Supporting Information

O-Benzyl Xanthate Esters under Ni/Photoredox Dual Catalysis: Selective Radical Generation and Csp^3-Csp^2 Cross-Coupling

Brandon A. Vara, Niki R. Patel and Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

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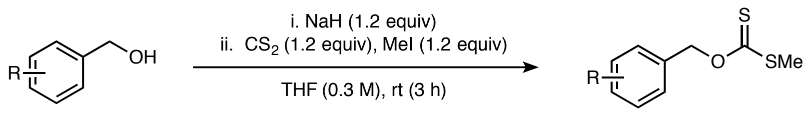
General considerations

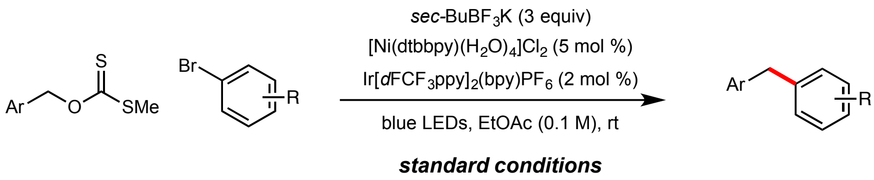
All reactions were carried out under an inert atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise noted. Conventional solvents (THF, Et_2O, CH_2Cl_2, toluene, xylenes) were dried using a solvent system. Ethyl acetate (99.8%, extra dry) was used as received, and all other reagents were purchased commercially and used as received, unless otherwise noted. $IrCl_3 \cdot xH_2O$ and [$NiCl_2$(dme)] were purchased from commercial sources. [Ni(dtbbpy)(H_2O)$_4$]Cl_2 precatalyst[1] and Ir[dFCF$_3$ppy]$_2$(bpy)PF_6 photocatalyst[2] were prepared following recent literature reports. Potassium alkyltrifluoroborates were purchased from commercial suppliers or prepared using a published procedure.[2] Column chromatography was performed by Combiflash(R) using RediSep Rf Gold Normal-Phase Silica(R) columns or RediSep Rf Alumina Neutral(R) columns. Photoredox reactions were irradiated with blue LED strips, and the temperature (~ 30 °C) was controlled using one external desk fan set up ~ 10 cm away from the photoreactor bed. Melting points (°C) are uncorrected. Mass spectra (ESI- or CI-TOF) were recorded using CH_2Cl_2, MeCN or MeOH as the solvent. NMR Spectra (^{1}H, ^{13}C {^{1}H}, ^{19}F {^{1}H}) were performed at 298 K. ^{1}H (500.4 MHz) and ^{13}C {^{1}H} (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm; $CHCl_3$: 7.26 ppm for ^{1}H nuclei and 77.00 for ^{13}C nuclei). ^{19}F {^{1}H} NMR (470.8 MHz) chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration.

General procedure for the preparation of benzyl xanthate esters



An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (1-1.2 equiv) was added under an Ar atmosphere followed by dry THF (0.3 M). The alcohol (1 equiv) was slowly added via syringe (oil) or slowly added (solid) to the stirring solution at rt. The reaction was capped under Ar and allowed to stir for 1 h at rt. Carbon disulfide (CS_2, 1.2 equiv) was then added via syringe at rt, stirred for 1 h, and the reaction was quenched with methyl iodiode (1.2 equiv), and stirred for an additional 30-60 min. The reaction was diluted with Et_2O, carefully quenched, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O (× 2) and then brine. The organics were dried ($MgSO_4$), filtered, and concentrated to a yellow oil or light yellow solid which often contained analytically pure xanthate ester to be employed directly in the next step. When needed, the resulting xanthate can be purified by column chromatography on silica gel, eluting with hexanes and EtOAc, to obtain products in pure form.

General procedure for the cross-coupling of benzyl xanthate esters

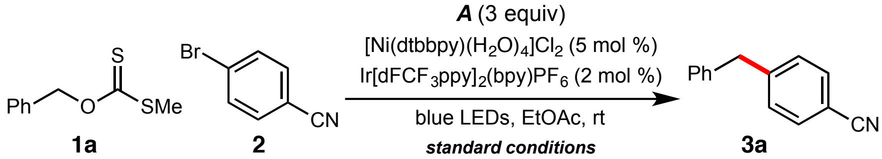


0.5 mmol scale reaction: An 8 mL sealable screw cap vial with septum was charged with the xanthate ester (0.5 mmol, 1.0 equiv) and the aryl bromide (0.5 mmol, 1.0 equiv), followed by addition of potassium *sec*-butyltrifluoroborate (246 mg, 1.5 mmol, 3.0 equiv), [Ni(dtbbpy)(H_2O)$_4$]Cl_2 (11.8 mg, 0.025 mmol, 5 mol %), and Ir[dFCF$_3$ppy]$_2$(bpy)PF_6 (10 mg, 0.01 mmol, 2 mol %) in succession. The vial was sealed, and three vacuum/argon cycles were carried out. Next, dry and degassed EtOAc (5.0 mL) was added. The vial containing all the reagents was further sealed with Parafilm, placed approximately 3-5 cm away from the blue LEDs (see Figure SI-1), and allowed to stirred for 48 h at rt. A fan was blown across the reaction setup to suppress the heat generated by the LED strips (the reaction temperatures are estimated to be ~30 °C). The crude reaction mixture was poured into a separatory funnel and diluted with Et_2O (10 mL) and H_2O (10 mL). The resulting organic layer was washed with H_2O (2 × 10 mL), then brine (10 mL), dried ($MgSO_4$), and concentrated. The crude residue was purified by column chromatography on silica gel, eluting with hexanes and EtOAc, to obtain products in pure form.

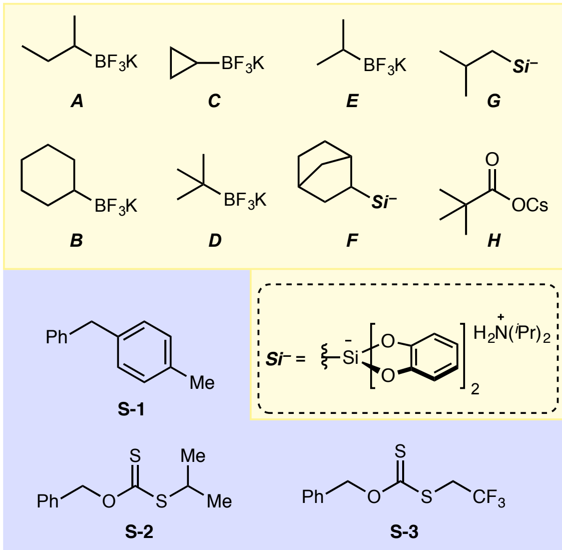
Figure SI–1. 0.5 mmol (left) scale photoredox cross-coupling reaction set-up.

Select reaction optimization studies

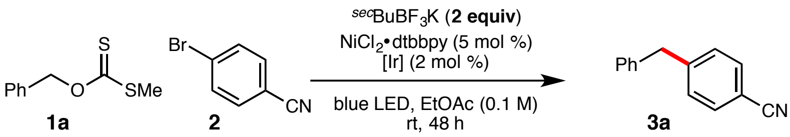
Studies examining various reaction conditions as deviated from the standard:



entry	variation from standard	% yield (HPLC)
1	***standard conditions***	94
2	+Cs_2CO_3 (3 equiv)	<5
3	+2,6-lutidine (3 equiv)	19
4	0.05 M EtOAc	95
5	0.2 M EtOAc	80
6	1 mol % [Ir]	61
7	4 mol % [Ir]	46
8	cyclohexyl BF_3K (**B**) (3 equiv) in place of **A**	48
9	cyclopropyl BF_3K (**C**) (3 equiv) in place of **A**	0
10	^{t}BuBF_3K (**D**) (3 equiv) in place of **A**	70
11	^{i}PrBF_3K (**E**) (3 equiv) in place of **A**	52
12	bicyclohexyl silicate **F** (2 equiv) in place of **A** in DMF	32
13	bicyclohexyl silicate **F** (2 equiv) in place of **A**	<5
14	*iso*-butyl silicate **G** (2 equiv) in place of **A** in DMF	53
15	cesium pivalate **H** (2 equiv) in place of **A**	<5
16	cesium pivalate **H** (2 equiv) in place of **A** in DMF	<5
17	pivalic acid/K_2CO_3 (3 equiv each) in place of **A**	<5
18	*p*-iodotoluene in place of **2** to yield **S-1**	<5
19	~40 ºC in place of room temperature	<10
20	phenol (-OPh) in place of Me (-SMe) xanthate ester ***A***	<5
21	^{i}Pr xanthate ester **S-2** in place of Me xanthate ester **1a**	82
22	SCH_2CF_3 xanthate ester **S-3** in place of Me xanthate ester **1a**	76



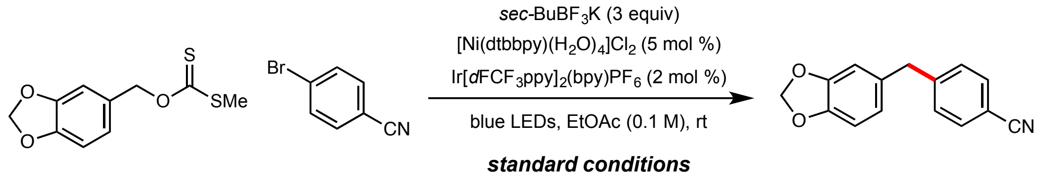
HPLC yield as compared to an internal standard.



cosolvent (1:1)	% conversion (HPLC)
-	70-80 (average)
toluene	64
cyclohexane	58
xylenes	75+byproduct
benzene	60
dioxane	27
H_2O	< 5

Attempts to lower RBF_3K loading (2 equiv) to promote C–O fragmentation in non-polar solvents was explored. Many radical-based fragmentation or HAT reactions, especially based on Sn and BEt_3 systems, are conducted in non-polar solvents (e.g., benzene, toluene, etc.),[3] yet polar organic solvents (EtOAc) are deemed necessary for the photoredox process. Addition of various non-polar organic co-solvents showed no additional benefit.

Reaction monitoring studies by ^{19}F NMR



General Procedure: Reaction was run according to standard photoredox cross-coupling conditions for benzyl xanthate esters (on 0.5 mmol scale), as described above. Upon reaction completion, hexafluorobenzene (internal standard, 0.75 mmol, 139.5 mg) was added to the reaction mixture and shaken. An aliquot (0.1 mL) was taken from the reaction mixture and diluted with DMSO-d_6 (0.5 mL), upon which a ^{19}F NMR was taken. This spectrum (Figure SI-2) shows full consumption of the alkyl trifluoroborate as compared to potassium *sec*-butyltrifluoroborate (–143.4 ppm in DMSO-*d6*, 1.5 mmol) at the start of the reaction.

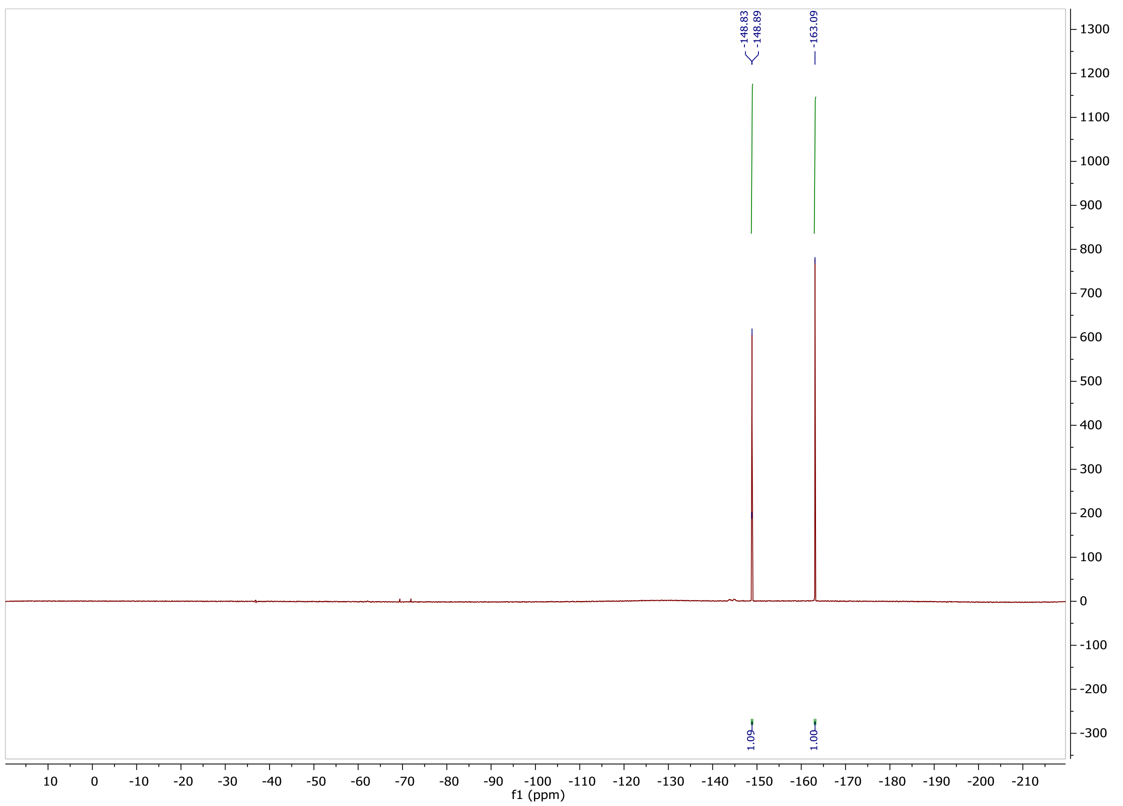


Figure SI-2. ^{19}F NMR ($CDCl_3$, 470.8 MHz) of reaction after completion (48 h) showing complete conversion of potassium sec-butyl trifluoroborate (-143.4 ppm in DMSO-d6) using 0.5 equivalent of hexafluorobenzene (compared to initial concentration of trifluoroborate) as internal standard

Cyclic Voltammetry of Dioxolane Benzyl Xanthate S12:

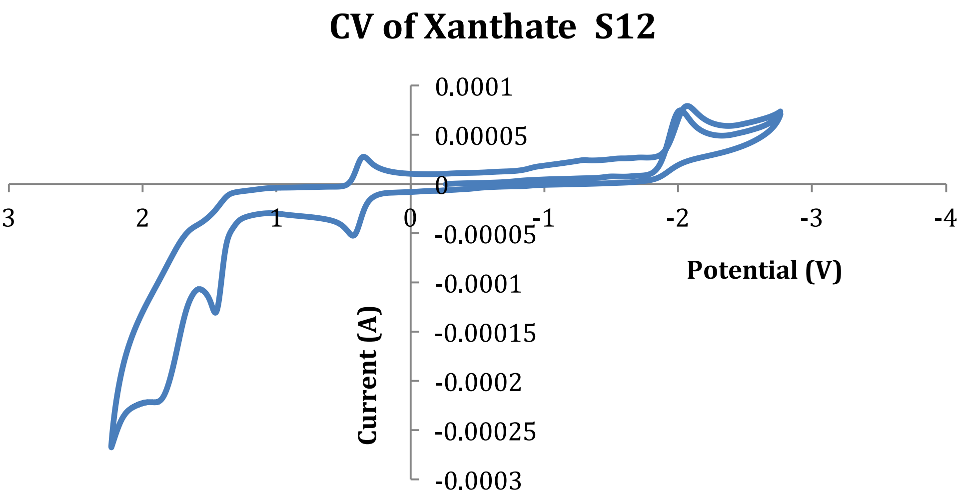
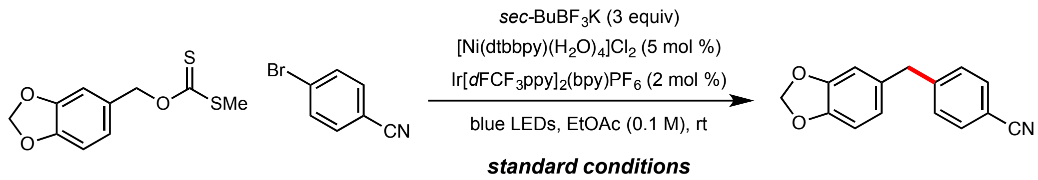


Figure SI–3. CV data of Xanthate S12

Reaction inhibition studies with *S*-*sec*-butyl *S*-methyl carbonodithioate



General Procedure: Reactions were run according to standard photoredox cross-coupling conditions for benzyl xanthate esters (on 0.5 mmol scale), as described above. Upon the start of the reaction, 0.1 mL aliquots were taken at various time points until reaction completion was observed. Aliquots were diluted with 0.9 mL EtOAc solution containing 4,4′-di-*tert*-butylbiphenyl (0.1 g 4,4′-di-*tert*-butylbiphenyl in 25 mL EtOAc). Reactions were monitored by HPLC.

A second reaction was carried out under the conditions described above with one variation: S-sec-butyl S-methyl carbonodithioate (0.7 equiv) was added at the start of the reaction. The reaction was monitored as described above.

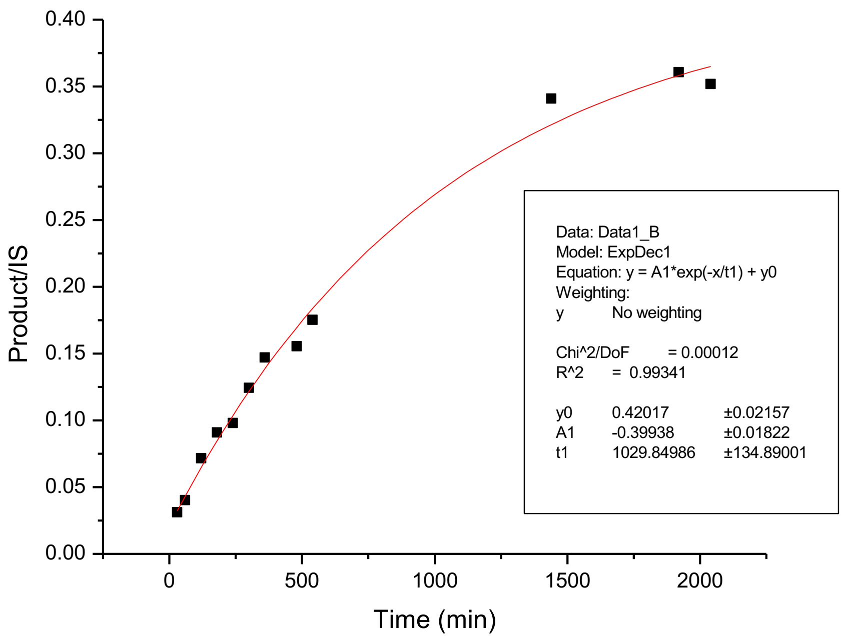
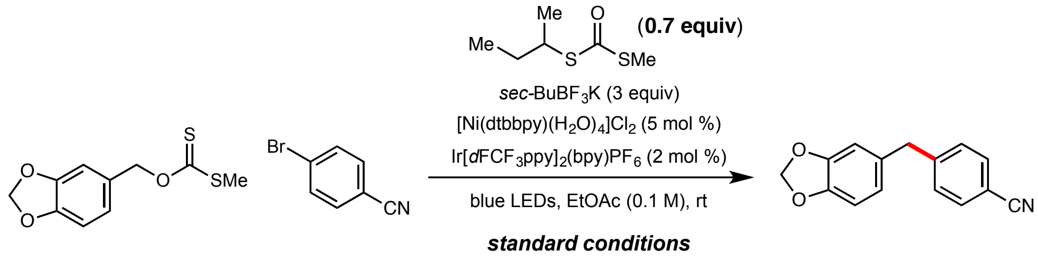


Figure SI-4. Plot of Product/IS vs. Time for reaction run under standard conditions



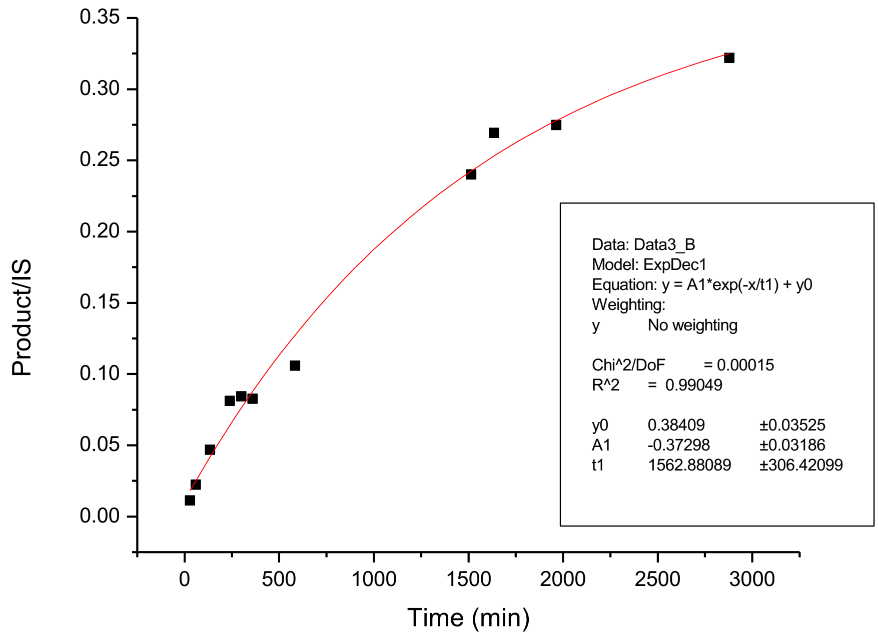


Figure SI-5. Plot of Product/IS vs. Time for reaction with 0.7 equiv *S*-*sec*-butyl *S*-methyl carbonodithioate

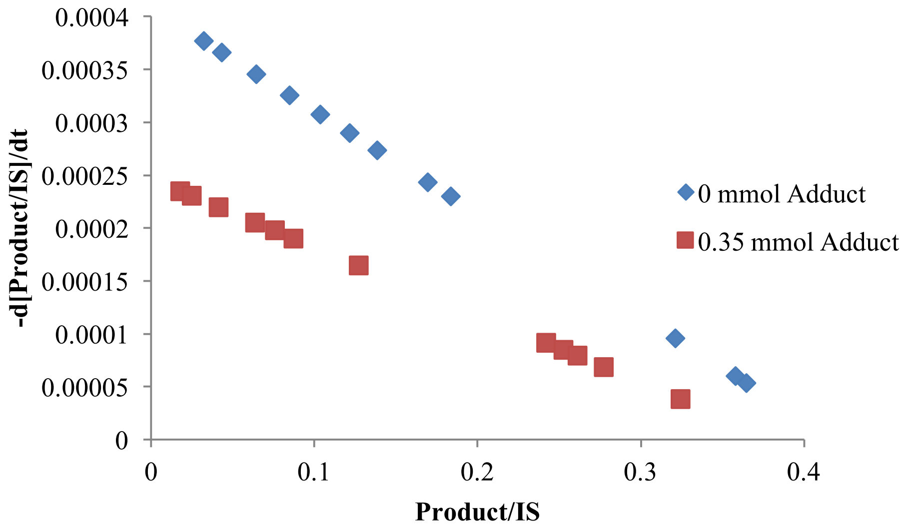
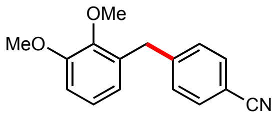
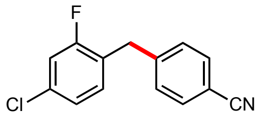


Figure SI-6. Plot showing inhibition of reaction rate with addition of 0.7 equiv S-sec-butyl S-methyl carbonodithioate

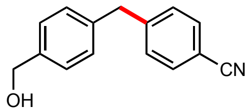
Compound Characterization Data



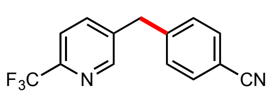
4-(2,3-Dimethoxybenzyl)benzonitrile (3c): obtained as a light tan oil (101 mg, 79%) following column flash chromatography (SiO_2, 0-7% EtOAc in hexanes);^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.54 (dd, *J* = 6.5, 1.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.72 (d, *J* = 7.5, 1.5 Hz, 1H), 4.03 (s, 2H), 3.86 (s, 3H), 3.71 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 152.9, 147.0, 133.2, 132.1, 129.5, 124.0, 122.3, 119.0, 111.2, 109.7, 60.4, 55.6, 36.2 ppm; IR: ν = 2932, 2840, 2227, 1606, 1597, 1585, 1504, 1474, 1430, 1414, 1269, 1222, 1168, 1113, 1071, 1005, 852 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{16}NO_2$ [M+H] 254.1181, found 254.1174.



4-(4-Chloro-2-fluorobenzyl)benzonitrile (3e): obtained as a colorless oil (82 mg, 67%) following column flash chromatography (SiO_2, 0-8% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.57 (dd, *J* = 6.5, 1.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10-7.07 (m, 3H), 4.00 (s, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 160.8 (d, $^{1}J_{CF}$ = 252 Hz), 144.8, 133.5 (d, $^{3}J_{CF}$ = 10.1 Hz), 132.4, 131.6 (d, $^{4}J_{CF}$ = 5.0 Hz), 129.4, 124.8 (d, $^{4}J_{CF}$ = 3.6 Hz), 124.7, 118.7, 116.4 (d, $^{2}J_{CF}$ = 24.5 Hz), 110.5, 34.6 (d, $^{3}J_{CF}$ = 2.5 Hz) ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –114.6 ppm; IR: ν = 3070, 2992, 2228, 1609, 1580, 1504, 1488, 1435, 1410, 1265, 1226, 1197, 1179, 1120, 1075, 925 cm^{-1}; HRMS (EI) m/z calc. for $C_{14}H_9ClFN$ $[M]^-$ 245.0408, found 245.0417.

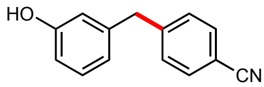


4-(4-(Hydroxymethyl)benzyl)benzonitrile (3f): obtained as a colorless oil (27 mg, 24%) following column flash chromatography (SiO_2, 5-40% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 4.03 (s, 2H), 1.62 (br s, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.6, 139.3, 138.8, 132.3, 129.6, 129.1, 127.5, 118.9, 110.1, 65.0, 41.6 ppm; IR: ν = 3403 (br), 3026, 2923, 2871, 2227, 1699, 1606, 1504, 1414, 1201, 1177, 1116, 1043, 1018, 861 cm^{-1}; HRMS (EI) m/z calc. for $C_{15}H_{13}NO$ $[M]^+$ 223.0997, found 223.0989. Oxidized (benzaldehyde) xanthate was unable to be completely removed from this sample, and is present as a 3.8% impurity by ^{1}H NMR integration (peaks @ 9.99 (br s, 1H), 5.64 (s, 2H), 4.72 (br s, 2H), 2.58 (s, 3H) ppm).

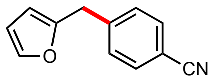


4-((6-(Trifluoromethyl)pyridin-3-yl)methyl)benzonitrile (3g): obtained as a colorless oil (68 mg, 52%) following column flash chromatography (SiO_2, 0-15% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.59 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 2.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.12 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.3, 146.7 (q, $^{2}J_{CF}$ = 40 Hz), 144.0, 138.2, 137.5, 132.7, 129.6, 121.5 ($^{1}J_{CF}$ = 297 Hz), 120.5 ($^{3}J_{CF}$ = 3.0 Hz), 118.5, 111.0, 38.8 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –67.82 ppm; IR: ν =

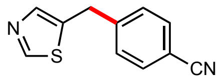
2992, 2229, 1609, 1505, 1416, 1401, 1336, 1306, 1254, 1176, 1130, 1085, 1028, 864 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{10}F_3N_2$ $[M+H]^+$ 263.0796, found 263.0798.



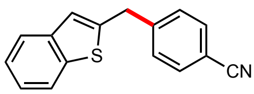
4-(3-Hydroxybenzyl)benzonitrile (3h): obtained as a tan solid (59 mg, 57%) following column flash chromatography (SiO_2, 0-15% EtOAc in hexanes). mp = 169-171 ºC; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.52 (dd, *J* = 6.5, 1.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 6.5, 2.5 Hz, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 5.89 (s, 1H), 3.96 (s, 2H), 2.12 (s, 1H); ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 156.0, 146.7, 141.0, 132.2, 129.8, 129.6, 121.1, 118.9, 115.9, 113.7, 109.6, 41.7 ppm; IR: ν = 3381 (br), 2994, 2228, 1599, 1588, 1503, 1486, 1455, 1345, 1271, 1228, 1177, 1152, 952 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{10}NO$ [M–H] 208.0762, found 208.0767.



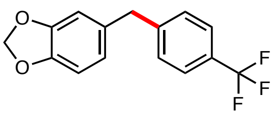
4-(Furan-2-ylmethyl)benzonitrile (3j): obtained as a colorless oil (56 mg, 61%) following column flash chromatography (SiO_2, 2-20% EtOAc in hexanes). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.32 (dd, *J* = 3.0, 2.0 Hz, 1H), 6.06 (d, *J* = 3.0 Hz, 1H), 4.03 (s, 2H); ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 152.5, 143.7, 142.0, 132.3, 129.4, 118.8, 110.5, 110.4, 107.0, 34.5 ppm; IR: ν = 2924, 2229, 1795, 1608, 1505, 1416, 1176, 1147, 1113, 1072, 1010, 938 cm^{-1}; HRMS (EI) m/z calc. for $C_{12}H_9NO$ [M] 183.0684, found 183.0682.



4-(Thiazol-5-ylmethyl)benzonitrile (3k): obtained as a tan oil (41 mg, 41%) following column flash chromatography (SiO_2, 5-40% EtOAc in hexanes). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.70 (s, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H); ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 152.9, 144.6, 141.6, 136.2, 132.5, 129.1, 118.5, 110.9, 32.8 ppm; IR: ν = 3082, 2991, 2228, 1607, 1507, 1406, 1315, 1240, 1177, 1105, 1021, 921 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_9N_2S$ [M+H] 201.0486, found 201.0466.

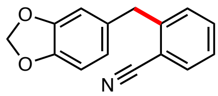


4-(Benzo[*b*]thiophen-2-ylmethyl)benzonitrile (3l): obtained as a light tan solid (66 mg, 54%) following column flash chromatography (SiO_2, 0-10-20% EtOAc in hexanes). mp = 122-124 ºC;^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 6.5, 2.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34-7.27 (m, 2H), 7.03 (s, 1H), 4.28 (s, 2H) ppm; ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 144.9, 142.7, 139.9, 132.3, 129.4, 125.4, 124.3, 124.0, 123.1, 122.5, 122.2, 118.8, 110.7, 36.9 ppm; IR: ν = 3057, 2227, 1607, 1505, 1458, 1436, 1414, 1177, 1114, 1089, 1015, 854 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{10}NS$ $[M–H]^-$ 248.0534, found 248.0541.

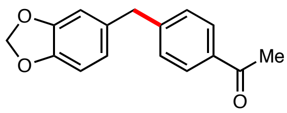


5-(4-(Trifluoromethyl)benzyl)benzo[d][1,3]dioxole (3m): obtained as a colorless oil (72 mg, 65%) following column flash chromatography (SiO_2, 0-15% EtOAc in hexanes). ^1H

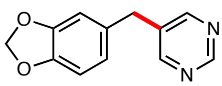
NMR ($CDCl_3$, 500.4 MHz): δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.69-6.61 (m, 2H), 5.94 (s, 2H), 3.95 (s, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.8, 146.1, 145.3, 133.7, 128.9, 128.4 ($^{2}J_{CF}$ = 32.3 Hz), 125.3 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 ($^{1}J_{CF}$ = 269.8 Hz), 121.7, 109.3, 108.2, 100.8, 41.3 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –62.3 ppm; IR: ν = 1488, 1322, 1244, 1160, 1117, 1105, 1065, 1038, 1018, 928, 802, 773 cm^{-1}; HRMS (EI) m/z calc. for $C_{15}H_{11}F_3O_2$ [M+] 280.0711, found 280.0723.



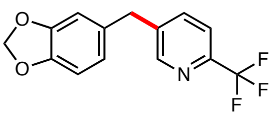
2-(Benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (3n): obtained as a light tan oil (57 mg, 48%) following column flash chromatography (SiO_2, 10-20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.64 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51 (td, *J* = 7.7, 1.4 Hz, 1H), 7.33-7.25 (m, 2H), 6.78-6.68 (m, 3H), 5.93 (s, 2H), 4.12 (s, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.0, 146.5, 145.2, 133.0, 133.0, 132.6, 130.1, 126.9, 122.2, 118.2, 112.6, 109.4, 108.5, 101.1, 40.0 ppm. IR: ν = 2920, 2364, 2226, 1601, 1475, 1254, 1038, 927, 816 cm^{-1}; HRMS: (ESI) m/z calc. for $C_{15}H_{12}NO_2$ [M+H] 238.0868, found 238.0861.



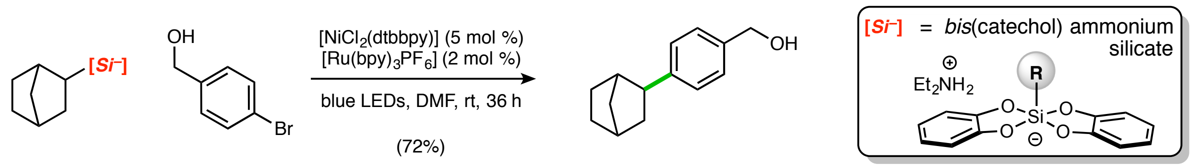
1-(4-(Benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)ethanone (3o): obtained as a colorless oil (76 mg, 69%) following column flash chromatography (SiO_2, 0-10-20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.93-7.86 (m, 2H), 7.32-7.23 (m, 2H), 6.75 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.69-6.62 (m, 2H), 5.93 (d, *J* = 1.1 Hz, 2H), 3.95 (s, 2H), 2.58 (d, *J* = 1.1 Hz, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 197.8, 148.0, 147.0, 146.3, 135.4, 133.9, 129.1, 128.8, 122.0, 109.5, 108.4, 101.0, 100.1, 41.7, 26.7 ppm; IR: ν = 1678, 1605, 1501, 1486, 1442, 1266, 1241, 1181, 1036, 926, 801, 770 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{15}O_3$ $[M+H]^+$ 255.1021, found 255.1023.



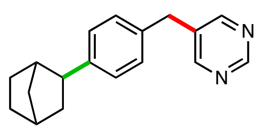
5-(Benzo[d][1,3]dioxol-5-ylmethyl)pyrimidine (3q): obtained as a light tan oil (97 mg, 90%) following column flash chromatography (SiO_2, 10-20-40% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.08 (s, 1H), 8.57 (s, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 2H), 5.95 (s, 2H), 3.89 (s, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 157.1, 157.0, 148.3, 146.7, 134.6, 132.1, 121.9, 109.3, 108.7, 101.3, 36.4 ppm; IR: ν = 1561, 1501, 1487, 1442, 1407, 1246, 1187, 1094, 1035, 925, 804, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_{12}H_{11}N_2O_2$ $[M+H]^+$ 215.0821, found 215.0827.



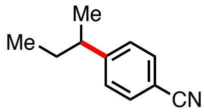
5-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-2-(trifluoromethyl)pyridine (3r): obtained as a colorless oil (102 mg, 72%) following column flash chromatography (SiO_2, 0-10-20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.82 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.79-6.70 (m, 3H), 5.93 (s, 2H), 4.14 (s, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 165.0, 147.8, 146.4, 146.2 (q, $^{3}J_{CF}$ = 4.0 Hz), 133.6 (q, $^{3}J_{CF}$ = 3.4 Hz), 131.9, 124.3 ($^{2}J_{CF}$ = 32.9 Hz), 123.6 ($^{1}J_{CF}$ = 272.1 Hz), 122.6, 122.0, 109.4, 108.4, 100.9, 44.1 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –62.3 ppm; IR: ν = 1606, 1487, 1442, 1325, 1241, 1122, 1077, 1037, 1016, 928, 807, 787 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{11}F_3NO_2$ $[M+H]^+$ 282.0742, found 282.0743.



(4-(Bicyclo[2.2.1]heptan-2-yl)phenyl)methanol (8): The reaction was carried out analogous to this group's recently reported findings.[4] An 8 mL sealable screw cap vial was charged with the aryl bromide (94.0 mg, 0.5 mmol, 1.0 equiv), the ammonium organobis(catecholato)silicate (265 mg, 0.6 mmol, 1.2 equiv), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (11.8 mg, 0.025 mmol, 5 mol %), and the photocatalyst $[Ru(bpy)_3](PF_6)_2$ (8.5 mg, 0.01 mmol, 2 mol %). The vial was sealed and three vacuum/argon cycles were carried out. Next, dry, degassed DMF (5.0 mL, 0.1 M) was added. The vial containing all the reagents was further sealed with Parafilm and placed approximately 3-5 cm away from the blue LEDs (as in Figure SI-1) and stirred for 36 h at rt. A fan was blown across the reaction setup to suppress the heat generated by the LED strips (the reaction temperatures are estimated to be ~30 °C). The crude reaction mixture was poured into a separatory funnel and diluted with H_2O (10 mL) and the resulting suspension was extracted with Et_2O (3 × 15 mL). The combined organic extracts were washed with a saturated solution of Na_2CO_3 (2 × 10 mL) then brine (10 mL), dried ($MgSO_4$), and concentrated.
The crude residue was purified by column flash chromatography (SiO_2, 0-5-10% EtOAc in hexanes) and the adduct was obtained as a colorless oil (73 mg, 72%). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.27 (d, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 4.63 (s, 2H), 2.76 (dd, J = 7.5, 5.5 Hz, 1H), 2.38 (s, 2H), 2.05 (br s, 1H), 1.82-1.77 (m, 1H), 1.70-1.54 (m, 4H), 1.41-1.37 (m, 1H), 1.32-1.28 (m, 1H), 1.22-1.20 (m, 1H) ppm; ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 147.1, 137.9, 127.2, 127.0, 65.1, 47.0, 42.9, 39.1, 36.8, 36.0, 30.5, 28.9 ppm; IR: ν = 3307 (br), 2948, 2838, 1513, 1454, 1418, 1368, 1311, 1298, 1210, 1138, 1027, 1009 cm^{-1}; HRMS (CI) m/z calc. for $C_{14}H_{18}O$ $[M]^+$ 202.1358, found 202.1364.

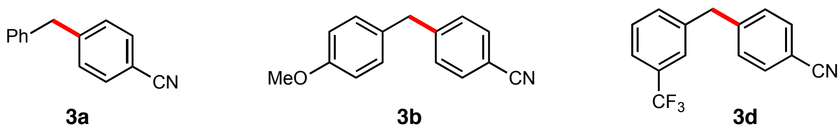


4-(4-(Hydroxymethyl)benzyl)benzonitrile (9): 0.42 mmol of **8** was employed to generate the crude xanthate ester, following the general procedure, and subjected to standard reaction coupling conditions, affording the title compound as a colorless oil (68 mg, 62%) following column flash chromatography (SiO_2, 5-35% EtOAc in hexanes). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 9.06 (s, 1H), 8.57 (s, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 3.93 (s, 2H), 2.71 (q, J = 7.5, 6.0 Hz, 1H), 2.33 (br s, 2H), 1.79-1.73 (m, 4H), 1.37-1.24 (m, 2H), 1.17 (d, J = 9.0 Hz, 1H), 1.02-0.87 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 157.0, 156.8, 146.4, 135.2, 134.5, 128.5, 127.6, 46.9, 42.9, 39.1, 36.8, 36.1, 36.0 30.5, 28.8 ppm; IR: ν = 3020, 2950, 2869, 1627, 1560, 1513, 1454, 1439, 1407, 1311, 1207, 1173, 1105, 1020, 920 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{21}N_2$ $[M+H]^+$ 265.1705, found 265.1700.



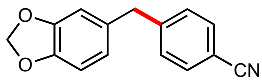
4-(*sec*-butyl)benzonitrile(10): prepared according to the general reaction parameters in the *absence* of any xanthate pronucleophile. The analytical data matches that of the previously reported compound: Liu, Z.; Dong, N.; Xu, M.; Sun, Z.; Tao, T. *J. Org. Chem.* **2013**, *78*, 7436.

Characterization for compounds not listed herein match the analytical data as previously reported:



3a **3b** **3d**

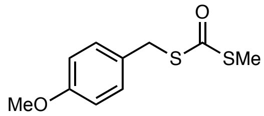
Benischke, A.D.; Knoll, I.; Rérat, A.; Gosmini, C; Knochel, P. *Chem. Commun.* **2016**, *52*, 3171.



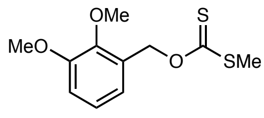
3p

Tellis, J.C.; Primer, D.N.; Molander, G.A. *Science* **2014**, *345*, 433.

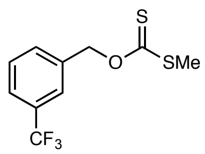
Supporting Characterization



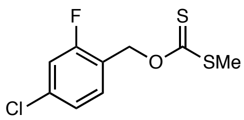
***O*-(4-Methoxybenzyl) *S*-methyl carbonodithioate (S1):** obtained as a dark yellow oil (1.02 g, 69%, 6.53 mmol scale) and subjected immediately to the next reaction. ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.57 (s, 2H), 3.81 (s, 3H), 2.55 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.5, 159.8, 130.04, 126.6, 113.8, 75.1, 55.1, 18.9 ppm; IR: ν = 2950, 2941, 1612, 1513, 1462, 1441, 1423, 1303, 1198, 1170, 1049, 1031, 963 cm^{-1}; *Material rapidly isomerizes to *S*-(4-methoxybenzyl) *S*-methyl carbonodithioate over 2 days when stored at 3 ºC. HRMS (EI) m/z calc. for $C_{10}H_{12}O_2S_2$ $[M]^+$ 228.0279, found 228.0283.



***O*-(2,3-Dimethoxybenzyl) *S*-methyl carbonodithioate (S2):** obtained crude as a yellow oil (1.65 g, 97%, 5.89 mmol scale). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.68 (s, 2H), 3.88 (s, 6H), 2.57 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.5, 152.7, 147.8, 128.6, 124.0, 122.0, 113.2, 70.8, 61.1, 55.8, 19.1 ppm; IR: ν = 2936, 2840, 1589, 1483, 1463, 1430, 1306, 1276, 1232, 1202, 1169, 1081, 1052, 1004, 976, 929 cm^{-1}; HRMS (CI) m/z calc. for $2[C_{11}H_{14}NaO_3S_2]$ $[2M+ Na]^+$ 539.0666, found 539.0668.

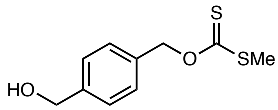


***S*-Methyl *O*-(3-(trifluoromethyl)benzyl) carbonodithioate (S3):** obtained as a yellow oil (1.40 g, 93%, 5.68 mmol scale). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.67 (s, 1H), 7.61 (dd, *J* = 8.0, 7.5 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 5.68 (s, 2H), 2.60 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.6, 135.8, 131.6, 131.0 (d, $^{2}J_{CF}$ = 31.3 Hz), 129.1, 125.4 (d, $^{3}J_{CF}$ = 3.8 Hz), 125.0 (d, $^{3}J_{CF}$ = 3.8 Hz), 123.9 (d, $^{1}J_{CF}$ = 270 Hz), 73.8, 19.2 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –62.7 ppm; IR: ν = 2973, 1452, 1425, 1369, 1329, 1211, 1198, 1165, 1123, 1099, 1064, 1002, 967 cm^{-1}; HRMS (EI) m/z calc. for $C_{10}H_9F_3OS_2$ $[M]^+$ 266.0047, found 266.0031.

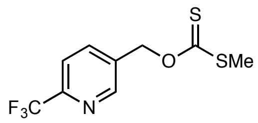


***O*-(4-Chloro-2-fluorobenzyl) *S*-methyl carbonodithioate (S4):** obtained as a yellow oil (1.30 g, 92%, 5.68 mmol scale). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.38 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 10.0 Hz, 1H), 7.13 (dd, *J* = 11.0, 2.0 Hz, 1H), 5.65 (s, 2H), 2.58 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.4, 160.8 (d, $^{1}J_{CF}$ = 252 Hz), 135.7 (d, $^{3}J_{CF}$ = 10.1 Hz), 131.6 (d, $^{4}J_{CF}$ = 5.0 Hz), 124.6 (d, $^{4}J_{CF}$ = 3.6 Hz), 120.8 (d, $^{2}J_{CF}$ = 14.6 Hz), 116.4 (d, $^{2}J_{CF}$ = 24.5 Hz), 68.0 (d, $^{3}J_{CF}$ = 3.5 Hz), 19.2 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –114.5

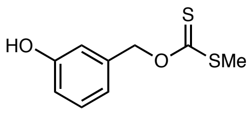
ppm; IR: ν = 2992, 1613, 1582, 1490, 1449, 1412, 1371, 1270, 1205, 1171, 1124, 1053, 966 cm^{-1}; HRMS (EI) m/z calc. for $C_9H_8ClFOS_2$ $[M]^+$ 249.9689, found 249.9703.



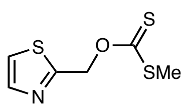
***O*-(4-(Hydroxymethyl)benzyl) *S*-methyl carbonodithioate (S5):** obtained as a light tan, crystalline solid (840 mg, 25%, 14.5 mmol scale) following recrystalization from dichloromethane then further purification by column flash chromatography (SiO_2, 50% EtOAc in hexanes). mp = 54-55 ºC; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.38 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.62 (s, 2H), 4.66 (s, 2H), 2.56 (s, 3H), 2.30 (s, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 215.6, 141.3, 133.9, 128.7, 127.0, 74.8, 64.7, 19.0 ppm; IR: ν = 3325 (br), 2920, 2872, 1421, 1368, 1225, 1194, 1175, 1112, 1052, 1017, 964 cm^{-1}; HRMS (EI) m/z calc. for $C_{10}H_{12}O_2S_2$ $[M]^+$ 228.0279, found 228.0268.



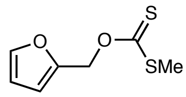
***S*-Methyl *O*-((6-(trifluoromethyl)pyridin-3-yl)methyl) carbonodithioate (S6):** obtained crude as a golden oil (740 mg, 98%, 2.82 mmol scale). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.76 (d, J = 2.0 Hz, 1H), 7.92 (dd, J = 8.0, 2.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 5.73 (s, 2H), 2.59 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 215.5, 149.6, 148.2 (q, $^2J_{CF}$ = 40 Hz), 137.2, 133.9, 121.3 ($^1J_{CF}$ = 297 Hz), 120.3 ($^3J_{CF}$ = 2.8 Hz), 70.8, 19.4 ppm; ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): –68.0 ppm; IR: ν = 2925, 1721, 1584, 1405, 1334, 1234, 1171, 1132, 1067, 1028, 969, 925, 856 cm^{-1}; HRMS (CI) m/z calc. for $C_9H_9F_3NOS_2$ $[M+H]^+$ 268.0078, found 268.0070.



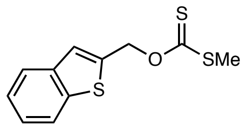
***O*-(3-Hydroxybenzyl) *S*-methyl carbonodithioate (S7):** obtained as a dark yellow oil (1.10 g, 64%, 8.06 mmol scale) following column chromatography (SiO_2, 20-30% EtOAc in hexanes). ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.26 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.90 (s, 1H), 6.85 (dd, J = 8.0, 2.0 Hz, 1H), 5.59 (s, 2H), 2.58 (s, 3H), 2.10 (s, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 215.7, 155.7, 136.4, 129.9, 120.6, 115.6, 115.2, 74.7, 19.4 ppm; IR: ν = 3389 (br), 2985, 2224, 1427, 1365, 1221, 1198, 1177, 1152, 952 cm^{-1}; HRMS (CI) m/z calc. for $C_9H_{11}O_2S_2$ $[M+H]^-$ 213.0044, found 213.0038.



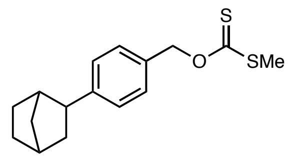
***S*-Methyl *O*-(thiazol-2-ylmethyl) carbonodithioate (S8):** obtained as a dark yellow oil (1.17 g, 97%, 5.89 mmol scale) and subjected immediately to the next reaction. ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.81 (s, 1H), 7.93 (s, 1H), 5.85 (s, 2H), 2.55 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 215.1, 154.9, 144.6, 131.2, 65.7, 19.2 ppm; the propensity for which this compound was prone to decomposition precluded the acquisition of the remaining analytical data.



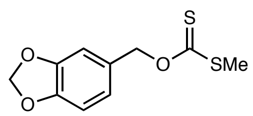
***O*-(Furan-2-ylmethyl) *S*-methyl carbonodithioate (S9):** obtained as a yellow oil (1.78 g, 93%, 10.2 mmol scale, ~85% purity) and subjected immediately to the next reaction. ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.45 (d, *J* = 1.0 Hz, 1H), 6.50 (d, *J* = 3.5 Hz, 1H), 6.38 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.57 (s, 2H), 2.55 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.3, 148.1, 143.6, 111.9, 110.6, 66.4, 19.1 ppm; IR: ν = 2962, 1646, 1499, 1424, 1275, 1231, 1191, 1171, 1050, 1013, 964 cm^{-1}; HRMS (EI) m/z calc. for $C_7H_8O_2S_2$ $[M]^+$ 187.9966, found 187.9985.



***O*-(Benzo[*b*]thiophen-2-ylmethyl) *S*-methyl carbonodithioate (S10):** obtained as a dark yellow, crystalline solid (740 mg, 96%, 3.04 mmol scale). mp = 38-39 ºC ; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.38-7.36 (m, 3H), 5.90 (s, 2H), 2.60 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.2, 140.6, 139.0, 137.2, 125.3, 124.9, 124.5, 123.9, 122.4, 69.6, 13.1 ppm; IR: ν = 2984, 2127, 1505, 1468, 1424, 1412, 1161, 1114, 1015, 895 cm^{-1}; HRMS (EI) m/z calc. for $C_{11}H_{10}OS_3$ $[M]^+$ 253.9894, found 253.9875.

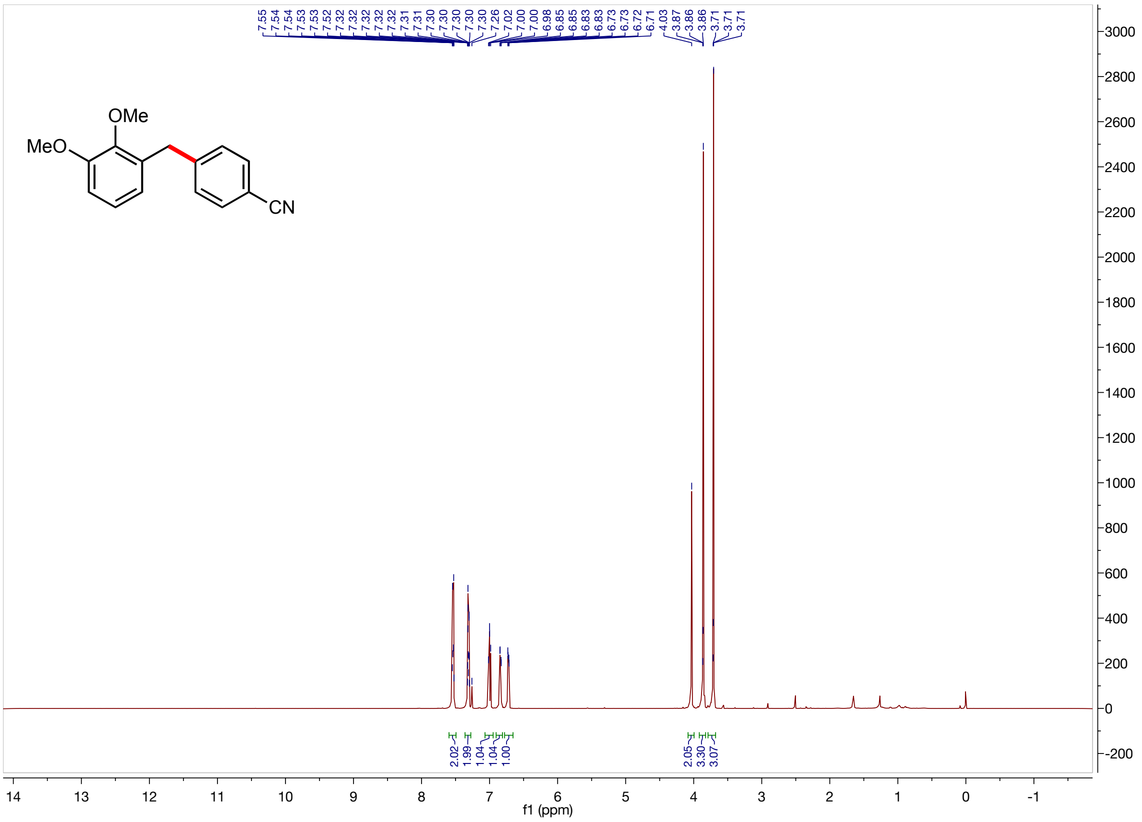


***O*-(4-(Bicyclo[2.2.1]heptan-2-yl)benzyl) *S*-methyl carbonodithioate (S11):** obtained as a yellow oil (123 mg, 99%, 0.42 mmol scale). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.62 (s, 2H), 2.76 (t, *J* = 5.0 Hz, 1H), 2.58 (s, 3H), 2.36 (m, 2H), 1.78 (ddd, *J* = 12.0, 9.0, 2.0 Hz, 1H), 1.67-1.52 (m, 4H), 1.38-1.35 (m, 1H), 1.30-1.27 (m, 1H), 1.20-1.18 (m, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.7, 148.3, 131.6, 128.6, 127.3, 75.2, 47.1, 42.8, 39.1, 36.8, 36.1, 30.5, 28.8, 19.0 ppm. This material was not isolated and used immediately in the next step.

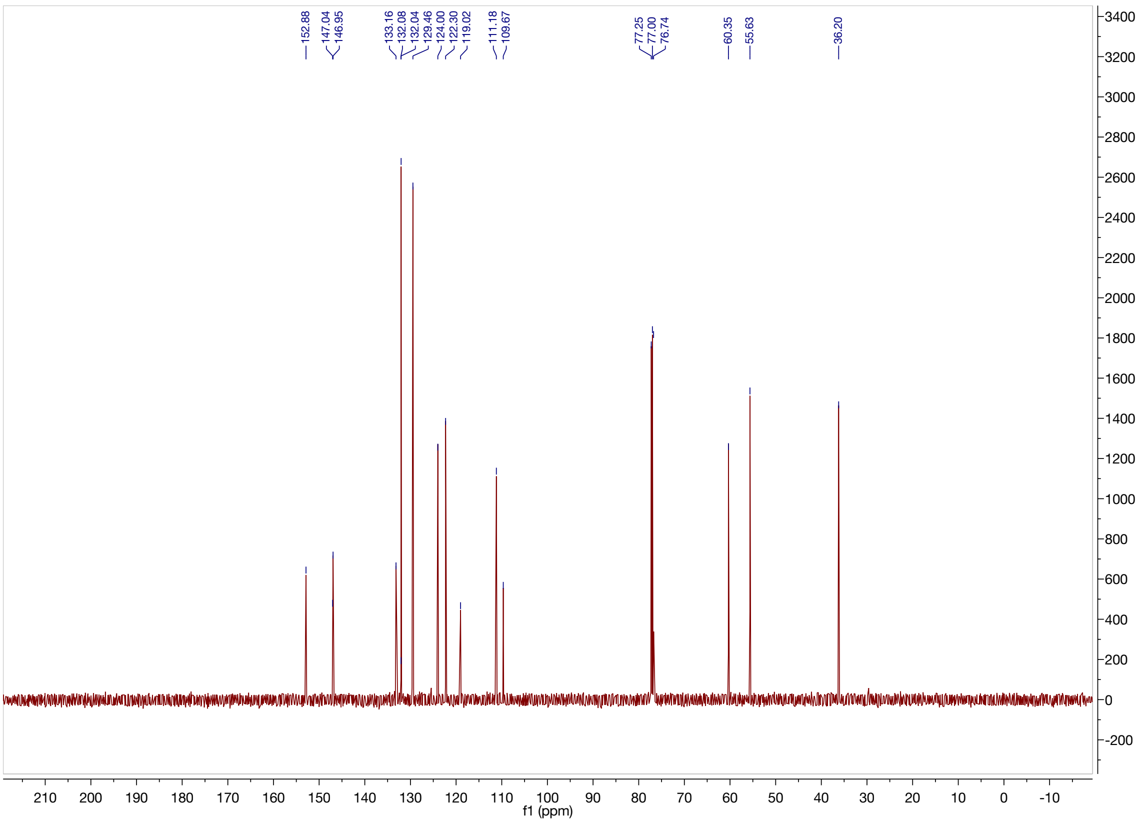


***O*-(Benzo[d][1,3]dioxol-5-ylmethyl) *S*-methyl carbonodithioate (S12)**: obtained as a light yellow solid (1.83 g, 94%, 8.00 mmol scale): mp = 35-37 ºC ; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 6.90 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 5.99 (s, 2H), 5.54 (s, 2H), 2.58 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 215.8, 148.1, 148.0, 128.5, 123.0, 109.4, 108.4, 101.4, 75.4, 19.2 ppm; IR: ν = 2961, 1501, 1488, 1444, 1246, 1218, 1194, 1035, 933, 926, 863, 827, 811 cm^{-1}; HRMS (ESI) m/z calc. for $C_{10}H_{11}O_3S_2$ [M+H] 243.0150, found 243.0145.

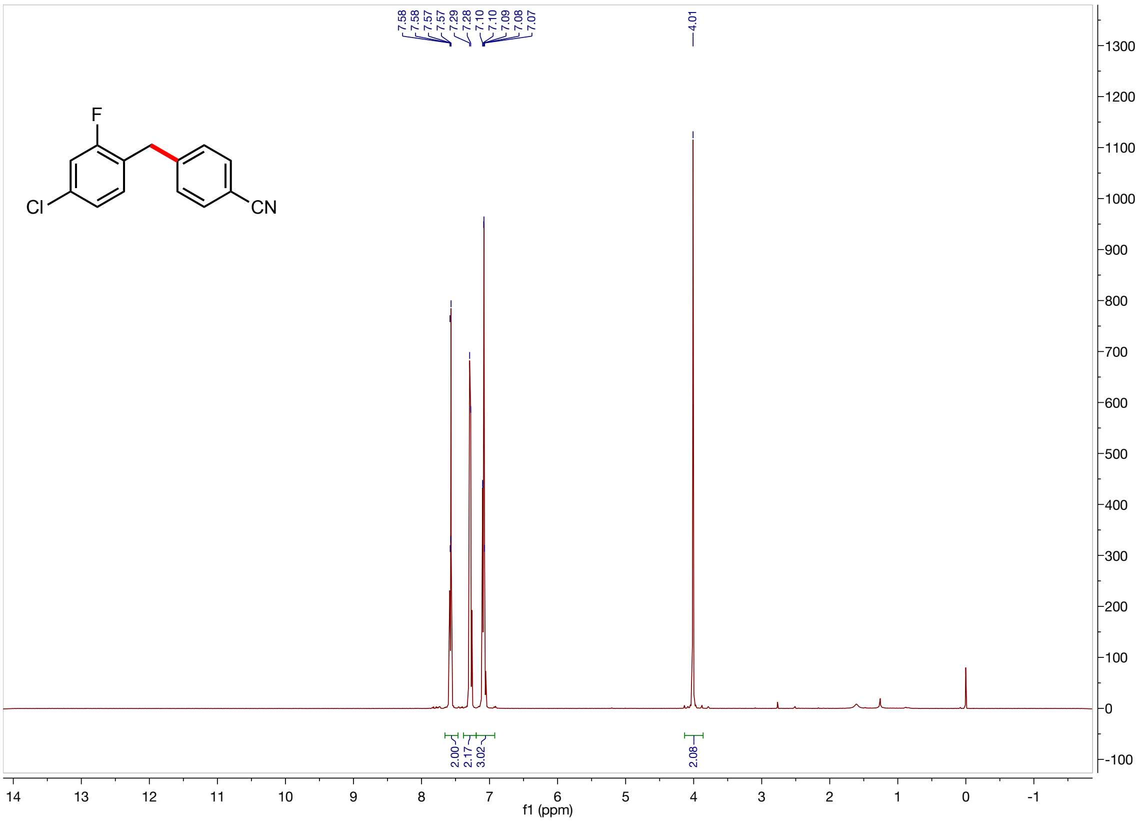
Spectral Data



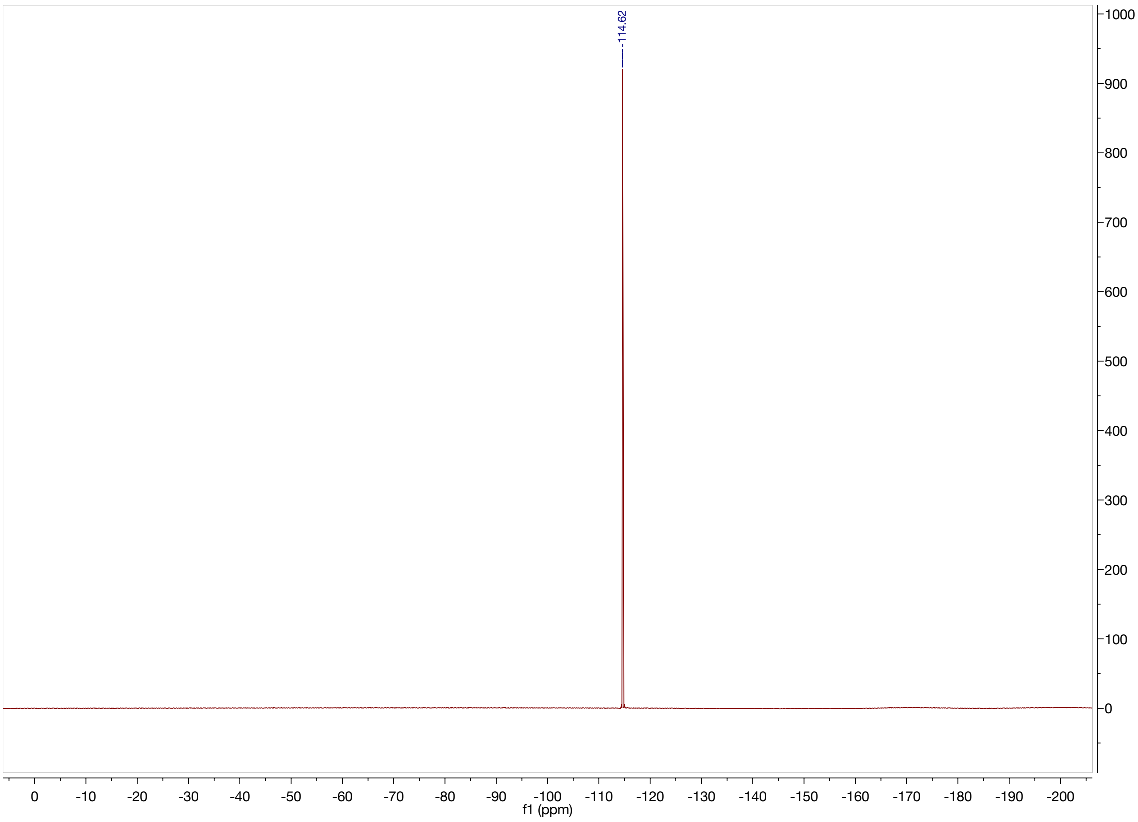
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(2,3-dimethoxybenzyl)benzonitrile (**3c**)



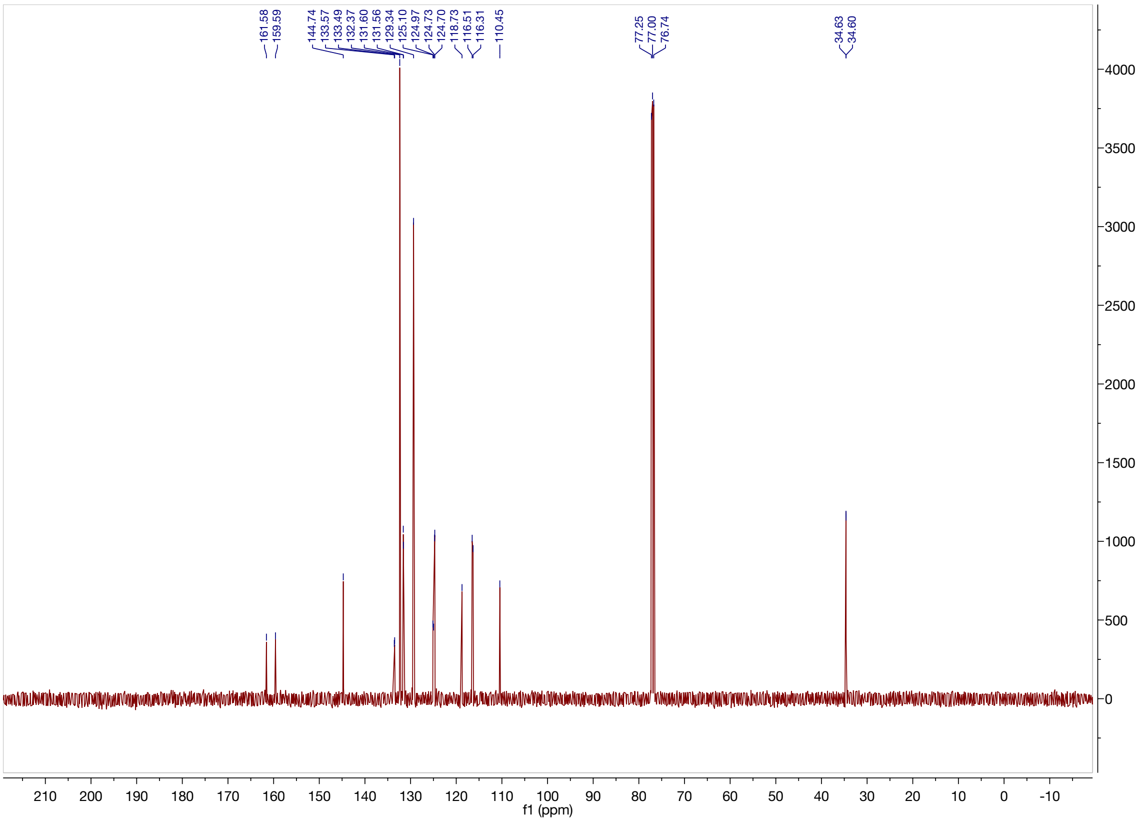
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(2,3-dimethoxybenzyl)benzonitrile (**3c**)



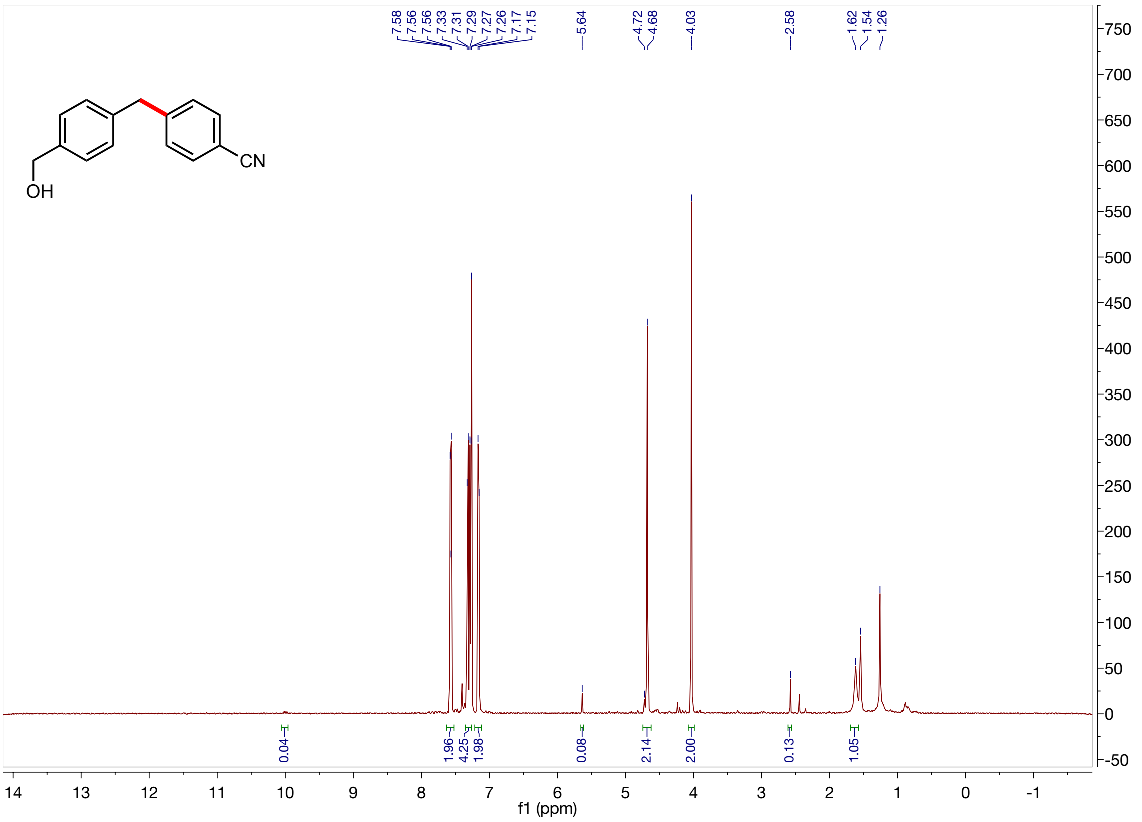
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(4-chloro-2-fluorobenzyl)benzonitrile (**3e**)



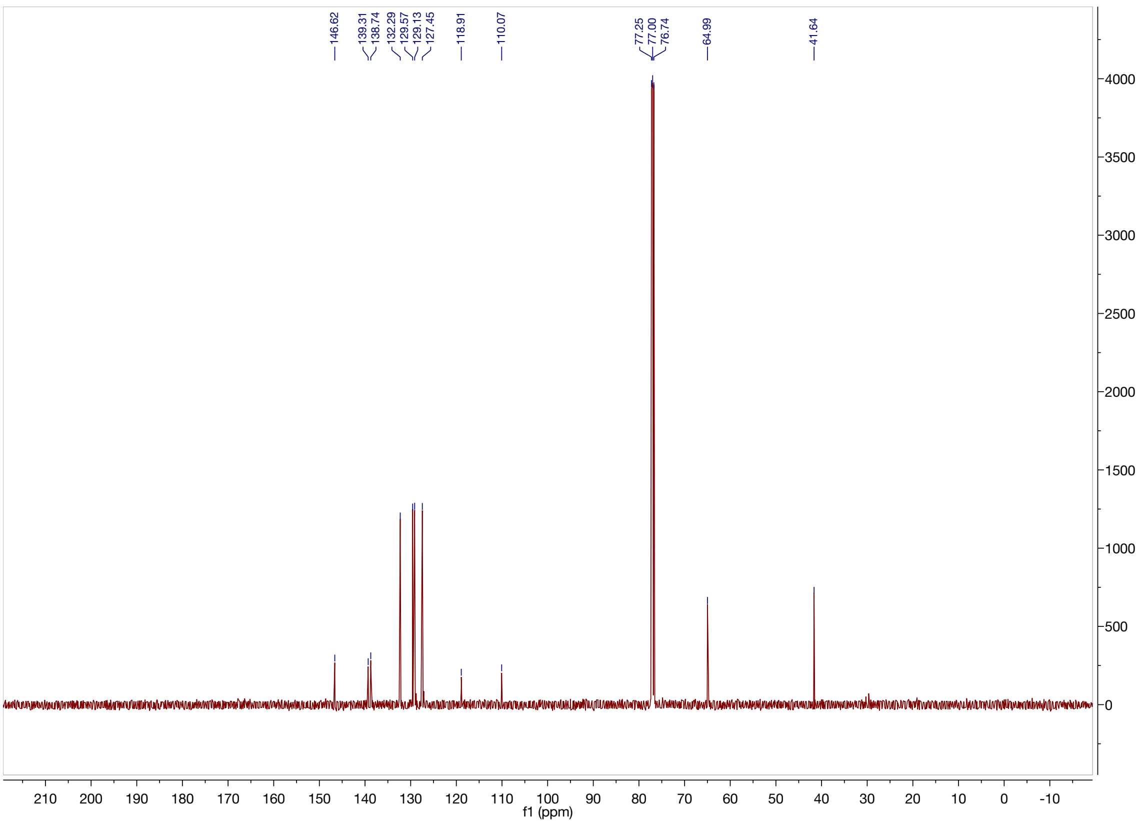
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 4-(4-chloro-2-fluorobenzyl)benzonitrile (**3e**)



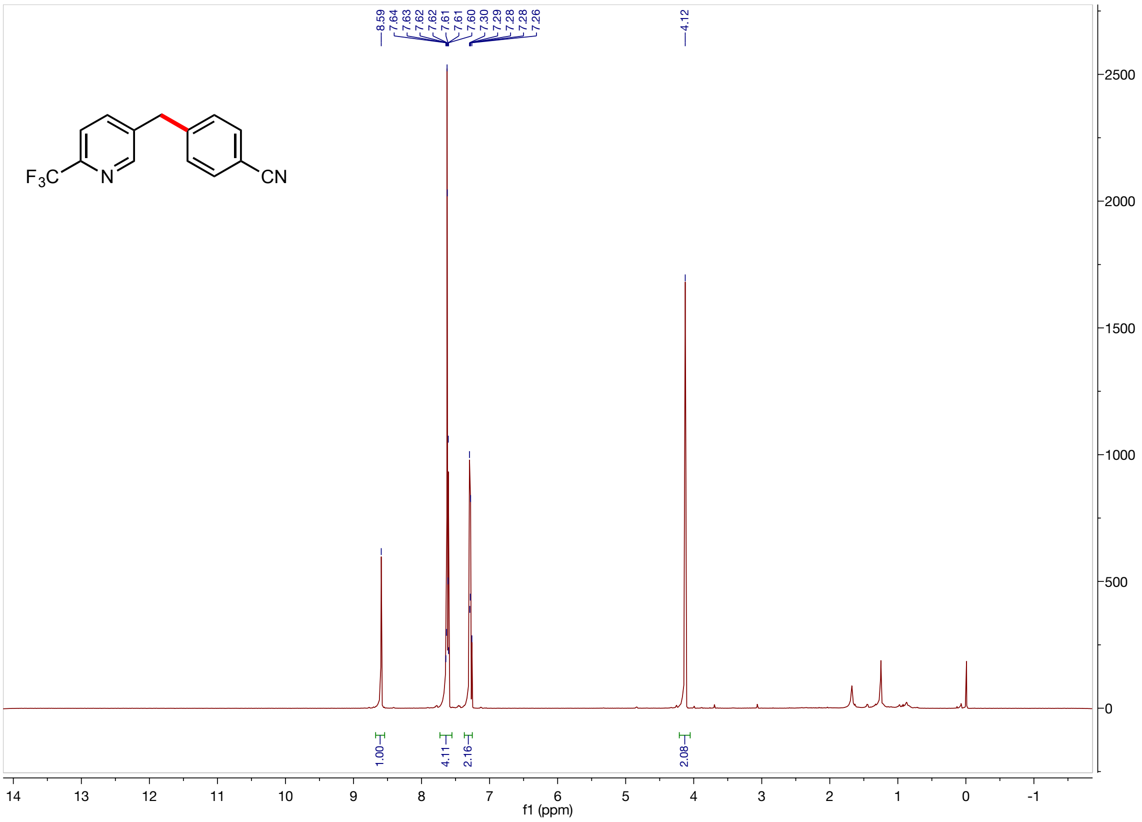
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz) of 4-(4-chloro-2-fluorobenzyl)benzonitrile (**3e**)



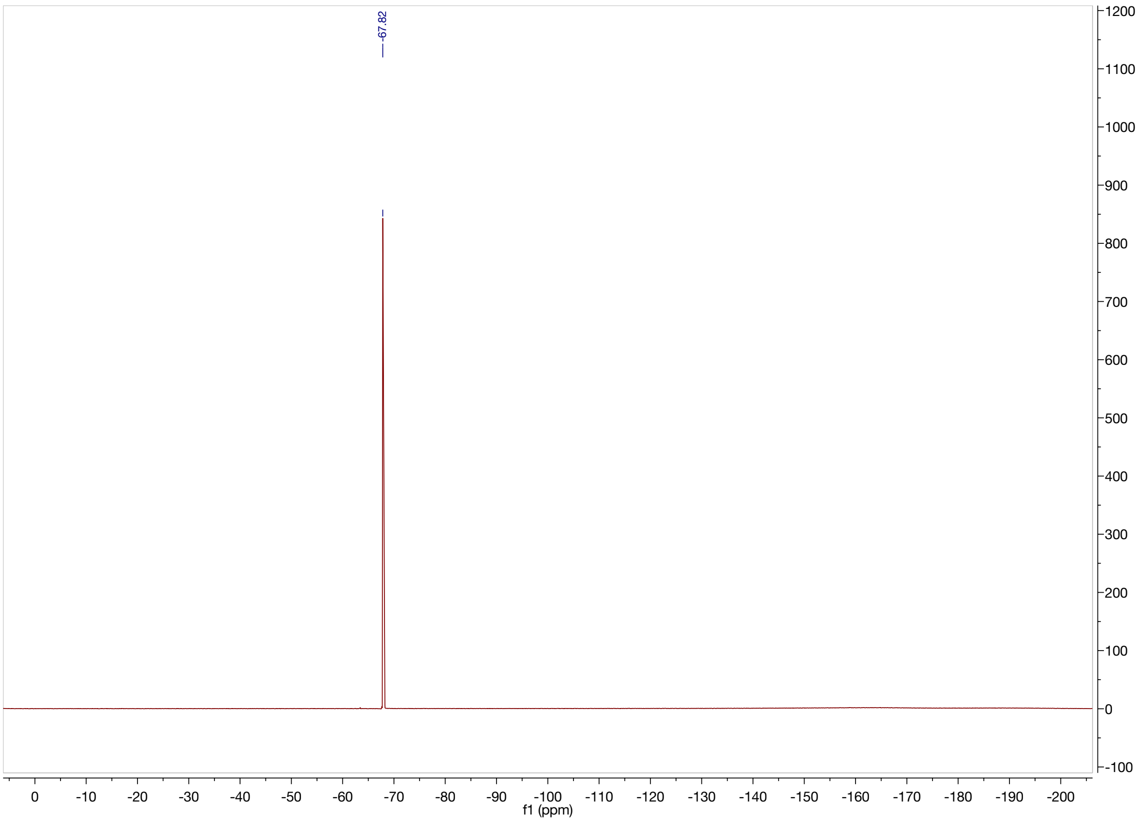
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(4-(hydroxymethyl)benzyl)benzonitrile (**3f**)



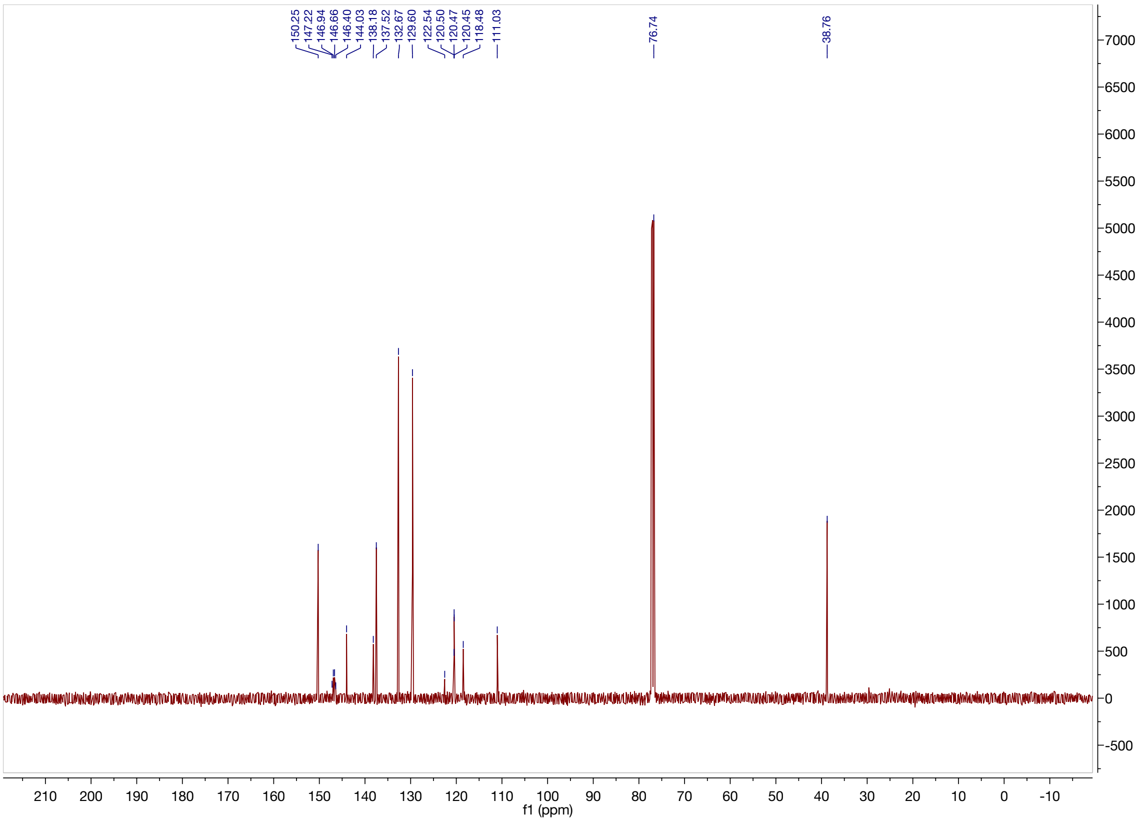
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(4-(hydroxymethyl)benzyl)benzonitrile (**3f**)



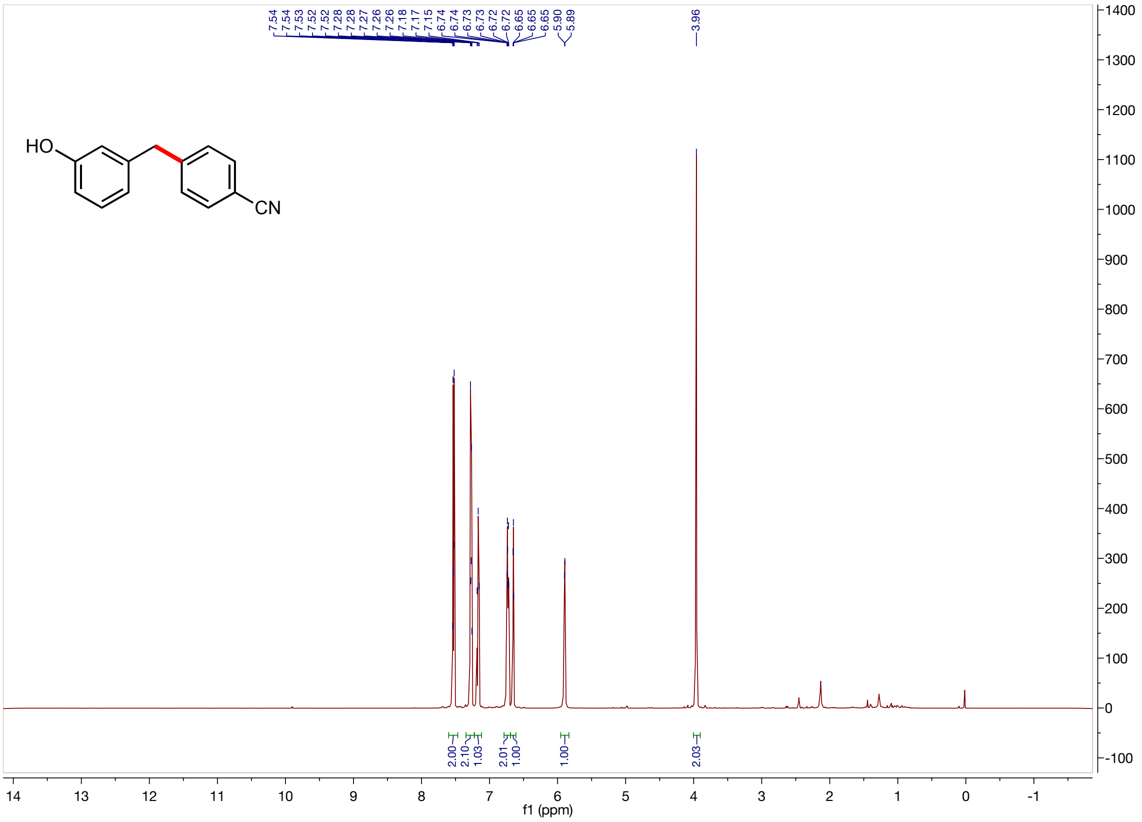
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-((6-(trifluoromethyl)pyridin-3-yl)methyl)benzonitrile (**3g**)



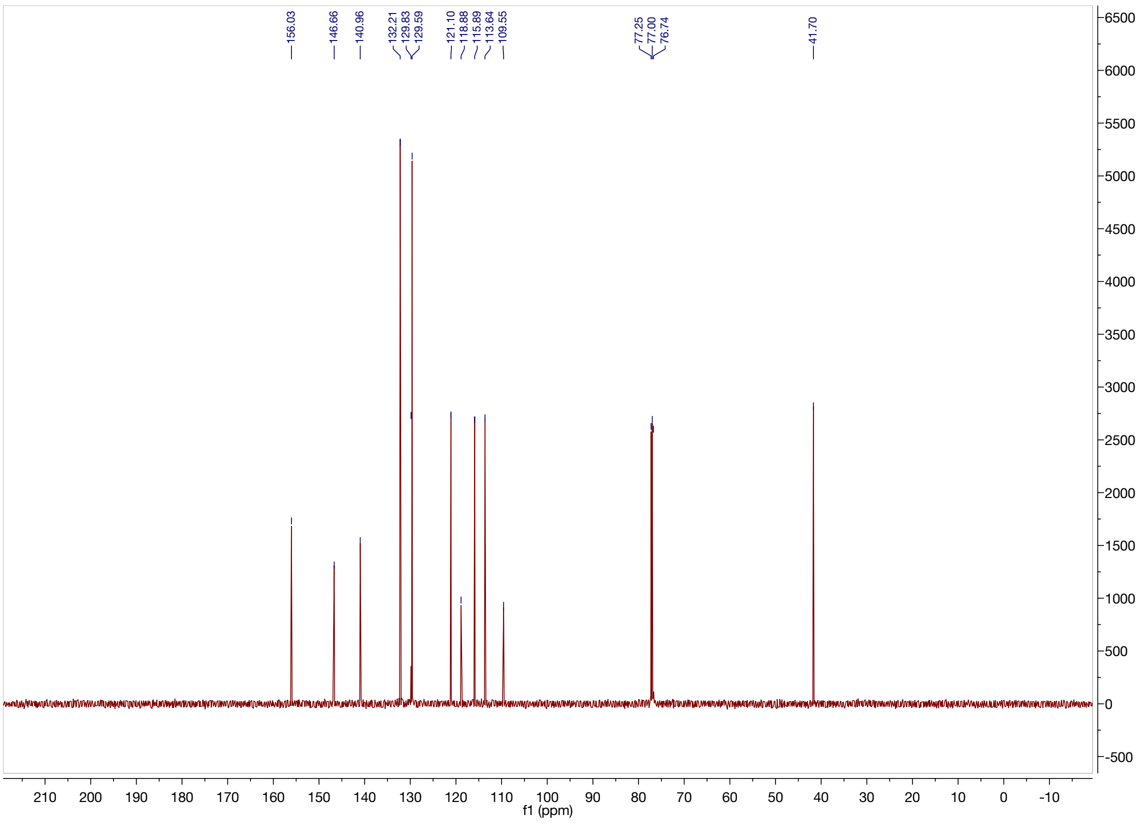
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 4-((6-(trifluoromethyl)pyridin-3-yl)methyl)benzonitrile (**3g**)



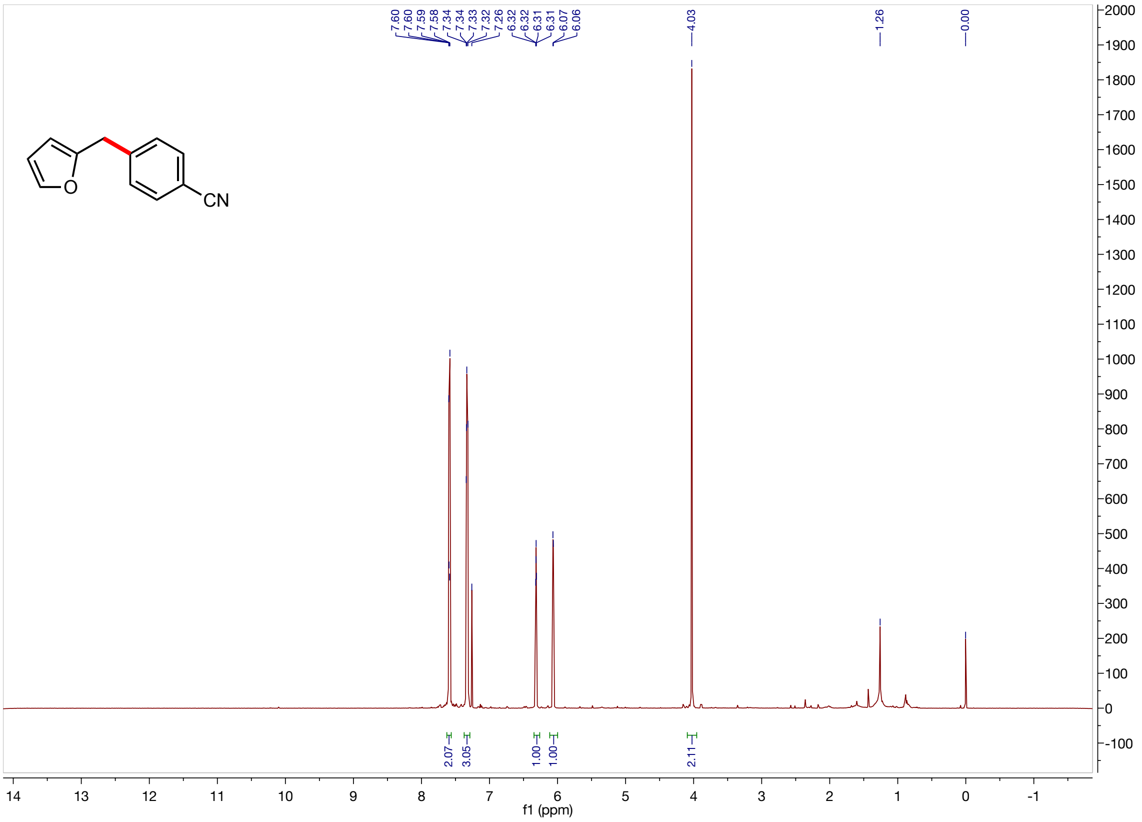
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-((6-(trifluoromethyl)pyridin-3-yl)methyl)benzonitrile (**3g**)



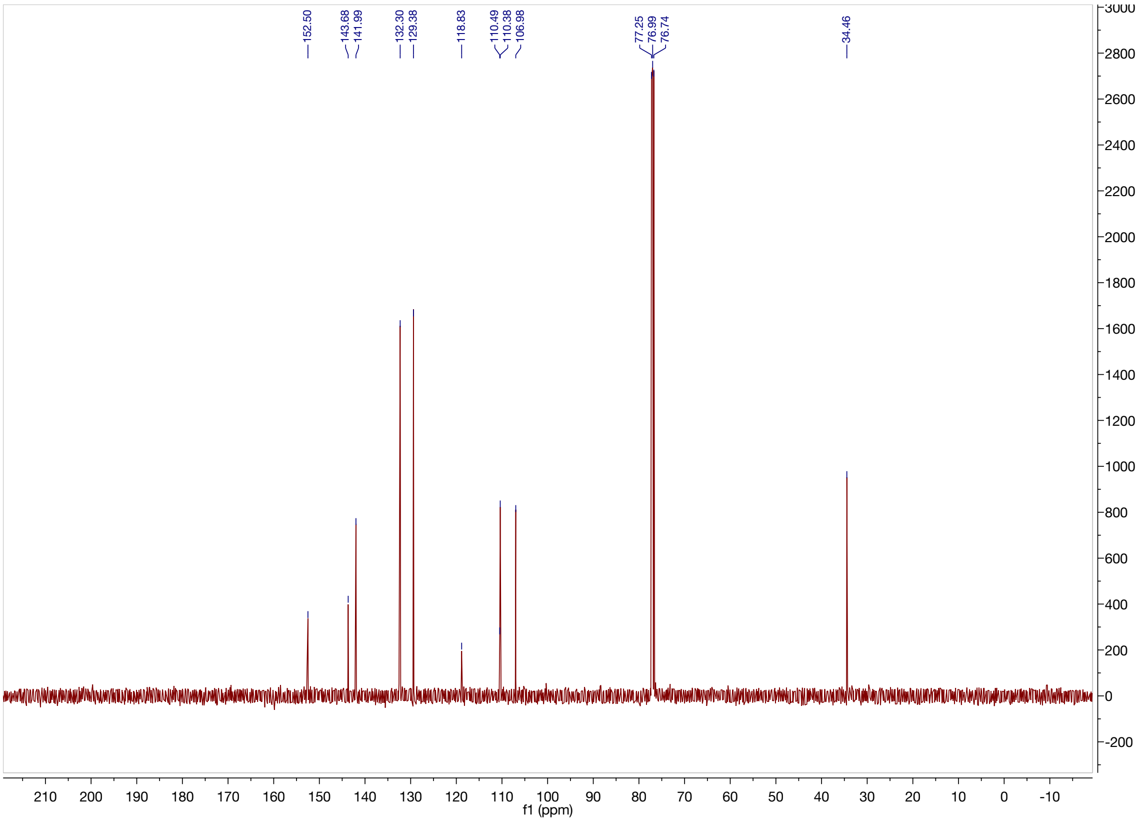
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(3-hydroxybenzyl)benzonitrile (**3h**)



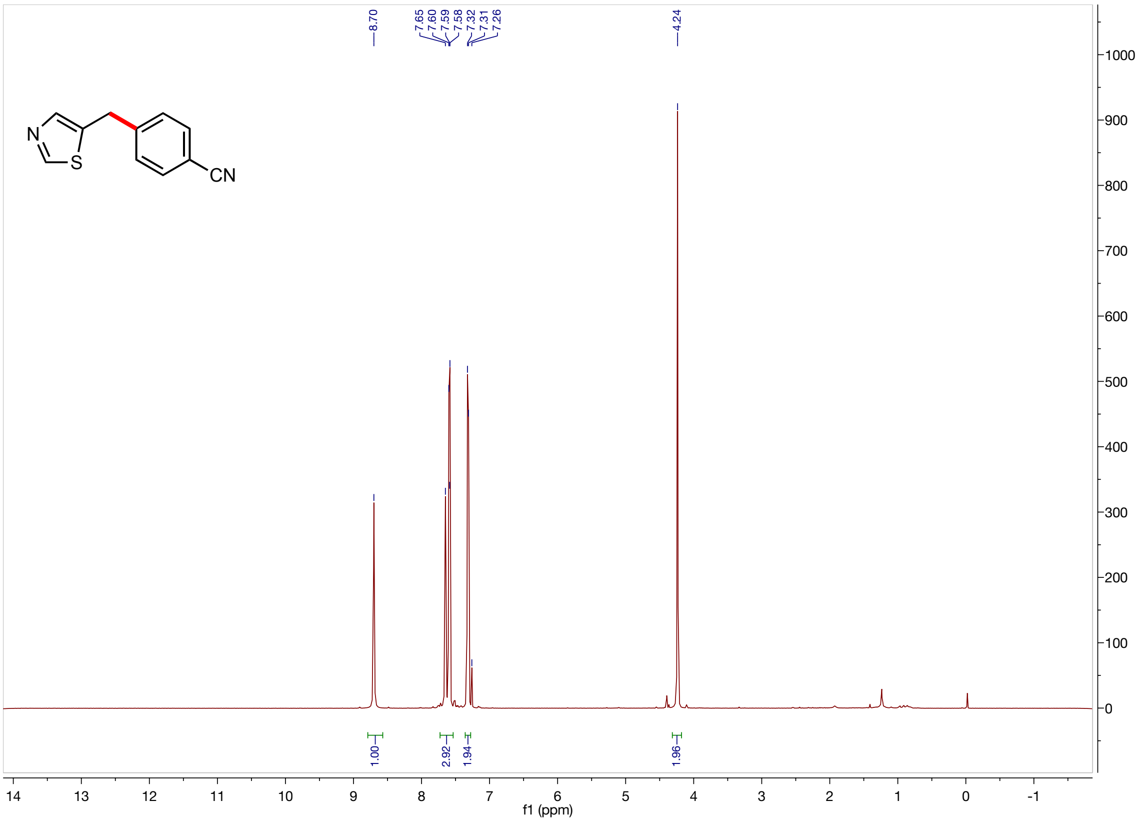
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(3-hydroxybenzyl)benzonitrile (**3h**)



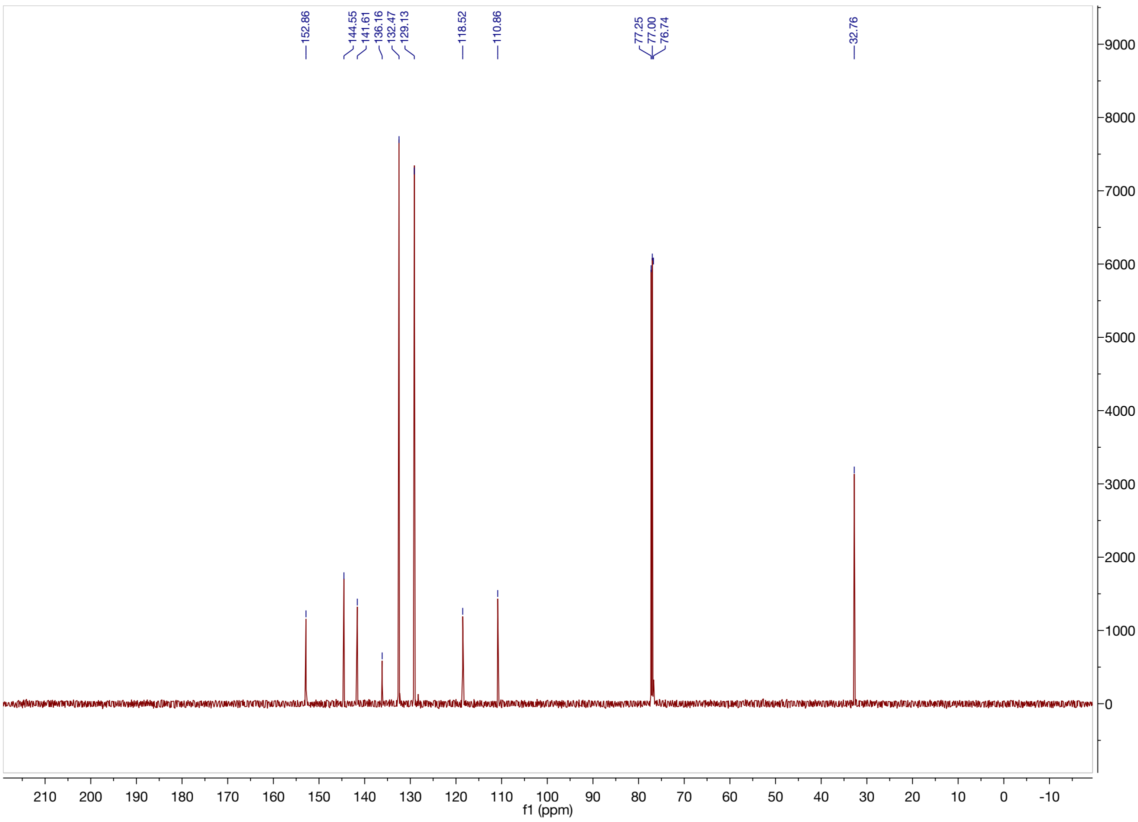
[1]H NMR ($CDCl_3$, 500.4 MHz) of 4-(furan-2-ylmethyl)benzonitrile (**3j**)



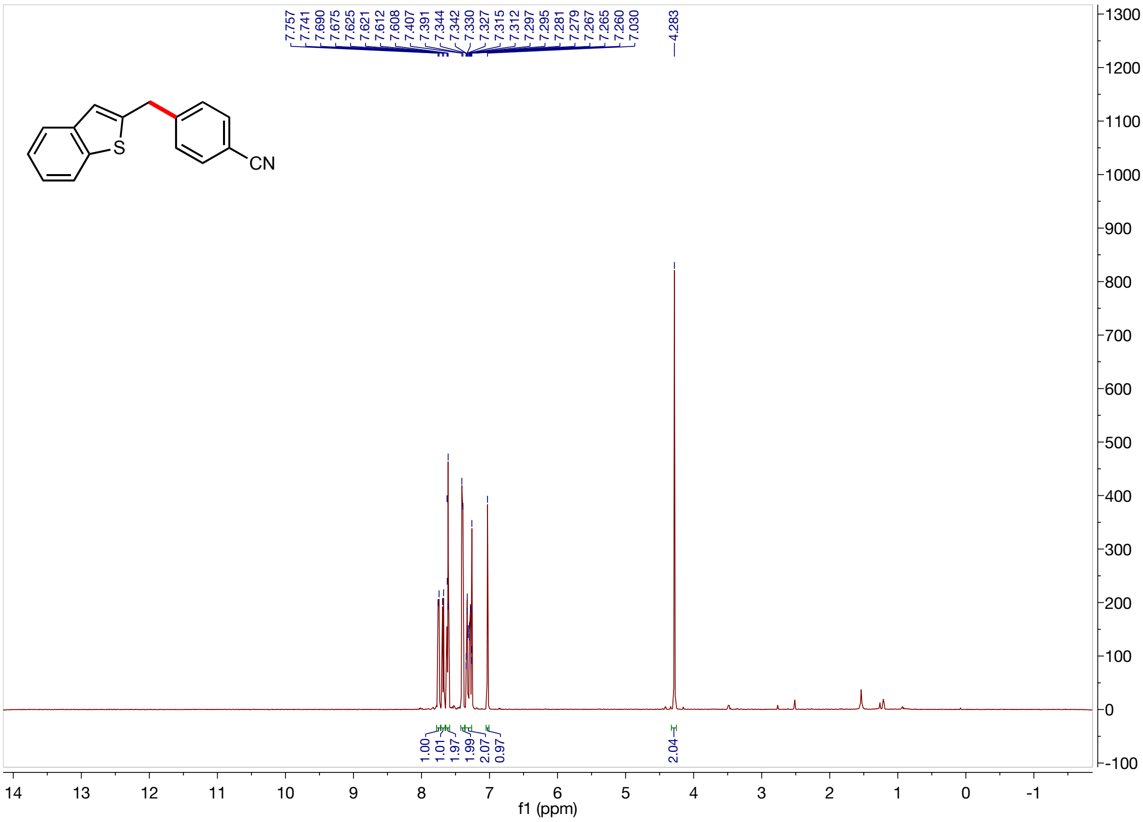
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of 4-(furan-2-ylmethyl)benzonitrile (**3j**)



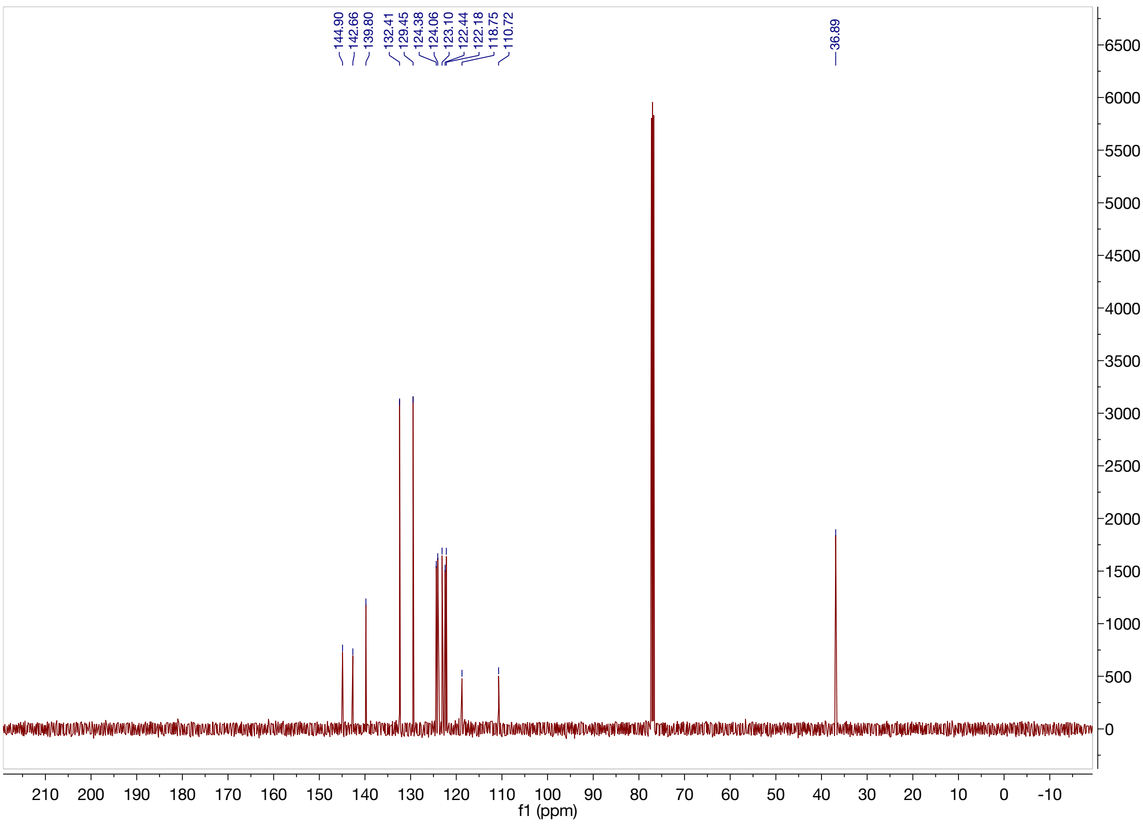
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(thiazol-5-ylmethyl)benzonitrile (**3k**)



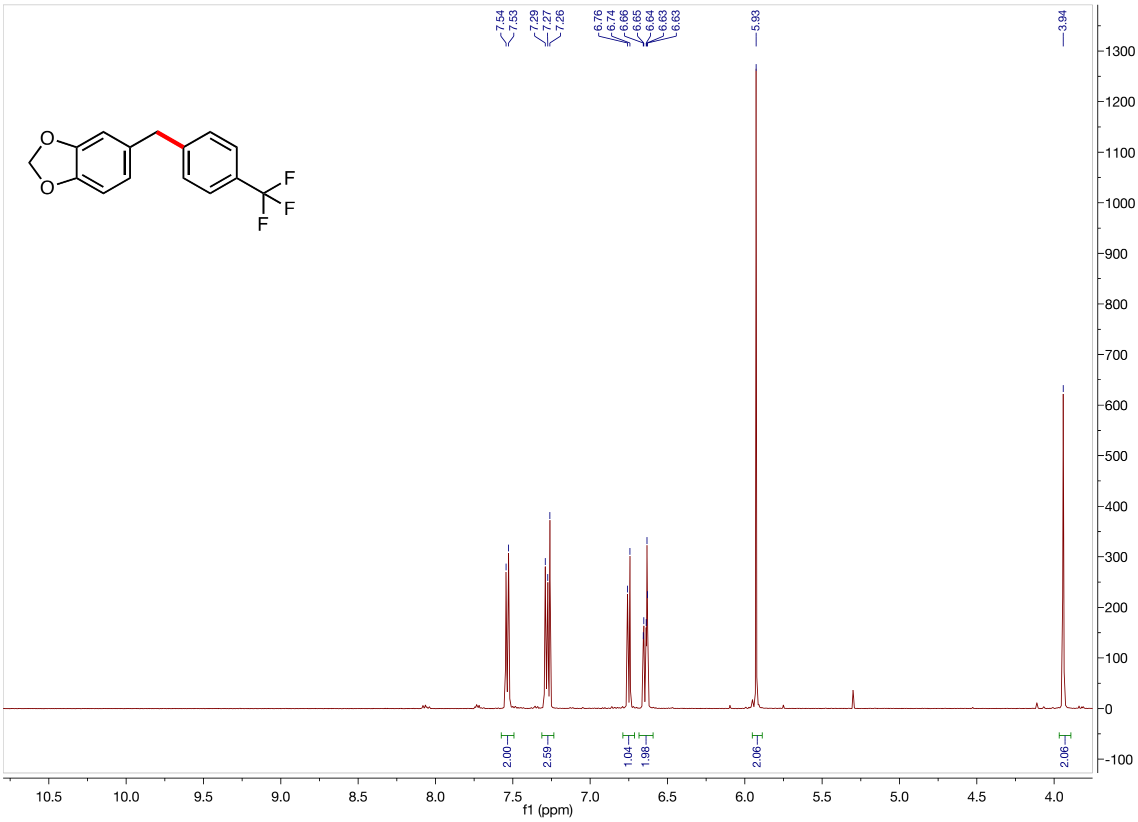
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(thiazol-5-ylmethyl)benzonitrile (**3k**)



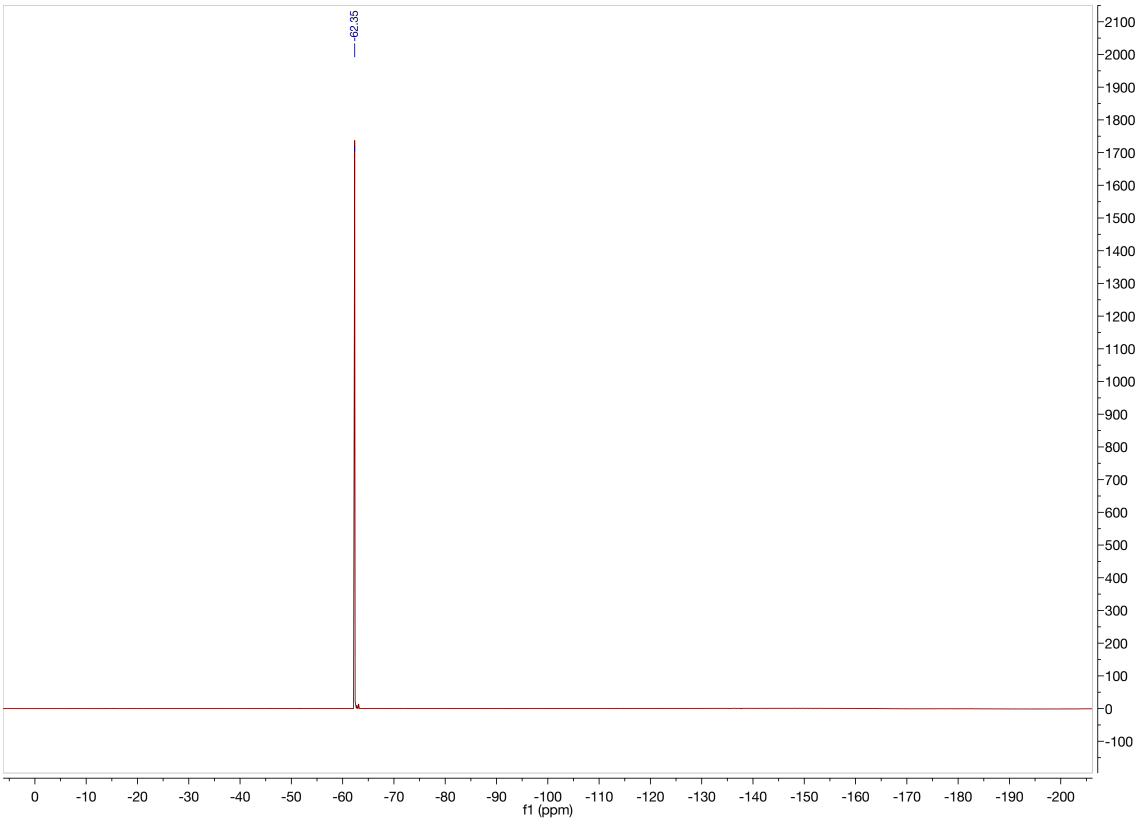
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(benzo[*b*]thiophen-2-ylmethyl)benzonitrile (**3l**)



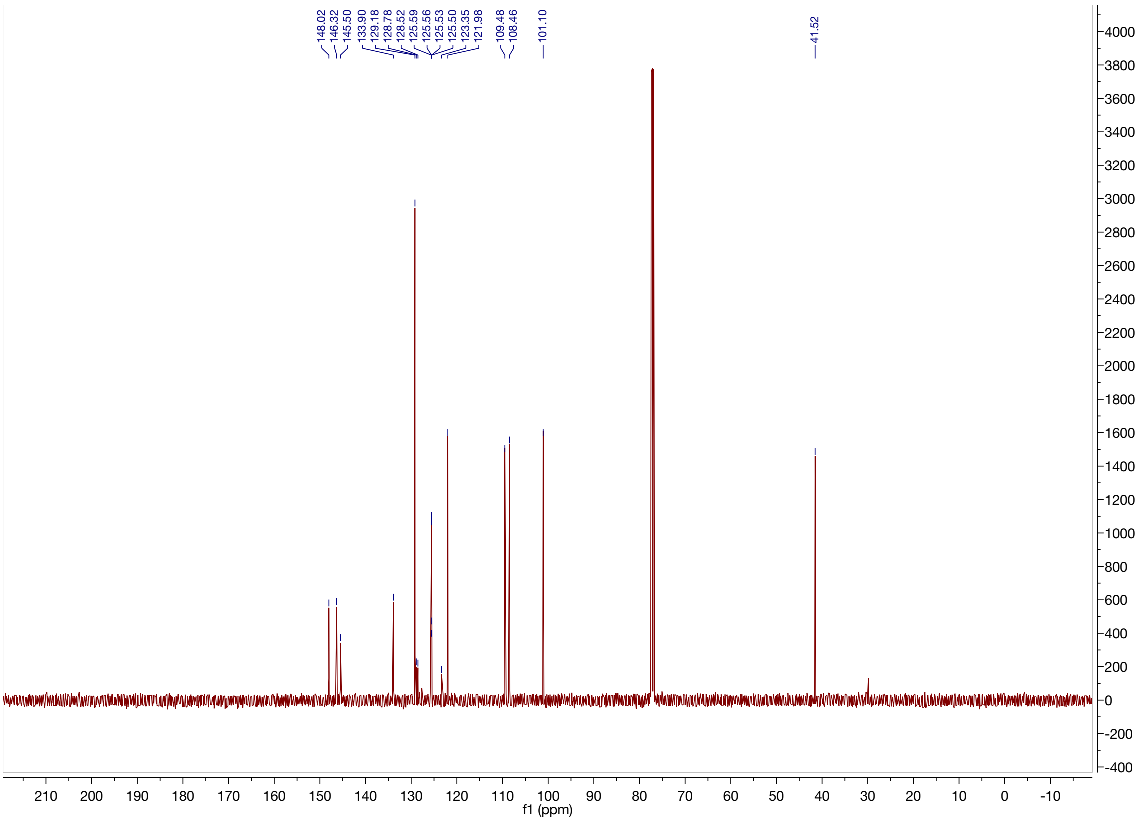
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(benzo[*b*]thiophen-2-ylmethyl)benzonitrile (**3l**)



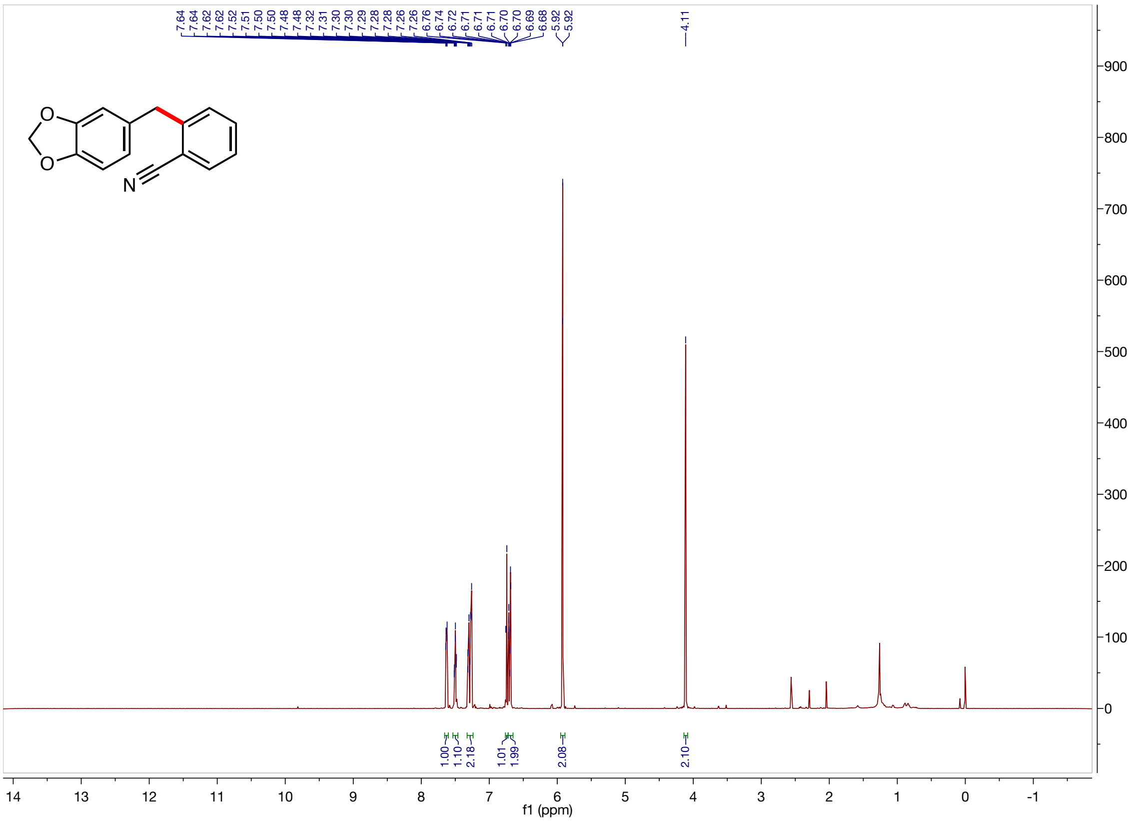
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 5-(4-(trifluoromethyl)benzyl)benzo[d][1,3]dioxole (**3m**)



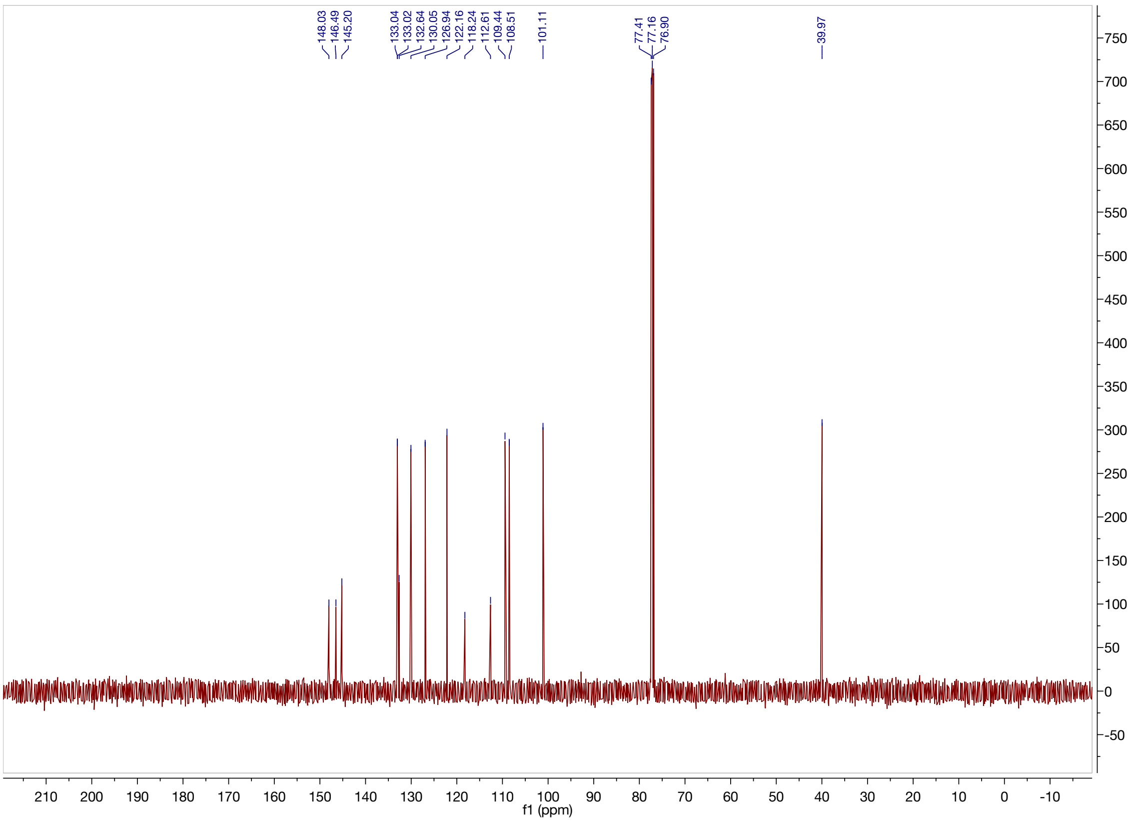
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 5-(4-(trifluoromethyl)benzyl)benzo[d][1,3]dioxole (**3m**)



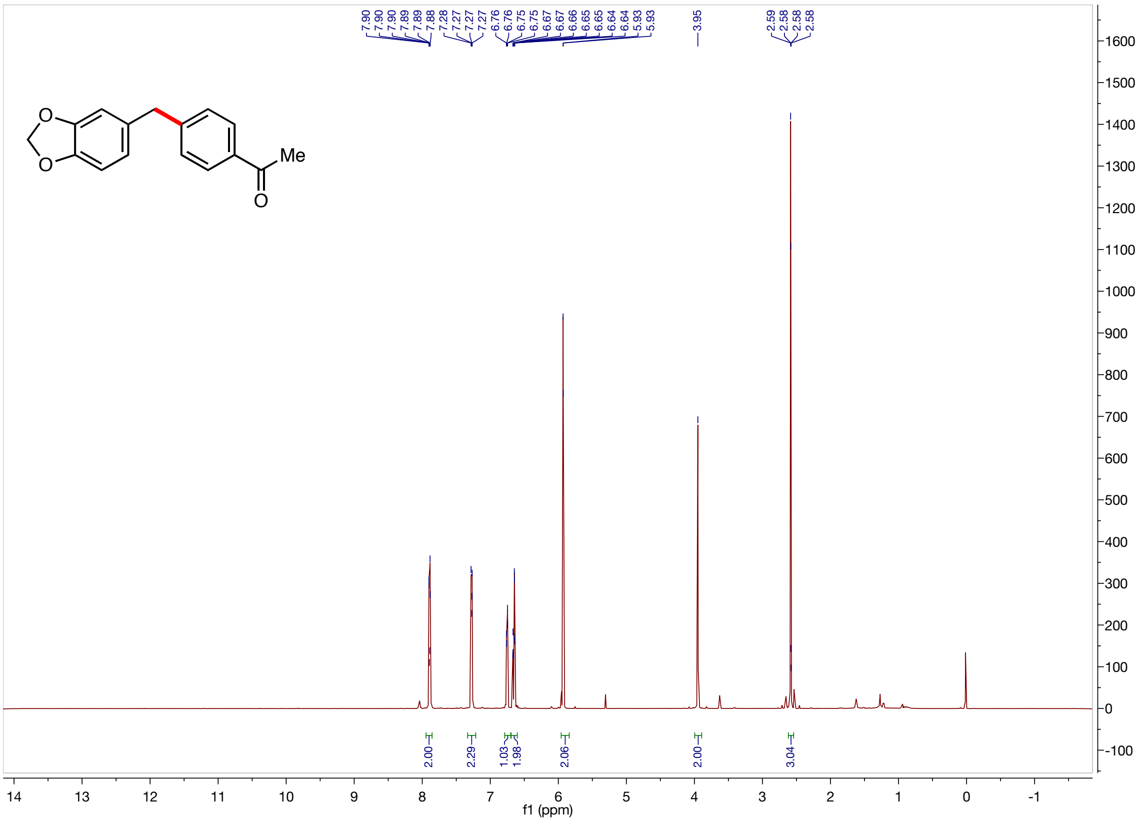
$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz) of 5-(4-(trifluoromethyl)benzyl)benzo[d][1,3]dioxole (**3m**)



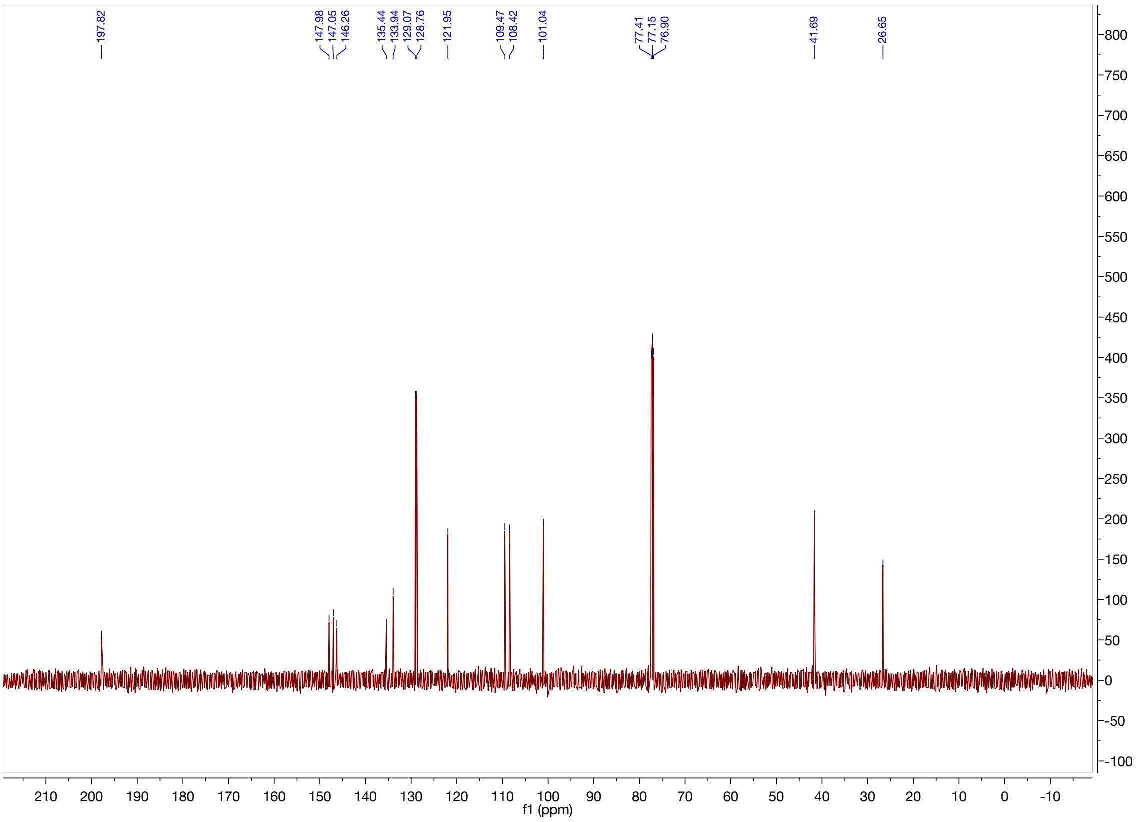
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (**3n**)



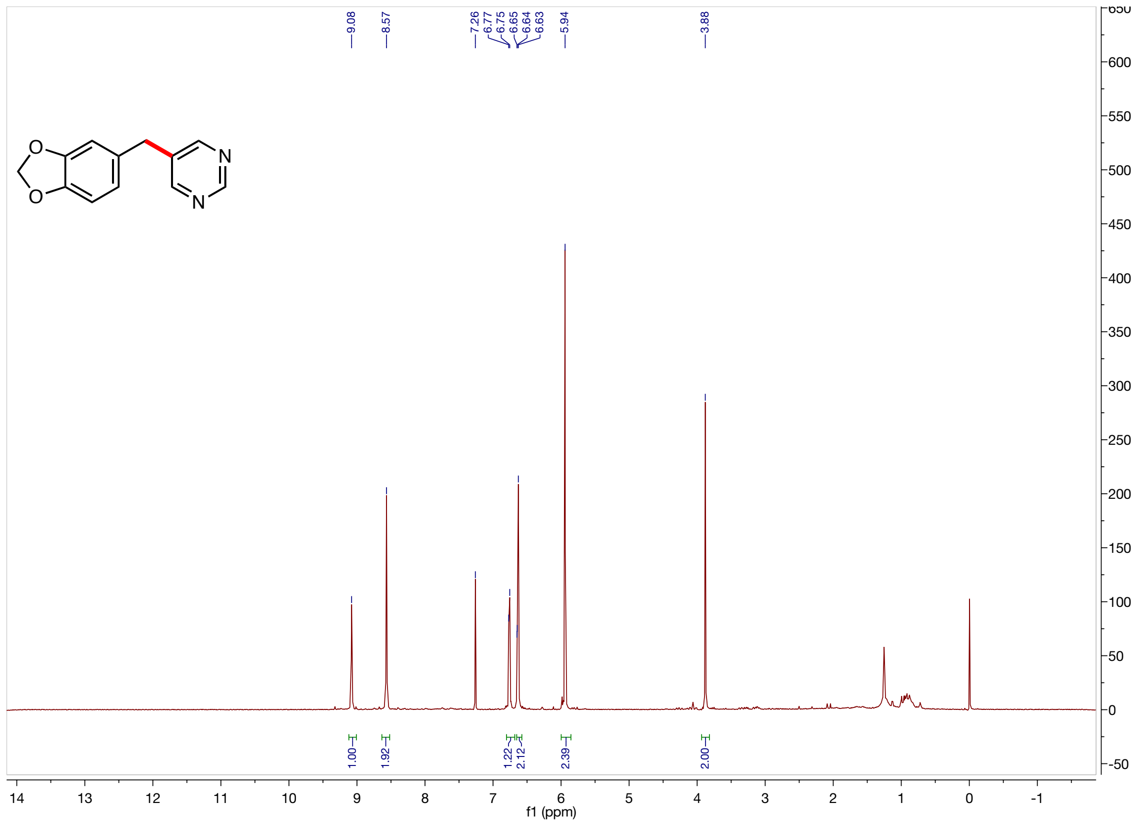
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (**3n**)



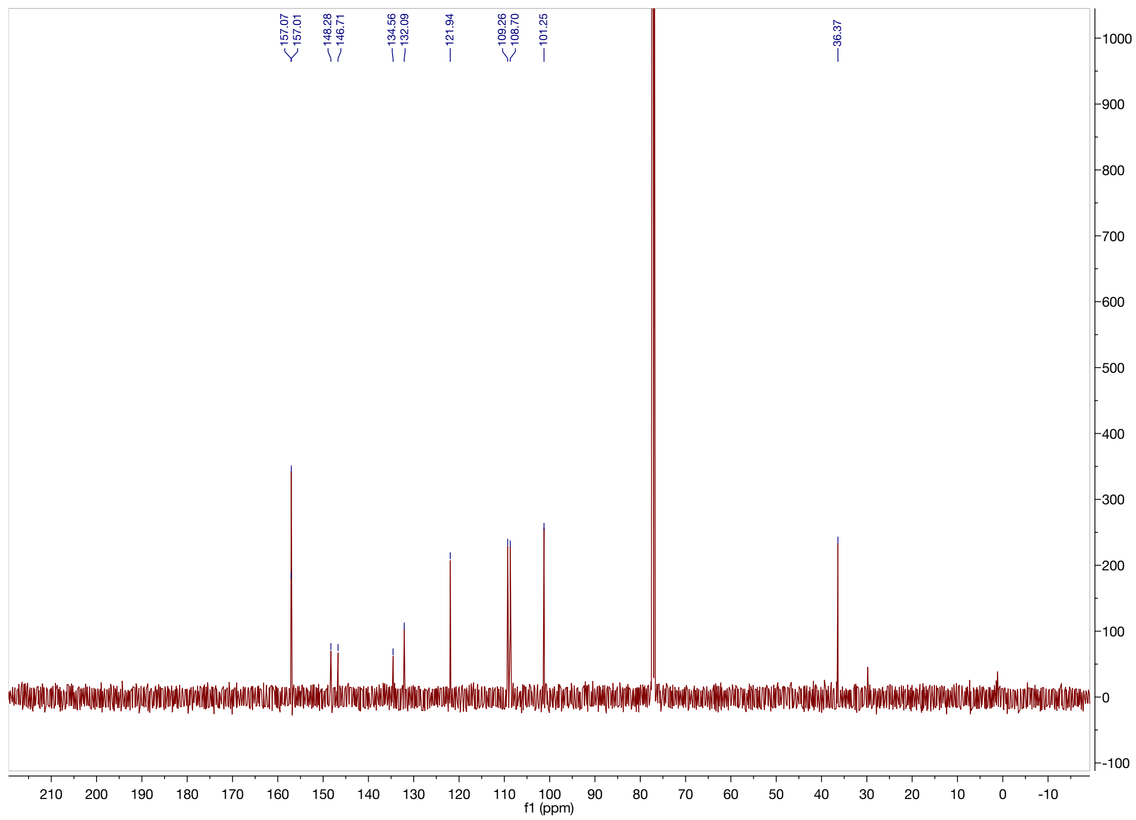
[1]H NMR ($CDCl_3$, 500.4 MHz) of 1-(4-(benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)ethanone (**3o**)



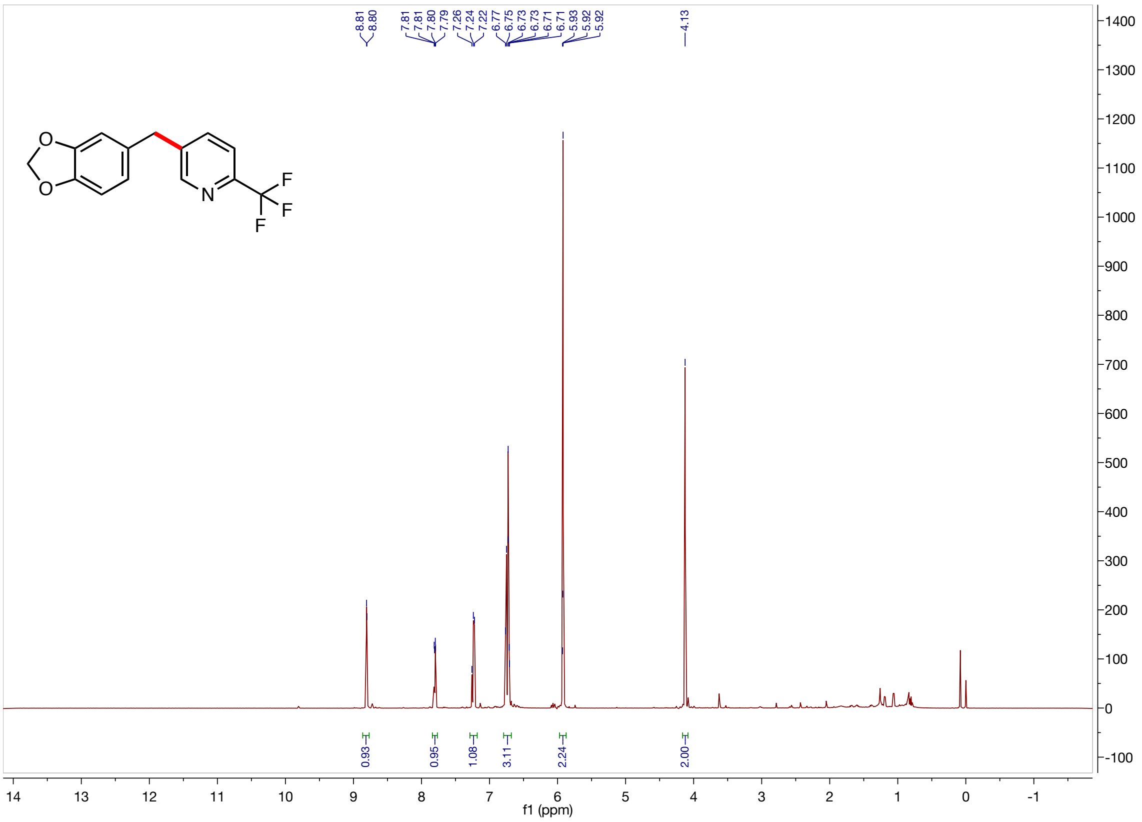
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)ethanone (**3o**)



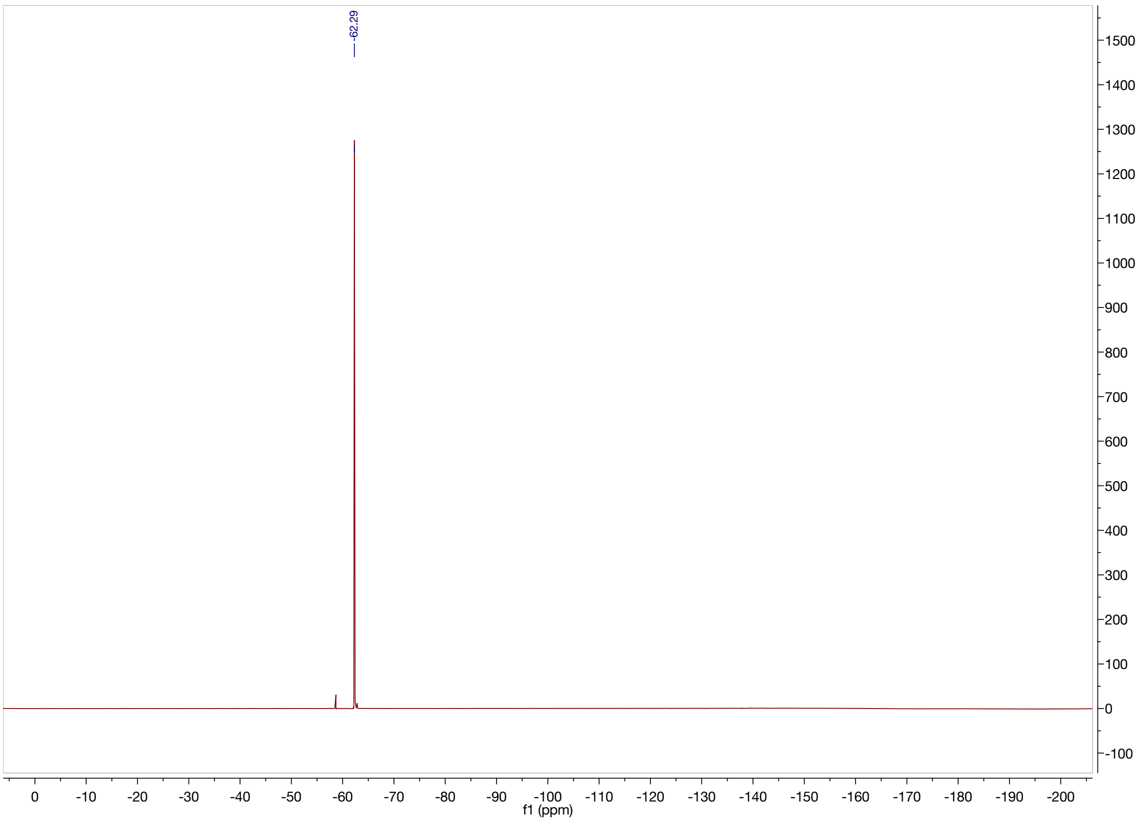
[1]H NMR ($CDCl_3$, 500.4 MHz) of 5-(benzo[d][1,3]dioxol-5-ylmethyl)pyrimidine (**3q**)



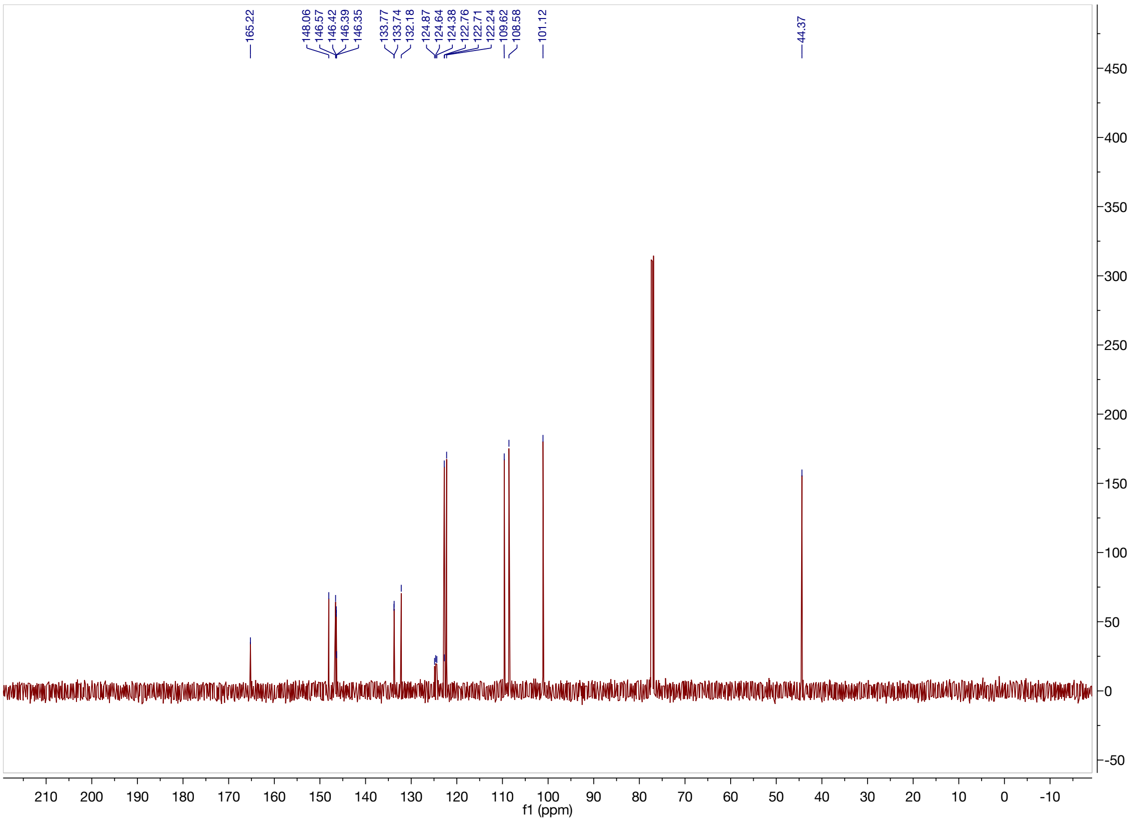
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of 5-(benzo[d][1,3]dioxol-5-ylmethyl)pyrimidine (**3q**)



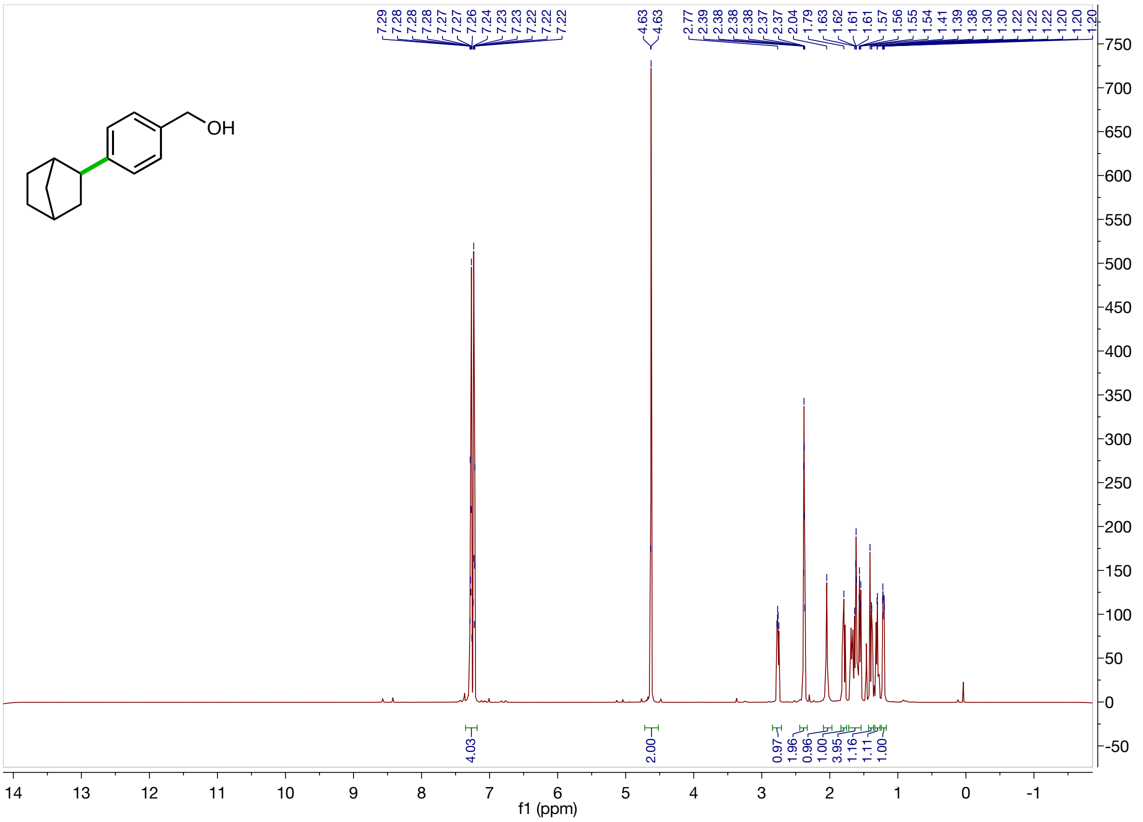
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-5-(trifluoromethyl)pyridine (**3r**)



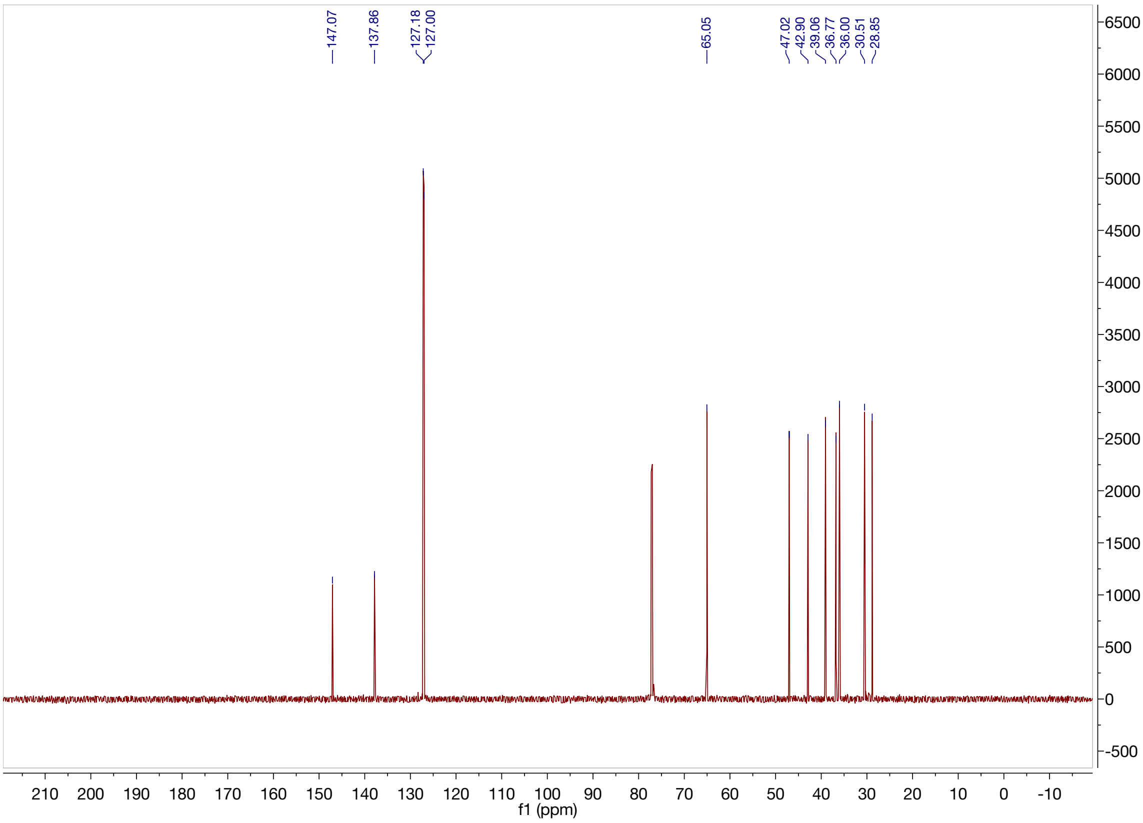
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-5-(trifluoromethyl)pyridine (**3r**)



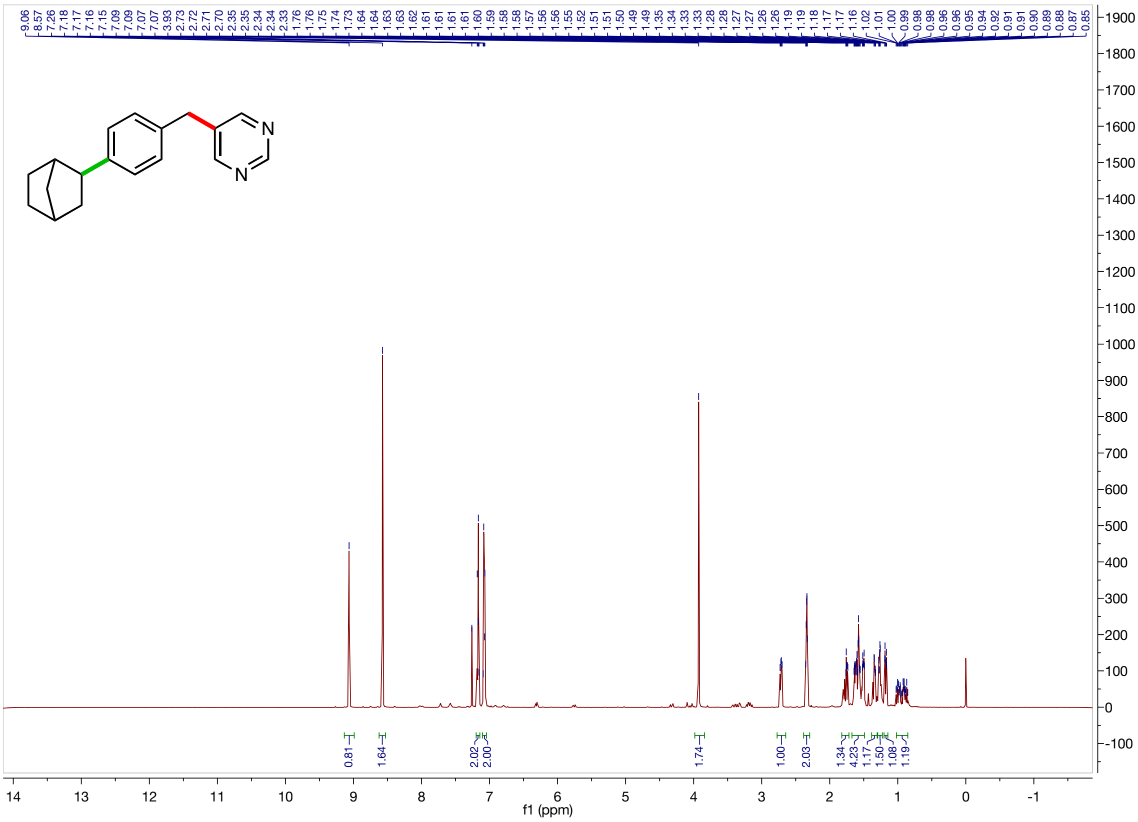
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-5-(trifluoromethyl)pyridine (**3r**)



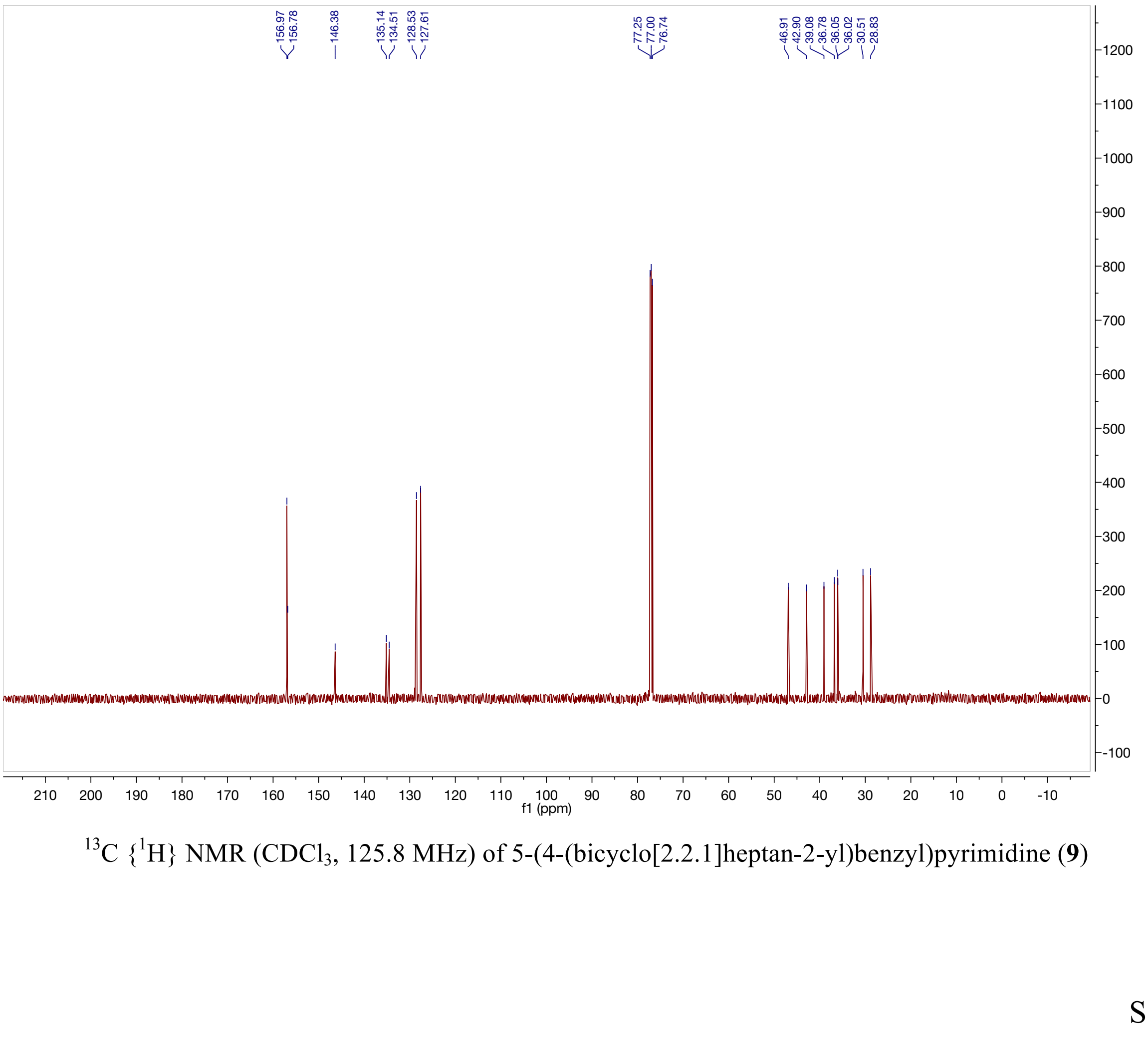
[1]H NMR ($CDCl_3$, 500.4 MHz) of (4-(bicyclo[2.2.1]heptan-2-yl)phenyl)methanol (**8**)



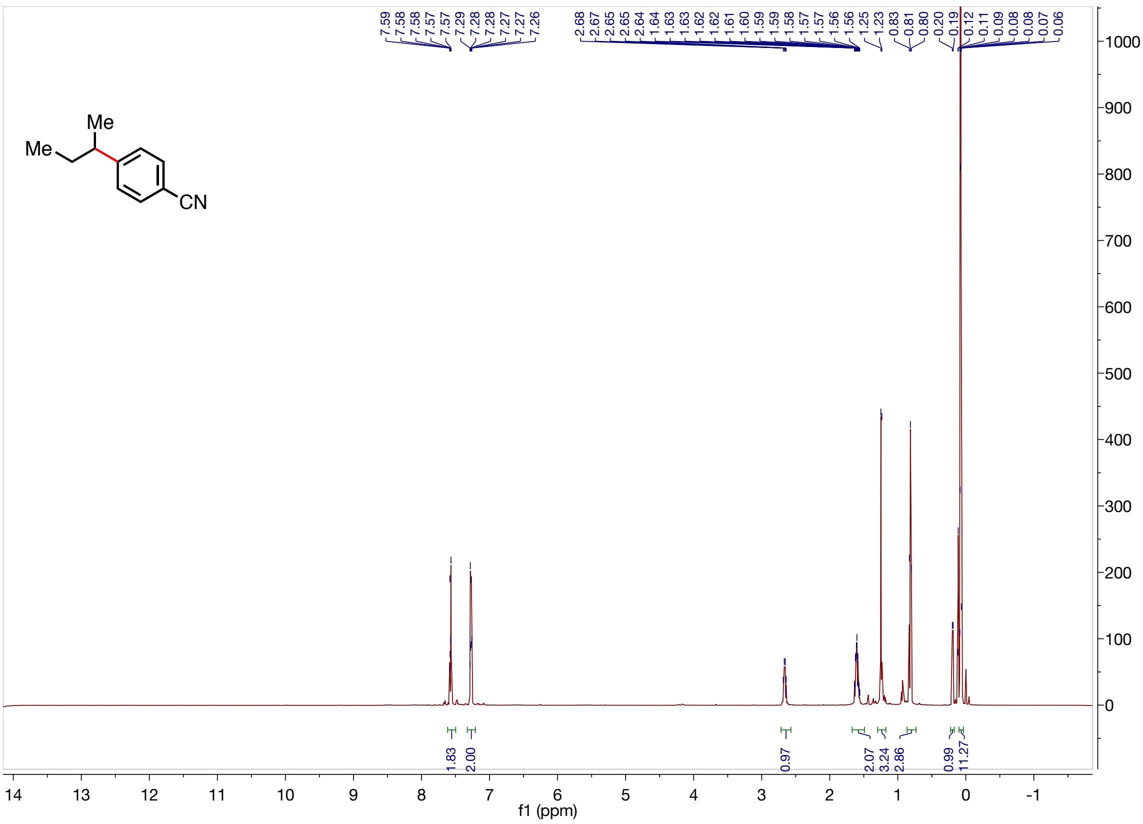
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of (4-(bicyclo[2.2.1]heptan-2-yl)phenyl)methanol (**8**)



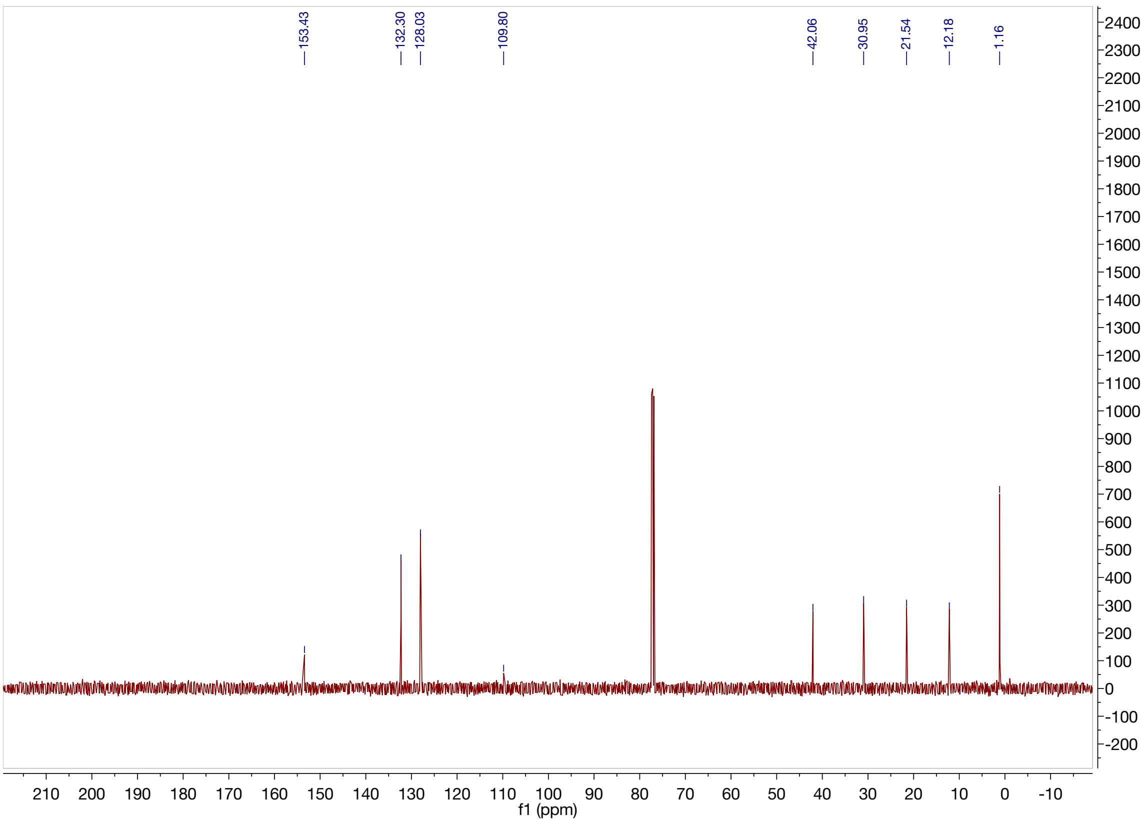
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 5-(4-(bicyclo[2.2.1]heptan-2-yl)benzyl)pyrimidine (**9**)



^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 5-(4-(bicyclo[2.2.1]heptan-2-yl)benzyl)pyrimidine (**9**)



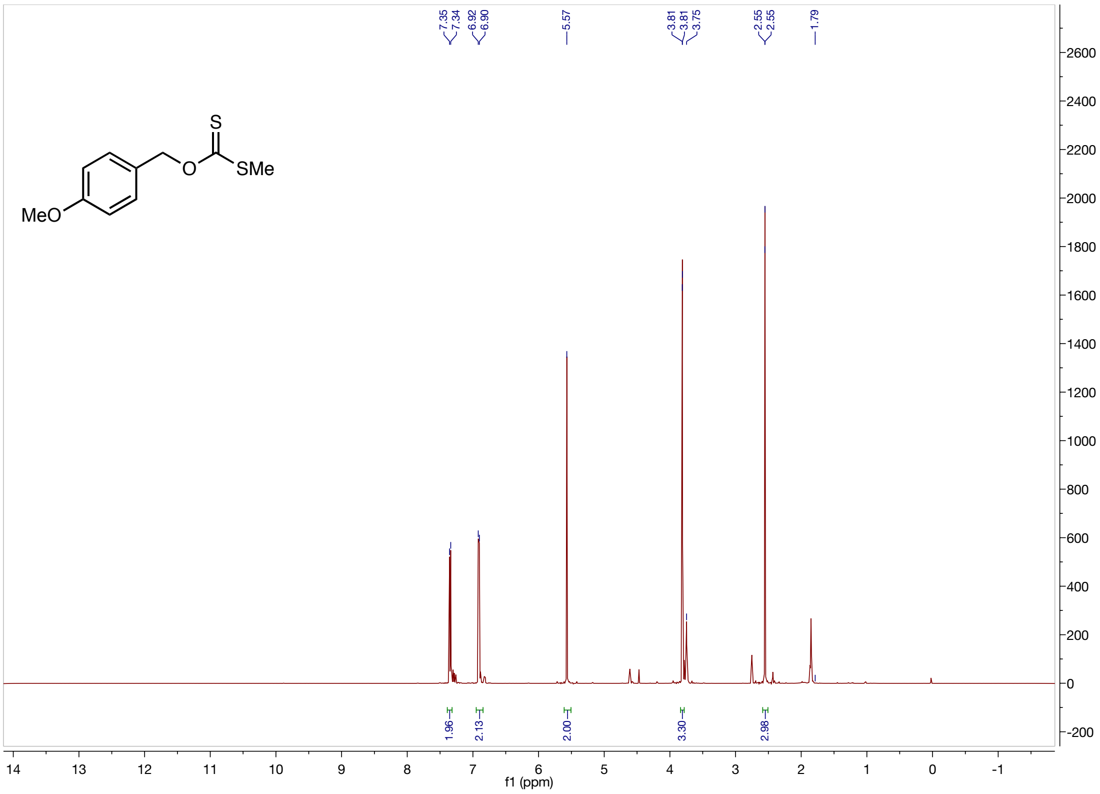
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(*sec*)butylbenzonitrile (**10**)



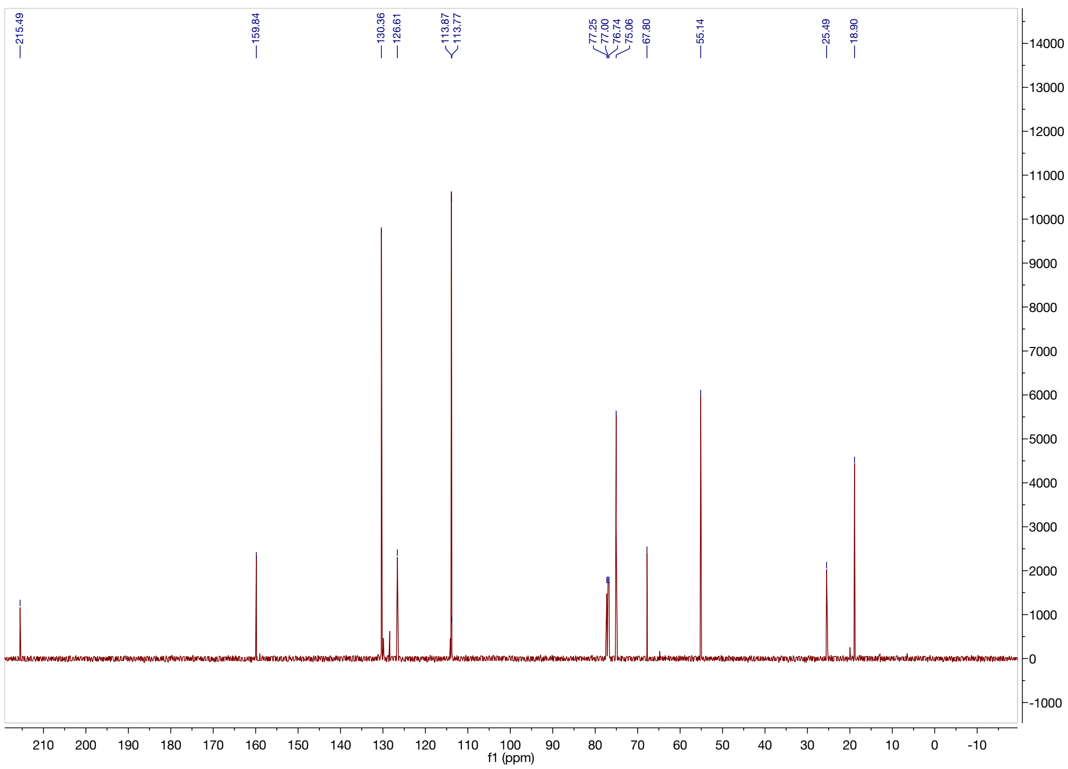
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(*sec*)butylbenzonitrile (**10**)

Spectral Data for Xanthates and Additional Compounds

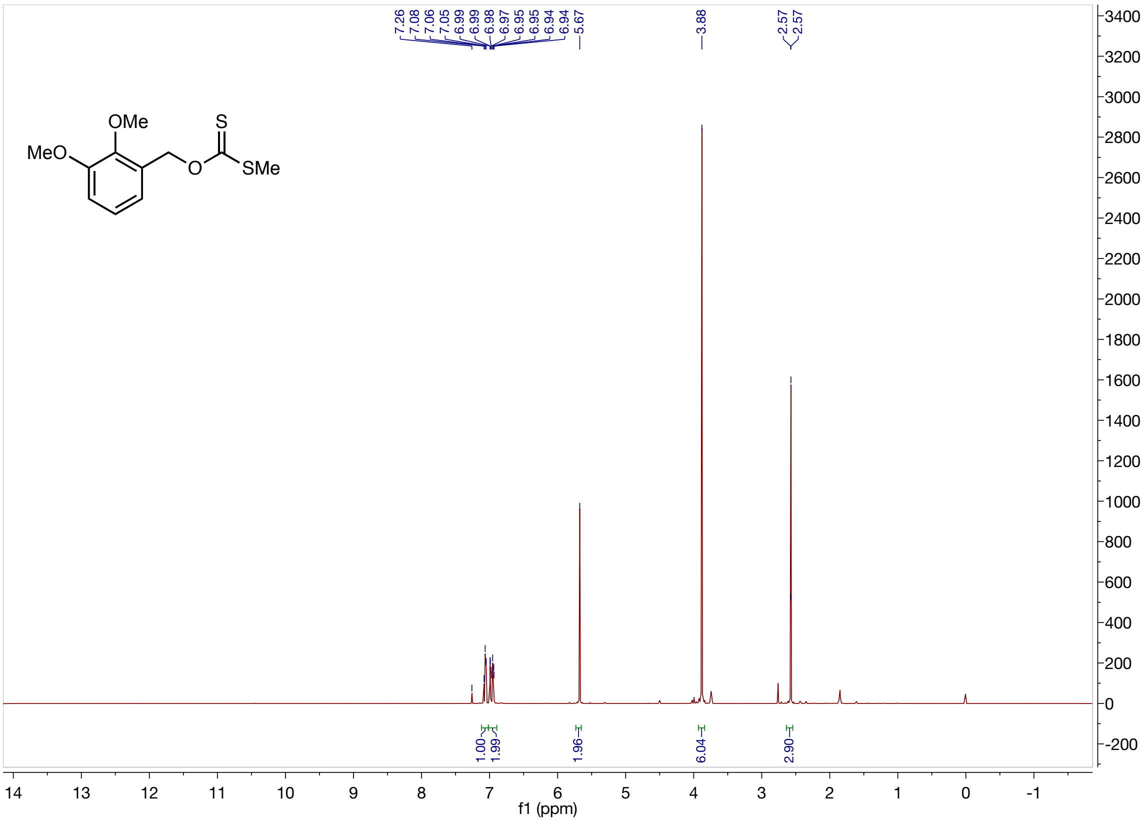
* Xanthates were prepared and isolated crude, and only purified in specific cases (see above)



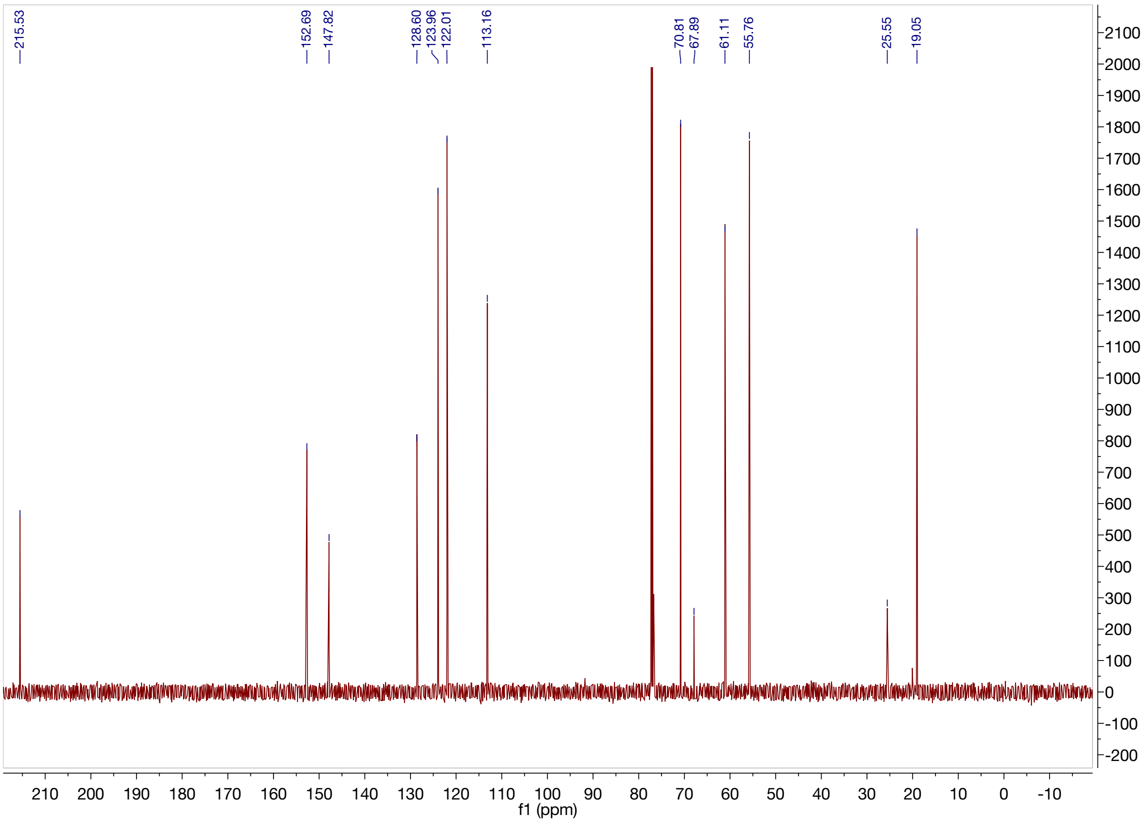
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(4-methoxybenzyl) *S*-methyl carbonodithioate (**S1**)



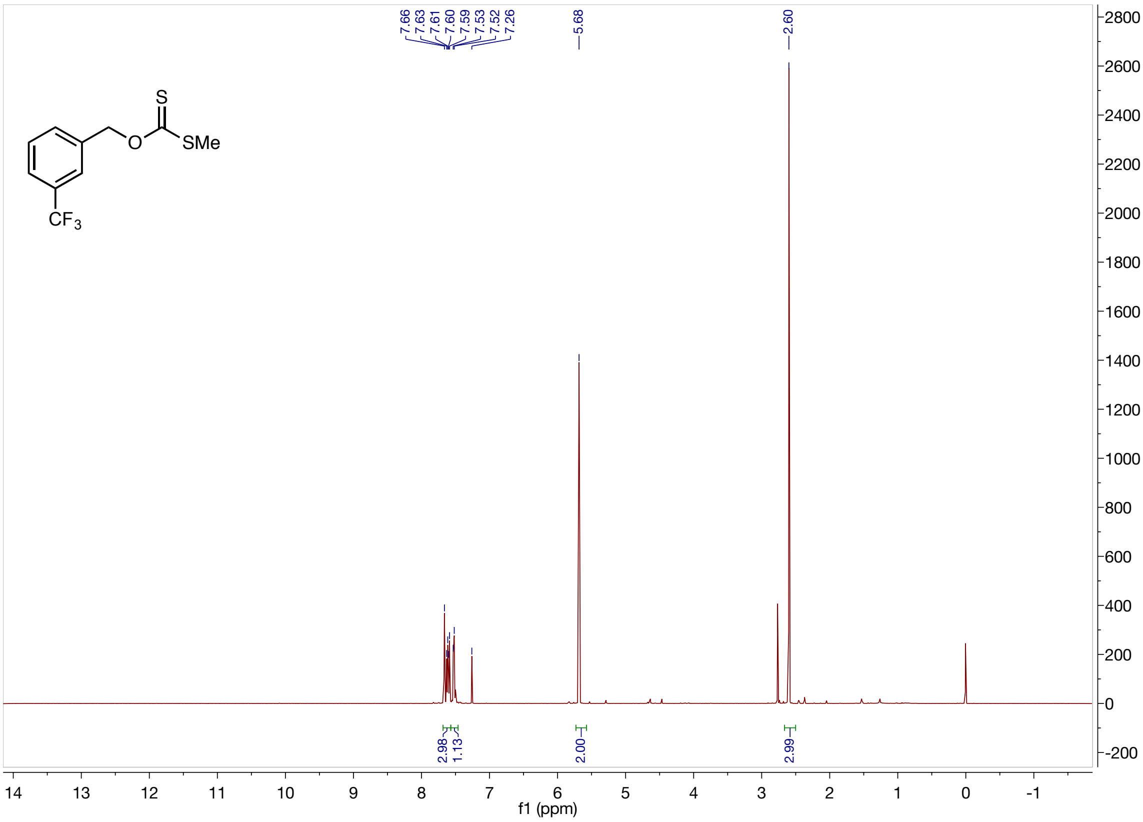
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(4-methoxybenzyl) *S*-methyl carbonodithioate (**S1**)



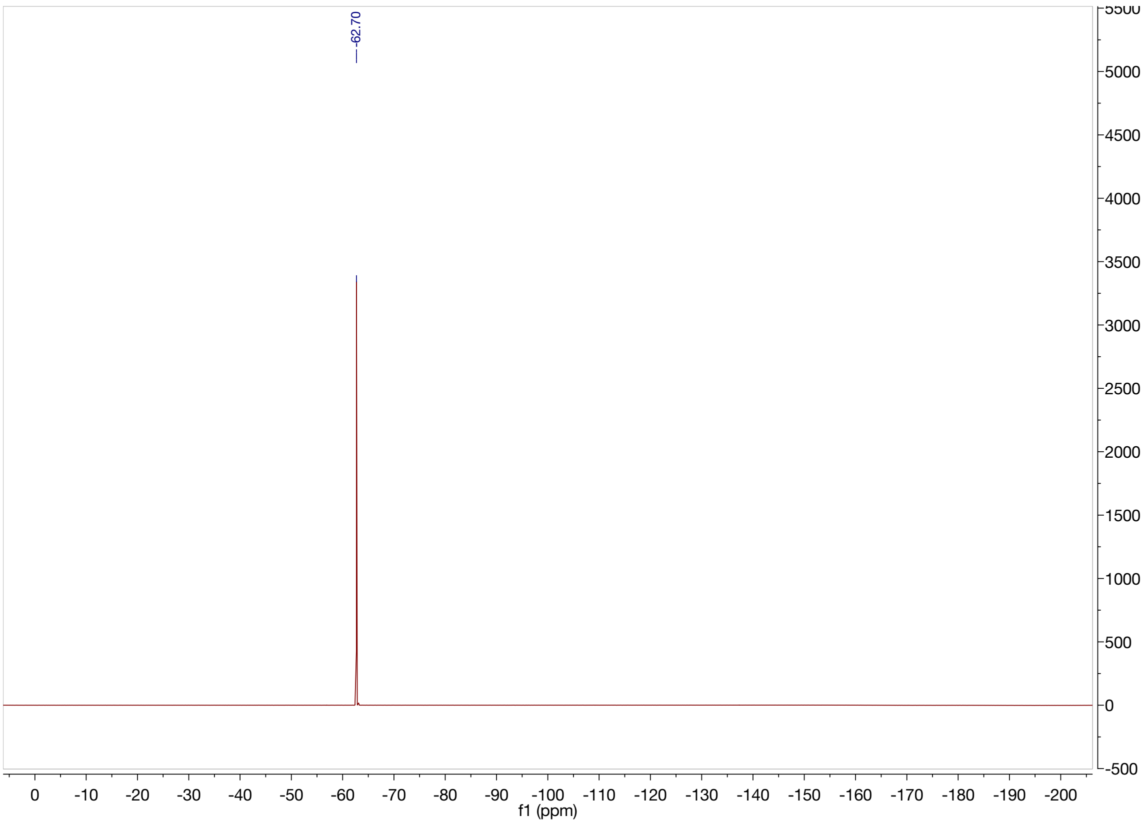
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(2,3-dimethoxybenzyl) *S*-methyl carbonodithioate (**S2**)



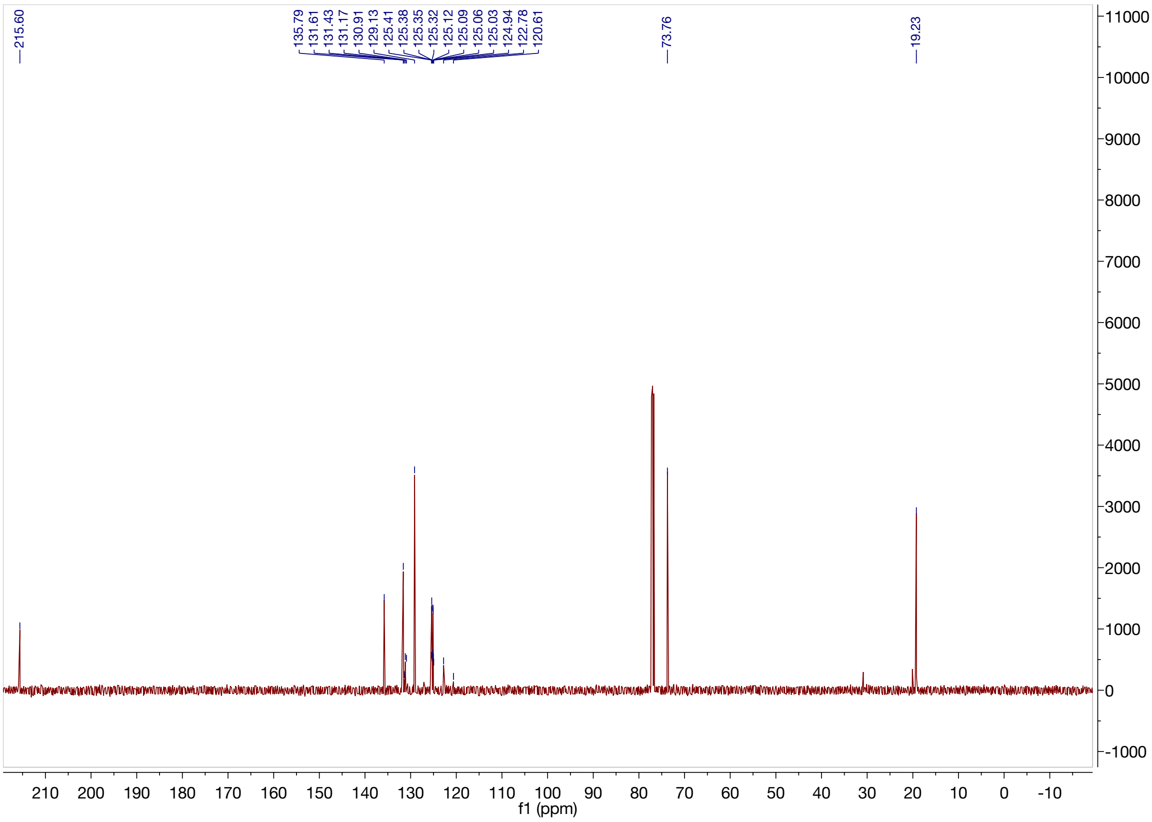
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(2,3-dimethoxybenzyl) *S*-methyl carbonodithioate (**S2**)



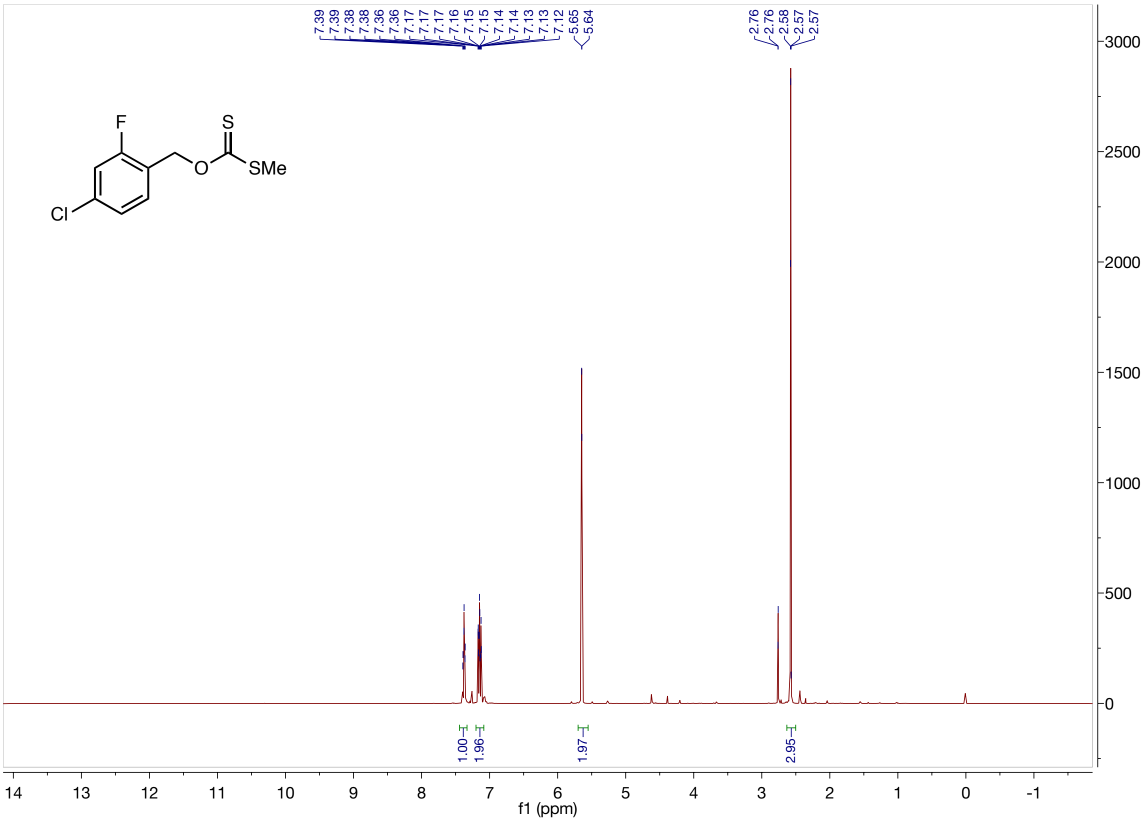
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *S*-methyl *O*-(3-(trifluoromethyl)benzyl) carbonodithioate (**S3**)



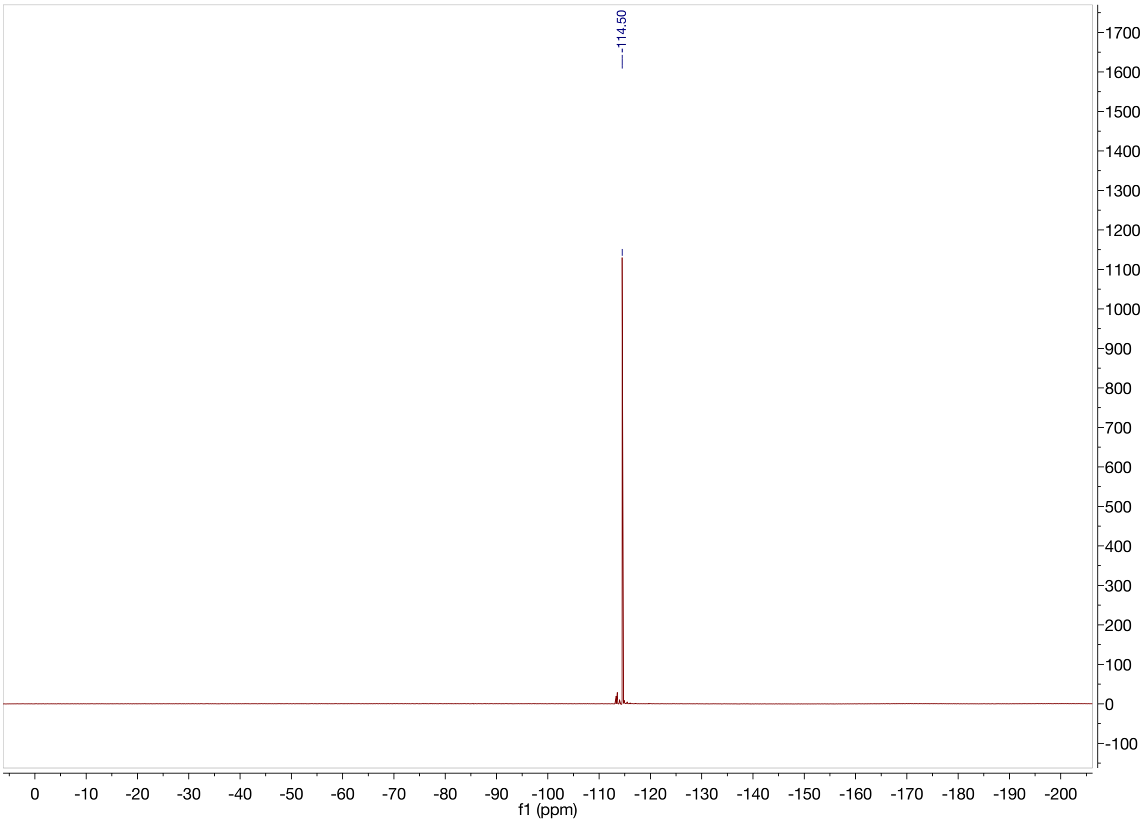
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of *S*-methyl *O*-(3-(trifluoromethyl)benzyl) carbonodithioate (**S3**)



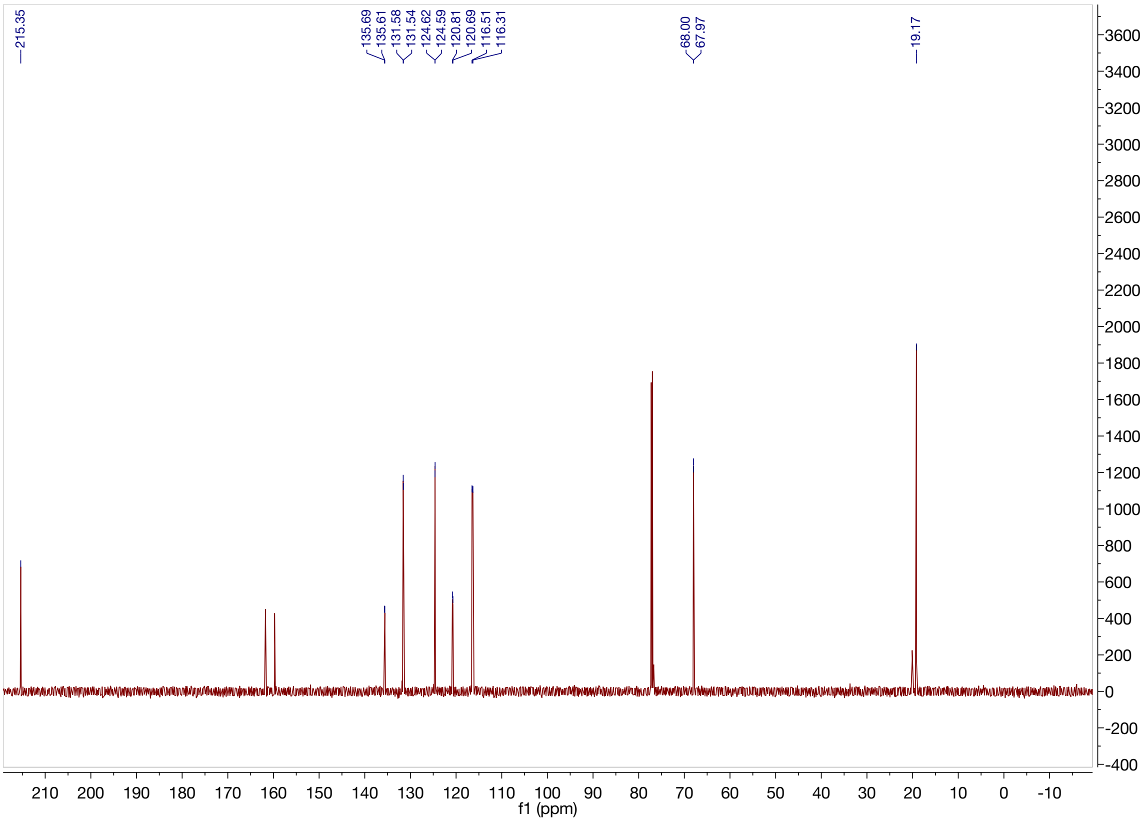
$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz) of *S*-methyl *O*-(3-(trifluoromethyl)benzyl) carbonodithioate (**S3**)



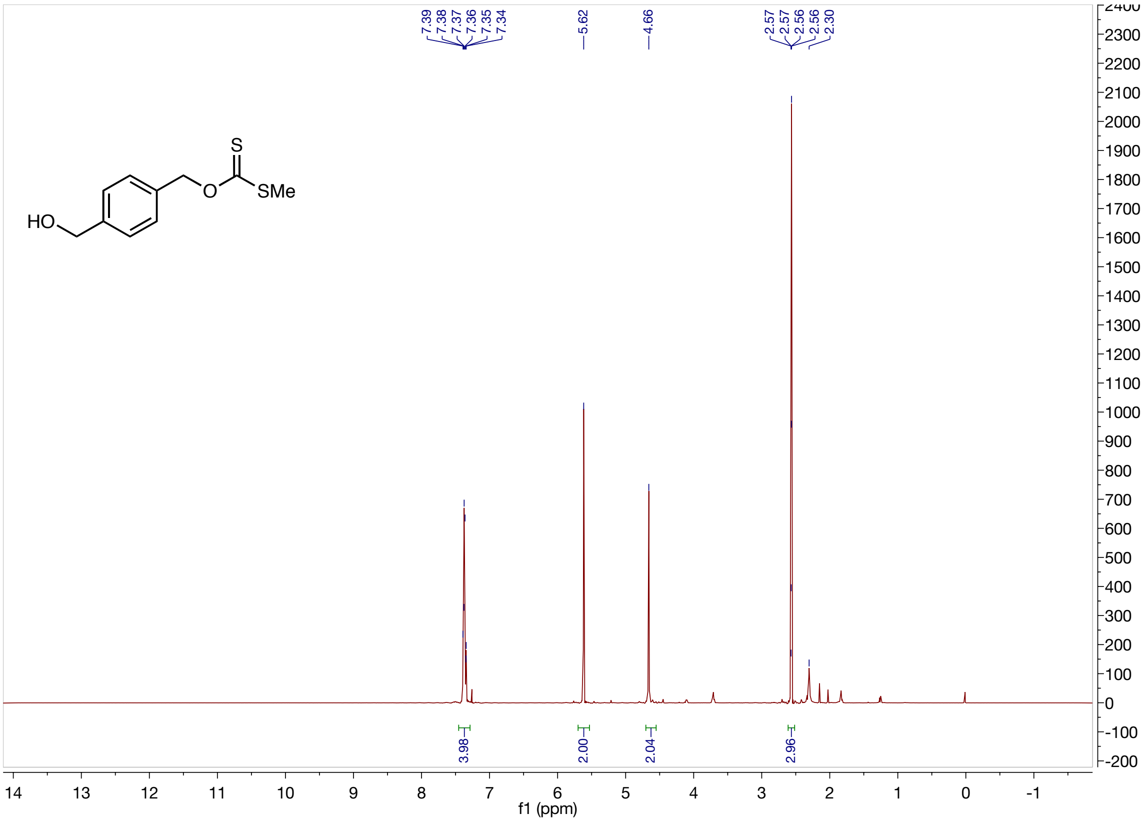
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(4-chloro-2-fluorobenzyl) *S*-methyl carbonodithioate (**S4**)



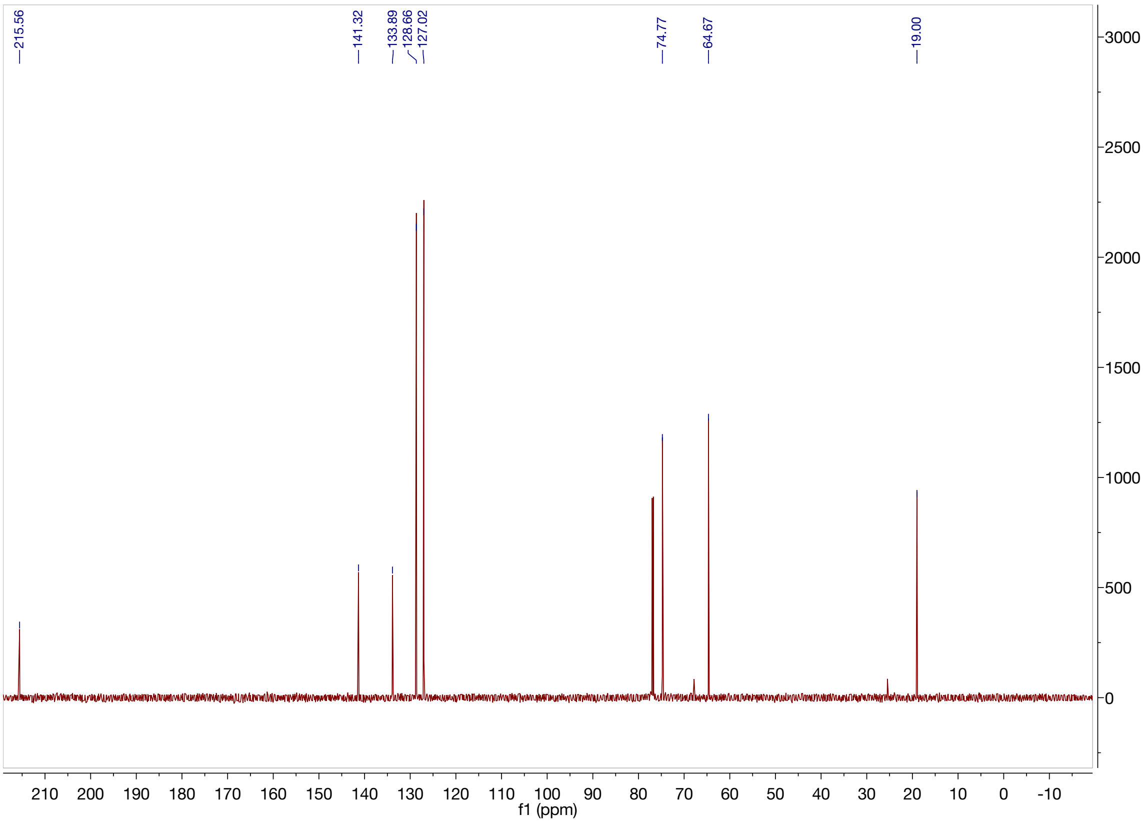
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of *O*-(4-chloro-2-fluorobenzyl) *S*-methyl carbonodithioate (**S4**)



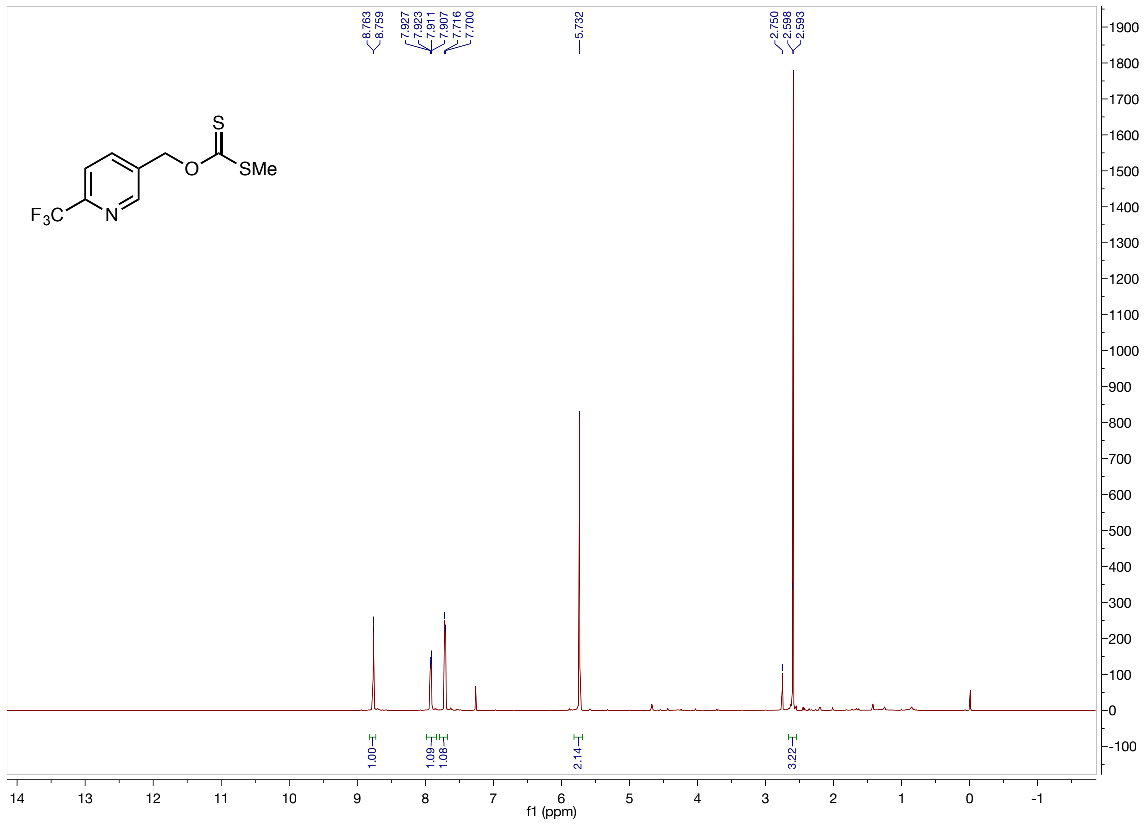
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(4-chloro-2-fluorobenzyl) *S*-methyl carbonodithioate (**S4**)



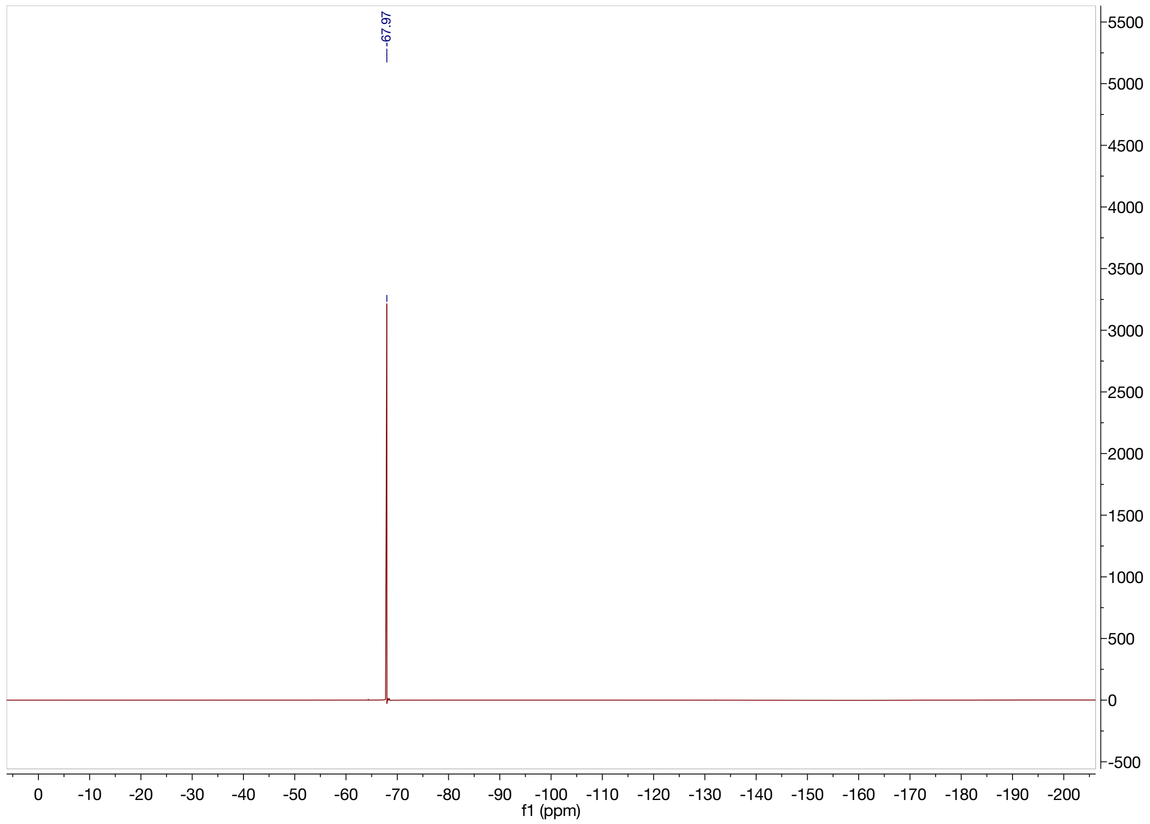
[1]H NMR ($CDCl_3$, 500.4 MHz) of *O*-(4-(hydroxymethyl)benzyl) *S*-methyl carbonodithioate (**S5**)



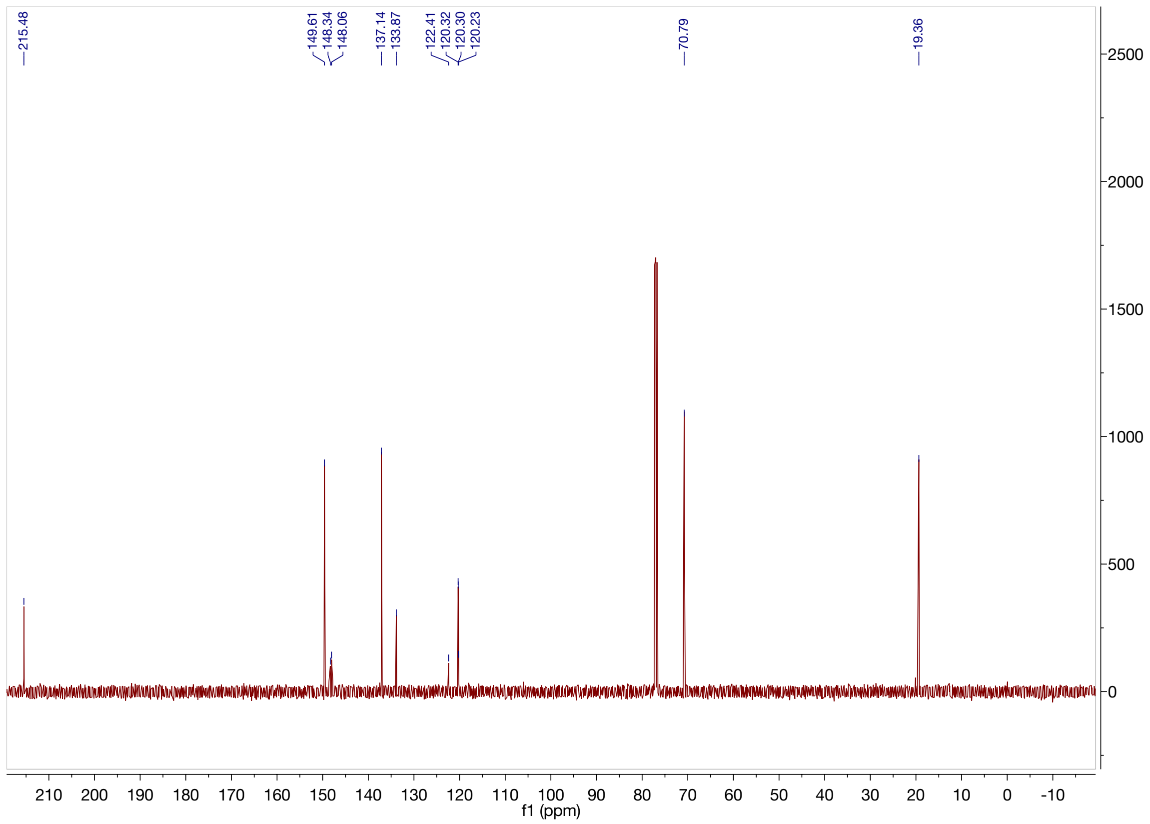
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(4-(hydroxymethyl)benzyl) *S*-methyl carbonodithioate (**S5**)



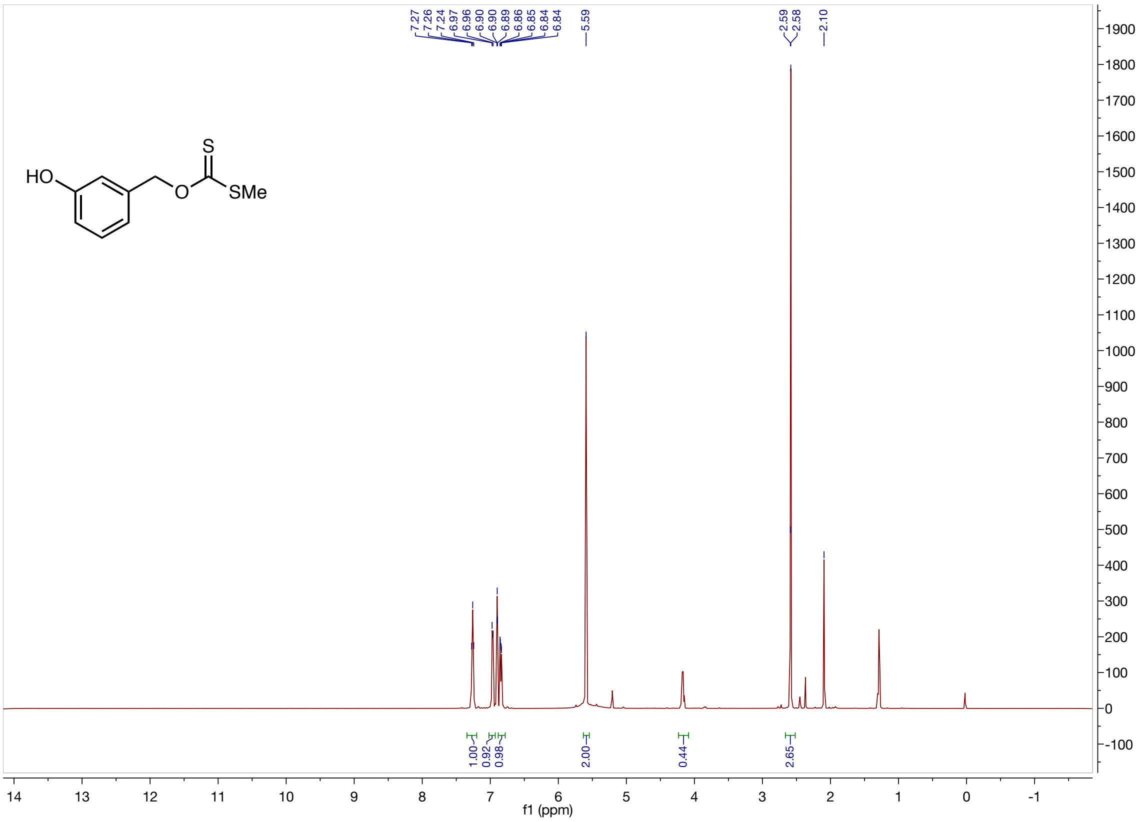
[1]H NMR ($CDCl_3$, 500.4 MHz) of *S*-methyl *O*-((6-(trifluoromethyl)pyridin-3-yl)methyl) carbonodithioate (**S6**)



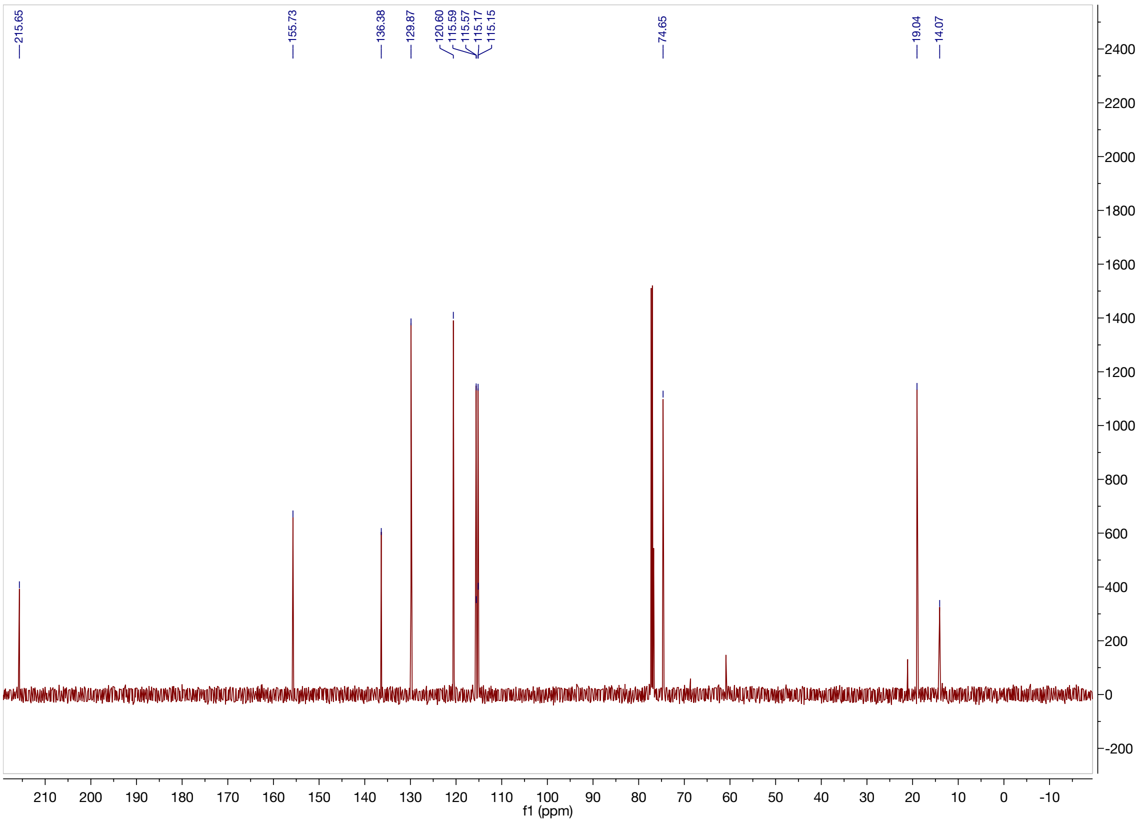
[19]F {[1]H} NMR ($CDCl_3$, 470.8 MHz) of *S*-methyl *O*-((6-(trifluoromethyl)pyridin-3-yl)methyl) carbonodithioate (**S6**)



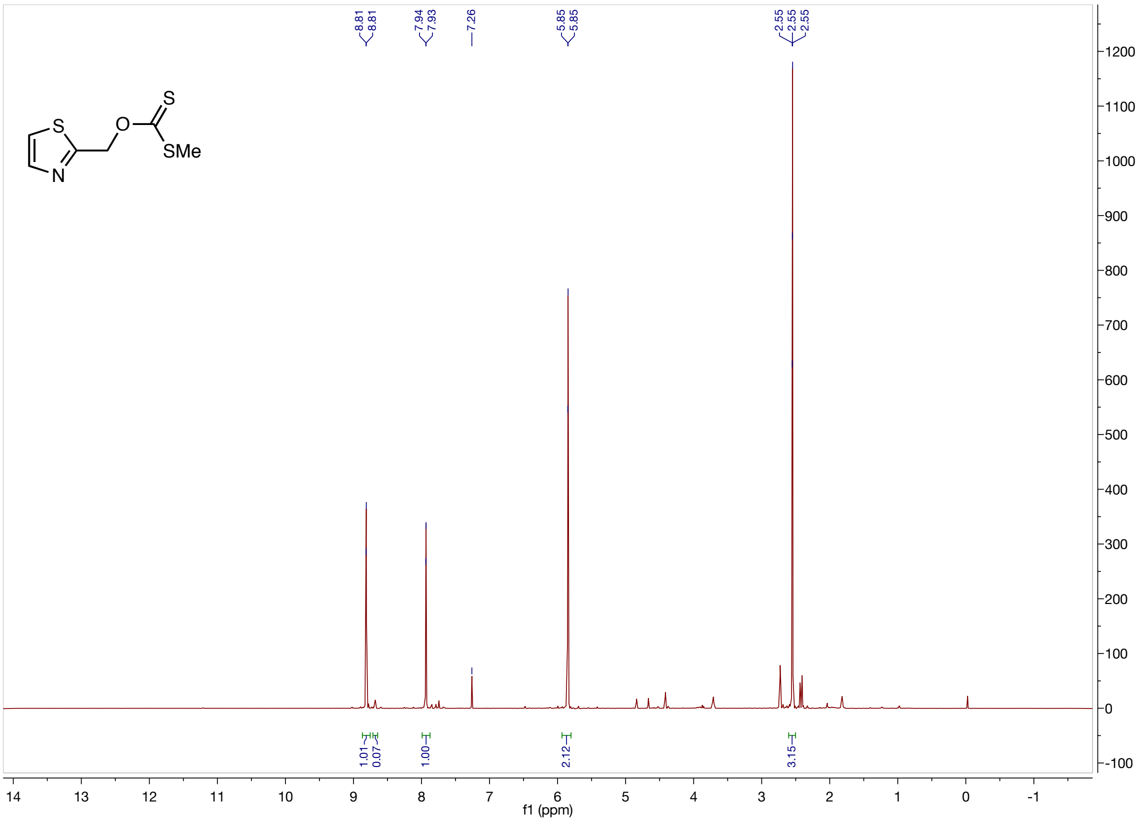
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *S*-methyl *O*-((6-(trifluoromethyl)pyridin-3-yl)methyl) carbonodithioate (**S6**)



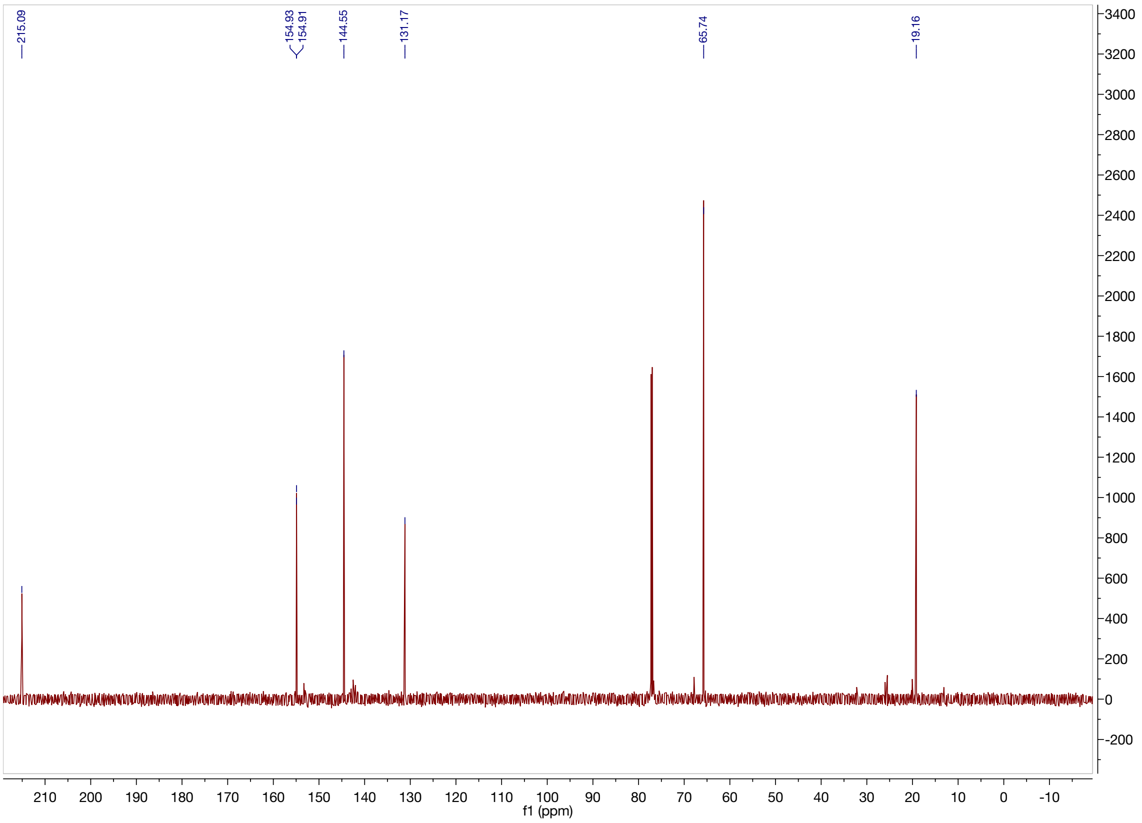
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(3-hydroxybenzyl) *S*-methyl carbonodithioate (**S7**)



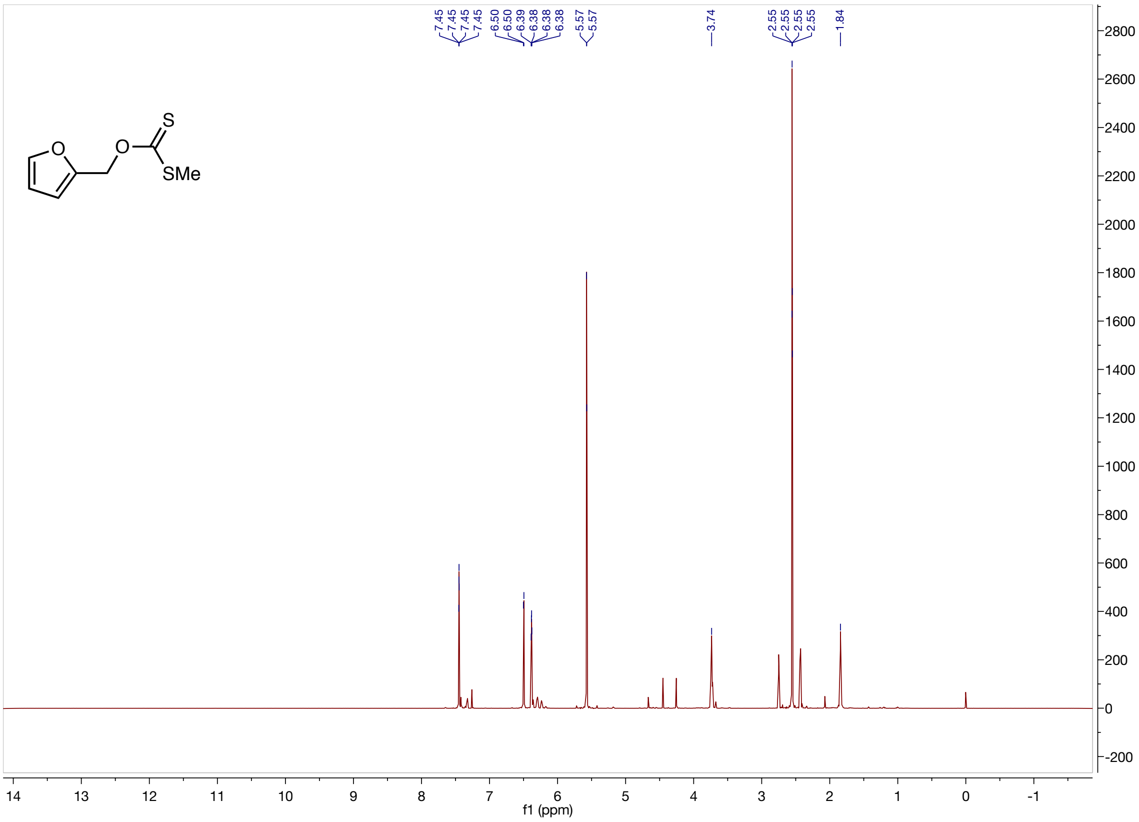
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(3-hydroxybenzyl) *S*-methyl carbonodithioate (**S7**)



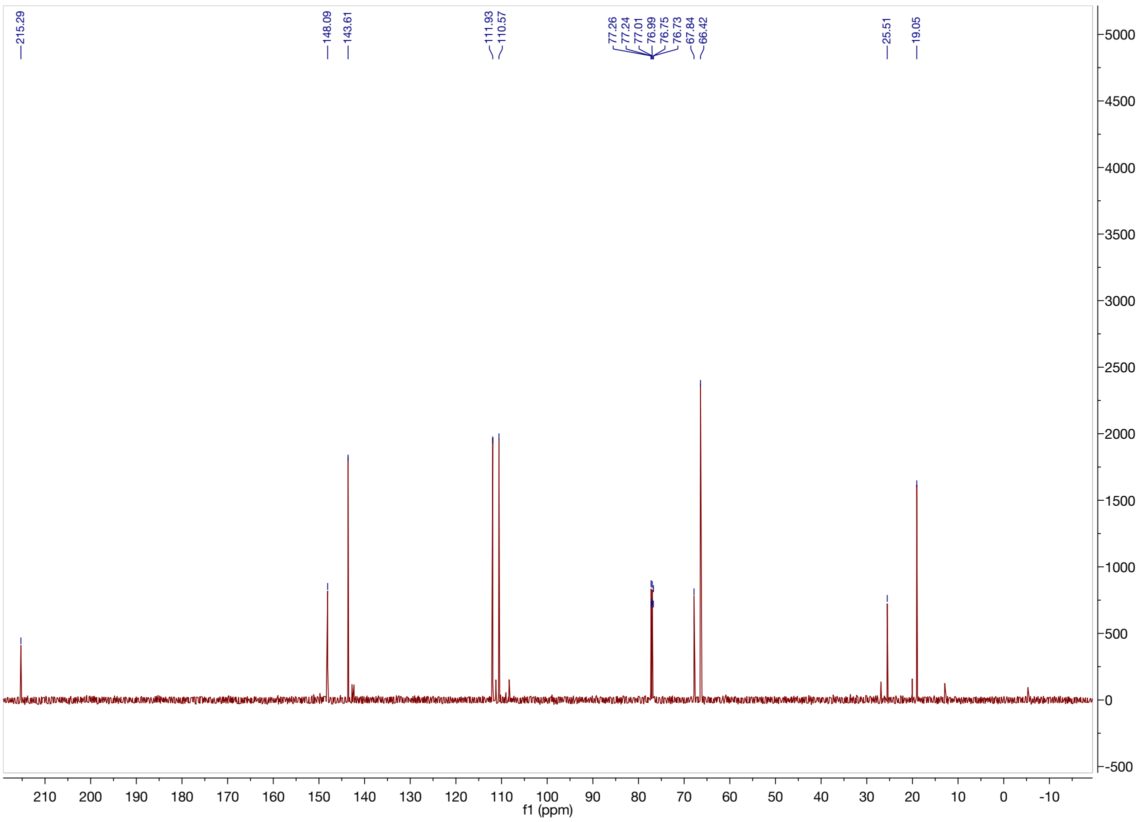
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *S*-methyl *O*-(thiazol-2-ylmethyl) carbonodithioate (**S8**)



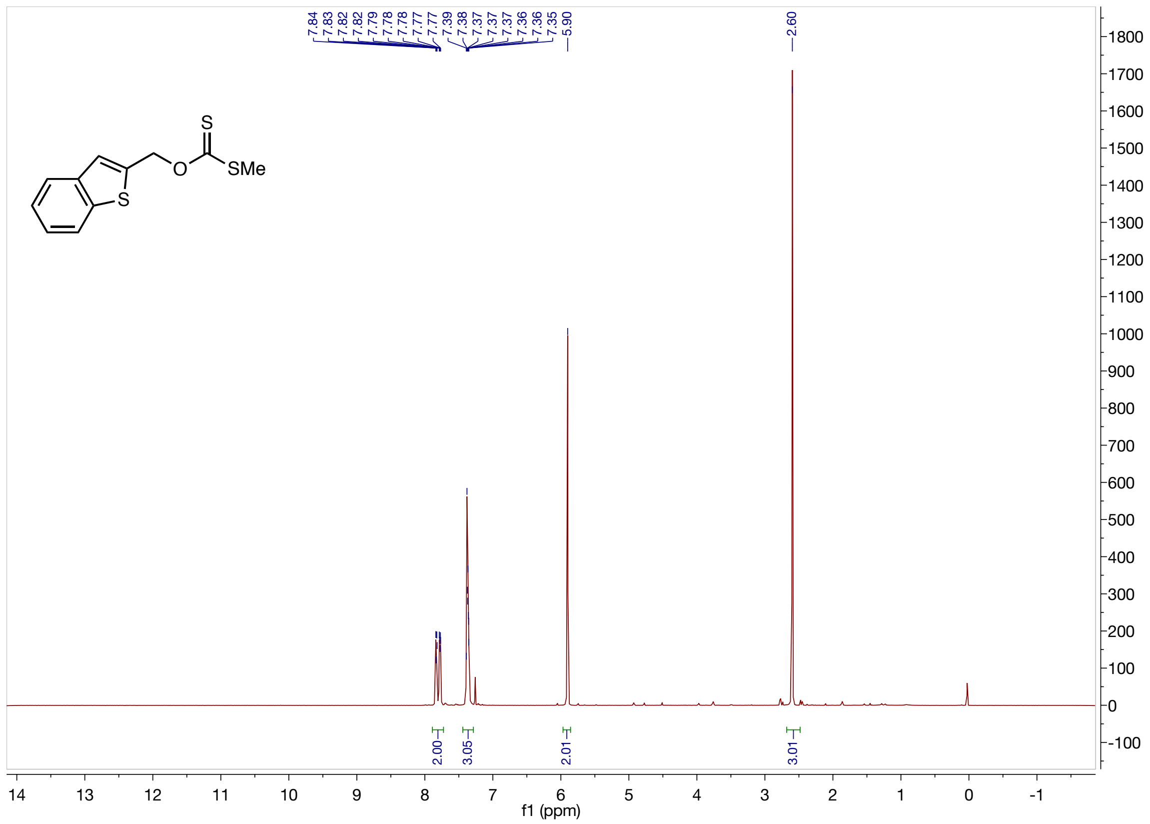
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *S*-methyl *O*-(thiazol-2-ylmethyl) carbonodithioate (**S8**)



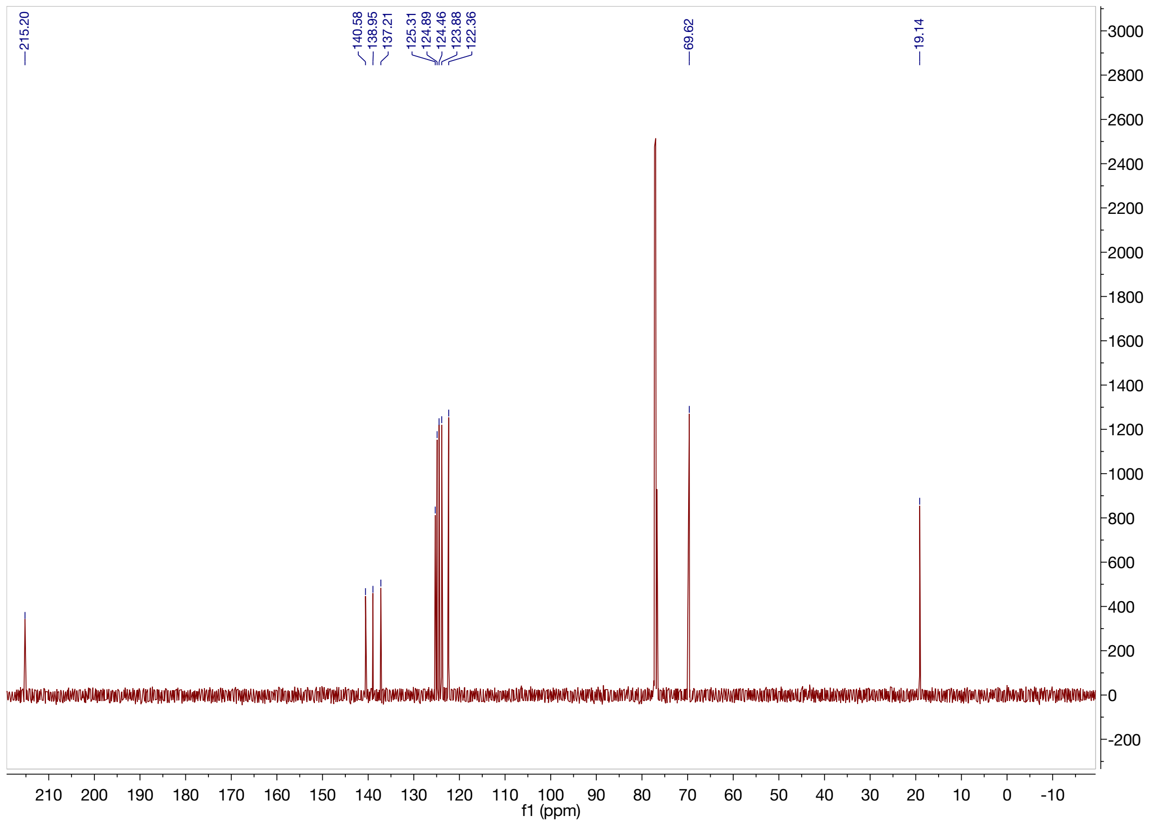
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(furan-2-ylmethyl) *S*-methyl carbonodithioate (**S9**)



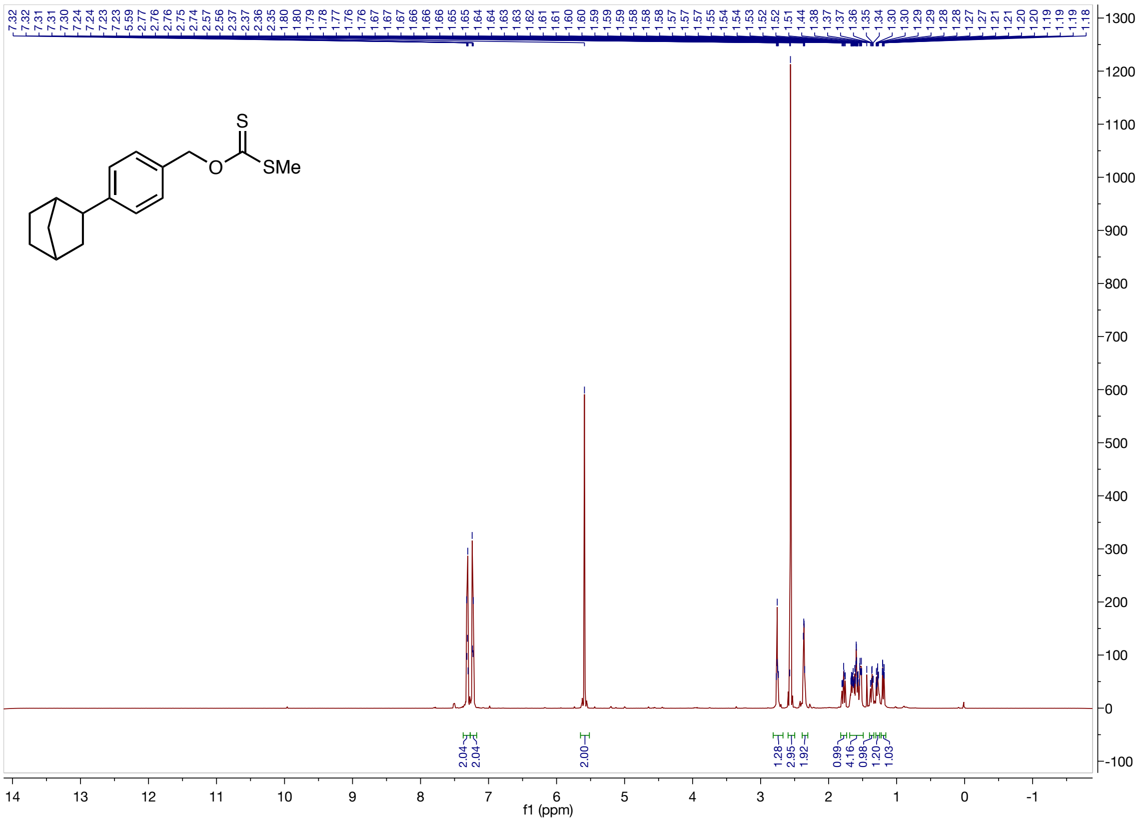
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(furan-2-ylmethyl) *S*-methyl carbonodithioate (**S9**)



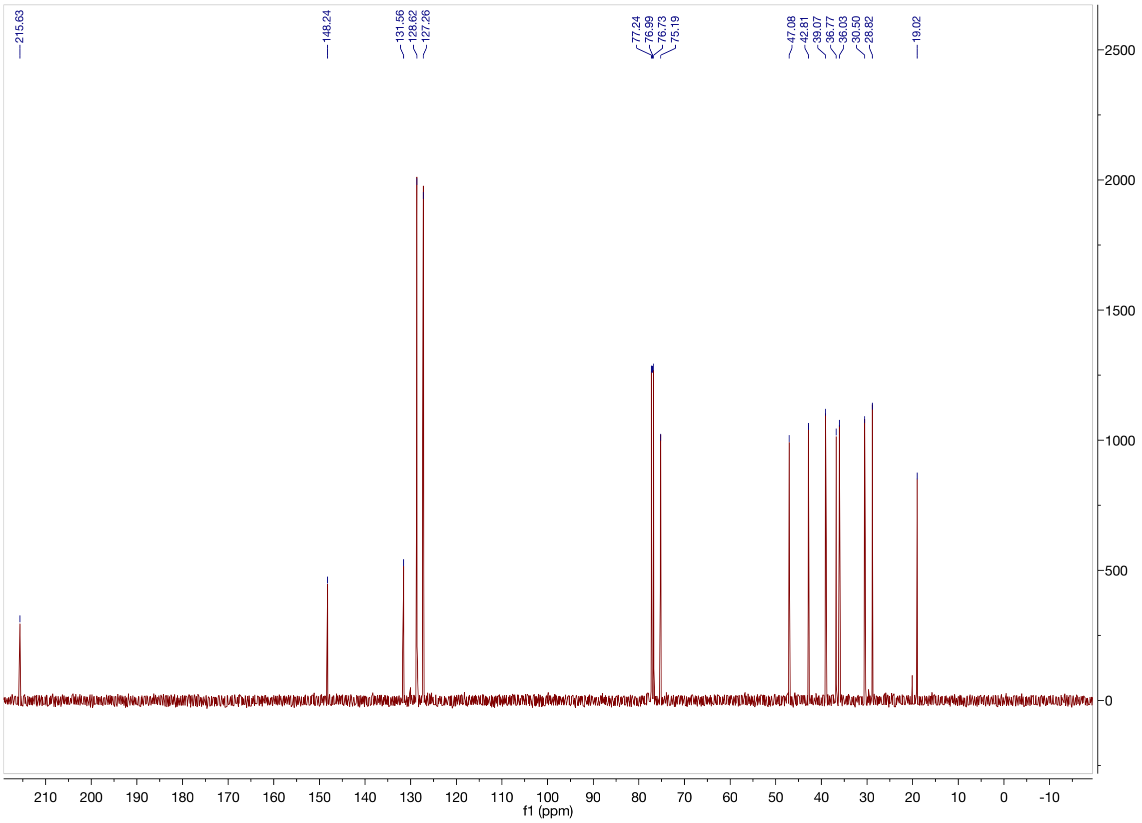
[1]H NMR ($CDCl_3$, 500.4 MHz) of *O*-(benzo[*b*]thiophen-2-ylmethyl) *S*-methyl carbonodithioate (**S10**)



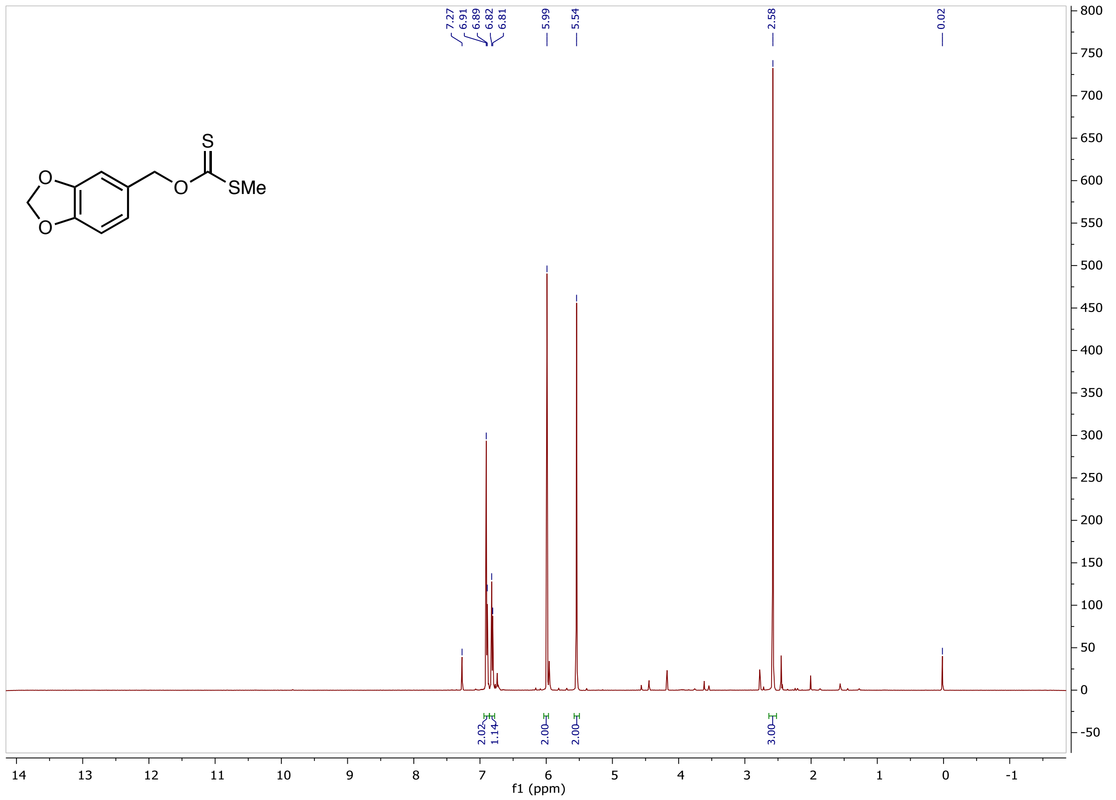
[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(benzo[*b*]thiophen-2-ylmethyl) *S*-methyl carbonodithioate (**S10**)



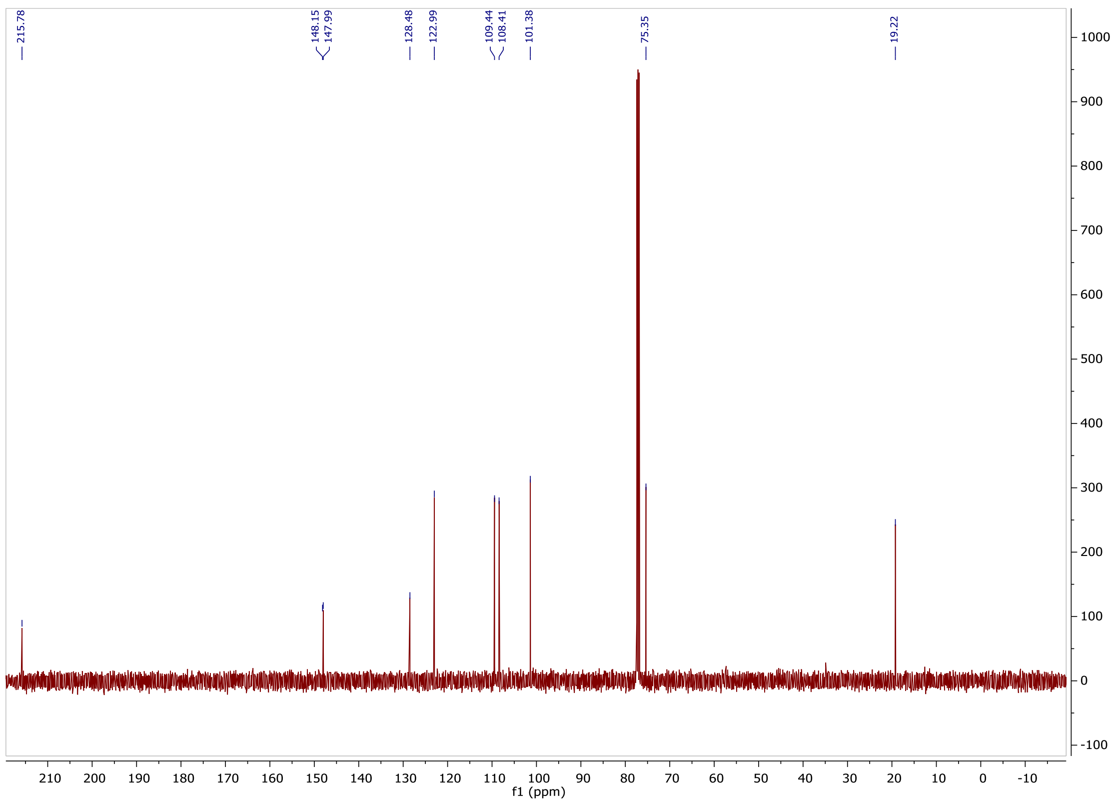
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *O*-(4-(bicyclo[2.2.1]heptan-2-yl)benzyl) *S*-methyl carbonodithioate (**S11**)



^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *O*-(4-(bicyclo[2.2.1]heptan-2-yl)benzyl) *S*-methyl carbonodithioate (**S11**)



[1]H NMR ($CDCl_3$, 500.4 MHz) of *O*-(benzo[d][1,3]dioxol-5-ylmethyl) *S*-methyl carbonodithioate (**S12**)



[13]C {[1]H} NMR ($CDCl_3$, 125.8 MHz) of O-(benzo[d][1,3]dioxol-5-ylmethyl) *S*-methyl carbonodithioate (**S12**)

[1] Gutiérrez-Bonet, A.; Tellis, J.C.; Matsui, J.K.; Vara, B.A.; Molander, G.A. *ACS Catal.* **2016**, *6*, 8004.
[2] Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc*. **2015**, *137*, 2195.
[3] Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415.
[4] Jouffroy, M.; Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, *138*, 475.