Supporting Information

**Ph₃P/I⁻-promoted dichlorination or dibromination of epoxide s with XCH₂CH₂X (X = Cl or Br)**

Jin Long, a,b Jia Chen, b Rong Li, a Zhuo Liu, a,b Xuan Xiao, a,b Jin-Hong Lin, b*

Xing-Zheng, a* Ji-Chang Xiao b*

a Institute of Pharmacy and Pharmacology, Hunan Province Cooperative Innovation Center for Molecular Target New Drug Study, University of South China, 28 Western Changsheng Road, Hengyang, Hunan, 421001, China.

b Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences 345 Lingling Road, Shanghai 200032, China.

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1. General information

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were detected on a 500 MHz, 400MHz or 300 MHz NMR spectrometer. Data for $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (J) in Hz). Mass spectra were obtained on a GC-MS or LC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

2. Optimization of the reaction conditions for dibromination

Table 1. Optimization of the reaction conditions for dibromination$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>ratio $^b$</th>
<th>temp. (°C)</th>
<th>time (h)</th>
<th>yield (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1.2:1.4</td>
<td>RT</td>
<td>4</td>
<td>69%</td>
</tr>
<tr>
<td>2</td>
<td>1:1.2:1.4</td>
<td>40</td>
<td>4</td>
<td>73%</td>
</tr>
<tr>
<td>3</td>
<td>1:1.2:1.4</td>
<td>60</td>
<td>4</td>
<td>67%</td>
</tr>
<tr>
<td>4</td>
<td>1:1.2:1.4</td>
<td>80</td>
<td>4</td>
<td>62%</td>
</tr>
<tr>
<td>5</td>
<td>1:1.2:1.4</td>
<td>40</td>
<td>1</td>
<td>76%</td>
</tr>
<tr>
<td>6</td>
<td>1:1.2:1.4</td>
<td>40</td>
<td>2</td>
<td>82%</td>
</tr>
<tr>
<td>7</td>
<td>1:1.2:1.4</td>
<td>40</td>
<td>3</td>
<td>75%</td>
</tr>
<tr>
<td>8</td>
<td>1:1.4:1.4</td>
<td>40</td>
<td>4</td>
<td>73%</td>
</tr>
<tr>
<td>9</td>
<td>1:1.2:1.4</td>
<td>40</td>
<td>5</td>
<td>82%</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: substrate 1a (0.25 mmol), Ph$_3$P, $^n$Bu$_4$NI and BrCH$_2$CH$_2$Br (2.5 mL) at the indicated temperature for the indicated time; RT = Room temperature; $^b$Molar ratio of 1a:Ph$_3$P:$^n$Bu$_4$NI; $^c$The yield was determined by $^1$H NMR with the use of PhCH$_3$ as an internal standard.
3. Typical procedure for the preparation of 2, 3

3.1 Procedure for the preparation of 2

![Chemical structure](image)

Epoxide 1a (1.0 equiv, 0.5 mmol, 60.1 mg), Ph₃P (1.2 equiv, 0.6 mmol, 157.4 mg), Ph₄BuNI (1.4 equiv, 0.7 mmol, 258.6 mg) and ClCH₂CH₂Cl (5.0 mL) were added into a 10 mL sealed tube under a N₂ atmosphere. The resulting mixture was stirred at 80 °C for 4 h. After the reaction solvent was removed by concentration under vacuum, the residue was subjected to flash column chromatography with hexane/ethyl acetate (100:1-4:1) as the eluent to afford the product 2a.

![Product 2a](image)

(1,2-dichloroethyl)benzene [1]: 64%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.27 (m, 5H), 4.99 (dd, J = 7.9, 6.6 Hz, 1H), 4.09 – 3.76 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.01, 129.17, 128.83, 127.41, 61.77, 48.36.

![Product 2b](image)

1-(1,2-dichloroethyl)-4-fluorobenzene [1]: 47%; ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.28 (m, 2H), 7.14 – 6.97 (m, 2H), 4.97 (dd, J = 8.4, 6.2 Hz, 1H), 3.97 (dd, J = 11.3, 6.2 Hz, 1H), 3.87 (dd, J = 11.3, 8.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.95 – -112.19 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 162.93 (d, J = 248.7 Hz), 133.89 (d, J = 3.4 Hz), 129.28 (d, J = 8.3 Hz), 115.82 (d, J = 21.8 Hz), 60.80, 48.23.
(2,3-dichloropropyloxy)benzene: 88%; $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 2H), 4.42 – 4.34 (m, 1H), 4.28 (d, $J = 5.8$ Hz, 2H), 4.01 – 3.87 (m, 2H). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 158.01, 129.68, 121.73, 114.80, 68.18, 57.39, 45.10.

1-(tert-butyl)-4-(2,3-dichloropropoxy)benzene: 86%; Light yellow liquid. $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 7.6$ Hz, 2H), 6.86 (d, $J = 7.4$ Hz, 2H), 4.41 – 4.18 (m, 3H), 4.03 – 3.80 (m, 2H), 1.29 (s, 9H). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 155.64, 144.38, 126.38, 114.15, 68.13, 57.35, 45.07, 34.11, 31.47. IR (neat) $\nu$ = 2962, 1514, 1459, 1364, 1295, 1246, 1185, 1036, 829 cm$^{-1}$; HRMS (EI) Calcd for C$_{13}$H$_{18}$Cl$_2$O$^+[M]^+$: 260.0735, Found: 260.0732.

((3,4-dichlorobutoxy)methyl)benzene: 73%; Colorless liquid. $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.25 (m, 5H), 4.52 (s, 2H), 4.41 – 4.22 (m, 1H), 3.81 – 3.69 (m, 2H), 3.68 – 3.63 (m, 2H), 2.37 – 2.23 (m, 1H), 1.99 – 1.85 (m, 1H). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 138.10, 128.44, 127.73, 127.65, 73.18, 66.30, 58.23, 48.78, 35.48. IR (neat) $\nu$ = 3030, 2921, 2864, 1455, 1361, 1116, 1028, 737, 698 cm$^{-1}$; HRMS (EI) Calcd for C$_{13}$H$_{18}$Cl$_2$O$^+[M]^+$: 232.0422, Found: 232.0429.
1-(2,3-dichloropropoxy)naphthalene Chloroform-d: 70%; Light yellow solid. mp 44°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 – 8.19 (m, 1H), 7.85 – 7.75 (m, 1H), 7.55 – 7.44 (m, 3H), 7.37 (t, $J = 7.9$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 4.56 – 4.37 (m, 3H), 4.11 – 3.93 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.65, 134.59, 127.59, 126.65, 125.68, 125.56, 125.52, 121.76, 121.32, 105.23, 68.34, 57.42, 45.12. IR (neat) ν = 1581, 1458, 1401, 1390, 1270, 1242, 1103, 1073, 1020, 932, 791, 769, 748 cm$^{-1}$; HRMS (EI) Calcd for C$_{13}$H$_{12}$Cl$_2$O$^+$: 254.0265, Found: 254.0274.

![2g]

4-(2,3-dichloropropoxy)-9H-carbazole: 67%; Light yellow solid. mp 96°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, $J = 7.8$ Hz, 1H), 8.02 (s, 1H), 7.44 – 7.36 (m, 2H), 7.29 – 7.23 (m, 1H), 7.06 (d, $J = 8.1$ Hz, 1H), 6.66 (d, $J = 7.9$ Hz, 1H), 4.63 – 4.49 (m, 3H), 4.16 – 4.04 (m, 1H), 4.06 – 4.00 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.33, 141.03, 138.79, 126.65, 125.28, 123.03, 122.36, 119.91, 112.84, 110.15, 104.44, 101.23, 68.01, 57.56, 45.16. IR (neat) ν = 3399, 1584, 1505, 1454, 1439, 1345, 1257, 1210, 1098, 784, 752, 729, 719 cm$^{-1}$; HRMS (EI) Calcd for C$_{15}$H$_{13}$Cl$_2$NO$^+$: 293.0374, Found: 293.0381.

![2h]

3-(2,3-dichloropropoxy)prop-1-ene: 84%; Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.96 – 5.80 (m, 1H), 5.34 – 5.12 (m, 2H), 4.20 – 4.11 (m, 1H), 4.05 (d, $J = 5.6$ Hz, 2H), 3.88 – 3.75 (m, 2H), 3.75 – 3.67 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.04, 117.78, 72.47, 70.19, 58.27, 45.26. IR (neat) ν = 2916, 1385, 1261, 1111, 1025, 873, 802, 618 cm$^{-1}$; HRMS (EI) Calcd for C$_6$H$_{10}$Cl$_2$O$^+$: 168.0109, Found: 168.0115.
2,3-dichloropropyl methacrylate: 88%; Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.15 (s, 1H), 5.62 (s, 1H), 4.55 – 4.39 (m, 2H), 4.33 – 4.23 (m, 1H), 3.82 – 3.75 (m, 2H), 1.95 (dd, $J$ = 1.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.59, 135.58, 126.65, 64.44, 56.79, 46.68, 18.27. IR (neat) ν = 2959, 1725, 1638, 1455, 1319, 1296, 1159, 946, 813 cm$^{-1}$.

1,2-dichlorododecane$^{[3]}$: 57%; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.07 – 3.95 (m, 1H), 3.78 – 3.58 (m, 2H), 2.02 – 1.89 (m, 1H), 1.75 – 1.62 (m, 1H), 1.44 – 1.18 (m, 16H), 0.86 (t, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 61.28, 48.28, 35.07, 31.90, 29.57, 29.53, 29.41, 29.32, 28.99, 25.82, 22.69, 14.12.

1,2-dichlorotetradecane: 74%; Colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.09 – 3.94 (m, 1H), 3.78 – 3.55 (m, 2H), 2.02 – 1.91 (m, 1H), 1.74 – 1.63 (m, 1H), 1.41 – 1.09 (m, 20H), 0.87 (t, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 61.26, 48.27, 35.07, 31.94, 29.68, 29.66, 29.63, 29.55, 29.43, 29.38, 29.00, 25.83, 22.72, 14.14. IR (neat) ν = 2854, 1466, 727, 664 cm$^{-1}$; HRMS (EI) Calcd for C$_{14}$H$_{28}$Cl$_2$[M]$^+$: 266.1568, Found: 266.1576.

1,2-dichlorooctane$^{[4]}$: 65%; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.14 – 3.92 (m, 1H), 3.78 – 3.58 (m, 2H), 2.05 – 1.86 (m, 1H), 1.78 – 1.63 (m, 1H), 1.60 – 1.47 (m, 1H), 1.46 – 1.20 (m, 7H), 0.88 (t, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 61.27, 48.28, 35.07, 31.60, 28.65, 25.78, 22.55, 14.04.
7,8-dichlorooct-1-ene[^3]: 62%; ¹H NMR (400 MHz, CDCl₃) δ 5.89 – 5.63 (m, 1H),
5.10 – 4.84 (m, 2H), 4.08 – 3.95 (m, 1H), 3.82 – 3.53 (m, 2H), 2.10 – 2.03 (m, 2H),
2.03 – 1.93 (m, 1H), 1.76 – 1.64 (m, 1H), 1.59 – 1.51 (m, 1H), 1.47 – 1.36 (m, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 138.43, 114.68, 61.08, 48.17, 34.84, 33.45, 28.18, 25.24.

### 3.2 Procedure for the preparation of 3

Epoxide 1a (1.0 equiv, 0.5 mmol, 60.1 mg), Ph₃P (1.2 equiv, 0.6 mmol, 157.4 mg),
Bu₄NI (1.4 equiv, 0.7 mmol, 258.6 mg) and BrCH₂CH₂Br (5.0 mL) were added into a
10 mL sealed tube under a N₂ atmosphere. The resulting mixture was stirred at 40 °C
for 2 h. After the reaction solvent was removed by concentration under vacuum, the
residue was subjected to flash column chromatography with hexane/ethyl acetate
(100:1-4:1) as the eluent to afford the product 3a.

(1,2-dibromoethyl)benzene[^5]: 57%; ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.29 (m,
5H), 5.13 (dd, J = 10.6, 5.5 Hz, 1H), 4.13 – 3.94 (m, 2H). ¹³C NMR (101 MHz,
CDCl₃) δ 138.62, 129.19, 128.87, 127.67, 50.89, 35.03.

1-(tert-butyl)-4-(2,3-dibromopropoxy)benzene: 62%; Light yellow liquid. ¹H NMR
(400 MHz, CDCl₃) δ 7.31 (d, J = 7.5 Hz, 2H), 6.87 (d, J = 7.5 Hz, 2H), 4.50 – 4.25 (m,
3H), 4.03 – 3.80 (m, 2H), 1.29 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 155.64, 144.37,
126.37, 114.25, 69.05, 47.84, 34.12, 32.82, 31.47. IR (neat) ν =2963, 2869, 1513,
1457, 1294, 1265, 1244, 1185, 1119, 1048, 831, 739, 705 cm\(^{-1}\); HRMS (EI) Calcd for \(\text{C}_{13}\text{H}_{18}\text{Br}_2\text{O}[\text{M}]^+\): 347.9724, Found: 347.9727.

![3c](image)

4-(2,3-dibromopropoxy)-9H-carbazole: 43%; Light yellow solid. mp 107°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.35 (d, \(J = 7.8\) Hz, 1H), 8.06 (s, 1H), 7.44 – 7.37 (m, 2H), 7.33 (t, \(J = 8.0\) Hz, 1H), 7.29 – 7.23 (m, 1H), 7.08 (d, \(J = 8.1\) Hz, 1H), 6.66 (d, \(J = 7.9\) Hz, 1H), 4.76 – 4.57 (m, 3H), 4.12 – 3.96 (m, 2H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.29, 141.01, 138.76, 126.62, 125.24, 123.16, 122.38, 119.88, 112.86, 110.09, 104.39, 101.22, 68.78, 47.84, 32.74. IR (neat) \(\nu = \)3400, 1583, 1504, 1452, 1439, 1344, 1301, 1255, 1212, 1203, 1093, 783, 751, 719 cm\(^{-1}\); HRMS (ESI) Calcd for \(\text{C}_{15}\text{H}_{13}\text{Br}_2\text{NO}[\text{M}]^+\): 381.9438.

![3d](image)

1,2-dibromododecane\(^6\): 53%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.21 – 4.10 (m, 1H), 3.83 (dd, \(J = 10.2, 4.4\) Hz, 1H), 3.61 (t, \(J = 10.0\) Hz, 1H), 2.20 – 2.04 (m, 1H), 1.85 – 1.67 (m, 1H), 1.45 – 1.17 (m, 16H), 0.86 (t, \(J = 6.6\) Hz, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 53.17, 36.36, 36.00, 31.88, 29.56, 29.52, 29.38, 29.30, 28.80, 26.74, 22.67, 14.12.

![3e](image)

1,2-dibromotetradecane\(^7\): 62%; \(^1\)H NMR (400 MHz, CDCl\(_3\))\(\delta\) 4.23 – 4.08 (m, 1H), 3.83 (dd, \(J = 10.2, 4.4\) Hz, 1H), 3.61 (t, \(J = 10.0\) Hz, 1H), 2.19 – 2.03 (m, 1H), 1.83 – 1.66 (m, 1H), 1.44 – 1.15 (m, 20H), 0.86 (t, \(J = 6.8\) Hz, 3H). \(^1\)C NMR (101 MHz,
CDCl$_3$ δ 53.19, 36.38, 36.05, 31.93, 29.66, 29.64, 29.61, 29.53, 29.39, 29.36, 28.82, 26.76, 22.70, 14.13.

4. References and Notes


5. Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra

$^1$H NMR

$^{13}$C NMR
$^{13}$C NMR

$^1$H NMR
$^{13}$C NMR

$^{1}$H NMR
$^{13}$C NMR

$^{1}H$ NMR
**$^{13}$C NMR**

![$^{13}$C NMR spectrum of 3b](image)

**$^1$H NMR**

![$^1$H NMR spectrum of 3c](image)
$^{13}$C NMR

$\text{CH}_3(\text{CH}_2)_x\text{Br}$

$3e$