

## Rhodium-Catalyzed Direct Oxidative Carbonylation of Aromatic C-H Bond with CO and Alcohols

Zheng-Hui Guan,<sup>†,‡</sup> Zhi-Hui Ren,<sup>†</sup> Stephen M. Spinella,<sup>‡</sup> Shichao Yu,<sup>‡</sup> Yong-Min Liang<sup>\*,†</sup> and Xumu Zhang<sup>\*,‡</sup>

*Department of Chemistry and Chemical Biology and Department of Pharmaceutical Chemistry, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854-8066, USA and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.*

(E-mail: [xumu@rci.rutgers.edu](mailto:xumu@rci.rutgers.edu))

### Context

<b>1. General information</b>	<b>S2</b>
<b>2. Typical procedure for carbonylation of 1 with CO and Alcohol</b>	<b>S2</b>
<b>3. Spectroscopic data for products 2</b>	<b>S2–S8</b>
<b>4. Copies of <math>^1\text{H}</math> NMR, <math>^{13}\text{C}</math> NMR and <math>^{19}\text{F}</math> NMR spectra</b>	<b>S9–S50</b>

### General information:

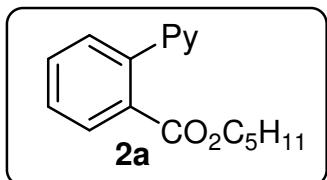
Column chromatography was carried out on silica gel.  $^1\text{H}$  NMR spectra were recorded on 500 MHz or 400 MHz in  $\text{CDCl}_3$  and  $^{13}\text{C}$  NMR spectra were recorded on 125 MHz or 100 MHz in  $\text{CDCl}_3$ . All new products were further characterized by HRMS; copies of their  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra are provided. Unless otherwise stated, all arenes and solvents were purchased from commercial suppliers and used without further purification. Other substrates (**1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1p**, **1q**, **1r**) were prepared according to the following literatures:

- (a) Liu, D.; Gao, W.; Dai, Q.; Zhang, X. *Org. Lett.* **2005**, 7, 4907-4910.
- (b) Kitamura, Y.; Sako, S.; Udzu, T.; Tsutsui, A.; Maegawa, T.; Monguchi, Y. and Sajiki, H. *Chem. Commun.*, **2007**, 5069–5071.

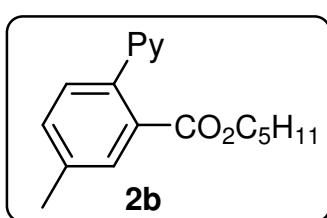
### Typical procedure for carbonylation of **1** with CO and Alcohol

A vial (5 mL) charged with arene **1** (0.1 mmol), *n*-pentanol (0.5 mmol), Oxone (185 mg, 0.3 mmol),  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (2 mol %) and toluene (2.0 mL) was stirred in a steel autoclave under CO (2 atm). After stirring at 110 °C for 8 h, the CO was released carefully and the solution was subjected to a short column of silica gel to remove the solid and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding products **2**.

### Spectroscopic data for products **2**

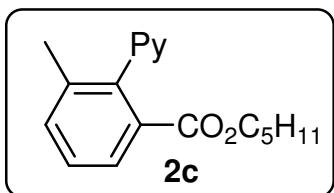


**2a:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) δ 8.65-8.64 (d,  $J = 4.0$  Hz, 1H), 7.85-7.83 (d,  $J = 7.5$  Hz, 1H), 7.76-7.73 (t,  $J = 7.5$  Hz, 1H), 7.55 (m, 2H), 7.49-7.46 (t,  $J = 7.5$  Hz, 2H), 7.26-7.24 (d,  $J = 7.5$  Hz, 1H), 4.09-4.06 (t,  $J = 6.5$  Hz, 2H), 1.44-1.40 (m, 2H), 1.24-1.21 (m, 2H), 1.13-1.08 (m, 2H), 0.86-0.83 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) δ 168.9, 158.9, 149.1, 140.9, 136.1, 131.9, 131.0, 129.8, 129.7, 128.3, 122.8, 122.0, 65.2, 28.0, 27.9, 22.3, 13.9. HRMS (ESI) Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_2$  ( $\text{MH}^+$ ): 270.1489, found ( $\text{MH}^+$ ): 270.1483.

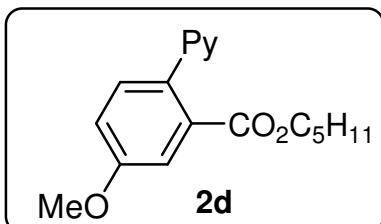


**2b:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) δ 8.64-8.63 (m, 1H), 7.73-7.70 (m, 1H), 7.63 (s, 1H), 7.46-7.43 (m, 2H), 7.37-7.35 (m, 1H), 7.24-7.21 (m, 1H), 4.08-4.05 (t,  $J = 6.5$  Hz, 2H), 2.44 (s, 1H), 1.44-1.38 (m, 2H), 1.26-1.19 (m, 2H), 1.11-1.07 (m, 2H), 0.85-0.82 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) δ 169.2, 158.9, 149.0, 138.3, 138.1, 136.0, 131.8, 131.6, 130.2, 129.7, 122.7, 121.8, 65.2, 28.0, 27.9, 22.3, 21.0, 13.9.

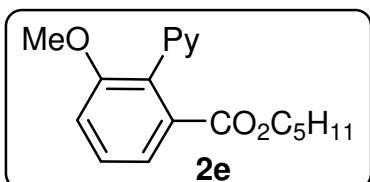
HRMS (ESI) Calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub> (MH<sup>+</sup>): 284.1645, found (MH<sup>+</sup>): 284.1638.



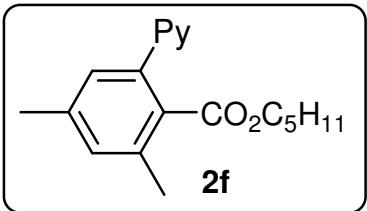
**2c:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.68-8.67 (m, 1H), 7.83-7.81 (m, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.75-7.71 (m, 1H), 7.44-7.42 (m, 1H), 7.38-7.35 (t, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 1H), 3.98-3.95 (t, *J* = 6.5 Hz, 2H), 2.12 (s, 1H), 1.37-1.33 (m, 2H), 1.27-1.23 (m, 2H), 1.19-1.14 (m, 2H), 0.88-0.85 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.7, 159.4, 149.1, 140.9, 137.1, 135.7, 133.7, 131.0, 127.9, 127.8, 124.0, 121.7, 65.0, 28.0, 27.9, 22.3, 20.1, 13.9. HRMS (ESI) Calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub> (MH<sup>+</sup>): 284.1645, found (MH<sup>+</sup>): 284.1643.



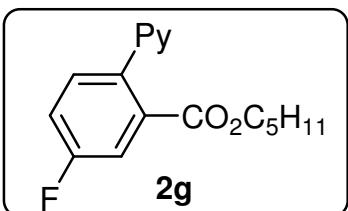
**2d:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.61-8.60 (m, 1H), 7.72-7.69 (m, 1H), 7.52-7.48 (m, 1H), 7.43-7.42 (m, 1H), 7.33-7.32 (m, 1H), 7.22-7.20 (m, 1H), 7.09-7.06 (m, 1H), 4.09-4.06 (t, *J* = 6.5 Hz, 2H), 3.91-3.88 (m, 3H), 1.43-1.39 (m, 2H), 1.26-1.20 (m, 2H), 1.11-1.07 (m, 2H), 0.86-0.82 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.0, 159.5, 158.5, 149.0, 136.1, 133.4, 133.2, 131.1, 122.6, 121.6, 116.9, 114.6, 65.3, 55.6, 28.0, 27.9, 22.2, 13.9. HRMS (ESI) Calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub> (MH<sup>+</sup>): 300.1594, found (MH<sup>+</sup>): 300.1588.



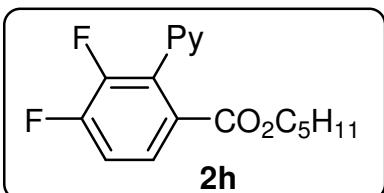
**2e:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.64-8.63 (d, *J* = 4.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.51-7.50 (d, *J* = 3.0 Hz, 1H), 7.45-7.39 (m, 2H), 7.24-7.21 (m, 1H), 7.13-7.11 (d, *J* = 8.0 Hz, 1H), 3.99-3.96 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 1.37-1.32 (m, 2H), 1.26-1.20 (m, 2H), 1.15-1.10 (m, 2H), 0.89-0.84 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.9, 157.0, 156.0, 148.9, 135.3, 133.3, 130.3, 129.2, 125.1, 122.0, 121.7, 114.2, 65.0, 56.1, 28.0, 27.9, 22.2, 13.9. HRMS (ESI) Calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub> (MH<sup>+</sup>): 300.1594, found (MH<sup>+</sup>): 300.1585.



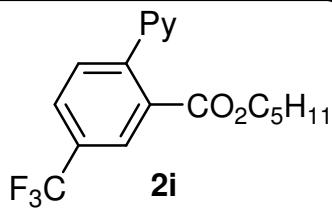
**2f:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62-8.61 (m, 1H), 7.72-7.69 (m, 1H), 7.53-7.51 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 1H), 7.26 (s, 1H), 7.22-7.19 (m, 1H), 7.09 (s, 1H), 4.07-4.04 (t,  $J = 6.5$  Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 1.43-1.40 (m, 2H), 1.23-1.18 (m, 2H), 1.08-1.05 (m, 2H), 0.84-0.81 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 158.4, 149.1, 139.3, 139.0, 136.3, 136.3, 131.3, 130.4, 127.3, 122.3, 121.9, 65.0, 27.9, 27.9, 22.3, 21.2, 19.7, 13.9. HRMS (ESI) Calcd for  $\text{C}_{19}\text{H}_{24}\text{NO}_2$  ( $\text{MH}^+$ ): 298.1802, found ( $\text{MH}^+$ ): 298.1796.



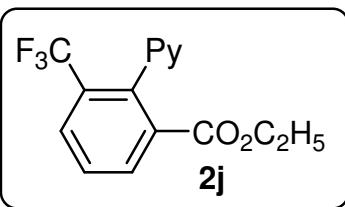
**2g:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63-8.62 (m, 1H), 7.75-7.71 (m, 1H), 7.54-7.51 (m, 2H), 7.44-7.42 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 1H), 7.26-7.24 (m, 2H), 4.09-4.07 (m, 2H), 1.45-1.41 (m, 2H), 1.27-1.21 (m, 2H), 1.13-1.08 (m, 2H), 0.87-0.82 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6 (d,  $J = 2.3$  Hz), 162.2 (d,  $J_{CF} = 248.1$  Hz), 157.8, 149.0, 137.0 (d,  $J_{CF} = 3.8$  Hz), 136.2, 133.7 (d,  $J_{CF} = 7.4$  Hz), 131.7 (d,  $J_{CF} = 7.9$  Hz), 122.7, 122.0, 117.9 (d,  $J_{CF} = 21.3$  Hz), 116.8 (d,  $J_{CF} = 23.6$  Hz), 65.5, 27.9, 27.8, 22.2, 13.8.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.32 - -113.37 (m). HRMS (ESI) Calcd for  $\text{C}_{17}\text{H}_{19}\text{FNO}_2$  ( $\text{MH}^+$ ): 288.1394, found ( $\text{MH}^+$ ): 288.1388.



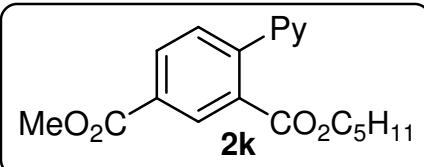
**2h:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68-8.67 (dd,  $J_1 = 4.5$  Hz,  $J_2 = 1.0$  Hz, 1H), 7.80-7.77 (m, 1H), 7.74-7.71 (m, 1H), 7.48-7.47 (d,  $J = 8.0$  Hz, 1H), 7.33-7.26 (m, 2H), 4.02-3.99 (t,  $J = 6.5$  Hz, 2H), 1.39-1.33 (m, 2H), 1.25-1.21 (m, 2H), 1.13-1.09 (m, 2H), 0.86-0.83 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2 (d,  $J = 2.3$  Hz), 152.6 (dd,  $J_{CF1} = 254.0$  Hz,  $J_{CF2} = 13.9$  Hz), 152.3 (d,  $J_{CF1} = 2.8$  Hz), 149.4, 148.2 (dd,  $J_{CF1} = 248.5$  Hz,  $J_{CF2} = 13.5$  Hz), 136.0, 131.6 (d,  $J_{CF} = 12.9$  Hz), 128.6 (d,  $J_{CF} = 3.6$  Hz), 126.4 (m), 124.7 (d,  $J_{CF} = 2.8$  Hz), 122.8, 116.7 (d,  $J_{CF} = 17.5$  Hz), 65.5, 27.9, 27.9, 22.2, 13.8.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -131.82 - -131.90 (m, 1F), -140.56 - -140.62 (m, 1F). HRMS (ESI) Calcd for  $\text{C}_{17}\text{H}_{18}\text{F}_2\text{NO}_2$  ( $\text{MH}^+$ ): 306.1300, found ( $\text{MH}^+$ ): 306.1292.



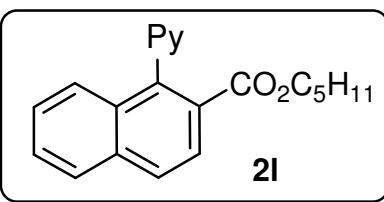
**2i:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66-8.65 (m, 1H), 8.08 (s, 1H), 7.81-7.76 (m, 2H), 7.69-7.67 (d,  $J = 8.5$  Hz, 1H), 7.50-7.48 (m, 1H), 7.32-7.29 (m, 1H), 4.12-4.09 (m, 2H), 1.45-1.40 (m, 2H), 1.25-1.21 (m, 2H), 1.12-1.08 (m, 2H), 0.87-0.82 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 157.4, 149.3, 144.1, 136.4, 132.7, 130.4 (d,  $J = 36.5$  Hz), 127.6 (q,  $J = 4$  Hz), 126.8 (q,  $J = 4$  Hz), 122.8, 124.4 (q,  $J = 270$  Hz), 122.8, 122.6, 65.7, 27.9, 27.8, 22.2, 13.8.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.15 (s). HRMS (ESI) Calcd for  $\text{C}_{18}\text{H}_{19}\text{F}_3\text{NO}_2$  ( $\text{MH}^+$ ): 338.1362, found ( $\text{MH}^+$ ): 338.1355.



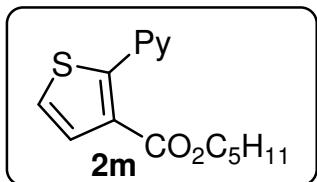
**2j:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64-8.63 (m, 1H), 8.13-8.12 (d,  $J = 8.0$  Hz, 1H), 7.92-7.91 (d,  $J = 8.0$  Hz, 1H), 7.76-7.73 (m, 1H), 7.62-7.59 (t,  $J = 8.0$  Hz, 1H), 7.40-7.38 (d,  $J = 7.5$  Hz, 1H), 7.33-7.31 (m, 1H), 4.05-4.00 (q,  $J = 7.0$  Hz, 2H), 1.01-0.98 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 156.2, 148.6, 140.1, 135.3, 133.6 (d,  $J = 32$  Hz), 129.5, 129.1 (q,  $J = 4$  Hz), 128.3, 124.8 (q,  $J = 272$  Hz,), 124.5, 122.5, 122.2, 61.2, 13.7.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -57.25 (s). HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NO}_2$  ( $\text{MH}^+$ ): 296.0893, found ( $\text{MH}^+$ ): 296.0886.



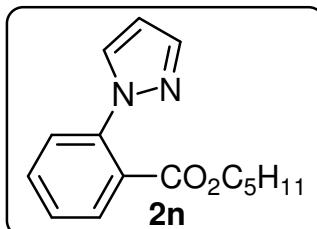
**2k:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66-8.65 (m, 1H), 8.47-8.47 (d,  $J = 1.5$  Hz, 1H), 8.21-8.19 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.78-7.75 (m, 1H), 7.64-7.63 (d,  $J = 8.0$  Hz, 1H), 7.50-7.49 (d,  $J = 8.0$  Hz, 1H), 7.30-7.26 (m, 1H), 4.11-4.09 (t,  $J = 6.5$  Hz, 2H), 3.96 (s, 3H), 1.47-1.43 (m, 2H), 1.26-1.21 (m, 2H), 1.14-1.09 (m, 2H), 0.87-0.82 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 166.0, 157.7, 149.2, 144.8, 136.3, 132.3, 131.8, 130.9, 130.1, 130.0, 122.8, 122.5, 65.5, 52.4, 28.0, 27.9, 22.2, 13.9. HRMS (ESI) Calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}_4$  ( $\text{MH}^+$ ): 328.1543, found ( $\text{MH}^+$ ): 328.1534.



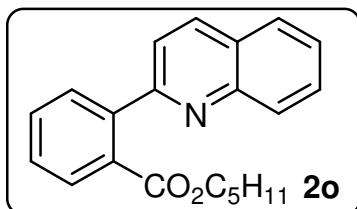
**2l:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78-8.77 (dd,  $J_1 = 5.0$  Hz,  $J_2 = 1.0$  Hz, 1H), 8.06-8.05 (d,  $J = 8.5$  Hz, 1H), 7.97-7.95 (d,  $J = 8.5$  Hz, 1H), 7.93-7.91 (d,  $J = 8.0$  Hz, 1H), 7.84-7.81 (m, 1H), 7.57-7.54 (m, 1H), 7.47-7.37 (m, 4H), 4.06-4.03 (t,  $J = 6.5$  Hz, 2H), 1.43-1.38 (m, 2H), 1.30-1.24 (m, 2H), 1.23-1.18 (m, 2H), 0.93-0.85 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 158.5, 149.3, 140.4, 135.7, 135.0, 132.1, 128.5, 127.9, 127.7, 127.6, 127.1, 126.8, 125.8, 125.1, 122.1, 65.2, 28.0, 28.0, 22.3, 13.9. HRMS (ESI) Calcd for  $\text{C}_{21}\text{H}_{22}\text{NO}_2$  ( $\text{MH}^+$ ): 320.1645, found ( $\text{MH}^+$ ): 320.1638.



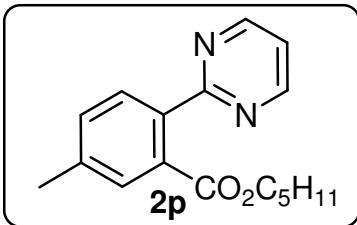
**2m:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64-8.62 (m, 1H), 7.86-7.84 (m, 1H), 7.73-7.70 (m, 1H), 7.51-7.50 (m, 1H), 7.34-7.33 (m, 1H), 7.27-7.24 (m, 1H), 4.23-4.20 (m, 2H), 1.65-1.61 (m, 2H), 1.33-1.26 (m, 4H), 0.89-0.87 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 151.8, 149.8, 149.1, 135.9, 130.2, 129.1, 125.9, 124.4, 122.9, 65.0, 28.2, 28.1, 22.3, 13.9. HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_2\text{S}$  ( $\text{MH}^+$ ): 276.1053, found ( $\text{MH}^+$ ): 276.1045.



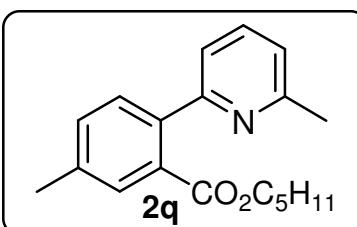
**2n:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.80 (d,  $J = 8.0$  Hz, 1H), 7.69-7.68 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.42 (m, 2H), 6.43-6.43 (d,  $J = 1.5$  Hz, 1H), 4.13-4.11 (t,  $J = 6.5$  Hz, 2H), 1.52-1.48 (m, 2H), 1.30-1.18 (m, 4H), 0.88-0.85 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 140.8, 139.3, 131.8, 130.4, 129.9, 128.0, 127.7, 125.3, 106.9, 65.6, 27.9, 27.9, 22.2, 13.8. HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2$  ( $\text{MH}^+$ ): 259.1441, found ( $\text{MH}^+$ ): 259.1433.



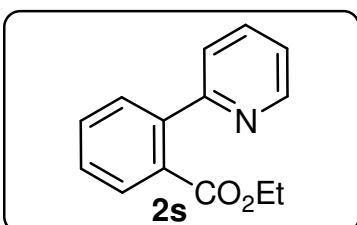
**2o:** oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20-8.18 (d,  $J = 8.5$  Hz, 1H), 8.13-8.11 (d,  $J = 8.5$  Hz, 1H), 7.92-7.90 (d,  $J = 8.0$  Hz, 1H), 7.85-7.84 (d,  $J = 8.0$  Hz, 1H), 7.73-7.70 (m, 1H), 7.67-7.66 (d,  $J = 7.5$  Hz, 1H), 7.61-7.49 (m, 4H), 4.03-4.00 (m, 2H), 1.26-1.19 (m, 2H), 1.01-0.97 (m, 2H), 0.86-0.81 (m, 2H), 0.67-0.64 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 158.9, 147.8, 141.3, 135.9, 131.9, 131.2, 130.0, 129.9, 129.6, 129.5, 128.5, 127.4, 126.9, 126.4, 121.2, 65.2, 27.9, 27.8, 22.1, 13.7. HRMS (ESI) Calcd for  $\text{C}_{21}\text{H}_{22}\text{NO}_2$  ( $\text{MH}^+$ ): 320.1645, found ( $\text{MH}^+$ ): 320.1633.



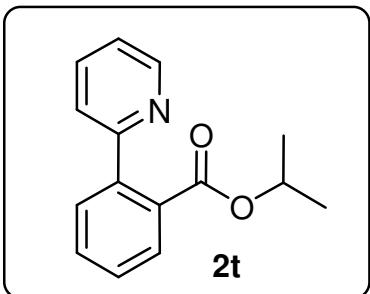
**2p:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.78-8.77 (m, 2H), 7.92-7.91 (d, *J* = 7.5 Hz, 1H), 7.52 (s, 1H), 7.39-7.37 (m, 1H), 7.21-7.19 (t, *J* = 5.0 Hz, 1H), 4.17-4.14 (t, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.53-1.48 (m, 2H), 1.28-1.22 (m, 2H), 1.19-1.14 (m, 2H), 0.88-0.83 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.8, 165.8, 156.8, 139.9, 133.2, 131.3, 129.9, 129.5, 118.8, 65.3, 28.1, 28.0, 22.3, 21.2, 13.9. HRMS (ESI) Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (MH<sup>+</sup>): 285.1598, found (MH<sup>+</sup>): 285.1590.



**2q:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61-7.58 (m, 2H), 7.44-7.43 (d, *J* = 7.5 Hz, 1H), 7.34-7.33 (m, 1H), 7.26-7.24 (m, 1H), 7.09-7.08 (d, *J* = 8.0 Hz, 1H), 4.07-4.04 (m, 2H), 2.57 (s, 3H), 2.42 (s, 3H), 1.42-1.39 (m, 2H), 1.26-1.20 (m, 2H), 1.09-1.06 (m, 2H), 0.85-0.82 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.4, 158.1, 157.6, 138.2, 138.1, 136.3, 131.9, 131.5, 130.1, 129.6, 121.3, 119.5, 65.1, 28.0, 27.9, 24.5, 22.3, 21.0, 13.9. HRMS (ESI) Calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>2</sub> (MH<sup>+</sup>): 298.1802, found (MH<sup>+</sup>): 298.1797.



**2s:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.65-8.64 (m, 1H), 7.85-7.84 (m, 1H), 7.75-7.74 (m, 1H), 7.56-7.55 (m, 2H), 7.48-7.45 (m, 2H), 7.28-7.26 (m, 1H), 4.16-4.12 (m, 2H), 1.08-1.04 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.7, 158.9, 148.9, 141.0, 136.1, 131.8, 131.1, 129.8, 129.8, 128.3, 122.9, 122.0, 60.9, 13.8.



**2t:** oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.65-8.63 (m, 1H), 7.84-7.82 (m, 1H), 7.75-7.72 (m, 1H), 7.55-7.52 (m, 2H), 7.48-7.45 (m, 2H), 7.27-7.25 (m, 1H), 5.06-5.01 (m, 1H), 1.09 (s, 3H), 1.08 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.2, 159.0, 149.0, 140.9, 136.1, 132.2, 130.9, 129.8, 129.7, 128.2, 122.9, 121.9, 68.5, 21.5.

