Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

# Catalytic Conversion of Ketones to Esters *via* C(O)-C Bond Cleavage under Transition-Metal free Conditions

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# 1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Most of the chemicals used in the catalytic reactions were purified according to standard procedure. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with $SiO_2$ (Silicycle Silica flash F60 (230-400 mesh). $^{1}H$ NMR (200, 400 or 500 MHz), $^{13}C$ NMR (50, 100 or 126 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.27 for $^{1}H$ (chloroform-d), δ 77.0 for $^{13}C$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

## 2. Experimental Section

**General procedure: Reaction of 1 with methanol**

In an oven dried screw cap reaction tube (15 mL), **1** (0.5 mmol), KO$^t$Bu (0.05 mmol), and methanol (1 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 12 h. After completion of the reaction the crude mixture was worked up with water and extracted using dichloromethane, followed by the solvent was removed under reduced pressure and finally the residue was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the corresponding esters.

**General procedure: Reaction of 1a with various alcohols**

In an oven dried screw cap reaction tube (15 mL), **1a** (0.5 mmol), KO$^t$Bu (0.05 mmol), and alcohol (**3a-3c** = 0.5 mL, **3d-3ae** = 4 eq.) were added in a gentle stream of argon. Then, the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 12 h. After completion of the reaction the crude mixture was worked up with water and extracted using dichloromethane, followed by the solvent was removed under reduced pressure and finally the residue was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the corresponding esters.

## 3. Mechanistic investigation

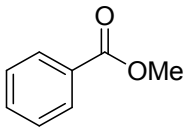
### 3.1 Deuterium labelling experiment

In an oven dried screw cap reaction tube (15 mL), **1** (0.5 mmol), KO$^t$Bu (0.05 mmol), and methanol-$D_4$ (1 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 12 h. After completion of the reaction the crude mixture was worked up with water and extracted using dichloromethane, followed by the solvent was removed under reduced pressure and finally the residue was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the product **2a-D** in 72% yield.

### 3.2 Reaction with radical scavengers

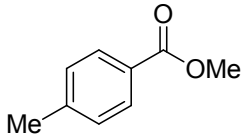
In an oven dried screw cap reaction tube (15 mL), **1** (0.5 mmol), KO$^t$Bu (0.05 mmol), radical quencher (0.5 mmol), and methanol (1 mL) were added in a gentle stream of argon. Then, the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 12 h. After completion of the reaction, internal standardmesitylene (0.5 mmol) was added into the crude and submitted to $^1$H NMR analysis for yield calculation.

## 4. Characterization Data



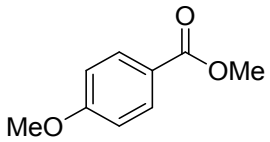

**Methyl Benzoate (2a)**[1]

Isolated yield = 88%. Pale yellow liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ7.99 - 7.94 (m, 2 H), 7.48 - 7.35 (m, 3 H), 3.83 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 167.05, 132.84, 130.12, 129.51, 128.29, 52.01 ppm. CAS Number: 93-58-3.



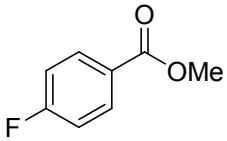

**Methyl 4-methylbenzoate (2b)**[1]

Isolated yield = 82%. White solid. $^{1}$H NMR (400 MHz, CHLOROFORM-d) δ = 7.93 (d, *J* = 8.1 Hz, 2 H), 7.23 (dd, *J* = 8.6, 0.6 Hz, 2 H), 3.89 (s, 3 H), 2.40 (s, 3 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-d) δ 167.17, 143.52, 129.57, 129.04, 127.40, 51.91, 21.61 ppm. CAS Number 99-75-2.



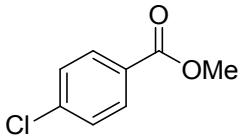

**Methyl 4-methoxybenzoate (2c)**[1]

Isolated yield = 91%. White solid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.01 - 7.97 (m, 2 H), 6.93 - 6.88 (m, 2 H), 3.88 (s, 3 H), 3.84 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.71, 163.22, 131.46, 122.48, 113.47, 55.25, 51.69 ppm. CAS Number: 121-98-2.



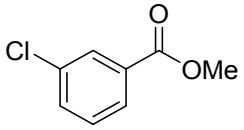

**Methyl 4-fluorobenzoate (2d)**[1]

Isolated yield = 71%. White solid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.02 - 7.95 (m, 2 H), 7.04 (t, *J* = 8.7 Hz, 2 H), 3.84 (s, 3 H) ppm. $^{13}$C NMR (50MHz, CHLOROFORM-d) δ 166.14, 132.20, 132.01, 115.71, 115.28, 52.17 ppm. CAS Number 403-33-8.



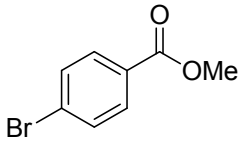

**Methyl 4-chlorobenzoate (2e)**[2]

Isolated yield = 77%. White solid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.88 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.13, 139.29, 130.90, 128.63, 128.53, 52.18 ppm. CAS Number: 1126-46-1.



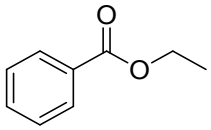

**Methyl 3-chlorobenzoate (2f)**

Isolated yield = 70%. White solid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.94 - 7.82 (m, 2 H), 7.47 - 7.43 (m, 1 H), 7.33 - 7.26 (m, 1 H), 3.85 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 165.81, 134.47, 132.89, 131.82, 129.62, 127.64, 52.34 ppm. CAS Number 2905-65-9.



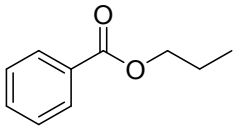

**Methyl 4-bromobenzoate (2g)**[2]

Isolated yield = 93%. White solid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.81 (d, *J* = 8.6 Hz, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.26, 131.64, 131.04, 128.97, 127.97, 52.22 ppm. CAS Number: 619-42-1.



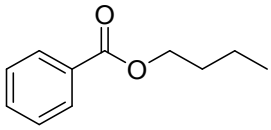

**Ethyl benzoate (3a)**[3]

Isolated yield = 84%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.05 (dd, *J* = 1.3, 8.3 Hz, 2 H), 7.56 - 7.40 (m, 3 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.40 (t, *J* = 7.2 Hz, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.60, 132.74, 130.49, 129.49, 128.26, 60.89, 14.28 ppm. CAS Number: 93-89-0.



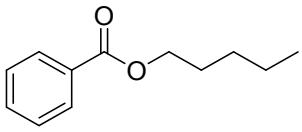
**Propyl benzoate (3b)**[3]

Isolated yield = 78%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.07 – 8.02 (m, 2 H), 7.46 - 7.34 (m, 3 H), 4.31 - 4.24 (m, 2 H), 1.84 - 1.74 (m, 2 H), 1.03 (t, *J* = 7.4 Hz, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.86, 132.74, 129.48, 128.26, 126.92, 66.49, 22.06, 10.46 ppm. CAS Number: 2315-68-6.



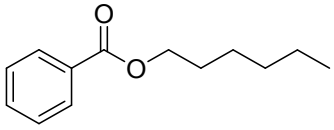
**Butyl benzoate (3c)**[3]

Isolated yield = 77%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.99 - 7.94 (m, 2 H), 7.47 - 7.35 (m, 3 H), 4.25 (t, *J* = 6.6 Hz, 2 H), 1.71 - 1.64 (m, 2 H), 1.46 - 1.38 (m, 2 H), 0.94 - 0.86 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.66, 132.74, 130.53, 129.50, 128.27, 64.79, 30.76, 19.25, 13.72 ppm. CAS Number: 136-60-7.



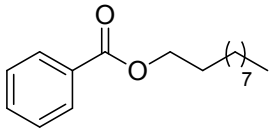
**Pentyl benzoate (3d)**[6]

Isolated yield = 70%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.07 – 8.02 (m, 2 H), 7.55 - 7.43 (m, 3 H), 4.32 (t, *J* = 6.6 Hz, 2 H), 1.77 - 1.74 (m, 2 H), 1.45 - 1.38 (m, 4 H), 0.96 - 0.89 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) δ 166.62, 132.71, 130.50, 129.47, 128.25, 65.05, 28.38, 28.15, 22.31, 13.93 ppm. CAS Number: 2049-96-9.



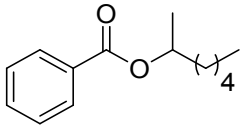
**Hexyl benzoate (3e)**[6]

Isolated yield = 69%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.95 - 7.90 (m, 2 H), 7.42 - 7.30 (m, 3 H), 4.19 (t, *J* = 6.6 Hz, 2 H), 1.68 - 1.60 (m, 2 H), 1.29 - 1.19 (m, 6 H), 0.81 - 0.75 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) δ 166.58, 132.69, 130.49, 129.46, 128.23, 65.05, 31.41, 28.63, 25.65, 22.49, 13.93, ppm. CAS Number: 6789-88-4.



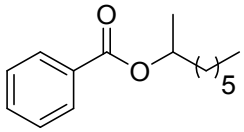
**Decyl benzoate (3f)**

Isolated yield = 66%. Pale yellow liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 7.98- 7.94 (m, 2 H), 7.50 - 7.31 (m, 3 H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.72 - 1.61 (m, 2 H), 1.34 - 1.19 (m, 14 H), 0.83 - 0.76 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.63, 132.72, 130.52, 129.49, 128.26, 65.10, 31.86, 29.50, 29.26, 28.70, 26.01, 22.64, 14.07 ppm. CAS Number: 36685-97-9.



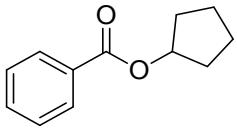
**Heptan-2-yl benzoate (3g)**

Isolated yield = 47%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.07 – 8.02 (m, 2H), 7.55 - 7.43 (m, 3 H), 5.16 (sxt, *J* = 6.3 Hz, 1 H), 1.76 - 1.58 (m, 2 H), 1.42-1.32 (m, 9H), 0.91 - 0.85 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) δ 166.21, 132.63, 130.92, 129.48, 128.24, 71.71, 36.00, 31.65, 25.08, 22.52, 20.04, 13.97 ppm. CAS Number: 6624-59-5.



**Octan-2-yl benzoate (3h)**

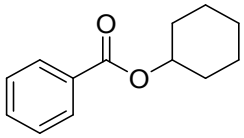
Isolated yield = 51%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.07 – 8.02 (m, 2 H), 7.55 - 7.40 (m, 3 H), 5.15 (sxt, *J* = 6.2 Hz, 1 H), 1.76 - 1.59 (m, 2 H), 1.35 - 1.27 (m, 11 H), 0.90 - 0.84 (m, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.21, 132.64, 130.94, 129.49, 128.24, 71.73, 36.05, 31.72, 29.15, 25.39, 22.57, 20.06, 14.04 ppm. CAS Number: 6938-51-8.



**Cyclopentyl benzoate (3i)**[5]

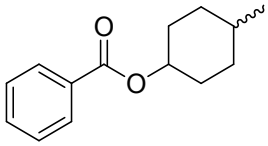
Isolated yield = 59%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.03 - 8.01 (m, 2 H), 7.56 - 7.52 (m, 1 H), 7.44 - 7.40 (m, 2 H), 5.43 - 5.40 (m, 1 H), 1.96 - 1.94 (m, 2 H) 1.86

- 1.81 (m, 4 H) 1.67 - 1.65 (m, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.34, 132.64, 130.87, 129.44, 128.22, 77.65, 32.76, 23.79 ppm. CAS Number: 32651-38-0.



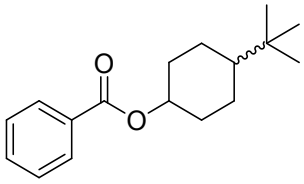
**Cyclohexyl benzoate (3j)**[1]

Isolated yield = 61%. Pale yellow liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.03 (d, *J* = 7.1 Hz, 2 H), 7.59 - 7.40 (m, 3 H), 5.08 - 4.99 (m, 1 H), 2.00 - 1.78 (m, 4 H), 1.62 - 1.42 (m, 6 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.58, 135.25, 133.26, 130.13, 128.86, 73.63, 32.26, 26.11, 24.27 ppm. CAS Number: 2412-73-9.



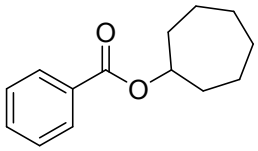
**4-Methylcyclohexyl benzoate (3k)**

Isolated yield = 55%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.05 (dd, *J*=9.6, 8.0 Hz, 2 H) 7.55 - 7.52 (m, 1 H) 7.46 – 7.41 (m, 2 H) 5.26 - 5.24 (m, 1 H) 4.94 – 4.90 (m, 1 H) 2.07 – 1.98 (m, 2 H) 1.80 – 1.77 (m, 1 H) 1.66 – 1.36 (m, 5 H) 1.13 – 1.09 (m, 1 H) 0.95 (brm, 3 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.11, 165.92, 132.66, 132.64, 131.12, 130.93, 129.49, 128.28, 128.22, 74.00, 70.32, 33.02, 31.73, 31.68, 31.50, 29.76, 29.69, 22.18, 21.83 ppm.



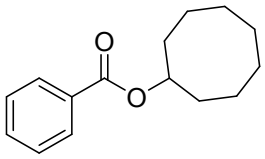
**4-(Tert-butyl)cyclohexyl benzoate (3l)**

Isolated yield = 52%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.06 - 8.03 (m, 2 H) 7.55 - 7.52 (m, 1 H) 7.46 – 7.41 (m, 2 H) 5.28 – 5.27 (m, 1 H) 4.92 – 4.85 (m, 1 H) 2.17 - 2.13 (m, 2 H) 1.88 - 1.84 (m, 1 H) 1.61 - 1.43 (m, 4 H) 1.20 - 1.16 (m, 2 H) 0.90 – 0.88 (d, *J*= 7.9 Hz, 9 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.14, 165.87, 132.63, 131.18, 130.93, 129.51, 129.45, 128.32, 128.22, 74.29, 70.01, 47.48, 47.15, 32.54, 32.32, 32.18, 30.69, 27.60, 27.44, 25.49, 21.83 ppm.



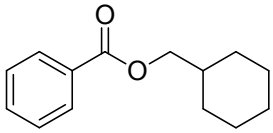
**Cycloheptyl benzoate (3m)**[8]

Isolated yield = 49%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 7.97 (d, *J* = 7.4 Hz, 2 H) 7.47 (t, *J* = 7.4 Hz, 1 H) 7.36 (t, *J* = 7.6 Hz, 2 H) 5.13 (tt, *J* = 8.1, 4.24 Hz, 1 H) 1.93 - 1.92 (m, 2 H) 1.77- 1.75 (m, 4 H) 1.56 - 1.44 (m, 6 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 165.92, 132.62, 131.05, 129.49, 128.24, 75.60, 33.82, 28.31, 22.92 ppm.



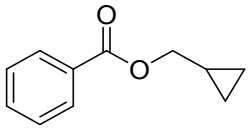
**Cyclooctyl benzoate (3n)**

Isolated yield = 48%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 7.96 (d, *J* = 7.4 Hz, 2 H) 7.46 (t, *J* = 7.4 Hz, 1 H) 7.35 (t, *J* = 7.6 Hz, 2 H) 5.16 - 5.10 (m, 1 H) 1.90 - 1.78 (m, 4 H) 1.74 - 1.66 (m, 2 H) 1.56 - 1.49 (m, 8 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 165.91, 132.59, 131.09, 129.47, 128.22, 75.61, 31.47, 27.15, 25.35, 22.90 ppm.



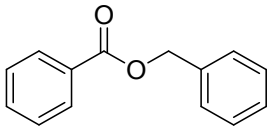
**Cyclohexylmethyl benzoate (3o)**[5]

Isolated yield = 70%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 7.95 (d, *J* = 7.3 Hz, 2 H) 7.44 (t, *J* = 7.4 Hz, 1 H) 7.33 (t, *J* = 7.7 Hz, 2 H) 4.03 (d, *J* = 6.3 Hz, 2 H) 1.74 - 1.57 (m, 6 H) 1.23 - 1.07 (m, 3 H) 1.02 – 0.89 (m, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.64, 132.74, 130.52, 129.49, 128.27, 70.02, 37.25, 29.73, 26.35, 25.68 ppm. CAS Number: 14135-40-1.



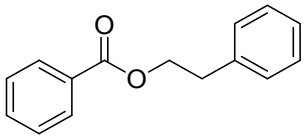
**Cyclopropylmethyl benzoate (3p)**[1]

Isolated yield = 59%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.08 - 8.06 (m, 2 H) 7.57 – 7.53 (m, 1 H) 7.46 – 7.42 (m, 2 H) 4.16 (d, *J* = 7.3 Hz, 2 H) 1.29 - 1.25 (m, 1 H) 0.62 - 0.59 (m, 2 H) 0.39 - 0.36 (m, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 166.73, 132.77, 130.51, 129.57, 128.28, 69.66, 9.89, 3.27 ppm.



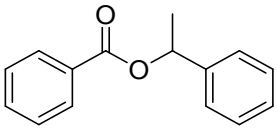
**Benzyl benzoate (3q)**[3]

Isolated yield = 82%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.09 – 8.05 (m, 2 H), 7.44 - 7.34 (m, 8 H), 5.35 (s, 2 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.28, 135.99, 132.90, 130.06, 129.59, 128.48, 128.26, 128.05, 66.56 ppm. CAS Number: 120-51-4.



**Phenethyl benzoate (3r)**[3]

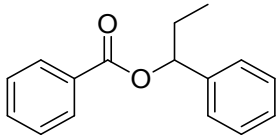
Isolated yield = 69%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.01 (td, *J* = 7.0, 1.7 Hz, 2 H), 7.54 (tt, *J* = 7.2, 2.4 Hz, 1 H), 7.41 (tt, *J* = 7.4, 1.2 Hz, 2 H), 7.23-7.18 (m, 5 H) 4.53 (t, *J* = 6.9 Hz, 2 H), 3.07 (t, *J* = 6.9, 2 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.57, 137.96, 132.96, 130.35, 129.61, 129.01, 128.59, 128.40, 126.64, 65.53, 35.29 ppm. CAS Number: 94-47-3.



**1-phenylethyl benzoate (3s)**[4]

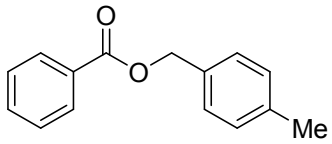
Isolated yield = 59%. Colourless liquid. $^{1}$H NMR (500 MHz, CHLOROFORM-d) δ 8.12 (d, *J* = 8.3 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.52 - 7.45 (m, 4 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 6.19 (q, *J* = 6.5 Hz, 1 H), 1.72 (d, *J* = 6.5 Hz, 3 H). $^{13}$C NMR (126 MHz,

CHLOROFORM-d) δ 165.83, 141.82, 132.94, 130.57, 129.68, 128.58, 128.36, 127.92, 126.08, 72.94, 22.44. CAS Number: 13358-49-1.



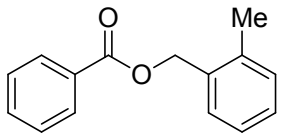
**1-phenylpropyl benzoate (3t)**

Isolated yield = 68%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.12 - 8.07 (m, 2 H), 7.47 - 7.24 (m, 8 H), 5.92 (t, *J* = 6.8 Hz, 1 H), 2.15 - 1.88 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) δ 165.86, 140.60, 132.85, 130.52, 129.59, 128.39, 128.31, 127.80, 126.45, 77.86, 29.54, 9.93 ppm. CAS Number: 58687-92-6.



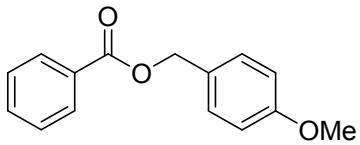

**4-Methyl benzyl benzoate (3u)**[4]

Isolated yield = 75%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.06 (td, *J* = 7.1, 1.1 Hz, 2H), 7.59-7.49 (m, 1H), 7.46-7.15 (m, 6H), 5.32 (s, 2H), 2.36 (s, 3H). $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.53, 138.13, 133.09, 133.01, 130.27, 129.73, 129.31, 128.39, 66.71, 21.26 ppm. CAS Number: 38418-10-9.



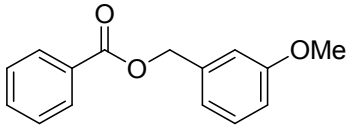

**2-Methyl benzyl benzoate (3v)**[4]

Isolated yield = 71%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.06 (td, *J* = 7.0 Hz, 1.5 Hz, 2H), 7.54 (tt, *J* = 7.3, 2.5 Hz, 1H), 7.46-7.36 (m, 3H), 7.29-7.14 (m, 3H), 5.37 (s, 2H), 2.41 (s, 3H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.46, 137.11, 134.05, 133.06, 130.46, 130.21, 129.73, 129.31, 128.61, 128.44, 126.11, 65.27, 19.06 ppm. CAS Number: 80716-36-5.



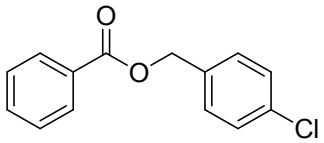
**4-Methoxy benzyl benzoate (3w)**

Isolated yield = 81%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.05 (td, *J* = 6.9, 1.6 Hz, 2H), 7.53 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.45-7.35 (m, 4H), 6.96-6.84 (tt, *J* = 8.7, 2.2 Hz, 2H), 5.29 (s, 2H), 3.79 (s, 3H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.54, 159.71, 132.98, 130.32, 130.11, 129.71, 128.37, 128.23, 114.02, 66.58, 55.31 ppm. CAS Number: 24318-41-0.



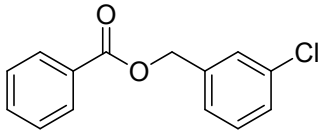

**3-Methoxy benzyl benzoate (3x)**

Isolated yield = 79%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.09 - 8.07 (m, 2 H) 7.58 - 7.51 (m, 1 H) 7.44 - 7.41 (m, 2 H) 7.30 (t, *J* = 7.9 Hz, 1 H) 7.03 – 6.99 (m, 2 H) 6.89 – 6.87 (m, 1 H) 5.34 (s, 2 H) 3.81 (s, 3 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.34, 159.72, 137.53, 132.99, 130.05, 129.65, 129.61, 128.32, 120.26, 113.61, 113.57, 66.47, 55.19 ppm.



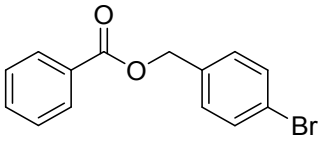

**4-Chloro benzyl benzoate (3y)**[3]

Isolated yield = 68%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.06 (d, *J* = 7.0, 2H), 7.57 (tt, *J* = 7.3, 2.2 Hz, 1H), 7.49–7.42 (m, 2H), 7.41-7.30 (m, 4H), 5.32 (s, 2H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.35, 134.59, 134.18, 133.20, 129.95, 129.72, 129.60, 128.83, 128.45, 65.90 ppm. CAS Number: 20386-93-0.



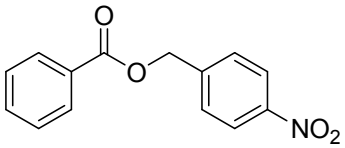

**3-Chloro benzyl benzoate (3z)**

Isolated yield = 67%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.07 (d, *J* = 7.4 Hz, 2 H) 7.56 - 7.54 (m, 1 H) 7.44- 7.42 (m, 3 H) 7.30 (br. s, 3 H) 5.32 (s, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.18, 138.01, 134.43, 133.15, 129.84, 129.78, 129.67, 128.39, 128.33, 128.06, 126.08, 65.69 ppm.



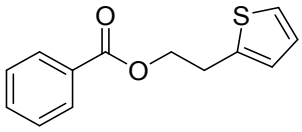
**4-Bromo benzyl benzoate** (**3aa**)[3]

Isolated yield = 63%. Colourless liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.06 (td, *J* = 6.9, 1.58 Hz, 2H), 7.56 (tt, *J* = 7.4, 1.7 Hz, 2H), 7.50-7.38 (m, 3H), 7.35-7.27 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 2H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-d) δ 166.32, 135.14, 133.22, 131.80, 129.90, 129.74, 128.48, 122.33, 65.92 ppm. CAS Number: 38612-13-4.



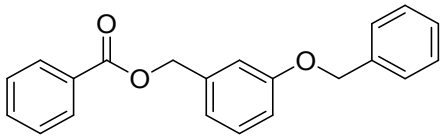
**4-Nitro benzyl benzoate(3ab)**[9]

Isolated yield = 46%. Pale yellow solid. $^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.17 (d, *J* = 8.6 Hz, 2 H) 8.01 (d, *J* = 7.3 Hz, 2 H) 7.54 - 7.51 (m, 3 H) 7.42 - 7.38 (m, 2 H) 5.39 (s, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 166.07, 147.71, 143.33, 133.44, 129.71, 129.44, 128.53, 128.30, 123.84, 65.15 ppm. CAS Number: 4457-41-4.



**2-(Thiophen-2-yl)ethyl benzoate (3ac)**[3]

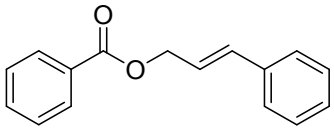
Isolated yield = 79%. Pale yellow liquid.$^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.08 – 8.03 (m, 2 H), 7.46 - 7.43 (m, 3 H), 7.14 (dd, *J* = 5.0, 1.3 Hz, 1 H), 6.95 - 6.91 (m, 2 H), 4.53 (t, *J* = 6.6 Hz, 2 H), 3.29 (t, *J* = 6.6 Hz, 2 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) δ 166.31, 139.92, 132.90, 130.05, 129.57, 128.29, 126.81, 125.51, 124.00, 65.08, 29.34 ppm.



**3-(Benzyloxy)benzyl benzoate (3ad)**

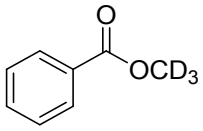
Isolated yield = 58%. Colourless liquid.$^{1}$H NMR (400 MHz, CHLOROFORM-*d*) δ 8.06 (d, *J* = 7.4 Hz, 2 H) 7.54 - 7.49 (m, 1 H) 7.54 - 7.23 (m, 8 H) 7.09 - 7.00 (m, 2 H) 6.94 (dd, *J* = 8.2, 2.31

Hz, 1 H) 5.32 (s, 2 H) 5.06 (s, 2 H) ppm. $^{13}$C NMR (101 MHz, CHLOROFORM-*d*) δ 166.31, 158.93, 137.57, 136.78, 132.98, 130.01, 129.65, 129.62, 128.53, 128.32, 127.93, 127.44, 120.48, 114.48, 69.94, 66.42 ppm.



**Cinnamyl benzoate (3ae)**[7]

Isolated yield = 63%. Pale yellow liquid. $^{1}$H NMR (200 MHz, CHLOROFORM-d) δ 8.03 - 7.98 (m, 2 H), 7.39 - 7.20 (m, 8 H), 6.69 - 6.61 (m, 1 H), 6.35 – 6.27 (m, 1 H), 4.89 (dd, *J* = 1.2, 6.3 Hz, 2 H) ppm. $^{13}$C NMR (50 MHz, CHLOROFORM-*d*) d 166.34, 136.19, 134.22, 132.95, 130.18, 129.62, 128.57, 128.33, 128.04, 126.61, 123.22, 65.48 ppm. CAS Number: 5320-75-2.



**Methyl Benzoate (2a-D)**

Isolated yield = 72%. Colourless liquid. $^{1}$H NMR (400 MHz, CHLOROFORM-d) δ 8.06 - 8.04 (m, 2 H), 7.56-7.55 (m, 1 H), 7.47 - 7.43 (m, 2 H) ppm. $^{13}$C NMR (101MHz, CHLOROFORM-d) δ 167.11, 132.87, 130.14, 129.53, 128.32 ppm.

## 5. References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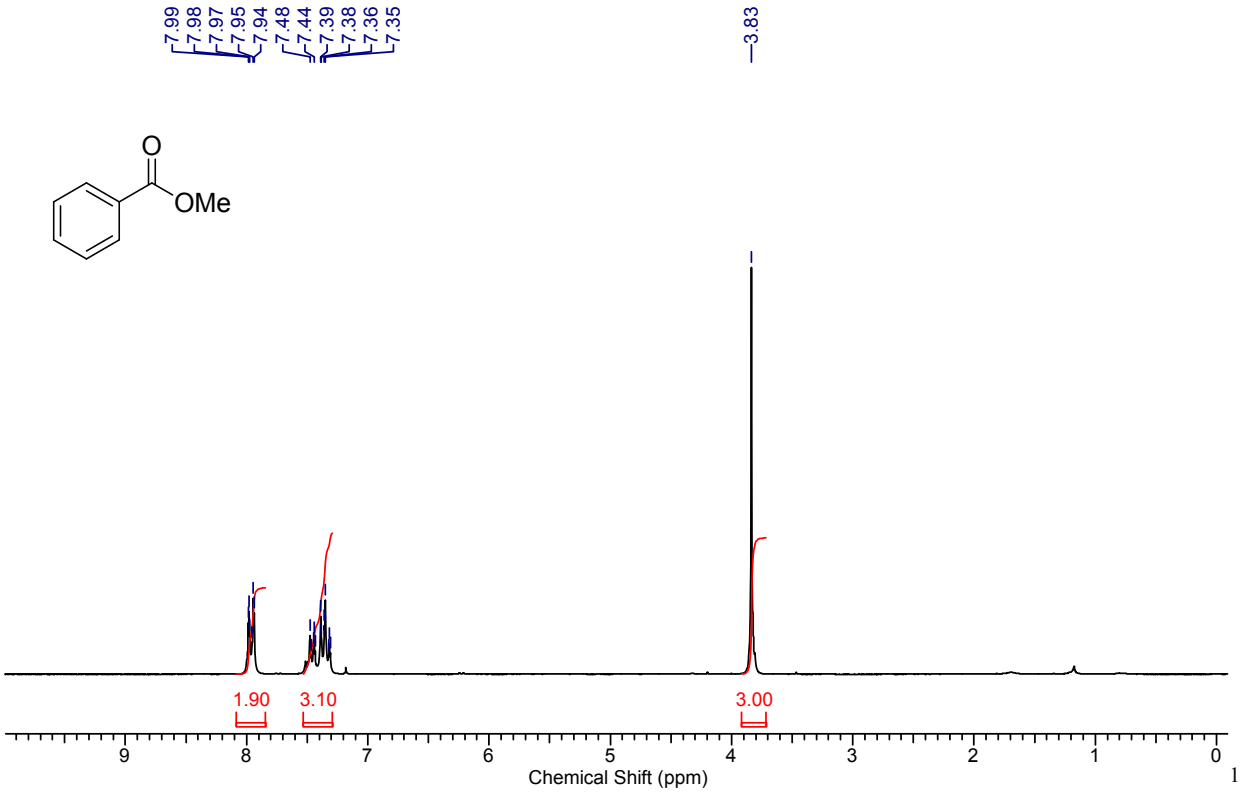
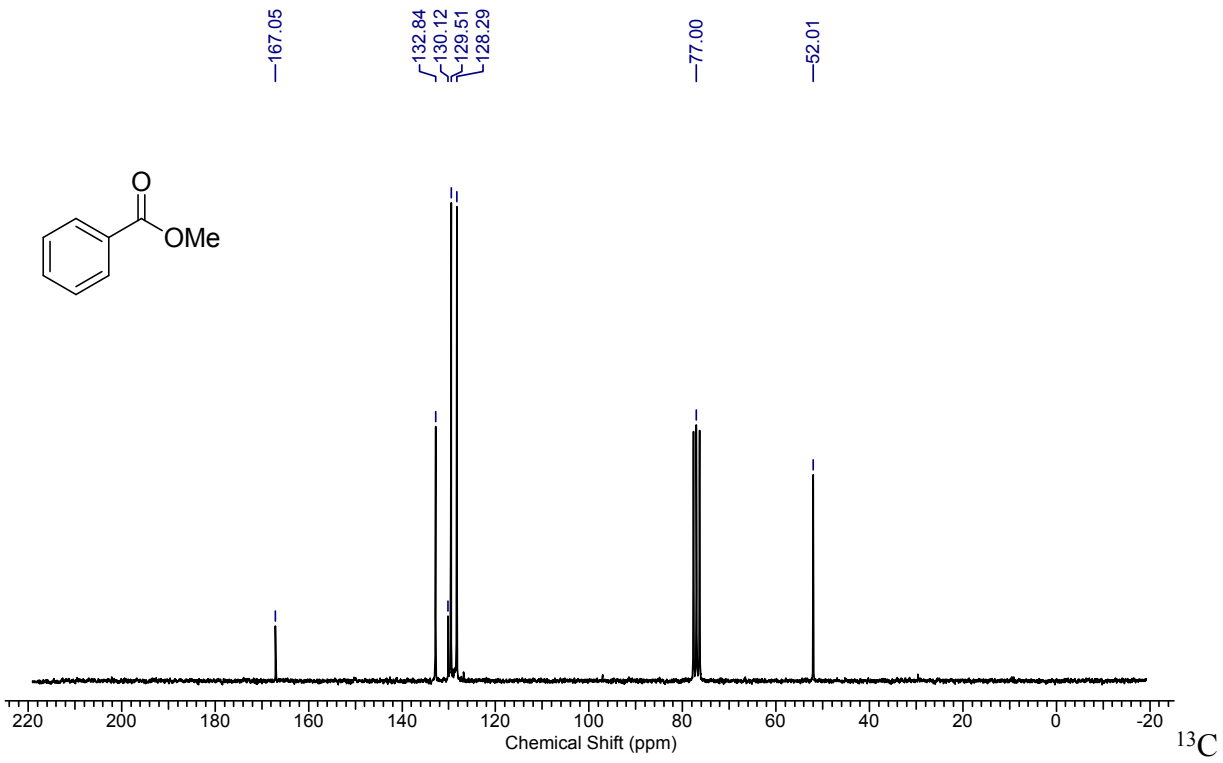
8. C. Zhang, G. Zhang, S. Luo, C. Wang and H. Li, *Org. Biomol. Chem.* 2018, **16**, 8467.
9. S. Gaspa, A. Porcheddu and L. De Lucaa, *Adv. Synth. Catal*. 2016, **358**, 154.

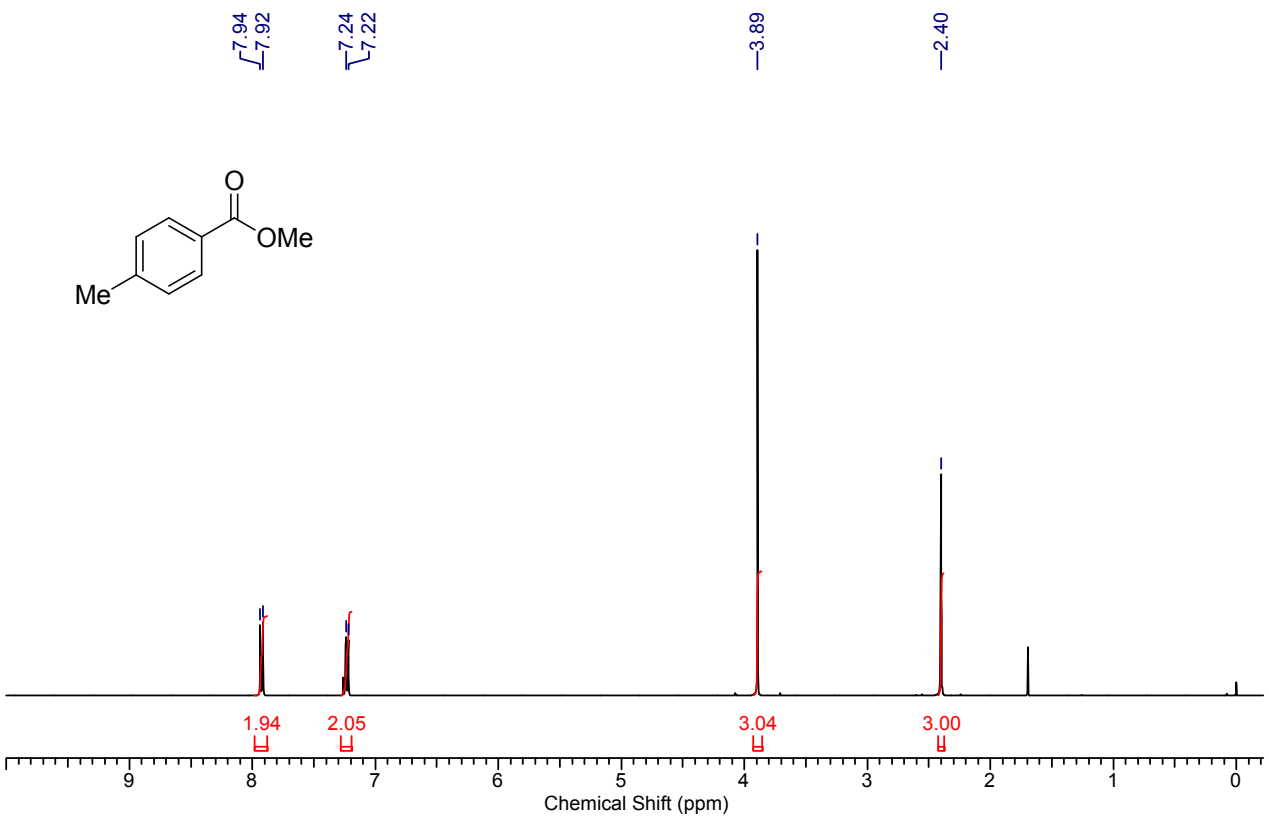
## 6. Copy of $^{1}H$ and $^{13}C$ NMR spectra



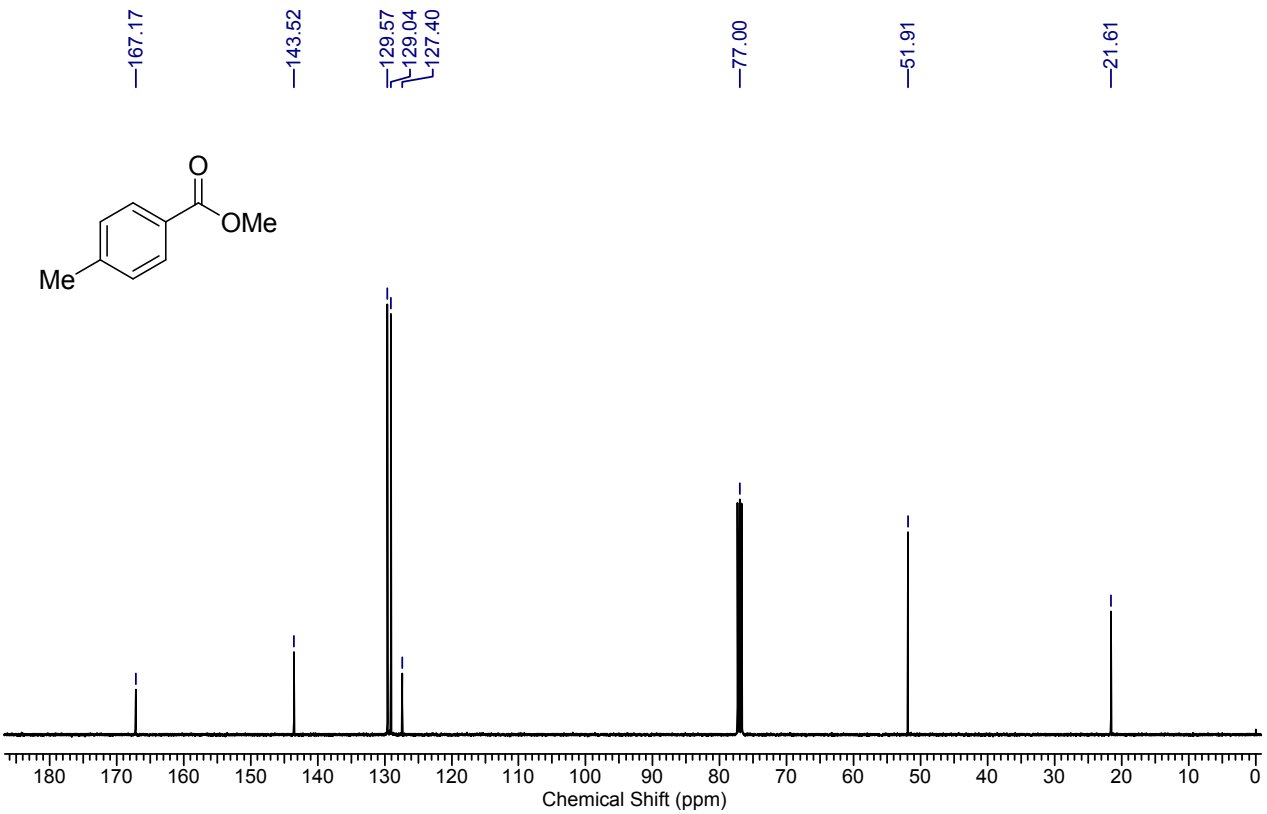

H NMR of **2a**



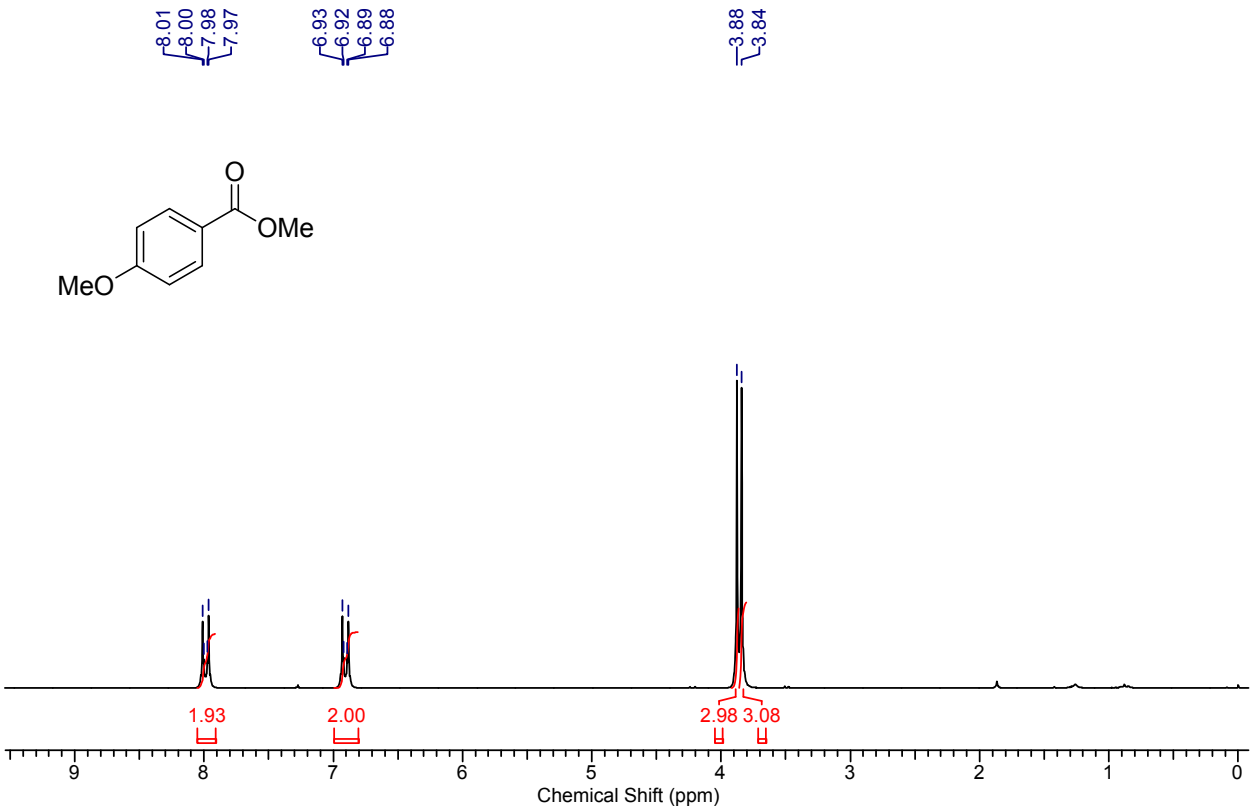

NMR of **2a**



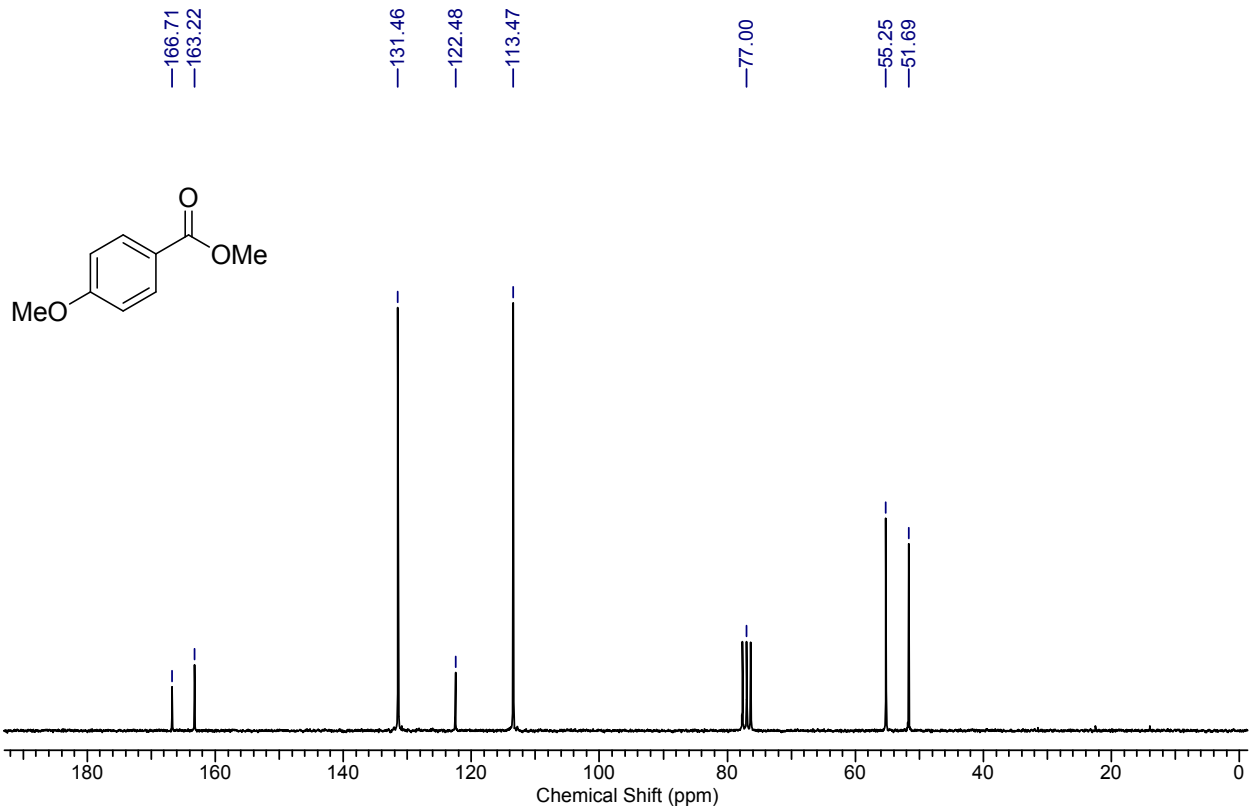

$^{1}$H NMR of **2b**



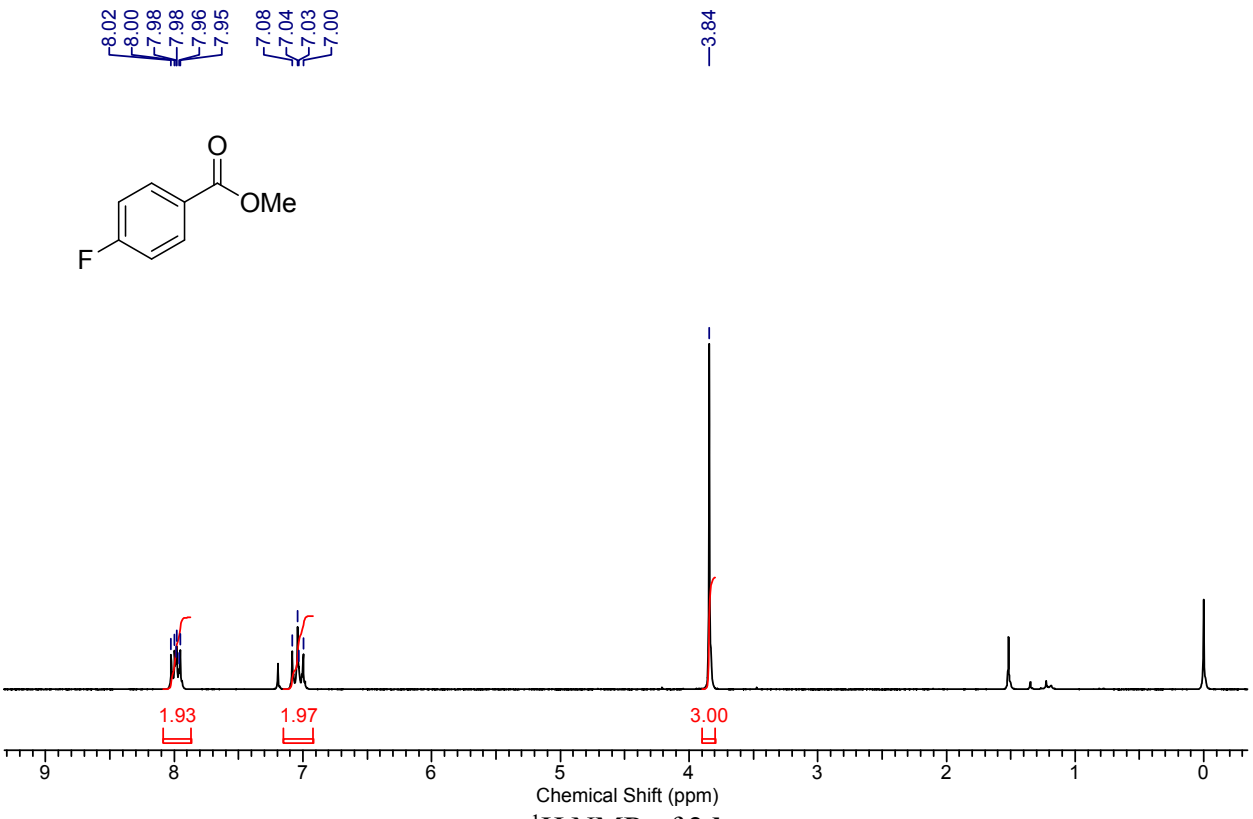

$^{13}$C NMR of **2b**



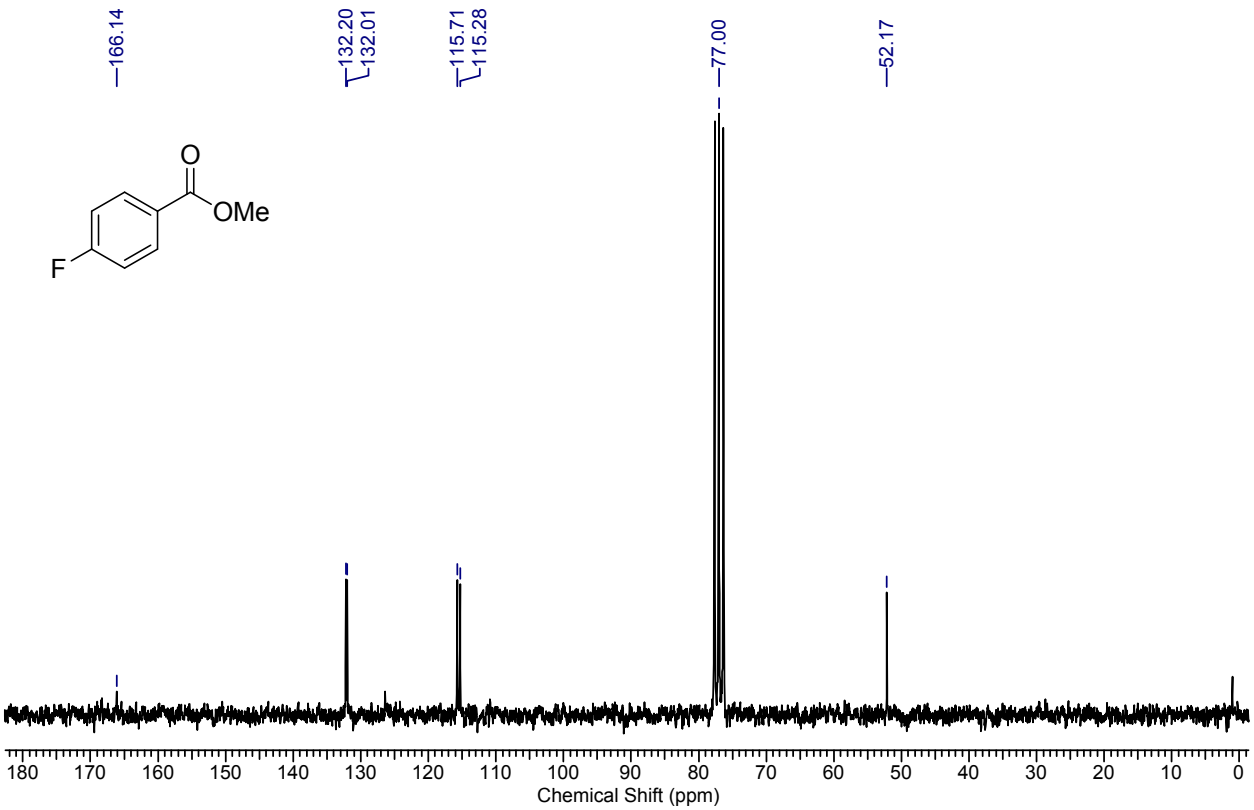

$^{1}$H NMR of **2c**



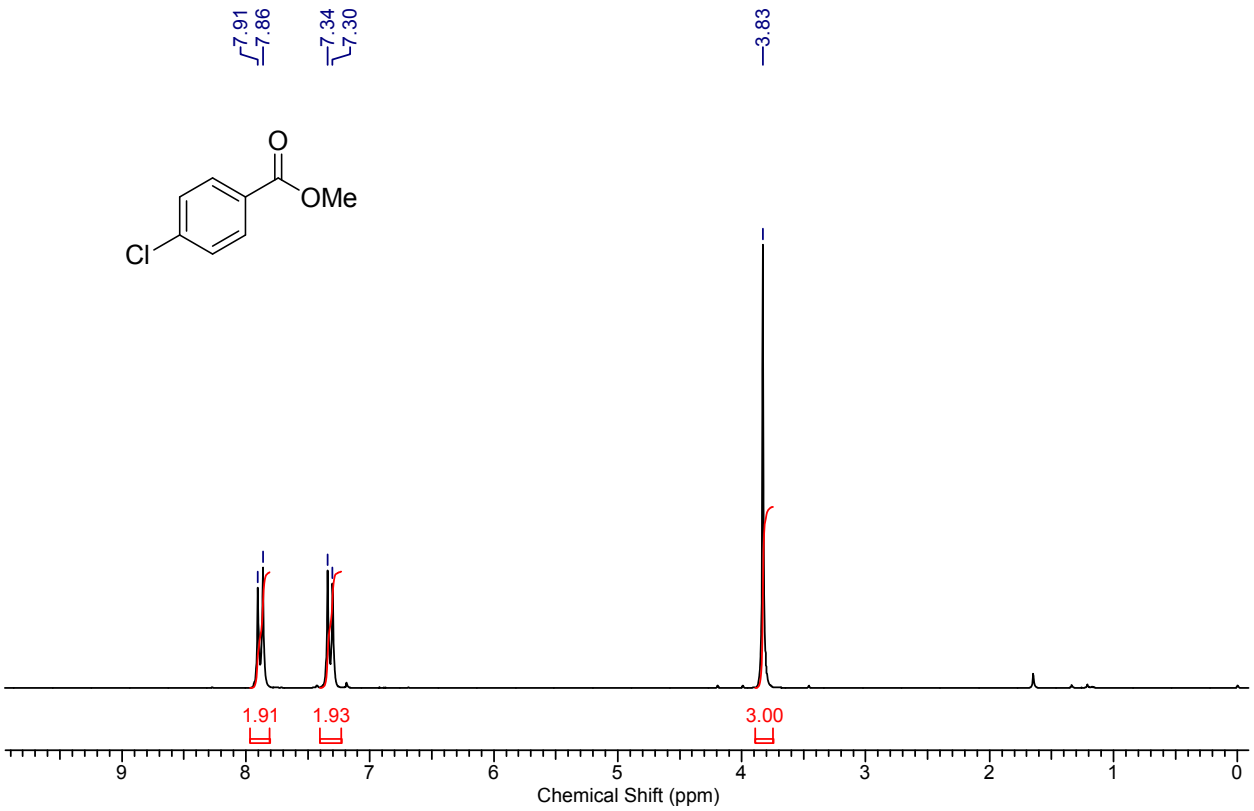

$^{13}$C NMR of **2c**



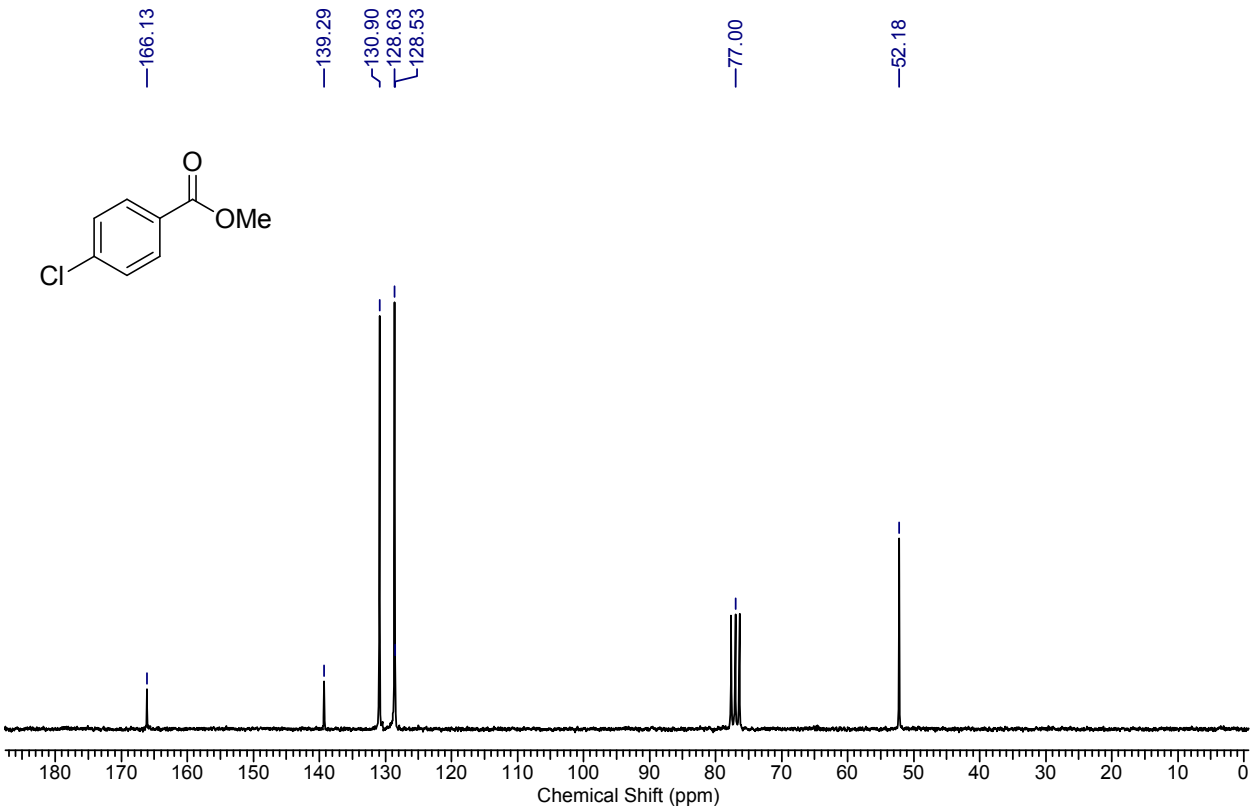

$^{1}$H NMR of **2d**



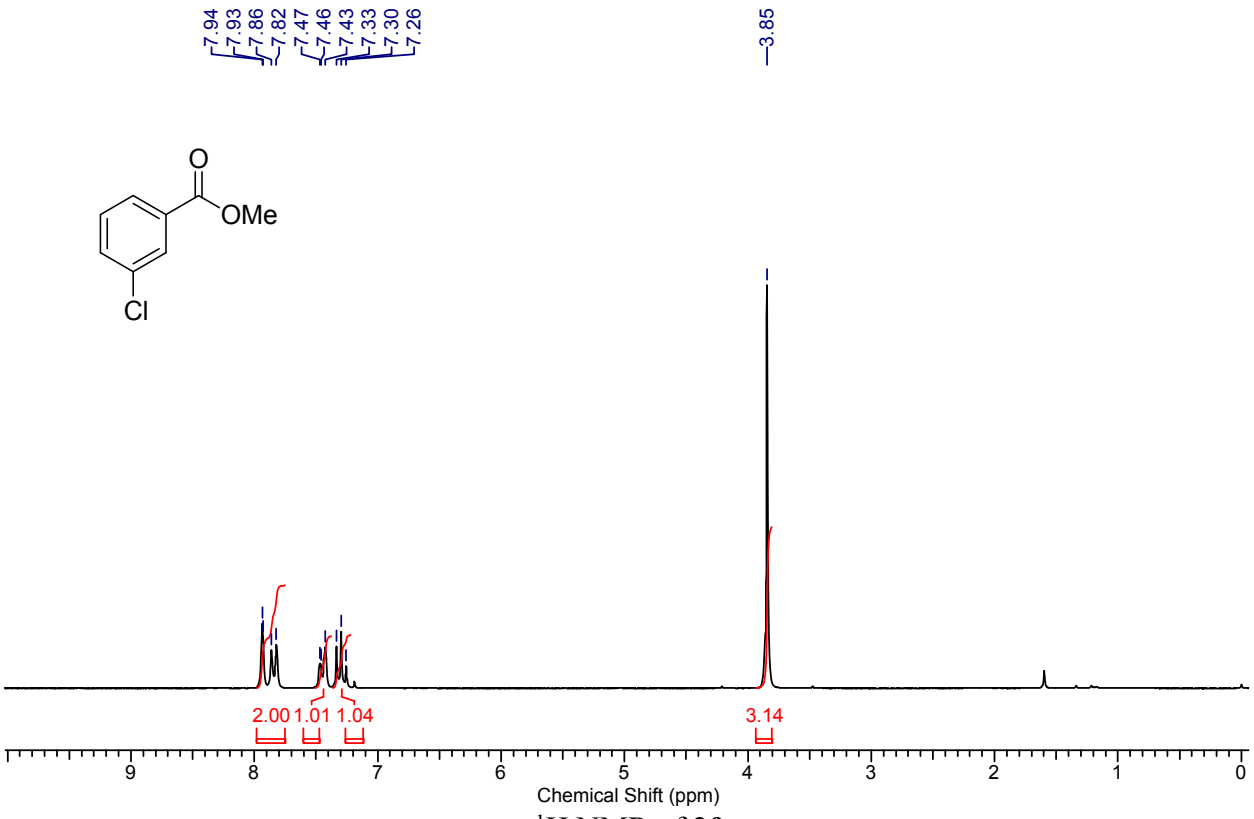

$^{13}$C NMR of **2d**



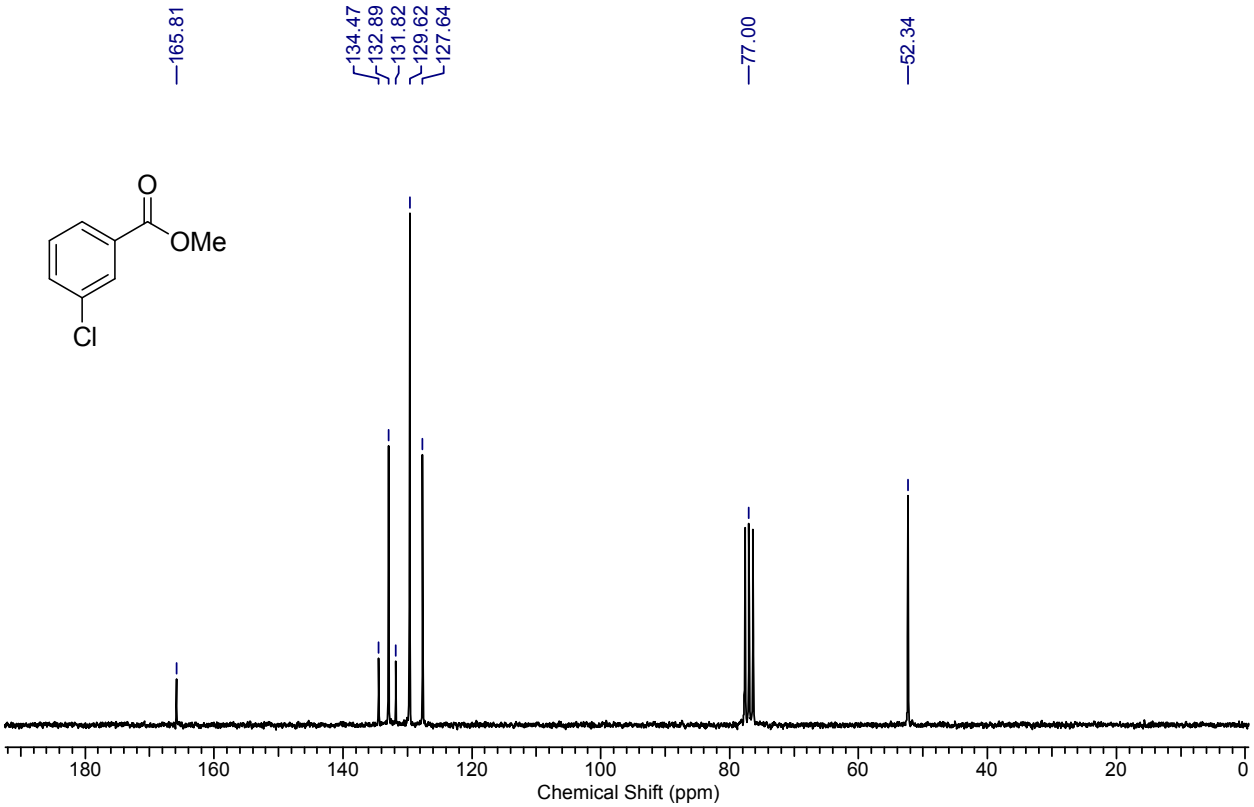

$^{1}$H NMR of **2e**



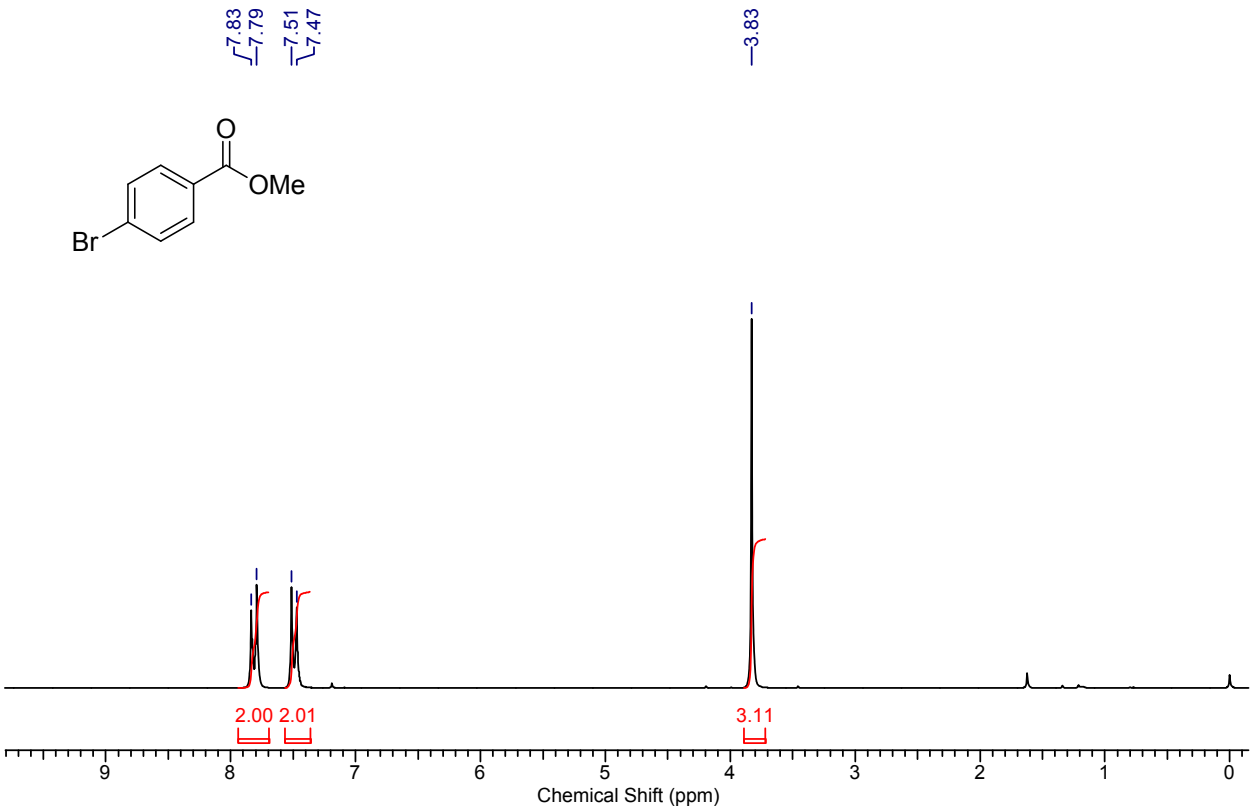

$^{13}$C NMR of **2e**



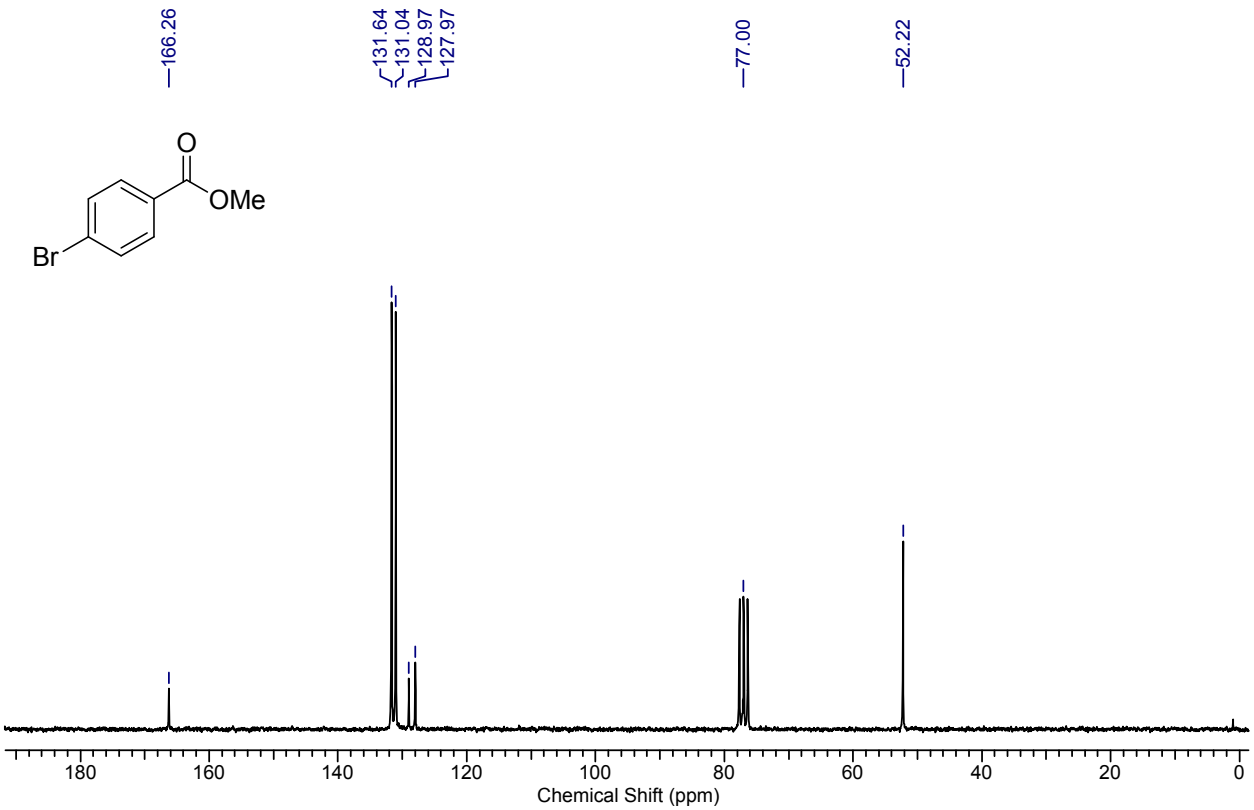

$^{1}$H NMR of **2f**



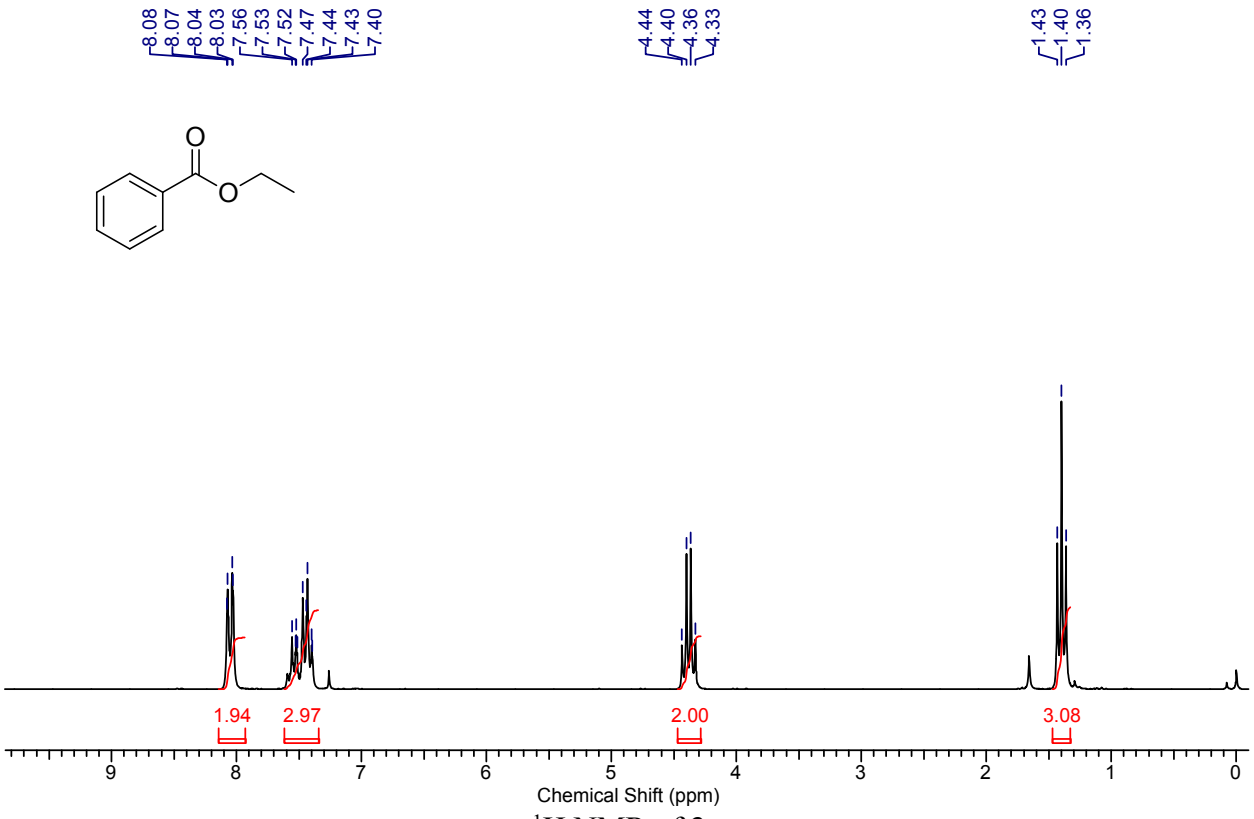

$^{13}$C NMR of **2f**



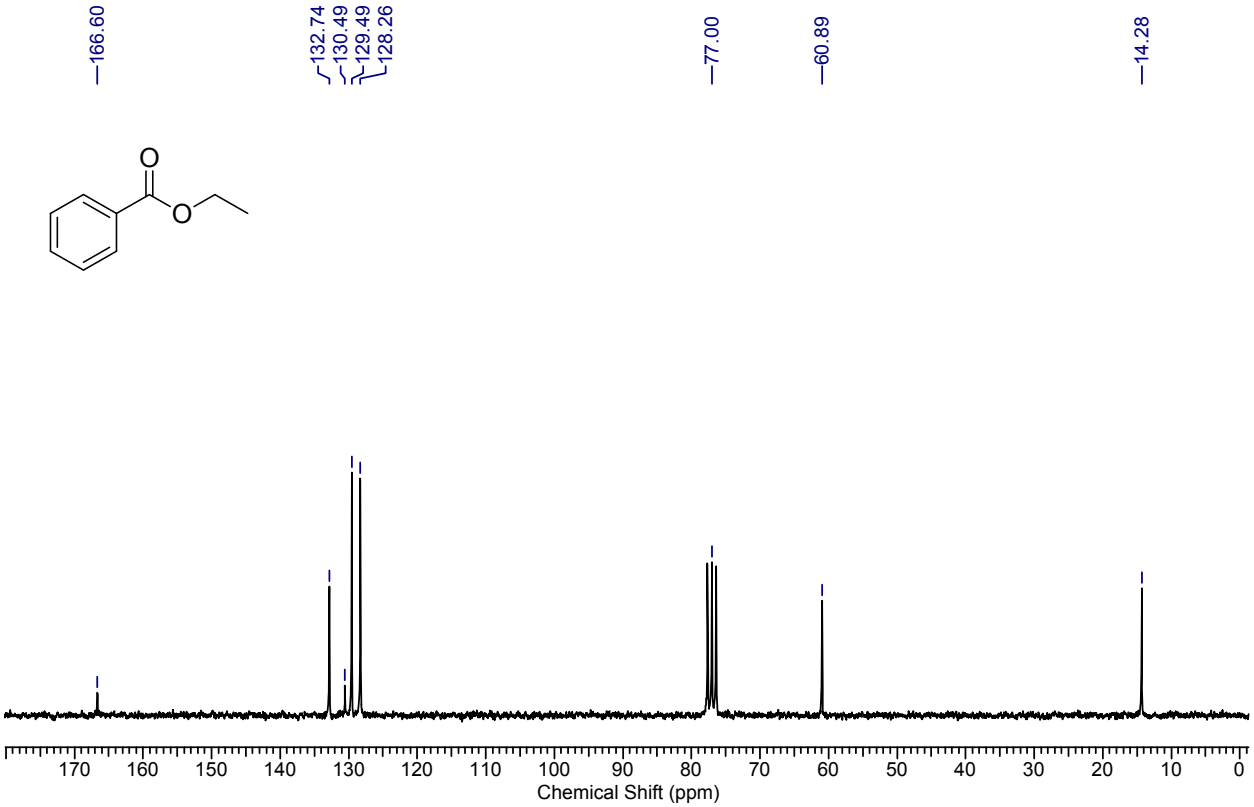

$^{1}$H NMR of **2g**



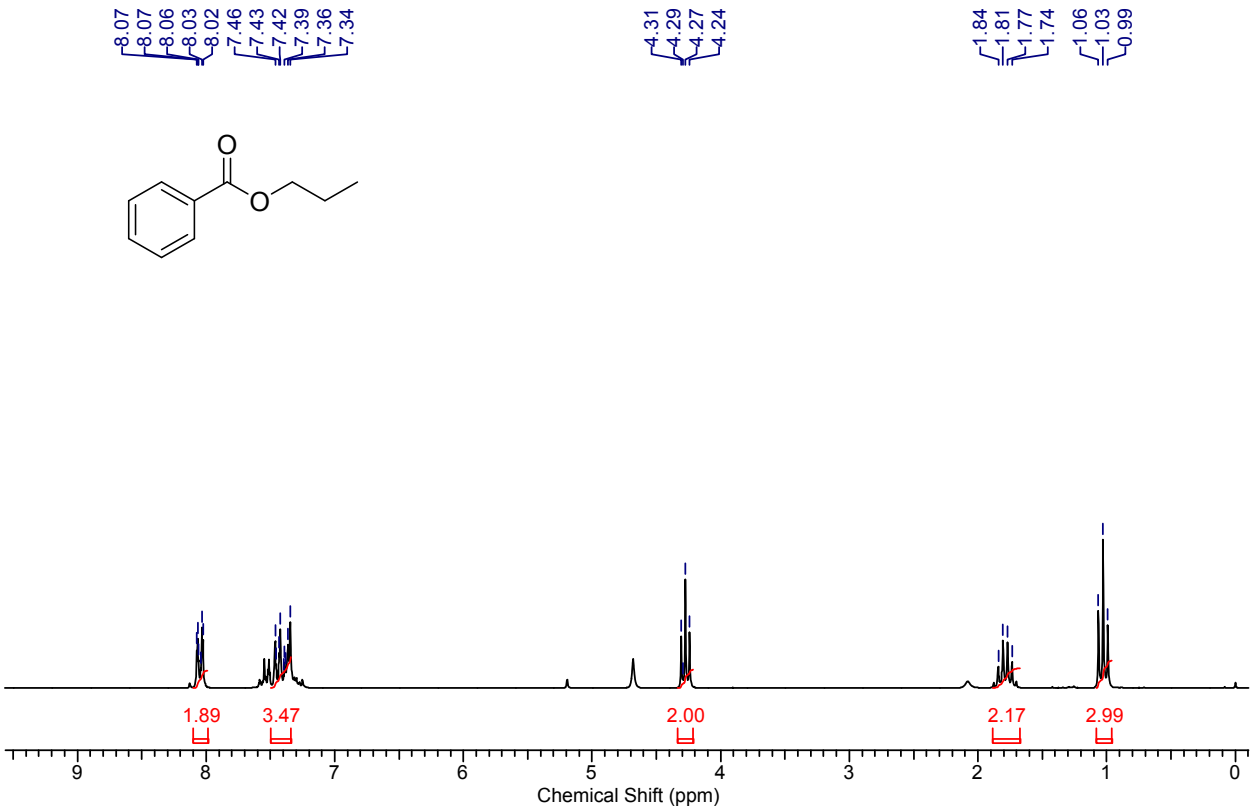

$^{13}$C NMR of **2g**



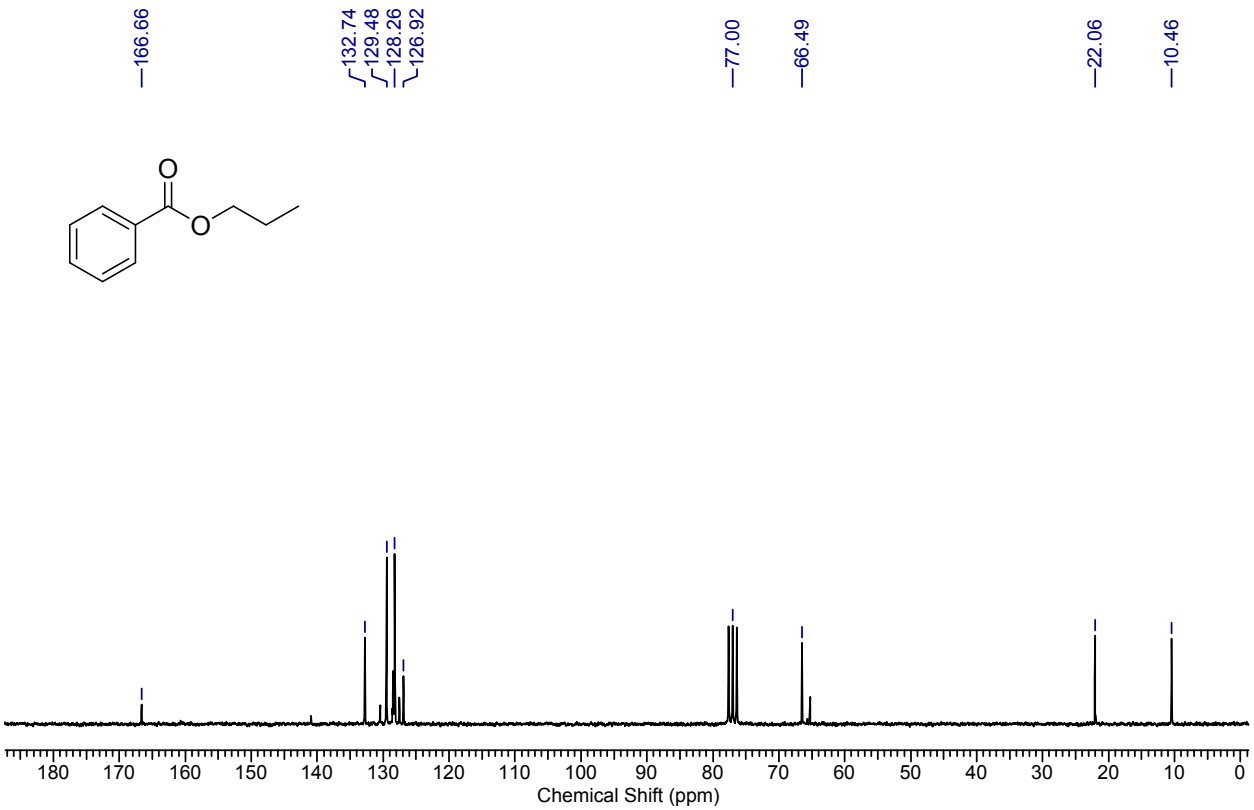

$^{1}$H NMR of **3a**




$^{13}$C NMR of **3a**




$^{1}$H NMR of **3b**

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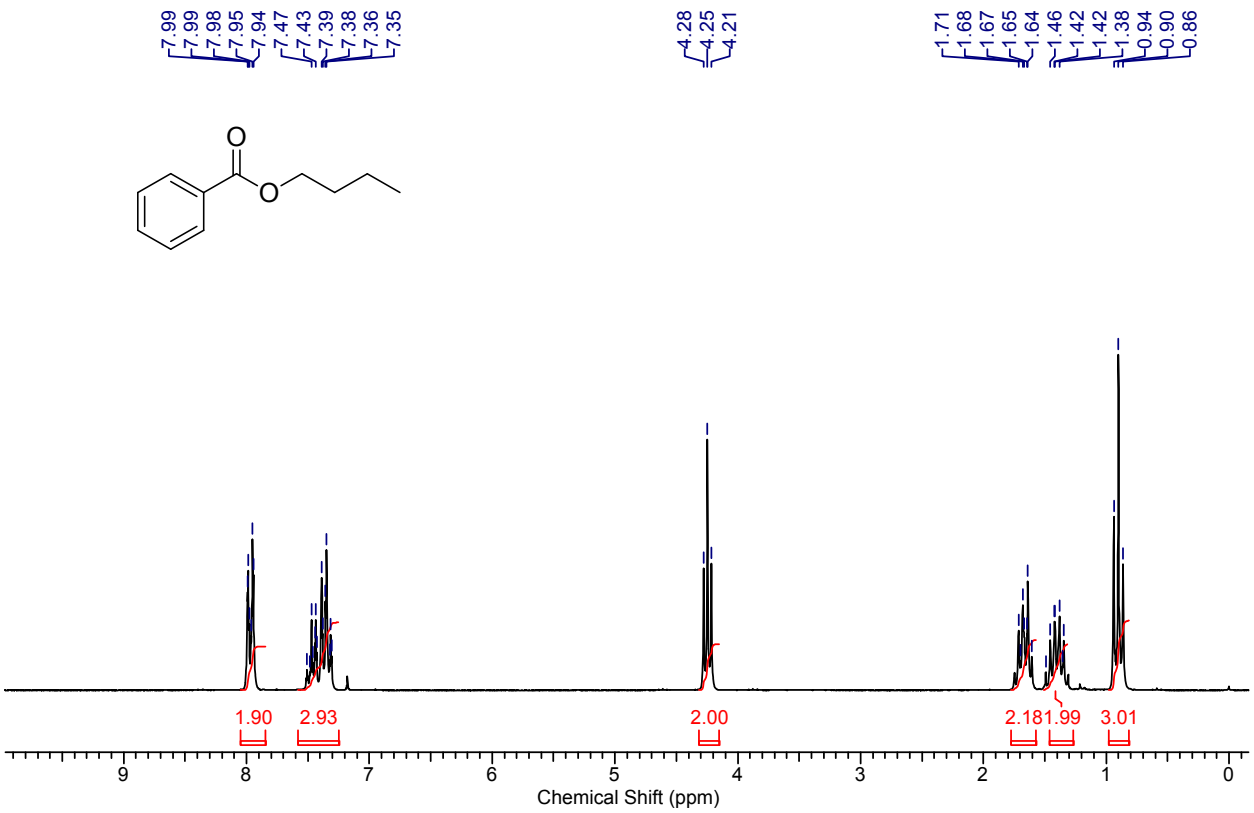
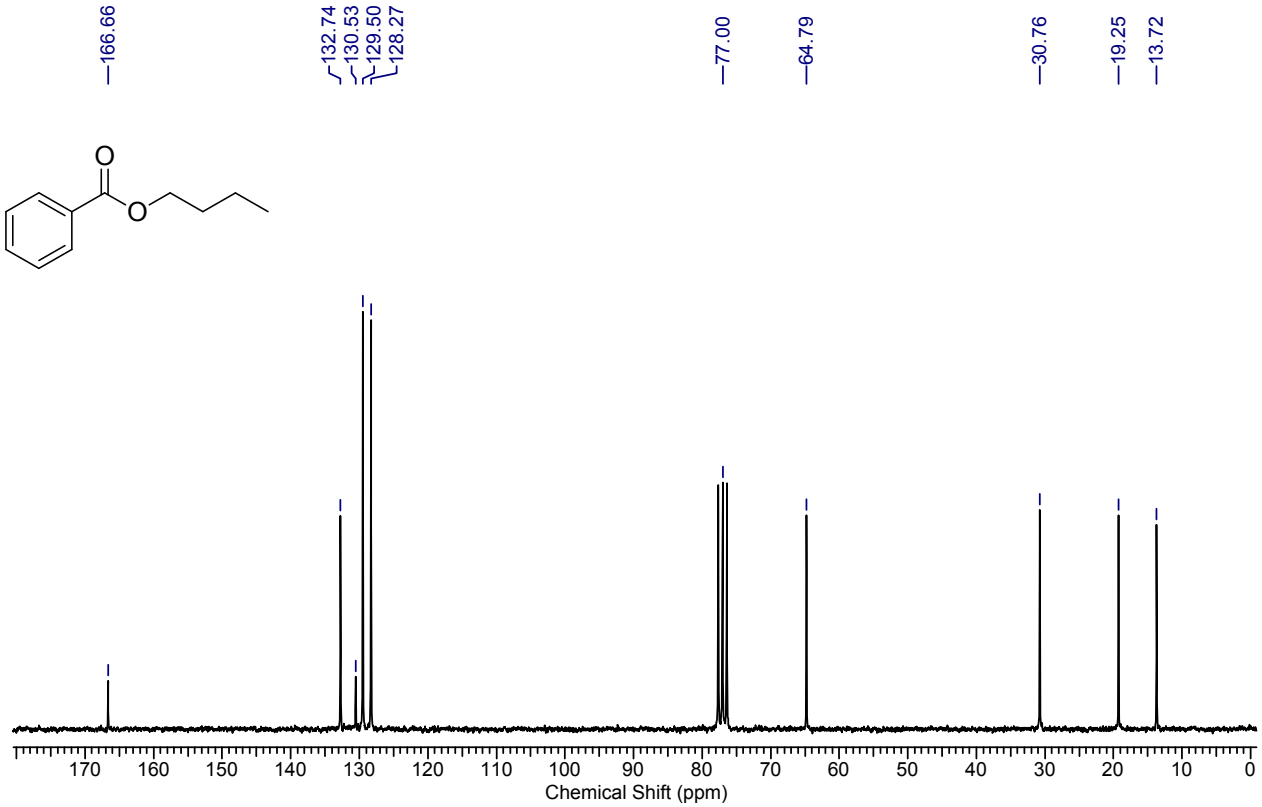
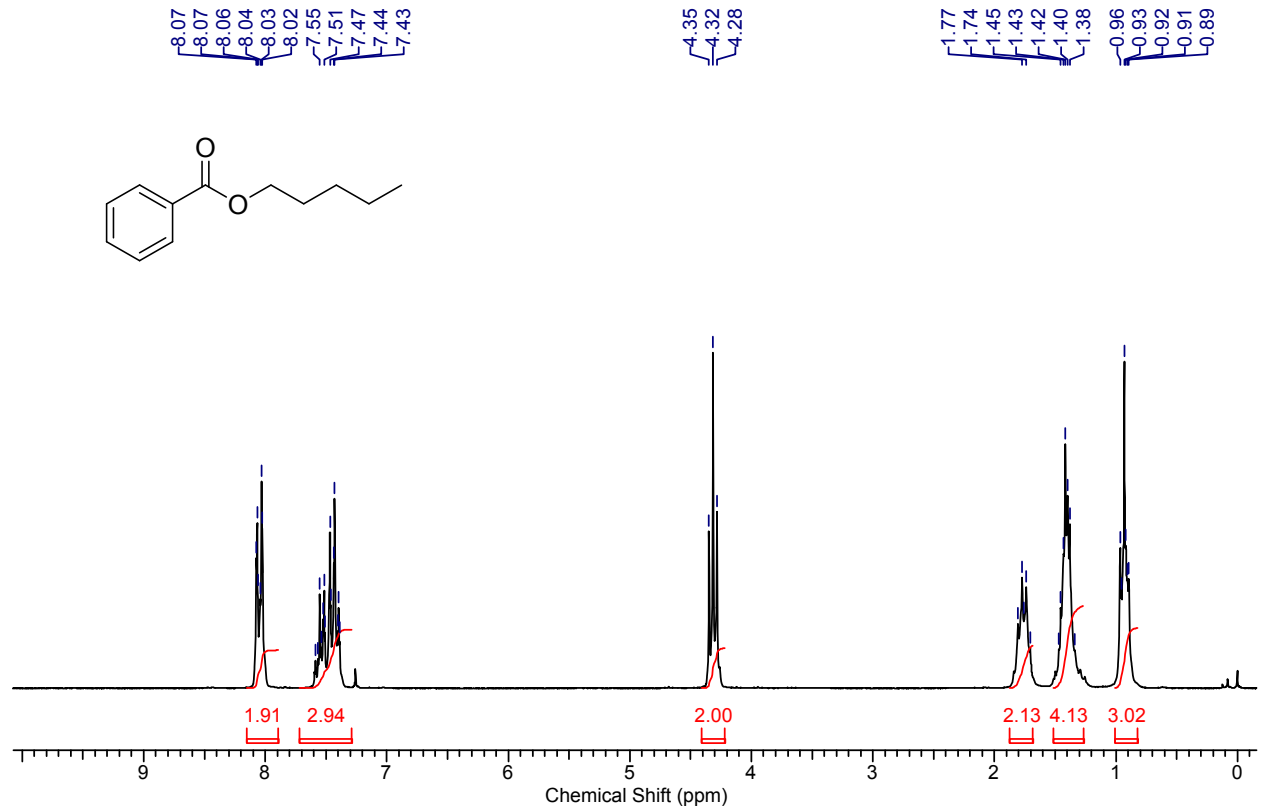


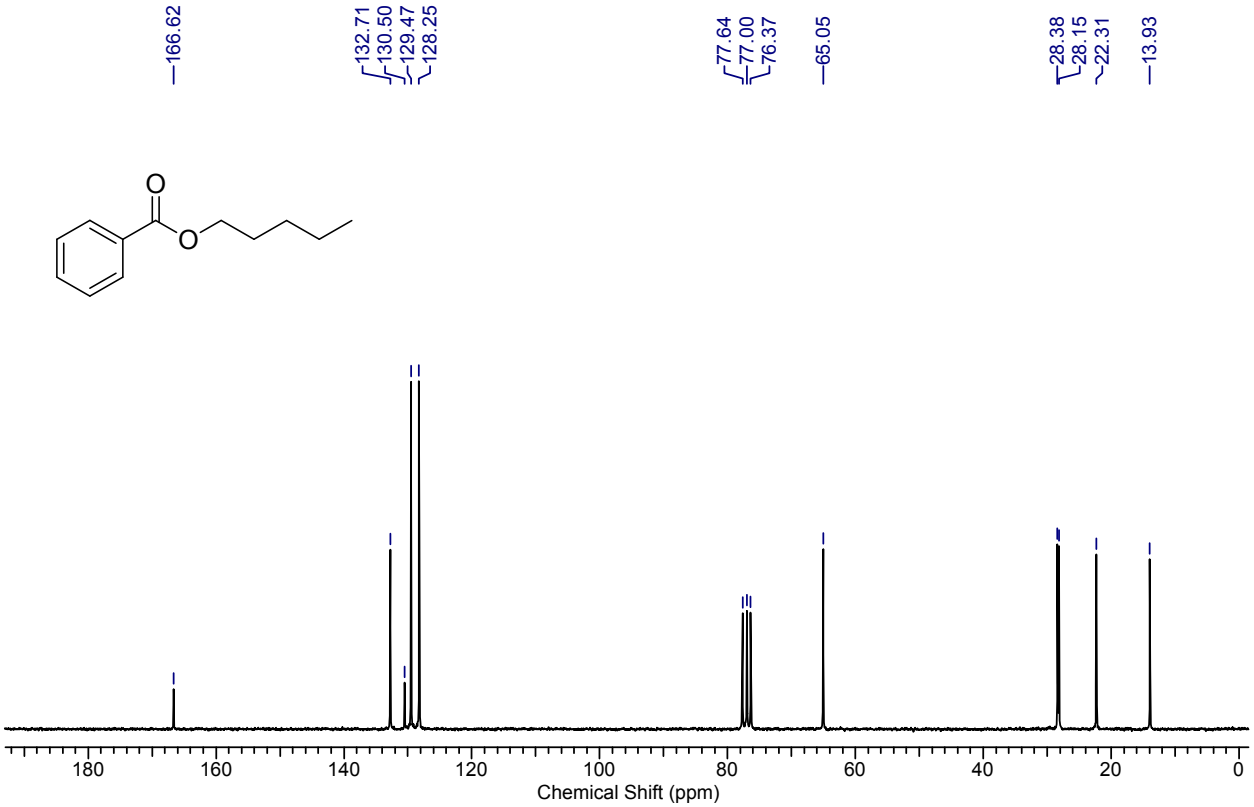

$^{1}$H NMR of **3c**



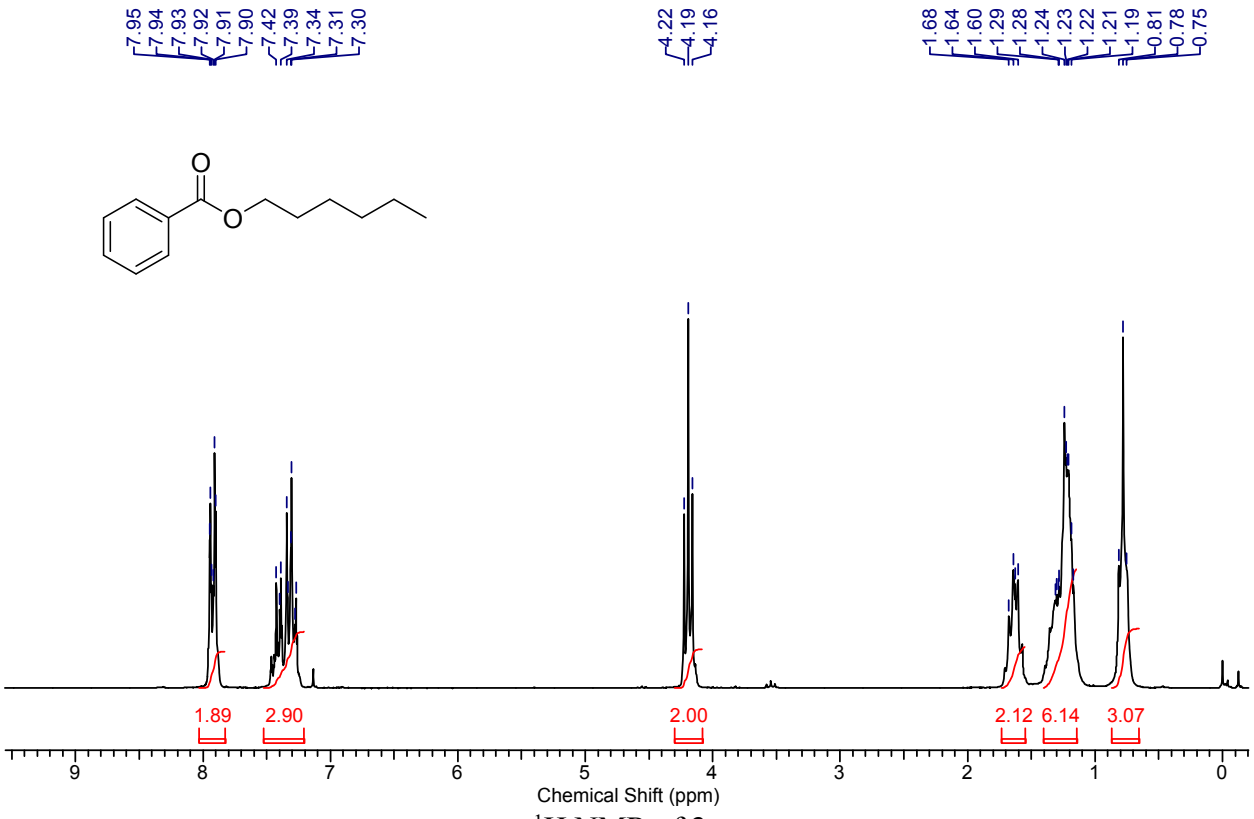

$^{13}$C NMR of **3c**



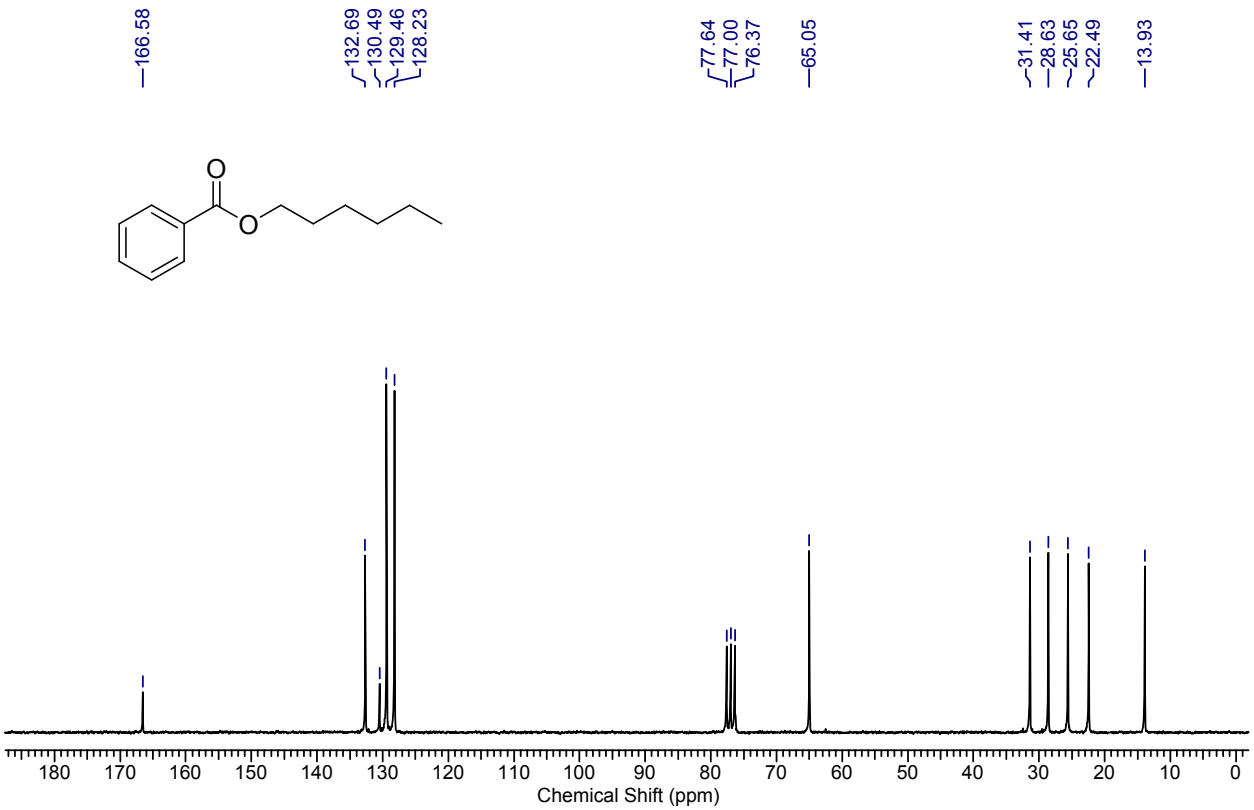

$^{1}$H NMR of **3d**




$^{13}$C NMR of **3d**




$^{1}$H NMR of **3e**

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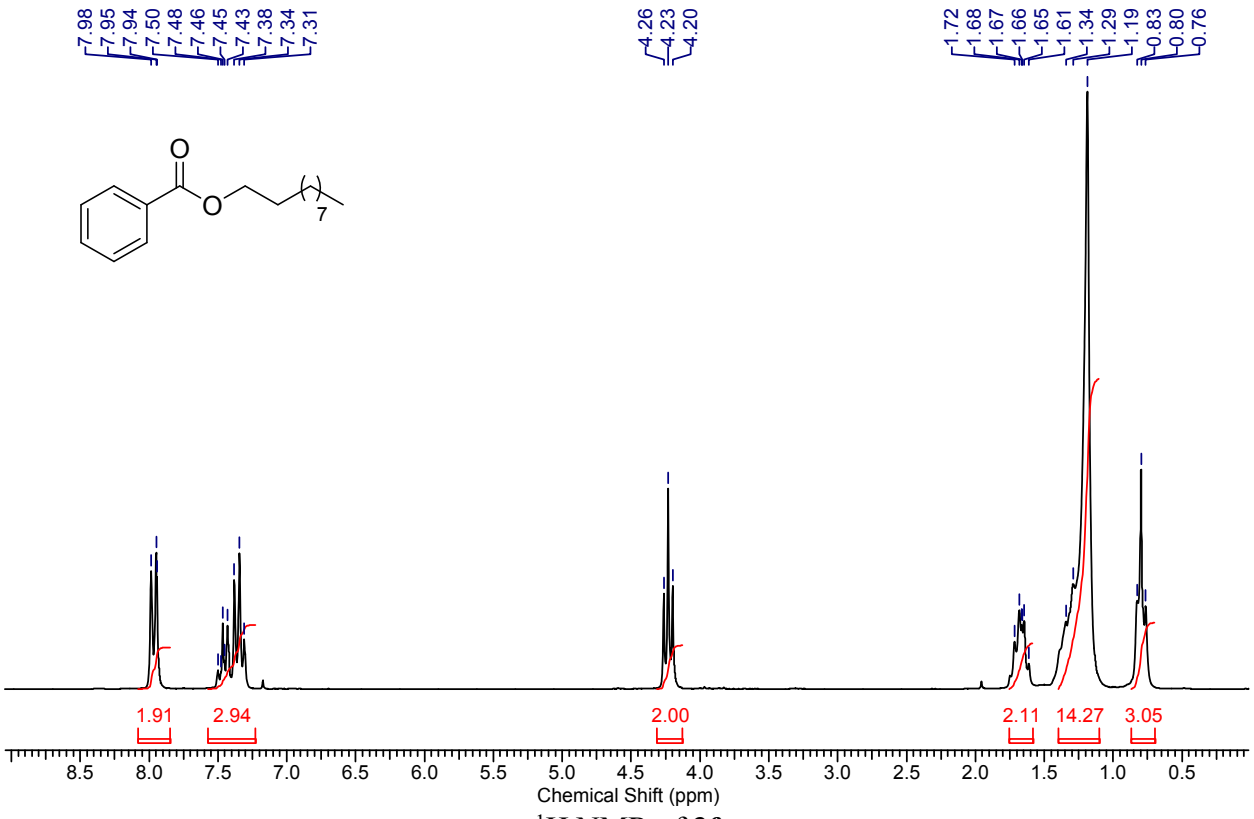
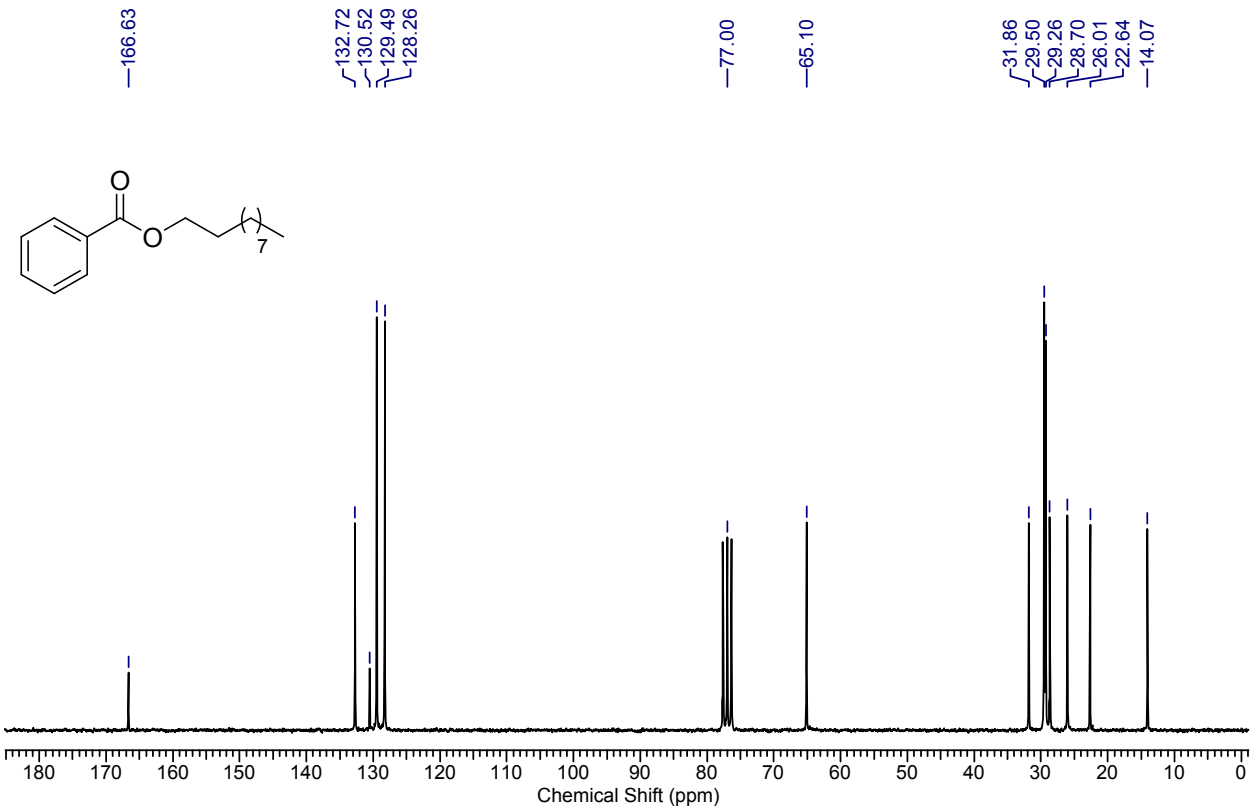
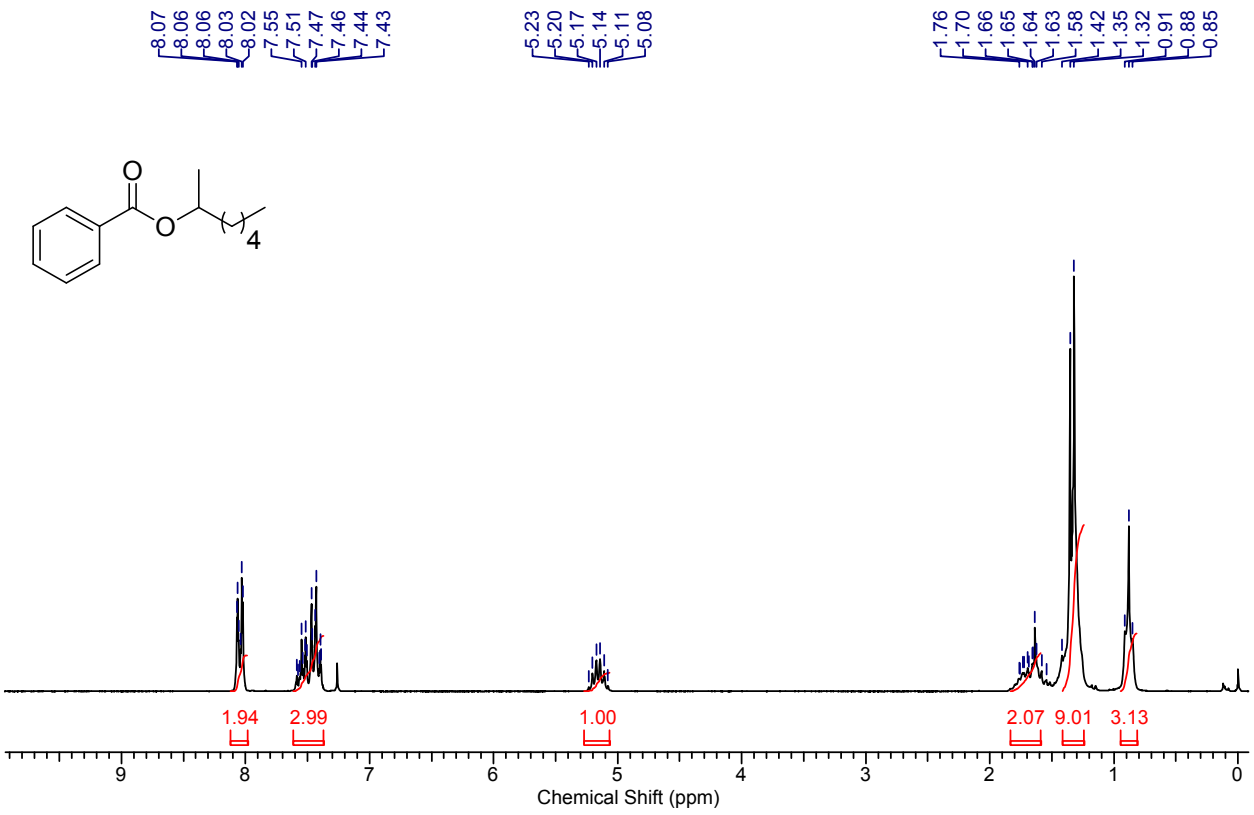


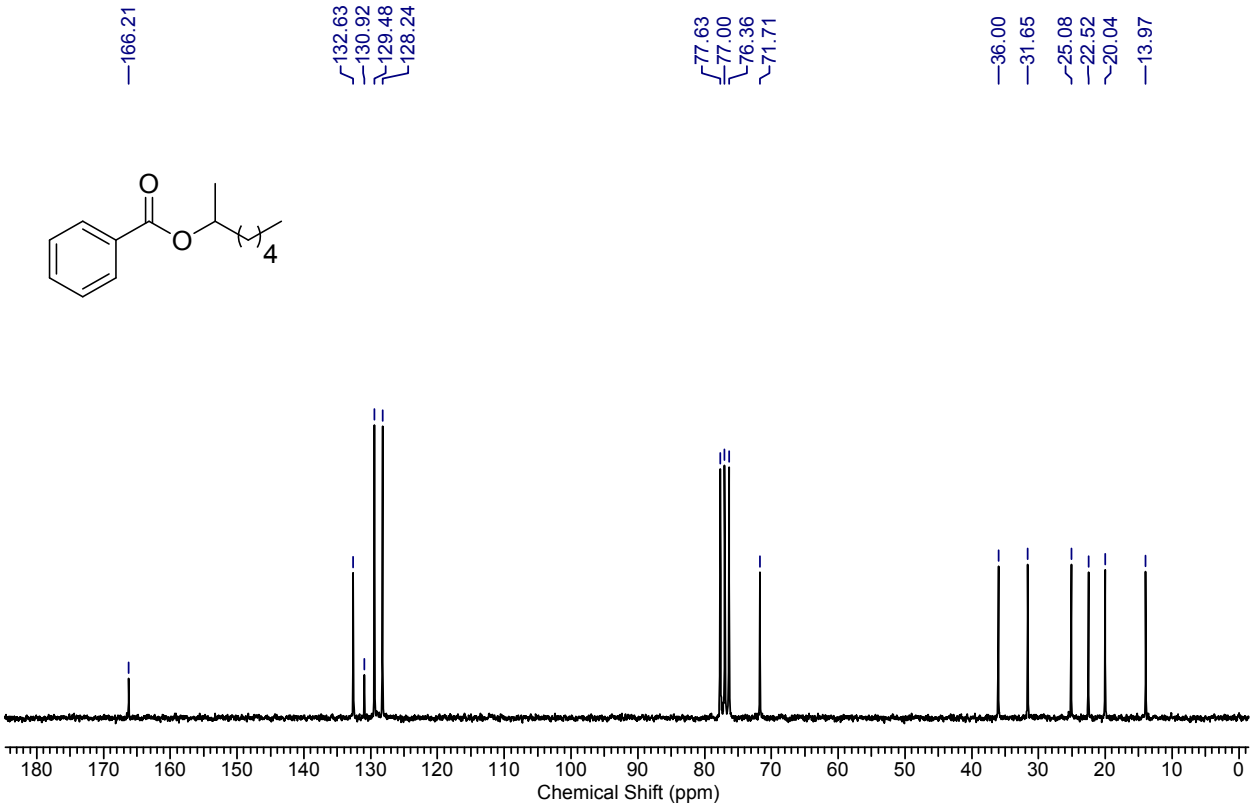

$^{1}$H NMR of **3f**



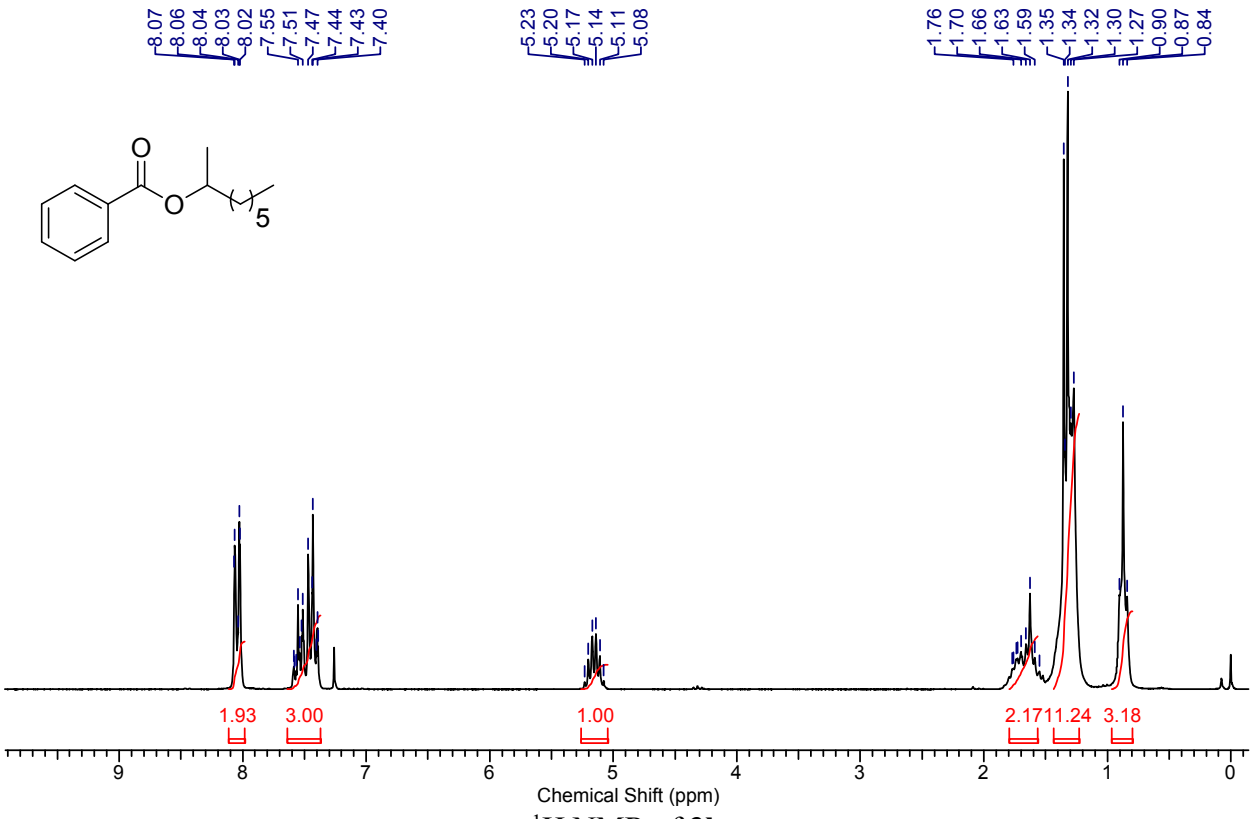

$^{13}$C NMR of **3f**



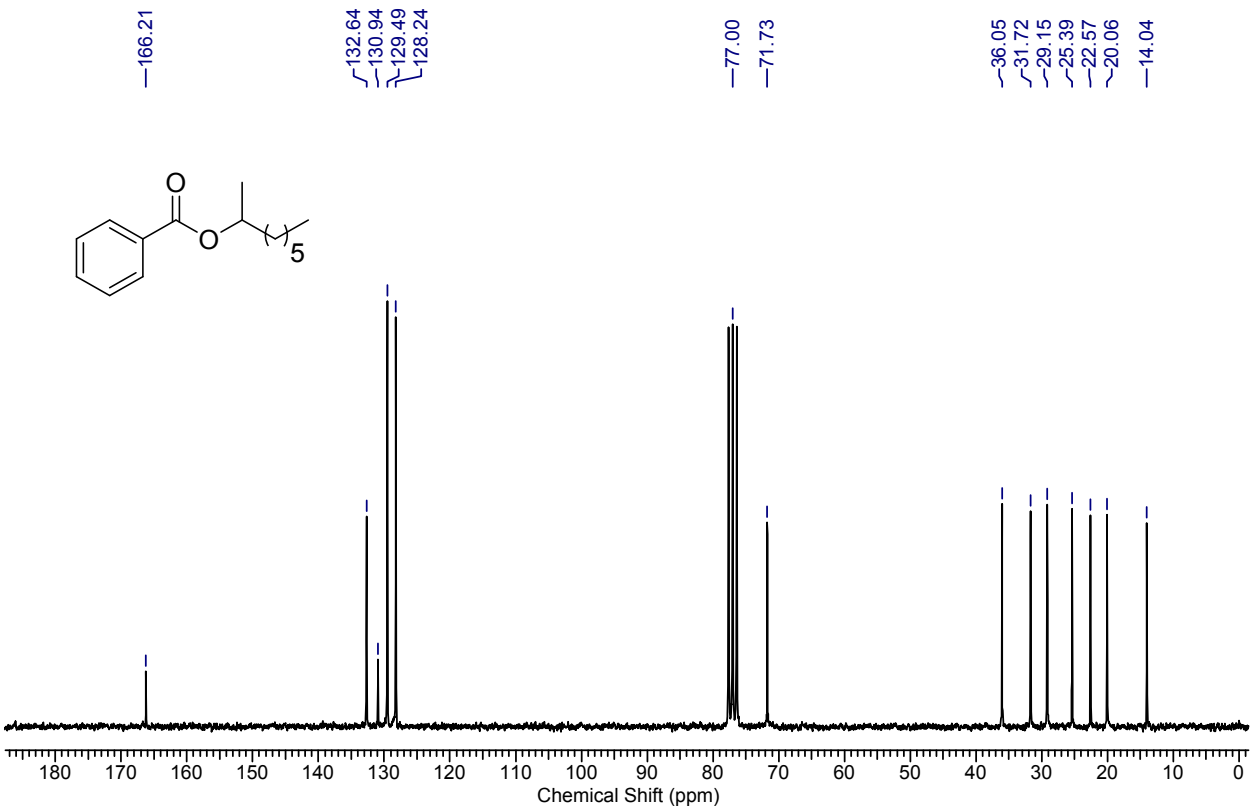

$^{1}$H NMR of **3g**



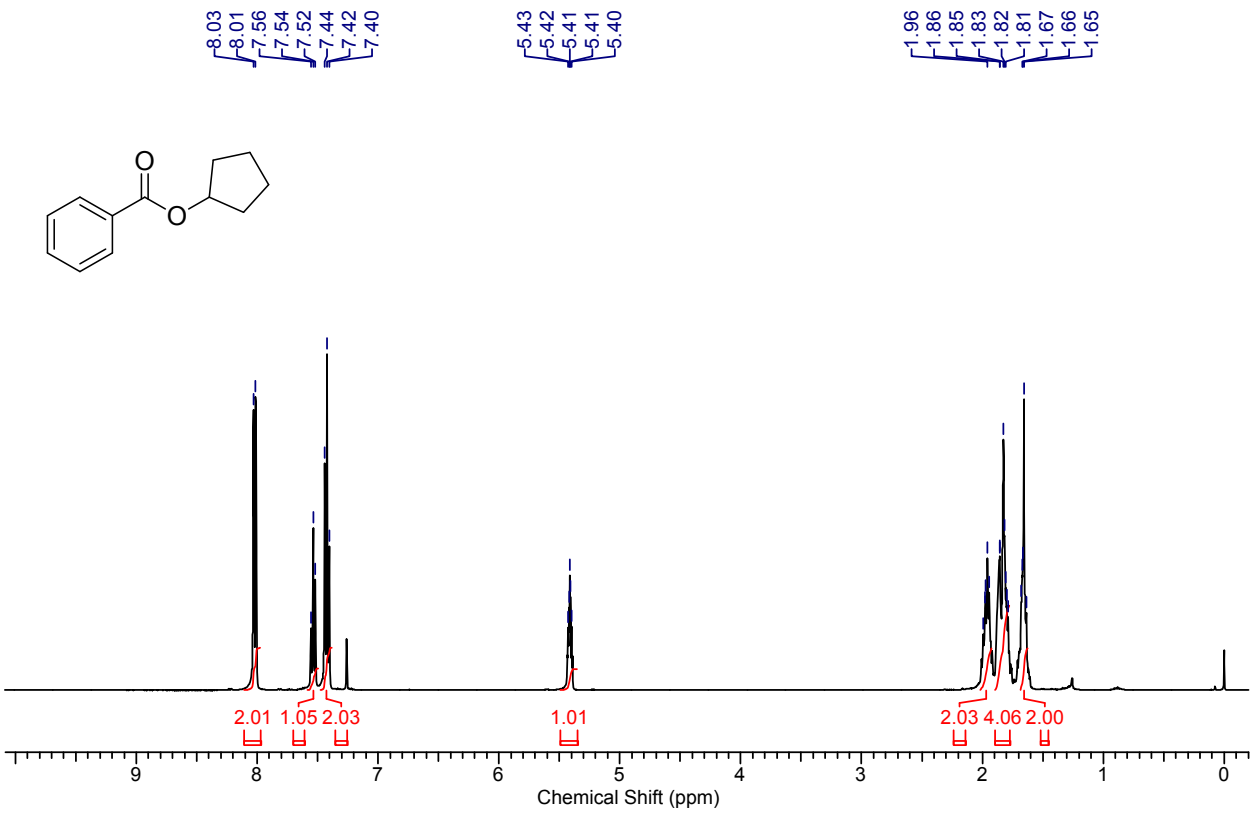

$^{13}$C NMR of **3g**



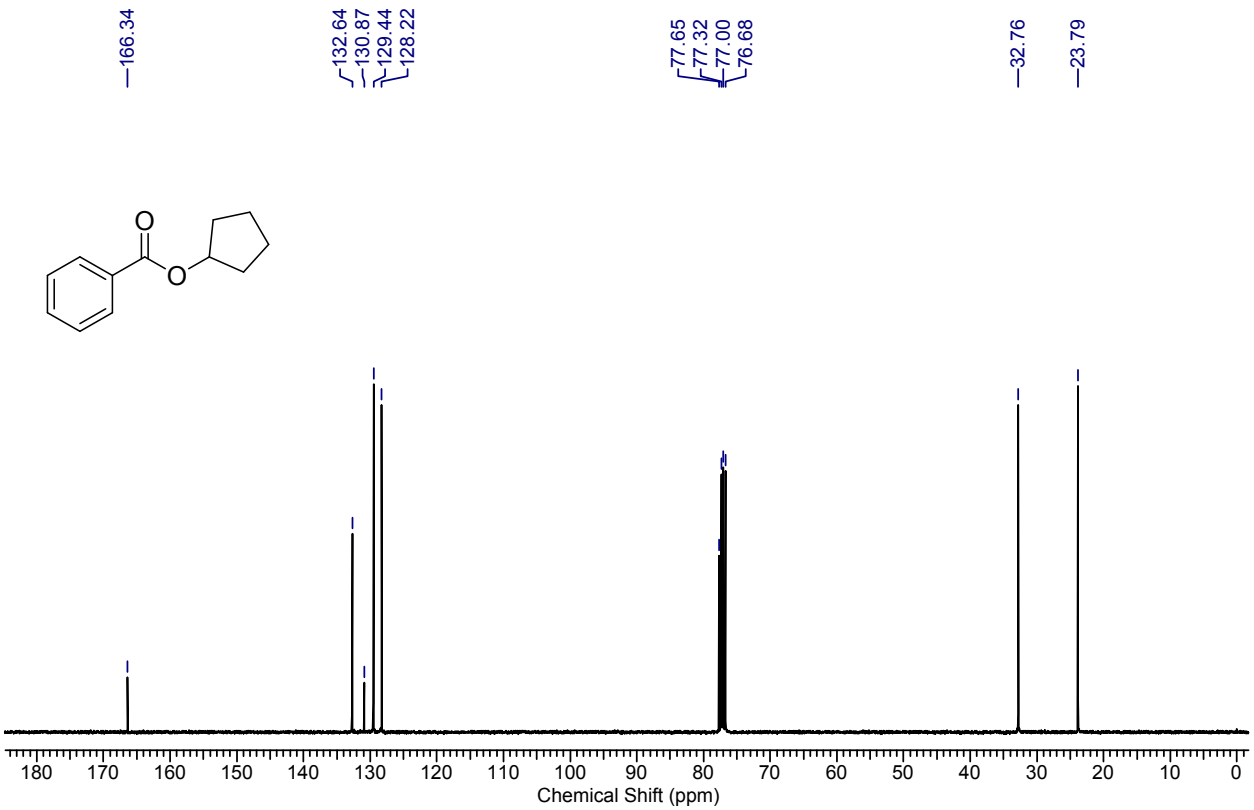

$^{1}$H NMR of **3h**



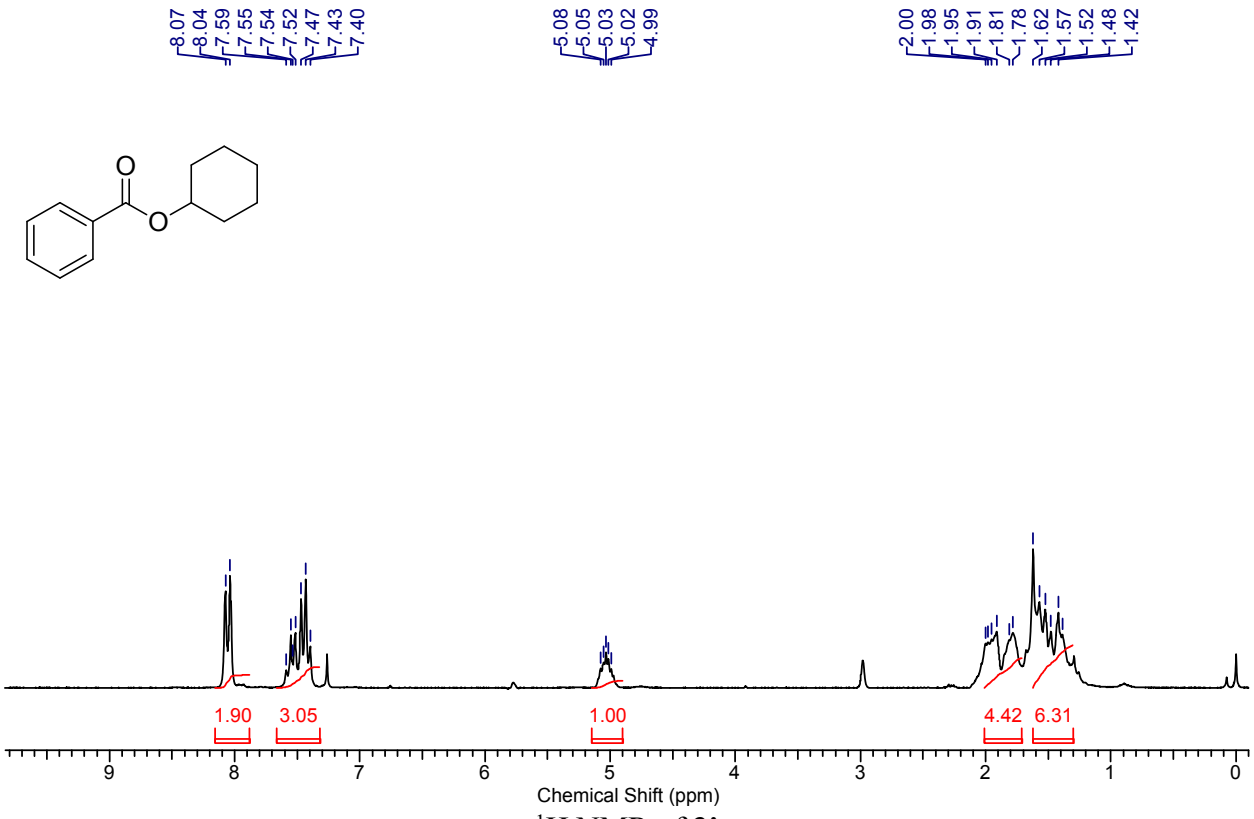

$^{13}$C NMR of **3h**



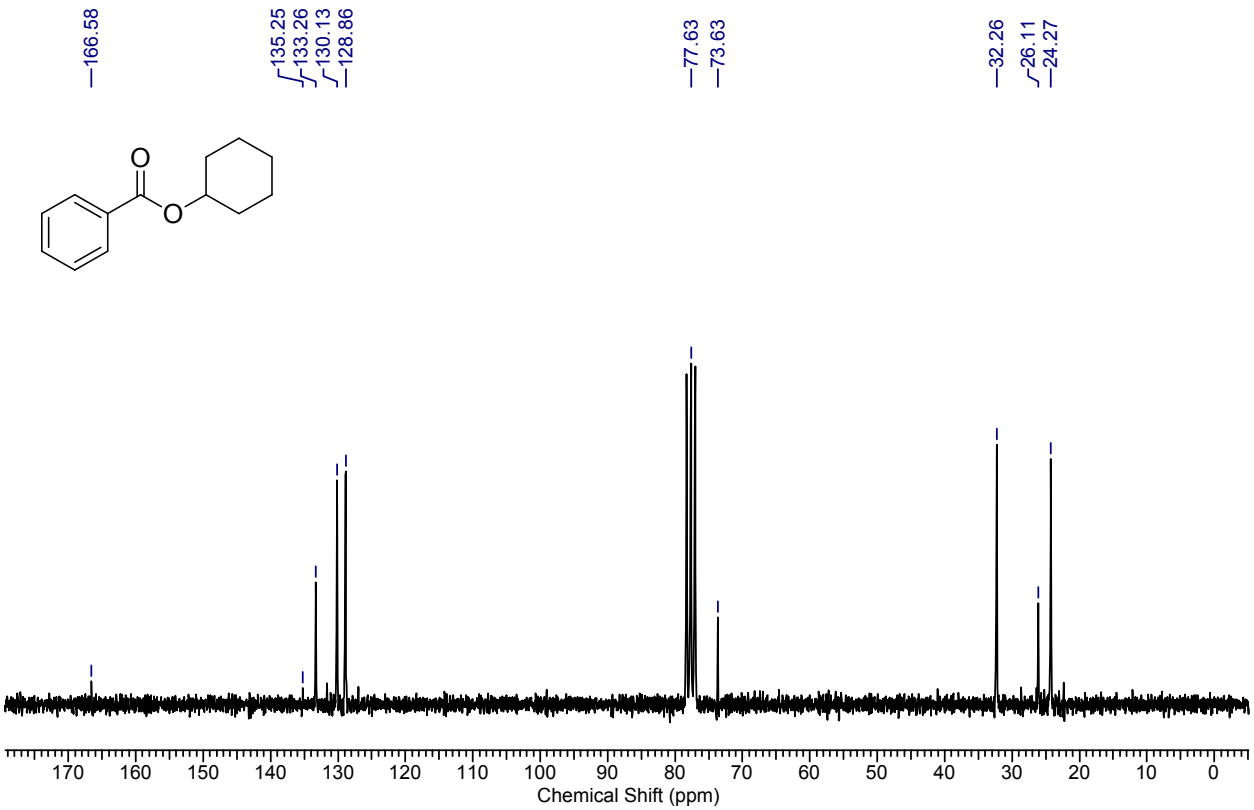

$^{1}$H NMR of **3i**




$^{13}$C NMR of **3i**




$^{1}$H NMR of **3j**

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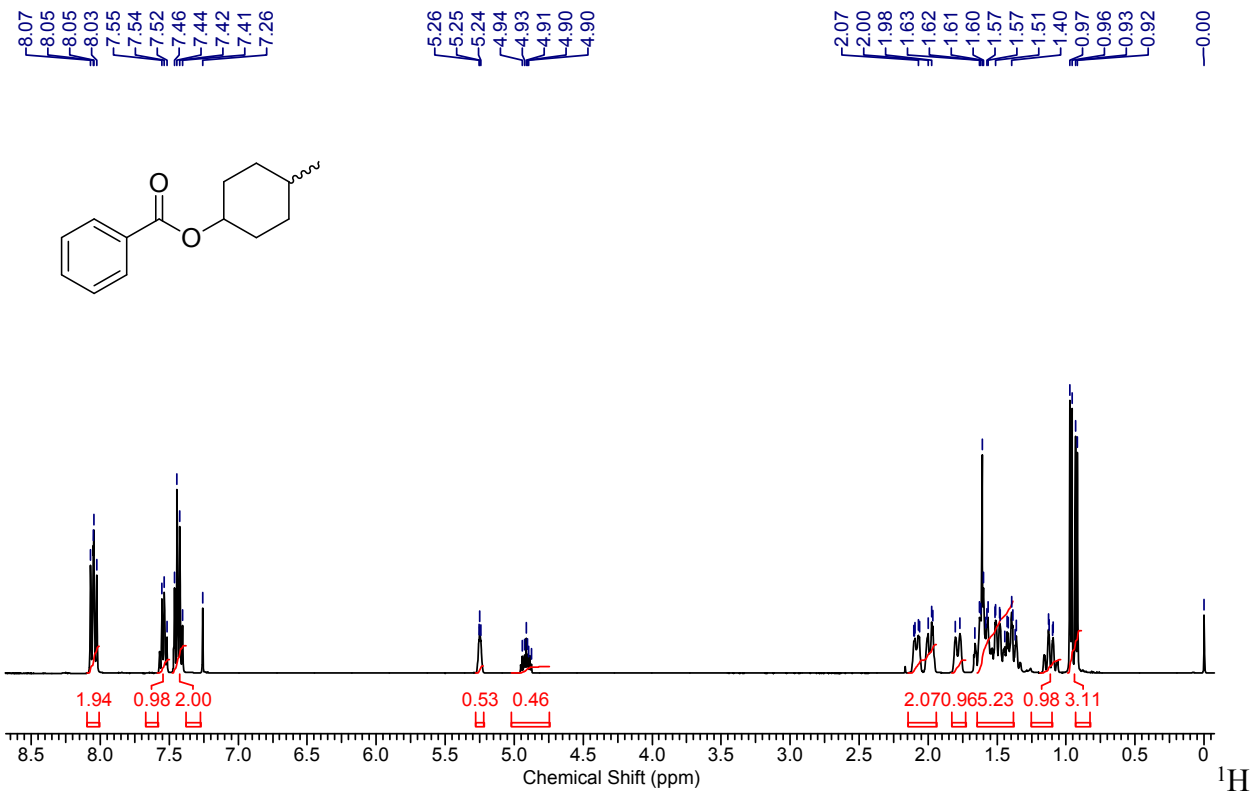
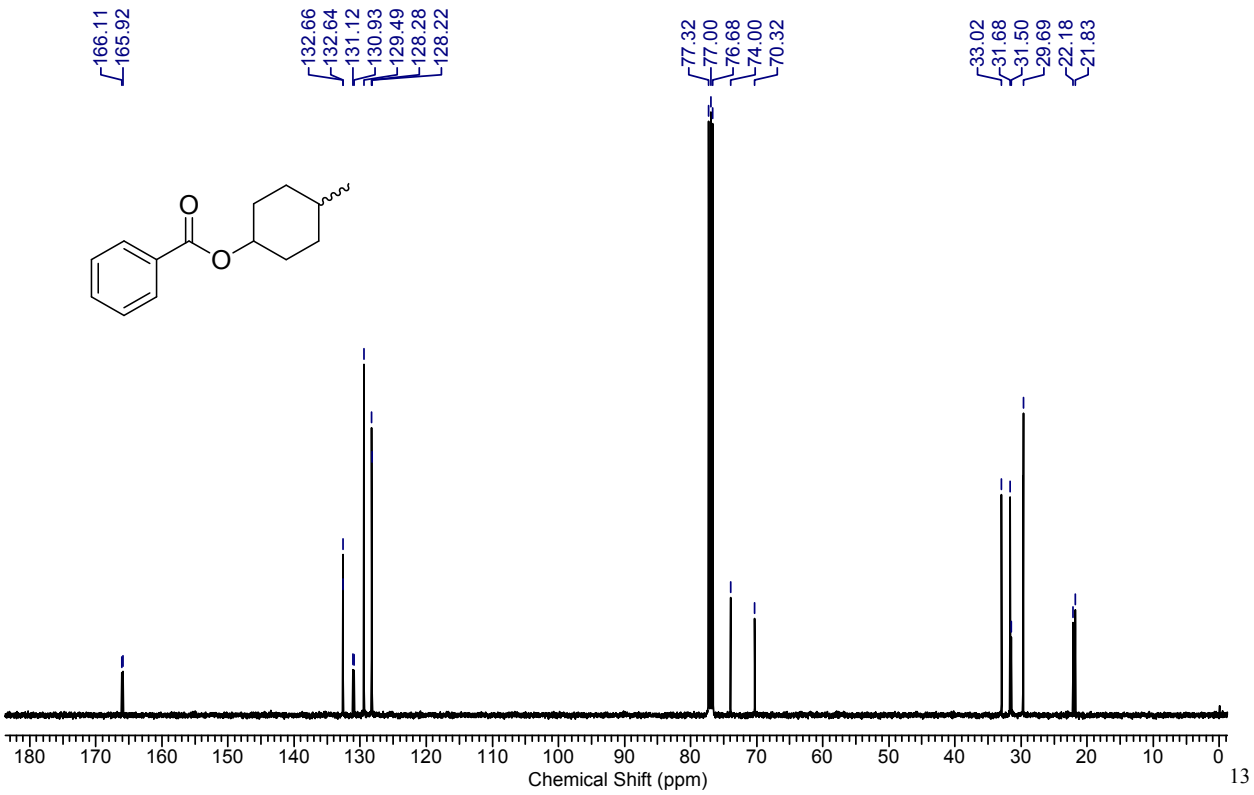



$^{1}$H NMR of **3k**

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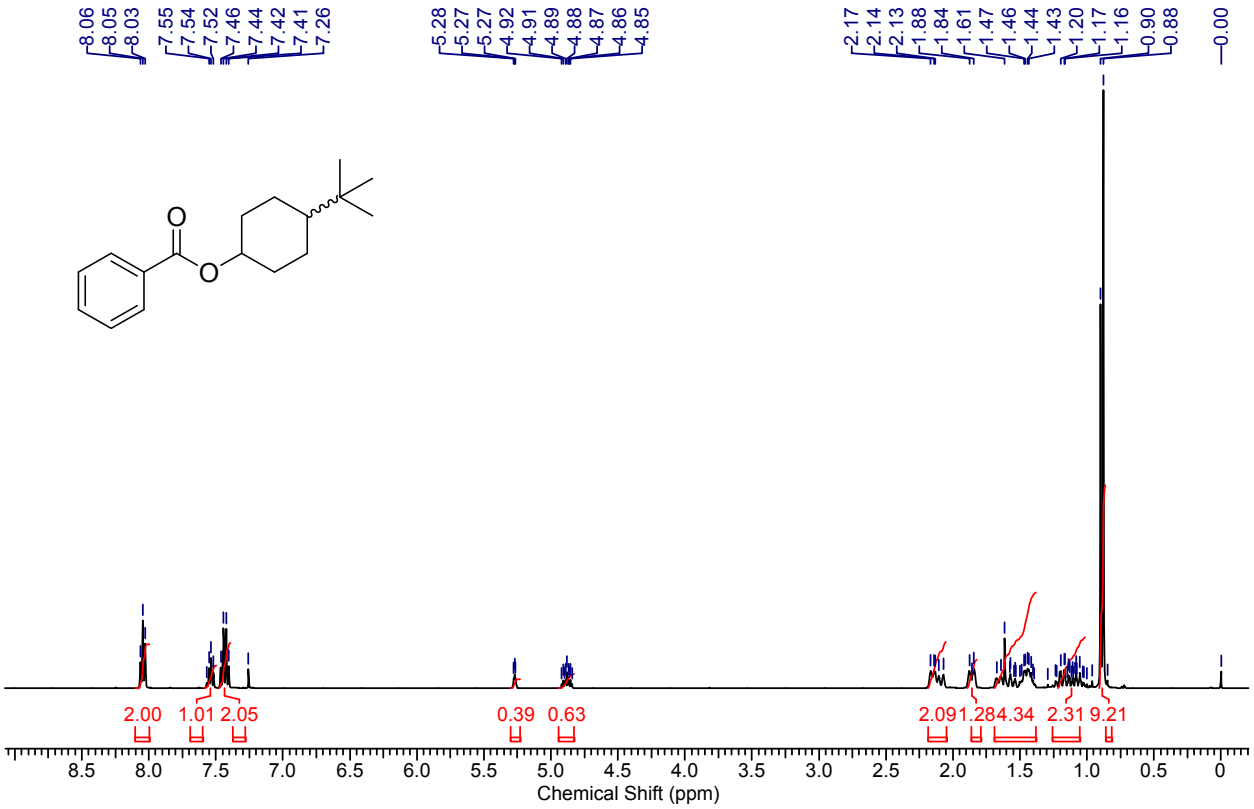
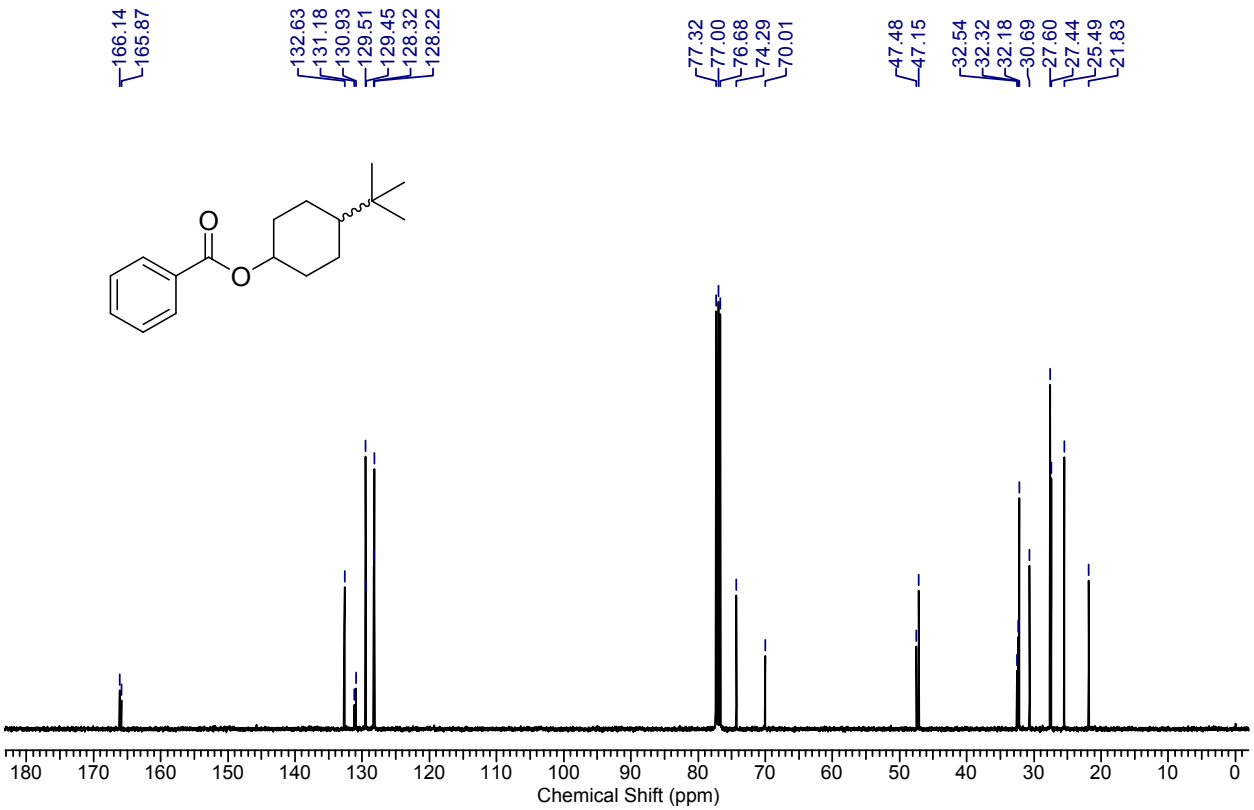
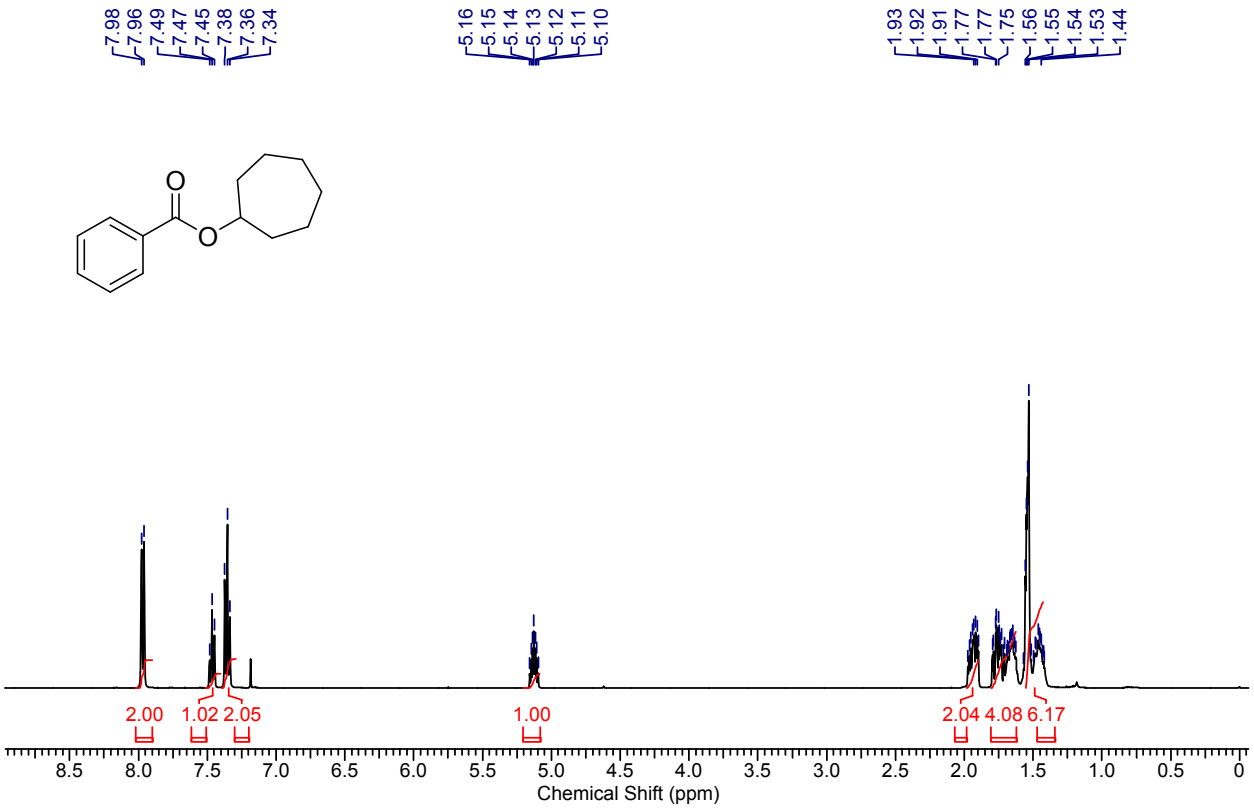
C NMR of **3k**



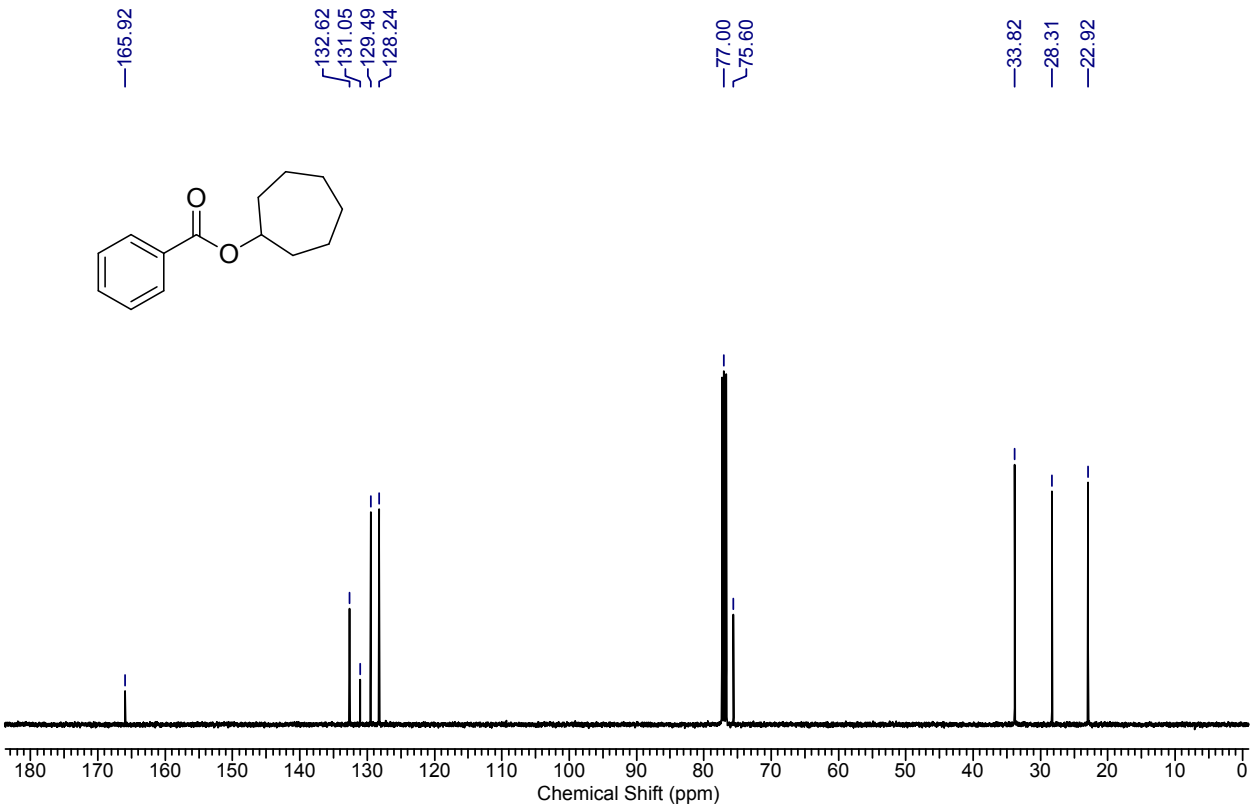

$^{1}$H NMR of **3l**



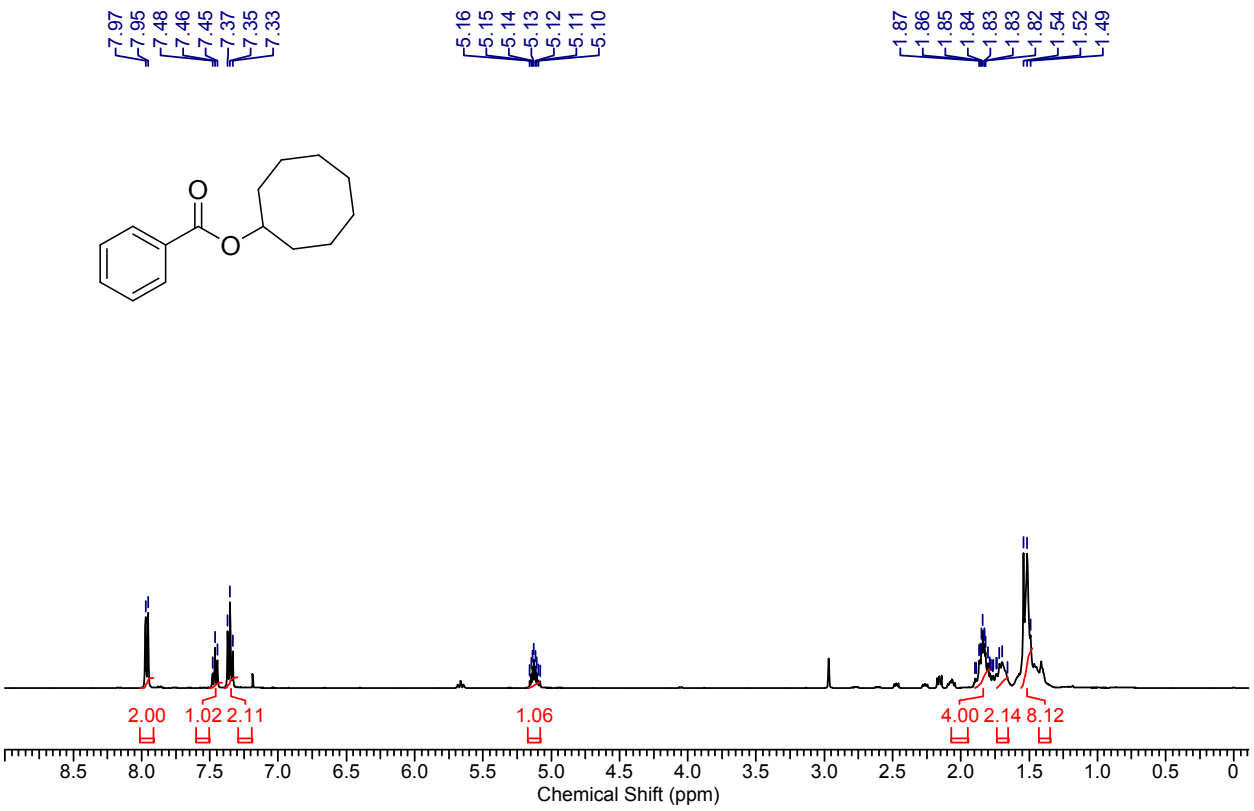

$^{13}$C NMR of **3l**



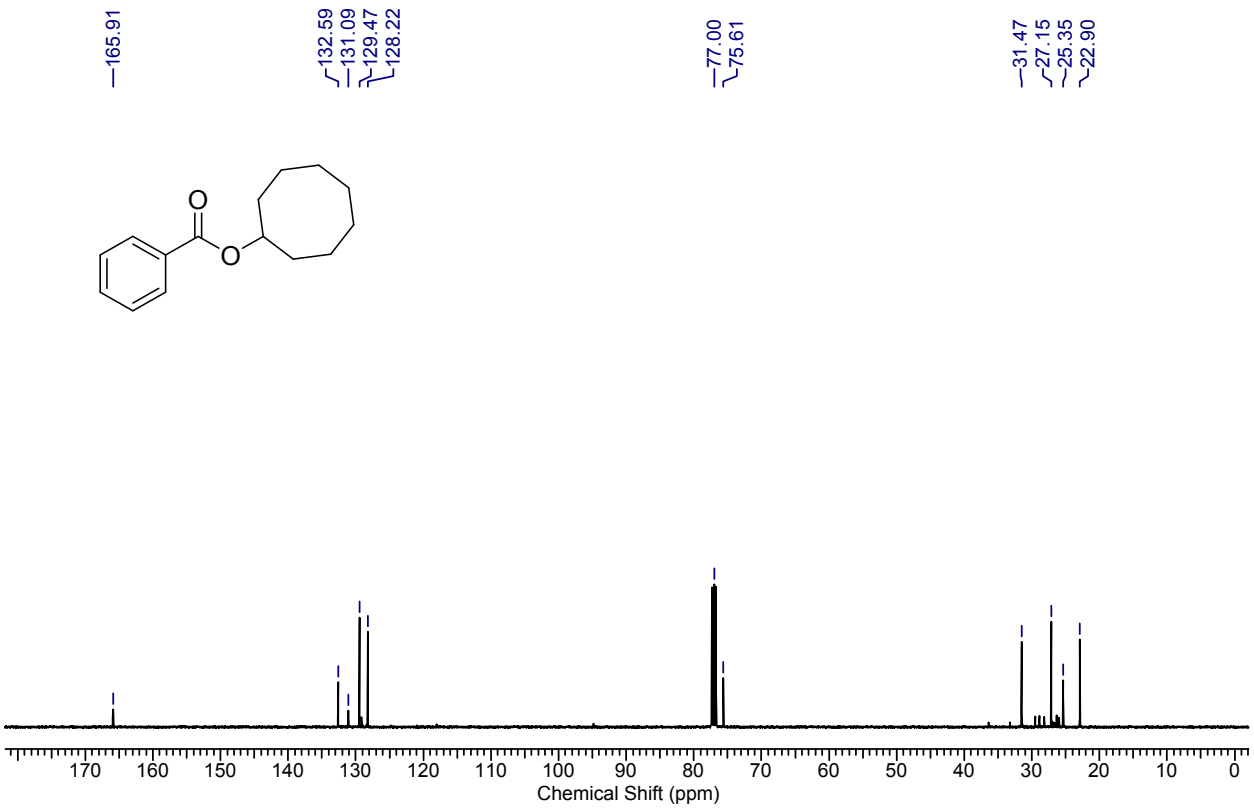

$^{1}$H NMR of **3m**



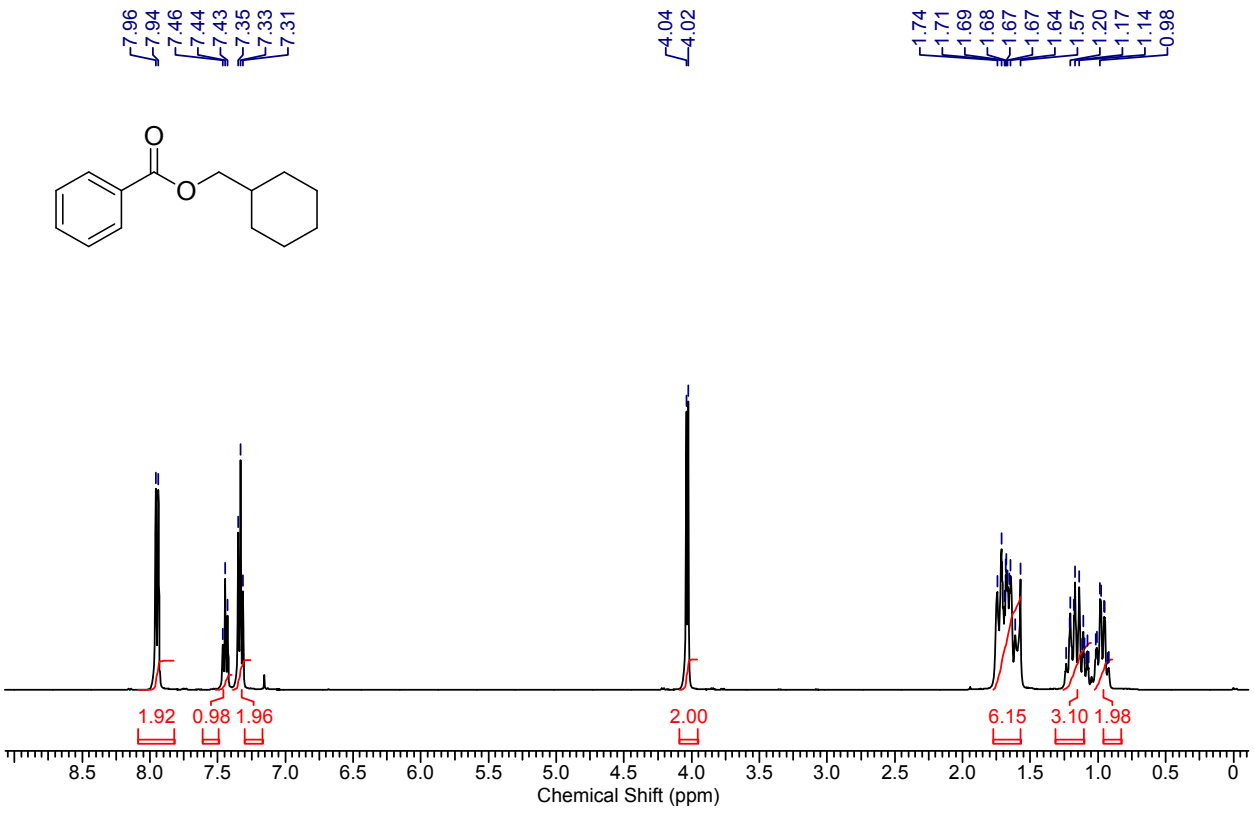

$^{13}$C NMR of **3m**



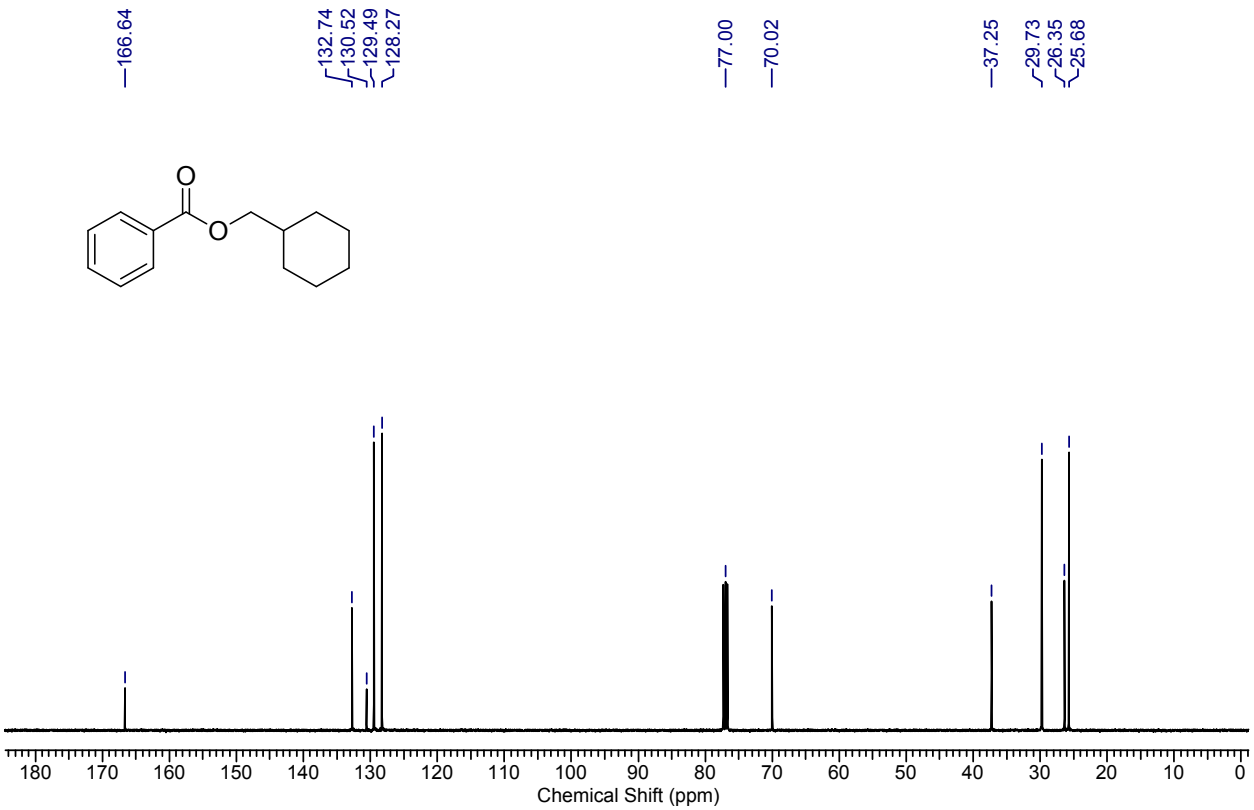

$^{1}$H NMR of **3n**




$^{13}$C NMR of **3n**




$^{1}$H NMR of **3o**

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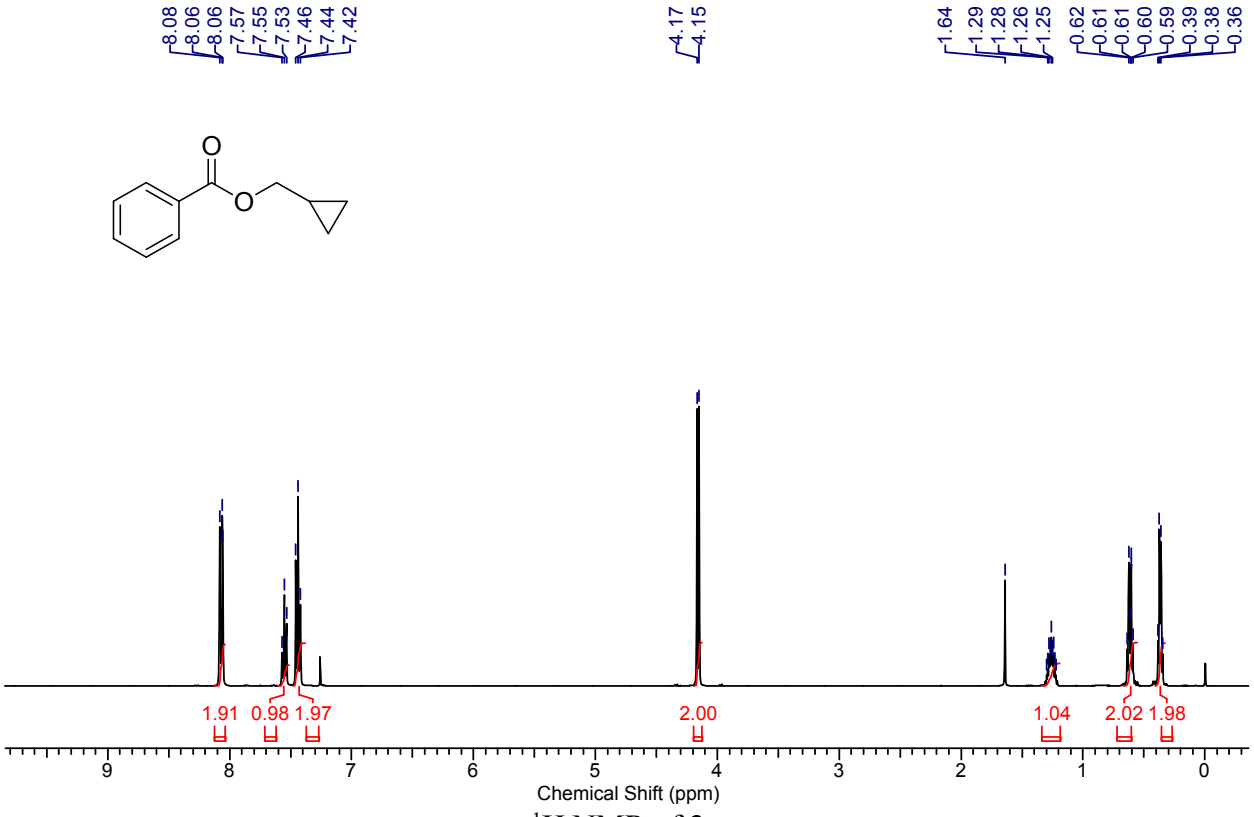
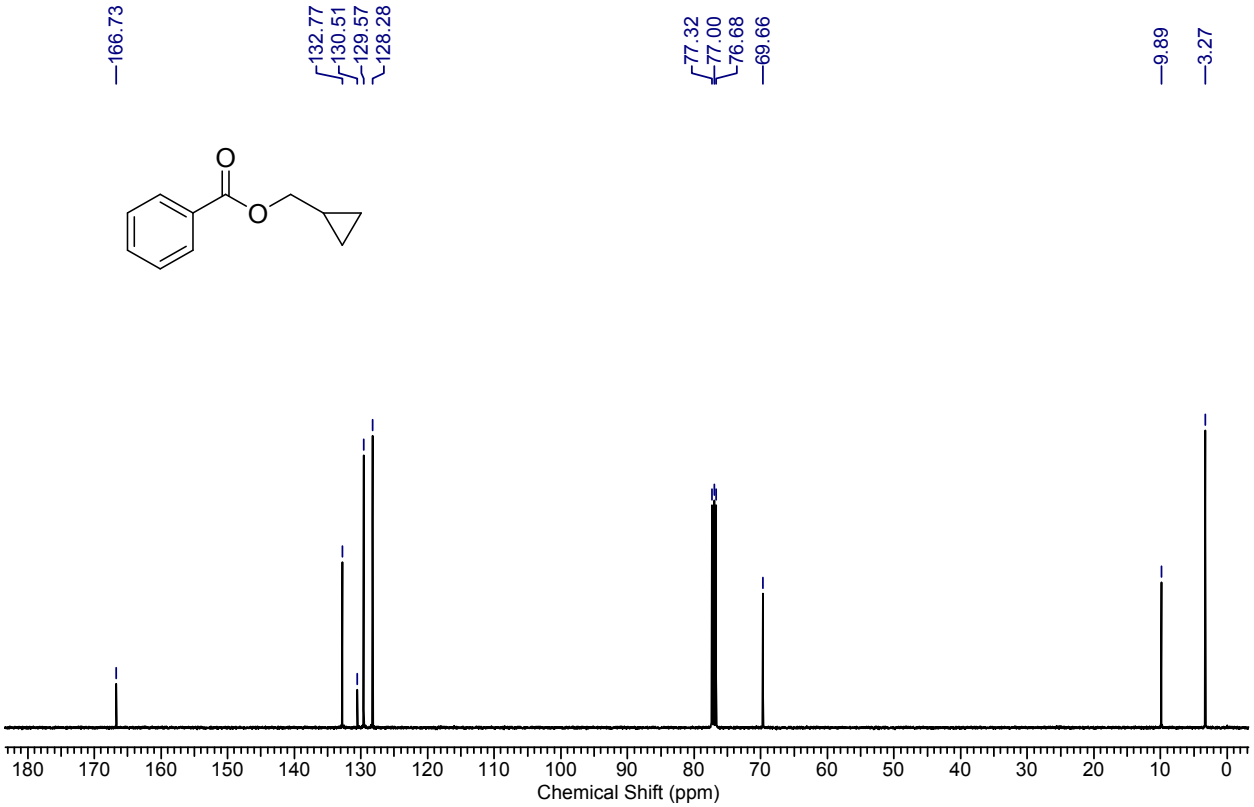
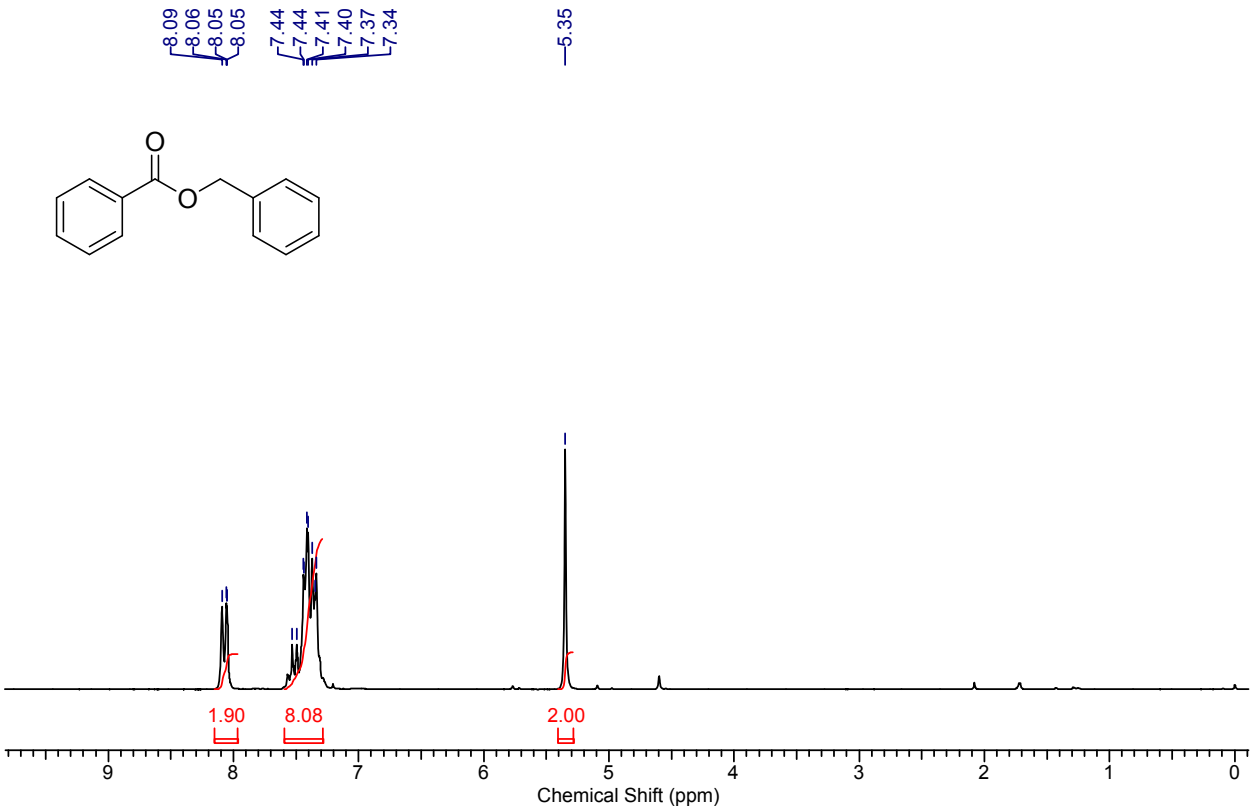


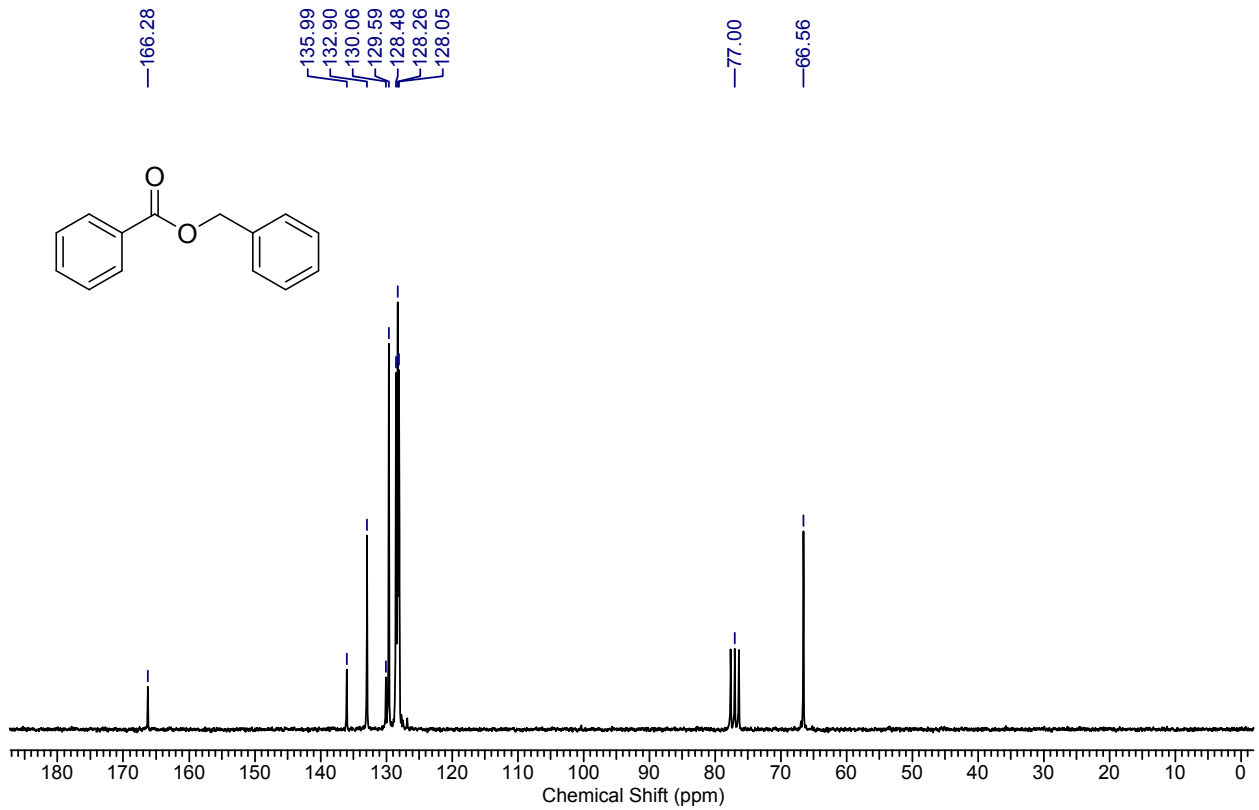

$^{1}$H NMR of **3p**



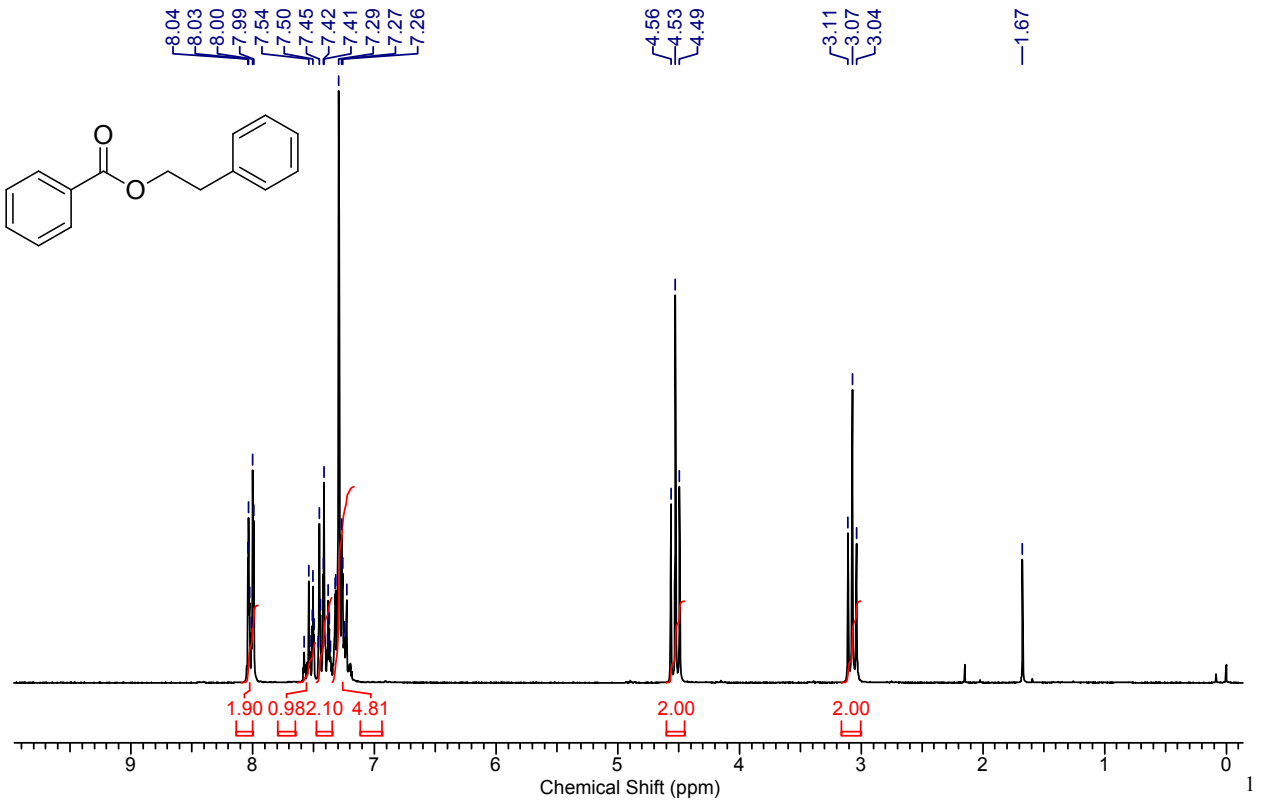

$^{13}$C NMR of **3p**



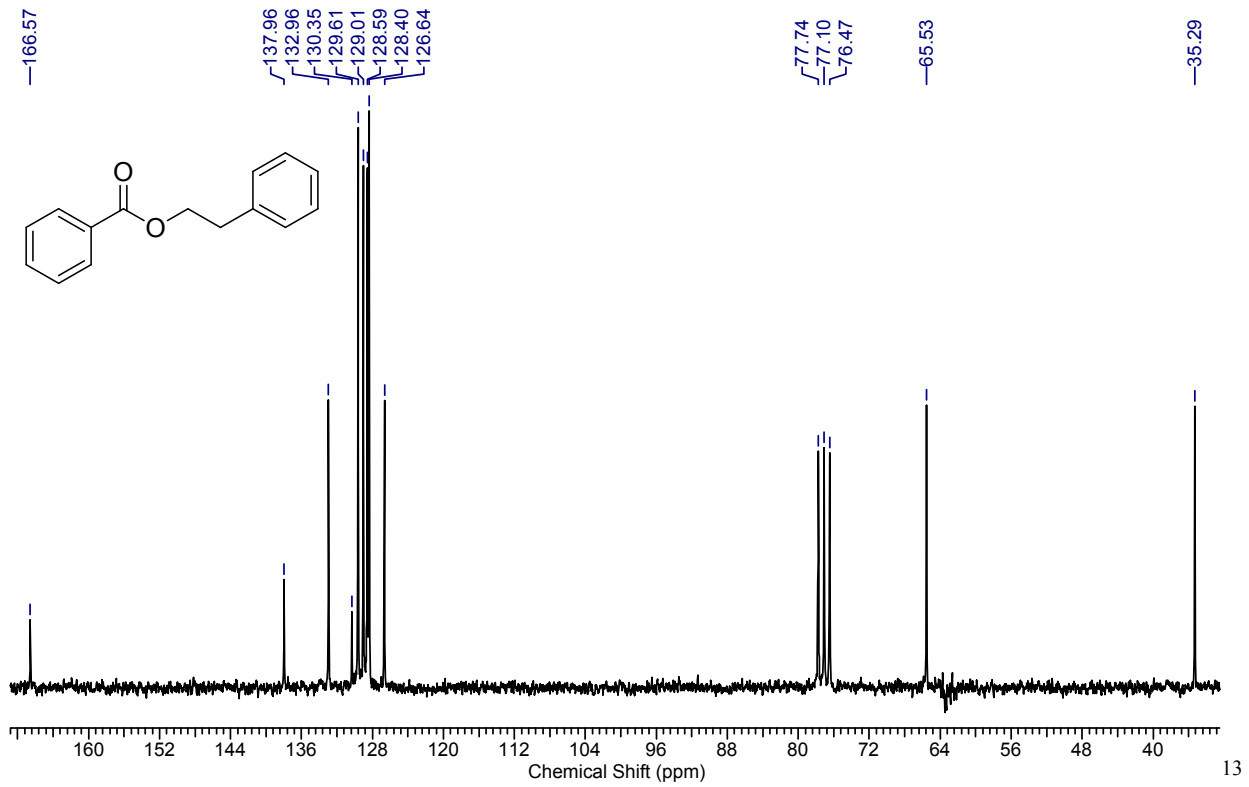

$^{1}$H NMR of **3q**




$^{13}$C NMR of **3q**




H NMR of **3r**

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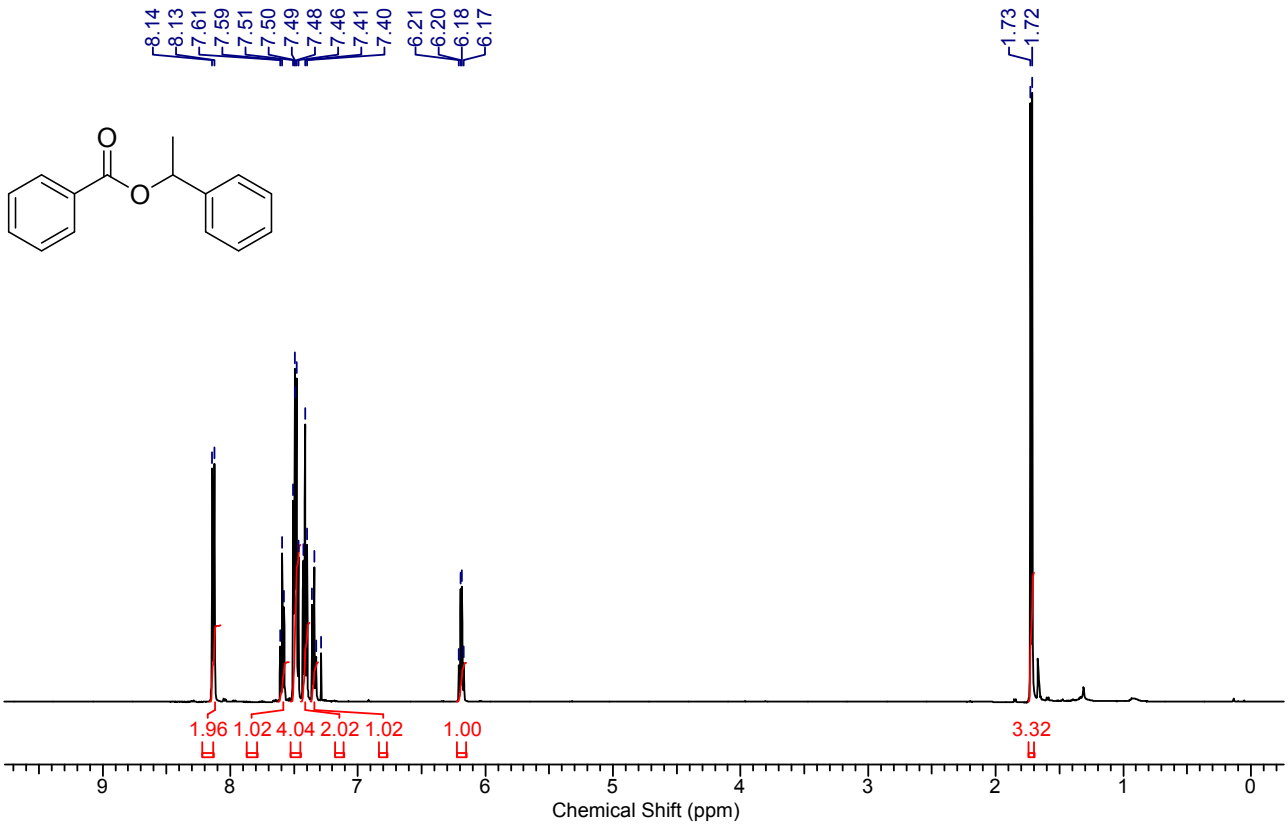
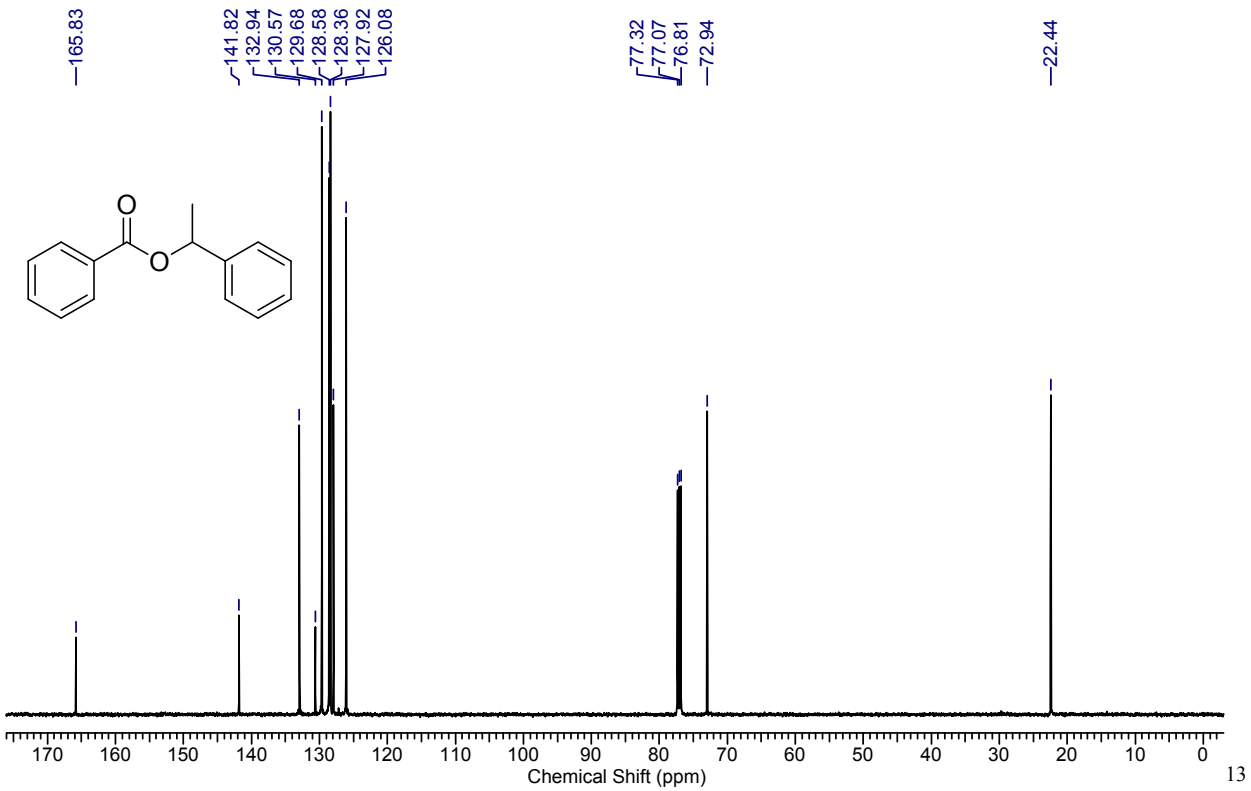
C NMR of **3r**




$^{1}$H NMR of **3s**

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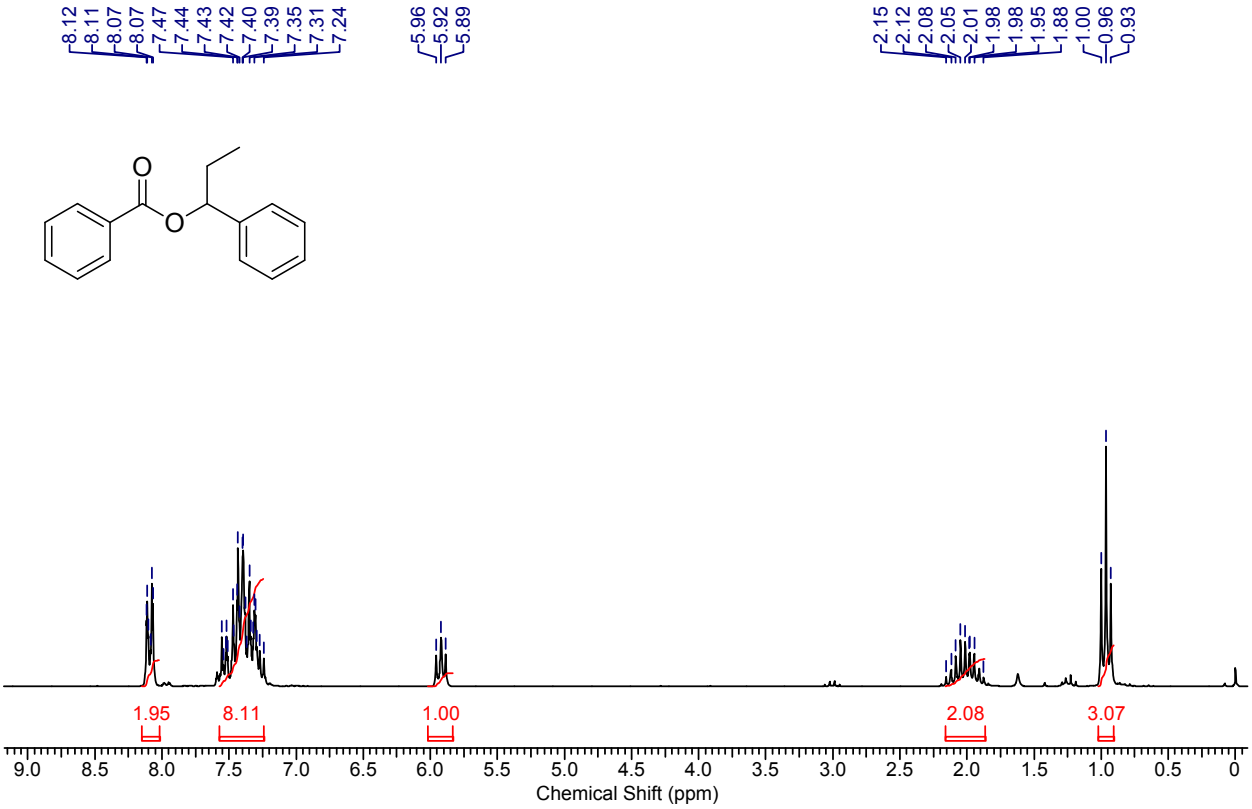
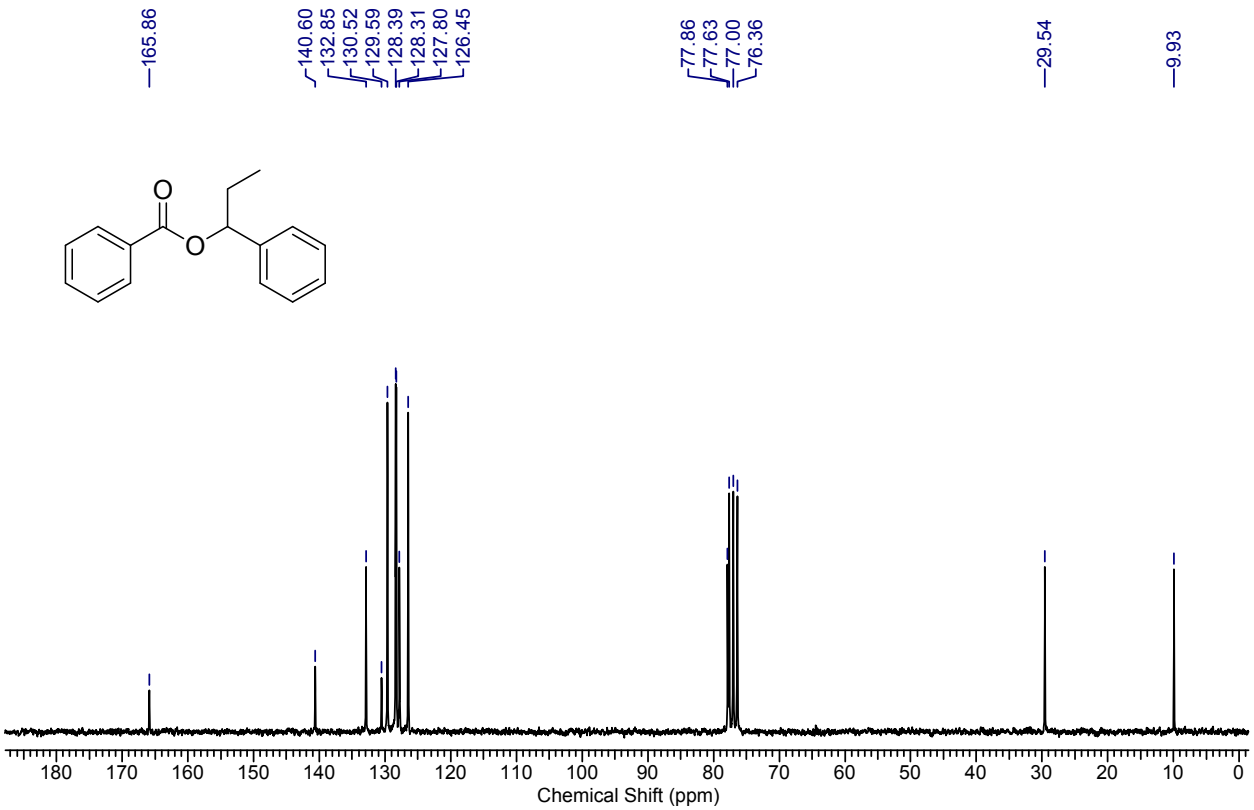
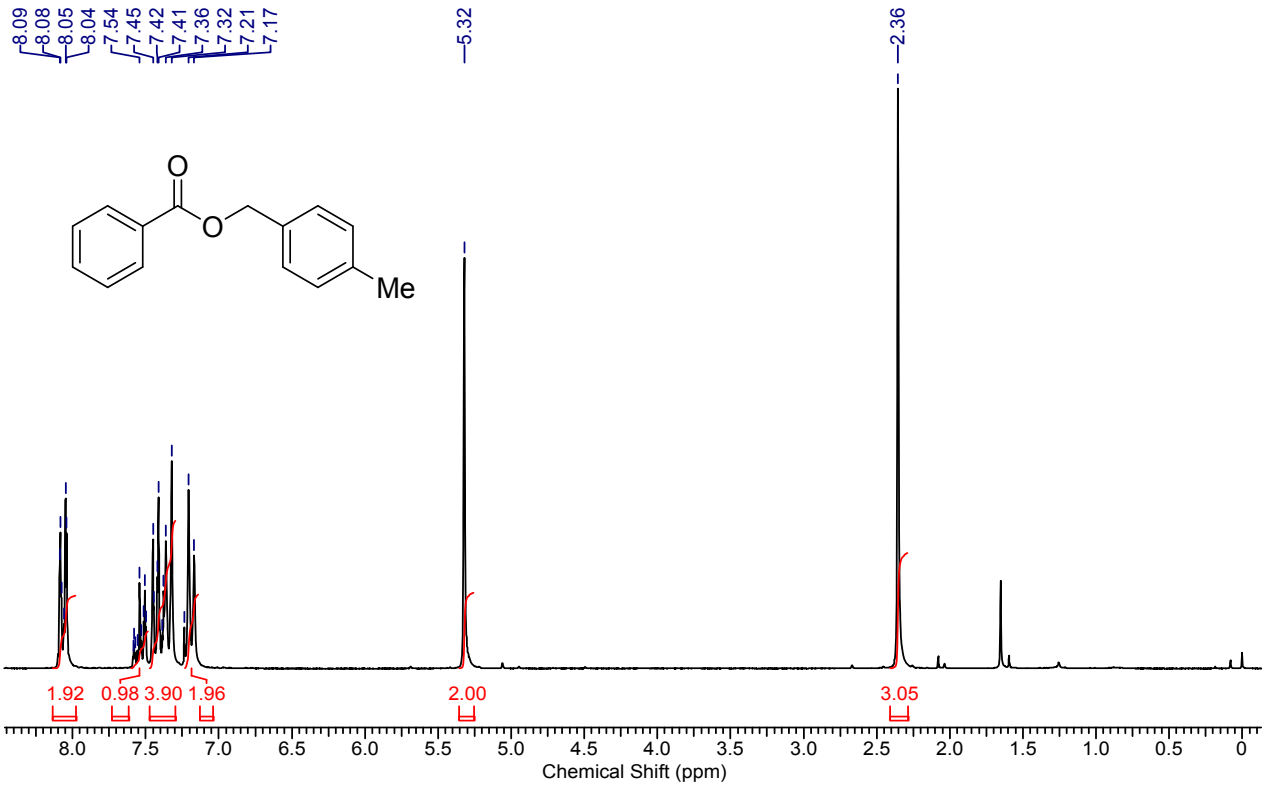
C NMR of **3s**



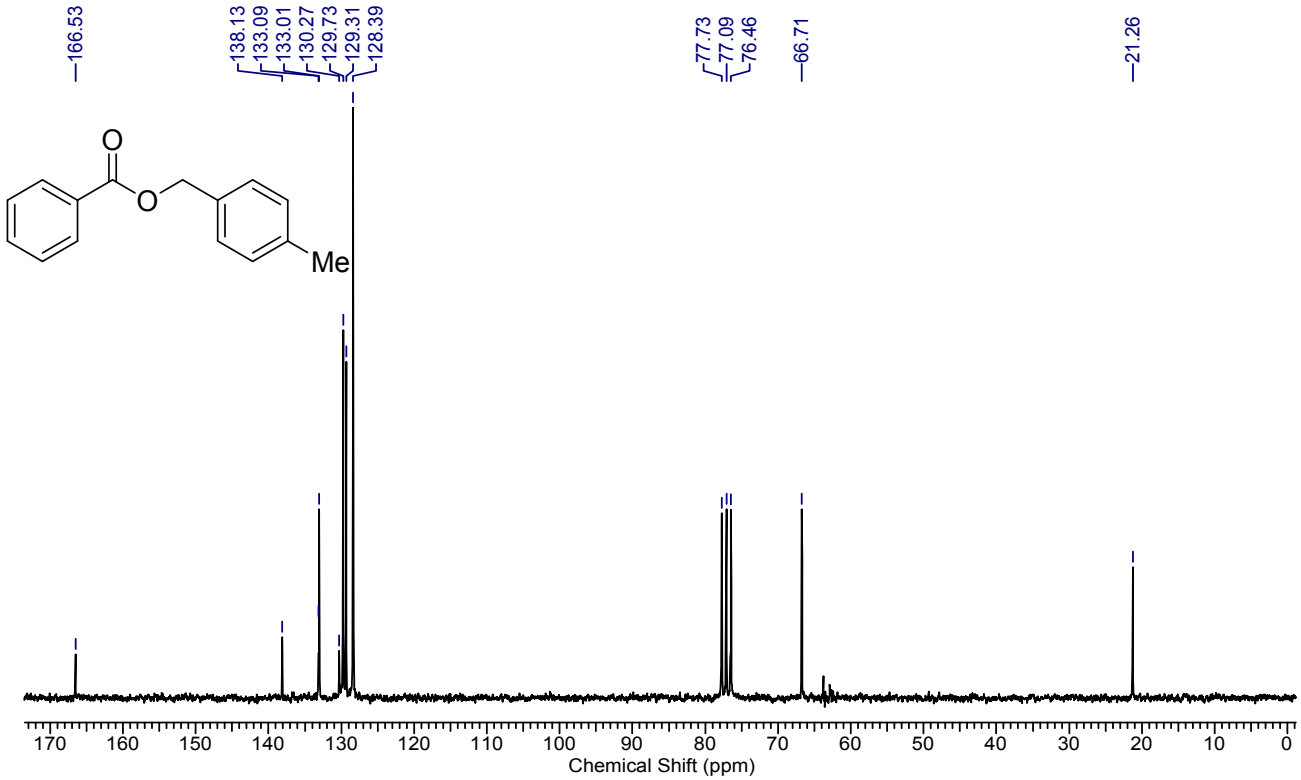

$^{1}$H NMR of **3t**



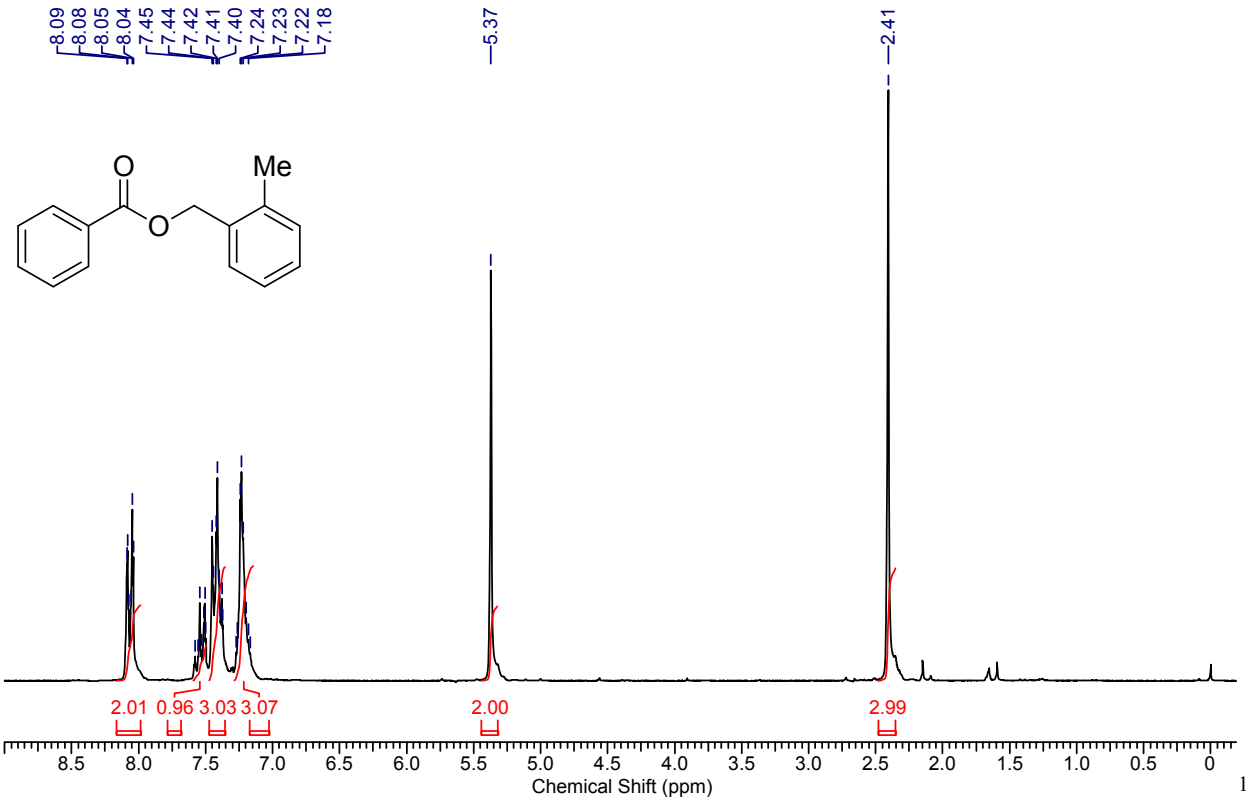

$^{13}$C NMR of **3t**



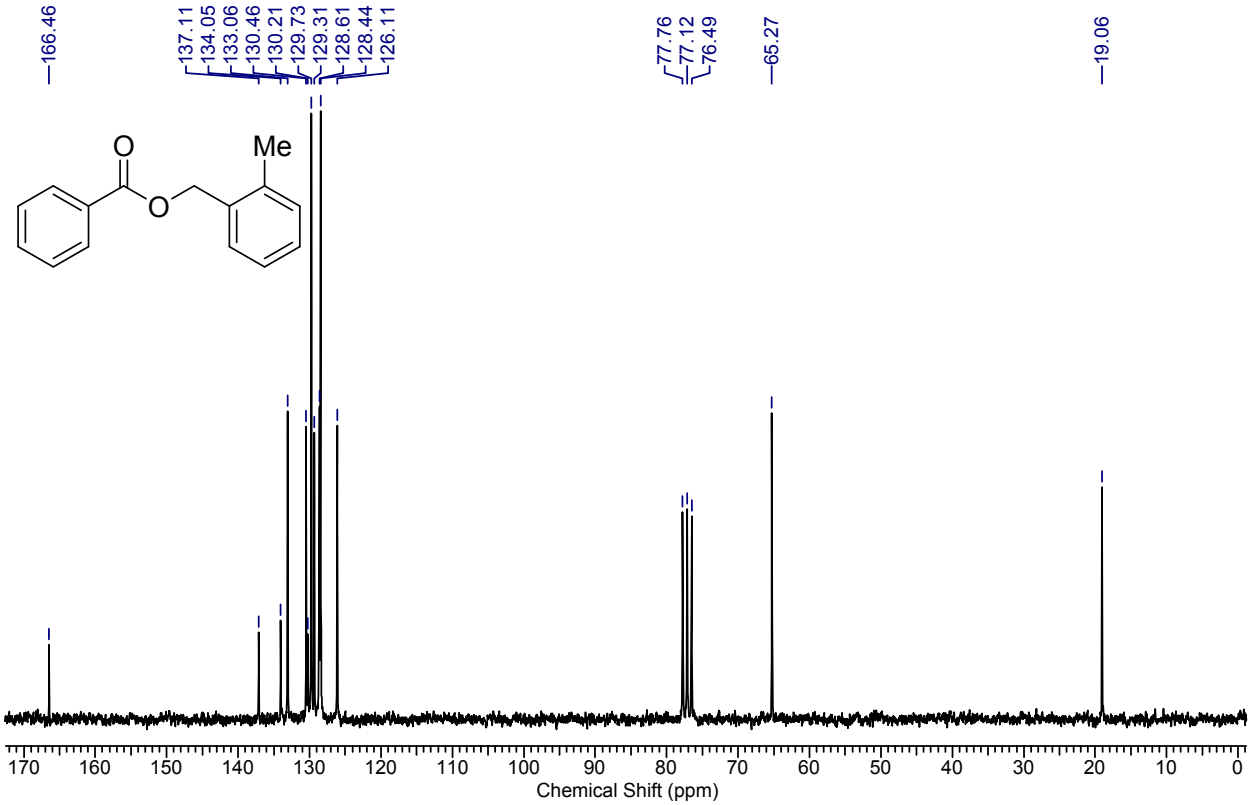

$^{1}$H NMR of **3u**



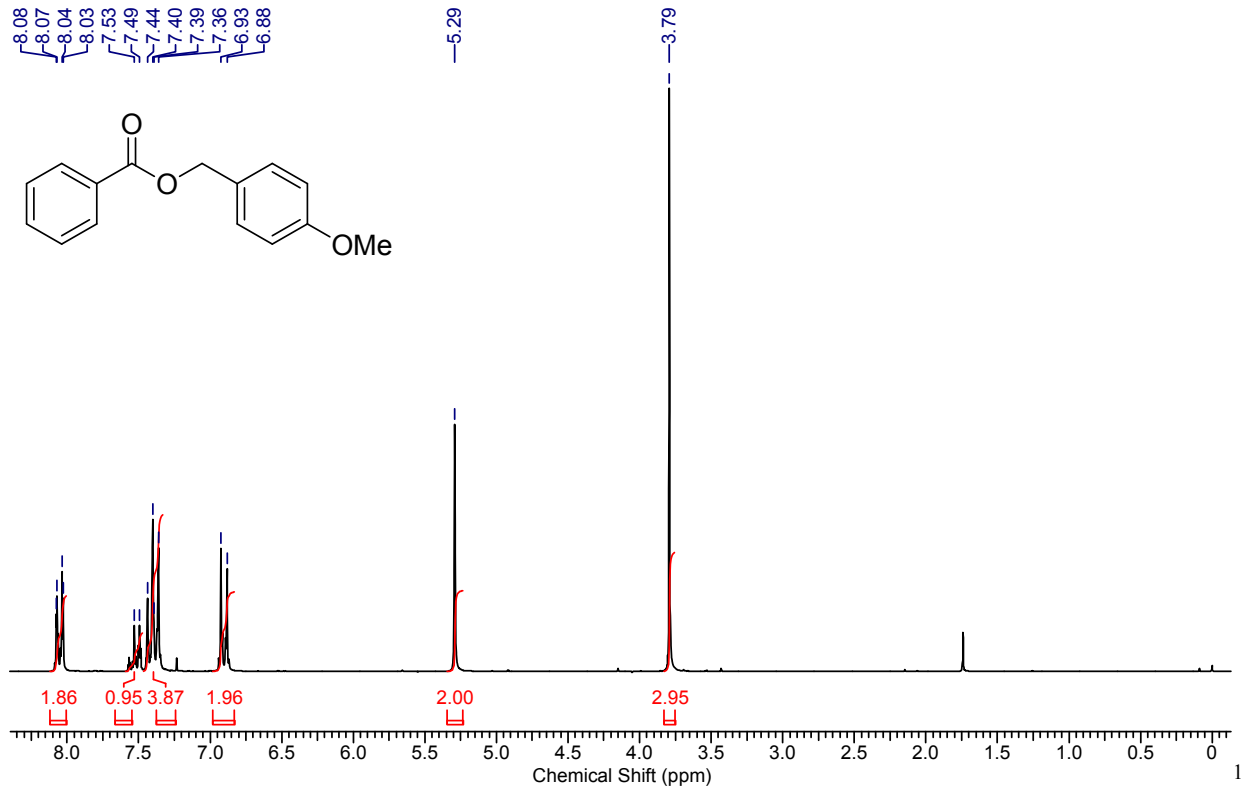

$^{13}$C NMR of **3u**



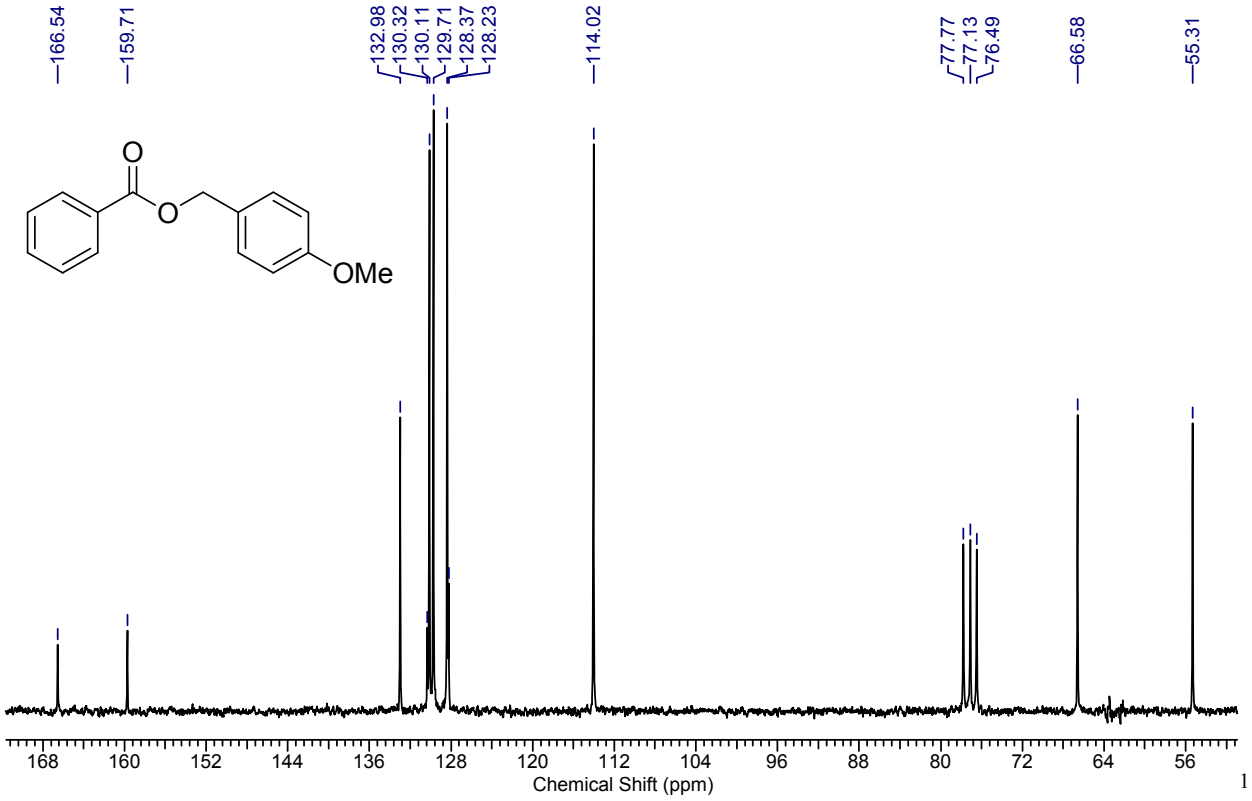

H NMR of **3v**



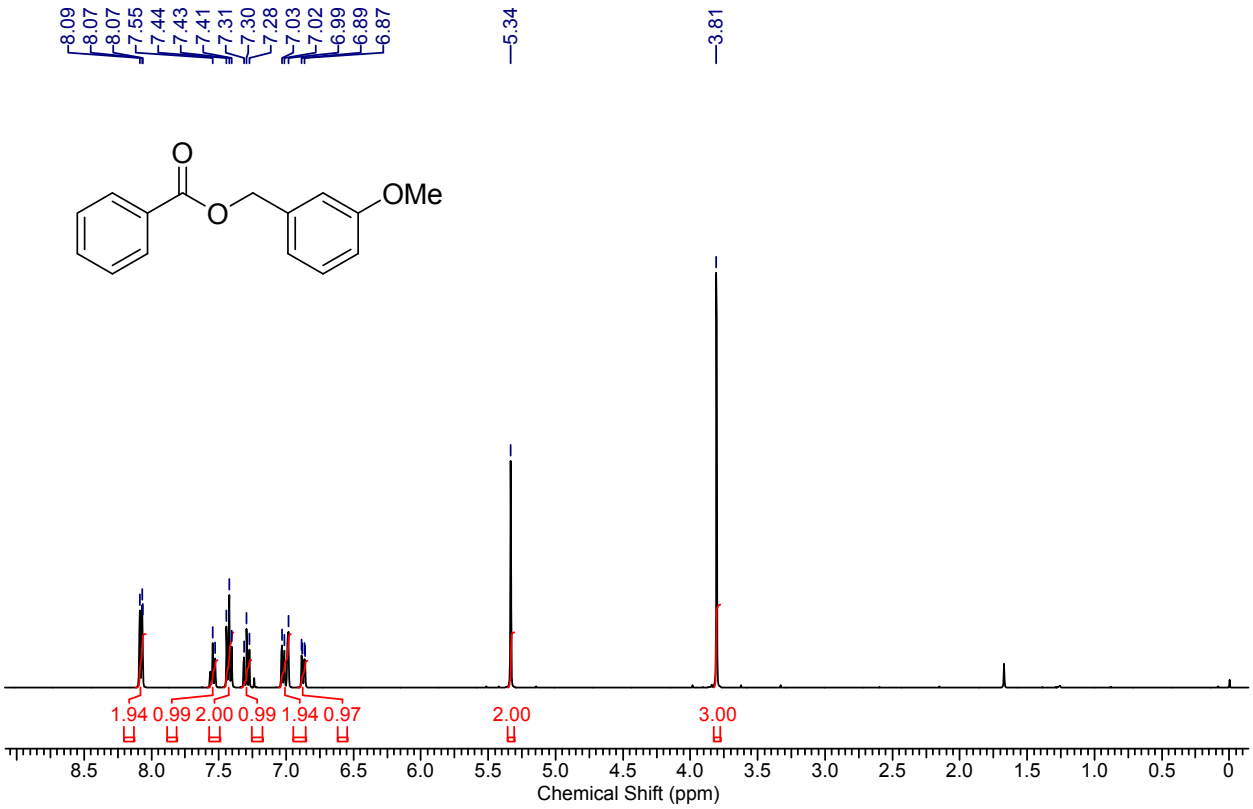

$^{13}$C NMR of **3v**



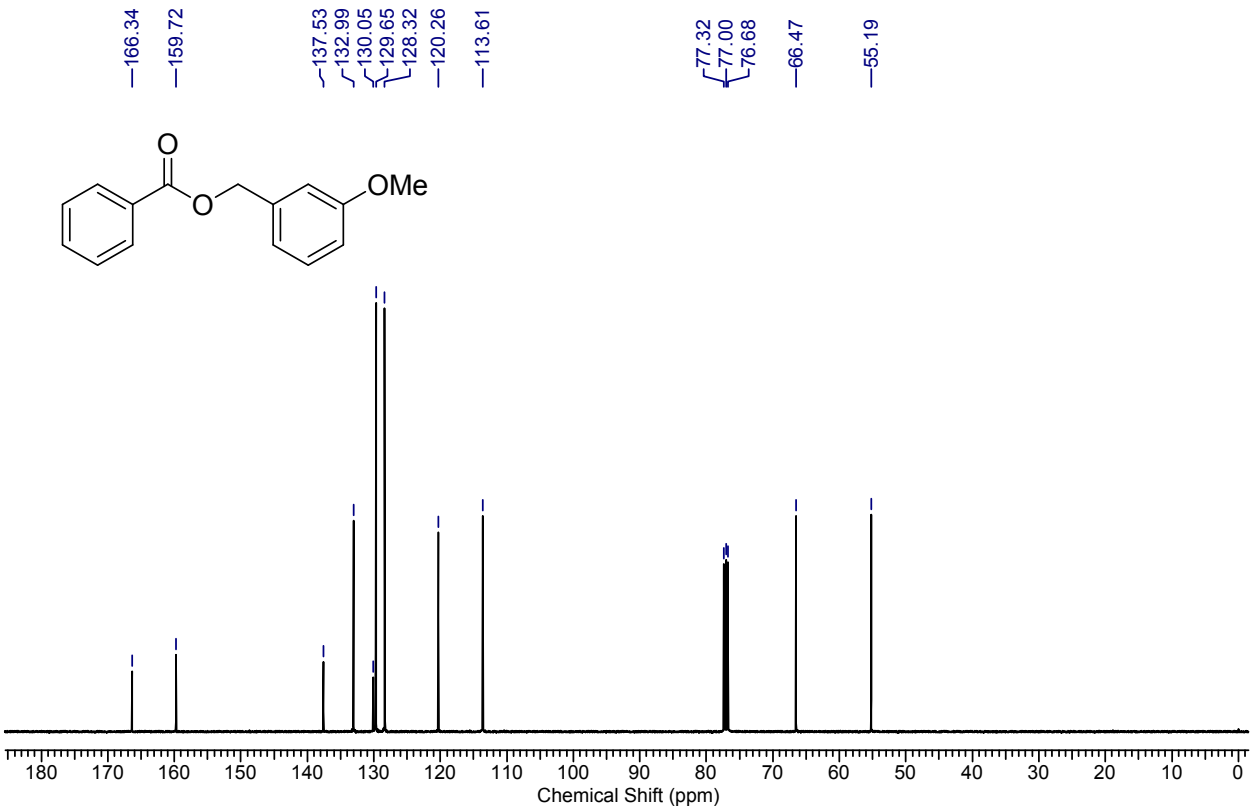

H NMR of **3w**



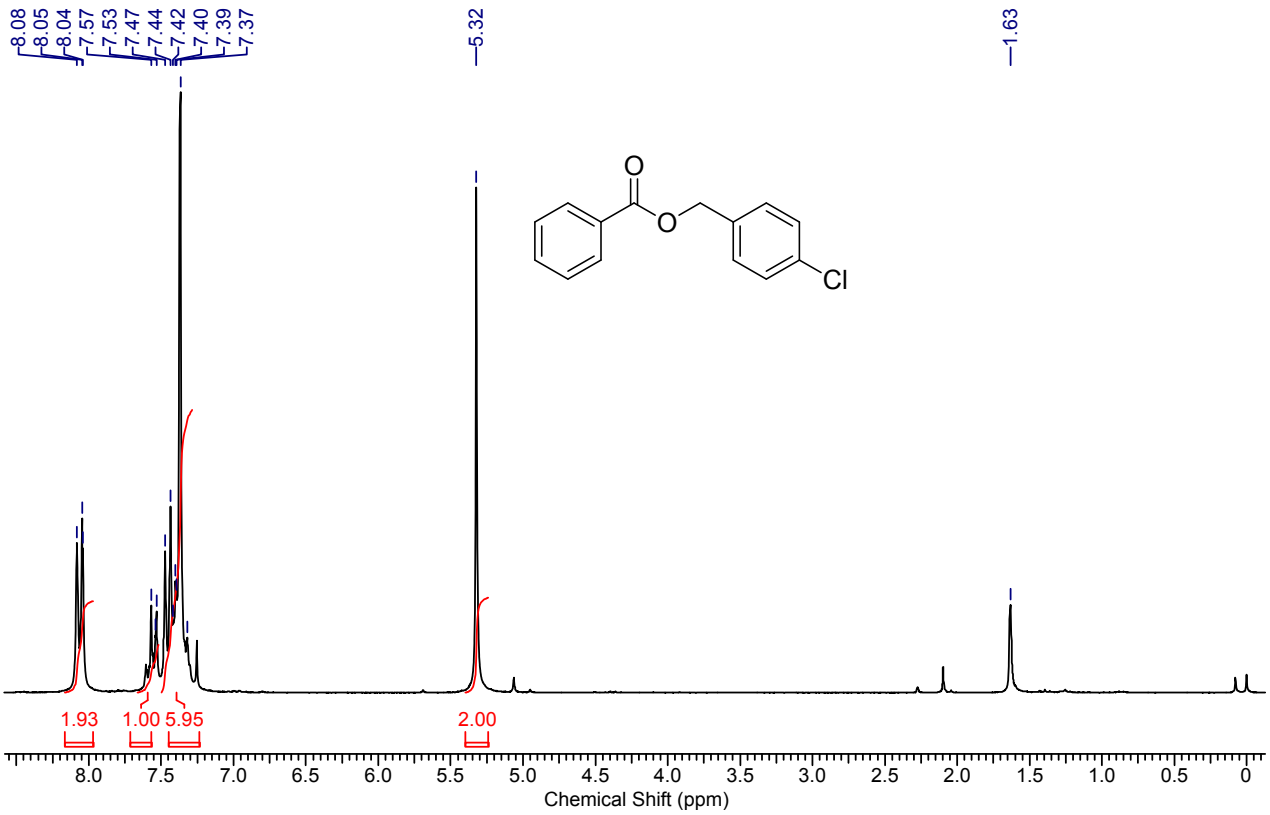

$^{3}$C NMR of **3w**




$^{1}$H NMR of **3x**

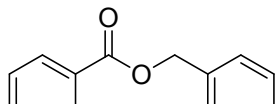


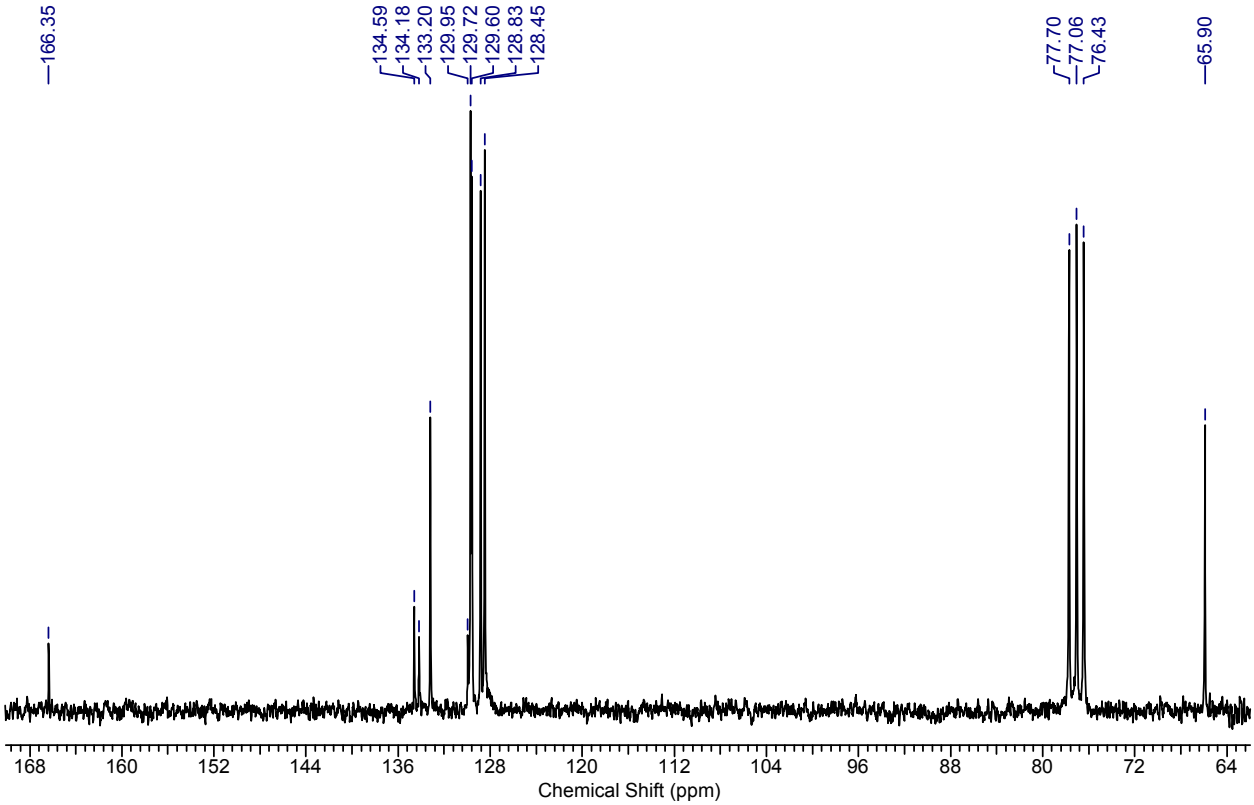

$^{13}$C NMR of **3x**



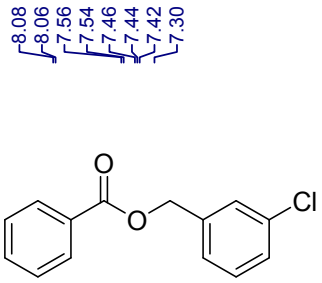

$^{1}$H NMR of **3y**

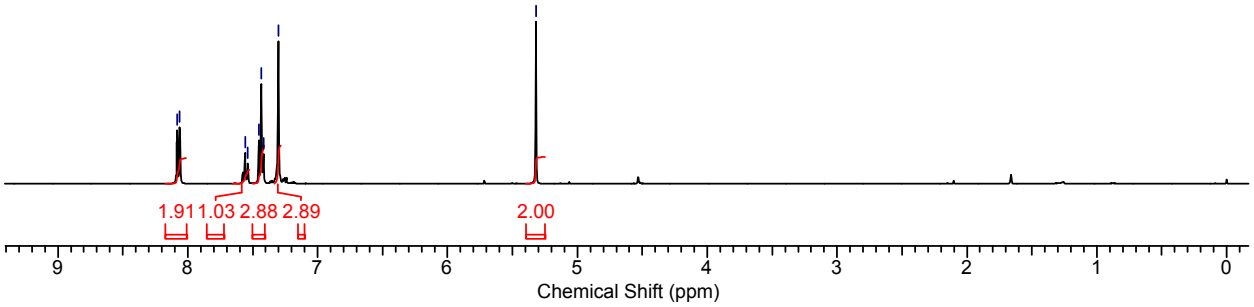




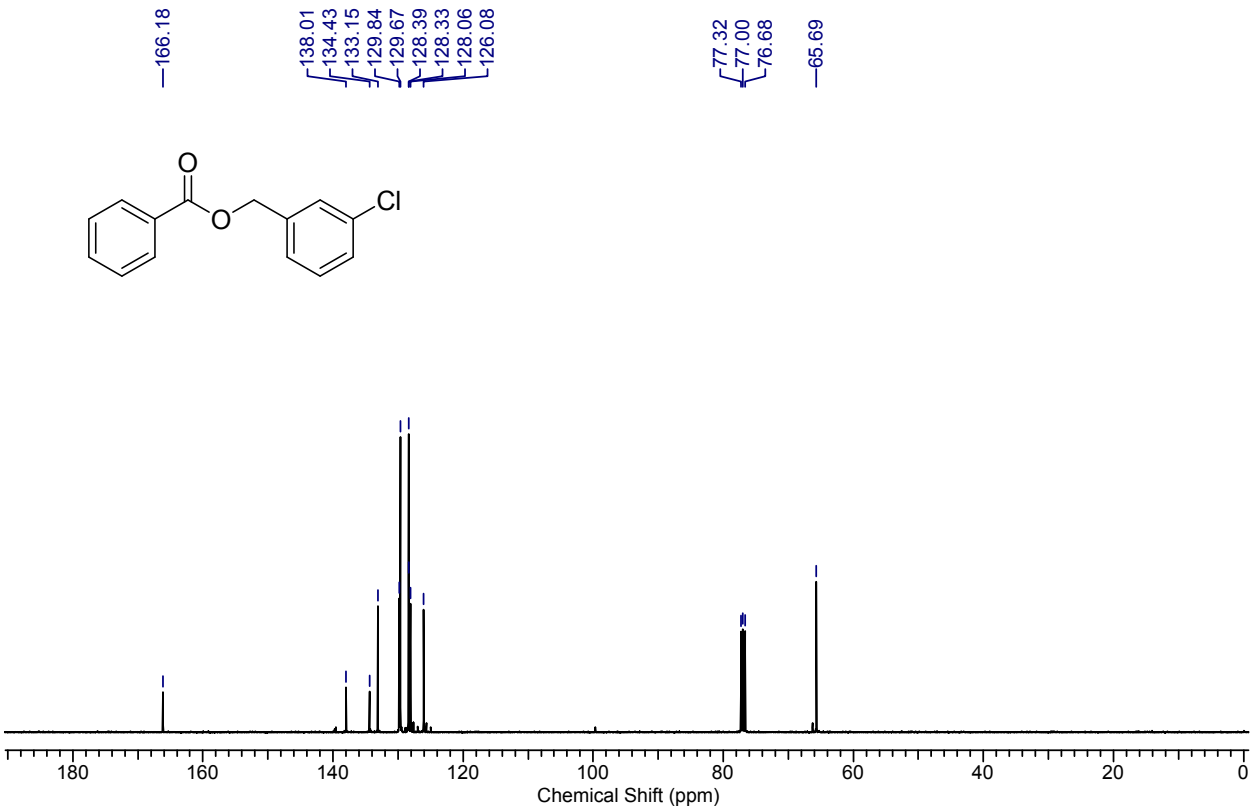



$^{13}$C NMR of **3y**

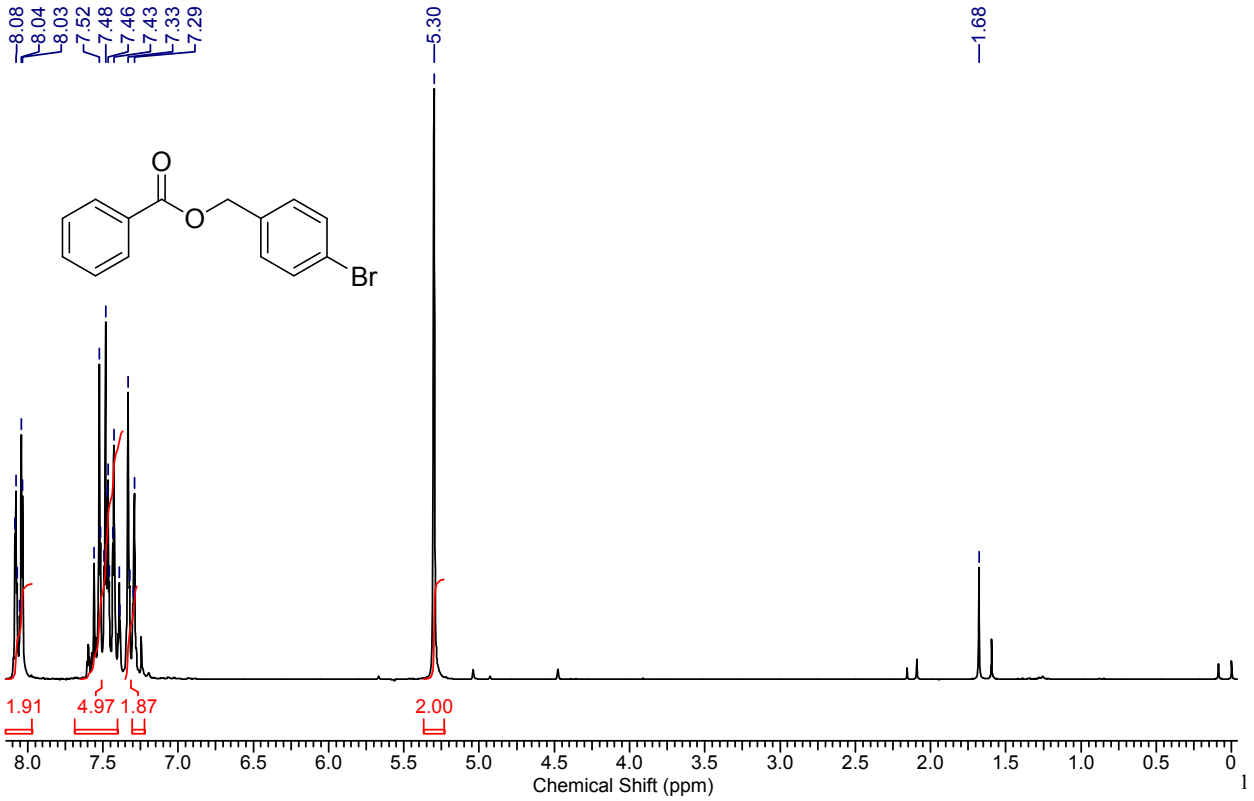


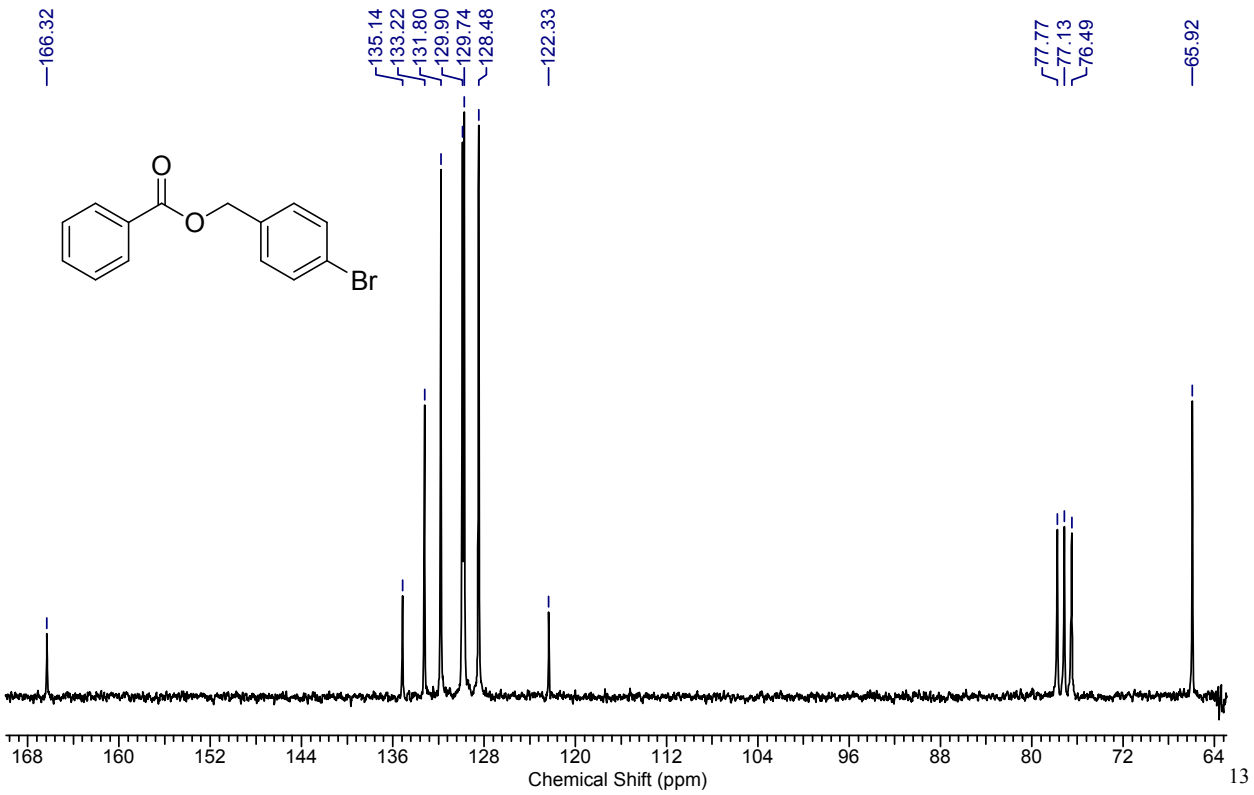

$^{1}$H NMR of **3z**



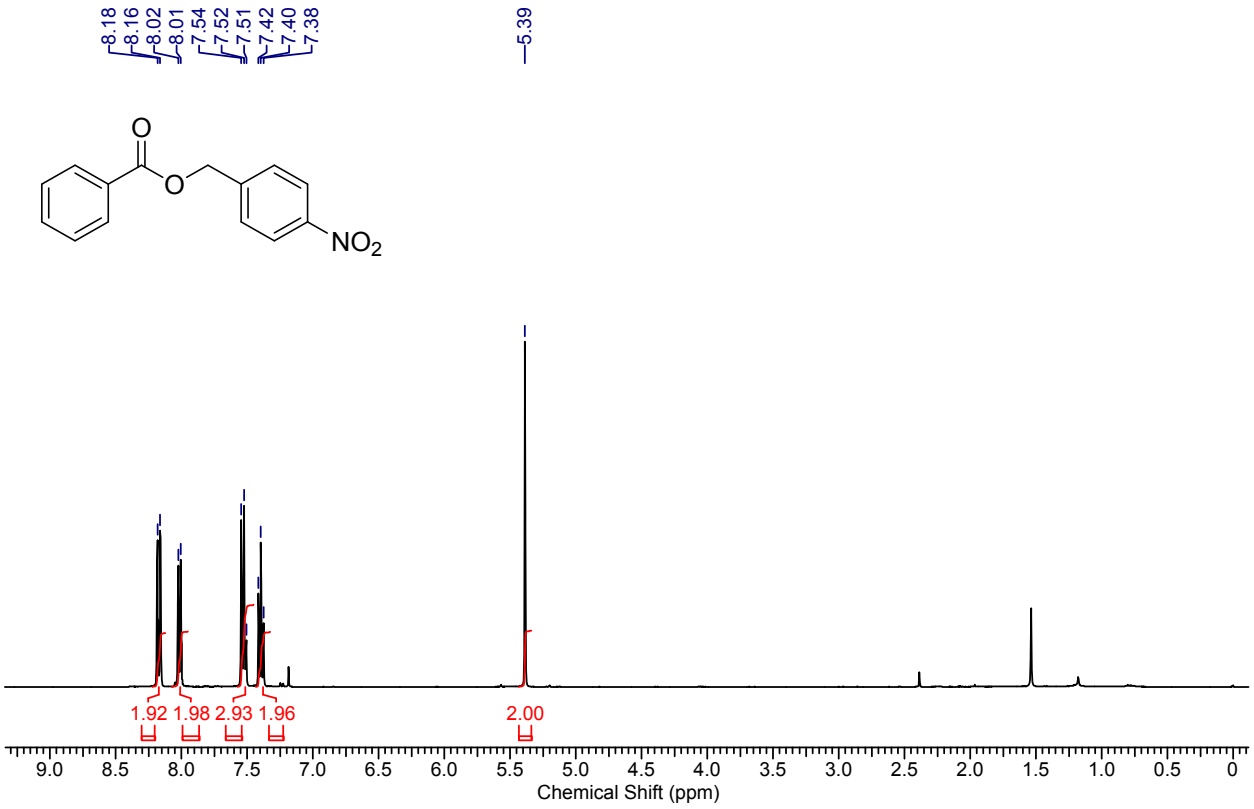

$^{13}$C NMR of **3z**



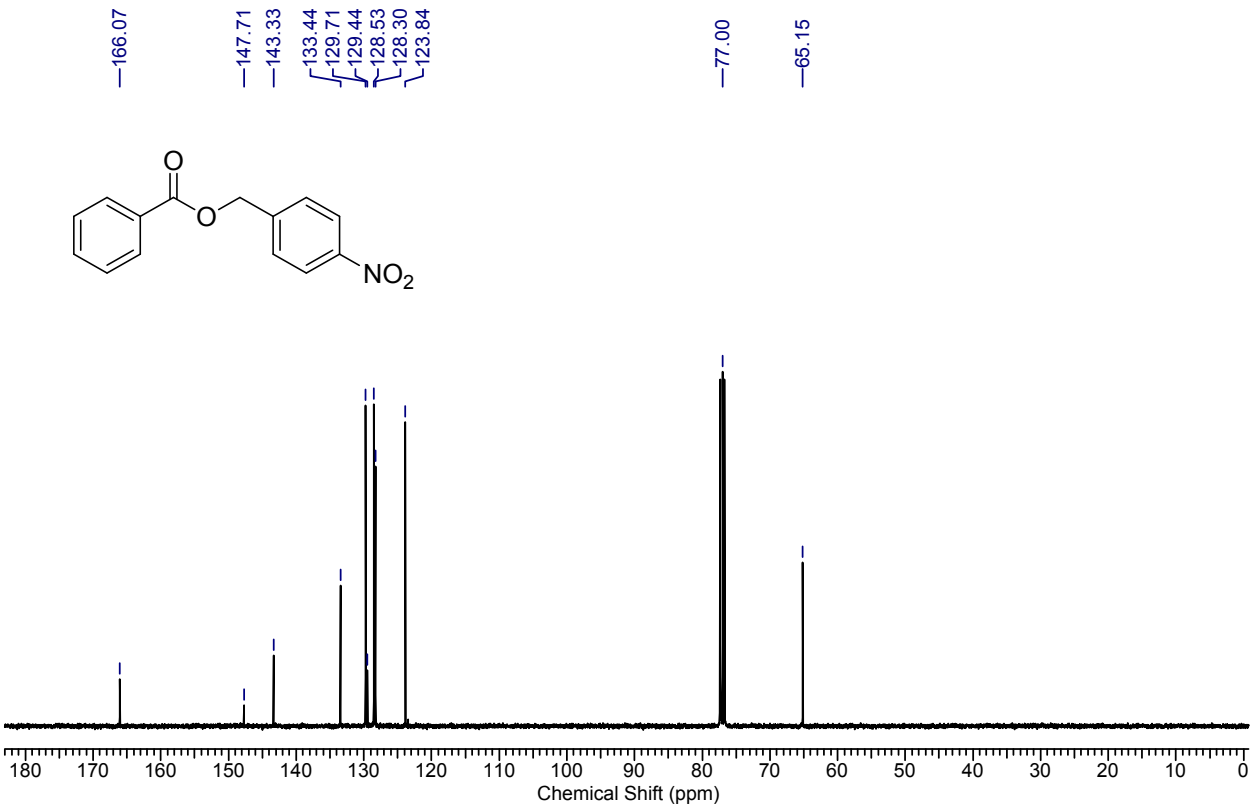

H NMR of **3aa**




C NMR of **3aa**




$^{1}$H NMR of **3ab**

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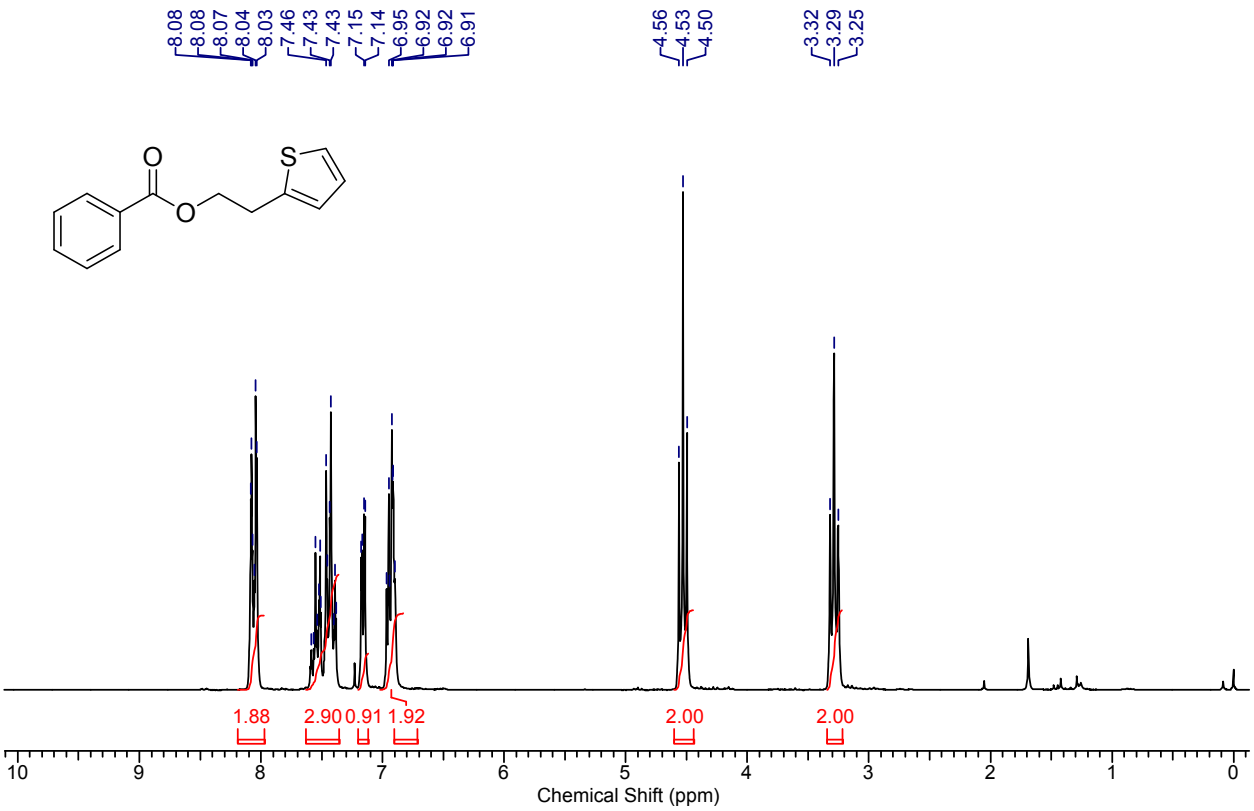
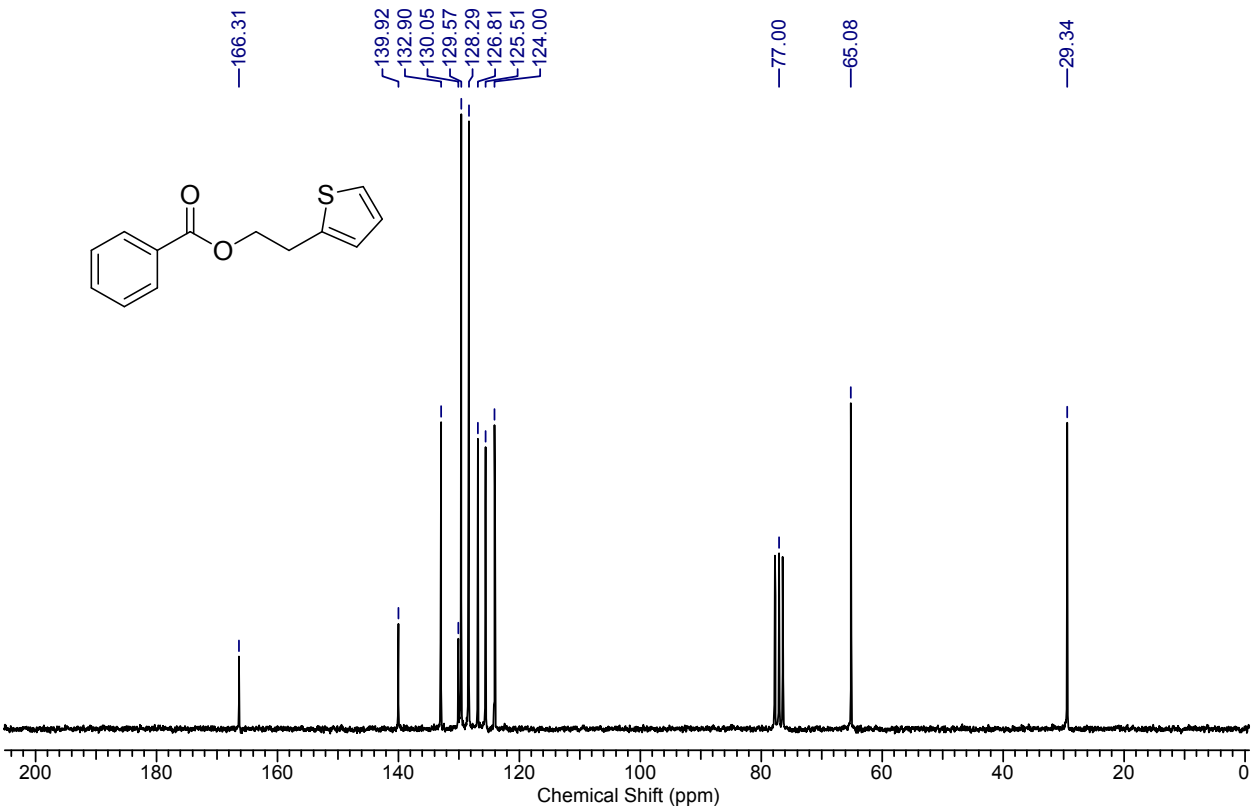
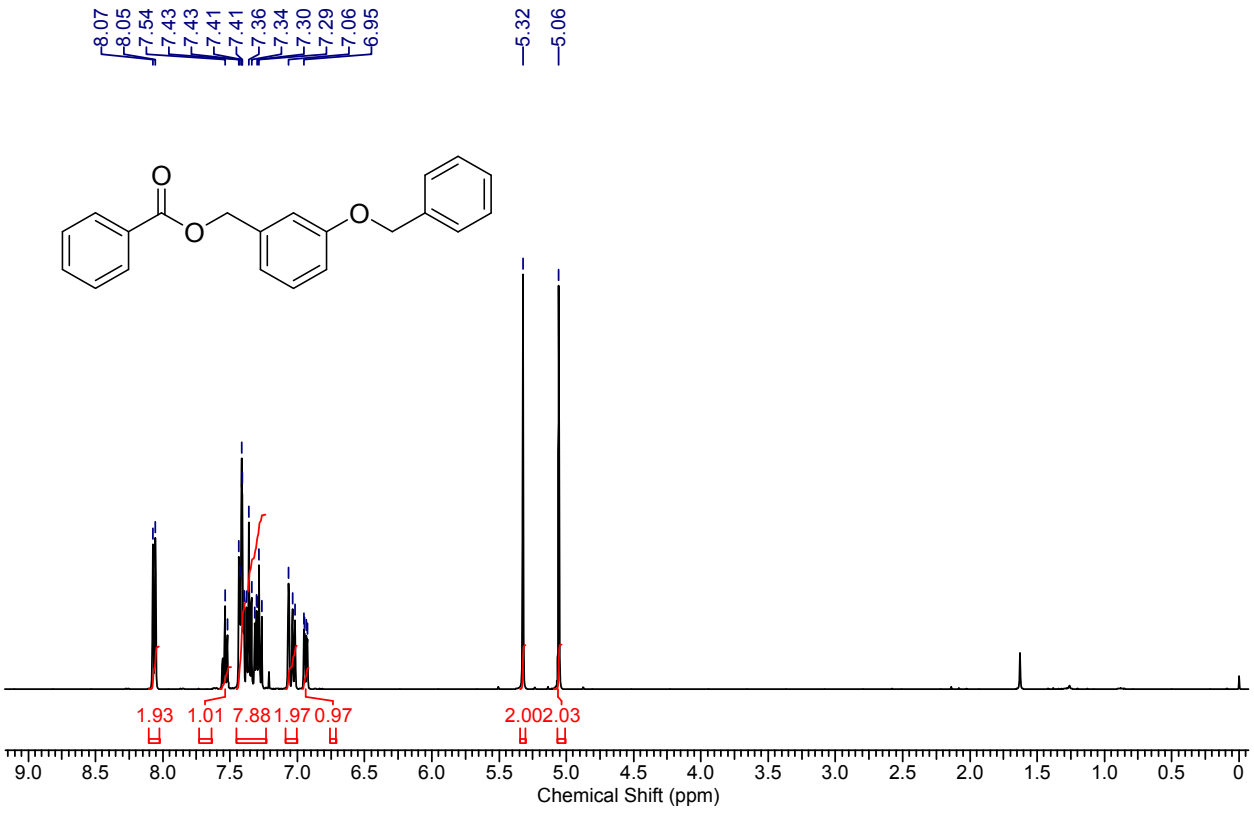


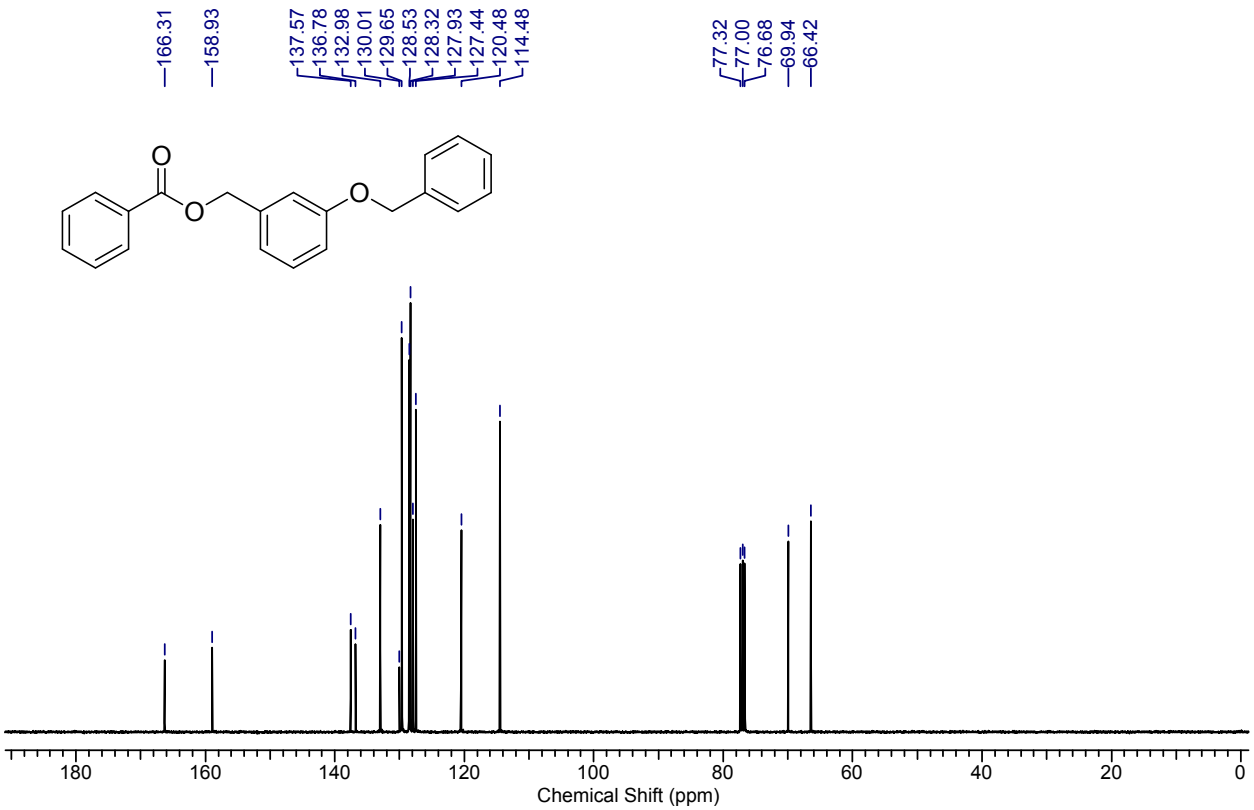

$^{1}$H NMR of **3ac**



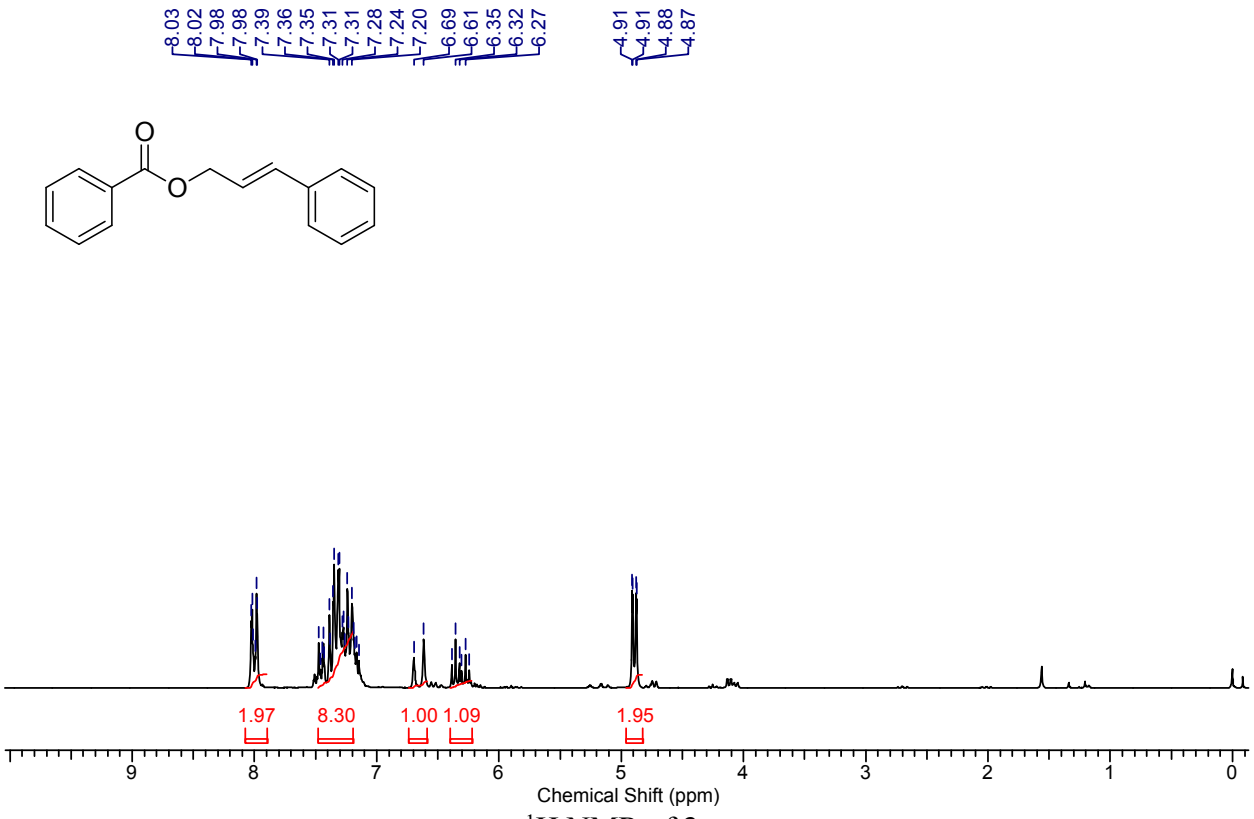

$^{13}$C NMR of **3ac**



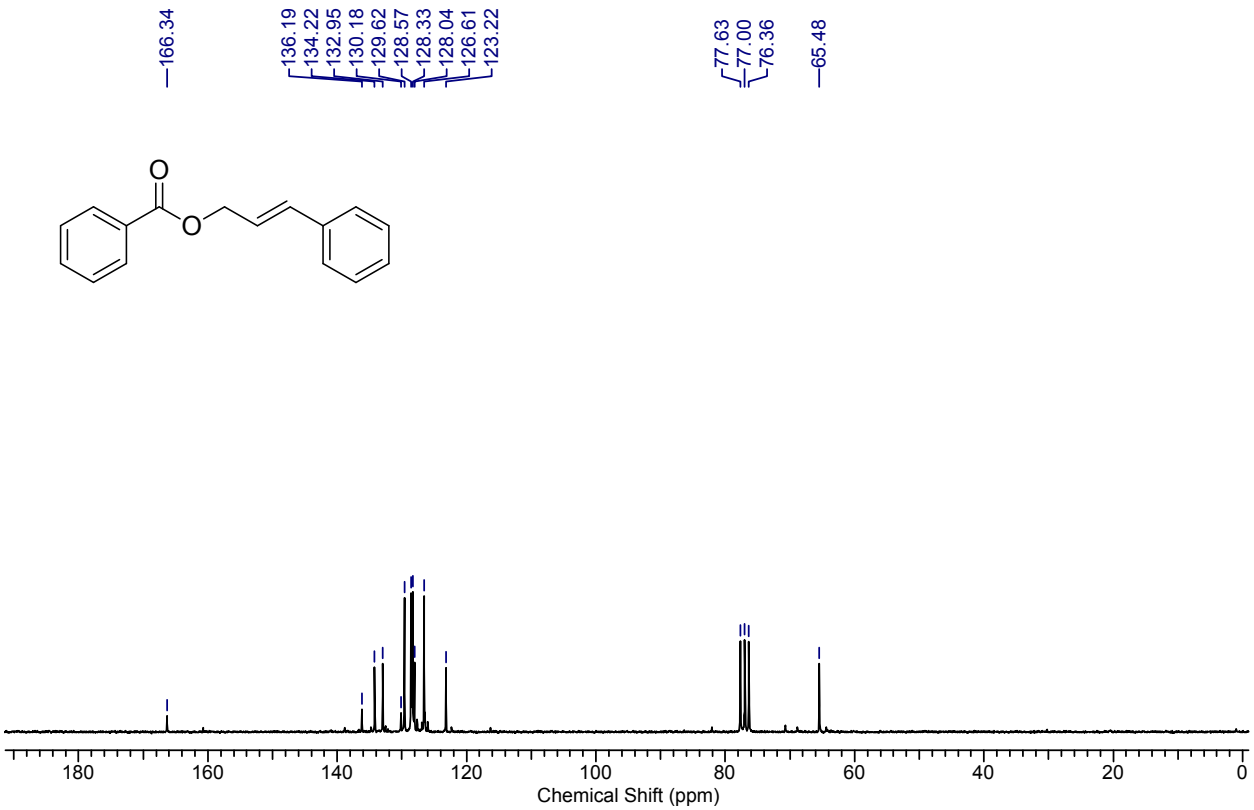

$^{1}$H NMR of **3ad**



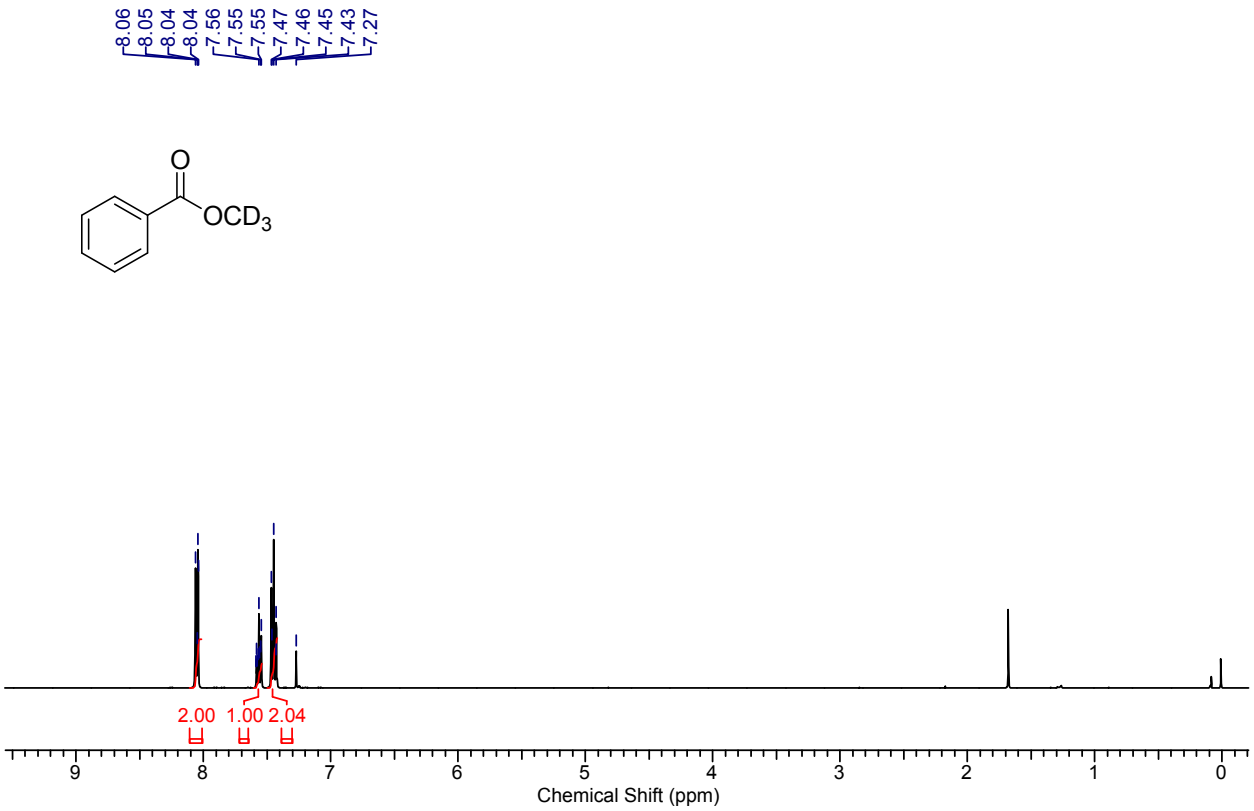

$^{13}$C NMR of **3ad**



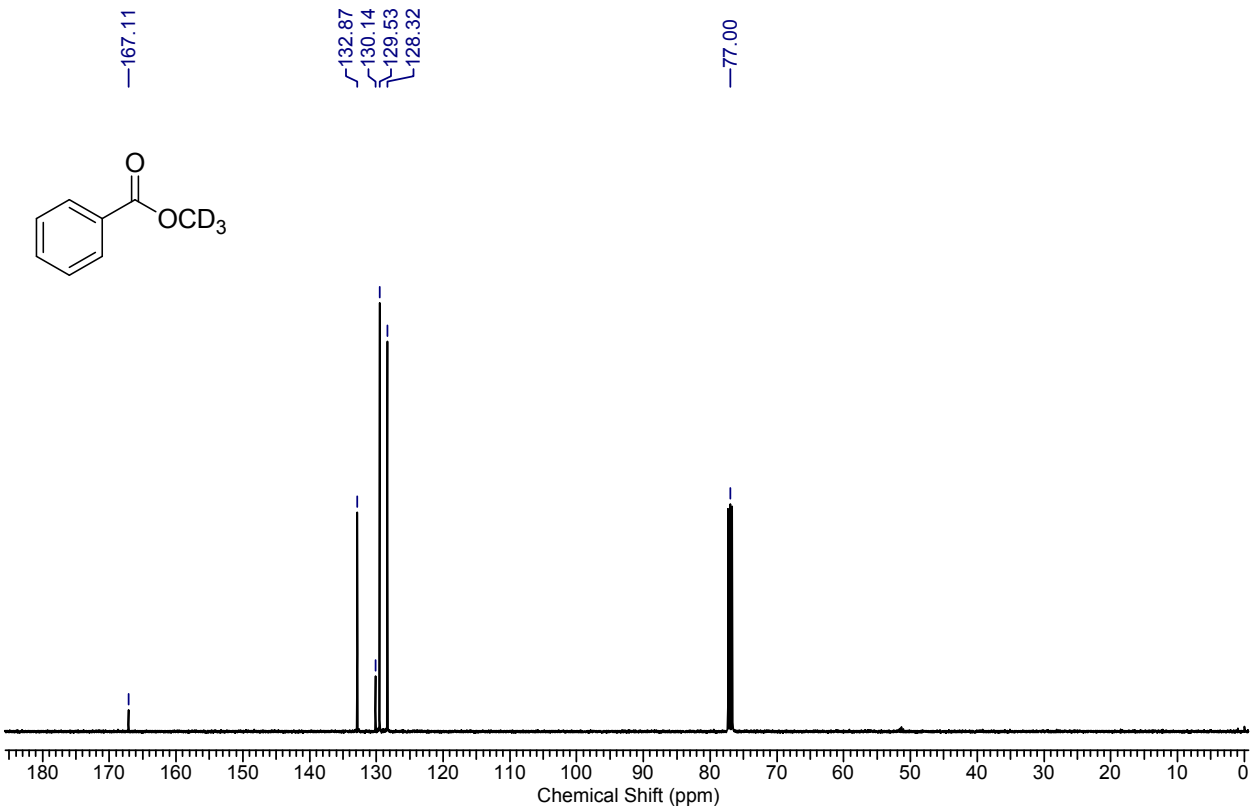

$^{1}$H NMR of **3ae**




$^{13}$C NMR of **3ae**




$^{1}$H NMR of **2a-D**




$^{13}$C NMR of **2a-D**