Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoorganocatalyzed and visible light photoredox catalysed trifluoromethylation of olefins and (hetero)aromatics in batch and continuous flow

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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 and THF from benzophenone/solvona® prior to use. Other solvents were used as purchased unless otherwise stated. The loading of the reactions was performed on air.

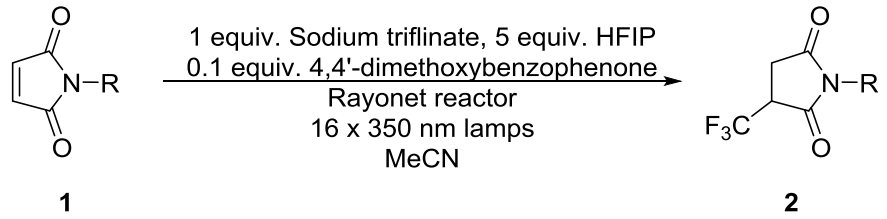
Commercial reagents were used as purchased without further purification.

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 nm) or by staining with aqueous potassium permanganate solutions.

^{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 NMR and ^{19}F NMR spectra are reported as δ/ppm. Assignments are aided by the use of DEPT-135, COSY, HMQC and HMBC spectra where necessary. IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer, only diagnostic absorbances (λ_{max}) are reported. Low resolution mass spectra were recorded on a Finnigan SSQ 7000 mass spectrometer (EI). Melting points were recorded on a Büchi Melting Point M-565 apparatus, at ambient pressure and are uncorrected.

Non-commercial maleimide derivatives were prepared by condensation of the corresponding primary amines with maleic anhydride.

2. Photoorganocatalysed trifluoromethylation



1 **2**

General procedure in batch

In a dry pyrex tube under argon, sodium triflinate (16 mg, 0.1 mmol, 1.0 equiv.), the maleimide derivative (0.1 mmol, 1.0 equiv.) and 4,4'-dimethoxybenzophenone (2.4 mg, 0.01 mmol, 0.1 equiv.) were dissolved in 5 mL of dry, degassed acetonitrile. HFIP (0.05 mL, 0.5 mmol, 5.0 equiv) was added to the solution. The milky solution was irradiated for 6 h, then evaporated and directly purified by column chromatography on silica gel eluting with a pentane/ethyl acetate mixture 10:1 to 4:1. For reactions on bigger scale, several experiments were conducted in parallel, and the reactions mixtures were combined prior purification.

The reaction under visible light was performed the same way, using a glass tube instead of a pyrex tube, and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv.) instead of 4,4'-dimethoxybenzophenone. Irradiation was performed with blue LEDs for 16-18 h.

General procedure in flow

The photo-flow setup was constructed similarly to our previous report:[1] 8 glass rods (length 40 cm, diameter 0.5 cm) were mounted onto a wooden plate (21×21×1 cm), and a Rotilabo®-FEP-tube (10 m, inner diameter 0.8 mm, outer diameter 1.58 mm, volume 5.0 mL) was wrapped around the rods. One end was connected to a steel needle and the other end was hanged above a receving flask. The wooden plate was placed onto a Rayonet reactor (RPR-200) equiped with 16 'black-light' lamps (8 W each, λ = 350 nm) with the rods inside the reactor.

In a dry round-bottom flask under argon, sodium triflinate (16 mg, 0.1 mmol, 1.0 equiv.), the maleimide derivative (0.1 mmol, 1.0 equiv.) and 4,4'-dimethoxybenzophenone (2.4 mg, 0.01 mmol, 0.1 equiv.) were dissolved in 5 mL of dry, degassed acetonitrile. HFIP (0.05 mL, 0.5 mmol, 5.0 equiv) was added to the solution. The milky solution was transferred to a 5 mL syringe and pumped into the photo-flow setup *via* a syringe pump (the flow rate was adapted to the setup to maintain a 30 minute retention time). After all the solution was pumped into the system, dry, degassed acetonitrile was

[1] Q. Lefebvre, M. Jentsch, M. Rueping, *Beilstein J. Org. Chem.*, **2013**, 9, 1883-1890.

pumped with the same flow rate to flush the tubing. The collected solution was evaporated and directly purified by chromatography on silica gel eluting with a pentane/ethyl acetate mixture 10:1 to 4:1. For reactions on bigger scale, a bigger flask and a bigger syringe were used.

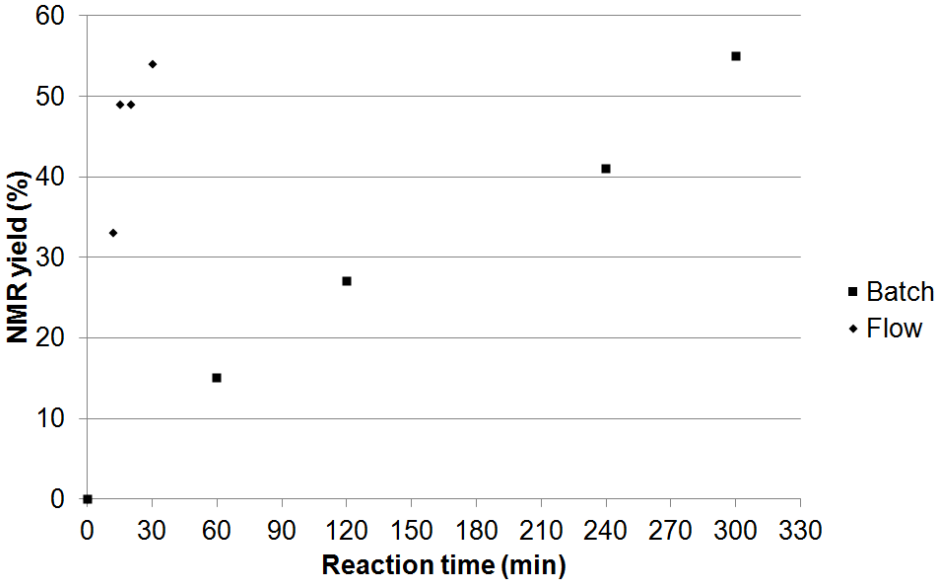
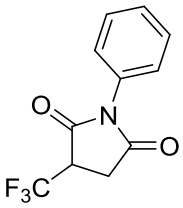


Figure S1. Comparison of the kinetic profiles of the trifluoromethylation of *N*-phenylmaleimide in batch and in flow.

1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2a



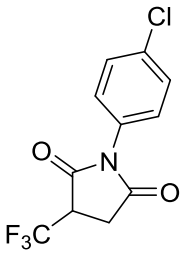
2a

0.4 mmol scale, colourless solid, 59 mg, 61%. In flow: 0.2 mmol scale, 26 mg, 54%. Under visible light: 0.2 mmol scale, 30 mg, 62%.

m.p. 105-107 °C; **FT-IR** ν_{max}(ATR) 2933 cm^{-1}, 1710 cm^{-1}, 1397 cm^{-1}, 1190 cm^{-1}, 1112 cm^{-1}, 680 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 2.98 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 5.2, 18.6 Hz), 3.11 (dd, 1H, CH$_a\underline{H}_b$, *J* 9.8, 18.6 Hz), 3.69 (ddq, 1H, C$\underline{H}$, *J* 5.2, 9.8 Hz, J_F 8.9 Hz), 7.23-7.26 (m, 2H, 2 × Ar-C$\underline{H}$), 7.40-7.50 (m, 3H, 3 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 29.7 (q, $\underline{C}H_2$, J_F 2.0 Hz), 44.6 (q, $\underline{C}$H, J_F 30.0 Hz), 123.9 (q, $\underline{C}F_3$, J_F 279.0 Hz), 126.5 (2 × Ar-$\underline{C}$H), 129.3 (Ar-$\underline{C}$H), 129.5 (2 × Ar-$\underline{C}$H), 131.2 ($\underline{C}$quat.), 168.8 (q, $\underline{C}$O, J_F 3.0 Hz), 172.6 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.82 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z*** (EI) 243 ($[M]^{\bullet+}$, 33%), 174 ($[M - CF_3]^+$, 100%). **HRMS** (ESI): calc. for [$C_{11}H_8O_2NF_3Na$] 266.0399, measured 266.0402.

1-(*p*-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2b

0.4 mmol scale, colourless solid, 43 mg, 39%. In flow: 0.2 mmol scale, 26 mg, 47%. Under visible light: 0.2 mmol scale, 30 mg, 54%.

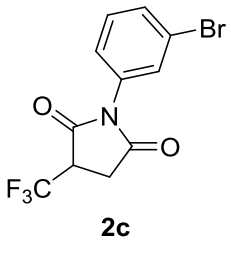


2b

m.p. 120-122 °C; **FT-IR** ν_{max}(ATR) 2956 cm^{-1}, 1712 cm^{-1}, 142 cm^{-1}, 1398 cm^{-1}, 1190 cm^{-1}, 1110 cm^{-1}, 955 cm^{-1}, 818 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.03 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 5.0, 18.7 Hz), 3.16 (dd, 1H, CH$_a$$\underline{H}_b$, *J* 10.0, 18.7 Hz), 3.73 (ddq, 1H, C$\underline{H}$, *J* 5.0, 10.0 Hz, J_F 8.8 Hz), 7.24 (d, 2H, 2 × Ar-C$\underline{H}$, *J* 8.7 Hz), 7.46 (d, 2H, 2 × Ar-C$\underline{H}$, *J* 8.7 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 29.7 (q, $\underline{C}H_2$, J_F 1.7 Hz), 44.7 (q, $\underline{C}$H, J_F 30.2 Hz), 123.8 (q, $\underline{C}F_3$, J_F 279.0 Hz), 127.7 (2 × Ar-$\underline{C}$H), 129.6 ($\underline{C}$quat.), 129.7 (2 × Ar-$\underline{C}$H), 135.3 ($\underline{C}$quat.), 168.5 (q, $\underline{C}$O, J_F 2.7 Hz), 172.2 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F – 68.78 (d, C$\underline{F}_3$, J_H 8.8 Hz); ***m/z*** (EI) 279 ($[M]^{\bullet+}$, 34%), 277 ($[M]^{\bullet+}$, 100%), 208 ($[M - CF_3]^+$, 25%). **HRMS** (ESI): calc. for [$C_{11}H_7O_2NClF_3Na$] 300.0015, measured 300.0010.

1-(*m*-bromophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2c

0.3 mmol scale, colourless solid, 45 mg, 47%.

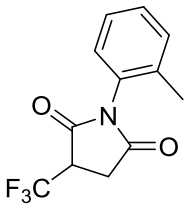


2c

m.p. 95-97 °C; **FT-IR** ν_{max}(ATR) 2930 cm^{-1}, 1712 cm^{-1}, 1385 cm^{-1}, 1184 cm^{-1}, 1115 cm^{-1}, 952 cm^{-1}, 677 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 3.04 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 5.1, 18.7 Hz), 3.17 (dd, 1H, CH$_a$$\underline{H}_b$, *J* 9.8, 18.7 Hz), 3.69 (ddq, 1H, C$\underline{H}$, *J* 5.1, 9.8 Hz, J_F 8.8 Hz), 7.24-7.27 (m, 1H, Ar-C$\underline{H}$), 7.37 (t, 1H, Ar-C$\underline{H}$, *J* 8.0 Hz), 7.48 (t, 1H, Ar-C$\underline{H}$, *J* 1.9 Hz), 7.56-7.59 (m, 1H, Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 29.7 (q, $\underline{C}H_2$, J_F 1.6 Hz), 44.7 (q, $\underline{C}$H, J_F 30.1 Hz), 122.8 ($\underline{C}$quat.), 123.8 (q, $\underline{C}F_3$, J_F 279.0 Hz), 125.1 (Ar-$\underline{C}$H), 129.6 (Ar-$\underline{C}$H), 130.7 (Ar-$\underline{C}$H), 132.3 ($\underline{C}$quat.), 132.5 (Ar-$\underline{C}$H), 168.3 (q, $\underline{C}$O, J_F 2.7 Hz), 172.0 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.78 (d, C$\underline{F}_3$, J_H 8.8 Hz); ***m/z*** (EI) 323 ($[M]^{\bullet+}$, 97%), 321 ($[M]^{\bullet+}$, 100%), 254 ($[M - CF_3]^+$, 25%), 252 ($[M - CF_3]^+$, 25%). **HRMS** (ESI): calc. for [$C_{11}H_7O_2NBrF_3Na$] 343.9505, measured 343.9506.

1-(*o*-tolyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2d

0.4 mmol scale, yellow solid, ~1.5:1 mixture of two diastereomers, 63 mg, 61%. Under visible light: 0.2 mmol scale, 34 mg, 66%.

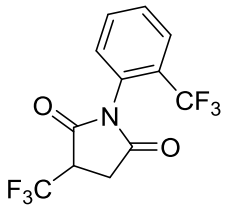


2d

m.p. 70-72 °C; **FT-IR** ν_{max}(ATR) 2959 cm^{-1}, 1717 cm^{-1}, 1373 cm^{-1}, 1187 cm^{-1}, 1115 cm^{-1}, 955 cm^{-1}, 674 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 2.13 (s, 6H, 2 × C$\underline{H}_3$), 2.98-3.04 (m, 2H, 2 × C$\underline{H}_a$H$_b$), 3.08-3.19 (m, 2H, 2 × CH$_a\underline{H}_b$), 3.63-3.80 (m, 2H, 2 × C$\underline{H}$), 7.03-7.07 (m, 2H, 2 × Ar-C$\underline{H}$), 7.28-7.40 (m, 6H, 6 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 17.4 (major $\underline{C}H_3$), 17.7 (minor $\underline{C}H_3$), 29.8 (2 × $\underline{C}H_2$), 44.3-45.3 (m, 2 × $\underline{C}$H), 119.8-128.1 (m, 2 × $\underline{C}F_3$), 127.2 (major Ar-$\underline{C}$H), 127.3 (minor Ar-$\underline{C}$H), 127.8 (major Ar-$\underline{C}$H), 128.0 (minor Ar-$\underline{C}$H), 130.2 (major Ar-$\underline{C}$H), 130.2 (minor Ar-$\underline{C}$H), 130.3 (2 × $\underline{C}$quat.), 131.4 (minor Ar-$\underline{C}$H), 131.5 (major Ar-$\underline{C}$H), 135.5 (minor $\underline{C}$quat.), 135.9 (major $\underline{C}$quat.), 168.7 (2 × $\underline{C}$O), 172.5 (minor $\underline{C}$O), 172.7 (major $\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.91-68.86 (m, 2 × C$\underline{F}_3$); ***m/z*** (EI) 257 ($[M]^{\bullet+}$, 5%), 188 ($[M - CF_3]^+$, 20%). **HRMS** (ESI): calc. for [$C_{12}H_{10}O_2NF_3Na$] 280.0556, measured 280.0556.

1-(*o*-trifluoromethylphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2e

0.4 mmol scale, yellow solid, 2:1 mixture of two diastereomers, 61 mg, 49%.

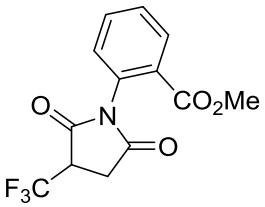


2e

m.p. 72-74 °C; **FT-IR** ν_{max}(ATR) 3397 cm^{-1}, 2926 cm^{-1}, 2660 cm^{-1}, 2309 cm^{-1}, 2094 cm^{-1}, 1892 cm^{-1}, 1730 cm^{-1}, 1188 cm^{-1}, 1123 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.04 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 4.9, 19.1 Hz), 3.08-3.15 (m, 2H, C$\underline{H}_a$H$_b$ & CH$_a\underline{H}_b$), 3.22 (dd, 1H, CH$_a\underline{H}_b$, *J* 10.1, 18.7 Hz), 3.69-3.76 (m, 1H, C$\underline{H}$), 3.78-3.84 (m, 1H, C$\underline{H}$), 7.20 (d, 1H, Ar-C$\underline{H}$, *J* 7.8 Hz), 7.24 (d, 1H, Ar-C$\underline{H}$, *J* 7.8 Hz), 7.62-7.73 (m, 4H, 4 × Ar-C$\underline{H}$), 7.82-7.83 (m, 2H, 2 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 29.9-30.0 (m, 2 × $\underline{C}H_2$), 44.9 (q, $\underline{C}$H, J_F 30.1 Hz), 45.0 (q, $\underline{C}$H, J_F 30.5 Hz), 122.7 (q, $\underline{C}F_3$, J_F 273.0 Hz), 122.9 (q, $\underline{C}F_3$, J_F 273.4 Hz), 123.7 (q, $\underline{C}F_3$, J_F 278.9 Hz), 123.8 (q, $\underline{C}F_3$, J_F 278.9 Hz), 127.8-127.9 (m, 2 × $\underline{C}$quat.), 128.5 (q, Ar-$\underline{C}$H, J_F 31.4 Hz), 128.9 (q, Ar-$\underline{C}$H, J_F 31.8 Hz), 129.3-129.4 (m, 2 × $\underline{C}$quat.), 130.6 (Ar-$\underline{C}$H), 130.7 (Ar-$\underline{C}$H), 130.8 (Ar-$\underline{C}$H), 130.9 (Ar-$\underline{C}$H), 133.5 (Ar-$\underline{C}$H), 133.7 (Ar-$\underline{C}$H), 168.3-168.4 (m, 2 × $\underline{C}$O), 172.2 ($\underline{C}$O), 172.3 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.9 (d, C$\underline{F}_3$, J_H 8.7 Hz), – 68.8-68.7 (m, C$\underline{F}_3$), – 61.7 (d, C$\underline{F}_3$, J_H 2.6 Hz), – 61.33 (s, C$\underline{F}_3$); ***m/z*** (EI) 311 ($[M]^{\bullet+}$, 5%), 242 ($[M - CF_3]^+$, 5%). **HRMS** (ESI): calc. for [$C_{12}H_7O_2NF_6Na$] 334.0279, measured 334.0273.

Methyl *o*-(2,5-dioxo-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate 2f

0.4 mmol scale, yellow oil, 2:1 mixture of two diastereomers, 58 mg, 48%.

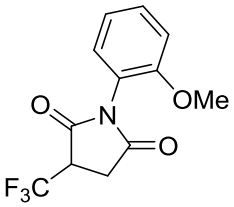


2f

FT-IR ν_{max}(ATR) 2953 cm^{-1}, 1717 cm^{-1}, 1264 cm^{-1}, 1186 cm^{-1}, 1115 cm^{-1}, 955 cm^{-1}, 685 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 3.00-3.15 (m, 2H, C$\underline{H}_2$), 3.77-3.89 (m, 4H, C$\underline{H}_3$ & C$\underline{H}$), 7.19-7.28 (m, 1H, Ar-C$\underline{H}$), 7.53-7.57 (m, 1H, Ar-C$\underline{H}$), 7.64-7.70 (m, 1H, Ar-C$\underline{H}$), 8.15-8.17 (m, 1H, Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 30.1 ($\underline{C}H_2$), 45.2 (q, $\underline{C}H$, J_F 30.5), 52.6 ($\underline{C}H_3$), 128.0 (q, $\underline{C}F_3$, J_F 283.2 Hz), 130.1 (2 × Ar-$\underline{C}$H), 132.0 (Ar-$\underline{C}$H), 133.6 (2 × $\underline{C}$quat.), 134.0 (Ar-$\underline{C}$H), 164.9 ($\underline{C}O_2$), 169.2 ($\underline{C}$O), 173.1 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.68 (d, C$\underline{F}_3$, *J* 8.9 Hz), – 67.90 (d, C$\underline{F}_3$, *J* 8.2 Hz); ***m/z*** (EI) 301 ($[M]^{\bullet+}$, 100%), 270 ($[M - OCH_3]^+$, 95%), 200 ($[M - CF_3 - HOCH_3]^+$, 35%). **HRMS** (ESI): calc. for [$C_{13}H_{10}O_4NF_3Na$] 324.0454, measured 324.0455.

1-(*o*-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2g

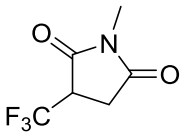
0.4 mmol scale, yellow oil, 1:1 mixture of diastereomers, 30 mg, 28%. In flow: 0.2 mmol scale, 27 mg, 49%.



2g

FT-IR ν_{max}(ATR) 2953 cm^{-1}, 1717 cm^{-1}, 1264 cm^{-1}, 1186 cm^{-1}, 1115 cm^{-1}, 955 cm^{-1}, 685 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.99-3.05 (m, 2H, 2 × C$\underline{H}_a$H$_b$), 3.12 (dd, 1H, CH$_a\underline{H}_b$, *J* 9.7, 18.6 Hz), 3.18 (dd, 1H, CH$_a\underline{H}_b$, *J* 10.1, 18.5 Hz), 3.66-3.73 (m, 1H, C$\underline{H}$), 3.75-3.80 (m, 1H, C$\underline{H}$), 3.79 (s, 3H, C$\underline{H}_3$), 3.80 (s, 3H, C$\underline{H}_3$), 7.02-7.07 (m, 4H, 4 × Ar-C$\underline{H}$), 7.10-7.14 (m, 2H, 2 × Ar-C$\underline{H}$), 7.42-7.45 (m, 2H, 2 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 29.9 (s, 2 × $\underline{C}H_2$), 44.8 (q, 2 × $\underline{C}$H, J_F 29.9 Hz), 55.9 ($\underline{C}H_3$), 56.0 ($\underline{C}H_3$), 112.3 (Ar-$\underline{C}$H), 112.4 (Ar-$\underline{C}$H), 119.8 ($\underline{C}$quat.), 120.0 ($\underline{C}$quat.), 121.0 (Ar-$\underline{C}$H), 121.2 (Ar-$\underline{C}$H), 123.9 (q, 2 × $\underline{C}F_3$, J_F 279.0 Hz), 128.9 (Ar-$\underline{C}$H), 129.2 (Ar-$\underline{C}$H), 131.4 (Ar-$\underline{C}$H), 131.5 (Ar-$\underline{C}$H), 154.5 ($\underline{C}$quat.), 154.7 ($\underline{C}$quat.), 168.5 ($\underline{C}$O), 168.7 ($\underline{C}$O), 172.4 ($\underline{C}$O), 172.7 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F – 68.89 (d, C$\underline{F}_3$, J_H 8.9 Hz), – 68.83 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z*** (EI) 301 ($[M]^{\bullet+}$, 100%), 270 ($[M - OCH_3]^+$, 95%), 200 ($[M - CF_3 - HOCH_3]^+$, 35%). **HRMS** (ESI): calc. for [$C_{12}H_{10}O_3NF_3$] 273.0607, measured 273.0608.

1-methyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2h

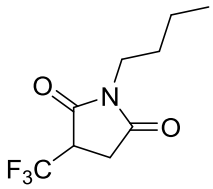


2h

0.1 mmol scale, directly analyzed by ^{1}H and ^{19}F NMR, 52%. Analytical data in accordance with literature.[2]

1-butyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2i

0.2 mmol scale, directly analyzed by ^{1}H and ^{19}F NMR, 42%. Isolated along with 3% of 4,4'-dimethoxybenzophenone.

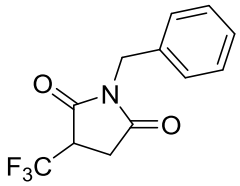


2i

FT-IR ν_{max}(ATR) 2960 cm^{-1}, 1708 cm^{-1}, 1351 cm^{-1}, 1253 cm^{-1}, 1188 cm^{-1}, 1115 cm^{-1}, 961 cm^{-1}, 981 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 0.92 (t, 3H, C$\underline{H}_3$, *J* 7.4 Hz), 1.27-1.33 (m, 2H, C$\underline{H}_2$), 1.54-1.59 (m, 2H, C$\underline{H}_2$), 2.84 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 4.8, 18.5 Hz), 2.96 (dd, 1H, CH$_a\underline{H}_b$, *J* 9.8, 18.5 Hz), 3.51-3.57 (m, 3H, C$\underline{H}_2$ & C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 13.7 ($\underline{C}H_3$), 20.0 ($\underline{C}H_2$), 29.6 (2 × $\underline{C}H_2$), 39.5 ($\underline{C}H_2$), 44.5 (q, $\underline{C}$H, J_F 29.9 Hz), 123.9 (q, $\underline{C}F_3$, J_F 278.7 Hz), 169.7 (q, $\underline{C}$O, J_F 2.8 Hz), 173.6 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F – 69.00 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z*** (EI) 224 ($[M + H]^+$, 35%), 223 ($[M]^{\bullet+}$, 25%), 181 ($[M - C_3H_7 + H]^+$, 50%), 168 ($[M - C_4H_9 + H_2]^+$, 100%).

1-benzyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2j

0.1 mmol scale, directly analyzed by ^{1}H and ^{19}F NMR, 55%. The reaction was repeated on 0.4 mmol scale, colourless oil, 42 mg, 41%. Under visible light: 0.2 mmol scale, 32 mg, 62%.



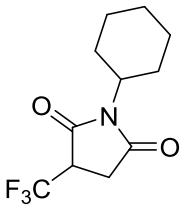
2j

FT-IR ν_{max}(ATR) 2958 cm^{-1}, 1710 cm^{-1}, 1346 cm^{-1}, 1253 cm^{-1}, 1173 cm^{-1}, 688 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 2.84 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 5.1, 18.6 Hz), 2.96 (dd, 1H, CH$_a\underline{H}_b$, *J* 9.7, 18.6 Hz), 3.55 (ddq, 1H, C$\underline{H}$, *J* 5.1, 9.7 Hz, J_F 8.9 Hz), 4.64-4.73 (m, 2H, C$\underline{H}_2$), 7.28-7.36 (m, 5H, 5 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 29.6 (q, $\underline{C}H_2$, J_F 2.1 Hz), 43.2 ($\underline{C}H_2$), 44.5 (q, $\underline{C}$H, J_F 30.0 Hz), 123.8 (q, $\underline{C}F_3$, J_F 278.8 Hz), 128.4 (Ar-$\underline{C}$H), 128.8 (2 × Ar-$\underline{C}$H), 128.9 (2 × Ar-$\underline{C}$H), 135.0 ($\underline{C}$quat.), 169.5 (q, $\underline{C}$O, J_F 3.0 Hz), 173.2 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F – 68.83 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z*** (EI) 257 ($[M]^{\bullet+}$, 100%). **HRMS** (ESI): calc. for $[C_{12}H_{10}O_2NF_3Na]$ 280.0550, measured 280.0556.

[2] C. Brulé, J.-P. Bouillon, C. Portella, *Tetrahedron*, **2004**, 60, 9849-9855.

1-cyclohexyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2k

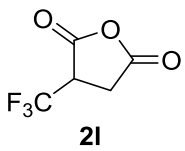
0.4 mmol scale, analyzed by ^{1}H and ^{19}F NMR, 41%. Isolated along with 10% of 4,4'-dimethoxybenzophenone. Under visible light: 0.2 mmol scale, 30 mg, 60%.



2k

FT-IR ν_{max}(ATR) 2923 cm^{-1}, 1458 cm^{-1}, 1067 cm^{-1}, 803 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.16-1.34 (m, 3H), 1.58 (d, 2H, C$\underline{H}_2$, *J* 10.8 Hz), 1.65 (d, 1H, *J* 12.8 Hz), 1.83 (d, 2H, C$\underline{H}_2$, *J* 13.5 Hz), 2.11 (m, 2H, C$\underline{H}_2$), 2.78 (dd, 1H, C$\underline{H}_a$H$_b$, *J* 4.8, 18.5 Hz), 2.91 (dd, 1H, CH$_a\underline{H}_b$, *J* 9.9, 18.5 Hz), 3.48 (ddq, 1H, C$\underline{H}$, *J* 4.8, 9.9 Hz, J_F 8.9 Hz), 3.99 (tt, 1H, C$\underline{H}$, *J* 3.8, 12.4 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 25.0 ($\underline{C}H_2$), 25.8 ($\underline{C}H_2$), 25.9 ($\underline{C}H_2$), 28.7 ($\underline{C}H_2$), 28.7 ($\underline{C}H_2$), 29.5 (q, $\underline{C}H_2$, J_F 1.7 Hz), 44.2 (q, $\underline{C}$H, J_F 29.7 Hz), 55.59 ($\underline{C}$H), 124.0 (q, $\underline{C}F_3$, J_F 278.8 Hz), 169.7 (q, $\underline{C}$O, J_F 2.6 Hz), 173.6 ($\underline{C}$O); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F – 69.20 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z*** (EI) 244 ($[M - 5]^{\bullet+}$, 35%), 227 ($[M - 12]^{\bullet+}$, 35%).

3-(trifluoromethyl)dihydrofuran-2,5-dione 2l



2l

Reaction performed starting from maleic anhydride. 0.1 mmol scale, analyzed by ^{1}H and ^{19}F NMR, 48%. The product could not be isolated, but condensation of the crude product with aniline and comparaison of the NMR with authentic **2a** confirmed the identity of the product.

Dimethyl 2-(trifluoromethyl)succinate 2m

Reaction performed starting from dimethyl maleate. 0.1 mmol scale, analyzed by ^{1}H and ^{19}F NMR, 51%. Analytical data in accordance with literature.[3]

1,3-Dimethyl-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione 2n

0.2 mmol scale (3 equiv. sulfinate, 14 h irradiation), white solid, 20 mg, 48%. Under visible light: 0.2 mmol scale (3 equiv. sulfinate), 30 mg, 72%. Analytical data in accordance with literature.[4]

[3] C. Botteghi, C. Lando, U. Matteoli, S. Paganelli, G. Menchi, *J. Fluorine Chem.*, **1997**, 83, 67-71

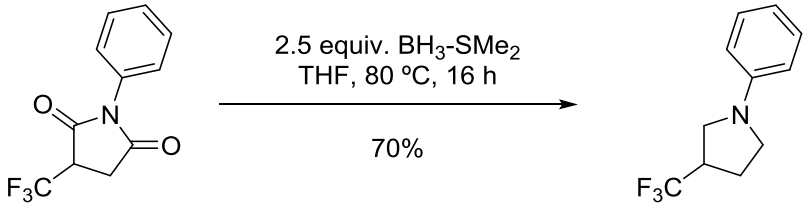
2-Phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine 2o

0.2 mmol scale (3 equiv. sulfinate, 6 h irradiation), white solid, 22 mg, 42%. Analytical data in accordance with literature.[5]

1,3,5-trimethoxy-2-(trifluoromethyl)benzene 2p

0.4 mmol scale (2 equiv. sulfinate, 6 h irradiation), white solid, 66 mg, 70%. Analytical data in accordance with literature.[6]

Reduction of 2a to 1-phenyl-3-(trifluoromethyl)pyrrolidine 3a



2a **3a**

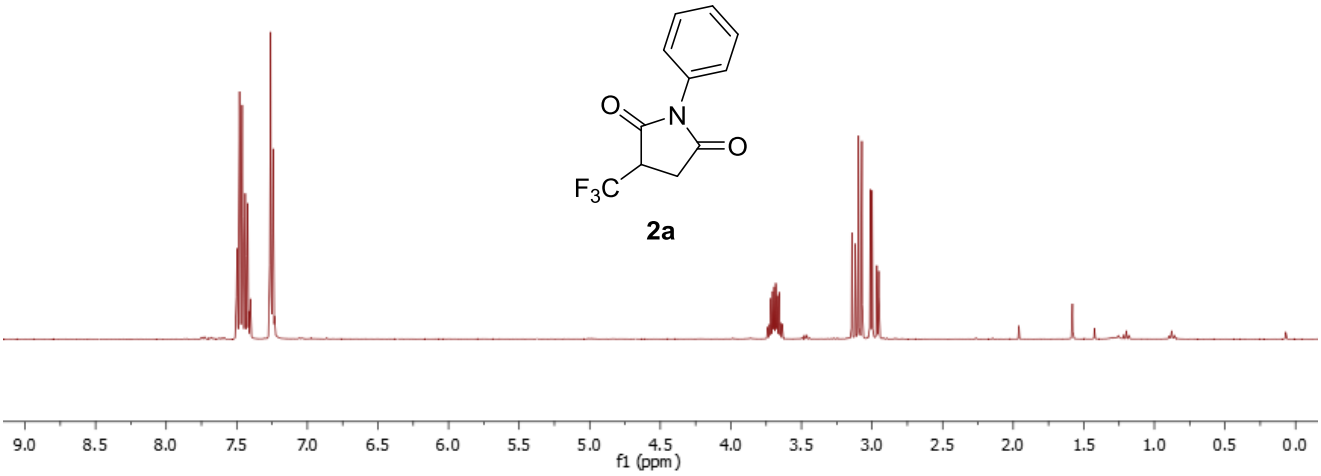
2a (24 mg, 0.1 mmol, 1.0 equiv.) was dissolved in 1 mL of dry THF in an oven-dried tube. BH_3-SMe_2 (2 M solution in THF, 0.125 mL, 0.25 mmol, 2.5 equiv) was added dropwise, the tube was sealed with a screw-cap and the solution was stirred at 80 ºC for 16 h. The mixture was carefuly quenched by addition of 1 mL of 2 M aqueous NaOH, extracted with diethyl ether and washed with brine. The combined organics were concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with pentane to give the product as a colourless oil (15 mg, 70%).

FT-IR ν_{max}(ATR) 2920 cm^{-1}, 2854 cm^{-1}, 1600 cm^{-1}, 1505 cm^{-1}, 1375 cm^{-1}, 1339 cm^{-1}, 1271 cm^{-1}, 1131 cm^{-1}, 1068 cm^{-1}, 747 cm^{-1}, 689 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.18-2.24 (m, 1H, C$\underline{H}_a$H$_b$), 2.26-2.31 (m, 1H, CH$_a$$\underline{H}_b$), 3.03-3.10 (m, 1H, C$\underline{H}$), 3.36-3.47 (m, 2H, C$\underline{H}_2$), 3.56 (t, 2H, C$\underline{H}_2$, *J* 9.2 Hz), 6.60 (d, 2H, 2 × Ar-C$\underline{H}$, *J* 8.2 Hz), 6.75 (t, 1H, Ar-C$\underline{H}$, *J* 7.3 Hz), 7.26 (app t, 2H, 2 × Ar-C$\underline{H}$, *J* 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ_C 25.3 (q, $\underline{C}H_2$, J_F 2.5 Hz), 42.4 (q, $\underline{C}$H, J_F 28.4 Hz), 47.1 ($\underline{C}H_2$), 47.4 (q, $\underline{C}H_2$, J_F 2.9 Hz), 112.3 (2 × Ar-$\underline{C}$H), 116.9 (Ar-$\underline{C}$H), 127.4 (q, $\underline{C}F_3$, J_F 277.3 Hz), 129.4 (2 × Ar-$\underline{C}$H), 147.4 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F – 71.23 (d, C$\underline{F}_3$, J_H 8.9 Hz); ***m/z***

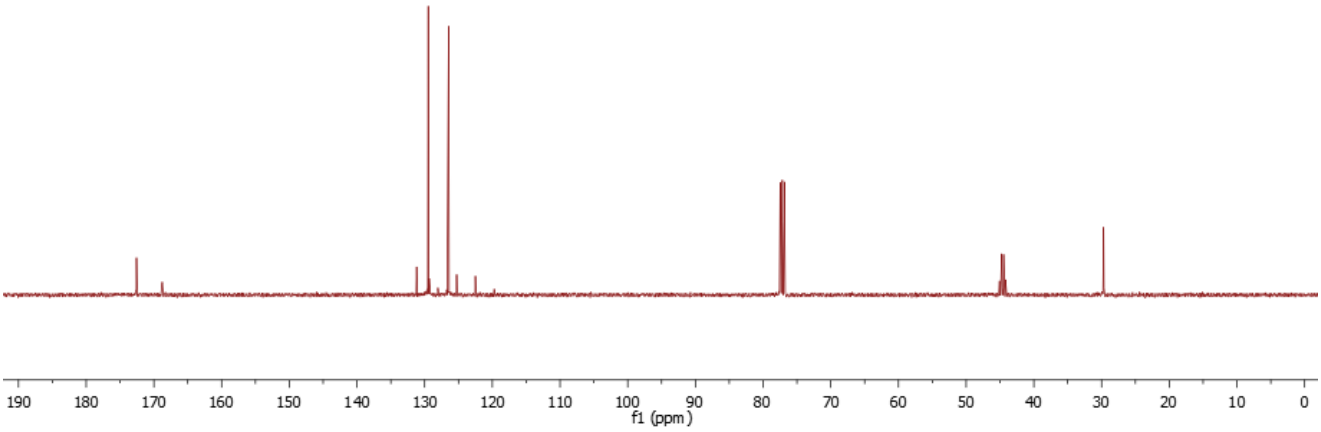
[4] Y.-Y. Yu, A. R. Ranade, G. I. Georg, *Adv. Synth. Catal.* **2014**, 356, 3510–3518
[5] K. Monir, A. K. Bagdi, M. Ghosh, A. Haajra, *J. Org. Chem.*, **2015**, 80, 1332-1337
[6] L. Cui, Y. Matusaki, N. Tada, T. Miura, B. Uno, A. Itoh, *Adv. Synth. Catal.* **2013**, 355, 2203–2207

(EI) 126 ($[M + H]^+$, 10%), 214 ($[M - H_2 + H]^+$, 100%). **HRMS** (ESI): calc. for $[C_{11}H_{13}NF_3]$ 216.0995, measured 216.0994.

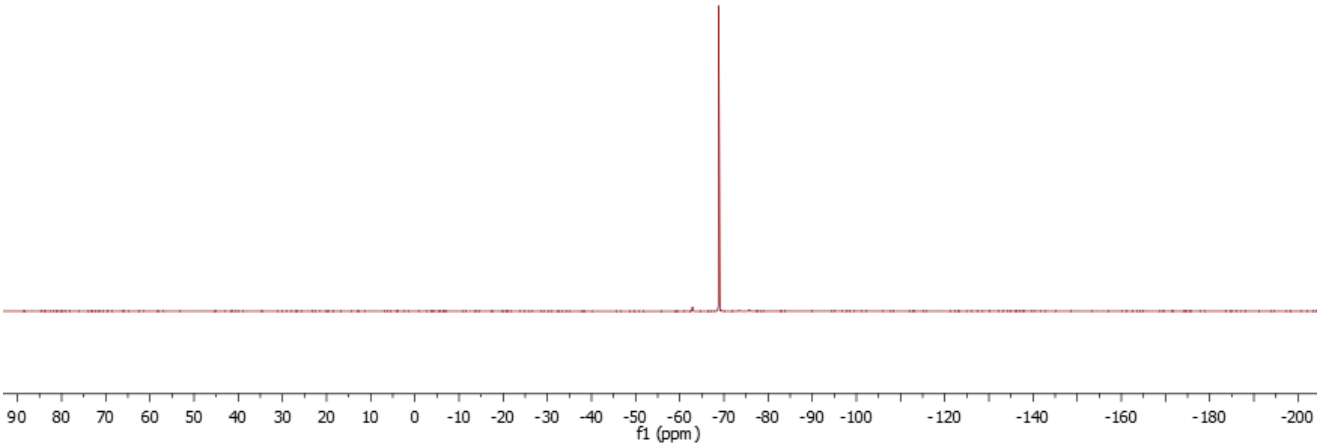
3. ^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds



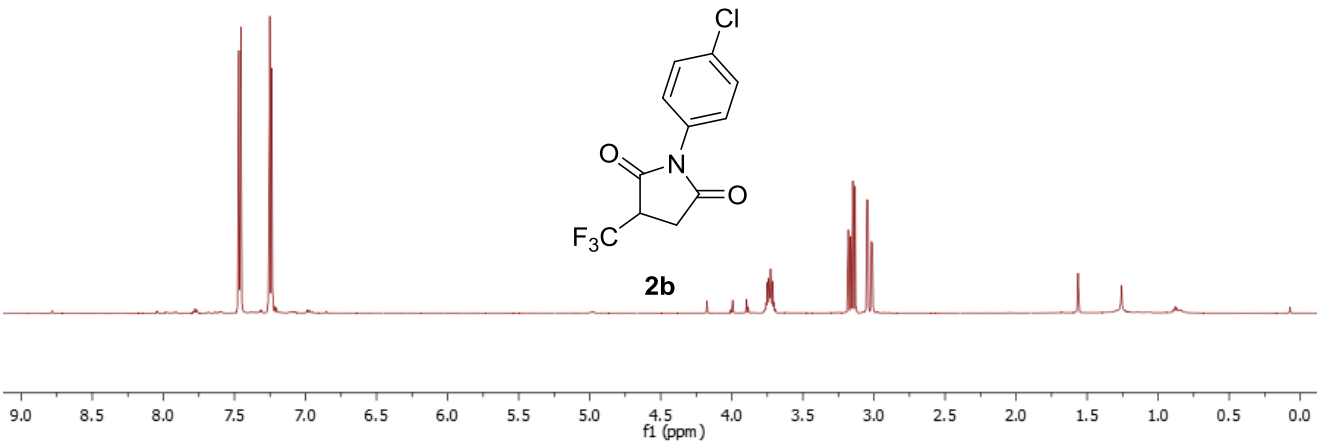
^{1}H NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2a



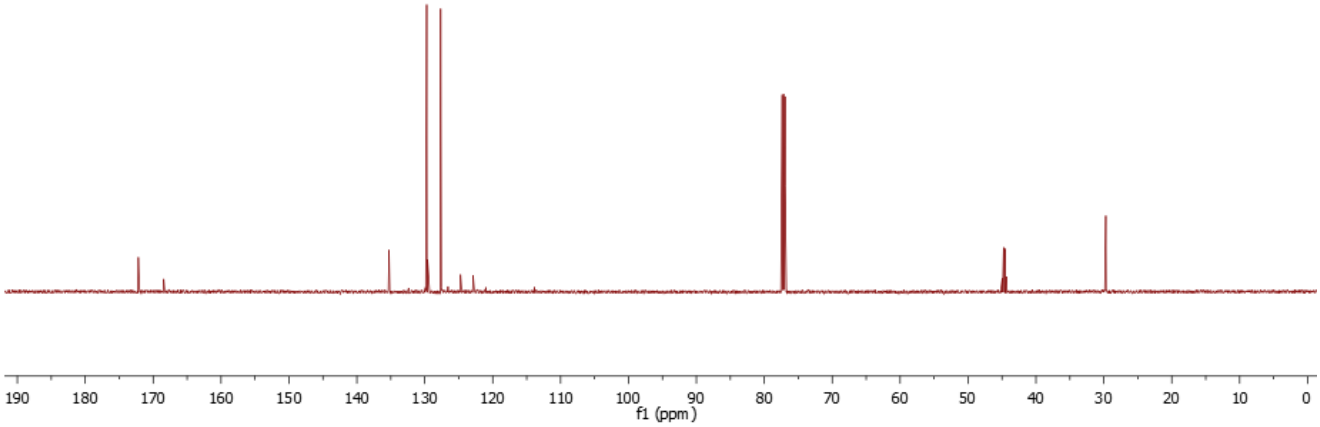
^{13}C NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2a



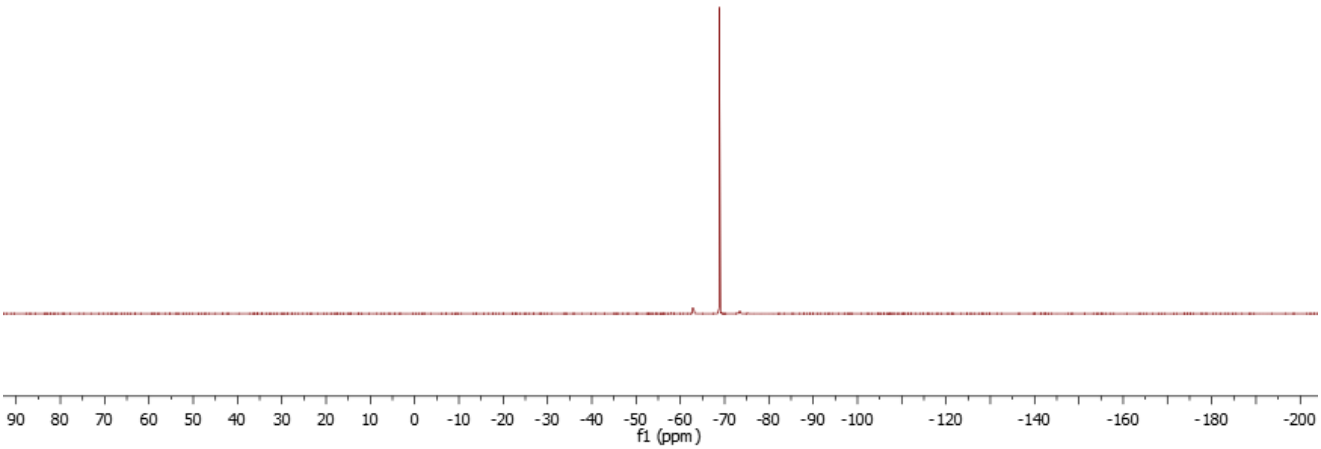
^{19}F NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2a



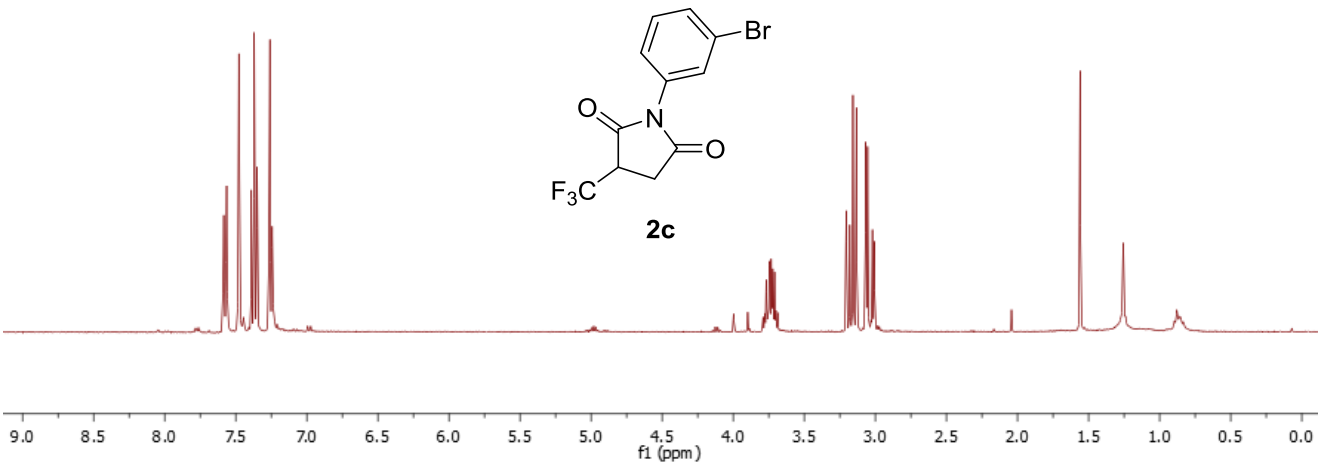
^{1}H NMR spectrum of 1-(*p*-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2b



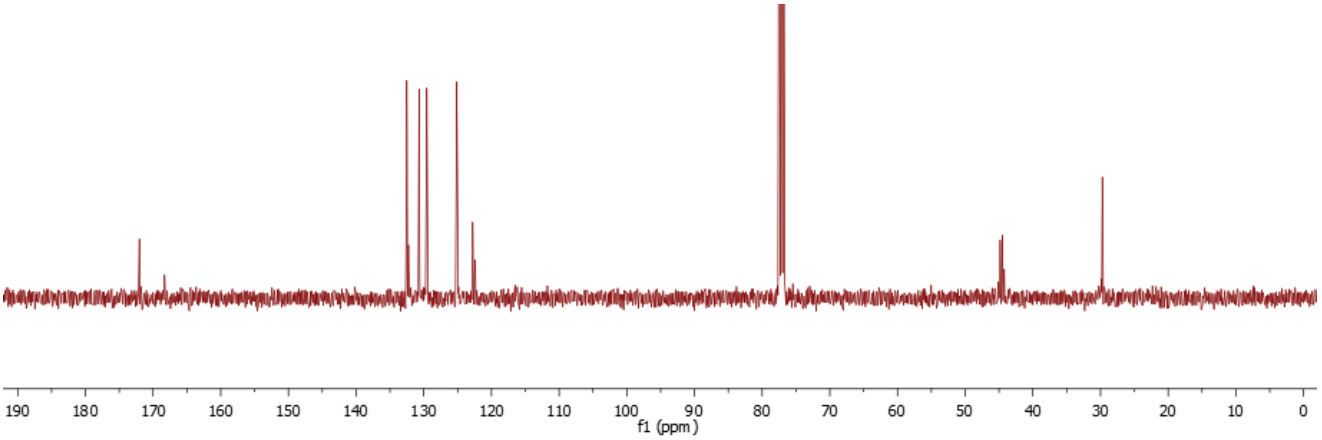
^{13}C NMR spectrum of 1-(*p*-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2b



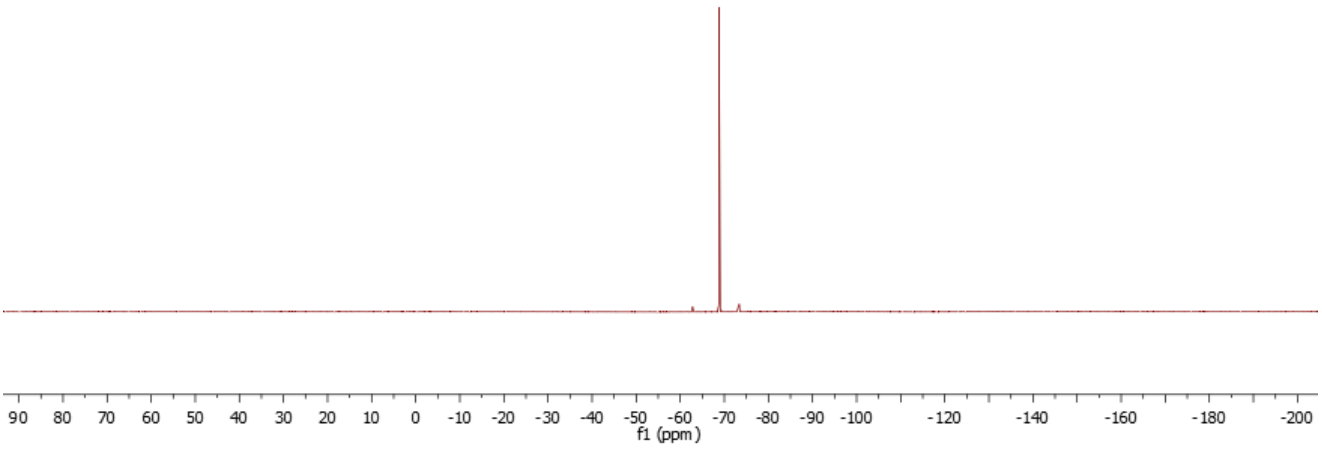
^{19}F NMR spectrum of 1-(*p*-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2b



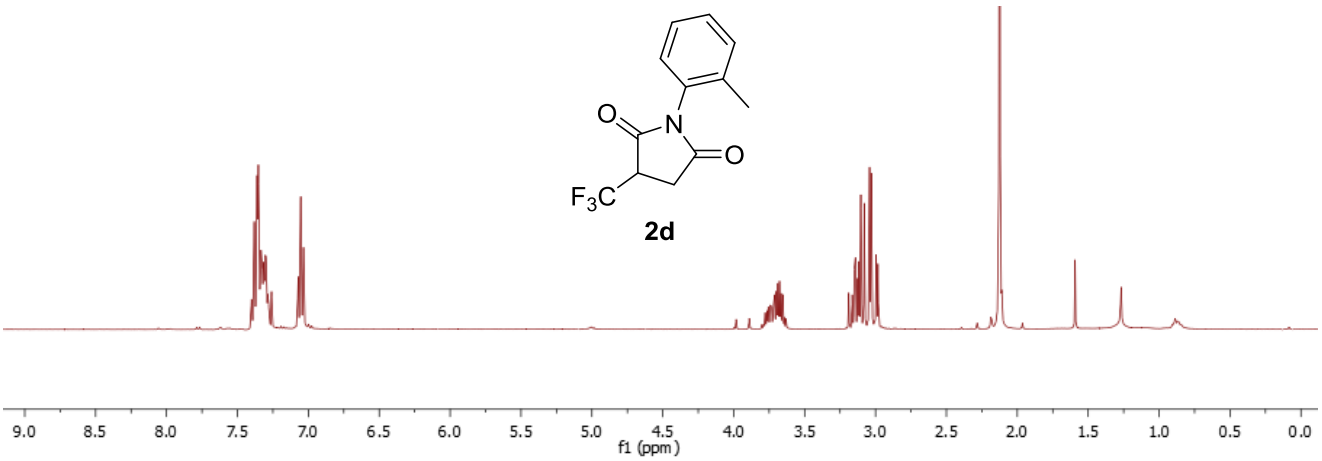
^{1}H NMR spectrum of 1-(*m*-bromophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2c



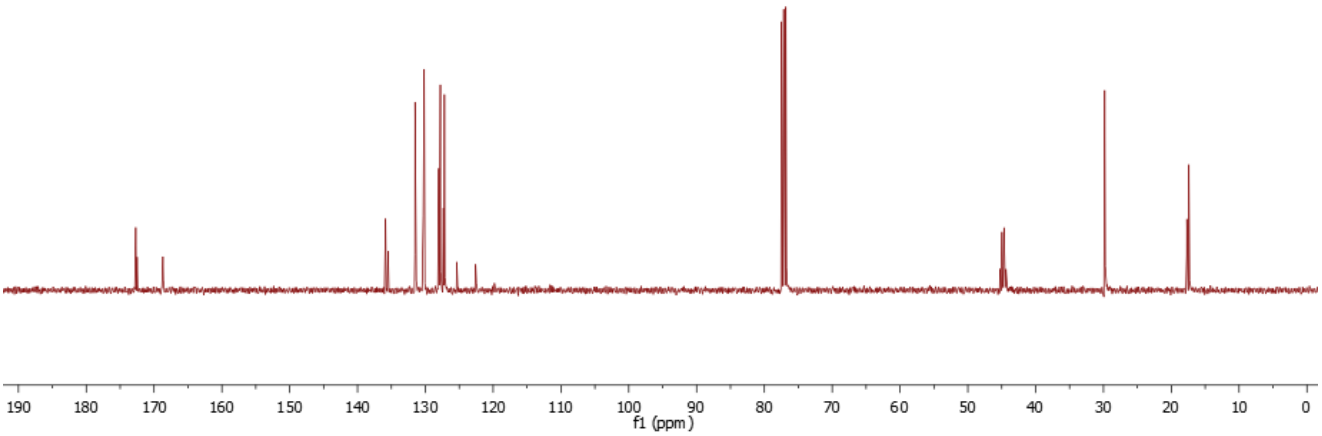
^{13}C NMR spectrum of 1-(*m*-bromophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2c



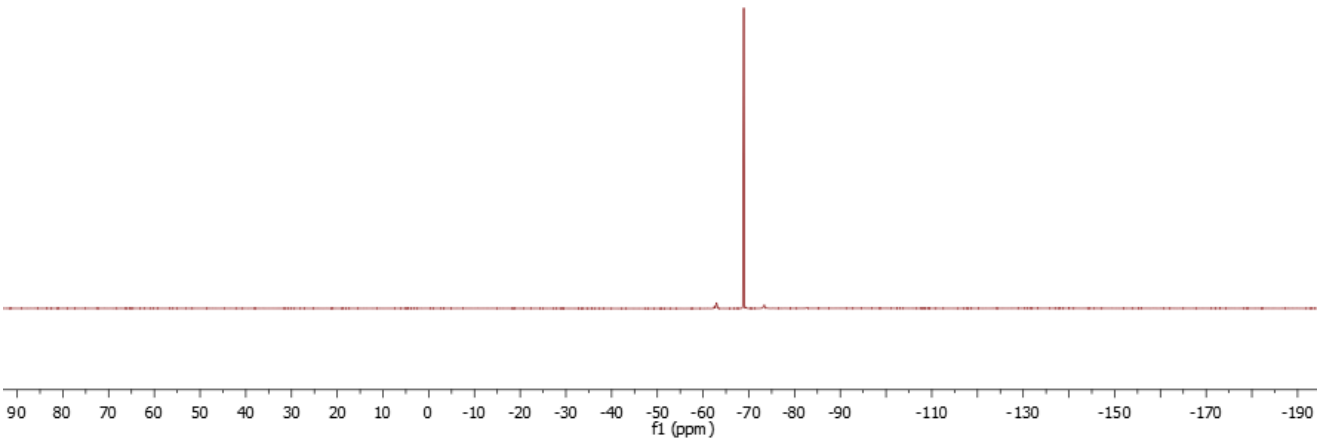
^{19}F NMR spectrum of 1-(*m*-bromophenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2c



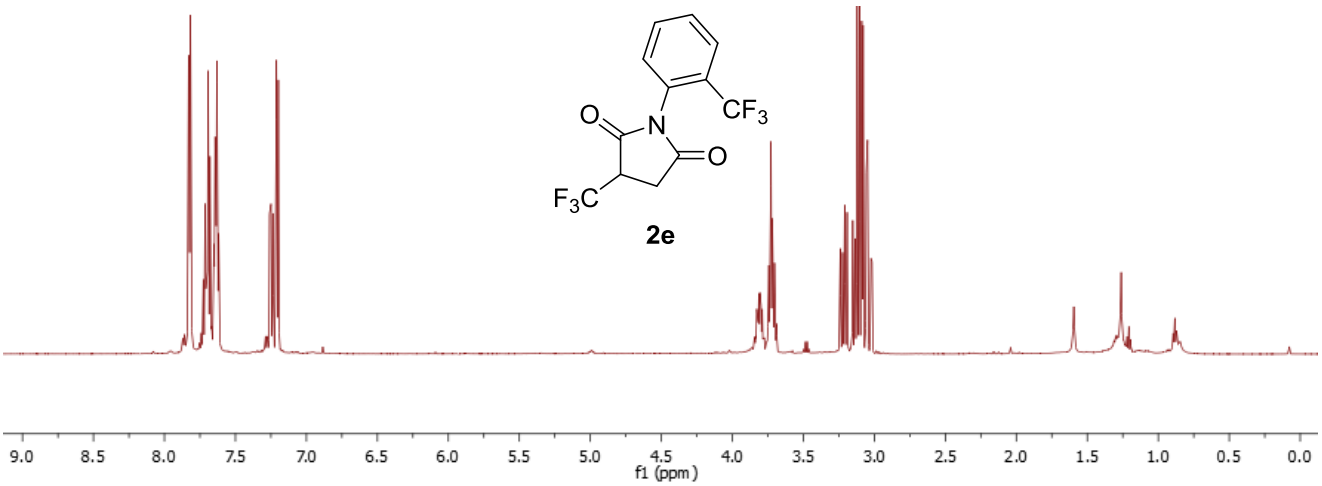
^{1}H NMR spectrum of 1-(*o*-tolyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2d



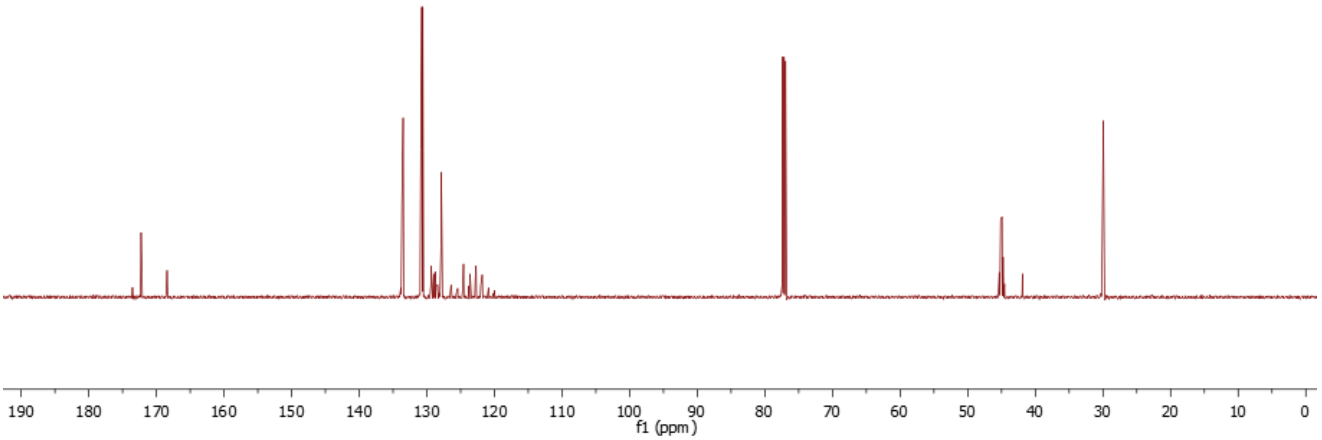
^{13}C NMR spectrum of 1-(*o*-tolyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2d



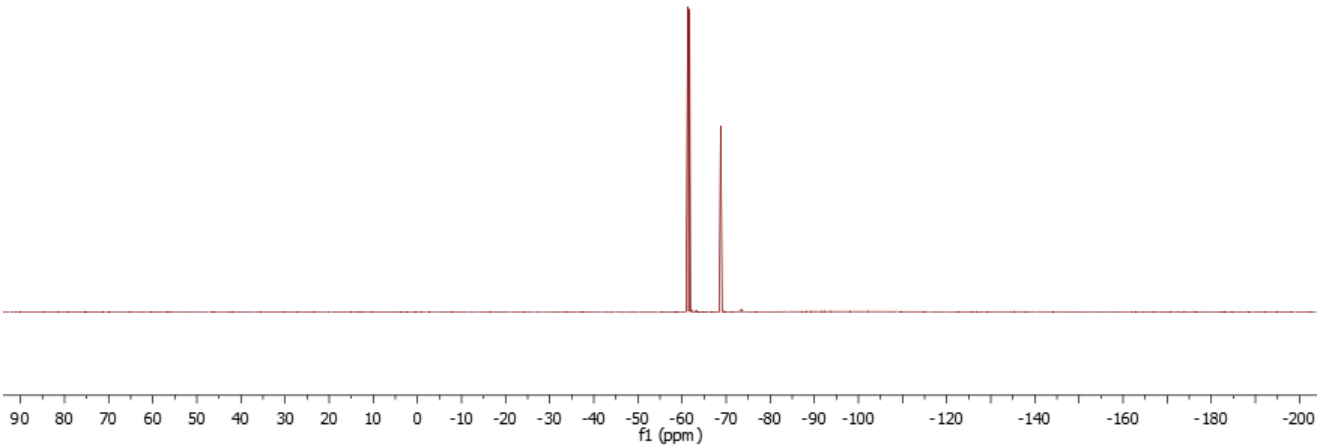
^{19}F NMR spectrum of 1-(*o*-tolyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2d



^{1}H NMR spectrum of 1-(*o*-trifluoromethylphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2e



^{13}C NMR spectrum of 1-(*o*-trifluoromethylphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2e



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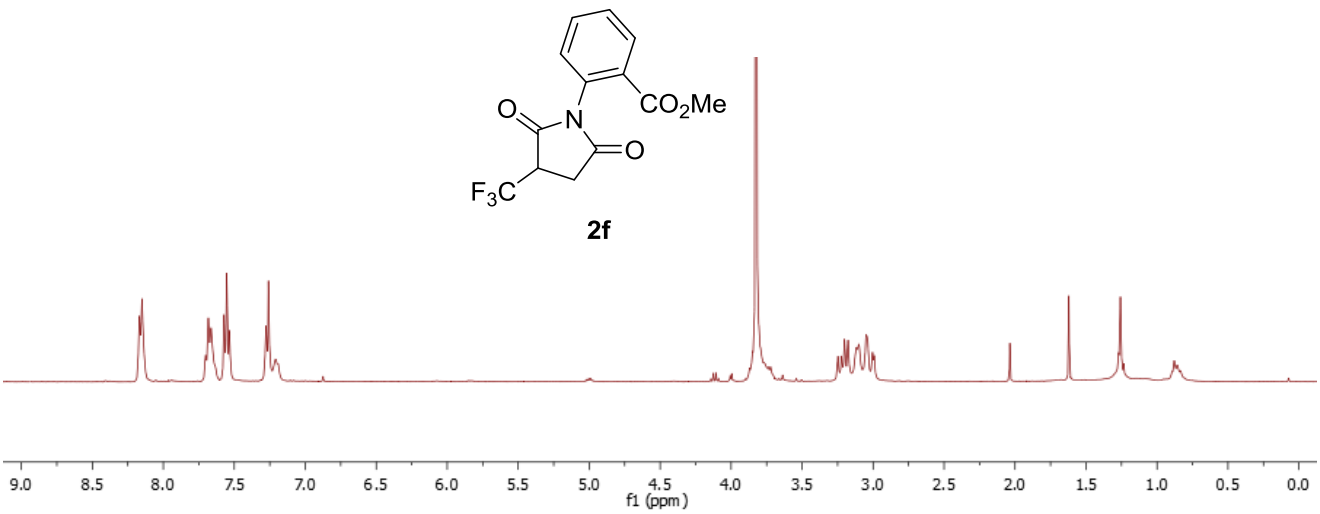
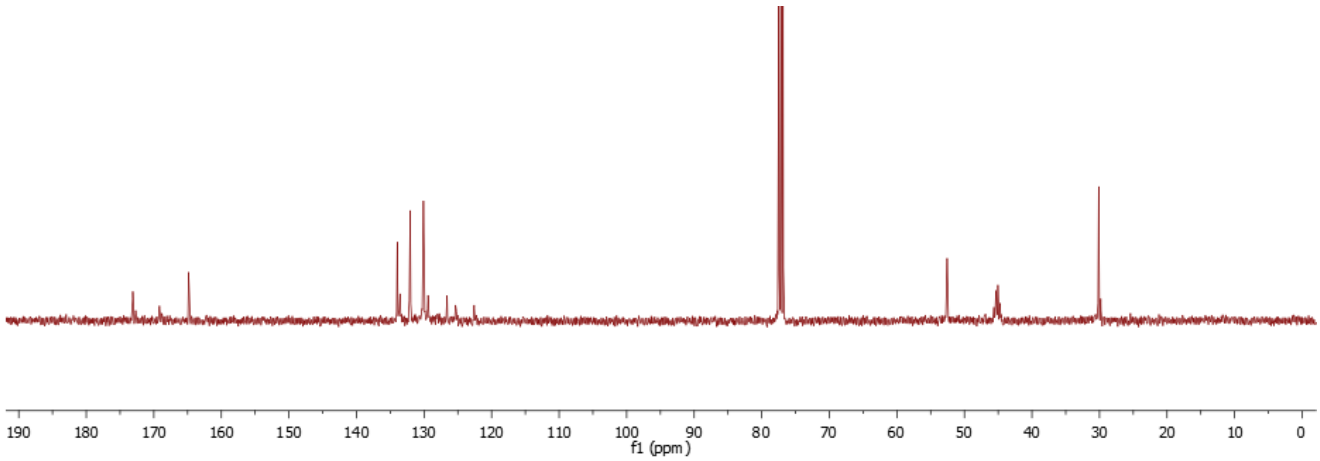
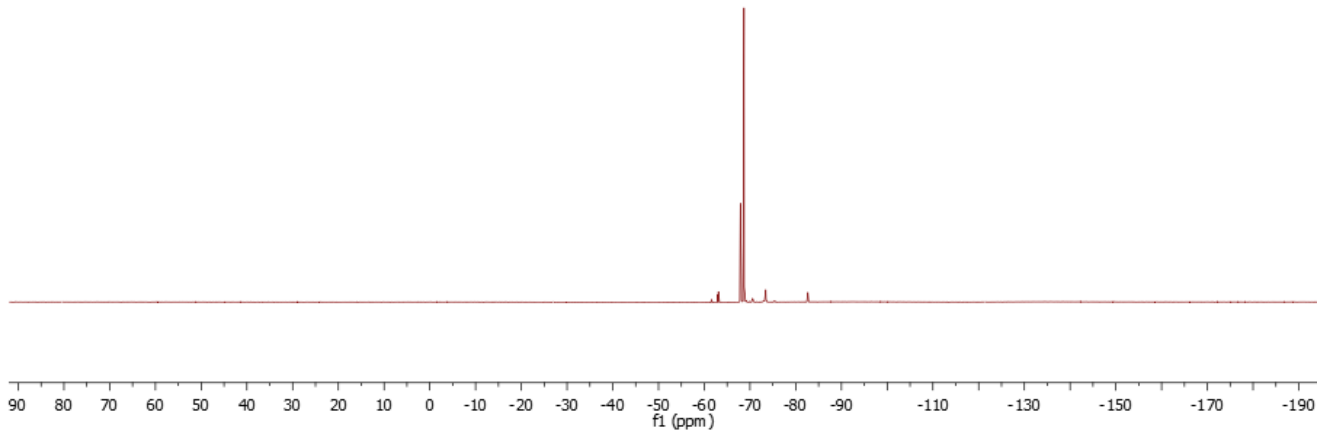


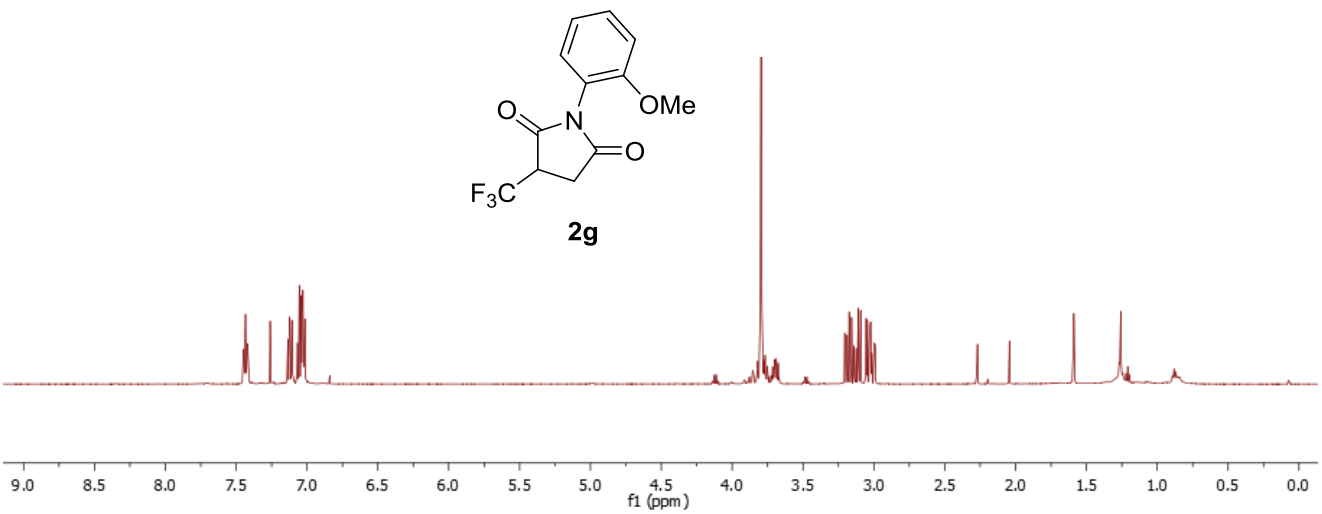
^{1}H NMR spectrum of Methyl *o*-(2,5-dioxo-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate 2f



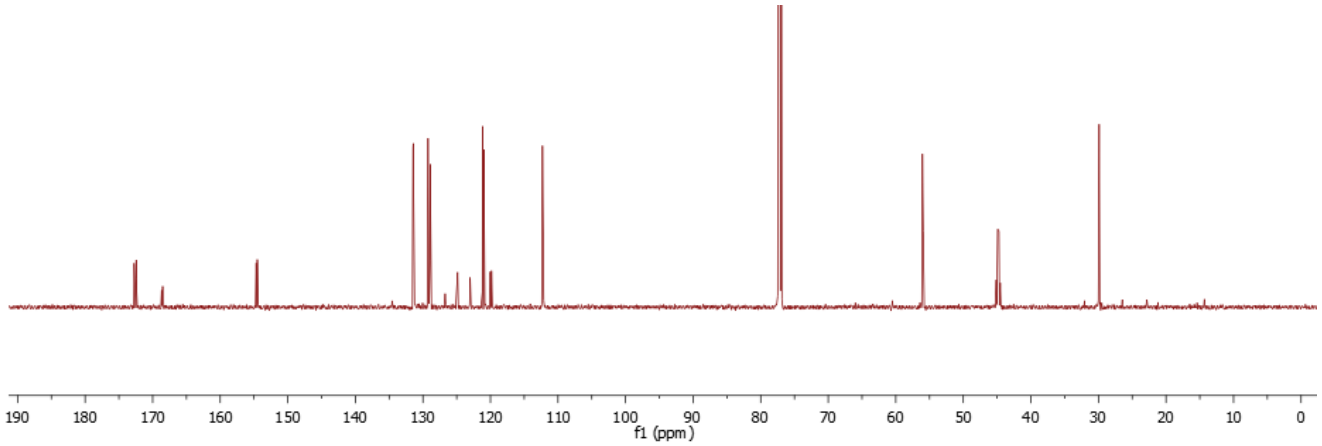
^{13}C NMR spectrum of Methyl *o*-(2,5-dioxo-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate 2f



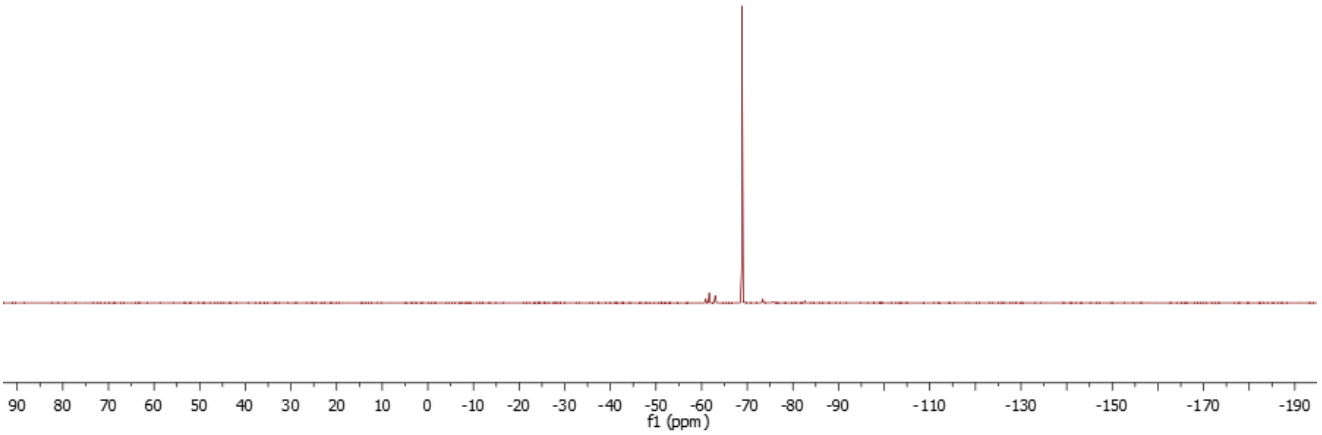
^{19}F NMR spectrum of Methyl *o*-(2,5-dioxo-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate 2f



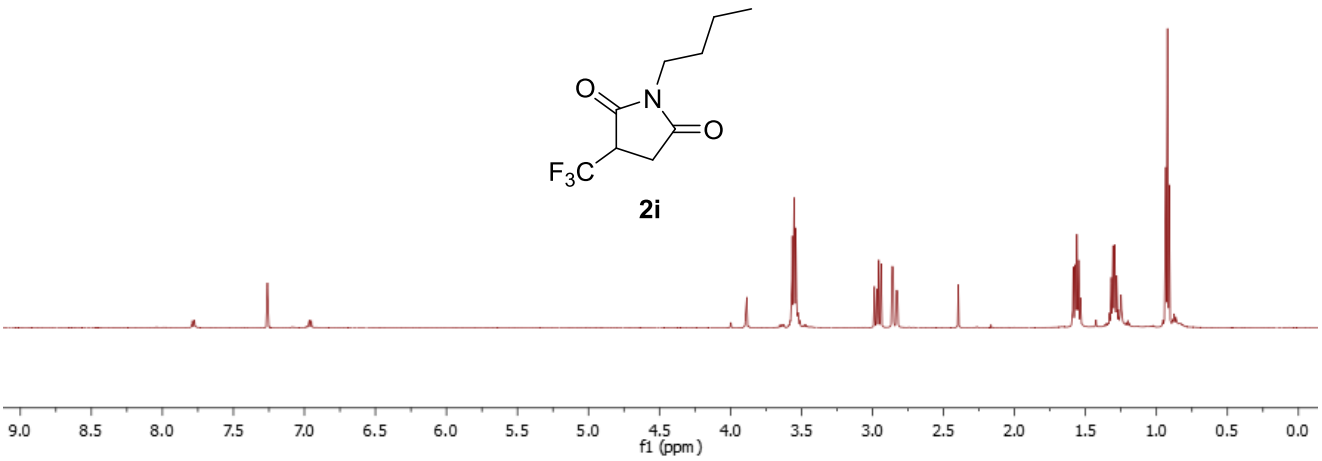
^{1}H NMR spectrum of 1-(*o*-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2g



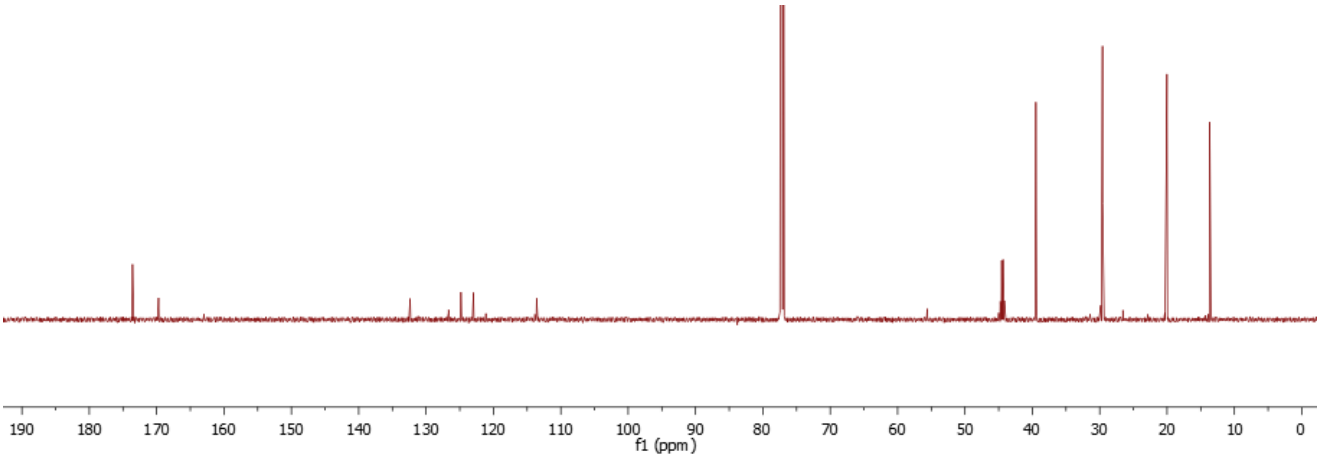
^{13}C NMR spectrum of 1-(*o*-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2g



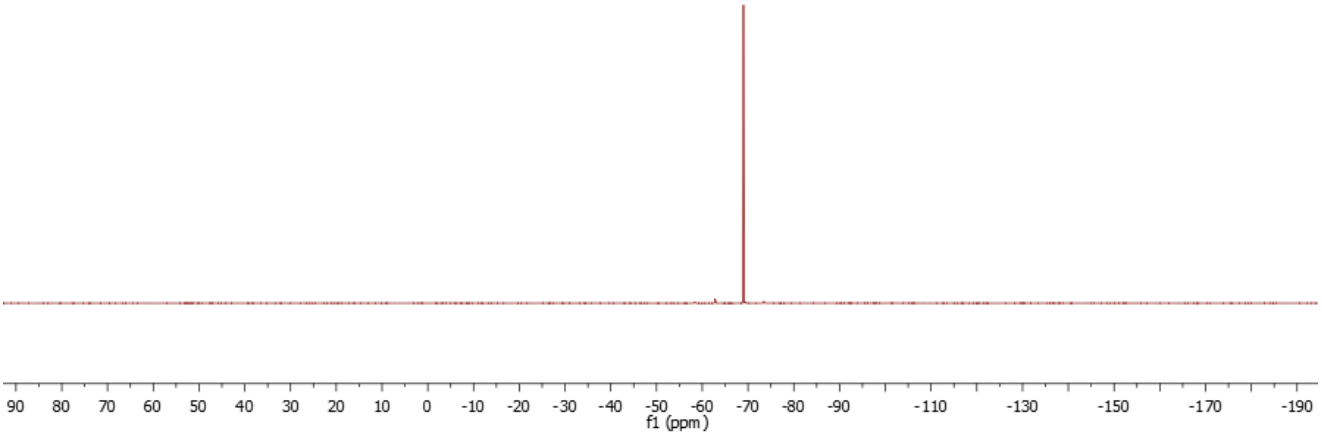
^{19}F NMR spectrum of 1-(*o*-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,5-dione 2g



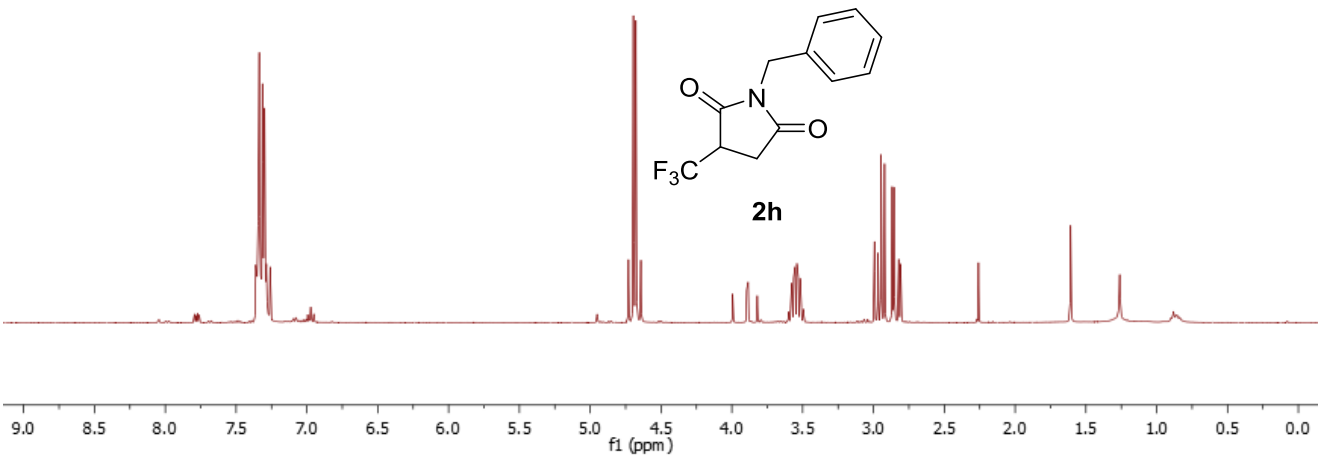
^{1}H NMR spectrum of 1-butyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2i with 3% 4,4' dimethoxybenzophenone



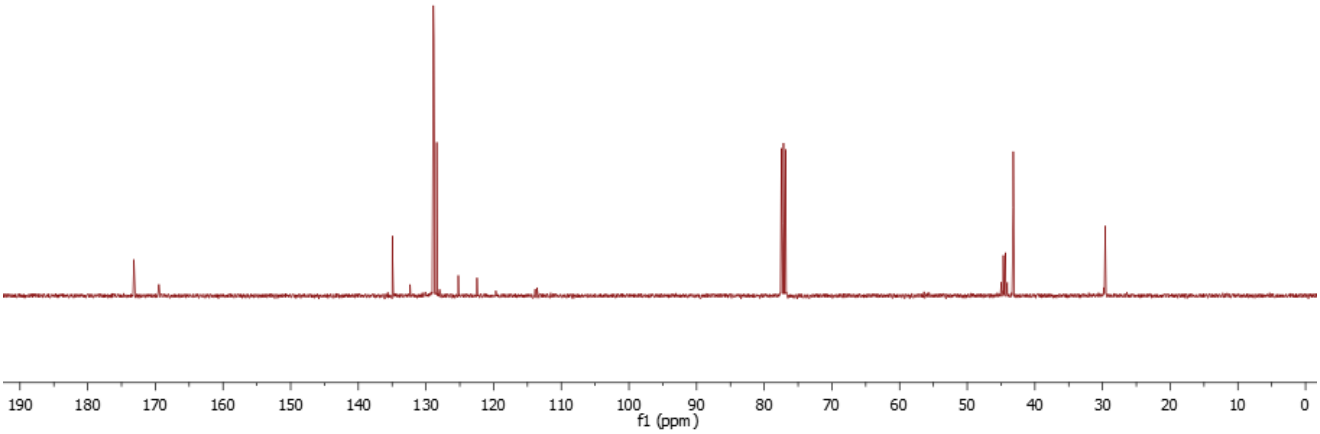
^{13}C NMR spectrum of 1-butyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2i with 3% 4,4' dimethoxybenzophenone



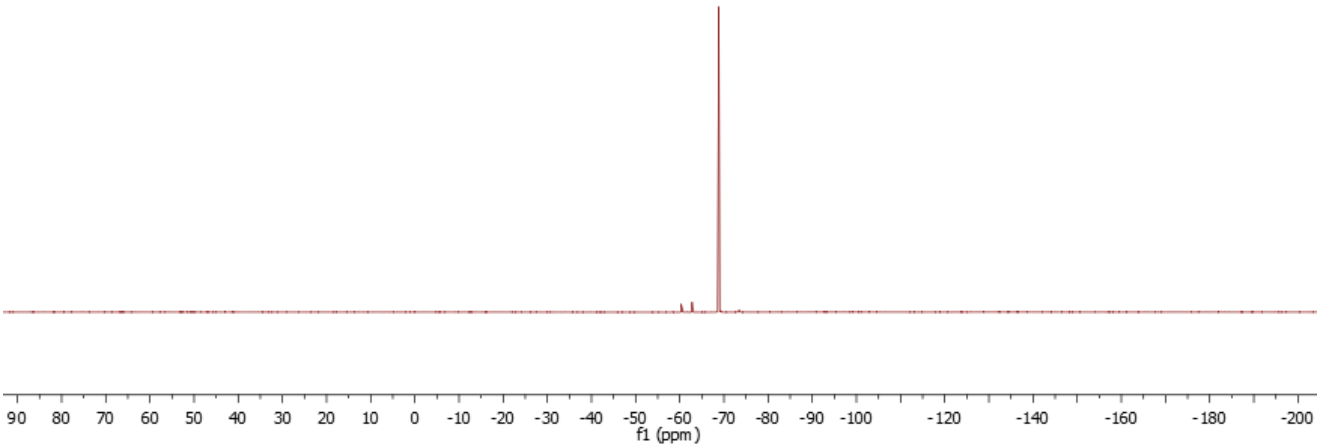
^{19}F NMR spectrum of 1-butyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2i with 3% 4,4' dimethoxybenzophenone



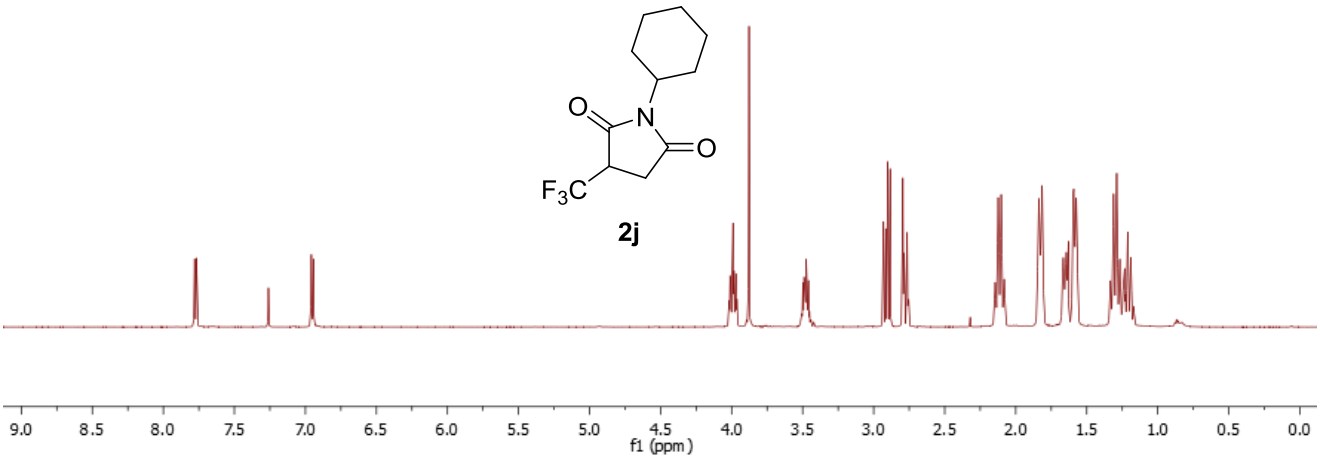
^{1}H NMR spectrum of 1-benzyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2j



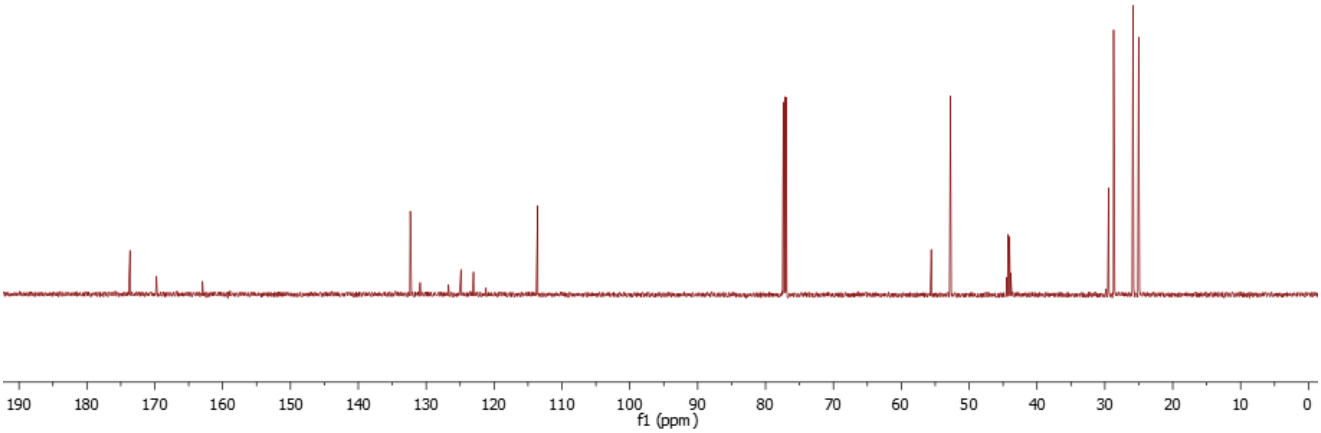
^{13}C NMR spectrum of 1-benzyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2j



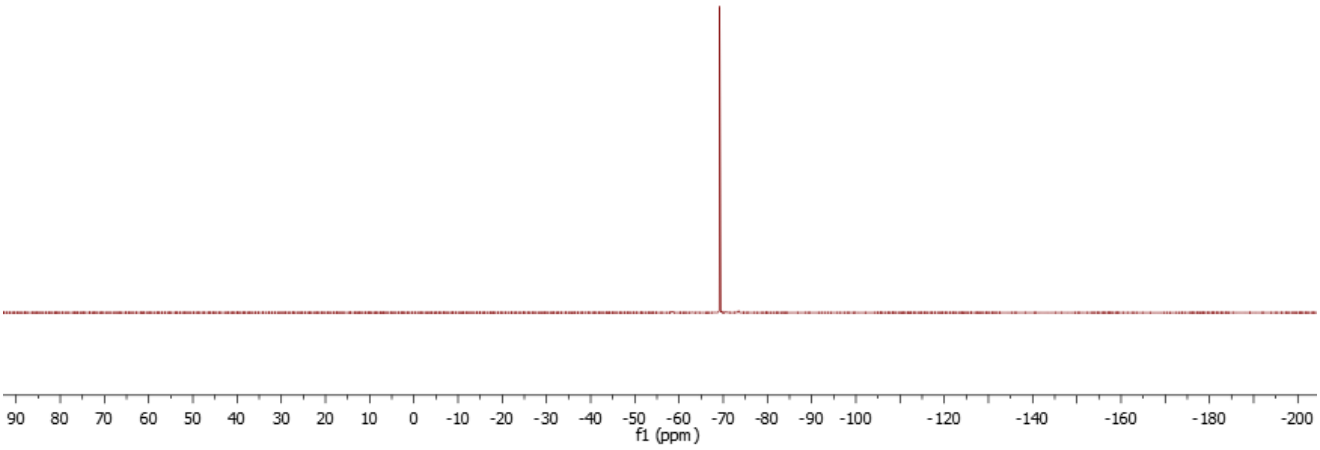
^{19}F NMR spectrum of 1-benzyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2j



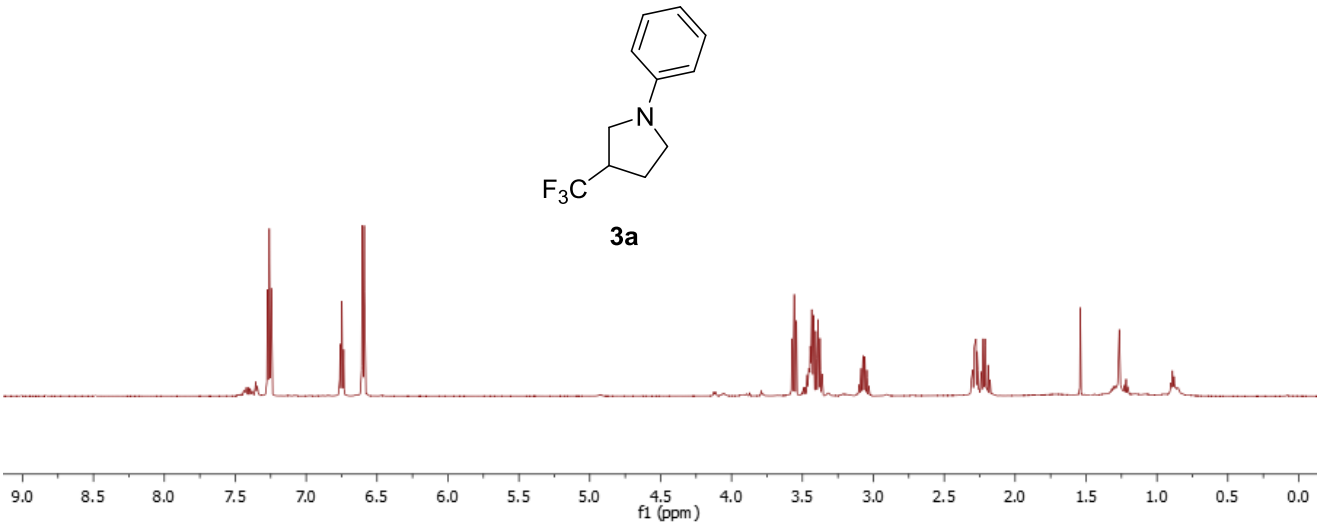
^{1}H NMR spectrum of 1-cyclohexyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2k with 10% 4,4' dimethoxybenzophenone



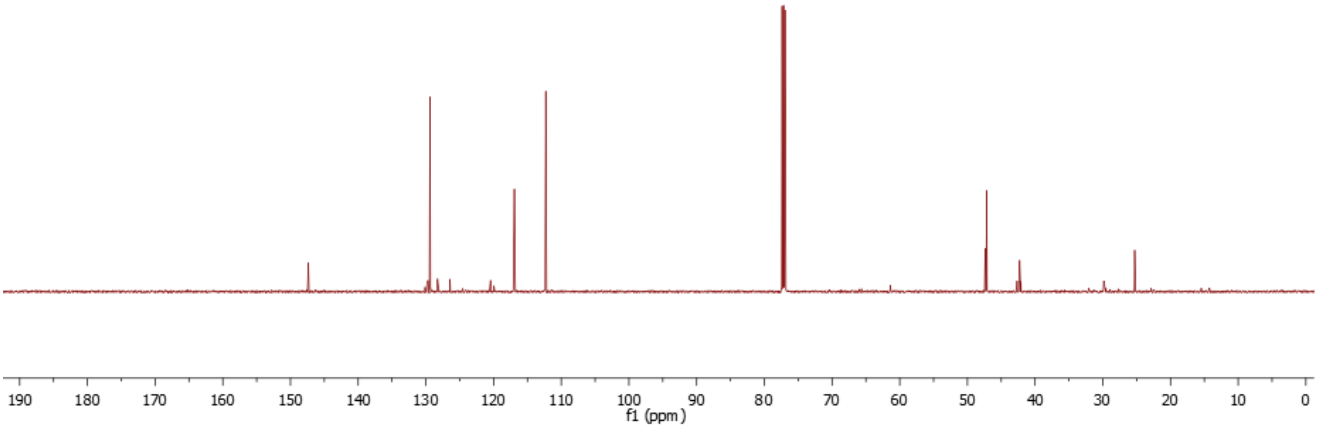
^{13}C NMR spectrum of 1-cyclohexyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2k with 10% 4,4' dimethoxybenzophenone



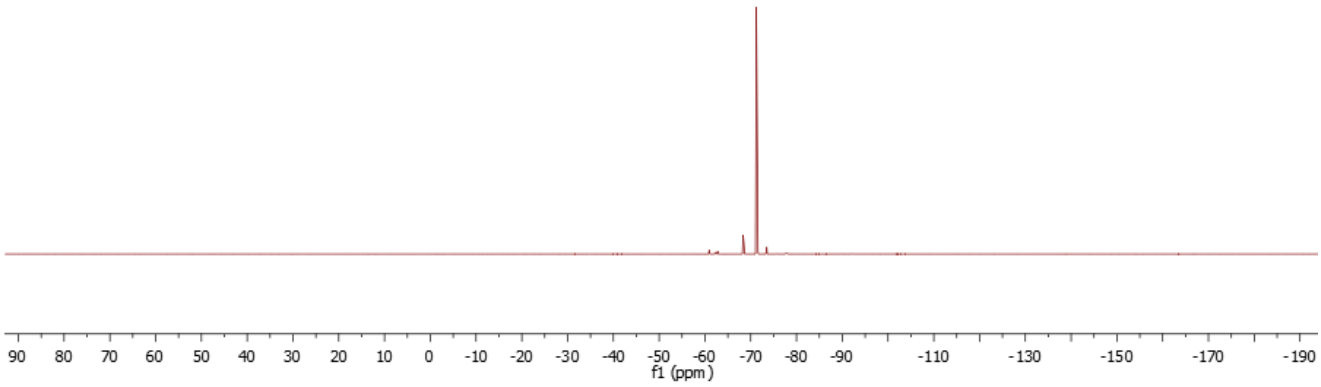
^{19}F NMR spectrum of 1-cyclohexyl-3-(trifluoromethyl)pyrrolidine-2,5-dione 2k with 10% 4,4' dimethoxybenzophenone



^{1}H NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine 3a



^{13}C NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine 3a



^{19}F NMR spectrum of 1-phenyl-3-(trifluoromethyl)pyrrolidine 3a