Supporting Information

Selective C-H Sulfenylation of Thiazoles via Thiazol-2-yl-phosphonium Salts

You Zi, Konrad Wagner, Fritz Schömberg and Ivan Vilotijevic

Institute of Organic Chemistry and Macromolecular Chemistry,
Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany

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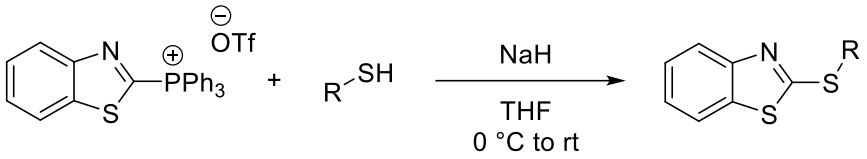
General remarks

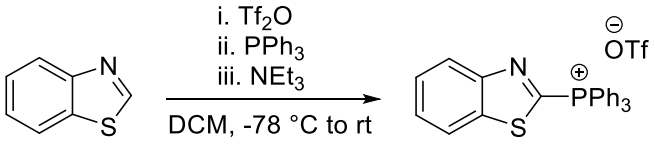
All the chemicals that are not mentioned in the subsequent parts were purchased from Merck, Alfa Aesar, Acros Organics, Fluorochem or TCI and used without further purification. The solvents if needed were dried according to standard conditions. For column chromatography and TLC (SiO_2, 60M, pore size 0.04 – 0.063 mm), products of Machery-Nagel were used. The TLC-glass-plates DURASIL consisted of a 0.25 mm layer of silica 60 with Fluorescence indicator UV254. TLCs were checked under UV-light (254 nm or 365 nm) and stained with an aq. $KMnO_4$-solution, PMA-stain, DNP or PAA. All ^{1}H, ^{13}C and ^{19}F NMR spectra were measured with a BRUKER 250 (^{13}C), BRUKER Fourier 300 (^{1}H, ^{13}C) or a BRUKER Avance 400 spectrometer (^{1}H, ^{13}C, ^{19}F). The chemical shift of each signal was registered in ppm. For 1H and 13C measurements, the chemical shift refers to TMS, showing a signal at 0 ppm. As an internal standard, the remaining protons or respectively the carbons of the corresponding deuterated solvent were used ($CDCl_3$, 7.26 ppm (1H-NMR), 77.16 ppm (^{13}C-NMR)). The chemical shift of the fluorine NMR was determined indirectly. For carbon spectra, a broadband decoupling was performed. High-resolution mass spectra (HRMS) were measured with EI or ESI ionisation by the MS plattform. A chromatographic purification was performed before each measurement. The Thermo Q-Exactive plus device for ESI-mass spectra was coupled to a binary UHPLC system. For EI-measurement, a GC-system was coupled to the Thermo Q-Exactive GC device. All the IRs were measured using the Shimadzu IR-Affinity-1 (FTIR) device.

General procedure for the thiolation of thiazole derivatives



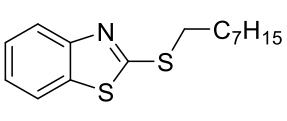
NaH (0.3 mmol) was added to the pronucleophile (0.3 mmol) in dry THF (0.1 M) under inert atmosphere at 0 °C. After stirring for half an hour at room temperature, the phosphonium salt (0.2 mmol) was added subsequently at 0 °C followed by three quick vacuum/nitrogen refills. The reaction mixture was warmed up to room temperature and quenched by addition of a small amount of water when it completed. The crude product was purified by column chromatography using ethyl acetate in petroleum ether.

General procedure for the synthesis of phosphonium salts



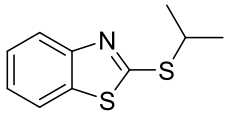
An oven dried round bottom flask equipped with a stirring bar was charged with the heterocycle (1.0 eq) and placed under a nitrogen atmosphere. After the addition of DCM (0.1 M), the reaction vessel was cooled to -78 °C and Tf_2O (1.0 eq) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes followed by the addition of PPh_3 (1.1 eq) in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and was stirred for another 30 minutes at -78 °C. NEt_3 (1.0 eq) was added dropwise via syringe and subsequently the reaction was warmed up to room temperature while stirring (approximately 15-30 minutes). The reaction was quenched by saturated NH_4Cl solution (approximately the same volume as DCM) and the mixture was transferred to a separatory funnel. The mixture was diluted with DCM and the resulting organic layer was washed three times with H_2O. The organic layer was dried (Na_2SO_4), filtered and concentrated under vacuo. An excess of chilled Et_2O (0 °C) was added to the concentrated solution which was first placed in an ultrasonic bath (approximately 15-30 minutes) then placed in a -20 °C refrigerator overnight. The resulting suspension was filtered and the solid was washed with chilled Et_2O (0 °C) and dried in vacuo to provide the pure phosphonium salt or purified by column chromatography.

2-(octylthio)benzo[d]thiazole (3a)[1]



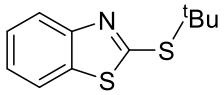
Yield: 97%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.99 – 7.82 (m, 1H), 7.82 – 7.70 (m, 1H), 7.42 (td, *J* = 8.2, 7.8, 1.2 Hz, 1H), 7.29 (td, *J* = 7.9, 1.1 Hz, 1H), 3.35 (t, *J* = 7.4 Hz, 2H), 1.83 (p, *J* = 7.3 Hz, 2H), 1.56 – 1.42 (m, 2H), 1.42 – 1.19 (m, 8H), 0.99 – 0.79 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 167.41, 153.37, 135.15, 125.97, 124.07, 121.44, 120.89, 33.64, 31.80, 29.20, 29.15, 29.07, 28.79, 22.66, 14.12.

2-(isopropylthio)benzo[d]thiazole (3b)[2]



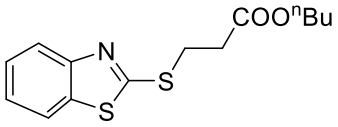
Yield: 92%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.71 (m, 1H), 7.43 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 4.10 (hept, *J* = 6.8 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.45, 153.42, 135.29, 125.97, 124.22, 121.61, 120.91, 39.47, 23.31.

2-(tert-butylthio)benzo[d]thiazole (3c)[3]



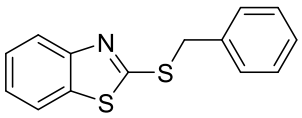
Yield: 99%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 8.1, 1.3, 0.6 Hz, 1H), 7.81 (ddd, *J* = 7.9, 1.4, 0.6 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.40 – 7.36 (m, 1H), 1.62 (s, 9H).

butyl 3-(benzo[d]thiazol-2-ylthio)propanoate (3d)



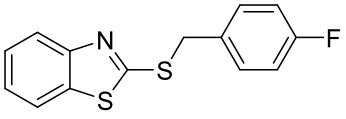
Yield: 21%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 1H), 7.78 – 7.74 (m, 1H), 7.46 – 7.39 (m, 1H), 7.34 – 7.28 (m, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.48 – 1.31 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.64, 166.05, 153.14, 135.28, 126.03, 124.28, 121.53, 120.99, 64.81, 34.42, 30.59, 28.21, 19.12, 13.70. **HRMS:** [EI]: m/z calculated for $C_{14}H_{17}NO_2S_2$ $[M]^+$ 295.0701, found 295.0701. **IR** (ATR): 2958, 1732, 1462, 1427, 1350, 1176, 999, 756 cm^{-1}.

2-(benzylthio)benzo[d]thiazole (3e)[4]



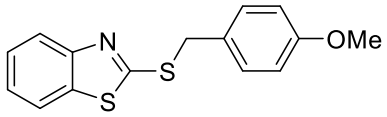
Yield: 96%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.2, 1.1 Hz, 1H), 7.76 (dd, J = 8.0, 1.2 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.40 – 7.27 (m, 4H), 4.63 (s, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.43, 153.17, 136.18, 135.34, 129.16, 128.73, 127.78, 126.08, 124.30, 121.57, 121.03, 37.72.

2-((4-fluorobenzyl)thio)benzo[d]thiazole (3f)[5]



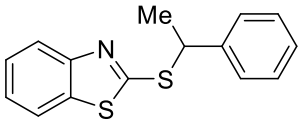
Yield: 99%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 1H), 7.81 – 7.74 (m, 1H), 7.49 – 7.39 (m, 3H), 7.36 – 7.28 (m, 1H), 7.10 – 6.95 (m, 2H), 4.59 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.02, 162.27 (d, *J* = 246.6 Hz), 153.07, 135.34, 132.13 (d, *J* = 3.3 Hz), 130.82 (d, *J* = 8.2 Hz), 128.52 (d, *J* = 12.2 Hz), 126.12, 124.39, 121.31 (d, *J* = 39.0 Hz), 115.60 (d, *J* = 21.6 Hz), 36.86.

2-((4-methoxybenzyl)thio)benzo[d]thiazole (3g)[6]



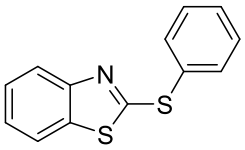
Yield: 99%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 1H), 7.79 – 7.73 (m, 1H), 7.48 – 7.37 (m, 3H), 7.35 – 7.27 (m, 1H), 6.91 – 6.85 (m, 2H), 4.58 (s, 2H), 3.80 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.61, 159.19, 153.18, 135.30, 130.37, 127.99, 126.06, 124.26, 121.53, 121.02, 114.12, 55.28, 37.34.

2-((1-phenylethyl)thio)benzo[d]thiazole (3h)[7]



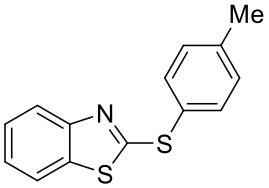
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 1H), 7.79 – 7.71 (m, 1H), 7.54 – 7.48 (m, 2H), 7.43 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.39 – 7.27 (m, 4H), 5.18 (q, *J* = 7.0 Hz, 1H), 1.87 (d, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 165.87, 153.20, 141.80, 135.43, 128.69, 127.78, 127.41, 126.01, 124.33, 121.71, 120.97, 47.58, 22.67.

2-(phenylthio)benzo[d]thiazole (3i)[3]



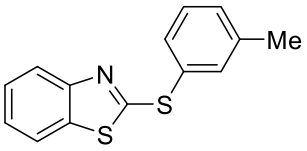
Yield: 82%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.90 (dt, J = 8.2, 0.9 Hz, 1H), 7.81 – 7.71 (m, 2H), 7.66 (dt, J = 7.8, 1.0 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.42 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.33 – 7.23 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.72, 153.93, 135.54, 135.39, 130.50, 129.94, 126.17, 124.33, 121.96, 120.80.

2-(*p*-tolylthio)benzo[d]thiazole (3j)[3]



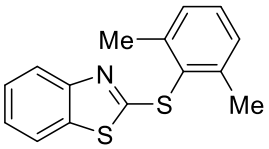
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.67 – 7.61 (m, 3H), 7.41 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.28 – 7.20 (m, 1H), 2.45 (s, 3H).

2-(*m*-tolylthio)benzo[d]thiazole (3k)[8]



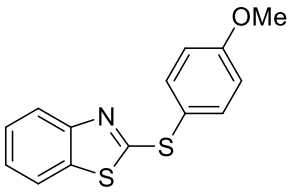
Yield: 94%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.66 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.45 – 7.35 (m, 2H), 7.35 – 7.31 (m, 1H), 7.27 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 170.10, 153.94, 139.99, 135.88, 135.53, 132.39, 131.32, 129.74, 129.56, 126.13, 124.27, 121.91, 120.77, 21.31.

2-((2,6-dimethylphenyl)thio)benzo[d]thiazole (3l)[9]



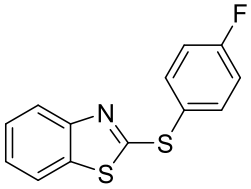
Yield: 93%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.67 – 7.57 (m, 1H), 7.44 – 7.33 (m, 2H), 7.30 – 7.21 (m, 3H), 2.56 (s, 6H).

2-((4-methoxyphenyl)thio)benzo[d]thiazole (3m)[10]



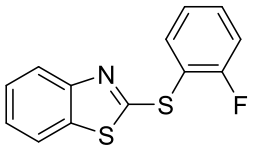
Yield: 83%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.87 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 7.71 – 7.61 (m, 3H), 7.40 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.25 (ddd, J = 8.0, 7.3, 1.2 Hz, 1H), 7.05 – 6.97 (m, 2H), 3.88 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 171.93, 161.70, 154.18, 137.60, 135.40, 126.09, 124.06, 121.75, 120.75, 120.17, 115.51, 55.48.

2-((4-fluorophenyl)thio)benzo[d]thiazole (3n)[11]



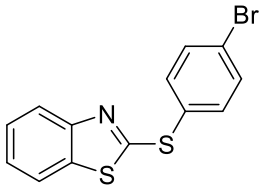
Yield: 77%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ7.89 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.80 – 7.63 (m, 3H), 7.42 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.35 – 7.09 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.54, 164.20 (d, *J* = 252.2 Hz,), 153.92, 137.79 (d, *J* = 8.8 Hz), 135.44, 126.26, 125.09 (d, *J* = 3.6 Hz), 124.41, 121.97, 120.82, 117.25 (d, *J* = 22.2 Hz).

2-((2-fluorophenyl)thio)benzo[d]thiazole (3o)



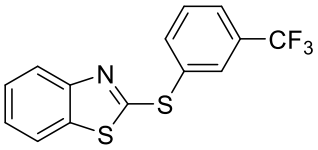
Yield: 81%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.75 (td, *J* = 7.7, 7.2, 1.9 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.60 – 7.50 (m, 1H), 7.42 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.32 – 7.22 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 167.40, 162.69 (d, *J* = 251.4 Hz), 153.80, 137.39, 135.62, 133.16 (d, *J* = 8.2 Hz), 126.23, 125.33 (d, *J* = 4.1 Hz), 124.51, 122.10, 120.84, 117.25, 116.85 (d, *J* = 22.7 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -104.89. **HRMS:** [EI]: m/z calculated for $C_{13}H_8FNS_2$ $[M]^+$ 261.0082, found 261.0082. **IR** (ATR): 3066, 1454, 1423, 1219, 1002, 817, 721 cm^{-1}.

2-((4-bromophenyl)thio)benzo[d]thiazole (3p)[11]



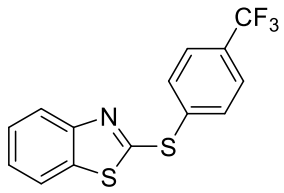
Yield: 91%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.93 – 7.86 (dt, J = 8.2, 0.9 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.61 – 7.55 (m, 4H), 7.43 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.30 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.07, 153.78, 136.56, 135.57, 133.13, 129.05, 126.31, 125.18, 124.59, 122.11, 120.88.

2-((3-(trifluoromethyl)phenyl)thio)benzo[d]thiazole (3q)[8]



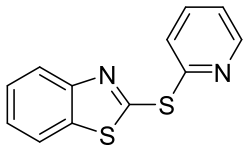
Yield: 91%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.97 – 7.89 (m, 2H), 7.79 – 7.69 (m, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.33 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.70, 153.66, 137.92, 135.66, 132.26 (d, *J* = 32.9 Hz), 131.59, 131.34 (q, *J* = 3.7 Hz), 130.29, 126.88 (q, *J* = 3.7 Hz), 126.41, 124.83, 123.40 (d, *J* =294 Hz), 122.29, 120.95.

2-((4-(trifluoromethyl)phenyl)thio)benzo[d]thiazole (3r)[11]



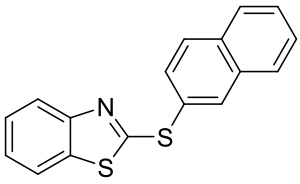
Yield: 86%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.77 – 7.66 (m, 3H), 7.46 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.34 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 165.77, 153.57, 135.83, 135.28, 134.12, 131.76 (q, J = 32 Hz), 126.57 (q, *J* = 3.7 Hz), 126.44, 124.99, 123.66 (q, *J* = 266 Hz), 122.41, 120.99.

2-(pyridin-2-ylthio)benzo[d]thiazole (3s)[12]



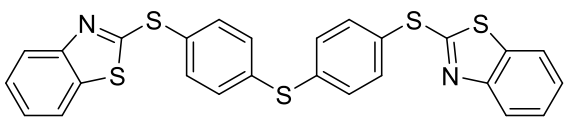
Yield: 65%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.61 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 8.00 (ddd, J = 8.1, 1.3, 0.7 Hz, 1H), 7.82 (ddd, J = 7.9, 1.4, 0.6 Hz, 1H), 7.68 (ddd, J = 8.0, 7.4, 1.9 Hz, 1H), 7.55 (dt, J = 8.0, 1.0 Hz, 1H), 7.47 (ddd, J = 8.2, 7.2, 1.4 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.24 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 162.51, 154.74, 152.72, 149.95, 137.42, 136.26, 126.23, 125.10, 125.07, 122.57, 122.48, 121.01.

2-(naphthalen-2-ylthio)benzo[d]thiazole (3t)[1]



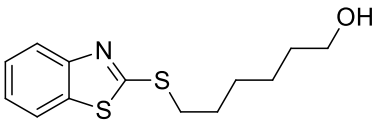
Yield: 90%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.30 (d, J = 1.7 Hz, 1H), 7.98 – 7.85 (m, 4H), 7.74 (dd, J = 8.6, 1.8 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.42 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.27 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.65, 153.94, 135.61, 135.52, 133.77, 133.74, 131.22, 129.77, 128.18, 127.91, 127.79, 127.04, 127.02, 126.20, 124.36, 121.99, 120.83.

bis(4-(benzo[d]thiazol-2-ylthio)phenyl)sulfane (3u)



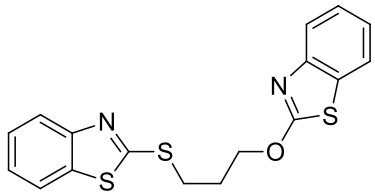
Yield: 66%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.2, 0.8 Hz, 2H), 7.74 – 7.66 (m, 6H), 7.49 – 7.40 (m, 6H), 7.31 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.25, 153.77, 137.93, 135.66, 135.59, 131.97, 129.29, 126.32, 124.62, 122.12, 120.89. **HRMS:** [EI]: m/z calculated for $C_{26}H_{16}N_2S_5$ $[M]^+$ 515.9917, found 515.9913. **IR** (ATR): 3063, 2924, 1570, 1454, 1423, 1385, 1092, 1076, 1007, 818, 748, 721 cm^{-1}.

6-(benzo[d]thiazol-2-ylthio)hexan-1-ol (3v)



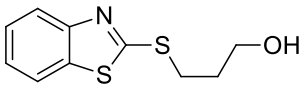
Yield: 70%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.25 – 7.18 (m, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.28 (t, *J* = 6.0 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.54 – 1.35 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 167.36, 153.24, 135.09, 126.04, 124.16, 121.42, 120.93, 62.79, 33.49, 32.52, 29.14, 28.48, 25.22. HRMS: [EI]: m/z calculated for $C_{13}H_{17}NOS_2$ $[M]^+$ 267.0752, found 267.0748. IR (ATR): 3282, 2927, 1647, 1539, 1458, 1307, 995, 756 cm^{-1}.

2-((3-(benzo[d]thiazol-2-yloxy)propyl)thio)benzo[d]thiazole (3w)



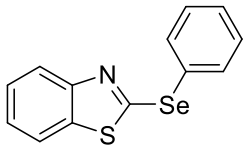
Yield: 33%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.36 – 7.25 (m, 2H), 7.24 – 7.13 (m, 2H), 4.67 (t, *J* = 6.0 Hz, 2H), 3.48 (t, *J* = 7.0 Hz, 2H), 2.42 – 2.29 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.63, 166.20, 153.20, 149.26, 135.24, 131.88, 126.02, 126.01, 124.27, 123.55, 121.53, 121.27, 120.96, 120.83, 69.94, 29.85, 28.76. HRMS: [EI]: m/z calculated for $C_{10}H_{12}NOS_2^+$ [M-benzothiazole+H]$^+$ 226.0355, found 226.0360. IR (ATR): 2924, 1716, 1624, 1535, 1427, 1249, 1219, 995, 756 cm^{-1}.

3-(benzo[d]thiazol-2-ylthio)propan-1-ol (3x)



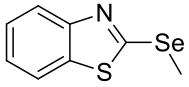
Yield: 45%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.25 – 7.18 (m, 1H), 3.68 (t, *J* = 5.9 Hz, 2H), 3.46 (t, *J* = 5.9 Hz, 2H), 1.95 (td, *J* = 11.1, 5.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 168.91, 152.41, 135.02, 126.24, 124.49, 121.06, 121.02, 59.02, 33.11, 29.83. HRMS: [EI]: m/z calculated for $C_{10}H_{11}NOS_2$ [M]$^+$ 225.0282, found 225.0278. IR (ATR): 3294, 2927, 1535, 1458, 1423, 1238, 1049, 995, 756 cm^{-1}.

2-(phenylselanyl)benzo[d]thiazole (3y)[3]



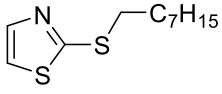
Yield: 77%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.72 – 7.67 (m, 1H), 7.55 – 7.38 (m, 4H), 7.32 – 7.24 (m, 1H).

2-(methylselanyl)benzo[d]thiazole (3aa)[13]



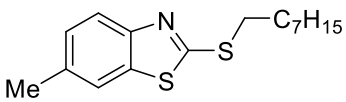
Yield: 67%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 1H), 7.72 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.39 – 7.29 (m, 1H), 7.27 – 7.19 (m, 1H), 2.62 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 160.08, 153.98, 136.26, 126.04, 124.20, 121.55, 120.93, 8.06.

2-(octylthio)thiazole (3ab)



Yield: 93%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 3.4 Hz, 1H), 7.20 (d, *J* = 3.4 Hz, 1H), 3.28 – 3.12 (m, 2H), 1.76 (p, *J* = 7.6, 7.2 Hz, 2H), 1.55 – 1.37 (m, 2H), 1.37 – 1.20 (m, 8H), 0.97 – 0.80 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.32, 143.60, 119.45, 35.51, 32.68, 30.12, 30.03, 29.96, 29.66, 23.54, 15.00. **HRMS** [EI]: m/z calculated for $C_{11}H_{19}NS_2$ [M]$^+$ 229.0959, found 229.0959. **IR** (ATR): ν = 2924, 2854, 1739, 1384, 1018, 864, 705 cm^{-1}

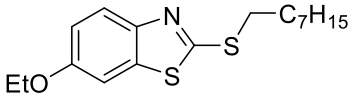
6-methyl-2-(octylthio)benzo[d]thiazole (3ac)



Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.22 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.33 (t, *J* = 6.0 Hz, 2H), 2.46 (s, 3H), 1.88 – 1.76 (m, 2H), 1.54 – 1.43 (m, 2H), 1.37 – 1.25 (m, 8H), 0.89 (t, *J* = 6.0

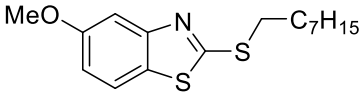
Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.04, 151.48, 135.31, 134.13, 127.41, 120.95, 120.76, 33.69, 31.79, 29.22, 29.13, 29.06, 28.78, 22.65, 21.40, 14.10. **HRMS:** [EI]: m/z calculated for $C_{16}H_{23}NS_2$ $[M]^+$ 293.1272, found 293.1265. **IR** (ATR): 2924, 2855, 1601, 1447, 1258, 1204, 1114, 1065, 995, 818 cm^{-1}.

6-ethoxy-2-(octylthio)benzo[d]thiazole (3ad)



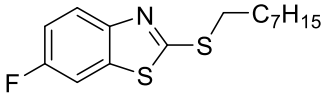
Yield: 86%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.31 (t, *J* = 7.4 Hz, 2H), 1.81 (p, *J* = 7.3 Hz, 2H), 1.54 – 1.40 (m, 5H), 1.40 – 1.18 (m, 8H), 0.89 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 156.28, 147.84, 136.47, 121.90, 115.16, 104.79, 64.09, 33.83, 31.79, 29.27, 29.13, 29.05, 28.77, 22.65, 14.84, 14.10. **HRMS:** [EI]: m/z calculated for $C_{17}H_{25}NOS_2$ $[M]^+$ 323.1378, found 323.1370. **IR** (ATR): 2924, 2855, 1601, 1447, 1258, 1204, 1115, 1065, 1038, 995, 937, 818 cm^{-1}.

5-methoxy-2-(octylthio)benzo[d]thiazole (3ae)



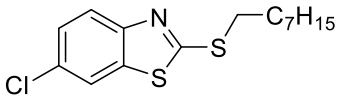
Yield: 95%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.88 (s, 3H), 3.33 (t, *J* = 6.0 Hz, 2H), 1.82 (p, *J* = 7.2 Hz, 2H), 1.54 – 1.42 (m, 2H), 1.36 – 1.24 (m, 8H), 0.89 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.60, 158.88, 154.57, 126.75, 121.07, 113.78, 104.47, 55.60, 33.69, 31.79, 29.15, 29.14, 29.06, 28.78, 22.65, 14.11. **HRMS:** [EI]: m/z calculated for $C_{16}H_{23}NOS_2$ $[M]^+$ 309.1221, found 309.1216. **IR** (ATR): 2928, 2855, 1744, 1597, 1466, 1416, 1319, 1026, 810 cm^{-1}.

6-fluoro-2-(octylthio)benzo[d]thiazole (3af)



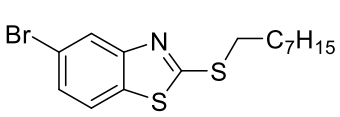
Yield: 94%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.35 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.05 (td, *J* = 8.9, 2.6 Hz, 1H), 3.24 (t, *J* = 7.4 Hz, 2H), 1.73 (p, *J* = 7.3 Hz, 2H), 1.46 – 1.33 (m, 2H), 1.32 – 1.16 (m, 8H), 0.80 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.84 (d, *J* = 3.0 Hz), 159.75 (d, *J* = 244.6 Hz), 150.01 (d, *J* = 1.8 Hz), 136.09 (d, *J* = 11.1 Hz), 122.12 (d, *J* = 9.2 Hz), 114.26 (d, *J* = 24.5 Hz), 107.37 (d, *J* = 26.9 Hz), 33.70, 31.78, 29.18, 29.12, 29.04, 28.76, 22.64, 14.10. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.55. **HRMS:** [EI]: m/z calculated for $C_{15}H_{20}FNS_2$ $[M]^+$ 297.1021, found 297.1020. **IR** (ATR): 2924, 2855, 1601, 1566, 1447, 1308, 1254, 1192, 995, 907, 810 cm^{-1}.

6-chloro-2-(octylthio)benzo[d]thiazole (3ag)



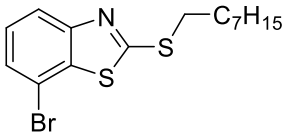
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.34 (t, *J* = 7.3 Hz, 2H), 1.83 (p, *J* = 7.3 Hz, 2H), 1.48 (p, *J* = 6.8 Hz, 2H), 1.37 – 1.25 (m, 8H), 0.89 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.10, 151.93, 136.31, 129.89, 126.67, 122.02, 120.54, 33.68, 31.77, 29.13, 29.12, 29.03, 28.75, 22.64, 14.10. **HRMS:** [EI]: m/z calculated for $C_{15}H_{20}ClNS_2$ $[M]^+$ 313.0726, found 313.0726. **IR** (ATR): 2920, 2855, 2191, 1431, 1300, 1261, 1196, 1103, 999, 814 cm^{-1}.

5-bromo-2-(octylthio)benzo[d]thiazole (3ah)



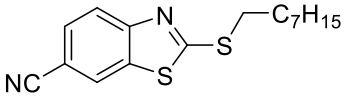
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.26 (t, *J* = 7.4 Hz, 2H), 1.74 (p, *J* = 7.3 Hz, 2H), 1.48 – 1.34 (m, 2H), 1.27 – 1.16 (m, 8H), 0.81 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.49, 154.48, 133.95, 127.03, 124.31, 121.84, 119.61, 33.63, 31.78, 29.13, 29.13, 29.04, 28.77, 22.65, 14.10. **HRMS:** [EI]: m/z calculated for $C_{15}H_{20}BrNS_2$ $[M]^+$ 357.0221, found 357.0227. **IR** (ATR): 2920, 2851, 1740, 1408, 1231, 1204, 1146, 1011, 891, 868 cm^{-1}.

7-bromo-2-(octylthio)benzo[d]thiazole (3ai)



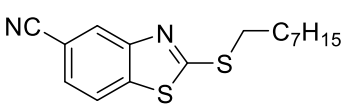
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.23 – 7.17 (m, 1H), 3.26 (t, *J* = 7.4 Hz, 2H), 1.75 (p, *J* = 7.3 Hz, 2H), 1.47 – 1.35 (m, 2H), 1.30 – 1.15 (m, 8H), 0.84 – 0.78 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.02, 153.20, 137.91, 127.19, 126.79, 120.10, 113.15, 33.71, 31.78, 29.12, 29.08, 29.03, 28.75, 22.64, 14.10. **HRMS:** [EI]: m/z calculated for $C_{15}H_{20}BrNS_2$ $[M]^+$ 357.0221, found 357.0224. **IR** (ATR): 2924, 2855, 1740, 1450, 1377, 999, 775 cm^{-1}.

2-(octylthio)benzo[d]thiazole-6-carbonitrile (3aj)



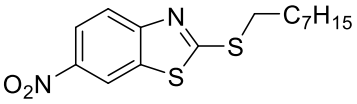
Yield: 98%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.37 (t, *J* = 7.3 Hz, 2H), 1.83 (p, *J* = 7.3 Hz, 2H), 1.56 – 1.41 (m, 2H), 1.41 – 1.17 (m, 8H), 0.96 – 0.82 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 172.94, 155.70, 135.66, 129.51, 125.34, 121.82, 118.81, 107.27, 33.73, 31.76, 29.10, 29.10, 29.01, 28.74, 22.63, 14.10. **HRMS:** [EI]: m/z calculated for $C_{16}H_{20}N_2S_2$ $[M]^+$ 304.1068, found 304.1068. **IR** (ATR): 2920, 2843, 2222, 1427, 1400, 1308, 1246, 1192, 1003, 826 cm^{-1}.

2-(octylthio)benzo[d]thiazole-5-carbonitrile (3ak)



Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.5 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.37 (t, *J* = 7.3 Hz, 2H), 1.83 (p, *J* = 7.3 Hz, 2H), 1.56 – 1.41 (m, 2H), 1.36 – 1.23 (m, 8H), 0.92 – 0.86 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 170.83, 153.00, 140.20, 126.56, 125.07, 121.86, 118.85, 109.65, 33.66, 31.77, 29.12, 29.06, 29.02, 28.75, 22.64, 14.11. **HRMS:** [EI]: m/z calculated for $C_{16}H_{20}N_2S_2$ $[M]^+$ 304.1068, found 304.1061. **IR** (ATR): 2924, 2855, 1744, 1431, 1412, 1018, 826 cm^{-1}.

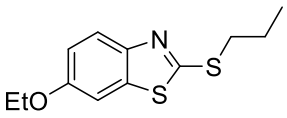
6-nitro-2-(octylthio)benzo[d]thiazole (3al)



Yield: 86%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.3 Hz, 1H), 8.29 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 3.40 (t, *J* = 7.4 Hz, 2H), 1.85 (p, *J* = 7.4 Hz, 2H), 1.55 – 1.43 (m, 2H), 1.40 – 1.25 (m, 8H), 0.89 (t, *J* = 6.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 174.64, 157.10, 143.96, 135.48,

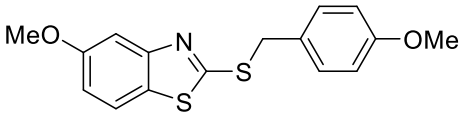
121.84, 121.12, 117.30, 33.79, 31.76, 29.10, 29.01, 28.99, 28.75, 22.63, 14.09. **HRMS:** [EI]: m/z calculated for $C_{15}H_{20}N_2O_2S_2$ $[M]^+$ 324.0966, found 324.0966. **IR** (ATR): 2924, 2851, 1512,1327, 1265, 1118, 1049, 1003, 829 cm^{-1}.

6-ethoxy-2-(propylthio)benzo[d]thiazole (3am)[14]



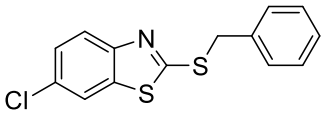
Yield: 80%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H), 1.85 (h, *J* = 7.3 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 163.91, 156.29, 147.83, 136.47, 121.90, 115.17, 104.78, 64.09, 35.72, 22.76, 14.84, 13.38.

5-methoxy-2-((4-methoxybenzyl)thio)benzo[d]thiazole (3an)[6]



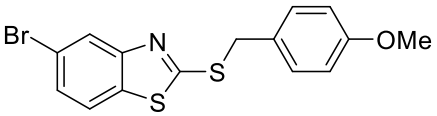
Yield: 83%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.41 – 7.34 (m, 2H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.91 – 6.83 (m, 2H), 4.55 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 167.72, 159.18, 158.94, 154.40, 130.33, 127.94, 126.92, 121.18, 114.11, 113.96, 104.57, 55.62, 55.28, 37.42.

2-(benzylthio)-6-chlorobenzo[d]thiazole (3ao)[15]



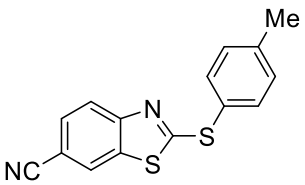
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.41 – 7.30 (m, 4H), 4.61 (s, 2H).

5-bromo-2-((4-methoxybenzyl)thio)benzo[d]thiazole (3ap)



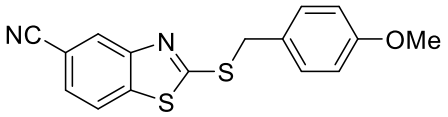
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.24 (m, 3H), 6.82 – 6.73 (m, 2H), 4.46 (s, 2H), 3.71 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.63, 159.23, 154.27, 134.10, 130.37, 127.80, 127.20, 124.39, 121.94, 119.68, 114.13, 55.29, 37.30. **HRMS:** [EI]: m/z calculated for $C_{15}H_{12}BrNOS_2$ $[M]^+$ 515.9917, found 364.9544. **IR** (ATR): 2916, 1608, 1508, 1419, 1246, 1172, 1014, 829, 794 cm^{-1}.

2-(p-tolylthio)benzo[d]thiazole-6-carbonitrile (3aq)



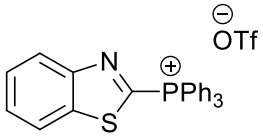
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 1H), 7.89 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.39 – 7.31 (m, 2H), 2.47 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 177.96, 157.47, 142.93, 136.68, 132.03, 130.50, 126.12, 126.03, 123.19, 119.69, 108.25, 22.43. **HRMS:** [EI]: m/z calculated for $C_{15}H_{10}N_2S_2$ $[M]^+$ 282.0285, found 282.0285. **IR** (ATR): 3089, 2229, 2739, 1431, 1381, 1006, 794 cm^{-1}.

2-((4-methoxybenzyl)thio)benzo[d]thiazole-5-carbonitrile (3ar)



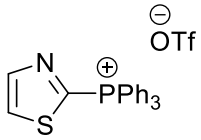
Yield: 99%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.5 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.35 – 7.24 (m, 2H), 6.84 – 6.75 (m, 2H), 4.51 (s, 2H), 3.72 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.98, 159.33, 152.82, 140.32, 130.40, 127.47, 126.71, 125.19, 121.96, 118.81, 114.18, 109.75, 55.30, 37.33. **HRMS:** [EI]: m/z calculated for $C_{16}H_{12}N_2OS_2$ $[M]^+$ 312.0391, found 312.0391. **IR** (ATR): 2920, 2229, 1739, 1508, 1435, 1249, 1172, 1006, 813 cm^{-1}.

benzo[d]thiazol-2-yltriphenylphosphonium trifluoromethanesulfonate (1a)[16]



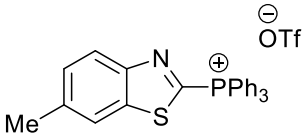
Yield: 87%. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, J = 7.4, 1.3 Hz, 1H), 8.16 (dd, J = 7.3, 1.3 Hz, 1H), 8.00 – 7.92 (m, 3H), 7.87 – 7.76 (m, 12H), 7.76 – 7.67 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 155.89, 155.66, 152.34, 151.11, 137.53, 136.63, 136.60, 134.58, 134.48, 131.03, 130.90, 129.20, 128.61, 125.61, 122.58, 116.77, 115.86.

triphenyl(thiazol-2-yl)phosphonium trifluoromethanesulfonate (1b)[16]



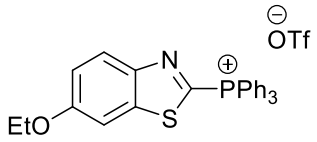
Yield: 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 3.0, 1.0 Hz, 1H), 8.45 (t, *J* = 3.1 Hz, 1H), 7.94 (dddd, *J* = 8.9, 7.1, 4.0, 2.0 Hz, 3H), 7.84 – 7.70 (m, 14H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.40, 136.37, 134.40, 134.29, 131.40, 130.91, 130.77, 116.48, 77.37, 77.25, 77.05, 76.73. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.82. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.03. **HRMS:** [EI]: m/z calculated for $C_{21}H_{17}NPS^+$ $[M]^+$ 346.0814, found 346.0814. **IR** (ATR): ν = 3067, 1480, 1261, 1146, 1107, 1030, 750 cm^{-1}.

(6-methylbenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1c)[16]



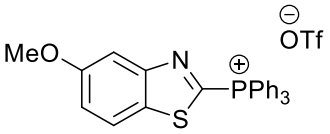
Yield: 68%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.90 (m, 4H), 7.86 – 7.77 (m, 12H), 7.56 (dd, *J* = 8.6, 1.7 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.30, 154.06, 150.44, 149.19, 140.38, 137.93, 136.57, 136.54, 134.52, 134.41, 130.99, 130.86, 130.57, 125.05, 121.79, 116.95, 116.04, 21.92. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.94. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.02. **HRMS:** [EI]: m/z calculated for $C_{26}H_{21}NPS^+$ $[M]^+$ 410.1127, found 410.1127. **IR** (ATR): ν = 3063, 1589, 1439, 1589, 1150, 1111, 1030, 810 cm^{-1}.

(6-ethoxybenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1d)[16]



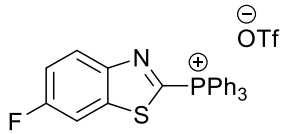
Yield: 21%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 9.0 Hz, 1H), 8.00 – 7.87 (m, 3H), 7.84 – 7.69 (m, 12H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.28 (dt, *J* = 9.2, 2.1 Hz, 1H), 4.21 – 4.07 (m, 2H), 1.44 (td, *J* = 7.0, 2.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.07, 150.75, 150.43, 147.43, 145.73, 140.13, 136.47, 136.43, 134.46, 134.32, 130.94, 130.76, 126.07, 123.04, 120.00, 118.79, 117.33, 116.12, 103.85, 64.70, 14.55. **^{31}P NMR** (162 MHz, $_{04}$_$CDCl_3$) δ 17.50. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.12. **HRMS:** [EI]: m/z calculated for $C_{27}H_{23}NOPS^+$ $[M]^+$ 440.1232, found 440.1232. **IR** (ATR): ν = 3067, 1597, 1462, 1439, 1258, 1150, 1107, 1030, 826 cm^{-1}.

(5-methoxybenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1e)[16]



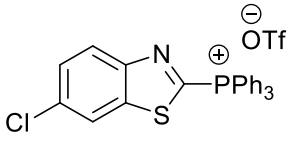
Yield: 59%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 4H), 7.84 – 7.76 (m, 13H), 7.34 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.59, 157.74, 157.51, 152.33, 151.08, 136.58, 136.55, 134.53, 134.42, 130.99, 130.86, 130.00, 122.63, 120.92, 116.92, 116.02, 106.09, 55.93. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.82. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.03. **HRMS:** [EI]: m/z calculated for $C_{26}H_{21}NOPS^+$ $[M]^+$ 426.1076, found 426.1065. **IR** (ATR): ν = 3055, 1585, 1439, 1260, 1146, 1111, 1026, 729 cm^{-1}.

(6-fluorobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1f)[16]



Yield: 54%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 9.2, 4.7 Hz, 1H), 8.00 – 7.91 (m, 3H), 7.87 – 7.77 (m, 13H), 7.49 – 7.43 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.69, 161.17, 152.69, 152.45, 152.24, 152.20, 151.00, 150.96, 139.13, 139.01, 136.67, 136.64, 134.55, 134.44, 131.06, 130.92, 127.18, 127.09, 118.28, 118.03, 116.60, 115.69, 108.89, 108.62. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.09. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.04. **HRMS:** [EI]: m/z calculated for $C_{25}H_{18}FNPS^+$ $[M]^+$ 414.0876, found 414.0876. **IR** (ATR): ν = 3067, 1601, 1558, 1466, 1439, 1261, 1142, 1107, 1030, 818 cm^{-1}.

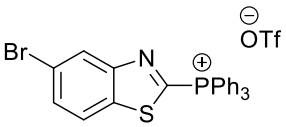
(6-chlorobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1g)[16]



Yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.1 Hz, 1H), 8.46 (d, *J* = 8.8 Hz, 1H), 8.05 (td, *J* = 7.4, 1.3 Hz, 3H), 7.97 – 7.94 (m, 6H), 7.90 – 7.85 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.63, 154.50, 154.42, 154.26, 139.28, 136.79,

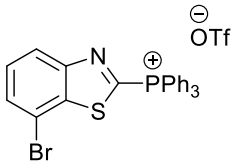
136.76, 135.30, 135.19, 133.93, 131.23, 131.10, 129.53, 126.87, 123.33, 117.25, 116.35. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.17. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -77.74. **HRMS:** [EI]: m/z calculated for $C_{25}H_{18}ClNPS^+$ $[M]^+$ 430.0581, found 430.0581. **IR** (ATR): ν = 3063, 1585, 1439, 1258, 1150, 1107, 1030, 822cm^{-1}.

(5-bromobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1h)[16]



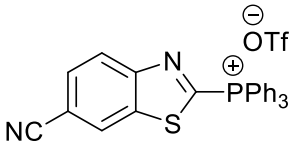
Yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 1.8 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 8.00 – 7.93 (m, 3H), 7.84 – 7.76 (m, 13H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.73, 156.50, 154.67, 153.45, 136.73, 136.70, 136.47, 134.58, 134.47, 132.26, 131.08, 130.95, 128.04, 124.07, 122.42, 122.42, 116.44, 115.54. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.42. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.04. **HRMS:** [EI]: m/z calculated for $C_{25}H_{18}BrNPS^+$ $[M]^+$ 474.0075, found 474.0073. **IR** (ATR): ν = 3063, 1585, 1439, 1261, 1150, 1107, 1026, 895, 729 cm^{-1}.

(7-bromobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1i)[16]



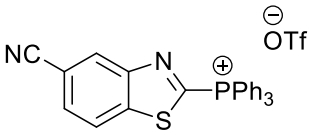
Yield: 42%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.87 (m, 3H), 7.81 – 7.71 (m, 13H), 7.60 (t, *J* = 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.31, 155.08, 153.32, 152.11, 140.46, 136.87, 136.84, 134.61, 134.50, 131.78, 131.18, 131.05, 130.02, 129.02, 128.21, 124.77, 116.28, 115.38, 114.14. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.60. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.03. **HRMS:** [EI]: m/z calculated for $C_{25}H_{18}BrNPS^+$ $[M]^+$ 474.0075, found 474.0071. **IR** (ATR): ν = 3063, 1740, 1439, 1261, 1146, 1107, 1030, 914, 795, 729 cm^{-1}.

(6-cyanobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1j)[16]



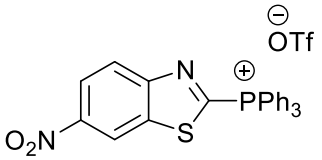
Yield: 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.4 Hz, 1H), 8.46 (d, *J* = 8.6 Hz, 1H), 8.06 – 7.94 (m, 3H), 7.92 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.88 – 7.75 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.53, 158.24, 157.87, 157.62, 138.85, 137.74, 137.69, 135.64, 135.47, 132.09, 131.87, 131.76, 129.20, 127.32, 118.47, 117.26, 115.81, 113.19. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.18. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.05. **HRMS:** [EI]: m/z calculated for $C_{21}H_{17}NPS^+$ $[M]^+$ 346.0814, found 346.0814. **IR** (ATR): ν = 3067, 1480, 1261, 1146, 1107, 1030, 750 cm^{-1}.

(5-cyanobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1k)[16]



Yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.5 Hz, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.01 – 7.94 (m, 3H), 7.85 – 7.79 (m, 13H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.97, 155.77, 154.92, 154.68, 141.84, 136.86, 136.83, 134.66, 134.55, 131.15, 131.02, 130.38, 129.75, 128.58, 128.45, 124.98, 117.63, 116.10, 115.19, 112.27. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.96. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -78.10. **HRMS:** [EI]: m/z calculated for $C_{26}H_{18}N_2PS^+$ $[M]^+$ 421.0923, found 421.0931. **IR** (ATR): ν = 3063, 1439, 1258, 1153, 1107, 1030, 729 cm^{-1}.

(6-nitrobenzo[d]thiazol-2-yl)triphenylphosphonium trifluoromethanesulfonate (1l)[16]



Yield: 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 2.3 Hz, 1H), 8.69 – 8.53 (m, 2H), 8.06 (td, *J* = 7.4, 1.3 Hz, 3H), 8.02 – 7.96 (m, 6H), 7.92 – 7.85 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.64, 160.46, 158.48, 158.24, 146.75, 138.37, 136.93, 136.90, 135.42, 135.31, 131.28, 131.15, 126.47, 123.56, 120.98, 116.90, 116.00. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.65. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -77.74. **HRMS:** [EI]: m/z calculated for $C_{21}H_{17}NPS^+$ $[M]^+$ 346.0814, found 346.0814. **IR** (ATR): ν = 3067, 1480, 1261, 1146, 1107, 1030, 750 cm^{-1}.

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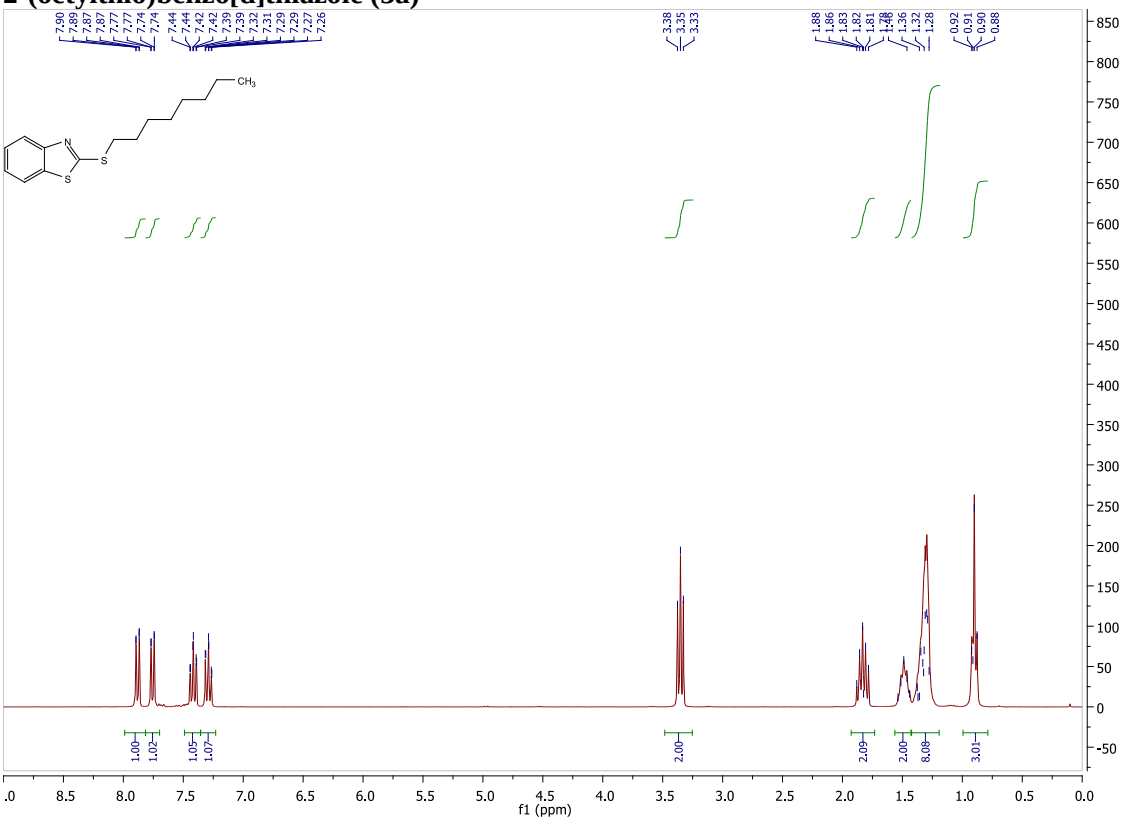
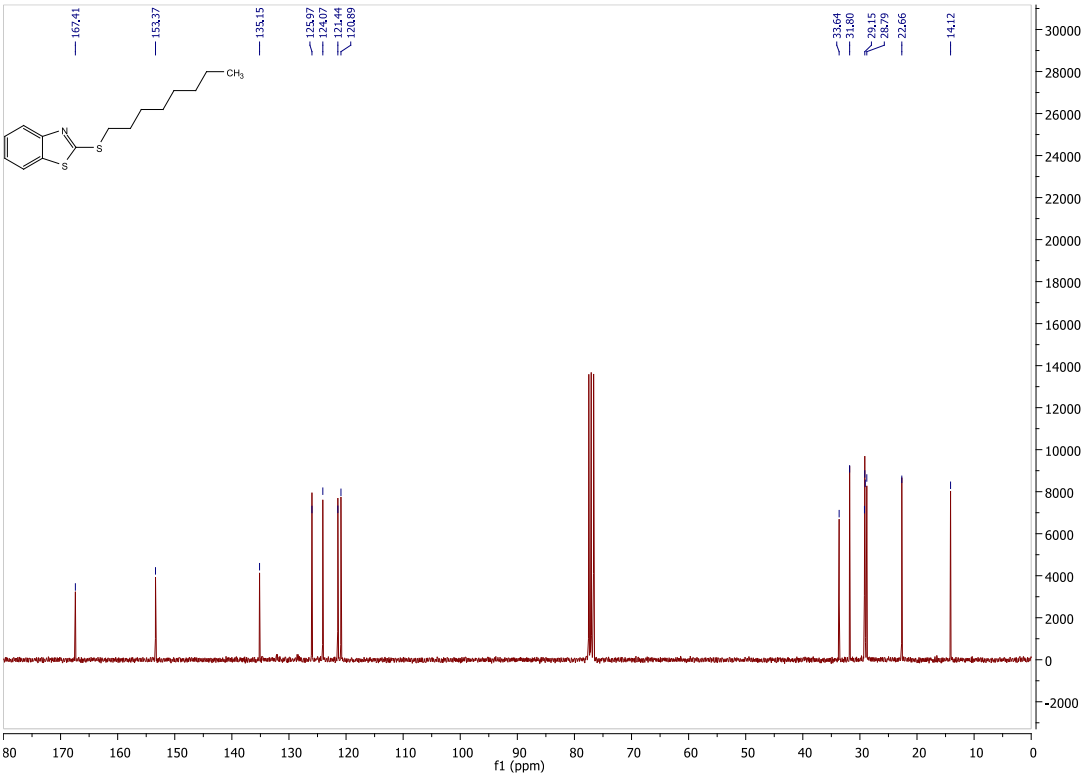
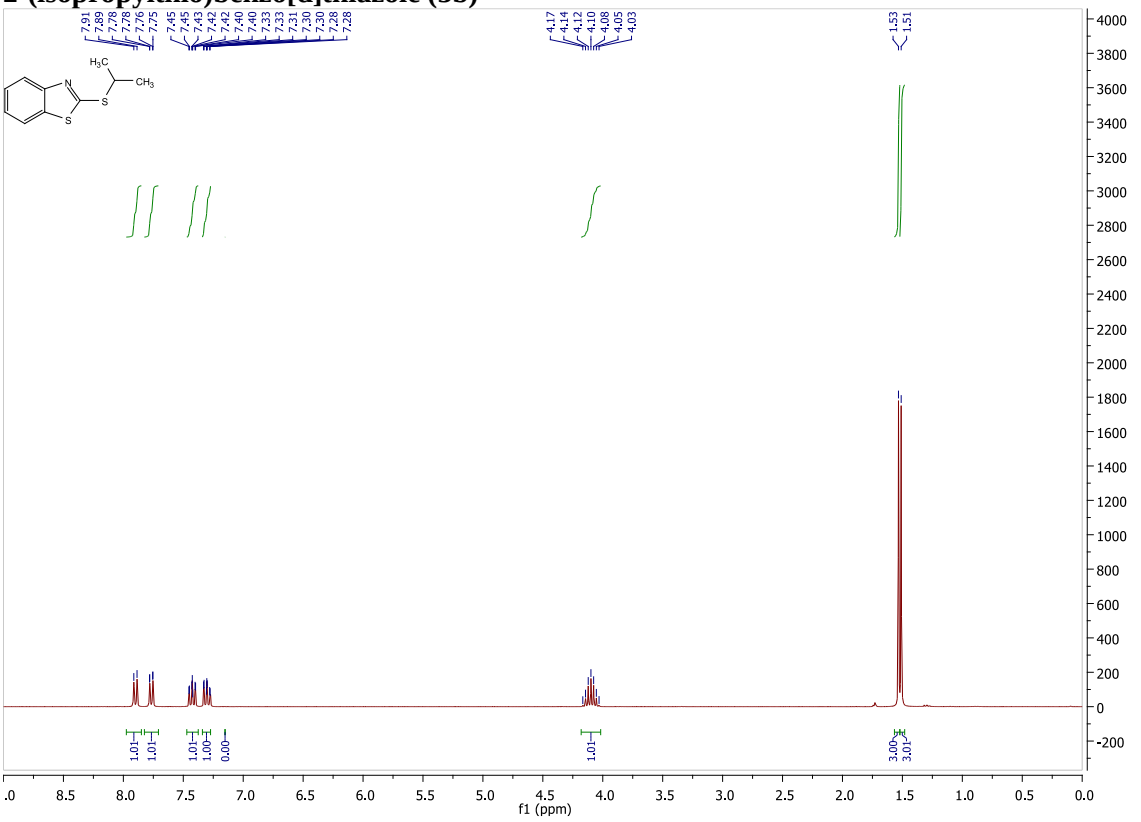
Copies of NMR spectra

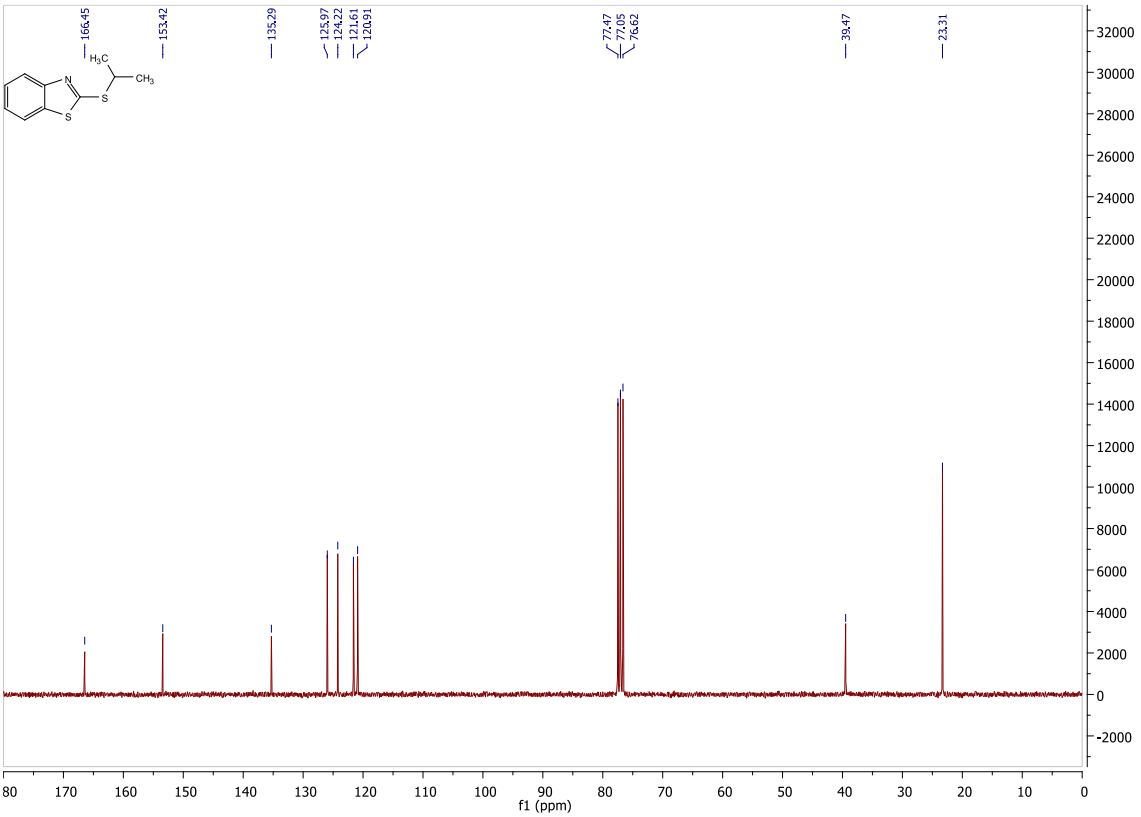
2-(octylthio)benzo[d]thiazole (3a)



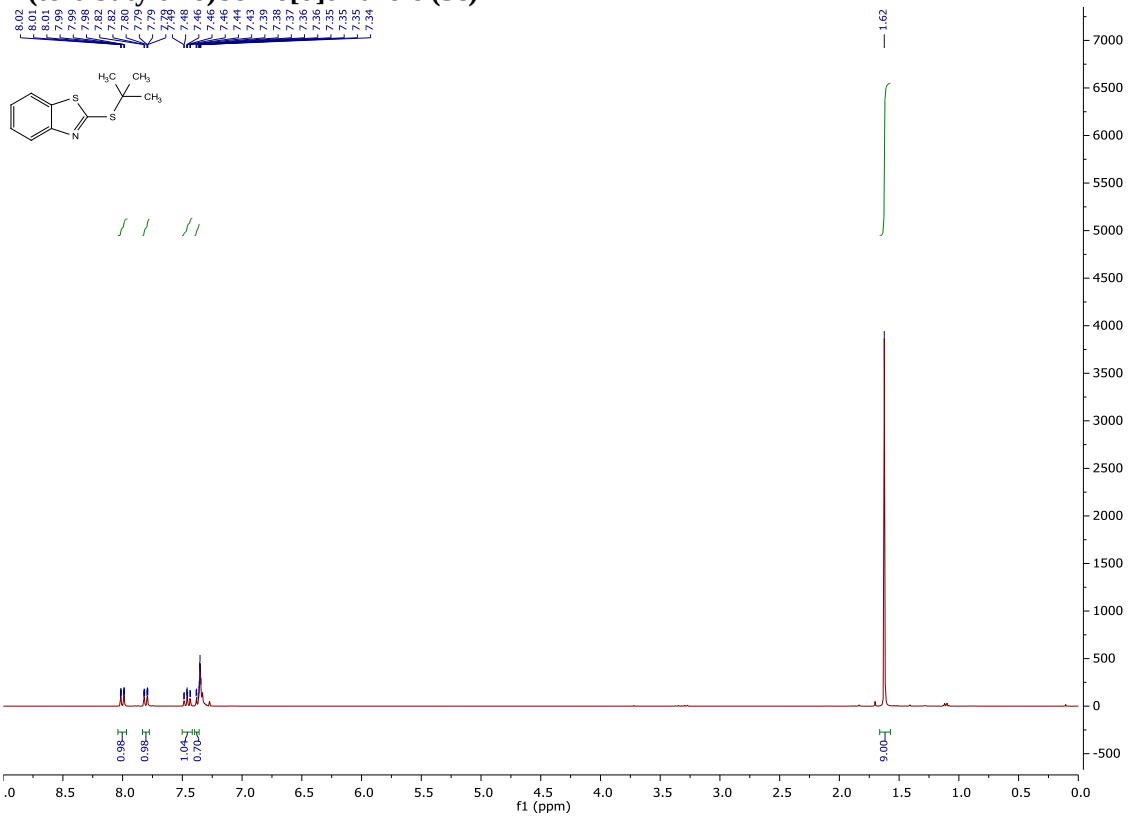


2-(isopropylthio)benzo[d]thiazole (3b)

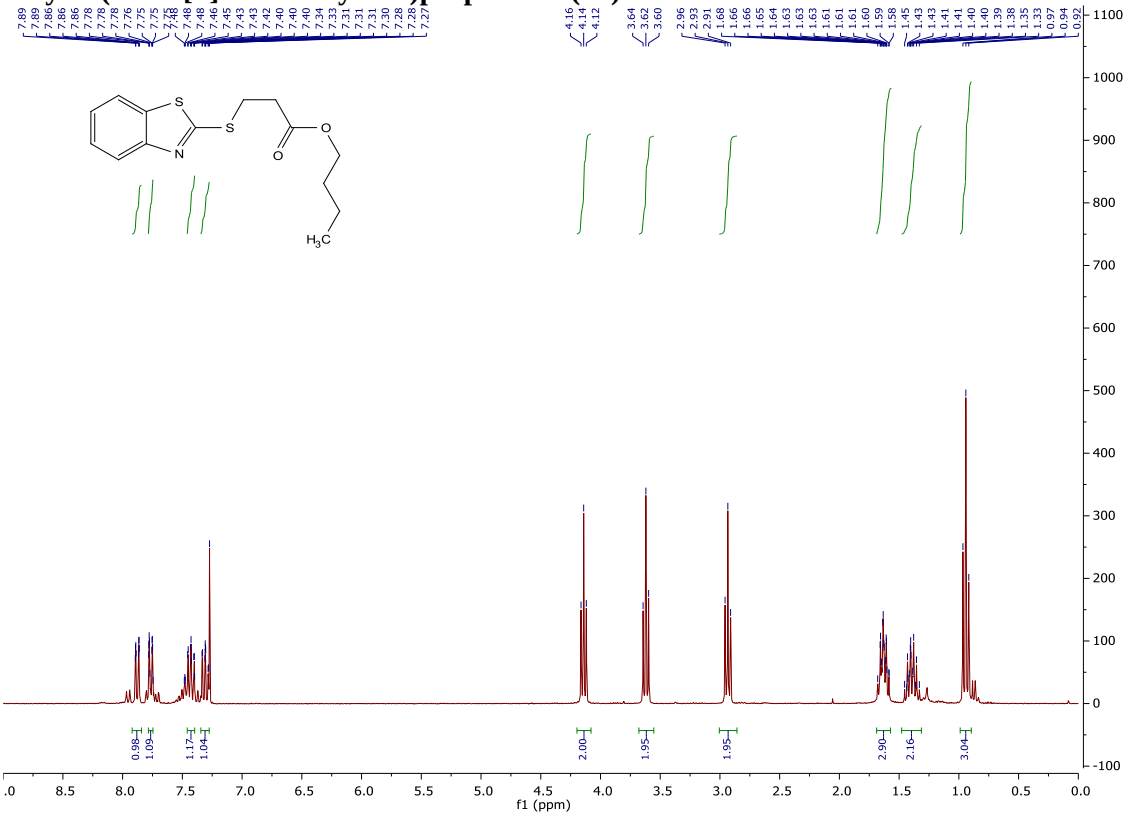


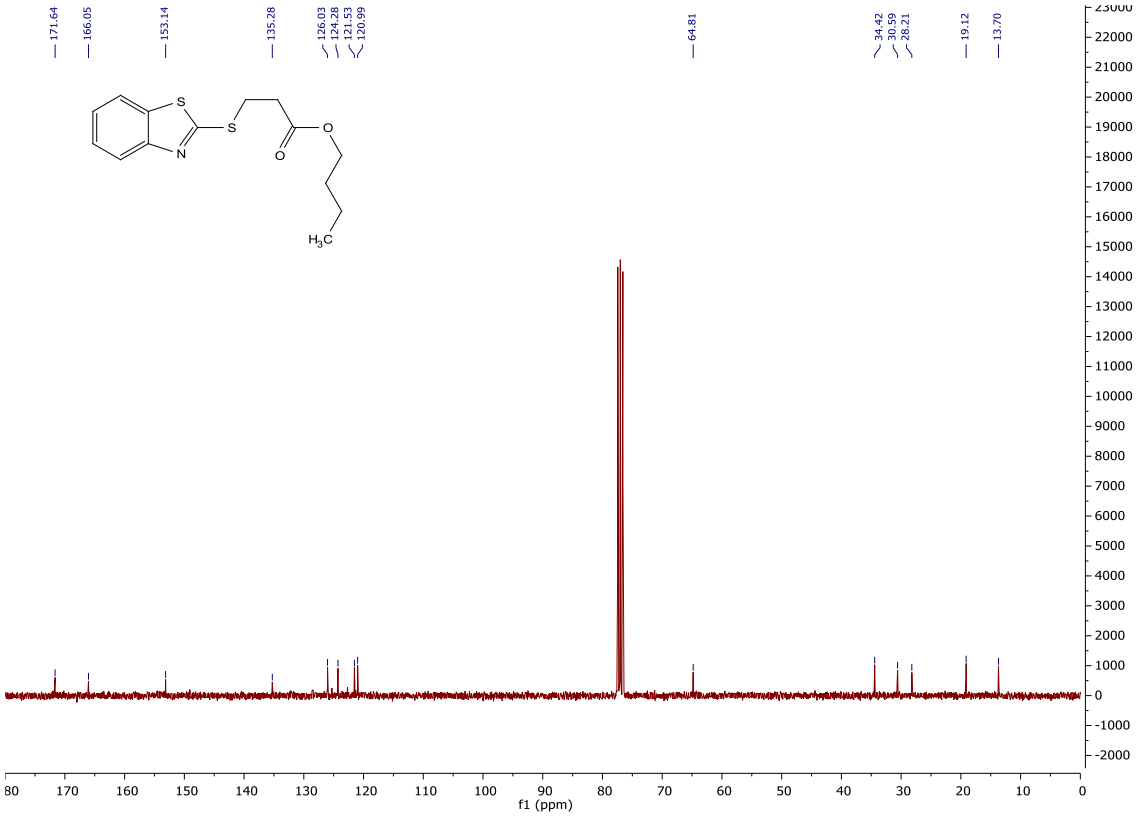


2-(tert-butylthio)benzo[d]thiazole (3c)

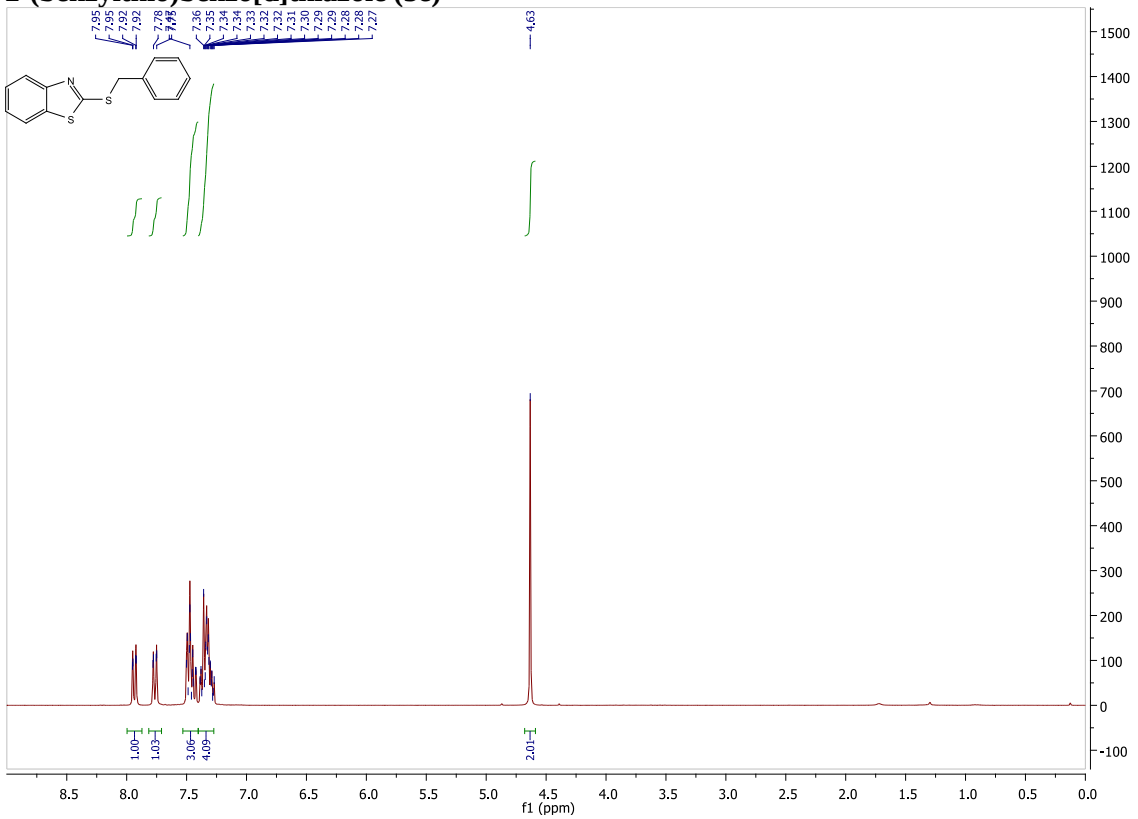


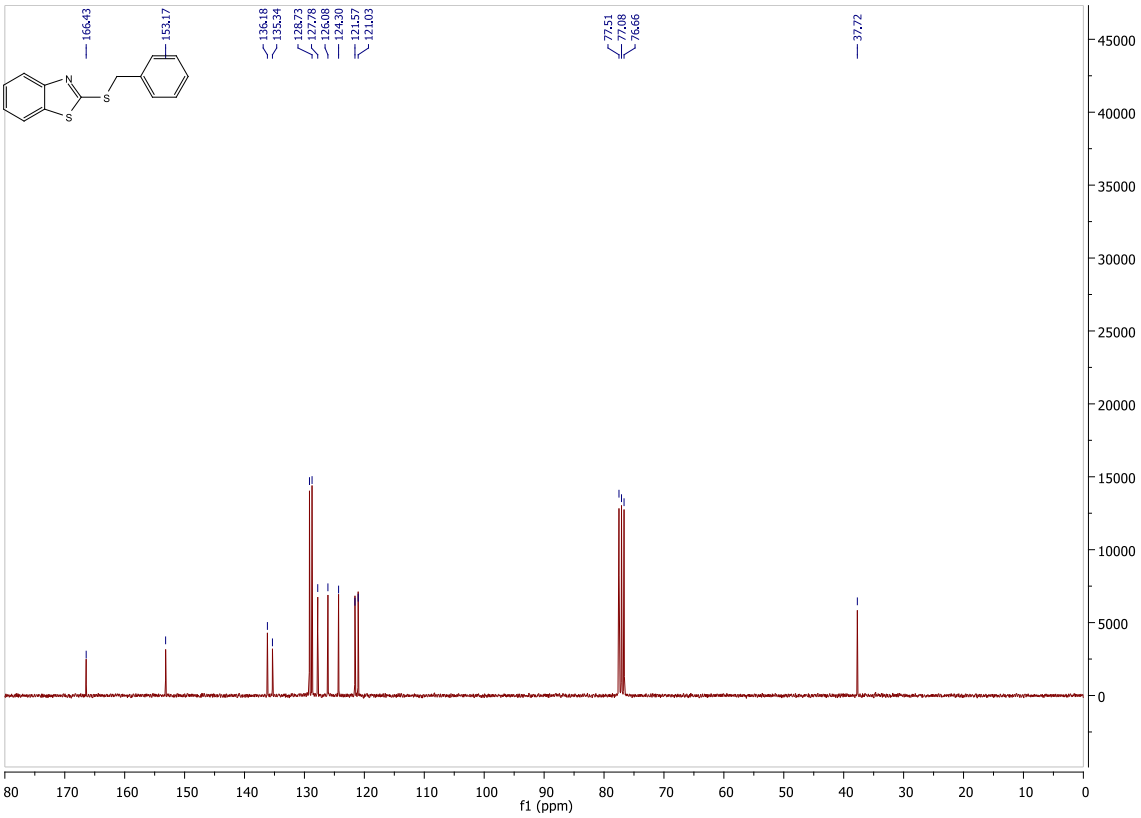
butyl 3-(benzo[d]thiazol-2-ylthio)propanoate (3d)



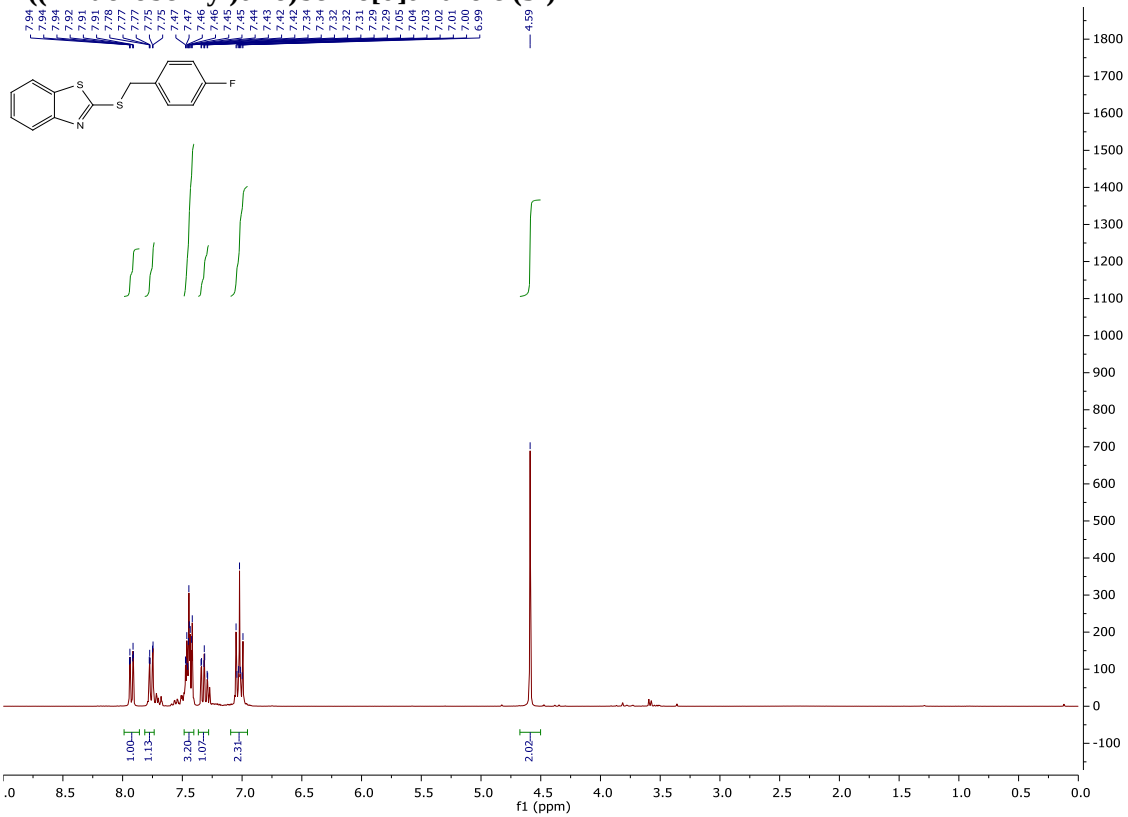


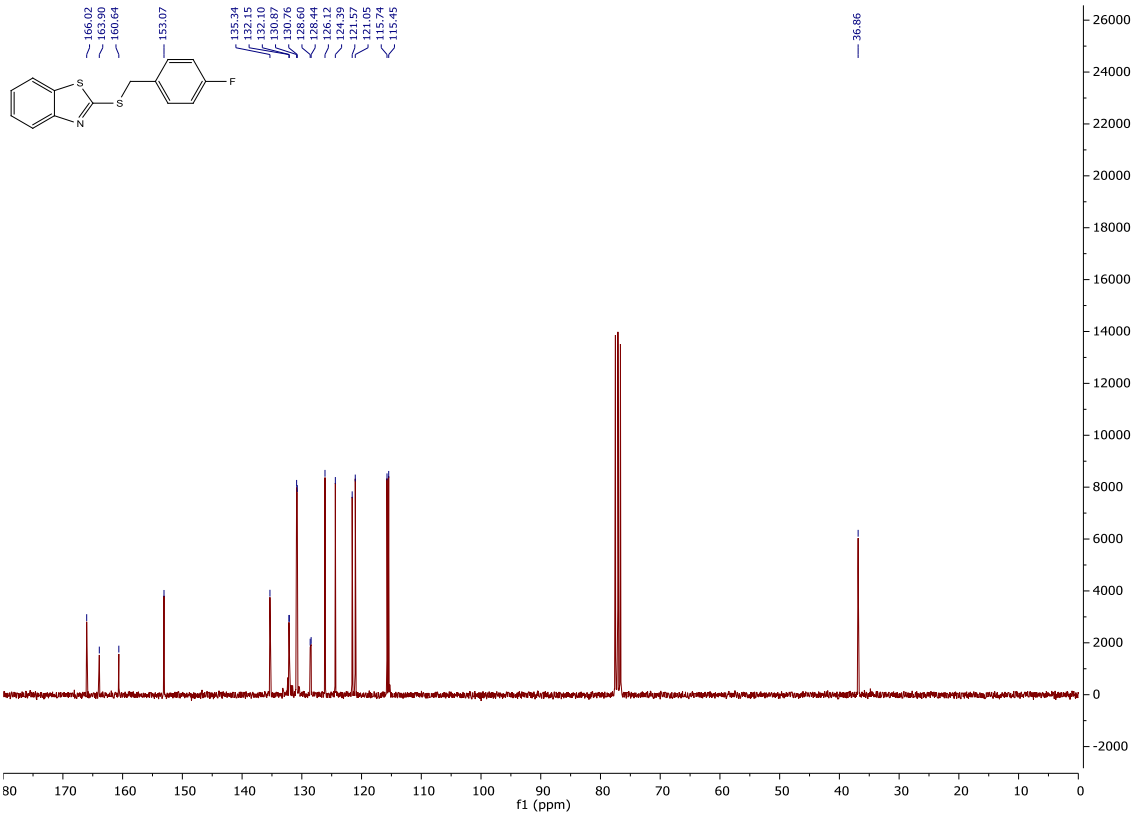
2-(benzylthio)benzo[d]thiazole (3e)



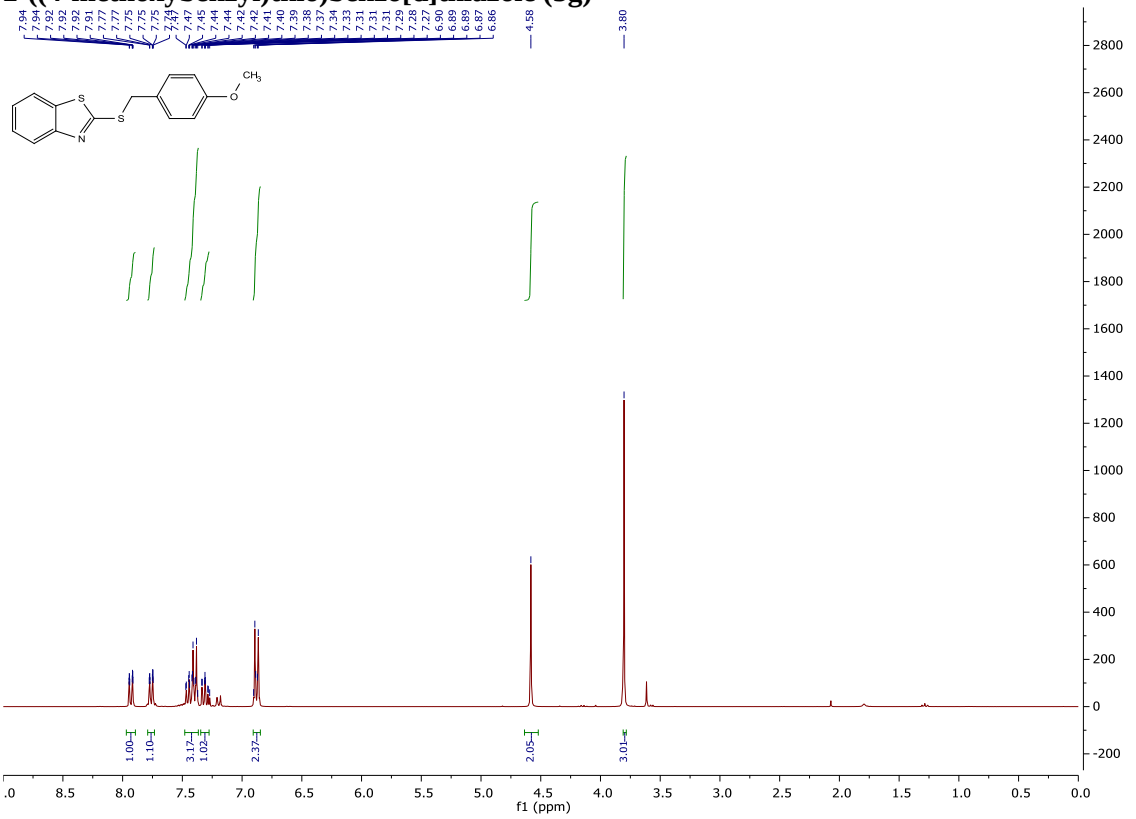


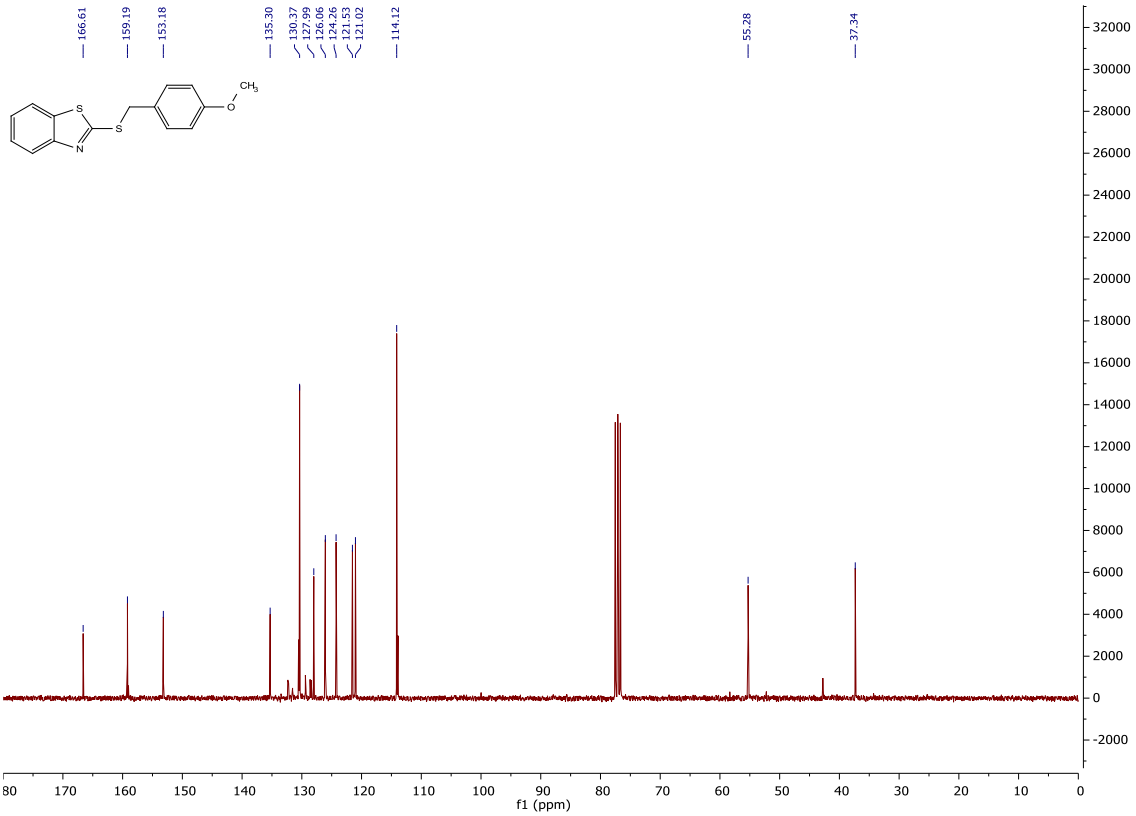
2-((4-fluorobenzyl)thio)benzo[d]thiazole (3f)



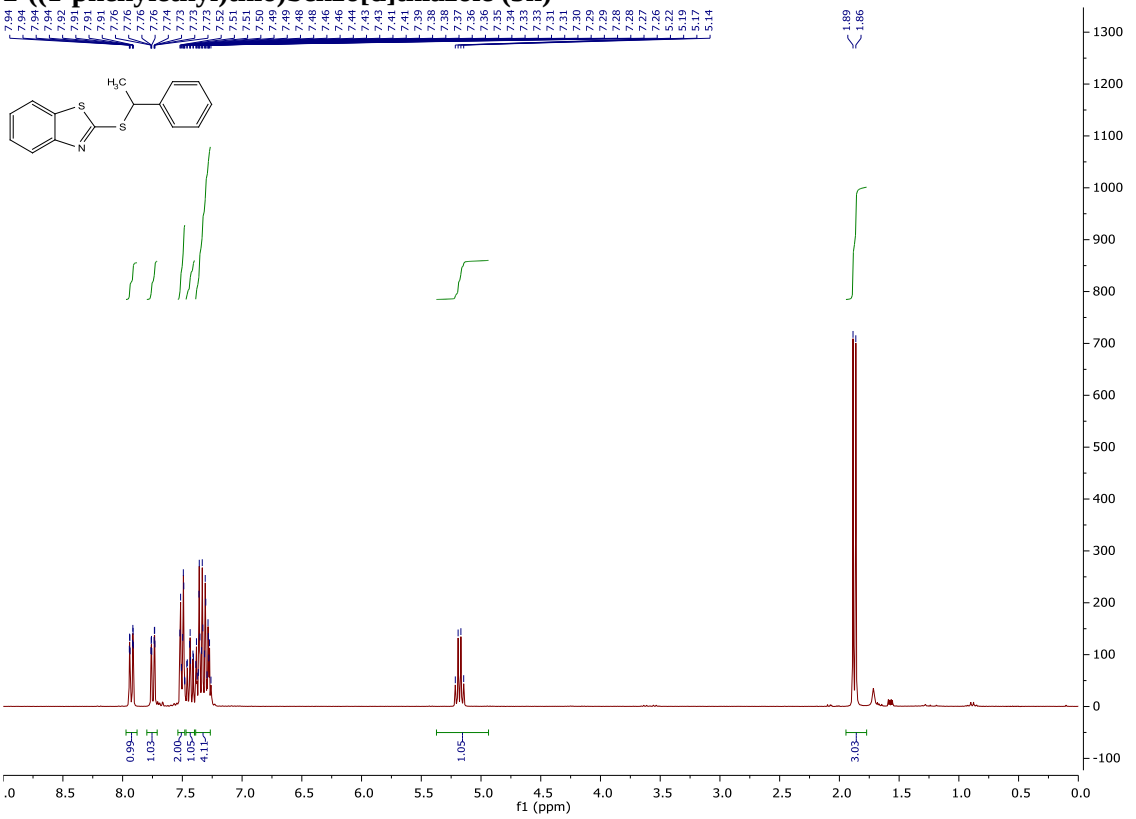


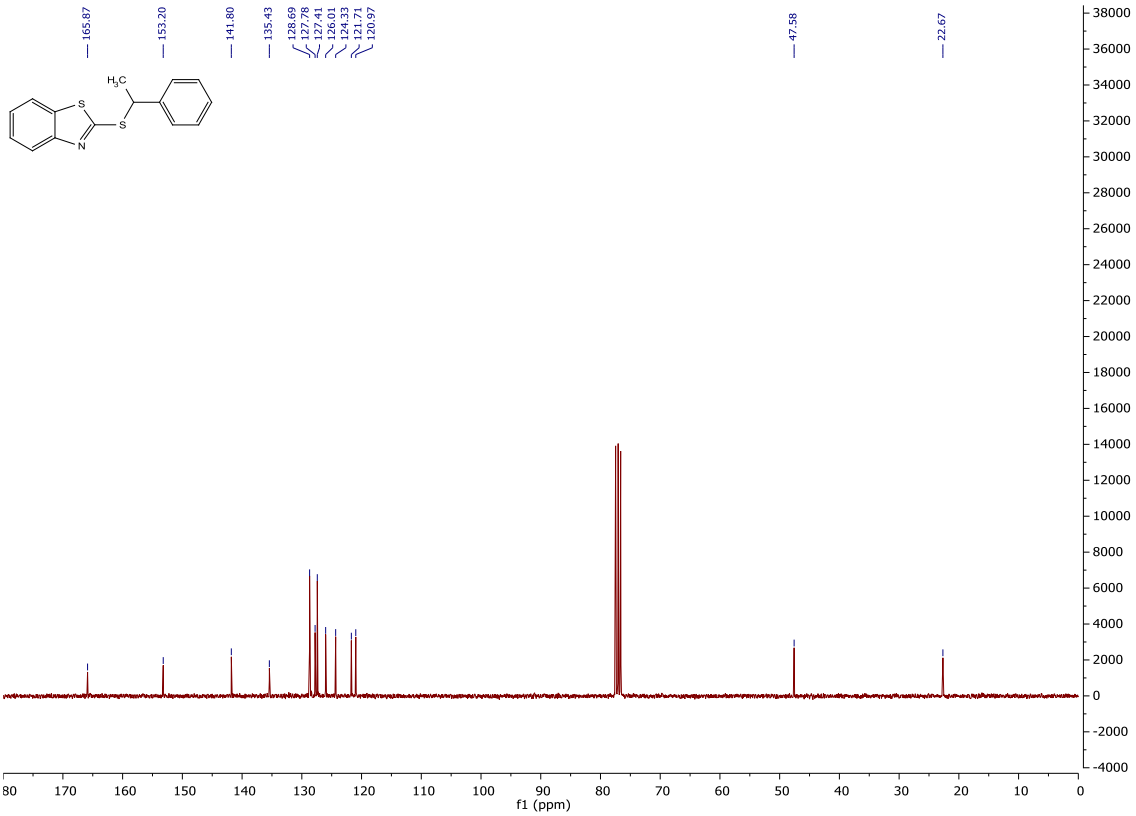
2-((4-methoxybenzyl)thio)benzo[d]thiazole (3g)



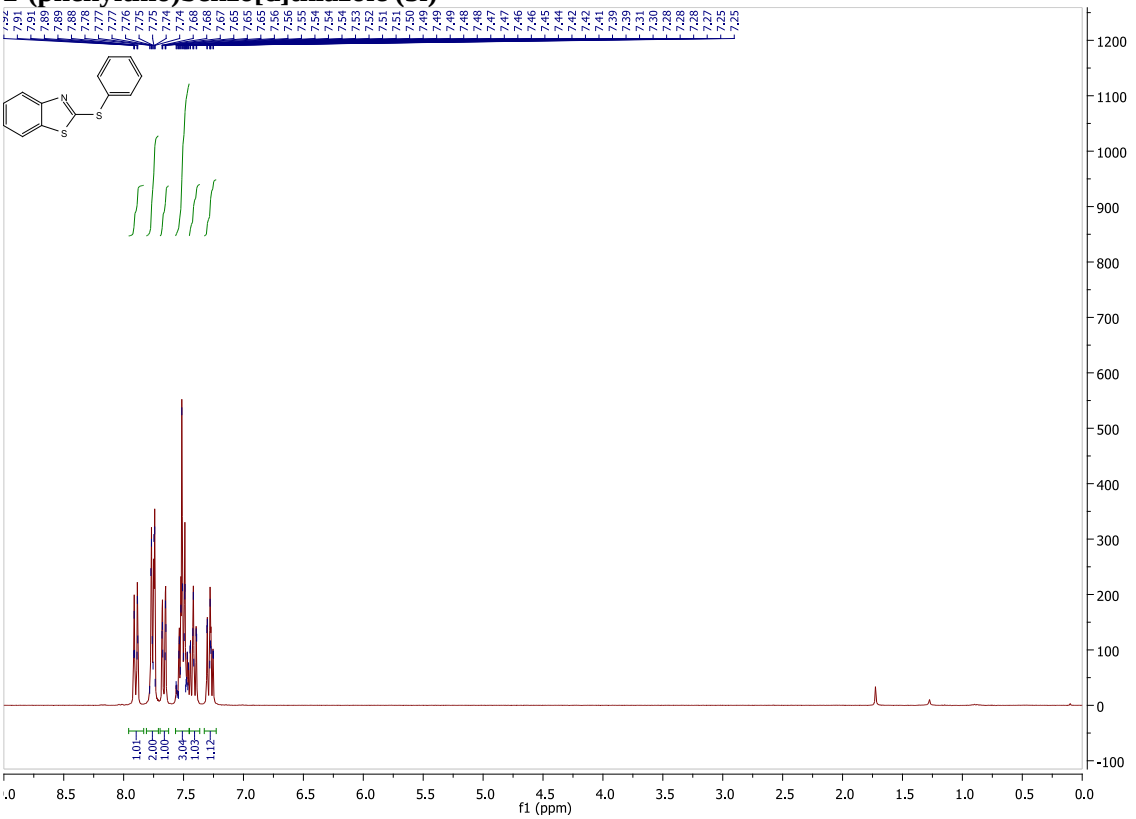


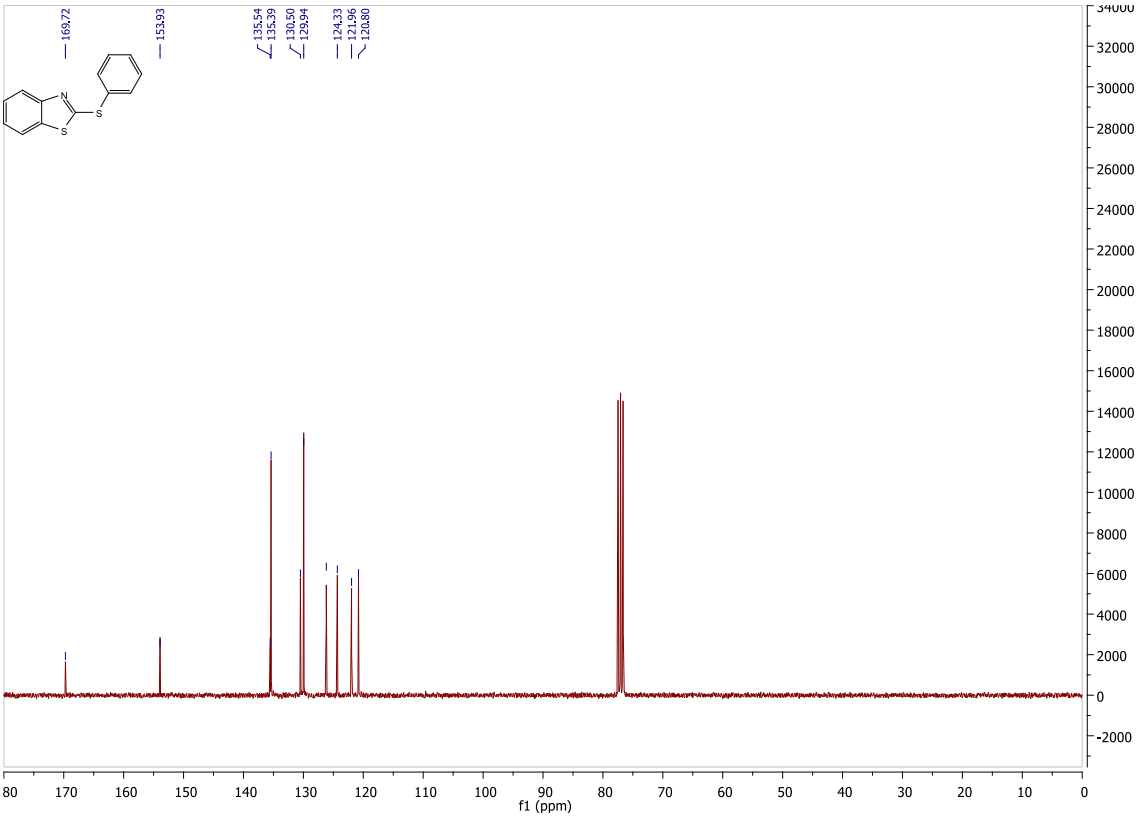
2-((1-phenylethyl)thio)benzo[d]thiazole (3h)



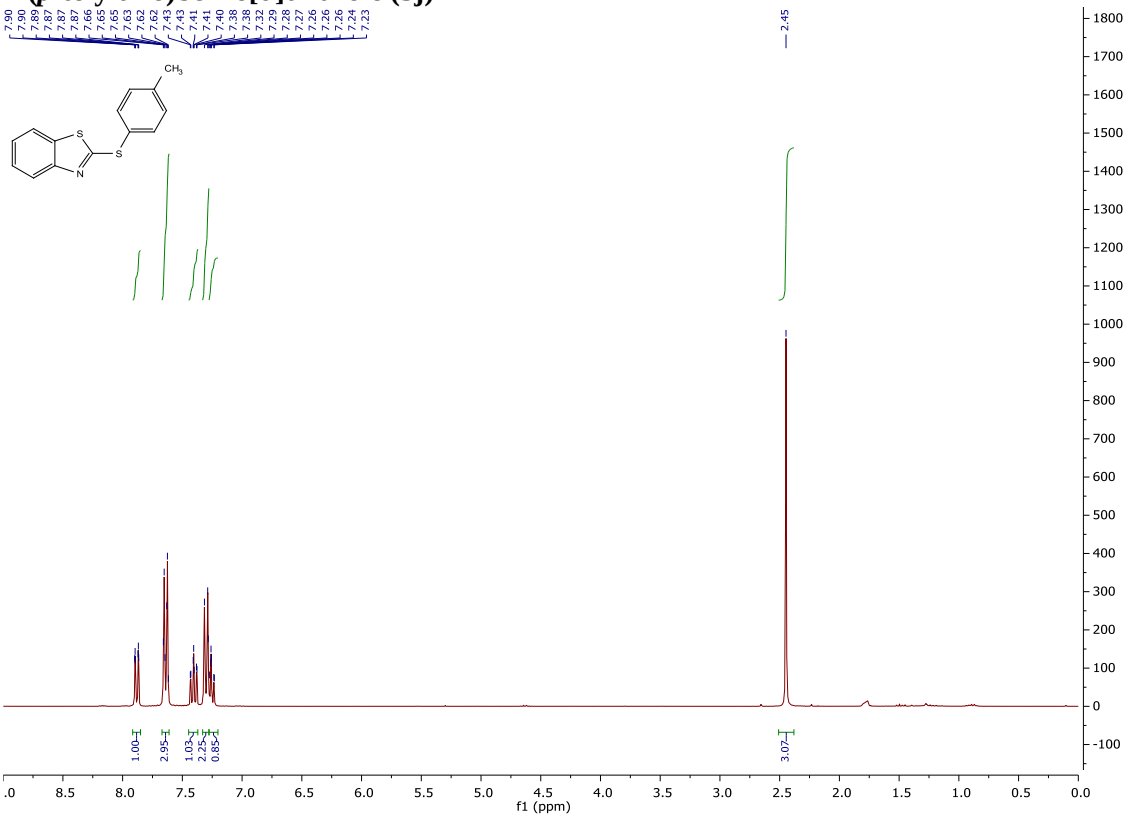


2-(phenylthio)benzo[d]thiazole (3i)

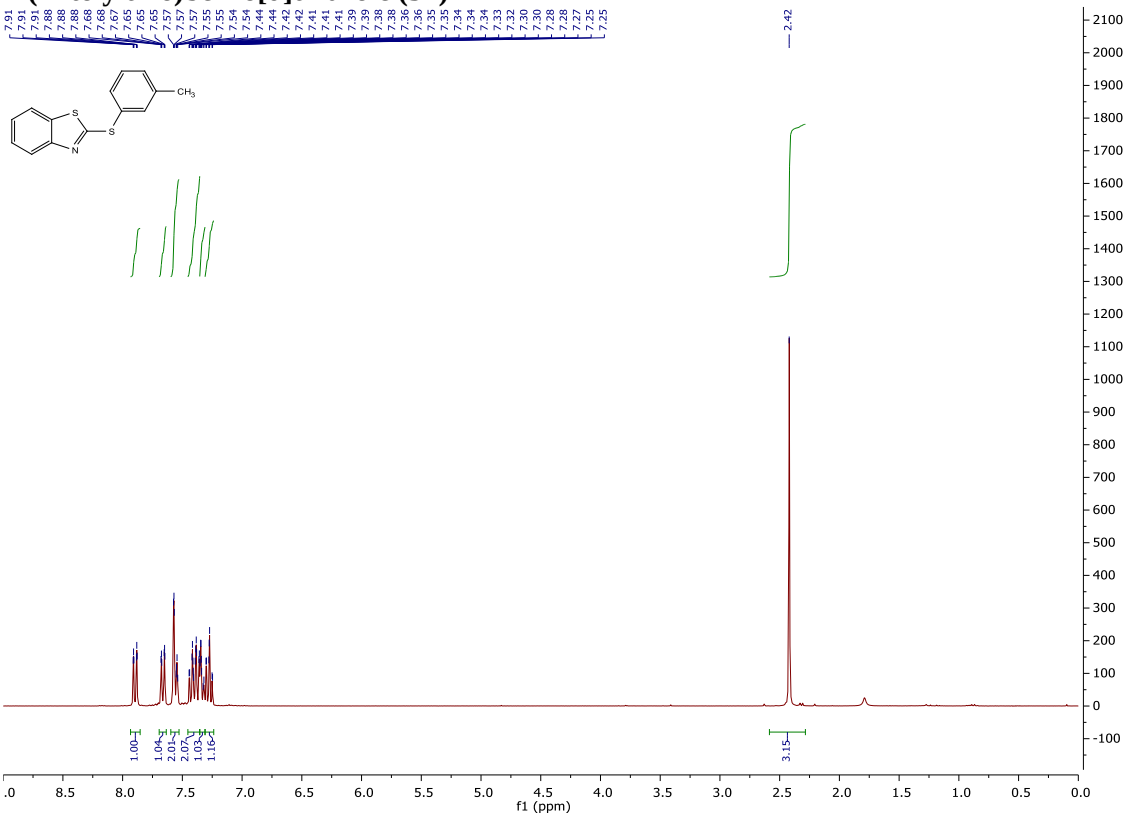


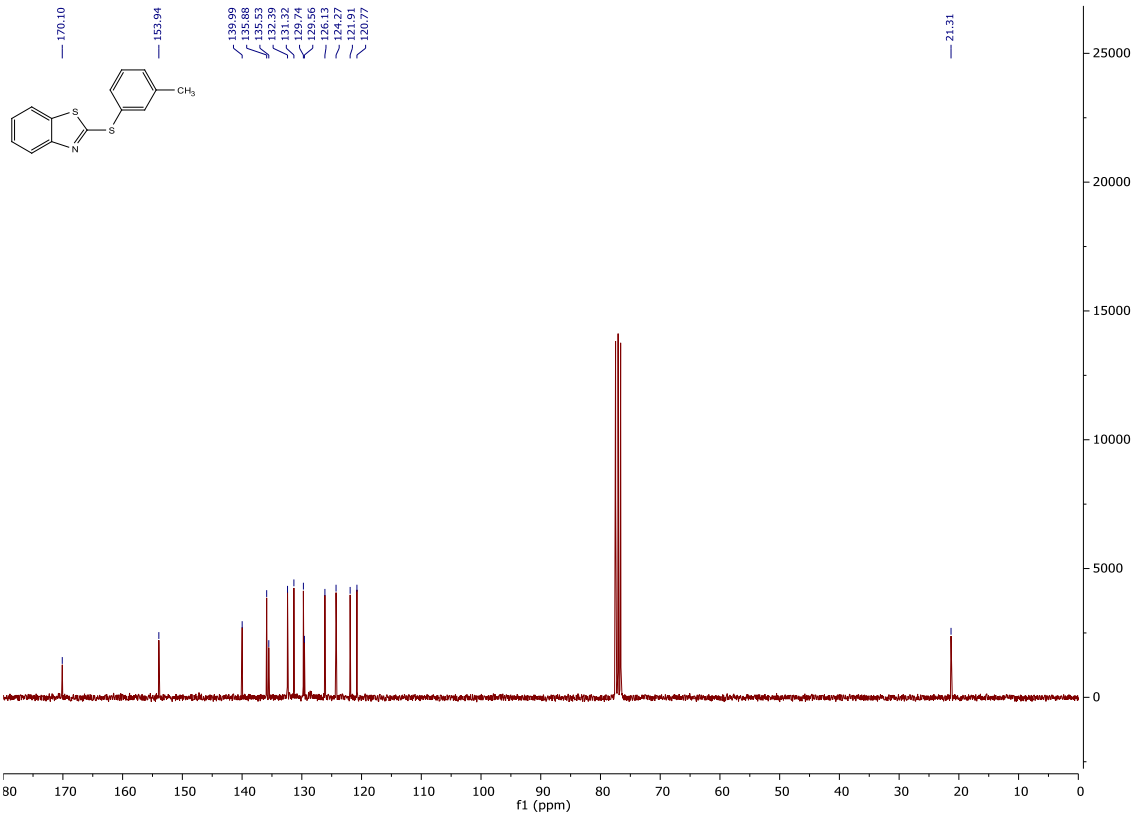


2-(*p*-tolylthio)benzo[d]thiazole (3j)

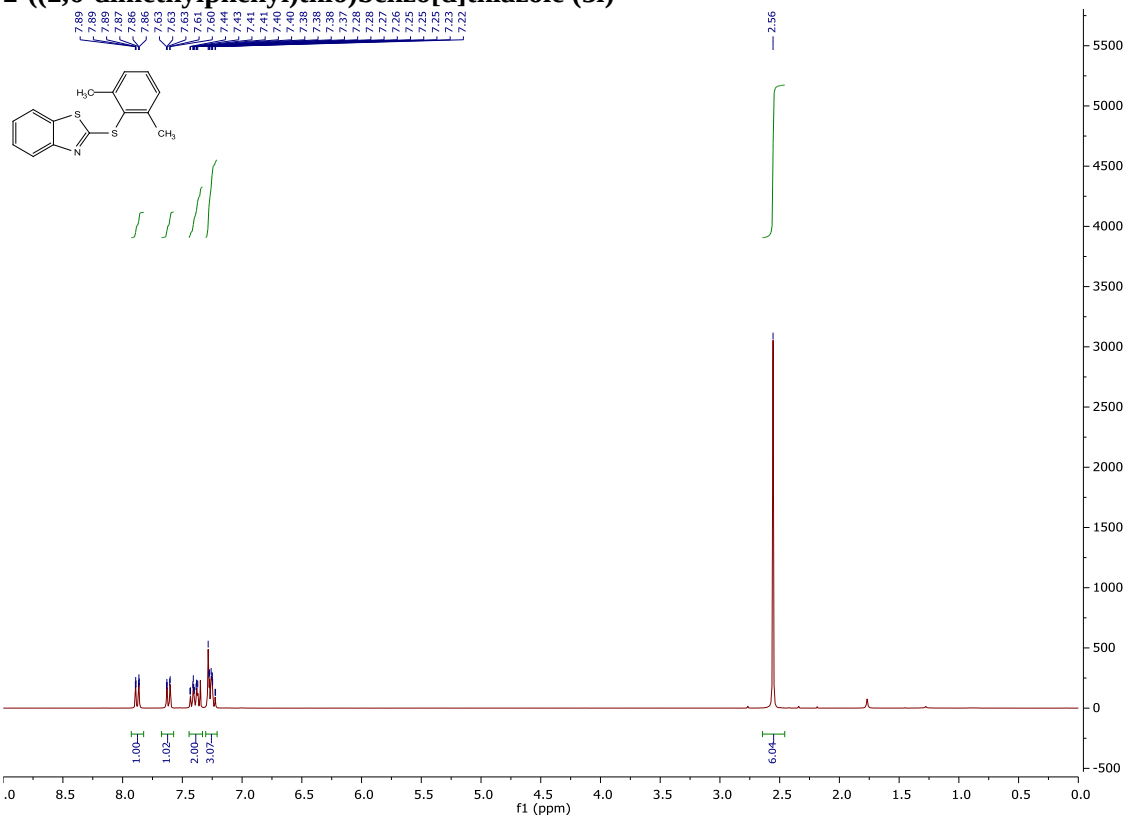


2-(*m*-tolylthio)benzo[d]thiazole (3k)

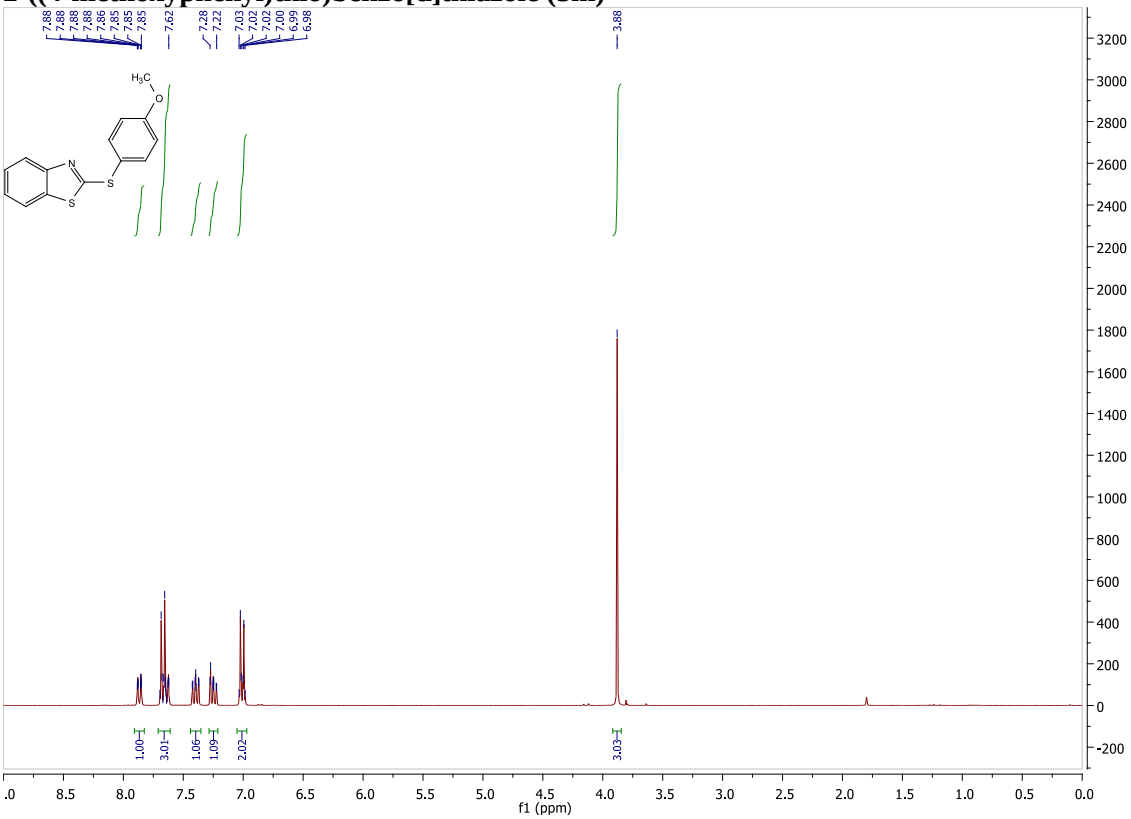


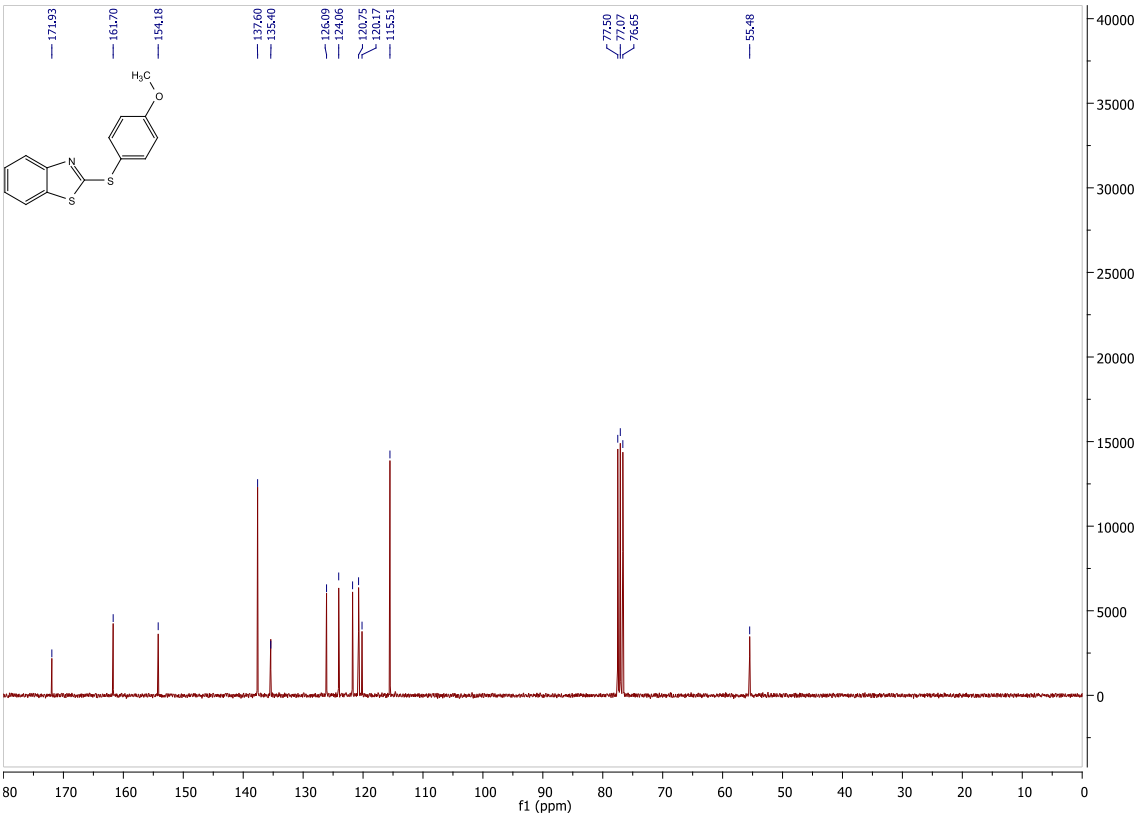


2-((2,6-dimethylphenyl)thio)benzo[d]thiazole (3l)

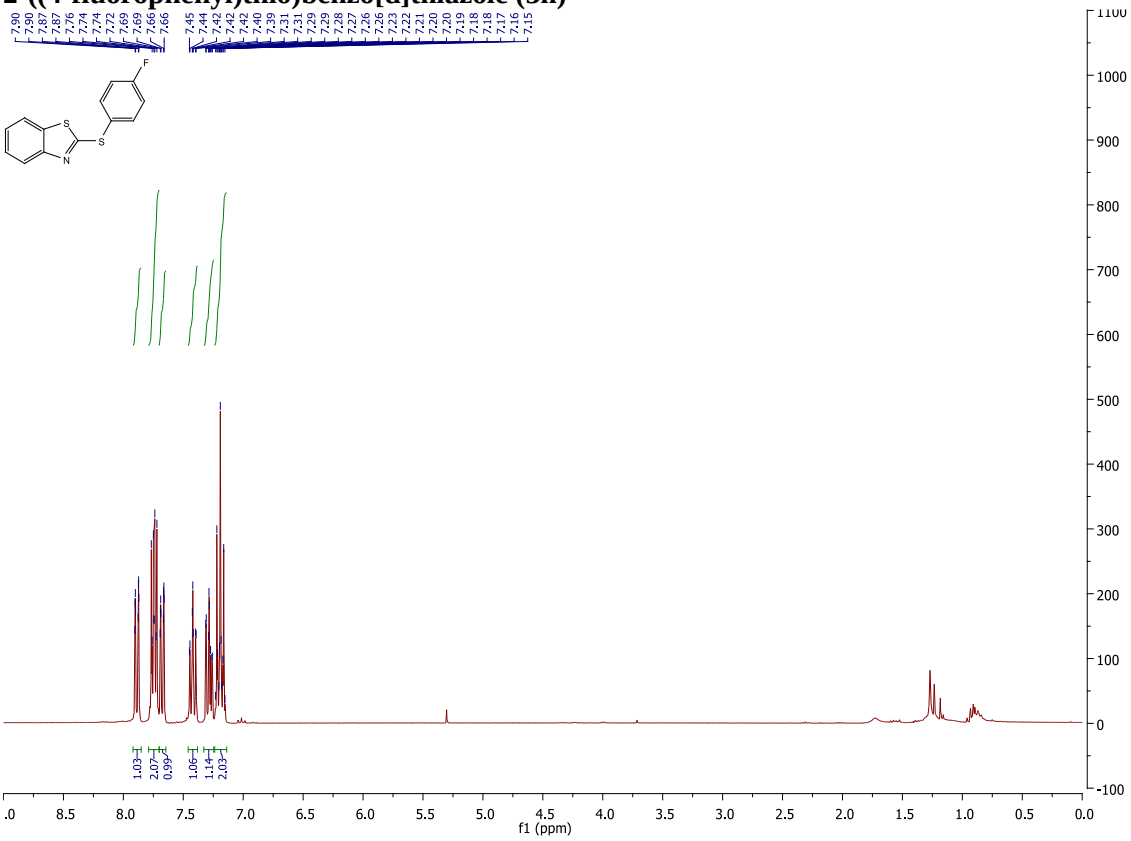


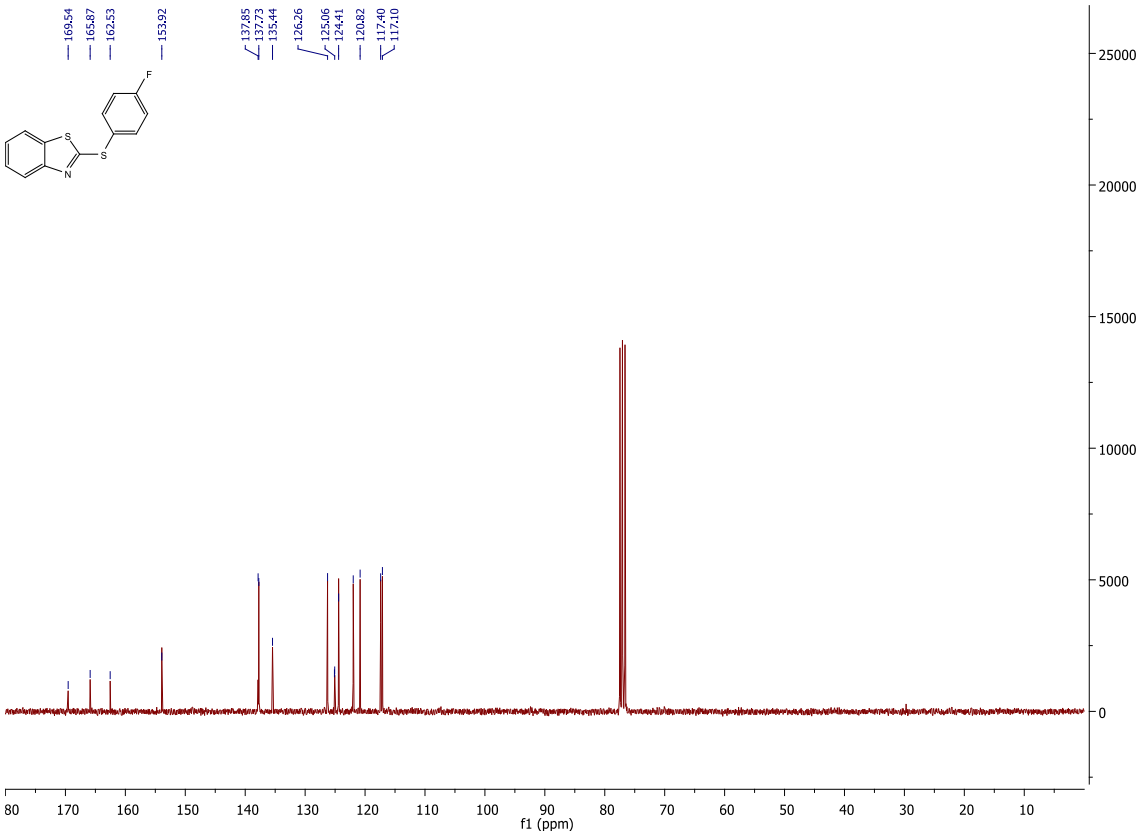
2-((4-methoxyphenyl)thio)benzo[d]thiazole (3m)



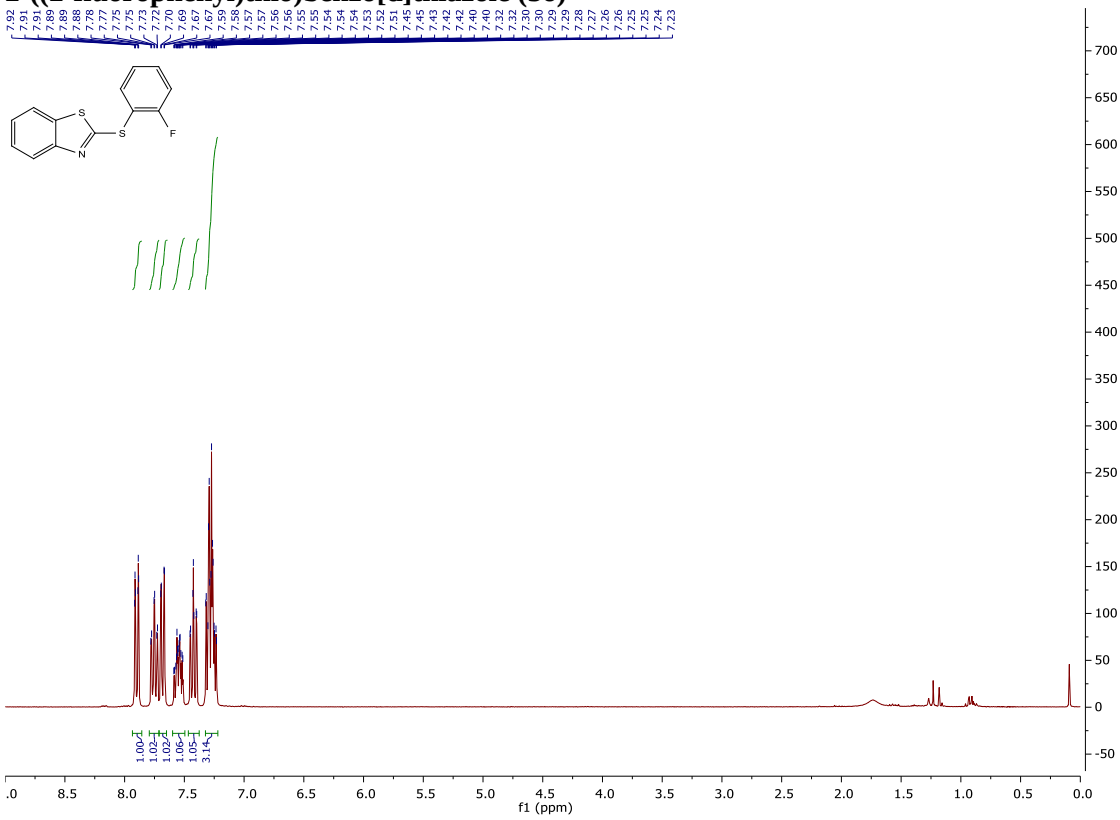


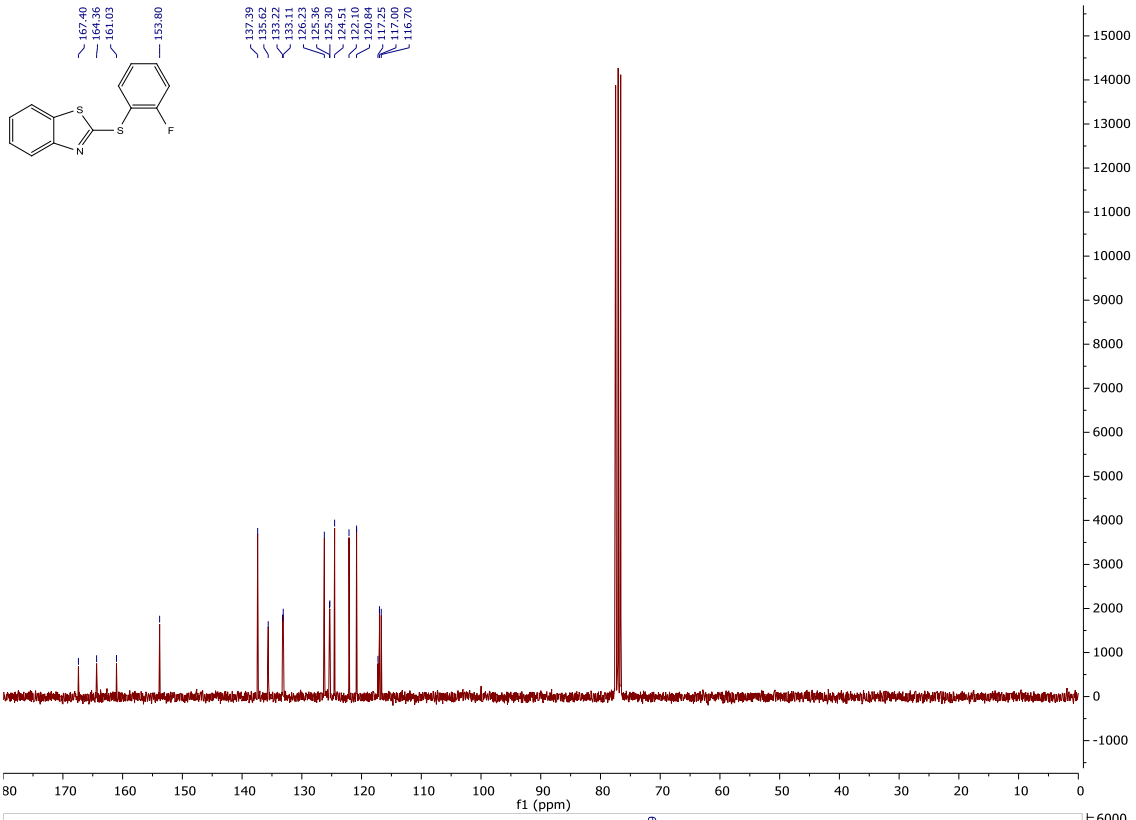
2-((4-fluorophenyl)thio)benzo[d]thiazole (3n)

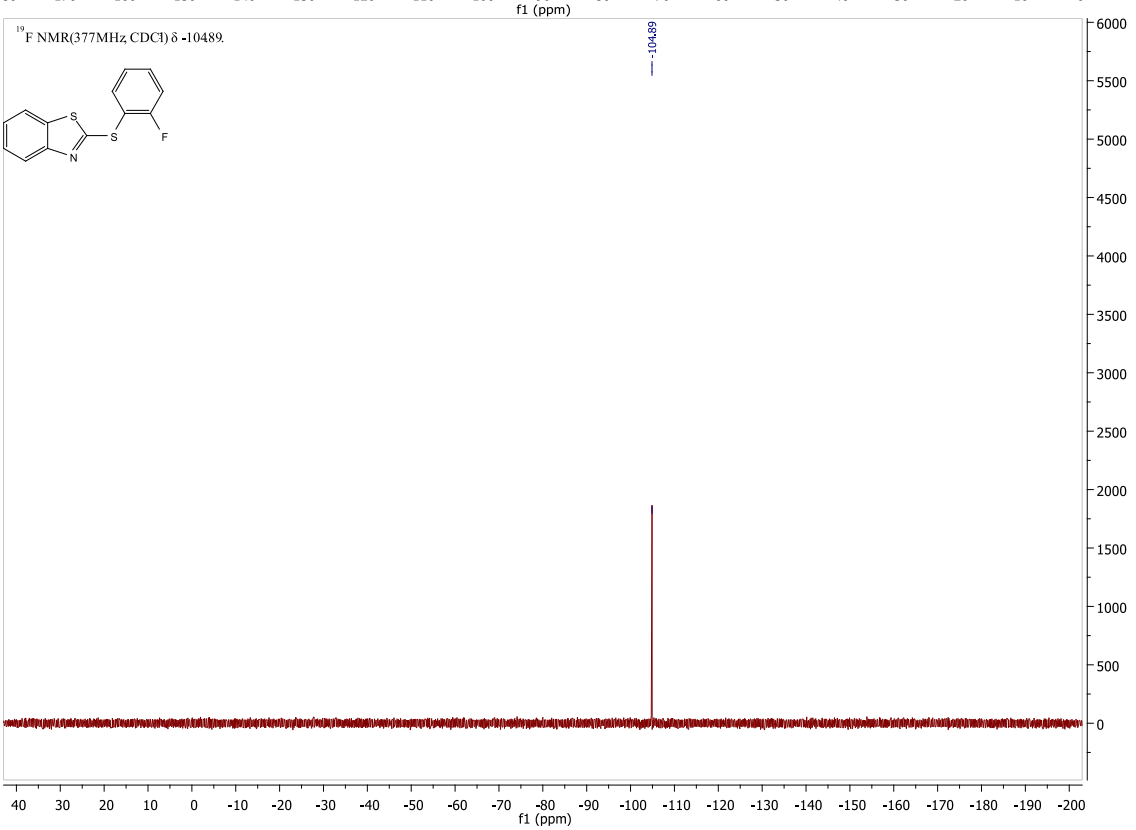




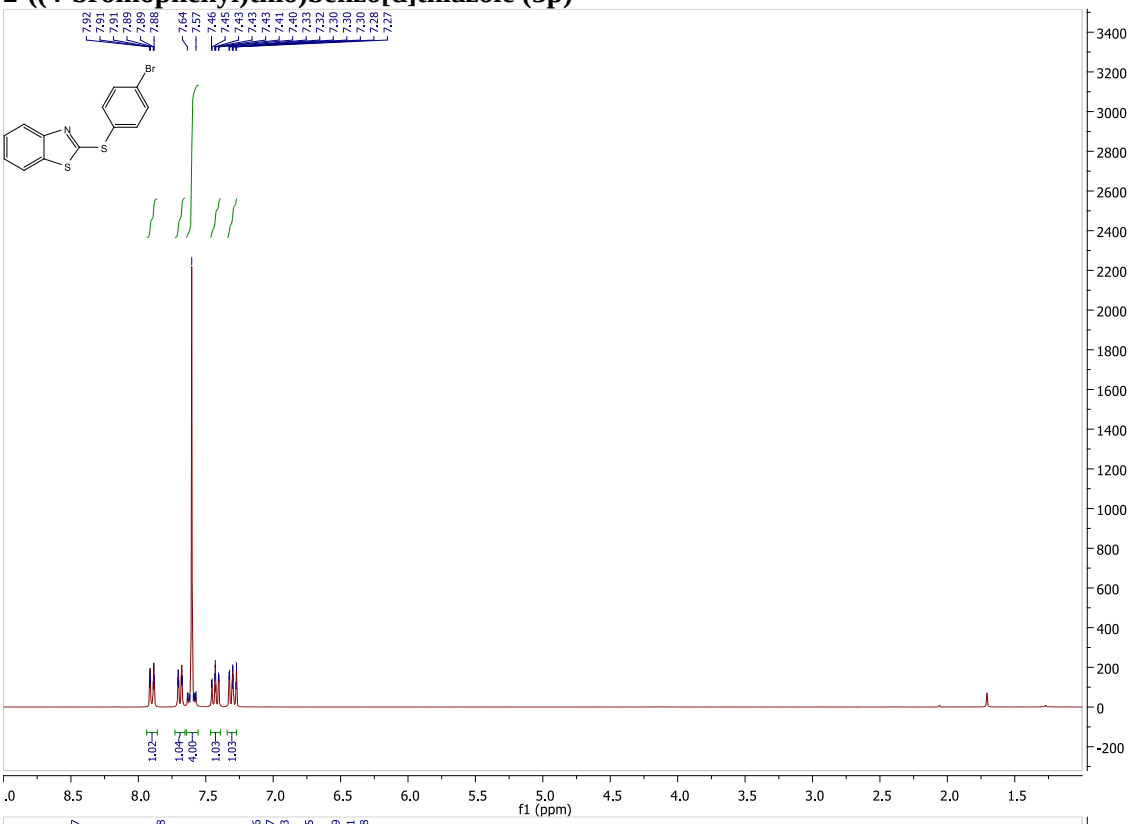
2-((2-fluorophenyl)thio)benzo[d]thiazole (3o)

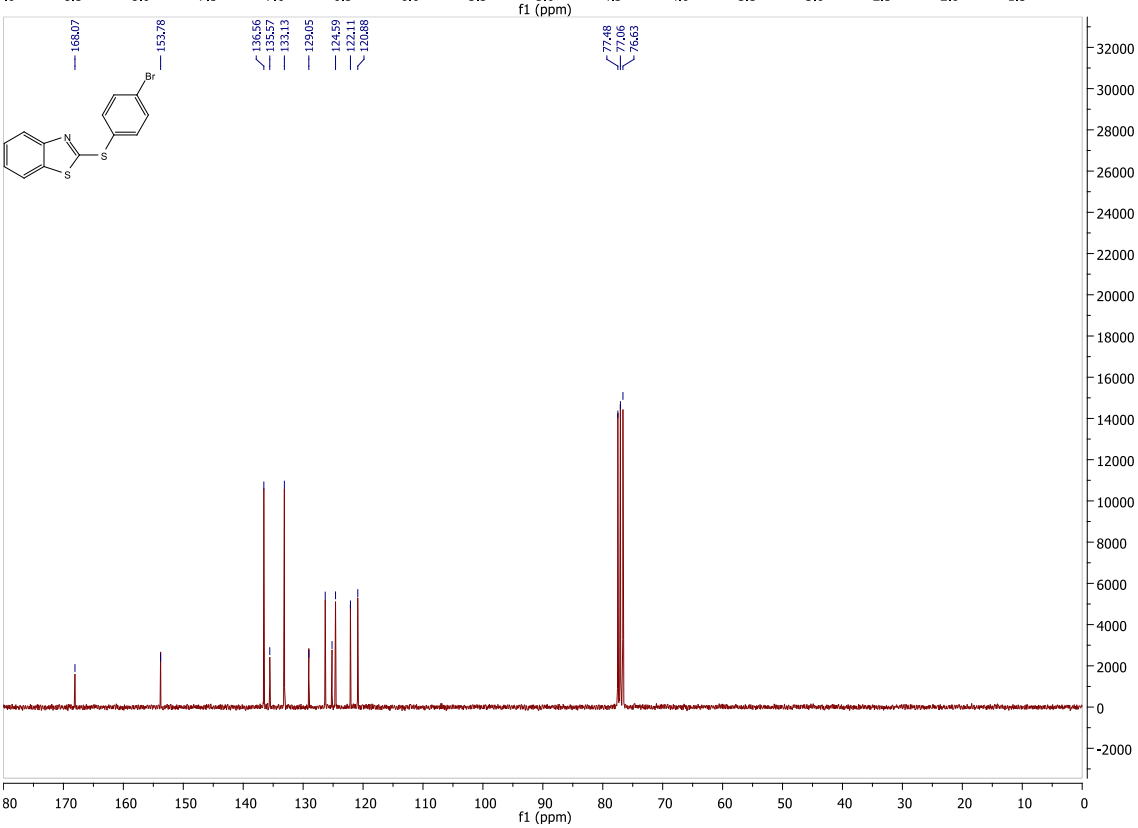



167.40
164.36
161.03
153.80
137.39
135.62
133.22
133.11
126.23
125.36
125.20
124.51
122.10
120.84
117.25
117.00
116.70
S
S
N
F
f1 (ppm)

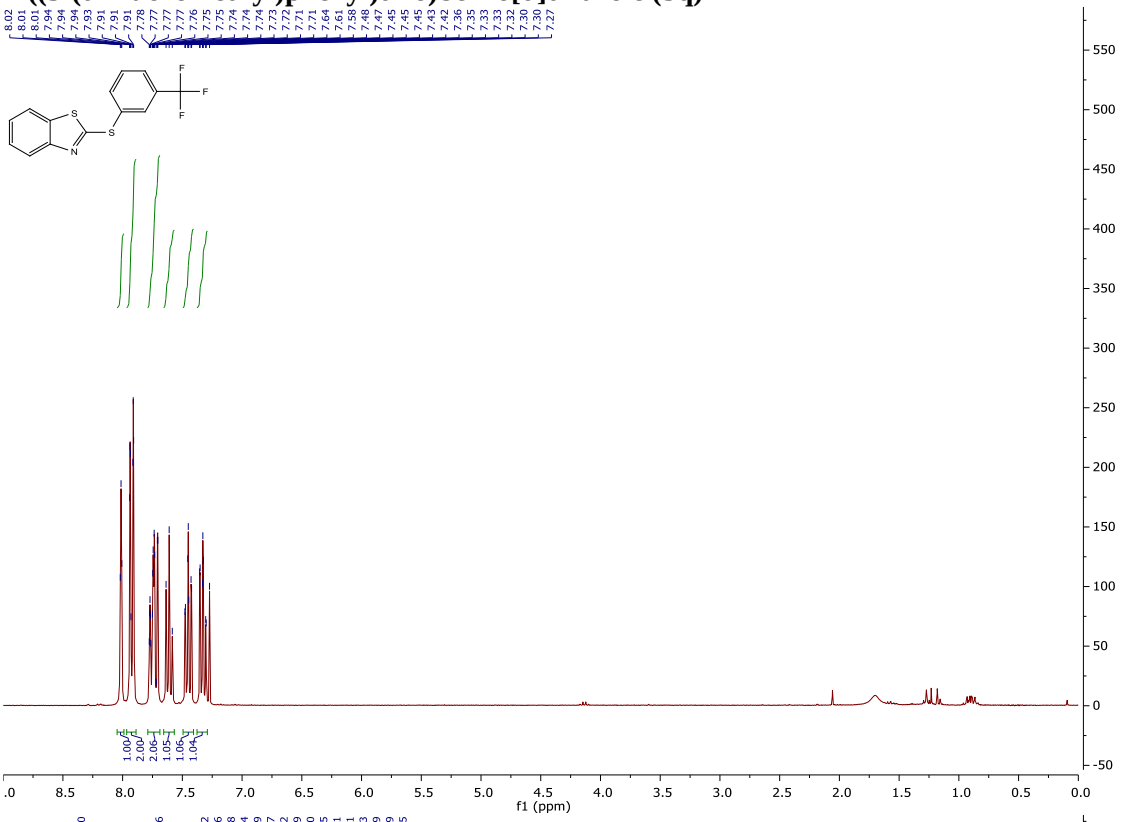

^{19}F NMR(377MHz, CDCl) δ -10489.
-104.89
S
S
N
F
f1 (ppm)

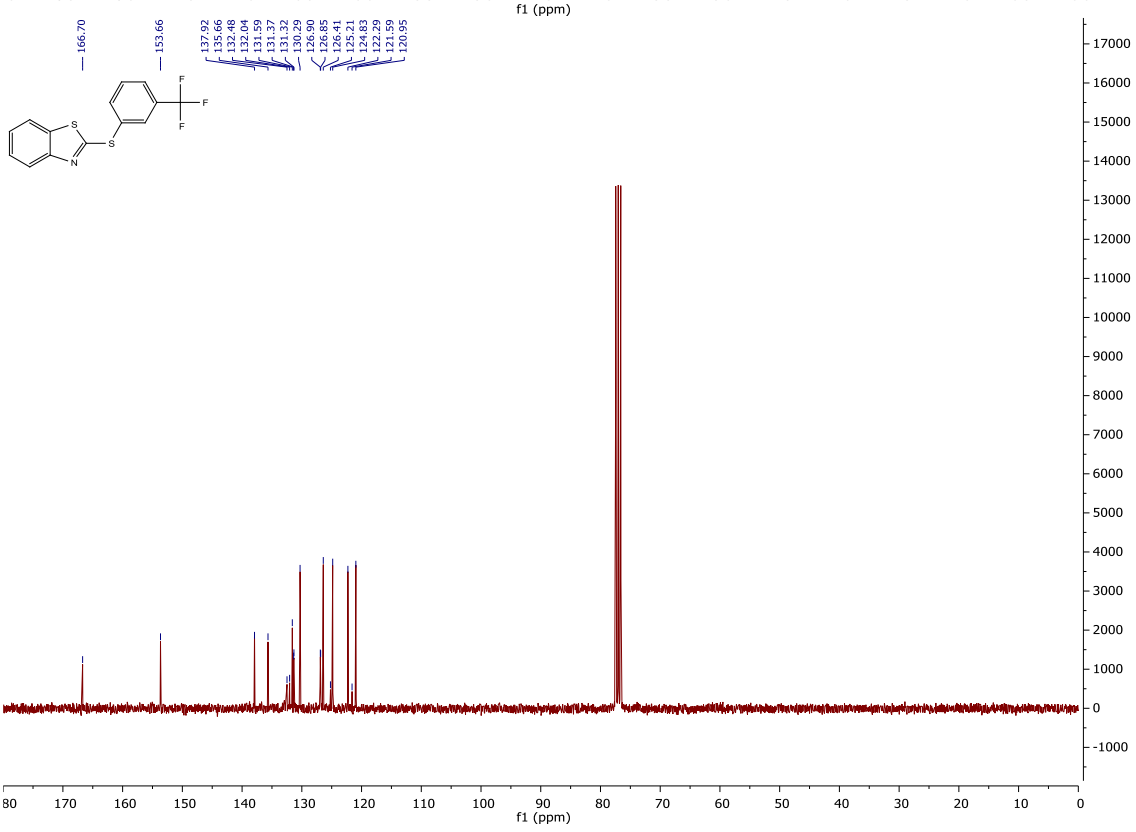
2-((4-bromophenyl)thio)benzo[d]thiazole (3p)



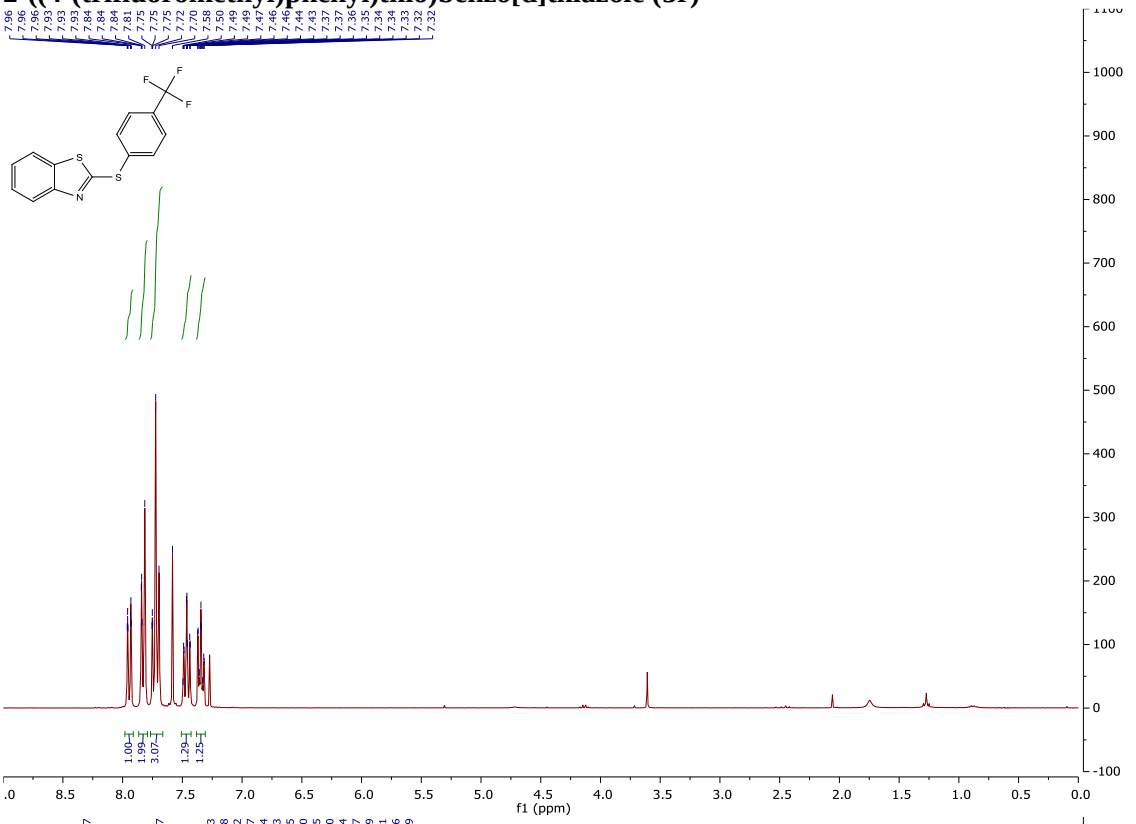


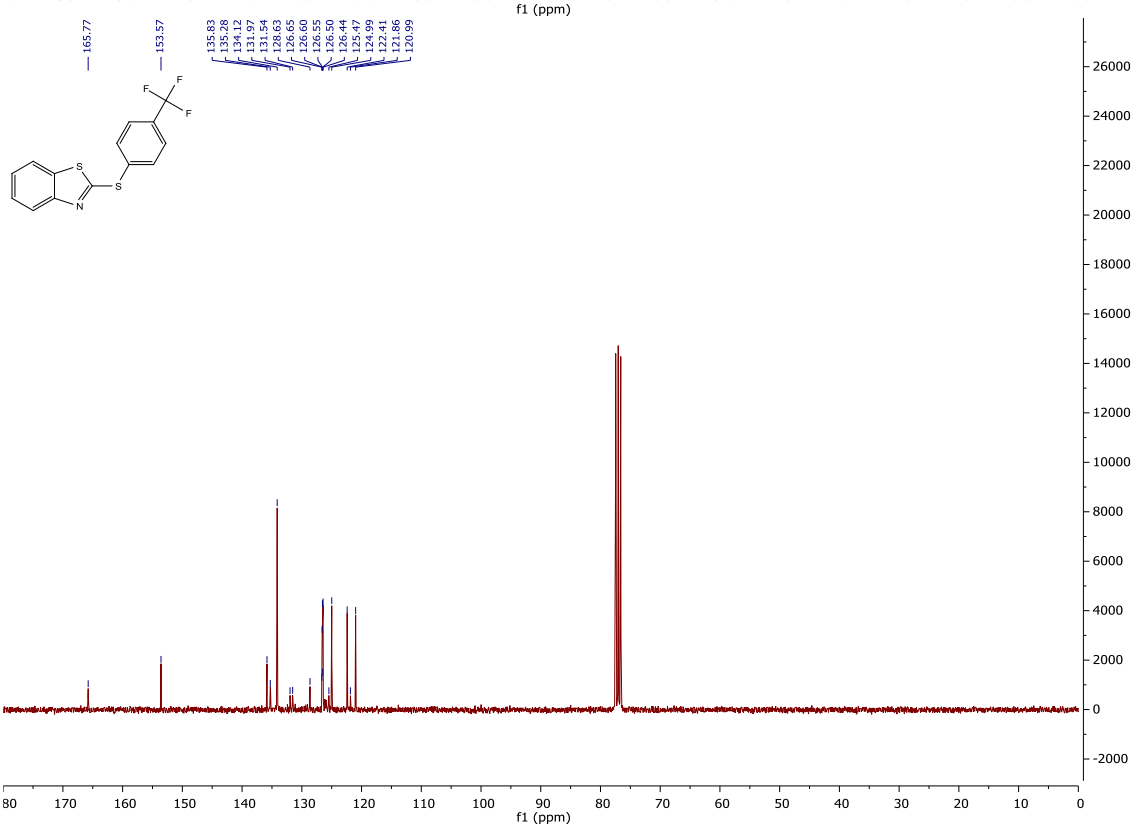
2-((3-(trifluoromethyl)phenyl)thio)benzo[d]thiazole (3q)



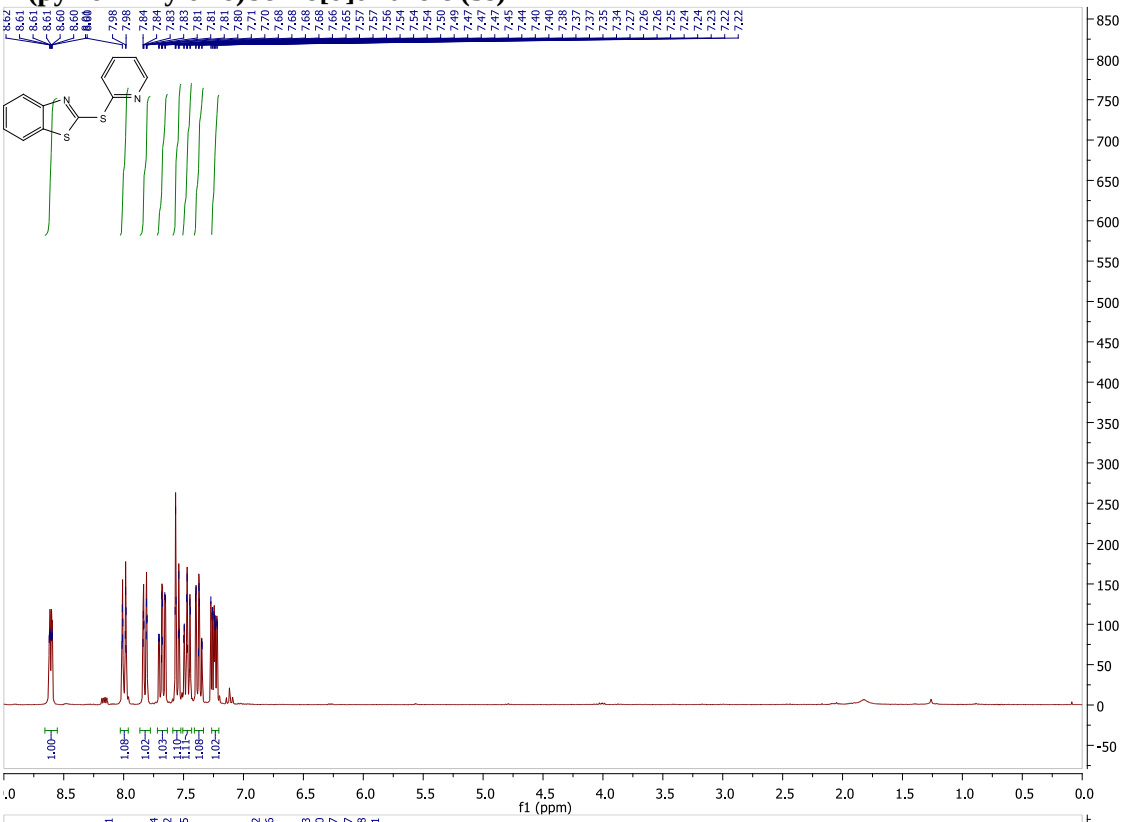


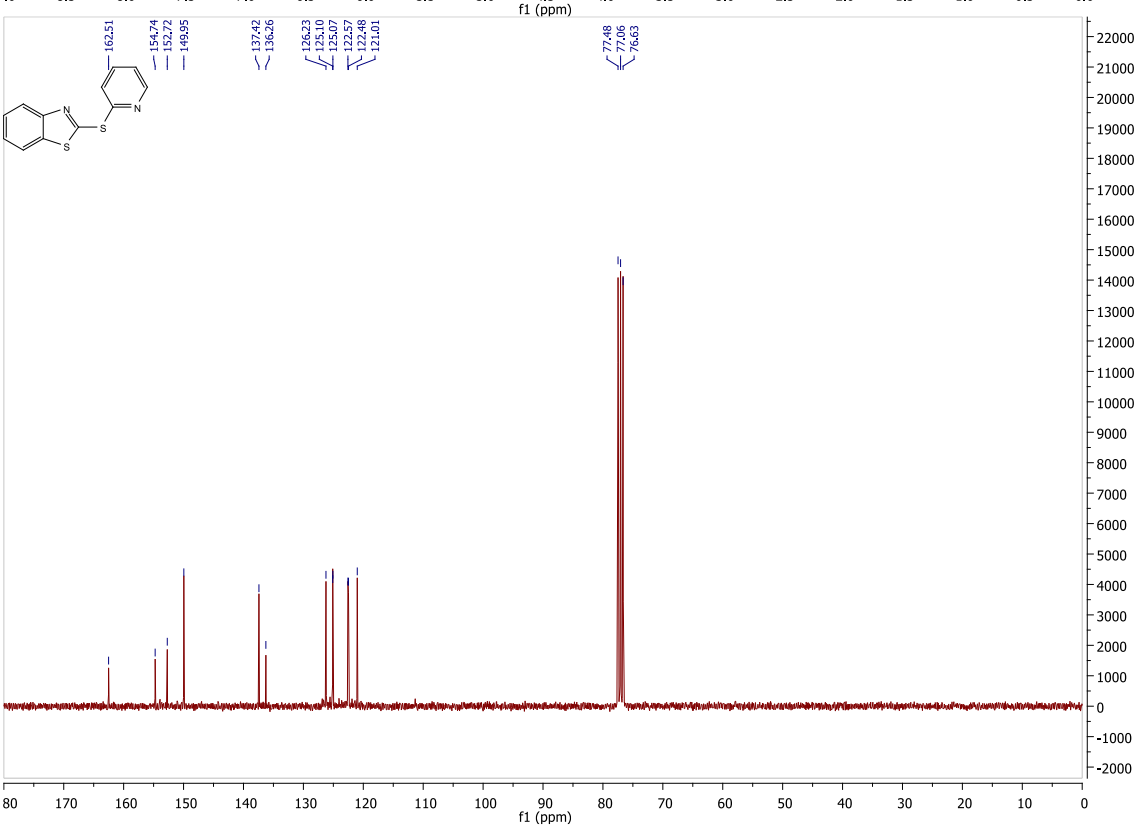
2-((4-(trifluoromethyl)phenyl)thio)benzo[d]thiazole (3r)



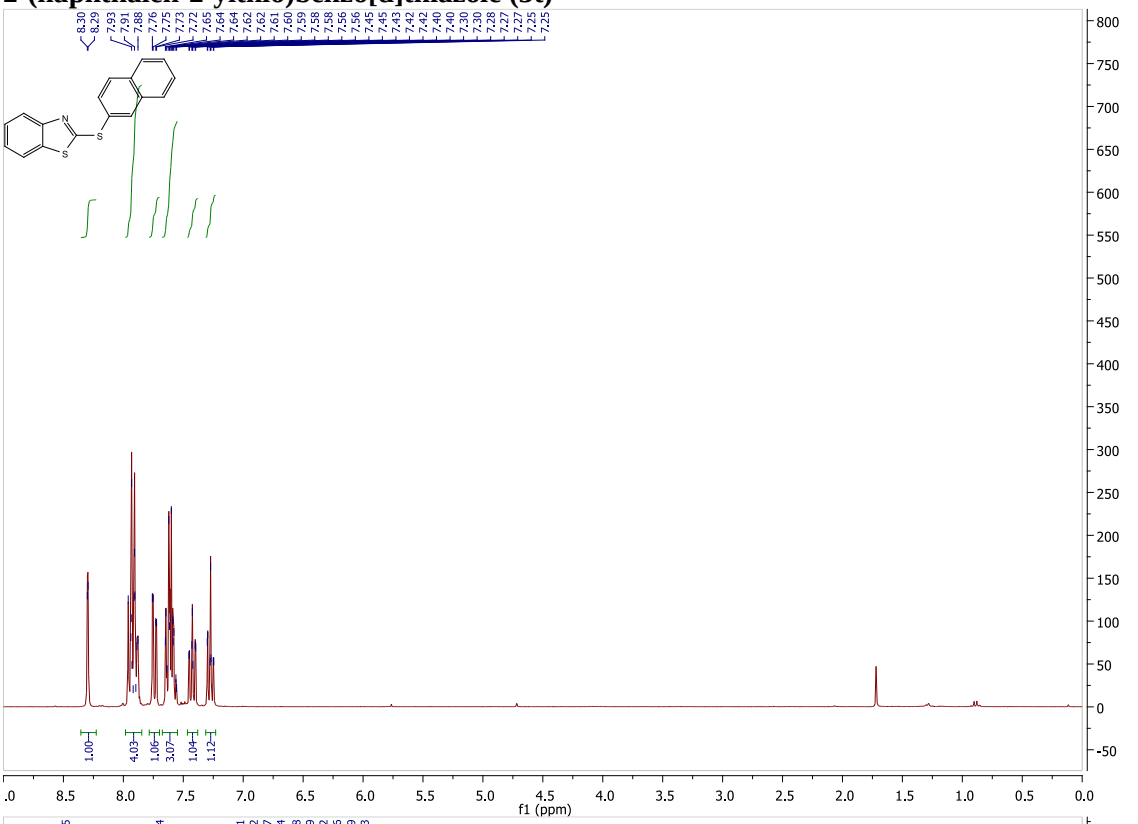


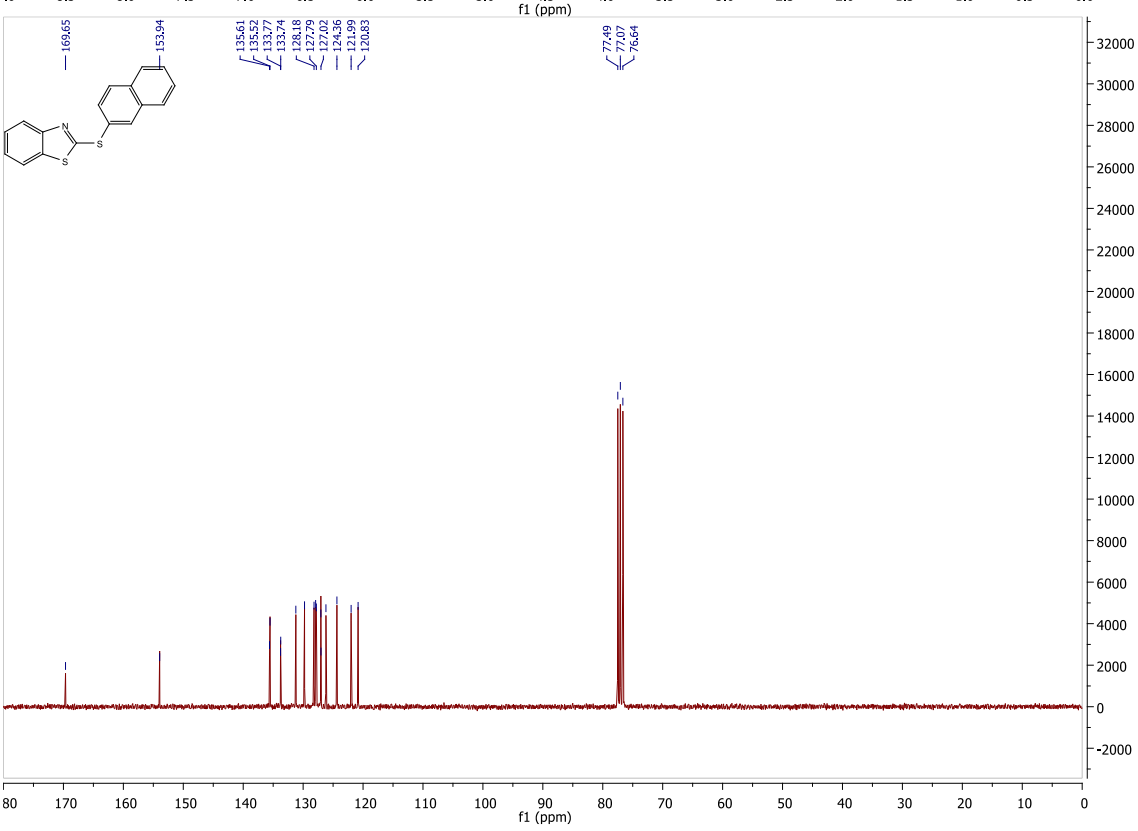
2-(pyridin-2-ylthio)benzo[d]thiazole (3s)



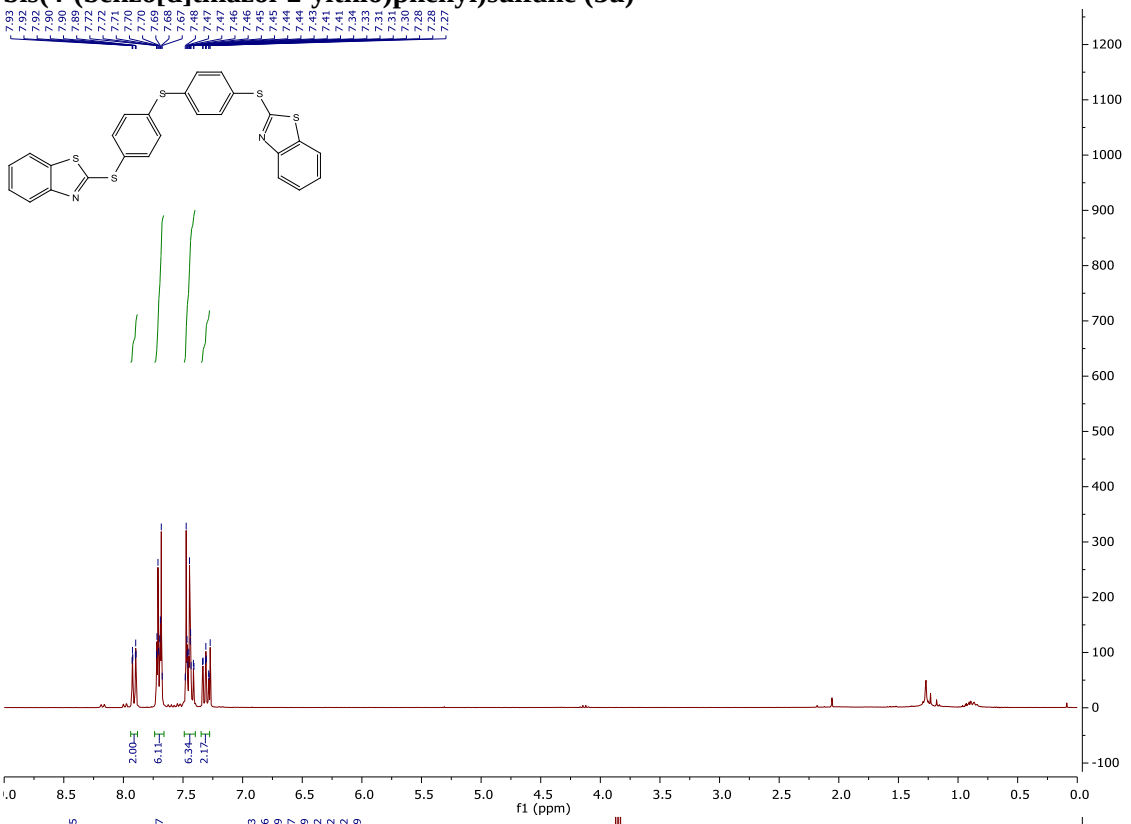


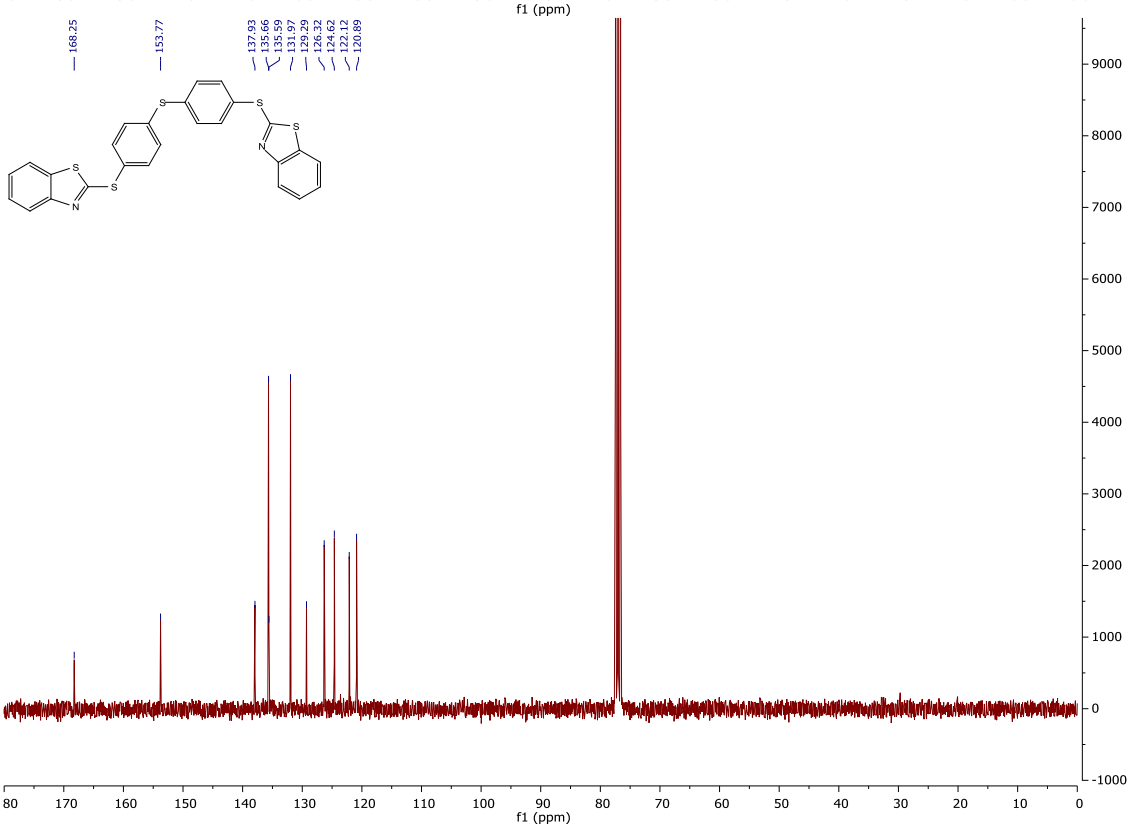
2-(naphthalen-2-ylthio)benzo[d]thiazole (3t)



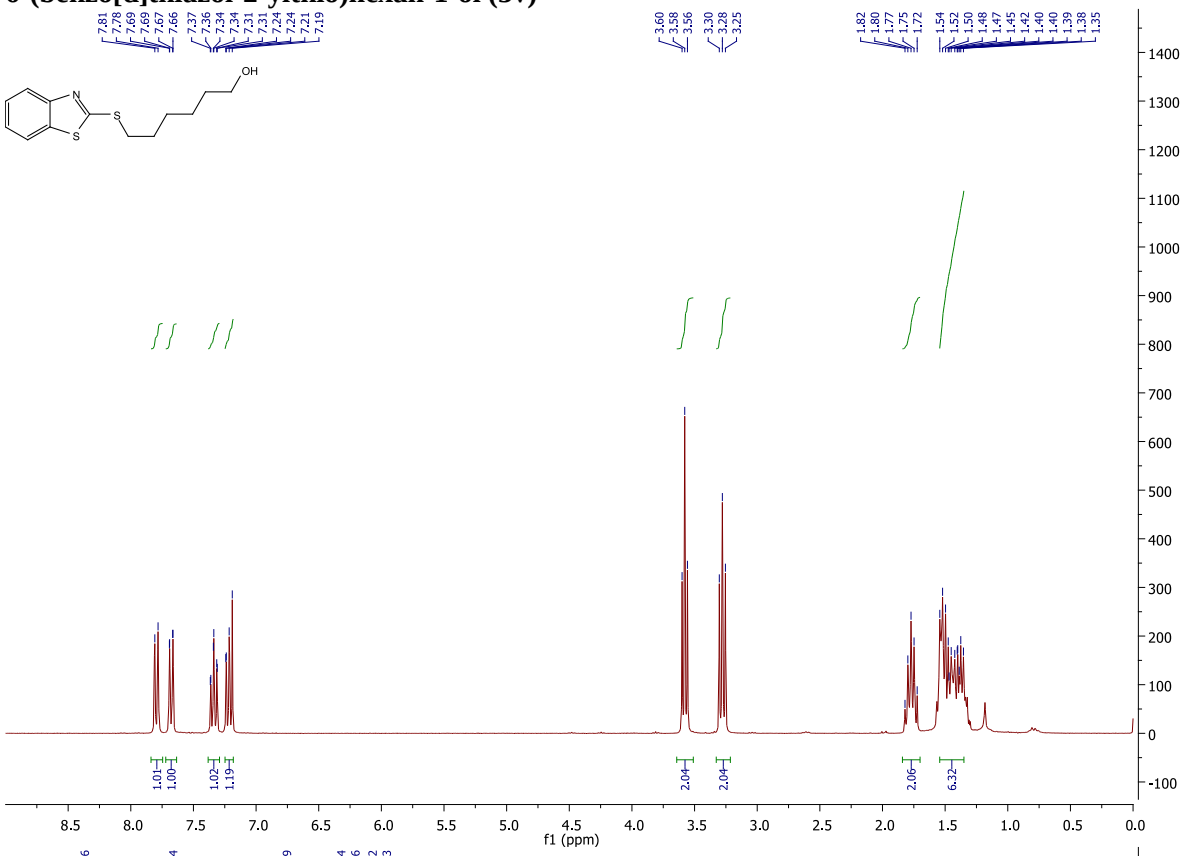


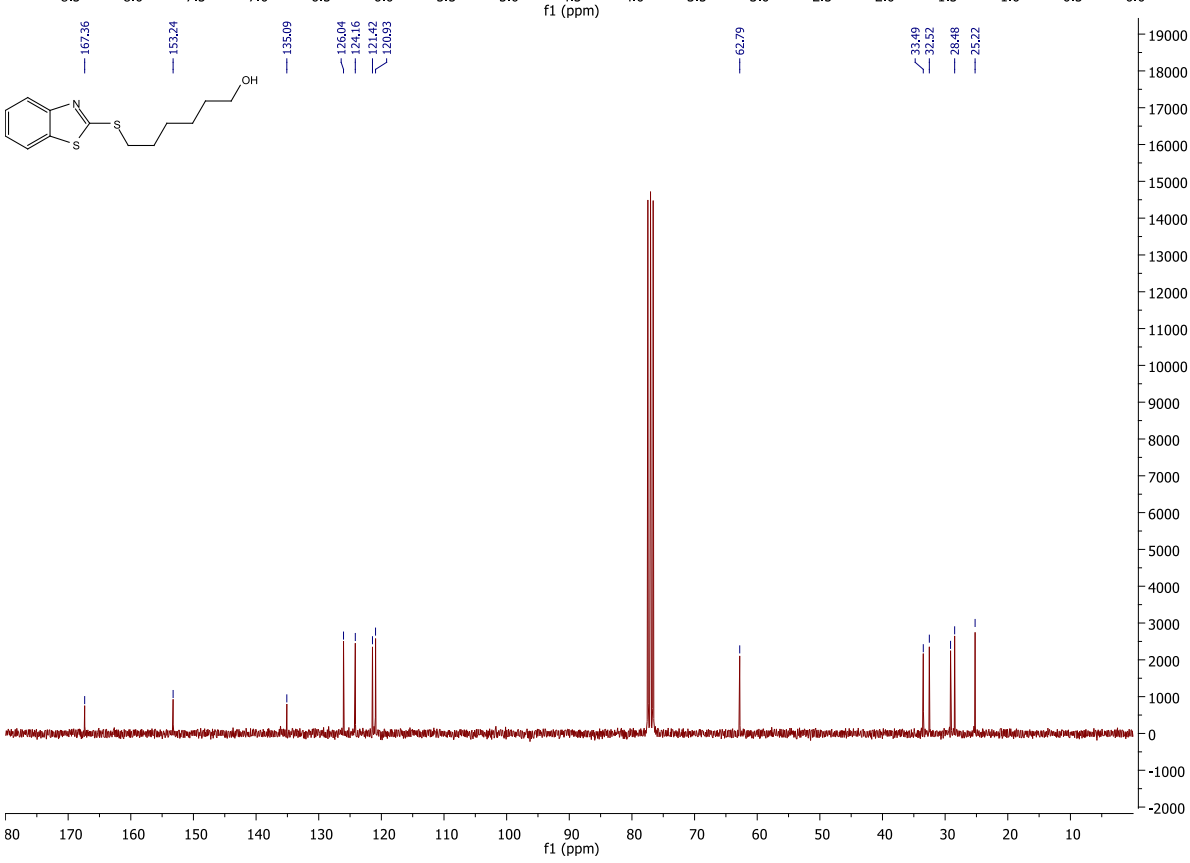
bis(4-(benzo[d]thiazol-2-ylthio)phenyl)sulfane (3u)



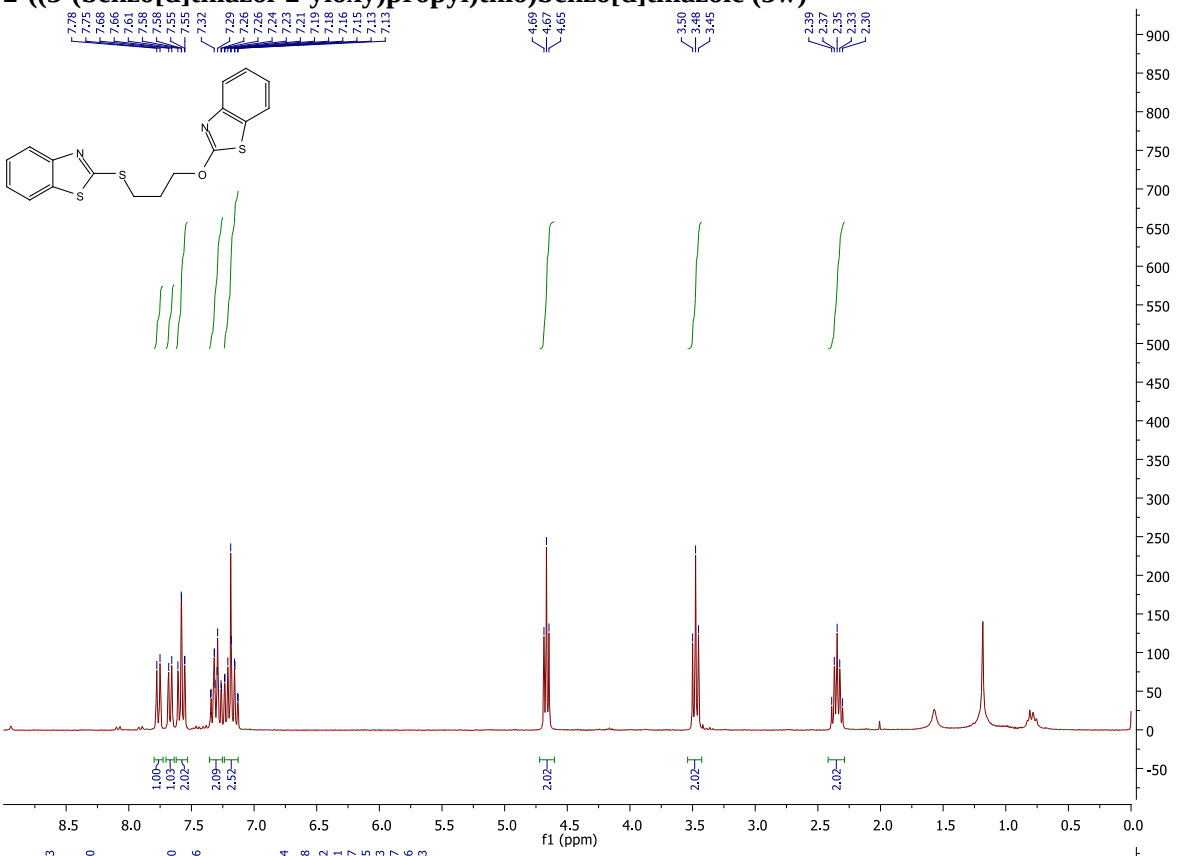


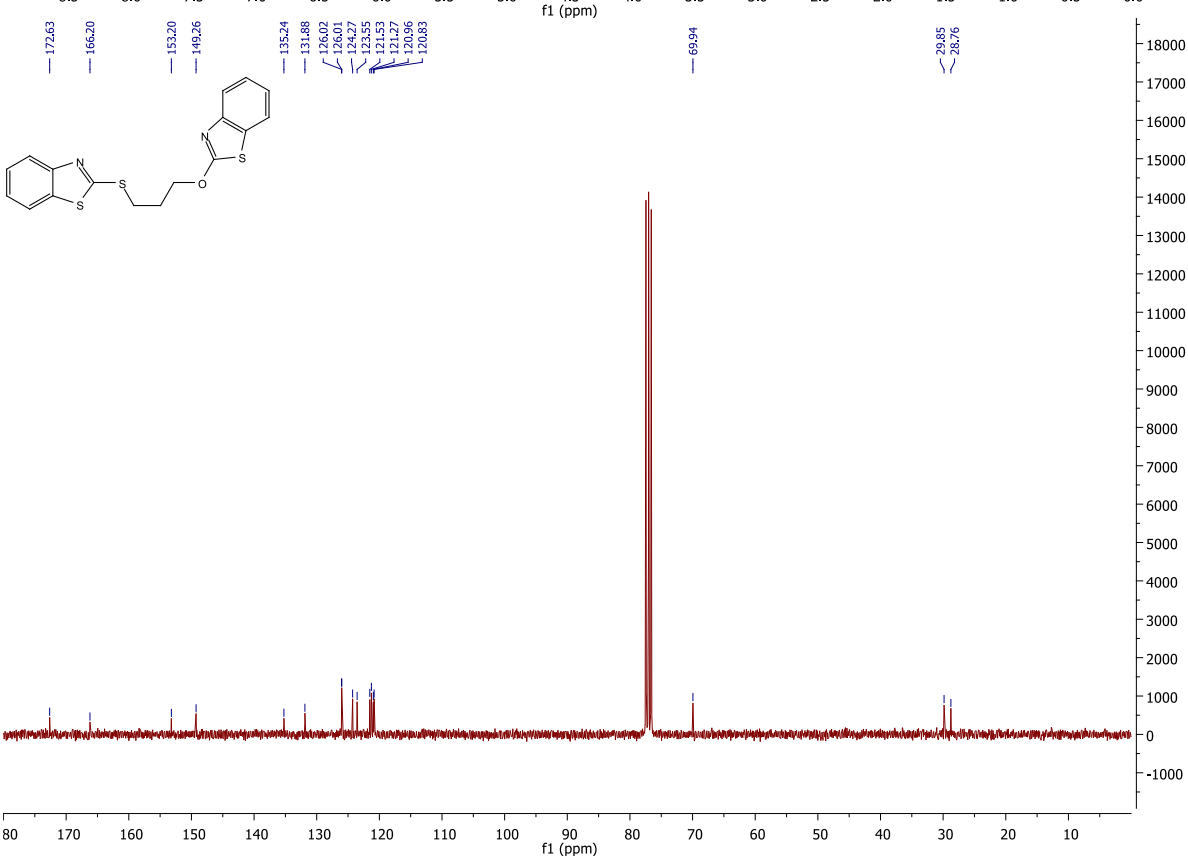
6-(benzo[d]thiazol-2-ylthio)hexan-1-ol (3v)



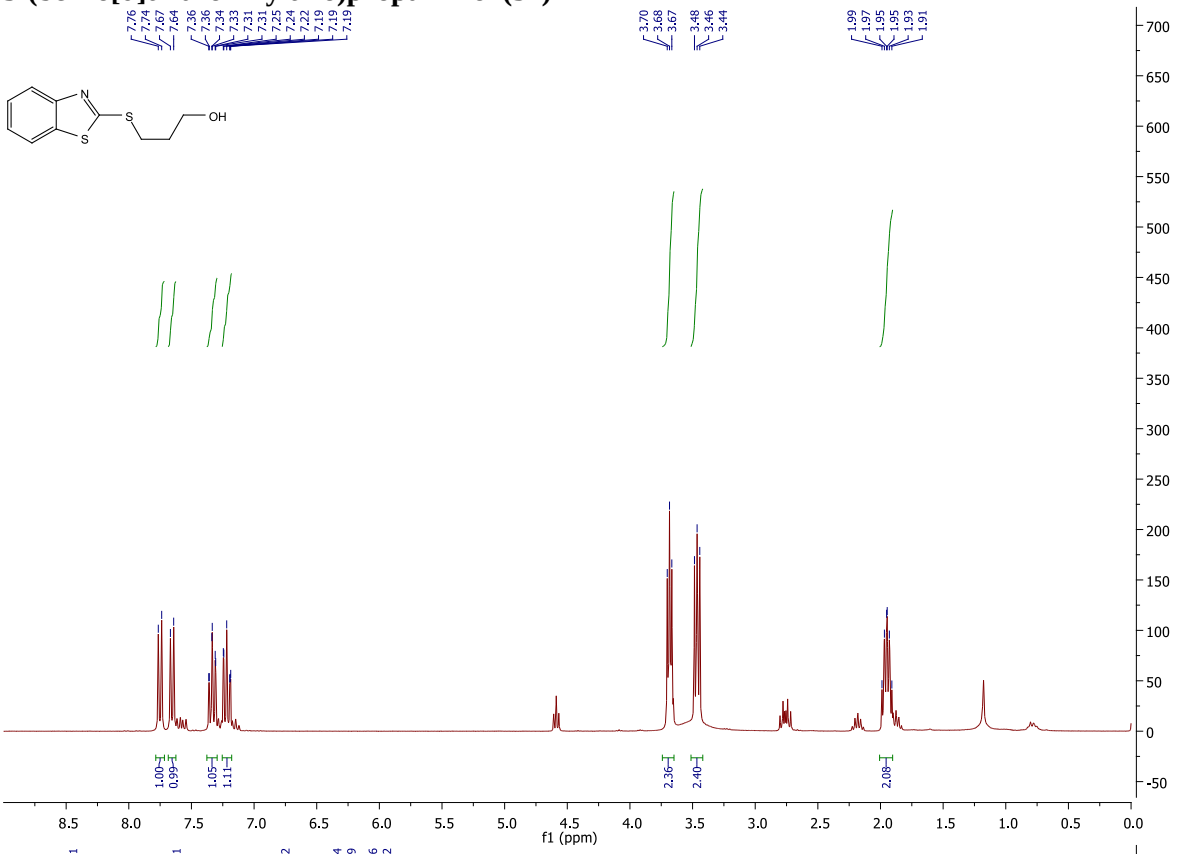


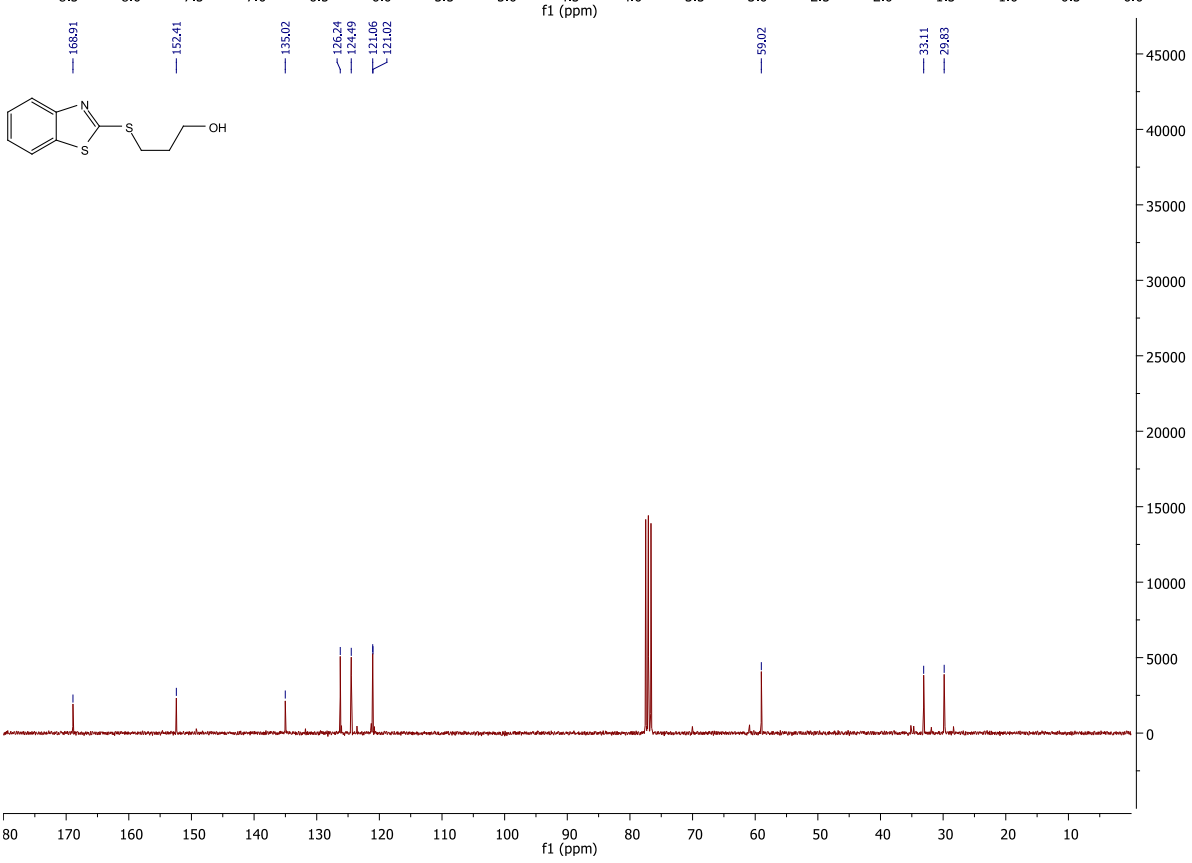
2-((3-(benzo[d]thiazol-2-yloxy)propyl)thio)benzo[d]thiazole (3w)



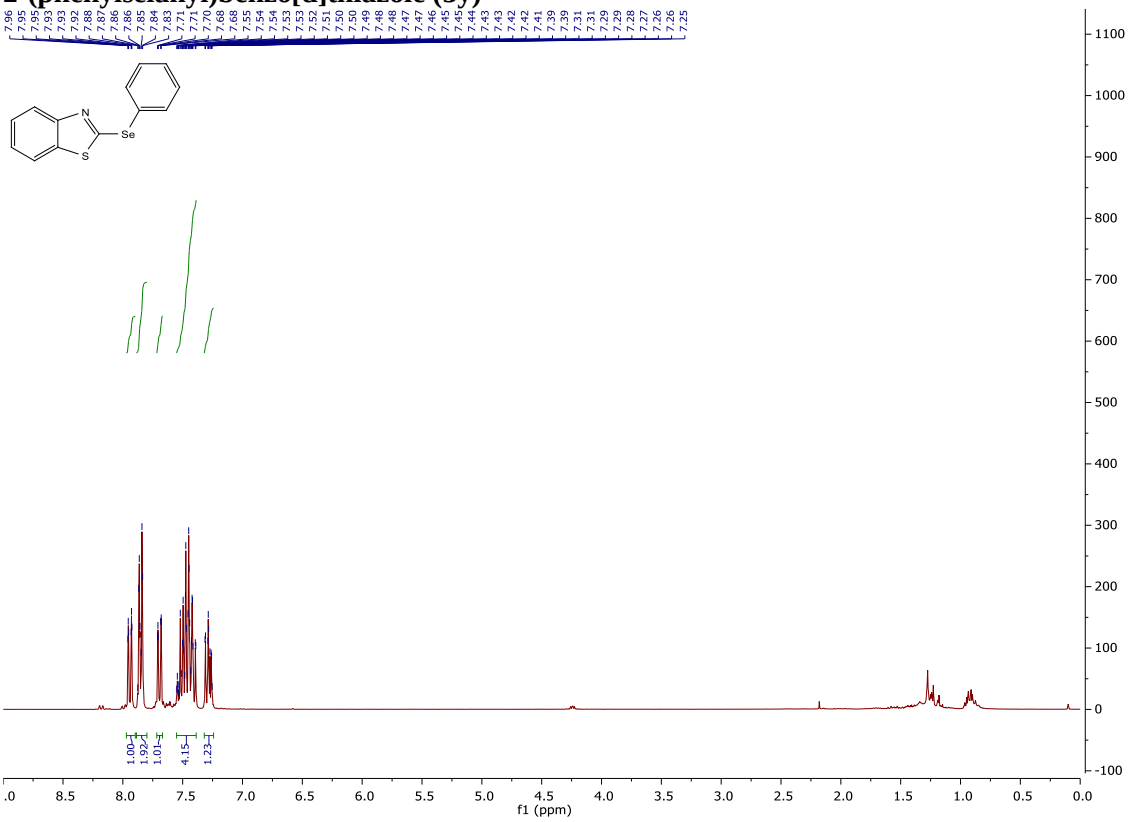


3-(benzo[d]thiazol-2-ylthio)propan-1-ol (3x)

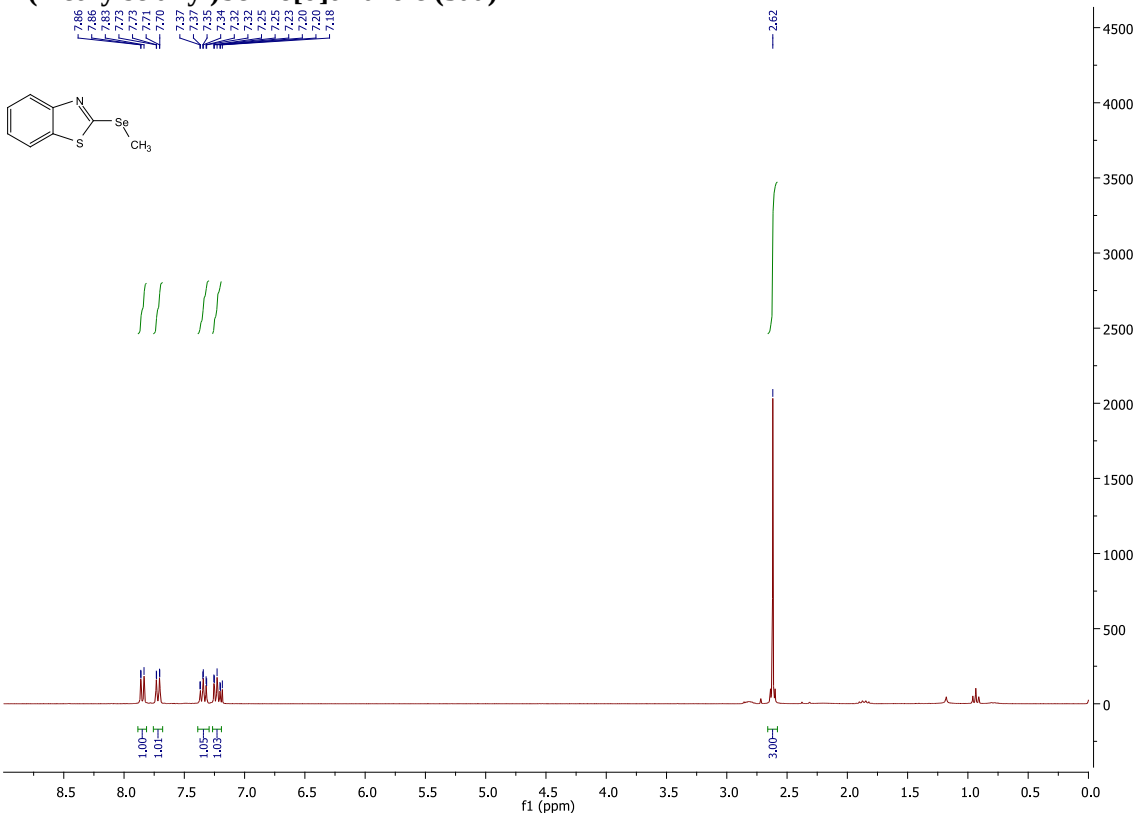


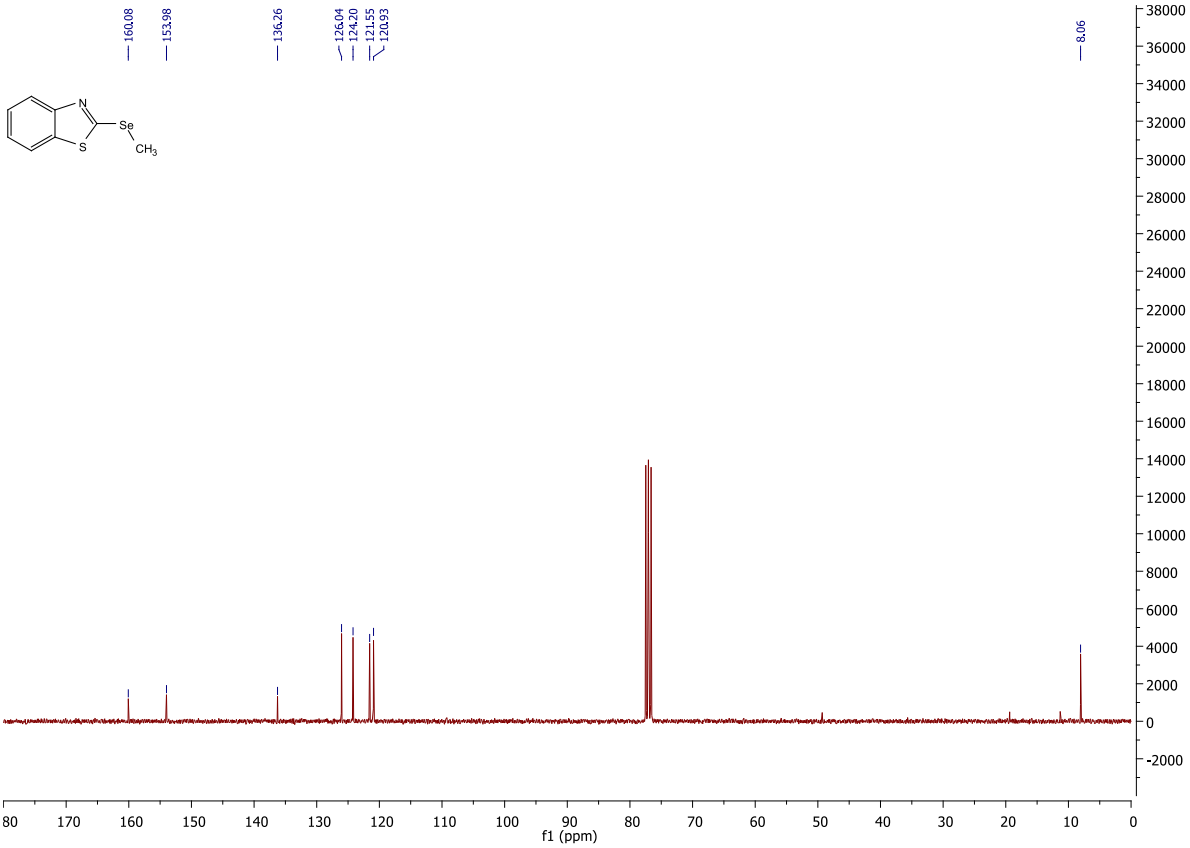


2-(phenylselanyl)benzo[d]thiazole (3y)

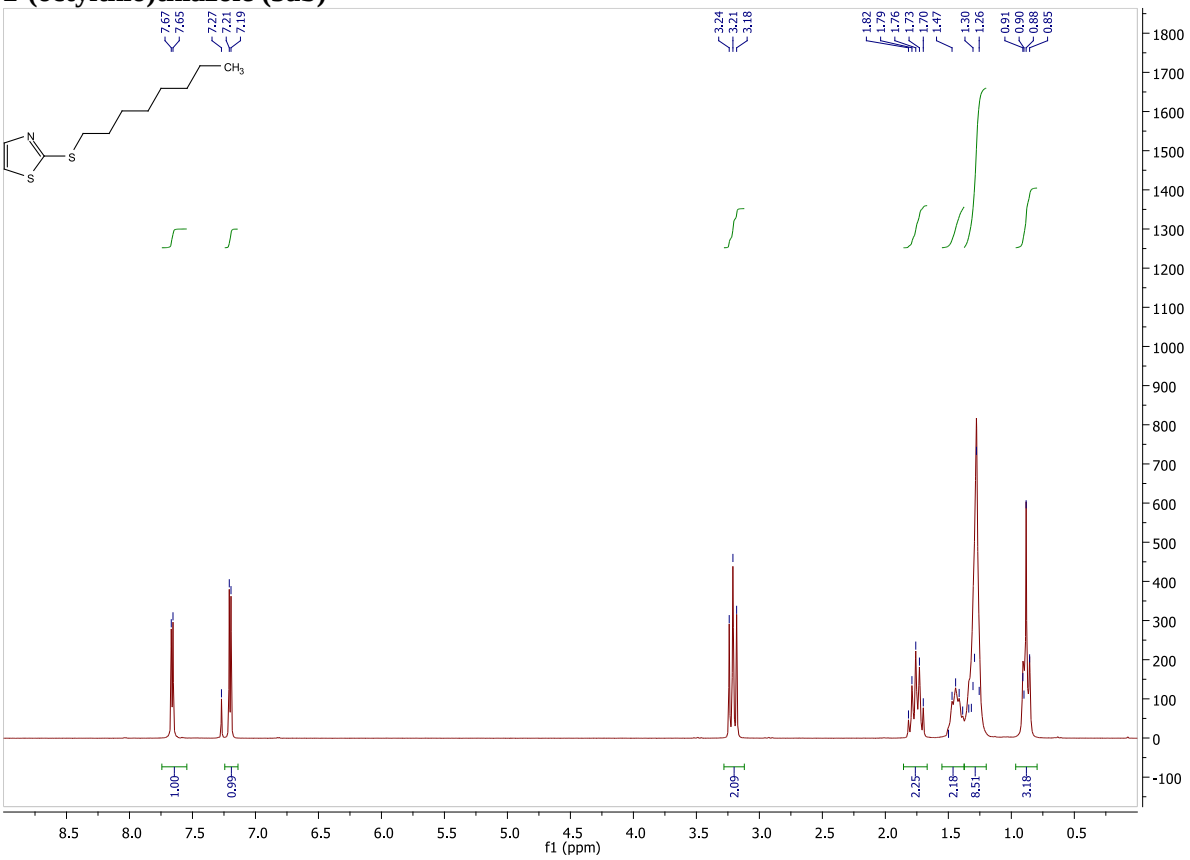


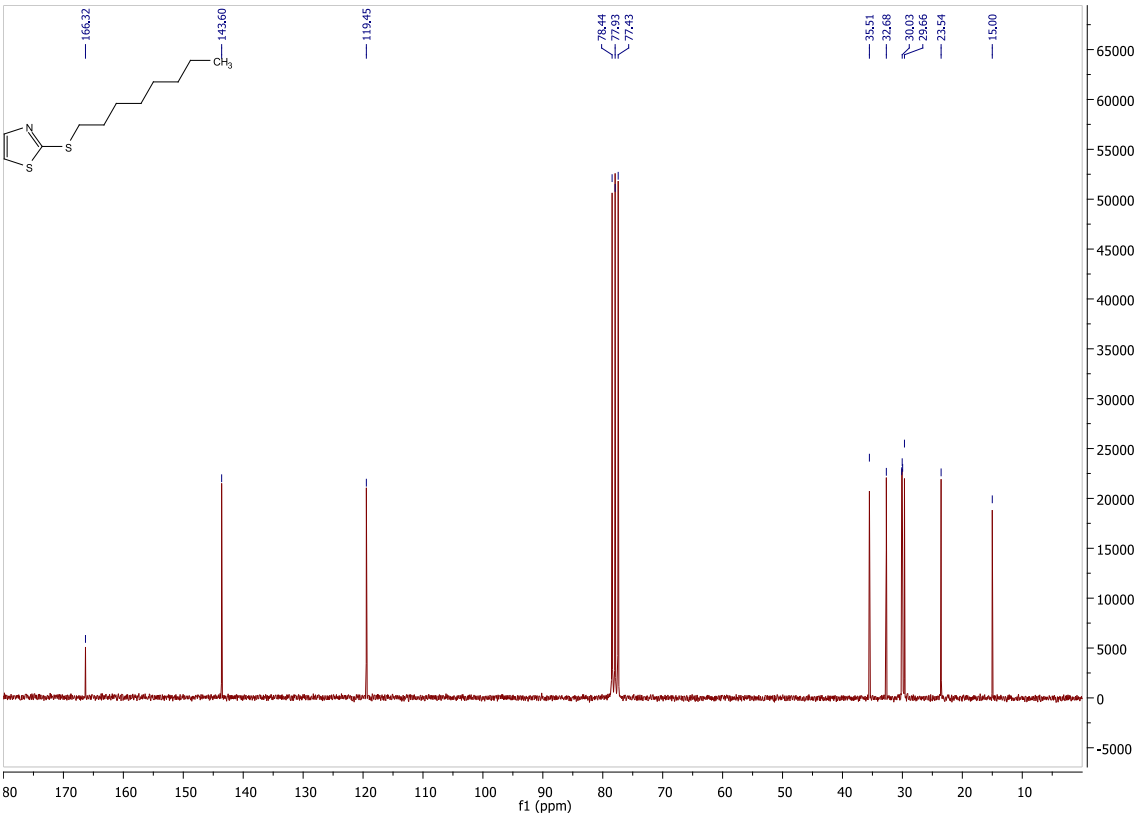
2-(methylselanyl)benzo[d]thiazole (3aa)



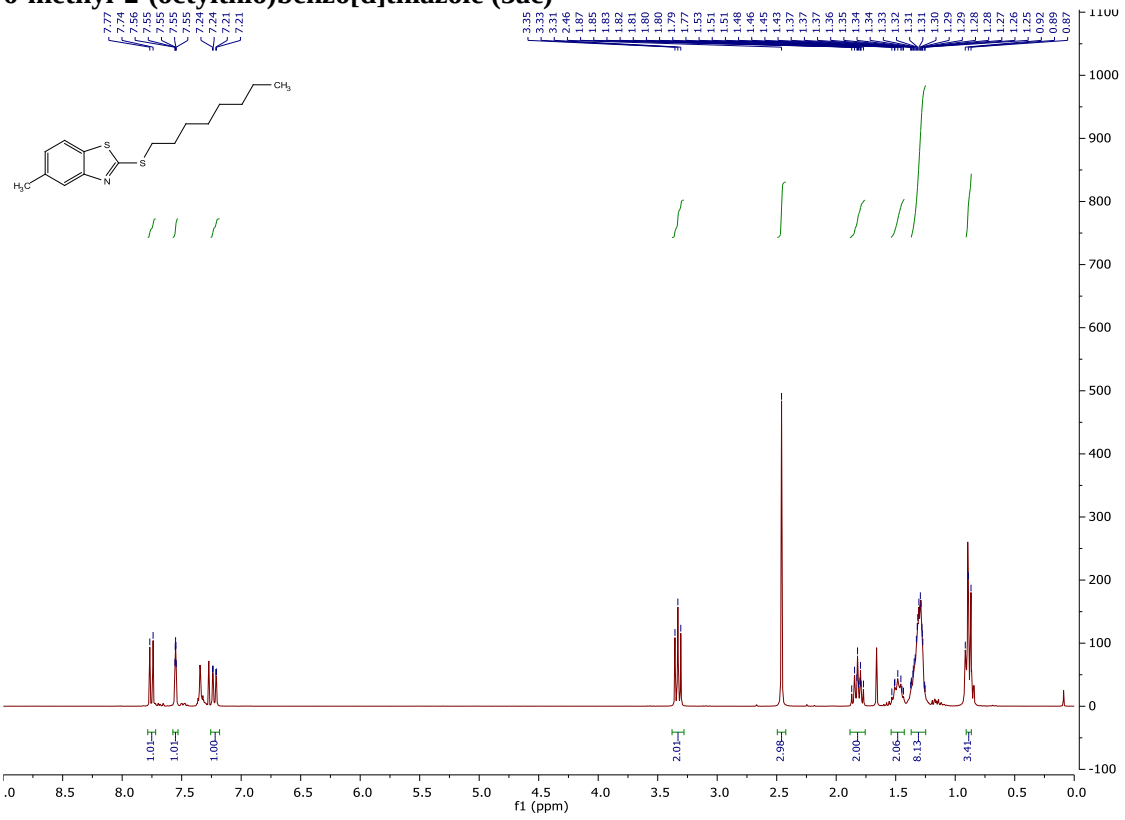


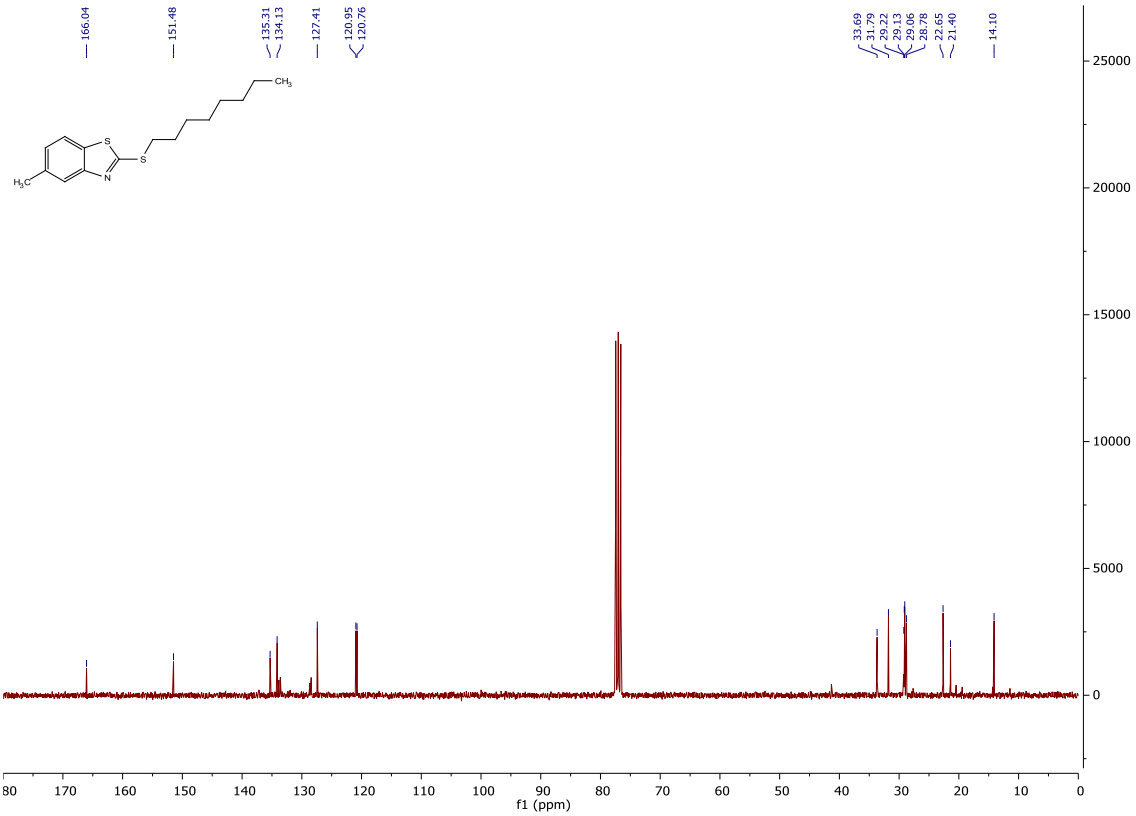
2-(octylthio)thiazole (3ab)



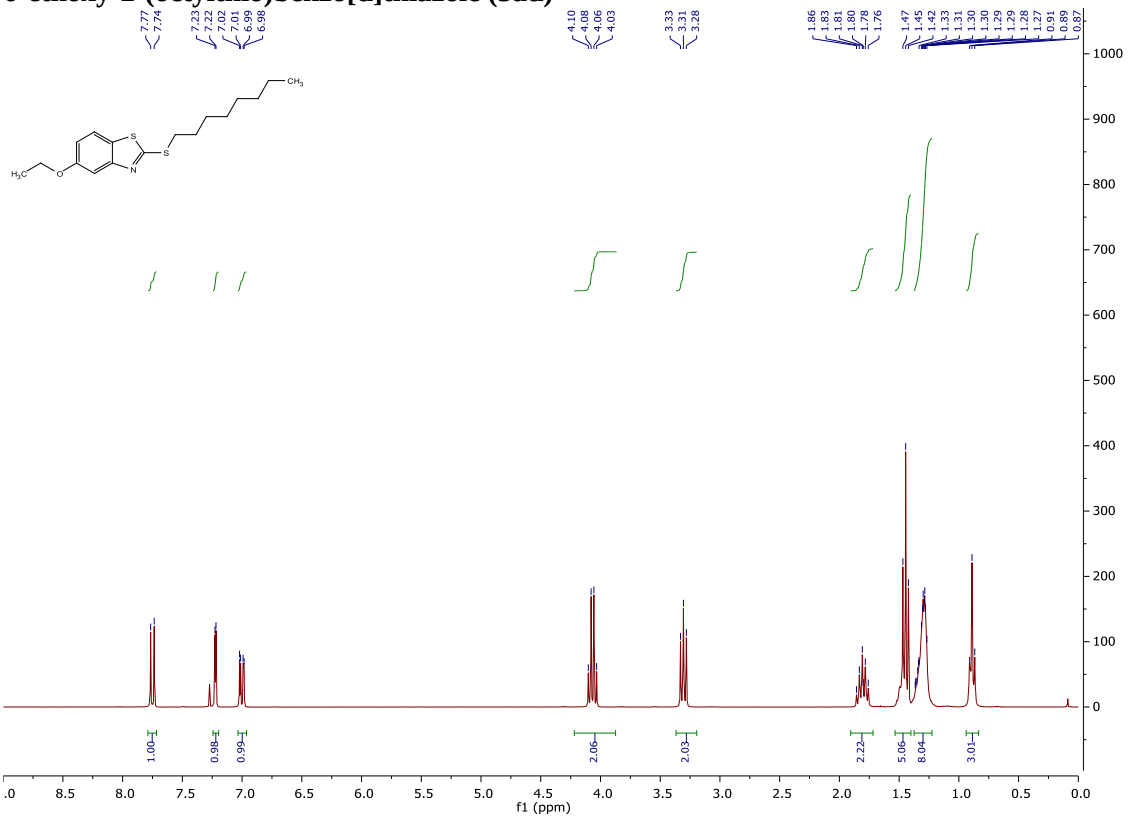


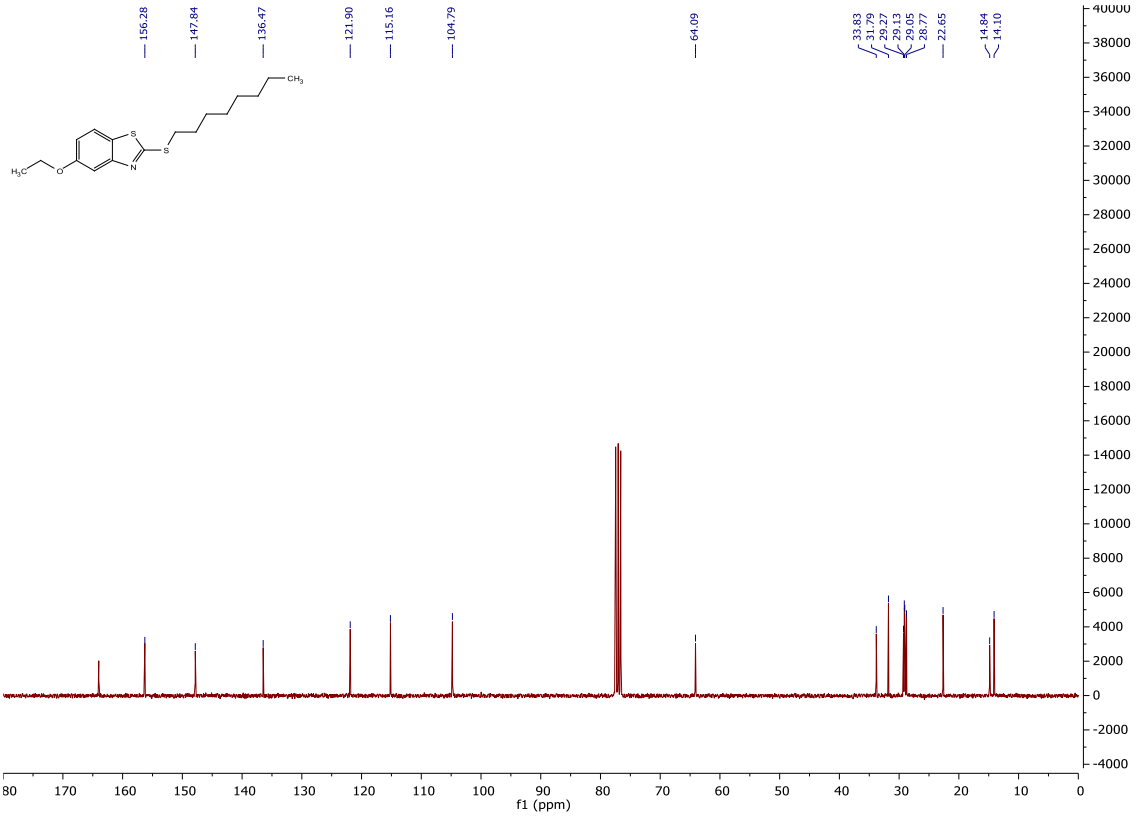
6-methyl-2-(octylthio)benzo[d]thiazole (3ac)



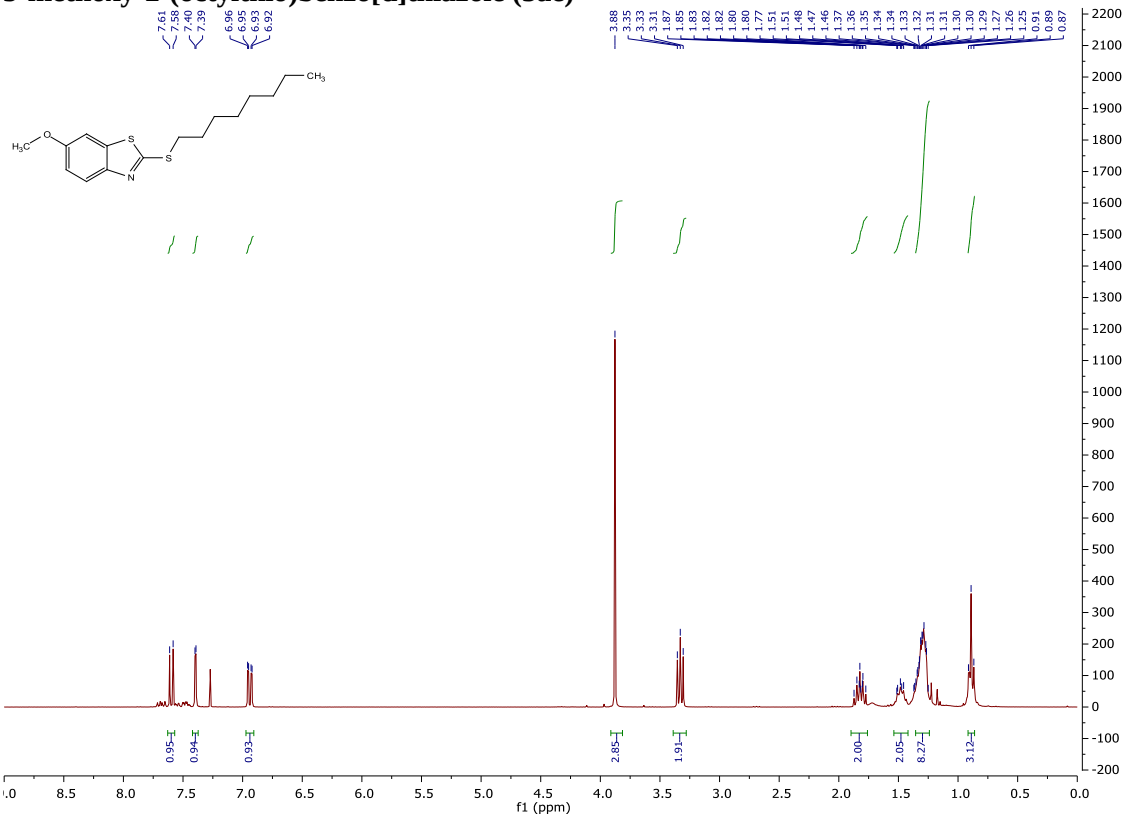


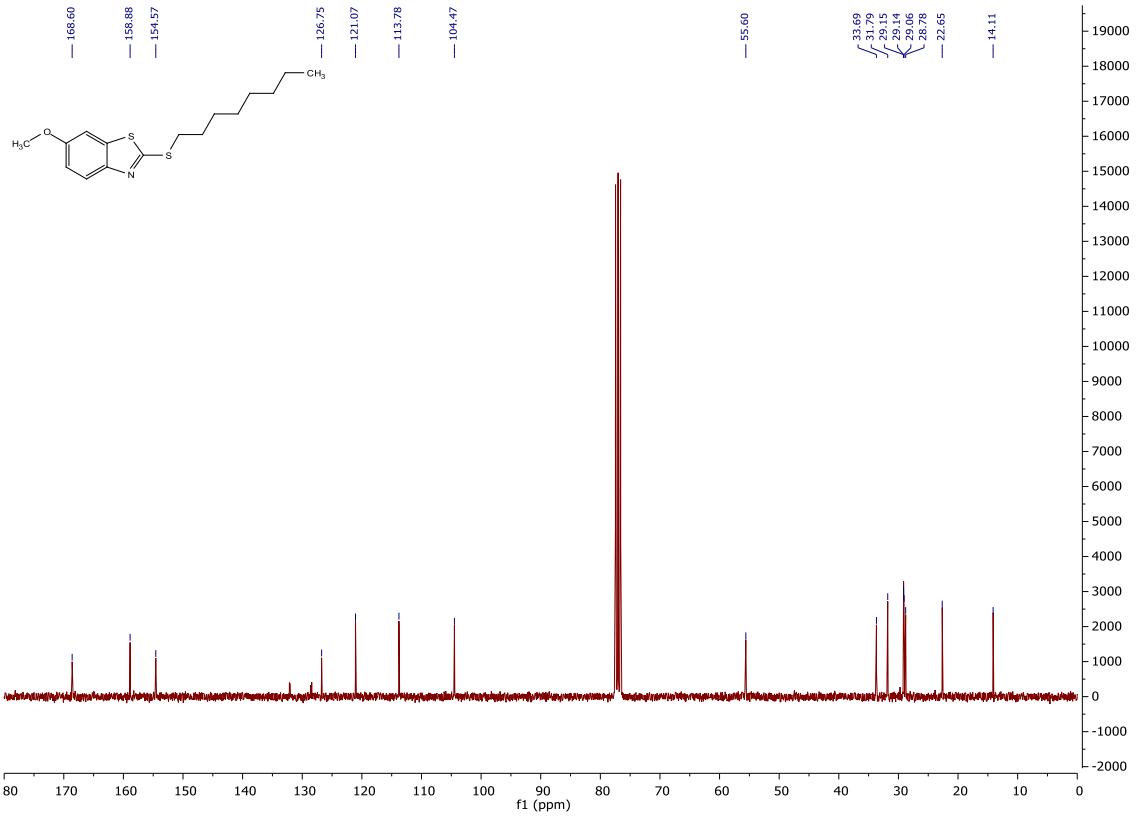
6-ethoxy-2-(octylthio)benzo[d]thiazole (3ad)



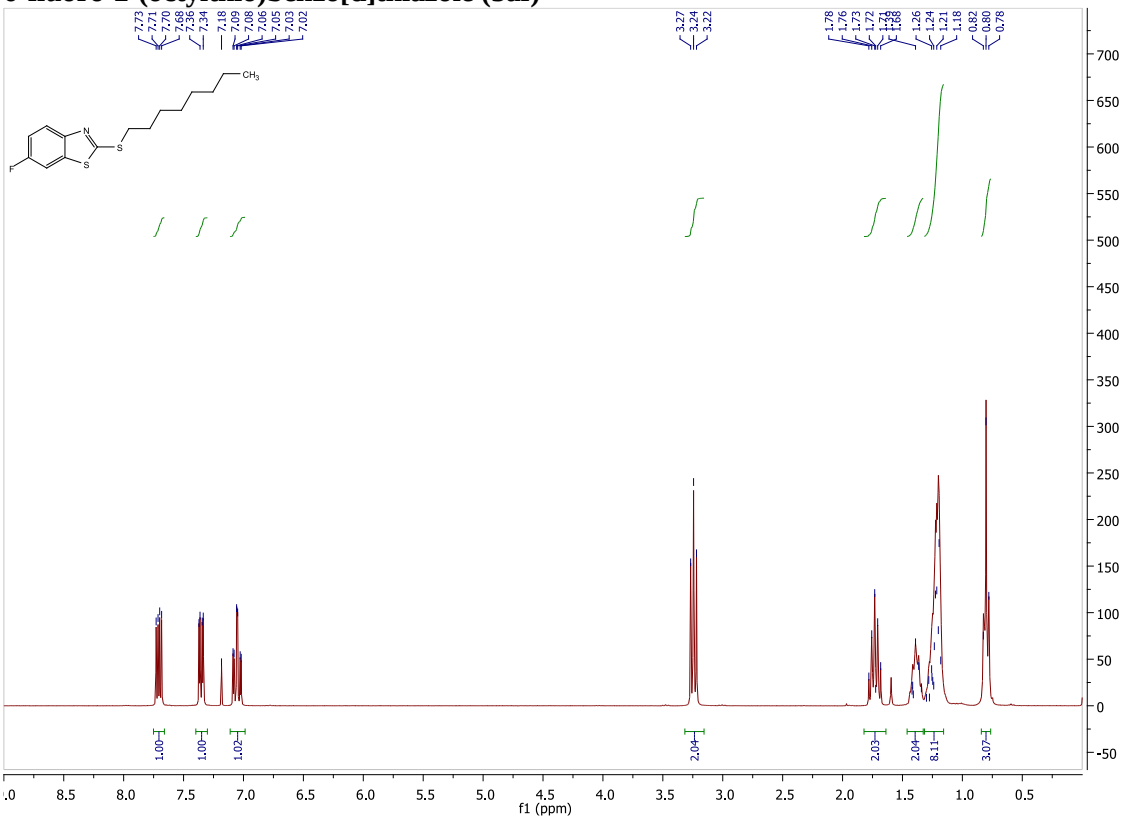


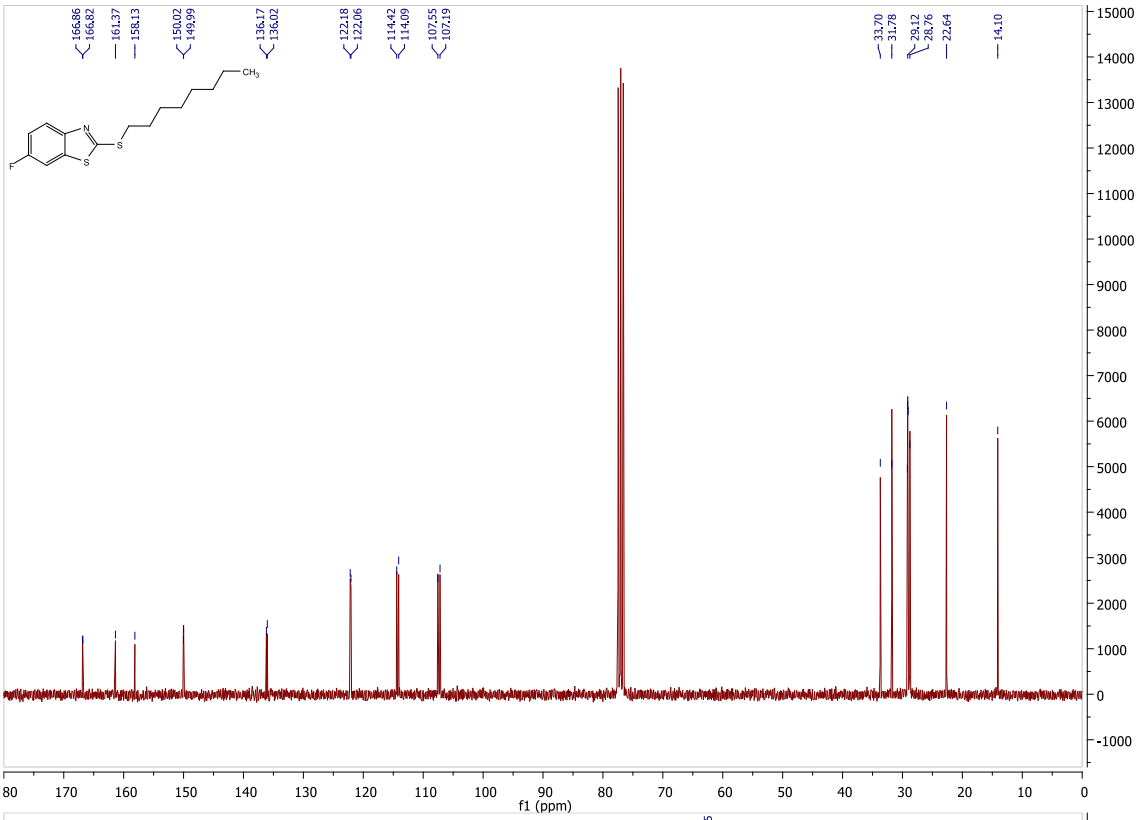
5-methoxy-2-(octylthio)benzo[d]thiazole (3ae)

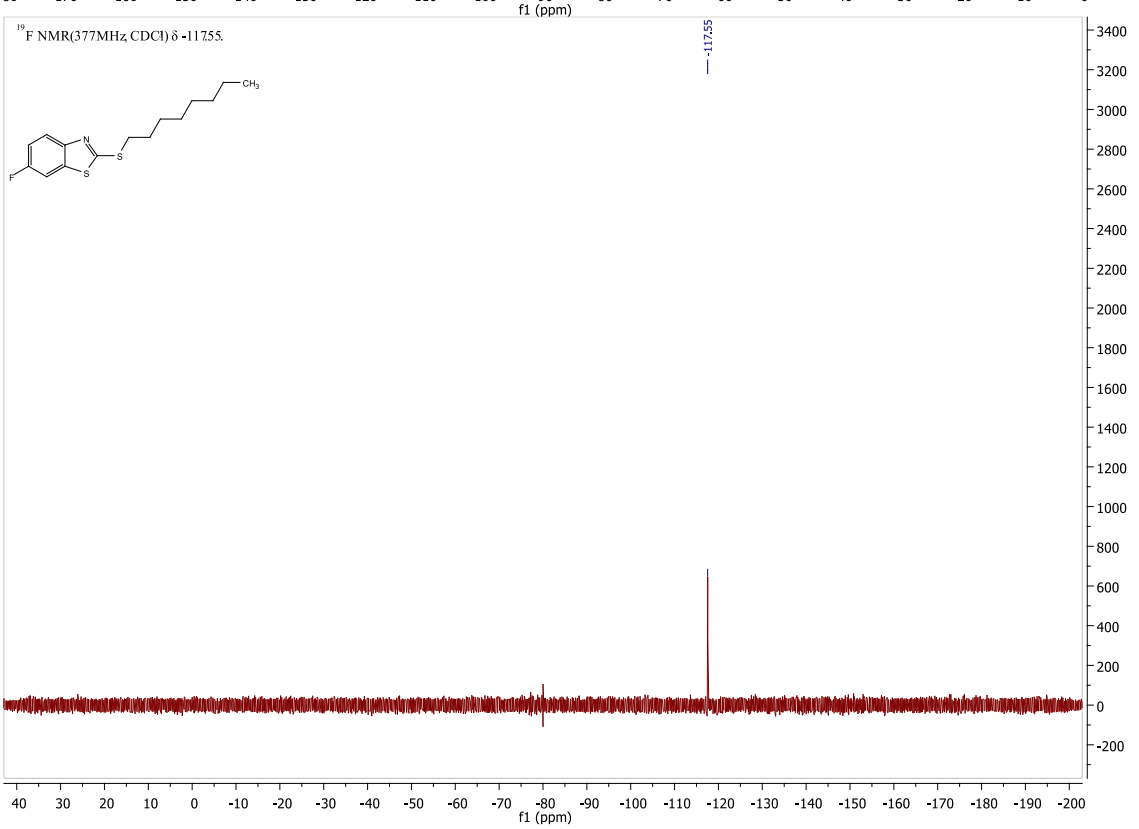




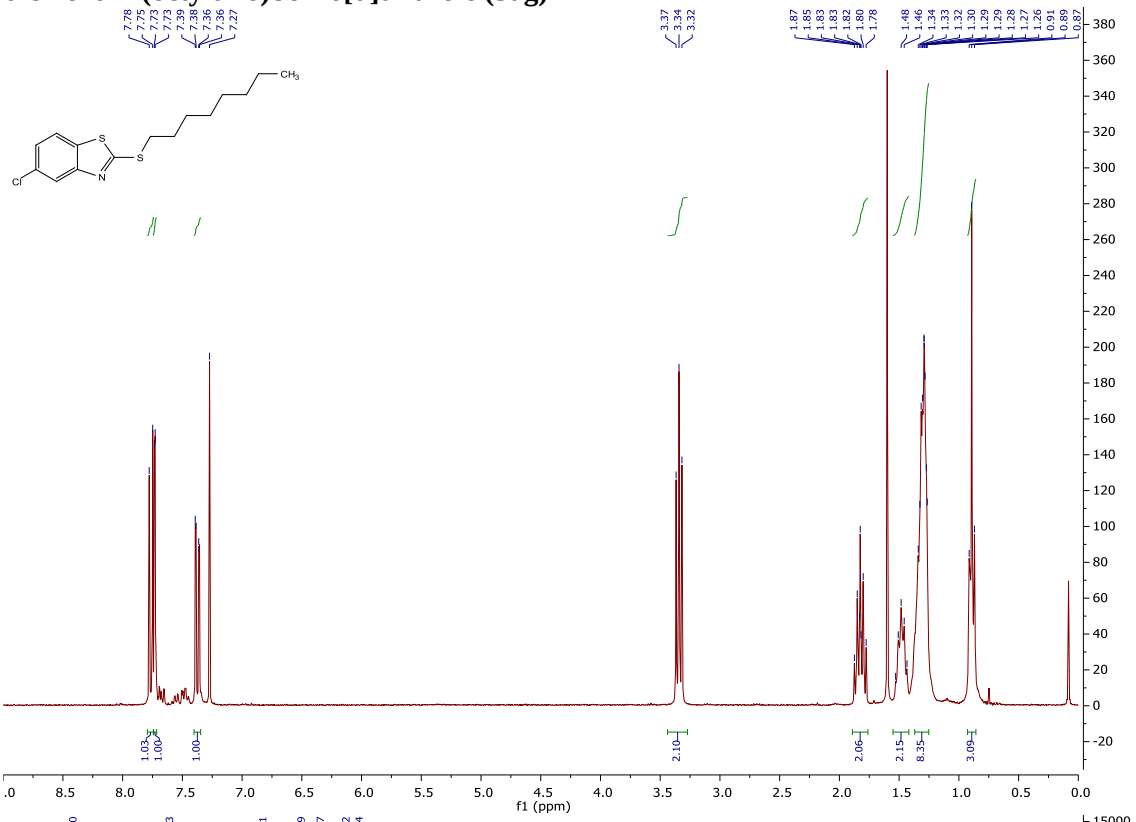
6-fluoro-2-(octylthio)benzo[d]thiazole (3af)

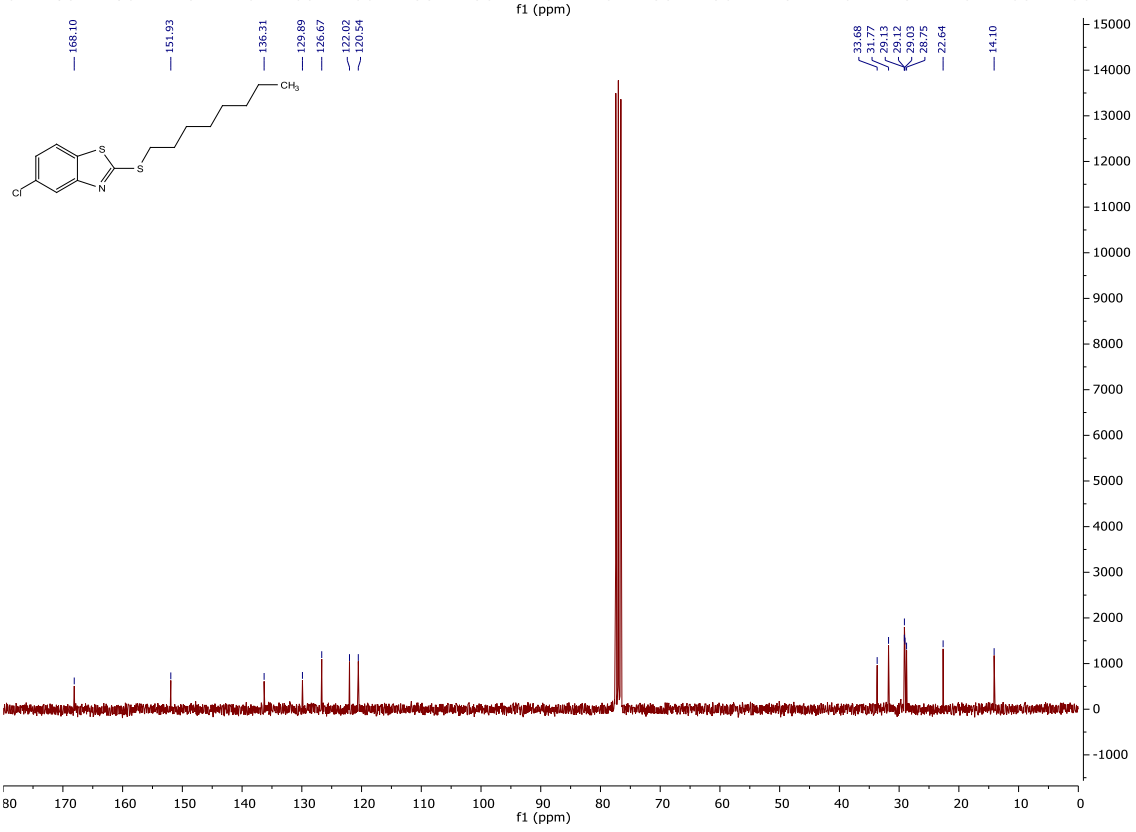



166.86
166.82
161.37
158.13
150.02
149.99
136.17
136.02
122.18
122.06
114.42
114.09
107.55
107.19
33.70
31.78
29.12
28.76
22.64
14.10
f1 (ppm)

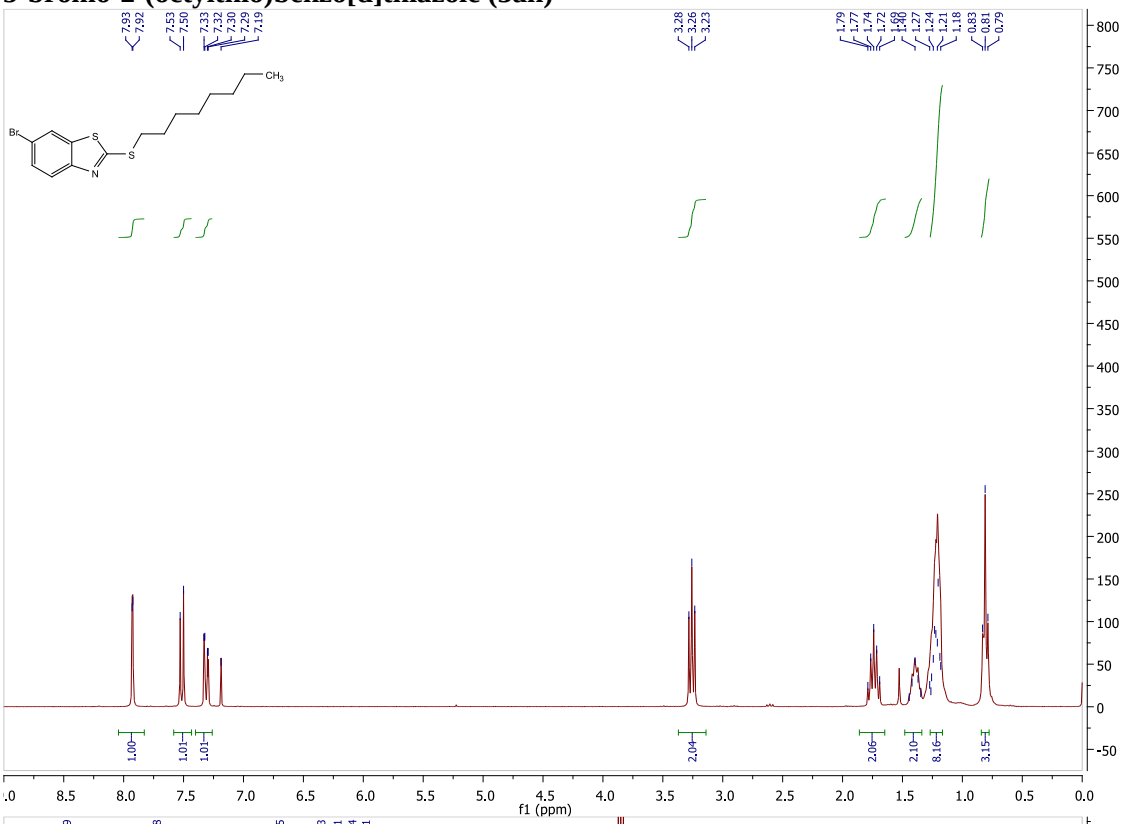

^{19}F NMR(377MHz, CDCl) δ -117.55.
-117.55
f1 (ppm)

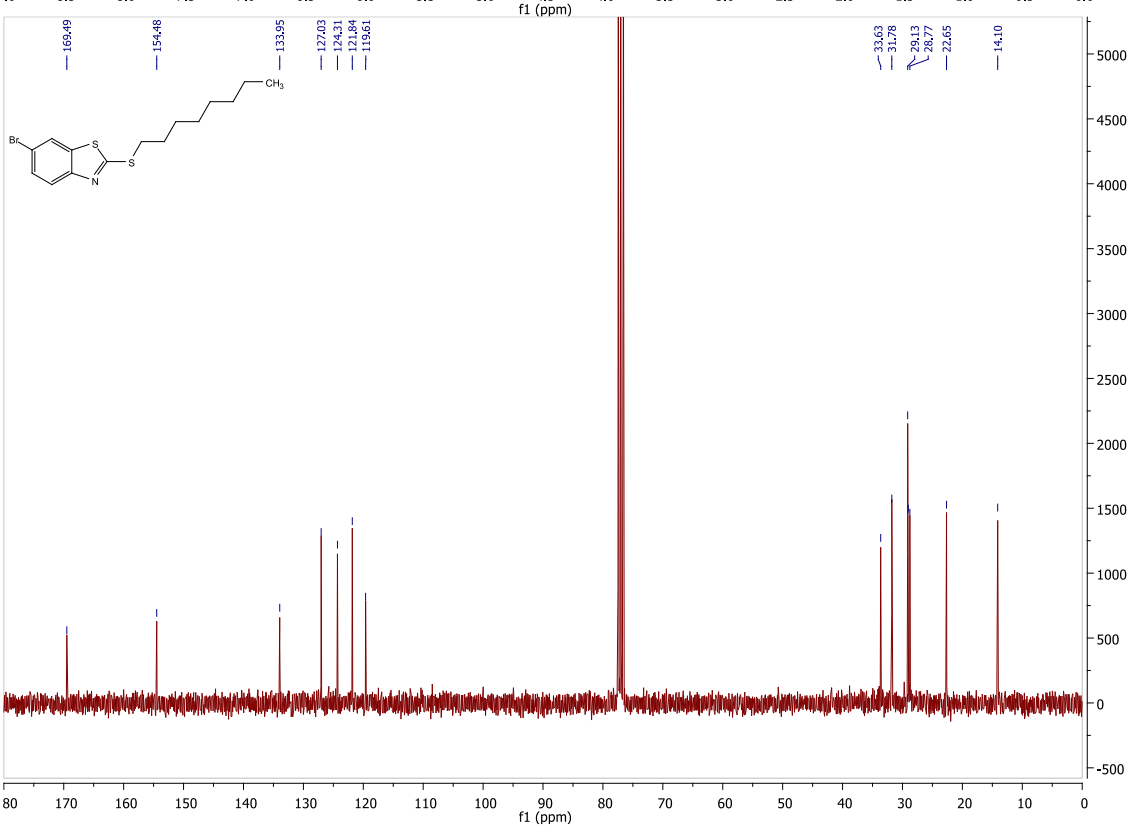
6-chloro-2-(octylthio)benzo[d]thiazole (3ag)



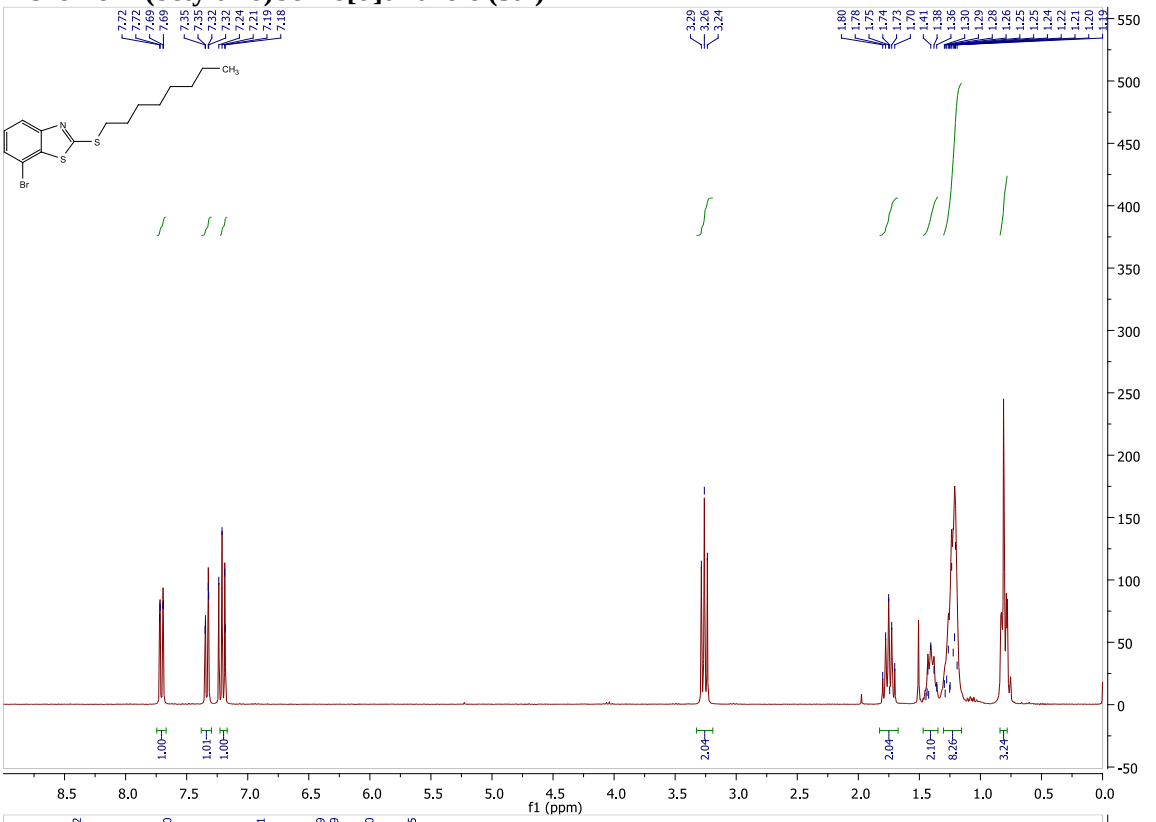


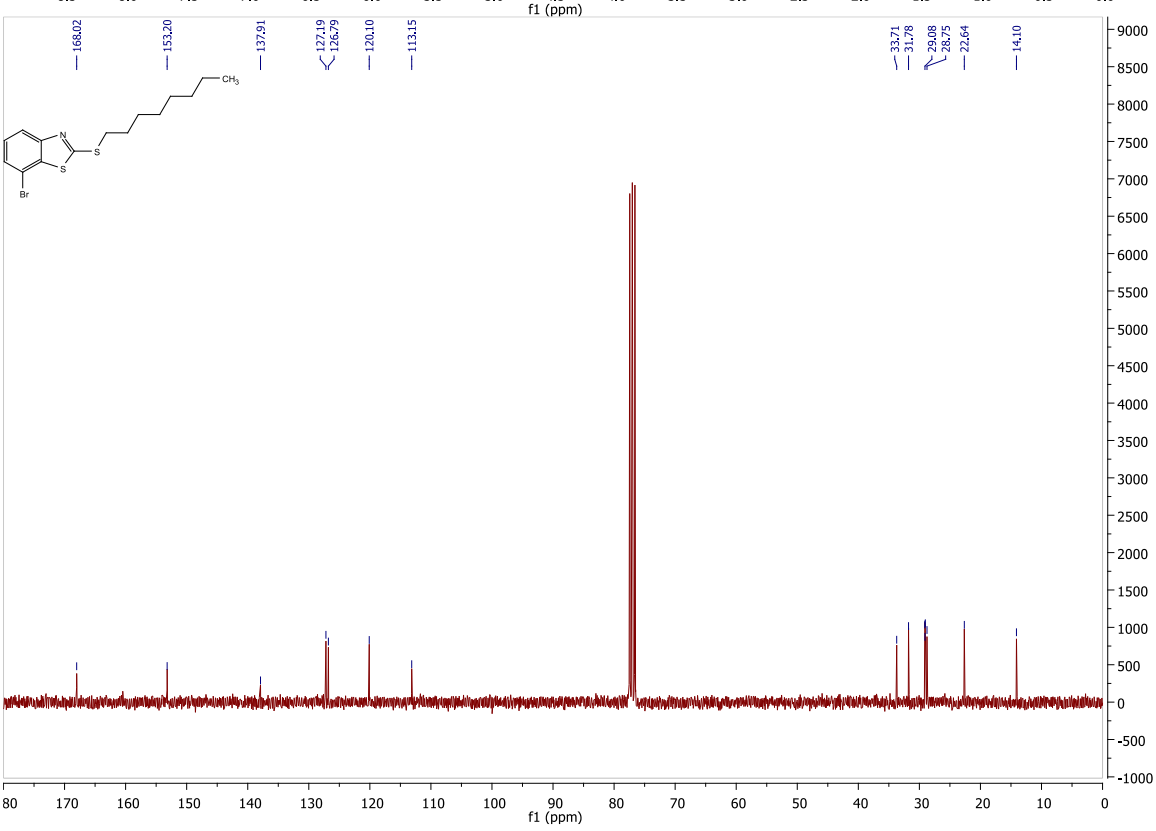
5-bromo-2-(octylthio)benzo[d]thiazole (3ah)



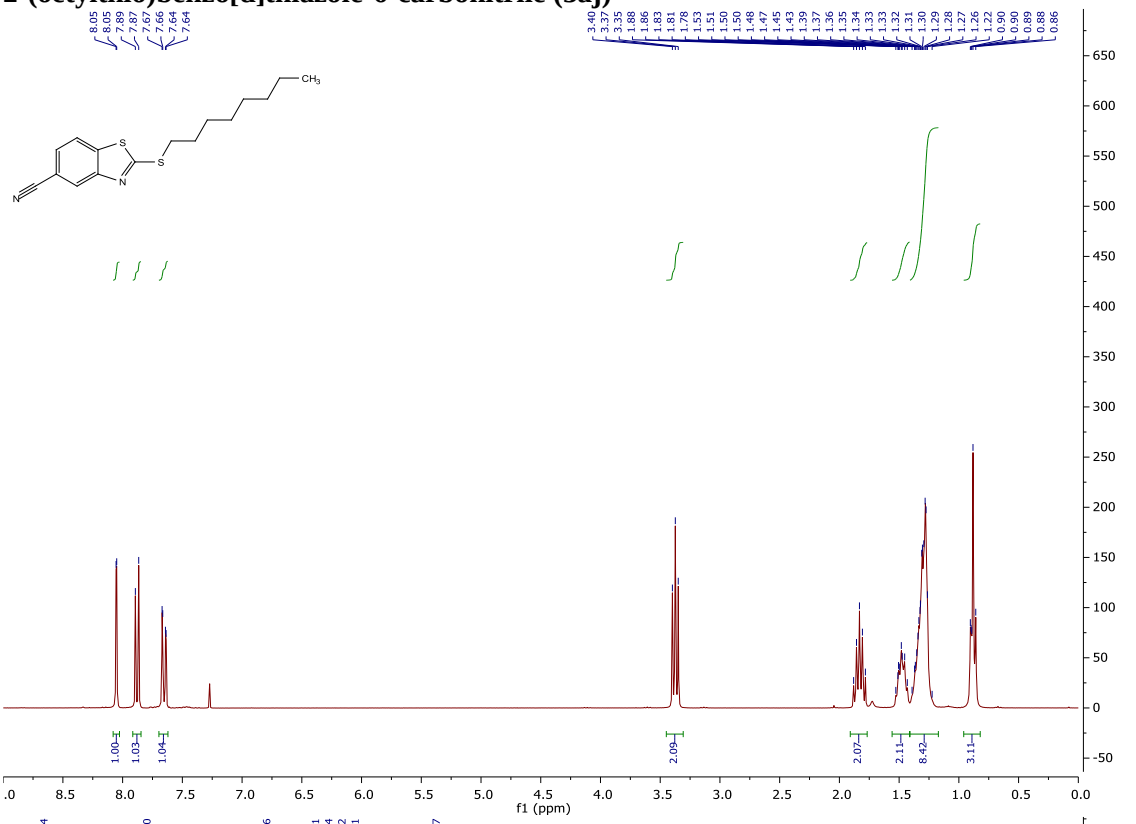


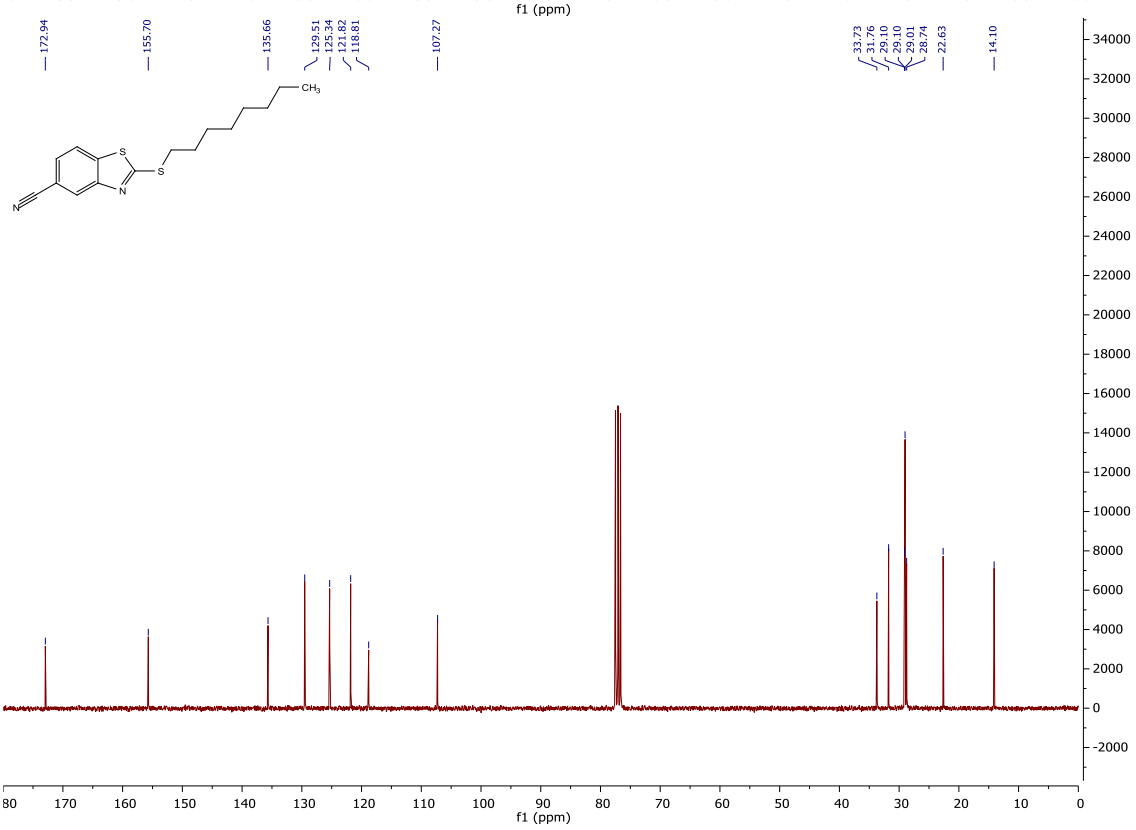
7-bromo-2-(octylthio)benzo[d]thiazole (3ai)



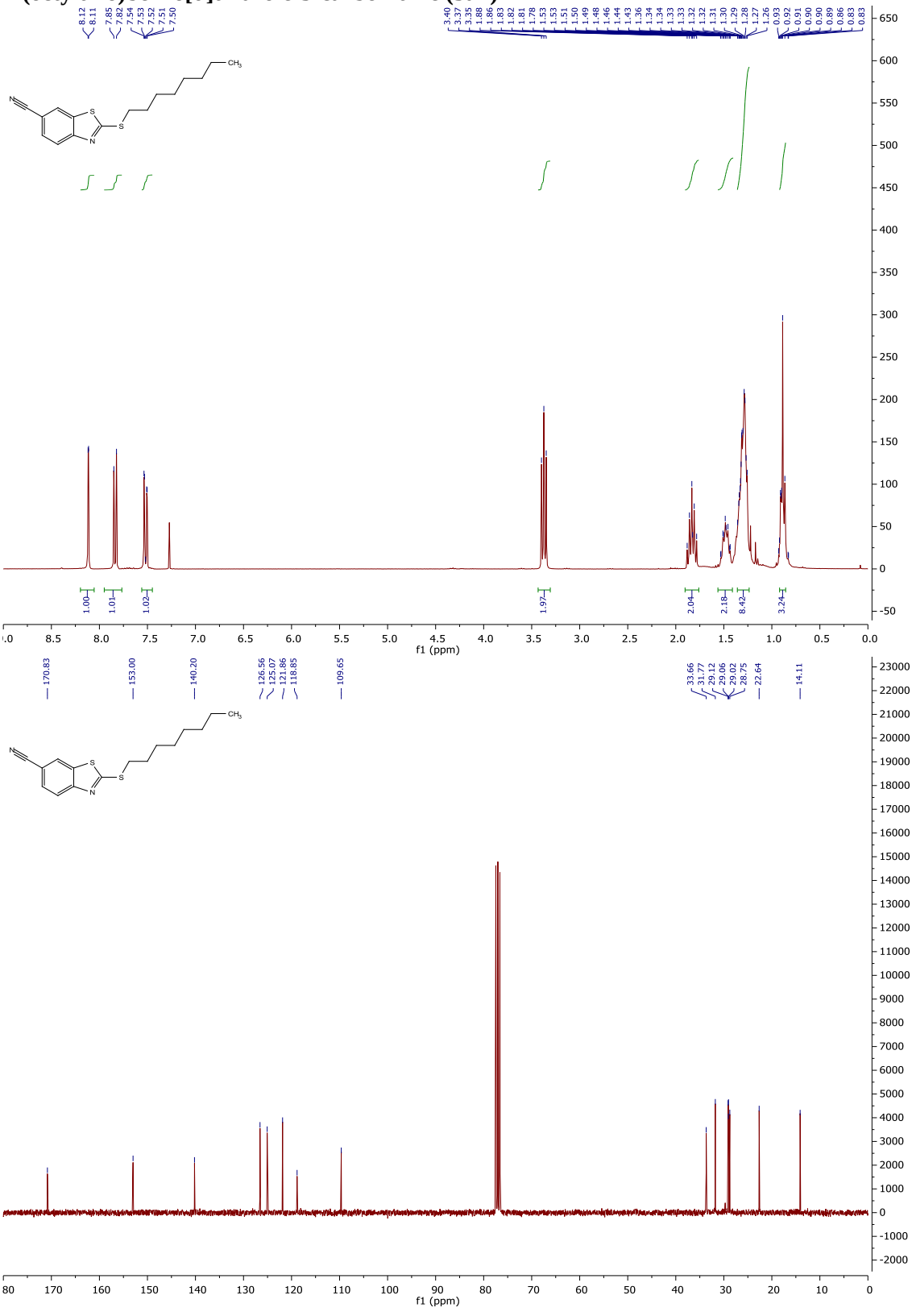


2-(octylthio)benzo[d]thiazole-6-carbonitrile (3aj)

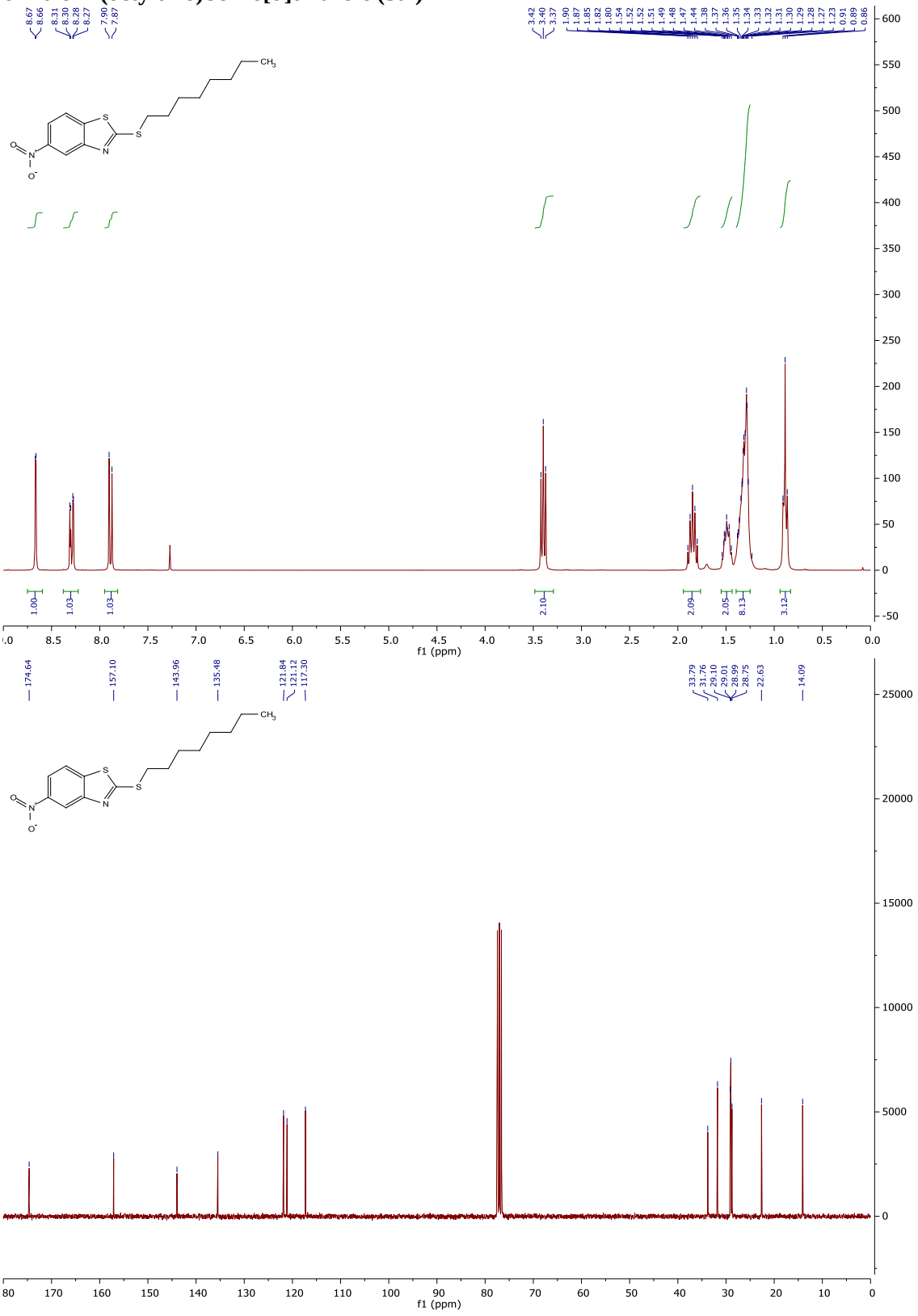




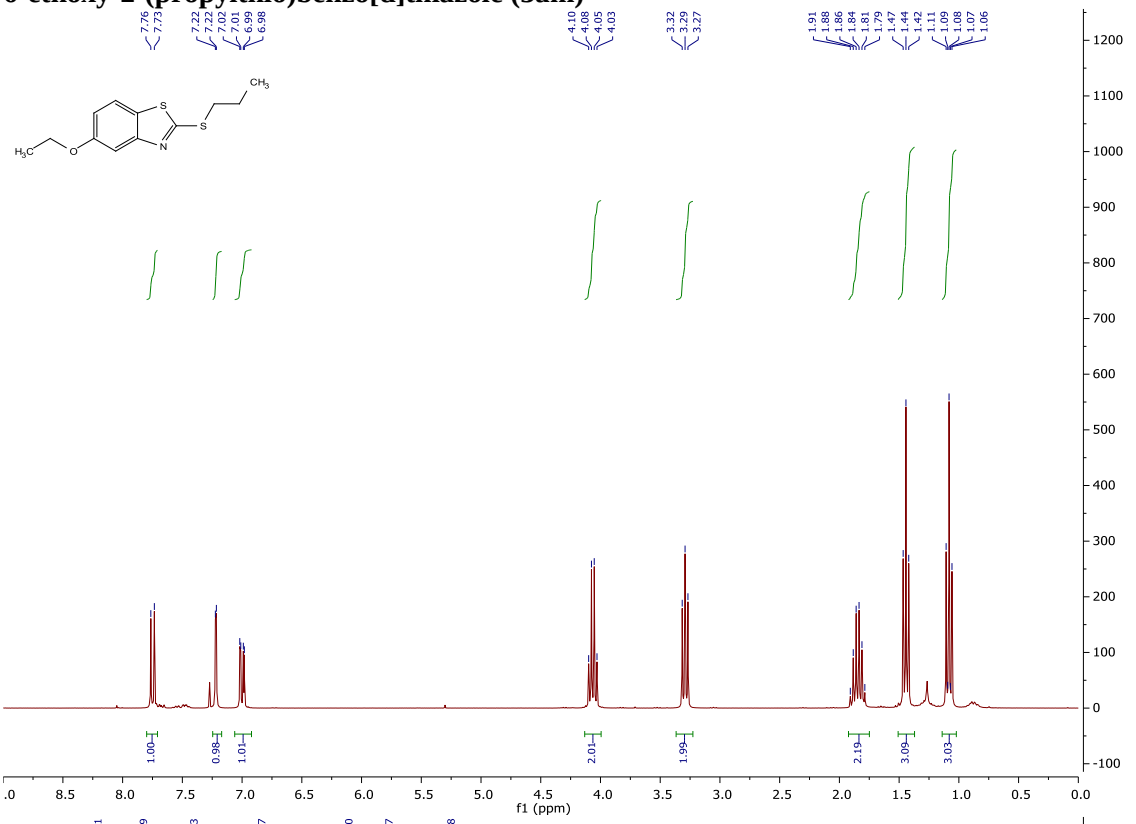
2-(octylthio)benzo[d]thiazole-5-carbonitrile (3ak)

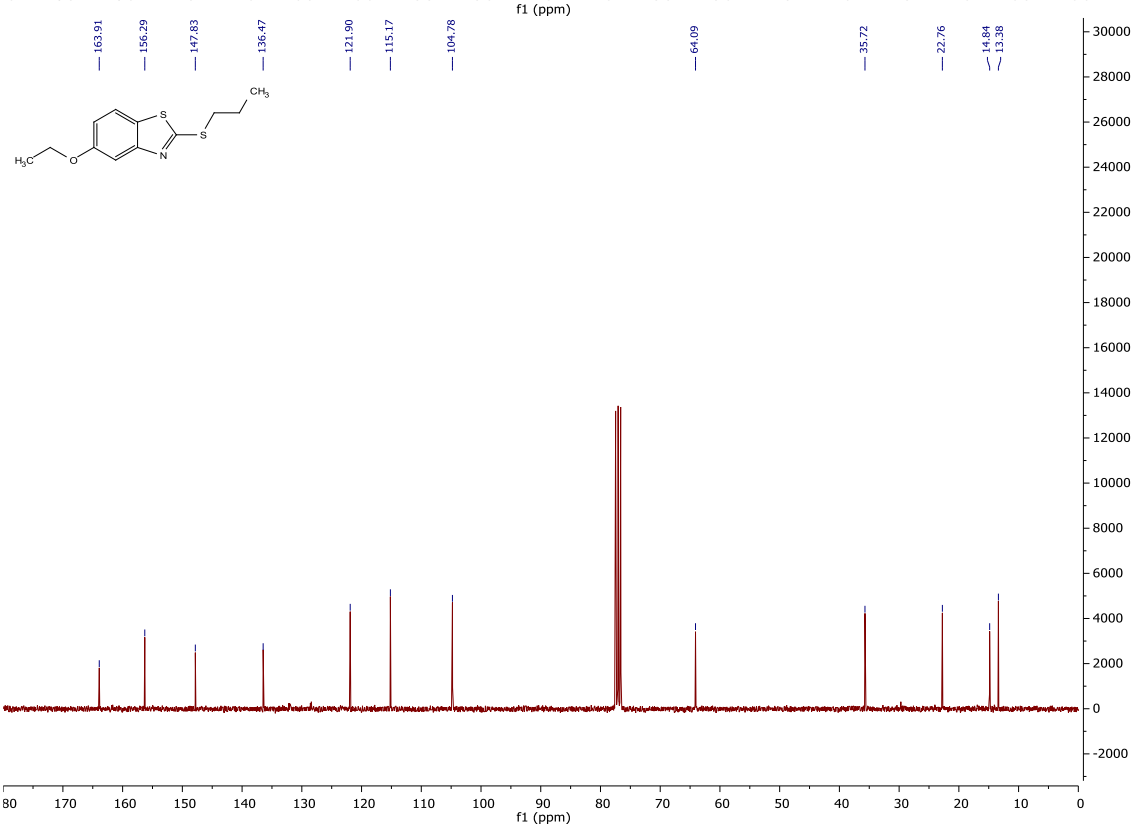


6-nitro-2-(octylthio)benzo[d]thiazole (3al)

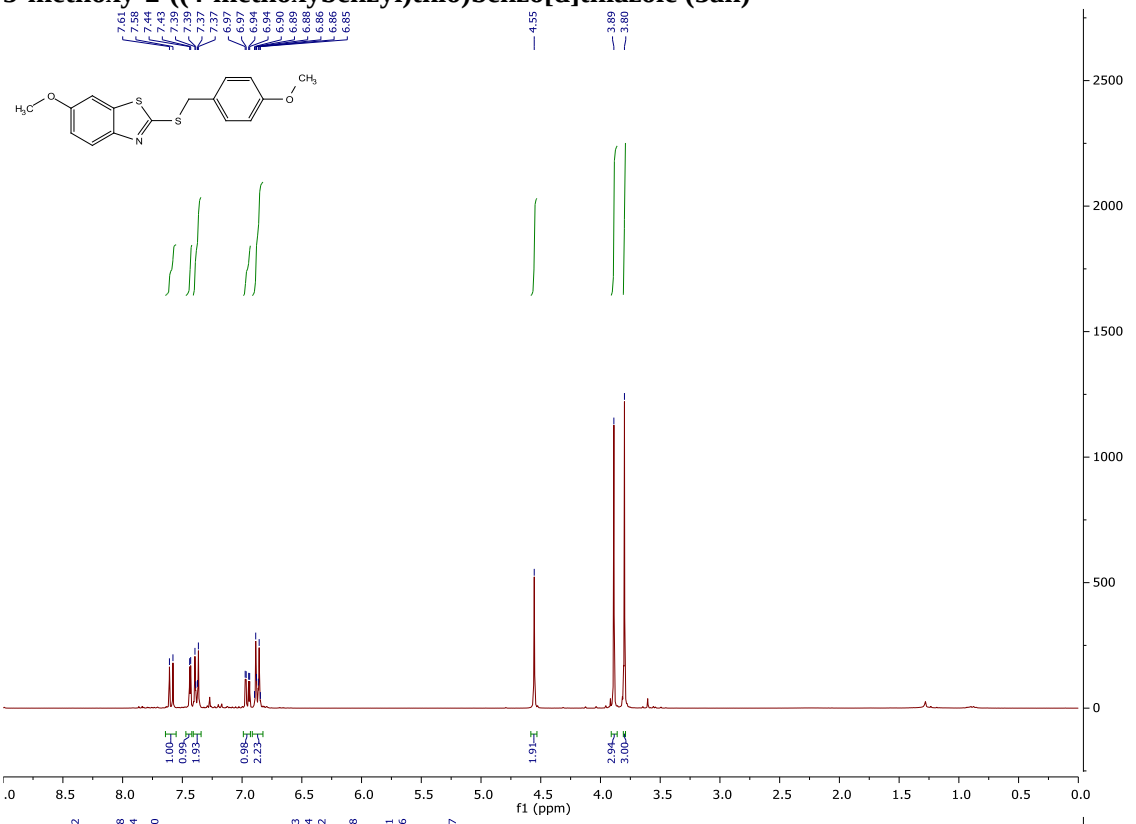


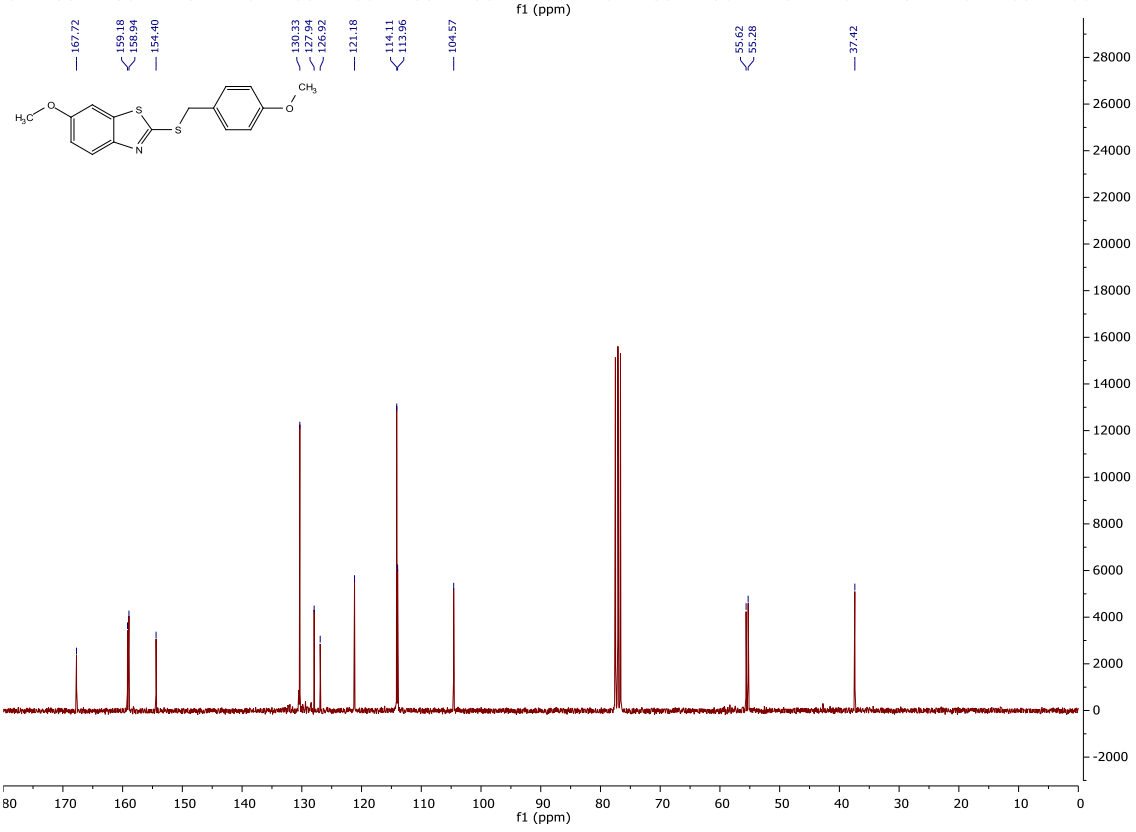
6-ethoxy-2-(propylthio)benzo[d]thiazole (3am)



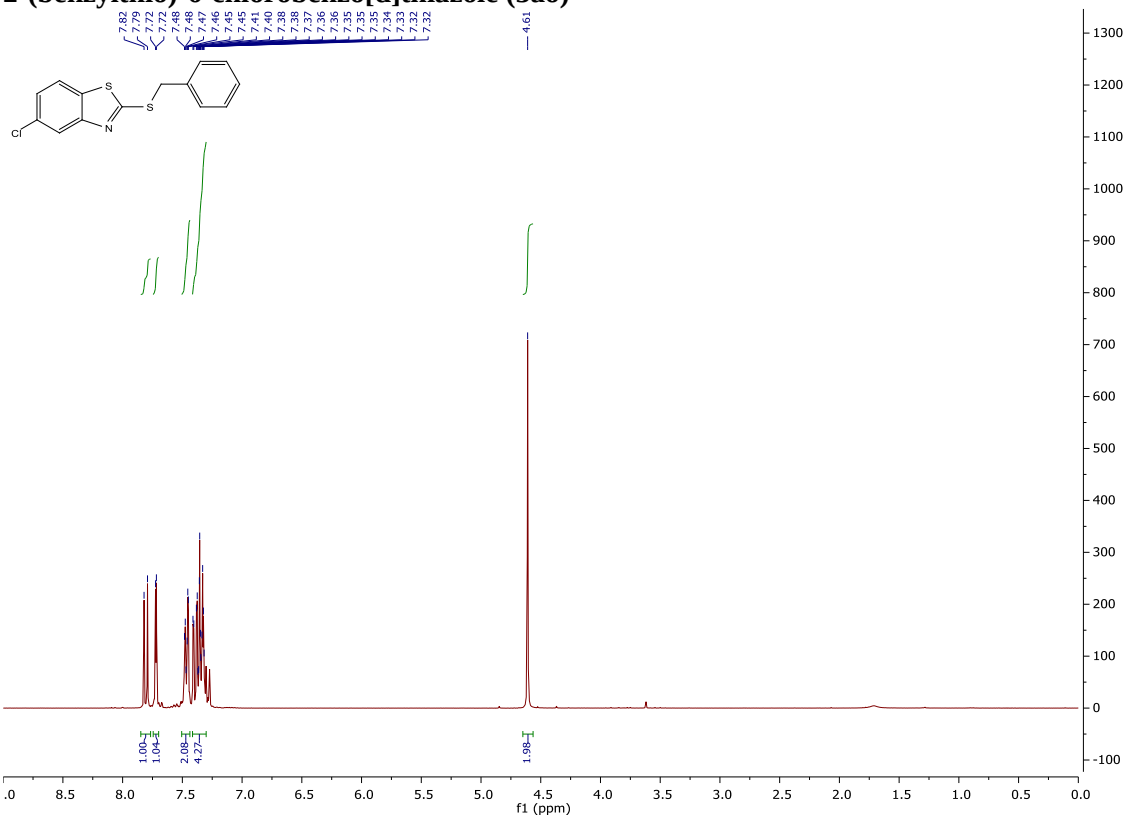


5-methoxy-2-((4-methoxybenzyl)thio)benzo[d]thiazole (3an)

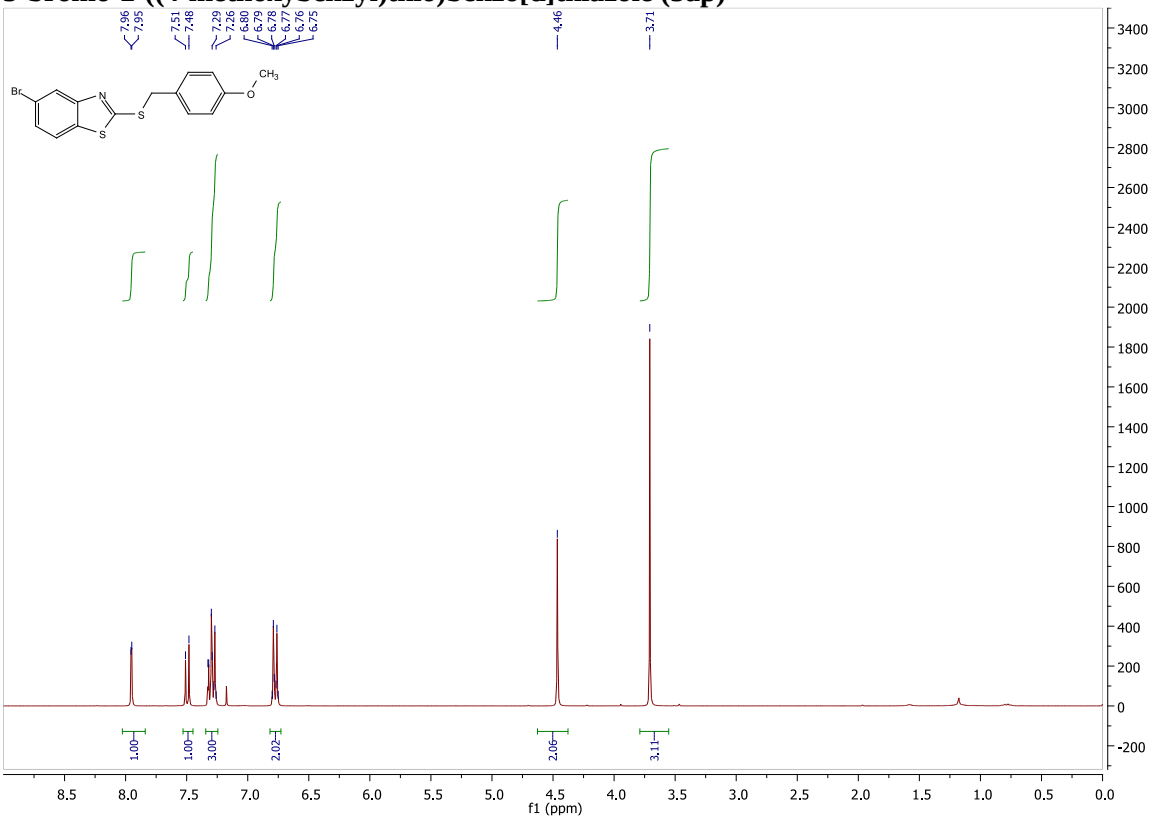


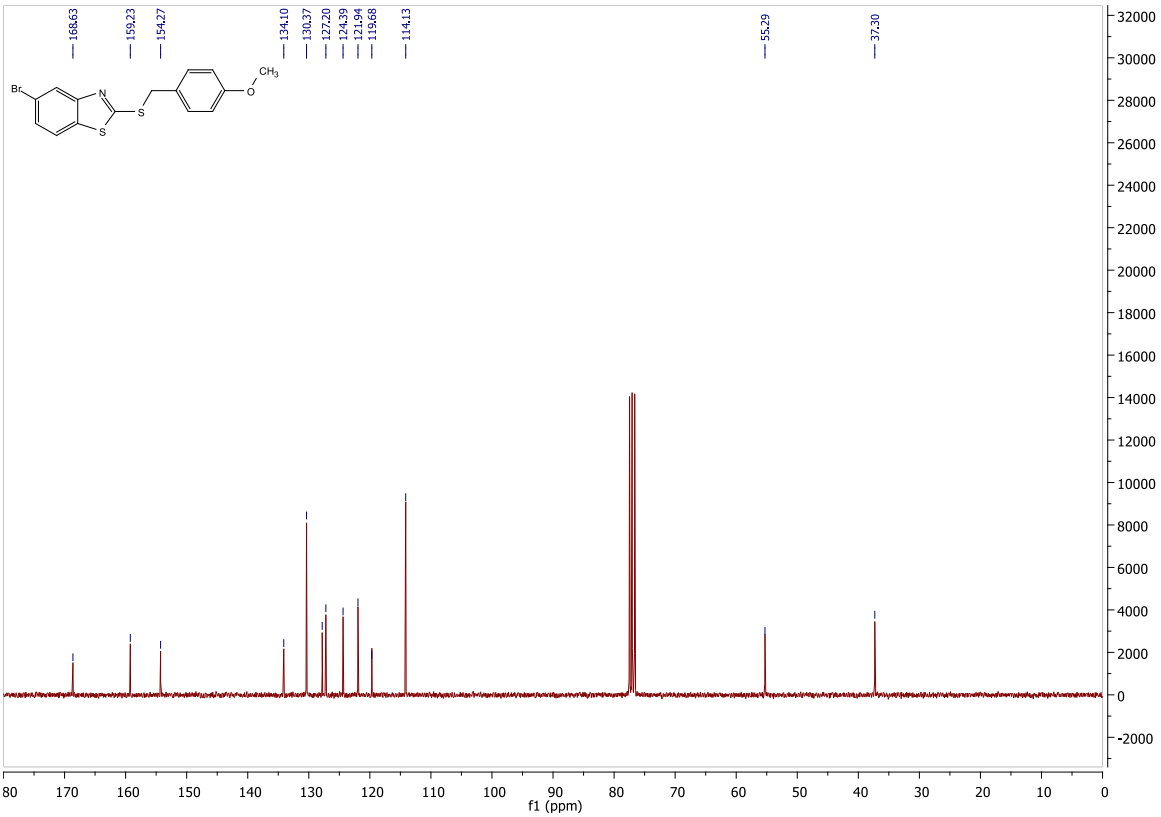


2-(benzylthio)-6-chlorobenzo[d]thiazole (3ao)

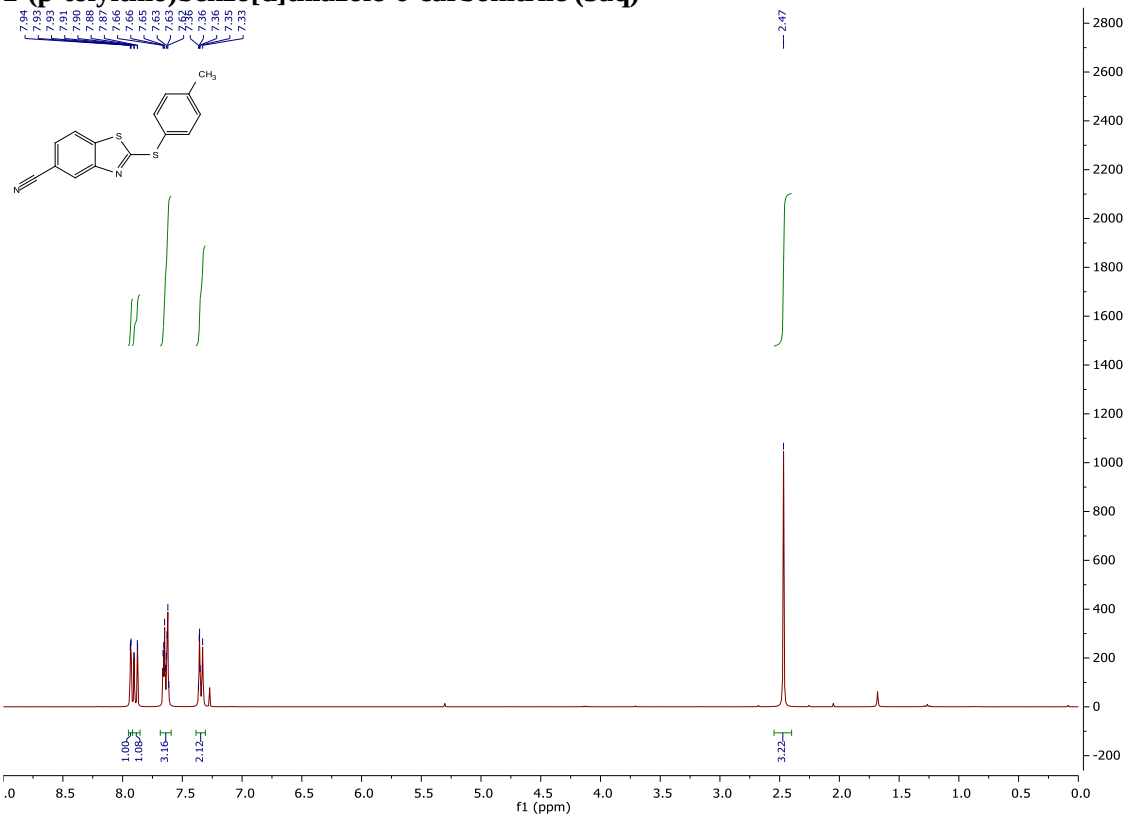


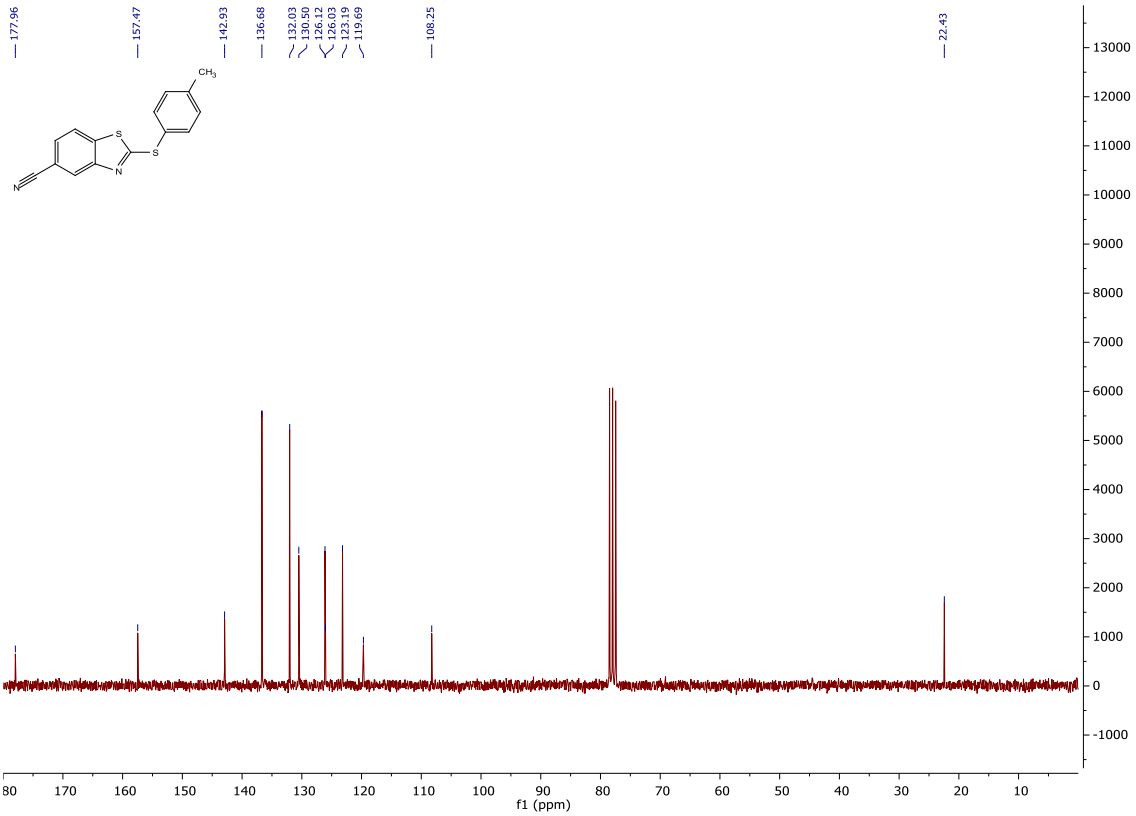
5-bromo-2-((4-methoxybenzyl)thio)benzo[d]thiazole (3ap)



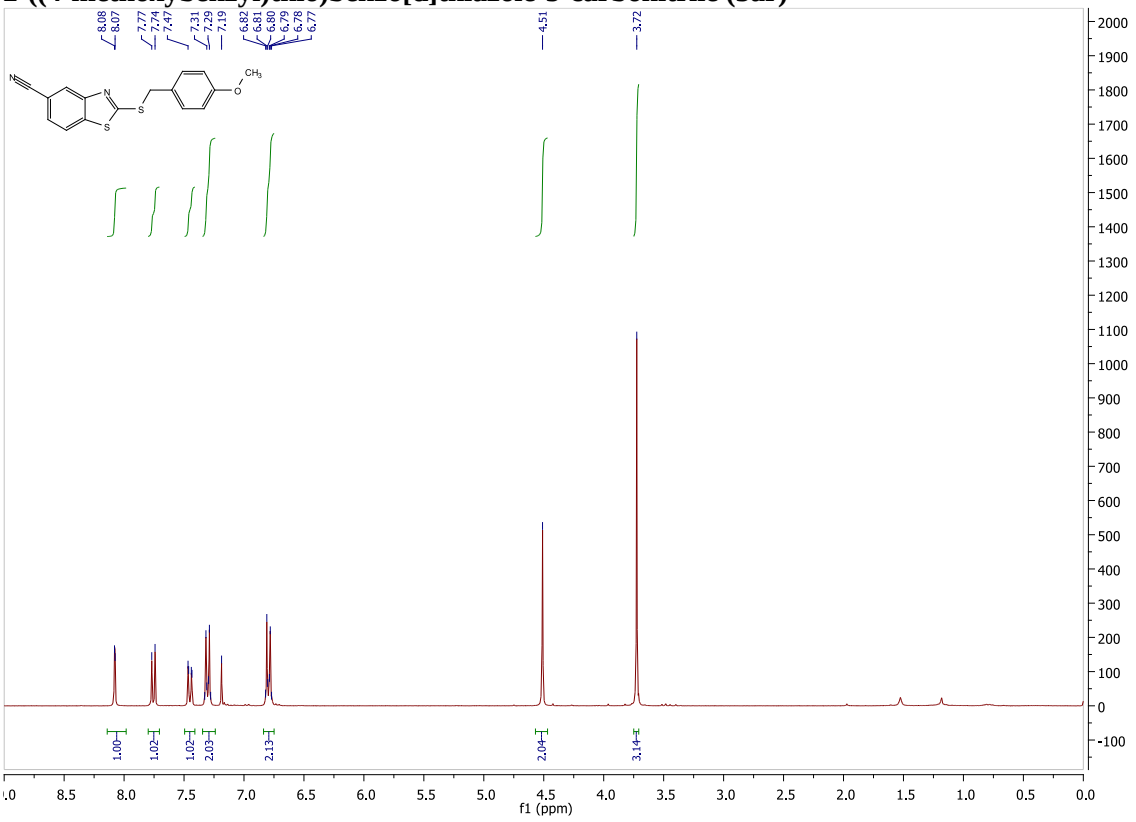


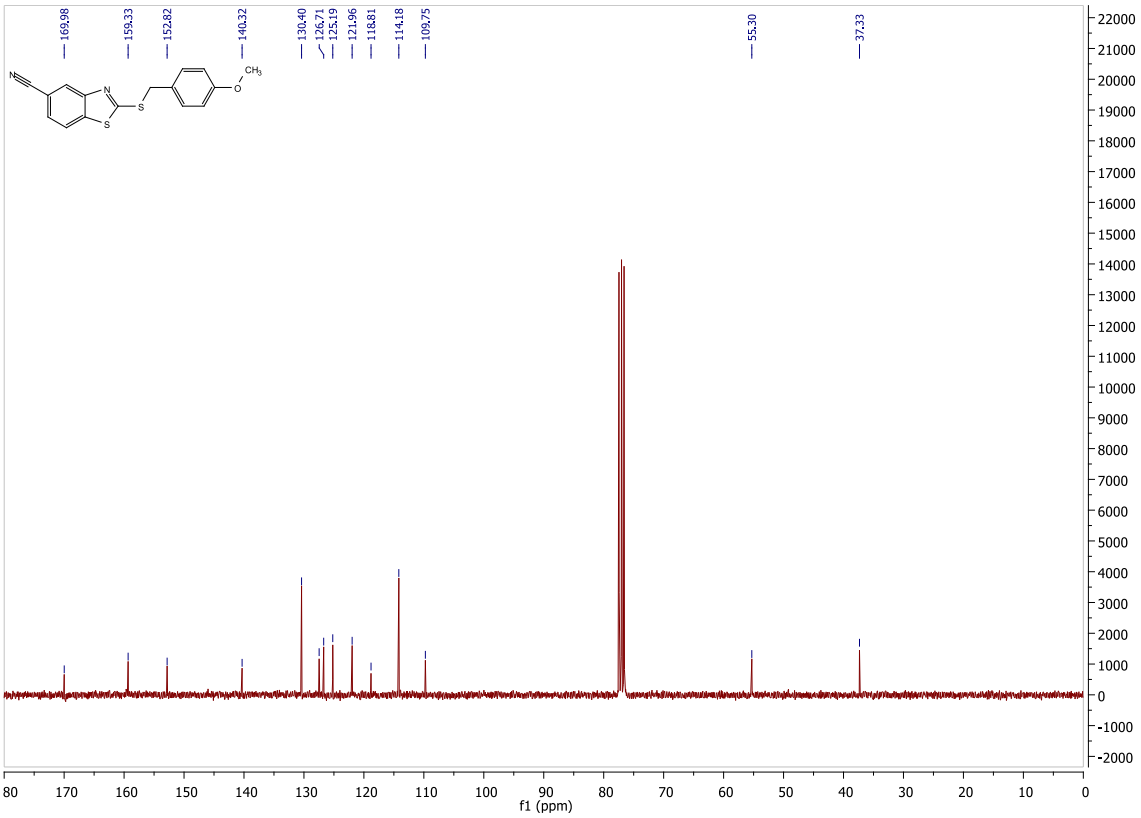
2-(p-tolylthio)benzo[d]thiazole-6-carbonitrile (3aq)



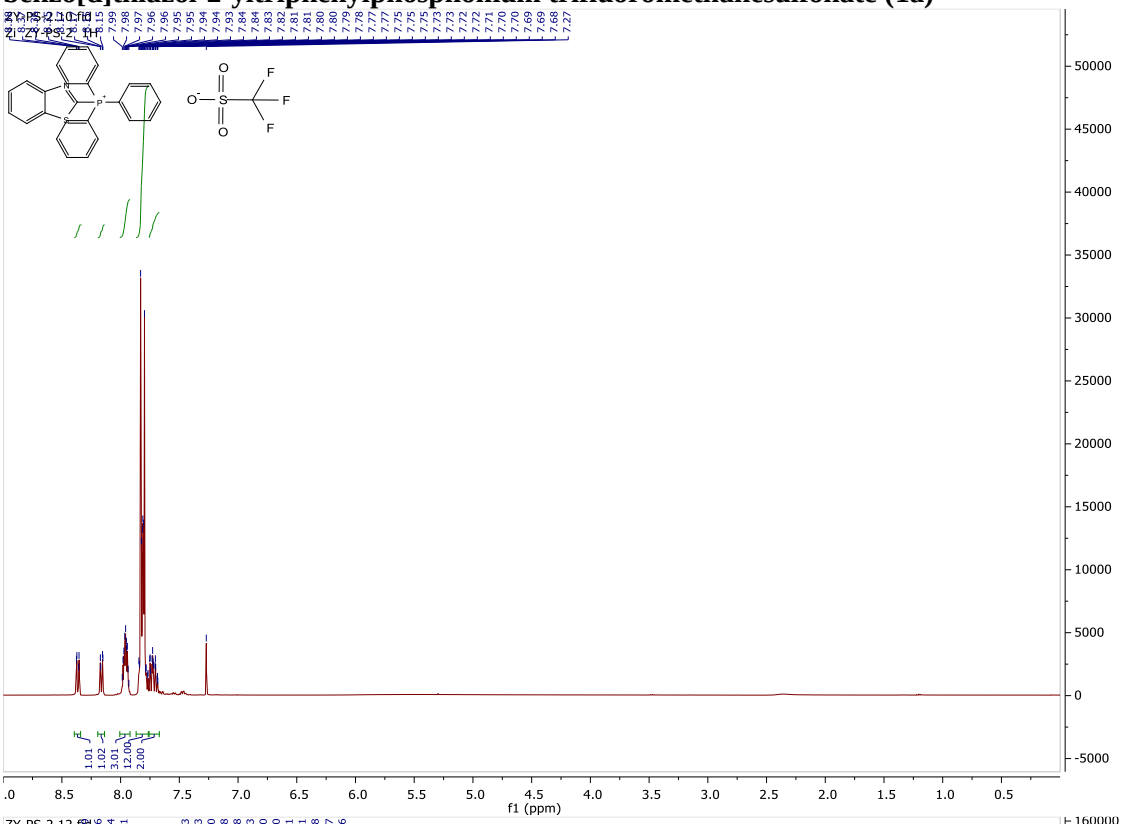


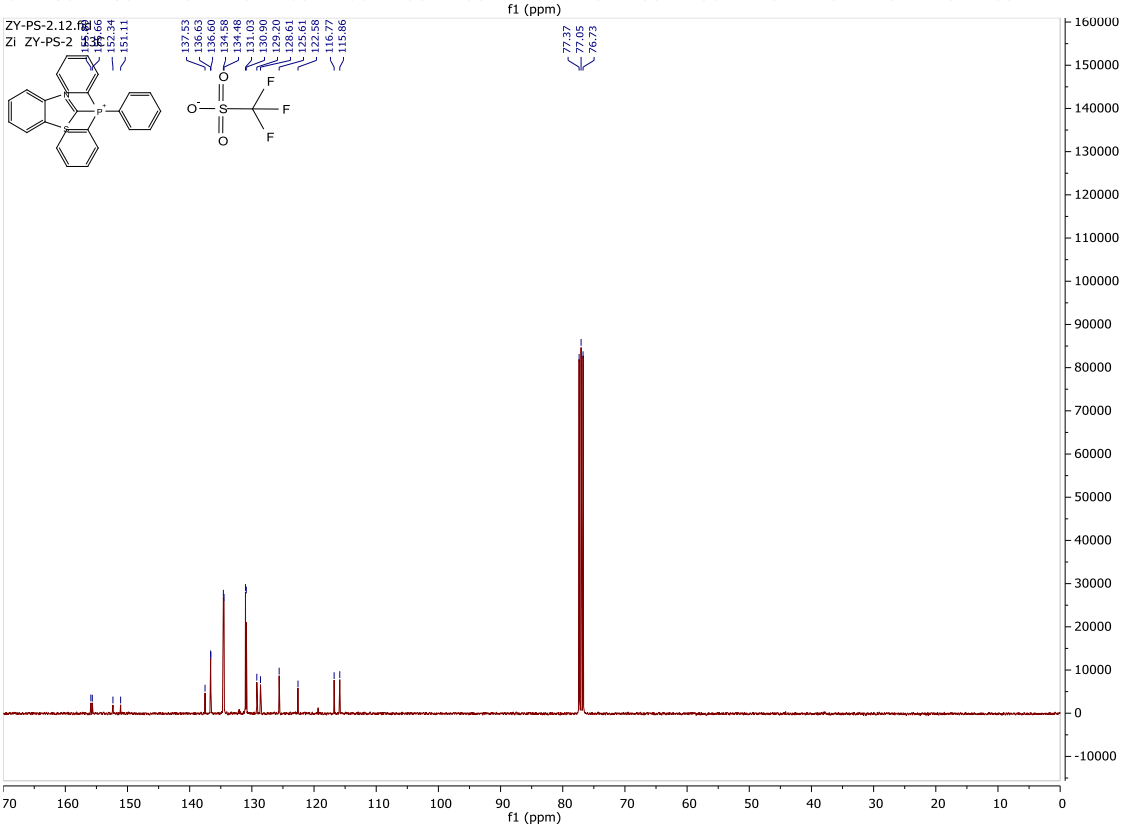
2-((4-methoxybenzyl)thio)benzo[d]thiazole-5-carbonitrile (3ar)



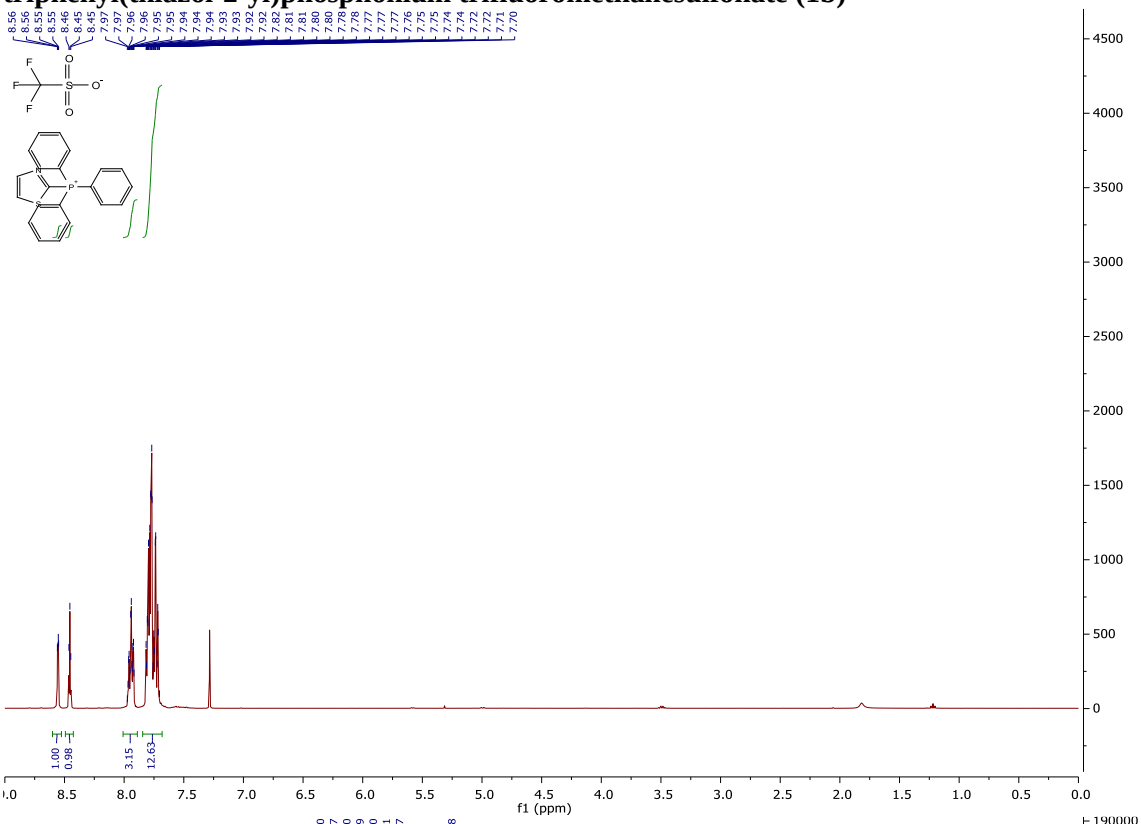

169.98
159.33
152.82
140.32
130.40
126.71
125.19
121.96
118.81
114.18
109.75
55.30
37.33
N
S
S
O
CH3
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

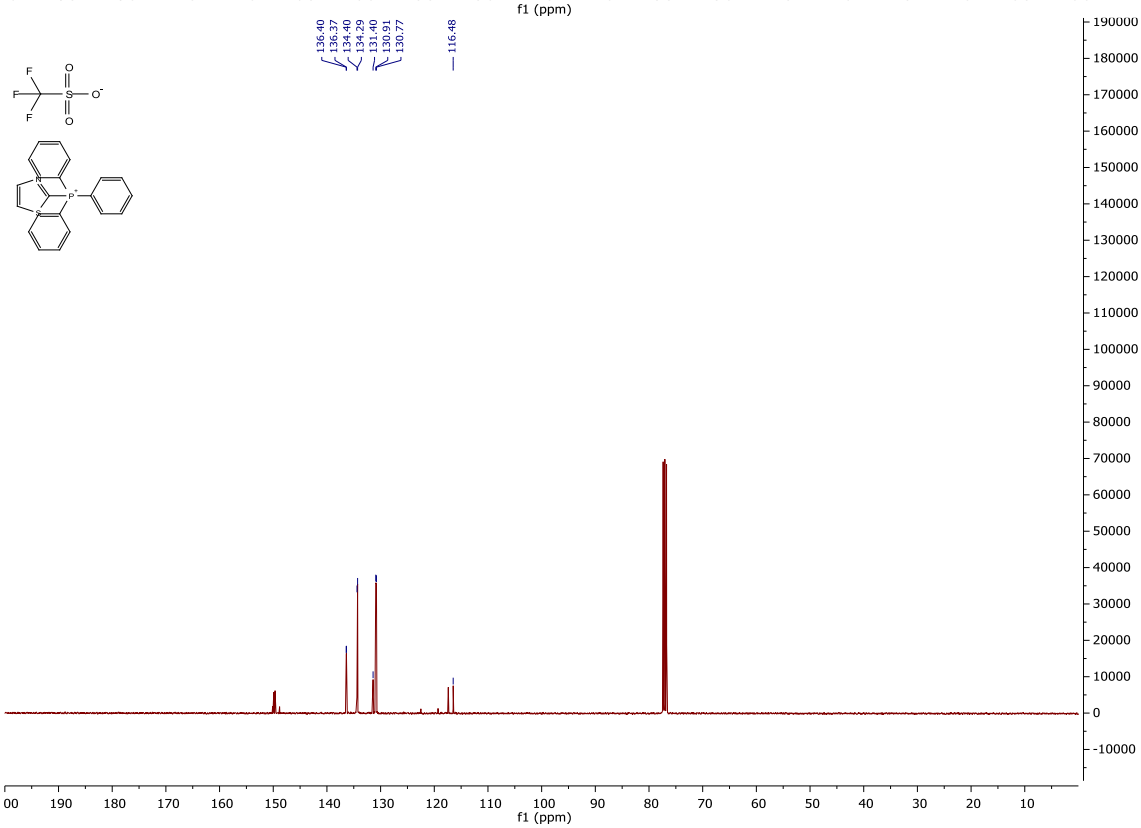
benzo[d]thiazol-2-yltriphenylphosphonium trifluoromethanesulfonate (1a)

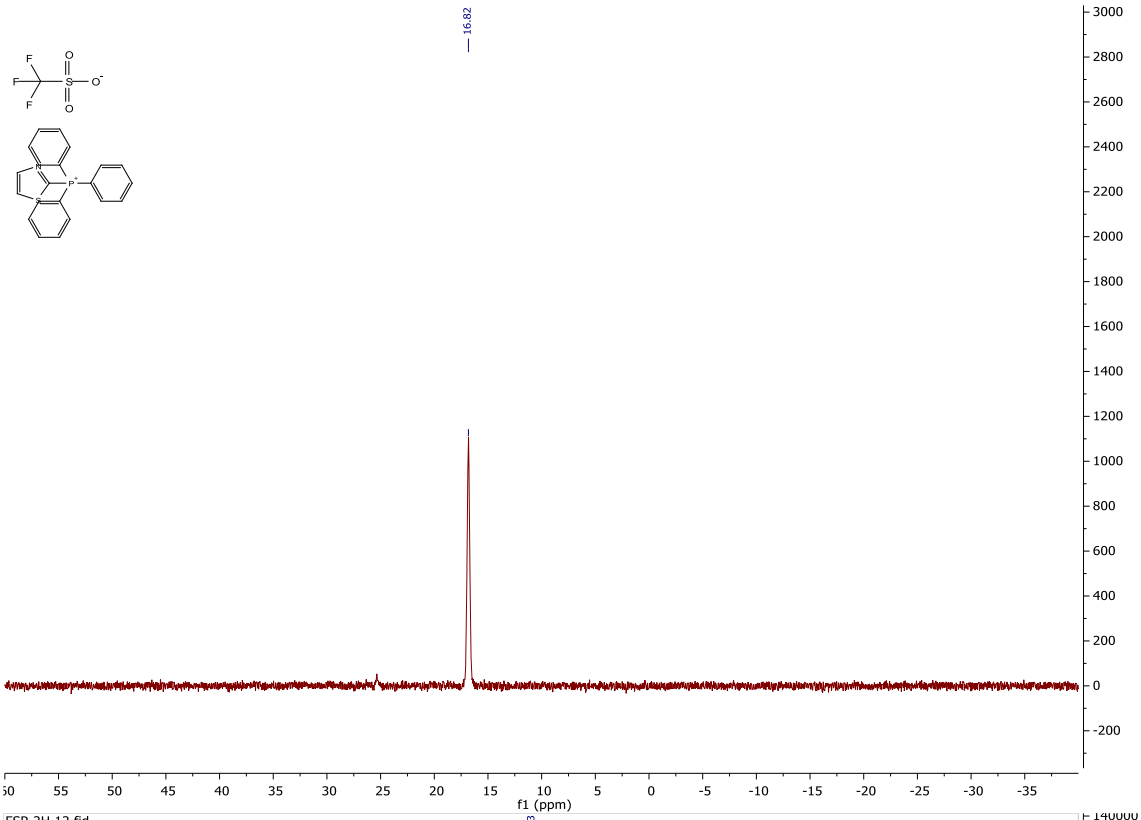


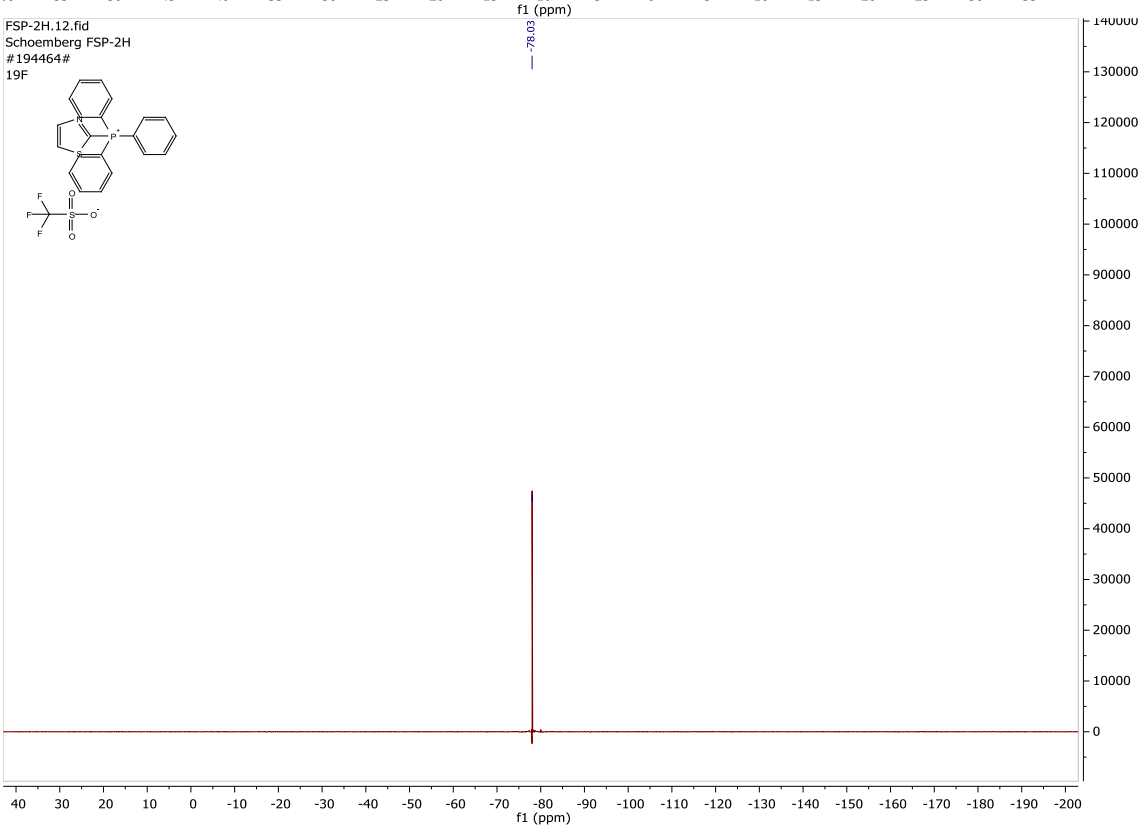


triphenyl(thiazol-2-yl)phosphonium trifluoromethanesulfonate (1b)






16.82
f1 (ppm)


FSP-2H.12.fid
Schoemberg FSP-2H
#194464#
19F
-78.03
f1 (ppm)