Supporting Information

Stereocontrol in Rare Earth Metal Triflate-Catalyzed 1,3-dipolar Cycloaddition Reaction of 2-Benzoprylium-4-olate with Aldehydes

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Experimental Section

General. ^{1}H NMR spectrum was recorded at 60 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. For preparative column chromatography, Wakogel C-300 and Silica gel 60 (Merck) were employed. Medium pressure liquid chromatography was carried out using a column packed with Silica gel 60 (Merck, size 0.040 – 0.063 mm). 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] Benzyloxyacetoaldehyde was prepared according to the procedure in the literature.[2] Other aldehydes were commercially available and purified by distillation or recrystallization prior to use. Benzene, diethyl ether, and THF were freshly distilled from a sodium benzophenone still under argon. CH_2Cl_2, $CHCl_3$, and $ClCH_2CH_2Cl$ were purified by distillation first from $CaCl_2$ and then CaH_2 under argon. $Sc(OTf)_3$, $Mg(OTf)_2$, and $Ln(OTf)_3$ were commercially available and were dried by heating in *vacuo* at 140 ºC for 8 h before use.

Typical Experimental Procedure for the Reaction of α-Diazoacetophenone 1 with Aldehyde: To a solution of aldehyde (1.0 mmol), $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol), $Yb(OTf)_3$ (31.1 mg, 0.05 mmol), and MS 4A (0.5 g) in diethyl ether (5.0 mL) was added diazoacetophenone **1** (102.1 mg, 0.5 mmol) in diethyl ether (5 mL) over a period of 1h at room temperature. After removal of MS 4A through celite, the reaction mixture was filtered through a plug of silica gel with AcOEt/hexane (1:1) as eluent. The solvent was removed *in vacuo* to give the mixture which was purified by medium pressure liquid chromatography (MPLC) (silica gel, 1:99 – 10:90 AcOEt/hexane).

5-methoxy-7-*exo*-phenyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (2a) and 5-methoxy-7-*endo*-phenyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (2b). The general procedure was followed using benzaldehyde (102 μL, 1 mmol). The crude mixture was analyzed by HPLC (WATERS Nova-Pak C18 column, 7:3 MeOH/H_2O, flow rate = 0.5 mL/min, *endo*-isomer: t_R = 22.5 min, *exo*-isomer: t_R = 41.1 min) using naphthalene as the internal standard. The products could be also separated by MPLC (silica gel, 1:99 – 3:97 AcOEt/hexane). The spectroscopic data were previously reported.[3]

5-methoxy-7-*exo*-(4-methoxyphenyl)-6.8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (3a) and 5-methoxy-7-*endo*-(4-methoxyphenyl)-6.8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (3b). The general procedure was followed using *p*-anisaldehyde (122 μL, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (1:99 – 3:97) gave 105.9 mg (67%) of **3a** and 15.5 mg (10%) of **3b**. The spectroscopic data were previously reported.[3]

5-methoxy-7-*exo*-(4-nitrophenyl)-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (4a) and 5-methoxy-7-*endo*-(4-nitrophenyl)-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (4b). The general procedure was followed using *p*-nitrobenzaldehyde (151.1 mg, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (2:98 – 10:90) gave 131.6 mg (81%) of **4a** and 29.1 mg (18%) of **4b**. The spectroscopic data were previously reported.[3]

5-methoxy-7-*exo*-propyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (5a) and 5-methoxy-7-*endo*-propyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (5b). The general procedure was followed using butyraldehyde (90 μL, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (1:99) gave mixture of **5a** and **5b** (111.3 mg, 89%) as colorless liquid. The *exo*/*endo* ratio was determined by ^{1}H NMR and HPLC analysis (WATERS Nova-Pak C18 column, 7 : 3 MeOH/H_2O, flow rate = 0.5 mL/min, *endo*-isomer t_R = 29.1 min, *exo*-isomer t_R = 37.2 min). IR spectrum and elemental analysis were obtained as a mixture of *exo*- and *endo*-isomers. IR (Neat) 2957, 2876, 1709 (C=O), 1605,1460, 1291, 1258, 1217, 1159, 1076, 1049, 993, 957, 466 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. found: C, 67.34; H, 6.53. The ^{1}H NMR spectrum of **5a** and **5b** was assigned as follows. **5a**: ^{1}H NMR (60 MHz, $CDCl_3$) δ = 0.7 – 2.2 (m, 7H, $CH_2CH_2CH_3$), 3.5 – 4.2 (m, 1H, H-7), 3.70 (s, 3H, OMe), 4.64 (s, 1H, H-1), 7.3 – 8.3 (m, 4H, ArH). **5b**: ^{1}H NMR (60 MHz, $CDCl_3$) δ = 0.7 – 2.2 (m, 7H, $CH_2CH_2CH_3$), 3.70 (s, 3H, OMe), 4.2 – 4.8 (m, 1H, H-7), 4.96 (d, *J* = 6.0 Hz, 1H, H-1), 7.3 – 8.3 (m, 4H, ArH).

5-methoxy-7-*exo*-(2-methylethyl)-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (6a) and , 5-methoxy-7-*endo*-(2-methylethyl)-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (6b). The general procedure was followed using isobutyraldehyde (91 μL, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (1:99) gave mixture of **6a** and **6b** (80.4 mg, 65%). The *exo*/*endo* ratio was determined by ^{1}H NMR and HPLC analysis (WATERS Nova-Pak C18 column, 7:3 MeOH:H_2O, flow rate = 0.5 mL/min, *endo*-isomer: t_R = 31.0 min, *exo*-isomer: t_R = 34.6 min). The spectrum data were previously reported.[3]

7-*exo*-cyclohexyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (7a) and 7-*endo*-cyclohexyl-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (7b). The general procedure was followed using cyclohexanecarboxaldehyde (121 μL, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (1:99) gave mixture of **7a** and **7b** (137.2 mg, 95%) as colorless oil. The *exo*/*endo* ratio was determined by ^{1}H NMR and HPLC analysis (WATERS Nova-Pak C18 column, 7:3 MeOH/H_2O, flow rate = 0.5 mL/min, *endo*-isomer t_R = 78.1 min, *exo*-isomer t_R = 101.2 min). IR and MS spectra were obtained as a mixture of *exo*- and *endo*-isomers. IR (Neat) 2928, 1738, 1707 (C=O), 1603, 1451, 1292, 1242, 1213, 1157, 1076, 1047, 1024, 957, 766, 610 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{20}O_4$ (M^+) 288.1362, found 288.1361. The ^{1}H NMR spectrum of **7a** and **7b** was assigned as follows. **7a**: ^{1}H NMR (60 MHz, $CDCl_3$) δ = 0.6 – 2.4 (m, 11H, *c*-hexyl), 3.52 (d, *J* = 8.1 Hz, 1H, H-7), 3.70 (s, 3H, OMe), 4.71 (s, 1H, H-1), 7.1 – 8.3 (m, 4H, ArH). **7b**: ^{1}H NMR (60 MHz, $CDCl_3$) δ = 0.6 – 2.4 (m, 11H, *c*-hexyl), 3.5 – 4.3 (m, 1H, H-7), 3.64 (s, 3H, OMe), 4.94 (d, *J* = 5.1 Hz, 1H, H-1), 7.1 – 8.3 (m, 4H, ArH).

7-*exo*-benzyloxymethyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (8a) and 7-*endo*-benzyloxymethyl-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (8b). The general procedure was followed using benzyloxyaectaldehyde (140 μL, 1 mmol). Purification by MPLC with elution by AcOEt/hexane (3:97) gave 146.5 mg (90%) of **8a** and 11.1 mg (7%) of **8b**. **8a**: colorless oil; IR (Neat) 2953, 2858, 1709 (C=O), 1603, 1458, 1296, 1258, 1215, 1161, 1084, 1046, 951, 764, 748, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ = 3.66 (s, 3H, OMe), 3.76 (d, *J* = 8.0 Hz, 2H, **CH_2**OBn), 3.9 – 4.3 (m, 1H, H-7), 4.66 (s, 2H, O**CH_2**Ph), 4.68 (s, 1H, H-1), 7.2 – 8.4 (m, 9H, ArH); HRMS (CI) calcd for $C_{19}H_{18}O_5$ (M^+) 326.1154, found 326.1126. **8b**: colorless crystals; mp = 67 – 69 °C; IR (KBr) 2957, 2895, 1711 (C=O), 1603, 1456, 1379, 1318, 1287, 1248, 1217, 1157, 1090, 1049, 1026, 1007, 976, 947, 889, 752, 704, 594 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ = 3.2 – 3.6 (m, 2H, **CH_2**OBn), 3.71 (s, 3H, OMe), 4.42 (s,

2H, O**CH$_2$**Ph), 4.5 – 4.9 (m, 1H, H-7), 5.02 (d, *J* = 6.0 Hz, 1H, H-1), 7.0 – 8.3 (m, 9H, ArH); HRMS (CI) calcd for $C_{19}H_{18}O_5$ (M^+) 326.1154, found 326.1163.

Reaction of 1 with Benzyloxyaectaldehyde in the Presence of Yb[(*S*)-BNP]$_3$. The reaction was carried out according to the general procedure using Yb[(*S*)-BNP]$_3$ (60.7 mg, 0.05 mmol) instead of Yb(OTf)$_3$. The enantiomeric excess was determined by chiral HPLC analysis (Daicel Chiralpak AS, 1:19 *i*-PrOH/hexane, Flow rate = 0.5 mL/min 35 °C, *exo*-isomer: t_R = 16.4 min (major) and 20.4 min (minor), *endo*-isomre: t_R = 15.4 min (major) and 18.7 min (minor).

References and Notes

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