Supporting Information

Chiral 2,6-Bis(oxazolinyl)pyridine–Rare Earth Metal Complexes as Catalysts for Highly Enantioselective 1,3-Dipolar Cycloaddition Reactions of 2-Benzopyrylium-4-olates

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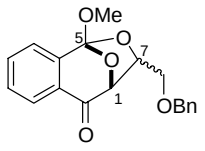
Experimental Section

General. Melting points are uncorrected. IR spectra were taken with FT/IR spectrophotometer. ^{1}H NMR spectra were run at 400 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded at 100 MHz using broadband proton decoupling. Chemical shifts are expressed in parts per million downfield from tetramethylsilane, using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard. High performance liquid chromatography was performed with chiral column shown below. For preparative column chromatography, Wakogel® C-300HG was employed. Medium-pressure liquid chromatography was carried out using a column packed with Wakogel® C-300HG. All reactions were carried out under an argon atmosphere in dried glassware.

Materials. *o*-(Methoxycarbonyl)-α-diazoacetophenone (**1**) and *o*-(isopropoxycarbonyl)-α-diazoacetophenone (**7**) was prepared by the procedure in the previous paper.[1] Benzyloxyacetaldehyde (**3a**) and its derivatives **3b** – **3f** were prepared according to the procedure in the literatures.[2] Benzyl pyruvate (**5b**) and its derivatives **5c** – **5g** and **5k** were prepared by the procedure in the literature.[3] 3-methyl-2-oxobutanoate **5h** and **5i** were prepared from 3-methyl-2-oxobutanoic acid sodium salt and corresponding benzyl bromide by the procedure in the literature.[2a] Benzyl glyoxylate (**5l**) and diethyl oxomalonate (**5m**) were prepared by the procedure in the literature.[4] 3-Acryloyl-2-oxazolidinone (**9**) was prepared according to the procedure in the literature.[5] Methyl pyruvate (**5a**), methyl benzoylformate (**5j**), $Rh_2(OAc)_4$, $Sc(OTf)_3$ and lanthanide triflates were commercially available, and used without further purification. 2,6-Bis(oxazolinyl)pyridines (Pybox) were prepared by the procedure in the literatures.[6] Powdered 4Å molecular sieves was commercially available and dried by *in vacuo* at 250 °C for 12 h before use. CH_2Cl_2 was purified by distillation first from $CaCl_2$ and then CaH_2 under argon. THF was freshly distilled from a sodium benzophenone still under argon.

General Procedure for the Reaction of α-Diazoacetophenone 1 with Benzyloxyacetaldehyde (3a) or Its Derivatives 3b – 3f: A solution of 2,6-bis[(4*S*)-(–)-4-isopropyl-2-oxazolin-2-yl]pyridine ((*S*,*S*)-Pybox-*i*-Pr, 15.1 mg, 0.05 mmol) in CH_2Cl_2 (1.5 mL) was added to a suspension of $Sc(OTf)_3$ (24.6 mg, 0.05 mmol) and powdered 4Å molecular sieves (MS 4A, 0.50 g) in CH_2Cl_2 (1 mL). After stirring the mixture for 2 h, a solution of benzyloxyacetaldehyde (**3a**) or its derivatives (1.0 mmol) in CH_2Cl_2 (2.5 mL) and $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol) were successively added. The mixture was cooled to –10 °C, and then a solution of diazoacetophenone **1** (102.1 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added over a period of 1 h. After removal of MS 4A through celite, the reaction mixture was filtered through a plug of silica gel (3 cm) with AcOEt/hexane (1:1, 80 mL) as an eluent. The solvent was removed *in vacuo* to give the mixture, which was purified by medium pressure liquid chromatography (MPLC) (silica gel, 1:99 – 5:95 AcOEt/hexane).

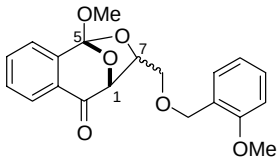
7-*Exo*-(benzyloxy)methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-4a) and 7-*Endo*-(benzyloxy)methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-4a).



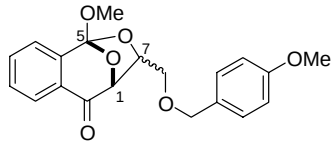
Benzyloxyaectaldehyde (**3a**, 150.2 mg, 140 μL, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 AcOEt/hexane) gave 18.7 mg (11%) of *exo*-**4a** and 139.2 mg (85%) of *endo*-**4a**. ***Exo*-4a**: Colorless oil; IR (Neat) 2953, 2858, 1709, 1603, 1458, 1296, 1258, 1215, 1161, 1084, 1046, 951, 764, 748, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.65 (3H, s), 3.69 (1H, dd, *J* = 6.6, 9.7 Hz), 3.75 (1H, dd, *J* = 5.6, 9.7 Hz), 4.04 (1H, dd, *J* = 5.6, 6.6 Hz), 4.62 (2H, s), 4.82 (1H, s), 7.28 – 7.40 (5H, m), 7.45 – 7.53 (1H, m), 7.61 – 7.67 (2H, m), 8.00 (1H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ =

49.7, 69.9, 72.8, 73.5, 81.4, 118.6, 122.6, 126.6, 127.7, 127.9, 128.2, 128.5, 129.3, 134.6, 137.6, 142.5, 192.9; MS (EI) m/z = 327 (M^++1), 296, 205, 163, 133, 105, 65, 37; HRMS (EI) Found: 326.1126. Calcd for $C_{19}H_{18}O_5$ (M^+): 326.1153; R_f = 0.42 (2:3 AcOEt/hexane). ***Endo*-4a**: Colorless prisms (ether–hexane); mp = 67 – 69 °C; $[\alpha]_D^{26}$ = –102 ^{o} (*c* 0.96, $CHCl_3$); IR (KBr) 2957, 2895, 1711, 1603, 1456, 1379, 1318, 1287, 1248, 1217, 1157, 1090, 1049, 1026, 1007, 976, 947, 889, 752, 704, 594 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.30 (1H, dd, *J* = 6.3, 10.7 Hz), 3.46 (1H, dd, *J* = 4.1, 10.7 Hz), 3.68 (3H, s), 4.32 (1H, d, *J* = 12.0 Hz), 4.42 (1H, d, *J* = 12.0 Hz), 4.60 – 4.65 (1H, m), 4.96 (1H, d, *J* = 5.6 Hz), 7.18 – 7.30 (5H, m), 7.41 – 7.44 (1H, m), 7.57 – 7.66 (2H, m), 7.92 (1H, d, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.6, 68.0, 73.5, 74.8, 81.7, 118.1, 122.6, 126.2, 127.7, 127.8, 128.3, 129.1, 129.3, 134.3, 137.3, 143.7, 192.4; HRMS (EI) Found: 326.1163. Calcd for $C_{19}H_{18}O_5$ (M^+): 326.1153. R_f = 0.35 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 13.7 min (minor) and 16.7 min (major). *Endo*-isomer: t_R = 12.3 min (minor) and 13.6 min (major).

5-Methoxy-7-*exo*-[(*o*-methoxybenzyl)oxy]methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-4b) and 5-Methoxy-7-*endo*-[(*o*-methoxybenzyl)oxy]methyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*endo*-4b). [(*o*-Methoxybenzyl)oxy]aectaldehyde (**3b**, 164.2 mg, 1.0 mmol) was used according to the general procedure. The reaction mixture was quenched by addition of NEt_3 (1.0 mL) and stirred for additional 1 h. Purification by MPLC (5:95 AcOEt/hexane) gave 21.4 mg (12%) of *exo*-**4b** and 124.6 mg (70%) of *endo*-**4b**. ***Exo*-4b**: Colorless prisms (ether–hexane); mp = 76 – 78.5 ^{o}C; IR (KBr) 3073, 3034, 3009, 2961, 2942, 2909, 2890, 2876, 2839, 1711, 1603, 1591, 1499, 1483, 1466, 1441, 1410, 1373, 1290, 1273, 1253, 1213, 1159, 1140, 1105, 1088, 1061, 1049, 1020, 966, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.66 (3H, s), 3.74 (1H, dd, *J* = 6.9, 9.9 Hz), 3.81 (1H, dd, *J* = 5.4, 9.9 Hz), 3.84 (3H, s), 4.06 (1H, dd, *J* = 5.4, 6.9 Hz), 4.66 (2H, s), 4.85 (1H, s), 6.87 – 6.98 (2H, m), 7.26 – 7.39 (2H, m), 7.46 – 7.50 (1H, m), 7.61 – 7.63 (2H, m), 8.00 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 357 (M^++1), 327, 298, 205, 163, 121, 91, 65, 27; HRMS (EI) Found: 356.1254. Calcd for $C_{20}H_{20}O_6$ (M^+): 356.1259; R_f = 0.51 (3:7 AcOEt/hexane). ***Endo*-4b**: Colorless prisms (ether–hexane); mp = 97.5 – 99.5 °C; $[\alpha]_D^{26}$ = –92 ^{o} (*c* 0.96, $CHCl_3$); IR (KBr) 3002, 2959, 2926, 2895, 2870, 2843, 1705, 1603, 1495, 1462, 1441, 1373, 1314, 1294, 1244, 1227, 1159, 1136, 1190, 1076, 1051, 1028, 974, 953, 943 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.32 (1H, dd, *J* = 6.8, 10.9 Hz), 3.49 (1H, dd, *J* = 4.1, 10.9 Hz), 3.68 (3H, s), 3.76 (3H, s), 4.40 (1H, d, *J* = 12.6 Hz), 4.48 (1H, d, *J* = 12.6 Hz), 4.63 – 4.67 (1H, m), 4.97 (1H, d, *J* = 5.6 Hz), 6.80 – 6.89 (2H, m), 7.16 – 7.24 (2H, m), 7.42 – 7.46 (1H, m), 7.58 – 7.66 (2H, m), 7.93 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 356 (M^+), 339, 324, 308, 221, 205, 177, 163, 149, 138, 121, 105, 91, 77, 56, 41, 27, 17; HRMS (EI) Found: 356.1249. Calcd for $C_{20}H_{20}O_6$ (M^+): 356.1259; R_f = 0.45 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 13.2 min (minor) and 15.0 min (major). *Endo*-isomer: t_R = 13.7 min (minor) and 16.3 min (major).

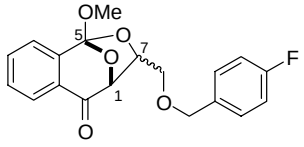


5-Methoxy-7-*exo*-[(*p*-methoxybenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*exo*-4c) and 5-Methoxy-7-*endo*-[(*p*-methoxybenzyl)oxy]methyl-6,8-dioxabenzo-[*c*]bicyclo[3.2.1]octan-2-one (*endo*-4c). [(*p*-Methoxybenzyl)oxy]aectaldehyde (**3c**, 164.2 mg, 1.0 mmol) was used according to the general procedure. The reaction mixture was quenched by addition of NEt_3 (1.0 mL) and stirred for additional 1 h. Purification by MPLC (5:95 AcOEt/hexane) gave 8.6 mg



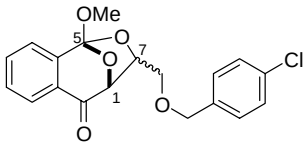
(5%) of *exo*-**4c** and 85.5 mg (48%) of *endo*-**4c**. ***Exo*-4c**: Colorless oil; IR (Neat) 2955, 2859, 1709, 1607, 1514, 1460, 1294, 1254, 1215, 1161, 1101, 1084, 1065, 1032, 951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.64 (3H, s), 3.65 (1H, dd, *J* = 6.8, 9.8 Hz), 3.72 (1H, dd, *J* = 5.5, 9.8 Hz), 3.81 (3H, s), 4.02 (1H, dd, *J* = 5.5, 6.8 Hz), 4.55 (2H, s), 4.80 (1H, s), 6.89 (2H, d, *J* = 8.3 Hz), 7.27 (2H, d, *J* = 8.3 Hz), 7.46 – 7.50 (1H, m), 7.61 – 7.63 (2H, m), 7.99 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 356 (M^+), 205, 163, 135, 105, 84, 55, 35, 14; HRMS (EI) Found: 356.1228. Calcd for $C_{20}H_{20}O_6$ (M^+): 356.1259; R_f = 0.48 (3:7 AcOEt/hexane). ***Endo*-4c**: Colorless prisms (ether–hexane); mp = 75 – 77 °C; $[\alpha]_D^{26}$ = –80 ^{o} (*c* 1.02, $CHCl_3$); IR (KBr) 3034, 2994, 2955, 2924, 2863, 2849, 2834, 2807, 1705, 1605, 1588, 1512, 1468, 1458, 1441, 1414, 1372, 1314, 1294, 1244, 1223, 1171, 1155, 1127, 1103, 1076, 1057, 1034, 1013, 976, 951, 889, 841, 816 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.26 (1H, dd, *J* = 6.6, 10.7 Hz), 3.41 (1H, dd, *J* = 4.4, 10.7 Hz), 3.68 (3H, s), 3.78 (3H, s), 4.25 (1H, d, *J* = 11.5 Hz), 4.36 (1H, d, *J* = 11.5 Hz), 4.59 – 4.63 (1H, m), 4.95 (1H, d, *J* = 5.6 Hz), 6.81 (2H, d, *J* = 8.3 Hz), 7.13 (2H, d, *J* = 8.3 Hz), 7.42 – 7.45 (1H, m), 7.58 – 7.66 (2H, m), 7.93 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 371 (M^++1), 358, 338, 320, 306, 279, 263, 253, 235, 221, 205, 188, 175, 164, 149, 136, 122, 105, 89, 78, 65, 52, 39, 28; HRMS (EI) Found: 356.1246. Calcd for $C_{20}H_{20}O_6$ (M^+): 356.1259; R_f = 0.42 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 27.9 min (major) and 42.5 min (minor). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 24.5 min (minor) and 27.5 min (major).

7-*Exo*-[(*p*-fluorobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-4d) and 7-*Endo*-[(*p*-fluorobenzyl)oxy]-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-4d). [(*p*-Fluorobenzyl)oxy]aectaldehyde (**3d**, 168.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (5:95 AcOEt/hexane) gave 29.4 mg (17%) of *exo*-**4d** and 139.2 mg (80%) of *endo*-**4d**. ***Exo*-4d**: Colorless oil; IR (Neat) 2955, 2863, 1711, 1603, 1510, 1460, 1294, 1260, 1223, 1159, 1084, 1065, 1046, 1028, 951, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.65 (3H, s), 3.69 (1H, dd, *J* = 6.6, 9.6 Hz), 3.74 (1H, dd, *J* = 5.6, 9.6 Hz), 4.03 (1H, dd, *J* = 5.6, 6.6 Hz), 4.58 (2H, s), 4.81 (1H, s), 6.99 – 7.07 (2H, m), 7.21 – 7.34 (2H, m), 7.47 – 7.51 (1H, m), 7.62 – 7.66 (2H, m), 8.00 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 345 (M^++1), 314, 294, 267, 239, 206, 164, 133, 109, 83, 57, 28; HRMS (EI) Found: 344.1076. Calcd for $C_{19}H_{17}FO_5$ (M^+): 344.1059; R_f = 0.46 (3:7 AcOEt/hexane). ***Endo*-4d**: Colorless needles (ether–hexane); mp = 112 – 114 °C; $[\alpha]_D^{26}$ = –98 ^{o} (*c* 1.00, $CHCl_3$); IR (KBr) 2963, 2919, 2897, 2857, 1709, 1603, 1512, 1460, 1447, 1379, 1318, 1292, 1248, 1223, 1155, 1132, 1092, 1073, 1049, 1026, 1007, 974, 947, 891, 858, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.31 (1H, dd, *J* = 6.3, 10.7 Hz), 3.46 (1H, dd, *J* = 4.4, 10.7 Hz), 3.68 (3H, s), 4.28 (1H, d, *J* = 11.7 Hz), 4.36 (1H, d, *J* = 11.7 Hz), 4.62 (1H, m), 4.96 (1H, d, *J* = 5.6 Hz), 6.93 – 6.97 (2H, m), 7.13 – 7.17 (2H, m), 7.41 – 7.45 (1H, m), 7.58 – 7.66 (2H, m), 7.90 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 345 (M^++1), 314, 294, 267, 239, 202, 177, 133, 105, 75, 50, 14; HRMS (EI) Found: 344.1068. Calcd for $C_{19}H_{17}FO_5$ (M^+): 344.1059; R_f = 0.39 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 20.1 min (minor) and 25.1 min (major). *Endo*-isomer (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 14.2 min (minor) and 16.1 min (major).

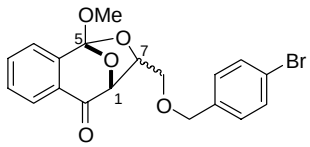


Supporting Information

7-*Exo*-[(*p*-chlorobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-4e) and 7-*Endo*-[(*p*-chlorobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]-octan-2-one (*endo*-4e). [(*p*-Chlorobenzyl)oxy]acetaldehyde (**3e**, 184.6 mg, 1.0 mmol) was used according to the general procedure. The reaction mixture was quenched by addition of NEt_3 (1.0 mL) and stirred for additional 1 h. Purification by MPLC (5:95 AcOEt/hexane) gave 40.7 mg (23%) of *exo*-**4e** and 111.5 mg (62%) of *endo*-**4e**. ***Exo*-4e**: Colorless oil; IR (Neat) 2953, 2863, 1711, 1603, 1493, 1460, 1296, 1260, 1217, 1161, 1088, 1065, 1047, 1026, 951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.65 (3H, s), 3.69 (1H, dd, *J* = 6.6, 9.8 Hz), 3.74 (1H, dd, *J* = 5.6, 9.8 Hz), 4.04 (1H, dd, *J* = 5.6, 6.6 Hz), 4.58 (2H, s), 4.81 (1H, s), 7.28 (2H, d, *J* = 8.2 Hz), 7.33 (2H, d, *J* = 8.2 Hz), 7.47 – 7.51 (1H, m), 7.62 – 7.63 (2H, m), 8.00 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 361 (M^++1), 330, 310, 275, 247, 205, 177, 139, 111, 75, 50, 28; HRMS (EI) Found: 360.0782. Calcd for $C_{19}H_{17}ClO_5$ (M^+): 360.0763; R_f = 0.59 (3 : 7 AcOEt/hexane). ***Endo*-4e**: Colorless needles (ether–hexane); mp = 103 – 106 °C; $[\alpha]_D^{26}$ = –77 ° (*c* 1.00, $CHCl_3$); IR (KBr) 2957, 2897, 2855, 1709, 1601, 1495, 1476, 1458, 1408, 1381, 1316, 1292, 1248, 1219, 1155, 1134, 1090, 1073, 1049, 1017, 974, 945, 891 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.31 (1H, dd, *J* = 6.3, 10.7 Hz), 3.46 (1H, dd, *J* = 4.4, 10.7 Hz), 3.68 (3H, s), 4.28 (1H, d, *J* = 12.0 Hz), 4.36 (1H, d, *J* = 12.0 Hz), 4.59 – 4.64 (1H, m), 4.96 (1H, d, *J* = 5.6 Hz), 7.10 (2H, d, *J* = 8.3 Hz), 7.23 (2H, d, *J* = 8.3 Hz), 7.40 – 7.44 (1H, m), 7.58 – 7.66 (2H, m), 7.90 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 361 (M^++1), 330, 310, 275, 255, 220, 188, 164, 127, 90, 63, 39, 14; HRMS (EI) Found: 360.0766. Calcd for $C_{19}H_{17}ClO_5$ (M^+): 360.0763; R_f = 0.53 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 15.9 min (minor) and 18.8 min (major). *Endo*-isomer: t_R = 13.7 min (minor) and 15.7 min (major).



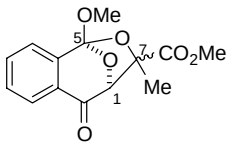
7-*Exo*-[(*p*-bromobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-4f) and 7-*Endo*-[(*p*-bromobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]-octan-2-one (*endo*-4f). [(*p*-Bromobenzyl)oxy]acetaldehyde (**3f**, 229.1 mg, 1.0 mmol) was used according to the general procedure. The reaction mixture was quenched by addition of NEt_3 (1.0 mL) and stirred for additional 1 h. Purification by MPLC (5:95 AcOEt/hexane) gave 56.8 mg (28%) of *exo*-**4f** and 98.0 mg (49%) of *endo*-**4f**. ***Exo*-4f**: Colorless oil; IR (Neat) 2953, 2859, 1713, 1603, 1487, 1460, 1294, 1260, 1217, 1161, 1084, 1046, 951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.65 (3H, s), 3.69 (1H, dd, *J* = 6.6, 9.8 Hz), 3.74 (1H, dd, *J* = 5.6, 9.8 Hz), 4.03 (1H, dd, *J* = 5.6, 6.6 Hz), 4.57 (2H, s), 4.81 (1H, s), 7.23 (2H, d, *J* = 8.0 Hz), 7.48 – 7.50 (3H, m), 7.62 – 7.63 (2H, m), 8.00 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 406 (M^++2), 388, 374, 356, 344, 329, 315, 301, 220, 205, 188, 177, 163, 133, 120, 105, 90, 77, 63, 50, 39, 26, 14; HRMS (EI) Found: 404.0276. Calcd for $C_{19}H_{17}BrO_5$ (M^+): 404.0259; R_f = 0.42 (3:7 AcOEt/hexane). ***Endo*-4f**: Colorless needles (ether–hexane); mp = 83 – 86 °C; $[\alpha]_D^{26}$ = –58 ° (*c* 1.01, $CHCl_3$); IR (KBr) 2955, 2895, 1709, 1599, 1489, 1458, 1402, 1379, 1314, 1290, 1248, 1217, 1155, 1134, 1090, 1073, 1049, 1024, 1012, 974, 945, 891, 839, 806 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.31 (1H, dd, *J* = 6.3, 10.7 Hz), 3.46 (1H, dd, *J* = 4.4, 10.7 Hz), 3.68 (3H, s), 4.26 (1H, d, *J* = 12.0 Hz), 4.35 (1H, d, *J* = 12.0 Hz), 4.60 – 4.64 (1H, m), 4.96 (1H, d, *J* = 5.6 Hz), 7.04 (2H, d, *J* = 8.3 Hz), 7.39 (2H, d, *J* = 8.3 Hz), 7.41 – 7.45 (1H, m), 7.58 – 7.66 (2H, m), 7.90 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 406 (M^++2), 374, 356, 329, 301, 275, 247, 220, 205, 188, 169, 157, 146, 133, 119, 105, 89, 76, 63, 50, 39, 27, 14; HRMS (EI) Found: 404.0280. Calcd for $C_{19}H_{17}BrO_5$ (M^+): 404.0259; R_f = 0.38 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane,



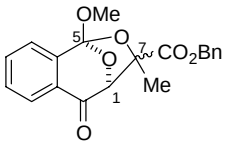
Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 17.3 min (minor) and 21.4 min (major). *Endo*-isomer: t_R = 14.6 min (minor) and 17.2 min (major).

General Procedure for the Reaction of α-Diazoacetophenone 1 with α-Keto Ester Derivatives 5a – 5l: A solution of 2,6-bis[(4*S*)-(–)-4-isopropyl-2-oxazolin-2-yl]pyridine ((*S*,*S*)-Pybox-*i*-Pr, 15.1 mg, 0.05 mmol) in CH_2Cl_2 (1.5 mL) was added to a suspension of $Sc(OTf)_3$ (24.6 mg, 0.05 mmol) and powdered 4Å molecular sieves (MS 4A, 0.50 g) in CH_2Cl_2 (1 mL). After stirring the mixture for 2 h, a solution of α-keto ester (1.0 mmol) in CH_2Cl_2 (2.5 mL), $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol) and trifluoroacetic acid (1M solution in CH_2Cl_2, 50 mL, 0.05 mmol) were successively added. The mixture was cooled to –25 °C, and then a solution of diazoacetophenone **1** (102.1 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added over a period of 1 h. After removal of MS 4A through celite, the reaction mixture was filtered through a plug of silica gel (3 cm) with AcOEt/hexane (1:1, 80 mL) as an eluent. The solvent was removed *in vacuo* to give the mixture, which was purified by medium pressure liquid chromatography (MPLC) (silica gel, 1:99 – 5:95 AcOEt/hexane).

5-Methoxy-7-*exo*-methoxycarbonyl-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6a) and 5-Methoxy-7-*endo*-methoxycarbonyl-7-*exo*-methyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*endo*-6a). Methyl pyruvate (**5a**, 102.1 mg, 90 μL, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 129.6 mg (94%) of *exo*-**6a** and 5.2 mg (4%) of *endo*-**6a**. ***Exo*-6a**: Colorless prisms (ether–hexane); mp = 84 – 86 °C; $[\alpha]_D^{23}$ = –133 ° (*c* 0.98, $CHCl_3$); IR (KBr) 3015, 2996, 2963, 1755, 1703, 1601, 1458, 1443, 1377, 1319, 1300, 1283, 1231, 1184, 1146, 1119, 1094, 1076, 1047, 1026, 976, 945, 909 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.31 (3H, s), 3.74 (3H, s), 3.87 (3H, s), 5.22 (1H, s), 7.48 – 7.53 (1H, m), 7.62 – 7.68 (2H, m), 8.00 (1H, d, *J* = 7.6 Hz); MS (EI) m/z = 279 (M^++1), 220, 191, 177, 163, 133, 104, 92, 76, 59, 50, 43, 38, 27, 14; Found: C, 60.40; H, 5.04%. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07%. R_f = 0.55 (3:7 AcOEt/hexane). ***Endo*-6a**: Colorless prisms (ether–hexane); mp = 60 – 62 °C; IR (KBr) 3007, 2961, 1752, 1705, 1603, 1464, 1453, 1312, 1279, 1254, 1194, 1132, 1090, 1073, 1055, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.84 (3H, s), 3.55 (3H, s), 3.73 (3H, s), 4.74 (1H, s), 7.46 – 7.50 (1H, m), 7.61 – 7.68 (2H, m), 7.92 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 279 (M^++1), 219, 177, 163, 133, 104, 76, 50, 43, 29, 14; Found: C, 60.58; H, 5.04%. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07%. R_f = 0.45 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 10.7 min (minor) and 12.4 min (major). *Endo*-isomer: t_R = 13.1 min (minor) and 17.2 min (major).



7-*Exo*-(benzyloxy)carbonyl-5-methoxy-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]-octan-2-one (*exo*-6b) and 7-*Endo*-(benzyloxy)carbonyl-5-methoxy-7-*exo*-methyl-6,8-dioxabenzo-[*c*]bicyclo [3.2.1]octan-2-one (*endo*-6b). Benzyl pyruvate (**5b**, 178.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 11.6 mg (7%) of *endo*-**6b** and 225.5 mg of a mixture of *exo*-**6b** and benzyl pyruvate (**5b**). The yield of *exo*-**6b** was calculated on the basis of ^1H NMR (162.0 mg, 92%). ***Exo*-6b**: Colorless oil; $[\alpha]_D^{28}$ = –115° (*c* 1.02, $CHCl_3$, 26wt% of **5b** was contained); IR (Neat) 3034, 2959, 1732, 1711, 1603, 1458, 1381,



1360, 1292, 1262, 1219, 1136, 1092, 1078, 1047, 1028 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.30 (3H, s), 3.62 (3H, s), 5.23 (1H, s), 5.24 (1H, d, *J* = 12.1 Hz), 5.33 (1H, d, *J* = 12.1 Hz), 7.36 – 7.40 (5H, m), 7.47 – 7.51 (1H, m), 7.60 – 7.66 (2H, m), 7.99 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.8, 50.4, 67.9, 79.2, 85.4, 118.9, 122.7, 126.4, 128.2, 128.5, 128.7, 128.8, 129.5, 134.8, 135.0, 143.2, 171.3, 191.5; MS (EI) m/z = 355 (M^++1), 339, 220, 177, 163, 133, 105, 91, 76, 65, 43; HRMS (EI) Found: 354.1072. Calcd for $C_{20}H_{18}O_6$ (M^+): 354.1102; R_f = 0.53 (3:7 AcOEt/hexane). ***Endo*-6b**: Colorless oil; IR (Neat) 3069, 3034, 2944, 2955, 1736, 1709, 1605, 1499, 1458, 1377, 1292, 1248, 1215, 1132, 1088, 1074, 1045, 951, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.84 (3H, s), 3.72 (3H, s), 4.74 (1H, s), 4.87 (1H, d, *J* = 12.2 Hz), 5.01 (1H, d, *J* = 12.2 Hz), 7.06 – 7.08 (2H, m), 7.25 – 7.29 (3H, m), 7.36 – 7.40 (1H, m), 7.57 – 7.66 (2H, m), 7.76 (1H, d, *J* = 7.8 Hz); MS (EI) m/z = 355 (M^++1), 339, 219, 177, 167, 133, 105, 92, 76, 65, 51, 39; HRMS (EI) Found: 354.1097. Calcd for $C_{20}H_{18}O_6$ (M^+): 354.1102; R_f = 0.44 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 17.0 min (minor) and 21.6 min (major). *Endo*-isomer (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 13.3 min (minor) and 17.6 min (major).

5-Methoxy-7-*exo*-[(4-methoxybenzyl)oxy]carbonyl-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6c) and 5-Methoxy-7-*endo*-[(4-methoxybenzyl)oxy]carbonyl-7-*exo*-methyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*endo*-6c). *p*-Methoxybenzyl pyruvate (**5c**, 208.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 7.9 mg (4%) of *endo*-cycloadduct and 220.8 mg of a mixture of *exo*-**6c** and pyruvate **5c**. The yield of *exo*-**6c** was calculated on the basis of ^1H NMR (192.6 mg, quant). ***Exo*-6c**: Colorless oil; $[\alpha]_D^{28}$ = –96° (*c* 0.97, $CHCl_3$, 16wt% of **5c** was contained); IR (Neat) 3002, 2957, 2839, 1734, 1709, 1610, 1588, 1516, 1460, 1379, 1289, 1254, 1219, 1177, 1115, 1092, 1078, 1047, 974, 949, 889, 849, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.29 (3H, s), 3.61 (3H, s), 3.82 (3H, s), 5.16 (1H, d, *J* = 11.8 Hz), 5.22 (1H, s), 5.27 (1H, d, *J* = 11.8 Hz), 6.88 – 6.92 (2H, m), 7.32 – 7.36 (2H, m), 7.47 – 7.51 (1H, m), 7.60 – 7.65 (2H, m), 7.97 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.9, 50.4, 55.3, 67.7, 79.2, 85.3, 113.9, 118.7, 122.6, 126.3, 127.0, 128.1, 129.3, 130.3, 134.6, 143.0, 159.7, 171.1, 191.2; MS (EI) m/z = 385 (M^++1), 219, 177, 163, 121, 77, 51, 43, 27, 14; HRMS (EI) Calcd for $C_{21}H_{20}O_7$ (M^+): 384.1208. Found: 384.1181; R_f = 0.58 (2:3 AcOEt/hexane). ***Endo*-6c**: Colorless oil; IR (Neat) 3011, 2940, 2843, 1753, 1698, 1603, 1586, 1514, 1454, 1383, 1248, 1140, 1086, 1061, 1030, 951, 924, 891, 806 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.82 (3H, s), 3.71 (3H, s), 3.81 (3H, s), 4.73 (1H, s), 4.80 (1H, d, *J* = 11.7 Hz), 4.96 (1H, d, *J* = 11.7 Hz), 6.78 – 6.82 (2H, m), 7.02 – 7.06 (2H, m), 7.37 – 7.41 (1H, m), 7.57 – 7.65 (2H, m), 7.75 – 7.77(1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.9, 49.9, 55.3, 67.5, 80.2, 86.2, 113.6, 119.5, 122.6, 126.0, 126.5, 128.5, 129.2, 130.1, 134.3, 141.7, 159.5, 169.2, 190.5; MS (EI) m/z = 385 (M^++1), 219, 177, 163, 133, 121, 105, 77, 51, 43, 27; Anal. Calcd for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24%. Found: C, 65.45; H, 5.51%; R_f = 0.48 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 24.1 min (minor) and 32.6 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 27.2 min (minor) and 51.0 min (major).

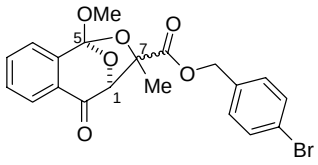
7-*Exo*-[(4-fluorobenzyl)oxy]carbonyl-5-methoxy-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*exo*-6d) and 7-*Endo*-[(4-fluorobenzyl)oxy]carbonyl-5-methoxy-7-*exo*-methyl-

6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6d). *p*-Fluorobenzyl pyruvate (**5d**, 196.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 6.2 mg (3%) of *endo*-**6d** and 204.7 mg of a mixture of *exo*-**6d** and pyruvate **5d**. The yield of *exo*-**6d** was calculated on the basis of ^{1}H NMR (165.6 mg, 89%). ***Exo*-6d**: Colorless oil; $[\alpha]_D^{28} = -100^o$ (*c* 1.07, $CHCl_3$, 7wt% of **5d** was contained); IR (Neat) 2998, 2959, 1730, 1711, 1605, 1512, 1460, 1381, 1290, 1260, 1223, 1157, 1117, 1092, 1078, 1047, 1028, 974, 949, 889, 851, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (3H, s), 3.61 (3H, s), 5.19 (1H, d, *J* = 12.0 Hz), 5.22 (1H, s), 5.30 (1H, d, *J* = 12.0 Hz), 7.05 – 7.09 (2H, m), 7.37 – 7.41 (2H, m), 7.48 – 7.52 (1H, m), 7.61 – 7.66 (2H, m), 7.98 – 8.00 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.9, 50.4, 67.1, 79.2, 85.3, 115.6 (d, $J_{C\text{-}F}$ = 21.7 Hz), 118.8, 122.6, 126.3, 128.0, 129.4, 130.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.7, 142.9, 162.6 (d, $J_{C\text{-}F}$ = 247.6 Hz), 171.0, 191.1; MS (EI) m/z = 373 (M^++1), 220, 191, 176, 163, 149, 134, 123, 105, 95, 89, 83, 77, 63, 57, 51, 44, 39, 29, 14; HRMS (EI) Calcd for $C_{20}H_{18}FO_6$ (M^++H): 373.1086. Found: 373.1064; R_f = 0.53 (2:3 AcOEt/hexane). ***Endo*-6d:** Colorless oil; IR (Neat) 3075, 2994, 2957, 1738, 1709, 1605, 1512, 1460, 1375, 1292, 1225, 1132, 1088, 1074, 1046, 951, 829 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83 (3H, s), 3.71 (3H, s), 4.74 (1H, s), 4.82 (1H, d, *J* = 12.1 Hz), 4.98 (1H, d, *J* = 12.1 Hz), 6.92 – 6.94 (2H, m), 7.03 – 7.07 (2H, m), 7.36 – 7.41 (1H, m), 7.57 – 7.65 (2H, m), 7.73 – 7.75 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.9, 49.9, 66.9, 80.1, 86.2, 115.2 (d, $J_{C\text{-}F}$ = 21.7 Hz), 119.6, 122.6, 125.9, 128.5, 129.2, 130.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 134.3, 141.7, 162.4 (d, $J_{C\text{-}F}$ = 245.0 Hz), 169.2, 190.5; MS (EI) m/z = 373 (M^++1), 220, 191, 176, 164, 149, 133, 120, 110, 105, 95, 89, 83, 77, 63, 57, 51, 44, 39, 29, 14; HRMS (EI) Calcd for $C_{20}H_{17}FO_6$ (M^+): 372.1008. Found: 372.1029; R_f = 0.47 (2:3 AcOEt/hexaen). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 19.0 min (minor) and 25.1 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 20.8 min (minor) and 36.6 min (major).

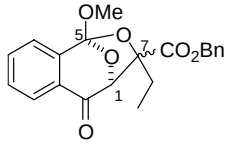
7-*Exo*-[(4-chlorobenzyl)oxy]carbonyl-5-methoxy-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*exo*-6e) and 7-*Endo*-[(4-chlorobenzyl)oxy]carbonyl-5-methoxy-7-*exo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6e). *p*-Chlorobenzyl pyruvate (**5e**, 212.6 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 5.9 mg (3%) of *endo*-**6e** and 217.2 mg of a mixture of *exo*-**6e** and pyruvate **5e**. The yield of *exo*-**6e** was calculated on the basis of ^{1}H NMR (179.9 mg, 92%). ***Exo*-6e**: Colorless needles (ether–hexane); mp 87 – 89 °C; $[\alpha]_D^{27} = -90^o$ (*c* 0.95, $CHCl_3$, 17wt% of **5e** was contained); IR (KBr) 3077, 3040, 3000, 2984, 2955, 2855, 1759, 1705, 1603, 1493, 1462, 1449, 1383, 1370, 1300, 1279, 1225, 1184, 1148, 1117, 1094, 1049, 1017, 976, 947, 885, 856, 839, 806 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (3H, m), 3.62 (3H, m), 5.20 (1H, d, *J* = 12.2 Hz), 5.21 (1H, s), 5.28 (1H, d, *J* = 12.2 Hz), 7.32 – 7.38 (4H, m), 7.48 – 7.52 (1H, m), 7.61 – 7.66 (2H, m), 7.98 – 8.00 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.9, 50.4, 67.0, 79.2, 85.3, 118.8, 122.6, 126.3, 128.0, 128.8, 129.4, 129.8, 133.3, 134.6, 134.7, 142.9, 171.0, 191.1; MS (EI) m/z = 389 (M^++1), 220, 191, 177, 163, 133, 125, 105, 89, 77, 63, 50, 43, 28, 14; HRMS (EI) Calcd for $C_{20}H_{18}ClO_6$ (M^++H): 389.0791. Found: 389.0783; Anal. Calcd for $C_{20}H_{17}ClO_6$: C, 61.78; H, 4.41%. Found: C, 61.86; H, 4.25%; R_f = 0.76 (2:3 AcOEt/hexane). ***Endo*-6e**: Colorless oil; IR (Neat) 3073, 2994, 2955, 2851, 1740, 1711, 1603, 1493, 1460, 1410, 1375, 1292, 1215, 1132, 1090, 1046, 951, 887, 835, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83 (3H, s), 3.71 (3H, s), 4.74 (1H, s), 4.82 (1H, d, *J* = 12.5 Hz), 4.97 (1H, d, *J* = 12.5 Hz), 6.97 – 6.99 (2H, m), 7.21 – 7.23 (2H, m), 7.35 – 7.41 (1H, m), 7.58 – 7.65 (2H, m), 7.72 – 7.74 (1H, m); ^{13}C

NMR (100 MHz, $CDCl_3$) 23.9, 49.9, 66.8, 80.1, 86.2, 119.6, 122.6, 125.9, 128.4, 129.3, 129.6, 132.7, 134.1, 134.3, 141.7, 169.1, 190.5; MS (EI) m/z = 389 (M^++1), 220, 191, 177, 164, 133, 127, 105, 99, 89, 77, 63, 51, 43, 29, 14; HRMS (EI) Calcd for $C_{20}H_{17}ClO_6$ (M^+): 388.0713. Found: 388.0742; Anal. Calcd for $C_{20}H_{17}ClO_6$: C, 61.78; H, 4.41%. Found: C, 61.69; H, 4.49%; R_f = 0.70 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 21.5 min (minor) and 28.1 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 21.8 min (minor) and 43.2 min (major).

(1*S*,5*S*,7*S*)-7-[(4-Bromobenzyl)oxy]carbonyl-5-methoxy-7-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6f) and 7-*Endo*-[(4-bromobenzyl)oxy]carbonyl-5-methoxy-7-*exo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6f). *p*-Bromobenzyl pyruvate (**5f**, 257.1 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (2:98 – 5:95 AcOEt/hexane) gave 7.2 mg (3%) of *endo*-**6f** and 249.7 mg of a mixture of *exo*-**6f** and pyruvate **5f**. The yield of *exo*-**6f** was calculated on the basis of ^{1}H NMR (193.8 mg, 89%). ***Exo*-6f**: Colorless needles (CH_2Cl_2–hexane); mp 89 – 90 °C; $[\alpha]_D^{29}$ –87° (*c* 1.04, $CHCl_3$, 22 wt% of **5f** was contained); IR (KBr) 2955, 1759, 1705, 1603, 1489, 1462, 1449, 1383, 1300, 1279, 1254, 1223, 1184, 1146, 1115, 1094, 1076, 1049, 1013, 976, 945, 885, 858, 837, 804 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (3H, s), 3.63 (3H, s), 5.18 (1H, d, *J* = 12.2 Hz), 5.21 (1H, s), 5.26 (1H, d, *J* = 12.2 Hz), 7.26 – 7.29 (2H, m), 7.48 – 7.54 (3H, m), 7.61 – 7.66 (2H, m), 7.97 – 8.00 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) 19.9, 50.4, 67.0, 79.2, 85.3, 118.8, 122.6, 122.7, 126.3, 128.0, 129.4, 130.0, 131.8, 133.8, 134.7, 142.9, 171.0, 191.1; MS (EI) m/z = 433 (M^++1), 220, 191, 176, 169, 162 ,133, 105, 90, 77, 63, 51, 39, 28, 14; HRMS (EI) Calcd for $C_{20}H_{18}BrO_6$ (M^++H): 433.0286. Found: 433.0300; Anal. Calcd for $C_{20}H_{17}BrO_6$: C, 55.44; H, 3.96%. Found: C, 55.53; H, 3.83%; R_f = 0.47 (3:7 AcOEt/hexane). ***Endo*-6f:** Colorless oil; IR (Neat) 2955, 1740, 1711, 1603, 1489, 1460, 1292, 1132, 1073, 1046, 949 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83 (3H, s), 3.72 (3H, s), 4.74 (1H, s), 4.80 (1H, d, *J* = 12.3 Hz), 4.96 (1H, d, *J* = 12.3 Hz), 6.90 – 6.93 (2H, m), 7.36 – 7.41 (3H, m), 7.58 – 7.65 (2H, m), 7.71 – 7.73 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 23.9, 49.9, 66.8, 80.1, 86.2, 119.6, 122.4, 122.6, 125.9, 128.5, 129.3, 129.9, 131.4, 133.3, 134.3, 141.7, 169.1, 190.5; MS (EI) m/z = 433 (M^++1), 248, 220, 191, 176, 164, 149, 135, 120, 105, 90, 76, 63, 51, 39, 26, 14; HRMS (EI) Calcd for $C_{20}H_{17}BrO_6$ (M^+): 432.0208. Found: 432.0186; Anal. Calcd for $C_{20}H_{17}BrO_6$: C, 55.44; H, 3.96%. Found: C, 55.27; H, 4.06%; R_f = 0.38 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 24.1 min (minor) and 31.4 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 23.9 min (minor) and 47.7 min (major).

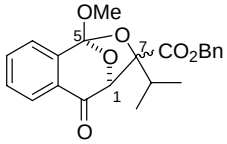


7-*Exo*-(benzyloxy)carbonyl-7-*endo*-ethyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6g) and 7-*Endo*-(benzyloxy)carbonyl-7-*exo*-ethyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*endo*-6g). Benzyl 2-oxobutanoate (**5g**, 197.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (1:99 – 3:97 AcOEt/hexane) gave 162.0 mg (87%) of *exo*-**6g** and 12.5 mg (7%) of *endo*-**6g**. ***Exo*-6g**: Colorless oil; $[\alpha]_D^{28}$ = –96° (*c* 1.03, $CHCl_3$); IR (Neat) 3034, 2957, 1732, 1711, 1603, 1460, 1289, 1250, 1217, 1157, 1134, 1119, 1096, 1078, 1051, 1024, 976, 945 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.78 (3H, t, *J* = 7.3 Hz), 1.34 – 1.43 (1H, m), 1.68 –



1.77 (1H, m), 3.64 (3H, s), 5.24 (1H, d, *J* = 12.0 Hz), 5.25 (1H, s), 5.33 (1H, d, *J* = 12.0 Hz), 7.34 – 7.42 (5H, m), 7.46 – 7.51 (1H, m), 7.60 – 7.66 (2H, m), 7.97 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.6, 27.4, 50.4, 67.7, 83.3, 85.2, 118.7, 122.6, 126.2, 128.1, 128.51, 128.55, 129.3, 134.6, 134.8, 143.1, 170.3, 191.1; MS (EI) m/z = 357 (M^+), 340, 233, 177, 163, 133, 105, 91, 76, 65, 57, 50, 39, 29; HRMS (EI) Calcd for $C_{21}H_{19}O_6$ (M^+–H): 355.1180. Found: 355.1190; Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47%. Found: C, 68.34; H, 5.41%; R_f = 0.74 (2:3 AcOEt/hexane). ***Endo*-6g**: Colorless oil; IR (Neat) 3034, 2955, 1736, 1709, 1603, 1460, 1460, 1381, 1292, 1252, 1132, 1109, 1078, 1049, 1028, 1007, 972, 943 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.01 (3H, t, *J* = 7.3 Hz), 2.01 – 2.10 (1H, m), 2.30 – 2.39 (1H, m), 3.71 (3H, s), 4.75 (1H, s), 4.85 (1H, d, *J* = 12.1 Hz), 5.10 (1H, d, *J* = 12.1 Hz), 7.09 – 7.11 (2H, m), 7.25 – 7.29 (3H, m), 7.37 – 7.41 (1H, m), 7.58 – 7.62 (1H, m), 7.66 – 7.67 (1H, m), 7.76 – 7.78 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.3, 31.1, 49.9, 67.6, 83.5, 85.7, 119.5, 122.7, 126.0, 128.2, 128.2, 128.4, 129.3, 134.36, 134.40, 141.6, 168.7, 190.4; MS (EI) m/z = 357 (M^+), 339, 234, 177, 163, 141, 133, 105, 92, 77, 65, 57, 51, 39, 29; Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47%. Found: C, 68.22; H, 5.70%; R_f = 0.66 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 14.3 min (minor) and 16.7 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 18.2 min (minor) and 36.0 min (major).

7-*Exo*-(4-benzyloxy)carbonyl-7-*endo*-isopropyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*exo*-6h) and 7-*Endo*-(4-benzyloxy)carbonyl-7-*exo*-isopropyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6h). Benzyl 3-methyl-2-oxobutanoate (**5h**, 206.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 185.0 mg (96%) of *exo*-**6h** and 13.2 mg (7%) of *endo*-**6h**.



***Exo*-6h**: Colorless oil; $[\alpha]_D^{28}$ –86° (*c* 1.00, $CHCl_3$); IR (Neat) 3069, 3034, 2959, 2855, 1730, 1603, 1497, 1460, 1395, 1373, 1354, 1289, 1217, 1144, 1099, 1071, 1044, 947, 891, 847 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.90 (3H, d, *J* = 6.8 Hz), 0.93 (3H, d, *J* = 6.8 Hz), 1.56 (1H, seqt, *J* = 6.8 Hz), 3.52 (3H, s), 5.27 (1H, d, *J* = 12.0 Hz), 5.32 (1H, d, *J* = 12.0 Hz), 5.46 (1H, s), 7.34 – 7.44 (5H, m), 7.46 – 7.50 (1H, m), 7.58 – 7.65 (2H, m), 7.97 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.3, 18.4, 33.6, 50.2, 67.6, 85.7, 87.0, 118.5, 122.4, 126.2, 128.2, 128.51, 128.54, 128.7, 129.2, 134.4, 134.8, 143.3, 169.1, 191.3; MS (EI) m/z = 383 (M^++1), 339, 248, 178, 163, 133, 104, 89, 77, 71, 65, 51, 39, 26; HRMS (EI) Calcd for $C_{22}H_{21}O_6$ (M^+–H): 381.1337. Found: 381.130; Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80%. Found: C, 69.13; H, 5.81%; R_f = 0.63 (3:7 AcOEt/hexane). ***Endo*-6h**: Colorless oil; IR (Neat) 3069, 3034, 2961, 2853, 1732, 1603, 1460, 1391, 1375, 1292, 1250, 1134, 1105, 1076, 1028, 945, 889 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.04 (3H, d, *J* = 6.8 Hz), 1.14 (3H, d, *J* = 6.8 Hz), 2.40 (1H, seqt, *J* = 6.8 Hz), 3.76 (3H, s), 4.79 (1H, d, *J* = 12.0 Hz), 4.88 (1H, s), 4.95 (1H, d, *J* = 12.0 Hz), 7.33 – 7.44 (5H, m), 7.46 – 7.50 (1H, m), 7.59 – 7.65 (2H, m), 7.96 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 16.6, 18.2, 35.6, 50.5, 67.3, 83.5, 85.3, 118.8, 123.1, 125.9, 128.2, 128.2, 128.6, 129.4, 134.3, 134.4, 141.2, 169.0, 190.2; MS (EI) m/z = 383 (M^++1), 339, 247, 177, 163, 133, 105, 91, 77, 65, 51, 43, 28; HRMS (EI) Calcd for $C_{22}H_{23}O_6$ (M^++H): 383.1493. Found: 383.1476; Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80%. Found: C, 68.86; H, 5.94%; R_f = 0.48 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:99 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 20.2 min (major) and 27.7 min (minor). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 18.9 min (minor) and 25.8 min (major).

7-*Exo*-(4-bromobenzyloxy)carbonyl-7-*endo*-isopropyl-5-methoxy-6,8-dioxabenzo[*c*]-bicyclo[3.2.1]octan-2-one (*exo*-6i) and 7-*Endo*-(4-bromobenzyloxy)carbonyl-7-*exo*-isopropyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6i). 4-Bromobenzyl 3-methyl-2-oxobutanoate (**5i**, 285.1 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (2:98 – 5:95 AcOEt/hexane) gave 219.5 mg (95%) of *exo*-**6i** and 10.3 mg (4%) of *endo*-**6i**. ***Exo*-6i**: Colorless oil; $[\alpha]_D^{28}$ –64° (*c* 0.90, $CHCl_3$); IR (Neat) 2959, 1732, 1707, 1603, 1489, 1462, 1289, 1258, 1217, 1165, 1142, 1101, 1071, 1044, 1015, 974, 945 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.89 (3H, d, *J* = 6.8 Hz), 0.92 (3H, d, *J* = 6.8 Hz), 1.56 (1H, seqt, *J* = 6.8 Hz), 3.53 (3H, s), 5.22 (1H, d, *J* = 12.2 Hz), 5.26 (1H, d, *J* = 12.2 Hz), 5.44 (1H, s), 7.29 – 7.32 (2H, m), 7.46 – 7.54 (3H, m), 7.59 – 7.65 (2H, m), 7.96 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.3, 18.4, 33.6, 50.2, 66.8, 85.7, 87.0, 118.6, 122.5, 122.7, 126.2, 128.2, 129.2, 130.3, 131.7, 133.8, 134.5, 143.2, 169.1, 191.2; MS (EI) m/z = 451 (M^++1), 417, 249, 178, 171, 164, 149, 134, 105, 90, 78, 71, 63, 51, 39, 26, 14; HRMS (EI) Calcd for $C_{22}H_{22}BrO_6$ (M^++H): 461.0598. Found: 461.0568; Anal. Calcd for $C_{22}H_{21}BrO_6$: C, 57.28; H, 4.59%. Found: C, 57.03; H, 4.65%; R_f = 0.57 (3:7 AcOEt/hexane). ***Endo*-6i:** Colorless prisms (ether–hexane); mp 124 – 126 °C; IR (KBr) 2980, 2951, 1728, 1703, 1597, 1489, 1464, 1441, 1381, 1343, 1292, 1236, 1154, 1103, 1074, 1047, 1026, 1003, 964, 893, 870, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.05 (3H, d, *J* = 6.8 Hz), 1.14 (3H, d, *J* = 6.8 Hz), 2.39 (1H, seqt, *J* = 6.8 Hz), 3.76 (3H, s), 4.72 (1H, d, *J* = 12.0 Hz), 4.88 (1H, s), 4.92 (1H, d, *J* = 12.0 Hz), 6.92 – 6.96 (2H, m), 7.35 – 7.40 (3H, m), 7.56 – 7.68 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 16.6, 18.2, 35.7, 50.5, 66.4, 83.5, 85.2, 118.8, 122.4, 123.1, 125.8, 128.1, 129.4, 130.4, 131.4, 133.3, 134.5, 141.1, 167.0, 190.2; MS (EI) m/z = 461 (M^++1), 418, 248, 203, 185, 176, 164, 135, 120, 105, 90, 78, 71, 63, 51, 41, 26, 14; HRMS (EI) Calcd for $C_{22}H_{21}BrO_6$ (M^+): 460.0521. Found: 460.0525; Anal. Calcd for $C_{22}H_{21}BrO_6$: C, 57.28; H, 4.59%. Found: C, 57.20; H, 4.55%; R_f = 0.43 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:99 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 29.5 min (major) and 39.7 min (minor). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R =21.6 min (minor) and 38.2 min (major).

5-Methoxy-7-*exo*-methoxycarbonyl-7-*endo*-phenyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6j) and 5-Methoxy-7-*endo*-methoxycarbonyl-7-*exo*-phenyl-6,8-dioxabenzo[*c*]bicyclo-[3.2.1]octan-2-one (*endo*-6j). Methyl benzoylformate (**5j**, 164.2 mg, 140 μL, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 102.1 mg (60%) of *exo*-**6j** and 47.2 mg (28%) of *endo*-**6j**. ***Exo*-6j**: Colorless prisms (ether–hexane); mp 109 – 111 °C; $[\alpha]_D^{28}$ +92.9° (*c* 0.97, $CHCl_3$); IR (KBr) 3071, 3007, 2955, 1734, 1713, 1603, 1493, 1451, 1290, 1260, 1229, 1157, 1103, 1078, 1030, 992, 972, 941, 891, 858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.77 (3H, s), 3.85 (3H, s), 5.75 (1H, s), 7.16 – 7.22 (5H, m), 7.34 – 7.40 (1H, m), 7.60 – 7.64 (2H, m), 7.71 – 7.73 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.3, 53.5, 84.3, 86.2, 119.5, 122.3, 125.1, 126.1, 128.3, 128.4, 128.7, 129.3, 132.8, 134.3, 141.7, 170.3, 189.9; MS (EI) m/z = 340 (M^+), 281, 176, 163, 133, 105, 77, 51, 28, 14; Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74%. Found: C, 66.95; H, 4.79%; R_f = 0.47 (3:7 AcOEt/hexane). ***Endo*-6j:** Colorless prisms (ether–hexane); mp 124 – 125 °C; $[\alpha]_D^{28}$ +14.4° (*c* 0.75, $CHCl_3$); IR (KBr) 3067, 3009, 2959, 2851, 1738, 1711, 1601, 1499, 1449, 1319, 1289, 1248, 1219, 1157, 1096, 1078, 1053, 968, 933, 909 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.49 (3H, s), 3.56 (3H, s), 5.43 (1H, s), 7.38 – 7.54 (4H, m), 7.65 – 7.76 (4H, m), 7.97 – 7.99 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.9, 53.0, 83.5, 86.5, 119.8, 122.9, 126.12, 126.17, 128.2, 128.5, 128.6, 129.6, 134.7, 137.1, 141.5, 168.6, 190.4; MS (EI) m/z = 341 (M^++1), 282, 253, 221, 176, 161, 145, 135,

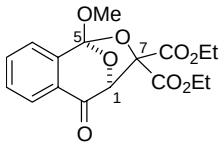
120, 106, 90, 75, 65, 59, 50, 39, 29, 14; Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74%. Found: C, 66.95; H, 4.79%; R_f = 0.36 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 11.9 min (minor) and 13.2 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 23.0 min (minor) and 39.9 min (major).

7-*Exo*-(benzyloxy)carbonyl-5-methoxy-7-*endo*-phenyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]-octan-2-one (*exo*-6k) and 7-*Endo*-(benzyloxy)carbonyl-5-methoxy-7-*exo*-phenyl-6,8-dioxabenzo-[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6k). Benzyl benzoylformate (**5k**, 240.3 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 155.3 mg (74%) of *exo*-**6k** and 44.5 mg (21%) of *endo*-**6k**. ***Exo*-6k**: Colorless needles (ether–hexane); mp 99 – 100 °C; $[\alpha]_D^{24}$ +68° (*c* 1.00, $CHCl_3$); IR (KBr) 3061, 2959, 1738, 1715, 1603, 1474, 1449, 1321, 1304, 1289, 1263, 1213, 1157, 1100, 1076, 1026, 976, 941, 891 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.56 (3H, s), 5.14 (1H, d, *J* =12.0 Hz), 5.37 (1H, d, *J* = 12.0 Hz), 5.76 (1H, s), 7.13 – 7.21 (5H, m), 7.32 – 7.38 (6H, m), 7.58 – 7.63 (2H, m), 7.68 – 7.70 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.2, 68.2, 84.3, 86.1, 119.4, 122.3, 125.1, 126.1, 128.3, 128.35, 128.42, 128.45, 128.49, 128.7, 129.3, 132.7, 134.3, 134.6, 141.7, 169.5, 190.0; MS (EI) m/z = 417 (M^++1), 385, 282, 267, 253, 249, 221, 193, 177, 164, 148, 133, 120, 106, 92, 76, 65, 50, 39, 28, 14; Anal. Calcd for $C_{25}H_{20}O_6$: C, 72.11; H, 4.84%. Found: C, 72.06; H, 4.81%; R_f = 0.52 (3:7 AcOEt/hexane). ***Endo*-6k**: Colorless oil; IR (Neat) 3067, 3032, 2955, 1736, 1711, 1603, 1497, 1449, 1377, 1294, 1252, 1161, 1049, 1003, 970, 937, 887, 851 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.00 (3H, s), 4.80 (1H, d, *J* = 12.2 Hz), 4.98 (1H, d, *J* = 12.2 Hz), 5.41 (1H, s), 6.96 – 6.98 (2H, m), 7.19 – 7.26 (3H, m), 7.38 – 7.45 (4H, m), 7.61 – 7.65 (1H, m), 7.70 – 7.73 (3H, m), 7.80 – 7.83 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.9, 67.8, 83.3, 86.7, 119.8, 122.8, 126.1, 126.2, 128.00, 128.04, 128.09, 128.2, 128.5, 128.6, 129.5, 134.2, 134.5, 137.1, 141.4, 168.1, 190.1; MS (EI) m/z = 417 (M^++1), 282, 253, 221, 176, 164, 133, 120, 106, 92, 78, 63, 51, 39, 28, 14; Anal. Calcd for $C_{25}H_{20}O_6$: C, 72.11; H, 4.84%. Found: C, 71.96; H, 4.88%. R_f = 0.46 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:49 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 39.7 min (minor) and 49.0 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 37.0 min (minor) and 98.1 min (major).

7-*Exo*-(bnezyloxy)carbonyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*exo*-6l) and 7-*Endo*-(bnezyloxy)carbonyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (*endo*-6l). Benzyl glyoxylate (164.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 – 5:95 AcOEt/hexane) gave 117.6 mg (69%) of *exo*-**6l** and 14.0 mg (8%) of *endo*-**6l**. ***Exo*-6l**: Colorless oil; IR (Neat) 3069, 3034, 2959, 1757, 1711, 1603, 1499, 1458, 1381, 1358, 1300, 1269, 1219, 1163, 1101, 1084, 1051, 1024, 970, 939, 889 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.77 (3H, s), 4.37 (1H, d, *J* = 1.0 Hz), 5.11 (1H, d, *J* = 1.0 Hz), 5.25 (1H, d, *J* = 12.1 Hz), 5.31 (1H, d, *J* = 12.1 Hz), 7.35 – 7.42 (5H, m), 7.48 – 7.52 (1H, m), 7.61 – 7.67 (2H, m), 7.98 – 8.00 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.8, 67.8, 72.0, 82.6, 119.7, 122.6, 126.6, 127.5, 128.4, 128.54, 128.58, 129.4, 134.6, 134.7, 142.0, 168.6, 191.0; MS (EI) m/z = 341 (M^++1), 327, 308, 220, 205, 192, 177, 162, 147, 132, 108, 92, 74, 65, 51, 44, 39, 28, 17; Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74%. Found: C, 66.93; H, 4.86%; R_f = 0.60 (2:3 AcOEt/hexane). ***Endo*-6l**: Colorless oil; IR (Neat) 3034, 2955, 1759,

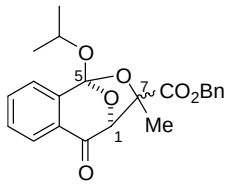
1709, 1603, 1460, 1385, 1352, 1294, 1215, 1188, 1159, 1080, 1053, 1026, 1003, 970, 941, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.69 (3H, s), 4.94 (1H, d, *J* = 12.1 Hz), 5.00 (1H, d, *J* = 6.1 Hz), 5.11 (1H, d, *J* = 12.1 Hz), 5.17 (1H, d, *J* = 6.1 Hz), 7.19 – 7.21 (2H, m), 7.30 – 7.33 (3H, m), 7.43 – 7.47 (1H, m), 7.61 – 7.65 (1H, m), 7.68 – 7.70 (1H, m), 7.86 – 7.88 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.0, 67.7, 73.7, 81.4, 119.4, 122.7, 126.2, 128.35, 128.39, 128.5, 128.9, 129.3, 134.3, 134.4, 142.0, 166.7, 190.5; MS (EI) m/z = 341 (M^++1), 205, 176, 164, 149, 133, 105, 92, 77, 65, 57, 51, 39, 29, 14; Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74%. Found: C, 67.06; H, 4.76%; R_f = 0.50 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 32.6 min (minor) and 35.5 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 31.0 min (minor) and 35.8 min (major).

7-Bis(ethoxycarbonyl)-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (6m).



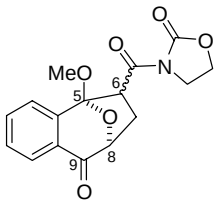
Diethyl oxomalonate (**5m**, 174.2 mg, 150 μL, 1.0 mmol) was used according to the general procedure. Purification by column chromatography (1:9 AcOEt/hexane) gave corresponding cycloadduct **6m** (174.7 mg, quant). Colorless liquid; IR (Neat) 2986, 1750, 1713, 1605, 1462, 1447, 1290, 1252, 1221, 1163, 1078, 1055, 1032, 934, 858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.10 (3H, t, *J* = 7.2 Hz), 1.35 (3H, t, *J* = 7.1 Hz), 3.68 (3H, s), 4.05 – 4.16 (2H, m), 4.34 – 4.44 (2H, m), 5.55 (1H, s), 7.46 – 7.54 (1H, m), 7.63 – 7.71 (2H, m), 7.94 – 7.96 (1H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.7, 14.2, 50.3, 62.97, 63.04, 82.4, 84.0, 120.4, 122.8, 126.0, 128.6, 129.7, 134.5, 141.1, 164.3, 165.8, 189.5; MS (EI) m/z = 351 (M^++1), 278, 203, 176, 163, 133, 105, 89, 77, 69, 50, 29, 14; Anal. Calcd for $C_{17}H_{18}O_8$: C, 58.29; H, 5.18%. Found: C, 55.25; H, 5.18%. R_f = 0.27 (3:7 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis [(DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow 0.5 mL/min, 35 °C) t_R = 12.4 min (minor), 16.4 min (major)].

7-*Exo*-(benzyloxy)carbonyl-5-isopropoxy-7-*endo*-methyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]-octan-2-one (*exo*-8b) and 7-*Endo*-(benzyloxy)carbonyl-5-isopropoxy-7-*exo*-methyl-6,8-dioxabenzo-[*c*]bicyclo[3.2.1]octan-2-one (*endo*-8b). *o*-Isopropoxycarbonyl-α-diazoacetophenone (**7**, 116.1 mg, 0.5 mmol) and benzyl pyruvate (**5b**, 178.2 mg, 1.0 mmol) was used according to the general procedure. Purification by MPLC (2:98 AcOEt/hexane) gave 18.4 mg (10%) of *endo*-**8b** and 164.8 mg of a mixture of *exo*-**8b** and pyruvate **5b**. The yield of *exo*-**8b** was calculated on the basis of ^1H NMR (129.4 mg, 67%). ***Exo*-8b**: Colorless oil; $[\alpha]_D^{29}$ = –107° (*c* 1.02, $CHCl_3$, 21wt% of benzyl pyruvate was contained); IR (Neat) 3069, 3036, 2990, 2967, 2934, 1732, 1707, 1602, 1499, 1456, 1360, 1296, 1223, 1134, 1090, 1047, 1030, 1015, 978, 947 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.16 (3H, d, *J* = 6.1 Hz), 1.26 (3H, d, *J* = 6.1 Hz), 1.29 (3H, s), 4.68 (1H, seqt, *J* = 6.1 Hz), 5.19 (1H, d, *J* = 12.0 Hz), 5.19 (1H, s), 5.36 (1H, d, *J* = 12.0 Hz), 7.36 – 7.42 (5H, m), 7.46 – 7.50 (1H, m), 7.60 – 7.64 (1H, m), 7.66 – 7.68 (1H, m), 7.96 – 7.98 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.0, 23.6, 23.7, 67.5, 67.9, 79.0, 84.9, 118.9, 122.9, 126.1, 127.9, 128.49, 128.53, 128.64, 129.2, 134.6, 134.8, 143.4, 171.3, 191.2; MS (EI) m/z = 383 (M^++1), 247, 205, 181, 163, 149, 105, 90, 78, 64, 52, 42, 26, 14; HRMS (EI) Calcd for $C_{22}H_{23}O_6$ (M^++H): 383.1493. Found: 383.1470; R_f = 0.61 (2:3 AcOEt/hexane). ***Endo*-8b:** Colorless oil; $[\alpha]_D^{29}$ = –33° (*c* 0.26, $CHCl_3$); IR (Neat) 3069, 3034, 2982, 2938, 2874, 1738, 1711, 1603, 1499, 1456, 1373, 1296, 1208, 1130, 1088, 1073, 1051, 1032, 1015, 949, 924, 885, 843, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.35 (3H, d, *J* = 6.3 Hz), 1.41 (3H, d, *J* = 6.3 Hz), 2.48 (3H,



s), 4.64 – 4.74 (1H, m), 4.71 (1H, s), 4.85 (1H, d, *J* = 12.2 Hz), 5.01 (1H, d, *J* = 12.2 Hz), 7.07 – 7.09 (2H, m), 7.26 – 7.29 (3H, m), 7.34 – 7.42 (1H, m), 7.57 – 7.61 (1H, m), 7.67 – 7.68 (1H, m), 7.73 – 7.75 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.8, 24.0, 24.1, 67.3, 67.6, 79.9, 85.9, 119.9, 122.9, 125.9, 128.2, 128.23, 128.28, 128.34, 129.1, 134.3, 134.4, 142.3, 169.4, 190.7; MS (EI) m/z = 383 (M^++1), 247, 205, 191, 162, 149, 132, 105, 92, 76, 65, 51, 39, 26, 14; HRMS (EI) Calcd for $C_{22}H_{23}O_6$ (M^++H): 383.1493. Found: 383.1470; R_f = 0.54 (2:3 AcOEt/hexane). The enantiomeric excess was determined by HPLC analysis. *Exo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 11.5 min (minor) and 16.6 min (major). *Endo*-isomer (DAICEL Chiralpak® AD, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C): t_R = 14.8 min (minor) and 24.9 min (major).

5,8-Epoxy-5-methoxy-6-*exo*-(2-oxazolidinoyl)carbonyl-9-oxo-6,7,8,9-tetrahydro-5*H*-benzo-cycloheptene (*exo*-10) and 5,8-Epoxy-5-methoxy-6-*endo*-(2-oxazolidinoyl)carbonyl-9-oxo-6,7,8,9-tetra-hydro-5*H*-benzocycloheptene (*endo*-10). A solution of 2,6-bis[(4*S*)-(–)-4-phenyl-2-oxazolin-2-yl]pyridine ((*S*,*S*)-Pybox-Ph, 18.5 mg, 0.05 mmol) in THF (1.5 mL) was added to a solution of $Yb(OTf)_3$ (31.0 mg, 0.05 mmol) in THF (1 mL). After stirring the mixture for 2 h, The solvent was removed *in vacuo* and resulting solid was dried *in vacuo* (< mmHg) at 120 °C for 5 h. A solution of Yb(III)–Pybox complex in CH_2Cl_2 (3 mL) was added to a suspension of 3-acryloyl-2-oxazolidinone (**9**, 144.1 mg, 1.0 mmol) and MS 4A (0.5 g) in CH_2Cl_2 (1 mL). After added $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol) and CH_2Cl_2 (1 mL), the mixture was cooled to –25 °C, and then a solution of diazoactophenone **1** (102.1 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added over a period of 6 h. After removal of MS 4A through celite, the reaction mixture was filtered through a plug of silica gel (3 cm) with AcOEt/hexane (1:1, 100 mL) as an eluent. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (3:7 AcOEt/hexane) to provide 149.5 mg (94%) of a mixture of *exo*-**10** and *endo*-**10**. The *exo*/*endo* ratio was determined by ^{1}H NMR analysis (*exo*:*endo* = 82:18). Colorless solid; $[\alpha]_D^{25}$ = +52 ° (*c* 0.99, $CHCl_3$, A mixture of *exo*-**10** and *endo*-**10** (88:12)); IR (KBr, A mixture of *exo*-**10** and *endo*-**10**) 2976, 2955, 2926, 2874, 1780, 1688, 1601, 1472, 1456, 1440, 1385, 1316, 1302, 1287, 1263, 1223, 1161, 1121, 1096, 1073, 1049, 1022, 1009, 978 cm^{-1}; Found: C, 60.59; H, 4.72; N, 4.24%. Calcd for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.77; N, 4.41%. ***Exo*-10**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.82 (1H, ddd, *J* = 1.7, 9.0, 13.7 Hz), 3.13 (1H, ddd, *J* = 3.9, 9.3, 13.7 Hz), 3.33 (3H, s), 3.9 – 4.0 (1H, m), 4.1 – 4.2 (1H, m), 4.2 – 4.5 (2H, m), 4.58 (1H, dd, *J* = 3.9, 9.0 Hz), 4.88 (1H, dd, *J* = 1.7, 9.3 Hz), 7.3 – 8.0 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.6, 43.0, 49.0, 53.9, 62.0, 80.2, 108.5, 124.7, 127.2, 129.2, 129.7, 134.3, 143.0, 153.1, 170.5, 194.6; R_f = 0.51 (ether). ***Endo*-10**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.22 (1H, ddd, *J* = 1.5, 5.6, 13.4 Hz), 2.72 (1H, ddd, *J* = 8.9, 10.9, 13.4 Hz), 3.4 – 3.5 (1H, m), 3.52 (3H, s), 3.6 – 3.8 (1H, m), 4.2 – 4.5 (2H, m), 4.78 (1H, dd, *J* = 1.5, 8.9 Hz), 5.00 (1H, dd, *J* = 5.6, 10.9 Hz), 7.3 – 8.0 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.6, 43.2, 46.8, 51.8, 61.9, 79.9, 108.2, 123.4, 126.9, 129.2, 130.2, 133.4, 142.3, 153.1, 170.5, 194.3; R_f = 0.45 (ether). The enantiomeric excess was determined by HPLC analysis (DAICEL Chiralpak® AS, 1:4 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 °C). *Exo*-isomer: t_R = 25.9 min (major) and 30.1 min (minor). *Endo*-isomer: t_R = 55.1 min (major) and 120.9 min (minor).



Supporting Information

X-ray crystallographci analysis of (–)-*exo*-6f

A. Crystal Data

Empirical Formula	$C_{20}H_{17}BrO_6$
Formula Weight	433.25
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 x 0.15 x 0.15 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20546 (6.1 – 60.1°)
Indexing Images	3 oscillations at 0.6 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 5.122(3) Å b = 17.263(8) Å c = 21.099(7) Å V = 1866(1) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.542 g/cm^3
F_{000}	880.00
μ(MoKα)	22.44 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Temperature	–120 °C
Voltage, Current	60 kV, 90 mA
Collimator Size	0.5 mm
Detector Aperture	280.0 mm x 256.0 mm
Data Images	44 exposures at 0.5 minutes per degree
Oscillation Range (ϕ = 0.0°, χ = 45°)	ω 130.0 – 190.0° with 5.0° step
Oscillation Range (ϕ = 180.0°, χ = 45°)	ω 0.0 – 160.0° with 5.0° step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	60.1°
No. of Reflections Measured	Total: 22517 Unique: 3129 (R_{int} = 0.029)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.5950 – 0.7140)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinemen	Full-matrix least-squares
Function Minimized	$\Sigma\, w\, (Fo^2 - Fc^2)^2$

Supporting Information

Least Squares Weights	$w = 1/[\sigma^2(Fo^2)]$
p-factor	0.0180
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations (I>–3.00σ(I), 2θ<60.07^o)	5399
No. Variables	245
Reflection/Parameter Ratio	22.04
Residuals: R; Rw	0.040; 0.052
Residuals: R1	0.026
No. of Reflections to calc R1	4613
Goodness of Fit Indicator	1.02
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.45 e^- /Å^3
Minimum peak in Final Diff. Map	–0.20 e^- /Å^3
Flack parameter	–0.003(5)

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Br(1)	0.47690(4)	0.67666(1)	0.487896(8)	3.494(4)
O(1)	1.1766(3)	0.11224(7)	0.42803(5)	3.73(3)
O(2)	0.6997(2)	0.24779(6)	0.31551(4)	1.96(2)
O(3)	0.7157(3)	0.19874(6)	0.21287(4)	2.82(3)
O(4)	1.0750(2)	0.19564(6)	0.27858(5)	2.26(2)
O(5)	0.9247(3)	0.38957(6)	0.30517(5)	3.07(3)
O(6)	1.1932(2)	0.36598(6)	0.38788(5)	2.35(2)
C(1)	0.8578(4)	0.07939(9)	0.34949(7)	2.20(3)
C(2)	0.7991(4)	0.0058(1)	0.37308(8)	2.87(4)
C(3)	0.6054(4)	–0.0380(1)	0.34441(8)	3.20(4)
C(4)	0.4687(4)	–0.00893(9)	0.29316(7)	2.95(4)
C(5)	0.5239(4)	0.06491(9)	0.26945(7)	2.49(3)
C(6)	0.7211(3)	0.10880(9)	0.29716(6)	1.92(3)
C(7)	0.7995(3)	0.18825(9)	0.27369(7)	2.16(3)
C(8)	0.8979(3)	0.26618(9)	0.36094(6)	1.79(3)
C(9)	1.1108(3)	0.20550(9)	0.34563(7)	2.16(3)
C(10)	1.0618(3)	0.12831(9)	0.37931(7)	2.41(3)
C(11)	0.7837(6)	0.2719(1)	0.18406(8)	4.64(5)
C(12)	0.7844(4)	0.26286(9)	0.42801(7)	2.42(3)
C(13)	1.0017(4)	0.34754(8)	0.34662(6)	2.02(3)
C(14)	1.2910(4)	0.44562(9)	0.38304(8)	2.68(4)
C(15)	1.0941(3)	0.50241(9)	0.40817(7)	2.18(3)
C(16)	0.9884(4)	0.55978(8)	0.36969(6)	2.72(3)
C(17)	0.8073(4)	0.6120(1)	0.39311(7)	2.85(4)
C(18)	0.7303(4)	0.60609(9)	0.45566(7)	2.39(3)
C(19)	0.8302(4)	0.5490(1)	0.49457(7)	2.99(4)
C(20)	1.0126(4)	0.49765(9)	0.47065(7)	2.79(4)
H(1)	0.8918	–0.0142	0.4085	3.434
H(2)	0.5664	–0.0883	0.3601	3.827

Table 1. (Continued from the preceding page)

H(3)	0.3360	–0.0393	0.2738	3.540
H(4)	0.4274	0.0850	0.2347	2.983
H(5)	1.2801	0.2249	0.3549	2.599
H(6)	0.9659	0.2805	0.1883	5.583
H(7)	0.6907	0.3125	0.2044	5.583
H(8)	0.7386	0.2708	0.1403	5.583
H(9)	0.9201	0.2705	0.4581	2.906
H(10)	0.7061	0.2136	0.4348	2.906
H(11)	0.6565	0.3022	0.4329	2.906
H(12)	1.4473	0.4501	0.4070	3.216
H(13)	1.3257	0.4572	0.3399	3.216
H(14)	1.0411	0.5632	0.3266	3.256
H(15)	0.7373	0.6512	0.3666	3.405
H(16)	0.7741	0.5451	0.5374	3.558
H(17)	1.0827	0.4587	0.4975	3.353

B_{eq} = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters

atom	U11	U22	U33	U12	U13	U23
Br(1)	0.0353(1)	0.0390(1)	0.0585(1)	–0.0001(1)	0.0031(1)	–0.01706(8)
O(1)	0.053(1)	0.0337(7)	0.0548(7)	0.0002(7)	–0.0287(7)	0.0068(6)
O(2)	0.0184(6)	0.0265(6)	0.0294(5)	0.0036(5)	–0.0026(5)	–0.0076(4)
O(3)	0.0517(9)	0.0304(6)	0.0252(5)	0.0040(6)	–0.0049(6)	–0.0016(4)
O(4)	0.0223(7)	0.0297(6)	0.0338(5)	0.0023(5)	0.0082(5)	–0.0010(4)
O(5)	0.0491(9)	0.0283(6)	0.0391(6)	–0.0015(6)	–0.0104(6)	0.0046(5)
O(6)	0.0242(7)	0.0230(6)	0.0421(6)	–0.0028(5)	–0.0071(5)	–0.0005(5)
C(1)	0.026(1)	0.0258(8)	0.0320(8)	–0.0004(7)	0.0029(7)	–0.0015(7)
C(2)	0.043(1)	0.0303(9)	0.0352(8)	–0.0036(9)	–0.0035(9)	0.0040(7)
C(3)	0.045(1)	0.031(1)	0.0454(9)	–0.0121(9)	0.0067(9)	–0.0014(8)
C(4)	0.032(1)	0.0358(9)	0.0443(9)	–0.0087(9)	0.0030(9)	–0.0145(7)
C(5)	0.028(1)	0.0344(8)	0.0323(7)	0.0028(9)	–0.0023(9)	–0.0101(6)
C(6)	0.0219(9)	0.0248(8)	0.0262(7)	0.0032(7)	0.0034(7)	–0.0060(6)
C(7)	0.0257(9)	0.0285(9)	0.0277(7)	0.0038(8)	–0.0002(7)	–0.0049(7)
C(8)	0.0170(8)	0.0255(8)	0.0254(7)	0.0005(7)	–0.0035(6)	–0.0011(6)
C(9)	0.0171(8)	0.0264(8)	0.0385(8)	–0.0001(7)	–0.0028(7)	–0.0027(7)
C(10)	0.026(1)	0.0269(8)	0.0389(8)	0.0030(8)	–0.0026(8)	0.0007(6)
C(11)	0.105(2)	0.033(1)	0.0383(9)	0.004(1)	–0.009(1)	0.0062(8)
C(12)	0.027(1)	0.0344(9)	0.0303(7)	–0.0027(8)	–0.0021(7)	–0.0015(7)
C(13)	0.0215(9)	0.0248(7)	0.0304(7)	0.0029(8)	0.0005(8)	–0.0027(5)
C(14)	0.026(1)	0.0263(9)	0.0491(9)	–0.0065(8)	0.0004(8)	–0.0026(7)
C(15)	0.024(1)	0.0225(8)	0.0361(8)	–0.0069(7)	–0.0011(7)	–0.0025(6)
C(16)	0.046(1)	0.0272(8)	0.0300(7)	–0.000(1)	0.006(1)	0.0030(6)
C(17)	0.046(1)	0.0283(9)	0.0341(9)	0.0041(9)	–0.0035(8)	0.0032(7)
C(18)	0.026(1)	0.0263(8)	0.0385(8)	–0.0061(8)	0.0004(8)	–0.0078(7)

Table 2. (Continued from the preceding page)

C(19)	0.042(1)	0.041(1)	0.0308(8)	–0.0036(9)	0.0058(8)	0.0023(7)
C(20)	0.039(1)	0.0346(8)	0.0326(7)	0.002(1)	–0.0014(9)	0.0079(6)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
Br(1)	C(18)	1.906(2)	O(1)	C(10)	1.217(2)
O(2)	C(7)	1.448(2)	O(2)	C(8)	1.432(2)
O(3)	C(7)	1.365(2)	O(3)	C(11)	1.444(2)
O(4)	C(7)	1.421(2)	O(4)	C(9)	1.437(2)
O(5)	C(13)	1.203(2)	O(6)	C(13)	1.350(2)
O(6)	C(14)	1.467(2)	C(1)	C(2)	1.397(2)
C(1)	C(6)	1.402(2)	C(1)	C(10)	1.484(2)
C(2)	C(3)	1.386(3)	C(3)	C(4)	1.383(2)
C(4)	C(5)	1.398(2)	C(5)	C(6)	1.392(2)
C(6)	C(7)	1.513(2)	C(8)	C(9)	1.546(2)
C(8)	C(12)	1.531(2)	C(8)	C(13)	1.532(2)
C(9)	C(10)	1.531(2)	C(14)	C(15)	1.503(2)
C(15)	C(16)	1.390(2)	C(15)	C(20)	1.385(2)
C(16)	C(17)	1.384(3)	C(17)	C(18)	1.381(2)
C(18)	C(19)	1.381(2)	C(19)	C(20)	1.383(3)
C(2)	H(1)	0.95	C(3)	H(2)	0.95
C(4)	H(3)	0.95	C(5)	H(4)	0.95
C(9)	H(5)	0.95	C(11)	H(6)	0.95
C(11)	H(7)	0.95	C(11)	H(8)	0.95
C(12)	H(9)	0.95	C(12)	H(10)	0.95
C(12)	H(11)	0.95	C(14)	H(12)	0.95
C(14)	H(13)	0.95	C(16)	H(14)	0.95
C(17)	H(15)	0.95	C(19)	H(16)	0.95
C(20)	H(17)	0.95			

Table 4. Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(7)	O(2)	C(8)	108.4(1)	C(7)	O(3)	C(11)	115.8(1)
C(7)	O(4)	C(9)	102.1(1)	C(13)	O(6)	C(14)	115.1(1)
C(2)	C(1)	C(6)	120.2(2)	C(2)	C(1)	C(10)	121.2(1)
C(6)	C(1)	C(10)	118.6(1)	C(1)	C(2)	C(3)	119.6(2)
C(2)	C(3)	C(4)	120.4(2)	C(3)	C(4)	C(5)	120.5(2)
C(4)	C(5)	C(6)	119.5(1)	C(1)	C(6)	C(5)	119.7(1)
C(1)	C(6)	C(7)	117.0(1)	C(5)	C(6)	C(7)	123.3(1)
O(2)	C(7)	O(3)	111.6(1)	O(2)	C(7)	O(4)	104.0(1)
O(2)	C(7)	C(6)	110.5(1)	O(3)	C(7)	O(4)	111.6(1)
O(3)	C(7)	C(6)	110.1(1)	O(4)	C(7)	C(6)	108.8(1)
O(2)	C(8)	C(9)	102.1(1)	O(2)	C(8)	C(12)	110.0(1)

Table 4. (Continued from the preceding page)

O(2)	C(8)	C(13)	108.5(1)	C(9)	C(8)	C(12)	115.8(1)
C(9)	C(8)	C(13)	109.6(1)	C(12)	C(8)	C(13)	110.4(1)
O(4)	C(9)	C(8)	101.3(1)	O(4)	C(9)	C(10)	109.4(1)
C(8)	C(9)	C(10)	112.1(1)	O(1)	C(10)	C(1)	124.7(1)
O(1)	C(10)	C(9)	120.8(1)	C(1)	C(10)	C(9)	114.5(1)
O(5)	C(13)	O(6)	124.4(1)	O(5)	C(13)	C(8)	125.6(1)
O(6)	C(13)	C(8)	110.0(1)	O(6)	C(14)	C(15)	111.0(1)
C(14)	C(15)	C(16)	121.3(1)	C(14)	C(15)	C(20)	120.0(1)
C(16)	C(15)	C(20)	118.7(2)	C(15)	C(16)	C(17)	121.1(1)
C(16)	C(17)	C(18)	119.0(2)	Br(1)	C(18)	C(17)	119.2(1)
Br(1)	C(18)	C(19)	119.8(1)	C(17)	C(18)	C(19)	121.0(2)
C(18)	C(19)	C(20)	119.4(1)	C(15)	C(20)	C(19)	120.9(1)
C(1)	C(2)	H(1)	120	C(3)	C(2)	H(1)	120
C(2)	C(3)	H(2)	119	C(4)	C(3)	H(2)	119
C(3)	C(4)	H(3)	119	C(5)	C(4)	H(3)	119
C(4)	C(5)	H(4)	120	C(6)	C(5)	H(4)	120
O(4)	C(9)	H(5)	111	C(8)	C(9)	H(5)	111
C(10)	C(9)	H(5)	111	O(3)	C(11)	H(6)	109
O(3)	C(11)	H(7)	109	O(3)	C(11)	H(8)	109
H(6)	C(11)	H(7)	109	H(6)	C(11)	H(8)	109
H(7)	C(11)	H(8)	109	C(8)	C(12)	H(9)	109
C(8)	C(12)	H(10)	109	C(8)	C(12)	H(11)	109
H(9)	C(12)	H(10)	109	H(9)	C(12)	H(11)	109
H(10)	C(12)	H(11)	109	O(6)	C(14)	H(12)	109
O(6)	C(14)	H(13)	109	C(15)	C(14)	H(12)	108
C(15)	C(14)	H(13)	109	H(12)	C(14)	H(13)	109
C(15)	C(16)	H(14)	119	C(17)	C(16)	H(14)	119
C(16)	C(17)	H(15)	120	C(18)	C(17)	H(15)	120
C(18)	C(19)	H(16)	120	C(20)	C(19)	H(16)	120
C(15)	C(20)	H(17)	119	C(19)	C(20)	H(17)	119

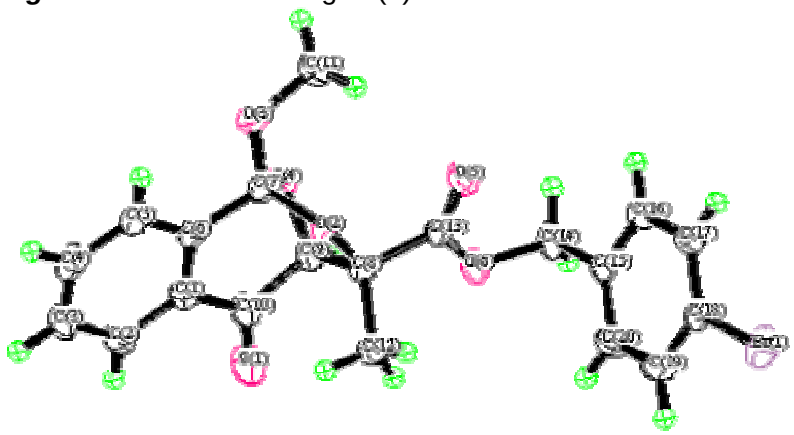
Table 5. Torsion Angles (^{o})

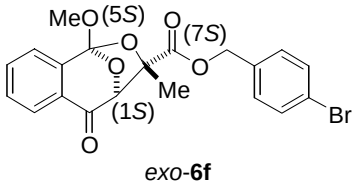
atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Br(1)	C(18)	C(17)	C(16)	–179.0(1)	Br(1)	C(18)	C(19)	C(20)	179.5(1)
O(1)	C(10)	C(1)	C(2)	–6.1(3)	O(1)	C(10)	C(1)	C(6)	173.1(2)
O(1)	C(10)	C(9)	O(4)	149.3(2)	O(1)	C(10)	C(9)	C(8)	–99.1(2)
O(2)	C(7)	O(3)	C(11)	58.3(2)	O(2)	C(7)	O(4)	C(9)	43.4(1)
O(2)	C(7)	C(6)	C(1)	–75.8(2)	O(2)	C(7)	C(6)	C(5)	104.3(2)
O(2)	C(8)	C(9)	O(4)	31.5(1)	O(2)	C(8)	C(9)	C(10)	–85.1(1)
O(2)	C(8)	C(13)	O(5)	1.8(2)	O(2)	C(8)	C(13)	O(6)	–178.7(1)
O(3)	C(7)	O(2)	C(8)	–143.2(1)	O(3)	C(7)	O(4)	C(9)	163.8(1)
O(3)	C(7)	C(6)	C(1)	160.5(1)	O(3)	C(7)	C(6)	C(5)	–19.4(2)
O(4)	C(7)	O(2)	C(8)	–22.7(1)	O(4)	C(7)	O(3)	C(11)	–57.6(2)
O(4)	C(7)	C(6)	C(1)	37.9(2)	O(4)	C(7)	C(6)	C(5)	–142.0(2)
O(4)	C(9)	C(8)	C(12)	151.0(1)	O(4)	C(9)	C(8)	C(13)	–83.3(1)
O(4)	C(9)	C(10)	C(1)	–33.8(2)	O(5)	C(13)	O(6)	C(14)	5.4(2)
O(5)	C(13)	C(8)	C(9)	112.5(2)	O(5)	C(13)	C(8)	C(12)	–118.8(2)

Table 5. (Continued from the preceding page)

O(6)	C(13)	C(8)	C(9)	–68.0(2)	O(6)	C(13)	C(8)	C(12)	60.8(2)
O(6)	C(14)	C(15)	C(16)	–119.2(2)	O(6)	C(14)	C(15)	C(20)	60.1(2)
C(1)	C(2)	C(3)	C(4)	–0.7(3)	C(1)	C(6)	C(5)	C(4)	–1.6(2)
C(1)	C(10)	C(9)	C(8)	77.8(2)	C(2)	C(1)	C(6)	C(5)	1.0(2)
C(2)	C(1)	C(6)	C(7)	–178.9(2)	C(2)	C(1)	C(10)	C(9)	177.1(2)
C(2)	C(3)	C(4)	C(5)	0.1(3)	C(3)	C(2)	C(1)	C(6)	0.1(3)
C(3)	C(2)	C(1)	C(10)	179.4(2)	C(3)	C(4)	C(5)	C(6)	1.1(3)
C(4)	C(5)	C(6)	C(7)	178.3(2)	C(5)	C(6)	C(1)	C(10)	–178.2(2)
C(6)	C(1)	C(10)	C(9)	–3.6(2)	C(6)	C(7)	O(2)	C(8)	93.9(1)
C(6)	C(7)	O(3)	C(11)	–178.5(2)	C(6)	C(7)	O(4)	C(9)	–74.5(1)
C(7)	O(2)	C(8)	C(9)	–5.6(1)	C(7)	O(2)	C(8)	C(12)	–129.2(1)
C(7)	O(2)	C(8)	C(13)	110.0(1)	C(7)	O(4)	C(9)	C(8)	–46.1(1)
C(7)	O(4)	C(9)	C(10)	72.5(1)	C(7)	C(6)	C(1)	C(10)	1.9(2)
C(8)	C(13)	O(6)	C(14)	–174.2(1)	C(10)	C(9)	C(8)	C(12)	34.4(2)
C(10)	C(9)	C(8)	C(13)	160.0(1)	C(13)	O(6)	C(14)	C(15)	72.2(2)
C(14)	C(15)	C(16)	C(17)	–179.9(2)	C(14)	C(15)	C(20)	C(19)	–179.5(2)
C(15)	C(16)	C(17)	C(18)	–0.5(3)	C(15)	C(20)	C(19)	C(18)	–0.6(3)
C(16)	C(15)	C(20)	C(19)	–0.2(3)	C(16)	C(17)	C(18)	C(19)	–0.4(3)
C(17)	C(16)	C(15)	C(20)	0.7(3)	C(17)	C(18)	C(19)	C(20)	0.9(3)

Figure 1. ORTEP Drawing of (–)-*exo*-**6f**





exo-**6f**

References and Notes

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1) (a) Suga, H.; Kakehi, A.; Ito, S.; Inoue, K.; Ishida, H.; Ibata, T. *Org. Lett.*, **2000**, *2*, 3145. (b) Suga, H.; Kakehi, A.; Ito, S.; Inoue, K.; Ishida, H.; Ibata, T. *Bull. Chem. Soc. Jpn.*, **2001**, *74*, 1115. (c) Ueda, K.; Ibata, T.; Takebayashi, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2779.

2) (a) Arndt, H. C.; Carroll, S. A. *Synthesis*, **1979**, 202. (b) Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 669 and references therein.

3) Yamamoto, Y.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Org. Chem.* **1986**, *51*, 886.

4) Jung, M. E.; Shishido, K.; Davis, L. H. *J. Org. Chem.* **1982**, *47*, 891.

5) Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt, P. *J. Am. Chem. Soc.* **1999**, *121*, 7559.

6) (*S*,*S*)-Pybox-*i*-Pr: (a) Totleben, M. J.; Prasad, J. S.; Simpson, J. H.; Chan, S. H.; Vanyo, D. J.; Kuehner, D. E.; Deshpande, R.; Kodersha, G. A. *J. Org. Chem.* **2001**, *66*, 1057. (b) Desimoni, G.; Faita, G.; Filippone, S.; Mella, M.; Zampori, M. G.; Zema, M. *Tetrahedron*, **2001**, *57*, 10203. (*S*,*S*)-Pybox-Ph: (c) Davies, I. W.; Gerena, L.; Lu, N.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **1996**, *61*, 9629. (*S*,*S*)-Pybox-TBSm: (d) Iwasa, S.; Nakamura, H.; Nishiyama, H. *Heterocycles*, **2000**, *52*, 939.