Synthesis of Unsymmetrical Ketones by Applying Visible-Light Benzophenone/Nickel Dual Catalysis for Direct Benzylic Acylation

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General methods:

Reactions: All reactions were carried out in oven-dried reaction-tubes under an argon or nitrogen atmosphere using Schlenk technique.

Reagents: All reagents were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar, TCI, ABCR, VWR, Chempur, Fluorochem or J&K Scientific. All the reagents obtained from commercial sources were used as received unless mentioned otherwise. **Toluene** and its derivatives used were of analytical reagent grade.

NMR Spectra: ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance Neo 400, Avance Neo 600; Varian Mercury Plus 300, VNMRS 400 and VNMRS 600 spectrometers. Spectra were calibrated relative to solvents' residual proton and carbon chemical shifts: $CHCl_3$ (δ = 7.26 ppm for ^{1}H NMR and δ = 77.16 ppm for ^{13}C NMR) and are reported in ppm. Coupling constants (*J*) are reported in Hertz (Hz). The multiplicity of the signals is given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

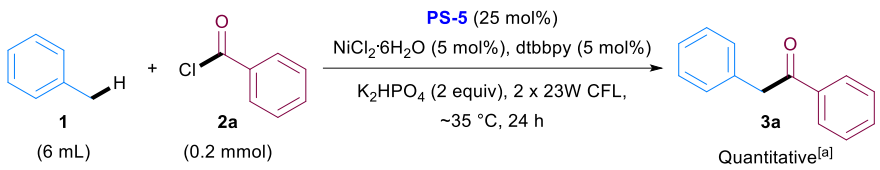
Thin layer chromatography (TLC) was performed to monitor the reactions using Merck silica gel aluminium plates with F-254 indicator and detection of compounds was done under UV light (254 nm).

Flash column chromatography (FCC) was performed using Macherey Nagel silica gel (particle size 0.040-0.063 mm) to purify products applying air pressure of about 0.2 bar.

Reaction setup: Reactions were set up in reaction tubes being irradiated from two sides with two OSRAM CFL-lamps (warm white, 23 W). Cooling with a fan was applied to keep the temperature at around 35 °C.

Control experiments:

Table S1.

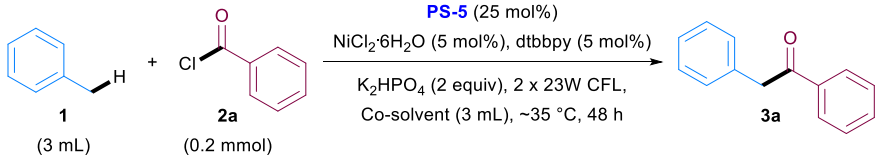


Standard Conditions

Entry	Deviation from standard conditions	Yield[a]
1	Without $NiCl_2·6H_2O$	2
2	Without dtbbpy	2
3	Without **PS-5**	0
4	In dark	0
5	Without K_2HPO_4	32

[a] Calculated, with CH_2Br_2 (14 µL, 0.2 mmol) as internal standard, from ^1H NMR spectra.

Table S2.



Entry	Co-solvent	Yield[a]
1	Acetonitrile	80
2	Benzene	80
3	Benzotrifluoride	60

[a] Calculated, with CH_2Br_2 (14 µL, 0.2 mmol) as internal standard, from ^1H NMR spectra.

General procedure:

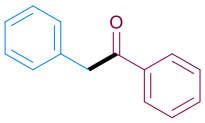
General procedure **GP1** for the synthesis of ketones **3**:

4-Benzoylphenyl acetate (**PS-5**) (12.0 mg, 0.05 mmol, 0.25 equiv), $NiCl_2·6H_2O$ (2.4 mg, 0.01 mmol, 0.05 equiv), dtbbpy (2.7 mg, 0.01 mmol, 0.05 equiv), K_2HPO_4 (69.7 mg, 0.4 mmol, 2.0 equiv) and acid chloride or acid anhydride (if solid, 0.2 mmol. 1 equiv) were taken in an oven-dried reaction-tube containing a teflon coated stirring bar and closed with a septum. Next, the tube was evacuated for 15 minutes and filled back with Argon before addition of degassed toluene or toluene derivative (6 mL) (analytical grade, degassed through a 30 min argon-purge) *via* syringe. Acid chloride or acid anhydride (if liquid, 0.2 mmol, 1.0 equiv) was added *via* syringe. The septum and the tube were sealed with parafilm and the reaction mixture was stirred under irradiation of two OSRAM CFL-lamps (warm white, 23 W). The setup was cooled with a fan

to keep the reaction temperature at ~35 °C. After 48 hours, the reaction was quenched with water (3 mL) and extracted with EtOAc (3x4 mL) The combined organic phase was filtered through $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to obtain the desired product.

Characterization of ketones 3:

1,2-Diphenylethan-1-one (3a):

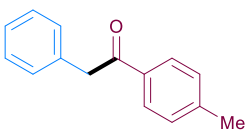


Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** to give **3a** as a white solid in 93% (36.4 mg, 0.185 mmol) isolated yield after column chromatography (hexane: Et_2O = 96.5:3.5; R_f = 0.38) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.39 – 7.36 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.10 – 7.05 (m, 3H), 4.10 (s, 2H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.6, 136.6, 134.6, 133.2, 129.5, 128.7, 128.7, 128.6, 126.9, 45.5 ppm. The spectral data were in accordance with the literature.[1]

Scale-up reaction: 4-Benzoylphenyl acetate (**PS-5**) (60.0 mg, 0.25 mmol, 0.25 equiv), $NiCl_2{\cdot}6H_2O$ (11.9 mg, 0.05 mmol, 0.05 equiv), dtbbpy (13.4 mg, 0.05 mmol, 0.05 equiv) and K_2HPO_4 (348.0 mg, 2.0 mmol, 2.0 equiv) were taken in a round-bottomed flask containing a teflon coated stirring bar and closed with a septum. Next, the flask was evacuated for 15 minutes and filled back with Argon before addition of degassed toluene ~~or toluene derivative~~ (30 mL) (analytical grade, degassed through a 30 min argon-purge) *via* syringe. Benzoylchloride (0.12 mL, 1.0 mmol, 1.0 equiv) was added *via* syringe. The septum and the tube were sealed with parafilm and the reaction mixture was stirred under irradiation of two OSRAM CFL-lamps (warm white, 23 W). The setup was cooled with a fan to keep the reaction temperature at ~35 °C. After 48 hours, the reaction was quenched with water (15 mL) and extracted with EtOAc (3x20 mL) The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexane: Et_2O = 97:3) to give **3a** as a white solid in 87% (171.8 mg, 0.87 mmol) yield.

This compound was also obtained when benzoic anhydride **4a** (45.2 mg, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** in presence of **20 mol% PS-5** with toluene (6 mL) to give **3a** as a white solid in 75% (29.4 mg, 0.150 mmol) isolated yield after column chromatography (hexane: Et_2O = 97:3).

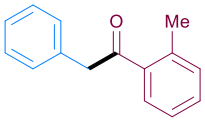
2-Phenyl-1-(*p*-tolyl)ethan-1-one (3b):



4-Methylbenzoyl chloride **2b** (26 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** in presence of **10 mol% PS-5** with toluene (6 mL) to give **3b** as a white solid in 73% (30.6 mg, 0.146 mmol) isolated yield after column chromatography (pentane: Et_2O = 97:3; R_f = 0.37). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H),

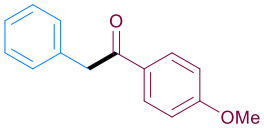
7.34 – 7.22 (m, 7H), 4.26 (s, 2H), 2.40 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 144.0, 134.8, 134.1, 129.4, 129.3, 128.8, 128.6, 126.8, 45.4, 21.6 ppm. The spectral data were in accordance with the literature.[1]

2-Phenyl-1-(*o*-tolyl)ethan-1-one (3c):



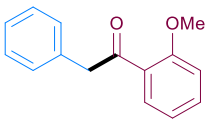
2-Methylbenzoyl chloride **2c** (26 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3c** as a colorless liquid in 65% (27.3 mg, 0.130 mmol) isolated yield after column chromatography (pentane: Et_2O = 97:3; R_f = 0.4). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.73-7.70 (m, 1H), 7.39-7.22 (m, 8H), 4.21 (s, 2H), 2.45 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.6, 138.7, 137.8, 134.6, 132.1, 131.5, 129.7, 128.8, 127.0, 125.8, 48.6, 21.4 ppm. The spectral data were in accordance with the literature.[2]

1-(4-Methoxyphenyl)-2-phenylethan-1-one (3d):



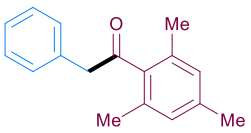
4-Methoxybenzoyl chloride **2d** (34.1 mg, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** in presence of **25 mol% PS-1** to give **3d** as a white solid in 74% (33.7 mg, 0.149 mmol) isolated yield after column chromatography (hexane: EtOAc = 95: 5; R_f = 0.24). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.2 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.26 (dd, *J* = 14.5, 7.4 Hz, 3H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.23 (s, 2H), 3.85 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.2, 163.5, 135.0, 130.9, 129.7, 129.4, 128.6, 126.8, 113.8, 55.5, 45.3 ppm. The spectral data were in accordance with the literature.[3]

1-(2-Methoxyphenyl)-2-phenylethan-1-one (3e):



2-Methoxybenzoyl chloride **2e** (34.1 mg, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** in presence of **25 mol% PS-2** with toluene (6 mL) to give **3e** as a colorless liquid in 58% (26.3 mg, 0.116 mmol) isolated yield after column chromatography (hexane: EtOAc = 95: 5; R_f = 0.35). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.6, 7.3, 1.8 Hz, 1H), 7.30 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.23 (dt, *J* = 8.7, 2.8 Hz, 3H), 7.00 – 6.95 (m, 2H), 4.30 (s, 2H), 3.92 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 200.2, 158.4, 135.2, 133.5, 130.7, 129.7, 128.3, 128.3, 126.6, 120.7, 111.5, 55.5, 50.2 ppm. The spectral data were in accordance with the literature.[4]

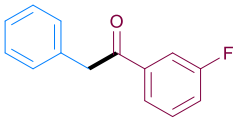
1-Mesityl-2-phenylethan-1-one (3f):



2,4,6-Trimethylbenzoyl chloride **2f** (33 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3f** as a white solid in 48% (23.1 mg, 0.097 mmol) isolated yield after column chromatography (pentane: Et_2O = 97:3;

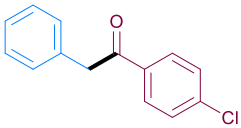
R_f = 0.6). **^{1}H NMR** (300 MHz $CDCl_3$) δ 7.35-7.26 (m, 3H), 7.22 (d, *J* = 7.0 Hz, 2H), 6.83 (s, 2H), 4.01 (s, 2H), 2.29 (s, 3H), 2.14 (s, 6H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.7, 139.3, 138.7, 133.4, 132.9, 130.0, 128.7, 128.6, 127.2, 51.9, 21.2, 19.3 ppm. The spectral data were in accordance with the literature.[4]

1-(3-fluorophenyl)-2-phenylethan-1-one (3g):



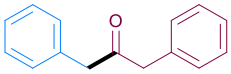
3-Fluorobenzoyl chloride **2g** (24.3 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3g** as a white solid in 60% (25.7 mg, 0.12 mmol) isolated yield after column chromatography (hexane: Et_2O = 97:3; R_f = 0.37). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.71 (dt, *J* = 9.4, 2.1 Hz, 1H), 7.46 (td, *J* = 8.0, 5.5 Hz, 1H), 7.36 (dd, *J* = 8.6, 6.6 Hz, 2H), 7.31 – 7.27 (m, 4H), 4.29 (s, 2H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.3, 162.9 (d, *J* = 247.2 Hz), 138.7 (d, *J* = 6.1 Hz), 134.1, 130.3 (d, *J* = 7.3 Hz), 129.4, 128.8, 127.1, 124.4, 120.2 (d, *J* = 21.8 Hz), 115.3 (d, *J* = 21.9 Hz), 45.7 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.7 (dd, *J* = 15.3, 7.2 Hz) ppm. The spectral data were in accordance with the literature.[5]

1-(4-Chlorophenyl)-2-phenylethan-1-one (3h):



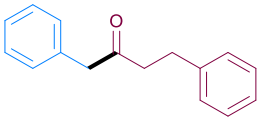
4-Chlorobenzoyl chloride **2h** (25.6 µL, 0.2 mmol, 1.0 equiv) was reacted for 24 hours according to **GP1** with toluene (6 mL) to give **3h** as a white solid in 60% (27.6 mg, 0.12 mmol) isolated yield after column chromatography (pentane: Et_2O = 98:2; R_f = 0.33). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26-7.23 (m, 3H), 4.24 (s, 2H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5, 139.7, 135.0, 134.3, 130.2, 129.5, 129.1, 128.9, 127.2, 45.7 ppm. The spectral data were in accordance with the literature.[6]

1,3-Diphenylpropan-2-one (3i):



2-Phenylacetyl chloride **2i** (26 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3i** as a colorless liquid in 70% (29.3 mg, 0.139 mmol) isolated yield after column chromatography (pentane: Et_2O = 97:3; R_f = 0.4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 6H), 7.20-7.18 (m, 4H), 3.76 (s, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 205.8, 134.1, 129.6, 128.8, 127.2, 49.2 ppm. The spectral data were in accordance with the literature.[7]

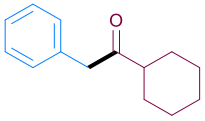
1,4-Diphenylbutan-2-one (3j):



Hydrocinnamoyl chloride **2j** (30 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3j** as a colorless liquid in 68% (30.7 mg, 0.137 mmol) isolated yield after column chromatography (pentane: Et_2O = 96:4; R_f = 0.4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 5H), 7.21-7.13 (m, 5H), 3.67 (s, 2H), 2.90-

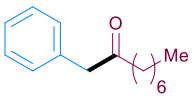
2.85 (m, 2H), 2.80-2.76 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.5, 141.0, 134.2, 129.5, 128.9, 128.6, 128.4, 127.1, 126.2, 50.5, 43.6, 29.9 ppm. The spectral data were in accordance with the literature.[3]

1-Cyclohexyl-2-phenylethan-1-one (3k):



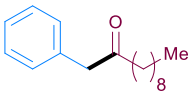
Cyclohexanecarbonyl chloride **2k** (27 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3k** as a colorless liquid in 59% (23.9 mg, 0.118 mmol) isolated yield after column chromatography (pentane: Et_2O = 97:3; R_f = 0.43). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26-7.09 (m, 5H), 3.64 (s, 2H), 2.37 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.77-1.53 (m, 5H), 1.35-1.07 (m, 5H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 211.3, 134.6, 129.6, 128.7, 126.9, 50.2, 48.0, 28.7, 25.9, 25.7 ppm. The spectral data were in accordance with the literature.[8]

1-Phenylnonan-2-one (3l):



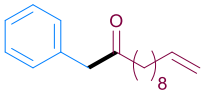
Octanoyl chloride **2l** (34 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3l** as a colorless liquid in 72% (31.4 mg, 0.144 mmol) isolated yield after column chromatography (pentane: Et_2O = 98:2; R_f = 0.47). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.27-7.24 (m, 1H), 7.21-7.19 (m, 2H), 3.67 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.54 (p, *J* = 7.1 Hz, 2H), 1.31 – 1.16 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.7, 134.5, 129.5, 128.8, 127.1, 50.3, 42.1, 31.8, 29.2, 29.1, 23.9, 22.7, 14.2 ppm. The spectral data were in accordance with the literature. [7]

1-Phenylundecan-2-one (3m):



Decanoyl chloride **2m** (42 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3m** as a colorless liquid in 57% (28.0 mg, 0.114 mmol) isolated yield after column chromatography (pentane: Et_2O = 98:2; R_f = 0.47). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.27-7.23 (m, 1H), 7.21-7.19 (m, 2H), 3.67 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.59-1.50 (m, 2H), 1.30 – 1.22 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.8, 134.5, 129.5, 128.8, 127.1, 50.3, 42.1, 32.0, 29.5, 29.5, 29.4, 29.2, 23.9, 22.8, 14.2 ppm. The spectral data were in accordance with the literature.[9]

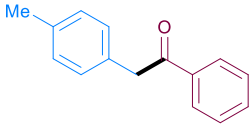
1-Phenyldodec-11-en-2-one (3n):



Undec-10-enoyl chloride **2n** (43 µL, 0.2 mmol, 1.0 equiv) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3n** as a colorless liquid in 47% (24.3 mg, 0.094 mmol) isolated yield after column chromatography (pentane: Et_2O = 96:4; R_f = 0.5). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.22 (m, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.96 – 4.94 (m, 1H), 3.70 (s, 2H), 2.46 (t,

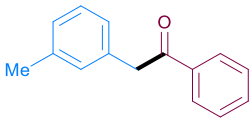
J = 7.4 Hz, 2H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.57 (p, *J* = 7.6 Hz, 2H), 1.38 (p, *J* = 7.2 Hz, 2H), 1.30 – 1.23 (m, 8H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.6, 139.2, 134.4, 129.4, 128.7, 127.0, 114.1, 50.2, 42.0, 33.8, 29.3, 29.3, 29.1, 29.0, 28.9, 23.7 ppm; IR (ATR): ṽ = 3418, 3070, 3030, 2925, 2854, 2662, 2328, 2094, 1712, 1639, 1495, 1454, 1411, 1362, 1184, 993, 909, 700 cm^{-1}; HRMS (ESI): calc. for $C_{18}H_{26}ONa$: 281.18759; found: 281.18748.

1-phenyl-2-(*p*-tolyl)ethan-1-one (3o):



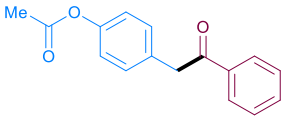
Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with *p*-xylene (6 mL) to give **3o** as a white solid in 79% (33.4 mg, 0.159 mmol) isolated yield after column chromatography (hexane: EtOAc = 96:4; R_f = 0.5). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.16 (q, *J* = 7.9 Hz, 4H), 4.25 (s, 2H), 2.33 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8, 136.7, 136.5, 133.1, 131.5, 129.4, 129.3, 128.6, 45.2, 21.1 ppm. The spectral data were in accordance with the literature.[10]

1-Phenyl-2-(*m*-tolyl)ethan-1-one (3p):



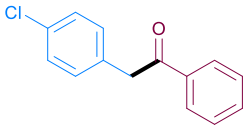
Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with *m*-xylene (6 mL) to give **3p** as a yellow oil in 73% (30.6 mg, 0.146 mmol) isolated yield after column chromatography (hexane: EtOAc = 96:4; R_f = 0.55). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.67 – 7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.08 (dd, *J* = 7.4, 3.6 Hz, 2H), 4.26 (s, 2H), 2.34 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8, 138.3, 136.7, 134.5, 133.1, 130.2, 128.7, 128.6, 127.7, 126.5, 45.5, 21.4 ppm. The spectral data were in accordance with the literature.[4]

4-(2-oxo-2-phenylethyl)phenyl acetate (3r):



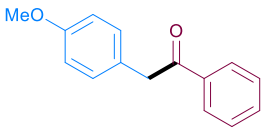
Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with *p*-tolyl acetate (6 mL) to give **3r** as a white solid in 39% (20.2 mg, 0.079 mmol) isolated yield after column chromatography [hexane: EtOAc = 95:5 (R_f = 0.25)→ 90:10 (R_f = 0.46)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 4.28 (s, 2H), 2.28 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 169.6, 149.8, 136.7, 133.4, 132.2, 130.6, 128.8, 128.7, 121.9, 44.8, 21.3 ppm. The spectral data were in accordance with the literature.[11]

2-(4-Chlorophenyl)-1-phenylethan-1-one (3s):



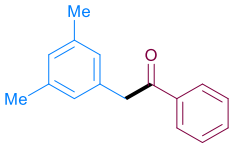
Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with 4-chlorotoluene (6 mL) to give **3s** as a white solid in 85% (39.4 mg, 0.171 mmol) isolated yield after column chromatography (hexane: Et_2O = 96:4; R_f = 0.44). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.59 – 7.56 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.21 – 7.19 (m, 2H), 4.26 (s, 2H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 197.1, 136.4, 133.4, 133.0, 132.9, 130.9, 128.8, 128.7, 128.5, 44.7 ppm. The spectral data were in accordance with the literature.[1]

2-(4-Methoxyphenyl)-1-phenylethan-1-one (3t):



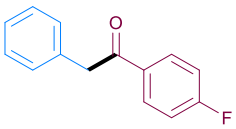
Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** in 1-methoxy-4-methylbenzene (6 mL) to give **3t** as a white solid in 56% (25.5 mg, 0.113 mmol) isolated yield after column chromatography (hexane: EtOAc = 95:5; R_f = 0.3). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.20 – 7.18 (m, 2H), 6.88 – 6.86 (m, 2H), 4.23 (s, 2H), 3.79 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.9, 158.6, 136.7, 133.1, 130.5, 128.6, 128.6, 126.5, 114.2, 55.3, 44.6 ppm. The spectral data were in accordance with the literature.[1]

2-(3,5-dimethylphenyl)-1-phenylethan-1-one (3u):



Benzoylchloride **2a** (23 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with mesitylene (6 mL) to give **3u** as a colorless oil in 38% (17.2 mg, 0.077 mmol) isolated yield after column chromatography (hexane: EtOAc = 96:4; R_f = 0.5). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.89 (s, 3H), 4.21 (s, 2H), 2.29 (s, 6H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.9, 138.2, 136.7, 134.3, 133.1, 128.7, 128.6, 127.2, 45.4, 21.3 ppm. The spectral data were in accordance with the literature.[**Fehler! Textmarke nicht definiert.**]

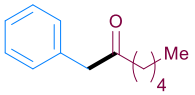
1-(4-fluorophenyl)-2-phenylethan-1-one (3v):



4-Fluorobenzoic anhydride (52.4 mg, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3v** as a white solid in 44% (19.0 mg, 0.089 mmol) isolated yield after column chromatography (hexane: Et_2O = 96.5:3.5; R_f = 0.38). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.26 (m, 3H), 7.14 – 7.11 (m, 2H), 4.26 (s, 2H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 196.1, 165.8 (d, *J* = 254.7 Hz), 134.3, 133.0 (d, *J* = 3.6 Hz), 131.3 (d, *J* = 9.7 Hz), 129.4, 128.7, 127.0, 115.8 (d, *J* = 22.2 Hz),

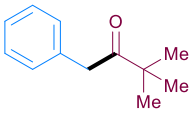
45.5 ppm; **^{19}F NMR** (564 MHz, $CDCl_3$) δ = -105.02 (ddd, *J* = 13.3, 8.1, 5.1 Hz) ppm. The spectral data were in accordance with the literature.[12]

1-Phenylheptan-2-one (3w):



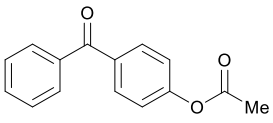
Caproic anhydride (46 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** in presence of **20 mol% PS-5** with toluene (6 mL) to give **3w** as a colorless liquid in 61% (23.2 mg, 0.122 mmol) isolated yield after column chromatography (hexane: Et_2O = 97:3; R_f = 0.48). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.22 (m, 2H), 3.70 (s, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.58 (p, *J* = 7.4 Hz, 2H), 1.33 – 1.21 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 208.6, 134.4, 129.4, 128.7, 127.0, 50.2, 42.0, 31.3, 23.4, 22.4, 13.9 ppm. The spectral data were in accordance with the literature.[13]

3,3-Dimethyl-1-phenylbutan-2-one (3x):



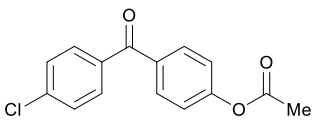
Pivalic anhydride (41 µL, 0.2 mmol, 1.0 equiv.) was reacted for 48 hours according to **GP1** with toluene (6 mL) to give **3x** as a colorless liquid in 44% (15.5 mg, 0.088 mmol) isolated yield after column chromatography (hexane: Et_2O = 97:3; R_f = 0.5). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 = (t, *J* = 7.5 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.21 – 7.20 (m, 2H), 3.83 (s, 2H), 1.23 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 212.8, 135.0, 129.6, 128.4, 126.6, 44.7, 43.3, 26.4 ppm. The spectral data were in accordance with the literature.[14]

Preparation of 4-benzoylphenyl acetate (PS-5)[15]:



According to a literature procedure, 4-hydroxybenzophenone (238.0 mg, 1.2 mmol), acetyl chloride (128 µL, 1.8 mmol) and triethylamine (336 µL, 2.4 mmol) were stirred in dichloromethane (20 mL) at 60 °C for 15 hours. After cooling to ambient temperature, the mixture was washed with water and the aqueous phase extracted with DCM (2 x 10 mL). The combined organic phase was filtered over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexane: EtOAc = 5:1; R_f = 0.52) to give **PS-5** as a white solid in 79% (227 mg, 0.944 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.79 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 195.7, 169.1, 154.0, 137.6, 135.2, 132.6, 131.8, 130.1, 128.5, 121.7, 21.3 ppm. The spectral data were in accordance with the literature.[15]

Preparation of 4-Acetoxy. 4-chlorobenzophenone (PS-4)[15]:

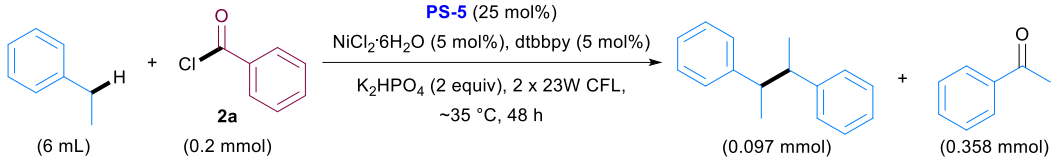


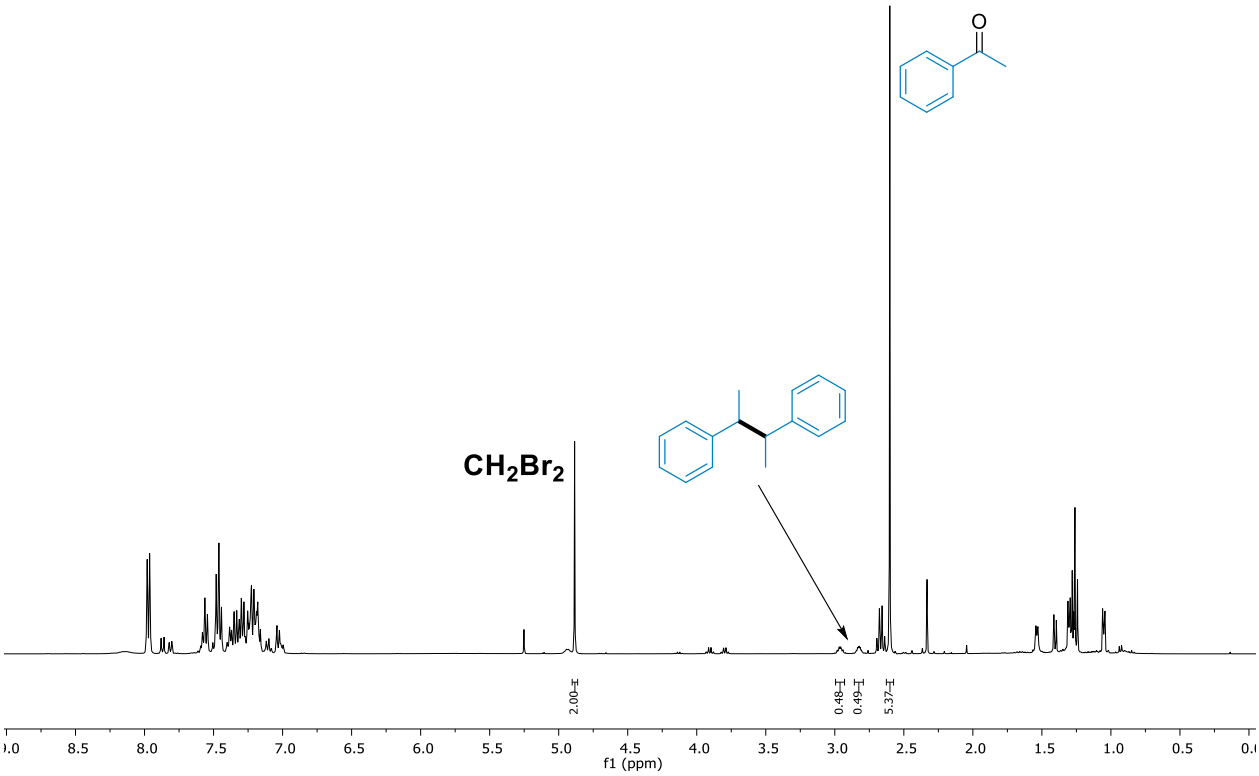
According to the literature procedure 4-hydroxy.4-chlorobenzophenone (280.0 mg, 1.2 mmol), acetyl chloride (128 µL, 1.8 mmol) and triethylamine

(336 µL, 2.4 mmol) were stirred in dichloromethane (20 mL) at 60 °C for 15 hours. After cooling to ambient temperature, the mixture was washed with water and the aqueous phase extracted with DCM (2 x 10 mL). The combined organic phase was filtered over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexane: EtOAc = 5:1; R_f = 0.55) to give **PS-4** as a white solid in 78% (256 mg, 0.932 mmol). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 -7.81 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.48-7.46 (m, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 2.35 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 194.4, 169.0, 154.2, 139.1, 135.9, 134.9, 131.7, 131.5, 128.9, 121.8, 21.3 ppm. The spectral data were in accordance with the literature.[16]

Reaction with Ethylbenzene:

Scheme S1:





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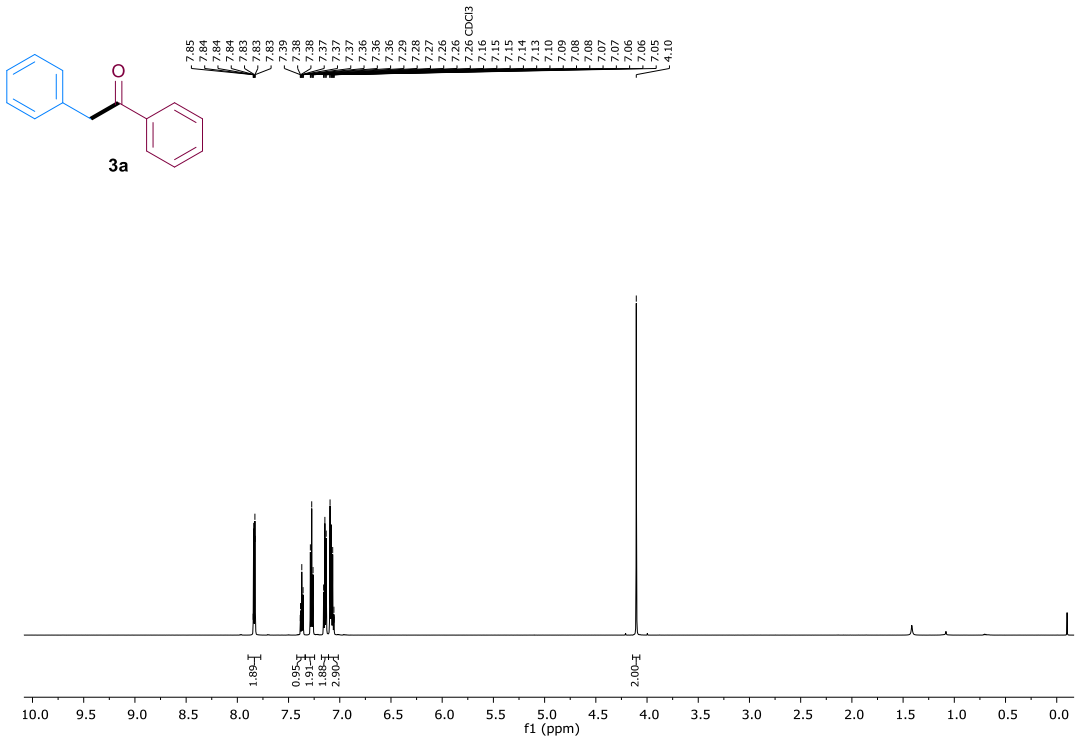
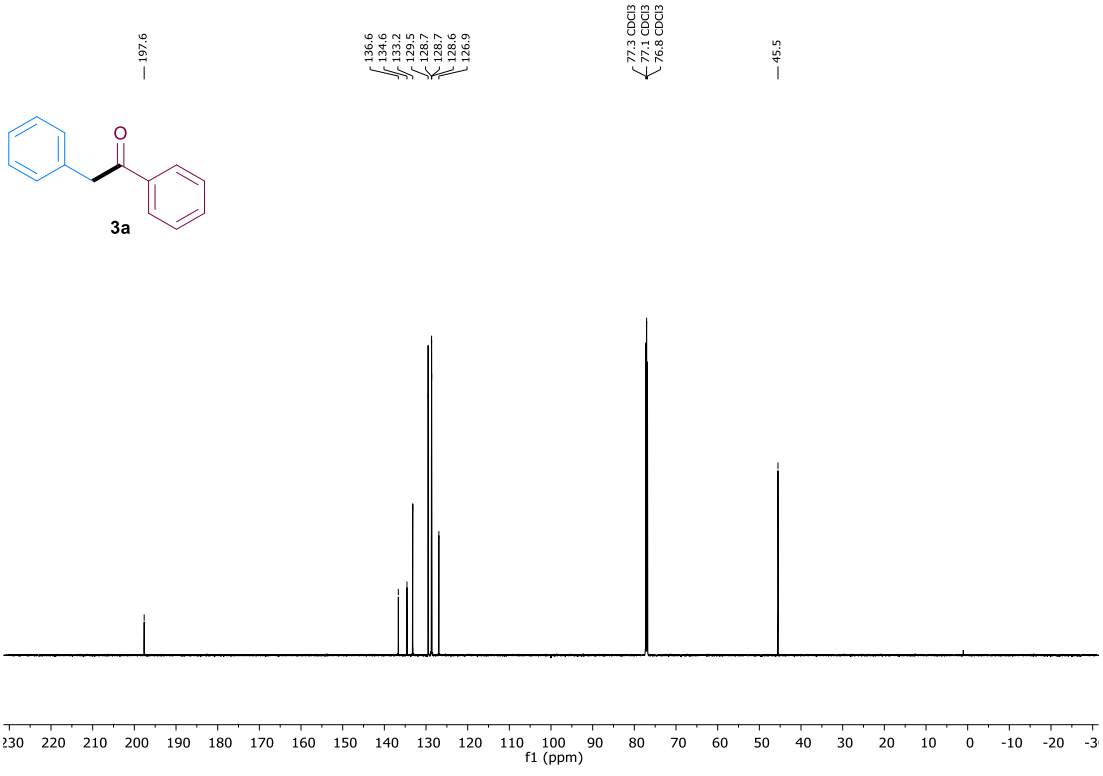
NMR spectra:

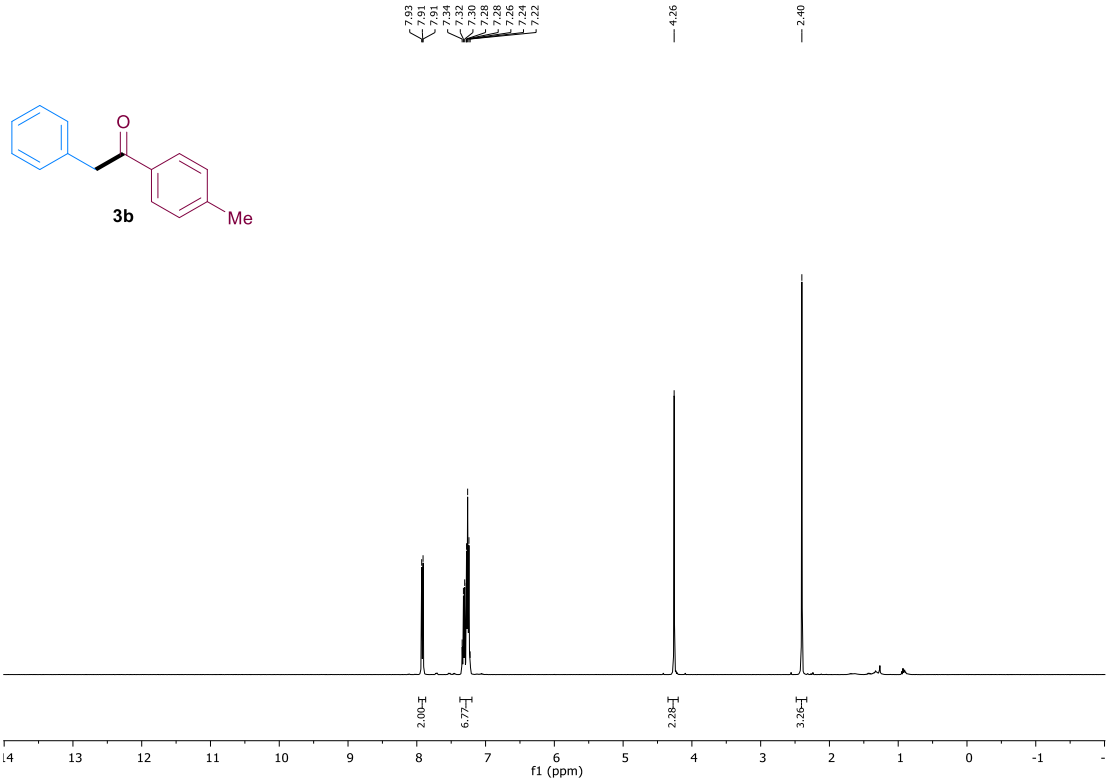
^{1}H-NMR (**3a**) [600 MHz, $CDCl_3$]



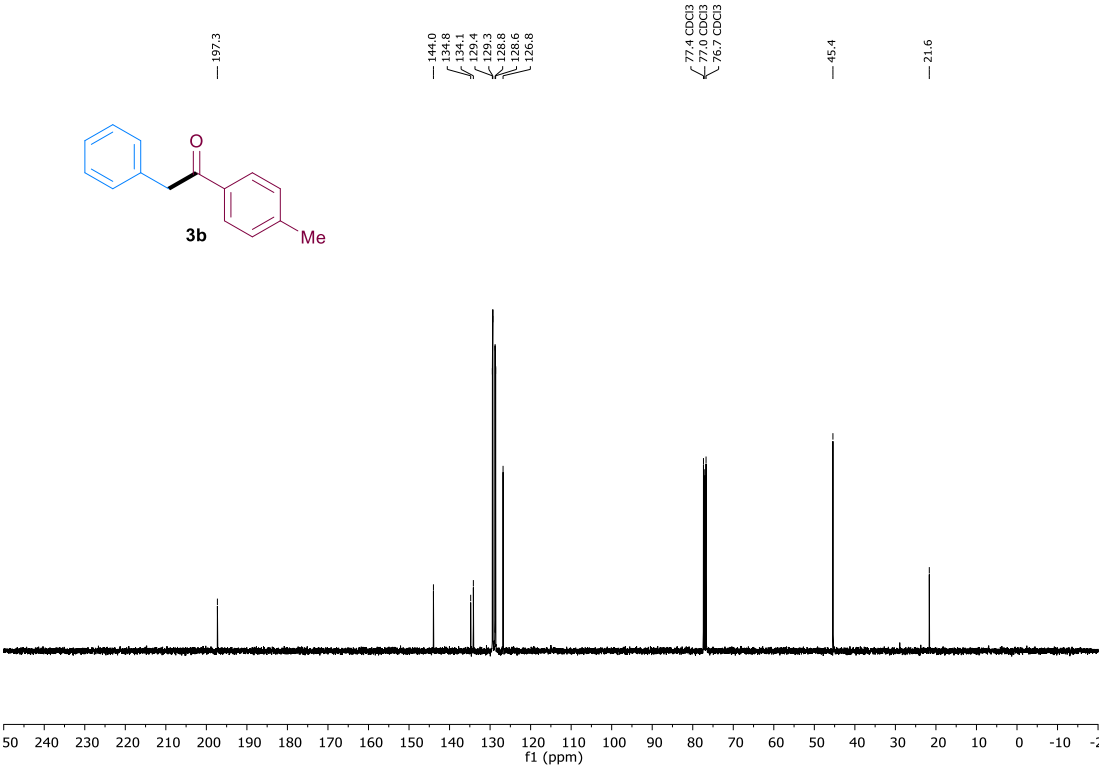
^{13}C-NMR (**3a**) [151 MHz, $CDCl_3$]



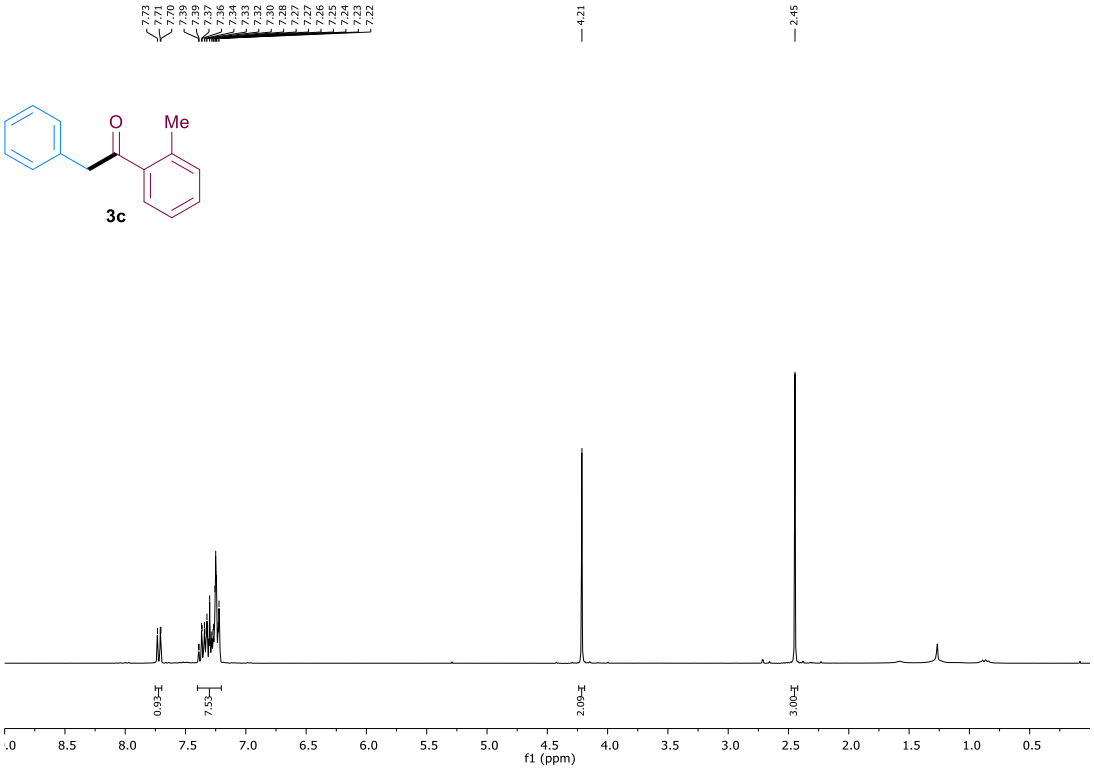
^{1}H-NMR (**3b**) [400 MHz, $CDCl_3$]



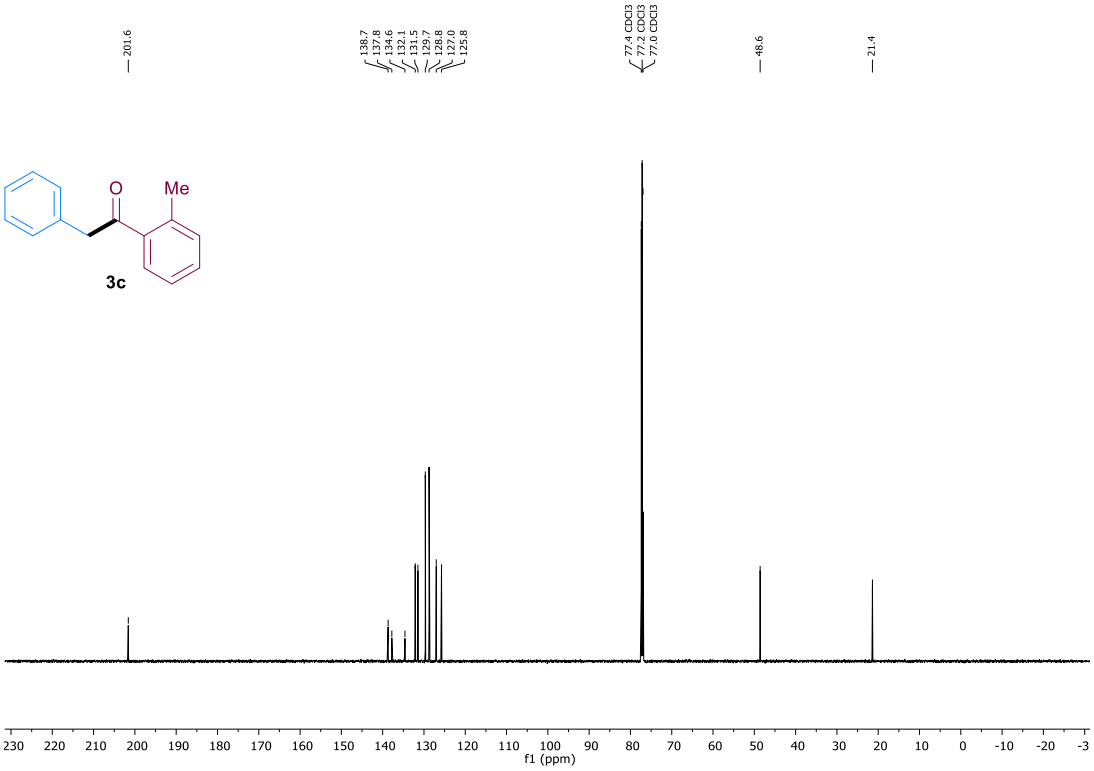
^{13}C-NMR (**3b**) [101 MHz, $CDCl_3$]



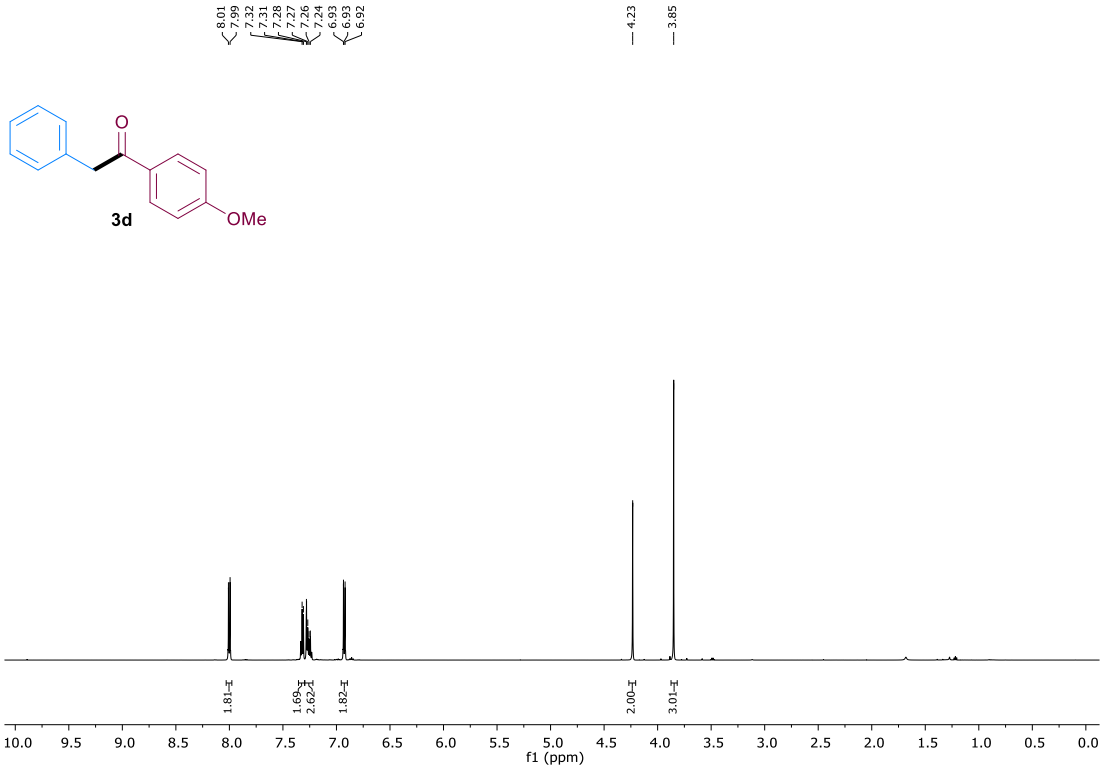
^{1}H-NMR (3c) [300 MHz, $CDCl_3$]



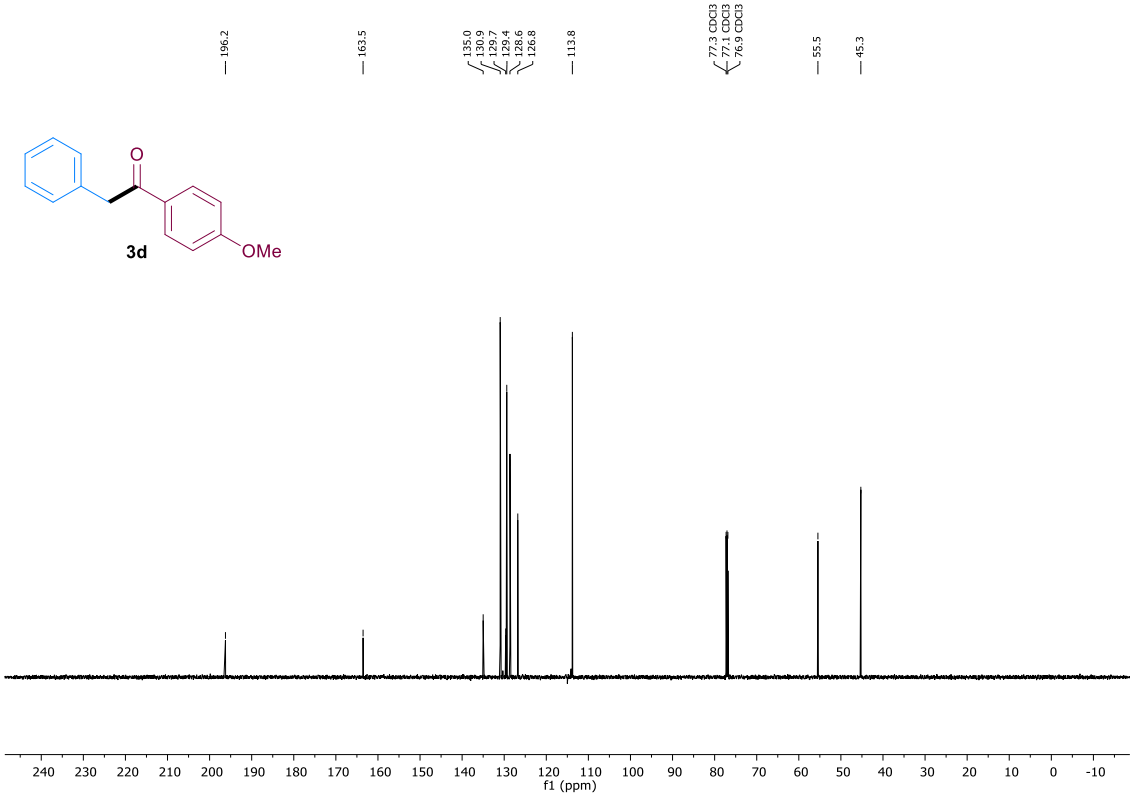
^{13}C-NMR (3c) [151 MHz, $CDCl_3$]



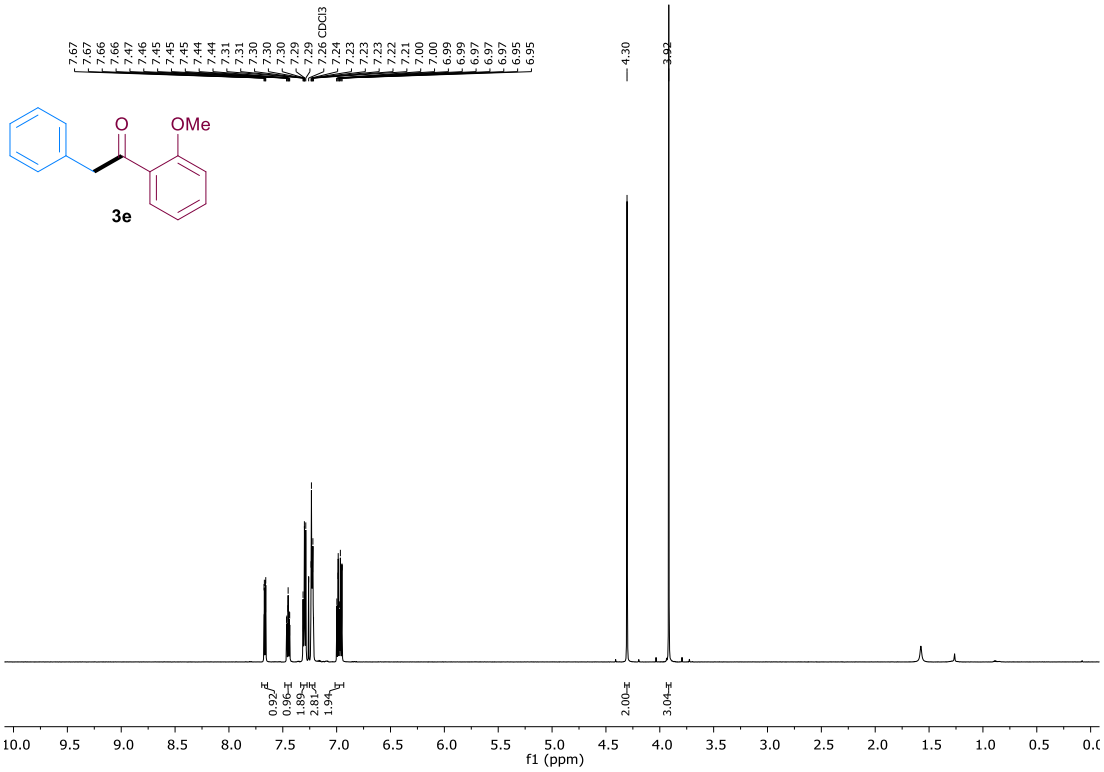
^{1}H-NMR (3d) [600 MHz, $CDCl_3$]



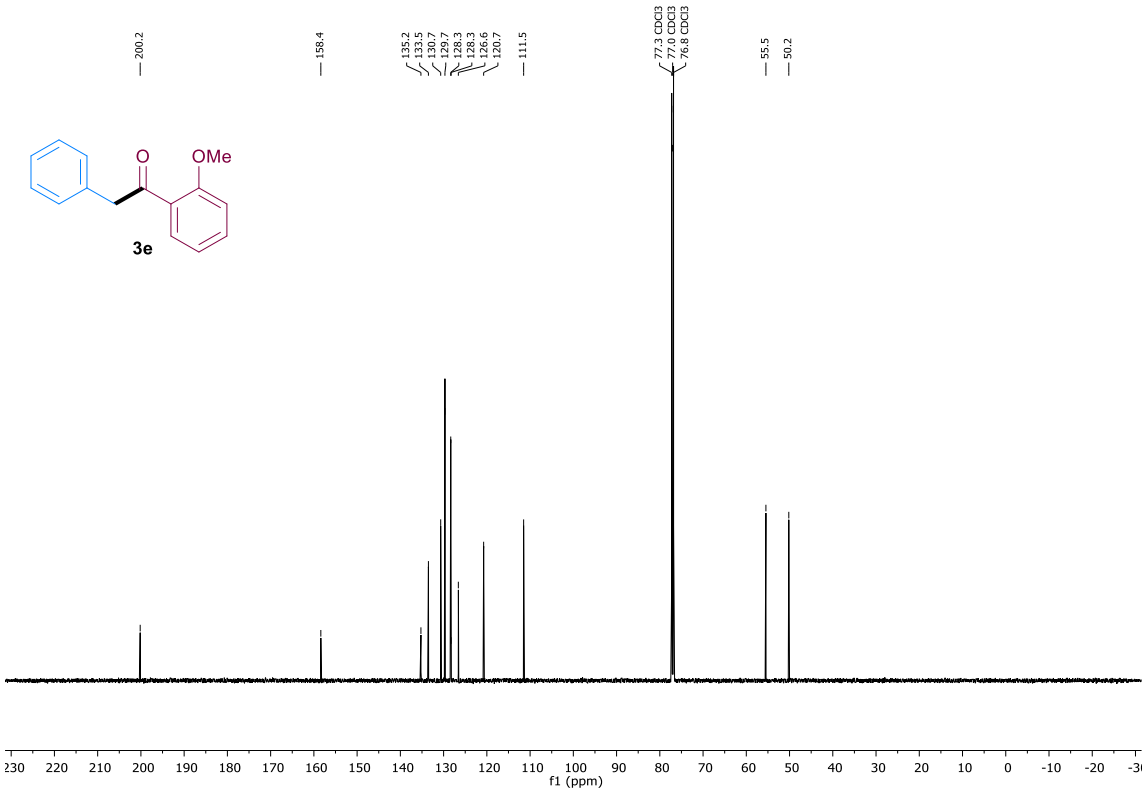
^{13}C-NMR (3d) [151 MHz, $CDCl_3$]



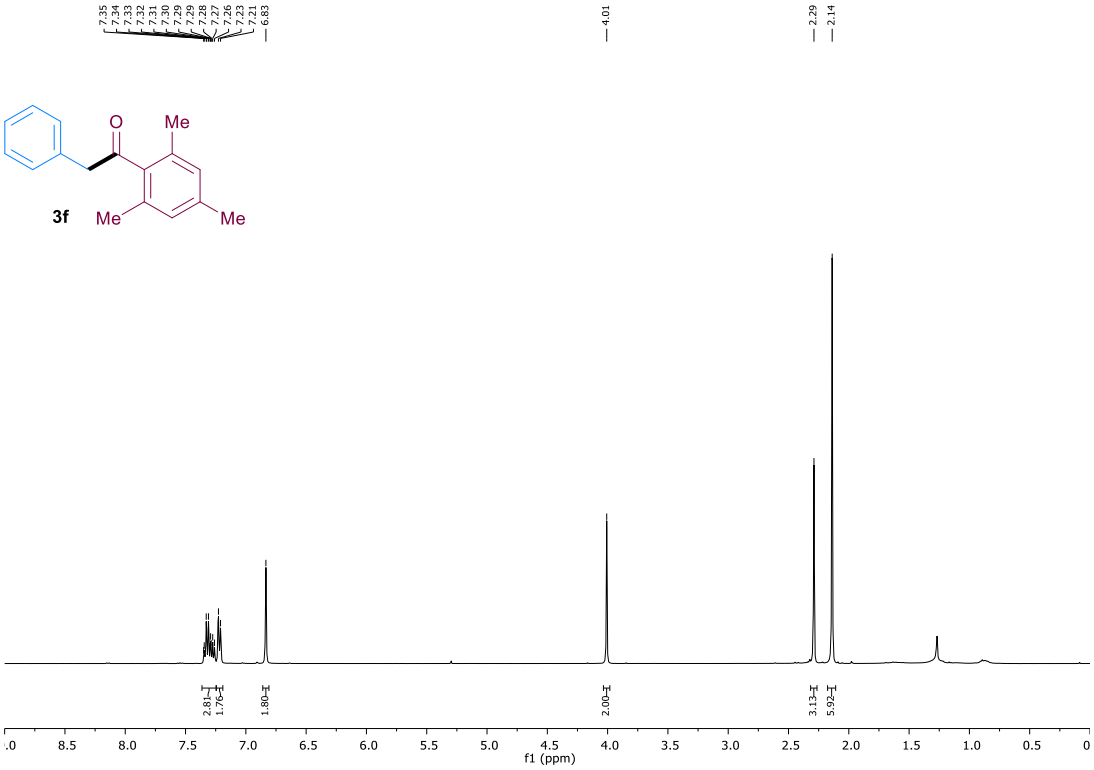
^{1}H-NMR (**3e**) [600 MHz, $CDCl_3$]



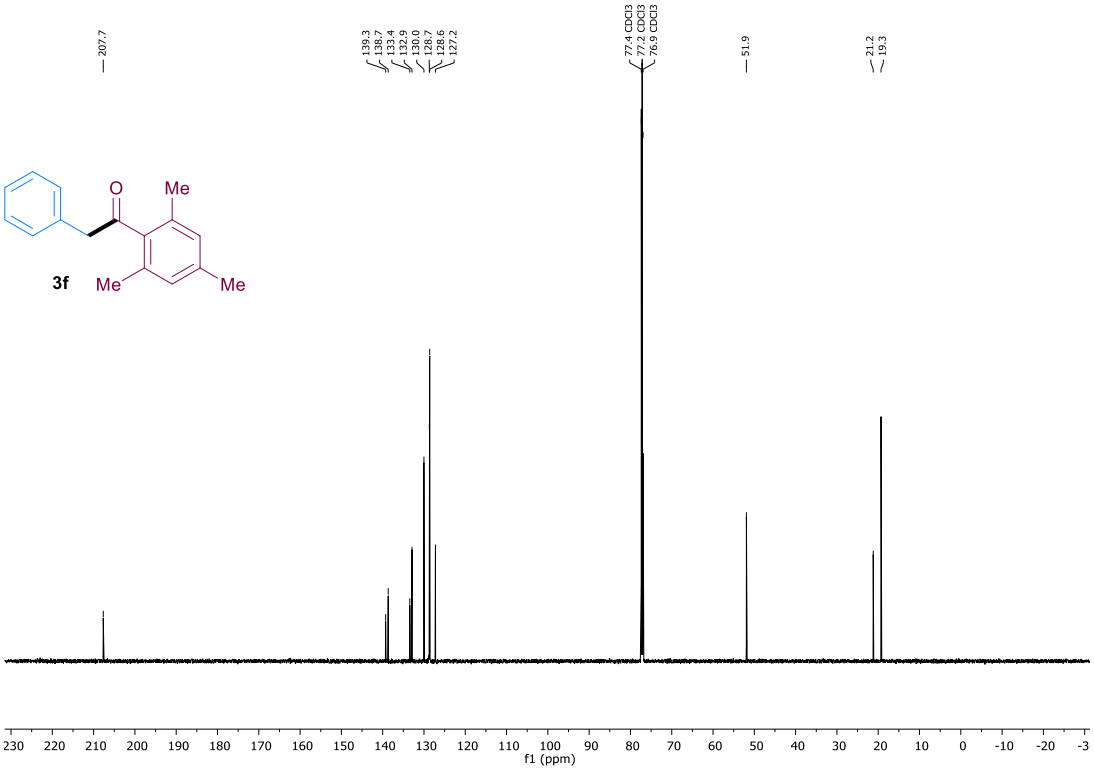
^{13}C-NMR (**3e**) [151 MHz, $CDCl_3$]



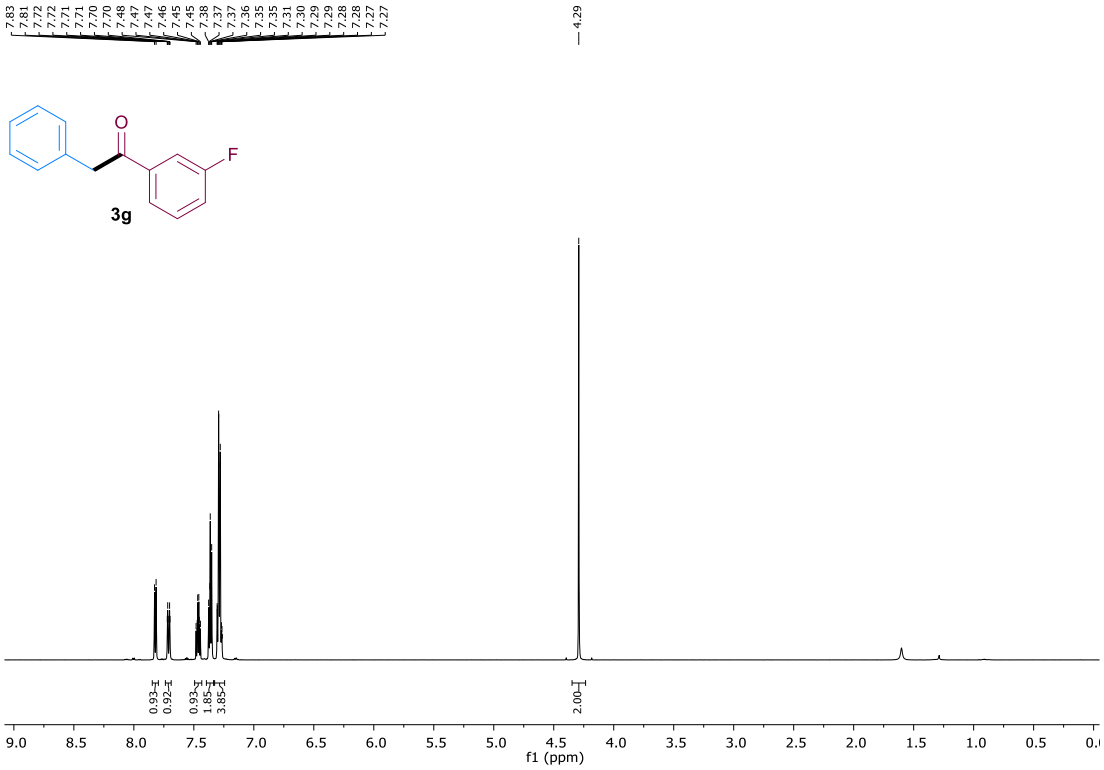
^{1}H-NMR (3f) [300 MHz, $CDCl_3$]



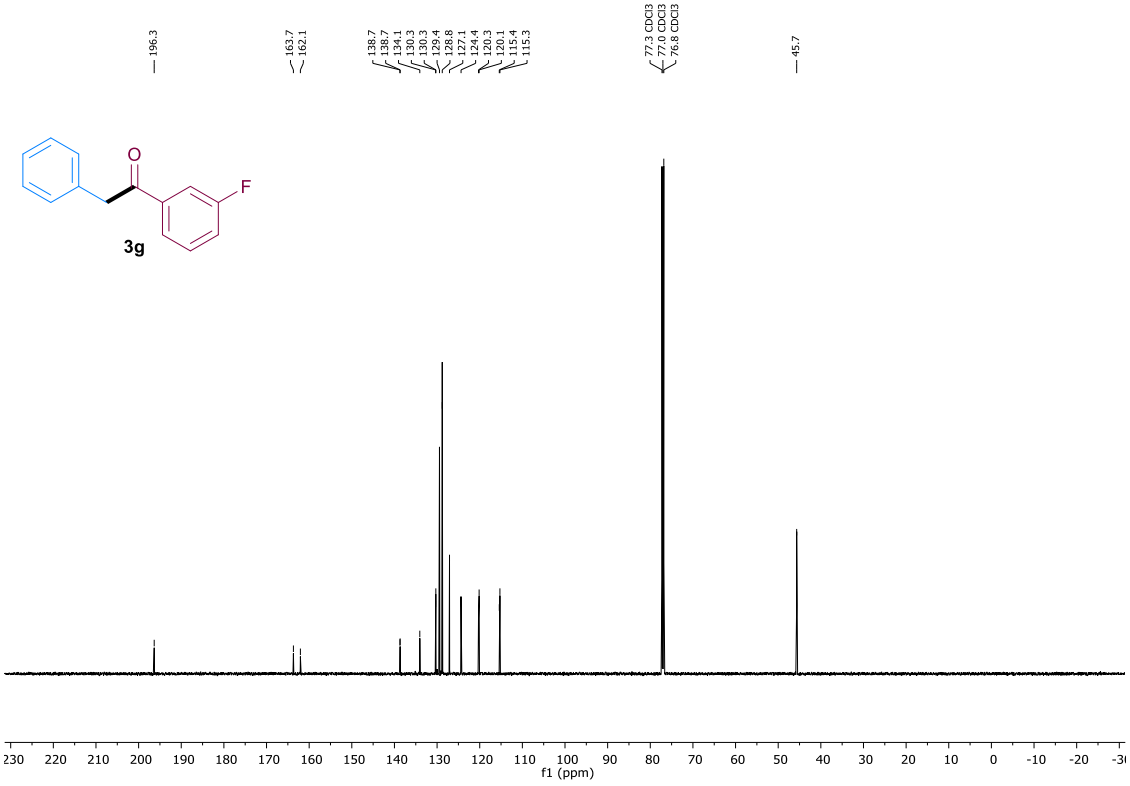
^{13}C-NMR (3f) [151 MHz, $CDCl_3$]



^{1}H-NMR (3g) [600 MHz, $CDCl_3$]

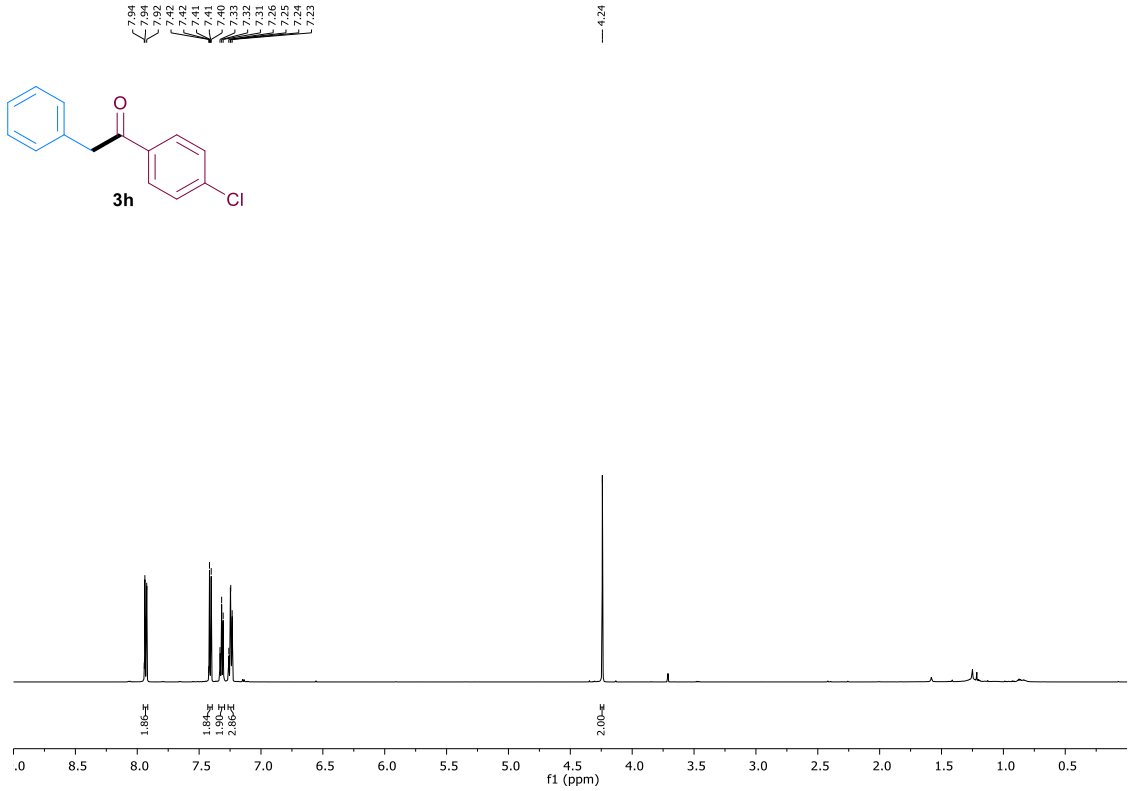


^{13}C-NMR (3g) [151 MHz, $CDCl_3$]

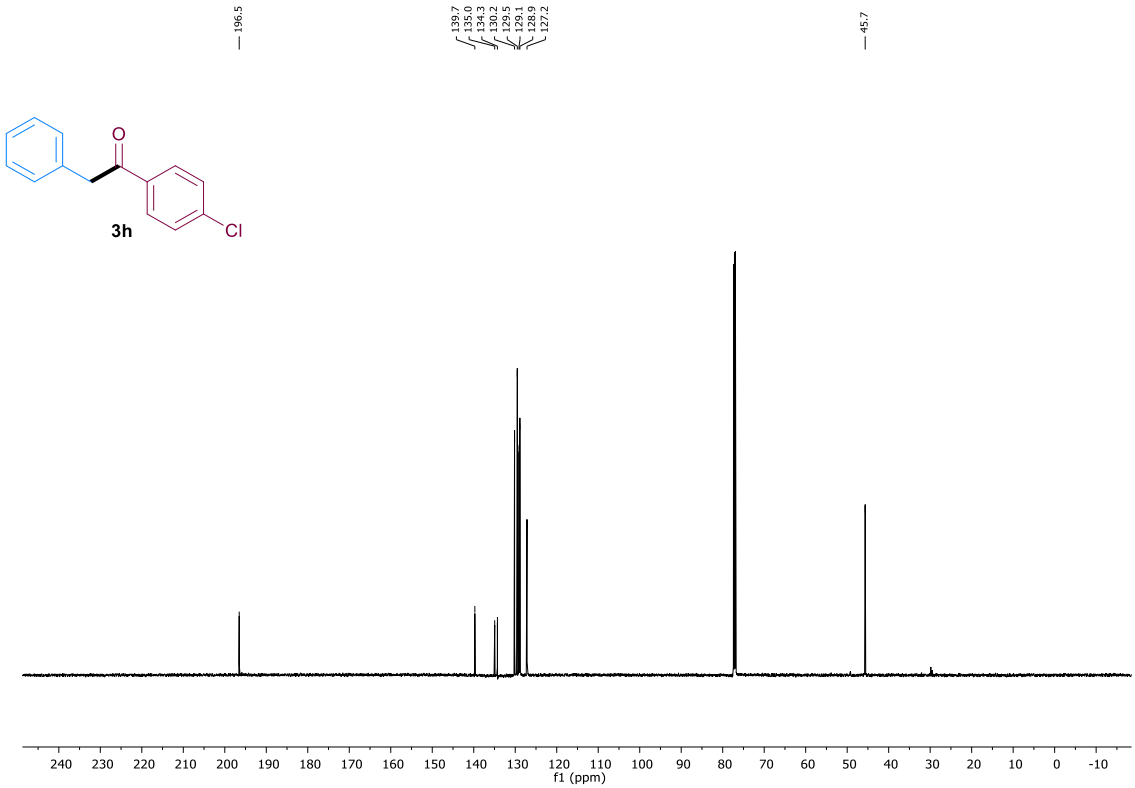


^{19}F-NMR (3g) [565 MHz, $CDCl_3$]

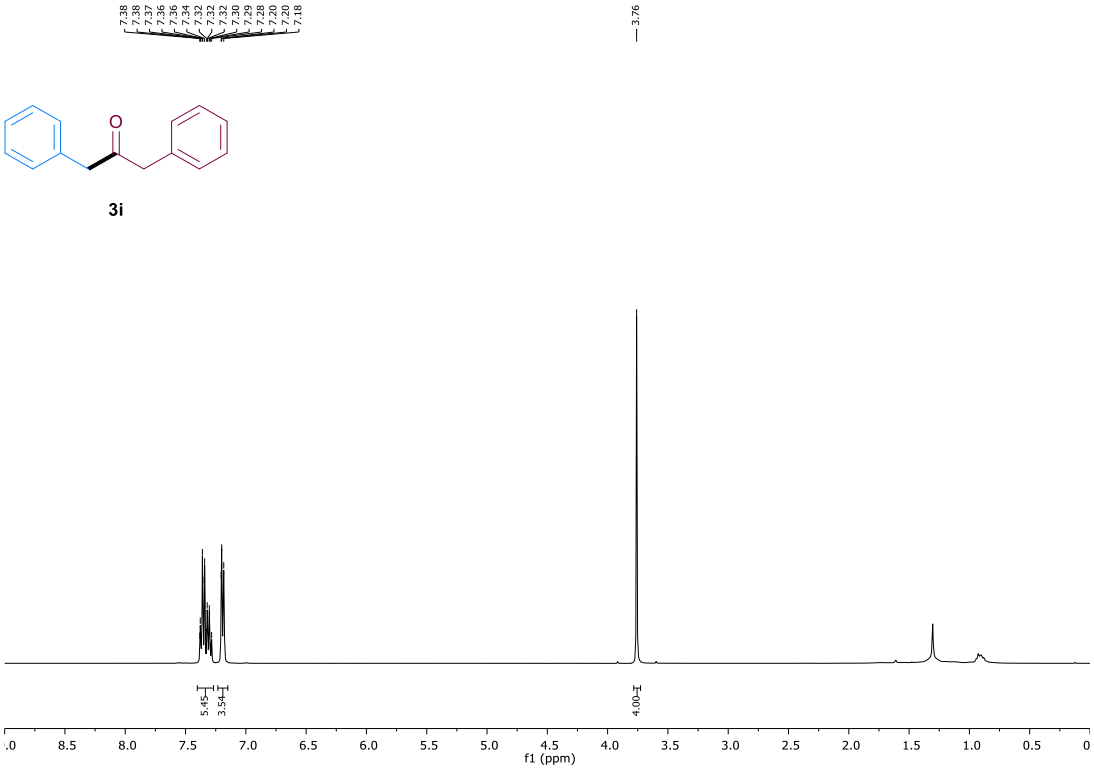
^{1}H-NMR (3h) [600 MHz, $CDCl_3$**]**



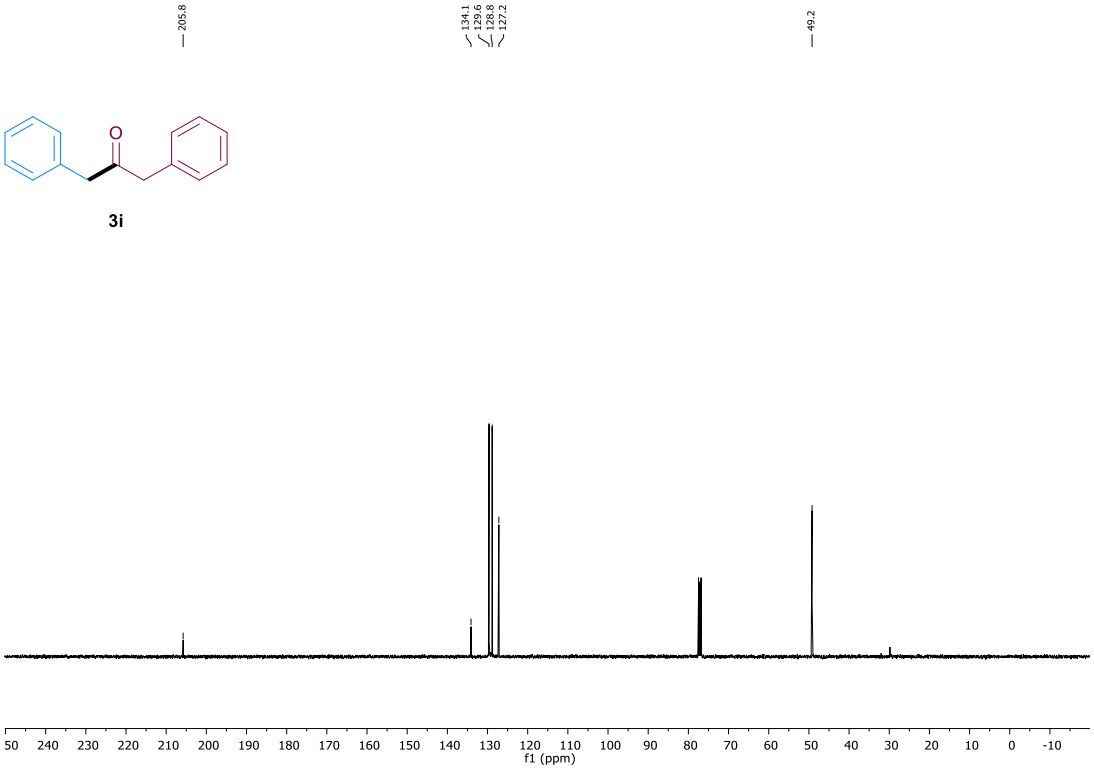
^{13}C-NMR (3h) [151 MHz, $CDCl_3$]



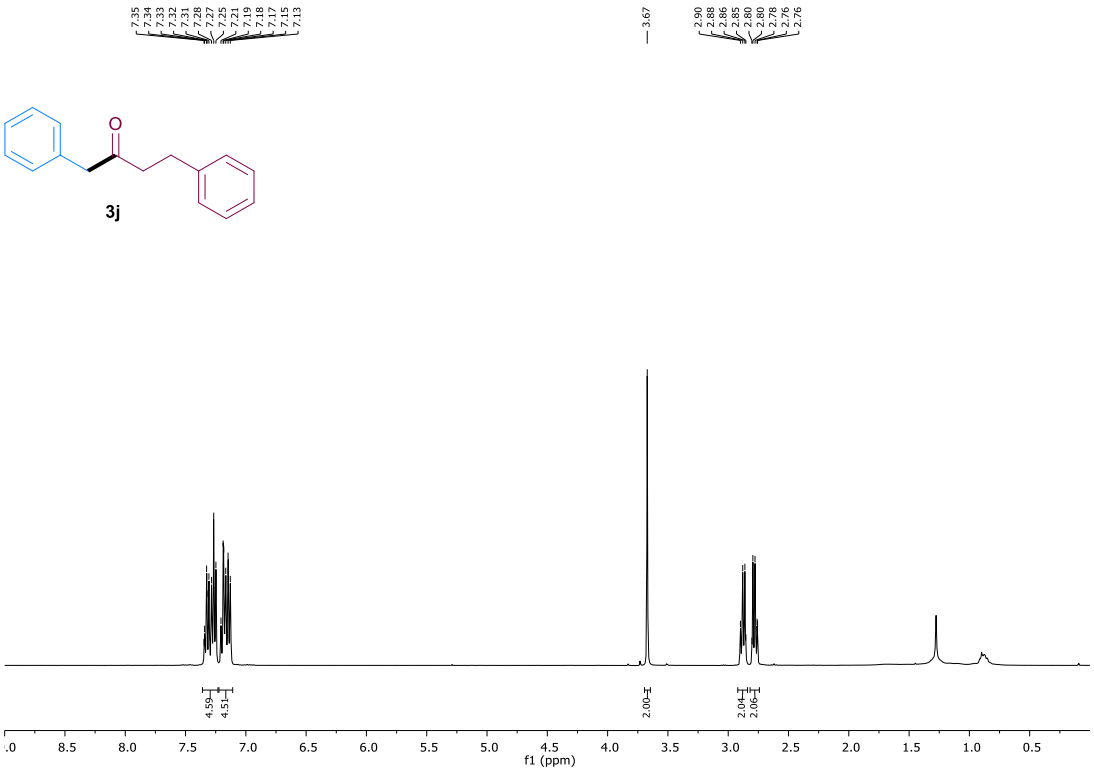
^{1}H-NMR (3i) [400 MHz, $CDCl_3$]



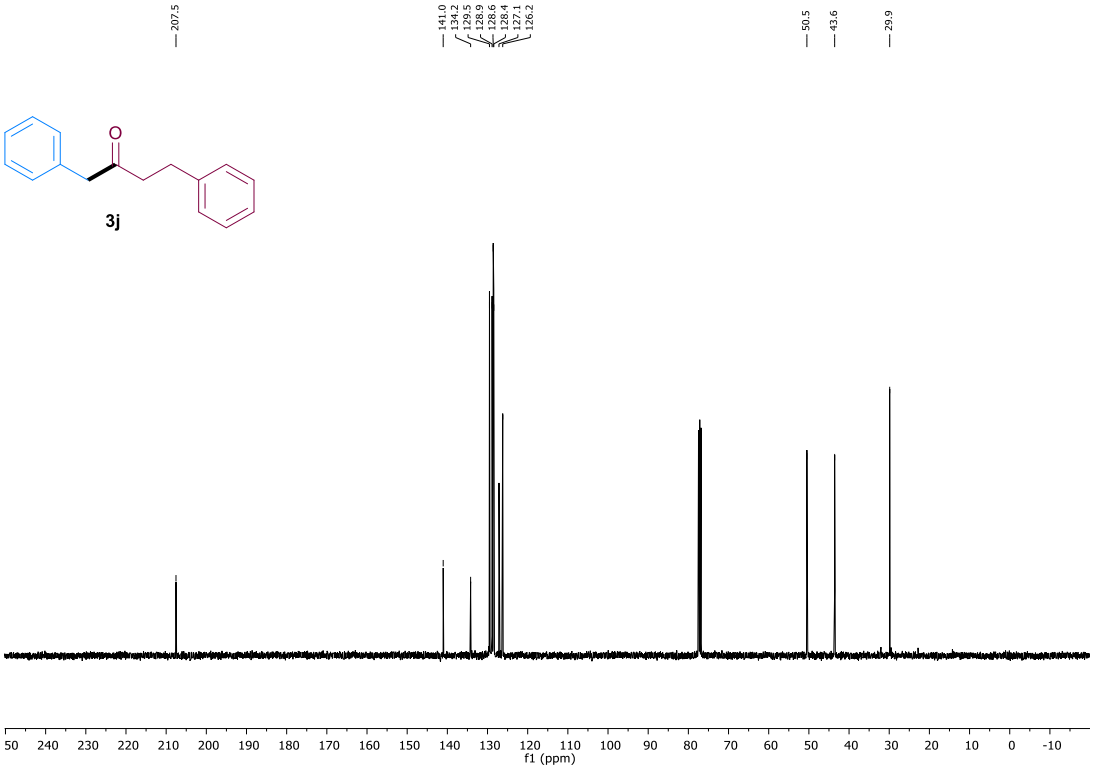
^{13}C-NMR (3i) [101 MHz, $CDCl_3$]



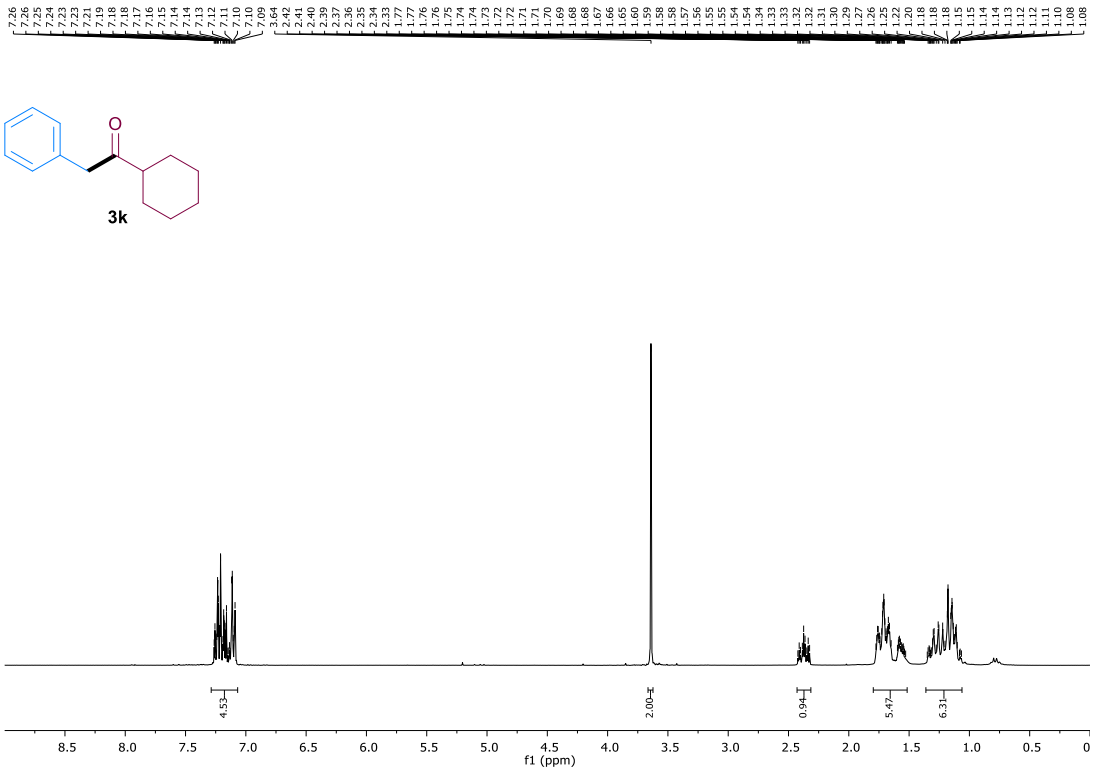
^{1}H-NMR (3j) [400 MHz, $CDCl_3$]



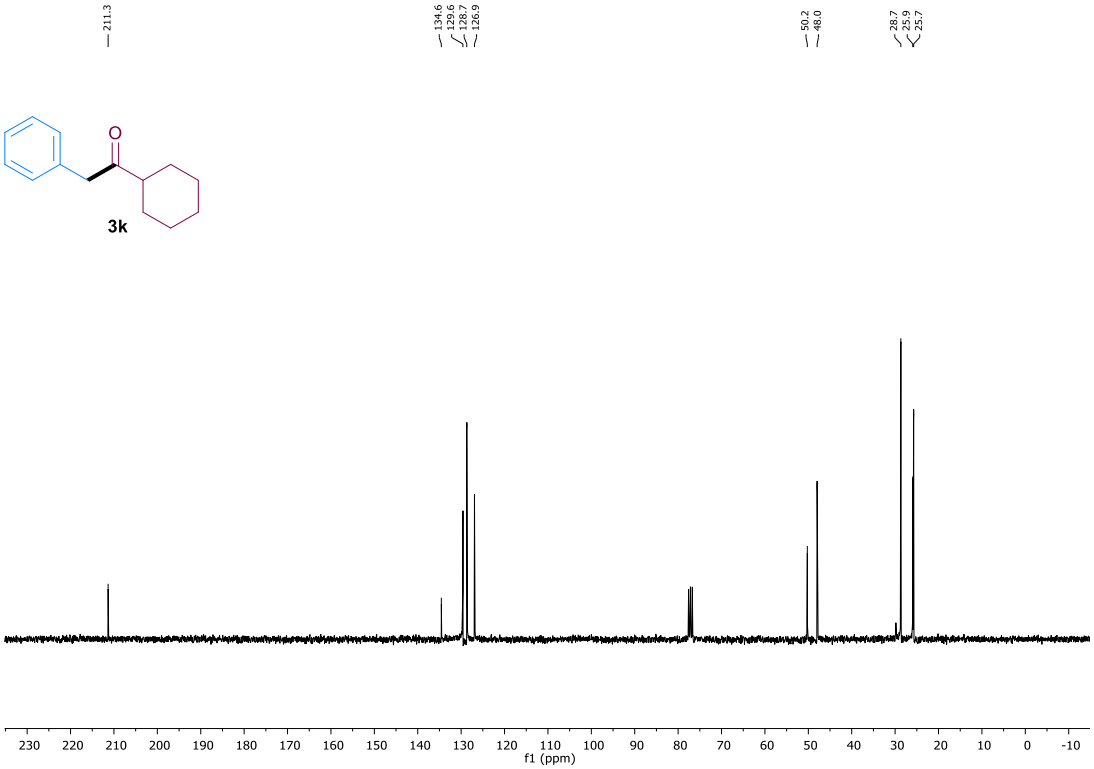
^{13}C-NMR (3j) [101 MHz, $CDCl_3$]



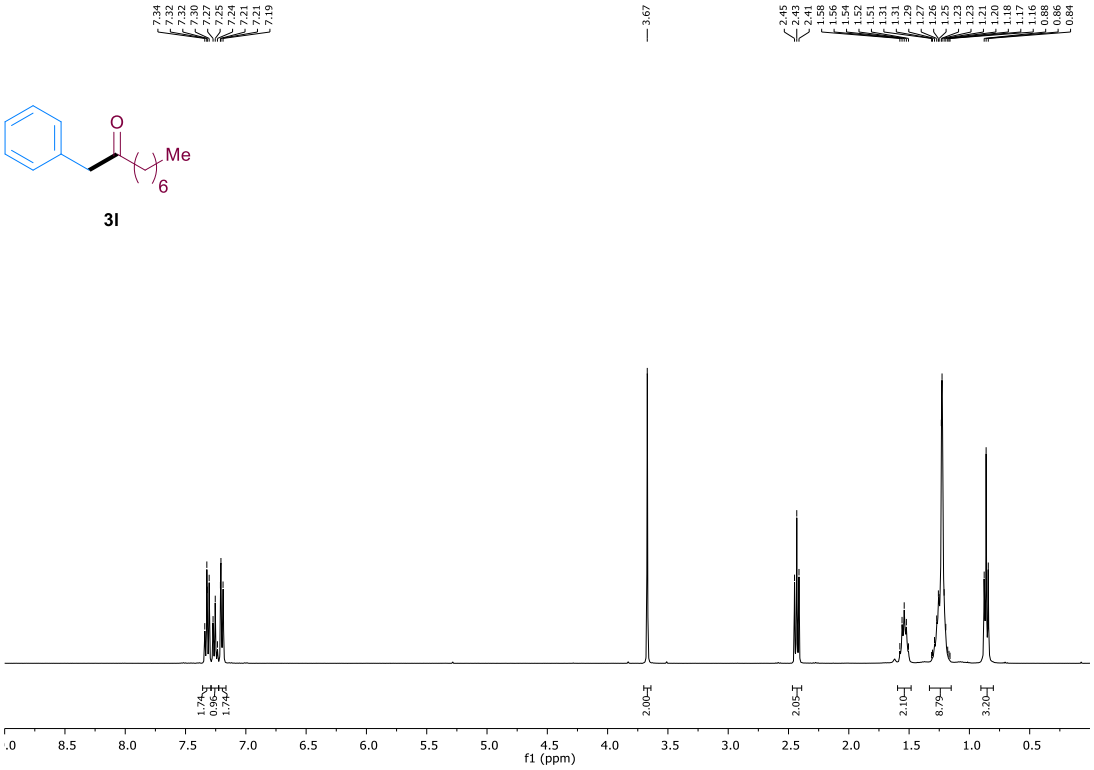
^{1}H-NMR (**3k**) [300 MHz, $CDCl_3$]



^{13}C-NMR (**3k**) [75 MHz, $CDCl_3$]

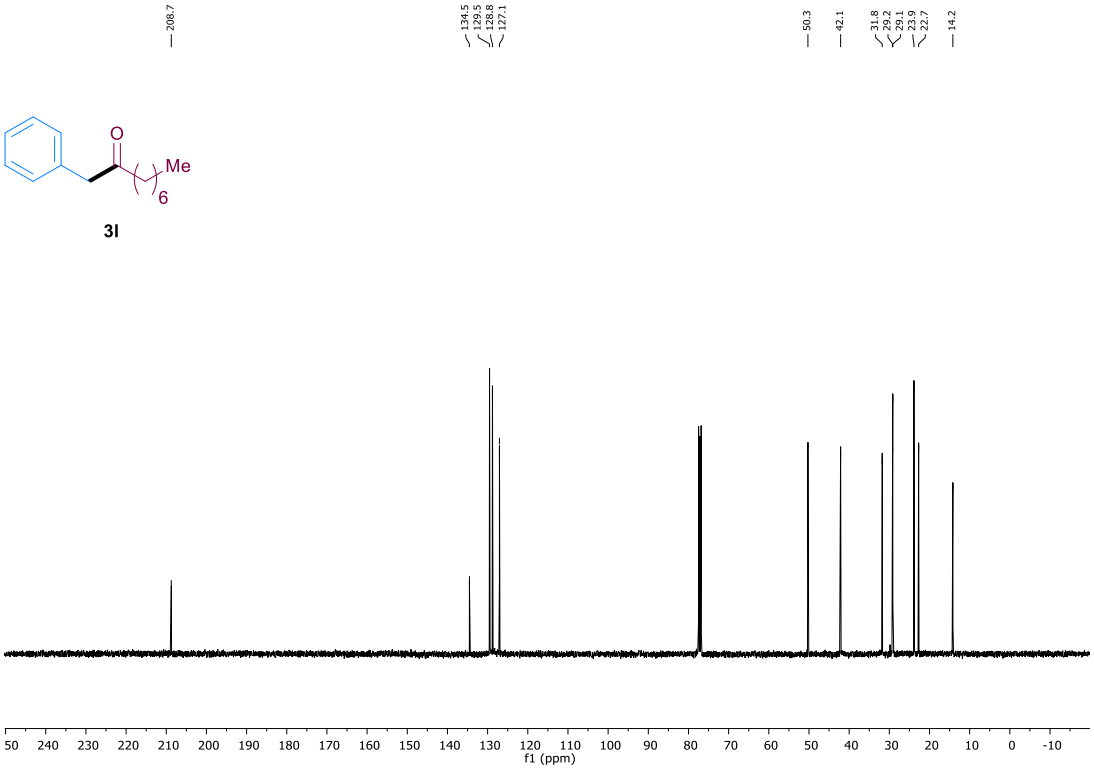


^{1}H-NMR (3l) [400 MHz, $CDCl_3$]



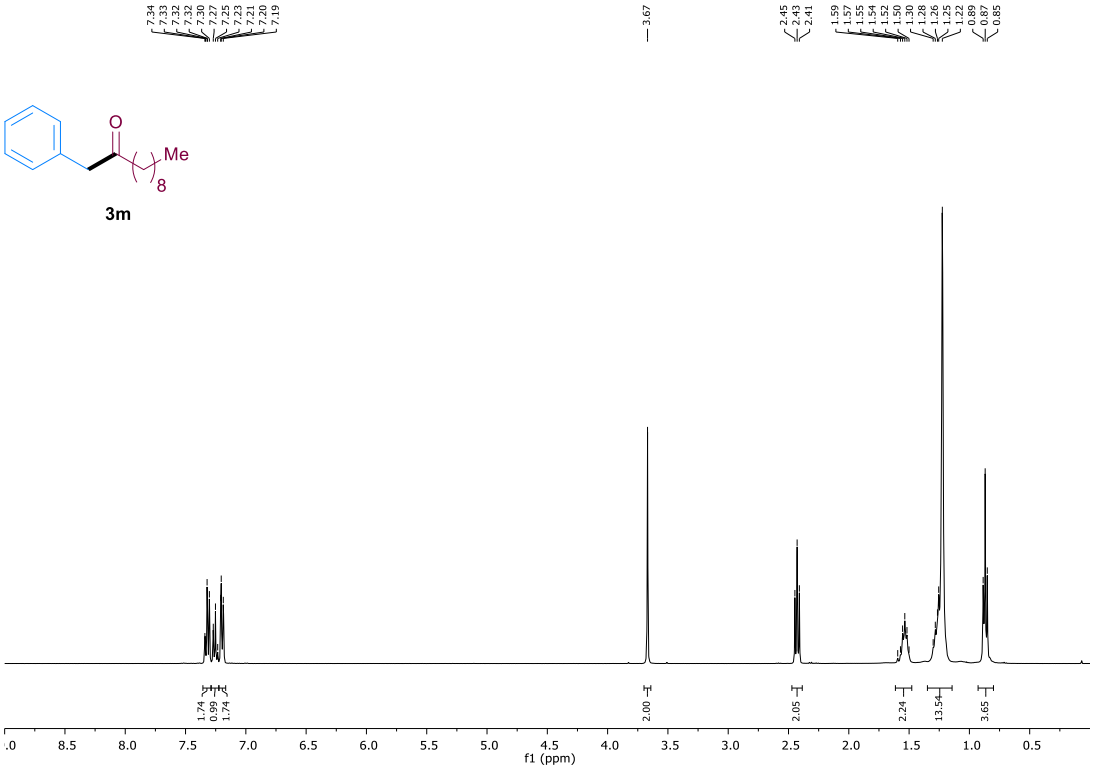
3l

^{13}C-NMR (3l) [101 MHz, $CDCl_3$]

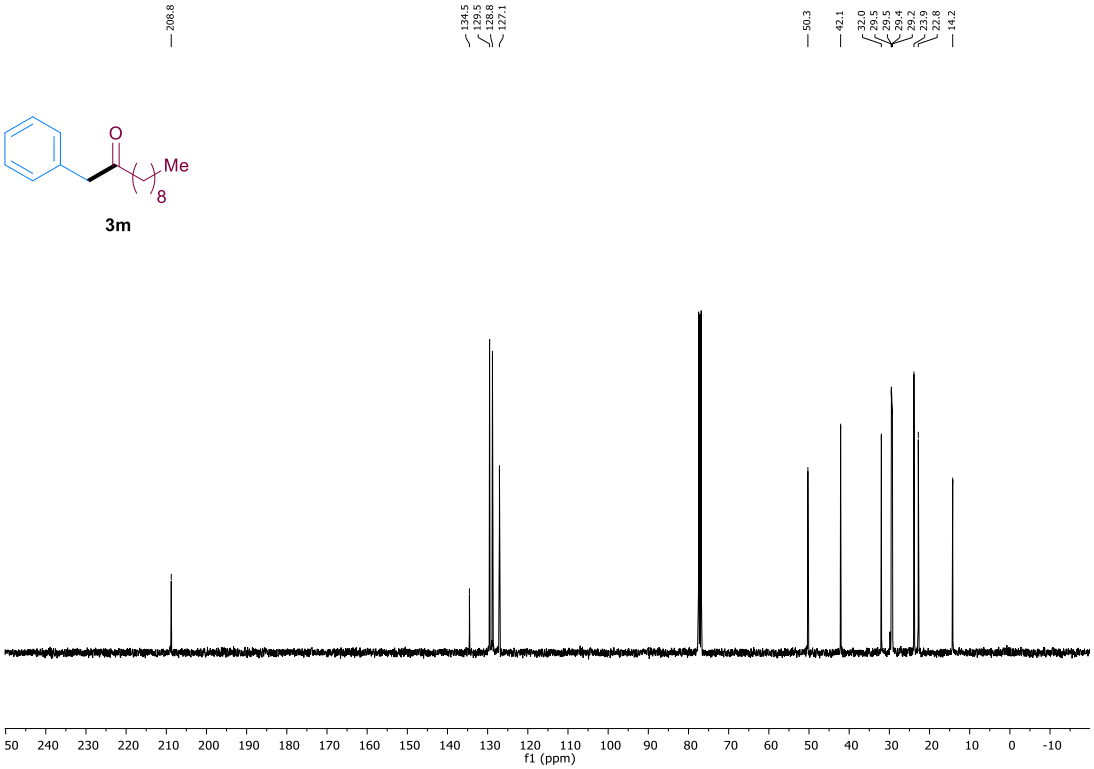


3l

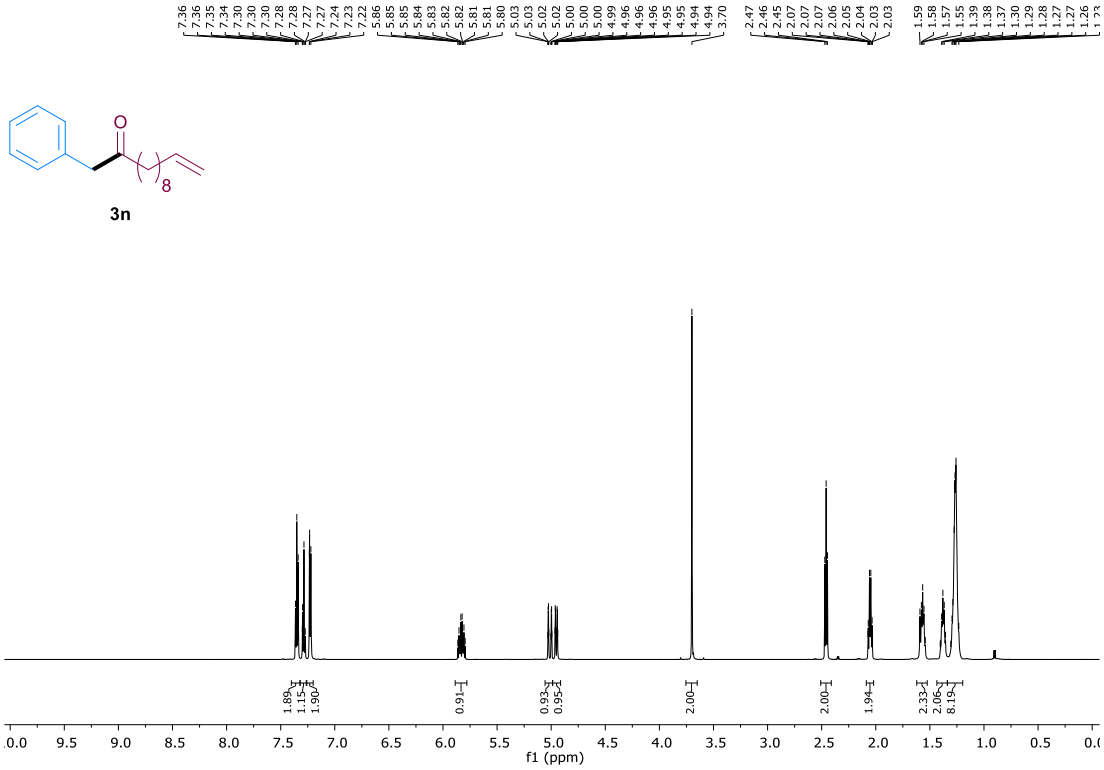
^{1}H-NMR (3m) [400 MHz, $CDCl_3$]



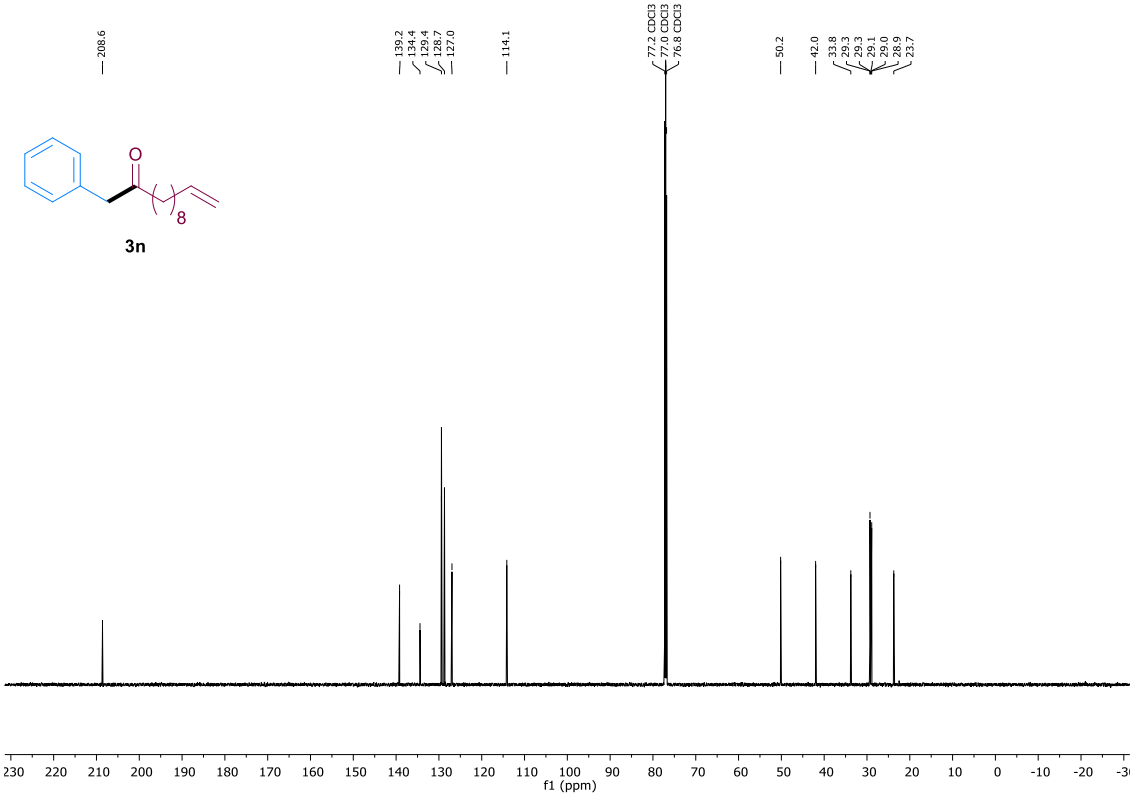
^{13}C-NMR (3m) [101 MHz, $CDCl_3$]



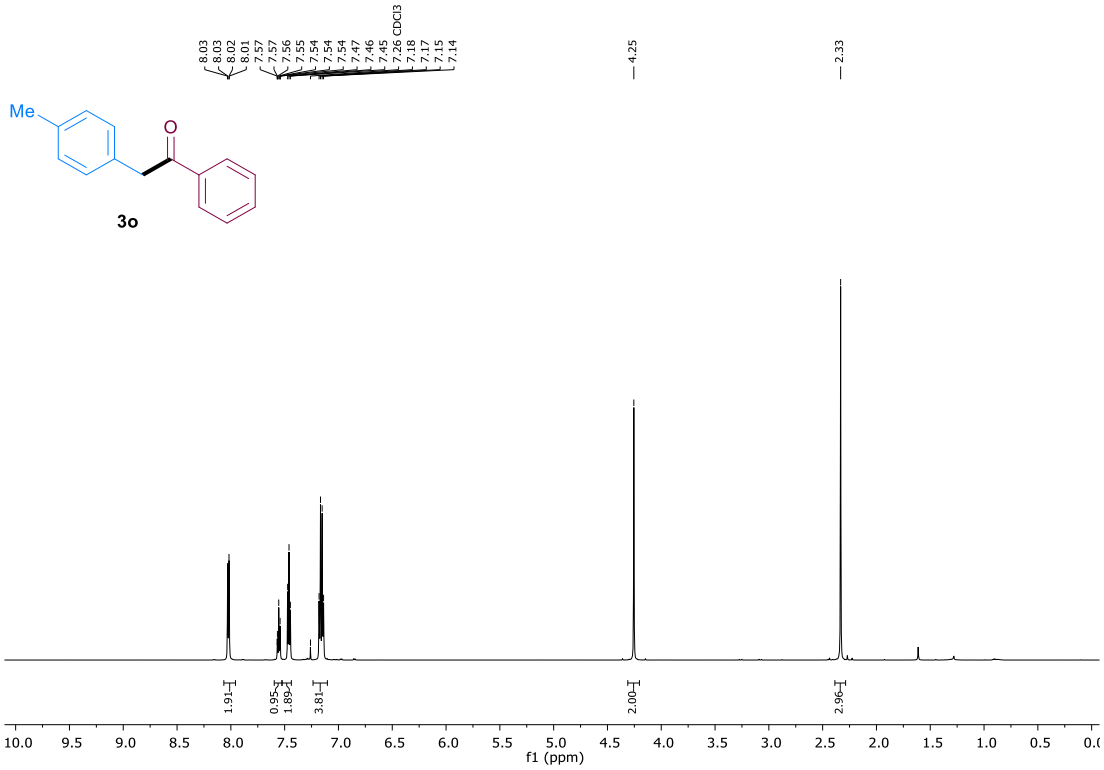
^{1}H-NMR (3n) [600 MHz, $CDCl_3$]



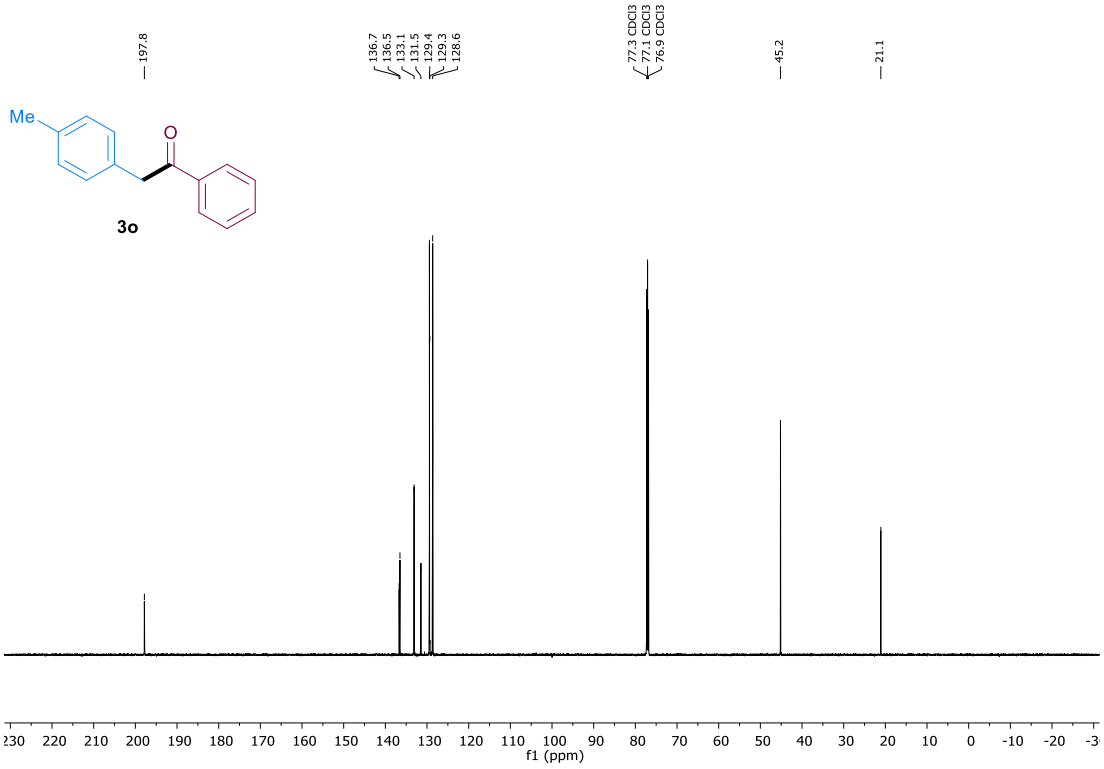
^{13}C-NMR (3n) [151 MHz, $CDCl_3$]



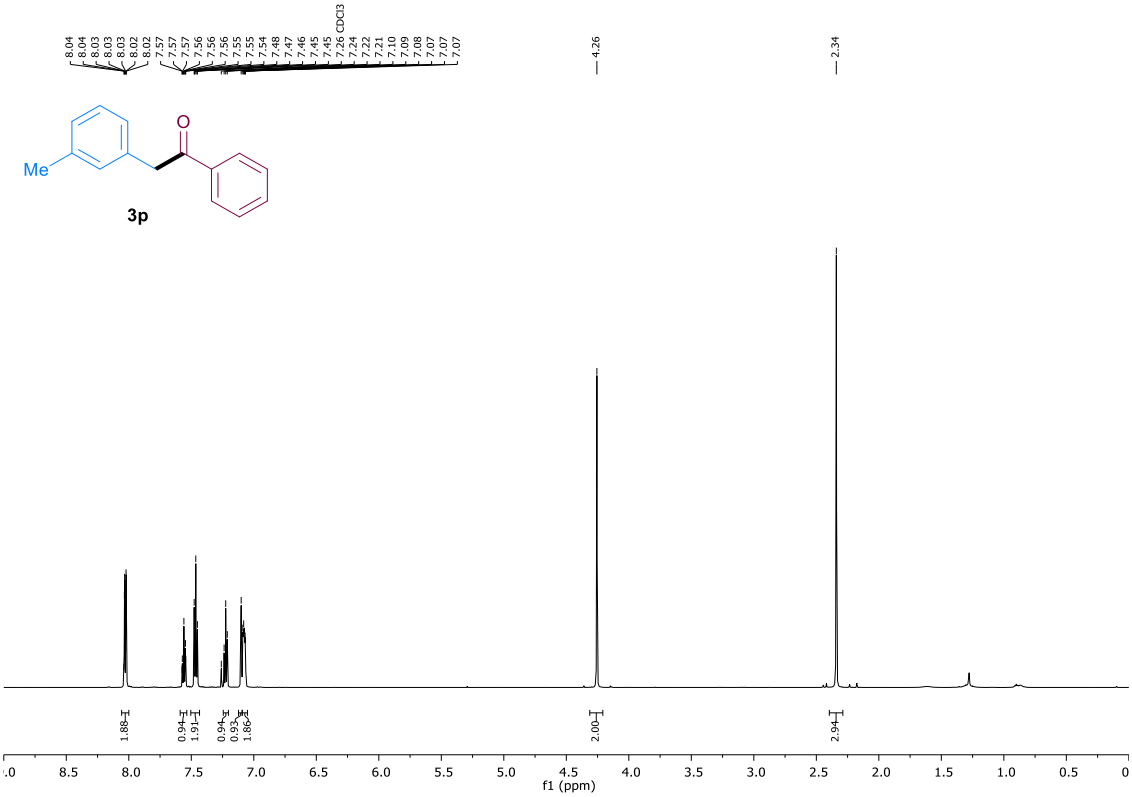
^{1}H-NMR (3o) [600 MHz, $CDCl_3$]



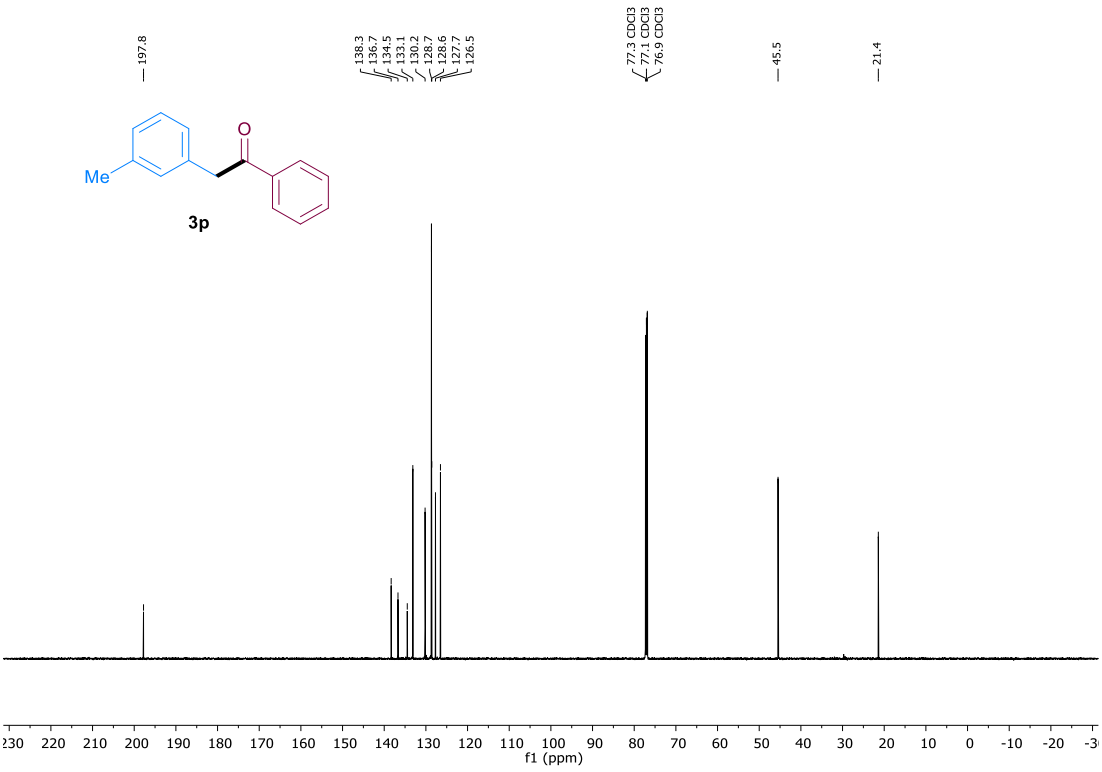
^{13}C-NMR (3o) [151 MHz, $CDCl_3$]



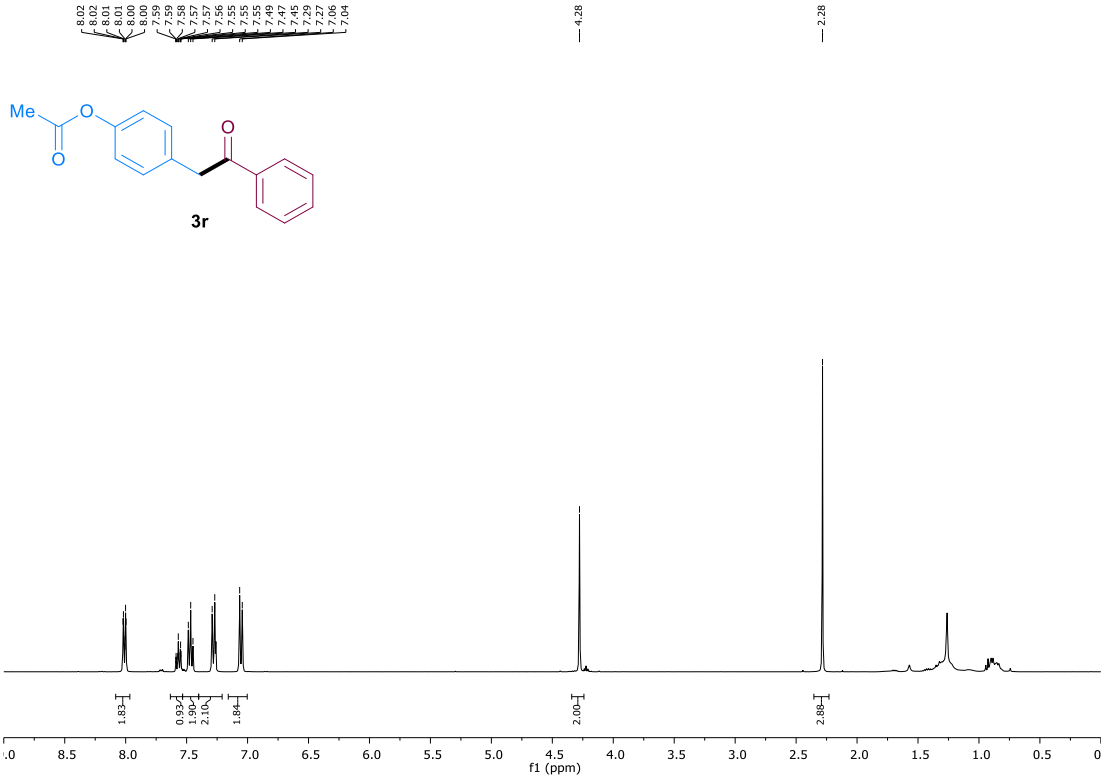
^{1}H-NMR (3p) [600 MHz, $CDCl_3$]



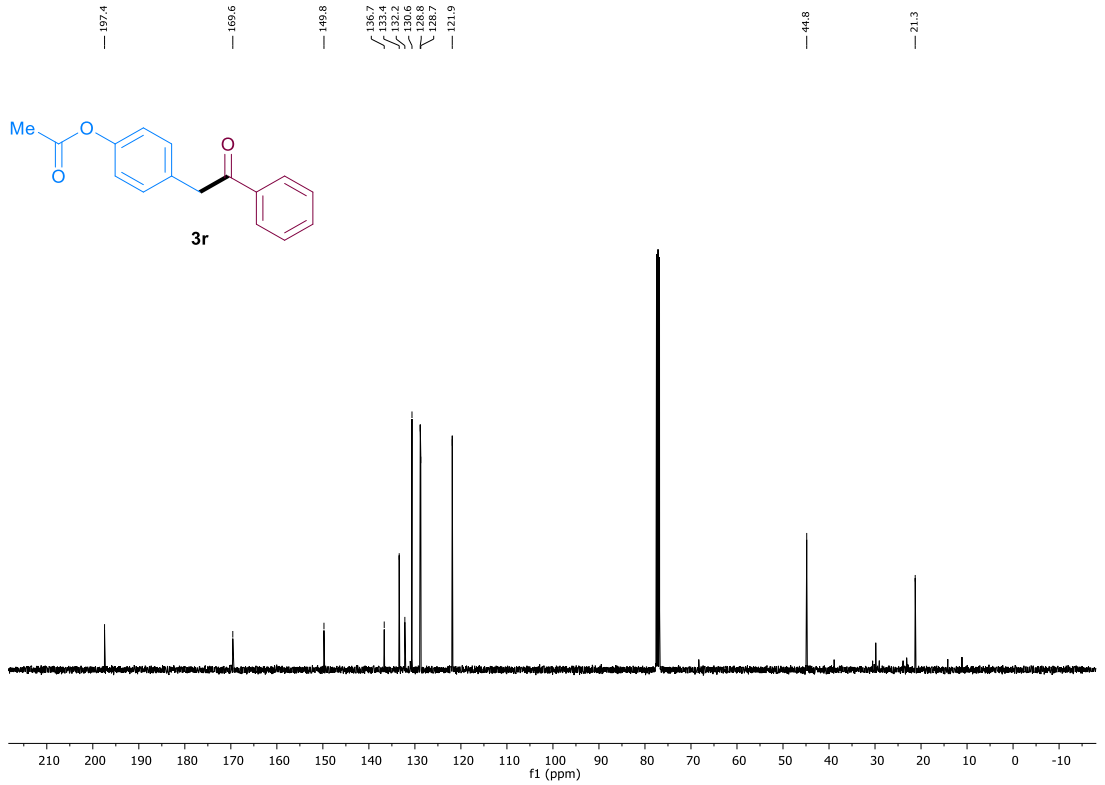
^{13}C-NMR (3p) [151 MHz, $CDCl_3$]



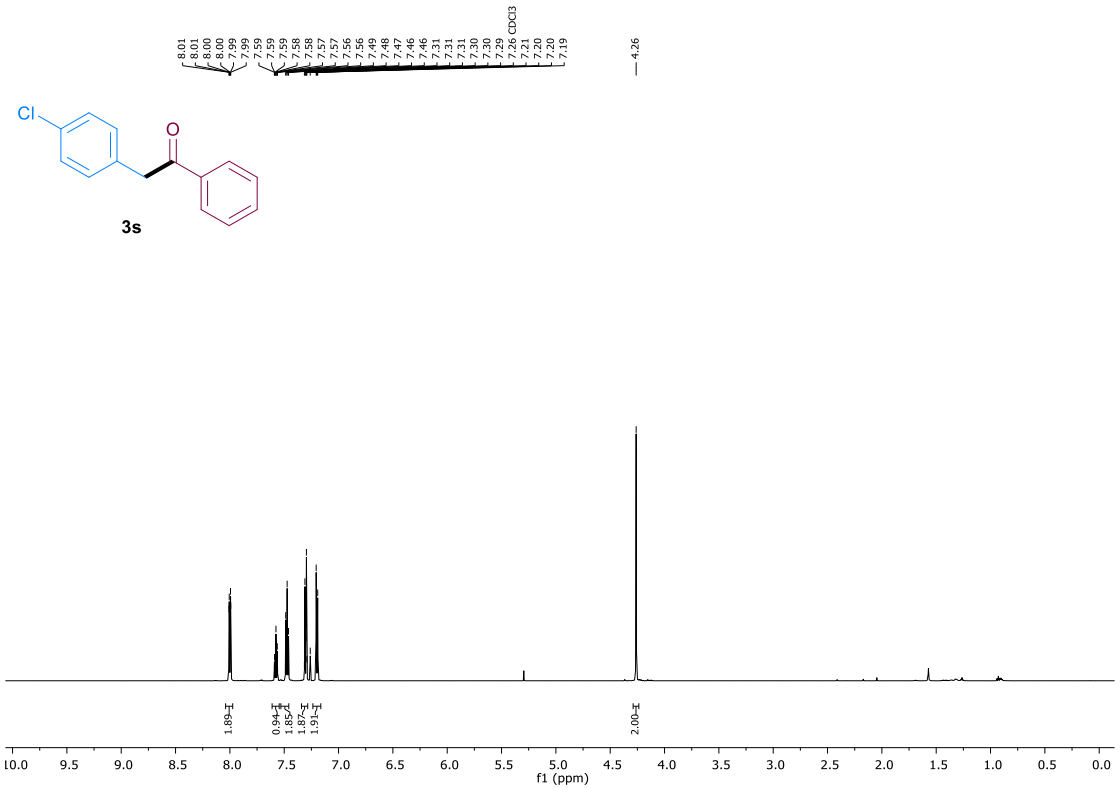
^{1}H-NMR (3r) [400 MHz, $CDCl_3$]



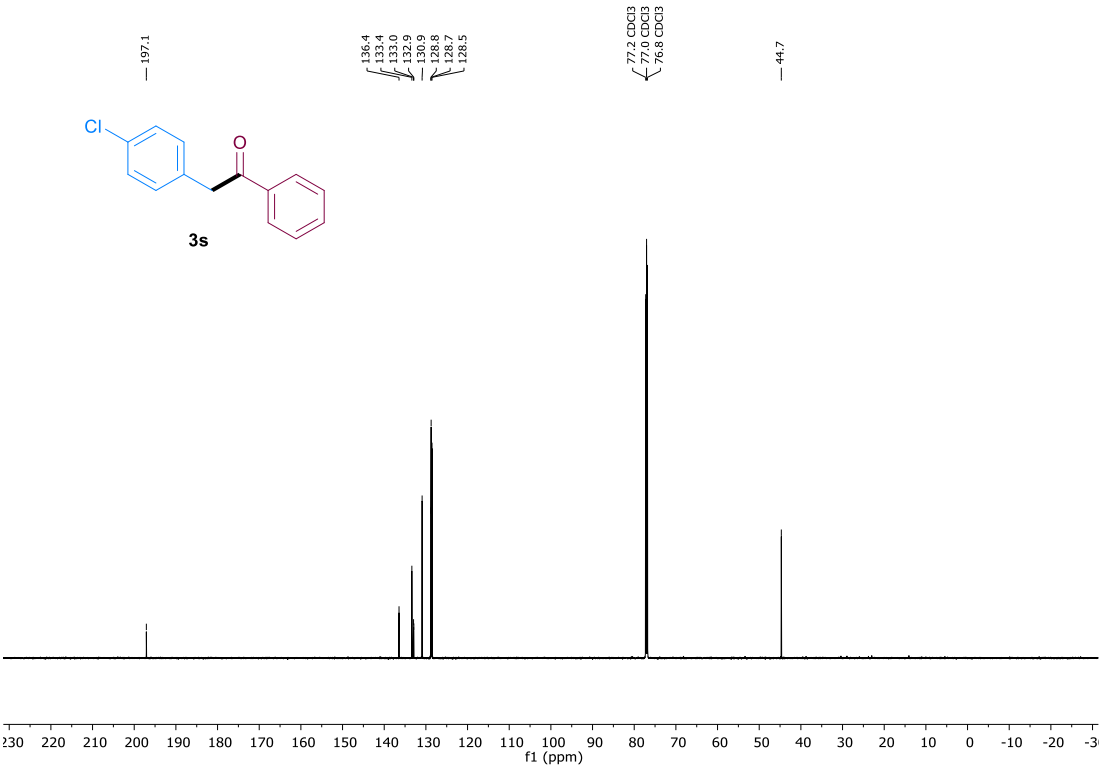
^{13}C-NMR (3r) [101 MHz, $CDCl_3$]



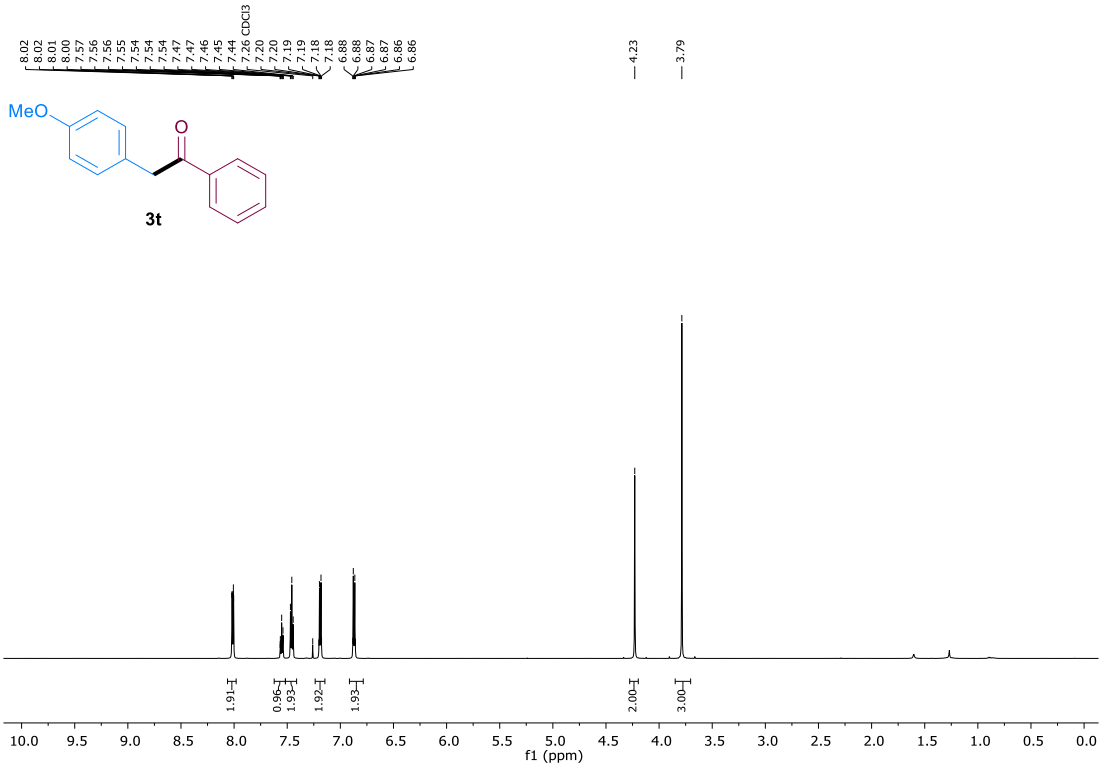
^{1}H-NMR (3s) [600 MHz, $CDCl_3$]



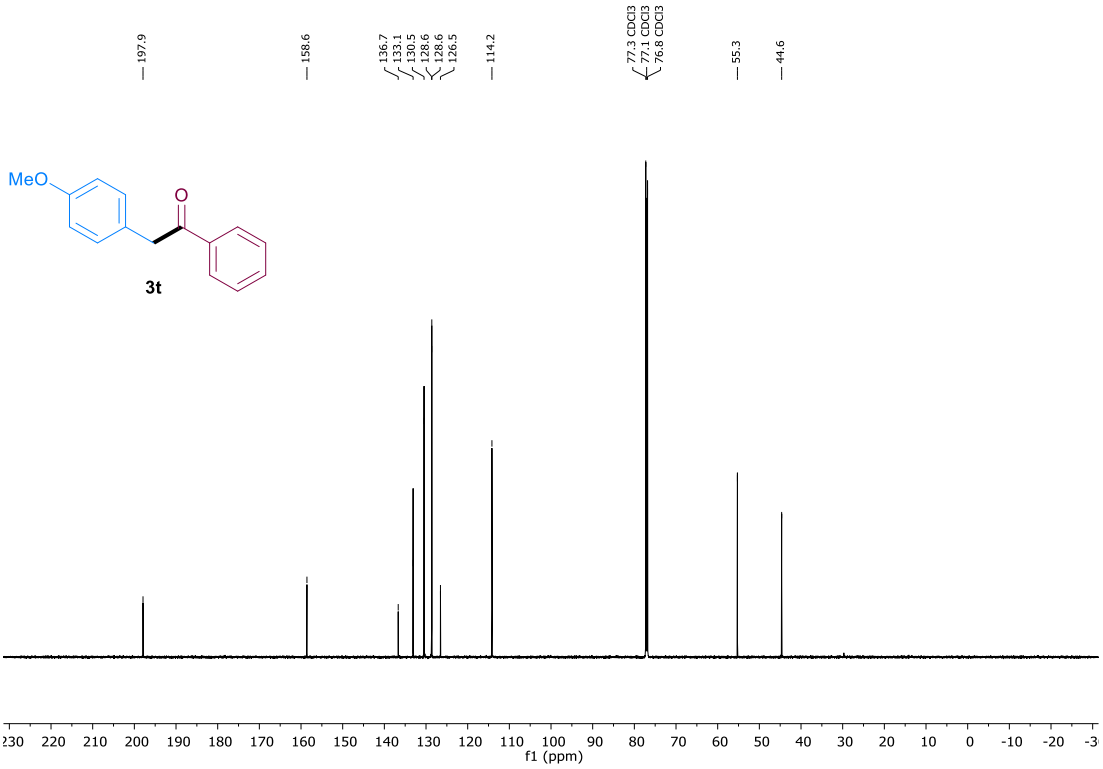
^{13}C-NMR (3s) [151 MHz, $CDCl_3$]



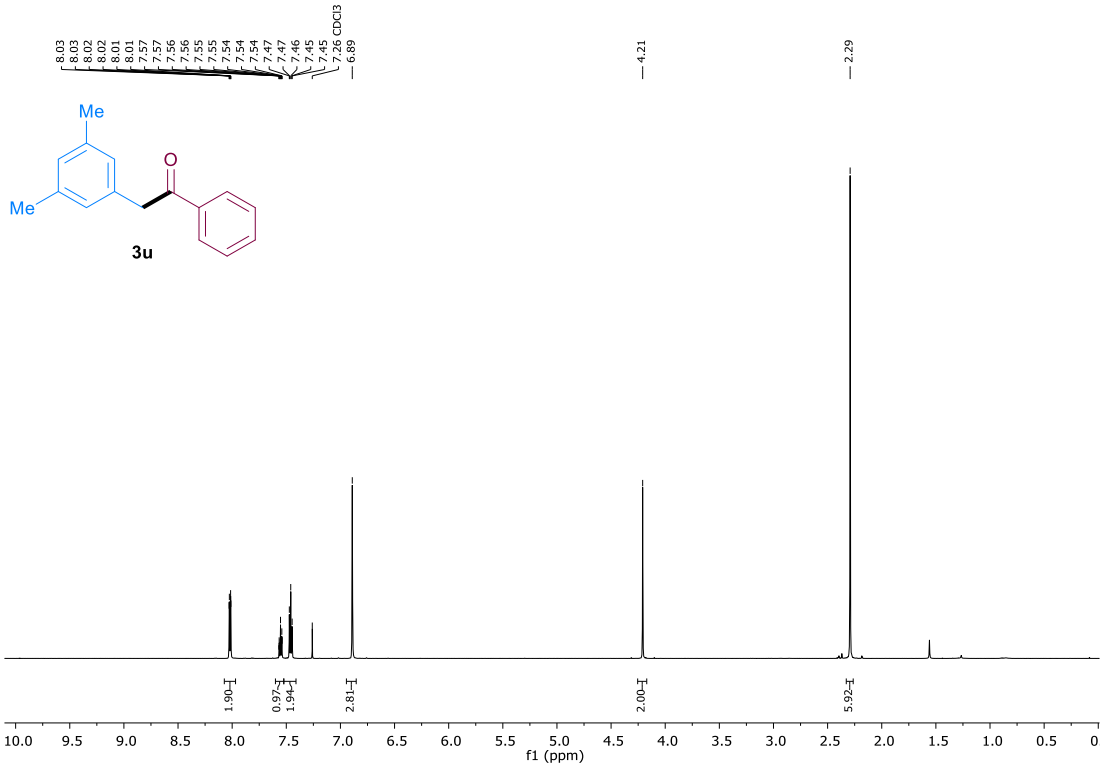
^{1}H-NMR (3t) [600 MHz, $CDCl_3$]



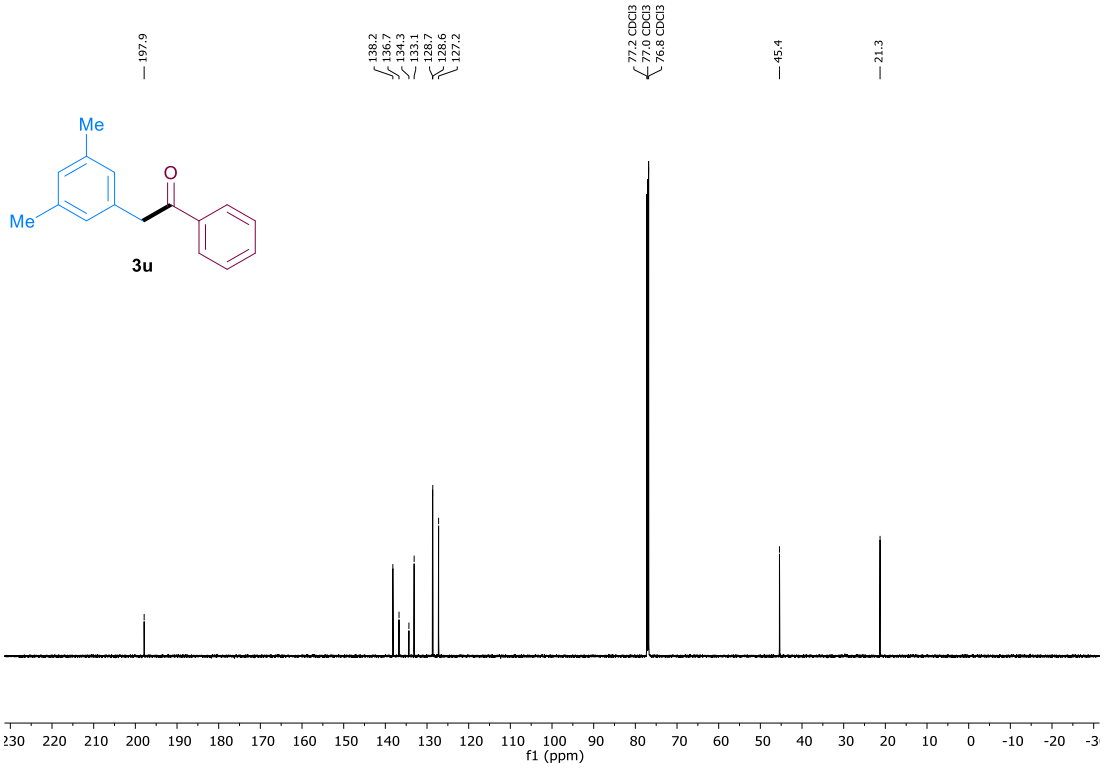
^{13}C-NMR (3t) [151 MHz, $CDCl_3$]



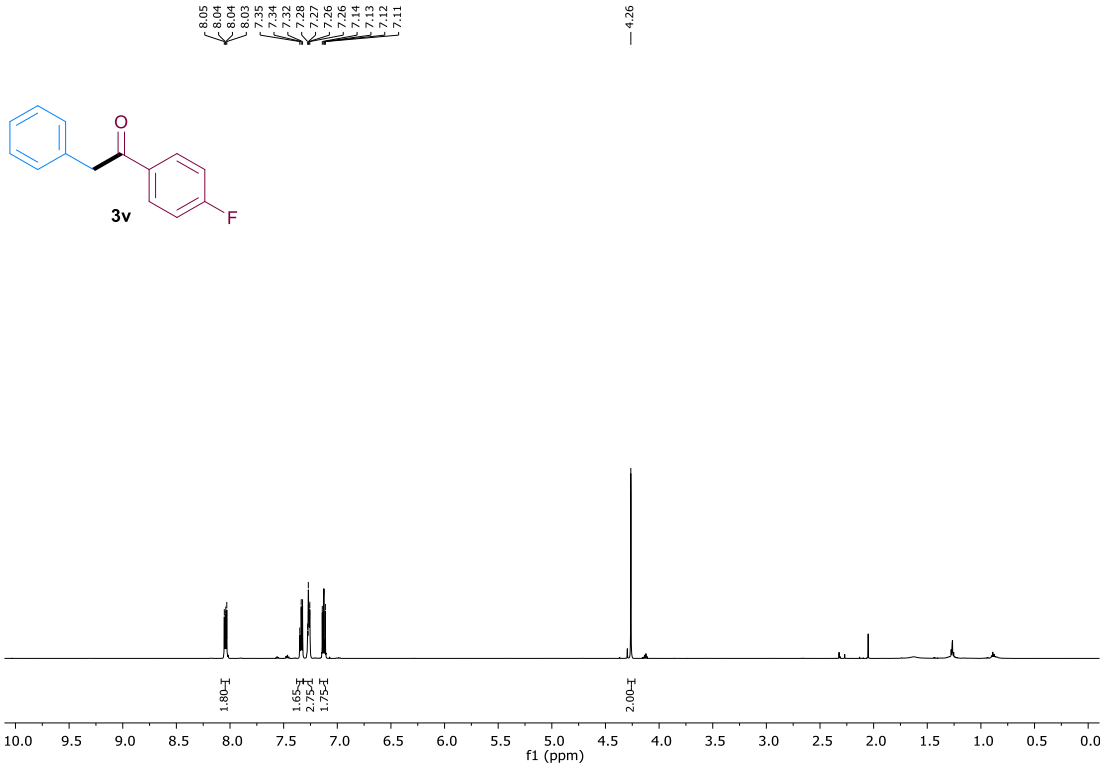
^{1}H-NMR (**3u**) [600 MHz, $CDCl_3$]



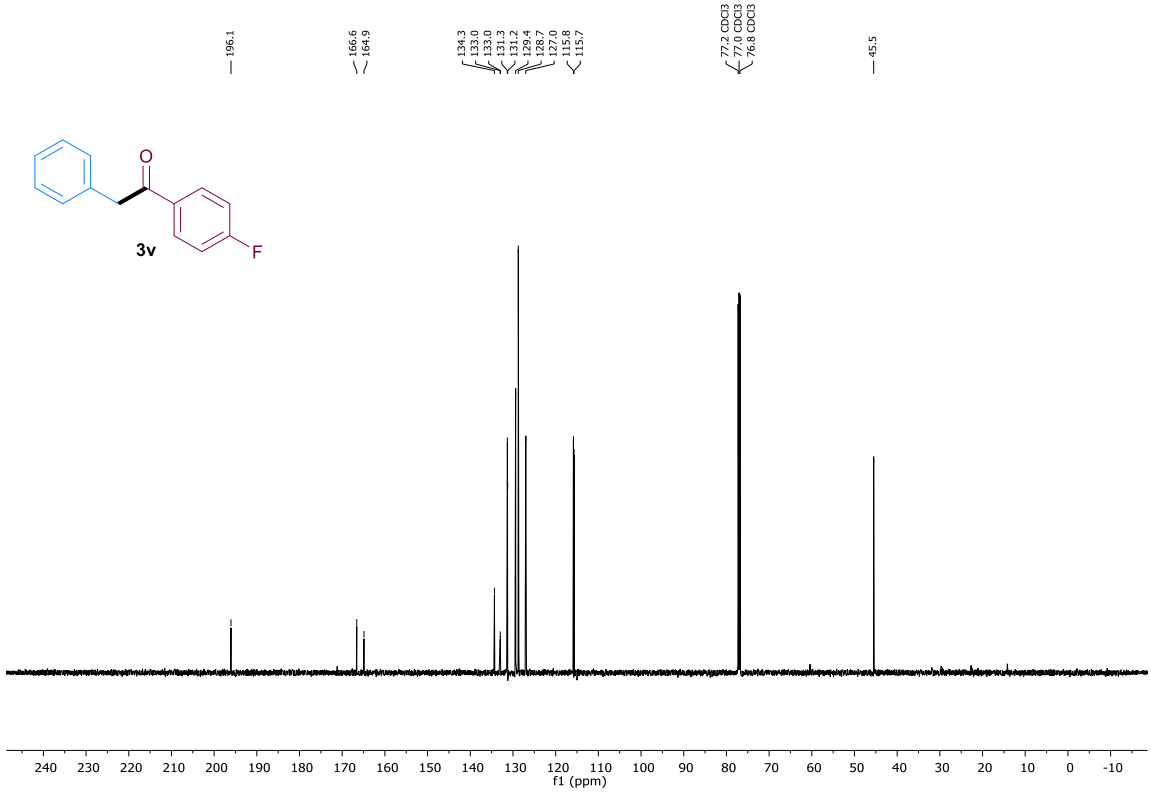
^{13}C-NMR (**3u**) [151 MHz, $CDCl_3$]



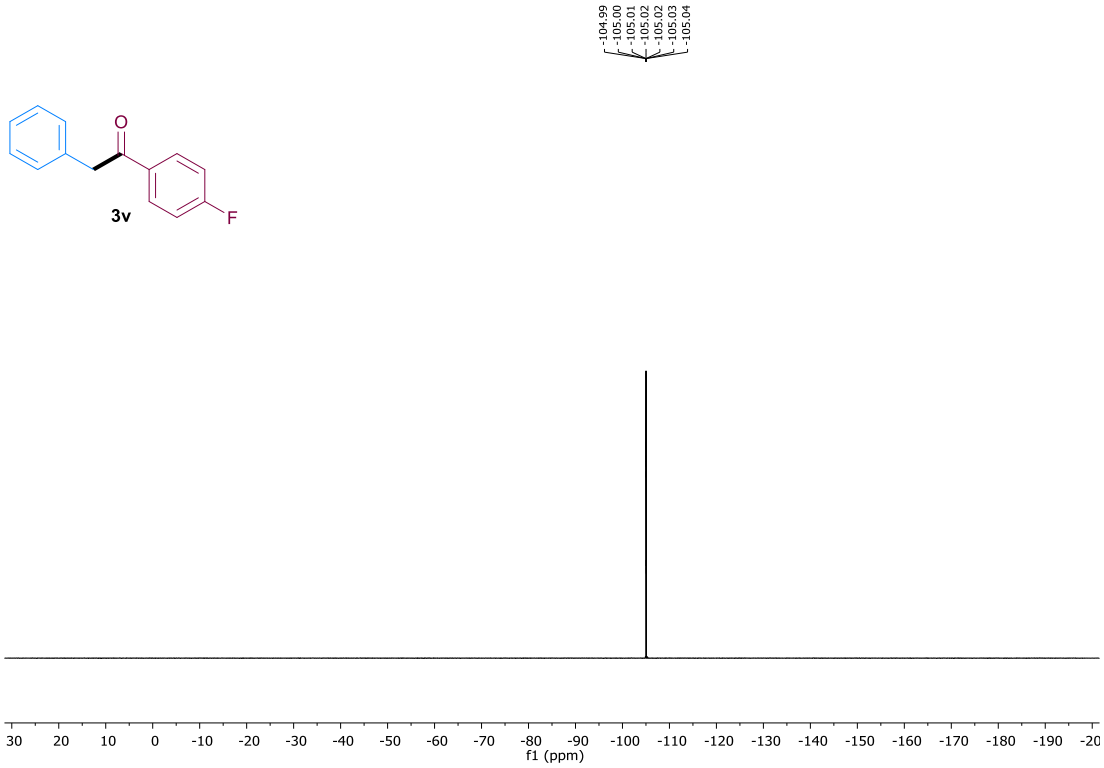
^{1}H-NMR (**3v**) [600 MHz, $CDCl_3$]



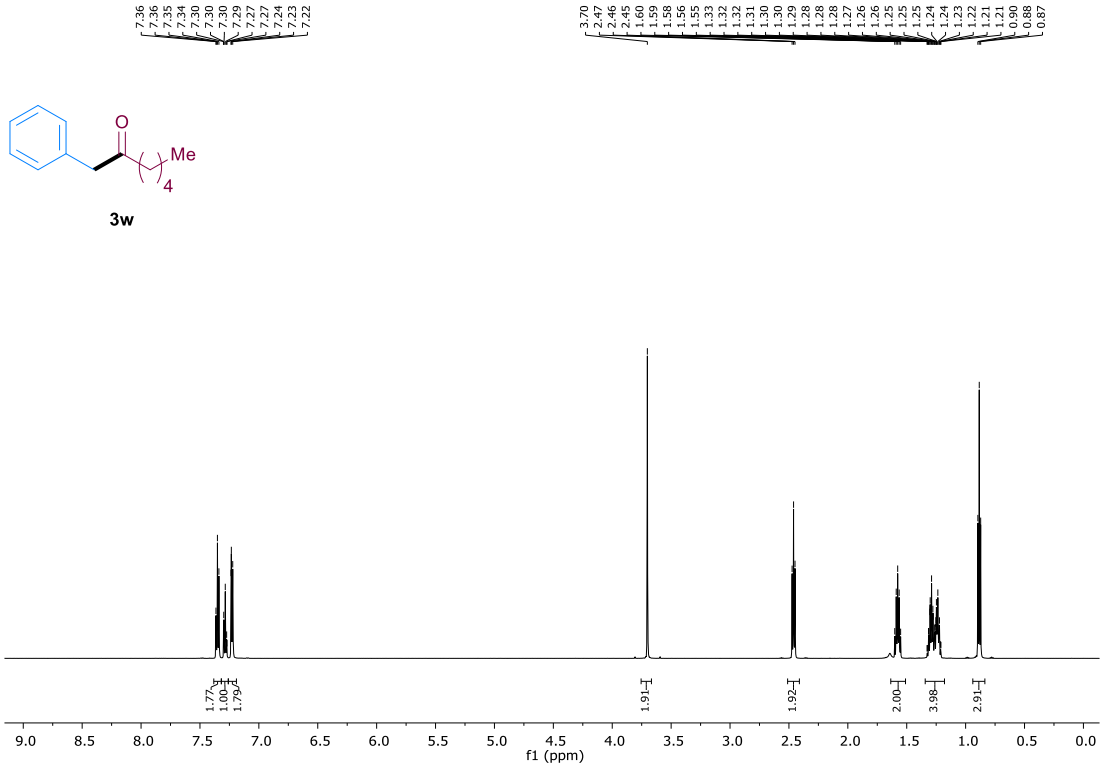
^{13}C-NMR (**3v**) [151 MHz, $CDCl_3$]



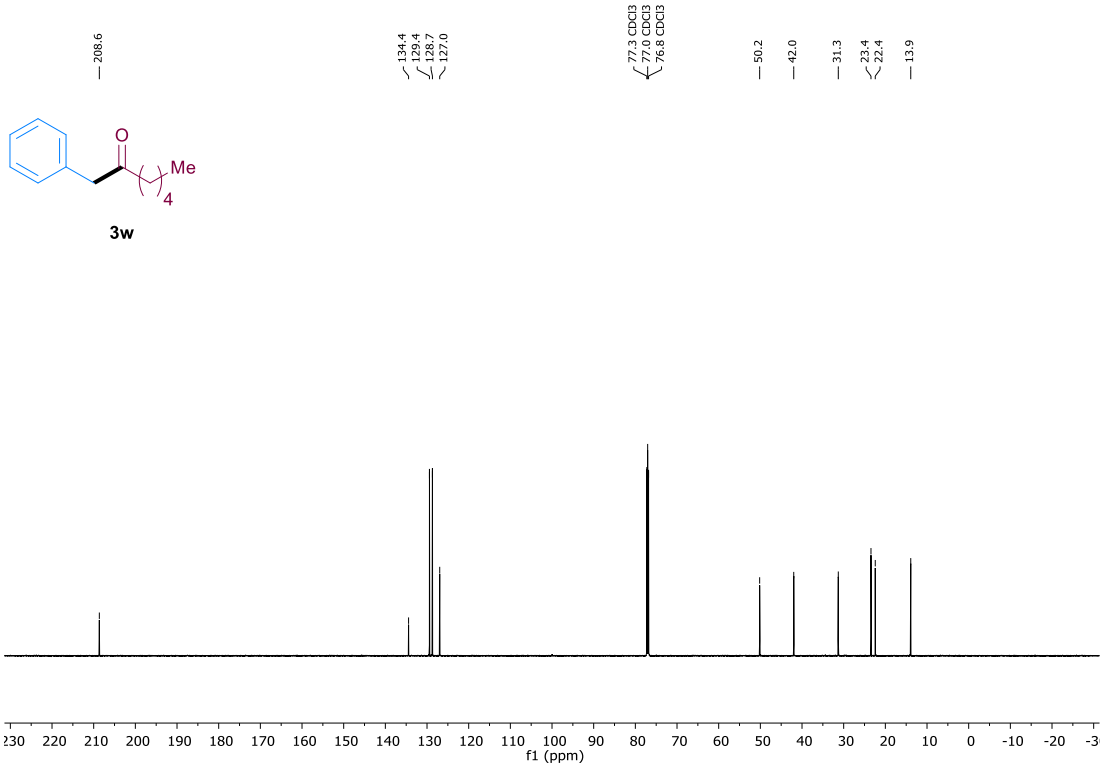
^{19}F-NMR (3v) [564 MHz, $CDCl_3$]



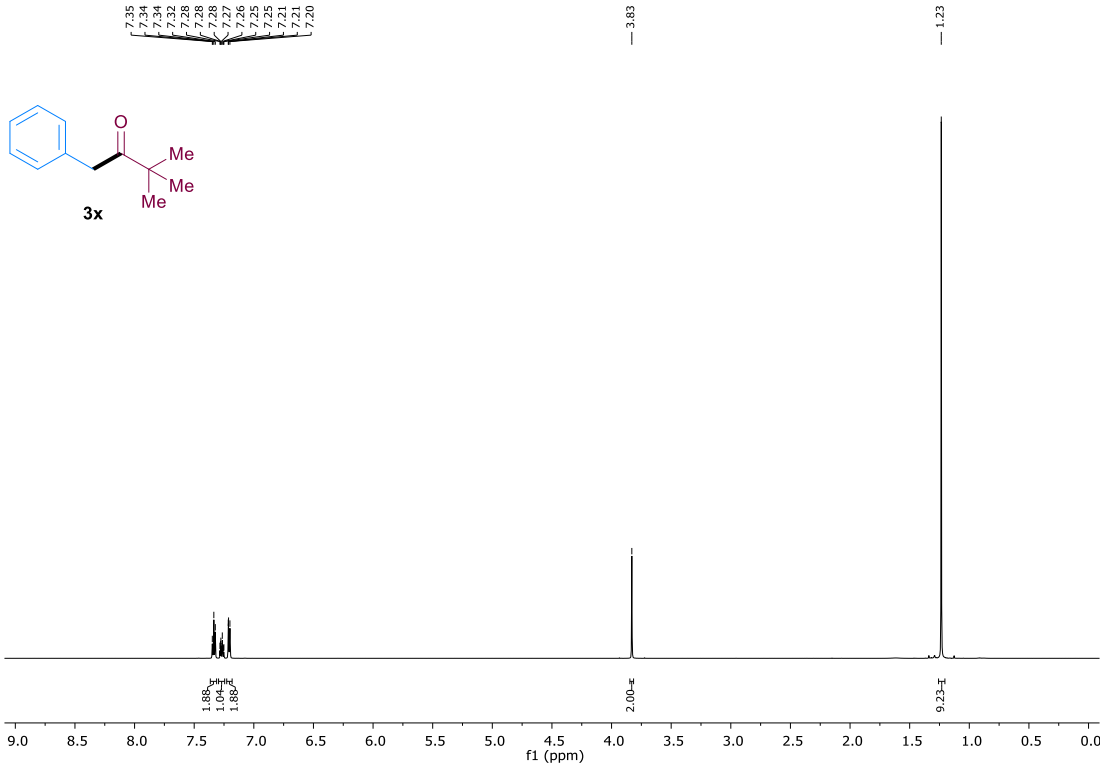
^{1}H-NMR (**3w**) [600 MHz, $CDCl_3$]



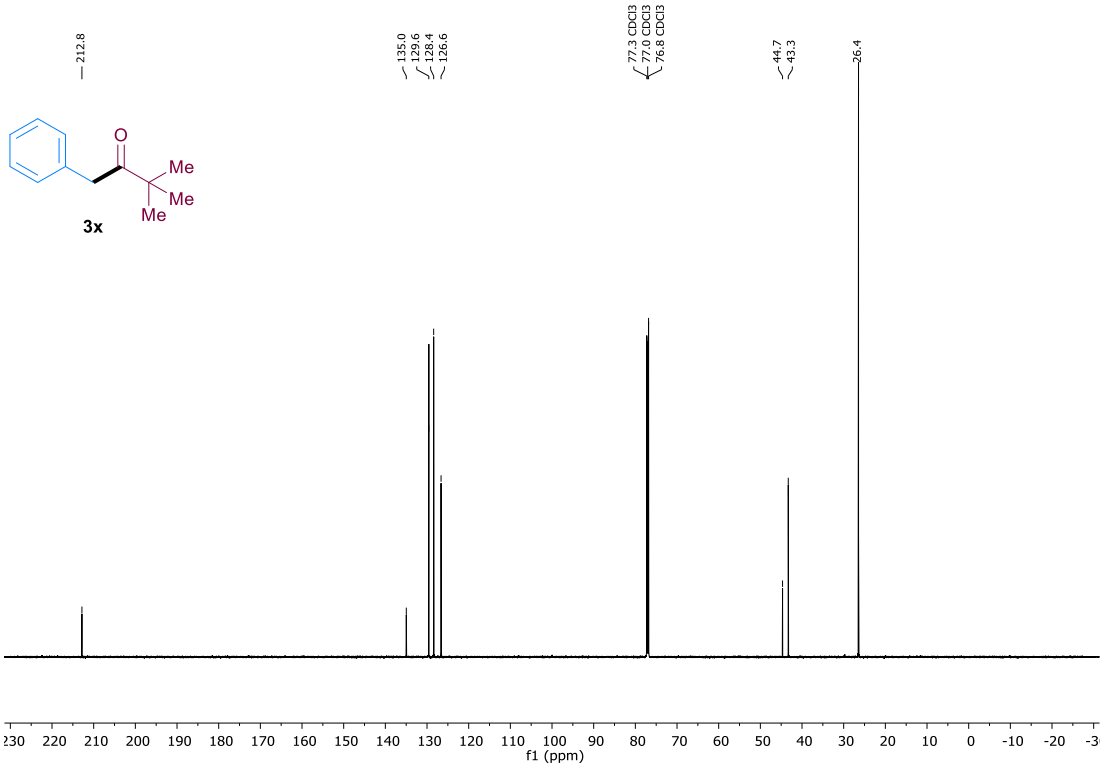
^{13}C-NMR (**3w**) [151 MHz, $CDCl_3$]



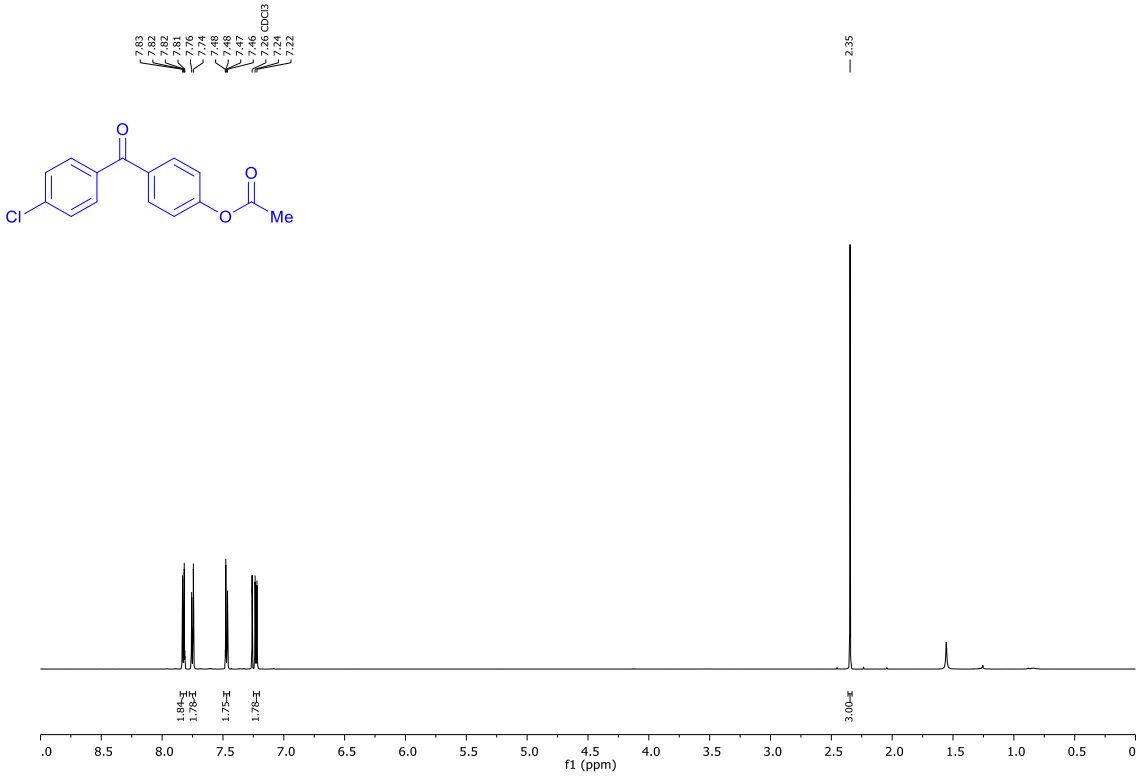
^{1}H-NMR (3x) [600 MHz, $CDCl_3$]



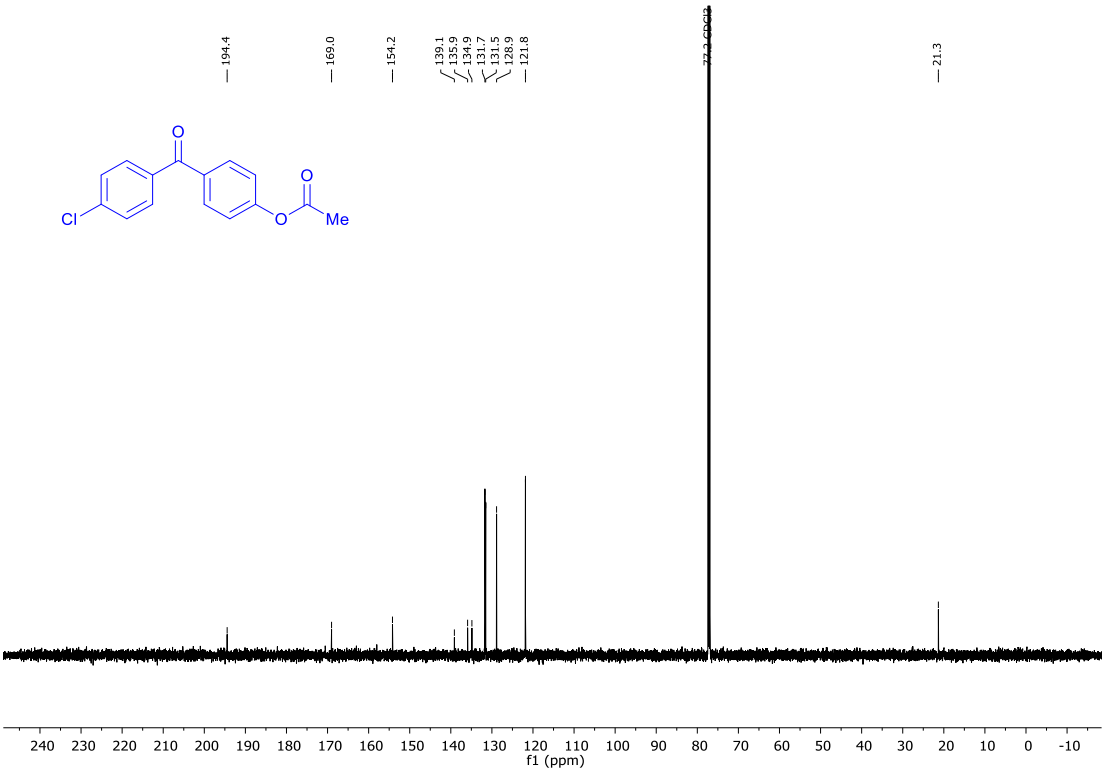
^{13}C-NMR (3x) [151 MHz, $CDCl_3$]



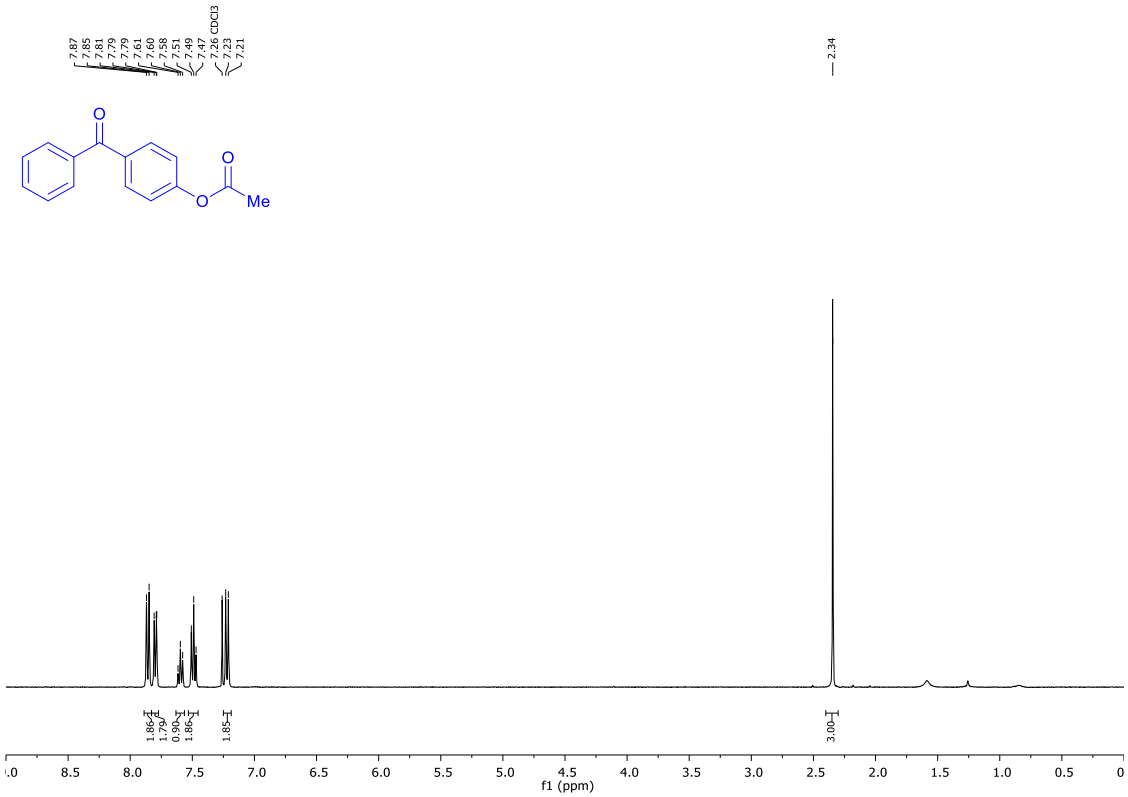
^{1}H-NMR (PS-4) [600 MHz, $CDCl_3$]



^{13}C-NMR (PS-4) [151 MHz, $CDCl_3$]



^{1}H-NMR (PS-5) [400 MHz, $CDCl_3$]



^{13}C-NMR (PS-5) [151 MHz, $CDCl_3$]