Supporting Information

"Revised"

Title

Catalytic Asymmetric Synthesis of Vicinal Diamine Derivatives Through Enantioselective *N*-Allylation Using Chiral π-Allyl Pd-Catalyst

Authored by

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The Contents of Supporting Information: Experimental procedures and characterization data for compounds **1a**-**1j**, **2a**, **2c**-**2i**, **4**-**6**, and reaction scheme for the determination of the absolute configuration of **2a**, **2d**, **2g**.

Experimental Section

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. In ^{1}H and ^{13}C NMR spectra, chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. Mass spectra were recorded by electron impact or chemical ionization. Column chromatography was performed on silica gel (75-150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 X 4 cm i. d. prepacked column (silica gel, 50 μm) with a UV detector. High-performance liquid chromatography (HPLC) was performed on a 25 x 0.4 cm i. d. chiral column with a UV detector.

Starting materials 1a-1j: Starting materials **1a-1j** were prepared from known diamines in accordance with following procedure.

***cis*-*N*,*N*'-Bis-(*p*-toluenesulfonyl)-1,2-diaminocyclohexane (1a)**. To a solution of *cis*-1,2-diaminocyclohexane (1.2 mL, 10 mmol, commercially available from Tokyo Kasei Kogyo Co. LTD) and Et_3N (4.15 mL, 30 mmol) in THF (20 mL) was added tosyl chloride (4.58 g, 24 mmol). After being stirred for 15 h at rt, the mixture was poured into 2% HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 3) gave **1a** (4.05 g, 96 %). **1a**: white solid; mp 167-168 °C; IR (KBr) 3281 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.71 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 8.2 Hz, 4H), 5.45 (d, *J* = 7.9 Hz, 2H), 3.12 (m, 2H), 2.42 (s, 6H), 1.14-1.46 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ: 143.2, 137.1, 129.5, 126.9, 53.5, 29.5, 21.7, 21.6; MS (*m*/*z*) 423 (MH^+); HRMS calcd for $C_{20}H_{27}N_2O_4S_2$ (MH^+) 423.1412, found 423.1398.

***cis*-*N*,*N*'-Bisbenzoyl-1,2-diaminocyclohexane (1b)**. **1b** was prepared from *cis*-1,2-diaminocyclohexane (0.6 mL, 5 mmol) in accordance with the general procedure for the synthesis of **1a**. Purification by column chromatography (hexane/AcOEt = 1) gave **1b** (1.35 g, 84 %). **1b**: white solid; mp 187-188 °C; IR (KBr) 3322, 1636 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.82 (d, *J* = 7.3 Hz, 4H), 7.32-7.52 (m, 8H), 4.28 (m, 2H), 1.92-2.10 (m, 2H), 1.56-1.78 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ: 167.9, 134.0, 131.3, 128.3, 126.9, 51.8, 28.6, 22.5; MS (*m*/*z*) 323 (MH^+); Anal calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88, N, 8.69. Found: C, 74.67; H, 6.57, N, 8.60.

***cis*-*N*,*N*'-Bis-(2-trifluoromethyl)phenylsulfonyl-1,2-diaminocyclohexane (1c)**. **1c** was prepared from *cis*-1,2-diaminocyclohexane (0.5 mL, 4 mmol) in accordance with the general

procedure for the synthesis of **1a**. Purification by column chromatography (hexane/AcOEt = 1) gave **1c** (1.73 g, 82 %). **1c**: white solid; mp 131-132 °C; IR (KBr) 3303 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 8.12-8.22 (m, 2H), 7.84-7.92 (m, 2H), 7.66- 7.76 (m, 4H), 5.05 (brd, *J* = 6.2 Hz, 2H), 3.43 (m, 2H), 1.63 (m, 2H), 1.24- 1.50 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ: 139.1, 131.8, 130.2, 127.7 (q, $J_{C\text{-}F}$ = 6.3 Hz), 126.7 (q, $J_{C\text{-}F}$ = 32.8 Hz), 124.1, 120.5, 54.2, 28.4, 21.3; MS (*m/z*) 531 (MH^+); HRMS calcd for $C_{20}H_{21}N_2O_4F_6S_2$ (MH^+) 531.0847, found 531.0879.

***cis*-*N*,*N*'-Bis-(2-nitro)phenylsulfonyl-1,2-diaminocyclohexane (1d)**. **1d** was prepared from *cis*-1,2-diaminocyclohexane (0.6 mL, 5 mmol) in accordance with the general procedure for the synthesis of **1a**. Purification by column chromatography (hexane/AcOEt = 1) gave **1d** (1.99 g, 82 %). **1d**: white solid; mp 183-184 °C; IR (KBr) 3345, 3316 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 8.03-8.10 (m, 2H), 7.83-7.90 (m, 2H), 7.69- 7.77 (m, 4H), 5.56 (d, *J* = 7.9 Hz, 2H), 3.64 (m, 2H), 1.25 - 1.62 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ: 147.0, 133.4, 132.7, 131.8, 129.6, 124.1, 54.2, 28.5, 21.1; MS (*m/z*) 485 (MH^+); Anal. calcd for $C_{18}H_{20}N_4O_8S_2$: C, 44.62; H, 4.16, N, 11.56. Found: C, 44.29; H, 4.48, N, 11.24.

***cis*-*N*,*N*'-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diaminocyclohexane (1e)**. To a solution of *cis*-1,2-diaminocyclohexane (0.8 mL, 7 mmol) and Et_3N (3 mL, 21 mmol) in THF (10 mL) was added 2,4,6-triisopropylbenzenesulfonyl chloride (4.2 g, 14 mmol). After being stirred for 15 h at 80 °C, the mixture was poured into 2% HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 5) gave **1e** (3.23 g, 71 %). **1e**: white solid; mp 84-85 °C; IR (KBr) 3389, 3265 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 4H), 4.97 (d, *J* = 7.9 Hz, 2H), 4.14 (sept, *J* = 6.7 Hz, 4H), 3.55 (m, 2H), 2.90 (sept, *J* = 6.7 Hz, 2H), 1.24 - 1.64 (m, 8H), 1.28 (d, *J* = 6.7 Hz, 24H), 1.26 (d, *J* = 6.7 Hz, 12H); ^{13}C-NMR ($CDCl_3$) δ: 152.6, 149.9, 132.8, 123.7, 53.0, 34.3, 29.9, 29.7, 25.2, 25.0, 23.8, 21.8; MS (*m/z*) 647 (MH^+); HRMS calcd for $C_{36}H_{59}N_2O_4S_2$ (MH^+) 647.3916, Found: 647.3961.

***cis*-*N*,*N*'-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diaminocyclopentane (1f)**. **1f** was prepared from *cis*-1,2-diaminocyclopentane[1] in accordance with the general procedure for the synthesis of **1e**. **1f**: white solid; mp 170-171 °C; IR (KBr) 3337, 3296 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 4H), 4.82 (brs, 2H), 4.11 (sept, *J* = 6.7 Hz, 4H), 3.64 (m, 2H), 2.90 (sept, *J* = 6.7 Hz, 2H),

1.00 - 1.88 (m, 6H), 1.27 (d, *J* = 6.7 Hz, 12H), 1.26 (d, *J* = 6.7 Hz, 24H); ^{13}C-NMR ($CDCl_3$) δ: 152.7, 150.0, 132.3, 123.7, 56.2, 34.3, 30.1, 29.9, 25.1, 23.8, 20.1; MS (*m/z*) 633 (MH^+); Anal. calcd for $C_{35}H_{56}N_2O_4S_2$: C, 66.41; H, 8.92, N, 4.43. Found: C, 66.07; H, 8.80, N, 4.23.

***meso-N,N'*-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diamino-1,2-diphenylethane (1g)**. **1g** was prepared from *meso*-1,2-diphenylethylenediamine (1.1 g, 5 mmol, commercially available from Aldrich) in accordance with the general procedure for the synthesis of **1e**. The reaction mixture was filtered, and the obtained crystal was washed with water and subsequently AcOEt (**1g**: 2.66 g, 71 %). **1g**: white solid; mp 248-249 °C; IR (KBr) 3302 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 6.98 - 7.16 (m, 10H), 6.62 (d, J = 7.3 Hz, 4H), 5.51 (d, *J* = 7.9 Hz, 2H), 4.88 (d, *J* = 7.9 Hz, 2H), 3.99 (sept, *J* = 6.7 Hz, 4H), 2.83 (sept, *J* = 6.7 Hz, 2H), 1.21 (d, *J* = 6.7 Hz, 12H), 1.144 (d, *J* = 6.7 Hz, 12H), 1.136 (d, *J* = 6.7 Hz, 12H); ^{13}C-NMR ($CDCl_3$) δ: 152.6, 149.8, 135.6, 132.6, 127.8, 127.4, 123.3, 61.5, 34.3, 30.0, 25.1, 25.0, 23.8; MS (*m/z*) 745 (MH^+); HRMS. calcd for $C_{44}H_{61}N_2O_4S_2$ (MH^+) 745.4073, found 745.4055.

***cis-N,N'*-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diaminocyclohexane (1h)**. **1h** was prepared from 1,3-diaminocyclohexane (0.4 mL, 3 mmol, *cis* and *trans* mixture, commercially available from Tokyo Kasei Kogyo Co. LTD) in accordance with the general procedure for the synthesis of **1e**. Purification by column chromatography (hexane/AcOEt = 5) gave **1h** (more polar, 1.16 g, 60 %) and the *trans*-isomer (less polar, 0.49 g, 25 %). **1h**: white solid; mp 201-202 °C; IR (KBr) 3290 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.13 (s, 4H), 4.24 (brd, *J* = 7.6 Hz, 2H), 4.07 (sept, *J* = 6.7 Hz, 4H), 3.16 (m, 2H), 2.90 (sept, *J* = 6.7 Hz, 2H), 2.12 (m, 1H), 1.85-1.95 (m, 2H), 1.70 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 12H), 1.22 (d, *J* = 6.7 Hz, 12H), 1.21 (d, *J* = 6.7 Hz, 12H), 0.94-1.32 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ: 152.5, 149.8, 133.0, 123.7, 51.3, 41.8, 34.3, 33.5, 29.8, 25.0, 25.0, 23.8, 22.8; MS (*m/z*) 647 (MH^+); HRMS. calcd for $C_{36}H_{59}N_2O_4S_2$ (MH^+) 647.3916, found 647.3913.

***N,N'*-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diamino-2-siloxypropane (1i)**. Bistrisylation of 1,3-diamino-2-propanol (0.9 g, 10 mmol, commercially available from Tokyo Kasei Kogyo Co. LTD) was performed in accordance with the general procedure for the synthesis of **1e**. Purification by column chromatography (hexane/AcOEt = 2.5) gave *N,N'*-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diamino-2-propanol. To a solution of *N,N'*-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diamino-2-propanol in THF (50 mL) was added NaH (2 g, 50

mmol) and TBSCl (4.5 g, 30 mmol) at 0 °C. After being stirred for 28 h at rt, the mixture was poured into aqueous $KHSO_4$ solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave **1i** (4.0 g, 54 %). **1i**: white solid; mp 129-130 °C; IR (KBr) 3351 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 4H), 4.93 (dd, *J* = 4.4, 8.8 Hz, 2H), 4.10 (sept, *J* = 6.7 Hz, 4H), 4.01 (m, 1H), 3.20 (ddd, *J* = 4.0, 8.8, 13.5 Hz, 2H), 2.98 (td, J = 5.3, 13.5 Hz, 2H), 2.91 (sept, *J* = 6.7 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 12H), 1.27 (d, *J* = 6.7 Hz, 12H), 1.27 (d, *J* = 6.7 Hz, 12H), 0.85 (s, 9H), 0.06 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 152.4, 149.7, 132.5, 123.6, 70.2, 44.6, 34.3, 29.9, 25.9, 25.1, 25.1, 23.8, 18.1, -4.6; MS (*m*/*z*) 737 (MH^+); HRMS. calcd for $C_{39}H_{69}N_2O_5S_2Si$ (MH^+) 737.4417, found 737.4385.

***trans*-*N*,*N*'-Bis-(2,4,6-triisopropyl)phenylulfonyl-1,2-diaminocyclohexane (1j)**. **1j** was prepared in accordance with the procedure described in the literature[2]. NMR data of **1j** coincided with that reported in the literature[2].

General procedure of catalytic asymmetric *N*-monoallylation of *meso*-diamides. Under Ar atmosphere, to a suspension of *tert*-BuOK (34 mg, 0.3 mmol) in toluene (1.5 mL) was added diamide **1e** (194 mg, 0.3 mmol). After being stirred for 5 min at rt, allylpalladium chloride dimer (4 mg, 0.011 mmol), (*R*,*R*)-Trost ligand (15 mg, 0.022 mmol) and allyl acetate (30 mg, 0.3 mmol) in 1,4-dioxane (1.5 mL) were added to the mixture at –15 °C, and then the reaction mixture was stirred for 23 h from –15 to 0 °C (in the reactions with **1a**, **1c** and **1d**, the mixture was stirred for 15 h at rt). The mixture was poured into 2 % HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **2e** (142 mg, 69 %). The ee (90 %ee) of **2e** was determined by HPLC analysis using a CHIRALCEL OD-H column [25 cm x 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.5 mL/min; (+)-**2e** (minor); t_R = 11.8 min, (-)-**2e** (major); t_R = 14.4 min].

(1*R*,2*S*)-*N*-Allyl-*N*,*N*'-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diaminocyclohexane (2e). **2e**: white solid; mp 130 - 131 °C; $[\alpha]_D$ = -13.6 (90 %ee, c = 1.0, $CHCl_3$); IR (KBr) 3394, 3283 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 2H), 7.14 (s, 2H), 5.86 (tdd, *J* = 6.5, 10.5, 16.7 Hz, 1H), 5.12 (d, *J* = 16.7 Hz, 1H), 5.12 (d, *J* = 7.0 Hz, 1H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.04-4.28 (m, 5H),

3.91-4.02 (m, 2H), 3.78 (m, 1H), 2.91 (sept, *J* = 6.9 Hz, 1H), 2.89 (sept, *J* = 6.9 Hz, 1H), 1.04-1.90 (m, 44H); ^{13}C-NMR ($CDCl_3$) δ: 152.9, 152.3, 151.2, 149.4, 136.0, 134.6, 131.7, 123.8, 123.6, 117.5, 59.0, 54.0, 48.1, 34.3, 34.2, 30.7, 30.0, 29.6, 26.8, 26.2, 25.2, 25.1, 25.1, 23.8, 19.2; MS (*m*/*z*) 687 (MH^+); Anal. calcd for $C_{39}H_{62}N_2O_4S_2$: C, 68.18; H, 9.10, N, 4.08. Found: C, 68.43; H, 8.86, N, 3.66.

(1*S*,2*R*)-*N*-Allyl-*N*,*N*'-bis-(*p*-toluenesulfonyl)-1,2-diaminocyclohexane (2a). **2a** was prepared from **1a** (254 mg, 0.6 mmol) in accordance with the general procedure for the synthesis of **2e** (the *N*-allylation reaction was performed at rt). Purification by column chromatography (hexane/AcOEt = 5) gave **2a** (189 mg, 68 %). The ee (52 %ee) of **2a** was determined by HPLC analysis using a CHIRALPACK AD column [25 cm x 0.46 cm i.d.; 20 % *i*-PrOH in hexane; flow rate, 1 mL/min; (-)-**2a** (major); t_R = 16.9 min, (+)-**2a** (minor); t_R = 19.6 min]. **2a**: white solid; mp 130 - 131 °C; $[\alpha]_D$ = -8.3 (52 %ee, c = 1.0, $CHCl_3$); IR (KBr) 3288 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.78 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.67 (brs, 1H), 5.43 (tdd, *J* = 6.2, 10.2, 17.0 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 3.84 (dd, *J* = 6.2, 16.1 Hz, 1H), 3.66 (dd, *J* = 6.2, 16.1 Hz, 1H), 3.45 (m, 1H), 3.37 (d, *J* = 12.9 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 1.70-1.92 (m, 3H), 1.10-1.52 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ: 143.1, 143.0, 138.3, 136.6, 134.9, 129.4, 129.4, 127.3, 126.8, 118.1, 60.7, 53.6, 50.5, 31.0, 26.9, 25.8, 21.7, 21.7, 18.9; MS (*m*/*z*) 463 (MH^+); Anal. calcd for $C_{23}H_{30}N_2O_4S_2$: C, 59.71; H, 6.54, N, 6.06. Found: C, 59.33; H, 6.55, N, 5.78.

(1*S,2*R**)-*N*-Allyl-*N*,*N*'-bis-(2-trifluoromethyl)phenylsulfonyl-1,2-diaminocyclohexane (2c).** **2c** was prepared from **1c** (159 mg, 0.3 mmol) in accordance with the general procedure for the synthesis of **2e** (the *N*-allylation reaction was performed at rt). Purification by column chromatography (hexane/AcOEt = 5) and subsequent MPLC (hexane/AcOEt = 3) gave **2c** (118 mg, 69 %). The ee (55 %ee) of **2c** was determined by HPLC analysis using a CHIRALPACK AD column [25 cm x 0.46 cm i.d.; 20 % *i*-PrOH in hexane; flow rate, 1 mL/min; (-)-**2c** (minor); t_R = 5.7 min, (+)-**2c** (major); t_R = 6.8 min]. **2c**: white solid; mp 135 - 136 °C; $[\alpha]_D$ = +16.1 (55 %ee, c = 1.0, $CHCl_3$); IR (KBr) 3314 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 8.20 (m, 1H), 8.11 (m, 1H), 7.84-7.92 (m, 2H), 7.63-7.77 (m, 4H), 5.63 (tdd, *J* = 6.5, 10.3, 17.0 Hz, 1H), 5.10 (brd, *J* = 6.0 Hz, 1H), 5.09 (dd, *J* = 1.2, 17.0 Hz, 1H), 4.97 (dd, *J* = 1.2, 10.3 Hz, 1H), 4.24 (dd, *J* = 6.5, 16.7 Hz, 1H), 4.13 (dd, *J* =

6.5, 16.7 Hz, 1H), 3.78-3.96 (m, 2H), 1.54-1.88 (m, 3H), 1.22-1.48 (m, 3H), 0.84-1.22 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ: 140.3, 138.8, 135.3, 132.6, 132.5, 132.1, 132.1, 131.8, 131.0, 128.3 (q, $J_{C\text{-}F}$ = 5.8 Hz), 128.2 (q, $J_{C\text{-}F}$ = 6.3 Hz), 124.5 (q, $J_{C\text{-}F}$ = 31.1 Hz), 120.9 (q, $J_{C\text{-}F}$ = 31.7 Hz), 117.5, 59.1, 55.2, 48.7, 30.6, 26.7, 25.7, 18.9; MS (*m*/*z*) 571 (MH^+); Anal. calcd for $C_{23}H_{24}F_6N_2O_4S_2$: C, 48.42; H, 4.24, N, 4.91. Found: C, 48.39; H, 4.54, N, 4.65.

(1*S*,2*R*)-*N*-Allyl-*N*,*N*'-bis-(2-nitro)phenylsulfonyl-1,2-diaminocyclohexane (2d). **2d** was prepared from **1d** (145 mg, 0.3 mmol) in accordance with the general procedure for the synthesis of **2e** (the *N*-allylation reaction was performed at rt). Purification by column chromatography (hexane/AcOEt = 3) gave **2d** (117 mg, 74 %). The ee (70 %ee) of **2d** was determined by HPLC analysis using a CHIRALPACK AD column [25 cm x 0.46 cm i.d.; 30 % *i*-PrOH in hexane; flow rate, 1 mL/min; (+)-**2d** (minor); t_R = 9.2 min, (-)-**2d** (major); t_R = 11.7 min]. **2d**: white solid; mp 63-64 °C; $[\alpha]_D$ = -125.0 (70 %ee, c = 1.0, $CHCl_3$); IR (KBr) 3349 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 8.00-8.10 (m, 2H), 7.82-7.90 (m, 1H), 7.56-7.78 (m, 5H), 5.67 (d, *J* = 9.1 Hz, 1H), 5.64 (m, 1H), 5.13 (d, *J* = 17.3 Hz, 1H), 4.98 (d, *J* = 10.3 Hz, 1H), 4.34 (dd, *J* = 6.2, 17.3 Hz, 1H), 4.26 (dd, *J* = 6.2, 17.3 Hz, 1H), 3.92-4.06 (m, 2H), 1.20-1.94 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ: 147.7, 147.5, 135.1, 134.5, 133.8, 133.5, 133.1, 133.0, 131.5, 131.5, 130.9, 125.2, 123.6, 117.5, 58.7, 56.3, 48.4, 30.7, 26.7, 25.6, 19.2; MS (*m*/*z*) 525 (MH^+); HRMS. calcd for $C_{21}H_{25}N_4O_8S_2$ (MH^+) 525.1114, found 525.1089.

(1*R,2*S**)-*N*-Allyl-*N*,*N*'-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diaminocyclopentane (2f).** **2f** was prepared from **1f** (127 mg, 0.2 mmol) in accordance with the general procedure for the synthesis of **2e**. Purification by column chromatography (hexane/AcOEt = 30) gave **2f** (114 mg, 85 %). The ee (71 %ee) of **2f** was determined by HPLC analysis using a CHIRALPACK AD-H column [25 cm x 0.46 cm i.d.; 0.5 % *i*-PrOH in hexane; flow rate, 1 mL/min; (-)-**2f** (major); t_R = 15.7 min, (+)-**2f** (minor); t_R = 20.6 min]. **2f**: white solid; mp 47-48 °C; $[\alpha]_D$ = -1.1 (71 %ee, c = 1.7, $CHCl_3$); IR (KBr) 3290 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 2H), 7.15 (s, 2H), 5.73 (m, 1H), 5.44 (brd, *J* = 3.5 Hz, 1H), 5.00-5.12 (m, 2H), 4.18 (sept, J = 6.7 Hz, 2H), 4.04-4.16 (m, 4H), 3.86 (dd, J = 7.6, 16.4 Hz, 1H), 3.78 (m, 1H), 2.90 (sept, J = 6.7 Hz, 2H), 1.64-1.98 (m, 4H), 0.84-1.48 (m, 38H); ^{13}C-NMR ($CDCl_3$) δ: 153.3, 152.4, 151.0, 150.1, 134.0, 133.2, 131.6, 123.9, 123.6, 118.4, 60.6, 55.1, 49.9, 34.3, 30.9, 29.9, 29.5, 27.9, 25.2, 25.1, 25.0, 24.9, 23.8, 23.7, 21.4; MS

(*m*/*z*) 673 (MH^+); Anal. calcd for $C_{38}H_{60}N_2O_4S_2$: C, 67.81; H, 8.99, N, 4.16. Found: C, 67.82; H, 8.97, N, 3.90.

(1*R*,2*S*)-*N*-Allyl-*N*,*N*'-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,2-diamino-1,2-diphenylethane (2g). **2g** was prepared from **1g** (186 mg, 0.25 mmol) in accordance with the general procedure for the synthesis of **2e**. Purification by column chromatography (hexane/AcOEt = 30) and subsequent MPLC (hexane/AcOEt = 20) gave **2g** (124 mg, 63 %). The ee (90 %ee) of **2g** was determined by HPLC analysis using a CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 1 mL/min; (+)-**2g** (minor); t_R = 7.9 min, (-)-**2g** (major); t_R = 11.6 min]. **2g**: white solid; mp 174-175 °C; $[\alpha]_D$ = -0.8 (90 %ee, c = 1.0, $CHCl_3$); IR (KBr) 3327, 3292 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 6.82-7.30 (m, 10H), 7.01 (s, 2H), 6.87 (s, 2H), 5.60-5.76 (m, 1H), 5.39 (t, *J* = 6.7 Hz, 1H), 5.34 (d, *J* = 6.7 Hz, 1H), 5.18 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.63 (d, *J* = 6.7 Hz, 1H), 4.21 (dd, *J* = 5.0, 17.0 Hz, 1H), 4.03 (dd, *J* = 7.3, 17.0 Hz, 4H), 3.62-3.82 (m, 4H), 2.68-2.90 (m, 2H), 1.20 (d, *J* = 7.3 Hz, 6H), 1.18 (d, *J* = 7.0 Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 6H), 1.04 (d, *J* = 6.2 Hz, 6H), 1.03 (d, *J* = 7.0 Hz, 6H), 1.00 (d, *J* = 7.3 Hz, 6H); ^{13}C-NMR ($CDCl_3$) δ: 153.0, 152.0, 151.2, 148.7, 137.7, 135.3, 134.2, 134.0, 131.6, 129.9, 128.4, 128.2, 127.7, 127.6, 127.4, 123.7, 122.9, 117.4, 64.4, 59.7, 47.2, 34.3, 30.0, 29.5, 25.0, 25.0, 24.8, 24.7, 23.9, 23.8; MS (*m*/*z*) 785 (MH^+); Anal. calcd for $C_{47}H_{64}N_2O_4S_2$: C, 71.90; H, 8.22, N, 3.57. Found: C, 71.76; H, 7.93, N, 3.35.

(1*R,3*S**)-*N*-Allyl-*N*,*N*'-bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diaminocyclohexane (2h)**. **2h** was prepared from **1h** (194 mg, 0.3 mmol) in accordance with the general procedure for the synthesis of **2e**. Purification by column chromatography (hexane/AcOEt = 10) gave **2h** (109 mg, 53 %). The ee (18 %ee) of **2h** was determined by HPLC analysis using a CHIRALPACK AD column [25 cm x 0.46 cm i.d.; 3 % *i*-PrOH in hexane; flow rate, 1 mL/min; **2h** (minor); t_R = 8.3 min, **2h** (major); t_R = 14.1 min]. **2h**: white solid; mp 66-67 °C; IR (KBr) 3295 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.15 (s, 2H), 7.11 (s, 2H), 5.69 (tdd, *J* = 6.2, 10.3, 17.3 Hz, 1H), 5.05 (dd, *J* = 1.2, 17.3 Hz, 1H), 4.99 (dd, *J* = 0.9, 10.3 Hz, 1H), 4.24 (brd, *J* = 7.6 Hz, 1H), 4.11 (sept, *J* = 6.7 Hz, 2H), 4.03 (sept, *J* = 6.7 Hz, 2H), 3.80 (dd, *J* = 6.5, 16.7 Hz, 1H), 3.72 (dd, *J* = 6.5, 16.7 Hz, 1H), 3.63 (tt, *J* = 3.5, 12.0 Hz, 2H), 3.19 (m, 1H), 2.90 (sept, *J* = 6.7 Hz, 2H), 1.16-2.08 (m, 7H), 1.16-1.30 (m, 36H), 1.00 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ: 152.8, 152.4, 151.0, 149.7, 135.8, 133.1, 131.4,

123.7, 116.9, 55.1, 52.1, 45.9, 34.4, 34.3, 33.8, 30.3, 29.8, 29.4, 25.0, 25.0, 23.8, 23.4; MS (*m*/*z*) 687 (MH^+); Anal. calcd for $C_{39}H_{62}N_2O_4S_2$: C, 68.18; H, 9.10, N, 4.08. Found: C, 67.92; H, 8.88, N, 3.83.

***N*-Allyl-*N*,*N*'-Bis-(2,4,6-triisopropyl)phenylsulfonyl-1,3-diamino-2-hydroxypropane (2i)**. **2i** was prepared from **1i** (184 mg, 0.25 mmol) in accordance with the general procedure for the synthesis of **2e**. Purification by column chromatography (hexane/AcOEt = 50) gave siloxy product. To a solution of the siloxy product in THF (2 mL) was added to TBAF (0.2 mL, 1M THF solution). After being stirred for 1.5 h at rt, the mixture was poured into water and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification by column chromatography (hexane/AcOEt = 3) gave hydroxy product **2i** (144 mg, 69 %). The ee (27 %ee) of **2i** was determined by HPLC analysis using a CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 1 % *i*-PrOH in hexane; flow rate, 1 mL/min; **2i** (minor); t_R = 24.2 min, **2i** (major); t_R = 28.2 min]. **2i**: white solid; mp 94-95 °C; IR (KBr) 3502, 3342 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.16 (s, 4H), 5.64 (tdd, *J* = 6.7, 10.0, 17.0 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.11 (t, *J* = 6.4 Hz, 1H), 4.11 (sept, *J* = 6.7 Hz, 2H), 4.01 (sept, *J* = 6.7 Hz, 2H), 3.94-4.18 (m, 1H), 3.82 (dd, *J* = 6.7, 15.0 Hz, 1H), 3.73 (dd, *J* = 6.7, 15.0 Hz, 1H), 3.37 (dd, *J* = 7.0, 15.2 Hz, 1H), 3.31 (dd, *J* = 5.6, 15.2 Hz, 1H), 3.11 (ddd, *J* = 3.5, 7.0, 13.0 Hz, 1H), 3.00 (td, *J* = 5.6, 13.0 Hz, 1H), 2.90 (sept, *J* = 6.7 Hz, 2H), 1.20-1.32 (m, 36H); ^{13}C-NMR ($CDCl_3$) δ: 153.3, 152.5, 151.2, 149.9, 132.4, 131.8, 130.4, 124.0, 123.7, 120.1, 67.2, 50.4, 49.3, 45.7, 34.3, 29.9, 29.6, 25.1, 25.0, 24.9, 23.8, 23.7; MS (*m*/*z*) 663 (MH^+); Anal. calcd for $C_{36}H_{58}N_2O_5S_2$: C, 65.22; H, 8.82, N, 4.23. Found: C, 65.24; H, 8.62, N, 3.92.

Kinetic resolution of *racemic*-diamides. Under Ar atmosphere, to a suspension of *tert*-BuOK (34 mg, 0.3 mmol) in tolene (1.5 mL) was added diamide **1j** (194 mg, 0.3 mmol). After being stirred for 5 min at rt, allylpalladium chloride dimer (4 mg, 0.011 mmol), (*R*,*R*)-Trost-ligand (15 mg, 0.022 mmol) and allyl acetate (20 μl, 0.18 mmol) in THF (1.5 mL) were added to the mixture at –78 °C, and then the reaction mixture was stirred for 10 h from –15 to -10 °C. The mixture was poured into 2 % HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 10) gave *N*-monoallylated product (120 mg, 58 %) and

1j (72 mg, 37%). The ee (92 %ee) of recovered **1j** was determined by HPLC analysis using a CHIRALCEL OD-H column [25 cm x 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**1j** (minor); t_R = 13.7 min, (+)-**1j** (major); t_R = 24.2 min].

(1*R*,2*R*)-*N*,*N*'-Bis-(2,4,6-triisopropyl)phenylulfonyl-1,2-diaminocyclohexane (1j). NMR data of **1j** coincided with that reported in the literature[2]. The absolute configuration of **1j** was determined by comparing (HPLC analysis using a chiral column) with authentic sample derived from commercially available (1*R*,2*R*)-1,2-diaminocyclohexane.

(1*R*,2*S*)-*N*-Allyl-*N*'-(3,4-dichlorophenyl)acetyl-1,2-diaminocyclohexane (4) [Deprotection of (2,4,6-triisopropyl)phenylsulfonyl group]. Ammonia was condensed to a two-necked flask that was equipped with a dry ice condenser and contained **2e** (1.4 g, 2.0 mmol) dissolved in a minimum amount of THF at –78 °C. After removal of the cold bath, small pieces of sodium metal were added to the reaction mixture until a deep blue color persisted for 15 min. After removal of ammonia by heating to 40 °C, the mixture was poured into saturated aqueous Na_2CO_3 solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. To a solution of the residue (**3**) in THF was added (3,4-dichlorophenyl)acetyl chloride (512 mg, 2.5 mmol). After being stirred for 10 h at rt, the mixture was poured into saturated aqueous Na_2CO_3 solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. Purification of the residue by column chromatography ($CHCl_3$/CH_3OH/NH_3 = 500/9/1) gave **4** (356 mg, 57 %). **4**: colorless oil; IR (neat) 3302, 1642 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.34 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.08 (dd, *J* = 1.8, 8.2 Hz, 1H), 6.48 (brd, *J* = 7.0 Hz, 1H), 5.67 (tdd, *J* = 5.9, 10.3, 17.0 Hz, 1H), 5.06 (dd, *J* = 1.6, 17.0 Hz, 1H), 5.01 (dd, *J* = 1.6, 10.3 Hz, 1H), 3.82 (m, 1H), 3.45 (s, 2H), 3.21 (dd, *J* = 5.9, 14.1 Hz, 1H), 2.99 (dd, *J* = 5.9, 14.1 Hz, 1H), 2.63 (m, 1H), 1.75 (brs, 1H), 1.12-1.70 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ: 168.7, 136.2, 135.3, 132.3, 130.9, 130.8, 130.2, 128.4, 115.8, 55.0, 49.6, 49.0, 42.9, 28.0, 27.7, 22.9, 20.9; MS (*m*/*z*) 341 (MH^+); HRMS. calcd for $C_{17}H_{22}Cl_2N_2O$ (MH^+) 341.1187. found 341.1176.

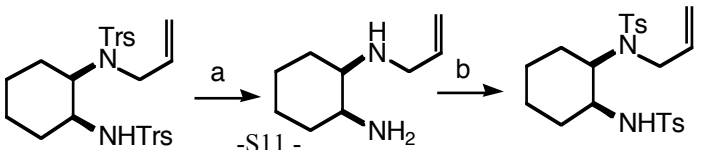
(1*R*,2*S*)-*N*,*N*-Diallyl-*N*'-(3,4-dichlorophenyl)acetyl-1,2-diaminocyclohexane (5). Under Ar atmosphere, to **4** (364 mg, 1.06 mmol) in toluene (5 mL) were added allylpalladium chloride dimer (13 mg, 0.035 mmol), dppe (28 mg, 0.07 mmol) and allyl acetate (120 mg, 1.2 mmol) in

THF (5 mL). After being stirred for 18 h at rt, the mixture was poured into saturated aqueous Na_2CO_3 solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 3) gave **5** (324 mg, 80 %). **5**: colorless oil; ^{1}H-NMR ($CDCl_3$) δ: 7.36-7.41 (m, 2H), 7.12 (dd, *J* = 2.1, 7.9 Hz, 1H), 6.05 (brd, *J* = 2.9 Hz, 1H), 5.63 (tdd, *J* = 6.4, 10.6, 16.7 Hz, 2H), 5.08 (d, *J* = 10.6 Hz, 2H), 5.06 (d, *J* = 16.7 Hz, 2H), 4.08 (m, 1H), 3.50 (s, 2H), 3.14 (dd, *J* = 6.4, 14.7 Hz, 2H), 3.07 (dd, *J* = 6.4, 14.7 Hz, 2H), 2.57 (td, J = 4.1, 11.1 Hz, 1H), 2.24 (m, 1H), 1.82 (m, 1H), 1.70 (m, 1H), 1.40 (m, 1H), 1.10-1.38 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ: 169.3, 135.3, 134.8, 132.5, 131.03, 131.00, 130.4, 128.5, 117.1, 58.6, 51.8, 46.9, 43.3, 28.8, 26.1, 24.9, 20.3; MS (*m/z*) 381 (MH^+); HRMS. calcd for $C_{20}H_{26}Cl_2N_2O$ (MH^+) 381.1500 . found 381.1523.

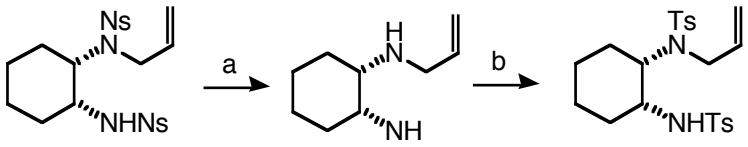
(1*R*,2*S*)-*N*-(3,4-dichlorophenyl)acetyl-1-(1-pyrrolidinyl)-2-aminocyclohexane (6). Under Ar atmosphere, to **5** (278 mg, 0.73 mmol) in CH_2Cl_2 (5 mL) was added Grubbs reagent (second generation, 31 mg, 0.037 mmol). After being stirred for 8.5 h at 40 °C, the mixture was poured into saturated aqueous Na_2CO_3 solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. Purification of the residue by column chromatography ($CHCl_3/CH_3OH/NH_3$ = 500/9/1) gave ring closing product (dihydropyrrole derivative) (117 mg, 45%). To ring closing product (117 mg, 0.33 mmol) in benzene (3 mL) was added Lindlar catalyst, and subsequently introduced H_2 gas. After being stirred for 11 h at rt, Lindlar catalyst was filtered off, and the solvent was removed in vacuo. Purification of the residue by column chromatography ($CHCl_3/CH_3OH/NH_3$ = 300/9/1) gave **6** (86 mg, 73%). NMR data of **6** coincided with that reported in the literature.[3] $[\alpha]_D$ value of **6** was measured as its fumarate salt.[3] $[\alpha]_D$ = +7.4 (CH_3OH, c = 0.2). lit. $[\alpha]_D$ = +9.2 (CH_3OH, c = 0.22)

The determination of absolute configurations of 2a, 2d and 2g.

The absolute configurations of **2a** and **2d** were determined by comparing with **2a** derived from **2e** and **2d**, respectively.



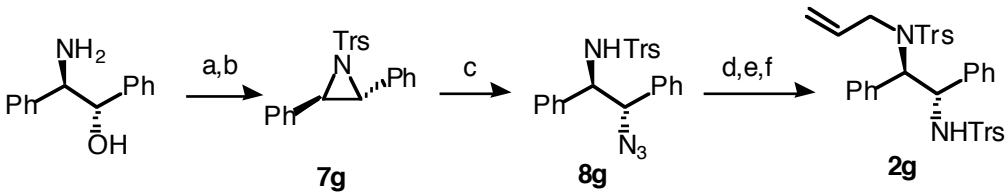
a) Na/liq.NH_3 b) TsCl (4 equiv), Et_3N (6 equiv), THF reflux, 24 h (2steps, 46%)



2d (70%ee) **3** **2a** (70%ee)

a) 4-*t*-BuC_6H_4SH (2.4 equiv), $CsCO_3$ (3 equiv), CH_3CN, rt, 10 h b) TsCl (4 equiv), Et_3N (6 equiv), THF reflux, 15 h (2steps, 38%)

The absolute configuration of **2g** was determined by comparing with the authentic sample derived from commercially available (1*S*,2*R*)-2-amino-1,2-diphenylethanol.



7g **8g** **2g**

a) TrsCl (1 equiv), Et_3N (2 equiv), THF, rt, 20 h (75%) b) MsCl (1.1 equiv), NaH (2 equiv), THF, rt, 20 h (64%) c) TBS-N_3 (1 equiv), TBAF (cat), THF, 50 °C, 10 h (97%) d) *t*-BuOK (1 equiv), (allyl-Pd-Cl)$_2$ (3.7 mol%), dppe (7.3 mol%), allyl acetate (1 equiv), toluene-dioxane, 0 °C, 5 h (71%) e) Ph_3P (1.1 equiv), H_2O (3 equiv), THF, rt, 12 h (36%) f) TrsCl (1 equiv), Et_3N (1 equiv), dioxane, 100 °C, 12 h (26%)

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