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Supporting Information

Copper-Catalyzed Trifluoromethylthiolation of Aryl Boronic Acids with A shelf-Stable Electrophilic Trifluoromethylthiolating Reagent

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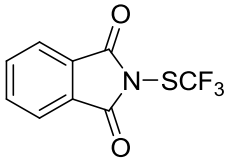
General information. All solvents were purified by standard method. ^{1}H NMR spectra were recorded on a 500 MHz, 400 MHz or 300 MHz. ^{19}F NMR were recorded on a 376 MHz or 282 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer and Agilent 400 or 500 MHz spectrometer. 1H NMR and 13C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Detection of melting point was conducted on the SGW X-4 microscopic melting point meter.

Materials. All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using.

Procedure for synthesis of *N*-(trifluoromethylthio)phthalimide and *N*-(Trifluoromethylthio)succinimide.

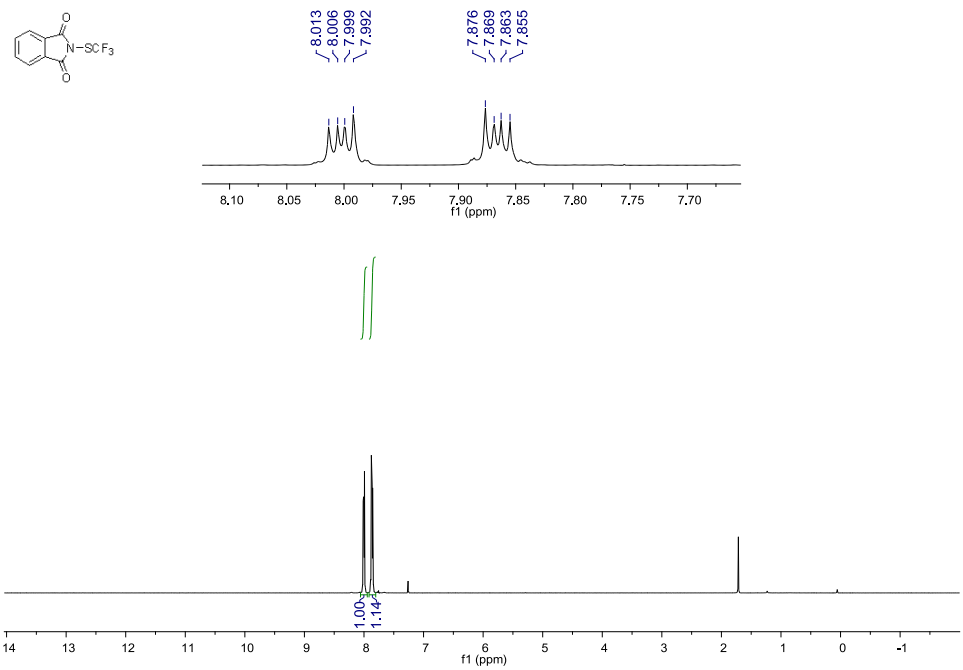
To a mixture of *N*-bromophthalimide (5.2 g, 23 mmol), $AgSCF_3$ (6.25 g, 30 mmol) in a 100 mL of round bottom flask was added dried CH_3CN (40 mL) under argon atmosphere. The mixture was stirred at room temperature for 3 h. Then the solvent was evacuated under rotary evaporator. The residue was added CH_2Cl_2 (20 mL), then filtered through a short plug of Celite. The filter was evacuated again under reduced pressure to give the title compound as a white solid (5.3 g, 93%).



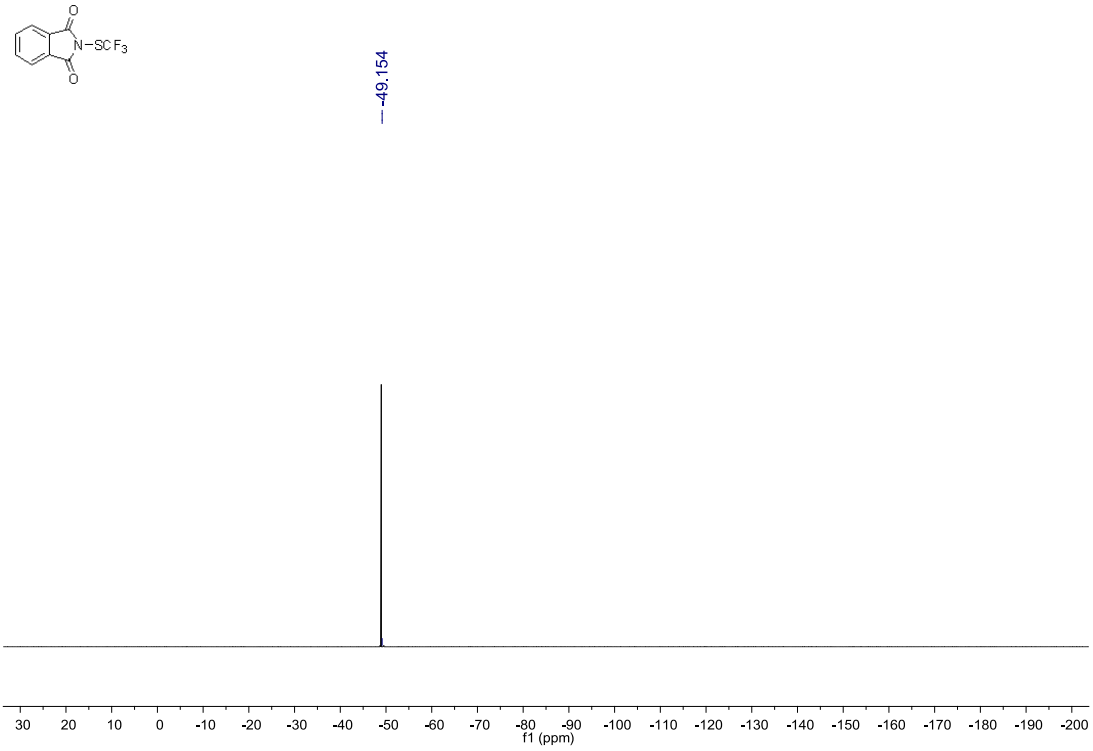
***N*-(trifluoromethylthio)phthalimide**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 5.5, 3.1 Hz, 2 H), 7.87 (dd, *J* = 5.5, 3.1 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -48.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.00, 135.40, 131.39, 127.84 (q, *J* = 316.6 Hz), 124.66 ppm. MS (ESI): 248.0 (M+H). HRMS: Calculated for $C_9H_4NO_2F_3S$: 246.9915; Found: 246.9911.

Reference: Munavalli, S.; Rohrbaugh, D. K.; Rossman, D. I.; Berg, F. J.; Wagner, G. W.; Durst, H. D. *Synthetic Commun.* **2000**, *30*, 2847.

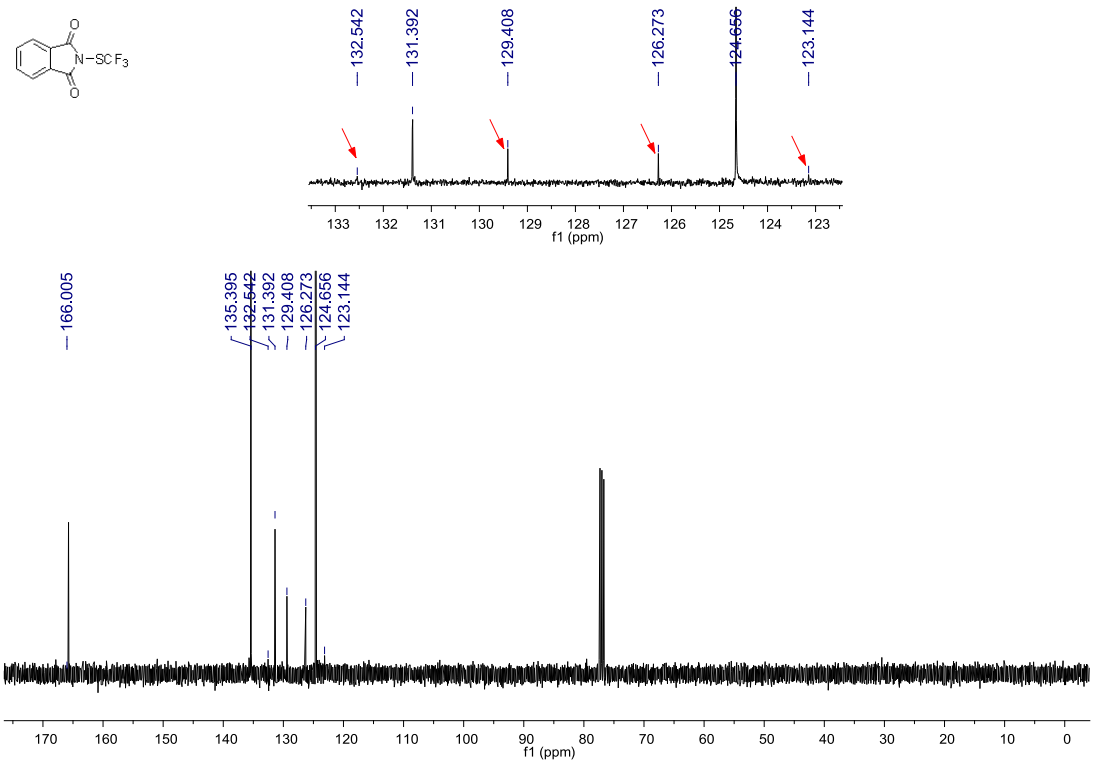
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *N*-(trifluoromethylthio)phthalimide

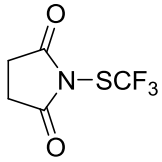


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of *N*-(trifluoromethylthio)phthalimide



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of *N*-(trifluoromethylthio)phthalimide

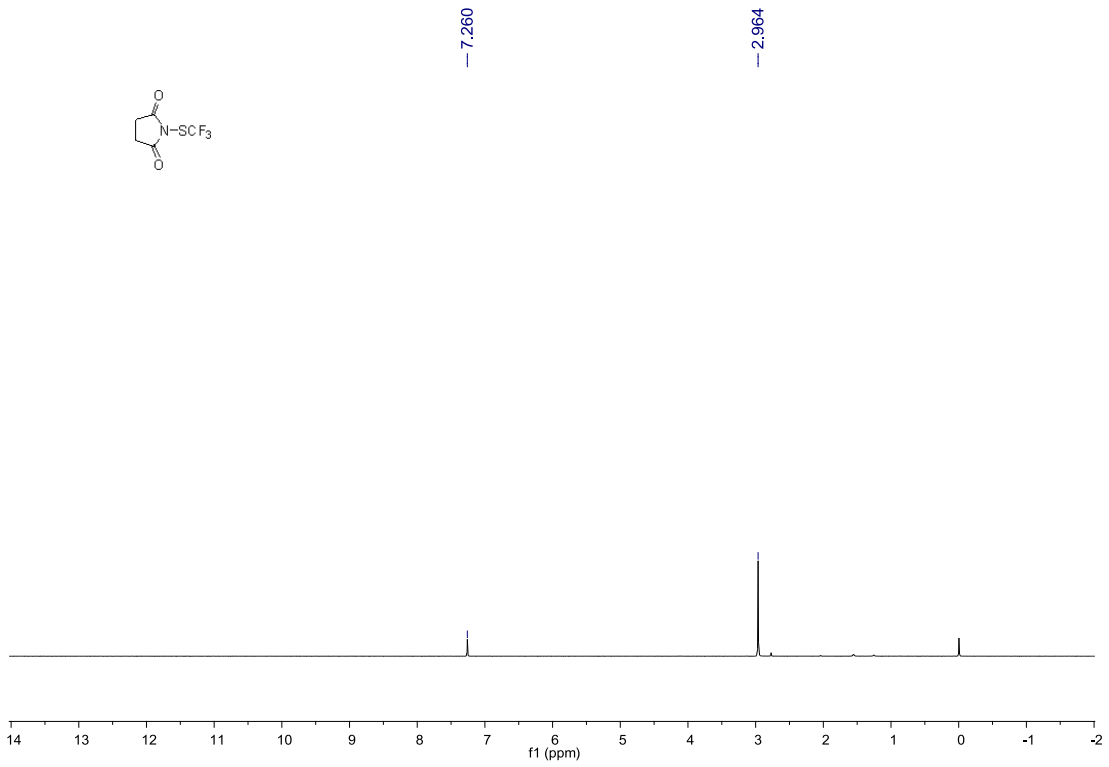




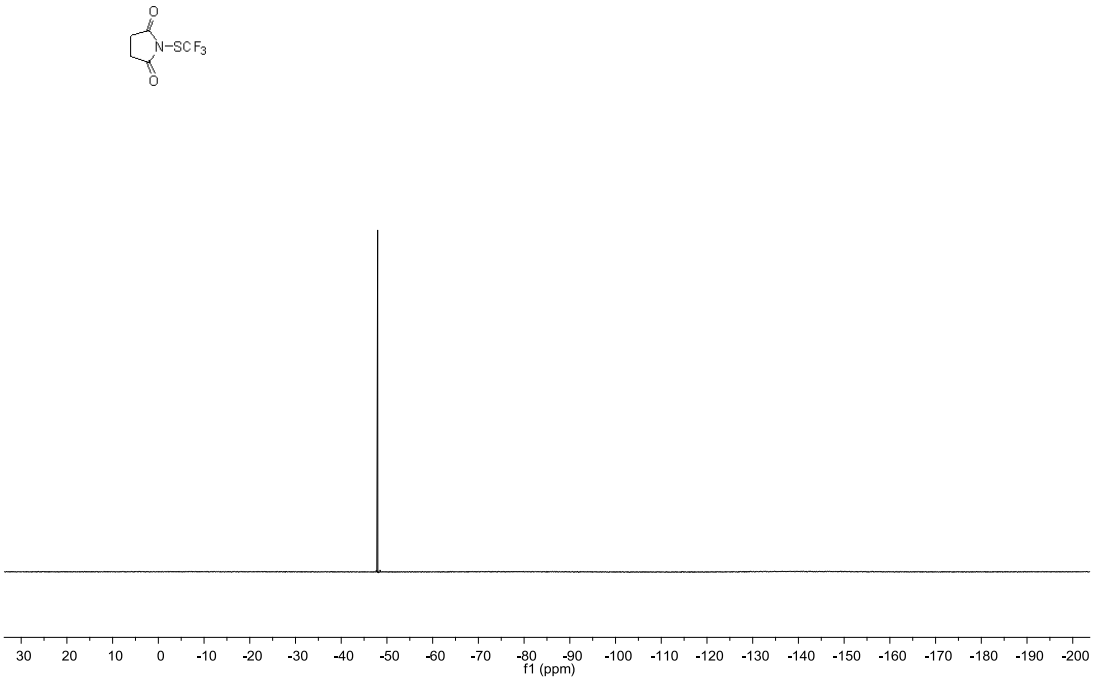
***N*-(Trifluoromethylthio)succinimide**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (s, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -48.16 (s, 3 F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.57, 127.71 (q, *J* = 314.2 Hz), 28.46 ppm. MS (ESI): 200.0 (M+H). HRMS: Calculated for $C_5H_4NO_2F_3S$: 198.9915; Found: 198.9914.

Reference: Haas,A.; Möller, G. *Chem. Ber.* **1996**, *129*, 1383.

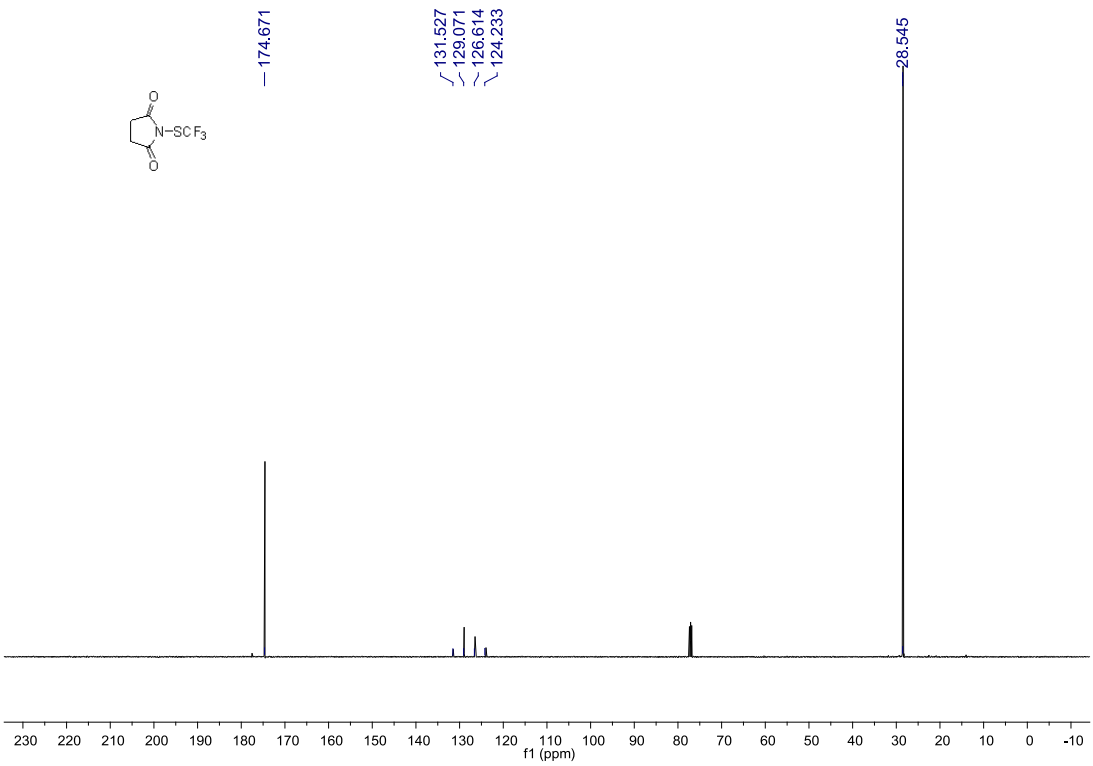
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *N*-(Trifluoromethylthio)succinimide



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of *N*-(Trifluoromethylthio)succinimide



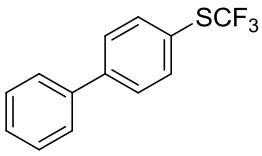
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of *N*-(Trifluoromethylthio)succinimide



General Procedures for Trifluoromethanesulfanylation of Boronic Acids with Reagent 1.

Aryl boronic acids (0.5 mmol, 1.0 equiv), reagent **1** (18.5 mg, 0.75 mmol, 1.5 equiv), Na_2CO_3 (2.7 mg, 0.25 mmol, 0.5 equiv), CuI (4.7 mg, 0.025 mmol, 0.05 equiv), 4,4'-di-*tert*-butylbipyridine (6.7 mg, 0.025 mmol, 0.05 equiv) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under Ar. 3 mL of freshly distilled diglyme was added into the Schlenk tube in a glove box. The reaction was stirred at 60 ^{o}C for 15 h. 25 mL of distilled water and 50 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (3 × 15 mL) and the combined organic extracts were washed with 50 mL of distilled water. The separated organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel and Kugelrohr distillation.

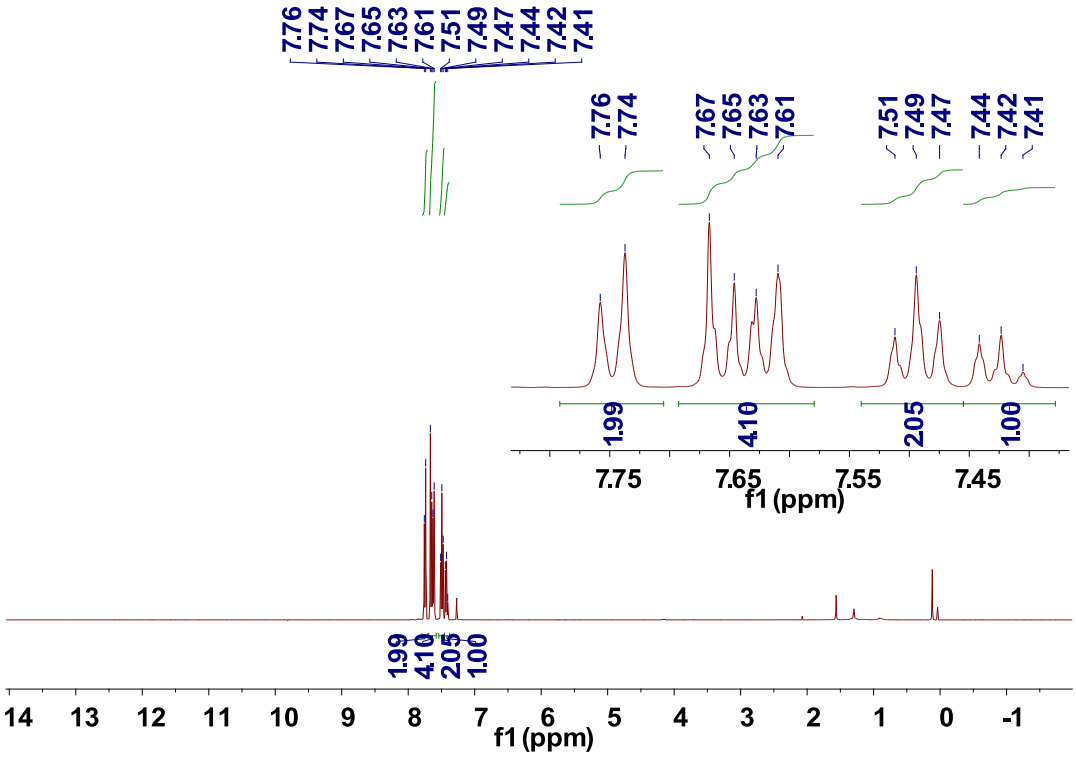
4-[(Trifluoromethyl)thio]biphenyl



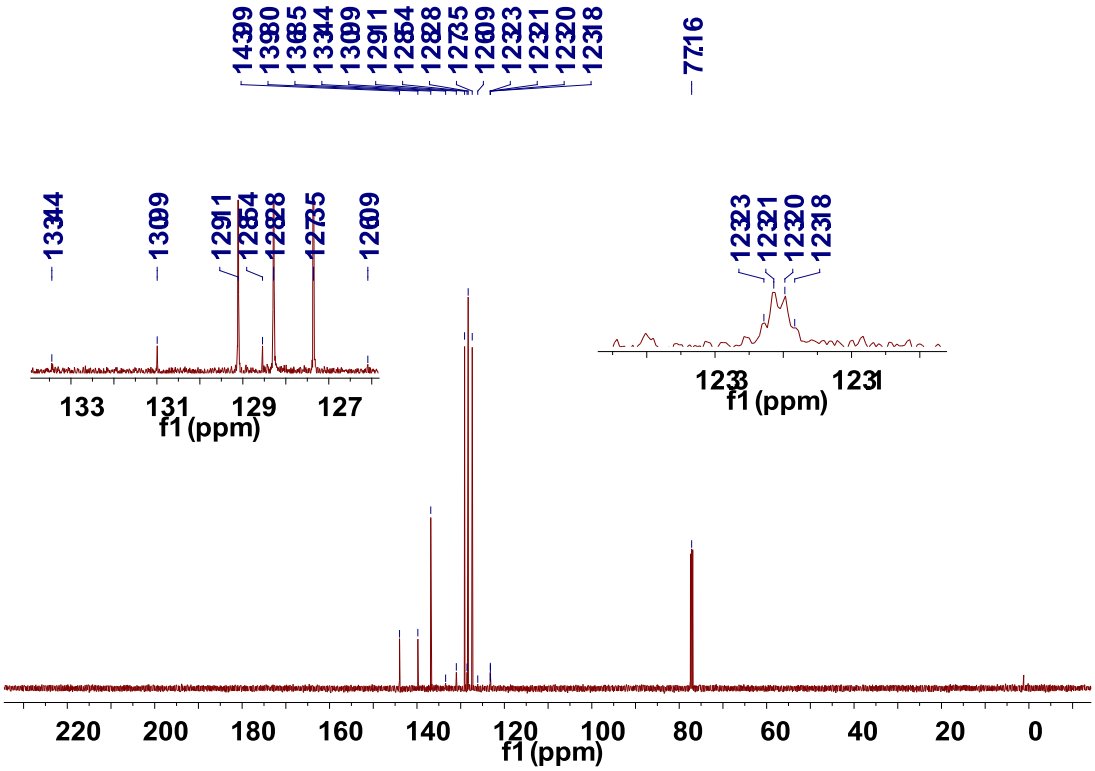
Obtained as a white solid in 80% yield (101.6 mg). ^{1}H NMR (400 M, $CDCl_3$, 293 K, TMS) δ 7.75 (d, *J* = 8.0 Hz, 2 H), 7.67- 7.61 (m, 4 H), 7.49 (t, *J* = 8.0 Hz, 2 H), 7.44-7.41 (m, 1 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.78 (s, 3 F) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 143.99, 139.80, 136.85, 129.76 (q, *J* = 308.2 Hz), 129.11, 128.28, 127.35, 123.20 (q, *J* = 2.5 Hz) ppm. GC-MS(EI) *m/z* (%) 254 (100), 185, 152, 115, 69. HRMS: Calculated for $C_{13}H_9F_3S$: 254.0377; Found: 254.0374.

Reference: Chen, C.; Xie, Y.; Chu, L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2012,** *51*, 2492.

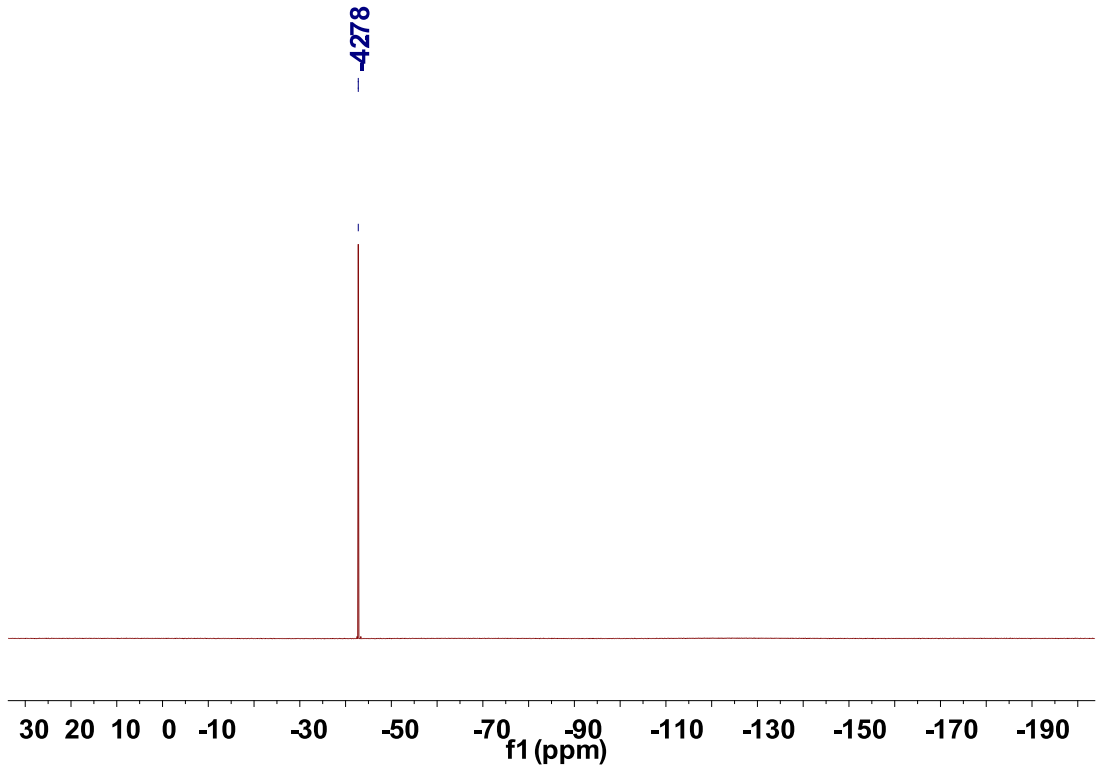
^{1}H NMR spectrum of 4-[(Trifluoromethyl)thio]biphenyl



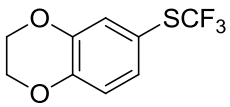
^{13}C NMR spectrum of 4-[(Trifluoromethyl)thio]biphenyl



^{19}F NMR spectrum of 4-[(Trifluoromethyl)thio]biphenyl

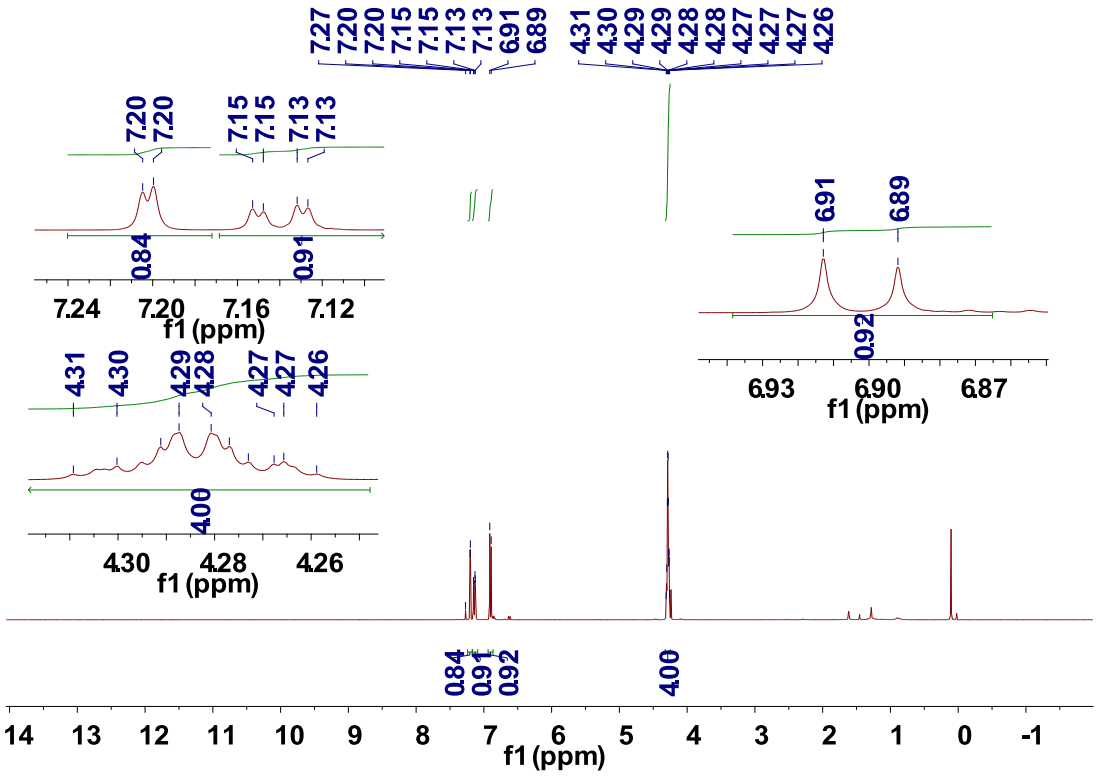


6-((Trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine

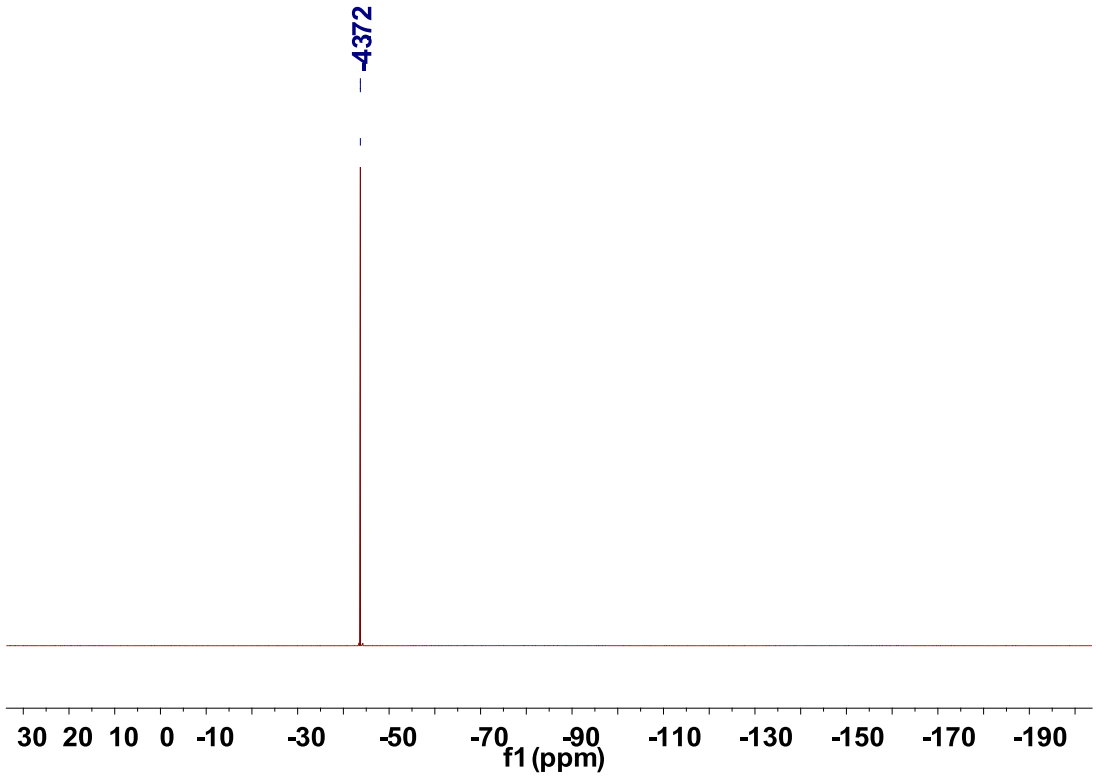


Obtained as a colorless oil in 85% yield (100.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.20 (d, *J* = 4.0 Hz, 1 H), 7.14 (dd, *J* = 8.0 Hz, 4.0 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 4.28 (m, 4 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.72 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 143.67, 141.25, 127.04 (q, *J* = 308.2 Hz), 127.45, 122.93, 115.60, 112.84 (q, *J* = 1.6 Hz), 61.84, 61.51 ppm; IR (ATR) ν_{max} 2968, 2937, 2887, 1601, 1580, 1494, 1460, 1305, 1286, 1113, 898, 874, 814, 756, 690 cm^{-1}. GC-MS (EI) *m/z* (%) 236.0 (100), 167. HRMS: Calculated for $C_9H_7O_2F_3S$: 236.0119; Found: 236.0119.

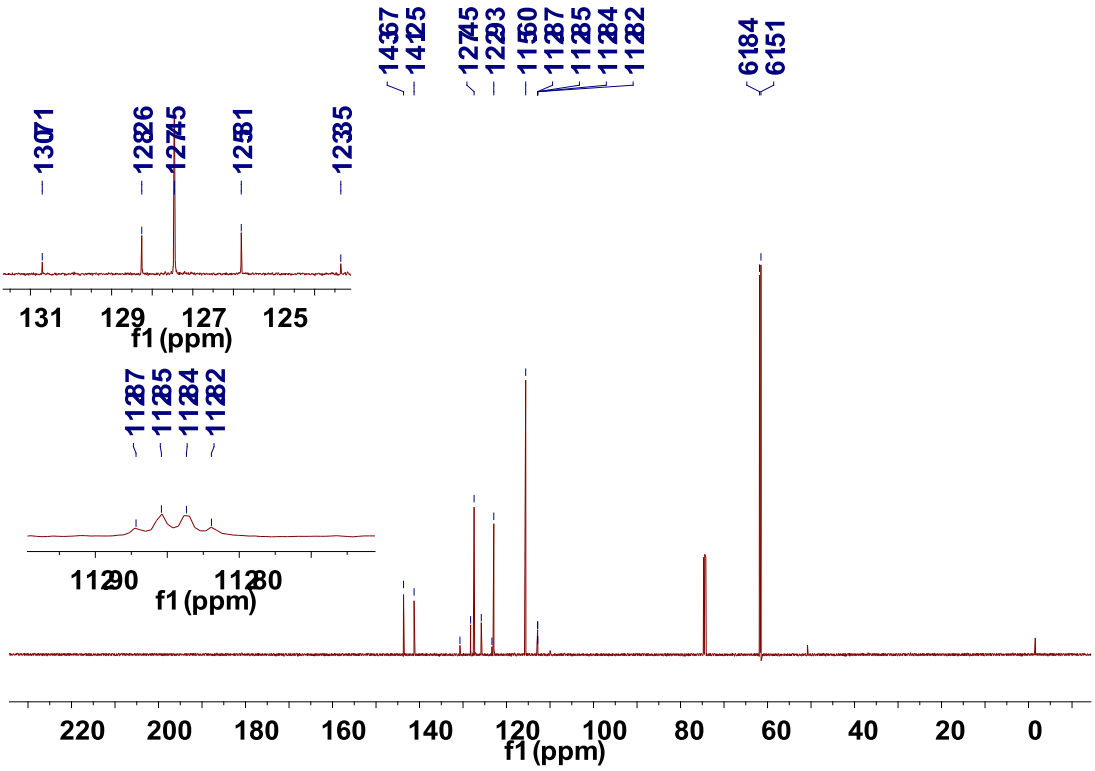
^{1}H NMR spectrum of 6-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine



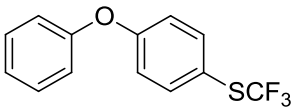
^{19}F NMR spectrum of 6-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine



^{13}C NMR spectrum of 6-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine



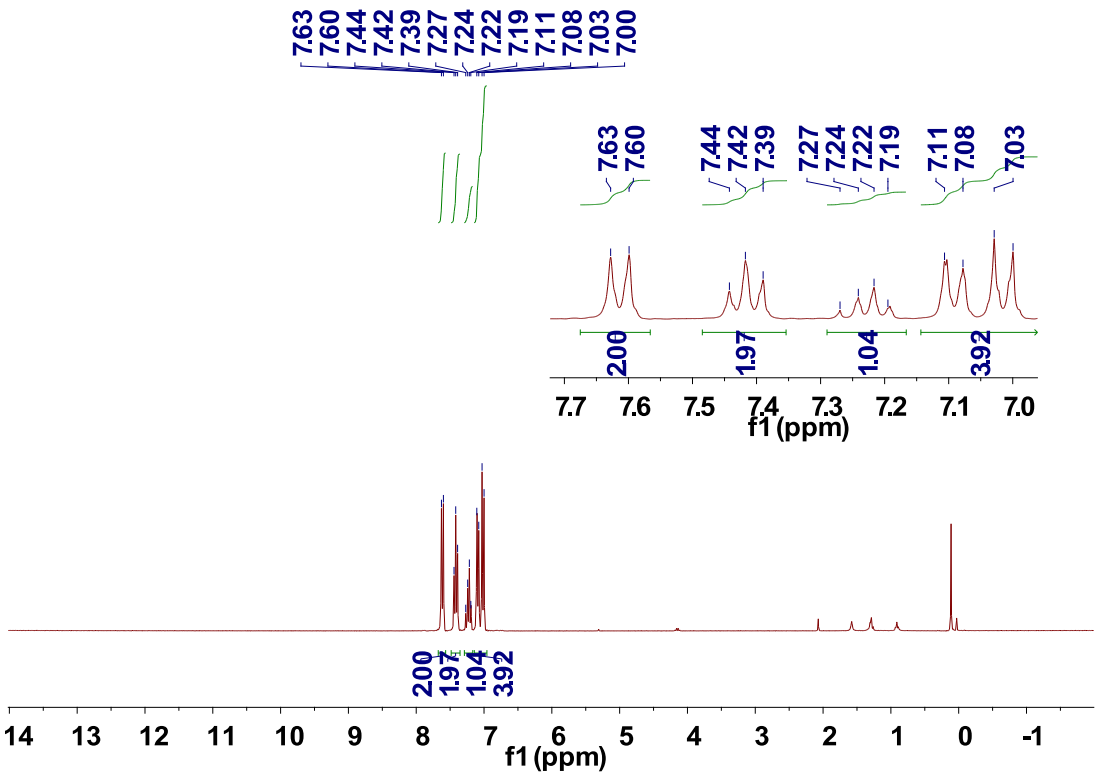
1-(Benzyloxy)-4-[(trifluoromethyl)thio]benzene



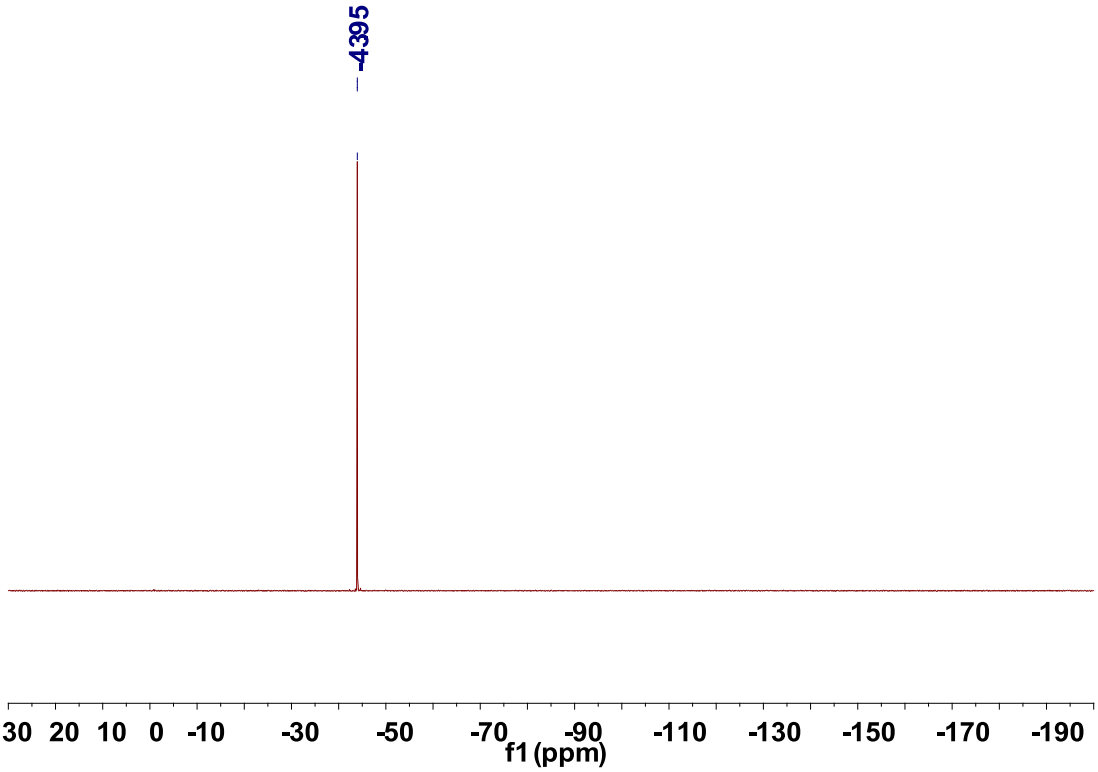
Obtained as white solid in 77% yield (104.0 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.62 (d, *J* = 9.0 Hz, 2 H), 7.42 (t, *J* = 9.0 Hz, 2 H), 7.22 (t, *J* = 9.0 Hz, 1 H), 7.11-7.00 (m, 4 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -43.95 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 160.54, 155.73, 138.38, 129.70 (q, *J* = 308.2 Hz), 130.20, 124.71, 120.22, 118.75, 117.37 (q, *J* = 2.5 Hz) ppm; GC-MS (EI) *m/z* (%) 270 (100), 201, 129, 77, 51. HRMS: Calculated for $C_{13}H_9F_3OS$: 270.0326; Found: 270.0327.

Reference: Chen, C.; Xie, Y.; Chu, L.-L.; Wang, R.- W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2012,** 51, 2492.

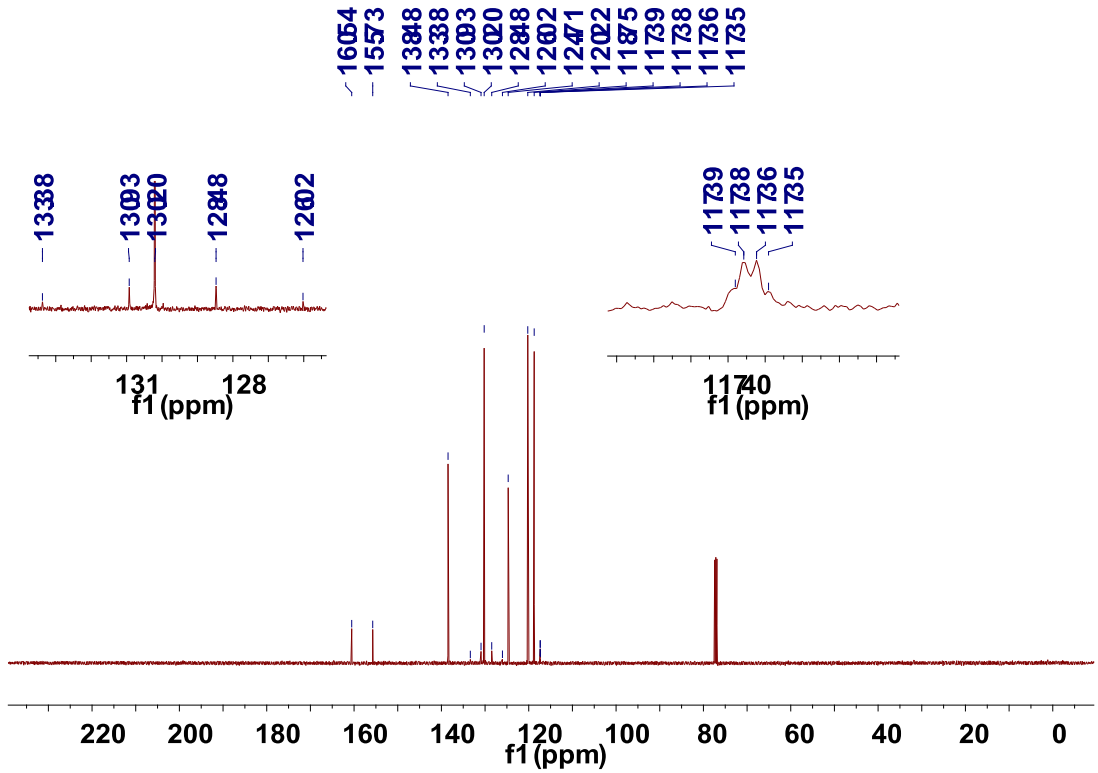
^{1}H NMR Spectrum of 1-(Benzyloxy)-4-[(trifluoromethyl)thio]benzene



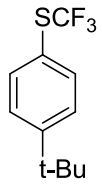
^{19}F NMR Spectrum of 1-(Benzyloxy)-4-[(trifluoromethyl)thio]benzene



^{13}C NMR Spectrum of 1-(Benzyloxy)-4-[(trifluoromethyl)thio]benzene



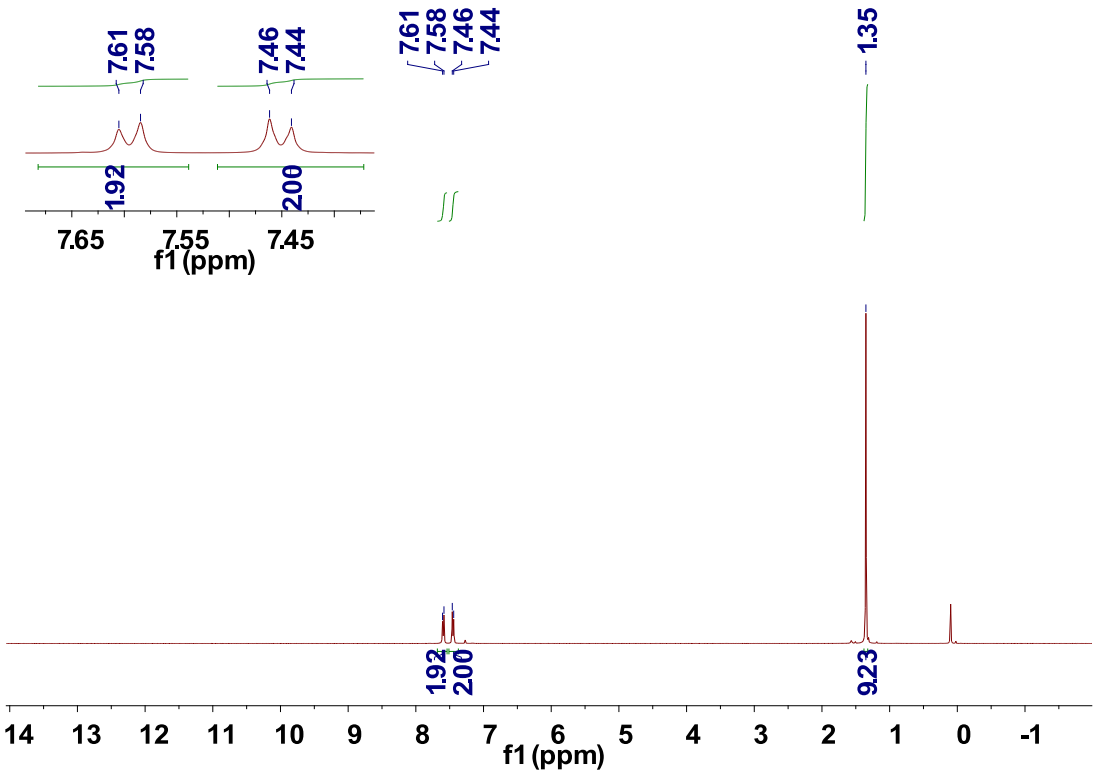
(4-(*tert*-Butyl)phenyl)(trifluoromethyl)sulfane



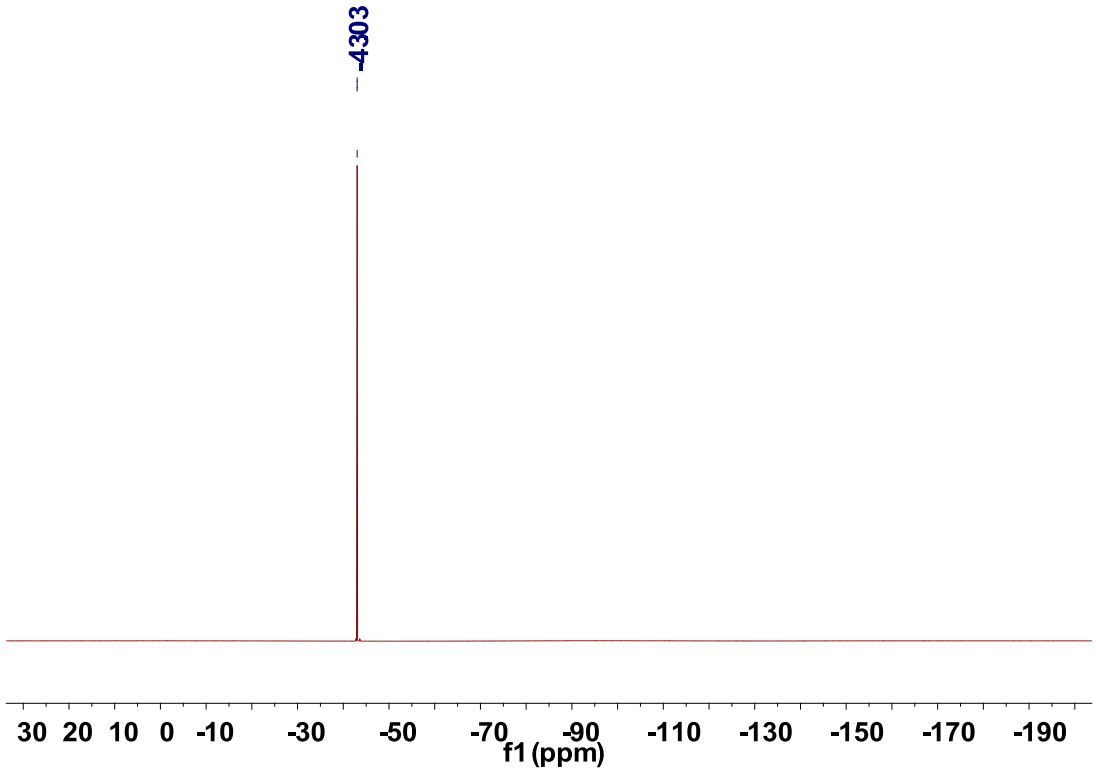
Obtained as a colorless oil in 82% yield (96.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.60 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 1.35 (s, 9 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.03 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 154.52, 136.29, 129.86 (q, *J* = 308.2 Hz), 126.73, 121.04 (q, *J* = 2.5 Hz), 35.02, 31.29 ppm. GC-MS (EI): *m/z* (%) 219.1 (100), 234.1. HRMS: Calculated for $C_{11}H_{13}F_3S$: 234.0690; Found: 234.0693.

Reference: Chen, C.; Xie, Y.; Chu, L.-L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2012,** *51*, 2492.

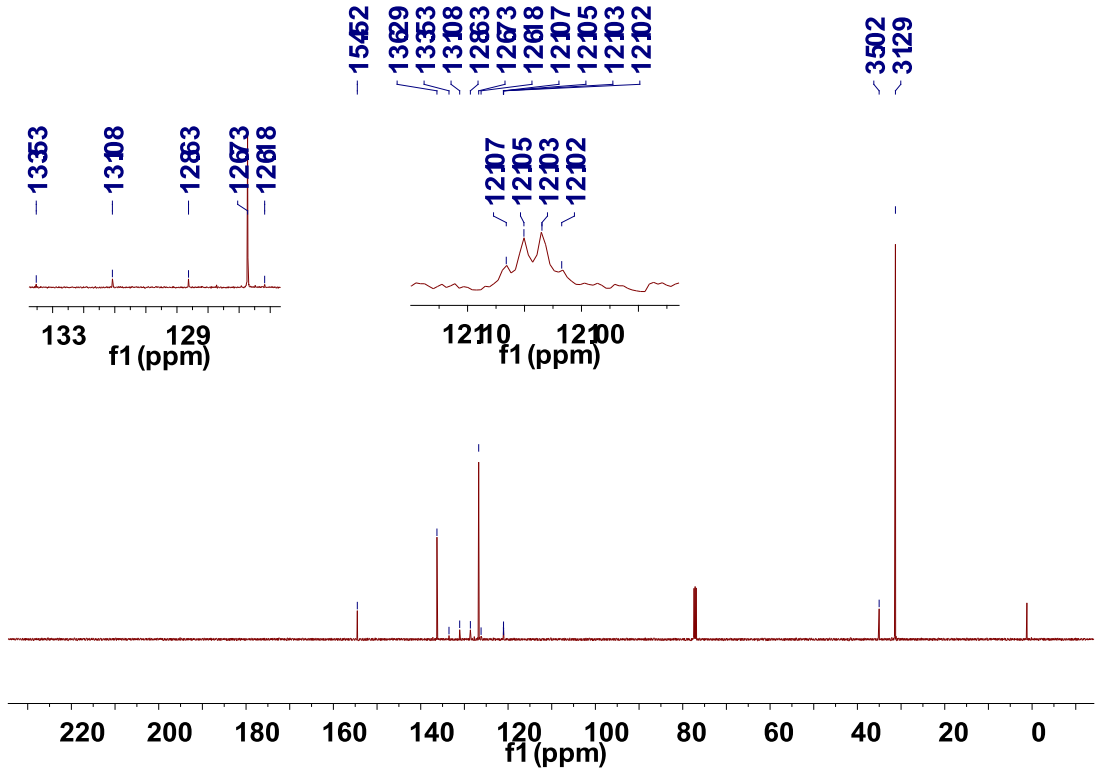
^{1}H NMR Spectrum of (4-(*tert*-butyl)phenyl)(trifluoromethyl)sulfane



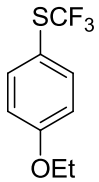
^{19}F NMR Spectrum of (4-(*tert*-butyl)phenyl)(trifluoromethyl)sulfane



^{13}C NMR Spectrum of (4-(*tert*-butyl)phenyl)(trifluoromethyl)sulfane

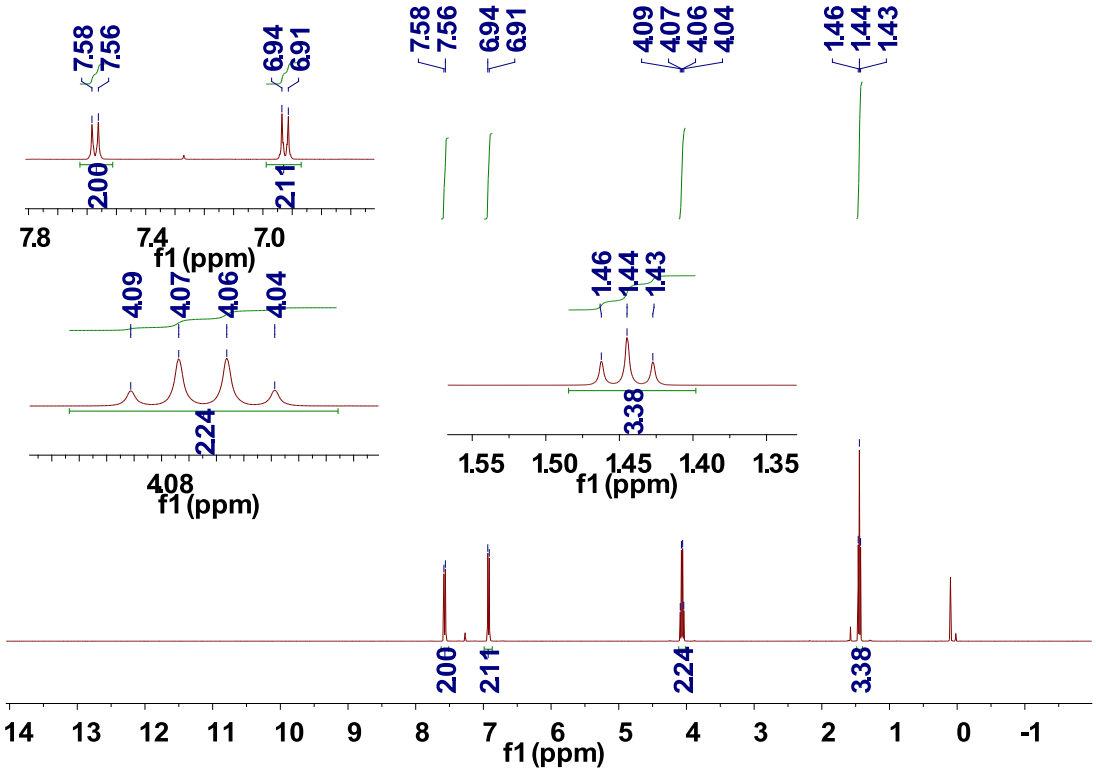


(4-Ethoxyphenyl)(trifluoromethyl)sulfane

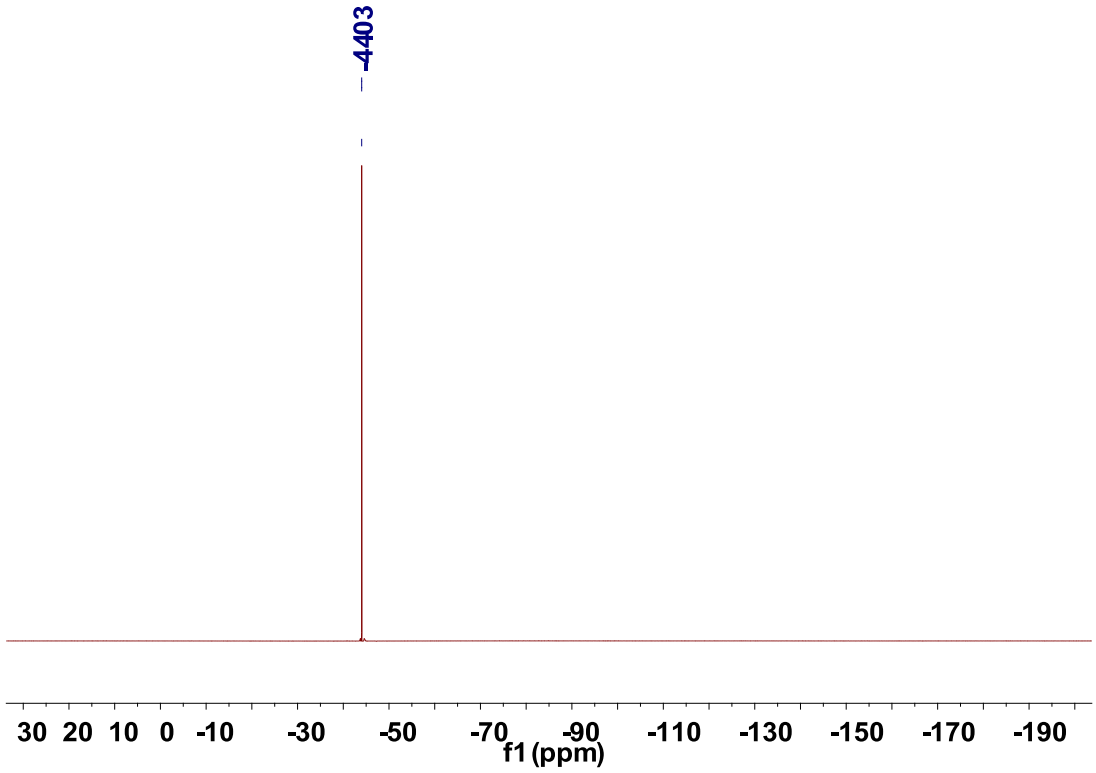


Obtained as a colorless oil in 90% yield (99.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.57 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 12.0 Hz, 2 H), 4.06 (q, *J* = 8.0 Hz, 2 H), 1.44 (t, 8.0 Hz, 3 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.03 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 161.40, 138.41, 129.80 (q, *J* = 308.2 Hz), 115.59, 114.70 (q, *J* = 2.5 Hz), 63.87, 14.80 ppm. IR (ATR) ν_{max} 2985.6, 2932.3, 1595.3, 1573.5, 1477.2, 1291.8, 1254.5, 1115.7, 827.0, 805.7, 736.1 cm^{-1}. GC-MS (EI) m/z (%) 222, 69 (100). HRMS: Calculated for $C_9H_9OSF_3$: 222.0326; Found: 222.0328.

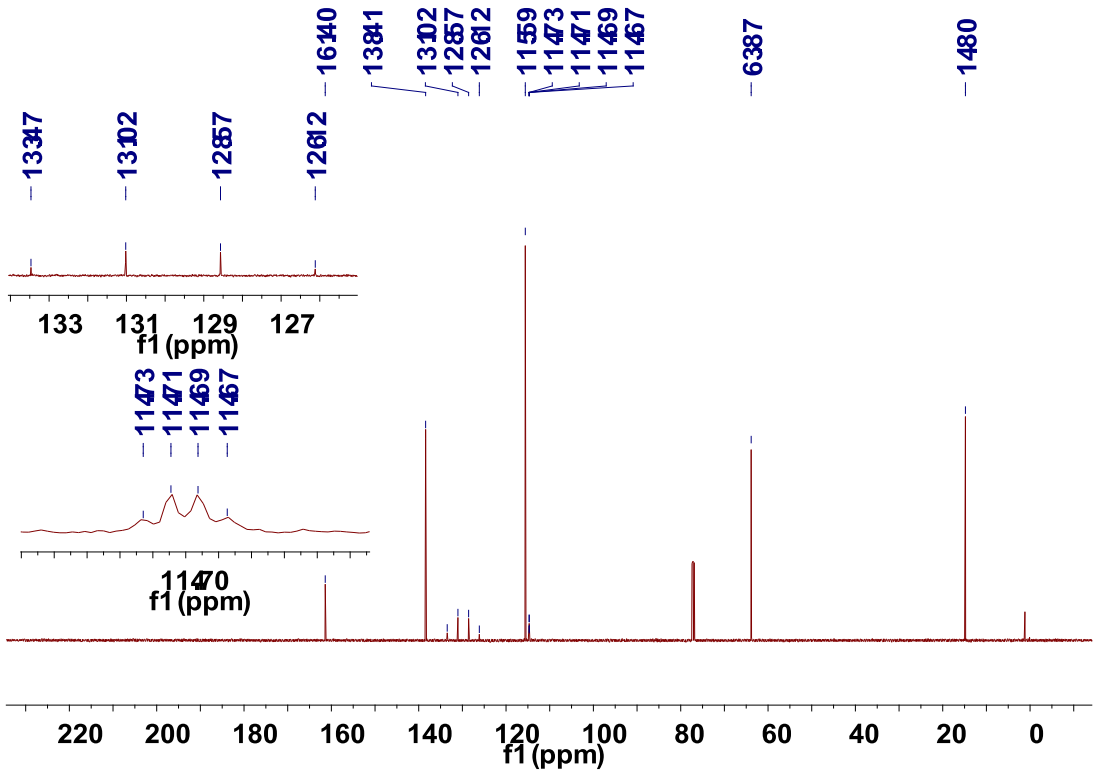
^{1}H NMR Spectrum of (4 - Ethoxyphenyl)(trifluoromethyl)sulfane



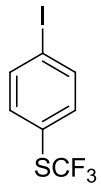
^{19}F NMR Spectrum of (4-Ethoxyphenyl)(trifluoromethyl)sulfane



^{13}C NMR Spectrum of (4 - Ethoxyphenyl)(trifluoromethyl)sulfane



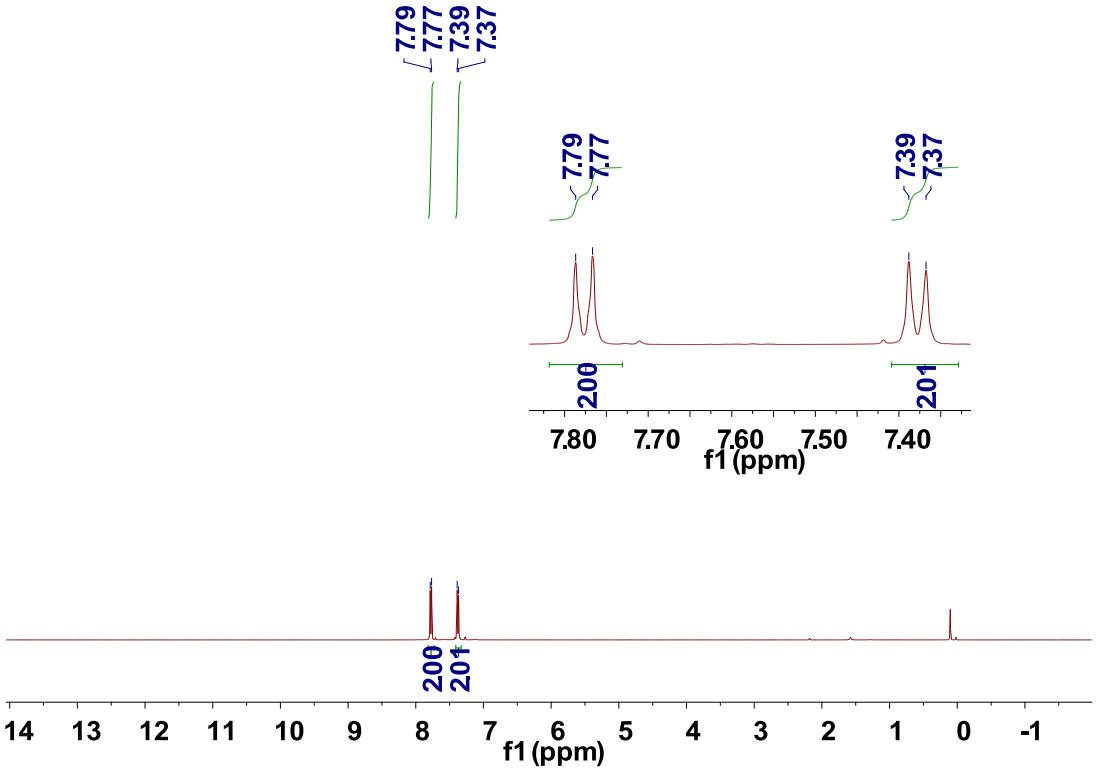
1-Iodo-4-[(trifluoromethyl)thio]benzene



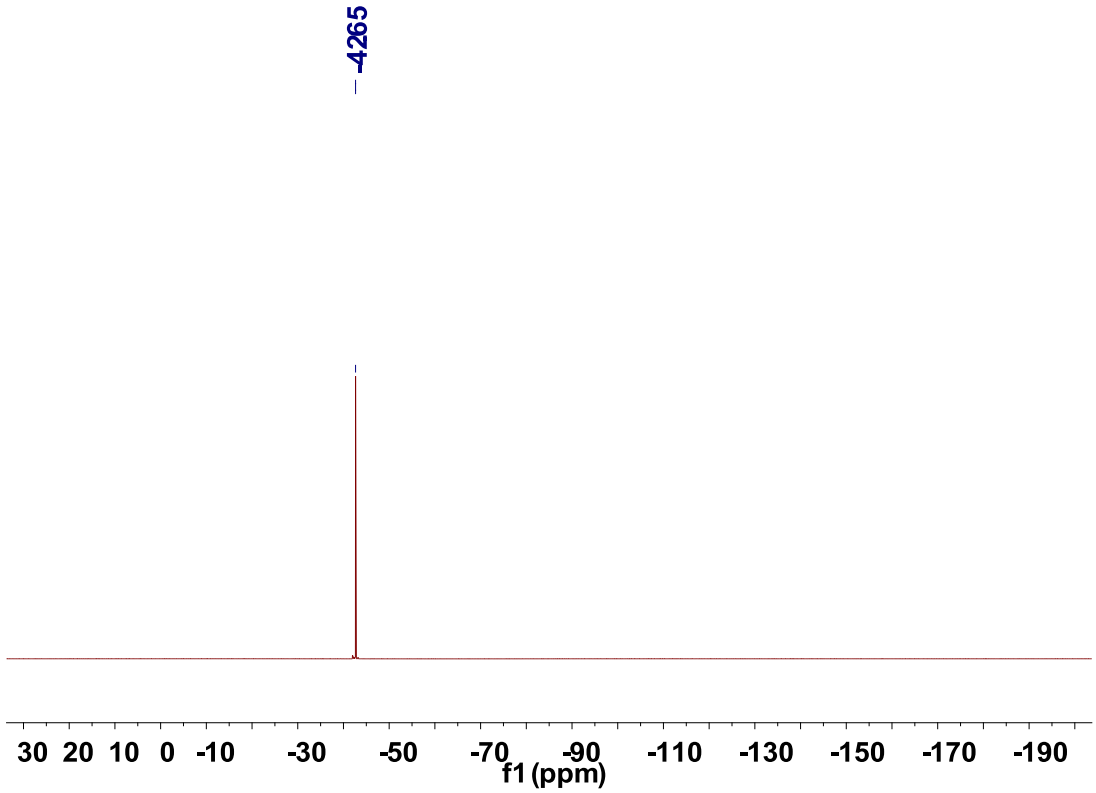
Obtained as a colorless oil in 80% yield (121.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.58 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.65 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 138.91, 137.85, 129.30 (q, *J* = 308.2 Hz), 124.34 (q, *J* = 2.5 Hz), 98.10 ppm. GC-MS (EI): *m/z* (%) 304.0 (100). HRMS: Calculated for $C_7H_4F_3IS$: 303.9030; Found: 303.9035.

Reference: Yagupol'skii, L. M.; Marenets, M. S. *Zhurnal Obshchei Khimii* **1954,** *24*, 885-91.

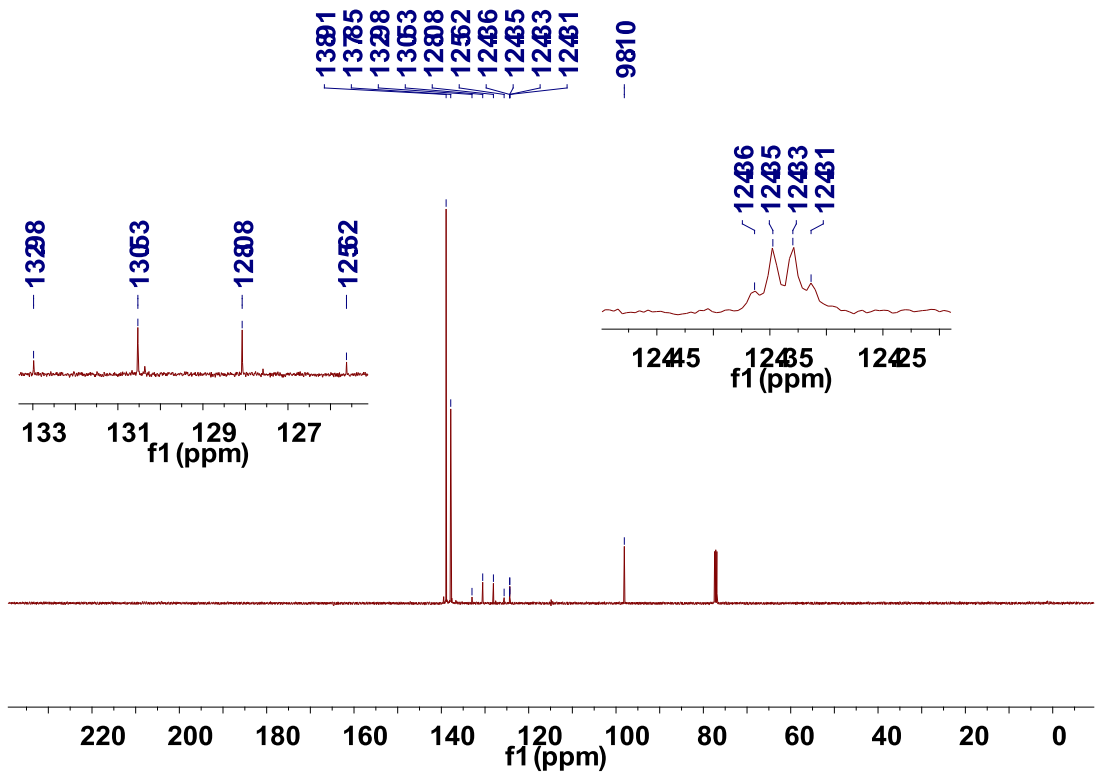
^{1}H NMR spectrum of 1-Iodo-4-[(trifluoromethyl)thio]benzene



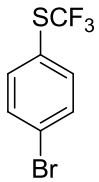
^{19}F NMR spectrum of 1-Iodo-4-[(trifluoromethyl)thio]benzene



^{13}C NMR spectrum of 1-Iodo-4-[(trifluoromethyl)thio]benzene



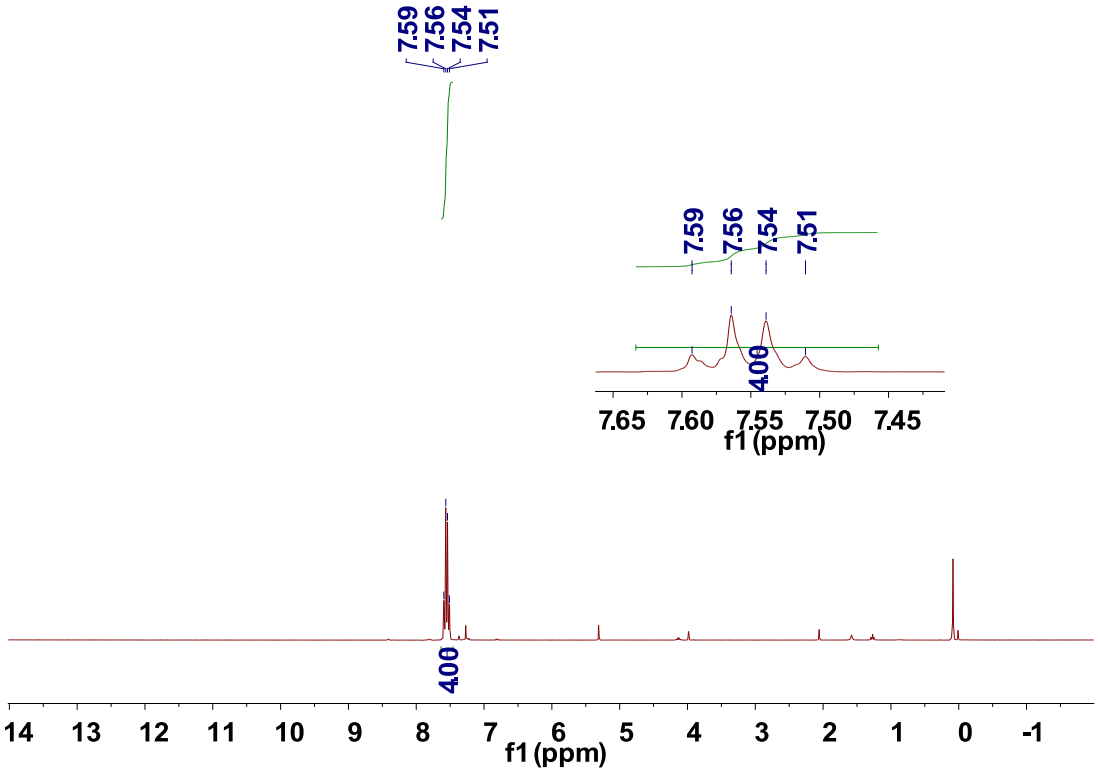
(4-Bromophenyl)(trifluoromethyl)sulfane



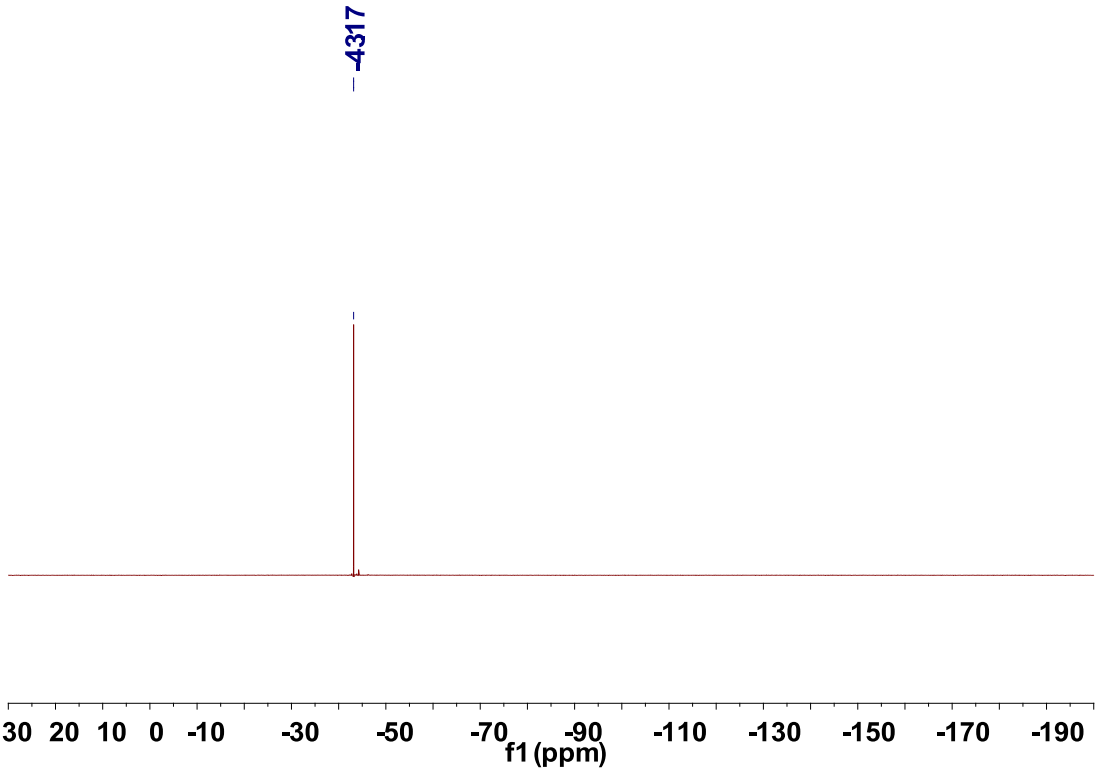
Obtained as a colorless oil in 90% yield (115.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.58 (d, *J* = 6.0 Hz, 2 H), 7.53 (d, *J* = 6.0 Hz, 2 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -43.17 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 137.88, 132.94, 129.3 (q, *J* = 309.5 Hz), 126.14, 123.55 (q, *J* = 2.5 Hz) ppm. GC-MS (EI): *m/z* (%) 256.0 (100). HRMS: Calculated for $C_7H_4BrF_3S$: 255.9169; Found: 255.9165.

Reference: Shao, X.-X.; Wang. X.-T.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2013,** *52*, 3457.

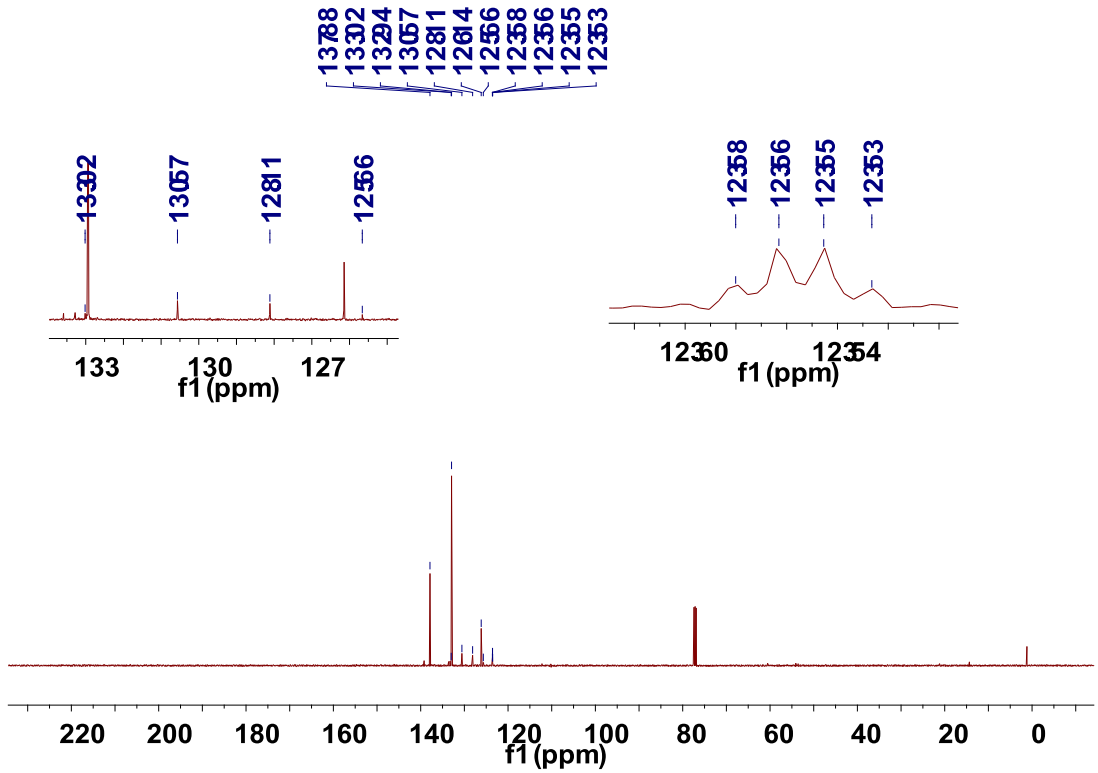
^{1}H NMR Spectrum of (4-Bromophenyl)(trifluoromethyl)sulfane



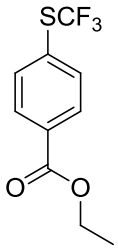
^{19}F NMR Spectrum of (4-Bromophenyl)(trifluoromethyl)sulfane



^{13}C NMR Spectrum of (4-Bromophenyl)(trifluoromethyl)sulfane



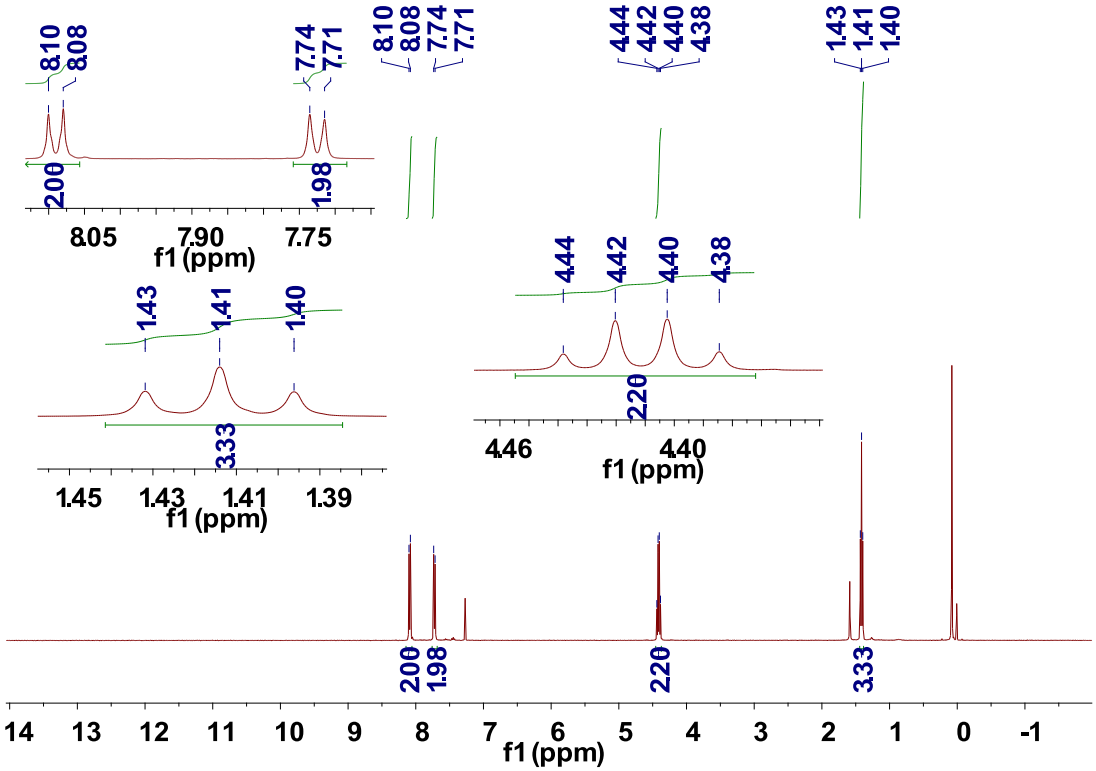
Ethyl 4-(trifluoromethylthio)benzoate



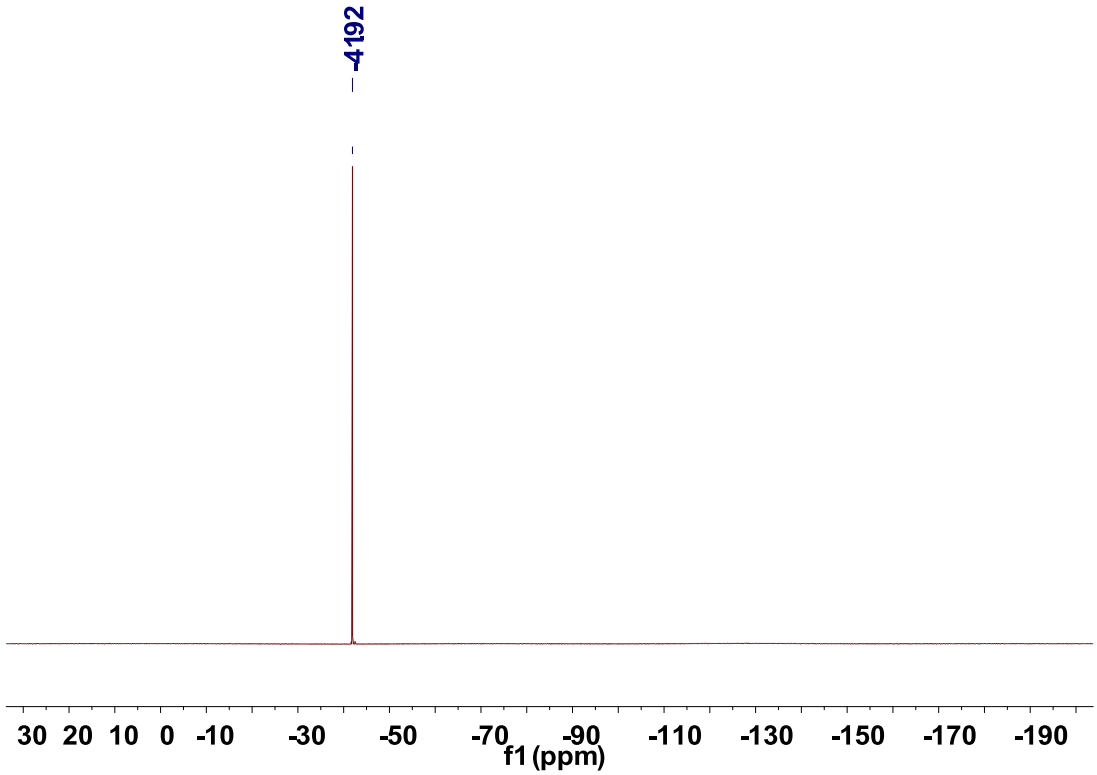
Obtained as a colorless oil in 93% yield (116.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.09 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 12.0 Hz, 2 H), 4.41 (q, *J* = 8.0 Hz, 2 H), 1.41 (t, *J* = 6.0 Hz, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -41.92 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 165.71, 135.70, 132.70, 129.46 (q, *J* = 308.0 Hz), 130.54, 129.87 (q, *J* = 2.5 Hz), 61.63, 14.42 ppm. GC-MS (EI): *m/z* (%) 205.0 (100), 250.1. HRMS: Calculated for $C_{10}H_9F_3O_2S$: 250.0275; Found: 250.0273.

Reference: Zhang, C.-P.; Vicic, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 183-185.

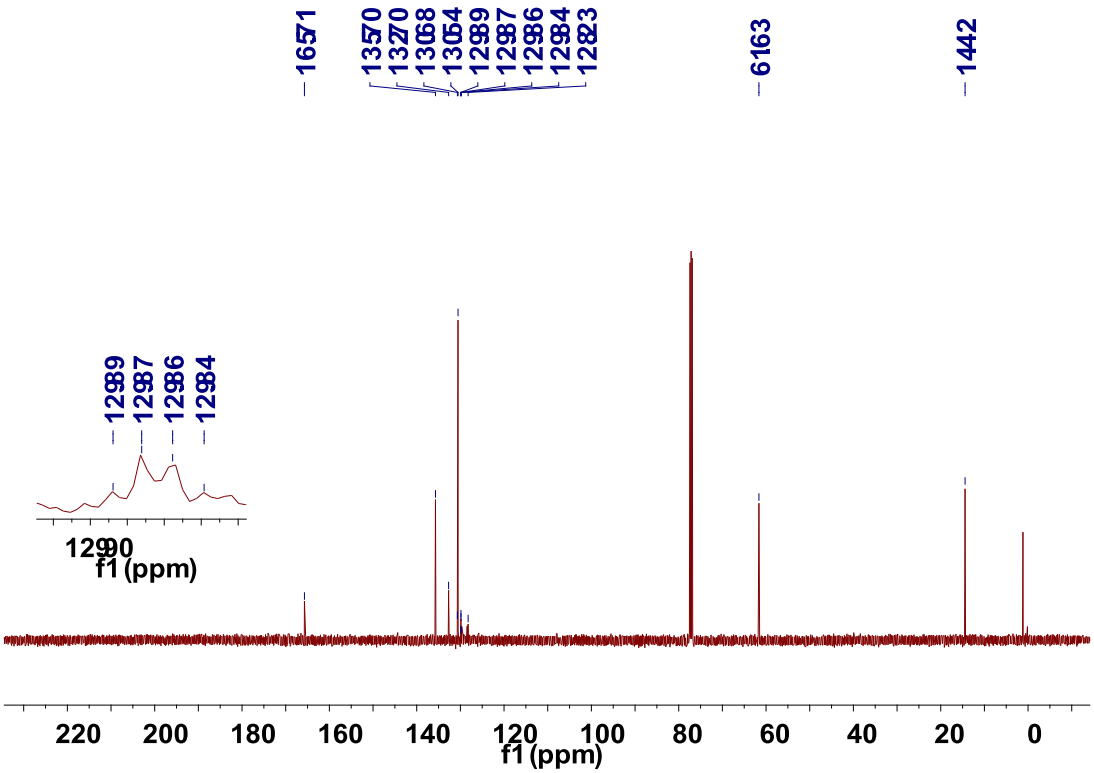
^{1}H NMR Spectrum of Ethyl 4-(trifluoromethylthio)benzoate



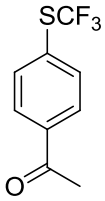
^{19}F NMR Spectrum of Ethyl 4-(trifluoromethylthio)benzoate



^{13}C NMR Spectrum of Ethyl 4-(trifluoromethylthio)benzoate



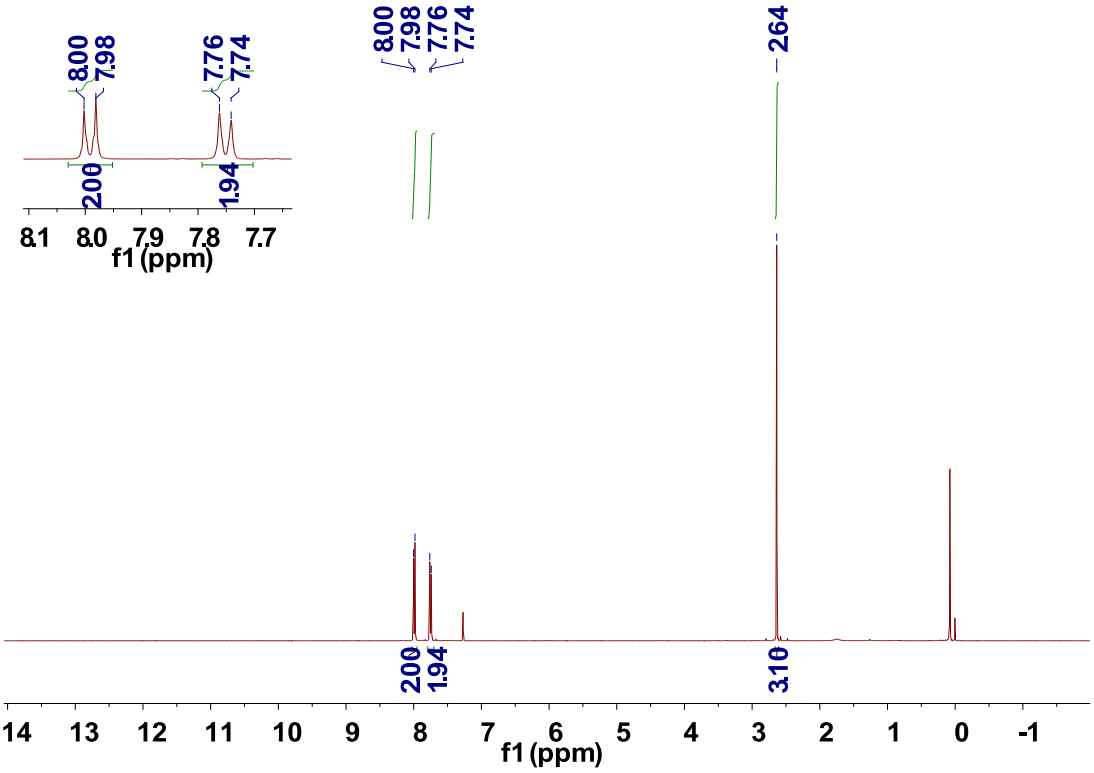
1-(4-((Trifluoromethyl)thio)phenyl)ethanone



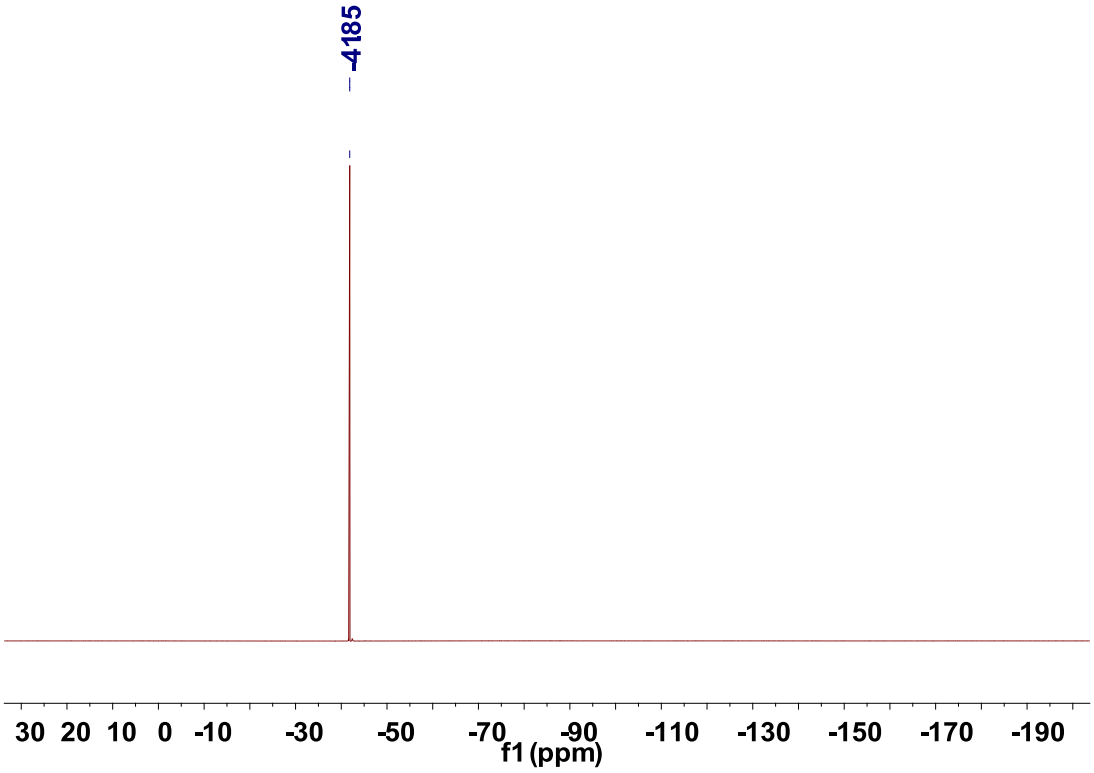
Obtained as a colorless oil in 89% yield (97.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.99 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 2.64 (s, 3 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.85 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 197.18, 138.64, 135.88, 129.41 (q, *J* = 309.5 Hz), 130.19 (q, *J* = 2.5 Hz）, 129.21, 26.86 ppm. GC-MS (EI): *m/z* (%) 205.0 (100), 220.1. HRMS: Calculated for $C_9H_7F_3OS$: 220.0170; Found: 220.0166.

Reference: Shao, X.-X.; Wang. X.-T.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2013,** *52*, 3457.

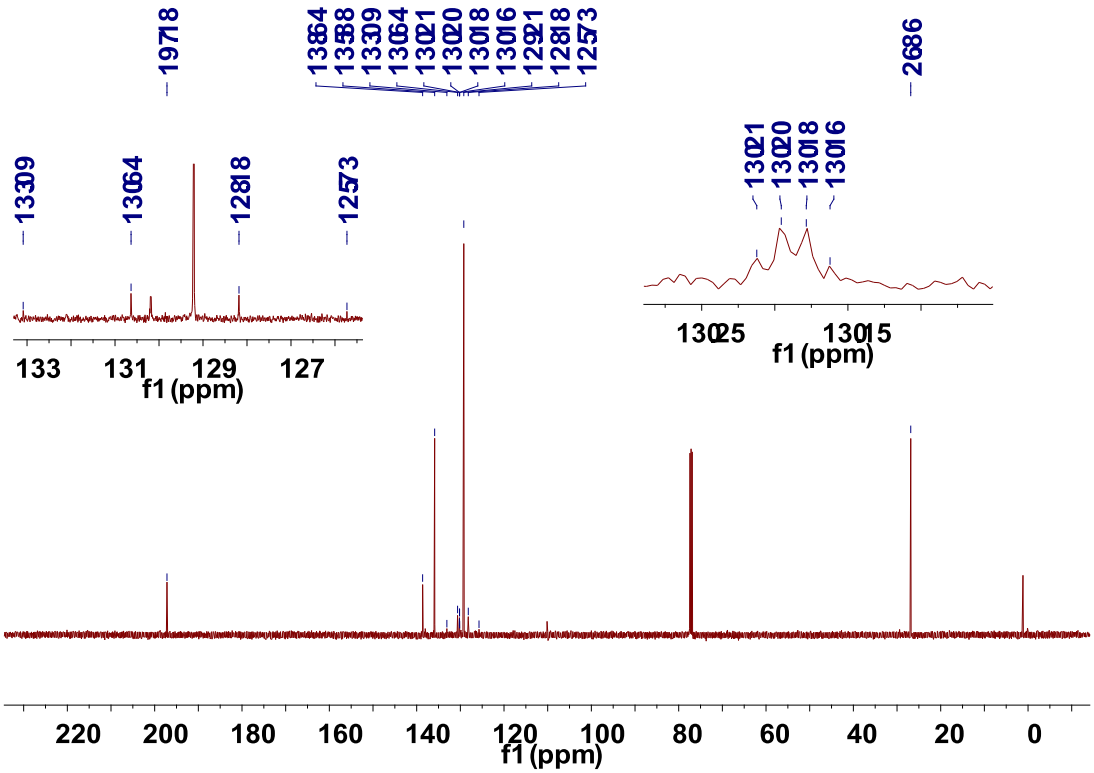
^{1}H NMR Spectrum of 1-(4-((Trifluoromethyl)thio)phenyl)ethanone



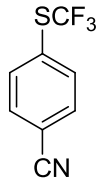
^{19}F NMR Spectrum of 1-(4-((Trifluoromethyl)thio)phenyl)ethanone



^{13}C NMR Spectrum of 1-(4-((Trifluoromethyl)thio)phenyl)ethanone



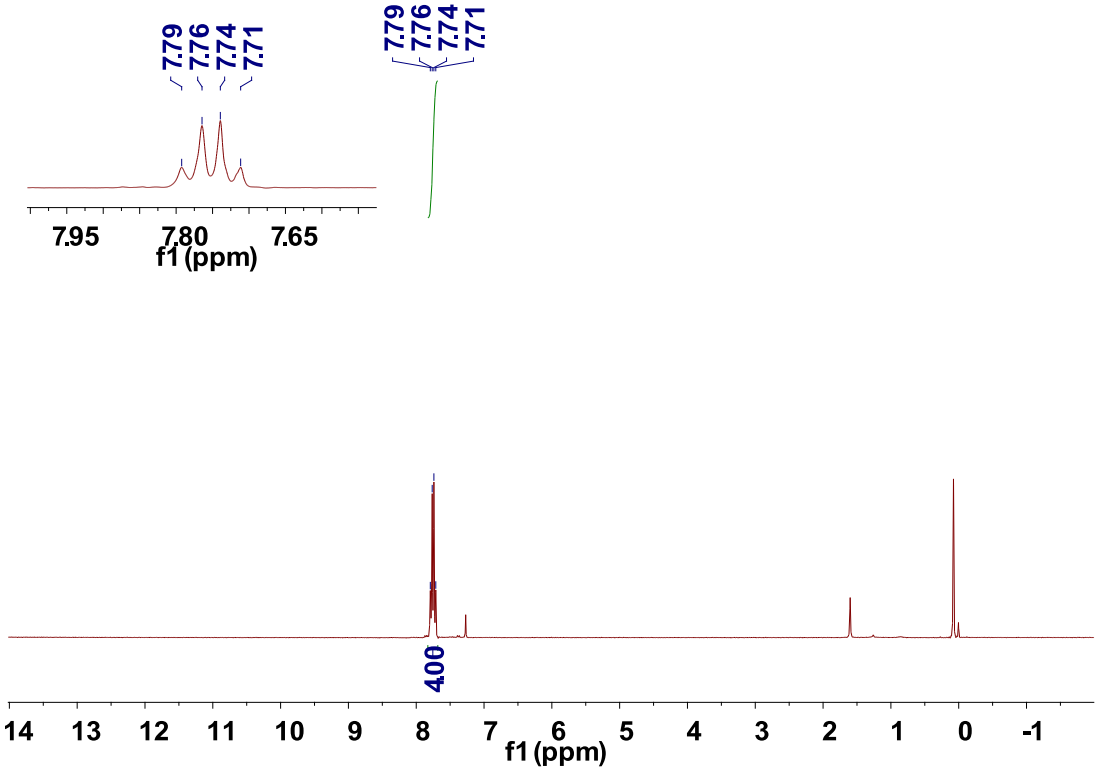
4- ((Trifluoromethyl)thio)benzonitrile



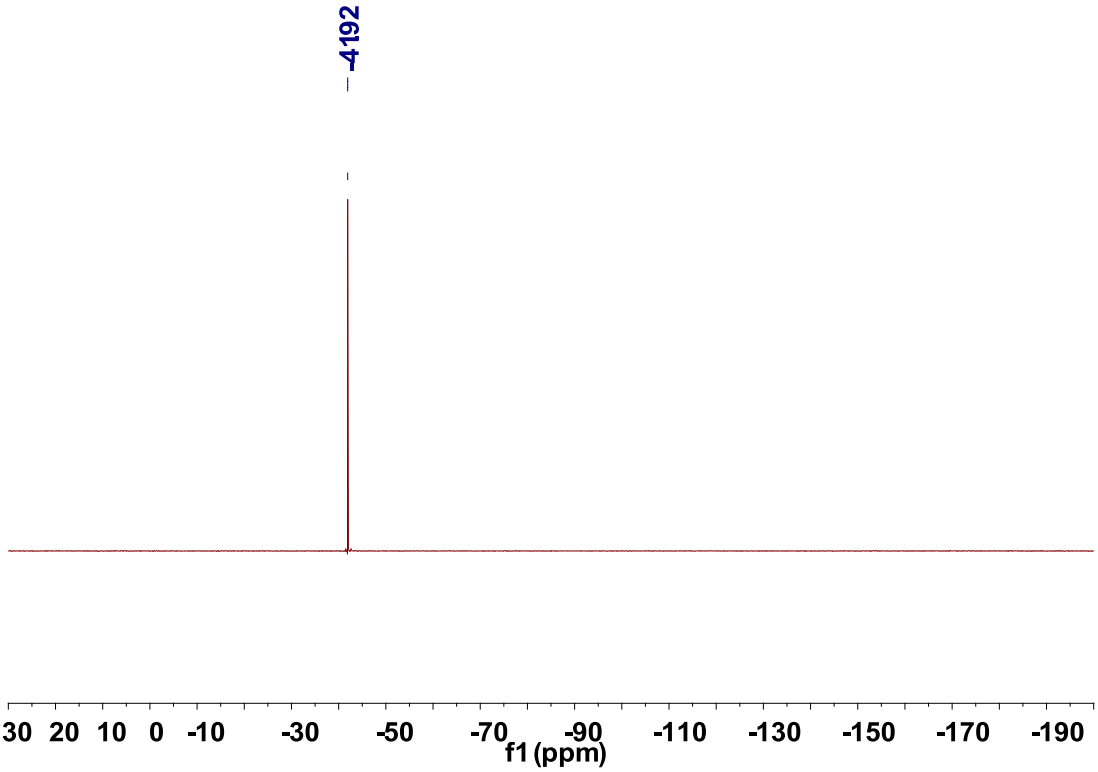
Obtained as a white solid in 92% yield (93.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.77 (d, *J* = 9.0 Hz, 2 H), 7.73 (d, *J* = 9.0 Hz, 2 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -41.92 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 136.12, 133.06, 129.16 (q, *J* = 309.5 Hz), 130.74 (q, *J* = 2.5 Hz), 117.75, 114.82 ppm; GC-MS(EI) *m/z* (%) 203, 134 (100). HRMS: Calculated for $C_8H_4F_3NS$: 203.0017; Found: 203.0014.

Reference: Chen, C.; Xie, Y.; Chu, L.-L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed* . **2012,** *51*, 2492.

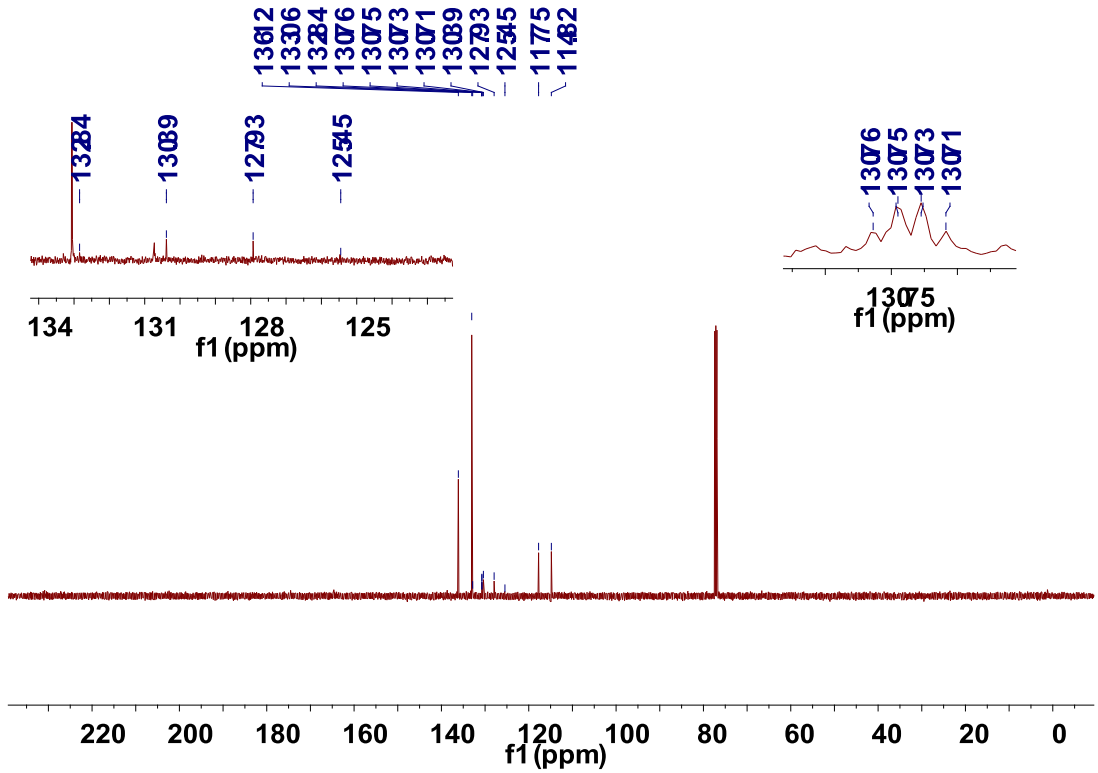
^{1}H NMR spectrum of 4- ((Trifluoromethyl)thio)benzonitrile



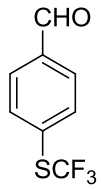
^{19}F NMR spectrum of 4- ((Trifluoromethyl)thio)benzonitrile



^{13}C NMR spectrum of 4- ((Trifluoromethyl)thio)benzonitrile



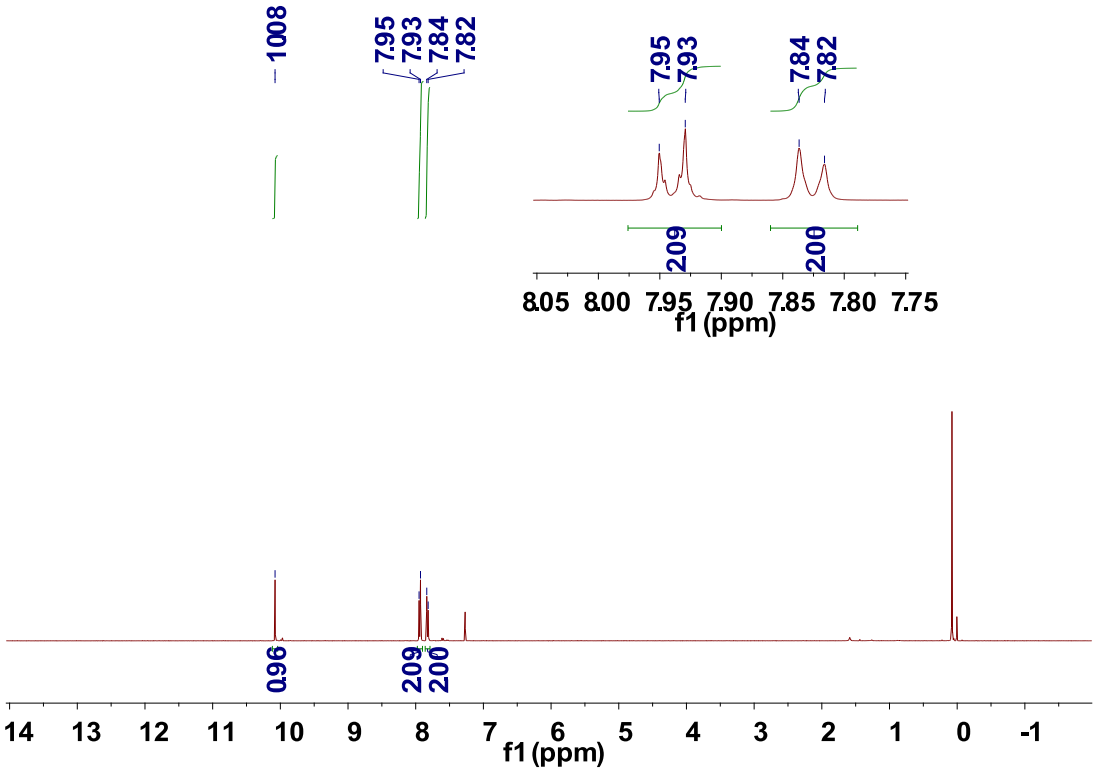
4- ((Trifluoromethyl)thio) benzaldehyde



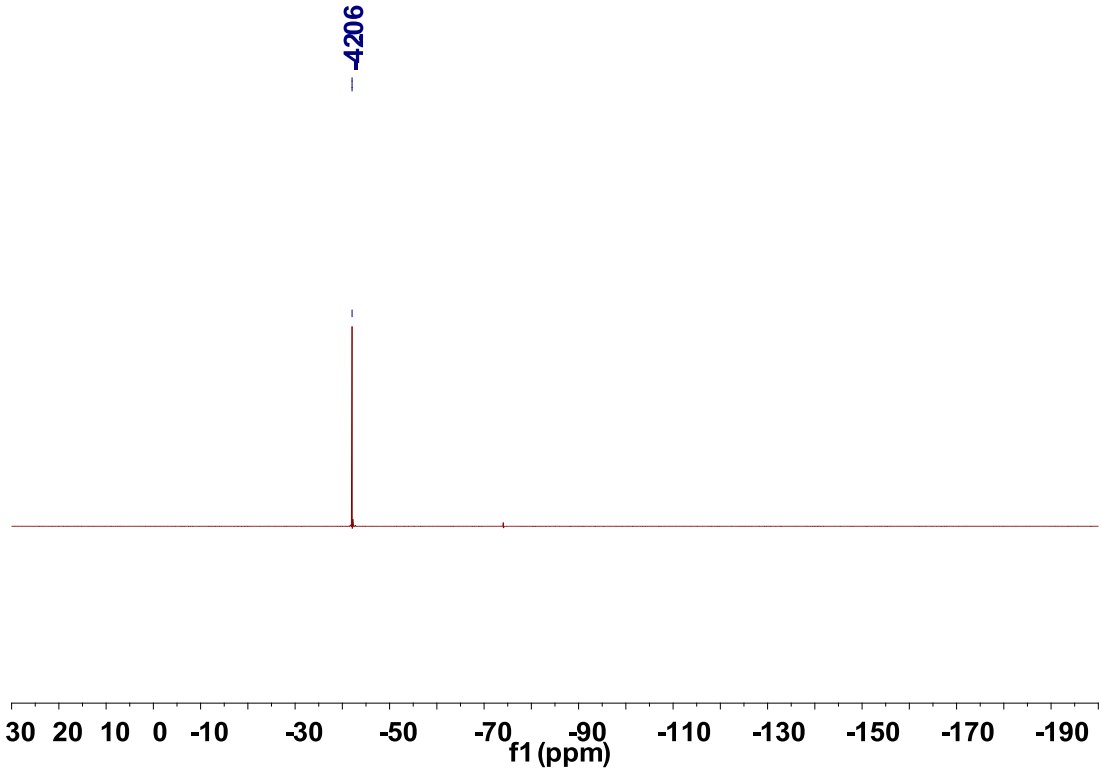
Obtained as a white solid in 87% yield (89.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.94 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -42.06 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 191.12, 137.56, 135.97, 129.30 (q, *J* = 308.2 Hz), 131.66 (q, *J* = 2.5 Hz), 130.30 ppm. GC-MS (EI): *m/z* (%) 205.0(100), 206.0. HRMS: Calculated for $C_8H_5F_3OS$: 206.0013; Found: 206.0014.

Reference: Nuria, R.; Mercedes, M.; Gregorio, A. *Adv. Syn. & Catal.* **2007**, *349*, 987.

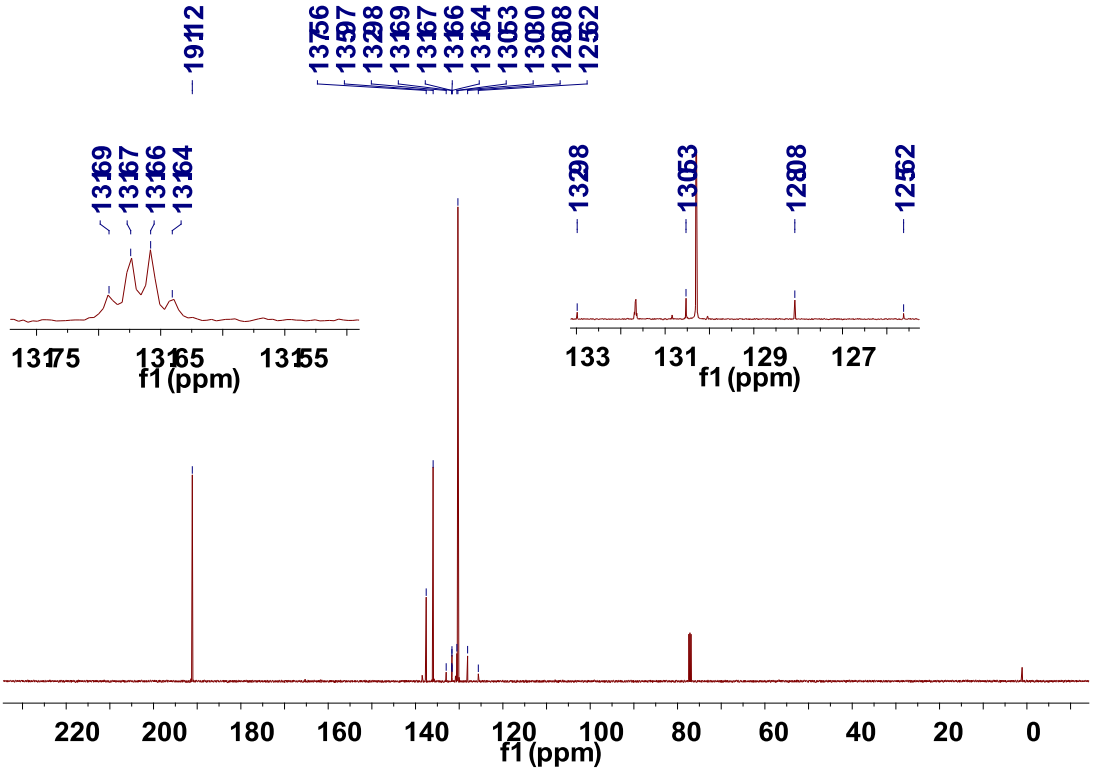
^{1}H NMR spectrum of 4- ((Trifluoromethyl)thio) benzaldehyde



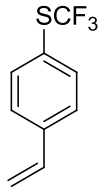
^{19} F NMR spectrum of 4-((Trifluoromethyl)thio) benzaldehyde



^{13}C NMR spectrum of 4-((Trifluoromethyl)thio) benzaldehyde



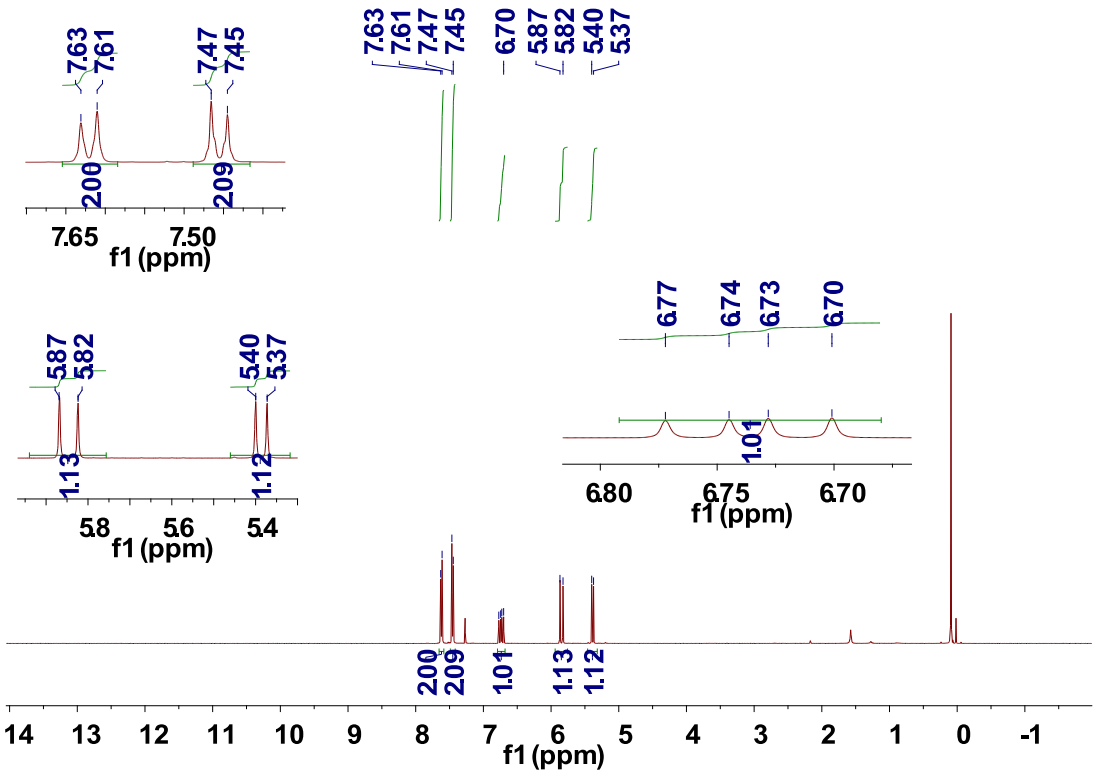
(Trifluoromethyl)(4-vinylphenyl)sulfane



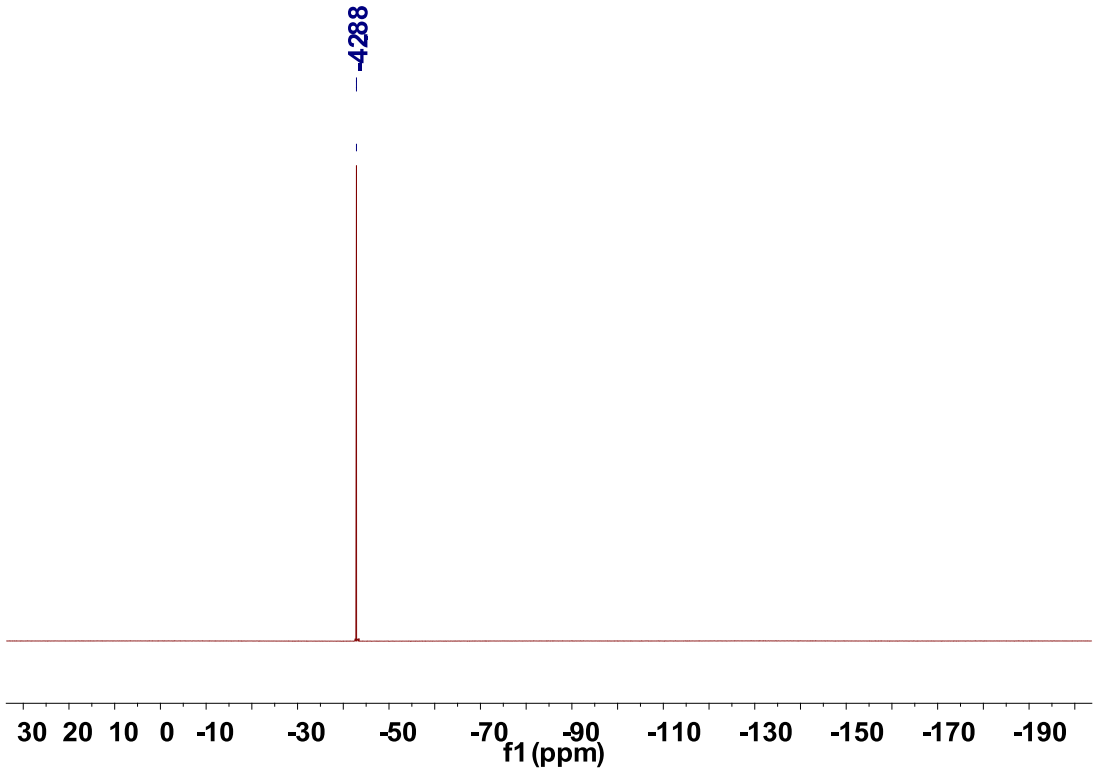
Obtained as a colorless oil in 79% yield (80.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.62 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 6.73 (dd, *J* = 12.0 Hz, 16.0 Hz, 1 H), 5.84 (d, *J* = 20.0 Hz, 1 H), 5.38 (d, *J* = 12.0 Hz, 1 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.88 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 140.26, 135.76, 133.38, 129.70 (q, *J* = 308.2 Hz), 127.29, 123.44 (q, *J* = 2.5 Hz), 116.51 ppm; GC-MS (EI) *m/z* (%) 204 (100). HRMS: Calculated for $C_9H_7F_3S$: 204.0221; Found: 204.0219.

Reference: Chen, C.; Xie, Y.; Chu, L.-L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2012**, *51*, 2492.

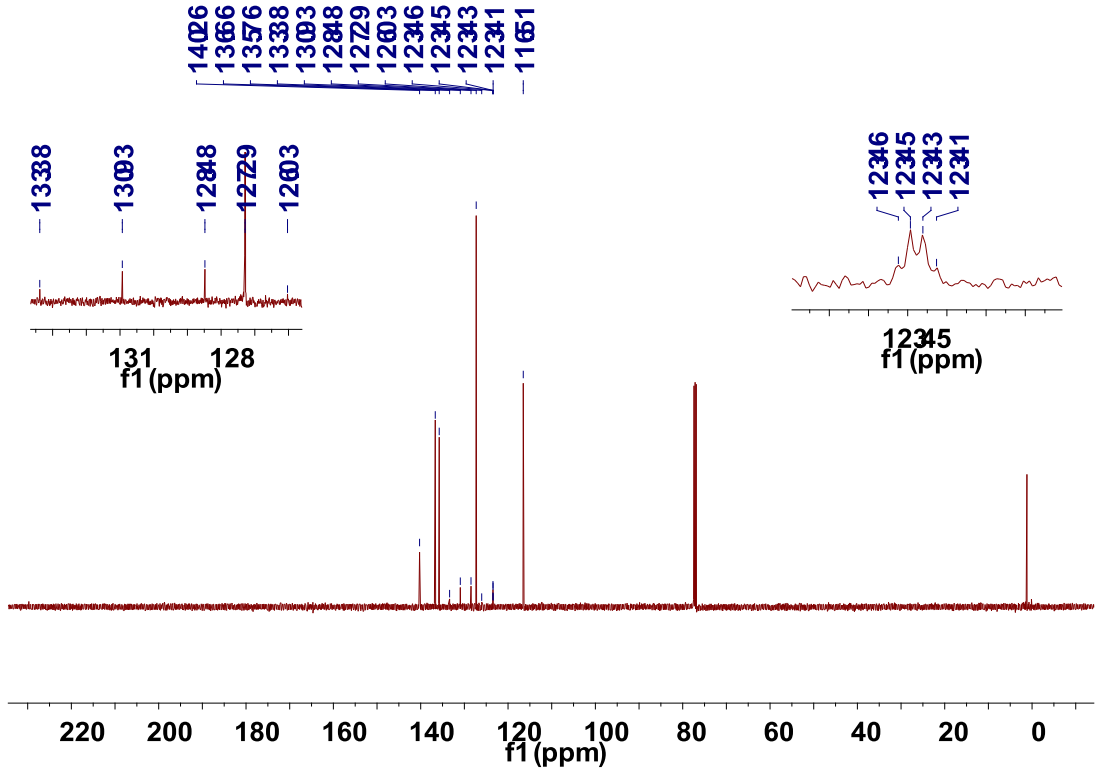
^{1}H NMR Spectrum of (Trifluoromethyl)(4-vinylphenyl)sulfane



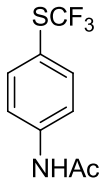
^{19}F NMR Spectrum of (Trifluoromethyl)(4-vinylphenyl)sulfane



^{13}C NMR Spectrum of (Trifluoromethyl)(4-vinylphenyl)sulfane



***N*-(4-((Trifluoromethyl)thio)phenyl)acetamide**

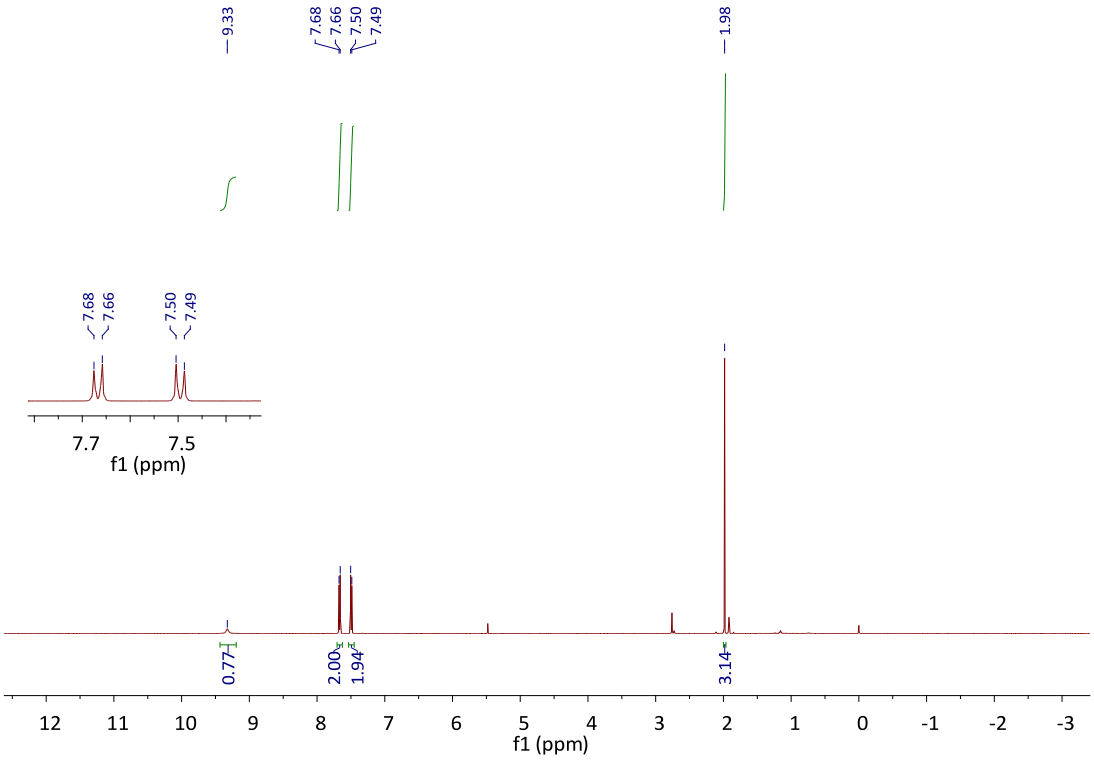


Obtained in 81% yield determined by ^{19}F NMR, trifluoromethylbenzene as internal standard, 56% isolated yield. ^{1}H NMR (500 MHz, d_6-acetone, 293 K, TMS) δ 9.33 (s, 1 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 1.98 (s, 3 H) ppm; ^{19}F NMR (376 MHz, d_6-acetone) δ -44.63 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, d_6-acetone, 293 K, TMS) δ 169.55, 143.57, 138.31, 130.87 (q, *J* = 307.0 Hz) , 120.74, 117.38 (q, *J* = 2.5 Hz), 24.48 ppm. GC-MS (EI): *m/z* (%) 124.0 (100), 235.0. HRMS: Calculated for $C_9H_8F_3NOS$: 235.0279; Found: 235.0277.

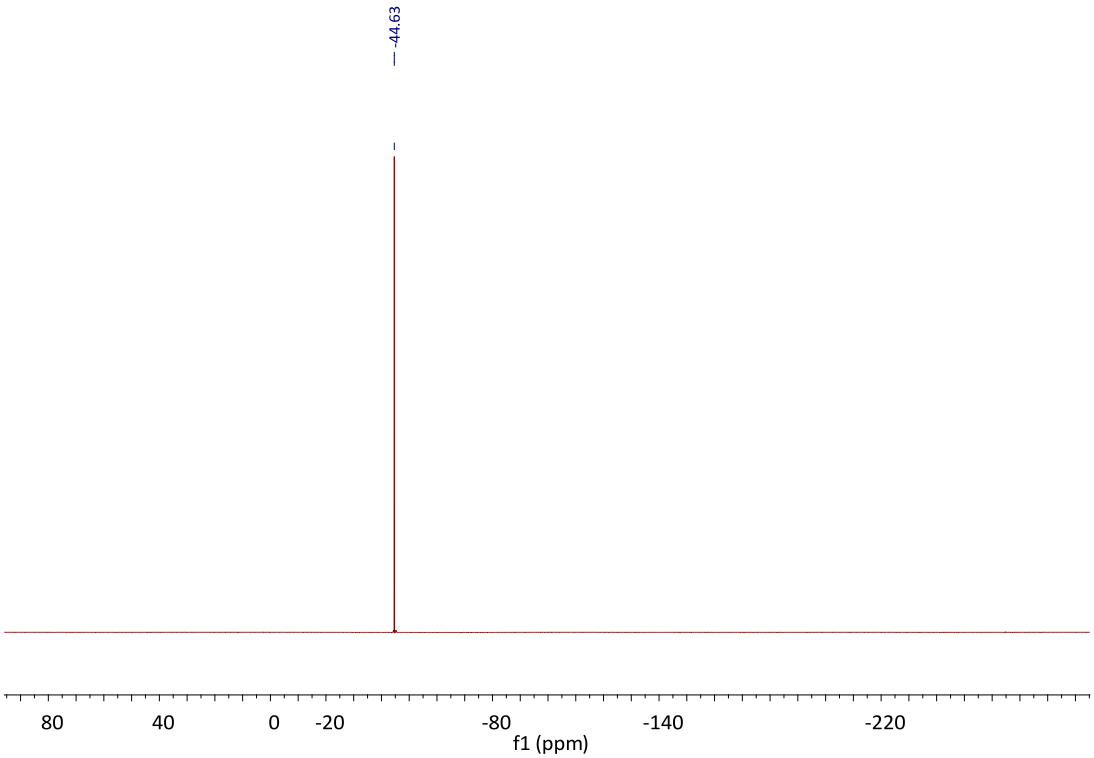
Reference: Kieltsch, I.; Eisenberger, P.; Togni, A. *Angew. Chem. Int. Ed.* **2007**, *46*,

754

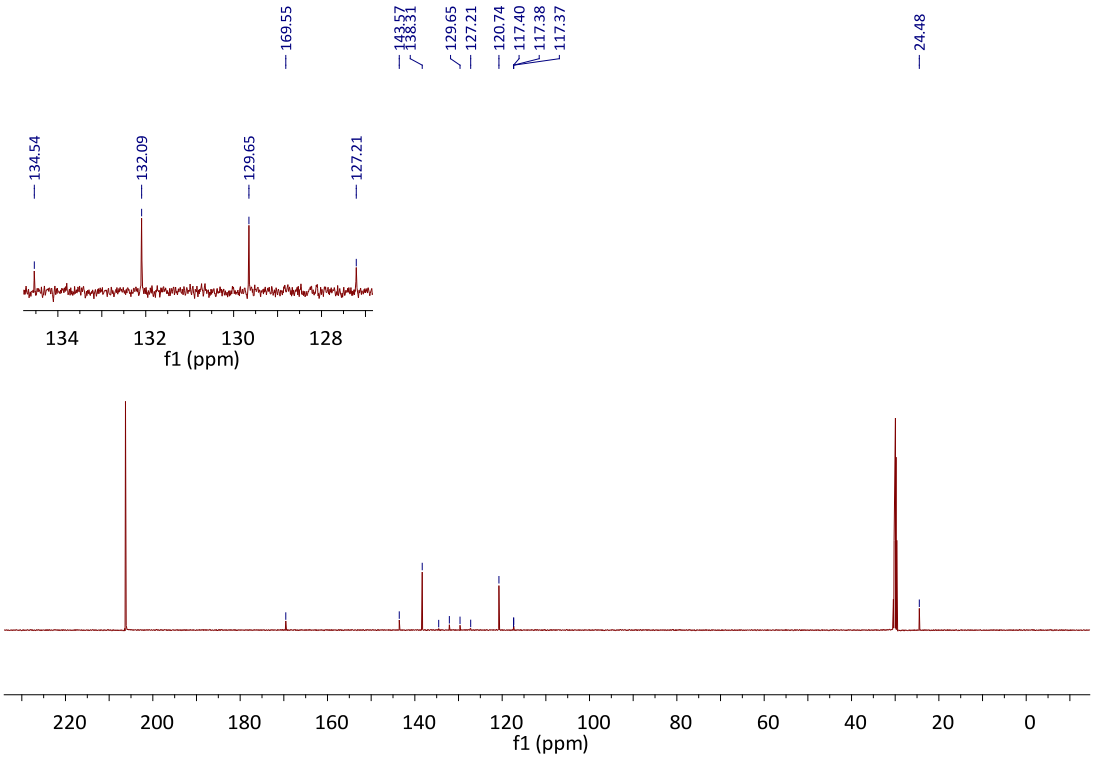
^{1}H NMR Spectrum of *N*-(4-((trifluoromethyl)thio)phenyl)acetamide



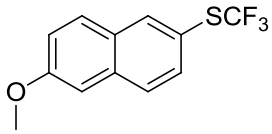
^{19}F NMR Spectrum N-(4-((trifluoromethyl)thio)phenyl)acetamide



^{13}C NMR Spectrum of *N*-(4-((trifluoromethyl)thio)phenyl)acetamide



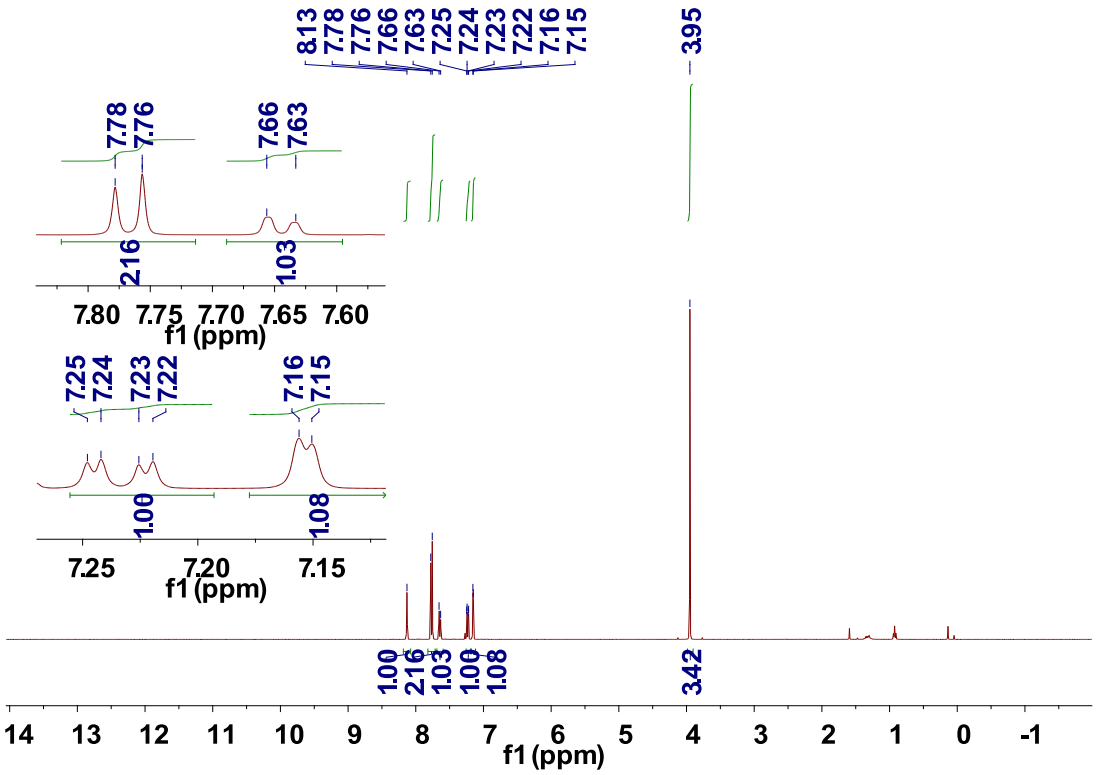
(6-Methoxynaphthalen-2-yl)(trifluoromethyl)sulfane



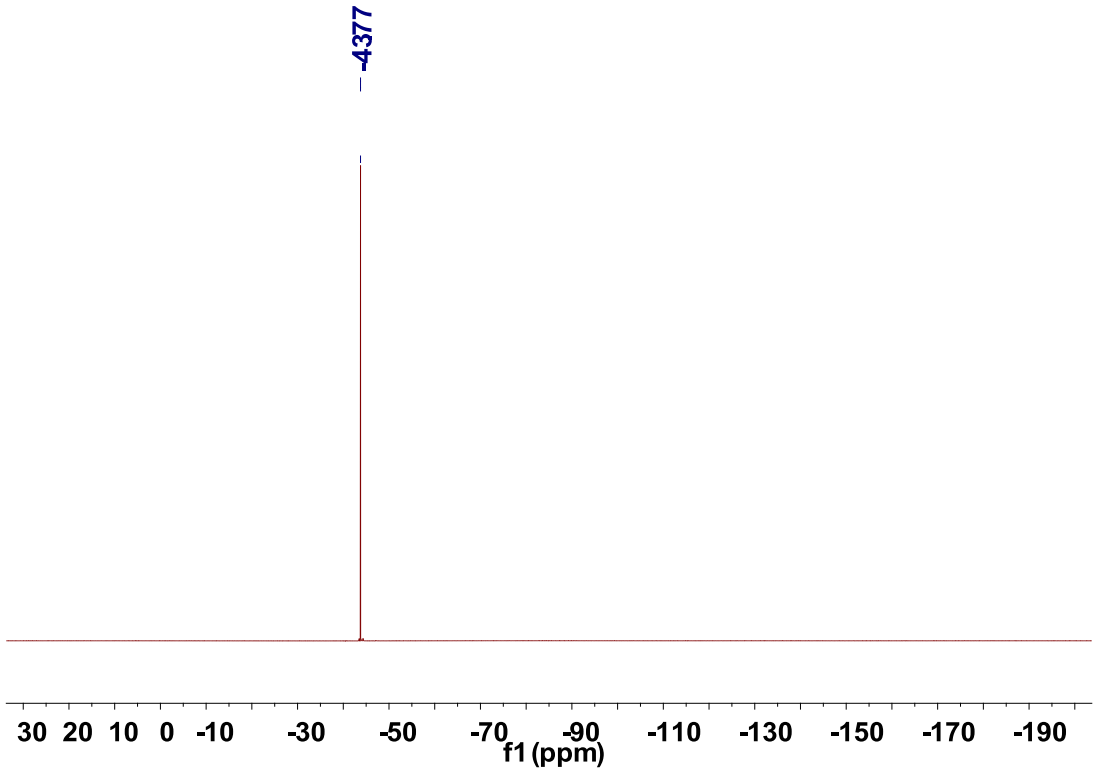
Obtained as white solid in 84% yield (108.4mg). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.13 (s, 1 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 12.0 Hz, 1 H), 7.23 (dd, *J* = 8.0 Hz, 4.0 Hz, 1 H), 7.15 (d, *J* = 12.0 Hz, 1 H), 3.95 (s, 3 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.77 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 159.35, 137.11, 135.63, 132.74, 129.85, 129.94 (q, *J* = 308.2 Hz), 128.71, 128.09, 120.09, 118.66 (q, *J* = 2.5 Hz), 105.73, 55.50 ppm. GC-MS (EI): *m/z* (%) 258.1 (100). HRMS: Calculated for $C_{12}H_9F_3OS$: 258.0326; Found: 258.0331.

Reference: Chen, C.; Xie, Y.; Chu, L.-L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2012,** *51*, 2492.

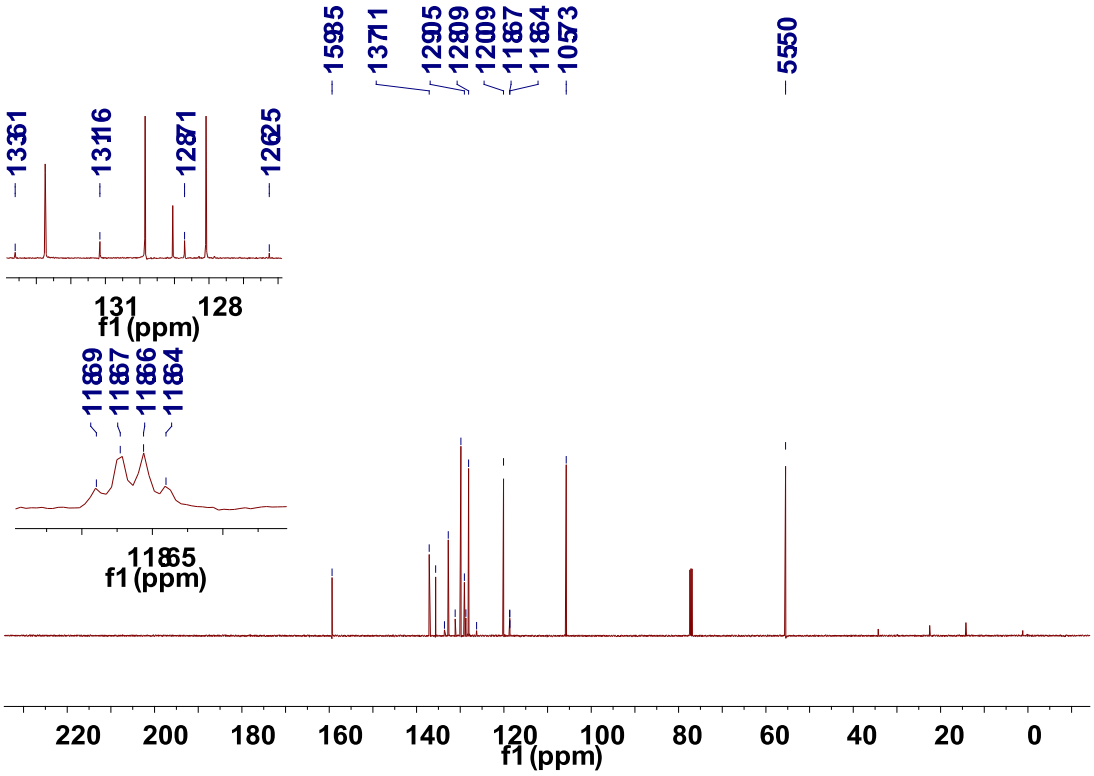
^{1}H NMR Spectrum of (6 - Methoxynaphthalen- 2- yl)(trifluoromethyl)sulfane



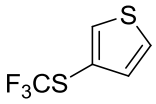
^{19}F NMR Spectrum of (6 - Methoxynaphthalen- 2- yl)(trifluoromethyl)sulfane



^{13}C NMR Spectrum of (6 - Methoxynaphthalen- 2- yl)(trifluoromethyl)sulfane



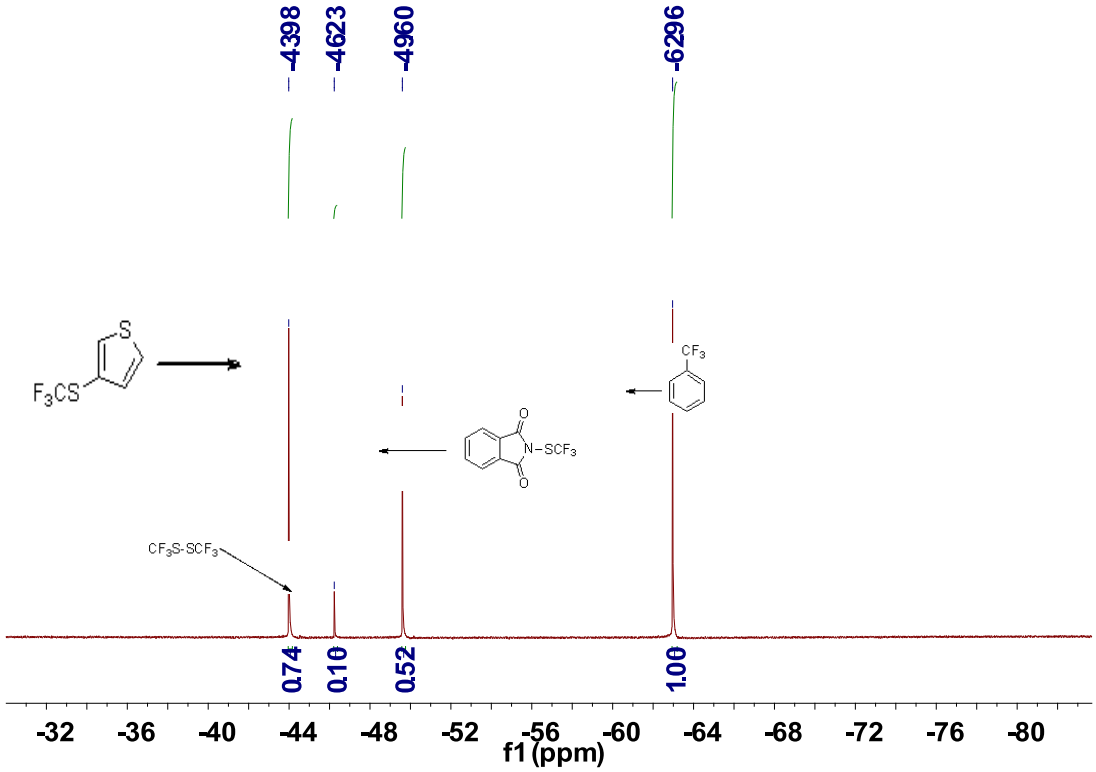
3-((Trifluoromethyl)thio)thiophene



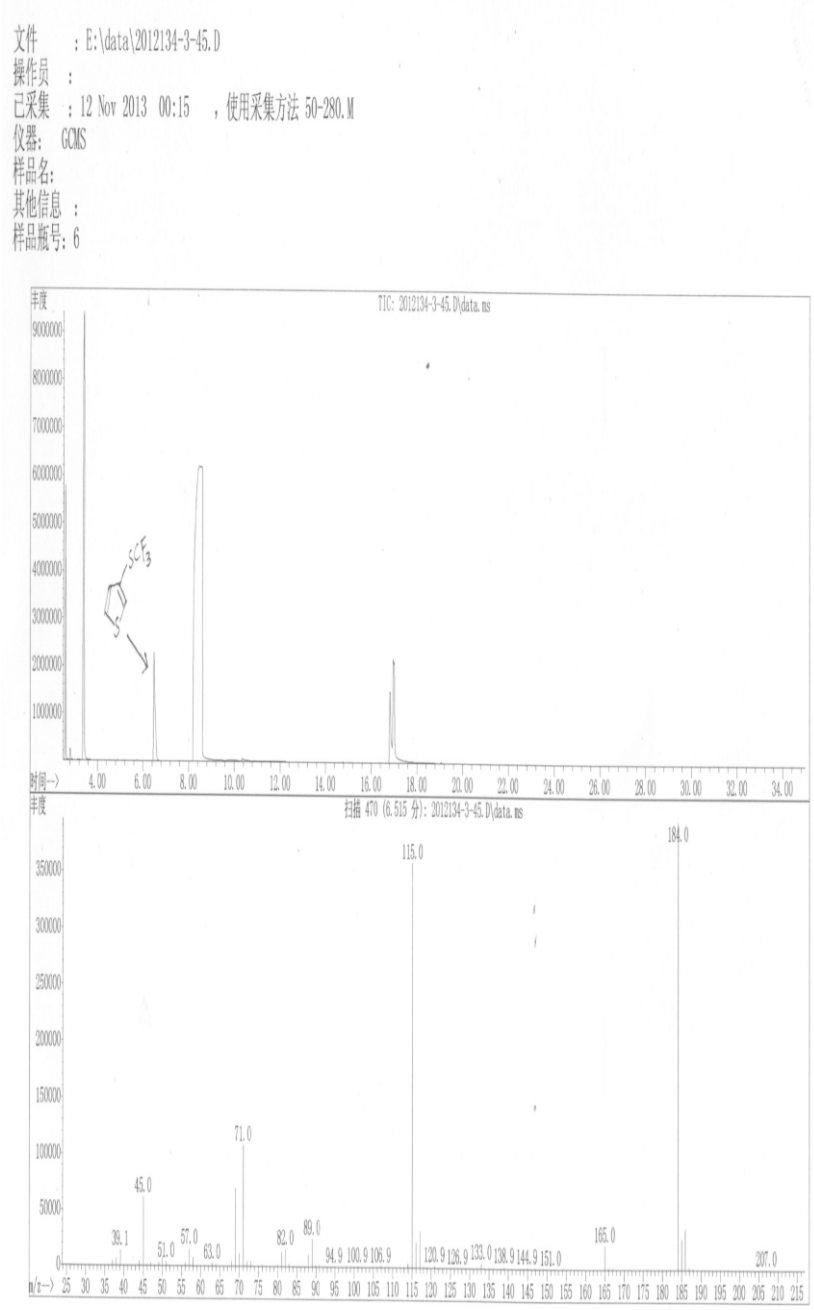
Obtained in 74% yield determined by ^{19}F NMR, trifluoromethylbenzene as internal standard. ^{19}F NMR (376 MHz, diglyme, 293 K, TMS) δ -43.98 ppm.

Reference: Zhang, C.-P.; Vicic, D. A. *Chem. Asian J.* **2012,** *7*, 1756.

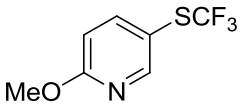
^{19}F NMR Spectroscopy of the reaction mixture for the preparation of 3-((trifluoromethyl)thio)thiophene.



GC/MS spectroscopy of the reaction mixture for the preparation of 3-((trifluoromethyl)thio)thiophene.



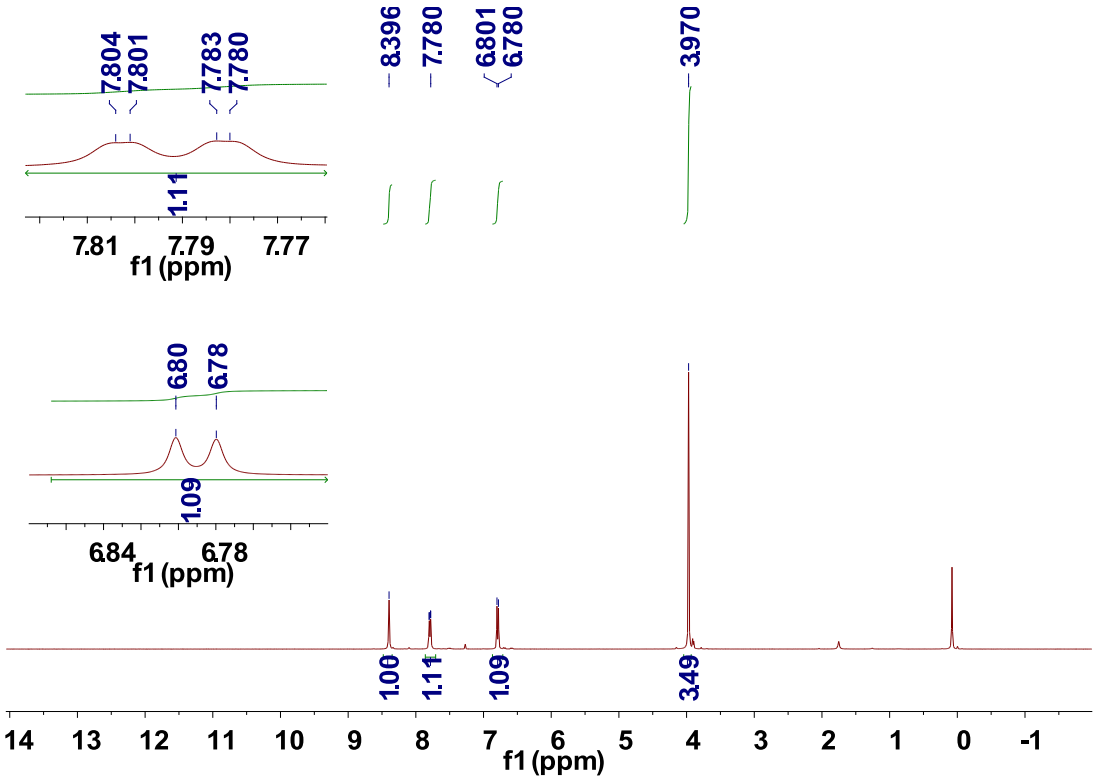
1-Methoxy- 5-((trifluoromethyl)thio)pyridine



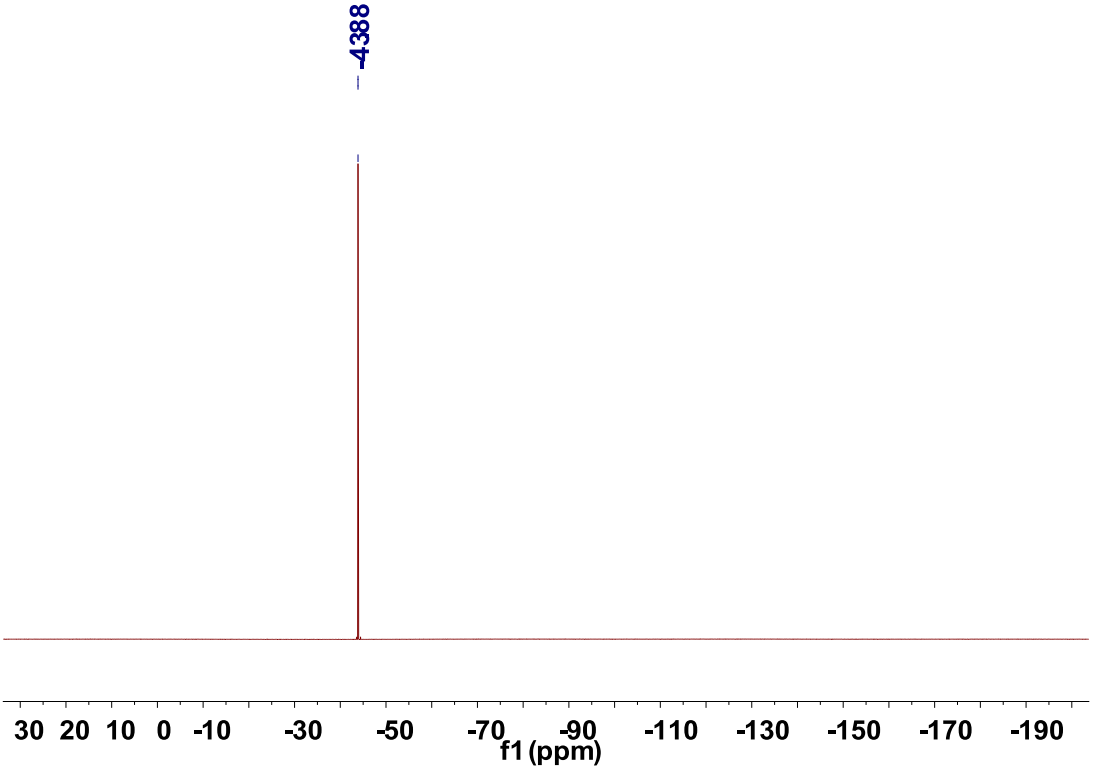
Obtained as a colorless oil in 62% yield (67.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 8.40 (s, 1 H), 7.79 (dd, *J* = 6.3 Hz, 0.9 Hz, 1 H), 6.79 (d, *J*= 6.0 Hz, 1 H), 3.97 (s, 3 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.88 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K, TMS) δ 165.90, 154.74, 146.04, 129.32 (q, *J* = 309.5 Hz), 113.17 (q, *J* = 2.5 Hz), 112.23, 54.11 ppm. GC-MS (EI): *m/z* (%) 209.1 (100). HRMS: Calculated for $C_7H_6F_3NOS$: 209.0122; Found: 209.0119.

Reference: Shao, X.-X.; Wang. X.-T.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2013,** *52*, 3457.

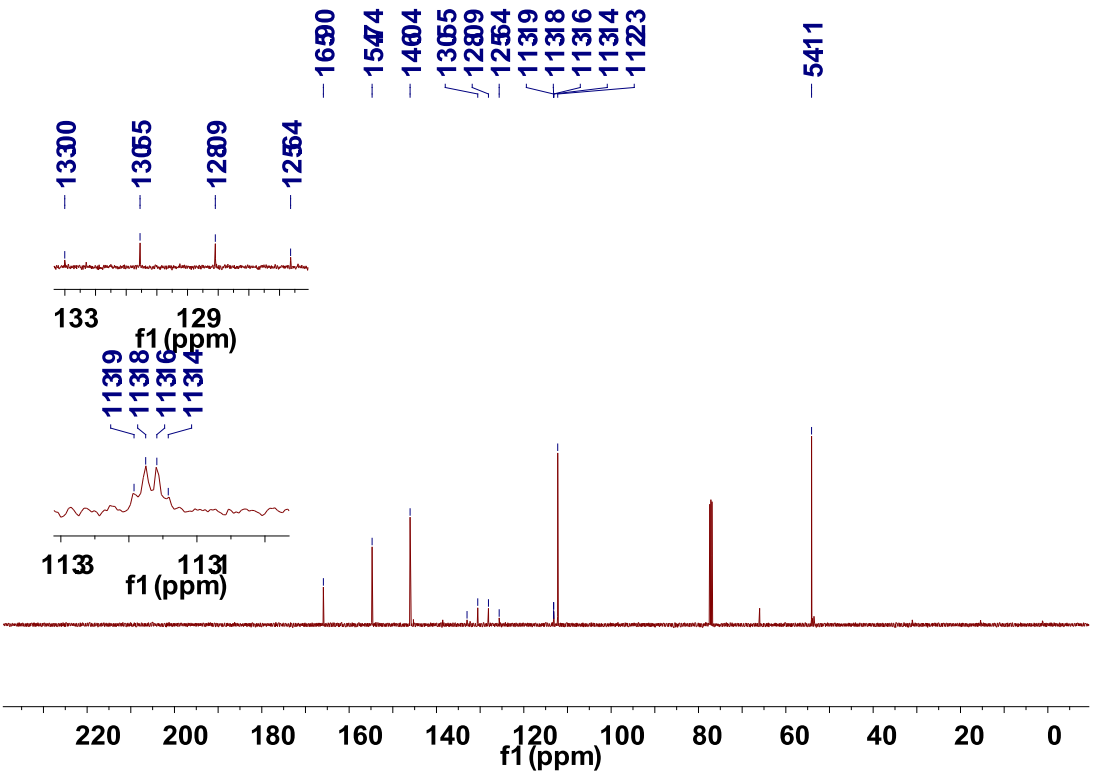
^{1}H NMR Spectrum of 1-Methoxy- 5-((trifluoromethyl)thio)pyridine



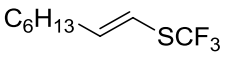
^{19}F NMR Spectrum of 1-Methoxy- 5-((trifluoromethyl)thio)pyridine



^{13}C NMR Spectrum of 1-Methoxy- 5-((trifluoromethyl)thio)pyridine



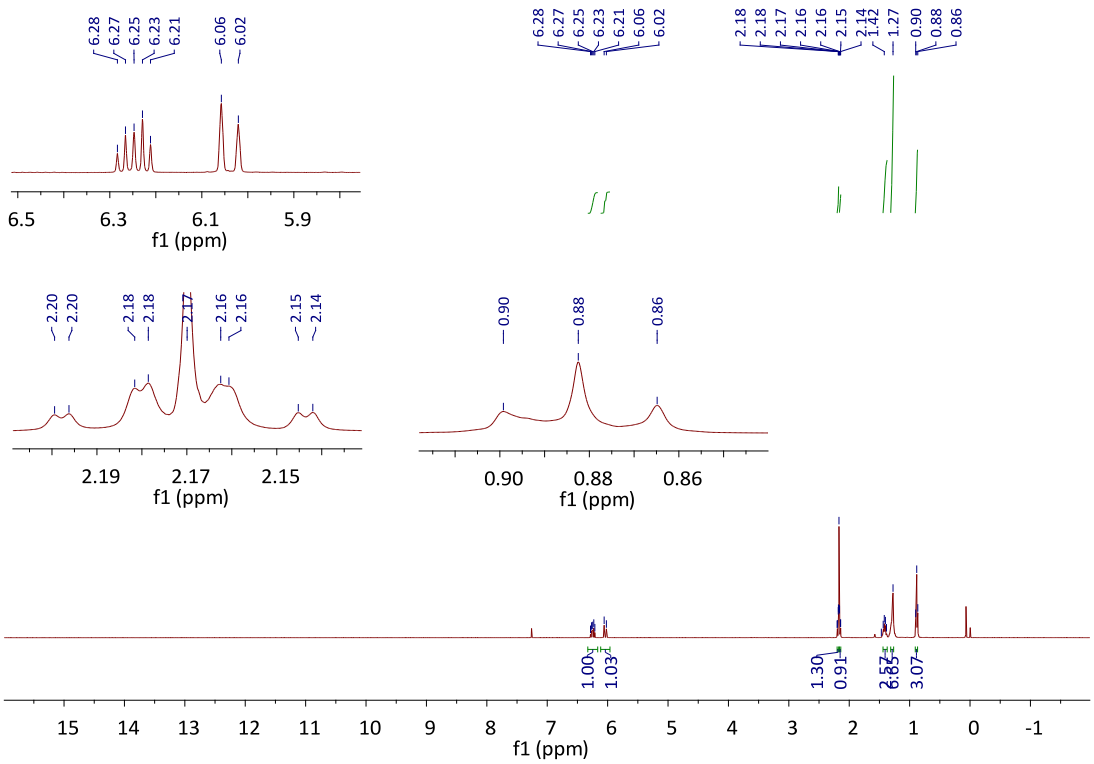
(E)-Oct-1-en-1-yl(trifluoromethyl)sulfane



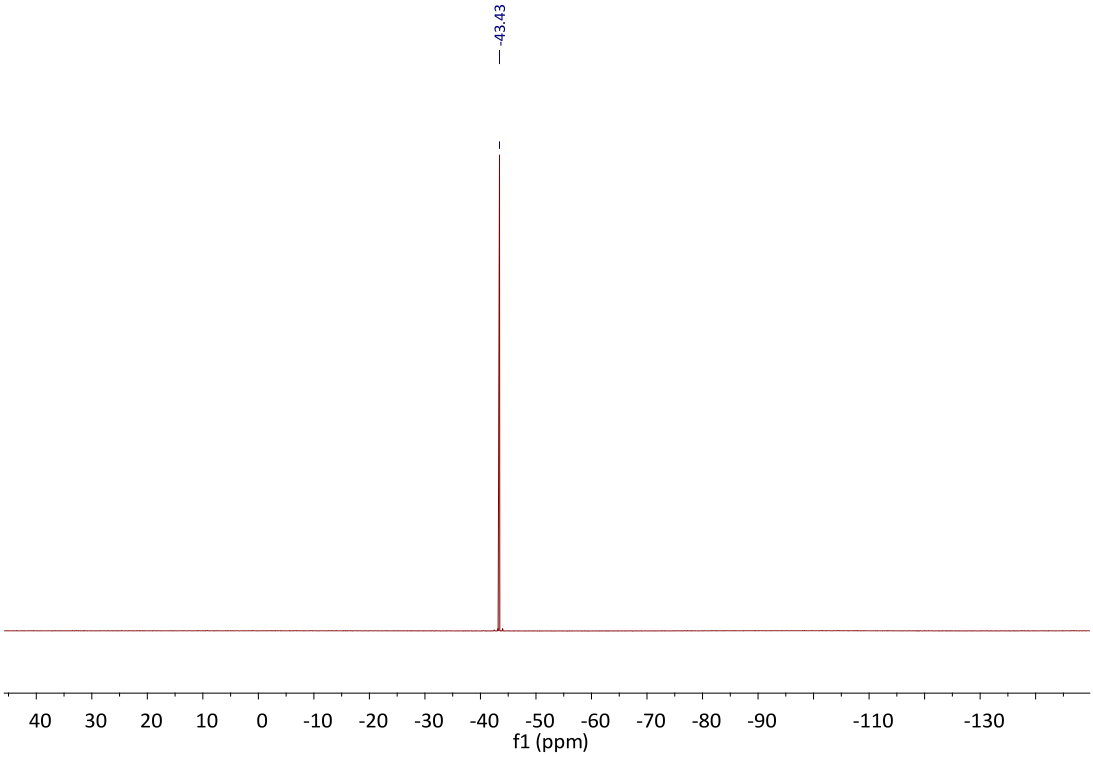
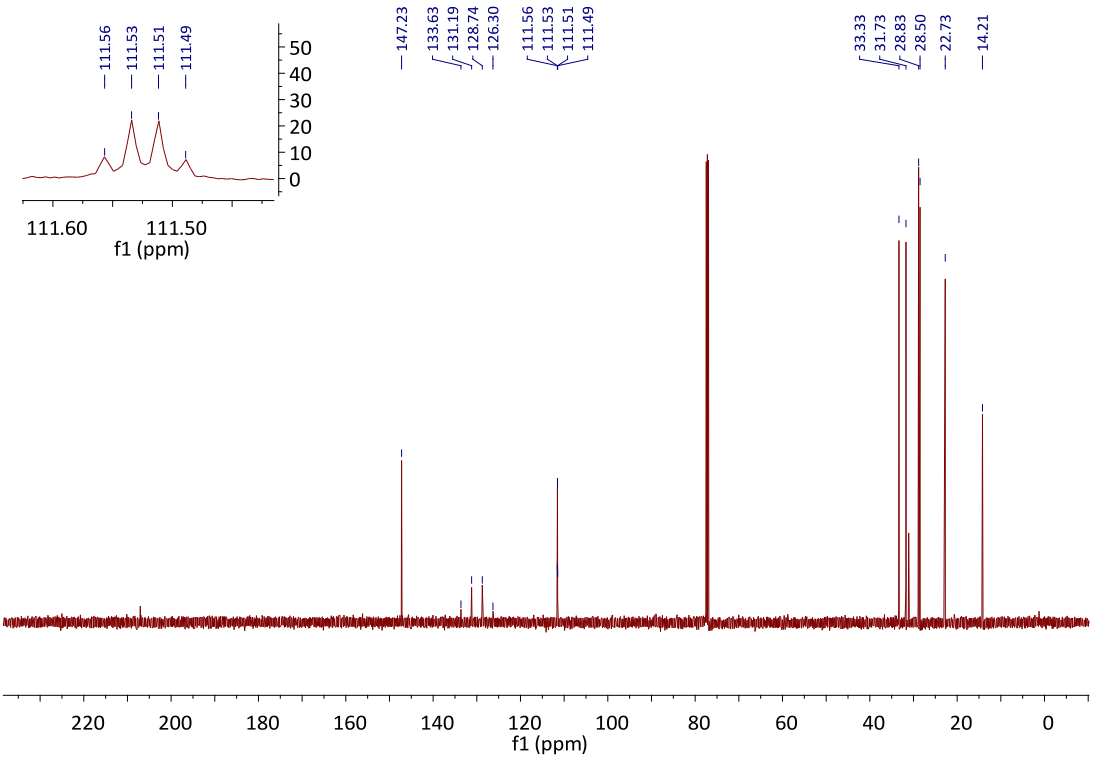
Obtained as a colorless oil, 74% yield as determined by ^{19}F NMR, trifluoromethylbenzene as internal standard，50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 6.28-6.22 (m, 1 H), 6.04 (d, *J* = 16.0 Hz, 1 H), 2.17 (qd, *J* = 7.1 Hz, 1.3 Hz, 2 H), 1.47-1.38 (m, 2 H), 1.33-1.25 (m, 6 H), 0.88 (t, *J* = 8.0 Hz, 3 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.43 (s, 3 F) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$, 293K, TMS) δ 147.23, 130.00 (q, *J* = 308.2 Hz), 111.52 (q, *J* = 2.5Hz), 33.33, 31.73, 28.83, 28.50, 22.73, 14.21 ppm. GC-MS (EI): *m/z* (%) 128.0 (100), 212.1. HRMS: Calculated for $C_9H_{15}F_3S$: 212.0847; Found: 212.0851.

Reference: Shao, X.-X.; Wang. X.-T.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2013**, *52*, 3457.

^{1}H NMR Spectrum of (E)-oct-1-en-1-yl(trifluoromethyl)sulfane



^{19}F NMR Spectrum of (E)-oct-1-en-1-yl(trifluoromethyl)sulfane



^{13}C NMR Spectrum of (E)-oct-1-en-1-yl(trifluoromethyl)sulfane