Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Dealkylative intercepted rearrangement reactions of sulfur ylides

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General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Carl Roth. Amino acetonitrile hydrochloride used in this manuscript was purchased from Alfa Aesar and Fluorochem, though it can be readily synthesized on 50 mmol scale in a single step starting from formaldehyde, ammonium hydroxide and sodium cyanide, followed by precipitation of the hydrochloride salt with 69% yield.[i]

Solvents used in reactions were p.A. grade. All reactions were performed under argon using degassed solvents. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR were recorded on a Varian AV600/AV400 or an Agilent DD2 400 NMR spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz).

HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

The following equipment was utilized for the addition of sodium nitrite: Syringe pump: Chemyx Inc. Model Fusion 710.

Important safety note

Safety hazards of diazo acetonitrile, described within this manuscript, have not been investigated. However, it should be noted this particular diazo compound was reported to be highly explosive.[ii]

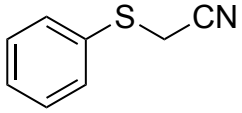
Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

Experimental Procedures

Standard procedure for the intercepted rearrangement reaction

Aminoacetonitrile hydrochloride (148 mg, 4.0 eq.), FePc (2.1 mg, 1 mol-%) and the corresponding substrate were placed in a reaction vessel. Then 100 µL $CHCl_3$ and 1.0 mL degassed water were added. The reaction mixture was heated to 40 °C and a solution of sodium nitrite (*c* = 4.8 mol/L, 1.0 mL, 4.8 eq., 132 mg) was added via syringe pump over 4 h. After the addition time the mixture was stirred for 10 h. The reaction mixture was then extracted three times with 10 mL of DCM. The combined organic layers were dried over $MgSO_4$ and the solvent removed. The crude product was purified by column chromatography on silica gel.

2-(Phenylthio)acetonitrile (**6a**)



Compound **6a** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 94% yield (56.3 mg):

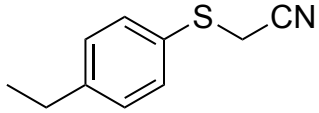
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.58 – 7.51 (m, 2H), 7.41 – 7.33 (m, 3H), 3.55 (s, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 132.4, 132.0, 129.5, 128.9, 116.4, 21.3 ppm.

MS (EI) *m/z*(%) = 149.7 ($[M]^+$, 30.5%), 148.9 ($[M - H]^+$, 35.1%), 109.0 ($[M - C_2H_2N]^+$, 100%).

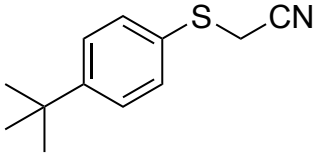
IR (KBr): 3900, 3652, 3379, 3167, 3061, 2968, 2930, 2838, 2662, 2326, 2245, 2178, 2111, 1992, 1947, 1921, 1807, 1733, 1669, 1582, 1477, 1438, 1399, 1305, 1282, 1236, 1158, 1072, 1027, 996, 923, 859, 743, 689 cm^{-1}.
The data is in accordance to the literature.[iii]

2-((4-Ethylphenyl)thio)acetonitrile (**6b**)



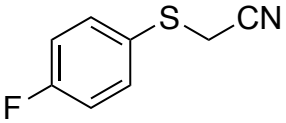
Compound **6b** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 91% yield (64.4 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.51 – 7.48 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 3.52 (s, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 145.7, 133.2, 129.1, 128.5, 116.6, 28.5, 21.9, 15.3 ppm.
MS (EI): *m/z*(%) = 177.4 ($[M]^+$, 100%), 162.4 ($[M - CH_3]^+$, 57.3%), 137.2 ($[M - C_2H_2N]^+$, 67.5%).
IR (KBr): 3864, 3660, 3425, 3167, 3025, 2967, 2931, 2873, 2668, 2330, 2245, 2173, 2109, 1970, 1911, 1795, 1659, 1596, 1554, 1492, 1459, 1402, 1328, 1277, 1232, 1181, 1115, 1093, 1054, 1016, 967, 925, 863, 825, 782, 706 cm^{-1}.
The data is in accordance to the literature.[ii]

2-((4-(*Tert*-butyl)phenyl)thio)acetonitrile (**6c**)



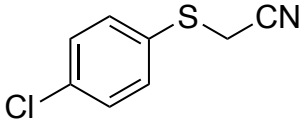
Compound **6c** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 74% yield (61.1 mg):
^{1}H NMR (600 MHz, Chloroform-*d)*: δ = 7.52 – 7.49 (m, 2H), 7.42 – 7.40 (m, 2H), 3.53 (s, 2H), 1.32 (s, 9H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 152.5, 132.7, 128.4, 126.6, 116.7, 34.7, 31.1, 21.8 ppm.
MS (EI): *m/z*(%) = 205.3 ($[M]^+$, 7.0%), 190.3 ($[M - CH_3]^+$, 12.5%), 121.4 ($[M - C_3H_3NS]^+$, 49.8%).
IR (KBr): 3914, 3887, 3780, 3703, 3663, 3633, 3439, 2920, 2855, 2746, 2424, 2314, 1959, 1851, 1728, 1629, 1540, 1439, 1384, 1262, 1159, 1030, 881, 825, 724 cm^{-1}.
The data is in accordance to the literature.[ii]

2-((4-Fluorophenyl)thio)acetonitrile (**6d**)



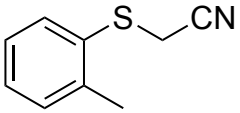
Compound **6d** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 76% yield (50.5 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.64 – 7.57 (m, 2H), 7.13 – 7.05 (m, 2H), 3.51 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 163.5 (d, *J* = 250.6 Hz), 135.9 (d, *J* = 8.6 Hz), 116.8 (d, *J* = 22.1 Hz), 116.3, 22.3 ppm.
^{19}F NMR (564 MHz, Chloroform-*d*): δ = -110.7 ppm.
MS(EI): *m/z*(%) = 166.9 ($[M]^+$, 5.0%), 127.2 ($[M - C_2H_2N]^+$, 100%).
IR (KBr): 3964, 3916, 3780, 3703, 3662, 3439, 2921, 2853, 2733, 2424, 2318, 2245, 2037, 1895, 1729, 1651, 1586, 1541, 1440, 1385, 1227, 1158, 1028, 924, 875, 826 cm^{-1}.
The data is in accordance to the literature.[iv]

2-((4-Chlorophenyl)thio)acetonitrile (**6e**)



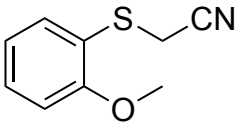
Compound **6e** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow solid in 89% yield (65.5 mg):
m.p.: 84.1 – 88.6 °C.
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.51 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.36 (m, 2H), 3.55 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 135.6, 134.1, 130.2, 129.8, 116.1, 21.6 ppm.
MS (EI): *m/z*(%) = 183.4 AND 185.3 ($[M]^+$, 46%; 18%), 143.2 AND 145.0 ($[M - C_2H_2N]^+$, 100%; 31.2%), 108.1 ($[M - C_2H_2NCl]^+$, 60%).
IR (KBr): 3830, 3165, 308, 3024, 2961, 2926, 2660, 2454, 2311, 2243, 2187, 2109 1896, 1781, 1729, 1638, 1571, 1475, 1402, 1304, 1262, 1229, 1178, 1092, 1007, 953, 922, 871, 810, 747, 725 cm^{-1}.
The data is in accordance to the literature.[ii]

2-(*o*-Tolylthio)acetonitrile (**6f**)



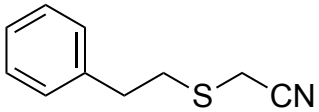
Compound **6f** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 95% yield (62.2 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.54 – 7.51 (m, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 3.54 (s, 2H), 2.49 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 140.4, 132.7, 131.1, 130.8, 129.0, 127.1, 116.3, 20.5, 20.4 ppm.
MS (EI): *m/z*(%) = 163.7 ($[M + H]^+$, 70.3%), 162.8 ($[M]^+$, 67.9%), 122.7 ($[M - C_2H_2N]^+$, 100%).
IR (KBr): 3060, 2968, 2930, 2246, 2162, 1727, 1589, 1462, 1397, 1278, 1228, 1168, 1074, 926, 861, 747 cm^{-1}.
The data is in accordance to the literature.[ii]

2-((2-Methoxyphenyl)thio)acetonitrile (**6g**)



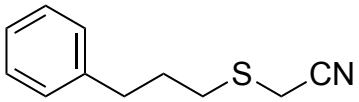
Compound **6g** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1 → 9:1) as a yellow oil in 95% yield (68.3 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.52 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.38 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.98 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.93 (s, 3H), 3.62 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 158.9, 134.4, 130.9, 121.3, 119.1, 116.6, 111.1, 55.8, 19.1 ppm.
MS (EI): *m/z*(%) = 179.9 ($[M + H]^+$, 24.2%), 179.1 ($[M]^+$, 100%), 139.0 ($[M - C_2H_2N]^+$, 36.8%).
IR (KBr): 3420, 3175, 2922, 2863, 2325, 2071, 1993, 1902, 1582, 1459, 1376, 1248, 1158, 1026, 962, 727 cm^{-1}.
The data is in accordance to the literature.[v]

2-(Phenethylthio)acetonitrile (**6h**)



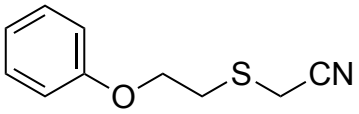
Compound **XXX** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 91% yield (64.6 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.33 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.25 – 7.23 (m, 2H), 3.21 (s, 2H), 3.02 (ddd, *J* = 8.1, 6.5, 1.8 Hz, 2H), 2.97 (ddd, *J* = 8.5, 6.3, 1.7 Hz, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 139.2, 128.6, 128.5, 126.7, 116.4, 35.4, 33.9, 17.1 ppm.
HRMS (ESI): mass found: 200.05040, calculated mass for $C_{10}H_{11}NNaS^+$: 200.05044.
IR (KBr): 3964, 3914, 3887, 3780, 3704, 3662, 3634, 3439, 3063, 3028, 2921, 2853, 2727, 2601, 2419, 2243, 1956, 1884, 1814, 1763, 1729, 1602, 1446, 1385, 1325, 1279, 1231, 1156, 1070, 1029, 921, 879, 843, 740, 703 cm^{-1}.

2-((3-Phenylpropyl)thio)acetonitrile (**6i**)



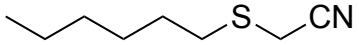
Compound **XXX** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 58% yield (44.1 mg):
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.32 – 7.25 (m, 2H), 7.19 (tt, *J* = 7.8, 1.3 Hz, 3H), 3.27 (s, 2H), 2.81 – 2.63 (m, 4H), 1.97 (ddd, *J* = 14.9, 8.2, 6.9 Hz, 2H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 140.7, 128.49, 128.41, 126.1, 116.4, 34.4, 31.9, 30.0, 16.9 ppm.
HRMS (ESI): mass found: 214.06654, calculated mass for $C_{11}H_{13}NNaS^{+}$: 214.06664.
IR (KBr): 3649, 3164, 3061, 3026, 2927, 2857, 2658, 2322, 2243, 2166, 2092, 1953, 1882, 1812, 1754, 1601, 1495, 1450, 1400, 1349, 1295, 1232, 1181, 1075, 1028, 970, 917, 863, 744, 700 cm^{-1}.

2-((2-Phenoxyethyl)thio)acetonitrile (**6j**)



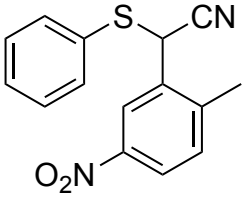
Compound **XXX** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 62% yield (48.0 mg):
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.32 – 7.25 (m, 2H), 6.97 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.92 – 6.86 (m, 2H), 4.26 (t, *J* = 5.8 Hz, 2H), 3.47 (s, 1H), 3.12 (t, *J* = 5.8 Hz, 2H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 158.0, 129.5, 121.3, 114.4, 68.0, 31.5, 17.9 ppm.
HRMS (ESI): mass found: 216.04507, calculated mass for $C_{10}H_{11}NONaS^{+}$: 216.04536.
IR (KBr): 3914, 3783, 3705, 3661, 3636, 3438, 3166, 3063, 3039, 2967, 2927, 2873, 2744, 2600, 2538, 2467, 2244, 2070, 2013, 1938, 1846, 1780, 1711, 1595, 1493, 1390, 1297, 1239, 1174, 1073, 1029, 924, 886, 838, 757, 692, 596, 511 cm^{-1}.

2-(Hexylthio)acetonitrile (**6k**)



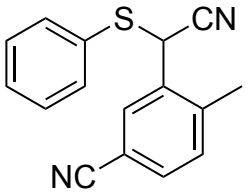
Compound **XXX** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 69% yield (43.5 mg):
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 3.27 (s, 2H), 2.79 – 2.67 (m, 2H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.29 (h, *J* = 3.8, 3.3 Hz, 4H), 0.90 – 0.82 (m, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 116.5, 32.6, 31.2, 28.5, 28.2, 22.4, 16.9, 13.9 ppm.
The data is in accordance to the literature.[v]

2-(2-Methyl-5-nitrophenyl)-2-(phenylthio)acetonitrile (**4o**)



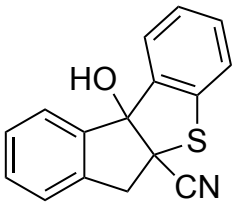
Compound **4o** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a colorless oil in 23% yield (26.0 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.11 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.38 – 7.33 (m, 2H), 5.03 (s, 1H), 2.60 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 146.2, 143.1, 135.8, 132.2, 132.0, 130.7, 129.5, 128.8, 123.8, 123.1, 117.1, 39.0, 19.3 ppm.
HRMS (ESI): mass found: 307.05133, calculated mass for $C_{15}H_{12}N_2O_2NaS^{+}$: 307.05117.
IR (KBr): 3892, 3625, 3407, 3066, 2922, 2853, 2645, 2343, 2244, 2197, 2155, 2086, 2022, 1956, 1863, 1801, 1736, 1588, 1517, 1471, 1340, 1248, 1153, 1085, 1021, 956, 896, 826, 730, 692 cm^{-1}.

3-(Cyano(phenylthio)methyl)-4-methylbenzonitrile (**4p**)



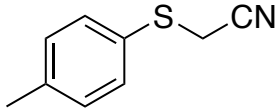
Compound **4p** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a colorless solid in 53% yield (56.0 mg):
m.p.: 99.2 – 103.4 °C.
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.54 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (ddt, *J* = 8.6, 7.5, 1.3 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.39 – 7.34 (m, 3H), 7.30 (d, *J* = 1.6 Hz, 1H), 4.98 (d, *J* = 0.9 Hz, 1H), 2.56 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 141.1, 135.9, 132.5, 132.1, 131.9, 131.4, 130.7, 129.5, 128.8, 117.8, 117.1, 110.4, 38.8, 19.4 ppm.
HRMS (ESI): mass found: 287.06149, calculated mass for $C_{16}H_{12}N_2NaS^+$: 287.06134.
IR (KBr): 3835, 3753, 3550, 3210, 3057, 2954, 2851, 2627, 2322, 2230, 2148, 2058, 2005, 1963, 1900, 1815, 1779, 1711, 1604, 1575, 1498, 1472, 1439, 1375, 1300, 1270, 1232, 1207, 1155, 1101, 1070, 1023, 970, 928, 894, 830, 790, 754, 734, 695 cm^{-1}.

10b-Hydroxy-6,10b-dihydro-5a*H*-benzo[*b*]indeno[1,2-*d*]thiophene-5a-carbonitrile (**4q**)



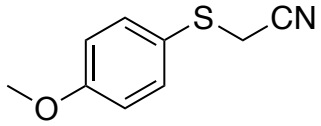
Compound **4q** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1 → 9:1 → 4:1) as a yellow solid in 33% yield (37.4 mg):
m.p.: 151.4 – 153.8 °C
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.65 – 7.62 (m, 1H), 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.33 – 7.27 (m, 3H), 7.16 – 7.13 (m, 1H), 3.90 (d, *J* = 16.7 Hz, 1H), 3.53 (d, *J* = 16.6 Hz, 1H), 3.05 (s, 1H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 139.3, 138.6, 138.5, 137.0, 130.2, 130.1, 128.6, 126.3, 125.0, 124.8, 124.6, 122.8, 119.1, 97.4, 60.7, 41.8 ppm.
HRMS (ESI): mass found: 288.04520, calculated mass for $C_{16}H_{11}NONaS^+$: 288.04536.
IR (KBr): 3748, 3409, 3066, 2905, 2845, 2459, 2318, 2239, 2177, 2075, 2014, 1967, 1920, 1796, 1719, 1587, 445, 1357, 1297, 1260, 1208, 1170, 1112, 1086, 1044, 986, 947, 925, 889, 819, 751 cm^{-1}.

2-(*p*-Tolylthio)acetonitrile (**6t**)



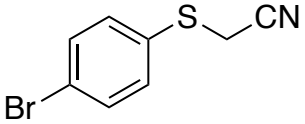
Compound **6t** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 59% yield (38.7 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.49 – 7.44 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 3.51 (s, 2H), 2.37 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 139.5, 133.2, 130.3, 128.3, 116.6, 22.0, 21.2 ppm.
MS (EI): *m/z*(%) = 163.9 ([M + H]$^+$, 10.4%); 163.1 ([M]$^+$,16.7%); 123.0 ([M – C_2H_2N]$^+$, 81.5%); 77.2 ([M – C_3H_5NS]$^+$, 58.9%).
IR (KBr): 3912, 3780, 3709, 3661, 3443, 2927, 2733, 2588, 2418, 2246, 2104, 1905, 1800, 1733, 1601, 1487, 1397, 1304, 1224, 1170, 1102, 1023, 940, 866, 806, 712 cm^{-1}.
The data is in accordance to the literature.[ii]

2-((4-Methoxyphenyl)thio)acetonitrile (**6u**)



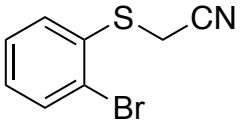
Compound **6u** was prepared according to general procedure and was obtained after column 6u (*n*-hexane : ethyl acetate 40:1 → 20:1 → 9:1) as a yellow oil in 67% yield (48.0 mg):
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.58 – 7.51 (m, 2H), 6.93 – 6.87 (m, 2H), 3.81 (s, 3H), 3.44 (s, 2H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 160.9, 136.0, 122.1, 116.6, 115.1, 55.3, 22.9 ppm.
MS (EI): *m/z*(%) = 179.1 ($[M]^+$, 64.2%); 139.1 ($[M - C_2H_2N]^+$, 100%).
IR (KBr): 3918, 3781, 36705, 3442, 3026, 2923, 2860, 2733, 2589, 2408, 2312, 2245, 2099, 1904, 1798, 1732, 1633, 1388, 1304, 1228, 1168, 1029, 925, 868, 806, 712 cm^{-1}.
The data is in accordance to the literature.[ii]

2-((4-Bromophenyl)thio)acetonitrile (**6w**)



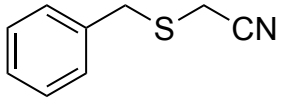
Compound **6w** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a colorless oil in 59% yield (53.9 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.54 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 3.56 (d, *J* = 1.0 Hz, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 134.1, 132.7, 130.9, 123.6, 116.1, 21.4 ppm.
MS(EI): *m/z*(%): 227.6; 229.6 ($[M + H]^+$, 89.7%; 93.9%); 187.3; 189.3 ($[M - C_2H_2N]^+$, 96.0%; 100%), 107.8 ($[M - C_2H_2NBr]^+$, 55.5%).
IR(KBr): 3159, 3063, 3015, 2961, 2925, 2857, 2658, 2455, 2326, 2242, 2171, 2107, 2022, 1918, 1833, 1737, 1634, 1563, 1472, 1404, 1327, 1300, 1230, 1177, 1087, 1001, 920, 872, 803, 738, 709, 689 cm^{-1}.
The data is in accordance to the literature.[v]

2-(2-Bromophenyl)thio)acetonitrile (**6x**)



Compound **6x** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 29% yield (26.6 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.38 (td, *J* = 7.7, 1.3 Hz, 1H), 7.23 (td, *J* = 7.8, 1.6 Hz, 1H), 3.67 (2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 133.6, 132.9, 132.8, 130.0, 128.5, 126.7, 115.8, 19.7 ppm.
MS (EI): *m/z*(%) = 227.4; 229.4 ($[M + H]^+$, 1.8%; 1.8%); 187.2; 189.1 ($[M - C_2H_2N]^+$, 1.0; 1.1%), 107.8 ($[M - C_2H_2NBr]^+$, 3.7%).
IR (KBr): 3919, 3780, 3706, 3440, 2922, 2854, 2725, 2398, 2313, 2245, 2095, 1899, 1726, 1631, 1564, 1440, 1387, 1252, 1159, 1024, 927, 869, 746 cm^{-1}.
The data is in accordance to the literature.[ii]

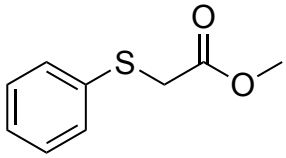
2-(Benzylthio)acetonitrile (**8**)



Compound **8** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1) as a yellow oil in 77% yield (50.2 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 3.92 (s, 2H), 3.08 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 135.6, 129.0, 128.8, 127.8, 116.2, 36.0, 15.8 ppm.

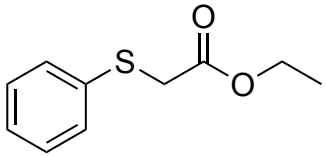
The data is in accordance to the literature.[v]

Methyl 2-(phenylthio)acetate (**10a**)



Compound **10a** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1 → 9:1) as a yellow oil in 74% yield (54.1 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.42 – 7.39 (m, 2H), 7.32 – 7.29 (m, 2H), 7.24 (ddt, *J* = 8.5, 6.7, 0.9 Hz, 1H), 3.72 (s, 3H), 3.66 (s, 2H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.1, 134.8, 129.9, 129.0, 127.0, 52.5, 36.5 ppm.
MS (EI) *m/z*(%) = 182.0 ($[M]^+$, 69.4%), 122.8 ($[M - C_2H_3O_2]^+$, 100%).
IR (KBr): 3915, 3779, 3704, 3663, 3633, 3441, 3065, 3003, 2920, 2851, 2425, 2316, 1957, 1861, 1737, 1626, 1555, 1438, 1384, 1282, 1070, 1021, 896, 836, 742 cm^{-1}.
The data is in accordance to the literature.[v]

Ethyl 2-(phenylthio)acetate (**10b**)



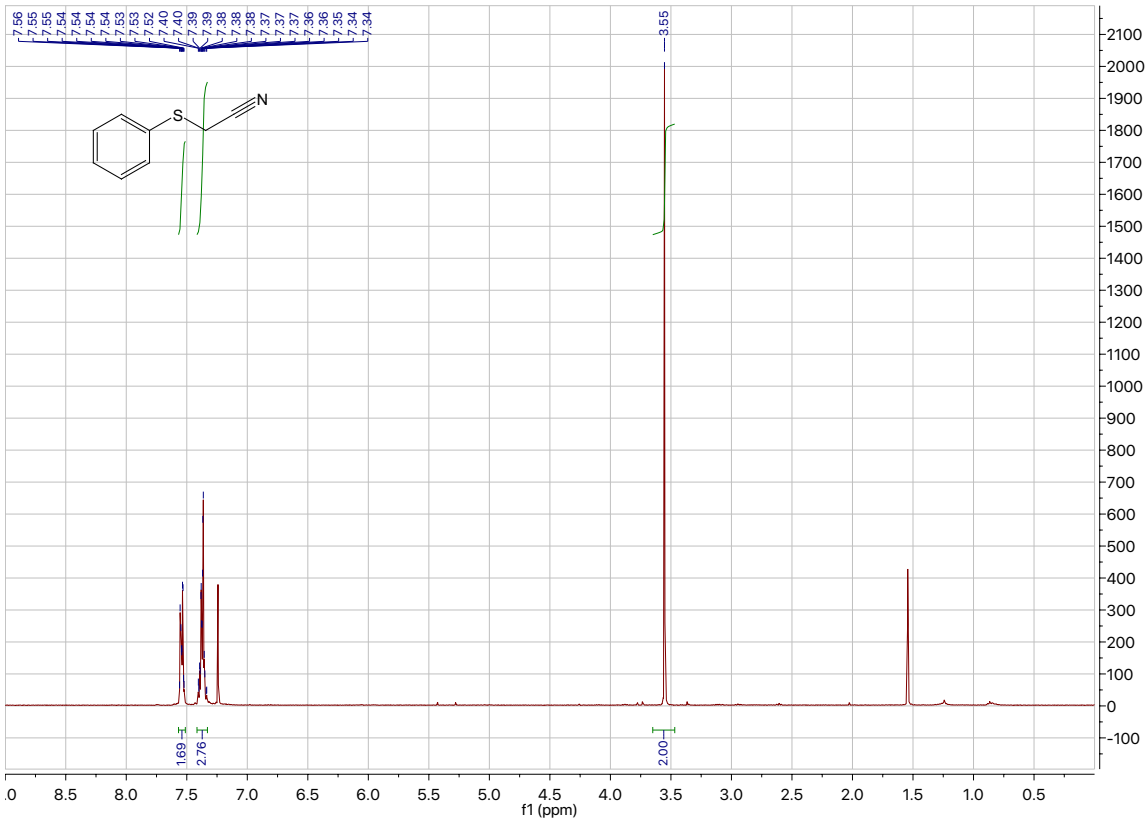
Compound **10b** was prepared according to general procedure and was obtained after column chromatography (*n*-hexane : ethyl acetate 40:1 → 20:1 → 9:1) as a yellow oil in 77% yield (60.7 mg):
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.41 (dt, *J* = 8.1, 1.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C NNR (151 MHz, Chloroform-*d*): δ = 169.6, 134.9, 129.9, 129.0, 126.9, 61.5, 36.7, 14.0 ppm.
MS (EI): *m/z*(%) = 196.7($[M]^+$, 49.5%), 122.8 ($[M - C_3H_5O_2]^+$, 100%), 108.6 ($[M - C_4H_7O_2]^+$, 38.6%), 77.4 ($[M - C_4H_7O_2S_2]^+$, 42.6%).
IR (KBr): 3915, 3779, 3701, 3662, 3635, 3444, 3061, 2982, 2929, 2663, 2419, 2321, 1957, 1879, 1733, 1580, 1474, 1444, 1384, 1280, 1144, 1026, 901, 843, 742 cm^{-1}.
The data is in accordance to the literature.[vi]

References

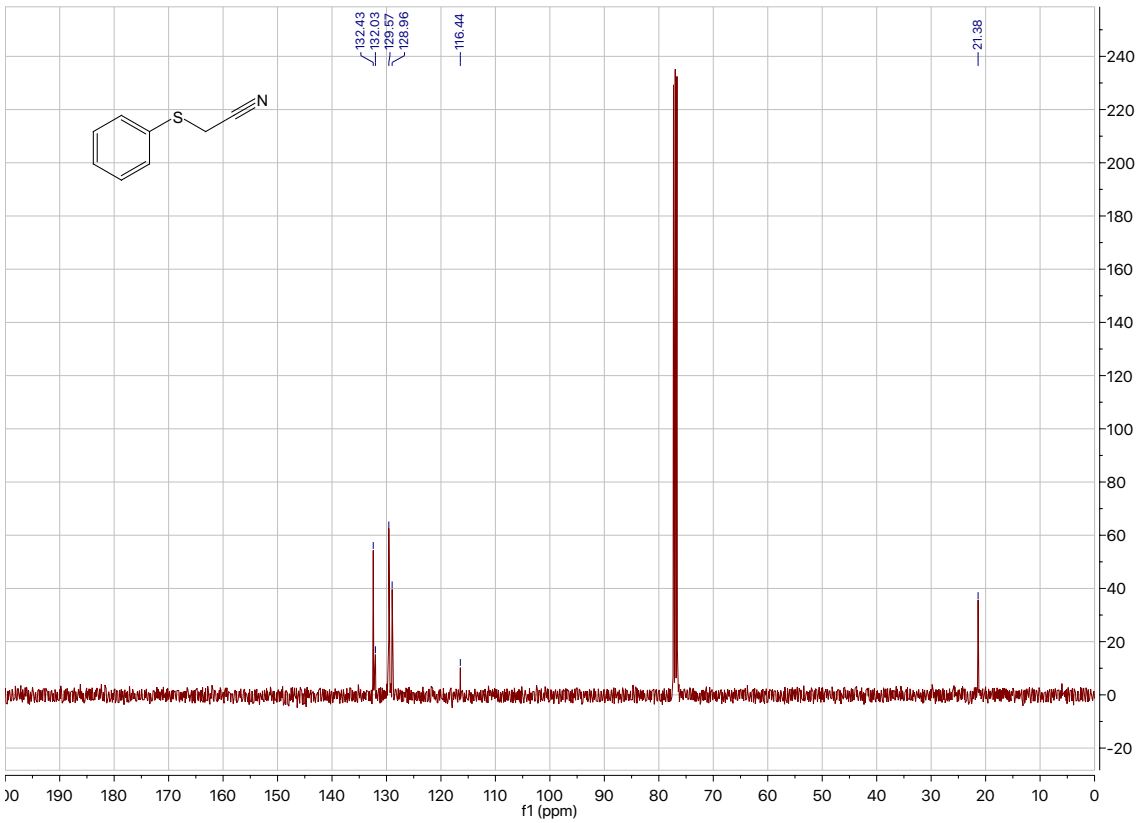
[i] B. Binkowski, L. P. Encell, M. Hall, M. B. Robers, M. R. Slater, K. V. Wood and M. G. Wood, WO2012061530, 2012, (Promega Corporation).
[ii] Q. Chen, Y. Huang, X. Wang, C. Wen, X. Yan and J. Zeng, *Tetrahedron Lett.*, 2017, **58**, 3928-3931.
[ii] D. D. Phillips and W. C. Champion, *J. Am. Chem. Soc.*, 1956, **78**, 5452
[iii] T. Miyazaki, S. Kasai, Y. Ogiwara and N. Sakai, *Eur. J. Org. Chem*., **2016**, 1043.
[iv] Tyagi, R. B. Bonn and R. Fasan, *Chem. Sci.,* 2015, **6**, 2488.
[v] C. Empel, K. J. Hock and R. M. Koenigs, *Org. Biomol. Chem*., 2018, **16**, 7129.

2-(Phenylthio)acetonitrile (**6a**)

^{1}H NMR (400 MHz, Chloroform-*d*)

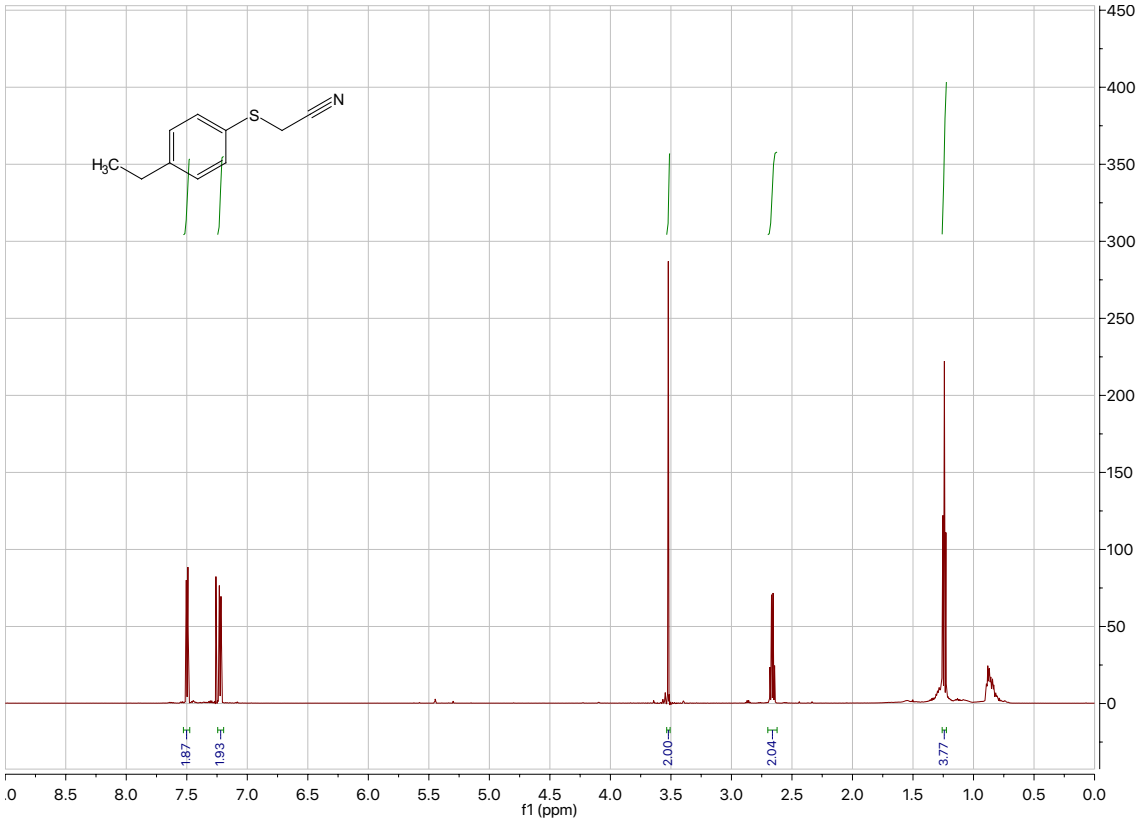


^{13}C NMR (101 MHz, Chloroform-*d*)

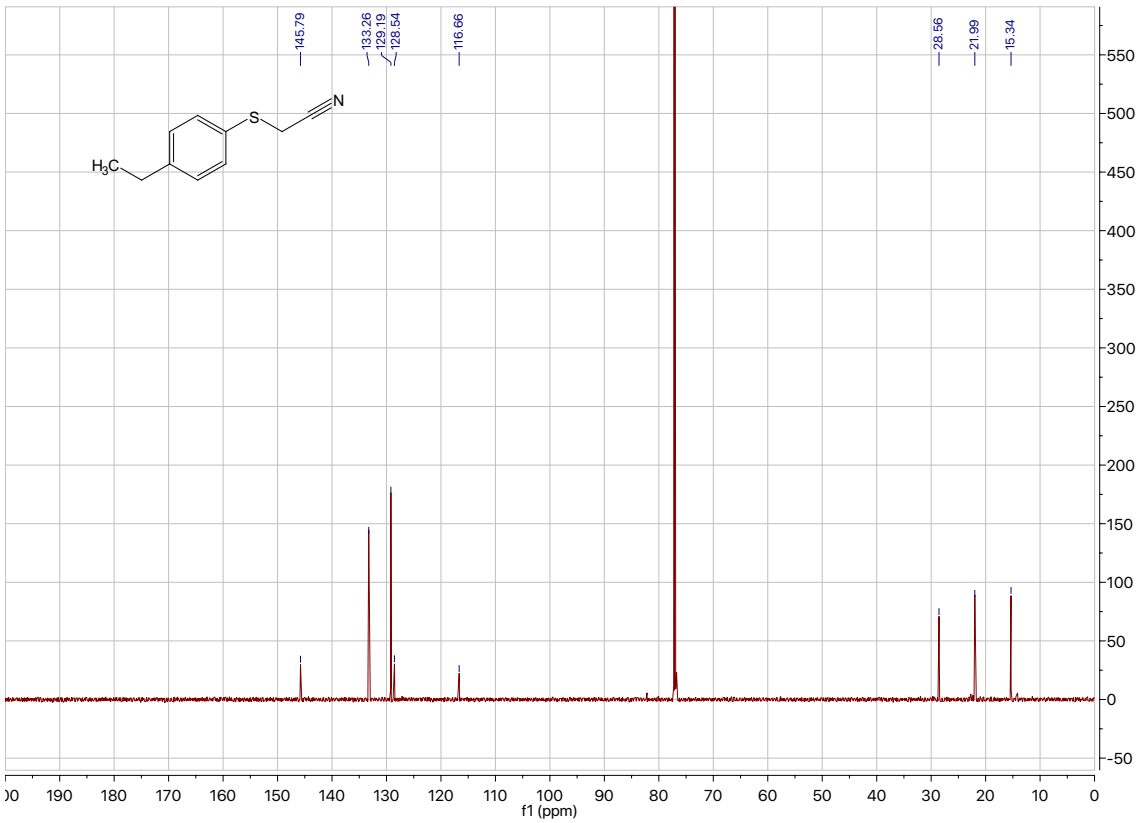


2-((4-Ethylphenyl)thio)acetonitrile (**6b**)

^{1}H NMR (600 MHz, Chloroform-*d*)

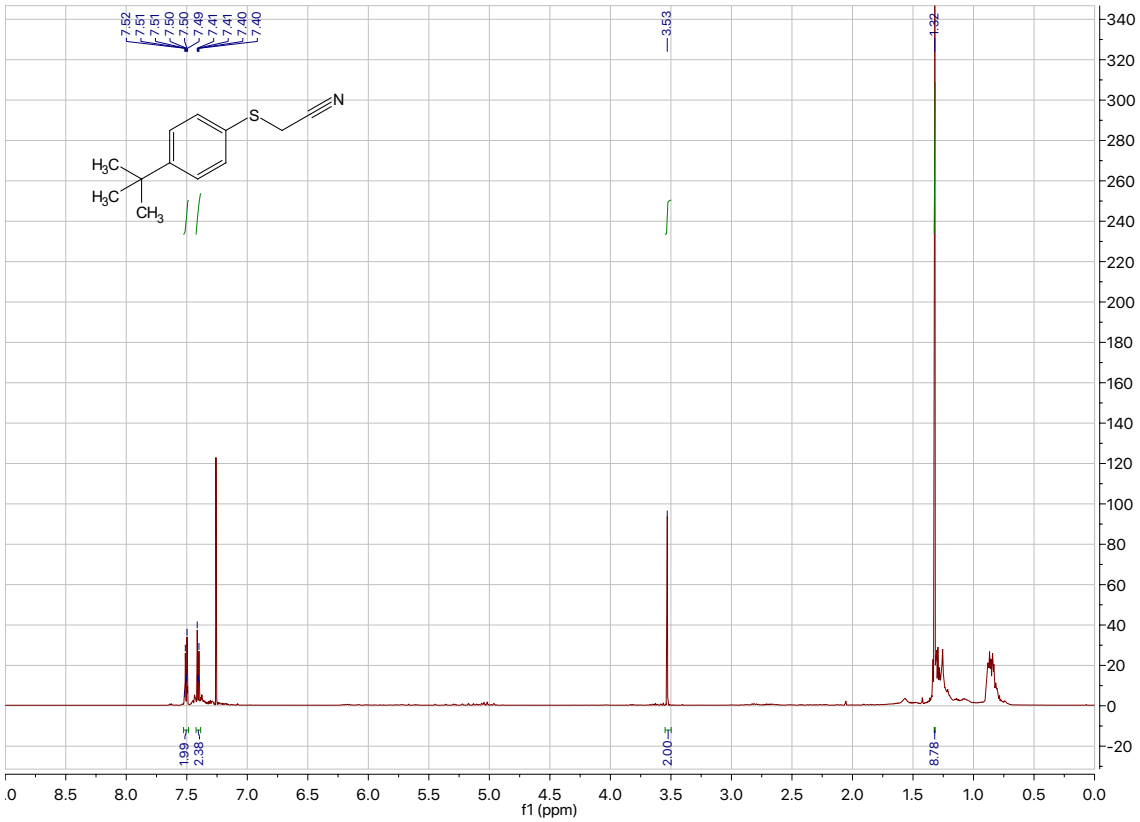


^{13}C NMR (151 MHz, Chloroform-*d*)

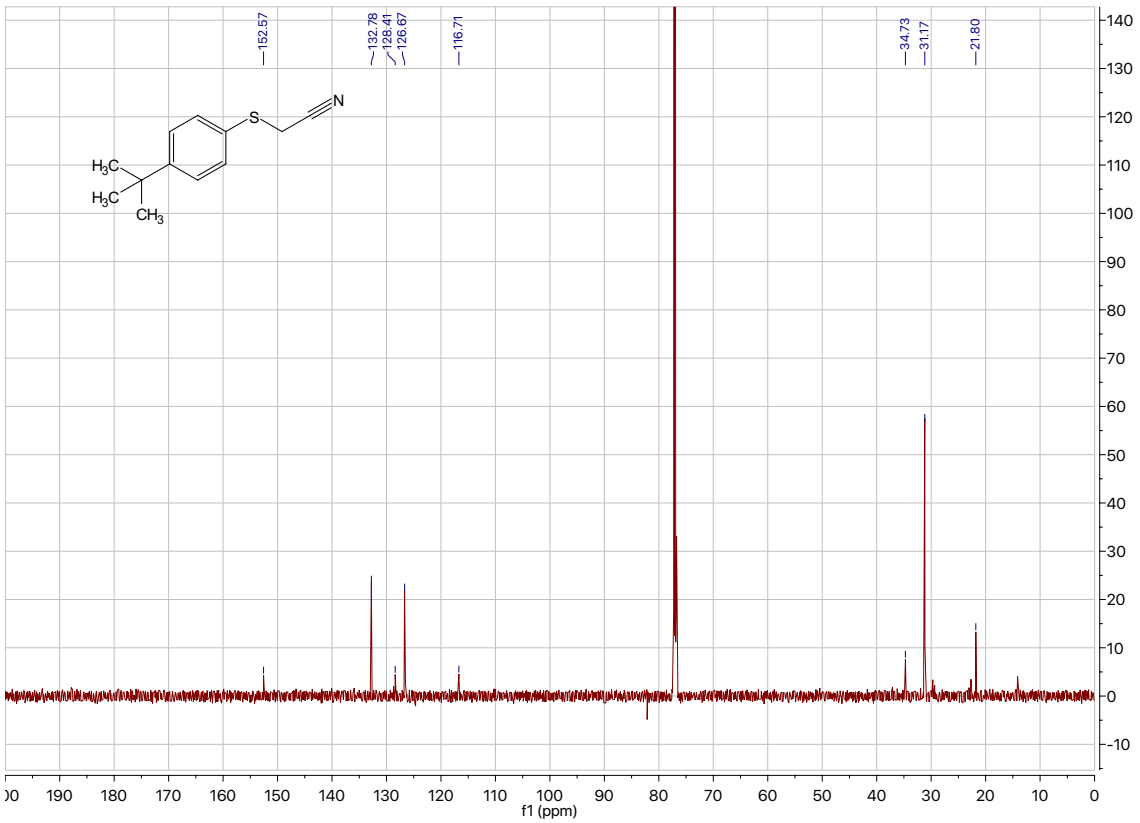


2-((4-(*Tert*-butyl)phenyl)thio)acetonitrile (**6c**)

^{1}H NMR (600 MHz, Chloroform-*d)*

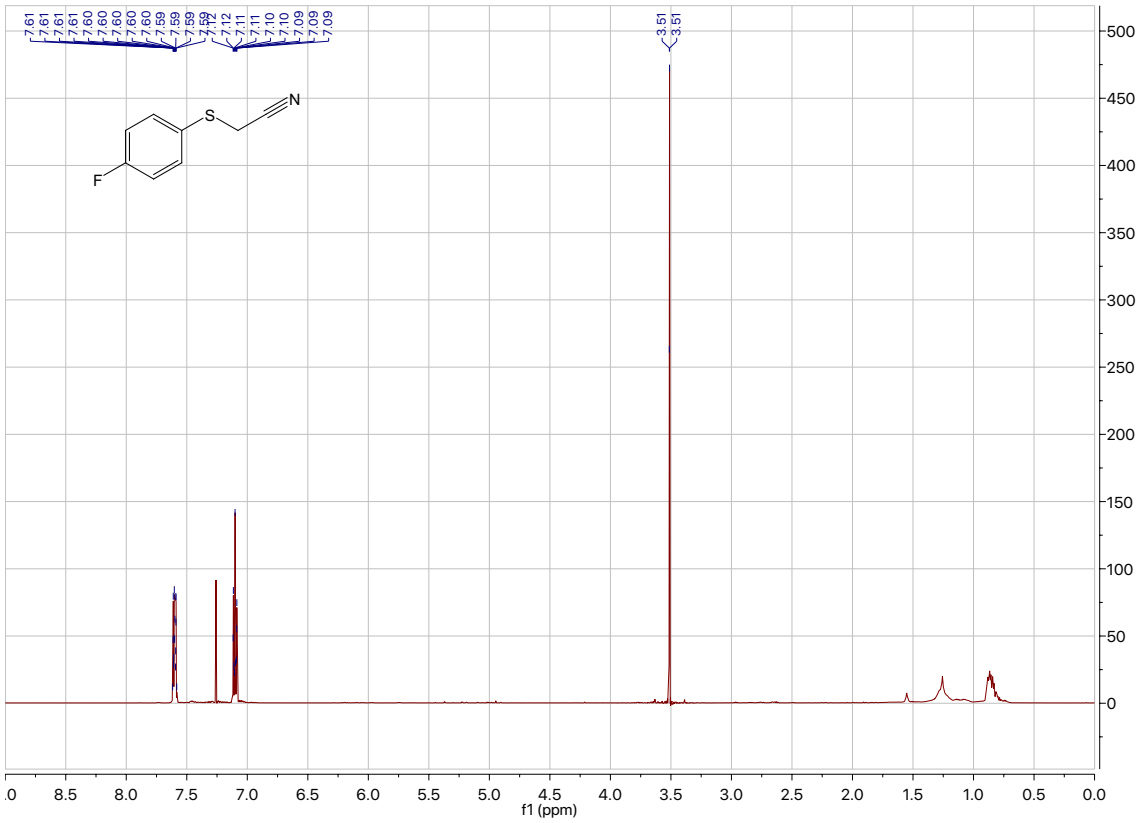


^{13}C NMR (151 MHz, Chloroform-*d*)

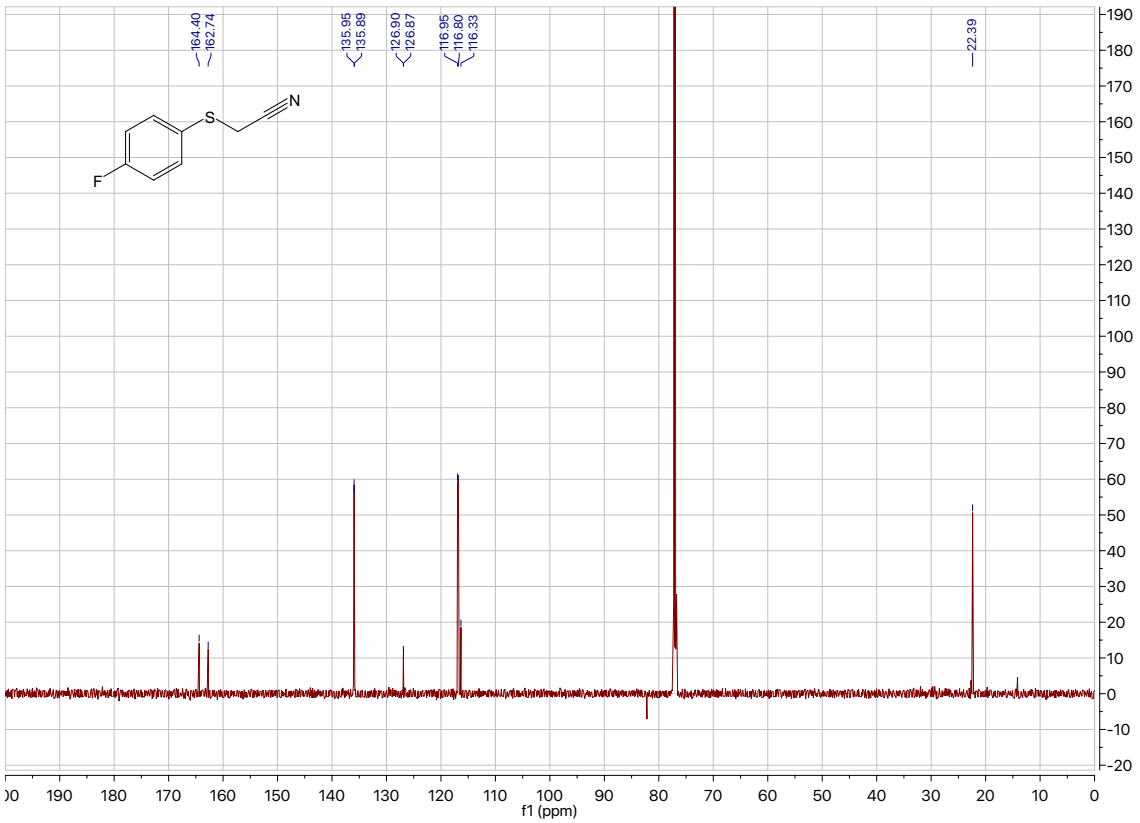


2-((4-Fluorophenyl)thio)acetonitrile (**6d**)

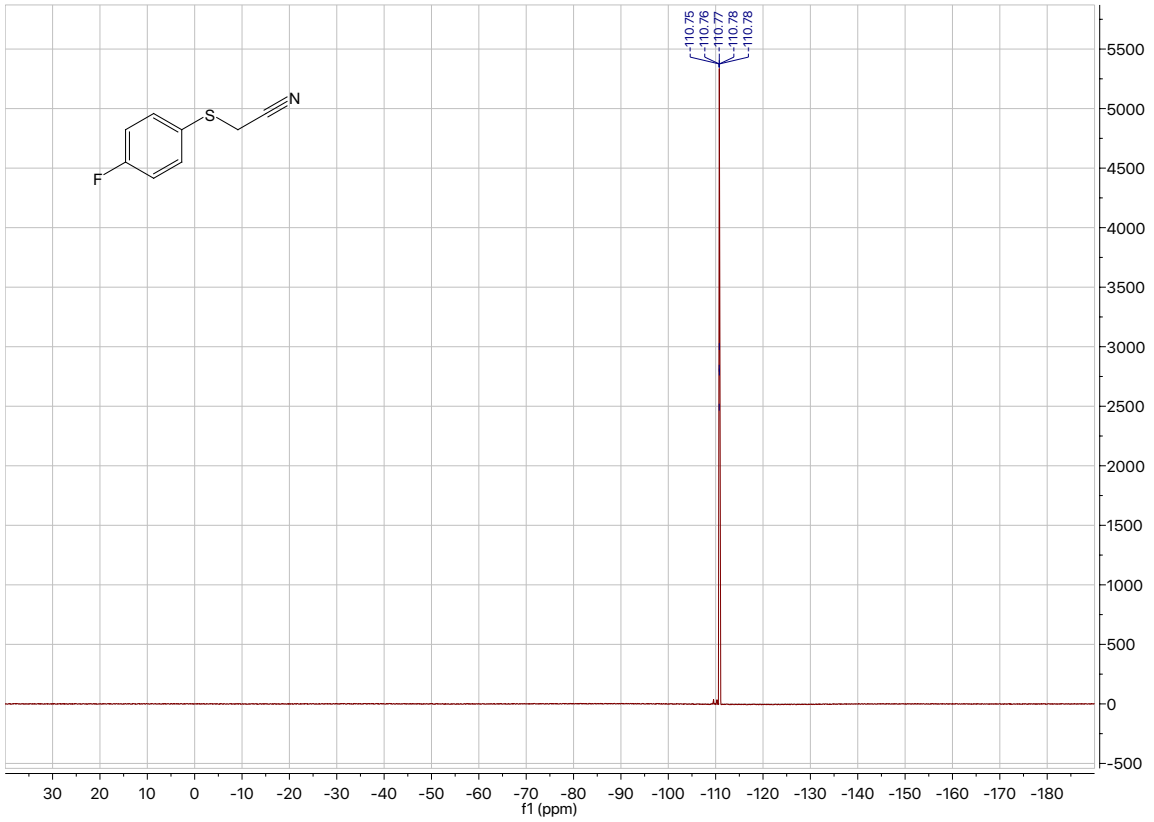
^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C NMR (151 MHz, Chloroform-*d*)

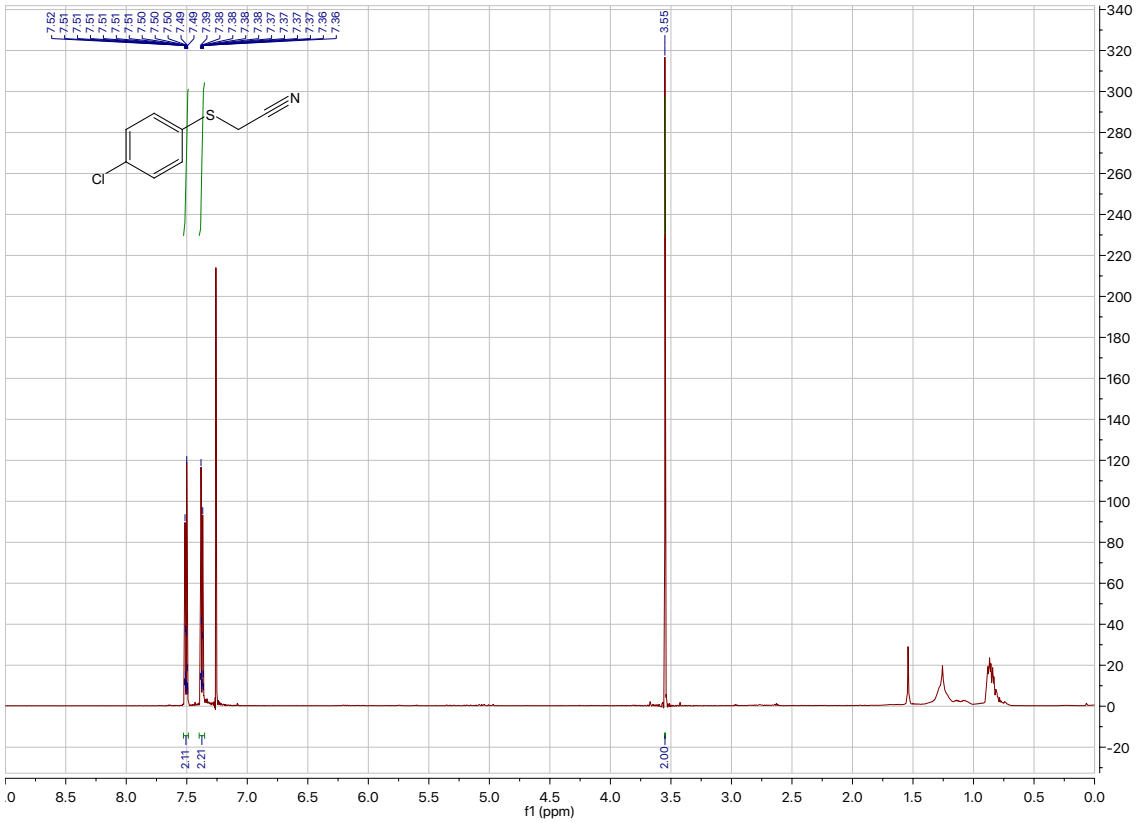


^{19}F NMR (564 MHz, Chloroform-*d*)

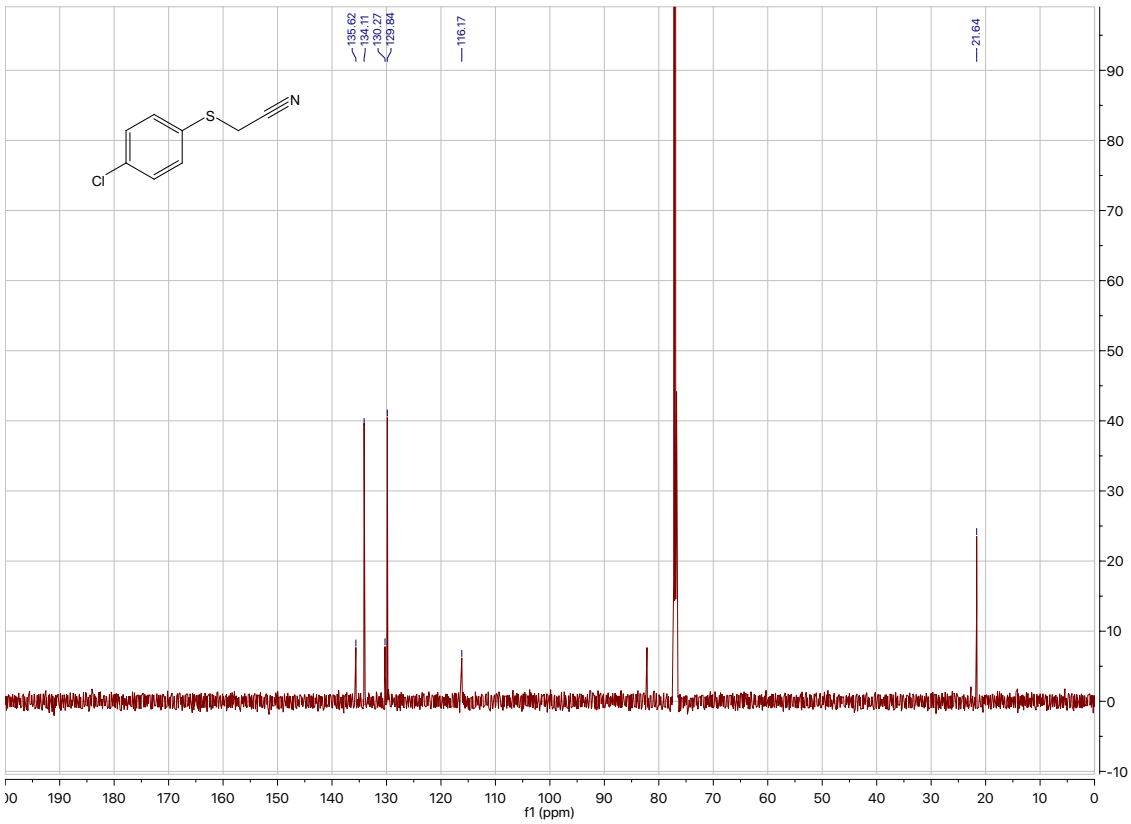


2-((4-Chlorophenyl)thio)acetonitrile (**6e**)

^{1}H NMR (600 MHz, Chloroform-*d*)

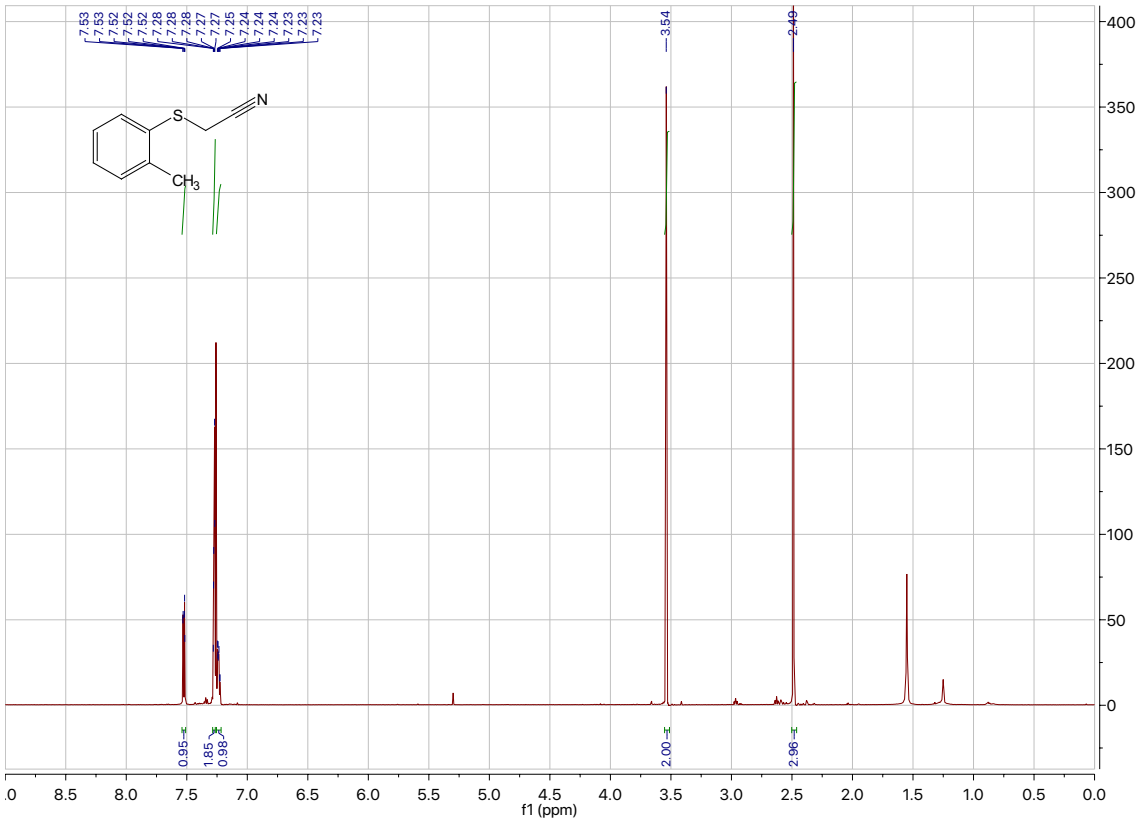


^{13}C NMR (151 MHz, Chloroform-*d*)

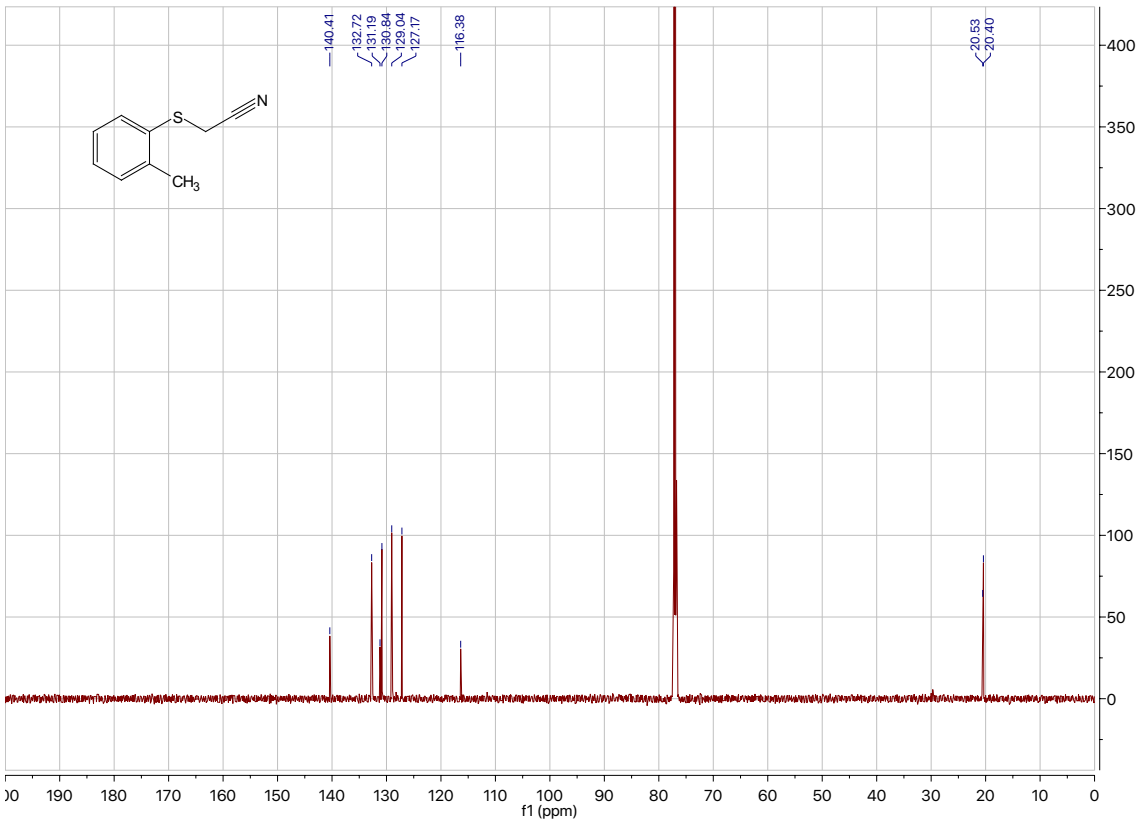


2-(*o*-Tolylthio)acetonitrile (**6f**)

^{1}H NMR (600 MHz, Chloroform-*d*)

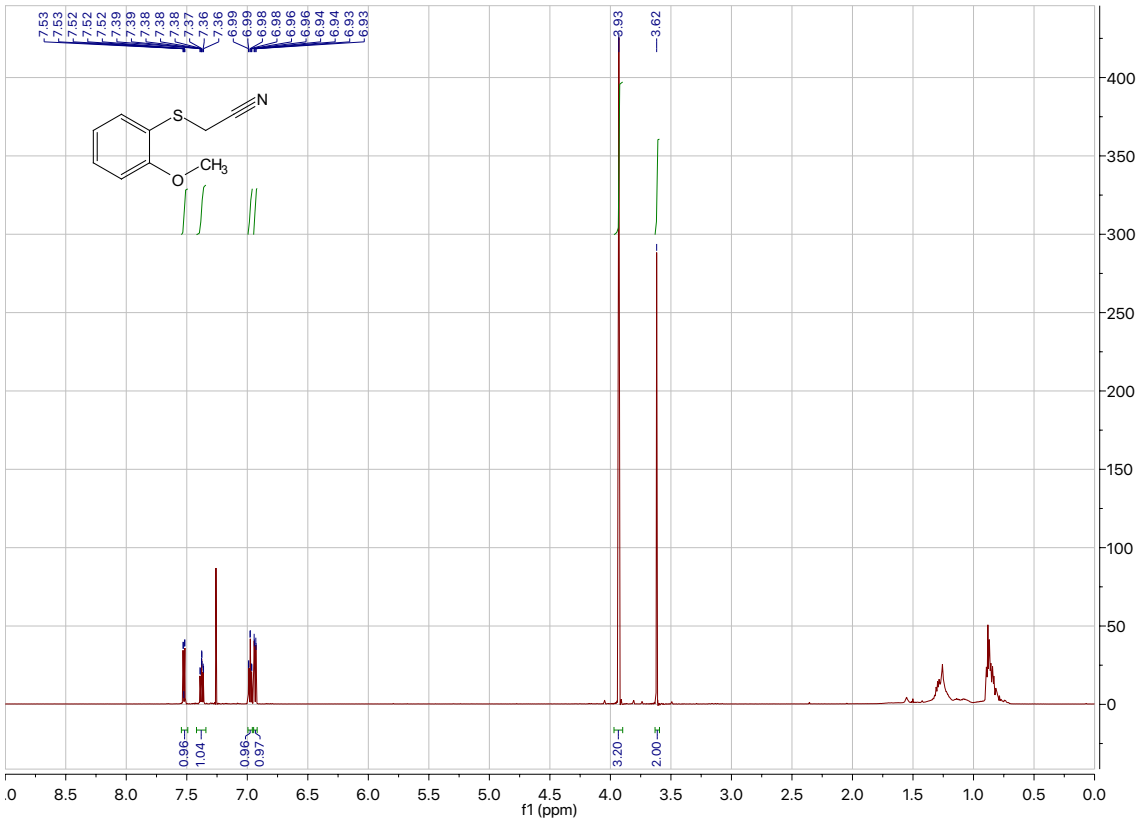


^{13}C NMR (151 MHz, Chloroform-*d*)

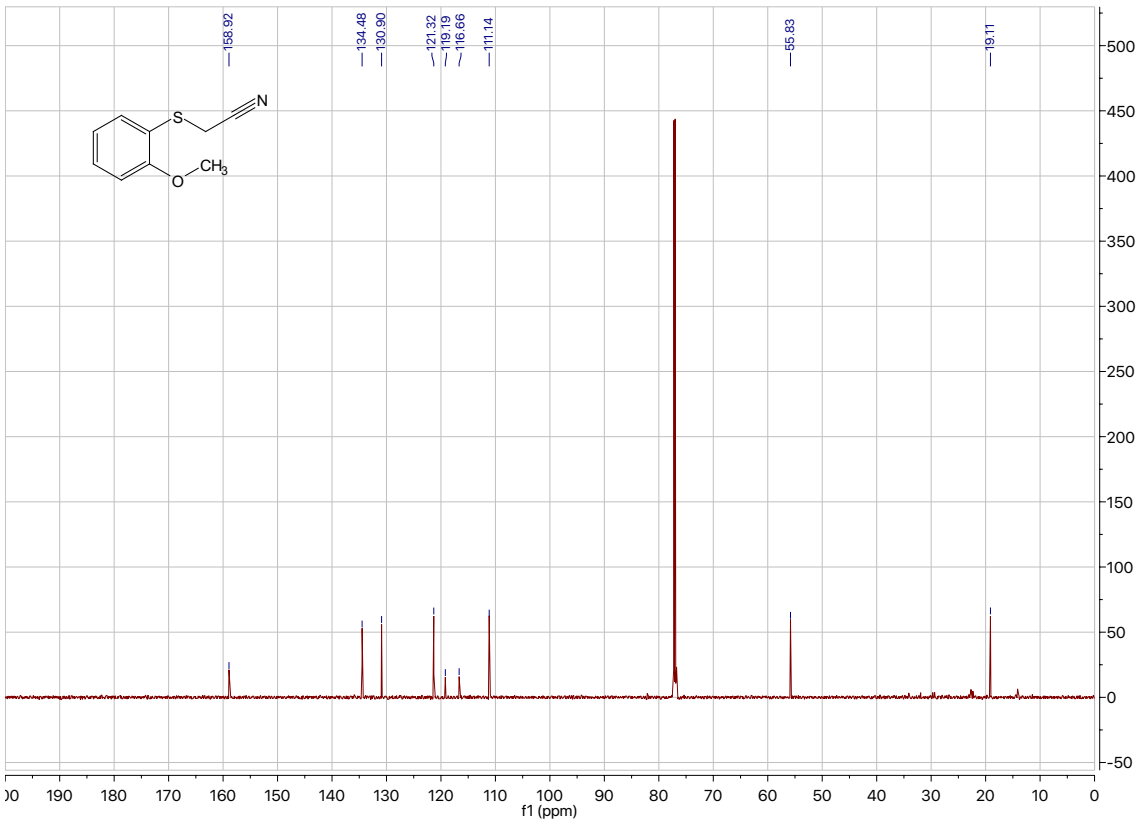


2-((2-Methoxyphenyl)thio)acetonitrile (**6g**)

^{1}H NMR (600 MHz, Chloroform-*d*)

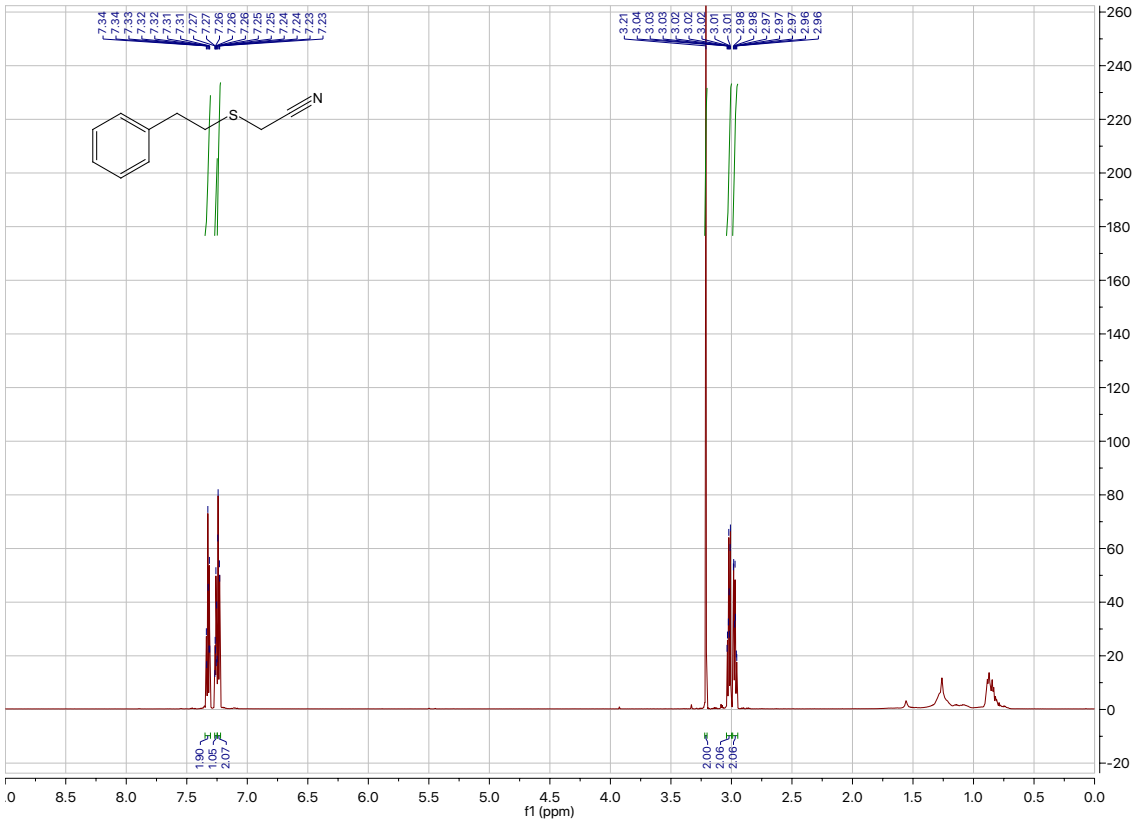


^{13}C NMR (151 MHz, Chloroform-*d*)

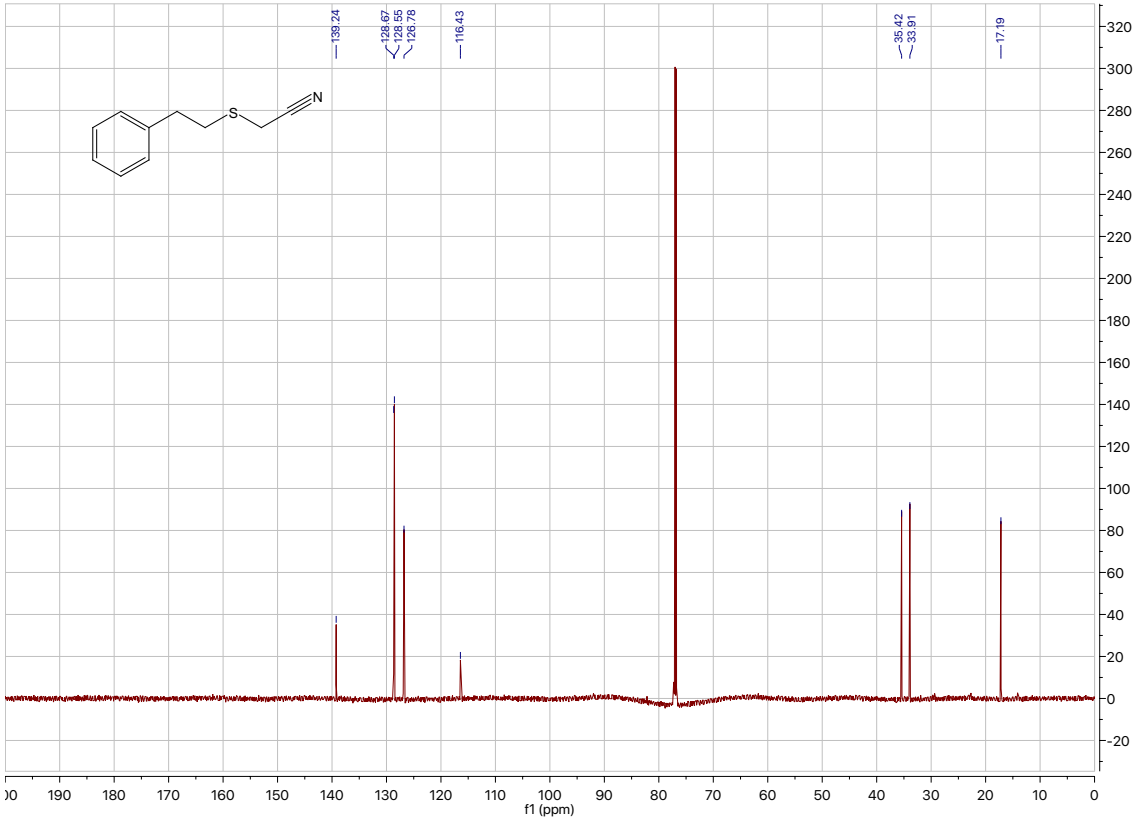


2-(Phenethylthio)acetonitrile (**6h**)

^{1}H NMR (400 MHz, Chloroform-*d*)

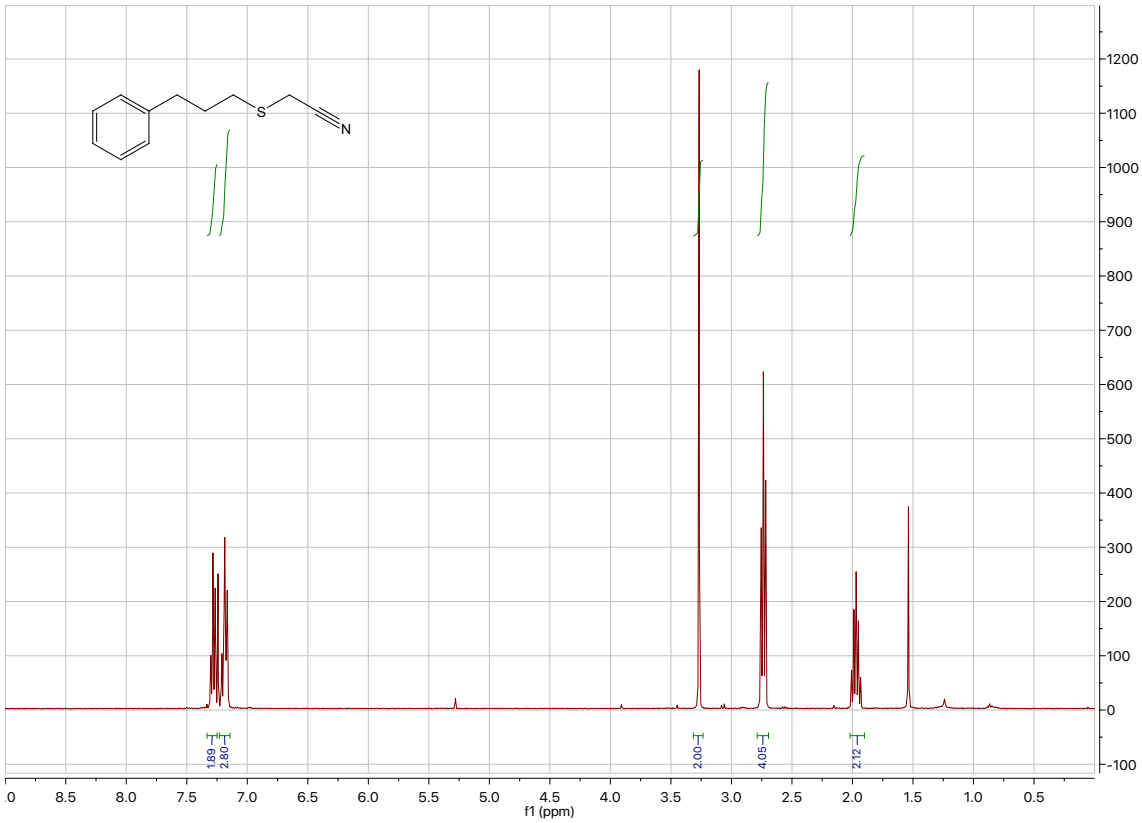


^{13}C NMR (101 MHz, Chloroform-*d*)

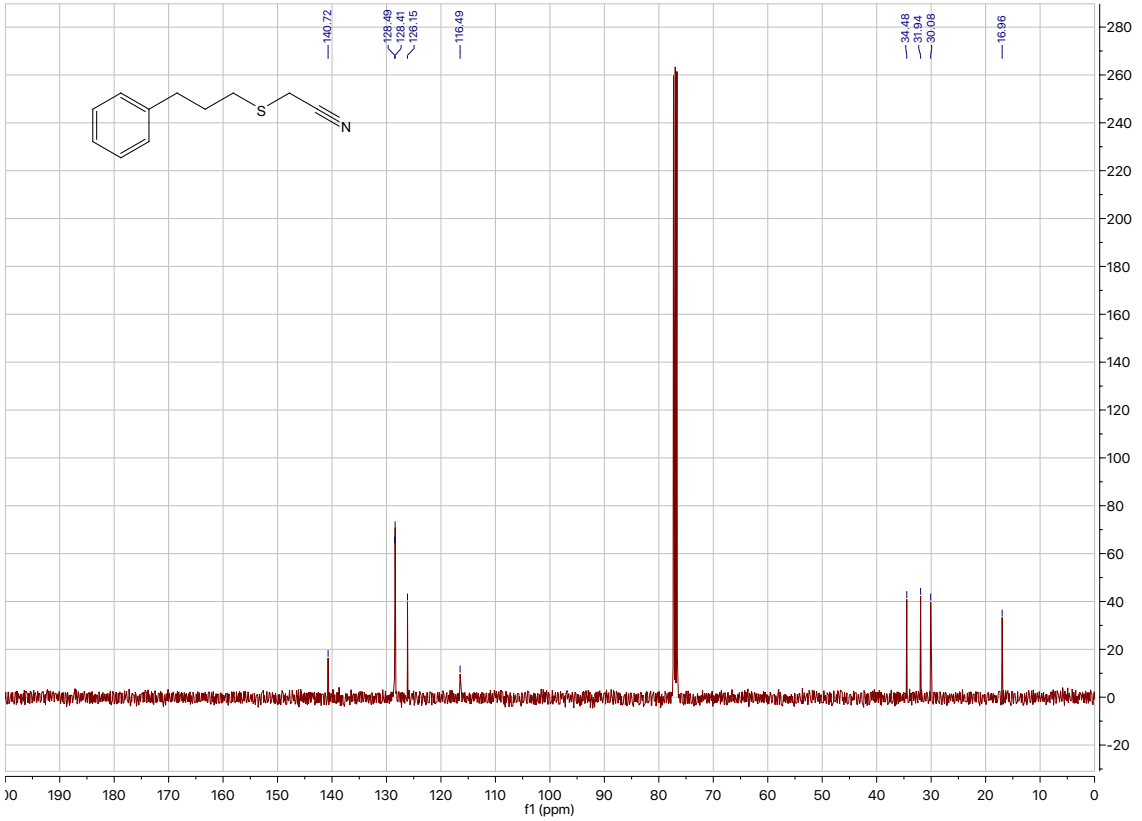


2-((3-Phenylpropyl)thio)acetonitrile (**6i**)

^{1}H NMR (400 MHz, Chloroform-*d*)

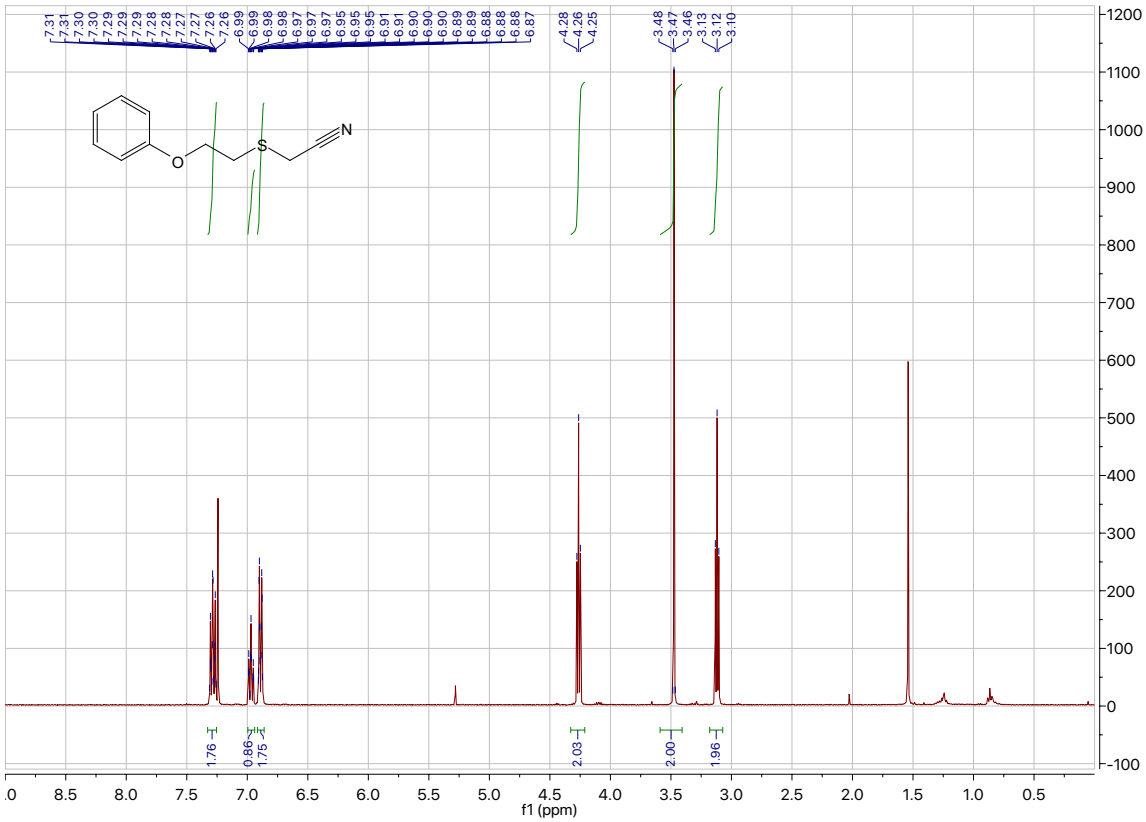


^{13}C NMR (101 MHz, Chloroform-*d*)

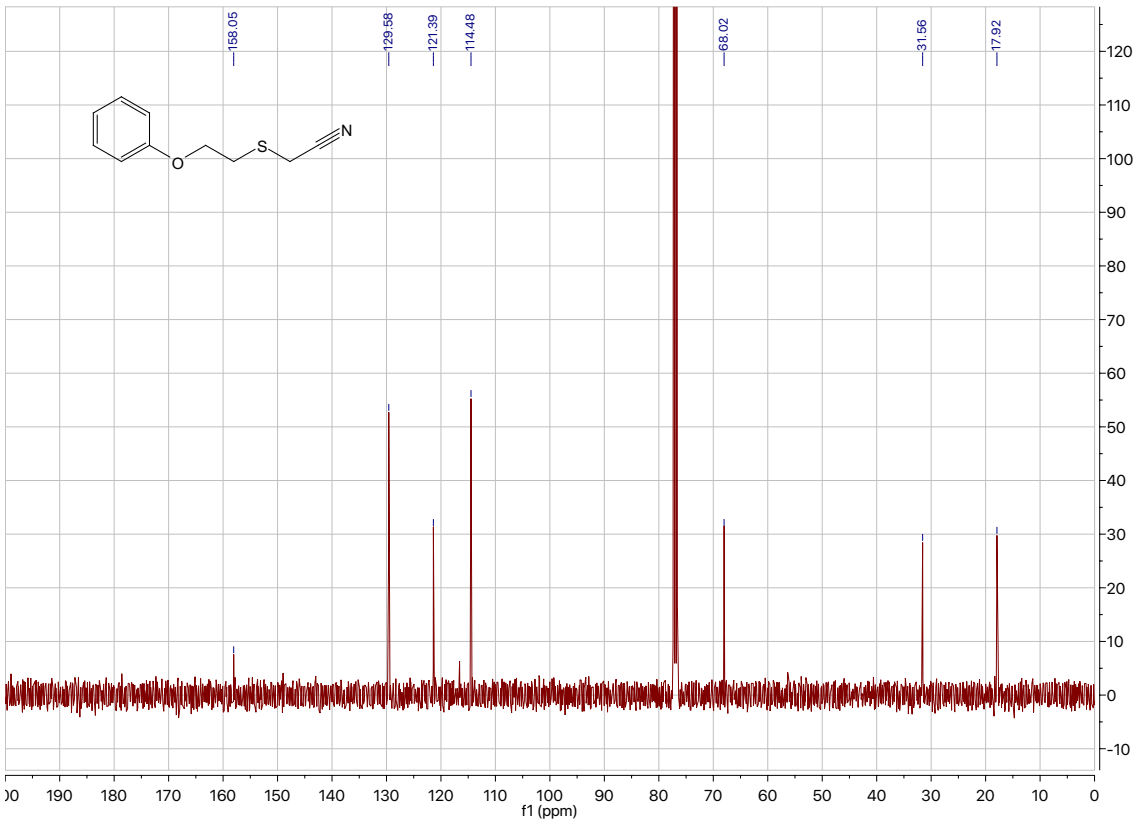


2-((2-Phenoxyethyl)thio)acetonitrile (**6j**)

^{1}H NMR (400 MHz, Chloroform-*d*)

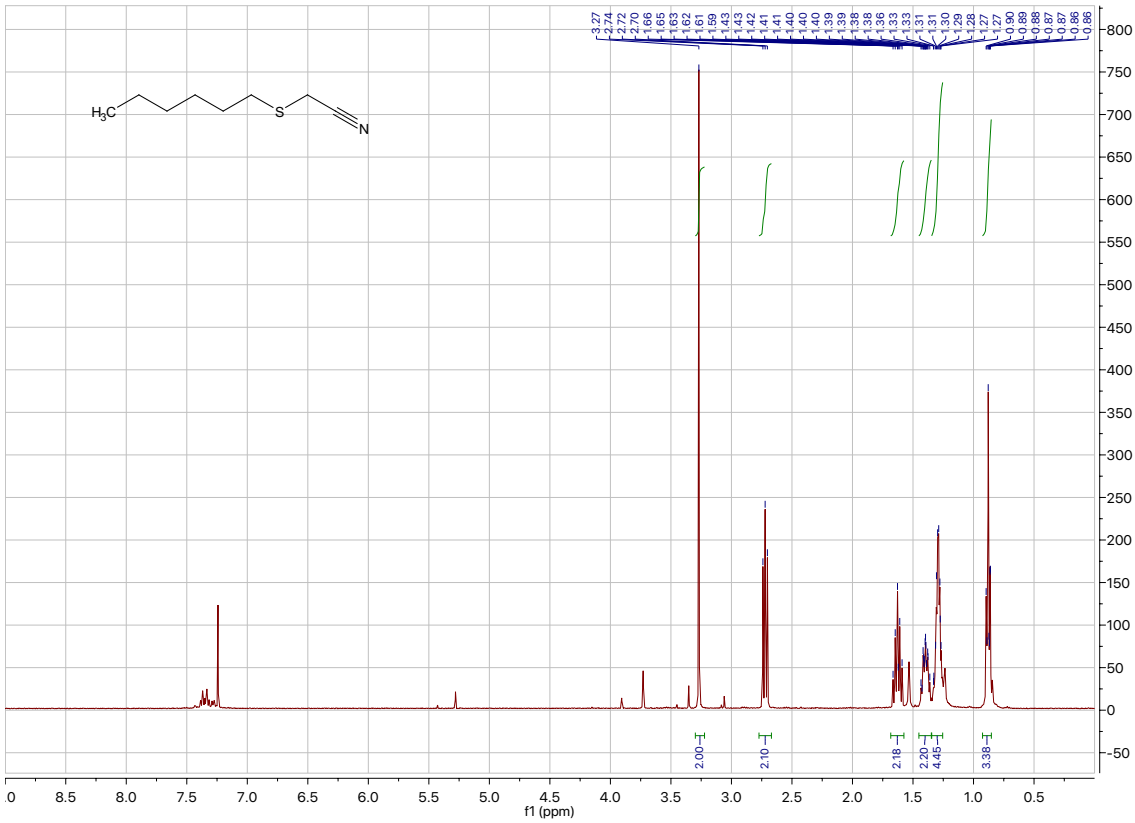


^{13}C NMR (101 MHz, Chloroform-*d*)

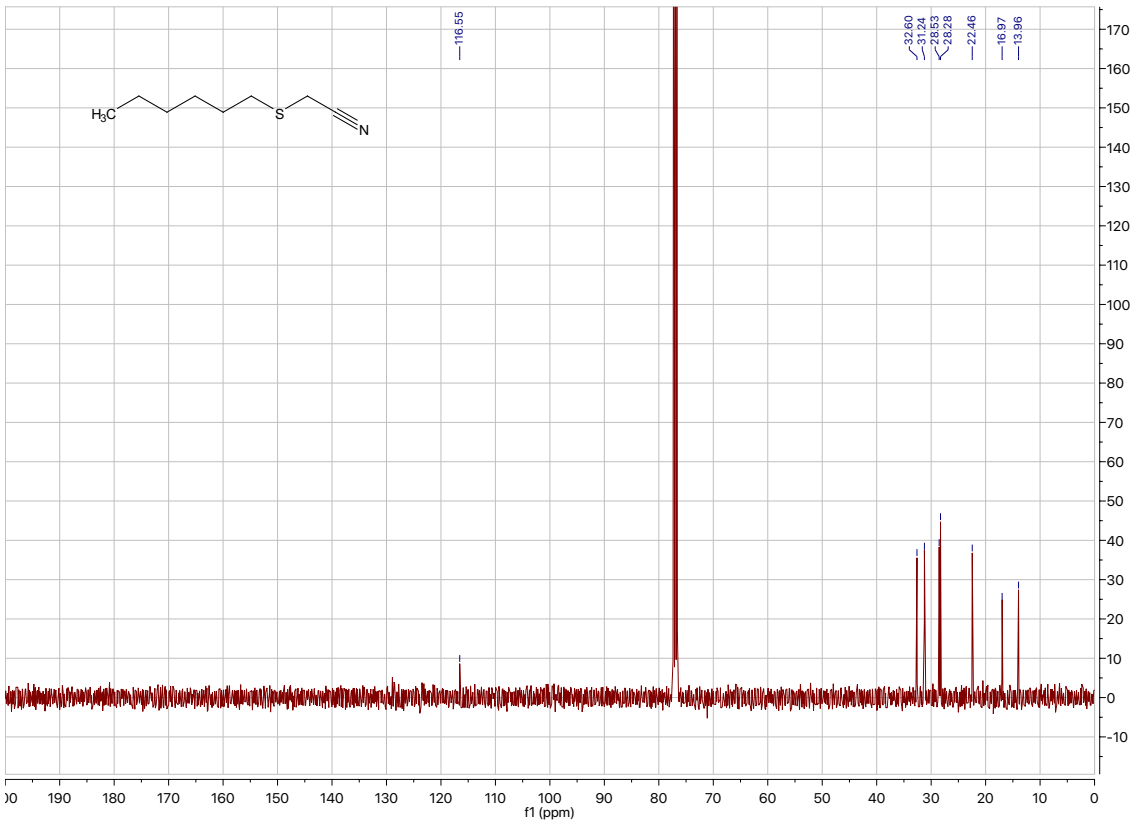


2-(Hexylthio)acetonitrile (**6k**)

^{1}H NMR (400 MHz, Chloroform-*d)*

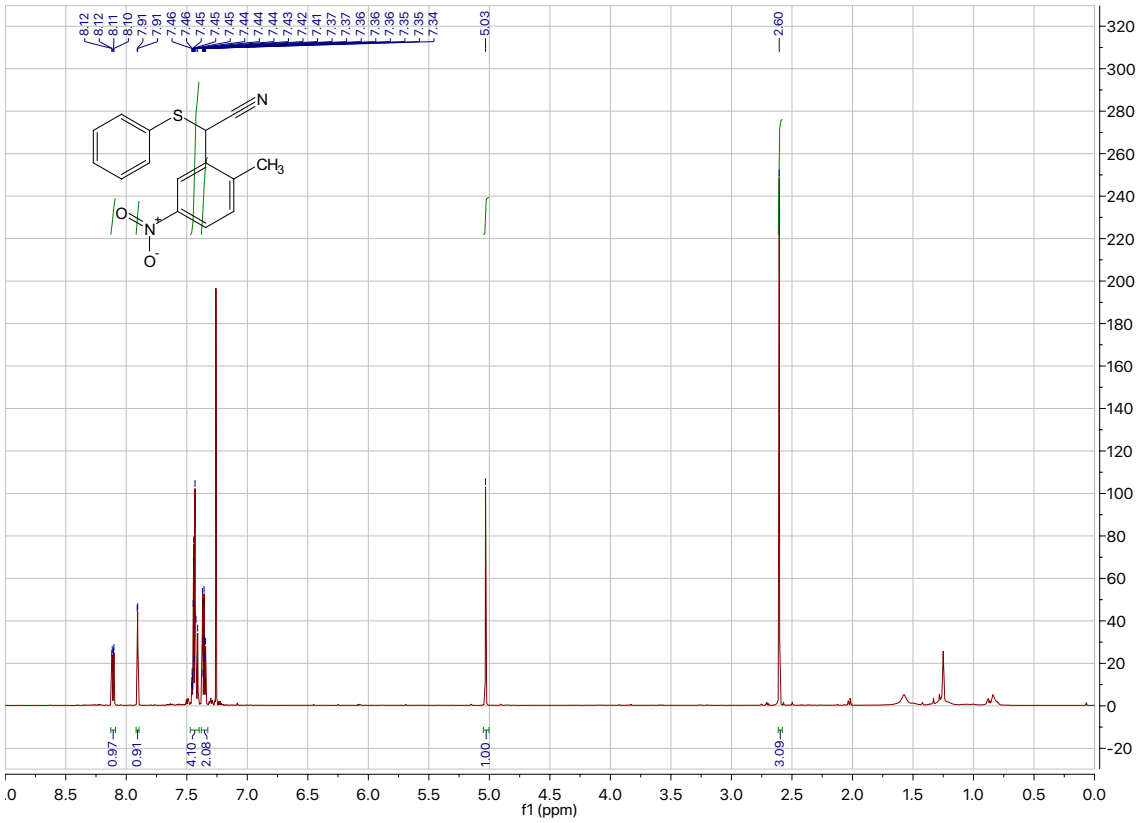


^{13}C NMR (101 MHz, Chloroform-*d)*

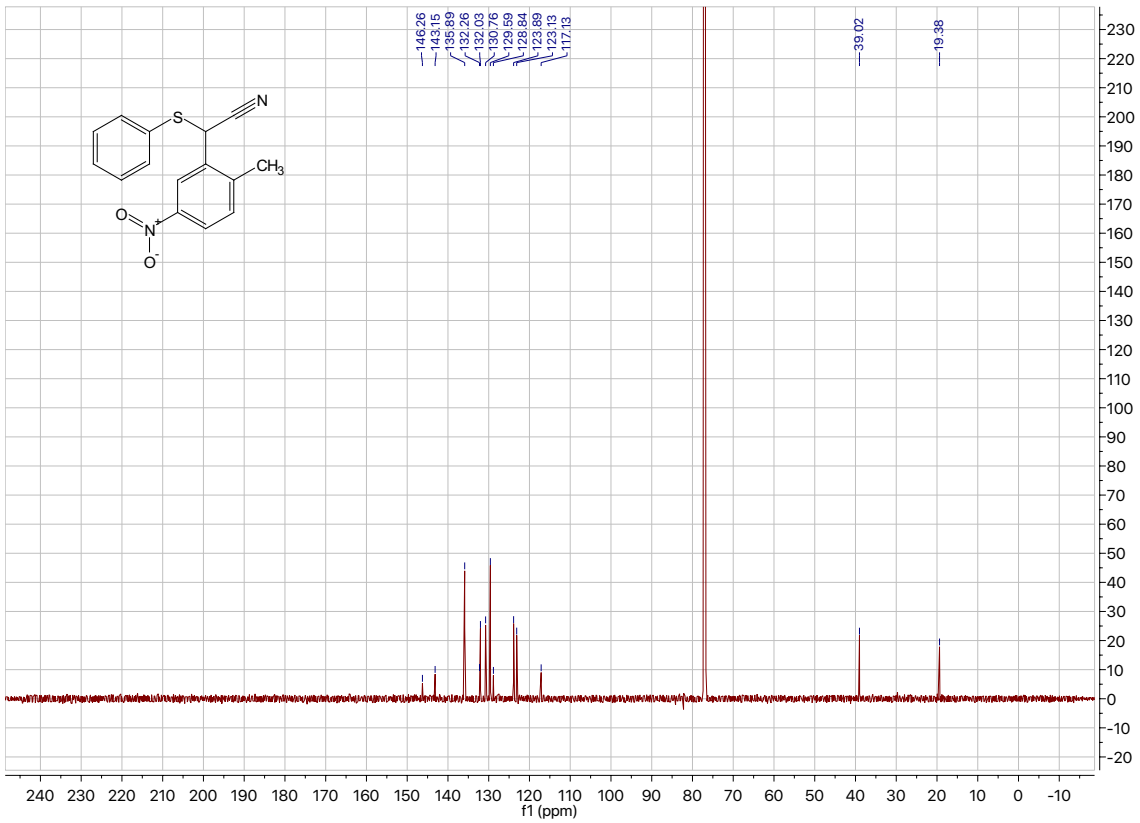


2-(2-Methyl-5-nitrophenyl)-2-(phenylthio)acetonitrile (**4o**)

^{1}H NMR (600 MHz, Chloroform-*d*)

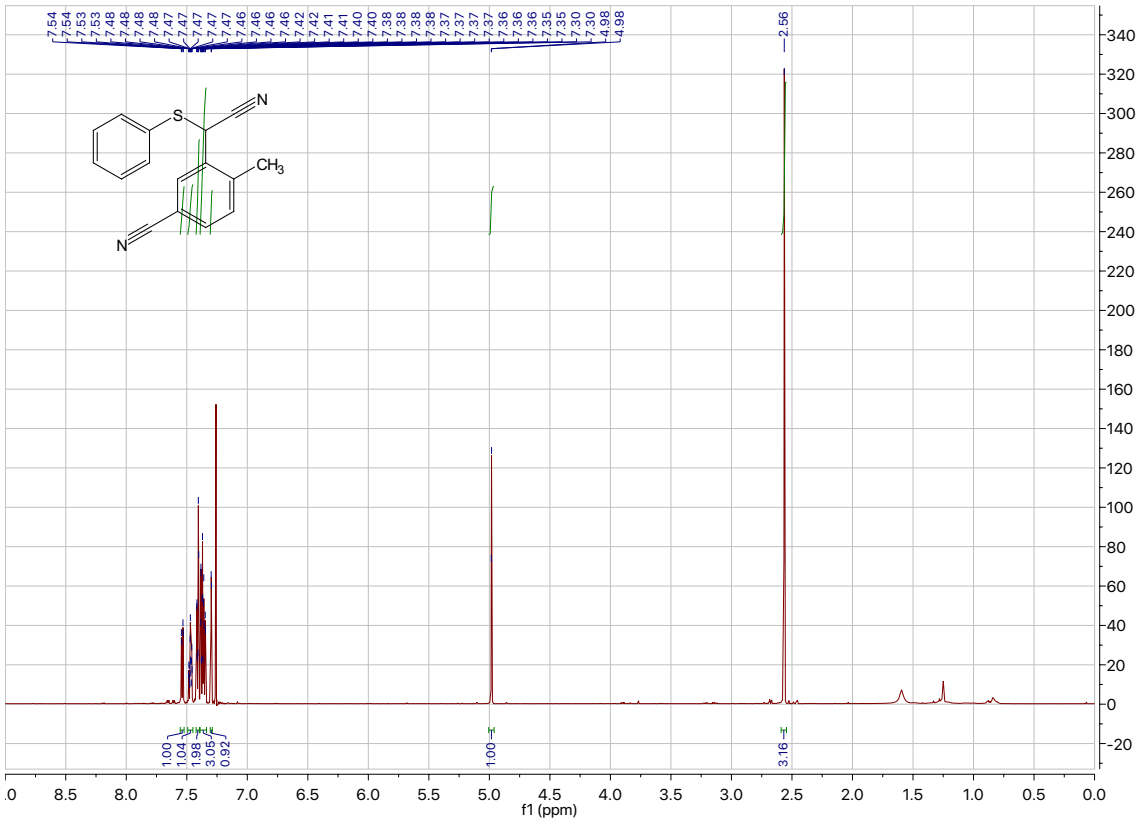


^{13}C NMR (151 MHz, Chloroform-*d*)

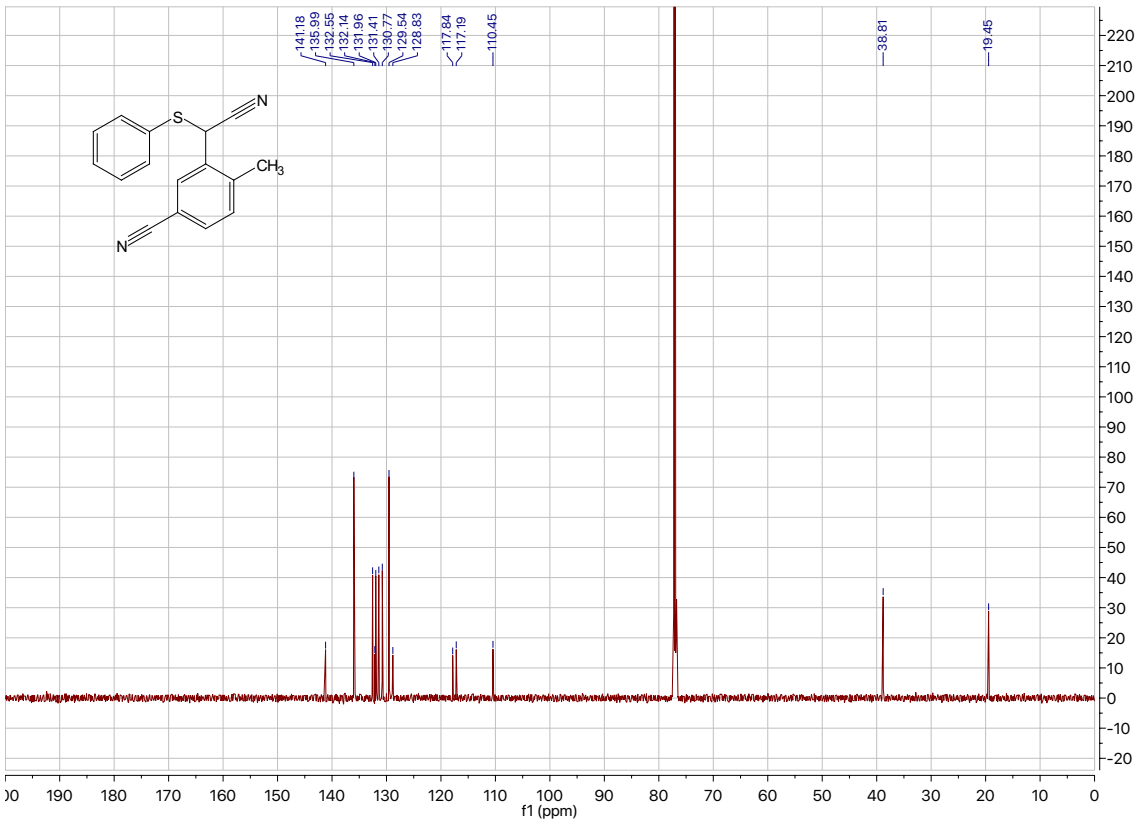


3-(Cyano(phenylthio)methyl)-4-methylbenzonitrile (**4p**)

^{1}H NMR (600 MHz, Chloroform-*d*)

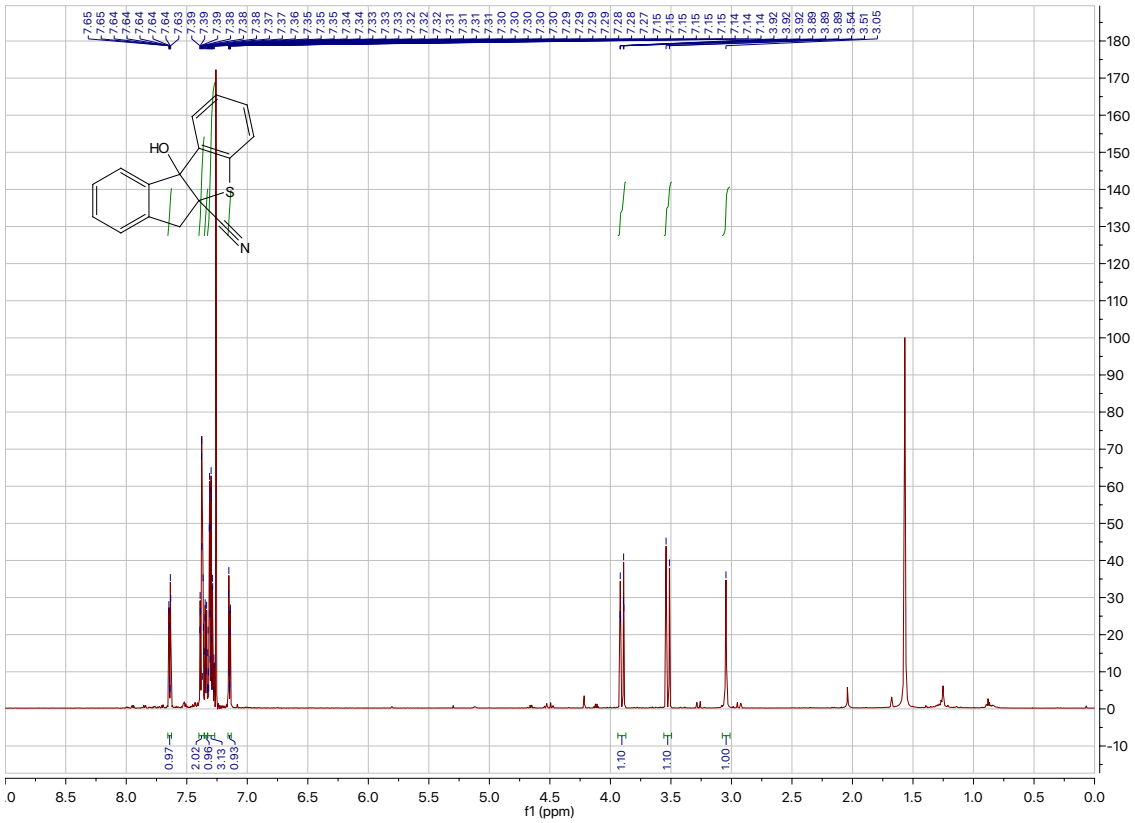


^{13}C NMR (151 MHz, Chloroform-*d*)

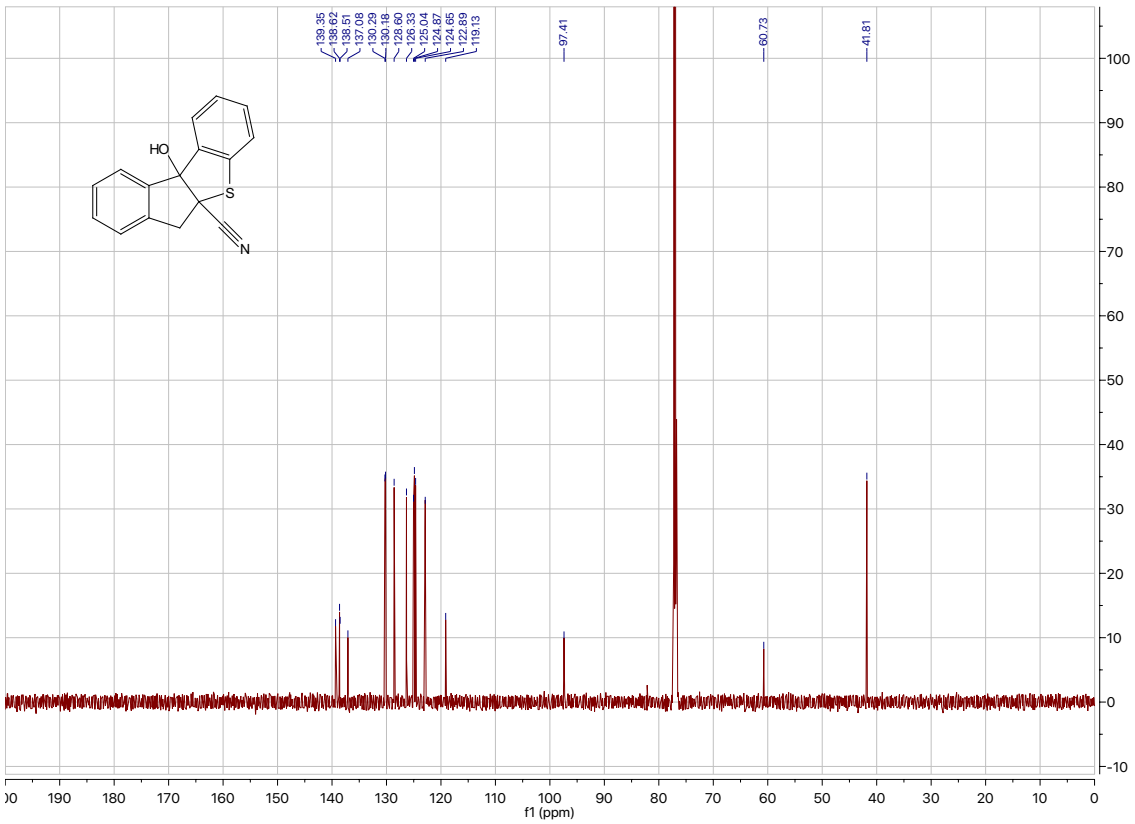


10b-Hydroxy-6,10b-dihydro-5a*H*-benzo[*b*]indeno[1,2-*d*]thiophene-5a-carbonitrile (**4q**)

^{1}H NMR (600 MHz, Chloroform-*d*)

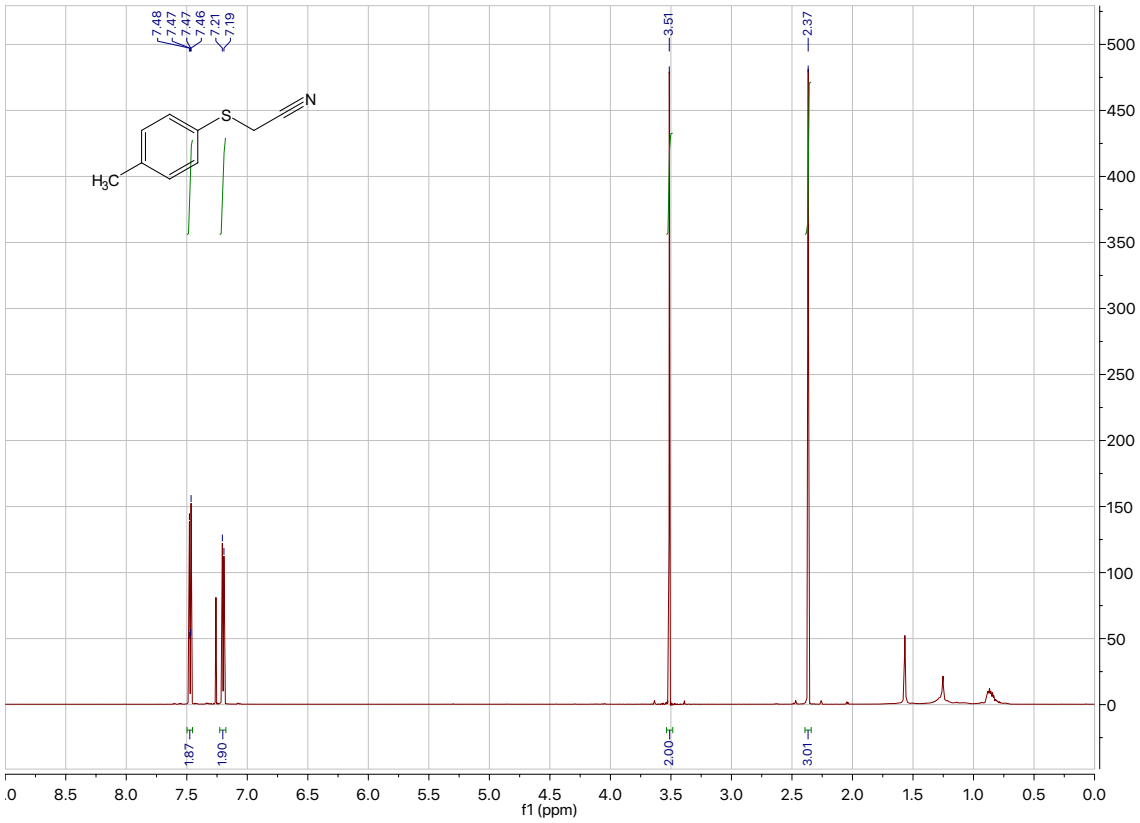


^{13}C NMR (151 MHz, Chloroform-*d*)

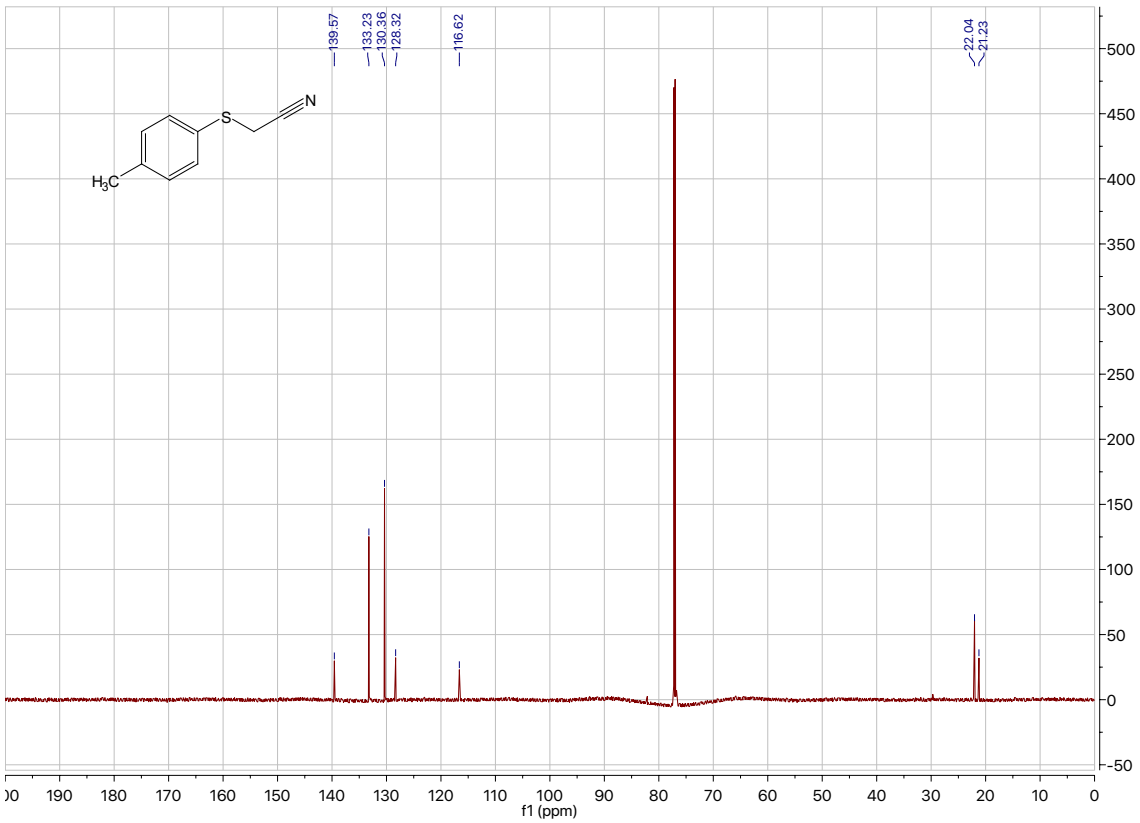


2-(*p*-Tolylthio)acetonitrile (**6t**)

^{1}H NMR (600 MHz, Chloroform-*d*)

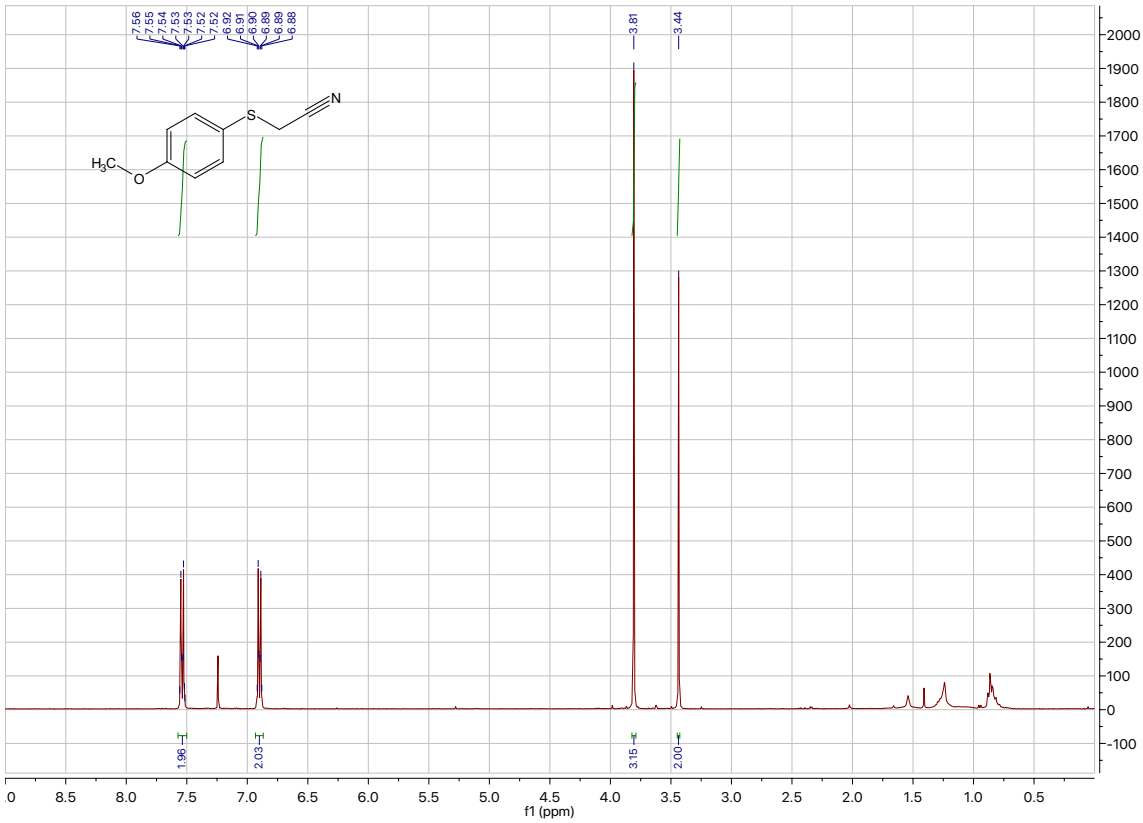


^{13}C NMR (151 MHz, Chloroform-*d*)

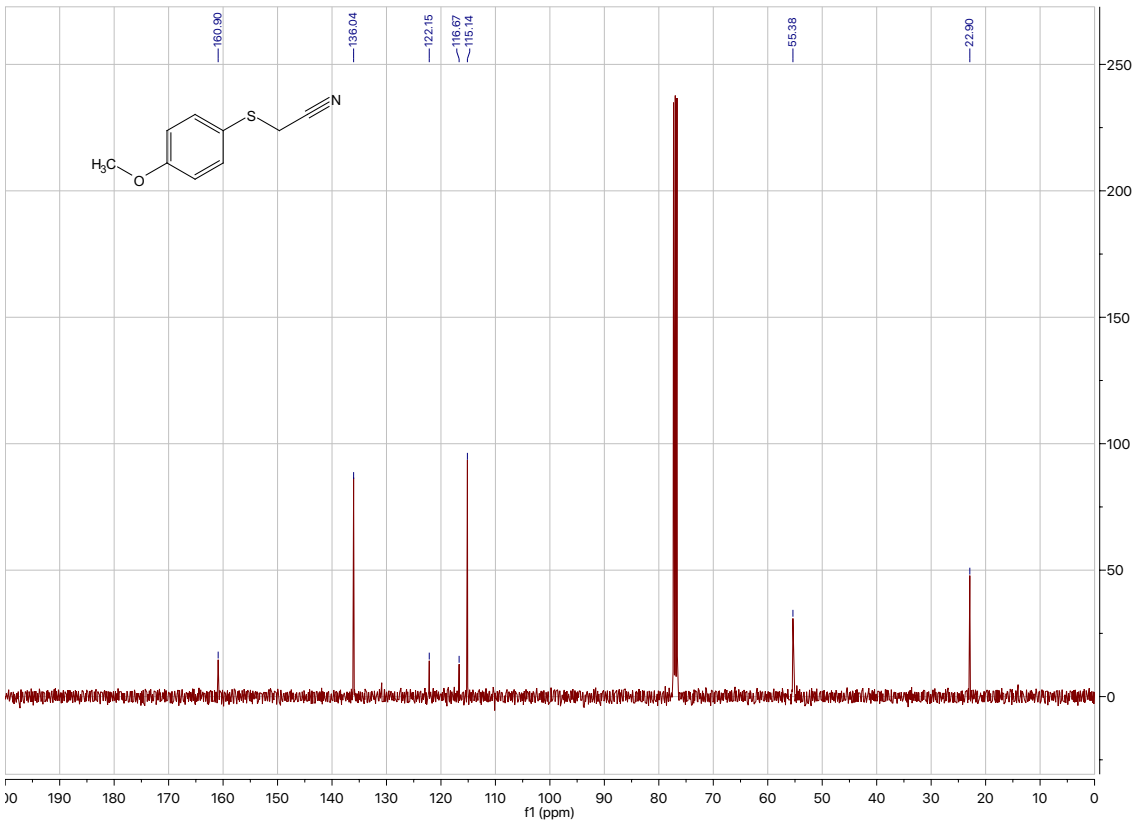


2-((4-Methoxyphenyl)thio)acetonitrile (**6u**)

^{1}H NMR (400 MHz, Chloroform-*d*)

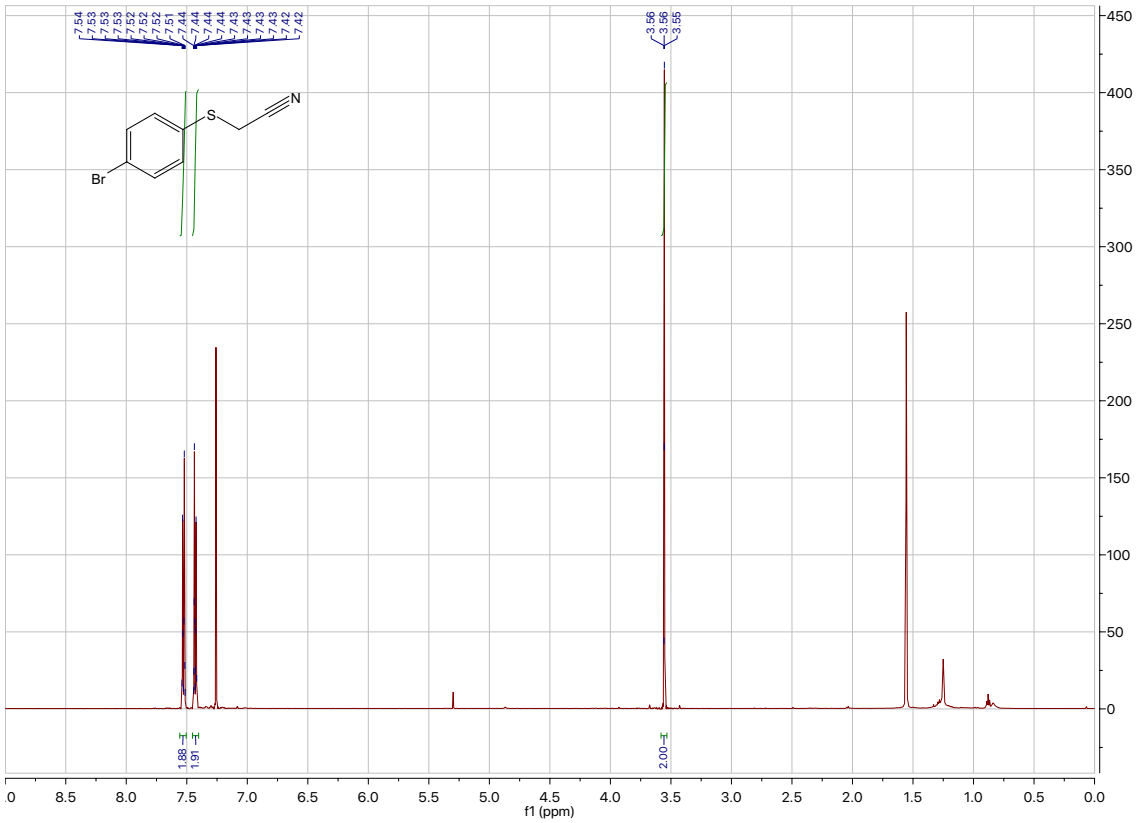


^{13}C NMR (101 MHz, Chloroform-*d*)

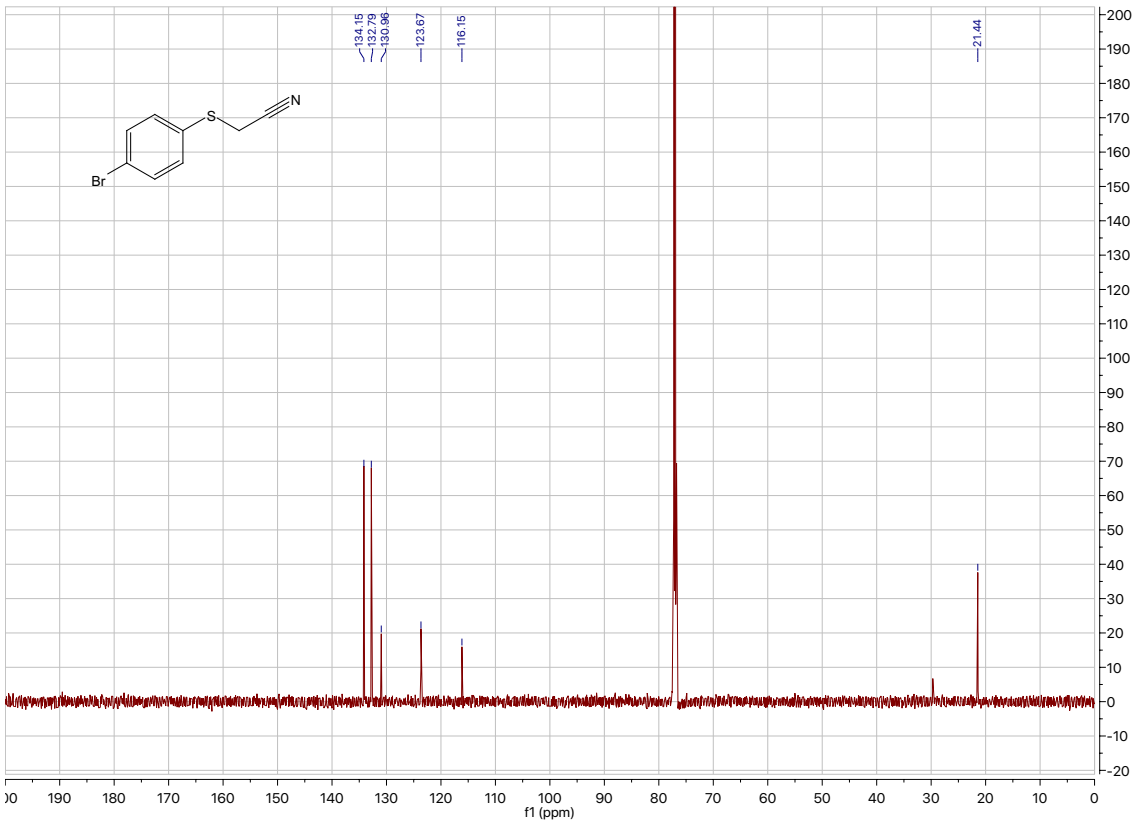


2-((4-Bromophenyl)thio)acetonitrile (**6w**)

^{1}H NMR (600 MHz, Chloroform-*d*)

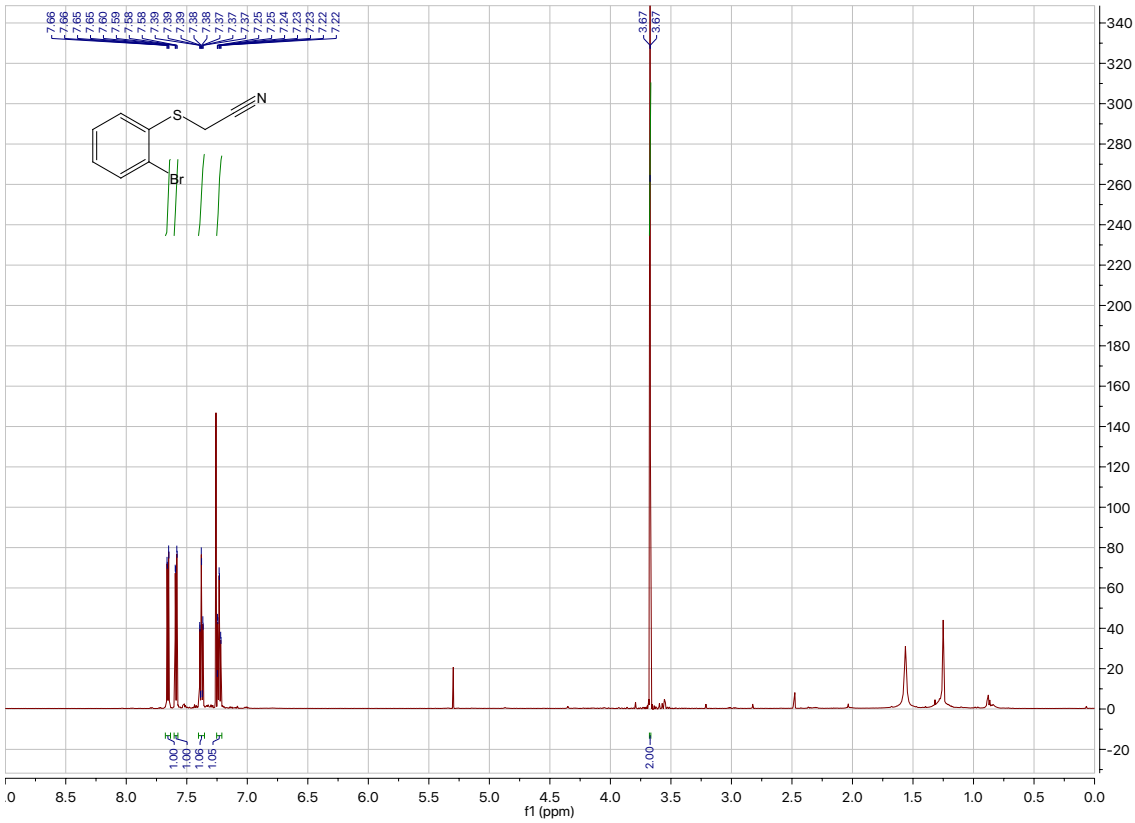


^{13}C NMR (151 MHz, Chloroform-*d*)

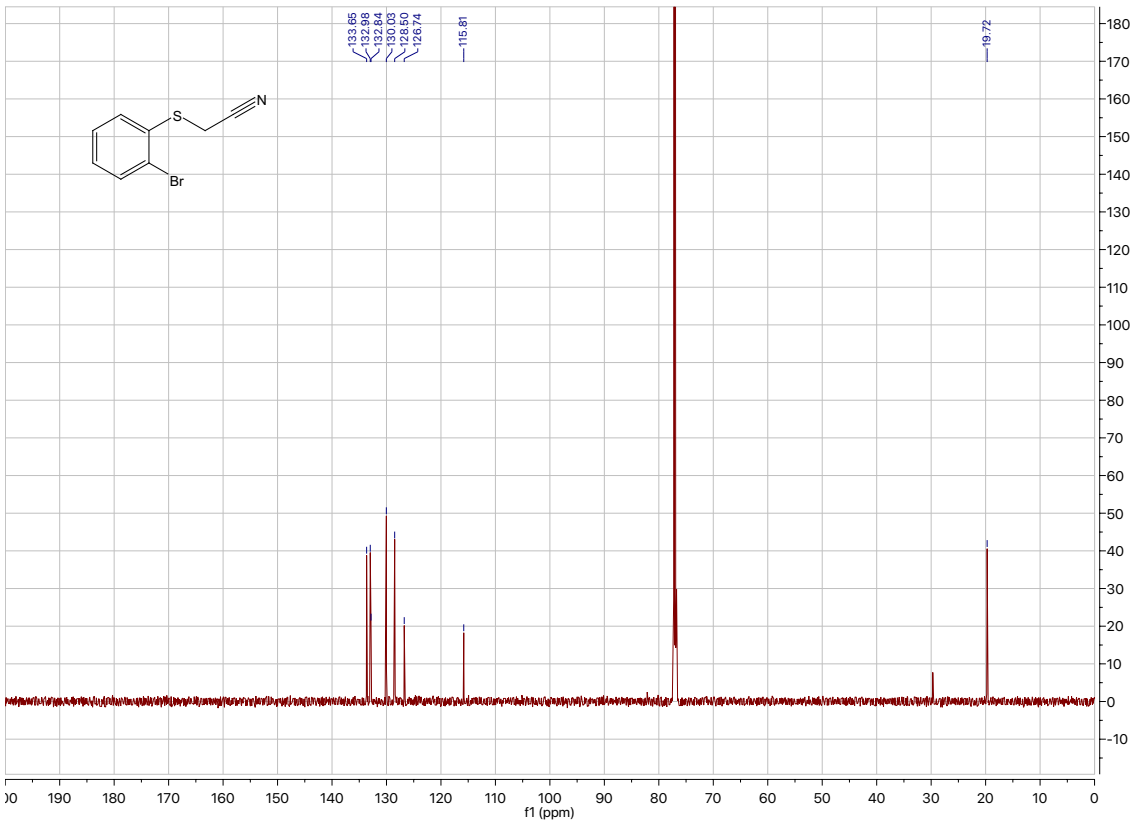


2-(2-Bromophenyl)thio)acetonitrile (**6x**)

^{1}H NMR (600 MHz, Chloroform-*d*)

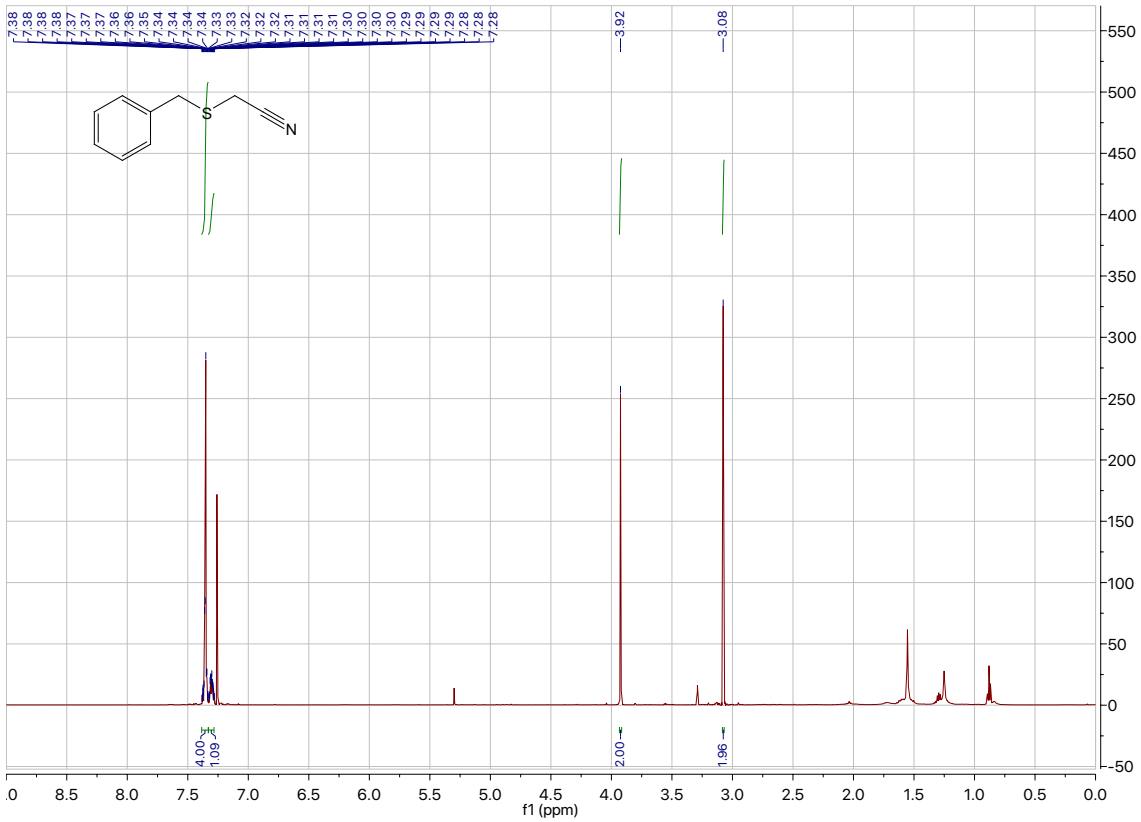


^{13}C NMR (151 MHz, Chloroform-*d*)

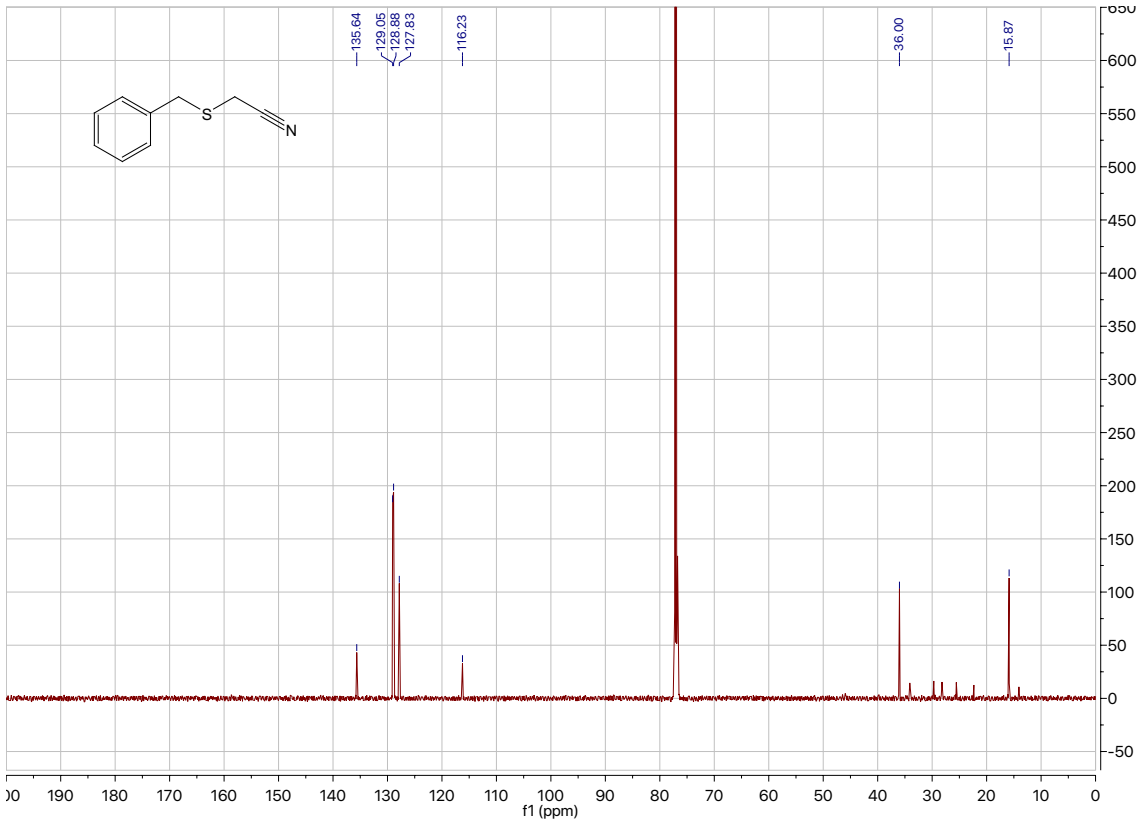


2-(Benzylthio)acetonitrile (**8**)

^{1}H NMR (600 MHz, Chloroform-*d*)

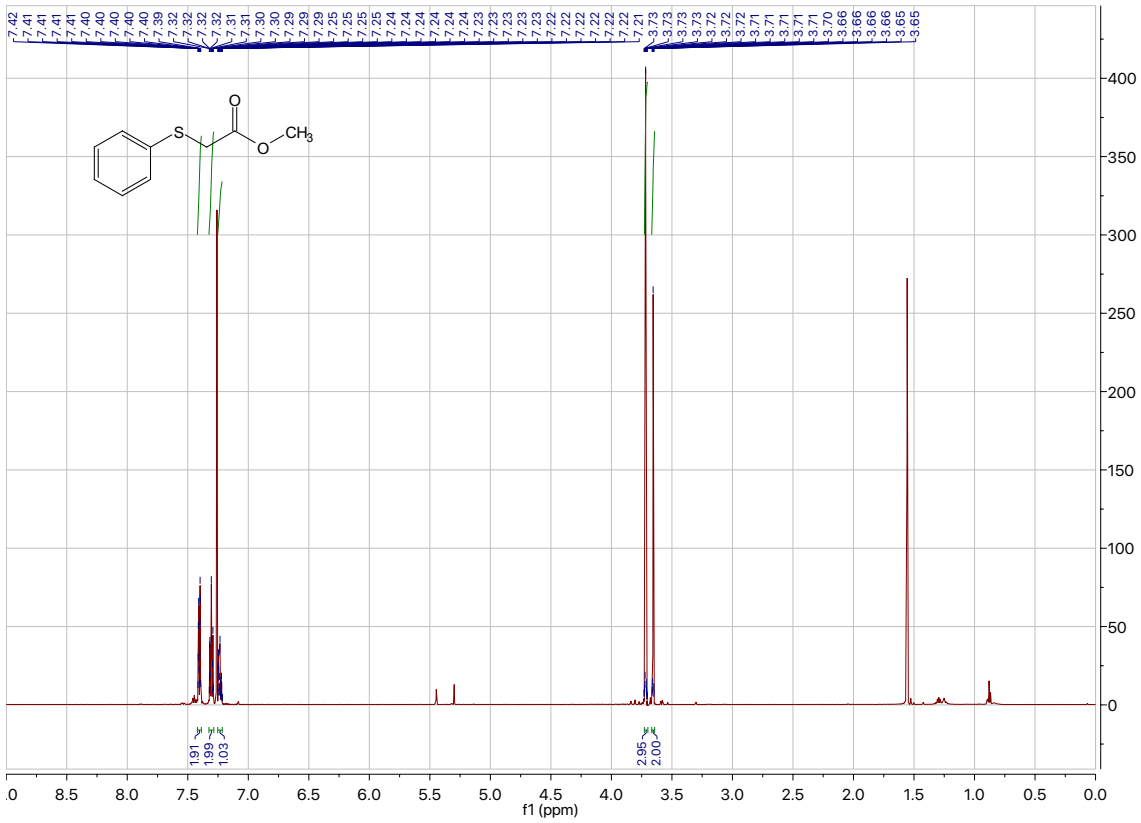


^{13}C NMR (151 MHz, Chloroform-*d*)

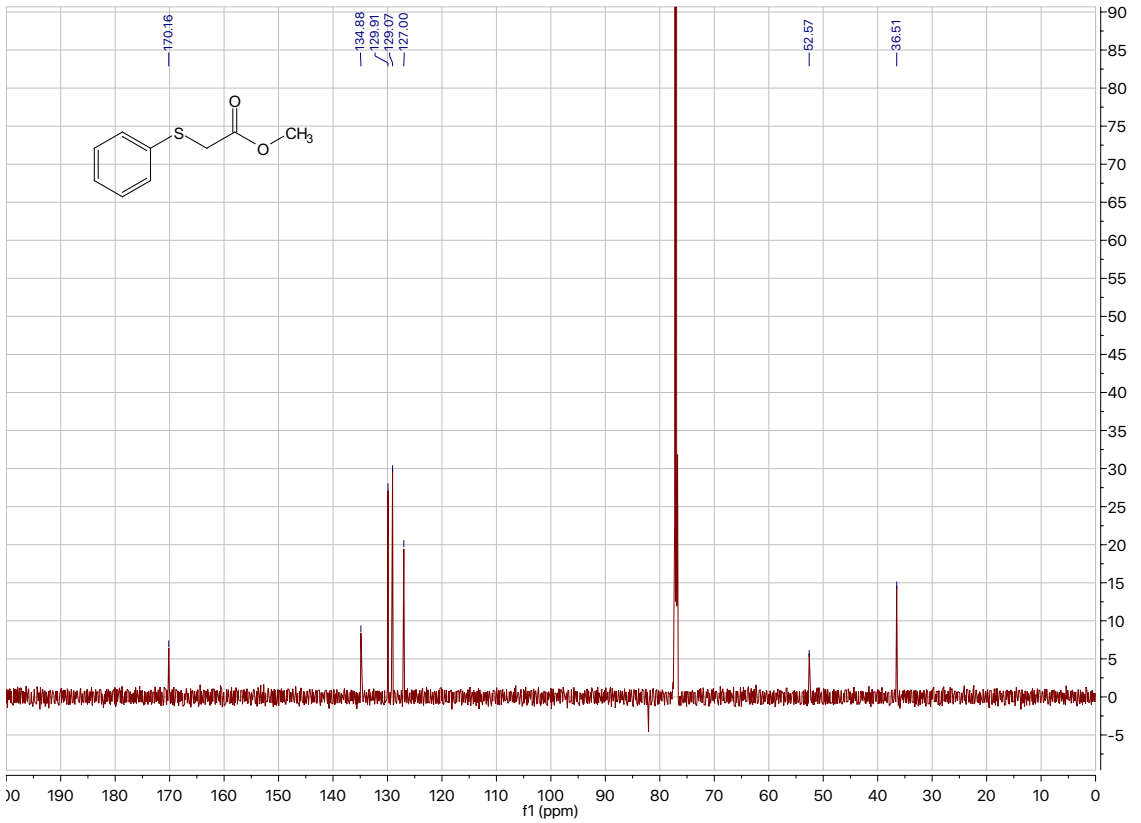


Methyl 2-(phenylthio)acetate (**10a**)

^{1}H NMR (600 MHz, Chloroform-*d*)

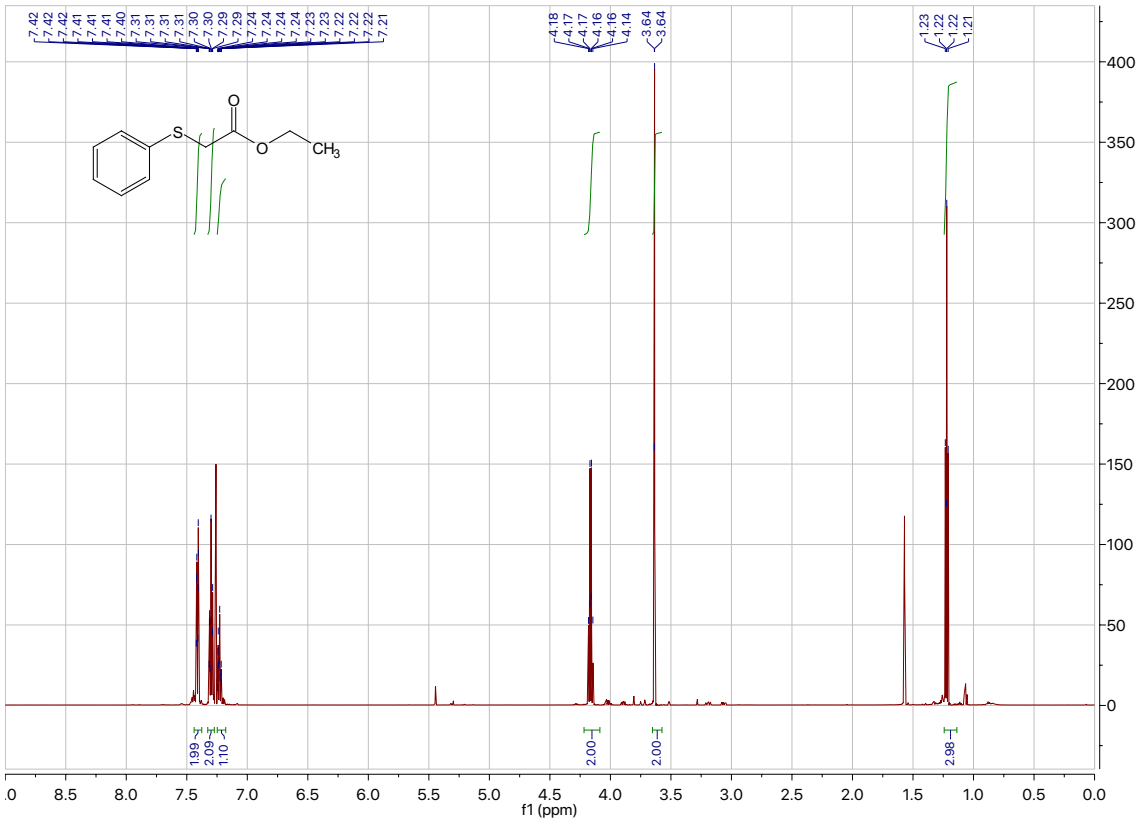


^{13}C NMR (151 MHz, Chloroform-*d*)



Ethyl 2-(phenylthio)acetate (**10b**)

^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C NNR (151 MHz, Chloroform-*d*)