Supporting Information

Enantioselective Enol Lactone Synthesis under the Double Catalytic Conditions

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General: Proton NMR spectra were recorded on JEOL LA 395 (395 MHz) NMR spectrometer. Proton chemical shifts are reported in parts per million downfield (δ) relative to internal tetramethylsilane (TMS, δ 0.00) or with the solvent reference as internal standard (CDCl_3 , δ 7.26). Data are reported as follows: chemical shift, multiplicity (s= singlet, d= doublet, t= triplet, q= quarted, o= octet, br= broad, m= multiplet), coupling constants (Hz), integration, and assignment. Carbon NMR spectra were recorded on JEOL LA 395 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million downfield (δ) relative to internal TMS with the respective solvent reference as the internal standard (CDCl_3 , δ 77.0). NMR data were collected at 27 °C unless otherwise stated. Elemental analyses were performed with Hitachi 026 CHN analyzer. Infrared (IR) spectra were recorded on SHIMADZU FTIR-8300 spectrophotometer, ν_{max} in cm^{-1} . Mass spectra were recorded with JEOL-JMS-70 spectrometer operating at ionization energy of 75 eV. Enantiomeric ratios were determined by chiral high performance liquid chromatography (HPLC) analysis (SHIMADZ LC-10Avp) attached by Daicel Chiral Cell AD, OD, ADH and ODH columns. Specific rotations were recorded with Horiba SEPA-200 polarimeter. Melting points were recorded on Yanagimoto melting point apparatus JANACO MP. Flash chromatography was performed using Silica Gel 60 (63~210 microns, spherical, neutral) from Kanto Chemicals, Inc.

Solvent and Materials: Cyclic diketones and 3,5-dimethylpyrazole were purchased from commercial supplies. 4-Bromo-3,5-dimethylpyrazole and 4-iodo-3,5-dimethylpyrazole were prepared from 3,5-dimethylpyrazole through bromination and iodination, respectively. (*E*)-2-Alkenoyl chlorides and unsaturated amides of pyrazoles amides were prepared according to methods reported previously.^{1,2} 3-Crotonoyl-2-oxazolidinone was prepared according to the reported procedure from crotonoyl chloride and 2-oxazolidinone which were purchased commercially.³

Preparation of 4-Bromo-3,5-dimethylpyrazole:

Bromine (10.1 mL, 0.39 mol, 1.50 equiv) was added over 1 hour to a solution of 3,5-dimethylpyrazole (25.0 g, 0.26 mol, 1.00 equiv) in anhydrous dichloromethane (520 mL) at -78 °C. The resulting solution was allowed to warm up to 0 °C and stirred for 5 min, followed by addition of saturated sodium thiosulfate pentahydrate until brownish color was diminished. The reaction mixture was neutralized by a saturated sodium hydrogen carbonate and extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate and concentrated in vacuo to provide desired product (46.0 g, quant) which was carried on without further purification: White solid; mp = 101 °C; IR (KBr) ν = 3172, 3136, 3091, 2926, 2843, 2773, 2729, 1582, 1471, 1414, 1302, 1148, 1096, 1042, 1001, 824, and 766 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.29 (6H, s, each of CH_3) and 11.56 (1H, br s, NH); ^{13}C NMR (CDCl_3) δ = 11.86 (each of CH_3), 94.17 (C-4), and 142.69 (C-3 and C-5); Mass (rel intensity, %) m/z = 176 (95, $\text{M}^+ + 2$), 175 (32, $\text{M}^+ + 1$), 174 (base peak, M^+), 173 (27), and 95 (57); HRMS Calcd for $\text{C}_5\text{H}_7\text{BrN}_2$ (M^+): 173.9793. Found: 173.9792.

Preparation of 4-Iodo-3,5-dimethylpyrazole:

3,5-Dimethylpyrazole (5.00 g, 52.0 mmol, 1.00 equiv) was added to a solution of periodic acid dehydrate (2.37g, 10.4 mmol, 0.20 equiv), sulfuric acid (52.0 mL), water (10.4 mL) and iodine (13.6 g, 107 mmol, 2.05 equiv) in acetic acid (52.0 mL) at room temperature. The resulting violet solution was allowed to heat up to 80 °C and stirred for 3 h. The reaction mixture was poured into saturated sodium thiosulfate pentahydrate (200 mL) to give yellow precipitate of 4-iodo-3,5-dimethylpyrazole (3.40 g, 30%): Yellow solid; mp = 146 °C; IR (KBr) ν = 3150, 3001, 2918, 1556, 1406, 1379, 1269, 1082, 1001, 787, and 692 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.31 (6H, s, each of CH_3) and 5.63 (1H, br s, NH); ^{13}C NMR (CDCl_3) δ = 12.93 (each of CH_3), 44.26 (C-4), and 146.76 (C-3 and C-5); Mass (rel intensity, %) m/z 223 (8, $\text{M}^+ + 1$), 155 (26), 139 (11), 138 (29), and 137 (58); HRMS: Calcd for $\text{C}_5\text{H}_8\text{IN}_2$ (M^{+1}): 222.9732. Found: 222.9729.

General Procedure for the Preparation of 1-(2-Alkenoyl)-3,5-dimethylpyrazoles, 4-Bromo-1-crotonoyl-3,5-dimethylpyrazole and 4-Iodo-1-crotonoyl-3,5-dimethylpyrazole (Method A):

Under nitrogen, a mixture of 3,5-dimethylpyrazole (5.00 g, 52.0 mmol, 1.00 equiv) and pyridine (4.41 mL, 54.6 mmol, 1.05 equiv) in anhydrous dichloromethane (106 mL) was added dropwise to crotonoyl chloride (4.41 mL, 54.6 mmol, 1.05 equiv) in dichloromethane (200 mL) at 0 °C, and the mixture was stirred for 3 h. The reaction mixture was poured into saturated sodium hydrogencarbonate and extracted with dichloromethane. The combined organic layers were washed with brine, dried with magnesium sulfate and concentrated in vacuo. The crude residue was passed through a flash silica gel column chromatography by eluting with 5% diethyl ether/hexane to provide analytically pure **4** (7.21 g, 84%).

Other unsaturated imide substrates **1b-i**, **1k-m**, **1o** and **1p** were prepared according to a similar procedure from 3,5-dimethylpyrazole and the corresponding (*E*)-2-alkenoyl chlorides which were prepared by the previously reported methods (Sibi, M. P.; Shay, J. J.; Jasperse, C. P. *J. Am. Chem. Soc.* **1998**, *120*, 6615-6616.).

The reaction of 4-iodo-3,5-dimethylpyrazole with crotonoyl chloride under similar conditions was completed in 12 h. After usual workup, the crude residue was purified through a silica gel column chromatography with diethyl ether to give **1c** which was purified through recrystallization from ethyl acetate and hexane. The 4-iodo-1-crotonoyl-3,5-dimethylpyrazole underwent partial decomposition during a silica gel column

chromatography.

(E)-1-Crotonoyl-3,5-dimethylpyrazole (4):

Colorless oil; IR (neat) ν = 3000, 1700, 1640, 1580, 1380, 1340, 1290, 1230, 1180, 1140, 1010, 960, 910, 830, and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.00 (3H, d, J_{4-3} = 6.6 Hz, H-4), 2.23 (3H, s, 5-Me of the pyrazole), 2.57 (3H, d, J = 0.7 Hz, 3-Me of the pyrazole), 5.97 (1H, s, H-4'), 7.19 (1H, dq, J_{3-2} = 15.5 Hz and J_{3-4} = 6.6 Hz, H-3), and 7.31 (1H, d, J_{2-3} = 15.5 Hz, H-2); ^{13}C NMR (CDCl_3) δ = 13.67 (5-Me of the pyrazole), 14.51 (3-Me of the pyrazole), 18.43 (C-4), 110.96 (C-4'), 122.58 (C-2), 144.25 (C-5'), 146.46 (C-3), 151.63 (C-3'), and 165.00 (C-1); Mass (rel intensity, %) m/z 165 (18, $\text{M}^+ + 1$), 164 (57, M^+), 153 (26), 150 (11), 149 (base peak), 136 (22), 135 (22), 121 (15), 109 (17), 108 (12), 107 (35), 106 (14), 105 (14), 97 (30), 96 (48), 95 (38), 89 (25), 78 (15), 77 (51), and 69 (70); HRMS Calcd for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}$ (M^+): 164.0950. Found: 164.0949.

(E)-4-Bromo-1-(2-crotonoyl)-3,5-dimethylpyrazole (7a):

White solid; mp = 65 $^{\circ}\text{C}$; IR (KBr) ν = 2978, 1780, 1641, 1569, 1487, 1439, 1404, 1373, 1350, 1294, 1290, 1232, 1082, 1024, 989, 966, 923, 829, 764, and 681 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.02 (3H, d, J_{4-3} = 5.3 Hz, H-4), 2.28 (3H, s, 5-Me of the pyrazole), 2.59 (3H, s, 3-Me of the pyrazole), 7.23 (1H, dq, J_{3-2} = 15.7 Hz and J_{3-4} = 5.3 Hz, H-3) and 7.31 (1H, d, J_{2-3} = 15.7 Hz, H-2); ^{13}C NMR (CDCl_3) δ = 12.71 (5-Me of the pyrazole), 13.59 (3-Me of the pyrazole), 18.66 (C-4), 102.17 (C-4'), 121.59 (C-2), 141.55 (C-5'), 147.68 (C-3), 150.36 (C-3'), and 164.46 (C-1); Mass (rel intensity, %) m/z 245 (16), 244 (91, $\text{M}^+ + 2$), 243 (12), 242 (90, M^+), 230 (11), 229 (84), 228 (12), 227 (95), 216 (21), 215 (17), 214 (24), 213 (11), 177 (12), 175 (23), 174 (74), 173 (14), 153 (35), 149 (11), 136 (21), 107 (36), 106 (20), 105 (13), 95 (27), 89 (30), 79 (13), 78 (19), 77 (55), 69 (base peak), 68 (17), 66 (10), 65 (16), and 58 (37). Anal. Calcd for $\text{C}_9\text{H}_{11}\text{BrN}_2\text{O}$: C, 44.47; H, 4.56; N, 11.52. Found: C, 44.47; H, 4.56; N, 11.52.

(E)-4-Iodo-1-(2-crotonoyl)-3,5-dimethylpyrazole (7b):

Yellow solid; mp = 76 $^{\circ}\text{C}$; IR (KBr) ν = 970, 2955, 2922, 1713, 1643, 1558, 1491, 1443, 1400, 1369, 1344, 1290, 1229, 1166, 1067, 1022, 986, 964, 923, 922, 841, 827, and 764 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.02 (3H, d, J_{4-3} = 5.6 Hz, H-4), 2.29 (3H, s, 5-Me of the pyrazole), 2.64 (3H, s, 3-Me of the pyrazole), 7.23 (1H, dq, J_{3-2} = 15.5 Hz and J_{3-4} = 5.6 Hz, H-3), and 7.30 (1H, d, J_{2-3} = 15.5 Hz, H-2); ^{13}C NMR (CDCl_3) δ =

14.50 (5-Me of the pyrazole), 15.64 (3-Me of the pyrazole), 18.70 (C-4), 73.08 (C-4'), 121.53 (C-2), 145.24 (C-5'), 147.83 (C-3), 153.01 (C-3'), and 164.21 (C-1); Mass (rel intensity, %) m/z 290 (5), 289 (12, M^+), 155 (27), 139 (11), 138 (30), and 137 (59); HRMS Calcd for $C_9H_{12}IN_2O$ ($M^+ + 1$): 290.9994. Found: 290.9995.

(E)-4-Bromo-1-(2-pentenoyl)-3,5-dimethylpyrazole (7c):

White solid; 1H NMR ($CDCl_3$) δ = 1.15 (3H, t, J_{5-4} = 7.5 Hz, H-5), 2.27 (3H, s, 5-Me of the pyrazole), 2.34-2.39 (2H, m, H-4), 2.59 (3H, s, 3-Me of the pyrazole), and 7.26-7.32 (2H, m, H-2 and H-3); ^{13}C NMR ($CDCl_3$) δ = 12.19 (5-Me of the pyrazole), 12.64 (3-Me of the pyrazole), 13.52 (C-5), 25.95 (C-4), 102.05 (C-4'), 119.18 (C-2), 141.41 (C-5'), 150.176 (C-3'), 153.70 (C-3), and 164.55 (C-1). Anal. Calcd for $C_{10}H_{13}BrN_2O$: C, 46.71; H, 5.10; N, 10.89. Found: C, 46.74; H, 5.08; N, 10.84.

(E)-4-Bromo-1-(2-hexenoyl)-3,5-dimethylpyrazole (7d):

White viscous oil; 1H NMR ($CDCl_3$) δ = 0.97 (3H, t, J_{6-5} = 7.2 Hz, H-6), 1.56 (2H, sex, $J_{5-6} = J_{5-4}$ = 7.2 Hz, H-5), 2.27 (3H, s, 5-Me of the pyrazole), 2.30-2.35 (2H, m, H-4), 2.59 (3H, s, 3-Me of the pyrazole), and 7.20-7.29 (2H, m, H-2 and H-3); ^{13}C NMR ($CDCl_3$) δ = 12.99 (5-Me of the pyrazole), 13.88 (3-Me of the pyrazole), 14.01 (C-6), 21.68 (C-5), 35.12 (C-4), 102.42 (C-4'), 120.47 (C-2), 141.80 (C-5'), 150.56 (C-3'), 152.71 (C-3), and 164.85 (C-1). Anal. Calcd for $C_{11}H_{15}BrN_2O$: C, 48.72; H, 5.58; N, 10.33. Found: C, 48.81; H, 5.59; N, 10.29.

(E)-4-Bromo-1-(4-methyl-2-pentenoyl)-3,5-dimethylpyrazole (7e):

Pale yellow solid; 1H NMR ($CDCl_3$) δ = 1.14 (6H, d, J_{CH-4} = 6.8 Hz, $CH(CH_3)_2$), 2.28 (3H, s, 5-Me of the pyrazole), 2.55 – 2.65 (1H, m, $CH(CH_3)_2$), 2.60 (3H, s, 3-Me of the pyrazole), 7.19 (1H, d, J_{2-3} = 15.7 Hz, H-2), and 7.31 (1H, d, J_{3-2} = 15.7 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ = 12.74 (5-Me of the pyrazole), 13.63 (3-Me of the pyrazole), 21.28 ($CH(CH_3)_2$), 31.69 ($CH(CH_3)_2$), 102.16 (C-4 of the pyrazole), 117.43 (C-2), 141.55 (C-5 of the pyrazole), 150.33 (C-3 of the pyrazole), 158.67 (C-3), and 164.94 (C-1). Anal. Calcd for $C_{11}H_{15}BrN_2O$: C, 48.72; H, 5.58; N, 10.33. Found: C, 48.60; H, 5.58; N, 10.25.

(E)-4-Bromo-1-(3-cyclohexyl-2-propenoyl)-3,5-dimethylpyrazole (7f):

Colorless solid; mp = 80 °C; ^1H NMR (CDCl_3) δ = 1.16 – 1.37 (5H, m, $c\text{-C}_6\text{H}_{11}$), 1.68 – 1.85 (5H, m, $c\text{-C}_6\text{H}_{11}$), 2.23 – 2.32 (1H, m, C_6H_{11}), 2.28 (3H, s, 5-Me of the pyrazole), 2.59 (3H, s, 3-Me of the pyrazole), and 7.18 – 7.26 (2H, m, H-2 and H-3); ^{13}C NMR (CDCl_3) δ = 12.74 (5-Me of the pyrazole), 13.63 (3-Me of the pyrazole), 25.67, 25.89, 31.67, 41.18 (each $c\text{-C}_6\text{H}_{11}$), 102.16 (C-4 of the pyrazole), 117.72 (C-2), 141.54 (C-5 of the pyrazole), 150.31 (C-3 of the pyrazole), 157.49 (C-3), and 165.01 (C-1). Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{BrN}_2\text{O}$: C, 54.03; H, 6.15; N, 9.00. Found: C, 53.47; H, 6.12; N, 8.93.

(E)-4-Bromo-1-[3-(2,4-hexadienyl)]-3,5-dimethylpyrazole (7g):

Pale yellow solid; mp = 89 °C; ^1H NMR (CDCl_3) δ = 1.89 (3H, dd, $J_{6,5} = 6.4$ and $J_{6,4} = 0.8$ Hz, H-6), 2.26 (3H, s, 5-Me of the pyrazole), 2.59 (1H, s, 3-Me of the pyrazole), 6.22-6.39 (2H, m, H-5 and H-4), 7.19 (1H, dd, $J_{2,3} = 15.6$ and $J_{2,4} = 0.4$ Hz, H-2), and 7.48 (1H, dd, $J_{3,2} = 15.6$ and $J_{3,4} = 10.4$ Hz, H-3); ^{13}C NMR (CDCl_3) δ = 12.62 (5-Me of the pyrazole), 13.49 (3-Me of the pyrazole), 18.77 (C-6), 101.95 (C-4 of the pyrazole), 117.58 (C-2), 130.37 (C-4), 141.27 (C-5 of the pyrazole), 147.25 (C-3 and C-5), 150.03 (C-3 of the pyrazole), and 165.01 (C-1). Anal. Calcd for $\text{C}_9\text{H}_{13}\text{BrN}_2\text{O}$: C, 49.09; H, 4.87; N, 10.41. Found: C, 48.93; H, 4.79; N, 10.30.

(E)-4-Bromo-1-[3-(2-furyl)-2-propenyl]-3,5-dimethylpyrazole (7h):

Colorless solid; mp = 120 °C; ^1H NMR (CDCl_3) δ = 2.30 (3H, s, 5-Me of the pyrazole), 2.63 (3H, s, 3-Me of the pyrazole), 6.51 (1H, dd, $J = 2.0$ and 3.6 Hz, Furyl), 6.75 (1H, $J = 3.6$ Hz, Furyl), 7.54 – 7.55 (1H, m, Furyl), 7.65 (1H, d, $J_{2,3} = 15.8$ Hz, H-2), and 7.75 (1H, $J_{3,2} = 15.8$ Hz, H-3); ^{13}C NMR (CDCl_3) δ = 12.76 (5-Me of the pyrazole), 13.62 (3-Me of the pyrazole), 102.29 (C-4 of the pyrazole), 112.59, 114.39, 116.24 (Furyl), 123.89 (C-2), 132.66 (q-C of Furyl), 141.43 (C-5 of the pyrazole), 145.32 (C-3), 151.51 (C-3 of the pyrazole), and 164.88 (C-1). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{BrN}_2\text{O}_2$: C, 48.84; H, 3.76; N, 9.49. Found: C, 48.83; H, 3.78; N, 9.54.

(E)-4-Bromo-1-[3-(methoxycarbonyl)-2-propenyl]-3,5-dimethylpyrazole (7i):

Colorless solid; mp = 90 °C; ^1H NMR (CDCl_3) δ = 2.89 (3H, s, 5-Me of the pyrazole), 2.61 (3H, s, 3-Me of the pyrazole), 3.85 (3H, s, COOMe), 7.04 (1H, d, $J_{3,2} = 15.9$ Hz, H-3), and 8.25 (1H, d, $J_{2,3} = 15.9$ Hz, H-2);

^{13}C NMR (CDCl_3) δ = 12.73 (5-Me of the pyrazole and COOMe), 13.42 (3-Me of the pyrazole), 52.39 (COOMe), 103.53 (C-4 of the pyrazole), 132.73, 134.24 (C-2 and C-3), 141.66 (C-5 of the pyrazole), 151.63 (C-3 of the pyrazole), 163.01 (COOMe), and 165.33 (C-1). Anal. Calcd for $\text{C}_9\text{H}_{11}\text{BrN}_2\text{O}_3$: C, 41.83; H, 3.86; N, 9.76. Found: C, 41.85; H, 3.89; N, 9.77.

(E)-4-Bromo-1-(3-phenyl-2-propenoyl)-3,5-dimethylpyrazole (7j):

Colorless solid; mp = 104 °C; ^1H NMR (CDCl_3) δ = 2.28 (3H, s, 5-Me of the pyrazole), 2.61 (3H, s, 3-Me of the pyrazole), 7.37 – 7.39 (3H, m, Ph), 7.62 – 7.64 (2H, m, Ph), and 7.88 (2H, m, H-2 and H-3); ^{13}C NMR (CDCl_3) δ = 12.65 (5-Me of the pyrazole), 13.54 (3-Me of the pyrazole), 102.26 (C-4 of the pyrazole), 116.62 (C-2), 128.62, 128.76, 130.63 (each Ph), 134.48 (q-C of Ph), 141.40 (C-5 of the pyrazole), 146.73 (C-3), 150.26 (C-3 of the pyrazole), and 164.06 (C-1). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{BrN}_2\text{O}$: C, 55.10; H, 4.29; N, 9.18. Found: C, 55.06; H, 4.32; N, 9.23.

(E)-4-Bromo-1-[3-(4-bromophenyl)-2-propenoyl]-3,5-dimethylpyrazole (7k):

Colorless solid; mp = 175 °C; ^1H NMR (CDCl_3) δ = 2.31 (3H, s, 5-Me of the pyrazole), 2.64 (3H, s, 3-Me of the pyrazole), 7.52 – 7.57 (4H, m, Ar), 7.83 (1H, d, $J_{2,3}$ = 15.9 Hz, H-2), and 7.90 (1H, $J_{3,2}$ = 15.9 Hz, H-3); ^{13}C NMR (CDCl_3) δ = 12.76 (5-Me of the pyrazole), 13.65 (3-Me of the pyrazole), 117.43 (C-4 of the pyrazole), 125.12 (C-2), 130.07, 132.16, 133.49 (each Ar), 137.24 (q-C of Ar), 141.62 (C-5 of the pyrazole), 145.42 (C-3), 150.66 (C-3 of the pyrazole), and 164.55 (C-1). Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}$: C, 43.78; H, 3.15; N, 7.29. Found: C, 43.65; H, 3.15; N, 7.36.

4-Bromo-1-[3-(5-bromo-2-methoxyphenyl)propanoyl]pyrazole:

Pale yellow solid; mp = 158 °C; ^1H NMR (CDCl_3) δ = 2.31 (3H, s, Me of the pyrazole), 2.63 (3H, s, Me of the pyrazole), 3.88 (3H, s, OMe), 6.80 (1H, d, J = 9.0 Hz, Ar), 7.45 (1H, dd, J = 2.4 and 9.0 Hz, Ar), 7.45 (1H, dd, J = 2.4 and 9.0 Hz, Ar), 7.80 (1H, d, J = 2.4 Hz, Ar), 7.85 (1H, d, $J_{2,3}$ = 15.9 Hz, H-2), and 8.20 (1H, d, $J_{3,2}$ = 15.9 Hz, H-3); ^{13}C NMR (CDCl_3) δ = 12.74, 13.61 (each Me of the pyrazole), 55.84 (OCH_3), 102.35 (C-4 of the pyrazole), 112.91, 113.00, 117.85 (each Ar), 125.56 (C-2), 130.89, 134.34, 140.20 (each q-C of Ar), 150.45 (C-5 of the pyrazole), 157.48 (C-3), and 164.73 (C-1).

4-Bromo-1-[3-(3,5-dibromophenyl)propanoyl]pyrazole:

Pale yellow solid; mp = 165 °C; ^1H NMR (CDCl_3) δ = 2.32 (3H, s, Me of the pyrazole), 2.63 (3H, s, Me of the pyrazole), 7.69 (1H, d, J = 1.6 Hz, Ar), 7.71 (2H, d, J = 1.6 Hz, Ar), 7.72 (1H, $J_{2,3}$ = 16.2 Hz, H-2), and 7.88 (1H, d, $J_{3,2}$ = 16.2 Hz, H-3); ^{13}C NMR (CDCl_3) δ = 12.74, 13.61 (each Me of the pyrazole), 102.86 (C-4 of the pyrazole), 119.67, (C-2), 123.46, 130.02 (each Ar), 135.66, 138.03 (each q-C of Ar), 141.67 (C-5 of the pyrazole), 143.24 (C-5 of the pyrazole), 150.96 (C-3), and 163.87 (C-1).

General Procedure for the Enantioselective Michael Addition / Cyclization Reactions Catalyzed by the Aqua Complex of (*R,R*)-DBFOX/Ph-Nickel(II) Perchlorate and TMP:

Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1**) with 4-bromo-1-crotonyl-3,5-dimethylpyrazole (**7a**) is described as a typical example: A mixture of (*R,R*)-DBFOX/Ph⁴ (17.9 mg, 0.039 mmol) and nickel (II) perchlorate hexahydrate (14.3 mg, 0.039 mmol) in THF (2 mL) was stirred at rt for 5 min. 4-Bromo-1-crotonyl-3,5-dimethylpyrazole (**7a**, 100 mg, 0.39 mmol) and acetic anhydride (0.07, 0.78 mmol) was added and the resulting solution was stirred at room temperature for an additional 5 min. 5,5-Dimethyl-1,3-cyclohexanedione (**1**, 109 mg, 0.78 mmol) and 2,2,6,6-tetramethylpiperidine (7 μL , 0.039 mmol) were added in this order and stirred for 5 h. The reaction mixture was poured into saturated ammonium chloride (2 mL) and extracted with ethyl acetate (4 mL x 3). The combined organic layers were washed with brine, dried with magnesium sulfate and concentrated in vacuo. The crude residue was passed through a flash silica gel column chromatography (eluted with hexane/diethyl ether (4:1 v/v)) to provide analytically pure **3a** (75.8 mg, 93%).

4,7,7-Trimethyl-3,4,5,6,7,8-hexahydrobenzopyrane-2(*H*),5-dione (3a**):**

Colorless solid; mp = 42 °C; $[\alpha]_{\text{D}}^{25}$ = -8.71 (98% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_{r} (minor) = 17.9 min, t_{r} (major) = 21.3 min, c 0.41, CHCl_3); IR (KBr) ν = 2961, 2920, 2991, 2871, 2831, 1784, 1735, 1649, 1456, 1435, 1418, 1381, 1367, 1340, 1323, 1306, 1292, 1231, 1202, 1157, 1119, 1080, 1070, 1028, 989, 968, 920, 891, 873, 849, 797, and 708 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.07 (3H, d, J = 7.0 Hz, 4- CH_3), 1.09 (3H, s, one of 7- CH_3), 1.12 (3H, s, the other of 7- CH_3), 2.30 (2H, s, H-8), 2.46 (1H, d, J_{gem} = 17.6 Hz, one of H-6), 2.47 (1H, br d, J_{gem} = 17.6, the other of H-6), 2.64 (1H, dd, J_{gem} = 15.6 and $J_{3,4}$ = 2.2 Hz, one of H-3), 2.65 (1H, dd, J_{gem} = 15.6 and $J_{3,4}$ = 6.3, the other of H-3), and 3.14 (1H, m, H-4); ^{13}C NMR (CDCl_3) δ = 19.32 (4- CH_3), 23.40, 27.87 (each of 7- CH_3), 28.51 (C-7), 32.48 (C-4), 36.00 (C-3), 40.88 (C-8), 50.62 (C-6), 118.10 (C-4a), 164.71 (C-8a), 166.65 (C-2), and 196.42 (C-5); Mass (rel intensity, %) m/z 208 (41, M^+), 193 (16), 181 (12), 180 (base peak), 166 (20), 165 (96), 124 (13), 96 (32), and 82 (15). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.21 %; H, 7.74 %. Found: C, 68.82 %; H, 7.74 %.

4-Ethyl-7,7-dimethyl-3,4,5,6,7,8-hexahydrobenzopyrane-2(*H*),5-dione (3b):

Colorless solid; mp = 49 °C; $[\alpha]_D^{25} = +11.17$ (93% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_r (minor) = 17.5 min, t_r (major) = 21.4 min, c 0.34, CHCl₃); IR (KBr) ν = 2966, 2928, 2874, 1790, 1736, 1713, 1462, 1416, 1389, 1346, 1323, 1296, 1246, 1207, 1157, 1119, 1092, 1069, 1030, 949, 926, 849, and 791 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.89 (3H, t, J = 7.2 Hz, CH₂CH₃), 1.11, 1.12 (3H each, s, 7-CH₃), 1.34, 1.50 (1H each, m, CH₂CH₃), 2.31 (1H, d, J_{gem} = 16.4 Hz, one of H-8), 2.32 (1H, d, J_{gem} = 16.4 Hz, the other of H-8), 2.42 (1H, d, J_{gem} = 17.8 Hz, one of H-6), 2.44 (1H, dd, J_{gem} = 17.8 and J = 1.6 Hz, the other of H-6), 2.60 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 7.2 Hz, one of H-3), 2.77 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 1.5 Hz, the other of H-3), and 2.98 (1H, m, H-4); ¹³C NMR (CDCl₃) δ = 10.77 (CH₂CH₃), 26.48, 27.73 (each of 7-CH₃), 28.63 (CH₂CH₃), 29.28 (C-7), 32.39 (C-4), 33.21 (C-3), 40.85 (C-8), 50.59 (C-6), 117.02 (C-4a), 165.12 (C-8a), 166.97 (C-2), and 196.63 (C-5); Mass (rel intensity, %) m/z 222 (74, M⁺), 194 (37), 193 (70), 180 (69), 179 (61), 166 (29), 165 (base peak), 137 (20), 124 (10), 109 (12), 96 (14), 95 (11), 83 (13), and 81 (12). Anal. Calcd for C₁₃H₁₈O₃: C, 70.24 %; H, 8.16 %. Found: C, 70.30; H, 8.23 %.

7,7-Dimethyl-4-propyl-3,4,5,6,7,8-hexahydrobenzopyrane-2(*H*),5-dione (3c):

Colorless low-melting solid; $[\alpha]_D^{25} = +6.26$ (91% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_r (minor) = 14.7 min, t_r (major) = 18.2 min, c 0.38, CHCl₃); IR (neat) ν = 2959, 2932, 2874, 1786, 1724, 1655, 1381, 1285, 1246, 1119, 1096, 1015, 926, 841 and 802 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.89 (3H, t, J = 7.0 Hz, MeCH₂CH₂), 1.10 (3H, s, one of 7-CH₃), 1.12 (3H, s, the other of 7-CH₃), 1.19 - 1.45 (4H, m, C₂H₄CH₃), 2.31 (1H, d, J_{gem} = 16.2, one of H-8), 2.32 (1H, d, J_{gem} = 16.2, the other of H-8), 2.42 (1H, d, J_{gem} = 17.8, one of H-6), 2.43 (1H, d, J_{gem} = 17.8, the other of H-6), 2.59 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 6.9 Hz, one of H-3), 2.75 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 1.7 Hz, the other of H-3), and 3.05 (1H, m, H-4); ¹³C NMR (CDCl₃) δ = 13.90 (C₂H₄CH₃), 19.67 (CH₂CH₂CH₃), 27.80, 27.84 (each of 7-CH₃), 28.64 (CH₂CH₂CH₃), 32.44 (C-7), 33.61 (C-4), 35.72 (C-3), 40.89 (C-8), 50.63 (C-6), 117.49 (C-4a), 165.04 (C-8a), 167.01 (C-2), and 196.62 (C-5); Mass (rel intensity, %) m/z 236 (88, M⁺), 218 (26), 208 (12), 194 (42), 193 (80), 180 (12), 179 (58), 167 (19), 166 (base peak), 165 (89), and 137 (21). Anal. Calcd for C₁₄H₂₀O₃: C, 71.16 %; H, 8.53 %. Found: C, 71.11 %; H, 8.55 %.

7,7-Dimethyl-4-(*iso*-propyl)-3,4,5,6,7,8-hexahydrobenzopyrane-2(*H*),5-dione (3d):

Colorless solid; mp = 83 °C; $[\alpha]_D^{25} = +29.76$ (96% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_r (minor) = 18.7 min, t_r (major) = 22.9 min, c 0.35, CHCl₃); IR (KBr) ν = 2963, 2928, 2870, 2824, 1794, 1670, 1651, 1466, 1420, 1373, 1315, 1292, 1269, 1227, 1200, 1165, 1142, 1115, 1030, 1007, 980, 953, 930, 903, 856, and 810 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.77 (3H, d, J = 7.0 Hz, one of CHMe₂), 0.85 (3H, d, J = 7.0 Hz, the other of CHMe₂), 1.05 (6H, s, 7-CH₃), 1.70 (1H, m, CHMe₂), 2.21 (1H, d, J_{gem} = 16.4, one of H-8), 2.28 (1H, d, J_{gem} = 16.4, the other of H-8), 2.38 (2H, s, H-6), 2.44 (1H, dd, J_{gem} = 16.4 and $J_{3,4}$ = 7.7 Hz, one of H-3), 2.74 (1H, dd, J_{gem} = 16.4 and $J_{3,4}$ = 1.2 Hz, the other of H-3), and 2.83 (1H, m, H-4); ¹³C NMR (CDCl₃) δ = 18.24, 20.09 (each of CHMe₂), 27.73, 28.72 (each of 7-CH₃), 30.64 (each of CHMe₂), 31.08 (C-7), 32.23 (C-4), 34.02 (C-3), 40.96 (C-8), 50.67 (C-6), 116.18 (C-4a), 165.41 (C-8a), 167.36 (C-2), and 196.72 (C-5); Mass (rel intensity, %) m/z 236 (50, M⁺), 195 (11), 194 (78), 193 (base peak), 179 (32), 166 (15), 165 (12), 161 (11), 138 (11), 137 (23), 95 (10), and 81 (13). Anal. Calcd for C₁₄H₂₀O₃: C, 71.16 %; H, 8.53 %. Found: C, 71.53 %; H, 8.78 %.

7,7-Dimethyl-4-cyclohexyl-3,4,5,6,7,8-hexahydrobenzopyrane-2(H),5-dione (3e):

Colorless solid; mp = 105 °C; $[\alpha]_D^{25} = +18.70$ (97% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_r (minor) = 14.9 min, t_r (major) = 18.8 min, c 0.43, CHCl₃); IR (KBr) ν = 2936, 2858, 1790, 1670, 1655, 1447, 1427, 1373, 1311, 1285, 1238, 1200, 1119, 1072, 1034, 980, 957, 930, 895, 845, 810, 791, and 718 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.84 - 0.96 (1H, m, C₆H₁₁), 1.07 - 1.28 (4H, m, C₆H₁₁), 1.11 (3H, s, one of 7-CH₃), 1.12 (3H, s, the other of 7-CH₃), 1.34 - 1.42 (1H, m, *c*-C₆H₁₁), 1.49-1.52 (1H, m, *c*-C₆H₁₁), 1.60-1.73 (1H, m, *c*-C₆H₁₁), 2.28 (1H, d, J_{gem} = 16.2 Hz, one of H-8), 2.236 (1H, d, J_{gem} = 16.2 Hz, the other of H-8), 2.44 (2H, br s, H-6), 2.48 (1H, dd, J_{gem} = 16.4 and $J_{3,4}$ = 7.7 Hz, one of H-3), 2.84 (1H, dd, J_{gem} = 16.4 and $J_{3,4}$ = 1.5 Hz, the other of H-3), and 2.90 (1H, m, H-4); ¹³C NMR (CDCl₃) δ = 26.09 (*c*-C₆H₁₁), 26.23, 28.01 (each of 7-CH₃), 28.67, 28.90, 30.56 (each of *c*-C₆H₁₁), 31.13 (C-7), 32.36 (C-4), 33.50 (C-3), 41.08 (C-8), 50.74 (C-6), 116.20 (C-4a), 165.44 (C-8a), 167.55 (C-2), and 196.87 (C-5); Mass (rel intensity, %) m/z 276 (80, M⁺), 259 (18), 258 (87), 248 (11), 235 (12), 234 (72), 194 (20), 193 (50), 167 (37), 166 (base peak), 165 (16), 154 (13), 153 (21), 137 (14), 110 (12), 83 (14), 82 (11), and 81 (14). Anal. Calcd for C₁₇H₂₄O₃: C, 73.88 %; H, 8.75 %. Found: C, 73.54 %; H, 8.82 %.

7,7-Dimethyl-4-(1-propenyl)-3,4,5,6,7,8-hexahydrobenzopyrane-2(H),5-dione (3f):

Colorless oil; $[\alpha]_D^{25} = -51.35$ (90% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_r (minor) = 12.5 min, t_r (major) = 16.9 min, c 0.33, CHCl₃); IR (neat) ν = 2953, 1713, 1612, 1385, 1250, 1204, 1169, 1119, 1061, 1038, 968, 887, and 860 cm⁻¹; ¹H NMR (CDCl₃) δ =

1.13 (6H, s, 7-CH₃), 1.63 (3H, dt, $J = 6.3$ and 1.2 Hz, CH=CHMe), 2.30 (1H, d, $J_{\text{gem}} = 16.2$, one of H-8), 2.34 (1H, d, $J_{\text{gem}} = 16.2$, the other of H-8), 2.44 (2H, s, H-6), 2.65 (1H, dd, $J_{\text{gem}} = 15.7$ and $J_{3-4} = 7.0$ Hz, one of H-3), 2.79 (1H, dd, $J_{\text{gem}} = 15.7$ and $J_{3-4} = 1.7$ Hz, the other of H-3), 3.65 (1H, m, H-4), 5.37 (1H, m, CH=CHMe), and 5.47 (1H, m, CH=CHMe); ¹³C NMR (CDCl₃) $\delta = 17.70$ (C₂H₂CH₃), 28.16, 28.39 (each of 7-CH₃), 30.32 (C-7), 32.44 (C-4), 34.31 (C-3), 40.84 (C-8), 50.52 (C-6), 115.75 (C-4a), 126.51, 128.43 (each of C₂H₂CH₃), 165.21 (C-8a), 166.35 (C-2), and 196.14 (C-5); Mass (rel intensity, %) m/z 234 (18, M⁺), 206 (18), 193 (12), 192 (23), 191 (base peak), 178 (19), 177 (65), 165 (15), 149 (16), 135 (25), 122 (31), 121 (24), 109 (12), 108 (33), 107 (35), 105 (17), 101 (68), 98 (13), 95 (22), 94 (17), 93 (17), 91 (48), 89 (11), 85 (12), 84 (29), 83 (64), 82 (18), 81 (22), 80 (21), 79 (65), 78 (25), 77 (77), 76 (11), 71 (16), 70 (32), 69 (23), 68 (18), 67 (33), 66 (33), 65 (36), 63 (12), 60 (11), 59 (67), and 58 (32). Anal. by HRMS: Calcd for C₁₄H₁₈O₃ (M⁺): 234.1256. Found: 234.1255.

7,7-Dimethyl-4-(2-furyl)-3,4,5,6,7,8-hexahydrobenzopyrane-2(H),5-dione (3g):

Colorless solid; mp = 70 °C; $[\alpha]_{\text{D}}^{25} = -60.69$ (89% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol 1 (9:1 v/v), 1 mL/min, t_{r} (minor) = 16.9 min, t_{r} (major) = 20.5 min, c 0.74, CHCl₃); IR (KBr) $\nu = 3151, 3121, 2966, 2936, 2878, 1790, 1763, 1709, 1647, 1589, 1504, 1423, 1373, 1327, 1304, 1258, 1234, 1215, 1196, 1180, 1146, 1103, 1011, 984, 914, 856, 806, 764, \text{ and } 613 \text{ cm}^{-1}$; ¹H NMR (CDCl₃) $\delta = 1.08$ (3H, s, one of 7-CH₃), 1.14 (3H, s, the other of 7-CH₃), 2.33 (2H, s, H-8), 2.48 (2H, s, H-6), 2.83 (1H, dd, $J_{\text{gem}} = 16.0$ and $J_{3-4} = 7.2$ Hz, one of H-3), 3.05 (1H, dd, $J_{\text{gem}} = 16.0$ and $J_{3-4} = 1.6$ Hz, the other of H-3), 4.37 (1H, d, $J_{4-3} = 7.2$ Hz, H-4), 6.06 (1H, dt, $J = 1.0$ and 3.1 Hz, Furyl), 6.24 (1H, dd, $J = 3.1$ and 1.9 Hz, Furyl), and 7.28 (1H, dd, $J = 1.0$ and 1.9 Hz, Furyl); ¹³C NMR (CDCl₃) $\delta = 27.69, 27.79$ (each 7-CH₃), 28.51 (C-7), 32.44 (C-4), 33.64 (C-3), 40.94 (C-8), 50.38 (C-6), 105.91, 110.24 (each Furyl), 113.87 (C-4a), 142.16 (Furyl), 152.66 (q-C of Furyl), 165.44 (C-8a), 166.12 (C-2), and 195.67 (C-5); Mass (rel intensity, %) m/z 260 (22, M⁺), 258 (50), 217 (17), 204 (20), 203 (14), 189 (23), 176 (29), 175 (21), 149 (20), 148 (77), 147 (21), 135 (18), 134 (39), 131 (20), 121 (57), 120 (83), 119 (29), 115 (24), 107 (24), 106 (76), 105 (39), 103 (22), 101 (14), 95 (19), 94 (44), 93 (26), 92 (79), 91 (89), 89 (26), 84 (14), 83 (35), 81 (37), 79 (26), 78 (base peak), 77 (87), 76 (17), 75 (13), 69 (13), 67 (13), 66 (18), 65 (44), 64 (16), 63 (24), and 60 (15). Anal. Calcd for C₁₅H₁₆O₄: C, 69.22 %; H, 6.20 %. Found: C, 69.13 %; H, 6.24 %.

7,7-Dimethyl-4-phenyl-3,4,5,6,7,8-hexahydrobenzopyrane-2(H),5-dione (3i):

Colorless solid; mp = 104 °C; $[\alpha]_{\text{D}}^{25} = -131.18$ (99% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (95:1 v/v), 1 mL/min, t_{r} (minor) = 25.0 min, t_{r} (major) = 28.0 min, c 0.51, CHCl₃); IR (KBr) $\nu = 3055, 3032, 2966, 2936, 2893, 2870, 1771, 1659, 1601, 1493, 1470, 1454, 1416, 1377,$

1342, 1315, 1273, 1242, 1211, 1184, 1161, 1115, 1038, 968, 922, 860, 772, 756, 725, 702, and 606 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.10 (3H, s, one of 7- CH_3), 1.15 (3H, s, the other of 7- CH_3), 2.32 (2H, s, H-8), 2.54 (2H, s, H-6), 2.79 (1H, d, J_{gem} = 16.2 Hz, one of H-3), 2.92 (1H, d, J_{gem} = 16.2 Hz, the other of H-3), 4.30 (1H, m, H-4), and 7.13 - 7.31 (5H, m, Ar); ^{13}C NMR (CDCl_3) δ = 28.10, 28.51 (each 7- CH_3), 32.54 (C-7), 33.83 (C-4), 36.31 (C-3), 41.03 (C-8), 50.59 (C-6), 116.07 (C-4a), 126.50, 127.46, 129.07 (each of CH, Ar), 140.51 (qC, Ar), 165.69 (C-8a), 165.97 (C-2), and 196.14 (C-5); Mass (rel intensity, %) m/z 270 (52, M^+), 243 (19), 242 (base peak), 241 (73), 227 (32), 185 (11), 171 (10), 158 (11), 115 (14), and 102 (11). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$: C, 75.53 %; H, 6.71 %. Found: C, 75.34 %; H, 6.72 %.

(4R)-7,7-Dimethyl-4-(4-bromophenyl)-3,4,5,6,7,8-hexahydrobenzopyrane-2(H),5-dione (3j):

Colorless prisms (from ethyl acetate / hexane); mp = 153 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = -130.78 (>99% ee estimated by chiral hplc analysis on Daicel Chiral Cell ODH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_{r} (minor) = 18.7 min, t_{r} (major) = 27.5 min, c 0.51, CHCl_3); IR (KBr) ν = 3055, 3032, 2966, 2936, 2893, 2870, 1771, 1659, 1601, 1493, 1470, 1454, 1416, 1377, 1342, 1315, 1273, 1242, 1211, 1184, 1161, 1115, 1038, 968, 922, 860, 772, 756, 725, 702, and 606 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.09 (3H, s, one of 7- CH_3), 1.15 (3H, s, the other of 7- CH_3), 2.32 (2H, s, H-8), 2.53 (2H, s, H-6), 2.90 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 2.5 Hz, one of H-3), 2.95 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 7.1 Hz, the other of H-3), 4.25 (1H, br d, J_{4-3} = 7.1 Hz, H-4), 7.02 - 7.04 (2H, m, Ar), and 7.40 - 7.42 (2H, m, Ar); ^{13}C NMR (CDCl_3) δ = 28.10, 28.60 (each 7- CH_3), 32.56 (C-7), 33.39 (C-4), 35.99 (C-3), 41.05 (C-8), 50.56 (C-6), 115.71 (C-4a), 121.42, 128.32 (each Ar), 132.20, 139.62 (q-C of Ar), 165.60 (C-8a), 165.91 (C-2), and 194.04 (C-5); Mass (rel intensity, %) m/z 350 (36), 348 (36, M^+), 323 (17), 322 (99), 321 (40), 320 (base peak), 319 (24), 307 (13), 305 (14), 241 (35), 185 (15), 129 (13), 115 (17), 101 (11), and 58 (51). Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{BrO}_3$: C, 58.47 %; H, 4.91 %. Found: C, 57.97 %; H, 4.87 %.

3,4-Dihydro-4-methyl-2H,5H-pyrano[3,2-b]phenalen-2,5-dione (11a):

Yellow solid; mp = 122 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = -36.47 (91% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_{r} (major) = 22.1 min, t_{r} (minor) = 24.2 min, c 0.91, CHCl_3); IR (KBr) ν = 3063, 2955, 2928, 2870, 1782, 1628, 1597, 1574, 1508, 1462, 1408, 1369, 1354, 1312, 1281, 1242, 1211, 1184, 1134, 1080, 1042, 1022, 988, 945, 899, 864, 845, 783, 744, and 664 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.28 (3H, d, J = 7.3 Hz, 4- CH_3), 2.82 (1H, dd, J_{3-4} = J_{gem} = 15.8 and J_{3-4} = 2.0 Hz, one of H-3), 2.93 (1H, dd, J_{gem} = 15.8 and J_{3-4} = 6.6 Hz, the other of H-3), 3.55-3.66 (1H, m, H-4), 7.59-7.74 (2H, m, Ar), 8.03-8.25 (3H, m, Ar), 8.60 (1H, dd, J = 7.6 and 1.3 Hz, Ar); ^{13}C NMR (CDCl_3) δ = 19.25 (4- CH_3), 24.33 (C-4), 35.75 (C-3), 121.69, 125.92, 126.28, 126.44, 126.87, 127.87, 130.25, 131.69, 132.54, 134.97

(each of Ar), 156.11 (C-11c), 166.42 (C-2), 182.59 (C-5); Mass (rel intensity, %) m/z 264 (46, M^+), 249 (17), 236 (33), 235 (20), 222 (21), 221 (based peak), 220 (11) and 165 (31). Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26 %; H, 4.58 %. Found: C, 76.99 %; H, 4.69 %.

3,4-Dihydro-4-(3,5-dibromophenyl)-2H,5H-pyrano[3,2-*b*]phenalen-2,5-dione (11b):

Yellow solid; mp = 122 °C; $[\alpha]_D^{25} = +26.66$ (89% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 29.5 min, t_r (minor) = 46.6 min, c 0.30, $CHCl_3$); IR (KBr) ν = 3055, 2939, 1782, 1628, 1597, 1582, 1555, 1508, 1408, 1369, 1350, 1304, 1254, 1231, 1188, 1134, 1026, 999, 972, 895, 849, 787, 741, and 683 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 3.11 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 1.7 Hz, one of H-3), 3.19 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 7.5 Hz, the other of H-3), 4.72 (1H, dd, J = 7.5 and 1.7 Hz, H-4), 7.36 (2H, d, J = 1.7 Hz, Ar), 7.55 (1H, t, J = 1.7 Hz, Ar), 7.74 (1H, dd, J = 8.2 and 7.5 Hz, Ar), 7.81 (1H, t, J = 7.5 Hz, Ar), 8.81 (1H, br d, J = 8.2 Hz, Ar), 8.27 (1H, dd, J = 8.2 and 1.2 Hz, Ar), 8.41 (1H, dd, J = 7.5 and 1.0 Hz, Ar), 8.63 (1H, dd, J = 7.2 and 1.2 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 34.44 (C-4), 35.95 (C-3), 111.63, 121.47, 123.68, 126.57, 126.64, 127.31, 127.57, 127.95 (each of Ar), 128.85, 131.03, 132.06, 133.54, 133.62, 135.62, 144.30 (each of qC, Ar), 157.80 (C-11c), 164.84 (C-2), 182.39 (C-5); Mass (rel intensity, %) m/z 486 (45), 485 (22), 484 (86), 483 (11, M^+), 482 (44), 458 (51), 457 (45), 456 (base peak), 455 (59), 454 (50), 453 (26), 221 (89), 181 (21), 180 (21), 165 (33), 153 (21), 149 (39), 122 (20), 111 (20), 109 (25), 107 (20), 105 (21), 101 (20), 97 (31), 91 (22), 89 (25), 85 (30), 83 (31), 81 (20), 77 (39), 71 (32), 69 (36), 59 (20) and 58 (86). HRMS: Calcd for $C_{22}H_{12}Br_2O_3$ (M^+): 483.9134. Found: 483.9138.

3,4-Dihydro-4,7-dimethyl-2H,5H-pyrano[4,3-*b*]pyran-2,5-dione (12a):

Colorless solid; mp = 128 °C; $[\alpha]_D^{25} = +15.60$ (98% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (19:1 v/v), 1 mL/min, t_r (major) = 19.1 min, t_r (minor) = 26.8 min, c 0.35, $CHCl_3$); IR (KBr) ν = 3086, 2966, 2932, 2878, 2677, 1798, 1709, 1655, 1628, 1597, 1551, 1447, 1408, 1377, 1327, 1300, 1277, 1238, 1177, 1123, 1080, 1038, 999, 968, 876, 837, 775 and 675 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 1.22 (3H, d, J = 7.2 Hz, 4- CH_3), 2.28 (3H, s, 7- CH_3), 2.73 (1H, dd, J_{gem} = 15.9 and J_{3-4} = 1.9 Hz, one of H-3), 2.83 (1H, dd, J_{gem} = 15.9 and J_{3-4} = 6.8 Hz, the other of H-3), 3.19-3.27 (1H, m, H-4), 5.93 (1H, br t, J = 0.5 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ = 19.02 (4- CH_3), 19.97 (7- CH_3), 24.96 (C-3), 35.73 (C-4), 98.83 (C-8), 105.28 (C-4a), 160.90, 162.65, 162.69, 165.20 (C-2, C-5, C-7a and C-8a); Mass (rel intensity, %) m/z 194 (46, M^+), 179 (63), 166 (62), 153 (12), 152 (14), 151 (85), 137 (40), 123 (14), 101 (18), 85 (18), 77 (11), 69 (10), 68 (11), 59 (22) and 58 (base peak). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85 %; H, 5.05 %.

5.19 %. Found: C, 61.73 %; H, 5.30 %.

3,4-Dihydro-4-(5-bromo-2-methoxy)-7-methyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione (12b):

Colorless solid; mp = 85 °C; $[\alpha]_D^{25} = -79.23$ (79% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 22.1 min, t_r (minor) = 31.0 min, c 0.13, CHCl₃); IR (KBr) ν = 3086, 2970, 2939, 2843, 1794, 1717, 1655, 1597, 1489, 1443, 1389, 1261, 1188, 1111, 1022, 991, 957, 806, 737 and 621 cm⁻¹; ¹H NMR (CDCl₃) δ = 2.27 (3H, s, 7-CH₃), 2.92 (1H, dd, J_{gem} = 16.9 and J_{3-4} = 1.7 Hz, one of H-3), 3.11 (1H, dd, J_{gem} = 16.9 and J_{3-4} = 8.9 Hz, the other of H-3), 3.72 (3H, s, OCH₃), 4.29 (1H, d, J_{4-3} = 8.9 Hz, H-4), 5.97 (1H, d, J = 0.5 Hz, H-8), 6.72 (1H, d, J = 8.7 Hz, Ar), and 7.31-7.35 (2H, m, Ar); ¹³C NMR (CDCl₃) δ = 20.06 (7-CH₃), 33.21, 33.92 (C-2 and C-3), 54.62 (OCH₃), 98.88 (C-8), 100.29 (C-4a), 112.39, 112.95, 116.06 (each of CH, Ar), 129.54, 131.76, 132.59 (each of qC, Ar), 156.13, 161.61, 163.18, 164.22 (C-2, C-5, C-7a and C-8a); Mass (rel intensity, %) m/z 367 (17), 366 (99), 365 (18), 364 (base peak, M⁺), 338 (60), 337 (13), 336 (63), 323 (15), 321 (15), 308 (14), 307 (81), 306 (14), 305 (81), 293 (36), 291 (29), 285 (13), 257 (13), 239 (10), 211 (19), 209 (18), 179 (12), 173 (14), 153 (19), 151 (28), 149 (20), 137 (10), 136 (14), 131 (13), 118 (14), 115 (14), 107 (15), 106 (12), 105 (11), 102 (15), 89 (23), 85 (21), 77 (25), 69 (16) and 58 (25). HRMS: Calcd for C₁₆H₁₃BrO₅ (M⁺): 363.9946. Found: 363.9946.

3,4-Dihydro-4-(3,5-dibromophenyl)-7-methyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione (12c):

Colorless solid; mp = 153 °C; $[\alpha]_D^{25} = +30.63$ (97% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 15.9 min, t_r (minor) = 21.3 min, c 0.33, CHCl₃); IR (KBr) ν = 3078, 2932, 2638, 1798, 1713, 1674, 1582, 1555, 1447, 1408, 1288, 1246, 1184, 1103, 1038, 995, 957, 911, 860, 818, 775, 741 and 687 cm⁻¹; ¹H NMR (CDCl₃) δ = 2.32 (3H, d, J = 0.5 Hz, 7-CH₃), 3.01 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 1.9 Hz, one of H-3), 3.11 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 7.7 Hz, the other of H-3), 4.30 (1H, dd, J = 7.7 and J = 1.9 Hz, H-4), 6.04 (1H, d, J = 0.5 Hz, H-8), 7.25 (2H, d, J = 0.5 and J = 1.7 Hz, Ar), and 7.58 (1H, t, J = 1.7 Hz, Ar); ¹³C NMR (CDCl₃) δ = 20.19 (7-CH₃), 34.67, 35.68 (C-3 and C-4), 98.85 (C-8), 101.61 (C-4a), 123.69, 128.50 (each of CH, Ar), 133.76, 143.36 (each of qC, Ar), 162.20, 162.26, 163.60, 164.31 (C-2, C-5, C-7a and C-8a); Mass (rel intensity, %) m/z 415 (32), 414 (11), 413 (65, M⁺), 411 (33), 387 (57), 386 (base peak), 385 (15), 384 (58), 342 (14), 259 (10), 193 (11), 179 (35), 151 (16), 137 (18), 113 (12), 85 (34) and 69 (11); HRMS: Calcd for C₁₅H₁₀Br₂O₄ (M⁺): 413.8926. Found: 413.8930.

4-Methyl-3,4,5,6-tetrahydronaphtho[1,2-*b*]pyran-2(*H*),5-dione (13a):

Colorless solid; mp = 115 °C; $[\alpha]_D^{25} = -55.00$ (93% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 13.5 min, t_r (minor) = 16.7 min, c 0.32, CHCl₃); IR (KBr) $\nu = 2970, 2839, 1778, 1713, 1647, 1628, 1574, 1493, 1454, 1385, 1366, 1327, 1234, 1142, 1111, 1084, 1042, 907, 876, 760, \text{ and } 640 \text{ cm}^{-1}$; ¹H NMR (CDCl₃) $\delta = 1.31$ (3H, d, $J = 7.0$ Hz, 4-CH₃), 2.84 (1H, dd, $J_{\text{gem}} = 15.9$ and $J_{3-4} = 1.7$ Hz, one of H-3), 2.95 (1H, dd, $J_{\text{gem}} = 15.9$ and $J_{3-4} = 7.0$ Hz, the other of H-3), 3.37 - 3.44 (1H, m, H-4), 7.33 - 7.39 (2H, m, Ar), 7.58 - 7.63 (1H, m, Ar), and 7.85 (1H, dd, $J = 7.9$ and 1.7 Hz, Ar); ¹³C NMR (CDCl₃) $\delta = 19.19$ (4-CH₃), 25.70 (C-4), 35.70 (C-3), 108.41 (C-4a), 113.67, 116.82, 122.57, 124.58, 132.62, 152.93 (each Ar), 156.47 (C-10b), 160.92, 164.82 (C-2 and C-5); Mass (rel intensity, %) m/z 231 (12, M⁺ + 1), 155 (26), 139 (11), 138 (29), and 137 (59). Anal. Calcd for C₁₃H₁₀O₄: C, 67.82 %; H, 4.38 %. Found: C, 67.76 %; H, 4.52 %.

4-Phenyl-3,4,5,6-tetrahydronaphtho[1,2-b]pyran-2(H),5-dione (13b):

Colorless solid; mp = 130 °C; $[\alpha]_D^{25} = -164.86$ (91% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 21.3 min, t_r (minor) = 31.0 min, c 0.33, CHCl₃); IR (KBr) $\nu = 3082, 3063, 3028, 2932, 1782, 1728, 1651, 1609, 1578, 1493, 1454, 1381, 1331, 1273, 1246, 1211, 1180, 1161, 1134, 1107, 1061, 1034, 999, 949, 907, 872, 833, 760, 702, \text{ and } 660 \text{ cm}^{-1}$; ¹H NMR (CDCl₃) $\delta = 3.12$ (1H, dd, $J_{\text{gem}} = 16.2$ and $J_{3-4} = 1.9$ Hz, one of H-3), 3.21 (1H, dd, $J_{\text{gem}} = 16.2$ and $J_{3-4} = 7.5$ Hz, the other of H-3), 4.52 (1H, dd, $J = 7.5$ and 1.9 Hz, H-4), 7.23 - 7.37 (7H, m, Ar), 7.57 - 7.61 (1H, m, Ar), and 7.88 (1H, dd, $J = 8.2$ and 1.5 Hz, Ar); ¹³C NMR (CDCl₃) $\delta = 35.77, 35.85$ (C-3 and C-4), 106.22 (C-4a), 113.40, 116.74, 122.66, 124.54, 126.52, 127.88, 129.17 (each of CH, Ar), 132.80, 139.29, 153.01 (each qC, Ar), 157.10 (C-10b), 160.61, 164.19 (C-2 and C-5); Mass (rel intensity, %) m/z 292 (48, M⁺), 265 (14), 264 (73), 263 (31), 249 (29), 153 (12), 149 (26), 144 (13), 121 (21), 89 (11), 77 (18), 59 (12), and 58 (base peak). Anal. Calcd for C₁₈H₁₂O₄: C, 73.97 %; H, 4.14 %. Found: C, 74.11 %; H, 4.12 %.

4-(4-Bromophenyl)-3,4,5,6-tetrahydronaphtho[1,2-b]pyran-2(H),5-dione (13c):

Colorless solid; mp = 149 °C; $[\alpha]_D^{25} = -110.98$ (93% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 28.5 min, t_r (minor) = 43.0 min, c 0.35,

CHCl₃); IR (KBr) ν = 3059, 2986, 2924, 1786, 1720, 1647, 1609, 1578, 1489, 1458, 1404, 1377, 1327, 1269, 1242, 1211, 1180, 1161, 1130, 1111, 1057, 988, 907, 829, 760, 637, and 606 cm⁻¹; ¹H NMR (CDCl₃) δ = 3.12 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 1.7 Hz, one of H-3), 3.23 (1H, dd, J_{gem} = 16.2 and J_{3-4} = 7.7 Hz, the other of H-3), 4.52 (1H, dd, J_{4-3} = 7.7 and 1.7 Hz, H-4), 7.14 - 7.17 (2H, m, Ar), 7.28 - 7.47 (4H, m, Ar), 7.62 - 7.67 (1H, m, Ar), and 7.92 (1H, dd, J = 7.9 and 1.7 Hz, Ar); ¹³C NMR (CDCl₃) δ = 35.42, 35.72 (C-3 and C-4), 105.76 (C-4a), 113.37, 116.95, 122.03, 124.76, 128.38, 132.39 (each of CH, Ar), 133.13, 138.34, 153.18 (each q-C of Ar), 157.38 (C-10b), 160.63, 163.88 (C-2 and C-5); Mass (rel intensity, %) m/z 372 (60), 370 (60, M⁺), 345 (18), 344 (99), 343 (36), 342 (base peak), 341 (18), 329 (17), 327 (18), 263 (38), 249 (26), 187 (11), 121 (48), 120 (16), 115 (13), and 92 (22); Anal. Calcd for C₁₈H₁₁BrO₄: C, 58.24 %; H, 2.99 %. Found: C, 58.22 %; H, 3.26 %.

4-(5-Bromo-2-methoxyphenyl)-3,4,5,6-tetrahydronaphtho[1,2-*b*]pyran-2(*H*),5-dione (13d):

Colorless plate (from di-*iso*-propyl ether / ethyl acetate); mp = 180 °C; $[\alpha]_D^{25}$ = -278.91 (84% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 21.3 min, t_r (minor) = 45.6 min, c 0.37, CHCl₃); IR (KBr) ν = 3414, 2939, 1790, 1717, 1639, 1609, 1578, 1489, 1458, 1404, 1377, 1327, 1285, 1246, 1223, 1169, 1138, 1111, 1061, 1026, 995, 941, 907, 810, 760, and 637 cm⁻¹; ¹H NMR (CDCl₃) δ = 3.02 (1H, dd, J_{3-4} = J_{gem} = 16.9 and 1.2 Hz, one of H-3), 3.14 (1H, dd, J_{3-4} = J_{gem} = 16.9 and 9.2 Hz, the other of H-3), 3.72 (3H, s, OCH₃), 4.45 (1H, br d, J_{4-3} = 9.2 Hz, H-4), 6.72 (1H, d, J = 6.7 Hz, Ar), 7.33 - 7.40 (4H, m, Ar), 7.59 - 7.63 (1H, m, Ar), and 7.95 (1H, dd, J = 7.9 and 1.4 Hz, Ar); ¹³C NMR (CDCl₃) δ = 33.83, 34.00 (C-3 and C-4), 54.66 (OCH₃), 103.19 (C-4a), 112.41, 113.01, 113.66, 116.82, 122.81, 124.53, 129.32, 131.92 (each Ar), 132.72, 132.87, 153.09, 156.17 (each q-C of Ar), 157.09 (C-10b), 160.72, 163.74 (C-2 and C-5); Mass (rel intensity, %) m/z 403 (21), 402 (98), 401 (21), 400 (base peak, M⁺), 375 (10), 374 (52), 373 (13), 372 (53), 359 (13), 357 (13), 344 (18), 343 (88), 342 (18), 341 (89), 329 (32), 327 (33), 293 (16), 211 (14), 209 (12), 187 (30), 173 (14), 139 (10), 131 (15), 121 (89), 120 (13), 118 (17), 115 (15), 103 (11), 102 (19), 101 (11), 93 (13), 92 (38), 89 (14), 88 (12), 77 (22), 76 (21), 75 (16), 65 (11), 64 (12), and 63 (15). Anal. Calcd for C₁₉H₁₃BrO₅ (M⁺): C, 56.88 %; H, 3.27 %. Found: C, 56.98 %; H, 3.24 %.

4-(3,5-Dibromophenyl)-3,4,5,6-tetrahydronaphtho[1,2-*b*]pyran-2(*H*),5-dione (13e):

Colorless solid; mp = 226 °C; $[\alpha]_D^{25}$ = -121.6 (98% ee estimated by chiral hplc analysis on Daicel Chiral Cell ADH, hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 18.3 min, t_r (minor) = 34.0 min, c 0.33, 1,4-dioxane); IR (KBr) ν = 3078, 2939, 1782, 1778, 1713, 1651, 1609, 1582, 1555, 1493, 1454, 1420, 1381,

1331, 1285, 1250, 1211, 1184, 1142, 1107, 1065, 1038, 1003, 907, 860, 768, 741, and 683 cm^{-1} ; ^1H NMR (CDCl_3) δ = 3.11 (1H, dd, J_{gem} = 16.2 and $J_{3,4}$ = 1.7 Hz, one of H-3), 3.23 (1H, dd, J_{gem} = 16.2 and $J_{3,4}$ = 7.7 Hz, the other of H-3), 4.47 (1H, dd, $J_{4,3}$ = 7.7 and 1.7 Hz, H-4), 7.31 (2H, dd, J = 1.7 and 0.5 Hz, Ar), 7.39-7.43 (2H, m, Ar), 7.59 (2H, t, J = 1.7 Hz, Ar), 7.64 - 7.69 (1H, m, Ar), and 7.93 (1H, dd, 8.2 and J = 1.5 Hz, *H*-Ar); ^{13}C NMR (CDCl_3) δ = 35.36, 35.63 (C-3 and C-4), 104.63 (C-4a), 113.20, 117.02, 122.97, 123.80, 124.86, 128.58 (each Ar), 133.41, 133.94, 143.08, 153.28 (each q-C of Ar), 157.89 (C-10b), 160.46, 163.22 (C-2 and C-5); Mass (rel intensity, %) m/z 452 (31), 451 (12), 450 (59, M^+), 448 (30), 423 (49), 422 (22), 421 (base peak), 420 (17), 419 (51), 343 (12), 341 (12), 329 (13), 327 (13), 215 (23), 187 (31), 153 (16), 149 (44), 136 (12), 121 (84), 120 (27), 107 (16), 106 (13), 105 (14), 101 (14), 97 (14), 95 (11), 93 (10), 92 (39), 91 (12), 89 (23), 85 (13), 83 (17), 78 (10), 77 (33), 71 (14), 69 (12), 59 (12), and 58 (53). Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{Br}_2\text{O}_4$: C, 48.03 %; H, 2.24 %. Found: C, 48.23 %; H, 2.25 %.

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