Electronic Supplementary Data

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

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3-p-Tolylpropiolic acid (2b)

Yield: 75%; colourless solid; mp 149.2 °C; IR: (CHCl₃, cm⁻¹): ʋ_max 536, 742, 908, 1018, 1176, 1209, 1412, 1601, 1673, 2228, 3009; ¹H NMR (200 MHz, DMSO-d₆): δ 2.35 (s, 3H), 7.27 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 13.74 (bs, 1H); ¹³C NMR (50 MHz, DMSO-d₆): δ 21.2, 63.1, 84.8, 115.8, 129.6, 132.6, 141.2, 154.3; Anal. Calcd for C₁₀H₈O₂ requires C, 74.99; H, 5.03; found C, 74.82; H, 4.92%.

3-(4-Chlorophenyl)propiolic acid (2c)

Yield: 71%; colourless solid; mp 191.3 °C; IR: (CHCl₃, cm⁻¹): ʋ_max 529, 754, 1083, 1209, 1384, 1488, 1700, 2239, 3428; ¹H NMR (200 MHz, DMSO-d₆): δ 7.53 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 13.91 (bs, 1H); ¹³C NMR (50 MHz, DMSO-d₆): δ 71.8, 83.2, 118.0, 129.4, 134.5, 136.0, 154.2; Anal. Calcd for C₉H₅ClO₂ requires C, 59.86; H, 2.79; Cl, 19.63; found C, 59.72; H, 2.80; Cl, 19.49%.

3-(3,4-Dimethoxyphenyl)propiolic acid (2d)

Yield: 82%; colourless solid; mp 154.7 °C; IR: (CHCl₃, cm⁻¹): ʋ_max 768, 1018, 1164, 1262, 1309, 1519, 1674, 2201, 2939; ¹H NMR (200 MHz, DMSO-d₆): δ 3.79 (s, 3H), 3.81 (s, 3H), 7.01-7.22, (m, 3H), 13.60 (bs, 1H); ¹³C NMR (50 MHz, DMSO-d₆): δ 55.8, 80.9, 85.8, 110.6, 112.1, 115.4, 126.9, 148.8, 151.5, 154.7; Anal. Calcd for C₁₁H₁₀O₄ 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: (CHCl₃, cm⁻¹): ʋ_max 699, 754, 1279, 1410, 1701, 2238, 3028; ¹H NMR (200 MHz, DMSO-d₆): δ 2.62-2.70 (m, 2H), 2.78-2.86 (m, 2H), 7.21-7.34, (m, 5H); ¹³C NMR (50 MHz, DMSO-d₆): δ 19.7, 33.1, 74.6, 87.7, 126.3, 128.3, 128.4, 139.8, 154.2; Anal. Calcd for C₁₀H₁₀O₂ 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: (CHCl₃, cm⁻¹): ʋ_max 725, 811, 1236, 1290, 1422, 1510, 1690, 2251, 2970; ¹H NMR (200 MHz, DMSO-d₆): δ 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); ¹³C NMR (50 MHz, DMSO-d₆): δ 20.0, 55.0,
81.9, 114.6, 129.8, 130.3, 133.3, 134.8; Anal. Calcd for C_{11}H_{10}O_{3} 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_{3}, cm^{-1}): \upsilon_{\text{max}} 1027, 1060, 1704, 2230, 3440; \textsuperscript{1}H NMR (200 MHz, DMSO-d_{6}): \delta 4.39 (s, 2H), 4.55 (s, 2H), 7.35 (s, 5H); \textsuperscript{13}C NMR (50 MHz, DMSO-d_{6}): \delta 56.9, 71.5, 79.3, 83.0, 126.0, 128.6, 137.5, 154.0; Anal. Calcd for C_{11}H_{10}O_{3} 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_{3}, cm^{-1}): \upsilon_{\text{max}} 700, 1101, 1257, 1712, 2240, 3028; \textsuperscript{1}H NMR (200 MHz, DMSO-d_{6}): \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); \textsuperscript{13}C NMR (50 MHz, DMSO-d_{6}): \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_{12}H_{12}O_{3} requires C, 70.37; H, 5.92; found C, 70.25; H, 5.76%.

3-Cyclopropylpropiolic acid (2i)

Yield: 70%; colourless solid, mp 63.9\degree C IR: (CHCl_{3}, cm^{-1}): \upsilon_{\text{max}} 1184, 1690, 2223, 3011; \textsuperscript{1}H NMR (200 MHz, DMSO-d_{6}): \delta 0.80-0.83 (m, 2H), 0.92-0.96 (m, 2H), 1.49-1.54 (m, 1H), 13.91 (bs, 1H); \textsuperscript{13}C NMR (50 MHz, DMSO-d_{6}): \delta 71.8, 83.2, 118.0, 129.4, 134.5, 136.0, 154.2; Anal. Calcd for C_{6}H_{6}O_{2} 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_{3}, cm^{-1}): \upsilon_{\text{max}} 755, 855, 1289, 1700, 2239, 2965; \textsuperscript{1}H NMR (200 MHz, DMSO-d_{6}): \delta 2.02 (qt, J = 6.7 Hz, 2H), 2.56 (m, 2H), 3.73, (t, J = 6.4 Hz, 2H); \textsuperscript{13}C NMR (50 MHz, CDCl_{3}): \delta 16.0, 20.7, 30.0, 43.0, 73.5, 89.5, 157.2; Anal. Calcd for C_{6}H_{7}ClO_{2} requires C, 49.17; H, 4.81 Cl, 24.19; found C, 49.05; H, 4.71; Cl, 24.12%.
Ethyl 3-phenylpropiolate (3ab)

Yield: 75%; colourless liquid; IR: (CHCl₃, cm⁻¹): \( \nu_{\text{max}} \) 757, 1174, 1192, 1286, 1708, 2210; \(^1\)H NMR (200 MHz, CDCl₃): \( \delta \) 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); \(^{13}\)C NMR (50 MHz, CDCl₃): \( \delta \) 14.1, 61.9, 80.8, 119.7, 128.5, 130.5, 132.9, 154.0; Anal. Calcd for C₁₁H₁₀O₂ requires C, 75.84; H, 5.79; found C, 75.68; H, 5.56%.

Butyl 3-phenylpropiolate (3ac)

Yield: 77%; colourless liquid; IR: (CHCl₃, cm⁻¹): \( \nu_{\text{max}} \) 688, 756, 1173, 1286, 1490, 1708, 2221; \(^1\)H NMR (200 MHz, CDCl₃): \( \delta \) 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); \(^{13}\)C NMR (50 MHz, CDCl₃): \( \delta \) 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 C₁₃H₁₄O₂ requires C, 77.20; H, 6.98; found C, 76.96; H, 6.74%.

Heptyl 3-propioolate (3ad)

Yield: 72%; colourless liquid; IR: (CHCl₃, cm⁻¹): \( \nu_{\text{max}} \) 689, 757, 1172, 1188, 1285, 1490, 1712, 2223, 2857; \(^1\)H NMR (200 MHz, CDCl₃): \( \delta \) 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 (dd, \( J = 6.3, 1.7 \) Hz, 2H); \(^{13}\)C NMR (50 MHz, CDCl₃): \( \delta \) 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 C₁₆H₂₀O₂ requires C, 78.65; H, 8.25; found C, 78.53; H, 8.08%.

Allyl 3-phenylpropiolate (3ae)

Yield: 62%; colourless liquid; IR: (CHCl₃, cm⁻¹): \( \nu_{\text{max}} \) 675, 1171, 1185, 1281, 1711, 2227; \(^1\)H NMR (200 MHz, CDCl₃): \( \delta \) 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); \(^{13}\)C NMR (50 MHz, CDCl₃): \( \delta \) 66.4, 80.5, 86.4, 119.3, 119.7, 128.5, 130.6, 131.3, 133.0, 153.5; Anal. Calcd for C₁₂H₁₀O₂ requires C, 77.40; H, 5.41; found C, 77.23; H, 5.85%.

Ethyl 3-\( p \)-tolylpropiolate (3b)

Yield: 89%; colourless liquid; IR: (CHCl₃, cm⁻¹): \( \nu_{\text{max}} \) 756, 1019, 1193, 1214, 1509, 1705, 2208; \(^1\)H NMR (200 MHz, CDCl₃): \( \delta \) 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); $^{13}$C NMR (50 MHz, CDCl$_3$): δ 14.1, 21.7, 61.8, 80.4, 86.4, 116.7, 129.3, 132.9, 141.0, 154.0; Anal. Calcd for C$_{12}$H$_{12}$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: (CHCl$_3$, cm$^{-1}$): $\nu_{\text{max}}$ 757, 1024, 1137, 1157, 1233, 1252, 1515, 1707, 2212; $^1$H NMR (200 MHz, CDCl$_3$): δ 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); $^{13}$C NMR (50 MHz, CDCl$_3$): δ 14.1, 62.0, 81.6, 84.5, 118.2, 129.0, 134.1, 137.0, 153.8; Anal. Calcd for C$_{11}$H$_9$ClO$_2$ requires C, 63.24; H, 4.12; Cl, 16.74%; found C, 63.24; H, 4.12; Cl, 16.74%.

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

Yield: 79%; colourless liquid; IR: (CHCl$_3$, cm$^{-1}$): $\nu_{\text{max}}$ 756, 1014, 1191, 1289, 1489, 1709, 2208; $^1$H NMR (200 MHz, CDCl$_3$): δ 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); $^{13}$C NMR (50 MHz, CDCl$_3$): δ 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 C$_{13}$H$_{14}$O$_4$ requires C, 66.66; H, 6.02; found C, 66.48; H, 5.95%.

Ethyl 4-($p$-tolyloxy)but-2-ynoate (3e)

Yield: 85%; colourless liquid; IR: (CHCl$_3$, cm$^{-1}$): $\nu_{\text{max}}$ 751, 1027, 1178, 1255, 1510, 1714, 2242; $^1$H NMR (200 MHz, CDCl$_3$): δ 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); $^{13}$C NMR (50 MHz, CDCl$_3$): δ 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 C$_{13}$H$_{14}$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: (CHCl$_3$, cm$^{-1}$): $\nu_{\text{max}}$ 1057, 1095, 1251, 1715, 2212; $^1$H NMR (200 MHz, CDCl$_3$): δ 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); $^{13}$C NMR (50 MHz, CDCl$_3$): δ 14.0, 56.6, 62.0, 78.4, 83.0, 128.1, 126.1, 128.5, 136.7, 153.0; Anal. Calcd for C$_{13}$H$_{14}$O$_3$ requires C, 71.54; H, 6.47; found C, 71.42; H, 6.34%.