

## Supporting Information

### Reusable Ionic Liquid-Catalyzed Oxidative Esterification of Carboxylic Acids with Benzylic Hydrocarbons *via* Benzylic Csp<sup>3</sup>-H Bond Activation under Metal-Free Conditions

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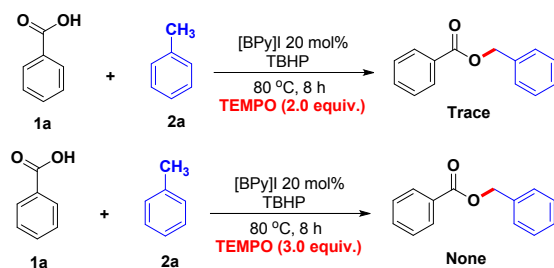
## **I . General methods**

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Alfa Aesar and Ark) and used without further purification except toluene. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F<sub>254</sub> plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (300-400 mesh) using a proper eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on 400 MHz NMR spectrometers (Varian Inova-400). Chemical shifts for protons were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to residual protium in the NMR solvents (CDCl<sub>3</sub> = δ 7.26). Chemical shifts for carbon resonances were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the carbon resonances of the solvents (CDCl<sub>3</sub> = δ 77.00). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet; d = doublet; t = triplet; m = multiplet. Coupling constants J were reported in hertz unit (Hz). Melting point (M. P.) were recorded on BÜCHI (M-560). High-resolution mass spectra (HRMS) were recorded on Thermo Q-Exactive.

## **II. General experimental procedure of the reaction between carboxylic acids and benzylic hydrocarbons**

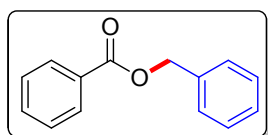
A reaction tube was charged with carboxylic acids (1 mmol), [BPy]I (0.0524 g, 20 mol%), benzylic hydrocarbons (2128 uL, 20 mmol) and TBHP (70% wt% in water, 192 uL, 1.4 mmol). The reaction mixture was stirred at 80 °C for 8 h. After the reaction was finished, the resulting mixture was allowed to cool to ambient temperature. The excess benzylic hydrocarbons was evaporated in vacuo. The mixture was extracted with ethyl acetate (3 × 10 mL), then the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing Na<sub>2</sub>SO<sub>4</sub> by filtration, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate as eluent to afford the respective product **3**.

### III. Control experiment on the reaction mechanism

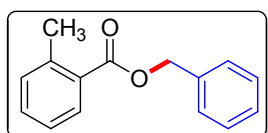


**Scheme 1** Reaction conditions: **1a** (1 mmol), **2a** (20 mmol), [BPy]I (20 mol%), TBHP (1.4 mmol, 70% in water), 80 °C, 8 h.

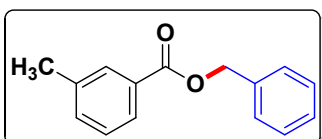
### IV. Characterization data of compounds obtained in this study



**benzyl benzoate 3a<sup>1</sup>**: (yield: 70%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06 (ddd, *J* = 7.2, 2.8, 1.6 Hz, 2 H), 7.51-7.46 (m, 1 H), 7.43-7.27 (m, 7 H), 5.33 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.15, 135.91, 132.82, 129.97, 129.51, 128.41, 128.19, 128.05, 127.98, 66.47.

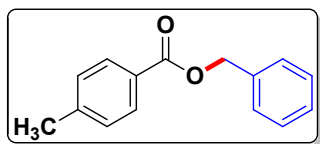


**benzyl 2-methylbenzoate 3b<sup>1</sup>**: (yield: 94%), colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96-7.93 (m, 1 H), 7.43-7.40 (m, 2 H), 7.37-7.30 (m, 4 H), 7.21-7.17 (m, 2 H), 5.32 (s, 2 H), 2.59 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.13, 140.22, 136.05, 131.92, 131.57, 130.57, 129.32, 128.45, 128.06, 128.05, 125.59, 66.35, 21.70.

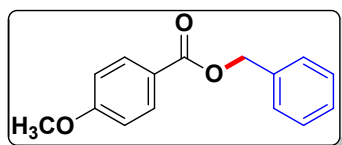


**benzyl 3-methylbenzoate 3c<sup>1</sup>**: (yield: 74%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.88-7.86 (m, 2 H), 7.44-7.41 (m, 2 H), 7.38-7.27 (m, 5 H), 5.33 (s, 2 H), 2.35 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.40, 137.98, 135.99, 133.64, 130.06,

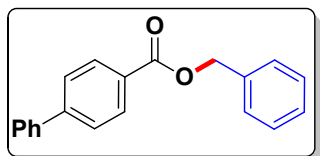
129.90, 129.54, 128.43, 128.21, 128.12, 128.05, 128.02, 126.71, 66.45, 21.10.



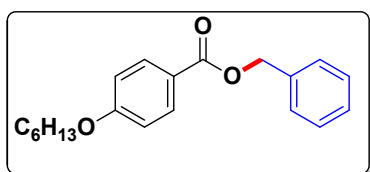
**benzyl 4-methylbenzoate 3d<sup>5</sup>:** (yield: 91%), yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97-7.95 (m, 2 H), 7.43-7.41 (m, 2 H), 7.38-7.30 (m, 3 H), 7.19 (dd, *J* = 8.5, 0.6 Hz, 2 H), 5.33 (s, 2 H), 2.36 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.31, 143.54, 136.09, 129.60, 128.95, 128.43, 128.02, 127.97, 127.28, 66.34, 21.51.



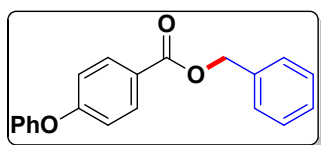
**benzyl 4-methoxybenzoate 3e<sup>1</sup>:** (yield: 75%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01 (d, *J* = 9.0 Hz, 2 H), 7.41 (dd, *J* = 4.1, 3.6 Hz, 2 H), 7.36-7.29 (m, 3 H), 6.87-6.85 (m, 2 H), 5.31 (s, 2 H), 3.75 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.85, 163.18, 136.09, 131.47, 128.31, 127.88, 127.84, 122.26, 113.38, 66.10, 55.09.



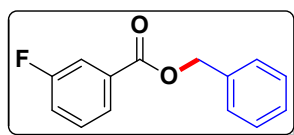
**benzyl [1,1'-biphenyl]-4-carboxylate 3f<sup>2</sup>:** (yield: 94%), faint yellow solid, m.p. 73-75 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.15-8.12 (m, 2 H), 7.66-7.59 (m, 4 H), 7.47-7.32 (m, 8 H), 5.38 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.26, 145.71, 139.93, 136.06, 130.19, 128.88, 128.82, 128.56, 128.20, 128.13, 128.11, 127.23, 127.01, 66.66.



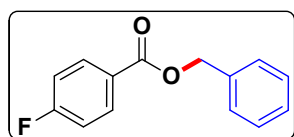
**benzyl 4-(hexyloxy)benzoate 3g:** (yield: 88%), faint yellow solid, m.p. 39-41 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03-8.00 (m, 2 H), 7.44-7.41 (m, 2 H), 7.38-7.31 (m, 3 H), 6.87-6.89 (m, 2 H), 5.32 (s, 2 H), 3.97 (t, *J* = 6.6 Hz, 2 H), 1.80-1.73 (m, 2 H), 1.44 (ddd, *J* = 10.5, 5.3, 3.3 Hz, 2 H), 1.37-1.29 (m, 4 H), 0.90 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.07, 162.96, 136.25, 131.60, 128.43, 127.99, 127.97, 122.14, 113.97, 68.08, 66.21, 31.45, 28.97, 25.56, 22.49, 13.93. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 313.17982, found: 313.17918.



**benzyl 4-phenoxybenzoate 3h:** (yield: 84%), yellow solid, m.p. 38-39 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04-8.02 (m, 2 H), 7.42-7.40 (m, 2 H), 7.36-7.29 (m, 5 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.04-7.01 (m, 2 H), 6.96-6.94 (m, 2 H), 5.32 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.70, 161.74, 155.44, 136.03, 131.69, 129.88, 128.44, 128.06, 127.98, 124.36, 124.28, 119.93, 117.17, 66.39. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 305.11722, found: 305.11645.

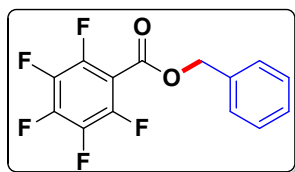


**benzyl 3-fluorobenzoate 3i<sup>8</sup>:** (yield: 88%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 (ddd, *J* = 7.8, 1.5, 1.1 Hz, 1 H), 7.75-7.71 (m, 1 H), 7.43-7.41 (m, 2 H), 7.38-7.31 (m, 4 H), 7.19 (m, 1 H), 5.34 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.06, 165.04, 163.60, 161.14, 135.60, 132.20, 132.12, 129.91, 129.83, 128.49, 128.23, 128.10, 125.30, 125.27, 120.02, 119.81, 116.52, 116.29, 66.88.

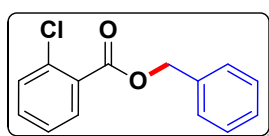


**benzyl 4-fluorobenzoate 3j<sup>1</sup>:** (yield: 88%), colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.11-8.06 (m, 2 H), 7.45-7.33 (m, 5 H), 7.09 (dd, *J* = 13.0, 4.5 Hz, 2 H), 5.35 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.00, 165.36, 164.48, 135.84, 132.23,

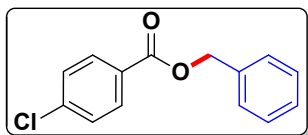
132.14, 128.56, 128.26, 128.15, 126.33, 126.30, 115.56, 115.34, 66.76.



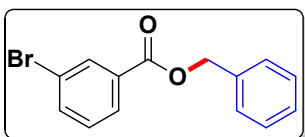
**benzyl 2,3,4,5,6-pentafluorobenzoate 3k<sup>3</sup>**: (yield: 73%), white solid, m.p. 82-84 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.44-7.36 (m, 5 H), 5.41 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 134.46, 128.72, 128.70, 128.34, 68.42.



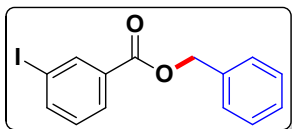
**benzyl 2-chlorobenzoate 3l<sup>1</sup>**: (yield: 92%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.82-7.80 (m, 1 H), 7.44-7.30 (m, 7 H), 7.24-7.20 (m, 1 H), 5.34 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.15, 135.37, 133.59, 132.42, 131.29, 130.86, 129.71, 128.39, 128.13, 126.36, 67.02.



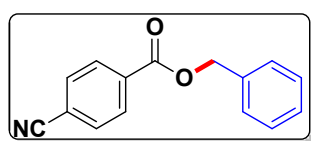
**benzyl 4-chlorobenzoate 3m<sup>1</sup>**: (yield: 92%), colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97-7.95 (m, 2 H), 7.42-7.30 (m, 7 H), 5.32 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.27, 139.25, 135.65, 130.90, 128.52, 128.45, 128.41, 128.18, 128.06, 66.73.



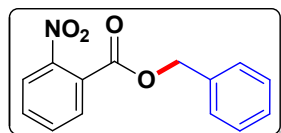
**benzyl 3-bromobenzoate 3n<sup>4</sup>**: (yield: 84%), colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.16 (t, *J* = 1.7 Hz, 1 H), 7.96-7.93 (m, 1 H), 7.59 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1 H), 7.42-7.39 (m, 2 H), 7.34 (ddd, *J* = 11.9, 8.5, 4.2 Hz, 3 H), 7.21 (t, *J* = 7.9 Hz, 1 H), 5.32 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.72, 135.70, 135.47, 132.39, 131.83, 129.72, 128.43, 128.19, 128.09, 128.05, 122.26, 66.86.



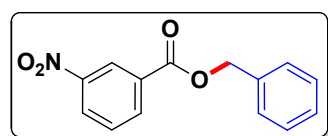
**benzyl 3-iodobenzoate 3o<sup>7</sup>**: (yield: 73%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.38-8.37 (m, 1 H), 8.00 (ddd, *J* = 7.8, 1.6, 1.1 Hz, 1 H), 7.83 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1 H), 7.43-7.32 (m, 5 H), 7.14-7.10 (m, 1 H), 5.33 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.71, 141.68, 138.33, 135.52, 131.84, 129.90, 128.71, 128.51, 128.27, 128.17, 93.75, 66.93.



**benzyl 4-cyanobenzoate 3p<sup>5</sup>**: (yield: 80%), white solid, m.p. 58-59 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.18-8.15 (m, 2 H), 7.74-7.72 (m, 2 H), 7.45-7.36 (m, 5 H), 5.39 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.70, 135.25, 133.87, 132.16, 130.13, 128.66, 128.54, 128.33, 117.88, 116.41, 67.44.

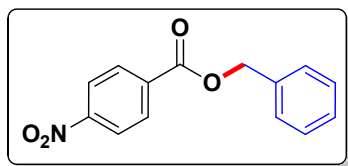


**benzyl 2-nitrobenzoate 3q<sup>1</sup>**: (yield: 86%), faint yellow solid, m.p. 103-104 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.82 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.70 (dd, *J* = 7.4, 1.7 Hz, 1 H), 7.61-7.52 (m, 2 H), 7.40-7.31 (m, 5 H), 5.33 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.97, 147.96, 134.61, 132.74, 131.67, 129.65, 128.44, 128.41, 128.35, 127.16, 123.67, 68.05.

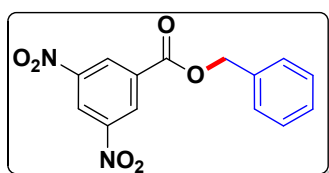


**benzyl 3-nitrobenzoate 3r<sup>1</sup>**: (yield: 76%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.85 (dd, *J* = 2.8, 1.1 Hz, 1 H), 8.40-8.36 (m, 2 H), 7.64-7.60 (m, 1 H), 7.47-7.45 (m, 2 H), 7.42-7.35 (m, 3 H), 5.41 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.09, 148.05, 135.17, 135.11, 131.67, 129.49, 128.54, 128.44, 128.28, 127.28,

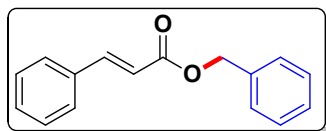
124.42, 67.40.



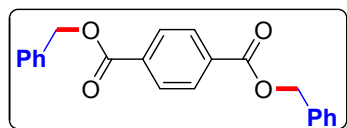
**benzyl 4-nitrobenzoate 3s<sup>1</sup>**: (yield: 87%), faint yellow solid, m.p. 84-85 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.29-8.22 (m, 4 H), 7.47-7.37 (m, 5 H), 5.41 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.46, 150.52, 135.44, 135.19, 130.76, 128.68, 128.59, 128.38, 123.49, 67.59.



**benzyl 3,5-dinitrobenzoate 3t<sup>1</sup>**: (yield: 93%), white solid, m.p. 117-118 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.22 (t, *J* = 2.1 Hz, 1 H), 9.17 (d, *J* = 2.1 Hz, 2 H), 7.50-7.40 (m, 5 H), 5.48 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.37, 148.65, 134.48, 133.83, 129.49, 129.03, 128.87, 128.80, 122.42, 68.61.

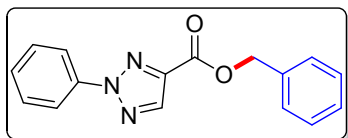


**benzyl cinnamate 3u<sup>1</sup>**: (yield: 65%), white solid, m.p. 37-39 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.72 (d, *J* = 16.0 Hz, 1 H), 7.48-7.46 (m, 2 H), 7.39-7.31 (m, 8 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 5.23 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.56, 144.99, 135.94, 134.19, 130.18, 128.73, 128.44, 128.13, 128.09, 127.95, 117.73, 66.17.

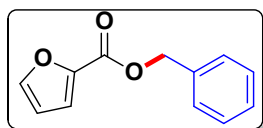


**dibenzyl terephthalate 3v<sup>6</sup>**: (yield: 48%), white solid, m.p. 94-95 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 4 H), 7.46-7.35 (m, 10 H), 5.38 (s, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.56, 135.61, 133.94, 129.64, 128.62, 128.39, 128.25, 67.11.

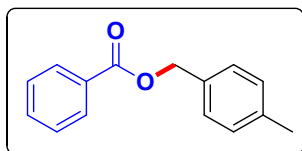




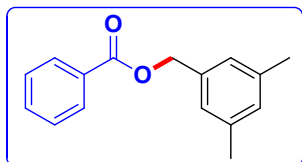
**benzyl 2-phenyl-2H-1,2,3-triazole-4-carboxylate 3w:** (yield: 85%), white solid, m.p. 72-74 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (s, 1 H), 8.15-8.12 (m, 2 H), 7.51-7.47 (m, 4 H), 7.42-7.35 (m, 4 H), 5.44 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.40, 140.73, 139.29, 137.86, 135.27, 129.32, 128.63, 128.61, 128.50, 119.56, 67.08. HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$ : 280.10805, found: 280.10773.



**benzyl furan-2-carboxylate 3x<sup>6</sup>:** (yield: 55%), yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (dd,  $J = 1.7, 0.8$  Hz, 1 H), 7.43-7.41 (m, 2 H), 7.38-7.31 (m, 3 H), 7.19 (dd,  $J = 3.5, 0.8$  Hz, 1 H), 6.47 (dd,  $J = 3.5, 1.7$  Hz, 1 H), 5.33 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.22, 146.18, 144.25, 135.33, 128.32, 128.10, 128.08, 117.92, 111.59, 66.22.

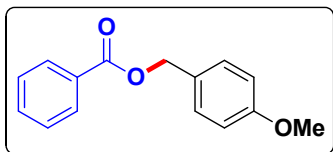


**4-methylbenzyl benzoate 4a<sup>9</sup>:** (yield: 78%), faint yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08-8.05 (m, 2 H), 7.51-7.47 (m, 1 H), 7.40-7.36 (m, 2 H), 7.04 (s, 2 H), 6.94 (s, 1 H), 5.27 (s, 2 H), 2.30 (s, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.26, 137.99, 135.78, 132.78, 130.12, 129.75, 129.56, 128.18, 125.93, 66.64, 21.12.

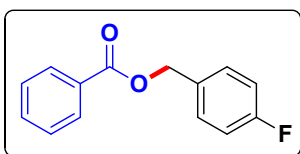


**3,5-dimethylbenzyl benzoate 4b<sup>9</sup>:** (yield: 82%), faint yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 7.3$  Hz, 2 H), 7.46 (t,  $J = 7.4$  Hz, 1 H), 7.37-7.30 (m, 4 H), 7.14 (d,  $J = 7.7$  Hz, 2 H), 5.29 (s, 2 H), 2.30 (s, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.14, 137.78, 132.88, 132.71, 130.03, 129.51, 129.46, 129.05, 128.84,

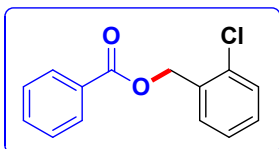
128.14, 128.11, 66.41, 20.98.



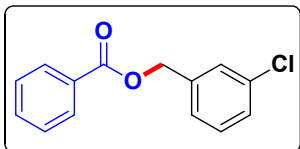
**4-methoxybenzyl benzoate 4c<sup>10</sup>**: (yield: 71%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05-8.03 (m, 2 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.37 (dd, *J* = 7.9, 6.6 Hz, 4 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 5.27 (s, 2 H), 3.74 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.22, 159.46, 132.73, 130.08, 129.86, 129.45, 128.13, 127.97, 113.76, 66.32, 55.00.



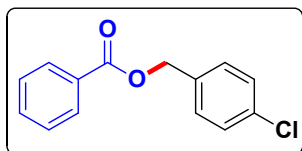
**4-fluorobenzyl benzoate 4d<sup>10</sup>**: (yield: 62%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06-8.04 (m, 2 H), 7.54-7.50 (m, 1 H), 7.42-7.38 (m, 4 H), 7.04 (dd, *J* = 9.7, 7.7 Hz, 2 H), 5.29 (d, *J* = 6.4 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.17, 163.75, 161.29, 132.95, 130.10, 130.02, 129.90, 129.54, 128.26, 115.52, 115.48, 115.31, 115.27, 65.82.



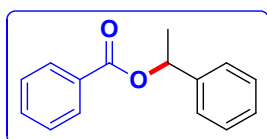
**2-chlorobenzyl benzoate 4e<sup>11</sup>**: (yield: 38%), yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.09-8.07 (m, 2 H), 7.56-7.48 (m, 2 H), 7.45-7.38 (m, 3 H), 7.27-7.23 (m, 2 H), 5.46 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.08, 133.66, 133.62, 133.02, 133.02, 129.84, 129.69, 129.63, 129.50, 129.41, 128.31, 126.80, 63.94.



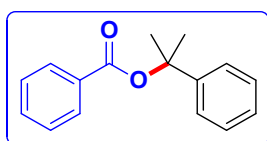
**3-chlorobenzyl benzoate 4f<sup>10</sup>**: (yield: 45%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (d, *J* = 7.2 Hz, 2 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 3 H), 7.29 (s, 3 H), 5.31 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.06, 137.97, 134.35, 133.06, 129.77, 129.72, 129.59, 128.31, 128.25, 127.98, 126.00, 65.61.



**4-chlorobenzyl benzoate 4g<sup>11</sup>**: (yield: 64%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07-8.04 (m, 2 H), 7.56-7.52 (m, 1 H), 7.40-7.32 (m, 6 H), 5.30 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.14, 134.46, 134.00, 133.03, 130.95, 129.80, 129.57, 129.54, 129.45, 128.72, 128.66, 128.31, 65.97, 65.73.



**(S)-1-phenylethyl benzoate 4h<sup>9</sup>**: (yield: 65%), faint yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96-7.94 (m, 2 H), 7.38-7.33 (m, 1 H), 7.32-7.19 (m, 6 H), 7.15-7.11 (m, 1 H), 6.01 (q, *J* = 6.6 Hz, 1 H), 1.52 (d, *J* = 6.6 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.56, 141.63, 132.73, 130.38, 129.46, 128.39, 128.16, 127.72, 125.87, 72.72, 22.24.



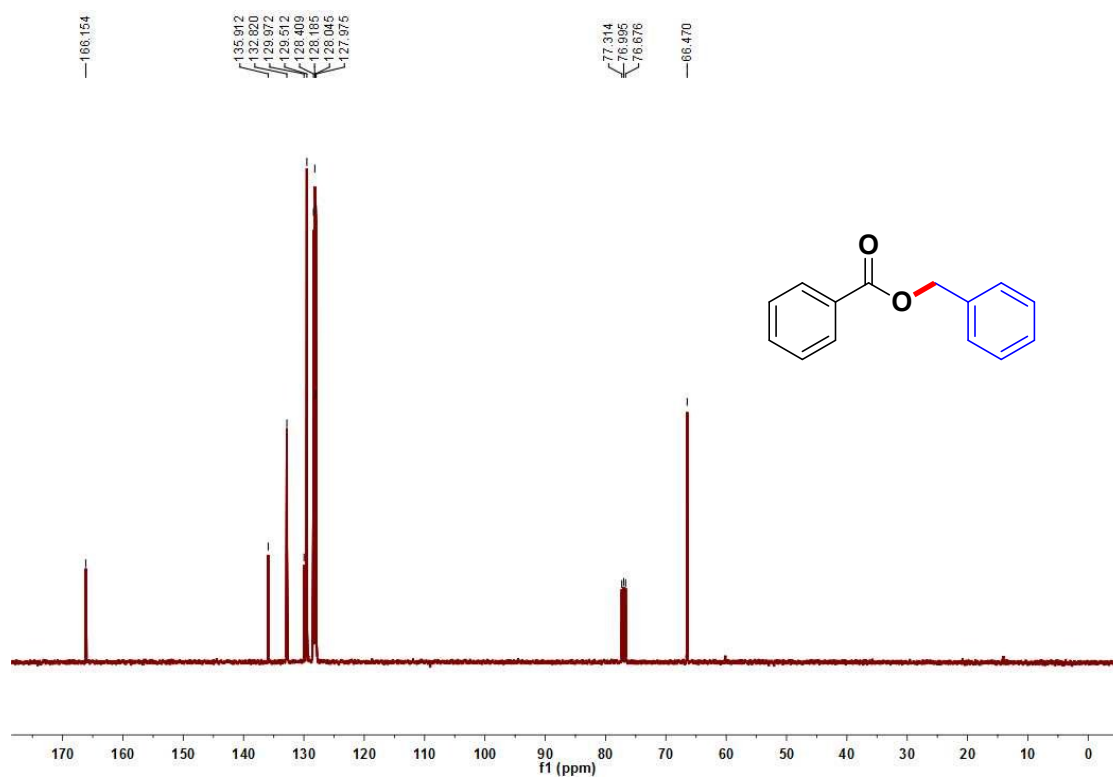
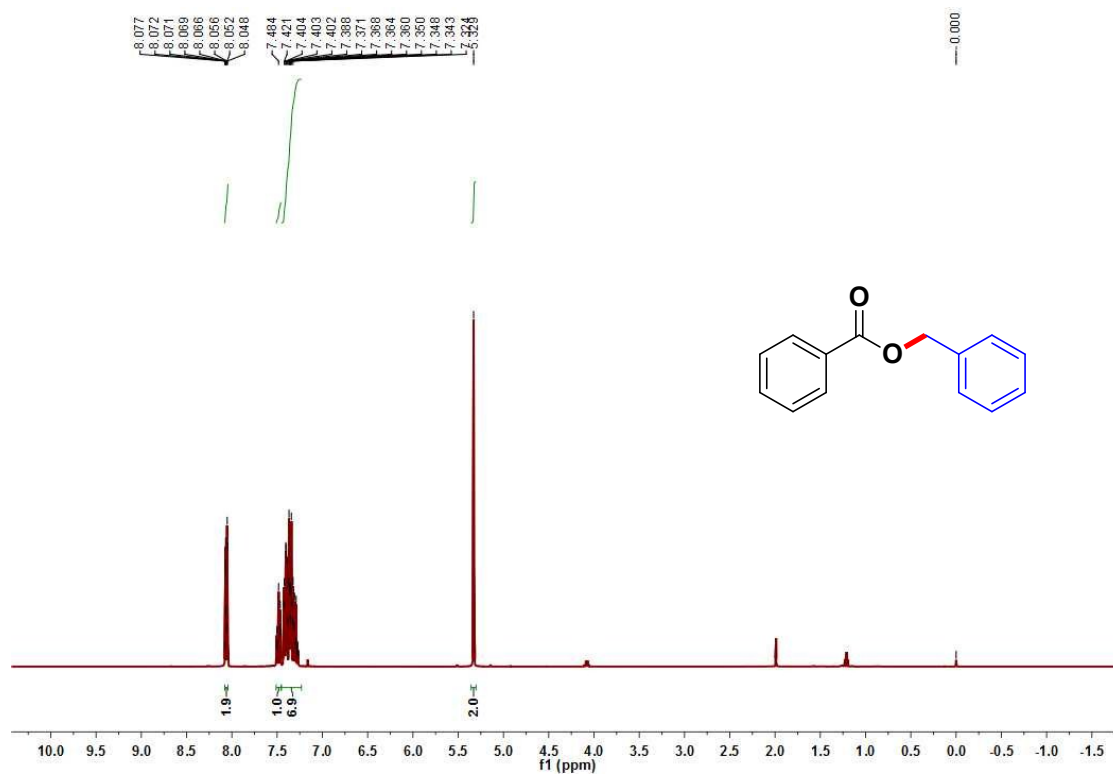
**2-phenylpropan-2-yl benzoate 4i<sup>9</sup>**: (yield: 50%), yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.43-7.38 (m, 4 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.3 Hz, 1 H), 1.91 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.02, 145.73, 132.57, 131.43, 129.45, 128.25, 128.18, 126.95, 124.19, 82.10, 28.68.

## V. References

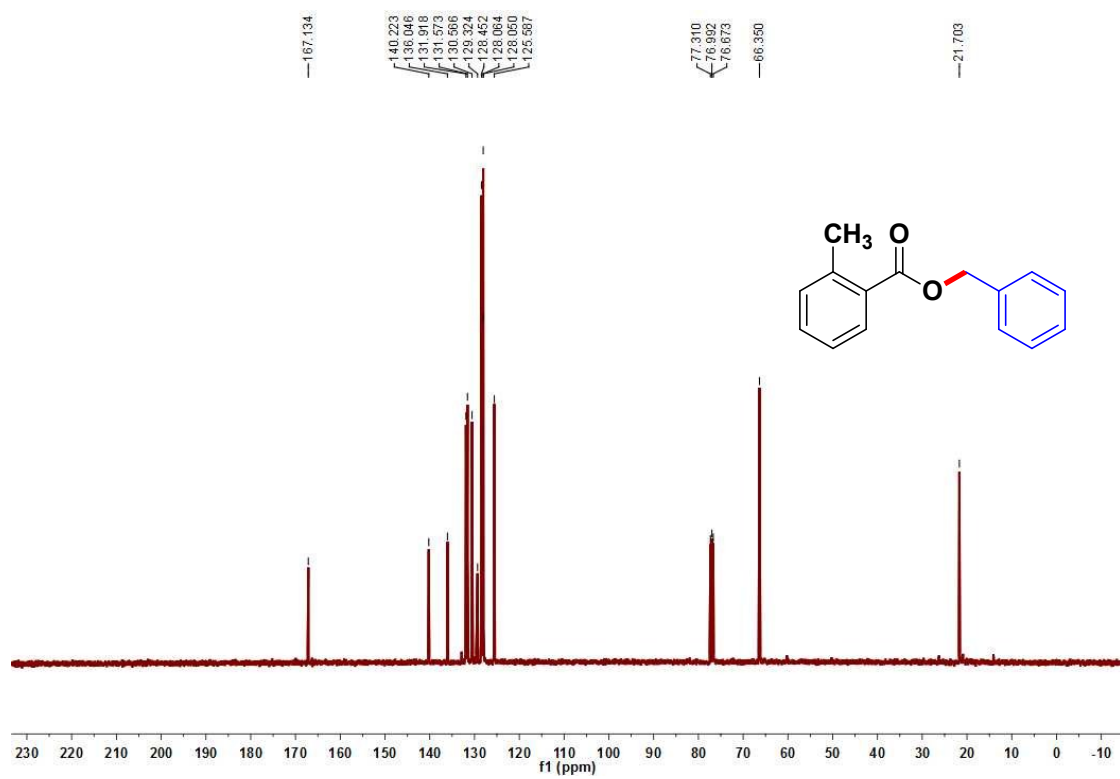
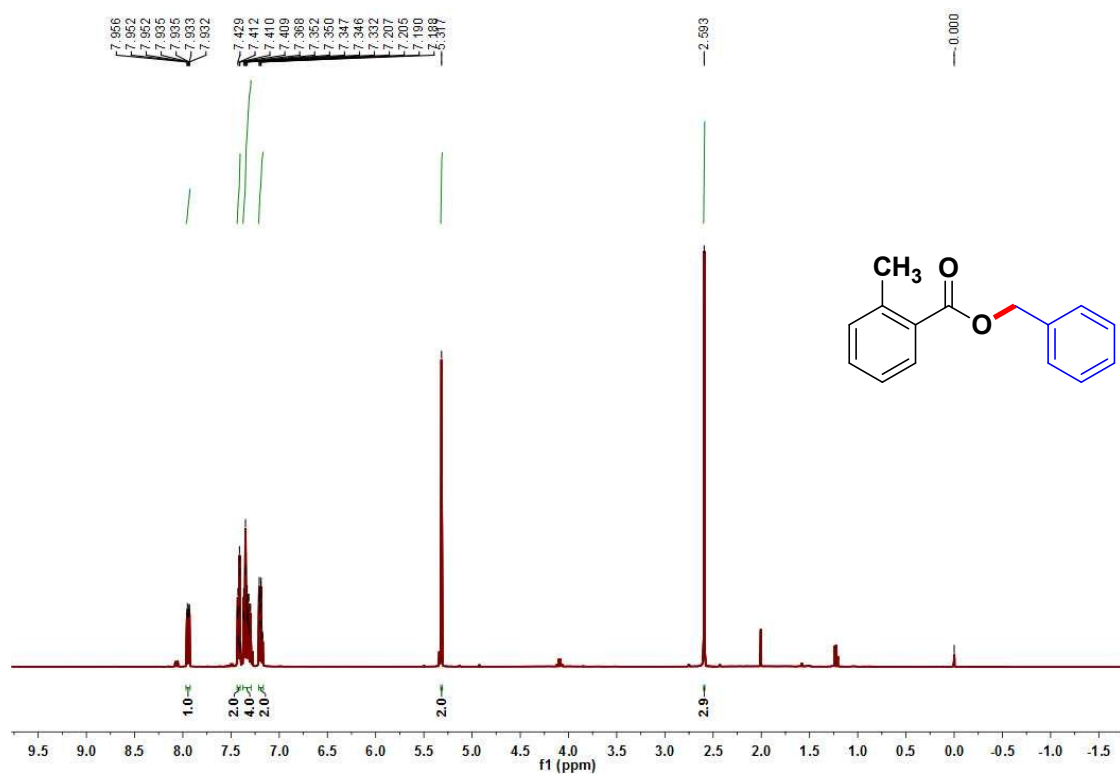
- 1 H. Liu, G. Shi, S. Pan, Y. Jiang and Y. Zhang, *Org. Lett.*, 2013, **15**, 4098.
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## VI. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

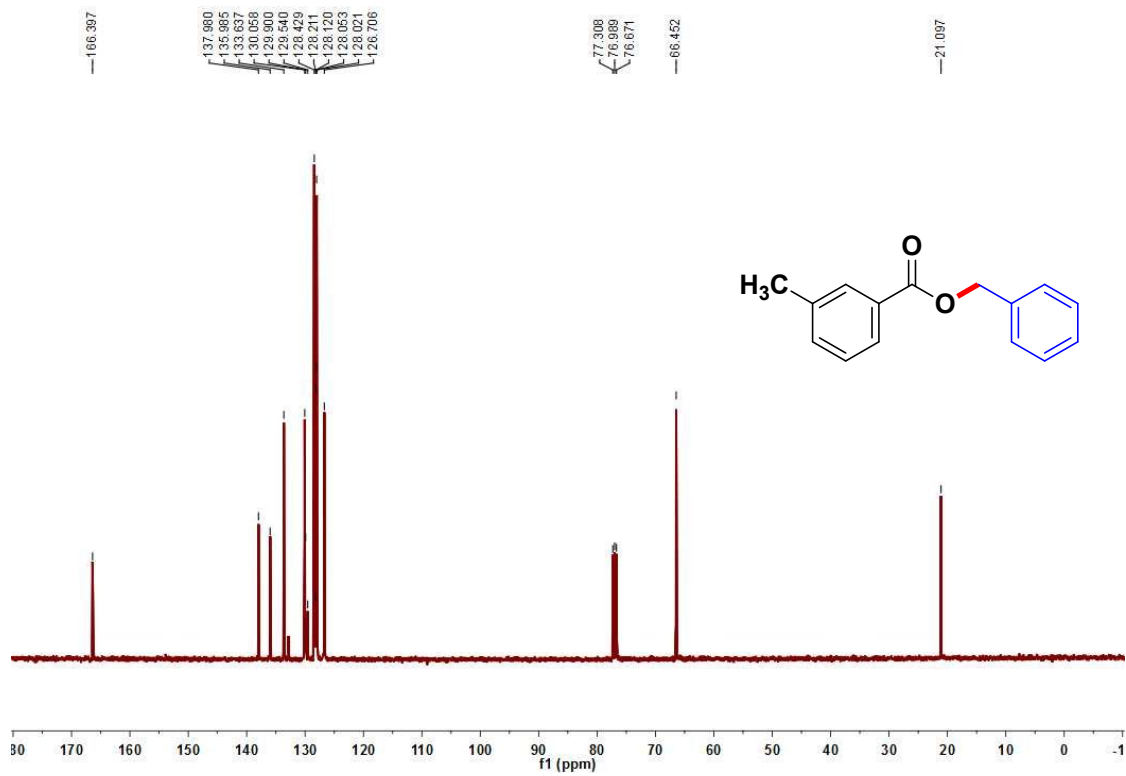
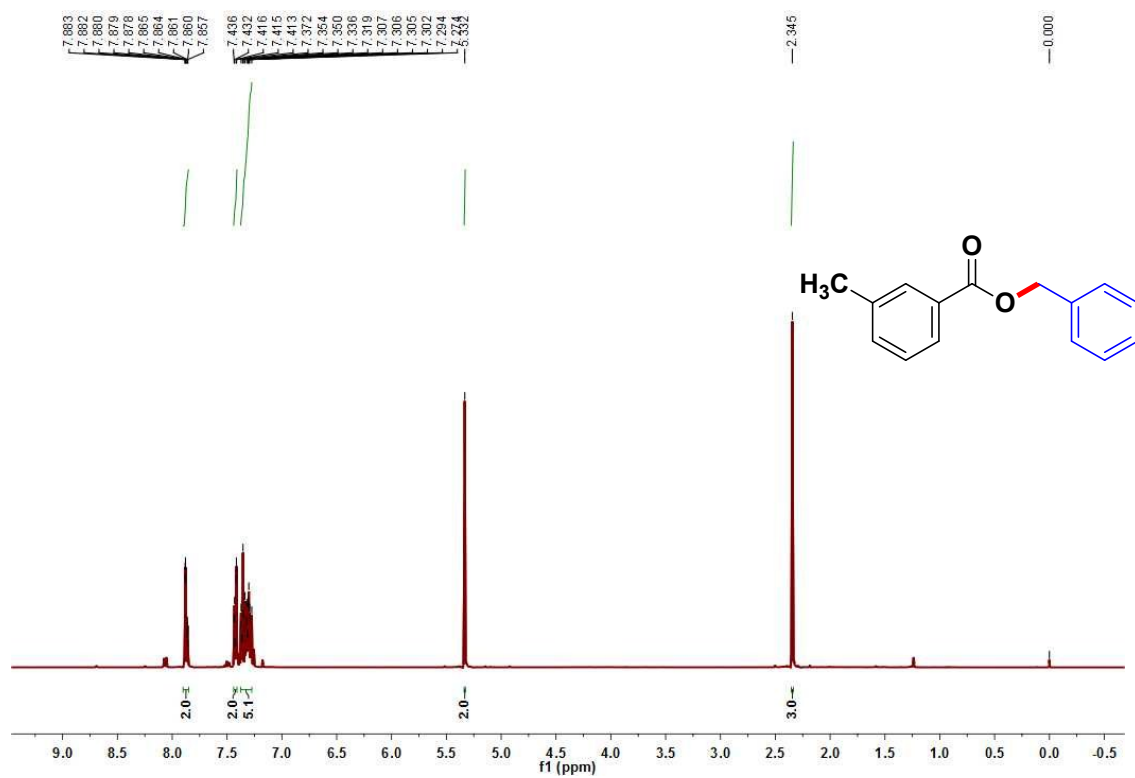
### 3a: benzyl benzoate



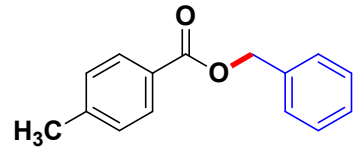
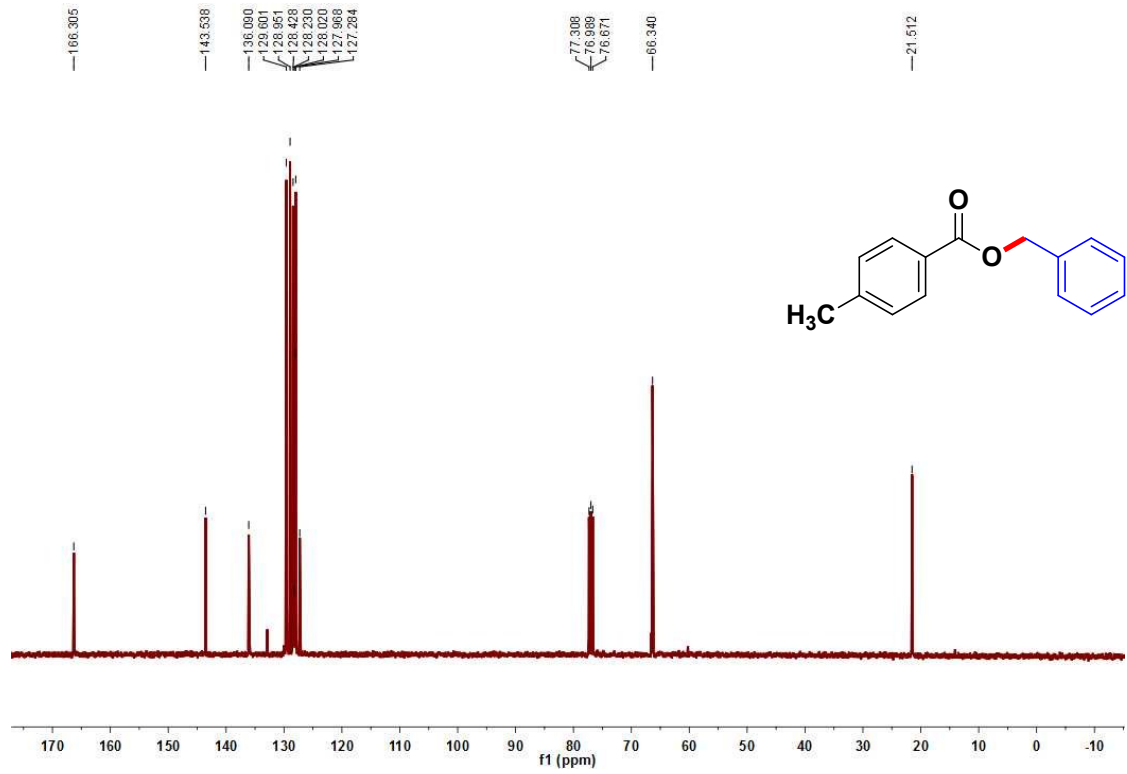
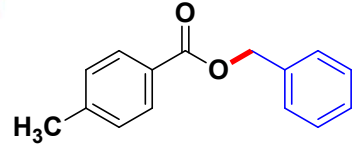
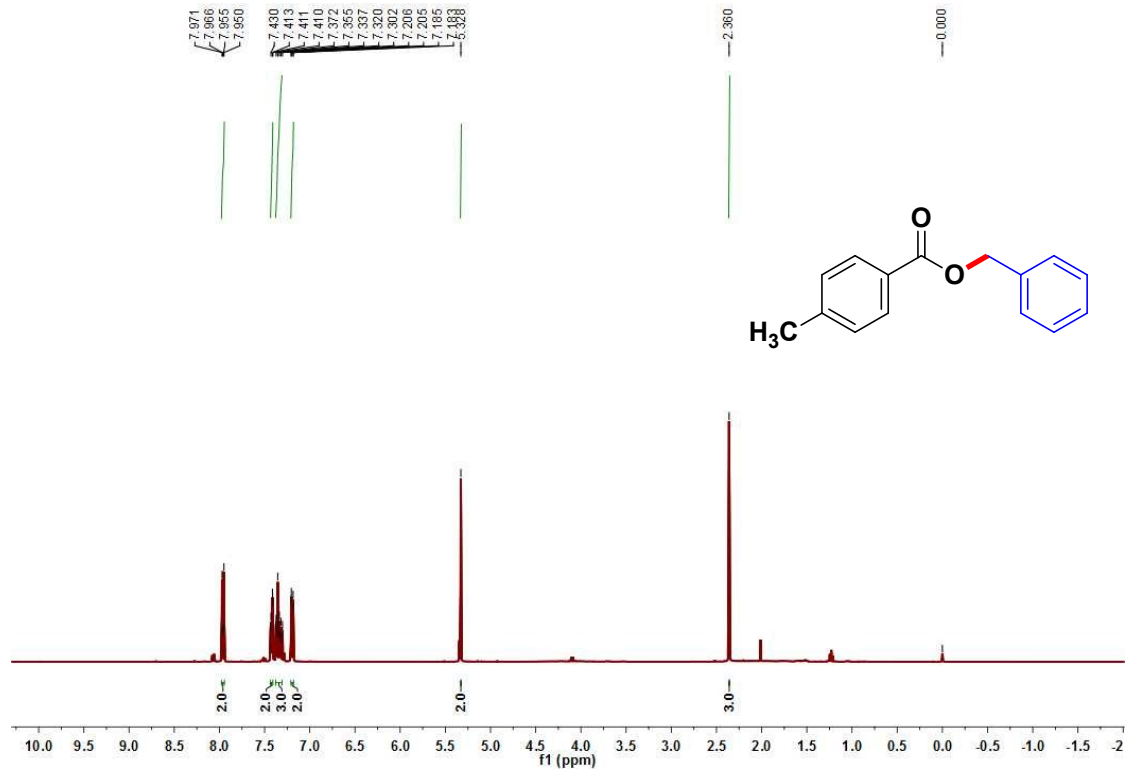
### 3b: benzyl 2-methylbenzoate



### 3c: benzyl 3-methylbenzoate

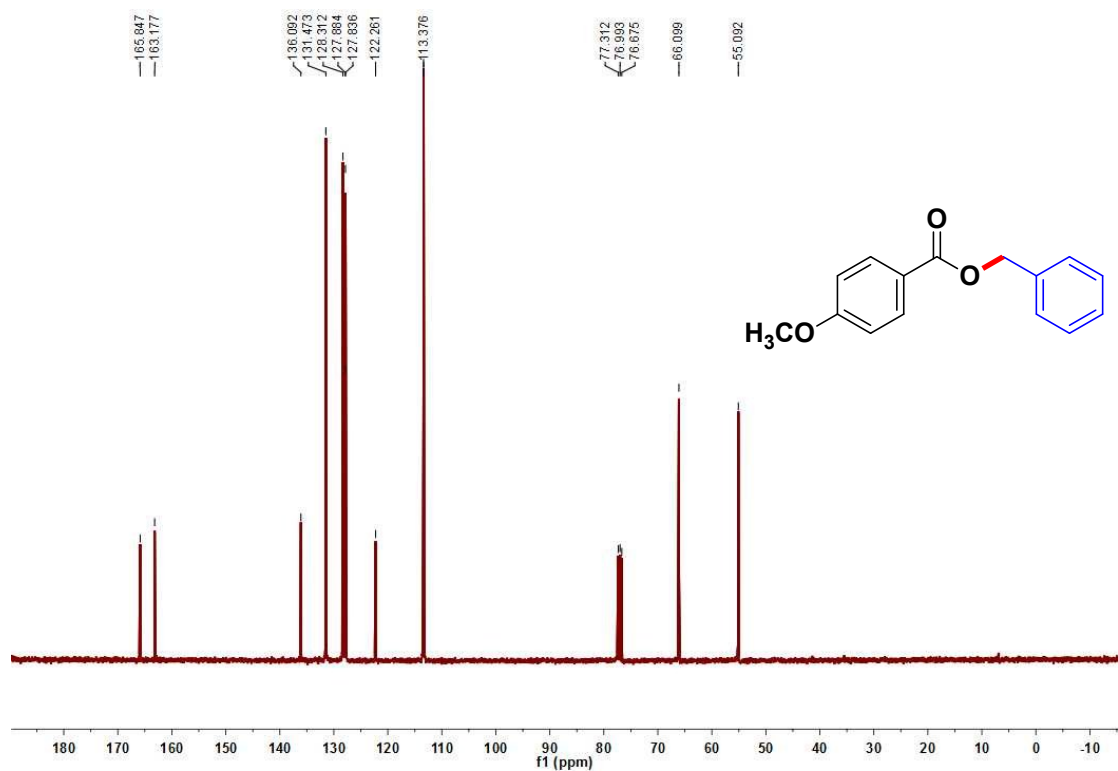
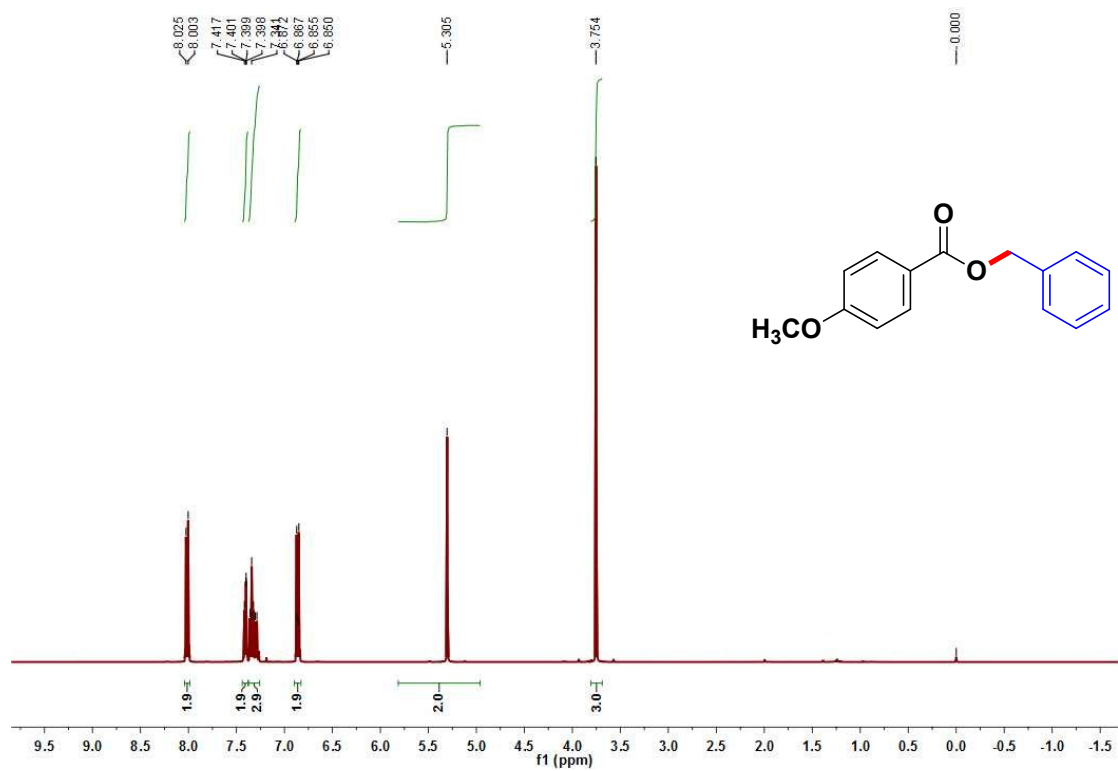


3d: benzyl 4-methylbenzoate

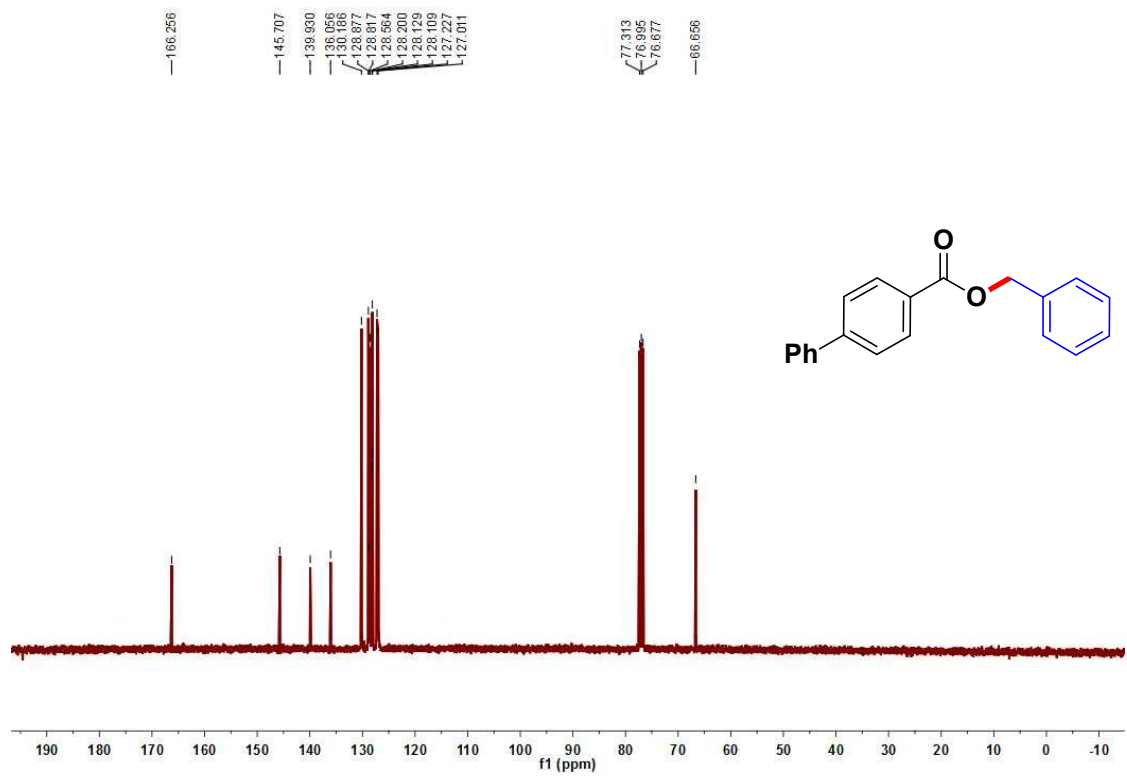
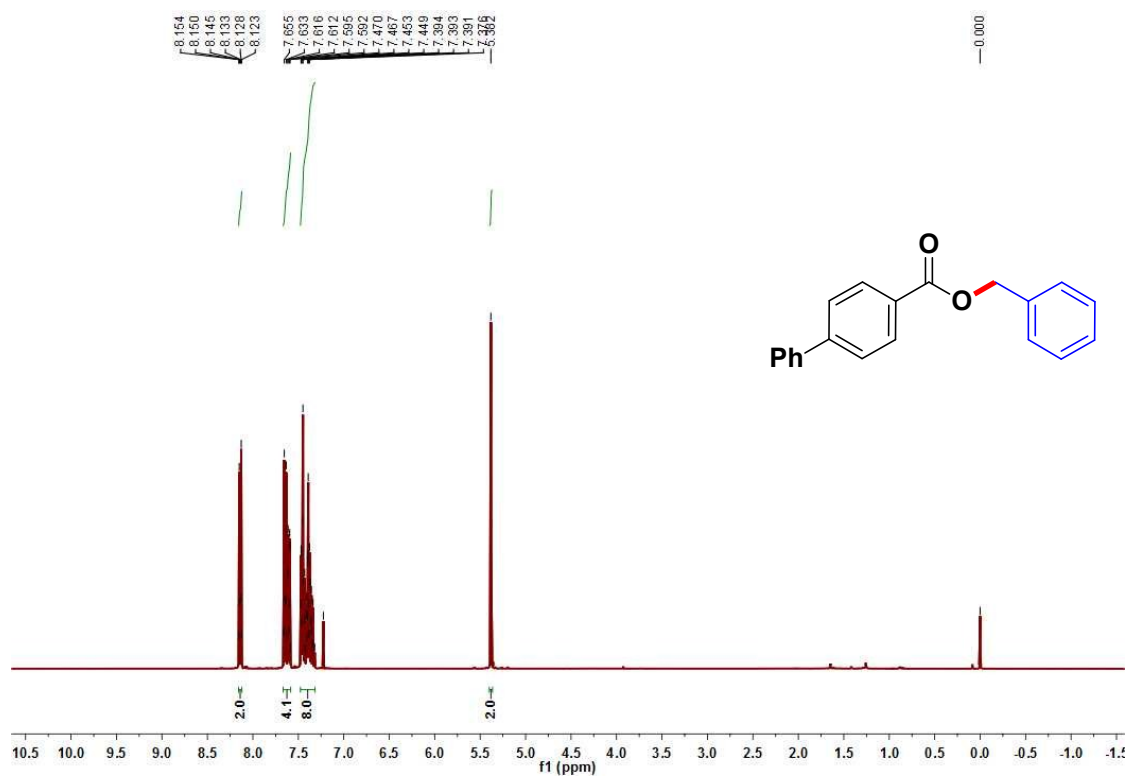




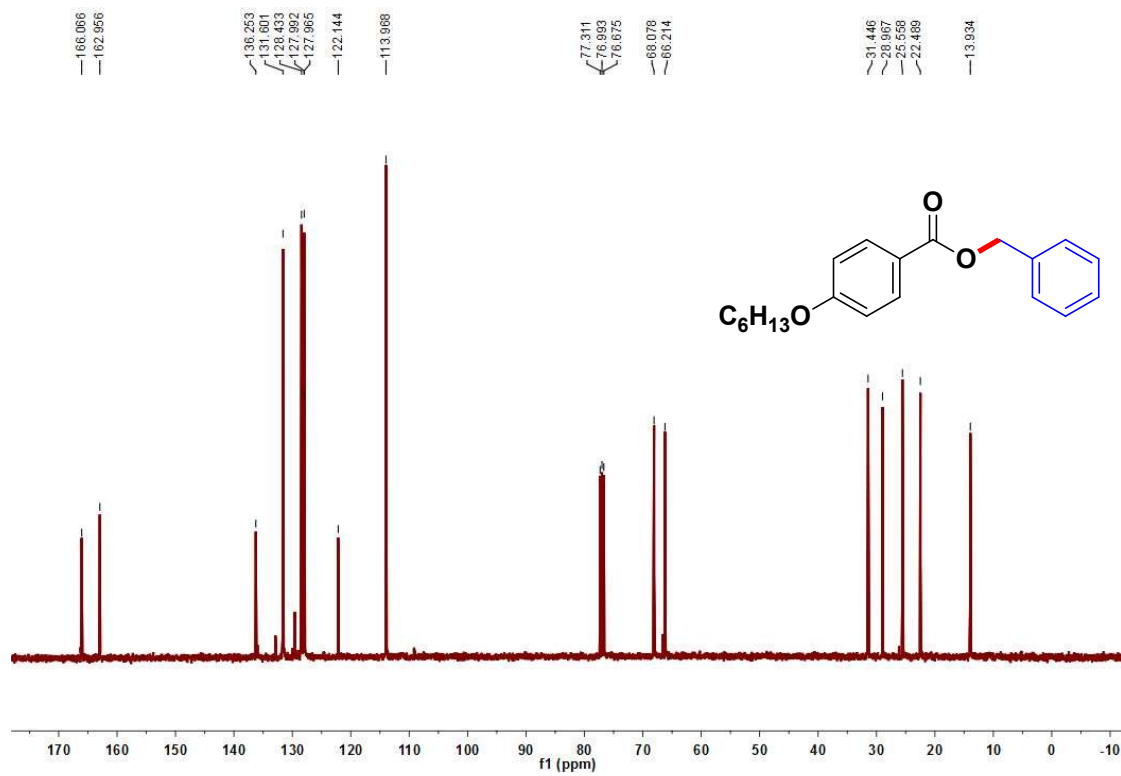
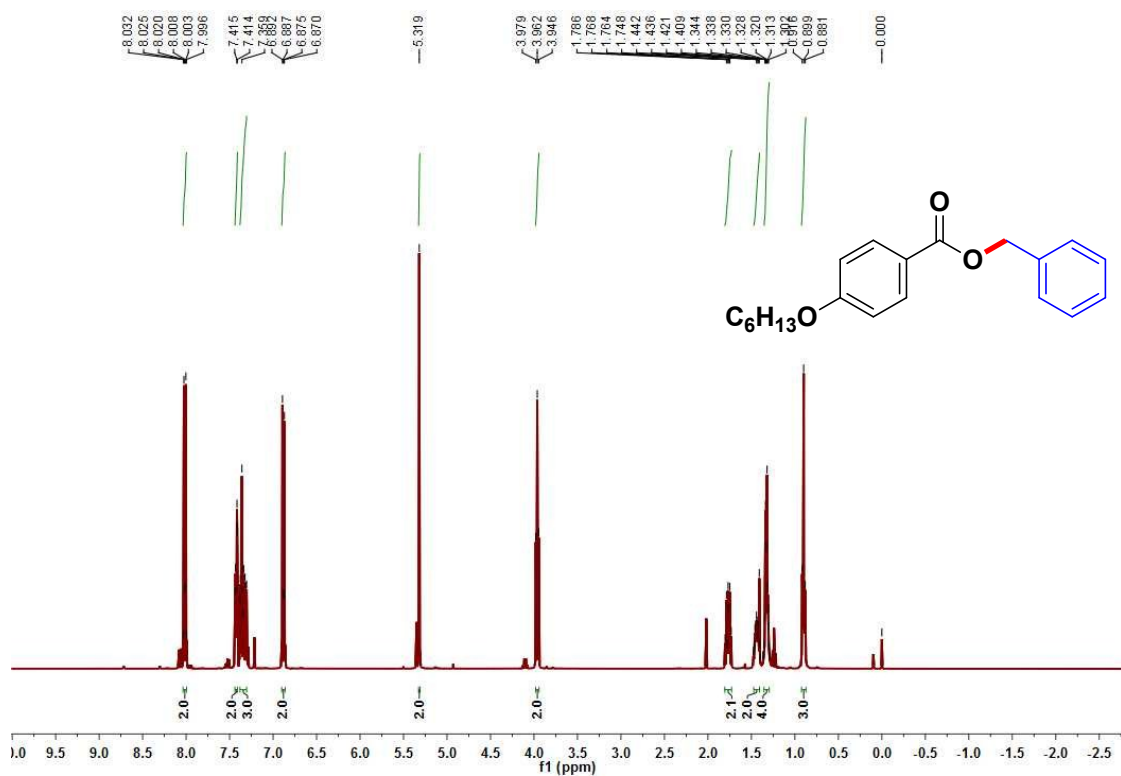
### 3e: benzyl 4-methoxybenzoate



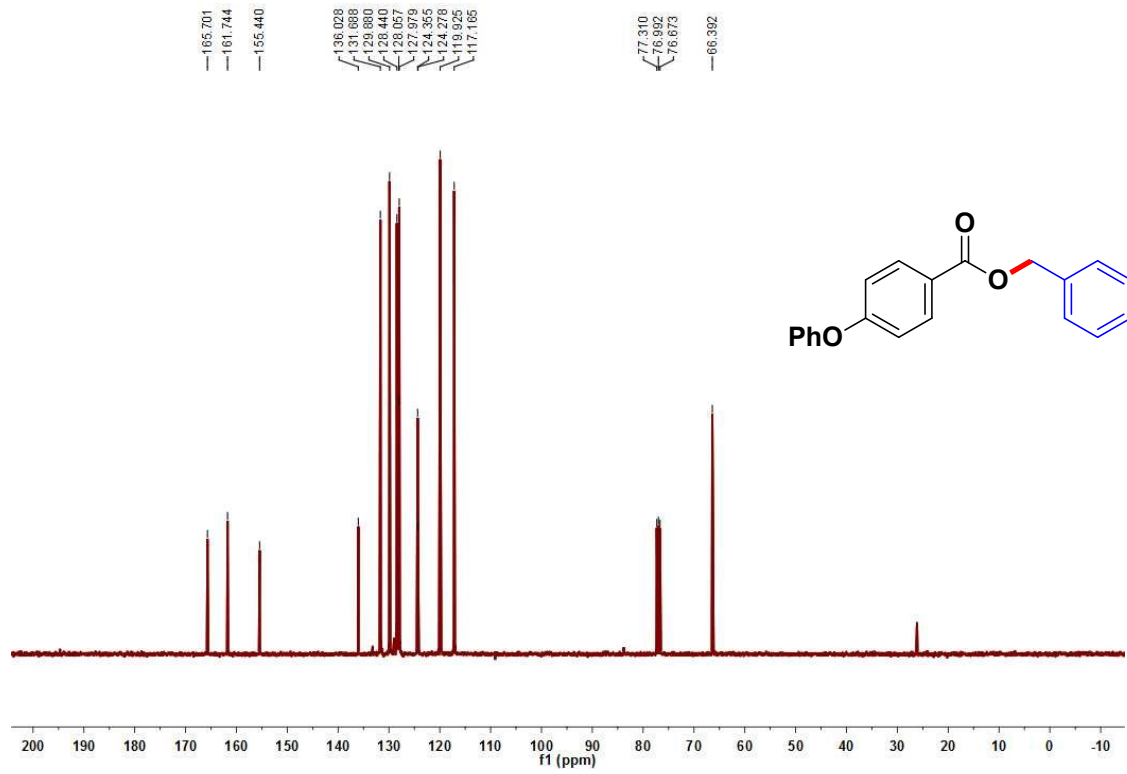
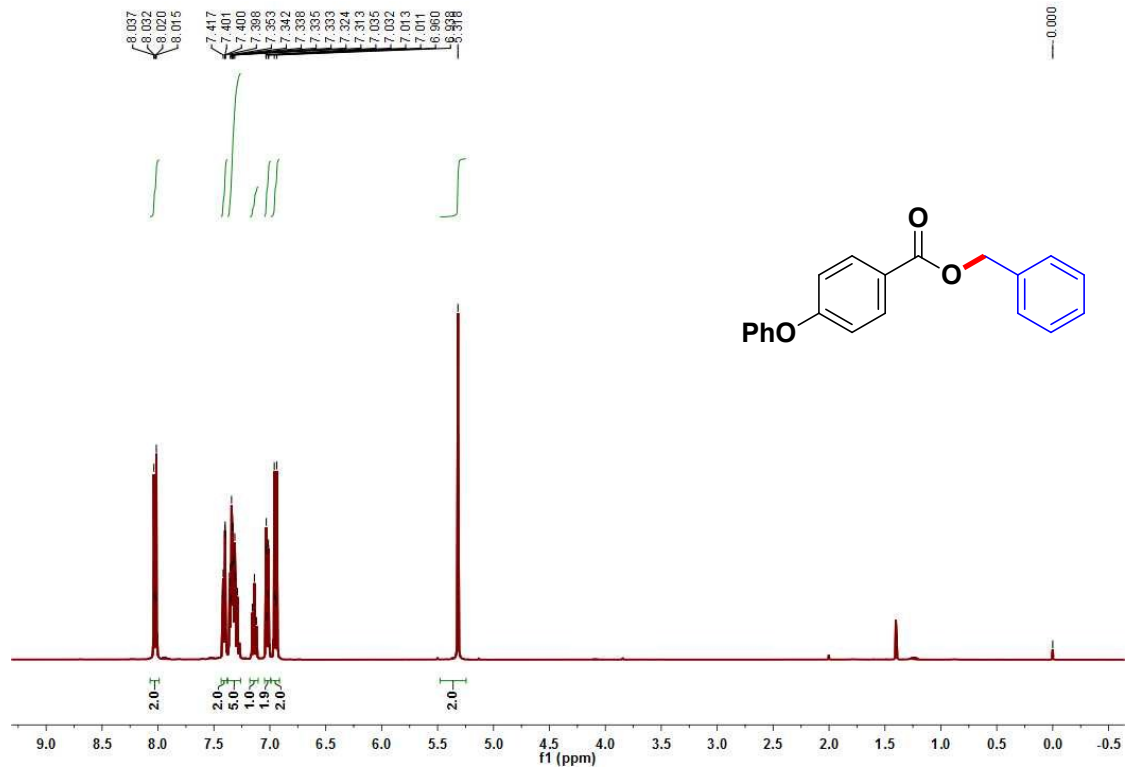
### 3f: benzyl [1,1'-biphenyl]-4-carboxylate



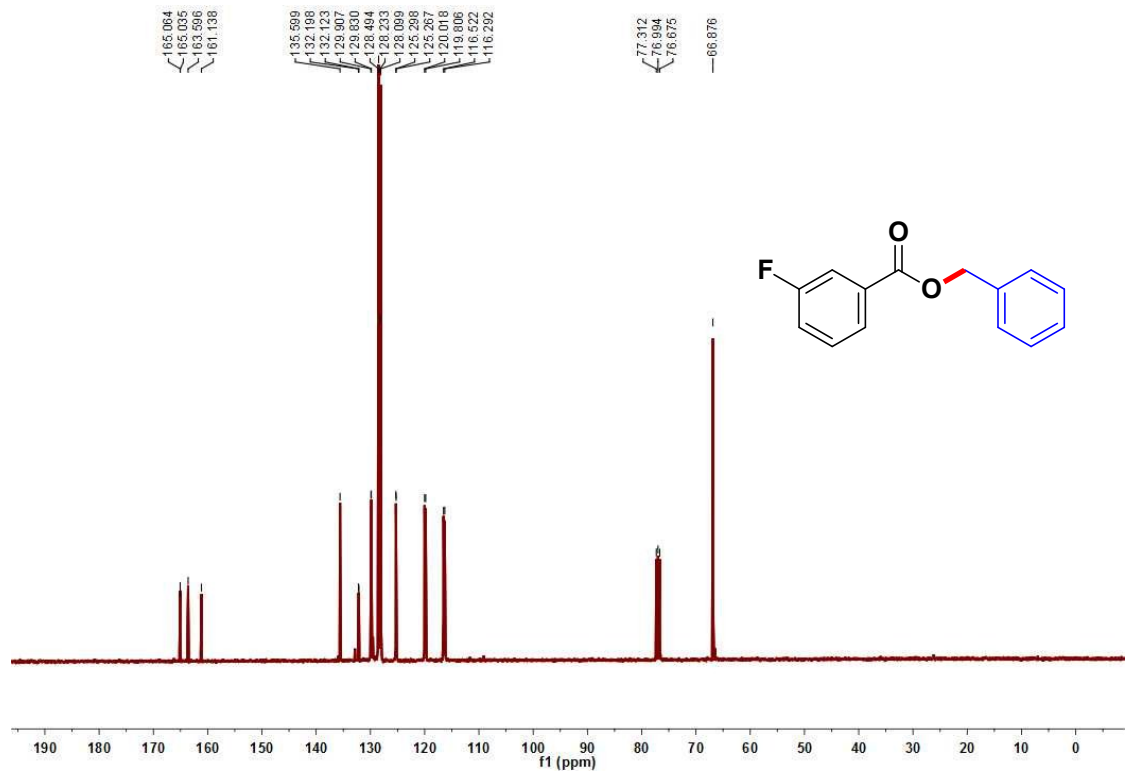
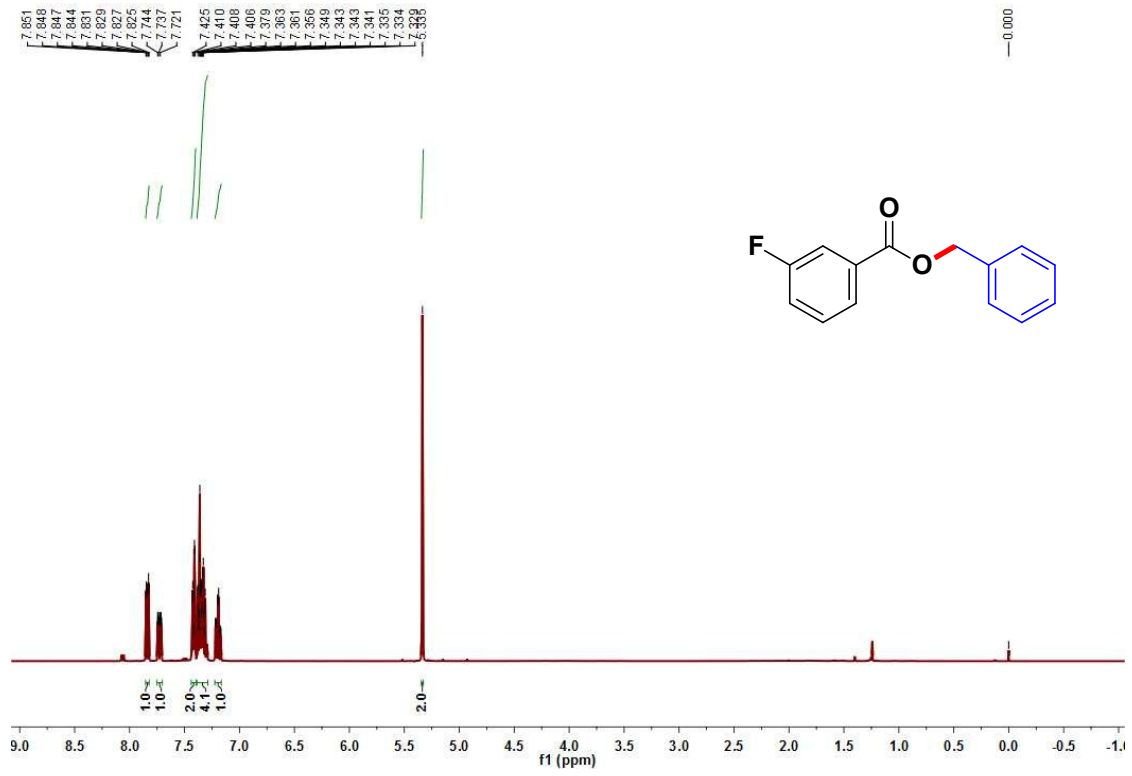
**3g: benzyl 4-(hexyloxy)benzoate**



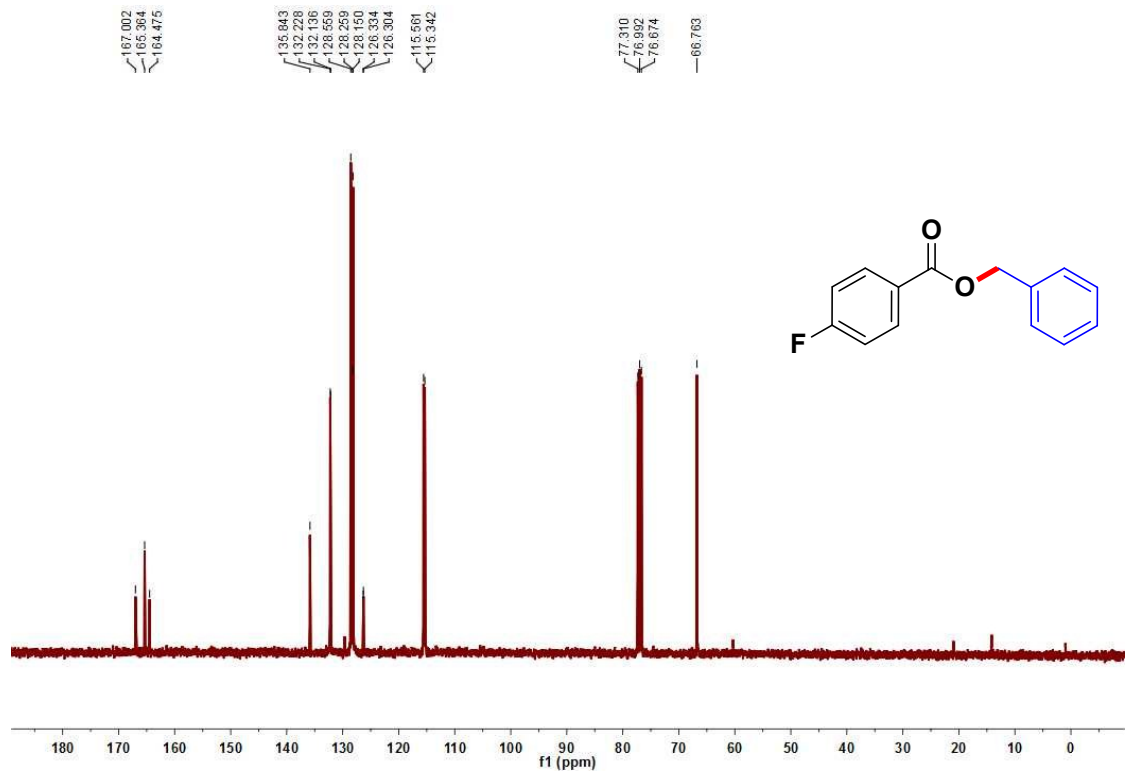
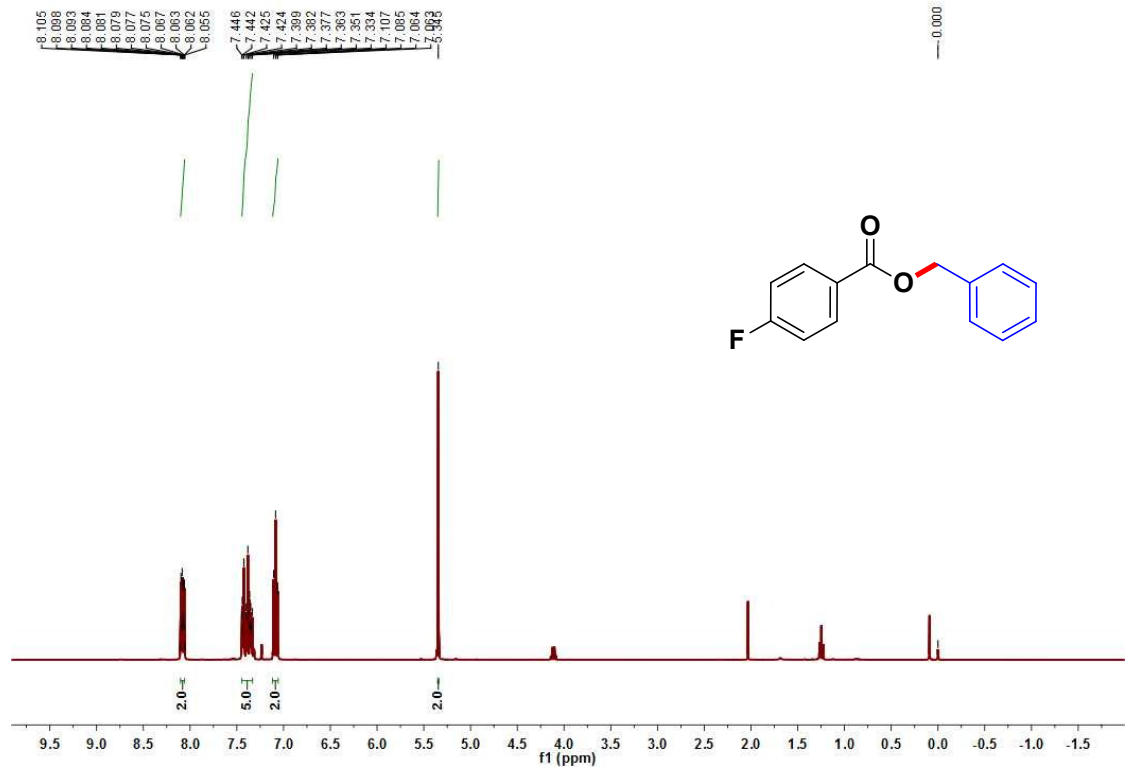
### 3h: benzyl 4-phenoxybenzoate



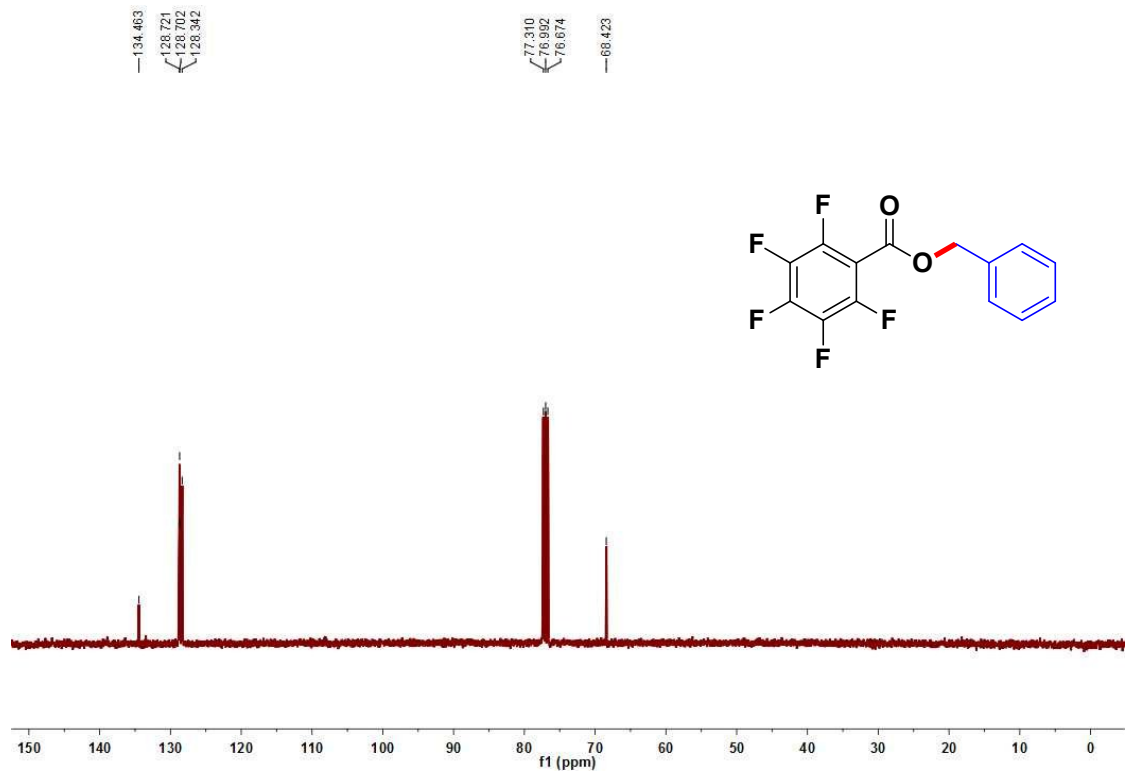
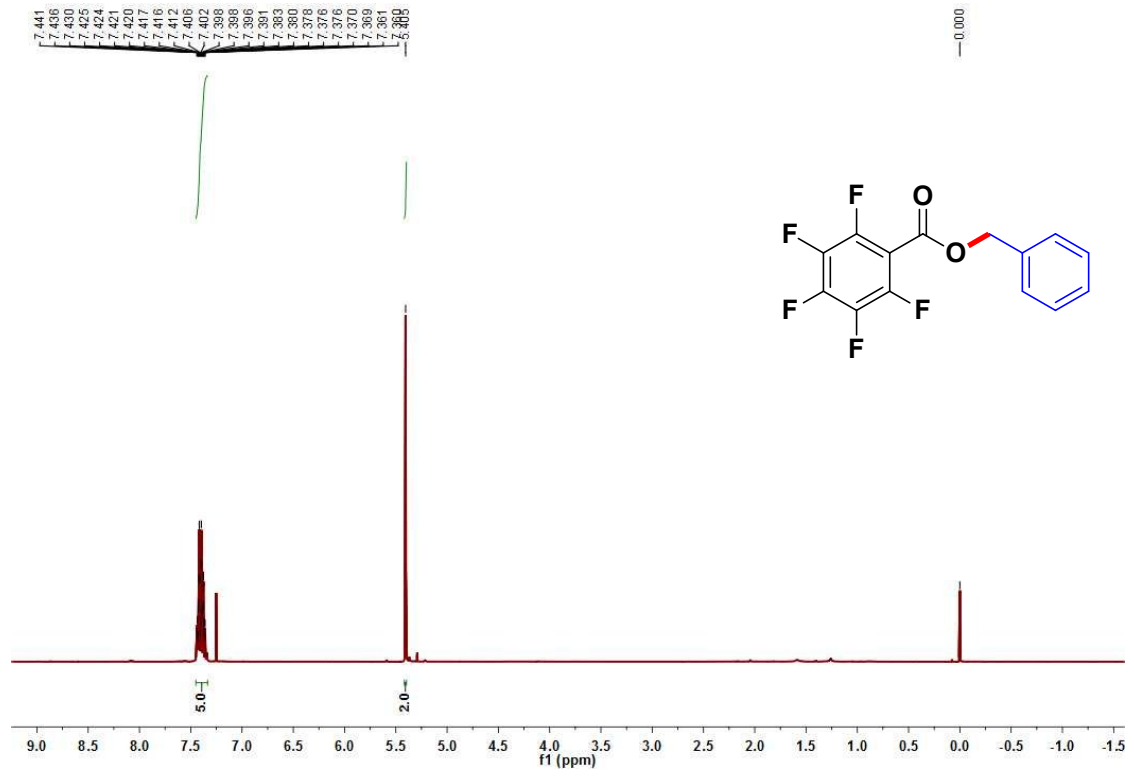
**3i: benzyl 3-fluorobenzoate**



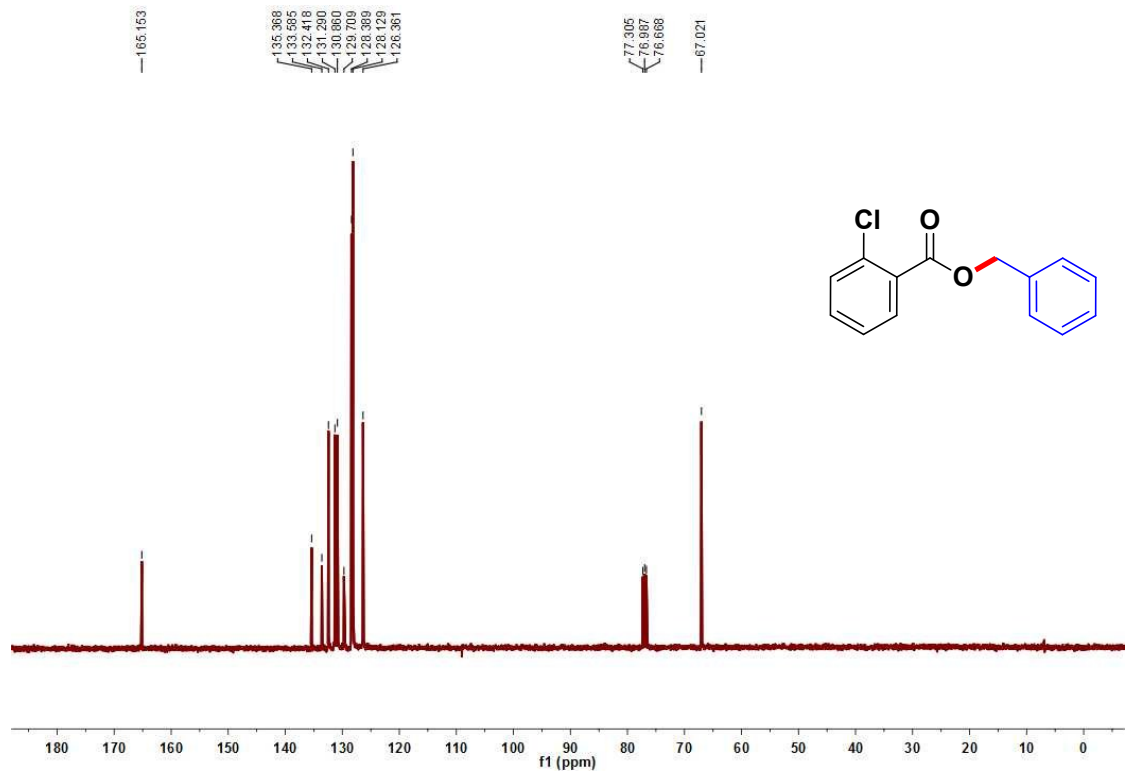
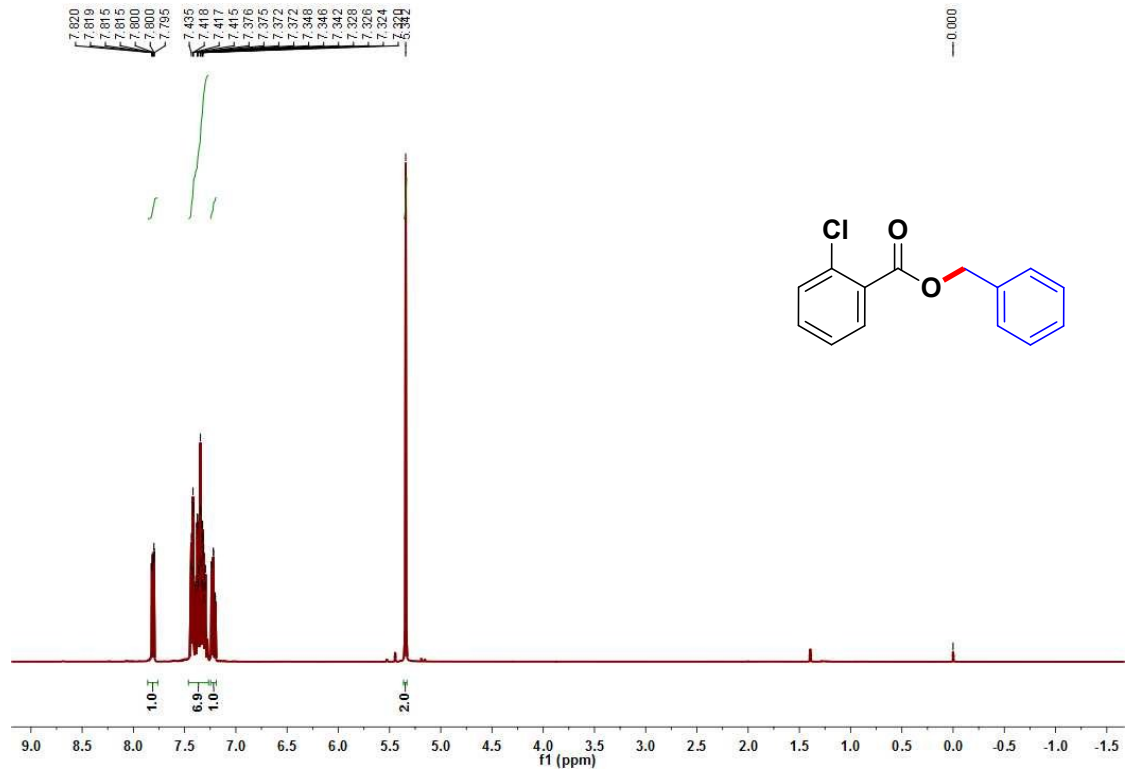
### 3j: benzyl 4-fluorobenzoate



**3k: benzyl 2,3,4,5,6-pentafluorobenzoate**

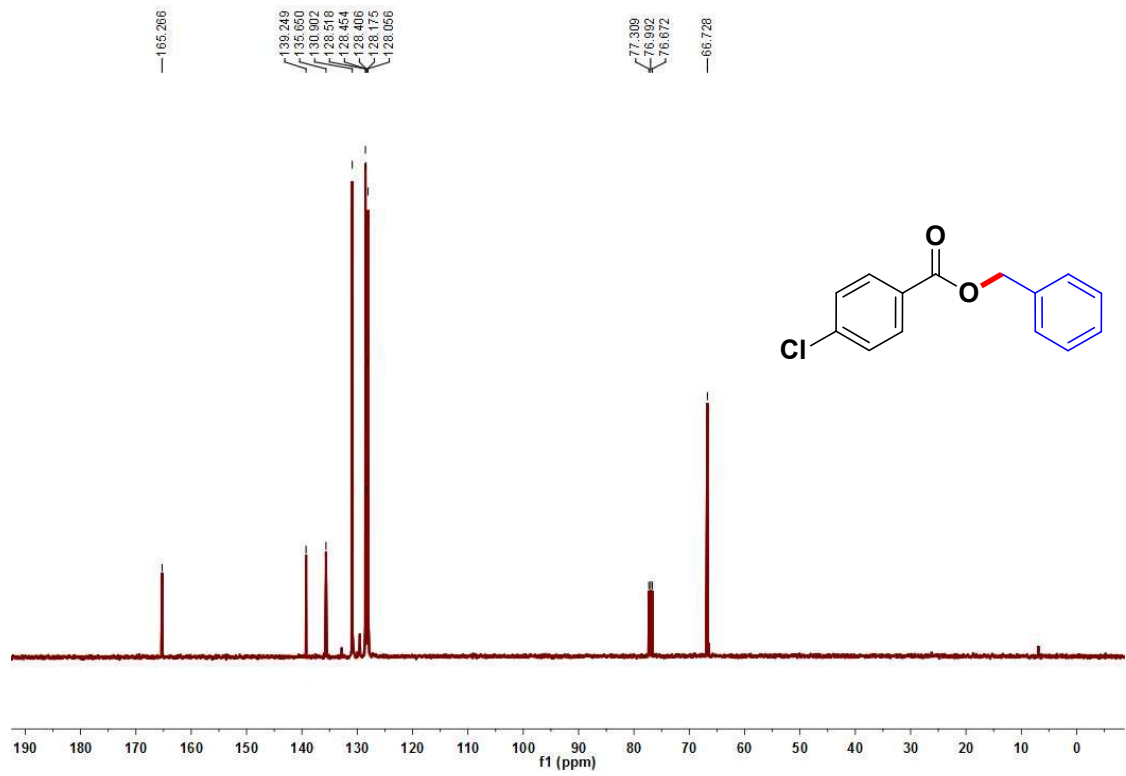
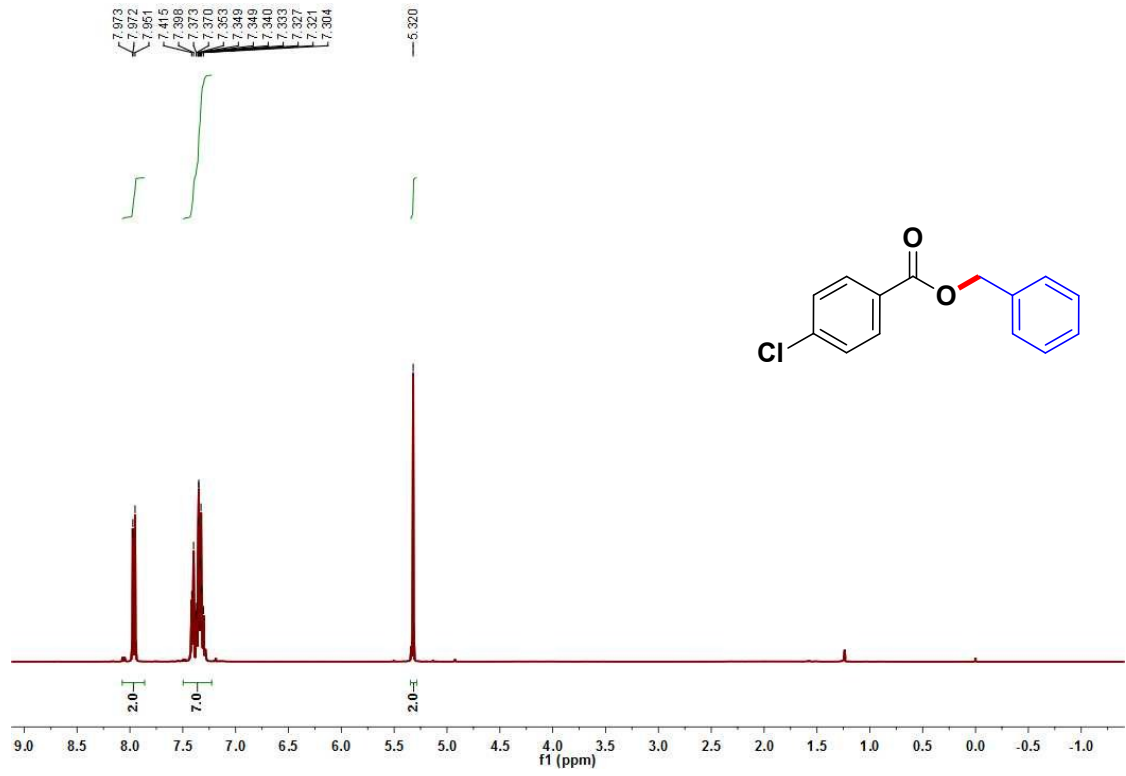


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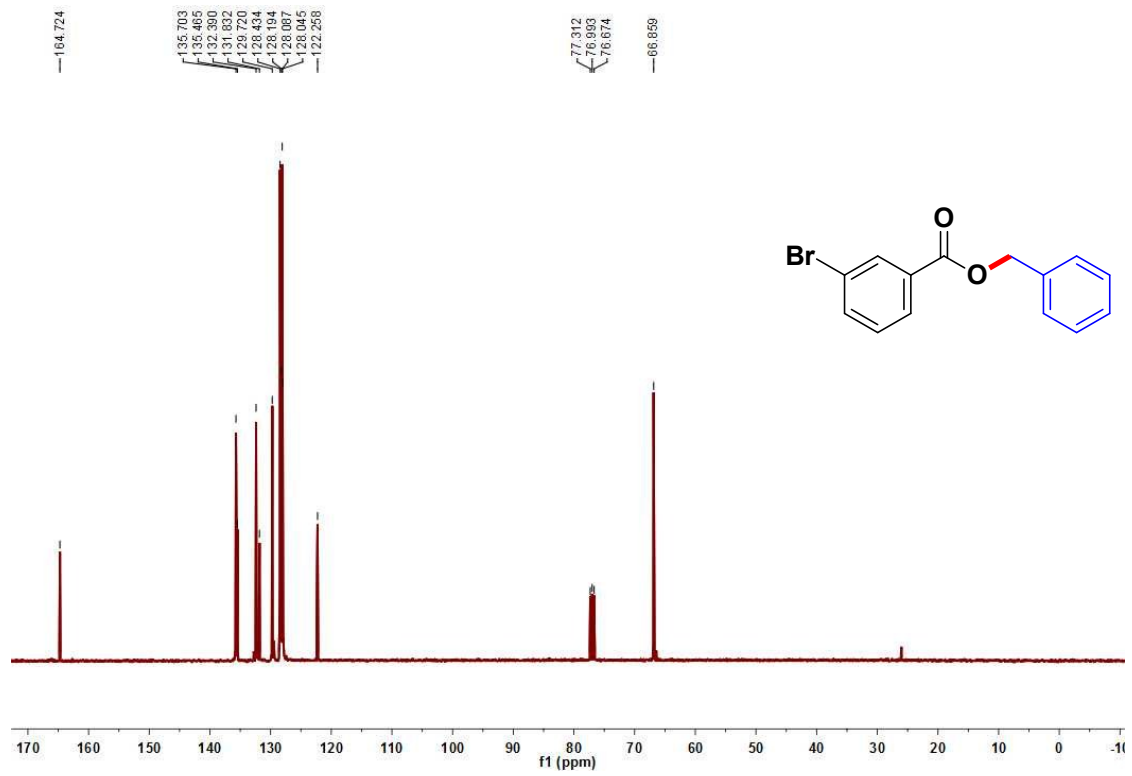
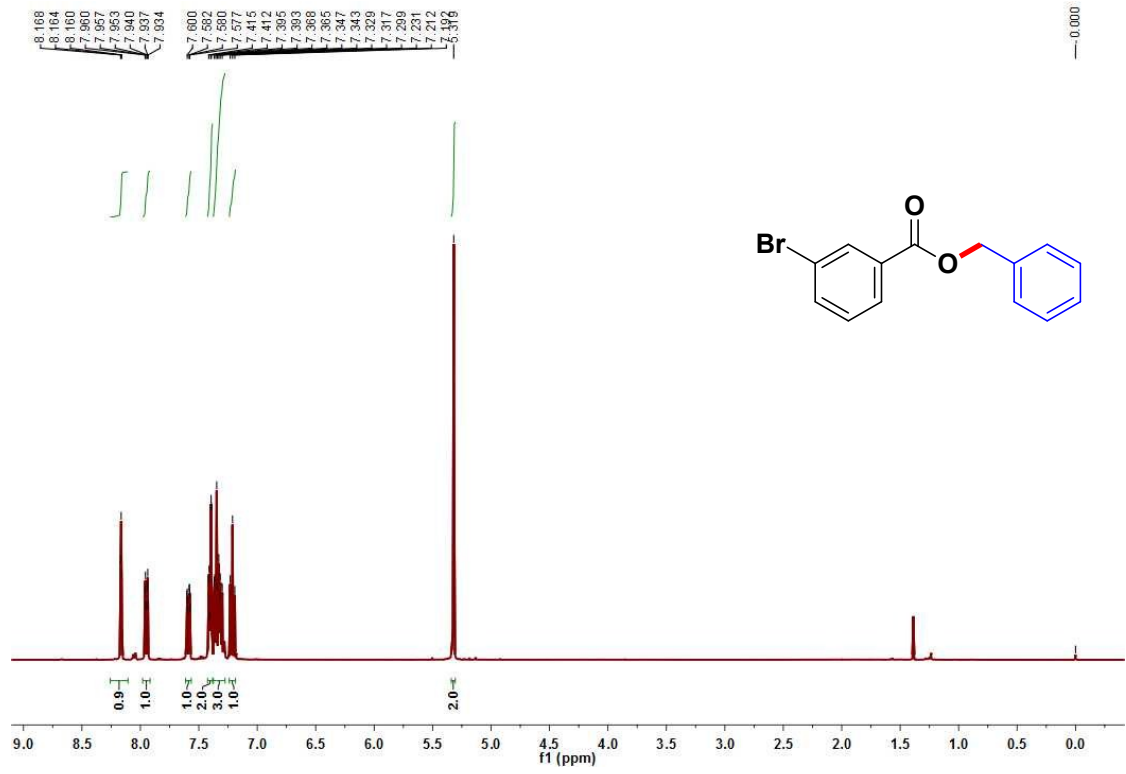




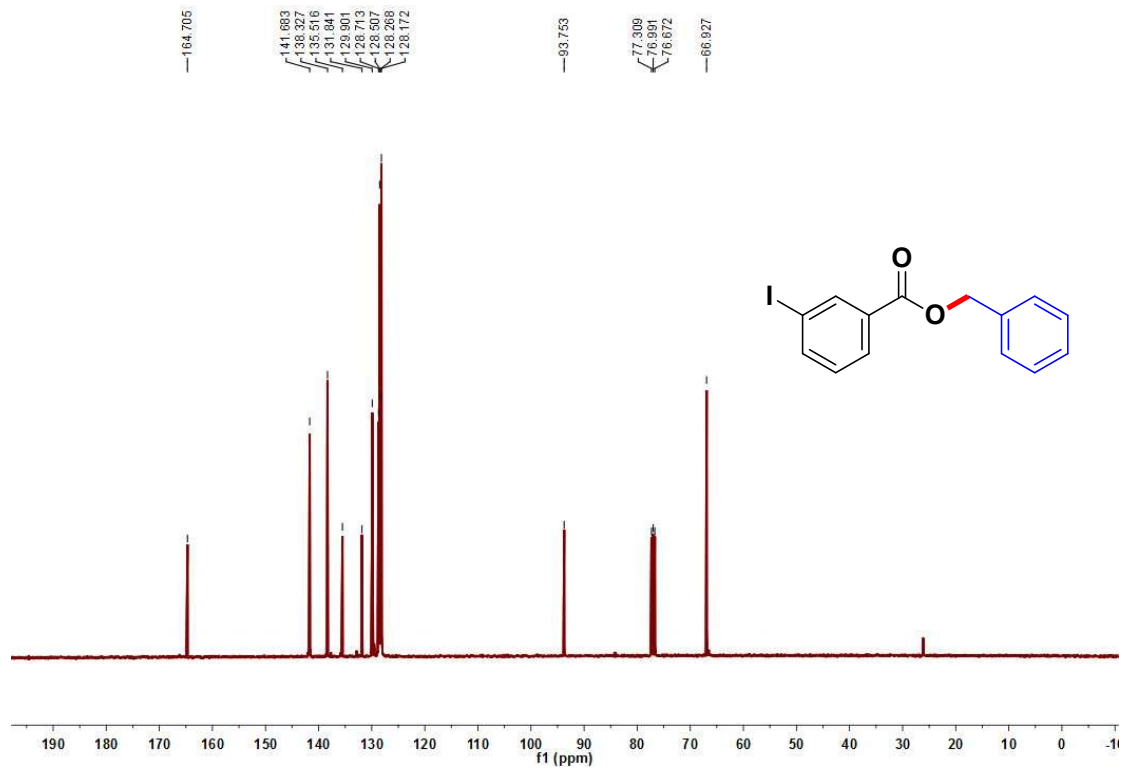
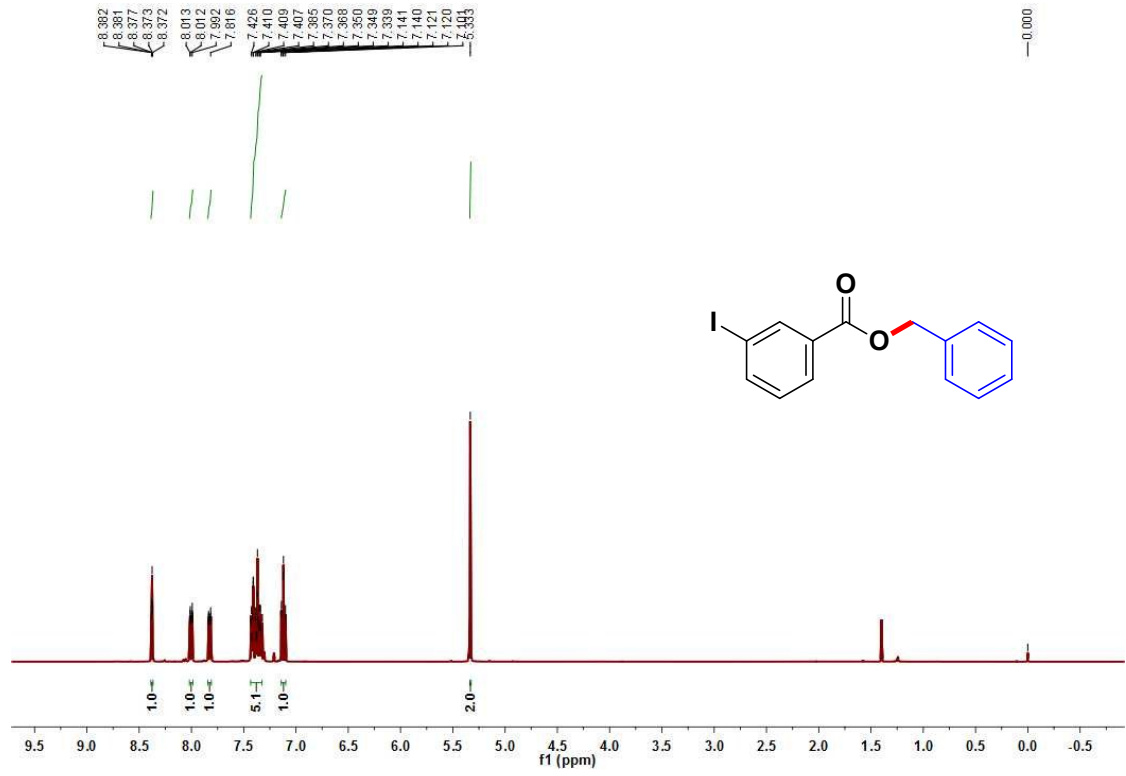
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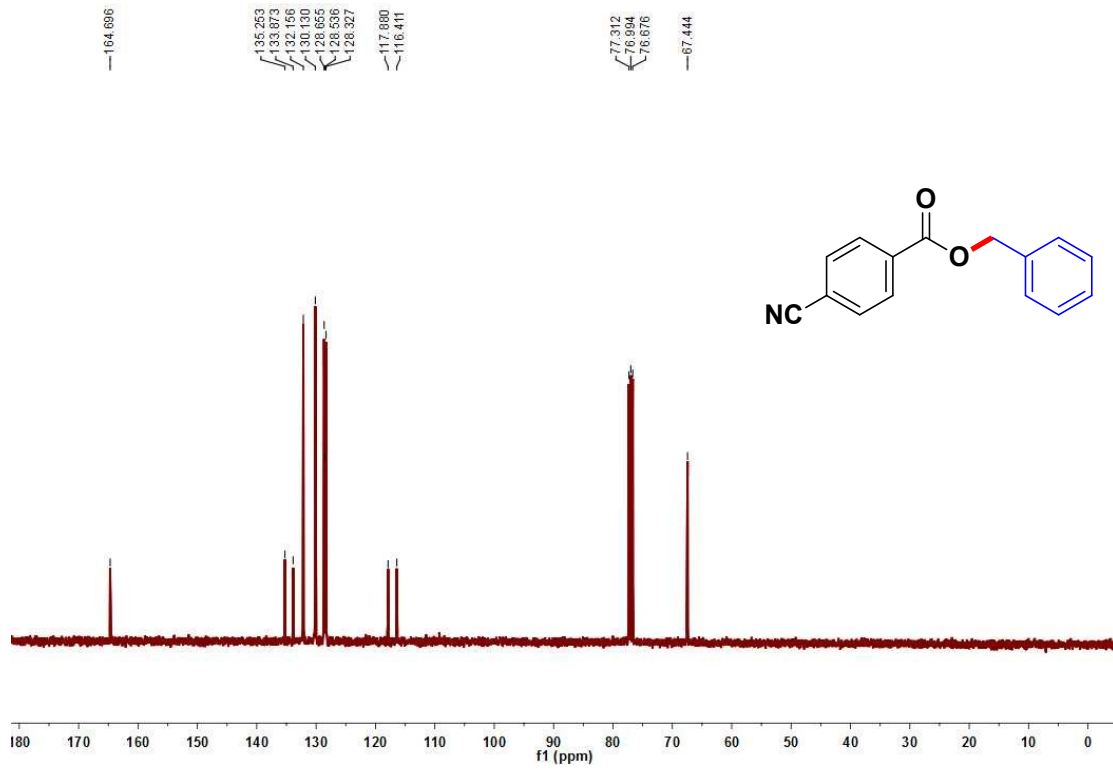
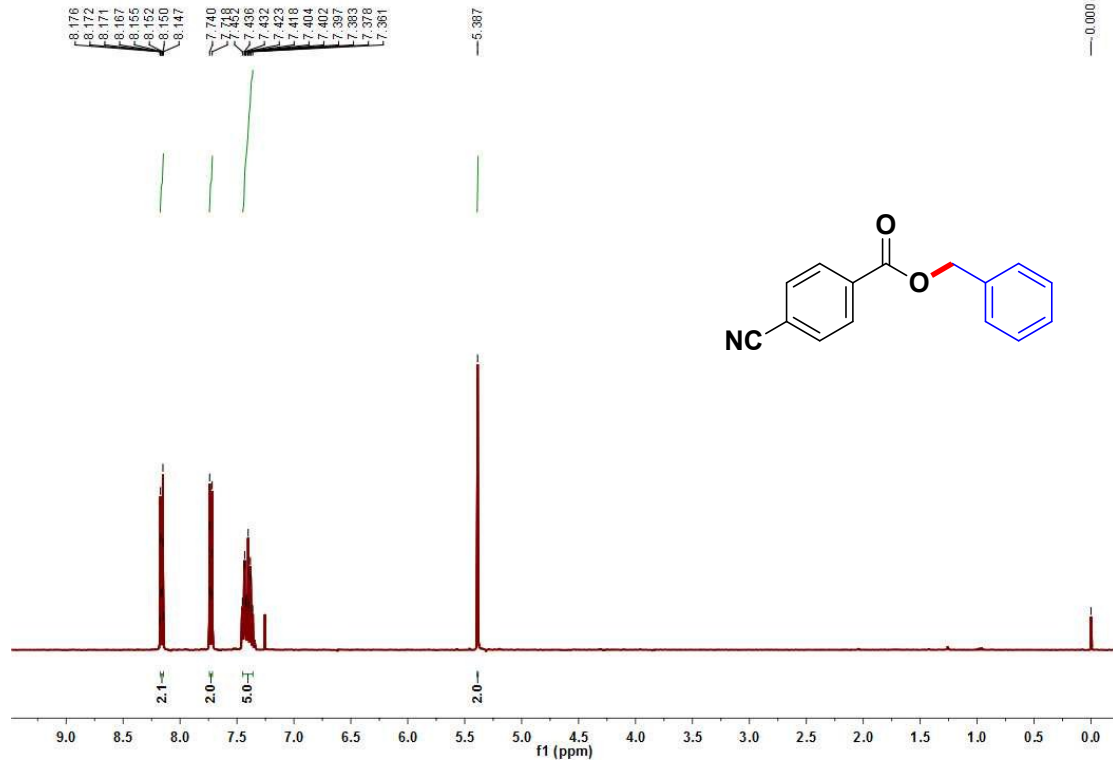
**3n: benzyl 3-bromobenzoate**



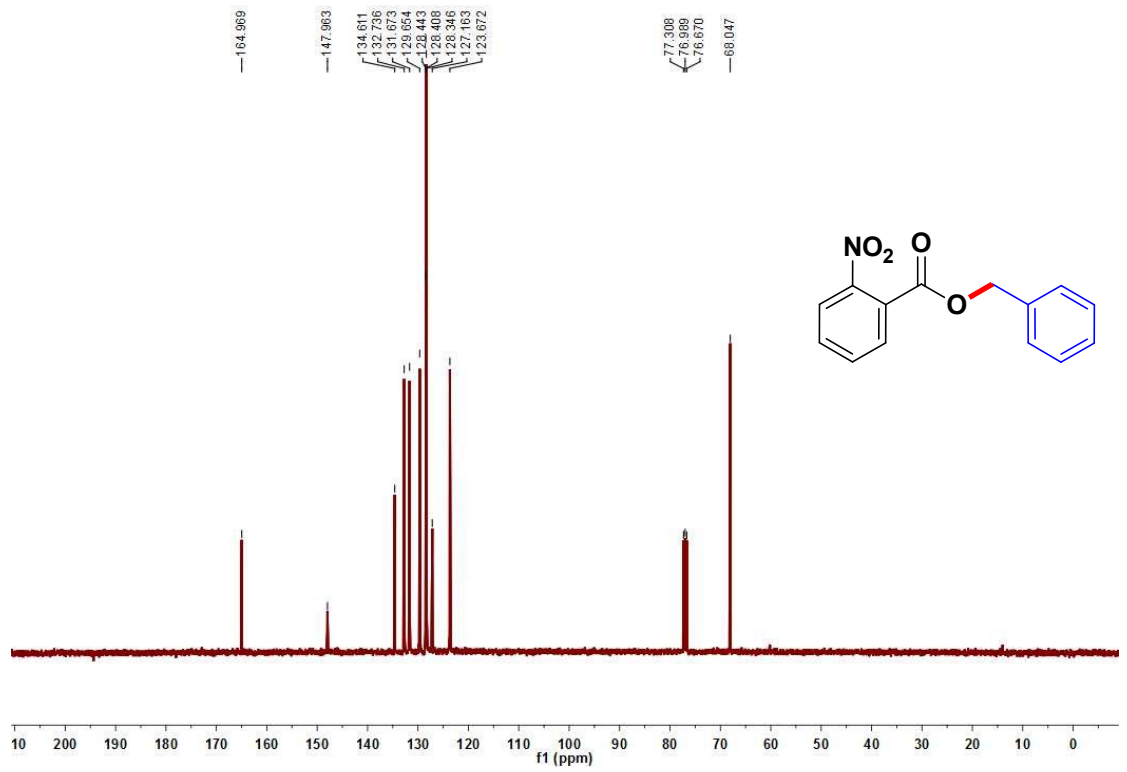
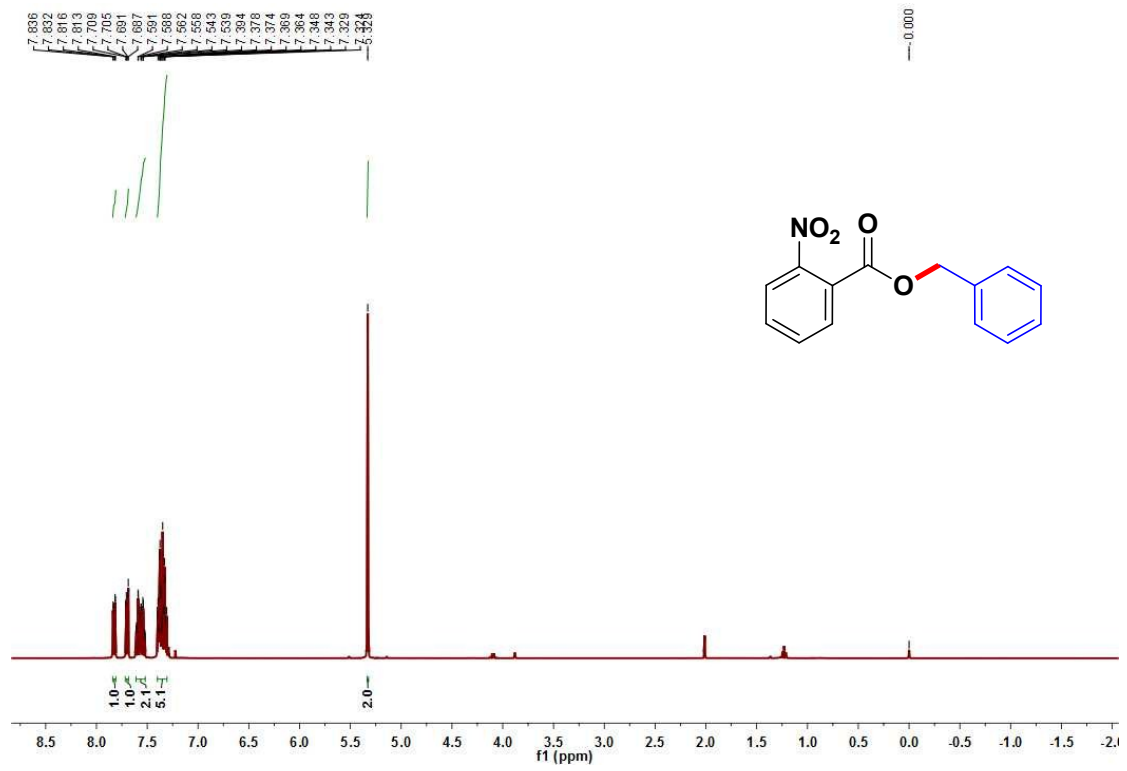
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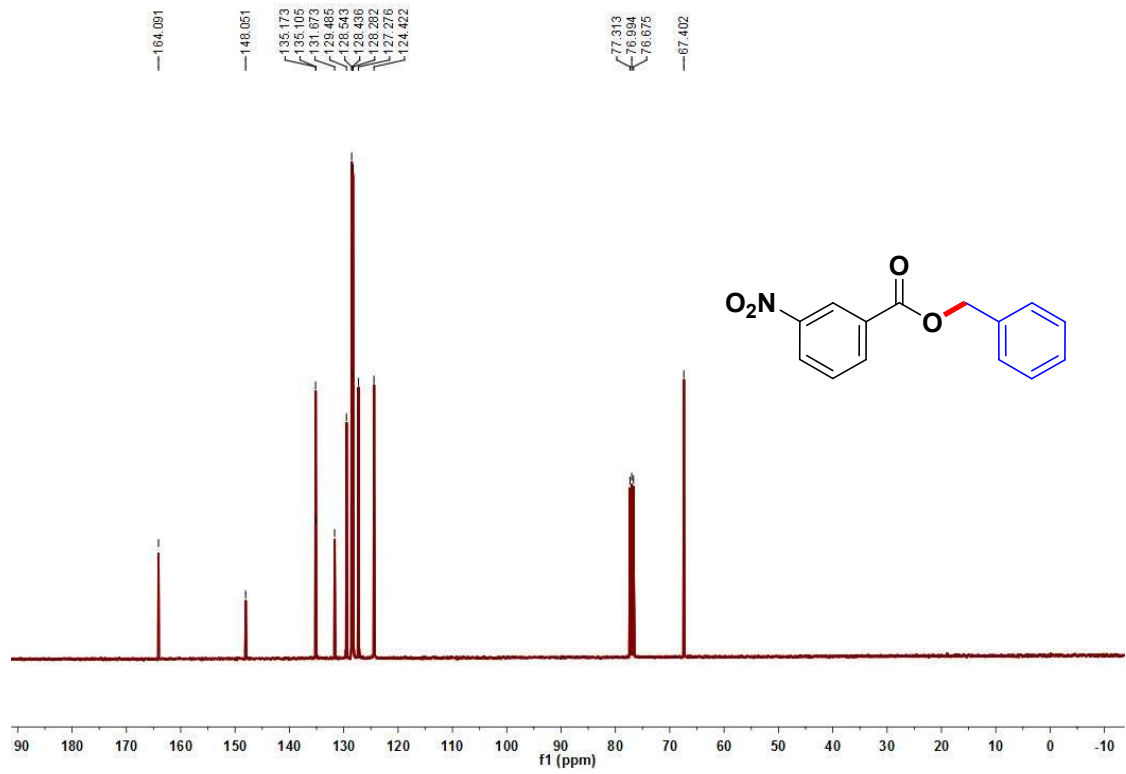
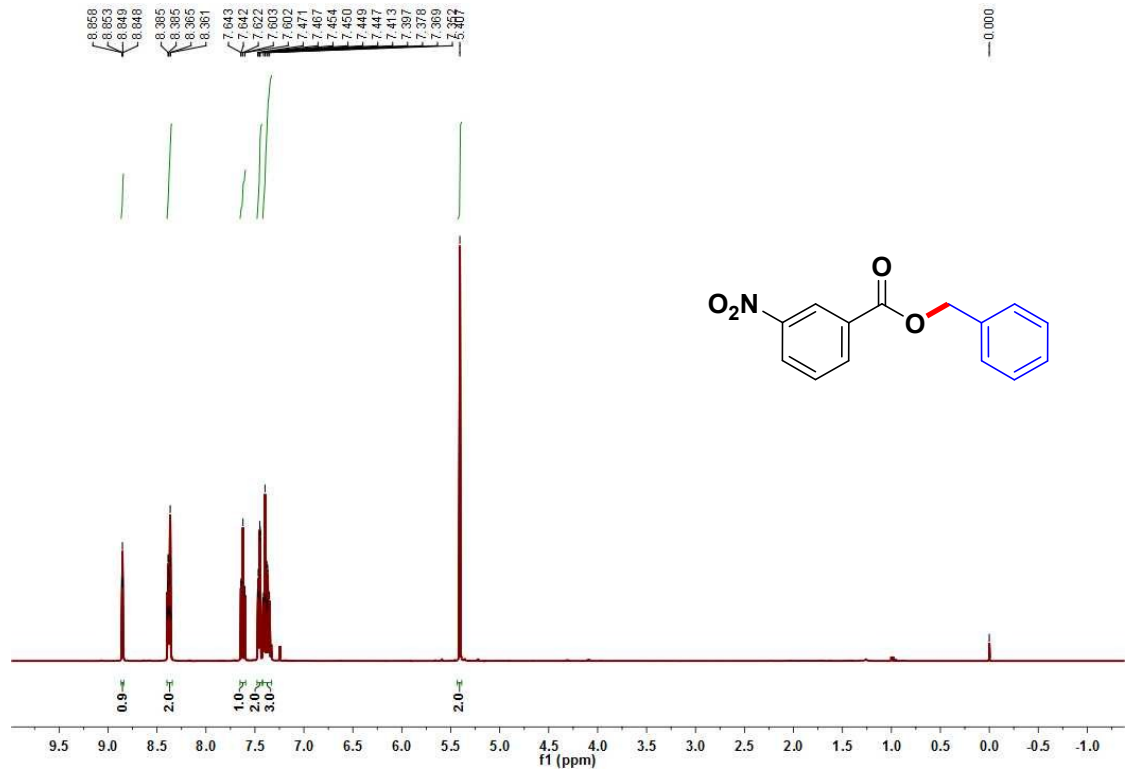
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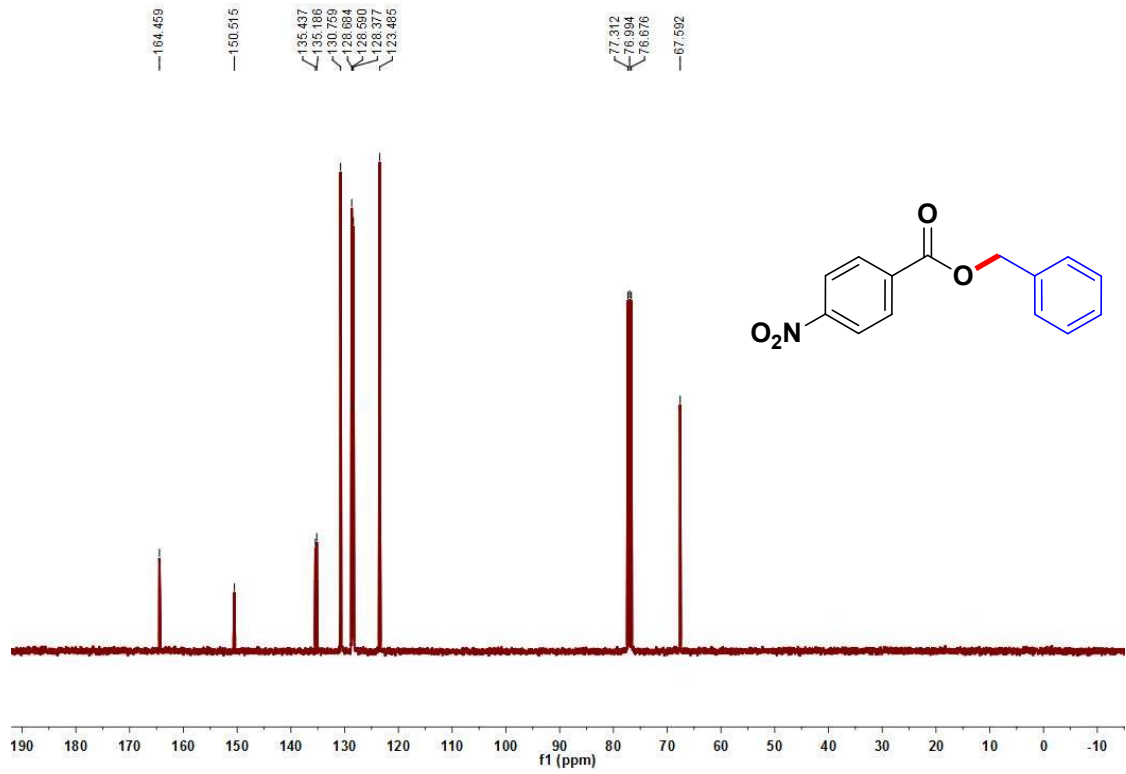
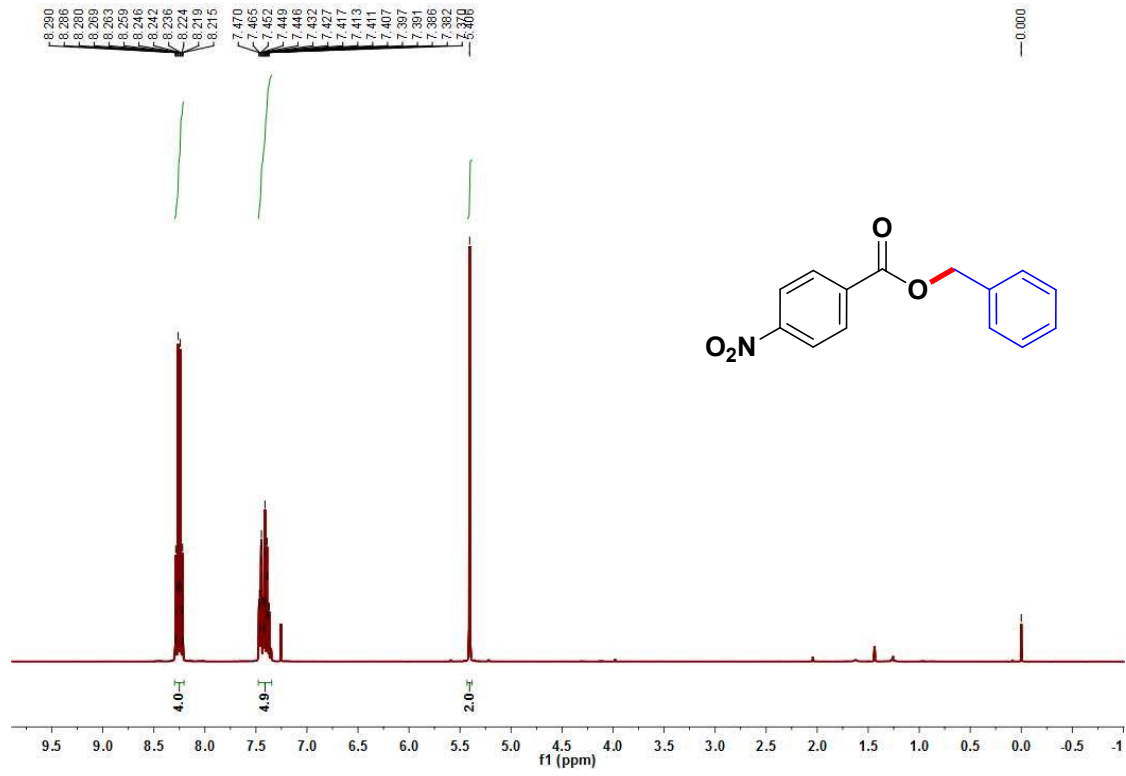
3q: benzyl 2-nitrobenzoate



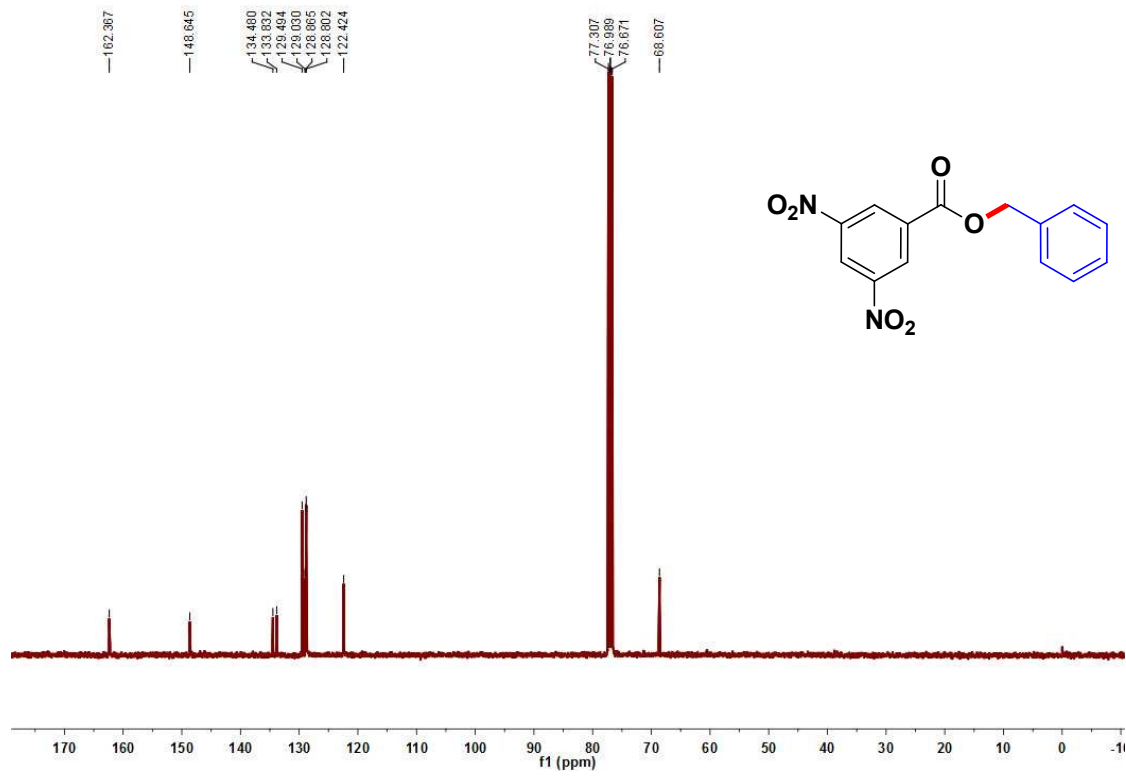
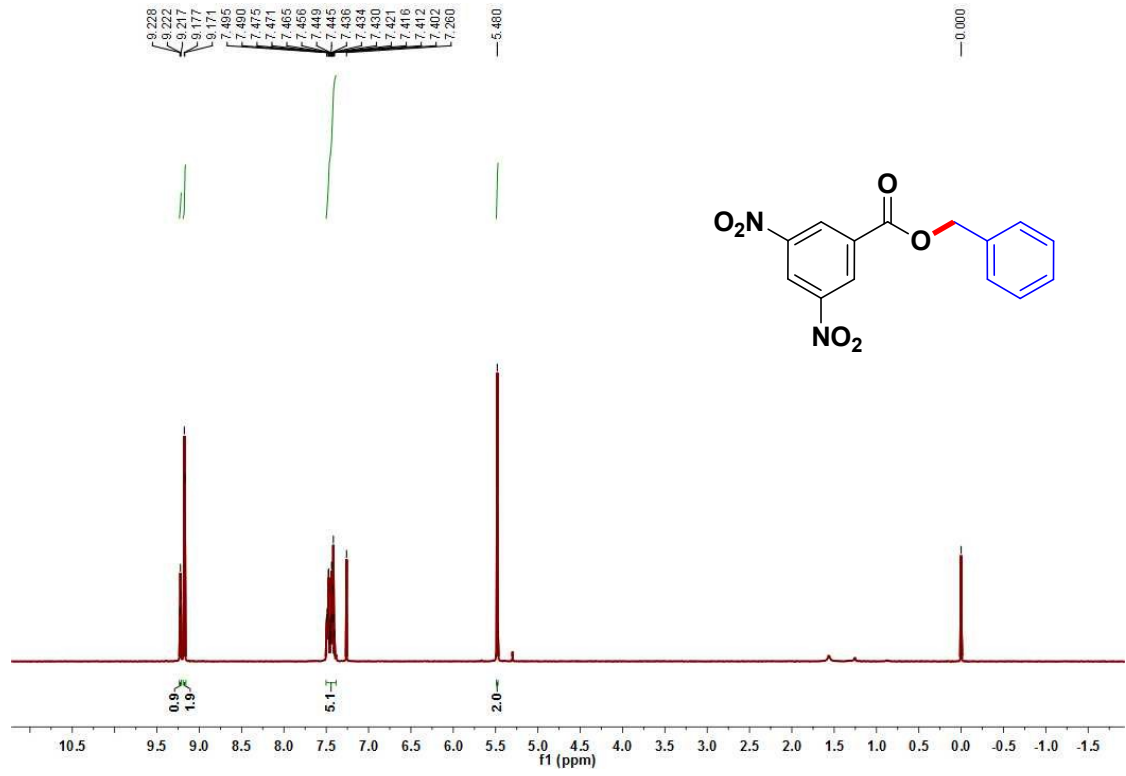
**3r: benzyl 3-nitrobenzoate**



3s: benzyl 4-nitrobenzoate

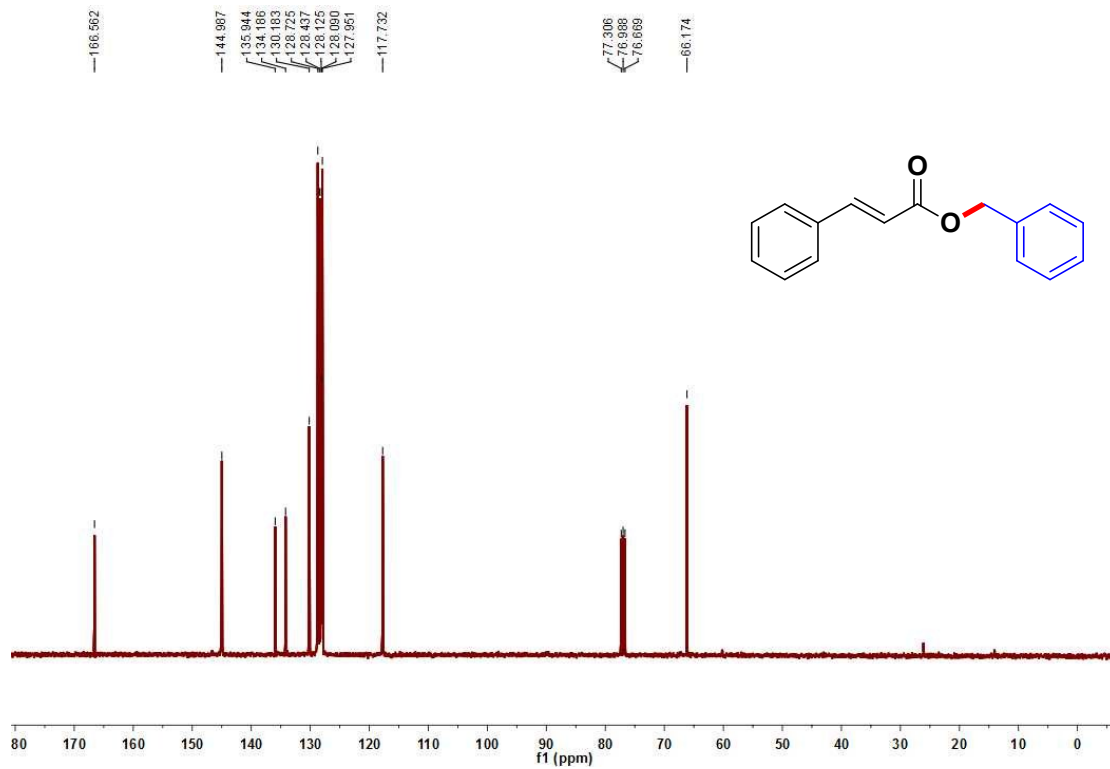
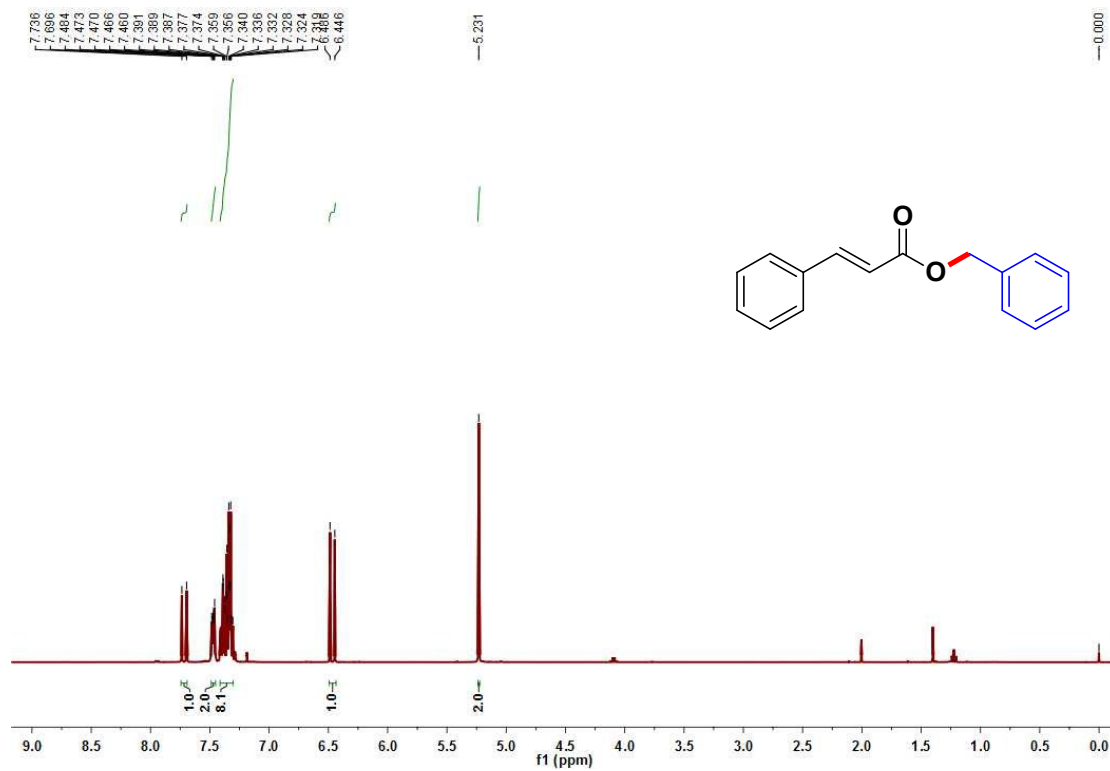


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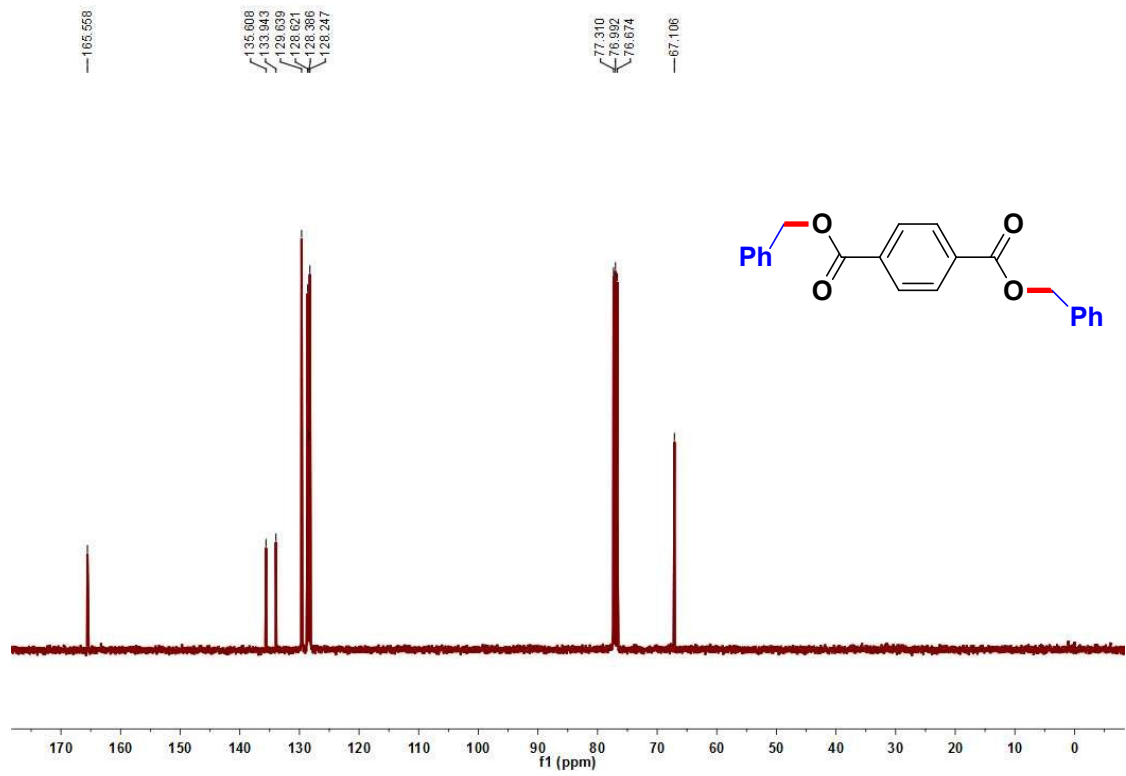
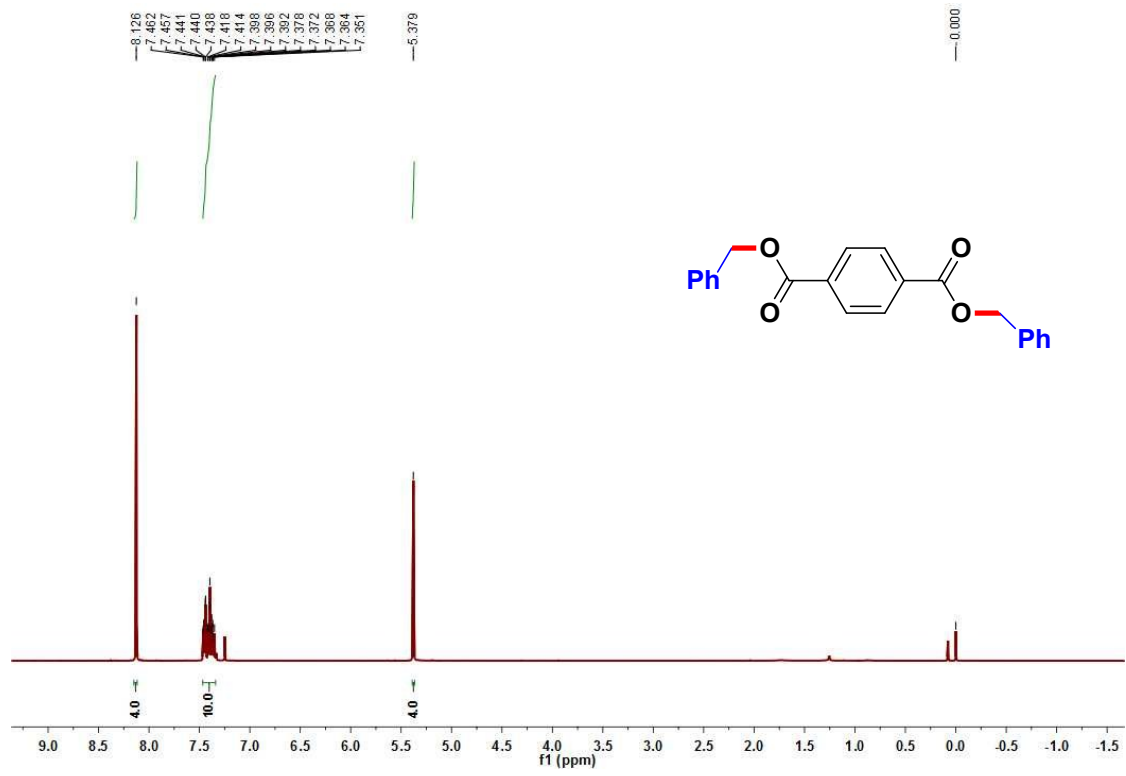




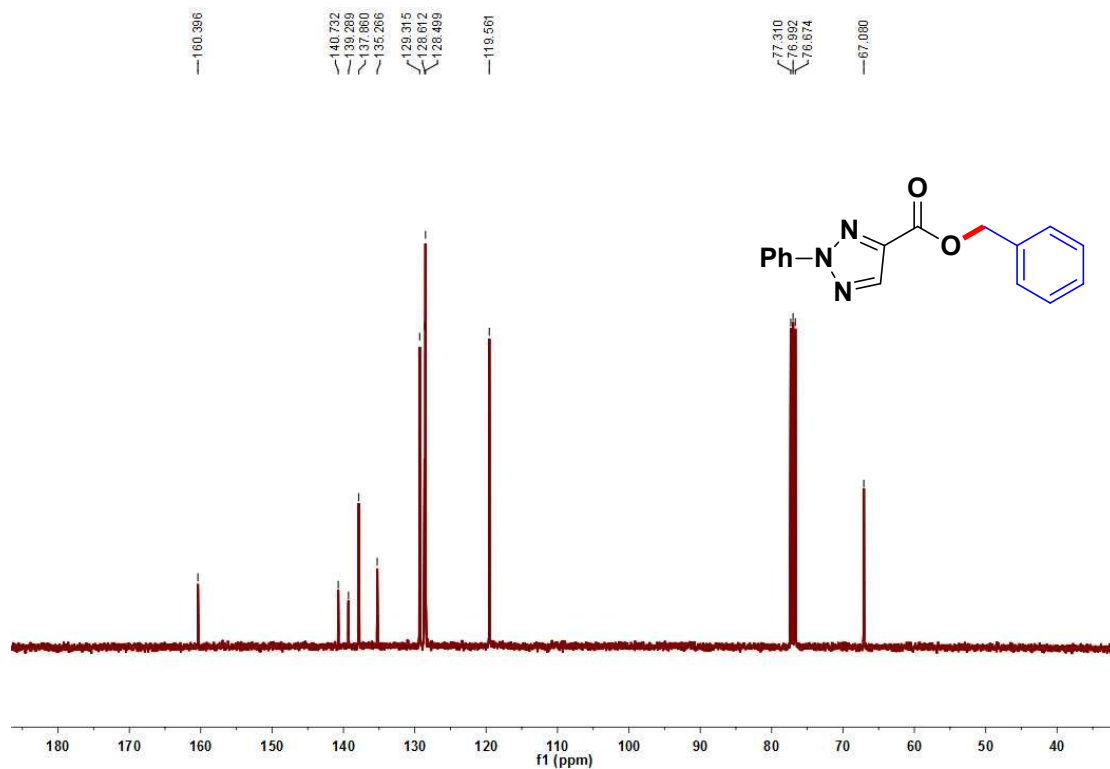
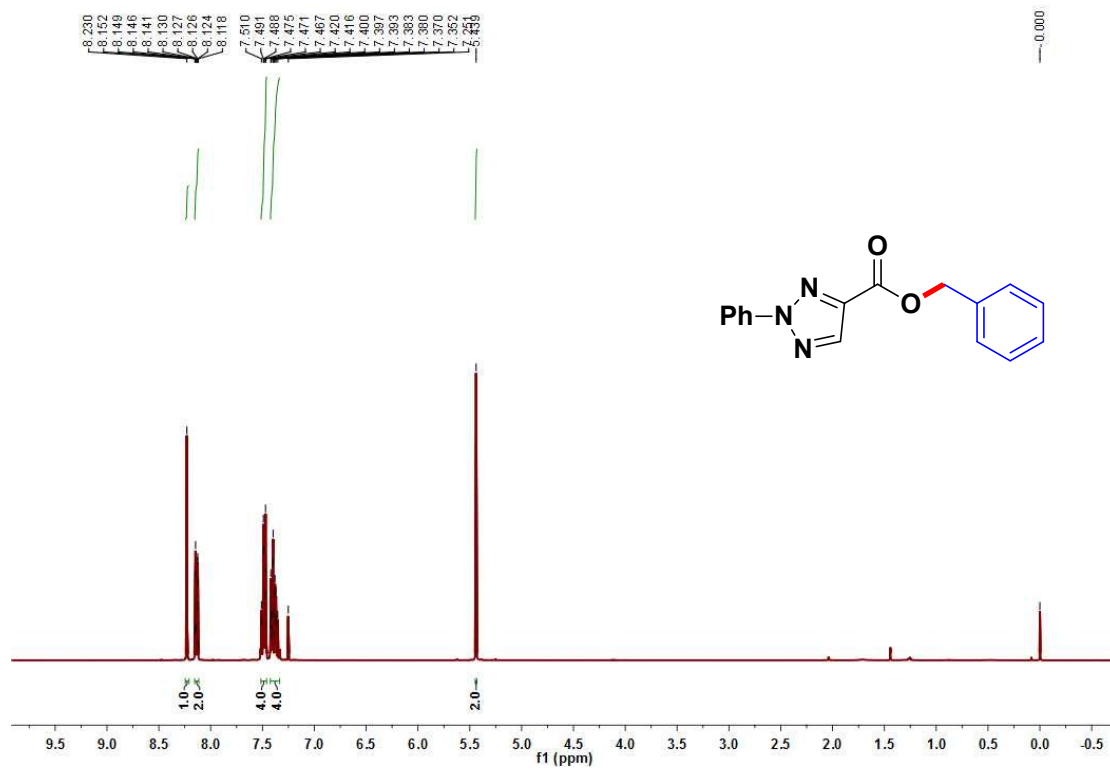
### 3u: benzyl cinnamate



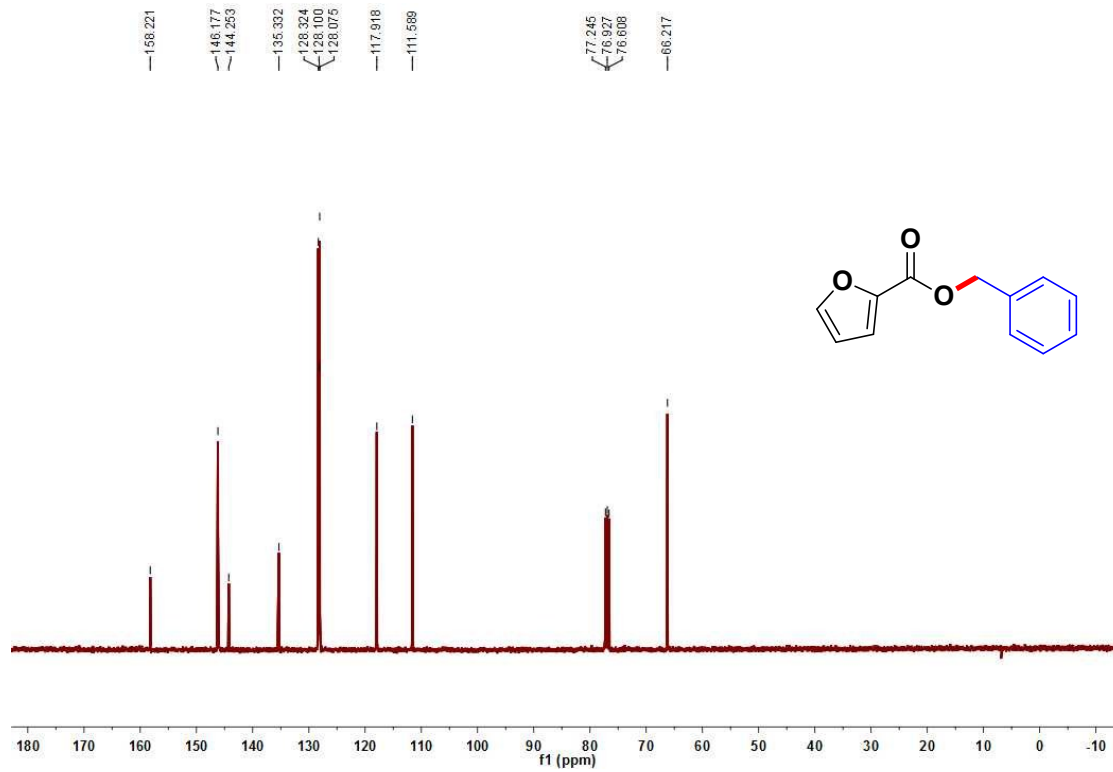
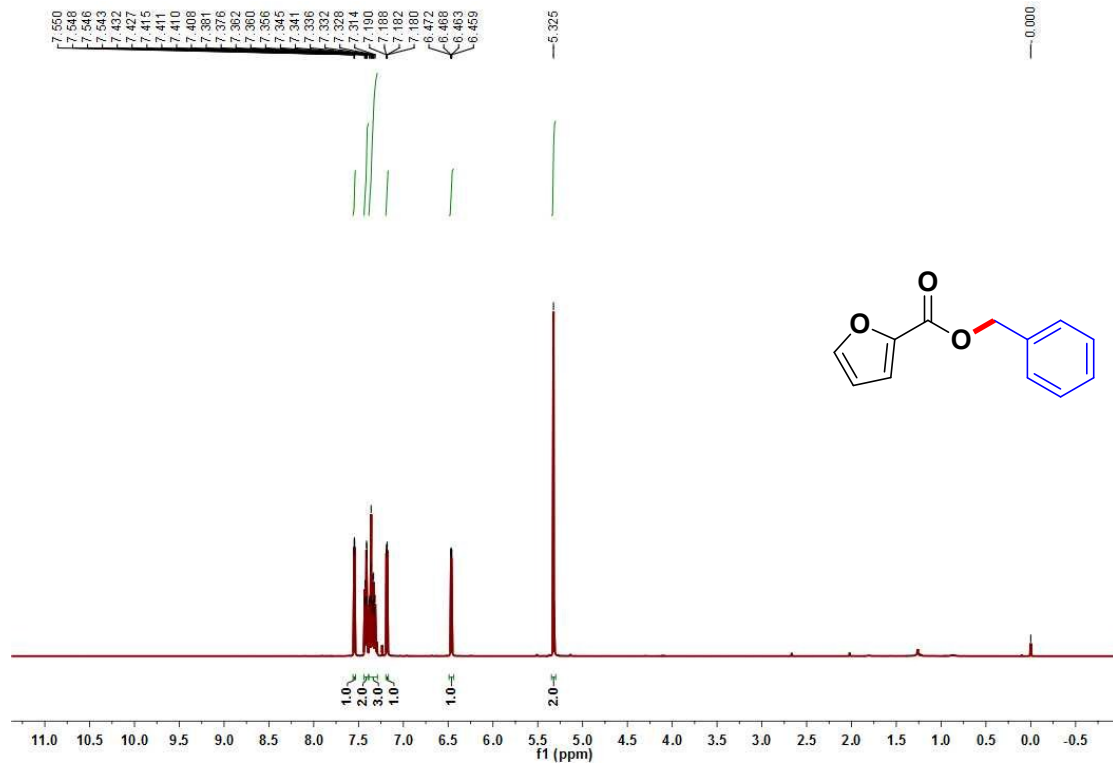
**3v: dibenzyl terephthalate**



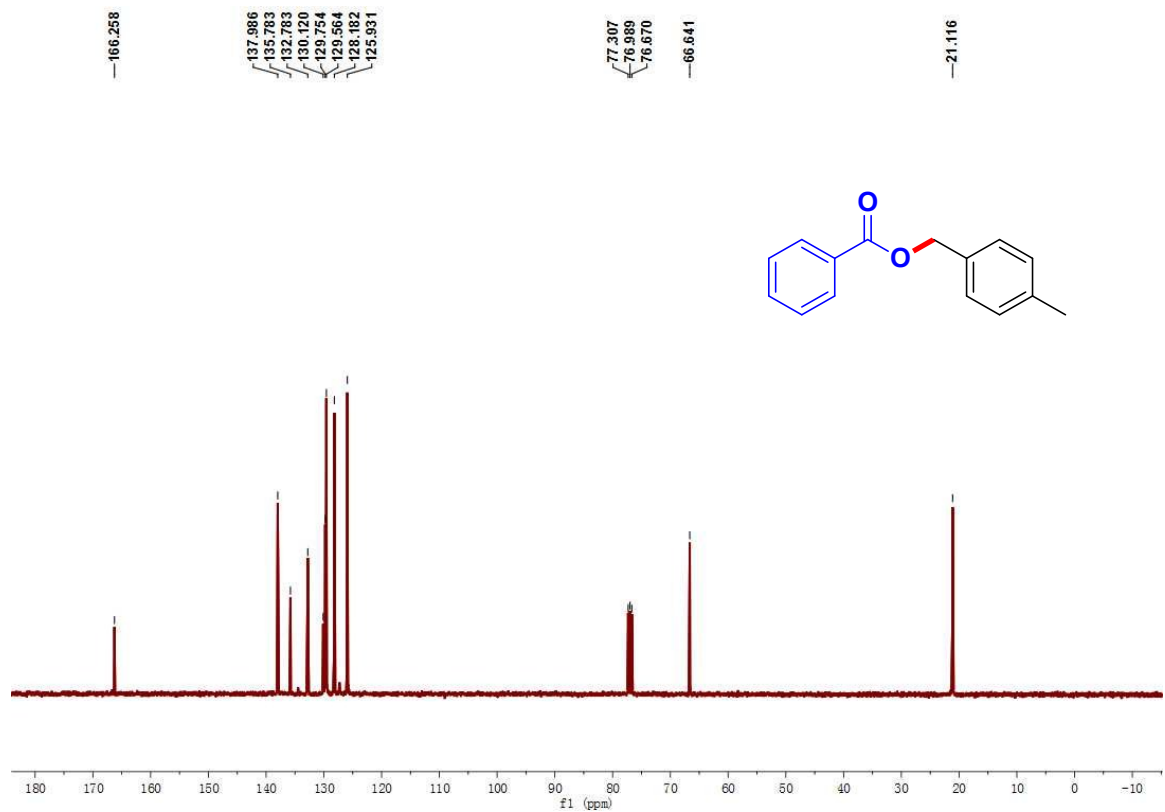
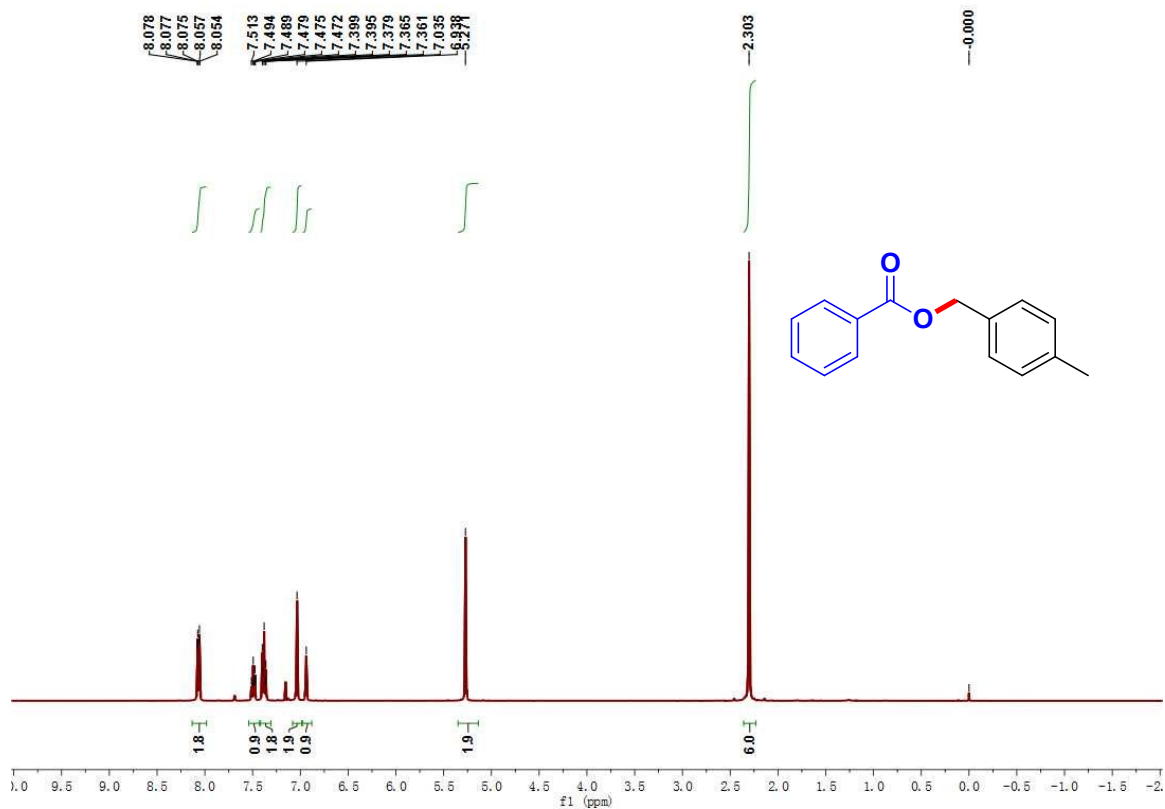
**3w: benzyl 2-phenyl-2H-1,2,3-triazole-4-carboxylate**



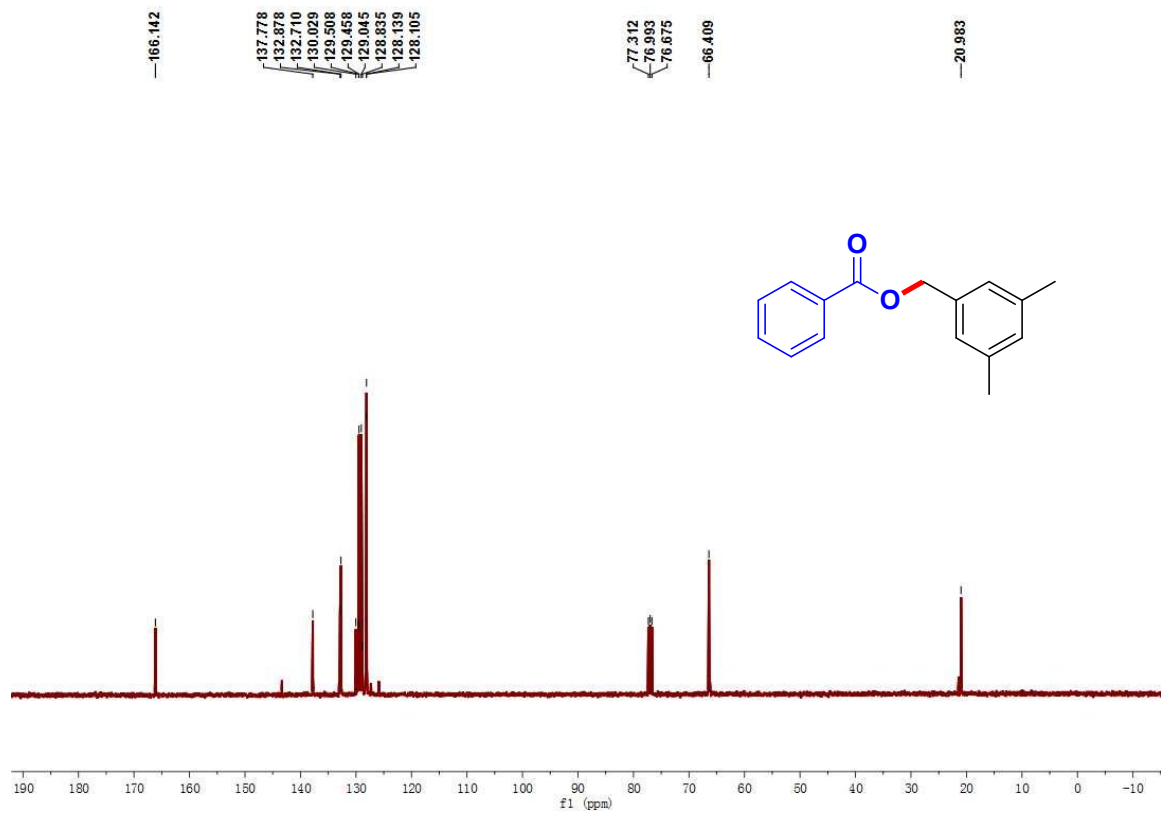
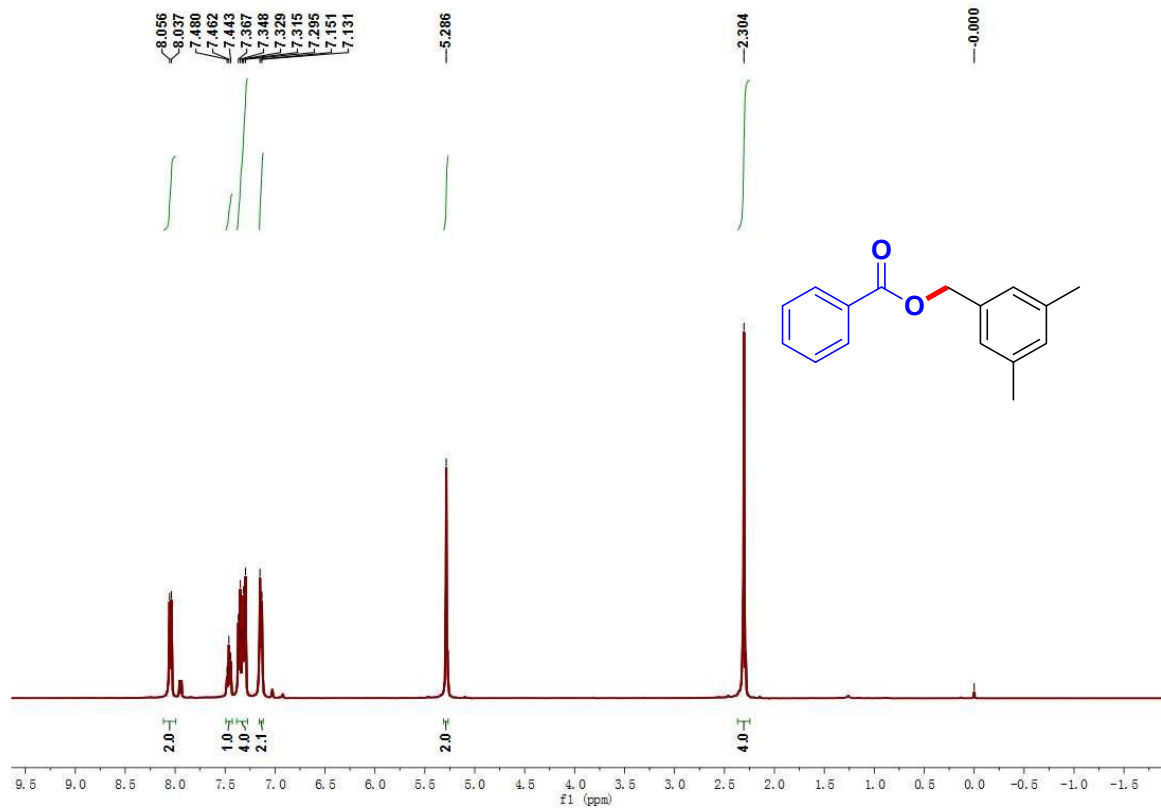
### 3x: benzyl furan-2-carboxylate



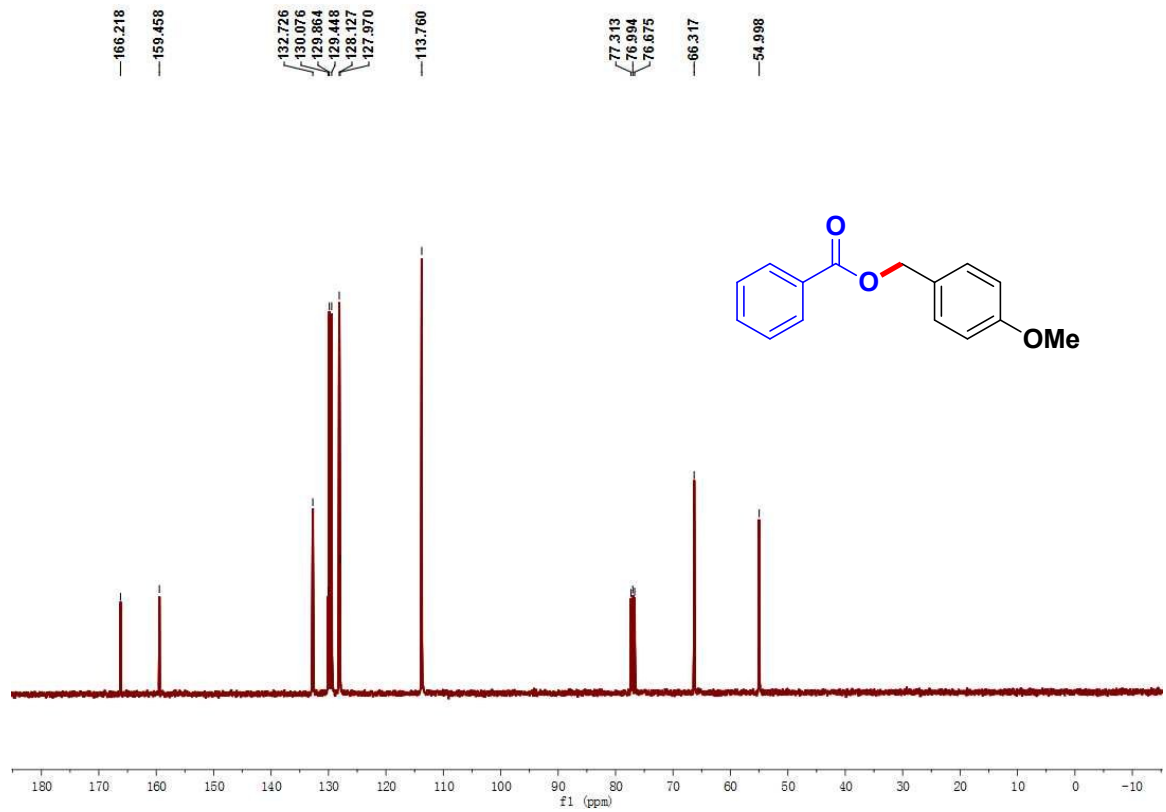
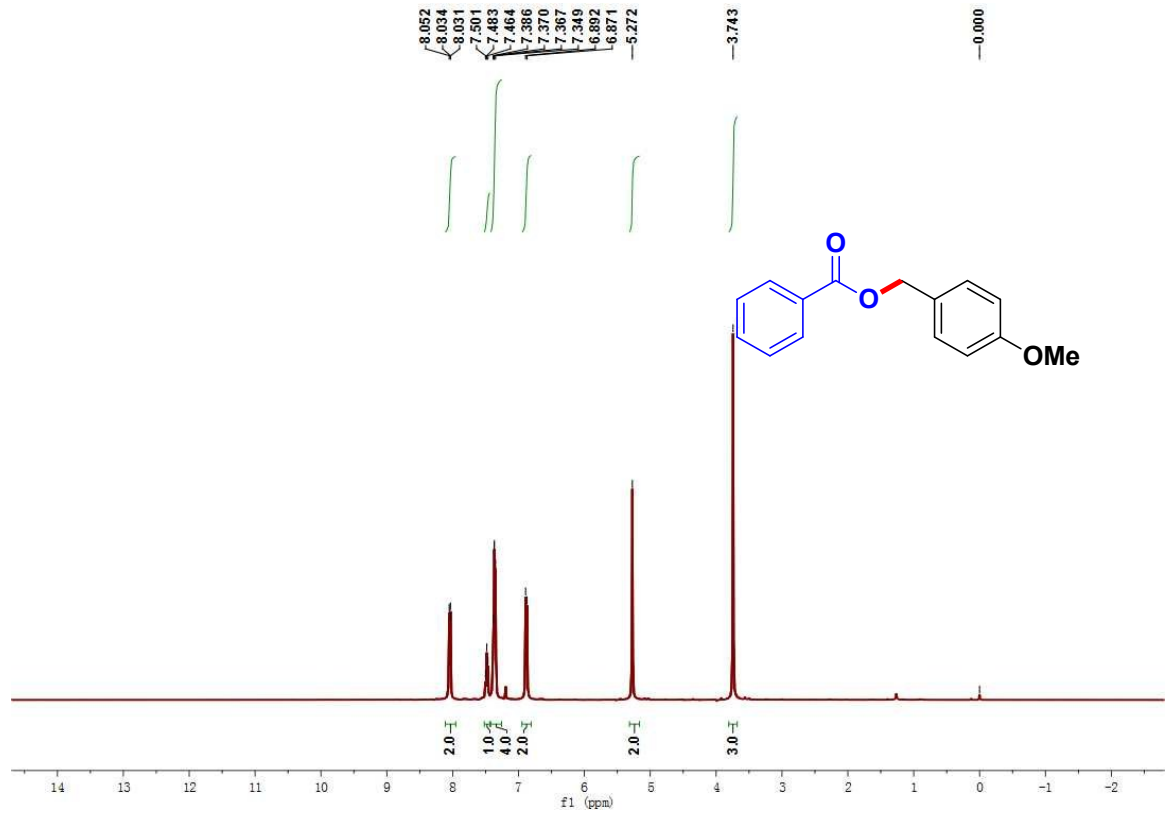
### 4a: 4-methylbenzyl benzoate



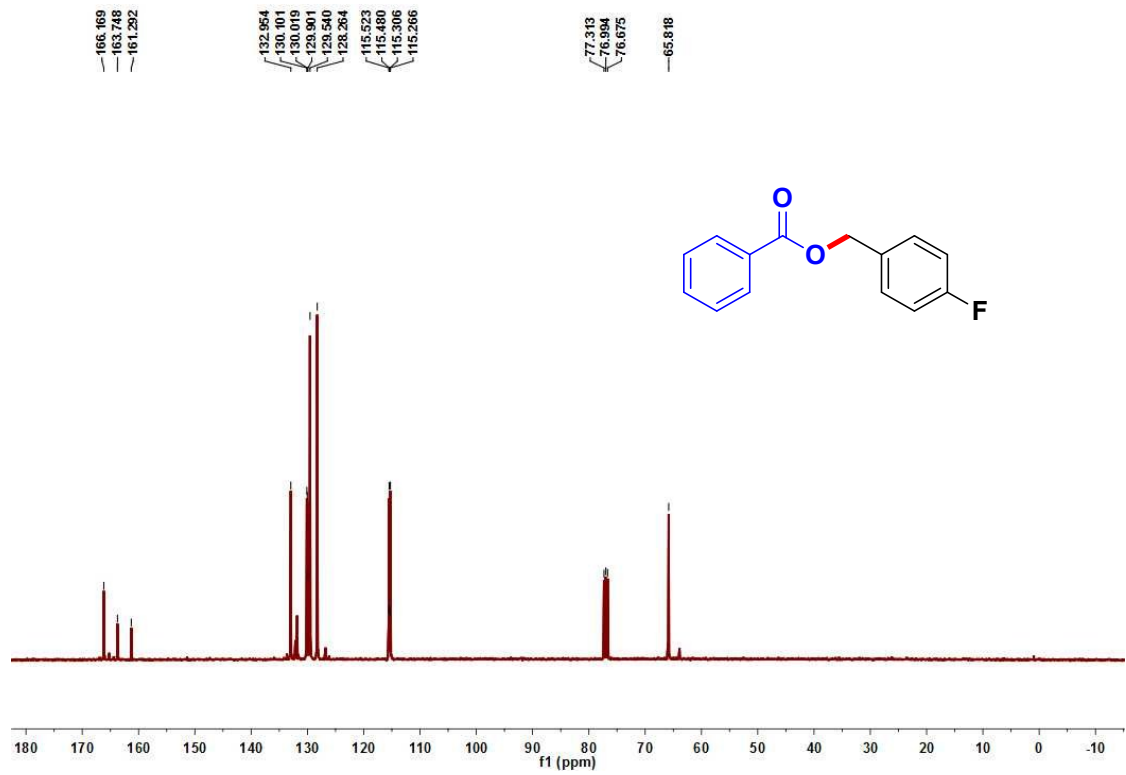
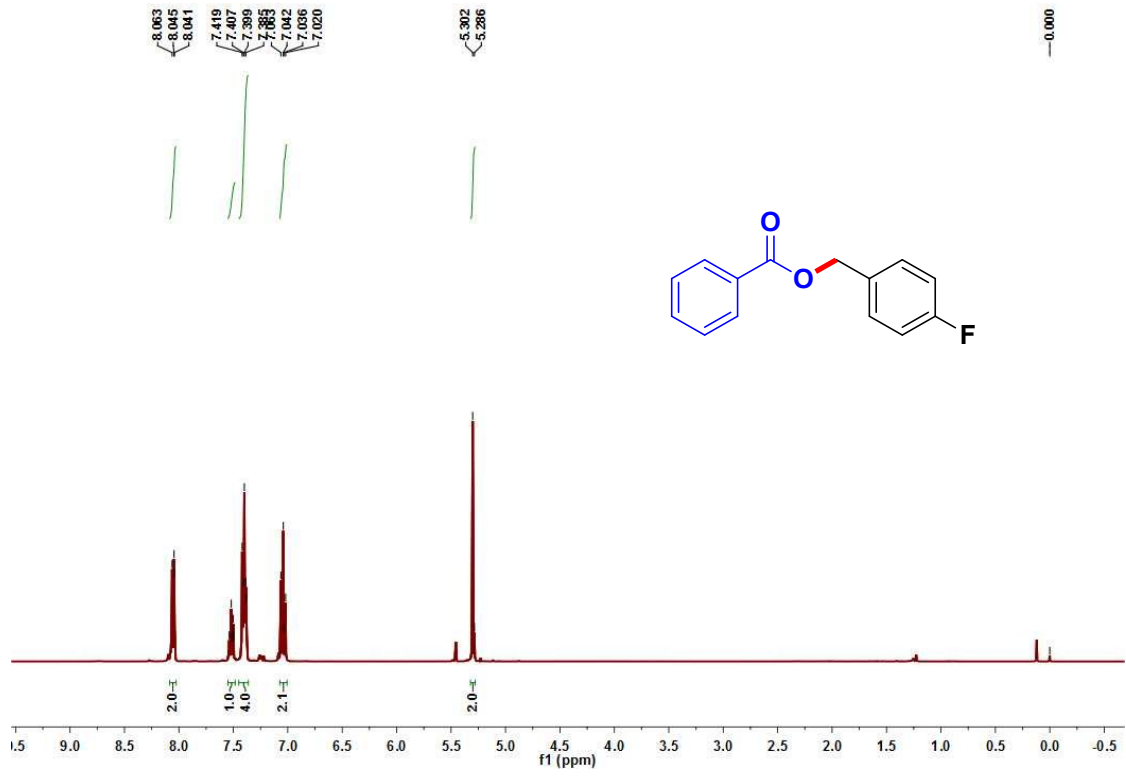
**4b: 3,5-dimethylbenzyl benzoate**



4c: 4-methoxybenzyl benzoate

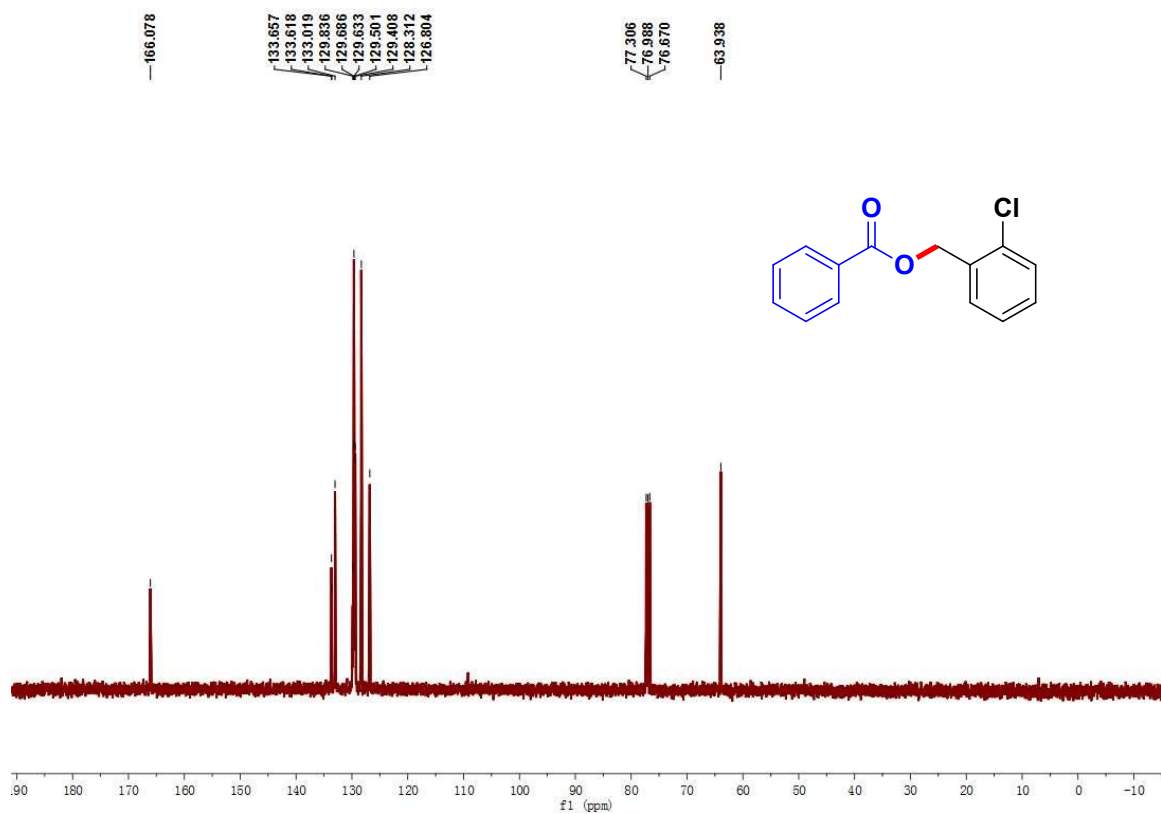
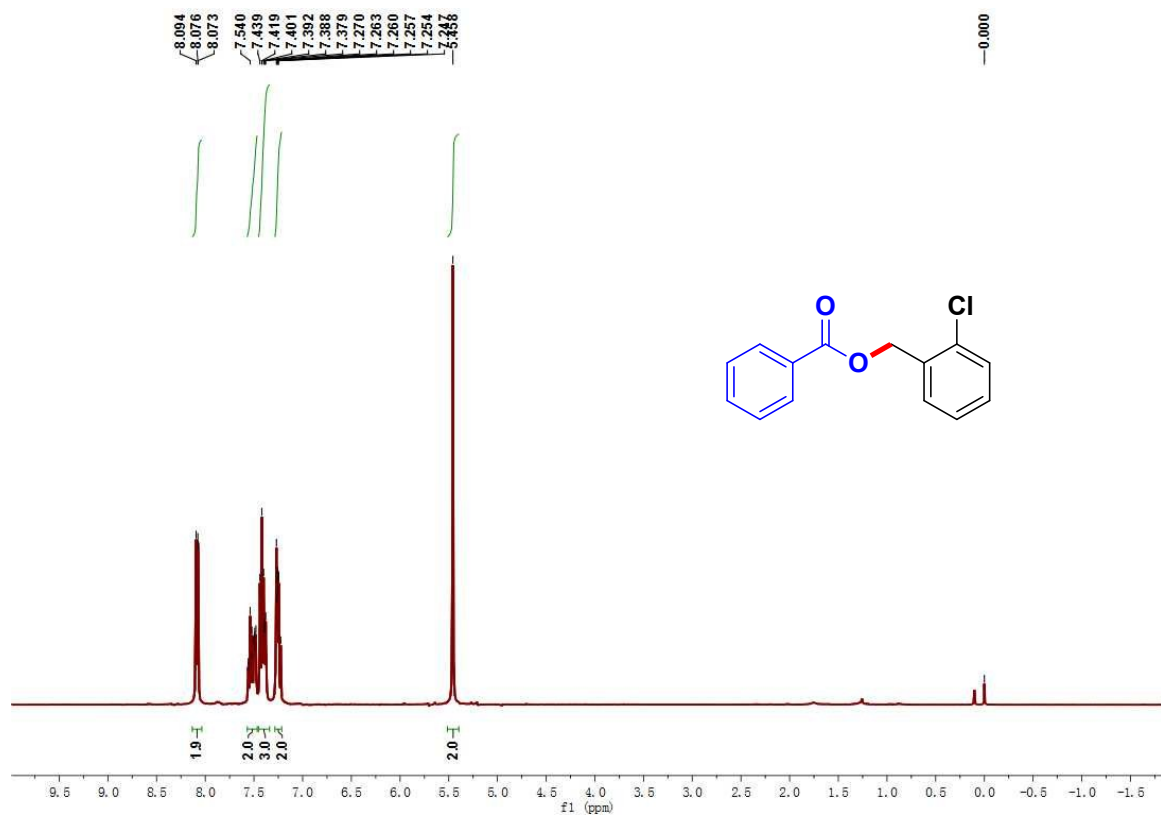


4d: 4-fluorobenzyl benzoate

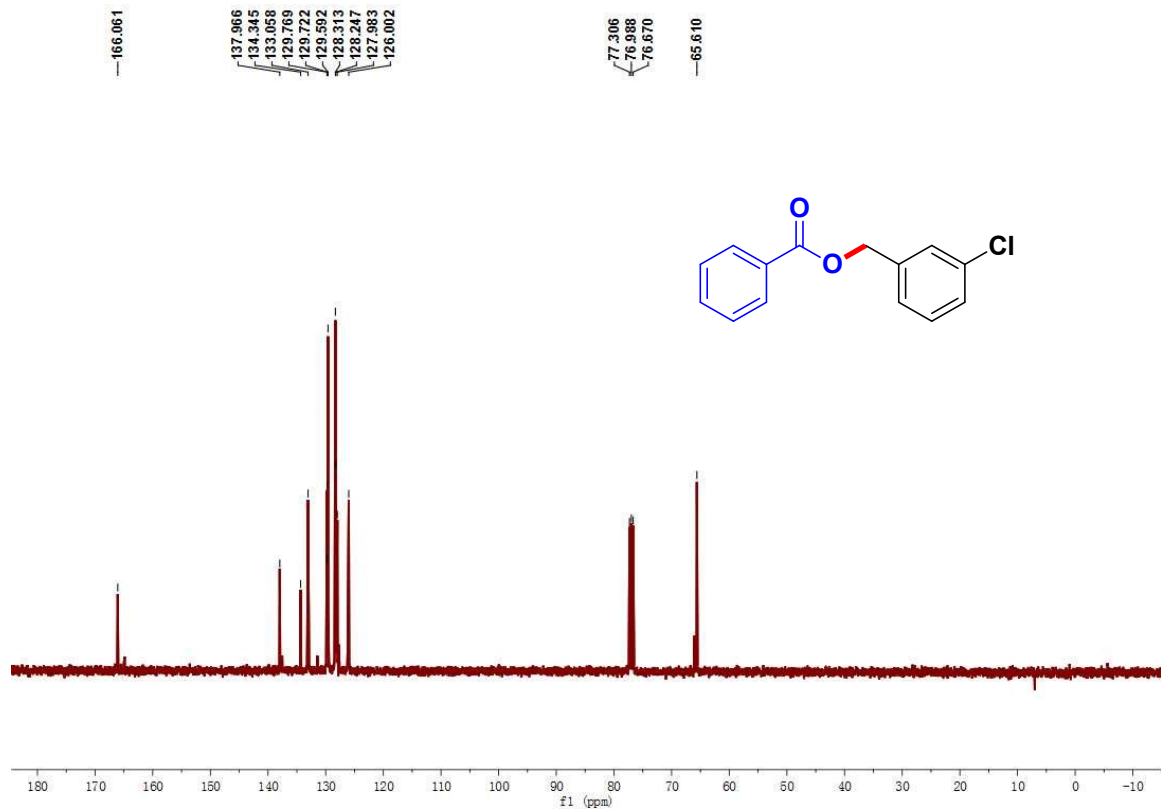
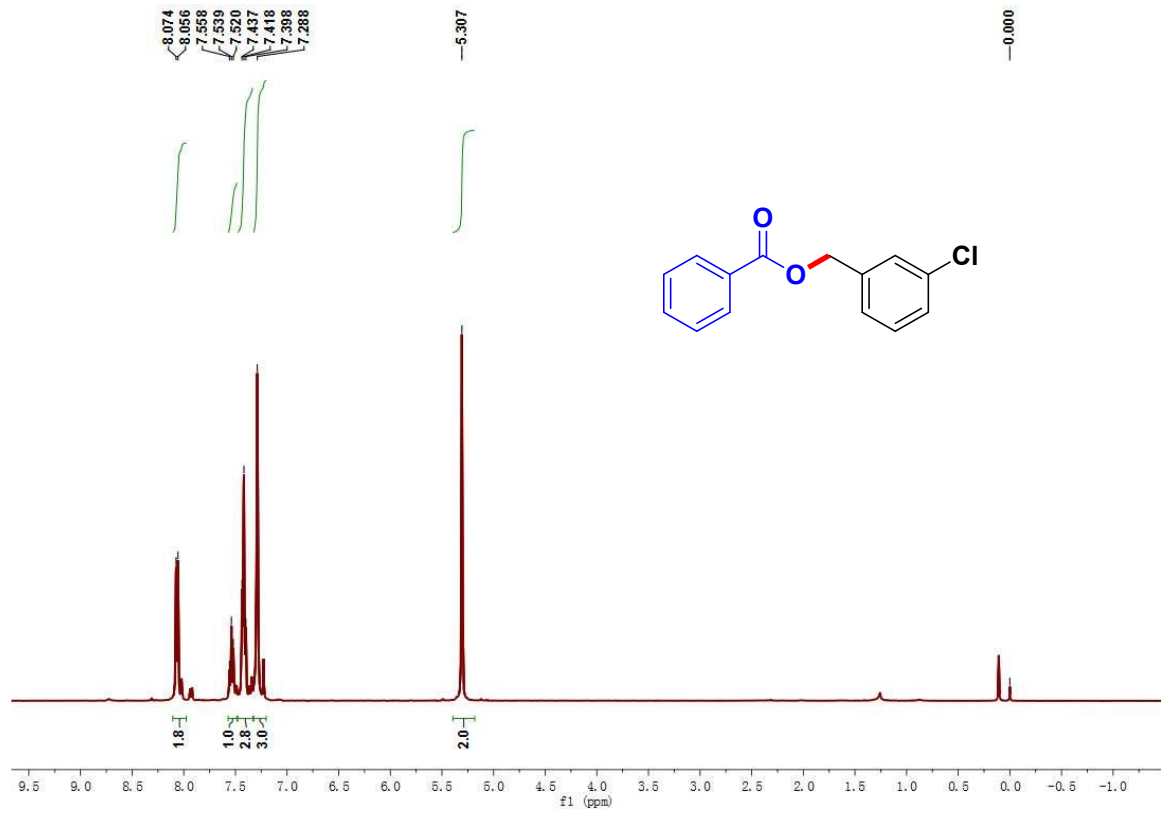




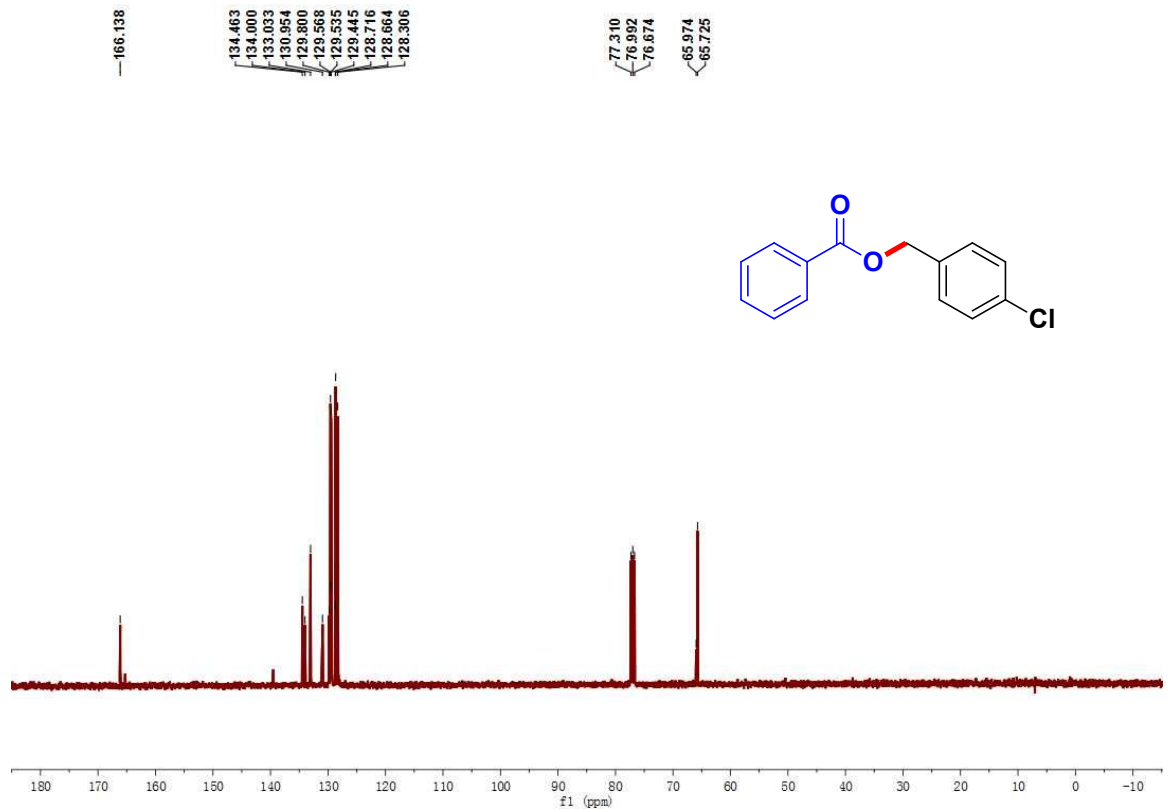
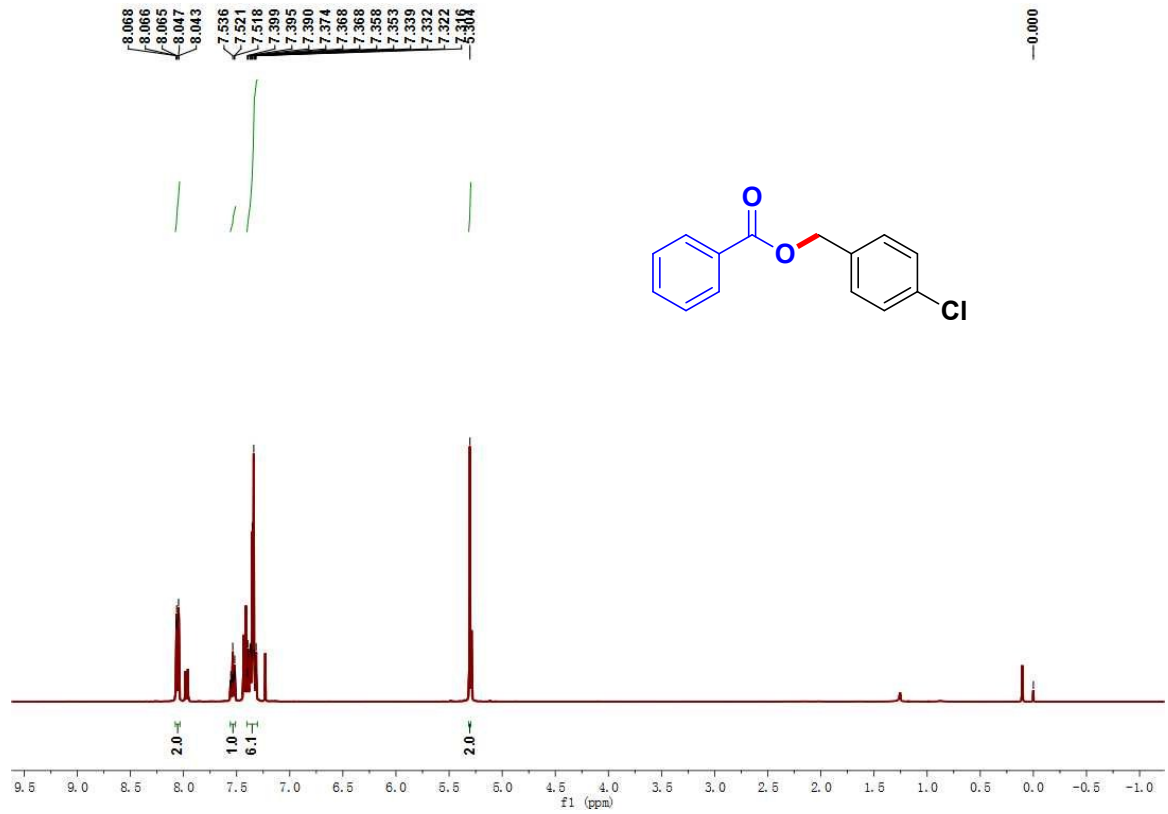
### 4e: 2-chlorobenzyl benzoate



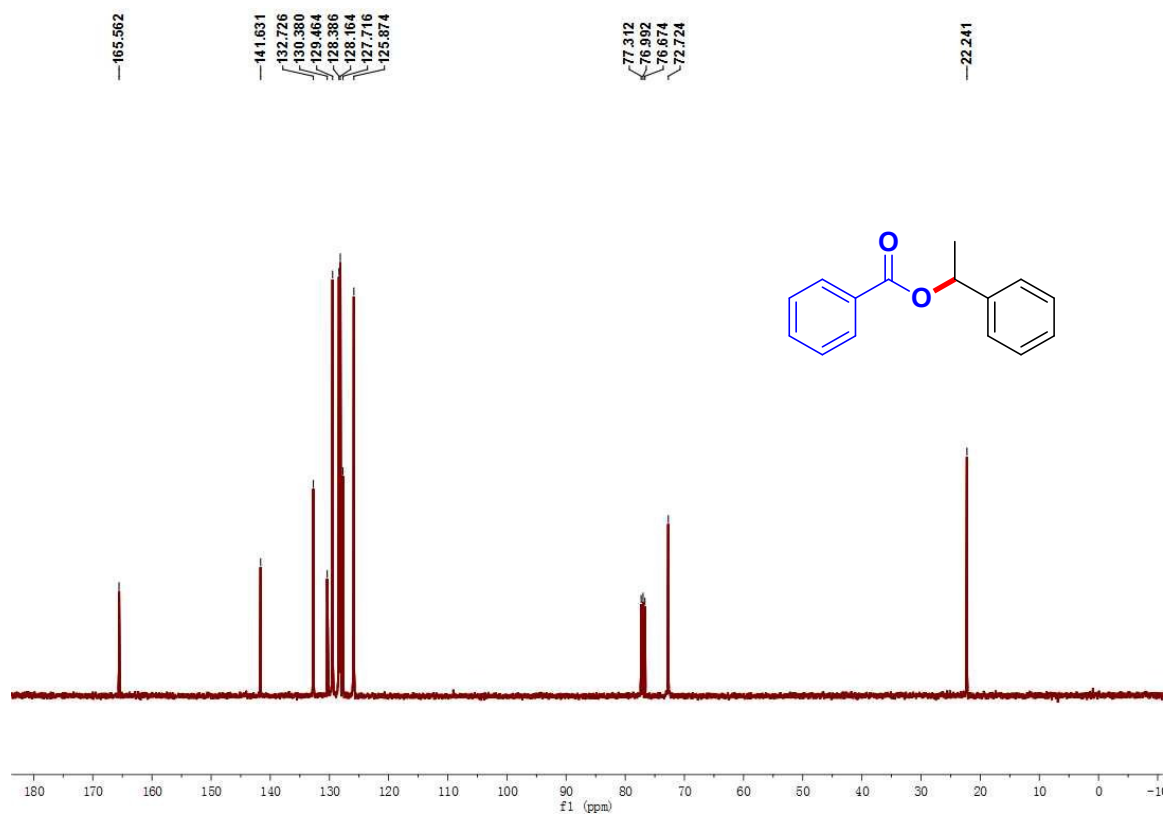
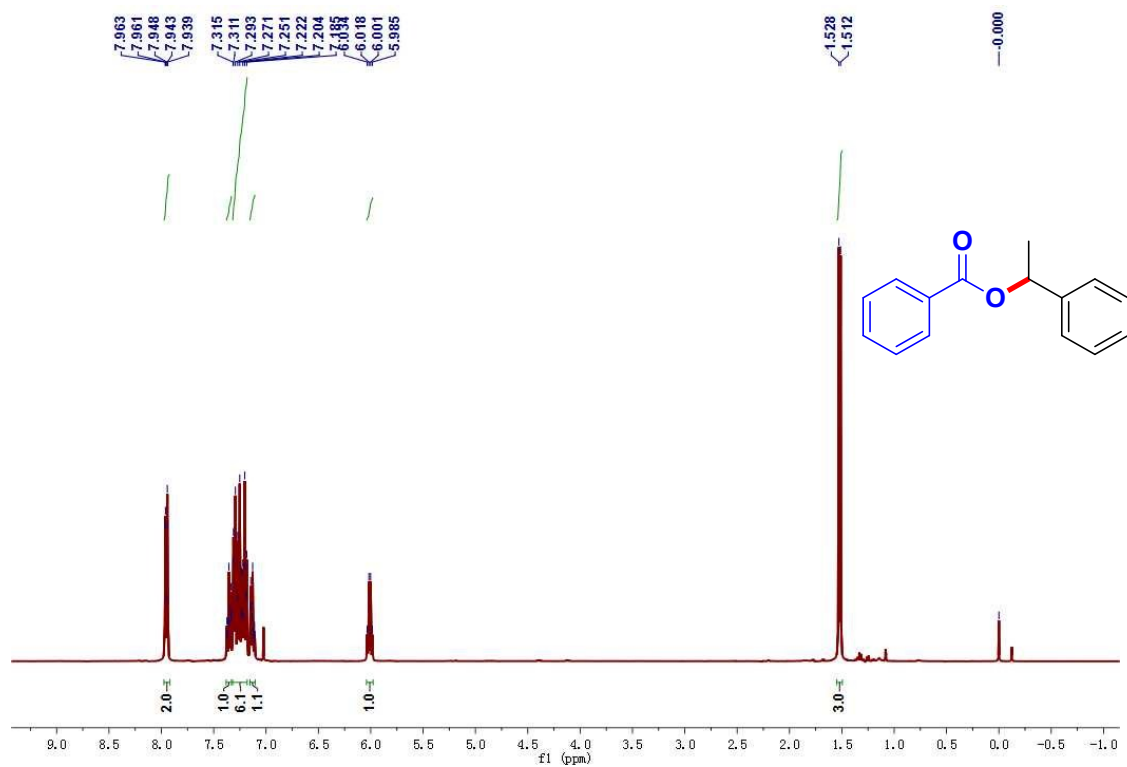
4f: 3-chlorobenzyl benzoate



4g: 4-chlorobenzyl benzoate



### 4h: (S)-1-phenylethyl benzoate



### 4i: 2-phenylpropan-2-yl benzoate

