SUPPORTING INFORMATION

Enantioselective Tandem O-Nitroso Aldol/Michael Reaction

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Experimental Section.

General Procedures.

All non aqueous reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry nitrogen unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using Whatman pre-coated silica gel flexible plates (0.25 mm) with F₂₅₄ indicator or Merck pre-coated silica gel plates with F₂₅₄ indicator. Visualization was accomplished by UV light (256 nm), with combination of potassium permanganate and/or Ninhydrin and/or phosphomolybdic acid, and/or ferric chloride solution as a indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by E. Merck. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted.

Commercial grade reagents and solvents were used without further purification except as indicated below. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under an atmosphere of dry argon. 2-Cycloheptene-1-one was distilled under P₂O₅. 1,4-Dioxaspiro[4,5]dec-6-en-8-one was prepared according to reported method.¹

Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ¹H, 100 MHz ¹³C), a Bruker Avance 500 (500 MHz ¹H, 125 MHz ¹³C). Chemical shift values (δ) are reported in ppm relative to Me₄Si (δ 0.0 ppm). The proton spectra are reported as follows d (multiplicity, number of protons, coupling constant *J*). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (heptet), m (multiplet) and br (broad).

Reference

(1) Kerr, W. J.; McLaughlin, M.; Morrison, A. J.; Pauson, P. L. *Org. Lett.* **2001**, 3, 2945-2948.

General procedure for tandem Diels-Alder reaction

To catalyst (0.40 mol) was added enone (2.0 mmol), nitrosobenzene (4.0 mmol) acetonitrile (4.0 mL). The mixture was allowed to warm to 40°C and was stirred at the same temperature for 15 hours. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel chromatography to afford Diels-Alder adduct.

8,8-Dimethyl-3-phenyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:9 EtOAc: Hexane) provided as a yellowish oil (64% yield, 99% ee). TLC R_f 0.7 (EtOAc/Hexane, 1:5); $[\alpha]_D^{29} +82.3^\circ$ ($c = 1.10$, CHCl_3); FTIR (CD_3Cl) ν_{max} 2962, 1743, 1595, 1489, 1028, 992 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.4$ Hz, 2 H), 7.09 (d, $J = 8.7$ Hz, 2 H), 7.00 (t, $J = 7.3$ Hz, 2 H), 4.18 - 4.19 (m, 1 H), 3.51 - 3.53 (m, 1 H), 2.71 (dd, $J = 18.7$ Hz, $J = 2.7$ Hz, 1 H), 2.48 (dd, $J = 18.7$ Hz, $J = 3.0$ Hz, 1 H), 2.31 (dd, $J = 14.5$ Hz, $J = 3.9$ Hz, 1 H), 1.81 (dd, $J = 14.5$ Hz, $J = 1.8$ Hz, 1 H), 1.57 (s, 3 H), 1.47 (s, 3 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 208.1, 149.9, 128.9, 122.4, 116.6, 78.2, 68.4, 39.8, 34.9, 33.1, 28.6, 27.2; MS (CI) Exact Mass Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_4$ ($\text{M}+\text{H}^+$): 232.1. Found: 232.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (97:3 hexane:2-propanol), 0.8 mL/min; major enantiomer $t_r = 11.1$ min, minor enantiomer $t_r = 10.6$ min. Enantiomer was obtained as a yellowish oil using D-tetrazole catalysis using the same method. (61% yield, 99% ee). $[\alpha]_D^{29} -79.7^\circ$ ($c = 0.56$, CHCl_3)

8, 12-Dioxaspiro-3-phenyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:19 EtOAc: CH_2Cl_2) provided as a yellowish oil (61% yield, 98% ee); TLC R_f 0.6 (EtOAc/ CH_2Cl_2 , 1:19); $[\alpha]_D^{28} -5.4^\circ$ ($c = 1.03$, CHCl_3); FTIR (CD_3Cl) ν_{max} 2979, 2892, 1747, 1597, 1489, 1227, 1064 cm^{-1} ; ^1H NMR (500 MHz, CD_3Cl) δ 7.31 (t, $J = 7.4$ Hz, 2 H), 7.13 (d, $J = 8.8$ Hz, 2 H), 7.02 (t, $J = 7.3$ Hz, 1 H) 4.32 (dd, $J = 3.6$ Hz, $J = 2.6$ Hz, 1 H), 4.10 - 4.15 (m, 1 H), 3.97 - 4.04 (m, 3 H), 3.92 (t, $J = 2.9$ Hz, 1 H), 2.91 (dd, $J = 15.2$ Hz, $J = 3.9$ Hz, 1 H), 2.88 (dd, $J = 18.5$ Hz, $J = 2.9$ Hz, 1 H) 2.66 (dd, $J = 18.5$

Hz, $J = 2.9$ Hz, 1 H), 2.28 (dd, $J = 15.2$ Hz, $J = 2.4$ Hz, 1 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 204.9, 148.9, 128.8, 122.9, 116.8, 105.5, 77.9, 64.9, 64.8, 64.4, 38.7, 64.5; MS (CI) Exact Mass Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 262.1. Found: 262.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (90:10 hexane:2-propanol), 1.0mL/min; major enantiomer $t_r = 20.5$ min, minor enantiomer $t_r = 17.3$ min

7-Phenyl-6-oxa-7-aza-bicyclo[3.2.2]nonan-9-one

Purification by flash column chromatography with elution by (1:1 Hexane: CH_2Cl_2) provided as a yellowish oil (51% yield, 99% ee); TLC R_f 0.7 (Hexane/ CH_2Cl_2 , 1:19); $[\alpha]_D^{29} -186.5^\circ$ ($c = 1.12$, CHCl_3); FTIR (CD_3Cl) ν_{max} 2946, 1736, 1597, 1489, 1204, 1102, 1038, 734 cm^{-1} ; ^1H NMR (500 MHz, CD_3Cl) δ 7.31 (t, $J = 7.4$ Hz, 2 H), 7.04 (d, $J = 8.8$ Hz, 2 H), 6.92 (t, $J = 7.4$ Hz, 1 H) 4.60 (br d, $J = 5.8$ Hz, 1 H), 4.36 – 4.39 (m, 1 H), 2.98 (dd, $J = 18.1$ Hz, $J = 5.5$ Hz, 1 H), 2.43 (dd, $J = 18.1$ Hz, $J = 2.1$ Hz, 1 H) 2.07 – 2.16 (m, 3 H), 1.86 – 1.96 (m, 1 H), 1.42 – 1.56 (m, 1 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 207.5, 150.0, 129.0, 121.0, 114.7, 83.6, 56.9, 38.8, 30.9, 29.7, 18.9; MS (CI) Exact Mass Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 218.1. Found: 218.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (90:10 hexane:2-propanol), 1.0mL/min; major enantiomer $t_r = 8.5$ min, minor enantiomer $t_r = 6.9$ min

3,8,8-Triphenyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:1 Hexane: CH_2Cl_2) provided as a yellowish crystal (56% yield, 99% ee); TLC R_f 0.7 (CH_2Cl_2); $[\alpha]_D^{30} +288.4^\circ$ ($c = 0.97$, CHCl_3); FTIR (CD_3Cl) ν_{max} 3058, 2361, 2337, 1743, 1596, 1449, 1394, 1032, 998, 909 cm^{-1} ; ^1H NMR (500 MHz, CD_3Cl) δ 7.31 (t, $J = 7.4$ Hz, 2 H), 7.04 (d, $J = 8.8$ Hz, 2 H), 6.92 (t, $J = 7.4$ Hz, 1 H) 4.60 (br d, $J = 5.8$ Hz, 1 H), 4.36 – 4.39 (m, 1 H), 2.98 (dd, $J = 18.1$ Hz, $J = 5.5$ Hz, 1 H), 2.43 (dd, $J = 18.1$ Hz, $J = 2.1$ Hz, 1 H) 2.07 – 2.16 (m, 3 H), 1.86 – 1.96 (m, 1 H), 1.42 – 1.56 (m, 1 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 207.5, 150.0, 129.0, 121.0, 114.7, 83.6, 56.9, 38.8, 30.9, 29.7, 18.9; MS (CI) Exact Mass Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 355.2. Found: 355.1. Enantiometric

excess was determined by HPLC with Chiralcel AD-H column (95:5 hexane:2-propanol), 1.0mL/min; major enantiomer t_r = 10.1 min, minor enantiomer t_r = 8.8 min

3-Phenyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:4 EtOAc: Hexane) provided as a yellowish oil (34% yield, 99% ee); TLC R_f 0.5 (EtOAc/Hexane 1 : 3); $[\alpha]_D^{27}$ -216.9° (c = 0.6, CHCl_3); FTIR (CD_3Cl) ν_{max} 2965, 1745, 1596, 1488, 1306, 1220, 1174, 986 cm^{-1} ; ^1H NMR (500 MHz, CD_3Cl) δ 7.31 (t, J = 7.4 Hz, 2 H), 7.12 (d, J = 8.7 Hz, 2 H), 7.00 (t, J = 7.3 Hz, 1 H) 4.19 – 4.22 (m, 2 H), 3.02 (br d, J = 18.2 Hz, 1 H), 2.47 (dd, J = 18.1 Hz, J = 3.1 Hz, 1 H) 2.26 – 2.40 (m, 2 H), 1.91 – 1.99 (m, 1 H), 1.61 – 1.68 (m, 1 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 207.1, 150.3, 129.0, 122.2, 116.2, 76.9, 56.1, 41.8, 22.4, 21.5; MS (CI) Exact Mass Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 204.1. Found: 204.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (90:10 hexane:2-propanol), 1.0mL/min; major enantiomer t_r = 23.4 min, minor enantiomer t_r = 10.0 min

3-(4-Bromo-phenyl)-8,8-dimethyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Solvent system was changed to $\text{CH}_2\text{Cl}_2/\text{MeCN}$ 1:1 (6 mL) was used instead of use of CH_2Cl_2 . Purification by flash column chromatography with elution by CH_2Cl_2 provided as a yellowish crystal (50% yield, 99% ee); TLC R_f 0.6 (CH_2Cl_2); $[\alpha]_D^{27}$ +68.1° (c = 2.17, CHCl_3); FTIR (CD_3Cl) ν_{max} 2962, 2871, 1742, 1587, 1485, 1436, 1028, 825 cm^{-1} ; ^1H NMR (400 MHz, CD_3Cl) δ 7.33 (d, J = 8.9 Hz, 2 H), 6.90 (d, J = 8.9 Hz, 2 H), 4.10 – 4.12 (m, 1 H), 3.40 - 3.42 (m, 1 H), 2.57 (dd, J = 18.7 Hz, J = 2.7 Hz, 1 H) 2.42 (dd, J = 18.7 Hz, J = 2.9 Hz, 1 H) 2.21 (dd, J = 14.6 Hz, J = 3.9 Hz, 1 H) 1.73 (dd, J = 14.5 Hz, J = 2.3 Hz, 1 H) 1.37 (s, 3 H), 1.01 (s, 3 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 207.4, 149.1, 131.8, 118.2, 114.8, 78.3, 68.3, 39.7, 35.0, 33.1, 28.6, 27.2; MS (CI) Exact Mass Calcd for $\text{C}_{14}\text{H}_{17}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 310.0. Found: 310.0. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (98:2 hexane:2-propanol), 1.0mL/min; major enantiomer t_r = 11.3 min, minor enantiomer t_r = 15.3 min

8,8-Dimethyl-3-*p*-tolyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:9 EtOAc: Hexane) provided as a yellowish crystal (46% yield, 98% ee); TLC R_f 0.5 (EtOAc/Hexane 1 : 5); $[\alpha]_D^{27} +44.4^\circ$ ($c = 1.32$, CHCl_3); FTIR (CD_3Cl) ν_{max} 2961, 1742, 1506, 1028, 994, 817 cm^{-1} ; ^1H NMR (400 MHz, CD_3Cl) δ 7.10 (d, $J = 8.1$ Hz, 2 H), 6.98 (d, $J = 8.5$ Hz, 2 H), 4.14 – 4.17 (m, 1 H), 3.42 – 3.45 (m, 1 H), 2.71 (dd, $J = 18.7$ Hz, $J = 2.7$ Hz, 1 H) 2.45 (dd, $J = 18.7$ Hz, $J = 3.0$ Hz, 1 H) 2.30 (dd, $J = 14.4$ Hz, $J = 4.0$ Hz, 1 H), 2.29 (s, 3 H), 1.79 (dd, $J = 14.5$ Hz, $J = 1.8$ Hz, 1 H) 1.47 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 208.3, 147.6, 132.0, 129.4, 116.8, 78.2, 68.6, 39.9, 34.7, 33.1, 28.6, 27.3, 20.6; $\text{C}_{15}\text{H}_{20}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 246.2. Found: 246.1. Enantiometric excess was determined by HPLC with Chiralcel OD-H column x 2 (99:1 hexane:2-propanol), 0.5 mL/min; major enantiomer $t_r = 38.3$ min, minor enantiomer $t_r = 40.7$ min

3-(3,5-Dimethyl-phenyl)-8,8-dimethyl-2-oxa-3-aza-bicyclo[2.2.2]octan-6-one

Purification by flash column chromatography with elution by (1:9 EtOAc: Hexane) provided as a yellowish crystal (52% yield, 98% ee); TLC R_f 0.5 (EtOAc/Hexane 1 : 5); $[\alpha]_D^{27} +70.8^\circ$ ($c = 0.67$, CHCl_3); FTIR (CD_3Cl) ν_{max} 2961, 2921, 2870, 1742, 1595, 1471, 1028, 1006 cm^{-1} ; ^1H NMR (400 MHz, CD_3Cl) δ 6.70 (s, 2 H), 6.64 (s, 1 H), 4.14 – 4.17 (m, 1 H), 3.47 – 3.51 (m, 1 H), 2.72 (dd, $J = 18.7$ Hz, $J = 2.7$ Hz, 1 H) 2.47 (dd, $J = 18.7$ Hz, $J = 3.0$ Hz, 1 H) 2.29 (dd, $J = 14.4$ Hz, $J = 3.9$ Hz, 1 H), 2.29 (s, 6 H), 1.79 (dd, $J = 14.5$ Hz, $J = 2.0$ Hz, 1 H) 1.46 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 208.4, 150.0, 138.5, 124.2, 114.3, 78.2, 68.2, 39.9, 35.0, 33.1, 28.6, 27.3, 21.5; $\text{C}_{16}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 260.2. Found: 260.2. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (97.5:2.5 hexane:2-propanol), 0.4 mL/min; major enantiomer $t_r = 13.7$ min, minor enantiomer $t_r = 12.8$ min

Reaction with 1-(Trimethylsilyloxy)-1,3-cyclohexadiene (normal Diels-Alder reaction)

To a solution of nitrosobenzene (107 mg, 1.0 mmol) in CH_2Cl_2 (4.0 mL) was added 1-(Trimethylsilyloxy)-1,3-cyclohexadiene (202 mg, 1.2 mmol). The reaction mixture was stirred for 5 h. and was concentrated under reduced pressure to afford crude cyclized product. The crude product was added THF and SiO_2 and was stirred for 3 h. Purification by flash column chromatography with elution by (1:4 EtOAc: Hexane) provided as a yellowish oil; TLC R_f 0.5 (EtOAc/Hexane 1 : 3); FTIR (CD_3Cl) ν_{max} 3375, 3060, 2939, 1734, 1595, 1489, 1301, 1173, 1007, 759 cm^{-1} ; ^1H NMR (400 MHz, CD_3Cl) δ 7.27 (t, J = 7.4 Hz, 2 H), 7.03 (d, J = 8.7 Hz, 2 H), 6.94 (t, J = 8.3 Hz, 1 H) 4.67 – 4.70 (m, 1 H), 4.14 (d, J = 3.3 Hz, 1 H), 2.53 – 2.67 (m, 2 H), 2.33 - 2.39 (m, 2 H), 2.13 – 2.20 (m, 1 H), 1.56 – 1.64 (m, 1 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 206.0, 151.1, 129.0, 122.2, 115.1, 72.6, 64.0, 44.2, 24.7, 21.6; MS (CI) Exact Mass Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 204.1. Found: 204.1

Results by using L-Proline as a catalyst

entry	R,R	yield, %	ee, %
1	1a : Me,Me	34	99
2	1b : H,H	8	99
3	1c : Ph,Ph	<1	-
4	1d : -(OCH ₂ CH ₂ O)-	36	98

General procedure for the preparation of trichloro acetic acid 4,4-dimethylcyclohexa-1,5-dienyl ester.

A mixture of Trichloro acetic anhydride (3 equiv), 4,4-Dimethylcyclohex-2-enone (1 equiv) and catalytic amount of $\text{TsOH} \cdot \text{H}_2\text{O}$ was stirred for 3 h at 90 °C. The reaction mixture was cooled to room temperature and diluted with Et_2O . The organic layer was washed with NaHCO_3 aq and water. The aqueous layer was extracted with Et_2O . The combined organic layer was dried over Na_2SO_4 and evaporated. Purification by silicagel column chromatography gave the desired dienyl ester.

Trichloro acetic acid 4,4-dimethylcyclohexa-1,5-dienyl ester.

Purification by flash column chromatography with elution by (1:100 EtOAc: Hexane) provided as a colorless oil (4% yield, 100 mmol scale). TLC R_f 0.68 (EtOAc/Hexane, 1:5); ^1H NMR (400 MHz, CDCl_3) δ 5.31 (dd, J = 10.0, 0.66 Hz, 1 H), 5.64 (dd, J = 10.0, 2.1 Hz, 1 H), 5.51 (td, J = 4.8, 2.0 Hz, 1 H), 2.29 (d, J = 2.0 Hz, 2 H), 1.10 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.3, 145.4, 141.5, 118.4, 110.9, 36.3, 31.4, 27.6

General procedure for the preparation of stanyloxy diene *in situ*. A mixture of dienyl ester (1 equiv) and tin methoxide (1.2 equiv) was stirred in THF (in the case of trimethyl stanyloxy diene) or neat (in the case of tributyl stanyloxy diene) at -20 °C for 1 h.

General procedure for the reaction of trimethyl stanyloxy diene with nitrosobenzene catalyzed by 1:1 (AgOTf·(*R*)-BINAP) complex. An oven-dried schlenk tube equipped with direct light excluded was charged with (*R*)-BINAP (10 mol%, 0.05 mmol) and AgOTf (10 mol%, 0.05 mmol). THF (2 mL) was added by syringe and the resulting mixture was stirred at room temperature for 20 min. After cooling to -78 °C, nitrosobenzene (1 equiv, 53.6 mg, 0.5 mmol) in THF (1 mL) and stanyloxy diene (1 equiv) prepared *in situ* before use was added in this order. The mixture was stirred at -78 °C for 1 h. The reaction mixture was quenched by cooled brine (20 mL) and the aqueous layer was extracted with ether (20 mLx2). The combined organic extracts were washed with brine, dried over Na_2SO_4 with cooling and concentrated under

reduced pressure after filtration. The residual crude product in THF was chromatographed with cooling on a two-layered column filled with Florisil® (upper layer) and silica gel (lower layer) using a mixture of ethyl acetate and hexane as the eluant to give the product.

4,4-Dimethyl-6-(*N*-phenyl aminoxy) cyclohex-2-enone

Purification by flash column chromatography with elution by (1:10 EtOAc: Hexane) provided as a yellowish powder (91% yield, 93% ee). TLC R_f 0.38 (EtOAc/Hexane, 1:3); $[\alpha]_D^{29}$ -152.9° ($c = 0.96$, CHCl_3); FTIR (CHCl_3) ν_{max} 3697, 2962, 1815, 1726, 1602, 1451, 1090, 830 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.94 (s, 1H, NH), 7.26 (t, 2H, $J = 8.4$ Hz, Ar- H), 6.95 (d, 3H, $J = 8.1$ Hz, Ar- H), 6.65 (dd, 1H, $J = 10.0, 2.0$ Hz, CH), 5.87 (d, 1H, $J = 10.0$, CH) 4.58 (dd, 1H, $J = 7.0, 5.6$ Hz, CH), 2.15 – 2.21 (m, 2H, CH_2), 1.28 (s, 3H, CH_3), 1.22 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 100 MHz) δ 199.0, 159.6, 148.2, 128.9 (2C), 125.3, 122.0, 114.4 (2C), 80.2, 40.9, 35.5, 30.7, 26.3; MS (CI) Exact Mass Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 232.1. Found: 232.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (40:1 hexane:2-propanol), 1.0 mL/min; major enantiomer $t_r = 22.1$ min, minor enantiomer $t_r = 24.2$ min

General procedure for the reaction of tributyl stanyloxy diene with nitrosobenzene catalyzed by 2:1 (AgOTf(*R*)-BINAP) complex. An oven-dried schlenk tube equipped with direct light excluded was charged with (*R*)-BINAP (4 mol%, 0.02 mmol) and AgOTf (10 mol%, 0.05 mmol). Ethylene glycol diethyl ether (2 mL) was added by syringe and the resulting mixture was stirred at room temperature for 20 min. After cooling to -78 °C, nitrosobenzene (1 equiv, 53.6 mg, 0.5 mmol) in ethylen glycol diethyl ether (1 mL) and tributyl stanyloxy diene prepared *in situ* before use (1 equiv) was added in this order. The mixture was stirred at -78 °C for 1 h. The reaction mixture was quenched by cooled brine (20 mL) and the aqueous layer was extracted with ether (20 mLx2). The combined organic extracts were washed with brine, dried over Na_2SO_4 with cooling and concentrated under reduced pressure after filtration. The residual crude product in ethylene glycol diethyl ether was chromatographed with cooling on a two-

layered column filled with Florisil[®] (upper layer) and silica gel (lower layer) using a mixture of ethyl acetate and hexane as the eluant to give the product.

4,4-Dimethyl-6-(*N*-phenyl hydroxyamino) cyclohex-2-enone

Purification by flash column chromatography with elution by (1:10 EtOAc: Hexane) provided as a yellowish powder (98% yield, >99% ee). TLC R_f 0.25 (EtOAc/Hexane, 1:3); $[\alpha]_D^{28}$ -155.7° ($c = 0.23$, CHCl_3); FTIR (CHCl_3) ν_{max} 3178, 2988, 1657, 1478, 1116, 803 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.27 (t, 2H, $J = 7.4$ Hz, Ar- H), 7.06 (d, 2H, $J = 8.6$ Hz, Ar- H), 6.95 (t, 1H, $J = 8.0$ Hz, Ar- H), 6.66 (dd, 1H, $J = 10.0, 2.0$ Hz, CH), 5.93 (d, 1H, $J = 10.0$, CH), 5.89 (s, 1H, OH), 4.52 (dd, 1H, $J = 13.6, 4.4$ Hz, CH), 1.31 – 1.43 (m, 2H, CH_2), 1.23 (s, 3H, CH_3), 1.16 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 100 MHz) δ 197.3, 159.7, 150.0, 128.8 (2C), 126.1, 121.3, 115.4 (2C), 66.3, 35.8, 34.6, 30.5, 25.5; MS (CI) Exact Mass Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ (M)⁺: 231.1. Found: 231.1. Enantiometric excess was determined by HPLC with Chiralcel AD-H column (40:1 hexane:2-propanol), 1.0 mL/min; major enantiomer $t_r = 37.8$ min, minor enantiomer $t_r = 40.1$ min

Crystallographic Experimental Section.

Data Collection

An irregular broken fragment (0.20 x 0.10 x 0.05 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A “hemisphere” data set was obtained which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.80 Å using 0.3° steps in ω using 20 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement

The space group was determined as $P2_1$ based on systematic absences and intensity statistics. Direct methods were used to locate all the Br atoms and many C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected Br, C, N and O atoms. Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for all non-hydrogen atoms and isotropic-riding for H atoms. No anomalous bond lengths or thermal parameters were noted. The Flack parameter is close to zero indicating the correct absolute structure. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Equations of interest:

$$R_{\text{int}} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$$

$$\text{GooF} = S = [\sum [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

where: $w = 1 / \sigma^2 (F_o^2) + (aP)^2 + bP$;

n = number of independent reflections;

q, a, b, P as defined in [1]

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 1. Crystal and structure refinement for Yama08.

Identification Code	Yama08
Empirical formula	$C_{14}H_{16}BrNO_2$
Formula weight	310.19
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space Group	$P2_1$
Unit cell dimensions	$a = 11.380(3)$ Å $\alpha = 90.0^\circ$ $b = 12.167(3)$ Å $\beta = 104.412(5)^\circ$ $c = 19.528(5)$ Å $\gamma = 90.0^\circ$
Volume	$2618.8(12)$ Å ³
Z	8
Density (calculated)	1.573 Mg/m ³
Absorption coefficient	3.133 mm ⁻¹
F(000)	1264
Crystal size, color, habit	0.20 x 0.10 x 0.05 mm, transparent, irregular
Theta range for data collection	$1.85 - 26.37^\circ$
Index ranges	$-13 \leq h \leq 14, -7 \leq k \leq 15, -23 \leq l \leq 24$
Reflections collected	14,563
Independent reflections	7,322 ($R_{int} = 0.0544$)
Reflections with $I > 4\sigma(F_o)$	6,170
Absorption correction	SADABS based on redundant diffractions
Max. and min. transmission	1.0, 0.746
Refinement method	Full-matrix least squares on F^2
Weighting scheme	$w = q [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2F_c^2)/3, a = 0.0326, b = 0.0, q = 1$
Data / restraints / parameters	7322 / 0 / 657
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0572, wR2 = 0.0988$
R indices (all data)	$R1 = 0.0711, wR2 = 0.1034$
Largest diff. peak and hole	0.743, -0.970 eÅ ⁻³