SUPPORTING INFORMATION

for

**"Divergent Regioselectivity in the Base-Promoted Reactions of Cyclic
Eight-Membered α -Ketols with Activated Halides"**

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(10 Pages)

General Procedure. A solution of the α -hydroxy ketone (50 mg, 0.36 mmol) in dry DMF (3.6 mL) was treated with dry sodium hydride (11 mg, 0.46 mmol), stirred at rt for 10 min, cooled to -15°C (or -30°C), and treated with the activated bromide, e.g., *p*-methoxybenzyl bromide (94 mg, 0.46 mmol). The reaction mixture was stirred at -15°C for 24 h, quenched with water, and extracted with ether. The combined organic phases were dried and evaporated to leave a residue that was purified by column chromatography on silica gel (elution with hexanes - ethyl acetate 97:3) to give 2-hydroxy-2-(4-methoxybenzyl)cyclooctanone as a white crystalline solid, mp 79°C .

Run 1: 56% yield (reaction conducted at -30°C); colorless oil; IR (film, cm^{-1}) 3474, 1700; ^1H NMR (300 MHz, CDCl_3) 5.74-5.60 (m, 1 H), 5.08-4.98 (m, 2 H), 3.90 (br s, 1 H), 2.76 (dt, $J = 12.2, 4.0$ Hz, 1 H), 2.41-2.28 (m, 2 H), 2.28-2.17 (m, 2 H), 1.96-1.91 (m, 1 H), 1.90-1.83 (m, 1 H), 1.82-1.55 (m, 4 H), 1.42-1.22 (m, 2 H), 1.02-0.87 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 218.6, 132.1, 118.5, 80.5, 44.5, 36.2, 33.2, 30.0, 25.4, 24.5, 22.8; ES HRMS m/z ($\text{C}_{11}\text{H}_{18}\text{O}_2\text{Na}^+$) calcd 205.1200, obsd 205.1216.

Run 2: 60% yield (reaction conducted at -30°C); colorless oil; IR (film, cm^{-1}) 3478, 1698; ^1H NMR (300 MHz, CDCl_3) 5.05-4.98 (m, 1 H), 3.85 (br s, 1 H), 2.79 (dt, $J = 12.2, 4.1$ Hz, 1 H), 2.33-2.30 (m, 2 H), 2.27-2.18 (m, 2 H), 2.00-1.87 (m, 2 H), 1.85-1.52 (m, 4 H), 1.69 (s, 3 H), 1.59 (s, 3 H), 1.48-1.26 (m, 2 H), 1.01-0.90 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 219.2, 135.3, 117.4, 80.7, 38.7, 36.2, 33.1, 30.2, 25.9, 25.5, 24.5, 22.9, 18.0; ES HRMS m/z ($\text{C}_{13}\text{H}_{22}\text{O}_2\text{Na}^+$) calcd 233.1512, obsd 233.1528.

Run 3: 42% yield (reaction conducted at -30 °C); colorless oil; IR (film, cm^{-1}) 3479, 1698; ^1H NMR (300 MHz, CDCl_3) 7.36-7.09 (m, 5 H), 3.84 (d, J = 1.6 Hz, 1 H), 2.89 (s, 2 H), 2.88 (dt, J = 12.3, 4.0 Hz, 1 H), 2.44-2.29 (m, 1 H), 2.27-2.22 (m, 1 H), 1.99-1.90 (m, 2 H), 1.86-1.57 (m, 4 H), 1.44-1.31 (m, 2 H), 0.98-0.84 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 218.3, 135.3, 130.0 (2C), 128.0 (2C), 126.7, 80.9, 46.2, 36.6, 33.0, 30.3, 25.3, 24.3, 22.8; ES HRMS m/z ($\text{C}_{15}\text{H}_{20}\text{O}_2\text{Na}^+$) calcd 255.1355, obsd 255.1360.

Run 4: 62% yield; white crystalline solid, mp 79 °C; IR (CHCl_3 , cm^{-1}) 3478, 1698; ^1H NMR (300 MHz, CDCl_3) 7.05-7.00 (m, 2 H), 6.81-6.76 (m, 2 H), 3.78 (br s, 1 H), 3.77 (s, 3 H), 2.90-2.79 (m, 1 H), 2.84 (s, 2 H), 2.41-2.30 (m, 1 H), 2.24 (dt, J = 12.0, 4.6 Hz, 1 H), 1.98-1.88 (m, 2 H), 1.84-1.58 (m, 4 H), 1.44-1.26 (m, 2 H), 0.99-0.85 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 218.5, 158.6, 131.0 (2C), 127.4, 113.6 (2C), 81.0, 55.2, 45.5, 36.8, 33.1, 30.3, 25.5, 24.5, 22.9; ES HRMS m/z ($\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}^+$) calcd 285.1461, obsd 285.1463.

Run 5: 43% yield; colorless oil; IR (film, cm^{-1}) 3474, 1702; ^1H NMR (500 MHz, CDCl_3) 7.51 (d, J = 8.1 Hz, 2 H), 7.25 (d, J = 8.1 Hz, 2 H), 3.85 (d, J = 1.4 Hz, 1 H), 2.96 (d, J = 13.7 Hz, 1 H), 2.92 (d, J = 13.7 Hz, 1 H), 2.92-2.86 (m, 1 H), 2.42-2.35 (m, 1 H), 2.31-2.27 (dt, J = 11.0, 4.6 Hz, 1 H), 2.01-1.91 (m, 2 H), 1.82-1.73 (m, 3 H), 1.68-1.61 (m, 1 H), 1.44-1.32 (m, 2 H), 0.96-0.88 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) 217.9, 139.5, 130.4 (2C), 129.1

(q, $J = 32.3$ Hz), 126.0 (q, $J = 3.8$ Hz, 2C), 124.2 (q, $J = 270.0$ Hz), 80.8, 45.8, 36.6, 33.2, 30.4, 25.4, 24.4, 22.8; ES HRMS m/z ($C_{16}H_{19}F_3O_2Na^+$) calcd 323.1229, obsd 323.1243.

Run 6: 40% yield; viscous yellow oil; IR (film, cm^{-1}) 3478, 1704; 1H NMR (300 MHz, $CDCl_3$) 7.28-7.20 (m, 1 H), 6.91 (d, $J = 1.8$ Hz, 2 H), 3.76 (d, $J = 1.1$ Hz, 1 H), 2.95 (d, $J = 13.6$ Hz, 1 H), 2.88 (d, $J = 13.6$ Hz, 1 H), 2.89-2.81 (m, 1 H), 2.45-2.35 (m, 1 H), 2.20 (dt, $J = 11.6, 4.3$ Hz, 1 H), 2.01-1.89 (m, 2 H), 1.86-1.50 (m, 4 H), 1.46-1.17 (m, 2 H), 1.29 (s, 18 H), 0.99-0.88 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 226.6, 150.3, 134.3 (2C), 124.3 (2C), 120.6, 81.1, 47.3, 37.0, 34.7, 33.4 (2C), 31.4 (6C), 30.3, 25.5, 24.4, 23.0; ES HRMS m/z ($C_{23}H_{36}O_2Na^+$) calcd 367.2607, obsd 367.2628.

Run 7: 45% yield; colorless oil; IR (film, cm^{-1}) 3478, 1694; 1H NMR (300 MHz, $CDCl_3$) 8.15-8.12 (m, 1 H), 7.84-7.80 (m, 1 H), 7.74 (d, $J = 8.1$ Hz, 1 H), 7.52-7.42 (m, 2 H), 7.37 (dd, $J = 8.1, 7.1$ Hz, 1 H), 7.27-7.24 (m, 1 H), 3.81 (d, $J = 1.7$ Hz, 1 H), 3.50 (d, $J = 14.1$ Hz, 1 H), 3.29 (d, $J = 14.1$ Hz, 1 H), 2.91 (dt, $J = 12.6, 3.9$ Hz, 1 H), 2.54-2.43 (m, 1 H), 2.24 (dt, $J = 11.5, 4.2$ Hz, 1 H), 2.04 (dt, $J = 15.0, 3.9$ Hz, 1 H), 1.95-1.88 (m, 1 H), 1.85-1.56 (m, 4 H), 1.44-1.26 (m, 2 H), 0.98-0.83 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 218.7, 133.9, 133.0, 132.1, 128.60, 128.55, 127.7, 125.7, 125.5, 125.0, 124.9, 81.6, 42.3, 37.2, 33.3, 30.5, 25.6, 24.4, 23.1; EI HRMS m/z ($C_{19}H_{22}O_2^+$) calcd 282.1614, obsd 282.1638.

Run 8: 40% yield; white solid, mp 131-132 °C; IR (film, cm^{-1}) 3474, 1698; ^1H NMR (500 MHz, CDCl_3) 8.32 (d, $J = 8.5$ Hz, 1 H), 7.88 (d, $J = 8.2$ Hz, 1 H), 7.67 (d, $J = 8.2$ Hz, 1 H), 7.62-7.59 (m, 1 H), 7.53 (d, $J = 7.1$ Hz, 1 H), 7.31-7.19 (m, 2 H), 6.85 (d, $J = 8.1$ Hz, 1 H), 6.68 (d, $J = 7.7$ Hz, 1 H), 6.59 (d, $J = 7.2$ Hz, 1 H), 4.66 (d, $J = 16.8$ Hz, 1 H), 4.60 (d, $J = 16.8$ Hz, 1 H), 3.84 (d, $J = 1.4$ Hz, 1 H), 3.71 (s, 3 H), 2.85 (d, $J = 14.3$ Hz, 1 H), 2.73 (d, $J = 14.3$ Hz, 1 H), 2.78-2.72 (m, 1 H), 2.29-2.17 (m, 2 H), 1.90-1.86 (m, 1 H), 1.82 (dt, $J = 15.0, 3.9$ Hz, 1 H), 1.78-1.69 (m, 3 H), 1.61-1.59 (m, 1 H), 1.33-1.21 (m, 2 H), 0.93-0.85 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) 218.6, 158.3, 136.8, 136.3, 133.6, 128.6, 128.2, 126.8 (2C), 126.2, 125.9, 125.53, 125.45, 124.0, 123.6, 123.4, 109.3, 81.4, 55.6, 42.1, 36.6, 33.2, 30.3, 27.9, 25.5, 24.4, 23.0; ES HRMS m/z ($\text{C}_{27}\text{H}_{30}\text{O}_3\text{Na}^+$) calcd 425.2087, obsd 425.2079.

Run 9: 61% yield (reaction at -30 °C); colorless oil; IR (film, cm^{-1}) 1708; ^1H NMR (300 MHz, CDCl_3) 6.00-5.80 (m, 1 H), 5.68-5.61 (m, 2 H), 5.37-5.29 (m, 1 H), 5.23-5.18 (m, 1 H), 4.05-3.99 (m, 2 H), 3.94-3.89 (m, 1 H), 3.19-3.07 (m, 1 H), 2.97 (ddd, $J = 12.6, 5.0, 4.3$ Hz, 1 H), 2.64-2.54 (m, 1 H), 2.32 (dt, $J = 12.5, 5.2$ Hz, 1 H), 2.13-2.03 (m, 1 H), 1.94-1.84 (m, 2 H), 1.64-1.53 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 215.4, 134.3, 130.85, 130.80, 117.0, 84.0, 70.7, 44.6, 29.8, 21.1, 20.3; ES HRMS m/z ($\text{C}_{11}\text{H}_{16}\text{O}_2\text{Na}^+$) calcd 203.1042, obsd 203.1051.

Run 10: 73% yield (reaction at -30 °C); colorless oil; IR (film, cm^{-1})

1709; ^1H NMR (300 MHz, CDCl_3) 5.70-5.59 (m, 2 H), 5.46-5.31 (m, 1 H), 4.06-3.94 (m, 2 H), 3.91-3.87 (m, 1 H), 3.16-3.03 (m, 1 H), 2.95 (dt, $J = 12.5, 4.6$ Hz, 1 H), 2.62-2.50 (m, 1 H), 2.30 (dt, $J = 12.3, 5.1$ Hz, 1 H), 2.13-2.03 (m, 1 H), 1.93-1.81 (m, 2 H), 1.74 (s, 3 H), 1.65 (s, 3 H), 1.62-1.52 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 215.6, 137.2, 130.81, 130.75, 120.8, 83.6, 66.4, 44.6, 30.0, 25.8, 21.1, 20.4, 18.1; ES HRMS m/z ($\text{C}_{13}\text{H}_{20}\text{O}_2\text{Na}^+$) calcd 231.1355, obsd 231.1363.

Run 11: 50% yield (reaction at -30 °C); colorless oil; IR (film, cm^{-1})

1708; ^1H NMR (300 MHz, CDCl_3) 7.40-7.27 (m, 5 H), 5.74-5.63 (m, 2 H), 4.59 (s, 2 H), 4.01-3.98 (dd, $J = 6.3, 2.5$ Hz, 1 H), 3.22-3.17 (m, 1 H), 3.02 (ddd, $J = 12.6, 5.0, 4.3$ Hz, 1 H), 2.67-2.60 (m, 1 H), 2.32 (dt, $J = 12.5, 5.3$ Hz, 1 H), 2.12-2.02 (m, 1 H), 1.99-1.88 (m, 2 H), 1.67-1.58 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 215.0, 137.9, 130.9, 130.8, 128.5, 127.8 (2C), 127.4 (2C), 84.3, 71.7, 44.5, 29.7, 21.1, 20.3; ES HRMS m/z ($\text{C}_{15}\text{H}_{18}\text{O}_2\text{Na}^+$) calcd 253.1199, obsd 253.1202.

Run 12: 70% yield; colorless oil; IR (film, cm^{-1}) 1707; ^1H NMR

(300 MHz, CDCl_3) 7.30-7.25 (m, 2 H), 6.91-6.86 (m, 2 H), 5.72-5.60 (m, 2 H), 4.50 (s, 2 H), 3.96 (dd, $J = 6.4, 2.7$ Hz, 1 H), 3.81 (m, 3 H), 3.22-3.09 (m, 1 H), 2.97 (ddd, $J = 12.4, 5.2, 4.4$ Hz, 1 H), 2.68-2.57 (m, 1 H), 2.29 (dt, $J = 12.4, 5.2$ Hz, 1 H), 2.12-2.02 (m, 1 H), 1.96-1.84 (m, 2 H), 1.64-1.55 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 215.1, 159.4, 130.8 (2C), 129.9, 129.1 (2C), 113.9 (2C),

83.9, 71.5, 55.3, 44.5, 29.8, 21.1, 20.3; ES HRMS m/z ($C_{16}H_{20}O_3Na^+$) calcd 283.1305, 283.1300.

Run 13: 51% yield; colorless oil; IR (film cm^{-1}) 1710; 1H NMR (500 MHz, $CDCl_3$) 7.68 (d, $J = 8.2$ Hz, 2 H), 7.54 (d, $J = 8.2$ Hz, 2 H), 5.77-5.70 (m, 2 H), 4.70 (d, $J = 12.4$ Hz, 1 H), 4.66 (d, $J = 12.4$ Hz, 1 H), 4.06-4.05 (m, 1 H), 3.23-3.16 (m, 1 H), 3.07-3.03 (m, 1 H), 2.71-2.64 (m, 1 H), 2.41 (dd, $J = 12.5, 5.3$ Hz, 1 H), 2.19-2.14 (m, 1 H), 2.04-1.96 (m, 2 H), 1.73-1.67 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 214.3, 141.9, 130.8, 130.7, 130.0 (q, $J = 32.3$ Hz), 127.3 (2C), 125.4 (q, $J = 3.6$ Hz, 2C), 124.1 (q, $J = 270.5$ Hz), 84.7, 70.9, 44.5, 29.6, 21.1, 20.3; ES HRMS m/z ($C_{16}H_{17}F_3O_2Na^+$) calcd 321.1073, obsd 321.1078.

Run 14: 43% yield; yellow viscous oil; IR (film, cm^{-1}) 1709; 1H NMR (300 MHz, $CDCl_3$) 7.38-7.36 (m, 1 H), 7.22-7.20 (m, 2 H), 5.74-5.62 (m, 2 H), 4.59 (d, $J = 0.6$ Hz, 2 H), 4.00-3.97 (m, 1 H), 3.30-3.17 (m, 1 H), 3.01 (ddd, $J = 12.6, 5.1, 4.3$ Hz, 1 H), 2.74-2.62 (m, 1 H), 2.30 (dt, $J = 12.5, 5.3$ Hz, 1 H), 2.14-2.06 (m, 1 H), 2.04-1.86 (m, 2 H), 1.66-1.55 (m, 1 H), 1.33 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) 215.4, 151.0, 137.0 (2C), 130.9 (2C), 121.8 (2C), 121.5, 84.3, 72.4, 44.6, 34.9 (2C), 31.5 (6C), 29.9, 21.1, 20.4; ES HRMS m/z ($C_{23}H_{34}O_2Na^+$) calcd 365.2451, obsd 365.2462.

Run 15: 69% yield; colorless oil; IR (film, cm^{-1}) 1707; 1H NMR (300 MHz, $CDCl_3$) 8.15-8.12 (m, 1 H), 7.90-7.82 (m, 2 H), 7.58-7.39 (m, 4 H),

5.73-5.61 (m, 2 H), 5.03 (d, $J = 4.9$ Hz, 2 H), 4.10-4.07 (m, 1 H), 3.22-3.11 (m, 1 H), 2.97 (ddd, $J = 12.7, 5.1, 4.5$ Hz, 1 H), 2.68-2.59 (m, 1 H), 2.29 (dt, $J = 12.4, 5.2$ Hz, 1 H), 2.17-2.05 (m, 1 H), 2.03-1.85 (m, 2 H), 1.67-1.55 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 214.9, 133.7, 133.3, 131.5, 130.9, 130.8, 128.8, 128.7, 126.3, 126.2, 125.9, 125.2, 123.7, 84.2, 70.3, 44.5, 29.8, 21.1, 20.4; ES HRMS m/z ($\text{C}_{19}\text{H}_{20}\text{O}_2\text{Na}^+$) calcd 303.1355, obsd 303.1351.

Run 16: 46% yield; colorless oil; IR (film, cm^{-1}) 1707, ^1H NMR (500 MHz, CDCl_3) 8.29 (d, $J = 8.4$ Hz, 1 H), 7.93 (d, $J = 8.1$ Hz, 1 H), 7.73 (d, $J = 8.2$ Hz, 1 H), 7.64 (t, $J = 8.0$ Hz, 1 H), 7.58 (t, $J = 7.8$ Hz, 1 H), 7.41 (t, $J = 7.9$ Hz, 1 H), 7.29 (t, $J = 7.6$ Hz, 1 H), 7.20 (d, $J = 7.6$ Hz, 1 H), 7.03 (d, $J = 8.2$ Hz, 1 H), 6.73 (d, $J = 7.1$ Hz, 1 H), 5.67-5.62 (m, 2 H), 4.61 (s, 2 H), 4.52 (d, $J = 11.9$ Hz, 1 H), 4.46 (d, $J = 11.9$ Hz, 1 H), 3.87-3.86 (m, 1 H), 3.80 (s, 3 H), 3.11-3.06 (m, 1 H), 2.80 (dt, $J = 12.7, 4.6$ Hz, 1 H), 2.53-2.47 (m, 1 H), 2.18 (td, $J = 12.5, 5.3$ Hz, 1 H), 2.02-1.97 (m, 1 H), 1.81-1.75 (m, 2 H), 1.50-2.44 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) 214.8, 158.2, 138.1, 136.0, 133.6, 132.1, 130.8, 130.7, 128.7, 127.6, 126.5, 126.3, 125.9, 125.6, 125.5, 123.7, 123.2, 121.1, 110.5, 84.2, 69.6, 55.7, 44.3, 29.4, 27.6, 21.0, 20.1; ES HRMS m/z ($\text{C}_{27}\text{H}_{28}\text{O}_3\text{Na}^+$) calcd 423.1931, obsd 423.1930.

2-(2-Naphthylmethyl)-3-methoxybenzyl Bromide. Potassium carbonate (473 mg, 3.42 mmol) and 2-(2-naphthylmethyl)-3-methoxybenzoic acid (500 mg, 1.71 mmol) were suspended in dry acetone (15 mL), treated with dimethyl sulfate (324 mg, 2.57 mmol), stirred at rt for 2 days, and filtered through Celite. The solid was rinsed with CH_2Cl_2 and the combined filtrates were

concentrated to afford the methyl ester as a brownish solid, mp 95-98 °C, which was used directly; quantitative yield; IR (CHCl₃, cm⁻¹) 1721; ¹H NMR (300 MHz, CDCl₃) 8.25 (d, *J* = 8.6 Hz, 1 H), 7.85 (dd, *J* = 7.9, 0.6 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.59-7.46 (m, 3 H), 7.36 (t, *J* = 8.0 Hz, 1 H), 7.24 (t, *J* = 8.1 Hz, 1 H), 7.11 (dd, *J* = 8.2, 1.0 Hz, 1 H), 6.68 (dd, *J* = 7.2, 1.1 Hz, 1 H), 4.83 (s, 2 H), 3.73 (s, 3 H), 3.62 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 168.2, 137.2, 133.6, 132.7, 132.2, 129.6, 128.6, 127.3, 126.0 (2C), 125.6, 125.4, 125.3, 123.8, 123.6, 122.4, 114.0, 55.9, 51.9, 28.6; ES HRMS *m/z* (C₂₀H₁₈O₃Na⁺) calcd 329.1148, obsd 329.1146.

The above ester (2.5 g, 8.17 mmol) was dissolved in dry ether (100 mL), treated with lithium aluminum hydride (466 mg, 12.25 mmol), stirred at rt for 24 h, quenched with methanol, and stirred for 1 h. Hydrochloric acid (1 M) was introduced and the product was extracted into ether (5 x 20 mL), and the combined ethereal phases were dried and concentrated. The residue was purified by chromatography on silica gel (elution with hexanes - ethyl acetate 4:1) to furnish 2.2 g (97%) of the primary carbinol as a white solid, mp 108 °C, IR (CHCl₃, cm⁻¹) 3363; ¹H NMR (300 MHz, CDCl₃) 8.28 (d, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 7.9 Hz, 1 H), 7.70 (d, *J* = 8.2 Hz, 1 H), 7.63-7.52 (m, 2 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.26 (t, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 1 H), 6.71 (d, *J* = 7.1 Hz, 1 H), 4.58 (s, 2 H), 4.55 (s, 2 H), 3.76 (s, 3 H), 1.61 (br s, 1 H); ¹³C NMR (75 MHz, CDCl₃) 158.2, 141.1, 136.4, 133.7, 132.2, 128.7, 127.9, 126.5 (2C), 126.0, 125.9, 125.6, 123.7, 123.4, 120.6, 110.4, 63.2, 55.8, 27.5; ES HRMS *m/z* (C₁₉H₁₈O₂Na⁺) calcd 301.1199, obsd 301.1201.

A solution of the preceding alcohol (1.00 g, 3.60 mmol) in dry ether (60 mL) was treated with a solution of phosphorus tribromide in ether (10 mL), stirred for 3 h, and quenched with water. The product was extracted into ether, and the combined ethereal layers were washed with saturated NaHCO₃ solution and brine. After

drying and solvent evaporation, the residue was purified by chromatography on silica gel (elution with hexanes - ethyl acetate 95:5) to afford 0.98 g (80%) of the bromide as a white solid, mp 85-87 °C; IR (CHCl₃, cm⁻¹) 1597, 1585, 1472; ¹H NMR (300 MHz, CDCl₃) 8.35-8.32 (m, 1 H), 7.92-7.89 (m, 1 H), 7.71 (d, *J* = 8.2 Hz, 1 H), 7.66-7.63 (m, 1 H), 7.61-7.53 (m, 1 H), 7.36-7.24 (m, 2 H), 7.10 (dd, *J* = 7.6, 1.0 Hz, 1 H), 6.97 (dd, *J* = 8.3, 0.7 Hz, 1 H), 6.70 (dd, *J* = 7.1, 1.1 Hz, 1 H), 4.67 (s, 2 H), 4.34 (s, 2 H), 3.76 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) 158.5, 138.2, 136.1, 133.7, 132.3, 128.8, 128.1, 127.3, 126.7, 126.1, 125.7, 125.6, 123.8, 123.5, 123.0, 111.3, 55.8, 31.9, 27.6; ES HRMS *m/z* (C₁₉H₁₇BrONa⁺) calcd 363.0355, obsd 363.0348.

2-Benzyloxycyclooctanone (9). A solution of **5** (600 mg, 4.2 mmol) in ether (10.5 mL) was treated with benzyl trichloroacetimidate (1.18 mL, 6.3 mmol) and triflic acid (19 µL, 0.21 mmol). The resulting solution was stirred for 40 h, treated with saturated NH₄Cl solution, and stirred for an additional hour. The product was extracted into ether and the combined organic phases were washed with NaHCO₃ solution, dried, and concentrated. The residue was purified by chromatography on silica gel (elution with hexane - ethyl acetate 10:1) to give **9** as a colorless oil (650 mg, 66%); IR (neat, cm⁻¹) 1707; ¹H NMR (300 MHz, CDCl₃) 7.37-7.28 (m, 5 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 3.94 (t, *J* = 5.7 Hz, 1 H), 2.67 (ddd, *J* = 13.0, 9.1, 3.6 Hz, 1 H), 2.30 (ddd, *J* = 13.0, 9.3, 3.6 Hz, 1 H), 2.09-1.99 (m, 3 H), 1.87-1.69 (m, 2 H), 1.59-1.31 (series of m, 5 H); ¹³C NMR (75 MHz, CDCl₃) 216.8, 137.9, 128.4 (2C), 127.8, 127.7 (2C), 83.3, 71.7, 39.4, 31.6, 26.9, 26.1, 25.2, 21.8; ES HRMS *m/z* (C₁₅H₂₀O₂Na⁺) calcd 255.1355, obsd 255.1364.