Supporting Information

Copper-Catalyzed Tandem Process: An Efficient Approach to 2-Substituted-1, 4-benzodioxanes

Yunyun Liu, Weiliang Bao*

Department of Chemistry, Xi Xi Campus, Zhejiang University, Hangzhou, Zhejiang 310028, P. R. China
Fax: (+86) -571-88273814; E-mail: wlbao@css.zju.edu.cn

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A. Experimental Procedure

**General Information.** All reactions were carried out in Schlenk tube and run under a N₂ atmosphere. All the copper sources, ligands and bases were commercially available. Organic solvents, also were commercially available, were dried over 4Å molecular sieves before used. 2-((2-iodophenoxy)methyl)oxirane were prepared according to the known literature.¹ Thin-layer chromatography (TLC) was carried out with 0.2 mm thick silica gel plates (GF 254) and visualized by UV light. All melting points are uncorrected. All products were confirmed by 1H NMR, 13C NMR. Unknown compounds were additionally confirmed by MS and HRMS. MS and HRMS were obtained using EI ionization. The NMR spectra were recorded in CDCl₃ on a 400 MHz instrument with TMS as internal standard. IR spectrums were taken in ATR apparatus.

**General Procedure for the Synthesis of 2-Substituted-1, 4-benzodioxanes.** A Schlenk tube was charged with CuBr (22 mg, 15% mol), 1,10-phenanthroline (57 mg, 30% mol), Cs₂CO₃ (650 mg, 2 mmol), phenol (113 mg, 1.2 mmol), evacuated and backfilled with nitrogen. Then 2-((2-iodophenoxy)methyl)oxirane (276 mg, 1.0 mmol), DMA (2 mL) were successively added. The reaction tube was quickly sealed and the contents were stirred at 120 ºC for 48 h. Then the cooled reaction mixture was dissolved in H₂O and extracted with Et₂O. The combined organic layer was dried (MgSO₄). The product was further purified by column chromatography (silica gel, PE-EtOAC).

**B. Spectra Data**

![Structure of 2-((2-iodophenoxy)methyl)oxirane](image)

2-((2-iodophenoxy)methyl)oxirane (1a): Oil, ¹H NMR (400MHz, CDCl₃): δ 7.76-7.74 (m, 1H), 7.29-7.24 (m, 1H), 6.83-6.81 (m, 1H), 6.73-6.69 (m, 1H), 4.28-4.25 (m, 1H), 4.04-4.00 (m, 1H), 3.37-3.36 (m, 1H), 2.90-2.87 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 156.98, 139.52, 129.55, 123.12, 112.56, 86.62, 69.27, 50.13, 44.74.

![Structure of 2-phenoxyethyl-2,3-dihydrobenzo[1,4]dioxin](image)

2-phenoxyethyl-2,3-dihydrobenzo[1,4]dioxin (3a): White solid, m.p. 35-36°C; ¹H NMR (400MHz, CDCl₃): δ 7.33 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.96-6.90 (m, 6H), 4.59-4.56 (m, 1H), 4.43 (dd, J = 1.4, 11.4Hz, 1H), 4.30-4.22 (m, 2H), 4.19-4.15
(m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.26, 143.18, 142.91, 129.55, 121.74, 121.53, 121.40, 117.40, 117.25, 114.56, 71.34, 66.24, 65.34; IR: $\nu$ = 3019, 2930, 2882, 1578, 1493, 1269, 1237, 1076, 745, 689 cm$^{-1}$.

2-(p-tolylxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3b): White solid, m.p. 56-57°C; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.11 (d, $J$ = 8.4Hz, 2H), 6.96-6.92 (m, 2H), 6.89-6.84 (m, 4H), 4.58-4.54 (m, 1H), 4.43-4.40 (m, 1H), 4.26-4.19 (m, 2H), 4.15-4.10 (m, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.22, 143.22, 142.96, 130.67, 130.00, 121.73, 121.52, 117.42, 117.26, 114.45, 71.41, 66.47, 65.39, 20.47; IR: $\nu$ = 3034, 2947, 2922, 2882, 1591, 1492, 235, 1041, 842, 739 cm$^{-1}$; EI-MS: m/z = 256 (M$^+$); HRMS (EI) calcd for C$_{16}$H$_{16}$O$_3$ 256.1099, found 256.1100.

2-((4-tert-butylphenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3c): White solid, m.p. 59-60°C; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.34 (d, $J$ = 7.6 Hz, 2H), 6.95-6.87 (m, 6H), 4.59-4.55 (m, 1H), 4.43-4.40 (m, 1H), 4.26-4.20 (m, 2H), 4.17-4.12 (m, 1H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.02, 144.14, 143.19, 142.92, 126.33, 121.71, 121.49, 117.38, 117.24, 114.03, 71.35, 66.32, 65.40, 34.09, 31.49; IR: $\nu$ = 3053, 2958, 2932, 2901, 2875, 1593, 1493, 1267, 1030, 841, 744 cm$^{-1}$; EI-MS: m/z = 298 (M$^+$); HRMS (EI) calcd for C$_{19}$H$_{22}$O$_3$ 258.1569, found 298.1566.

2-(m-tolylxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3d): Oil; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.15 (t, $J$ = 8.0Hz, 1H), 6.92-6.88 (m, 2H), 6.85-6.82 (m, 2H), 6.78 (d, $J$ = 7.8Hz, 1H), 6.74-6.70 (m, 2H), 4.54-4.50 (m, 1H), 4.38-4.35 (m, 1H), 4.23-4.15 (m, 2H), 4.11-4.07 (m, 1H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.31, 143.22, 142.95, 139.66, 129.31, 122.23, 121.74, 121.53, 117.42, 117.26, 115.44, 111.44, 71.37, 66.20, 65.37, 21.49; IR: $\nu$ = 3048, 2977, 2921, 1590, 1490, 1248, 1043, 848, 780, 745 cm$^{-1}$; EI-MS: m/z = 256 (M$^+$). HRMS (EI) calcd for C$_{16}$H$_{16}$O$_3$ 256.1099, found 256.1101.
2-(o-tolyloxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3e): Oil; $^1$H NMR (400MHz, CDCl$_3$): δ 720-7.16 (m, 2H), 6.96-6.92 (m, 3H), 6.90-6.84 (m, 3H), 4.62-4.58 (m, 1H), 4.46 (dd, $J = 1.6, 11.4$ Hz, 1H), 4.31-4.24 (m, 2H), 4.20-4.16 (m, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.35, 143.21, 143.03, 130.84, 126.91, 126.86, 121.72, 121.50, 121.10, 117.35, 117.24, 111.04, 71.42, 66.35, 65.51, 16.15; IR: $\nu = 3053, 2923, 2882, 1592, 1491, 1239, 1044, 743$ cm$^{-1}$. 

2-((2,4-di-tert-butylphenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3f): Oil; $^1$H NMR (400MHz, CDCl$_3$): δ 7.34 (s, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.90-6.86 (m, 4H), 6.80 (d, $J = 8.4$ Hz, 1H), 4.62-4.60 (m, 1H), 4.48-4.45 (m, 1H), 4.27-4.19 (m, 3H), 1.40 (s, 9H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.64, 143.30, 143.15, 142.95, 137.30, 124.10, 123.39, 121.73, 121.45, 117.39, 117.16, 111.22, 71.50, 66.28, 65.79, 35.01, 34.27, 31.53, 29.90; IR: $\nu = 3057, 2961, 2857, 2878, 1591, 1493, 1235, 1061, 811, 749$ cm$^{-1}$; EI-MS: $m/z = 354$ (M$^+$); HRMS (EI) calcd for C$_{23}$H$_{30}$O$_3$ 354.2195, found 354.2204.

2-((4-chlorophenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3g): White solid, m.p. 81-82°C; $^1$H NMR (400MHz, CDCl$_3$): δ 7.23 (d, $J = 8.4$ Hz, 2H), 6.89 (t, $J = 4.8$ Hz, 2H), 6.86-6.83 (m, 4H), 4.56-4.51 (m, 1H), 4.39-4.36 (m, 1H), 4.22-4.17 (m, 2H), 4.13-4.09 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 157.04, 143.20, 142.61, 129.40, 126.37, 121.79, 121.57, 117.35, 117.24, 115.84, 71.22, 66.61, 65.15; IR: $\nu = 3076, 3042, 2961, 2886, 2852, 1588, 1492, 1240, 1043, 853, 753$ cm$^{-1}$; EI-MS: $m/z = 276$ (M$^+$); HRMS (EI) calcd for C$_{15}$H$_{13}$ClO$_3$ 276.0553, found 276.0559.

2-((2,4-dichlorophenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3h): White solid, m.p. 70-71°C; $^1$H NMR (400MHz, CDCl$_3$): δ 7.37 (s, 1H), 7.18 (d, $J = 8.4$Hz, 1H), 6.92-6.85 (m, 5H), 4.61-4.59 (m, 1H), 4.45-4.42(m, 1H), 4.31-4.26 (m, 2H), 4.20-4.16 (m,
\[ \text{H}_3\text{CO} \]

2-((2-acetylphenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3i): Oil; \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 7.72 (d, \(J = 7.6\) Hz, 1H), 7.44 (t, \(J = 7.6\)Hz, 1H), 7.02 (t, \(J = 7.6\)Hz, 1H), 6.94 (d, \(J = 8.4\)Hz, 1H), 6.90-6.84 (m, 4H), 4.63-4.59 (m, 1H), 4.41-4.38 (m, 1H), 4.33-4.20 (m, 3H), 2.63 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.42, 157.35, 142.96, 142.61, 133.60, 130.53, 128.63, 121.92, 121.67, 121.39, 117.36 117.28, 112.44, 71.19, 66.95, 65.16, 31.88; IR: \(\nu = 3072, 2985, 2886, 2742, 1685, 1598, 1490, 1334, 1243, 1045, 831, 752 \text{ cm}^{-1}\); EI-MS: \(m/z = 284(M^+)\); HRMS (EI) calcd for C\(_{17}\)H\(_{16}\)O\(_4\) 284.1049, found 284.1050.

\[ \text{CHO} \]

2-((4-formylphenoxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3j): White solid, m.p. 60-61°C; \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 9.89 (s 1H), 7.85 (d, \(J = 8.0\)Hz, 2H), 7.04 (d, \(J = 8.0\)Hz, 2H), 6.92-6.87 (m, 4H), 4.62-4.58 (m, 1H), 4.41-4.38 (m, 1H), 4.34-4.30 (m, 1H), 4.26-4.22 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.71, 163.11, 143.00, 142.63, 131.97, 130.46, 121.89, 121.68, 117.38, 117.30, 114.81, 71.06, 66.46, 64.97; IR: \(\nu = 3038, 2907, 2883, 2742, 1685, 1598, 1490, 1243, 1046, 830, 749 \text{ cm}^{-1}\).

\[ \text{2-((naphthalen-2-yloxy)methyl)-2,3-dihydrobenzo[1,4]dioxine (3k):} \]

White solid, m.p. 80-81°C; \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 7.81-7.74 (m, 3H), 7.48 (t, \(J = 7.6\)Hz, 1H), 7.39 (t, \(J = 7.6\)Hz, 1H), 7.26-7.19 (m, 2H), 7.00-6.95 (m, 2H), 6.93-6.90 (m, 2H), 4.67-4.63 (m, 1H), 4.48-4.45 (m, 1H), 4.39 (dd, \(J = 4.8, 10.0\) Hz, 1H), 4.31-4.26 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 156.23, 143.18, 142.92, 134.39, 129.59, 129.23, 127.67, 126.82, 126.53, 123.96, 121.81, 121.56, 118.63, 117.46, 117.30, 106.91, 71.36, 66.33, 65.34; IR: \(\nu = 3051, 2977, 2919, 1593, 1492, 1250, 1055, 848, 747 \text{ cm}^{-1}\); EI-MS: \(m/z = 292(M^+)\); HRMS (EI) calcd for C\(_{19}\)H\(_{16}\)O\(_3\) 292.1099, found 292.1105.
7-methyl-2-(phenoxymethyl)-2,3-dihydrobenz[1,4]dioxine (3l): White solid, m.p. 55-56°C; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.33 (t, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.78 (s, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 4.59-4.55 (m, 1H), 4.40 (dd, $J = 2.0$, 11.2 Hz, 1H), 4.29-4.15 (m, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.29, 142.44, 140.86, 131.42, 129.54, 122.06, 121.35, 117.70, 116.85, 114.55, 71.37, 66.22, 65.29, 20.66; IR: $\nu$ = 3103, 2973, 2921, 2875, 1588, 1499, 1240, 1058, 800, 750 cm$^{-1}$.

7-methyl-2-(p-tolyloxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3m): White solid, m.p. 80-81°C; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.12 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 7.2$ Hz, 1H), 6.77 (s, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 4.57-4.53 (m, 1H), 4.40-4.38 (m, 1H), 4.26-4.18 (m, 2H), 4.15-4.10 (m, 1H), 2.32 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.23, 142.48, 140.87, 131.39, 130.62, 129.96, 122.02, 117.71, 116.83, 114.43, 71.42, 66.45, 65.34, 20.66, 20.45; IR: $\nu$ = 3034, 2992, 2926, 2879, 1589, 1507, 1240, 1058, 842, 747 cm$^{-1}$; EI-MS: $m/z$ = 270(M$^+$); HRMS (EI) calcd for C$_{17}$H$_{18}$O$_3$ 270.1256, found 270.1258.

7-methyl-2-(m-tolyloxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3n): White solid, m.p. 50-51°C; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.21 (t, $J = 7.6$ Hz, 1H), 6.83-6.81 (m, 2H), 6.78-6.76 (m, 3H), 6.69 (d, $J = 8.0$ Hz, 1H), 4.58-4.56 (m, 1H), 4.41-4.38 (m, 1H), 4.28-4.19 (m, 2H), 4.17-4.13 (m, 1H), 2.37 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.29, 142.44, 140.85, 139.62, 131.41, 129.26, 122.16, 122.02, 117.70, 116.83, 115.37, 111.40, 71.36, 66.14, 65.30, 21.47, 20.65; IR: $\nu$ = 3034, 2951, 2921, 2879, 1583, 1506, 1255, 1060, 802, 767, 747 cm$^{-1}$; EI-MS: $m/z$ = 270(M$^+$); HRMS (EI) calcd for C$_{17}$H$_{18}$O$_3$ 270.1256, found 270.1253.

2-((4-chlorophenoxy)methyl)-7-methyl-2,3-dihydrobenzo[1,4]
dioxane (3a): White solid, m.p. 84-85°C; $^1$H NMR (400MHz, CDCl$_3$): δ 7.25 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.4$Hz, 1H), 6.74 (s, 1H), 6.67 (d, $J = 8.0$Hz, 1H), 4.56-4.52 (m, 1H), 4.36 (m, 1H), 4.23-4.17 (m, 2H), 4.12 (dd, $J = 6.4$, 9.8Hz, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.90, 142.29, 140.82, 131.51, 129.39, 126.29, 122.11, 117.67, 116.85, 115.84, 71.25, 66.61, 65.10, 20.63; IR: $\nu = 3053, 2958, 2928, 2867, 1590, 1492, 1242, 1012, 822, 748 \text{ cm}^{-1}$; EI-MS: $m/z = 290(M^+)$; HRMS (EI) calcd for C$_{16}$H$_{15}$ClO$_3$ 290.0710, found 290.0710.

![7-chloro-2-(phenoxymethyl)-2,3-dihydrobenzo[1,4]dioxine (3p)](image)

Oil; $^1$H NMR (400MHz, CDCl$_3$): δ 7.31 (t, $J = 7.6$Hz, 2H), 7.00, (t, $J = 7.2$ Hz, 1H), 6.94-6.92 (m, 3H), 6.83 (br, 2H), 4.58-4.53 (m, 1H), 4.41-4.39 (m, 1H), 4.27-4.19 (m, 2H), 4.16-4.12 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.12, 143.40, 141.91, 129.59, 126.13 121.50, 121.48, 118.03, 117.49, 114.49, 71.44, 65.97, 65.23; IR: $\nu = 3072, 2981, 2926, 2882, 1585, 1487, 1237, 1031, 802, 752 \text{ cm}^{-1}$.

C. References


D. Copies of $^1$H NMR and $^{13}$C NMR spectra