Highly Enantioselective 1,3-Dipolar Cycloaddition Reactions of 2-Benzopyrylium-4-olate Catalyzed by Chiral Lewis Acids

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Experimental Section

General. Melting points were determined on a Yanaco MP-13 melting point apparatus and are uncorrected. IR spectra were taken with a JASCO FT/IR-5300S spectrophotometer. ^1H NMR spectra were recorded on a JEOL JNM-LA400 (400 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on JEOL JNM-LA400 (100 MHz) spectrometer 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-resolution mass spectra were obtained on HITACHI M-80B spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN recorder. High performance liquid chromatography was performed on a SHIMADZU LC-VP system. Optical rotations were recorded with a JASCO P-1010 polarimeter. 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**) was prepared by the procedure in the previous paper.¹ Benzyloxyacetaldehyde (**3**) and its derivatives **4** – **8** were prepared according to the procedure in the literatures.² Benzyl pyruvate (**10**) was prepared by the procedure in the literature.³ 3-Acryloyl-2-oxazolinone (**11**) was prepared according to the procedure in the literature.⁴ Methyl pyruvate (**9**), $\text{Rh}_2(\text{OAc})_4$, $\text{Sc}(\text{OTf})_3$ and $\text{Yb}(\text{OTf})_3$ were commercially available, and used without further purification. 2,6-Bis(oxazolinyl)pyridines were prepared by the procedure in the literatures.⁵ Powdered 4 Å 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.

General Procedure for the Reaction of α -Diazoacetophenone **1 with Benzyloxyacetaldehyde (**3**) or its Derivatives **4** – **8**:** 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 $\text{Sc}(\text{OTf})_3$ (24.6 mg, 0.05 mmol) and powdered 4 Å molecular sieves (MS 4A, 0.50 g) in CH_2Cl_2 (1.0 mL). After stirring the mixture for 2 h, $\text{Rh}_2(\text{OAc})_4$ (4.4 mg, 0.01 mmol) and a solution of benzyloxyacetaldehyde or its derivatives (1.0 mmol) in CH_2Cl_2 (2.5 mL) 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

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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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 7-*Endo*-(benzyloxy)methyl-5-methoxy-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one.

Benzyloxyacetaldehyde (**3**) (150.2 mg, 140 μ L, 1.0 mmol) was used according to the general procedure. Purification by MPLC (3:97 AcOEt/hexane) gave 18.7 mg (11%) of *exo*-cycloadduct and 139.2 mg (85%) of *endo*-cycloadduct. ***Exo*-cycloadduct:** Colorless oil; IR (Neat) 2953, 2858, 1709, 1603, 1458, 1296, 1258, 1215, 1161, 1084, 1046, 951, 764, 748, 700 cm^{-1} ; ^1H 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; HRMS (EI) Found: 326.1126. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$ (M^+): 326.1153; R_f = 0.42 (2:3 AcOEt/hexane). ***Endo*-cycloadduct:** Colorless prisms; mp = 67 – 69 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{26}$ = -102° (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 (100MHz, 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 $\text{C}_{19}\text{H}_{18}\text{O}_5$ (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 $^\circ\text{C}$). *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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 5-Methoxy-7-*endo*-[(*o*-methoxybenzyl)oxy]methyl-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one.

[(*o*-Methoxybenzyl)oxy]acetaldehyde (**4**) (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*-cycloadduct and 124.6 mg (70%) of *endo*-cycloadduct. ***Exo*-cycloadduct:** Colorless prisms; mp = 76 – 78.5 $^\circ\text{C}$; 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); HRMS (EI) Found: 356.1254. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_6$ (M^+): 356.1259; R_f = 0.51 (3:7 AcOEt/hexane). ***Endo*-cycloadduct:** Colorless prisms; mp = 97.5 – 99.5 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{26}$ = -92° (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); HRMS (EI) Found: 356.1249. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_6$ (M^+): 356.1259; R_f = 0.45 (3:7 AcOEt/hexane). The enantiomeric excess was determined by

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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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 5-Methoxy-7-*endo*-[(*p*-methoxybenzyl)oxy]methyl-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one. [(*p*-Methoxybenzyl)oxy]acetaldehyde (**5**) (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*-cycloadduct and 85.5 mg (48%) of *endo*-cycloadduct. **Exo-cycloadduct:** 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); HRMS (EI) Found: 356.1228. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_6$ (M^+): 356.1259; R_f = 0.48 (3:7 AcOEt/hexane). **Endo-cycloadduct:** Colorless prisms; mp = 75 – 77 °C; $[\alpha]_D^{26}$ = -80° (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); HRMS (EI) Found: 356.1246. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_6$ (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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 7-*Endo*-[(*p*-fluorobenzyl)oxy]-5-methoxy-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one. [(*p*-

Fluorobenzyl)oxy]acetaldehyde (**6**) (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*-cycloadduct and 139.2 mg (80%) of *endo*-cycloadduct. **Exo-cycloadduct:** 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); HRMS (EI) Found: 344.1076. Calcd for $\text{C}_{19}\text{H}_{17}\text{FO}_5$ (M^+): 344.1059; R_f = 0.46 (3:7 AcOEt/hexane). **Endo-cycloadduct:** Colorless needles; mp = 112 – 114 °C; $[\alpha]_D^{26}$ = -98° (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

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(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); 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).

7-*Exo*-[(*p*-chlorobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 7-*Endo*-[(*p*-chlorobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one.

[(*p*-Chlorobenzyl)oxy]acetaldehyde (**7**) (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*-cycloadduct and 111.5 mg (62%) of *endo*-cycloadduct. **Exo-cycloadduct**: 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, $CDCl_3$) $\delta = 3.65$ (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); 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-cycloadduct**: Colorless needles; mp = 103 – 106 °C; $[\alpha]_D^{26} = -77^\circ$ (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, $CDCl_3$) $\delta = 3.31$ (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); 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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 7-*Endo*-[(*p*-bromobenzyl)oxy]methyl-5-methoxy-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one.

[(*p*-Bromobenzyl)oxy]acetaldehyde (**8**) (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*-cycloadduct and 98.0 mg (49%) of *endo*-cycloadduct. **Exo-cycloadduct**: Colorless oil; IR (Neat) 2953, 2859, 1713, 1603, 1487,

1460, 1294, 1260, 1217, 1161, 1084, 1046, 951 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) $\delta = 3.65$ (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); 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-cycloadduct**: Colorless needles; mp = 83 – 86 °C; $[\alpha]_D^{26} = -58^\circ$ (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, $CDCl_3$) $\delta =$

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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); 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).

5-Methoxy-7-*exo*-methoxycarbonyl-7-*endo*-methyl-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 5-Methoxy-7-*endo*-methoxycarbonyl-7-*exo*-methyl-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one. A solution of (*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 MS 4A (0.50 g) in CH_2Cl_2 (1.0 mL). After stirring the mixture for 2 h, $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol), a solution of methyl pyruvate (**9**) (102.1 mg, 90 μ L, 1.0 mmol) in CH_2Cl_2 (2.5 mL), and pyruvic acid (1 M solution in CH_2Cl_2 , 50 μ L, 0.05 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*, and the residue was purified by MPLC (3:97 – 5:95 AcOEt/hexane) to provide 118.2 mg (84%) of *exo*-cycloadduct and 5.3 mg (4%) of *endo*-cycloadduct. **Exo-cycloadduct:** Colorless prisms; mp = 84 – 86 °C; $[\alpha]_D^{23} = -133$ ° (c 1.01, $CHCl_3$); 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, $CDCl_3$) $\delta = 1.31$ (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). 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-cycloadduct:** Colorless prisms; 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, $CDCl_3$) $\delta = 1.84$ (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); 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-dioxabenzoc[bicyclo[3.2.1]octan-2-one and 7-*Endo*-(benzyloxy)carbonyl-5-methoxy-7-*exo*-methyl-6,8-dioxabenzoc[bicyclo[3.2.1]octan-2-one. A solution of (*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 MS 4A (0.50 g) in CH_2Cl_2 (1.0 mL). After stirring the mixture for 2 h, $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol), a solution of benzyl pyruvate (**10**) (178.2 mg, 1.0 mmol) in CH_2Cl_2 (2.5 mL), and pyruvic acid (1 M solution in CH_2Cl_2 , 0.1 mL, 0.1 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*, and the residue was purified by MPLC (3:97 – 5:95 AcOEt/hexane) to provide 10.8 mg (6%) of *endo*-

Supporting Information

cycloadduct and 204.6 mg of a mixture (54:46) of *exo*-cycloadduct and benzyl pyruvate. The yield of *exo*-cycloadduct was calculated from ^1H NMR (143.9 mg, 82%). ***Exo*-cycloadduct:** Colorless oil; $[\alpha]_{\text{D}}^{28} = -103^\circ$ (*c* 1.14, CHCl_3 , containing benzyl pyruvate (21 wt%)); 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) $\delta = 1.30$ (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) $\delta = 19.8, 50.4, 67.9, 79.2, 85.4, 118.9, 122.7, 126.4, 128.2, 128.5, 128.7, 128.8, 129.5, 134.8, 135.0, 143.2, 171.3, 191.5$; HRMS (EI) Found: 354.1072. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_6$ (M^+): 354.1102; $R_f = 0.53$ (3:7 AcOEt/hexane). ***Endo*-cycloadduct:** 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) $\delta = 1.84$ (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); HRMS (EI) Found: 354.1097. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_6$ (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 $^\circ\text{C}$): $t_{\text{R}} = 17.0$ min (minor) and 21.6 min (major). *Endo*-isomer (Daicel Chiralpak AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min, 35 $^\circ\text{C}$): $t_{\text{R}} = 13.3$ min (minor) and 17.6 min (major).

5,8-Epoxy-5-methoxy-6-*exo*-(2-oxazolidinoyl)carbonyl-9-oxo-6,7,8,9-tetrahydro-5H-benzocycloheptene and 5,8-Epoxy-5-methoxy-6-*endo*-(2-oxazolidinoyl)carbonyl-9-oxo-6,7,8,9-tetrahydro-5H-benzocycloheptene. 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 CH_2Cl_2 (1.5 mL) was added to a suspension of $\text{Yb}(\text{OTf})_3$ (31.0 mg, 0.05 mmol) and MS 4A (0.50 g) in CH_2Cl_2 (1.0 mL). After stirring the mixture for 2 h, $\text{Rh}_2(\text{OAc})_4$ (4.4 mg, 0.01 mmol) and a solution of 3-acryloyl-2-oxazolidinone (**11**) (144.1 mg, 1.0 mmol) in CH_2Cl_2 (2.5 mL) 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 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,

80 mL) as an eluent. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (3:7 – 1:1 AcOEt/hexane) to provide 141.6 mg (89%) of a mixture of *exo*- and *endo*-cycloadducts. The *exo/endo* ratio was determined by ^1H NMR analysis (*exo:endo* = 88:12). Colorless solid; $[\alpha]_{\text{D}}^{25} = +52^\circ$ (*c* 0.99, CHCl_3 , A mixture of *exo*- and *endo*-cycloadducts (88:12)); IR (KBr, A mixture of *exo*- and *endo*-cycloadducts) 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 $\text{C}_{16}\text{H}_{15}\text{NO}_6$: C, 60.57; H, 4.77; N, 4.41%. ***Exo*-cycloadduct:** ^1H NMR (CDCl_3 , 400 MHz) $\delta = 1.82$ (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) $\delta = 28.6, 43.0, 49.0, 53.9, 62.0, 80.2, 108.5, 124.7, 127.2, 129.2, 129.7, 134.3, 143.0, 153.1, 170.5, 194.6$; $R_f = 0.51$ (ether). ***Endo*-cycloadduct:** ^1H NMR (CDCl_3 , 400 MHz) $\delta = 2.22$ (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) $\delta = 29.6, 43.2, 46.8, 51.8, 61.9, 79.9, 108.2, 123.4, 126.9, 129.2, 130.2, 133.4, 142.3, 153.1, 170.5, 194.3$; $R_f = 0.45$ (ether). The enantiomeric excess was determined by HPLC analysis (Daicel

Supporting Information

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).

References and Notes

- 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.
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DFILE
 COMNT
 DATIM Sat Sep 7 08:01:04 2002
 OBNUC 1H
 EXMOD non
 OBFRQ 399.65 MHz
 OBSET 130.00 KHz
 OBFIN 4300.0 Hz
 POINT 32768
 FREQU 7993.6 Hz
 SCANS 4
 ACQTM 4.099 sec
 PD 2.901 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 24.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

Sat Sep 7 08:18:56 2002
1H
non

¹ H	399.65 MHz
	130.00 KHz
	4300.0 Hz
	32768
	7993.6 Hz
	4
	4.099 sec
	2.901 sec
	5.8 us
	24.5 °C
CDCl ₃	0.00 ppm
	0.12 Hz
	20

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

Sat Sep 7 08:54:15 2002
 1H
 non

399.65 MHz
 130.00 KHz
 4300.0 Hz
 32768
 7993.6 Hz
 4
 4.099 sec
 2.901 sec
 5.8 us
 1H
 24.6 c
 CDCL3
 0.00 ppm
 0.12 Hz
 19

Endo-cycloadduct

DFILE
 COMNT
 DATIM
 OBNUC 1H
 EXMOD non
 OBFRQ 399.65 MHz
 OBSET 130.00 KHz
 OBFIN 4300.0 Hz
 POINT 32768
 FREQU 7993.6 Hz
 SCANS 4
 ACQTM 4.099 sec
 PD 2.901 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 24.6 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 20

Sat Sep 7 09:06:36 2002
 1H
 non

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRO
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

Sat Sep 7 09:23:24 2002
 1H
 non
 399.65 MHz
 130.00 KHz
 4300.0 Hz
 32768
 7993.6 Hz
 4
 4.099 sec
 2.901 sec
 5.8 us
 1H
 24.5 c
 CDCL3
 0.00 ppm
 0.12 Hz
 20

Endo-cycloadduct

DFILE
 COMNT
 DATIM Sat Sep 7 09:34:11 2002
 OBNUC 1H
 EXMOD non
 OBFRQ 399.65 MHz
 OBSET 130.00 KHz
 OBFIN 4300.0 Hz
 POINT 32768
 FREQU 7993.6 Hz
 SCANS 4
 ACQTM 4.099 sec
 PD 2.901 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 20

DFILE
 COMNT
 DATIM Sat Sep 7 09:42:50 2002
 OBNUC 1H
 EXMOD non
 OBFRQ 399.65 MHz
 OBSET 130.00 KHz
 OBFIN 4300.0 Hz
 POINT 32768
 FREQU 7993.6 Hz
 SCANS 4
 ACQTM 4.099 sec
 PD 2.901 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 24.3 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

Sat Sep 7 09:55:52 2002
 1H
 non

399.65 MHz
 130.00 KHz
 4300.0 Hz
 32768
 7993.6 Hz
 4
 4.099 sec
 2.901 sec
 5.8 us
 1H
 24.6 c
 CDCL3
 0.00 ppm
 0.12 Hz
 19

Exo-cycloadduct

+

Benzyl pyruvate

(Exo-cycloadduct:Benzy pyruvate = 66:34)

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRO
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

Thu Aug 29 08:30:05 2002
 1H
 non

399.65 MHz
 130.00 KHz
 4300.0 Hz
 32768
 7993.6 Hz
 4
 4.099 sec
 2.901 sec
 5.8 us
 1H
 24.5 c
 CDCL3
 0.00 ppm
 0.12 Hz
 20

Exo/Endo Mixture
 (Exo:Endo = 88:12)

Endo-cycloadduct

Racemate

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@KI.C02 01/06/30 14:13:50

Sample Name : KI-250-2

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AS, i-PrOH:HEXANE = 1:19, FLOW = 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	12.166	5708958	208624			49.3874	
	2	13.416	5850584	187450	V		50.6126	
TOTAL			11559542	396074			100	

91%ee (-)

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@KI.C02 01/10/04 10:37:52

Sample Name : KI-284-2 (ENDO)

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AS, i-PrOH:HEXANE = 1:19, FLOW = 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	11.319	59593	2233			3.2711	
	2	12.274	80540	2971	V		4.421	
	3	13.61	1681634	54619	V		92.3079	
TOTAL			1821766	59823			100

Exo-cycloadduct

Racemate

C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@KI.C01 02/01/17 10:15:26

Sample Name : KI-325-1

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AS, i-PrOH:HEXANE = 1:19, FLOW = 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	10.464	1200436	58697			49.976	
	2	11.772	1201591	45209	V		50.024	
TOTAL			2402027	103906			100	

78%ee (-)

C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@KI.C01 02/09/19 18:28:52

Sample Name : KI-427-1 (EXO)

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AS, 1:19 i-PrOH/HEXANE, FLOW 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	10.743	617281	29032			10.9489	
	2	11.66	11922	532	V		0.2115	
	3	12.392	5008635	169344	SV		88.8396	
TOTAL			5637838	198907			100

Exo-cycloadduct

Racemate

C-RSA CHROMATOPAC CH=1 Report No.=15 DATA=1:@KI.C06 02/06/04 15:41:40

Sample Name : KI-381-1 (EXO)

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AD, 1:19 i-PrOH/HEXANE, FLOW 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	16.723	1236	69			0.0491	
	3	17.526	1258183	55400	V		50.0208	
	6	22.423	1255900	42996	V		49.93	
TOTAL			2515318	98465			100	

87%ee (-)

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@KI.C01 02/09/21 18:55:50

Sample Name : KI-429-1 (EXO)

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AD, 1:19 i-PrOH/HEXANE, FLOW 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	17.01	298787	13369			6.3406	
	2	21.631	4413471	153623	S		93.6594	
TOTAL			4712258	166992			100

Exo-cycloadduct

Racemate

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@KI.C01 02/09/14 13:37:28

Sample Name : KI-348-1

Sample ID :

Operator : KEI INOUE

Comment : CHIRALPAK AS, 1:4 i-PrOH/HEXANE, FLOW 0.5 mL/min, 35 oC

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	26.207	1006007	11958			49.9888	
	2	30.732	1006458	8119	V		50.0112	
TOTAL			2012465	20077			100	

98%ee (+)

C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@SH.C01 02/05/28 10:28:56

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	25.897	2532798	32144			98.9632	
	2	30.137	26534	232	V		1.0367	
TOTAL			2559331	32376			100	