Electronic Supplementary Information

Electrochemical Oxidative C(sp^3)–H/O–H Cross-Coupling for the Synthesis of α-Acyloxyketones

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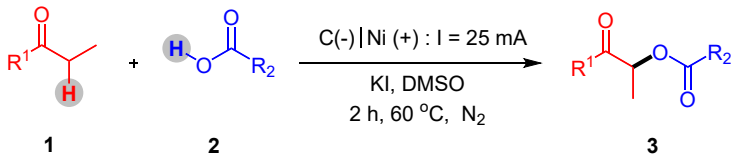
1. General information

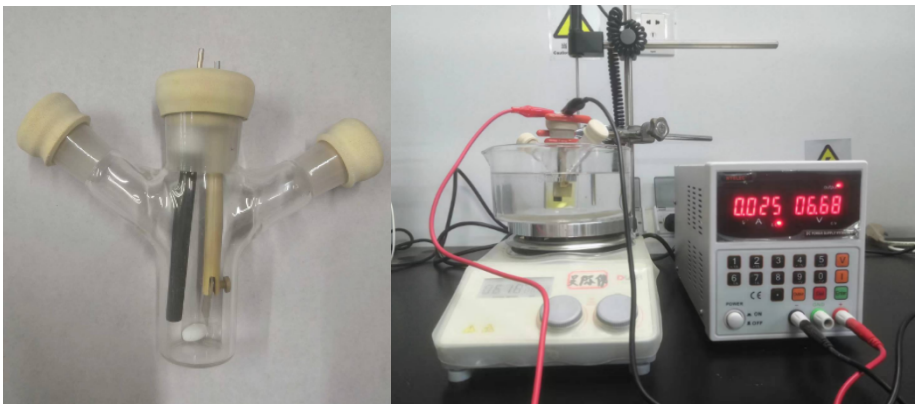
All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm, hard) and cathodic electrode was nickel plate (1.5 cm × 1.5 cm × 0.1 cm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks, respectively.

2. General procedures

General procedures:

Scheme S1 General procedures.



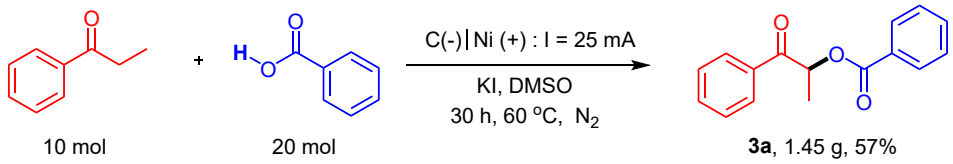


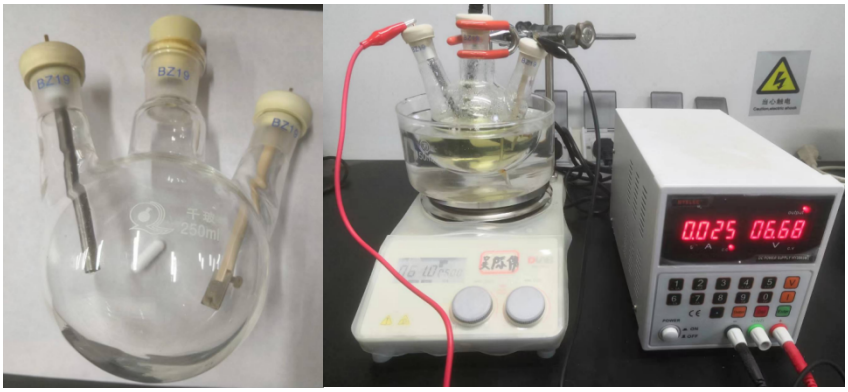
In a 25 mL three-necked bottle equipped with a magnetic stir bar, C rod (ϕ 6 mm, hard) was used as anode and Ni (1.5 cm × 1.5 cm × 0.1 cm) was used as cathode. Acid **2** (0.6 mmol – 3.0 mmol), KI (1.0 mmol, 166.0 mg) were added and charged with N_2 for three times. The phenylacetone **1** (0.3 mmol) and DMSO (10.0 mL) were added sequently to the bottle via syringes.

The Electrolysis experiment was performed at 25 mA for 2 hours. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (10 mL x 3). The organic layers were combined, dried with Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

General procedures for gram-scale synthesis

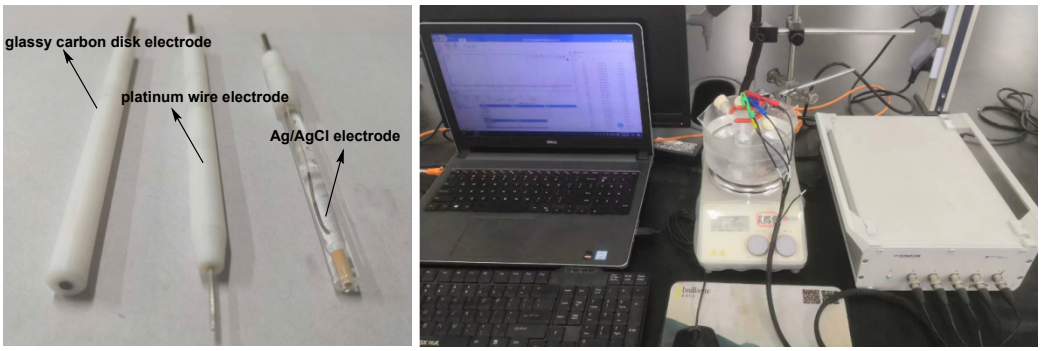
Scheme S2 Gram-scale synthesis.





In a 250 mL three-necked bottle equipped with a magnetic stir bar, C rod (ϕ 6 mm, hard) was used as anode and Ni (1.5 cm × 1.5 cm × 0.1 cm) was used as cathode. Benzoic acid **2a** (20.0 mmo1, 2.44g), KI (10.0 mmol, 1.66 g) were added and charged with N_2 for three times. The propiophenone **1a** (10.0 mmol, 1.34 g) and DMSO (100.0 mL) were added sequently to the bottle via syringes. The Electrolysis experiment was performed at 25 mA for 30 h. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (100 mL x 3). The organic layers were combined, dried with Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

3. Electrochemical procedures for cyclic voltammetry



Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at 35 °C. The working electrode was a steady glassy carbon disk electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10.0 mL of DMSO and 0.1 mmol of $^{n}Bu_4NBF_4$ were added to the electrochemical cell in all experiments. The scan rate was 0.05 V/s, from 0 V to 2.0 V

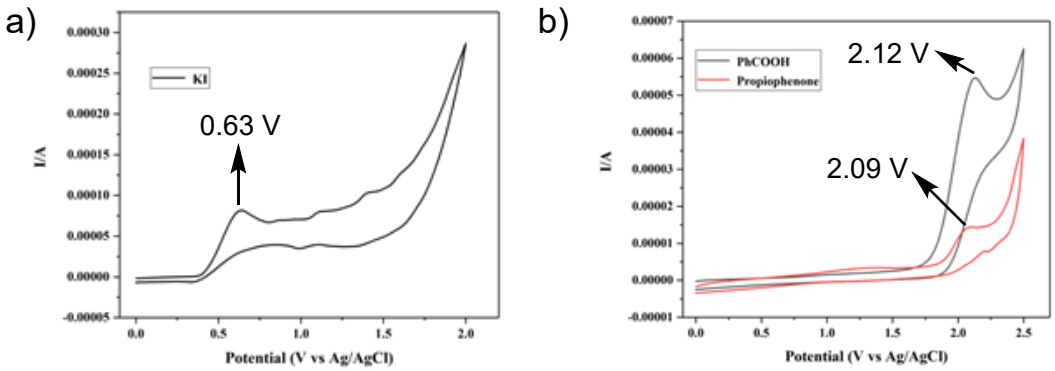
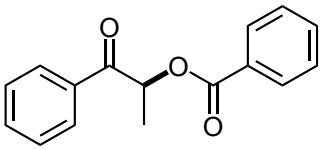


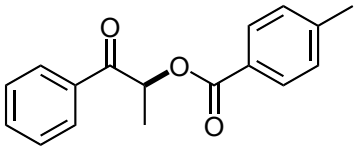
Figure S1. a) Cyclic voltammetry of KI (0.1 mmol) in DMSO (10 mL) with $^{n}Bu_4NBF_4$ (0.1 mmol) under nitrogen at a scan rate of v = 0.05 V/s, from 0 V to 2.0 V. b) Cyclic voltammetry of PhCOOH (0.1 mmol) and propiophenone (0.1 mmol) in DMSO (10 mL) with $^{n}Bu_4NBF_4$ (0.1 mmol) under nitrogen at a scan rate of v = 0.05 V/s, from 0 V to 2.5 V.

4. Detail descriptions for products

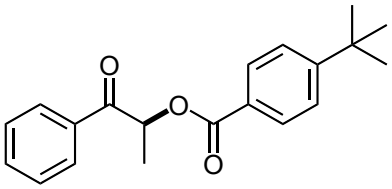


1-Oxo-1-phenylpropan-2-yl benzoate 3a[1]: 59.5mg, 78% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.59 (q, *J* = 7.5 Hz, 2H), 7.47 (dt, *J* = 15.7,

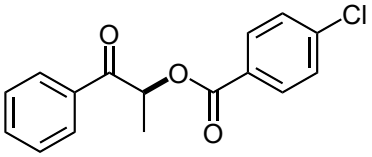
7.7 Hz, 4H), 6.21 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.75, 166.00, 134.48, 133.60, 133.30, 129.88, 129.50, 128.82, 128.54, 128.41, 71.88, 17.21.



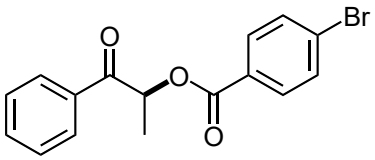
1-Oxo-1-phenylpropan-2-yl 4-methylbenzoate 3b[1]: 72.4 mg, 90% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.5 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.19 (q, *J* = 7.0 Hz, 1H), 2.40 (s, 3H), 1.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.90, 166.05, 144.04, 134.51, 133.55, 129.91, 129.12, 128.79, 128.53, 126.74, 71.71, 21.71, 17.19.



1-Oxo-1-phenylpropan-2-yl 4-(tert-butyl)benzoate 3c[2]: 84.3 mg, 91% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 7.4 Hz, 4H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.39 (dd, *J* = 10.4, 8.2 Hz, 4H), 6.12 (q, *J* = 6.9 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.85, 164.97, 155.97, 133.48, 132.51, 128.73, 127.75, 127.50, 125.65, 124.36, 70.65, 34.08, 30.06, 16.12.

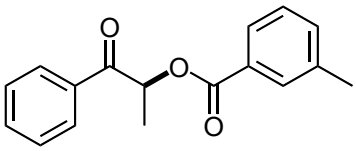


1-Oxo-1-phenylpropan-2-yl 4-chlorobenzoate 3d[1]: 45.0 mg, 52% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 14.6, 8.0 Hz, 4H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.20 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.53, 165.15, 139.80, 134.33, 133.71, 131.27, 128.86, 128.78, 128.51, 127.95, 72.11, 17.23.

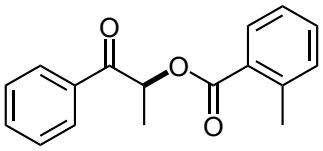


1-Oxo-1-phenylpropan-2-yl 4-bromobenzoate 3e[1]: 63.8 mg, 64% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 15.4, 8.1 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 3H), 7.50 (t, *J* = 7.7 Hz, 2H), 6.20 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50, 165.29, 134.32,

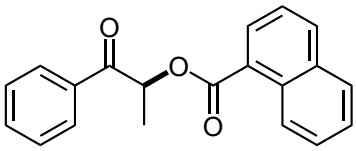
133.71, 131.78, 131.39, 128.86, 128.51, 128.40, 72.13, 17.23.



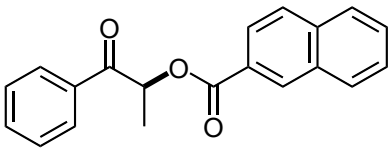
1-Oxo-1-phenylpropan-2-yl 3-methylbenzoate 3f[1]: 66.0 mg, 82% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 9.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.20 (q, *J* = 7.0 Hz, 1H), 2.39 (s, 3H), 1.67 (d, *J* = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 196.83, 166.17, 138.20, 134.46, 134.08, 133.59, 130.37, 129.37, 128.80, 128.53, 128.31, 127.03, 71.80, 21.25, 17.20.



1-Oxo-1-phenylpropan-2-yl 2-methylbenzoate 3g[1]: 61.9 mg, 77% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 2H), 6.30 (q, *J* = 7.0 Hz, 1H), 2.52 (s, 3H), 1.57 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.21, 166.78, 139.78, 134.39, 134.30, 132.92, 132.13, 130.71, 129.50, 129.31, 128.85, 126.52, 72.57, 21.43, 17.42.

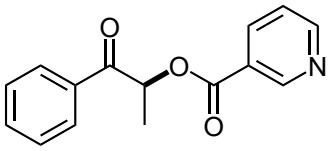


1-Oxo-1-phenylpropan-2-yl 1-naphthoate 3h[2]: 61.1 mg, 67% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.04 (t, *J* = 7.5 Hz, 3H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 12.5, 7.1 Hz, 2H), 7.51 (q, *J* = 6.9 Hz, 4H), 6.32 (q, *J* = 7.0 Hz, 1H), 1.72 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.98, 166.94, 134.52, 133.77, 133.68, 133.64, 128.86, 128.54, 128.50, 127.84, 126.44, 126.25, 125.78, 124.52, 72.00, 17.26.

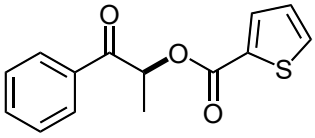


1-Oxo-1-phenylpropan-2-yl 2-naphthoate 3i[1]: 65.7 mg, 72% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.70 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.12 – 7.93 (m, 5H), 7.84 – 7.53 (m, 5H), 6.37 (q, J = 6.9 Hz, 1H), 1.64 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.13, 165.75, 135.68,

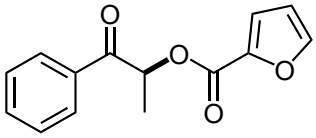
134.46, 134.26, 132.53, 131.32, 129.90, 129.54, 129.30, 129.03, 128.90, 128.24, 127.60, 126.82, 125.26, 72.90, 17.59.



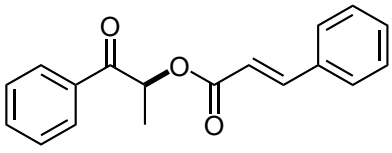
1-Oxo-1-phenylpropan-2-yl nicotinate 3j[2]: 27.6 mg, 36% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.78 (d, *J* = 3.4 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 7.9, 4.9 Hz, 1H), 6.22 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.27, 164.72, 153.74, 151.13, 137.35, 134.14, 133.83, 128.92, 128.51, 125.49, 123.37, 72.42, 17.26.



1-Oxo-1-phenylpropan-2-yl thiophene-2-carboxylate 3k[1]: 51.6 mg, 66% yield, oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 3.6 Hz, 1H), 7.59 (t, *J* = 5.8 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.12 – 7.09 (m, 1H), 6.16 (q, *J* = 7.0 Hz, 1H), 1.65 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.59, 161.60, 134.37, 134.19, 133.67, 133.09, 132.88, 128.84, 128.57, 127.88, 72.25, 17.40.

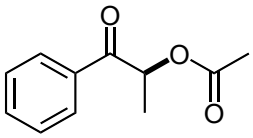


1-Oxo-1-phenylpropan-2-yl furan-2-carboxylate 3l[3]: 51.3 mg, 70% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 11.2 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 3.7 Hz, 1H), 6.52 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.19 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 157.91, 146.81, 144.04, 134.29, 133.69, 128.84, 128.56, 118.95, 112.01, 71.88, 17.45.

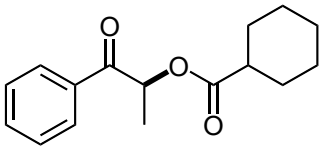


1-Oxo-1-phenylpropan-2-yl cinnamate 3m[3]: 67.3 mg, 80% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m,

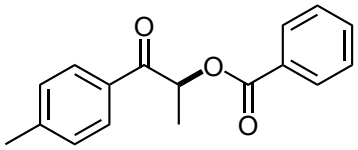
4H), 7.40 – 7.35 (m, 3H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.12 (q, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.97, 166.29, 145.98, 134.45, 134.26, 133.64, 130.53, 128.93, 128.84, 128.56, 128.25, 117.22, 71.47, 17.27.



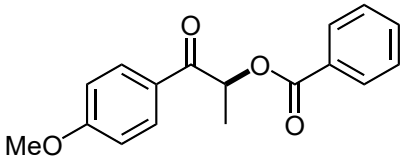
1-Oxo-1-phenylpropan-2-yl acetate 3n[3]: 30.6 mg, 53% yield, oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.97 (q, *J* = 7.0 Hz, 1H), 2.15 (s, 3H), 1.53 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.94, 170.48, 134.34, 133.62, 128.80, 128.46, 71.44, 20.75, 17.16.



1-Oxo-1-phenylpropan-2-yl cyclohexanecarboxylate 3o[4]: 60 mg, 77% yield, oil liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 6.01 (q, *J* = 7.0 Hz, 1H), 2.43 – 2.34 (m, 1H), 1.82 (t, *J* = 14.1 Hz, 2H), 1.66 (s, 2H), 1.57 (d, *J* = 11.7 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.37 – 1.17 (m, 5H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.22, 174.87, 134.33, 134.26, 129.41, 128.77, 42.16, 29.04, 28.83, 25.75, 25.11, 25.04, 17.27.

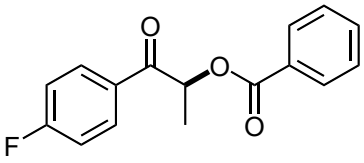


1-Oxo-1-(*p*-tolyl)propan-2-yl benzoate 3p[1]: 45.8 mg, 57% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.19 (q, *J* = 7.0 Hz, 1H), 2.42 (s, 3H), 1.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.27, 165.99, 144.55, 133.25, 131.89, 129.89, 129.58, 129.50, 128.67, 128.39, 71.82, 21.72, 17.31.

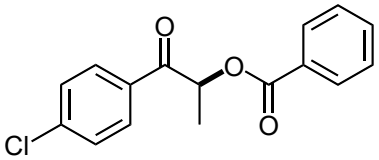


1-(4-Methoxyphenyl)-1-oxopropan-2-yl benzoate 3q[1]: 35.0 mg, 41% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.44 (t,

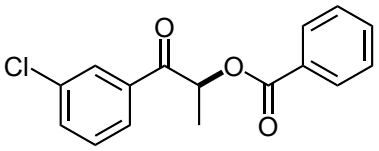
J = 7.3 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.18 (q, *J* = 6.4 Hz, 1H), 3.87 (s, 2H), 1.66 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.15, 166.04, 163.92, 133.27, 130.84, 129.90, 129.60, 128.41, 127.29, 114.05, 71.68, 55.54, 17.41.



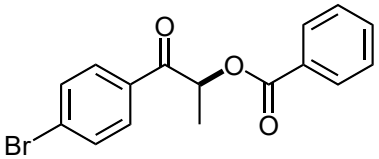
1-(4-Fluorophenyl)-1-oxopropan-2-yl benzoate 3r[1]: 49.8 mg, 61% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 6.17 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.26, 166.00, 165.99 (d, J_{C-F} = 257), 133.41, 131.26 (d, J_{C-F} = 9.4 Hz), 130.86 (d, J_{C-F} = 3.0 Hz), 129.89, 129.38, 128.47, 116.05 (d, J_{C-F} = 21.9 Hz), 71.78, 17.16. ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.94.



1-(4-Chlorophenyl)-1-oxopropan-2-yl benzoate 3s[1]: 70.0 mg, 81% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 15.2, 7.3 Hz, 2H), 6.13 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.69, 165.97, 140.10, 133.42, 132.78, 129.94, 129.88, 129.31, 129.18, 128.46, 71.79, 17.08.

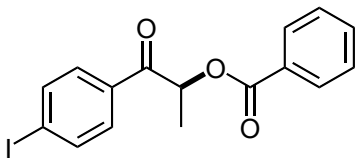


1-(3-Chlorophenyl)-1-oxopropan-2-yl benzoate 3t[1]: 62.2 mg, 72% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.98 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 13.1, 7.1 Hz, 2H), 7.45 (t, *J* = 8.1 Hz, 3H), 6.11 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.75, 165.98, 136.04, 135.18, 133.53, 133.43, 130.15, 129.88, 129.27, 128.62, 128.46, 126.54, 71.89, 17.07.

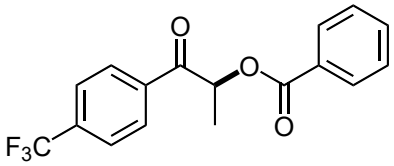


1-(4-Bromophenyl)-1-oxopropan-2-yl benzoate 3u[1]: 53.8 mg, 54% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.53 (m, 3H), 7.45 (t, *J* = 7.7

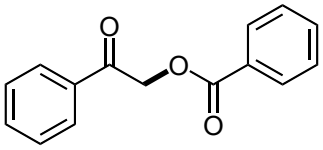
Hz, 2H), 6.12 (q, J = 6.9 Hz, 1H), 1.66 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.07, 166.13, 133.59, 133.36, 132.34, 130.18, 130.04, 129.46, 129.01, 128.62, 71.94, 17.23.



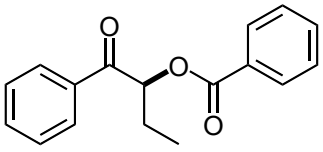
1-(4-Iodophenyl)-1-oxopropan-2-yl benzoate 3v: 63.8 mg, 56% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.3 Hz, 1H), 7.88 (d, J = 10.6 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 6.14 (q, J = 7.0 Hz, 1H), 1.68 (d, J = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.21, 165.96, 138.17, 137.85, 133.73, 133.44, 131.28, 129.90, 129.32, 128.48, 71.74, 17.10. HRMS (ESI) calcd for $C_{16}H_{13}INaO_3$, $[M+Na]^+$ 402.9802, found 402.9807.



1-Oxo-1-(4-(trifluoromethyl)phenyl)propan-2-yl benzoate 3w[5]: 60.8 mg, 61% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 4H), 7.77 (d, J = 8.2 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 6.18 (q, J = 7.0 Hz, 1H), 1.70 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.15, 166.01, 137.34, 134.96, 134.63, 133.53, 129.90, 129.19, 128.88, 128.51, 125.90 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.85, 122.14, 71.99, 16.91. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.21.

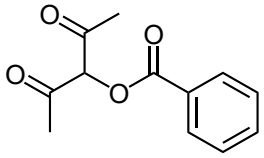


2-Oxo-2-phenylethyl benzoate 3x[1]: 58.3 mg, 81% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (dd, J = 10.9, 7.6 Hz, 4H), 7.72 (t, J = 7.4 Hz, 2H), 7.59 (t, J = 7.8 Hz, 4H), 5.78 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.21, 165.76, 134.52, 134.35, 134.16, 129.84, 129.64, 129.45, 129.37, 128.31, 67.66.

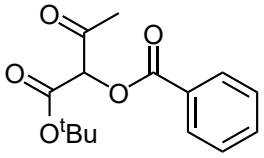


1-Oxo-1-phenylbutan-2-yl benzoate 3y[2]: 29.8 mg, 37% yield, oil liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 7.5 Hz, 2H), 8.03 (d, J = 7.3 Hz, 2H), 7.71 (t, J = 7.3 Hz, 2H), 7.58 (dd, J = 14.7, 7.4 Hz, 4H), 6.19 (dd, J = 7.9, 4.2 Hz, 1H), 2.12 – 1.80 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C

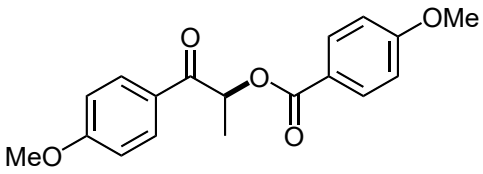
NMR (101 MHz, DMSO-d_6) δ 196.57, 165.76, 134.65, 134.40, 134.15, 129.76, 129.65, 129.51, 129.36, 128.80, 77.13, 24.92, 10.00.



2,4-Dioxopentan-3-yl benzoate 3z[6]: 20.5 mg, 31% yield, oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$, keto and enol tautomers) δ 14.52 (s, 0.51H, enol), 8.18 (d, *J* = 7.3 Hz, 1.14H, enol), 8.13 (d, *J* = 7.2 Hz, 3.80H, keto), 7.71 – 7.60 (m, 2.66H, keto and enol), 7.57 – 7.45 (m, 5.11H, keto and enol), 5.74 (s, 1H, keto), 2.41 (s, 6.13H, keto), 2.07 (s, 3.04H, enol). ^{13}C NMR (101 MHz, $CDCl_3$, keto and enol tautomers) δ 199.11, 184.96, 171.55, 165.17, 164.97, 134.01, 133.81, 130.22, 130.01, 128.83, 128.72, 128.52, 128.44, 85.32, 27.54, 20.86.



1-(*tert*-Butoxy)-1,3-dioxobutan-2-yl benzoate 3aa[6]: 36.7 mg, 44% yield, oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.63 (s, 1H), 2.43 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.05, 165.19, 163.39, 133.81, 130.09, 128.59, 84.15, 78.64, 27.92, 27.47.

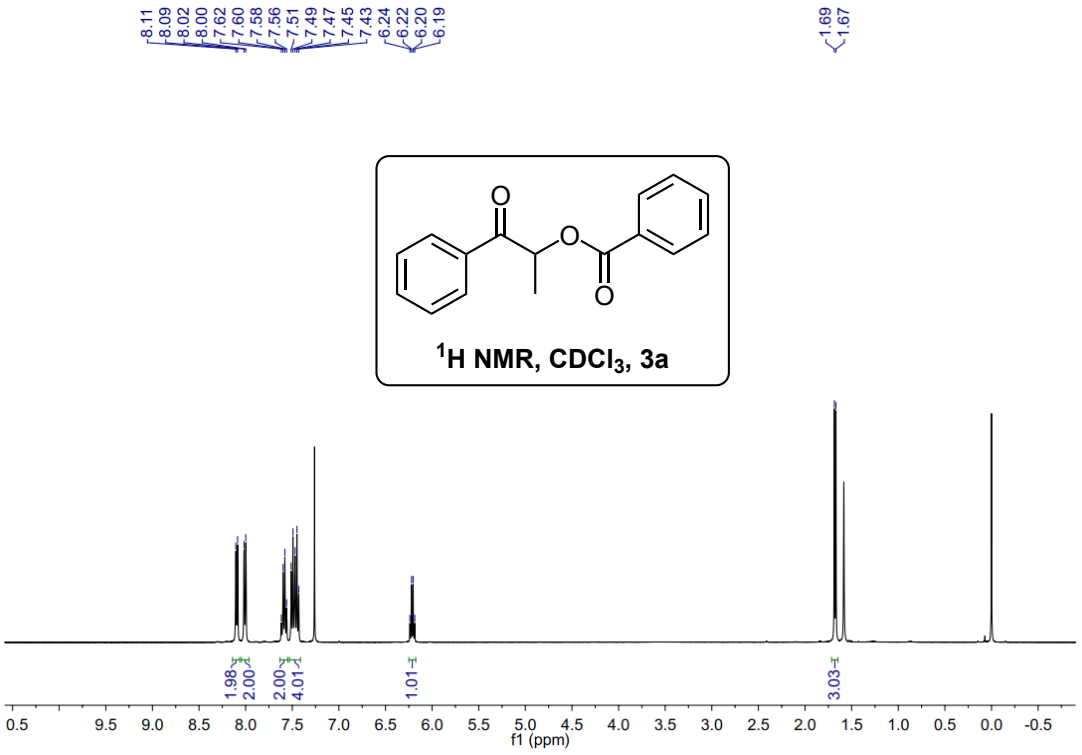


1-(4-Methoxyphenyl)-1-oxopropan-2-yl 4-methoxybenzoate 3ab[7]: 57.5 mg, 61% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 20.4, 8.8 Hz, 4H), 6.93 (dd, *J* = 13.7, 8.9 Hz, 4H), 6.15 (q, *J* = 6.9 Hz, 1H), 3.86 (d, *J* = 4.1 Hz, 6H), 1.64 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.39, 165.74, 163.85, 163.62, 131.99, 130.92, 127.35, 121.97, 114.01, 113.65, 71.36, 55.54, 55.48, 17.41.

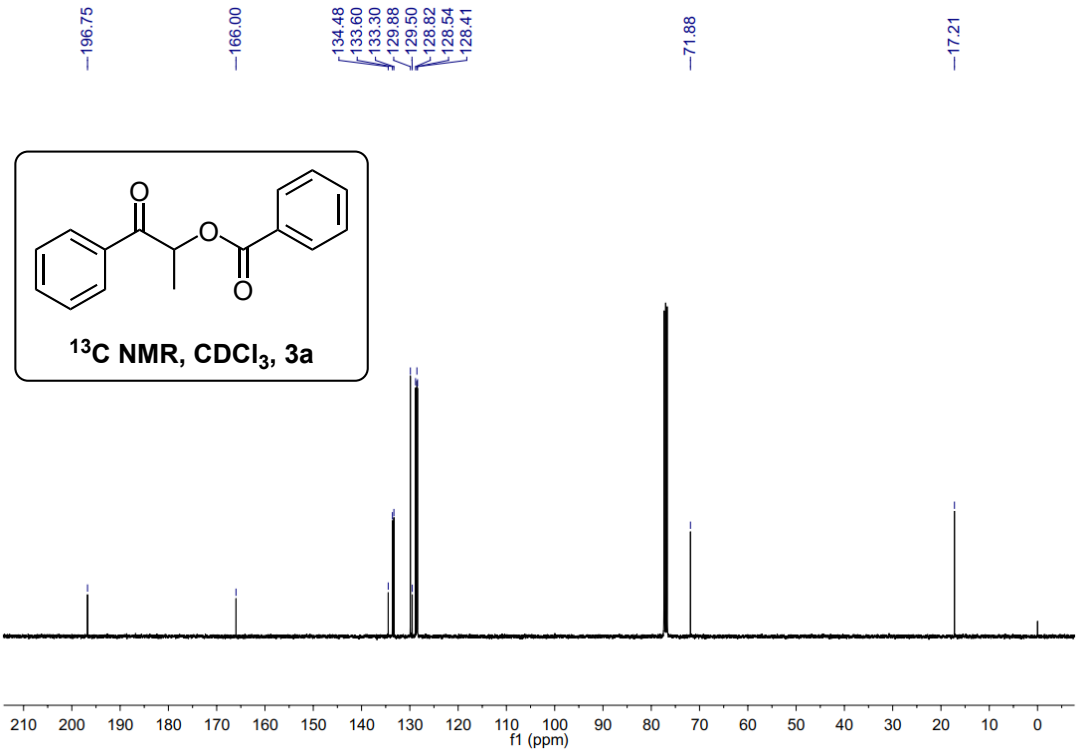
4. Copies of product NMR spectra

1-Oxo-1-phenylpropan-2-yl benzoate (3a)

^{1}H NMR

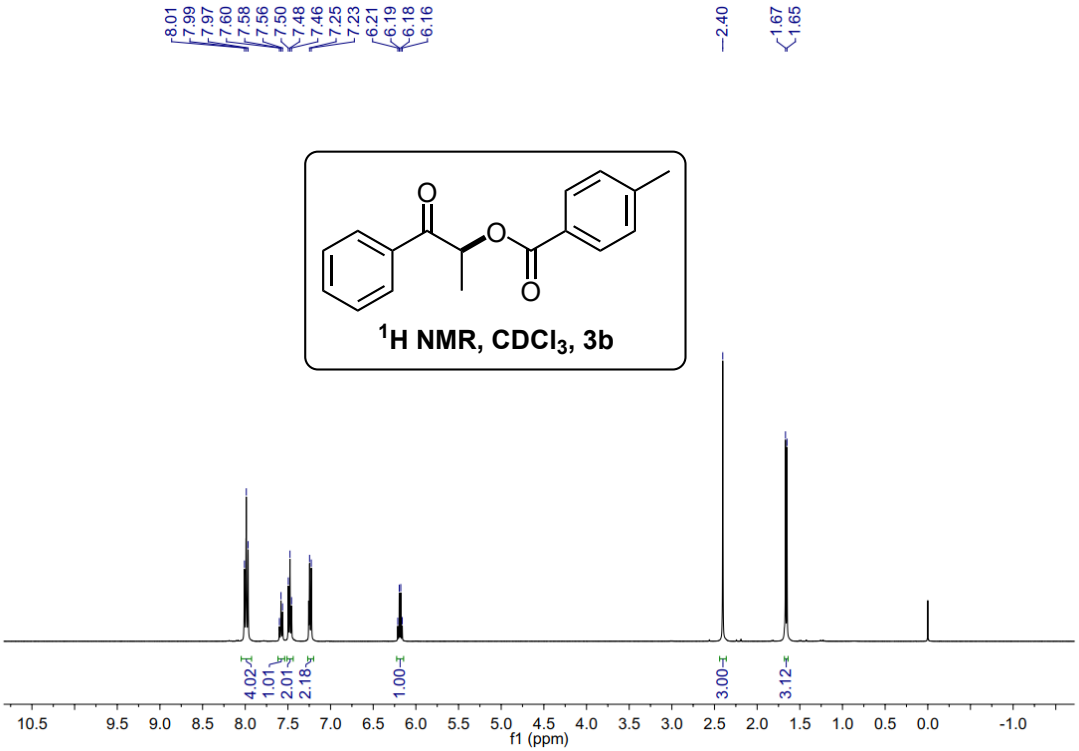


^{13}C NMR

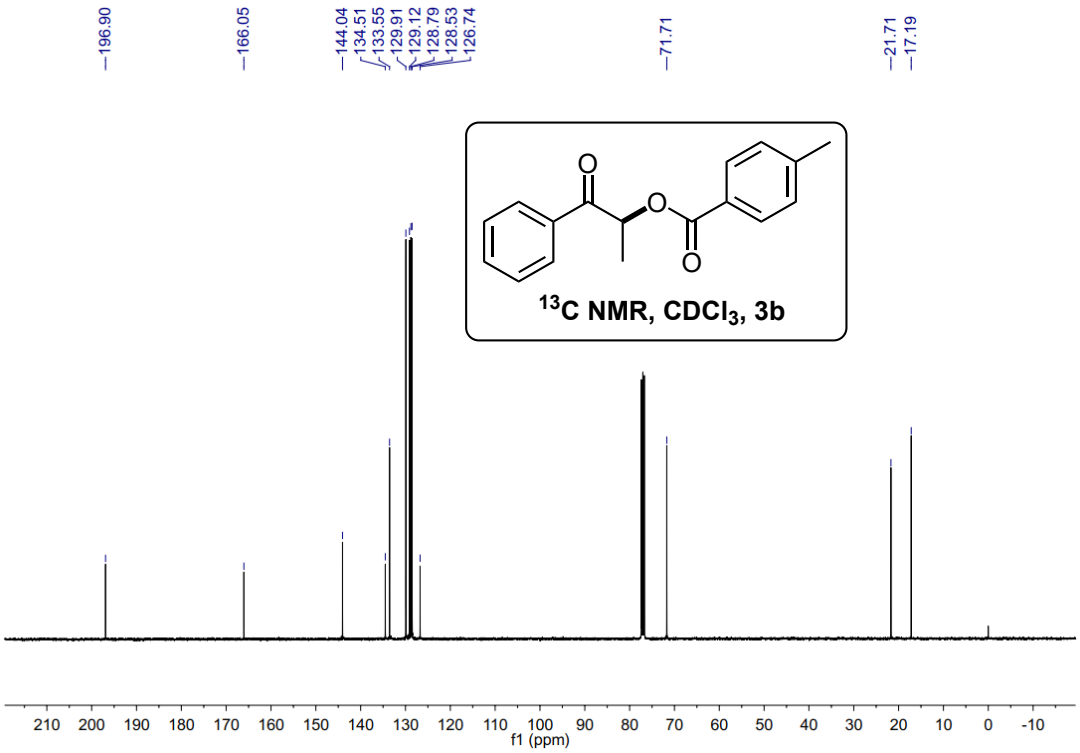


1-Oxo-1-phenylpropan-2-yl 4-methylbenzoate (3b)

^{1}H NMR

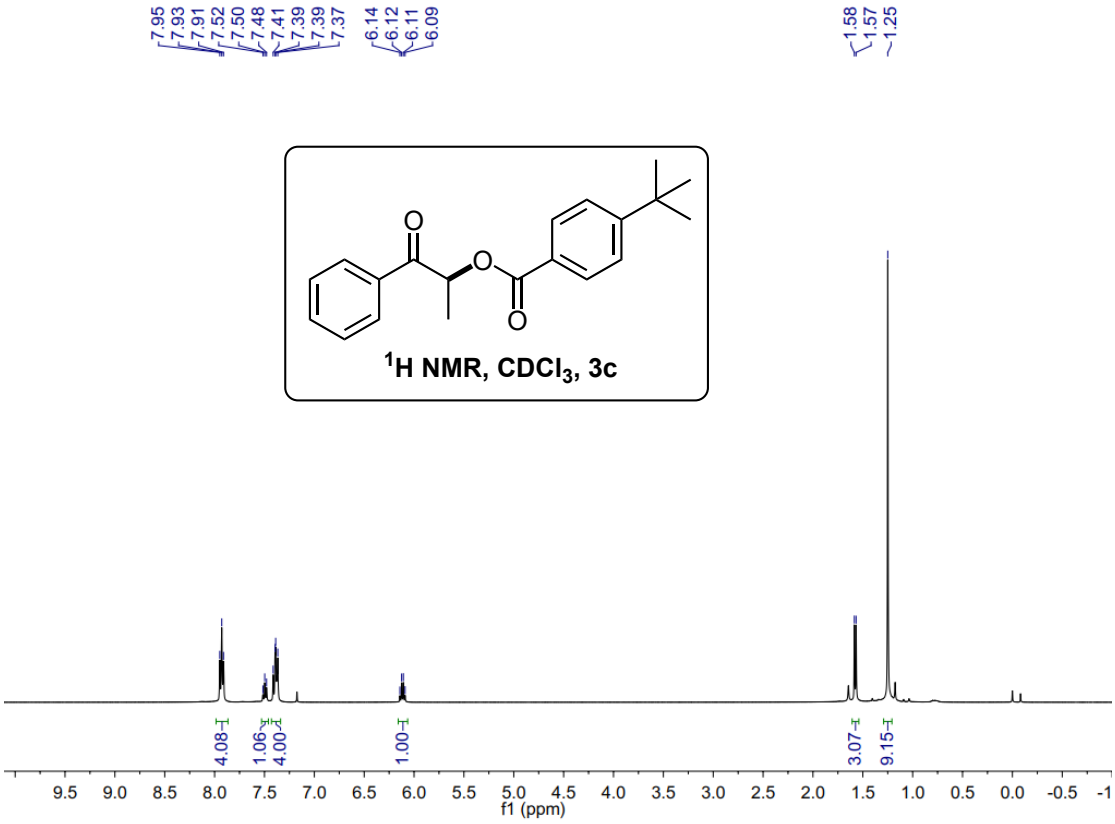


^{13}C NMR

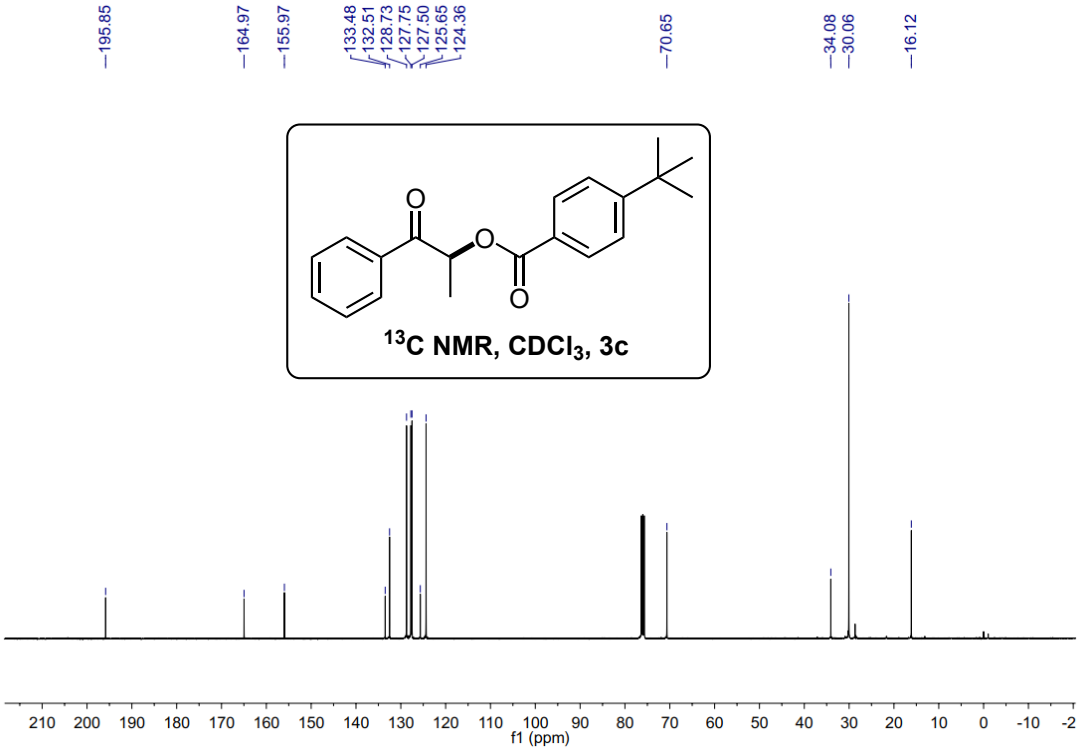


1-Oxo-1-phenylpropan-2-yl 4-(tert-butyl)benzoate (3c)

^{1}H NMR

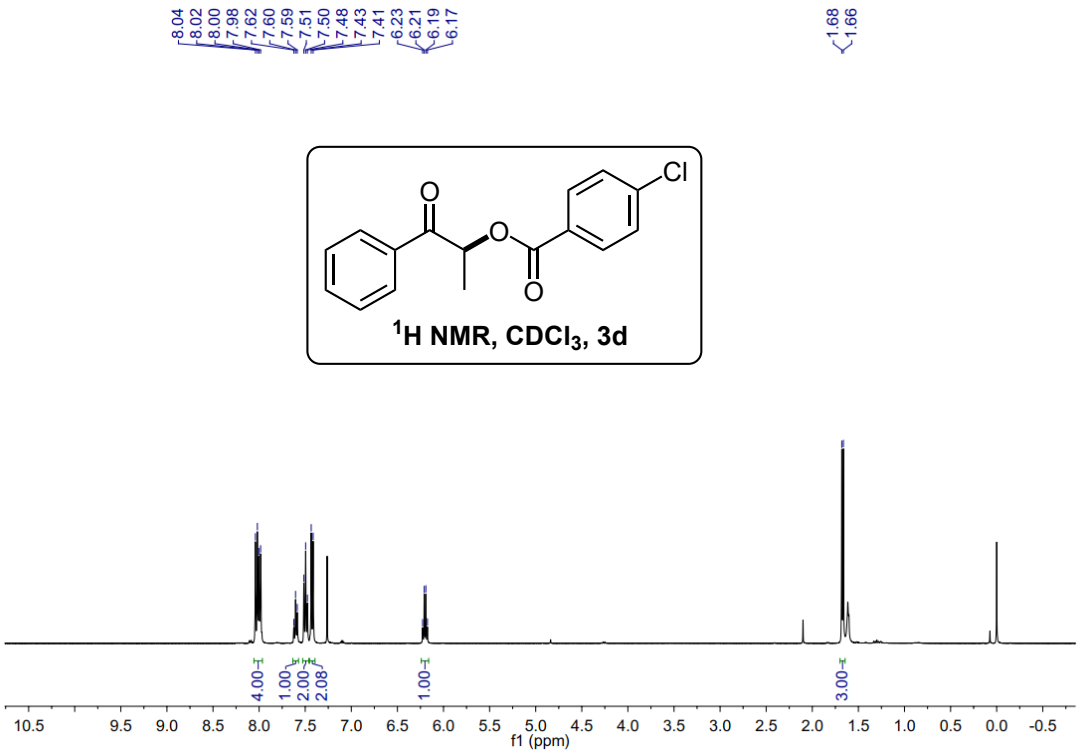


^{13}C NMR

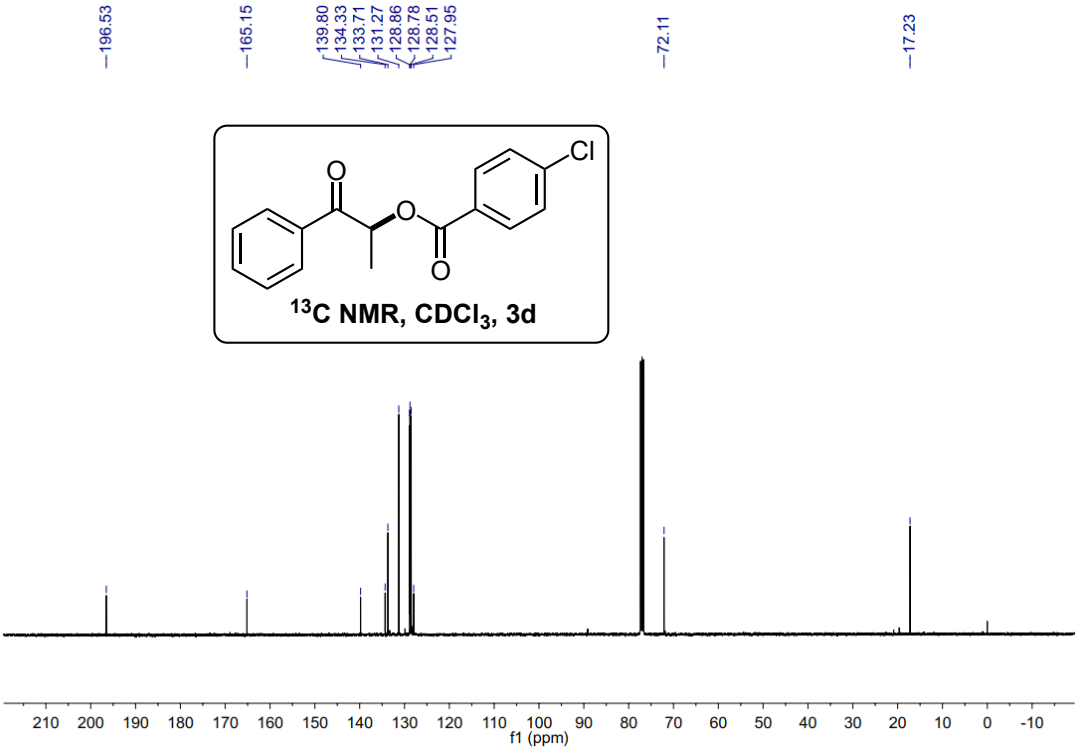


1-Oxo-1-phenylpropan-2-yl 4-chlorobenzoate (3d)

^{1}H NMR

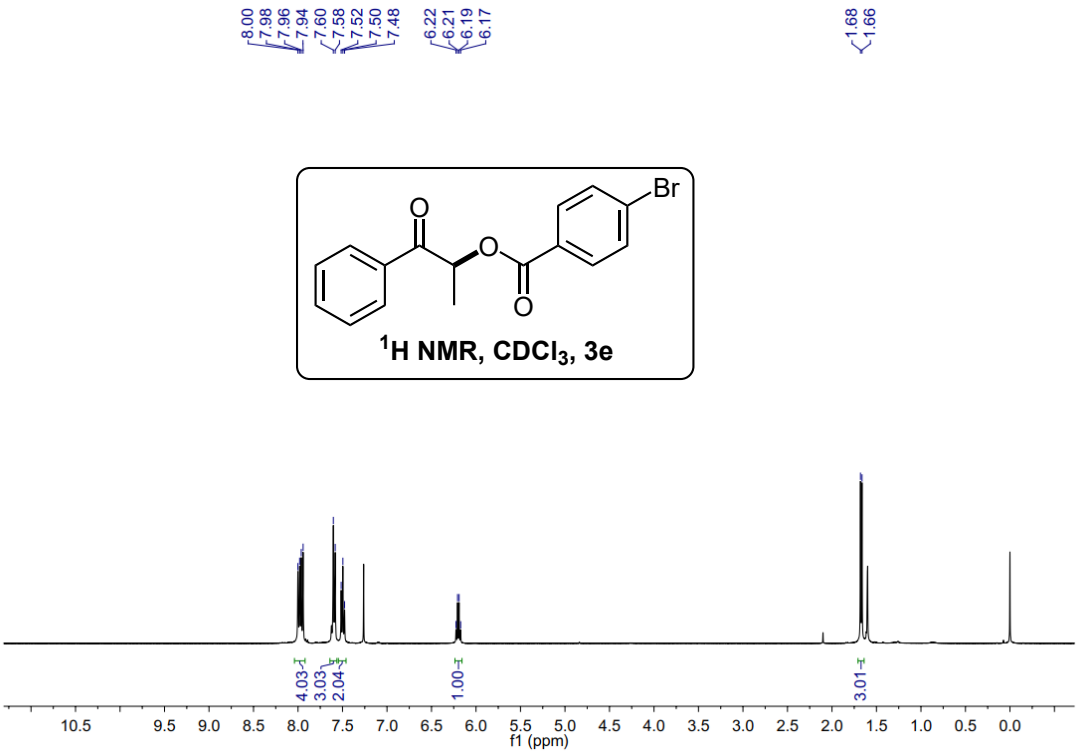


^{13}C NMR

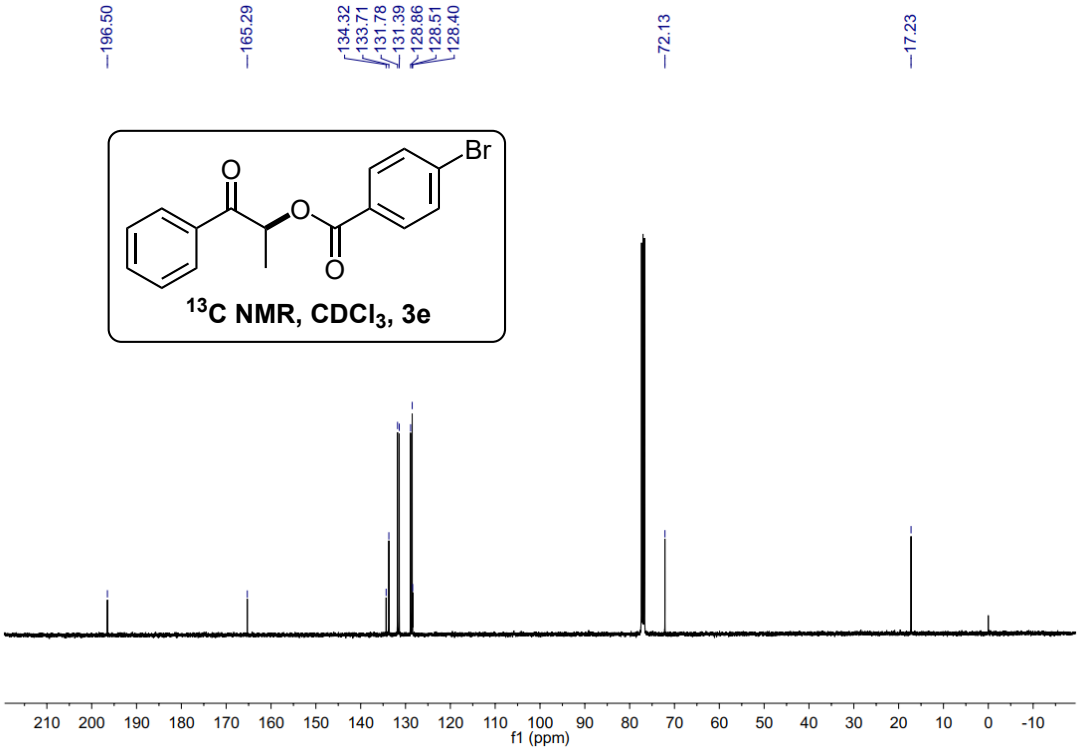


1-Oxo-1-phenylpropan-2-yl 4-bromobenzoate (3e)

^{1}H NMR

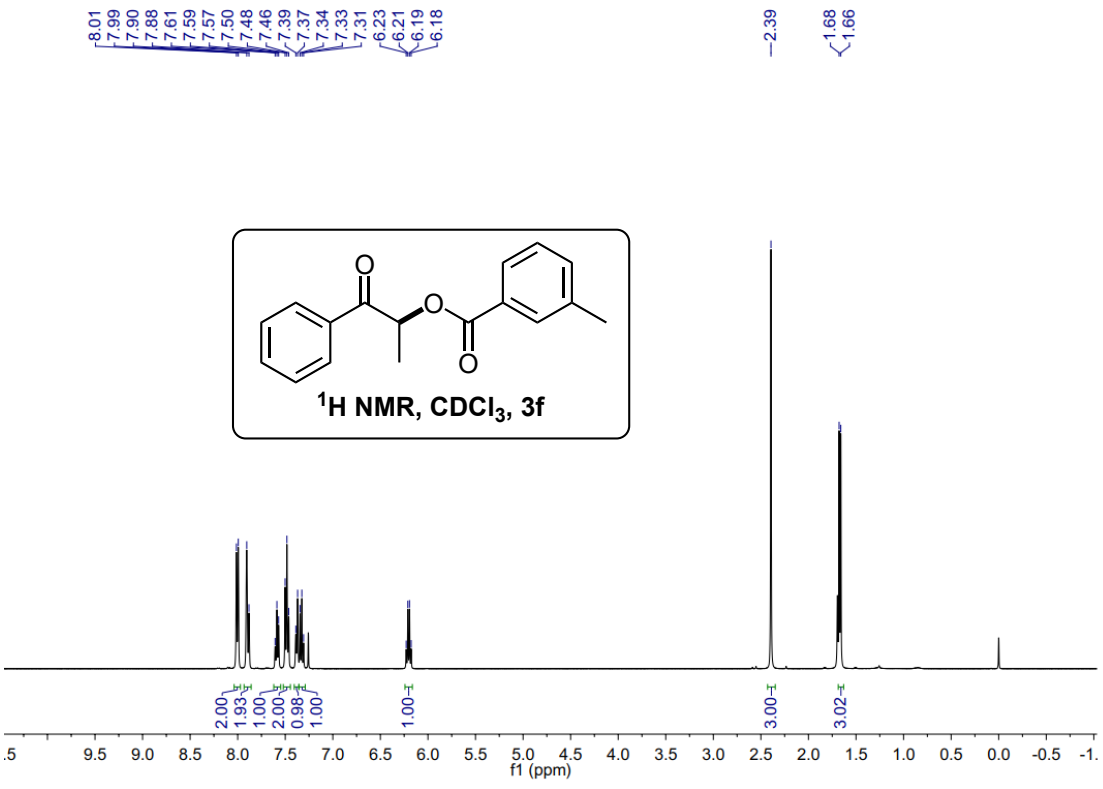


^{13}C NMR

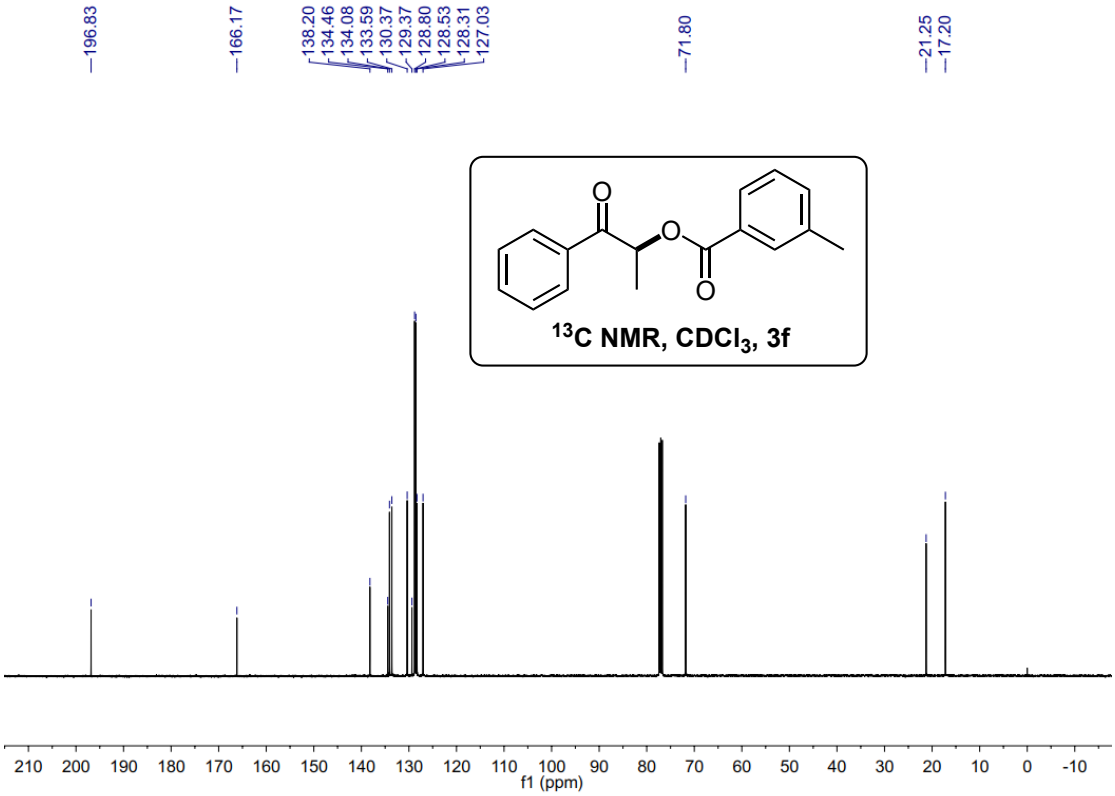


1-Oxo-1-phenylpropan-2-yl 3-methylbenzoate (3f)

^{1}H NMR

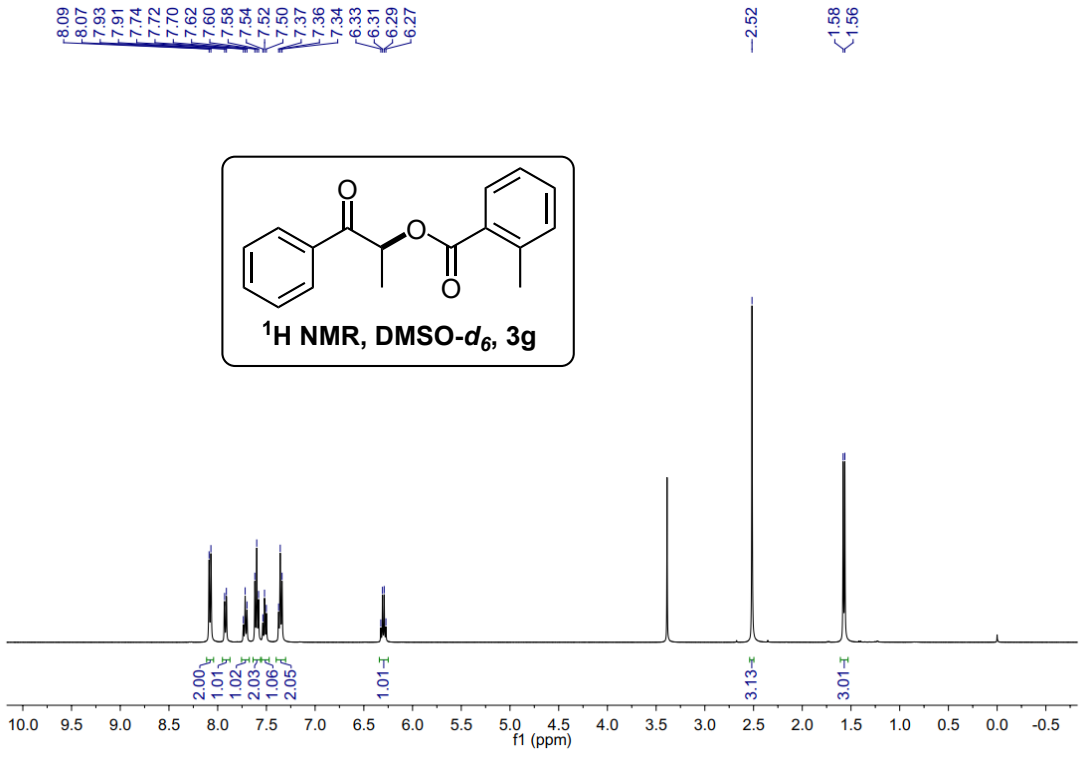


^{13}C NMR

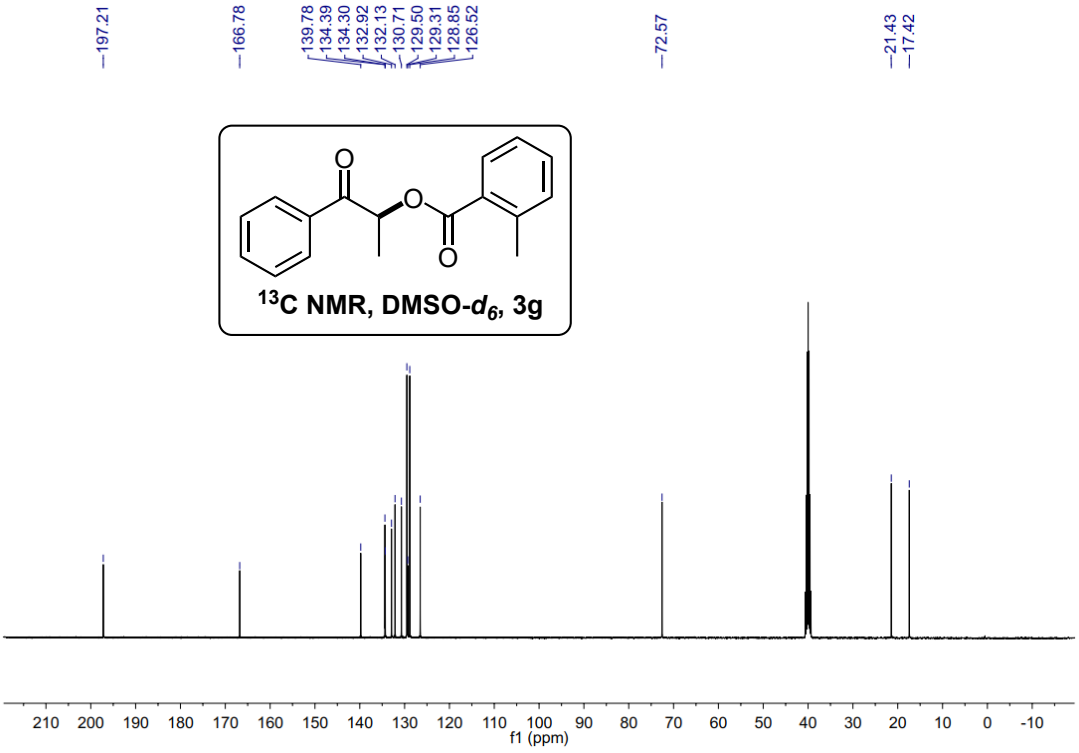


1-Oxo-1-phenylpropan-2-yl 2-methylbenzoate (3g)

^{1}H NMR

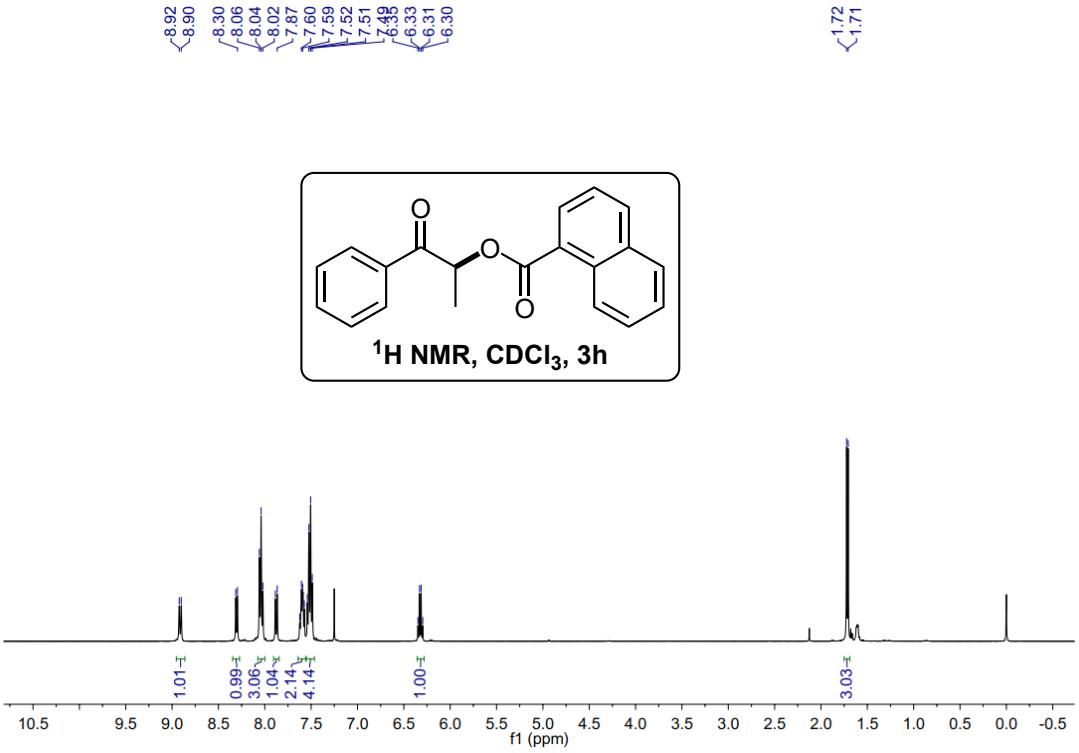


^{13}C NMR

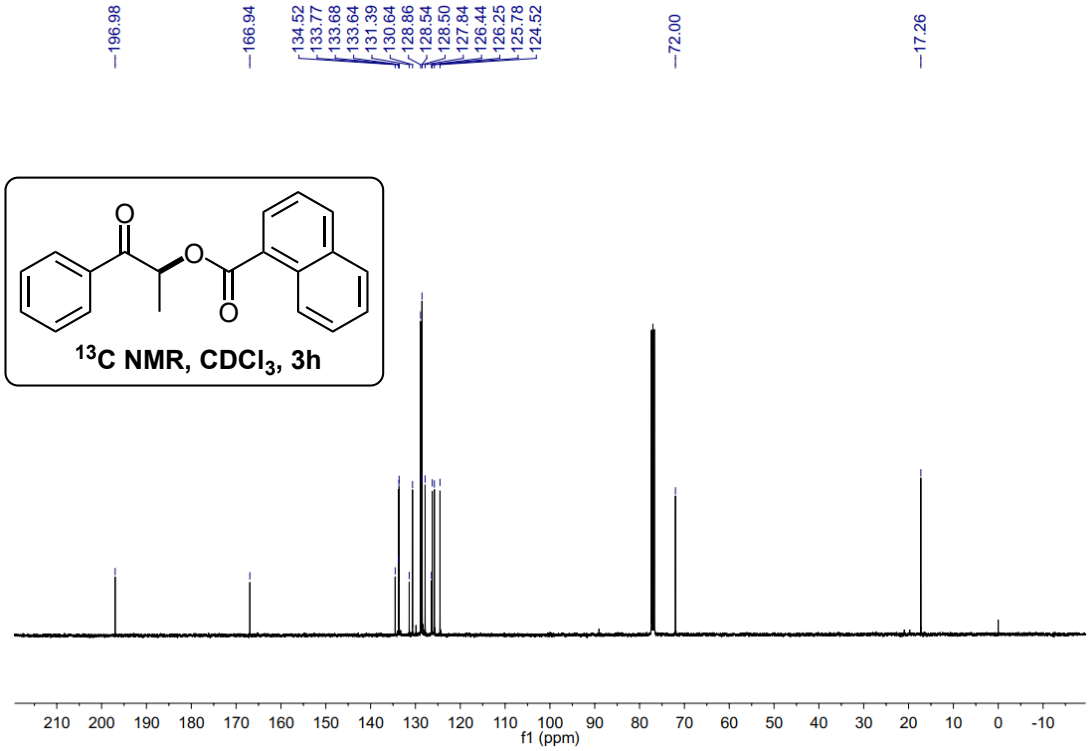


1-Oxo-1-phenylpropan-2-yl 1-naphthoate (3h)

^{1}H NMR

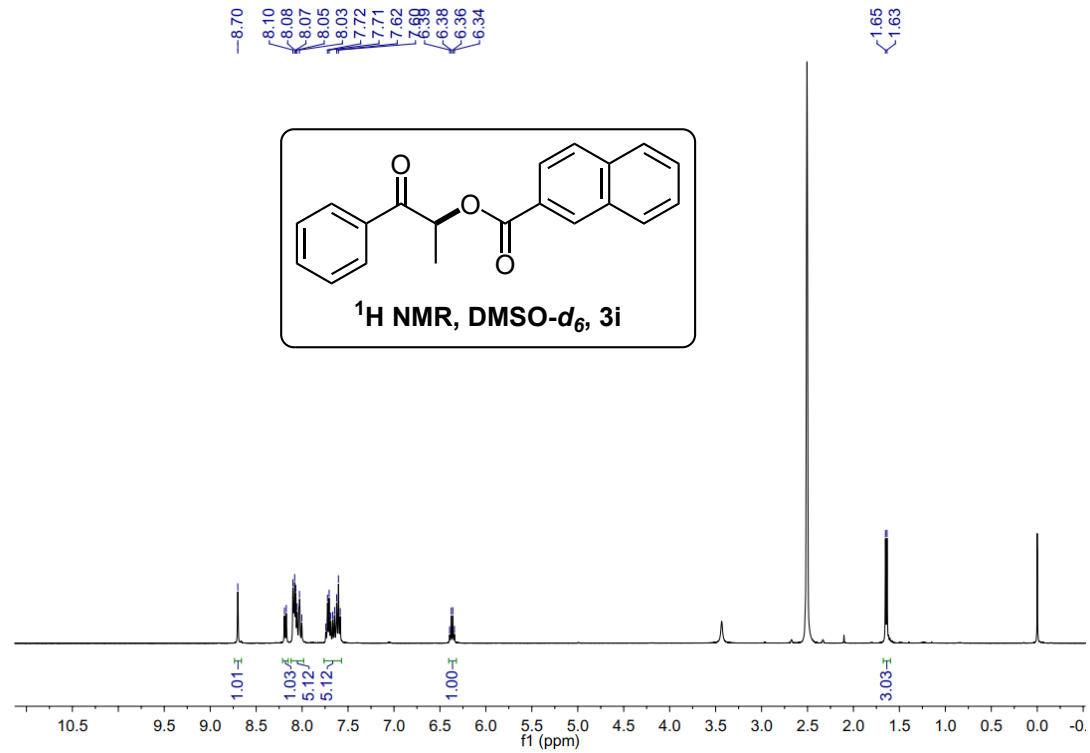


^{13}C NMR

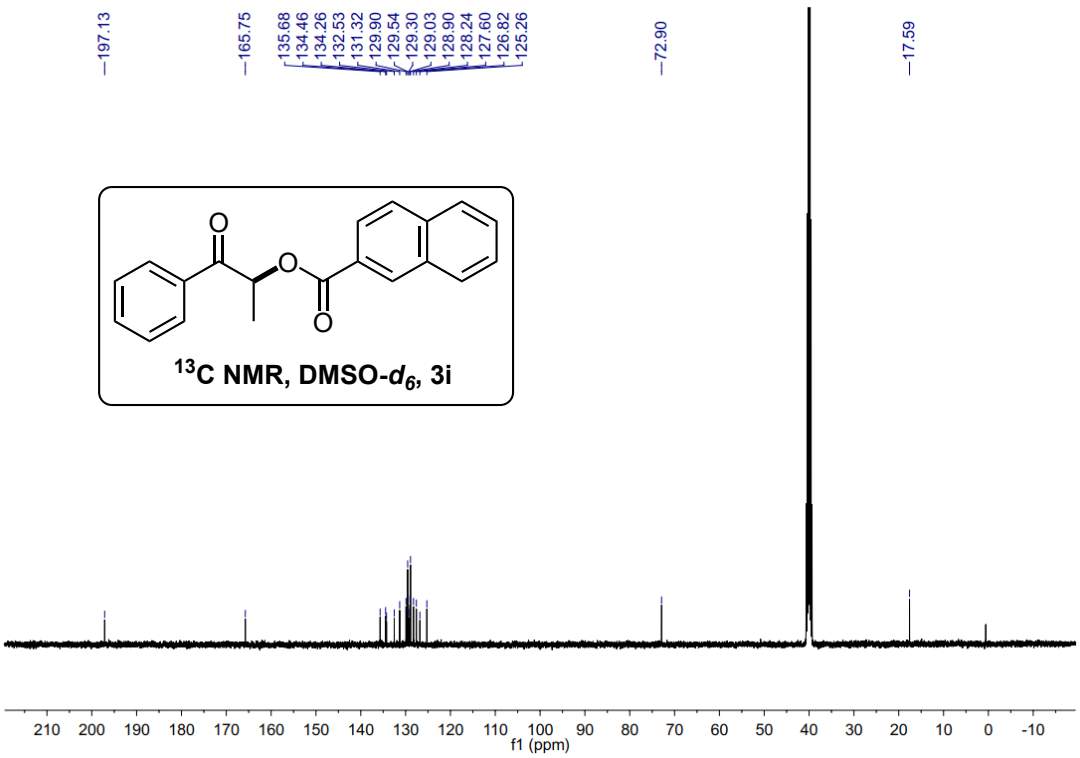


1-Oxo-1-phenylpropan-2-yl 2-naphthoate (3i)

^{1}H NMR

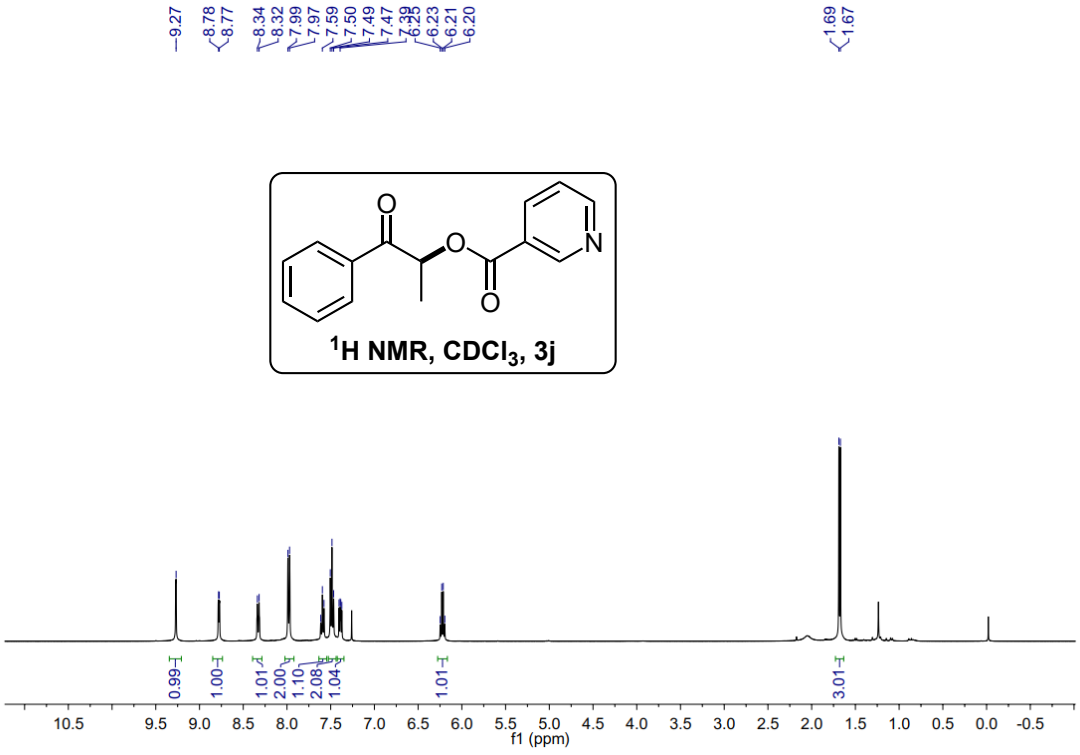


^{13}C NMR

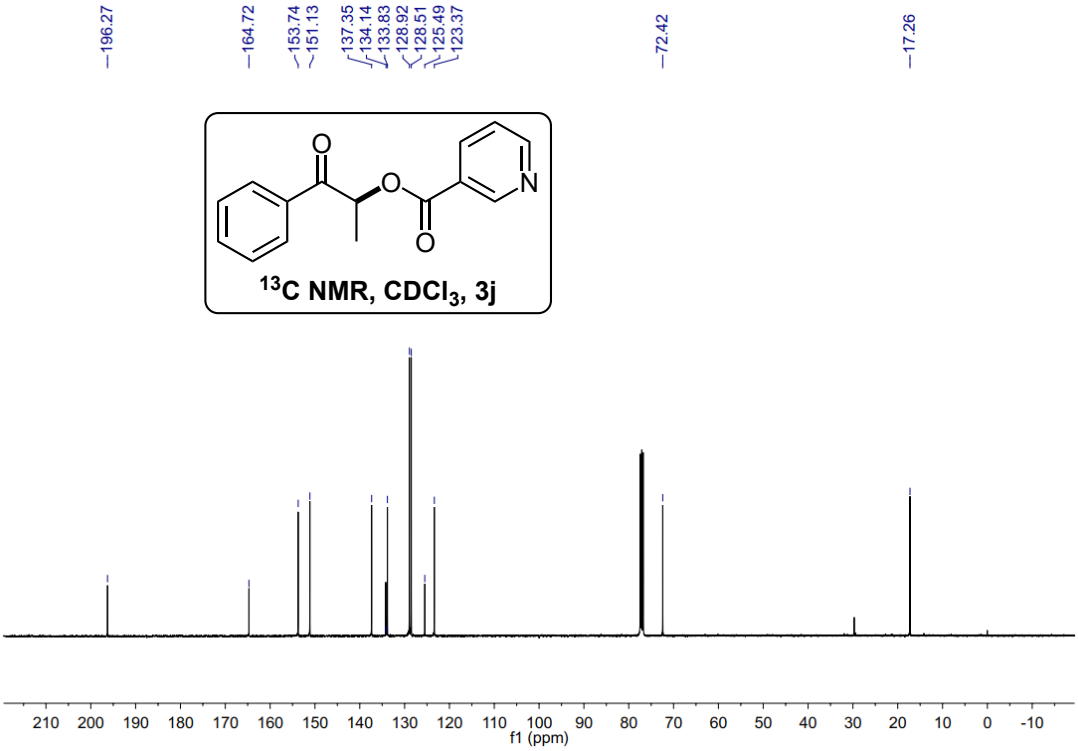


1-Oxo-1-phenylpropan-2-yl nicotinate (3j)

^{1}H NMR

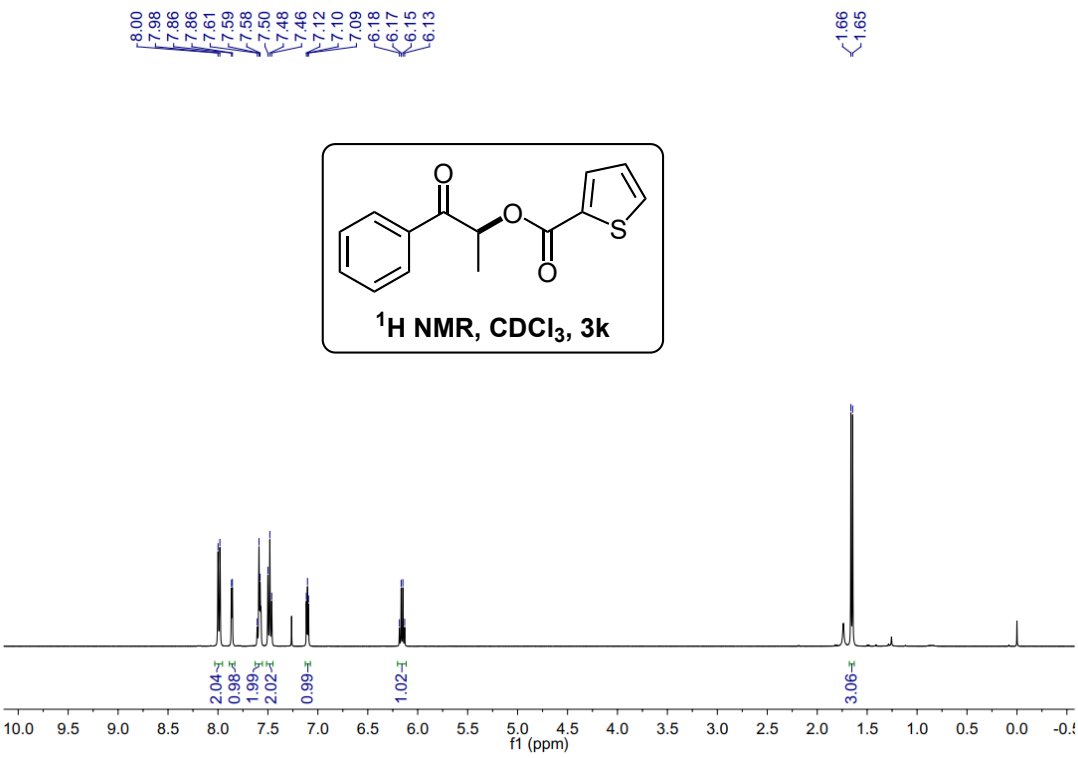


^{13}C NMR

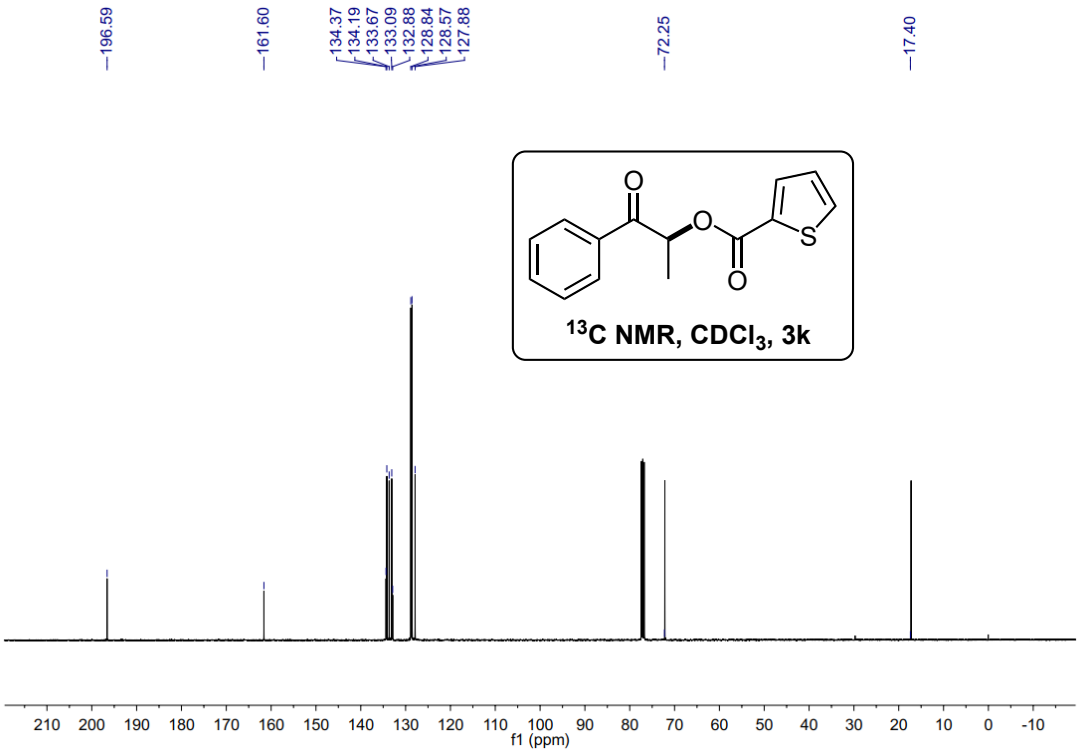


1-Oxo-1-phenylpropan-2-yl thiophene-2-carboxylate (3k)

^{1}H NMR

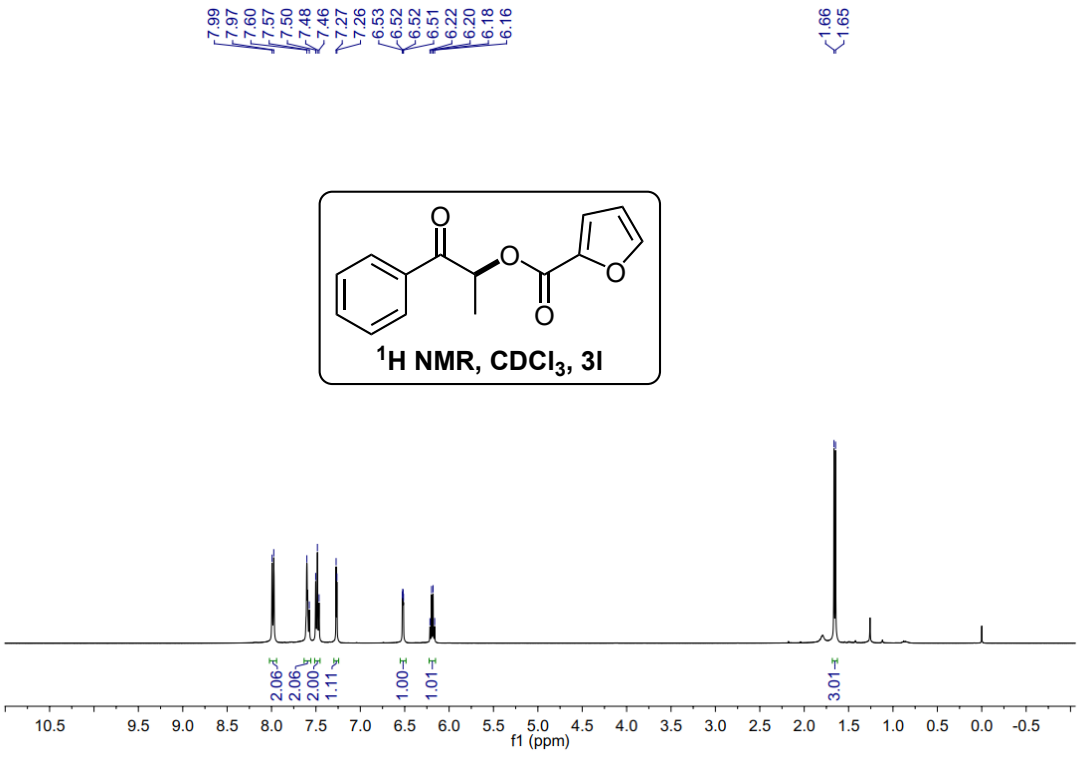


^{13}C NMR

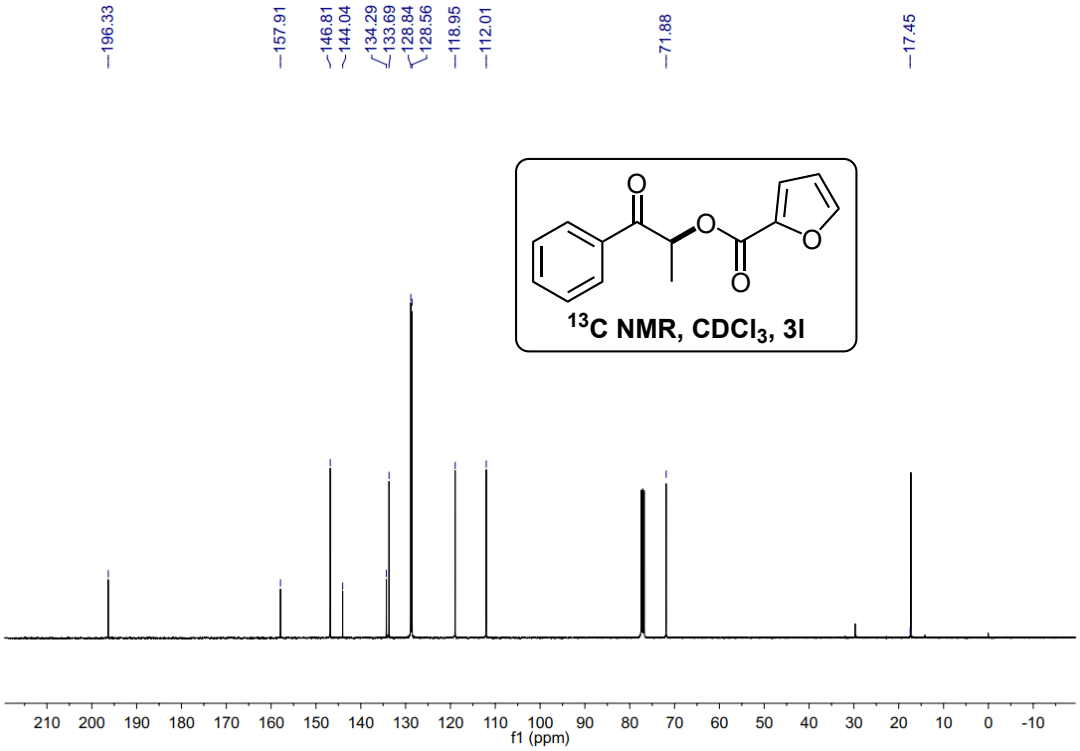


1-Oxo-1-phenylpropan-2-yl furan-2-carboxylate (3l)

^{1}H NMR

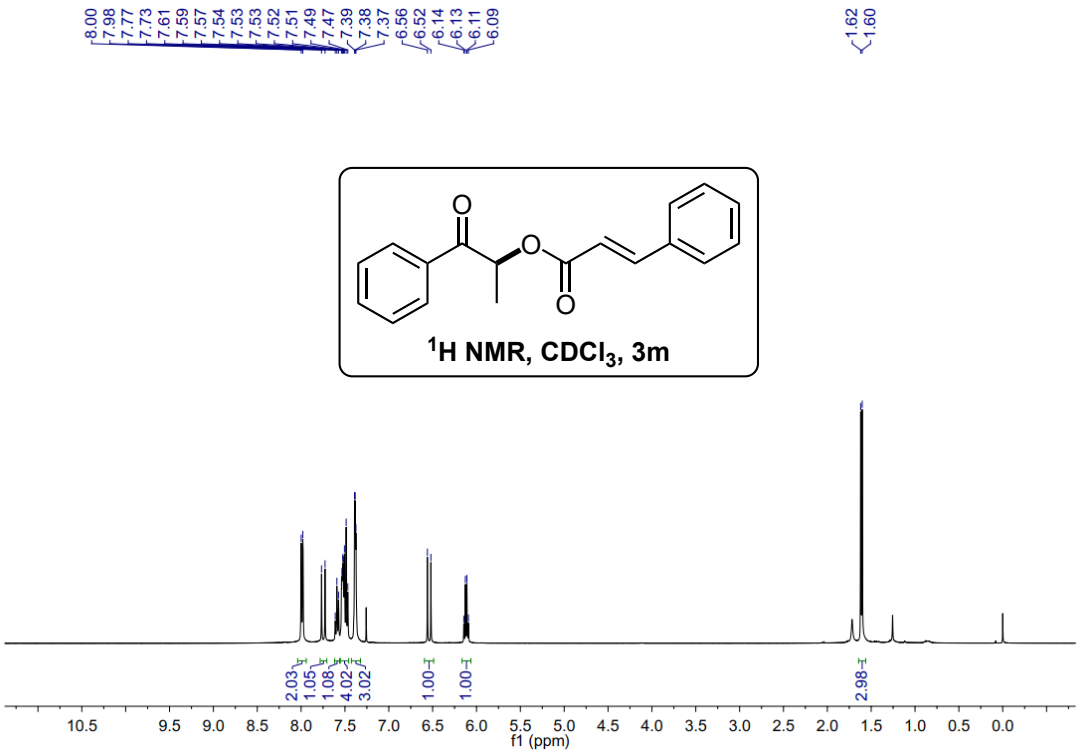


^{13}C NMR

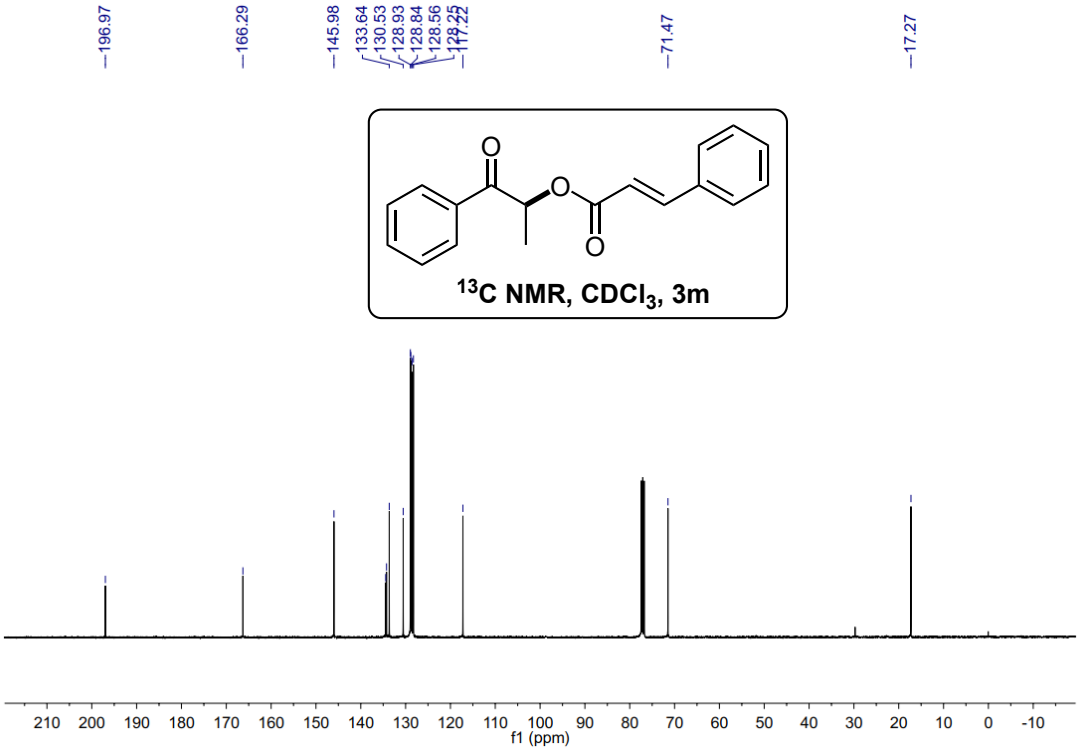


1-Oxo-1-phenylpropan-2-yl cinnamate (3m)

^{1}H NMR

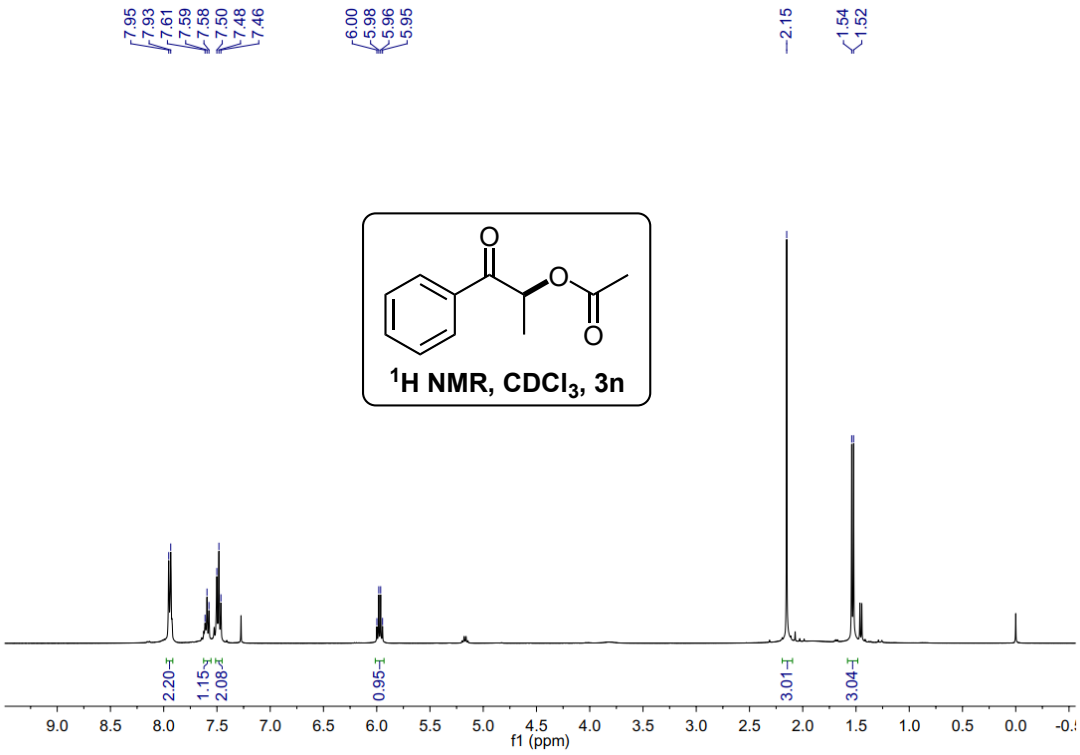


^{13}C NMR

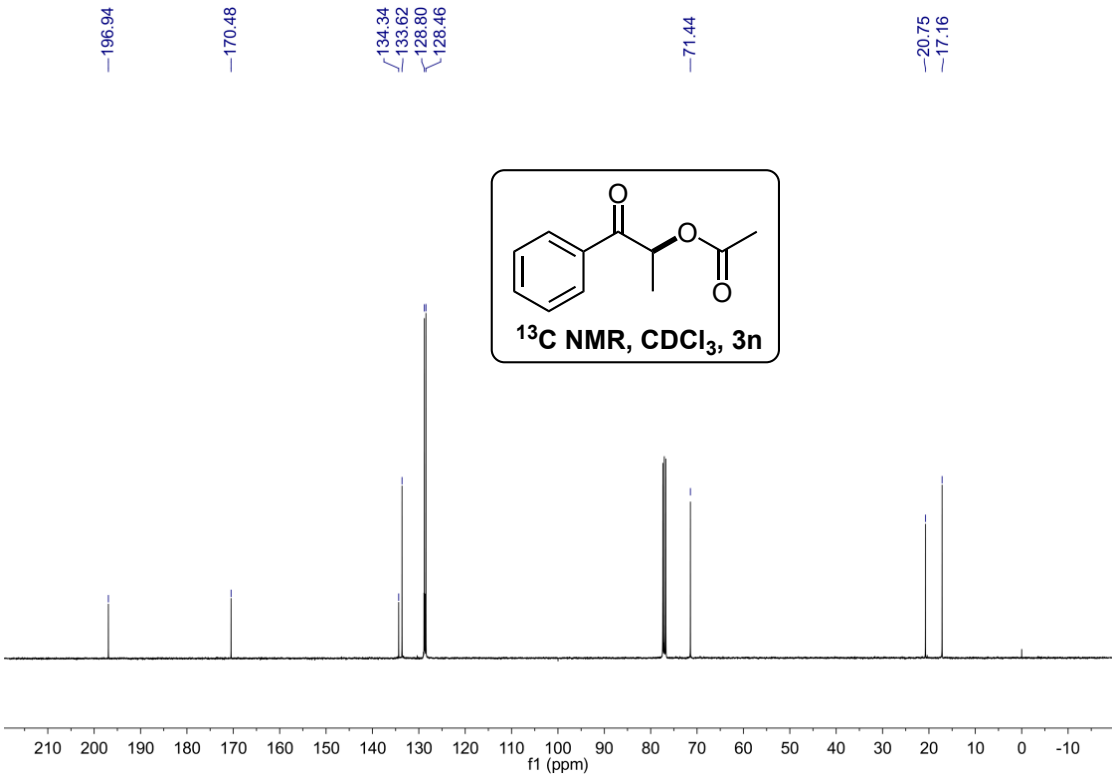


1-Oxo-1-phenylpropan-2-yl acetate (3n)

^{1}H NMR

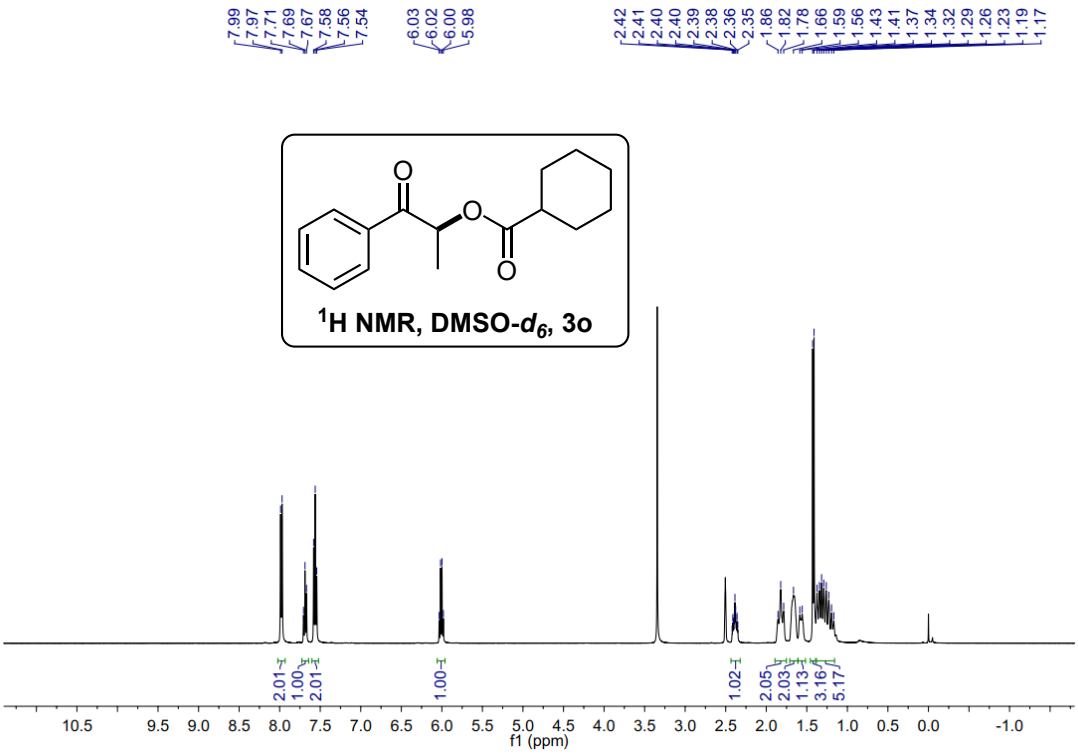


^{13}C NMR

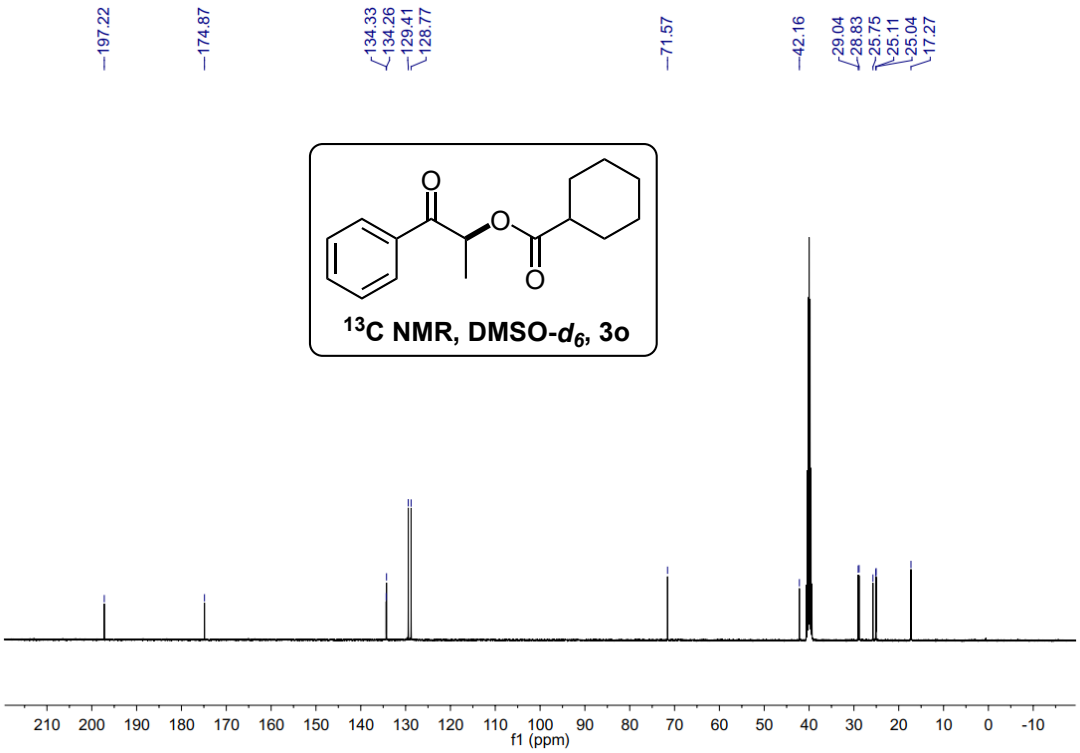


1-Oxo-1-phenylpropan-2-yl cyclohexanecarboxylate (3o)

^{1}H NMR

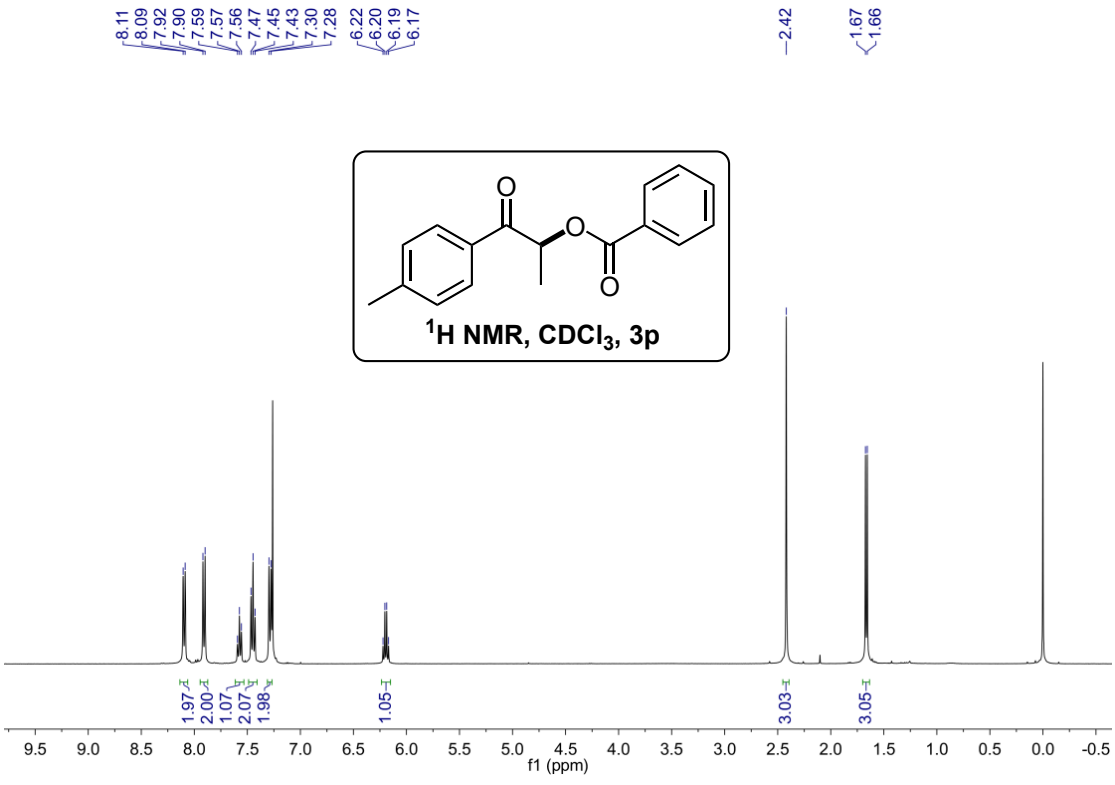


^{13}C NMR

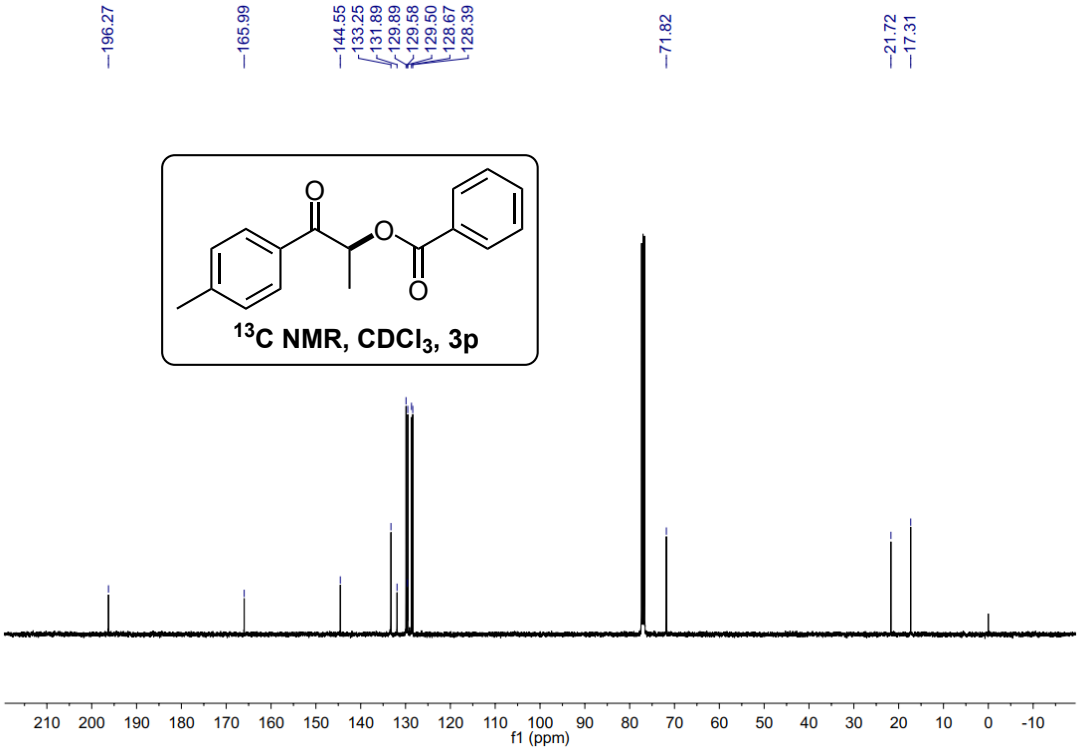


1-Oxo-1-(*p*-tolyl)propan-2-yl benzoate (3p)

^{1}H NMR

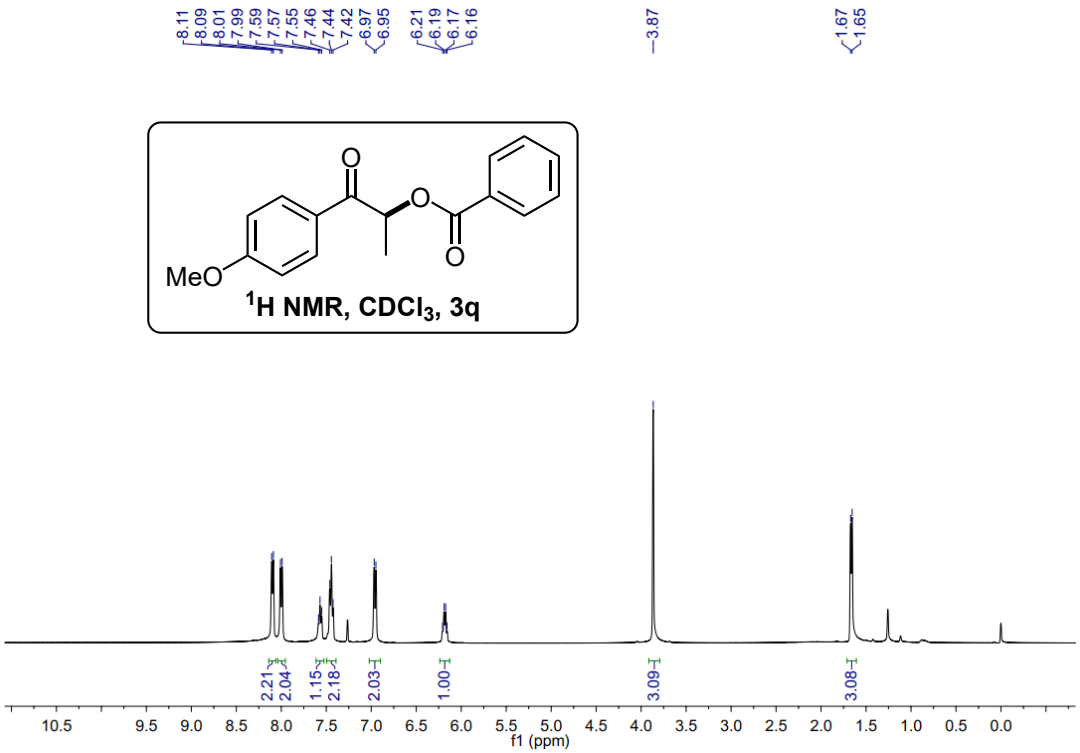


^{13}C NMR

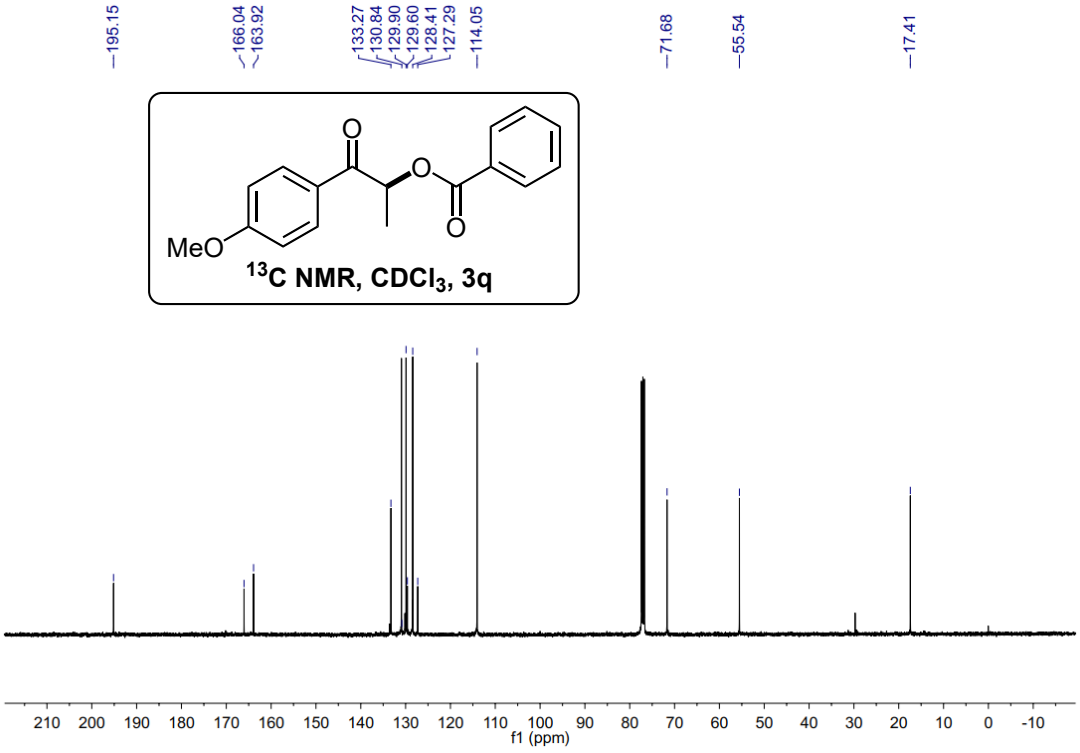


1-(4-Methoxyphenyl)-1-oxopropan-2-yl benzoate (3q)

^{1}H NMR

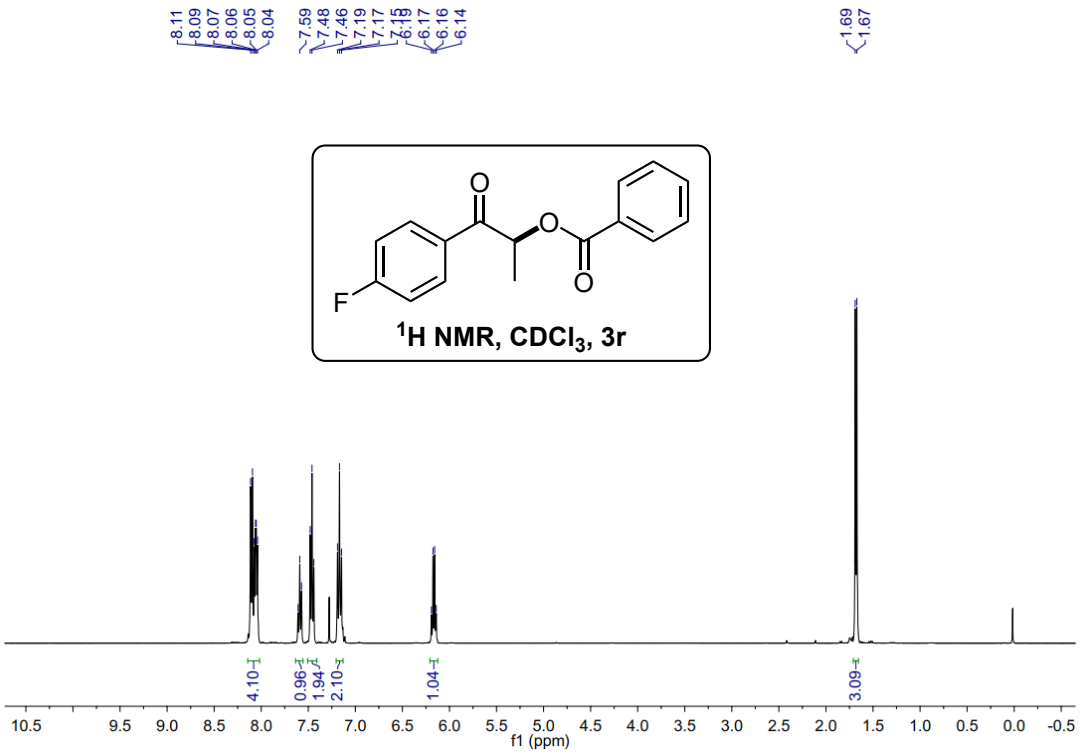


^{13}C NMR

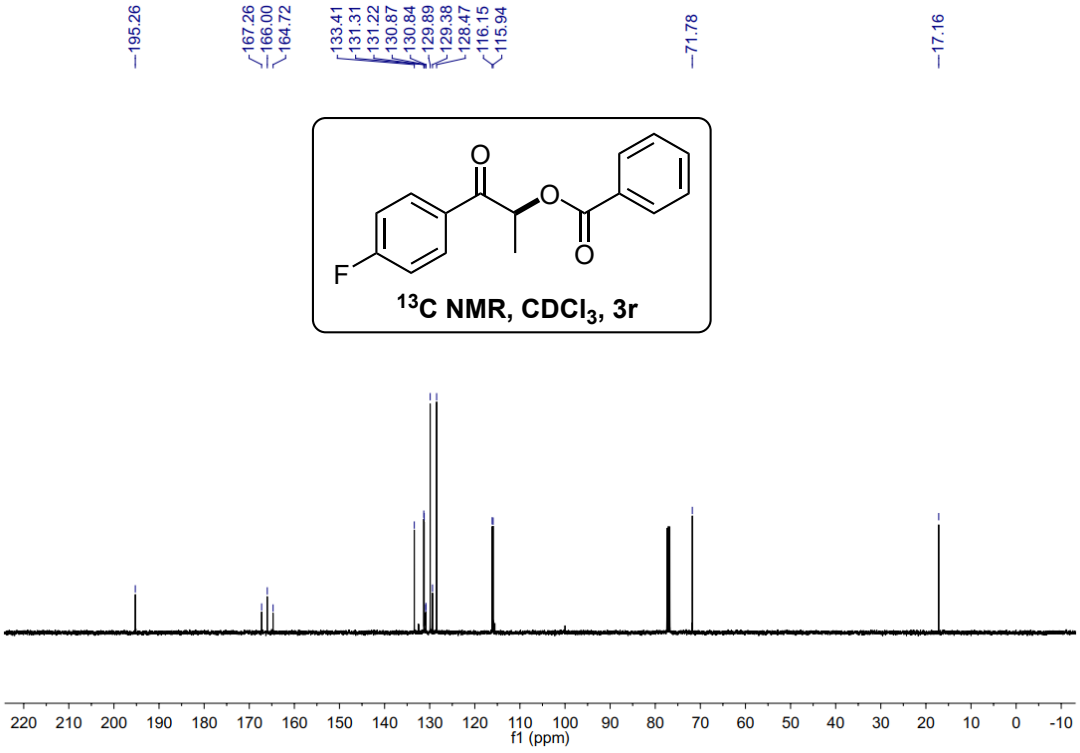


1-(4-Fluorophenyl)-1-oxopropan-2-yl benzoate (3r)

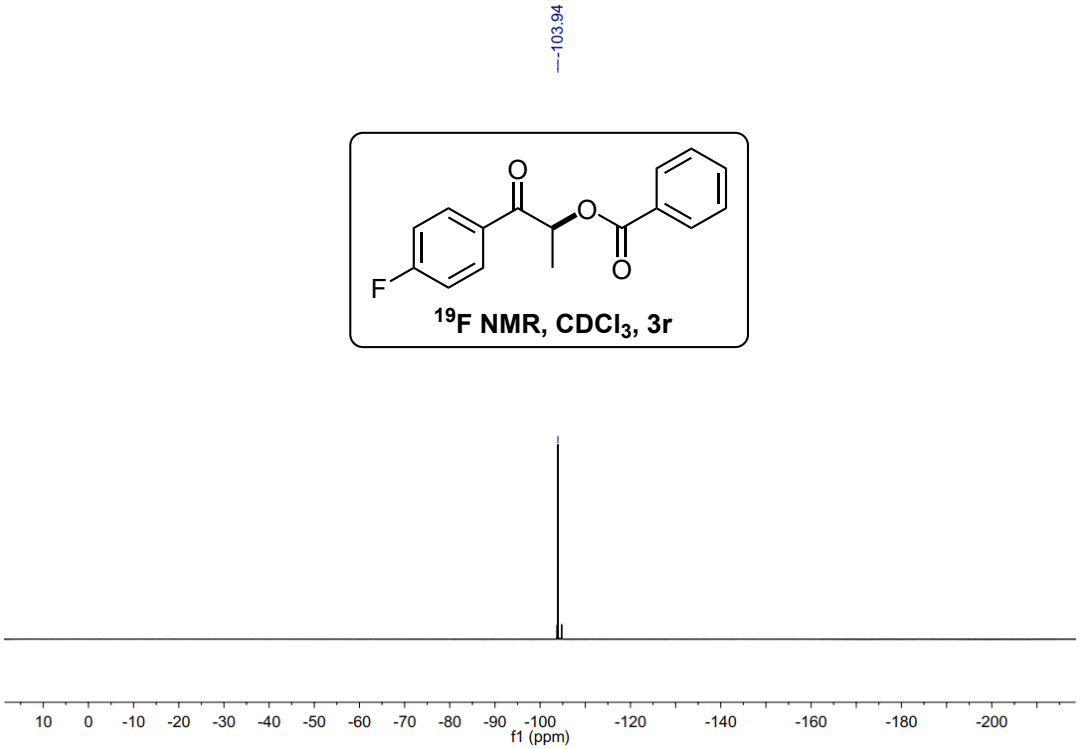
^{1}H NMR



^{13}C NMR

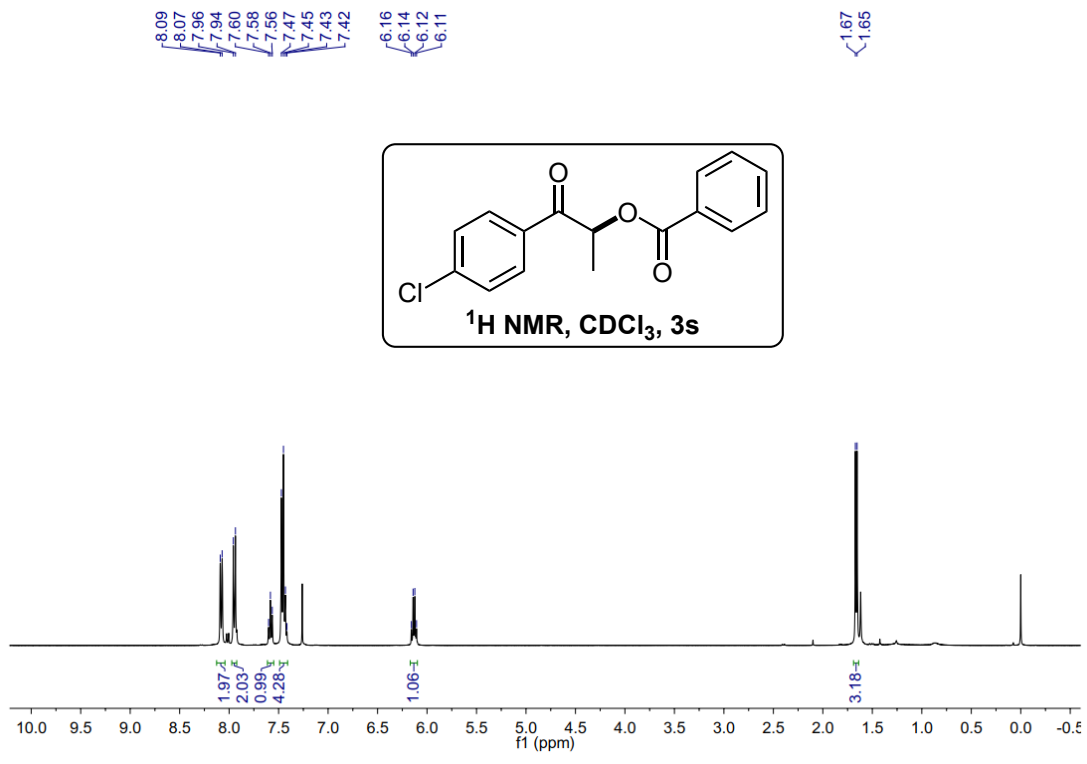

195.26
167.26
166.00
164.72
133.41
131.31
131.22
130.87
130.84
129.89
129.38
128.47
116.15
115.94
71.78
17.16
O
O
O
F
13C NMR, CDCl3, 3r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR

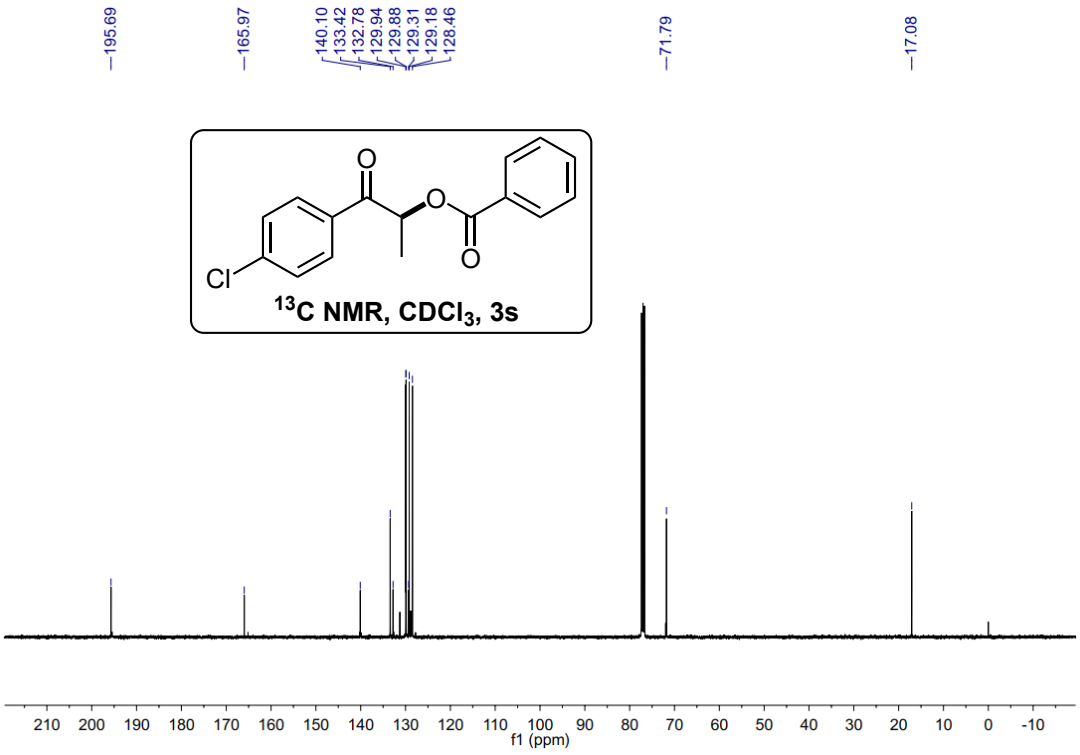

103.94
O
O
O
F
19F NMR, CDCl3, 3r
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

1-(4-Chlorophenyl)-1-oxopropan-2-yl benzoate (3s)

^{1}H NMR

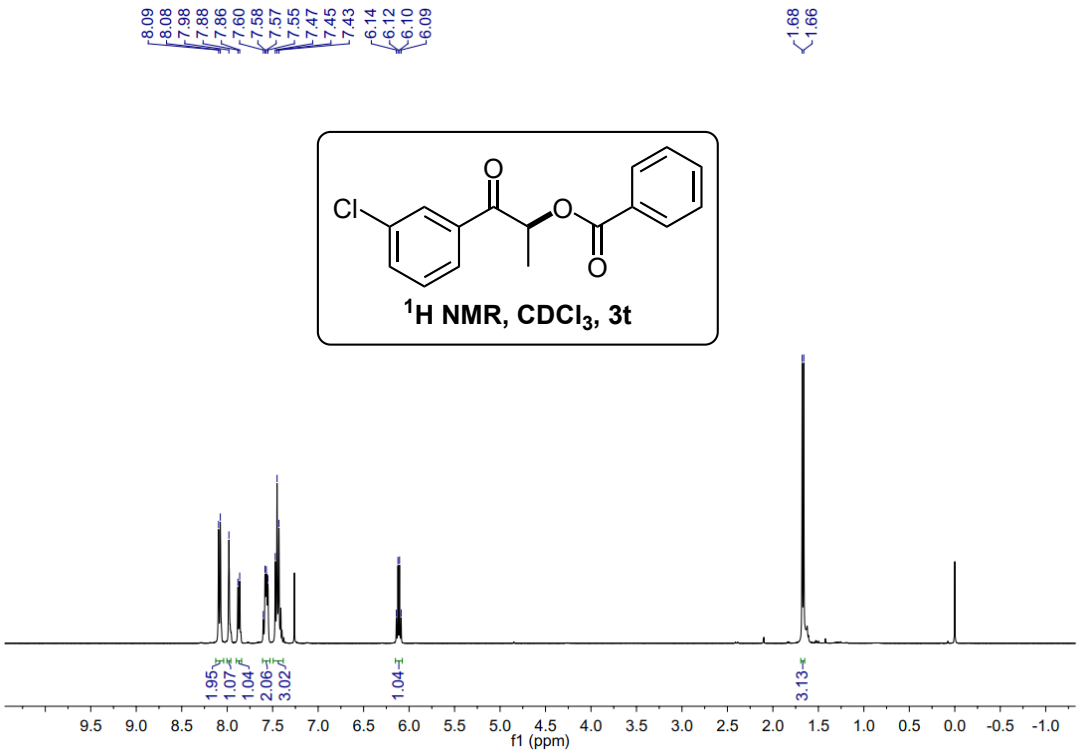


^{13}C NMR

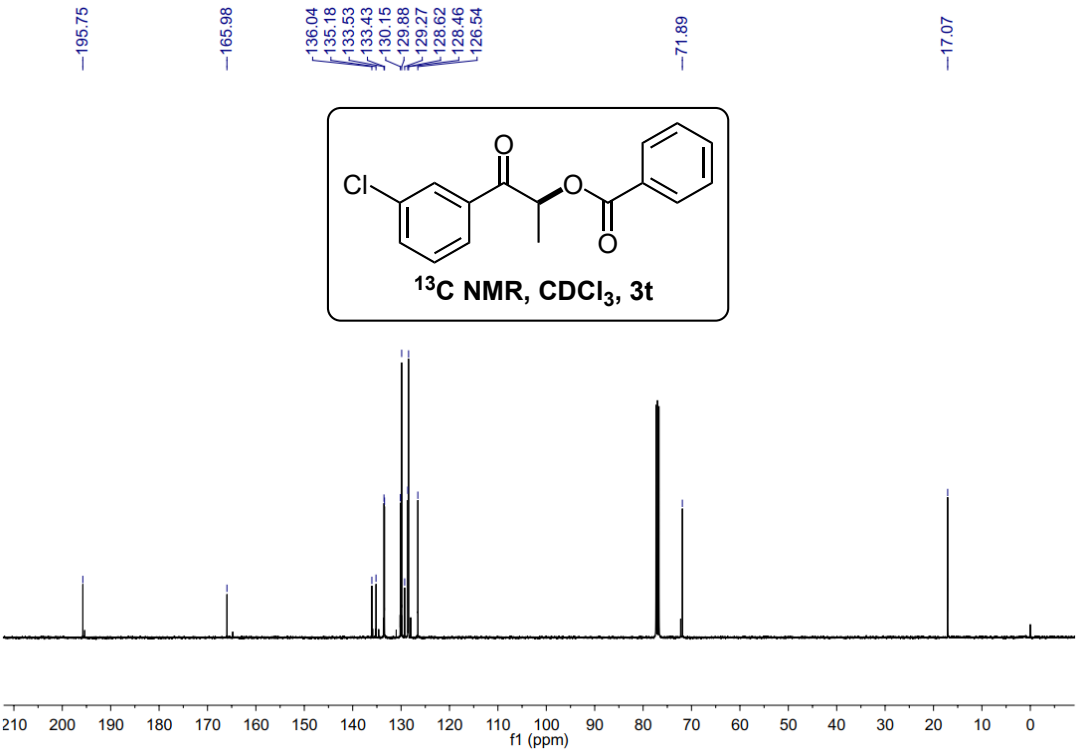


1-(3-Chlorophenyl)-1-oxopropan-2-yl benzoate (3t)

^{1}H NMR

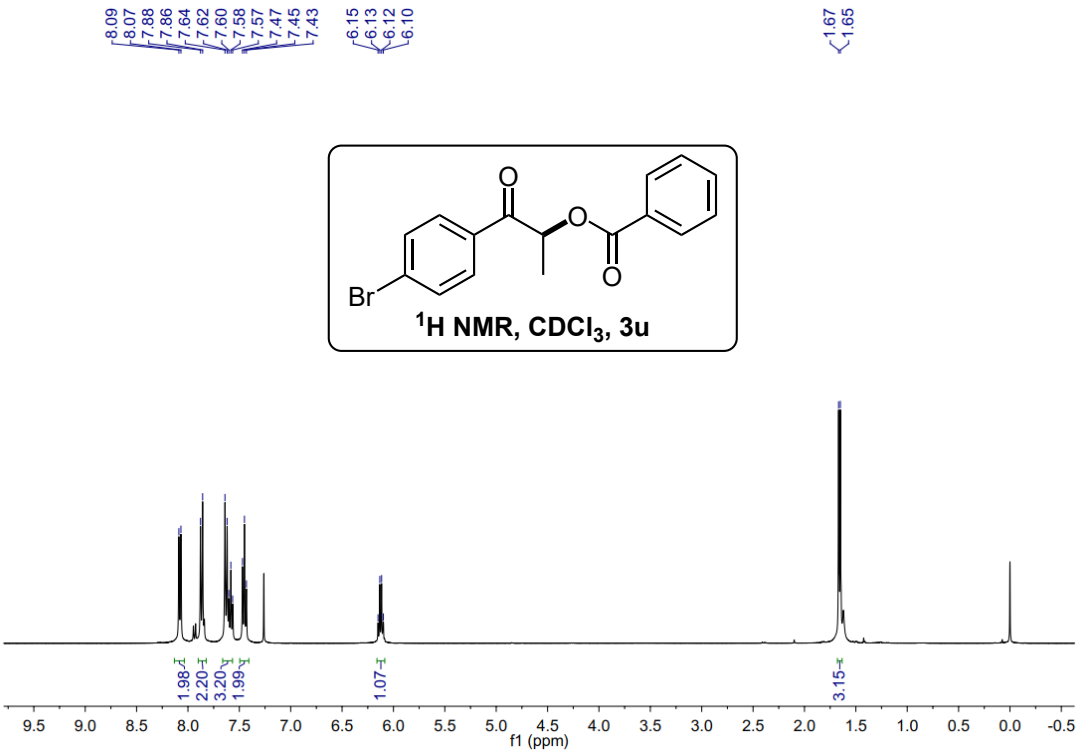


^{13}C NMR

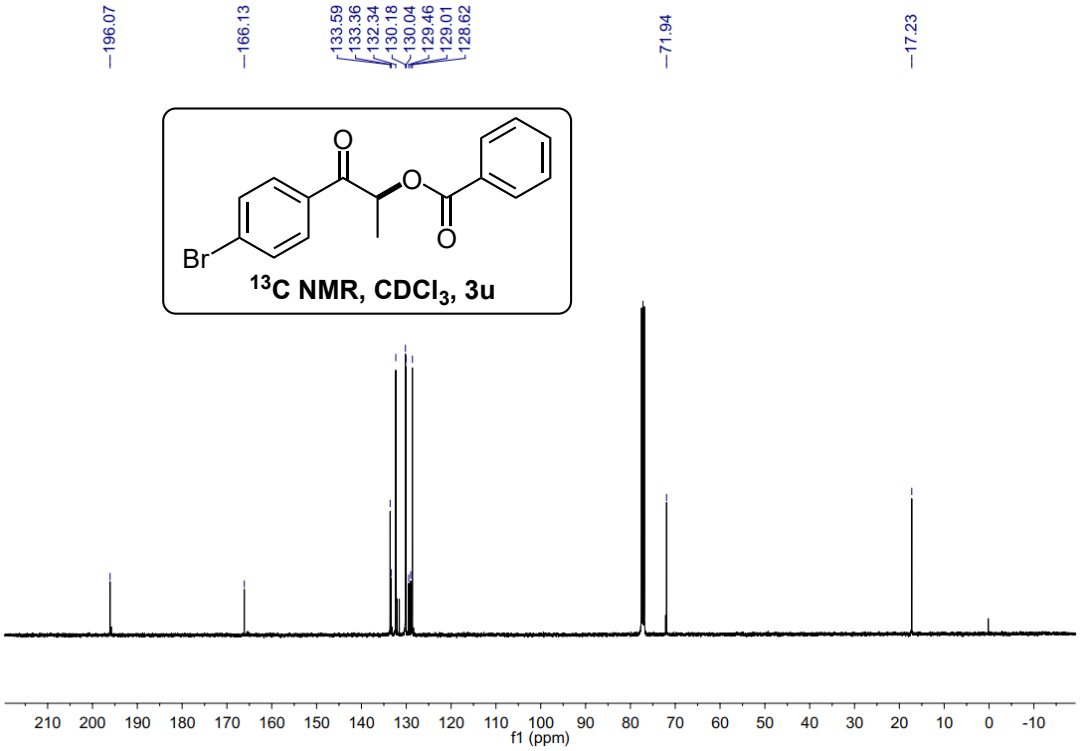


1-(4-Bromophenyl)-1-oxopropan-2-yl benzoate (3u)

^{1}H NMR

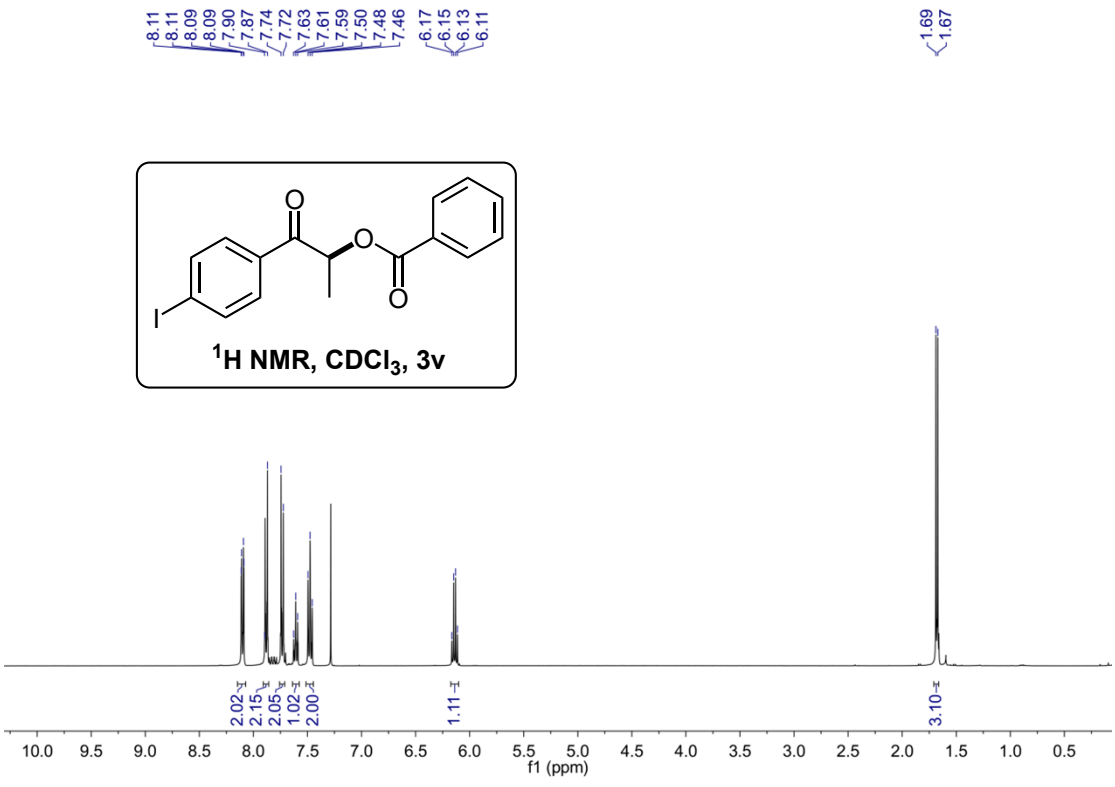


^{13}C NMR

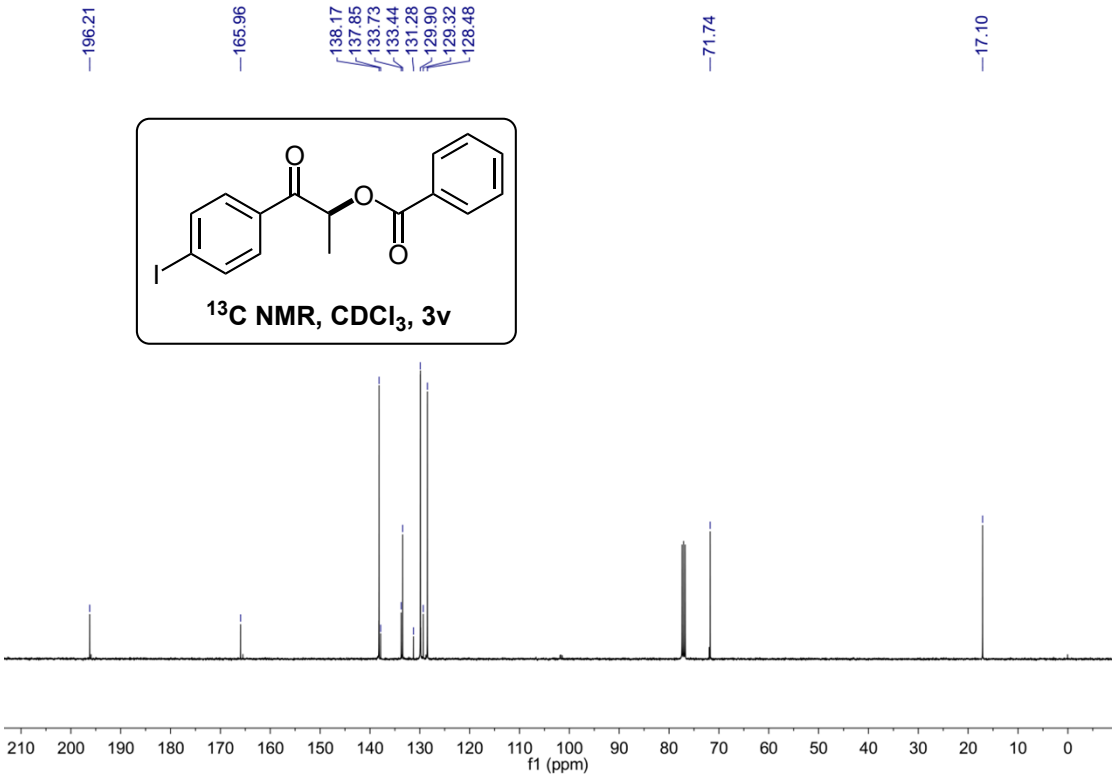


1-(4-Iodophenyl)-1-oxopropan-2-yl benzoate (3v)

^{1}H NMR

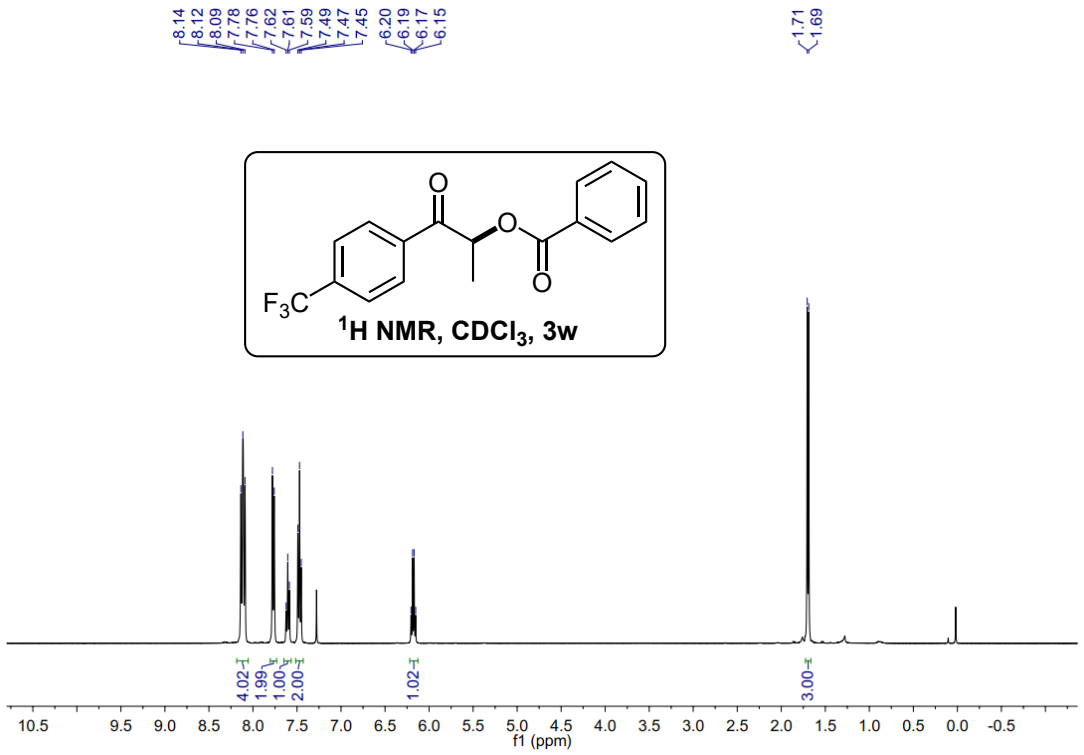


^{13}C NMR

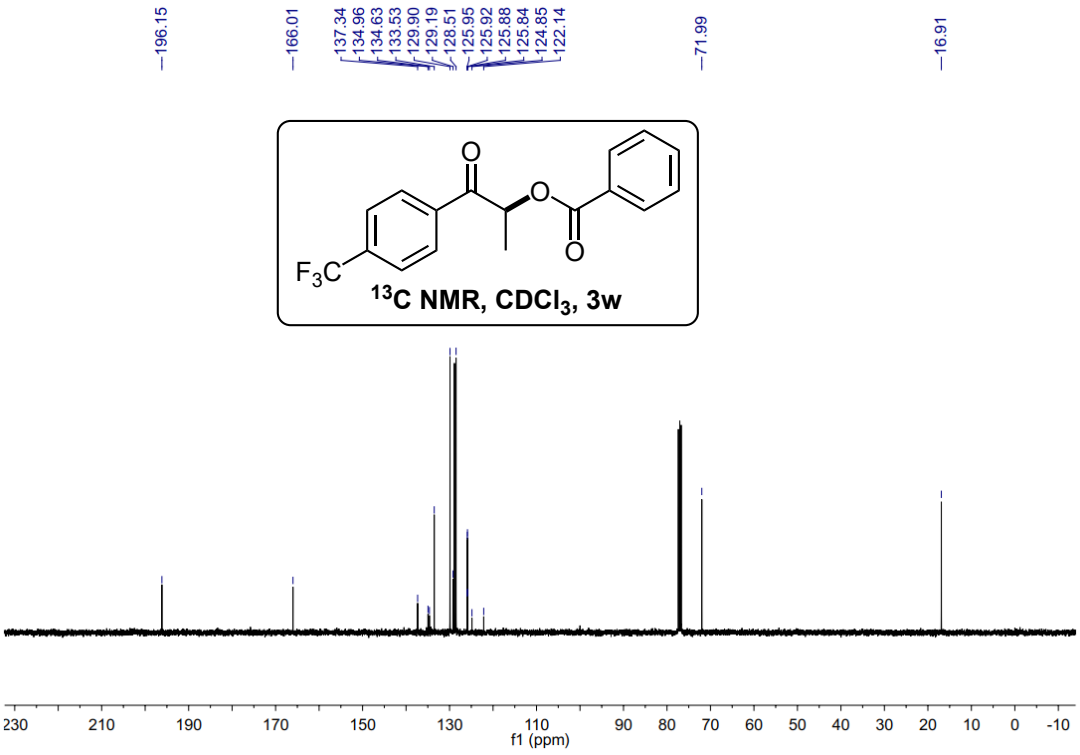


1-Oxo-1-(4-(trifluoromethyl)phenyl)propan-2-yl benzoate (3w)

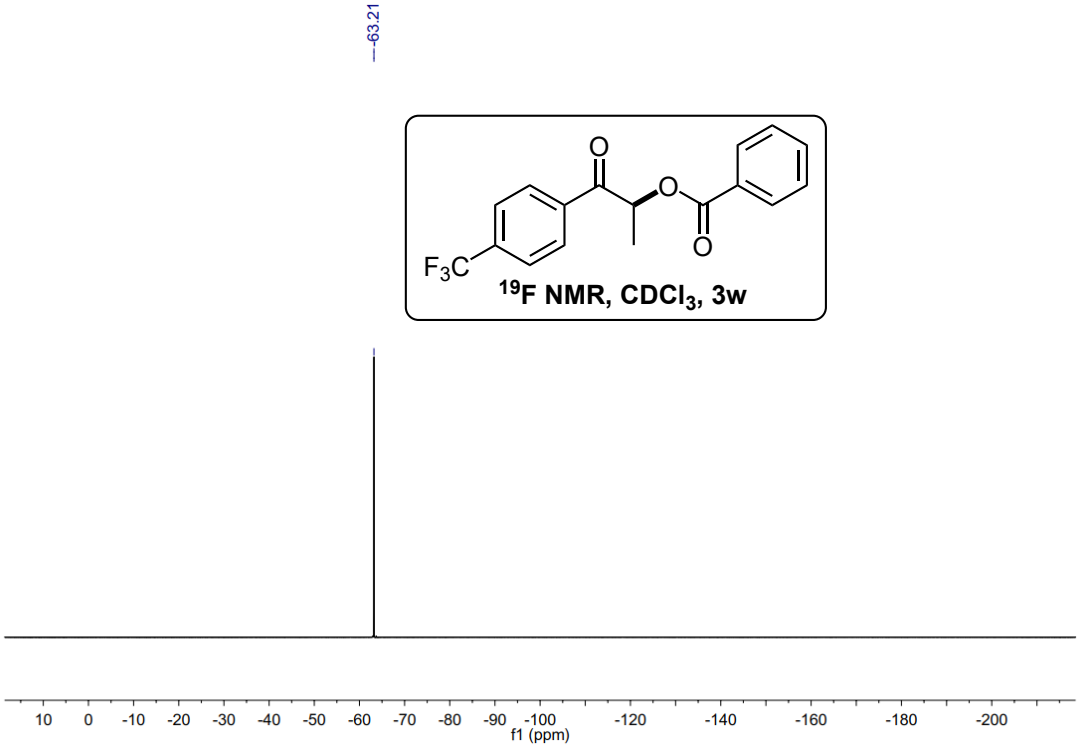
^{1}H NMR



^{13}C NMR

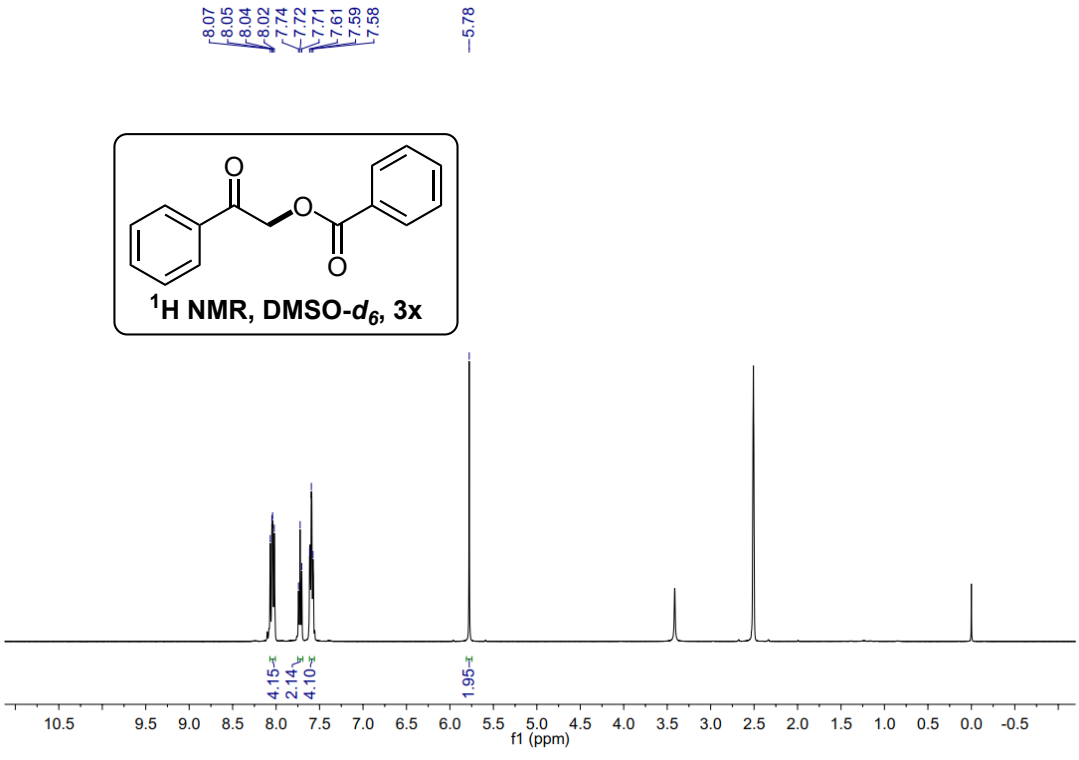

196.15
166.01
137.34
134.96
134.63
133.53
129.90
129.19
128.51
125.95
125.92
125.88
125.84
124.85
122.14
71.99
16.91
O
O
O
F3C
13C NMR, CDCl3, 3w
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR

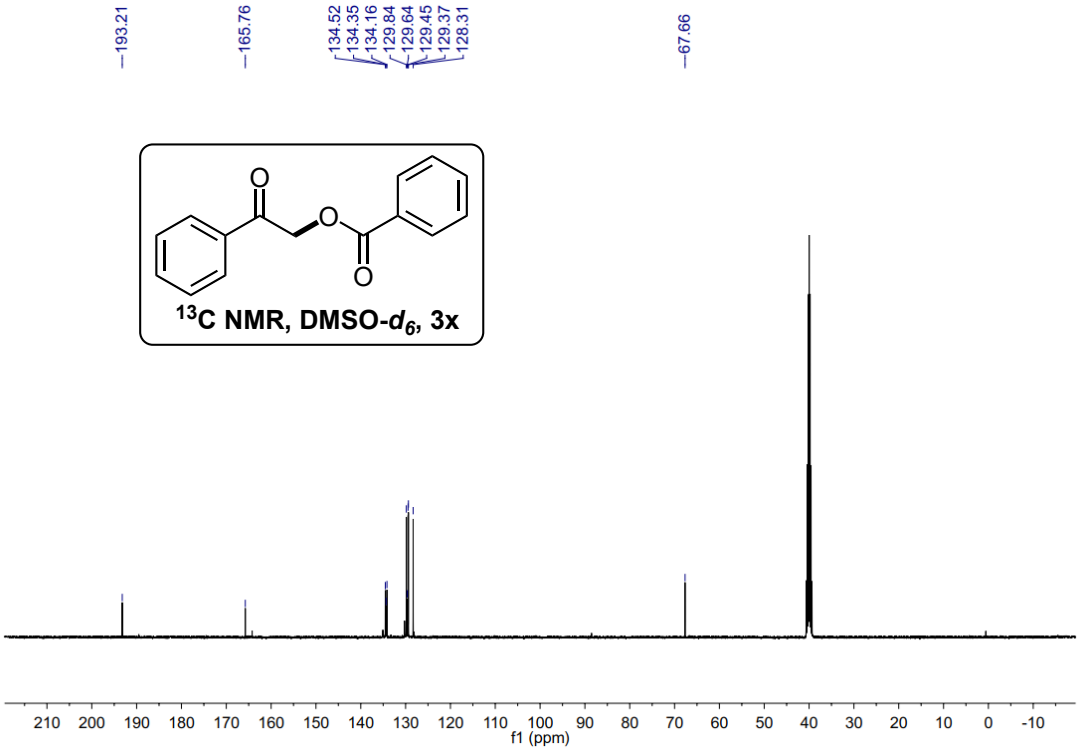

63.21
O
O
O
F3C
19F NMR, CDCl3, 3w
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

2-Oxo-2-phenylethyl benzoate (3x)

^{1}H NMR

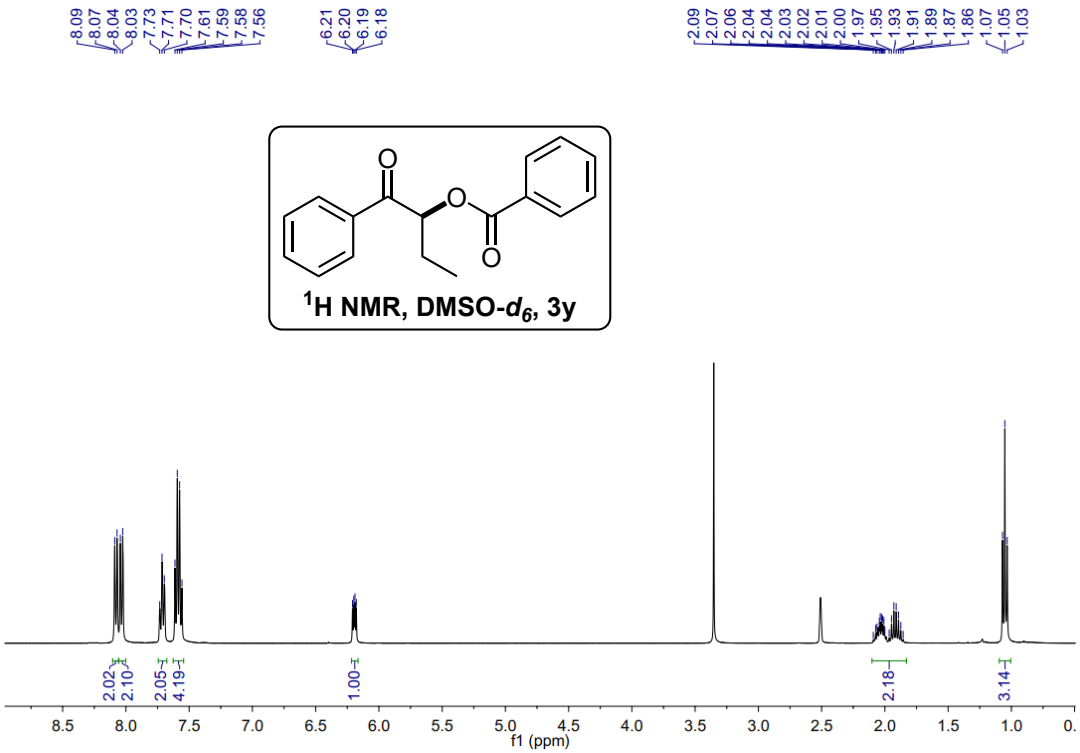


^{13}C NMR

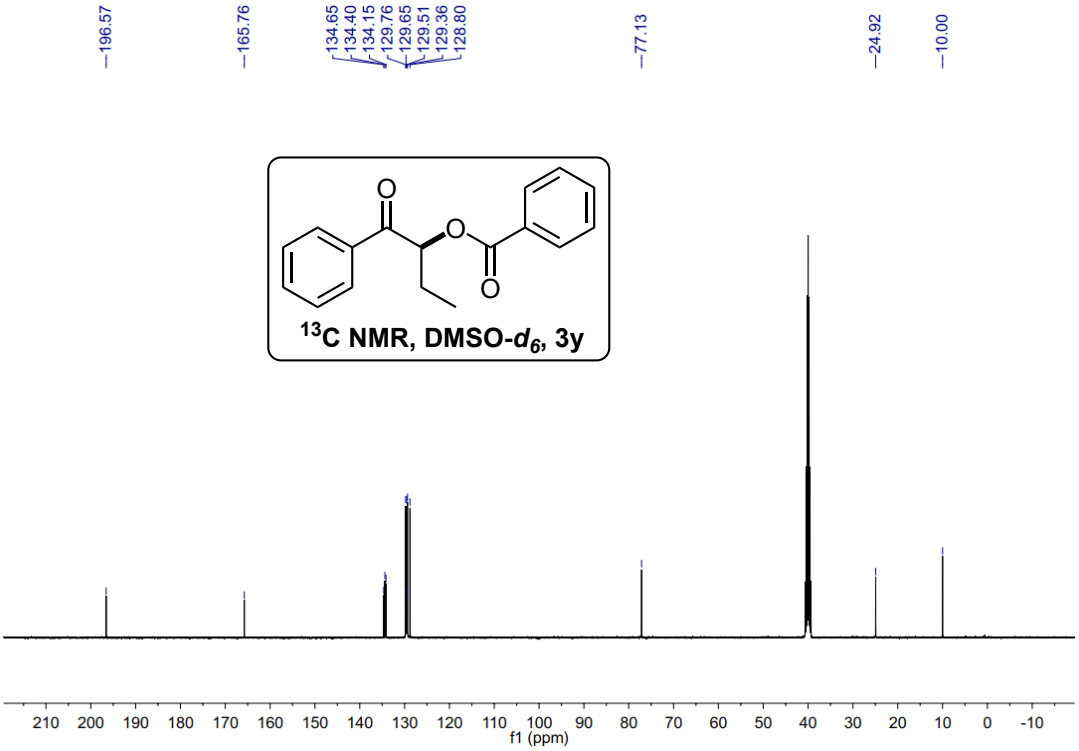


1-Oxo-1-phenylbutan-2-yl benzoate (3y)

^{1}H NMR

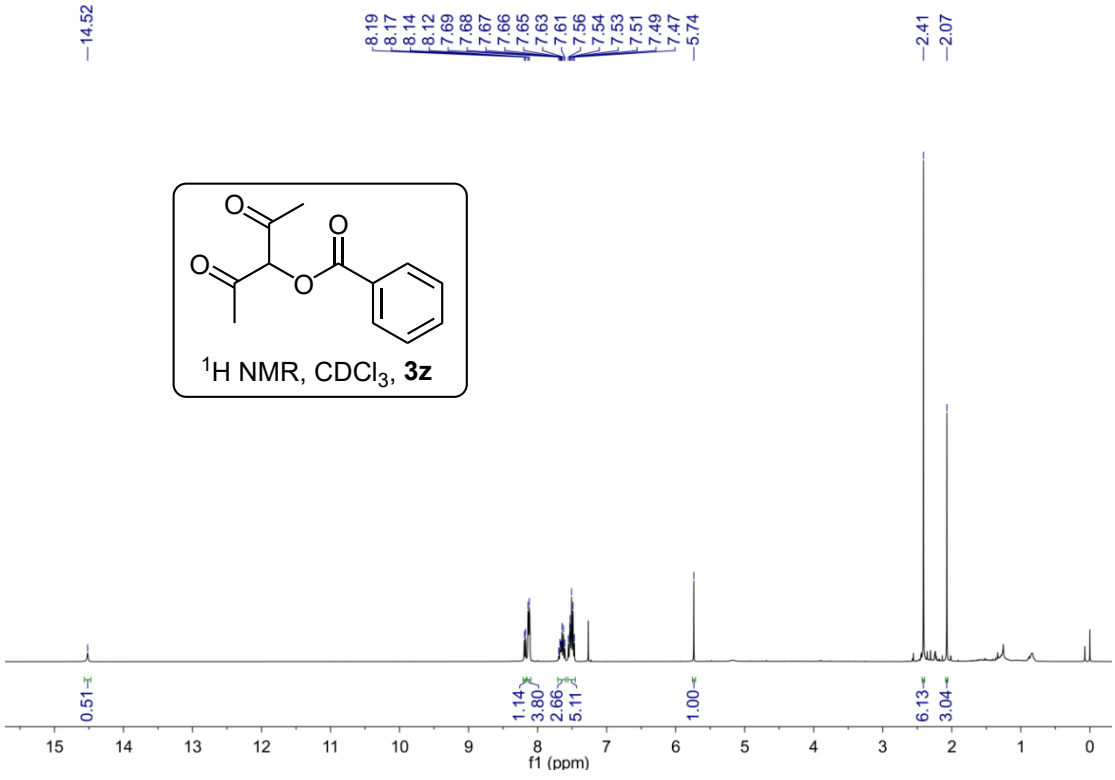


^{13}C NMR

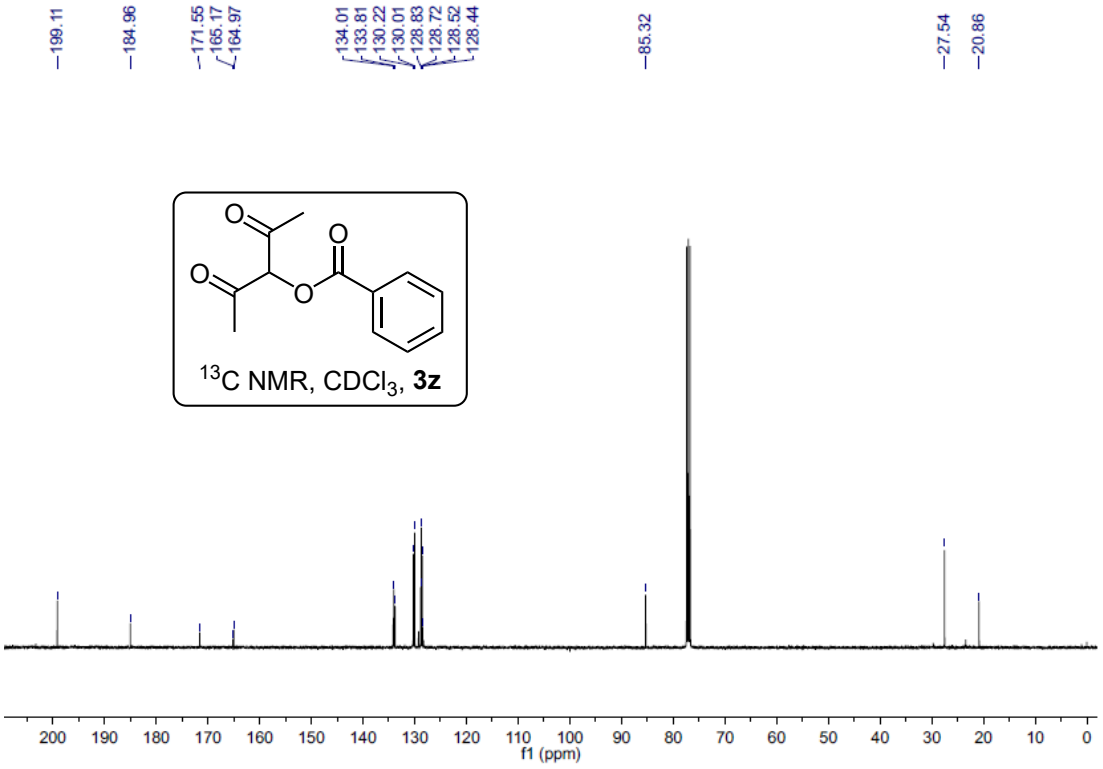


2,4-Dioxopentan-3-yl benzoate (3z)

^{1}H NMR

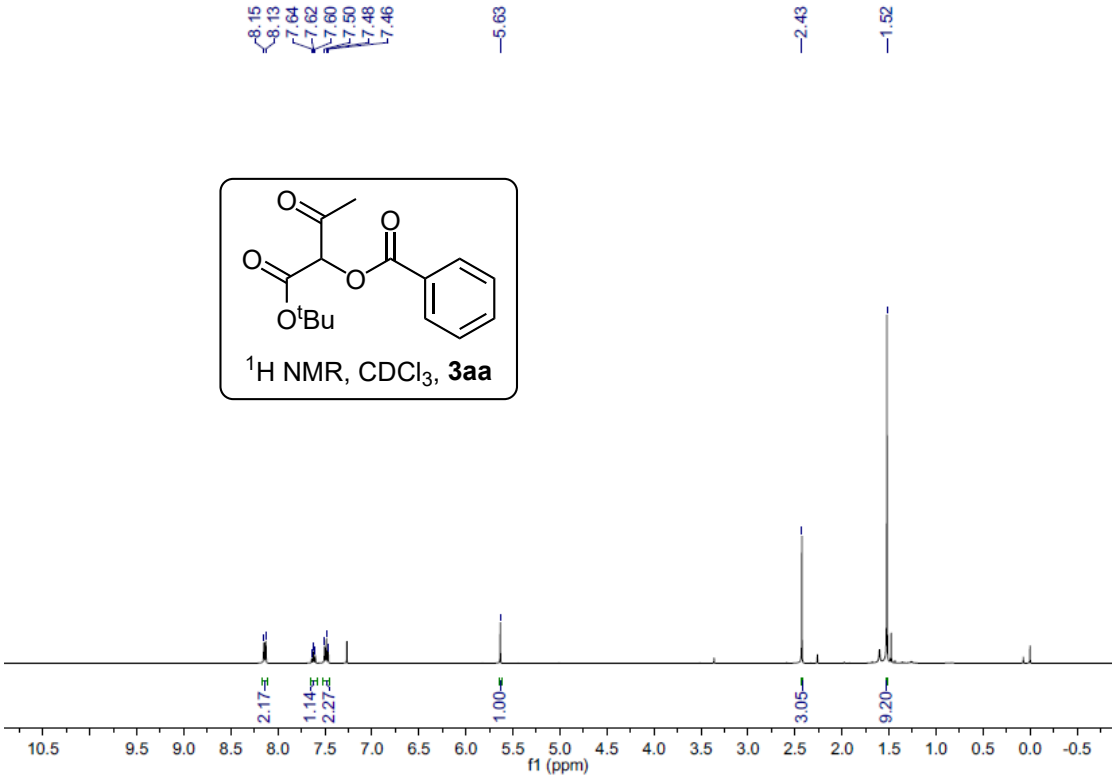


^{13}C NMR

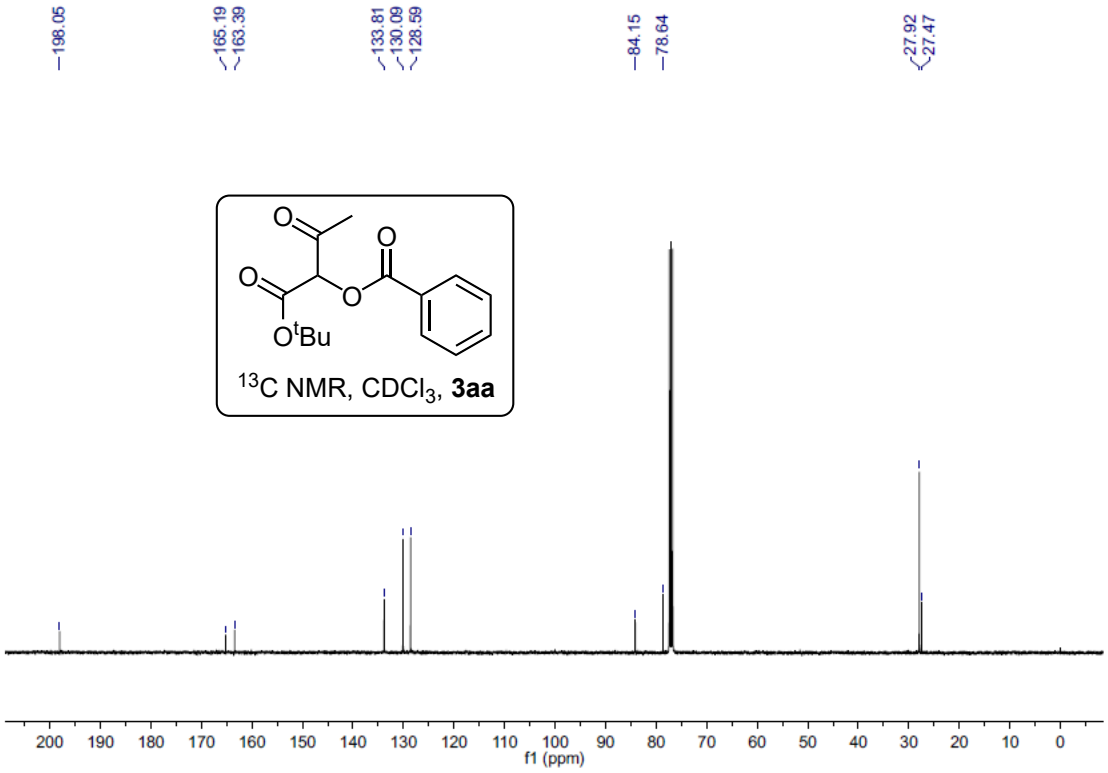


1-(*tert*-Butoxy)-1,3-dioxobutan-2-yl benzoate (3aa)

^{1}H NMR

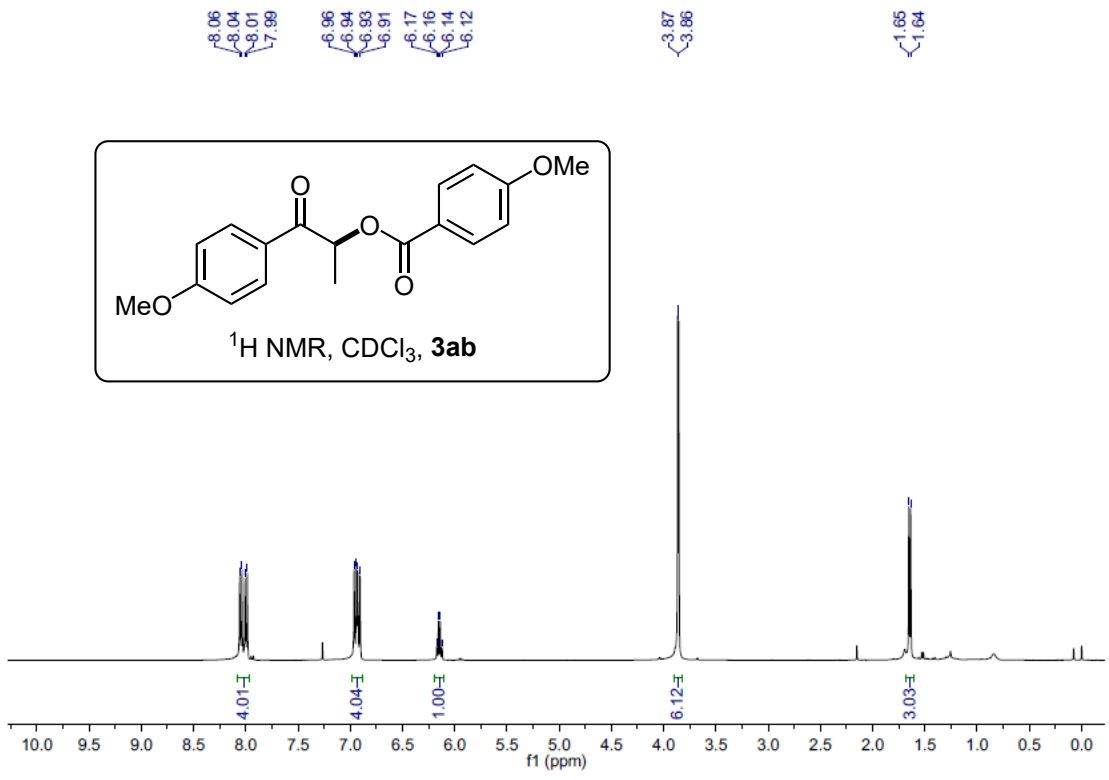


^{13}C NMR

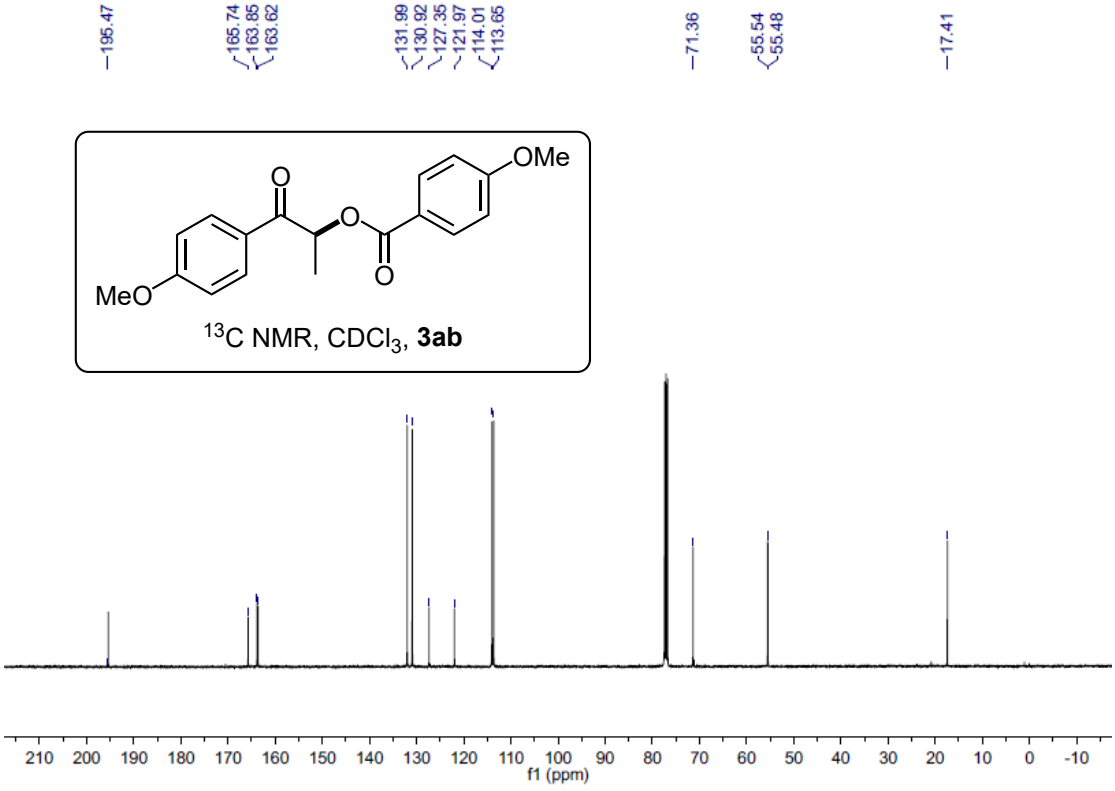


1-(4-Methoxyphenyl)-1-oxopropan-2-yl 4-methoxybenzoate (3ab)

^{1}H NMR



^{13}C NMR



5. References

[1] J. Li, Z. Yang, T. Yang, J. Yi, C. Zhou, Copper-catalyzed α-C–H acyloxylation of carbonyl compounds with terminal alkynes, *New J. Chem.,* 2018, **42**, 1581.

[2] C. Li, T. Jin, X. Zhang, C. Li, X. Jia, J. Li, Bu_4NI-Catalyzed α-Oxyacylation of Carbonyl Compounds with Toluene Derivatives, *Org. Lett.,* 2016, **18**, 1916.

[3] X. Huang, X. Liang, J. Yuan, Z. Ni, Y. Zhou, Y. Pan, Aerobic copper catalyzed α-oxyacylation of ketones with carboxylic acids, *Org. Chem. Front.,* 2017, **4**, 163.

[4] F. Zhu, Z.-X. Wang, Bu_4NI-catalyzed α-acyloxylation reaction of ethers and ketones with aldehydes and tert-butyl hydroperoxide, *Tetrahedron*, 2014, **70**, 9819.

[5] Z. Zhou, J. Cheng, J.-T. Yu, Bu_4NI-catalyzed direct α-oxyacylation of diarylethanones with acyl peroxides, *Org. Biomol. Chem.,* 2015, **13**, 9751.

[6] M. Uyanik, D. Suzuki, T. Yasui, K. Ishihara, In Situ Generated (Hypo)Iodite Catalysts for the Direct α-Oxyacylation of Carbonyl Compounds with Carboxylic Acids, *Angew. Chem. Int. Ed.,* 2011, **50**, 5331.

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