

## Supporting Information

### Synthesis of Phenacyl Bromides $K_2S_2O_8$ -mediated Tandem

### Hydroxybromination and Oxidation of Styrenes in Water

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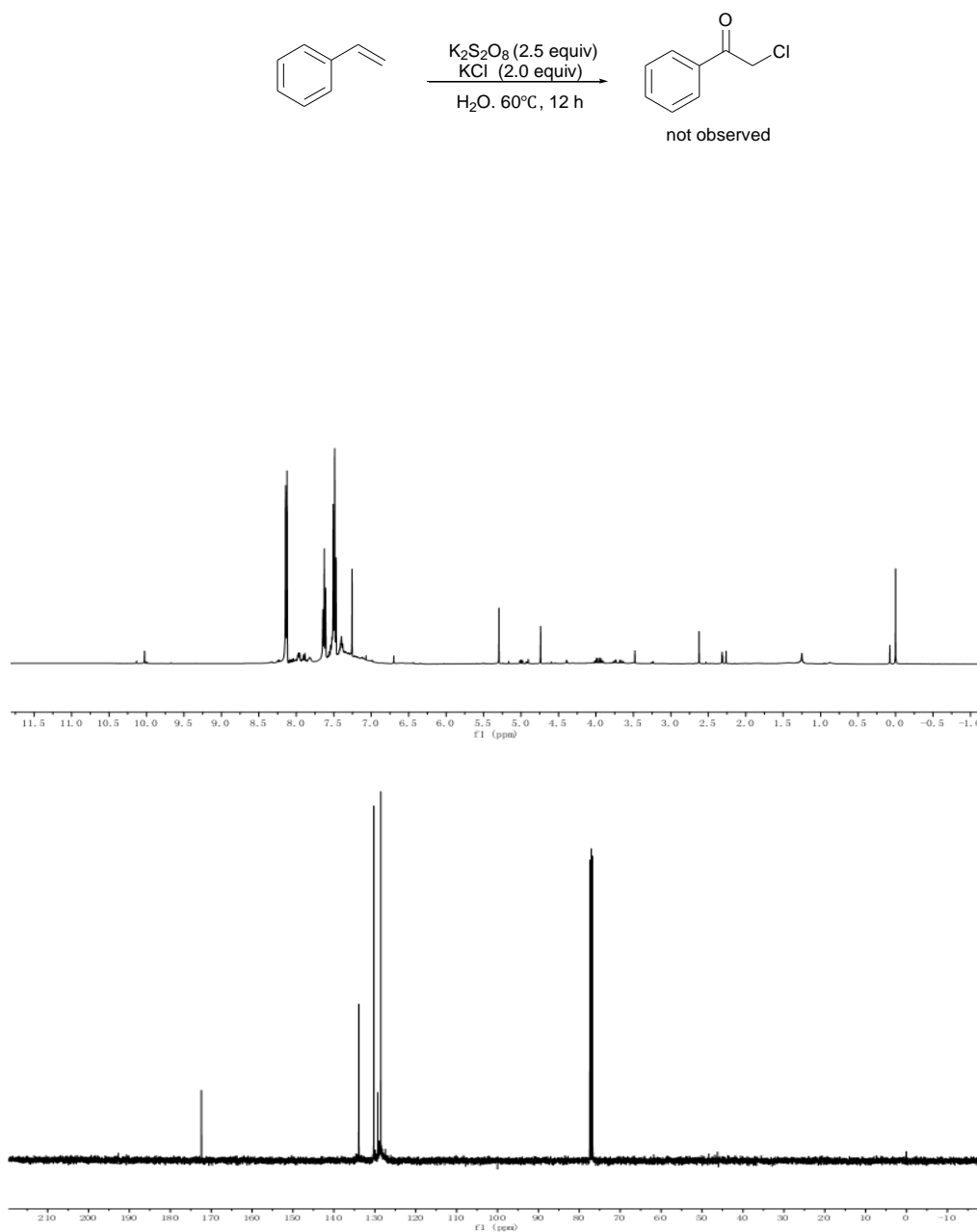
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### General Consideration:

All solvents and reagents were purchased from the suppliers and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in  $\text{CDCl}_3$  at room temperature on the Bruker spectrometer (400 MHz  $^1\text{H}$ ). 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  $\text{K}_2\text{O}_2\text{S}_8$**



**Figure S2. NMR spectra of the mixture of the reaction of styrene with KI in the presence of  $K_2O_2S_8$**

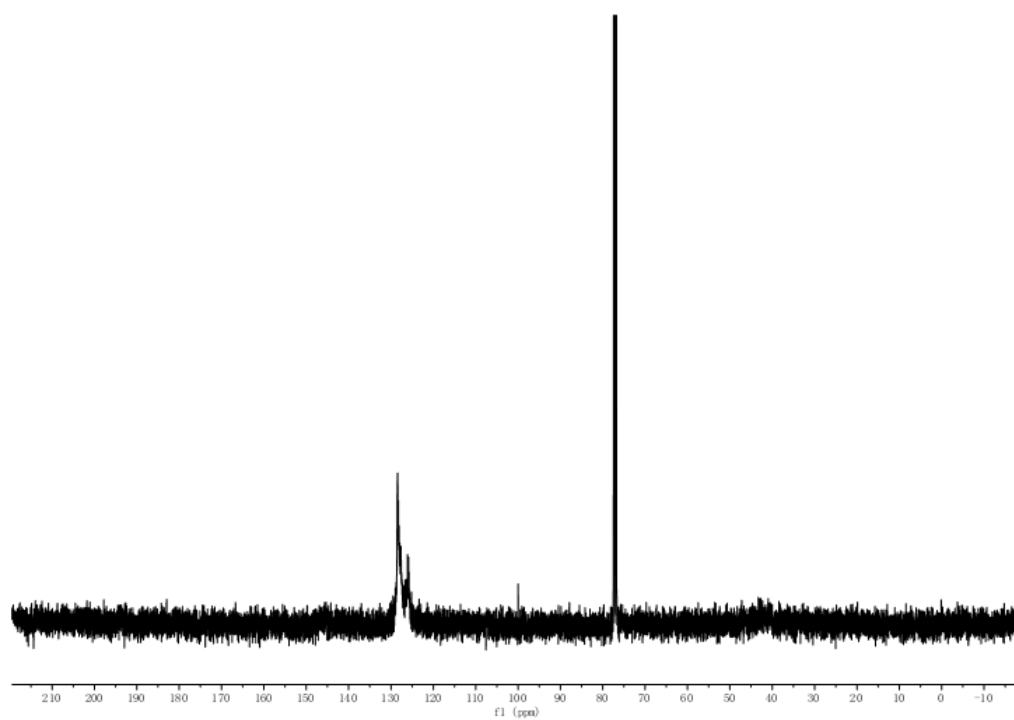
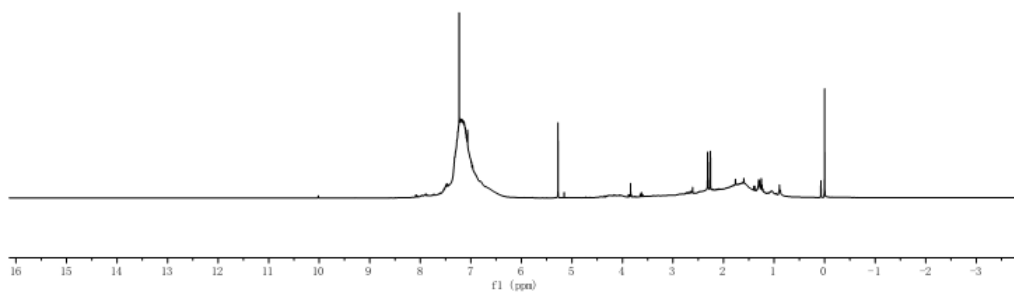
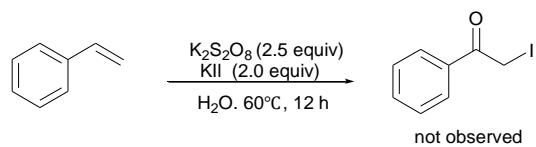


Figure S3. GC/MS spectra of the mixture of the reaction of 1-octene with KBr in the presence of  $K_2O_2S_8$

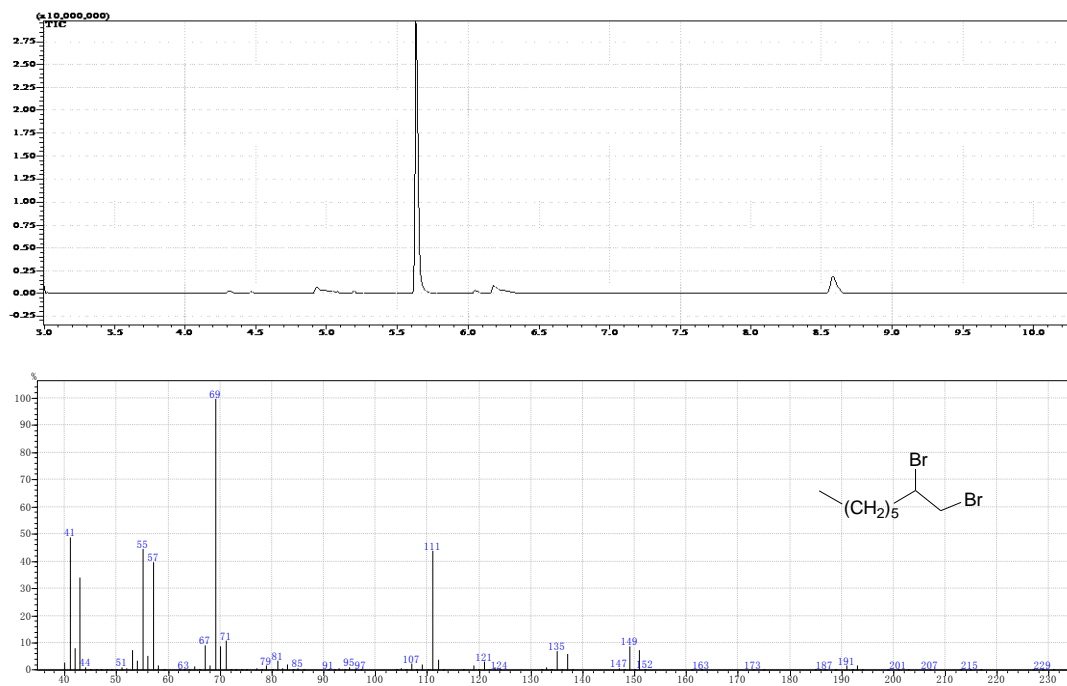
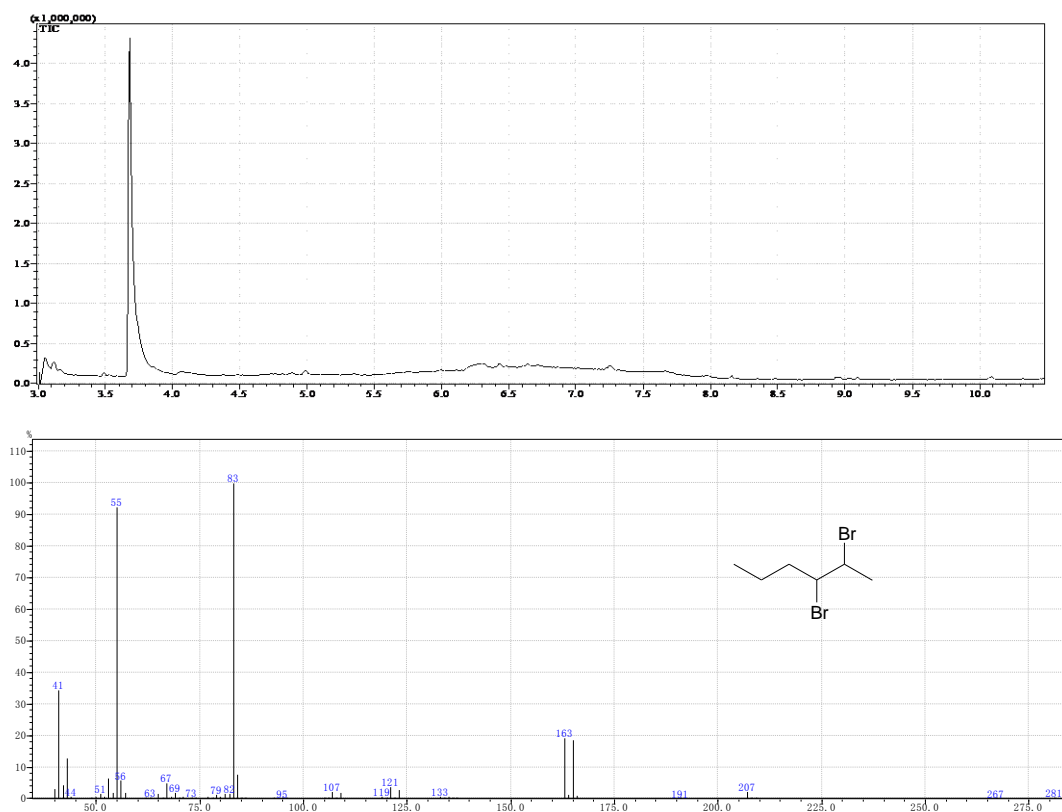
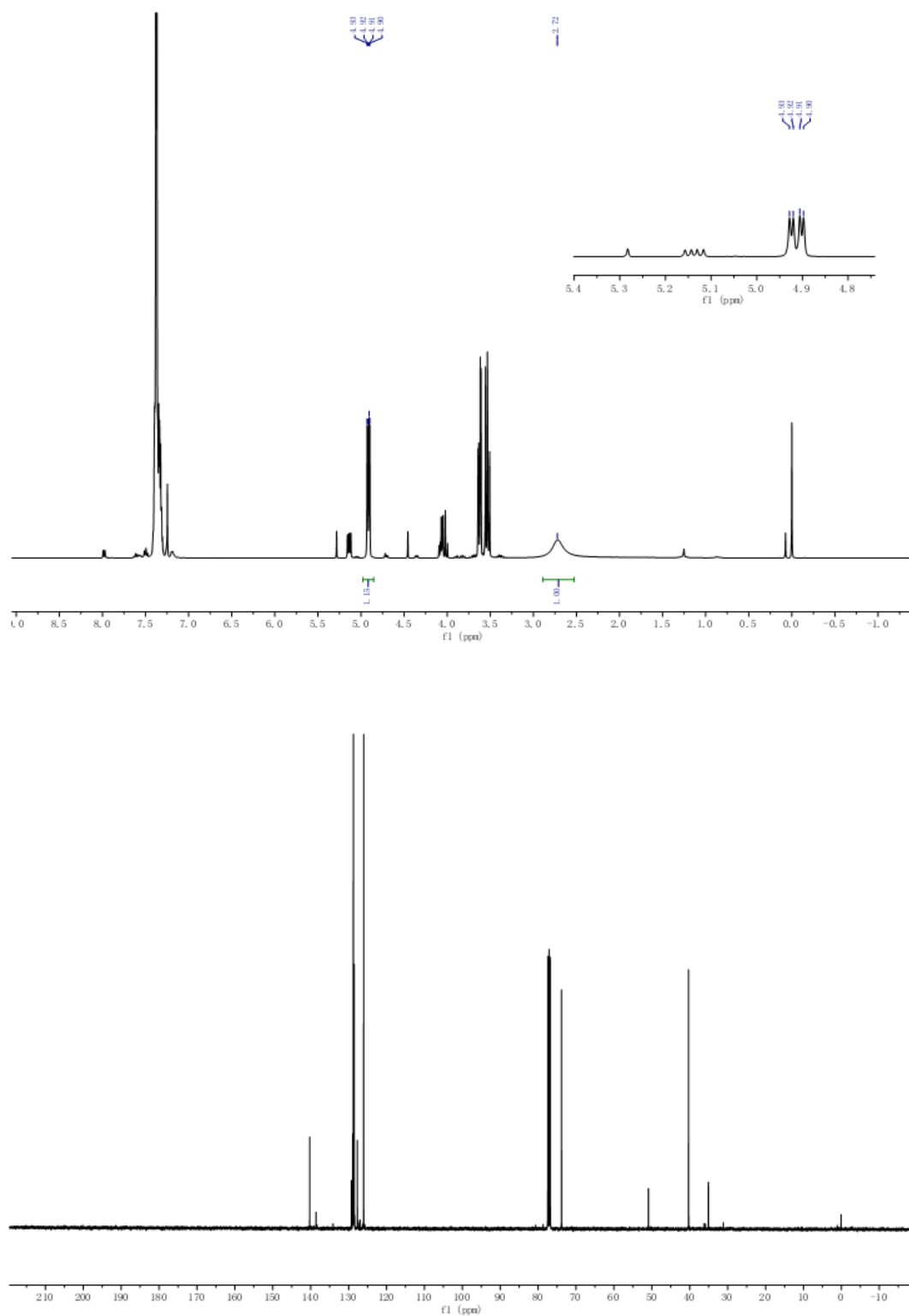
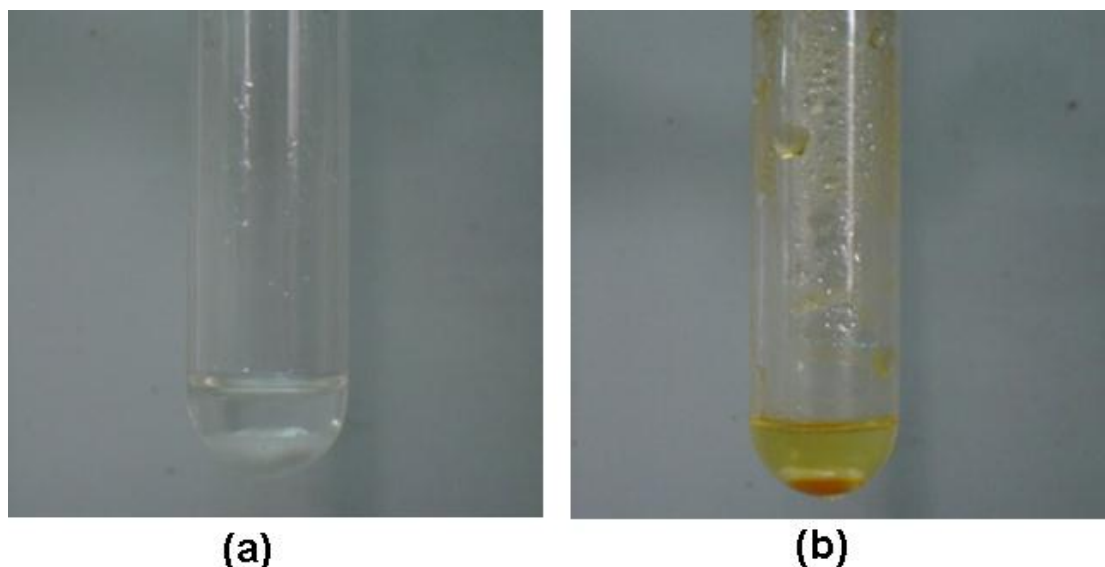


Figure S4. GC/MS spectra of the mixture of the reaction of *trans*-2-hexene with KBr in the presence of  $K_2O_2S_8$



**Figure S5. NMR spectra of the mixture of the reaction of styrene with KBr in the presence of  $K_2O_2S_8$  for 0.5 h**

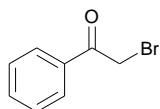




**Figure S6.** Bromine formation: (a) prior to heating; (b) after the reaction was complete.

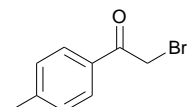
### Characterization Data for Selected Compounds

#### Phenacyl bromide (2a)



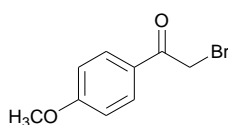
Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 76%, colorless solid, m.p.: 48-50 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.47 (s, 2 H), 7.50 (t,  $J = 8.0$  Hz, 2 H), 7.62 (t,  $J = 8.0$  Hz, 1 H), 7.99 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$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

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



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

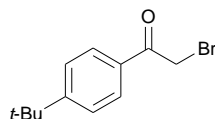
#### 4-Methoxyphenacyl bromide (2c)



Flash chromatography (petroleum ether/ dichloromethane, 2/1); Yield: 24%, colorless solid, m.p.:

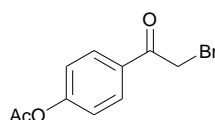
69-71 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.89 (s, 3 H), 4.41 (s, 2 H), 6.96 (d,  $J = 8.0$  Hz, 2 H), 7.97 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  30.89, 55.62, 114.08, 126.85, 131.39, 164.14, 189.99; LRMS:  $m/z$  calcd for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

#### 4-*tert*-Butylphenacyl bromide (2d)



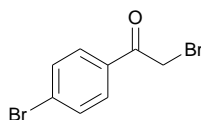
Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 62%, colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.35 (s, 9 H), 4.45 (s, 2 H), 7.51 (d,  $J = 8.0$  Hz, 2 H), 7.93 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  31.02, 31.05, 125.88, 128.96, 131.35, 157.94, 190.97; LRMS:  $m/z$  calcd for  $\text{C}_{12}\text{H}_{15}\text{BrO}$  (M+H): 256, found: 256;

#### 4-Acetoxyphenacyl bromide (2e)



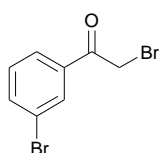
Flash chromatography (petroleum ether/ dichloromethane, 1/1); Yield: 42%, colorless solid, m.p.: 68-70 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  2.35 (s, 9 H), 4.44 (s, 2 H), 7.24 (d,  $J = 8.0$  Hz, 2 H), 8.04 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 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-Bromophenacyl bromide (2f)



Flash chromatography (petroleum ether/ dichloromethane, 2/1); Yield: 82%, colorless solid, m.p.: 108-110 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  30.42, 129.37, 130.46, 132.26, 132.61, 190.46; LRMS:  $m/z$  calcd for  $\text{C}_8\text{H}_6\text{Br}_2\text{O}$  (M+H): 279, found: 279; Anal. Calcd for  $\text{C}_8\text{H}_6\text{Br}_2\text{O}$ : Elemental Analysis: C, 34.57; H, 2.18; Found: C, 34.72; H, 2.12;

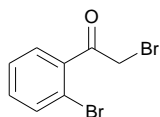
#### 3-Bromophenacyl bromide (2g)



Flash chromatography (petroleum ether/ dichloromethane, 4/1); Yield: 74%, colorless solid, m.p.: 48-51 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  30.51, 123.22, 127.52, 130.46, 131.94, 135.60, 136.87, 190.07; LRMS:  $m/z$  calcd for  $\text{C}_8\text{H}_6\text{Br}_2\text{O}$  (M+H): 279, found: 279; Anal. Calcd for  $\text{C}_8\text{H}_6\text{Br}_2\text{O}$ : Elemental Analysis: C, 34.57; H, 2.18; Found: C, 34.61; H,

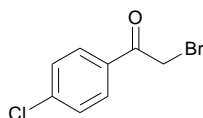
2.22;

#### 2-Bromophenacyl bromide (2h)



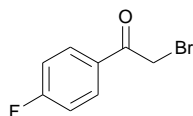
Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 41%, pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.35 (s, 9 H), 4.51 (s, 2 H), 7.34-7.49 (m, 3 H), 7.63-7.33 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  33.72, 119.02, 127.22, 129.64, 132.33, 134.07, 138.51, 194.97; LRMS:  $m/z$  calcd for  $\text{C}_8\text{H}_6\text{Br}_2\text{O}$  (M+H): 279, found: 279;

#### 4-Chlorophenacyl bromide (2i)



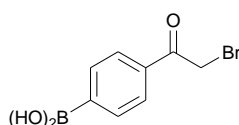
Flash chromatography (petroleum ether/ dichloromethane, 4/1); Yield: 90%, colorless solid, m.p.: 93-96 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.42 (s, 2 H), 7.48 (d,  $J = 8.0$  Hz, 2 H), 7.94 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$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

#### 4-Fluorophenacyl bromide (2j)



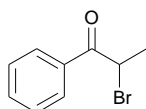
Flash chromatography (petroleum ether/ dichloromethane, 5/1); Yield: 88%, colorless solid, m.p.: 47-49 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.42 (s, 2 H), 7.18 (t,  $J = 8.0$  Hz, 2 H), 8.02-8.05 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  30.50, 116.03, 116.25, 1313.72, 131.82, 189.87; LRMS:  $m/z$  calcd for  $\text{C}_8\text{H}_6\text{BrFO}$  (M+H): 218, found: 218; Anal. Calcd for  $\text{C}_8\text{H}_6\text{BrFO}$ : Elemental Analysis: C, 44.27; H, 2.79; Found: C, 44.40; H, 2.52;

#### 4-(bromoacetyl)phenylboronic acid (2k)



Flash chromatography (petroleum ether/ dichloromethane, 6/1); Yield: 77%, colorless solid, m.p.: 104-106 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  30.49, 129.27, 130.52, 132.40, 132.75, 190.49; Anal. Calcd for  $\text{C}_8\text{H}_8\text{BBrO}$ : Elemental Analysis: C, 39.56; H, 3.32; Found: C, 39.62; H, 3.23;

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

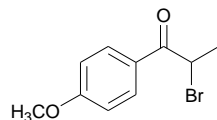


Flash chromatography (petroleum ether/ dichloromethane, 8/1); Yield: 73%, colorless solid, m.p.: 108-110 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.91 (d,  $J = 8.0$  Hz, 3 H), 5.30 (q,  $J = 4.0$  Hz, 1 H),



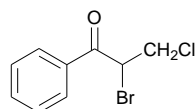
7.47-7.60 (m, 2 H), 7.60-7.62 (m, 1 H), 8.02-8.04 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  20.15, 41.18, 128.78, 128.95, 133.74, 134.01, 190.37; LRMS:  $m/z$  calcd for  $\text{C}_9\text{H}_9\text{BrO}$  (M+H): 214, found: 214; Anal. Calcd for  $\text{C}_9\text{H}_9\text{BrO}$ : Elemental Analysis: C, 50.73; H, 4.26; Found: C, 50.80; H, 4.21;

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



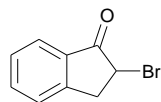
Flash chromatography (petroleum ether/ dichloromethane, 1/1); Yield: 21%, pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.89 (d,  $J = 8.0$  Hz, 3 H), 3.89 (s, 3 H), 5.27 (q,  $J = 4.0$  Hz, 1 H), 6.96 (d,  $J = 8.0$  Hz, 2 H), 8.02 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$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

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



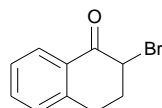
Flash chromatography (petroleum ether/ dichloromethane, 6/1); Yield: 34%, colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.95 (q,  $J = 4.0$  Hz, 1 H), 4.36 (t,  $J = 8.0$  Hz, 1 H), 5.30 (q,  $J = 4.0$  Hz, 1 H), 7.53 (t,  $J = 8.0$  Hz, 2 H), 7.65 (t,  $J = 8.0$  Hz, 1 H),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

### 2-Bromo-1-indanone (2o)



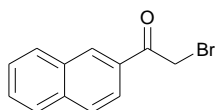
Flash chromatography (petroleum ether/ dichloromethane, 3/1); Yield: 53%, yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.42 (dd,  $J = 4.0, 4.0$  Hz, 1 H), 3.83 (dd,  $J = 4.0, 4.0$  Hz, 1 H), 4.65 (dd,  $J = 4.0, 4.0$  Hz, 1 H), 7.44 (t,  $J = 8.0$  Hz, 2 H), 7.67 (t,  $J = 8.0$  Hz, 1 H), 7.84 (d,  $J = 8.0$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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  $\text{C}_9\text{H}_7\text{BrO}$  (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;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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  $\text{C}_{10}\text{H}_9\text{BrO}$  (M+H): 226, found: 226; Anal. Calcd for  $\text{C}_{10}\text{H}_9\text{BrO}$ : Elemental Analysis: C, 53.36; H, 4.03; Found: C, 53.18; H, 3.86;

**Bromomethyl 2-naphthyl ketone (2q)**



Flash chromatography (petroleum ether/ dichloromethane, 3/2); Yield: 35%, purplish-brown solid, m.p.: 82-84 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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  $\text{C}_{12}\text{H}_9\text{BrO}$ : Elemental Analysis: C, 57.86; H, 3.64; Found: C, 57.74; H, 3.56;

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra

