

# Electronic Supplementary Data

## **Cu-exchanged montmorillonite K10-catalyzed direct carboxylation of terminal alkynes with carbon dioxide**

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### 3-p-Tolylpropionic acid (2b)

Yield: 75%; colourless solid; mp 149.2 °C; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  536, 742, 908, 1018, 1176, 1209, 1412, 1601, 1673, 2228, 3009; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.35 (s, 3H), 7.27 (d,  $J$  = 7.9 Hz, 2H), 7.50 (d,  $J$  = 8.0 Hz, 2H), 13.74 (bs, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  21.2, 63.1, 84.8, 115.8, 129.6, 132.6, 141.2, 154.3; Anal. Calcd for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub> requires C, 74.99; H, 5.03; found C, 74.82; H, 4.92%.

### 3-(4-Chlorophenyl)propionic acid (2c)

Yield: 71%; colourless solid; mp 191.3 °C {lit<sup>15b</sup>: 191-192.7 °C}; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  529, 754, 1083, 1209, 1384, 1488, 1700, 2239, 3428; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  7.53 (d,  $J$  = 8.5 Hz, 2H), 7.64 (d,  $J$  = 8.5 Hz, 2H), 13.91 (bs, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  71.8, 83.2, 118.0, 129.4, 134.5, 136.0, 154.2; Anal. Calcd for C<sub>9</sub>H<sub>5</sub>ClO<sub>2</sub> requires C, 59.86; H, 2.79; Cl, 19.63; found C, 59.72; H, 2.80; Cl, 19.49%.

### 3-(3,4-Dimethoxyphenyl)propionic acid (2d)

Yield: 82%; colourless solid; mp 154.7 °C IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  768, 1018, 1164, 1262, 1309, 1519, 1674, 2201, 2939; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.79 (s, 3H), 3.81 (s, 3H), 7.01-7.22, (m, 3H), 13.60 (bs, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  55.8, 80.9, 85.8, 110.6, 112.1, 115.4, 126.9, 148.8, 151.5, 154.7; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub> requires C, 64.07; H, 4.89; found C, 63.95; H, 4.76%.

### 5-Phenylpent-2-ynoic acid (2e)

Yield: 94%; yellow colour liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  699, 754, 1279, 1410, 1701, 2238, 3028; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.62-2.70 (m, 2H), 2.78-2.86 (m, 2H), 7.21-7.34, (m, 5H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  19.7, 33.1, 74.6, 87.7, 126.3, 128.3, 128.4, 139.8, 154.2; Anal. Calcd for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub> requires C, 75.84; H, 5.79; found C, 75.75; H, 5.65%.

### 4-(p-Tolyloxy)but-2-ynoic acid (2f)

Yield: 88%; brownish solid; mp 105.5 °C IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  725, 811, 1236, 1290, 1422, 1510, 1690, 2251, 2970; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.24 (s, 3H), 4.98 (s, 2H), 6.86-6.92 (m, 2H), 7.10 (d,  $J$  = 8.3 Hz, 2H), 13.90(s, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  20.0, 55.0,

81.9, 114.6, 129.8, 130.3, 133.3, 134.8; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub> requires C, 69.46; H, 5.30; found C, 69.34; H, 5.16%.

#### 4-(Benzyloxy)but-2-ynoic acid (2g)

Yield: 76%; yellow colour liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  1027, 1060, 1704, 2230, 3440; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  4.39 (s, 2H), 4.55 (s, 2H), 7.35 (s, 5H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  56.9, 71.5, 79.3, 83.0, 126.0, 128.6, 137.5, 154.0; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub> requires C, 69.46; H, 5.40; found C, 69.16; H, 5.21%.

#### 4-(Phenethyloxy)but-2-ynoic acid (2h)

Yield: 83%; yellow colour liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  700, 1101, 1257, 1712, 2240, 3028; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.84 (t, *J* = 6.9 Hz, 2H), 3.69 (t, *J* = 6.8 Hz, 2H), 4.35 (s, 5H), 7.33-7.19 (m, 5H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  35.3, 57.3, 70.7, 79.0, 83.3, 126.3, 128.4, 129.0, 138.8, 153.9; Anal. Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>3</sub> requires C, 70.37; H, 5.92; found C, 70.25; H, 5.76%.

#### 3-Cyclopropylpropionic acid (2i)

Yield: 70%; colourless solid, mp 63.9°C IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  1184, 1690, 2223, 3011; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  0.80-0.83 (m, 2H), 0.92-0.96 (m, 2H), 1.49-1.54 (m, 1H), 13.91 (bs, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-d<sub>6</sub>):  $\delta$  71.8, 83.2, 118.0, 129.4, 134.5, 136.0, 154.2; Anal. Calcd for C<sub>6</sub>H<sub>6</sub>O<sub>2</sub> requires C, 60.45; H, 5.49; found C, 60.34; H, 5.35%.

#### 6-Chlorohex-2-ynoic acid (2j)

Yield: 88%; yellow colour liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  755, 855, 1289, 1700, 2239, 2965; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.02 (qt, *J* = 6.7 Hz, 2H), 2.56 (m, 2H), 3.73 (t, *J* = 6.4 Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  16.0, 20.7, 30.0, 43.0, 73.5, 89.5, 157.2; Anal. Calcd for C<sub>6</sub>H<sub>7</sub>ClO<sub>2</sub> requires C, 49.17; H, 4.81 Cl, 24.19; found C, 49.05; H, 4.71; Cl, 24.12%.

### Ethyl 3-phenylpropionate (3ab)

Yield: 75%; colourless liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  757, 1174, 1192, 1286, 1708, 2210; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.37 (t,  $J = 7.2$  Hz, 3H), 4.29 (q,  $J = 7.2$  Hz, 2H), 7.33-7.45 (m, 3H), 7.56-7.57 (dd,  $J = 8.21, 1.89$  Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 61.9, 80.8, 119.7, 128.5, 130.5, 132.9, 154.0; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub> requires C, 75.84; H, 5.79; found C, 75.68; H, 5.56%.

### Butyl 3-phenylpropionate (3ac)

Yield: 77%; colourless liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  688, 756, 1173, 1286, 1490, 1708, 2221; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.97 (t,  $J = 7.2$  Hz, 3H), 1.36-1.54 (m, 2H), 1.71 (quin,  $J = 8.1$  Hz, 2H), 4.23 (t,  $J = 6.7$  Hz, 2H), 7.33-7.44 (m, 3H), 7.56-7.61 (dd,  $J = 6.3, 1.7$  Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  13.7, 19.1, 30.5, 65.7, 80.8, 85.9, 119.8, 128.5, 130.5, 132.9, 154.0; Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> requires C, 77.20; H, 6.98; found C, 76.96; H, 6.74%.

### Heptyl 3-propionate (3ad)

Yield: 72%; colourless liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  689, 757, 1172, 1188, 1285, 1490, 1712, 2223, 2857; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (br s, 3H), 1.30 (br s, 10H), 1.65-1.78 (m, 2H), 4.22 (t,  $J = 6.7$  Hz, 2H), 7.33-7.44 (m, 3H), 7.56-7.61 (m, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 22.6, 35.8, 28.5, 28.9, 31.7, 66.0, 80.8, 85.8, 119.8, 128.5, 130.4, 132.9, 154.0; Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>2</sub> requires C, 78.65; H, 8.25; found C, 78.53; H, 8.08%.

### Allyl 3-phenylpropionate (3ae)

Yield: 62%; colourless liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  675, 1171, 1185, 1281, 1711, 2227; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  4.71 (d,  $J = 5.8$  Hz, 2H), 5.29-5.45 (m, 2H), 5.88-6.08 (m, 1H), 7.34-7.49 (m, 3H), 7.58 (d,  $J = 6.6$  Hz, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  66.4, 80.5, 86.4, 119.3, 119.7, 128.5, 130.6, 131.3, 133.0, 153.5; Anal. Calcd for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub> requires C, 77.40; H, 5.41; found C, 77.23; H, 5.85%.

### Ethyl 3-*p*-tolylpropionate (3b)

Yield: 89%; colourless liquid; IR: (CHCl<sub>3</sub>, cm<sup>-1</sup>):  $\nu_{\max}$  756, 1019, 1193, 1214, 1509, 1705, 2208; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.36 (t,  $J = 7.1$  Hz, 3H), 2.38 (s, 3H), 4.30 (q,  $J = 7.2$  Hz, 2H),

7.15 (d,  $J = 7.3$  Hz, 2H), 7.46 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 21.7, 61.8, 80.4, 86.4, 116.7, 129.3, 132.9, 141.0, 154.0; Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  requires C, 76.57; H, 6.43; found C, 76.42; H, 6.34%.

#### Ethyl 3-(4-chlorophenyl)propiolate (3c)

Yield: 75%; colourless liquid; IR: ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  757, 1024, 1137, 1157, 1233, 1252, 1515, 1707, 2212;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.36 (t,  $J = 7.2$  Hz, 3H), 4.27 (q,  $J = 7.2$  Hz, 2H), 7.32-7.39 (m, 2H), 7.54-7.49 (m, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 62.0, 81.6, 84.5, 118.2, 129.0, 134.1, 137.0, 153.8; Anal. Calcd for  $\text{C}_{11}\text{H}_9\text{ClO}_2$  requires C, 63.32; H, 4.35; Cl, 16.99; found C, 63.24; H, 4.12; Cl, 16.74%.

#### Ethyl 3-(3,4-dimethoxyphenyl)propiolate (3d)

Yield: 79%; colourless liquid; IR: ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  756, 1014, 1191, 1289, 1489, 1709, 2208;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.36 (t,  $J = 7.2$  Hz, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 4.30 (q,  $J = 7.2$  Hz, 2H), 6.81 (d,  $J = 8.3$  Hz, 1H), 7.07 (d,  $J = 1.5$  Hz, 1H), 7.20-7.25 (m, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 55.8, 61.7, 79.9, 86.8, 110.9, 111.5, 115.2, 127.1, 148.7, 151.4, 154.0; Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_4$  requires C, 66.66; H, 6.02; found C, 66.48; H, 5.95%.

#### Ethyl 4-(*p*-tolylloxy)but-2-ynoate (3e)

Yield: 85%; colourless liquid; IR: ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  751, 1027, 1178, 1255, 1510, 1714, 2242;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H), 2.29 (s, 3H), 4.20 (q,  $J = 7.2$  Hz, 2H), 4.76 (s, 2H), 6.81 (d,  $J = 8.6$  Hz, 2H), 7.07 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 20.5, 55.6, 62.0, 78.5, 81.8, 114.7, 130.0, 131.2, 152.8, 155.3; Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3$  requires C, 71.51; H, 6.47; found C, 71.38; H, 6.32%.

#### Ethyl 4-(benzyloxy)but-2-ynoate (3f)

Yield: 84%; colourless liquid; IR: ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  1057, 1095, 1251, 1715, 2212;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32 (t,  $J = 7.20$  Hz, 3H), 4.26 (q,  $J = 7.20$  Hz, 2H), 4.27 (s, 2H), 4.61 (s, 2H), 7.32 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 56.6, 62.0, 78.4, 83.0, 128.1, 126.1, 128.5, 136.7, 153.0; Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3$  requires C, 71.54; H, 6.47; found C, 71.42; H, 6.34%.