Supporting Information

Nonselective Bromination – Selective Debromination Strategy: Selective Bromination of Unsymmetrical Ketone on Singly Activated Carbon against Doubly Activated Carbon.

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Acetophenone (3a). Concentrated hydrobromic acid (5 mL) was added to the mixture of 2'-bromoacetophenone (**3b**, 200 mg, 1.0 mmol), sodium hydrosulfite (200 mg, 1.15 mmol, 1.15 equiv) and acetic acid (10 mL) in a one-neck flask (100 mL) with stirring at room temperature. The mixture was refluxed for 4 h and was basified with aqueous NaHCO₃ and extracted with EtOAc, then the organic layer was dried (Na₂SO₄) and concentrated *in vacuo*. The residue was purified by flash column chromatography (40% EtOAc/hexane) to give **3a** (107 mg, 0.89 mmol, 89%): ¹H NMR (200 MHz, CDCl₃) δ 7.92–8.02 (m, 2H), 7.41–7.63 (m, 3H), 2.61 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 198.1, 137.1, 133.1, 128.5, 128.2, 26.5.

3'-Nitroacetophenone (4a). ¹H NMR (200 MHz, CDCl₃) δ 8.76 (t, *J* = 2.0 Hz, 1H), 8.43 (ddd, *J* = 8.0, 2.2, 1.0 Hz, 1H), 8.33 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 2.73 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 195.5, 148.2, 138.0, 133.7, 129.8, 127.2, 122.9, 26.5.

2-Bromoacetophenone (3b). ¹H NMR (200 MHz, CDCl₃) δ 7.95–8.04 (m, 2H), 7.45–7.68 (m, 3H), 4.46 (s, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 191.2, 133.9, 128.9, 128.8, 30.9.

3'-Nitro-2-bromoacetophenone (4b). ¹H NMR (200 MHz, CDCl₃) δ 8.81 (t, *J* = 2.0 Hz, 1H), 8.48 (ddd, *J* = 8.0, 2.2, 1.0 Hz, 1H), 8.35 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 4.54 (s, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 189.3, 148.4, 135.0, 134.4, 130.2, 128.0, 123.7, 30.1.

General procedure for Table 2. Br₂ (1.22 g, 7.63 mmol, 1.00 equiv) dissolved in acetic acid (5 mL) was added to the mixture of phenylacetone (**5a**, 1.02 g, 7.61 mmol) and acetic acid (5 mL) in a

vial (20 mL) with stirring at room temperature and the reaction mixture was stirred for 10 min at room temperature and extracted with methylene chloride, then the organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was passed through short silica column to give crude mixture (1.56 g) including **5a** (0.18 mmol, 3%), **5b** (6.27 mmol, 83%), **5c** (0.06 mmol, 1%), and **5e** (0.63 mmol, 8%) (The percentages were measured by NMR integral).

1-Phenyl-2-propanone (5a). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.15-7.40 (m, 5H), 3.68 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 206.1, 134.0, 129.1, 128.4, 126.7, 50.6, 28.9.

1-Bromo-1-phenyl-2-propanone (5b). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.34-7.44 (m, 5H), 5.44 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 199.0, 135.1, 129.1, 129.0, 128.7, 56.2, 26.1. MS (CI) 215 (M^++1), 213 (M^++1), 175, 173, 163, 161, 135, 133 (100), 117, 105, 91, 57, 43.

1-Bromo-3-phenyl-2-propanone (5c). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.20-7.35 (m, 5H), 3.94 (s, 2H), 3.91 (s, 2H). ^{13}C NMR (50 MHz, CDCl_3) δ 199.2, 133.2, 129.4, 128.9, 127.5, 46.8, 33.3. MS (CI) 215 (M^++1), 213 (M^++1), 175, 173, 163, 161, 145, 143, 135 (100), 133, 119, 105, 91.

1,3-Dibromo-1-phenyl-2-propanone (5e). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.30-7.50 (m, 5H), 5.84 (s, 1H), 4.23 (d, $J = 12.8$ Hz, 1H), 4.04 (d, $J = 12.8$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 192.8, 134.2, 129.5, 129.1, 128.9, 51.3, 30.8. MS (CI) 295 (M^++1), 293 (M^++1), 291 (M^++1), 213, 211, 133 (100), 131, 104, 91.

1-Phenyl-1,3-butanedione (6a). (keto form:enol form = 0.09 : 1.0) (enol form) ^1H NMR (200 MHz, CDCl_3) δ 16.19 (bs, 1H), 7.80-7.90 (m, 2H), 7.30-7.60 (m, 3H), 6.17 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 193.7, 183.3, 134.8, 132.2, 128.5, 126.9, 96.6, 25.7. **(keto form)** ^1H NMR (200 MHz, CDCl_3) δ 4.09 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 128.7.

2-Bromo-1-phenyl-1,3-butanedione (6b). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.90-8.00 (m, 2H), 7.60-7.70 (m, 1H), 7.40-7.60 (m, 2H), 5.65 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 198.2, 189.9, 134.5, 133.6, 129.2, 129.0, 52.9, 27.1.

4-Bromo-1-phenyl-1,3-butanedione (6c). (enol form) ^1H NMR (200 MHz, CDCl_3) δ 15.63 (bs, 1H), 7.87-7.92 (m, 2H), 7.40-7.60 (m, 3H), 6.45 (s, 1H), 3.97 (s, 2H). ^{13}C NMR (50 MHz, CDCl_3) δ 188.4, 184.0, 133.9, 132.9, 128.7, 127.1, 95.4, 31.2.

2,4-Dibromo-1-phenyl-1,3-butanedione (6e). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 8.00 (dd, $J = 7.0, 1.4$ Hz, 2H), 7.67 (t, $J = 7.3$ Hz, 1H), 7.47-7.57 (m, 2H), 6.12 (s, 1H), 4.43 (d, $J = 13.8$ Hz, 1H), 4.30 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 192.0, 189.7, 134.7, 133.2, 129.2, 129.0, 49.4, 32.0.

Ethyl Acetoactate (7a). (keto form:enol form = 1.0 : 0.1) (keto form) ^1H NMR (200 MHz, CDCl_3) δ 4.21 (q, $J = 7.2$ Hz, 2H), 3.46 (s, 2H), 2.28 (s, 3H), 1.29 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 200.4, 166.9, 61.0, 49.8, 29.8, 13.8. **(enol form)** ^1H NMR (200 MHz, CDCl_3) δ 12.12 (bs, 1H), 4.98 (s, 1H), 1.96 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 175.2, 89.5, 59.6, 20.8, 14.0.

Ethyl 2-Bromoacetoacetate (7b). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 4.77 (s, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 2.45 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 196.3, 165.1, 63.1, 49.1, 26.4, 13.8. MS (CI) 211 ($\text{M}^+ + 1$), 209 ($\text{M}^+ + 1$), 183, 181, 131 (100), 103, 85.

Ethyl 4-Bromoacetoacetate (7c). (keto form:enol form = 1.0 : 0.21) (keto form) ^1H NMR (200 MHz, CDCl_3) δ 4.21 (q, $J = 7.2$ Hz, 2H), 4.08 (s, 2H), 3.71 (s, 2H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 194.3, 166.4, 61.6, 46.0, 33.8, 13.9. **(enol form)** ^1H NMR (200 MHz, CDCl_3) δ 11.99 (s, 1H), 5.29 (s, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 3.87 (s, 2H), 1.30 (t, $J = 7.0$ Hz, 3H). MS (CI) 211 ($\text{M}^+ + 1$), 209 ($\text{M}^+ + 1$, 100), 165, 163, 131, 129, 101, 85, 47.

Ethyl 2,2-Dibromoacetoacetate (7d). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 4.36 (q, $J = 7.1$ Hz, 2H), 2.58 (s, 3H), 1.33 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 190.9, 163.6, 64.7, 59.8, 23.5, 13.7. MS (CI) 291 ($\text{M}^+ + 1$), 289 ($\text{M}^+ + 1$), 287 ($\text{M}^+ + 1$), 263, 261, 256, 245, 243, 241, 211, 209, 207, 131 (100), 105, 85, 47.

2-Acetyl-2-bromo- α -tetralone (8b). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.93 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.42 (td, $J = 7.6, 1.4$ Hz, 1H), 7.14-7.26 (m, 2H), 3.19 (ddd, $J = 17.2, 9.2, 4.8$ Hz, 1H),

3.02 (dt, $J = 17.6, 5.2$ Hz, 1H), 2.81 (ddd, $J = 14.2, 9.4, 5.0$ Hz, 1H), 2.58 (s, 3H), 2.43 (dt, $J = 14.8, 5.0$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 200.0, 189.1, 142.3, 134.1, 129.5, 128.5, 128.3, 126.8, 68.4, 33.5, 27.8, 26.4.

General procedure for Table 3. Br_2 (1.23 g, 7.69 mmol, 1.02 equiv) dissolved in acetic acid (5 mL) was added to the mixture of phenylacetone (**5a**, 1.02 g, 7.57 mmol) acetic acid (5 mL) in a vial (20 mL) with stirring at room temperature and the the reaction mixture was enveloped by the cap. The mixture was stirred for 24 h at room temperature and extracted with methylene chloride, then the organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was passed through short silica column to give crude mixture (1.63 g) including **5a** (0.81 mmol, 11%), **5b** (4.13 mmol, 55%), **5c** (0.96 mmol, 13%), and **5e** (1.47 mmol, 20%) (The percentages were measured by NMR integral).

4,4-Dibromo-1-phenyl-1,3-butanedione (6f). (enol form) ^1H NMR (200 MHz, CDCl_3) δ 14.89 (bs, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.46-7.64 (m, 3H), 6.66 (s, 1H), 5.95 (s, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 188.8, 181.9, 133.1, 132.9, 128.8, 127.1, 92.0, 39.6.

Ethyl 4-Bromoacetoacetate (7f). (keto form:enol form = 1.0 : 0.25) (keto form) ^1H NMR (200 MHz, CDCl_3) δ 6.02 (s, 1H), 4.24 (q, $J = 7.0$ Hz, 2H), 3.96 (s, 2H), 1.30 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 188.7, 166.1, 61.9, 42.0, 41.8, 14.0. **(enol form)** ^1H NMR (200 MHz, CDCl_3) δ 12.10 (bs, 1H), 5.92 (s, 1H), 5.42 (s, 1H), 4.26 (q, $J = 6.8$ Hz, 2H), 1.32 (t, $J = 7.0$ Hz, 3H).

2-Acetyl- α -tetralone (8a). (enol form) ^1H NMR (200 MHz, CDCl_3) δ 16.36 (bs, 1H), 7.94 (dd, $J = 7.2, 1.6$ Hz, 1H), 7.27-7.45 (m, 2H), 7.20 (dd, $J = 6.8, 1.0$ Hz, 1H), 2.88 (t, $J = 8.0$ Hz, 2H), 2.62 (t, $J = 7.8$ Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 193.8, 176.8, 140.7, 131.8, 131.0, 127.5, 126.7, 125.7, 105.9, 28.1, 23.8, 22.6.

2-Bromoacetyl- α -tetralone (8c). (enol form) ^1H NMR (200 MHz, CDCl_3) δ 15.82 (bs, 1H), 7.91 (d, $J = 7.2$ Hz, 1H), 7.20-7.45 (m, 2H), 7.18 (d, $J = 7.2$ Hz, 1H), 4.03 (s, 3H), 2.87 (t, $J = 7.8$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (50 MHz, CDCl_3) δ 184.0, 181.2, 141.3, 132.6, 130.8,

127.7, 126.8, 126.1, 105.6, 28.5, 27.8, 22.5.

2-Bromoacetyl-2-bromo- α -tetralone (8d). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 8.03 (dd, J = 8.0, 1.0 Hz, 1H), 7.54 (td, J = 7.6, 1.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 8.4 Hz, 1H), 4.79 (d, J = 14.4 Hz, 1H), 4.66 (d, J = 14.2 Hz, 1H), 3.23 (ddd, J = 17.6, 10.8, 4.4 Hz, 1H), 3.03 (dt, J = 17.2, 4.4 Hz, 1H), 2.81 (ddd, J = 15.0, 10.6, 4.6 Hz, 1H), 2.48 (dt, J = 15.0, 4.4 Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 194.7, 189.1, 142.7, 134.7, 129.4, 128.9, 128.8, 127.3, 65.8, 33.7, 33.6, 26.4.

General procedure for Table 4. Br_2 (2.40 g, 15.0 mmol, 2.0 equiv) dissolved in acetic acid (5 mL) was added to the mixture of phenylacetone (**5a**, 1.01 g, 7.50 mmol) acetic acid (5 mL) in a vial (20 mL) with stirring at room temperature and the reaction mixture was enveloped by the cap. The mixture was stirred for 24 h at room temperature and extracted with methylene chloride, then the organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was passed through short silica column to give crude mixture (2.20 g) including **5b** (0.29 mmol, 4%), **5c** (0.06 mmol, 1%), **5e** (5.80 mmol, 77%), and **5g**, (1.16 mmol, 15%) (The percentages were measured by NMR integral).

General procedure for Table 5. Br_2 (10.5 g, 65.6 mmol, 2.2 equiv) dissolved in acetic acid (15 mL) was added to the mixture of phenylacetone (**5a**, 4.0 g, 29.85 mmol) acetic acid (10 mL) concentrated hydrobromic acid (5 mL) and in a one-neck flask (100 mL) with stirring at room temperature. The mixture was stirred for 6 h at room temperature and acetone (50 mL) was added. After stirring for 24 h at room temperature, the reaction mixture concentrated *in vacuo* was extracted with methylene chloride, then the organic layer was dried (Na_2SO_4) and concentrated for 10 h *in vacuo*. The residue was passed through short silica column to give crude mixture (6.09 g) including **5a** (1.52 mmol, 5%), **5b** (1.01 mmol, 3%), **5c** (25.25 mmol, 85%), and **5e**, (1.01 mmol, 3%) (The percentages were measured by NMR integral). The reaction mixture was purified by flash column chromatography (5% EtOAc/hexane) to give pure **5c** (4.81 g, 16.5 mmol, 76%).

1-Bromo-1-phenyl-3,3-dibromo-2-propanone (5g). (keto form) ^1H NMR (200 MHz, CDCl_3) δ 7.51-7.56 (m, 2H), 7.37-7.42 (m, 3H), 6.16 (s, 1H), 6.03 (s, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 187.7, 134.5, 129.8, 129.1, 46.4, 38.9. MS (CI) 375 (M^++1), 373 (M^++1), 371 (M^++1), 369 (M^++1), 293, 291, 289, 213, 211, 133 (100).