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Supporting Information

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Catalytic Asymmetric Nitroso Diels-Alder Reaction with Acyclic Dienes

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General Procedures. Diels–Alder reactions were performed in flame-dried 10mL Schlenk flasks. All other reactions were performed in flame-dried round bottom flasks. The flasks were fitted with rubber septa and reactions were conducted under an atmosphere of nitrogen. Flash chromatography was performed using silica gel 60 (230-400 mesh) from E. Merck.

Materials. Commercial reagents were purchased from Aldrich, Acros, Lancaster, or STREM and used as received. (2*Z*,4*E*)-3-Trialkyl-silyl-2,4-hexadienes **1a-1c** were prepared by treatment of 4-hexene-3-one (Aldrich) with triethylamine and the trialkylsilyl trifluoromethanesufornate ester in CH_2Cl_2 at 0°C and distilled prior to use.[1] Other dienes **1c-1m** were prepared by treatment of corresponding enone with triethylamine and triisopropylsilyl trifluoromethanesufornate in CH_2Cl_2 at 0°C and purified by silica gel chromatography.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) were recorded on Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C), or Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C). Chemical shift values (δ) are reported in ppm relative to Me_4Si (δ 0.0 ppm). Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. Infrared (IR) spectra were obtaine using a Nicolet 20 SXB FTIR. High-performance liquid chromatography (HPLC) was performed on a Varian Prostar Series equipped with a variable wavelength detector using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

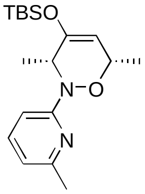
Reference

(1) Dossetter, A. G.; Jamison, T. F.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **1999**, *43*, 2398–2400.

General Procedure for Catalytic Asymmetric nitroso Diels-Alder Reaction

A 10 mL Schrenk tube equipped with magnetic stir bar was charged with Cu(I)($CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol) and (*S*)-(–) DIFLUOPHOS (35.8 mg, 0.0525 mmol). The mixture was dried under vacuum for 10 min and was flushed thoroughly with N_2 gas, three times. CH_2Cl_2 (4 mL) was added by syringe and the resulting colorless solution was stirred for 1 h at room temperature. After cooling the solution to –85 °C, 6-methyl-2-nitrosopyridine **2** (61 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) was slowly added and stirred for 10 min at the same temperature. Diene (0.6 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to this dark blue solution. The reaction mixture was gradually warmed to –20 °C in 5 h and was stirred at –20 °C for additional 1 h. The crude product was purified by silica gel chromatography to afford the Diels–Alder adduct.:

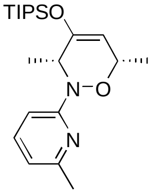
3b



Purification by flash column chromatography with elution by hexanes: ethyl acetate: triethylamine (95:5:0.02) provided as colorless oil (88% yield). Enantiometric excess was determined by HPLC with Chiralcel AD-H column ((99.5:0.5 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 3.9 min, minor enantiomer t_r = 4.3 min) to have 84% ee.

TLC *R_f* 0.7 (9:1 hexanes: ethy acetate); $[\alpha]^{28}_{D}$ = –185.4° (c = 0.57, $CHCl_3$; for product with 84% ee); FTIR (CD_3Cl) υ_{max} 2931, 2859, 1669, 1577, 1456, 1338, 1209 cm^{-1}; ^1H NMR (400 MHz, CD_3Cl) δ 7.44 (t, *J* = 7.8 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 6.58 (d, *J* = 7.3 Hz, 1 H), 4.65 – 4.77 (m, 3 H), 2.41 (s, 3 H), 1.24 – 1.29 (m, 6 H), 0.95 (s, 9 H), 0.21 (s, 3 H), 0.19 (s, 3 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 159.2, 156.6, 152.5, 137.7, 114.7, 106.2, 104.2, 71.7, 53.9, 25.6, 24.4, 20.0, 18.0, 14.3, -4.3, -4.8.

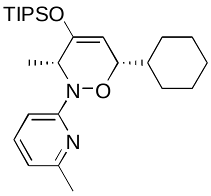
3c



Purification by flash column chromatography with elution by hexanes: ethyl acetate: (95:5) provided as colorless oil (95% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.6:0.4 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 7.6 min, minor enantiomer t_r = 8.8 min) to have 99% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{27}_{D}$ = –196.8° (c = 0.77, $CHCl_3$; for product with 99% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1668, 1578, 1456, 1213 cm^{-1}; ^1H NMR (400 MHz, CD_3Cl) δ 7.44 (dd, *J* = 8.2 Hz, 7.5 Hz,1 H), 6.91 (d, *J* = 8.3 Hz, 1 H), 6.58 (d, *J* = 7.3 Hz, 1 H), 4.75 (dq, *J* = 1.5 Hz, *J* = 6.5 Hz), 4.71 (br s, 1 H), 4.67 (br q, *J* = 6.5 Hz, 1 H), 2.41 (s, 3 H), 1.28 (d, *J* = 6.5 Hz, 3 H), 1.26 (d, *J* = 6.5 Hz, 3 H), 1.15 – 1.28 (m, 3 H), 1.12 (s, 12 H), 1.10 (s, 6 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 159.3, 156.6, 152.6, 137.7, 114.7, 106.2, 102.9, 71.9, 54.2, 24.4, 20.0, 18.0, 14.2, 12.6; MS (CI) Exact Mass Calcd for $C_{21}H_{37}N_2O_2Si$ $(M+H)^+$: 377.3. Found: 377.2.

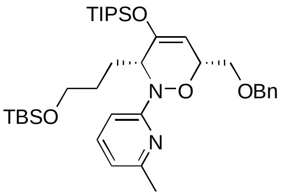
3d



Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (93% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.6:0.4 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 7.8 min, minor enantiomer t_r = 7.0 min) to have 91% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{27}_D$ = –116.8° (c = 0.69, $CHCl_3$; for product with 91% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1667, 1588, 1577, 1449, 1311, 1211, 1195 cm^{-1}; ^{1}H NMR (400 MHz, CD_3Cl) δ 7.43 (dd, *J* = 8.1 Hz, *J* = 7.5 Hz, 1 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 6.57 (d, *J* = 7.2 Hz, 1 H), 4.75 (dq, *J* = 1.5 Hz, *J* = 6.5 Hz, 1 H), 4.71 (br s, 1 H), 4.37 (br d, *J* = 5.0 Hz, 1 H), 2.40 (s, 3 H), 1.43 – 1.91 (m, 6 H), 1.16 – 1.29 (m, 11 H), 1.11 (s, 12 H), 1.10 (s, 6 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 159.4,156.5, 153.0, 137.6, 114.5, 106.3, 99.6, 79.4, 54.2, 41.8, 28.8, 27.9, 26.5, 26.3, 26.2, 24.4 18.0, 14.6, 12.6; MS (CI) Exact Mass Calcd for $C_{26}H_{45}N_2O_2Si$ $(M+H)^+$: 445.3. Found: 445.2.

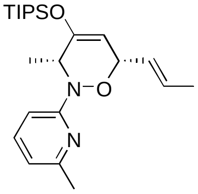
3e



Purification by flash column chromatography with elution by hexanes: ethyl acetate: triethylamine (90:10:1) provided as a yellowish oil (86% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.5:0.5 hexane:2-propanol), 1.0 mL/min; major enantiomer t_r = 8.7 min, minor enantiomer t_r = 6.6 min) to have 95% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{24}_D$ = –81.9° (c = 0.29, $CHCl_3$; for product with 95% ee); FTIR (CD_3Cl) υ_{max} 2947, 2866, 1671, 1590, 1577, 1452, 1254, 1211, 1096, 835 cm^{-1}; ^{1}H NMR (400 MHz, CD_3Cl) δ 7.42 (dd, *J* = 8.2 Hz, *J* = 7.4 Hz, 1 H), 7.26 – 7.38 (m, 5 H), 6.91 (d, *J* = 8.3 Hz, 1 H), 6.55 (d, *J* = 7.3 Hz, 1 H), 4.92 (ddd, *J* = 8.7 Hz, *J* = 3.8 Hz, *J* = 1.8 Hz, 1 H), 4.77 – 4.82 (m, 1 H), 4.68 (d, *J* = 12.2 Hz 1 H), 4.61 (d, *J* = 1.3 Hz, 1 H), 4.57 (d, *J* = 12.2 Hz 1 H), 3.55 – 3.65 (m, 3 H), 3.49 (dd, *J* = 10.6 Hz, *J* = 3.9 Hz 1 H), 2.36 (s, 3 H), 1.92 – 2.03 (m, 1 H), 1.72 – 1.87 (m, 1 H), 1.60 – 1.71 (m, 2 H), 1.10 – 1.26 (m, 3 H), 1.08 (d, *J* = 2.7 Hz, 12 H), 1.06 (d, *J* = 2.6 Hz, 6 H), 0.87 (s, 9 H), 0.01 (s, 6 H); ^{13}C NMR (100 MHz, CD$_3$Cl) δ 159.0, 156.5, 153.3, 138.2, 137.7, 128.3, 127.6, 114.4, 106.0, 97.7, 73.4, 72.9, 72.3, 63.2, 56.3, 29.9, 27.5, 26.0, 24.3, 18.0, 12.6, -5.3; MS (CI) Exact Mass Calcd for $C_{36}H_{61}N_2O_4Si_2$ (M+H)$^+$: 641.4. Found: 641.3. Enantiometric excess was determined by HPLC with Chiralcel OD-H column (99.5:0.5 hexane:2-propanol), 1.0 mL/min; major enantiomer t_r = 8.7 min, minor enantiomer t_r = 6.6 min.

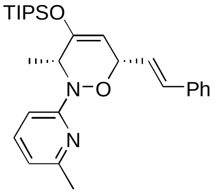
3f



Purification by flash column chromatography with elution by hexanes: ethyl acetate (19:1) gave the product as colorless oil (91% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.9:0.1 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 33.2 min, minor enantiomer t_r = 11.7 min. To have 96% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{27}_{D}$ = –117.7° (c = 0.68, CHCl$_3$; for product with 96% ee); FTIR (CD$_3$Cl) υ_{max} 2945, 2867, 1664, 1590, 157, 1454, 1340, 1208, 1065, 883 cm^{-1}; ^{1}H NMR (400 MHz, CD$_3$Cl) δ 7.36 (dd, *J* = 8.2 Hz, *J* = 7.5 Hz, 1 H), 6.85 (d, *J* = 8.3 Hz, 1 H), 6.51 (d, *J* = 7.3 Hz, 1 H), 5.78 (ddq, *J* =15.3, *J* = 0.7 Hz, *J* = 6.6 Hz, 1 H), 5.42 (ddq, *J* = 15.3 Hz, *J* = 7.8 Hz, *J* = 1.7 Hz, 1 H), 4.88 (br d *J* = 7.8 Hz), 4.66 – 4.73 (m, 1 H), 4.62 (d, *J* = 0.9 Hz, 1 H), 2.34 (s, 3 H), 1.70 (dd, *J* = 9.6 Hz, *J* = 1.6 Hz, 3 H), 1.23 (d, *J* = 6.6 Hz, 3 H), 1.15 – 1.20 (m, 3 H), 1.05 (s, 12 H), 1.08 (s, 6 H); ^{13}C NMR (100 MHz, CD$_3$Cl) δ 159.3, 156.6, 153.0, 137.7, 131.1, 129.2, 114.7, 106.4, 100.8, 76.7, 54.2, 24.4, 18.0, 17.9, 14.4, 12.6; MS (CI) Exact Mass Calcd for $C_{23}H_{39}N_2O_2Si$ $(M+H)^+$: 403.3. Found: 403.1.

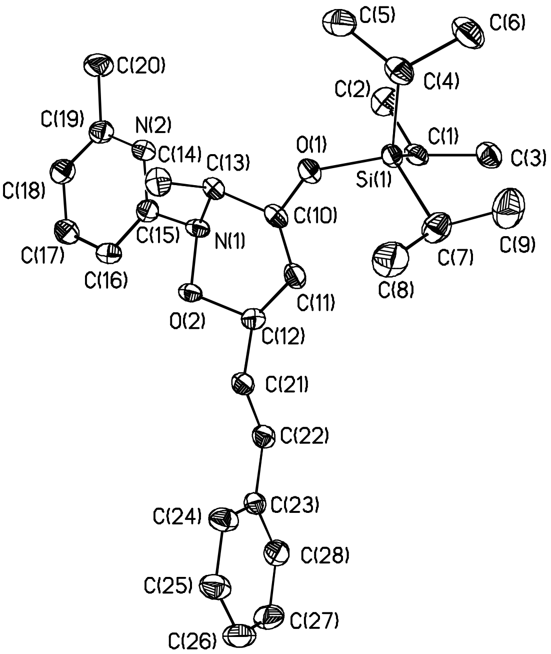
3g



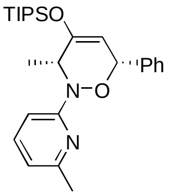
Purification by flash column chromatography with elution by hexanes: ethyl acetate: triethylamine (95:5:1) gave the product as colorless crystal (84% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.9:0.1 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 30.6 min, minor enantiomer t_r = 25.7 min.) to have 85% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{25}_D = -47.0°$ (c = 0.90, $CHCl_3$; for product with 85% ee); FTIR (CD_3Cl) υ_{max} 2944, 2867, 1665, 1578, 1456, 1337, 1211, 1122, 1066, 964, 884 cm^{-1}; ^1H NMR (500 MHz, CD_3Cl) δ 7.34 – 7.39 (m, 3 H), 7.22 – 7.26 (m, 2 H), 7.17 – 7.20 (m, 1 H), 6.89 (d, *J* = 8.3 Hz, 1 H), 6.62 (d, *J* = 15.9 Hz, 1 H), 6.52 (d, *J* = 7.4 Hz, 1 H), 6.09 (dd, *J* = 15.9 Hz, *J* = 7.7 Hz, 1 H), 5.10 (br d, *J* = 7.8 Hz, 1 H), 4.75 (dq, *J* = 1.5 Hz, *J* = 6.5 Hz, 1 H), 4.69 (br d, *J* = 1.1 Hz), 2.34 (s, 3 H), 1.27 (d, *J* = 6.6 Hz, 3 H), 1.08 – 1.20 (m, 3 H), 1.04 (d, *J* = 2.2 Hz, 12 H), 1.03 (d, *J* = 2.1 Hz, 6 H),; ^{13}C NMR (100 MHz, CD_3Cl) δ 159.3, 156.6, 153.4, 137.8, 136.4, 133.7, 128.6, 128.0, 127.1, 126.7, 114.9, 106.5, 100.3, 76.9, 54.4, 24.4, 18.0, 14.4, 12.6; MS (CI) Exact Mass Calcd for $C_{23}H_{39}N_2O_2Si$ $(M+H)^+$: 465.3. Found: 465.1.

X-ray structure analysis was performed with this compound.



3h

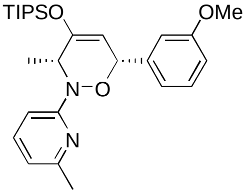


Purification by flash column chromatography with elution by hexanes: ethylacetate: triethylamine (95:5:1) provided as a colorless oil (95% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.8:0.2 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 27.4 min, minor enantiomer t_r = 19.4 min.) to have 81% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{25}_D$ = –103.9° (c = 0.77, $CHCl_3$; for product with 81% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1665, 1577, 1337, 1210, 1065 cm^{-1}; ^{1}H NMR (400 MHz, CD_3Cl) δ 7.35 – 7.48 (m, 6 H), 6.93 (d, *J* = 8.3 Hz, 1 H), 6.60 (d, *J* = 7.4 Hz, 1 H), 5.57 (s, 1 H), 4.87 (dq, *J* = 1.5 Hz, *J* = 6.5 Hz, 1 H), 4.85 (d, *J* = 1.0, 1 H), 2.43 (s, 3 H), 1.40 (d, *J* = 6.5 Hz, 3 H), 1.15 – 1.28 (m, 3 H), 1.12 (s, 12 H), 1.10 (s, 6 H);

^{13}C NMR (100 MHz, CD_3Cl) δ 159.3, 156.6, 153.3, 139.3, 137.8, 128.7, 128.5, 128.4, 115.0, 106.7, 101.1, 78.7, 54.5, 24.4, 18.0, 14.6, 12.6; MS (CI) Exact Mass Calcd for $C_{26}H_{39}N_2O_2Si$ $(M+H)^+$: 439.3. Found: 439.1.

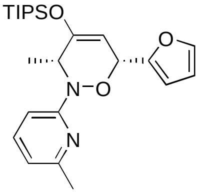
3i



Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (91% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.8:0.2 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 34.7 min, minor enantiomer t_r = 25.8 min.) to have 99% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{26}_{D} = -106.3°$ (c = 0.57, $CHCl_3$; for product with 99% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1665, 1589, 1454, 1210, 882 cm^{-1}; ^{1}H NMR (500 MHz, CD_3Cl) δ 7.43 (dd, *J* = 8.1 Hz, *J* = 7.5 Hz, 1 H), 7.31 (dd, *J* = 7.9 Hz, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 7.01 (s, 1 H), 6.93 (d, *J* = 8.2 Hz, 1 H), 6.91 (dd, *J* = 7.7 Hz, 2.7 Hz, 1 H), 6.60 (d, *J* = 7.3 Hz, 1 H), 5.54 (s, 1 H), 4.87 (dq, *J* = 1.3 Hz, *J* = 6.5 Hz, 1 H), 4.83 (s, 1 H), 3.83 (s, 3 H), 2.43 (s, 3 H), 1.40 (d, *J* = 6.5 Hz, 1 H), 1.19 – 1.27 (m, 3 H), 1.12 (d, *J* = 2.5 Hz, 12 H), 1.10 (d, *J* = 2.5 Hz, 6 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 159.7, 159.2, 156.6, 153.3, 140.9, 137.8, 129.5, 120.8, 115.0, 114.5, 113.5, 106.7, 100.9, 78.6, 55.2, 54.5, 24.4, 18.0, 14.6, 12.6; MS (CI) Exact Mass Calcd for $C_{25}H_{43}N_2O_4Si$ $(M+H)^+$: 469.3. Found: 469.1.

3j

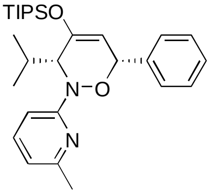


Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (91% yield). Enantiometric excess was determined by

HPLC with Chiralcel OD-H column ((99.5:0.5 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 10.4 min, minor enantiomer t_r = 8.5 min.) to have 95% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{25}_D$ = –120.6° (c = 0.82, $CHCl_3$; for product with 95% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1668, 1590, 1577, 1454, 1338, 1211, 1065, 833 cm^{-1}; ^1H NMR (500 MHz, CD_3Cl) δ 7.45 (dd, *J* = 8.2 Hz, *J* = 7.8 Hz, 1 H), 7.45 (dd, *J* = 1.7 Hz, *J* = 0.8 Hz, 1 H), 6.99 (d, *J* = 8.3 Hz, 1 H), 6.62 (d, *J* = 7.4 Hz, 1 H), 6.41 (d. *J* = 3.2 Hz, 1 H), 6.39 (dd, *J*= 3.1 Hz, *J* = 1.8 Hz, 1 H), 5.65 (s, 1 H), 4.90 (d, *J* = 1.4 Hz, 1 H), 4.85 (dq, *J* = 1.7 Hz, *J* = 6.6 Hz, 1 H), 2.43 (s, 3 H), 1.34 (d, *J* = 6.5 Hz, 3 H), 1.21 – 1.30 (m, 3 H), 1.14 (d, *J* = 5.7 Hz, 12 H), 1.12 (d, *J* = 5.8 Hz, 6 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 159.1, 156.6, 154.5, 152.7, 143.0, 137.8, 115.1, 110.4, 109.2, 106.7, 97.8, 71.3, 54.7, 24.4, 18.0, 14.2, 12.6; MS (CI) Exact Mass Calcd for $C_{24}H_{37}N_2O_3Si$ $(M+H)^+$: 429.3. Found: 429.1.

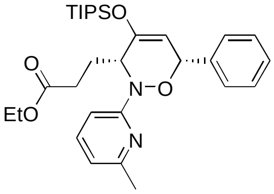
3k



Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (97% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.8:0.2 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 13.3 min, minor enantiomer t_r = 11.8 min.) to have 96% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{26}_D$ = –143.6° (c = 0.57, $CHCl_3$; for product with 96% ee); FTIR (CD_3Cl) υ_{max} 2929, 2866, 1668, 1590, 1453, 1339, 1210, 882 cm^{-1}; ^1H NMR (400 MHz, CD_3Cl) δ 7.36 – 7.48 (m, 6 H), 6.95 (d, *J* = 8.3 Hz, 1 H), 6.56 (d, *J* = 7.2 Hz, 1 H), 5.45 – 5.47 (m, 1 H), 5.02 – 5.04 (m, 1 H), 4.84 (br s, 1 H), 2.38 – 2.43 (m, 1 H), 2.38 (s, 3 H), 1.06 – 1.25 (m, 27 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 159.4, 156.7, 151.3, 139.1, 137.7, 128.7, 128.6, 128.5, 114.0, 105.7, 101.5, 75.1, 59.9, 30.4, 24.4, 20.1, 19.8, 18.1, 18.0, 12.6; MS (CI) Exact Mass Calcd for $C_{28}H_{43}N_2O_2Si$ $(M+H)^+$: 467.3. Found: 467.2.

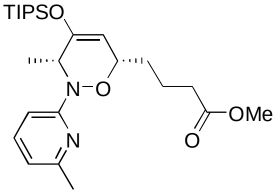
3l



Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (94% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99:1 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 12.2 min, minor enantiomer t_r = 10.0 min.) to have 88% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{26}_D$ = –101.8° (c = 0.66, $CHCl_3$; for the pruduct with 88% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1735, 1669, 1589, 1576, 1455, 1212 cm^{-1}; ^1H NMR (400 MHz, CD_3Cl) δ 7.35 – 7.49 (m, 6 H), 6.95 (d, *J* = 8.3 Hz, 1 H), 6.59 (d, *J* = 7.3 Hz, 1 H), 5.50 (t, *J* = 1.6 Hz, 1 H), 5.04 – 5.10 (m, 1 H), 4.82 (d, *J* = 0.84, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 2.51 – 2.58 (m, 2 H), 2.39 (s, 3 H), 2.27 – 2.37 (m, 2 H), 1.21 (t, *J* = 7.2, 2 H), 1.16 – 1.27 (m, 3 H), 1.16 (d, *J* = 5.4 Hz, 12 H), 1.08 (d, *J* = 5.4 Hz, 6 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 173.7, 158.8, 156.7, 151.6, 138.8, 137.8, 128.8, 128.6, 128.4, 114.6, 106.0, 101.2, 76.0, 60.1, 55.3, 31.6, 26.6, 24.3, 18.0, 14.2, 12.5; MS (CI) Exact Mass Calcd for $C_{30}H_{45}N_2O_4Si$ $(M+H)^+$: 525.3. Found: 525.2.

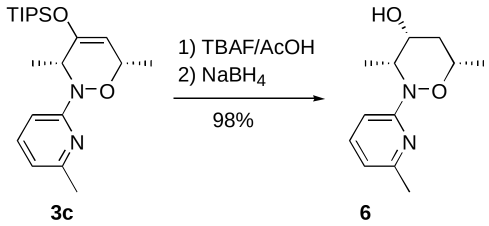
3m



Purification by flash column chromatography with elution by hexanes: ethyl acetate (95:5) provided as a colorless oil (96% yield). Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99:1 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 10.0 min, minor enantiomer t_r = 8.8 min.) to have 93% ee.

TLC R_f 0.8 (5:1 hexanes: ethyl acetate); $[\alpha]^{26}_D$ = –149.1° (c = 0.85, $CHCl_3$; for product with 93% ee); FTIR (CD_3Cl) υ_{max} 2945, 2867, 1742, 1669, 1590, 1576, 1454, 1337, 1237, 1166, 883, 785, 685 cm^{-1}; ^1H NMR (500 MHz, CD_3Cl) δ 7.44 (dd, *J* = 8.1 Hz, *J* = 7.5 Hz, 1 H), 6.87 (d, J = 8.3 Hz, 1 H), 6.59 (d, J = 7.3 Hz, 1 H), 4.74 (dq, J = 1.7 Hz, J = 6.5 Hz, 1 H), 4.68 (s, 1 H), 4.58 (br t, J = 6.0 Hz, 1 H), 3.67 (s, 3 H), 2.40 (s, 3 H), 2.40 (t, J = 7.2 Hz, 2 H), 1.78 – 1.94 (m, 2 H), 1.59 – 1.63 (m, 2 H), 1.26 (d, J = 6.5 Hz, 3 H), 1.19 – 1.24 (m, 3 H) 1.13 (s, 12 H), 1.10 (s, 6 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 173.9, 159.3, 156.6, 153.0, 137.7, 114.8, 106.2, 101.2, 75.4, 54.5, 51.5, 34.0, 33.9, 24.4, 20.7, 18.0, 14.3, 12.6; MS (CI) Exact Mass Calcd for $C_{25}H_{43}N_2O_4Si$ $(M+H)^+$: 463.3. Found: 463.2.

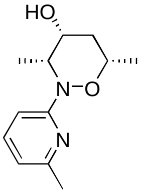
Conversion to Protected Amino Alcohol



To a solution of **3c** (1.50 g, 4.0 mmol) in THF (30 mL) was added AcOH (264 mg, 4.4 mmol). After cooloing the solution to –78 °C, tetrabutylammonium fluoride (1.0M in THF, 4.4mL, 4.4mmol) was added and was allowed to warm to room temperature. The mixture was stirred for 2 h and diluted with Et_2O (30 mL). The organic layer was washed with sat. NH_4Cl (aq) (15 mL), sat. $NaHCO_3$ (aq) (15 mL) and brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure.

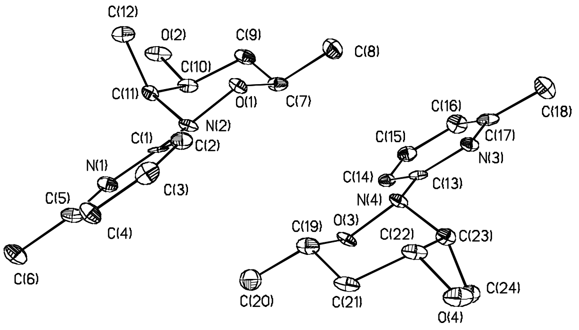
To a cooled solution (0 °C) of this residue in MeOH (20 mL) was added $NaBH_4$ (166 mg 4.4 mmol). After stirring at same temperature for 2 h, the mixture was concentrated under reduced pressure and was diluted with Et_2O (40 mL). The organic layer was washed with sat. NH_4Cl (aq) (20 mL), sat. $NaHCO_3$ (aq) (20 mL) and brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography to give **6** as a colorless oil* (871 mg, 3.9 mmol, 98% yield in 2 steps).

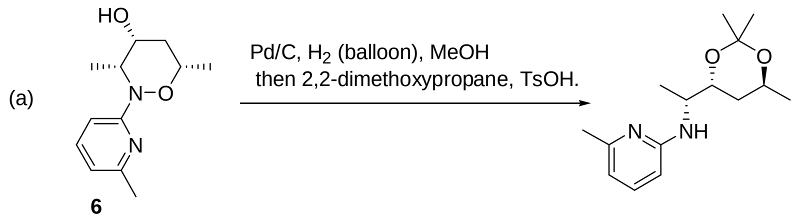
6



TLC R_f 0.6 (2:1 hexanes: ethyl acetate); $[\alpha]^{26}_{D}$ −107.4° (c = 0.76, CHCl$_3$); FTIR (CD$_3$Cl) υ_{max} 3384, 2975, 2939, 1578, 1452, 1375, 1337, 1149, 1100, 1053, 785 cm^{-1}; ^{1}H NMR (500 MHz, CD$_3$Cl) δ 7.44 (dd, *J* = 8.0 Hz, *J* = 7.7 Hz, 1 H), 6.88 (d, *J* = 8.3 Hz, 1 H), 6.60 (d, *J* = 7.4 Hz, 1 H), 4.83 (dq, *J* = 5.8 Hz, *J* = 6.0 Hz,1 H), 4.18 – 4.22 (m, 1 H), 3.99 (ddq, *J* = 11.3 Hz, *J* = 2.7 Hz, *J* = 6.3 Hz, 1 H), 2.41 (s, 3 H), 1.83 (ddd, *J* = 12.6 Hz, *J* = 5.0 Hz, *J* = 2.4 Hz, 1 H), 1.64 (dd, *J* = 12.4 Hz, *J* = 11.5 Hz, 1 H), 1.30 (d, *J* = 6.3 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, CD$_3$Cl) δ 159.7, 156.6, 138.0, 115.0, 106.5, 74.3, 74.2, 67.4, 55.1, 36.7, 24.3, 20.0, 6.8; MS (CI) Exact Mass Calcd for $C_{12}H_{19}N_2O_2$ (M+H)$^+$: 223.1. Found: 223.1.

*racemic sample gave a crystal suitable for X-ray structure analysis.

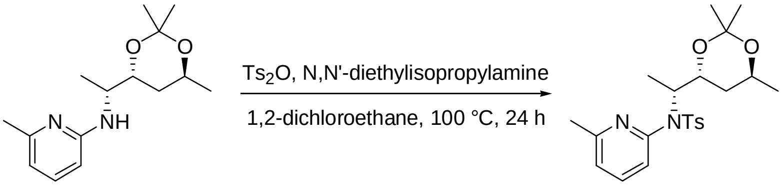




(a) To a solution of **6** (777 mg, 3.5 mmol) in MeOH (15 mL) was added 10% (dry basis) wet Pd/C (78 mg) and AcOH (264 mg, 4.4 mmol). The flask was flushed thoroughly with H$_2$ gas (x 3) and was stirred vigorously at 45 °C for 3 h. The mixture was cooled to room temperature and was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure.

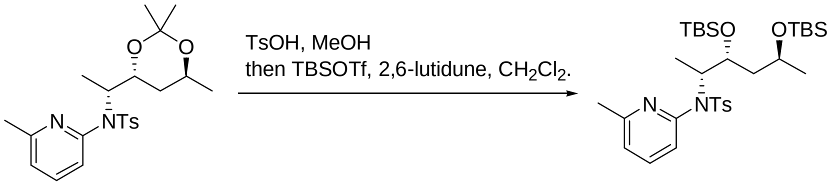
To this residue was added 2,2-dimethoxypropane (15 mL) and TsOH-H_2O (1.9 mg 0.01 mmol). The mixture was warmed to 80 °C. After stirring for 2 h at this temperature, the reaction mixture was concentrated under reduced pressure. The organic layer was diluted with Et_2O (15 mL) and was washed with sat. $NaHCO_3$ (aq) (15 mL) and brine (15 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was used for next reaction without further purification.

(b)



(b) To this crude mixture was added 1,2-dichloroethane (10 mL), *N*,*N*'-diisopropylethylamine (3.6 mL, 21 mmol) and Ts_2O (3.4 g, 10.5 mmol). The mixture was warmed to 100 °C and was stirred at same temperature for 24 h. The reaction mixture was cooled to room temperature and was diluted with CH_2Cl_2 (30 mL). The organic layer was washed with sat. NH_4Cl (aq) (10 mL), sat. $NaHCO_3$ (aq) (10 mL) and brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography to give tosylate as a brownish oil (1.17 g, 2.8 mmol, 80% yield from **6**).

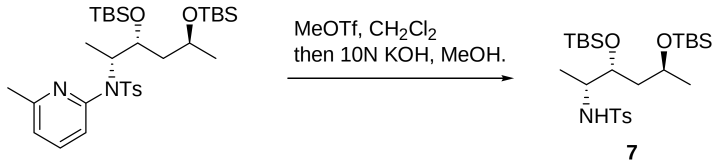
(c)



(c) To this tosylate (418 mg, 1.0 mmol) was added MeOH (10 mL) and TsOH-H_2O (1.9 mg 0.01 mmol). The mixture was warmed to 60°C and was stirred for 2 h. The reaction mixture was concentrated under reduced pressure and was diluted with Et_2O (15 mL). The organic layer was washed with NH_4Cl (10 mL), sat. $NaHCO_3$ (aq) (10 mL) and brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure.

The cooled (0 °C) solution of this residue in CH_2Cl_2 (10 mL) was added 2,6-Lutidine (0.51 mL, 4.4 mmol) and TBSOTf (0.51 mL, 2.2 mmol), in this order. The mixture was allowed to warm to room temperature and was stirred for 2 h. Sat. $NaHCO_3$ (aq) (10 mL) was added to the reaction mixture and the organic phase was extracted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography to give the product as colorless oil (576 mg, 0.95 mmol, 95% yield).

(d)

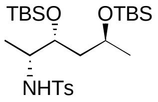


7

(d) To a cooled (0 °C) solution of this colorless oil (485 mg. 0.8 mmol) in CH_2Cl_2 (10 mL) was added MeOTf (144 mg, 0.88 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Na_2CO_3 (10 mL) was added to this solution and was stirred vigorously for 15 min. The organic layer was washed with brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure.

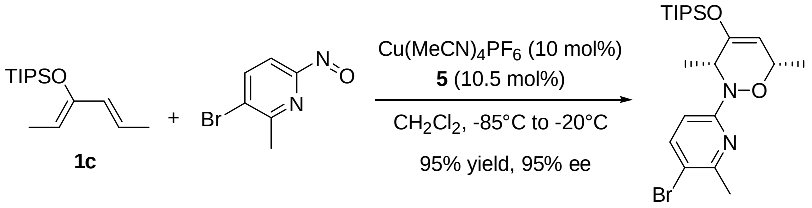
To a solution of the residue in MeOH (5 mL) was added 10N KOH (aq) (10 mL). The mixture was warmed to 60 °C and was stirred for 2 h. The mixture was concentrated under reduced pressure and was diluted by Et_2O (10 mL). Organic phase was washed with sat. NH_4Cl (aq) (10 mL x 2), sat. $NaHCO_3$ (aq) (10 mL) and brine (10 mL) and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography to give **7** as a white solid. (371 mg, 0.72 mmol, 90%)

7

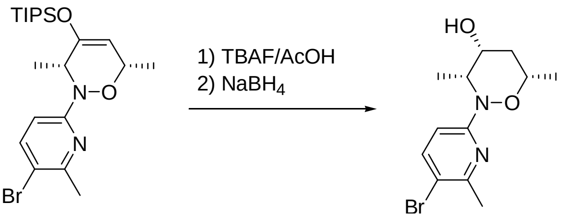


FTIR (CD_3Cl) υ_{max} 3276, 2929, 2856, 1472, 1331, 1256, 1162, 1074, 835 cm^{-1}; ^{1}H NMR (500 MHz, CD_3Cl) δ 7.76 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 7.9 Hz, 2 H), 4.62 (d, *J* = 8.9 Hz, 1 H), 3.85 – 3.88 (m, 1 H), 3.57 – 3.61 (m, 1 H), 3.37 – 3.41 (m, 1 H), 2.41 (s, 3 H), 1.52 – 1.56 (m, 1 H), 1.26 – 1.32 (m, 1 H), 1.00 (d, *J* = 6.3 Hz, 3 H), 0.99 (d, *J* = 6.3 Hz, 3 H), 0.88 (s, 9 H), 0.86 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 142.9, 138.6, 129.5, 127.1, 73.4, 66.4, 53.5, 44.0, 25.9, 25.8, 24.3, 21.4, 19.0, 18.0, 17.9, -4.0, -4.2, -4.4, -4.7

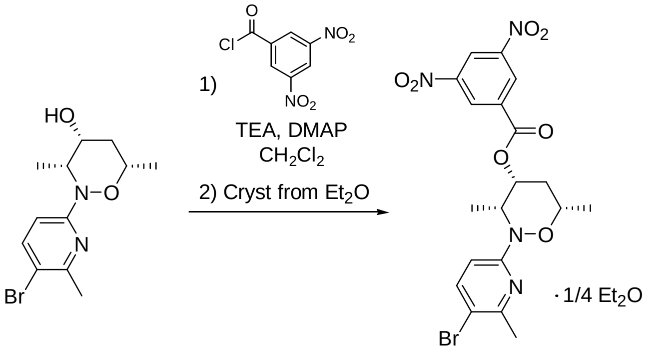
Determination of absolute configuration



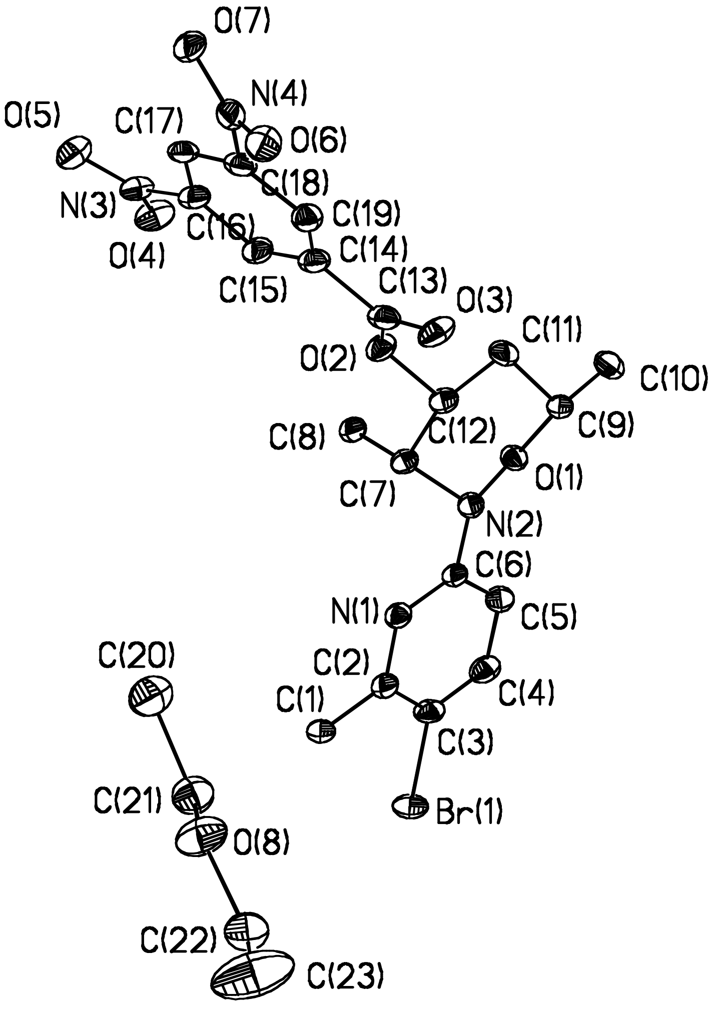
The reaction of 5-bromo-6-methyl-2-nitrosopyridine with **1c** was performed following the general procedure for catalytic asymmetric nitroso Diels–Alder reaction. Enantiometric excess was determined by HPLC with Chiralcel OD-H column ((99.8:0.2 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 10.4 min, minor enantiomer t_r = 14.0 min.) to have 95% ee.



This Diels–Alder adduct was further converted to alcohol by following the procedure above. See: conversion from **3c** to **6**.



To a solution of this alcohol in CH_2Cl_2 was added TEA (2.6 eq), DMAP (0.1 eq) and 3,5-dinitrobenzoicacid chloride (1.3 eq) and was stirred for 2 h. The reaction mixture was diluted with CH_2Cl_2 and the organic phase was washed with water and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography (9:1 hexanes: ethylacetate). This was crystallized from Et_2O to afford yellowish crystal, suitable for X-ray analysis. TLC R_f 0.6 (5:1 hexanes: ethylacetate); FTIR (CD_3Cl) υ_{max} 3101, 2978, 1734, 1570, 1436, 1344, 1276, 117, 1094 cm^{-1}; ^1H NMR (400 MHz, CD_3Cl) δ 9.26 (t, *J* = 2.1 Hz, 1 H), 9.17 (d, *J* = 2.1 Hz, 2 H), 7.64 (d, *J* = 8.7 Hz, 1 H), 6.83 (d, *J* = 8.7 Hz, 1 H), 5.54 (ddd, *J* = 11.7 Hz, *J* = 6.3 Hz, *J* = 5.5 Hz, 1 H) 5.13 (dq, *J* = 5.8 Hz, *J* = 6.0 Hz, 1 H), 4.21 (ddq, *J* = 11.3 Hz, *J* = 2.5 Hz, *J* = 6.4 Hz, 1 H), 3.48 (q, *J* = 7.0 Hz, 1 H), 2.52 (s, 3 H), 2.15 (ddd, *J* = 11.8 Hz, *J* = 5.2 Hz, *J* = 2.4 Hz, 1 H), 1.94 (dd, *J* = 12.4 Hz, *J* = 12.0 Hz, 1 H), 1.38 (d, *J* = 6.3 Hz, 3 H), 1.25 (d, *J* = 6.6 Hz, 3 H), 1.21 (d, *J* = 7.0 Hz, 1.5 H); ^{13}C NMR (100 MHz, CD_3Cl) δ 161.6, 157.5, 155.0, 148.7, 141.3, 133.8, 129.4, 122.6, 111.5, 109.0, 74.5, 72.3, 65.9, 51.7, 33.4, 29.7, 24.8, 19.5, 15.3, 8.0.


O(7)
N(4)
O(5)
C(17)
O(6)
C(18)
N(3)
C(19)
C(16)
C(14)
O(4)
C(15)
C(13)
O(3)
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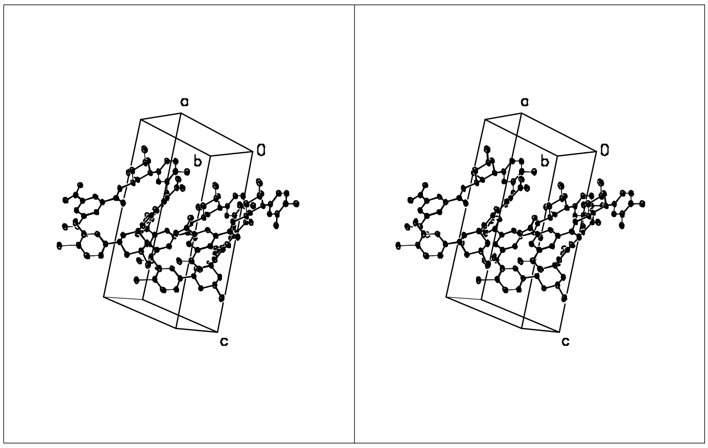
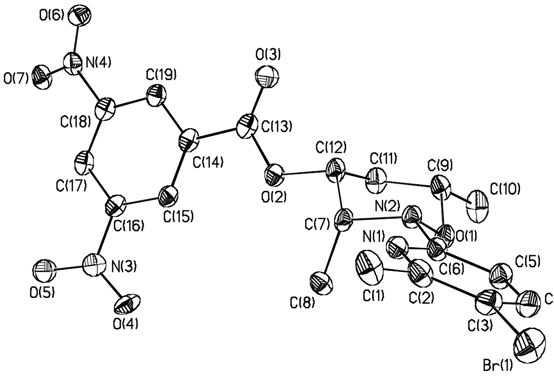
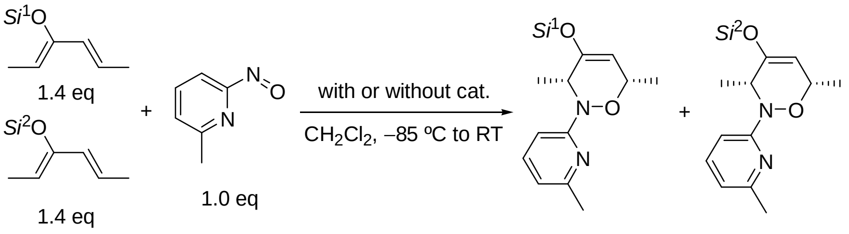




Competetive Reaction (eq. 1)



(1)

Si^1 = TIPS, Si^2 = TMS			
no catalysis	>99	:	<1
with $CuPF_6(MeCN)_4$-DIFLUORPHOS	>99 (99% ee)	:	<1
Si^1 = TIPS, Si^2 = TBS			
no catalysis	3	:	1
with $CuPF_6(MeCN)_4$-DIFLUORPHOS	11 (99% ee)	:	1

Without catalysis

To a cooled (–85 °C) solution of mixture of silyloxydienes (0.7 mmol each) in CH_2Cl_2 (4 mL) was added a solution of 6-Methyl-2-nitrosopyridine (0.5 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was allowed to warm to room temperature in 5 h and was stirred for additional 1 h. The mixture was concentrated under reduced pressure and purified through SiO_2 column.

TIPS vs TMS: **3c** was obtained (179 mg, 0.47 mmol).

TIPS vs TBS: Mixture of **3b** and **3c** was obtained (154 mg). The ratio of **3b**: **3c** (1: 3) was determined by ^{1}H NMR.

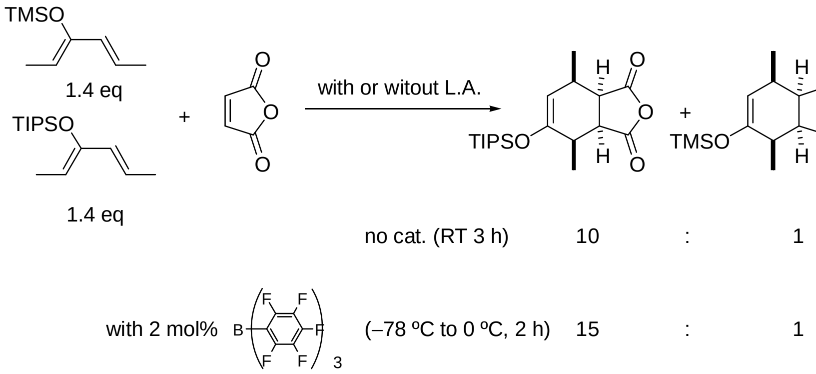
With catalysis

A 10 mL schrenk tube equipped with magnetic stir bar was charged with Cu(I)$(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol) and (*S*)-(-) DIFLUOPHOS (35.8 mg, 0.0525 mmol). The mixture was dried under vacuum for 10 min and was flushed thoroughly with N_2 gas, three times. CH_2Cl_2 (4 mL) was added by syringe and the resulting colorless solution was stirred for 1 h at room temperature. After cooling the solution to –85 °C, a solution of mixture of silyloxydienes (0.7 mmol each) in CH_2Cl_2 (1 mL) was added and stirred for 10 min. A solution 6-metyl-2-nitrosopyridine **2** in CH_2Cl_2 (1 mL) was added dropwise (30 min) to the solution. After the addition, the reaction mixture was gradually warmed to –20 °C in 5 h and was stirred at –20 °C for additional 1 h. The crude product was purified by silica gel chromatography.

TIPS vs. TMS: **3c** was obtained (179 mg, 0.47 mmol, 99% ee).

TIPS vs. TBS: Mixture of **3b** and **3c** was obtained (162 mg 99% ee for **3c**). The ratio of **3b**: **3c** (1: 11) was determined by ^{1}H NMR. Enantiometric excess was determined by HPLC with Chiralcel OD-H column (99.6:0.4 hexane:2-propanol), 0.5 mL/min; major enantiomer t_r = 7.6 min, minor enantiomer t_r = 8.8 min.

Competetive Reaction (eq. 2)

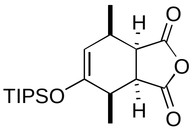


Without catalysis

To a cooled (0 °C) solution of mixture of silyloxydienes (0.7 mmol each) in CH_2Cl_2 (4 mL) was added a solution of maleic anhydryde (0.5 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 3 h. The mixture was concentrated under reduced pressure and purified by silica gel chromatography. The mixture of two products was obtained (160 mg). The ratio (10: 1) was determined by ^{1}H NMR.

With catalysis

To a cooled (–78 °C) solution of mixture of silyloxydienes (0.7 mmol each) in CH_2Cl_2 (4 mL) was added tris(pentafluorophenyl)borane (0.01 mmol). The mixture was added maleic anhydryde (0.5 mmol) and was allowed to warm to 0 °C in 2 h. The mixture was concentrated under reduced pressure and purified by silica gel chromatography. The mixture of two products was obtained (168 mg). The ratio (15: 1) was determined by ^{1}H NMR.

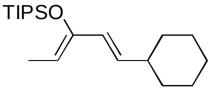


FTIR (CD_3Cl) υ_{max} 1854, 1773, 1664, 1458, 1347, 1295, 1209, 1088, 1068, 1018, 933, 883, 850, 714 cm^{-1}; ^{1}H NMR (500 MHz, CD_3Cl) δ 4.58 (dd, *J* = 3.4 Hz, *J* = 2.5 Hz, 1 H), 3.27 (dd, *J* = 9.2 Hz, *J* = 6.1 Hz, 1 H), 3.18 (dd, *J* = 9.2 Hz, *J* = 6.1 Hz, 1 H), 2.59 – 2.63 (m, 1 H), 2.44 – 2.48 (m, 1 H), 1.41 (d, *J* = 7.3 Hz, 3 H), 1.37 (d, *J* = 7.3Hz, 1 H), 1.13

– 1.20 (m, 3 H), 1.04 (d, *J* = 2.7 Hz, 12 H), 1.02 (d, *J* = 2.6 Hz, 6 H); ^{13}C NMR (125 MHz, CD_3Cl) δ 171.6, 171.4, 153.4, 103.1, 47.0, 46.6, 34.1, 30.5, 17.9, 17.8, 17.2, 12.5.

Spectrum Data of Dienes

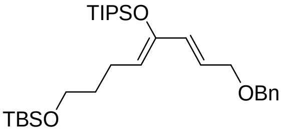
1d



(2*Z*,4*E*): (2*E*,4*E*) (>15: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 5.80 (d, *J* = 15.6 Hz, 1 H), 5.77 (dd, *J* = 15.6 Hz, *J* = 5.8 Hz, 1 H), 4.69 (q, *J* = 7.0 Hz, 1 H), 1.96 – 2.05 (m, 1 H), 1.67 – 1.76 (m, 4 H), 1.64 (d, *J* = 6.9 Hz, 3 H), 1.05 – 1.32 (m, 27 H).

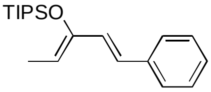
1e



(2*Z*,4*E*): (2*E*,4*E*) (>30: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.27 – 7.35 (m, 5 H), 6.07 (d, *J* = 15.5 Hz, 1 H), 5.88 (dt, *J* = 15.4 Hz, *J* = 5.9 Hz, 1 H), 4.74 (t, *J* = 7.2 Hz, 1 H), 4.51 (s, 2 H), 4.08 (d, *J* = 5.9 Hz, 2 H), 3.62 (t, *J* = 6.5 Hz, 2 H), 2.18 (dt, *J* = 7.4 Hz, *J* = 7.2 Hz, 2 H), 1.52 – 1.62 (m, 2 H), 1.11 – 1.23 (m, 3 H), 1.09 – 1.13 (m, 18 H), 0.89 (s, 9 H), 0.03 (s, 3 H), -0.01 (s, 3 H).

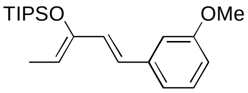
1h



(2*Z*,4*E*): (2*E*,4*E*) (>9: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.21 – 7.34 (m, 5 H), 6.69 (d, *J* = 15.9 Hz, 1 H), 6.57 (d, *J* = 15.9 Hz, 1 H), 4.95 (q, *J* = 7.1 Hz, 1 H), 1.76 (d, *J* = 7.1 Hz, 3 H), 1.22 – 1.29 (m, 3 H), 1.17 (s, 12 H), 1.12 (s, 6 H).

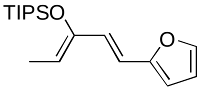
1i



(2*Z*,4*E*): (2*E*,4*E*) (>5: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.23 (d, *J* = 8.0 Hz, *J* = 7.7Hz, 1 H), 6.97 (d, *J* = 7.7 Hz, 1 H), 6.92 (t, *J* = 2.1 Hz, 1 H), 6.77 (dd, *J* = 7.9 Hz, J = 1.9 Hz, 1 H), 6.66 (d, *J* = 15.9 Hz, 1 H), 6.55 (d, *J* = 15.9 Hz, 1 H), 4.96 (q, *J* = 7.1 Hz, 1 H), 3.83 (s, 3 H), 1.74 (d, *J* = 7.1 Hz, 3 H), 1.22 – 1.29 (m, 3 H), 1.16 (s, 12 H), 1.14 (s, 6 H).

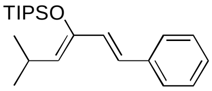
1j



(2*Z*,4*E*): (2*E*,4*E*) (>7: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.35 (s, 1 H), 6.50 (d, *J* = 15.7 Hz, 1 H), 6.50 (d, *J* = 15.8 Hz, 1 H), 6.44 (d, *J* = 15.8 Hz, 1 H), 6.37 (dd, *J* = 3.3 Hz, *J* = 1.9 Hz, 1 H), 6.21 (d, *J* = 3.3 Hz, 1 H), 4.94 (q, *J* = 7.2 Hz, 1 H), 1.72 (d, *J* = 7.1 Hz, 3 H), 1.22 – 1.29 (m, 3 H), 1.17 (s, 12 H), 1.12 (s, 6 H).

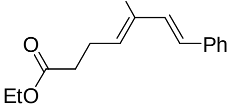
1k



(2*Z*,4*E*): (2*E*,4*E*) (4: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.11 – 7.26 (m, 5 H), 6.57 (d, *J* = 15.9 Hz, 1 H), 6.44. (d, *J* = 15.8) 4.64 (d, *J* = 9.6 Hz, 1 H), 2.67 – 2.74 (m, 1 H), 1.15 – 1.19 (m, 3 H), 1.07 (s, 12 H), 1.05 (s, 6 H),

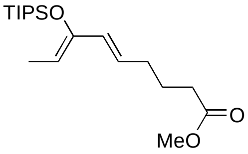
1l



(2*Z*,4*E*): (2*E*,4*E*) (>25: 1)

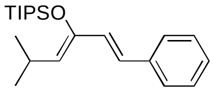
^{1}H NMR (400 MHz, CD_3Cl) δ 7.21 – 7.38 (m, 5 H), 6.71 (d, *J* = 15.9 Hz, 1 H), 6.54 (d, *J* = 15.9 Hz, 1 H), 4.87 (t, *J* = 7.3 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 1 H), 2.51 (dt, *J* = 7.6 Hz, *J* = 7.3 Hz, 2 H), 2.38 (t, *J* = 7.7, 2 H), 1.22 – 1.31 (m, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.15 (s, 12 H), 1.14 (s, 6 H).

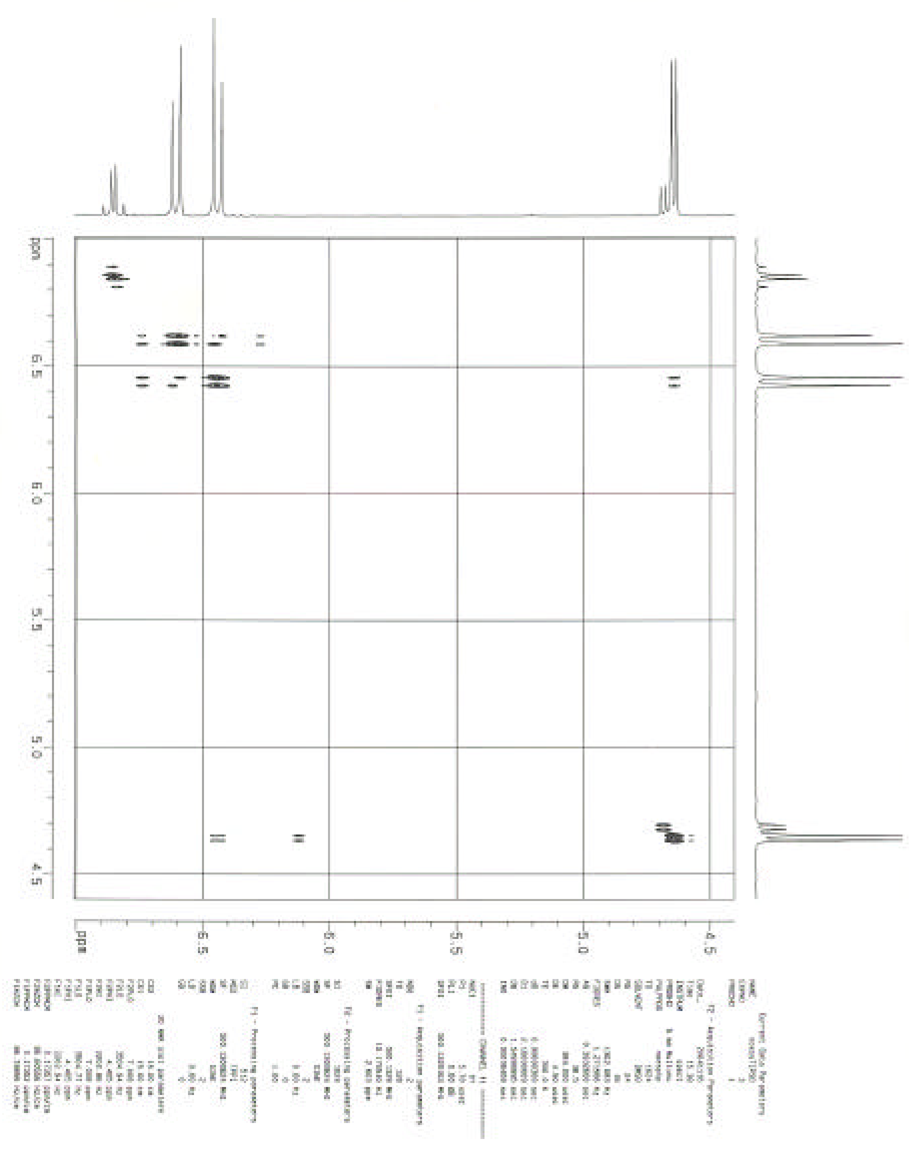
1m

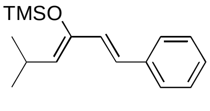


(2*Z*,4*E*): (2*E*,4*E*) (>9: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 5.85 (d, *J* = 15.5 Hz, 1 H), 5.74 (dt, *J* = 15.4 Hz, *J* = 6.8 Hz, 1 H), 4.70 (d, *J* = 7.1 Hz, 1 H), 3.66 (s, 3 H), 2.31 (t, *J* = 7.6 Hz, 2 H), 2.15 (dt, *J* = 7.3 Hz, *J* = 7.1 Hz, 2 H), 1.73 (tt, *J* = 7.4 Hz, *J* = 7.1 Hz, 2 H), 1.64 (d, *J* = 7.0 Hz, 3 H), 1.05 – 1.18 (m, 21 H).

NOESY spectrum of 





(2*Z*, 4*E*): (2*E*, 4*E*) (4: 1)

^{1}H NMR (400 MHz, CD_3Cl) δ 7.18 – 7.43 (m, 5 H), 6.52 (d, *J* = 15.9 Hz, 1 H), 6.44. (d, *J* = 15.8) 4.80 (d, *J* = 9.7 Hz, 1 H), 2.66 – 2.73 (m, 1 H), 1.15 – 1.19 (m, 3 H), 1.00 (s, 12 H), 1.05 (s, 6 H), 4.51 (s, 2 H), 4.08 (d, *J* = 5.9 Hz, 2 H), 3.62 (t, *J* = 6.5 Hz, 2 H), 2.14 – 2.22 (m, 2 H), 1.52 – 1.62 (m, 2 H), 1.11 – 1.23 (m, 3 H), 1.09 – 1.13 (m, 18 H), 1.01 (d, *J* = 6.7 Hz, 6 H), 0.28 (s, 9 H)

NOESY spectrum of