

# Rhodium-catalyzed direct *ortho* C-H olefination of phenol derivatives

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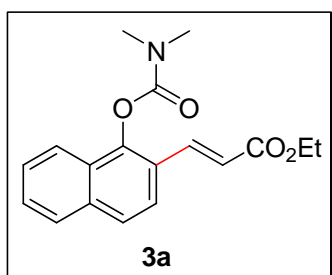
## **I. General Methods**

[RhCp\*Cl<sub>2</sub>]<sub>2</sub>, AgSbF<sub>6</sub>, and Cu(OAc)<sub>2</sub> were purchased from commercial suppliers and used as received unless otherwise noted. Phenol carbamates are synthesized according to the reported procedure.<sup>1</sup> All reactions were carried out under air unless otherwise stated. Commercial solvents and reagents were used without further purification. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q-ToF Premier Spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Bruker Avance 300, 400 and 500 MHz spectrometers. Chemical shifts for <sup>1</sup>H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe<sub>4</sub> (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe<sub>4</sub> (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

## **II. General procedure for the direct olefination of phenol carbamate derivatives**

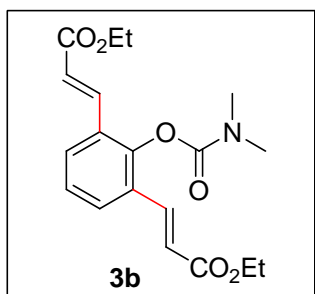
The phenol carbamate (0.1 mmol, 1equiv), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 0.025 equiv), AgSbF<sub>6</sub> (0.01 mmol, 0.1 equiv), Cu(OAc)<sub>2</sub> and 1,2-dimethoxyethane (0.5 mL) were placed in a glass vial under air. Ethyl acrylate (0.2 mmol, 2 equiv) was then added and the reaction was heated to 110°C for 24 h. The reaction was then filtered and concentrated *in vacuo* to give a crude product that was purified by column chromatography.

### III. Spectroscopic data of products



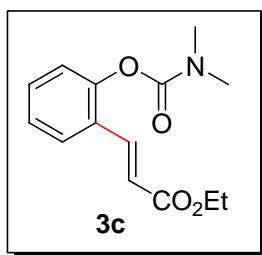
#### (E)-ethyl 3-(1-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate:

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.34 (t, *J*=7.12 Hz, 3H), 3.09 (s, 3H), 3.35 (s, 3H), 4.28 (q, *J*=7.13, 2H), 6.54 (d, *J*=16.07, 1H), 7.49-7.54 (m, 2H), 7.67-7.72 (m, 2H), 7.97 (d, *J*=16.06 Hz, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.7, 37.0, 60.5, 119.9, 122.2, 122.8, 124.0, 126.1, 127.1, 127.4, 127.9, 135.3, 138.1, 146.7, 154.3, 166.9 ppm; **HRMS (ESI, m/z):** calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 336.1212, found: 336.1220.



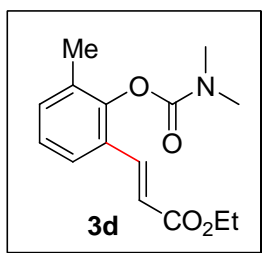
#### (2E,2'E)-diethyl 3,3'-(2-(dimethylcarbamoyloxy)-1,3-phenylene)diacrylate:

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.15 Hz, 6H), 3.04 (s, 3H), 3.26 (s, 3H), 4.26 (q, *J*=7.13, 4H), 6.44 (d, *J*=16.04, 1H), 7.25-7.29 (m, 1H), 7.65 (d, *J*=7.82, 2H), 7.75 (d, *J*=16.08 Hz, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.2, 36.6, 37.0, 60.6, 120.8, 126.2, 128.8, 129.2, 137.7, 148.7, 153.7, 166.5 ppm; **HRMS (ESI, m/z):** calcd for C<sub>19</sub>H<sub>23</sub>NO<sub>6</sub> [M+Na]<sup>+</sup> 384.1423, found: 384.1435.



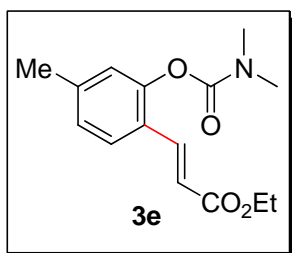
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.14 Hz, 3H), 3.03 (s, 3H), 3.18 (s, 3H), 4.26 (q, *J*=7.14, 2H), 6.44 (d, *J*=16.07, 1H), 7.16-7.24 (m, 2H), 7.36-7.40 (m, 1H), 7.62 (d, *J*=7.72 Hz, 1H), 7.84 (d, *J*=16.07, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.5, 36.8, 60.5, 119.8, 123.4, 125.7, 127.2, 127.3, 131.0, 138.3, 150.1, 154.3, 166.8 ppm; **HRMS (ESI, m/z):** calcd for C<sub>14</sub>H<sub>17</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 286.1055, found: 286.1068.



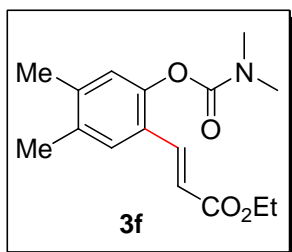
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3-methylphenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.32 (t, *J*=7.13 Hz, 3H), 2.21 (s, 3H), 3.03 (s, 3H), 3.20 (s, 3H), 4.25 (q, *J*=7.14, 2H), 6.42 (d, *J*=16.03, 1H), 7.13 (t, *J*=7.64 Hz, 1H), 7.24 (d, *J*=7.41 Hz, 1H), 7.46 (d, *J*=7.73, 1H), 7.77 (d, *J*=16.05, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 16.2, 36.5, 36.9, 60.4, 119.8, 124.9, 125.7, 128.0, 131.9, 132.7, 138.7, 148.8, 153.8, 166.9 ppm; **HRMS (ESI, m/z):** calcd for C<sub>15</sub>H<sub>19</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 300.1212, found: 300.1225.



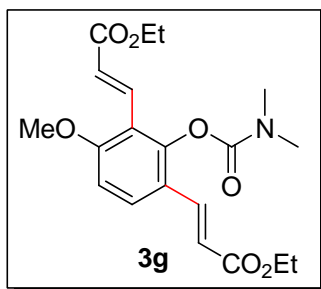
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-4-methylphenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.32 (t, *J*=7.14 Hz, 3H), 2.36 (s, 3H), 3.03 (s, 3H), 3.17 (s, 3H), 4.25 (q, *J*=7.14, 2H), 6.39 (d, *J*=16.10, 1H), 6.99 (s, 1H), 7.03 (d, *J*=8.24 Hz, 1H), 7.51 (d, *J*=7.94, 1H), 7.80 (d, *J*=16.09, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 21.3, 36.5, 36.8, 60.4, 118.6, 123.8, 124.4, 126.7, 127.0, 138.3, 141.8, 150.0, 154.4, 167.0 ppm; **HRMS (ESI, m/z):** calcd for C<sub>15</sub>H<sub>19</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 300.1212, found: 300.1222.



**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-4,5-dimethylphenyl)acrylate:**

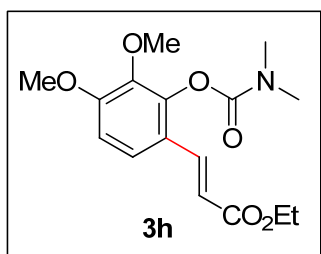
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.32 (t, *J*=7.13 Hz, 3H), 2.24 (s, 3H), 2.25 (s, 3H), 3.02 (s, 3H), 3.16 (s, 3H), 4.24 (q, *J*=7.12, 2H), 6.39 (d, *J*=16.05, 1H), 6.93 (s, 1H), 7.37 (s, 1H), 7.77 (d, *J*=16.05, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 19.2, 19.9, 36.5, 36.8, 60.3, 118.4, 124.2, 124.4, 128.0, 134.1, 138.4, 140.5, 148.1, 154.6, 167.1 ppm; **HRMS (ESI, m/z):** calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 314.1368, found: 314.1371.



**(2E,2'E)-diethyl 3,3'-(2-(dimethylcarbamoyloxy)-4-methoxy-1,3-phenylene)diacrylate:**

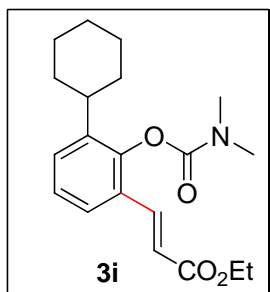
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.30-1.35 (m, 6H), 3.03 (s, 3H), 3.25 (s, 3H), 3.93 (s, 3H), 4.22-4.28 (m, 4H), 6.33 (d, *J*=16.00, 1H), 6.73 (d, *J*=16.24, 1H), 6.85 (d, *J*=8.88, 1H), 7.61 (d, *J*=8.86, 1H), 7.67-7.75 (m, 2H) ppm; **<sup>13</sup>C NMR**

(100 MHz, CDCl<sub>3</sub>): δ 14.3, 14.3, 36.5, 37.0, 56.0, 60.3, 60.4, 108.9, 118.0, 118.2, 121.5, 123.2, 128.8, 134.3, 137.9, 150.1, 153.5, 160.9, 166.9, 167.5 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>7</sub> [M+Na]<sup>+</sup> 414.1529, found: 414.1531.



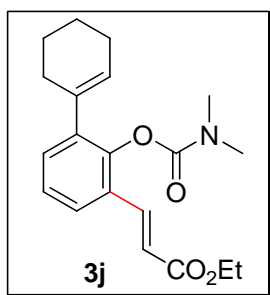
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3,4-dimethoxyphenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.32 (t, *J*=7.13 Hz, 3H), 3.04 (s, 3H), 3.19 (s, 3H), 3.85(s, 3H), 3.89 (s, 3H), 4.24 (q, *J*=7.12, 2H), 6.34 (d, *J*=16.05, 1H), 6.81(d, *J*=8.85, 1H), 7.32 (d, *J*=8.85, 1H), 7.73 (d, *J*=16.02, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.6, 36.9, 56.0, 60.3, 60.7, 109.7, 117.7, 121.6, 122.1, 138.4, 141.8, 144.4, 154.1, 155.0, 167.1 ppm; **HRMS (ESI, m/z):** calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>6</sub> [M+Na]<sup>+</sup> 346.1267, found: 346.1268.



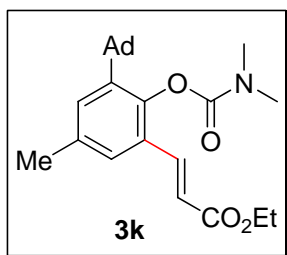
**(E)-ethyl 3-(3-cyclohexyl-2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.30-1.38 (m, 8H), 1.74-1.77 (m, 1H), 1.84-1.86 (m, 4H), 2.60 (s, 1H), 3.04 (s, 3H), 3.21 (s, 3H), 4.24 (q, *J*=7.13, 2H), 6.40 (d, *J*=16.03, 1H), 7.20(t, *J*=7.74, 1H), 7.31 (d, *J*=7.65, 1H), 7.46 (d, *J*=7.72, 1H), 7.75 (d, *J*=16.06, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 26.1, 26.9, 36.5, 36.9, 38.0, 60.4, 119.7, 124.6, 126.0, 128.2, 128.9, 139.0, 141.0, 147.8, 154.4, 166.9 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>27</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 368.1838, found: 368.1846.



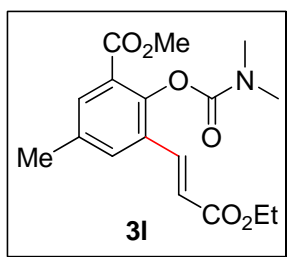
**(E)-ethyl 3-(3-cyclohexenyl-2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.32 (t, *J*=7.13, 3H), 1.62-1.65 (m, 2H), 1.71-1.73 (m, 2H), 2.12 (s, 2H), 2.24 (s, 2H), 2.99 (s, 3H), 3.12 (s, 3H), 4.25 (q, *J*=7.09, 2H), 5.71 (s, 1H), 6.42 (d, *J*=16.10, 1H), 7.15-7.22 (m, 2H), 7.49 (d, *J*=7.38, 1H), 7.81 (d, *J*=16.08, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 22.0, 23.1, 25.5, 29.1, 36.4, 36.8, 60.4, 119.7, 125.4, 125.6, 127.3, 128.3, 131.0, 134.4, 138.8, 139.0, 147.4, 154.1, 166.9 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 366.1681, found: 366.1685.



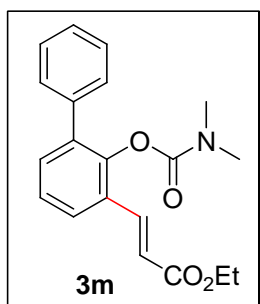
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3-adamantyl-5-methylphenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.31 (t, *J*=7.11, 3H), 1.72-1.80 (m, 6H), 1.90-1.93 (m, 3H), 2.09-2.13 (m, 6H), 2.33 (s, 3H), 3.05 (s, 3H), 3.26 (s, 3H), 4.23 (q, *J*=7.08, 2H), 6.36 (d, *J*=15.91, 1H), 7.17 (s, 1H), 7.28 (s, 1H), 7.60 (d, *J*=15.93, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 21.2, 28.9, 36.6, 36.9, 37.0, 37.0, 41.3, 60.3, 119.4, 125.6, 129.0, 130.1, 134.9, 139.4, 142.1, 147.0, 154.7, 166.9 ppm; **HRMS (ESI, m/z):** calcd for C<sub>25</sub>H<sub>33</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 434.2307, found: 434.2309.



**(E)-methyl 2-(dimethylcarbamoyloxy)-3-(3-ethoxy-3-oxoprop-1-enyl)-5-methylbenzoate:**

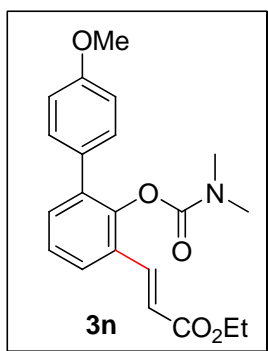
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.13, 3H), 2.38 (s, 3H), 3.04 (s, 3H), 3.19 (s, 3H), 3.85 (s, 3H), 4.26 (q, *J*=7.13, 2H), 6.43 (d, *J*=16.06, 1H), 7.59 (s, 1H), 7.81-7.85 (m, 2H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.2, 20.8, 36.6, 36.9, 52.1, 60.5, 120.7, 124.3, 129.2, 131.7, 133.7, 135.1, 137.8, 147.7, 154.2, 165.0, 166.6 ppm; **HRMS (ESI, m/z):** calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>6</sub> [M+Na]<sup>+</sup> 358.1267, found: 358.1275.



**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)biphenyl-3-yl)acrylate:**

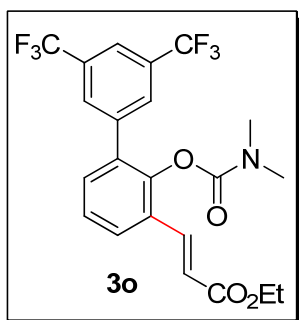
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.13, 3H), 2.79 (s, 3H), 2.92 (s, 3H), 4.26 (q, *J*=7.14, 2H), 6.47 (d, *J*=16.10, 1H), 7.25-7.42 (m, 7H), 7.62-7.64 (m, 1H), 7.83 (d, *J*=16.08, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.3, 36.7, 60.5, 120.2, 126.0, 126.4, 127.5, 128.0, 128.8, 128.9, 132.4, 136.6, 137.5, 138.7, 147.4, 153.8, 166.8 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 362.1368, found: 362.1378.





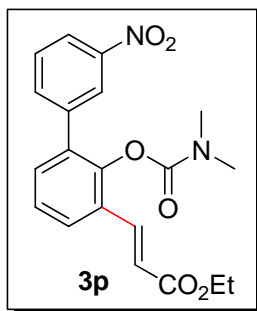
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-4'-methoxybiphenyl-3-yl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.13, 3H), 2.82 (s, 3H), 2.97 (s, 3H), 3.84 (s, 3H), 4.26 (q, *J*=7.13, 2H), 6.46 (d, *J*=16.05, 1H), 6.91-6.95 (m, 2H), 7.25-7.29 (m, 1H), 7.33-7.37 (m, 3H), 7.58-7.61 (m, 1H), 7.82 (d, *J*=16.07, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.4, 36.7, 55.2, 60.4, 113.5, 120.1, 126.0, 126.1, 128.8, 129.8, 130.1, 132.5, 136.2, 138.7, 147.5, 153.8, 159.0, 166.8 ppm; **HRMS (ESI, m/z):** calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub> [M+Na]<sup>+</sup> 392.1474, found: 392.1480.



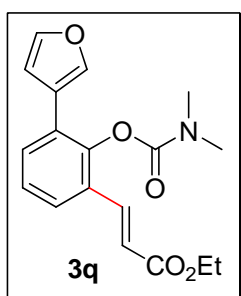
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3',5'-bis(trifluoromethyl)biphenyl-3-yl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.34 (t, *J*=7.14, 3H), 2.82 (s, 3H), 2.97 (s, 3H), 4.27 (q, *J*=7.15, 2H), 6.50 (d, *J*=16.03, 1H), 7.36-7.44 (m, 2H), 7.72 (dd, *J*<sub>1</sub>=7.69, *J*<sub>2</sub>=1.64, 1H), 7.80 (d, *J*=16.04, 1H), 7.88 (s, 1H), 7.92 (s, 2H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.1, 36.7, 60.6, 121.1, 121.2, 121.3, 121.3, 121.3, 121.4, 121.9, 124.6, 126.5, 128.0, 129.2, 129.5, 131.1, 131.4, 131.7, 131.9, 132.1, 133.5, 137.8, 139.5, 147.2, 153.2, 166.6 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>19</sub>F<sub>6</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 498.1116, found: 498.1124.



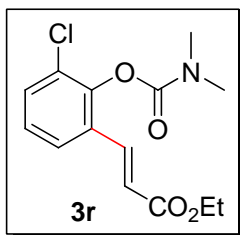
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3'-nitrophenyl-3-yl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.34 (t, *J*=7.14, 3H), 2.81 (s, 3H), 3.02 (s, 3H), 4.27 (q, *J*=7.13, 2H), 6.50 (d, *J*=16.04, 1H), 7.35-7.38 (m, 1H), 7.42-7.44 (m, 1H), 7.58-7.62 (m, 1H), 7.69-7.71 (m, 1H), 7.77-7.83 (m, 2H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.3, 36.8, 60.6, 120.9, 122.4, 123.8, 126.4, 127.6, 129.3, 129.3, 132.0, 134.1, 135.1, 138.0, 139.1, 147.2, 148.0, 153.3, 166.6 ppm; **HRMS (ESI, *m/z*):** calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub> [M+Na]<sup>+</sup> 407.1219, found: 407.1225.



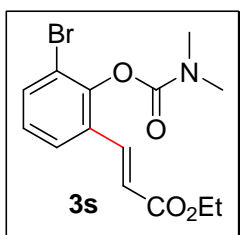
**(E)-ethyl 3-(2-(dimethylcarbamoyloxy)-3-(furan-3-yl)phenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.12, 3H), 2.98 (s, 3H), 3.19 (s, 3H), 4.26 (q, *J*=7.15, 2H), 6.45 (d, *J*=16.02, 1H), 6.64 (s, 1H), 7.25-7.29 (m, 1H), 7.47-7.50 (m, 2H), 7.55-7.57 (m, 1H), 7.65 (s, 1H), 7.78 (d, *J*=16.00, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 36.5, 36.9, 60.5, 110.2, 120.4, 121.5, 126.1, 126.2, 127.6, 129.1, 130.9, 138.4, 140.2, 142.9, 147.2, 153.7, 166.7 ppm; **HRMS (ESI, *m/z*):** calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>5</sub> [M+Na]<sup>+</sup> 352.1161, found: 352.1169.



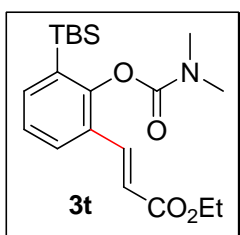
**(E)-ethyl 3-(3-chloro-2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  1.33 (t,  $J=7.13$  Hz, 3H), 3.05 (s, 3H), 3.21 (s, 3H), 4.26 (q,  $J=7.11$ , 2H), 6.44 (d,  $J=16.10$ , 1H), 7.18 (t,  $J=7.93$  Hz, 1H), 7.43-7.45 (m, 1H), 7.51-7.53 (m, 1H), 7.76 (d,  $J=16.07$ , 1H) ppm;  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  14.2, 36.6, 37.0, 60.6, 121.2, 125.7, 126.5, 128.8, 130.3, 131.4, 137.7, 146.6, 153.1, 166.5 ppm; **HRMS (ESI,  $m/z$ ):** calcd for  $\text{C}_{14}\text{H}_{16}\text{ClNO}_4$   $[\text{M}+\text{Na}]^+$  320.0666, found: 320.0679.



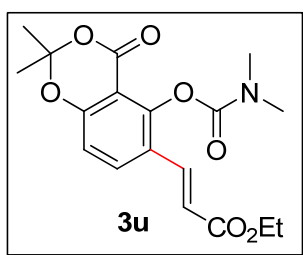
**(E)-ethyl 3-(3-bromo-2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  1.33 (t,  $J=7.12$  Hz, 3H), 3.05 (s, 3H), 3.22 (s, 3H), 4.26 (q,  $J=7.13$ , 2H), 6.43 (d,  $J=16.06$ , 1H), 7.12 (t,  $J=7.92$  Hz, 1H), 7.55-7.61 (m, 2H), 7.75 (d,  $J=16.07$ , 1H) ppm;  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  14.3, 36.7, 37.0, 60.6, 118.4, 121.2, 126.4, 127.0, 130.5, 134.5, 137.9, 147.7, 153.0, 166.4 ppm; **HRMS (ESI,  $m/z$ ):** calcd for  $\text{C}_{14}\text{H}_{16}\text{BrNO}_4$   $[\text{M}+\text{Na}]^+$  364.0160, found: 364.0170.



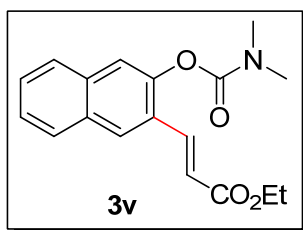
**(E)-ethyl 3-(3-(tert-butyldimethylsilyl)-2-(dimethylcarbamoyloxy)phenyl)acrylate:**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 0.25 (s, 3H), 0.30 (s, 3H), 0.89 (s, 9H), 1.32 (t, *J*=7.13 Hz, 3H), 3.01 (s, 3H), 3.20 (s, 3H), 4.24 (q, *J*=7.10, 2H), 6.39 (d, *J*=15.98, 1H), 7.21-7.25 (m, 1H), 7.49 (d, *J*=7.29 Hz, 1H), 7.62-7.66 (m, 2H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ -5.4, -4.8, 14.3, 17.4, 26.7, 36.5, 36.8, 60.4, 119.8, 125.4, 127.9, 128.5, 131.2, 138.4, 138.9, 154.7, 154.8, 166.8 ppm; **HRMS (ESI, m/z):** calcd for C<sub>20</sub>H<sub>31</sub>NO<sub>4</sub>Si [M+Na]<sup>+</sup> 400.1920, found: 400.1927.



**(E)-ethyl 3-(5-(dimethylcarbamoyloxy)-2,2-dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-6-yl)acrylate:**

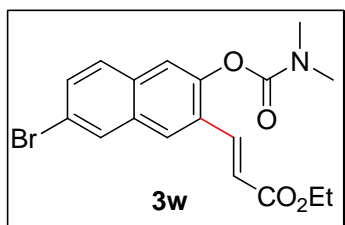
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.33 (t, *J*=7.12 Hz, 3H), 1.75 (s, 6H), 3.03 (s, 3H), 3.21 (s, 3H), 4.26 (q, *J*=7.14, 2H), 6.38 (d, *J*=16.19, 1H), 6.87 (d, *J*=8.76, 1H), 7.79 (d, *J*=8.80, 1H), 7.84 (d, *J*=16.18, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 14.3, 25.6, 36.9, 60.6, 106.4, 108.5, 114.7, 119.4, 123.2, 133.7, 136.9, 150.9, 153.6, 157.9, 158.0, 166.7 ppm; **HRMS (ESI, m/z):** calcd for C<sub>18</sub>H<sub>21</sub>NO<sub>7</sub> [M+Na]<sup>+</sup> 386.1216, found: 386.1227.



**(E)-ethyl 3-(3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate:**

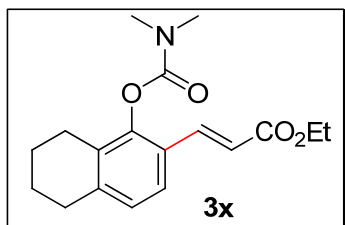
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 1.35 (t, *J*=7.16 Hz, 3H), 3.06 (s, 3H), 3.22 (s, 3H), 4.28 (q, *J*=7.14, 2H), 6.58 (d, *J*=16.00, 1H), 7.43-7.50 (m, 2H), 7.62 (s, 1H), 7.76 (d, *J*=7.89, 1H), 7.83 (d, *J*=7.65, 1H), 7.93 (d, *J*=16.05, 1H), 8.10 (s,

1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.3, 36.6, 36.9, 60.5, 120.3, 120.3, 126.1, 127.0, 127.4, 127.4, 128.0, 128.2, 131.0, 134.4, 139.0, 147.3, 154.5, 166.8 ppm; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{19}\text{NO}_4$   $[\text{M}+\text{Na}]^+$  336.1212, found: 336.1204.



**(E)-ethyl 3-(7-bromo-3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate:**

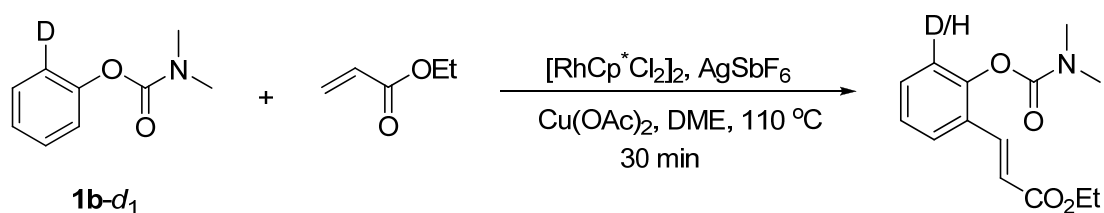
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.35 (t,  $J=7.08$  Hz, 3H), 3.06 (s, 3H), 3.22 (s, 3H), 4.28 (q,  $J=7.08$ , 2H), 6.56 (d,  $J=16.05$ , 1H), 7.53-7.55 (m, 1H), 7.60-7.63 (m, 2H), 7.80 (d,  $J=16.07$ , 1H), 7.98 (s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.3, 36.6, 36.9, 60.6, 119.9, 120.3, 121.1, 126.9, 128.2, 129.0, 130.1, 130.7, 132.0, 132.8, 138.4, 147.6, 154.2, 166.6 ppm; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{18}\text{BrNO}_4$   $[\text{M}+\text{Na}]^+$  414.0317, found: 414.0305.



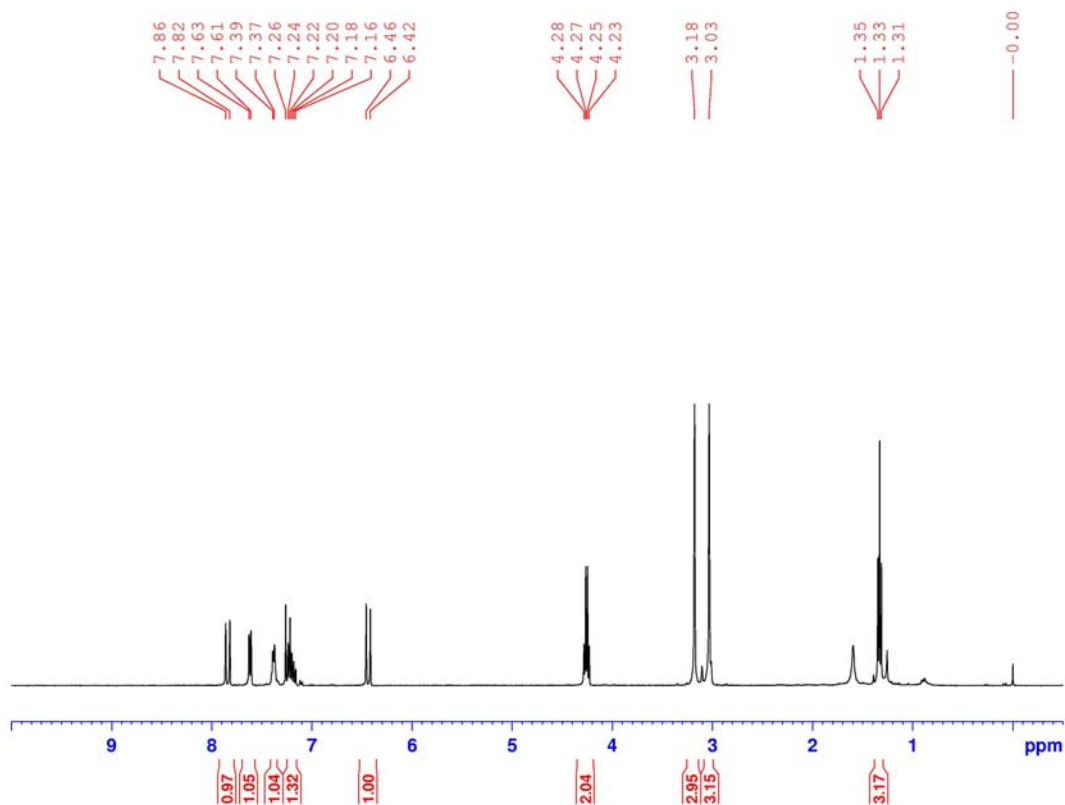
**(E)-ethyl 3-(1-(dimethylcarbamoyloxy)-5,6,7,8-tetrahydronaphthalen-2-yl)acrylate:**

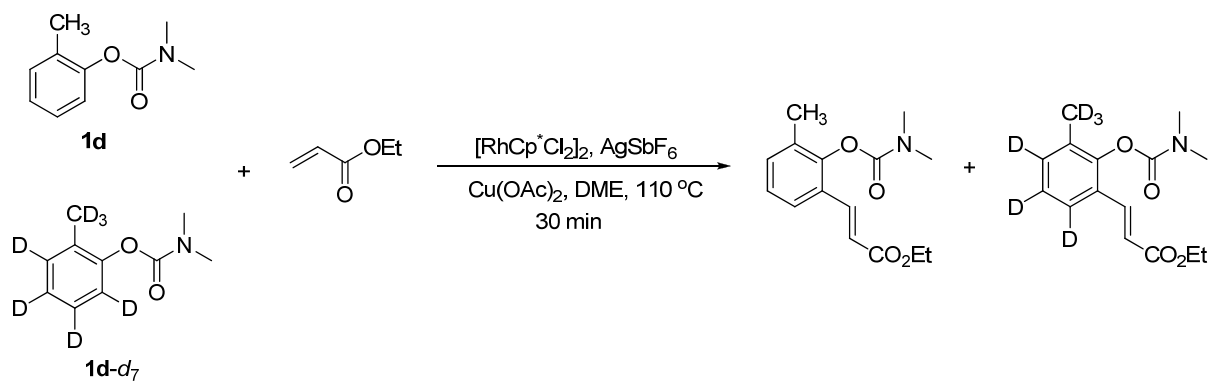
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32 (t,  $J=7.08$  Hz, 3H), 1.77 (s, 4H), 2.59 (s, 2H), 2.77 (s, 2H), 3.03 (s, 3H), 3.19 (s, 3H), 4.24 (q,  $J=7.13$ , 2H), 6.38 (d,  $J=16.05$ , 1H), 6.96 (d,  $J=8.09$ , 1H), 7.37 (d,  $J=8.08$ , 1H), 7.74 (d,  $J=16.03$ , 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.3, 22.3, 22.3, 23.2, 29.6, 36.5, 36.8, 60.3, 118.5, 123.8, 125.1, 126.8, 131.0, 138.8, 141.6, 148.5, 153.9, 167.1 ppm; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_4$   $[\text{M}+\text{Na}]^+$  340.1525, found: 340.1538.

#### IV. Deuterium labelling and kinetic isotope effect studies

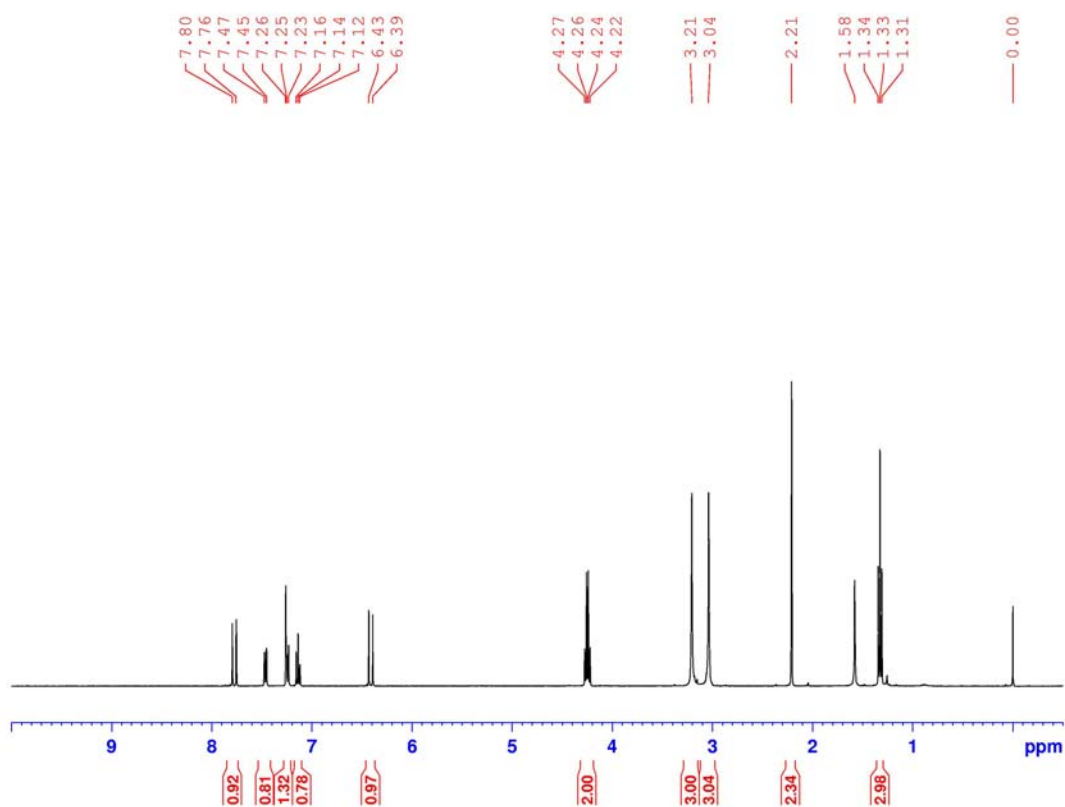


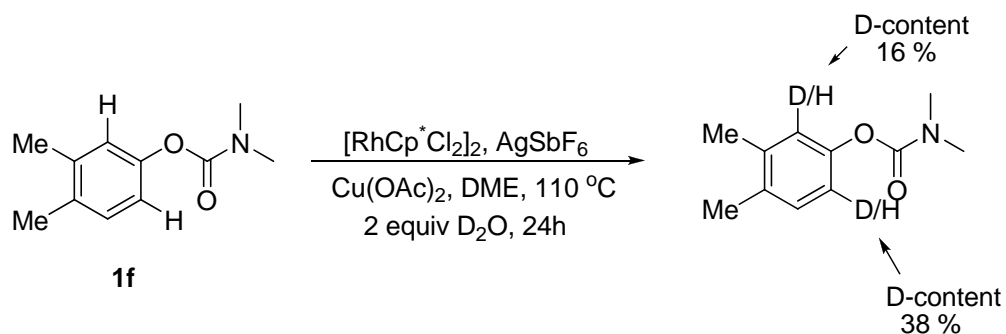
**1b-d<sub>1</sub>** (0.2 mmol, 1equiv), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 0.025 equiv), AgSbF<sub>6</sub> (0.01 mmol, 0.1 equiv), Cu(OAc)<sub>2</sub> and 1,2-dimethoxyethane (0.5 mL) were placed in a glass vial under air. Ethyl acrylate (0.1 mmol, 1 equiv) was then added and the reaction was heated to 110°C for 30 min. The reaction was then filtered and concentrated *in vacuo* to give a crude product that was purified by column chromatography.



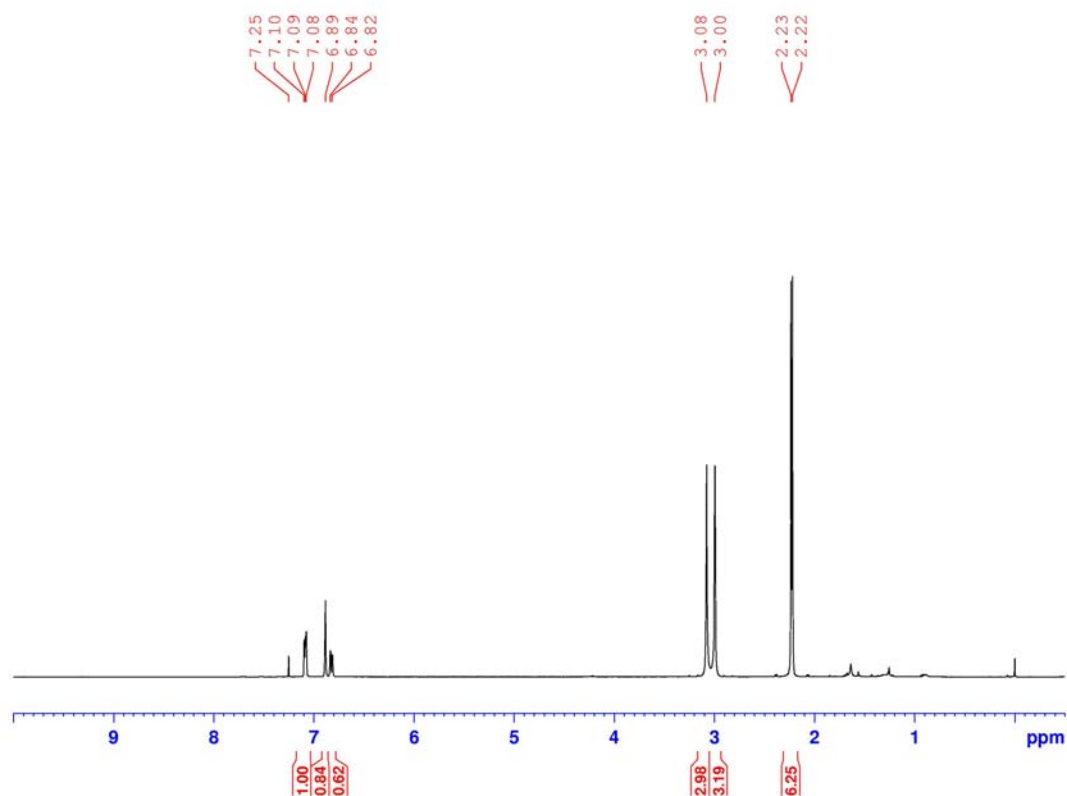


**1d** (0.1 mmol, 1 equiv), **1d-d<sub>7</sub>** (0.1 mmol, 1 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (0.0025 mmol, 0.025 equiv),  $\text{AgSbF}_6$  (0.01 mmol, 0.1 equiv),  $\text{Cu(OAc)}_2$  and 1,2-dimethoxyethane (0.5 mL) were placed in a glass vial under air. Ethyl acrylate (0.1 mmol, 1 equiv) was then added and the reaction was heated to  $110^\circ\text{C}$  for 30 min. The reaction was then filtered and concentrated *in vacuo* to give a crude product that was purified by column chromatography.

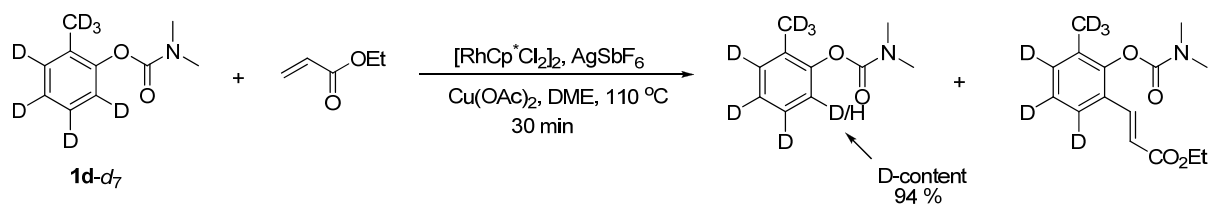




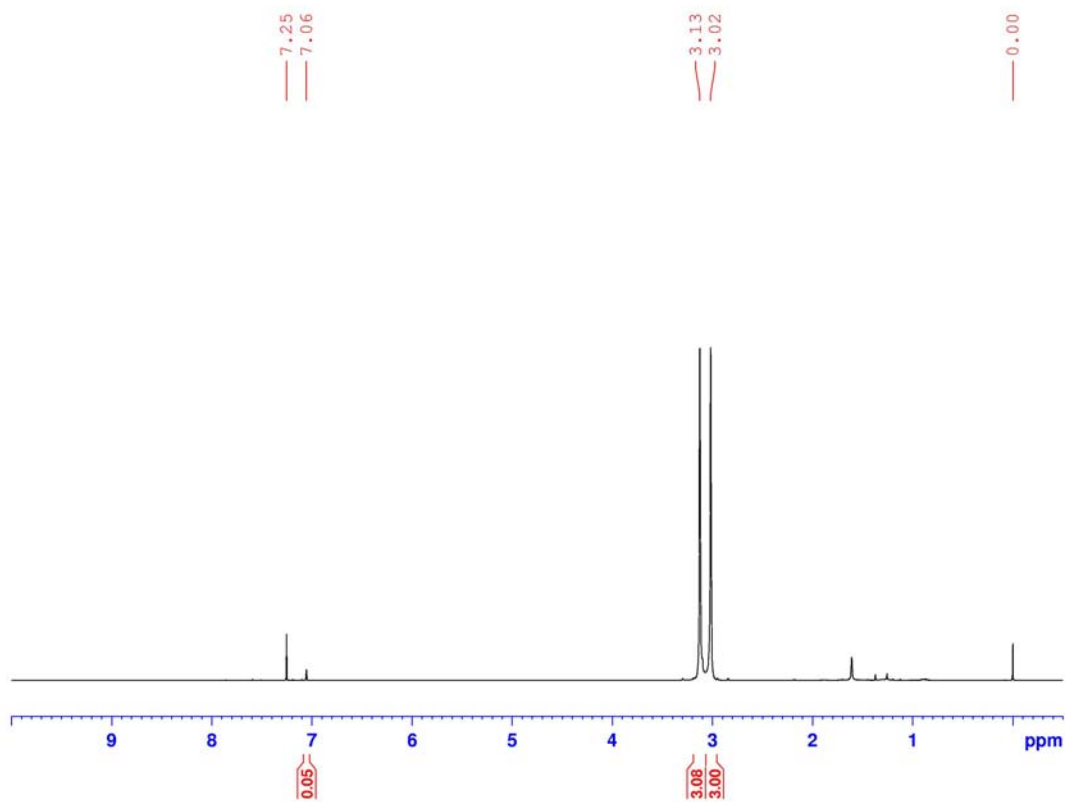
**1f** (0.1 mmol, 1equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (0.0025 mmol, 0.025 equiv),  $\text{AgSbF}_6$  (0.01 mmol, 0.1 equiv),  $\text{Cu}(\text{OAc})_2$ ,  $\text{D}_2\text{O}$  (0.2 mmol, 2 equiv) and 1,2-dimethoxyethane (0.5 mL) were placed in a glass vial under air. The mixture was heated to  $110^\circ\text{C}$  for 30 min. The reaction was then filtered and concentrated *in vacuo* to give a crude product that was purified by column chromatography.







**1d-d<sub>7</sub>** (0.1 mmol, 1equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (0.0025 mmol, 0.025 equiv),  $\text{AgSbF}_6$  (0.01 mmol, 0.1 equiv),  $\text{Cu(OAc)}_2$ , and 1,2-dimethoxyethane (0.5 mL) were placed in a glass vial under air. Ethyl acrylate (0.2 mmol, 2 equiv) was then added and the reaction was heated to  $110^\circ\text{C}$  for 30 min. The reaction was then filtered and concentrated *in vacuo* to give a crude product that was purified by column chromatography.



Reference:

- (1) X. Zhao, C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 5837.

## VI. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products

