Supporting Information

Synthesis of Phenacyl Bromides $K_2S_2O_8$-mediated Tandem Hydroxybromination and Oxidation of Styrenes in Water
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General Consideration:

All solvents and reagents were purchased from the suppliers and used without further purification. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ at room temperature on the Bruker spectrometer (400 MHz $^1$H). The chemical-shifts scale is based on internal TMS.

Figure S1. NMR spectra of the mixture of the reaction of styrene with KCl in the presence of K$_2$O$_2$S$_8$
Figure S2. NMR spectra of the mixture of the reaction of styrene with KI in the presence of K$_2$O$_2$S$_8$

\[
\text{苯乙烯} \xrightarrow{\text{K}_2\text{S}_2\text{O}_8(2.5 \text{ equiv})} \xrightarrow{\text{KI}(2.0 \text{ equiv})} \text{不观察}
\]

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Figure S3. GC/MS spectra of the mixture of the reaction of 1-octene with KBr in the presence of K$_2$O$_2$S$_8$

Figure S4. GC/MS spectra of the mixture of the reaction of trans-2-hexene with KBr in the presence of K$_2$O$_2$S$_8$
Figure S5. NMR spectra of the mixture of the reaction of styrene with KBr in the presence of \( \text{K}_2\text{O}_2\text{S}_8 \) for 0.5 h
Figure S6. Bromine formation: (a) prior to heating; (b) after the reaction was complete.

Characterization Data for Selected Compounds

**Phenacyl bromide (2a)**

![Phenacyl bromide (2a)](image)

Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 76%, colorless solid, m.p.: 48-50 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 4.47 (s, 2 H), 7.50 (t, $J = 8.0$ Hz, 2 H), 7.62 (t, $J = 8.0$ Hz, 1 H), 7.99 (d, $J = 8.0$ Hz, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 31.03, 128.91, 128.97, 133.94, 134.03, 191.33; LRMS: m/z calcd for C$_8$H$_7$BrO (M+H): 200, found: 200; Anal. Calcd for C$_8$H$_7$BrO: Elemental Analysis: C, 48.27; H, 3.54; Found: C, 48.31; H, 3.48;

**4-Methylphenacyl bromide (2b)**

![4-Methylphenacyl bromide (2b)](image)

Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 72%, colorless solid, m.p.: 46-48 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.44 (s, 3 H), 4.45 (s, 2 H), 7.30 (d, $J = 8.0$ Hz, 2 H), 7.89 (d, $J = 8.0$ Hz, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 21.48, 30.85, 129.06, 129.56, 131.40, 145.05, 190.98; LRMS: m/z calcd for C$_9$H$_9$BrO (M+H): 214, found: 214; Anal. Calcd for C$_9$H$_9$BrO: Elemental Analysis: C, 50.73; H, 4.26; Found: C, 50.92; H, 4.08;

**4-Methoxyphenacyl bromide (2c)**

![4-Methoxyphenacyl bromide (2c)](image)

Flash chromatography (petroleum ether/ dichloromethane, 2/1); Yield: 24%, colorless solid, m.p.:
69-71 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.89 (s, 3 H), 4.41 (s, 2 H), 6.96 (d, \(J = 8.0\) Hz, 2 H),
7.97 (d, \(J = 8.0\) Hz, 2 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 30.89, 55.62, 114.08, 126.85, 131.39,
164.14, 189.99; LRMS: m/z calcd for \(\text{C}_9\text{H}_9\text{Br}_2\text{O}_2\) (M+H): 230, found: 230; Anal. Calcd for
\(\text{C}_9\text{H}_9\text{Br}_2\text{O}_2\): Elemental Analysis: C, 47.19; H, 3.96; Found: C, 47.32; H, 3.75;

4-\textit{tert}-Butylyphenacetyl bromide (2d)

Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 62%, colorless oil; \(^1\)H
NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.35 (s, 9 H), 4.45 (s, 2 H), 7.51 (d, \(J = 8.0\) Hz, 2 H), 7.93 (d, \(J = 8.0\)
Hz, 2 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 31.02, 31.05, 125.88, 131.35, 157.94, 190.97;
LRMS: m/z calcd for \(\text{C}_{12}\text{H}_{13}\text{BrO}\) (M+H): 256, found: 256;

4-Acetoxyphenacetyl bromide (2e)

Flash chromatography (petroleum ether/ dichloromethane, 1/1); Yield: 42%, colorless solid, m.p.:
68-70 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.35 (s, 9 H), 4.44 (s, 2 H), 7.24 (d, \(J = 8.0\) Hz, 2 H),
8.04 (d, \(J = 8.0\) Hz, 2 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 20.99, 21.26, 30.75, 122.18, 128.20,
130.72, 154.93, 168.63, 190.24; LRMS: m/z calcd for \(\text{C}_{10}\text{H}_9\text{BrO}_3\) (M+H): 258, found: 258; Anal.
Calcd for \(\text{C}_{10}\text{H}_9\text{BrO}_3\): Elemental Analysis: C, 46.72; H, 3.53; Found: C, 46.63; H, 3.42;

4-Bromophenacetyl bromide (2f)

Flash chromatography (petroleum ether/ dichloromethane, 2/1); Yield: 82%, colorless solid, m.p.:
108-110 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.41 (s, 2 H), 7.65 (d, \(J = 8.0\) Hz, 2 H), 7.86 (d, \(J = 8.0\)
Hz, 2 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 30.42, 129.37, 130.46, 132.26, 132.61, 190.46; LRMS:
m/z calcd for \(\text{C}_9\text{H}_9\text{Br}_2\text{O}\) (M+H): 279, found: 279; Anal. Calcd for \(\text{C}_9\text{H}_9\text{Br}_2\text{O}\): Elemental Analysis:
C, 34.57; H, 2.18; Found: C, 34.72; H, 2.12;

3-Bromophenacetyl bromide (2g)

Flash chromatography (petroleum ether/ dichloromethane, 4/1); Yield: 74%, colorless solid, m.p.:
48-51 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.35 (s, 9 H), 4.43 (s, 2 H), 7.39 (d, \(J = 8.0\) Hz, 1 H),
7.73-7.76 (m,1 H), 7.90-7.93 (m, 1 H), 8.12 (s, 1 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 30.51, 123.22,
127.52, 130.46, 131.94, 135.60, 136.87, 190.07; LRMS: m/z calcd for \(\text{C}_9\text{H}_9\text{Br}_2\text{O}\) (M+H): 279,
found: 279; Anal. Calcd for \(\text{C}_9\text{H}_9\text{Br}_2\text{O}\): Elemental Analysis: C, 34.57; H, 2.18; Found: C, 34.61; H,
2-Bromophenacyl bromide (2h)

![Chemical structure of 2-Bromophenacyl bromide (2h)](image)

Flash chromatography (petroleum ether/dichloromethane, 3/1); Yield: 41%, pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.35 (s, 9 H), 4.51 (s, 2 H), 7.34-7.49 (m, 3 H), 7.63-7.33 (m, 1 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 33.72, 119.02, 127.22, 129.64, 132.33, 134.07, 138.51, 194.97; LRMS: m/z calc'd for C$_8$H$_7$BrO (M+H): 279, found: 279;

4-Chlorophenacyl bromide (2i)

![Chemical structure of 4-Chlorophenacyl bromide (2i)](image)

Flash chromatography (petroleum ether/dichloromethane, 4/1); Yield: 90%, colorless solid, m.p.: 93-96 $^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 4.42 (s, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 7.94 (d, J = 8.0 Hz, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 30.44, 129.27, 130.40, 132.21, 140.57, 190.25; LRMS: m/z calc'd for C$_8$H$_6$BrClO (M+H): 234, found: 234; Anal. Calcd for C$_8$H$_6$BrClO: Elemental Analysis: C, 41.15; H, 2.59; Found: C, 41.42; H, 2.32;

4-Fluorophenacyl bromide (2j)

![Chemical structure of 4-Fluorophenacyl bromide (2j)](image)

Flash chromatography (petroleum ether/dichloromethane, 5/1); Yield: 88%, colorless solid, m.p.: 47-49 $^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 4.42 (s, 2 H), 7.18 (t, J = 8.0 Hz, 2 H), 8.02-8.05 (m, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 30.50, 116.03, 116.25, 1313.72, 131.82, 189.87; LRMS: m/z calc'd for C$_8$H$_5$BrFO (M+H): 218, found: 218; Anal. Calcd for C$_8$H$_5$BrFO: Elemental Analysis: C, 44.27; H, 2.79; Found: C, 44.40; H, 2.52;

4-(bromoacetyl)phenylboronic acid (2k)

![Chemical structure of 4-(bromoacetyl)phenylboronic acid (2k)](image)

Flash chromatography (petroleum ether/dichloromethane, 6/1); Yield: 77%, colorless solid, m.p.: 104-106 $^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 4.42 (s, 2 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.86 (d, J = 8.0 Hz, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 30.49, 129.27, 130.52, 132.40, 132.75, 190.49; Anal. Calcd for C$_8$H$_6$BrBO: Elemental Analysis: C, 39.56; H, 3.32; Found: C, 39.62; H, 3.23;

2-Bromo-1-phenyl-1-propanone (2l)

![Chemical structure of 2-Bromo-1-phenyl-1-propanone (2l)](image)

Flash chromatography (petroleum ether/dichloromethane, 8/1); Yield: 73%, colorless solid, m.p.: 108-110 $^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.91 (d, J = 8.0 Hz, 3 H), 5.30 (q, J = 4.0 Hz, 1 H),
7.47-7.60 (m, 2 H), 7.60-7.62 (m, 1 H), 8.02-8.04 (m, 2 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 20.15, 41.18, 128.78, 128.95, 133.74, 134.01, 190.37; LRMS: m/z calcd for C\(_9\)H\(_8\)BrO (M+H): 214, found: 214; Anal. Calcd for C\(_9\)H\(_8\)BrO: Elemental Analysis: C, 50.73; H, 4.26; Found: C, 50.80; H, 4.21;

2-Bromo-1-(4-methoxyphenyl)-1-propanone (2m)

Flash chromatography (petroleum ether/ dichloromethane, 1/1); Yield: 21%, pale yellow oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.89 (d, \(J\) = 8.0 Hz, 3 H ), 3.89 (s, 3 H ), 5.27 (q, \(J\) = 4.0 Hz, 1 H ), 6.96 (d, \(J\) = 8.0 Hz, 2 H ), 8.02 (d, \(J\) = 8.0 Hz, 2 H ); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 20.26, 41.46, 55.59, 113.98, 126.79, 133.34, 163.94, 192.03; LRMS: m/z calcd for C\(_{10}\)H\(_{11}\)BrO\(_2\) (M+H): 244, found: 244;

3-Chloro-2-bromo-1-phenyl-1-propanone (2n)

Flash chromatography (petroleum ether/ dichloromethane, 6/1); Yield: 34%, colorless oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.95 (q, \(J\) = 4.0 Hz, 1 H ), 4.36 (t, \(J\) = 8.0 Hz, 1 H ), 5.30 (q, \(J\) = 4.0 Hz, 1 H ), 7.53 (t, \(J\) = 8.0 Hz, 2 H ), 7.65 (t, \(J\) = 8.0 Hz, 1 H ), 8.04 (d, \(J\) = 8.0 Hz, 2 H ); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 42.10, 42.24, 129.98, 129.00, 133.69, 134.45, 190.71; LRMS: m/z calcd for C\(_9\)H\(_8\)BrClO (M+H): 248, found: 248;

2-Bromo-1-indanone (2o)

Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 53%, yellow oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.42 (dd, \(J\) = 4.0, 4.0 Hz, 1 H ), 3.83 (dd, \(J\) = 4.0, 4.0 Hz, 1 H ), 4.65 (dd, \(J\) = 4.0, 4.0 Hz, 1 H ), 7.44 (t, \(J\) = 8.0 Hz, 2 H ), 7.67 (t, \(J\) = 8.0 Hz, 1 H ), 7.84 (d, \(J\) = 8.0 Hz, 1 H ); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 38.01, 44.04, 125.10, 126.43, 128.30, 133.60, 135.94, 151.09, 199.51; LRMS: m/z calcd for C\(_9\)H\(_8\)O (M+H): 212, found: 212;

2-Bromo-1-tetralone (2p)

Flash chromatography (petroleum ether/ dichloromethane, 1/1); Yield: 65%, yellow solid, m.p.: 39-42 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.48-2.55 (m, 2 H ), 2.94 (tt, \(J\) = 4.0, 4.0 Hz, 1 H ), 3.28-3.36 (m, 1 H ), 4.74 (t, \(J\) = 4.0 Hz, 1 H ), 7.27-7.38 (m, 2 H ), 7.51-7.56 (m, 1 H ), 8.10 (d, \(J\) = 8.0 Hz, 1 H ); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 25.81, 31.60, 50.51, 127.17, 128.70, 128.83, 129.89, 134.22, 143.01, 190.69; LRMS: m/z calcd for C\(_{10}\)H\(_8\)BrO (M+H): 226, found: 226; Anal. Calcd for C\(_{10}\)H\(_8\)BrO: Elemental Analysis: C, 53.36; H, 4.03; Found: C, 53.18; H, 3.86;
**Bromomethyl 2-naphthyl ketone (2q)**

![Chemical Structure of Bromomethyl 2-naphthyl ketone (2q)](image)

Flash chromatography (petroleum ether/ dichloromethane, 3/2); Yield: 35%, purplish-brown solid, m.p.: 82-84 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.58 (s, 1 H), 7.56-7.65 (m, 2 H), 7.87-8.01 (m, 4 H), 8.50 (s, 1 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 30.83, 124.13, 127.13, 127.90, 128.88, 129.12, 129.75, 131.03, 131.24, 132.33, 135.89, 191.50; Anal. Calcd for C\(_{12}\)H\(_9\)BrO: Elemental Analysis: C, 57.86; H, 3.64; Found: C, 57.74; H, 3.56;
$^1$H and $^{13}$C NMR Spectra