Advanced Synthesis & Catalysis

Supporting Information

Catalytic Enantioselective Tandem Carbonyl Ylide Formation/1,3-Dipolar Cycloaddition Reactions of α-Diazo Ketones with Aromatic Aldehydes Using Dirhodium(II) Tetrakis[*N*-benzene-fused-phthaloyl-(*S*)-valinate]

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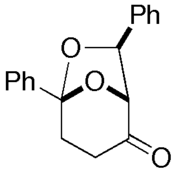
Supporting Information

General. Melting points were determined on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-EX 270 (270 MHz) or AL 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; δ_H 0.00). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. ^{13}C NMR spectra were recorded on JEOL JNM-EX 270 (67.8 MHz) or AL 400 (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$; δ 77.0). Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). EI-MS spectra were obtained on a JEOL JMS-HX 110 spectrometer. Column chromatography was carried out on Kanto silica gel 60 N (63-210 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on JASCO PU-980 intelligent HPLC pump with JASCO UV-970 intelligent UV/VIS detector. Detection was performed at 254 or 220 nm. Chiralpak AD-H and Chiralcel OD-H columns (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratio were determined with Shimadzu C-R6A or C-R8A chromatopac integrator or JASCO-Borwin analysis system.

All non-aqueous reactions were carried out in flame-dried glassware under argon atmosphere. Reagents and solvents were purified by standard means.

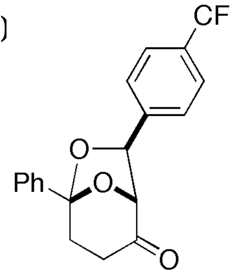
5,7-*exo*-Diphenyl-6,8-dioxabicyclo[3.2.1]octan-2-one (7a)[1]



Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5a** (91.0 mg, 0.45 mmol) and **6a** (96.0

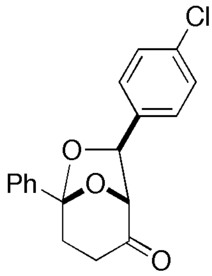
mg, 0.90 mmol), **7a** (60.4 mg, 48%, colorless oil) was obtained; TLC R_f 0.50 (5:1 benzene/Et_2O); $[\alpha]^{21}_{,\mathrm{D}}$ +34.1 (*c* 1.24, $CHCl_3$) for 78% ee; IR (film) ν 3063, 2934, 1734, 1451 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.41–2.59 (2H, m, C*H*$_2$), 2.68 (1H, dddd, *J* = 17.3, 7.8, 3.2, 1.4 Hz, C*H*$_2$), 2.83 (1H, dt, *J* = 17.3, 8.6 Hz, C*H*$_2$), 4.49 (1H, s, COC*H*), 5.29 (1H, s, ArC*H*), 7.16–7.23 (5H, m, *Ar*), 7.36–7.48 (3H, m, *Ar*), 7.64–7.70 (2H, m, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 33.0 (CH_2), 37.2 (CH_2), 80.6 (CH), 87.0 (CH), 109.7 (C), 125.1 (CH), 125.9 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.6 (C), 139.2 (C), 140.0 (C), 204.6 (C); LRMS (EI) *m/z* 280 (M^+), 223, 174, 158, 105, 77. The enantiomeric excess of **7a** was determined to be 78% by HPLC using Daicel Chiralpak AD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 220 nm): t_R = 6.0 min for the minor enantiomer; t_R = 7.5 min for the major enantiomer.

5-Phenyl-7-*exo*-(4-trifluoromethylphenyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (7c)



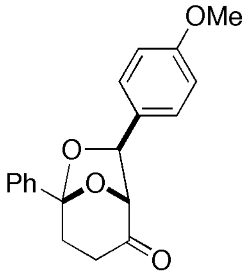
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5a** (60.6 mg, 0.30 mmol) and **6c** (104.5 mg, 0.60 mmol), **7c** (72.0 mg, 69%, colorless oil) was obtained; TLC R_f 0.41 (5:1 benzene/Et_2O); $[\alpha]^{22}_{,\mathrm{D}}$ +38.8 (*c* 1.28, $CHCl_3$) for 91% ee; IR (KBr) ν 2847, 1732, 1327 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.35–2.50 (2H, m, C*H*$_2$), 2.62 (1H, dddd, *J* = 17.6, 8.0, 2.8, 1.2 Hz, C*H*$_2$), 2.74 (1H, dt, *J* = 17.6, 8.4 Hz, C*H*$_2$), 4.40 (1H, s, COC*H*), 5.26 (1H, s, ArC*H*), 7.17–7.21 (2H, m, *Ar*), 7.33–7.41 (5H, m, *Ar*), 7.54–7.59 (2H, m, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.2 (CH_2), 37.2 (CH_2), 79.9 (CH, d, *J* = 9.5 Hz), 86.8 (CH, d, *J* = 7.1 Hz), 109.9 (C), 123.7 (CF_3, q, *J* = 271.5 Hz), 125.0 (CH, d, *J* = 48.9 Hz), 126.1 (CH), 128.3 (CH), 128.5 (CH, d, *J* = 38.1 Hz), 130.1 (C, q, *J* = 32.1 Hz), 138.7 (C), 143.6 (C), 203.8 (C); LRMS (EI) *m/z* 348 (M^+), 329, 291, 226, 174, 105, 77; HRMS (EI) calcd for $C_{19}H_{15}F_3O_3$ (M^+) 348.0973, found 348.0960; Anal. Calcd for $C_{19}H_{15}F_3O_3$: C, 65.52; H, 4.34. Found: C, 65.29; H, 4.39. The enantiomeric excess of **7c** was determined to be 91% by HPLC using Daicel Chiralcel OD-H column (9:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 220 nm): t_R = 8.3 min for the minor enantiomer; t_R = 9.9 min for the major enantiomer.

7-*exo*-(4-Chlorophenyl)-5-phenyl-6,8-dioxabicyclo[3.2.1]octan-2-one (7d)



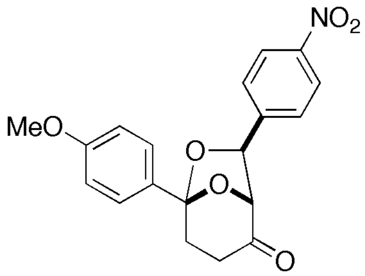
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5a** (60.6 mg, 0.30 mmol) and **6d** (84.0 mg, 0.60 mmol), **7d** (64.1 mg, 68%, colorless oil) was obtained; TLC R_f 0.41 (5:1 benzene/Et_2O); $[\alpha]^{22}_{,\mathrm{D}}$ +34.9 (*c* 1.09, $CHCl_3$) for 88% ee; IR (film) ν 3034, 2934, 1736, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34–2.48 (2H, m, C*H*$_2$), 2.60 (1H, dddd, *J* = 17.6, 8.0, 2.8, 1.2 Hz, C*H*$_2$), 2.73 (1H, dt, *J* = 17.6, 8.4 Hz, C*H*$_2$), 4.37 (1H, s, COC*H*), 5.18 (1H, s, ArC*H*), 6.99–7.04 (2H, m, *Ar*), 7.12–7.15 (2H, m, *Ar*), 7.32–7.44 (3H, m, *Ar*), 7.54–7.59 (2H, m, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 33.0 (CH_2), 37.0 (CH_2), 79.9 (CH), 86.9 (CH), 109.8 (C), 125.0 (CH), 127.3 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 134.0 (C), 138.5 (C), 139.0 (C), 204.4 (C); LRMS (EI) *m/z* 314 (M^+), 192, 174, 157, 132, 105, 77; HRMS (EI) calcd for $C_{18}H_{15}ClO_3$ (M^+) 314.0710, found 314.0724; Anal. Calcd for $C_{18}H_{15}ClO_3$: C, 68.68; H, 4.80; Cl, 11.26. Found: C, 68.42; H, 4.85; Cl, 10.99. The enantiomeric excess of **7d** was determined to be 88% by HPLC using Daicel Chiralcel OD-H column

(9:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 220 nm): t_R = 8.9 min for the minor enantiomer; t_R = 10.0 min for the major enantiomer.



7-*exo*-(4-Methoxyphenyl)-5-phenyl-6,8-dioxabicyclo[3.2.1]octan-2-one (**7e**)

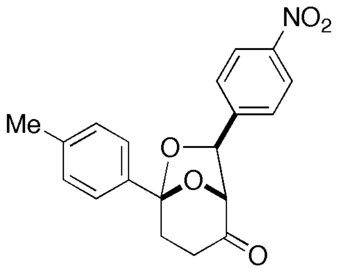
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5a** (60.6 mg, 0.30 mmol) and **6e** (81.7 mg, 0.60 mmol), **7e** (23.9 mg, 26%, pale yellow oil) was obtained; TLC R_f 0.50 (5:1 benzene/Et_2O); $[\alpha]^{21}{}_{,D}$ +21.7 (*c* 0.44, $CHCl_3$) for 76% ee; IR (film) ν 2934, 2837, 1732, 1613, 1514 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.40–2.56 (2H, m, CH_2), 2.61–2.72 (1H, m, CH_2), 2.82 (1H, dt, *J* = 17.8, 8.6 Hz, CH_2), 3.75 (3H, s, $ArOCH_3$), 4.46 (1H, s, COC*H*), 5.25 (1H, s, ArC*H*), 6.76–6.80 (2H, m, *Ar*), 7.09–7.13 (2H, m, *Ar*), 7.37–7.47 (3H, m, *Ar*), 7.65–7.69 (2H, m, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 33.1 (CH_2), 37.2 (CH_2), 55.2 (CH_3), 80.4 (CH), 87.1 (CH), 109.5 (C), 113.9 (CH), 125.1 (CH), 127.3 (CH), 128.4 (CH), 128.6 (CH), 132.2 (C), 139.3 (C), 159.5 (C), 204.8 (C); LRMS (EI) *m/z* 310 (M^+), 188, 174, 146, 132, 105, 77; HRMS (EI) calcd for $C_{19}H_{18}O_4$ (M^+) 310.1205, found 310.1192. The enantiomeric excess of **7e** was determined to be 76% by HPLC using Daicel Chiralcel OD-H column (9:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 220 nm): t_R = 10.2 min for the minor enantiomer; t_R = 17.6 min for the major enantiomer.



5-(4-Methoxyphenyl)-7-*exo*-(4-nitrophenyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (7f)

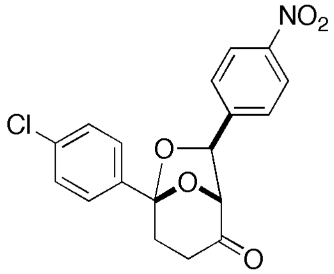
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5b** (93.0 mg, 0.40 mmol) and **6b** (121 mg, 0.80 mmol), **7f** (95.2 mg, 67%, white solid) was obtained; TLC R_f 0.50 (5:1 benzene/Et_2O); mp 128.5–129.5 °C (hexane/EtOAc); $[\alpha]^{20}{}_{,D}$ +67.2 (*c* 1.27, $CHCl_3$) for 88% ee; IR (KBr) ν 3439, 2940, 1736, 1613, 1526, 1348 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.41–2.61 (2H, m, CH_2), 2.64–2.88 (2H, m, CH_2), 3.87 (3H, s, OCH_3), 4.47 (1H, s, COC*H*), 5.35 (1H, s, ArC*H*), 6.98 (2H, d, *J* = 9.2 Hz, *Ar*), 7.35 (2H, d, *J* = 8.6 Hz, *Ar*), 7.58 (2H, d, *J* = 9.2 Hz, *Ar*), 8.12 (2H, d, *J* = 8.6 Hz, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 33.0 (CH_2), 36.9 (CH_2), 55.3 (CH_3), 79.6 (CH), 86.7 (CH), 110.3 (C), 113.8 (CH), 123.7 (CH), 126.3 (CH), 126.8 (CH), 131.0 (C), 147.2 (C), 147.7 (C), 160.0 (C), 204.1 (C); LRMS (EI) *m/z* 355 (M^+), 298, 135, 77; HRMS (EI) calcd for $C_{19}H_{17}NO_6$ (M^+) 355.1056, found 355.1059; Anal. Calcd for $C_{19}H_{17}NO_6$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.38; H, 4.92; N, 3.91. The enantiomeric excess of **7f** was determined to be 88% by HPLC using Daicel Chiralpak AD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 15.9 min for the major enantiomer; t_R = 18.3 min for the minor enantiomer.

5-(4-Methylphenyl)-7-*exo*-(4-nitrophenyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (7g)



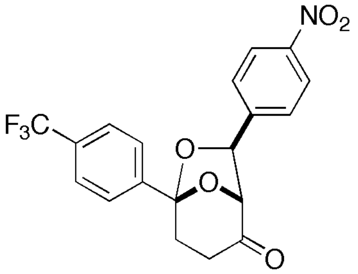
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5c** (64.9 mg, 0.30 mm) and **6b** (91.0 mg, 0.80 mmol), **7g** (61.0 mg, 60%, pale yellow solid) was obtained; TLC R_f 0.34 (5:1 benzene/Et_2O); mp 166.0–167.0 °C (hexane/EtOAc); $[\alpha]^{22}{}_{,D}$ +66.9 (*c* 1.16, $CHCl_3$) for 88% ee; IR (KBr) ν 2996, 2936, 1740, 1605, 1524, 1342 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.42 (3H, s, ArC*H*$_3$), 2.40–2.60 (2H, m, C*H*$_2$), 2.64–2.88 (2H, m, C*H*$_2$), 4.47 (1H, s, COC*H*), 5.35 (1H, s, ArC*H*), 7.25–7.28 (2H, m, *Ar*), 7.32–7.37 (2H, m, *Ar*), 7.51–7.55 (2H, m, *Ar*), 8.09–8.14 (2H, m, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.2 (CH_3), 33.0 (CH_2), 36.9 (CH_2), 79.6 (CH), 86.6 (CH), 110.4 (C), 123.6 (CH), 124.9 (CH), 126.8 (CH), 129.2 (CH), 135.8 (C), 138.8 (C), 147.1 (C), 147.7 (C), 204.0 (C); LRMS (EI) *m/z* 339 (M^+), 282, 119; HRMS (EI) calcd for $C_{19}H_{17}NO_5$ (M^+) 339.1106, found 339.1112; Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.22; H, 5.08; N, 4.12. The enantiomeric excess of **7g** was determined to be 88% by HPLC using Daicel Chiralpak AD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 12.0 min for the major enantiomer; t_R = 13.5 min for the minor enantiomer.

5-(4-Chlorophenyl)-7-*exo*-(4-nitrophenyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (7h)



Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5d** (71.0 mg, 0.30 mmol) and **6b** (91.0 mg, 0.60 mmol), **7h** (86.3 mg, 80%, white solid) was obtained; TLC R_f 0.38 (5:1 benzene/Et_2O); mp 148.5–149.0 °C; $[\alpha]^{21}{}_{,D}$ +63.5 (*c* 1.32, $CHCl_3$) for 89% ee; IR (KBr) ν 3447, 1740, 1603, 1520, 1346 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40–2.56 (2H, m, CH_2), 2.68–2.86 (2H, m, CH_2), 4.49 (1H, s, COC*H*), 5.37 (1H, s, ArC*H*), 7.31 (2H, d, *J* = 8.8 Hz, *Ar*), 7.44 (2H, d, *J* = 8.8 Hz, *Ar*), 7.59 (2H, d, *J* = 8.8 Hz, *Ar*), 8.11 (2H, d, *J* = 8.8 Hz, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9 (CH_2), 36.9 (CH_2), 79.6 (CH), 86.6 (CH), 109.8 (C), 123.7 (CH), 126.3 (CH), 126.7 (CH), 128.7 (CH), 134.9 (C), 137.2 (C), 146.6 (C), 147.6 (C), 203.4 (C); LRMS (EI) *m/z* 359 (M^+), 302, 139. HRMS (EI) calcd for $C_{18}H_{14}ClNO_5$ (M^+) 359.0560, found 359.0551; Anal. Calcd for $C_{18}H_{14}ClNO_5$: C, 60.09; H, 3.92; N, 3.89; Cl, 9.85. Found: C, 59.91; H, 4.06; N, 3.78; Cl, 9.80. The enantiomeric excess of **7h** was determined to be 89% by HPLC using Daicel Chiralcel OD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 15.3 min for the minor enantiomer; t_R = 18.6 min for the major enantiomer.

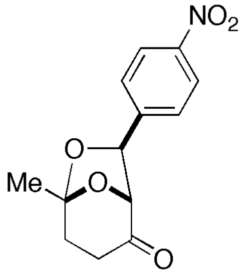
7-*exo*-(4-Nitrophenyl)-5-(4-trifluoromethylphenyl)-6,8-dioxabicyclo-[3.2.1]octan-2-one (7i)



Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5e** (81.0 mg, 0.30

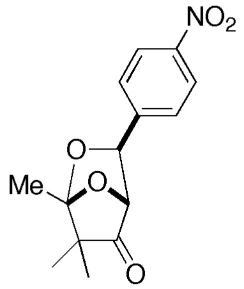
mmol) and **6b** (91.0 mg, 0.60 mmol), **7i** (87.2 mg, 74%, white solid) was obtained; TLC R_f 0.27 (5:1 benzene/Et$_2$O); mp 158.0–159.0 °C; $[\alpha]^{22}{}_{,D}$ +51.5 (*c* 1.29, CHCl$_3$) for 89% ee; IR (KBr) ν 3439, 1740, 1603, 1524, 1337 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.41–2.58 (2H, m, C*H*$_2$), 2.71–2.89 (2H, m, C*H*$_2$), 4.52 (1H, s, COC*H*), 5.40 (1H, s, ArC*H*), 7.30 (2H, d, *J* = 8.8 Hz, *Ar*), 7.74 (2H, d, *J* = 8.0 Hz, *Ar*), 7.79 (2H, d, *J* = 8.0 Hz, *Ar*), 8.12 (2H, d, *J* = 8.8 Hz, *Ar*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.9 (CH$_2$), 36.9 (CH$_2$), 79.7 (CH), 86.6 (CH), 109.7 (C), 123.7 (CH), 123.8 (CF$_3$, q, *J* = 270.6 Hz,), 125.4 (CH), 125.6 (CH, q, *J* = 3.3 Hz), 126.6 (CH), 131.1 (C, q, *J* = 33.0 Hz), 142.4 (C), 146.5 (C), 147.7 (C), 203.1 (C); LRMS (EI) *m/z* 393 (M$^+$), 374, 336, 242, 229, 203, 173, 145; HRMS (EI) calcd for $C_{19}H_{14}F_3NO_5$ (M$^+$) 393.0824, found 393.0818; Anal. Calcd for $C_{19}H_{14}F_3NO_5$: C, 58.02; H, 3.59; N, 3.56. Found: C, 57.94; H, 3.71; N, 3.52. The enantiomeric excess of **7i** was determined to be 89% by HPLC using Daicel Chiralpak AD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 15.2 min for the major enantiomer; t_R = 21.4 min for the minor enantiomer.

5-Methyl-7-*exo*-(4-nitrophenyl)-6,8-dioxabicyclo[3.2.1]octan-2-one (7j)



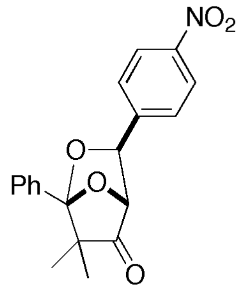
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5f** (140 mg, 1.0 mmol) and **6b** (302 mg, 2.0 mmol), **7j** (38 mg, 14%, white solid) was obtained; TLC R_f 0.23 (5:1 benzene/Et$_2$O); mp 126.0–127.0 °C; $[\alpha]^{22}{}_{,D}$ +2.4 (*c* 1.20, CHCl$_3$) for 19% ee; IR (KBr) ν 3441, 2955, 2934, 1728, 1603, 1522, 1348 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.81 (3H, s, C*H*$_3$), 2.26–2.31 (2H, m, COCC*H*$_2$), 2.59–2.66 (2H, m, COC*H*$_2$), 4.35 (1H, s, COC*H*), 5.15 (1H, s, ArC*H*), 7.54 (2H, d, *J* = 8.6 Hz, *Ar*), 8.23 (2H, d, *J* = 8.6 Hz, *Ar*); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 23.9 (CH$_3$), 32.4 (CH$_2$), 34.8 (CH$_2$), 79.2 (CH), 86.5 (C), 109.8 (C), 123.8 (CH), 126.7 (CH), 147.4 (C), 147.8 (C), 204.5 (C); LRMS (EI) *m/z* 263 (M$^+$), 221, 203, 165, 112, 99; HRMS (EI) calcd for $C_{13}H_{13}NO_5$ (M$^+$) 263.0793, found 263.0800; Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.34; H, 5.05; N, 5.34. The enantiomeric excess of **7j** was determined to be 19% by HPLC using Daicel Chiralpak AD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 11.9 min for the minor enantiomer; t_R = 15.2 min for the major enantiomer.

6-*exo*-(4-Nitrophenyl)-3,3,4-trimethyl-5,7-dioxabicyclo[2.2.1]heptan-2-one (7k)



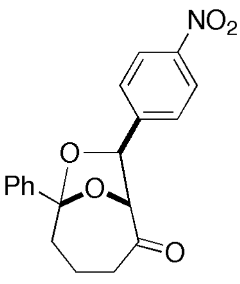
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5g** (15 mg, 0.10 mmol) and **6b** (30 mg, 0.20 mmol), **7k** (20.5 mg, 74%, white solid) was obtained; TLC R_f 0.54 (5:1 benzene/Et$_2$O); mp 133.0–134.0 °C; $[\alpha]^{26}{}_{,D}$ –25.4 (*c* 0.87, CHCl$_3$) for 12% ee; IR (KBr) ν 3441, 2973, 2940, 1769, 1607, 1526, 1346 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.14 (3H, s, C*H*$_3$), 1.19 (3H, s, C*H*$_3$), 1.75 (3H, s, C*H*$_3$), 4.47 (1H, s, COC*H*), 4.90 (1H, s, ArC*H*), 7.53 (2H, d, *J* = 8.3 Hz, *Ar*), 8.24 (2H, d, *J* = 8.3 Hz, *Ar*); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 14.7 (CH$_3$), 18.9 (CH$_3$), 20.6 (CH$_3$), 52.8 (C), 76.5 (CH), 85.7 (CH), 115.1 (C), 123.7 (CH), 127.1 (CH), 146.1 (C), 147.9 (C), 212.6 (C); LRMS (EI) *m/z* 277 (M$^+$), 207, 165, 126, 97, 70; HRMS (EI) calcd for $C_{14}H_{15}NO_5$ (M$^+$) 277.0950, found 277.0958; Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.64; H, 5.56; N, 4.94. The enantiomeric excess of **7k** was determined to be 12% by HPLC using Daicel Chiralcel OD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 7.0 min for the major enantiomer; t_R = 8.4 min for the minor enantiomer.

3,3-Dimethyl-6-*exo*-(4-nitrophenyl)-4-phenyl-5,7-dioxabicyclo[2.2.1]heptan-2-one (7l)



Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5h** (21.6 mg, 0.10 mmol) and **6b** (30 mg, 0.20 mmol), **7l** (21 mg, 62%, white solid) was obtained; TLC R_f 0.66 (5:1 benzene/Et_2O); mp 149.0–150.0 ºC; IR (KBr) ν 3437, 2907, 1773, 1599, 1518, 1346 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (3H, s, C*H*$_3$), 1.30 (3H, s, C*H*$_3$), 4.67 (1H, s, COC*H*), 5.11 (1H, s, ArC*H*), 7.41 (2H, d, *J* = 8.6 Hz, *Ar*), 7.49–7.51 (3H, m, *Ar*), 7.60–7.66 (2H, m, *Ar*), 8.15 (2H, d, *J* = 8.6 Hz, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.6 (CH_3), 20.8 (CH_3), 54.6 (C), 76.5 (CH), 85.5 (CH), 115.3 (C), 123.6 (CH), 126.0 (CH), 127.2 (CH), 128.3 (CH), 129.4 (CH), 132.4 (C), 145.8 (C), 147.9 (C), 212.0 (C); LRMS (EI) *m/z* 339 (M^+), 269, 131, 105; HRMS (EI) calcd for $C_{19}H_{17}NO_5$ (M^+) 339.1106, found 339.1109; Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.28; H, 5.17; N, 4.24. The enantiomeric excess of **7l** was determined to be <1% by HPLC using Daicel Chiralcel OD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 8.0 min, 10.0 min.

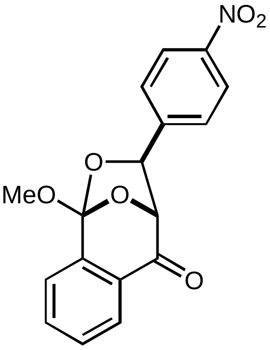
8-*exo*-(4-Nitrophenyl)-6-phenyl-7,9-dioxabicyclo[4.2.1]nonan-2-one (7m)



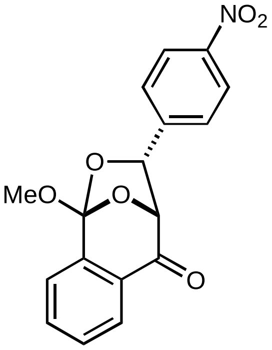
Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5i** (86.5 mg, 0.40 mmol) and **6b** (121 mg, 0.80 mmol), **7m** (81 mg, 60%, pale yellow solid) was obtained; TLC R_f 0.64 (5:1 benzene/Et_2O); mp 156.0–157.0 ºC (hexane/EtOAc); $[\alpha]^{21}{}_{,D}$ –0.94 (*c* 1.24, $CHCl_3$) for 79% ee, $[\alpha]^{22}{}_{,D}$ –22.5 (*c* 1.01, C_6H_6); IR (KBr) ν 3414, 3065, 2949, 1415, 1605, 1520, 1346 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.87–2.04 (2H, m, C*H*$_2$), 2.08–2.20 (1H, m, C*H*$_2$), 2.40 (1H, dt, *J* = 14.6, 3.5 Hz, C*H*$_2$), 2.54–2.62 (1H, m, C*H*$_2$), 3.04–3.15 (1H, m, C*H*$_2$), 4.54 (1H, d, *J* = 1.1 Hz, COC*H*), 5.47 (1H, d, *J* = 1.1 Hz, ArC*H*), 7.24–7.27 (2H, m, *Ar*), 7.39–7.45 (3H, m, *Ar*), 7.55–7.59 (2H, m, *Ar*), 8.02–8.06 (2H, d, *J* = 8.6 Hz, *Ar*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 19.1 (CH_2), 41.5 (CH_2), 42.7 (CH_2), 83.6 (CH), 87.8 (CH), 115.7 (C), 123.6 (CH), 124.7 (CH), 126.6 (CH), 128.3 (CH), 128.4 (CH), 142.5 (C), 147.5 (C), 147.9 (C), 213.7 (C); LRMS (EI) *m/z* 339 (M^+), 311, 268, 234, 217, 105, 77; HRMS (EI) calcd for $C_{19}H_{17}NO_5$ (M^+) 339.1106, found 339.1109. The enantiomeric excess of **7m** was determined to be 79% by HPLC using Daicel Chiralcel OD-H column (5:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 13.3 min for the minor enantiomer; t_R = 14.7 min for the major enantiomer.

7-*exo*-(4-Nitrophenyl)-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (7n)[2] and 7-*endo*-(4-Nitrophenyl)-5-methoxy-6,8-dioxabenzo[*c*]bicyclo[3.2.1]octan-2-one (8c)[2]

Following the representative procedure for the tandem carbonyl ylide formation/1,3-dipolar cycloaddition, starting from **5j** (20.4 mg, 0.10 mmol) and **6b** (30.2 mg, 0.20 mmol), **7n** (7.8 mg, 24%, pale yellow solid) and **8c** (12.9 mg, 39%, pale yellow solid) were obtained;



7n: TLC R_f 0.46 (5:1 benzene/Et$_2$O); mp 147.0–148.0 ºC (lit.[2] mp 147.5-148.8 for racemate); $[\alpha]^{21}_{,\mathrm{D}}$ –0.78 (*c* 0.50, CHCl$_3$) for <1% ee; IR (KBr) ν 3306, 1698, 1593, 1522, 1350 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.79 (3H, s, OC*H*$_3$), 4.94 (2H, s, ArC*H* and COC*H*), 7.54–7.60 (1H, m, *Ar*), 7.67–7.72 (4H, m, *Ar*), 8.05–8.08 (1H, m, *Ar*), 8.29–8.32 (2H, m, *Ar*). The enantiomeric excess of **7n** was determined to be <1% by HPLC using Daicel Chiralpak AD-H column (9:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 19.3 min for the major enantiomer; t_R = 22.1 min for the minor enantiomer.



8c: TLC R_f 0.21 (5:1 benzene/Et$_2$O); mp 152.0–154.0 ºC (lit.[2] mp 147.5-148.8 for racemate); $[\alpha]^{21}_{,\mathrm{D}}$ –8.21 (*c* 0.58, CHCl$_3$) for 6% ee; IR (KBr) ν 3470, 1713, 1699, 1599, 1520, 1345 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.79 (3H, s, OC*H*$_3$), 5.22 (1H, d, *J* = 5.9 Hz, ArC*H*), 5.70 (1H, d, *J* = 5.9 Hz, COC*H*), 7.11 (2H, d, *J* = 8.1 Hz, *Ar*), 7.47 (1H, dt, J = 7.6, 1.1 Hz, *Ar*), 7.66–7.79 (3H, m, *Ar*), 8.04 (2H, d, *J* = 8.1 Hz, *Ar*). The enantiomeric excess of **8c** was determined to be 6% by HPLC using Daicel Chiralcel OD-H column (9:1 hexane/2-propanol; flow rate = 1.0 mL/min; detection: 254 nm): t_R = 12.5 min for the major enantiomer; t_R = 20.6 min for the minor enantiomer.

Reference

[1] A. Padwa, G. E. Fryxell, L. Zhi, *J. Am. Chem. Soc.* **1990**, *112*, 3100.

[2] T. Ibata, J. Toyoda, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1787.