Electronic Supplementary Material (ESI) for Chemical Communications

Acyl hydrazides as acyl donors for the synthesis of diaryl and aryl alkyl ketones

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General Experimental

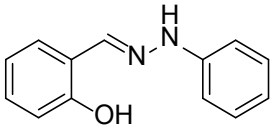
All reagents were purchased from Aldrich or AlfaAesar and were used as received without further purification unless otherwise stated. All reactions were carried out with HPLC gradient grade water (demineralised) purchased from Fisher Scientific. All hydroacylation reactions were carried out in carousel tubes (15 cm × 2 cm) equipped with an octagon-shaped magnetic stirrer bar (12.7 mm × 3 mm). Where described below, petrol refers to petroleum ether (b.p. 40-60 °C). All reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates (254 μm). Flash column chromatography was carried out with Kiesegel 60M 0.04/0.063 mm (200-400 mesh) silica gel. ^{1}H NMR spectra were recorded at 400 MHz, 500 MHz and 600 MHz and ^{13}C NMR at 100 MHz, 125 MHz and 150 MHz on Bruker AMX400, AMX500 and AMX600 spectrometers. ^{19}F NMR spectra were recorded at 376 MHz on Bruker AMX400 at ambient temperature unless otherwise stated, in $CDCl_3$ or d_6-DMSO (see below). The chemical shifts (δ) for ^{1}H and ^{13}C are quoted relative to residual signals of the solvent on the ppm scale. Coupling constants (*J* values) are reported in Hertz (Hz) and are H-H coupling constants unless otherwise stated. Signal multiplicities in ^{13}C NMR were determined using the distortionless enhancement by phase transfer (DEPT) spectral editing technique. Where applicable, only the peaks for the major rotamers of acyl hydrazides and ketones are assigned in the ^{1}H and ^{19}F NMR spectra. Mass spectra were obtained on a VG70-SE mass spectrometer. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode. Melting points were measured with a Gallenkamp apparatus and are uncorrected.

General method for the titration of Grignard reagents

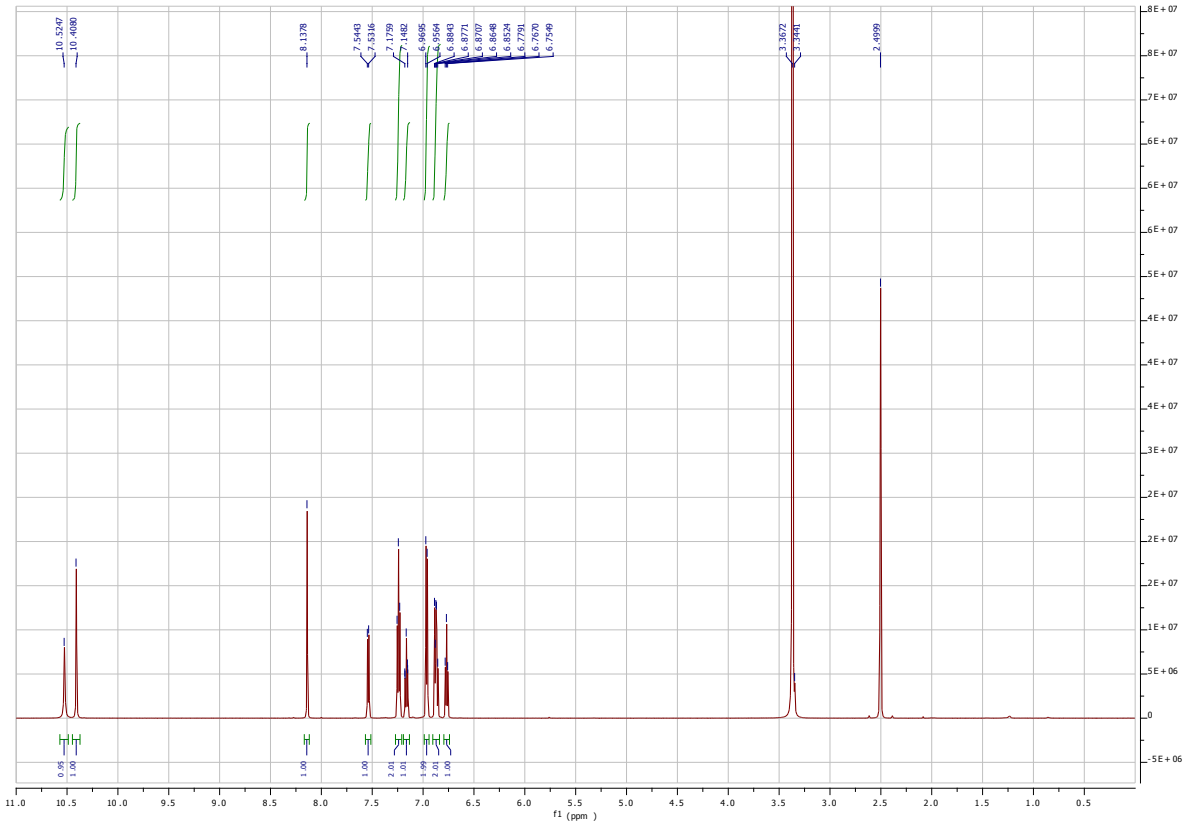
Grignard reagents were titrated against salicylaldehydephenylhydrazone. An accurately weighed sample of salicylaldehydephenylhydrazone was dissolved in dry THF (10 mL) and

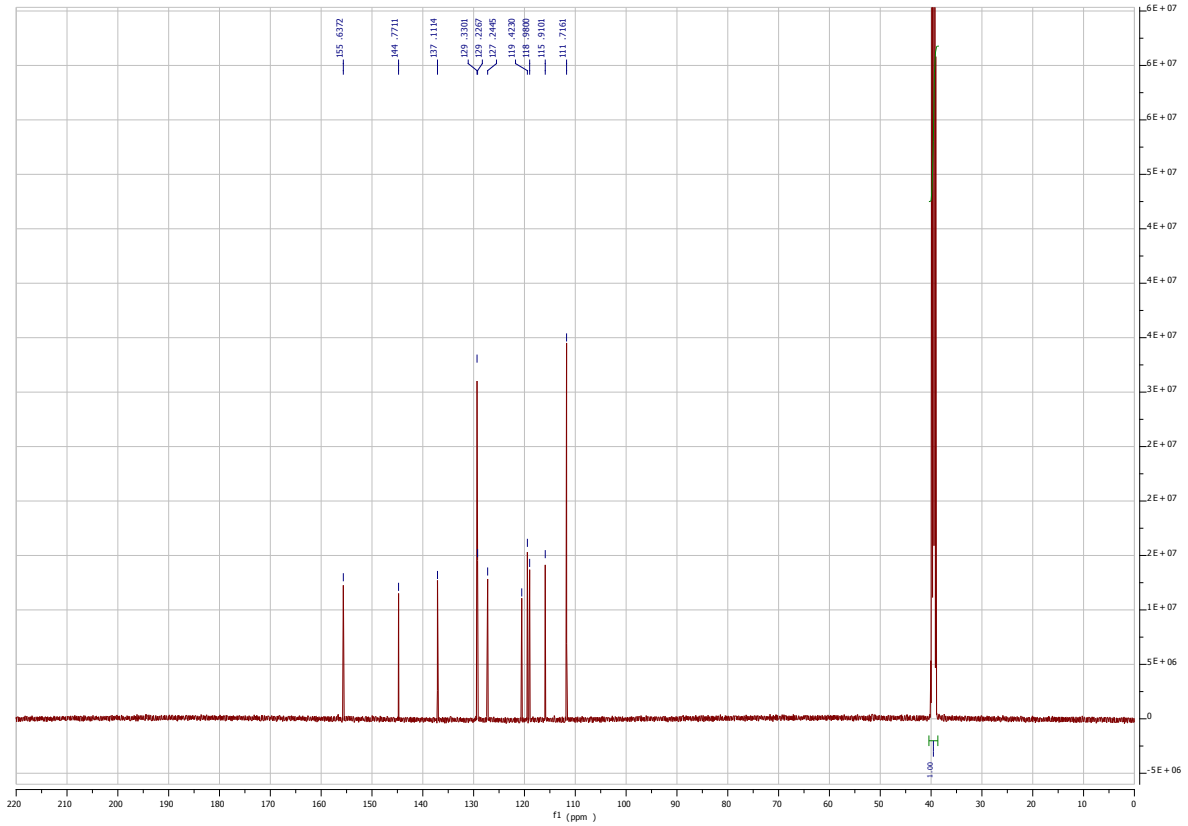
stirred at room temperature under an inert nitrogen atmosphere. Grignard reagent was carefully added, dropwise using a gas tight syringe. A yellow color (mono anion) formed initially, the end point was apparent from the intense orange color change. Experiments were performed in triplicate.

Salicylaldehydephenylhydrazone[1]



Phenylhydrazine (2.92 g, 27.0 mmol, 1 eq) was dissolved in 95% ethanol (10 mL) and stirred while salicylaldehyde (3.30 g, 27.0 mmol, 1 eq) in 95% ethanol (15 mL) was added in one portion. A white precipitate formed after 1 min. The reaction was stirred for 30 min and then cooled to –15 °C. The greenish solid was collected by vacuum filtration and washed with ice-cold ethanol to afford the product as a light green solid (4.60 g, 21.7 mmol, 80%). **^{1}H NMR (600 MHz, d_6-DMSO)** δ 10.52 (s, 1H), 10.41 (s, 1H), 8.14 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.8 Hz, 2H), 7.18-7.16 (m, 1H), 6.97 (d, J = 7.9 Hz, 2H), 6.88-6.75 (m, 2H), 6.76 (t, J = 7.3 Hz, 1H); **^{13}C NMR (150 MHz, d_6-DMSO)** δ 155.6 (C), 144.8 (C), 137.1 (CH), 129.3 (CH), 129.2 (CH), 127.2 (CH), 120.5 (C), 119.4 (CH), 119.0 (CH), 115.9 (CH), 111.7 (CH); **m.p.** 139-141 °C.

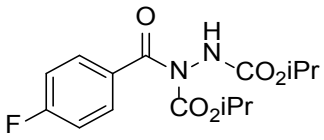




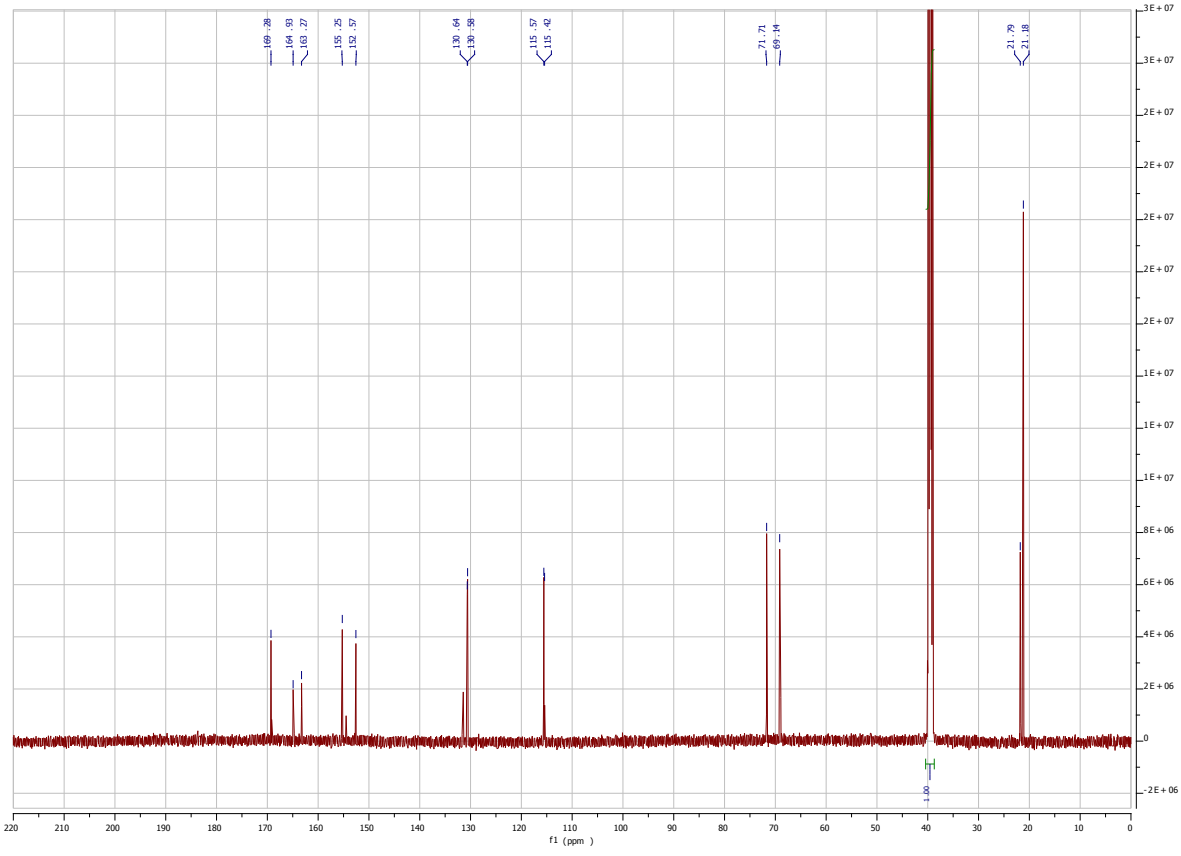
General Procedure for the hydroacylation of DIAD with various aldehydes

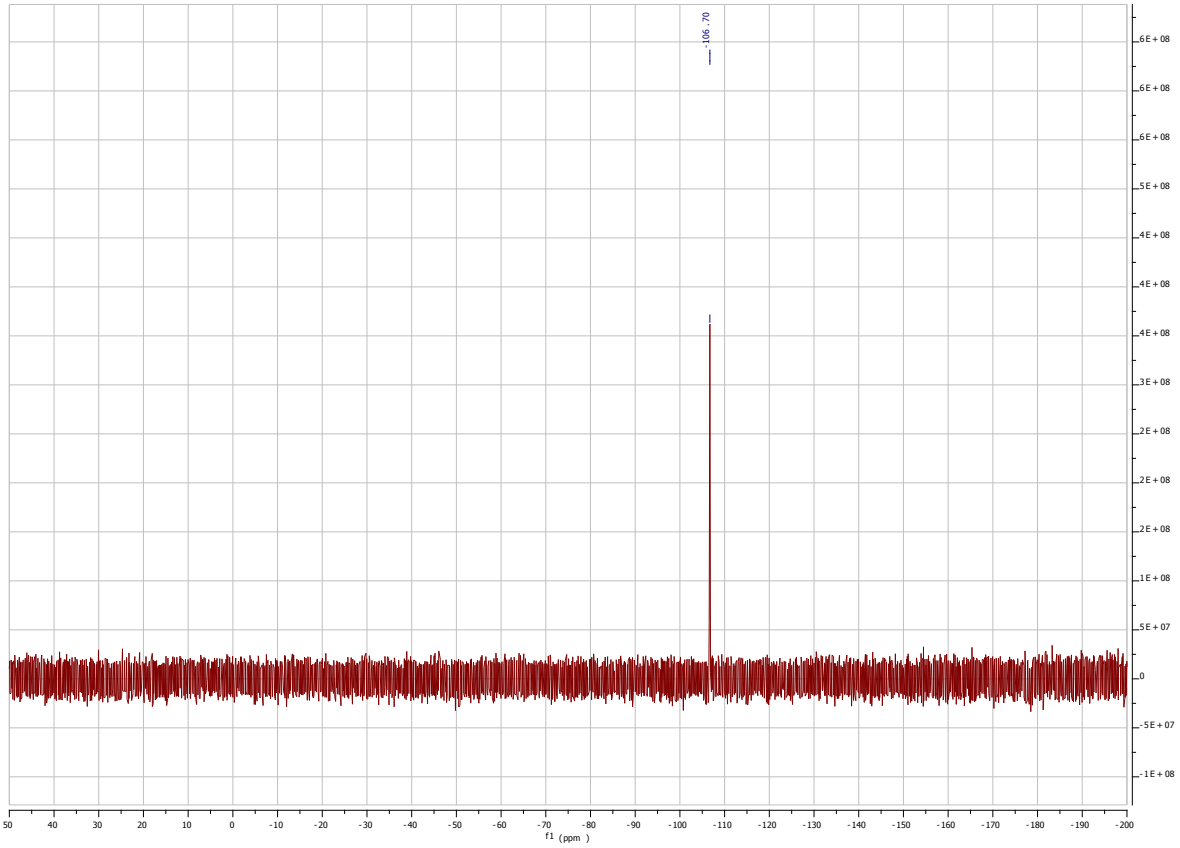
Aldehyde (1.0 mmol) was added to a mixture of azodicarboxylate (1.2 mmol) and H_2O (500 µL) and the reaction mixture stirred at 300 rpm at 21 °C in a stoppered carousel tube for 96 h. The solvent was removed *in vacuo* and the product purified as described below.

Diisopropyl 1-(4-fluorobenzoyl)hydrazine-1,2-dicarboxylate[2] (1a)

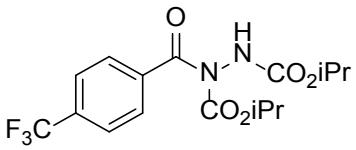


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(4-fluorobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (245 mg, 0.75 mmol, 75%). **^{1}H NMR (400 MHz, 100 °C, d_6-DMSO)** δ 9.43 (br s, NH, 1H), 7.68-7.64 (m, 2H), 7.29-7.24 (m, 2H), 4.89-4.80 (m, 2H), 1.22 (d, J = 6.2 Hz, 6H), 1.13 (d, J = 6.3 Hz, 6H); **^{13}C NMR (150 MHz, d_6-DMSO)** δ 169.3 (C), 164.9 (CH), 164.1 (d, $J_{C\text{-}F}$ = 249.0 Hz, C), 155.3 (C), 152.6 (C), 131.5 (CH), 130.6 (d, $J_{C\text{-}F}$ = 9.0 Hz, CH), 115.5 (d, $J_{C\text{-}F}$ = 9.0 Hz, CH), 71.7 (CH), 69.1 (CH), 21.8 (CH_3), 21.2 (CH_3); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -106.7 (s, 1F); **IR** (thin film) 3379, 1709, 1603, 1259, 1103 cm^{-1}; **LRMS (CI)** 327 (40, $[M+H]^+$), 307 (30), 241 (70), 227 (33), 199 (100); **HRMS (CI)** calcd. for $C_{15}H_{20}FN_2O_5$ $[M+H]^+$ 327.1356, observed 327.1355; **m.p.** 100-102 °C (recrystallized from *n*-heptane).

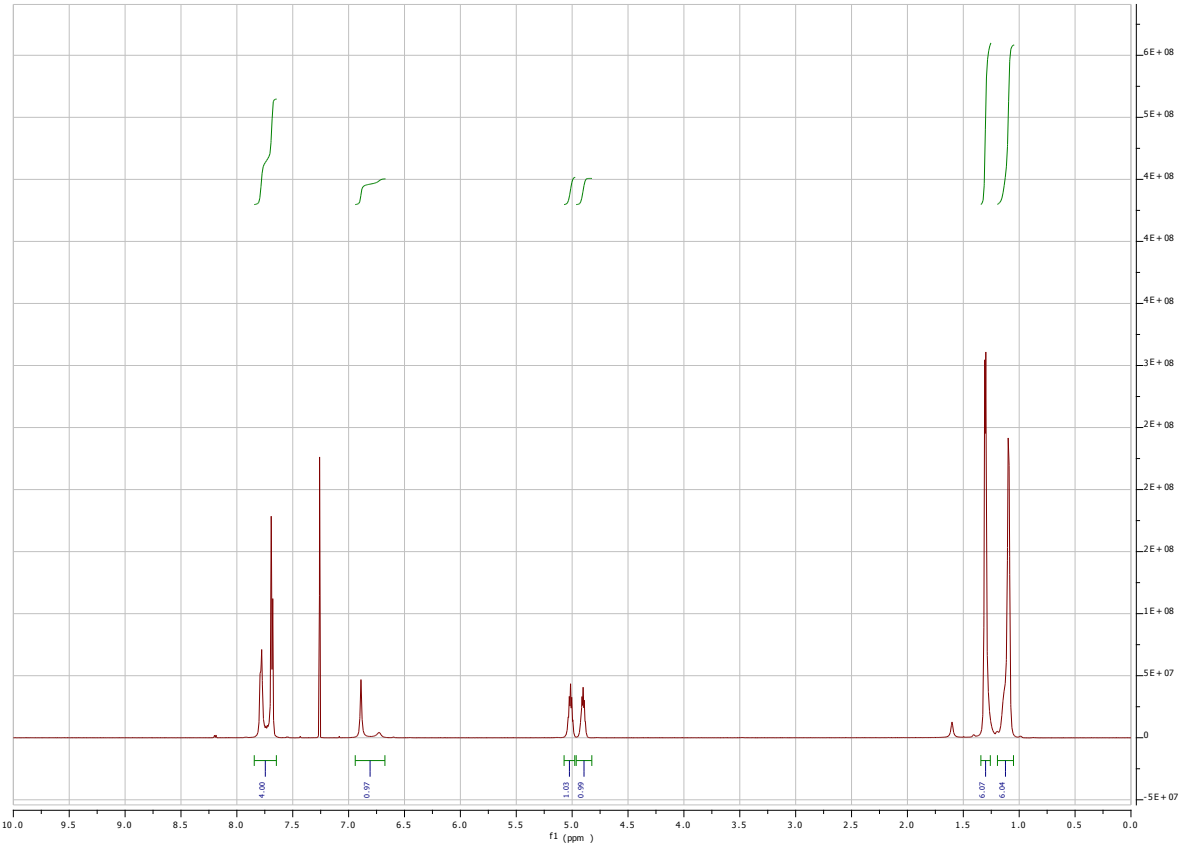


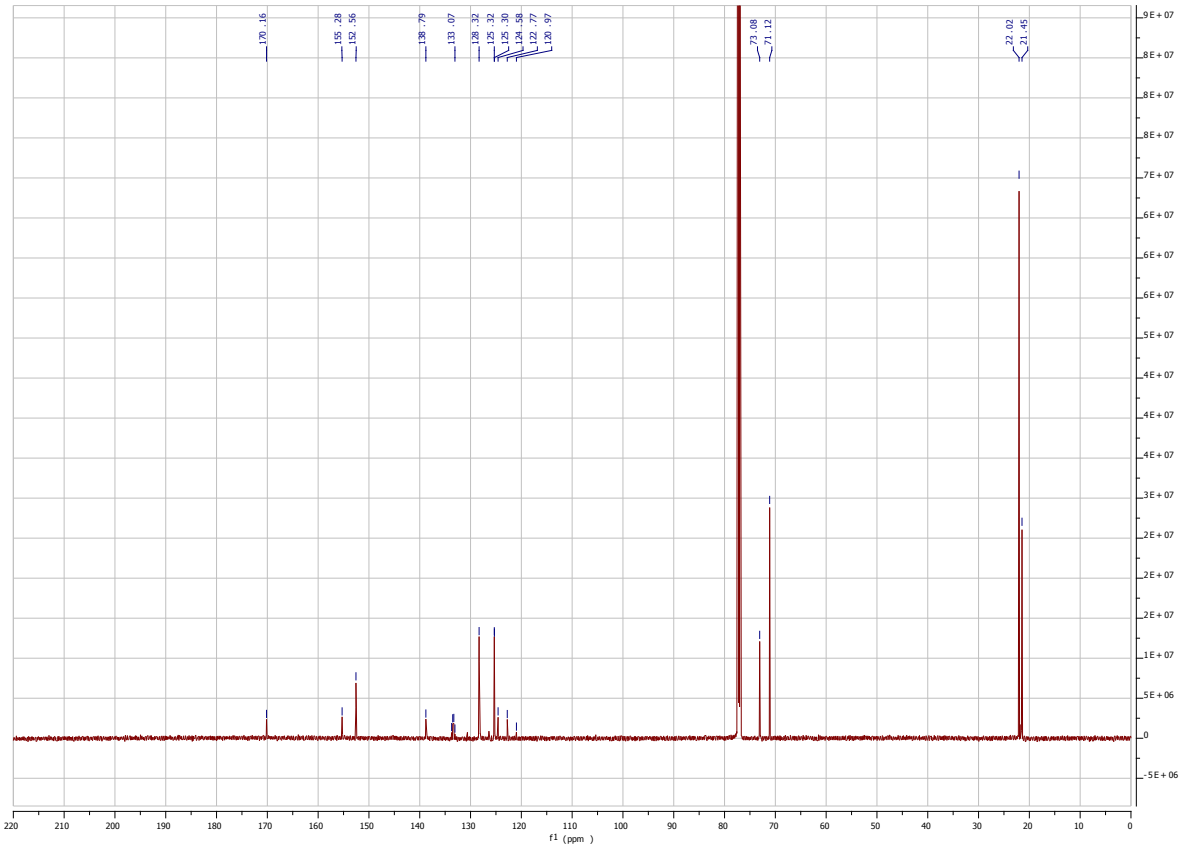


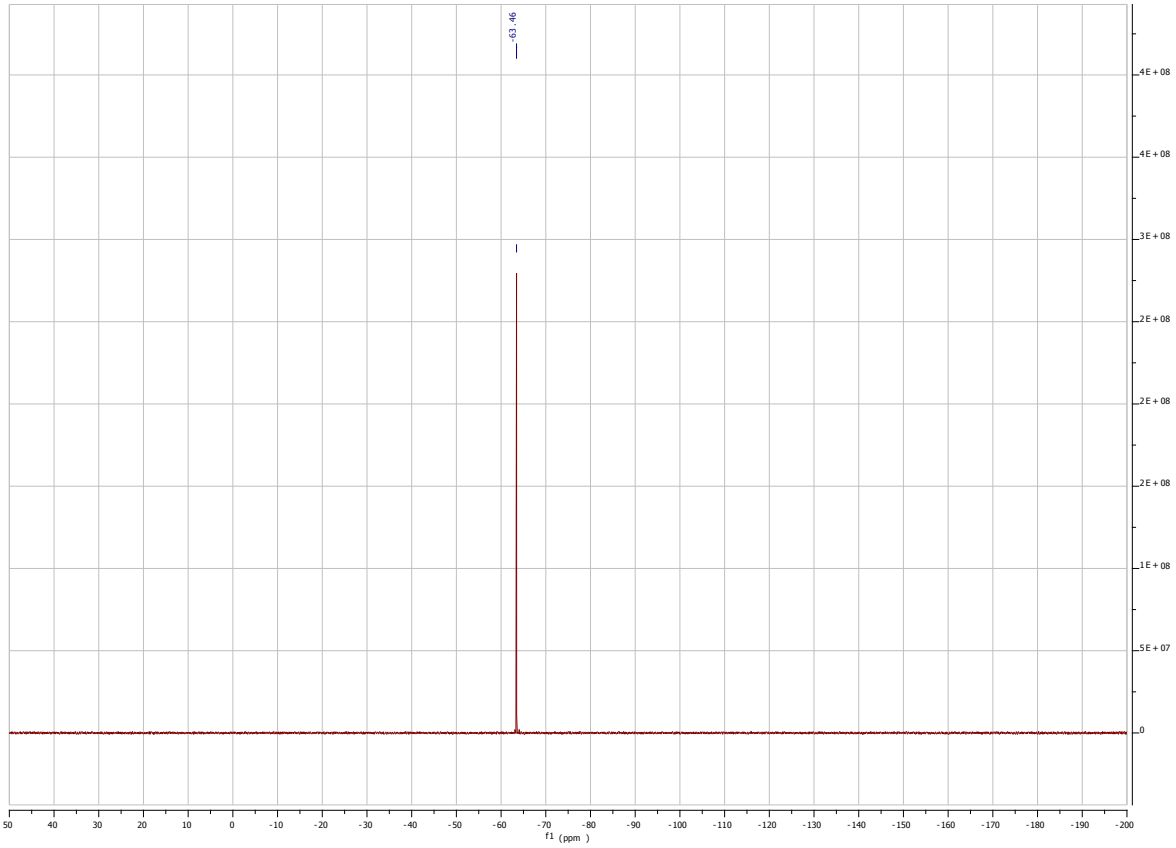
Diisopropyl 1-(4-(trifluoromethyl)benzoyl)hydrazine-1,2-dicarboxylate (1b)



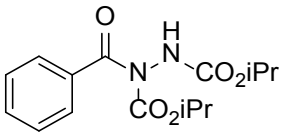
Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(4-(trifluoromethyl)benzoyl)hydrazine-1,2-dicarboxylate as a white solid (229 mg, 0.61 mmol, 61%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.80-7.75 (m, 2H), 7.74-7.66 (m, 2H), 6.89-6.82 (br s, NH, 1H), 5.03-5.00 (m, 1H), 4.92-4.89 (m, 1H), 1.30 (d, J = 6.3, 6H), 1.09 (d, J = 6.2 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.2 (C), 155.3 (C), 152.6 (C), 138.8 (C), 133.3 (q, $J_{C\text{-}F}$ = 32.0 Hz, C), 128.3 (CH), 123.7 (q, $J_{C\text{-}F}$ = 271 Hz, C), 125.3 (CH), 73.1 (CH), 71.1 (CH), 22.0 (CH_3), 21.5 (CH_3); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -63.5 (s, CF_3, 3F); **IR** (thin film) 3305, 2985, 1708, 1620, 1323, 1245, 1168, 1127, 1100, 1064, 919 cm^{-1}; **LRMS (CI)** 377 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{16}H_{20}F_3N_2O_5$ $[M+H]^+$ 377.1324, observed 377.1332; **m.p.** 91-93 °C (recrystallized from *n*-heptane).



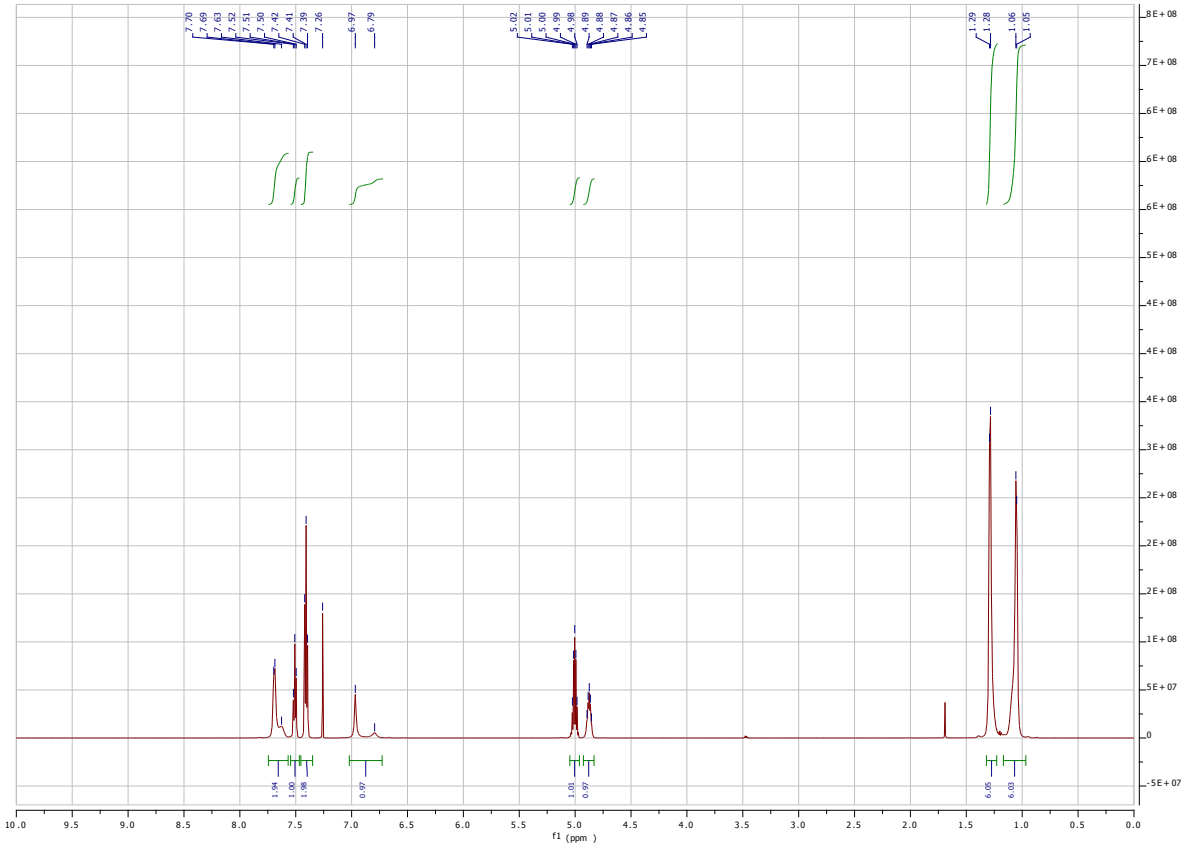


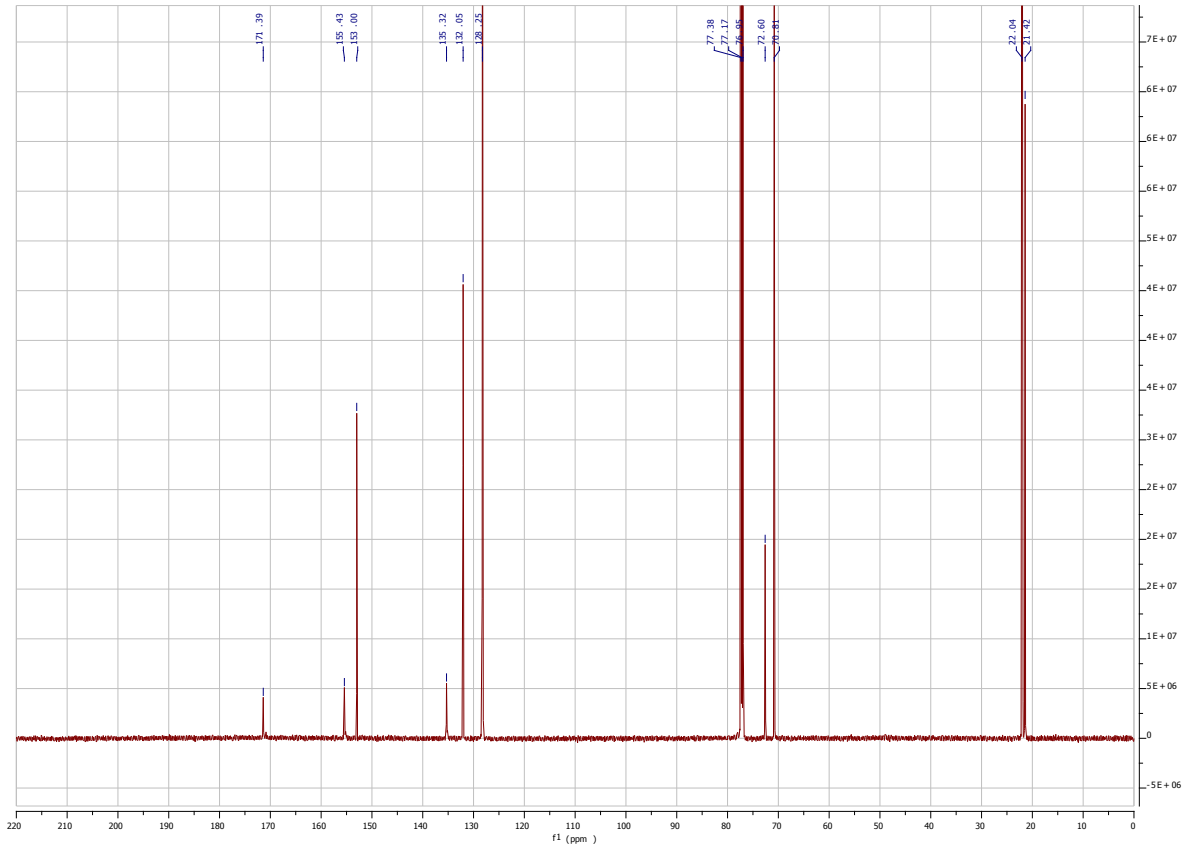


Diisopropyl 1-benzoylhydrazine-1,2-dicarboxylate[2] (1c)

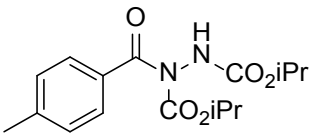


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-benzoylhydrazine-1,2-dicarboxylate as a white solid (206 mg, 0.67 mmol, 67%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73-7.58 (m, 2H), 7.51 (t, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 6.97 (br s, NH, 1H), 5.00 (septet, *J* = 6.1 Hz, 1H), 4.89-4.85 (m, 1H), 1.29 (d, *J* = 6.1 Hz, 6H), 1.05 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.4 (C), 155.4 (C), 153.0 (C), 135.3 (CH), 128.3 (CH), 128.0 (CH), 72.6 (CH), 70.8 (CH), 22.0 (CH_3), 21.4 (CH_3); **IR** (thin film) 3308, 2982, 1707, 1248, 1102 cm^{-1}; **LRMS (CI)** 309 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{15}H_{21}N_2O_5$ $[M+H]^+$ 309.1451, observed 309.1450; **m.p.** 118-120 °C (recrystallized from *n*-heptane).

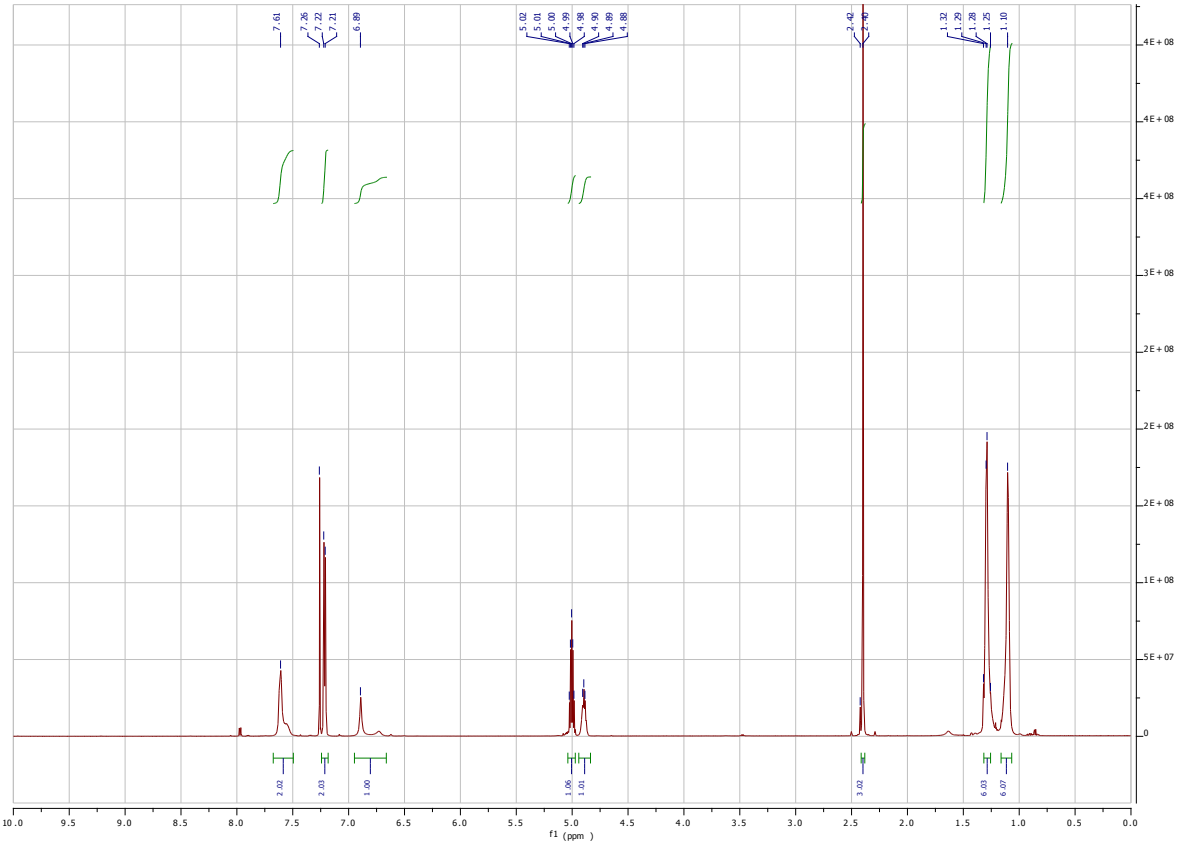


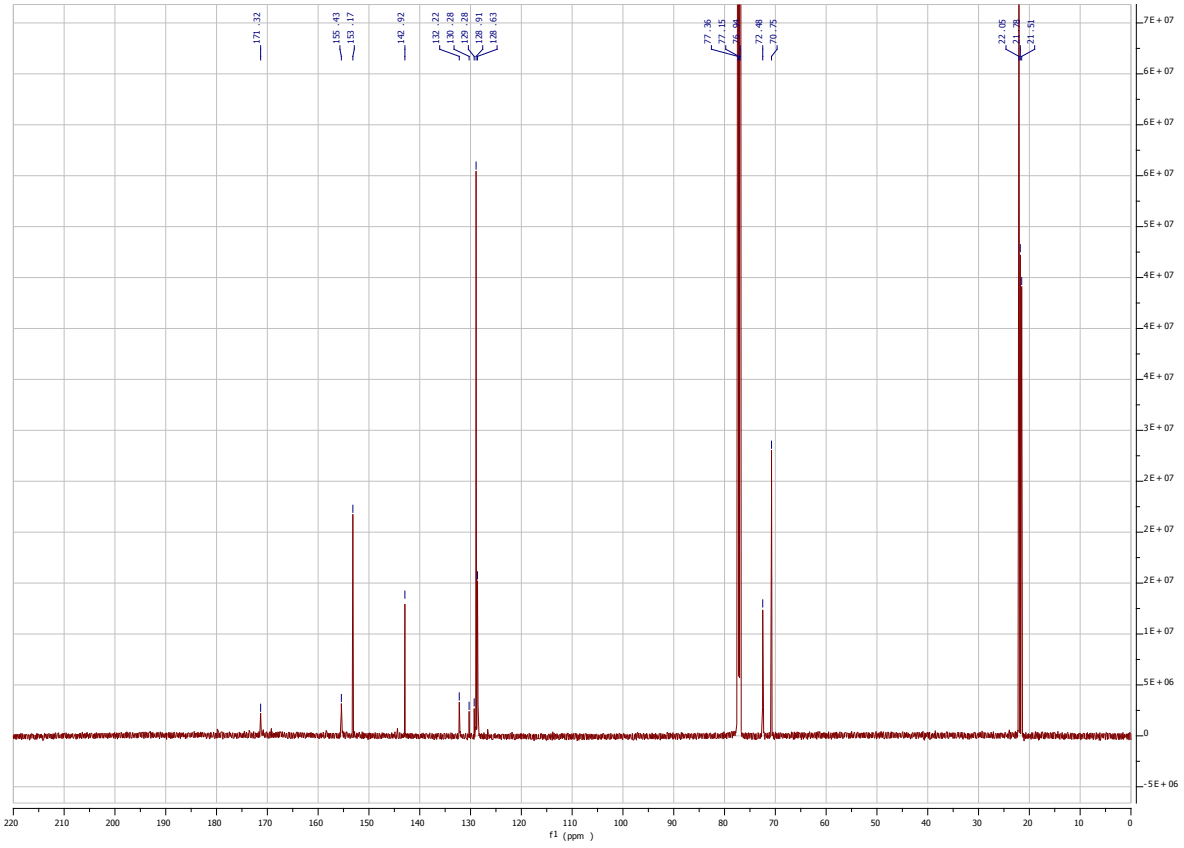


Diisopropyl 1-(4-(methyl)benzoyl)hydrazine-1,2-dicarboxylate[3] (1d)

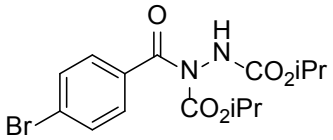


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(4-(methyl)benzoyl)hydrazine-1,2-dicarboxylate as a white solid (200 mg, 0.62 mmol, 62%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.66-7.50 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.89-6.82 (br s, NH, 1H), 5.03-4.98 (m, 1H), 4.90-4.88 (m, 1H), 2.40 (s, 3H), 1.29 (d, *J* = 6.3, 6H), 1.09 (d, *J* = 6.2, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.3 (C), 155.4 (C), 153.2 (C), 142.9 (C), 132.2 (C), 130.3 (CH), 129.3 (CH), 128.9 (CH), 128.6 (CH), 72.5 (CH), 70.8 (CH), 22.1 (CH_3), 21.8 (CH_3), 21.5 (CH_3); **IR** (thin film) 3307, 2982, 1736, 1704, 1375, 1246, 1145, 1102 cm^{-1}; **LRMS (CI)** 323 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{16}H_{23}N_2O_5$ $[M+H]^+$ 323.1607, observed 323.1615; **m.p.** 99-101°C (recrystallized from *n*-heptane).

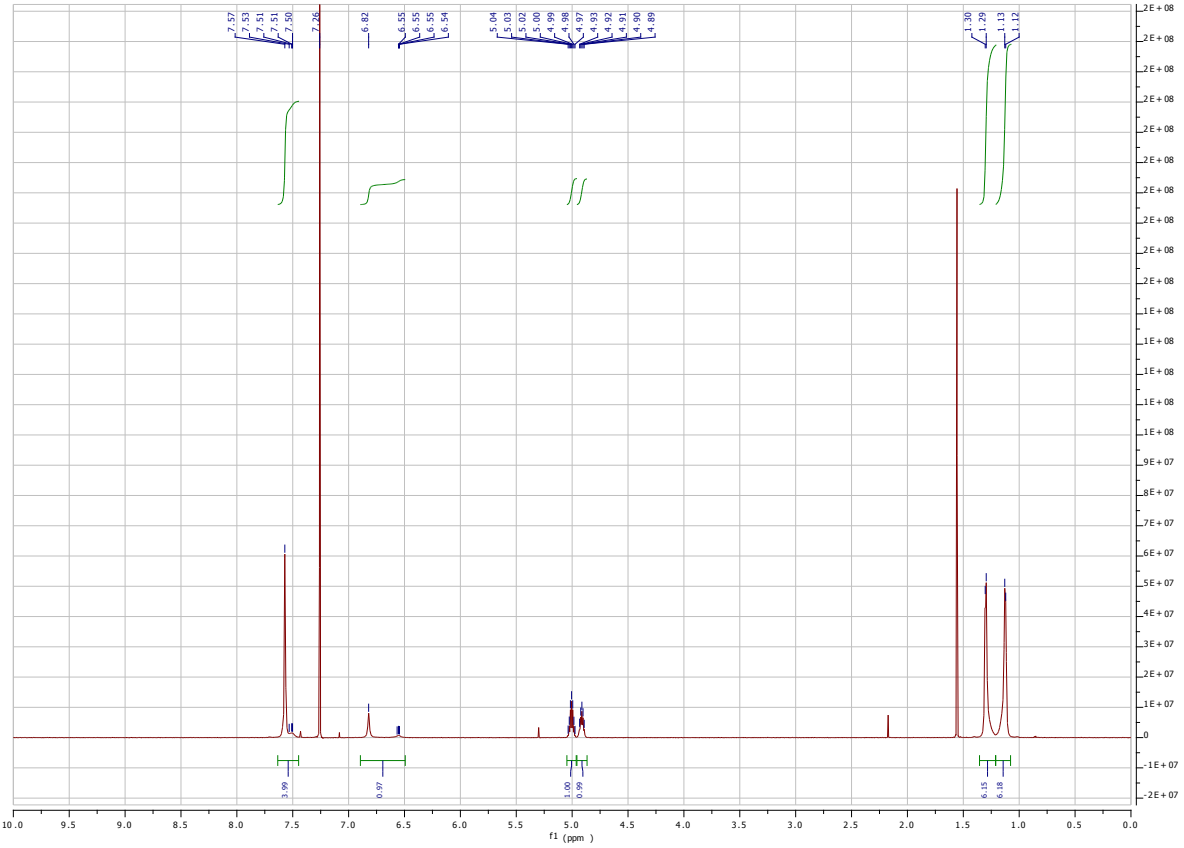


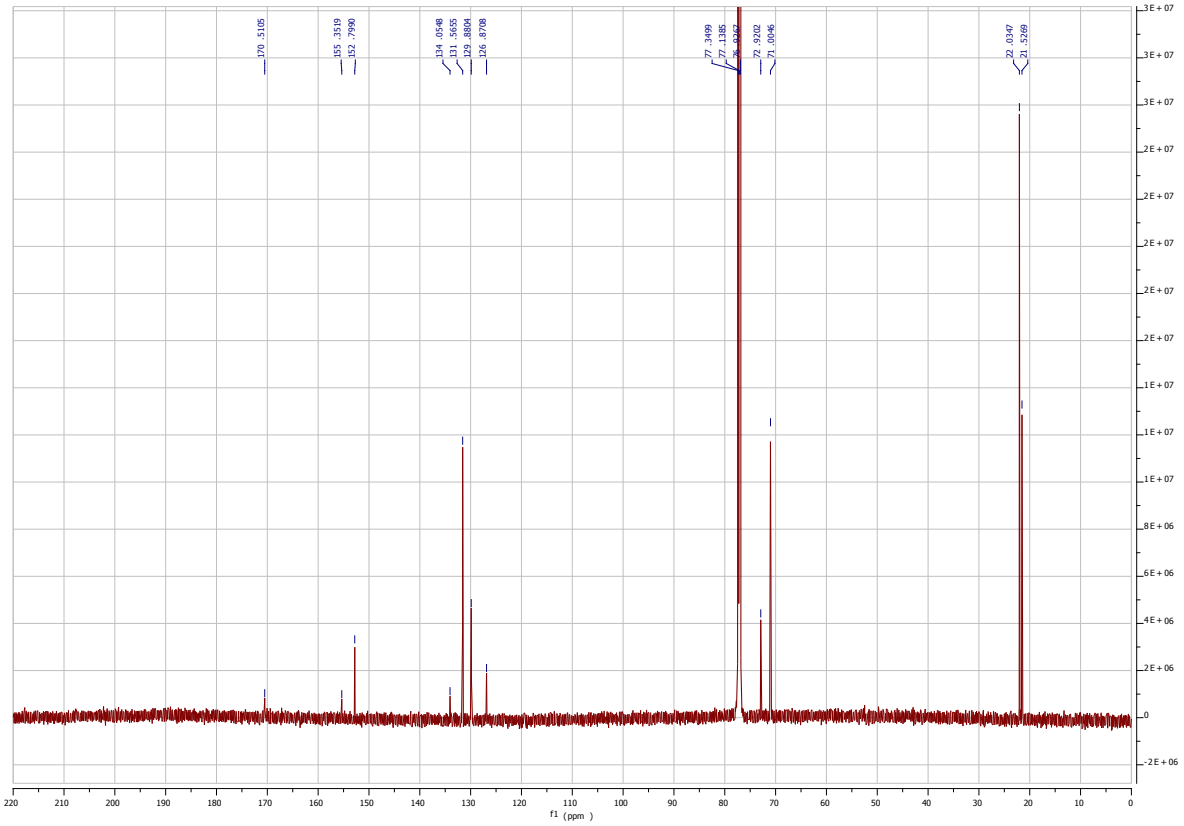


Diisopropyl 1-(4-bromobenzoyl)hydrazine-1,2-dicarboxylate[4] (1e)

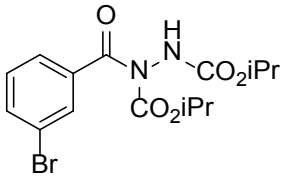


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(4-bromobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (232 mg, 0.60 mmol, 60%). **^{1}H NMR (600 MHz,$CDCl_3$)** δ 7.57-7.50 (m, 4H), 6.82 (br s, NH, 1H), 5.03 (septet, J = 6.2 Hz, 1H), 4.93-4.89 (m, 1H), 1.30 (d, J = 6.2, 6H), 1.13 (d, J = 6.2, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.5 (C), 155.4 (C), 152.8 (C), 134.1 (C), 131.6 (CH), 129.9 (CH), 126.9 (C), 72.9 (CH), 71.0 (CH), 22.0 (CH_3), 21.5 (CH_3); **IR** (thin film) 3305, 2982, 1708, 1589, 1255, 1101, 919 cm^{-1}; **LRMS (CI)** 389 (10, $[M^{81}Br+H]^+$), 387 (10, $[M^{79}Br+H]^+$), 185 (100, $[M^{81}Br\text{-}C_8H_{15}N_2O_4]^+$), 183 (100, $[M^{79}Br\text{-}C_8H_{15}N_2O_4]^+$); **HRMS (CI)** calcd. for $C_{15}H_{20}BrN_2O_5$ $[M^{79}Br+H]^+$ 387.0556, observed 387.0566; **m.p.** 102-105 °C (recrystallized from *n*-heptane).

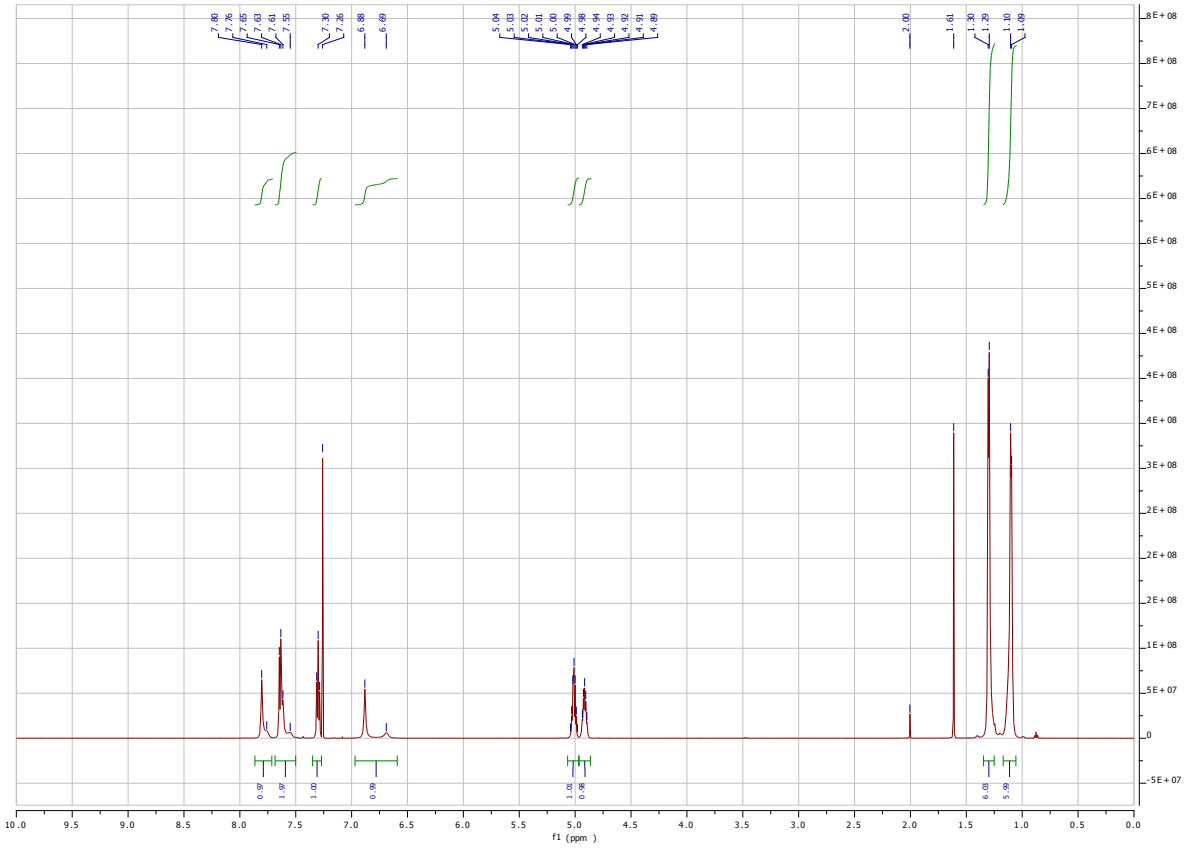


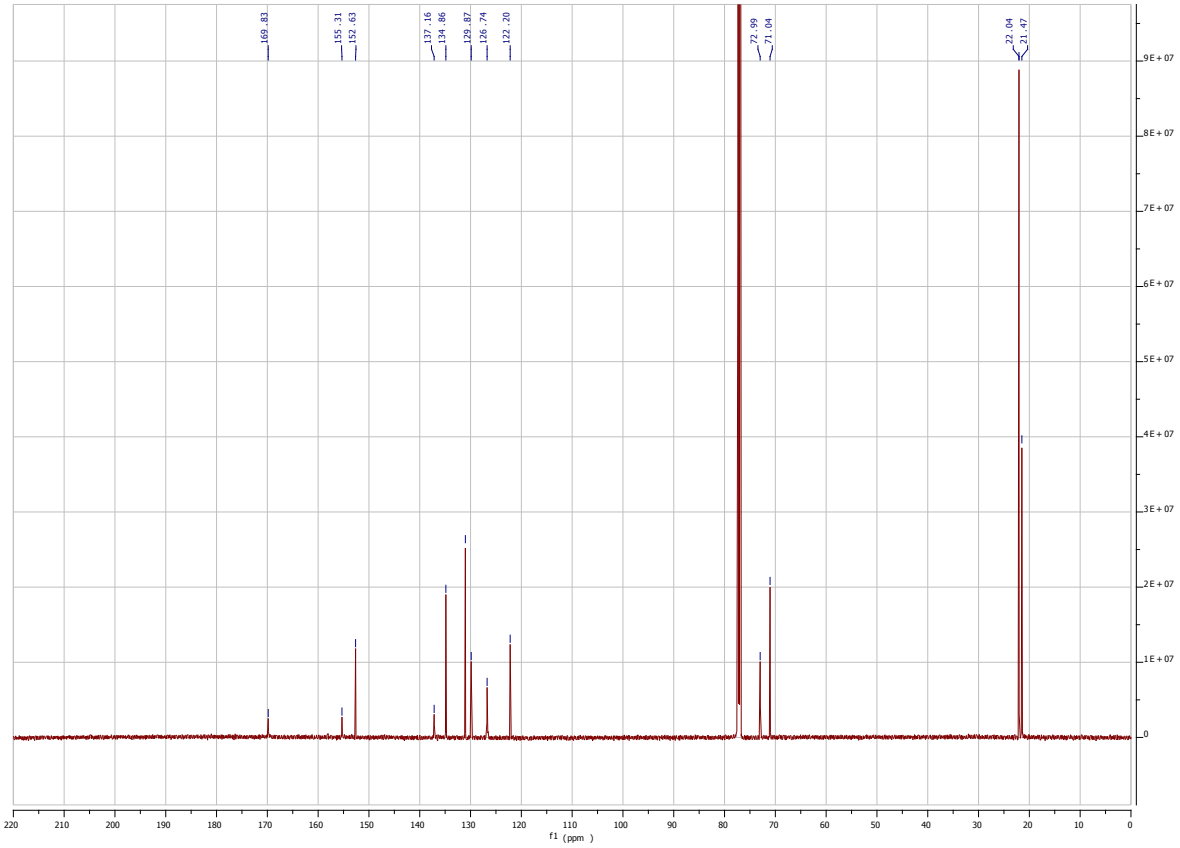


Diisopropyl 1-(3-bromobenzoyl)hydrazine-1,2-dicarboxylate (1f)

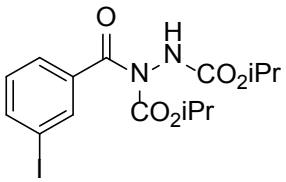


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(3-bromobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (231 mg, 0.60 mmol, 60%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84-7.72 (m, 1H), 7.66-7.53 (m, 2H), 7.30 (t, J = 6.1 Hz, 1H), 6.88 (br s, NH, 1H), 5.01 (septet, J = 6.2 Hz, 1H), 4.96-4.87 (m, 1H), 1.29 (d, J = 6.2, 6H), 1.10 (d, J = 6.2, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.8 (C), 155.3 (C), 152.6 (C), 137.2 (CH), 134.9 (CH), 131.0 (CH), 129.9 (CH), 126.7 (CH), 122.2 (C), 73.0 (CH), 71.0 (CH), 22.0 (CH_3), 21.5 (CH_3); **IR** (thin film) 3311, 2983, 1707, 1245, 1244, 1099 cm^{-1}; **LRMS (CI)** 389 (15, $[M^{81}Br+H]^+$), 387 (15, $[M^{79}Br+H]^+$), 185 (100, $[M^{81}Br\text{-}C_8H_{15}N_2O_4]^+$), 183 (100, $[M^{79}Br\text{-}C_8H_{15}N_2O_4]^+$); **HRMS (CI)** calcd. for $C_{15}H_{20}BrN_2O_5$ $[M^{79}Br+H]^+$ 387.0556, observed 387.0561; **m.p.** 139-140 °C (recrystallized from *n*-heptane).

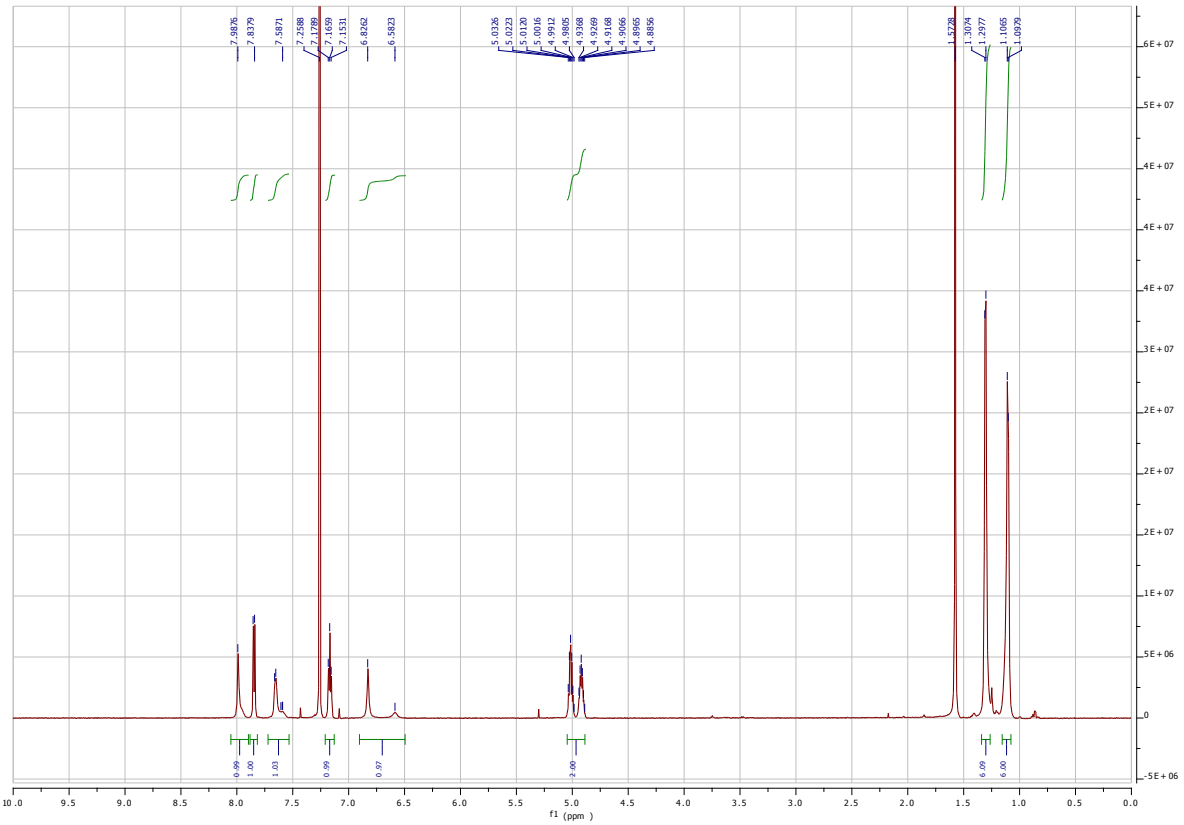


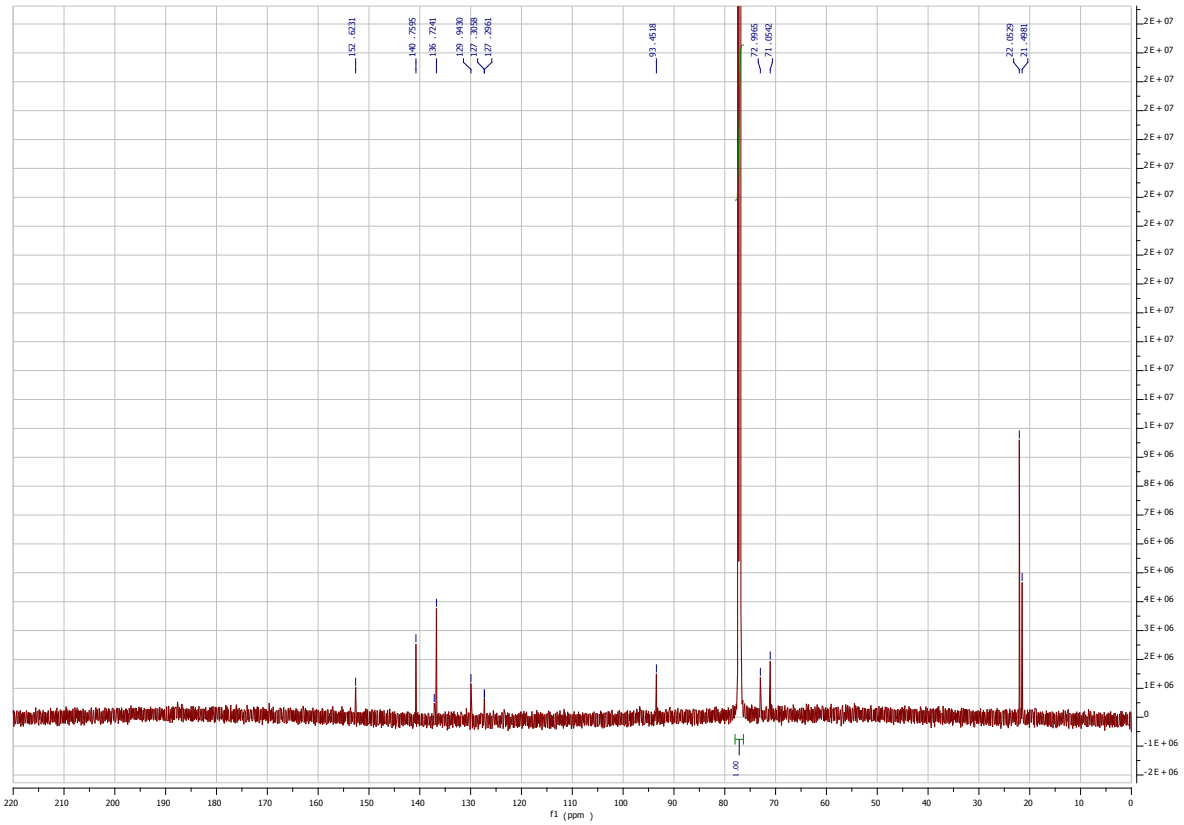


Diisopropyl 1-(3-iodobenzoyl)hydrazine-1,2-dicarboxylate (1g)

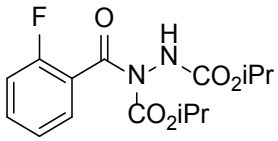


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(3-iodobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (265 mg, 0.61 mmol, 61%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.66-7.59 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.83-6.58 (m, NH), 5.01 (septet, *J* = 6.2 Hz, 1H), 4.95-4.89 (m, 1H), 1.30 (d, *J* = 5.8 Hz, 6H), 1.10 (d, *J* = 5.2 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 152.6 (C), 140.8 (CH), 137.2 (C), 136.7 (CH), 130.8 (C), 129.9 (CH), 127.3 (C), 127.3 (CH), 93.5 (C), 73.0 (CH), 71.1 (CH), 22.1 (CH_3), 21.5 (CH_3); **IR** (thin film) 3317, 2981, 1709, 1250, 1101 cm^{-1}; **LRMS (CI)** 435 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{15}H_{20}IN_2O_5$ $[M+H]^+$ 435.0417, observed 435.0421; **m.p.** 156-159 °C (recrystallized from *n*-heptane).

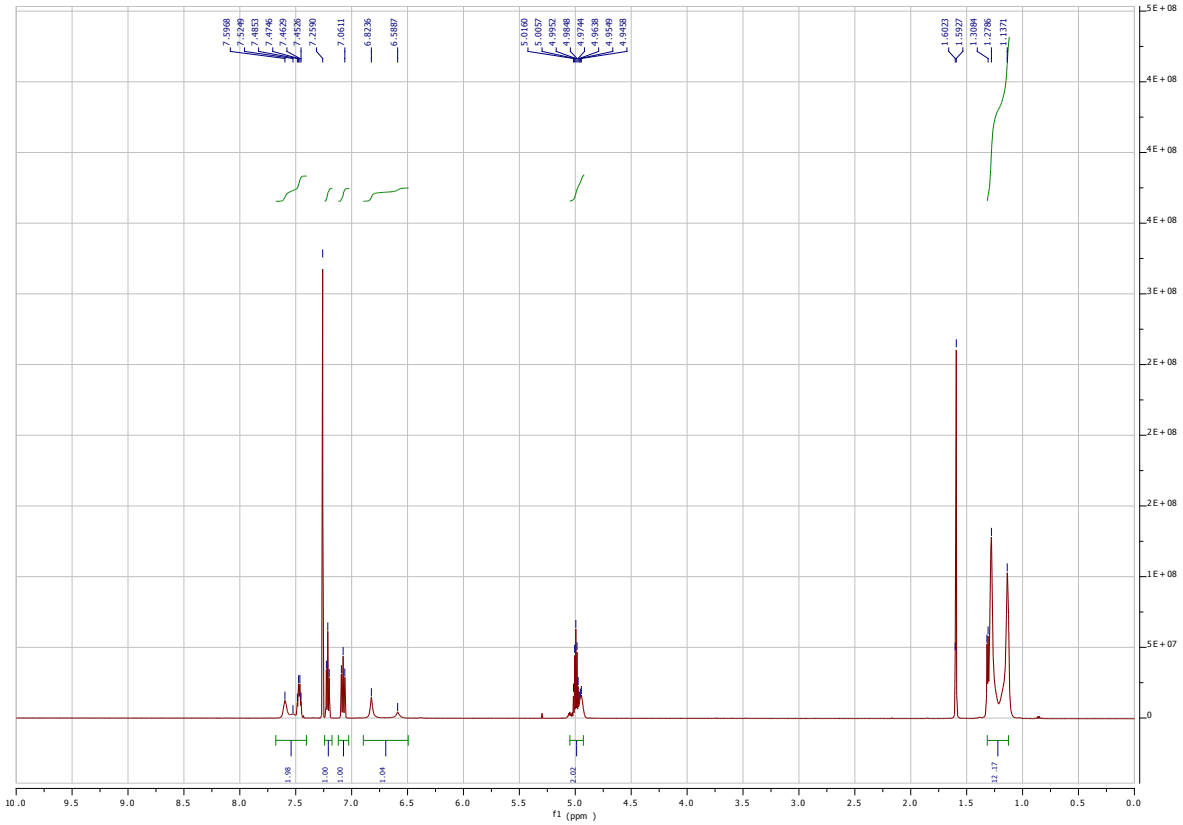


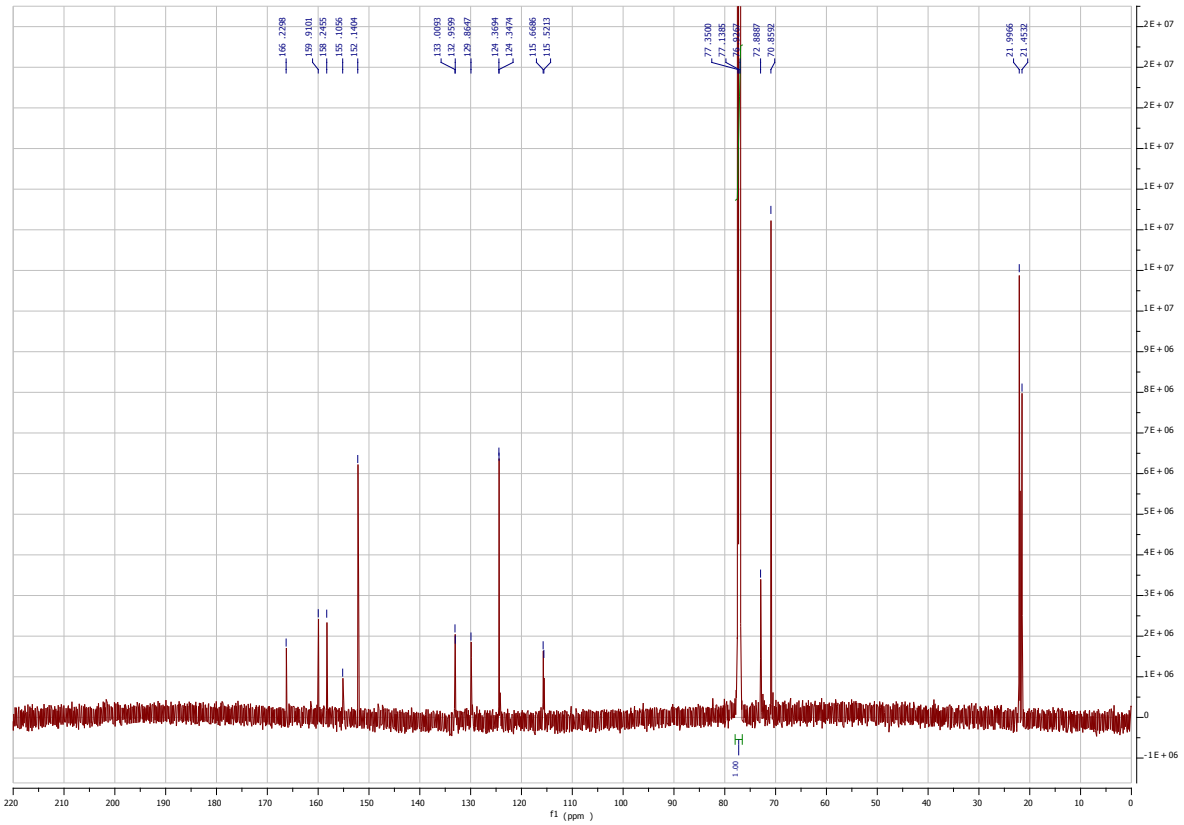


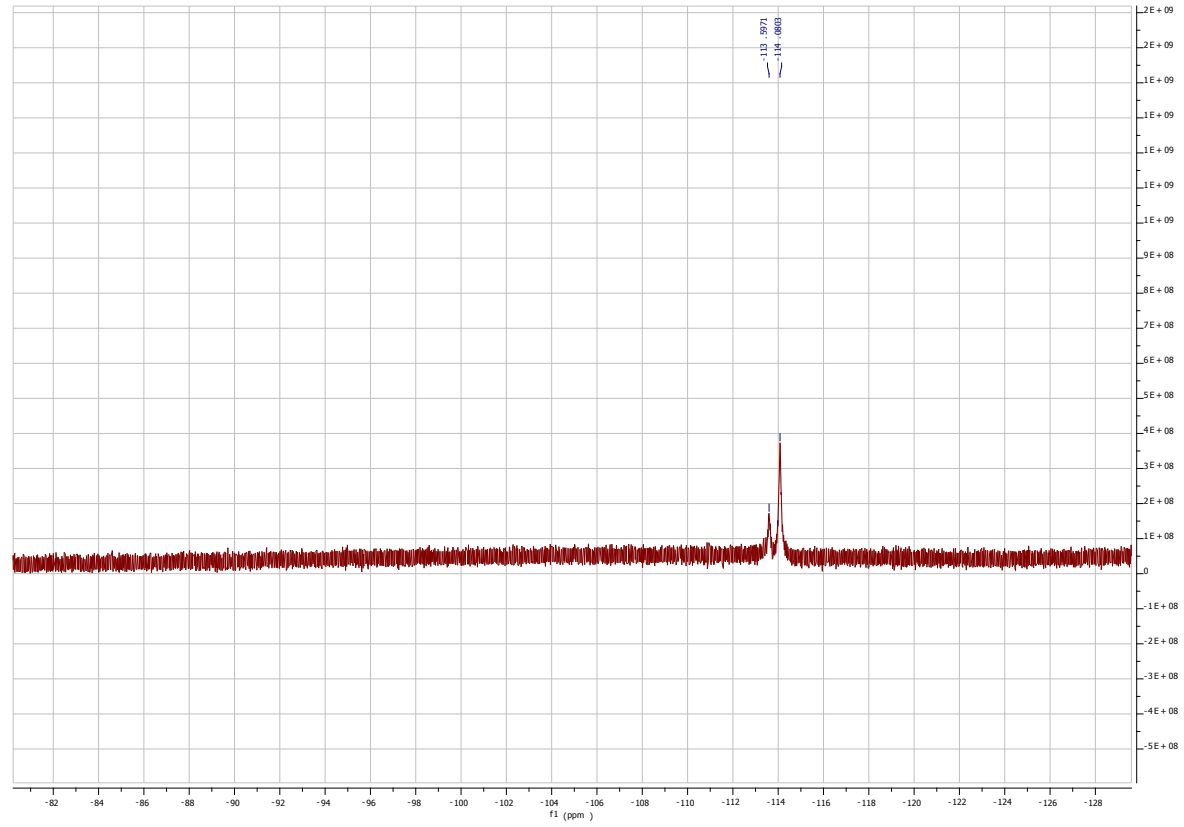
Diisopropyl 1-(2-fluorobenzoyl)hydrazine-1,2-dicarboxylate (1h)



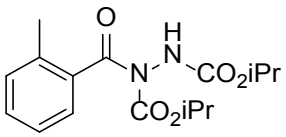
Purification by column chromatography (5%-25% Et_2O/Petrol) gave as diisopropyl 1-(2-fluorobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (202 mg, 0.62 mmol, 62%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60-7.45 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 9.2 Hz, 1H), 6.82-6.59 (m, NH, 1H), 4.97 (m, 2H), 1.32-1.14 (m, 12H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 166.2 (C), 159.2 (d, $J_{C\text{-}F}$ = 249.7 Hz, C), 155.1 (C), 152.1 (C), 133.5 (d, $J_{C\text{-}F}$ = 7.4 Hz, CH), 129.9 (CH), 124.3 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH), 115.5 (d, $J_{C\text{-}F}$ = 22.1 Hz, CH), 72.9 (CH), 70.9 (CH), 22.0 (CH_3), 21.5 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.1 (m, 1F); **IR** (thin film) 3308, 2983, 1710, 1709, 1231, 1099 cm^{-1}; **LRMS (CI)** 327 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{15}H_{20}FN_2O_5$ $[M+H]^+$ 327.1356, observed 327.1349; **m.p.** 128-130 °C (recrystallized from *n*-heptane).



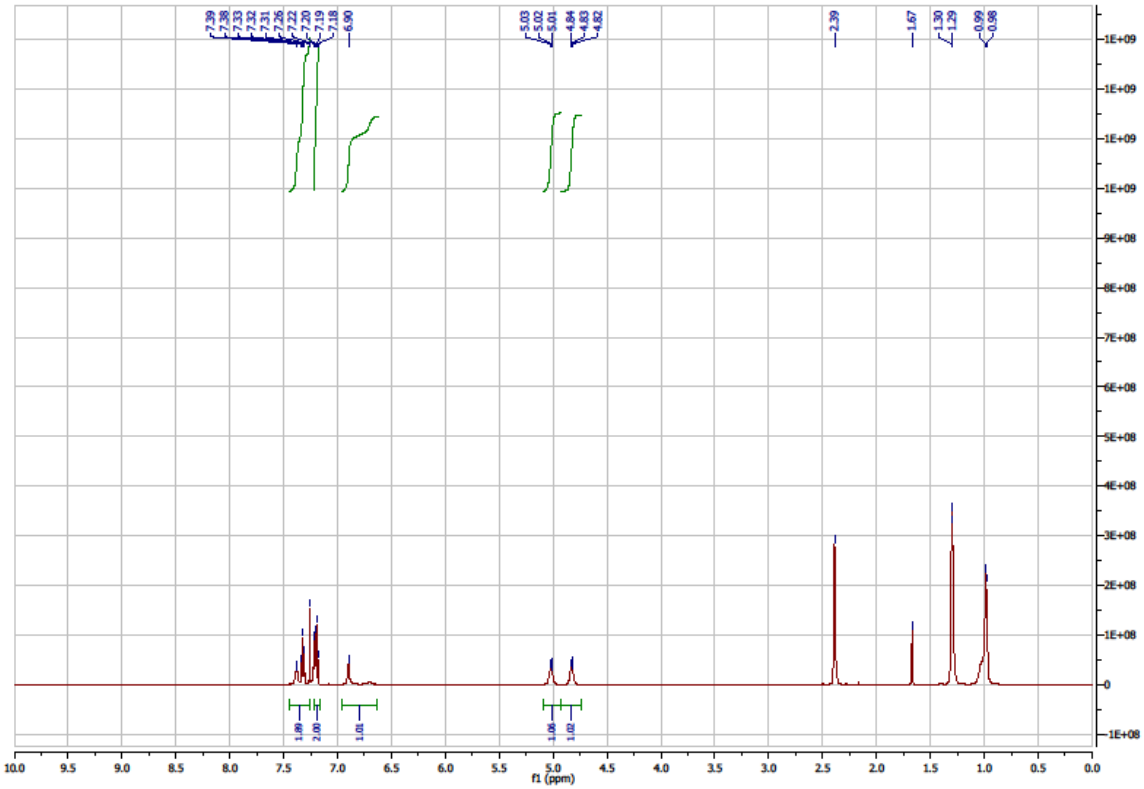


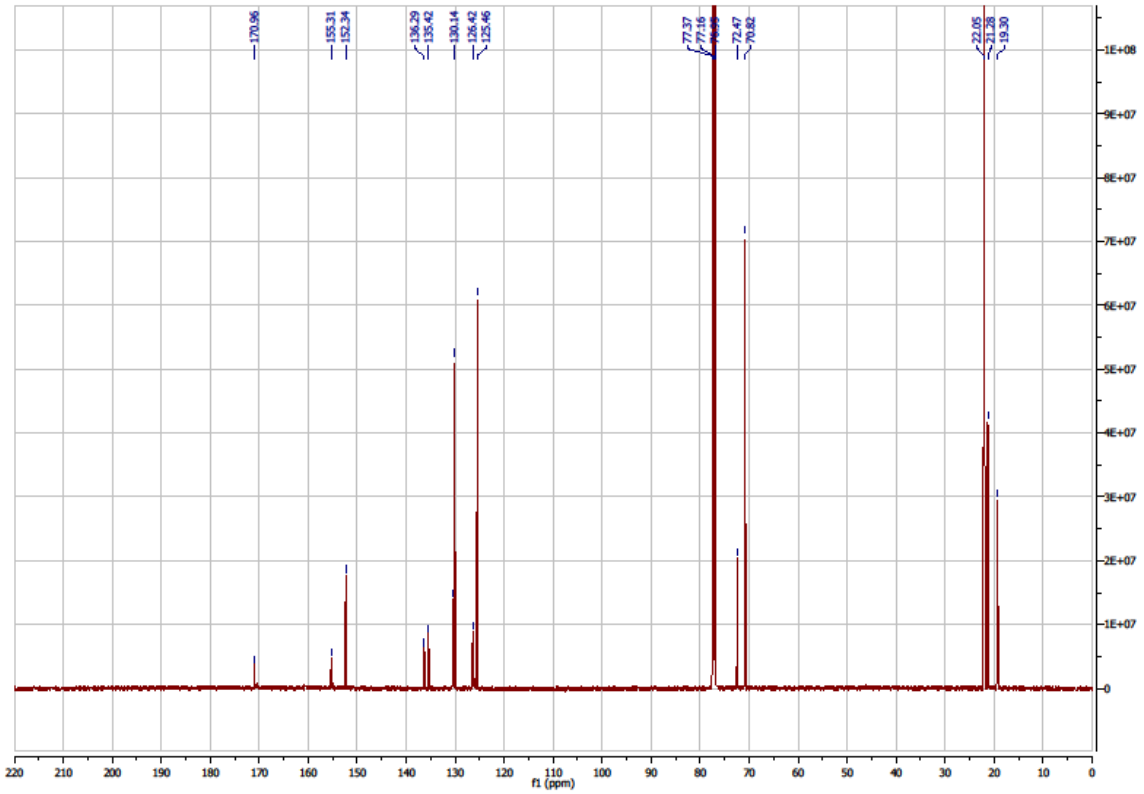


Diisopropyl 1-(2-methylbenzoyl)hydrazine-1,2-dicarboxylate (1i)

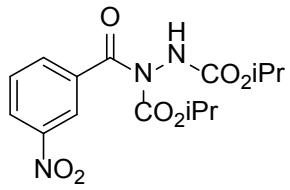


Purification by column chromatography (5%-25% Et_2O: Et_2O/Petrol) gave diisopropyl 1-(2-methylbenzoyl)hydrazine-1,2-dicarboxylate as a white solid (184 mg, 0.57 mmol, 57%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39-7.35 (m, 1H), 7.34-7.30 (m, 1H), 7.24-7.16 (m, 2H), 6.90 (br s, NH, 1H), 5.06-4.97 (m, 1H), 4.87-4.79 (m, 1H), 2.39 (s, 3H), 1.30 (d, J = 5.7 Hz, 6H), 1.02-0.98 (m, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.0 (C), 155.3 (C), 152.3 (C), 136.3 (C), 135.4 (C), 130.4 (CH), 130.1 (CH), 126.4 (CH), 125.5 (CH), 72.5 (CH), 70.8 (CH), 22.1 (CH_3), 21.3 (CH_3), 19.3 (CH_3); **IR** (thin film) 3308, 2982, 1707, 1248, 1102 cm^{-1}; **LRMS (CI)** 323 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{16}H_{22}N_2O_5$ $[M+H]^+$ 323.1607, observed 323.1602; **m.p.** 82-84 °C (recrystallized from *n*-heptane).

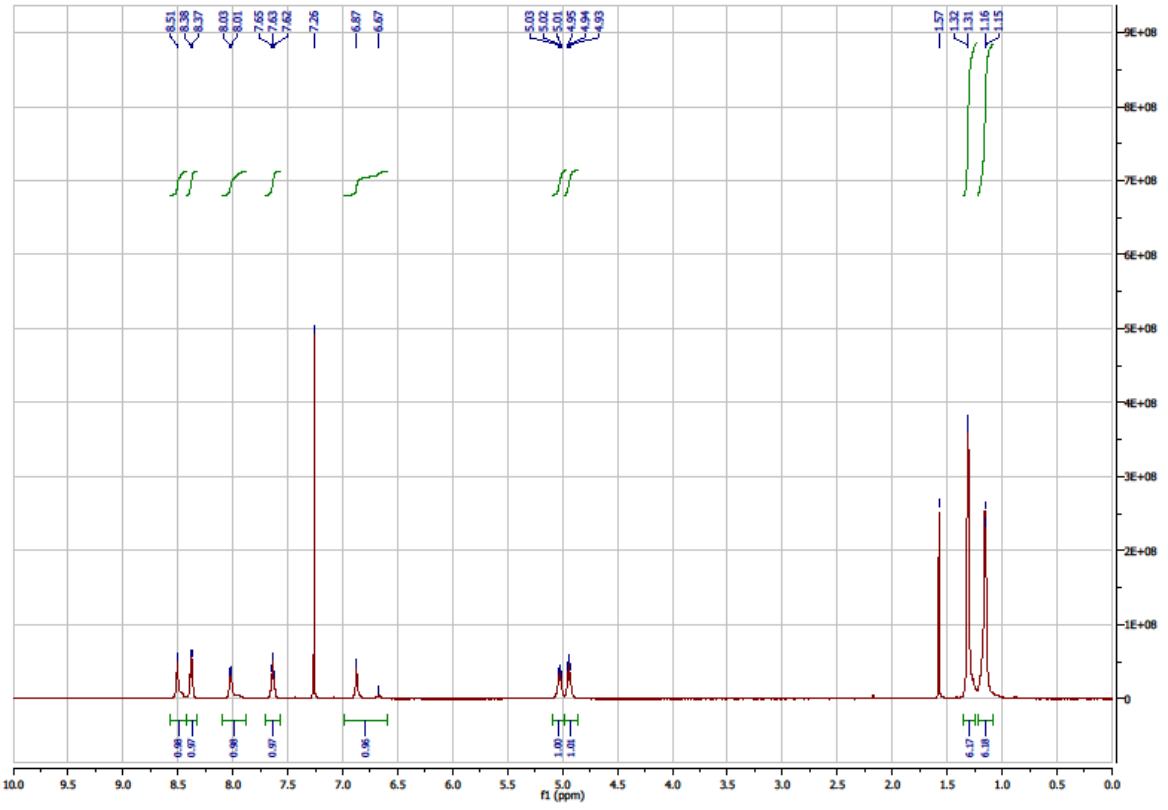


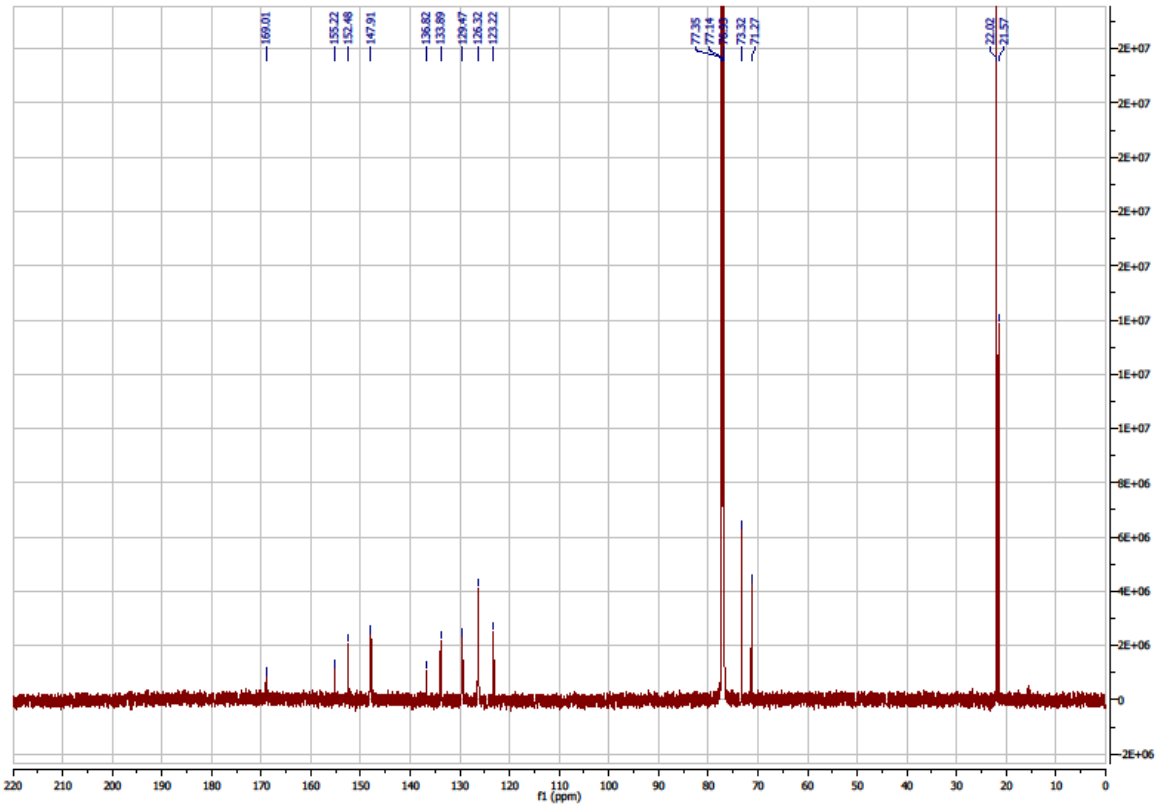


Diisopropyl 1-(3-nitrobenzoyl)hydrazine-1,2-dicarboxylate (1j)

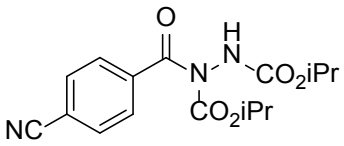


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(3-nitrobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (202 mg, 0.57 mmol, 57%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.54-8.43 (m, 1H), 8.40-8.36 (m, 1H), 8.05-7.91 (m, 1H), 7.69-7.65-7.60 (m, 1H), 6.67 (br s, NH, 1H), 5.08-4.99 (m, 1H), 4.98-4.91 (m, 1H), 1.31 (d, J = 5.7, 6H), 1.15 (d, J = 4.5, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.0 (C), 155.2 (C), 152.5 (C), 147.9 (C), 136.8 (C), 133.9 (CH), 129.5 (CH), 126.3 (CH), 123.2 (C), 73.3 (CH), 71.3 (CH), 22.0 (CH_3), 21.6 (CH_3); **IR** (thin film) 3310, 2984, 1715, 1534, 1350, 1258, 1102 cm^{-1}; **LRMS (CI)** 354 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{15}H_{20}N_3O_7$ $[M+H]^+$ 354.1301, observed 354.1319; **m.p.** 114-116 °C (recrystallized from *n*-heptane).

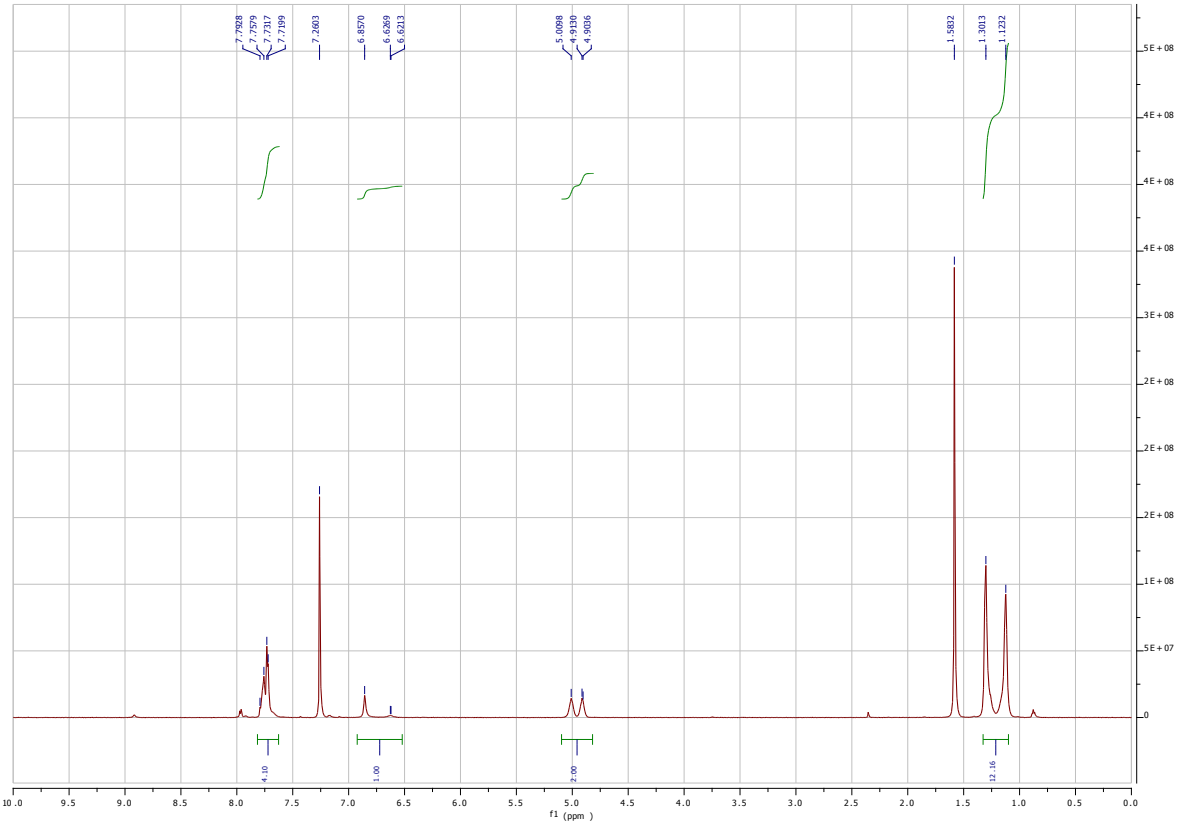


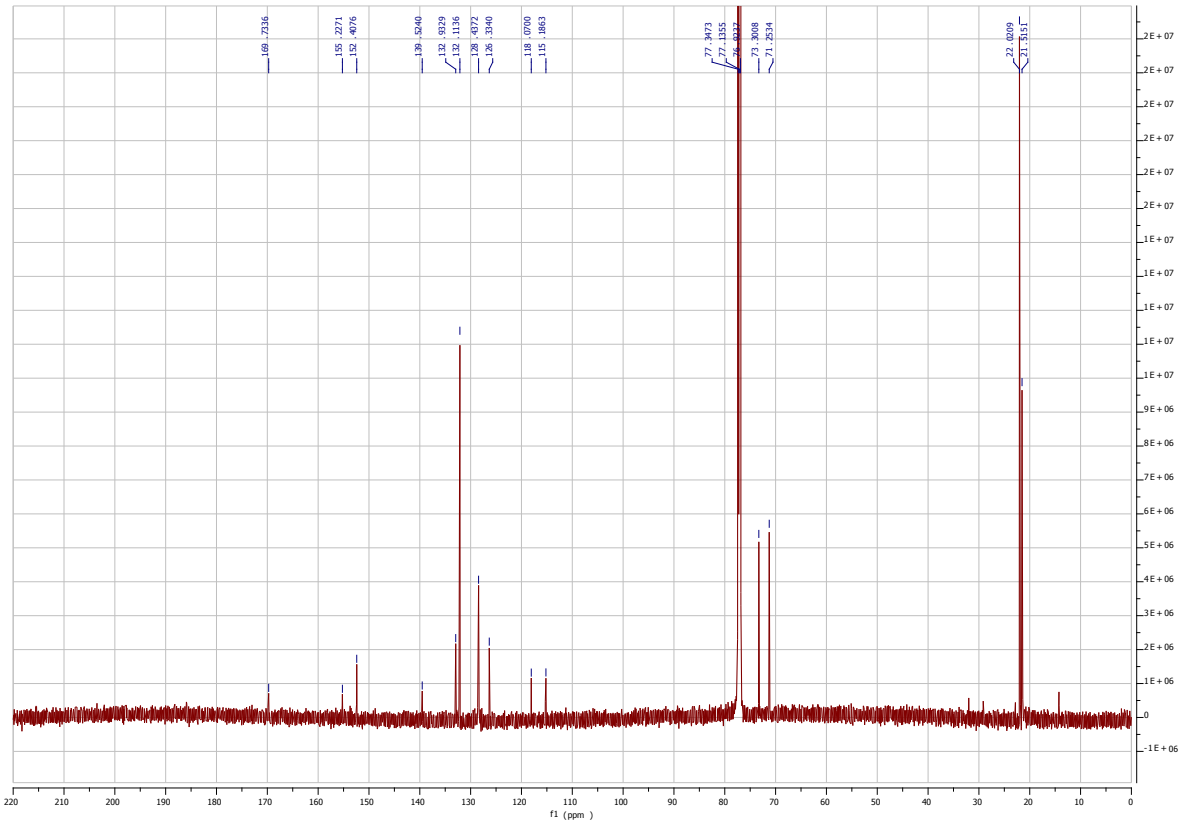


Diisopropyl 1-(4-cyanobenzoyl)hydrazine-1,2-dicarboxylate (1k)

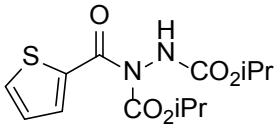


Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(4-cyanobenzoyl)hydrazine-1,2-dicarboxylate as a white solid (213 mg, 0.64 mmol, 64%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79-7.71 (m, 4H), 6.86-6.62 (m, NH, 1H), 5.00-4.95 (m, 2H), 1.30-1.12 (m, 12H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7 (C), 155.2 (C), 152.4 (C), 139.5 (C), 132.9 (CH), 132.1 (CH), 128.4 (CH), 126.3 (CH), 118.1 (C), 115.2 (C), 73.3 (CH), 71.3 (C), 22.0 (CH_3), 21.5 (CH_3); **IR** (thin film) 3307, 2984, 2232, 1707, 1232, 1099, 850 cm^{-1}; **LRMS (CI)** 334 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{16}H_{20}N_3O_5$ $[M+H]^+$ 334.1403, observed 334.1402; **m.p.** 82-86 °C (recrystallized from *n*-heptane).

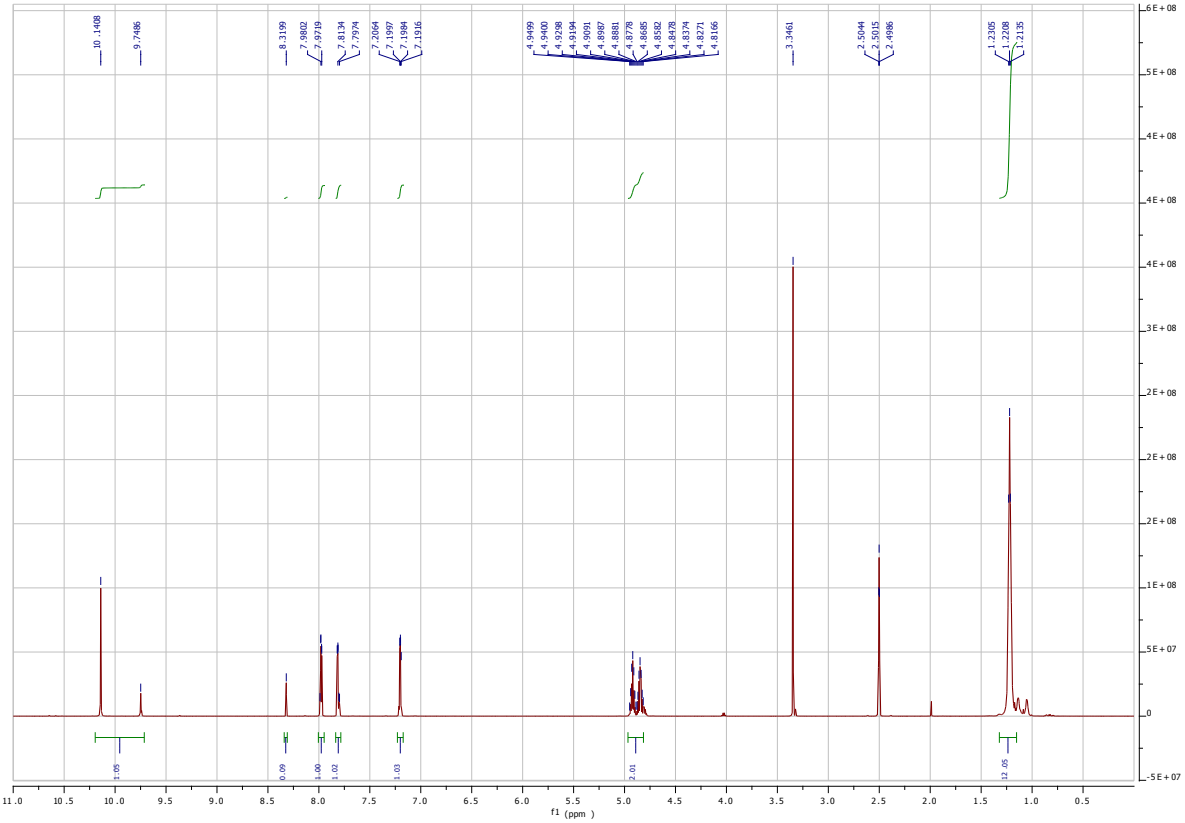


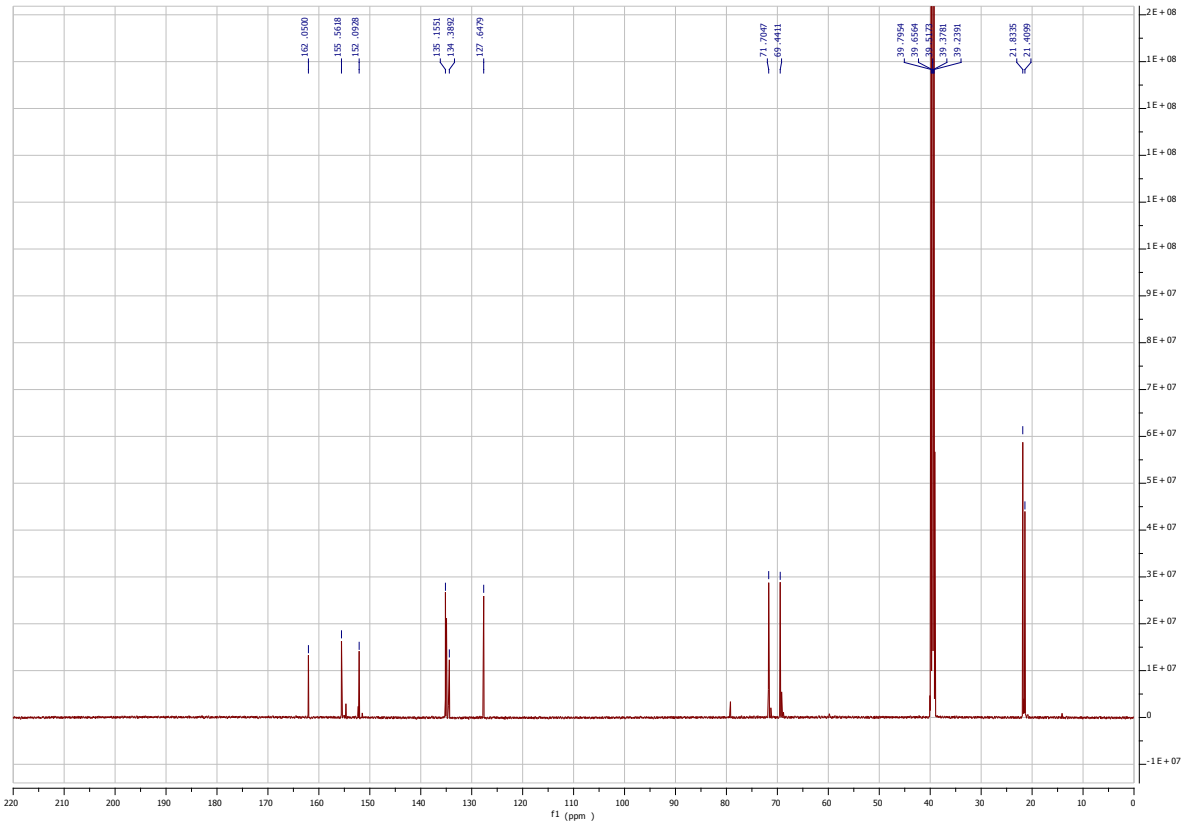


Diisopropyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate (1l)



Purification by column chromatography (5%-25% Et_2O/Petrol) gave diisopropyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate as pink oil (203 mg, 0.65 mmol, 65%). **^{1}H NMR (600 MHz, DMSO-d$_6$)** δ 10.14 (s, NH, 1H), 7.98 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.82 (dd, *J* = 3.84, 1.3 Hz, 1H), 7.20 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.92 (septet, *J* = 6.2 Hz, 1H), 4.85 (septet, *J* = 6.1 Hz, 1H), 1.24-1.20 (m, 12H); **^{13}C NMR (150 MHz, DMSO-d$_6$)** δ 162.1 (C), 155.6 (C), 154.7 (C), 152.1 (C), 135.2 (CH), 135.0 (CH), 127.7 (CH), 71.8 (CH), 69.4 (CH), 21.9 (CH_3), 21.4 (CH_3); **IR** (thin film) 3311, 2982, 1712, 1236, 1106, 1046 cm^{-1}; **LRMS (CI)** 315 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{13}H_{19}N_2O_5S$ $[M+H]^+$ 315.1015, observed 315.1007.

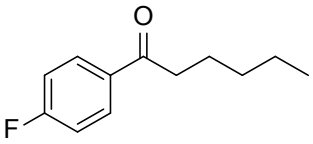




General procedure for alkyl aryl ketone synthesis

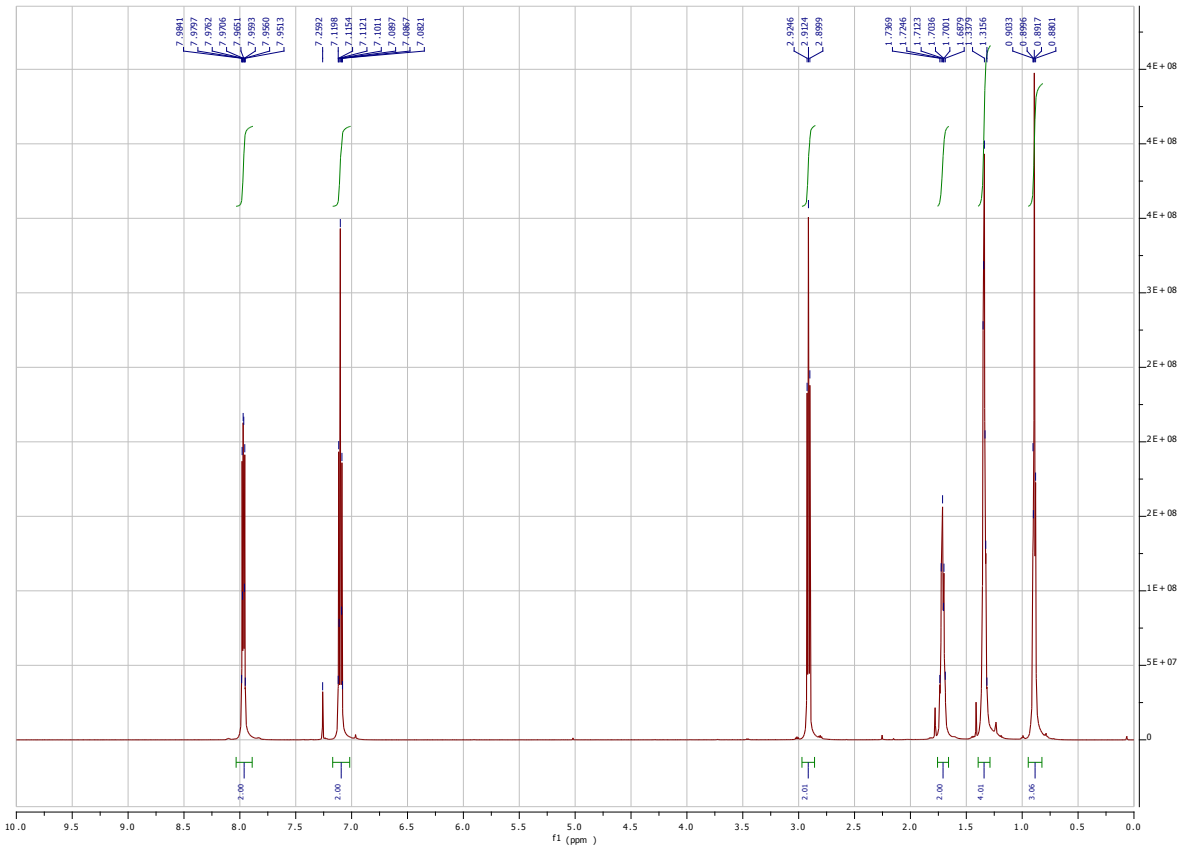
To a flame-dried three-necked flask, under an inert atmosphere, was added a solution of acyl hydrazide (0.5 mmol) in THF (10 mL). *n*-Pentylmagnesium bromide (1.25 mmol) was then added to the stirring solution in one portion at –78 °C. After 30 min, the reaction was quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and the solvent was removed in *vacuo*. The resultant crude residue was purified as described below.

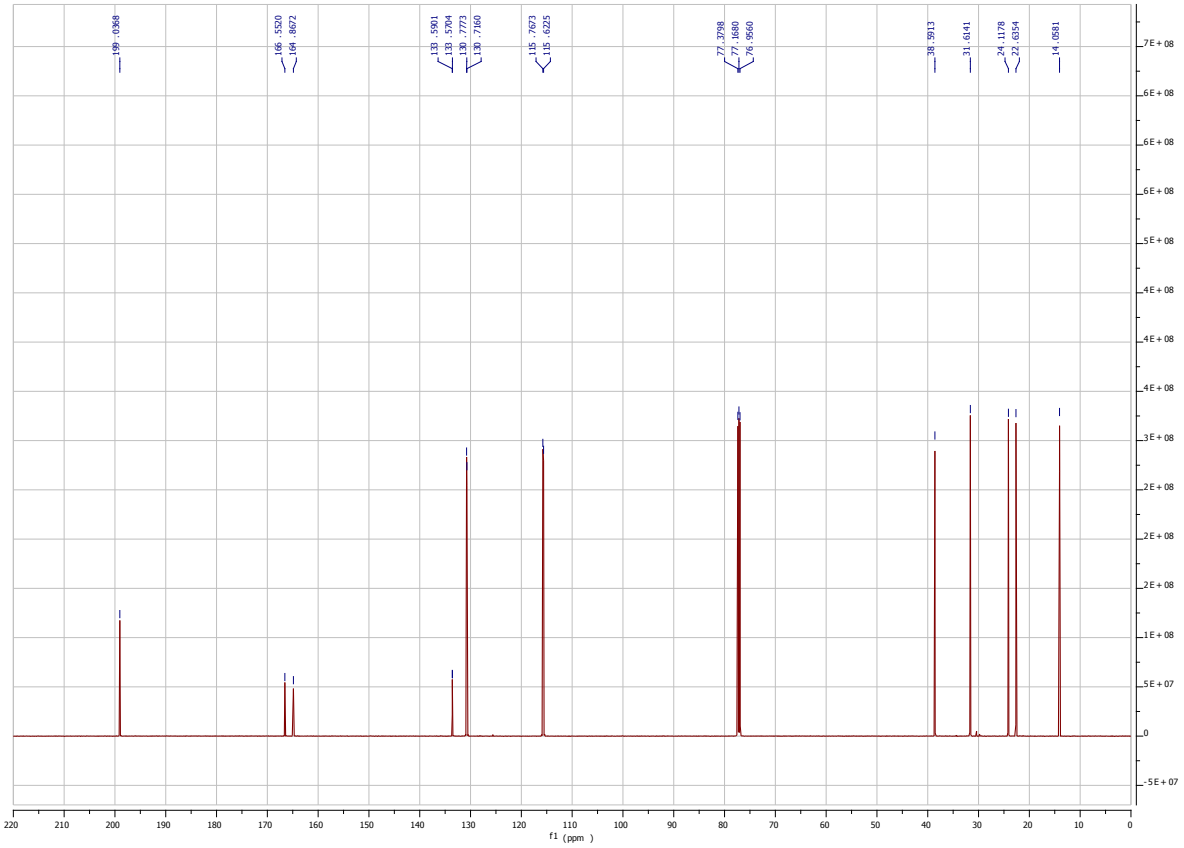
1-(4-Fluorophenyl)hexan-1-one[5] (3aa)

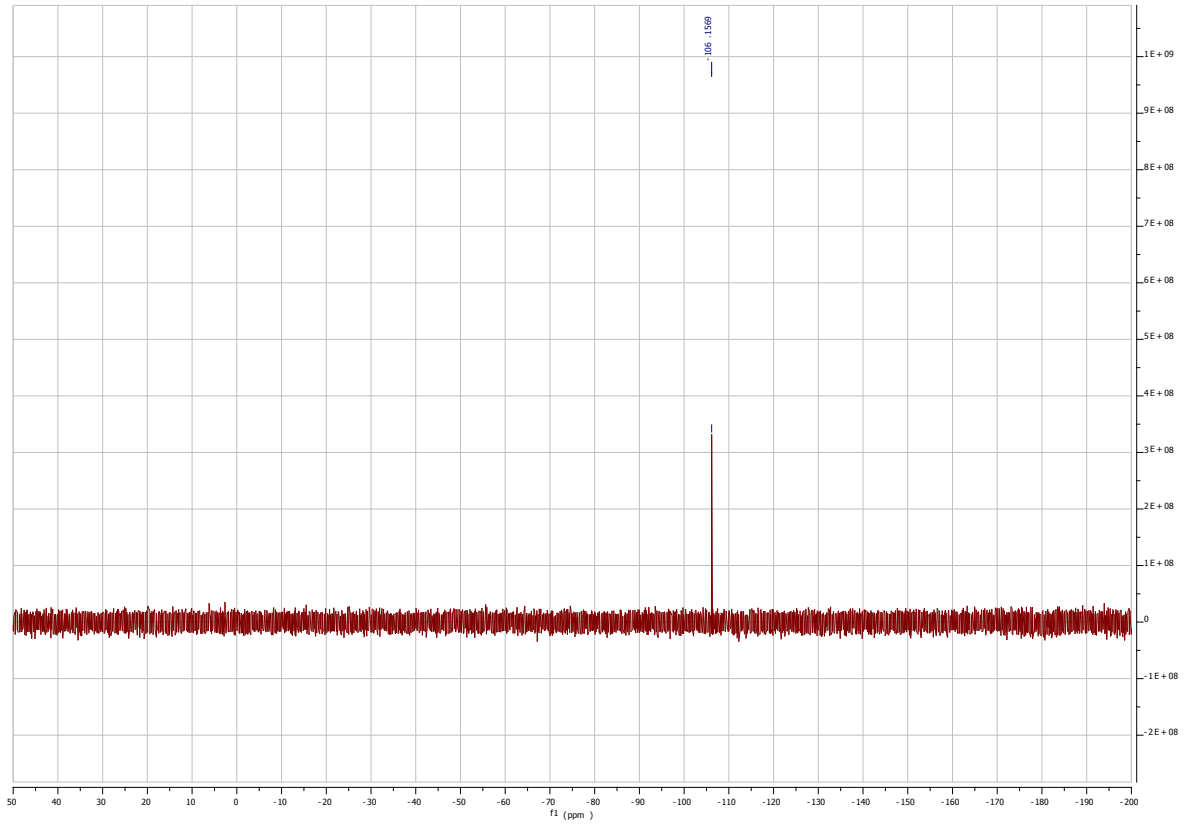


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(4-fluorophenyl)hexan-1-one as a white solid (76 mg, 0.39 mmol, 78%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98-7.95 (m, 2H), 7.11-7.08 (m, 2H), 2.91 (t, J = 7.4 Hz, 2H), 1.74-1.69 (m, 2H), 1.35-1.32 (m, 4H), 0.91-0.88 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.0 (C), 165.7 (d, $J_{C\text{-}F}$ = 252.7 Hz,

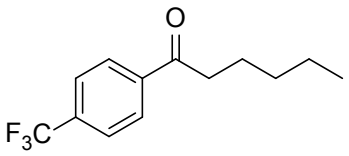
CF), 133.6 (d, $J_{C\text{-}F}$ = 3.0 Hz, CH), 130.7 (d, $J_{C\text{-}F}$ = 9.5 Hz, CH), 115.7 (d, $J_{C\text{-}F}$ = 21.7 Hz, C), 38.6 (CH_2), 31.6 (CH_2), 24.1 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -106.2 (s, 1F); **IR** (thin film) 1675, 1507, 1452, 1017 cm^{-1}; **LRMS (EI)** 194 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{12}H_{15}FO$ $[M]^+$ 194.1107, observed 194.1110; **m.p.** 41-43 °C (recrystallized from *n*-heptane).



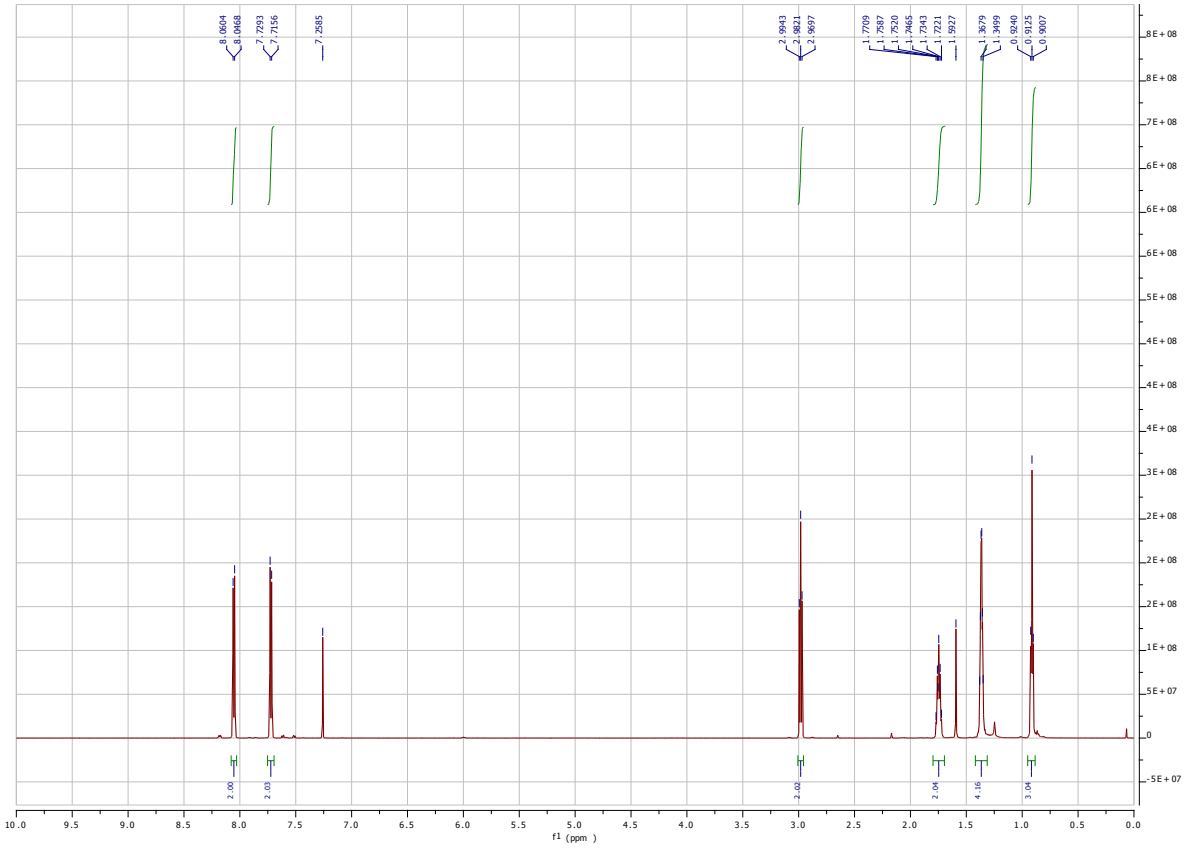


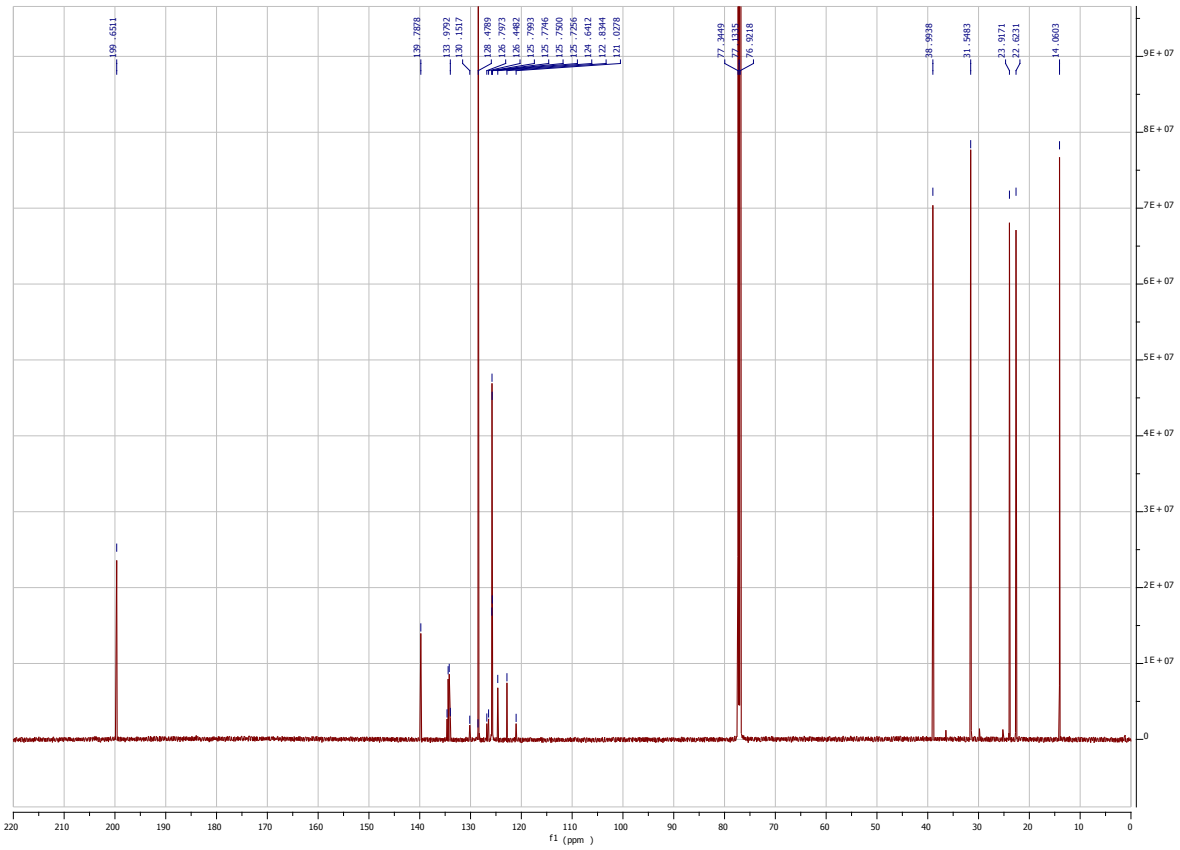


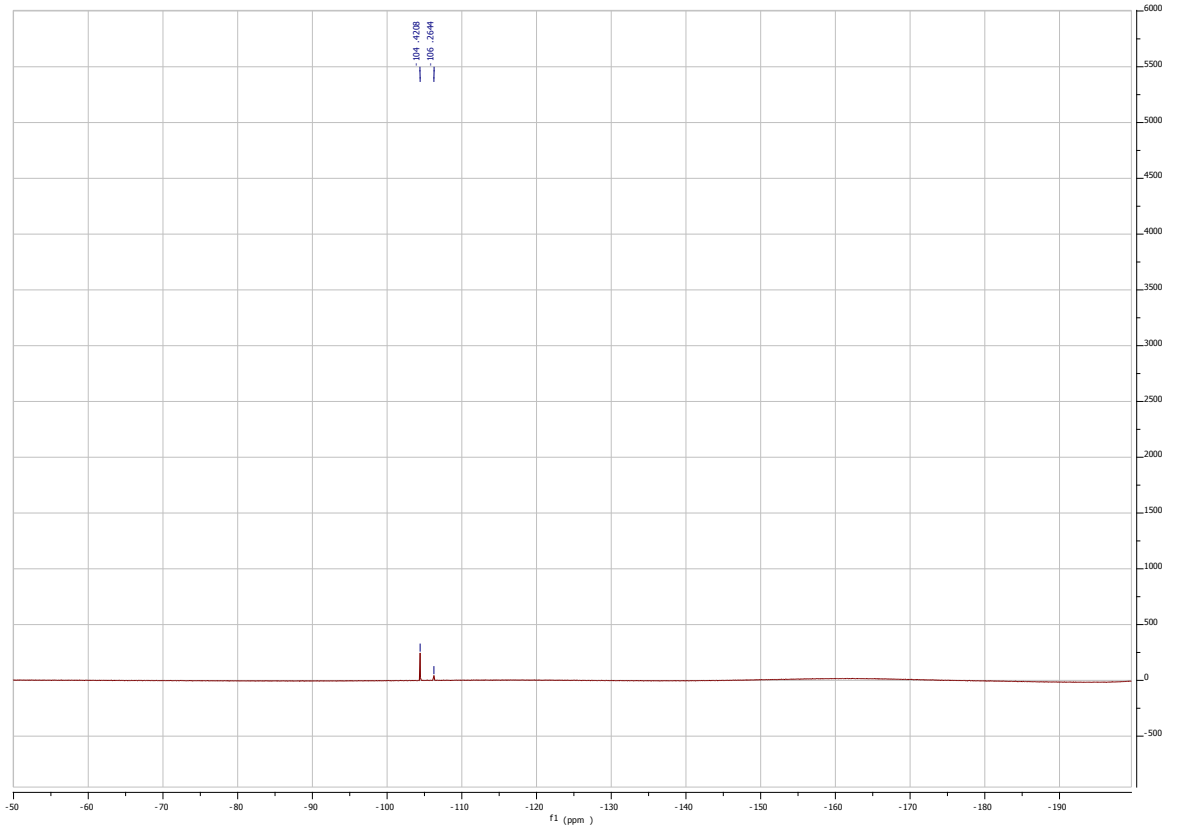
1-(4-(Trifluoromethyl)phenyl)hexan-1-one[6] (3ba)



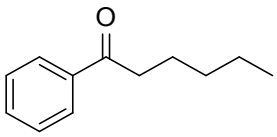
Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(4-(trifluoromethyl)phenyl)hexan-1-one as a white solid (94 mg, 0.39 mmol, 77%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 2.98 (t, J = 7.4 Hz, 2H), 1.77-1.72 (m, 2H), 1.36-1.35 (m, 4H), 0.92-0.90 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.7 (C), 139.8 (C), 134.2 (q, J_{C-F} = 129.7 Hz, C), 128.5 (q, J_{C-F} = 167.7 Hz, CH), 123.7 (q, J_{C-F} = 271.4 Hz, CF_3), 125.8 (q, J_{C-F} = 3.7 Hz, CH), 39.0 (CH_2), 31.5 (CH_2), 23.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -104.4 (m, 3F); **IR** (thin film) 2985, 1682, 1410, 1329, 1167, 1130, 1069, 1014, 831 cm^{-1}; **LRMS (EI)** 244 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{13}H_{15}F_3O$ $[M]^+$ 244.1075, observed 244.1070; **m.p.** 31-35 °C (recrystallized from petroleum ether).



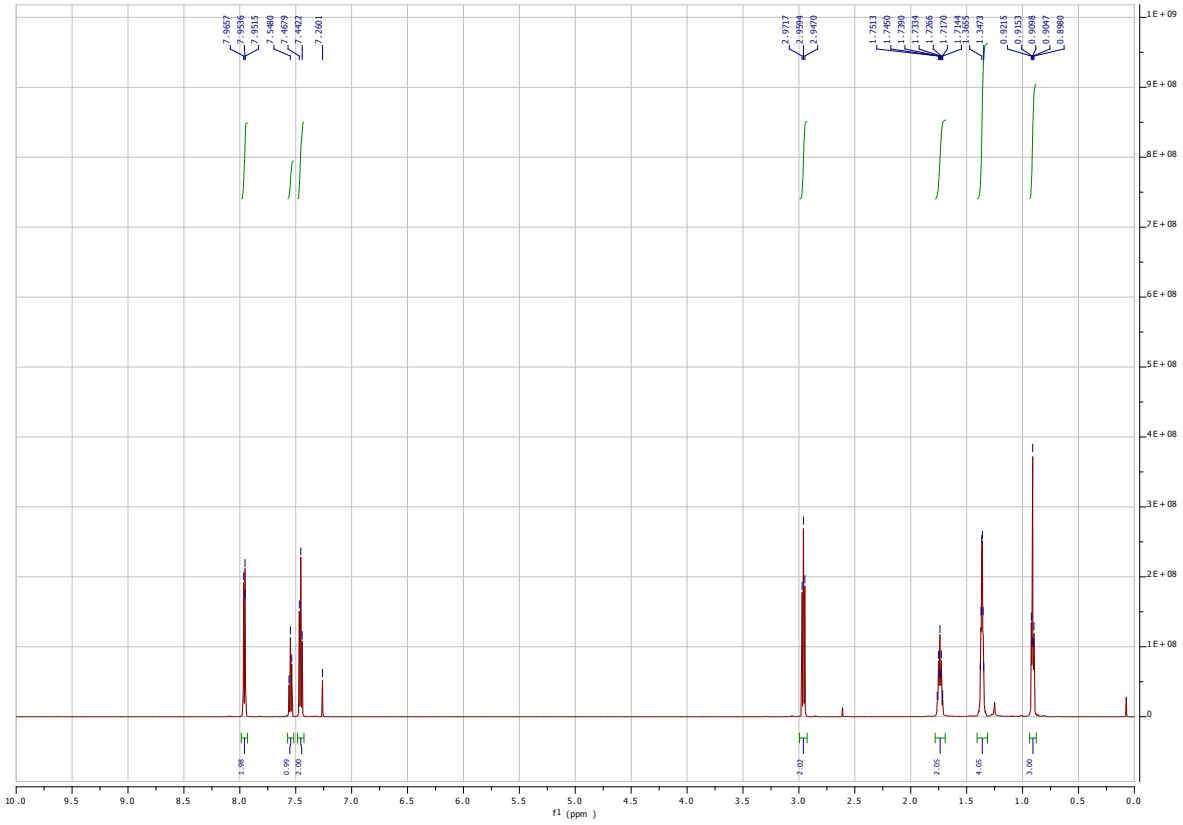


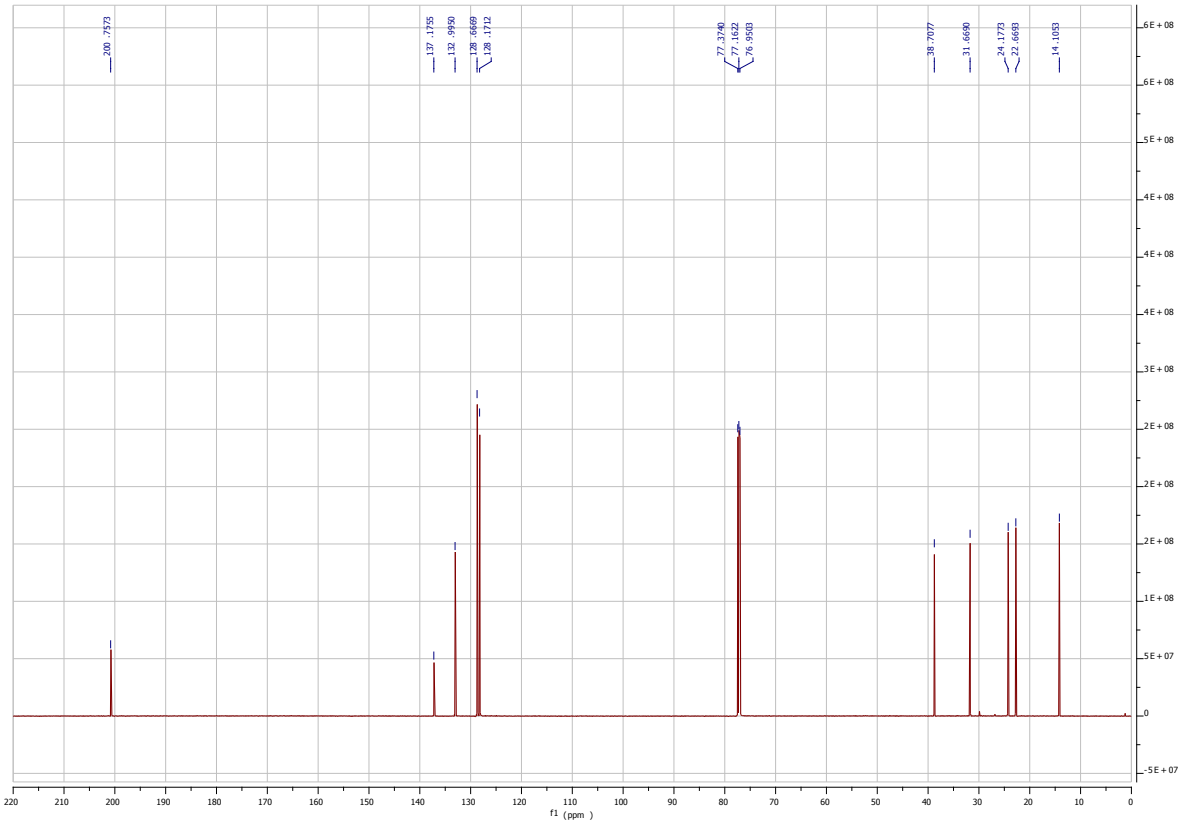


1-Phenylhexan-1-one[7] (3ca)

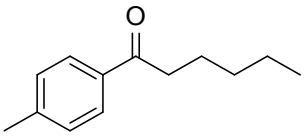


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-phenylhexan-1-one as clear oil (63 mg, 0.36 mmol, 71%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98-7.94 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.75-1.72 (m, 2H), 1.38-1.34 (m, 4H), 0.93-0.89 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 200.8 (C), 137.2 (C), 133.0 (CH), 128.7 (CH), 128.2 (CH), 38.7 (CH_2), 31.7 (CH_2), 24.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3); **IR** (thin film) 1737, 1657, 1415, 984 cm^{-1}; **LRMS (EI)** 176 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{12}H_{16}O$ $[M]^+$ 176.1201, observed 176.1211.

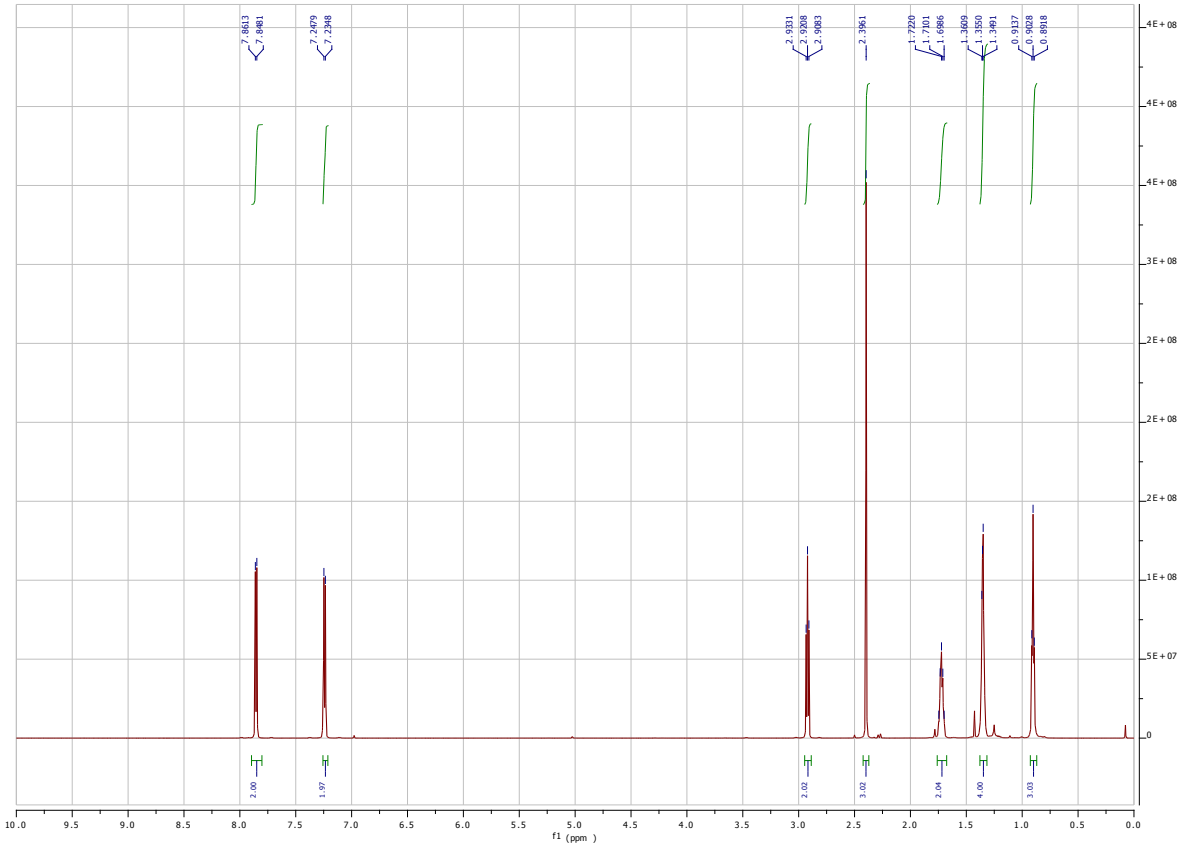


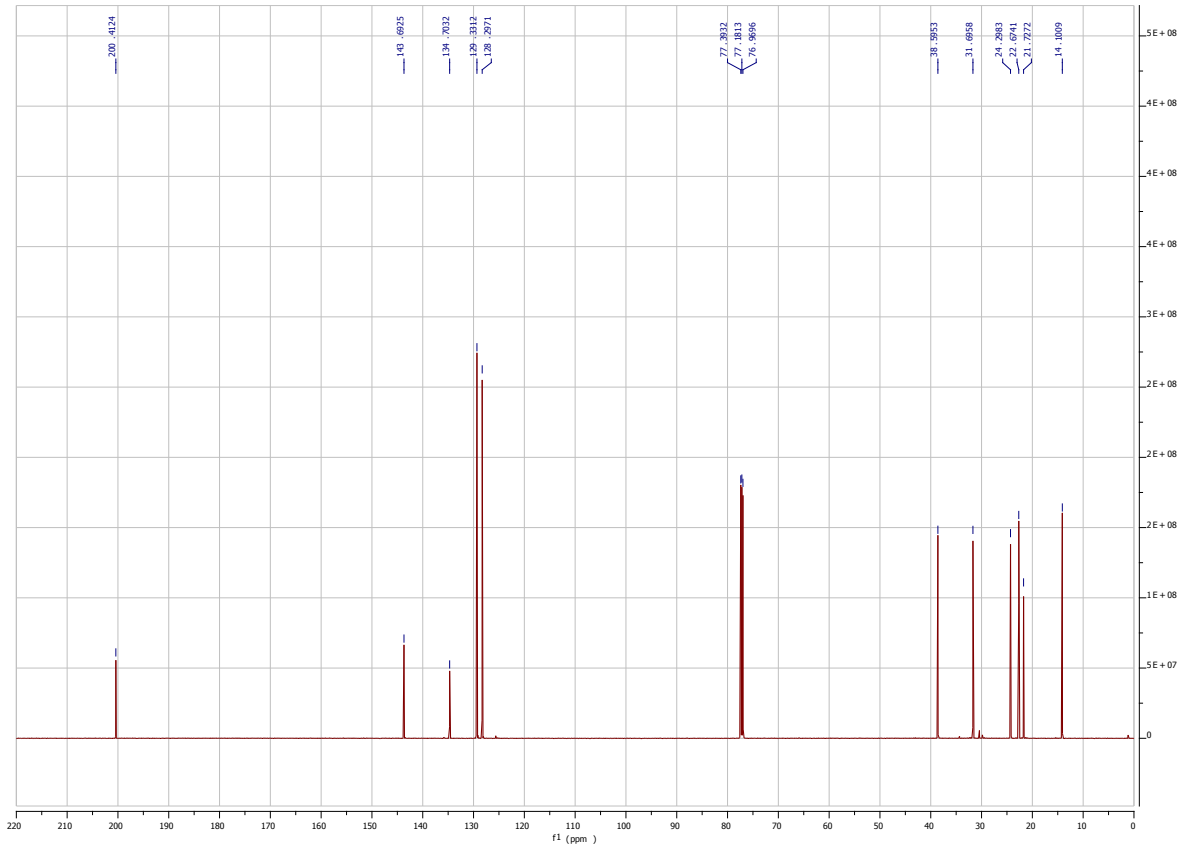


1-(*p*-Tolyl)hexan-1-one[5] (3da)

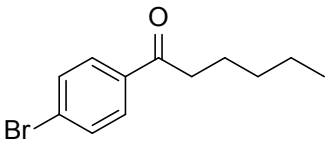


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(*p*-tolyl)hexan-1-one as a colourless oil (65 mg, 0.34 mmol, 68%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.72-1.69 (m, 2H), 1.37-1.34 (m, 4H), 0.92-0.89 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 200.4 (C), 143.7 (C), 137.7 (C), 129.3 (CH), 128.3 (CH), 38.6 (CH_2), 31.7 (CH_2), 24.3 (CH_2), 22.7 (CH_2), 21.7 (CH_3), 14.1 (CH_3); **IR** (thin film) 2984, 1665, 1017, 830 cm^{-1}; **LRMS (EI)** 190 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{13}H_{18}O$ $[M]^+$ 190.1358, observed 190.1364.

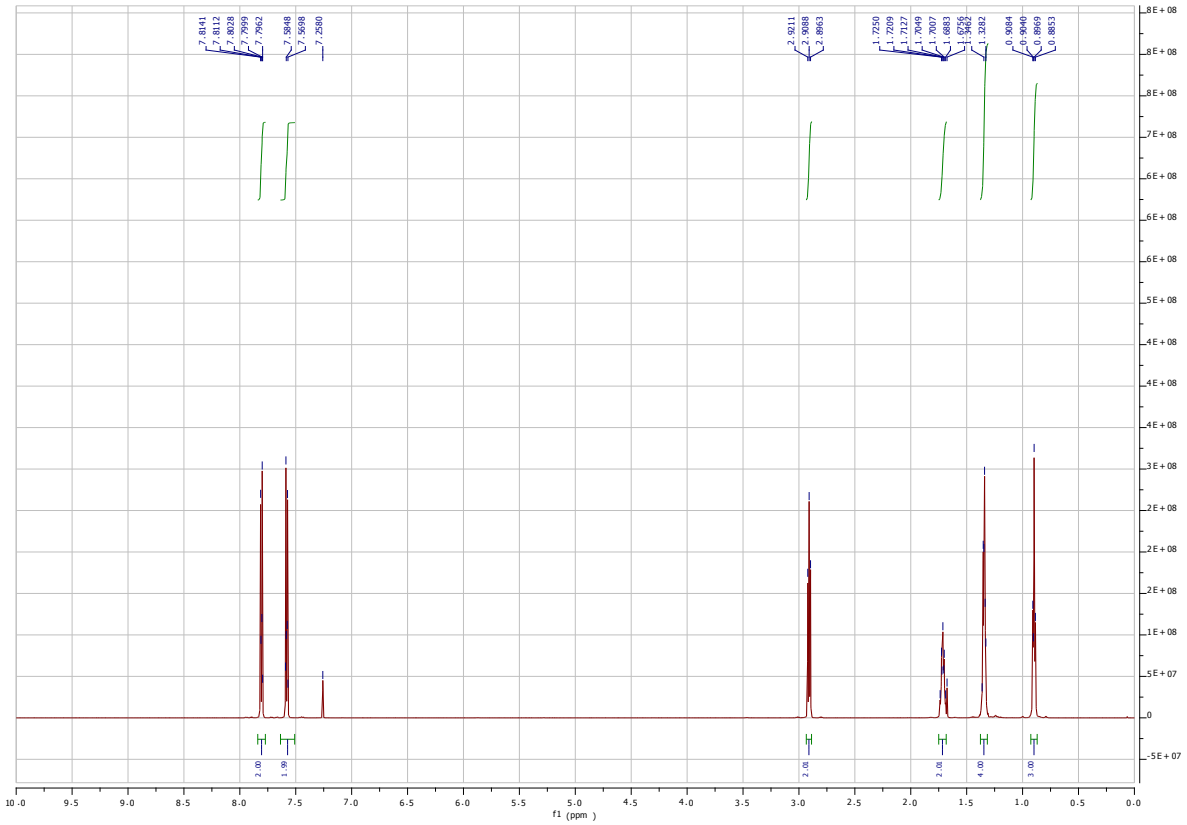


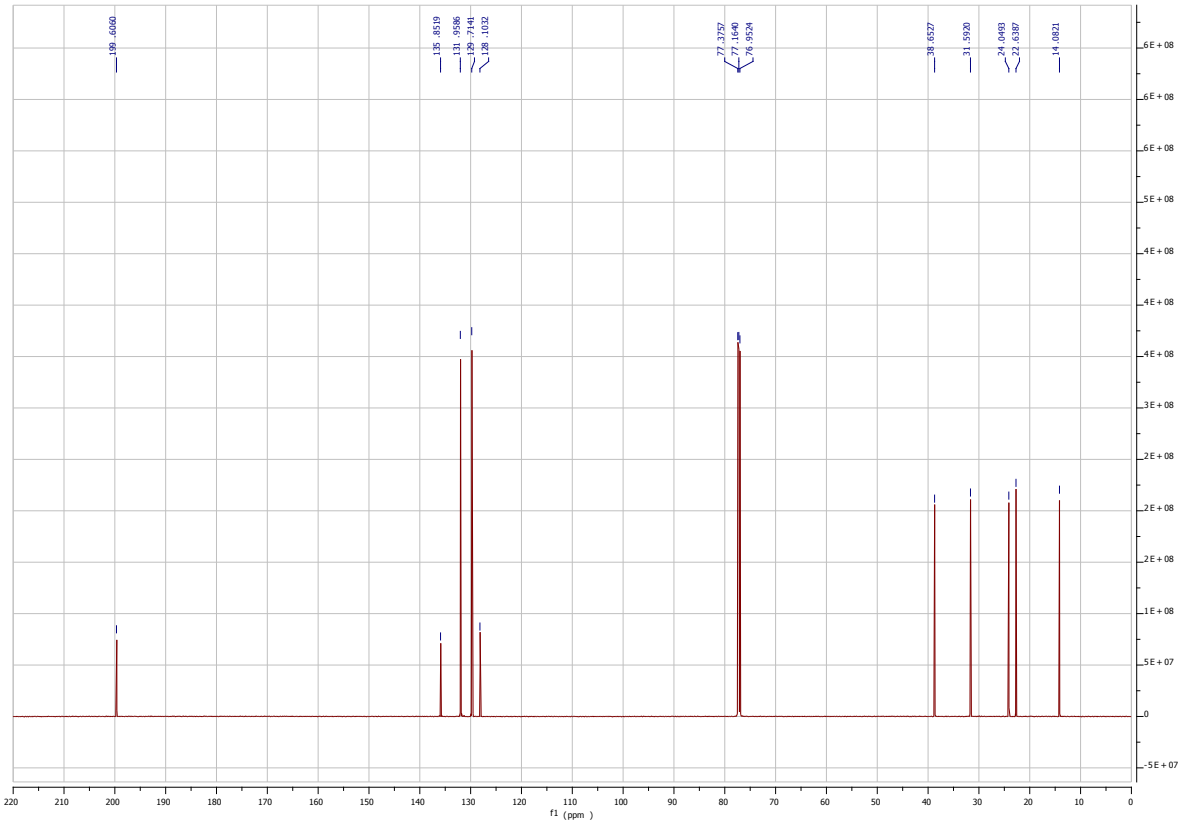


1-(4-Bromophenyl)hexan-1-one[8] (3ea)

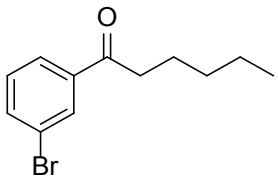


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(4-bromophenyl)hexan-1-one as a colourless oil (102 mg, 0.40 mmol, 79%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81-7.79 (m, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.72-1.68 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.6 (C), 135.9 (C), 132.0 (CH), 129.7 (CH), 128.1 (C), 38.7 (CH_2), 31.6 (CH_2), 24.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **IR** (thin film) 2964, 1676, 1585, 1401, 1201, 819 cm^{-1}; **LRMS (EI)** 256 (100, $[M^{81}Br]^+$), 254 (100, $[M^{79}Br]^+$); **HRMS (EI)** calcd. for $C_{12}H_{15}BrO$ $[M^{79}Br]^+$ 254.0306, observed 254.0304.

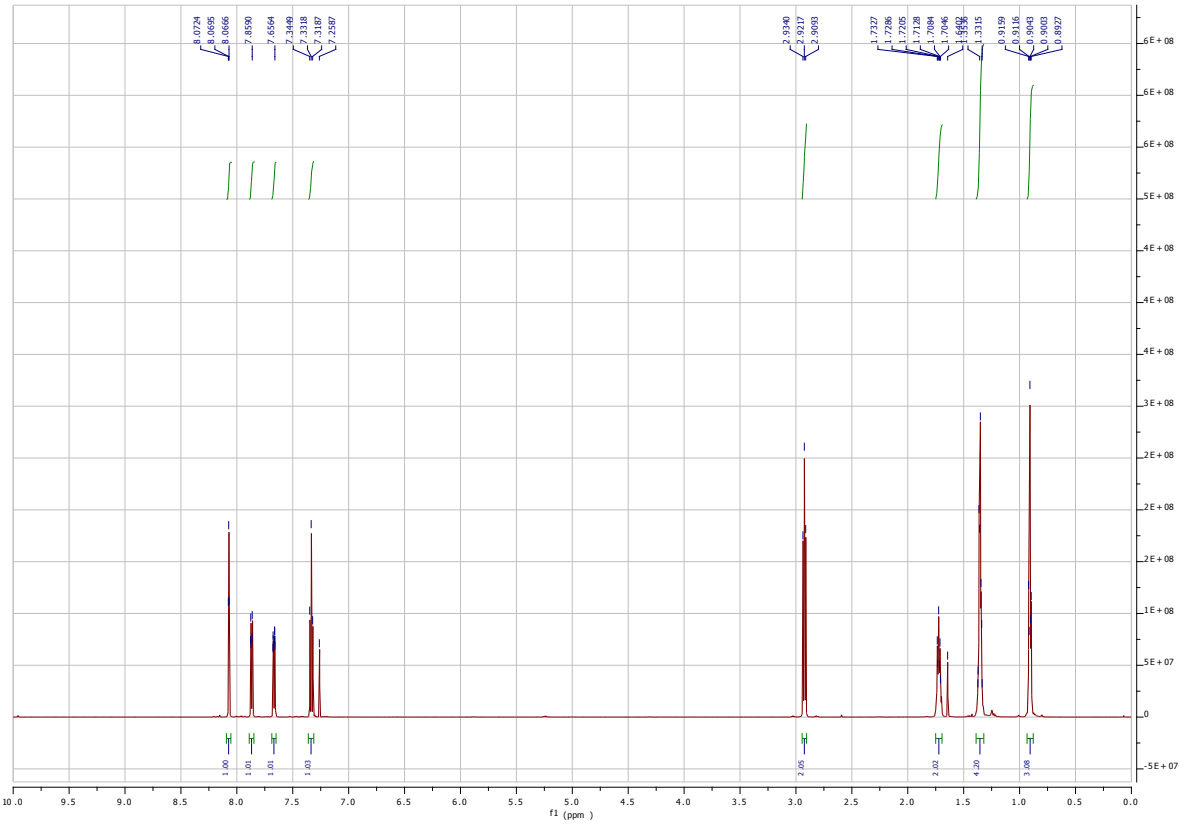


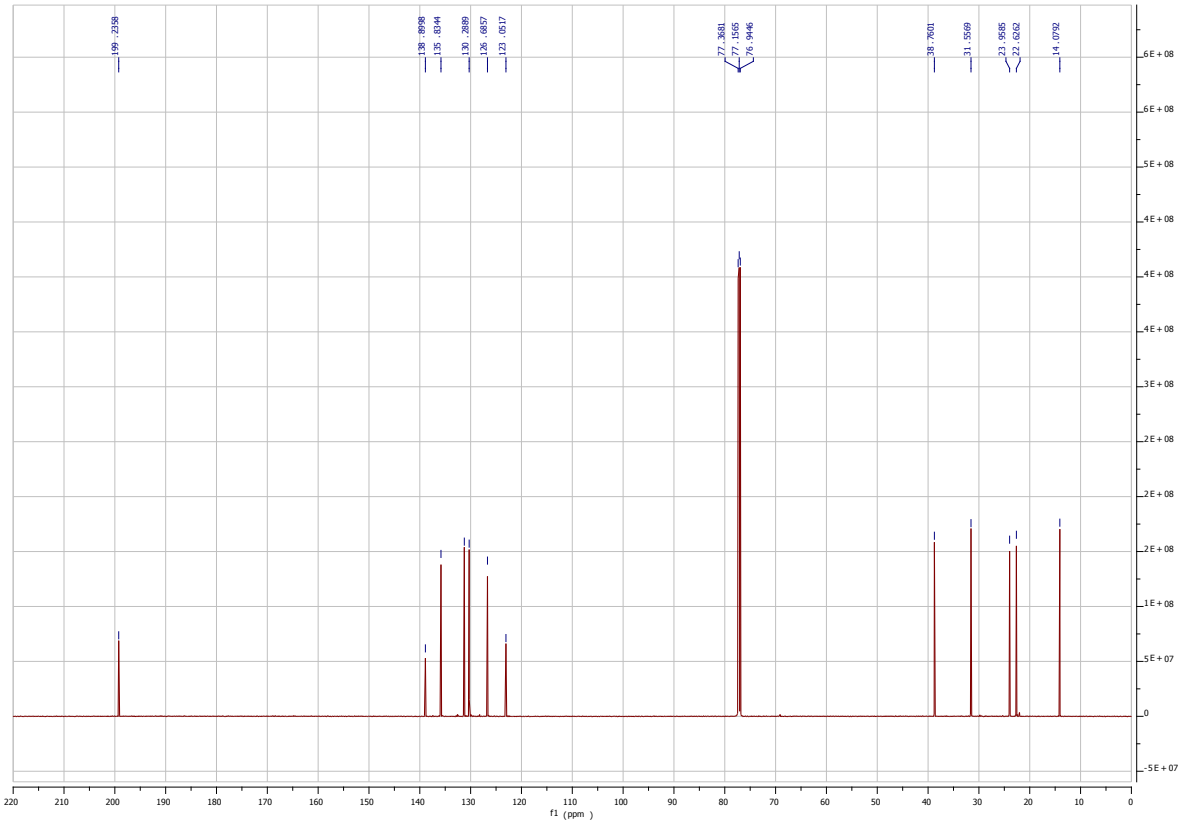


1-(3-Bromophenyl)hexan-1-one[5] (3fa)

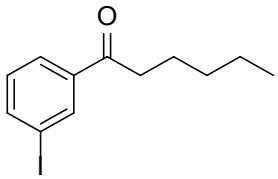


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(3-bromophenyl)hexan-1-one as a colourless oil (92 mg, 0.36 mmol, 72%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (t, *J* = 1.7 Hz, 1H), 7.88-7.85 (m, 1H), 7.68-7.65 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 1.73-1.70 (m, 2H), 1.36-1.32 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.2 (C), 138.9 (C), 135.8 (CH), 131.2 (CH), 130.3 (CH), 126.7 (CH), 123.1 (C), 38.8 (CH_2), 31.6 (CH_2), 24.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **IR** (thin film) 2952, 1676, 1586, 819 cm^{-1}; **LRMS (CI)** 256 (100, $[M^{81}Br]^+$), 254 (100, $[M^{79}Br]^+$); **HRMS (CI)** calcd. for $C_{12}H_{15}BrO$ $[M^{79}Br]^+$ 254.0306, observed 254.0301.

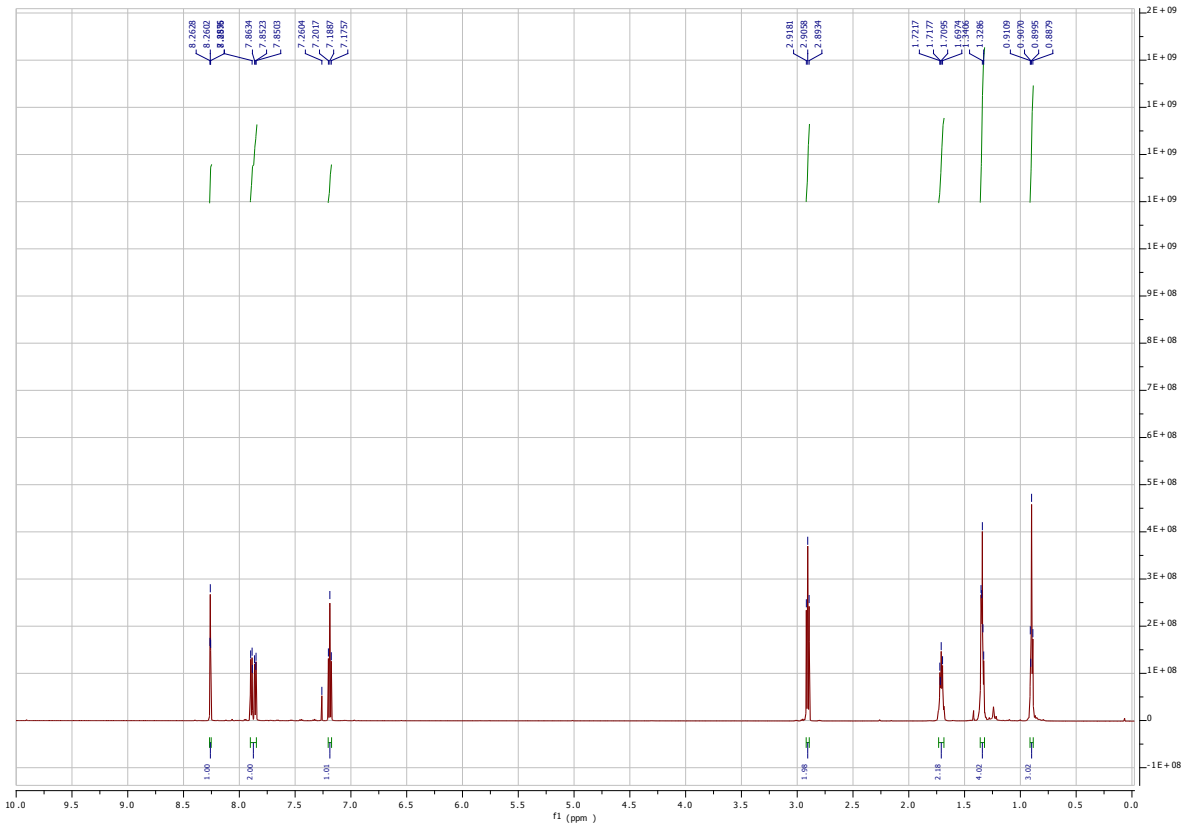


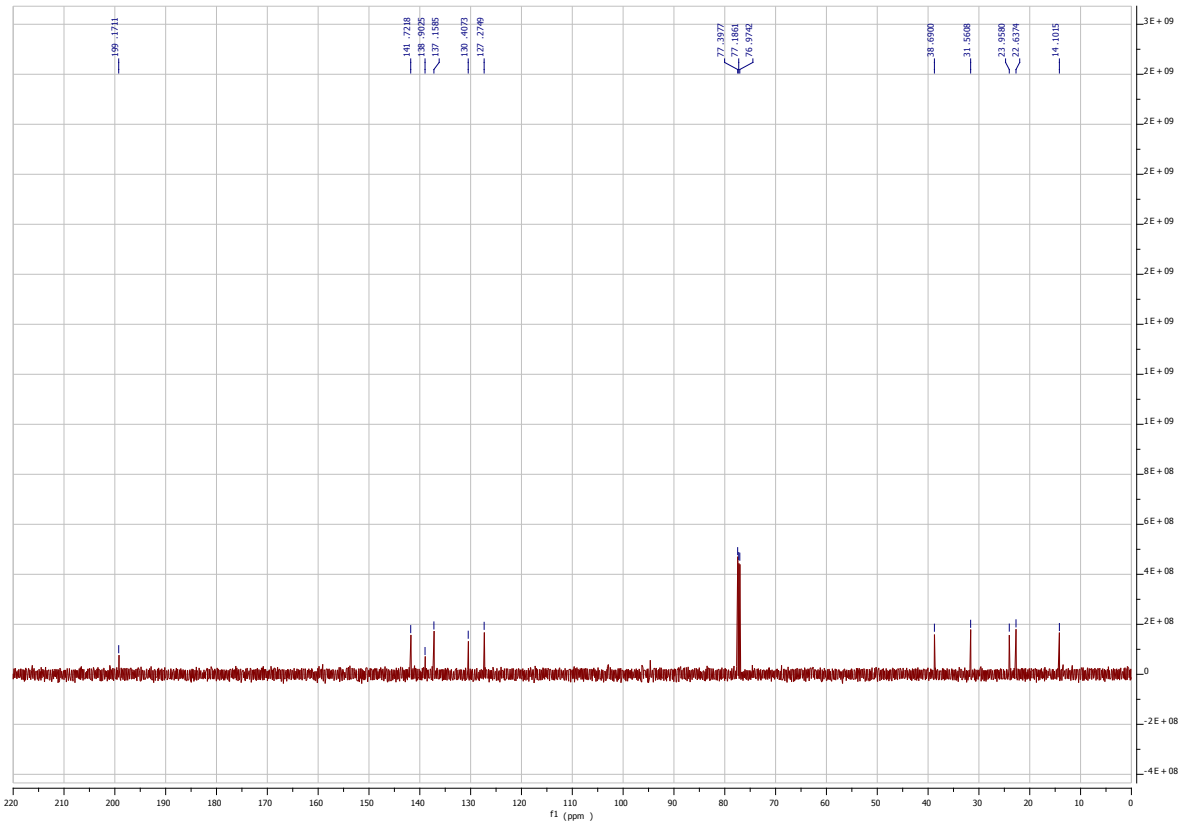


1-(3-Iodophenyl)hexan-1-one (3ga)

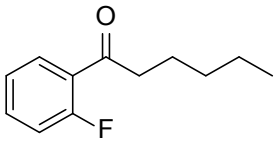


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(3-iodophenyl)hexan-1-one as a colourless oil (115 mg, 0.38 mmol, 76%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (t, *J* = 1.6 Hz, 1H), 7.89-7.85 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.72-1.69 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.2 (C), 141.7 (CH), 138.9 (C), 137.2 (CH), 130.4 (CH), 127.3 (CH), 94.5 (C), 38.7 (CH_2), 31.6 (CH_2), 24.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **IR** (thin film) 2912, 1670, 1590, 1201, 901 cm^{-1}; **LRMS (EI)** 302 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{12}H_{15}IO$ $[M]^+$ 302.0168, observed 302.0163.

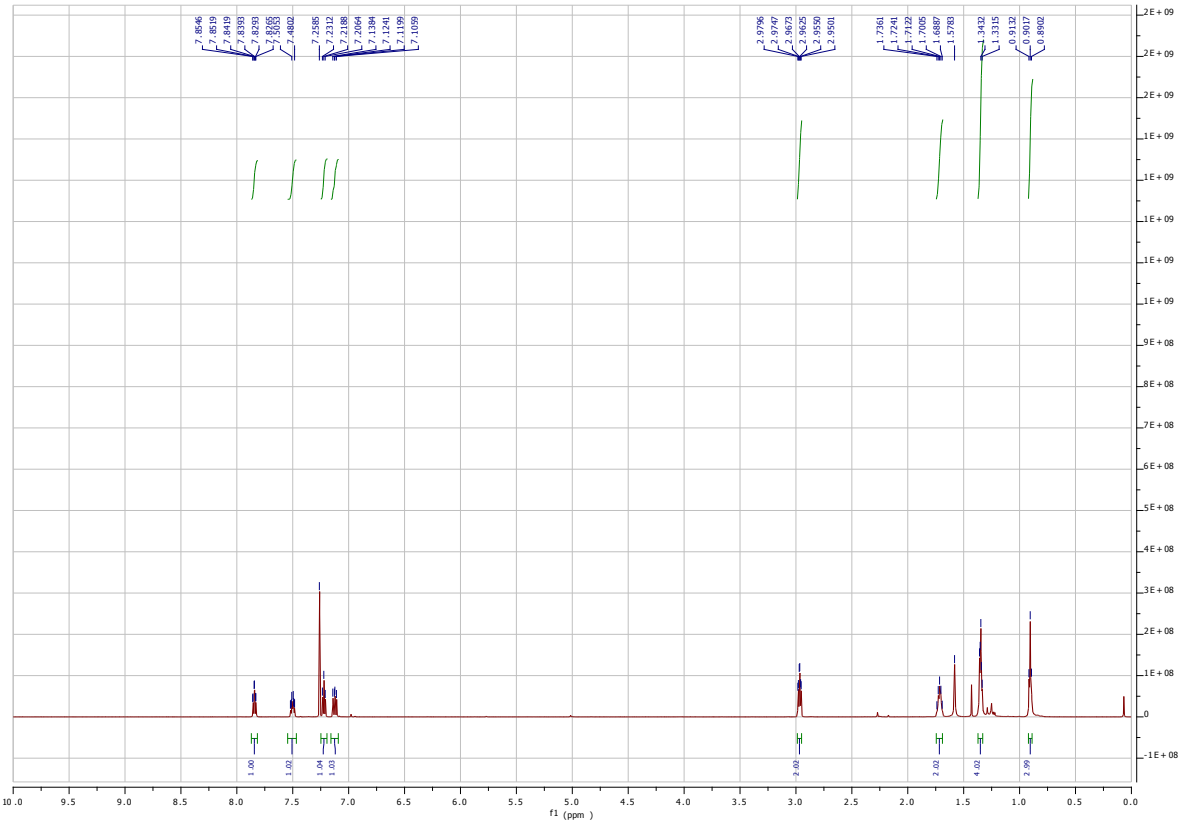


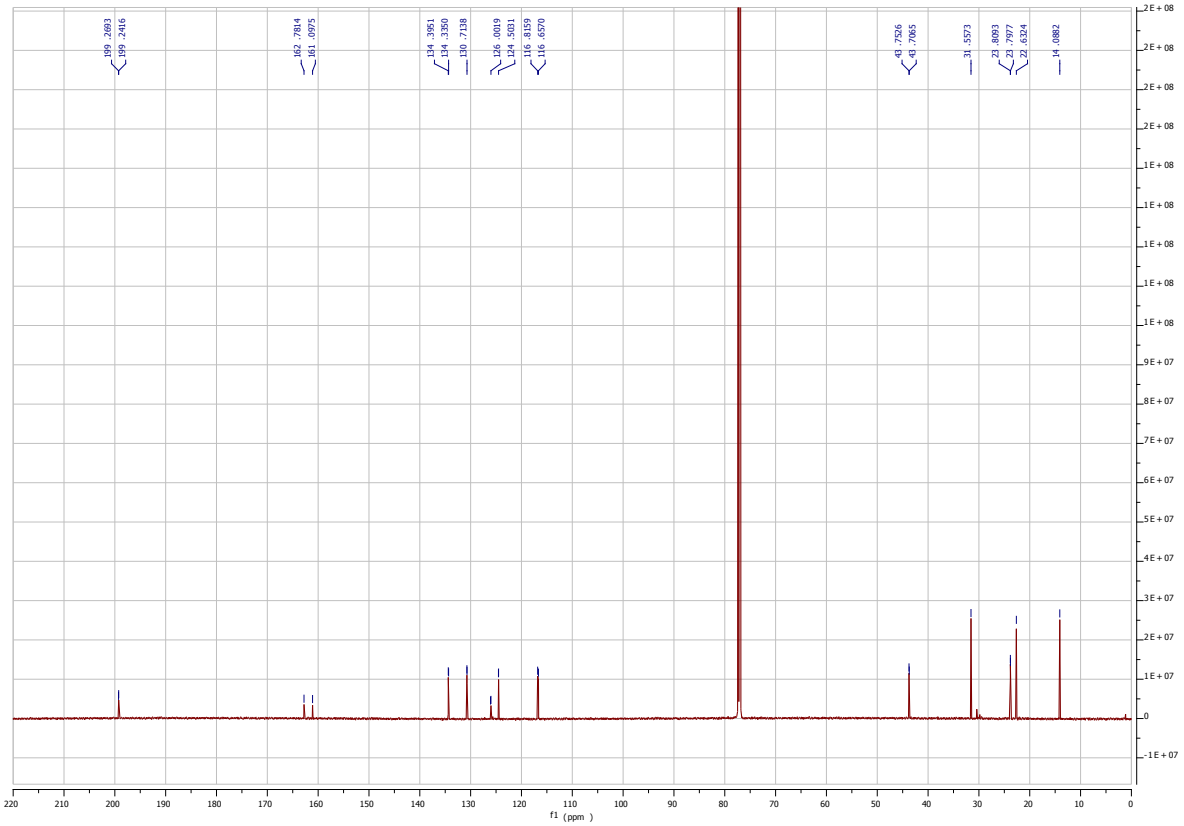


1-(2-Fluorophenyl)hexan-1-one[9] (3ha)

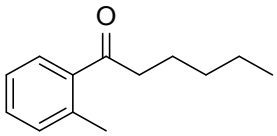


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(2-fluorophenyl)hexan-1-one as a colourless oil (35 mg, 0.18 mmol, 36%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84 (dt, J = 7.6 Hz, $J_{H\text{-}F}$ = 1.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.14-7.11 (m, 1H), 2.97 (dt, J = 7.4 Hz, $J_{H\text{-}F}$ = 2.9 Hz, 2H), 1.74-1.69 (m, 2H), 1.36-1.33 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.3 (d, $J_{C\text{-}F}$ = 4.2 Hz, C), 162.4 (d, $J_{C\text{-}F}$ = 252.6 Hz, CF), 134.4 (d, $J_{C\text{-}F}$ = 9.0 Hz, CH), 130.7 (d, $J_{C\text{-}F}$ = 2.7 Hz, CH), 126.0 (d, $J_{C\text{-}F}$ = 13.2 Hz, C), 124.5 (d, $J_{C\text{-}F}$ = 3.4 Hz, CH), 116.7 (d, $J_{C\text{-}F}$ = 23.8 Hz, CH), 43.7 (d, $J_{C\text{-}F}$ = 6.9 Hz, CH_2), 31.6 (CH_2), 23.8 (d, $J_{C\text{-}F}$ = 1.7 Hz, CH_2), 22.6 (CH_2), 14.1 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -109.7 (s, 1F); **IR** (thin film) 2934, 1675, 1507, 1452, 1017 cm^{-1}; **LRMS (EI)** 194 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{12}H_{15}FO$ $[M]^+$ 194.1107, observed 194.1110.

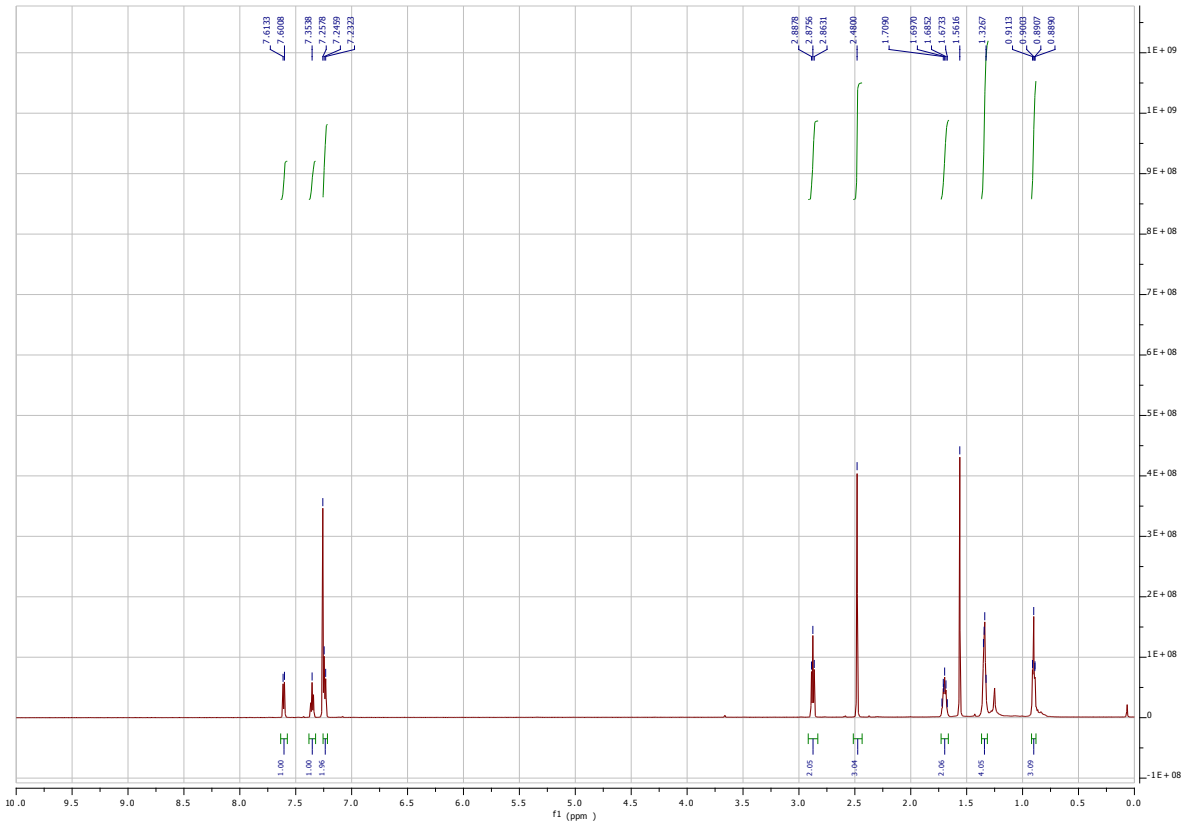


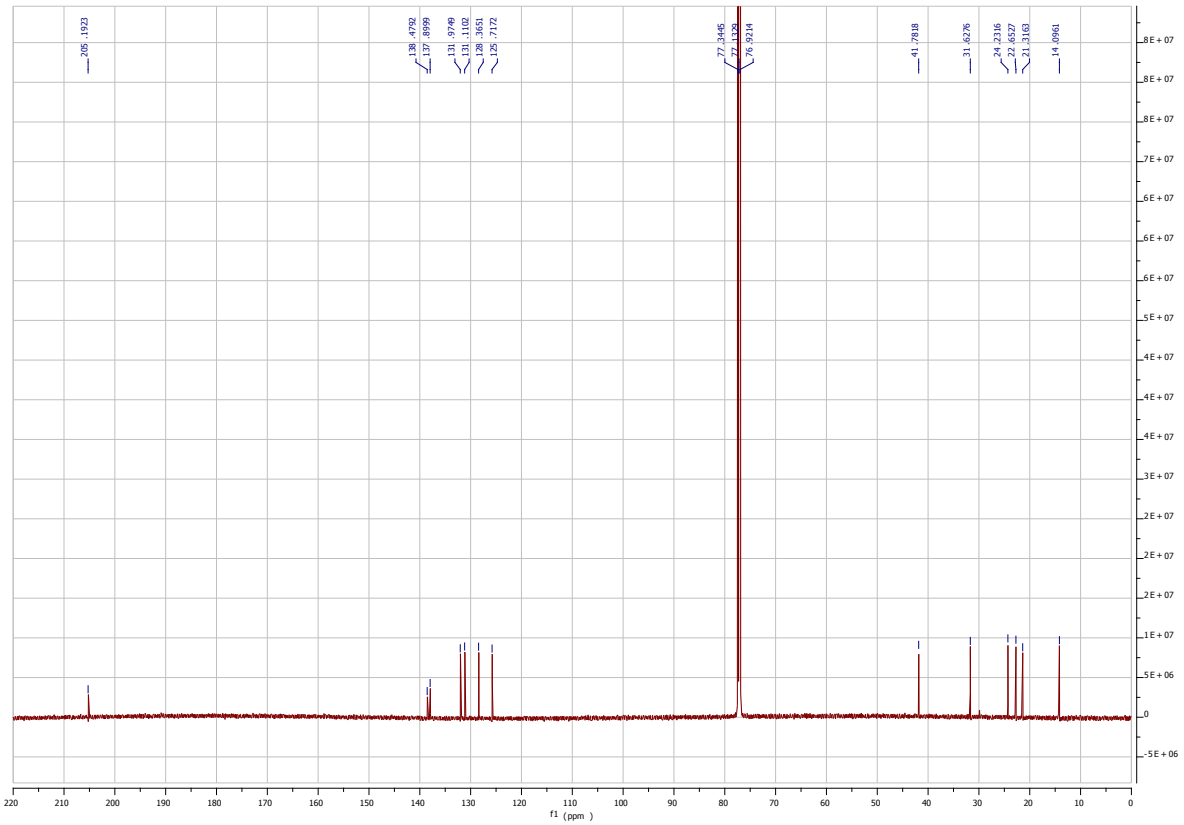


1-(*o*-Tolyl)hexan-1-one[10] (3ia)

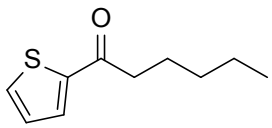


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(*o*-tolyl)hexan-1-one as a colourless oil (42 mg, 0.22 mmol, 44%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 8.2 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 1.72-1.67 (m, 2H), 2.48 (s, 3H), 1.33-1.32 (m, 4H), 0.93-0.88 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.2 (C), 138.5 (C), 137.9 (C), 132.0 (CH), 131.1 (CH), 128.4 (CH), 125.7 (CH), 41.8 (CH_2), 31.6 (CH_2), 24.2 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.1 (CH_3); **IR** 2956, 2926, 2857, 1656, 1455, cm^{-1}; **LRMS (CI)** 191 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{13}H_{19}O$ $[M+H]^+$ 191.1430, observed 191.1429.

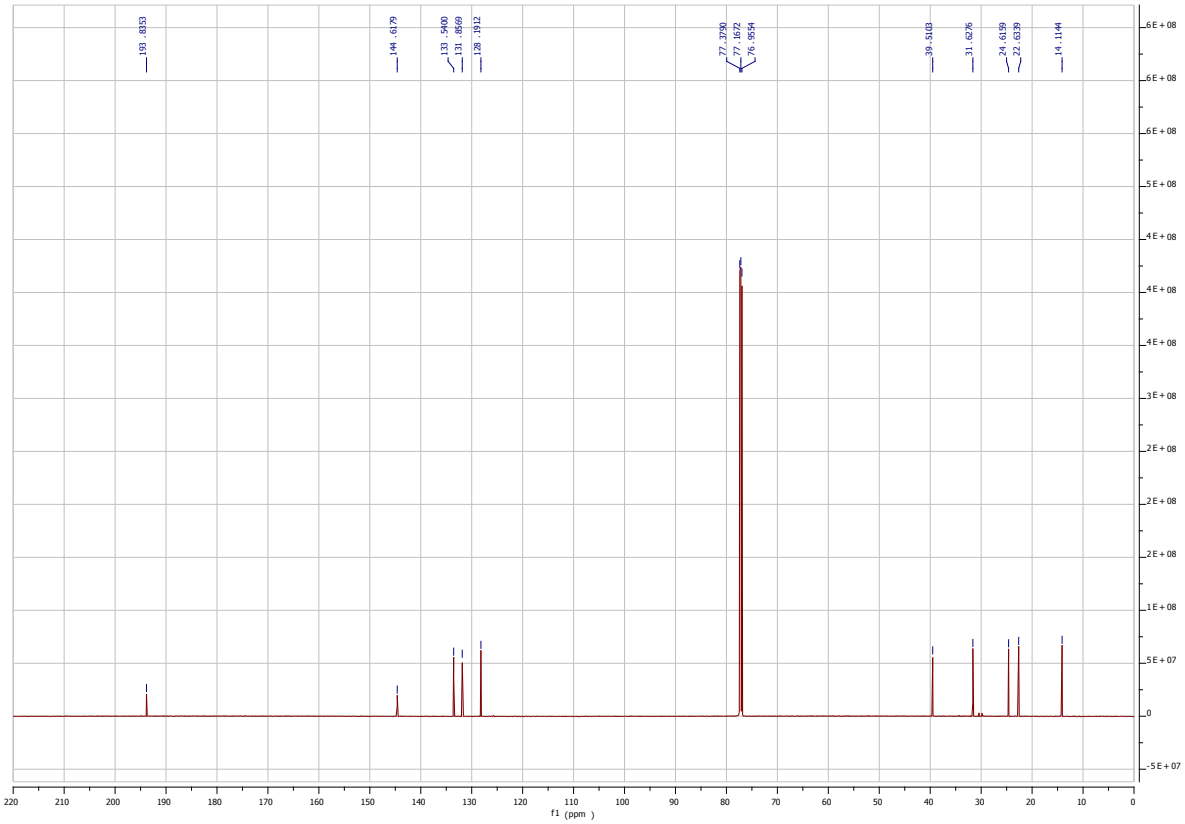




1-(Thiophen-2-yl)hexan-1-one[5] (3la)



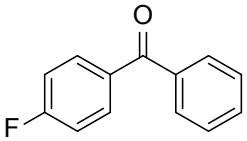
Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(thiophen-2-yl)hexan-1-one as a colourless oil (0.67 mg, 0.37 mmol, 74%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 3.7 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.12 (t, *J* = 4.3 Hz, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.76-1.72 (m, 2H), 1.37-1.33 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.9 (C), 144.6 (C), 133.5 (CH), 131.9 (CH), 128.2 (CH), 39.5 (CH_2), 31.6 (CH_2), 24.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3); **IR** (thin film) 2955, 2927, 2858, 1658, 1518, 1459, 1237, 1058 cm^{-1}.



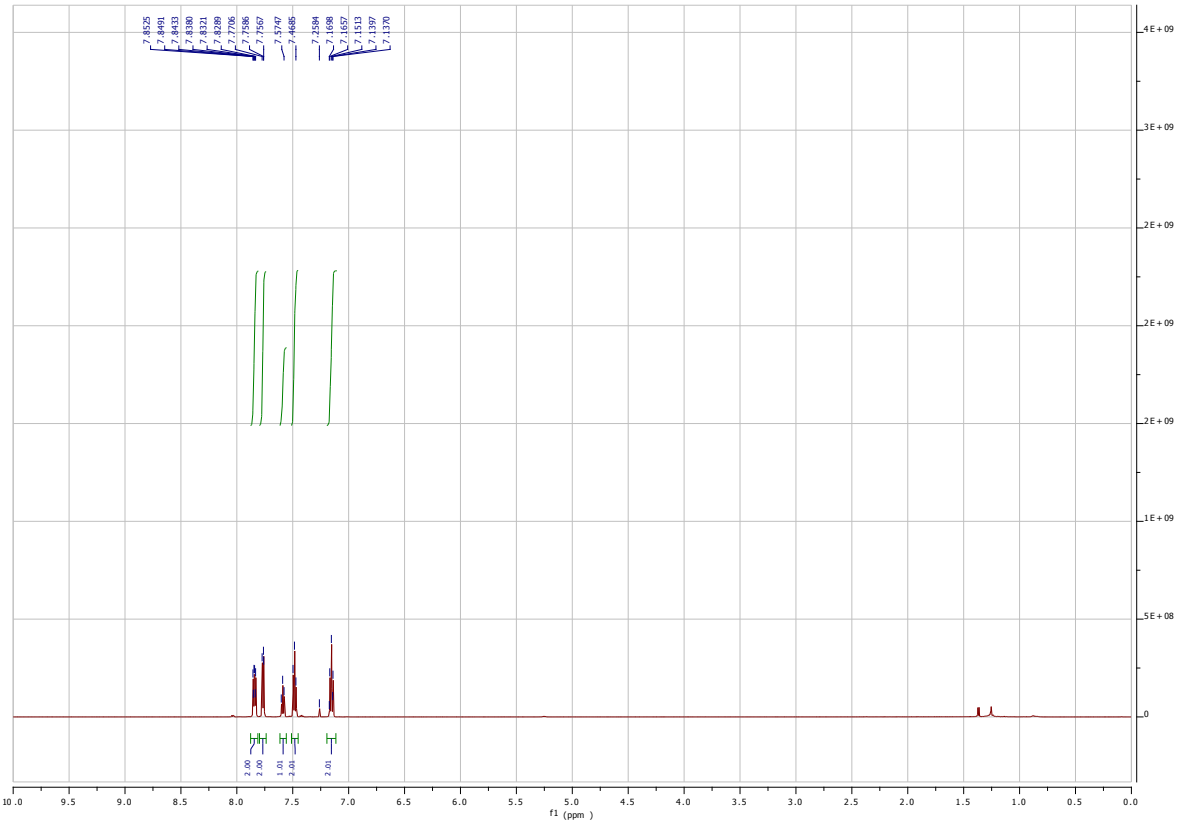
General procedure for diaryl ketone synthesis

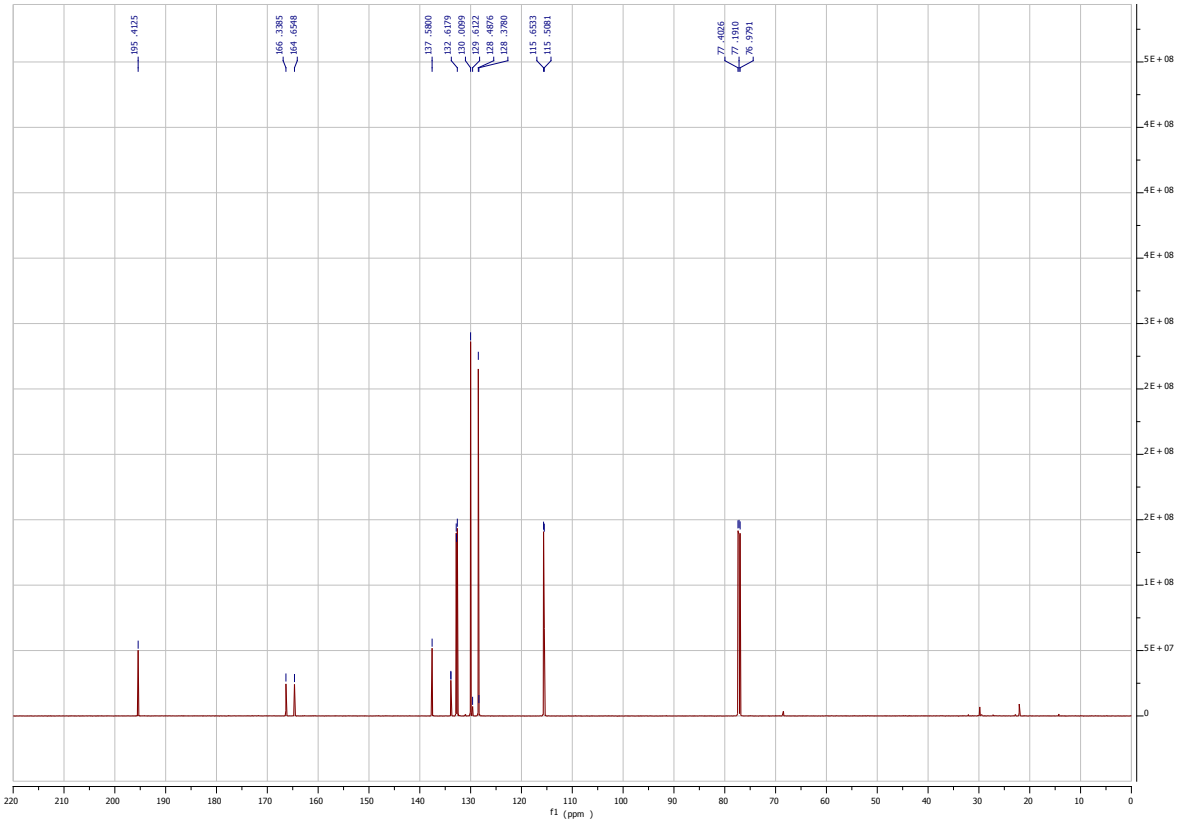
To a flame-dried, three necked flask, under an inert atmosphere, was added a solution of acyl hydrazide (0.5 mmol) in THF (10 mL). Phenylmagnesium bromide (1.25 mmol) was then added to the stirring solution in one portion at –78 °C. After 30 min, the reaction was warmed to 0 °C over 30 min. After this time, the reactions was quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was washed with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and solvent removed in *vacuo*. The crude residue was purified as described below.

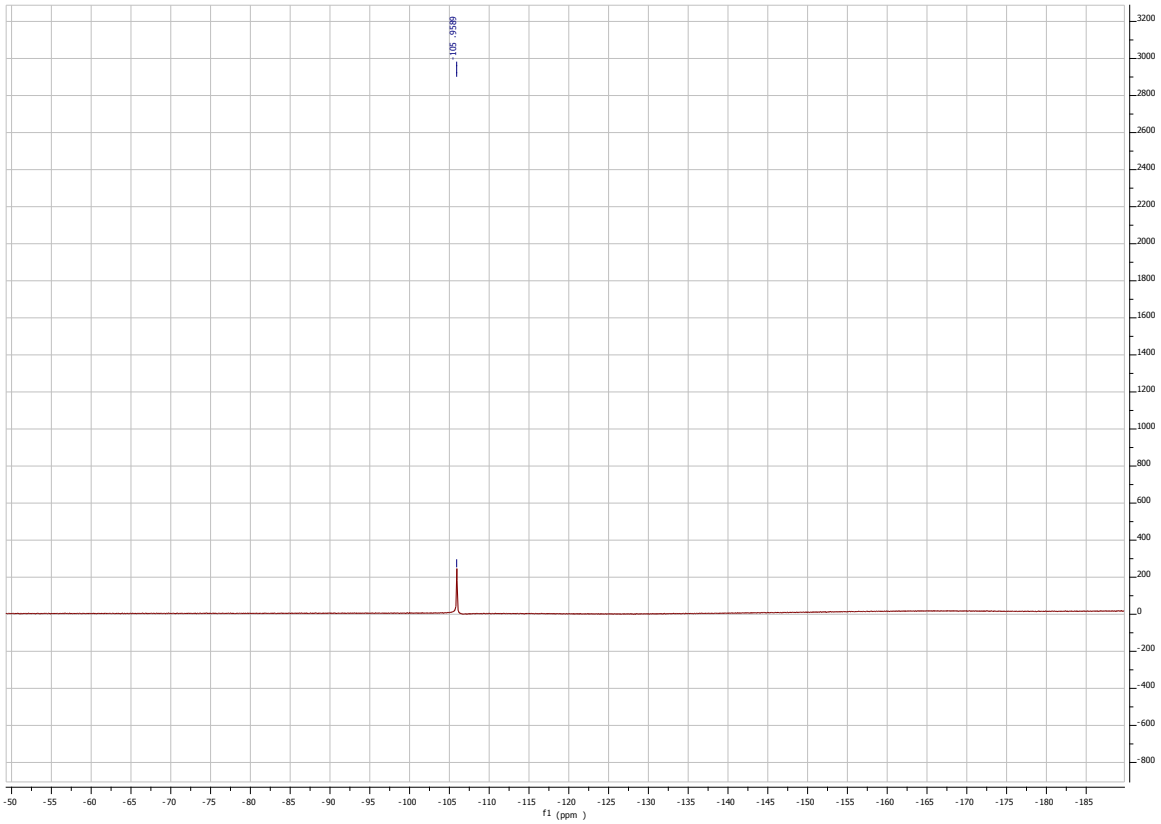
(4-Fluorophenyl)(phenyl)methanone[11] (3ab)



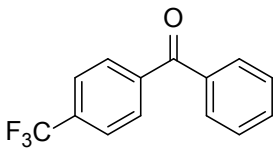
Purification by column chromatography (1%-5% Et_2O/Petrol) gave (4-fluorophenyl)(phenyl)methanone as a colourless oil (78 mg, 0.39 mmol, 78%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85-7.82 (m, 2H), 7.78-7.75 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.45 (m, 2H), 7.17-7.13 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.4 (C), 166.5 (d, $J_{C\text{-}F}$ = 252.6 Hz, C), 137.6 (C), 133.9 (d, $J_{C\text{-}F}$ = 2.9 Hz, C), 132.8 (d, $J_{C\text{-}F}$ = 9.1 Hz, CH), 132.6 (CH), 130.0 (CH), 128.5 (CH), 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz, CH); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -106.0 (s, 1F); **IR** (thin film) 1656, 1598, 1446, 1275, 698cm^{-1}; **LRMS (EI)** 200 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{13}H_9FO$ $[M]^+$ 200.0637, observed 200.0635.



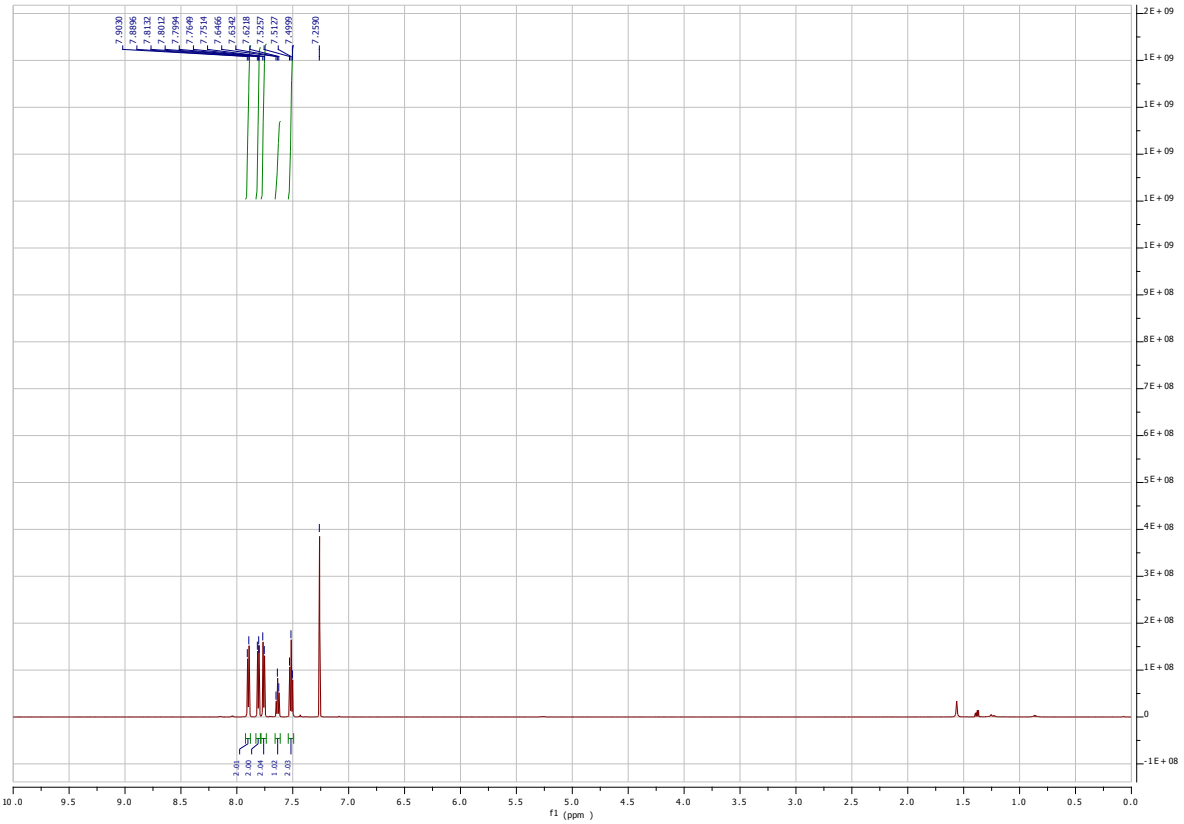


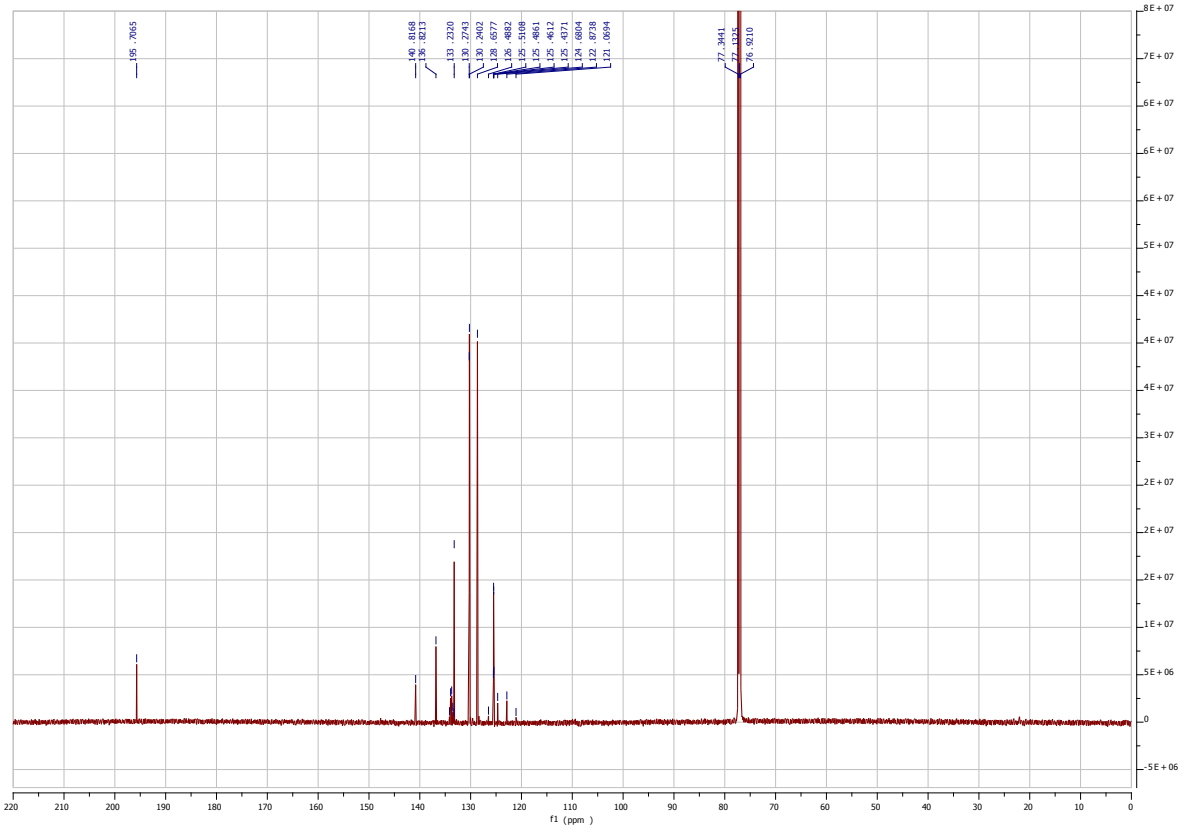


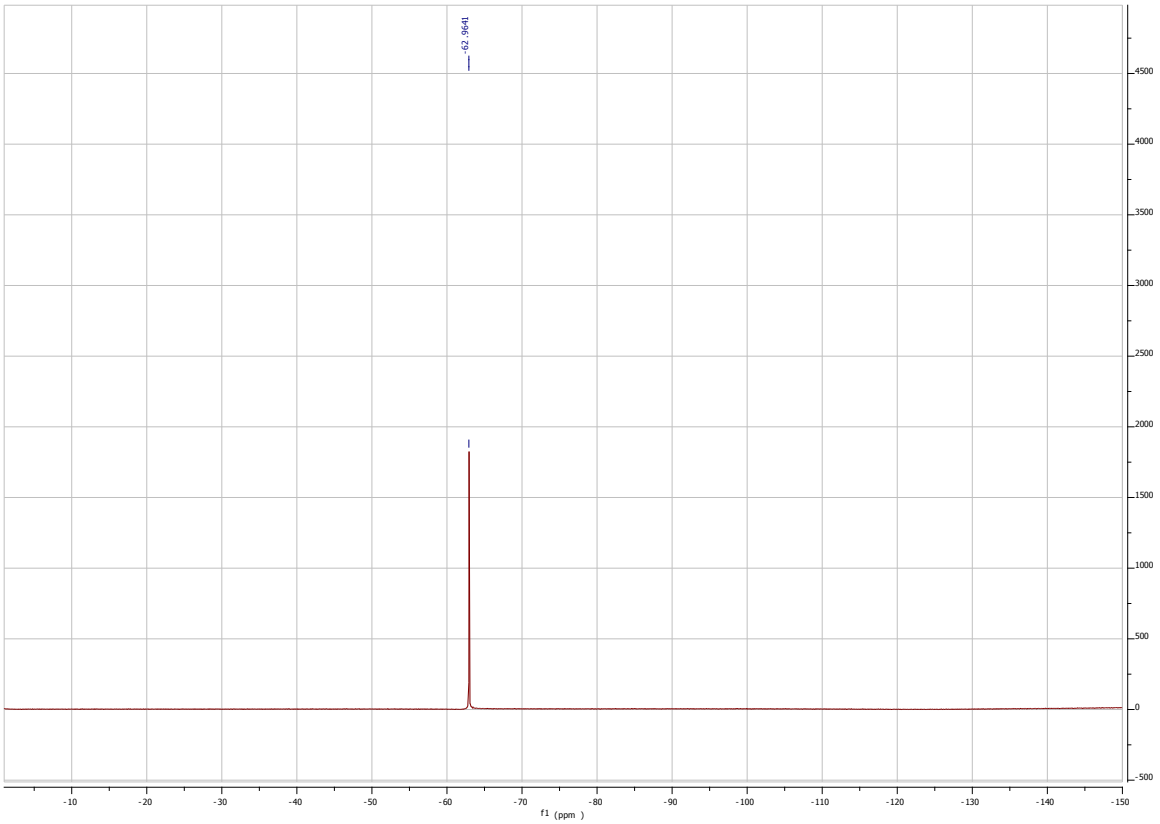
Phenyl(4-(trifluoromethyl)phenyl)methanone[12] (3bb)



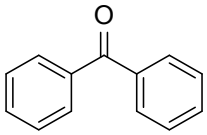
Purification by column chromatography (1%-5% Et_2O/Petrol) gave phenyl(4-(trifluoromethyl)phenyl)methanone as a clear solid (109 mg, 0.43 mmol, 87%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.89 (d, J = 8.0 Hz, 2H), 7.82-7.88 (m, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.65-7.61 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.7 (C), 140.8 (C), 136.8 (C), 133.8 (q, J_{C-F} = 32.5 Hz, C), 133.3 (CH), 130.3 (m, CH), 128.7 (CH), 125.5 (q, J_{C-F} = 3.7 Hz, CH), 123.5 (q, J_{C-F} = 270.9 Hz, C); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.0 (s, CF_3, 3F); **IR** (thin film) 1654, 1604, 1275, 729 cm^{-1}; **LRMS (CI)** 250 (100, $[M]^+$); **HRMS (CI)** calcd. for $C_{14}H_9F_3O$ $[M]^+$ 250.0601, observed 250.0615; **m.p.** 110-113 °C (recrystallized from *n*-heptane).



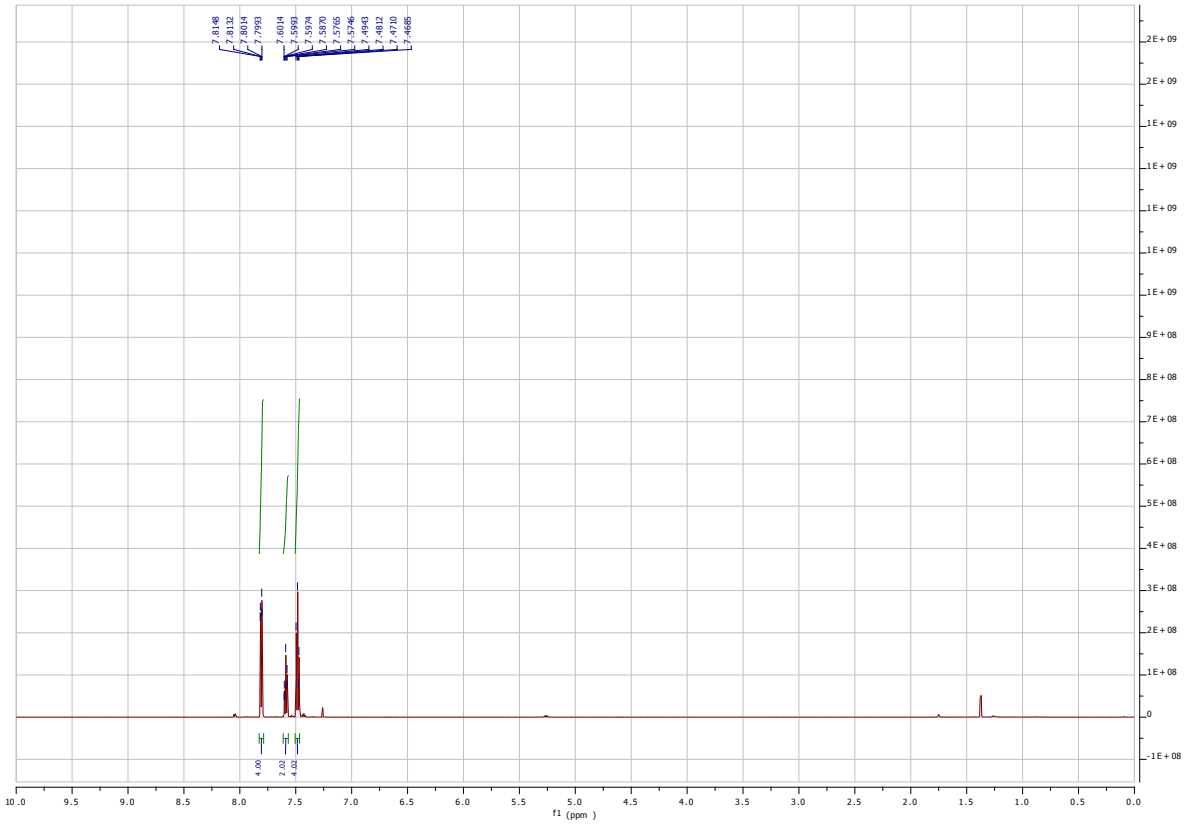


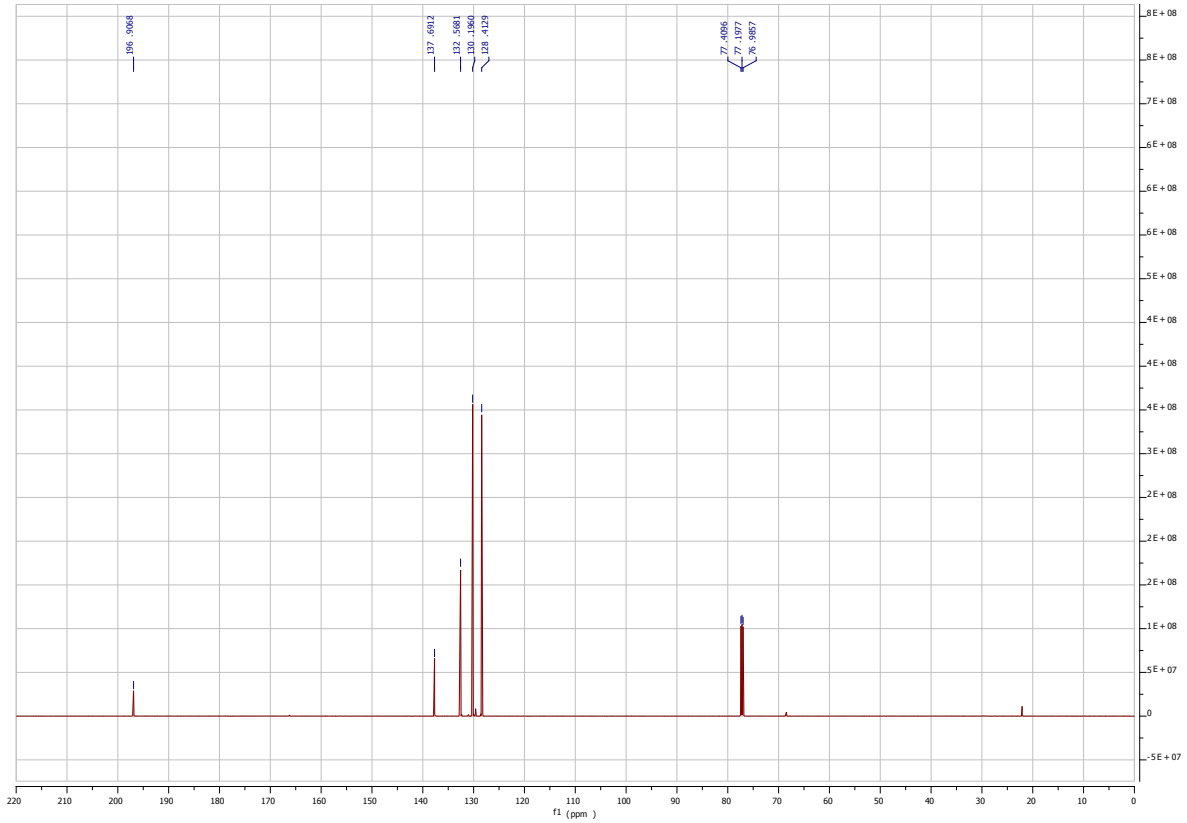


Benzophenone[13] (3cb)

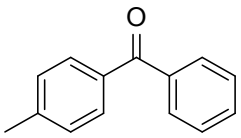


Purification by column chromatography (1%-5% Et_2O/Petrol) gave benzophenone as a clear oil (67 mg, 0.37 mmol, 73%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82-7.80 (m, 4H), 7.60-7.57 (m, 2H), 7.49-7.47 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 196.9 (C), 137.69 (C), 132.6 (CH), 130.2 (CH), 128.4 (CH); **IR** (thin film) 1656, 1577, 1317, 1275, 701 cm^{-1}; **LRMS (EI)** 182 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{13}H_{10}O$ $[M]^+$ 182.0732, observed 182.0727.

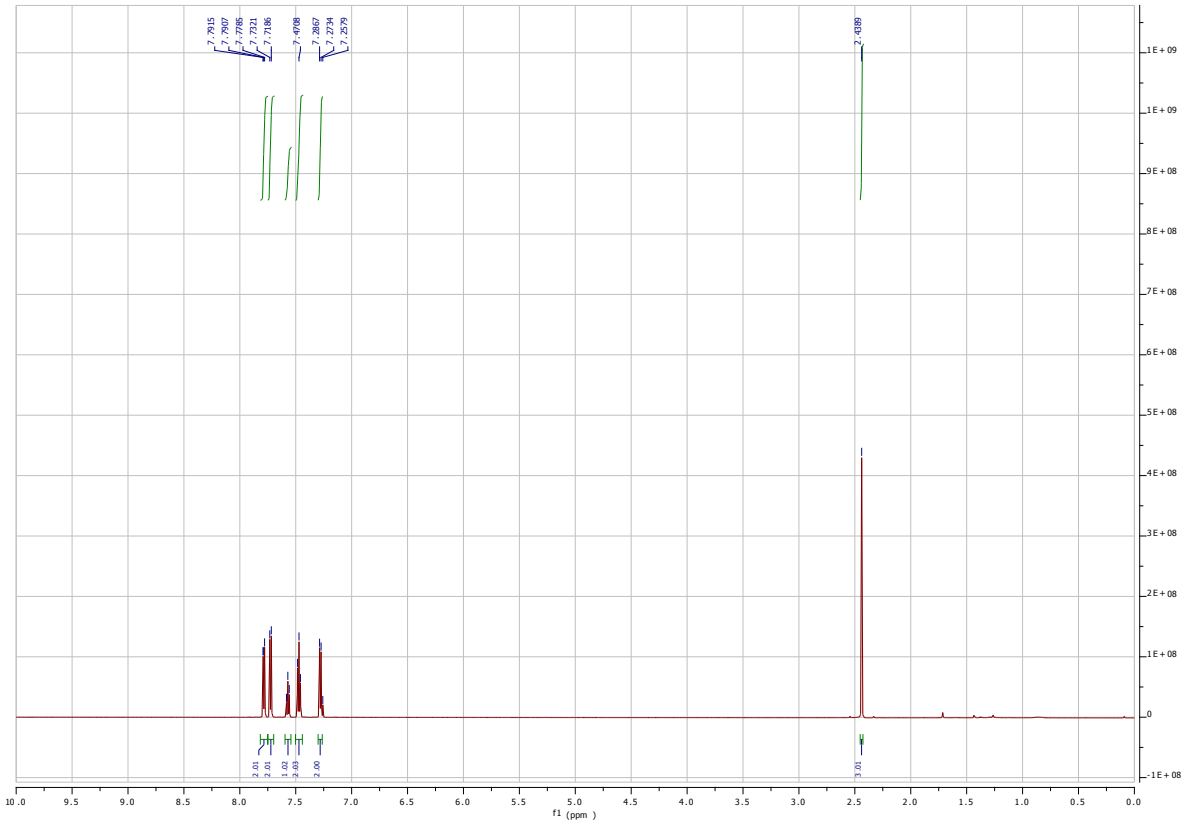


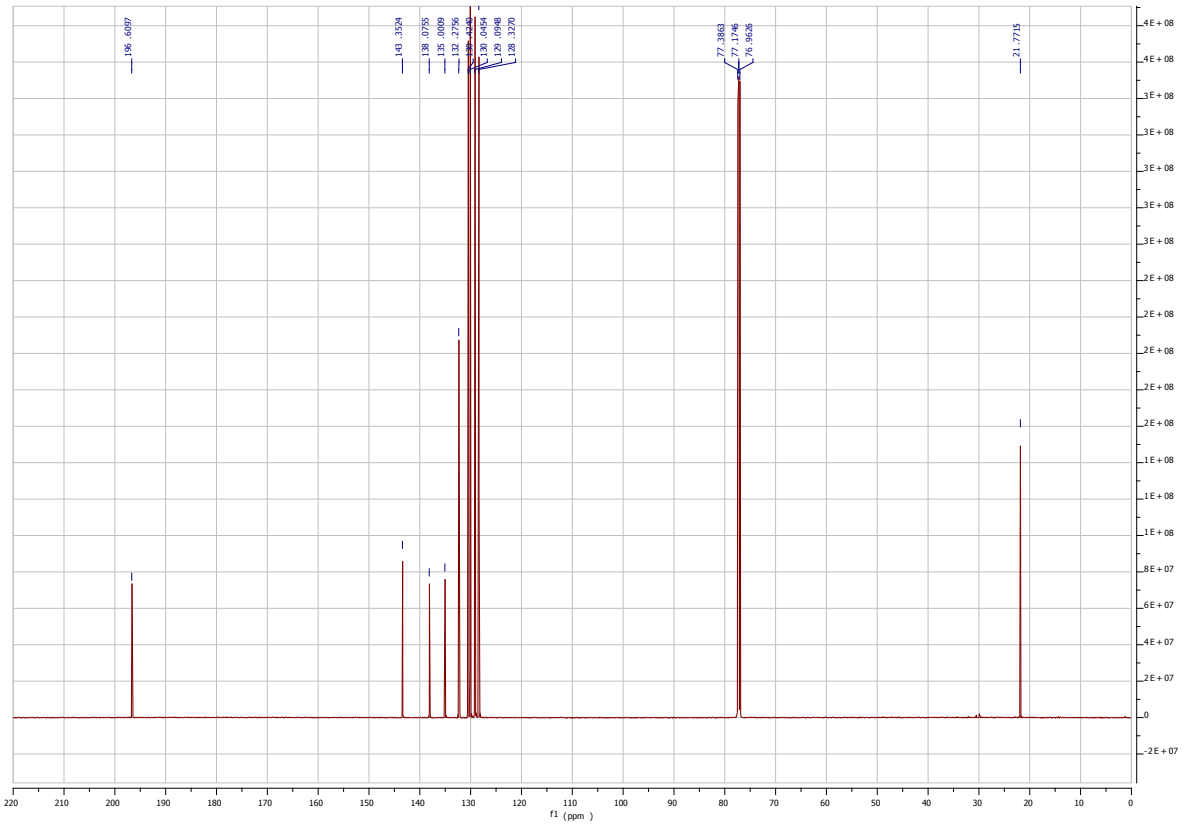


Phenyl(p-tolyl)methanone[14] (3db)

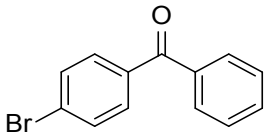


Purification by column chromatography (1%-5% Et_2O/Petrol) gave phenyl(*p*-tolyl)methanone as a clear oil (69 mg, 0.35 mmol, 70%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79-7.76 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 196.6 (C), 143.4 (C), 138.1 (C), 135.0 (C), 132.3 (CH), 130.4 (CH), 130.0 (CH), 129.1 (CH), 128.3 (CH), 21.8 (CH_3); **IR** (thin film) 1654, 1604, 1275, 698 cm^{-1}; **LRMS (EI)** 196 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{14}H_{12}O$ $[M]^+$ 196.0888, observed 196.0883.

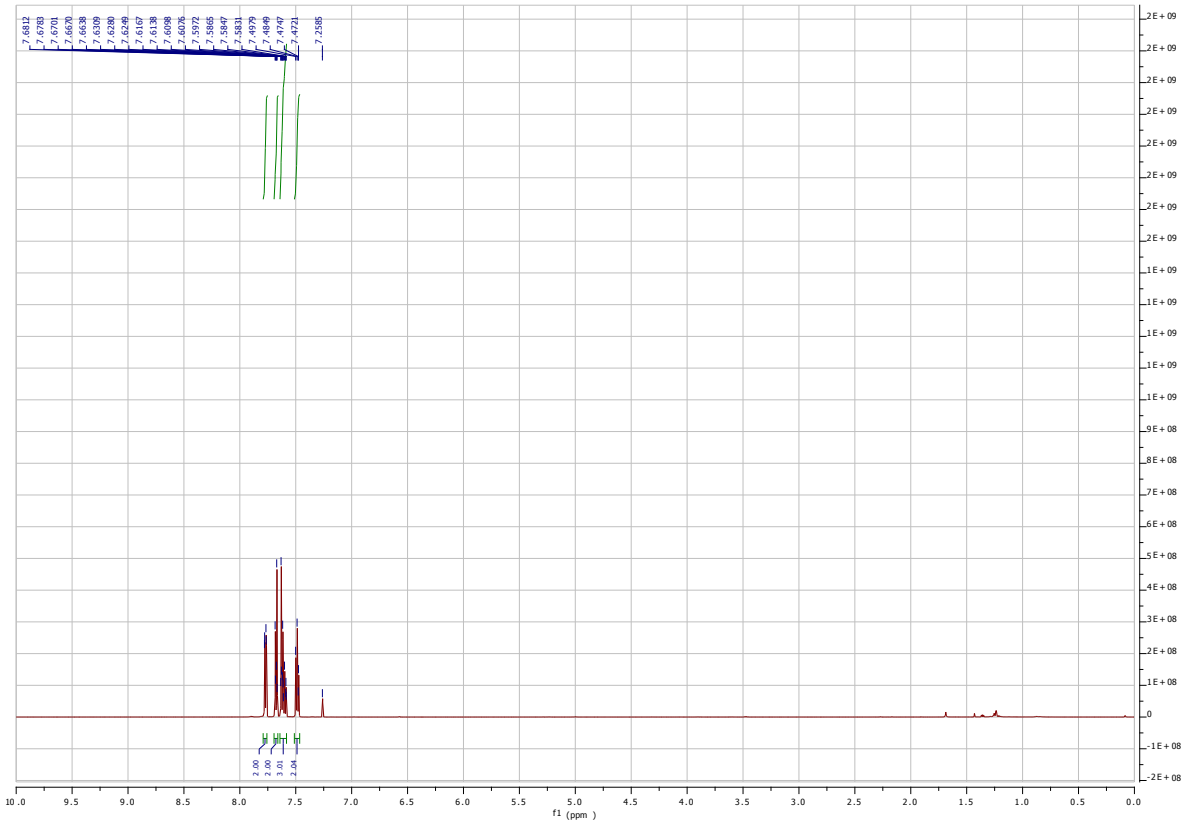


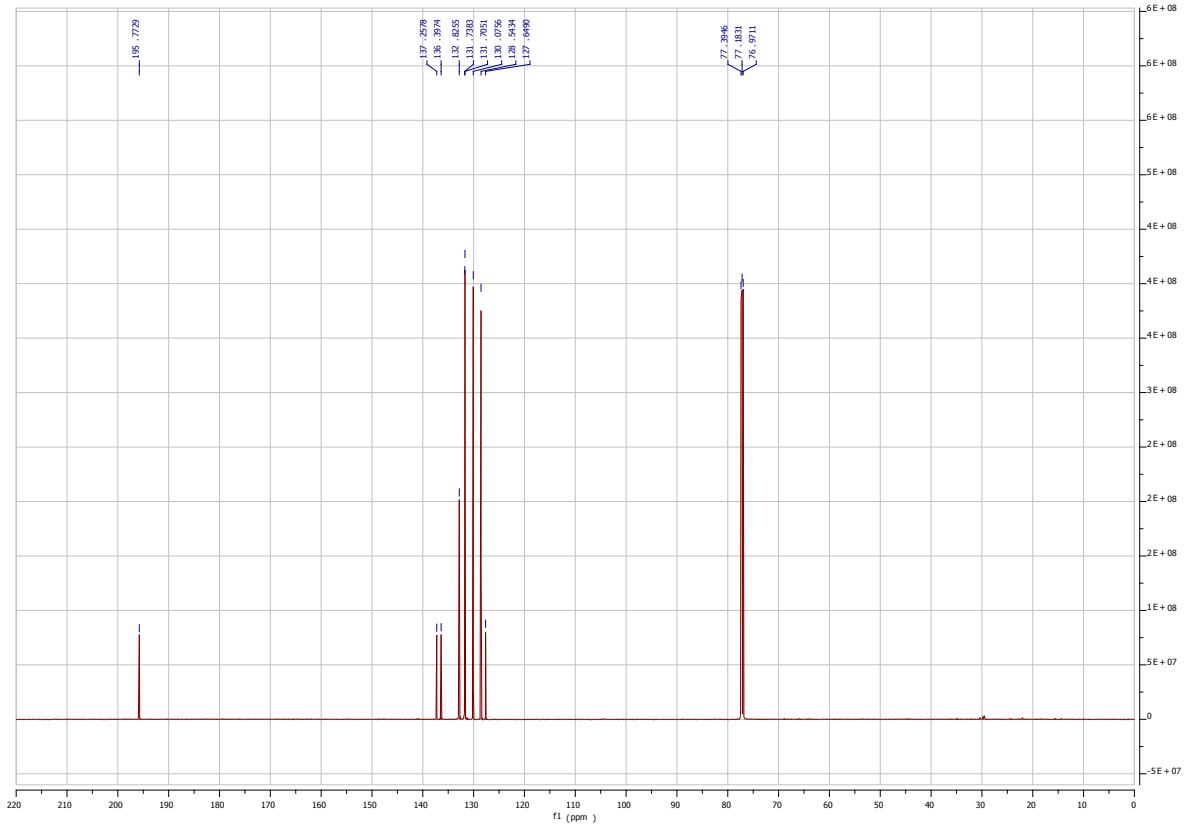


(4-Bromophenyl)(phenyl)methanone[15] (3eb)

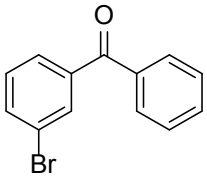


Purification by column chromatography (1%-5% Et_2O/Petrol) gave (4-bromophenyl)(phenyl)methanone as a clear oil (92 mg, 0.36 mmol, 71%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79-7.76 (m, 2H), 7.68-7.65 (m, 2H), 7.63-7.58 (m, 3H), 7.50-7.47 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.8 (C), 137.3 (C), 136.4 (C), 132.8 (CH), 131.7 (CH), 131.7 (CH), 130.1 (CH), 128.5 (CH), 127.6 (CH); **IR** (thin film) 1649, 1600, 1250, 922, 729 cm^{-1}; **LRMS (EI)** 262 (100, $[M^{81}Br]^+$), 260 (100, $[M^{79}Br]^+$); **HRMS (EI)** calcd. for $C_{13}H_9BrO$ $[M^{79}Br]^+$ 259.9837, observed 259.9835.

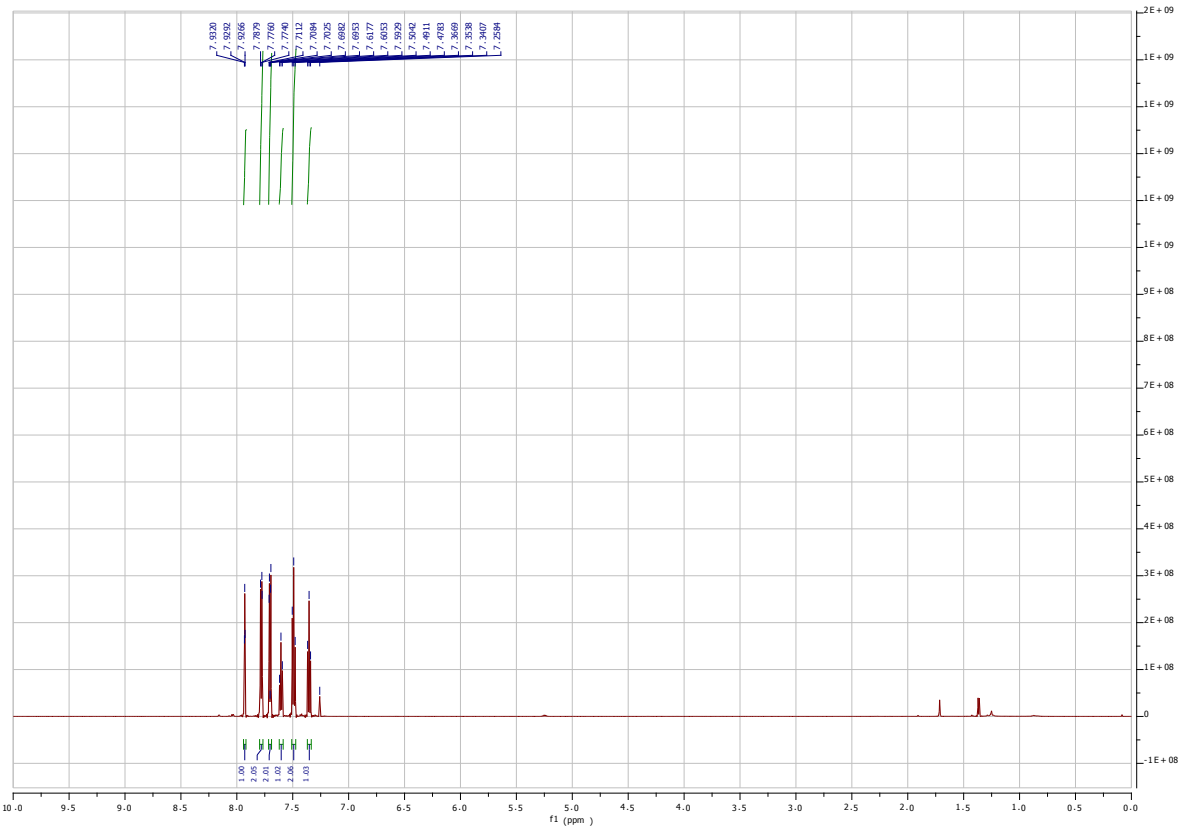


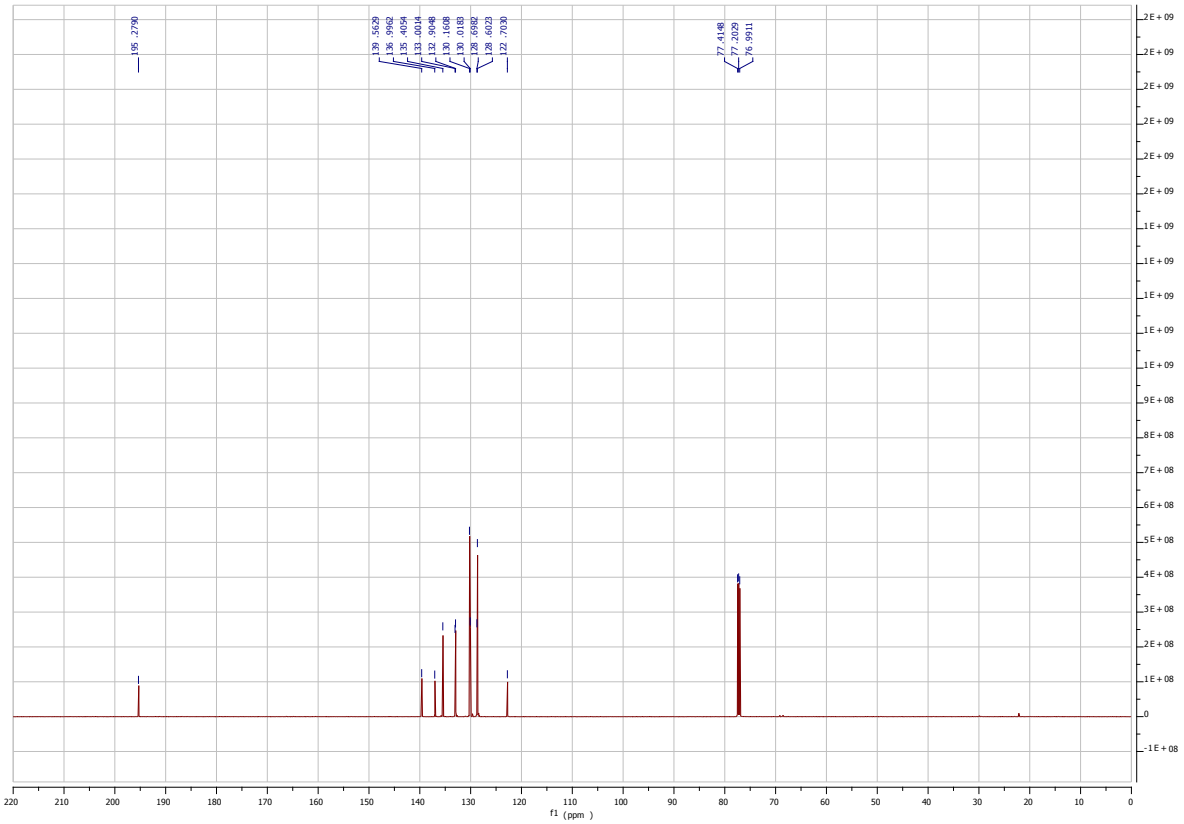


(3-Bromophenyl)(phenyl)methanone[16] (3fb)

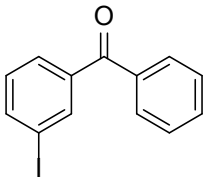


Purification by column chromatography (1%-5% Et_2O/Petrol) gave (3-bromophenyl)(phenyl)methanone as a clear oil (120 mg, 0.46 mmol, 92%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (t, *J* = 1.6 Hz, 1H), 7.79-7.77 (m, 2H), 7.71 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.62-7.59 (m, 1H), 7.50-7.48 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.3 (C), 139.6 (C), 137.0 (C), 135.4 (CH), 133.0 (CH), 132.9 (CH), 130.2 (CH), 130.0 (CH), 128.7 (CH), 128.6 (CH), 122.7 (C); **IR** (thin film) 1649, 1599, 1260, 937, 729 cm^{-1}; **LRMS (EI)** 262 (100, $[M^{81}Br]^+$), 260 (100, $[M^{79}Br]^+$); **HRMS (EI)** calcd. for $C_{13}H_9BrO$ $[M^{79}Br]^+$ 259.9837, observed 259.9835.

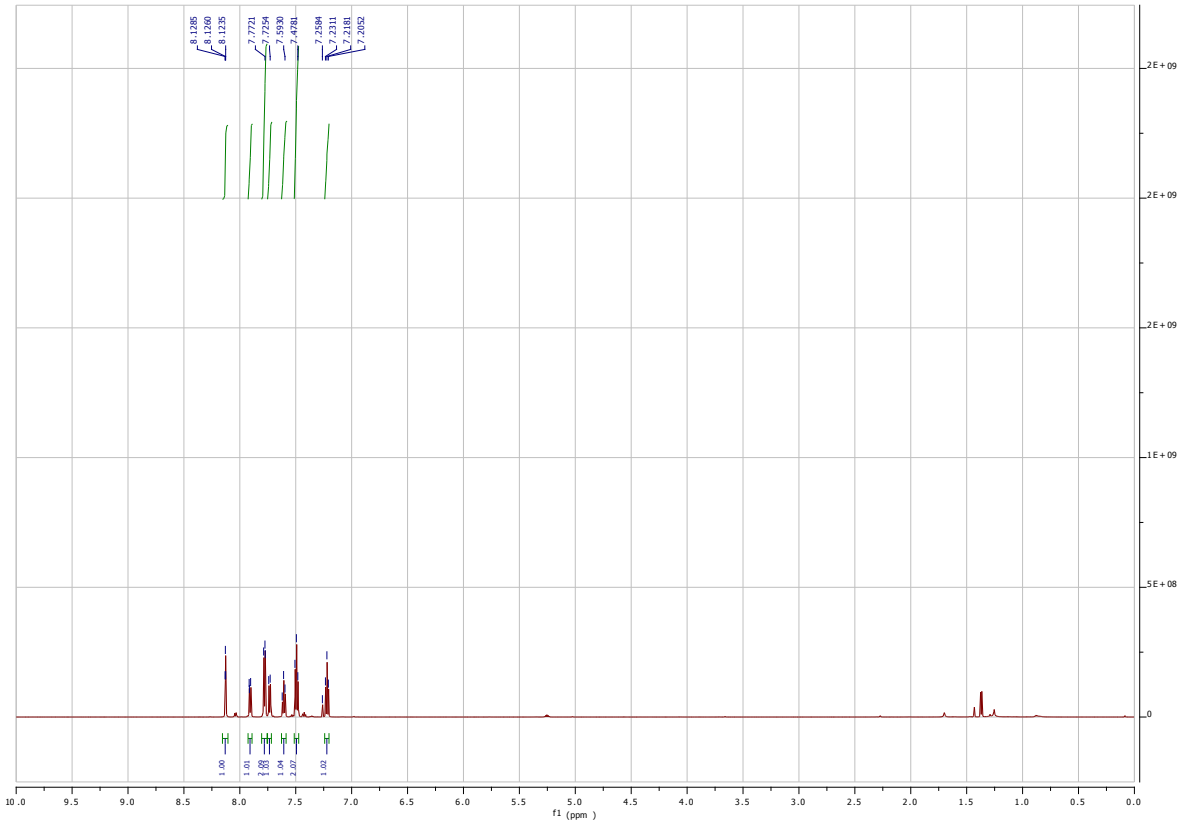


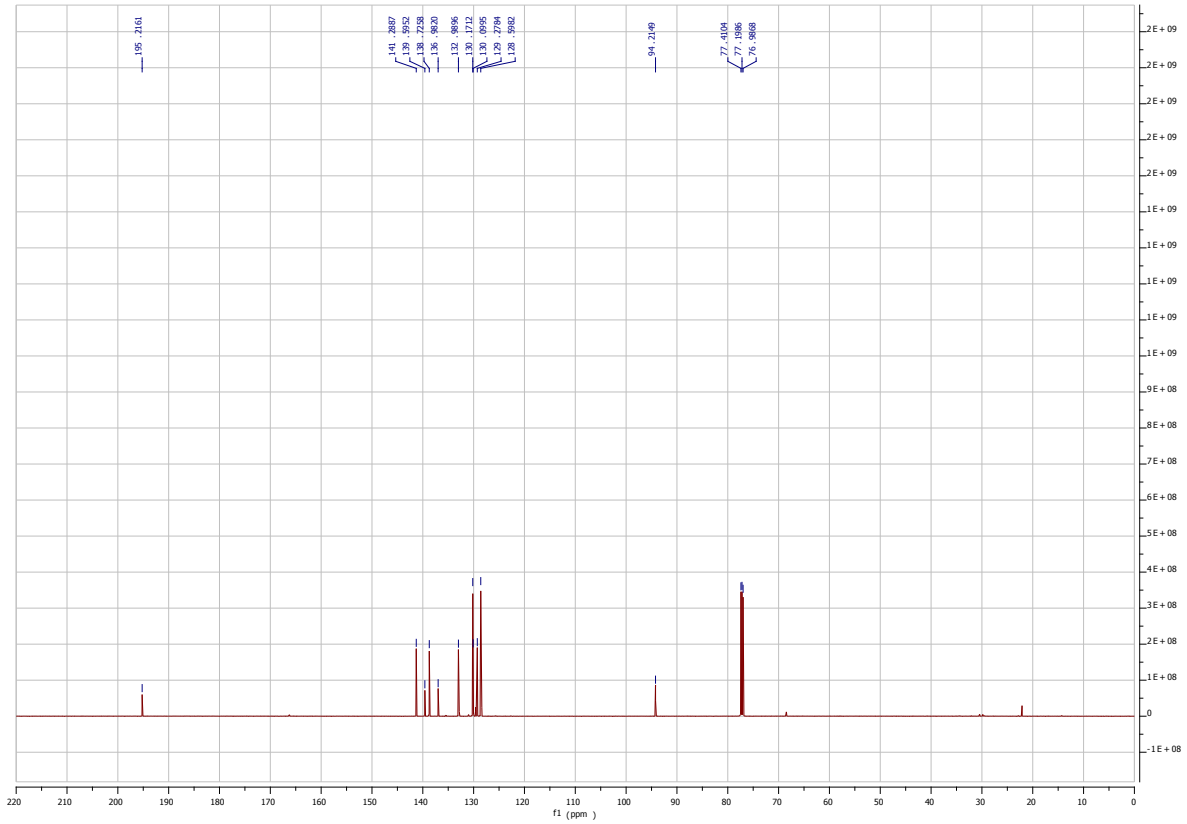


(3-iodophenyl)(phenyl)methanone[17] (3gb)

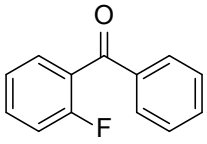


Purification by column chromatography (1%-5% Et_2O/Petrol) gave (3-iodophenyl)(phenyl)methanone as a colourless oil (111 mg, 0.36 mmol, 72%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14-8.11 (m, 1H), 7.92-7.89 (m, 1H), 7.79-7.76 (m, 2H), 7.74-7.68 (m, 1H), 7.62-7.59 (m, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.2 (C), 141.3 (CH), 139.6 (C), 138.7 (CH), 137.0 (C), 133.0 (CH), 130.2 (CH), 130.1 (CH), 129.3 (CH), 128.6 (CH), 94.2 (C); **IR** (thin film) 1680, 1580, 1313, 937, 698 cm^{-1}; **LRMS (ES^+)** 308 (100, $[M+H]^+$); **HRMS (ES^+)** calcd. for $C_{13}H_{10}IO$ $[M+H]^+$ 308.9776, observed 308.9770.

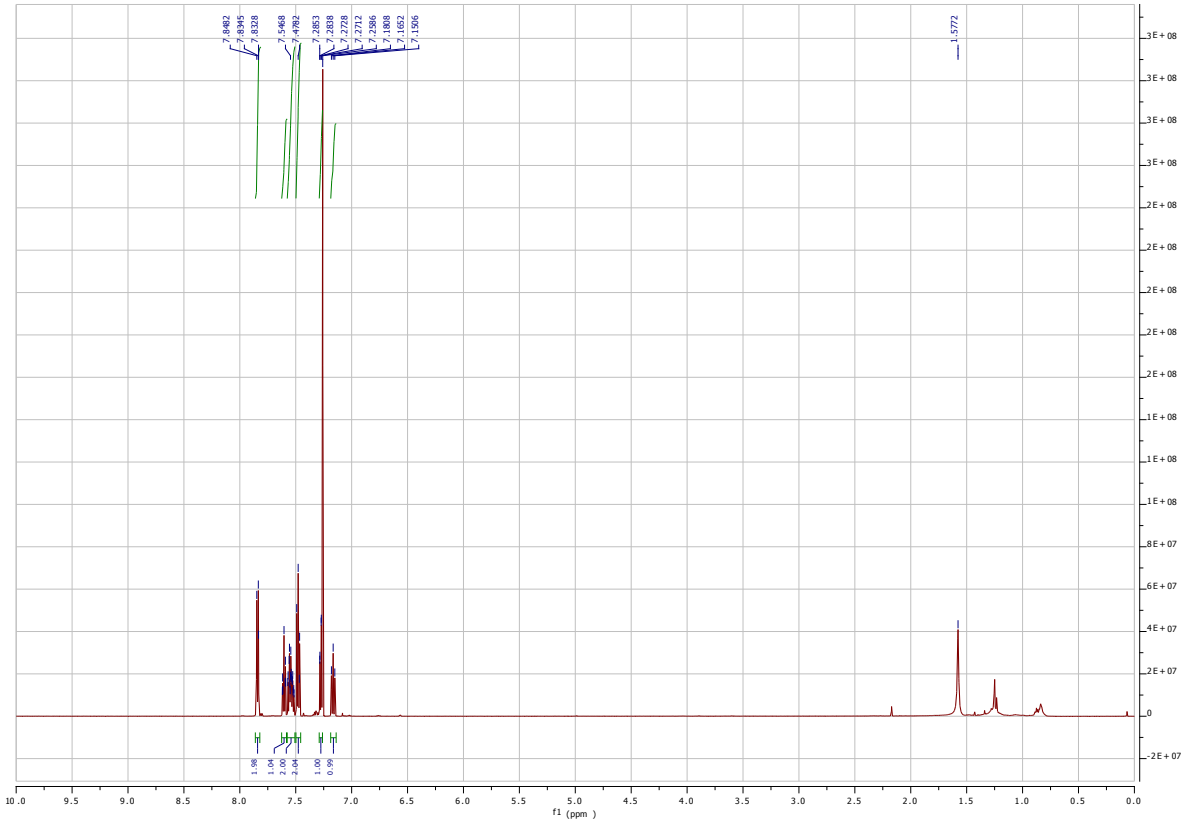


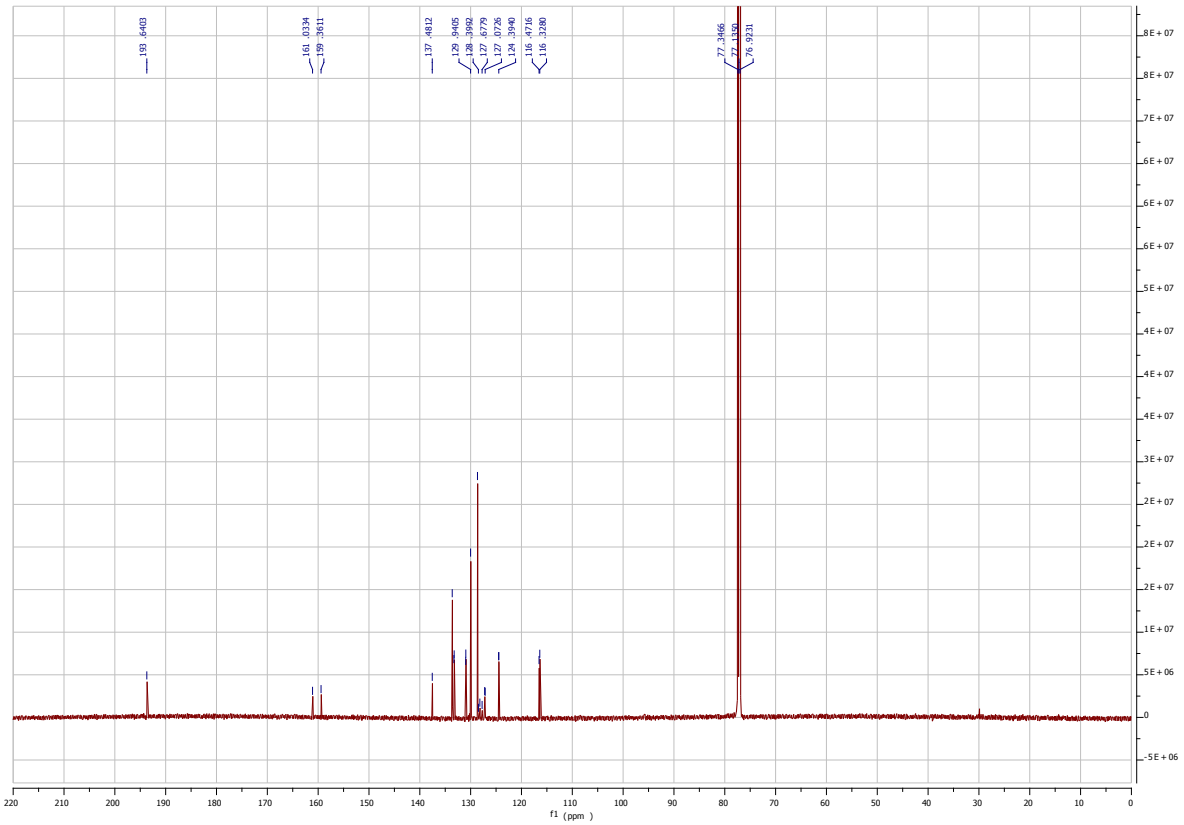


(2-Fluorophenyl)(phenyl)methanone[18] (3hb)

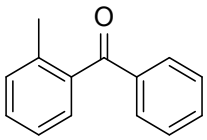


Purification by column chromatography (1%-5% Et_2O/Petrol) gave (2-fluorophenyl)(phenyl)methanone as a colourless oil (74 mg, 0.37 mmol, 74%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85-7.82 (m, 2H), 7.61 (dt, J = 7.4 Hz, $J_{H\text{-}F}$ = 1.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.49-7.46 (m, 2H), 7.27 (dt, J = 7.5 Hz, $J_{H\text{-}F}$ = 1.0 Hz, 1H), 7.17 (t, J = 9.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.6 (C), 160.2 (d, $J_{C\text{-}F}$ = 250.8 Hz, C), 137.5 (C), 133.6 (CH), 133.2 (d, $J_{C\text{-}F}$ = 8.2 Hz, CH), 130.9 (d, $J_{C\text{-}F}$ = 2.8 Hz, CH), 129.9 (CH), 128.6 (CH), 127.1 (d, $J_{C\text{-}F}$ = 14.7 Hz, C), 124.4 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH) 116.4 (d, $J_{C\text{-}F}$ = 21.5 Hz, CH); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.0 (s, 1F)**; IR** (thin film) 1685, 1584, 1440, 1313, 922, 731 cm^{-1}; **LRMS (EI)** 201 (100, $[M+H]^+$); **HRMS (EI)** calcd. for $C_{13}H_{10}FO$ $[M+H]^+$ 201.0716, observed 201.0710.

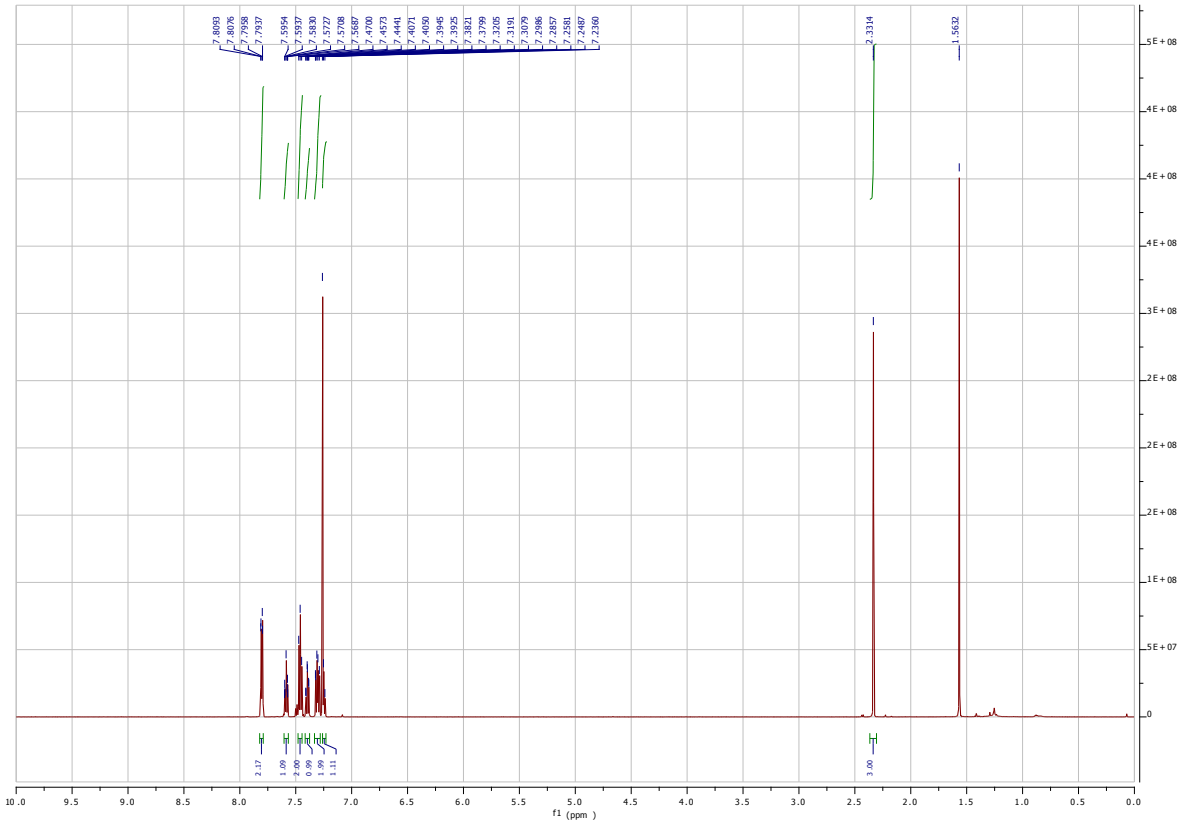


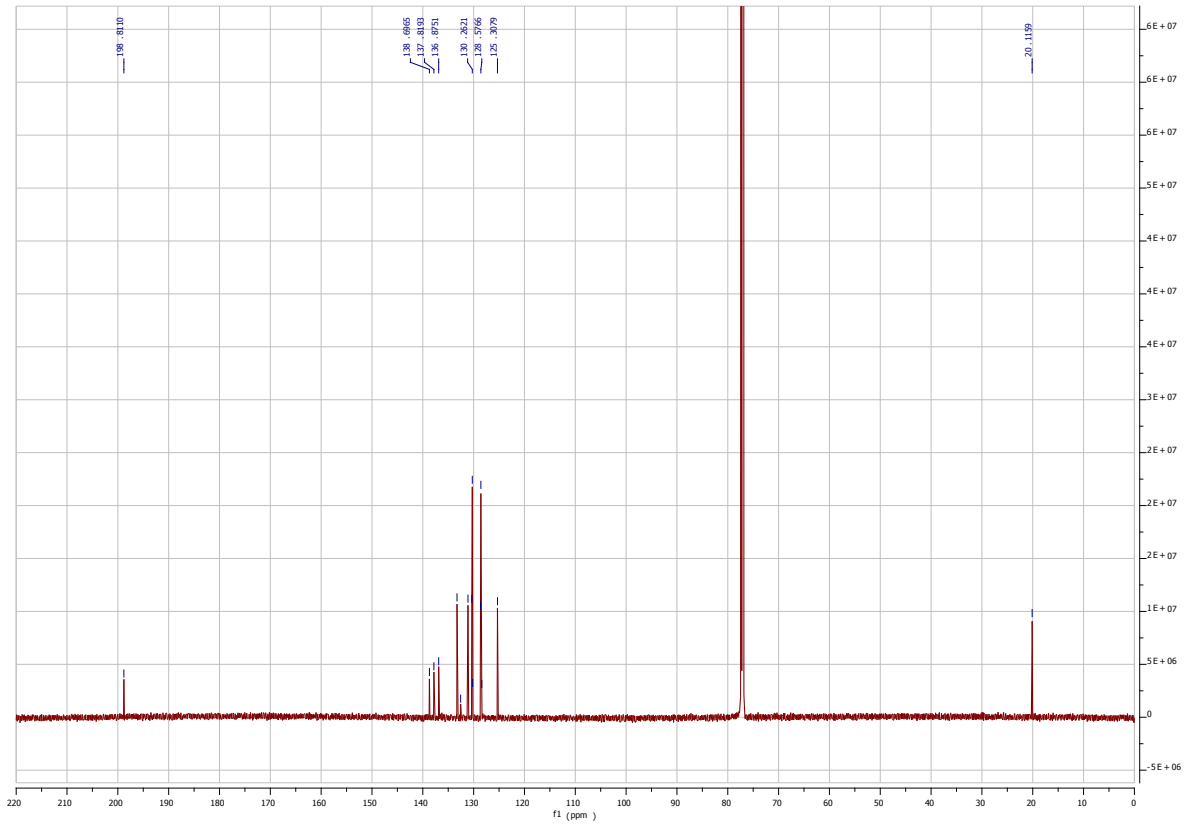


Phenyl(o-tolyl)methanone[19] (3ib)

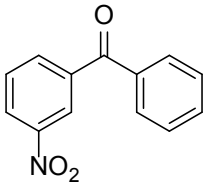


Purification by column chromatography (1%-5% Et_2O/Petrol) gave phenyl(*o*-tolyl)methanone as a clear oil (72 mg, 0.37 mmol, 73%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82-7.79 (m, 2H), 7.61-7.57 (m, 1H), 7.47-7.44 (m, 2H), 7.42-7.38 (m, 1H), 7.32-7.28 (m, 2H), 7.27-7.24 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 198.8 (C), 138.7 (C), 137.8 (C), 136.9 (C), 133.3 (CH), 131.1 (CH), 130.4 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 125.3 (CH), 20.1 (CH_3); **IR** (thin film) 1654, 1603, 1339, 1262, 937, 729 cm^{-1}; **LRMS (EI)** 196 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{14}H_{12}O$ $[M]^+$ 196.0888, observed 196.0883.

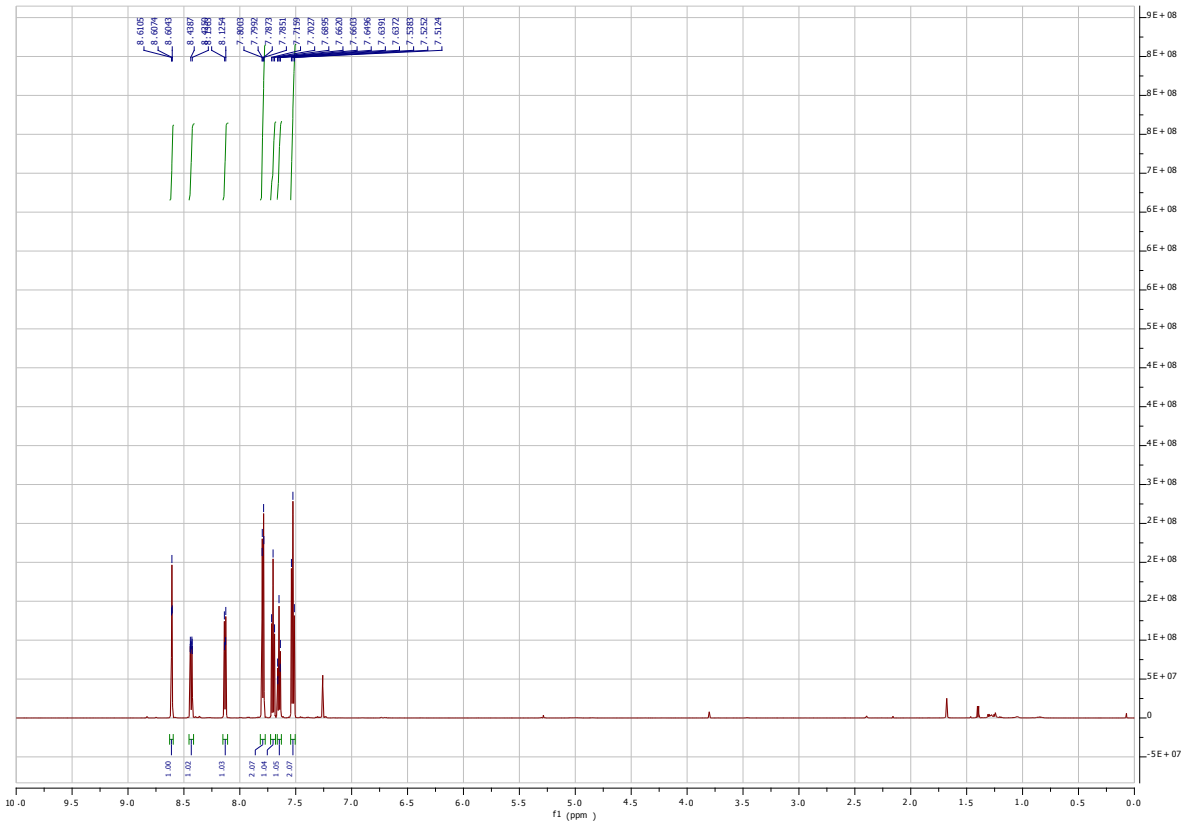


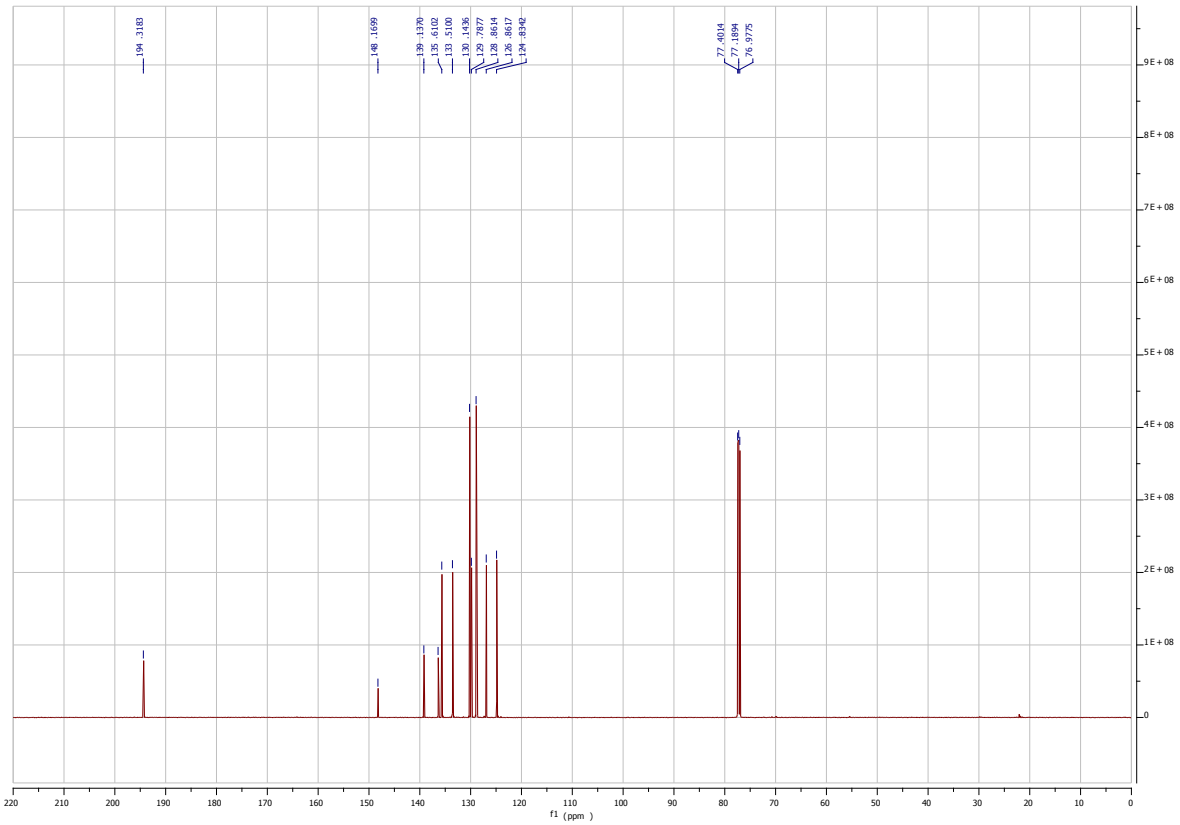


(3-Nitrophenyl)(phenyl)methanone[20] (3jb)

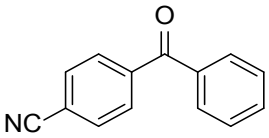


Purification by column chromatography (1%-5% Et_2O/Petrol) gave (3-nitrophenyl)(phenyl)methanone as a clear oil (87 mg, 0.39 mmol, 77%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.61 (t, *J* = 1.9 Hz, 1H), 8.43 (dq, *J* = 8.3 Hz, 1.0 Hz, 1H), 8.15-8.11 (m, 1H), 7.81-7.75 (m, 2H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.66-7.62 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.3 (C), 148.2 (C), 139.1 (C), 136.3 (C), 135.6 (CH), 133.5 (CH), 130.1 (CH), 129.8 (CH), 128.9 (CH), 126.9 (CH), 124.8 (CH); **IR** (thin film) 1664, 1532, 1348, 1274, 1090, 708 cm^{-1}; **LRMS (EI)** 227 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{13}H_9NO_3$ $[M]^+$ 227.0582, observed 227.0580.

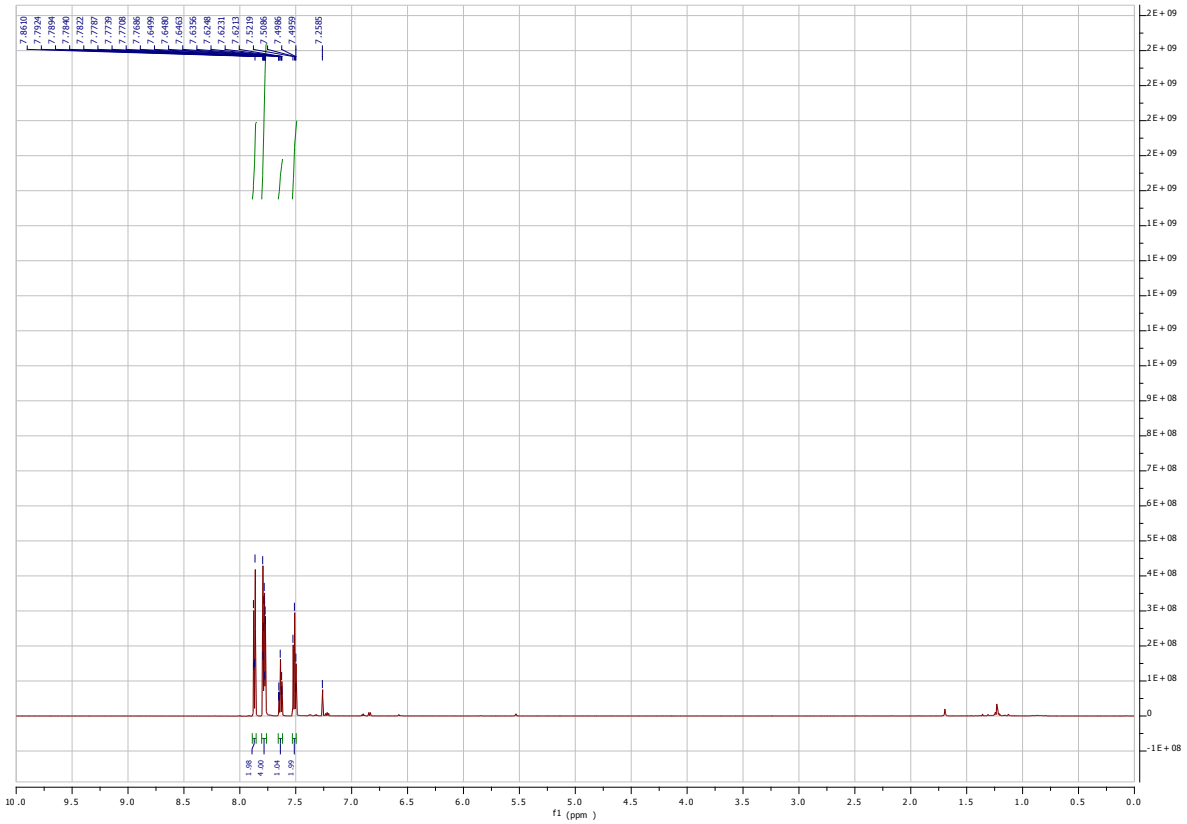


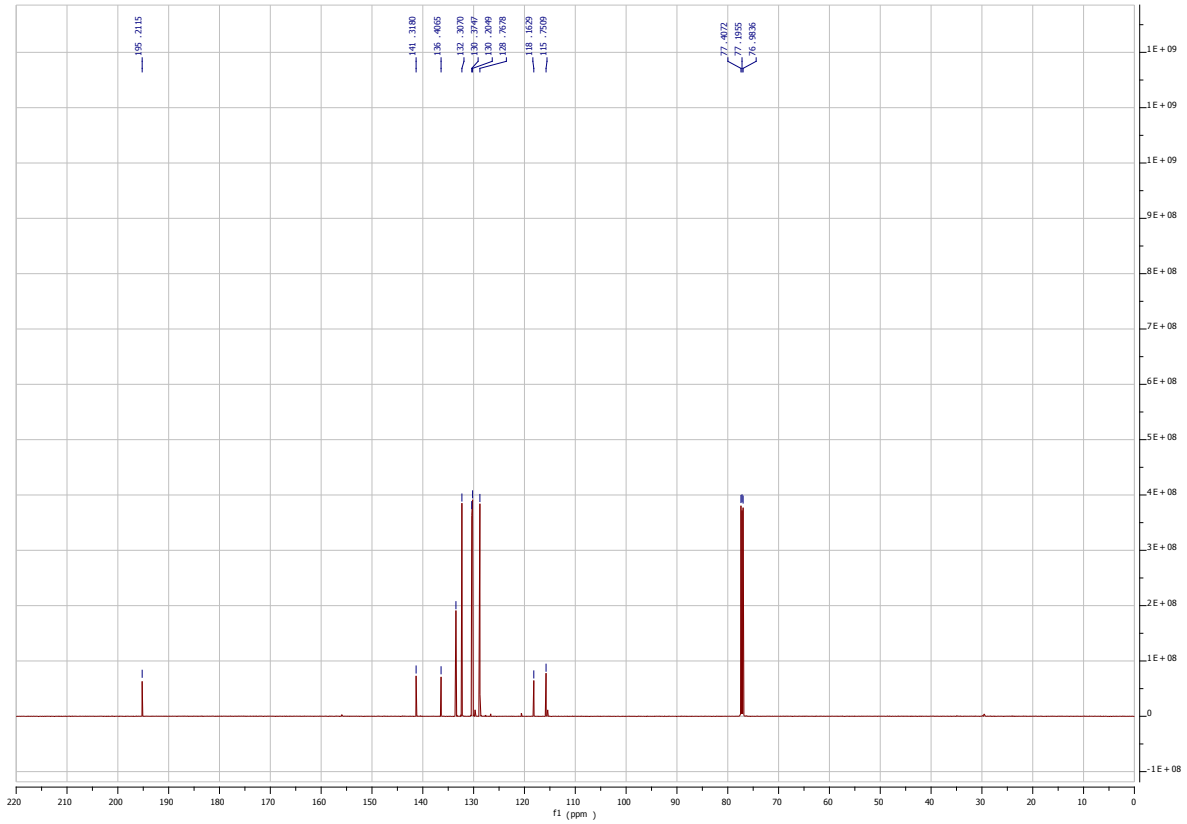


4-Benzoylbenzonitrile[12] (3kb)

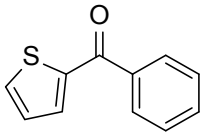


Purification by column chromatography (1%-5% Et_2O/Petrol) gave 4-benzoylbenzonitrile as a clear oil (79 mg, 0.38 mmol, 76%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87-7.86 (m, 2H), 7.79-7.77 (m, 4H), 7.65-7.62 (m, 1H), 7.52-7.50 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.2 (C), 141.3 (C), 136.4 (C), 133.5 (CH), 132.3 (CH), 130.4 (CH), 130.2 (CH), 128.8 (CH), 118.2 (C), 115.8 (C); **IR** (thin film) 2227, 1648, 1595, 1309, 1279, 693 cm^{-1}; **LRMS (EI)** 207 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{14}H_9NO$ $[M]^+$ 207.0684, observed 207.0682.

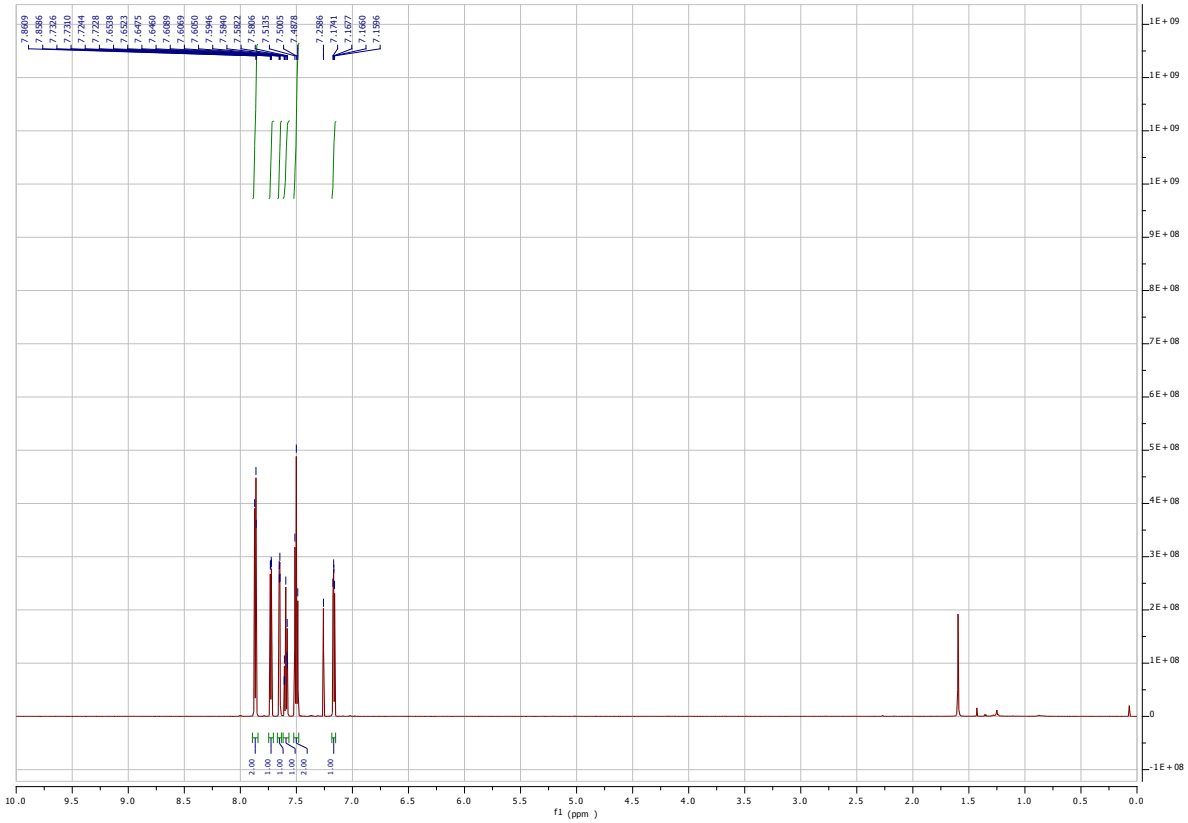


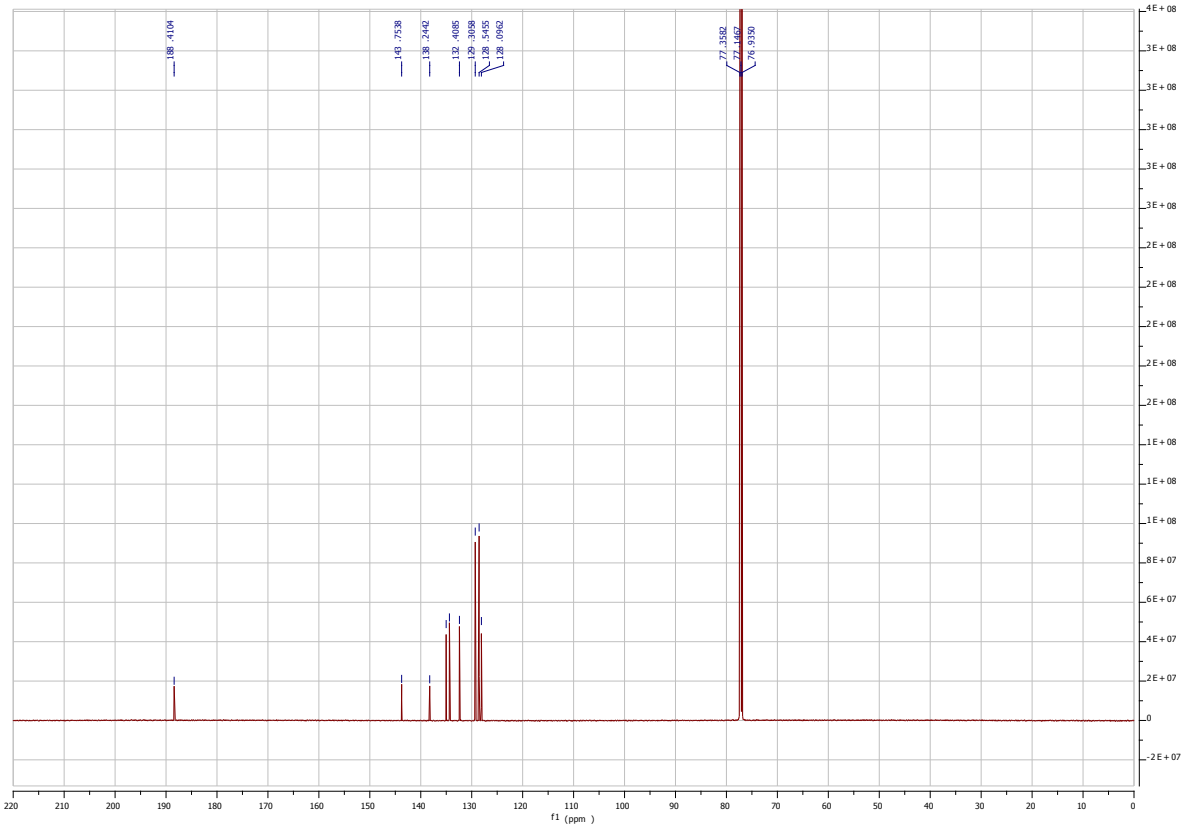


Phenyl(thiophen-2-yl)methanone[19] (3lb)

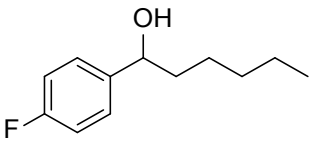


Purification by column chromatography (1%-5% Et_2O/Petrol) gave phenyl(thiophen-2-yl)methanone as a clear oil (72 mg, 0.38 mmol, 76%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87-7.85 (m, 2H), 7.73 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.65 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.61-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.17 (dd, *J* = 4.9, 3.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 188.4 (C), 143.8 (C), 138.2 (C), 135.0 (CH), 134.4 (CH), 132.4 (CH), 129.3 (CH), 128.5 (CH), 128.1 (CH); **IR** (thin film) 3099, 1630, 1597, 1410, 1352, 1284, 1052 cm^{-1}.

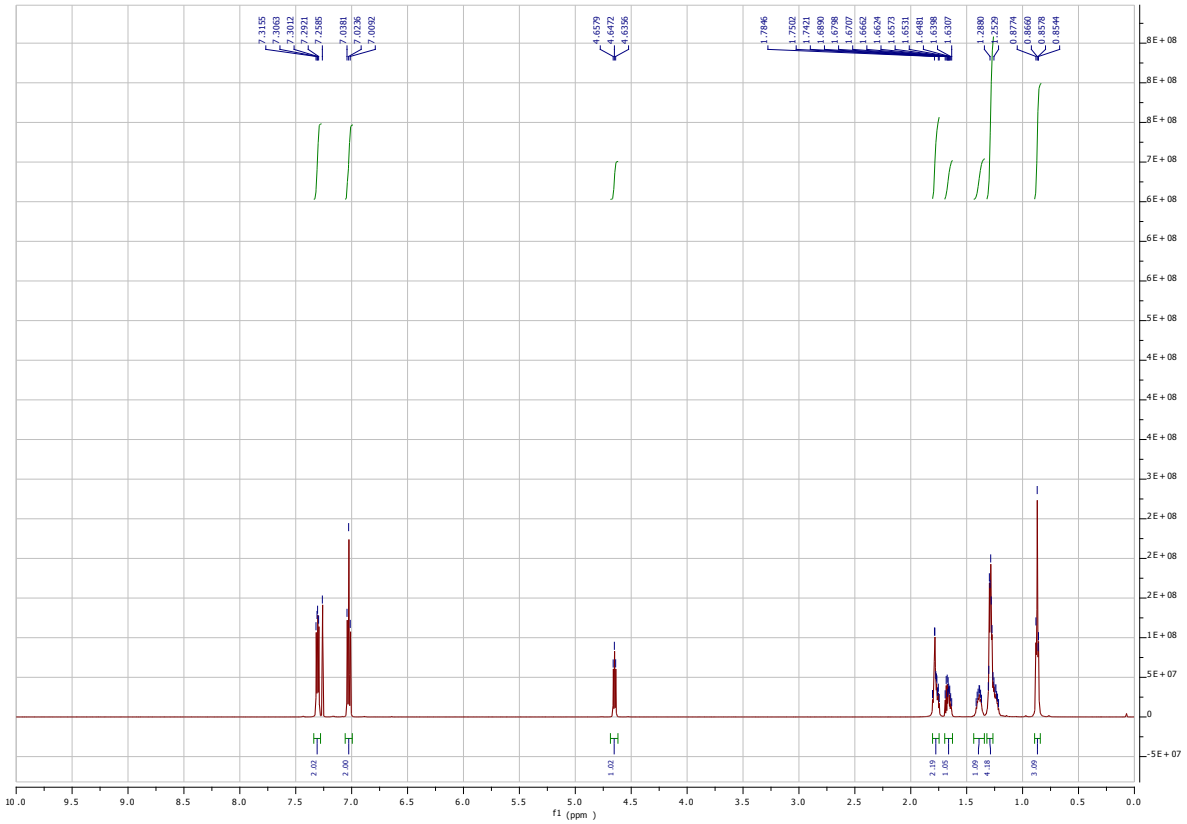


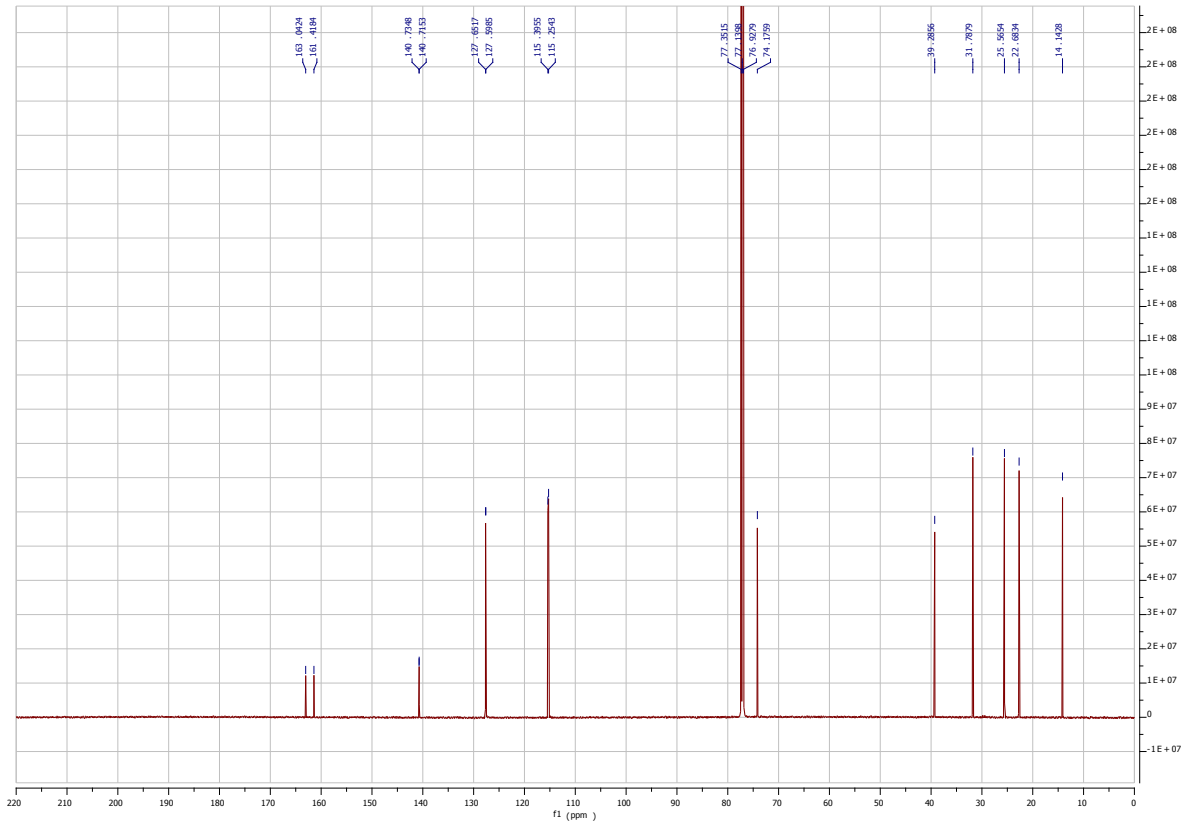


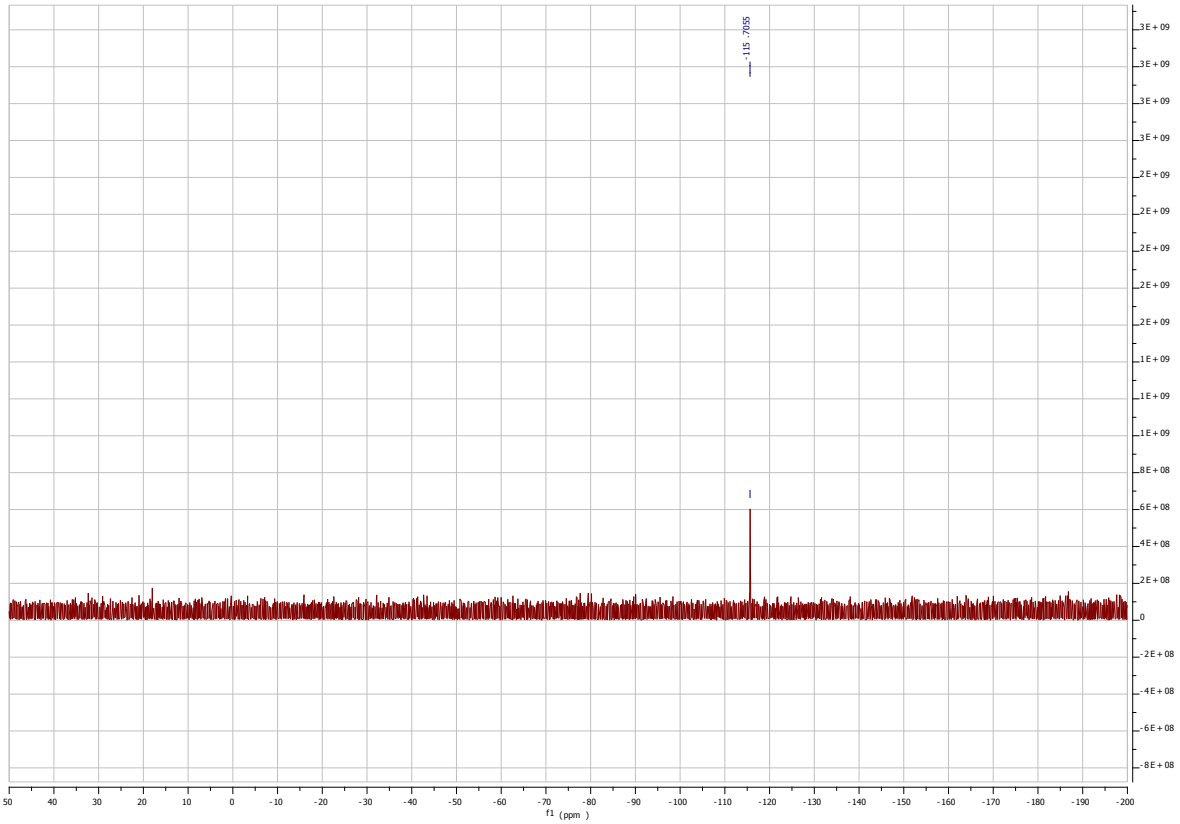
1-(4-Fluorophenyl)hexan-1-ol[21] (4)



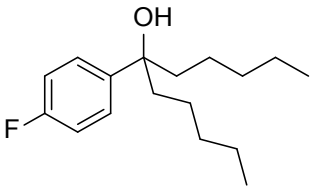
Purification by column chromatography (1%-15% Et_2O/Petrol) of the crude residue in the reaction for the formation of 1-(4-fluorophenyl)hexan-1-one also gave 1-(4-fluorophenyl)hexan-1-ol as a colourless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32-7.26 (m, 2H), 7.04-7.01 (m, 2H), 4.65 (t, J = 6.7 Hz, 1H), 1.80-1.74 (m, 2H), 1.69-1.63 (m, 1H), 1.41-1.36 (m, 1H), 1.30-1.21 (m, 4H), 0.88-0.85 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.0 (d, $J_{C\text{-}F}$ = 243.6 Hz, CF), 140.7 (d, $J_{C\text{-}F}$ = 3.0 Hz, C), 127.7 (d, $J_{C\text{-}F}$ = 8.0 Hz, CH), 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz, CH), 74.2 (CH), 39.3 (CH_2), 31.8 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.7 (s, 1F); **IR** (thin film) 3356, 2960, 1600, 1510, 1445, 1369, 1210, 1150, 1091, 1044, 975 cm^{-1}; **LRMS (CI)** 219 (100, $[M+Na]^+$); **HRMS (CI)** calcd. for $C_{12}H_{18}FO$ $[M+H]^+$ 197.1342, observed 197.1346.



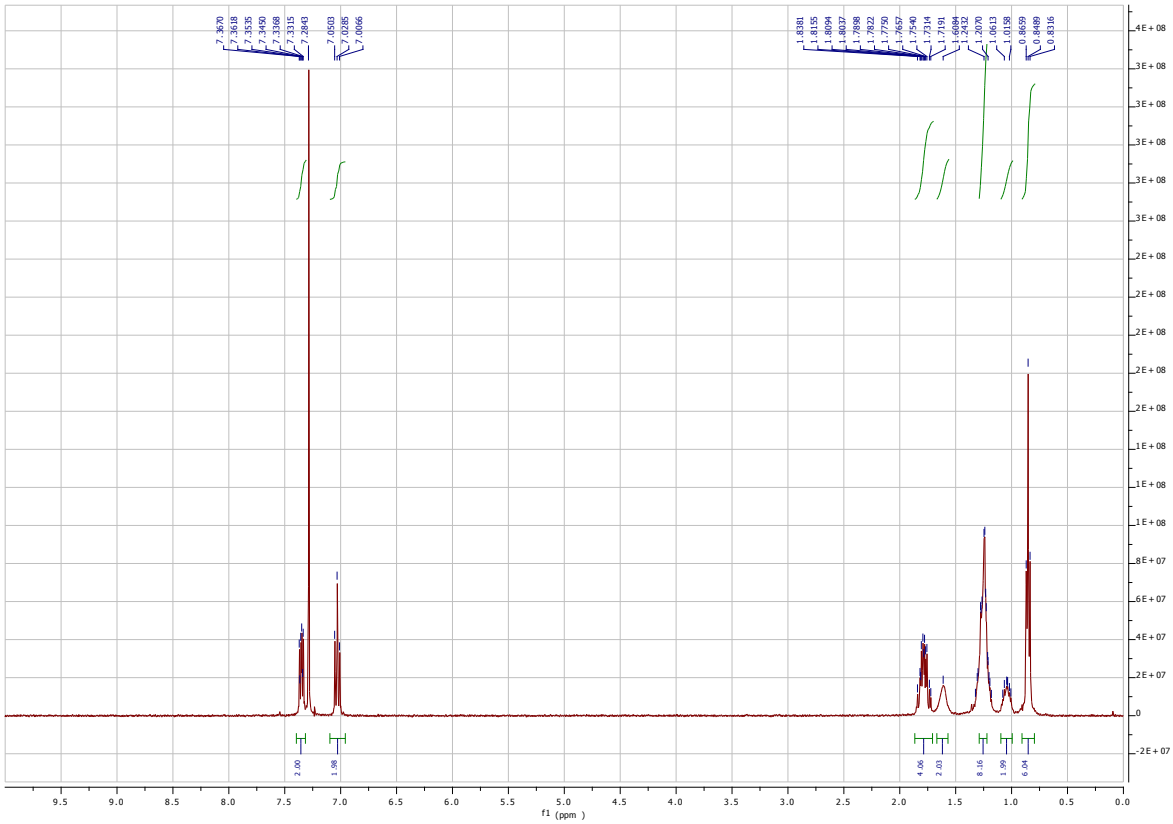


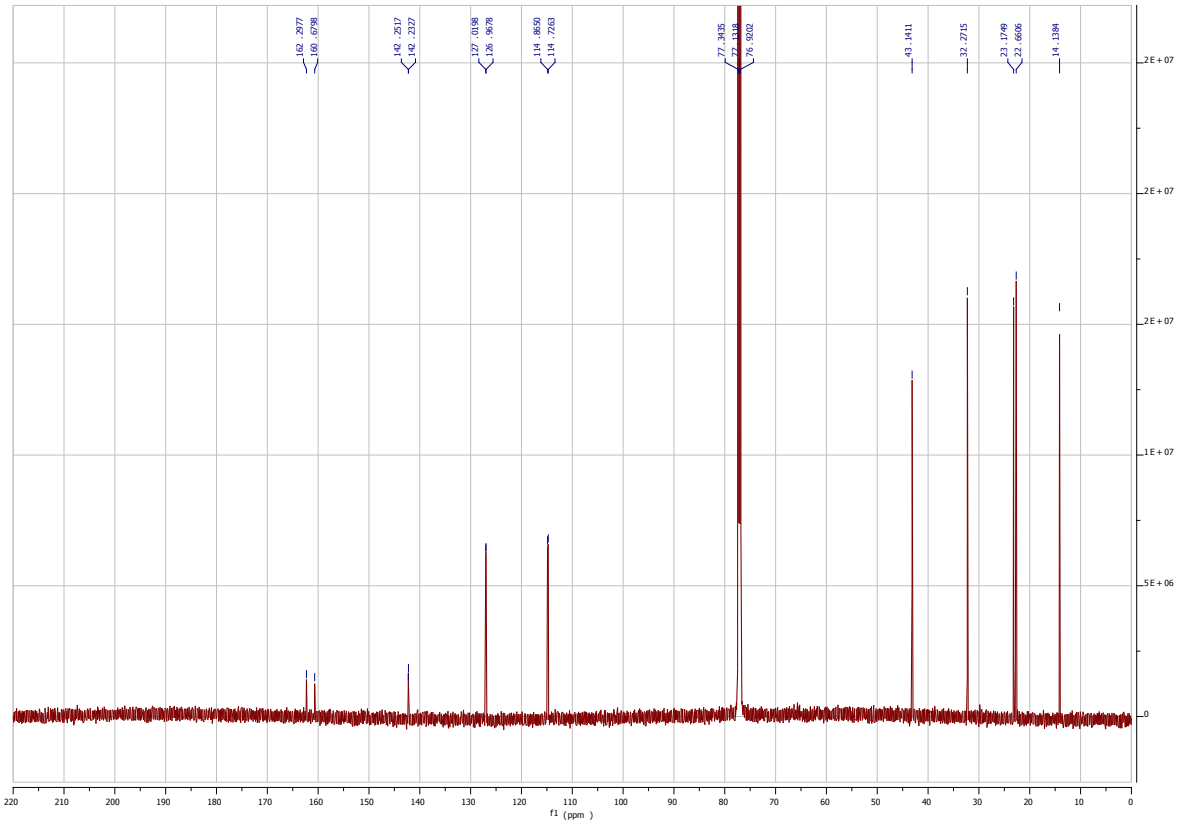


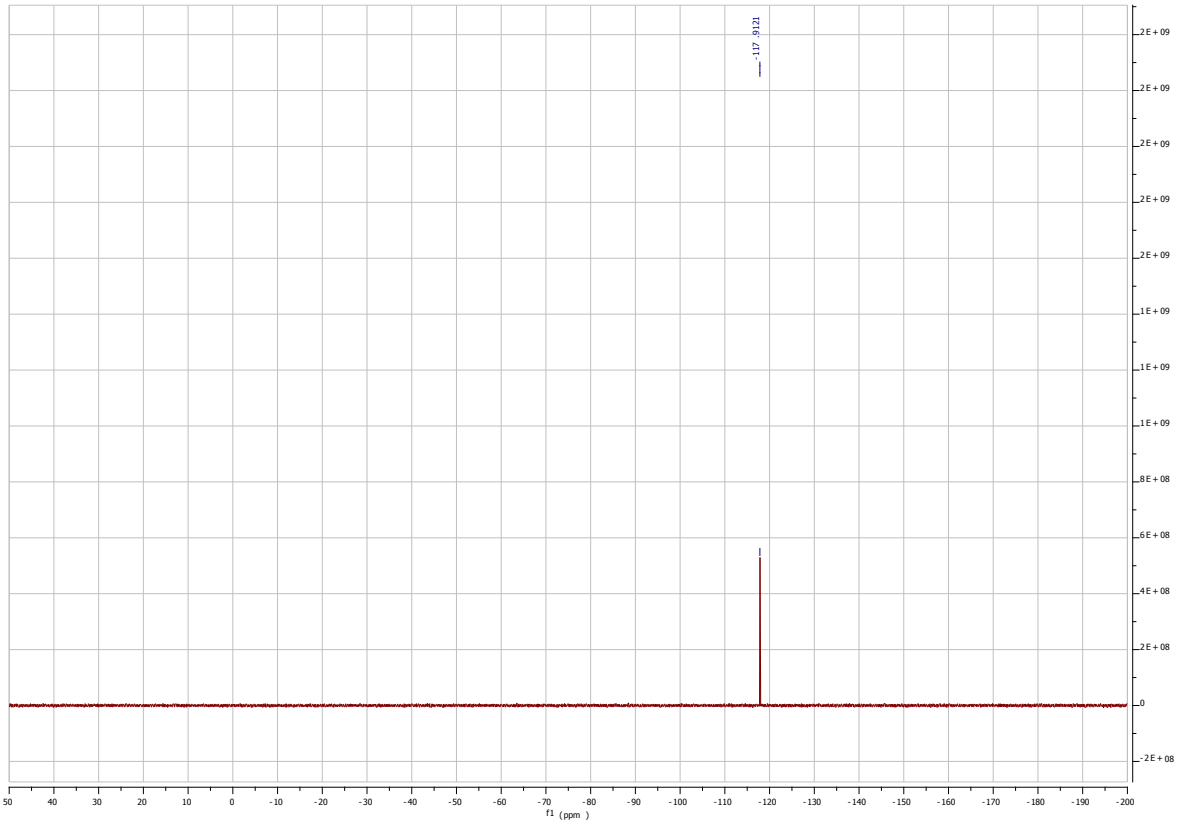
6-(4-Fluorophenyl)undecan-6-ol (5)



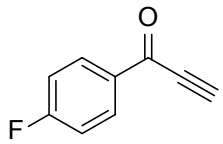
Purification by column chromatography (1%-15% Et_2O/Petrol) of the crude residue in the reaction for the formation of 1-(4-fluorophenyl)hexan-1-one also gave 6-(4-fluorophenyl)undecan-6-ol as a clear oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36-7.33 (m, 2H), 7.05-7.00 (m, 2H), 1.84-1.72 (m, 4H), 1.66-1.56 (m, 2H), 1.32-1.18 (m, 8H), 1.08-1.00 (m, 2H), 0.87-0.83 (m, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 161.5 (d, $J_{C\text{-}F}$= 242.7 Hz, CF), 142.2 (d, $J_{C\text{-}F}$ = 2.8 Hz, C), 127.0 (d, $J_{C\text{-}F}$ = 7.8 Hz, CH), 114.8 (d, $J_{C\text{-}F}$ = 20.8 Hz, CH), 43.1 (CH_2), 32.3 (CH_2), 23.2 (CH_2), 22.7 (CH_2), 14.2 (CH_3); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -117.9 (s, 1F); **IR** (thin film) 3356, 2960, 1600, 1510, 1445, 1369, 1091, 1044, 975 cm^{-1}; **LRMS (CI)** 289 (100, $[M+Na]^+$); **HRMS (CI)** calcd. for $C_{17}H_{28}FO$ $[M+H]^+$ 267.2046, observed 267.2051.



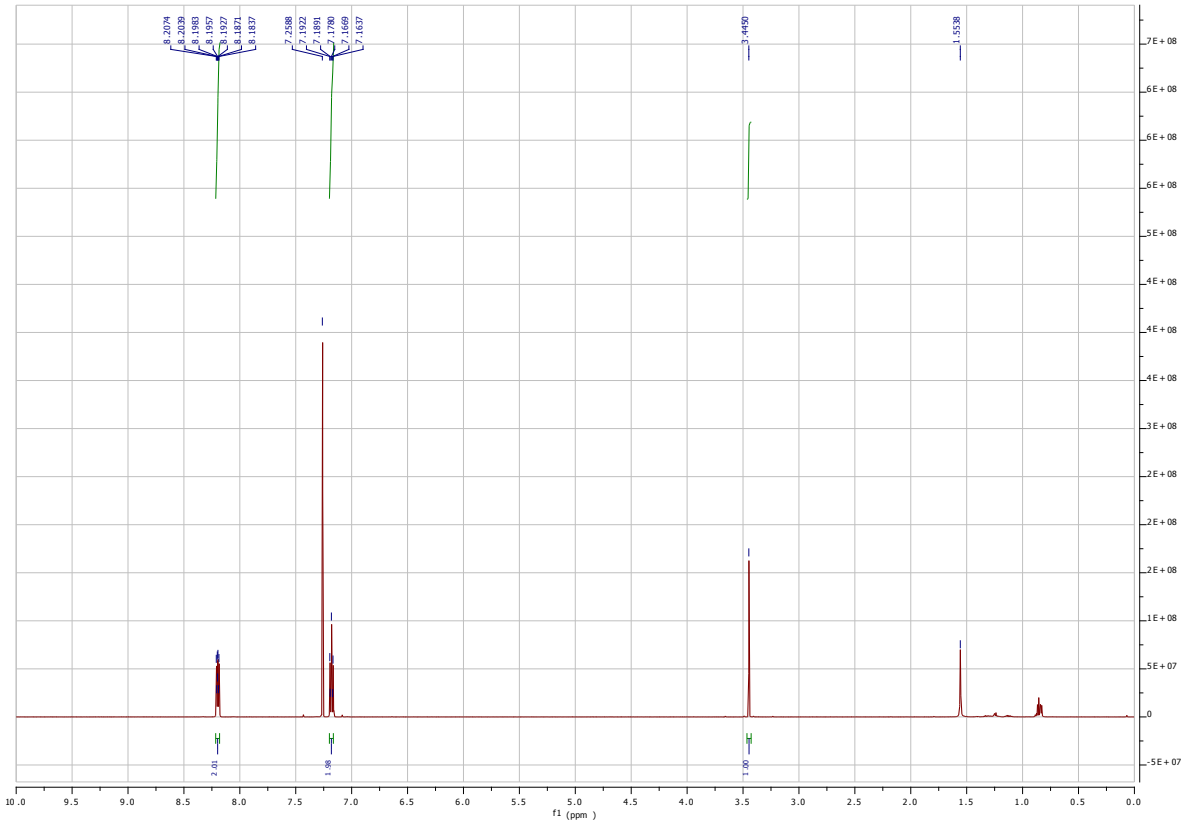


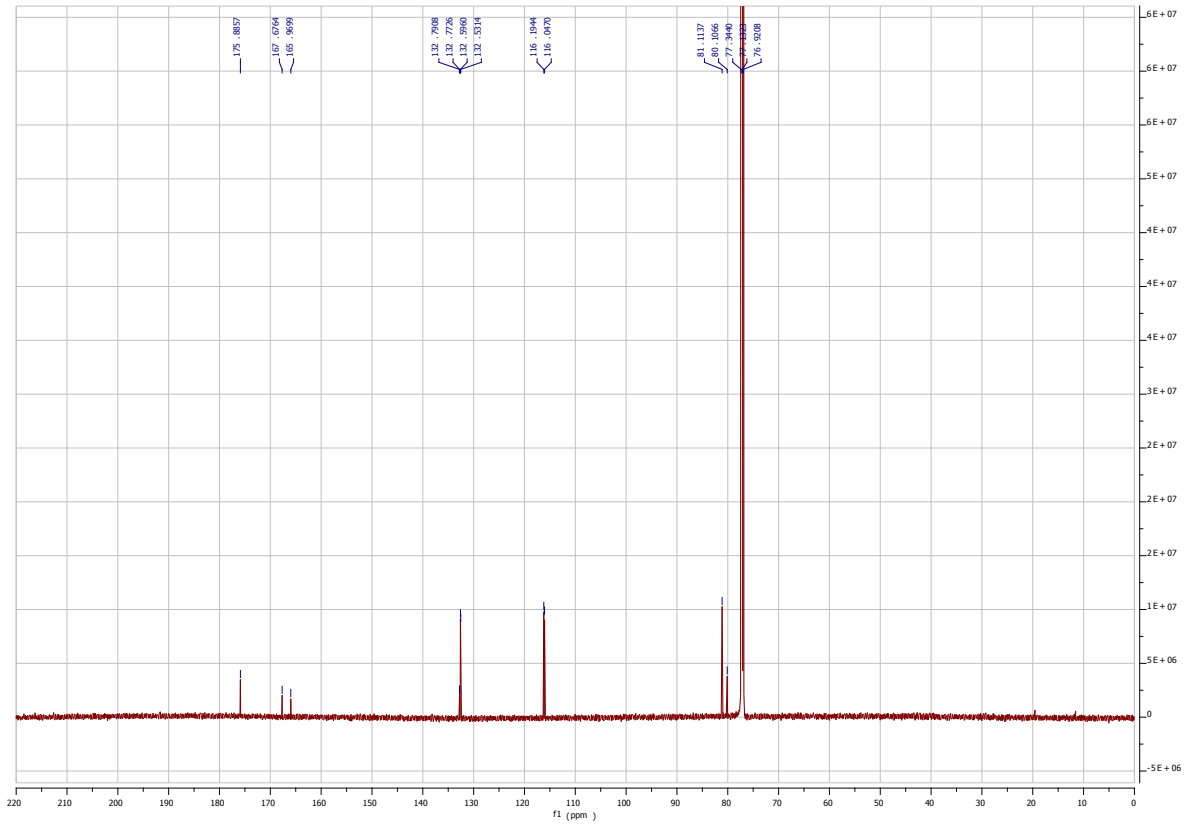


1-(4-Fluorophenyl)prop-2-yn-1-one[22] (6)

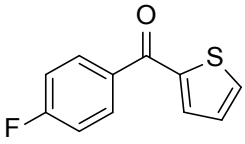


Applied general procedure for the diaryl ketone synthesis (see above). Purification by column chromatography (1%-8% Et_2O/Petrol) gave 1-(4-fluorophenyl)prop-2-yn-1-one as a white solid (58 mg, 0.38 mmol, 76%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.22-8.18 (m, 2H), 7.20-7.16 (m, 2H), 3.45 (s, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 175.9 (C), 166.2 (d, $J_{C\text{-}F}$ = 256.0 Hz, C), 132.8 (d, $J_{C\text{-}F}$ = 2.7 Hz, C), 132.6 (d, $J_{C\text{-}F}$ = 9.7 Hz, CH), 116.1 (d, $J_{C\text{-}F}$ = 22.1 Hz, C), 81.1 (C), 80.1 (CH); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -102.3 (s, 1F); **IR** (thin film) 3211, 2092, 1650, 1592, 1503, 1409, 1252, 1232, 1015 cm^{-1}; **LRMS (CI)** 149 (100, $[M+H]^+$); **HRMS (CI)** calcd. for C_9H_6FO $[M+H]^+$ 149.0403, observed 149.0398, **m.p.** 50-53 °C.

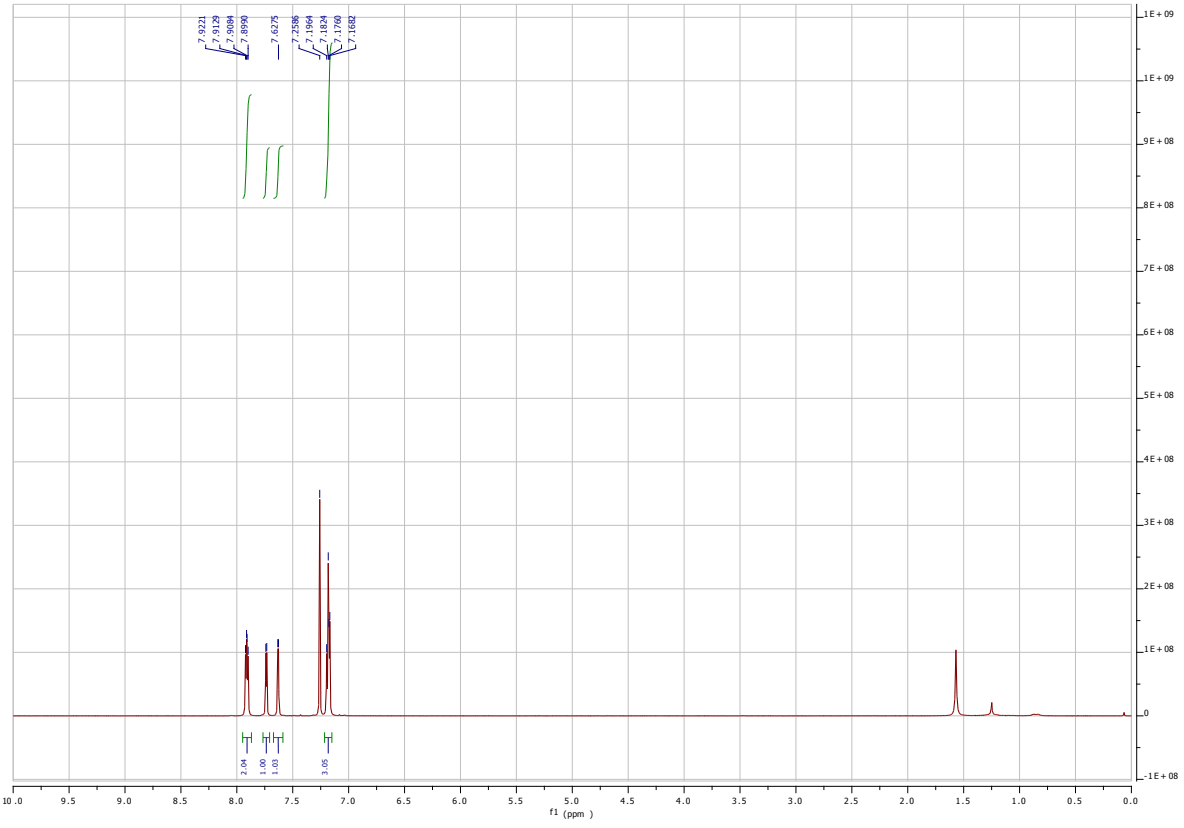


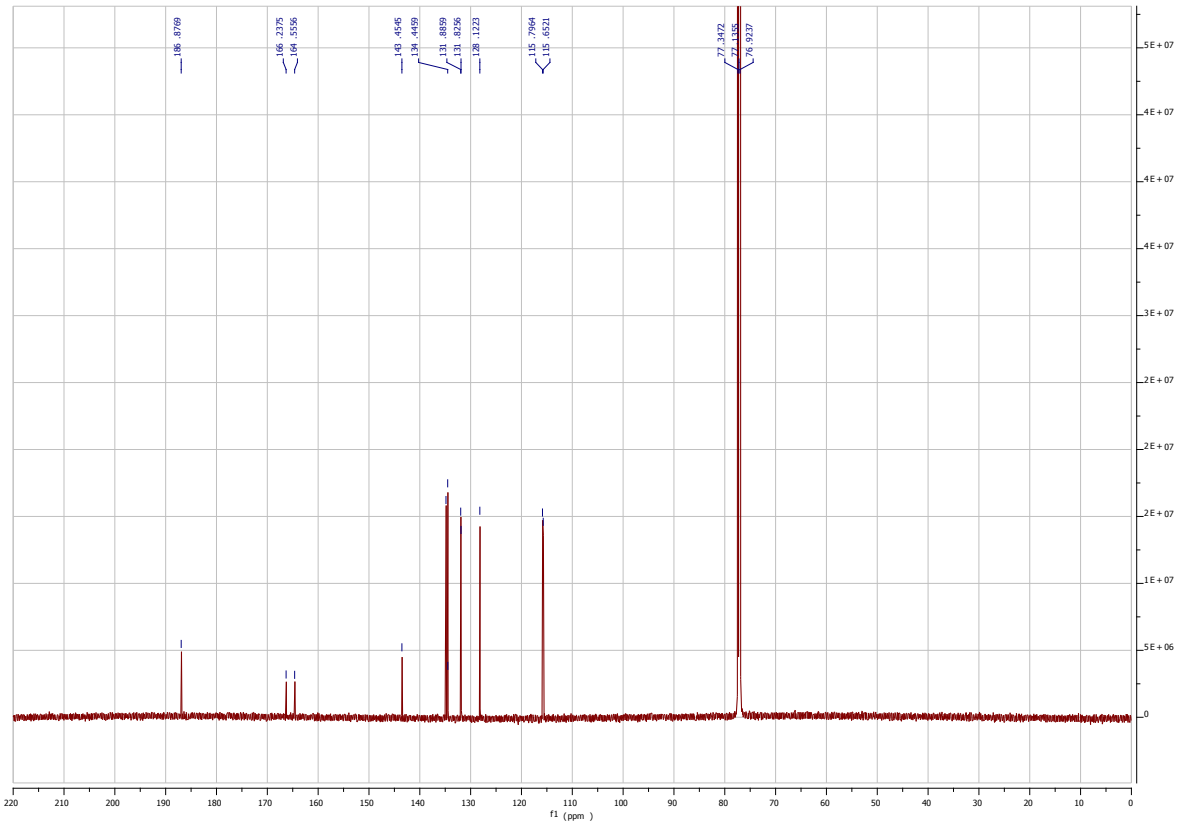


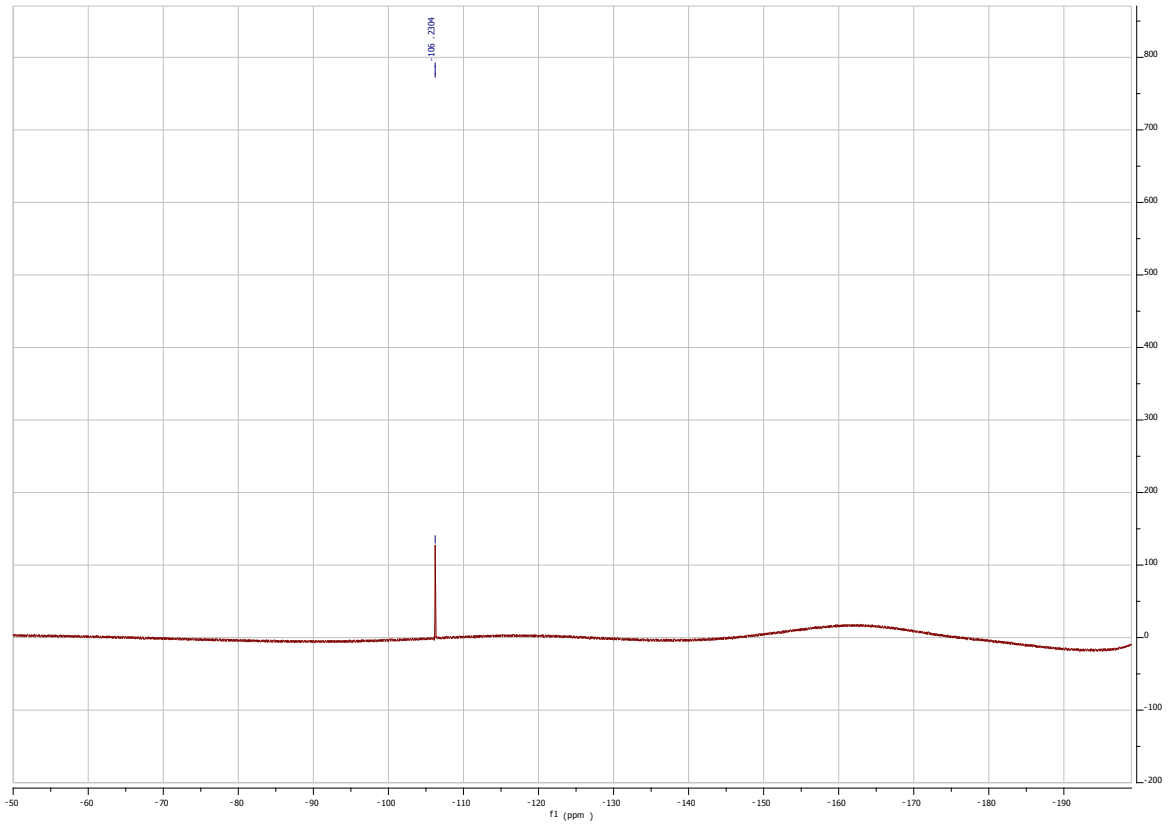
(4-Fluorophenyl)(thiophen-2-yl)methanone[23] (7)



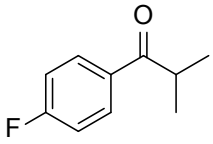
Applied general procedure for the diaryl ketone synthesis (see above). Purification by column chromatography (1%-5% Et_2O/Petrol) gave (4-fluorophenyl)(thiophen-2-yl)methanone as a colourless oil (73 mg, 0.36 mmol, 71%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92-7.88 (m, 2H), 7.74 (d, J = 4.9 Hz, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.20-7.17 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 186.9 (C), 165.5 (d, $J_{C\text{-}F}$ = 252.3 Hz, C), 143.5 (C), 134.8 (CH), 134.4 (CH), 134.4 (d, $J_{C\text{-}F}$ = 3.5 Hz, C), 131.9 (d, $J_{C\text{-}F}$ = 9.0 Hz, CH), 128.1 (CH), 115.7 (d, $J_{C\text{-}F}$ = 21.6 Hz, CH); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -106.2 (s, 1F); **IR** 3025, 1635, 1285, 1240, 1230, 1150, 1049, 758 cm^{-1}; **LRMS (CI)** 207 (100, $[M+H]^+$); **HRMS (CI)** calcd. for $C_{11}H_8FOS$ $[M+H]^+$ 207.0258, observed 207.0276; **m.p.** 88-93 °C.



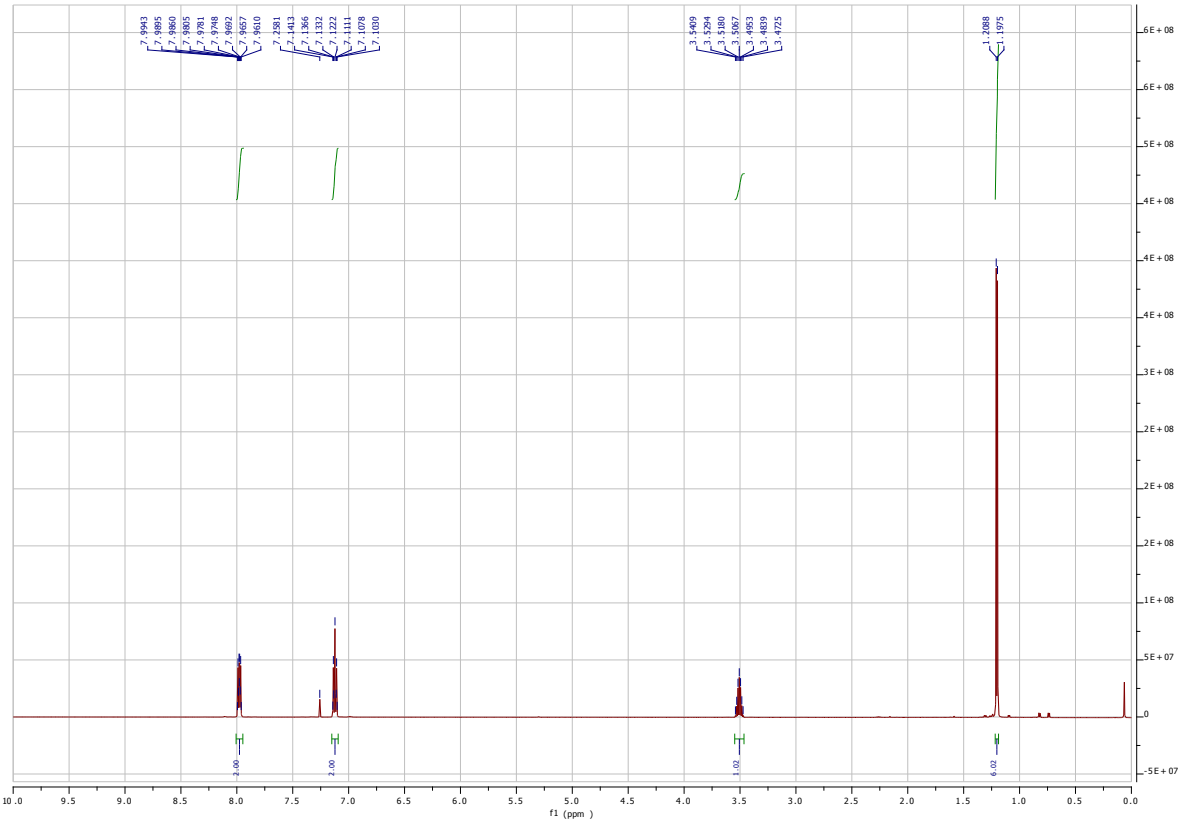


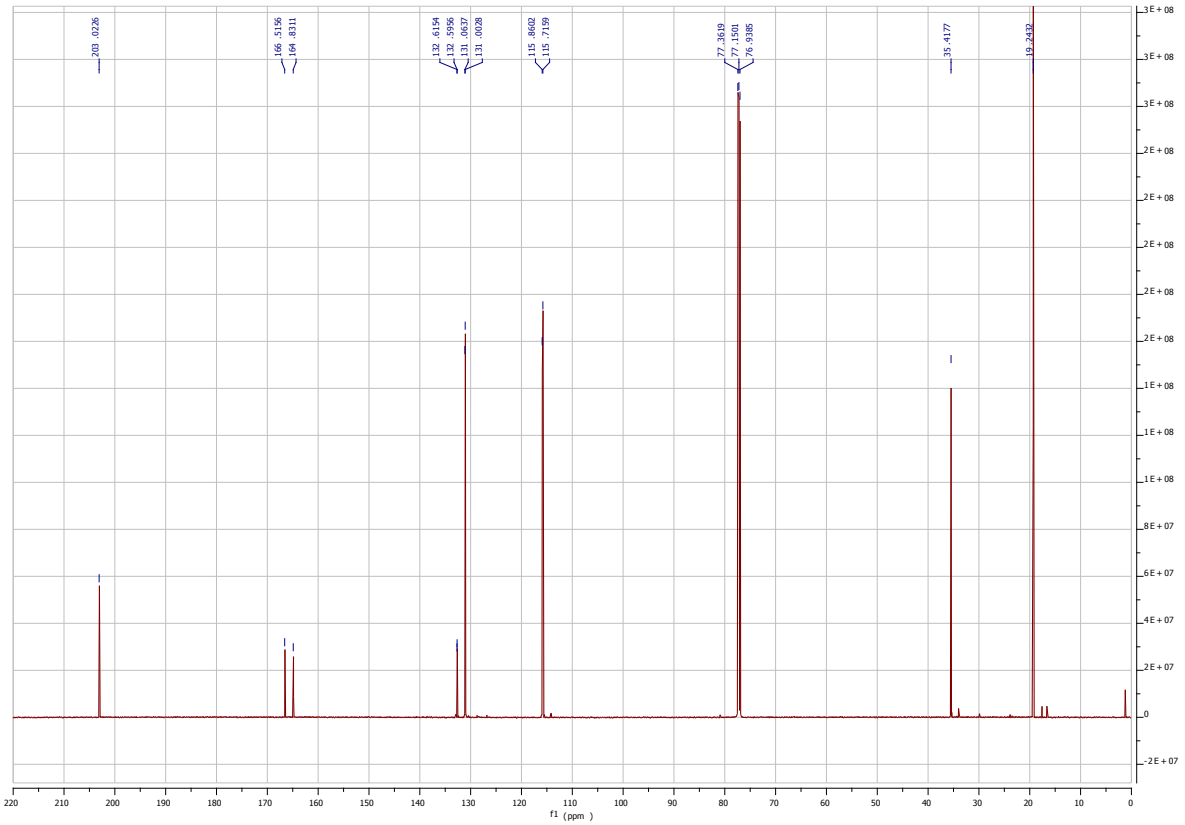


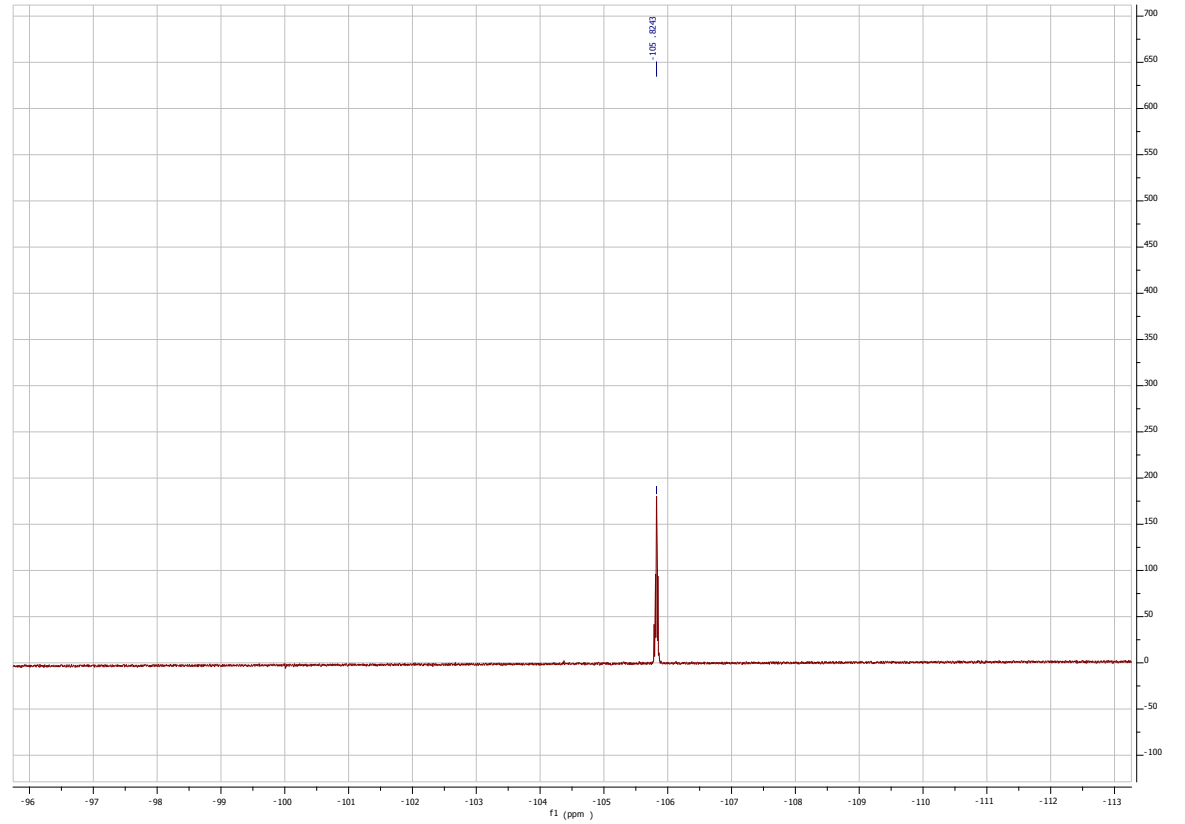
1-(4-Fluorophenyl)-2-methylpropan-1-one[24] (8)



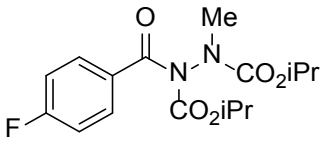
Applied general procedure for the alkyl aryl ketone synthesis (see above). Purification by column chromatography (1%-5% Et_2O/Petrol) gave 1-(4-fluorophenyl)-2-methylpropan-1-one as a colourless oil (58 mg, 0.35 mmol, 70%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99-7.96 (m, 2H), 7.16-7.10 (m, 2H), 3.51 (septet, J = 6.8 Hz, 1H), 1.20 (d, J = 6.8 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 203.0 (C), 166.5 (d, $J_{C\text{-}F}$ = 252.7 Hz, C), 132.6 (d, $J_{C\text{-}F}$ = 3.0 Hz, C), 131.0 (d, $J_{C\text{-}F}$ = 9.1 Hz, CH), 115.8 (d, $J_{C\text{-}F}$ = 21.6 Hz, CH), 35.4 (CH), 19.2 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -105.8; **IR** (thin film) 1681, 1595, 1219, 1152, 845 cm^{-1}; **LRMS (EI)** 166 (100, $[M]^+$); **HRMS (EI)** calcd. for $C_{10}H_{11}FO$ $[M]^+$ 166.0794, observed 166.0790.



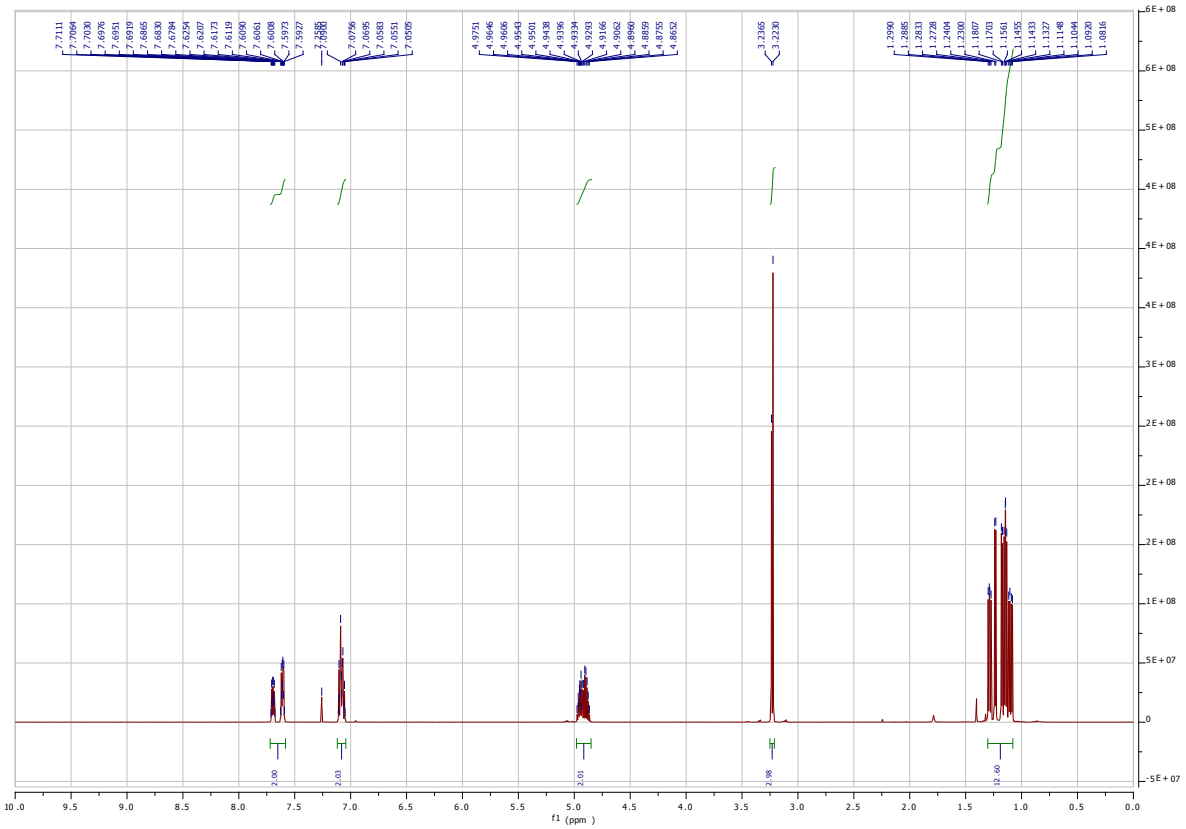


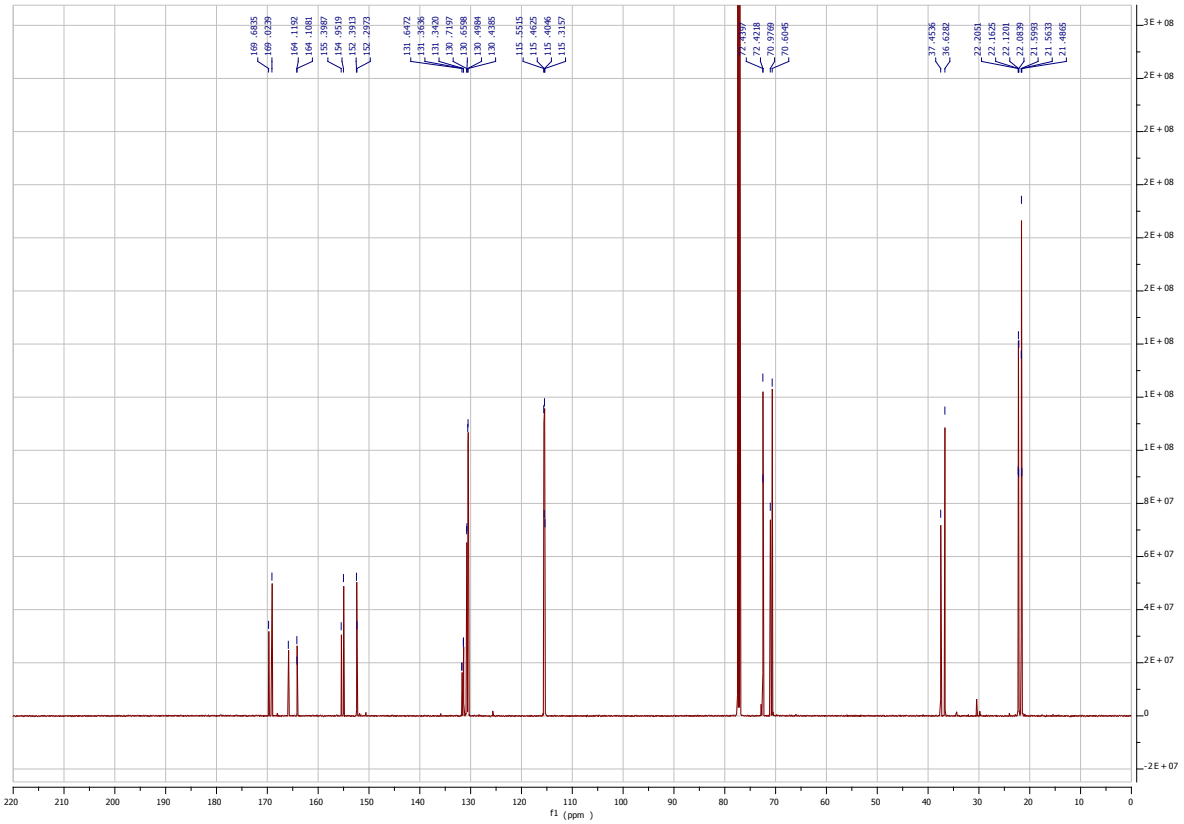


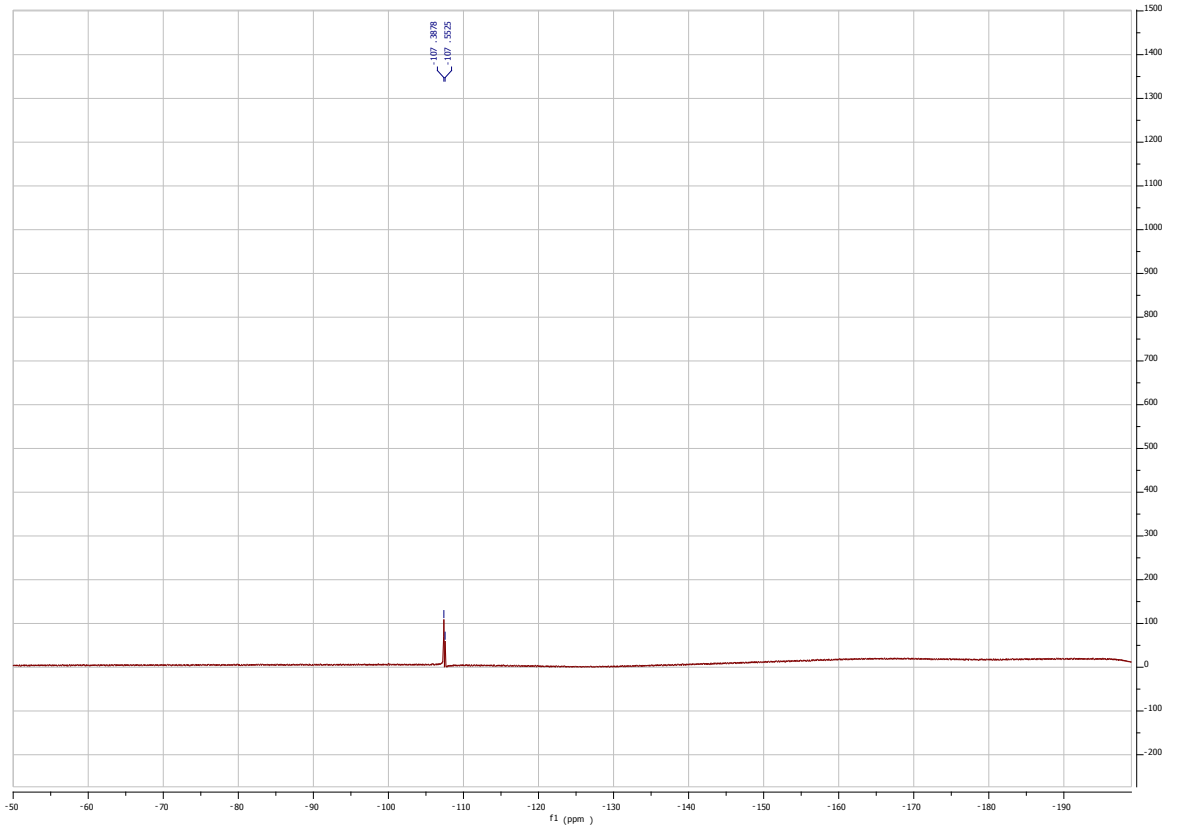
Diisopropyl 1-(4-fluorobenzoyl)-2-methylhydrazine-1,2-dicarboxylate (12)



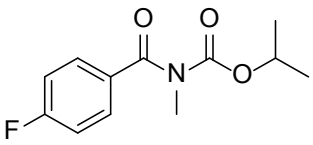
To a solution of **1a** (1.63 g, 5.0 mmol) in DMF (40 mL) was added caesium carbonate (1.95 g, 6.0 mmol) and methyl iodide (374 µL, 6.0 mmol). The reaction was complete after 21 h. Purification by column chromatography (5-25% Et_2O/Petrol) gave diisopropyl 1-(4-fluorobenzoyl)-2-methylhydrazine-1,2-dicarboxylate as a colourless oil (1.19 g, 3.50 mmol, 70%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.71-7.59 (m, 2H), 7.11-7.05 (m, 2H), 4.98-4.87 (m, 2H), 3.25-3.21 (m, 3H), 1.33-1.08 (m, 12H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.0 (C), 164.1 (C), 155.4 (d, $J_{C\text{-}F}$ = 268.1 Hz, CF), 152.4 (C), 152.3 (C), 131.4 (d, $J_{C\text{-}F}$ = 3.2 Hz, C), 130.4 (d, $J_{C\text{-}F}$ = 9.0 Hz, CH), 115.5 (d, $J_{C\text{-}F}$ = 22.0 Hz, CH), 72.4 (CH), 70.6 (CH), 36.6 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 21.6 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -107.4 (m, 1F); **IR** (thin film) 1709, 1579, 1231, 1115 cm^{-1}; **LRMS (ES$^+$)** 341.1525 (100, $[M+H]^+$); **HRMS (ES$^+$)** calcd. for $C_{16}H_{22}FO_5$ $[M+H]^+$ 341.1513, observed 341.1525.



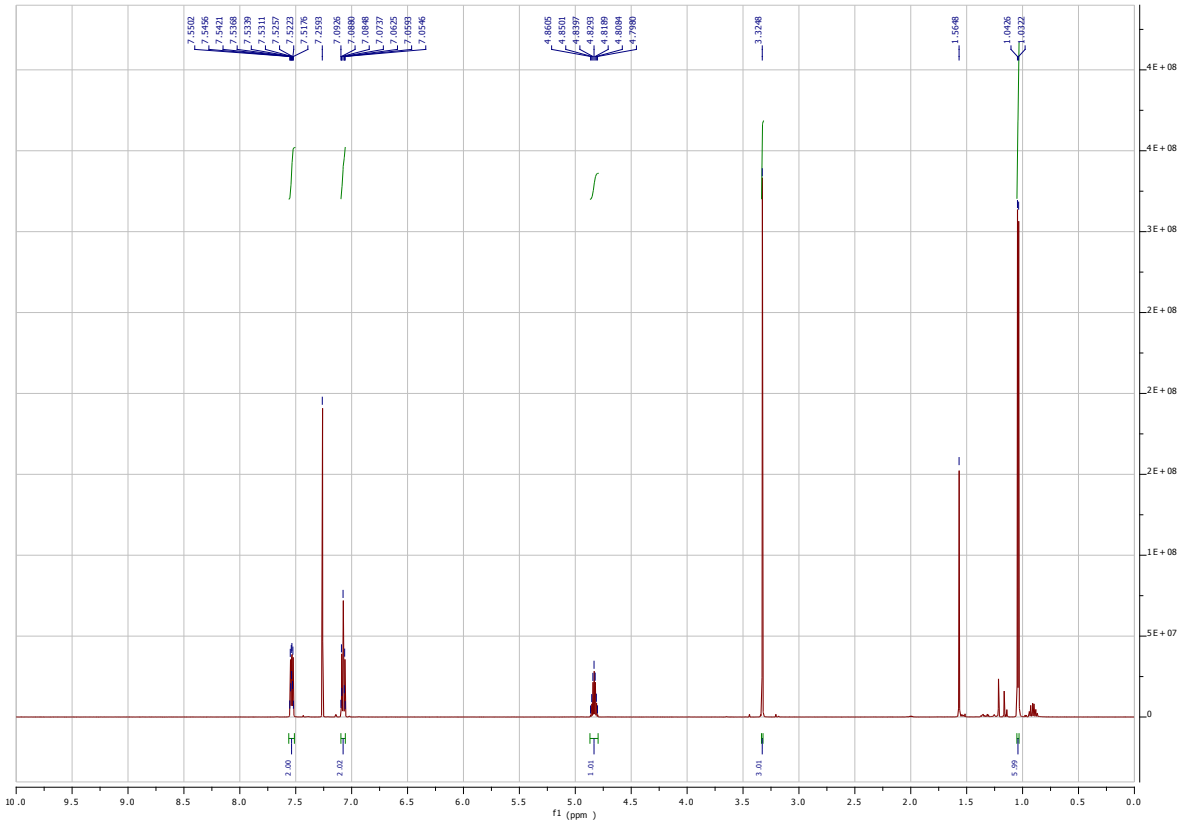


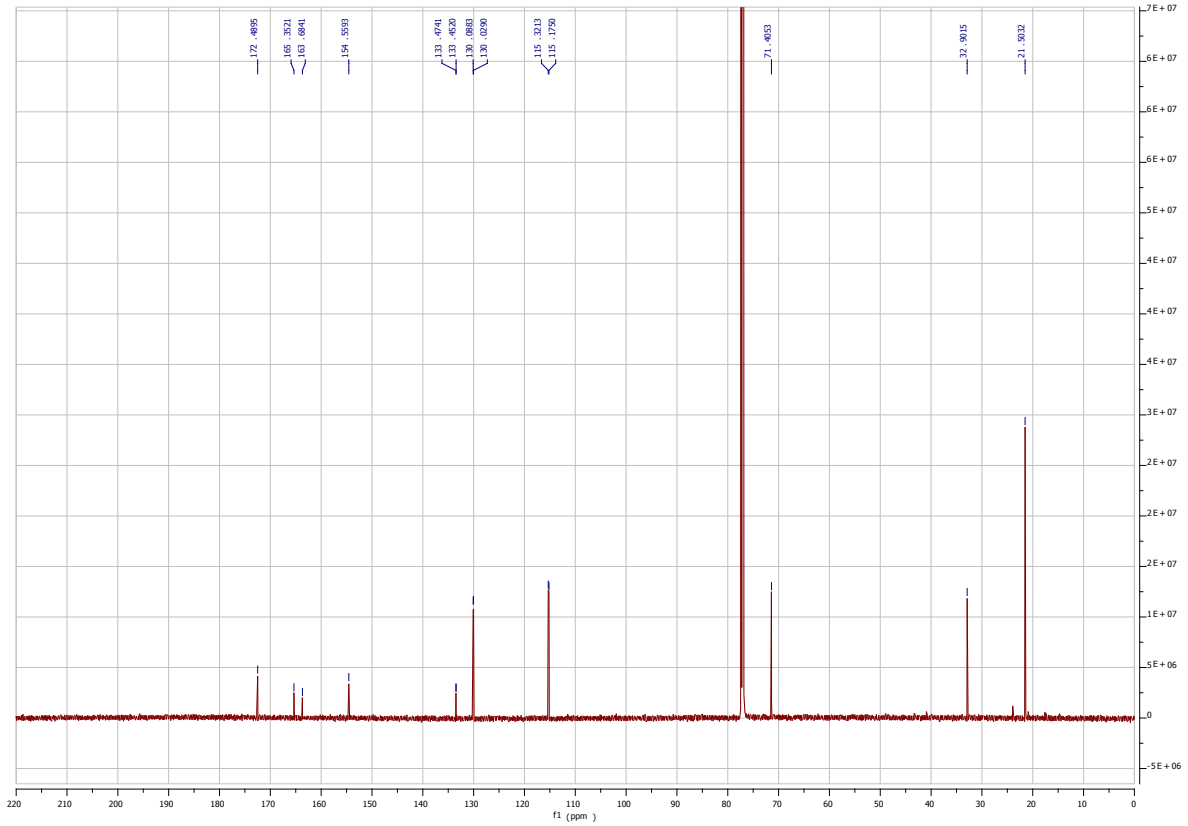


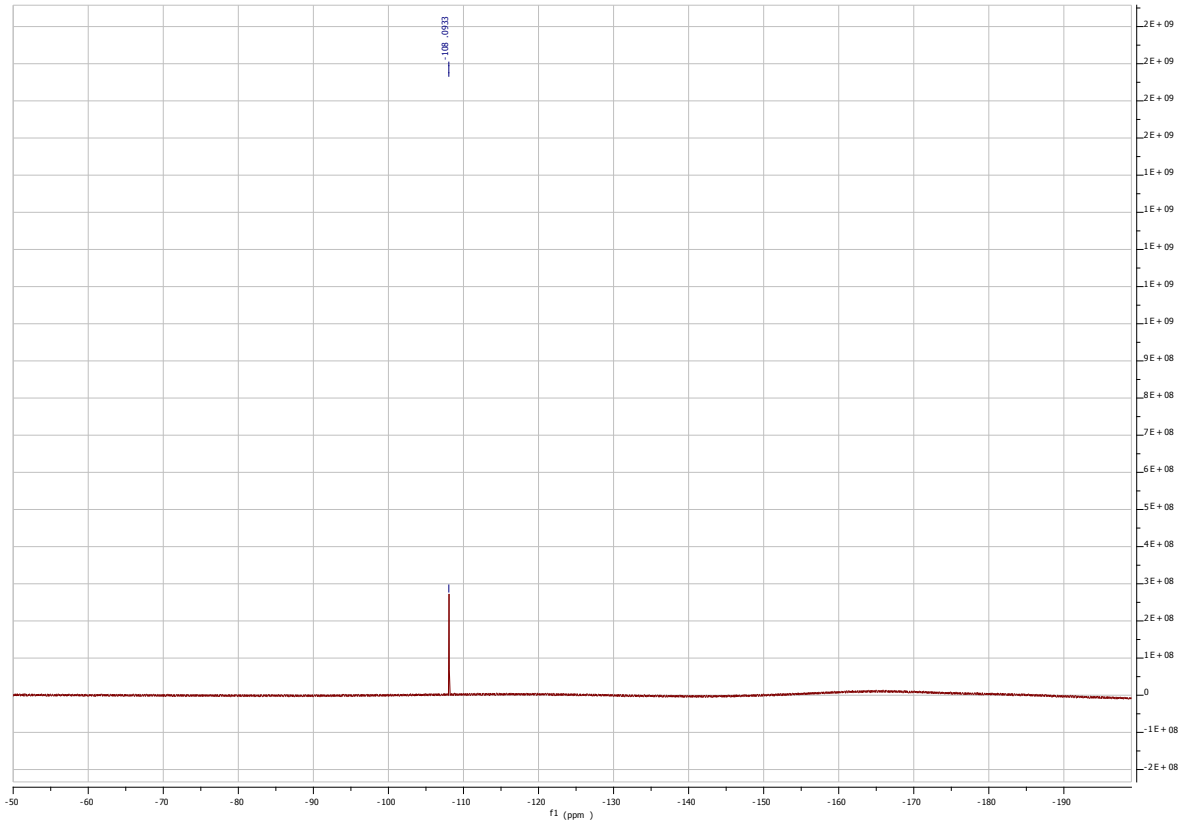
Isopropyl (4-fluorobenzoyl)(methyl)carbamate (13)



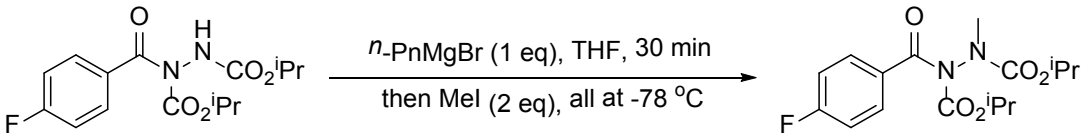
Sodium hydride (660 mg, 16.5 mmol) was added to a stirring solution of *N*-methylbenzamide (500 mg, 3.30 mmol) in THF (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and isopropyl chloroformate (13 mL, 13.2 mmol) was added in one portion. After 2 h, the reaction was quenched with saturated ammonium chloride solution (10 mL). The organic layer was extracted with Et_2O (3 x 20 mL) and dried ($MgSO_4$). The solvent was then removed *in vacuo* and the crude residue purified by column chromatography (10%-25% Et_2O/Petrol) to afford isopropyl (4-fluorobenzoyl)(methyl)carbamate as a colourless oil (765 mg, 3.20 mmol, 97%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56-7.52 (m, 2H), 7.19-7.15 (m, 2H), 4.83 (septet, J = 6.2 Hz, 1H), 3.32 (s, 3H), 1.03 (d, J = 6.2 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 172.5 (C), 164.5 (d, $J_{C\text{-}F}$ = 250.2 Hz, C), 154.6 (C), 133.5 (d, $J_{C\text{-}F}$ = 3.3 Hz, C), 130.1 (d, $J_{C\text{-}F}$ = 35.6 Hz, CH), 115.2 (d, $J_{C\text{-}F}$ = 21.9 Hz, CH), 71.4 (CH), 32.9 (CH_3), 21.5 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -108.1 (s, 1F); **IR** (thin film) 1718, 1600, 1216 cm^{-1}; **LRMS (ES$^+$)** 240 (100, $[M+H]^+$); **HRMS (ES$^+$)** calcd. for $C_{12}H_{15}FNO_3$ $[M+H]^+$ 240.1036, observed 240.1040.



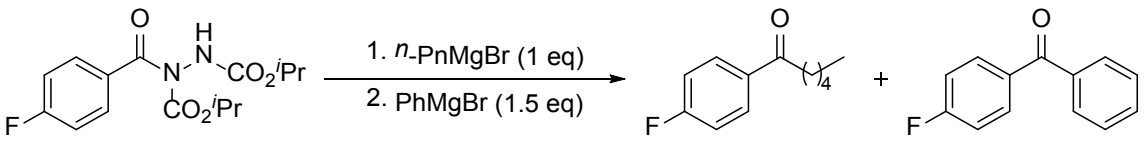




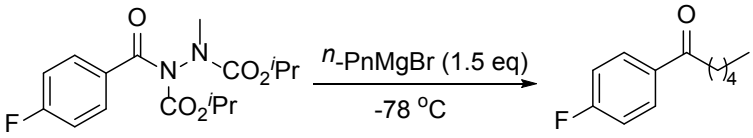
Reactions detailed in Scheme 1



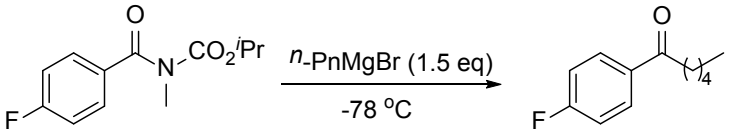
To a flame-dried three-necked flask, under an inert atmosphere, was added a solution of acyl hydrazide **1a** (163 mg, 0.5 mmol) in THF (10 mL). *n*-Pentylmagnesium bromide (93 µL, 0.5 mmol) was then added to the stirring solution in one portion at –78 °C. After 30 min, methyl iodide (62 µL, 1.0 mmol) was added and the reaction stirred at –78 °C for a further 30 min. The reaction was then quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and the solvent was removed in *vacuo*. The resultant crude residue was purified by column chromatography (5%-25% Et_2O/Petrol) to give diisopropyl 1-(4-fluorobenzoyl)-2-methylhydrazine-1,2-dicarboxylate as a colourless oil (148 mg, 0.43 mmol, 87%). Data for this compound matched that as described above for diisopropyl 1-(4-fluorobenzoyl)-2-methylhydrazine-1,2-dicarboxylate **12**.



To a flame-dried three-necked flask, under an inert atmosphere, was added a solution of acyl hydrazide **1a** (163 mg, 0.5 mmol) in THF (10 mL). *n*-Pentylmagnesium bromide (93 µL, 0.5 mmol) was then added to the stirring solution in one portion at –78 °C. After 30 min, phenylmagnesium bromide (119 µL, 0.75 mmol) was added and the reaction stirred at 0 °C for a further 30 min. The reaction was then quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and the solvent was removed in *vacuo.* The resultant crude residue was purified by column chromatography (5%-25% Et_2O/Petrol) to give 1-(4-fluorophenyl)hexan-1-one as a white solid (4 mg, 0.02 mmol, 4%) and (4-fluorophenyl)(phenyl)methanone as a colourless oil (72 mg, 0.36 mmol, 71%). Data for these compounds matched that as described above for 1-(4-fluorophenyl)hexan-1-one **3aa** and (4-fluorophenyl)(phenyl)methanone **3ab**.



To a flame-dried three-necked flask, under an inert atmosphere, was added a solution of diisopropyl 1-(4-fluorobenzoyl)-2-methylhydrazine-1,2-dicarboxylate **12** (170 mg, 0.5 mmol) in THF (10 mL). *n*-Pentylmagnesium bromide (119 µL, 0.75 mmol) was then added to the stirring solution in one portion and the reaction stirred for 30 min at –78 °C. The reaction was then quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and the solvent was removed in *vacuo.* The resultant crude residue was purified by column chromatography (5%-25% Et_2O/Petrol) to give 1-(4-fluorophenyl)hexan-1-one as a white solid (39 mg, 0.19 mmol, 38%). Data for this compound matched that as described above for 1-(4-fluorophenyl)hexan-1-one **3aa**.



To a flame-dried three-necked flask, under an inert atmosphere, was added a solution of isopropyl (4-fluorobenzoyl)(methyl)carbamate **13** (120 mg, 0.5 mmol) in THF (10 mL). *n*-Pentylmagnesium bromide (119 µL, 0.75 mmol) was then added to the stirring solution in one portion and the reaction stirred for 30 min at –78 °C. The reaction was then quenched with pre-cooled (*ca.* 4 °C) saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), the organic layers combined, dried ($MgSO_4$), filtered under vacuum and the solvent was removed in *vacuo*. The resultant crude residue was purified by column chromatography (5%-25% Et_2O/Petrol) to give 1-(4-fluorophenyl)hexan-1-one as a white solid (37 mg, 0.18 mmol, 36%). Data for this compound matched that as described above for 1-(4-fluorophenyl)hexan-1-one **3aa**.

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