Electronic Supplementary Material (ESI) for ChemComm.

Hydrotrifluoromethylthiolation of α-Diazo Esters - Synthesis of α-SCF_3 substituted Esters

Supporting Information

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1. General Information

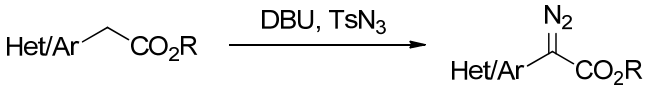
All reactions were performed with oven-dried glassware and under an inert atmosphere (argon) unless otherwise stated. Acetonitrile was distilled from calcium hydride prior to use. Pentane was distilled. Other solvents were used as purchased unless otherwise stated. Commercial reagents were used as purchased without further purification. Copper (I) trifluorothiolate was prepared according to literature.[1]

Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was carried out using Merck Kieselgel 60 silica gel (230-400 mesh). Thin-layer chromatography was carried out using Merck Kieselgel 60 F_{254} (230-400 mesh) fluorescent treated silica and were visualized under UV light (250 and 354 nm) or by staining with aqueous potassium permanganate solution.

^{1}H NMR spectra were recorded in deuterated solvents on Bruker or Varian spectrometers at 300, 400 or 600 MHz, with residual protic solvent as the internal standard. ^{13}C NMR spectra were recorded in deuterated solvents on Bruker or Varian spectrometers at 75, 100 or 125 MHz, with the central peak of the deuterated solvent as the internal standard. ^{19}F NMR spectra were recorded in deuterated solvents on Bruker or Varian spectrometers at 376 or 564 MHz. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz) rounded to the nearest 0.1 Hz. The ^{1}H NMR spectra are reported as δ/ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant *J*/Hz). The ^{13}C and ^{19}F NMR spectra are reported as δ/ppm, with multiplicity and coupling constant (*J*/Hz) where relevant. Assignments are aided by the use of DEPT-135, COSY, HMQC and HMBC spectra where necessary. IR spectra were recorded on a Perkin Elmer 1760 FTIR spectrometer, only diagnostic absorbances (λ_{max}) are reported. Low resolution mass spectra were recorded on a Thermo Finnigan SSQ 7000 mass spectrometer (EI).

2. Preparation of starting materials

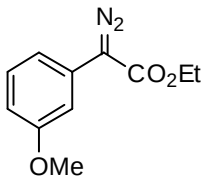
General procedure for diazotisation of arylacetate esters



DBU (14 mmol, 1.4 equiv.) was added to a mixture of ester (10 mmol, 1 equiv.) and *p*-ABSA (12 mmol, 1.2 equiv.) in anhydrous acetonitrile (30 mL). The reaction mixture was stirred at room temperature overnight. Upon completion of the reaction as indicated by thin layer chromatography (TLC), the reaction mixture was diluted with distilled water (20 mL) and extracted with diethyl ether (3 × 10 mL). After washing with a 10% aqueous NH_4Cl solution (3 × 10 mL) and brine (3 × 10 mL), the combined organic extracts were dried over magnesium sulphate and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with the mentioned solvents mixture to afford the diazo product.

Note regarding ^{13}C NMR data: in many cases, the quaternary carbon bearing the diazo function could not be observed by NMR even with extended acquisition time. The authenticity of the compound was attested by the bright yellow or red colour of the substance, by its characteristic IR-band in the 2080-2090 cm^{-1} region and by mass spectrometry.

Preparation and characterisation of ethyl *m*-methoxyphenyl diazoacetate 1d

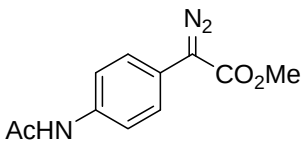


1d

Prepared according to the general procedure on 3 mmol scale of ethyl *m*-methoxyphenyl acetate. The crude mixture was purified by column chromatography on silica gel eluting with hexane/ethyl acetate 10:1 to afford the title product as a red solid (521 mg, 79%).

FT-IR ν_{max}(KBr) 2977, 2085, 1687, 1230, 1034, 769 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.34 (t, 3H, C<u>*H*</u>$_3$, *J* = 7.1 Hz), 3.82 (s, 3H, OC<u>*H*</u>$_3$), 4.33 (q, 2H, C<u>*H*</u>$_2$, *J* = 7.1 Hz), 6.73 (ddd, 1H, Ar-C<u>*H*</u>, *J* = 8.2, 2.5, 0.8 Hz), 6.99 (ddd, 1H, Ar-C<u>*H*</u>, *J* = 7.9, 1.8, 0.8 Hz), 7.17 (app t., 1H, Ar-C<u>*H*</u>, *J* = 2.5 Hz), 7.29 (app t., 1H, Ar-C<u>*H*</u>, *J* = 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.6 (<u>C</u>H$_3$), 55.4 (O<u>C</u>H$_3$), 61.1 (<u>C</u>H$_2$), 109.8 (Ar-<u>C</u>H), 111.6 (Ar-<u>C</u>H), 116.1 (Ar-<u>C</u>H), 127.3 (<u>C</u>quat.), 130.0 (Ar-<u>C</u>H), 160.2 (<u>C</u>quat.), 165.3 (<u>C</u>quat.); ***m/z*** (EI) 220 ($[M]^{\bullet+}$, 55%), 148 ($[M - C(O)OC_2H_5]^+$, 60%).

Preparation and characterisation of methyl *p*-acetylaminophenyl diazoacetate 1j

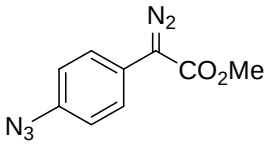


1j

Prepared according to the general procedure on 0.7 mmol scale of methyl *p*-acetylaminophenyl acetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/ethyl acetate 1:1 to afford the title product as an orange solid (99 mg, 61%).

FT-IR ν_{max}(KBr) 3331, 2090, 1690, 1517, 1244, 1153, 818 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.16 (s, 3H, C*H*$_3$), 3.85 (s, 3H, C*H*$_3$), 7.40 (d, 2H, 2 × Ar-C*H*, *J* = 8.7 Hz), 7.43 (br. s., 1H, N*H*), 7.53 (d, 2H, 2 × Ar-C*H*, *J* = 8.7 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 24.7 (*C*H$_3$), 52.2 (*C*H$_3$), 120.6 (2 × Ar-*C*H), 121.0 (*C*quat.), 124.9 (2 × Ar-*C*H), 136.1 (*C*quat.), 166.0 (*C*quat.), 168.5 (*C*quat.); ***m/z*** (EI) 233 ($[M]^{\bullet+}$, 25%), 175 ($[M - C(O)OCH_3]^+$, 65%).

Preparation and characterisation of methyl *p*-azidophenyl diazoacetate 1k



1k

Prepared according to the general procedure on 0.7 mmol scale of methyl *p*-azidophenyl acetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as an orange oil (127 mg, 84%).

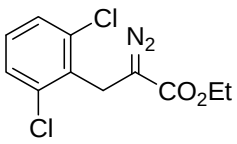
FT-IR ν_{max}(ATR) 2079, 1689, 1499, 1285, 1234, 825 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 3.87 (s, 3H, C*H*$_3$), 7.05 (d, 2H, 2 × Ar-C*H*, *J* = 8.8 Hz), 7.47 (d, 2H, 2 × Ar-C*H*, *J* = 8.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 52.2 (*C*H$_3$), 119.8 (2 × Ar-*C*H), 122.1 (*C*quat.), 125.5 (2 × Ar-*C*H), 137.8 (*C*quat.), 165.7 (*C*quat.); ***m/z*** (EI) 217 ($[M]^{\bullet+}$, 75%), 189 ($[M - N_2]^+$, 60%).

Preparation and characterisation of ethyl 3-(*2,6*-dichlorophenyl)-2-diazopropanoate 1o

Under a nitrogen atmosphere, a solution of acetoacetate (30 mmol, 1.5 equiv.) in THF (10 mL) was added dropwise to a stirred suspension of NaH (60 % dispersion in mineral oil, 1.2 g, 30 mmol, 1.5 equiv.) in THF (15 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After the mixture became clear, a solution of the *2,6*-dichlorobenzyl bromide (20 mmol, 1equiv.) in THF (10 mL) was added dropwise, and the reaction mixture was refluxed for 12h. The resulting mixture was cooled down to room temperature, quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with dichloromethane. The combined organic

layers were dried over sodium sulfate and evaporated, and the residue was purified by column chromatography to afford the pure *β*-ketoester.

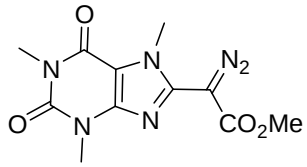
DBU (5.0 mmol, 1.2 equiv.) was added dropwise under nitrogen to a solution of *β*-ketoester (4.17 mmol, 1.0 eq.) and 4-methylbenzenesulfonyl azide (5.0 mmol, 1.2 equiv.) in acetonitrile at 0 °C. The resulting solution was stirred at 0 °C for 3 h and slowly brought to room temperature. Upon completion of the reaction as indicated by thin layer chromatography (TLC), the mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with pentane/ethyl acetate 20:1 to afford the title product as a orange oil (831 mg, 73%).



1o

FT-IR ν_{max}(ATR) 2983, 2088, 1694, 1438, 1271, 1102, 774 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.27 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 3.98 (s, 2H, C$\underline{H}_2$), 4.24 (q, 2H, C$\underline{H}_2$, J = 7.1 Hz), 7.16 (t, 1H, Ar-C$\underline{H}$, J = 8.1 Hz), 7.32 (d, 2H, 2 × Ar-C$\underline{H}$, J = 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.6 (C$\underline{H}_3$), 24.9 (C$\underline{H}_2$), 61.1 (C$\underline{H}_2$), 128.6 (2 × Ar-C$\underline{H}$), 129.2 (Ar-C$\underline{H}$), 132.7 (C$\underline{quat.}$), 136.2 (2 × C$\underline{quat.}$); ***m/z*** (EI) 272 ($[M]^{\bullet+}$, 10%), 209 ($[M - N_2Cl]^+$, 10%), 159 ($[C_7H_5Cl_2]^+$, 100%).

Preparation and characterisation of methyl caffeinodiazoacetate 1p

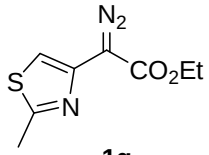


1p

Prepared according to the general procedure on 0.5 mmol scale of methyl caffeinoacetate.[2] The crude solid was washed with methanol to yield 70 mg of the title product as a yellow solid. The mother liquor was evaporated and the residue was purified by column chromatography on silica gel eluting with pentane/acetone 2:1 to afford 117 mg of the title product as a greenish solid (187 mg, 47%).

FT-IR ν_{max}(KBr) 2957, 2120, 1703, 1662, 1439, 1295, 1071, 742 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.40 (s, 3H, C$\underline{H}_3$), 3.55 (s, 3H, C$\underline{H}_3$), 3.87 (s, 3H, C$\underline{H}_3$), 3.93 (s, 3H, C$\underline{H}_3$); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 28.1 (C$\underline{H}_3$), 29.9 (C$\underline{H}_3$), 34.0 (C$\underline{H}_3$), 52.9 (C$\underline{H}_3$), 84.6 (C$\underline{quat.}$), 109.8 (C$\underline{quat.}$), 139.9 (C$\underline{quat.}$), 148.0 (C$\underline{quat.}$), 151.2 (C$\underline{quat.}$), 155.2 (C$\underline{quat.}$), 163.4 (C$\underline{quat.}$); ***m/z*** (EI) 292 ($[M]^{\bullet+}$, 50%), 234 ($[M - C(O)OCH_3 + H]^+$, 100%).

Preparation and characterisation of ethyl (2-methylthiazol-4-yl)diazoacetate 1q

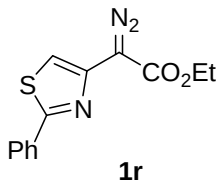


1q

Prepared according to the general procedure on 5 mmol scale of ethyl (2-methylthiazol-4-yl)acetate. The crude mixture was purified by column chromatography on silica gel eluting with hexane/ethyl acetate 4:1 to afford the title product as a red solid (1.0 g, 95%).

FT-IR ν_{max}(KBr) 2982, 2100, 1700, 1265, 1124, 749 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 1.34 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 2.67 (s, 3H, C$\underline{H}_3$), 4.33 (q, 2H, C$\underline{H}_2$, J = 7.1 Hz), 7.36 (s, 1H, HetAr-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 14.6 ($\underline{C}H_3$), 19.2 ($\underline{C}H_3$), 61.2 ($\underline{C}H_2$), 110.3 (HetAr-$\underline{C}$H), 139.0 ($\underline{C}$quat.), 165.3 ($\underline{C}$quat.), 165.6 ($\underline{C}$quat.); ***m/z*** (EI) 211 ($[M]^{\bullet+}$, 15%), 139 ($[M - C(O)OC_2H_5]^+$, 35%).

Preparation and characterisation of ethyl (2-phenylthiazol-4-yl)diazoacetate 1r



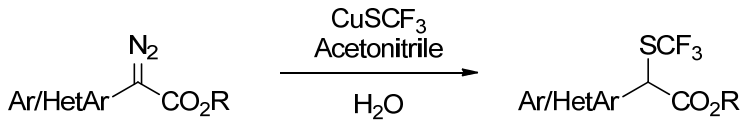
1r

Prepared according to the general procedure on 2 mmol scale of ethyl (2-phenylthiazol-4-yl)acetate. The crude mixture was purified by column chromatography on silica gel eluting with hexane/ethyl acetate 40:1 to afford the title product as a red solid (481 mg, 88%).

FT-IR ν_{max}(KBr) 3124, 2094, 1689, 1511, 1266, 1127, 1055, 774, 686 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 1.37 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 4.37 (q, 2H, C$\underline{H}_2$, J = 7.1 Hz), 7.41-7.45 (m, 3H, 3 × Ar-C$\underline{H}$), 7.54 (s, 1H, HetAr-C$\underline{H}$), 7.91-7.94 (m, 2H, 2 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 14.7 ($\underline{C}H_3$), 61.3 ($\underline{C}H_2$), 110.7 (HetAr-$\underline{C}$H), 126.6 (2 × Ar-$\underline{C}$H), 129.1 (2 × Ar-$\underline{C}$H), 130.3 (Ar-$\underline{C}$H), 133.3 ($\underline{C}$quat.), 140.6 ($\underline{C}$quat.), 167.3 ($\underline{C}$quat.), 167.5 ($\underline{C}$quat.); ***m/z*** (EI) 273 ($[M]^{\bullet+}$, 100%), 201 ($[M - C(O)OC_2H_5]^+$, 90%).

1. Hydrotrifluoromethylthiolation of diazo compounds by $CuSCF_3$

General procedure for hydrotrifluoromethylthiolation experiments

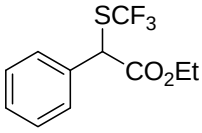


Note: Neither use of degassed acetonitrile nor concentration change within the range of 0.05-0.2 mol/L had a significant impact on the yield of this reaction. However, quality of $CuSCF_3$ evaluated by ^{19}F NMR- proved to be of critical importance: when a batch of 90% purity, contaminated by HF_2^-, was used, yields dropped under 40%. The copper salt used in our studies was typically 97-99% pure, obtained by a single recrystallisation from crude product.

$CuSCF_3$ (40 mg, 0.24 mmol, 1.2 equiv.) was loaded into a dry tube under argon atmosphere and dissolved in dry acetonitrile (0.5 or 1 mL). The colourless solution was stirred at 0°C for 2 min, then the diazo compound (0.2 mmol, 1.0 equiv.) was added per syringe through a septum as a solution in 0.5 mL of dry acetonitrile if solid, neat otherwise. The yellow solution was stirred at 0°C for 3h, then water (36 µL, 2 mmol, 10 equiv.) was added. The mixture was stirred at room temperature for an additional 3h, resulting in a troubled mixture with copper salts precipitating. The reaction mixture was quenched by aqueous hydrochloric acid (1M, 2 mL). The aqueous phase was extracted with diethyl ether (3 × 2 mL), and the combined organic layers were concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with a pentane/diethyl ether mixture to afford the trifluoromethylthiolated product.

Note regarding ^{13}C NMR data: in some cases, the extremities of the quartet assigned to the quaternary carbon bearing three fluorine atoms were not resolved from the baseline. The two middle peaks were then used to determine the chemical shift and the multiplicity of this signal.

Preparation and characterisation of ethyl phenyl(trifluoromethylthio)acetate 2a

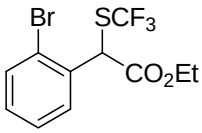


2a

Prepared according to the general procedure on 0.2 mmol scale of ethyl phenyldiazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless oil (37 mg, 70%).

FT-IR ν_{max}(ATR) 2986, 1741, 1155, 1115 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.25 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 4.16-4.28 (AA' system, 2H, C$\underline{H}_2$), 5.05 (s, 1H, C$\underline{H}$), 7.34-7.39 (m, 3H, 3 × Ar-C$\underline{H}$), 744-7.46 (m, 2H, 2 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 ($\underline{C}H_3$), 51.6 (q, $\underline{C}$H, $J_{C\text{-}F}$ = 2.0 Hz), 62.8 ($\underline{C}H_2$), 128.3 (2 × Ar-$\underline{C}$H), 129.2 (Ar-$\underline{C}$H), 129.2 (2 × Ar-$\underline{C}$H), 130.0 (q, $\underline{C}$quat., $J_{C\text{-}F}$ = 308 Hz), 134.2 ($\underline{C}$quat.), 169.1 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.18 (SC$\underline{F}_3$); ***m/z*** (EI) 264 ($[M]^{\bullet+}$, 20%), 191 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of ethyl (*o*-bromophenyl)(trifluoromethylthio)acetate 2b

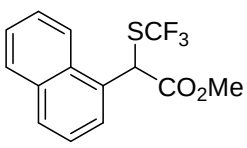


2b

Prepared according to the general procedure on 0.2 mmol scale of ethyl (*o*-bromophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless oil (37 mg, 54%).

FT-IR ν_{max}(ATR) 2985, 1743, 1160, 1114, 1023, 748 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 4.18-4.29 (AA' system, 2H, C$\underline{H}_2$), 5.63 (s, 1H, C$\underline{H}$), 7.21 (app. td, 1H, Ar-C$\underline{H}$, J = 8.0, 1.6 Hz), 7.34 (app. td, 1H, Ar-C$\underline{H}$, J = 7.8, 1.2 Hz), 7.56 (dd, 1H, Ar-C$\underline{H}$, J = 7.8, 1.6 Hz), 7.61 (dd, 1H, Ar-C$\underline{H}$, J = 8.0, 1.2 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 ($\underline{C}H_3$), 50.7 (q, $\underline{C}$H, $J_{C\text{-}F}$ = 2.0 Hz), 63.0 ($\underline{C}H_2$), 124.3 ($\underline{C}$quat.), 128.3 (Ar-$\underline{C}$H), 129.9 (q, $\underline{C}$quat., $J_{C\text{-}F}$ = 308 Hz), 130.0 (Ar-$\underline{C}$H), 130.5 (Ar-$\underline{C}$H), 133.6 (Ar-$\underline{C}$H), 134.2 ($\underline{C}$quat.), 168.5 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.11 (SC$\underline{F}_3$); ***m/z*** (EI) 345 ($[M + H]^{\bullet+}$, 10%), 343 ($[M + H]^{\bullet+}$, 10%), 271 ($[M - C(O)OC_2H_5]^+$, 100%), 269 ($[M - C(O)OC_2H_5]^+$, 100%), 263 ($[M - Br]^+$, 90%).

Preparation and characterisation of methyl (1-naphtyl)(trifluoromethylthio)acetate 2c



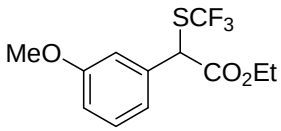
2c

Prepared by slight modification of the general procedure (stirred at 0 °C for 20h) on 0.2 mmol scale of methyl (1-naphtyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless foam

(44 mg, 70%).

FT-IR ν_{max}(ATR) 2956, 1746, 1116, 784 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.77 (s, 3H, C$\underline{H}_3$), 5.85 (s, 1H, C$\underline{H}$), 7.48 (dd, 1H, Ar-C$\underline{H}$, J = 8.1, 7.3 Hz), 7.56 (ddd, 1H, Ar-C$\underline{H}$, J = 8.0, 6.9, 1.0 Hz), 7.63 (ddd, 1H, Ar-C$\underline{H}$, J = 8.5, 6.9, 1.4 Hz), 7.67 (dd, 1H, Ar-C$\underline{H}$, J = 7.3, 1.0 Hz), 7.88 (d, 1H, Ar-C$\underline{H}$, J = 8.1 Hz), 7.91 (d, 1H, Ar-C$\underline{H}$, J = 8.0 Hz), 8.11 (d, 1H, Ar-C$\underline{H}$, J = 8.5 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 48.0 ($\underline{C}H_3$), 53.7 ($\underline{C}$H), 122.7 (Ar-$\underline{C}$H), 125.5 (Ar-$\underline{C}$H), 126.5 (Ar-$\underline{C}$H), 127.2 (Ar-$\underline{C}$H), 127.4 (Ar-$\underline{C}$H), 129.4 (Ar-$\underline{C}$H), 129.4 ($\underline{C}$quat.), 130.0 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 308 Hz), 130.2 (Ar-$\underline{C}$H), 130.5 ($\underline{C}$quat.), 134.2 ($\underline{C}$quat.), 170.0 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.60 (SC$\underline{F}_3$); ***m/z*** (EI) 300 ($[M]^{\bullet+}$, 100%), 241 ($[M - C(O)OCH_3]^+$, 50%), 199 ($[M - SCF_3]^+$, 100%).

Preparation and characterisation of ethyl (*m*-methoxyphenyl)(trifluoromethylthio)acetate 2d

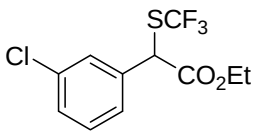


2d

Prepared according to the general procedure on 0.2 mmol scale of ethyl (*m*-methoxyphenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a colourless oil (44 mg, 75%).

FT-IR ν_{max}(ATR) 2981, 1741, 1599, 1483, 1268, 1118, 773 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C$\underline{H}_3$, J = 7.2 Hz), 3.81 (s, 3H, OC$\underline{H}_3$), 4.15-4.29 (AA' system, 2H, C$\underline{H}_2$), 5.01 (s, 1H, C$\underline{H}$), 6.89 (ddd, 1H, Ar-C$\underline{H}$, J = 8.3, 2.5, 0.8 Hz), 6.99 (app. t, 1H, Ar-C$\underline{H}$, J = 1.8 Hz), 7.02 (d, 1H, Ar-C$\underline{H}$, J = 7.7 Hz), 7.28 (app. t, 1H, Ar-C$\underline{H}$, J = 7.7 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 ($\underline{C}H_3$), 51.5 (q, $\underline{C}$H, $J_{C\text{-}F}$ = 2.1 Hz), 55.5 (OC$\underline{H}_3$), 62.8 ($\underline{C}H_2$), 113.8 (Ar-$\underline{C}$H), 114.8 (Ar-$\underline{C}$H), 120.6 (Ar-$\underline{C}$H), 130.0 (q, $\underline{C}$quat., $J_{C\text{-}F}$ = 308 Hz), 130.3 (Ar-$\underline{C}$H), 135.4 ($\underline{C}$quat.), 160.1 ($\underline{C}$quat.), 169.0 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.22 (SC$\underline{F}_3$); ***m/z*** (EI) 294 ($[M]^{\bullet+}$, 70%), 221 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of ethyl (*m*-chlorophenyl)(trifluoromethylthio)acetate 2e



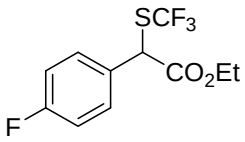
2e

Prepared according to the general procedure on 0.1 mmol scale of ethyl (*m*-chlorophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product in 90% purity as a yellow oil (18 mg, 70%). An

analytically pure sample of the product was obtained by converting the residual starting material to the corresponding *p*-methoxybenzylamino derivative following recent literature.[3] The pure title product was a colourless oil.

FT-IR ν_{max}(ATR) 2926, 1740, 1460, 1115, 1024, 761, 688 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C<u>*H*</u>$_3$, J = 7.1 Hz), 4.14-4.32 (AA' system, 2H, C<u>*H*</u>$_2$), 4.99 (s, 1H, C<u>*H*</u>), 7.32-7.35 (m, 3H, 3 × Ar-C<u>*H*</u>), 7.46-7.47 (m, 1H, Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 (<u>*C*</u>H_3), 51.1 (q, <u>*C*</u>H, $J_{C\text{-}F}$ = 1.6 Hz), 63.0 (<u>*C*</u>H_2), 126.5 (Ar-<u>*C*</u>H), 128.5 (Ar-<u>*C*</u>H), 129.5 (Ar-<u>*C*</u>H), 129.8 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ = 308 Hz), 130.5 (Ar-<u>*C*</u>H), 135.1 (<u>*C*</u>quat.), 136.3 (<u>*C*</u>quat.), 168.5 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –41.02 (SC<u>*F*</u>$_3$); ***m/z*** (EI) 298 ($[M]^{\bullet+}$, 15%), 227 ($[M - C(O)OC_2H_5]^+$, 35%), 225 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of ethyl (*p*-fluorophenyl)(trifluoromethylthio)acetate 2f

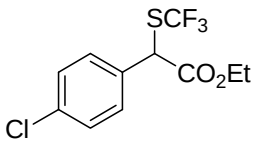


2f

Prepared by slight modification of the general procedure (stirred at r.t. for 20h after water was added) on 0.1 mmol scale of ethyl (*p*-fluorophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a yellow oil (15 mg, 53%).

FT-IR ν_{max}(ATR) 2986, 1741, 1510, 1284, 1232, 1156, 1115 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C<u>*H*</u>$_3$, J = 7.1 Hz), 4.16-4.28 (AA' system, 2H, C<u>*H*</u>$_2$), 5.03 (s, 1H, C<u>*H*</u>), 7.05-7.09 (m, 2H, 2 × Ar-C<u>*H*</u>), 7.42-7.46 (m, 2H, 2 × Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 (<u>*C*</u>H_3), 50.9 (q, <u>*C*</u>H, $J_{C\text{-}F}$ = 2.0 Hz), 62.9 (<u>*C*</u>H_2), 116.3 (d, 2 × Ar-<u>*C*</u>H, $J_{C\text{-}F}$ = 21.9 Hz), 129.9 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ = 308 Hz), 130.1 (d, <u>*C*</u>quat., $J_{C\text{-}F}$ = 3.3 Hz), 130.2 (d, 2 × Ar-<u>*C*</u>H, $J_{C\text{-}F}$ = 8.4 Hz), 163.1 (d, <u>*C*</u>quat., $J_{C\text{-}F}$ = 249.0 Hz), 168.9 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –112.16 (m, Ar-<u>*F*</u>), –41.01 (SC<u>*F*</u>$_3$); ***m/z*** (EI) 282 ($[M]^{\bullet+}$, 15%), 209 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of ethyl (*p*-chlorophenyl)(trifluoromethylthio)acetate 2g

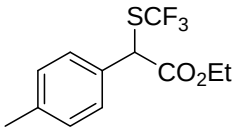


2g

Prepared according to the general procedure on 0.2 mmol scale of ethyl (*p*-chlorophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a yellow oil (36 mg, 60%).

FT-IR ν_{max}(ATR) 2986, 1742, 1491, 1296, 1273, 1115, 831, 759 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.25 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 4.16-4.28 (AA' system, 2H, C*H*$_2$), 5.02 (s, 1H, C*H*), 7.35 (d, 2H, 2 × Ar-C*H*, *J* = 8.6 Hz), 7.40 (d, 2H, 2 × Ar-C*H*, *J* = 8.6 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 (*C*H$_3$), 51.0 (q, *C*H, $J_{C\text{-}F}$ = 2.0 Hz), 63.0 (*C*H$_2$), 129.5 (2 × Ar-*C*H), 129.7 (2 × Ar-*C*H), 129.8 (q, *C*quat., $J_{C\text{-}F}$ = 308 Hz), 132.9 (*C*quat.), 135.3 (*C*quat.), 168.7 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.01 (SC*F*$_3$); ***m/z*** (EI) 300 ($[M]^{\bullet+}$, 10%), 298 ($[M]^{\bullet+}$, 30%), 227 ($[M - C(O)OC_2H_5]^+$, 40%), 225 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of ethyl (*p*-tolyl)(trifluoromethylthio)acetate 2h

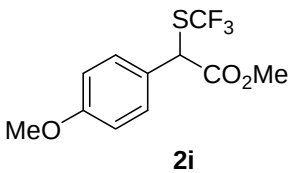


2h

Prepared according to the general procedure on 0.1 mmol scale of ethyl (*p*-tolyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a yellow oil (19 mg, 68%).

FT-IR ν_{max}(ATR) 2985, 1741, 1301, 1155, 1115, 1025 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 1.24 (t, 3H, C*H*$_3$, *J* = 7.1 Hz), 2.34 (s, 3H, C*H*$_3$), 4.12-4.28 (AA' system, 2H, C*H*$_2$), 5.00 (s, 1H, C*H*), 7.17 (d, 2H, 2 × Ar-C*H*, *J* = 7.9 Hz), 7.32 (d, 2H, 2 × Ar-C*H*, *J* = 7.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 14.0 (*C*H$_3$), 21.3 (*C*H$_3$) 51.3 (q, *C*H, $J_{C\text{-}F}$ = 1.8 Hz), 62.6 (*C*H$_2$), 114.1 (*C*quat.), 128.2 (2 × Ar-*C*H), 129.9 (2 × Ar-*C*H), 139.2 (*C*quat.), 169.2 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –41.23 (SC*F*$_3$); ***m/z*** (EI) 278 ($[M]^{\bullet+}$, 40%), 205 ($[M - C(O)OC_2H_5]^+$, 100%).

Preparation and characterisation of methyl (*p*-methoxyphenyl)(trifluoromethylthio)acetate 2i



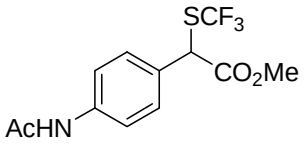
2i

Prepared according to the general procedure on 0.1 mmol scale of methyl (*p*-methoxyphenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a yellow oil (15 mg, 51%).

FT-IR ν_{max}(ATR) 2958, 2842, 1744, 1610, 1512, 1441, 1297, 1256, 1112, 1032, 834, 532 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.76 (s, 3H, C*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 5.04 (s, 1H, C*H*), 6.89 (d, 2H, 2 × Ar-C*H*, *J* = 8.8 Hz), 7.36 (d, 2H, 2 × Ar-C*H*, *J* = 8.8 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 50.9 (q, *C*H, $J_{C\text{-}F}$ = 2.1 Hz), 53.5 (*C*H$_3$), 55.5 (*C*H$_3$), 114.7 (2 × Ar-*C*H), 125.7 (*C*quat.), 129.6

(2 × Ar-<u>C</u>H), 129.9 (q, <u>C</u>quat., $J_{C\text{-}F}$ = 308 Hz), 160.3 (<u>C</u>quat.), 168.8 (<u>C</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.26 (SC<u>F_3</u>); ***m/z*** (EI) 280 ($[M]^{\bullet+}$, 30%), 221 ($[M - C(O)OC_2H_5]^+$, 25%), 179 ($[M - SCF_3]^+$, 100%).

Preparation and characterisation of methyl (*p*-acetylaminophenyl)(trifluoromethylthio) acetate 2j

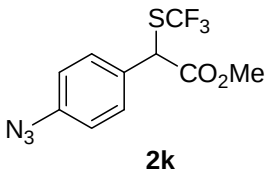


2j

Prepared by slight modification of the general procedure (stirred at r.t. for 20h after water was added) on 0.1 mmol scale of methyl (*p*-acetylaminophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 1:1 to pure ether to afford the title product as a colourless foam (25 mg, 78%).

FT-IR ν_{max}(ATR) 3253, 1743, 1659, 1109, 745 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.17 (s, 3H, C<u>H_3</u>), 3.75 (s, 3H, C<u>H_3</u>), 5.04 (s, 1H, C<u>H</u>), 7.38 (d, 2H, 2 × Ar-C<u>H</u>, J = 8.5 Hz), 7.52 (d, 2H, 2 × Ar-C<u>H</u>, J = 8.5 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 24.7 (<u>C</u>H_3), 51.0 (q, <u>C</u>H, $J_{C\text{-}F}$ = 2.0 Hz), 53.6 (<u>C</u>H_3), 120.4 (2 × Ar-<u>C</u>H), 129.1 (2 × Ar-<u>C</u>H), 129.5 (<u>C</u>quat.), 129.9 (q, <u>C</u>quat., $J_{C\text{-}F}$ = 308 Hz), 138.8 (<u>C</u>quat.), 168.7 (<u>C</u>quat.), 169.6 (<u>C</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.16 (SC<u>F_3</u>); ***m/z*** (EI) 307 ($[M]^{\bullet+}$, 35%), 206 ($[M - SCF_3]^+$, 100%).

Preparation and characterisation of methyl (*p*-azidophenyl)(trifluoromethylthio)acetate 2k

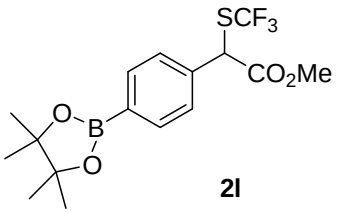


2k

Prepared by slight modification of the general procedure (stirred at r.t. for 20h after water was added) on 0.1 mmol scale of methyl (*p*-azidophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a colourless oil (24 mg, 86%).

FT-IR ν_{max}(ATR) 2955, 2122, 1746, 1292, 1117 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.77 (s, 3H, C<u>H_3</u>), 5.05 (s, 1H, C<u>H</u>), 7.03 (d, 2H, 2 × Ar-C<u>H</u>, J = 8.6 Hz), 7.44 (d, 2H, 2 × Ar-C<u>H</u>, J = 8.6 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 50.9 (q, <u>C</u>H, $J_{C\text{-}F}$ = 2.1 Hz), 53.7 (<u>C</u>H_3), 119.8 (2 × Ar-<u>C</u>H), 129.8 (q, <u>C</u>quat., $J_{C\text{-}F}$ = 308 Hz), 129.9 (2 × Ar-<u>C</u>H), 130.6 (<u>C</u>quat.), 141.2 (<u>C</u>quat.), 169.3 (<u>C</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.09 (SC<u>F_3</u>); ***m/z*** (EI) 291 ($[M]^{\bullet+}$, 60%), 232 ($[M - C(O)OCH_3]^+$, 35%).

Preparation and characterisation of methyl [*p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y)phenyl](trifluoromethylthio)acetate 2l

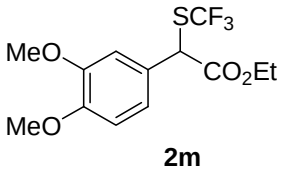


2l

Prepared by slight modification of the general procedure (stirred at r.t. for 20h after water was added) on 0.1 mmol scale of methyl [*p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y)phenyl]diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a colourless oil (26 mg, 69%).

FT-IR ν_{max}(ATR) 2982, 1744, 1359, 1106, 857 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.36 (s, 12H, 4 × C$\underline{H}_3$), 3.75 (s, 3H, C$\underline{H}_3$), 5.07 (s, 1H, C$\underline{H}$), 7.44 (d, 2H, 2 × Ar-C$\underline{H}$, J = 8.2 Hz), 7.82 (d, 2H, 2 × Ar-C$\underline{H}$, J = 8.2 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 25.0 (4 × $\underline{C}H_3$), 51.6 (q, $\underline{C}$H, $J_{C\text{-}F}$ = 2.1 Hz), 53.6 ($\underline{C}H_3$), 84.2 (2 × $\underline{C}$quat.), 127.6 (2 × Ar-$\underline{C}$H), 129.9 (q, $\underline{C}$quat., $J_{C\text{-}F}$ = 308 Hz), 135.7 (2 × Ar-$\underline{C}$H), 136.9 ($\underline{C}$quat.), 169.4 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.15 (SC$\underline{F}_3$); ***m/z*** (EI) 376 ($[M]^{\bullet+}$, 45%), 317 ($[M - C(O)OCH_3]^+$, 100%), 275 ($[M - SCF_3]^+$, 70%).

Preparation and characterisation of ethyl (*3,4*-dimethoxyphenyl)(trifluoromethylthio) acetate 2m

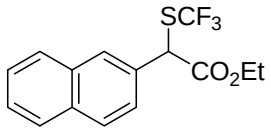


2m

Prepared according to the general procedure on 0.076 mmol scale of ethyl (*3*,*4*-dimethoxyphenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a colourless oil (15 mg, 61%).

FT-IR ν_{max}(ATR) 2967, 1739, 1516, 1460, 1264, 1117, 1026, 759 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C$\underline{H}_3$, J = 7.1 Hz), 3.88 (s, 3H, OC$\underline{H}_3$), 3.89 (s, 3H, OC$\underline{H}_3$), 4.15-4.29 (AA' system, 2H, C$\underline{H}_2$), 5.00 (s, 1H, C$\underline{H}$), 6.83 (dd, 1H, Ar-C$\underline{H}$, J = 8.3 Hz), 6.97 (d, 1H, Ar-C$\underline{H}$, J = 2.1 Hz), 6.99 (dd, 1H, Ar-C$\underline{H}$, J = 8.3, 2.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.1 ($\underline{C}H_3$), 51.4 ($\underline{C}$H), 56.0 (O$\underline{C}H_3$), 56.1 (O$\underline{C}H_3$), 62.7 ($\underline{C}H_2$), 111.0 (Ar-$\underline{C}$H), 111.3 (Ar-$\underline{C}$H), 121.0 (Ar-$\underline{C}$H), 126.0 ($\underline{C}$quat.), 129.9 (q, $\underline{C}$quat., $J_{C\text{-}F}$ = 308 Hz), 149.5 ($\underline{C}$quat.), 149.8 ($\underline{C}$quat.), 169.3 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.19 (SC$\underline{F}_3$); ***m/z*** (EI) 324 ($[M]^{\bullet+}$, 60%), 251 ($[M - C(O)OC_2H_5]^+$, 40%), 223 ($[M - SCF_3]^+$, 100%).

Preparation and characterisation of ethyl (2-naphtyl)(trifluoromethylthio)acetate 2n

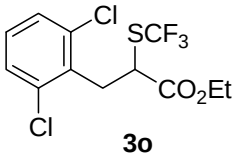


2n

Prepared according to the general procedure on 0.2 mmol scale of ethyl (2-naphtyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless foam (43 mg, 68%).

FT-IR ν_{max}(ATR) 1740, 1301, 1145, 1104, 1015, 812, 750 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.26 (t, 3H, C*H*$_3$, *J* = 7.1 Hz), 4.17-4.31 (AA' system, 2H, C*H*$_2$), 5.24 (s, 1H, C*H*), 7.51-7.54 (m, 2H, 2 × Ar-C*H*), 7.57 (dd, 1H, Ar-C*H*, *J* = 8.5, 1.9 Hz), 7.84-7.88 (m, 3H, 3 × Ar-C*H*), 7.93 (d, 1H, Ar-C*H*, *J* = 1.5 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 (*C*H$_3$), 51.9 (q, *C*H, $J_{C\text{-}F}$ = 2.0 Hz), 62.8 (*C*H$_2$), 125.3 (Ar-*C*H), 126.9 (Ar-*C*H), 127.0 (Ar-*C*H), 127.9 (2 × Ar-*C*H), 128.3 (Ar-*C*H), 129.3 (Ar-*C*H), 130.0 (q, *C*quat., $J_{C\text{-}F}$ = 308 Hz), 131.4 (*C*quat.), 133.3 (*C*quat.), 133.4 (*C*quat.), 169.1 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.00 (SC*F*$_3$); ***m/z*** (EI) 314 ($[M]^{\bullet+}$, 90%), 241 ($[M - C(O)OC_2H_5]^+$, 100%), 213 ($[M - SCF_3]^+$, 70%).

Preparation and characterisation of ethyl 3-(*2,6*-dichlorophenyl)-2-(trifluoromethylthio) propanoate 2o



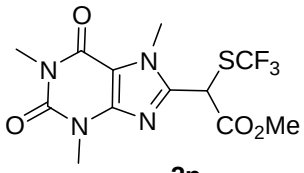
3o

Ethyl 3-(*2,6*-dichlorophenyl)diazopropanoate (34.7 mg, 0.1 mmol, 1.0 eq.) was loaded into a dry tube under argon atmosphere and dissolved in 0.5 mL of dry acetonitrile. The yellow solution was stirred at –40°C for 10 min, then $CuSCF_3$ (24.5 mg, 0.15 mmol, 1.5 eq.) was added per syringe through a septum as a solution in 0.5 mL of dry acetonitrile. The yellow solution was stirred at –40°C for 40 minutes, then the reaction mixture was quenched by aqueous hydrochloric acid (1M, 2 mL). The aqueous phase was extracted with diethyl ether (3 × 2 mL), and the combined organic layers were concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel eluting with pentane/ethyl acetate 20:1 to afford the title product as a colourless oil (23 mg, 66%).

FT-IR ν_{max}(ATR) 3462, 2984, 2116, 1740, 1565, 1439, 1297, 1113, 1033, 774 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 1.22 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 3.48-3.62 (AA' system, 2H, C*H*$_2$), 4.19 (q, 2H, C*H*$_2$, *J* = 7.2 Hz), 4.30 (t, 1H, C*H*, *J* = 8.3 Hz), 7.17 (dd, 1H, Ar-C*H*, *J* = 8.5, 7.6 Hz), 7.32 (s, 1H, Ar-C*H*), 7.34 (s, 1H, Ar-C*H*); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 13.8 (*C*H$_3$), 33.5 (*C*H$_2$), 45.1 (*C*H) 62.3 (*C*H$_2$), 128.4 (2 × Ar-*C*H), 129.1 (Ar-*C*H), 132.7 (*C*quat.), 136.0 (2 × *C*quat.),

169.9 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –40.78 (SC*F*$_3$); ***m/z*** (EI) 313 ([M − Cl]$^+$, 10%), 311 ([M − Cl]$^+$, 30%), 247 ([M − SCF_3]$^+$, 60%), 245 ([M − SCF_3]$^+$, 100%).

Preparation and characterisation of methyl caffeino(trifluoromethylthio)acetate 2p

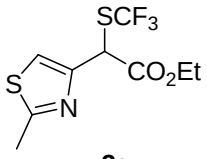


2p

Prepared by slight modification of the general procedure (stirred at r.t. for 20h after water was added) on 0.1 mmol scale of methyl caffeinodiazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/acetone 8:1 to 4:1 to afford the title product as a yellowish oil (19 mg, 52%).

FT-IR ν_{max}(ATR) 3488, 2952, 1747, 1466, 1114, 1007, 744 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 3.40 (s, 3H, C*H*$_3$), 3.55 (s, 3H, C*H*$_3$), 3.85 (s, 3H, C*H*$_3$), 4.04 (s, 3H, C*H*$_3$), 5.34 (s, 1H, C*H*); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 28.2 (*C*H$_3$), 30.1 (*C*H$_3$), 32.6 (*C*H$_3$), 44.0 (q, *C*H, $J_{C\text{-}F}$ = 2.3 Hz), 54.5 (*C*H$_3$), 108.9 (*C*quat.), 129.6 (q, *C*quat., $J_{C\text{-}F}$ = 309 Hz), 144.9 (*C*quat.), 147.8 (*C*quat.), 151.6 (*C*quat.), 155.5 (*C*quat.), 165.8 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –41.08 (SC*F*$_3$); ***m/z*** (EI) 366 ([M]$^{\bullet+}$, 100%), 265 ([M − SCF_3]$^+$, 55%).

Preparation and characterisation of ethyl (2-methylthiazol-4-yl)(trifluoromethylthio)acetate 2q

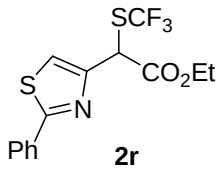


2q

Prepared by slight modification of the general procedure (stirred at –30°C for 20h, without addition of water) on 0.2 mmol scale of ethyl (2-methylthiazol-4-yl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 4:1 to afford the title product as a colourless oil (29 mg, 51%).

FT-IR ν_{max}(ATR) 2985, 1744, 1282, 1116, 1026, 755 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.29 (t, 3H, C*H*$_3$, J = 7.2 Hz), 2.71 (s, 3H, C*H*$_3$), 4.22-4.32 (AA' system, 2H, C*H*$_2$), 5.26 (s, 1H, C*H*) 7.25 (d, 1H, HetAr-C*H*, J = 0.5 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 (*C*H$_3$), 19.4 (*C*H$_3$), 47.4 (q, *C*H, $J_{C\text{-}F}$ = 2.1 Hz), 62.9 (*C*H$_2$), 117.8 (HetAr-*C*H), 130.0 (q, *C*quat., $J_{C\text{-}F}$ = 308 Hz), 147.6 (*C*quat.), 167.4 (*C*quat.), 168.3 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –41.17 (SC*F*$_3$); ***m/z*** (EI) 286 ([M + H]$^+$, 30%), 285 ([M]$^{\bullet+}$, 30%), 212 ([M − C(O)OC_2H_5]$^+$, 100%).

Preparation and characterisation of ethyl (2-phenylthiazol-4-yl)(trifluoromethylthio)acetate 2r



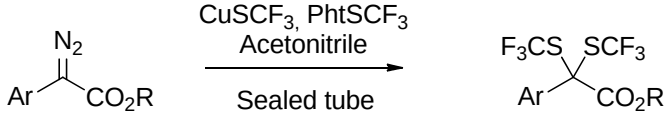
2r

Prepared by slight modification of the general procedure (stirred at –30°C for 20h, without addition of water) on 0.1 mmol scale of ethyl (2-phenylthiazol-4-yl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 4:1 to afford the title product as a colourless oil (19 mg, 55%).

FT-IR ν_{max}(ATR) 3112, 2985, 1742, 1462, 1278, 1111, 1025, 763 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 1.31 (t, 3H, C<u>*H*</u>$_3$, *J* 7.1 Hz), 4.22-4.32 (AA' system, 2H, C<u>*H*</u>$_2$), 5.36 (s, 1H, C<u>*H*</u>), 7.41 (s, 1H, HetAr-C<u>*H*</u>), 7.43-7.45 (m, 3H, 3 × Ar-C<u>*H*</u>), 7.92-7.96 (m, 2H, 2 × Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 14.1 (<u>*C*</u>H_3), 47.6 (q, <u>*C*</u>H, $J_{C\text{-}F}$ = 2.0 Hz), 62.9 (<u>*C*</u>H_2), 117.9 (HetAr-<u>*C*</u>H), 126.8 (2 × Ar-<u>*C*</u>H), 129.1 (2 × Ar-<u>*C*</u>H), 130.6 (Ar-<u>*C*</u>H), 130.0 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ = 308 Hz), 133.2 (<u>*C*</u>quat.), 149.2 (<u>*C*</u>quat.), 168.3 (<u>*C*</u>quat.), 169.2 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –41.08 (SC<u>*F*</u>$_3$); ***m/z*** (EI) 348 ($[M + H]^+$, 90%), 347 ($[M]^{\bullet+}$, 100%), 274 ($[M - C(O)OC_2H_5]^+$, 90%).

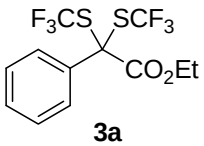
2. Double trifluoromethylthiolation of diazo compounds by $CuSCF_3$ and $PhtSCF_3$

General procedure for double trifluoromethylthiolation experiments



The solid diazo compound (0.1 mmol, 1.0 equiv.) and *N*-trifluoromethylthiophtalimide ($PhtSCF_3$, 29 mg, 0.12 mmol, 1.2 equiv.) were loaded into a dry tube under argon atmosphere and dissolved in dry acetonitrile (0.5 mL). The yellow solution was stirred at 0 °C for 2 min, then $CuSCF_3$ (18 mg, 0.11 mmol, 1.1 equiv.) was added per syringe through a septum as a solution in 0.5 mL of dry acetonitrile. The tube was sealed, and the yellow solution was stirred at room temperature for 16h. The reaction mixture was then quenched by aqueous hydrochloric acid (1M, 2 mL), the aqueous phase was extracted with diethyl ether (3 × 2 mL), and the combined organic layers were concentrated *in vacuo*. The residue was dissolved in $CDCl_3$ (0.8 mL), transferred to a NMR tube and trifluorotoluene (12 µL, 0.1 mmol) was added as internal standard. The yields of both mono- and di-substituted products were determined by ^{19}F NMR. Where relevant, the reaction mixture was purified by chromatography on silica gel eluting with a pentane/diethyl ether mixture to afford the ditrifluoromethylthiolated product. Note regarding ^{13}C NMR data: in all cases, the quaternary carbon bearing the two trifluoromethylthio groups could not be observed by NMR even with extended acquisition time. The authenticity of the compound was attested by the absence of diastereotopicity of the ethyl group and the chemical shift in ^{19}F NMR, typical for a quaternary SCF_3 group.

Preparation and characterisation of ethyl phenyldi(trifluoromethylthio)acetate 3a

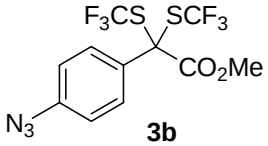


3a

An analytically pure sample was obtained by slight modification of the general procedure, although in low yield, most probably due to the volatility of the product.

FT-IR ν_{max}(ATR) 2927, 1738, 1451, 1242, 1102, 1020 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.27 (t, 3H, C<u>*H*</u>$_3$, J = 7.2 Hz), 4.32 (q, 2H, C<u>*H*</u>$_2$, J = 7.2 Hz), 7.39-7.43 (m, 3H, 3 × Ar-C<u>*H*</u>), 7.58-7.59 (m, 2H, 2 × Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 13.7 (<u>*C*</u>H$_3$), 64.6 (<u>*C*</u>H$_2$), 127.1 (2 × Ar-<u>*C*</u>H), 128.6 (q, 2 × <u>*C*</u>quat., $J_{C\text{-}F}$ = 311 Hz), 129.0 (2 × Ar-<u>*C*</u>H), 129.9 (Ar-<u>*C*</u>H), 134.9 (<u>*C*</u>quat.), 167.8 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –37.90 (2 × SC<u>*F*</u>$_3$); ***m/z*** (EI) 291 ([M − C(O)OC_2H_5]$^+$, 35%), 163 ([M − SCF_3]$^+$, 100%).

Preparation and characterisation of methyl (*p*-azidophenyl)di(trifluoromethylthio)acetate 3b

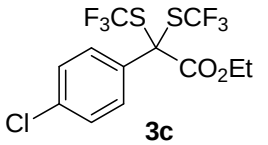


3b

Prepared by slight modification of the general procedure (stirred at 0°C for 3h followed by addition of $PhtSCF_3$, stirred at r.t. for 20h) on 0.1 mmol scale of methyl (*p*-azidophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 20:1 to afford the title product as a colourless oil (27 mg, 69%).

FT-IR ν_{max}(ATR) 2960, 2127, 1744, 1296, 1100 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.86 (s, 3H, C*H*$_3$), 7.04-7.08 (m, 2H, 2 × Ar-C*H*), 7.56-7.59 (m, 2H, 2 × Ar-C*H*); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 55.0 (*C*H$_3$), 119.5 (2 × Ar-*C*H), 128.4 (q, 2 × *C*quat., $J_{C\text{-}F}$ = 311 Hz), 129.0 (2 × Ar-*C*H), 131.0 (*C*quat.), 141.9 (*C*quat.), 168.1 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –38.08 (2 × SC*F*$_3$); ***m/z*** (EI) 391 ($[M]^{\bullet+}$, 25%), 290 ($[M - SCF_3]^+$, 80%).

Preparation and characterisation of ethyl (*p*-chlorophenyl)di(trifluoromethylthio)acetate 3c

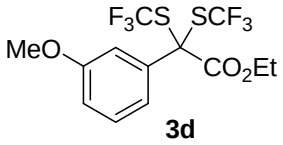


3c

Prepared according to the general procedure on 0.1 mmol scale of ethyl (*p*-chlorophenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless oil (30 mg, 75%).

FT-IR ν_{max}(ATR) 2926, 2859, 1729, 1512, 1249, 1077 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.28 (t, 3H, C*H*$_3$, *J* = 7.2 Hz), 4.32 (q, 2H, C*H*$_2$, *J* = 7.2 Hz), 7.38-7.40 (m, 2H, 2 × Ar-C*H*), 7.53-7.56 (m, 2H, 2 × Ar-C*H*); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 13.7 (*C*H$_3$), 64.8 (*C*H$_2$), 128.4 (q, 2 × *C*quat., $J_{C\text{-}F}$ = 311 Hz), 128.8 (2 × Ar-*C*H), 129.2 (2 × Ar-*C*H), 133.4 (*C*quat.), 136.1 (*C*quat.), 167.4 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –37.85 (2 × SC*F*$_3$); ***m/z*** (EI) 325 ($[M - C(O)OC_2H_5]^+$, 30%), 297 ($[M - SCF_3]^+$, 100%).

Preparation and characterisation of ethyl (*m*-methoxyphenyl)di(trifluoromethylthio)acetate 3d



3d

Prepared according to the general procedure on 0.1 mmol scale of ethyl (*m*-methoxyphenyl)diazoacetate. The crude mixture was purified by column chromatography on silica gel eluting with pentane/diethyl ether 50:1 to afford the title product as a colourless oil (23 mg, 58%).

FT-IR ν_{max}(ATR) 2988, 1742, 1240, 1107 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.28 (t, 3H, C<u>*H*</u>$_3$, *J* = 7.1 Hz), 3.82 (s, 3H, OC<u>*H*</u>$_3$), 4.31 (q, 2H, C<u>*H*</u>$_2$, *J* = 7.1 Hz), 6.92 (ddd, 1H, Ar-C<u>*H*</u>, *J* = 8.2, 2.4, 0.6 Hz), 7.13 (app t, 1H, Ar-C<u>*H*</u>, *J* = 2.2 Hz), 7.16 (dd, 1H, Ar-C<u>*H*</u>, *J* = 7.9, 1.6 Hz), 7.32 (app t, 1H, Ar-C<u>*H*</u>, *J* = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 13.7 (<u>*C*</u>H$_3$), 55.6 (O<u>*C*</u>H$_3$), 64.6 (<u>*C*</u>H$_2$), 113.3 (Ar-<u>*C*</u>H), 115.1 (Ar-<u>*C*</u>H), 119.3 (Ar-<u>*C*</u>H), 128.6 (q, 2 × <u>*C*</u>quat., $J_{C\text{-}F}$ = 311 Hz), 136.3 (<u>*C*</u>quat.), 159.9 (<u>*C*</u>quat.), 167.7 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –37.92 (2 × SC<u>*F*</u>$_3$); ***m/z*** (EI) 394 ($[M]^{\bullet+}$, 50%), 321 ($[M - C(O)OC_2H_5]^+$, 35%), 293 ($[M - SCF_3]^+$, 100%).

3. Mechanistic studies by ^{1}H and ^{19}F NMR

Kinetics of the monotrifluoromethylthiolation of ethyl phenyldiazoacetate

$CuSCF_3$ (20 mg, 0.12 mmol, 1.2 equiv.) was loaded into an NMR tube under argon atmosphere and dissolved in dry deuterated acetonitrile (0.5 mL) at 0 °C. Trifluorotoluene (12 µL, 0.1 mmol) was added as internal standard. The tube was shaken and the ^{1}H and ^{19}F spectra were recorded at 100 and 376 MHz respectively on a Varian spectrometer cooled at 0 °C. The diazo compound (0.1 mmol, 1.0 equiv.) was then added per syringe as a solution in 0.5 mL of dry deuterated acetonitrile. The yellow solution was shaken and the spectra were recorded several times at 0 °C. *Slow rise of a peak at – 42.14 ppm was observed by ^{19}F NMR, indicating the formation of the proto-product.* After two hours, deuterated water (36 µL, 2 mmol, 10 equiv.) was added at 0 °C. The tube was shaken and the spectra were recorded several times at 0 °C. *Slow rise of a peak at – 42.12 ppm was observed by ^{19}F NMR, indicating the formation of the deutero-product.* The spectrometer was then warmed up to room temperature and the spectra were recorded again.

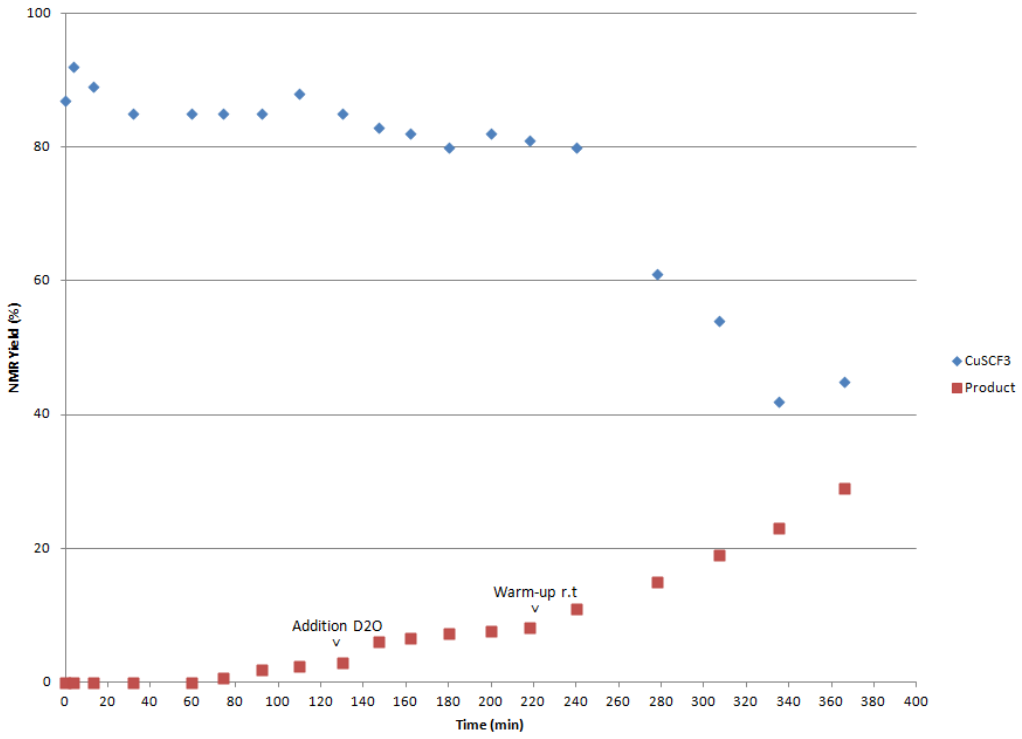


Figure S1. Kinetic study of $CuSCF_3$ consumption and product formation by ^{1}H and ^{19}F NMR.

Interactions between $CuSCF_3$, $PhtSCF_3$ and ethyl phenyldiazoacetate

$CuSCF_3$ (16.5 mg, 0.1 mmol, 1.0 equiv.) was loaded into an NMR tube under argon atmosphere and dissolved in dry deuterated acetonitrile (0.5 mL) at 0 °C. The tube was shaken and the ^{19}F spectrum was recorded at 376 MHz on a Varian spectrometer at r.t. (S2.1). $PhtSCF_3$ (24.7 mg, 0.1 mmol, 1.0 equiv.) was then added per syringe as a solution in 0.5 mL of dry deuterated acetonitrile. The tube was shaken and the spectrum was recorded (S2.2). *Immediate formation of a peak at – 47.4 ppm was observed by ^{19}F NMR, indicating the formation of $(CF_3S)_2$.* After standing one day at r.t., the spectrum was recorded (S2.3) and after one additional day, trifluorotoluene (12 µL, 0.1 mmol) was added as internal standard and the spectrum recorded (S2.4). The amounts of $CuSCF_3$, disulfide and $PhtSCF_3$ were 0.55, 0.32 and 0.61 mmol respectively, which expressed only 10% decomposition. The diazo compound (0.1 mmol, 1.0 equiv.) was then added per syringe. The yellow solution was shaken and the spectrum was recorded (S2.5). *Slow rise of two peaks at – 42.1 ppm and – 39.3 ppm were observed by ^{19}F NMR, indicating the formation of the mono- and ditrifluoromethylthiolated products, respectively.* After standing for one day at r.t., the spectrum was recorded (S2.6).

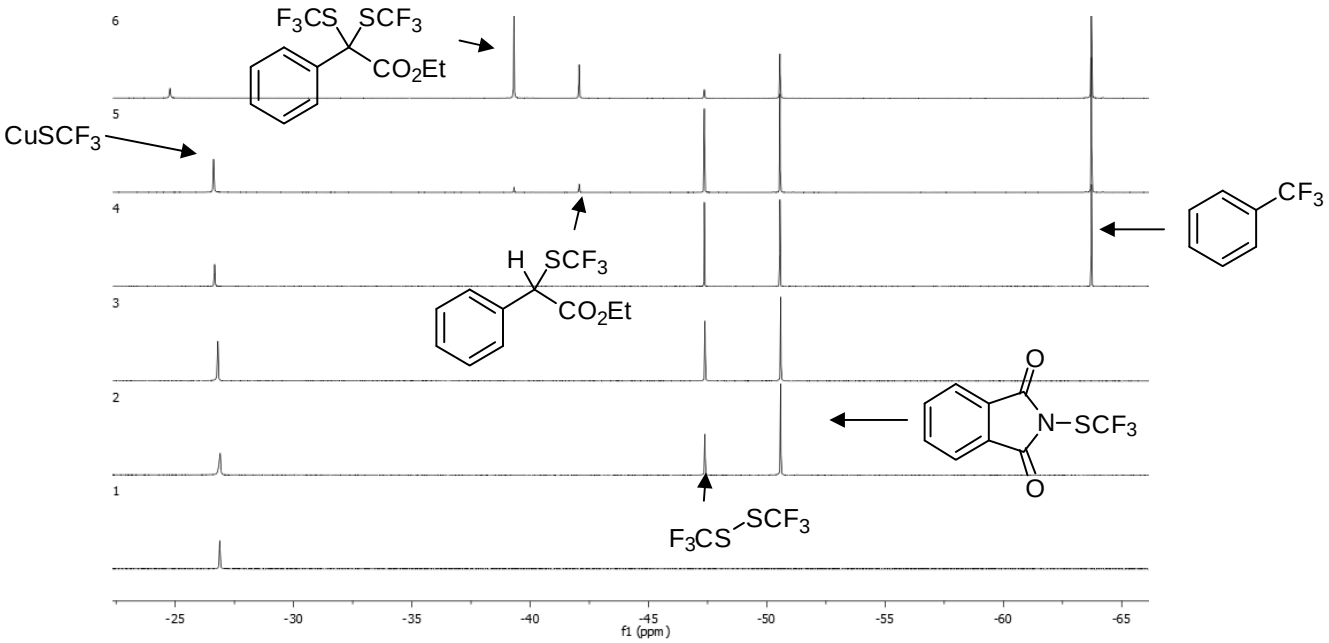


Figure S2. Quantitative study of the interactions between $CuSCF_3$, $PhtSCF_3$ and ethyl phenyldiazoacetate by ^{19}F NMR.

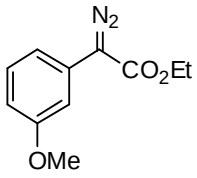
6. References

(1) Clark, J. H.; Jones, C. W.; Kybett, A. P.; McClinton, M. A.; Miller, J. M.; Bishop, D.; Blade, R. J. *J. Fluorine Chem.* **1990**, *48*, 249–253.

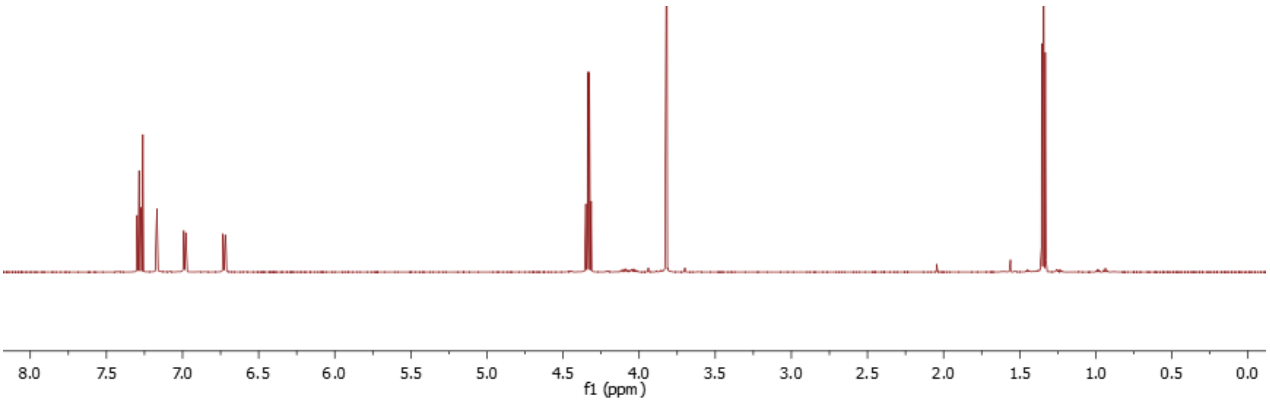
(2) Zylber, J.; Ouazzani-Chahdi, L.; Lefort, D.; Chiaroni, A.; Riche, C. *Tetrahedron* **1989**, *45*, 721–732.

(3) Hansen, S. R.; Spangler, J. E.; Hansen, J. H.; Davies, H. M. L. *Org. Lett.* **2012**, *14*, 4626–4629.

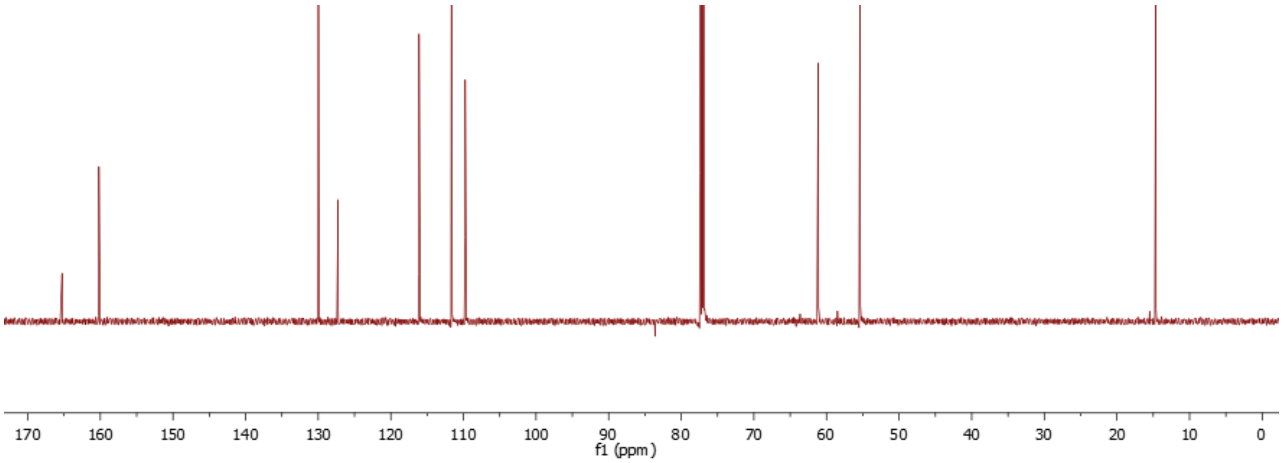
7. ^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds.



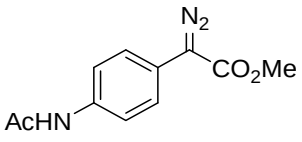
1d



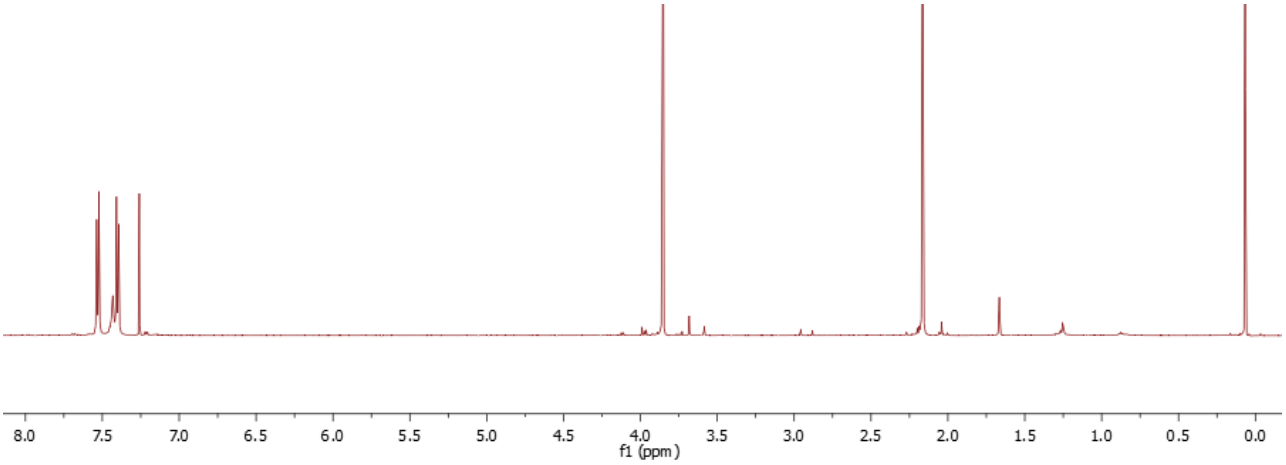
^{1}H NMR spectrum of ethyl *m*-methoxyphenyl diazoacetate 1d



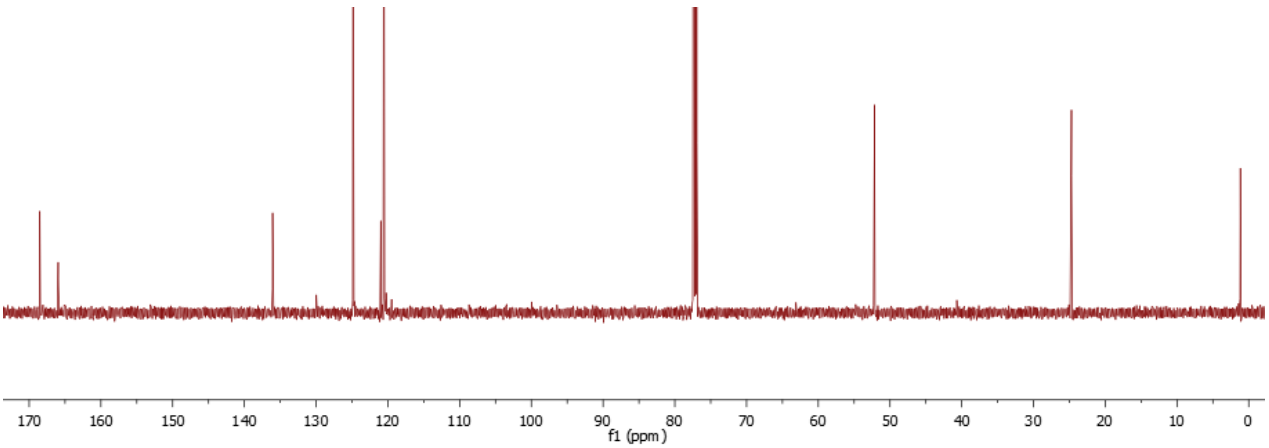
^{13}C NMR spectrum of ethyl *m*-methoxyphenyl diazoacetate 1d



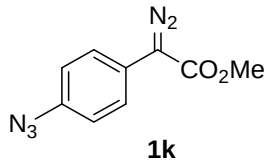
1j



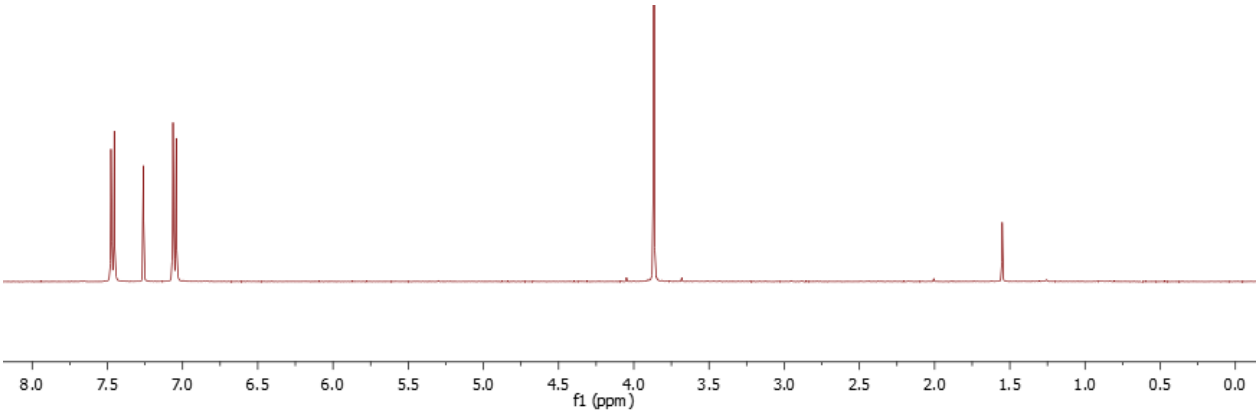
^{1}H NMR spectrum of methyl *p*-acetylaminophenyl diazoacetate 1j



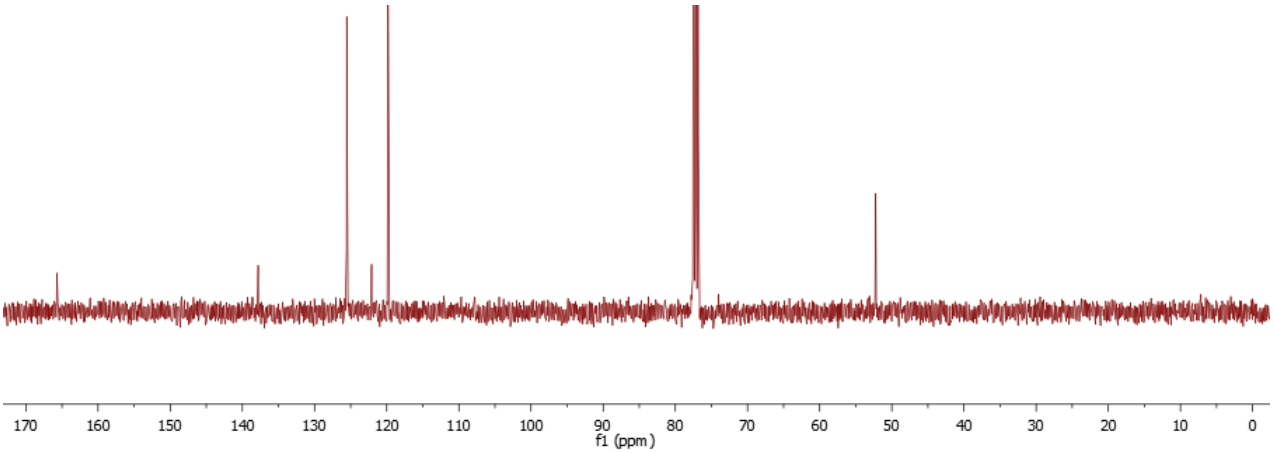
^{13}C NMR spectrum of methyl *p*-acetylaminophenyl diazoacetate 1j



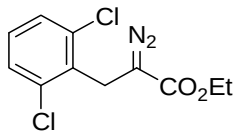
1k



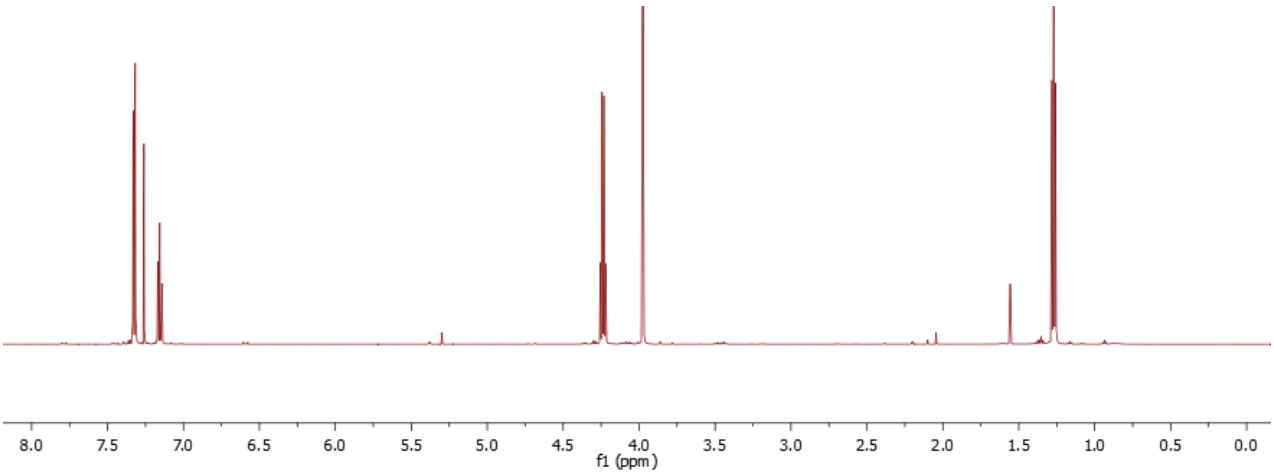
^{1}H NMR spectrum of methyl *p*-azidophenyl diazoacetate 1k



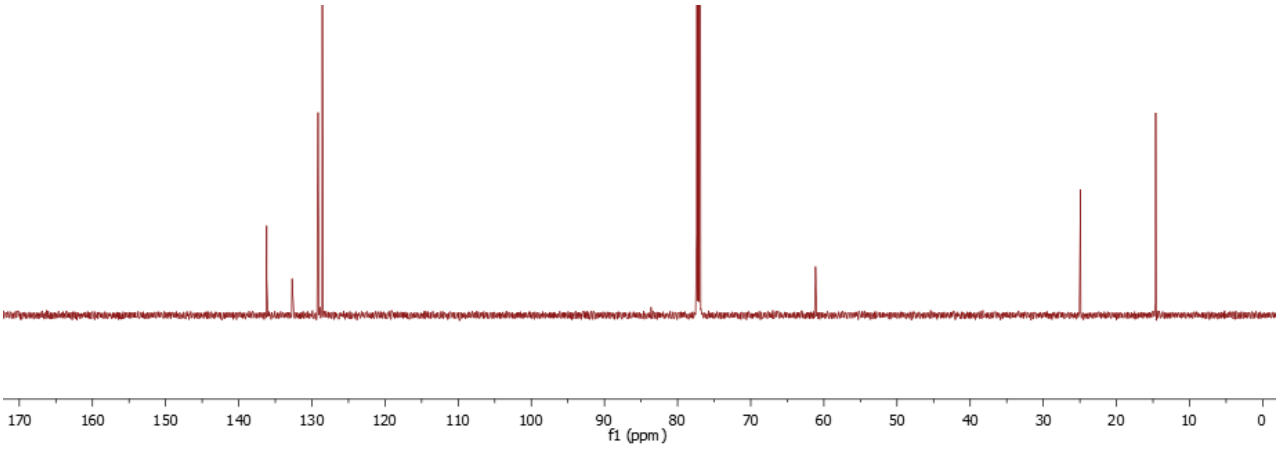
^{13}C NMR spectrum of methyl *p*-azidophenyl diazoacetate 1k



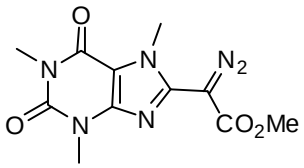
1o



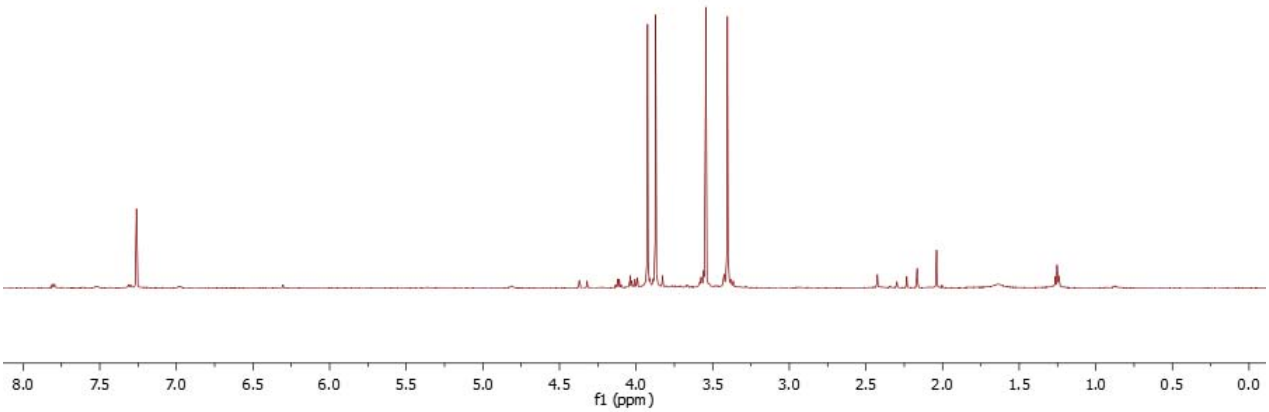
^{1}H NMR spectrum of ethyl 3-(*o*,*o*-dichlorophenyl)-2-diazopropanoate 1o



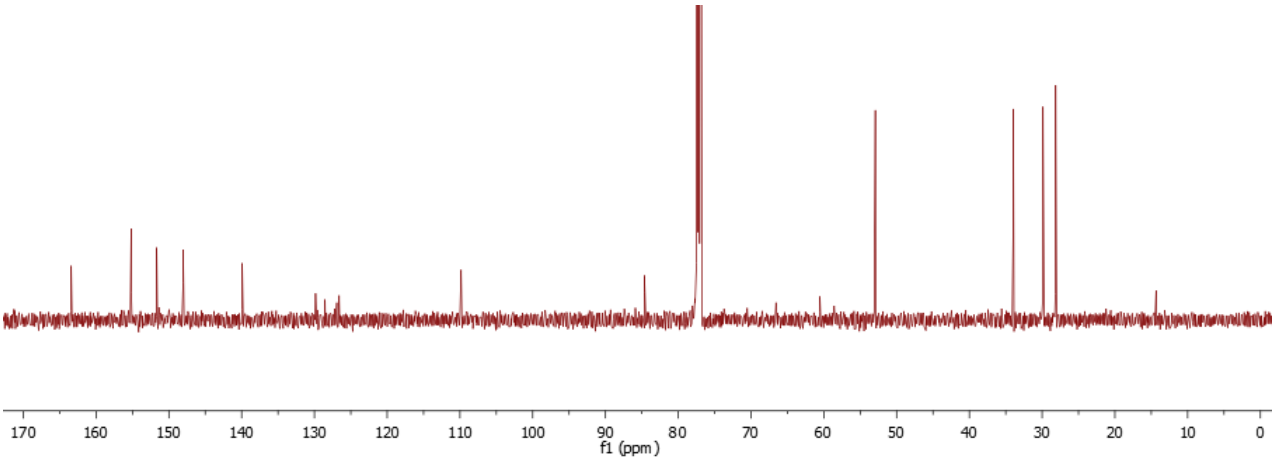
^{13}C NMR spectrum of ethyl 3-(*o*,*o*-dichlorophenyl)-2-diazopropanoate 1o



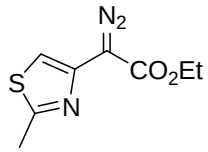
1p



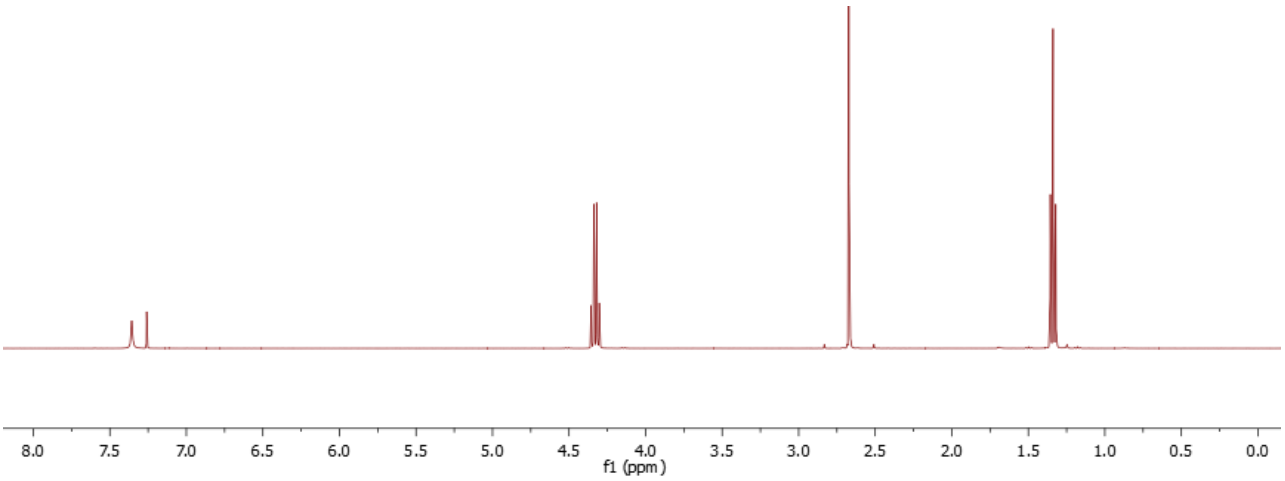
^{1}H NMR spectrum of methyl caffeinodiazoacetate 1p



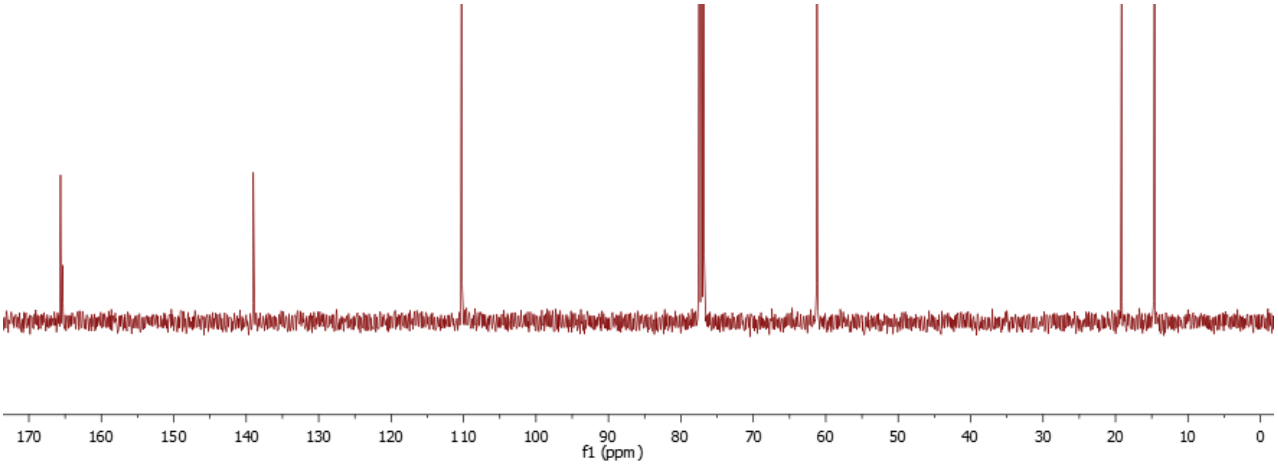
^{13}C NMR spectrum of methyl caffeinodiazoacetate 1p



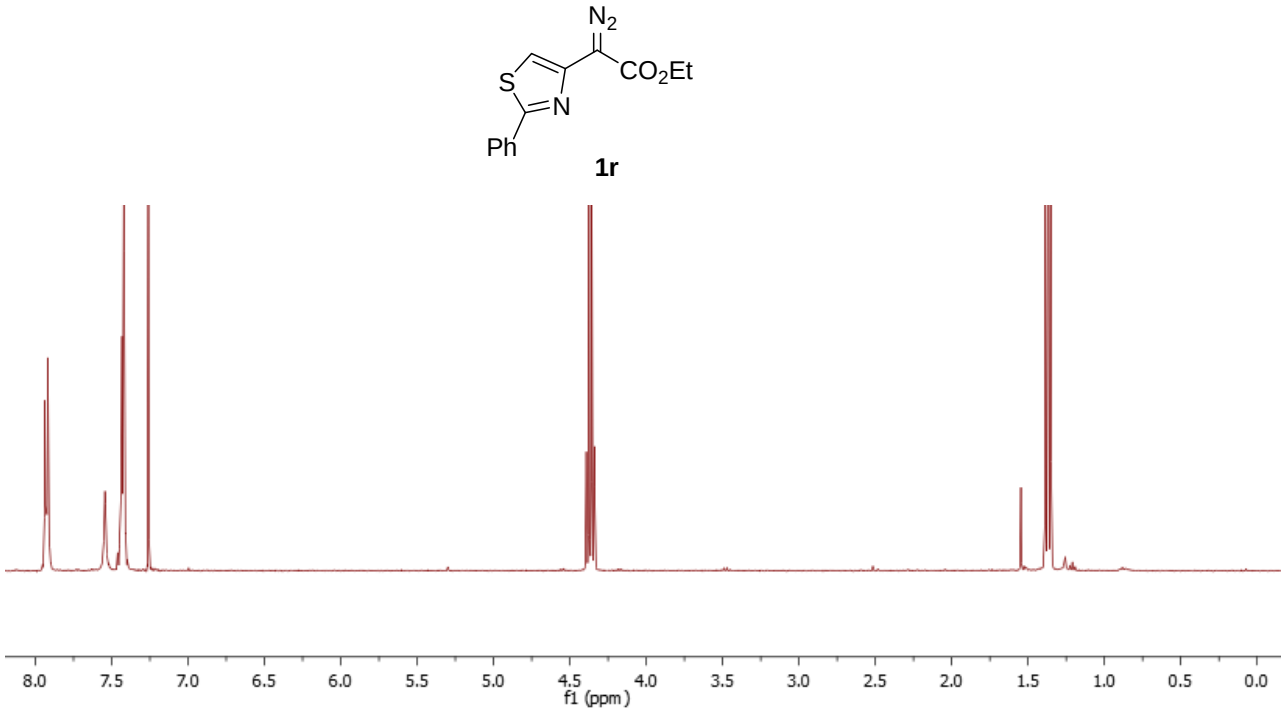
1q



^{1}H NMR spectrum of ethyl (2-methylthiazol-4-yl)diazoacetate 1q

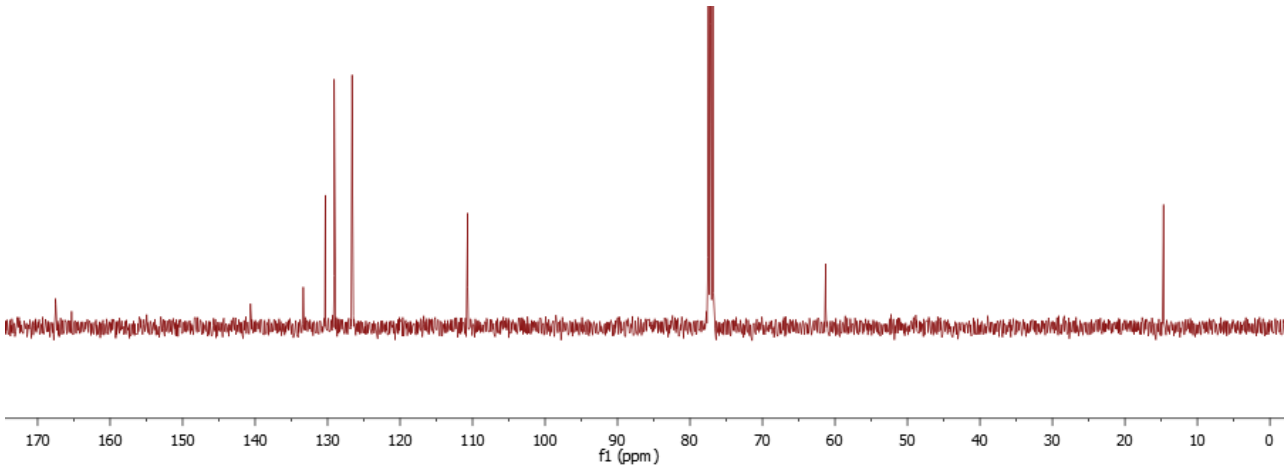


^{13}C NMR spectrum of ethyl (2-methylthiazol-4-yl)diazoacetate 1q

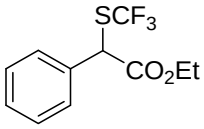


1r

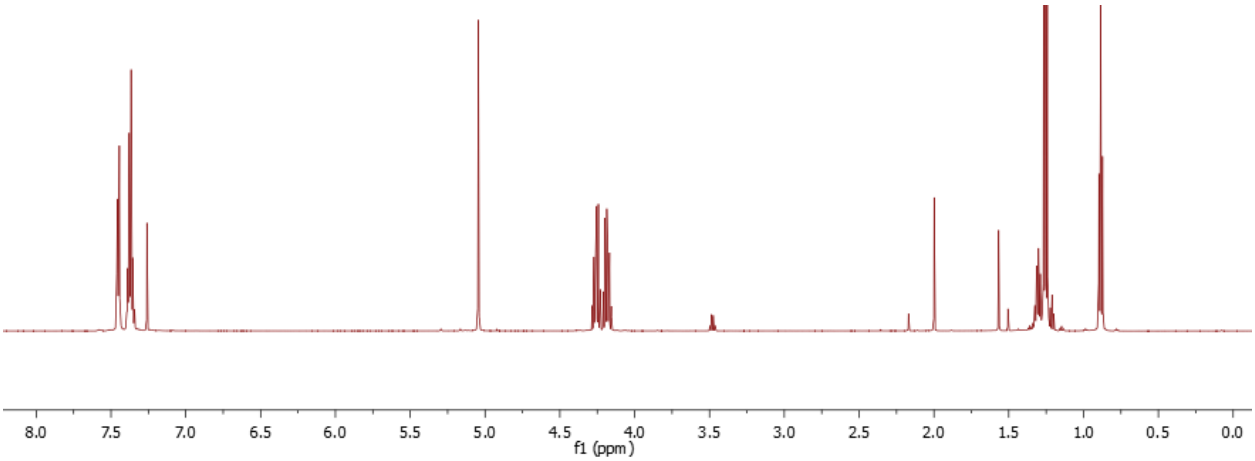
^{1}H NMR spectrum of ethyl (2-phenylthiazol-4-yl)diazoacetate 1r



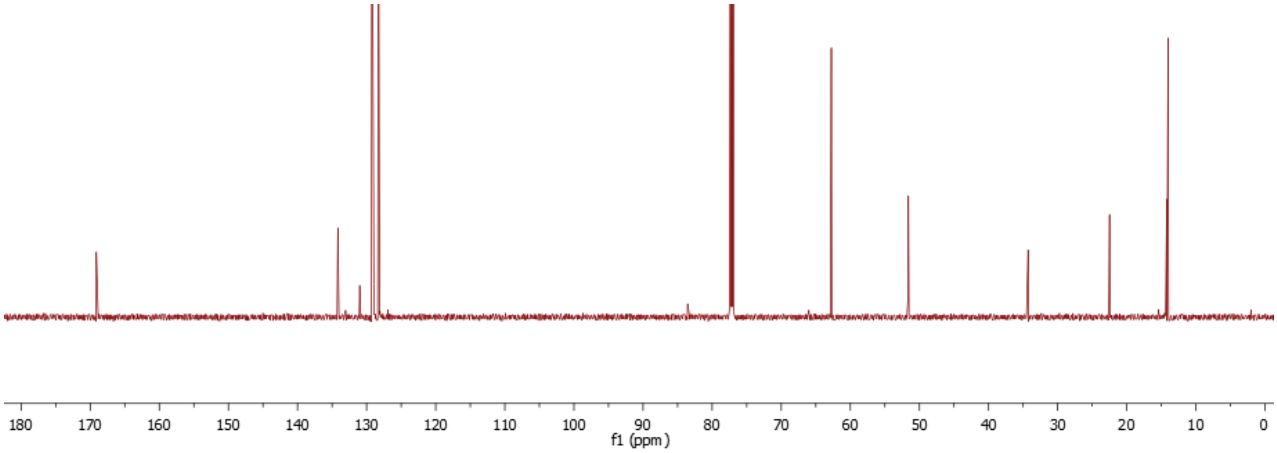
^{13}C NMR spectrum of ethyl (2-phenylthiazol-4-yl)diazoacetate 1r



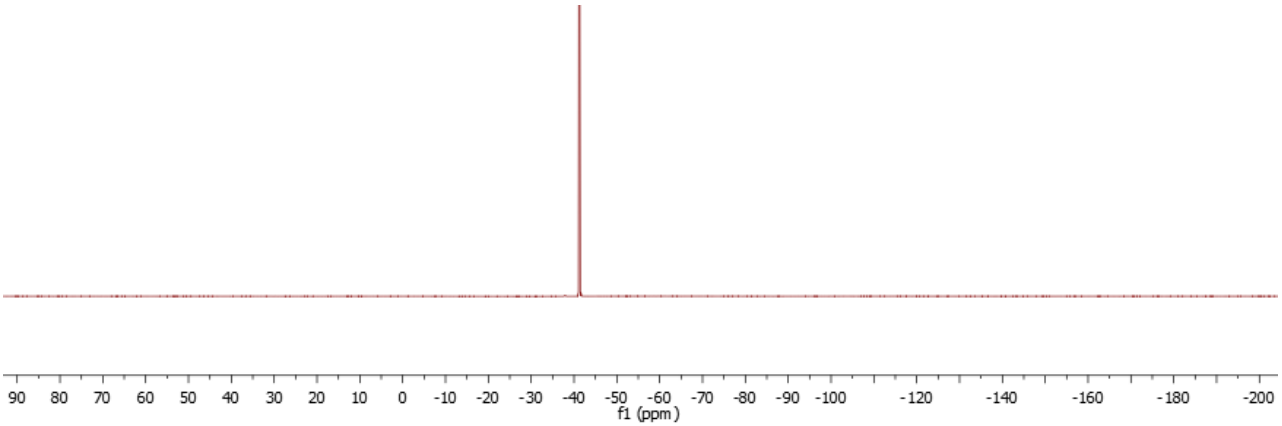
2a



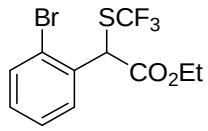
^{1}H NMR spectrum of ethyl phenyl(trifluoromethylthio)acetate 2a



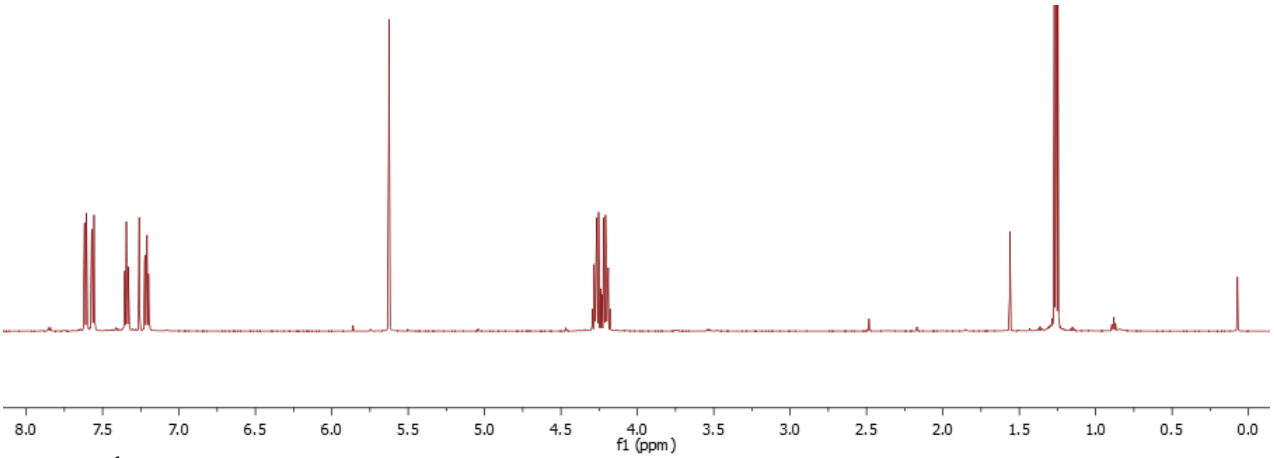
^{13}C NMR spectrum of ethyl phenyl(trifluoromethylthio)acetate 2a



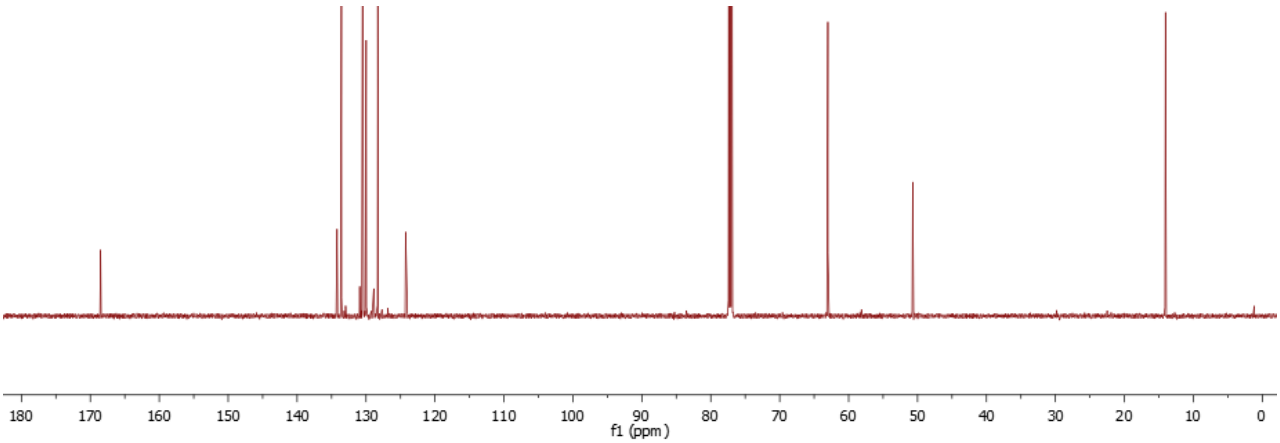
^{19}F NMR spectrum of ethyl phenyl(trifluoromethylthio)acetate 2a



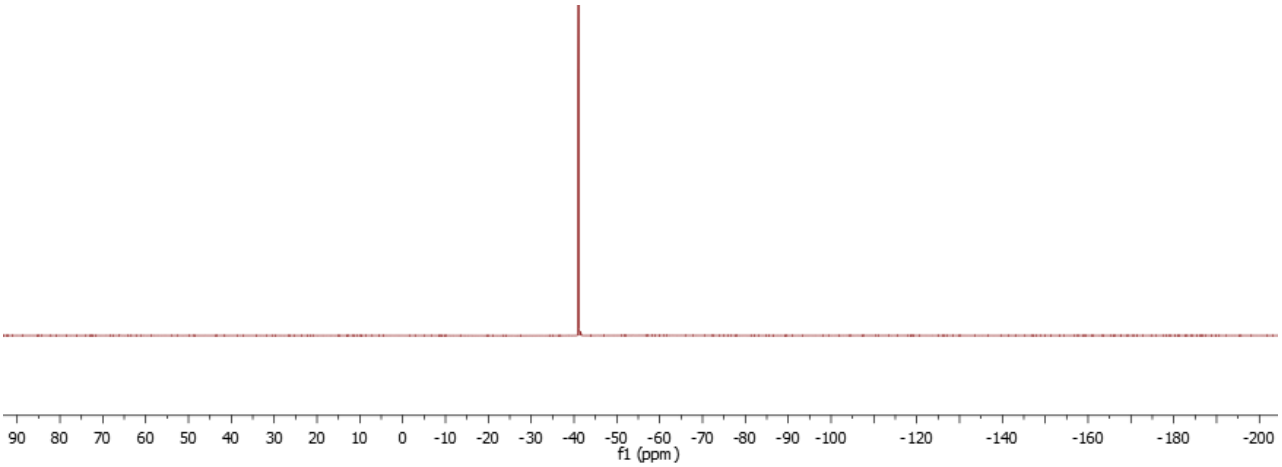
2b



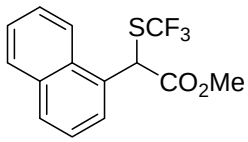
^{1}H NMR spectrum of ethyl (*o*-bromophenyl)(trifluoromethylthio)acetate 2b



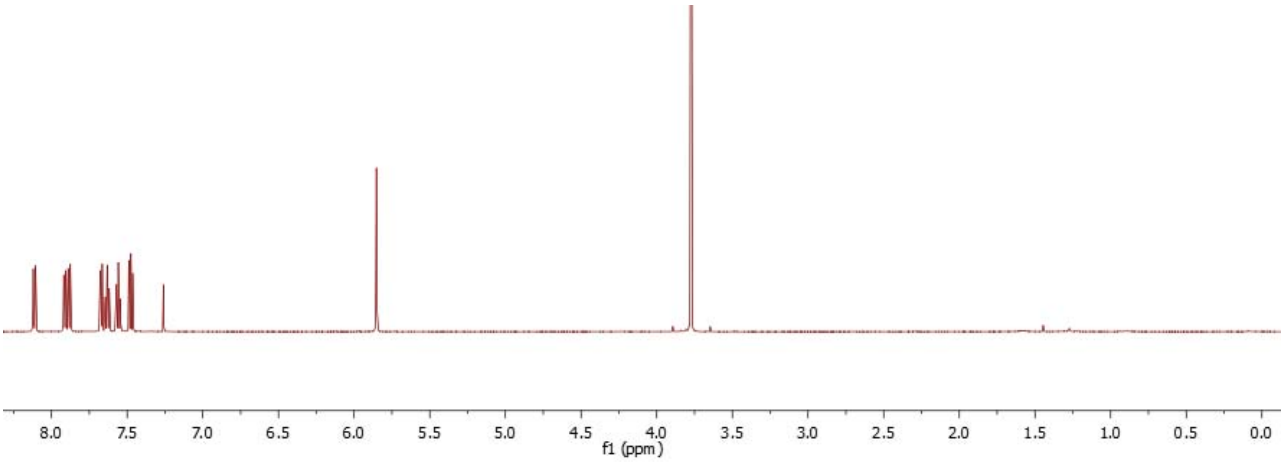
^{13}C NMR spectrum of ethyl (*o*-bromophenyl)(trifluoromethylthio)acetate 2b



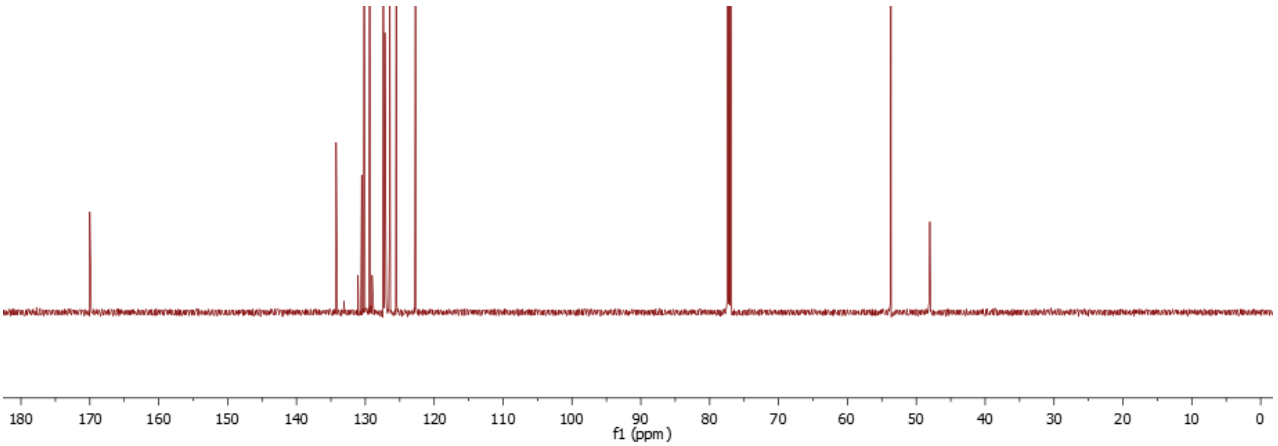
^{19}F NMR spectrum of ethyl (*o*-bromophenyl)(trifluoromethylthio)acetate 2b



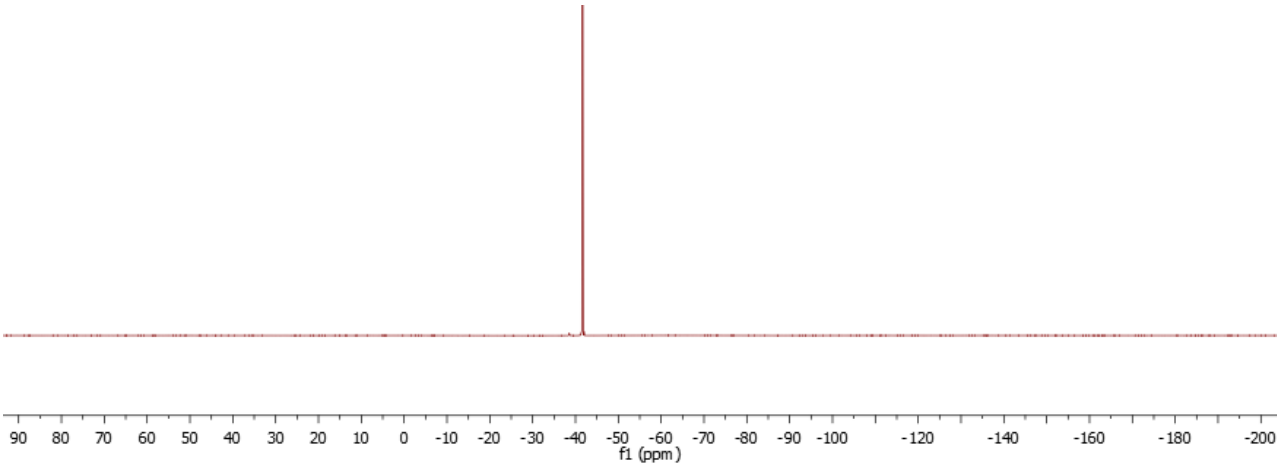
2c



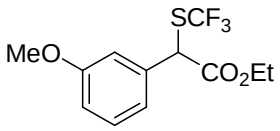
^{1}H NMR spectrum of methyl (1-naphtyl)(trifluoromethylthio)acetate 2c



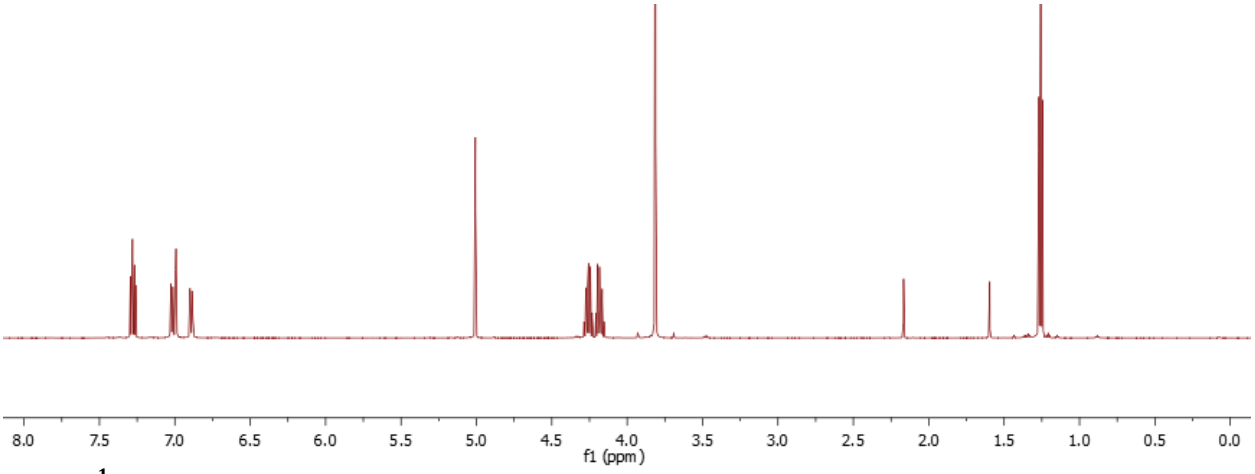
^{13}C NMR spectrum of methyl (1-naphtyl)(trifluoromethylthio)acetate 2c



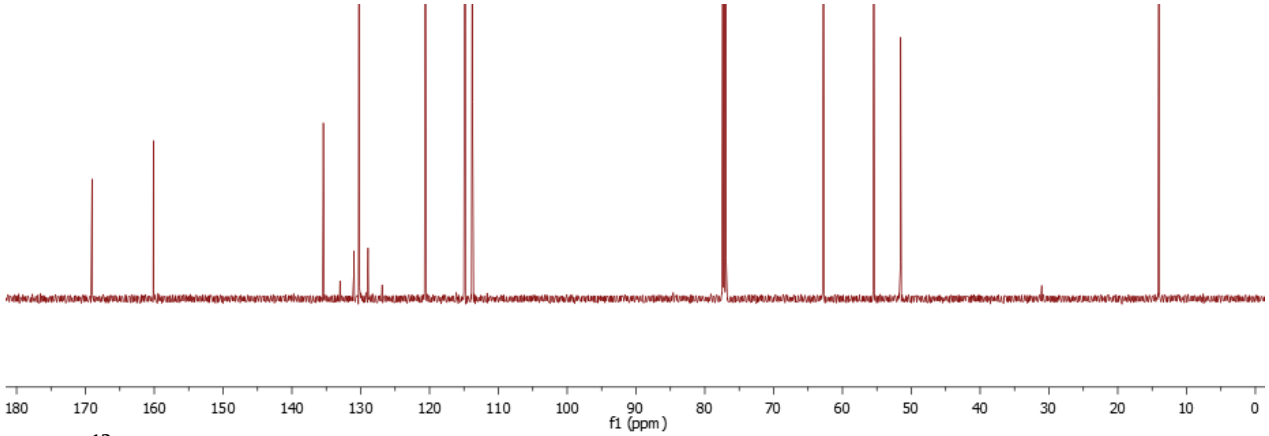
^{19}F NMR spectrum of methyl (1-naphtyl)(trifluoromethylthio)acetate 2c



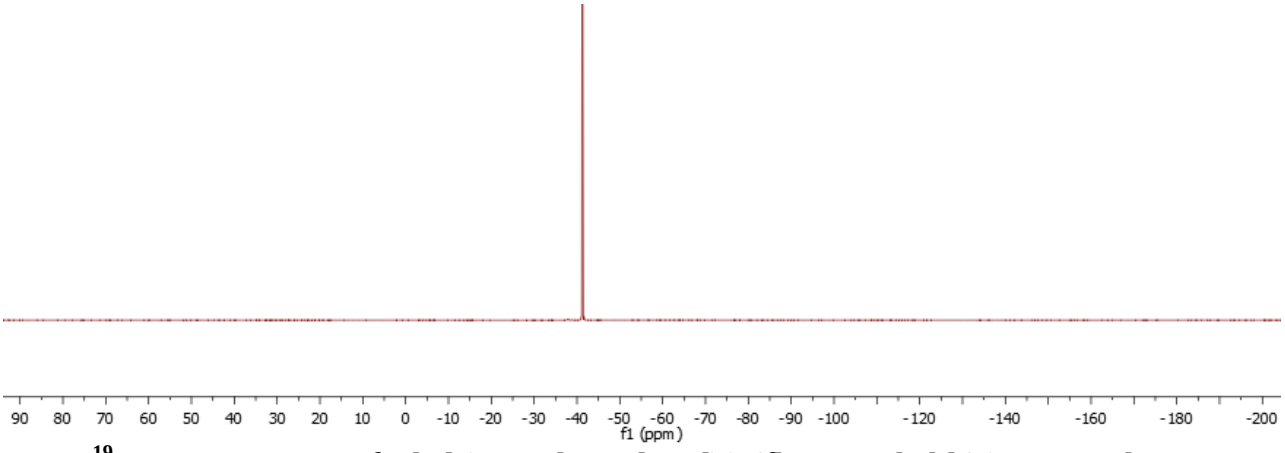
2d



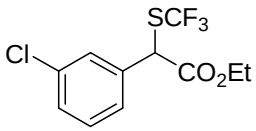
^{1}H NMR spectrum of ethyl (*m*-methoxyphenyl)(trifluoromethylthio)acetate 2d



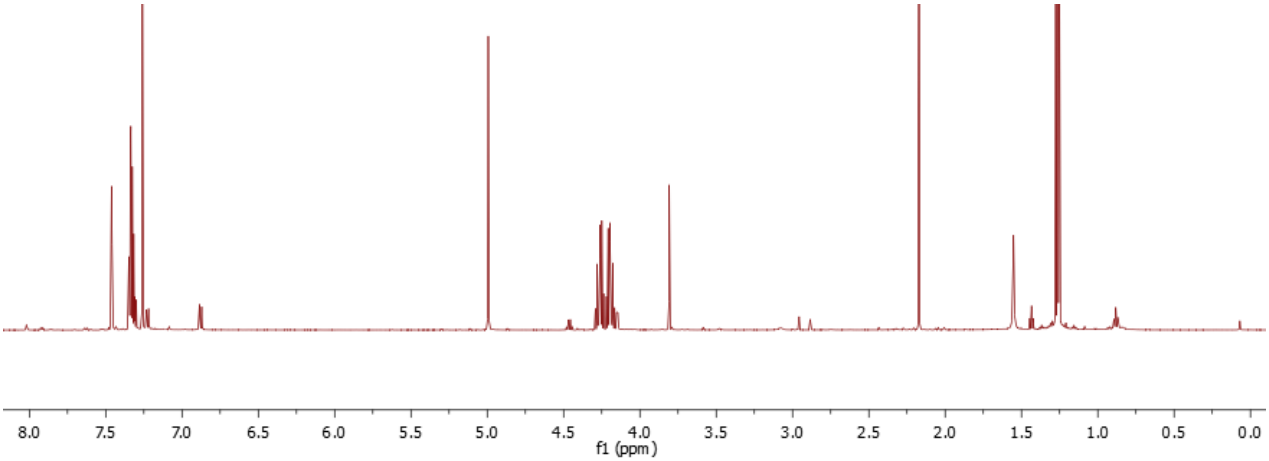
^{13}C NMR spectrum of ethyl (*m*-methoxyphenyl)(trifluoromethylthio)acetate 2d



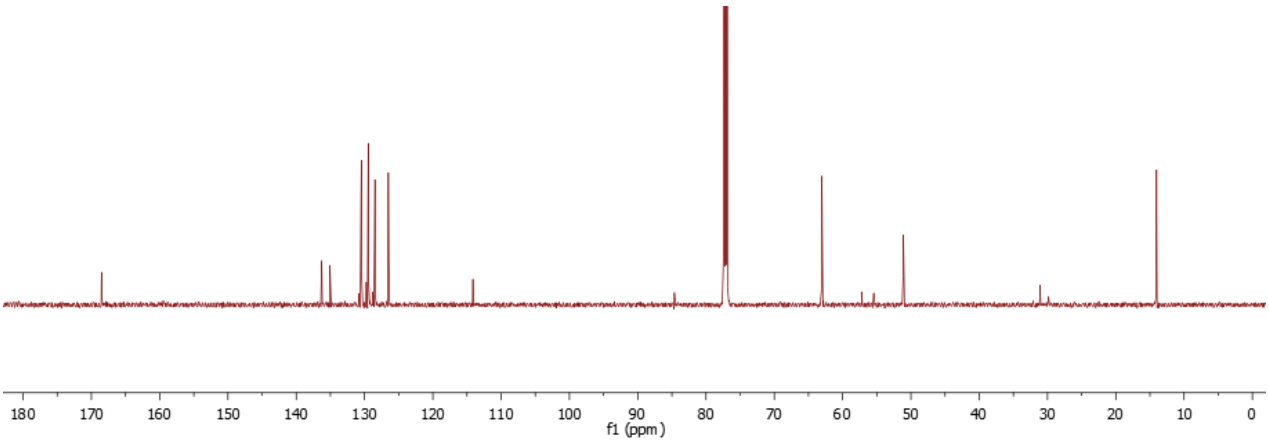
^{19}F NMR spectrum of ethyl (*m*-methoxyphenyl)(trifluoromethylthio)acetate 2d



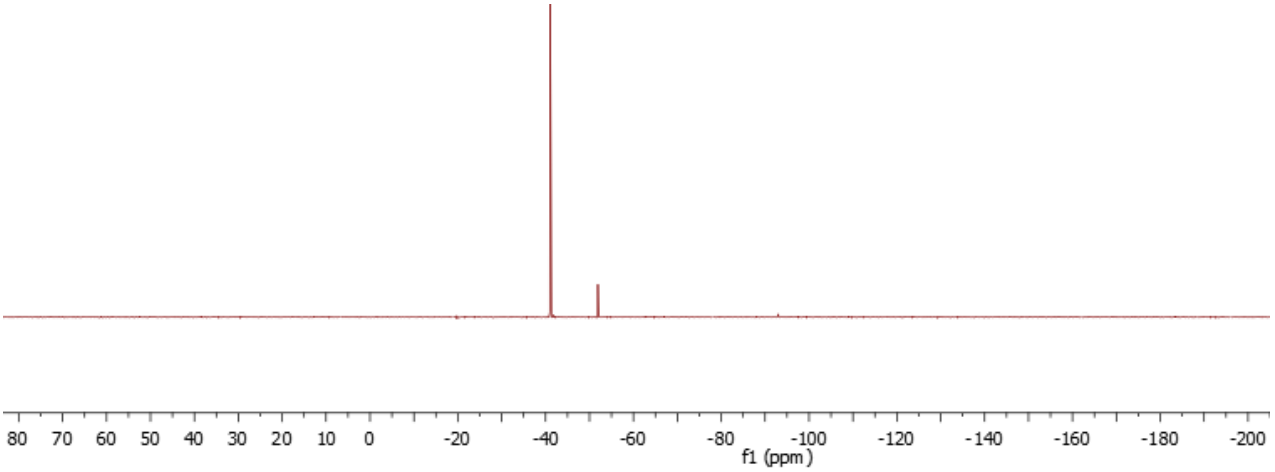
2e



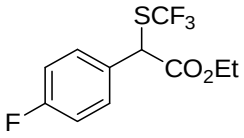
^{1}H NMR spectrum of ethyl (*m*-chlorophenyl)(trifluoromethylthio)acetate 2e



^{13}C NMR spectrum of ethyl (*m*-chlorophenyl)(trifluoromethylthio)acetate 2e



^{19}F NMR spectrum of ethyl (*m*-chlorophenyl)(trifluoromethylthio)acetate 2e



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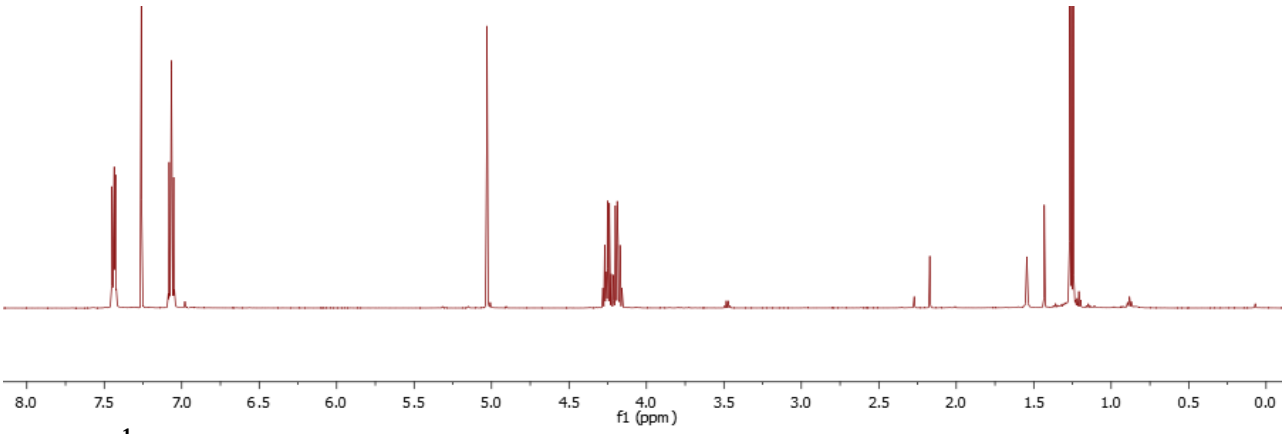
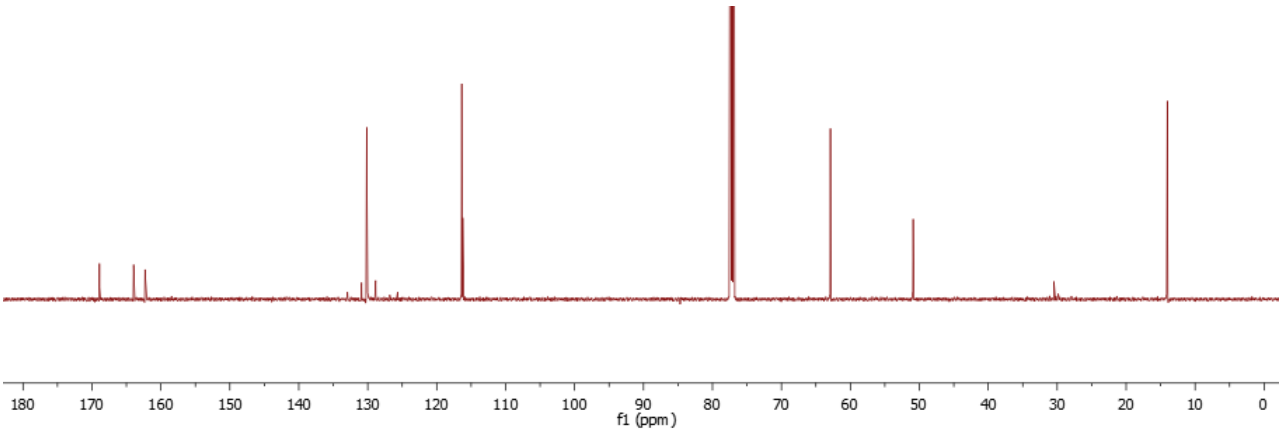
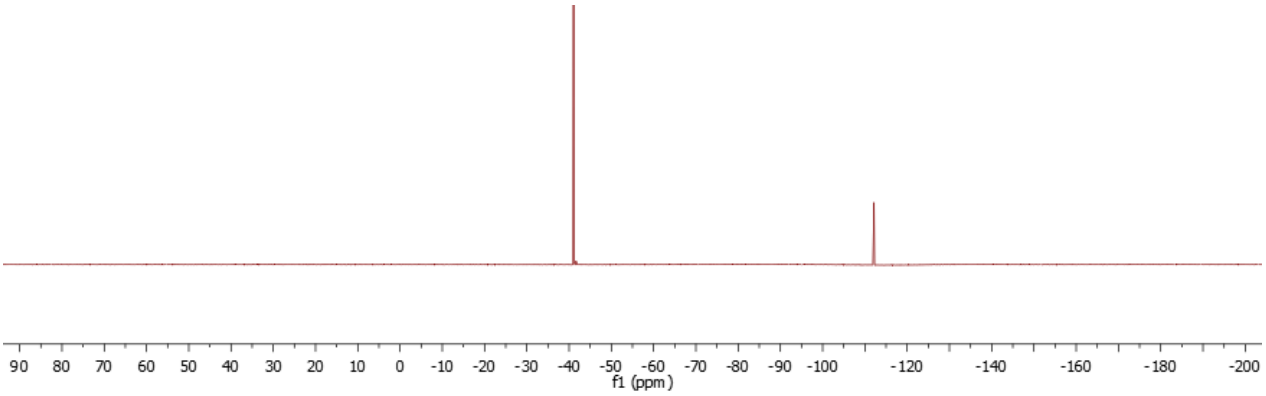


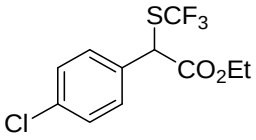
^{1}H NMR spectrum of ethyl (*p*-fluorophenyl)(trifluoromethylthio)acetate 2f



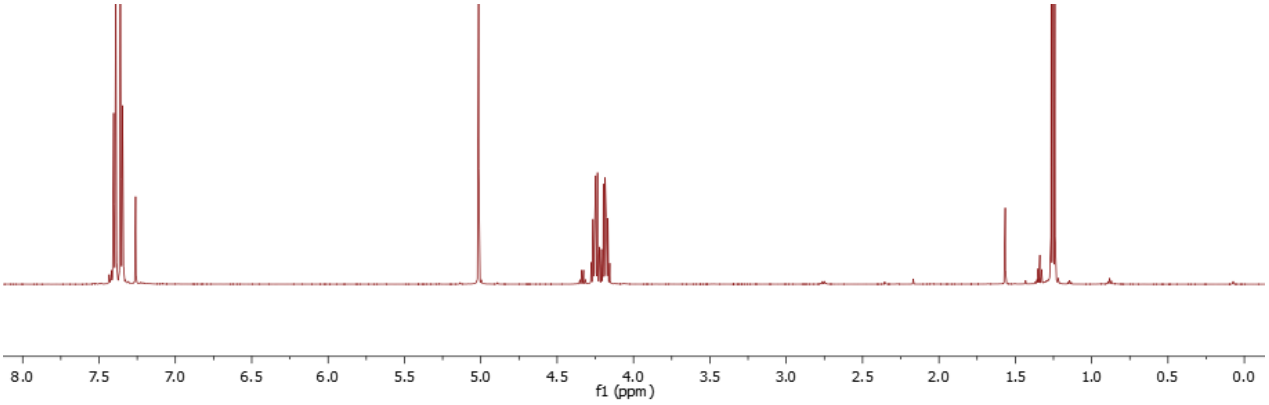
^{13}C NMR spectrum of ethyl (*p*-fluorophenyl)(trifluoromethylthio)acetate 2f



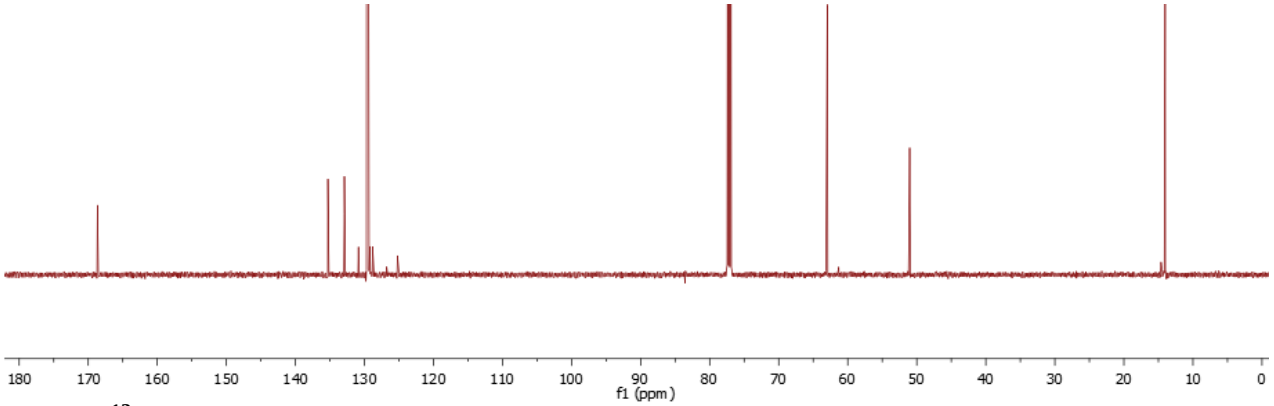
^{19}F NMR spectrum of ethyl (*p*-fluorophenyl)(trifluoromethylthio)acetate 2f



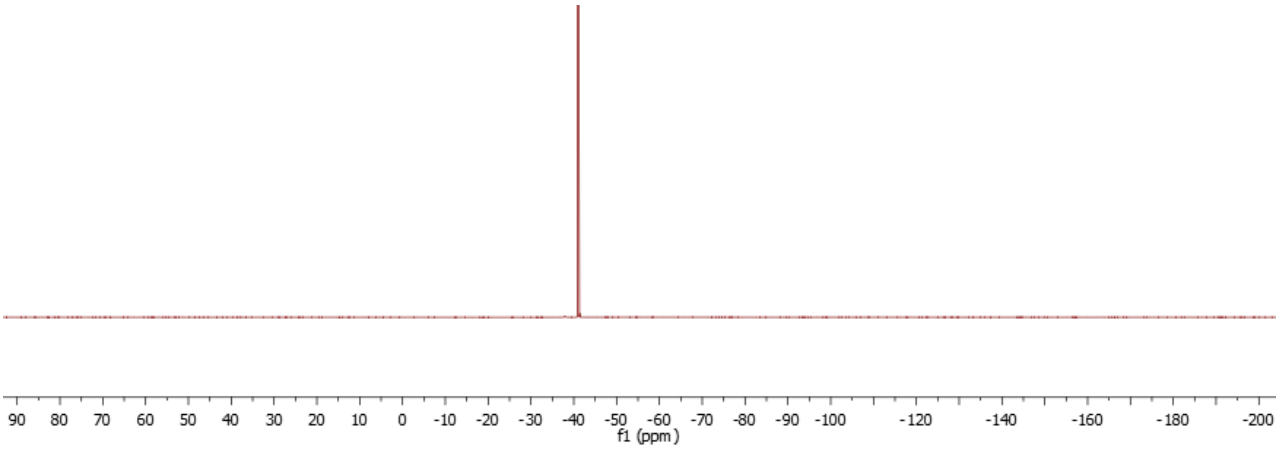
2g



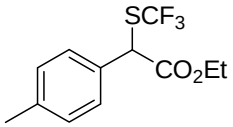
^{1}H NMR spectrum of ethyl (*p*-chlorophenyl)(trifluoromethylthio)acetate 2g



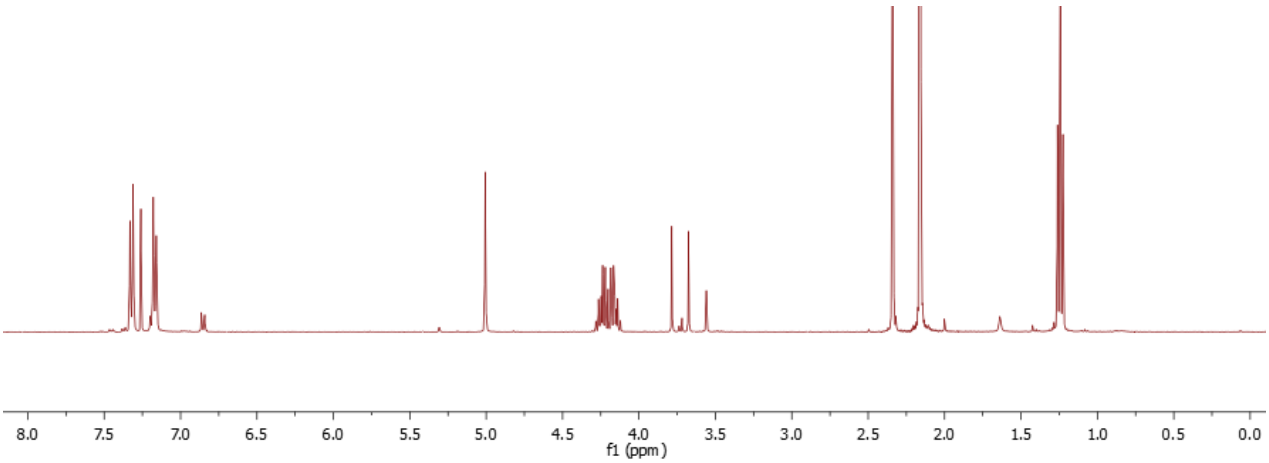
^{13}C NMR spectrum of ethyl (*p*-chlorophenyl)(trifluoromethylthio)acetate 2g



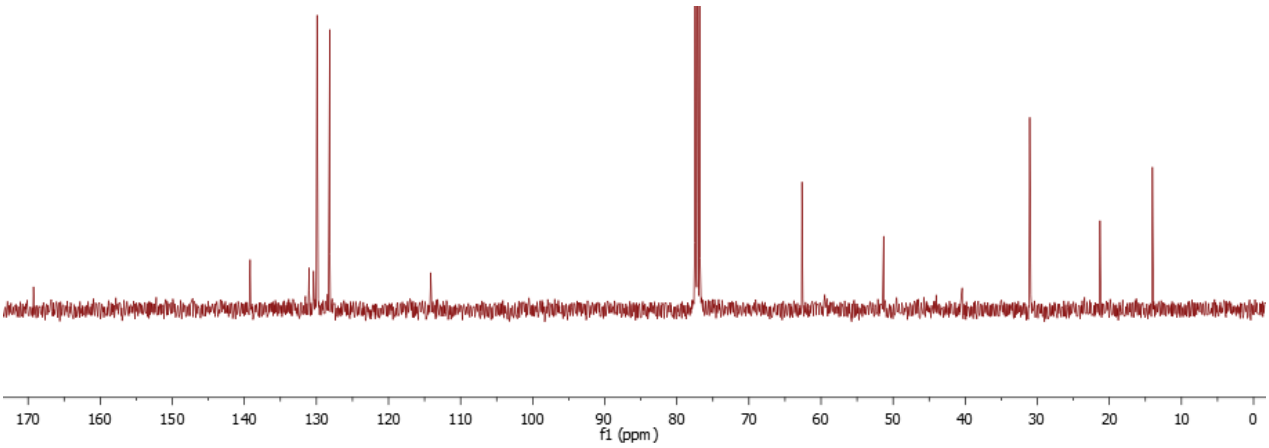
^{19}F NMR spectrum of ethyl (*p*-chlorophenyl)(trifluoromethylthio)acetate 2g



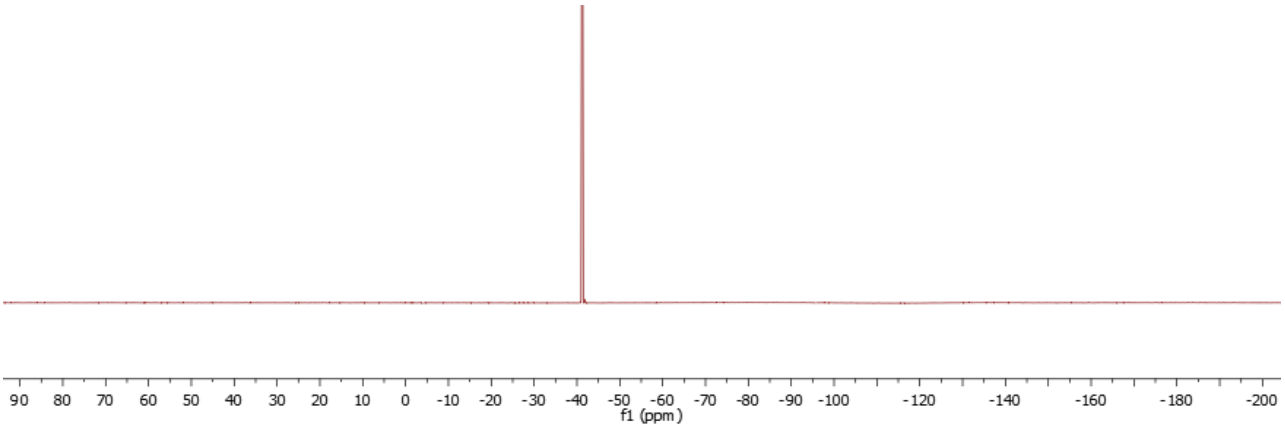
2h



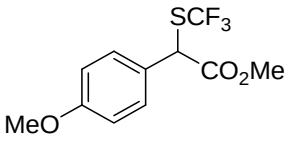
^{1}H NMR spectrum of ethyl (*p*-tolyl)(trifluoromethylthio)acetate 2h



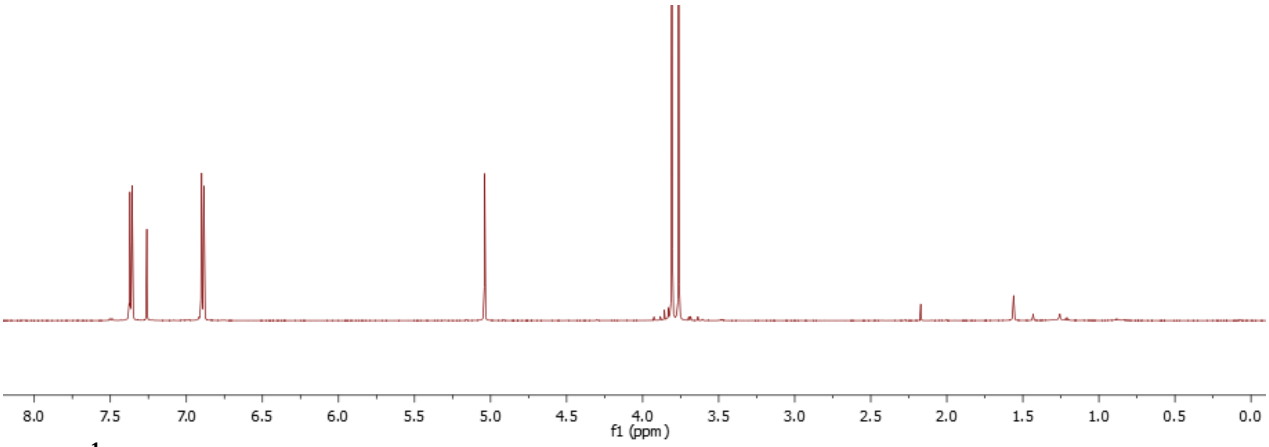
^{13}C NMR spectrum of ethyl (*p*-tolyl)(trifluoromethylthio)acetate 2h



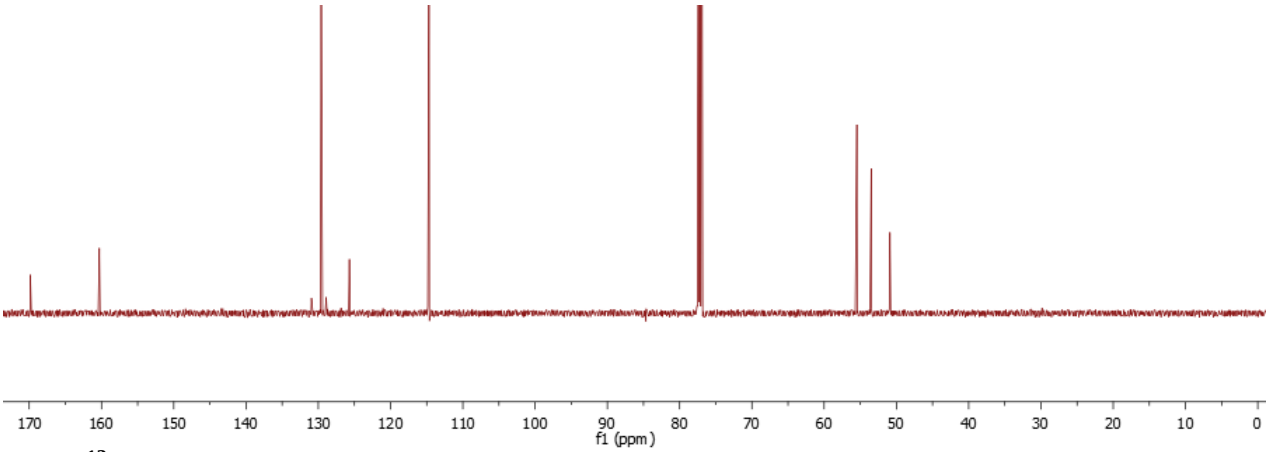
^{19}F NMR spectrum of ethyl (*p*-tolyl)(trifluoromethylthio)acetate 2h



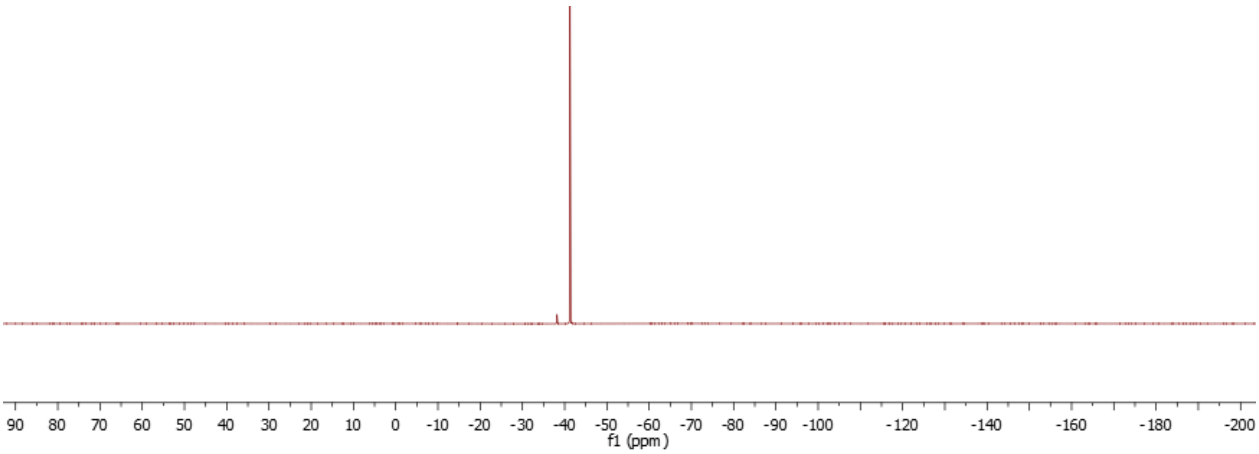
2i



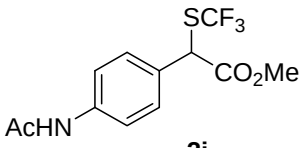
^{1}H NMR spectrum of methyl (*p*-methoxyphenyl)(trifluoromethylthio)acetate 2i



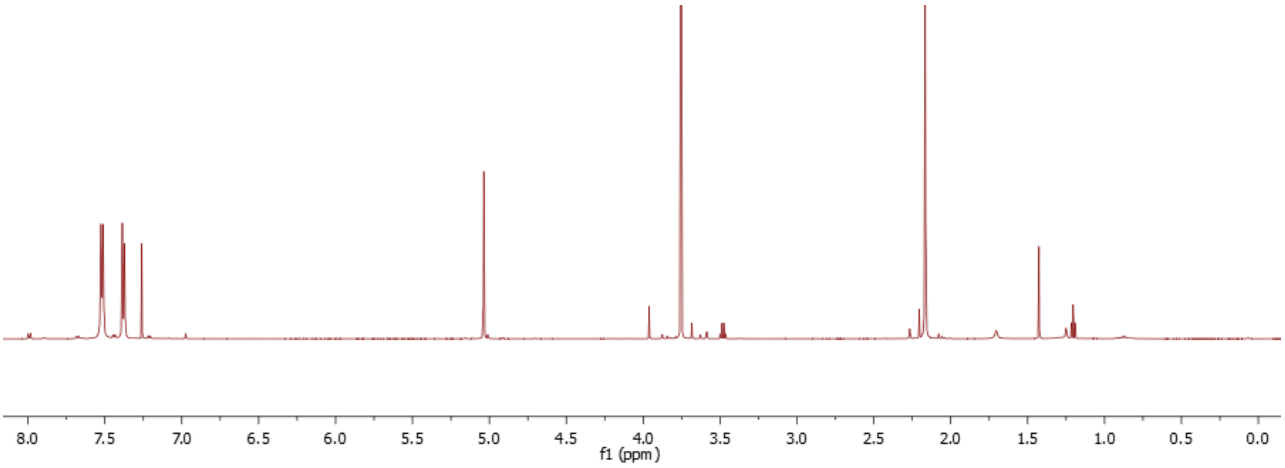
^{13}C NMR spectrum of methyl (*p*-methoxyphenyl)(trifluoromethylthio)acetate 2i



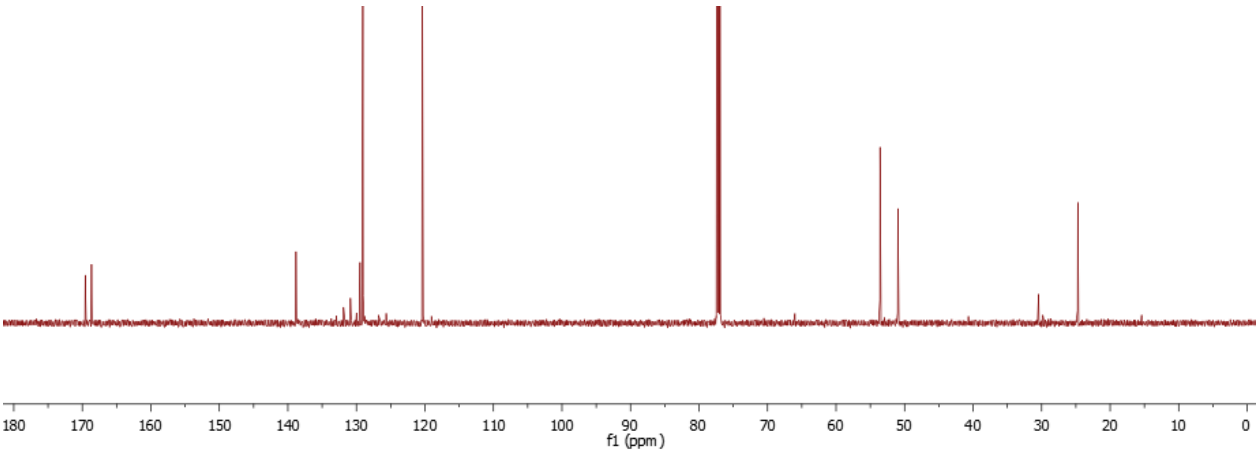
^{19}F NMR spectrum of methyl (*p*-methoxyphenyl)(trifluoromethylthio)acetate 2i



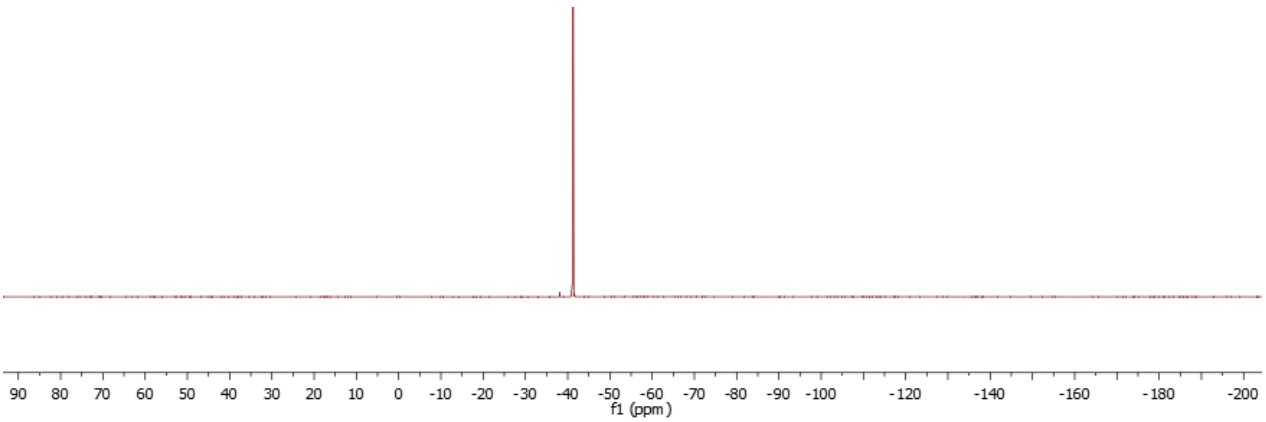
2j



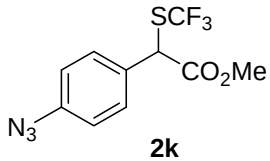
^{1}H NMR spectrum of methyl (*p*-acetylaminophenyl)(trifluoromethylthio)acetate 2j



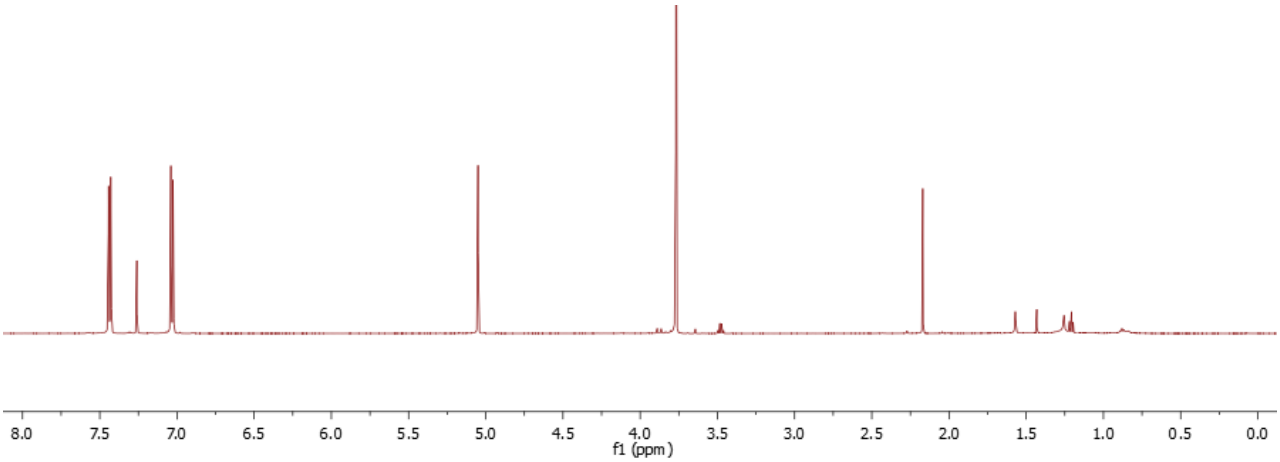
^{13}C NMR spectrum of methyl (*p*-acetylaminophenyl)(trifluoromethylthio)acetate 2j



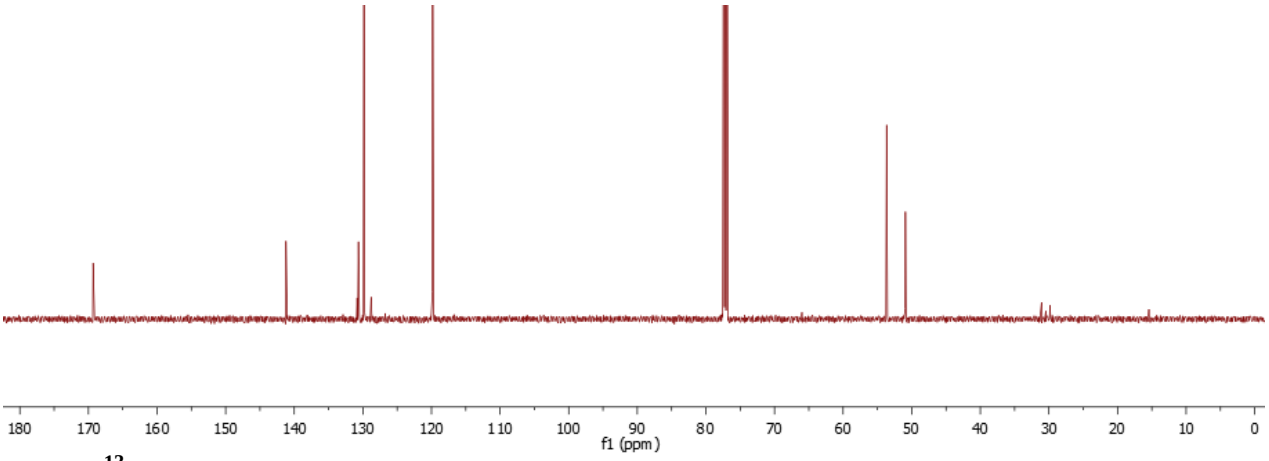
^{19}F NMR spectrum of methyl (*p*-acetylaminophenyl)(trifluoromethylthio)acetate 2j



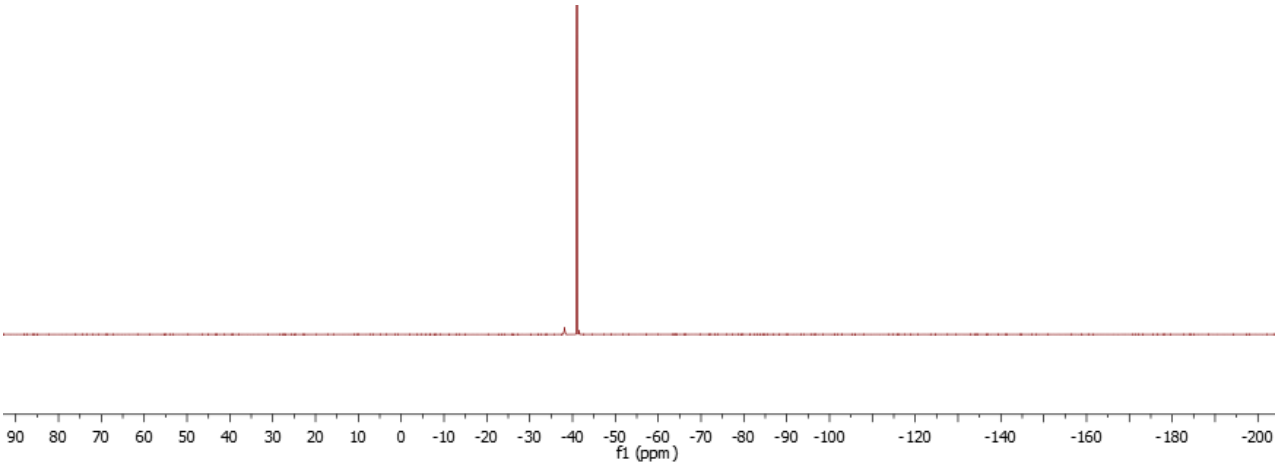
2k



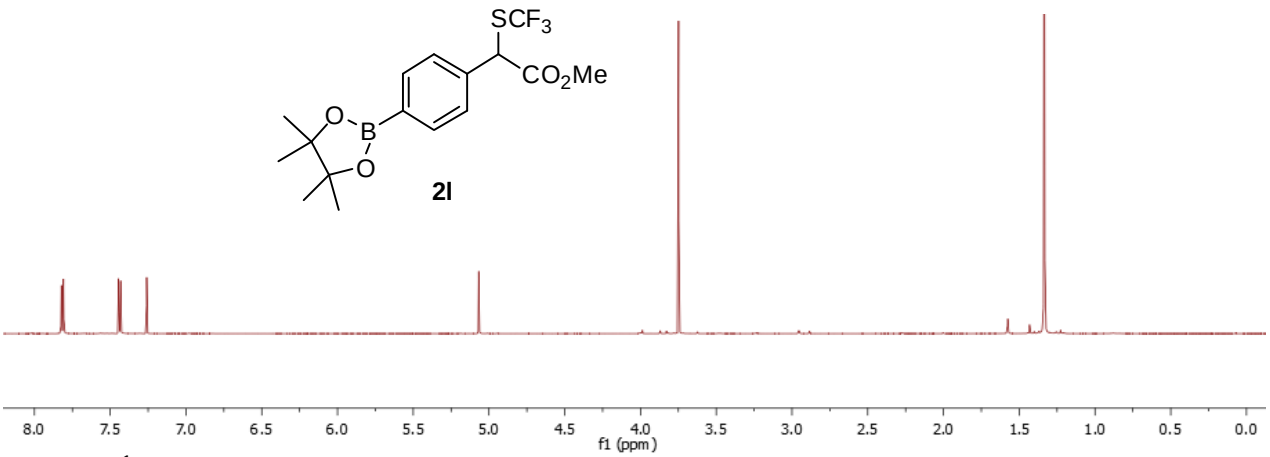
^{1}H NMR spectrum of methyl (*p*-azidophenyl)(trifluoromethylthio)acetate 2k



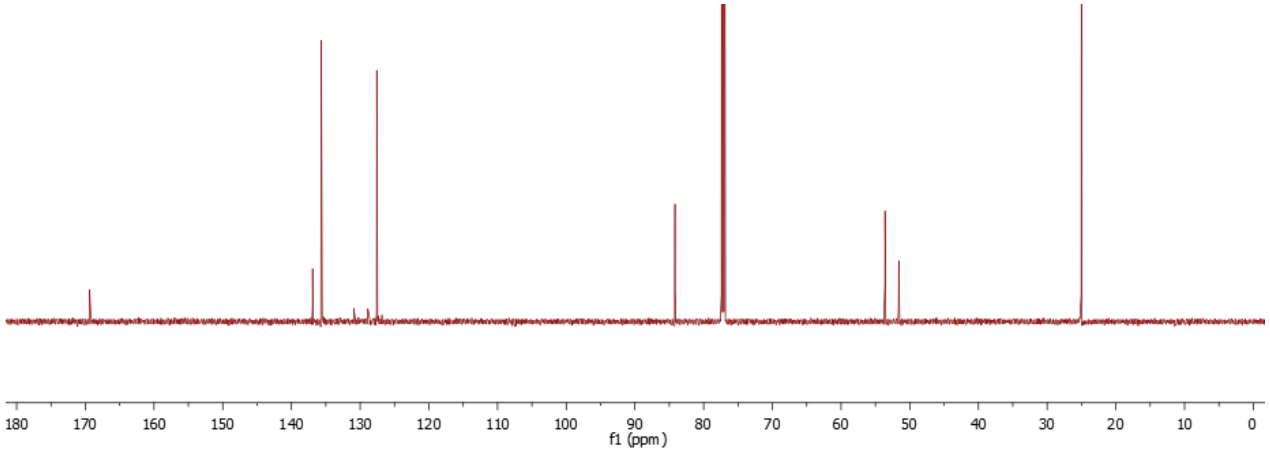
^{13}C NMR spectrum of methyl (*p*-azidophenyl)(trifluoromethylthio)acetate 2k



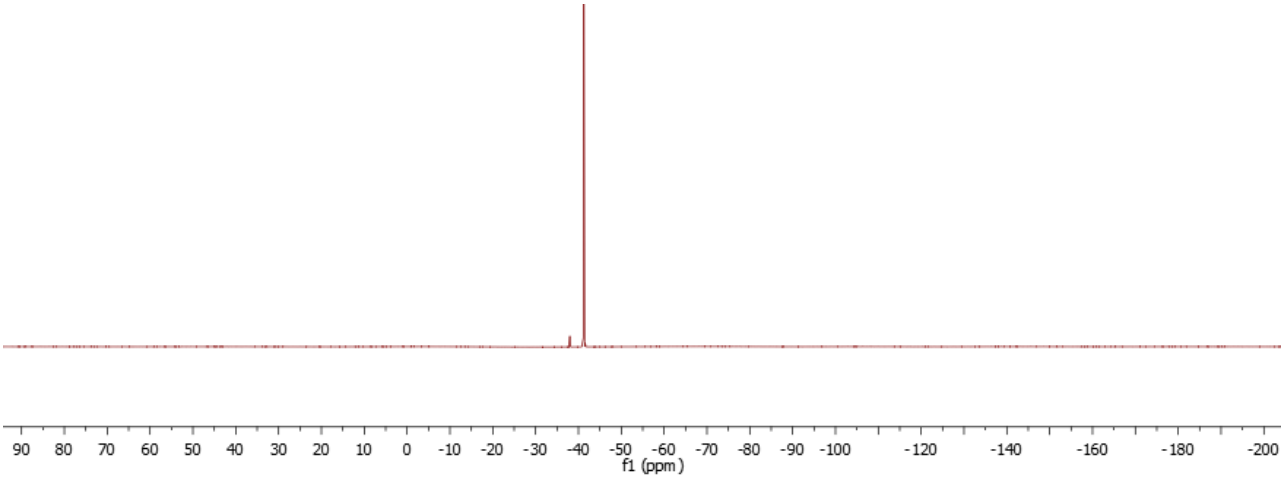
^{19}F NMR spectrum of methyl (*p*-azidophenyl)(trifluoromethylthio)acetate 2k



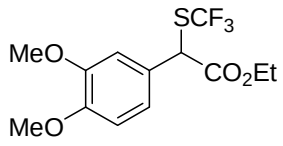
^{1}H NMR spectrum of methyl [*p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y)phenyl](trifluoromethylthio)acetate 2l



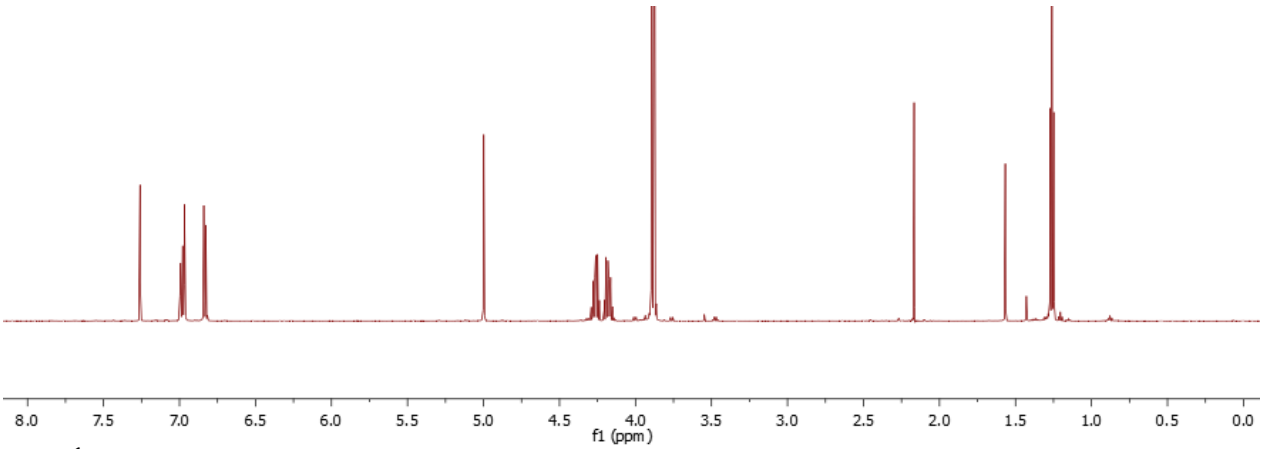
^{13}C NMR spectrum of methyl [*p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y)phenyl](trifluoromethylthio)acetate 2l



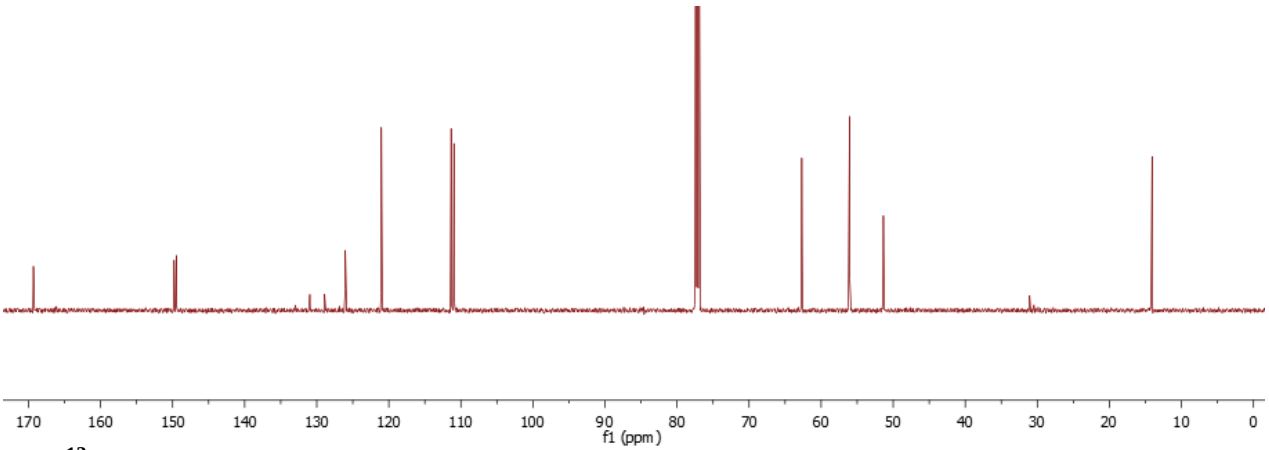
^{19}F NMR spectrum of methyl [*p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y)phenyl](trifluoromethylthio)acetate 2l



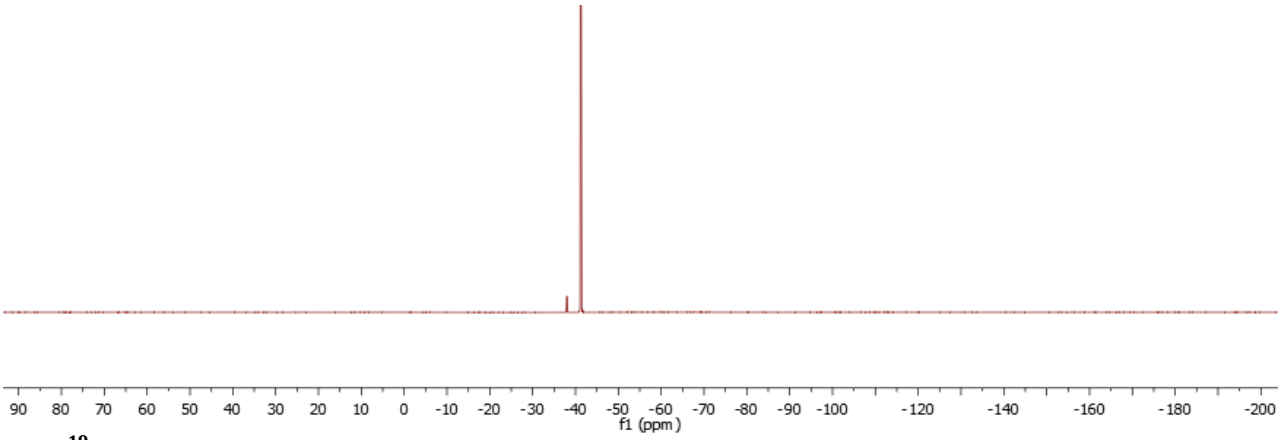
2m



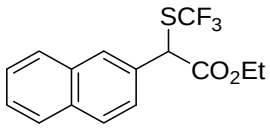
^{1}H NMR spectrum of ethyl (*3,4*-dimethoxyphenyl)(trifluoromethylthio)acetate 2m



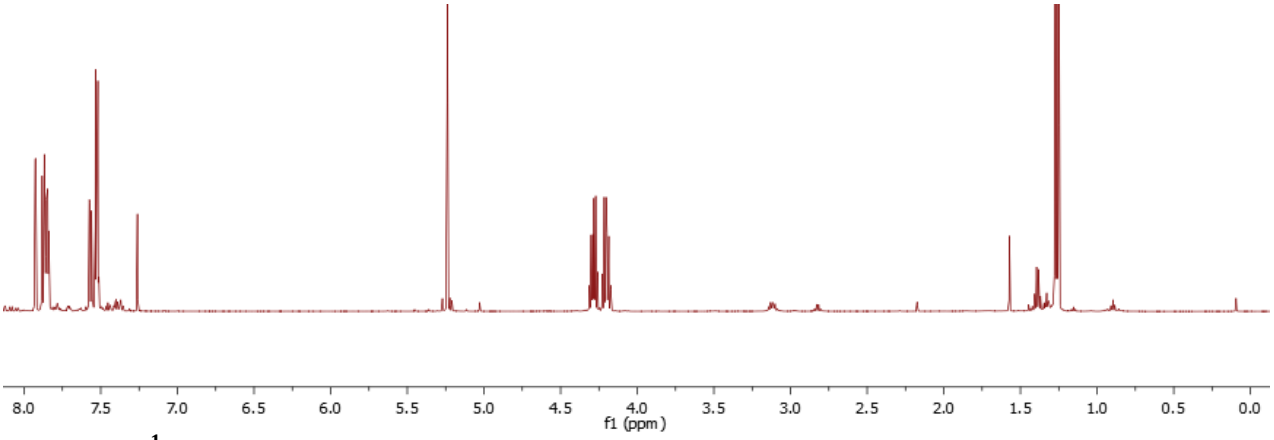
^{13}C NMR spectrum of ethyl (*3,4*-dimethoxyphenyl)(trifluoromethylthio)acetate 2m



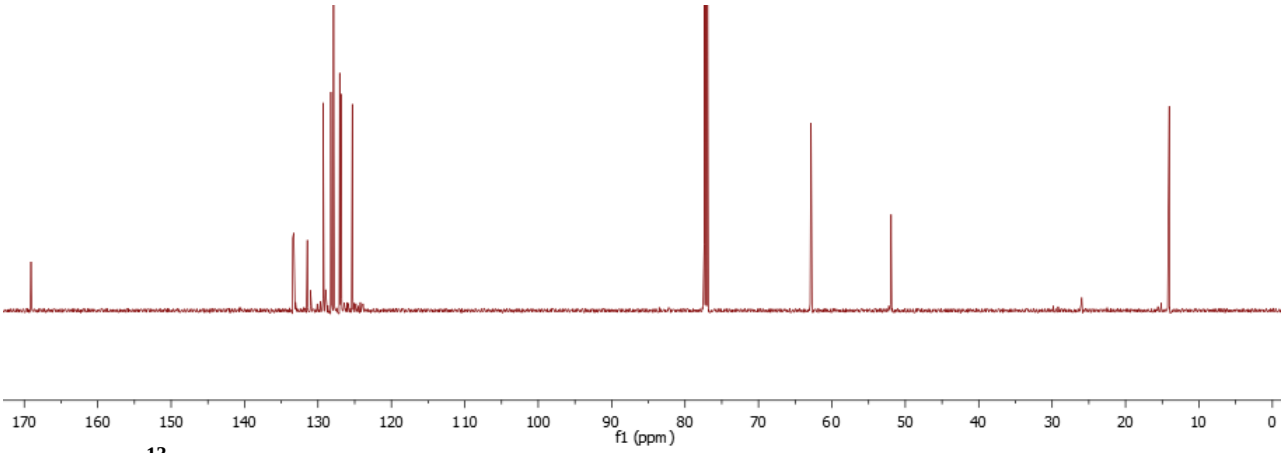
^{19}F NMR spectrum of ethyl (*3,4*-dimethoxyphenyl)(trifluoromethylthio)acetate 2m



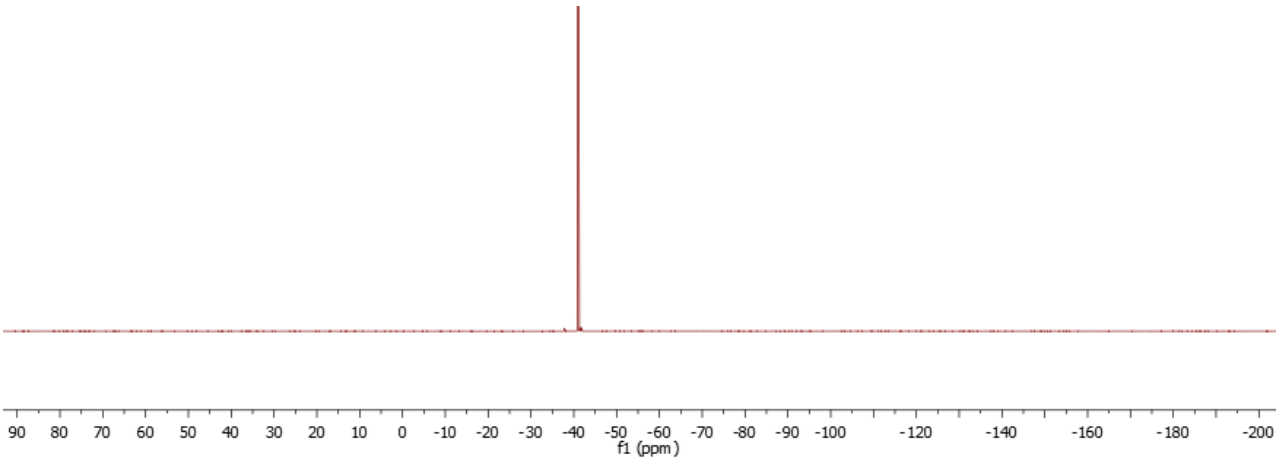
2n



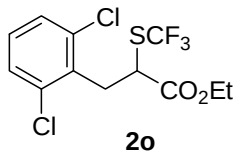
^{1}H NMR spectrum of ethyl (2-naphtyl)(trifluoromethylthio)acetate 2n



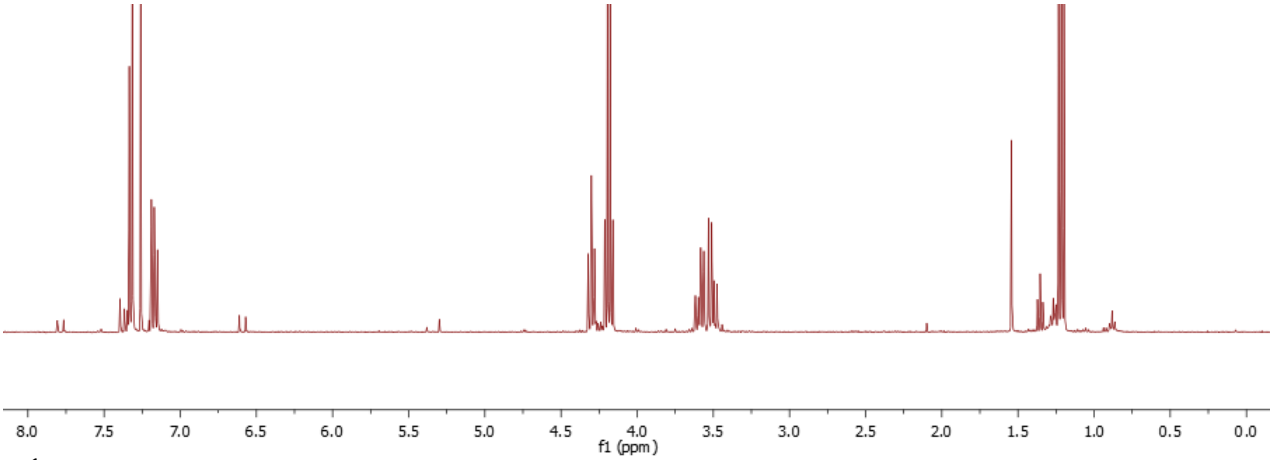
^{13}C NMR spectrum of ethyl (2-naphtyl)(trifluoromethylthio)acetate 2n



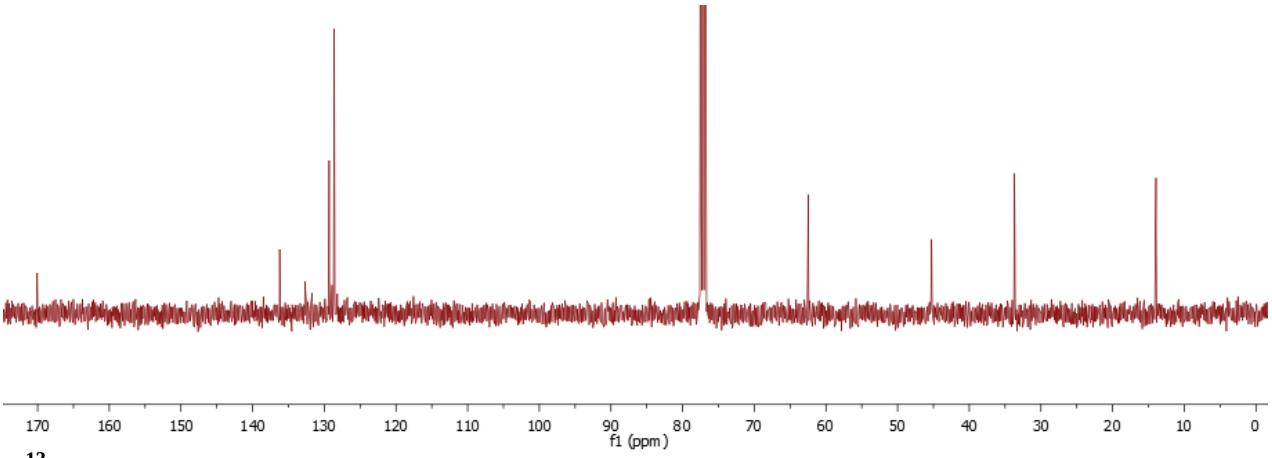
^{19}F NMR spectrum of ethyl (2-naphtyl)(trifluoromethylthio)acetate 2n



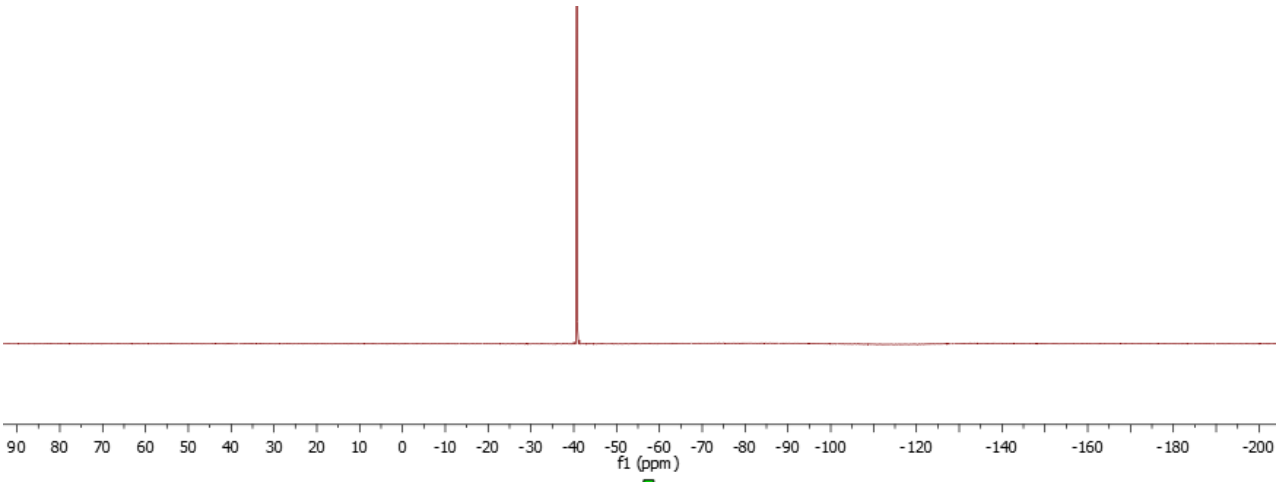
2o



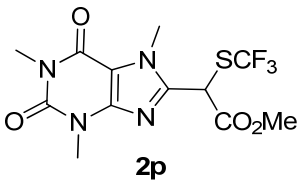
^{1}H NMR spectrum of ethyl 3-(*3,4*-dichlorophenyl)-2-(trifluoromethylthio)propanoate 2o



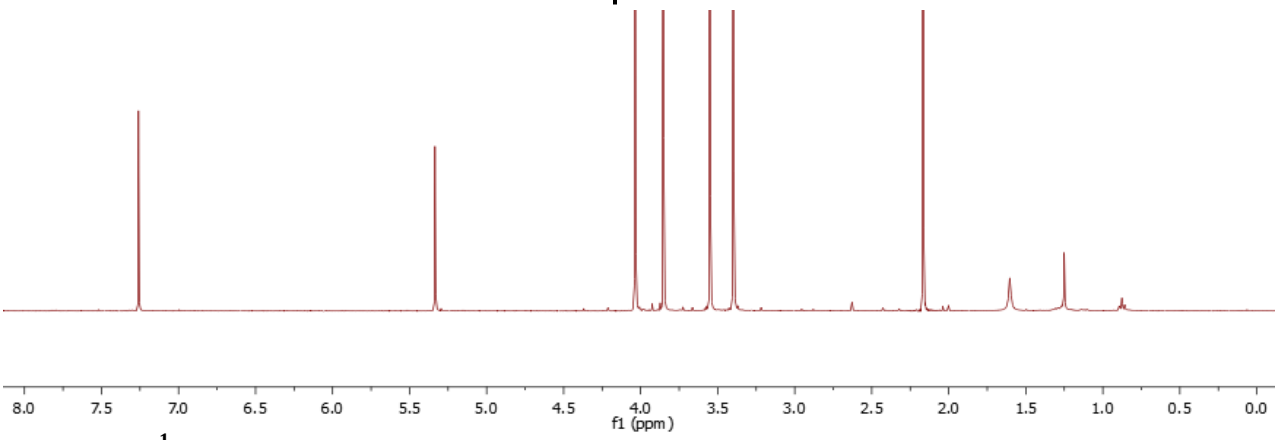
^{13}C NMR spectrum of ethyl 3-(*3,4*-dichlorophenyl)-2-(trifluoromethylthio)propanoate 2o



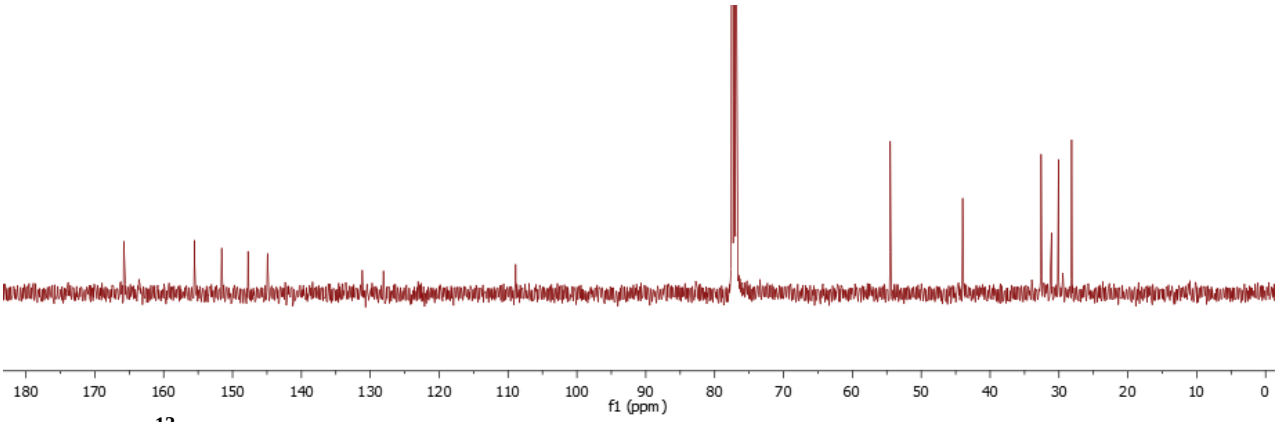
^{19}F NMR spectrum of ethyl 3-(*3,4*-dichlorophenyl)-2-(trifluoromethylthio)propanoate 2o



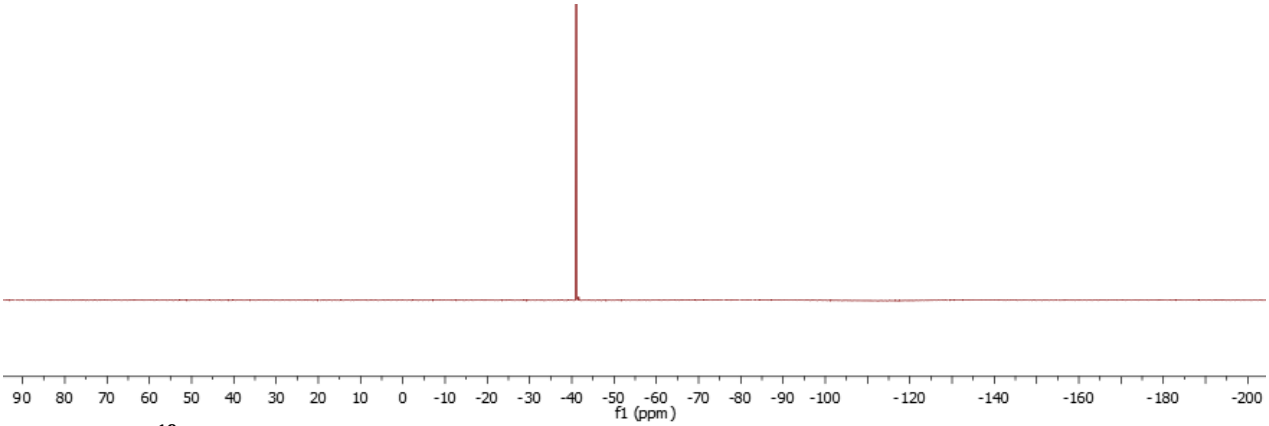
2p



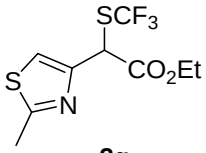
^{1}H NMR spectrum of methyl caffeino(trifluoromethylthio)acetate 2p



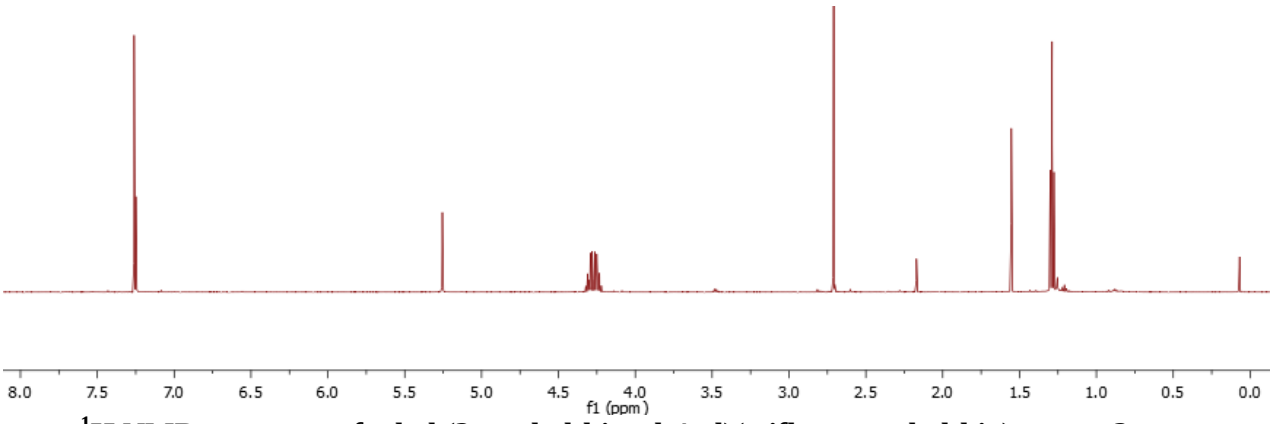
^{13}C NMR spectrum of methyl caffeino(trifluoromethylthio)acetate 2p



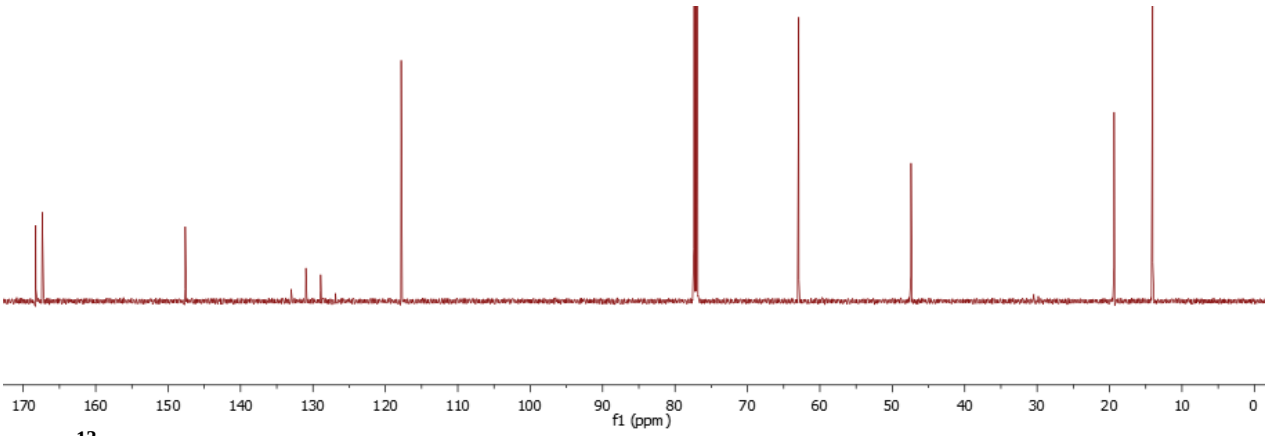
^{19}F NMR spectrum of methyl caffeino(trifluoromethylthio)acetate 2p



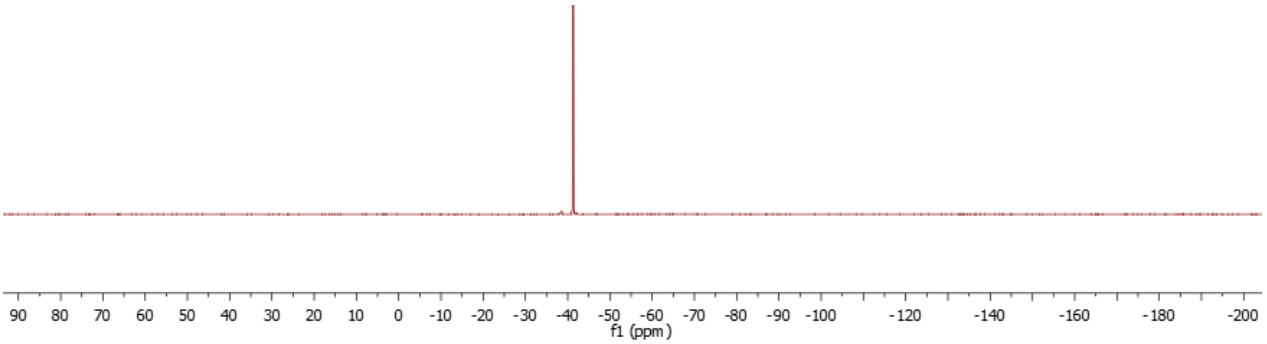
2q



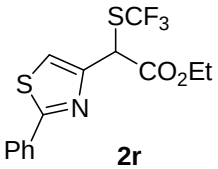
^{1}H NMR spectrum of ethyl (2-methylthiazol-4-yl)(trifluoromethylthio)acetate 2q



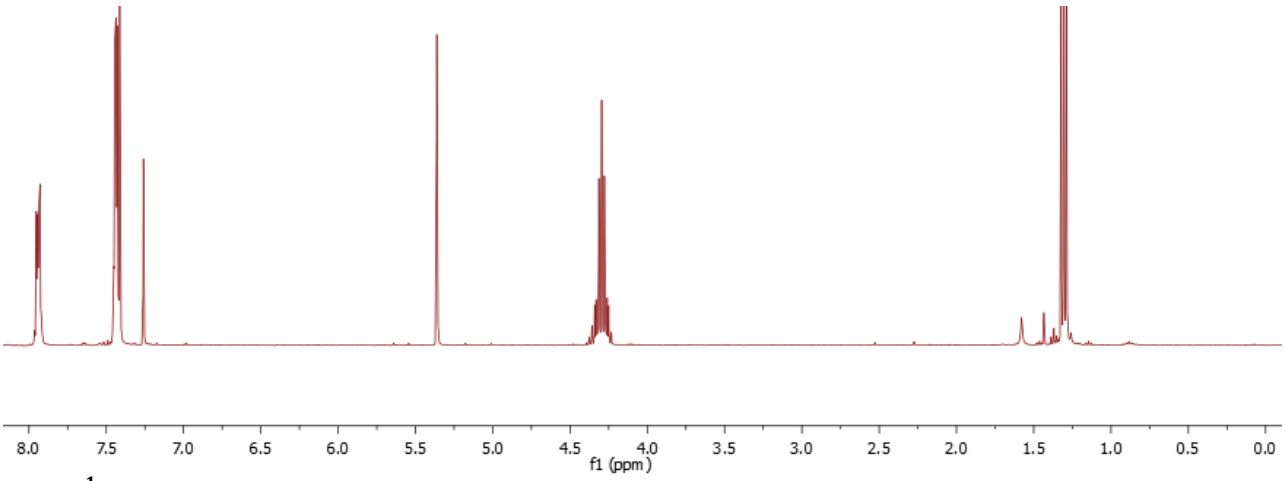
^{13}C NMR spectrum of ethyl (2-methylthiazol-4-yl)(trifluoromethylthio)acetate 2q



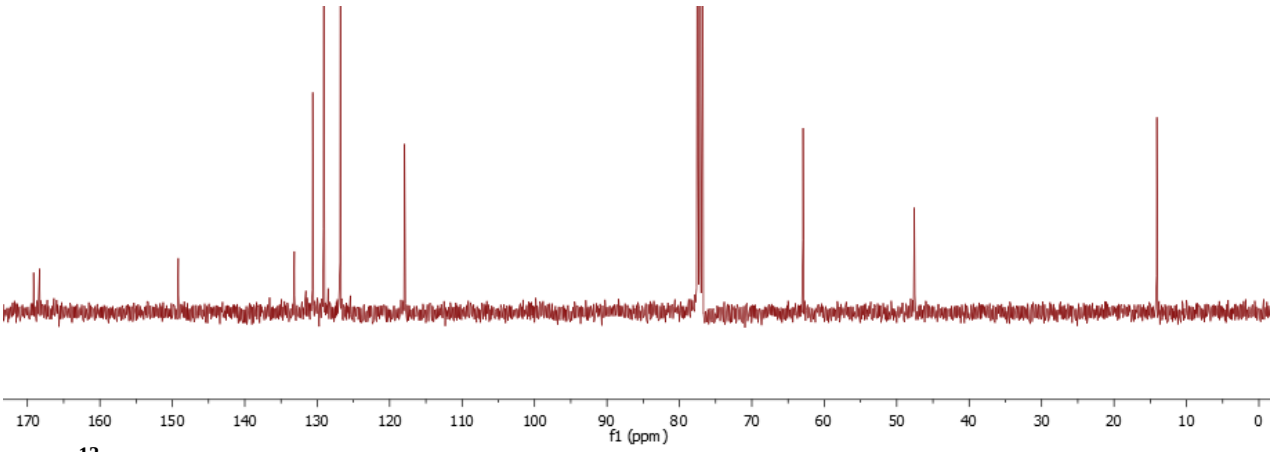
^{19}F NMR spectrum of ethyl (2-methylthiazol-4-yl)(trifluoromethylthio)acetate 2q



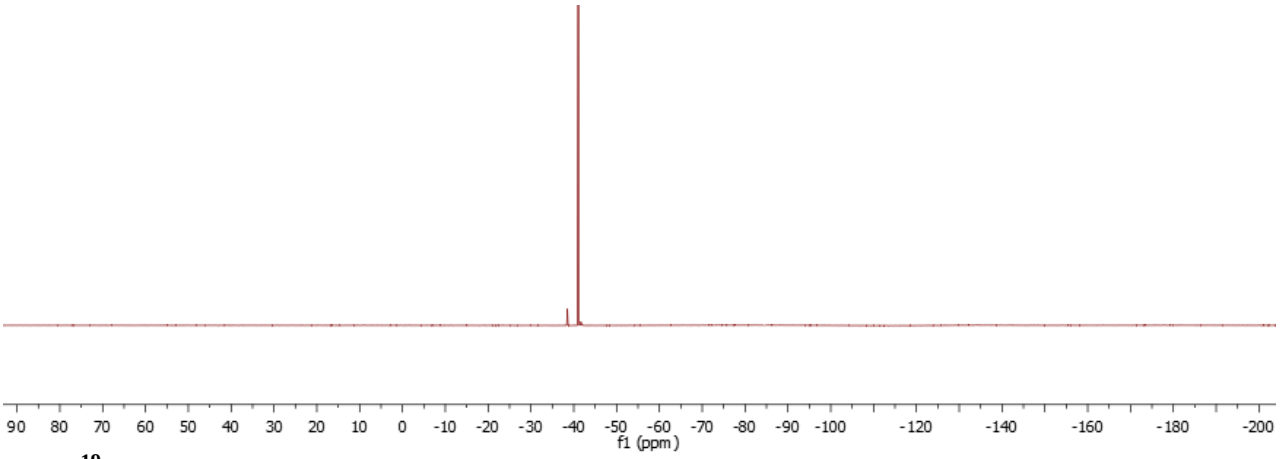
2r



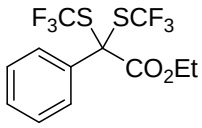
^{1}H NMR spectrum of ethyl (2-phenylthiazol-4-yl)(trifluoromethylthio)acetate 2r



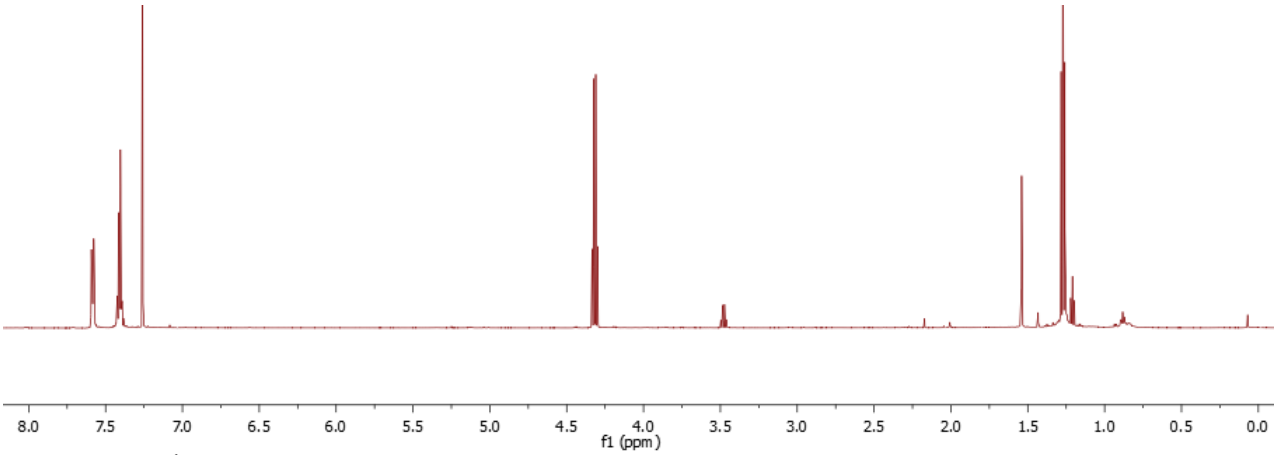
^{13}C NMR spectrum of ethyl (2-phenylthiazol-4-yl)(trifluoromethylthio)acetate 2r



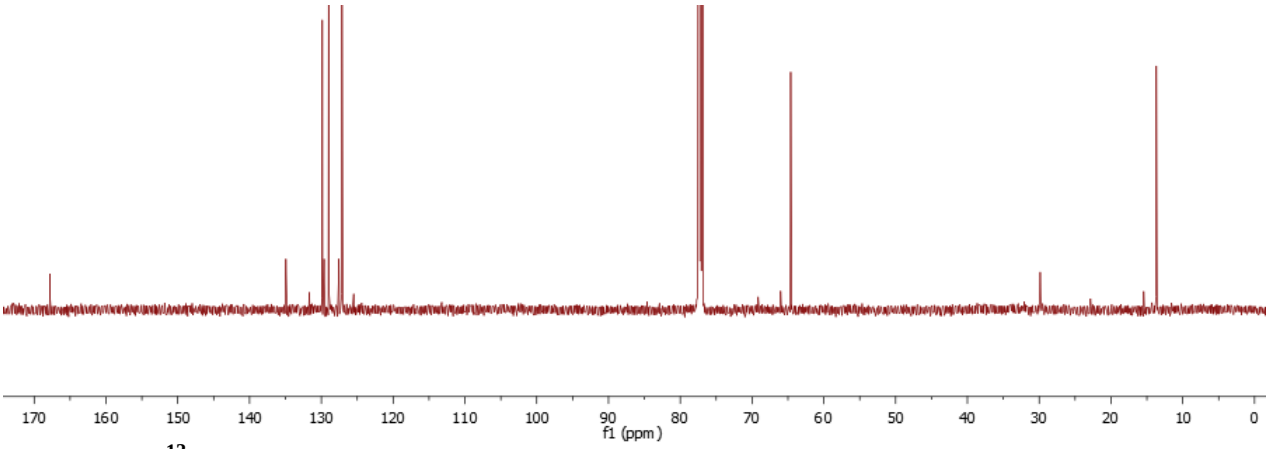
^{19}F NMR spectrum of ethyl (2-phenylthiazol-4-yl)(trifluoromethylthio)acetate 2r



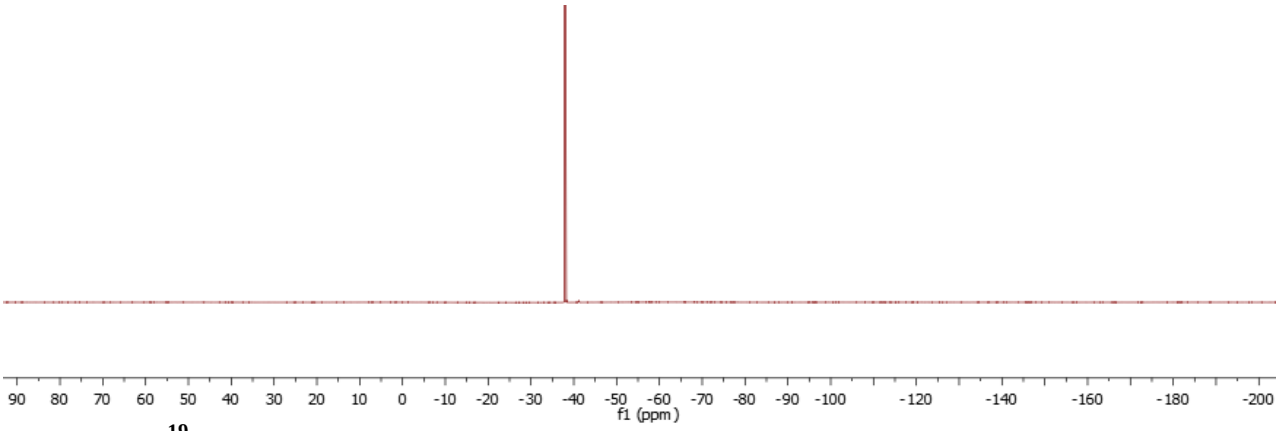
3a



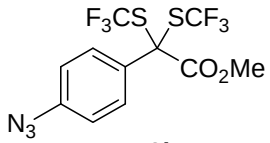
^{1}H NMR spectrum of ethyl phenyldi(trifluoromethylthio)acetate 3a



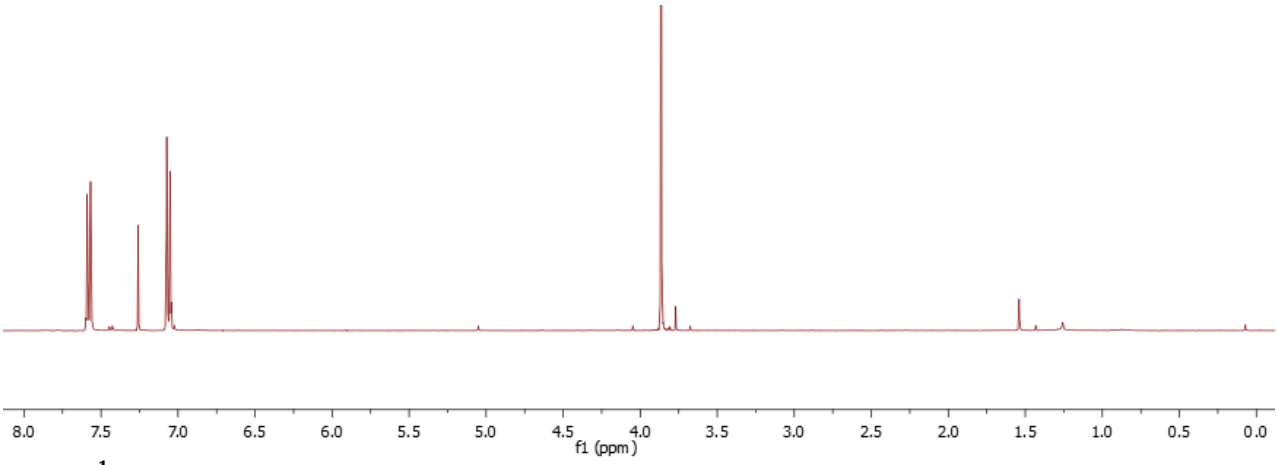
^{13}C NMR spectrum of ethyl phenyldi(trifluoromethylthio)acetate 3a



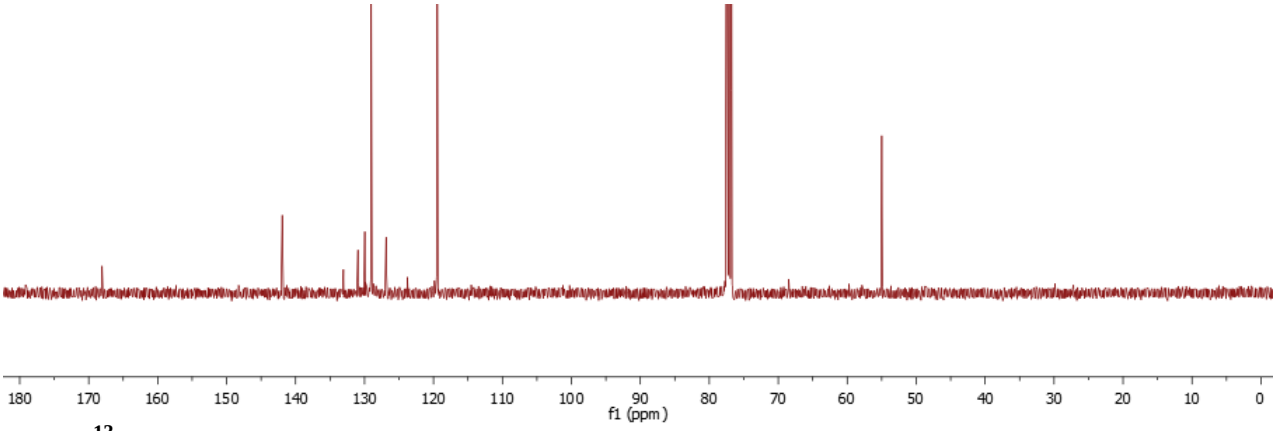
^{19}F NMR spectrum of ethyl phenyldi(trifluoromethylthio)acetate 3a



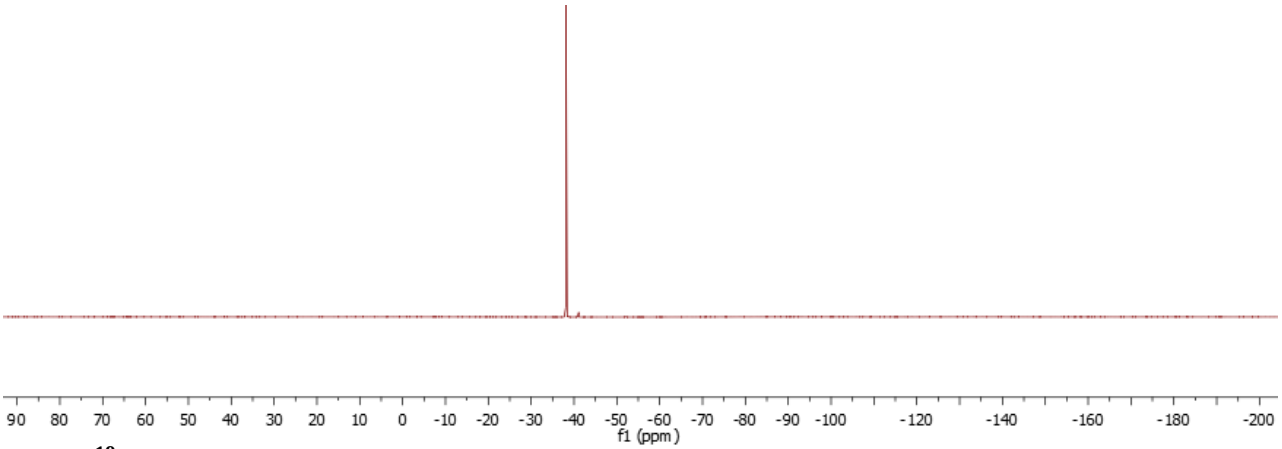
3b



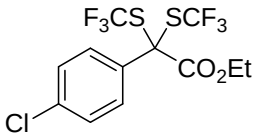
^{1}H NMR spectrum of methyl (*p*-azidophenyl)di(trifluoromethylthio)acetate 3b



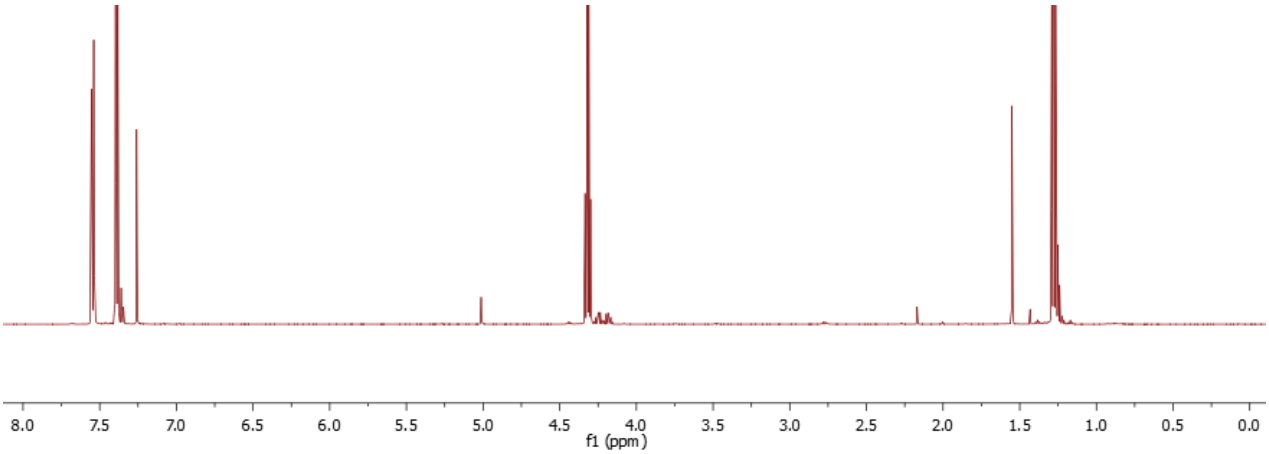
^{13}C NMR spectrum of methyl (*p*-azidophenyl)di(trifluoromethylthio)acetate 3b



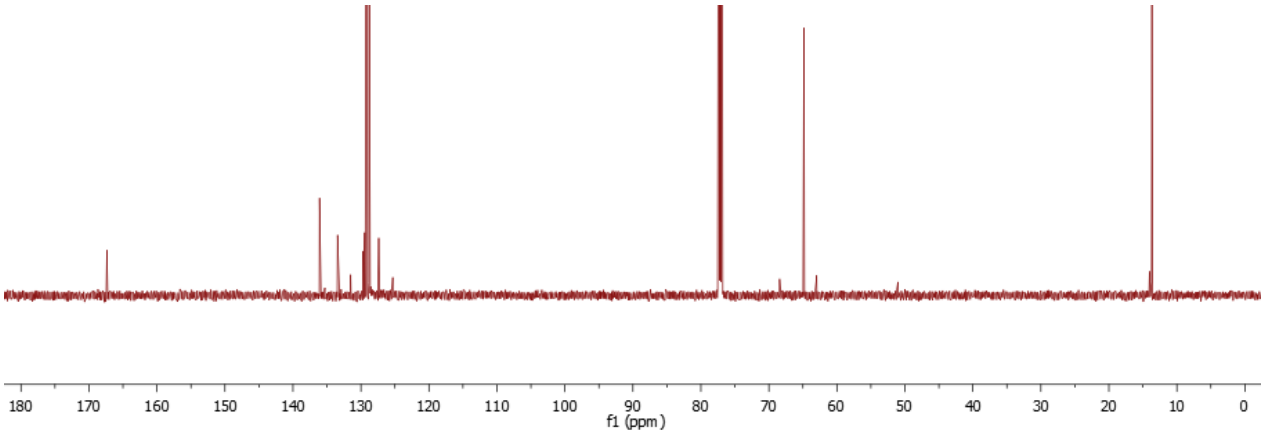
^{19}F NMR spectrum of methyl (*p*-azidophenyl)di(trifluoromethylthio)acetate 3b



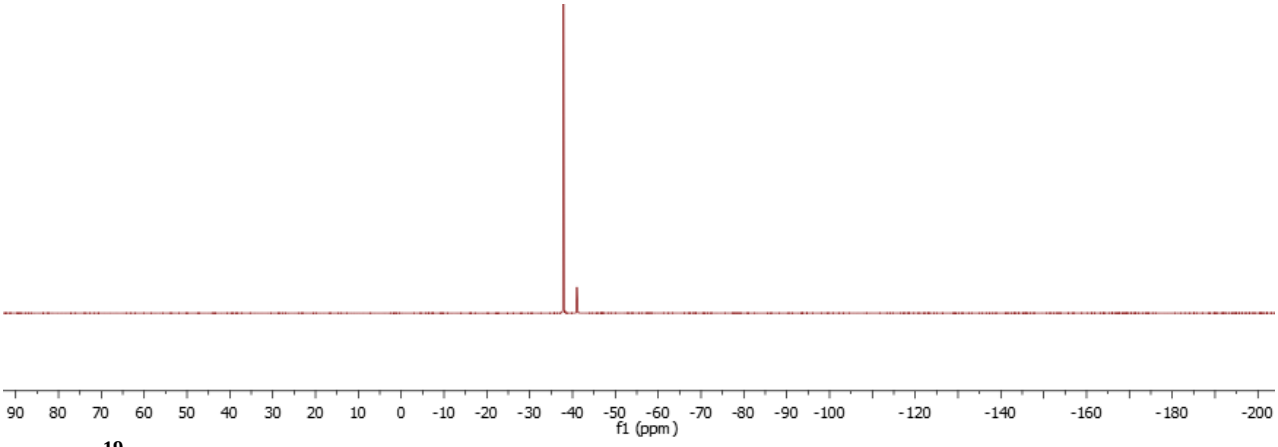
3c



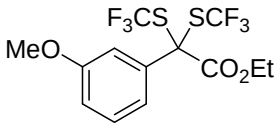
^{1}H NMR spectrum of ethyl (*p*-chlorophenyl)di(trifluoromethylthio)acetate 3c



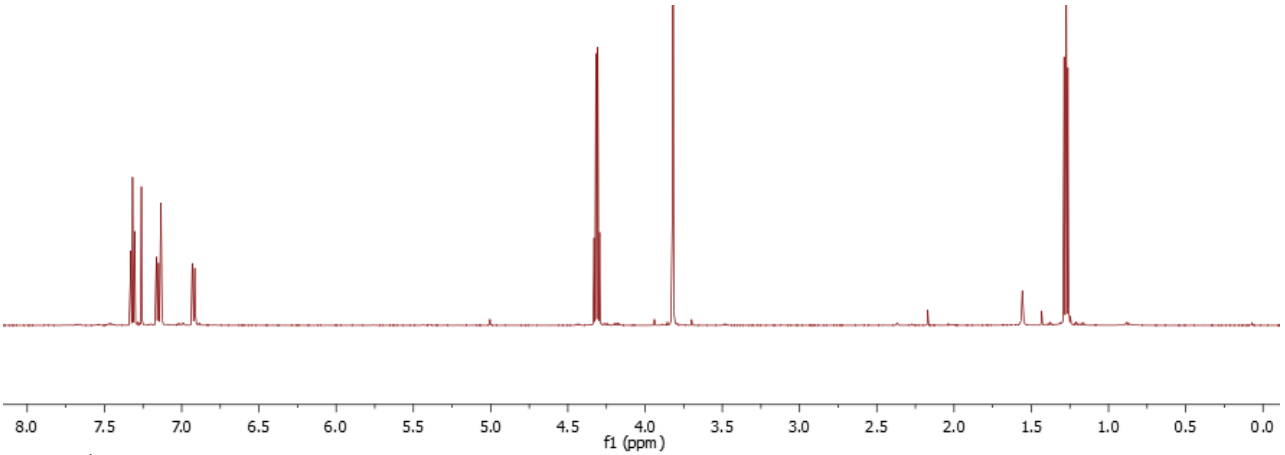
^{13}C NMR spectrum of ethyl (*p*-chlorophenyl)di(trifluoromethylthio)acetate 3c



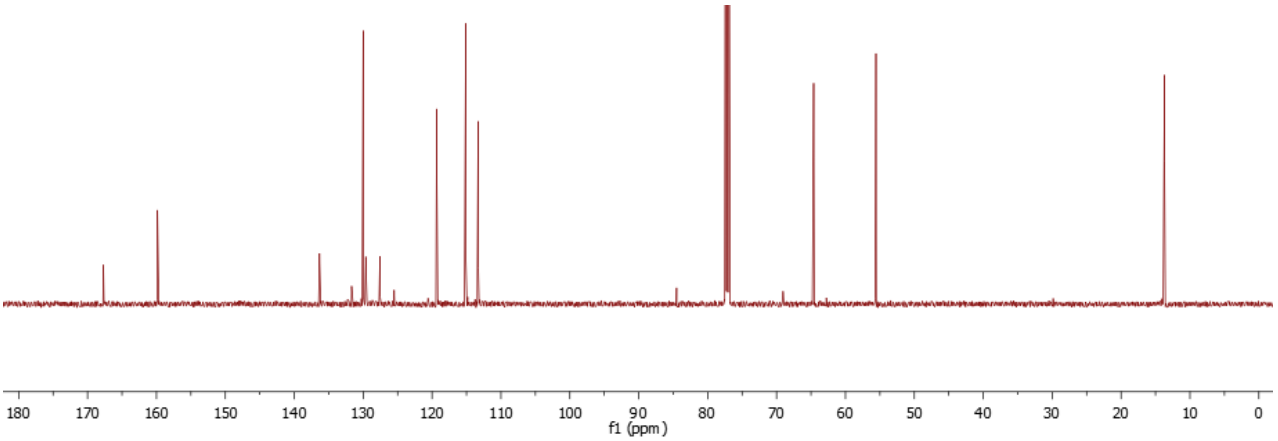
^{19}F NMR spectrum of ethyl (*p*-chlorophenyl)di(trifluoromethylthio)acetate 3c



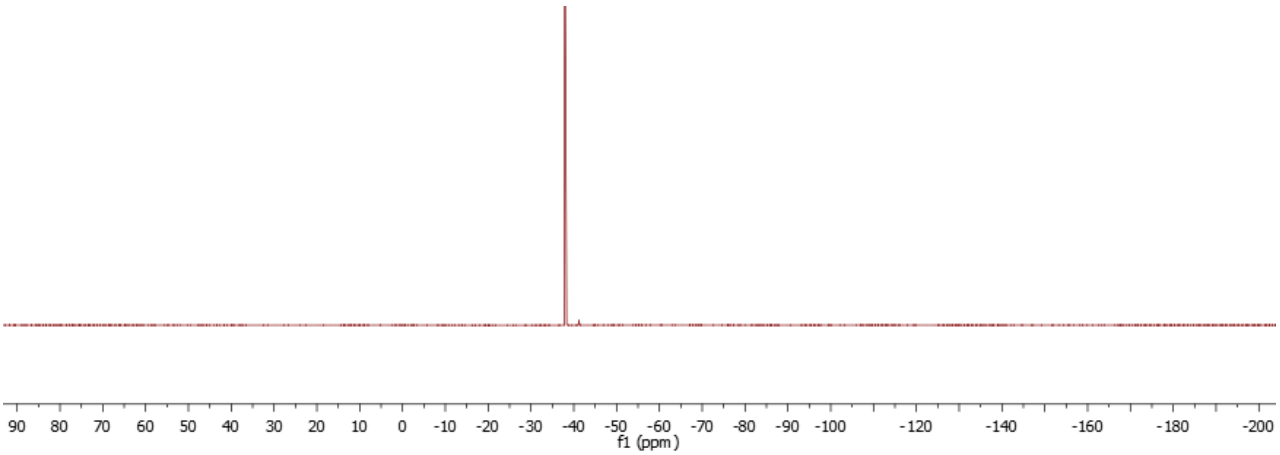
3d



^{1}H NMR spectrum of ethyl (*m*-methoxyphenyl)di(trifluoromethylthio)acetate 3d



^{13}C NMR spectrum of ethyl (*m*-methoxyphenyl)di(trifluoromethylthio)acetate 3d



^{19}F NMR spectrum of ethyl (*m*-methoxyphenyl)di(trifluoromethylthio)acetate 3d