Catalyst- and base-free visible light-enabled radical relay trihalomethylation/functional group-migration/carbonylation with CX_3SO_2Cl

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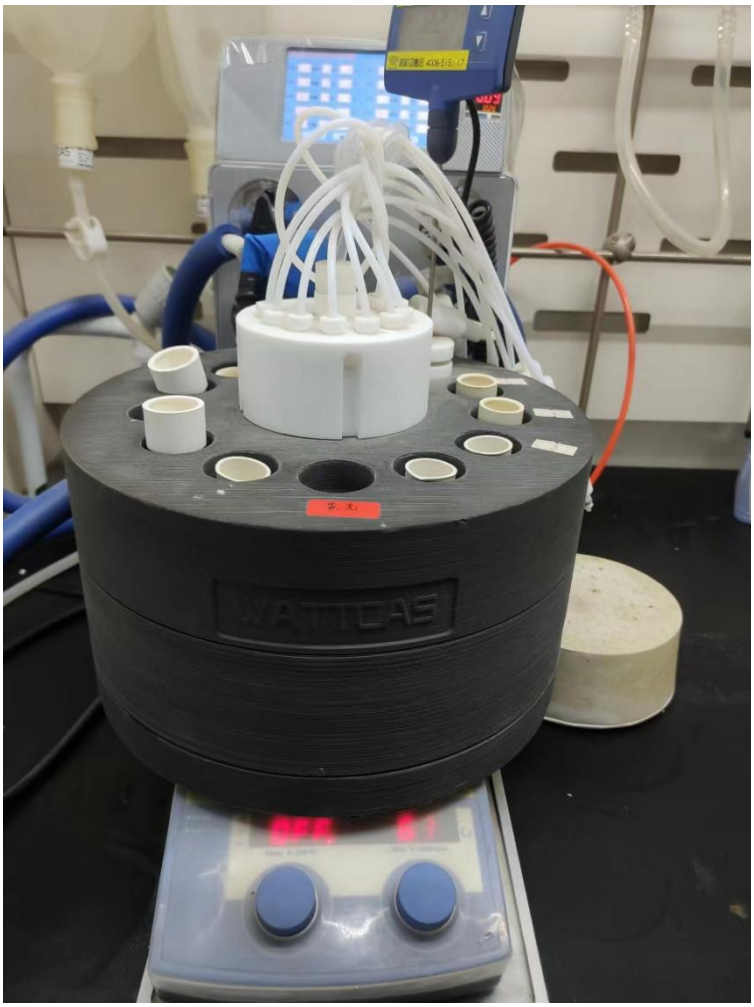
Supporting Information

1.General information

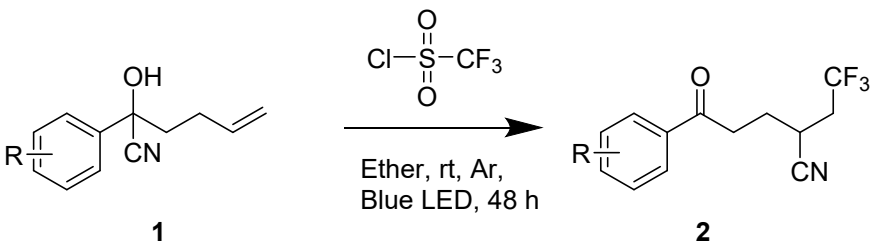
Unless otherwise noted, all reactions were carried out in flame-dried quartz tube under argon atmosphere. Anhydrous solvents were purified and dried by standard procedures. All commercially available reagents were used as received. Otherwise, diethylether was purchased from Sino pharm chemical reagent, $ClSO_2CF_3$ were purchased from Makllin. Other reagents were purchased from Innochem.diethylether were distilled over $LiAlH_4$ before use. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Melting points were measured on SGW® X-4 melting point apparatus and uncorrected. ^1H NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer at room temperature. Chemical shifts (ppm) were referenced to tetramethylsilane (TMS, δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were obtained by the same NMR spectrometer. Data for ^1H NMR were reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. High-Resolution Mass Spectrometry (HRMS) were performed on an ThermoFisher LTQ Orbitrap XL for HRMS. The starting materials **1** and **4** were prepared according to the literature[1-3]

2.Reaction equipment and details



Our Photocatalytic Parallel Reactor is cooled by circulating water, which can ensure that the reaction temperature is kept at about 26±3℃, and the distance between the light source and the reaction quartz tube is 0.4 cm, the power is 3W.

2.1. General procedure for synthesis of 2

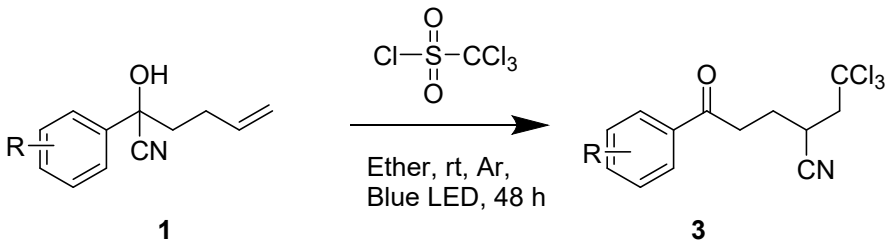


1 **2**

To a 25 mL of flame-dried quartz tube were added 2-hydroxy-2-arylhex-5-enenitrile **1** (0.5 mmol, 1.0 equiv), The mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (0.1ml, 2.0 equiv.) and diethylether (2.5

mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under educed pressure. The residue was purified by chromatography on silica gel (PE / EtOAc), eluting with the mixture of ethyl acetate/petroleum ether to give products **2.**

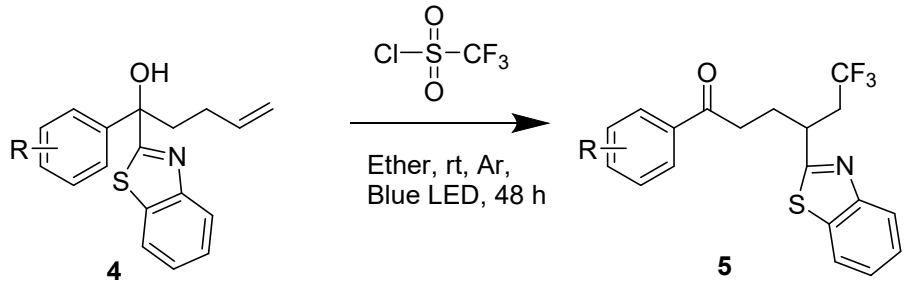
2.2 General procedure for synthesis of 3



1 **3**

To a 25 mL of flame-dried quartz tube were added 2-hydroxy-2-arylhex-5-enenitrile **1** (0.5 mmol, 1.0 equiv.), the mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CCl_3$ (0.272g, 1.25mmol, 2.5 equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under reduced pressure. The residue was purified by chromatography on silica gel (PE / EtOAc), eluting with the mixture of ethyl acetate/petroleum ether to give products **3.**

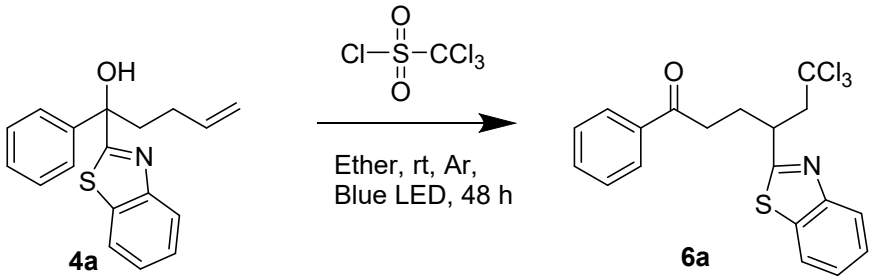
2.3. General procedure for synthesis of 5



4 **5**

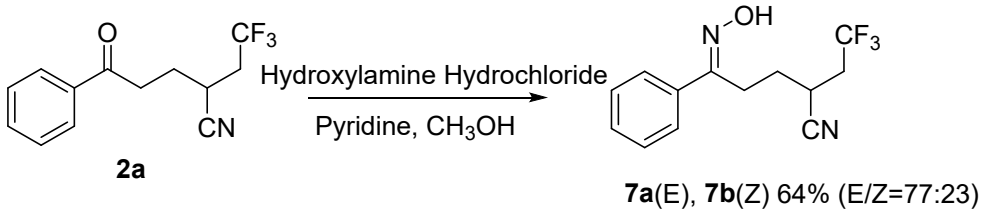
To a 25 mL of flame-dried quartz tube were added 1-(benzo[d]thiazol-2-yl)-1-arylpent-4-en-1-ol **4** (0.5 mmol, 1.0 equiv.), the mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (0.1ml, 2.0 equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under reduced pressure. The residue was purified by chromatography on silica gel (PE / EtOAc), eluting with the mixture of ethyl acetate/petroleum ether to give products **5.**

2.4 General procedure for synthesis of 6



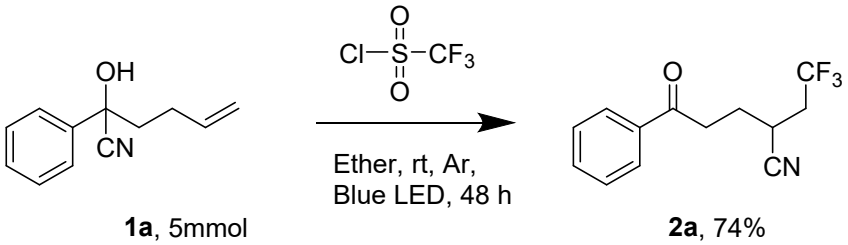
To a 25 mL of flame-dried quartz tube were added 1-(benzo[d]thiazol-2-yl)-1-phenylpent-4-en-1-ol **4a** (0.147g, 0.5 mmol, 1.0 equiv.), the mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CCl_3$ (0.272g, 1.25mmol, 2.5 equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under reduced pressure. The residue was purified by chromatography on silica gel (PE / EtOAc = 10:1), eluting with the mixture of ethyl acetate/petroleum ether to give products **6a** (0.161g, 78%).

2.5 Transformation of the Product



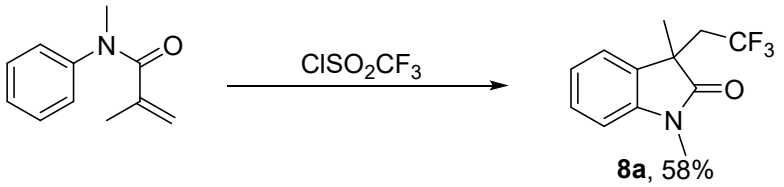
To a 25 mL of quartz tube were added 5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanenitrile **2a** (0.048g, 0.2 mmol, 1.0 equiv.), hydroxylamine Hydrochloride (0.021g, 0.3 mmol, 1.0 equiv.), pyridine (0.039g, 0.5 mmol, 1.0 equiv.), CH_3OH (2ml). The mixture was stirred in air atmosphere for 12 h. After completion, adding silica gel (2g), concentrated under reduced pressure. The product was separate by PLC prepared plates (0.5mm, PE / EtOAc = 20:1), get products **7.**

2.6. Gram-scale reaction



To a 25 mL of flame-dried quartz tube were added 2-hydroxy-2-arylhex-5-enenitrile **1** (5 mmol, 1.0 equiv), the mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (1 ml, 2.0 equiv.) and diethylether (5 mL). The mixture was stirred for 48 h under 25 W blue LED irradiation at room temperature. After completion, adding silica gel (5 g), concentrated under educed pressure. The residue was purified by chromatography on silica gel (PE / EtOAc), eluting with the mixture of ethyl acetate/petroleum ether to give products **2.**

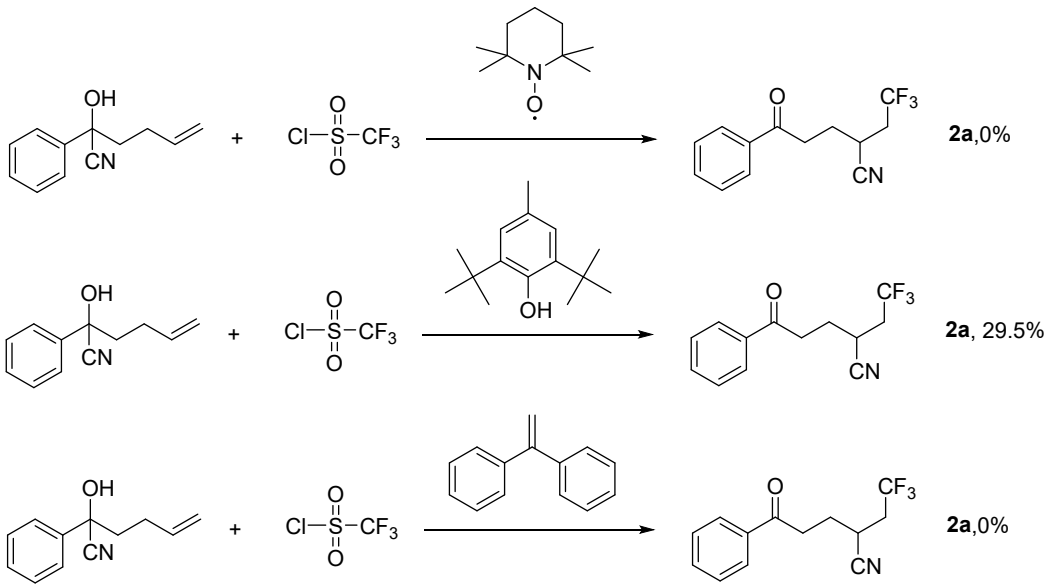
2.6 The free radical clock experiment: synthesis of 8



8a, 58%

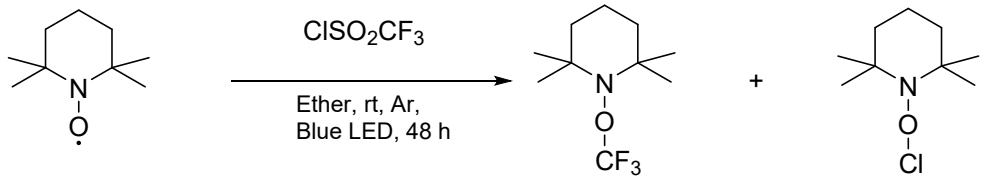
To a 25 mL of flame-dried quartz tube were added N-methyl-N-phenylmethacrylamide (0.087g, 0.5 mmol, 1.0 equiv.), the mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (0.1ml, 2.0 equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under reduced pressure. The residue was purified by chromatography on silica gel (PE / EtOAc = 10:1), eluting with the mixture of ethyl acetate/petroleum ether to give products **8** (0.070g, 58%).

2.7 General procedure for Free-radical inhibition experiments



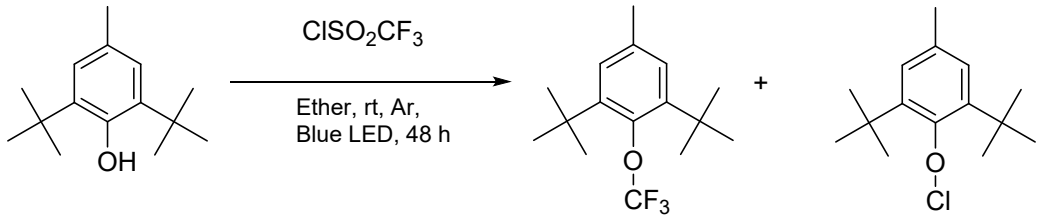
To a 25 mL of flame-dried quartz tube were added 2-hydroxy-2-phenylhex-5-enenitrile **1a** (0.094g, 0.5 mmol, 1.0 equiv.), TEMPO (0.312g, 2.0 mmol, 4.0 equiv.), or BHT (0.440g, 2.0 mmol, 4.0 equiv.), or 1,1-Diphenylethylene (0.360g, 2.0 mmol, 4.0 equiv.). The mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (0.1ml, 2.0equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, adding silica gel (2g), concentrated under reduced pressure, and was purified by chromatography on silica gel.

2.8 General procedure for Free-radical trapping experiments



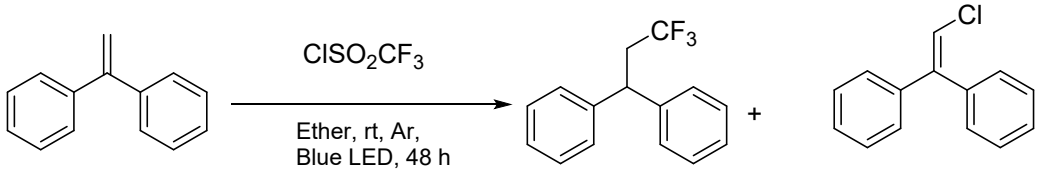
8b, HRMS calculated for 226.1413, found: 226.1407.

8c, HRMS calculated : 192.1149, found: 192.1144.



8d, HRMS calculated for: 289.1773, found: 289.1771.

8e, HRMS calculated for : 255.1510, found: 255.1501.

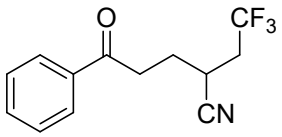


8f, HRMS calculated for: 249.0896, found: 249.0900.

8g, HRMS calculated for: 215.0622, found: 215.0615.

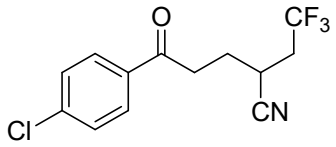
To a 25 mL of flame-dried quartz tube were added TEMPO (0.312g, 2.0 mmol, 2.0 equiv.), or BHT (0.440g, 2.0 mmol, 2.0 equiv.), or 1,1-Diphenylethylene (0.360g, 2.0 mmol, 2.0 equiv.). The mixture was evacuated and backfilled with argon for three times, then add $ClSO_2CF_3$ (0.1ml, 1.0equiv.) and diethylether (2.5 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature. After completion, capture compound by HRMS.

3. Analytical Data for products



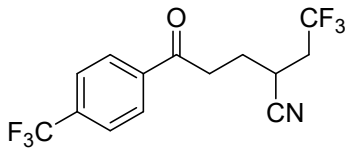
5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanenitrile (2a)

White solid, melting point：82-85℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 2H), 3.28 (t, *J* = 6.0 Hz, 2H), 3.10-3.19 (m, 1H), 2.52-2.67 (m, 1H), 2.37-2.50 (m, 1H), 2.21-2.31 (m, 1H), 2.10 – 1.97 (m, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 197.77, 136.25, 133.81, 128.91, 128.11, 125.12 (q, *J* = 277.0 Hz), 119.54, 36.82 (q, *J* = 30.0 Hz), 35.13, 26.42, 25.15 (q, *J* = 3.0 Hz).^{19}F NMR (376 MHz, Chloroform-d) δ -64.77.HRMS (ESI-TOF) m/z [M +H^+] calculated for $C_{13}H_{13}F_3NO^+$: 256.0944, found: 256.0940.



5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2b)

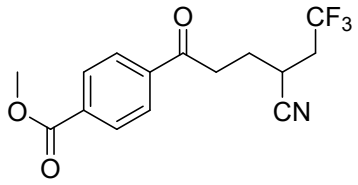
Yellow solid,melting point: 90-95℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.18-3.12 (m, 1H), 2.66-2.57 (m, 1H), 2.50-2.43 (m, 1H), 2.32-2.23 (m, 1H), 2.09-2.00 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.46, 140.09, 134.48, 129.40, 129.09, 125.05 (q, *J* = 277.2 Hz), 119.39, 36.58 (q, *J* = 30.0 Hz), 35.03, 26.17, 24.98 (q, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.75. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{13}H_{10}ClF_3NO^-$: 288.0408, found: 288.0410.



5-oxo-2-(2,2,2-trifluoroethyl)-5-(4-(trifluoromethyl)phenyl)pentanenitrile5-(2-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2c)

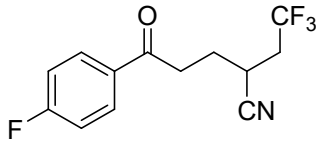
White solid, melting point: 54-56℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ8.11 (d, J =

8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 3.34-3.31 (m, 1H), 3.19-3.14 (m, 1H), 2.67-2.60 (m, 1H), 2.50-2.44 (m, 1H), 2.34-2.28 (m, 1H), 2.12-2.06 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.78, 138.72, 134.89 (q, *J* = 32.9 Hz), 128.37, 125.88 (q, *J* = 3.6 Hz), 124.99 (q, *J* = 277.4 Hz), 123.48 (q, *J* = 272.8 Hz), 119.30, 36.64 (q, *J* = 29.9 Hz), 35.41, 26.08, 24.98 (q, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -63.20, -64.79. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{10}F_6NO^-$: 322.0672, found: 322.0674.



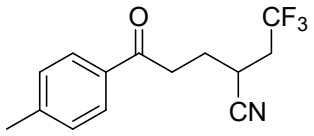
methyl 4-(4-cyano-6,6,6-trifluorohexanoyl)benzoate (2d)

White solid, melting point: 84-86℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.1 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 3.96 (s,3H), 3.31 (t, *J* = 6.7 Hz, 2H), 3.19-3.18 (m, 1H), 2.65-2.56 (m, 1H), 2.49-2.40 (m, 1H), 2.32-2.24 (m, 1H), 2.10-2.01 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.15, 166.04, 139.27, 134.43, 129.99, 127.93, 124.98 (q, *J* = 277.3 Hz), 119.28, 52.52, 36.72 (q, *J* = 30.0 Hz), 35.46, 31.57, 26.20, 25.03 (q, *J* = 2.9 Hz), 22.64, 14.10. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.76. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{15}H_{15}F_3NO_3^+$ 314.0998, found: 314.0995



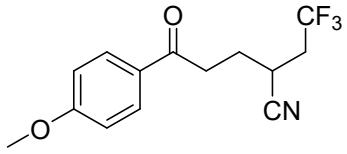
5-(4-fluorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2e)

White solid, melting point: 41-43℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04-8.01(m, 2H), 7.18 (t, *J* = 8.6 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.18-3.10 (m, 1H), 2.64-2.53 (m, 1H), 2.50-2.38 (m, 1H), 2.25-2.22 (m, 1H), 2.08-1.98 (m, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 196.00, 166.08, (d, *J* = 255.8 Hz), 132.63 (d, *J* = 3.0 Hz), 130.71 (d, *J* = 9.4 Hz) ,124.98 (q, *J* = 277.2 Hz), 119.34, 115.98 (d, *J* = 22.1 Hz), 36.77 (q, *J* = 30.1 Hz), 34.97 26.31 25.06 (q, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.76, 104.03. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{13}H_{12}F_4NO^+$: 274.0849, found: 274.0846.



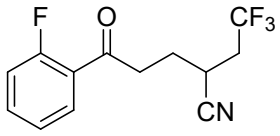
5-oxo-5-(p-tolyl)-2-(2,2,2-trifluoroethyl)pentanenitrile (2f)

White solid, melting point: 69-71℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 3.20-3.13 (m, 1H), 2.65-2.54 (m, 1H), 2.51-2.41 (m, 4H), 2.32-2.23 (m, 1H), 2.09-2.01 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.31, 144.63, 133.73, 129.47, 128.13, 125.03 (q, *J* = 277.6 Hz), 119.46, 36.69 (q, *J* = 30.3 Hz), 34.88, 26.41, 25.07 (q, *J* = 2.8 Hz), 21.69 (q, *J* = 6.3 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.76. HRMS (ESI-TOF) m/z [M + H^{+}] calculated for $C_{14}H_{15}F_3NO^{+}$: 270.1100, found: 270.1095.



5-(4-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2g)

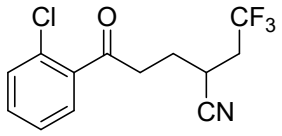
Colourless liquid, R_f = 0.19 (PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 3.20-3.13 (m, 1H), 2.65-2.59 (m, 1H), 2.57-2.39 (m, 4H), 2.32-2.22 (m, 1H), 2.09-2.02 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 197.22, 144.60, 133.79, 129.47, 128.13, 125.01 (q, *J* = 277.9 Hz), 119.39, 36.81 (q, *J* = 30.2 Hz), 34.88, 26.46, 25.12 (q, *J* = 3.0 Hz), 21.67. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.76. HRMS (ESI-TOF) m/z [M+Na^{+}] calculated for $C_{14}H_{14}F_3NO_2Na^{+}$: 308.0869, found: 308.0880.



5-(2-fluorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2h)

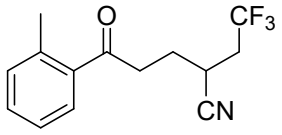
White solid, melting point：48-51℃. ^{1}H NMR (400 MHz, Chloroform-*d*) 7.93-7.89 (m, 1H), 7.60-7.54 (m, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.18 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.31-3.26 (m, 2H), 3.18-3.11 (m, 1H), 2.67-2.53 (m, 1H), 2.50-2.37(m, 1H), 2.29-2.21 (m, 1H), 2.09-2.01 (m, 1H), ^{13}C NMR (101 MHz, Chloroform-d) δ 196.11(d, *J* = 0.3Hz), 162.47(d, *J* = 256.1Hz), 135.51(d, *J* = 9.1Hz), 130.81(d, *J* = 2.5Hz), 125.74(q,

J = 278.4 Hz), 125.01, 124.89 (d, *J* = 3.4 Hz), 119.55, 117.12(d, *J* = 26.0 Hz), 40.25(d, *J* = 8.4 Hz), 36.96 (q, *J* = 30.1 Hz), 26.57(d, *J* = 2.1 Hz), 25.21(q, *J* = 3.3 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.75, 108.58. HRMS (ESI-TOF) m/z [M +H^+] calculated for $C_{13}H_{12}F_4NO^+$: 274.0849, found: 274.0845.



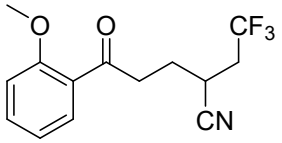
5-(2-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2i)

Colourless liquid, R_f = 0.14 (PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.37 (t, *J* = 6.8 Hz, 1H), 3.27 (t, *J* = 7.0 Hz, 2H), 3.21 – 3.06 (m, 1H), 2.69 – 2.53 (m, 1H), 2.52 – 2.37 (m, 1H), 2.34 – 2.18 (m, 1H), 2.17 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 200.76, 138.30, 132.32, 131.00, 130.77, 129.04, 127.16, 125.01 (q, *J* = 277.3 Hz), 119.25, 39.41, 36.59 (q, *J* = 29.4 Hz), 26.36 (q, *J* = 4.8 Hz), 24.92 (d, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.75. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{13}H_{10}ClF_3NO^-$: 288.0408, found: 288.0410.



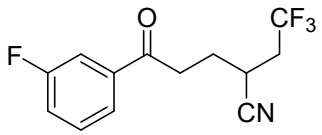
5-oxo-5-(o-tolyl)-2-(2,2,2-trifluoroethyl)pentanenitrile (2j)

Faint yellow solid, melting point: 35-38°C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.43-7.39 (m, 1H), 7.31-7.26 (m, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 3.16-3.09 (m, 1H), 2.62-2.56 (m, 1H), 2.51 (s,3H), 2.46-2.38 (m, 1H), 2.27-2.19 (m, 1H), 2.05-1.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 201.21, 138.64, 136.67, 132.29, 132.01, 128.72, 125.94, 125.01 (q, *J* = 277.3 Hz,), 119.37, 37.62, 36.76 (q, *J* = 30.0 Hz,), 26.53, 25.03 (q, *J* = 3.0 Hz,), 21.57. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.76. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{14}H_{15}F_3NO^+$: 270.1100, found: 270.1096.



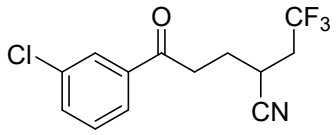
5-(2-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2k)

Yellow liquid, Rf = 0.14(PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 6.92 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.19 (t, *J* = 6.9 Hz, 2H), 3.05-2.89 (m, 1H), 2.54-2.43 (m, 1H), 2.38-2.27 (m, 1H), 3.15-3.07 (m, 1H), 1.96-1.87 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 199.77, 158.94, 134.23, 130.42, 127.13, 125.13 (q, *J* = 277.3 Hz), 120.77, 119.64, 111.67, 55.54, 40.35, 36.69 (q, *J* = 29.9 Hz), 26.83, 25.09 (q, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.79. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{13}F_3NO_2^+$: 284.0903, found: 284.0905.



5-(3-fluorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2l)

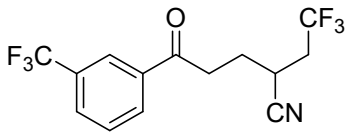
White liquid, R_f = 0.58 (PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 1H), 7.48 (m, 1H), 7.31 (m, 1H), 3.24-3.27 (m, 2H), 3.18-3.10 (m, 1H), 2.67-2.53 (m, 1H), 2.50-2.38 (m,1H), 2.31-2.22 (m, 1H), 2.08-1.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.41 (d, *J* = 2.04Hz), 162.92 (d, *J* = 249.5Hz), 138.20(d,*J* = 6.2Hz), 130.55 (d, *J* = 7.8Hz), 124.98 (q, *J* = 278.3Hz), 123.80 (d, *J* = 3.1Hz), 120.76 (d, *J* = 21.4Hz), 119.30, 114.75 (d, *J* = 22.6Hz), 36.72(q,*J* = 30.3Hz), 35.26, 26.21, 25.02 (q, *J* = 2.8Hz).^{19}F NMR (376 MHz, Chloroform-d) δ -64.76, -111.35. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{13}H_{12}F_4NO^+$: 274.0849, found: 274.0845.



5-(3-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2m)

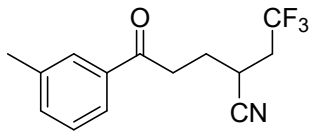
Yellow liquid, R_f = 0.13(PE:EA = 10:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (s,1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 3.28 (t, *J* = 6.6 Hz, 2H), 3.19-3.12 (m, 1H), 2.68-2.55 (m, 1H), 2.50-2.39 (m, 1H), 2.31-2.23 (m, 1H), 2.09-2.00 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.39, 137.62, 135.19, 133.64, 130.18 , 128.13, 126.11, 124.98 (q, *J* = 277.8 Hz), 119.31, 36.71 (q, *J* = 28.2 Hz,), 35.22, 26.16, 25.02 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz,

Chloroform-d) δ -64.74. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{13}H_{10}ClF_3NO^-$: 288.0408, found: 288.0411.



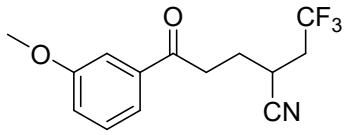
5-oxo-2-(2,2,2-trifluoroethyl)-5-(3-(trifluoromethyl)phenyl)pentanenitrile (2n)

Yellow oil liquid, R_f = 0.11(PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.22-3.15 (m, 1H), 2.68-2.57 (m, 1H), 2.53-2.42 (m, 1H), 2.35-2.06 (m, 1H), 2.13-2.03 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.30, 136.61, 131.49 (q, *J* = 33.1 Hz), 131.15, 130.10 (q, *J* = 3.5 Hz), 129.56, 124.97 (q, *J* = 277.3 Hz), 124.86 (q, *J* = 3.9 Hz), 123.58 (q, *J* = 276.0 Hz), 119.28, 36.71 (q, *J* = 30.6 Hz), 35.25, 26.12, 25.00 (q, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.83, -64.77. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{10}F_6NO^-$: 322.0672, found: 322.0674.



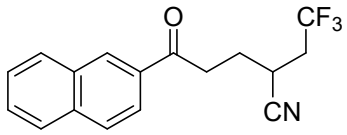
5-oxo-5-(m-tolyl)-2-(2,2,2-trifluoroethyl)pentanenitrile (2o)

Colourless liquid, R_f = 0.14(PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.44-7.37 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 3.16 (m,1H), 2.65-2.56 (m, 1H), 2.50-2.38 (m, 4H), 2.31-2.23 (m, 1H), 2.09-2.01 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.90, 138.66, 136.21, 134.47, 128.68, 128.55, 125.23, 125.01 (q, *J* = 279.4 Hz), 119.45, 36.73 (q, *J* = 25.9 Hz), 35.08, 26.36, 25.07 (q, *J* = 2.6 Hz), 21.35 (q, *J* = 5.2 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.77. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{14}H_{15}F_3NO^+$: 270.1100, found: 270.1095.



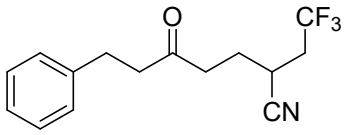
5-(3-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2p)

Colourless liquid, R_f = 0.32(PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.48-7.49 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.16-7.13 (m, 1H), 3.87 (s, 3H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.18-3.11 (m, 1H), 2.63-2.55 (m, 1H), 2.50-2.37 (m, 1H), 2.30-2.22 (m, 1H), 2.08-1.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.50, 159.97, 137.52, 129.82, 125.00 (q, *J* = 277.3 Hz), 120.64, 120.15, 119.39, 112.25, 55.50, 36.78 (q, *J* = 30.1 Hz), 35.16, 26.42, 25.07 (q, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.77. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{14}H_{15}F_3NO_2^+$: 286.1049, found: 286.1045



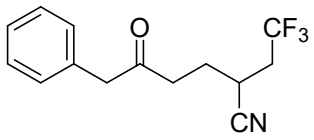
5-(naphthalen-2-yl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanenitrile (2q)

Yellow solid, melting point: 109-112℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.04-8.00 (m, 2H), 7.93-7.88 (m, 2H), 7.65-7.56 (m, 2H), 3.44-3.40 (m, 2H), 3.23-3.15 (m, 1H), 2.69-2.56 (m, 1H), 2.53-2.40 (m, 1H), 2.37-2.29 (m, 1H), 2.14-2.05 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.55, 135.84, 133.51, 132.47, 129.93, 129.66, 128.84, 128.75, 127.85, 127.05, 125.02 (q, *J* = 277.1 Hz), 123.49, 119.46, 36.82 (q, *J* = 30.1 Hz), 35.13, 26.51, 25.16 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.74. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{17}H_{13}F_3NO^-$: 304.0954, found: 304.0956.



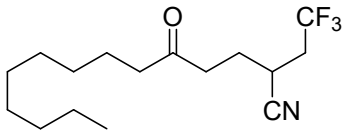
5-oxo-7-phenyl-2-(2,2,2-trifluoroethyl)heptanenitrile (2r)

Colourless liquid, R_f = 0.39(PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.2 Hz, 2H), 3.04-2.96 (m, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.55-2.47 (m, 1H), 2.39-2.30 (m, 1H), 2.09-2.01 (m, 1H), 1.88-1.80 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 207.74, 140.54, 128.62, 128.30, 126.33, 124.99 (q, *J* = 276.9 Hz), 119.28, 44.28, 39.22, 36.54 (q, *J* = 29.9 Hz), 29.70, 25.77, 24.82 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.78. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{15}H_{15}F_3NO^-$: 282.1111, found: 282.1113.



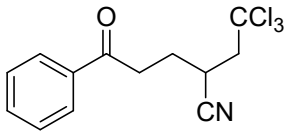
5-oxo-6-phenyl-2-(2,2,2-trifluoroethyl)hexanenitrile (2s)

Faint yellow liquid, R_f = 0.51(PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.21 (m, 5H), 3.73 (s,2H), 3.00-2.93 (m, 1H), 2.75-2.71 (m, 2H), 2.51-2.42 (m, 1H), 2.33-2.28 (m, 1H), 2.05-1.96 (m, 1H), 1.85-1.76 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 206.16, 133.46, 129.35, 128.98, 127.42, 124.91 (q, *J* = 277.5 Hz), 119.16, 50.22, 38.16, 36.60 (q, *J* = 30.0 Hz), 25.94, 24.78 (q, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -64.83. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{13}F_3NO^-$: 268.0954, found: 268.0957.



5-oxo-2-(2,2,2-trifluoroethyl)tetradecanenitrile (2t)

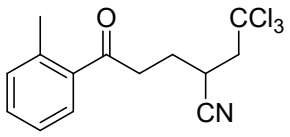
Colourless liquid, R_f = 0.39(PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.00-2.92 (m, 1H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.50-2.41 (m, 1H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.33-2.25 (m, 1H), 2.02-1.94 (m, 1H), 1.80-1.68 (m, 1H), 1.51 (t, *J* = 6.8 Hz, 2H), 1.20 (s, 12H), 0.81 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 208.89, 125.00 (q, *J* = 277.2 Hz), 119.27, 42.93, 38.82, 36.58 (q, *J* = 30.0 Hz), 31.82, 29.37, 29.33, 29.21, 29.14, 25.86, 24.84 (q, *J* = 3.0 Hz), 23.76, 22.62, 14.03. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.89. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{16}H_{26}F_3NO^-$: 304.1893, found: 304.1895.



5-oxo-5-phenyl-2-(2,2,2-trichloroethyl)pentanenitrile (3a)

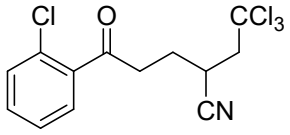
White solid, melting point: 104-107℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.23-3.15 (m, 4H), 2.83 (d, *J* = 13.4 Hz, 1H), 2.25-2.17 (m, 1H), 2.05-1.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.69, 136.24, 133.67, 128.81, 128.04, 120.40, 96.56, 56.49, 35.07,

28.67, 27.27. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{13}H_{12}Cl_3NONa^+$: 325.98767, found: 325.98779.



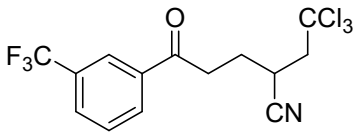
5-oxo-5-(o-tolyl)-2-(2,2,2-trichloroethyl)pentanenitrile (3b)

White solid, melting point: 77-82℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz), 7.21 (q, *J* = 6.5 Hz, 1H), 3.22-3.12 (m,4H), 2.81 (d, *J* = 12.5 Hz, 1H), 2.44 (s, 3H), 2.21-2.13 (m, 1H), 2.04-1.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 201.28, 138.59, 136.76, 132.27, 131.98, 128.76, 125.94, 120.39, 96.56, 56.44, 37.68, 28.62, 27.42, 21.60. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{13}Cl_3NO^-$: 316.0068, found: 316.0069.



5-(2-chlorophenyl)-5-oxo-2-(2,2,2-trichloroethyl)pentanenitrile (3c)

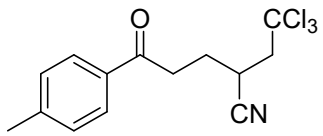
Colourless liquid, R_f = 0.12(PE:EA = 5:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55-7.53 (m, 1H), 7.46-7.41 (m, 2H), 7.38-7.34 (m, 1H), 3.30-3.23 (m, 4H), 2.91 (d, *J* = 13.1 Hz, 1H), 2.32-2.25 (m, 1H), 2.16-2.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 200.80, 138.30, 132.36, 130.92, 129.14, 127.17, 120.24, 96.53, 56.27, 39.43, 28.51, 27.27. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{13}H_{12}Cl_4NO^+$:337.9667, found: 337.9655.



5-oxo-2-(2,2,2-trichloroethyl)-5-(3-(trifluoromethyl)phenyl)pentanenitrile (3d)

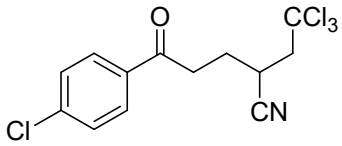
Yellow liquid , R_f = 0.13(PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s,1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 3.27-3.17 (m, 4H), 2.85 (d, *J* = 13.0 Hz, 1H), 2.29-2.20 (m, 1H), 2.10-2.01 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.34, 136.69, 131.49 (q, *J* = 33.0 Hz),

131.17, 130.06 (q, J = 3.6 Hz), 129.55, 124.87 (q, J = 4.0 Hz), 123.58 (q, J = 272.6 Hz), 120.26, 96.46, 56.47, 35.27, 28.60, 27.06. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.79. HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{10}Cl_3F_3NO^-$: 369.9785, found: 369.9787.



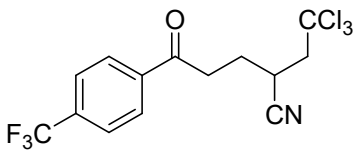
5-oxo-5-(p-tolyl)-2-(2,2,2-trichloroethyl)pentanenitrile (3e)

White solid, melting point: 101-102℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 7.9 Hz, 2H), 7.35-7.28 (m, 2H), 3.24-3.16 (q, J = 7.1 Hz, 4H), 2.84 (d, J = 12.8 Hz, 1H), 2.36 (s, 3H), 2.26-2.18 (m, 1H), 2.05-1.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.90, 138.66, 136.27, 134.44, 128.68, 128.56, 125.26, 120.43, 96.53, 56.54, 35.11, 28.70, 27.32, 21.38. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{14}H_{14}Cl_3NO^-$: 318.0213, found: 318.0204.



5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trichloroethyl)pentanenitrile (3f)

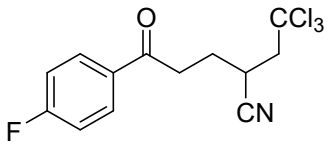
Yellow solid, melting point: 105-107℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H), 3.23-3.15 (m, 4 H), 2.83 (d, J = 12.8 Hz, 1 H), 2.25-2.17 (m, 1 H), 2.05-1.99 (m, 1 H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.44, 140.16, 134.55, 129.44, 129.14, 120.30, 96.50, 56.48, 35.08, 28.64, 27.17. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{13}H_{11}Cl_4NONa^+$: 363.94280, found: 363.94406.



5-oxo-2-(2,2,2-trichloroethyl)-5-(4-(trifluoromethyl)phenyl)pentanenitrile (3g)

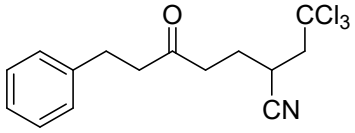
Yellow solid, melting point: 88-96℃ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 3.25-3.15 (m, 4H), 2.83 (d, J = 12.9 Hz, 1H),

2.26-2.18 (m, 1H), 2.08-1.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.77, 138.82, 134.81 (q, *J* = 32.8 Hz), 128.39, 125.87 (q, *J* = 3.7 Hz), 123.50 (q, *J* = 272.8 Hz), 120.26, 96.49, 56.39, 35.43, 28.57, 27.01. ^{19}F NMR (376 MHz, Chloroform-d) δ -63.13.HRMS (ESI-TOF) m/z [M - H^+] calculated for $C_{14}H_{10}Cl_3F_3NO^-$: 369.9785, found: 369.9786.



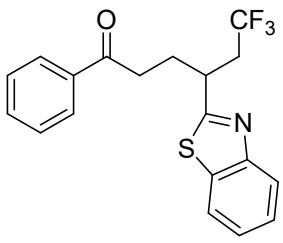
5-(4-fluorophenyl)-5-oxo-2-(2,2,2-trichloroethyl)pentanenitrile (3h)

Colourless liquid, R_f = 0.10(PE:EA = 10:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.28, 5.7 Hz, 2H), 7.18 (m, 2H), 4.48-4.43 (m, 1H), 3.39 (dd, *J* = 15.66, 5.7 Hz, 1H), 3.29-3.21 (m, 3H), 2.58-2.52 (m, 1H), 2.24-2.16 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 196.84, 165.91 (d, *J* = 254.8 Hz), 133.09 (d, *J* = 2.9 Hz), 130.66 (d, *J* = 9.3 Hz), 115.81 (d, *J* = 22.0 Hz), 96.55, 62.51, 57.33, 35.03, 33.10. ^{19}F NMR (376 MHz, Chloroform-d) δ -104.74. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{13}H_{12}Cl_3FNO^+$: 321.9963, found: 321.9953.



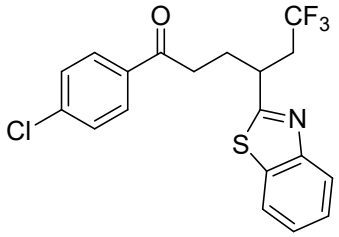
5-oxo-7-phenyl-2-(2,2,2-trichloroethyl)heptanenitrile (3i)

Colourless liquid, R_f = 0.16(PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22-7.17 (m, 2H), 7.15-7.08 (m, 3H), 3.11-3.02 (m, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.73-2.67 (m, 3H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.02-1.93 (m, 1H), 1.84-1.75 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 207.73, 140.57, 128.64, 128.32, 126.35, 120.26, 96.55, 56.31, 44.34, 39.25, 29.73, 28.44, 26.69. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{15}H_{16}Cl_3NONa^+$: 354.01897, found: 354.01953.



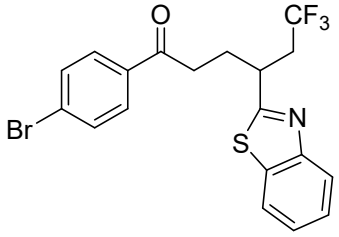
4-(benzo[d]thiazol-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (5a)

Colourless liquid, Rf = 0.16(PE:EA = 10:1). ^{1}H NMR (500 MHz, CDCl3), 8.02 (d, J = 8.1 Hz, 1H), 7.89-7.87 (m, 3H), 7.56-7.49 (m, 2H), 7.44-7.40 (m, 3H), 3.74-3.69 (m, 1H), 3.02-2.99 (m, 2H), 2.78-2.54(m, 2H), 2.49-2.40 (m, 1H), 2.38-2.32 (m, 1H), ^{13}C NMR (126 MHz, Chloroform-d) δ 198.62, 172.08, 153.03, 136.61, 134.66, 133.18, 128.58, 127.96, 126.24, 126.12 (d, J = 277.38 Hz), 125.26, 123.00, 121.72, 39.34 (q, J = 28.43 Hz), 37.97 (d, J = 2.55 Hz), 35.28, 30.00. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.04. HRMS (ESI-TOF) m/z [M + H^{+}] calculated for $C_{19}H_{17}F_3NOS^{+}$: 364.0972, found: 364.0977.



4-(benzo[d]thiazol-2-yl)-1-(4-chlorophenyl)-6,6,6-trifluorohexan-1-one (5b)

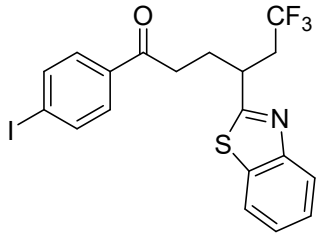
White solid, melting point: 87-95℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31-7.25 (m, 3H), 3.62-3.55 (m, 1H), 2.92-2.78 (m, 3H), 2.60-2.47 (m, 1H), 2.36-2.18 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.39, 171.92, 153.03, 139.65, 134.87, 134.64, 129.38, 128.90, 126.29, 126.11 (q, *J* = 277.4 Hz), 125.32, 123.01, 121.75, 39.33 (q, *J* = 28.5 Hz), 37.90 (q, *J* = 2.5 Hz), 35.23, 29.87. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.01. HRMS (ESI-TOF) m/z [M + H^{+}] calculated for $C_{19}H_{16}ClF_3NOS^{+}$: 398.05877, found: 398.05893.



4-(benzo[d]thiazol-2-yl)-1-(4-bromophenyl)-6,6,6-trifluorohexan-1-one (5c)

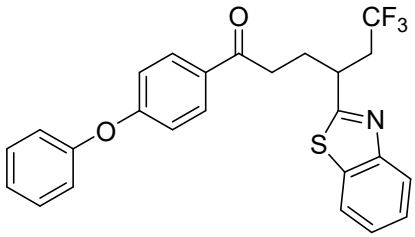
White solid, melting point: 109-112℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.62-3.56 (m, 1H), 2.92-2.79 (m, 3H), 2.61-2.48 (m, 1H), 2.37-2.19 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ

197.59, 171.93, 152.97, 135.26, 134.61, 131.90, 129.49, 128.40, 126.31, 126.09 (q, *J* = 277.4 Hz), 125.34, 122.99, 121.76, 39.34 (q, *J* = 28.5 Hz), 37.88 (q, *J* = 2.5 Hz), 35.22, 29.85. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.02. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{19}H_{15}BrF_3NOSNa^+$: 463.99020, found: 463.99081.



4-(benzo[d]thiazol-2-yl)-6,6,6-trifluoro-1-(4-iodophenyl)hexan-1-one (5d)

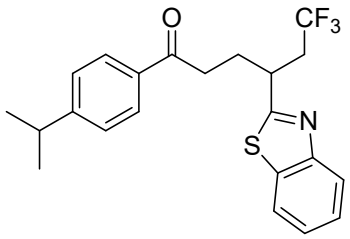
White solid, melting point: 109-111℃. ^{1}H NMR (500 MHz, Chloroform-*d*)8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 3.71 (s,1H), 3.01-2.92 (m, 3H), 2.69-2.64 (m, 1H), 2.46-2.42 (m, 1H), 2.39-2.31 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.90, 171.92, 152.96, 137.91, 135.79, 134.60, 129.35, 126.31, 126.08 (q, *J* = 277.4 Hz), 125.34, 122.99, 121.75, 101.20, 39.34 (q, *J* = 28.6 Hz), 37.88 (q, *J* = 2.5 Hz), 35.16, 29.84. ^{19}F NMR (376 MHz, Chloroform-d) δ -64.03. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{19}H_{15}IF_3NOSNa^+$: 511.97633, found: 511.97717.



4-(benzo[d]thiazol-2-yl)-6,6,6-trifluoro-1-(4-phenoxyphenyl)hexan-1-one (5e)

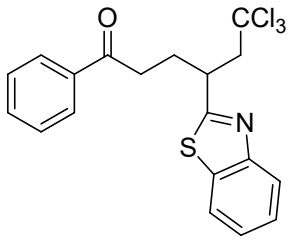
White solid, melting point: 96-98℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ , 7.87 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 3H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.60-3.53 (m, 1H), 2.89-2.75 (m, 3H), 2.57-2.44 (m, 1H), 2.33-2.15 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.16, 172.13, 162.07, 155.45, 153.08, 134.71, 131.29, 130.27, 130.08, 126.26, 126.20 (q, *J* = 277.4 Hz), 125.28, 124.67, 123.02, 121.76, 120.18, 117.30, 39.32 (q, *J* = 28.4 Hz), 38.00 (q, *J* = 2.5 Hz), 35.05, 30.15. ^{19}F NMR (376 MHz, Chloroform-d) δ -63.93. HRMS (ESI-TOF) m/z [M + H^+] calculated for

$C_{25}H_{21}F_3NO_2S^+$: 456.1240, found: 456.1264.



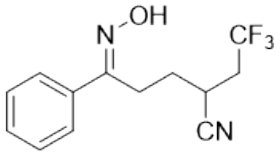
4-(benzo[d]thiazol-2-yl)-6,6,6-trifluoro-1-(4-isopropylphenyl)hexan-1-one (5f)

White solid, melting point: 104-107℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.61-3.54 (m, 1H), 2.88-2.76 (m, 4H), 2.58-2.45 (m, 1H), 2.32-2.18 (m, 2H), 1.11 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 198.31, 172.17, 154.74, 153.10, 134.71, 134.51, 128.25, 126.68, 126.22, 126.20 (q, *J* = 277.4 Hz), 125.24, 123.01, 121.74, 39.32 (q, *J* = 28.5 Hz), 38.01 (q, *J* = 2.4 Hz), 35.18, 34.23, 30.15, 23.62. ^{19}F NMR (376 MHz, Chloroform-d) δ -63.97. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{22}H_{22}F_3NOSNa^+$: 430.12244, found: 430.12460.



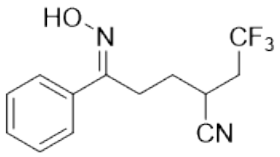
4-(benzo[d]thiazol-2-yl)-6,6,6-trichloro-1-phenylhexan-1-one (6a)

Yellow liquid, R_f = 0.13(PE:EA = 10:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, J_1 = 8.03, J_2 = 3.6 Hz,3H), 7.53 (dt, , *J* = 23.86, 7.5 Hz, 2H), 7.44-7.39 (m, 3H), 3.91-3.86 (m, 1H), 3.81 (dd, J_1 = 14.85, J_2 = 7.6 Hz, 1H), 3.21 (dd, J_1 = 2.70, J_2 = 14.9 Hz, 1H), 3.10-2.98 (m, 1H), 2.51-2.38 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 198.67, 173.02, 153.07, 136.66, 134.88, 133.17, 128.59, 127.97, 126.17, 125.17, 122.99, 121.70, 98.29, 59.50, 41.91, 35.42, 31.28. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{19}H_{17}Cl_3NOSH^+$: 412.00909, found: 412.00919.



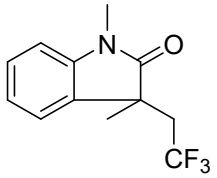
(E)-5-(hydroxyimino)-5-phenyl-2-(2,2,2-trifluoroethyl)pentanenitrile (7a)

Colourless liquid, R_f = 0.17(PE:EA = 5:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.91 (s,1H), 7.64-7.62 (m, 2H), 7.45 (t, *J* = 2.0 Hz, 2H), 3.08-3.05 (m, 2H), 2.99-2.93 (m, 1H), 2.63-2.52 (m, 1H), 2.47-2.37 (m, 1H), 2.03 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 157.34, 134.51, 129.86, 128.93, 126.13, 125.03 (d, *J* = 277.3 Hz), 119.32, 36.21 (q, *J* = 30.0 Hz), 28.67, 25.58 (q, *J* = 3.0 Hz), 23.38.^{19}F NMR (376 MHz, Chloroform-d) δ -64.84. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{13}H_{14}IF_3NO_2^+$: 271.1053, found: 271.1042.



(Z)-5-(hydroxyimino)-5-phenyl-2-(2,2,2-trifluoroethyl)pentanenitrile (7b)

Colourless liquid, R_f = 0.28(PE:EA = 5:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s,1H), 7.46-7.41 (m, 4H), 3.10-3.04 (m, 1H), 2.88-2.74 (m, 2H), 2.60-2.505 (m, 1H), 2.40-2.30 (m, 1H), 2.05-1.908 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.12, 132.56, 129.39, 128.52, 127.66, 125.01 (q, *J* = 277.3 Hz) , 119.28, 36.43 (q, *J* = 30.0Hz) , 32.39, 28.65, 24.91 (q, *J* = 2.8Hz).^{19}F NMR (376 MHz, Chloroform-d) δ -64.83. HRMS (ESI-TOF) m/z [M + Na^+] calculated for $C_{13}H_{14}IF_3NO_2^+$: 271.1053, found: 271.1042.



1,2,3-trimethyl-3-(trifluoromethyl)indoline (8a)

Colourless liquid, R_f = 0.25(PE:EA = 10:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (td, J_1 = 7.7Hz, J_2 = 1.0 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 3.25 (s, 3H), 2.83 (dq, *J* = 15.2, 10.0 Hz, 1H), 2.67 (dq, *J* = 15.2, 10.0 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 178.46,

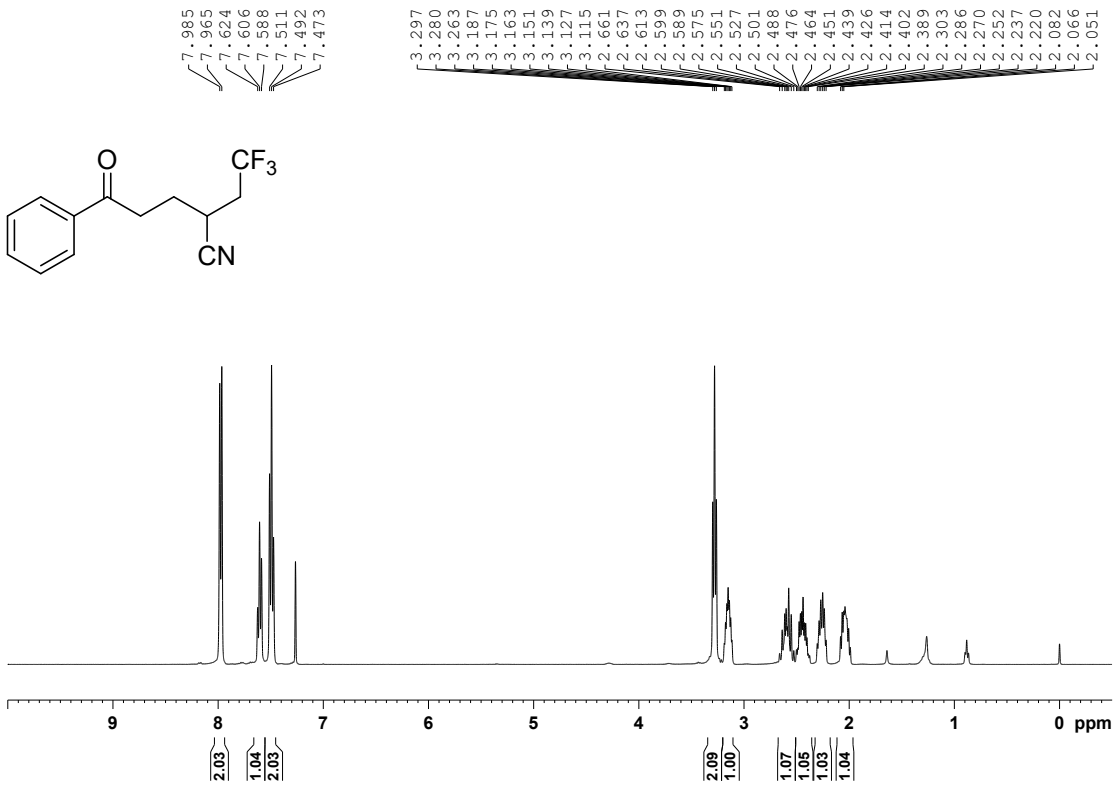
142.88, 131.04, 128.51, 125.26 (q, J = 278.2 Hz), 123.54, 122.62, 108.42, 44.37 (q, J = 2.1 Hz), 40.65 (q, J = 28.3 Hz), 26.38, 24.95.^{19}F NMR (376 MHz, Chloroform-d) δ -61.96. HRMS (ESI-TOF) m/z [M + H^+] calculated for $C_{12}H_{12}F_3NOH^+$: 244.0943, found: 244.093

References

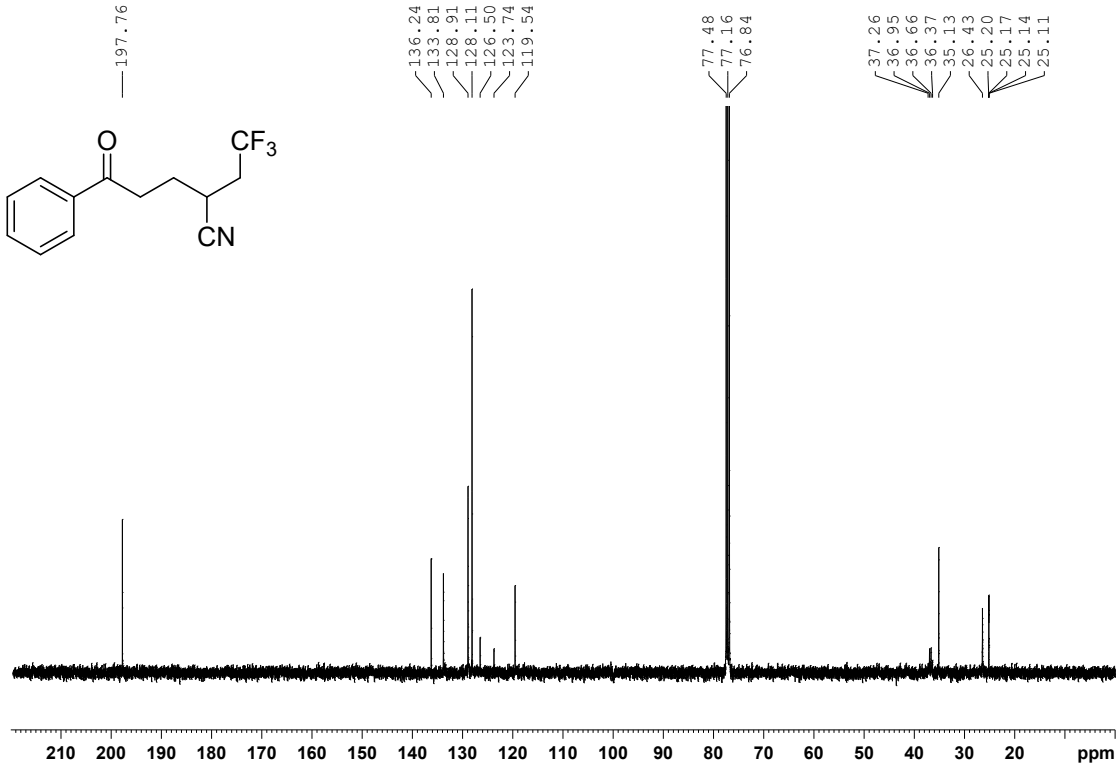
1. Zhang, Y.; Yin, Z.; Wang, H.; Wu, X.-F., Iron-catalyzed carbonylative cyclization of γ, δ-unsaturated aromatic oxime esters to functionalized pyrrolines. *Chem. Commun.* 2020, **56,** 7045-7048.
2. Kwon, Y.; Wang, Q., Copper-catalyzed 1, 2-aminocyanation of unactivated alkenes via cyano migration. *Org. Lett.* 2020, **22**, 4141-4145.
3. Tian, T.; Wang, X.; Lv, L.; Li, Z., Iron-catalyzed acylation-functionalization of unactivated alkenes with aldehydes. *Chem. Commun.* 2020, **56**, 14637-14640.

Copies of [1] H, [13]C and [19]F NMR Spectra for products

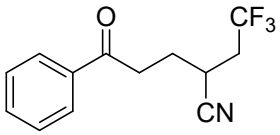
(2a) [1]H NMR (400 MHz, CDCl3)



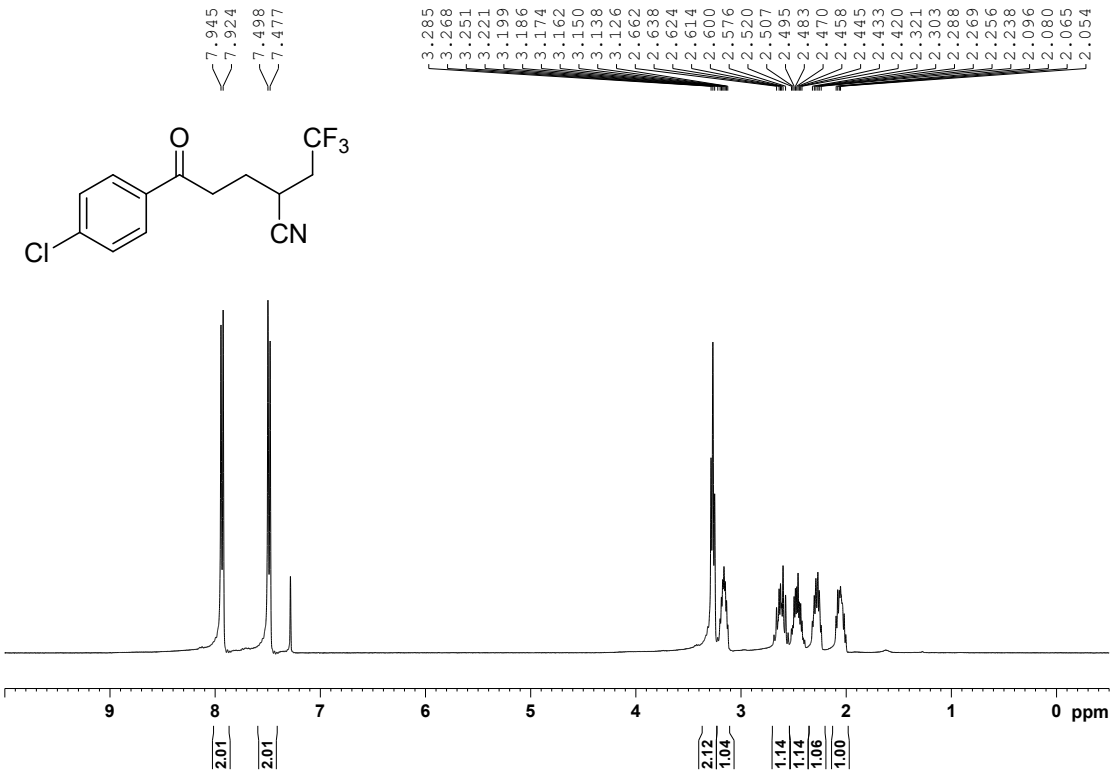
(2a) [13]C NMR (101 MHz, CDCl3)



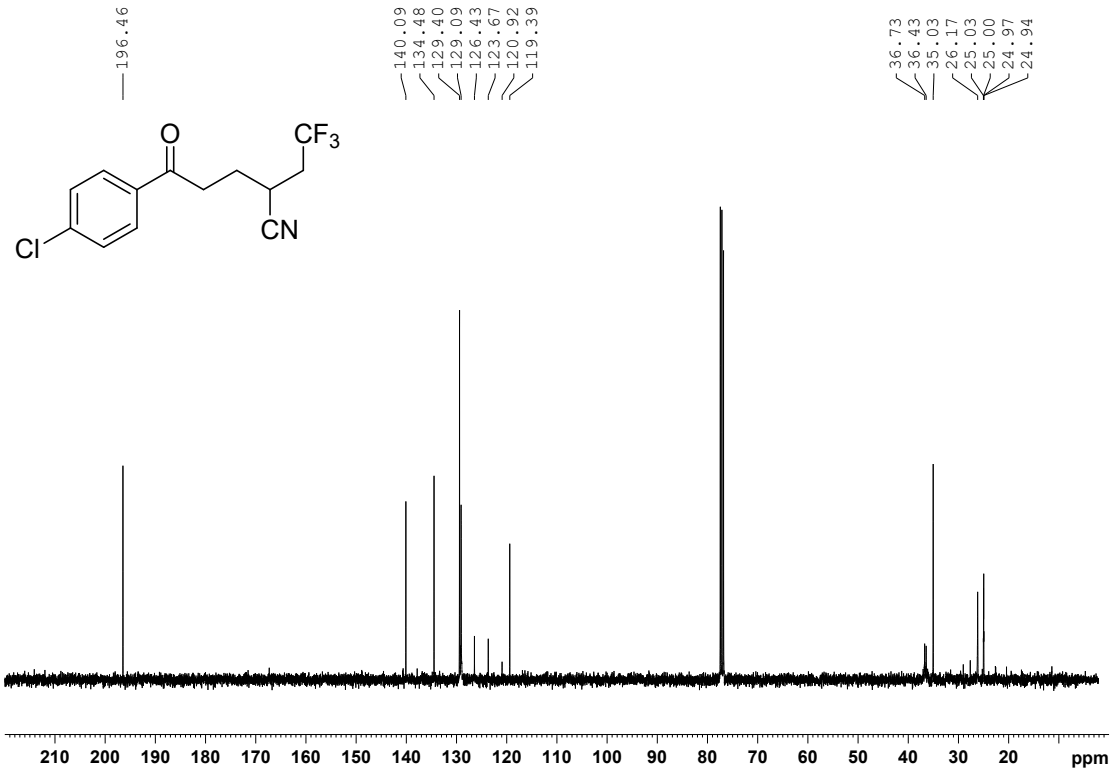
(2a) ^{19}F NMR (376 MHz, CDCl3)



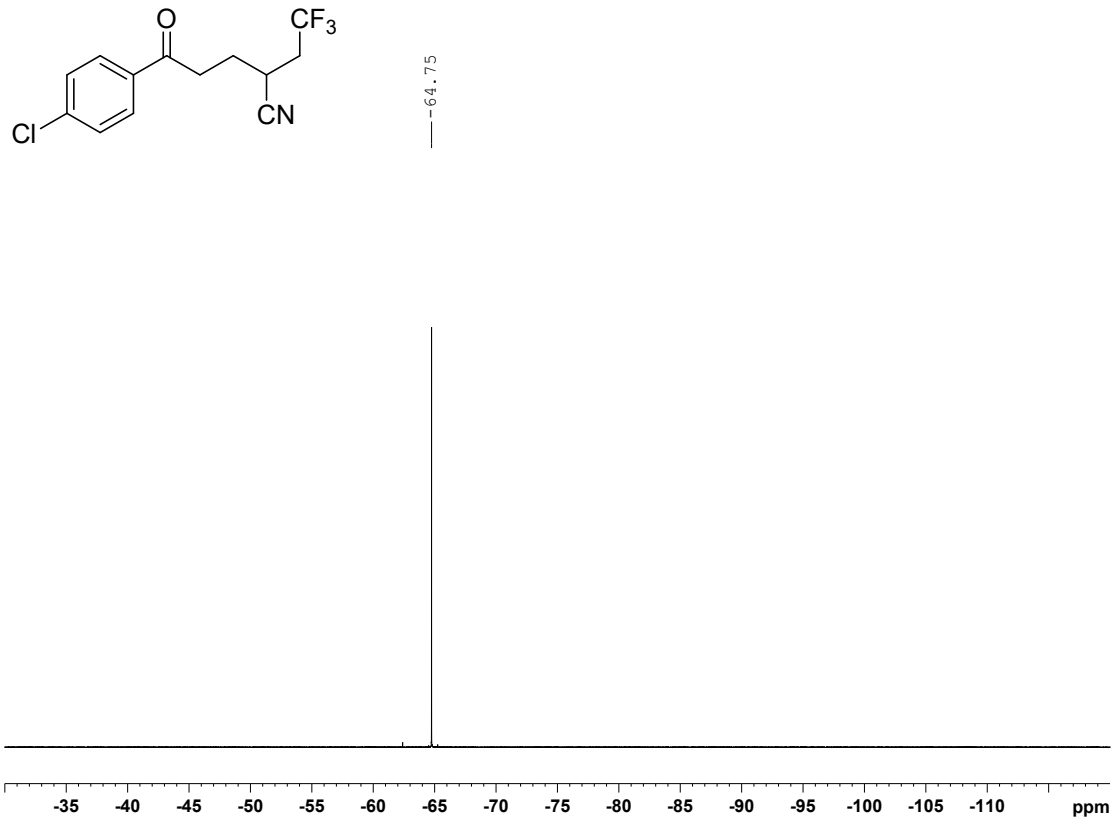
(2b) ^{1}H NMR (400 MHz, CDCl3)



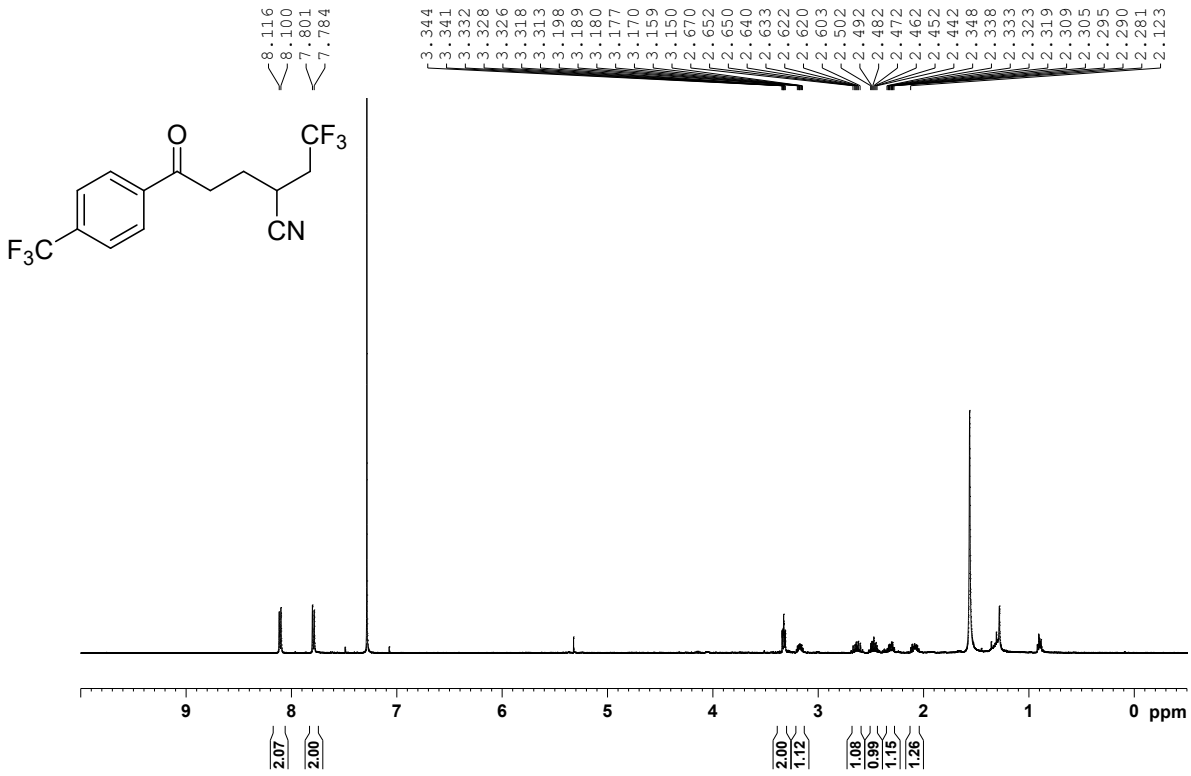
(2b) ^{13}C NMR (101 MHz, CDCl3)



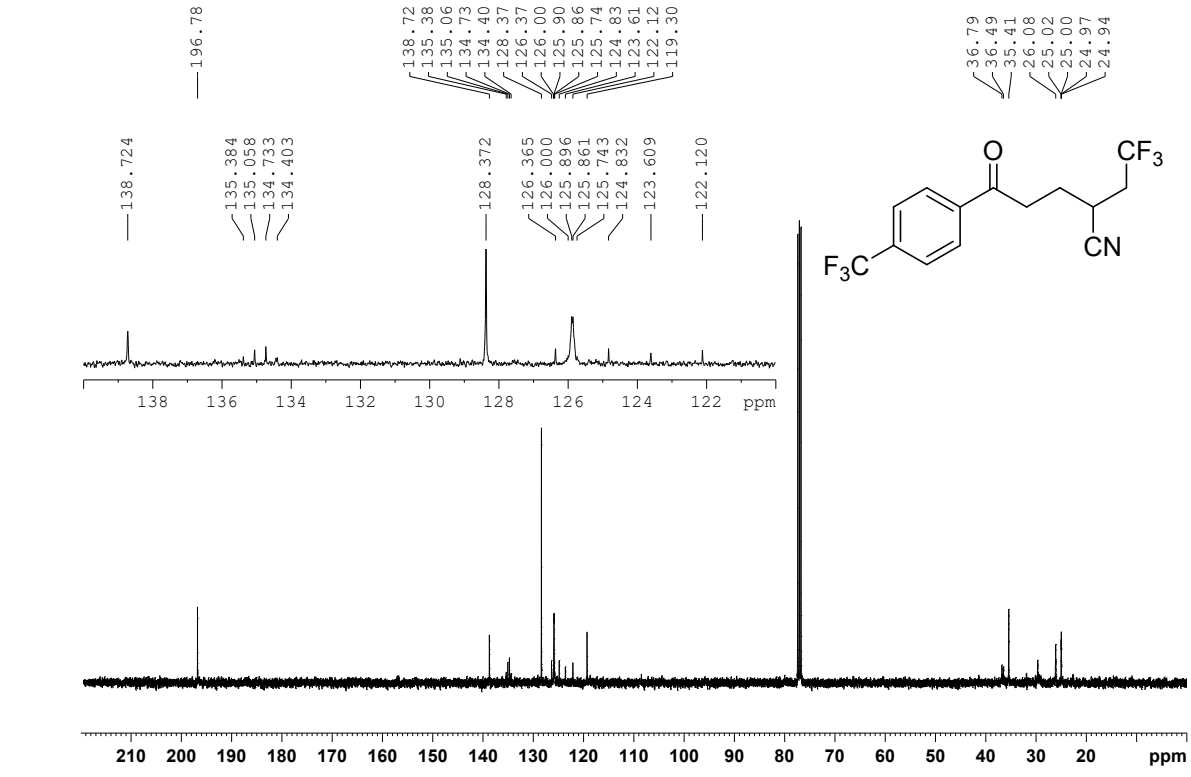
(2b) ^{19}F NMR (376 MHz, CDCl3)



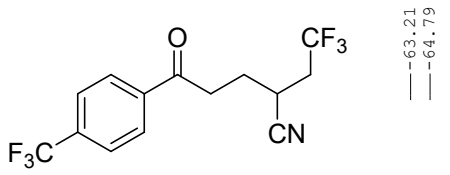
(2c) ^{1}H NMR (500 MHz, CDCl3)

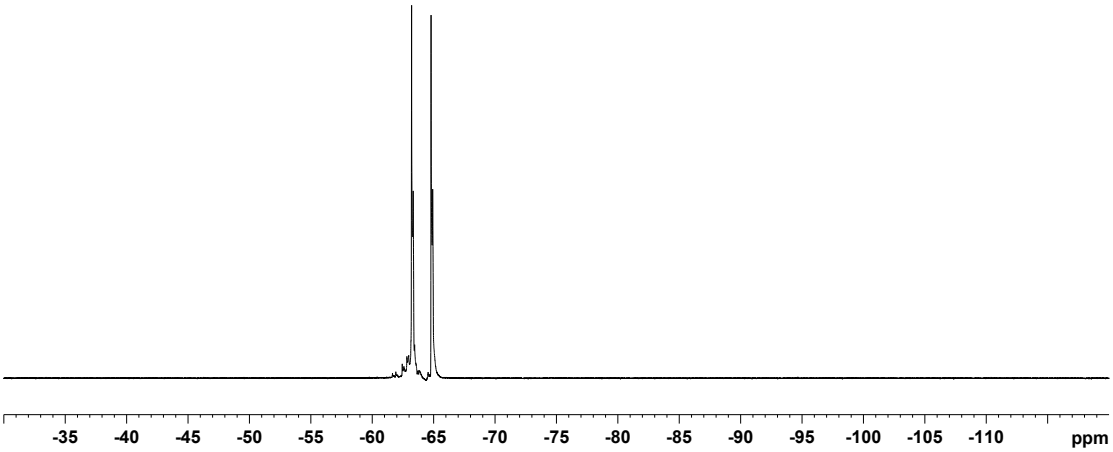


(2c) ^{13}C NMR (101 MHz, CDCl3)

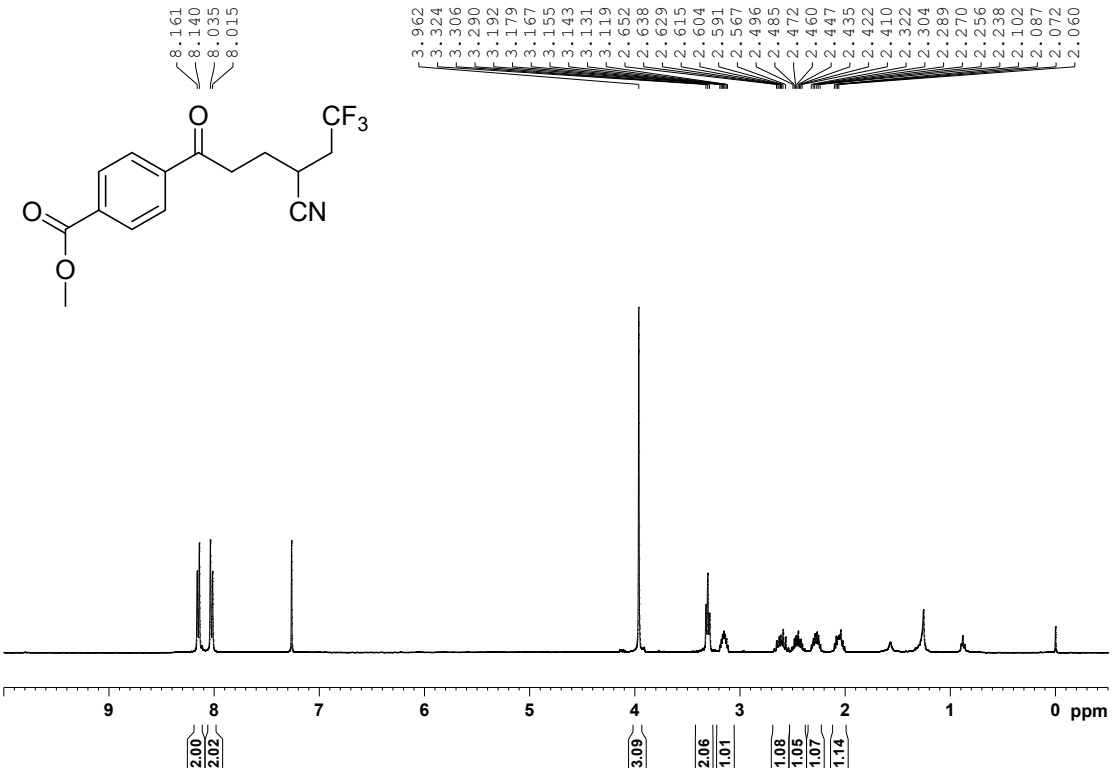


(2c) ^{19}F NMR (376 MHz, CDCl3)

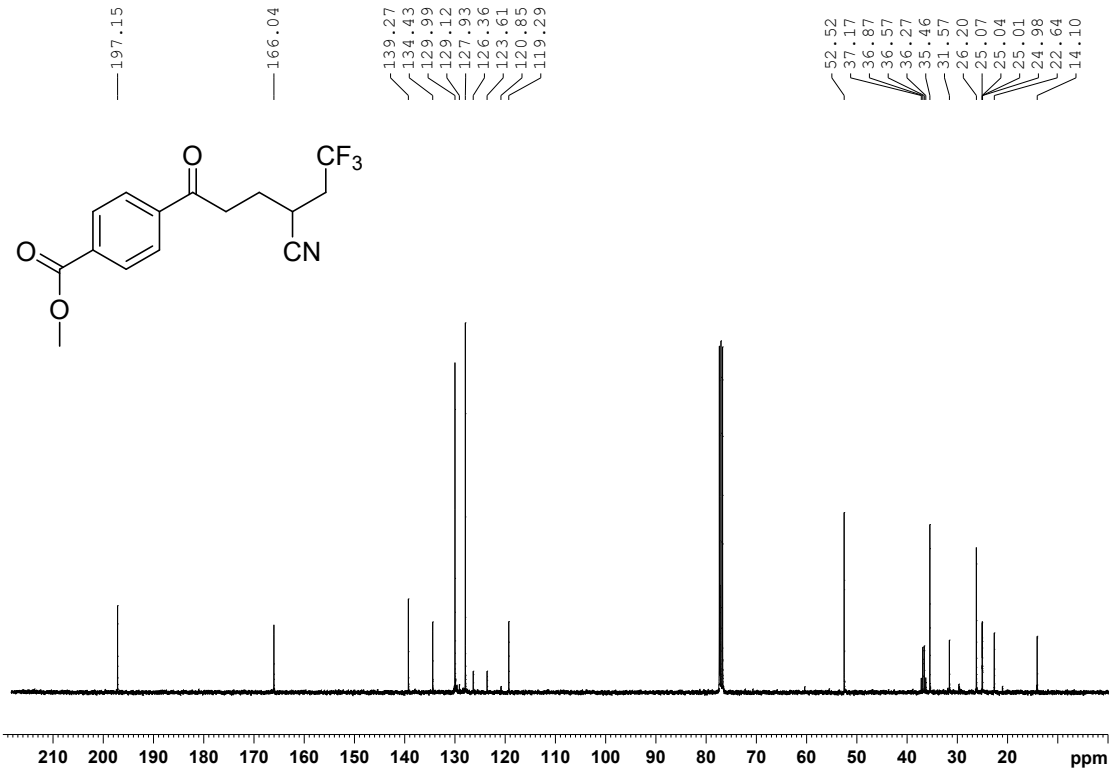




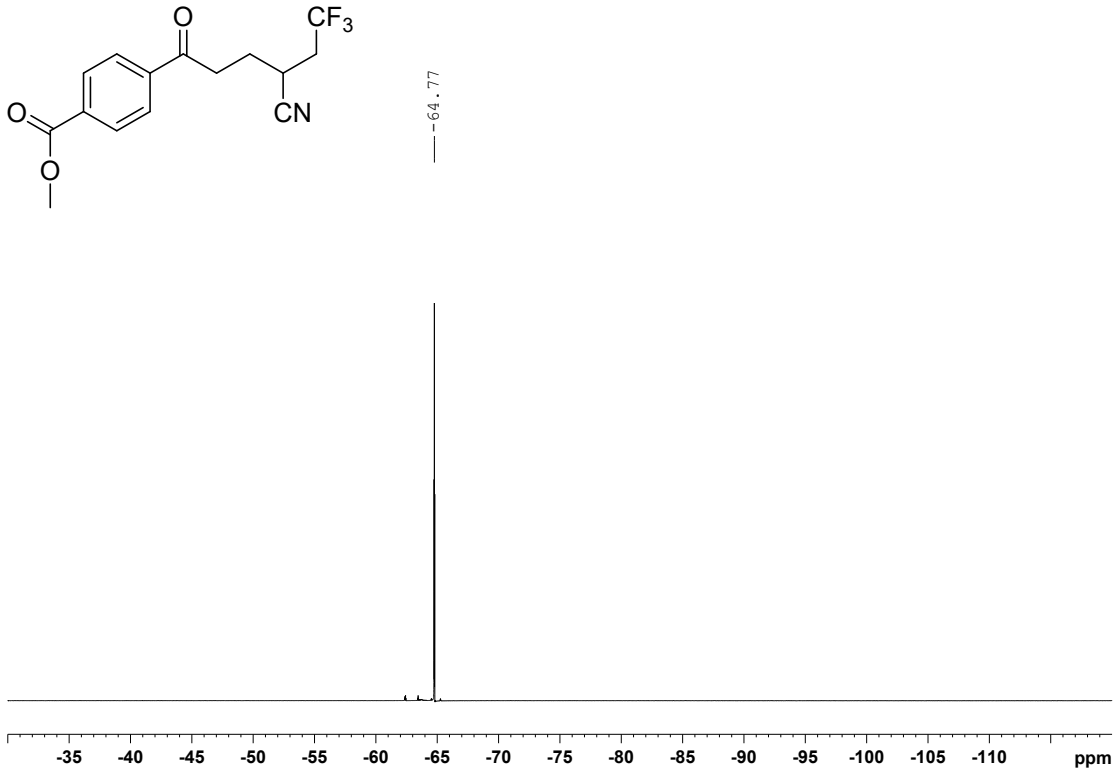
(2d) ^{1}H NMR (400 MHz, CDCl3)



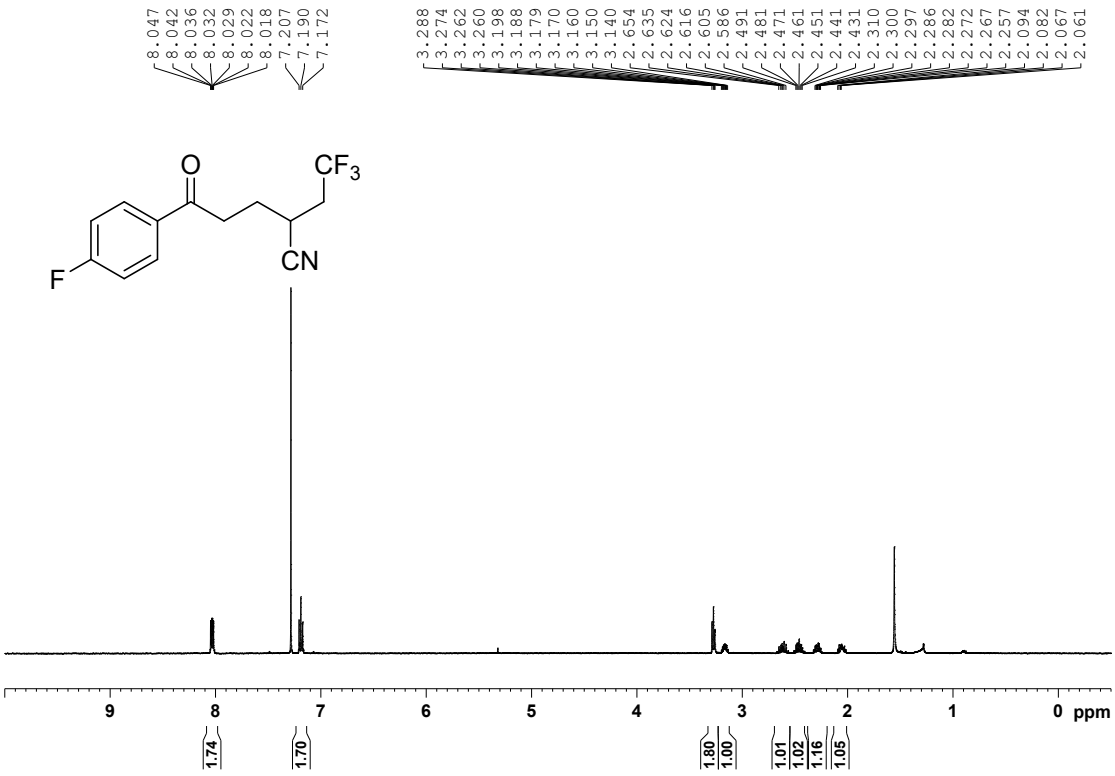
(2d) ^{13}C NMR (101 MHz, CDCl3)



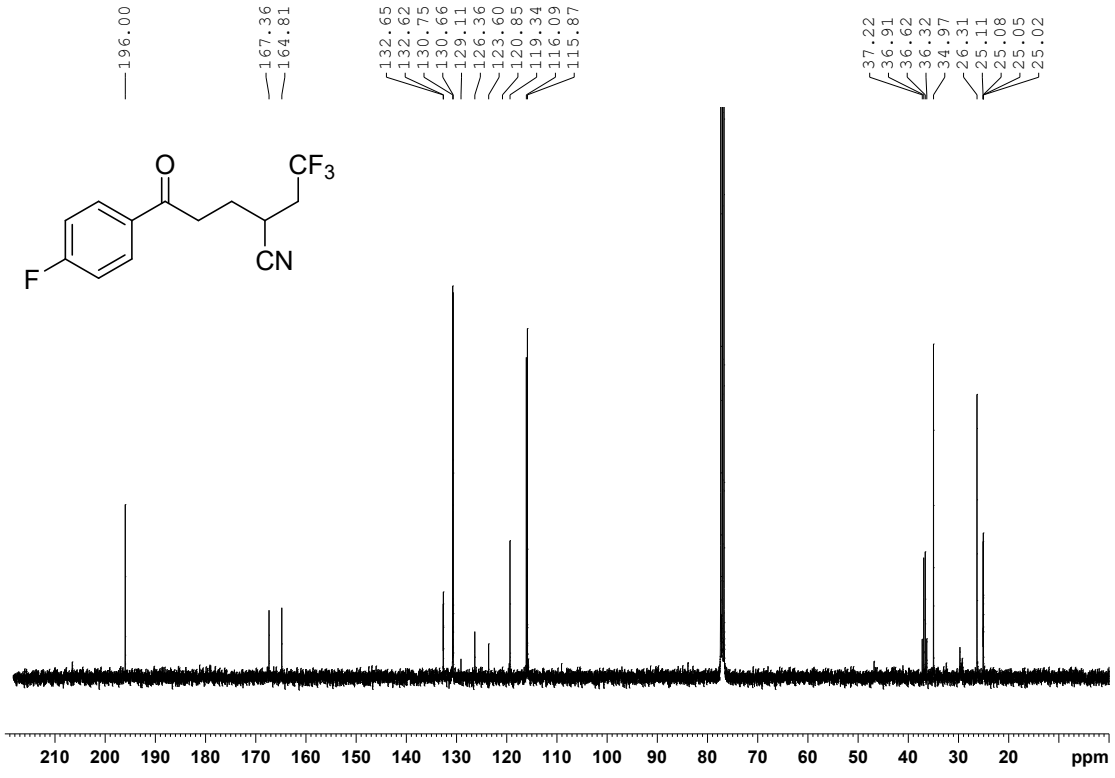
(2d) ^{19}F NMR (376 MHz, CDCl3)



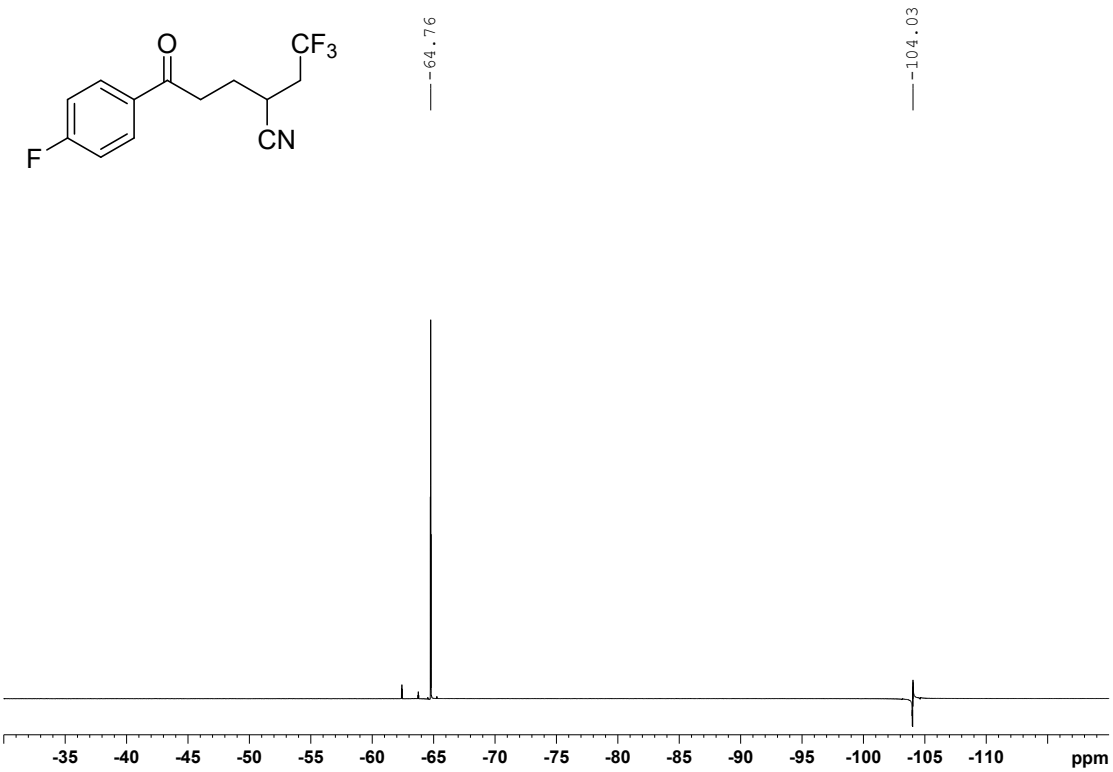
(2e) ^{1}H NMR (400 MHz, CDCl3)



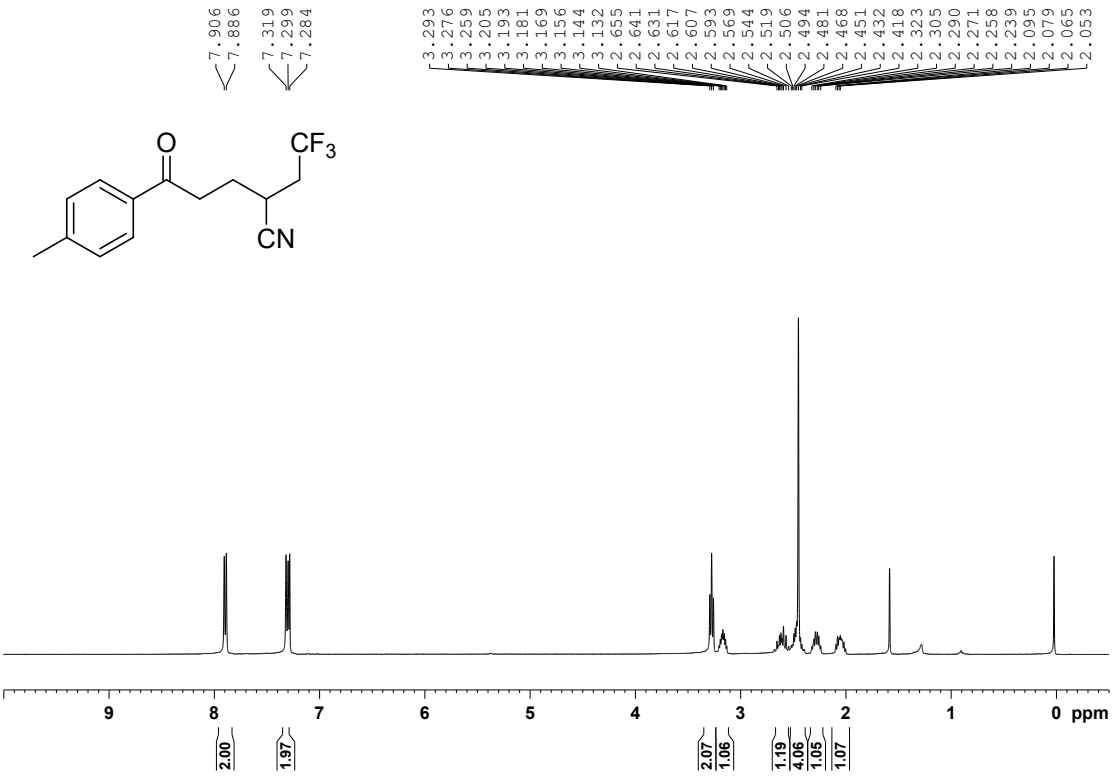
(2e) ^{13}C NMR (101 MHz, CDCl3)



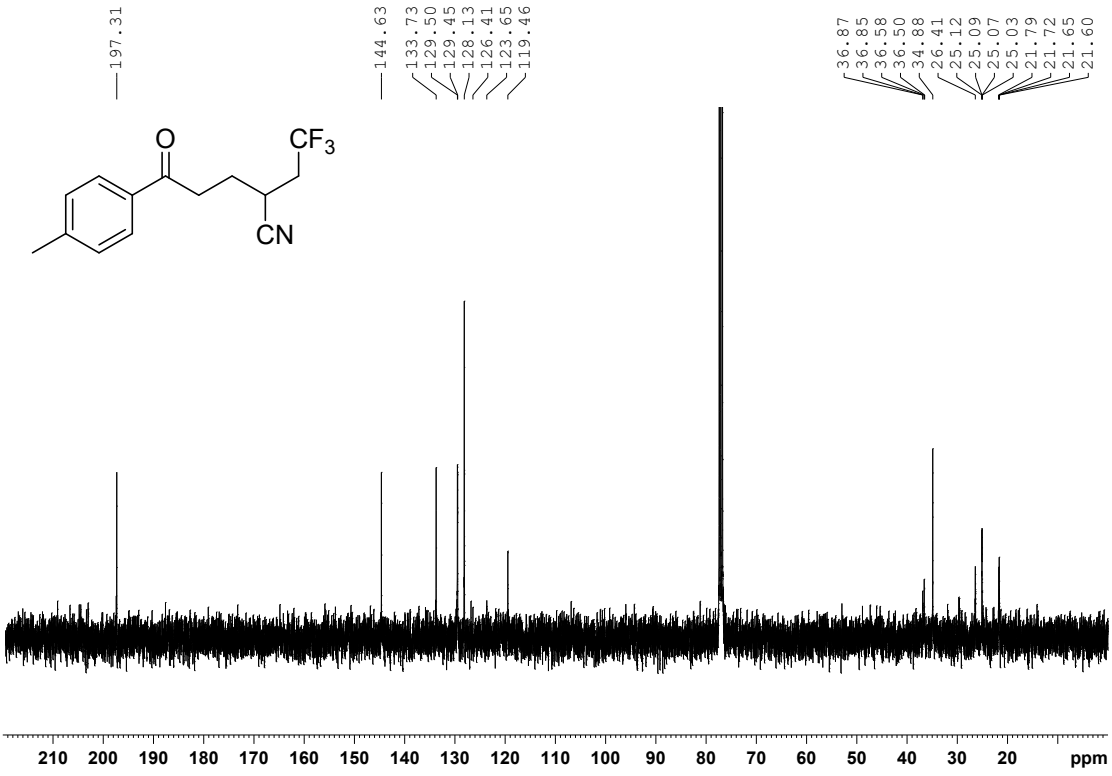
(2e) ^{19}F NMR (376 MHz, CDCl3)



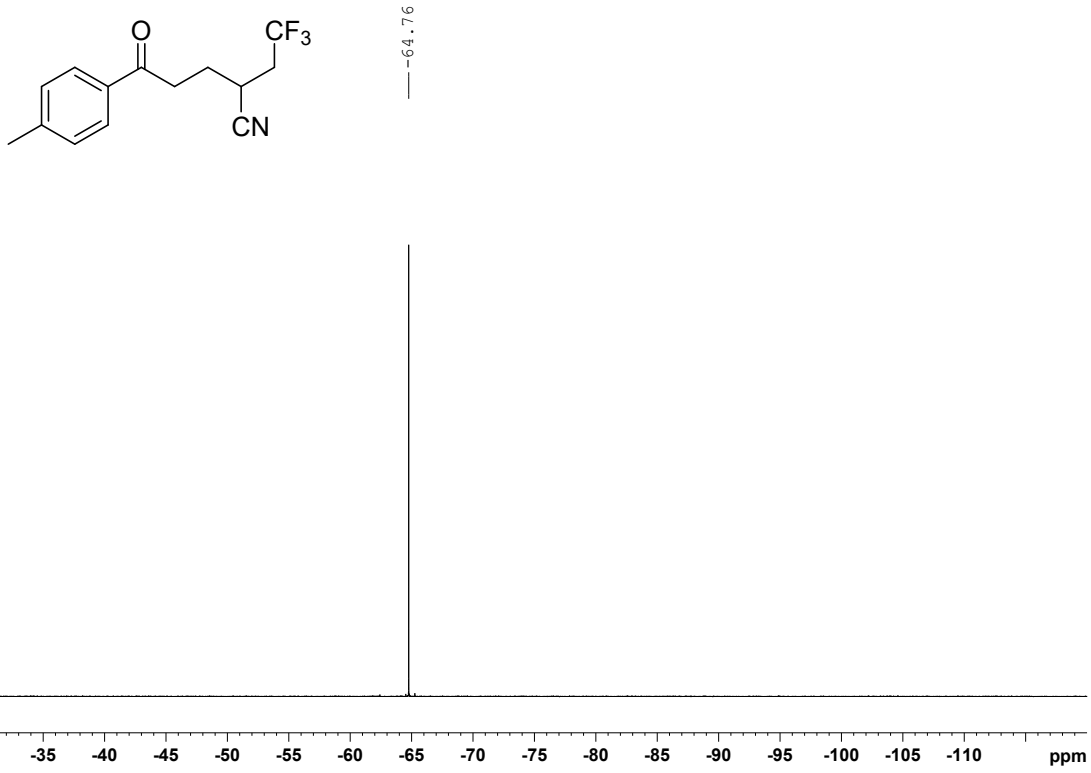
(2f)^{1}H NMR (400 MHz, CDCl3)



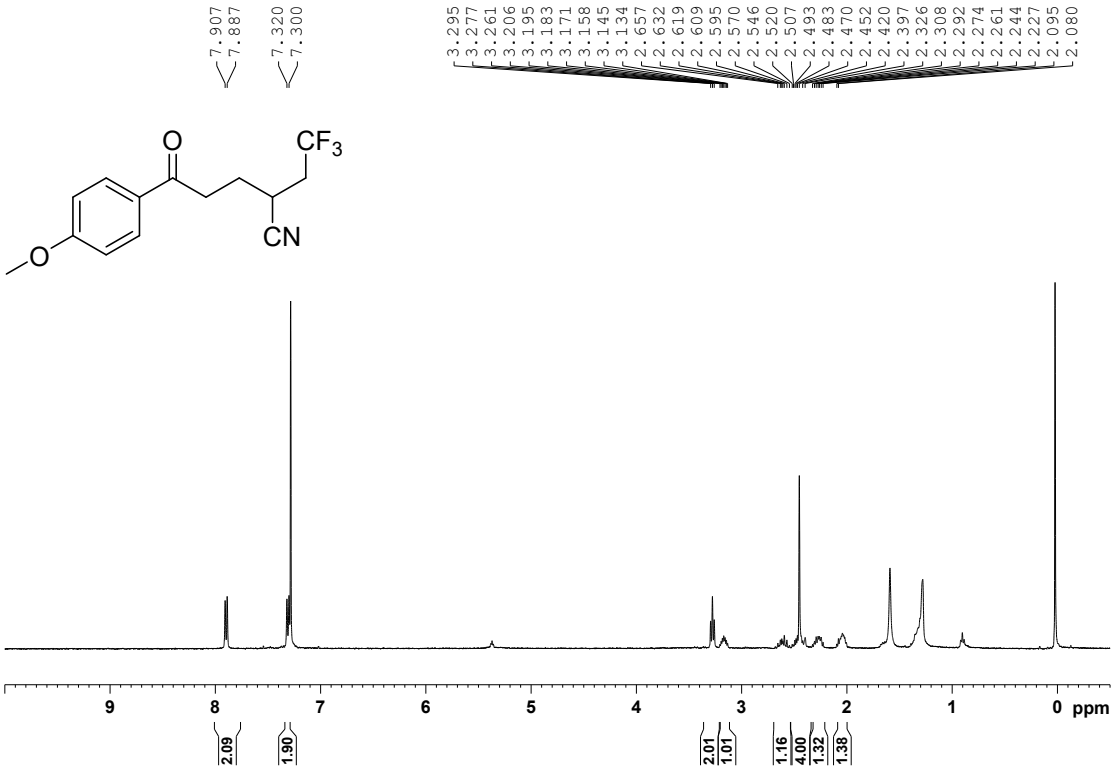
(2f) ^{13}C NMR (101 MHz, CDCl3)



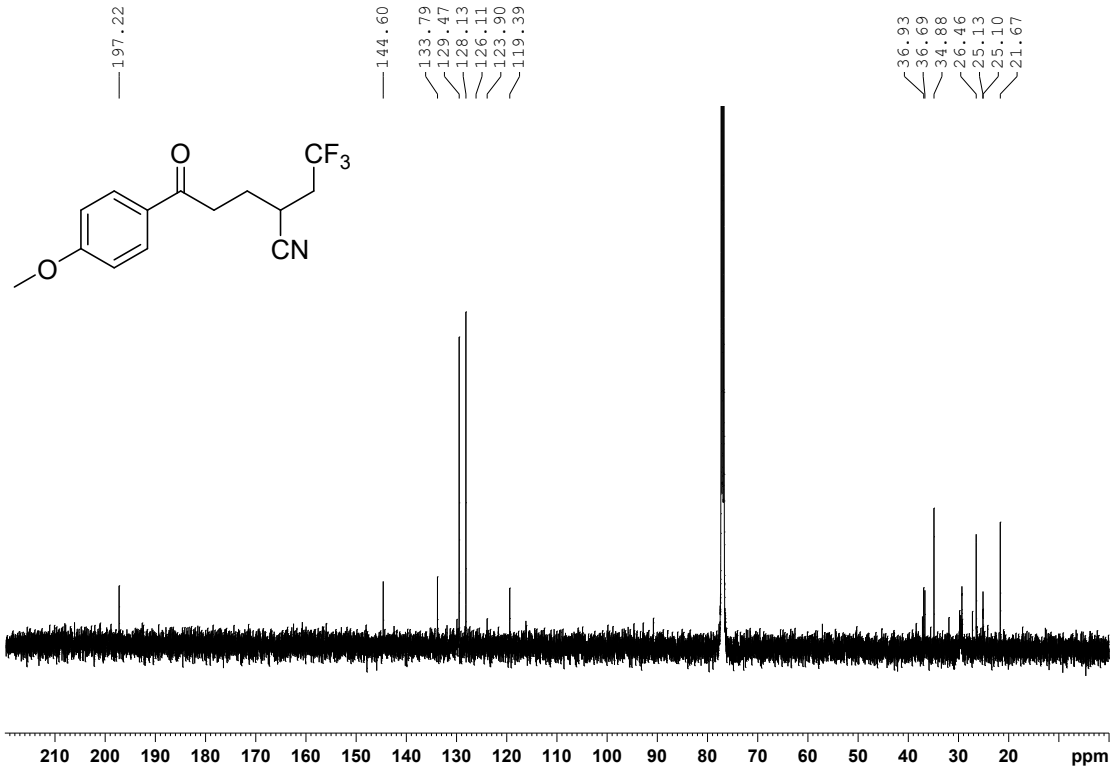
(2f) ^{19}F NMR (376 MHz, CDCl3)



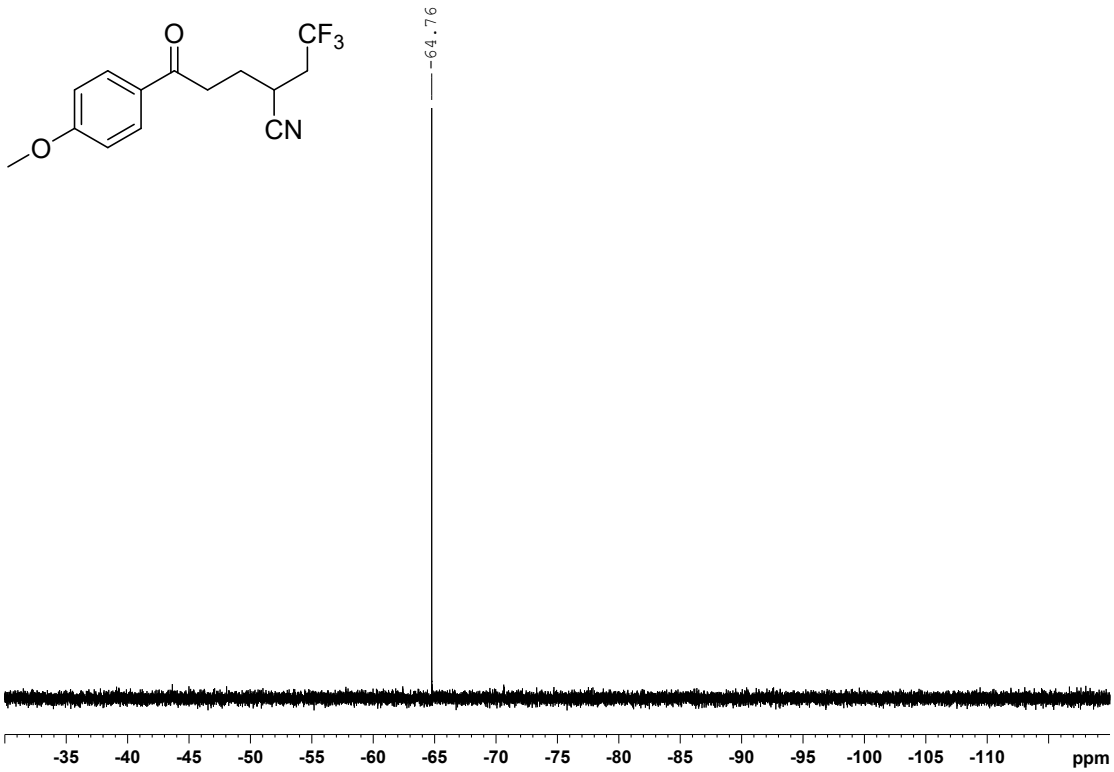
(2g) ^{1}H NMR (400 MHz, CDCl3)



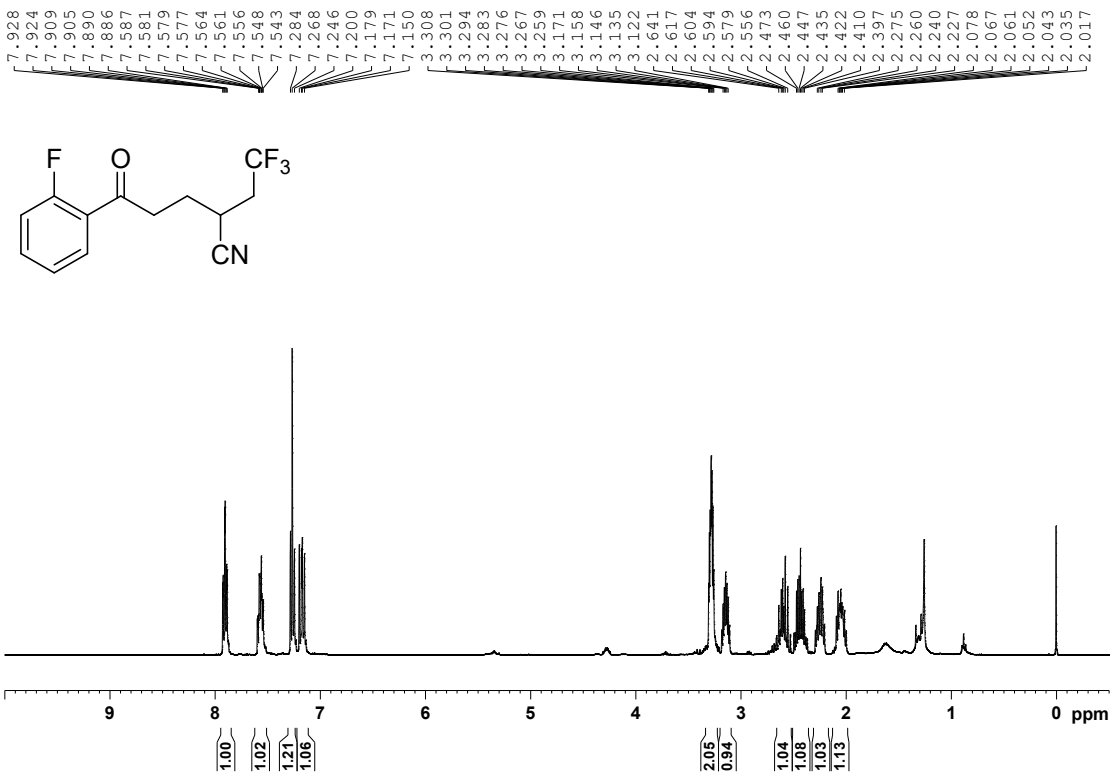
(2g) ^{13}C NMR (101 MHz, CDCl3)



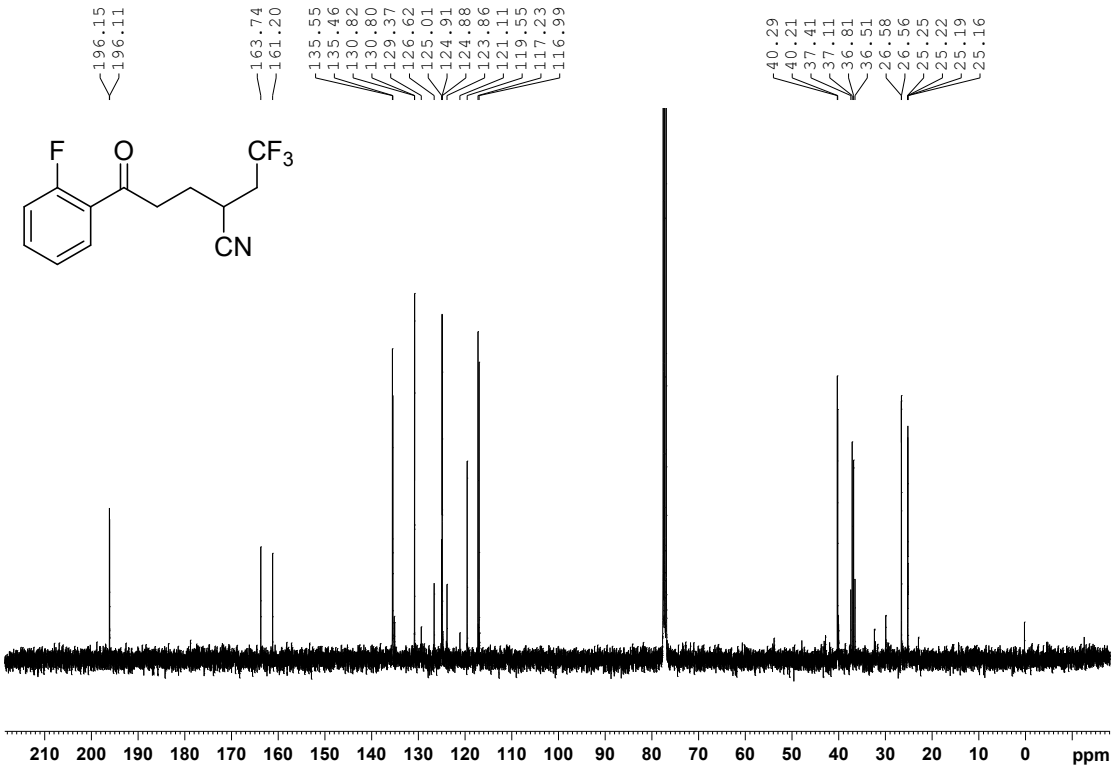
(2g) ^{19}F NMR (376 MHz, CDCl3)



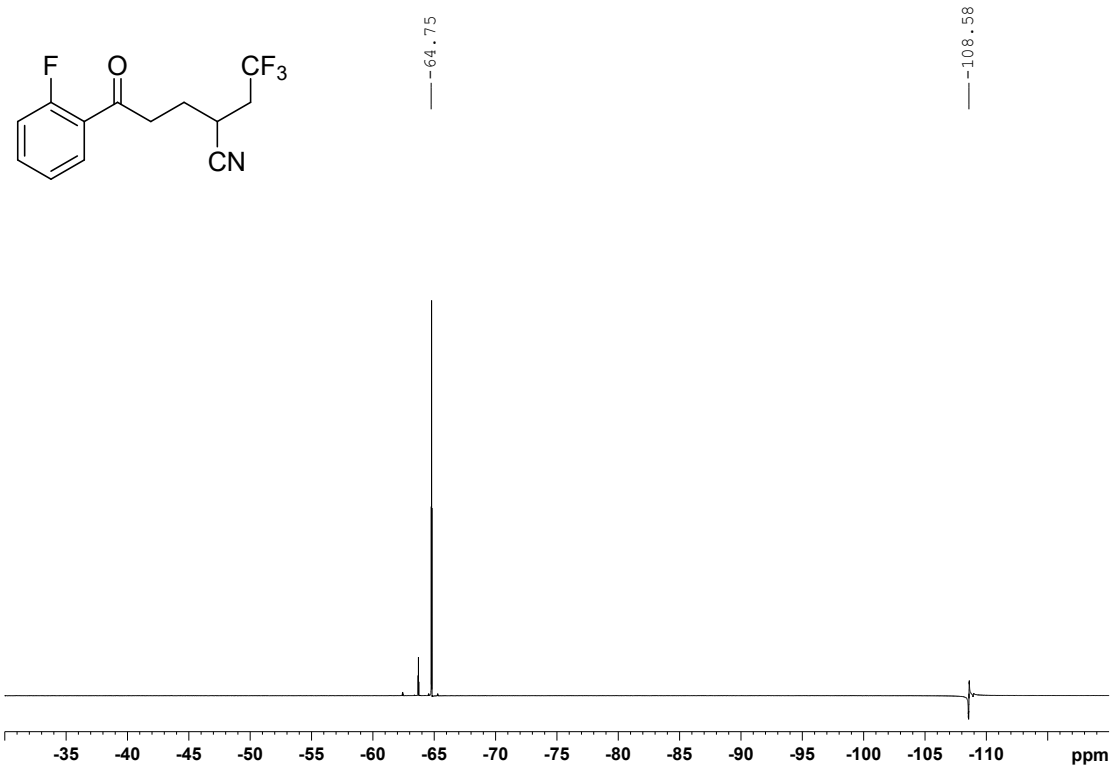
(2h) ^{1}H NMR (400 MHz, CDCl3)



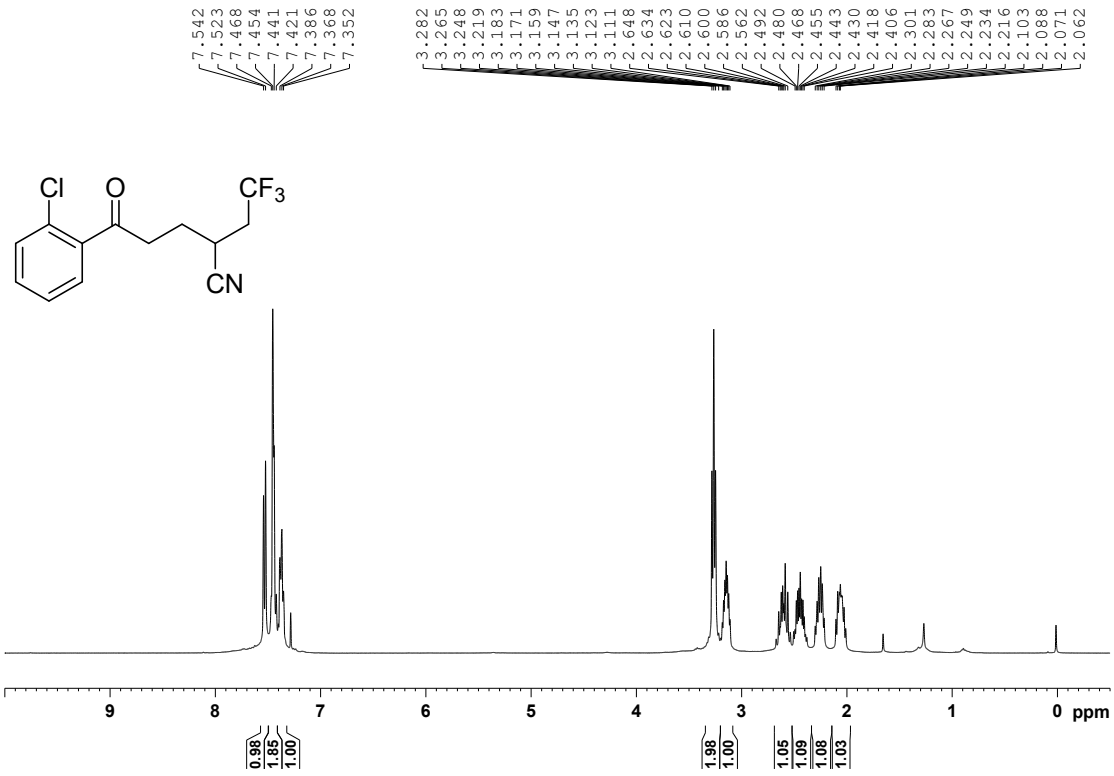
(2h) ^{13}C NMR (101 MHz, CDCl3)



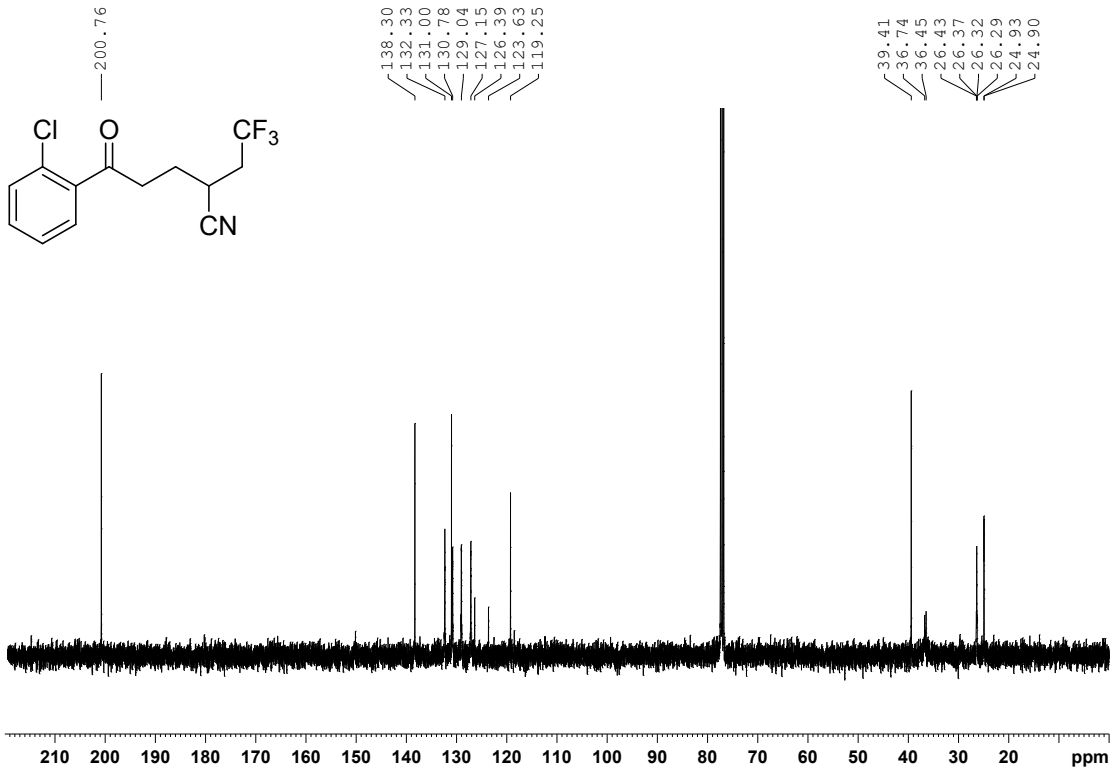
(2h) ^{19}F NMR (376 MHz, CDCl3)



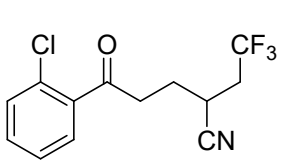
(2i)^{1}H NMR (400 MHz, CDCl3)



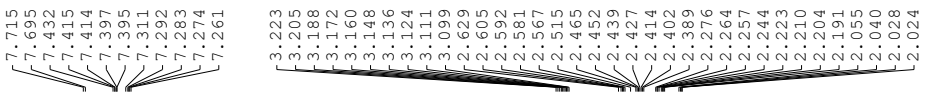
(2i) ^{13}C NMR (101 MHz, CDCl3)

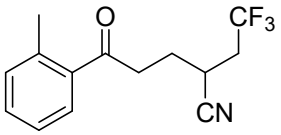


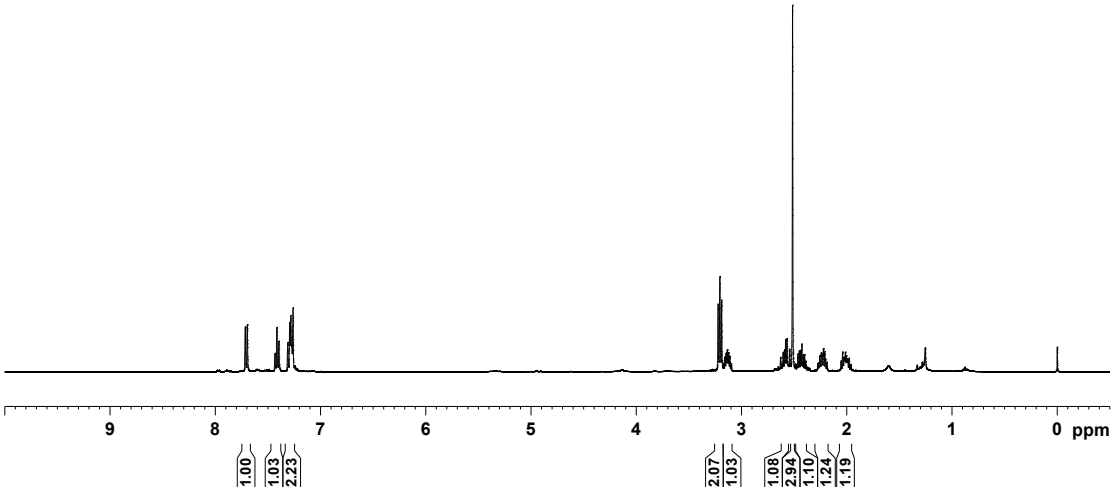
(2i) ^{19}F NMR (376 MHz, CDCl3)



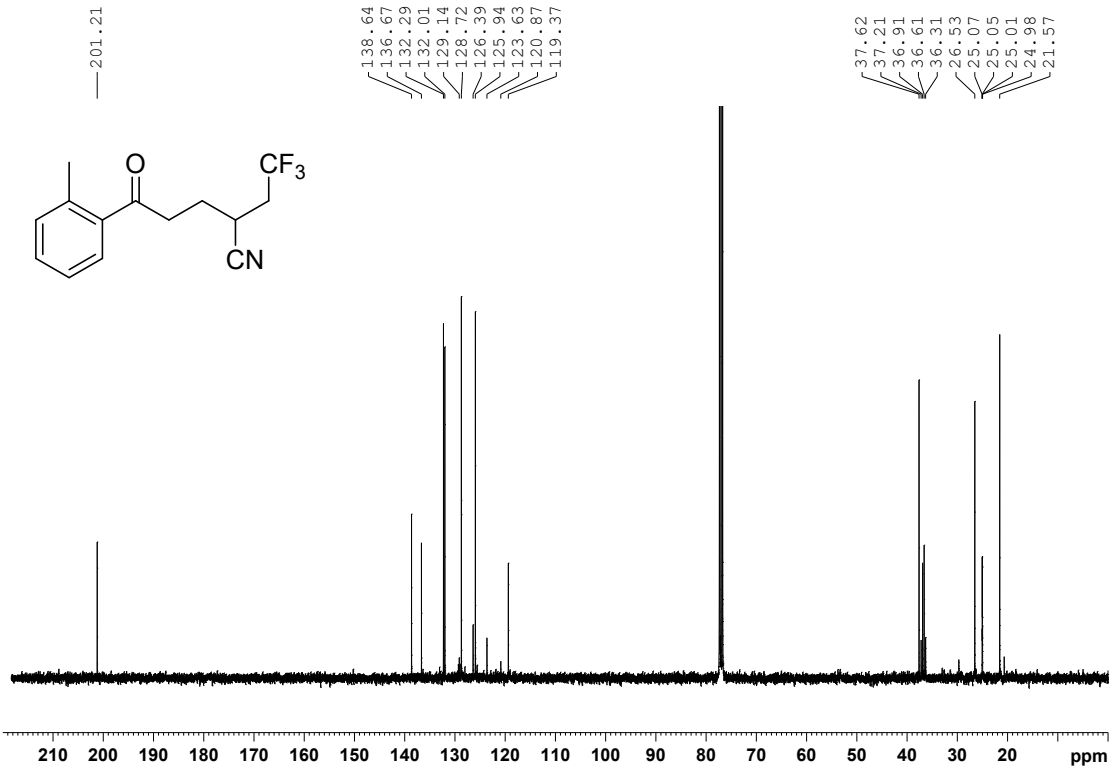
(2j) ^{1}H NMR (400 MHz, CDCl3)



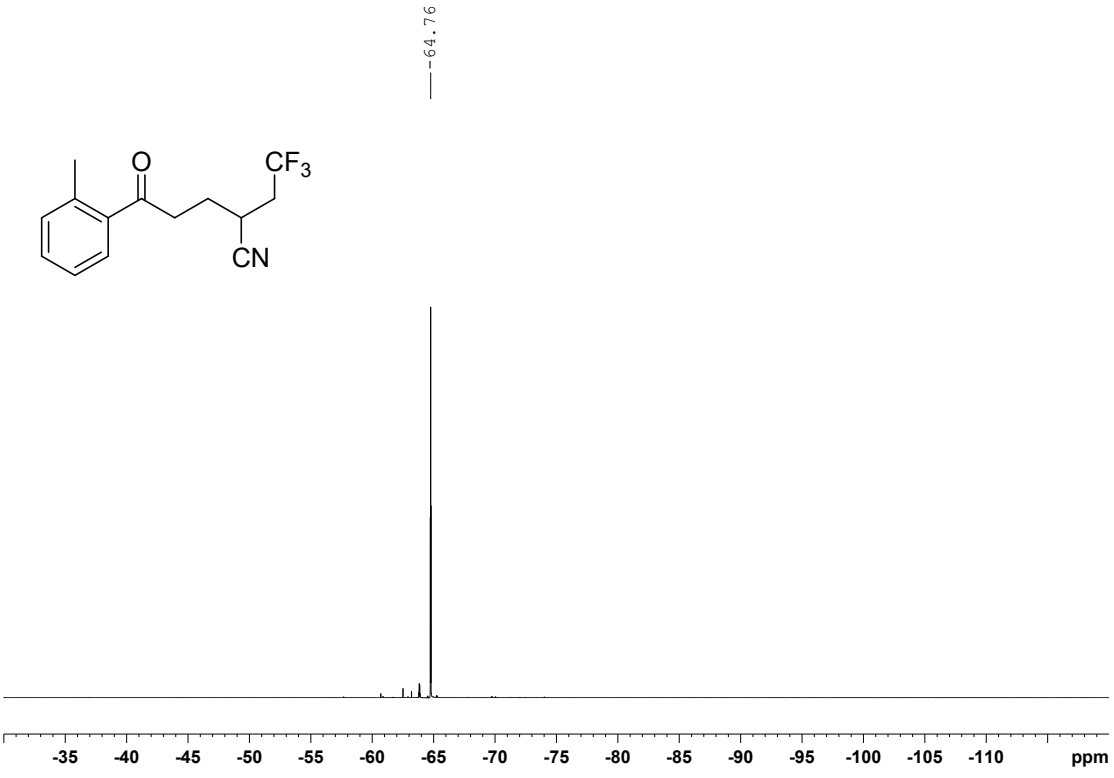




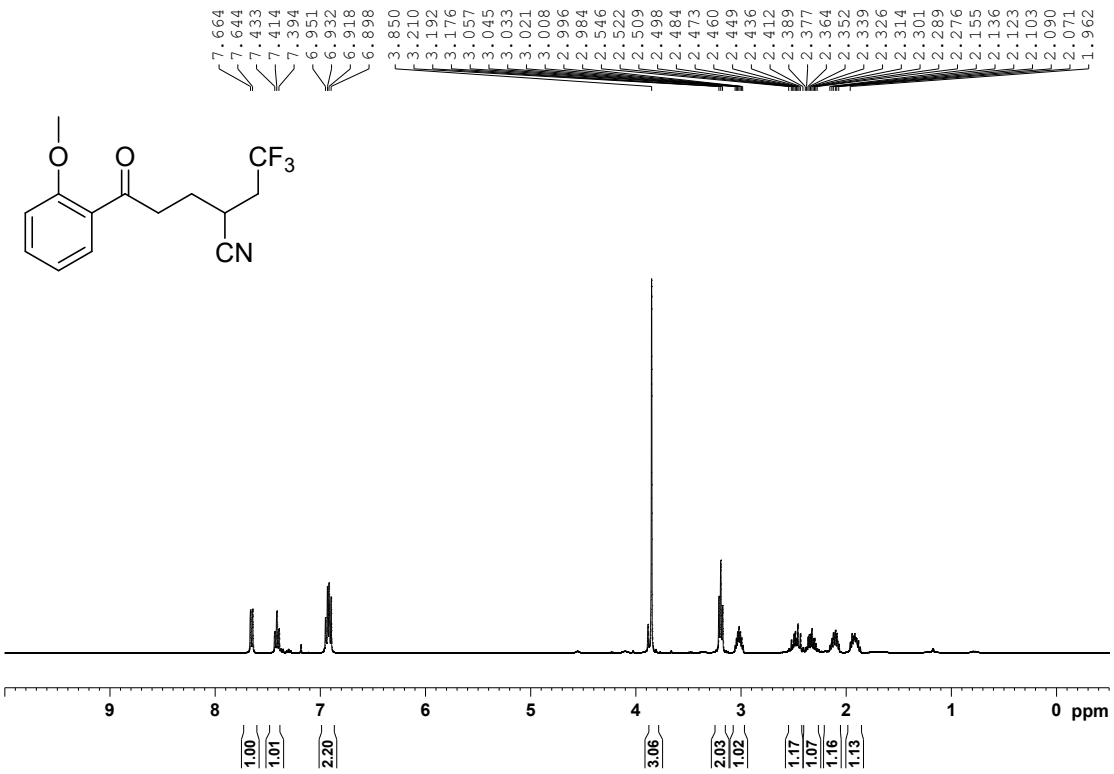
(2j) ^{13}C NMR (101 MHz, CDCl3)



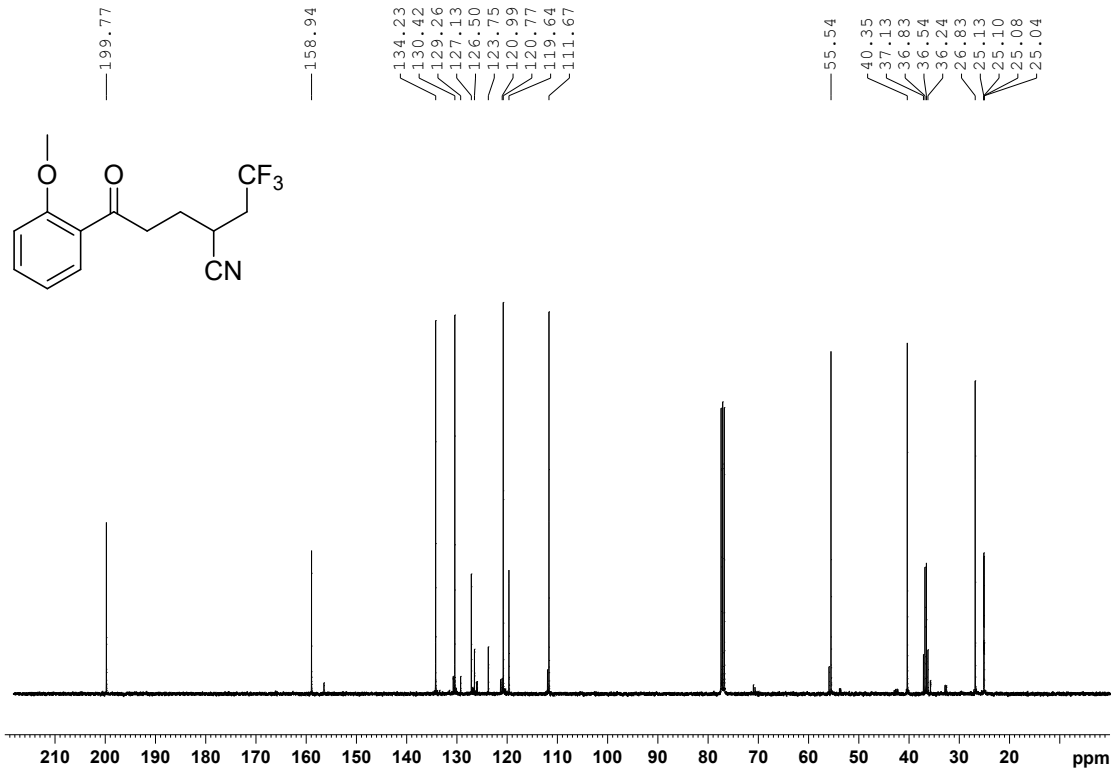
(2j) ^{19}F NMR (376 MHz, CDCl3)



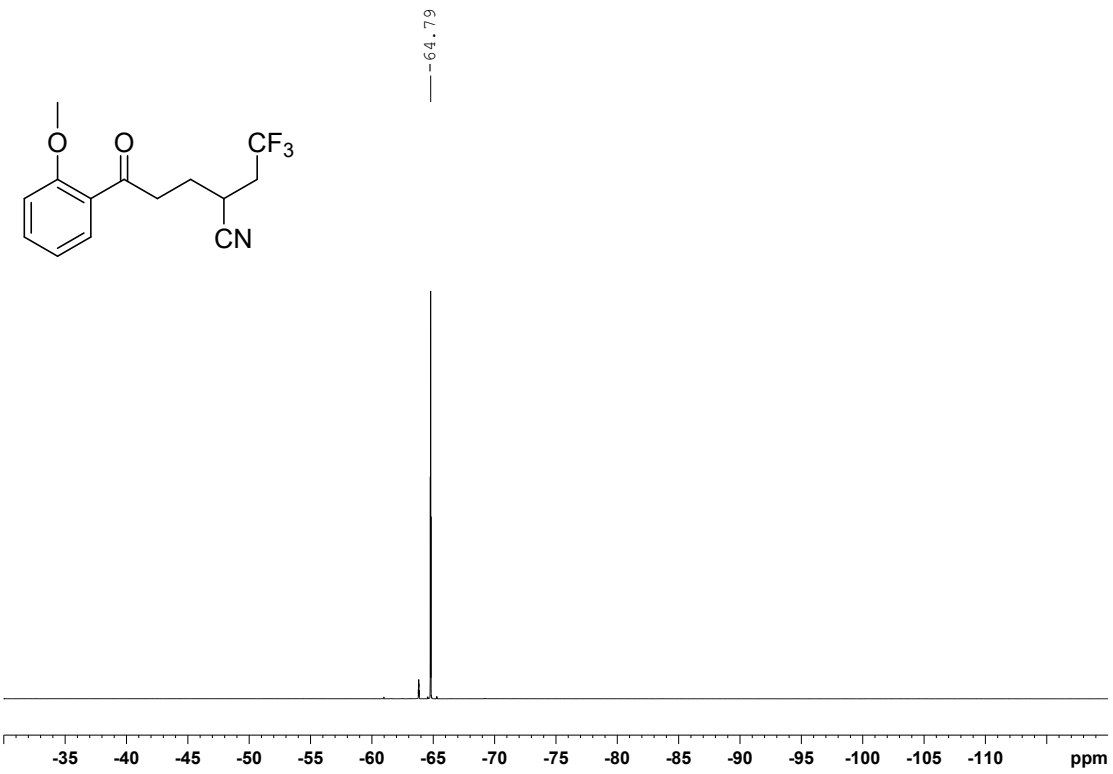
(2k) ^{1}H NMR (400 MHz, CDCl3)



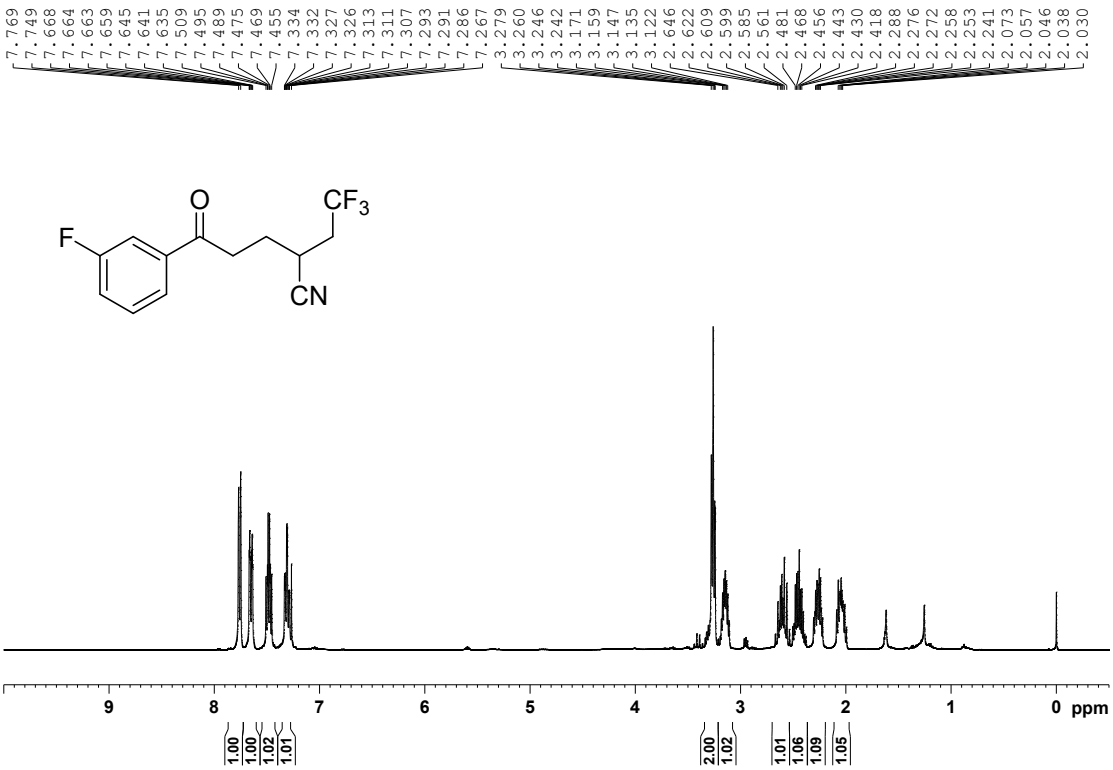
(2k) ^{13}C NMR (101 MHz, CDCl3)



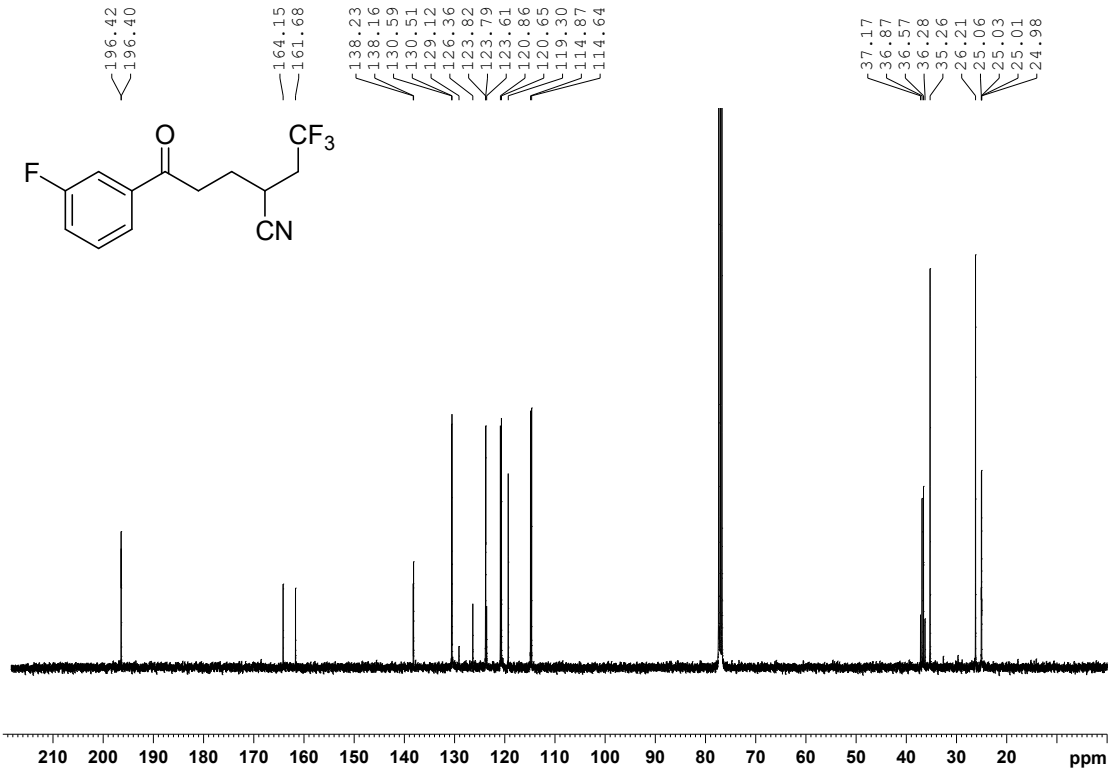
(2k) ^{19}F NMR (376 MHz, CDCl3)



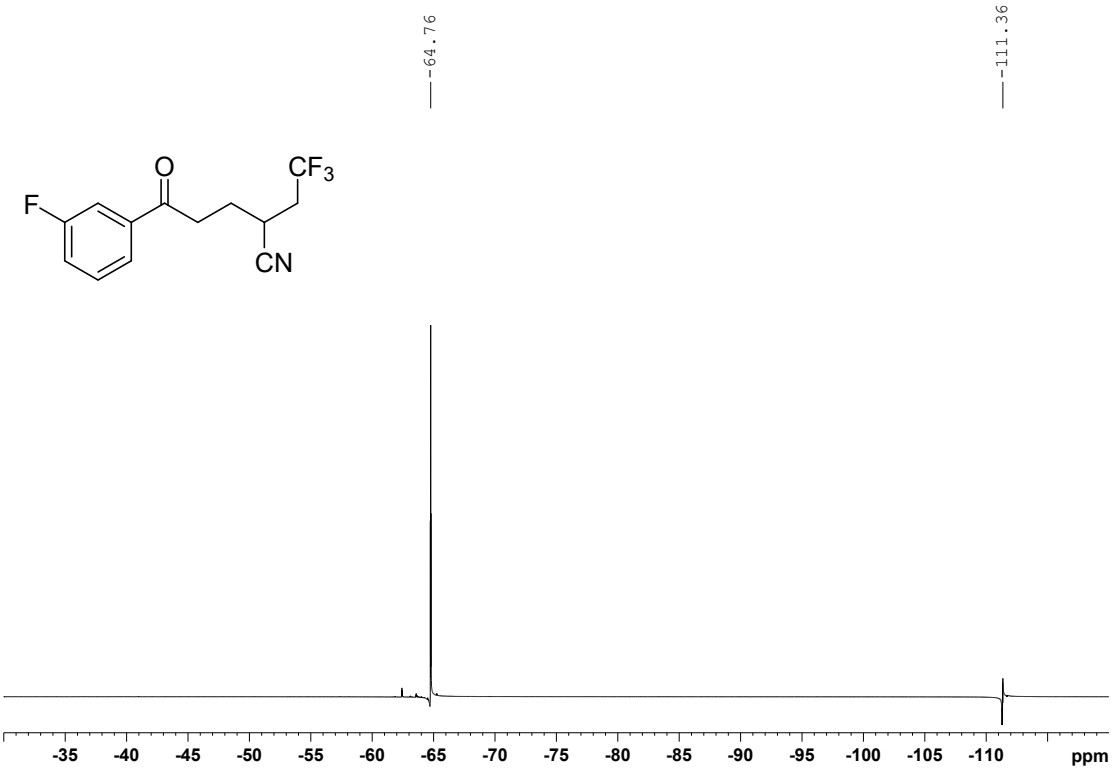
(2l) ^{1}H NMR (400 MHz, CDCl3)



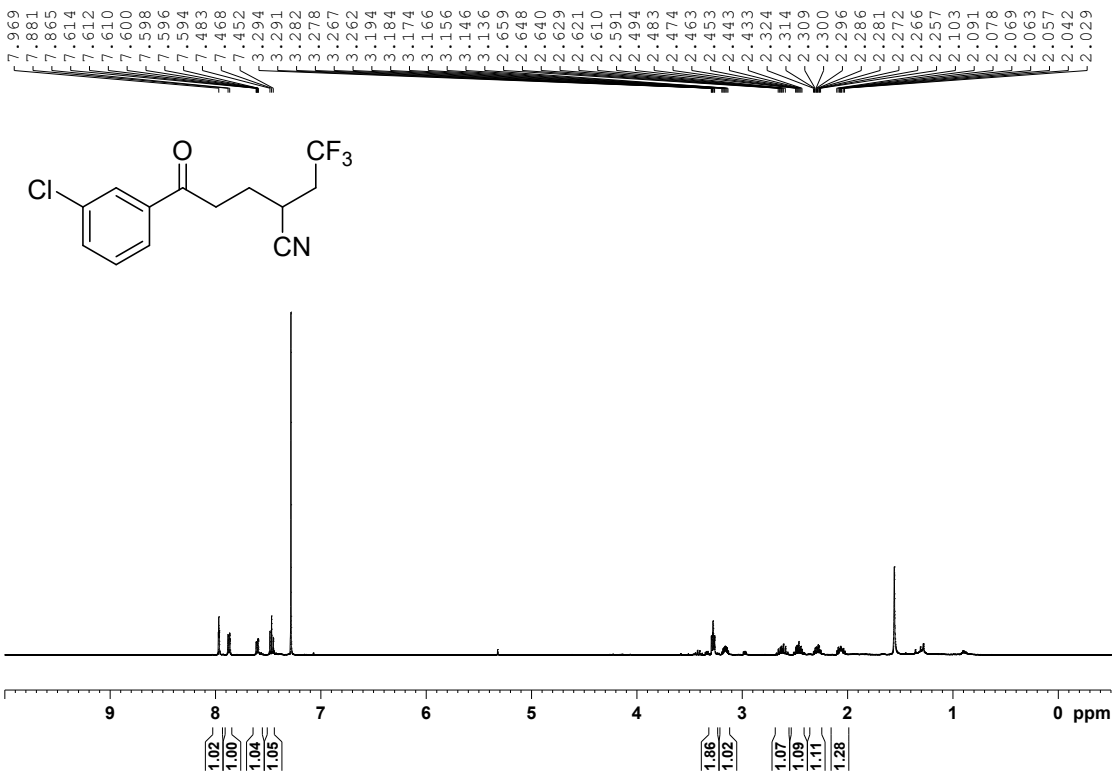
(2l) ^{13}C NMR (101 MHz, CDCl3)



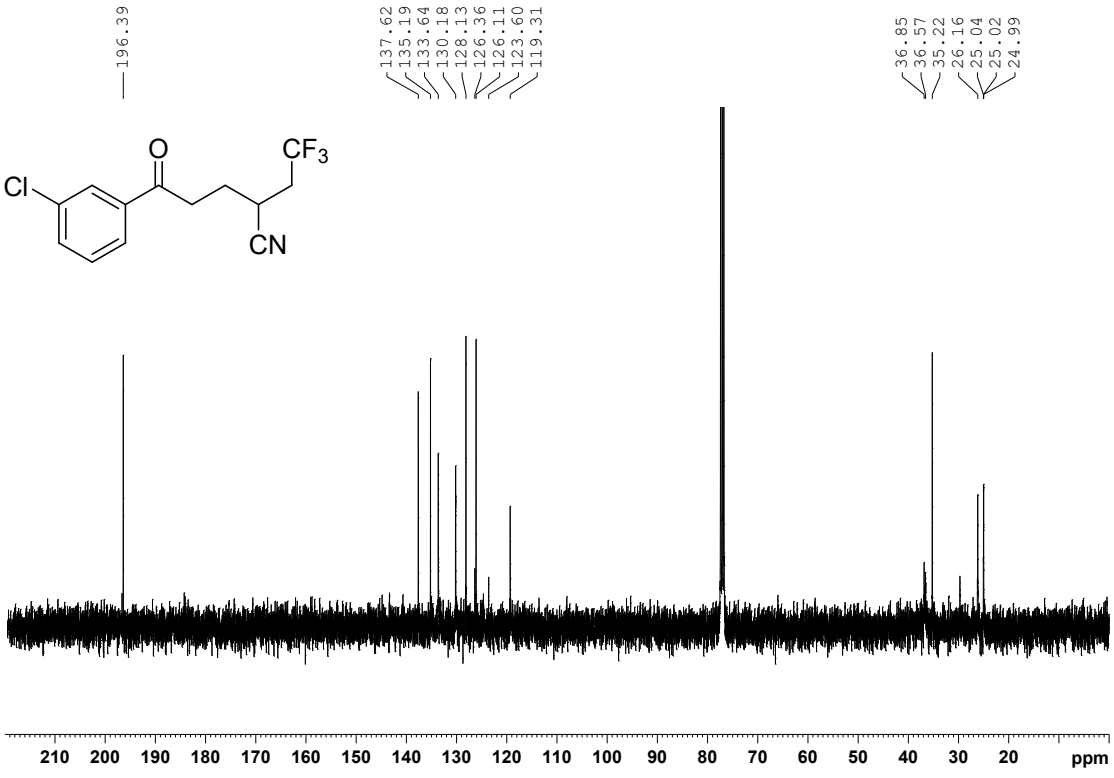
(2l) ^{19}F NMR (376 MHz, CDCl3)



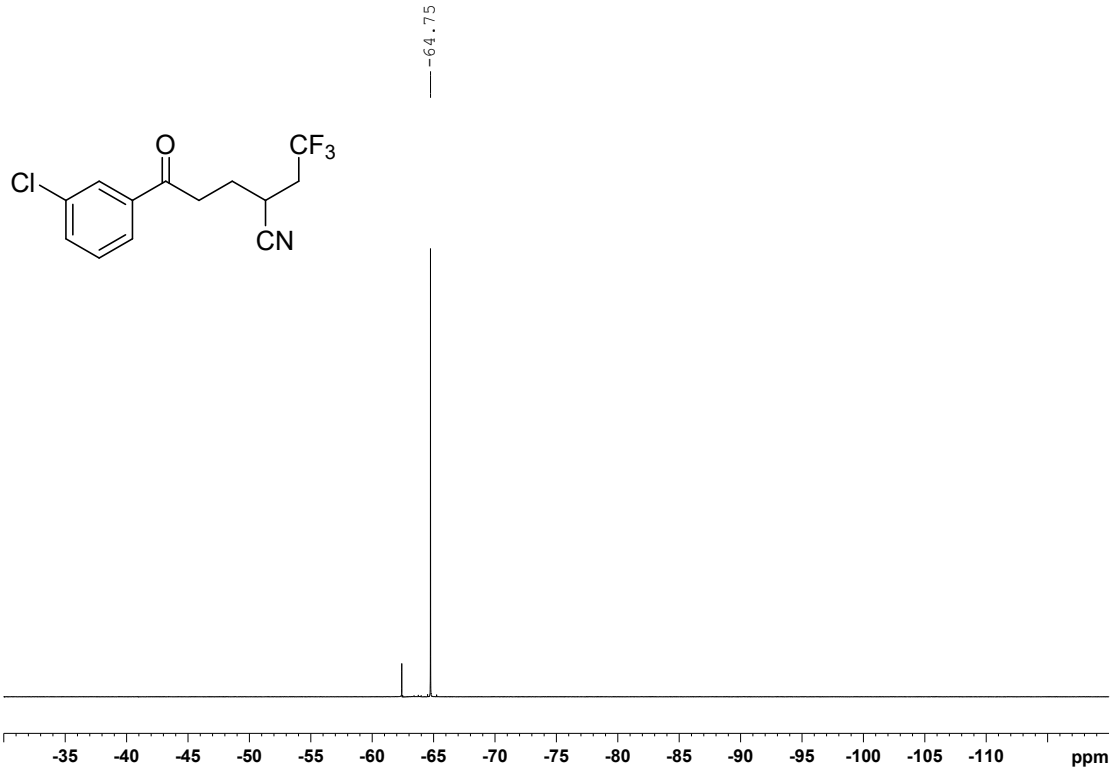
(2m) ^{1}H NMR (500 MHz, CDCl3)



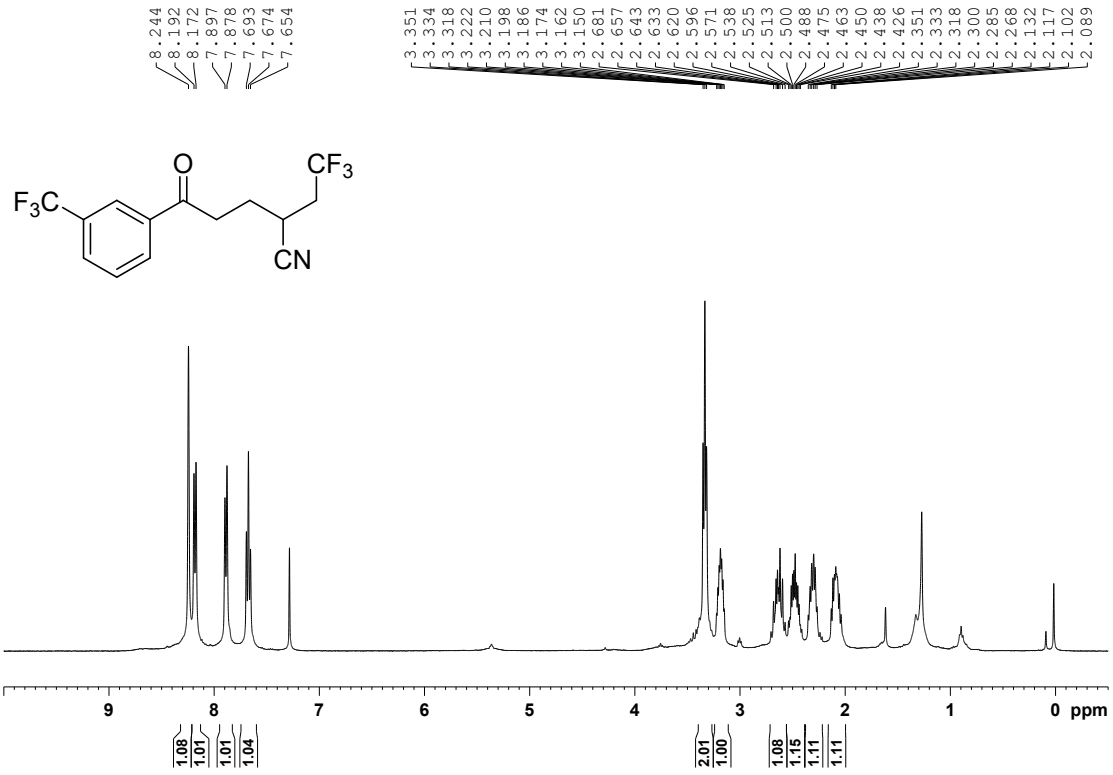
(2m) ^{13}C NMR (101 MHz, CDCl3)



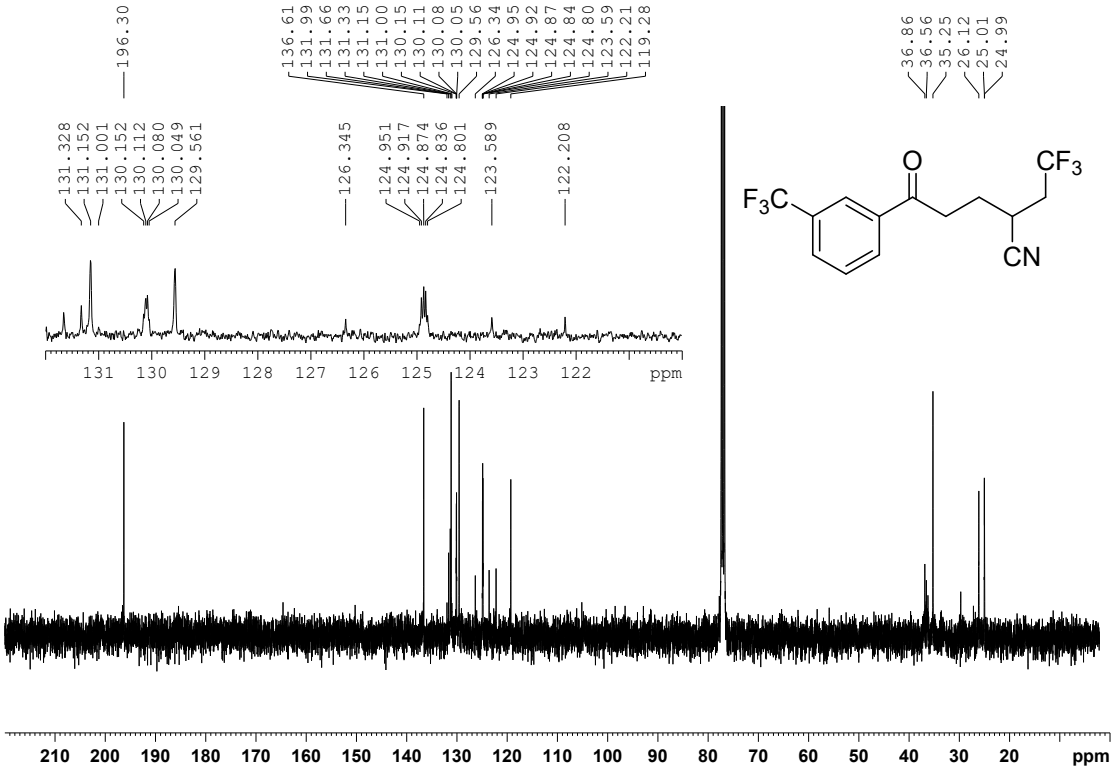
(2m) ^{19}F NMR (376 MHz, CDCl3)



(2n) ^{1}H NMR (400 MHz, CDCl3)

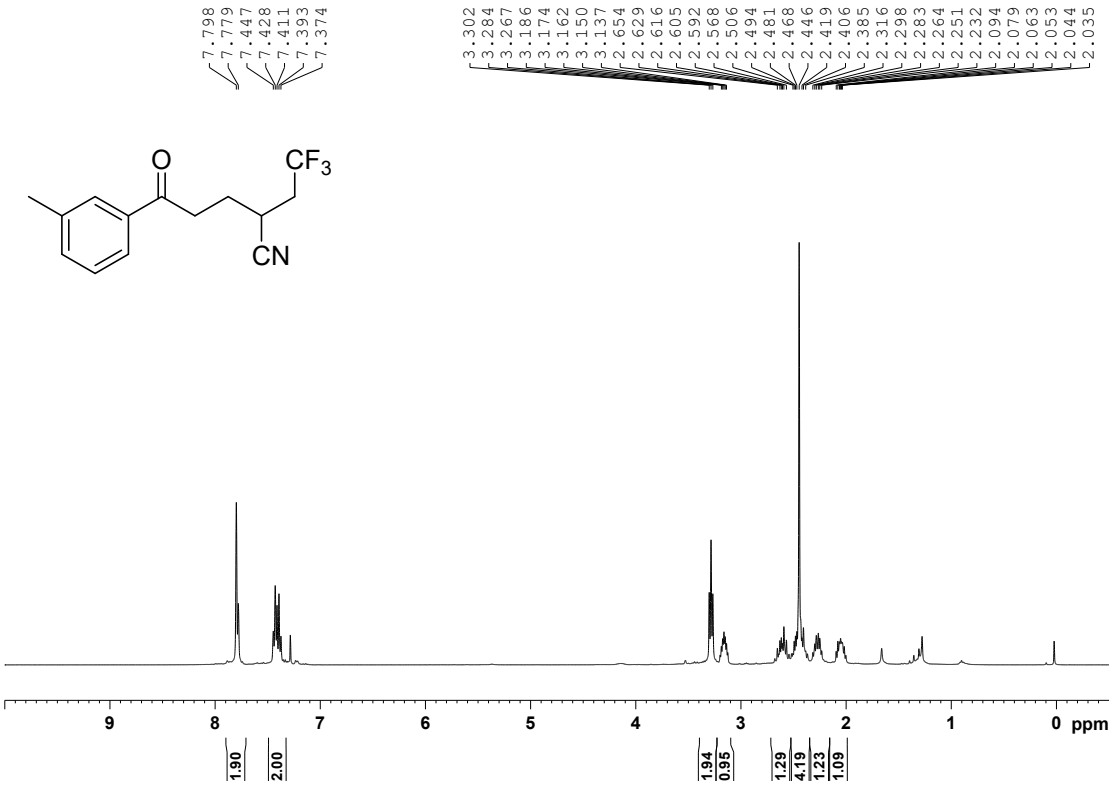


(2n) ^{13}C NMR (101 MHz, CDCl3)

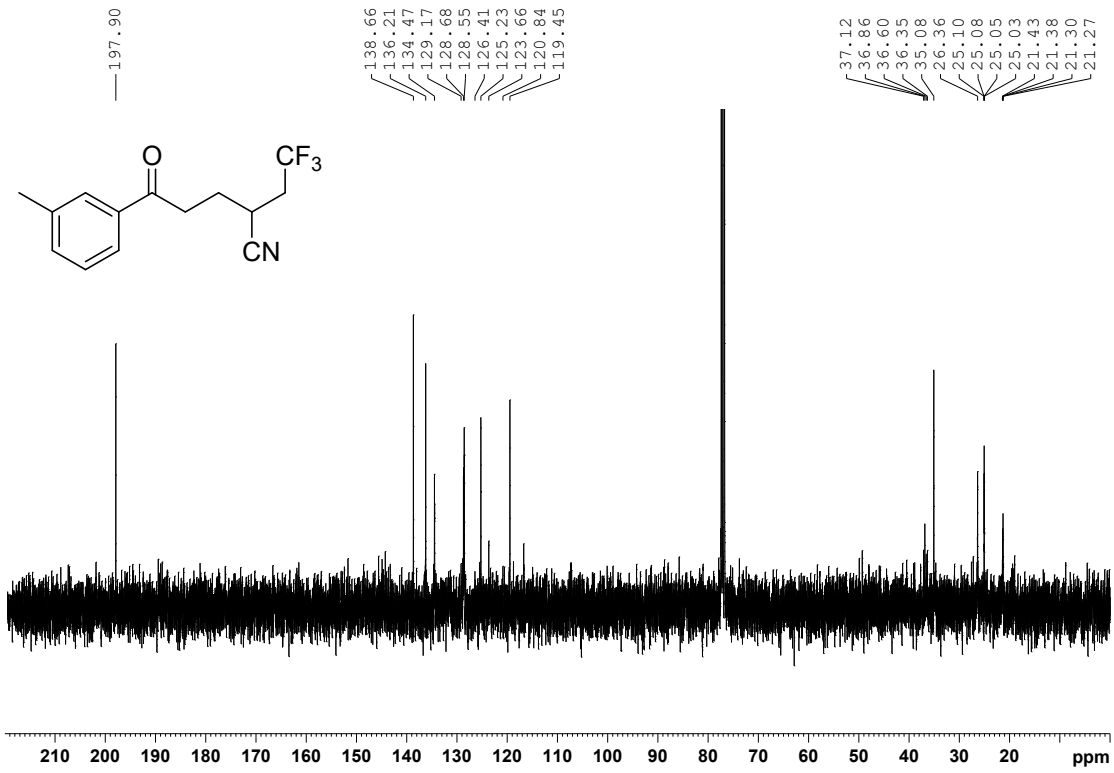


(2n) ^{19}F NMR (376 MHz, CDCl3)

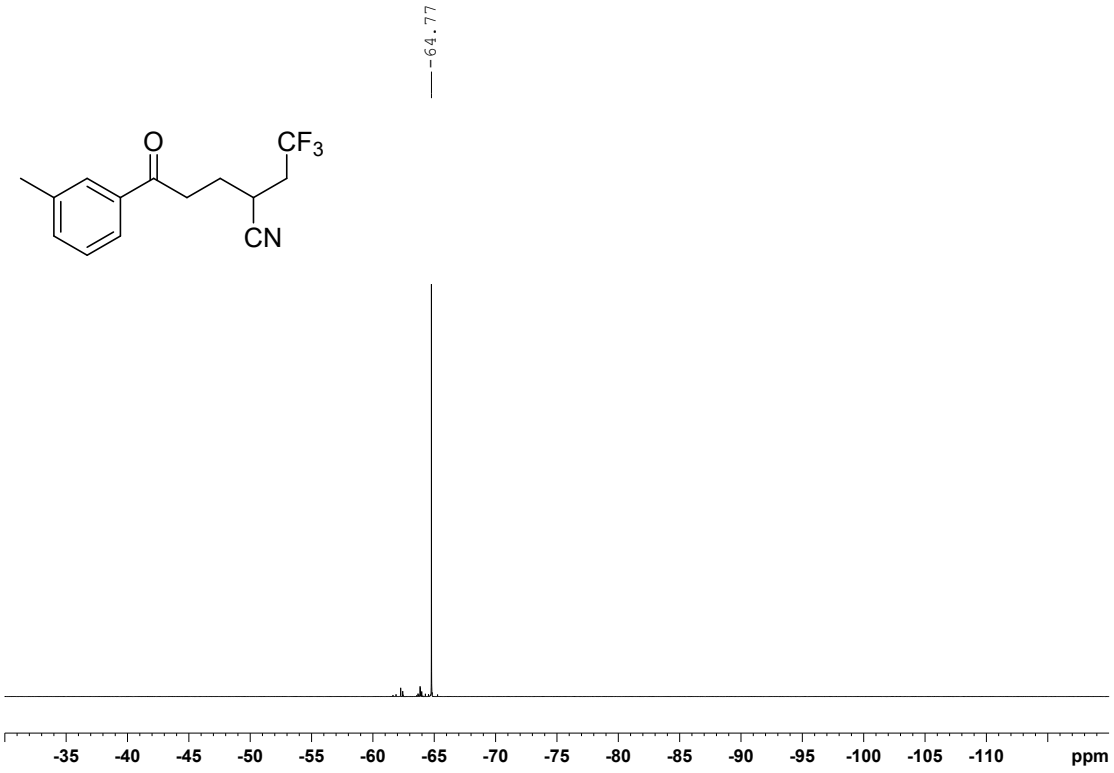
(2o) ^{1}H NMR (400 MHz, CDCl3)



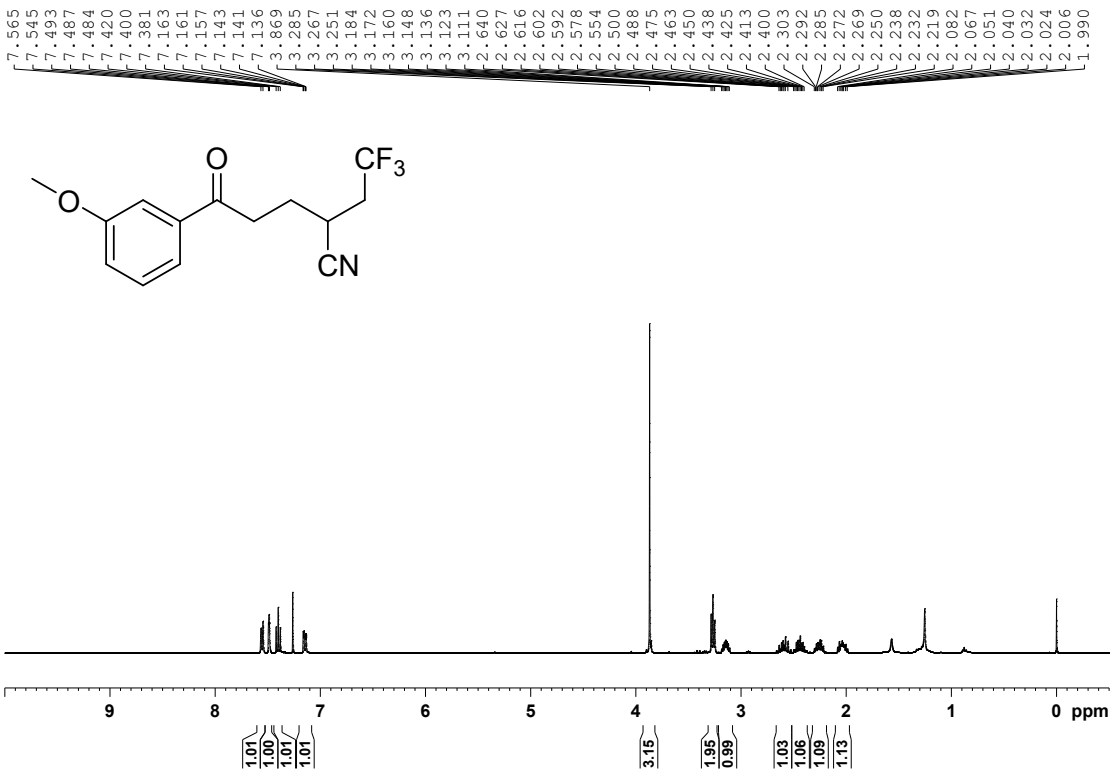
(2o) ^{13}C NMR (101 MHz, CDCl3)



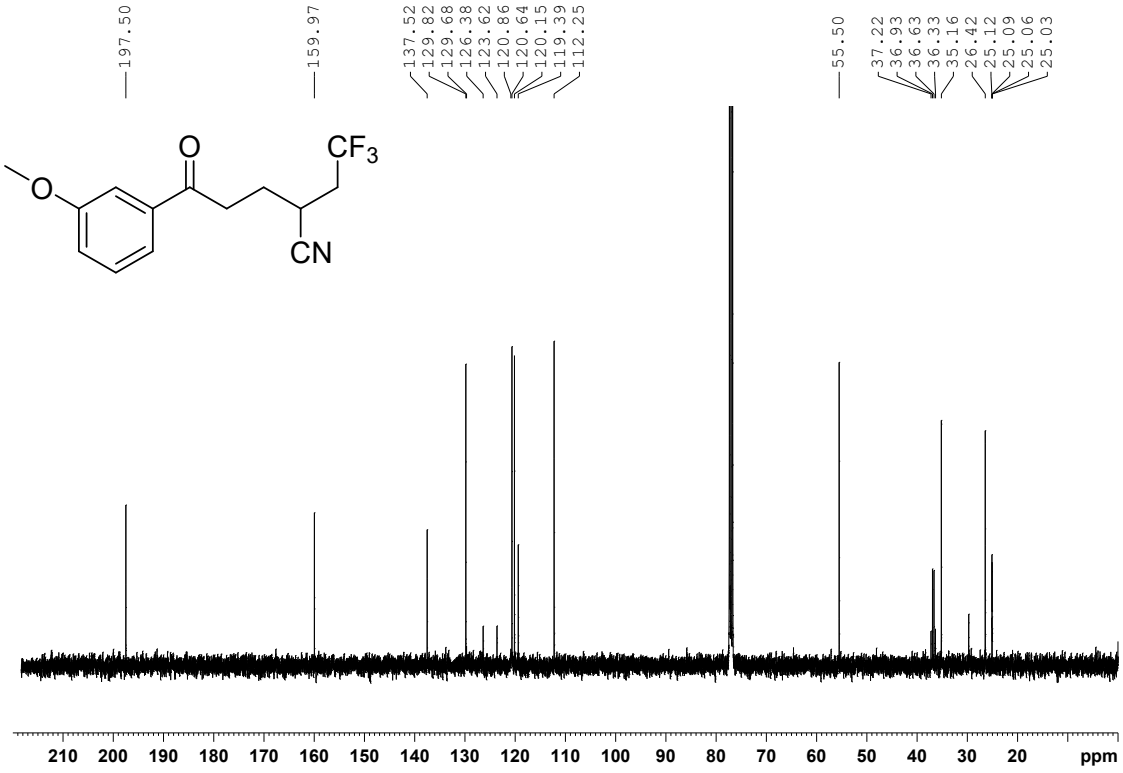
(2o) ^{19}F NMR (376 MHz, CDCl3)



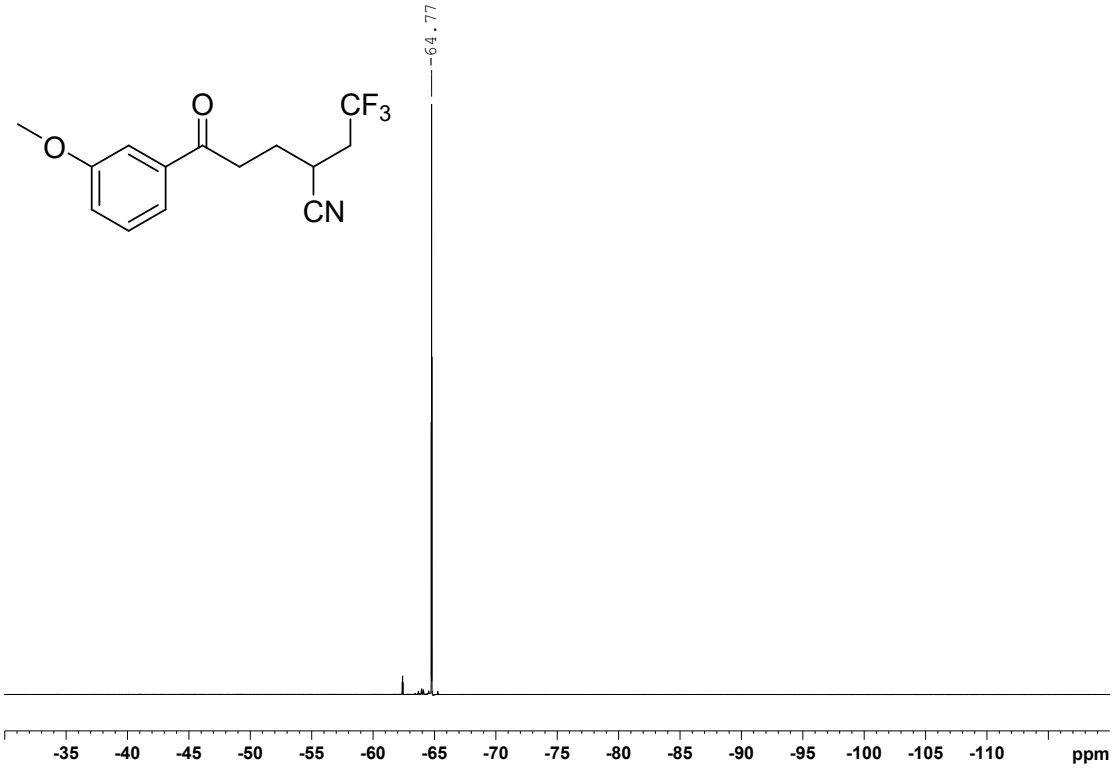
(2p) ^{1}H NMR (400 MHz, CDCl3)



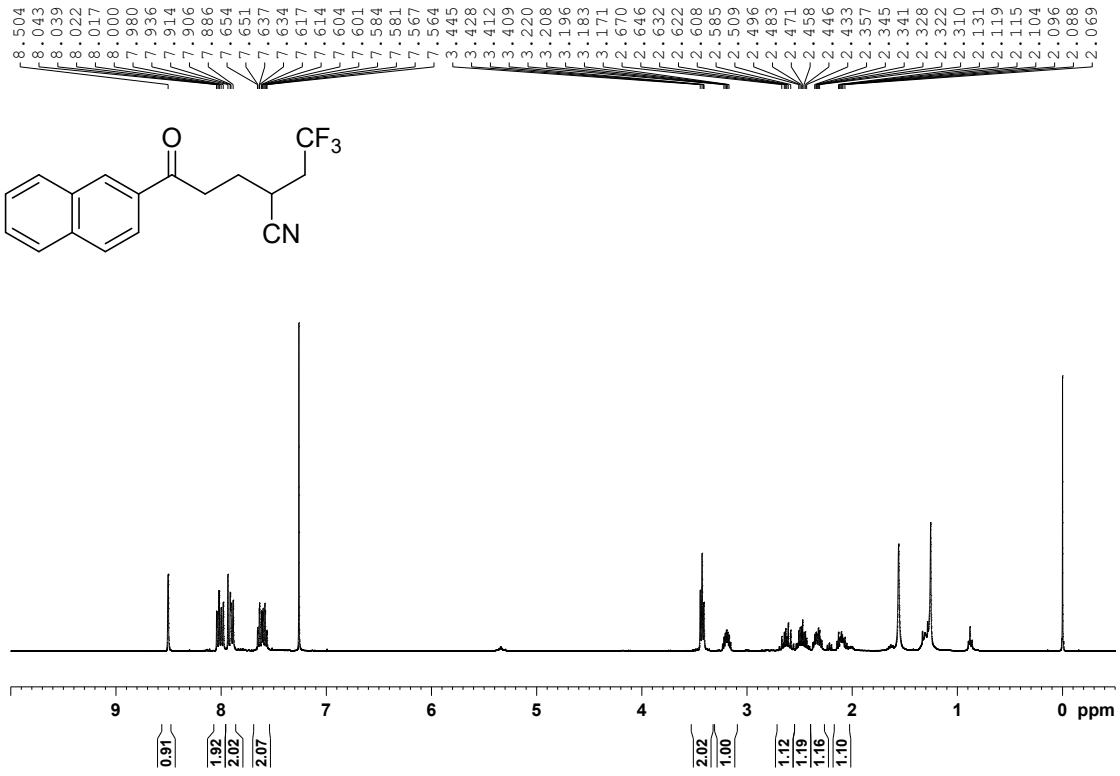
(2p) ^{13}C NMR (101 MHz, CDCl3)



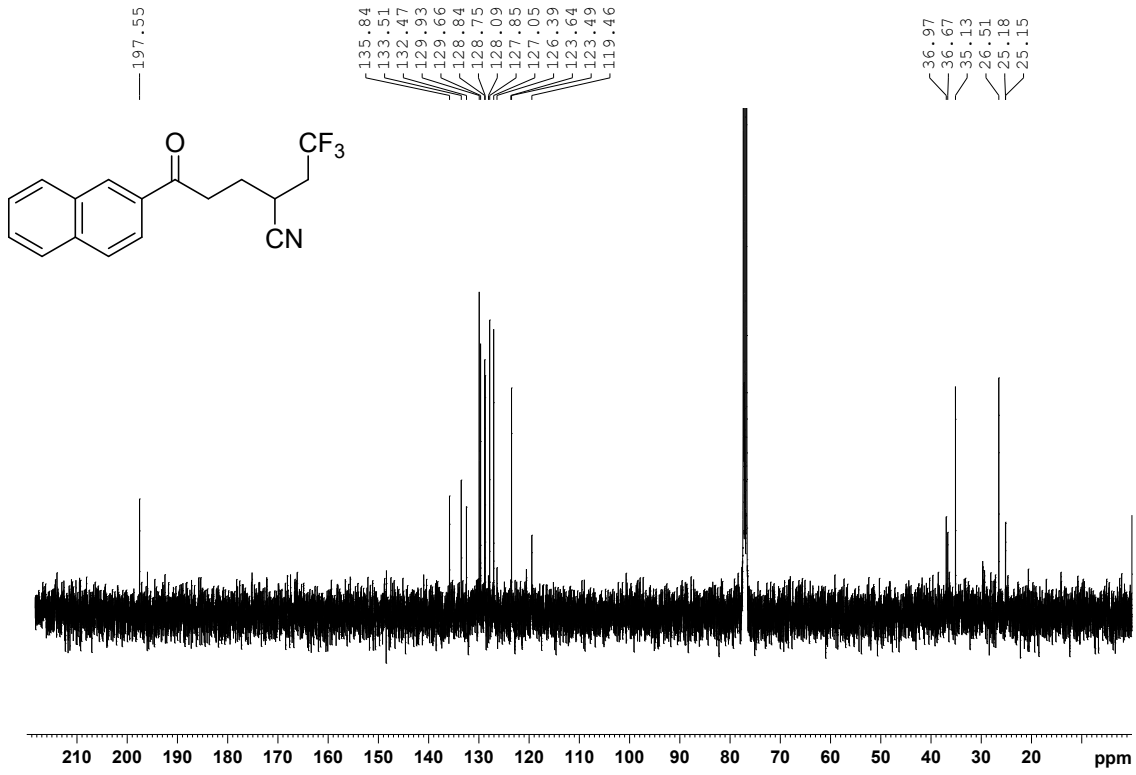
(2p) ^{19}F NMR (376 MHz, CDCl3)



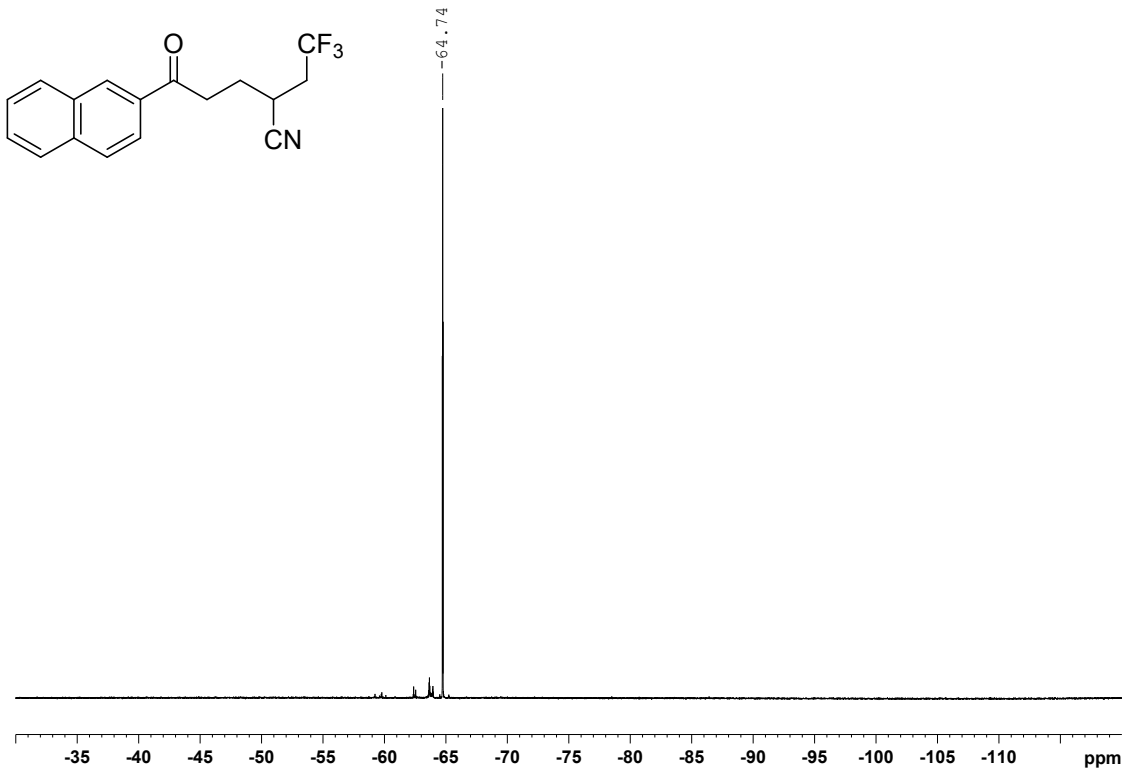
(2q) ^{1}H NMR (400 MHz, CDCl3)



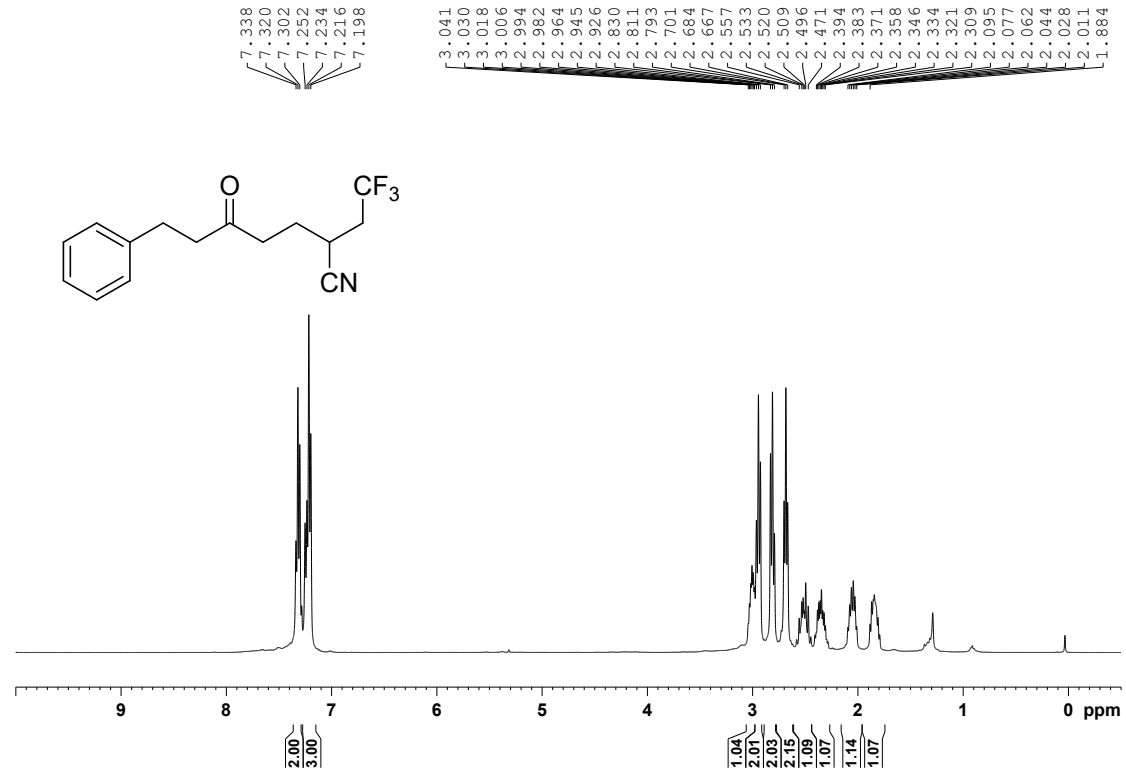
(2q) ^{13}C NMR (101 MHz, CDCl3)



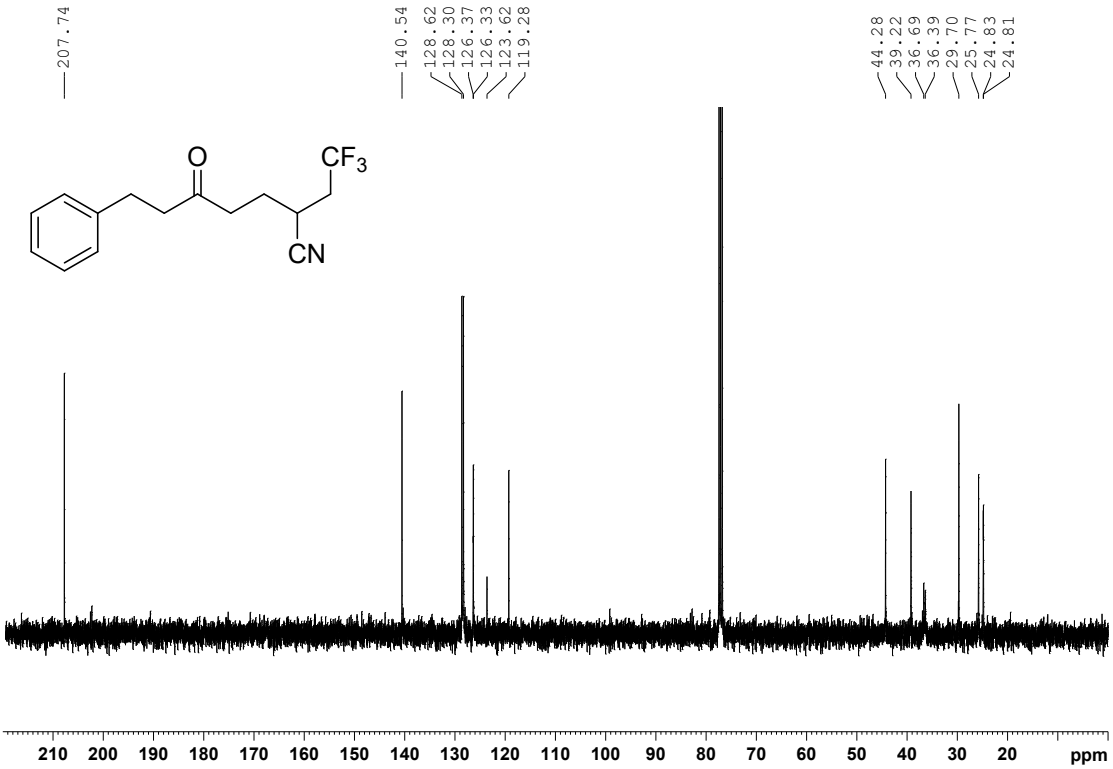
(2q) ^{19}F NMR (376 MHz, CDCl3)



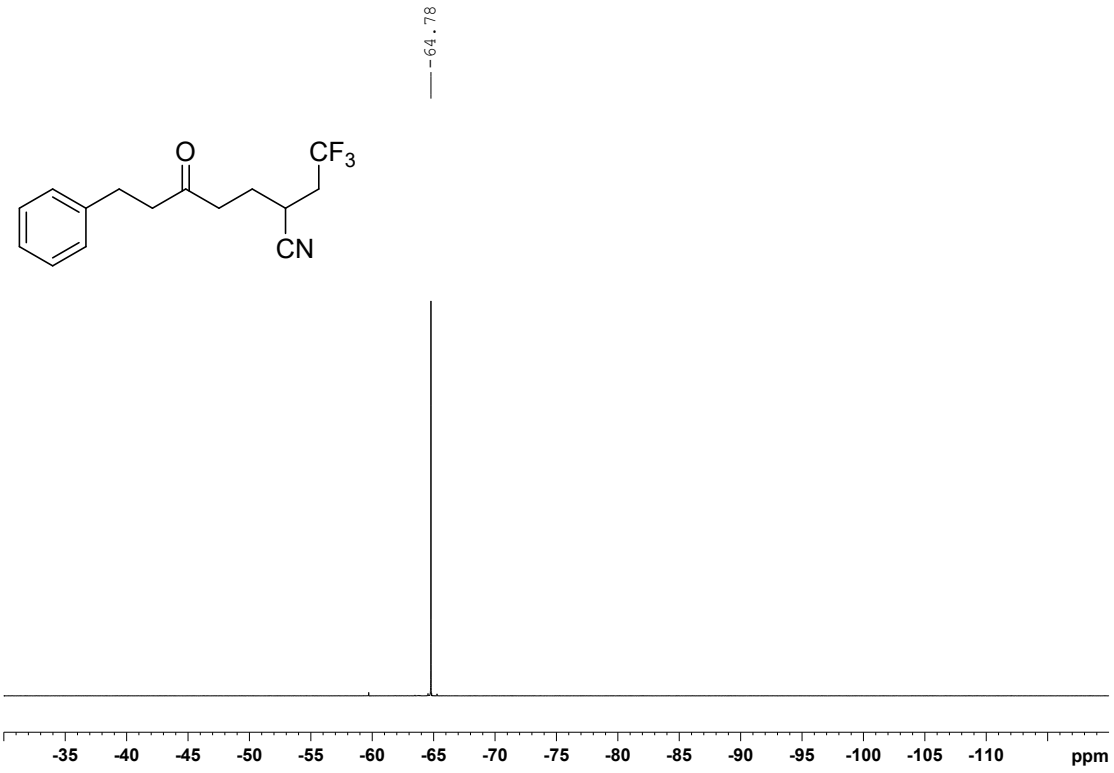
(2r) ^{1}H NMR (400 MHz, CDCl3)



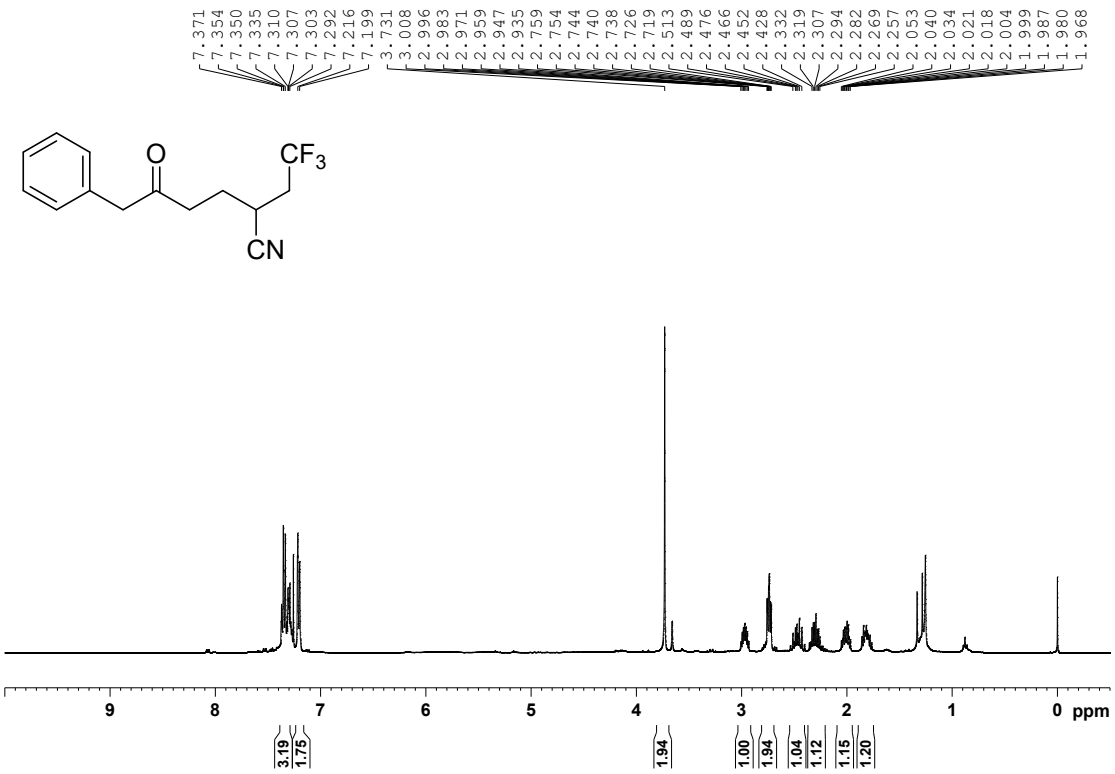
(2r) ^{13}C NMR (101 MHz, CDCl3)



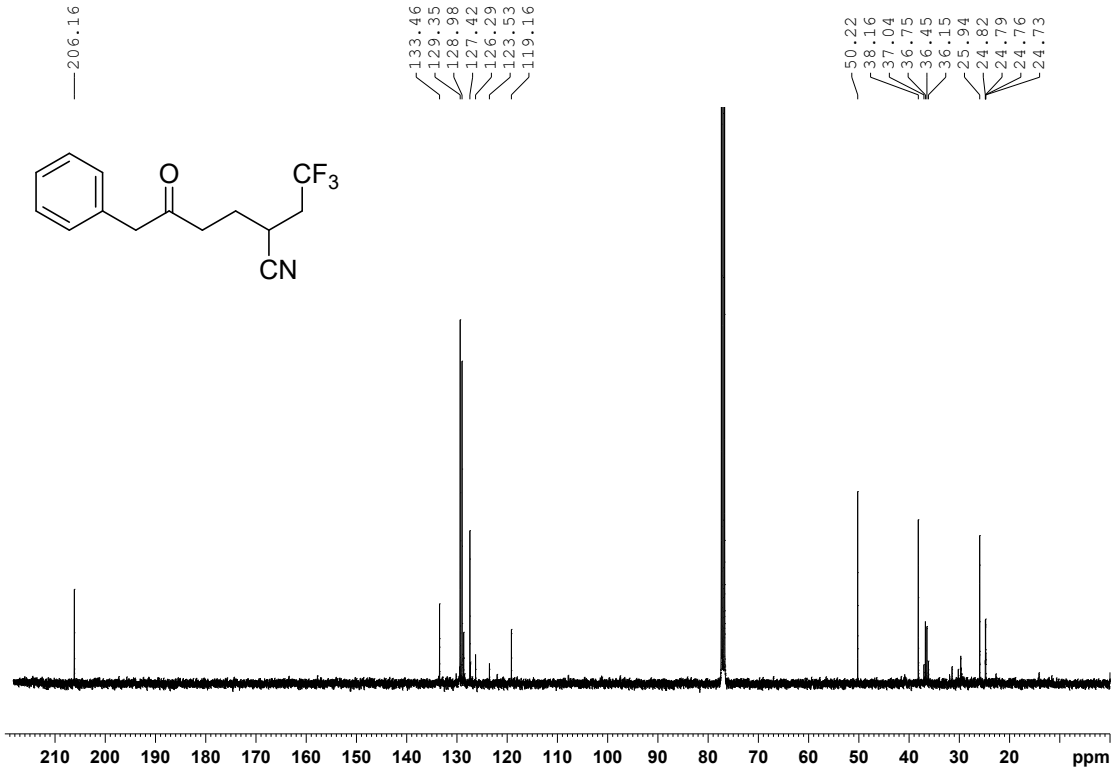
(2r) ^{19}F NMR (376 MHz, CDCl3)



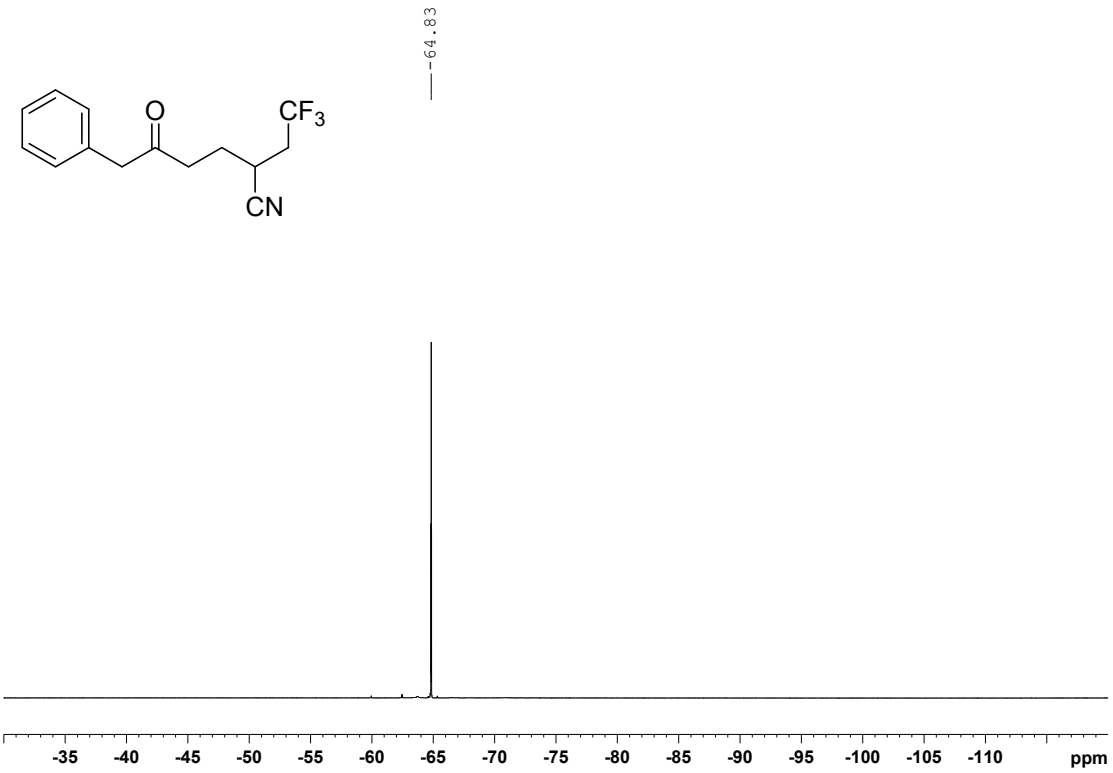
(2s) ^{1}H NMR (400 MHz, CDCl3)



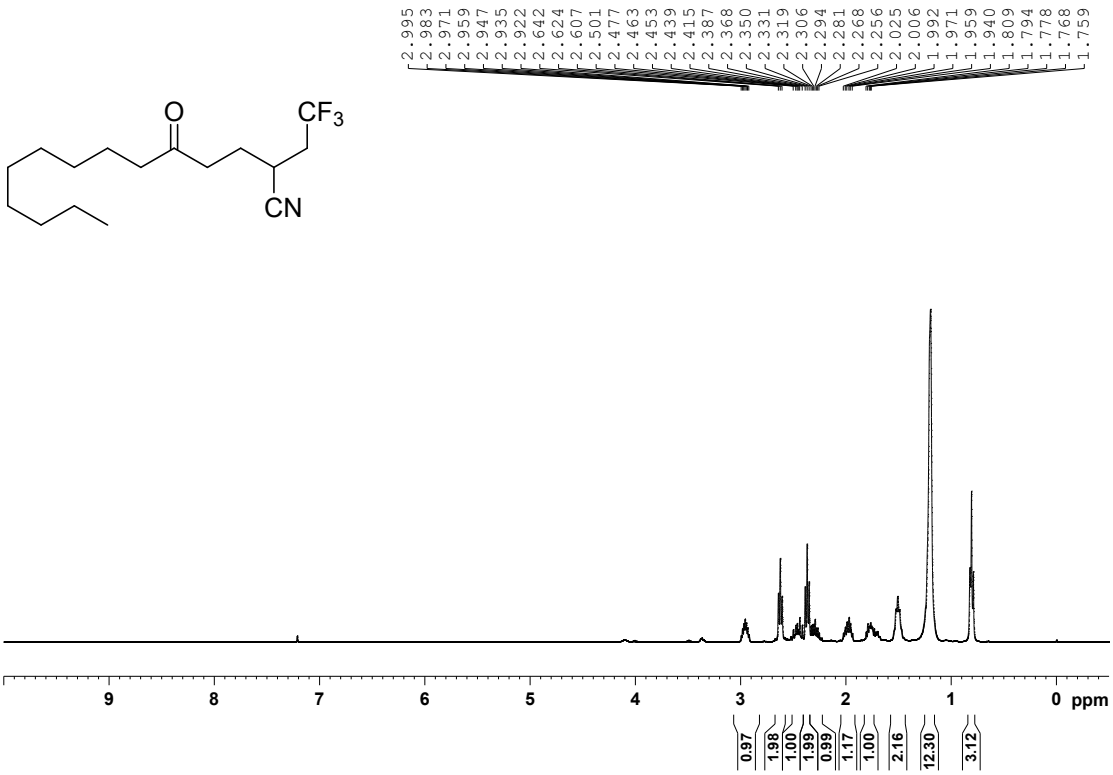
(2s) ^{13}C NMR (101 MHz, CDCl3)



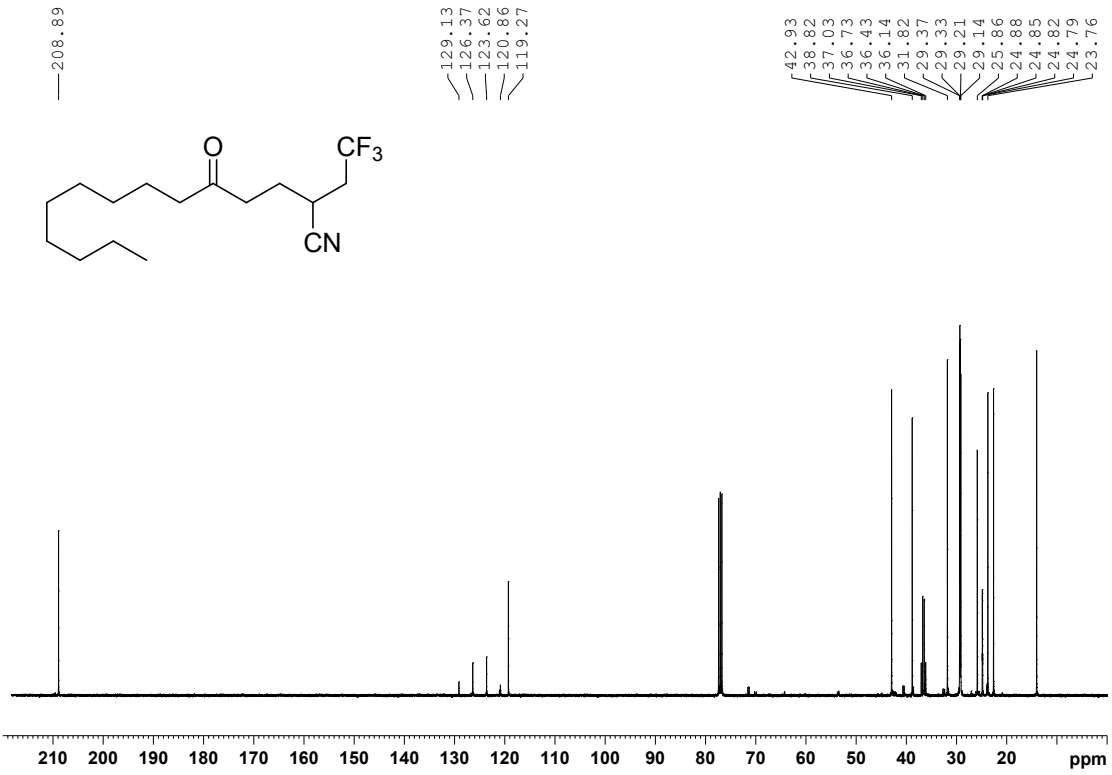
(2s) ^{19}F NMR (376 MHz, CDCl3)



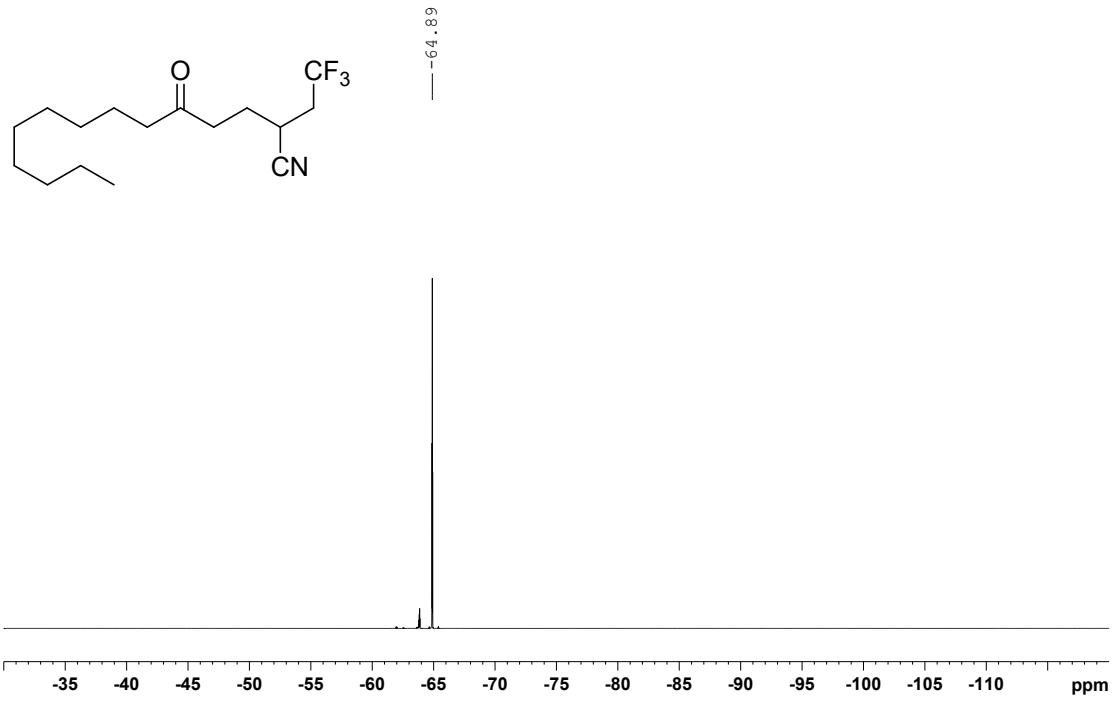
(2t) ^{1}H NMR (400 MHz, CDCl3)



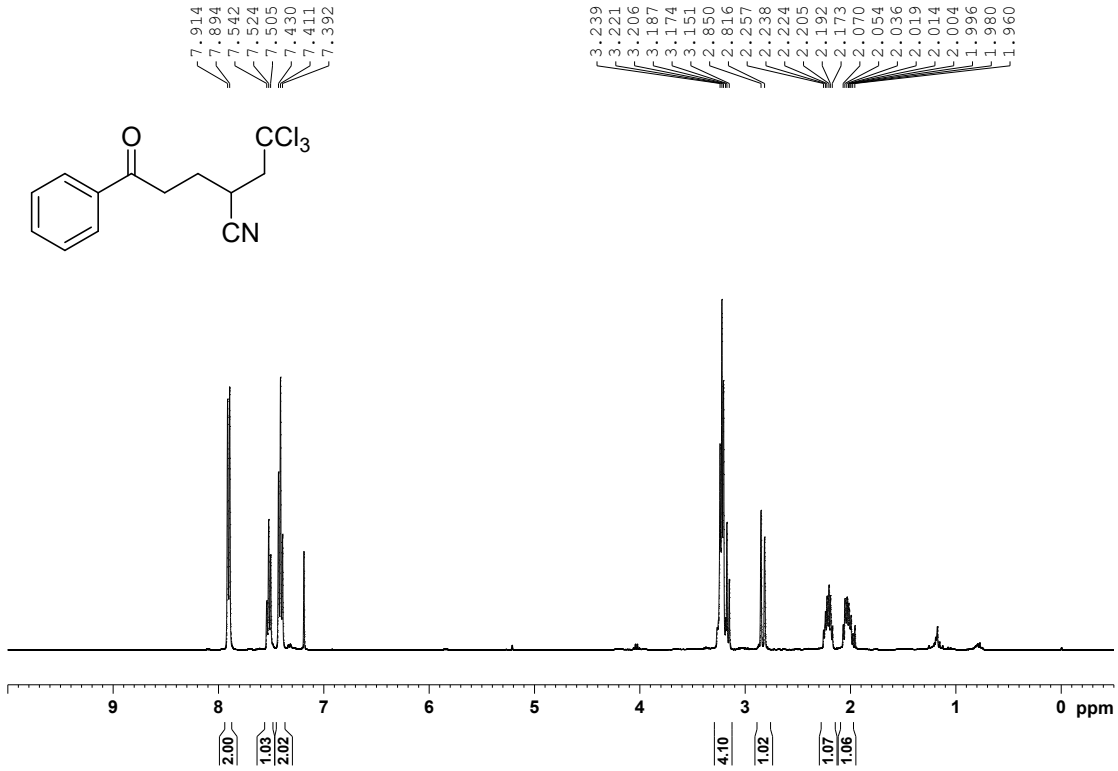
(2t) ^{13}C NMR (101 MHz, CDCl3)



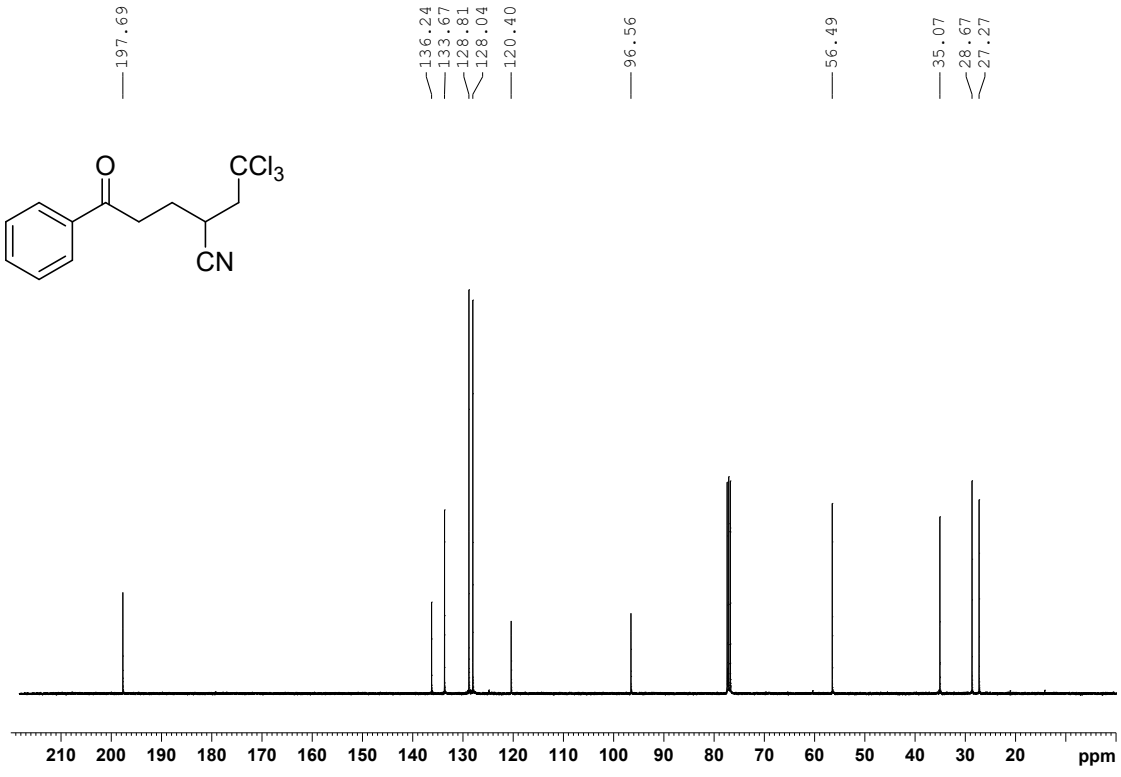
(2t) ^{19}F NMR (376 MHz, CDCl3)



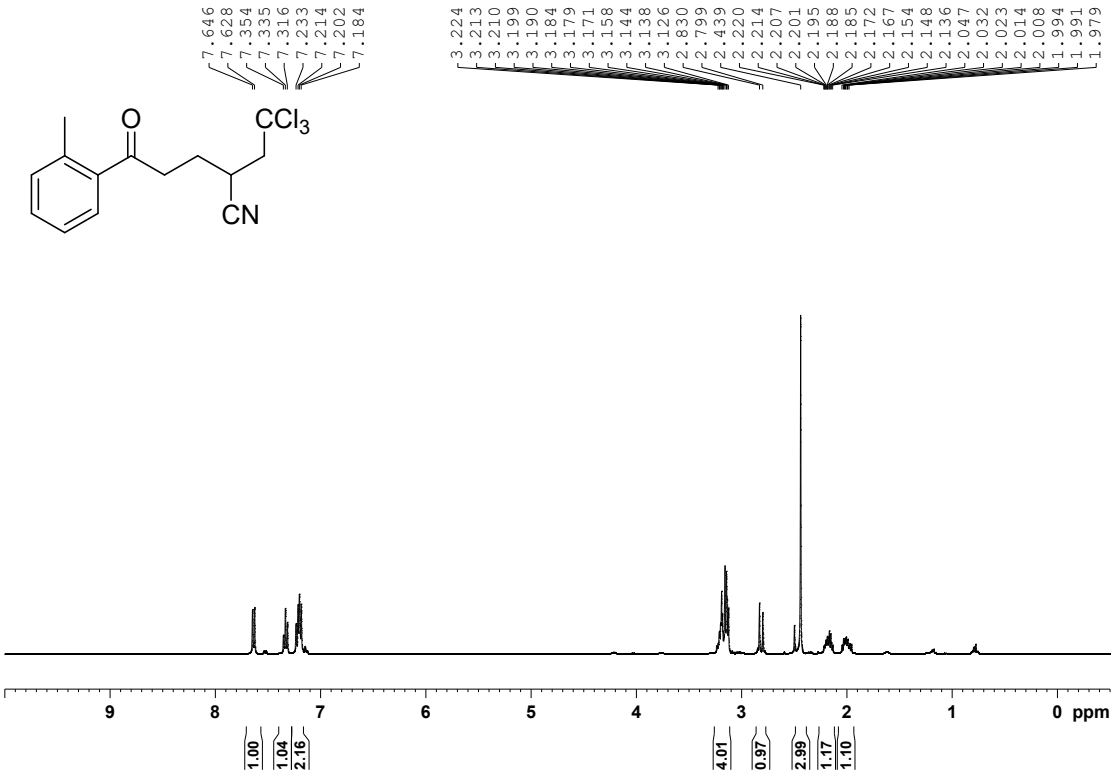
(3a) ^{1}H NMR (400 MHz, CDCl3)



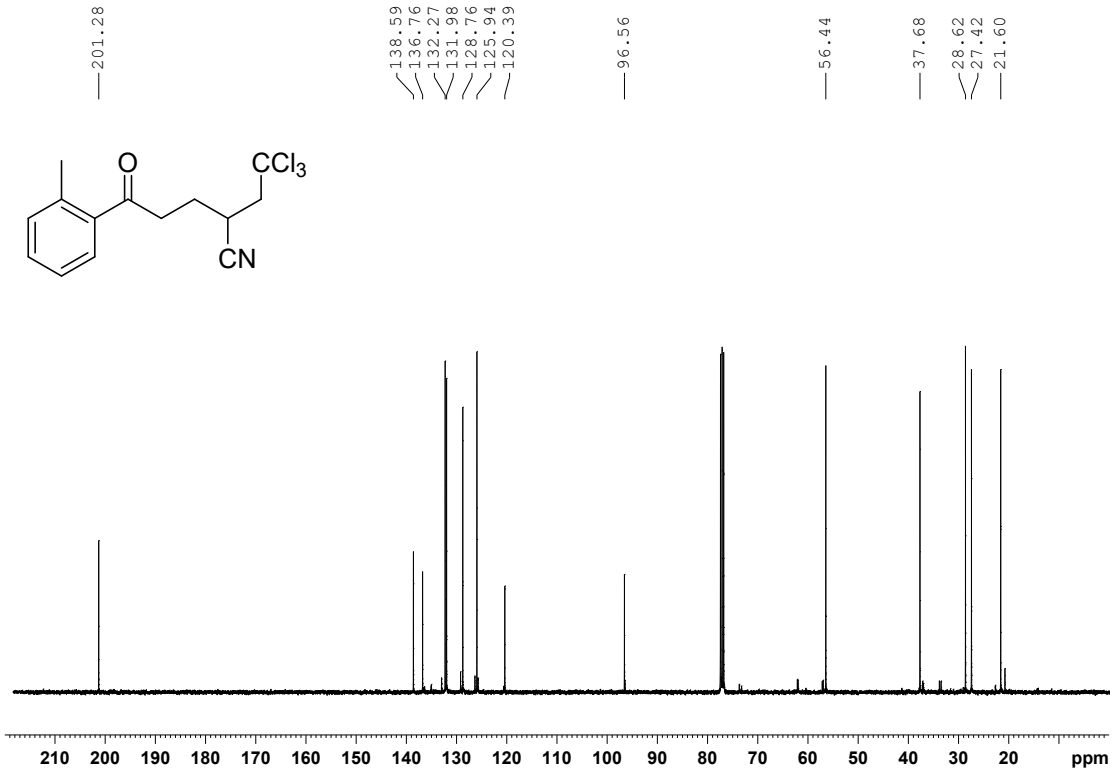
(3a) ^{13}C NMR (101 MHz, CDCl3)



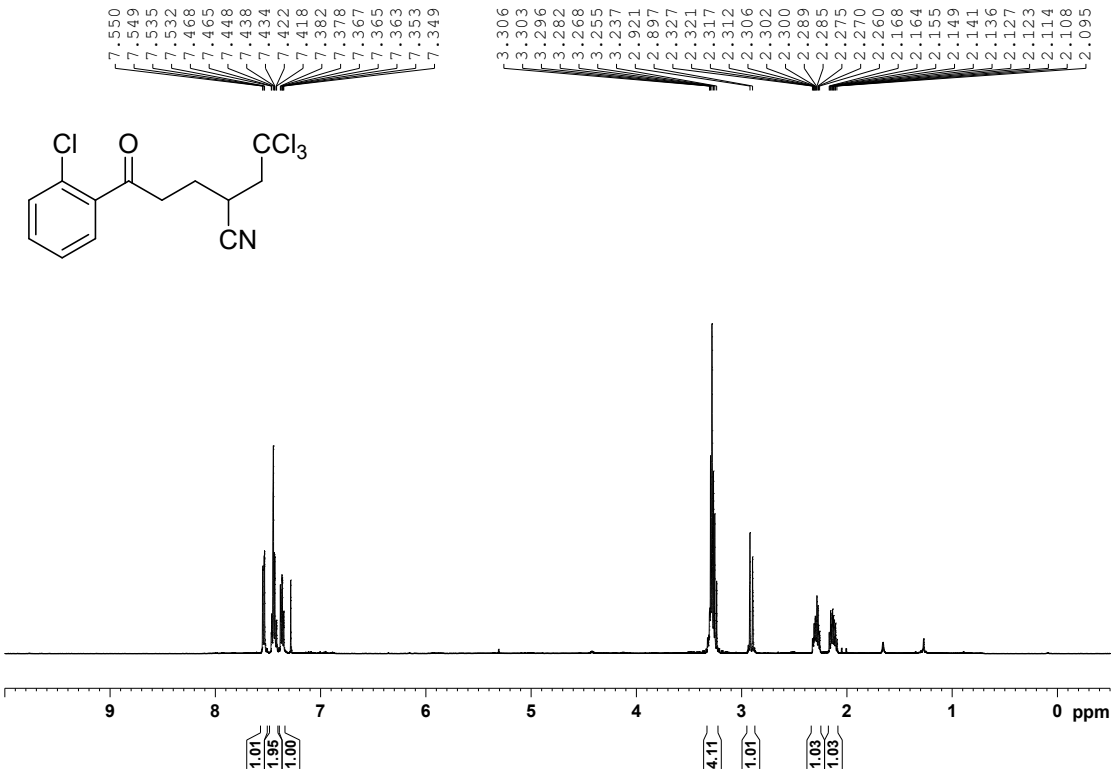
(3b) ^{1}H NMR (400 MHz, CDCl3)



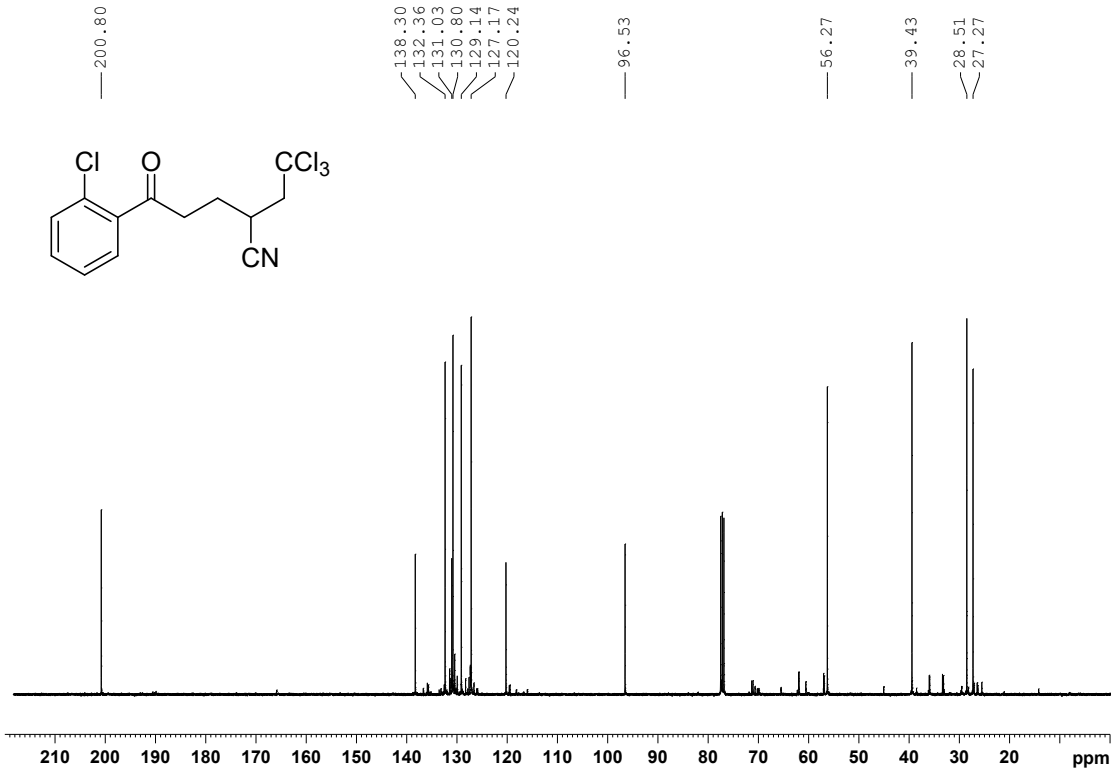
(3b) ^{13}C NMR (101 MHz, CDCl3)



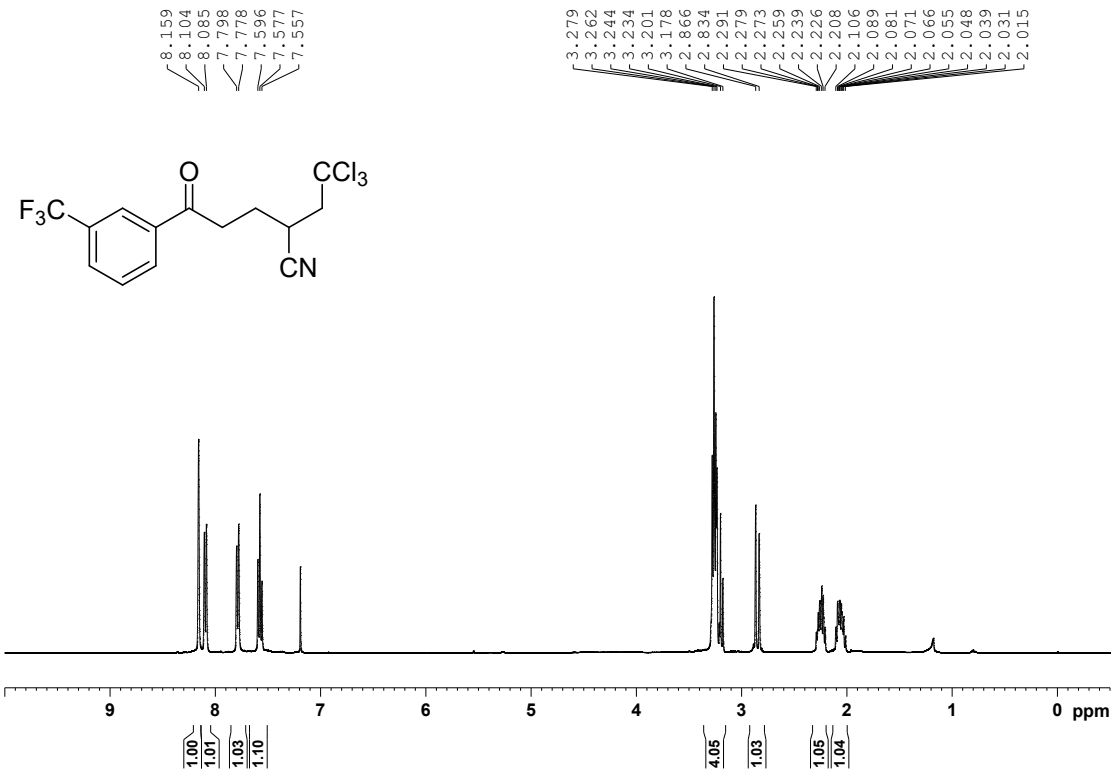
(3c) ^{1}H NMR (400 MHz, CDCl3)



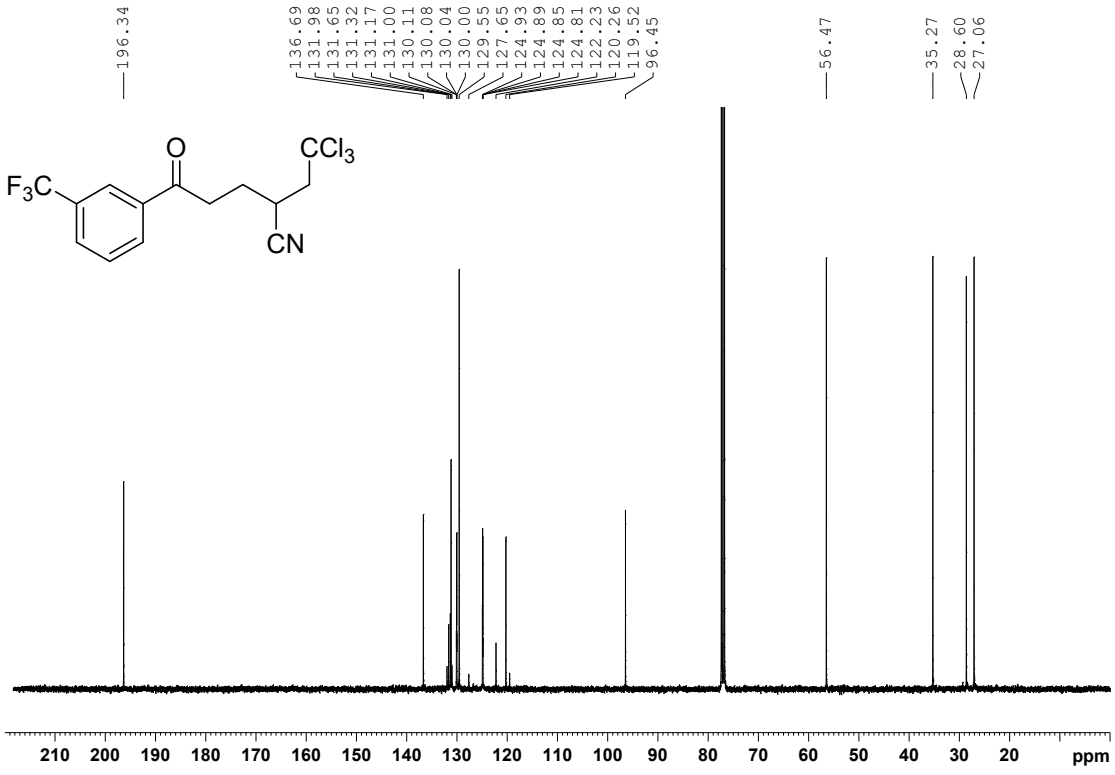
(3c) ^{13}C NMR (101 MHz, CDCl3)



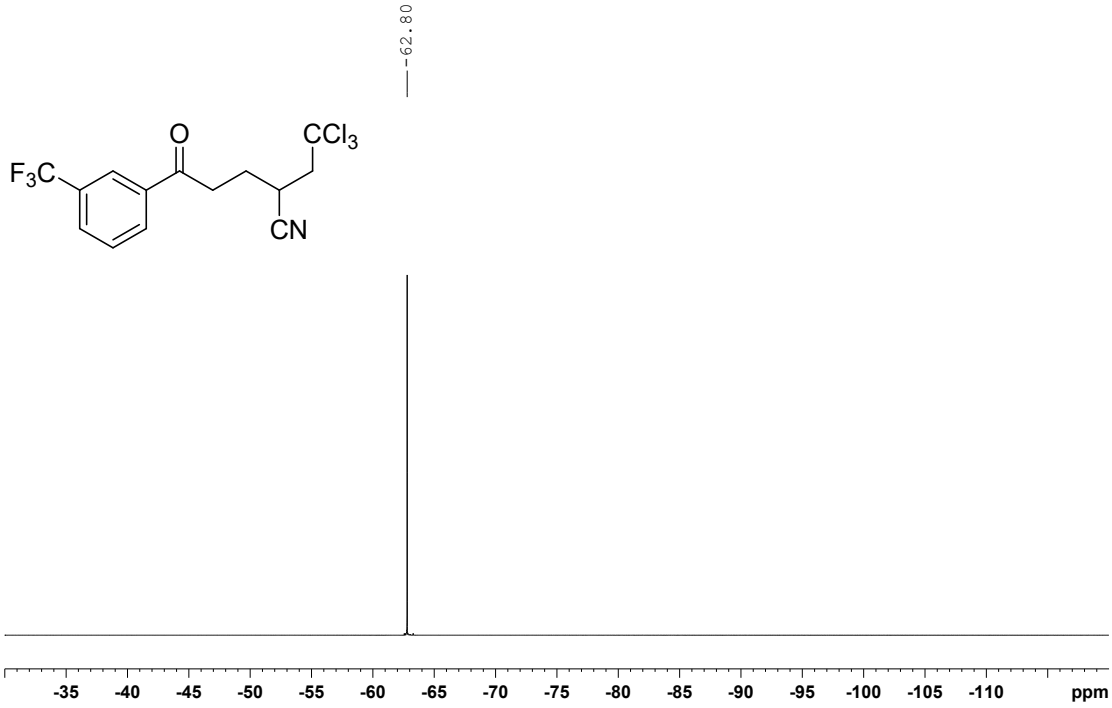
(3d) ^{1}H NMR (400 MHz, CDCl3)



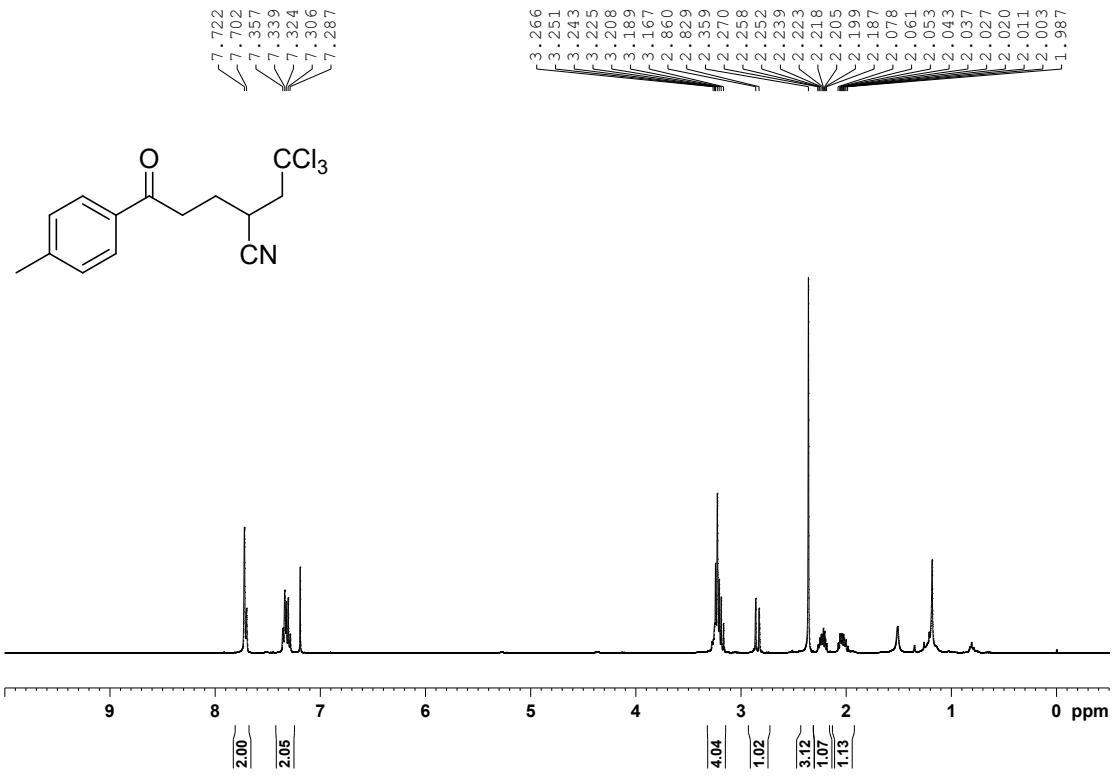
(3d) ^{13}C NMR (101 MHz, CDCl3)



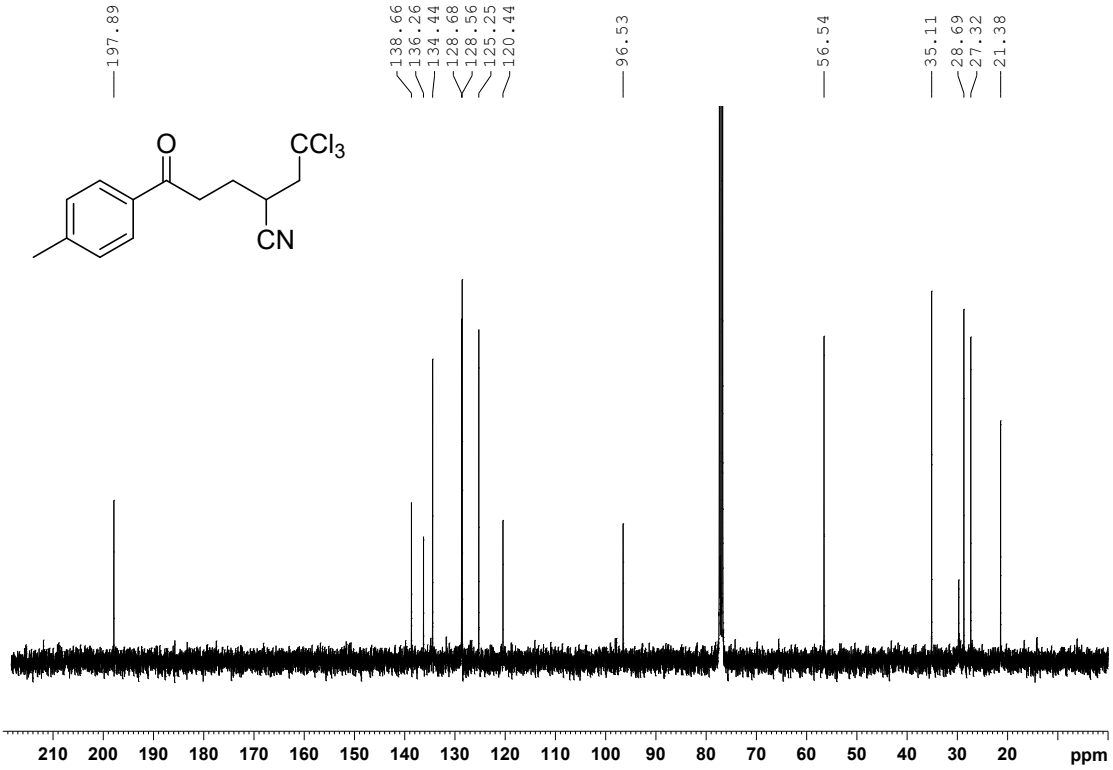
(3d) ^{19}F NMR (376 MHz, CDCl3)



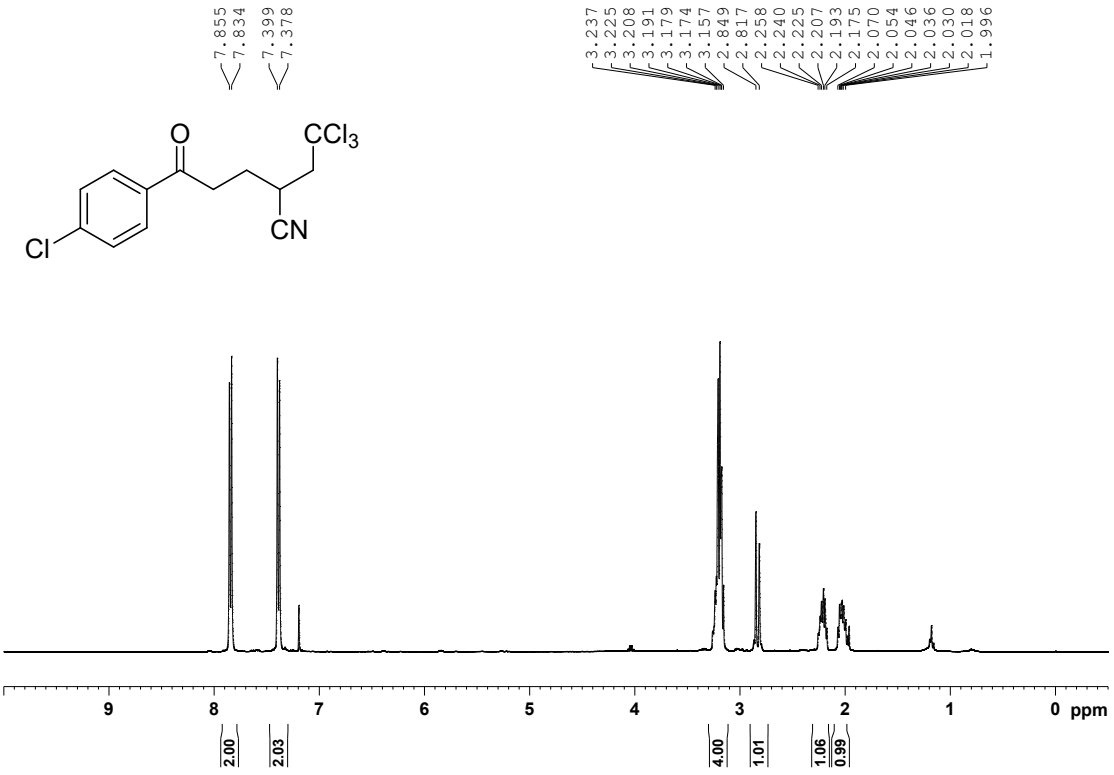
(3e) ^{1}H NMR (400 MHz, CDCl3)



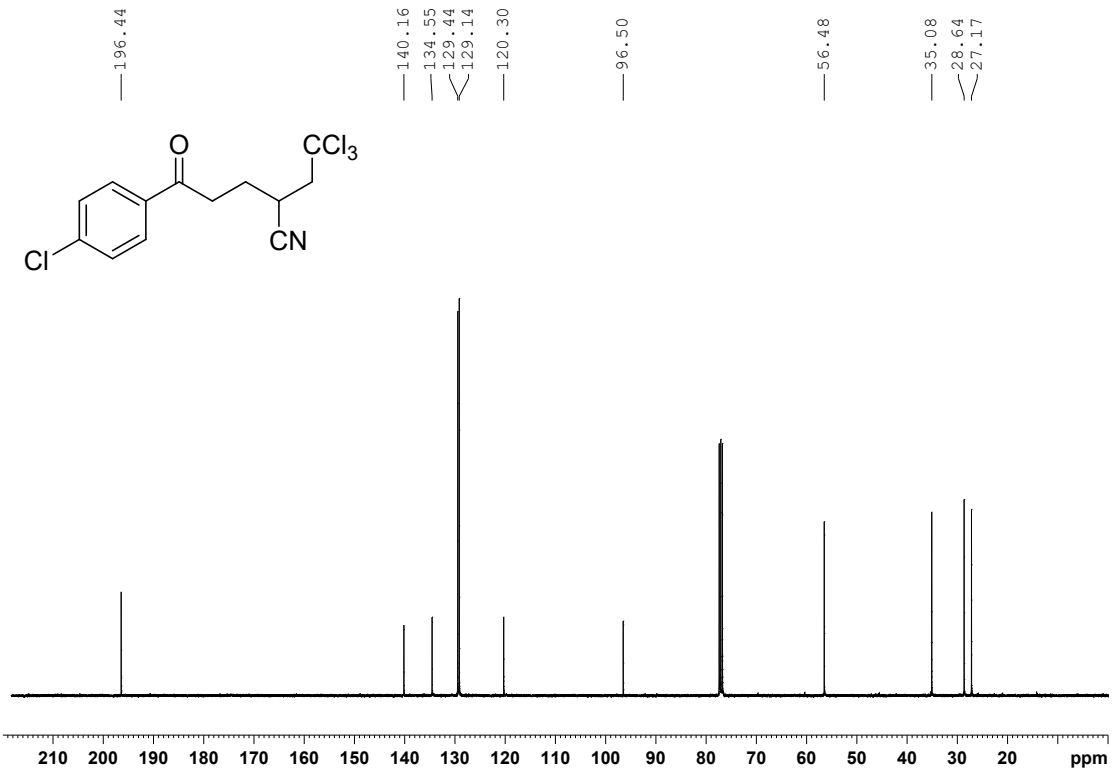
(3e) ^{13}C NMR (101 MHz, CDCl3)



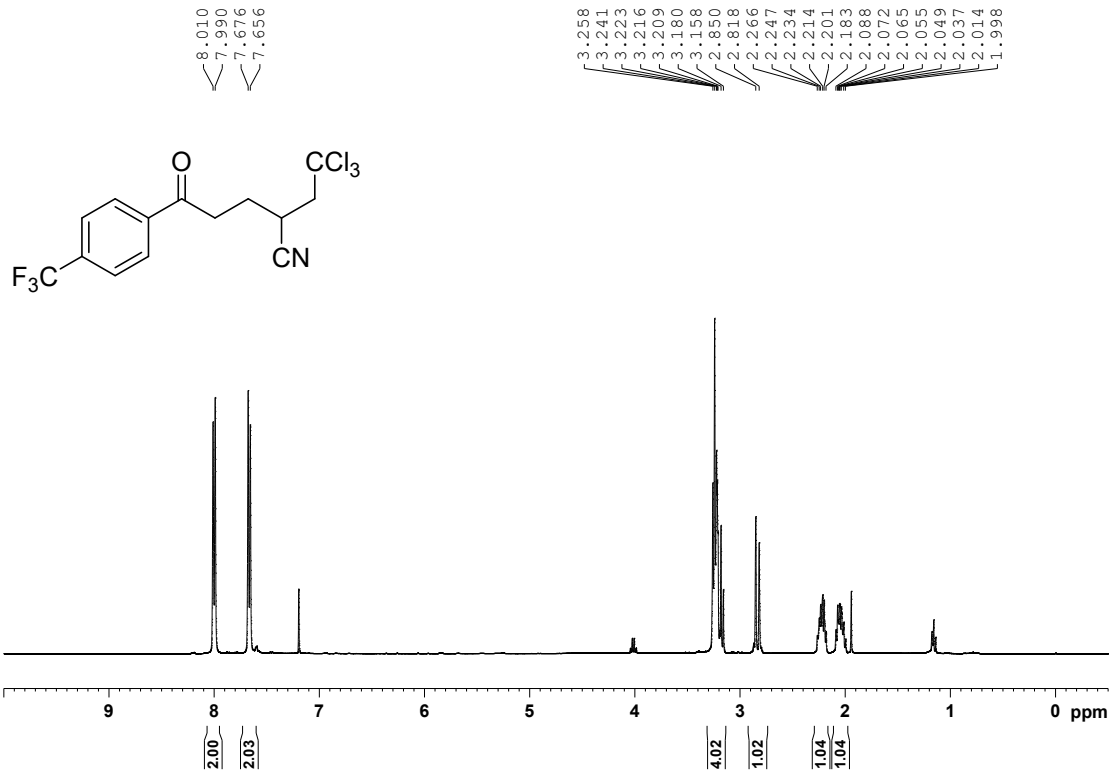
(3f) ^{1}H NMR (400 MHz, CDCl3)



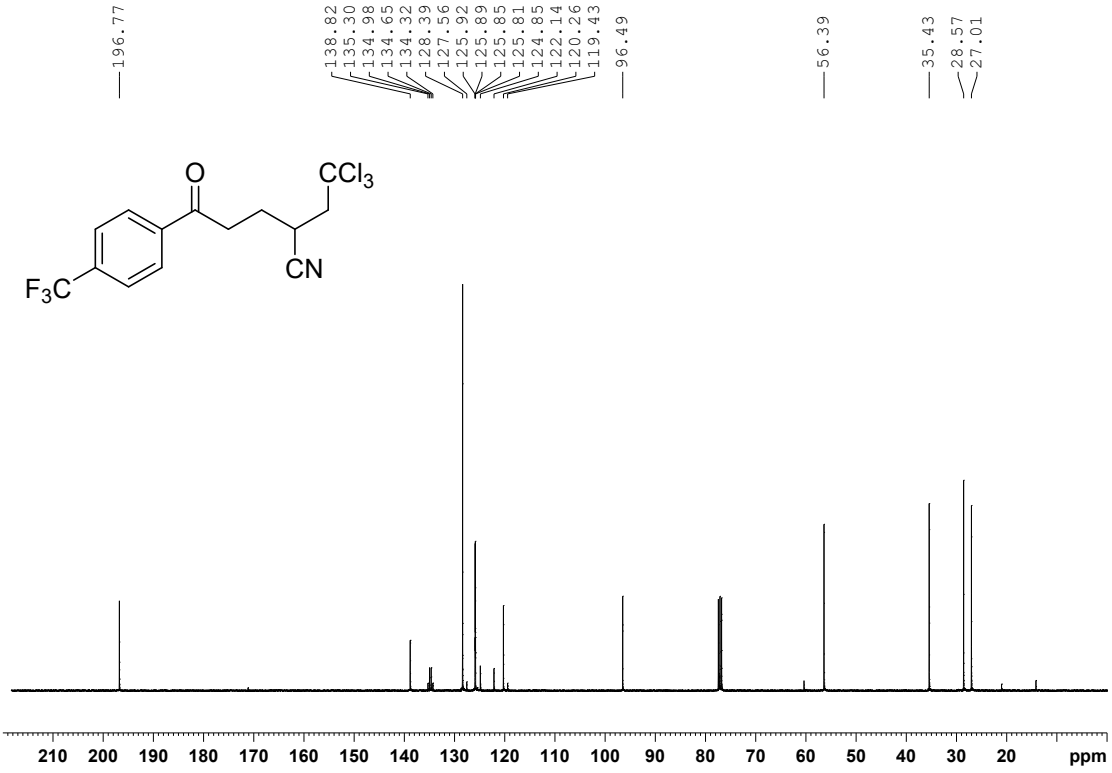
(3f) ^{13}C NMR (101 MHz, CDCl3)



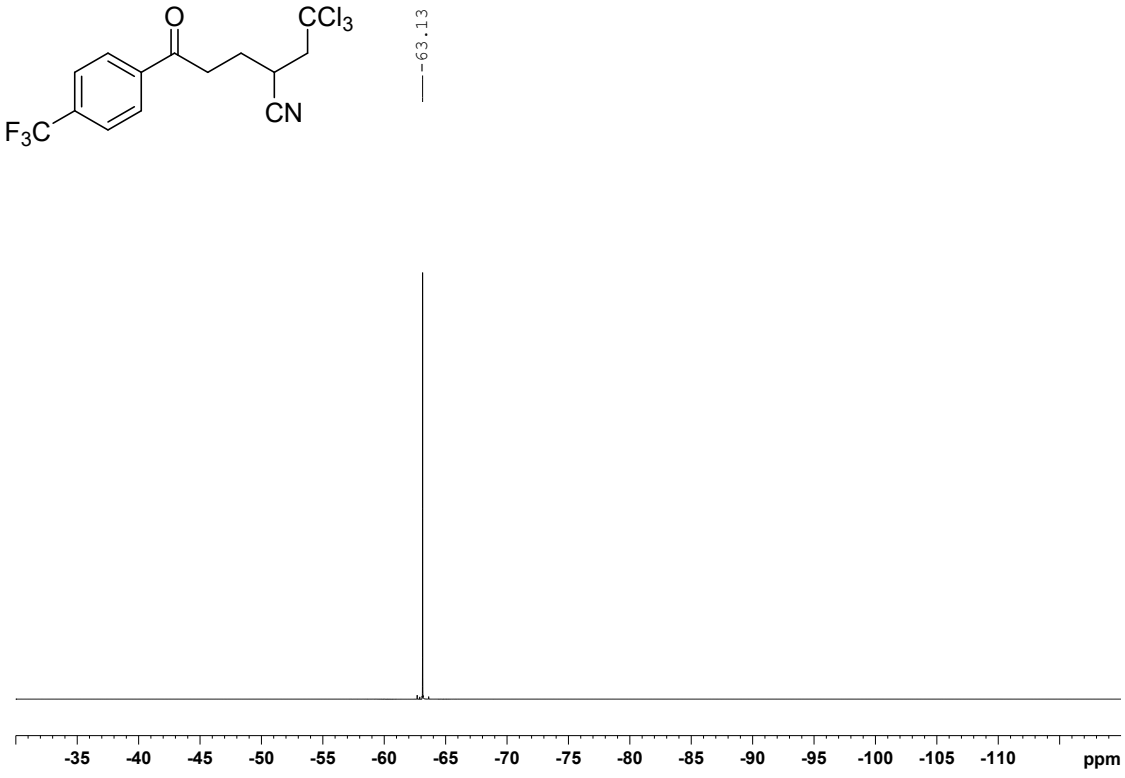
(3g) ^{1}H NMR (400 MHz, CDCl3)



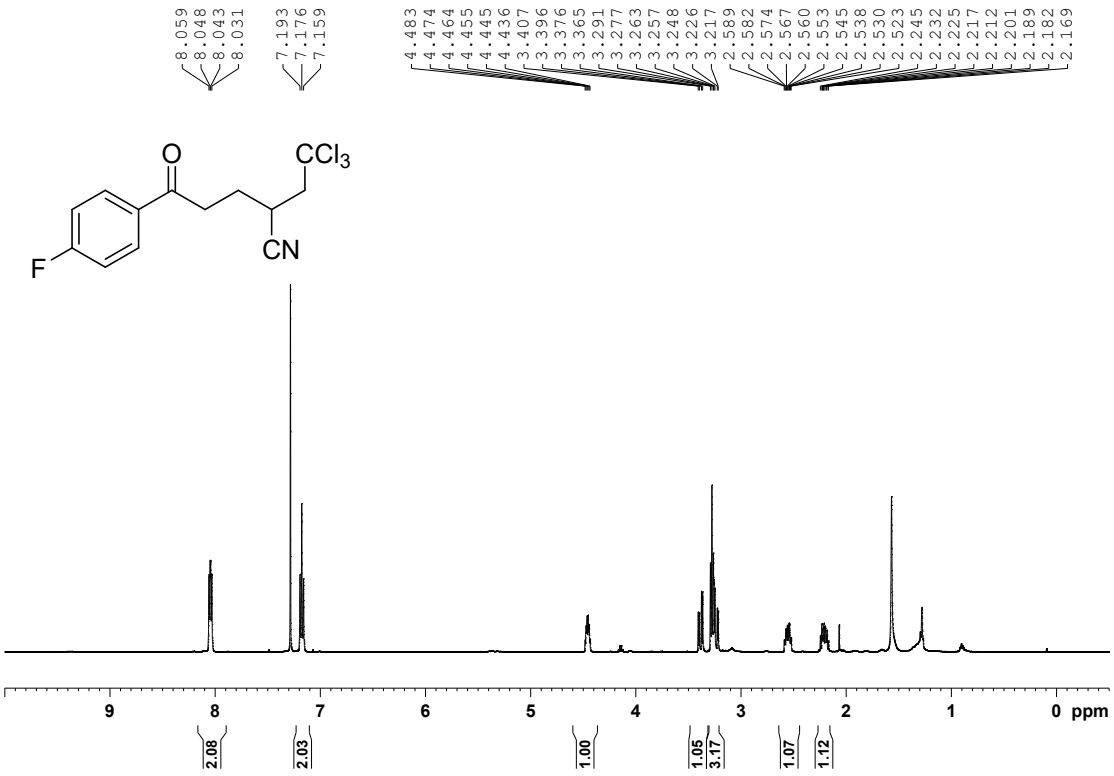
(3g) ^{13}C NMR (101 MHz, CDCl3)



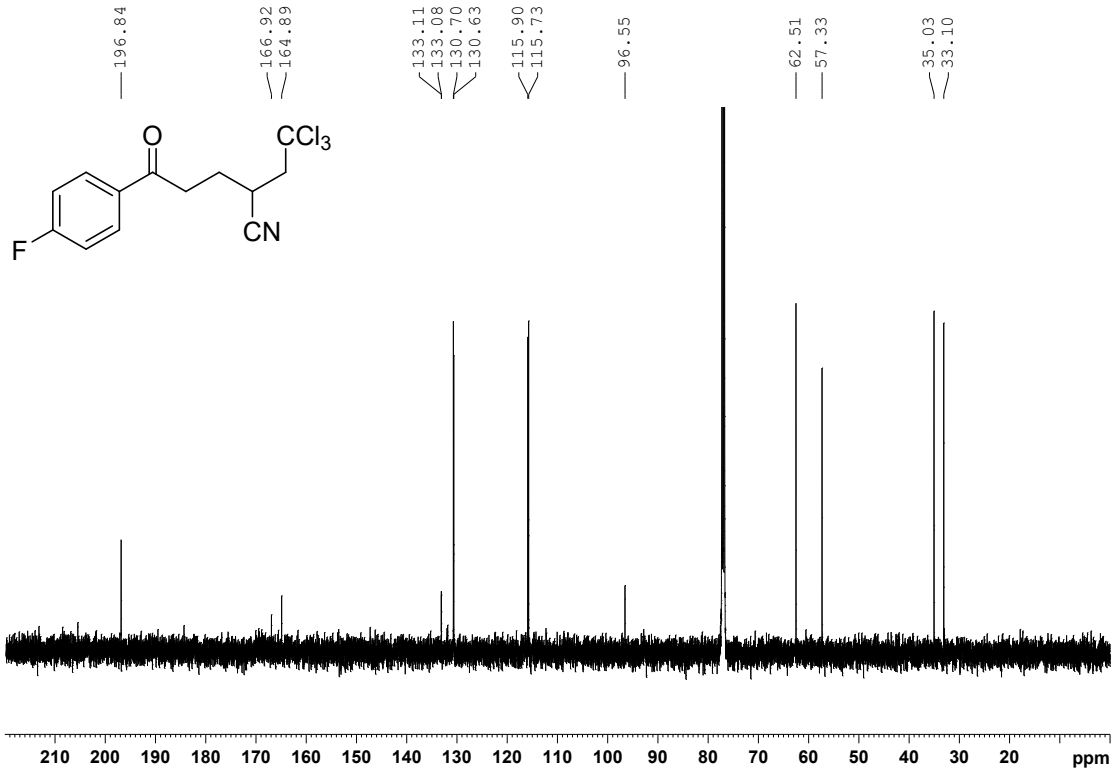
(3g) ^{19}F NMR (376 MHz, CDCl3)



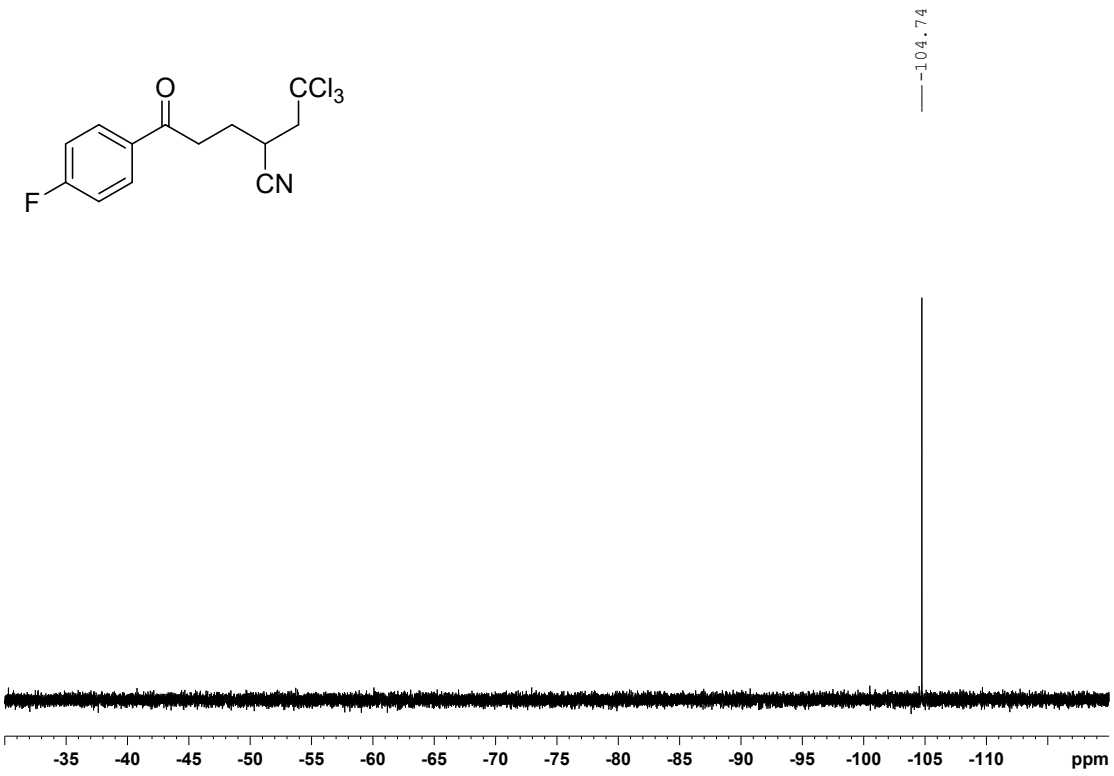
(3h) ^{1}H NMR (400 MHz, CDCl3)



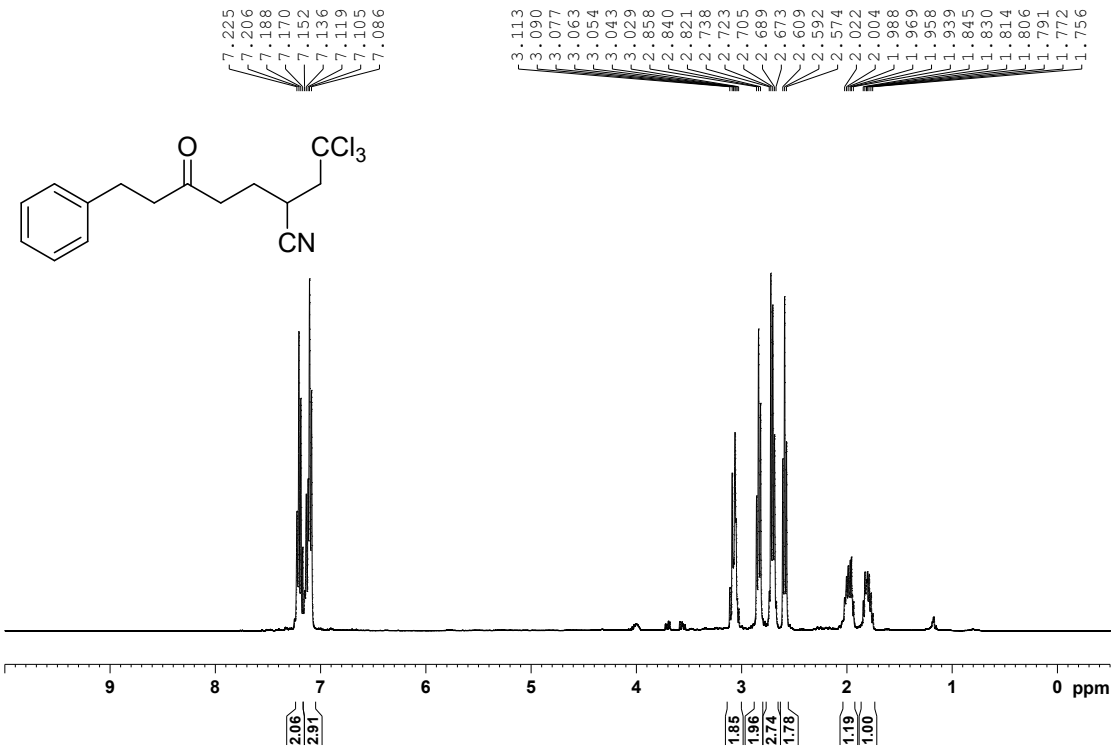
(3h) ^{13}C NMR (101 MHz, CDCl3)



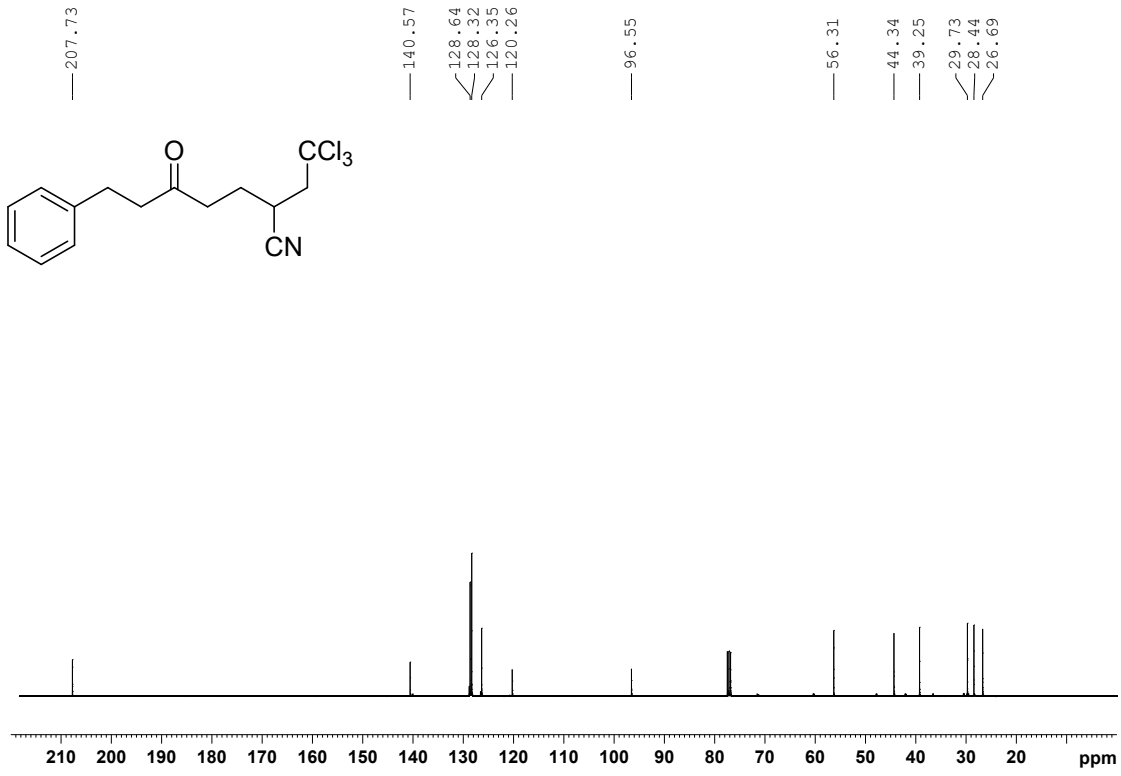
(3h) ^{19}F NMR (376 MHz, CDCl3)



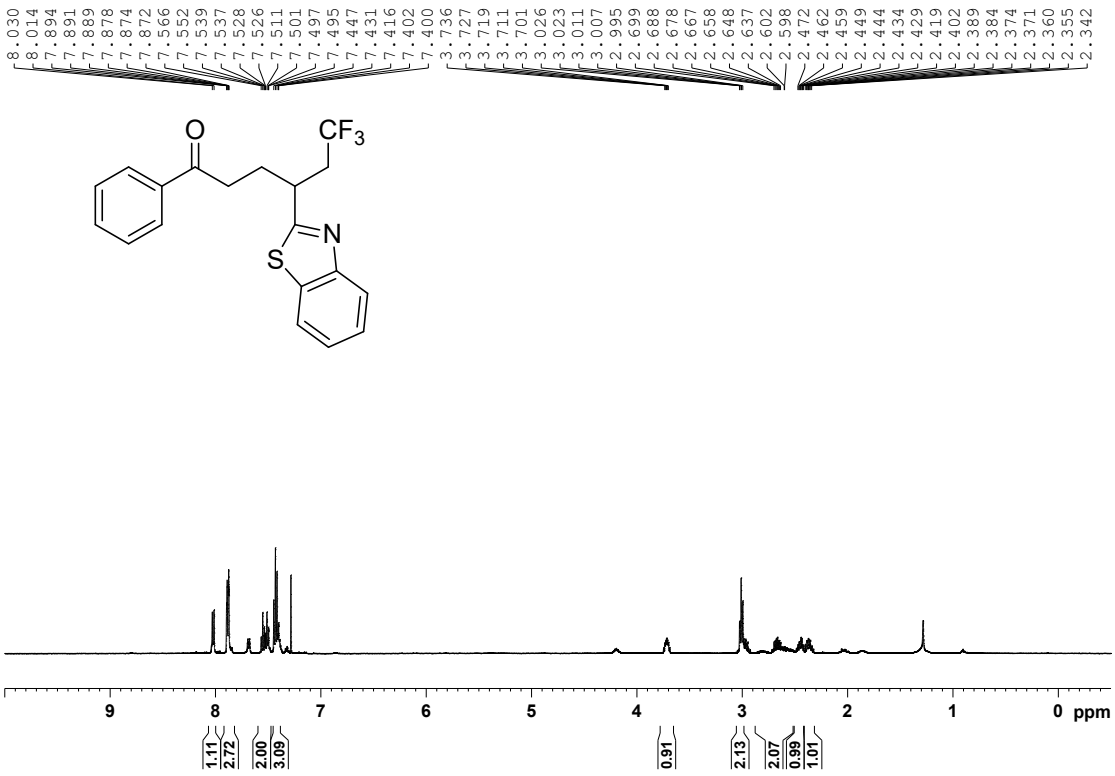
(3i) ^{1}H NMR (500 MHz, CDCl3)



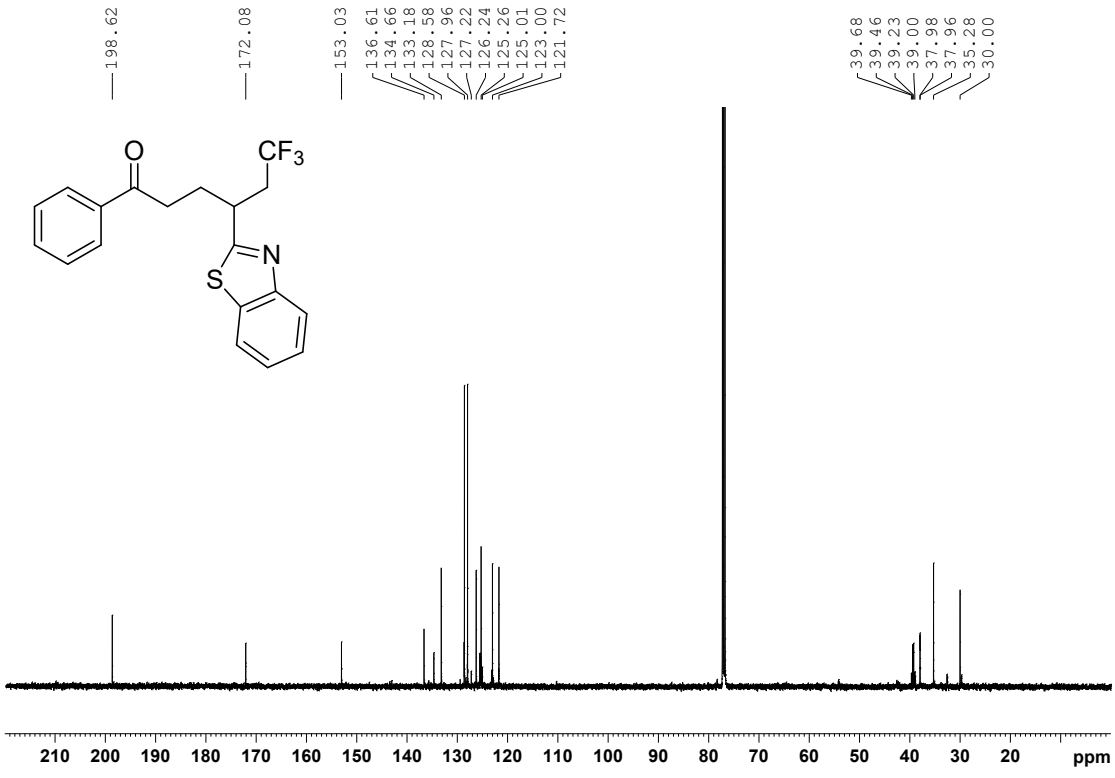
(3i) ^{13}C NMR (126 MHz, CDCl3)



(5a) ^{1}H NMR (500 MHz, CDCl3)

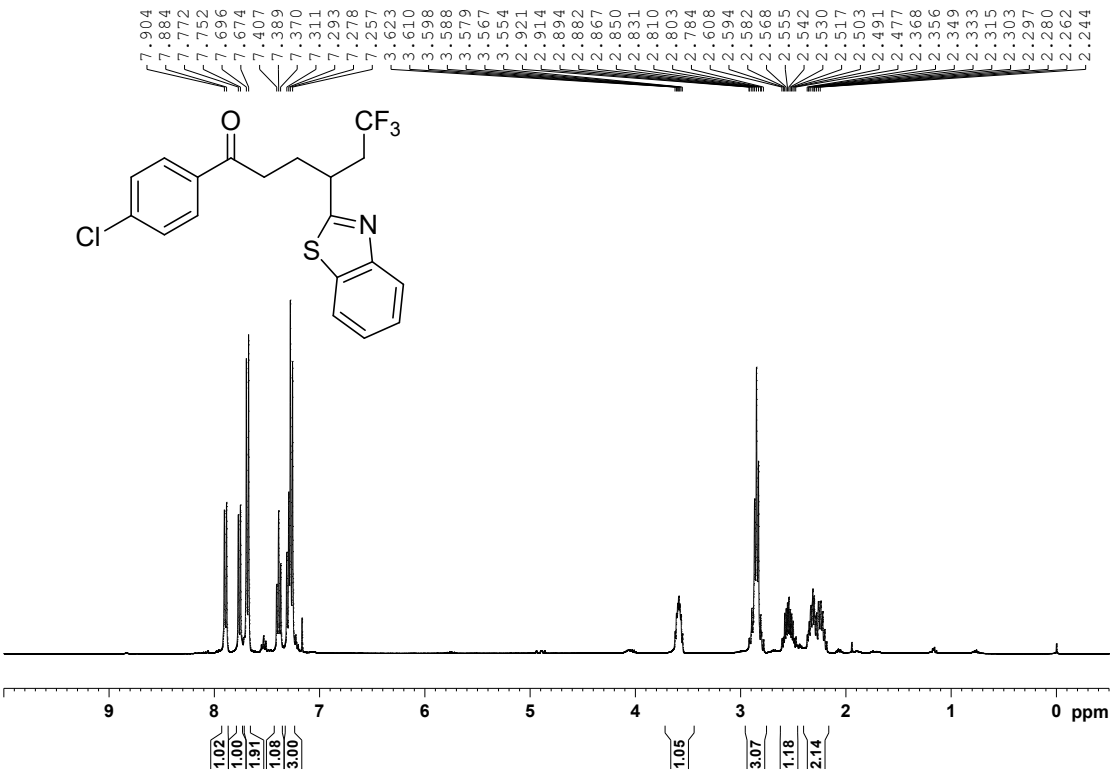


(5a) ^{13}C NMR (126 MHz, CDCl3)

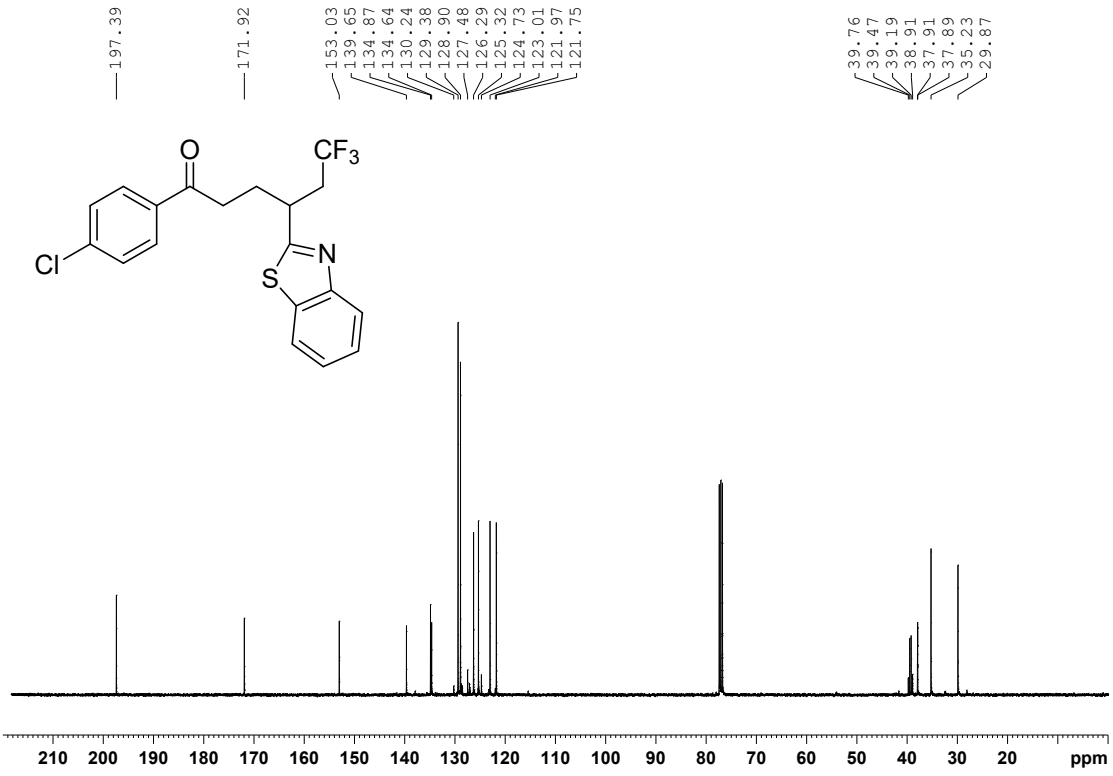


(5a) ^{19}F NMR (376 MHz, CDCl3)

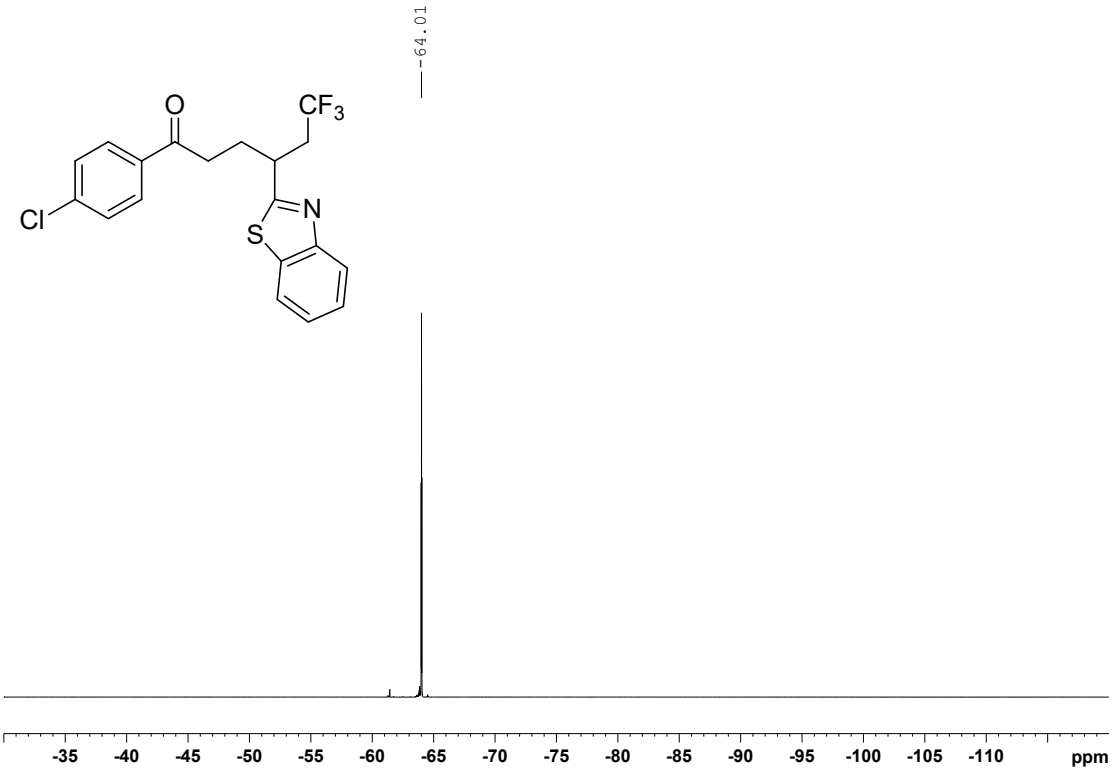
(5b) ^{1}H NMR (400 MHz, CDCl3)



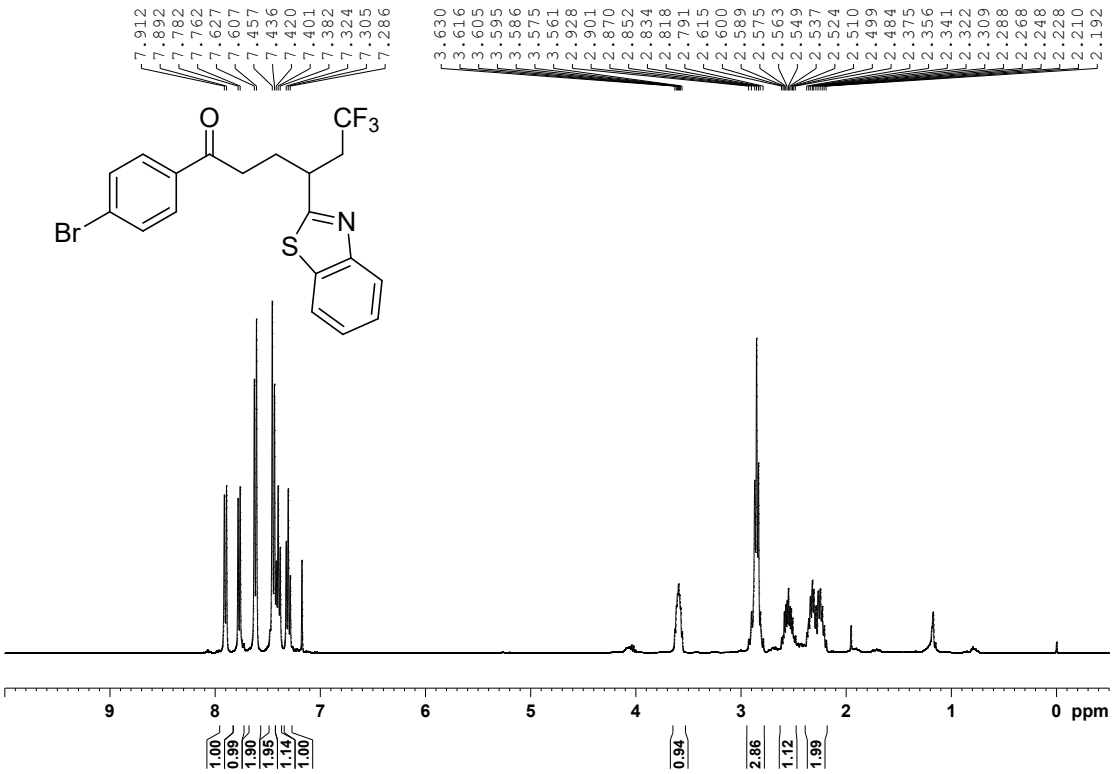
(5b) ^{13}C NMR (101 MHz, CDCl3)



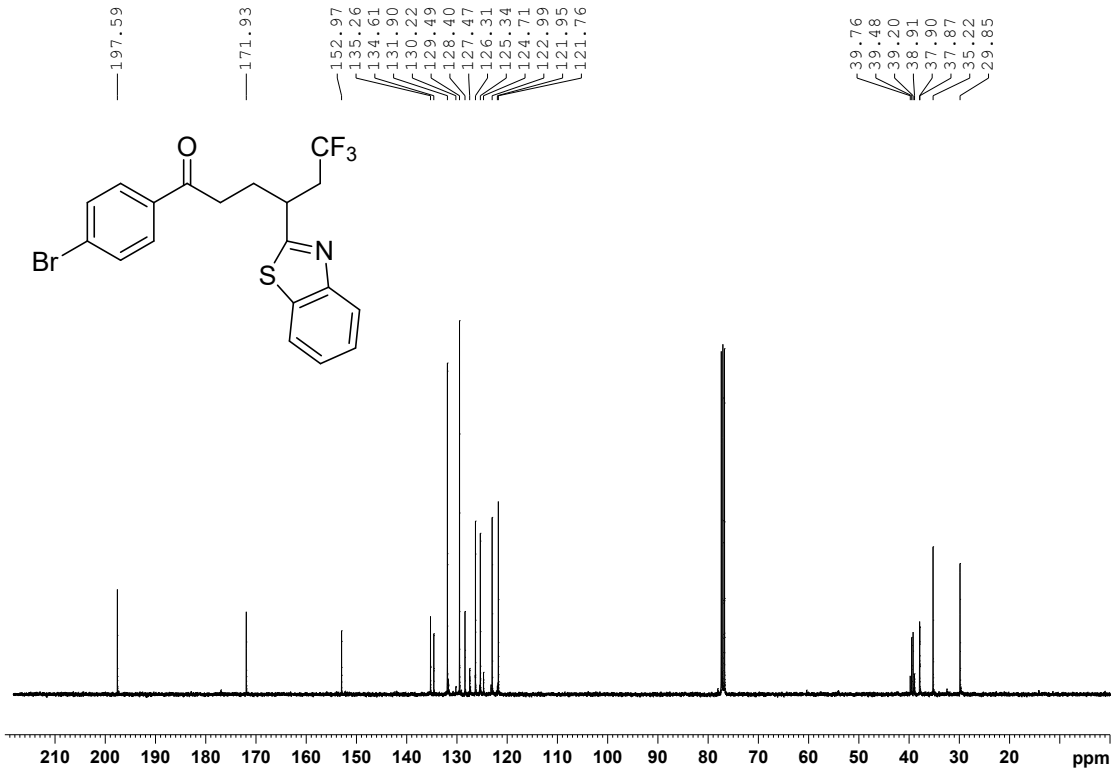
(5b) ^{19}F NMR (376 MHz, CDCl3)



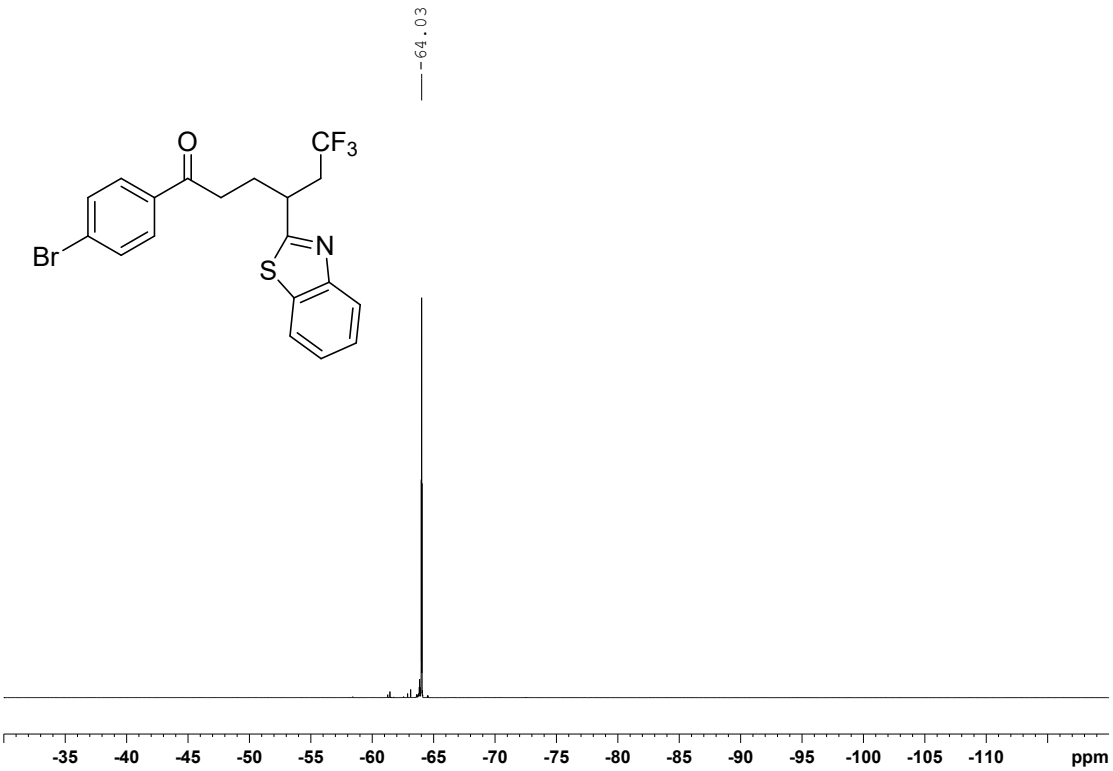
(5c) ^{1}H NMR (400 MHz, CDCl3)



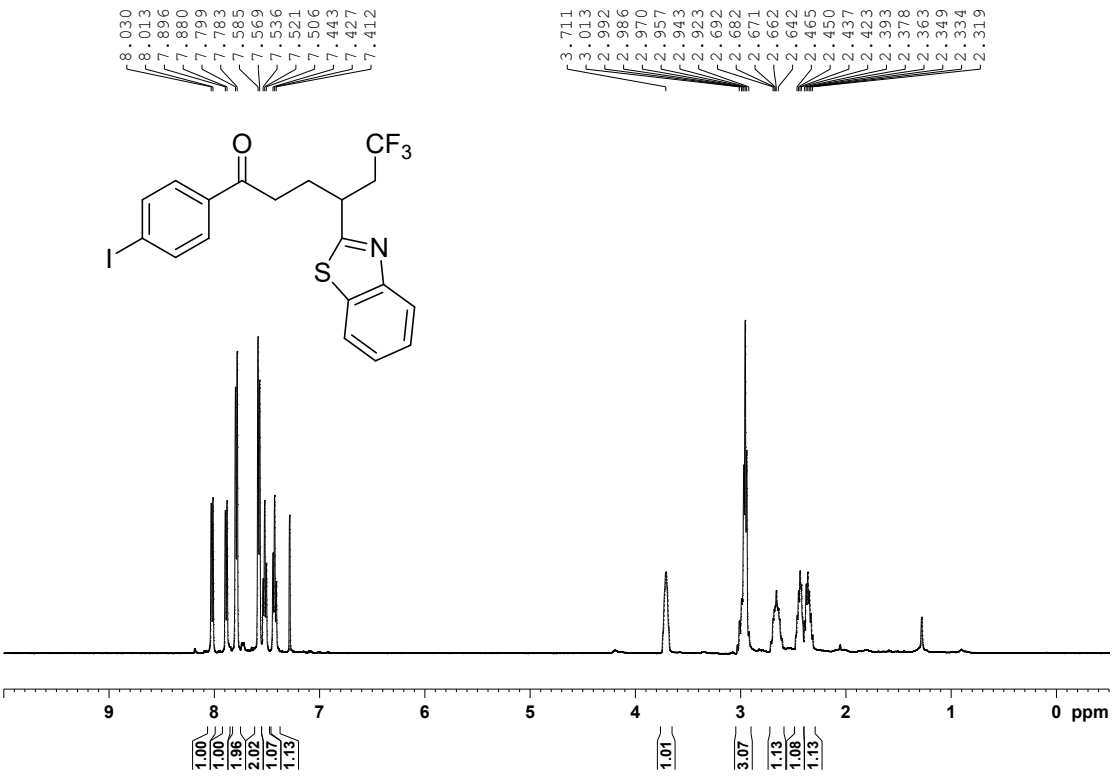
(5c) ^{13}C NMR (101 MHz, CDCl3)



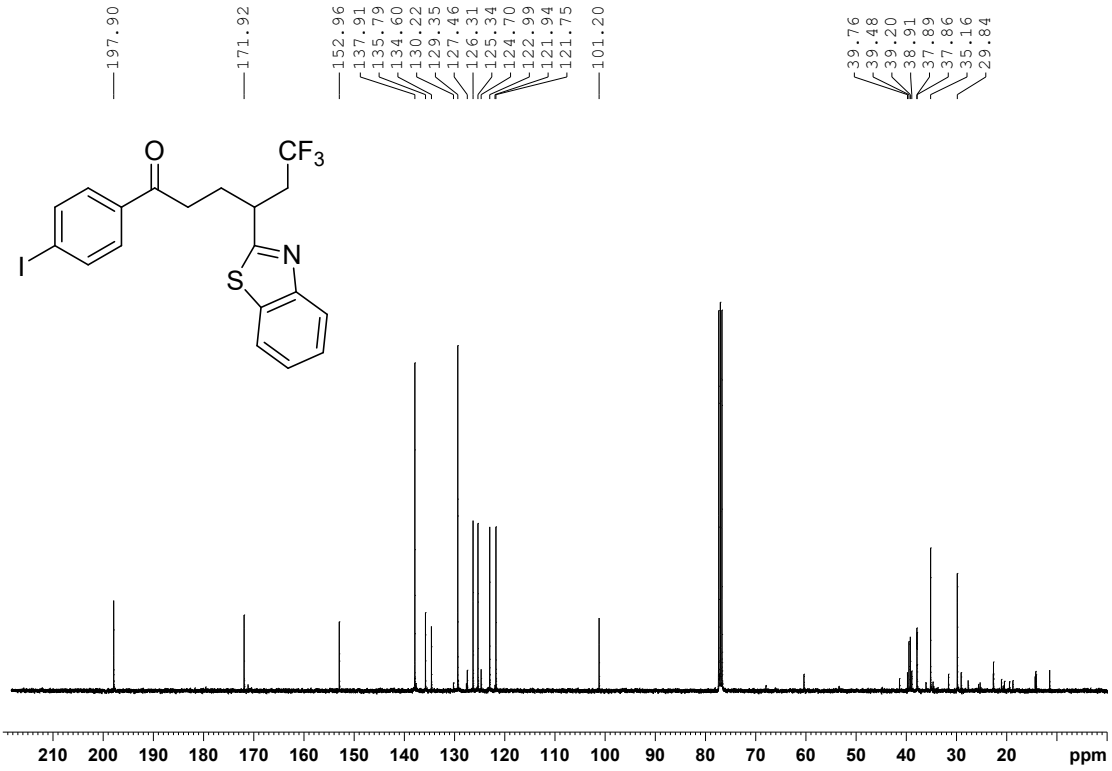
(5c) ^{19}F NMR (376 MHz, CDCl3)



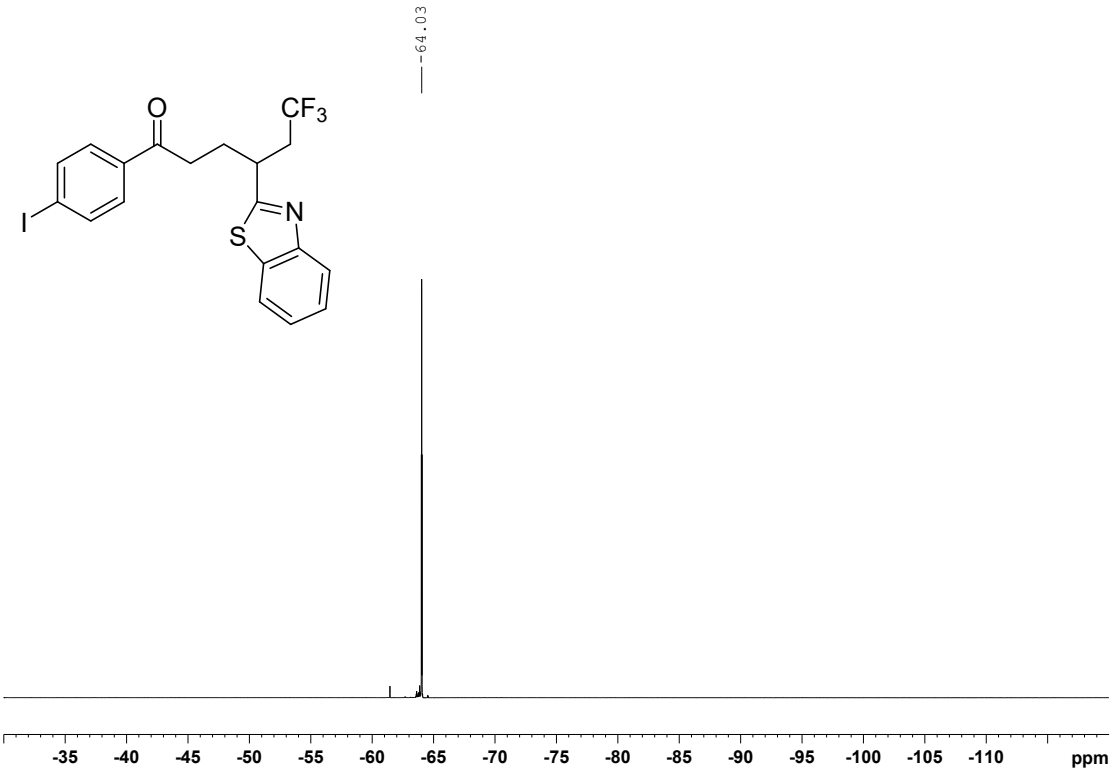
(5d) ^{1}H NMR (500 MHz, CDCl3)



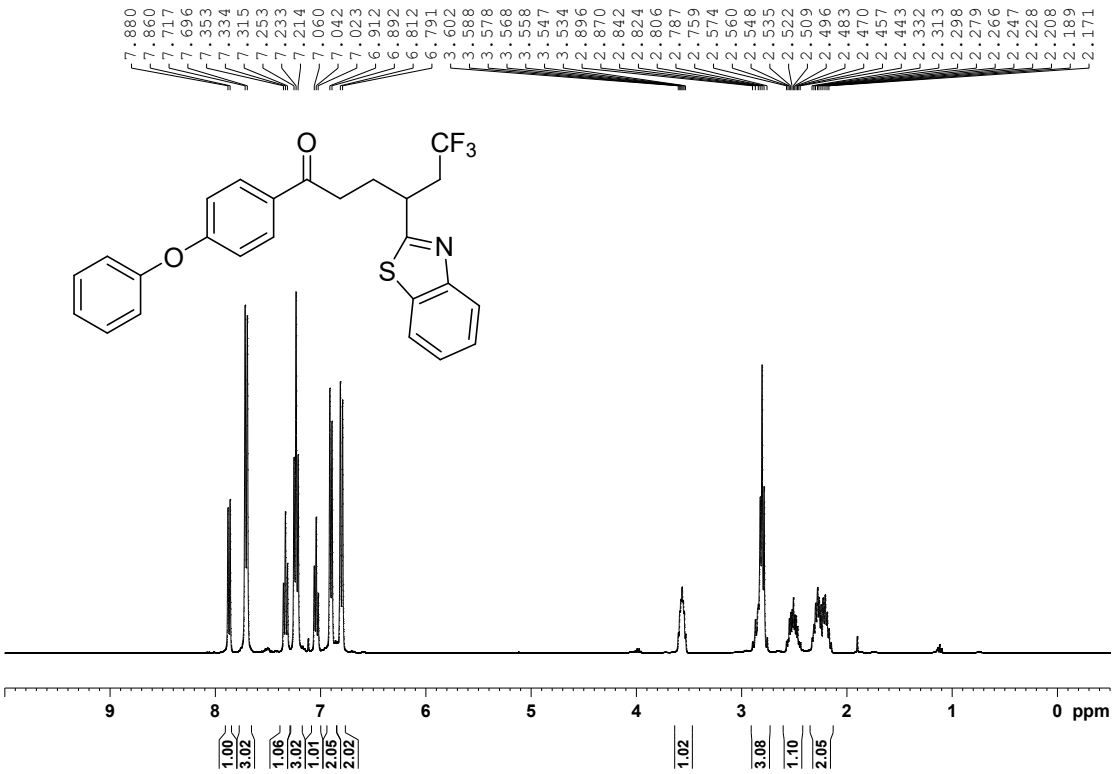
(5d) ^{13}C NMR (101 MHz, CDCl3)



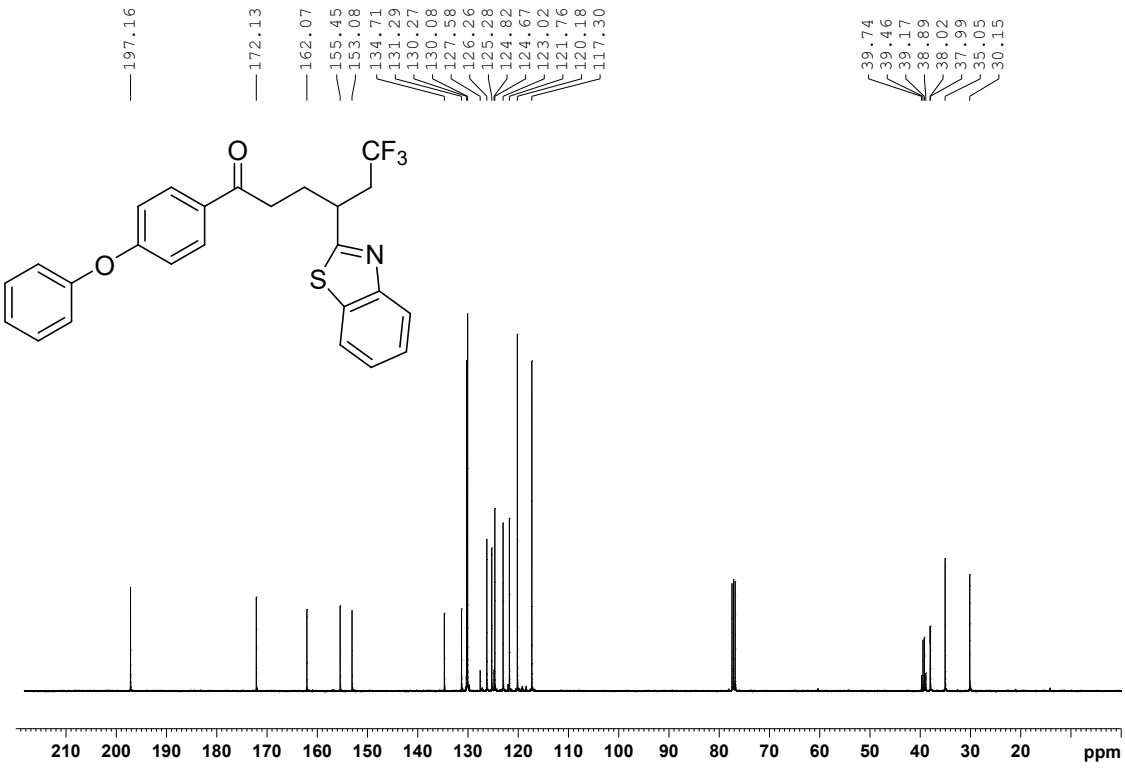
(5d) ^{19}F NMR (376 MHz, CDCl3)



(5e) ^{1}H NMR (400 MHz, CDCl3)

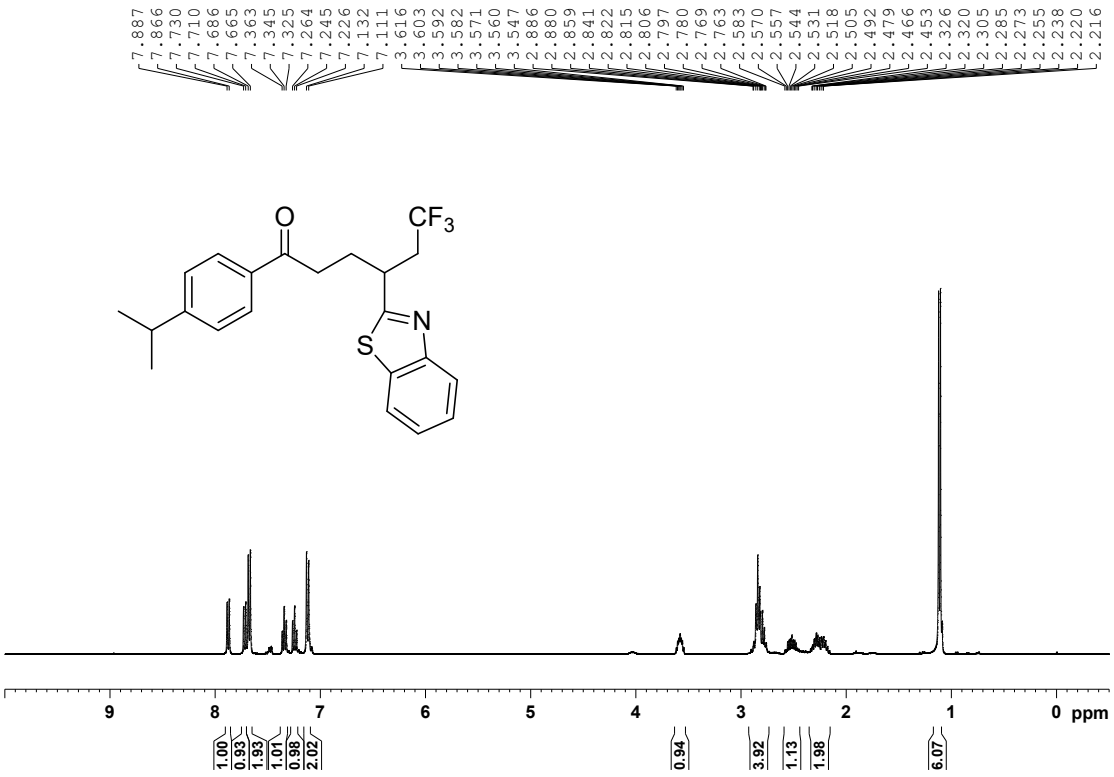


(5e) ^{13}C NMR (101 MHz, CDCl3)

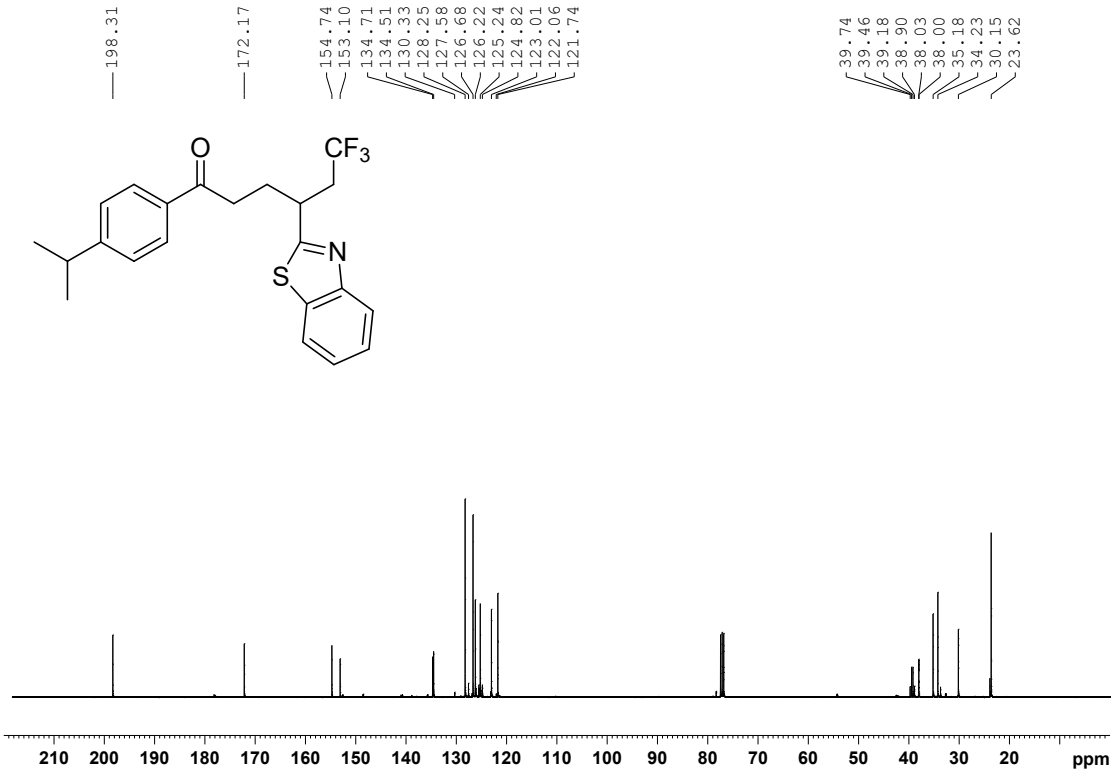


(5e) ^{19}F NMR (376 MHz, CDCl3)

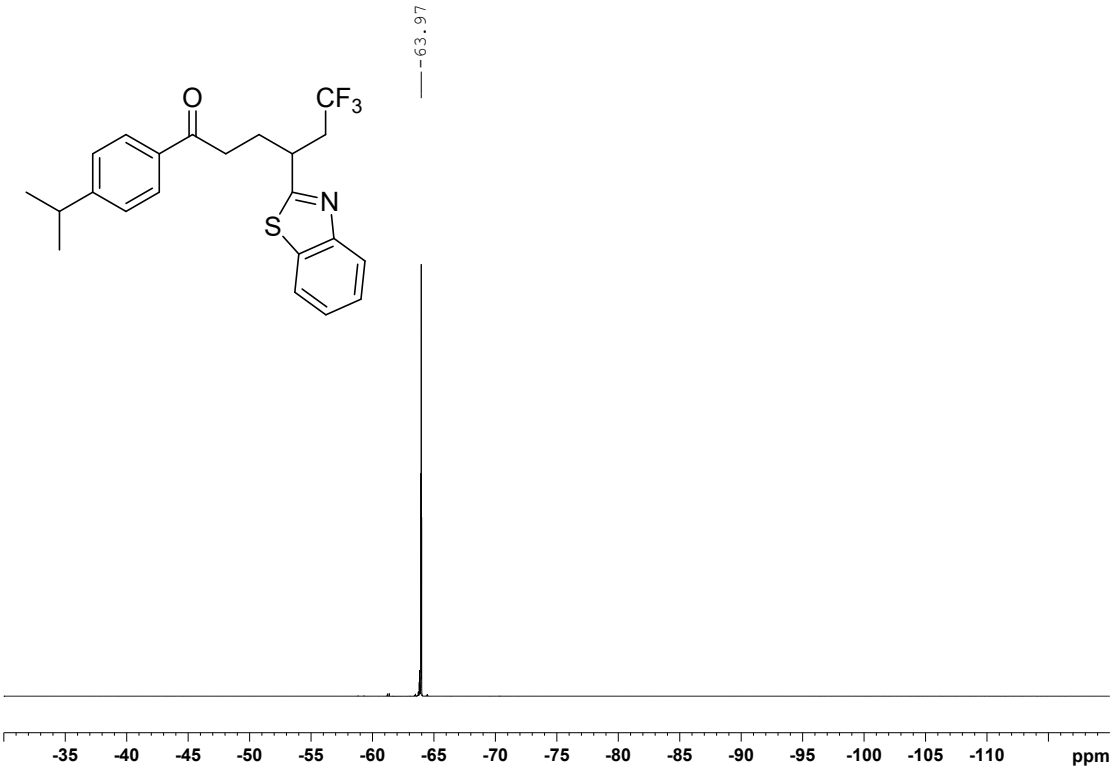
(5f) ^{1}H NMR (400 MHz, CDCl3)



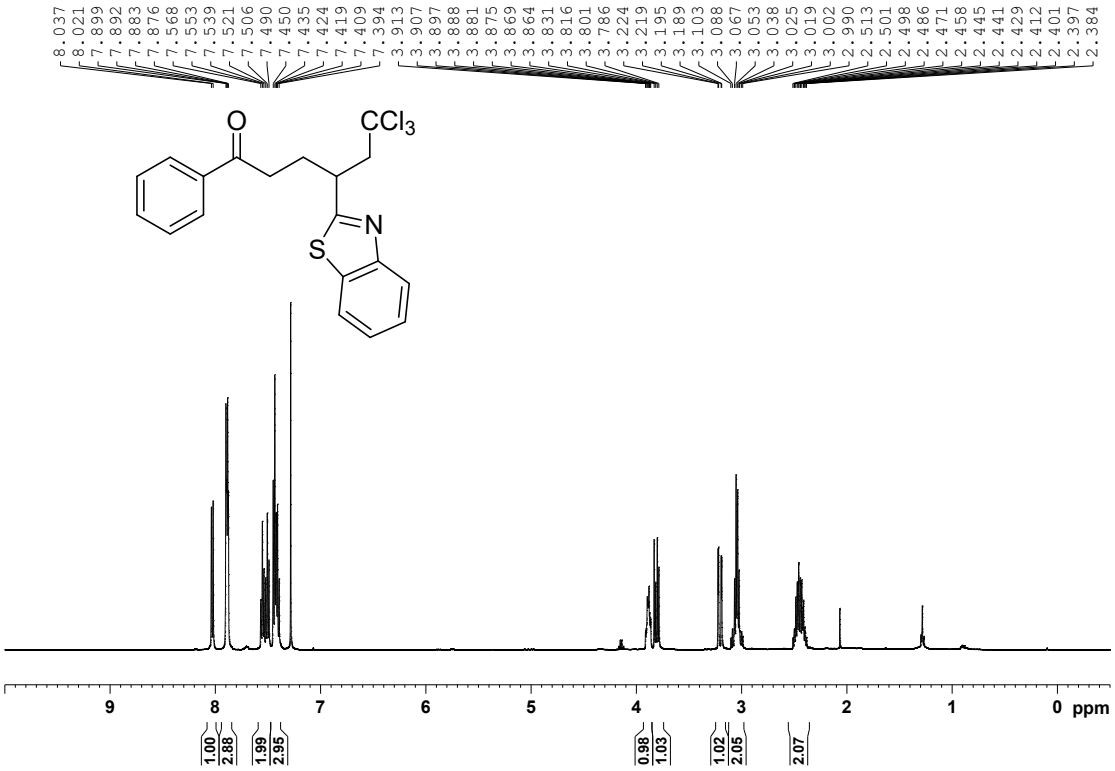
(5f) ^{13}C NMR (101 MHz, CDCl3)



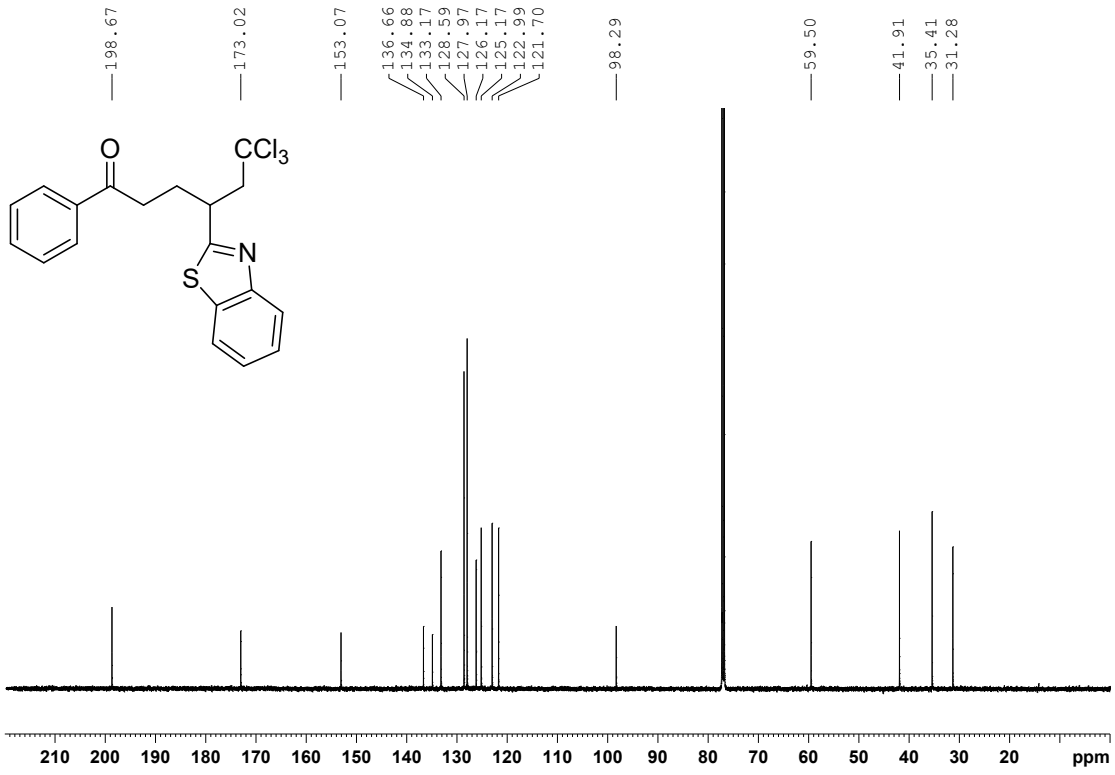
(5f) ^{19}F NMR (376 MHz, CDCl3)



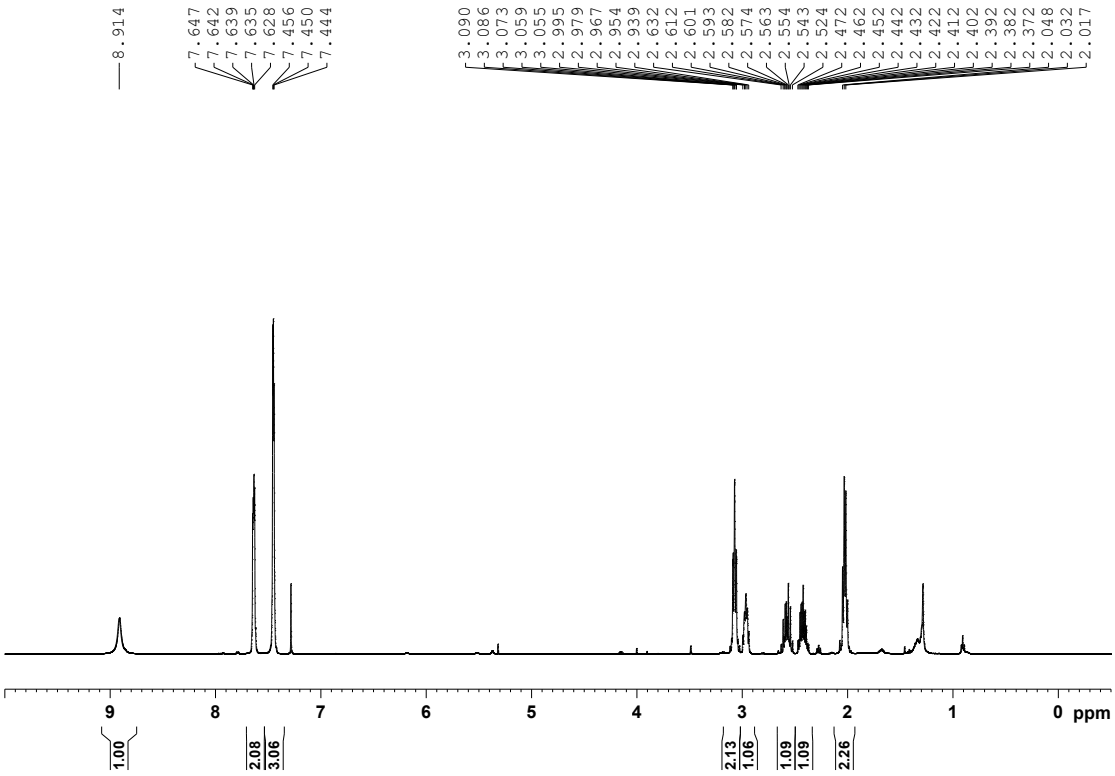
(6a) ^{1}H NMR (500 MHz, CDCl3)



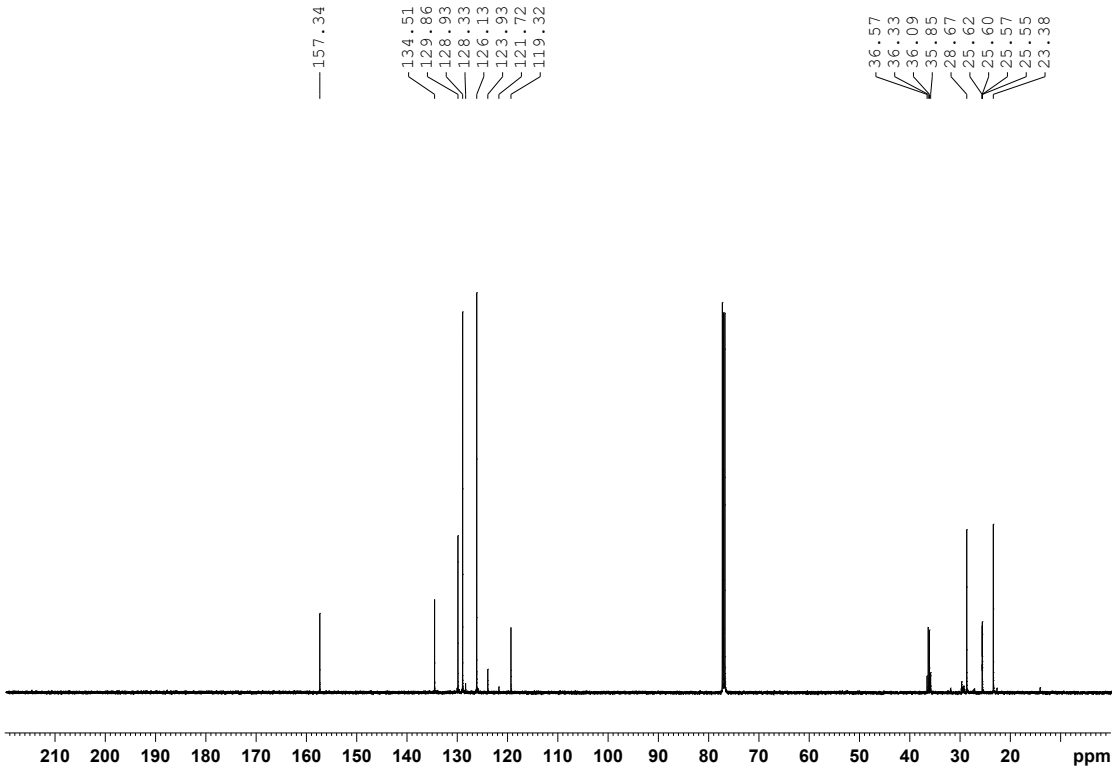
(6a) ^{13}C NMR (126 MHz, CDCl3)



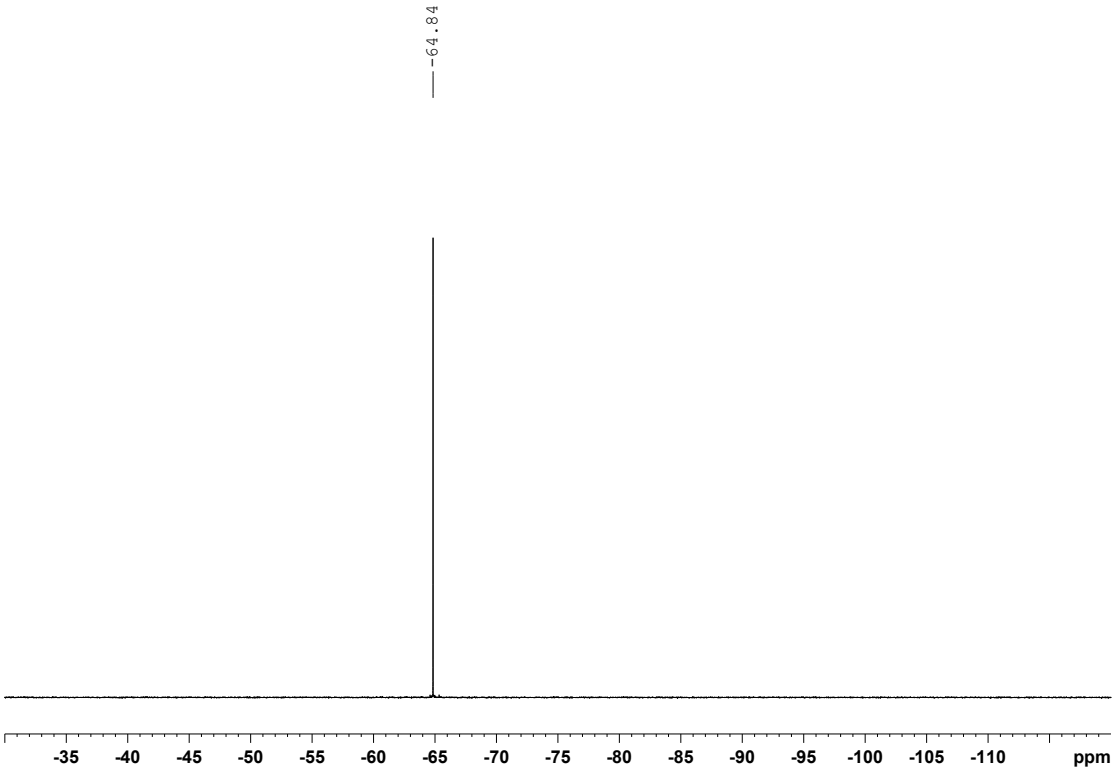
(7a) ^{1}H NMR (500 MHz, CDCl3)



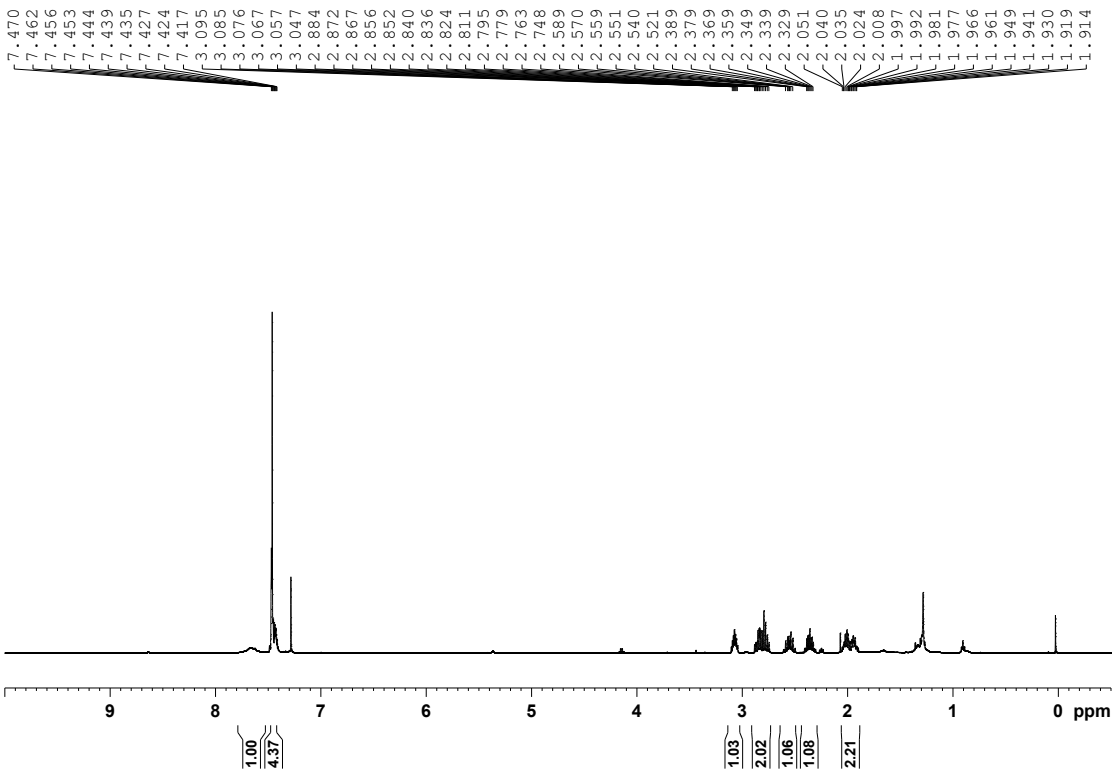
(7a) ^{13}C NMR (126 MHz, CDCl3)



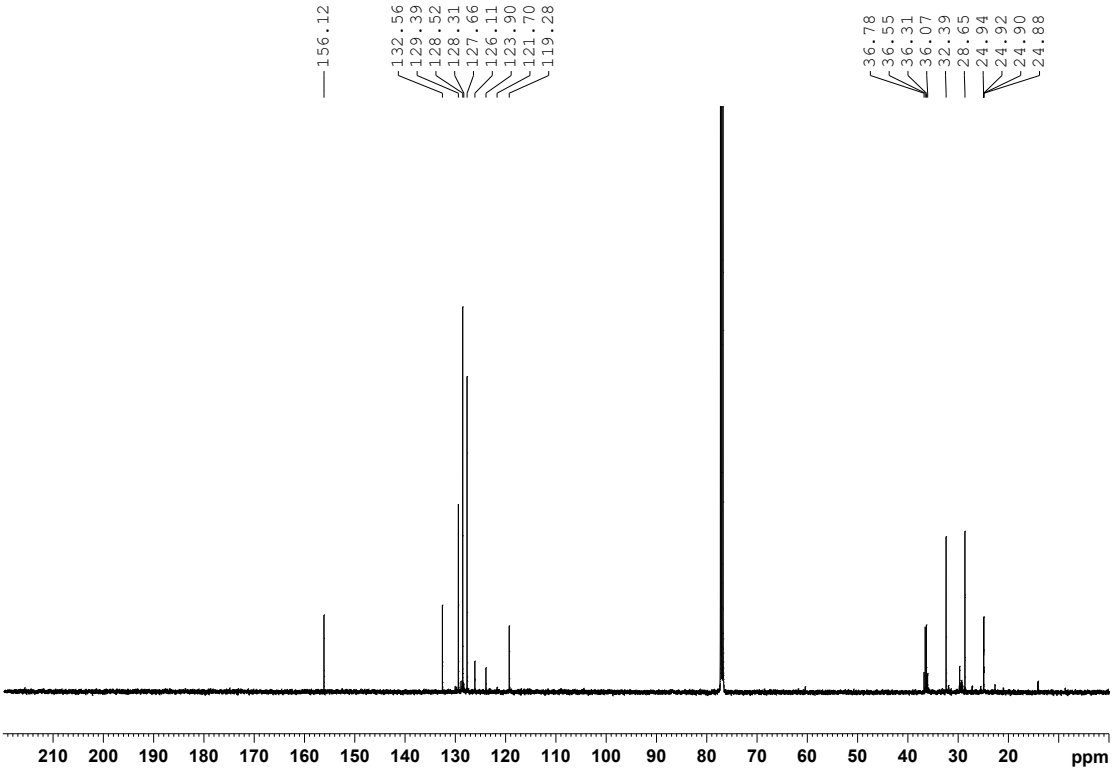
(7a) ^{19}F NMR (376 MHz, CDCl3)



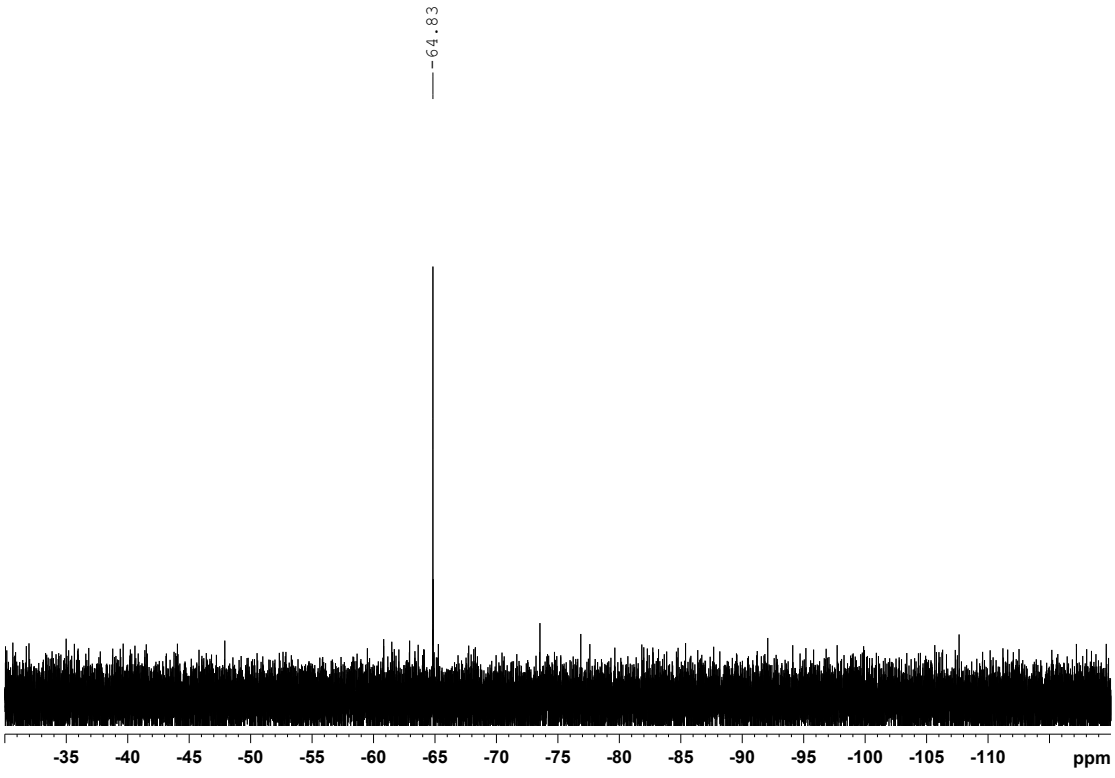
(7b) ^{1}H NMR (500 MHz, CDCl3)



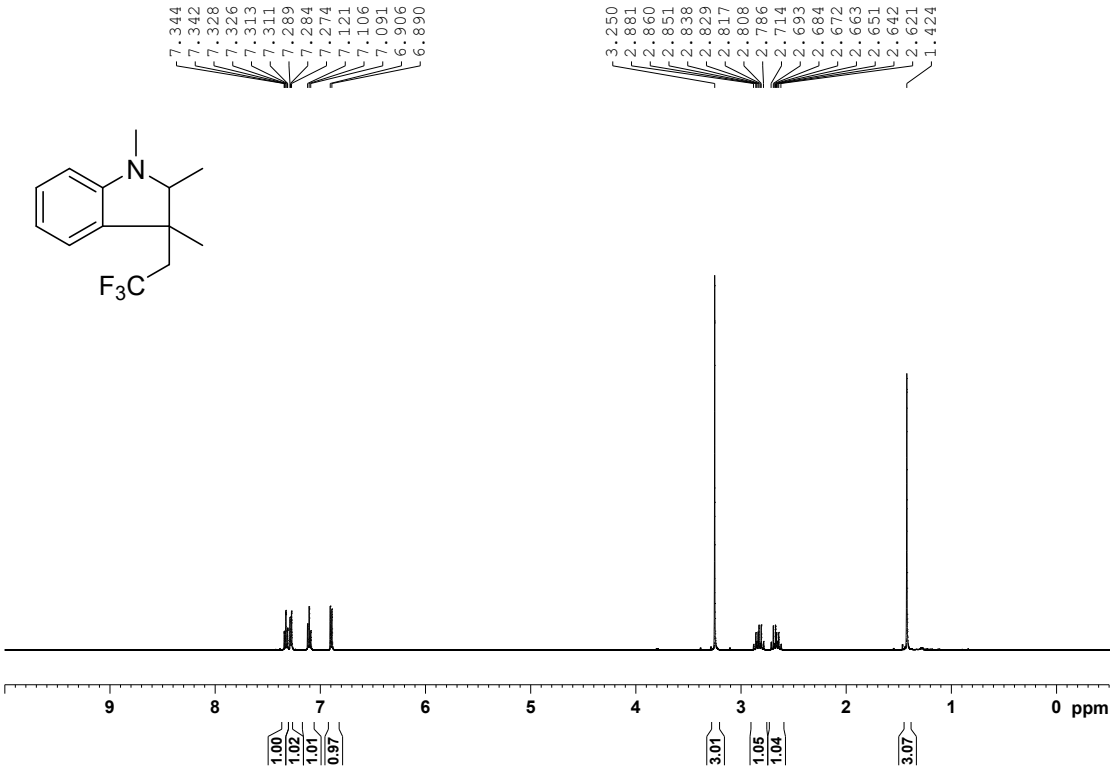
(7b) ^{13}C NMR (126 MHz, CDCl3)



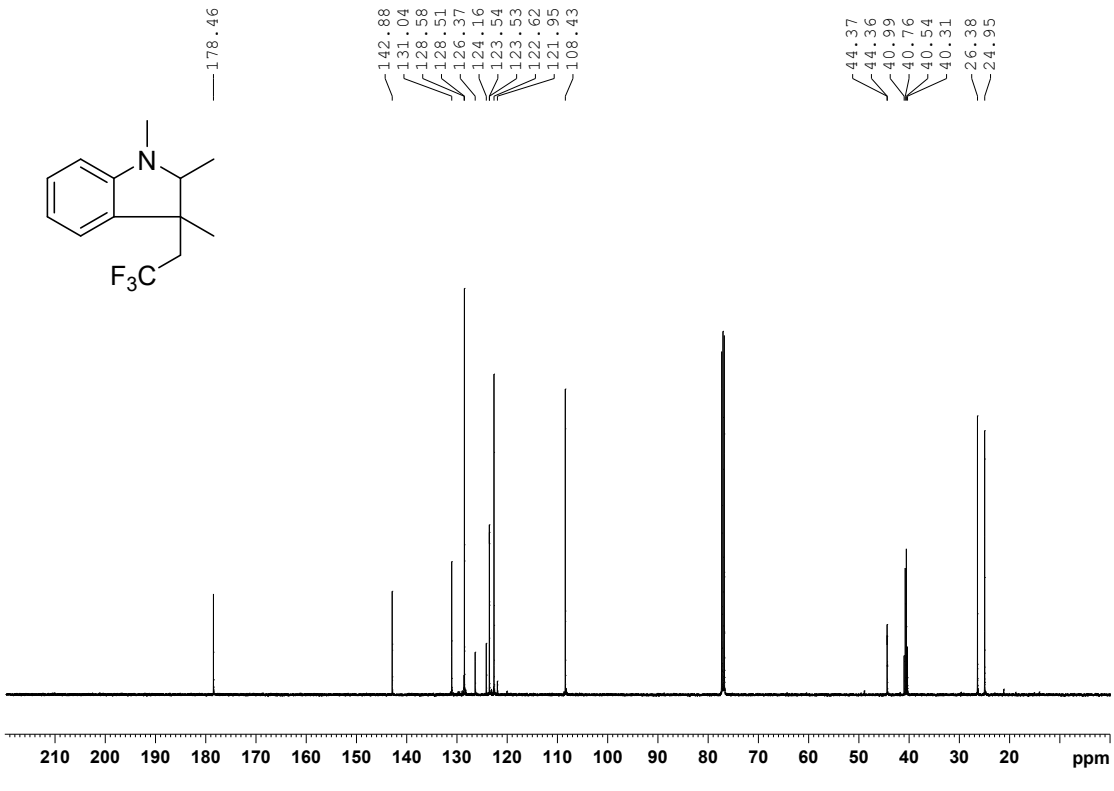
(7b) ^{19}F NMR (376 MHz, CDCl3)



(8a) ^{1}H NMR (500 MHz, CDCl3)



(8a) ^{13}C NMR (126 MHz, CDCl3)



(8a) ^{19}F NMR (376 MHz, CDCl3)