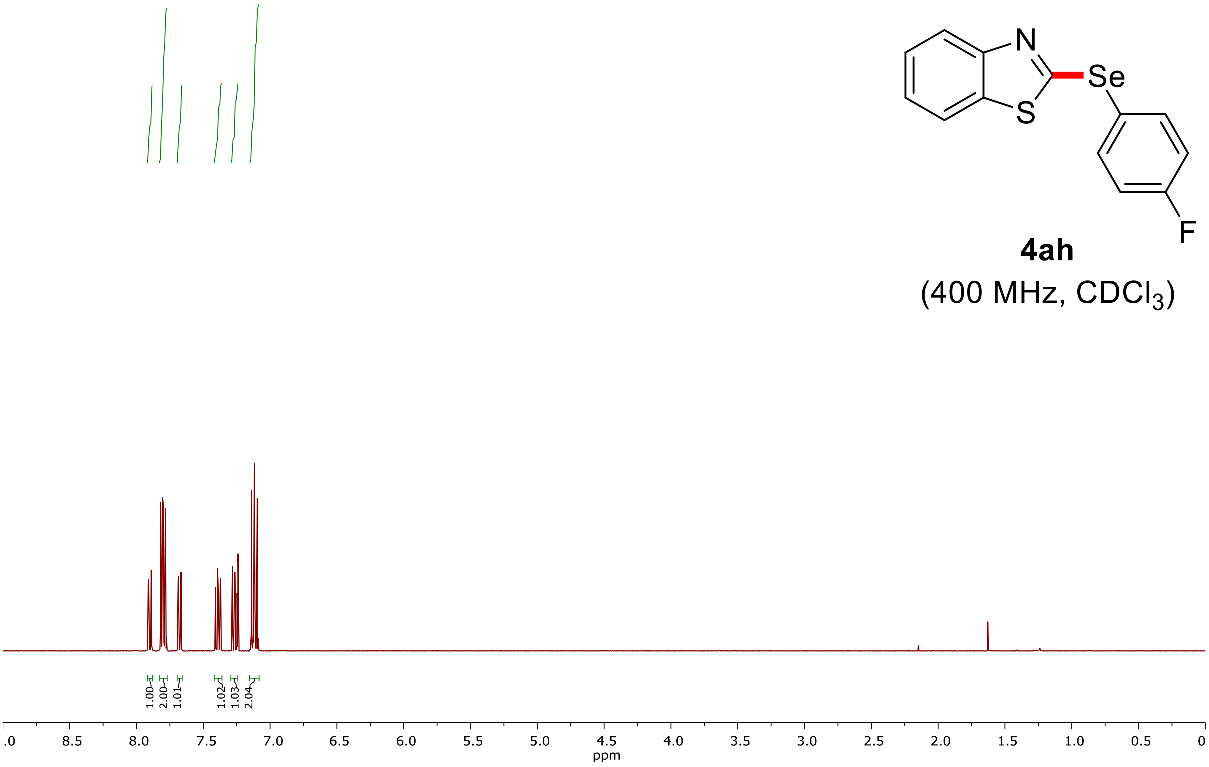
4ag

(101 MHz, CDCl$_3$)



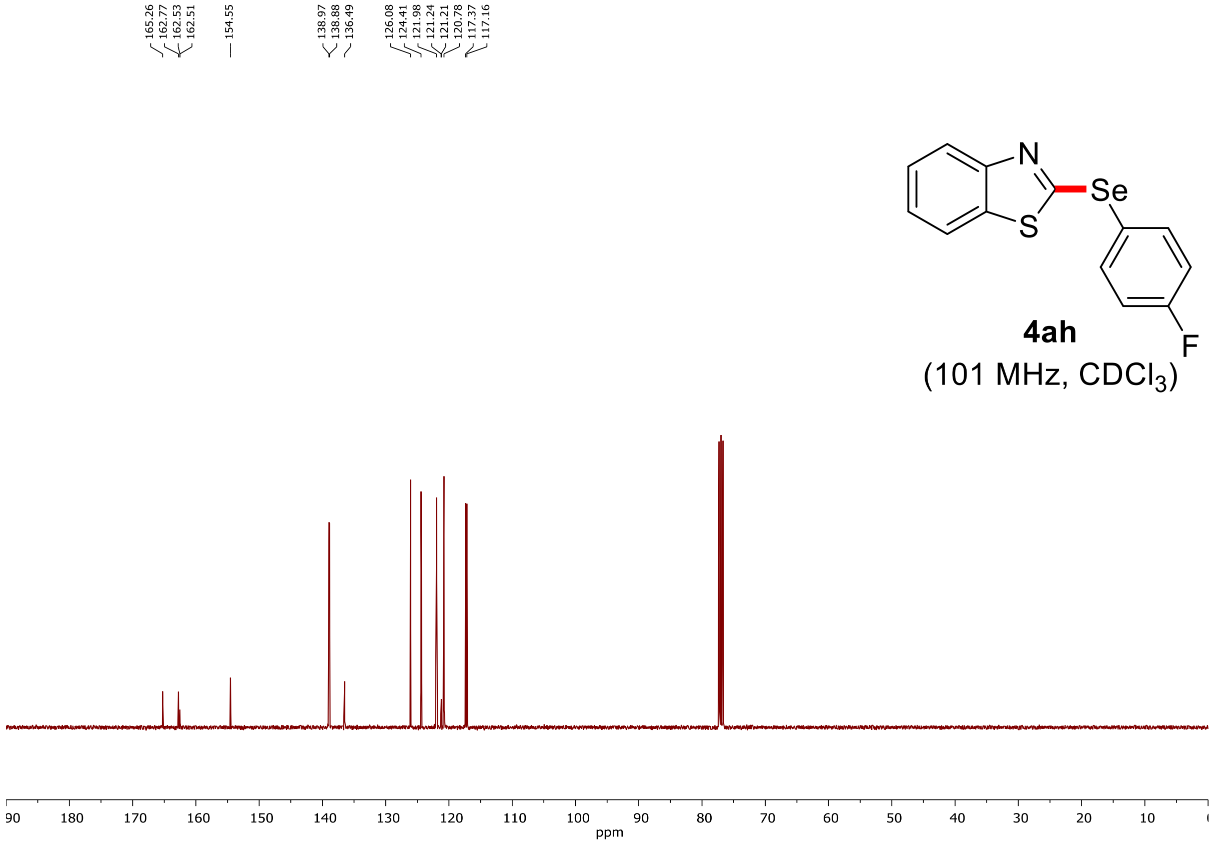
4ag

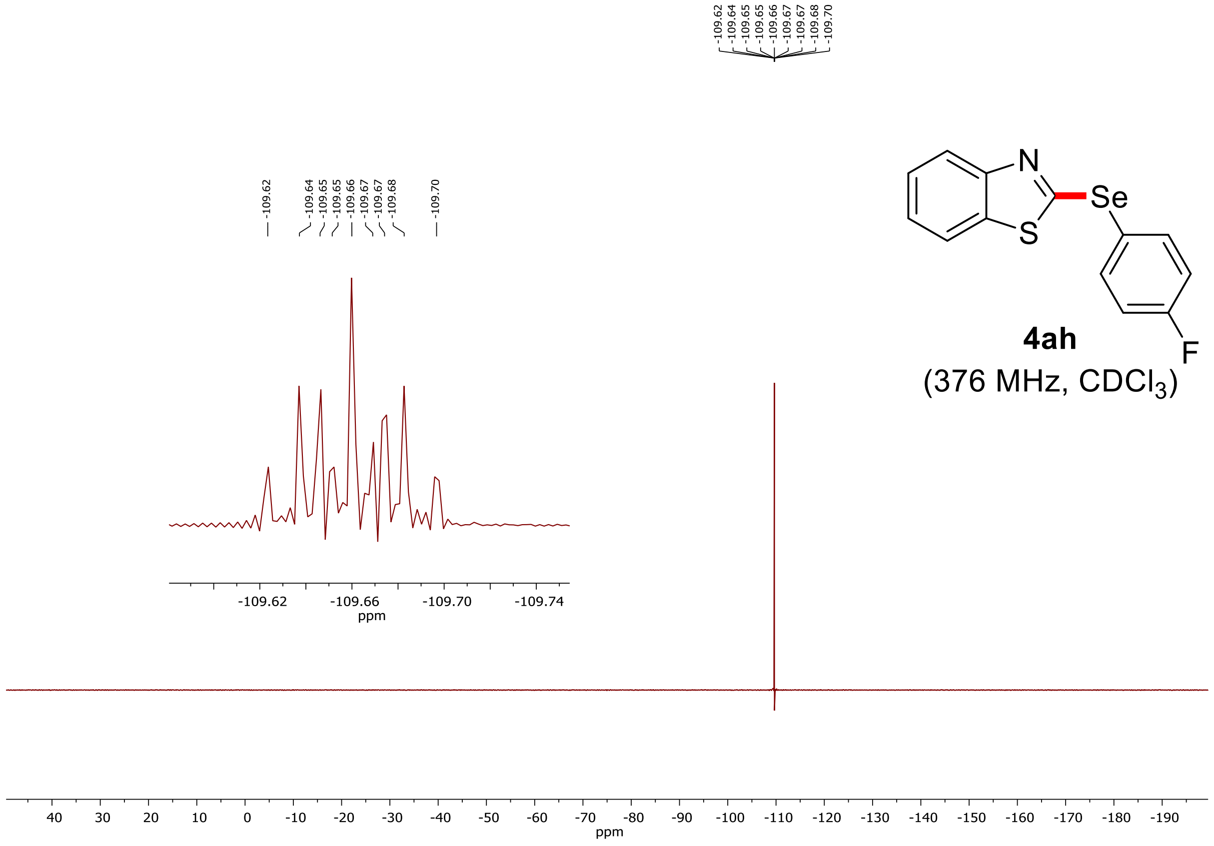
(376 MHz, $CDCl_3$)

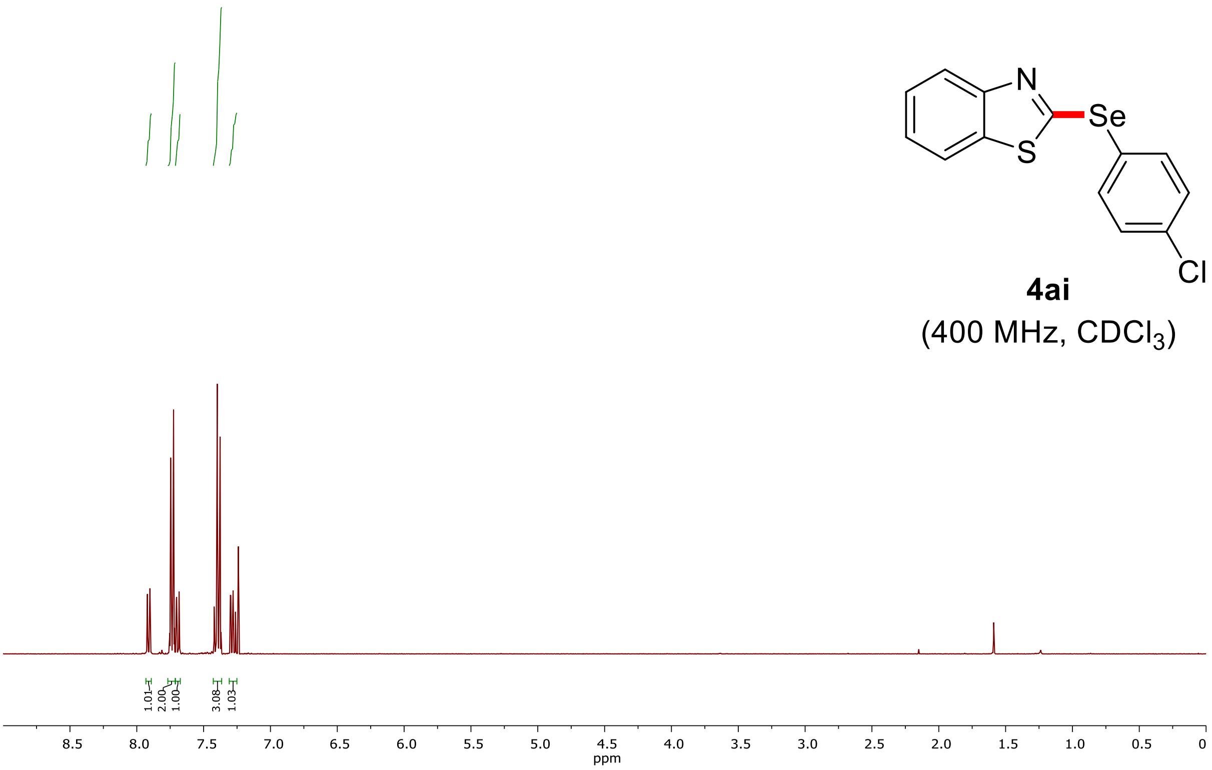


4ah

(400 MHz, $CDCl_3$)

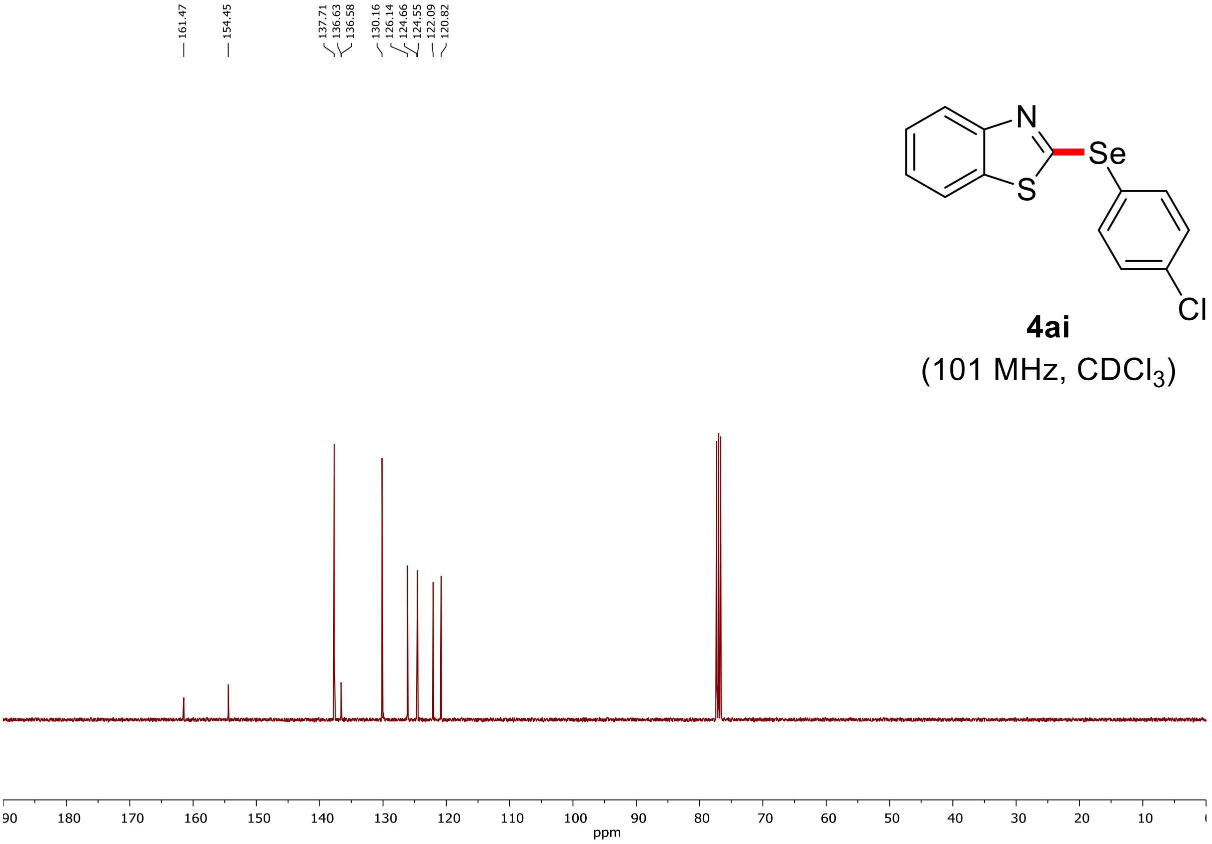

165.26
162.77
162.53
162.51
154.55
138.97
138.88
136.49
126.08
124.41
121.98
121.24
121.21
120.78
117.37
117.16
N
Se
S
F
4ah
(101 MHz, CDCl$_3$)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-109.62
-109.64
-109.65
-109.65
-109.66
-109.67
-109.67
-109.68
-109.70
N
Se
S
F
4ah
(376 MHz, CDCl$_3$)
-109.62
-109.64
-109.65
-109.65
-109.66
-109.67
-109.67
-109.68
-109.70
-109.62
-109.66
-109.70
-109.74
ppm
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm



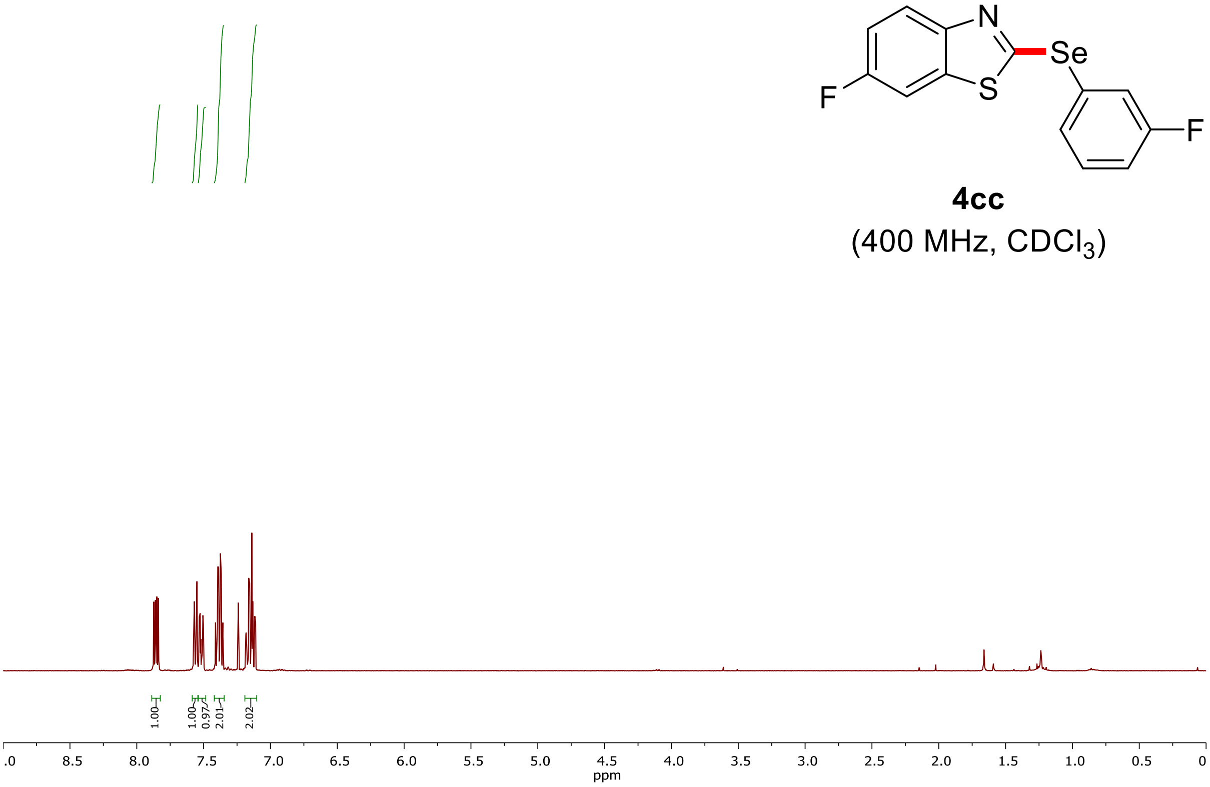
4ai

(400 MHz, $CDCl_3$)



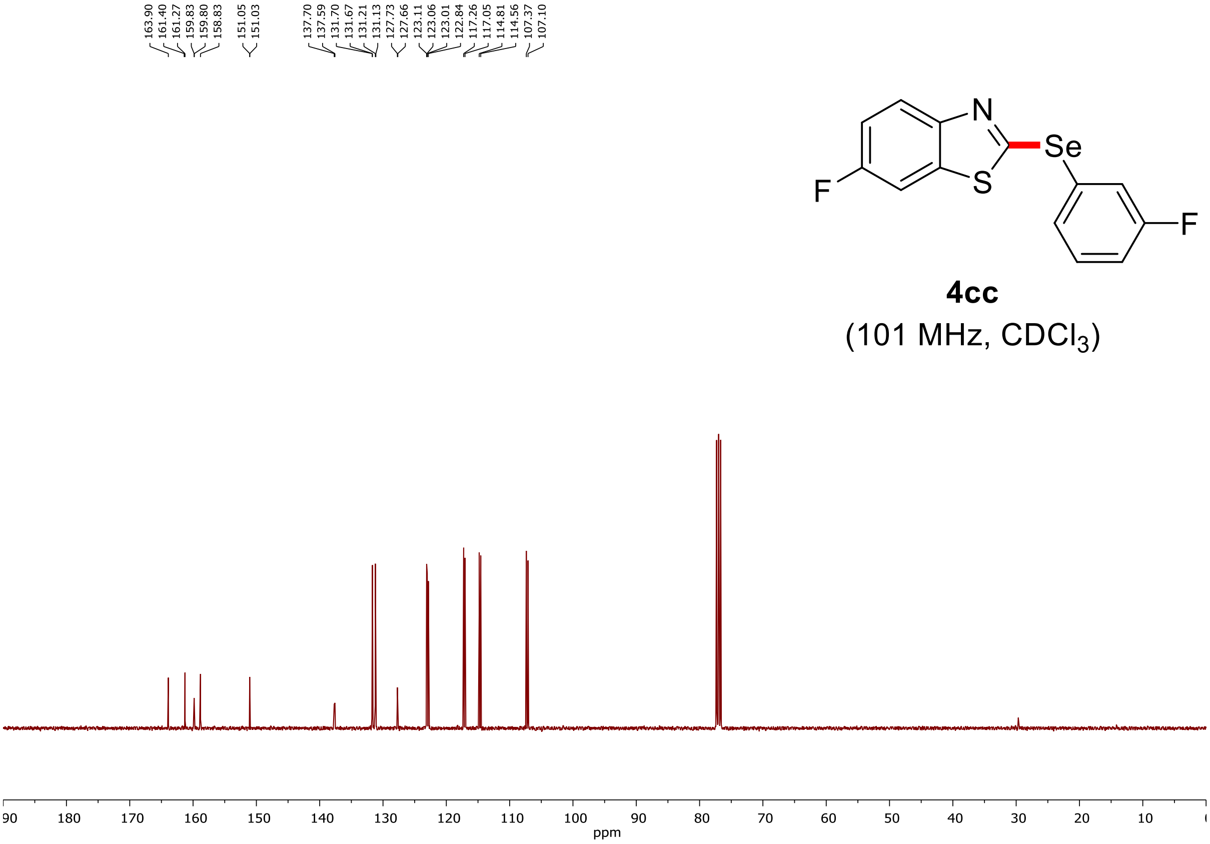
4ai

(101 MHz, $CDCl_3$)



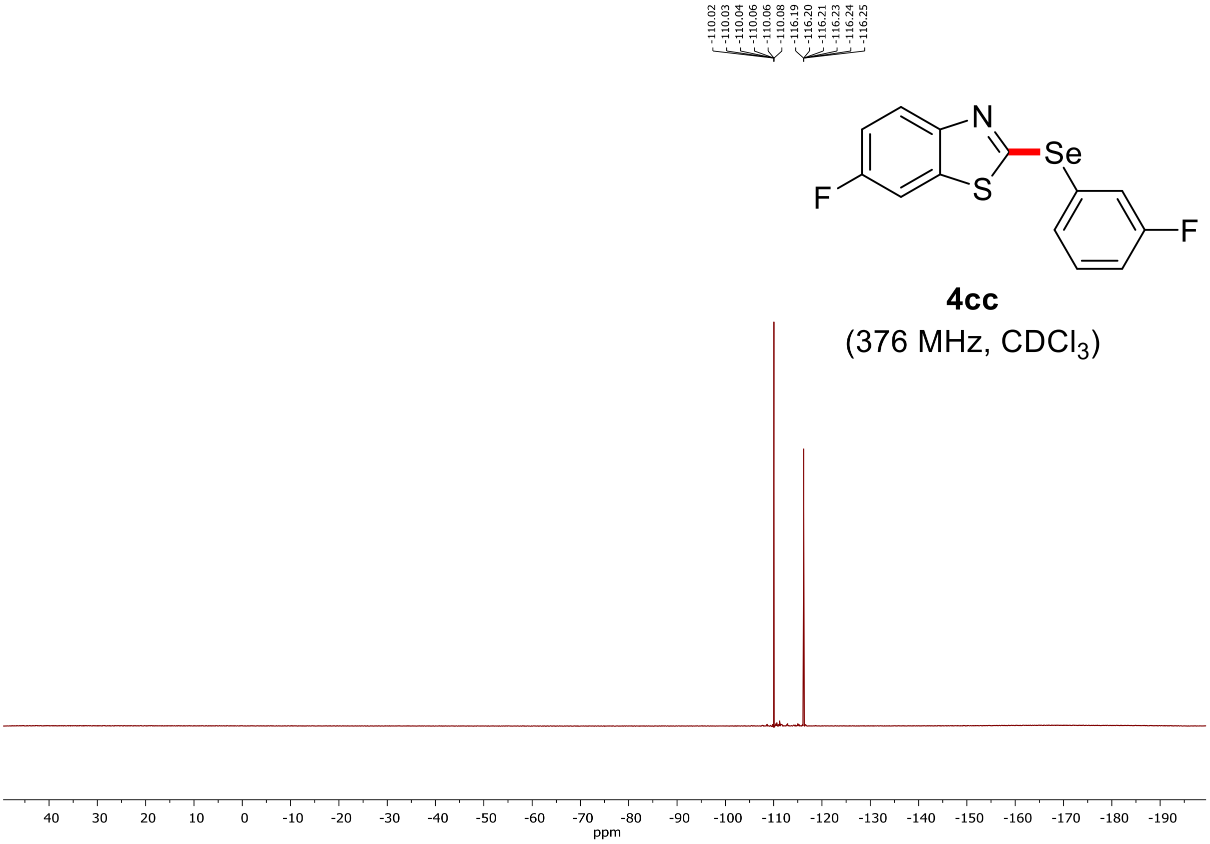
4cc

(400 MHz, CDCl$_3$)

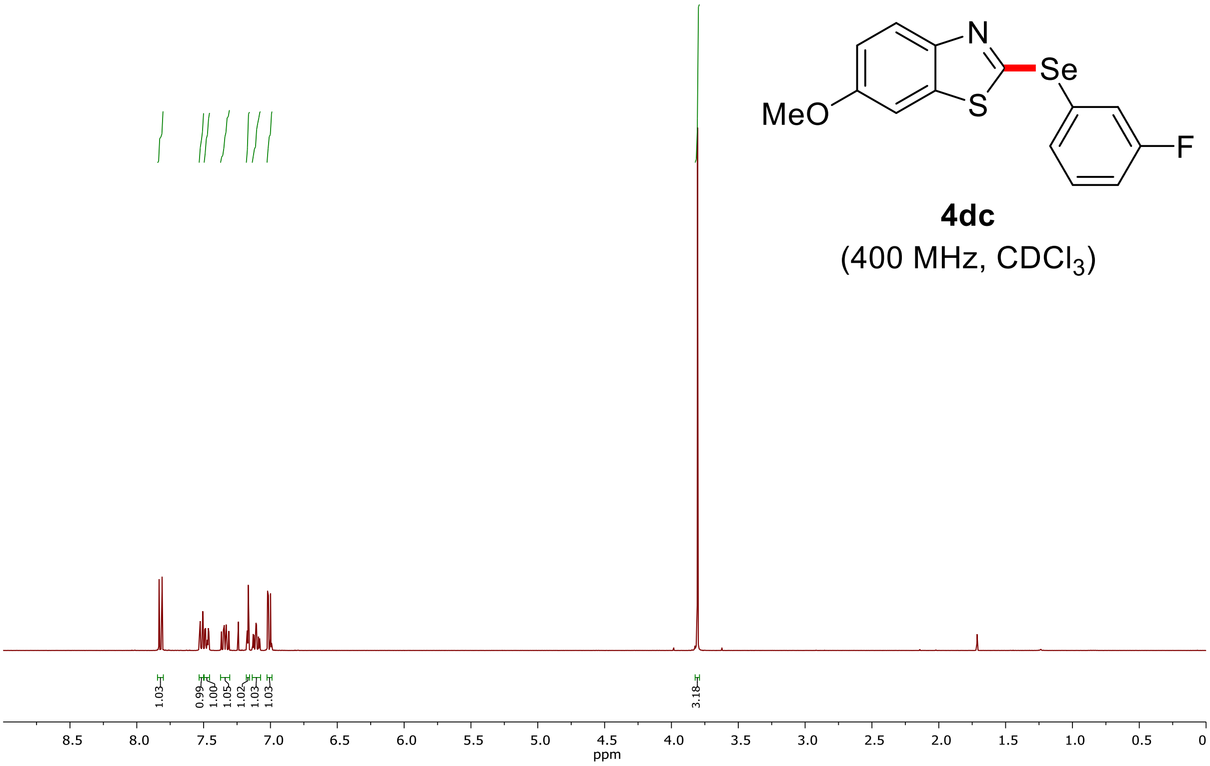


4cc

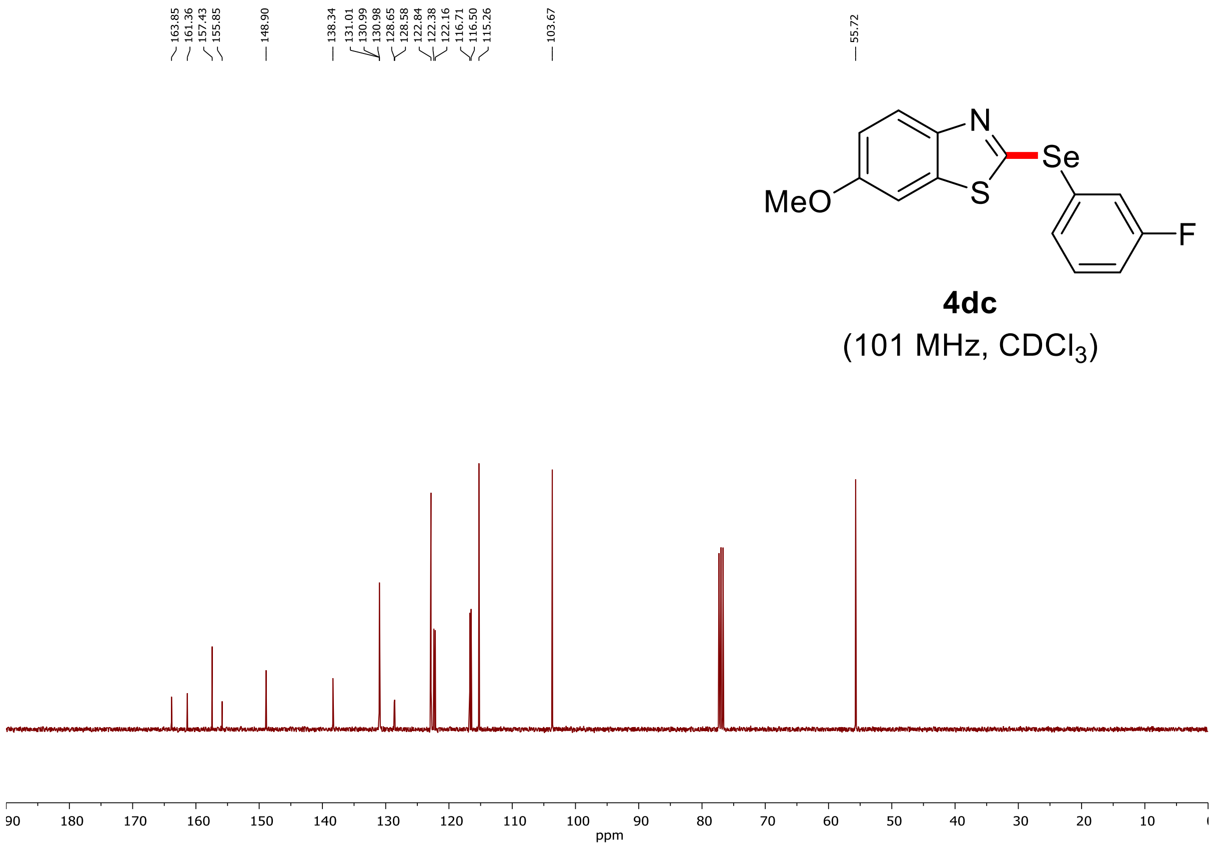
(101 MHz, CDCl$_3$)

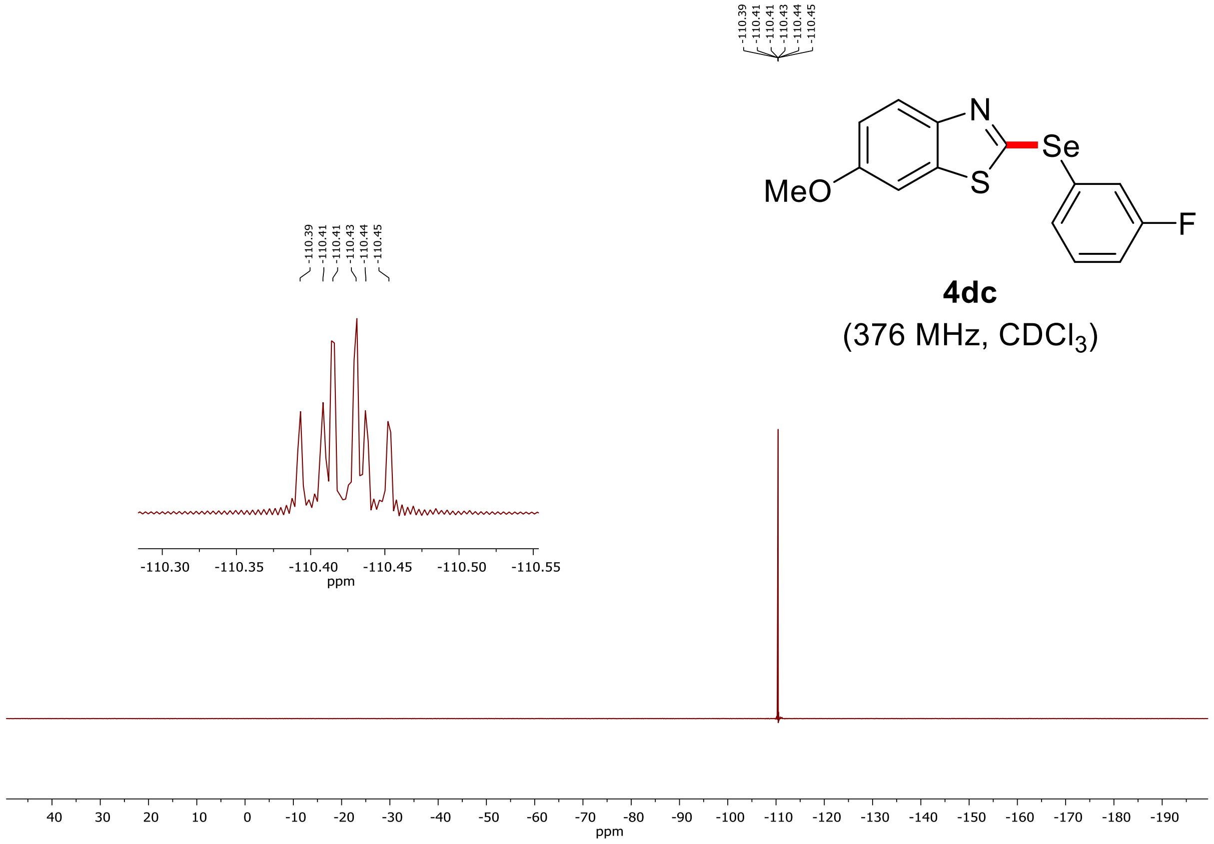


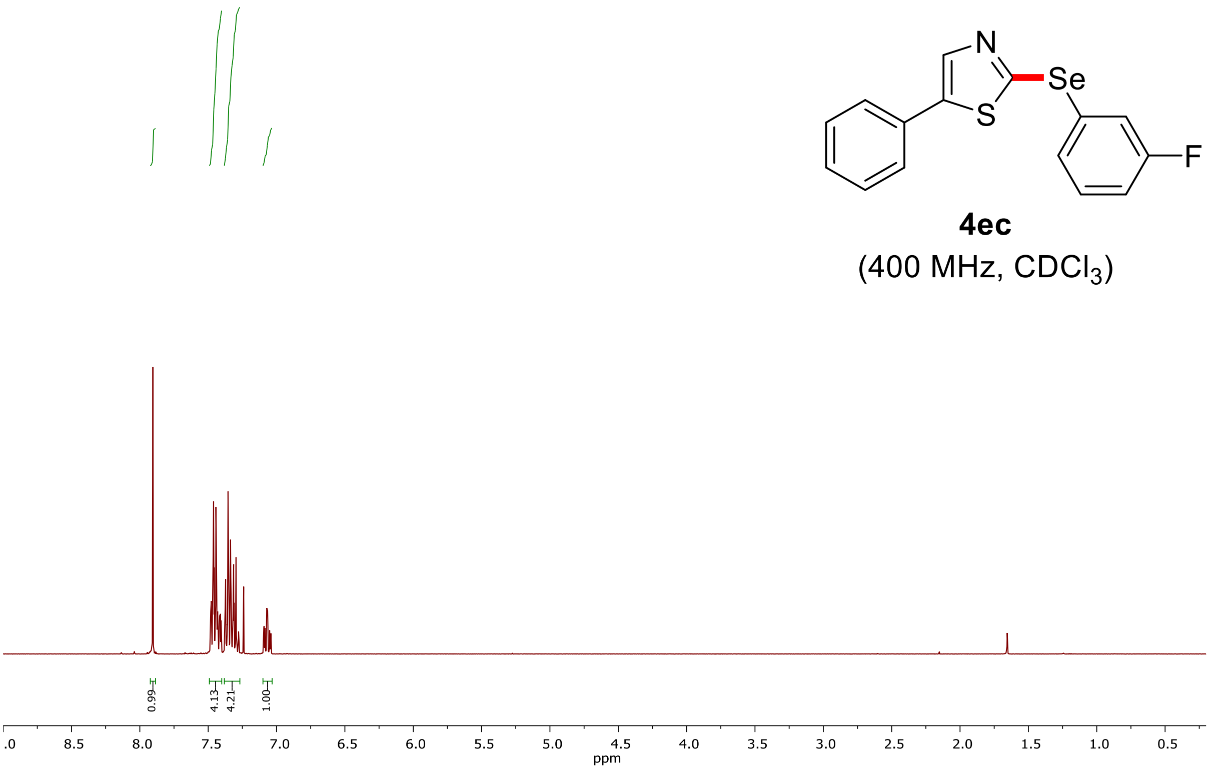
4cc
(376 MHz, $CDCl_3$)



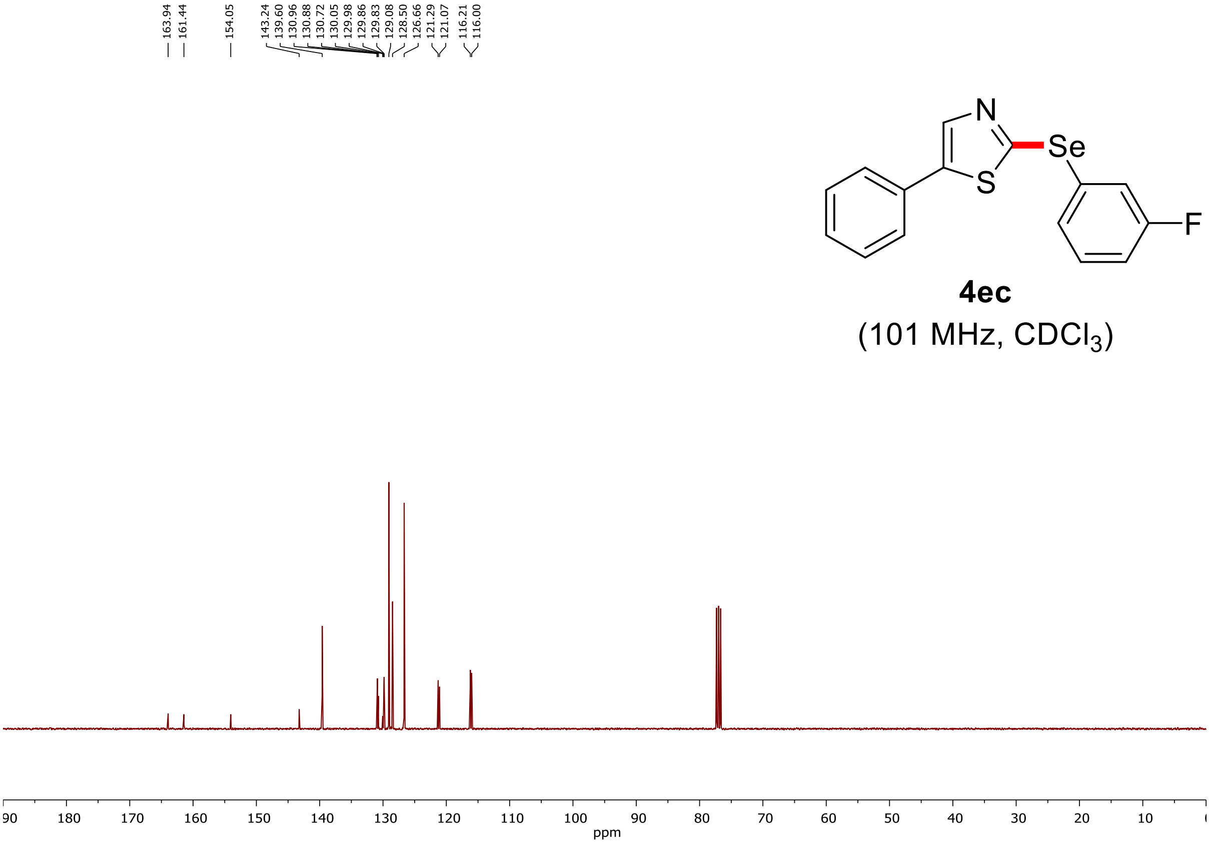
4dc
(400 MHz, $CDCl_3$)


163.85
161.36
157.43
155.85
148.90
138.34
131.01
130.99
130.98
128.65
128.58
122.84
122.38
122.16
116.71
116.50
115.26
103.67
55.72
N
Se
MeO
S
F
4dc
(101 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

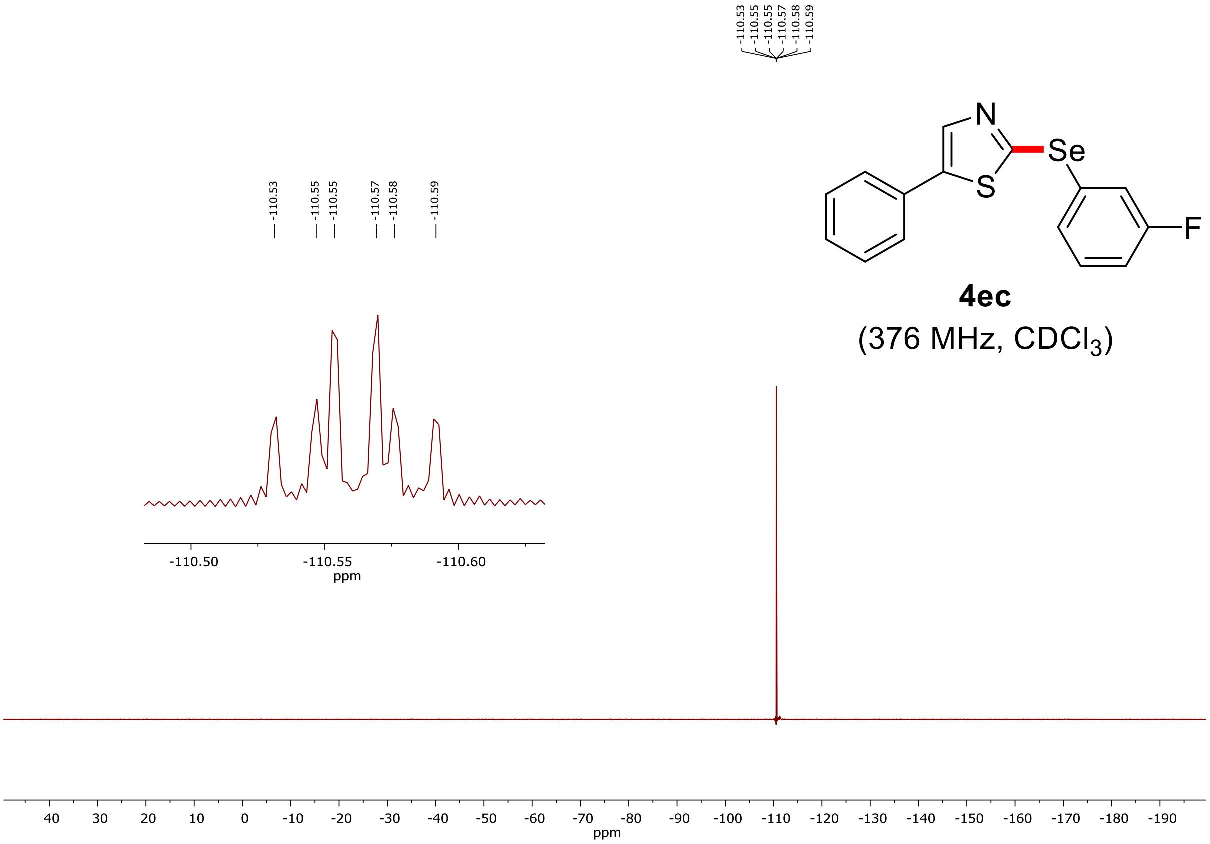

-110.39
-110.41
-110.41
-110.43
-110.44
-110.45
N
Se
MeO
S
F
4dc
(376 MHz, CDCl3)
-110.39
-110.41
-110.41
-110.43
-110.44
-110.45
-110.30
-110.35
-110.40
-110.45
-110.50
-110.55
ppm
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm



4ec
(400 MHz, $CDCl_3$)

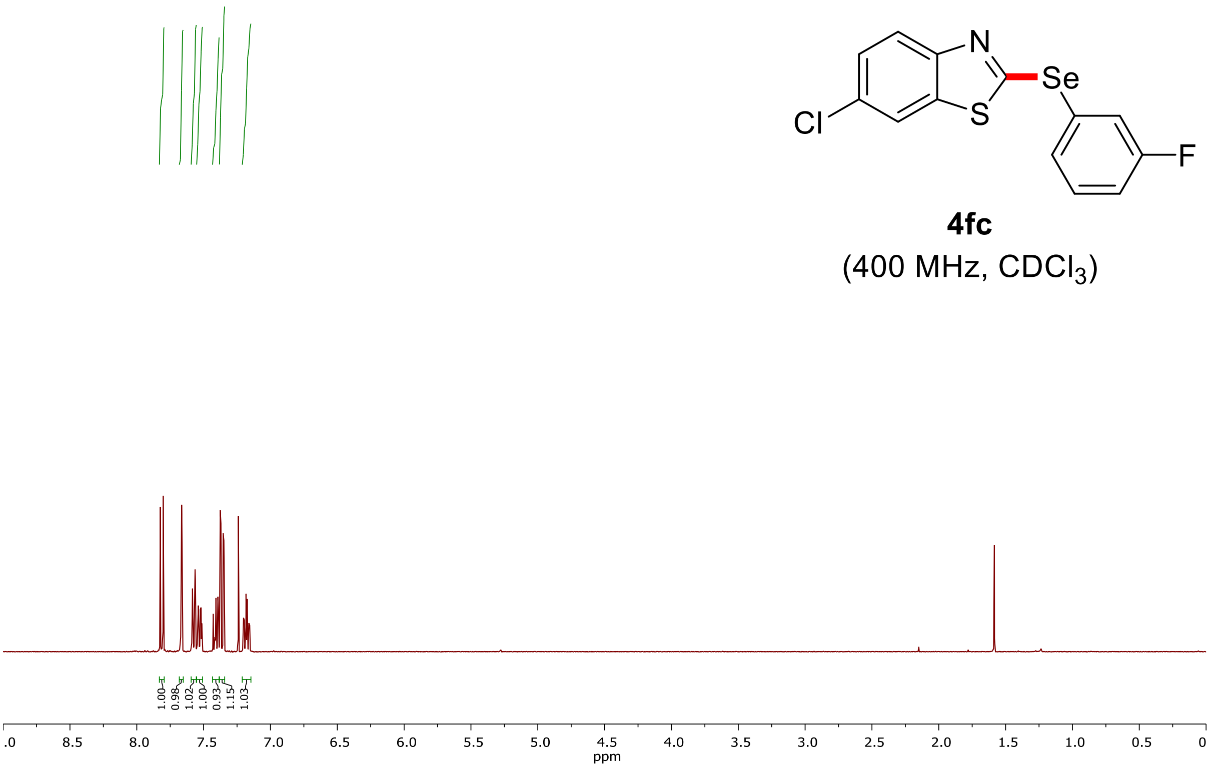


4ec
(101 MHz, $CDCl_3$)



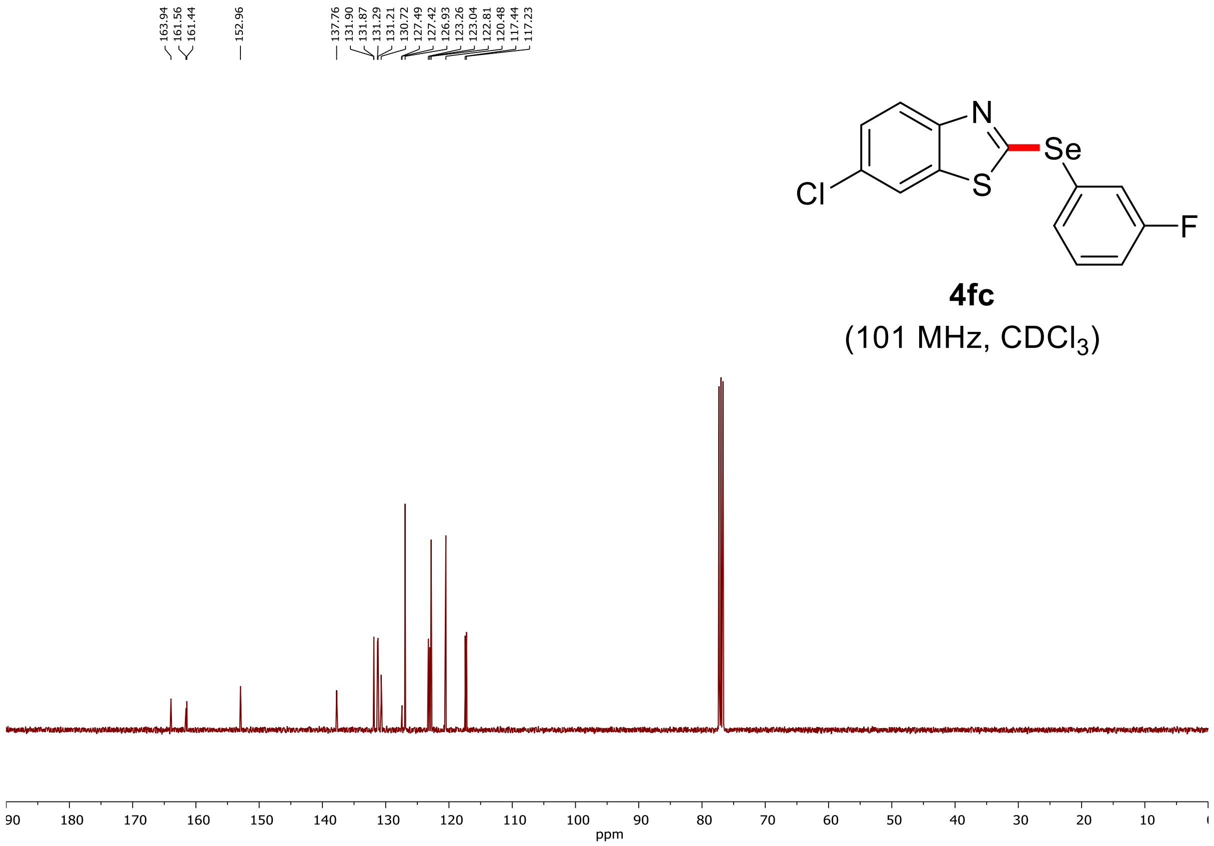
4ec

(376 MHz, $CDCl_3$)

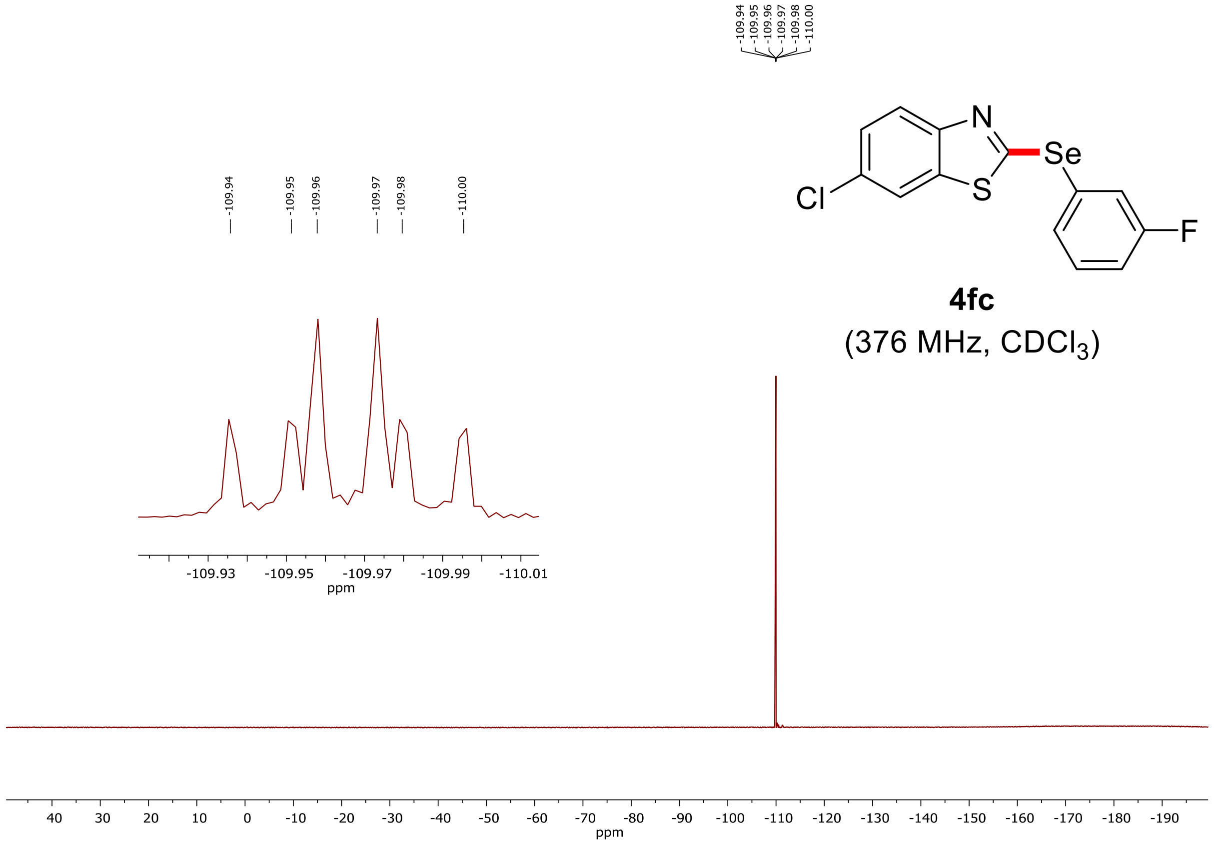


4fc

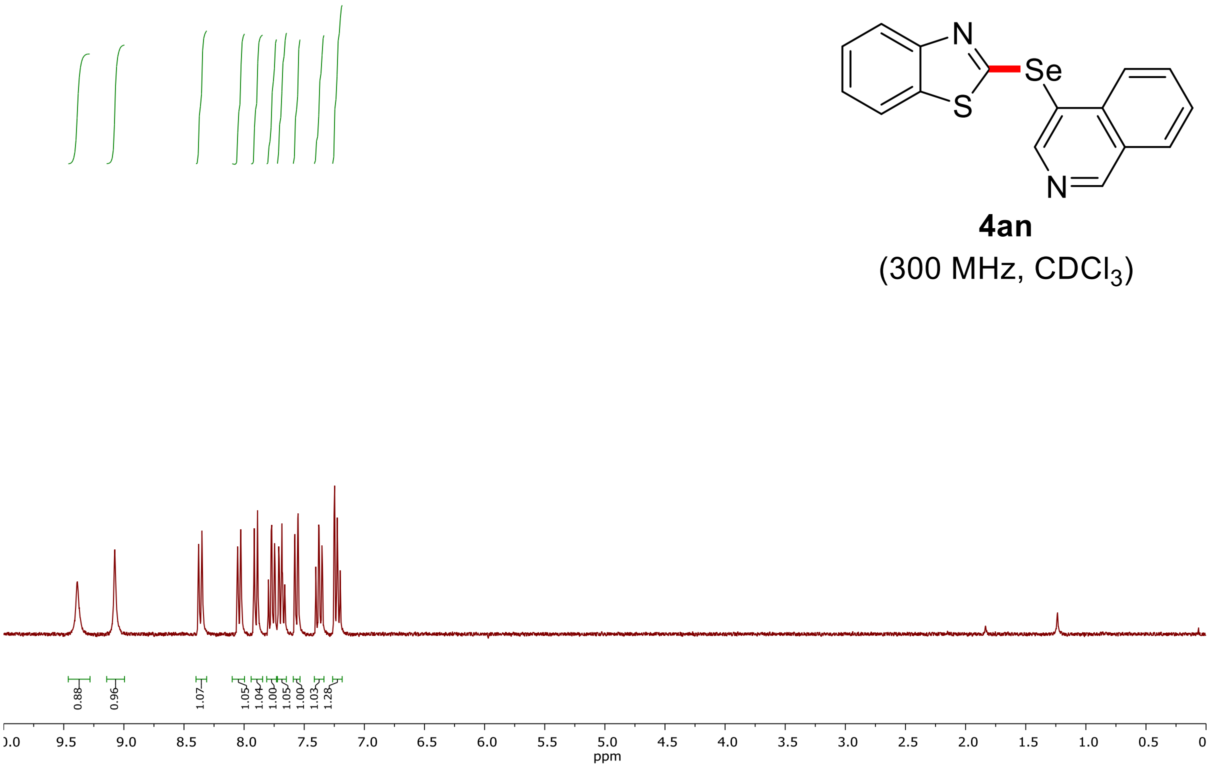
(400 MHz, $CDCl_3$)



4fc
(101 MHz, CDCl$_3$)

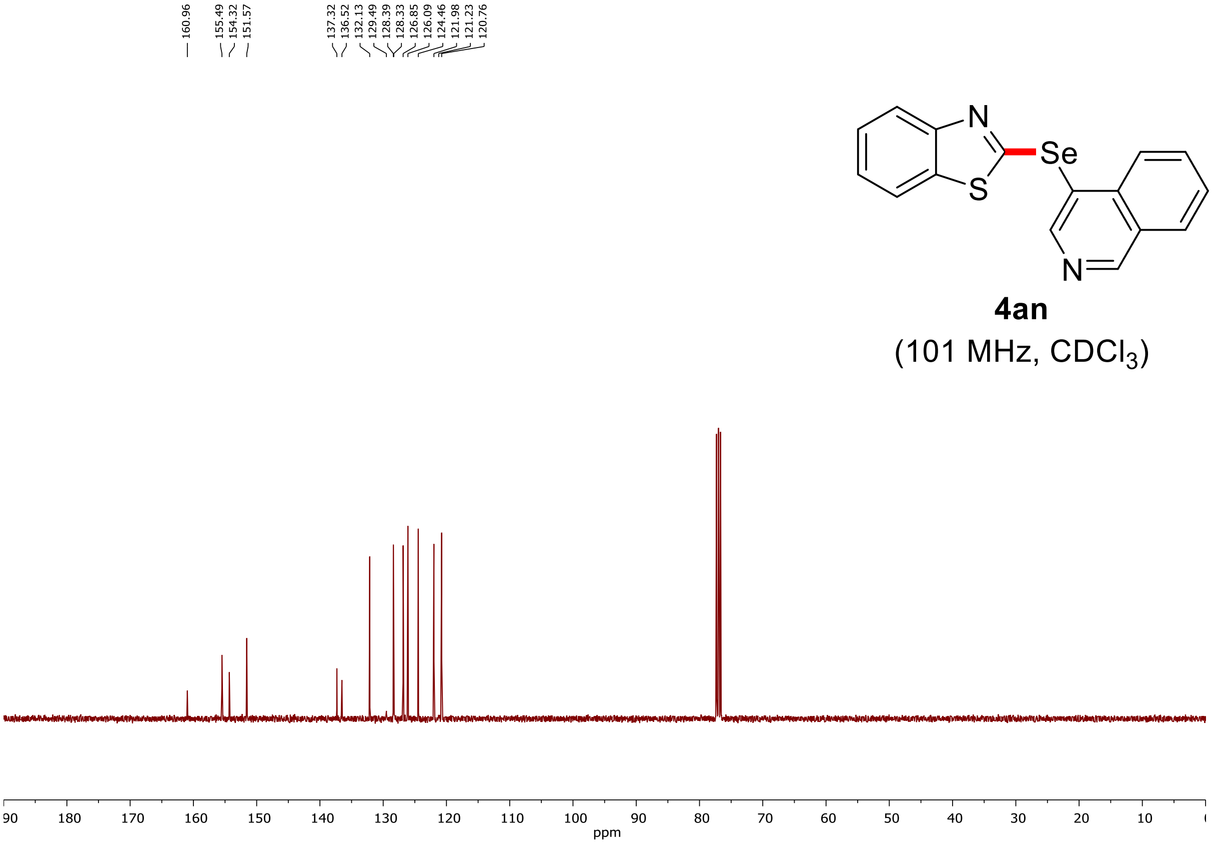


4fc
(376 MHz, CDCl$_3$)



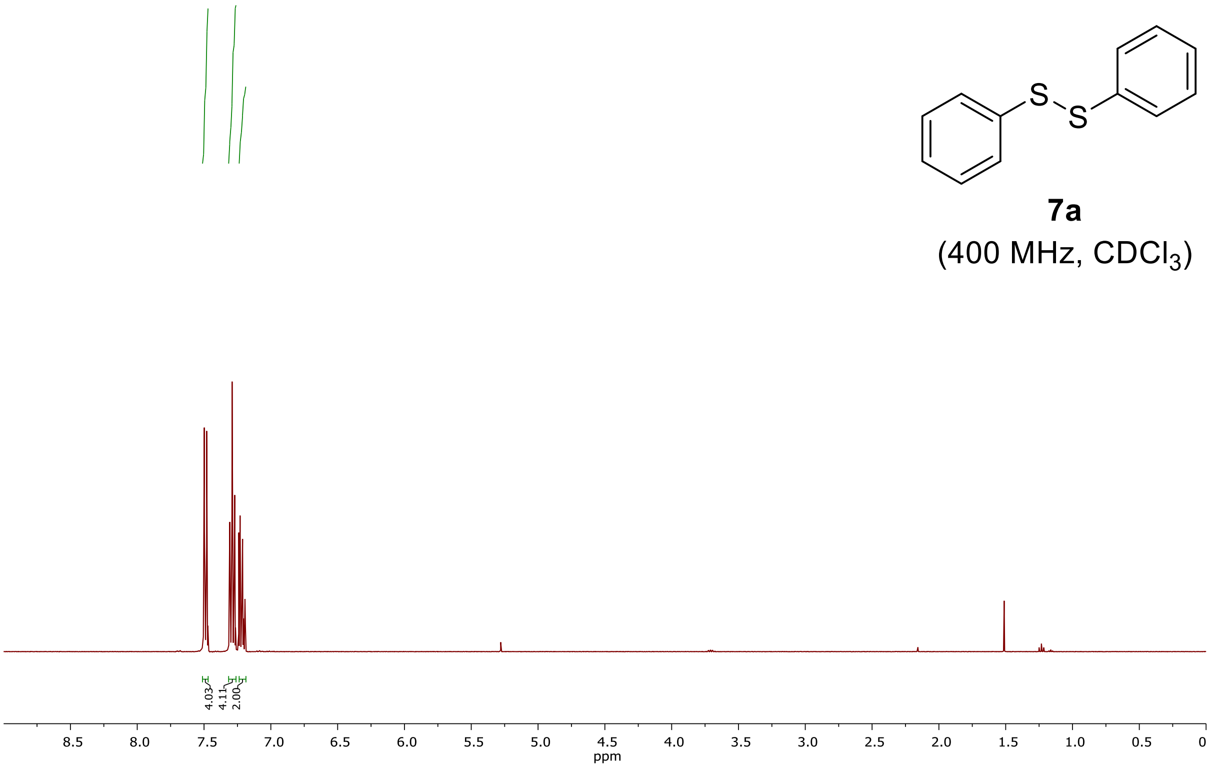
4an

(300 MHz, $CDCl_3$)

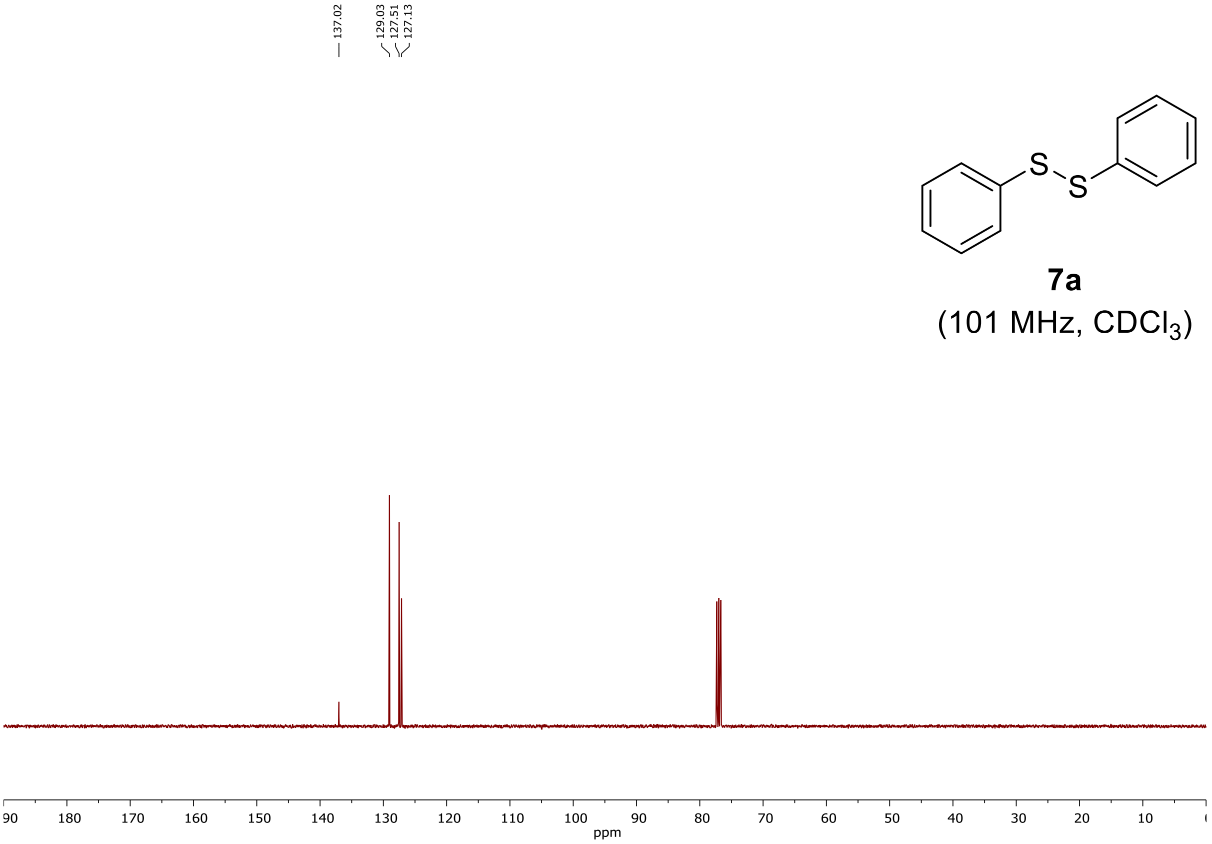


4an

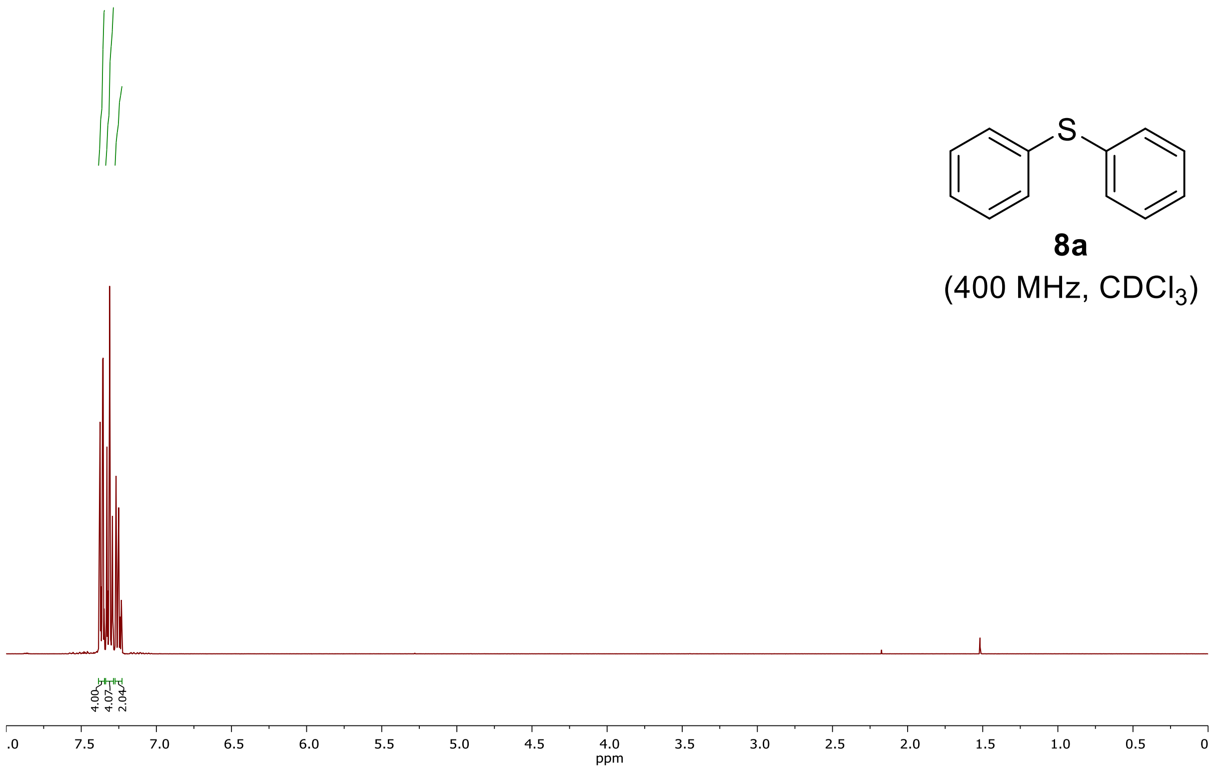
(101 MHz, $CDCl_3$)

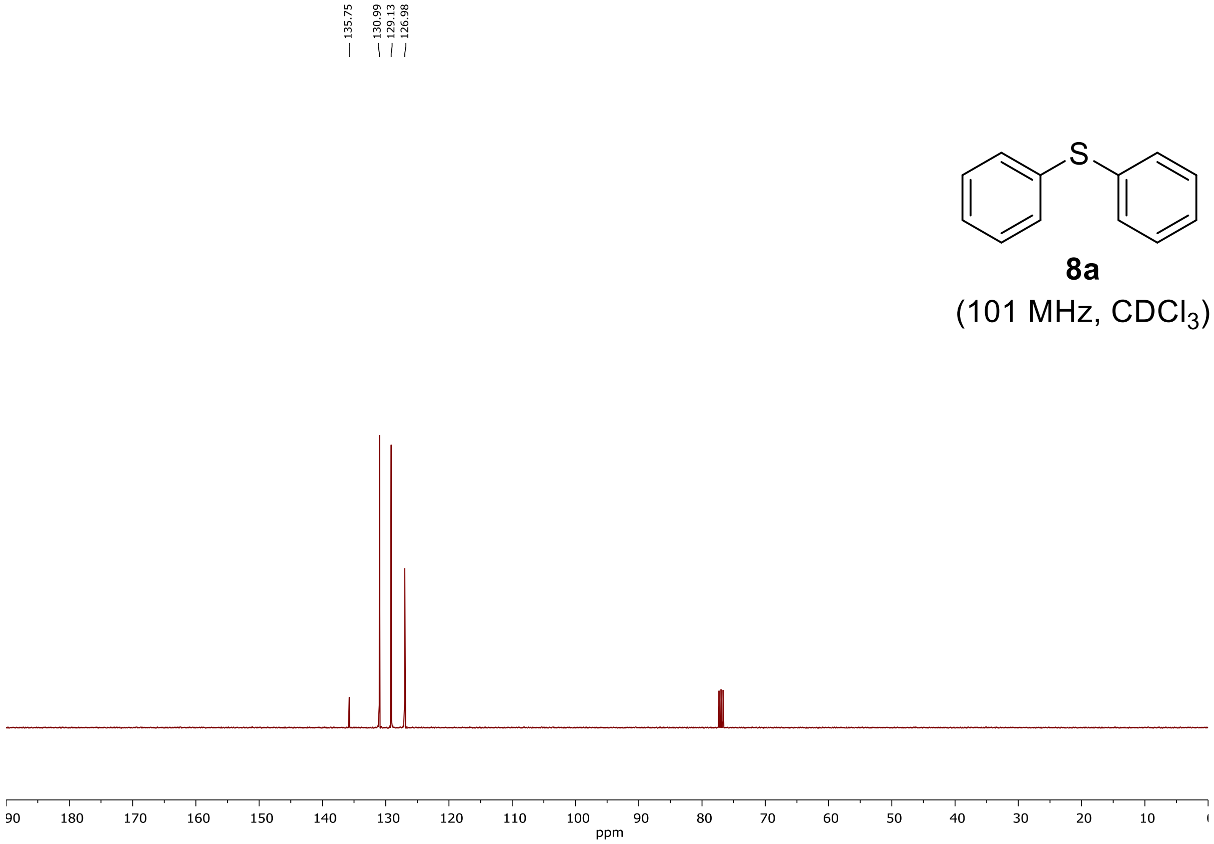


7a
(400 MHz, $CDCl_3$)

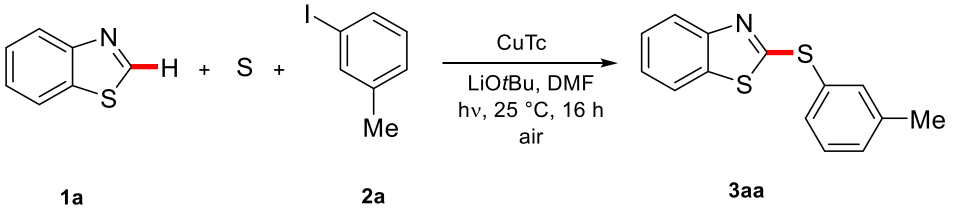


7a
(101 MHz, $CDCl_3$)


8a
(400 MHz, CDCl$_3$)
4.00
4.07
2.04
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

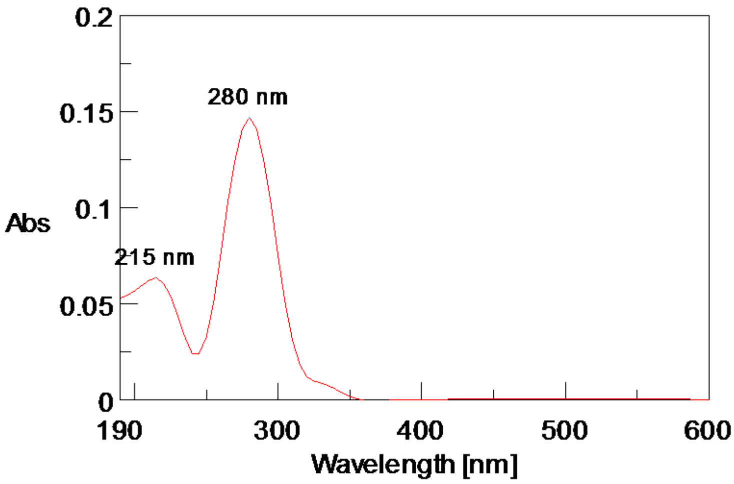

135.75
130.99
129.13
126.98
8a
(101 MHz, CDCl$_3$)
90
180
170
160
150
140
130
120
110
100
90
ppm
80
70
60
50
40
30
20
10

UV-visible absorption spectra

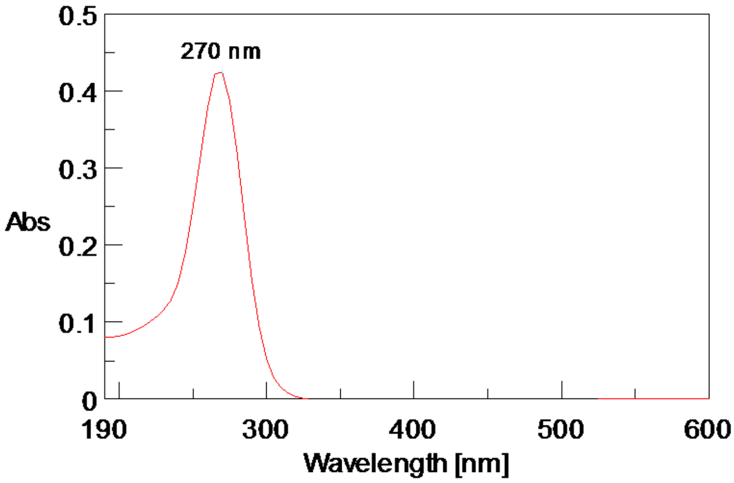


The UV-visible absorption spectra of reaction components and combination were measured in DMF (1×10-5 M). The results showed that the reagents, catalyst and the reaction mixture are absorbing light under UV region which facilitate the Cu-catalyzed C–H chalcogenation process.

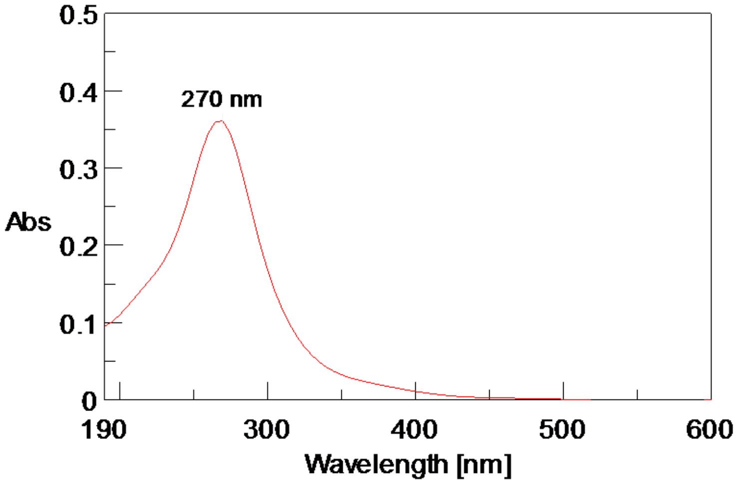
Benzothiazole (1a):



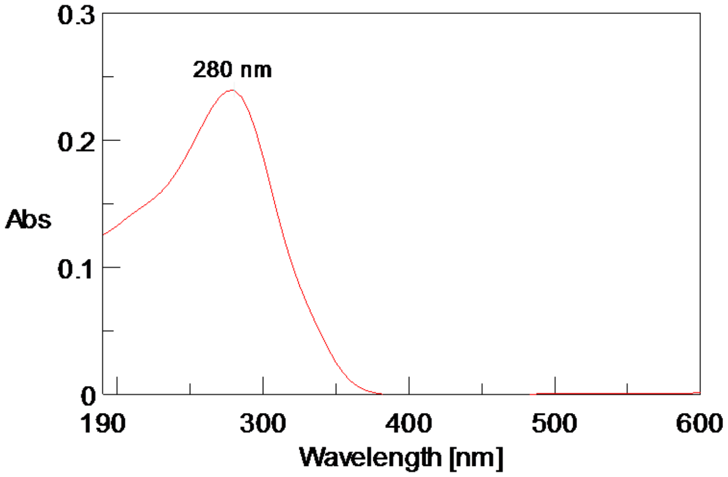
3-Iodotoluene (2a):



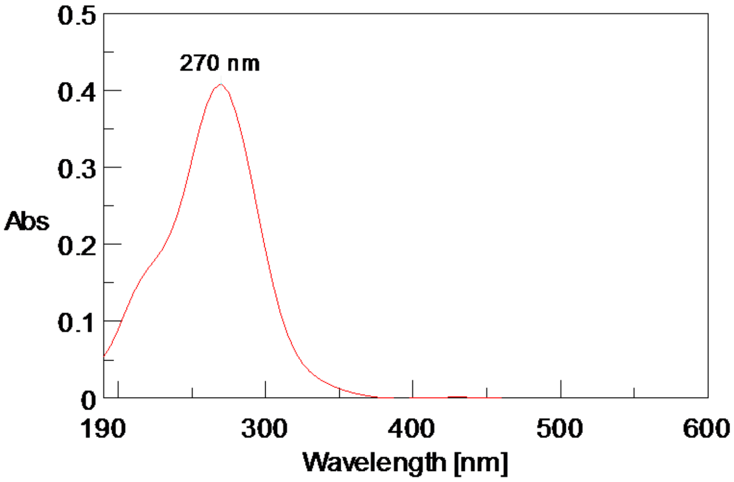
Copper(I)-thiophene-2-carboxylate (CuTc):



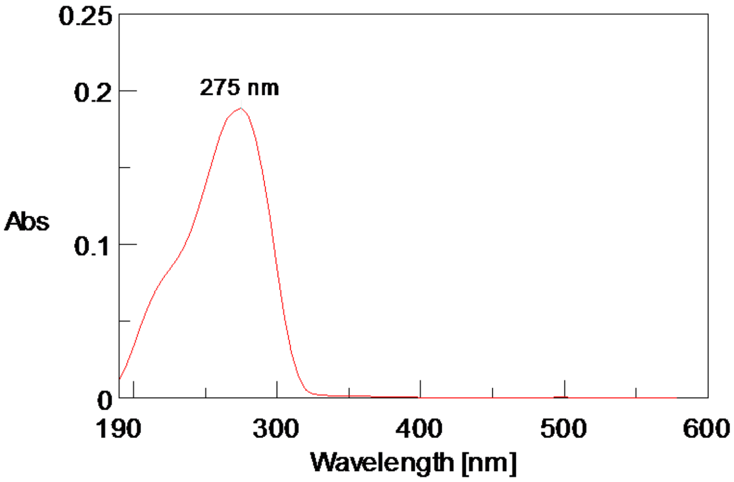
Product 3aa:



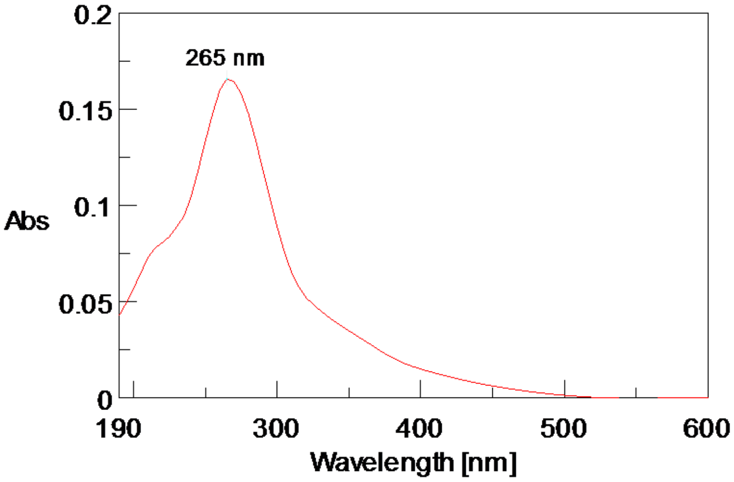
Mixture of 1a and CuTc:



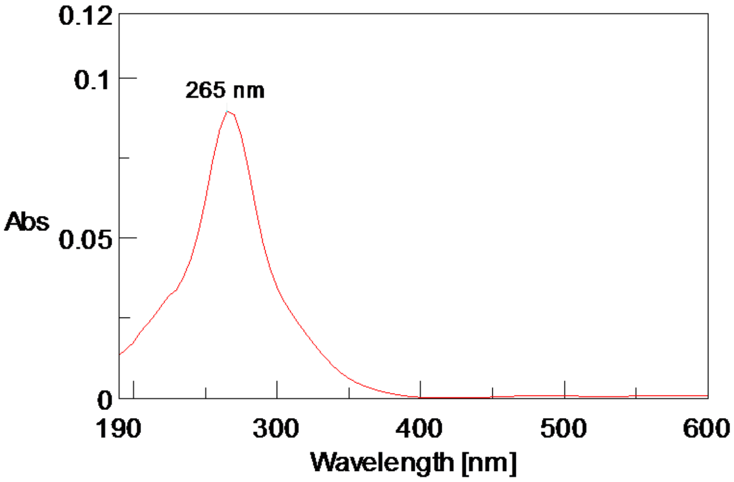
Mixture of 1a and LiO*t*Bu:



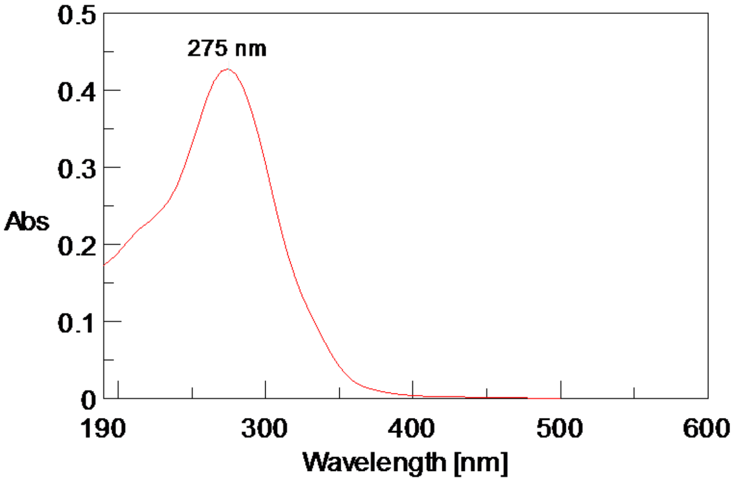
Mixture of 1a, LiO*t*Bu and CuTc:



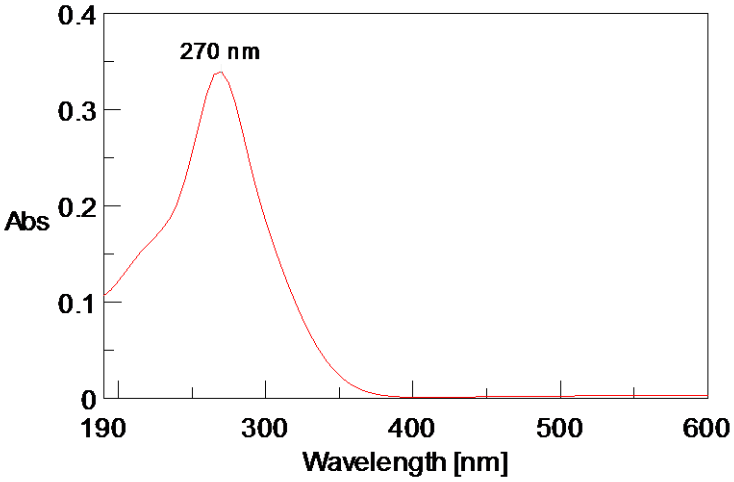
Mixture of 2a and CuTc:



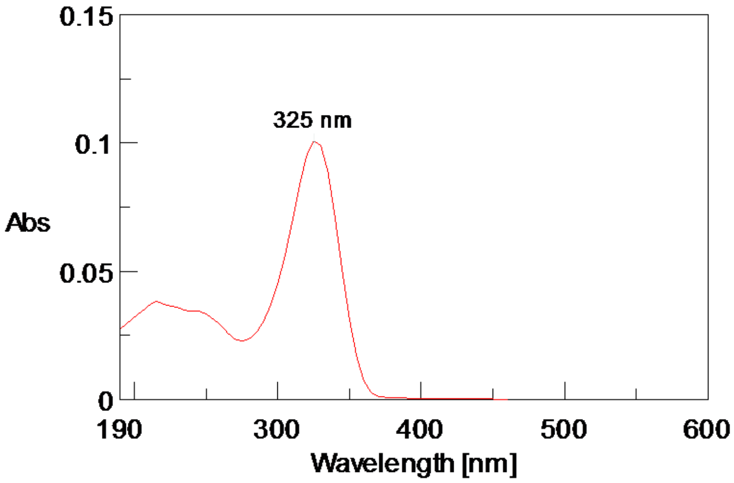
Mixture of 3aa and CuTc:



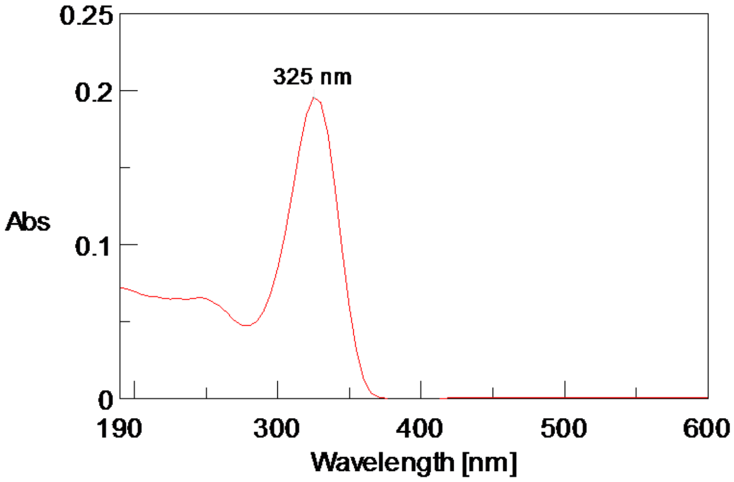
Diphenyl disulfide (7a):



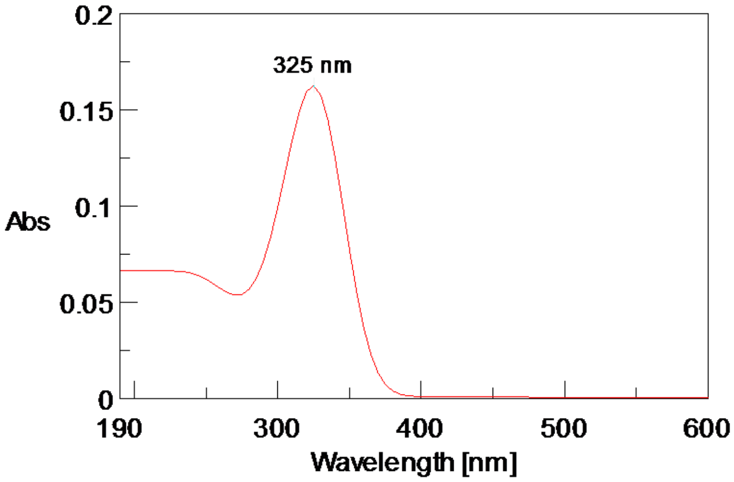
Reaction mixture for the synthesis of 3aa—Before light irradiation:



Reaction mixture for the synthesis of 3aa—after 1 h light irradiation:



Reaction mixture for the synthesis of 3aa—after 3 h light irradiation:



Reaction mixture for the synthesis of 3aa—after 16 h light irradiation: