Supporting Information

CuO/CNTs-catalyzed Heterogeneous process: A Convenient Strategy to Prepared Furan Derivatives from Electron-deficient Alkynes and α-hydroxy Ketones

Hua Cao,*[a] Huan-Feng Jiang,*[b] Xiao-Song Zhou,[c] Chao-Rong Qi,[b] Yuan-Guang Lin,[a] Jian-Yong Wu[a] and Qi-Mei Liang[a]

[a] School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou 510006, P.R. of China

[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P.R. of China

[c] School of Chemistry Science & Technology, and Development Center for New Materials Engineering & Technology, Universities of Guangdong, Zhanjiang Normal University, Zhanjiang 524048, PR China

hua.cao@mail.scut.edu.cn; *jianghf@scut.edu.cn*

Experimental Section

General method

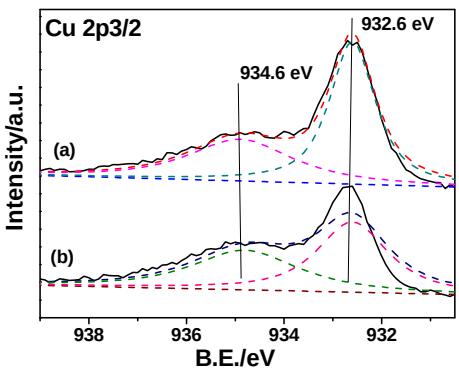
General. All reactions were performed at the room temperature under air atmosphere in a round bottom flask equipped with magnetic stir bar. ^{1}H NMR spectra and ^{13}H NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and referenced to 7.26 ppm and 77.0 ppm for chloroform solvent respectively with TMS as internal standard. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS–QP5050A at an ionization voltage of 70 eV equipped with a DB–WAX capillary column (internal diameter = 0.25 mm, length = 30 m). Elemental analysis was performed on a Vario EL elemental analyzer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

Synthesis of CuO/CNTs[1]

In a typical synthesis, 25 ml 0.25 M $Cu(NO_3)_2$ solution was slowly dropped into 30 ml of 0.5 M $(NH_4)_2CO_3$ solution under vigorous stirring to obtain a precipitate. Then 25 ml 1.0% polyethylene glycol (molecular weight: 10,000, Aldrich) was slowly dropped into the solution, then 100 g multi-walled carbon nanotubes (Shenzhen Nanotech Port) was added. The mixture was stirred for 30 min and then transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and put into a preheated oven to perform hydrothermal treatment at 150 ^oC for 10 h. After hydrothermal processing, the product was collected and washed with copious amounts of distilled water and absolute alcohol three times, respectively, then dried in air at 80 ^oC overnight, which we denote as CuO/CNTs(containing 15.4% CuO).

General procedure for the synthesis of dimethyl 4,5-diethylfuran-2,3-dicarboxylate (4aa).

Diethyl but-2-ynedioate (**1a** 1.0 mmol), 3-hydroxybutan-2-one (**2a** 1.1 mmol) and DABCO (5% mol) were stirred in CH_2Cl_2 at room temperature for 15min. And then the solution was evaporated to dryness under reduced pressure and the pure sample of **3a** was obtained by column chromatography. Subsequently, **3a**, CuO/CNTs(6% mol)/CH_3CO_2H(10% mol) and DMF(3mL) were added and stirred at 60 ^oC for 8h.. After completion of the reaction (monitored by TLC), the reaction mixture turned clear and the CuO/CNTs were deposited on the button. The catalyst was recovered by filtration and washed 3 times by water (3×3 mL).The aqueous solution was extracted with diethyl ether (3×8 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solution was evaporated to dryness under reduced pressure and the crude product was separated by column chromatography to give a pure sample of **4aa**.



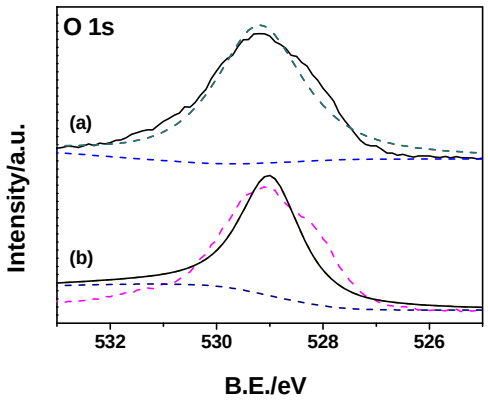


Figure 2. XPS of Cu 2p and O 1s survey spectrum of as-prepared sample: (a) before reaction; (b) after reaction

Diethyl 4,5-dimethylfuran-2,3-dicarboxylate (4aa)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.37 (q, J = 7.2 Hz 2H), 2.29 (s, 3H), 2.00 (s, 3H), 1.33-1.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.9, 157.9, 152.1, 140.0, 126.5, 116.5, 61.3, 61.1, 14.2, 14.1, 11.7, 8.50; MS (EI) m/z (%):240, 194, 166, 138, 110. $C_{12}H_{16}O_5$: Calcd. C, 59.99; H, 6.71; Found: C, 60.32; H, 6.73.

Diethyl 4-methylfuran-2,3-dicarboxylate (4ab)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31(s, 1H), 4.34-4.40 (m, 4H), 2.10 (s, 3H), 1.35-1.39(m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4, 157.8, 143.0, 142.2, 125.3, 122.0, 61.5, 61.4, 14.2, 14.1, 8.52; MS (EI) m/z (%):226, 185, 180, 153, 110; $C_{11}H_{14}O_5$: Calcd. C, 58.40; H, 6.24; Found: C, 58.76; H, 5.66.

Diethyl 4,5-di(furan-2-yl)furan-2,3-dicarboxylate (4ac)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, J=0.8 Hz, 1H), 7.47 (d, J=0.8 Hz, 1H), 6.96 (d, J=3.6 Hz, 1H), 6.79 (d, J=3.6 Hz, 1H), 6.48-6.53 (m, 2H), 4.36-4.43 (m, 4H), 1.34-1.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.3, 157.4, 144.0, 143.8, 142.5, 126.1, 111.8, 111.5, 111.0, 62.0, 62.6, 14.2, 14.0; MS (EI) m/z (%):344, 299, 272, 244, 215, 171, 158, 115, 95. $C_{18}H_{16}O_7$: Calcd. C, 62.79; H, 4.68; Found: C, 63.25; H, 5.42.

Diethyl 4,5-di(thiophen-2-yl)furan-2,3-dicarboxylate (4ad)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93(d, *J*=8.8 Hz, 1H), 7.46 (d, *J*=8.8 Hz, 1H), 7.25 (d, *J*=8.8 Hz, 1H), 6.79-6.97 (m, 3H), 4.41(d, *J*=7.2 Hz, 2H), 4.26 (d, *J*=7.2 Hz, 2H), 1.39 (d, *J*=7.2 Hz, 3H), 1.22 (d, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 159.4, 152.1, 139.0, 132.3, 130.8, 128.6, 128.2, 126.3, 114.3, 61.6, 61.2; MS (EI) m/z (%):376, 341, 277, 205, 111, 105, 73; $C_{18}H_{16}O_5S_2$: Calcd. C, 57.43; H, 4.28; Found: C, 57.78; H, 4.23.

Diethyl 4,5-dip-tolylfuran-2,3-dicarboxylate (4ae)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J*=8.4 Hz, 2H), 7.06-7.25 (m, 6H), 4.41 (q, *J*=7.2 Hz, 2H), 4.26 (q, *J*=7.2 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 2.31(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 157.9, 152.2, 139.4, 139.1, 138.0, 129.4, 129.2, 129.0, 128.4, 128.0, 127.3, 126.7, 126.4, 122.0, 61.6, 61.3, 21.4, 21.3, 14.2, 13.9; MS (EI) m/z (%):392, 320, 292, 263, 219, 189, 119, 91,65. $C_{24}H_{24}O_5$: Calcd. C, 73.45; H, 6.16; Found: C, 72.99; H, 6.10.

Diethyl 4,5-diphenylfuran-2,3-dicarboxylate (4af)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.51 (m, 3H), 7.29-7.38 (m, 7H), 4.22-4.43 (m, 4H), 1.19-1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 157.93, 152.0, 140.1, 134.4, 131.0, 129.5, 129.3, 129.1, 128.7, 128.6, 128.5, 127.6, 126.8,126.7, 121.3, 61.8, 61.5, 14.2, 13.9; MS (EI) m/z (%):364, 333, 305, 277, 219, 202, 119, 91; $C_{22}H_{20}O_5$: Calcd. C, 72.51; H, 5.53; Found: C, 72.52; H, 5.62.

Diethyl 4,5-bis(4-methoxyphenyl)furan-2,3-dicarboxylate (4ag)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, *J*=9.2 Hz, 2H),7.25 (d, *J*=8.8 Hz, 2H), 6.90 (d, *J*=8.8 Hz, 2H), 6.79 (d, *J*=9.2 Hz, 2H), 4.41 (q, *J*=7.2 Hz, 2H), 4.26 (q, *J*=7.2 Hz, 2H),3.64 (s, 3H), 3.79 (s, 3H), 1.35 (t, *J*=7.2 Hz, 3H), 1.22 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 160.1, 159.4, 158.0, 152.1, 139.0, 130.8, 128.5, 128.3, 123.3, 121.8, 120.9, 114.3, 113.9, 61.6, 61.3, 55.6, 55.2, 14.2, 13.9; MS (EI) m/z (%):424, 352, 295, 251, 207, 135, 77, 44; $C_{24}H_{24}O_7$: Calcd. C, 67.91; H, 5.70; Found: C, 68.37; H, 5.65.

Diethyl 4-(4-methoxyphenyl)-5-methylfuran-2,3-dicarboxylate (4ah)

^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.22 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 9.6 Hz, 2H), 4.39 (q, J = 8.0 Hz, 2H), 4.27 (q, J = 8.0 Hz, 2H), 3.82 (s, 3H), 2.39 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 164.0, 159.1, 157.8, 152.4, 139.3, 130.0, 126.7, 122.9, 122.2, 114.0, 61.6, 61.2, 55.2, 14.1, 13.9, 12.5; MS (EI) m/z (%): 332, 304, 287, 259, 232, 187, 115; $C_{18}H_{20}O_6$: Calcd. C, 65.05; H, 6.07; Found: C, 65.22; H, 5.93.

Diethyl 5-methyl-4-phenylfuran-2,3-dicarboxylate (4ai)

^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.22-7.34 (m, 5H), 4.29 (q, J = 7.2 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 163.9, 157.8, 152.6, 139.5, 131.7, 130.7, 128.8, 128.3, 127.7, 126.6, 122.6, 111.4, 61.6, 61.2, 14.2, 13.9, 12.6; MS (EI) m/z (%): 302, 257, 229, 202, 185, 128, 77; $C_{17}H_{18}O_5$: Calcd. C, 67.54; H, 6.00; Found: C, 67.30; H, 6.14.

Diethyl 4-ethyl-5-methylfuran-2,3-dicarboxylate (4aj)

^{1}H NMR ($CDCl_3$, 400 Hz) δ 4.28-4.36 (m, 4H), 2.39 (d, J = 7.6 Hz, 2H), 2.27 (s, 3H), 1.29-1.36 (m, 6H), 1.07 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 164.1, 157.9, 151.8, 139.7, 122.8, 110.8, 61.4, 61.0, 16.9, 14.7, 14.1, 14.0, 11.7; MS (EI) m/z (%): 254, 208, 179, 162, 135, 108; $C_{13}H_{18}O_5$: Calcd. C, 61.40; H, 7.14; Found: C, 61.16; H, 7.20.

Dimethyl 4,5-dimethylfuran-2,3-dicarboxylate (4ba)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.90 (s, 3H), 3.88 (s, 3H), 2.30 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ164.2, 158.3, 152.2, 140.0, 126.3, 116.8, 52.3, 52.1, 11.7, 8.59; MS (EI) m/z (%):212, 180, 151, 122, 94, 66. $C_{10}H_{12}O_5$: Calcd. C, 56.60; H, 5.70; Found: C, 56.41; H, 5.71.

Dimethyl 4-methylfuran-2,3-dicarboxylate (4bb)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32(s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.10 (d, J = 1.2 Hz 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 158.2, 143.1, 142.3, 125.0, 122.3, 52.4, 52.3, 8.60; MS (EI) m/z (%):198, 167, 127, 115, 87; $C_9H_{10}O_5$: Calcd. C, 54.55; H,

5.09; Found: C, 54.73; H, 5.69.

Dimethyl 4,5-di(furan-2-yl)furan-2,3-dicarboxylate (4bc)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J=1.2 Hz, 1H), 7.64 (d, J=3.6 Hz, 1H), 7.56 (d, J=0.8 Hz, 1H), 6.95 (d, J=3.6 Hz, 1H), 6.78 (d, J=3.2 Hz, 1H), 6.64 (d, J=1.6 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 157.8, 149.3, 143.9, 142.6, 124.7, 113.0, 111.9, 111.6, 110.2, 52.9, 52.5; MS (EI) m/z (%):316, 287, 229, 95; $C_{16}H_{12}O_7$: Calcd. C, 60.76; H, 3.82; Found: C, 61.09; H, 5.44.

Dimethyl 4,5-di(thiophen-2-yl)furan-2,3-dicarboxylate (4bd)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.46 (m, 3H), 6.98-7.16 (m, 3H), 3.93 (s, 3H), 3.81 (s, 3H),; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.2, 158.0, 149.5, 139.4, 130.0, 129.5, 129.4, 128.3, 127.9, 127.8, 127.5, 114.7, 52.7, 52.4; MS (EI) m/z (%):348, 317, 261, 190, 111; $C_{16}H_{12}O_5S_2$: Calcd. C, 55.16; H, 3.47; Found: C, 55.51; H, 3.50.

Dimethyl 4,5-dip-tolylfuran-2,3-dicarboxylate (4be)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, J=8.4 Hz, 2H), 7.16-7.23 (m, 4H), 7.06 (d, J=8.0 Hz, 2H), 3.92 (s, 3H), 3.77 (s, 3H), 2.37 (s, 3H), 2.31(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.1, 158.3, 152.3, 139.4, 139.3, 138.0, 129.5, 129.3, 129.2, 128.4, 127.9, 126.7, 126.3, 122.1, 52.6, 52.3, 21.4, 21.3; MS (EI) m/z (%):364, 337, 277, 219, 202, 119, 91, 65; $C_{22}H_{20}O_5$: Calcd. C, 72.51; H, 5.53; Found: C, 72.89; H, 5.50.

Dimethyl 4,5-diphenylfuran-2,3-dicarboxylate (4bf)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.51 (m, 10H), 3.94 (s, 3H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.9, 158.3, 152.1, 139.7, 130.8, 129.6, 129.5, 129.2, 128.9, 128.5, 128.4, 127.3, 126.8, 122.7, 52.6, 52.4; MS (EI) m/z (%):336, 305, 209, 189, 151, 77; $C_{20}H_{16}O_5$: Calcd. C, 71.42; H, 4.79; Found: C, 71.76; H, 5.66.

Dimethyl 4,5-bis(4-methoxyphenyl)furan-2,3-dicarboxylate (3ag)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, J=8.8 Hz, 2H),7.24 (d, J=8.8 Hz, 2H), 6.90 (d, J=9.2 Hz, 2H), 6.79 (d, J=8.0 Hz, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 3.78 (s,

3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.2, 160.2, 159.5, 158.3, 152.2, 139.0, 130.7, 128.5, 128.3, 123.1, 121.7, 121.0, 114.3, 114.0, 55.3, 55.2, 52.6, 52.2; MS (EI) m/z (%):396, 309, 251, 207, 152, 135, 77, 59; $C_{22}H_{20}O_7$: Calcd. C, 66.66; H, 5.09; Found: C, 66.34; H, 5.42.

Dimethyl 4-(4-chlorophenyl)-5-phenylfuran-2,3-dicarboxylate (4bk)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.49 (m, 2H), 7.27-7.38 (m, 7H), 3.94 (s, 3H), 3.79 (s, 3H),; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 158.1, 152.2, 140.1, 134.5, 130.9, 129.4, 129.2, 128.6, 126.9, 121.4, 100.0, 52.7, 52.4; MS (EI) m/z (%):370, 343, 283, 207, 189, 165, 105, 77; $C_{20}H_{15}ClO_5$: Calcd. C, 64.79; H, 4.08; Found: C, 64.41; H, 4.10.

Ethyl 2,4,5-trimethylfuran-3-carboxylate (4ca)[2-4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (q, J = 7.2 Hz, 2 H), 2.50 (s, 3 H), 2.17 (s, 3 H), 2.05 (s, 3 H), 1.35 (t, J = 7.2 Hz, 3 H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 157.3, 145.9, 114.8, 113.9, 59.7, 14.3, 14.2, 11.0, 10.0.

Ethyl 2,4 -dimethylfuran-3-carboxylate (4cb)[2-4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J=1.6 Hz, 1H), 4.28 (q, J=7.2 Hz, 2H,), 2.53 (s, 3H), 2.13 (d, J=l.6 Hz, 3H,), 1.35 (t, 3H, J=7.2 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 160.1, 137.7, 121.2, 113.5, 59.9, 14.4, 10.1.

Ethyl 4,5-dimethylfuran-3-carboxylate (4da) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 4.28 (q, 2H, J=8.0 Hz), 2.21 (s, 3H), 2.11 (s, 3H), 1.33 (t, 3H, J=8.0 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 149.5, 146.1, 119.3, 114.4, 59.9, 14.4, 11.3, 9.0.

Ethyl 4,5-dimethyl-2-phenylfuran-3-carboxylate (4ea) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.79 (m, 2 H); 7.30−7.42 (m, 3H), 4.26 (q, J = 7.2 Hz, 2 H), 2.28 (s, 3 H), 2.12 (s, 3 H), 1.28 (t, J = 7.2 Hz, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 155.0,147.5 130.7, 128.6, 128.2, 127.8, 116.2, 114.6, 60.2,

14.1, 11.2, 9.9;

(4,5-dimethyl-2-phenylfuran-3-yl)(phenyl)methanone(3fa)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.84(m, 2 H), 7.27−7.51 (m, 5 H), 7.05−7.22 (m, 3 H), 2.33 (s, 3 H), 1.92 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 151.6, 147.8, 137.8, 133.1, 130.1, 129.9, 128.3, 128.1, 128.0, 126.7, 122.3, 116.4, 11.5, 8.9;

Methyl 4,5-dimethyl-2-pentylfuran-3-carboxylate(4ga)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80(s, 3H), 2.88 (t, J = 8.0 Hz, 2H), 2.16 (s, 3 H), 2.05 (s, 3 H), 1.54−1.62 (m, 2H), 1.28−1.35 (m, 4H), 0.87 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 161.5, 145.8, 114,3, 113.1, 50.7, 31.3, 28.0, 27.9, 13.8, 11.0, 9.9;

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