Electronic Supplementary Information

Synthesis of unsymmetrical ketones via dual catalysed cross-coupling of α,β-unsaturated carboxylic acids with aryldiazonium salts

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1. General Information Materials.

^{1}H, ^{13}C and ^{19}F Spectra were recorded on a JEOL ECZ 500R FT NMR spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz, & ^{19}F NMR at 471 MHz) and Bruker Avance Neo 600 MHz NMR spectrometer (^{1}H NMR at 600 MHz, ^{13}C NMR at 150 MHz, & ^{19}F NMR at 564 MHz. Chemical shifts for protons and carbons are reported in parts per million downfield from tetramethylsilane, and are referenced to the residual deuterium in the solvent (^{1}H NMR: $CDCl_3$ at 7.26 ppm) and carbon of the solvent peak (^{13}C NMR: $CDCl_3$ at 77.16 ppm) respectively. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, brs = broad singlet, and m = multiplet), coupling constant (*J*) (Hz), and integration. Mass spectra were recorded on a SCIEX X500R QTOF mass spectrometer. Thin layer chromatography (TLC) was performed using Merck Kieselgel 60 GF 254 plates (thickness 0.25 mm). Visualization of TLC was performed with a 254 nm UV lamp. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the crude products was done by column chromatography using aluminum oxide active neutral according to Brockmann activity I, II 70-230 mesh. All the reactions were carried out in oven-dried open glass vessels. Yield refers to the isolated analytically pure material.

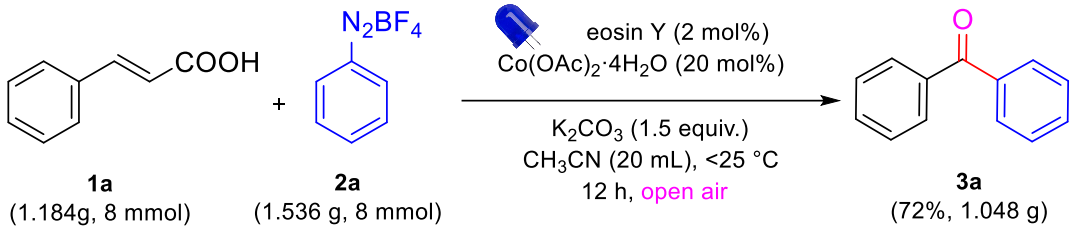
All the reagents and solvents were purchased from Sigma-Aldrich, Merck, and TCI Chemicals. The chemicals were used as such without any further purification, whereas the solvents were purified by standard methods prior to their use. All the aryldiazonium tetrafluoroborates were prepared by known procedure.[1]

2. General Experimental Procedure for the Synthesis of the Products 3.

A mixture of α,β-unsaturated carboxylic acid **1** (1.0 mmol, 1.0 equiv.), aryldiazonium tetrafluoroborate **2** (1.0 mmol, 1.0 equiv.), $Co(OAc)_2 \cdot 4H_2O$ (50 mg, 0.2 mmol, 0.2 equiv.), K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv.), eosin Y (13 mg, 0.02 mmol, 0.02 equiv.), and CH_3CN (3.0 mL), contained in a 25-mL round-bottom flask, was irradiated by Luxeon rebel Blue LED (470 nm) while stirring at room temperature for 8-12 h. The distance from the light source to the irradiation vessel was approximately 1.5 cm, and no filters were used. After completion of the reaction (monitored through TLC), the mixture was quenched using a saturated aqueous solution of sodium bicarbonate (15 mL), and then extracted with ethyl acetate (2×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography using n-hexane and ethyl acetate (0-1% v/v) as eluent to afford the pure product **3**.

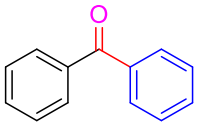
3. Gram Scale Synthesis of Benzophenone 3a.

A mixture of cinnamic acid **1a** (1.184g, 8 mmol), benzenediazonium tetrafluoroborate **2a** (1.536 g, 8 mmol), $Co(OAc)_2 \cdot 4H_2O$ (0.398 g, 20 mol%), K_2CO_3 (1.66 g, 1.5 equiv.), eosin Y (0.110 g, 2 mol%), and CH_3CN (20 mL), contained in a 50-mL round-bottom flask, was irradiated by Luxeon rebel Blue LED (470 nm) while stirring at room temperature for 12 h. After completion of the reaction (monitored through TLC), the mixture was quenched using a saturated aqueous solution of sodium bicarbonate, and then extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography using n-hexane as eluent to afford the pure product **3a** (72%, 1.048 g).



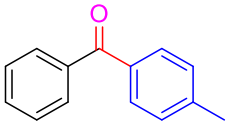
4. Physical and Spectral Data

Benzophenone(3a):[2]



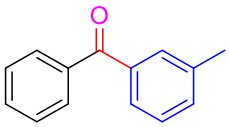
White solid (149 mg, 82% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 49-52 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.0, 128.3.

Phenyl(*p*-tolyl)methanone (3b):[2]



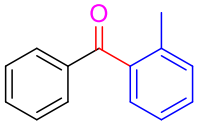
White solid (167 mg, 85% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 57-58 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.6, 143.3, 138.0, 135.0, 132.2, 130.4, 130.0, 129.1, 128.3, 21.7.

Phenyl(*m*-tolyl)methanone (**3c**): [2]



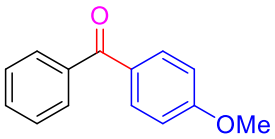
Colorless liquid (149 mg, 75% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.63 (s, 1H), 7.58 (d, *J* = 6.5 Hz, 2H), 7.49 (t, *J* = 7.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.1, 138.3, 137.9, 137.8, 133.3, 132.4, 130.6, 130.2, 128.4, 128.2, 127.5, 21.5.

Phenyl(*o*-tolyl)methanone (**3d**):[2]



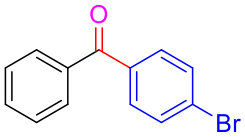
Colorless liquid (131 mg, 67% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.5 8 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.7, 138.7, 137.8, 136.8, 133.2, 131.1, 130.3, 130.2, 128.6, 128.6, 125.3, 20.1.

(4-Methoxyphenyl)(phenyl)methanone (**3e**):[2]



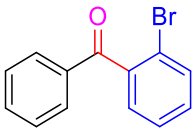
White solid (187 mg, 88% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 60-62 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H) 3.88 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.7, 163.3, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.6.

(4-Bromophenyl)(phenyl)methanone (**3f**):[3]



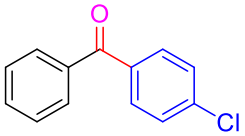
White solid (204 mg, 78% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 79-80 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.64-7.59 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.8, 137.4, 136.5, 132.8, 131.8, 131.7, 130.1, 128.6, 127.7.

(2-Bromophenyl)(phenyl)methanone (**3g**):[4]



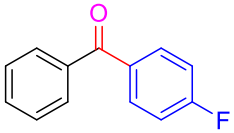
White solid (159 mg, 61% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 42-44 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49-7.44 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.0, 140.8, 136.3, 133.9, 133.4, 131.3, 130.4, 129.1, 128.8, 127.3, 119.7.

(4-Chlorophenyl)(phenyl)methanone (**3h**):[2]



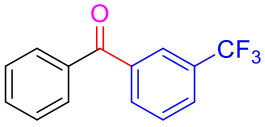
White solid (160 mg, 74% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 75-78 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (t, *J* = 8.0 Hz, 4H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49-7.44 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.6, 139.0, 137.4, 136.0, 132.8, 131.6, 130.1, 128.8, 128.5.

(4-Fluorophenyl)(phenyl)methanone (**3i**):[2]



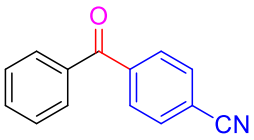
White solid (142 mg, 71% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 47-48 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (t, *J* = 6.5 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.4, 166.5 (d, *J* = 254.3 Hz) 137.6, 133.9 (d, *J* = 2.6 Hz), 132.8 (d, *J* = 9.6 Hz) 132.6, 130.0, 128.5, 115.7(d, *J* = 22.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.8.

Phenyl(3-(trifluoromethyl)phenyl)methanone (**3j**).[5]



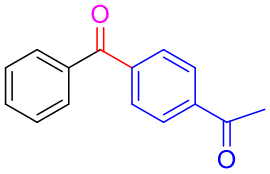
White solid (172 mg, 69% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 52-54 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.99 (t, *J* = 8.0 Hz, 1H), 7.90-7.85 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67-7.62 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.4, 137.6, 136.9, 133.3, 133.2, 131.6 (q, *J* = 30.8 Hz), 130.2, 129.6 (q, *J* = 3.5 Hz), 126.4, 129.1, 129.0 (q, *J* = 2.4 Hz), 126.9 (q, *J* = 2.9 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}F_3O$ 251.0678; Found: 251.0680.

4-Benzoylbenzonitrile (**3k**):[2]



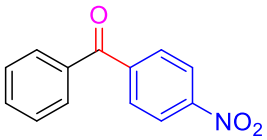
White solid (128 mg, 62% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 111-113 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.80-7.78 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.2, 141.4, 136.5, 133.5, 132.3, 130.4, 130.2, 128.8, 118.1, 115.8.

1-(4-Benzoylphenyl)ethan-1-one (**3l**).[3]



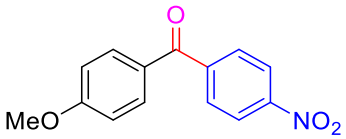
White solid (143 mg, 64% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 84-86 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 2.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.7, 196.1, 141.5, 139.7, 137.1, 133.1, 130.3, 130.2, 128.6, 128.3, 27.1.

(4-Nitrophenyl)(phenyl)methanone (**3m**):[6]



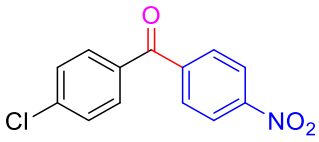
Light orange solid (125 mg, 55% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p.135-137 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.9, 150.0, 143.0, 136.4, 133.6, 130.8, 130.2, 128.8, 123.7.

(4-Methoxyphenyl)(4-nitrophenyl)methanone (**3n**):[6]



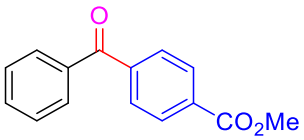
Light yellow solid (162 mg, 63% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 126-128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.6, 164.1, 149.7, 143.9, 132.8, 130.4, 129.1, 123.6, 114.1, 55.8.

(4-Chlorophenyl)(4-nitrophenyl)methanone (**3o**):[5]



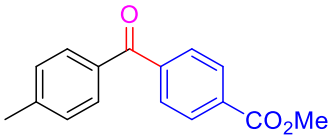
Yellow solid (133 mg, 51% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 100-102 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.7, 150.1, 142.6, 140.3, 134.7, 131.6, 130.7, 129.2, 123.8.

Methyl 4-benzoylbenzoate (**3p**):[2]



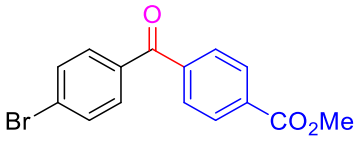
White solid (173 mg, 72% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 106-108 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.2, 166.5, 141.5, 137.1, 133.4, 133.1, 130.3, 129.9, 129.7, 128.6, 52.6.

Methyl 4-(4-methylbenzoyl)benzoate (**3q**):[7]



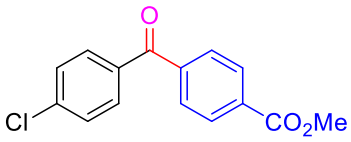
White solid (193 mg, 76% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 124-126 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 3.97 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.9, 166.5, 144.1, 141.9, 134.4, 133.1, 130.5, 129.8, 129.6, 129.3, 52.6, 21.9.

Methyl 4-(4-bromobenzoyl)benzoate (**3r**):[7]



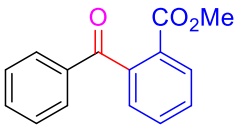
White solid (220 mg, 69% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 175-177 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.64 (m, 4H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.1, 166.4, 141.0, 135.8, 133.6, 132.0, 131.7, 129.8, 129.8, 128.3, 52.7.

Methyl 4-(4-chlorobenzoyl)benzoate (**3s**):[7]



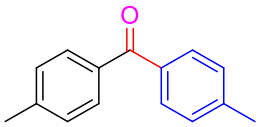
White solid (181 mg, 66% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 160-162 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.7, 166.2, 140.9, 139.5, 135.2, 133.4,131.4 129.6, 129.6, 128.8, 52.4.

Methyl 2-benzoylbenzoate (**3t**):[5]



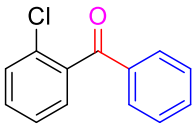
White solid (125 mg, 52% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 51-53 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59-7.54 (m, 2H), 7.45-7.41 (m, 3H), 3.61 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.9, 166.3, 141.6, 137.1, 132.9, 132.3, 130.0, 129.5, 129.1, 128.4, 127.7, 52.0.

Di-p-tolylmethanone (**3u**):[5]



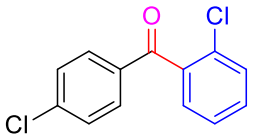
White solid (187 mg, 89% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 92-94 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 2.44 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.4, 143.1, 135.4, 130.3, 129.0, 21.8.

(2-Chlorophenyl)(phenyl)methanone (**3v**):[8]



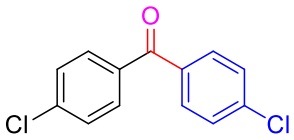
White solid (136 mg, 63% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 43-45 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.47-7.46 (m, 4H), 7.38 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.4, 138.8, 136.6, 133.8, 131.5, 131.3, 130.2, 129.3, 128.7, 126.8.

(2-Chlorophenyl)(4-chlorophenyl)methanone (**3w**):[9]



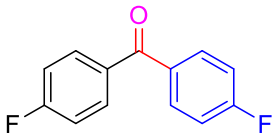
White solid (128 mg, 51% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 63-65 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.42 (m, 4H), 7.38 – 7.35 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.1, 140.3, 138.2, 134.9, 131.5, 131.5, 131.3, 130.2, 129.2, 129.1, 126.9.

Bis(4-chlorophenyl)methanone (**3x**):[5]



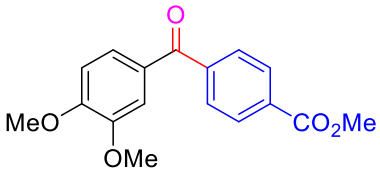
White solid (170 mg, 68% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 145-147 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.0 Hz, 4H), 7.48 (d, *J* = 7.0 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.4, 139.3, 135.7, 131.5, 128.9.

Bis(4-fluorophenyl)methanone (**3y**):[10]



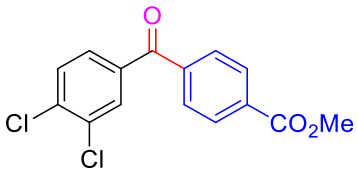
White solid (135 mg, 62% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 0/100). m.p. 106-108 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (t, *J* = 6.0 Hz, 4H), 7.18 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.0, 166.4 (d, *J* = 252.7 Hz), 133.9 (d, *J* = 2.7 Hz), 132.7 (d, *J* = 9.3 Hz), 115.8, 115.64, (d, *J* = 21.9 Hz).

Methyl 4-(3,4-dimethoxybenzoyl)benzoate (**3z**):[11]



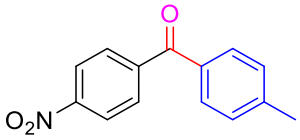
White solid (240 mg, 80% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 10/90). m.p. 134-136 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 1.2 Hz, 1H), 7.36 (dd, *J* = 1.8 Hz, 6.6 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 6H), 3.94 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 195.0, 166.6, 153.6, 149.3, 142.3, 132.9, 129.8, 129.6, 125.9, 112.0, 110.0, 56.3, 56.2, 52.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}O_5$ 301.1071; Found: 301.1071.

Methyl 4-(3,4-dichlorobenzoyl)benzoate (**3aa**):



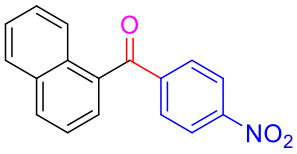
White solid (188 mg, 61% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 133-135 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.63-7.61 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H) 3.96 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.7, 166.2, 140.4, 137.7, 136.6, 133.8, 133.4, 131.9, 130.7, 129.8, 129.7, 129.1, 52.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}Cl_2O_3$ 309.0080; Found: 309.0089.

(4-Nitrophenyl)(*p*-tolyl)methanone (**3ab**):[5]



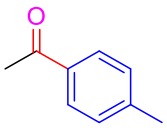
Yellow solid (113 mg, 47% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 121-123 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.7, 149.9, 144.7, 143.5, 133.8, 130.7, 130.5, 129.5, 123.7, 21.9.

Naphthalen-1-yl(4-nitrophenyl)methanone (**3ac**):[12]



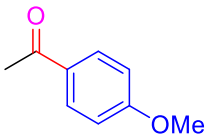
Yellow solid (138 mg, 51% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). m.p. 90-92 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.59-7.53 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.2, 150.4, 143.5, 134.8, 134.0, 132.8, 131.3, 130.9, 129.1, 128.8, 128.1, 127.0, 125.5, 124.4, 123.8.

1-(*p*-Tolyl)ethan-1-one (**3ad**):[13]



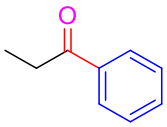
Colorless liquid (92 mg, 69% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.0, 144.0, 134.9, 129.4, 128.6, 26.7, 21.8.

1-(4-Methoxyphenyl)ethan-1-one (**3ae**):[13]



Colorless liquid (115 mg, 77% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 197.0, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5.

Propiophenone (**3af**):[13]



Colorless liquid (78 mg, 58% Yield). Purification by column chromatography (ethyl acetate/hexane, v/v = 1/99). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 3.03 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 201.0, 137.0, 133.0, 128.7, 128.1, 31.9, 8.4.

4. References:

1. B. Xing, C. Ni, J. Hu, *Angew. Chem. Int. Ed.* **2018**, *57*, 9896 –9900.
2. J. Zhang, P. Zhang, L. Shao, R. Wang, Y. Ma, M. Szostak, *Angew. Chem. Int. Ed.* 2022, *61*, e202114146.
3. D-L. Zhu, Q. Wu, Young, D. J.; H. Wang, Z.-G. Ren, H.-X. Li, *Org. Lett.* **2020**, *22*, 6832–6837.
4. Z. Zhu, Z. Wang, Y. Jian, H. Sun, G. Zhang, J. M. Lynam, C. R. McElroy, T. J. Burden, R. L. Inight, I. J. S. Fairlamb, W. Zhang, Z. Gao, Green Chem. 2021, 23, 920-926.
5. W. Hao, H. Liu, L. Yin, M. Cai, *J. Org. Chem.* **2016**, *81*, 4244–4251.
6. Y. Suzuki, S. Ota, Y. Fukuta, Y. Ueda, M. Sato, *J. Org. Chem.* **2008**, 73, 2420–2423.
7. J. Dansereau, S. Gautreau, A. Gagnon, *ChemistrySelect* **2017**, *2*, 2593-2599.
8. K. Cheng, G. Wang, M. Meng, C. Qi, *Org. Chem. Front.* **2017**, 4, 398-403.
9. R. Parella, Naveen, A. Kumar, S. A. Babu, *Tetrahedron Lett.* **2013**, *54*, 1738–1742.
10. M. Shee, N. D. P. Singh, Adv. Synth. Catal. **2022**, 364, 2032-2039.
11. D. Sukeguchi, S. P. Singh, M. R. Reddy, H. Yoshiyama, R. A. Afre, Y. Hayashi, H. Inukai, T. Soga, S. Nakamura, N. Shibata, T. Toru, *Beilstein J. Org. Chem.* **2009**, *5*, doi:10.3762/bjoc.5.7.
12. Y. Fu, Y. Yang, H. M Hügel, Z. Du, K. Wang, D. Huanga, Y. Hua, *Org. Biomol. Chem.* **2013**, *11*, 4429-4432.
13. G. Oss, J. Ho, T. V. Nguyen, *Eur. J. Org. Chem.* **2018**, *29*, 3974-3981.

6. ORTEP diagram of the product 3k.

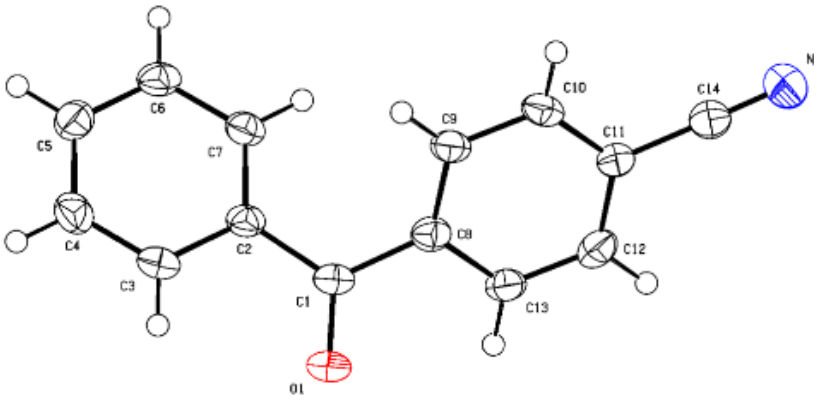
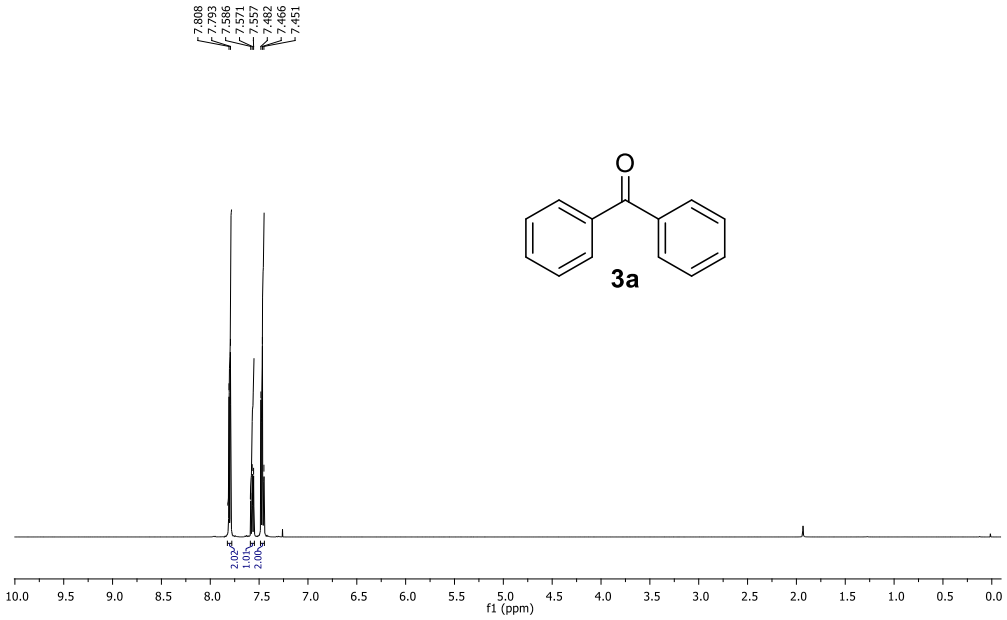


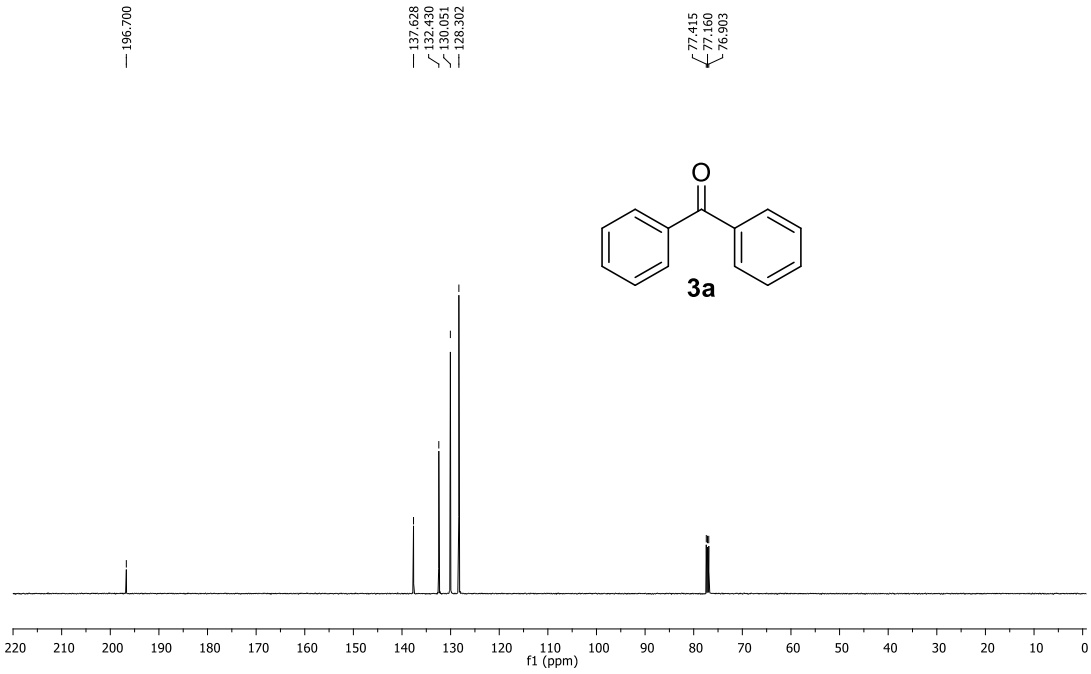
Figure 2. ORTEP diagram of the product **3k** (CCDC 2262537)

7. Copies of ^{1}H, ^{19}F, and ^{13}C Spectra of the Products 3.

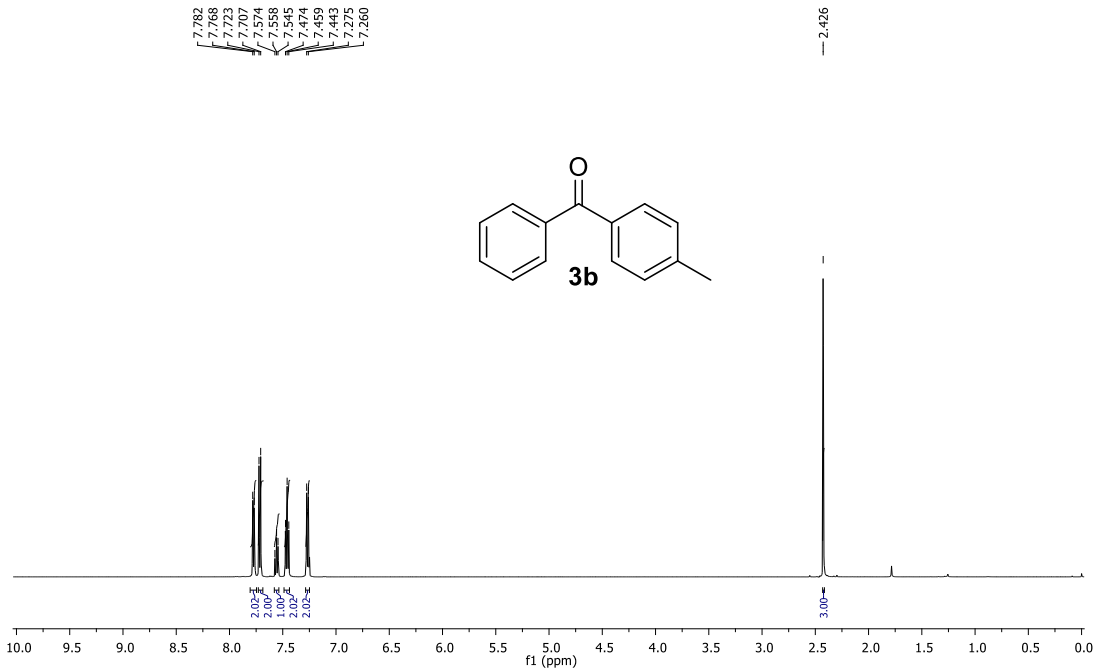
^{1}H NMR (500 MHz, $CDCl_3$)



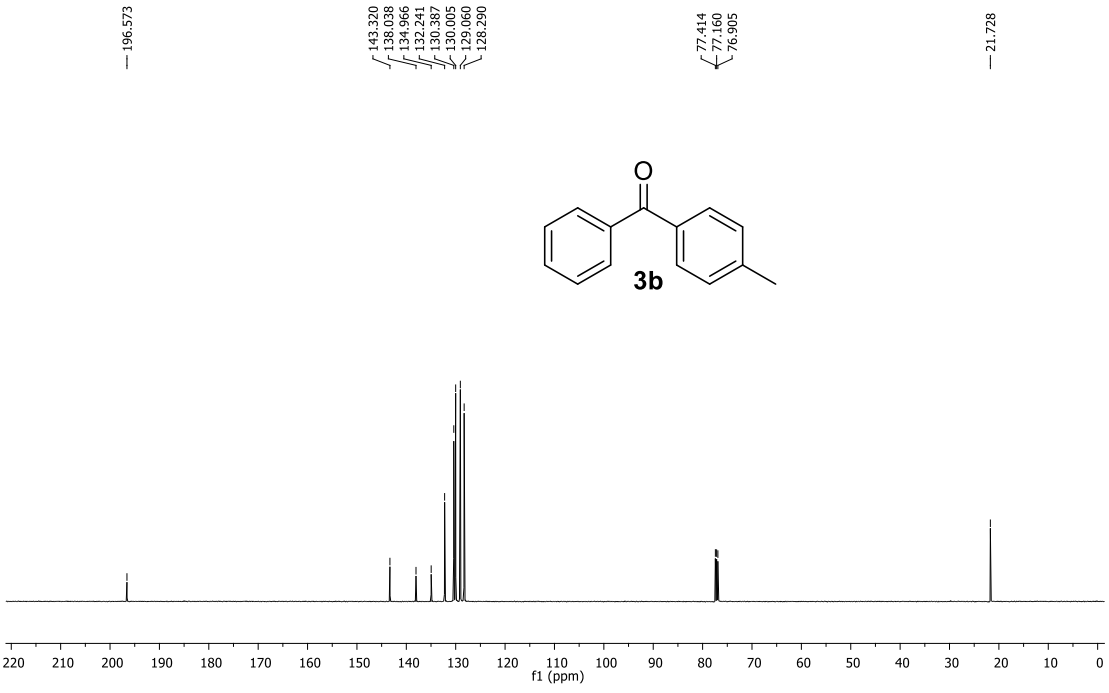
^{13}C NMR (126 MHz, $CDCl_3$)



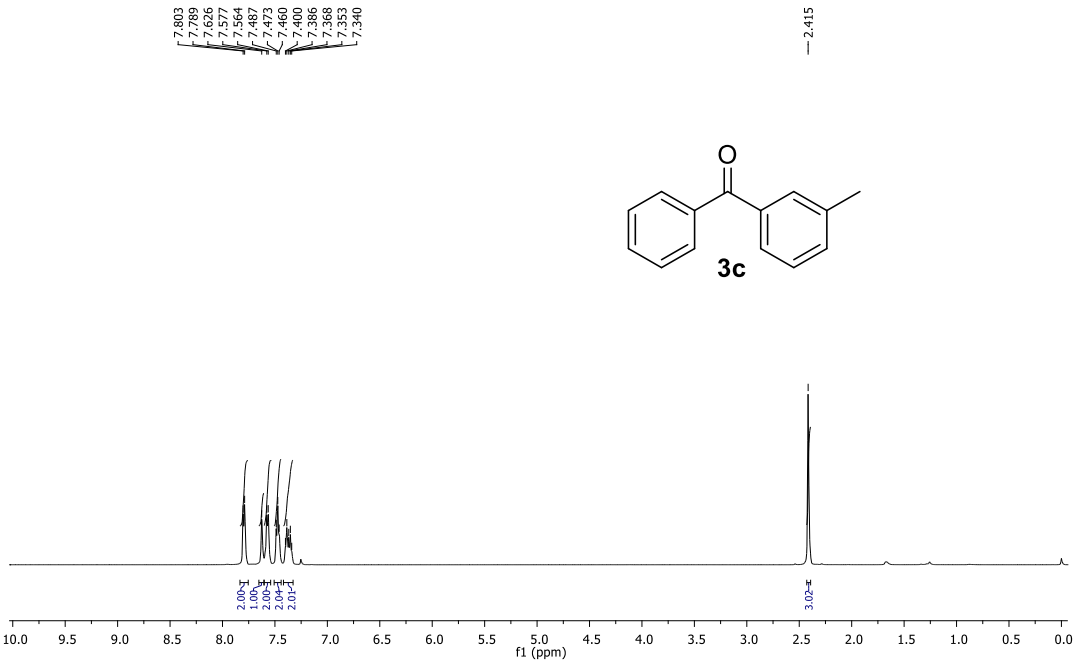
^{1}H NMR (500 MHz, $CDCl_3$)



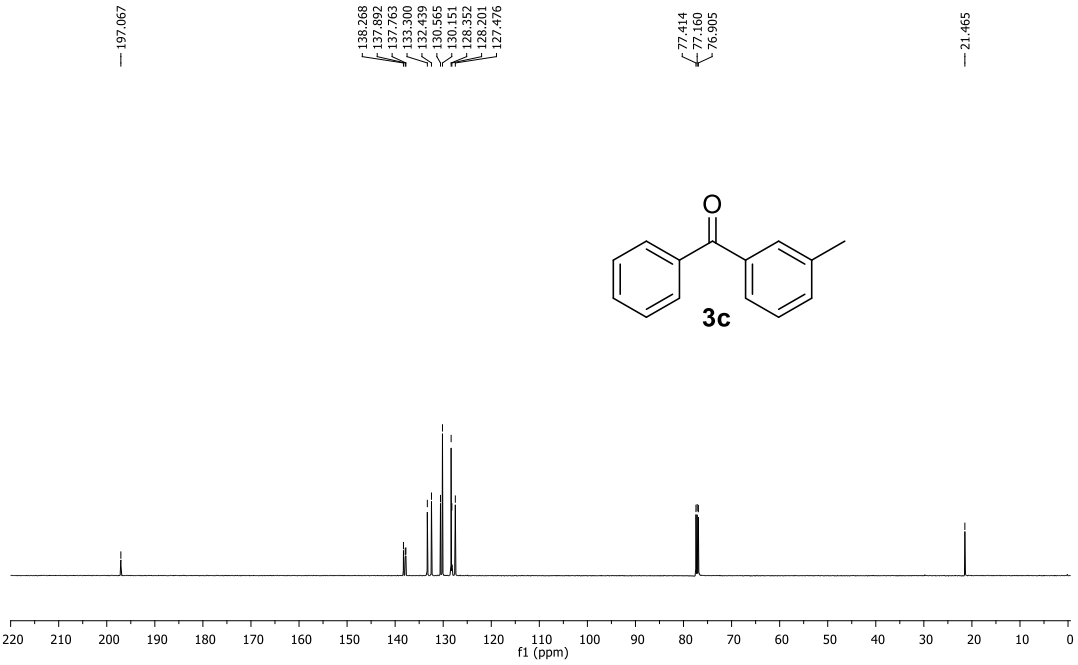
^{13}C NMR (126 MHz, $CDCl_3$)



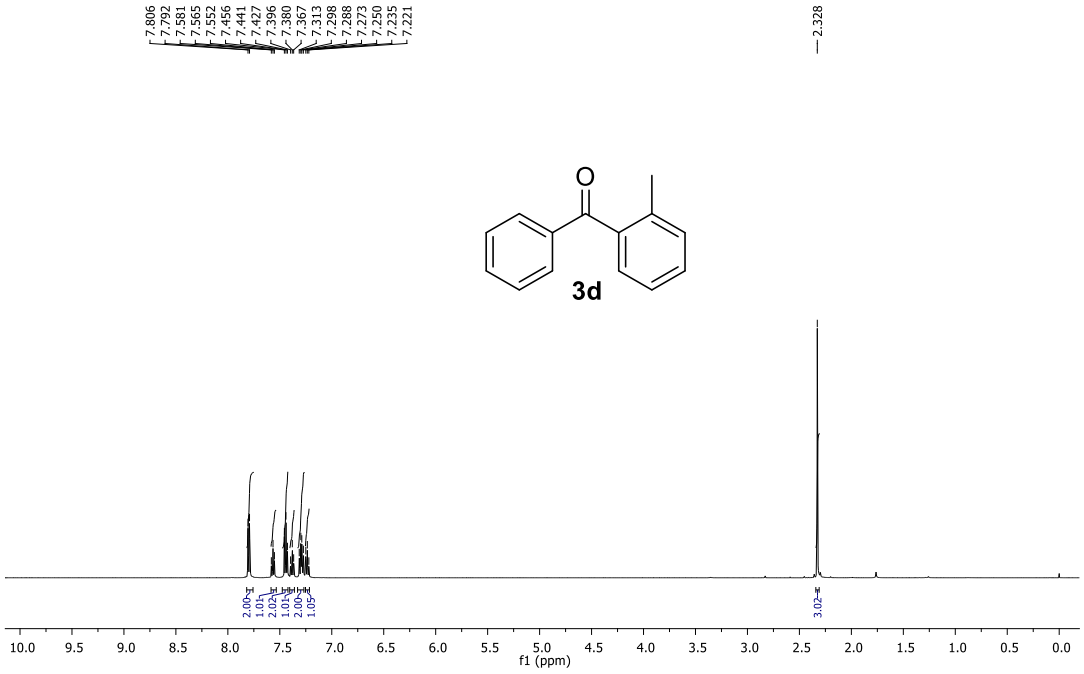
^{1}H NMR (500 MHz, $CDCl_3$)



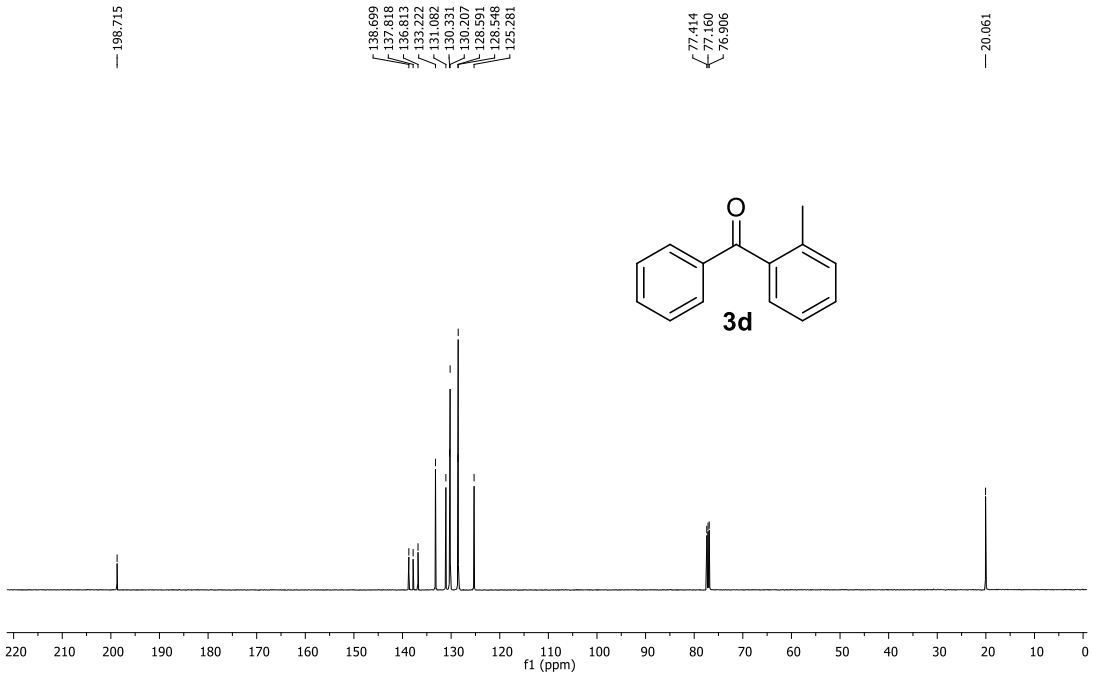
^{13}C NMR (126 MHz, $CDCl_3$)



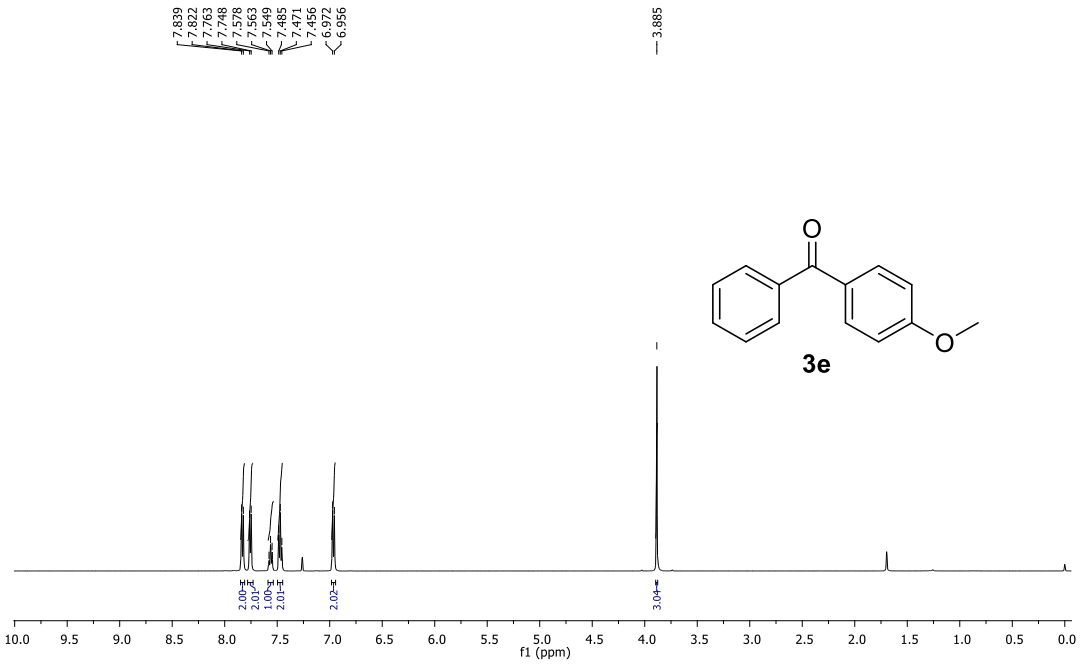
^{1}H NMR (500 MHz, $CDCl_3$)



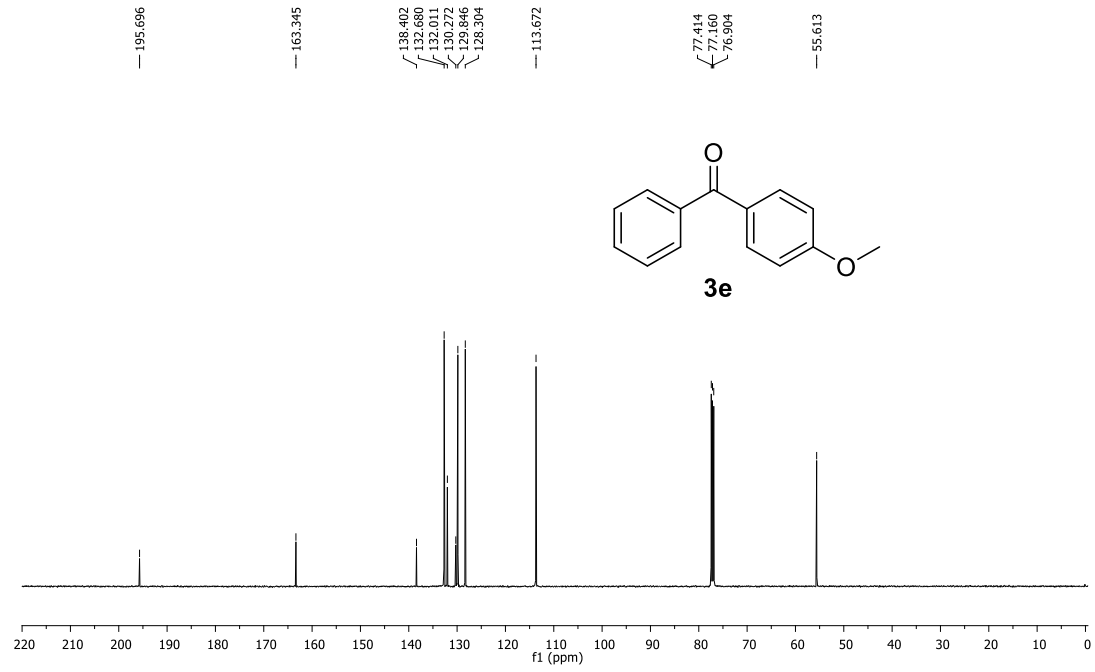
^{13}C NMR (126 MHz, $CDCl_3$)



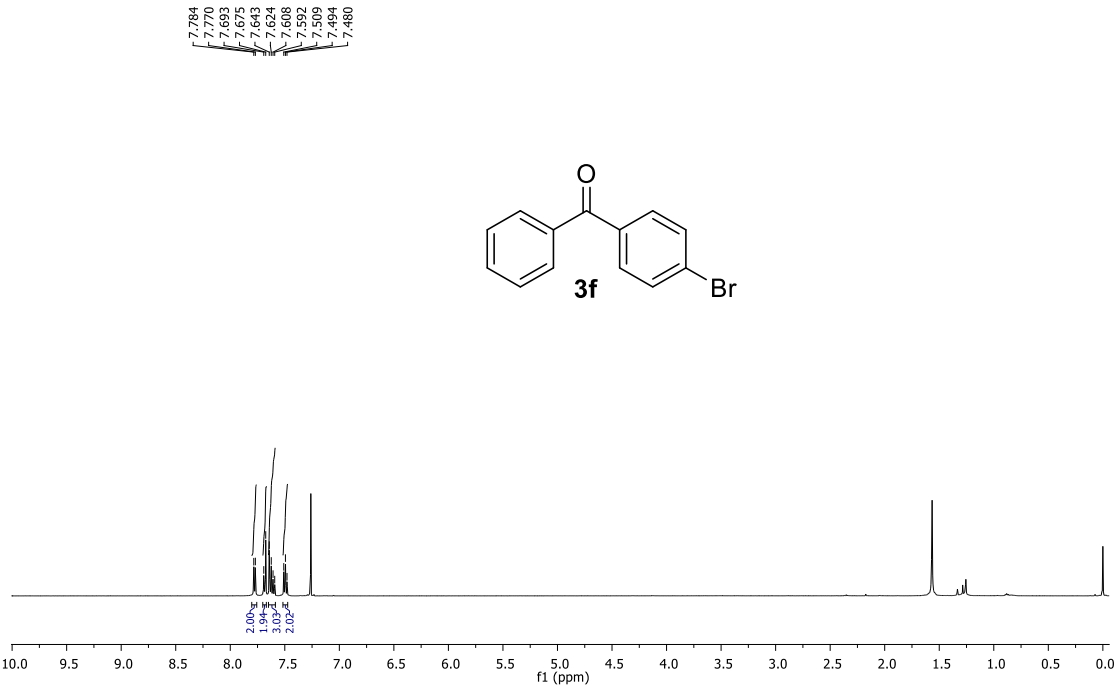
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

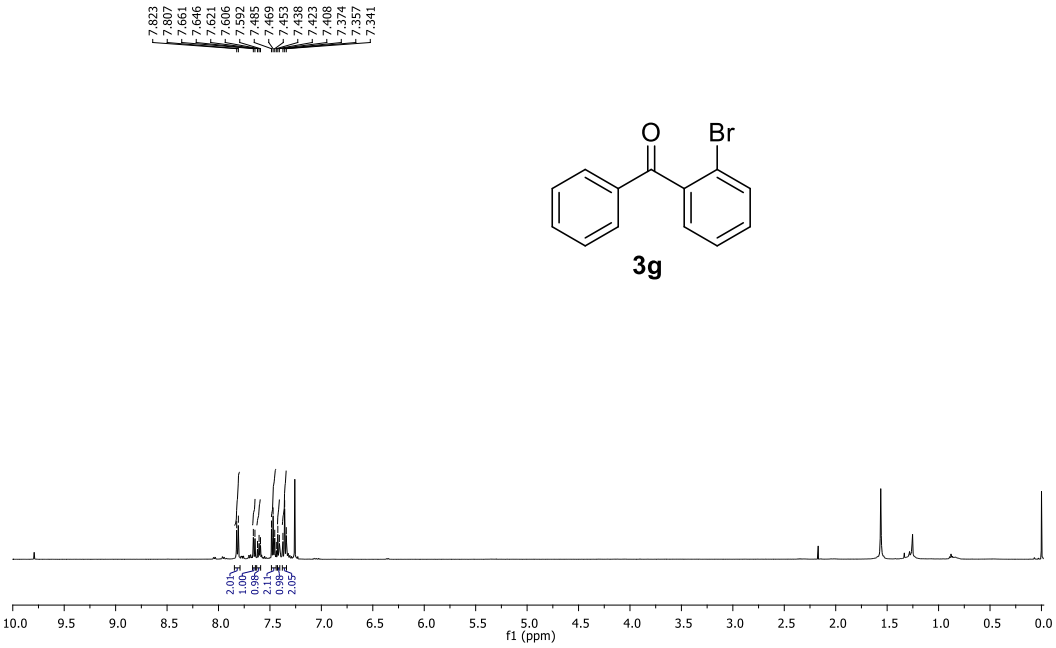


^{1}H NMR (500 MHz, $CDCl_3$)

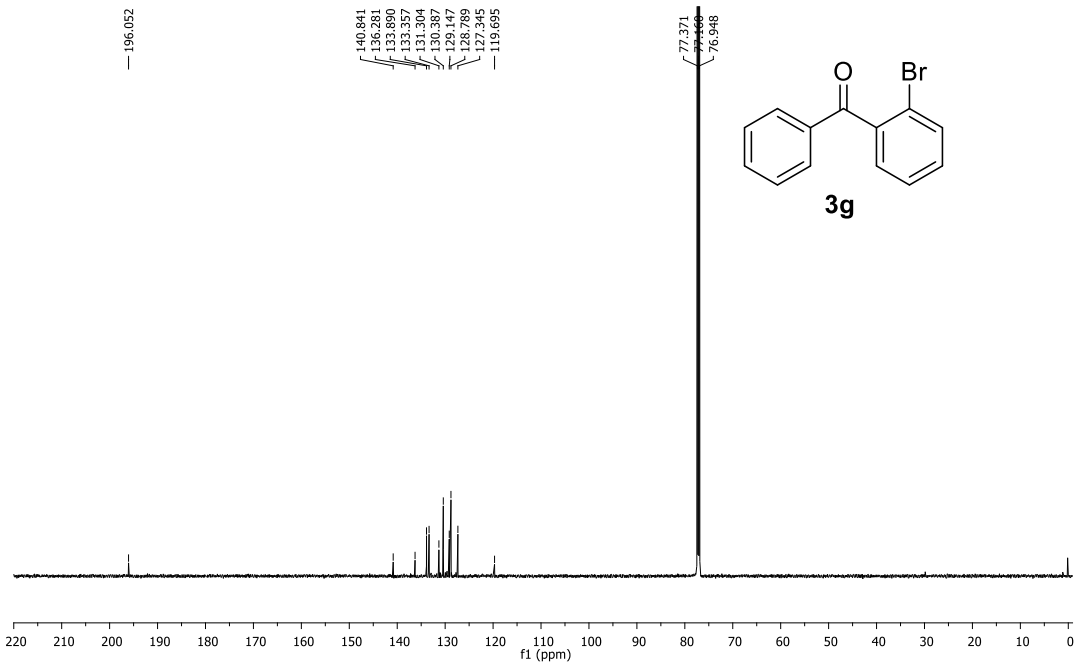


^{13}C NMR (126 MHz, $CDCl_3$)

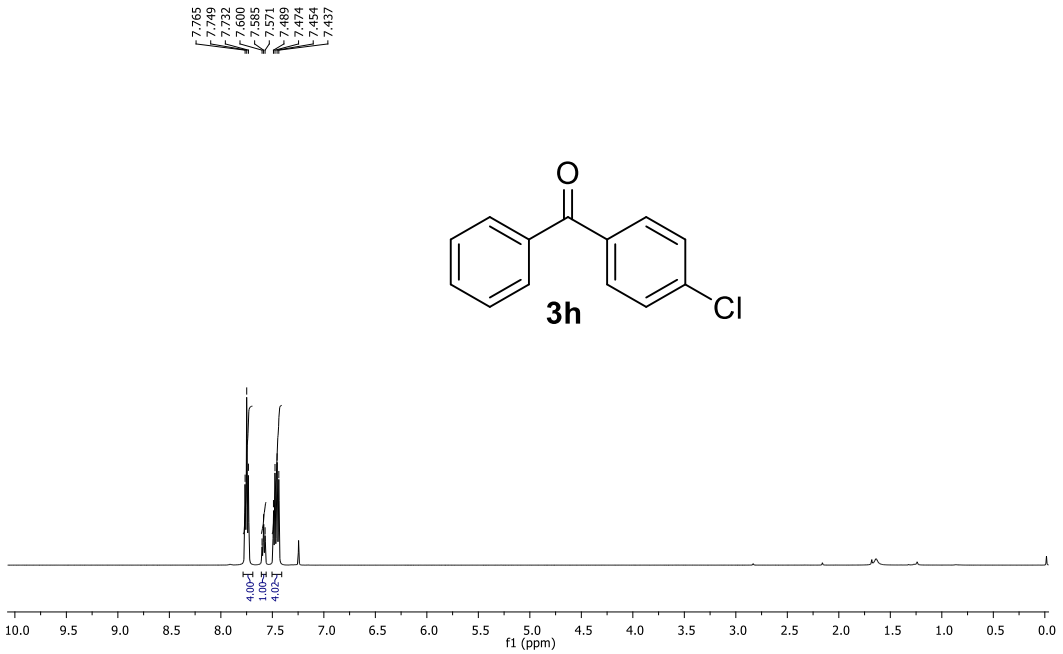
^{1}H NMR (500 MHz, $CDCl_3$)



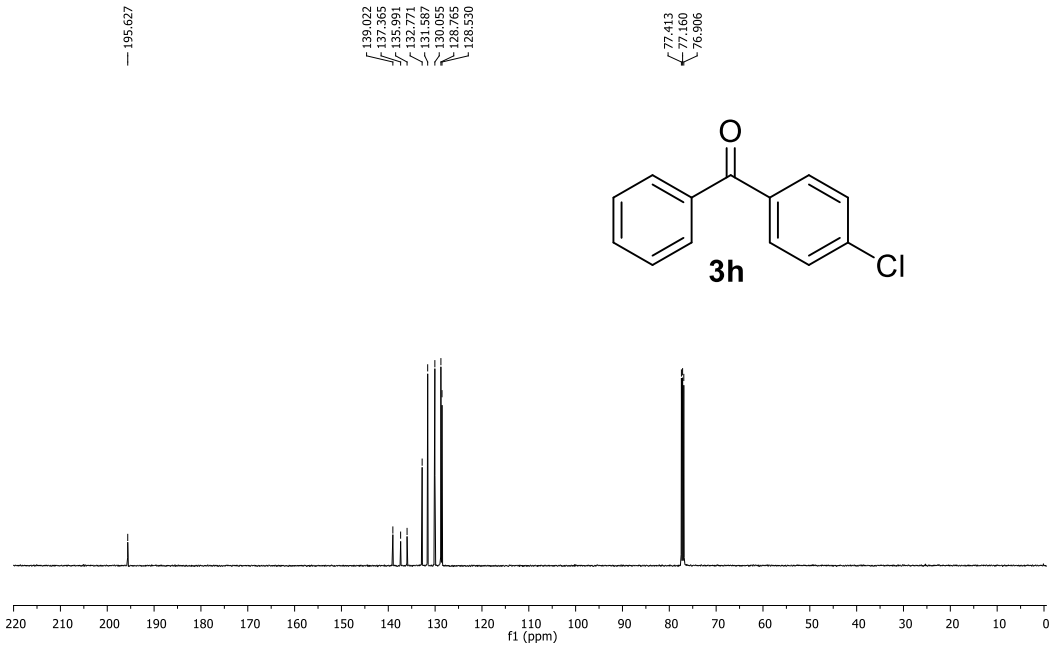
^{13}C NMR (126 MHz, $CDCl_3$)



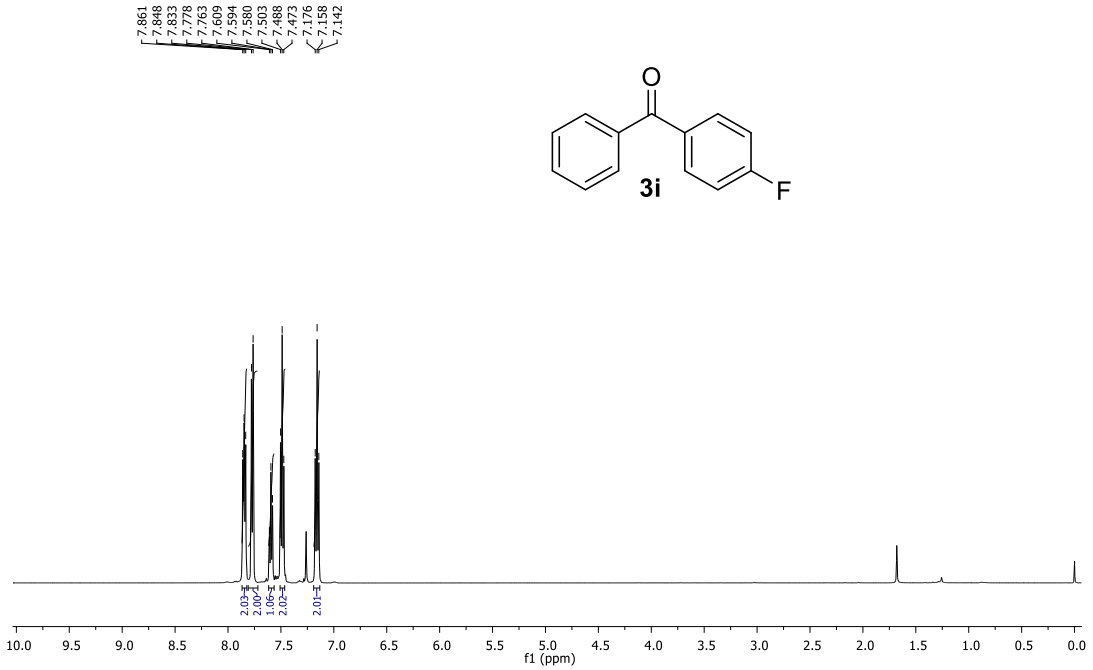
^{1}H NMR (500 MHz, $CDCl_3$)



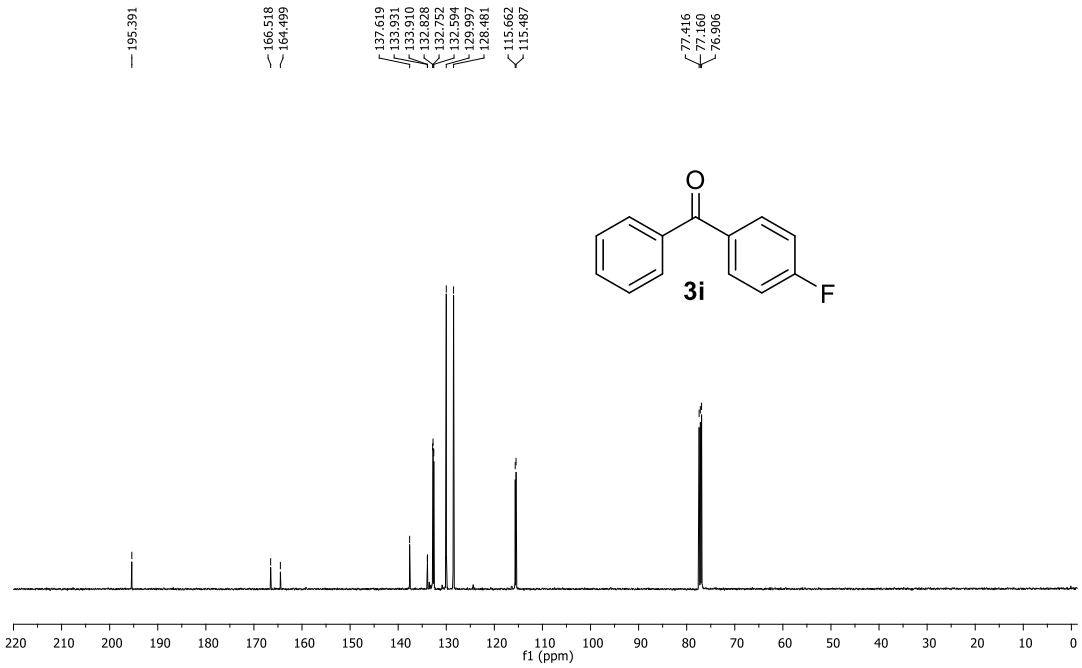
^{13}C NMR (126 MHz, $CDCl_3$)



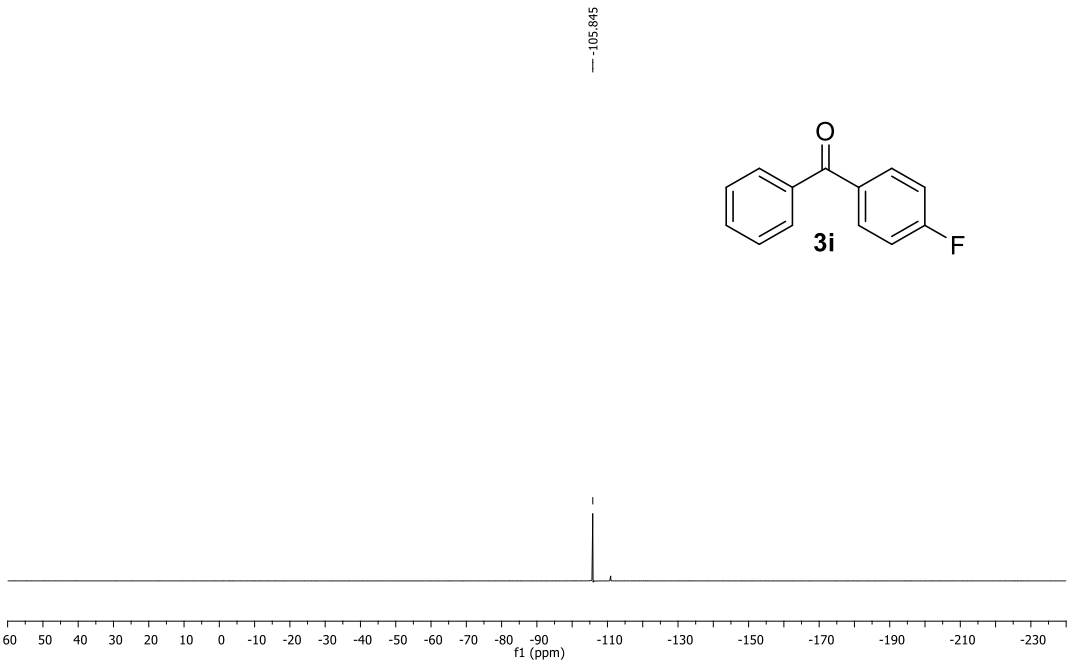
^{1}H NMR (500 MHz, $CDCl_3$)



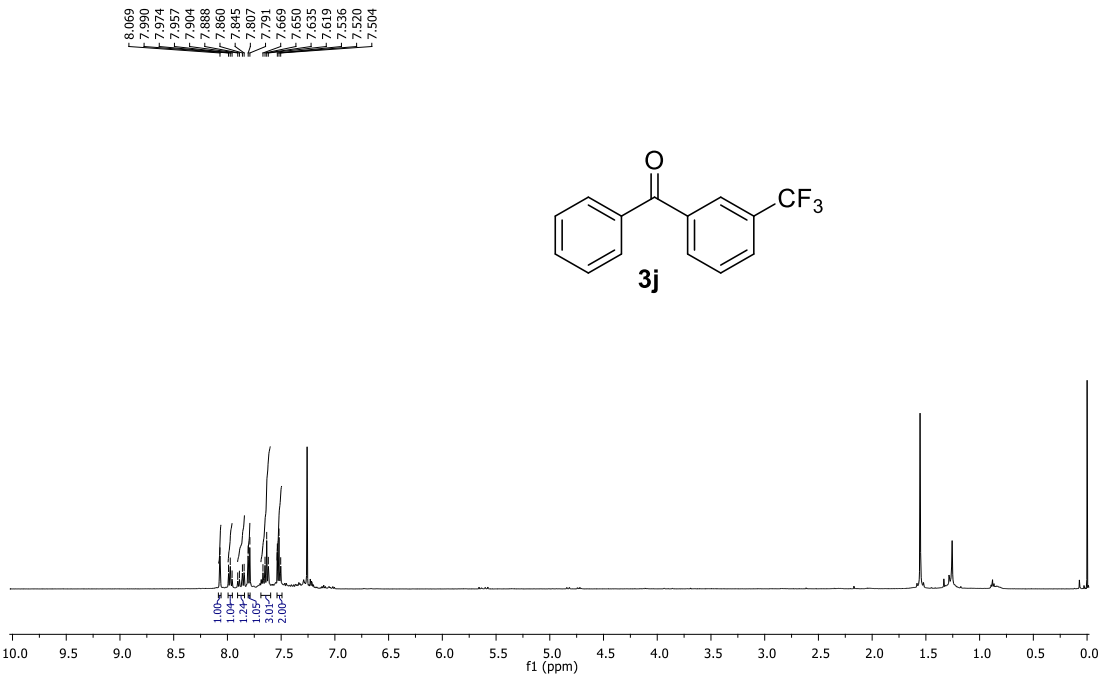
^{13}C NMR (126 MHz, $CDCl_3$)



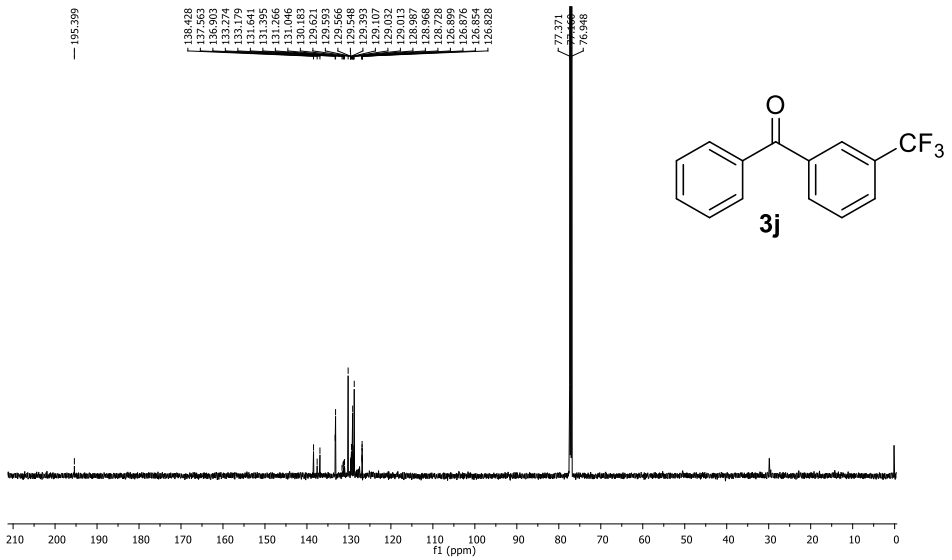
^{19}F NMR (471 MHz, $CDCl_3$)



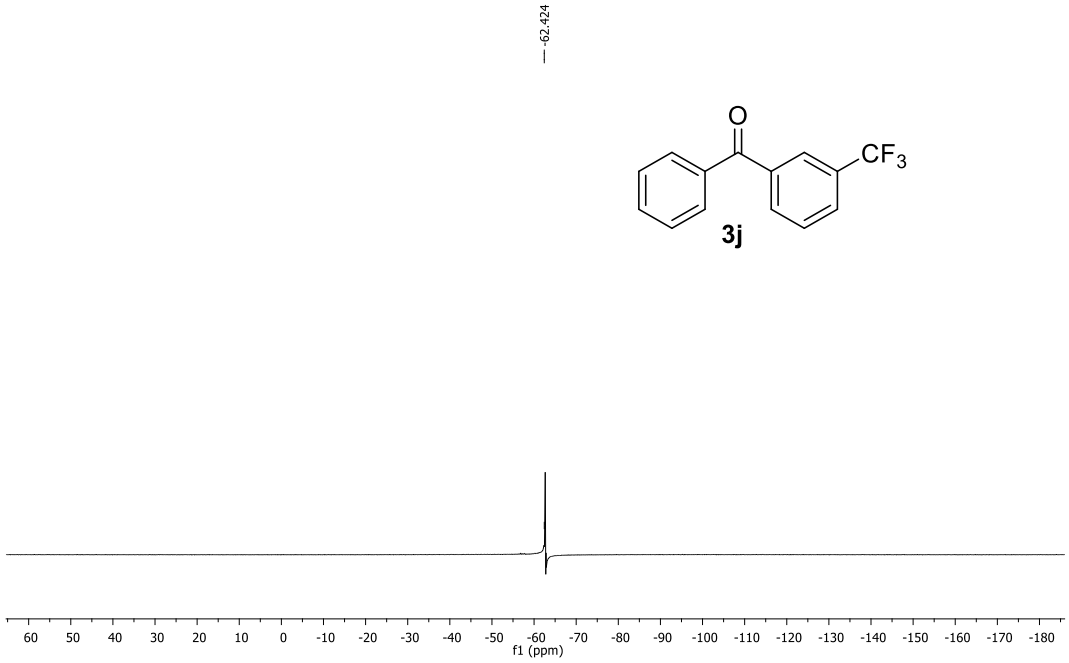
^{1}H NMR (500 MHz, $CDCl_3$)



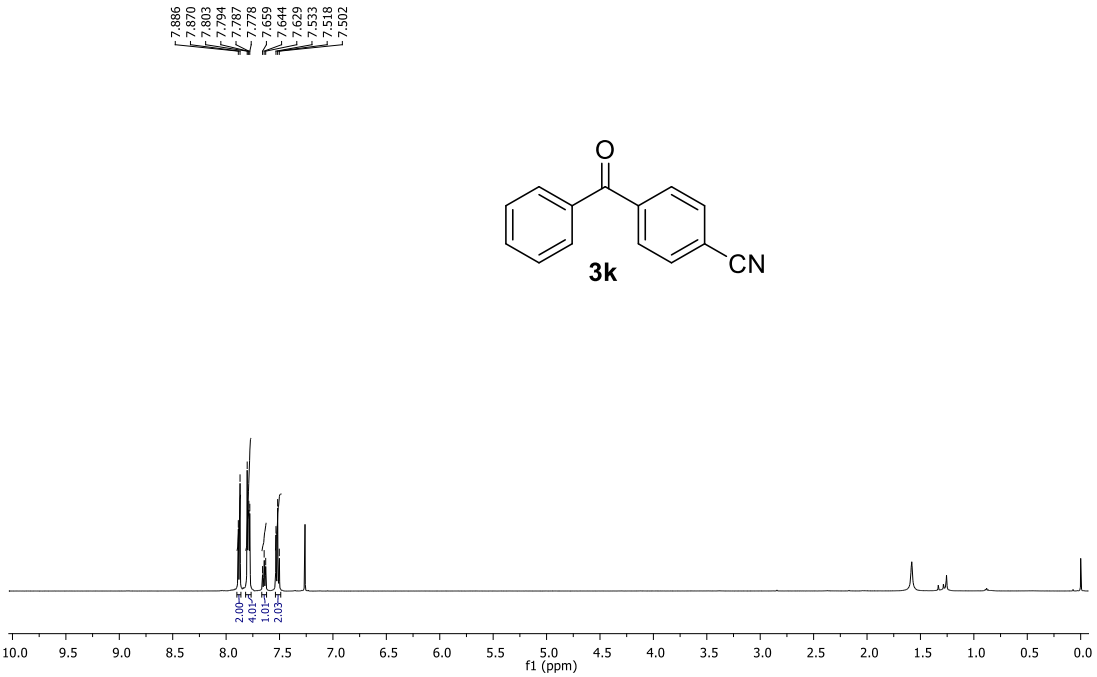
^{13}C NMR (126 MHz, $CDCl_3$)



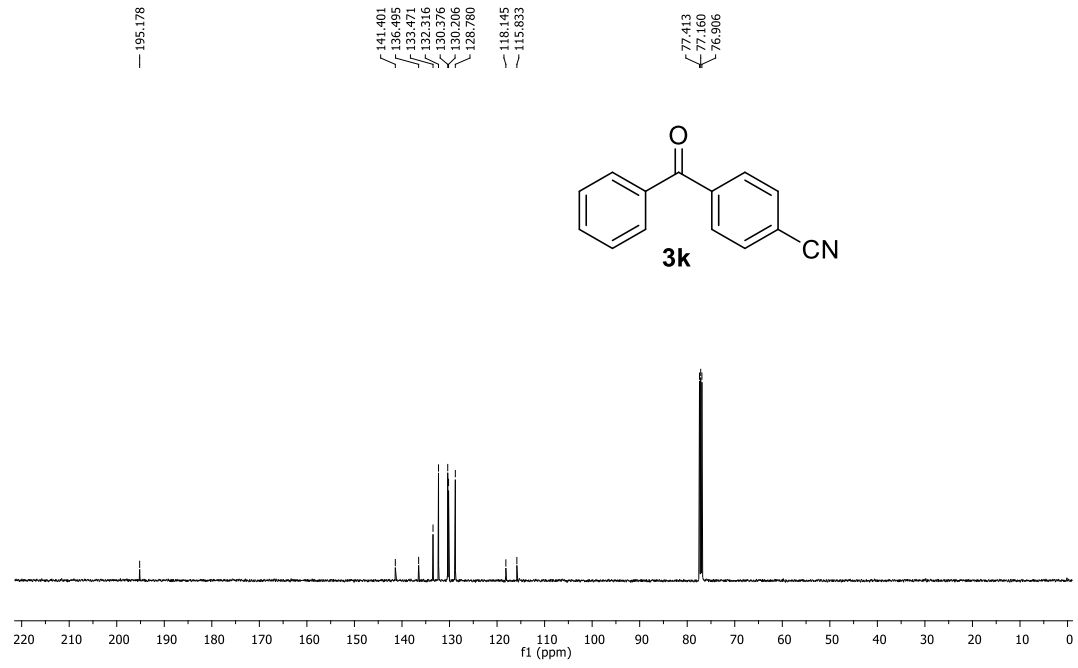
^{19}F NMR (471 MHz, $CDCl_3$)



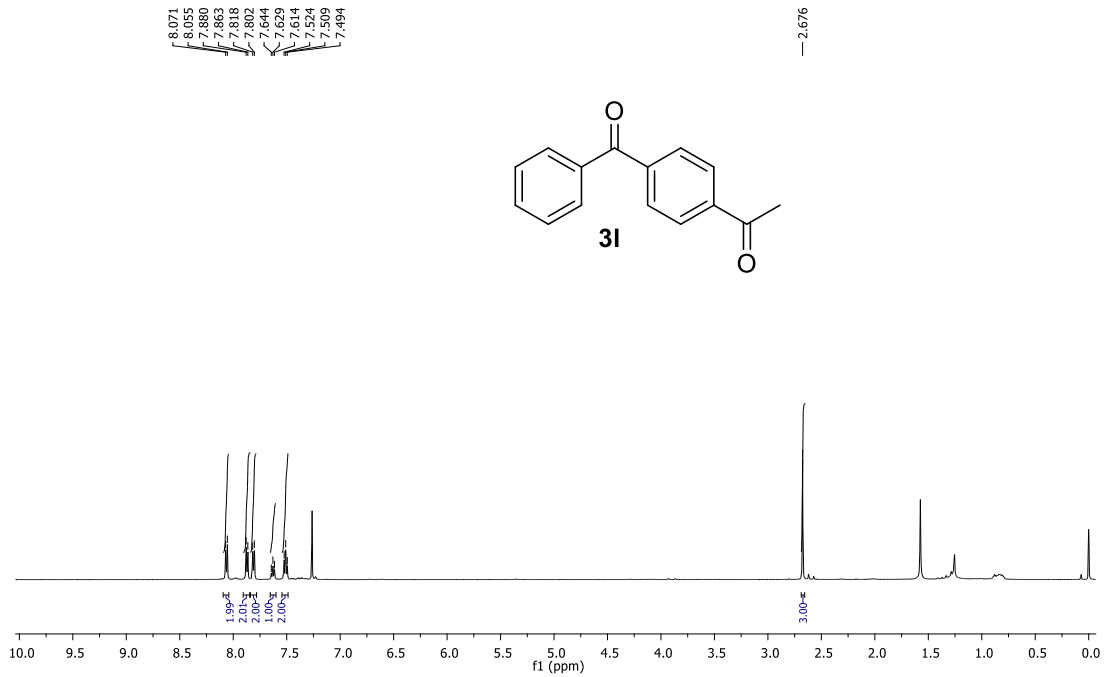
^{1}H NMR (500 MHz, $CDCl_3$)



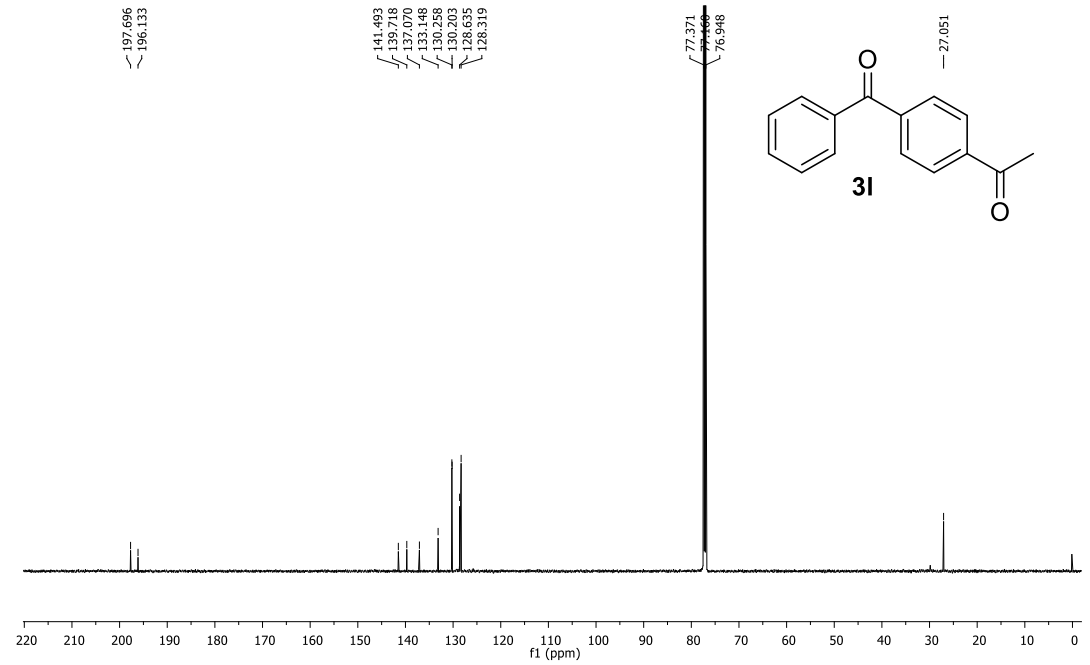
^{13}C NMR (126 MHz, $CDCl_3$)



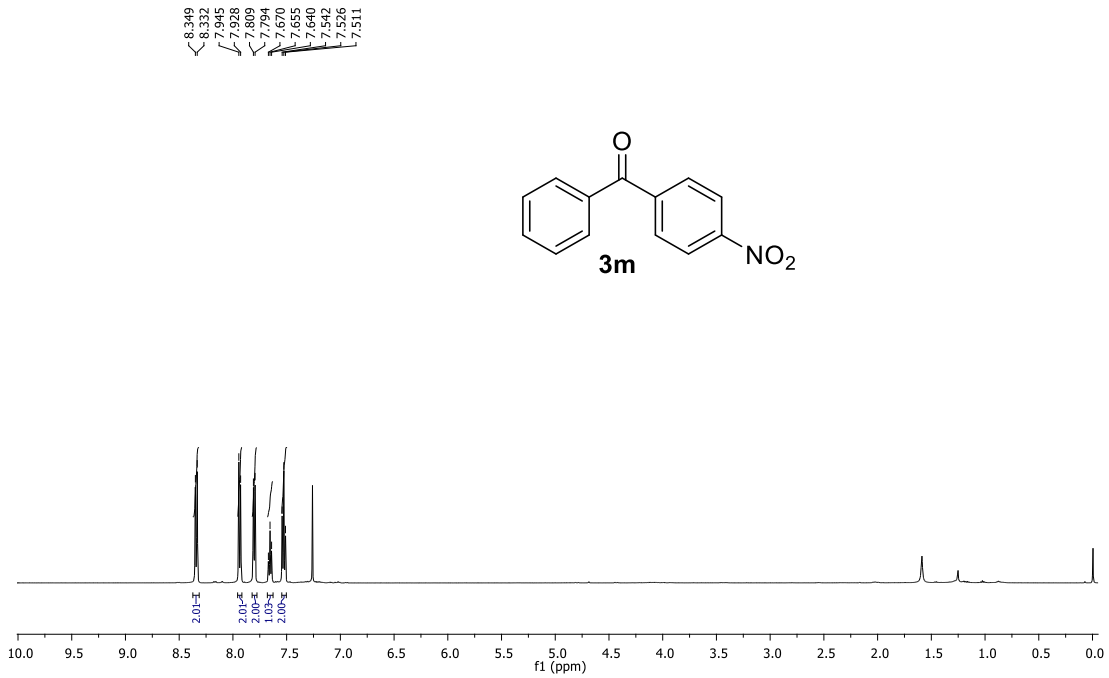
^{1}H NMR (500 MHz, $CDCl_3$)



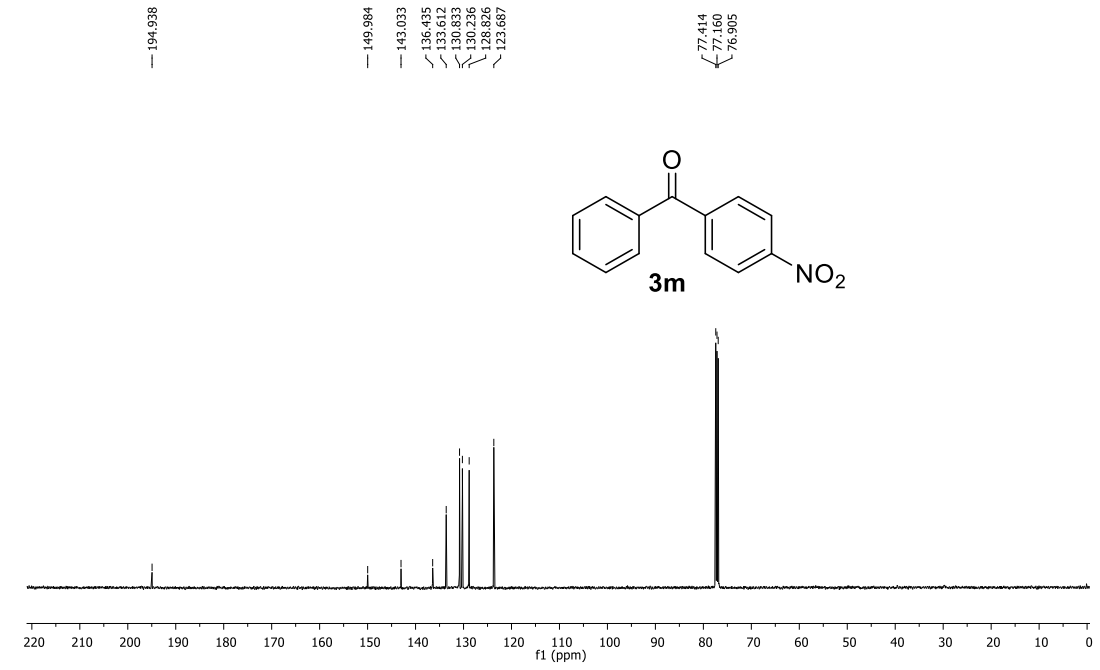
^{13}C NMR (126 MHz, $CDCl_3$)



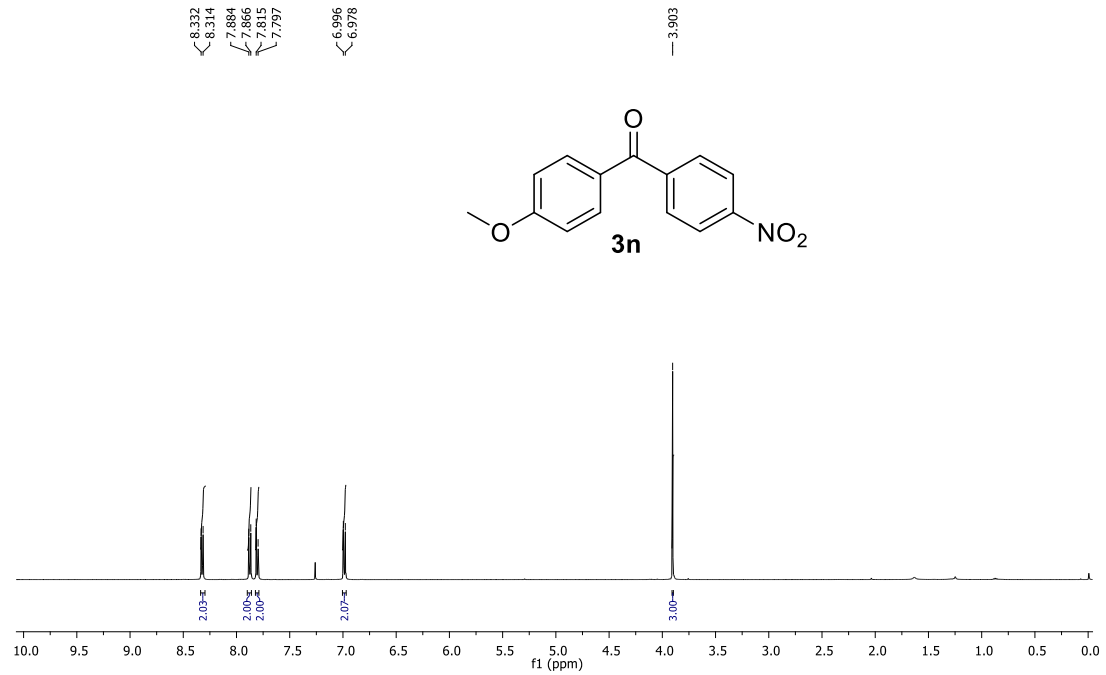
^{1}H NMR (500 MHz, $CDCl_3$)



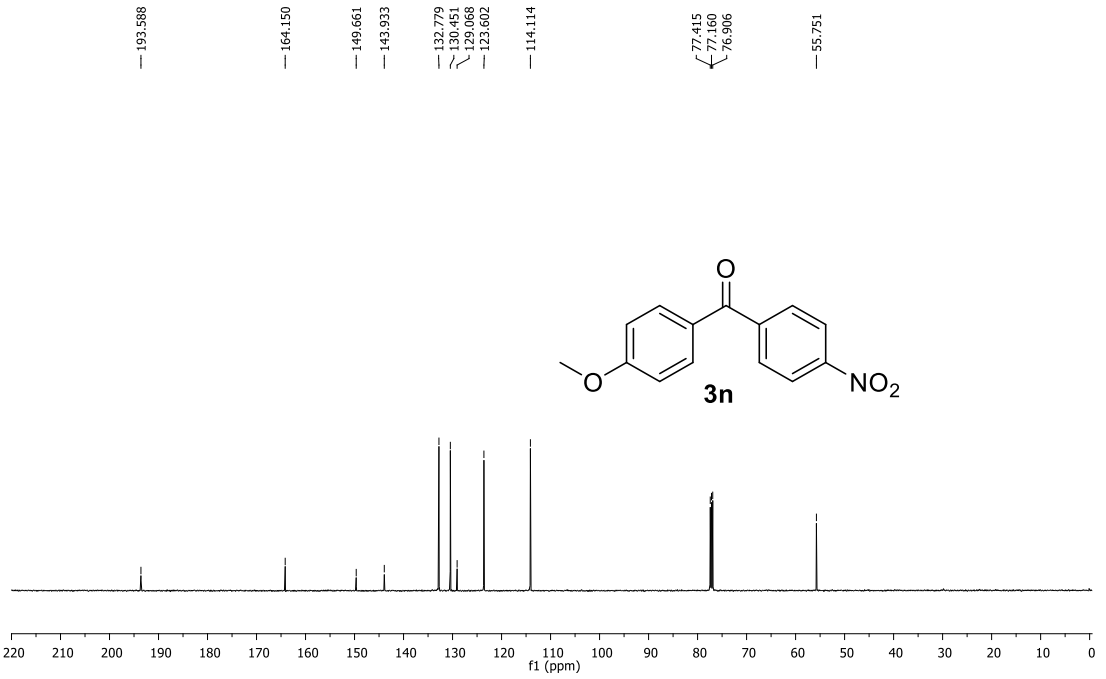
^{13}C NMR (126 MHz, $CDCl_3$)



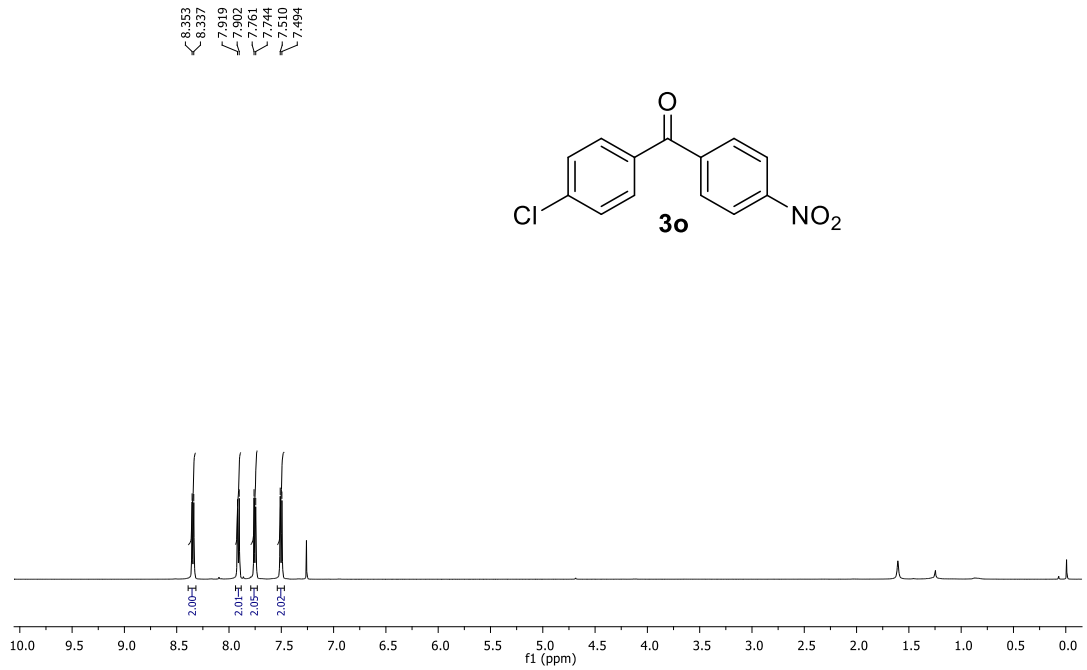
^{1}H NMR (500 MHz, $CDCl_3$)



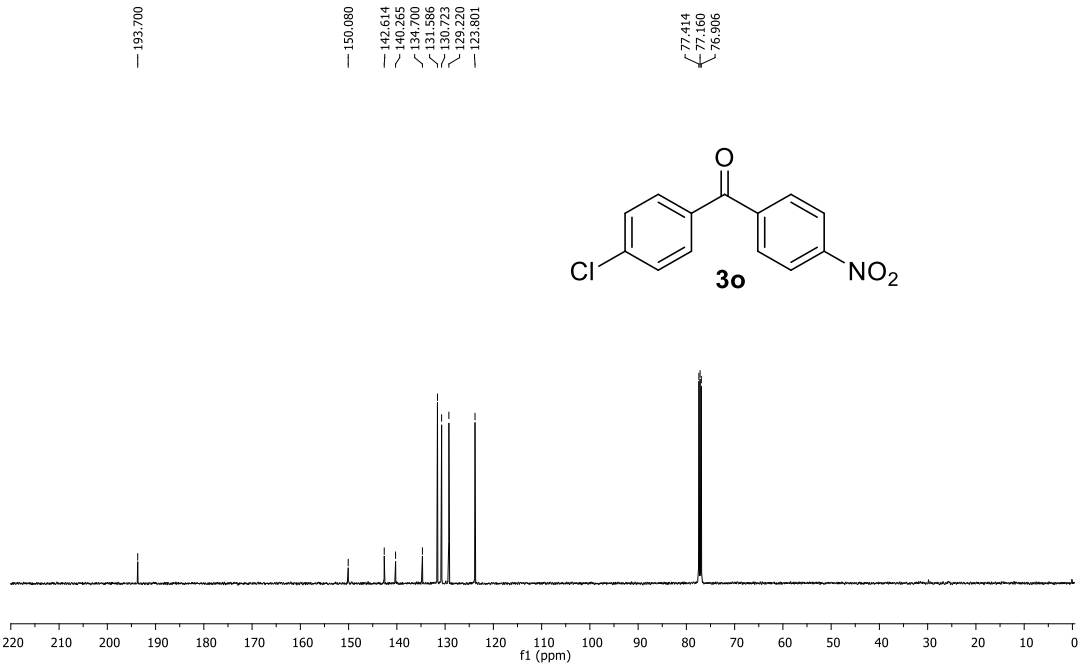
^{13}C NMR (126 MHz, $CDCl_3$)



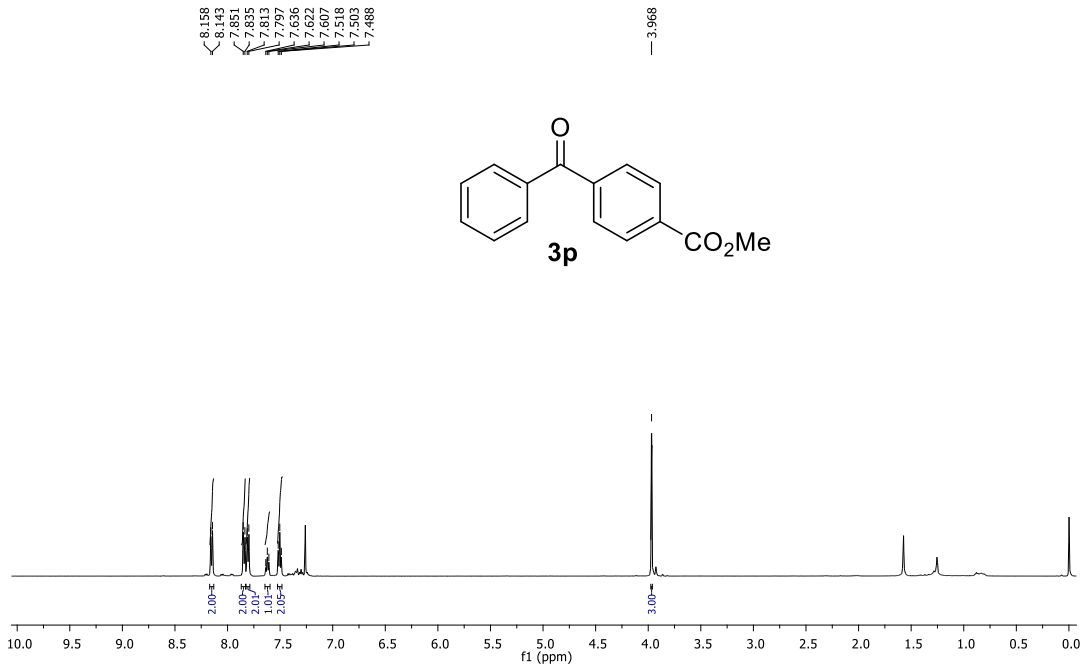
^{1}H NMR (500 MHz, $CDCl_3$)



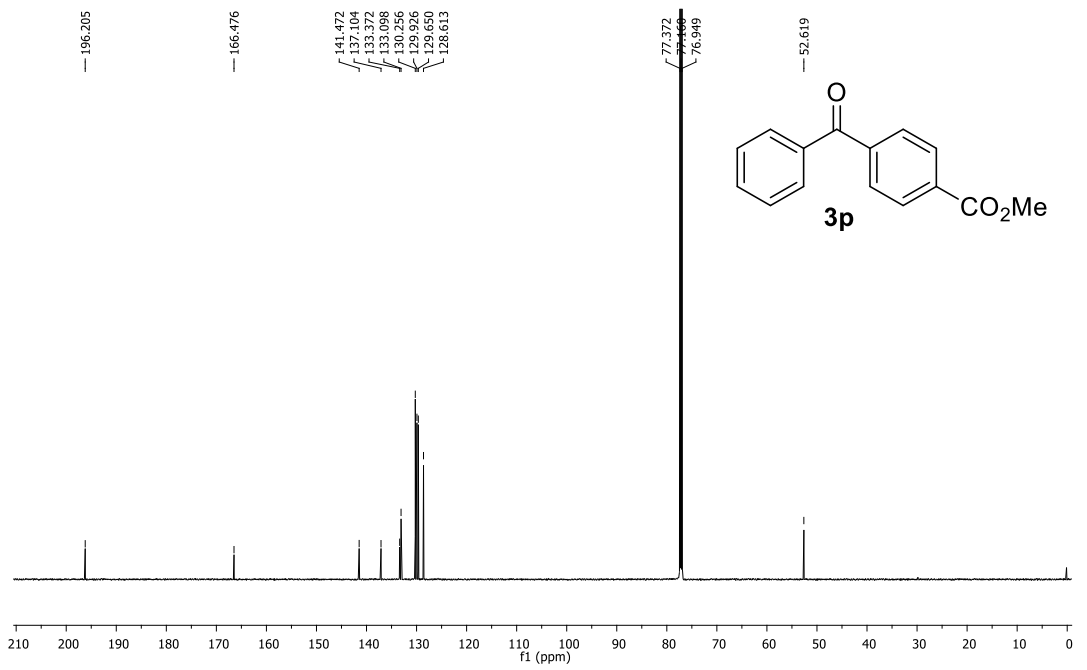
^{13}C NMR (126 MHz, $CDCl_3$)



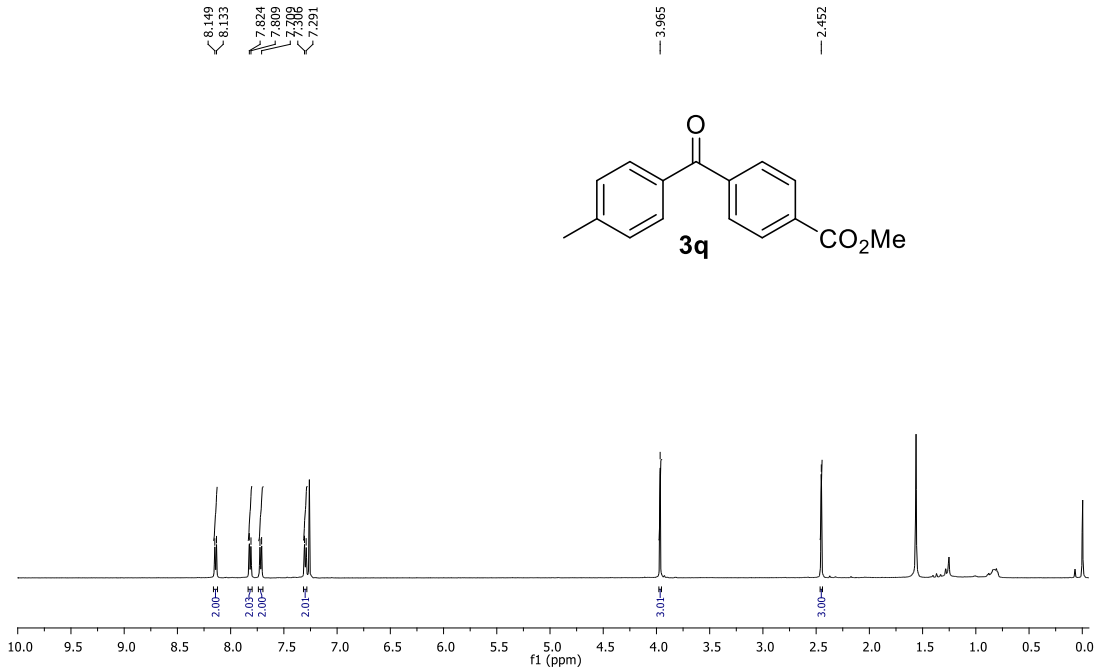
^{1}H NMR (500 MHz, $CDCl_3$)



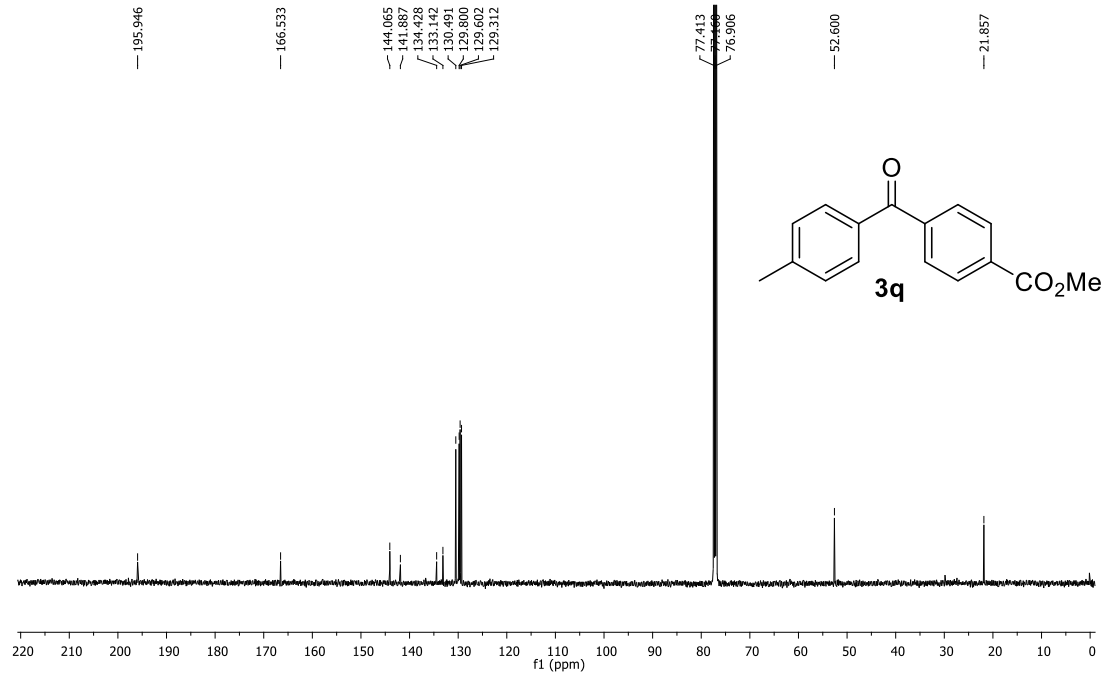
^{13}C NMR (126 MHz, $CDCl_3$)



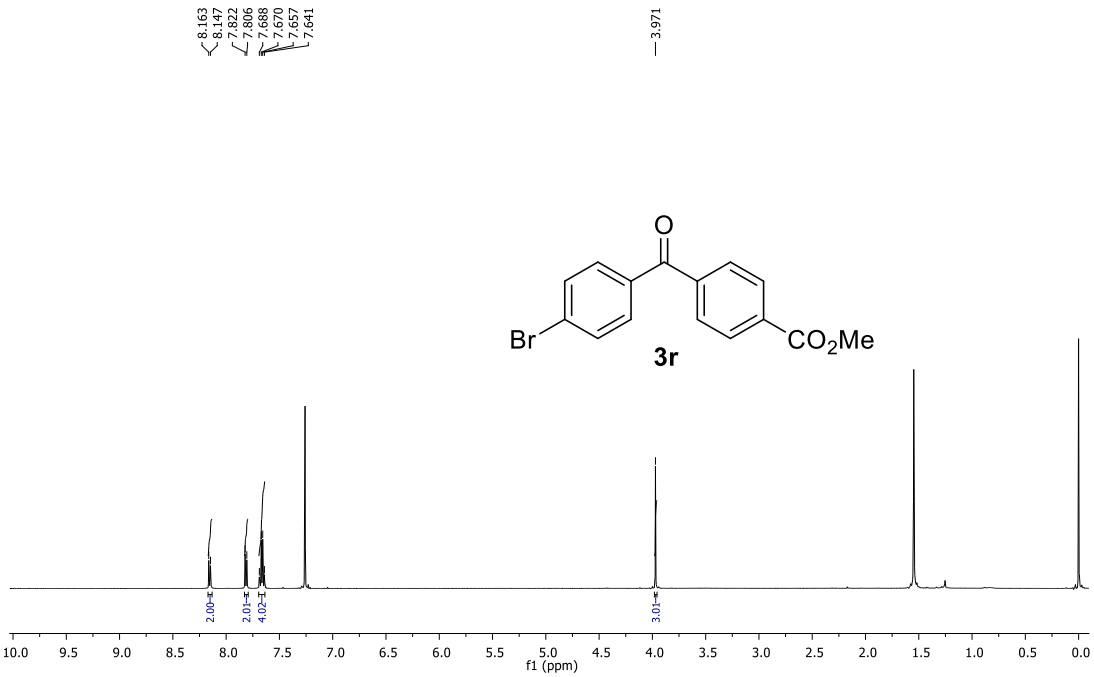
^{1}H NMR (500 MHz, $CDCl_3$)



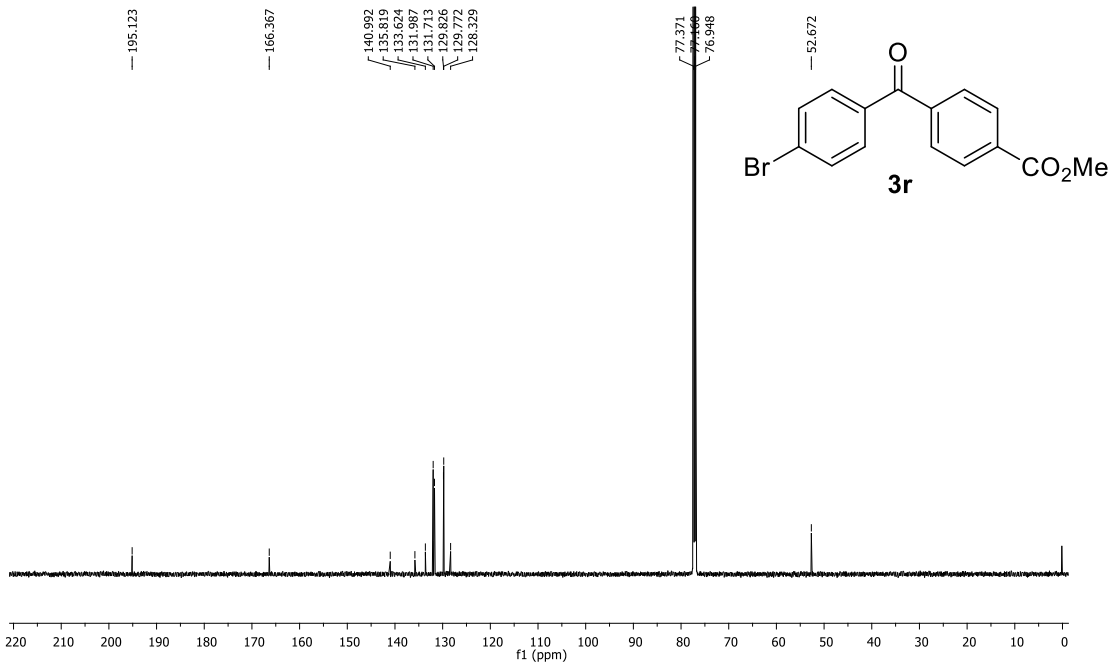
^{13}C NMR (126 MHz, $CDCl_3$)



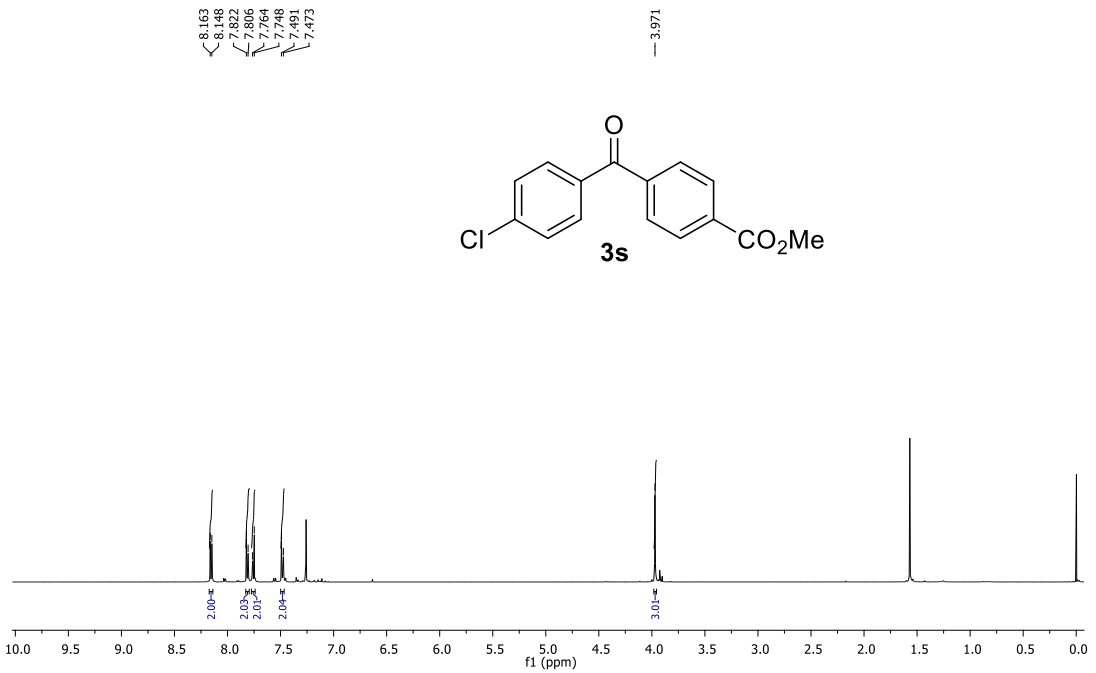
^{1}H NMR (500 MHz, $CDCl_3$)



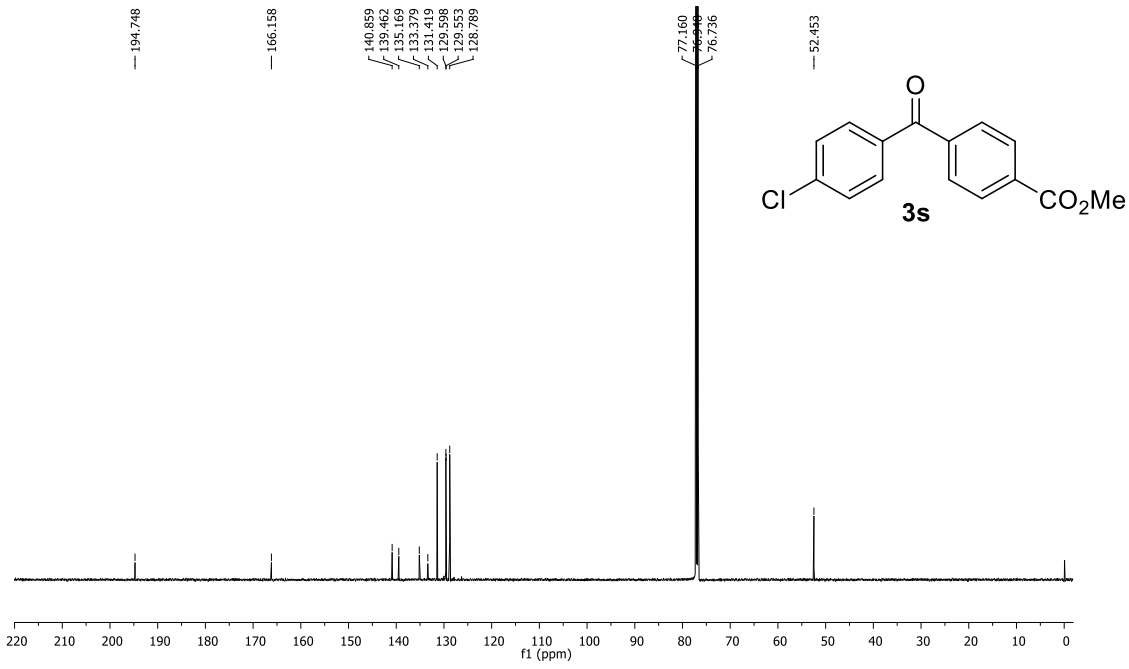
^{13}C NMR (126 MHz, $CDCl_3$)



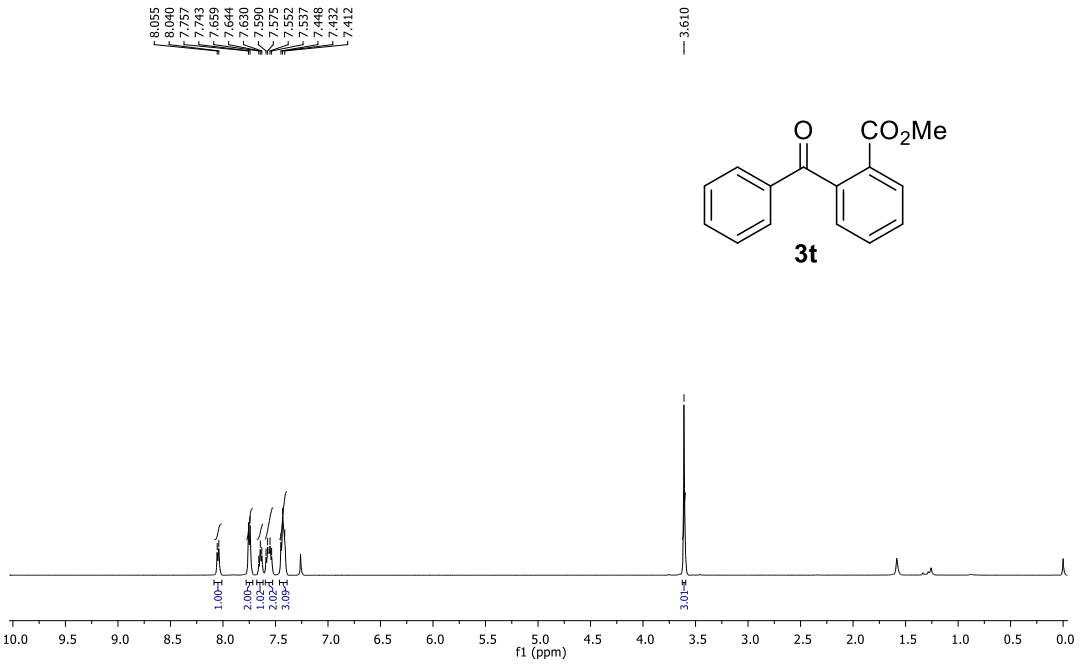
^{1}H NMR (500 MHz, $CDCl_3$)



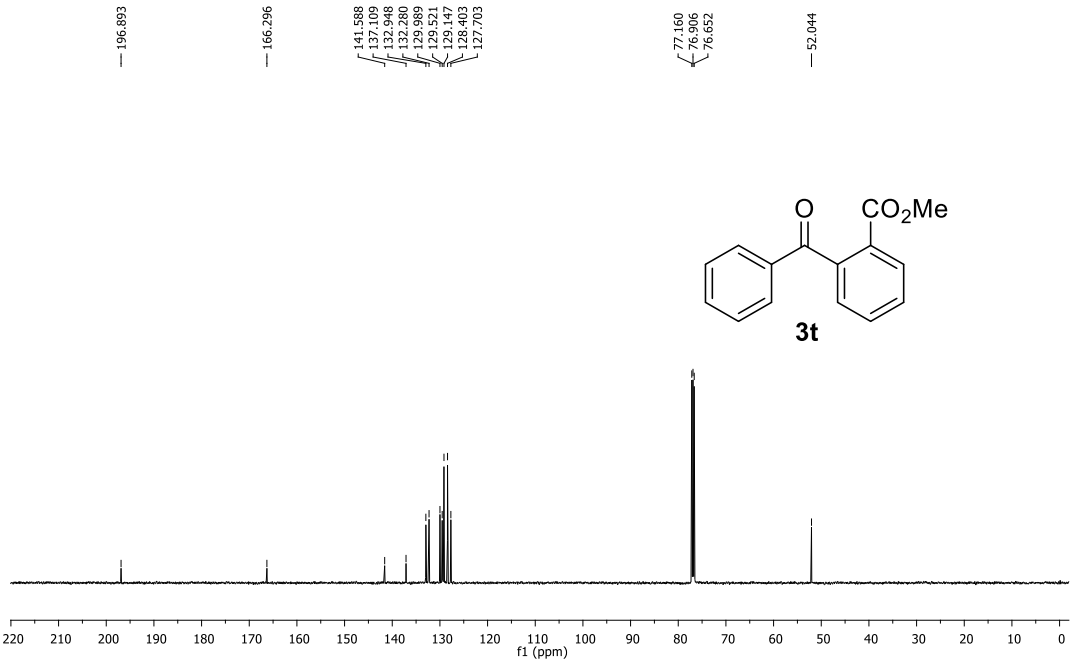
^{13}C NMR (126 MHz, $CDCl_3$)



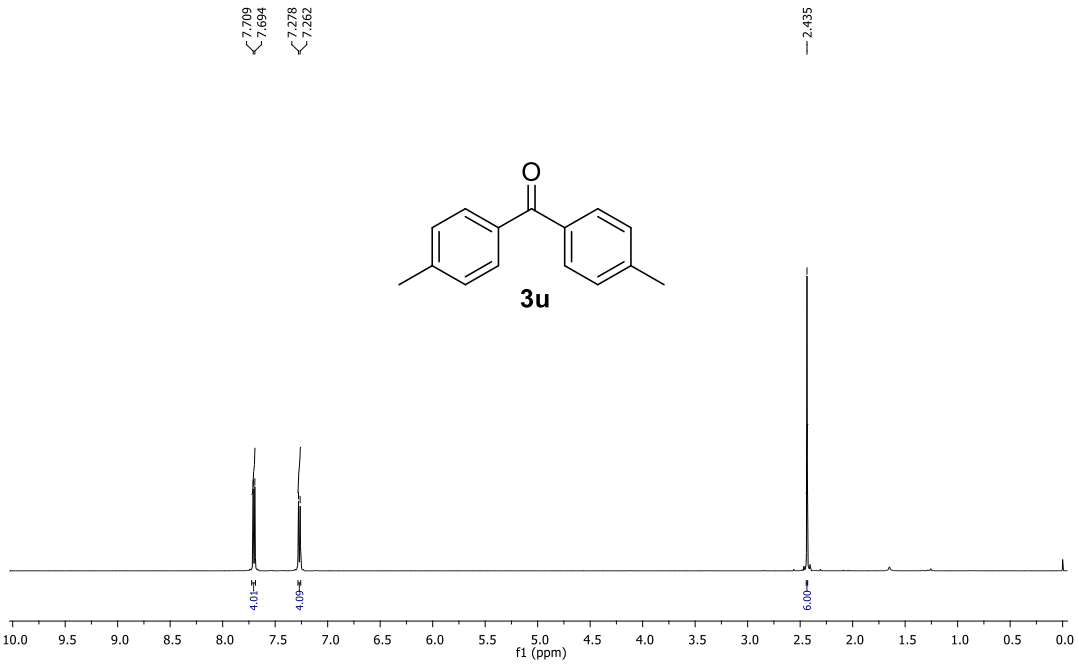
^{1}H NMR (500 MHz, $CDCl_3$)



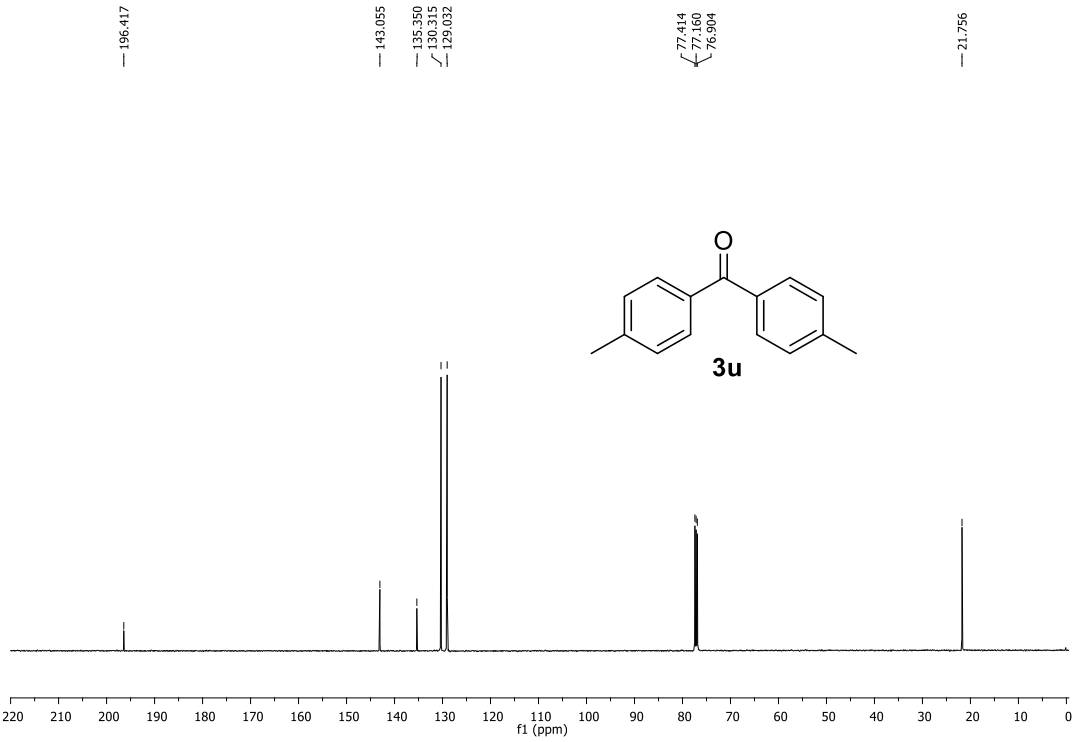
^{13}C NMR (126 MHz, $CDCl_3$)



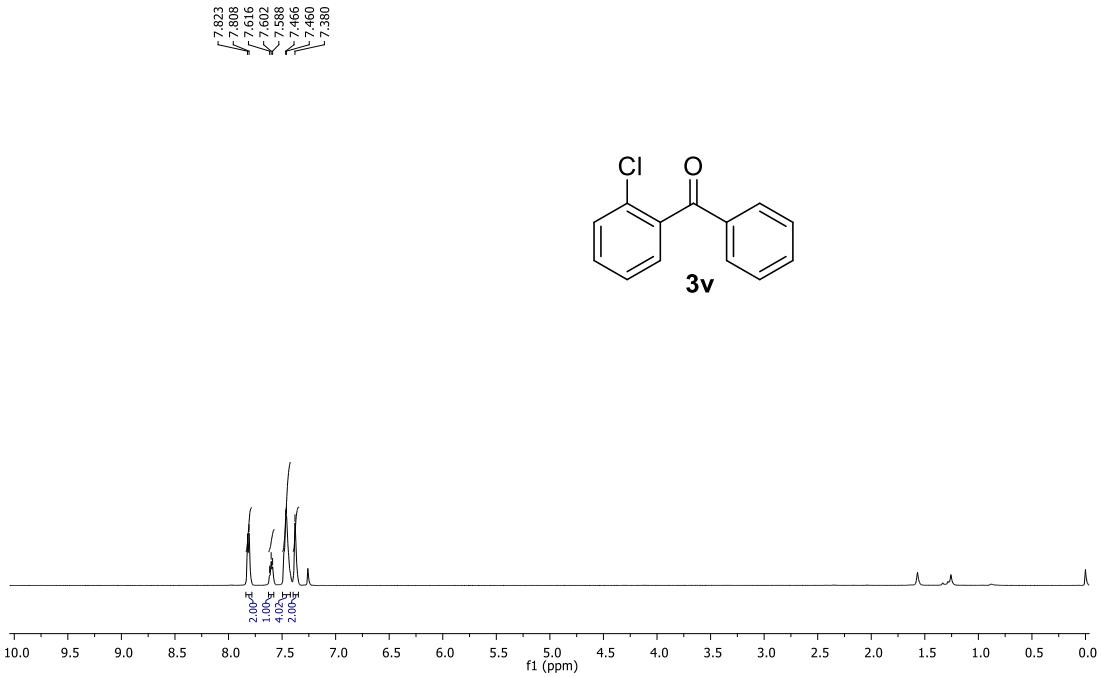
^{1}H NMR (500 MHz, $CDCl_3$)



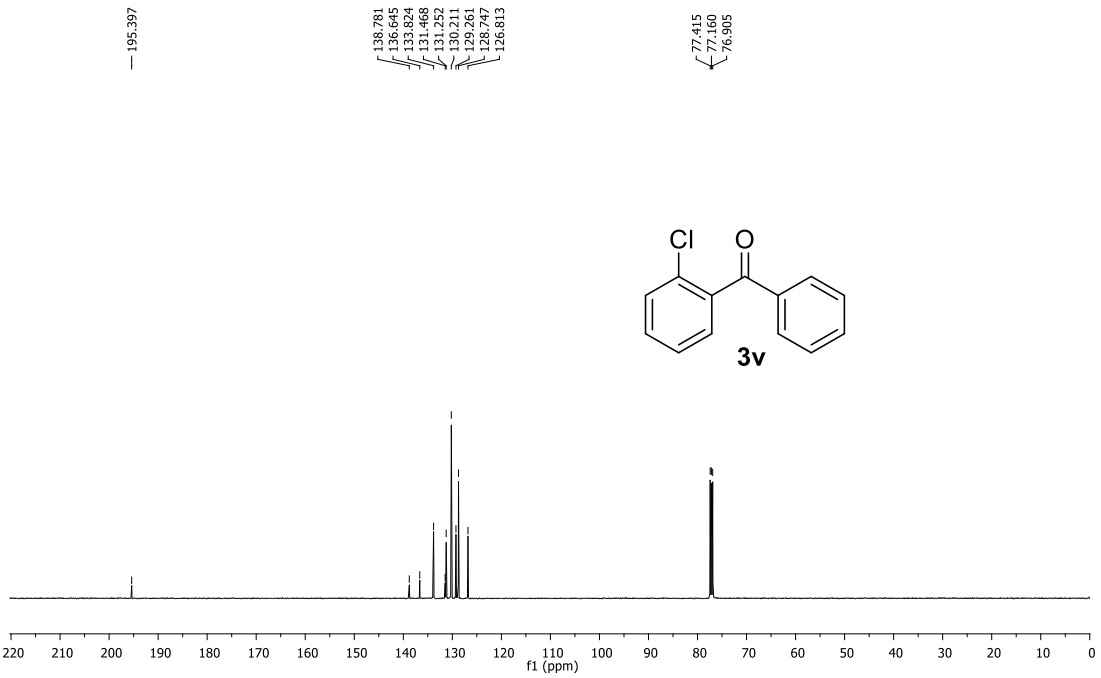
^{13}C NMR (126 MHz, $CDCl_3$)



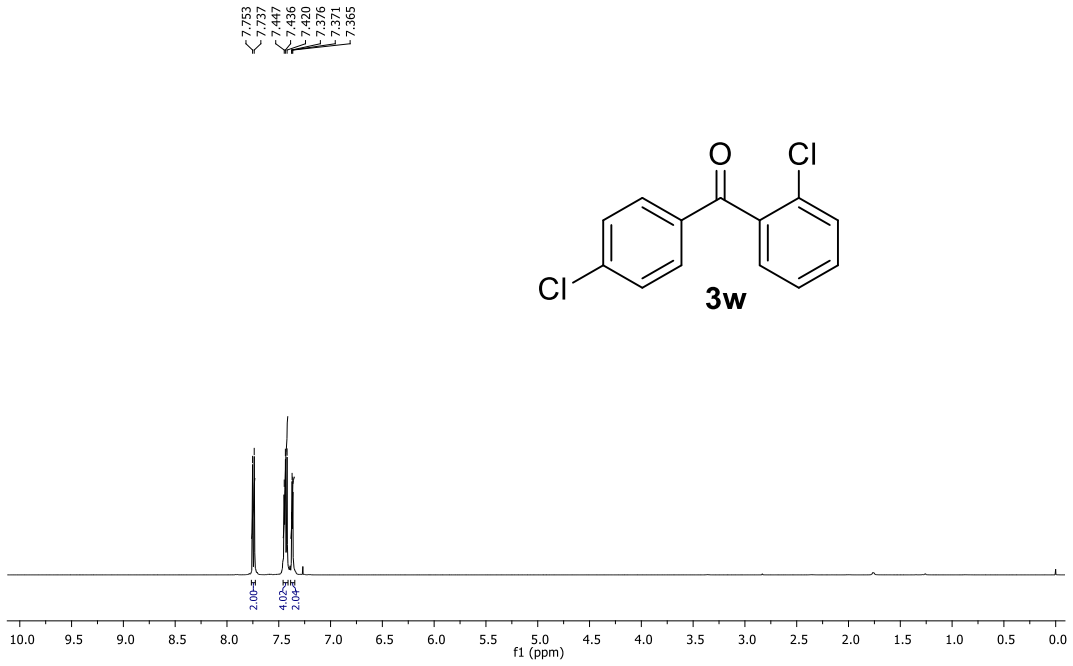
^{1}H NMR (500 MHz, $CDCl_3$)



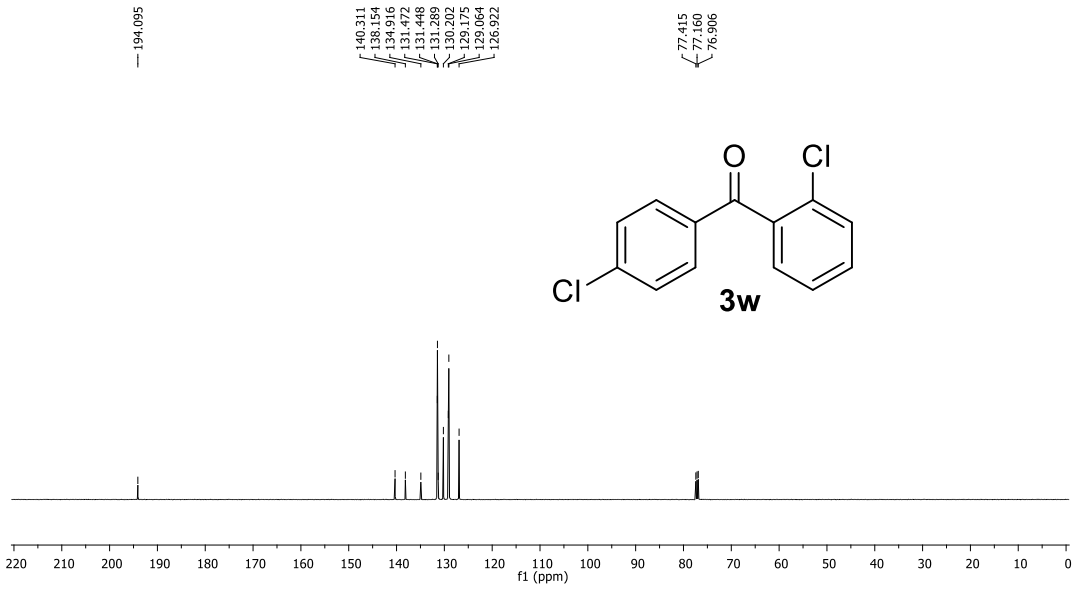
^{13}C NMR (126 MHz, $CDCl_3$)



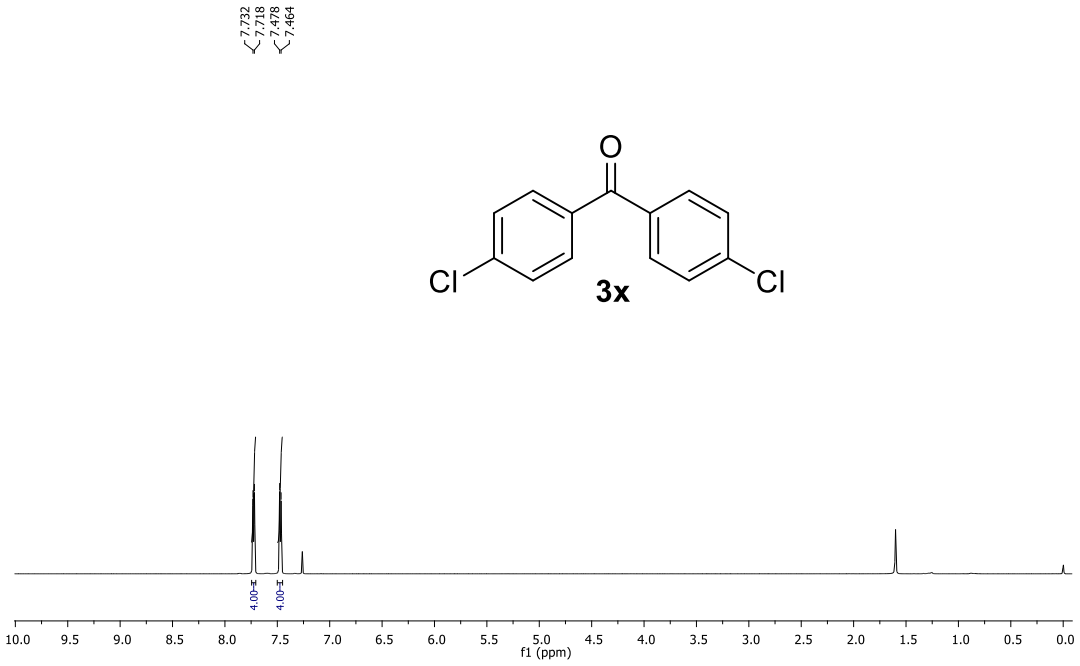
^{1}H NMR (500 MHz, $CDCl_3$)



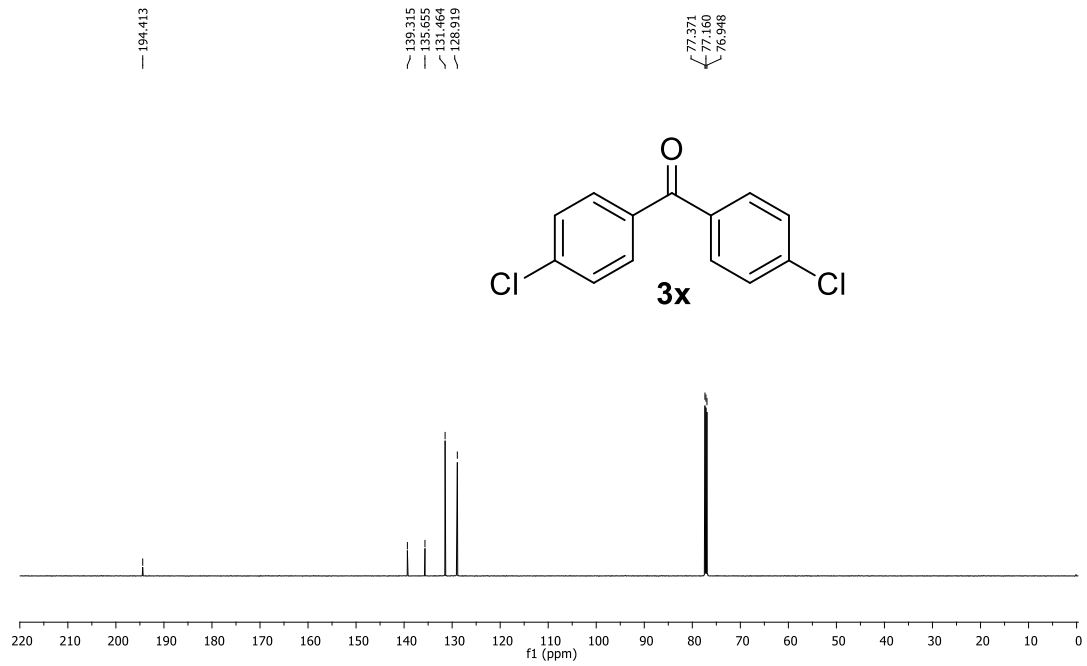
^{13}C NMR (126 MHz, $CDCl_3$)



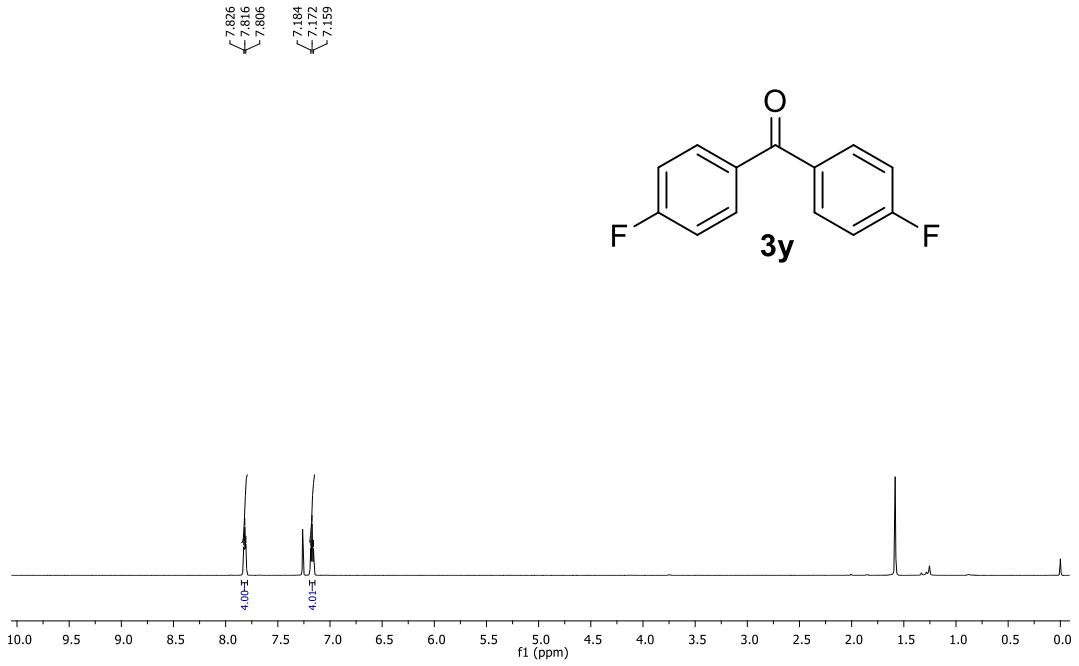
^{1}H NMR (600 MHz, $CDCl_3$)



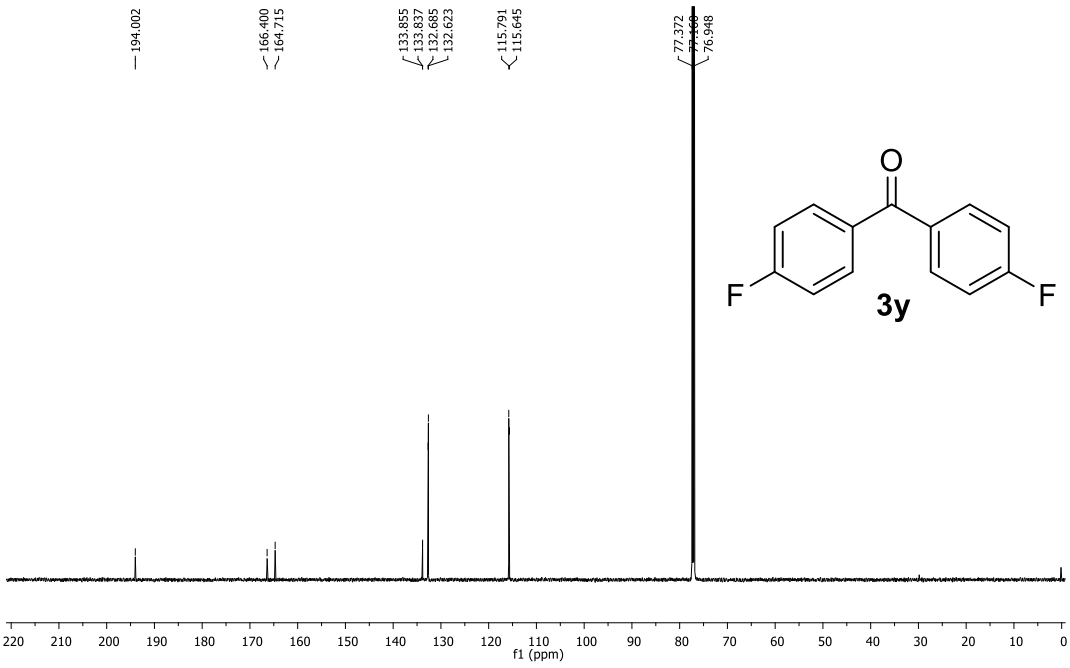
^{13}C NMR (150 MHz, $CDCl_3$)



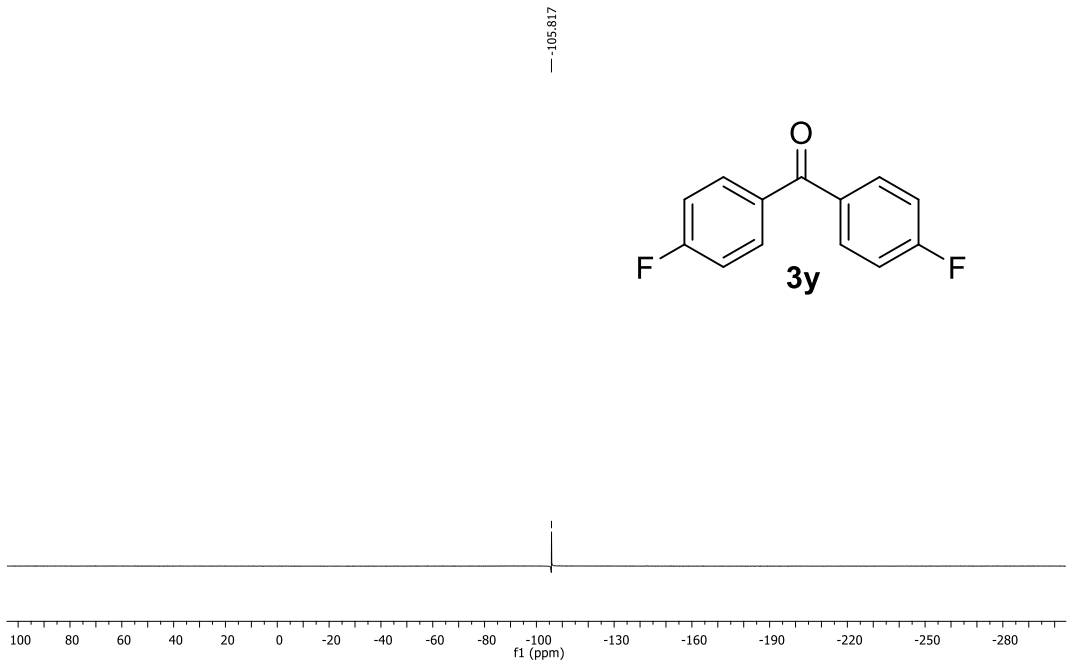
^{1}H NMR (600 MHz, $CDCl_3$)



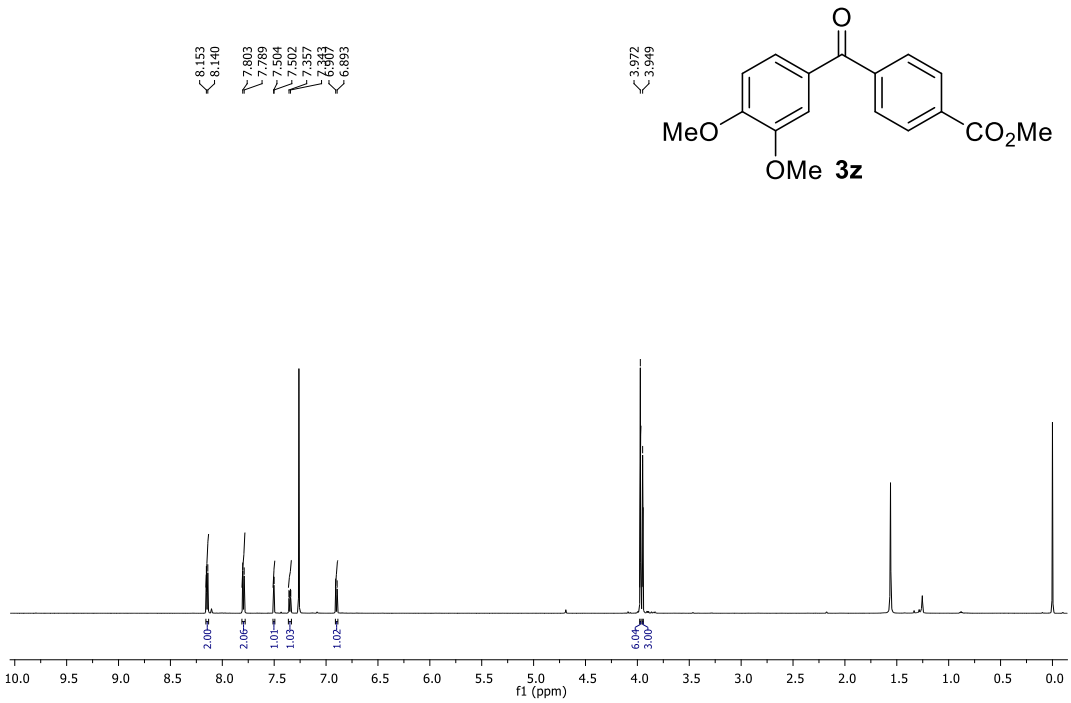
^{13}C NMR (150 MHz, $CDCl_3$)



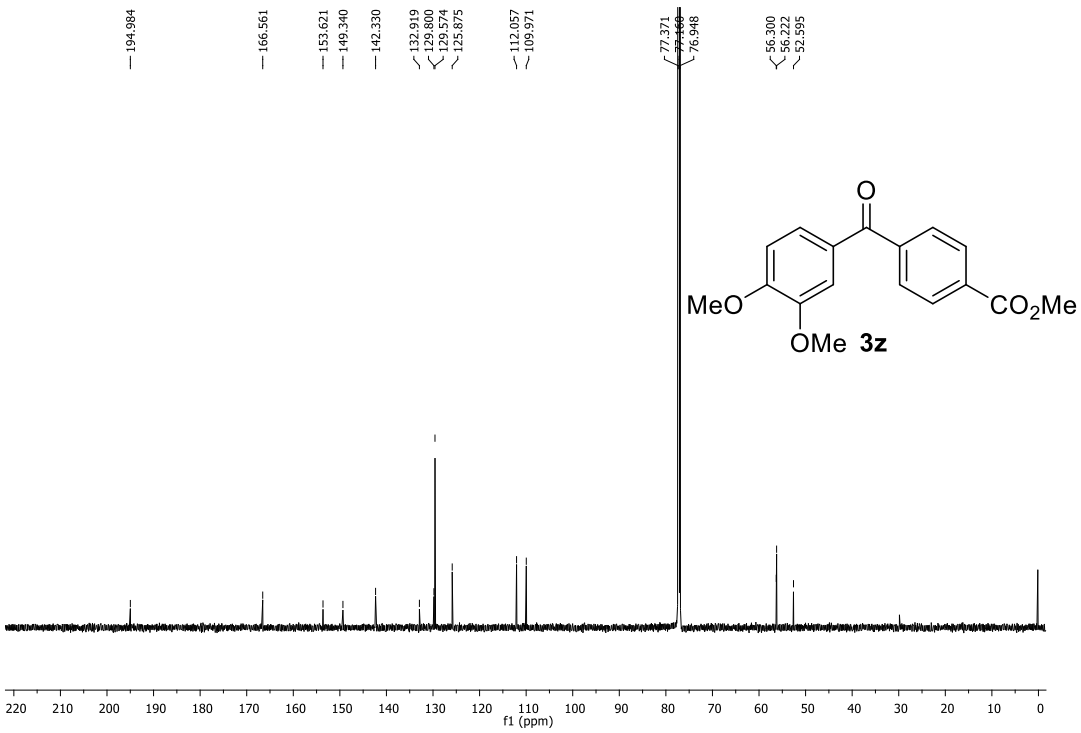
^{19}F NMR (471 MHz, $CDCl_3$)



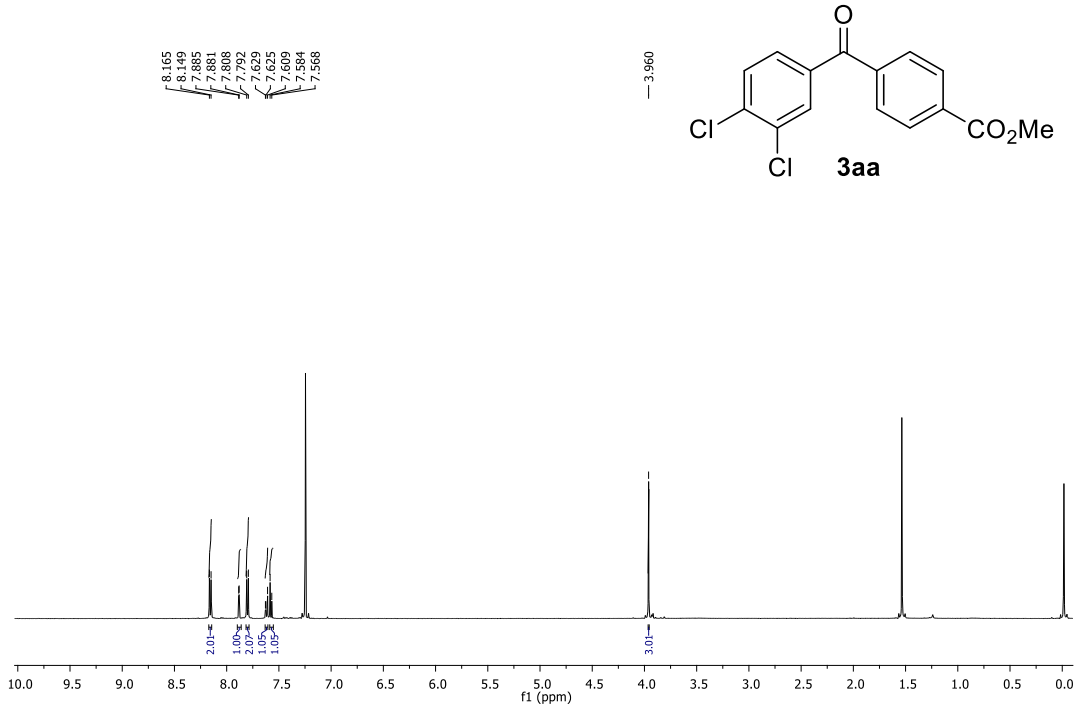
^{1}H NMR (600 MHz, $CDCl_3$)



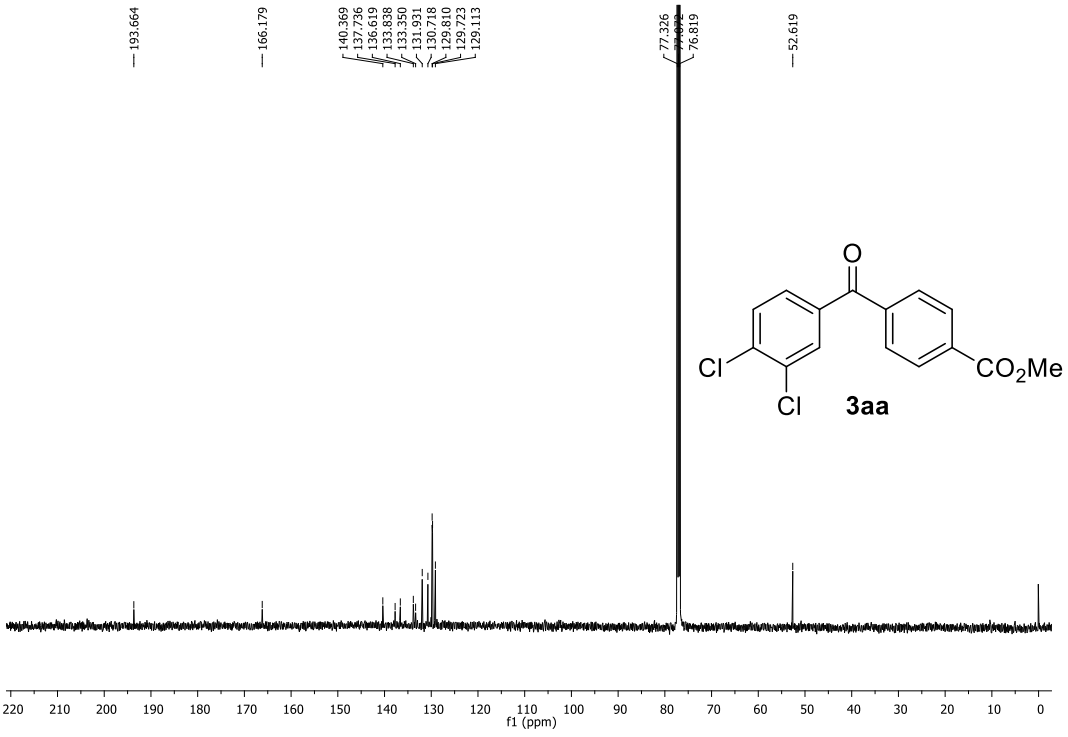
^{13}C NMR (150 MHz, $CDCl_3$)



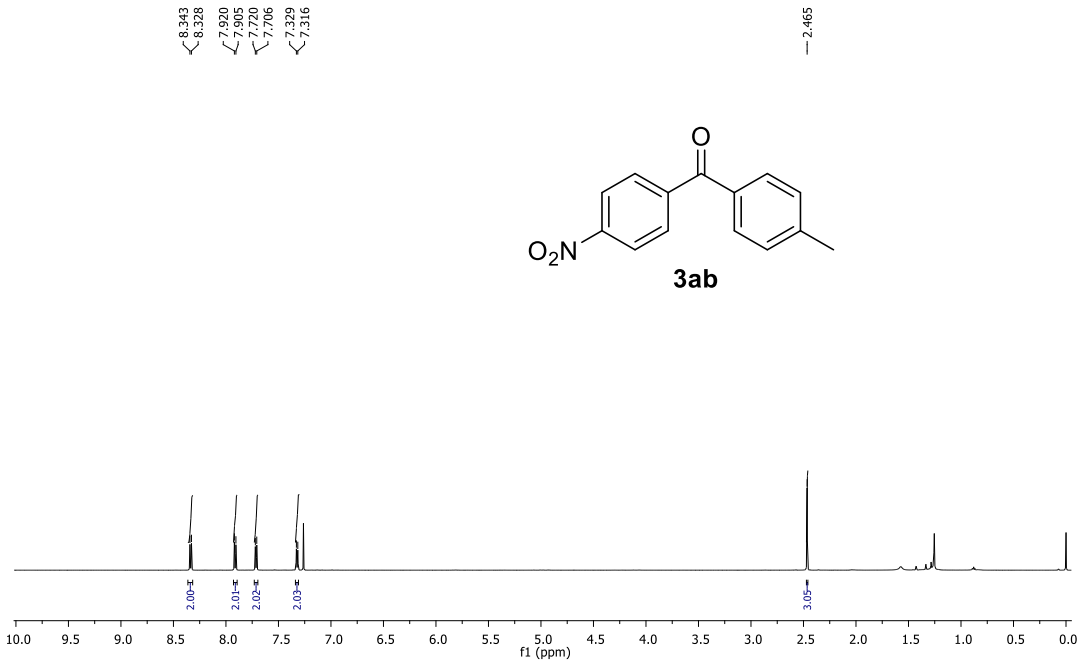
^{1}H NMR (500 MHz, $CDCl_3$)



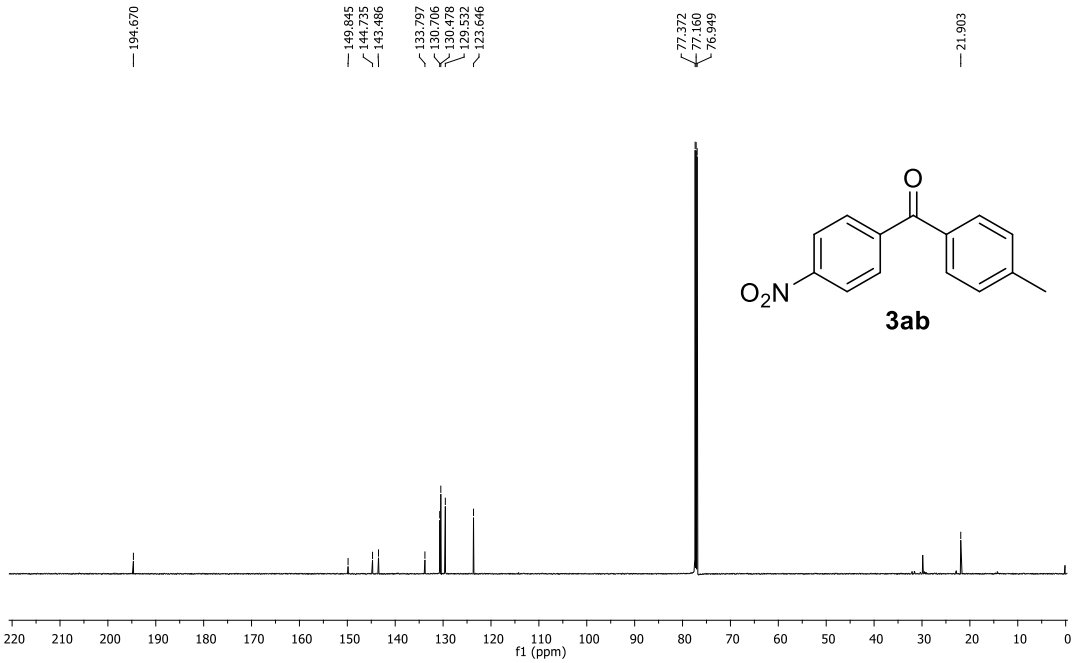
^{13}C NMR (126 MHz, $CDCl_3$)



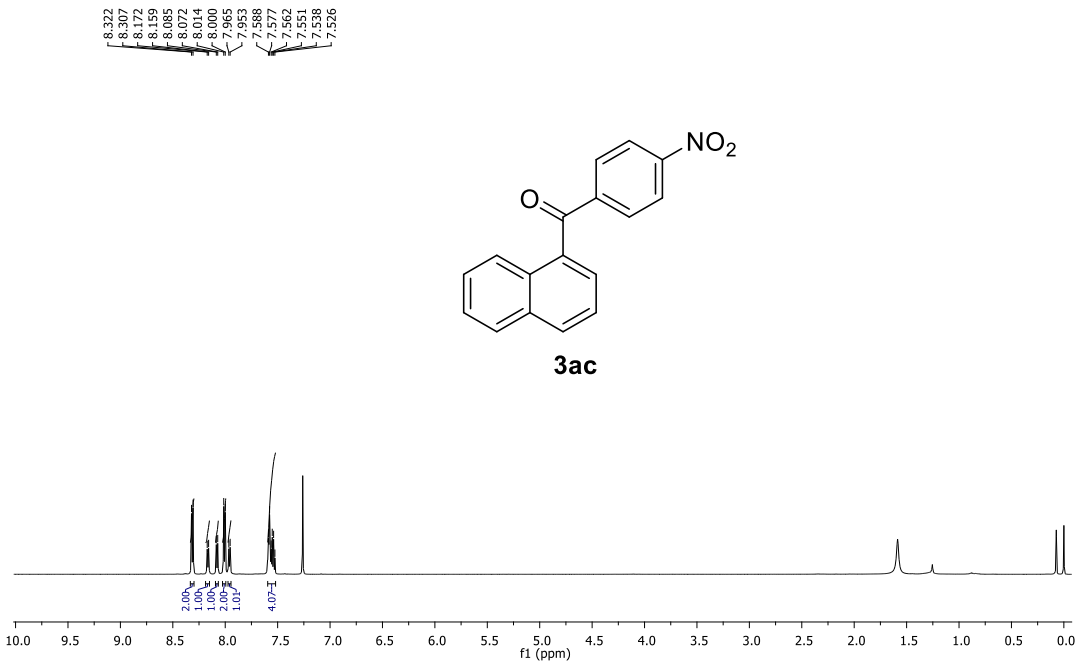
^{1}H NMR (600 MHz, $CDCl_3$)



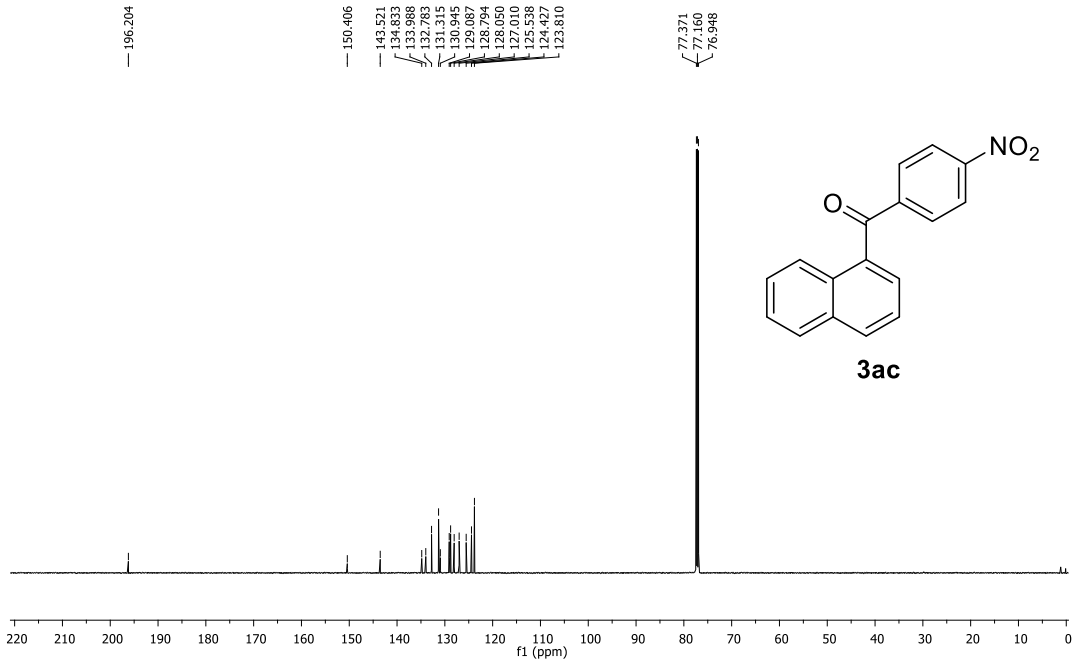
^{13}C NMR (150 MHz, $CDCl_3$)



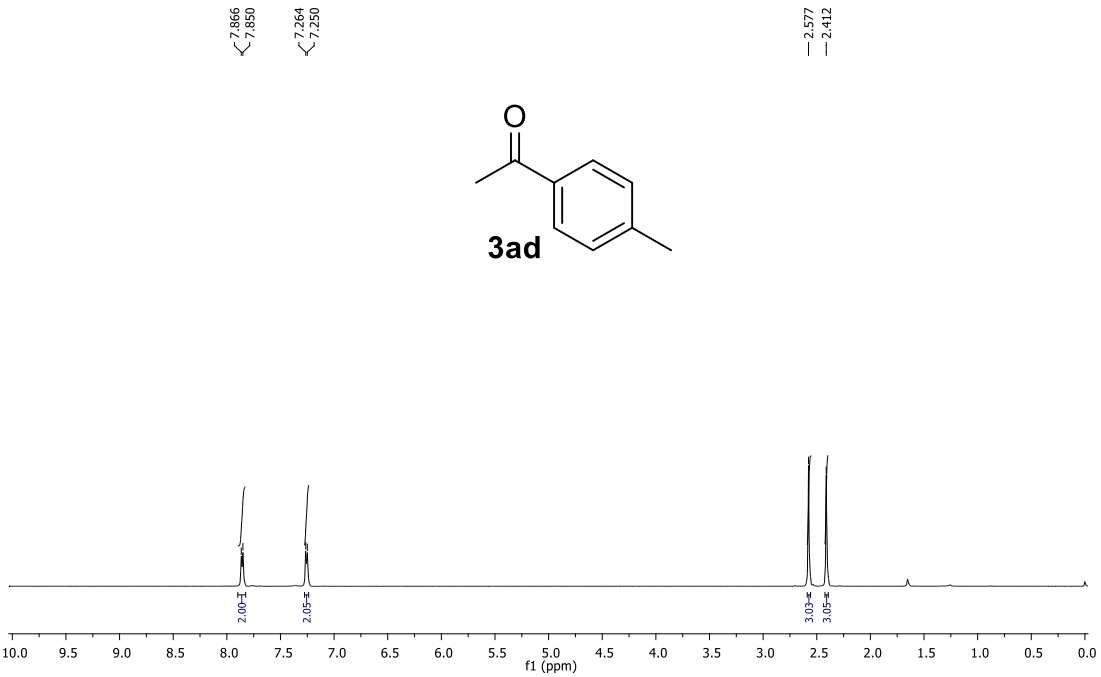
^{1}H NMR (600 MHz, $CDCl_3$)



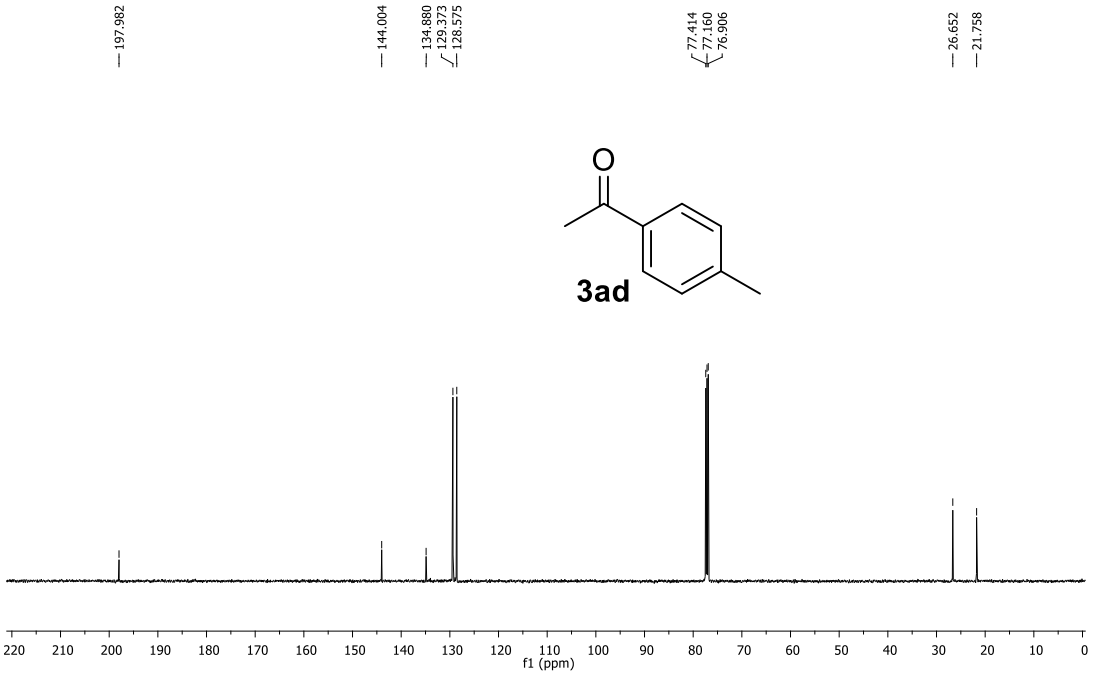
^{13}C NMR (150 MHz, $CDCl_3$)



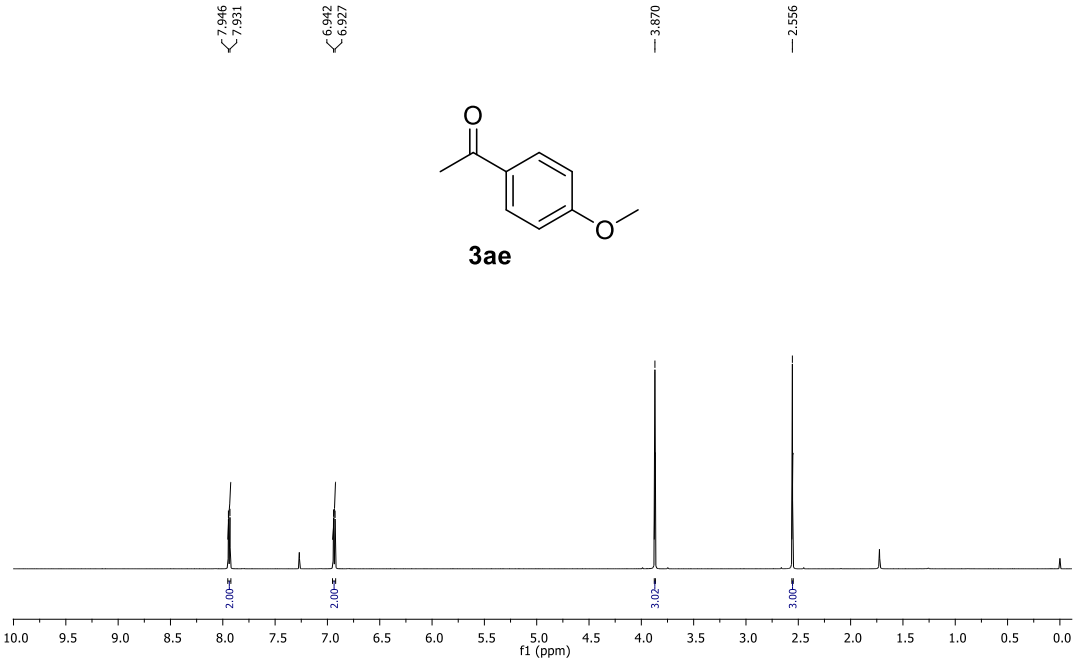
^{1}H NMR (500 MHz, $CDCl_3$)



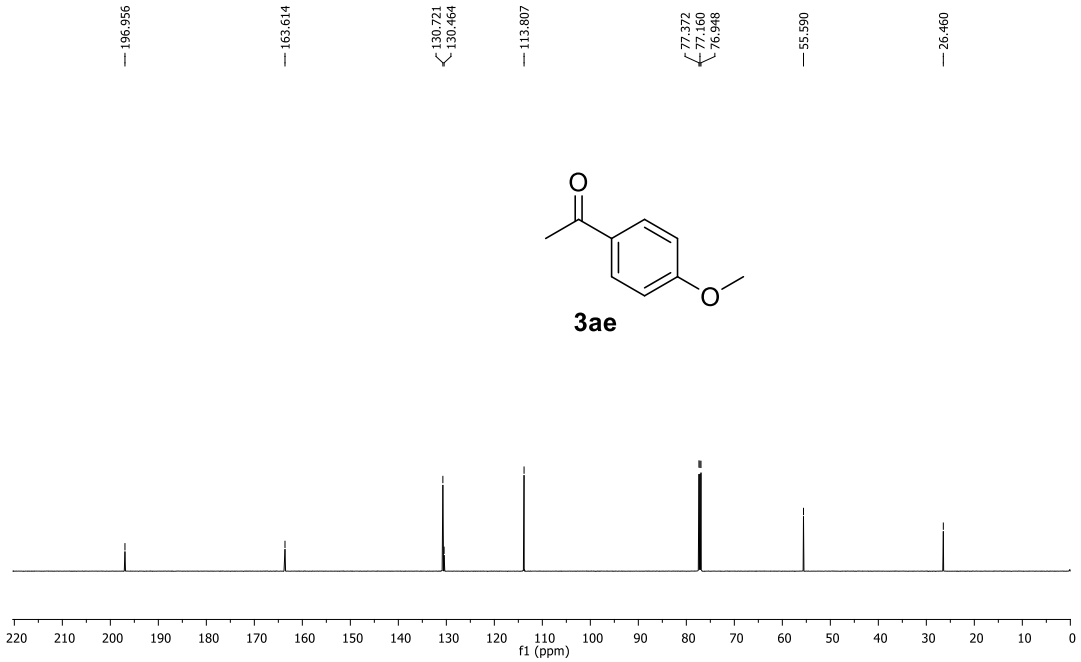
^{13}C NMR (126 MHz, $CDCl_3$)



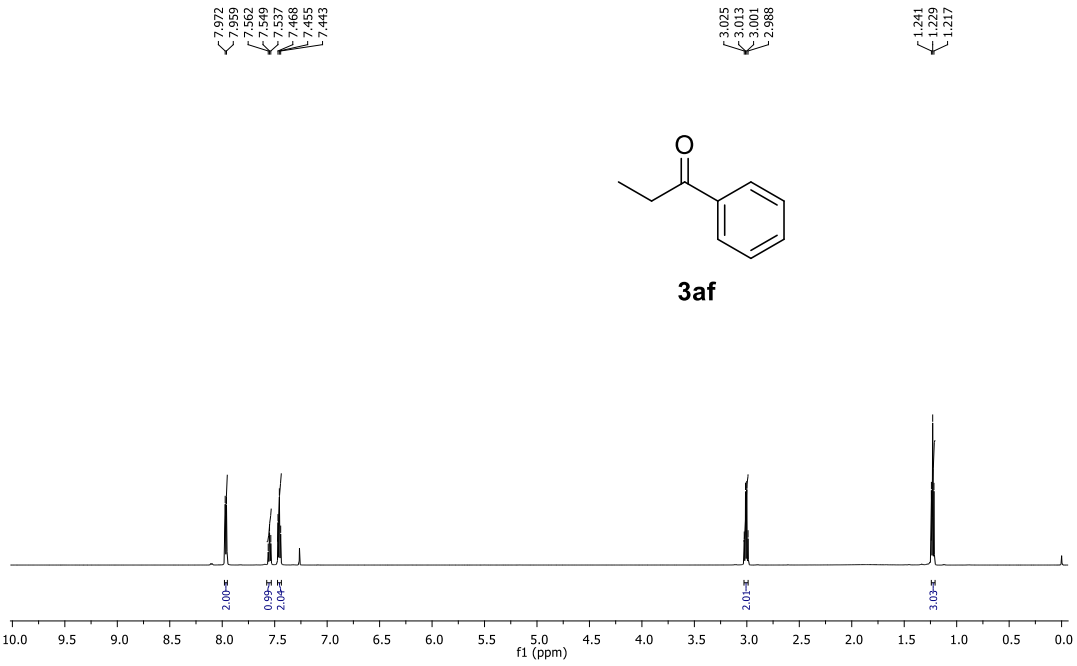
^{1}H NMR (600 MHz, $CDCl_3$)



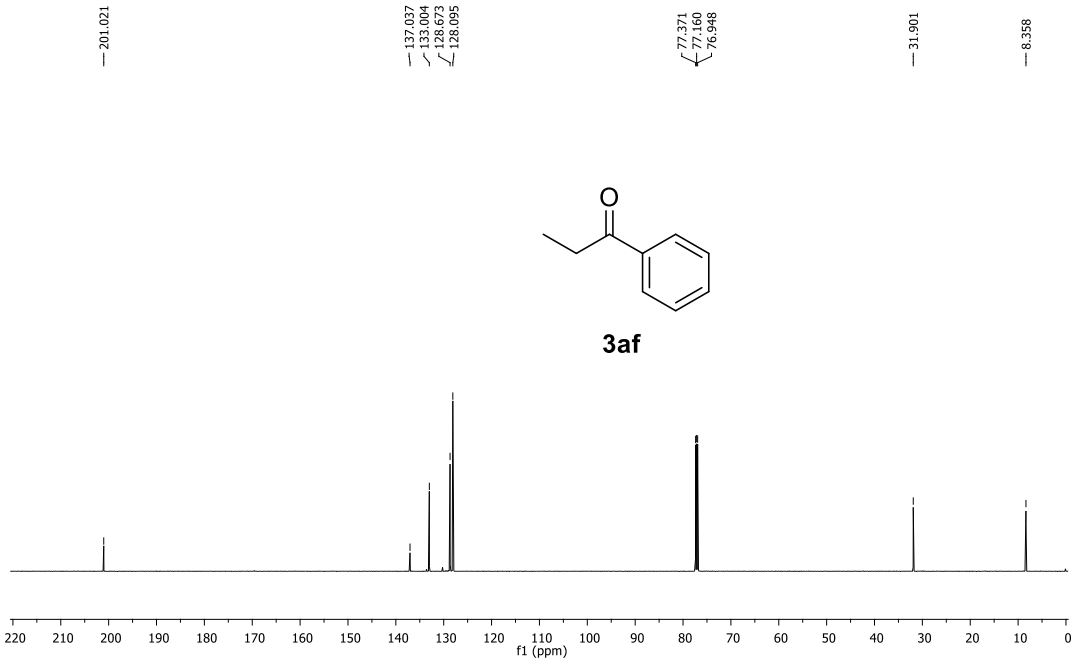
^{13}C NMR (150 MHz, $CDCl_3$)



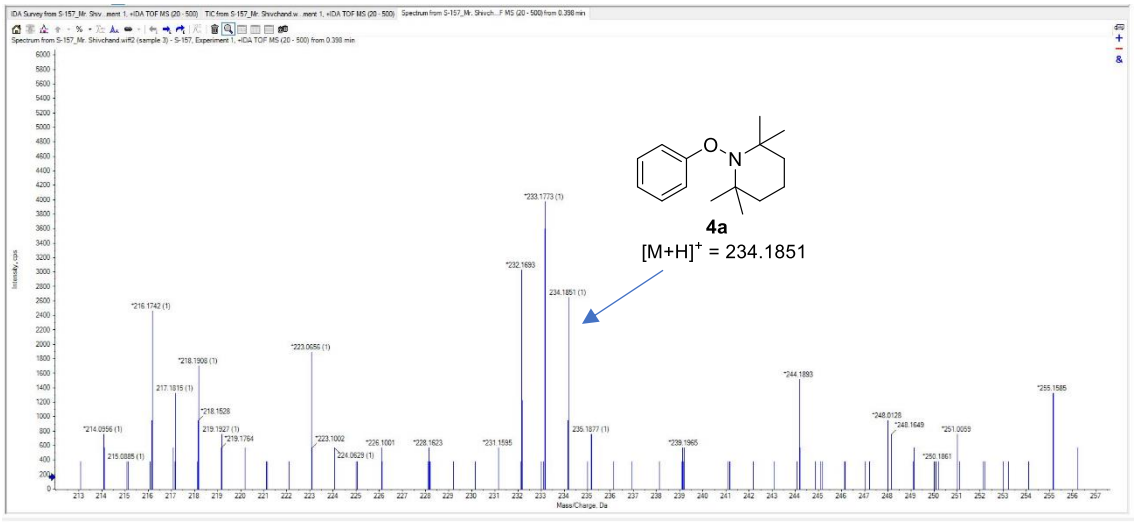
^{1}H NMR (600 MHz, $CDCl_3$)



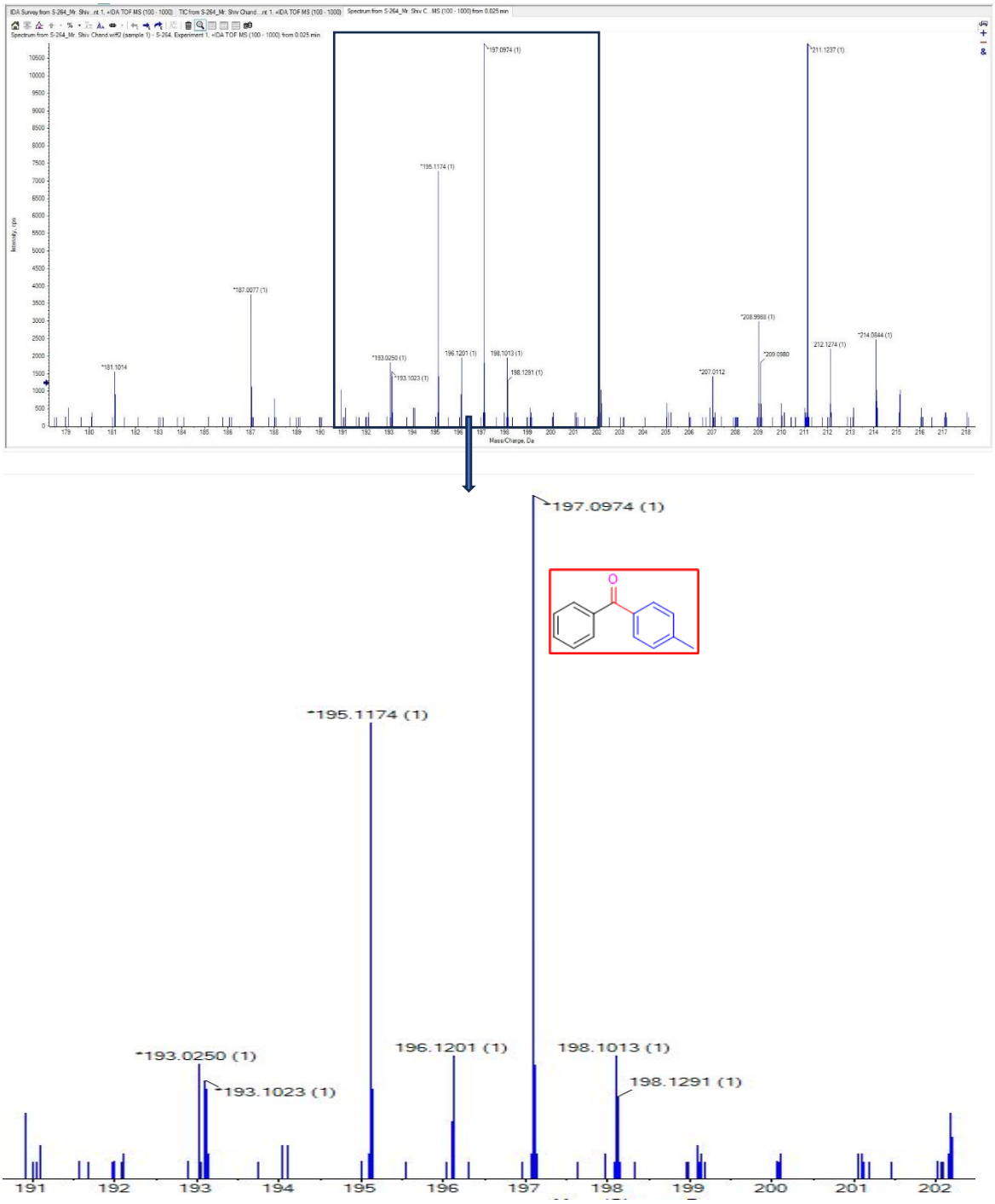
^{13}C NMR (150 MHz, $CDCl_3$)



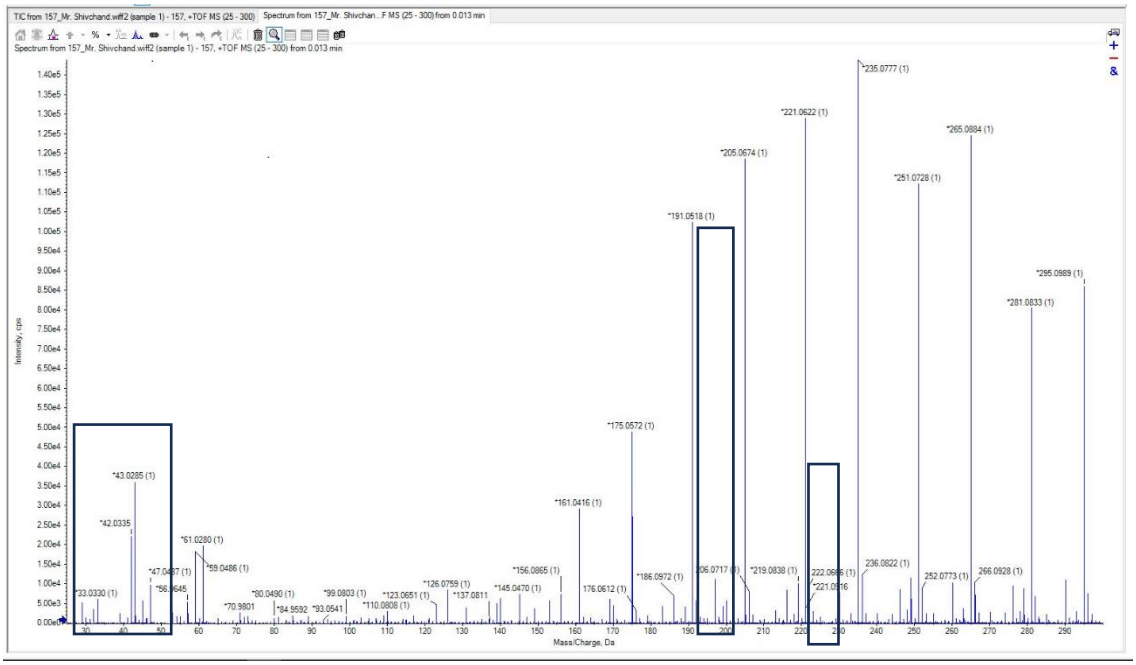
8. HRMS Data of TEMPO Adduct and Other Species.

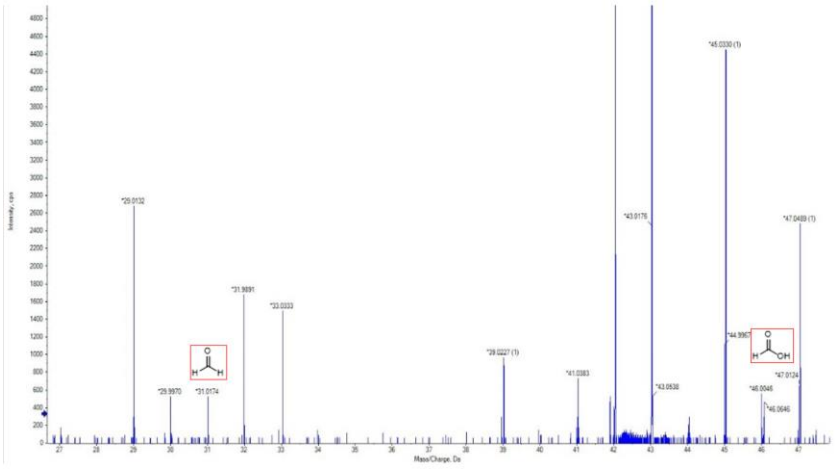


HRMS data of isotope-labeling experiment.



HRMS data of crude reaction mixture.





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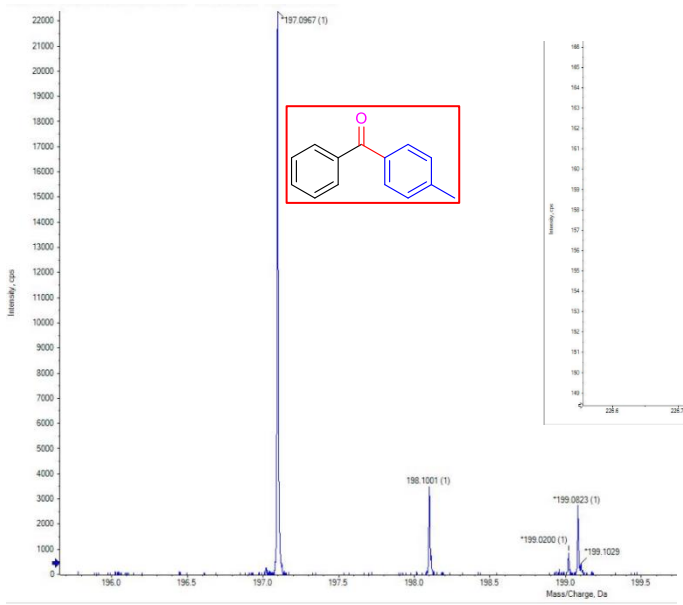

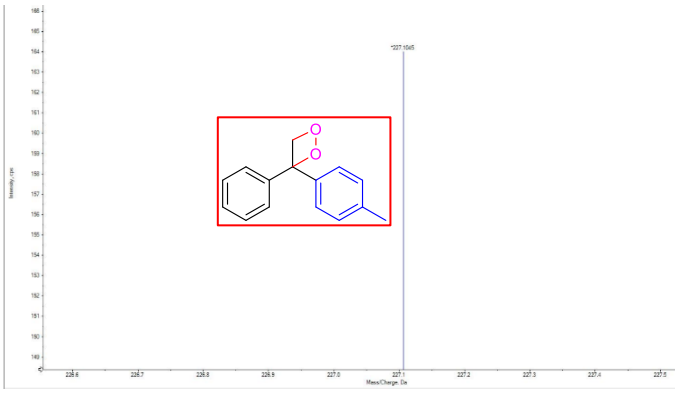

9. LED Setup.