Supporting Information for

Copper-Catalyzed Highly Efficient Ester Formation from Carboxylic acids /Esters and Formates

Jun Liu, a Changdong Shao, a Yanghui Zhang, a,b,* Guangfa Shi, a Shulei Pan a

Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai, 200092, China. *To correspondence should be addressed. Email:

zhangyanghui@tongji.edu.cn

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**General Information:** Cu(O Tf)$_2$ was purchased from Accela ChemBio Co., Ltd.. Solvent was dried by molecular sieve 5A. Unless otherwise noted, the other commercial materials were used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded with Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. $^1$H NMR spectra were recorded in CDCl$_3$ and referenced to residual CHCl$_3$ at 7.26 ppm, and $^{13}$C NMR spectra were referenced to the central peak of CDCl$_3$ at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance.

**I. General procedure for screening of reaction conditions:** A 50 mL sealed tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with Cu(O Tf)$_2$ (18.1 mg, 0.05 mmol), followed by benzoic acid (61.1 mg, 0.5 mmol), n-pentyl formate, TBHP, and solvents. After the reaction mixture was stirred at 130 °C for 12 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with saturated aqueous NaHCO$_3$ (5 mL) and brine (5 mL, twice). The organic phase was dried (Na$_2$SO$_4$) and concentrated in vacuo. The yield was determined by $^1$H NMR analysis of crude product using CHCl$_3$ as the internal standard.
Table 1. Survey of Reaction Conditions

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>2a</th>
<th>solvent</th>
<th>oxidant</th>
<th>yield %&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
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<td>1,4-dioxane</td>
<td>K$_2$S$_2$O$_8$</td>
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<tr>
<td>2</td>
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<td>CH$_2$CN</td>
<td>K$_2$S$_2$O$_8$</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
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<td>K$_2$S$_2$O$_8$</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
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<td>K$_2$S$_2$O$_8$</td>
<td>5</td>
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<tr>
<td>5</td>
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<td>DCE</td>
<td>K$_2$S$_2$O$_8$</td>
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</tr>
<tr>
<td>6</td>
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<td>DCE</td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>oxone</td>
<td>&lt;3</td>
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<tr>
<td>8</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>AcOOH</td>
<td>17</td>
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<tr>
<td>9</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>DCP</td>
<td>78</td>
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<tr>
<td>10</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>DTBP</td>
<td>91</td>
</tr>
<tr>
<td>11</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>TBHP</td>
<td>94</td>
</tr>
<tr>
<td>12</td>
<td>4.0 equiv.</td>
<td>DCE</td>
<td>TBHP</td>
<td>54&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>13</td>
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<td>DCE</td>
<td>TBHP</td>
<td>&lt;3&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>3.0 equiv.</td>
<td>DCE</td>
<td>TBHP</td>
<td>93(85)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
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<td>DCE</td>
<td>TBHP</td>
<td>66</td>
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<td>1.0 equiv.</td>
<td>DCE</td>
<td>TBHP</td>
<td>49</td>
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<tr>
<td>17</td>
<td>3.0 equiv.</td>
<td>DCE</td>
<td>----</td>
<td>24</td>
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<td>3.0 equiv.</td>
<td>DCE</td>
<td>TBHP</td>
<td>&lt;3&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>19</td>
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<td>DCE</td>
<td>TBHP</td>
<td>67&lt;sup&gt;c&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup> The yields were determined by $^1$H NMR analysis of crude products using CHCl$_3$/CHCl$_2$ as the internal standard. DBPT = tert-Butyl peroxide, TBHP = tert-Butyl hydroperoxide, DCP = Dicumyl peroxide, DCE = 1,2-Dichloroethane.

Reaction condition: 1a (0.5 mmol), 2a (3.0 equiv), Cu(OTf)$_2$ (10% mol), TBHP (2.0 equiv), 130 °C, 12 h, all of the reactions were run under air.<sup>b</sup> Cu(OTf)$_2$ = 5% mol, <sup>c</sup> Cu(OTf)$_2$ = 1% mol, <sup>d</sup> isolated yield.<sup>e</sup> No Cu(OTf)$_2$ / 110 °C.

II. General procedure for Cu-catalyzed esterification/transesterification of carboxylic acids/esters: A 50 mL sealed tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with Cu(OTf)$_2$ (18.1 mg, 0.05 mmol) followed by carboxylic acid or benzoates (0.5 mmol), formats (1.5 mmol), THBP (100.2 μL, 1.0 mmol), and DCE (1.0 mL). After the reaction mixture was stirred at 130°C for 12 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with saturated aqueous NaHCO$_3$ (5 mL) and brine (5
mL, twice). The organic phase was dried (Na$_2$SO$_4$) and concentrated *in vacuo*. The residue was purified by silica gel preparative TLC to give the corresponding product.

**Scheme 1.** Copper-Catalyzed Pentylation of Various Aromatic Carboxylic Acids.

![Chemical reaction scheme]

**Scheme 1.** Copper-Catalyzed Pentylation of Various Aromatic Carboxylic Acids.
### Table 2 Copper-Catalyzed Esterification of Benzoic Acids with Various Formates.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>3ab</td>
<td>82%</td>
</tr>
<tr>
<td>2</td>
<td>2c</td>
<td>3ac</td>
<td>51%$^b$</td>
</tr>
<tr>
<td>3</td>
<td>2d</td>
<td>3ad</td>
<td>47%</td>
</tr>
<tr>
<td>4</td>
<td>2e</td>
<td>3ae</td>
<td>0%</td>
</tr>
</tbody>
</table>

### Table 3 Copper-Catalyzed Transesterification of Benzoates with Pentyl Formate.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>yield</th>
<th>entry</th>
<th>substrate</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3af</td>
<td>91%</td>
<td>4</td>
<td>3ah</td>
<td>86%</td>
</tr>
<tr>
<td>2</td>
<td>3ag</td>
<td>72%</td>
<td>5</td>
<td>3ai</td>
<td>74%</td>
</tr>
<tr>
<td>3</td>
<td>3ac</td>
<td>92%</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
III. Characterization of the synthesized compounds

pentyl benzoate (3aa)

\[
\text{Colorless oil; } ^1H \text{ NMR (400 MHz, CDCl}_3): \delta = 8.05 (d, J = 7.8 \text{ Hz}, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 4.32 (t, J = 6.7 \text{ Hz}, 2H), 1.84-1.69 (m, 2H), 1.49-1.31 (m, 4H), 0.93 (t, J = 6.7 \text{ Hz}, 3H). ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta = 166.64, 132.73, 130.52, 129.49, 128.27, 65.08, 28.41, 28.18, 22.34, 13.95. \text{ HRMS (ESI-TOF) } m/z: \text{ calcd for C}_{12}H_{16}NaO}_2^+: 215.1043 (M + Na)^+, \text{ found: 215.1042.}
\]

pentyl 2-methylbenzoate (3ba)

\[
\text{Colorless oil; } ^1H \text{ NMR (400 MHz, CDCl}_3): \delta = 7.92-7.90 (m, 1H), 7.43-7.36 (m, 1H), 7.29-7.20 (m, 2H), 4.30 (t, J = 6.8 \text{ Hz}, 2H), 2.60 (s, 3H), 1.81-1.71 (m, 2H), 1.49-1.33 (m, 4H), 0.93 (t, J = 7.2 \text{ Hz}, 3H). ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta = 167.77, 139.96, 131.75, 131.60, 130.47, 130.02, 125.63, 64.88, 28.43, 28.26, 22.34, 21.70, 13.96. \text{ HRMS (ESI-TOF) } m/z: \text{ calcd for C}_{13}H_{18}NaO}_2^+: 229.1199 (M + Na)^+, \text{ found: 229.1201.}
\]

pentyl 3-methylbenzoate (3ca)

\[
\text{Colorless oil; } ^1H \text{ NMR (400 MHz, CDCl}_3): \delta = 7.91-7.81 (m, 2H), 7.40-7.28 (m, 2H), 4.31 (t, J = 6.8 \text{ Hz}, 2H), 2.40 (s, 3H), 1.83-1.71 (m, 2H), 1.49-1.30 (m, 4H), 0.93 (t, J = 7.2 \text{ Hz}, 3H). ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta = 166.84, 138.05, 133.50, 130.47, 130.04, 128.18, 126.64, 65.04, 28.44, 28.18, 22.35, 21.25, 13.96. \text{ HRMS (ESI-TOF) } m/z: \text{ calcd for C}_{13}H_{18}NaO}_2^+: 229.1199 (M + Na)^+, \text{ found: 229.1196.}
\]

pentyl 4-methylbenzoate (3da)

\[
\text{Colorless oil; } ^1H \text{ NMR (400 MHz, CDCl}_3): \delta = 7.94 (d, J = 8.0 \text{ Hz}, 2H), 7.23 (d, J = 8.0 \text{ Hz}, 2H), 4.30 (t, J = 6.8 \text{ Hz}, 2H), 2.40 (s, 3H), 1.83-1.70 (m, 2H), 1.49-1.32 (m, 4H), 0.93 (t, J = 6.8 \text{ Hz}, 3H). ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta = 166.70, 143.32,
pentyl 2-fluorobenzoate (3ea)

Colorless oil; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.97-7.87 \) (m, 1H), \( 7.55-7.43 \) (m, 1H), \( 7.23-7.07 \) (m, 2H), \( 4.32 \) (t, \( J = 6.8 \) Hz, 2H), \( 1.82-1.68 \) (m, 2H), \( 1.48-1.31 \) (m, 4H), \( 0.92 \) (t, \( J = 6.8 \) Hz, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 164.46 \) (d, \( J_{C,F} = 3.6 \) Hz), \( 161.89 \) (d, \( J_{C,F} = 258.2 \) Hz), \( 134.19 \) (d, \( J_{C,F} = 8.9 \) Hz), \( 131.99 \), \( 123.81 \) (d, \( J_{C,F} = 3.9 \) Hz), \( 119.07 \) (d, \( J_{C,F} = 9.8 \) Hz), \( 116.85 \) (d, \( J_{C,F} = 22.3 \) Hz), \( 65.39 \), \( 28.39 \), \( 28.04 \), \( 22.59 \), \( 13.88 \). HRMS (ESI-TOF) \( m/z \): calcd for \( C_{12}H_{15}FNaO_2^+ \): 233.0948 (M + Na)^+, found: 233.0949.

pentyl 3-fluorobenzoate (3fa)

Colorless oil; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.87-7.79 \) (m, 1H), \( 7.76-7.67 \) (m, 1H), \( 7.45-7.35 \) (m, 1H), \( 7.29-7.19 \) (m, 1H), \( 4.31 \) (t, \( J = 6.8 \) Hz, 2H), \( 1.82-1.70 \) (m, 2H), \( 1.48-1.30 \) (m, 4H), \( 0.93 \) (t, \( J = 7.2 \) Hz, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.46 \) (d, \( J_{C,F} = 3.0 \) Hz), \( 162.53 \) (d, \( J_{C,F} = 254.3 \) Hz), \( 132.71 \) (d, \( J_{C,F} = 7.4 \) Hz), \( 129.90 \) (d, \( J_{C,F} = 7.7 \) Hz), \( 125.23 \) (d, \( J_{C,F} = 3.1 \) Hz), \( 119.79 \) (d, \( J_{C,F} = 21.2 \) Hz), \( 116.39 \) (d, \( J_{C,F} = 22.8 \) Hz), \( 65.47 \), \( 28.35 \), \( 28.14 \), \( 22.31 \), \( 13.91 \). HRMS (ESI-TOF) \( m/z \): calcd for \( C_{12}H_{15}FNaO_2^+ \): 233.0948 (M + Na)^+, found: 233.0944.

pentyl 4-fluorobenzoate (3ga)

Colorless oil; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.11-7.99 \) (m, 2H), \( 7.16-7.05 \) (m, 2H), \( 4.30 \) (t, \( J = 6.8 \) Hz, 2H), \( 1.81-1.70 \) (m, 2H), \( 1.47-1.31 \) (m, 4H), \( 0.92 \) (t, \( J = 7.2 \) Hz, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.67 \), \( 165.66 \) (d, \( J_{C,F} = 252.0 \) Hz), \( 132.01 \) (d, \( J_{C,F} = 9.2 \) Hz), \( 126.77 \) (d, \( J_{C,F} = 3.0 \) Hz), \( 115.39 \) (d, \( J_{C,F} = 21.8 \) Hz), \( 65.23 \), \( 28.39 \), \( 28.16 \), \( 22.32 \), \( 12.93 \). HRMS (ESI-TOF) \( m/z \): calcd for \( C_{12}H_{15}FNaO_2^+ \): 233.0948 (M + Na)^+, found: 233.0942.

pentyl 4-chlorobenzoate (3ha)

129.52, 128.97, 127.81, 64.88, 28.43, 28.18, 22.33, 21.57, 13.93. HRMS (ESI-TOF) \( m/z \): calcd for \( C_{13}H_{18}NaO_2^+ \): 229.1199 (M + Na)^+, found: 229.1199.
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.97$ (d, $J = 8.8$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 4.30 (t, $J = 6.7$ Hz, 2H), 1.85-1.70 (m, 2H), 1.47-1.32 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 165.76$, 139.20, 130.90, 128.99, 128.63, 65.35, 28.37, 28.15, 22.32, 13.93. HRMS (ESI-TOF) m/z: calcd for C$_{12}$H$_{15}$ClNaO$_2$+: 249.0653 (M + Na)$^+$, found: 249.0629.

pentyl 4-bromobenzoate (3ia)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 4.30 (t, $J = 6.7$ Hz, 2H), 1.82-1.69 (m, 2H), 1.47-1.29 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 165.84$, 131.60, 131.02, 129.40, 127.82, 65.34, 28.34, 28.12, 22.30, 13.92. HRMS (ESI-TOF) m/z: calcd for C$_{12}$H$_{15}$BrNaO$_2$+: 293.0148 (M + Na)$^+$, found: 293.0153.

pentyl 4-iodobenzoate (3ja)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.78$ (d, $J = 8.6$ Hz, 2H), 7.73 (d, $J = 8.6$ Hz, 2H), 4.30 (t, $J = 6.7$ Hz, 2H), 1.82-1.69 (m, 2H), 1.47-1.28 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 166.09$, 137.64, 130.96, 129.99, 100.47, 65.35, 28.35, 28.13, 22.31, 13.94. HRMS (ESI-TOF) m/z: calcd for C$_{12}$H$_{15}$INaO$_3$+: 341.0009 (M + Na)$^+$, found: 341.0009.

pentyl 4-methoxybenzoate (3ka)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.99$ (d, $J = 8.9$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 4.27 (t, $J = 6.7$ Hz, 2H), 3.84 (s, 3H), 1.81-1.67 (m, 2H), 1.49-1.32 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 166.39$, 163.22, 131.48, 123.00, 113.52, 64.77, 55.35, 28.46, 28.20, 22.34, 13.94. HRMS (ESI-TOF) m/z: calcd for C$_{13}$H$_{18}$NaO$_3$+: 245.1148 (M + Na)$^+$, found: 245.1145.

pentyl 4-(trifluoromethyl)benzoate (3la)
Colorless oil; $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta = 8.25$ (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 4.34 (t, $J = 6.7$ Hz, 2H), 1.81-1.67 (m, 2H), 1.49-1.32 (m, 4H), 0.92 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta = 165.44, 134.31$ (q, $J_{\text{C,F}} = 32.4$ Hz), 133.74, 129.92, 125.35 (q, $J_{\text{C,F}} = 3.7$ Hz), 123.65 (q, $J_{\text{C,F}} = 271.0$ Hz), 65.69, 28.33, 28.14, 22.32, 13.93.

**pentyl 4-nitrobenzoate (3ma)**

Colorless oil; $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta = 8.28$ (d, $J = 8.9$ Hz, 2H), 8.11 (d, $J = 8.9$ Hz, 2H), 4.36 (t, $J = 6.8$ Hz, 2H), 1.85-1.71 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta = 164.69, 150.46, 135.86, 130.60, 123.45, 66.06, 28.27, 28.08, 22.28, 13.89$. HRMS (ESI-TOF) $m/z$: calcd for C$_{12}$H$_{15}$NNaO$_4$+: 260.0893 (M + Na)$^+$, found: 260.0881.

**pentyl 4-acetylbenzoate (3na)**

Colorless oil; $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta = 8.12$ (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 8.4$ Hz, 2H), 4.34 (t, $J = 6.7$ Hz, 2H), 2.64 (s, 3H), 1.85-1.70 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta = 197.50, 165.77, 140.15, 134.30, 129.75, 128.15, 65.60, 28.35, 28.15, 26.83, 22.32, 13.94$. HRMS (ESI-TOF) $m/z$: calcd for C$_{14}$H$_{18}$NaO$_3^+$: 257.1148 (M + Na)$^+$, found: 257.1148.

**pentyl 4-hydroxybenzoate (3oa)**

Colorless oil; $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.8$ Hz, 2H), 7.89 (d, $J = 8.8$ Hz, 2H), 6.74 (br, 1H), 4.29 (t, $J = 6.6$ Hz, 2H), 1.81-1.69 (m, 2H), 1.47-1.29 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta = 167.09, 160.32, 131.88, 122.56, 115.25, 65.14, 28.42, 28.18, 22.33, 13.94$. HRMS (ESI-TOF) $m/z$: calcd for C$_{12}$H$_{16}$NaO$_3^+$: 231.0992 (M + Na)$^+$, found: 231.0986.
pentyl [1,1'-biphenyl]-2-carboxylate (3pa)

![Chemical structure of pentyl [1,1'-biphenyl]-2-carboxylate](image)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.87-7.79\) (m, 1H), 7.67-7.50 (m, 1H), 7.47-7.28 (m, 7H), 4.03 (t, \(J = 6.8\) Hz, 2H), 1.42-1.29 (m, 2H), 1.26-1.16 (m, 2H), 1.10-0.99 (m, 2H), 0.84 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 169.00, 142.31, 141.54, 131.43, 131.00, 130.62, 129.70, 128.35, 128.00, 127.14, 127.10, 65.18, 27.91, 27.86, 22.24, 13.85.\)

HRMS (ESI-TOF) \(m/z\): calcd for C\(_{18}\)H\(_{20}\)NaO\(_2^+\): 291.1356 (M + Na), found: 291.1367.

pentyl 3,5-dimethylbenzoate (3qa)

![Chemical structure of pentyl 3,5-dimethylbenzoate](image)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.66\) (s, 2H), 7.18 (s, 1H), 4.30 (t, \(J = 6.7\) Hz, 2H), 2.36 (s, 6H), 1.83-1.70 (m, 2H), 1.47-1.34 (m, 4H), 0.94 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 166.98, 137.90, 134.38, 130.40, 127.20, 64.96, 28.43, 28.16, 22.33, 21.11, 13.93.\)

HRMS (ESI-TOF) \(m/z\): calcd for C\(_{14}\)H\(_{20}\)NaO\(_2^+\): 243.1356 (M + Na), found: 243.1351.

pentyl 2-naphthoate (3ra)

![Chemical structure of pentyl 2-naphthoate](image)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.62\) (s, 1H), 8.13-8.02 (m, 1H), 7.96 (d, \(J = 7.6\) Hz, 1H), 7.88 (d, \(J = 8.4\) Hz, 2H), 7.63-7.48 (m, 2H), 4.39 (t, \(J = 6.8\) Hz, 2H), 1.89-1.77 (m, 2H), 1.54-1.36 (m, 4H), 0.96 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 166.78, 135.44, 132.48, 130.88, 129.29, 128.08, 128.03, 127.76, 127.70, 126.52, 125.22, 65.24, 28.46, 28.20, 22.36, 13.96.\)

HRMS (ESI-TOF) \(m/z\): calcd for C\(_{16}\)H\(_{18}\)NaO\(_2^+\): 265.1199 (M + Na), found: 265.1197.

pentyl 3,5-dinitrobenzoate (3sa)

![Chemical structure of pentyl 3,5-dinitrobenzoate](image)
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.26-9.20 (m, 1H), 9.18-9.11 (m, 2H), 4.30 (t, $J = 6.8$ Hz, 2H), 1.90-1.77 (m, 2H), 1.50-1.34 (m, 4H), 0.94 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 162.53, 148.66, 134.16, 129.37, 122.25, 67.11, 28.22, 27.99, 22.27, 13.89.

**penty 1-methyl-4-nitrobenzoate(3ta)**

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.01 (s, 1H), 7.97 (s, 2H), 4.34 (t, $J = 6.8$ Hz, 2H), 2.62 (s, 3H), 1.85-1.72 (m, 2H), 1.49-1.30 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 164.88, 151.79, 134.11, 133.89, 133.38, 127.97, 124.50, 65.94, 28.30, 28.10, 22.30, 20.03, 13.92. HRMS (ESI-TOF) m/z: calcd for C$_{13}$H$_{17}$NNaO$_4$$: 274.1050 (M + Na)$^+$, found: 274.1027.

**pentyl 2-chloro-4-nitrobenzoate(3ua)**

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.31 (d, $J = 2.4$ Hz, 1H), 8.18-8.11 (m, 2H), 7.94 (d, $J = 8.4$ Hz, 1H), 4.38 (t, $J = 6.8$ Hz, 2H), 1.85-1.73 (m, 2H), 1.49-1.31 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 164.34, 149.34, 136.28, 134.64, 131.89, 125.94, 121.40, 66.60, 28.17, 28.05, 22.24, 13.90. HRMS (ESI-TOF) m/z: calcd for C$_{12}$H$_{14}$ClNNaO$_4$$: 294.0504 (M + Na)$^+$, found: 294.0508.

**pentyl cyclohexanecarboxylate(3va)**

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 4.00 (t, $J = 6.7$ Hz, 2H), 2.30-2.17 (m, 1H), 1.91-1.09 (m, 16H), 0.86 (t, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 176.02, 64.09, 43.17, 28.95, 28.28, 28.00, 25.70, 25.37, 22.22, 13.83. HRMS (ESI-TOF) m/z: calcd for C$_{12}$H$_{22}$NaO$_2$$: 221.1512 (M + Na)$^+$, found: 221.1511.

**pentyl octanoate(3wa)**

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 4.00 (t, $J = 6.8$ Hz, 2H), 2.23 (t, $J = 7.6$ Hz, 2H), 1.67-1.47 (m, 4H), 1.36-1.14 (m, 12H), 0.95-0.71 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 173.75, 64.20, 34.26, 31.58, 29.02, 28.84, 28.28, 28.01, 24.92,
22.49, 22.22, 13.90, 13.80. HRMS (ESI-TOF) m/z: calcd for C_{13}H_{26}NaO_{2}+: 237.1825 (M + Na)^+, found: 237.1823.

**pental 2-phenylacetate(3xa)**

![Chemical Structure](attachment:image.png)

Colorless oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.40-7.24\) (m, 5H), 4.11 (t, \(J = 6.8\) Hz, 2H), 3.64 (s, 2H), 1.72-1.57 (m, 2H), 1.45-1.25 (m, 4H), 0.91 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 171.65, 134.18, 128.21, 128.49, 126.98, 64.99, 41.47, 28.23, 27.97, 22.24, 13.91\). HRMS (ESI-TOF) m/z: calcd for C\(_{13}\)H\(_{18}\)NaO\(_2\)^+: 229.1199 (M + Na)^+, found: 229.1194.

**pental 3-phenylpropanoate(3ya)**

![Chemical Structure](attachment:image.png)

Colorless oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.38-7.17\) (m, 5H), 4.09 (t, \(J = 6.8\) Hz, 2H), 2.98 (t, \(J = 7.7\) Hz, 2H), 2.65 (t, \(J = 7.7\) Hz, 2H), 1.70-1.57 (m, 2H), 1.41-1.25 (m, 4H), 0.92 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 172.99, 140.56, 128.44, 128.26, 126.20, 64.62, 35.92, 30.99, 28.29, 28.02, 22.29, 13.93\). HRMS (ESI-TOF) m/z: calcd for C\(_{14}\)H\(_{20}\)NaO\(_2\)^+: 243.1356 (M + Na)^+, found: 243.1355.

**pental cinnamate(3za)**

![Chemical Structure](attachment:image.png)

Colorless oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.69\) (d, \(J = 16.0\) Hz, 1H), 7.58-7.47 (m, 2H), 7.44-7.36 (m, 3H), 6.45 (d, \(J = 16.0\) Hz, 1H), 4.20 (t, \(J = 6.8\) Hz, 2H), 1.78-1.67 (m, 2H), 1.45-1.32 (m, 4H), 0.99-0.86 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 172.99, 140.56, 128.44, 128.26, 126.20, 64.62, 35.92, 30.99, 28.29, 28.02, 22.29, 13.93\). HRMS (ESI-TOF) m/z: calcd for C\(_{14}\)H\(_{18}\)NaO\(_2\)^+: 241.1199 (M + Na)^+, found: 241.1200.

**propyl benzoate(3ab)**

![Chemical Structure](attachment:image.png)

Colorless oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.05\) (d, \(J = 7.6k\) Hz, 2H), 7.60-7.48 (m, 1H), 7.48-7.33 (m, 2H), 4.28 (t, \(J = 6.6\) Hz, 2H), 1.89-1.67 (m, 2H), 1.03 (t, \(J = 7.2\) Hz, 3H).
7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 166.51, 132.65, 130.44, 129.40, 128.18, 66.38, 22.02, 10.39. HRMS (ESI-TOF) $m/z$: calcd for C$_{10}$H$_{12}$NaO$_2^+$: 187.0730 (M + Na)$^+$, found: 187.0732.

**isopropyl benzoate(3ac)**

\[
\begin{align*}
\text{Colorless oil; } &^1\text{H NMR (400 MHz, CDCl$_3$): } \delta = 8.09-7.97 \text{ (m, 2H), 7.59-7.50} \text{ (m, 1H),} \\
&7.48-7.37 \text{ (m, 2H), 5.31-5.19} \text{ (m, 1H), 1.37} \text{ (d, } J = 6.4 \text{ Hz, 6H). } ^{13}\text{C NMR (100 MHz, CDCl$_3$): } \delta = 166.07, 132.64, 130.90, 129.46, 128.21, 68.29, 21.92. \text{ HRMS (ESI-TOF) } m/z: \text{ calcd for C$_{10}$H$_{12}$NaO$_2^+$: 187.0730 (M + Na)$^+$, found: 187.0730.}
\end{align*}
\]

**cyclohexyl benzoate(3ad)**

\[
\begin{align*}
\text{Colorless oil; } &^1\text{H NMR (400 MHz, CDCl$_3$): } \delta = 8.09-80.2 \text{ (m, 2H), 7.59-7.51} \text{ (d, } J = 7.4 \text{ Hz, 1H), 7.47-7.40} \text{ (m, 2H), 5.10-4.96} \text{ (m, 1H), 2.02-1.89} \text{ (m, 2H), 1.95-1.71} \text{ (m, 2H), 1.59-1.30} \text{ (m, 6H). } ^{13}\text{C NMR (100 MHz, CDCl$_3$): } \delta = 165.98, 132.64, 131.01, 129.51, 128.24, 73.01, 31.64, 25.48, 23.65. \text{ HRMS (ESI-TOF) } m/z: \text{ calcd for C$_{13}$H$_{16}$NaO$_2^+$: 227.1043 (M + Na)$^+$, found: 227.1042.}
\end{align*}
\]
IV. NMR spectra

Compound 3aa

$^1$H NMR

$^1$H NMR spectrum of Compound 3aa showing the proton resonances.

$^{13}$C NMR

$^{13}$C NMR spectrum of Compound 3aa showing the carbon resonances.
Compound 3ba

$^1$H NMR

13C NMR
Compound 3ca

$^1$H NMR

$^1^3$C NMR
Compound 3da

$^1$H NMR

$^1$C NMR
**Compound 3ea**

**$^1$H NMR**

![$^1$H NMR spectrum of Compound 3ea](image)

**$^{13}$C NMR**

![$^{13}$C NMR spectrum of Compound 3ea](image)
Compound 3fa

$^1$H NMR

$^{13}$C NMR
Compound 3ga

$^1$H NMR

$^{13}$C NMR
Compound 3ha

$^1$H NMR

$^1$C NMR
Compound 3ia

$^1$H NMR

$^1$C NMR
Compound 3ja

$^1$H NMR

$^{13}$C NMR
Compound 3ka

$^1$H NMR

$^1^3$C NMR
Compound 3ma

$^1$H NMR

$^1$C NMR
Compound 3na

$^1$H NMR

$^1$C NMR
Compound 30a

$^1$H NMR

$^13$C NMR
Compound 3pa

$^1$H NMR

$^{13}$C NMR
Compound 3qa

$^1$H NMR

$^1$C NMR

$^{13}$C NMR
Compound 3ra

$^1$H NMR

$^{13}$C NMR
Compound 3sa

**$^1$H NMR**

![Chemical structure](image1)

**$^{13}$C NMR**

![Chemical structure](image2)
Compound 3ta

$^1$H NMR

$^{13}$C NMR
Compound 3ua

$^1$H NMR

$^{13}$C NMR
Compound 3va

$^1$H NMR

$^{13}$C NMR
Compound 3wa

$^1$H NMR

$^{13}$C NMR
Compound 3xa

$^1$H NMR

$^{13}$C NMR
Compound 3ya

$^1$H NMR

$^1$C NMR

$^1$H NMR

$^1$C NMR
Compound 3za

$^1$H NMR

$^1$C NMR
Compound 3ab

$^1$H NMR

$^{13}$C NMR
Compound 3ac

\(^1\text{H NMR}\)

\(^{13}\text{C NMR}\)
Compound 3ad

$^1$H NMR

$^{13}$C NMR