Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 3559–3570

TETRAHEDRON: *ASYMMETRY*

Syntheses of C_2-symmetric vicinal diamines derived from tartaric acid

Andreas Scheurer,[a,b] Paul Mosset [a,*] and Rolf W. Saalfrank [b,*]

[a] *Laboratoire de Synthèses et Activations de Biomolécules, CNRS ESA 6052, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, F-35700 Rennes, France*

[b] *Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestraβe 42, D-91054 Erlangen, Germany*

Received 29 July 1999; accepted 11 August 1999

Abstract

C_2-symmetric vicinal diamines **3b**–**f**, derived from L-tartaric acid, with increasingly bulky terminal ether functionalities were prepared using two distinct sequences. Diamines **3b**,**c** were obtained from the corresponding vicinal diols **4b**,**c**, while diamines **3d**–**f** were generated from dihydroxydiazide **7** via deprotection–reprotection strategies.

1. Introduction

During the past decade, remarkable progress has been made in the field of metal-catalyzed asymmetric syntheses.[1,2] The design of numerous effective enantiomerically pure catalysts is based on C_2-symmetric diamines,[3] such as 1,2-diphenylethylenediamine and 1,2-diaminocyclohexane. Recently, we reported on the efficient synthesis of non-cyclic vicinal diamine (2*S*,3*S*)-2,3-diaminobutane-1,4-diol **2** and (2*S*,3*S*)-1,4-bis(benzyloxy)-2,3-diaminobutane **3a**, starting from diethyl L-tartrate (+)-**1**[4] (Scheme 1).

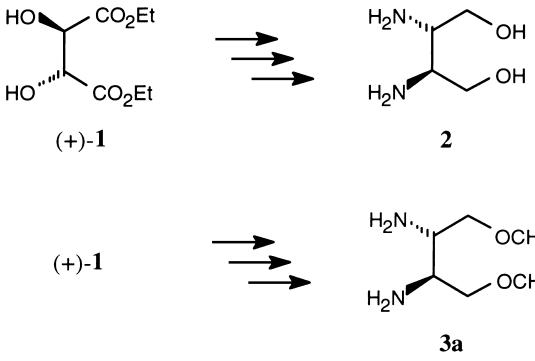
In order to test the influence of different (2*S*,3*S*)-2,3-diaminobutane-1,4-diether ligands on the catalytic effect of the corresponding chelate complexes, we synthesized the diamines **3b**[5] and **3c**–**f**, respectively. Hitherto, the diamines **3c**–**f** with bulky substituents such as 2-naphthylmethoxy, triphenylmethoxy, (*t*-butyldimethylsilyl)oxy and (*t*-butyldiphenylsilyl)oxy were unknown (Scheme 2).

2. Results and discussion

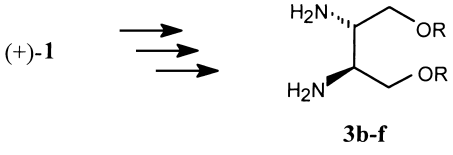
The diols[6] **4a**–**c** were converted to the vicinal diamines **3a**–**c** by a three step sequence. Standard mesylation of **4a**–**c** afforded dimesylates **5a**–**c** which were converted to diazides **6a**–**c** with sodium

* Corresponding authors. E-mail: mosset@ensc-rennes.fr

0957-4166/99/$ - see front matter
PII: S0957-4166(99)00353-5



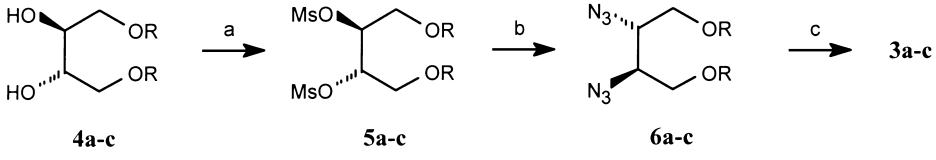
Scheme 1.



3	b	c	d	e	f
R	Me	CH_2-2-naphthyl	CPh_3	Si*t*-$BuMe_2$	Si*t*-$BuPh_2$

Scheme 2.

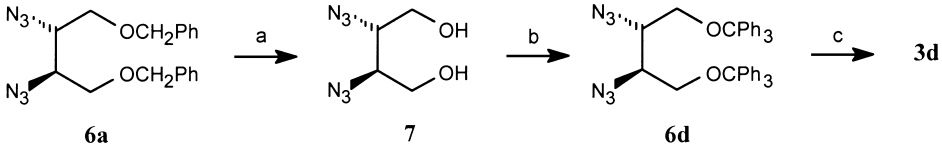
azide in DMSO.[7] Catalytic hydrogenation of the azide functions of **6a–c** using palladium on charcoal afforded the diamines **3a–c**[8] without touching the protecting groups. While the reduction of **6a**,**b** could be performed in methanol, diazide **6c** was reduced in THF[9] (Scheme 3).



3-6	a	b	c
R	CH_2Ph	Me	CH_2-2-naphthyl

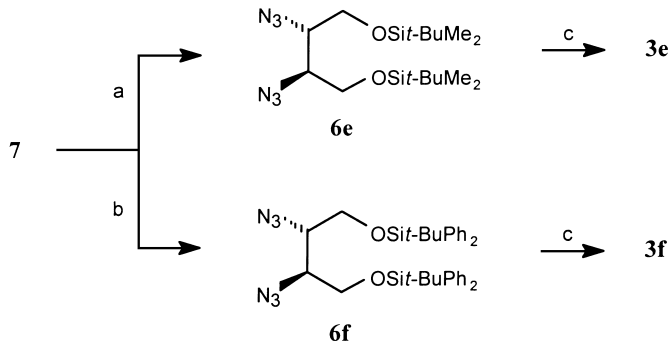
Scheme 3. (a) MsCl, Et_3N, CH_2Cl_2, 0°C, 1 h, 99% for **4a** and **4b**, quant. for **4c**. (b) NaN_3, DMSO, 80°C, 24 h, 88% for **5a**, 95% for **5b**, 85% for **5c**. (c) H_2, Pd/C, MeOH or THF for **3a**, MeOH for **3b**, THF for **3c**, ca. 20°C, 18 h, quant.

(2*S*,3*S*)-1,4-Bis(triphenylmethoxy)-2,3-diaminobutane **3d** was synthesized from diazide **6a**, which was first deprotected with boron trichloride dimethyl sulfide complex to give diol **7**.[4] Reprotection of the hydroxyl groups of **7** using 1-tritylpyridinium tetrafluoroborate in acetonitrile[10,11] yielded diazide **6d**. Hydrogenation of diazide **6d** with Pearlman's catalyst in THF[12] afforded diamine **3d** in excellent yield (Scheme 4).



Scheme 4. (a) $BCl_3 \cdot Me_2S$, CH_2Cl_2, ca. 20°C, 2–3 h, 81%. (b) $TrBF_4 \cdot Py$, CH_3CN, 65°C, 8 h, 82%. (c) H_2, $Pd(OH)_2$/C, THF, ca. 20°C, 18 h, quant.

The diamines **3e**,**f** were prepared starting from diol **7**, which was first protected by silylation in DMF with *t*-butyldimethylchlorosilane[13] or *t*-butyldiphenylchlorosilane[14], respectively, to give **6e**,**f** in good yield. Subsequent catalytic hydrogenation of **6e**,**f** with palladium on carbon in THF generated the corresponding diamines **3e**,**f** (Scheme 5).



Scheme 5. (a) *t*-BuMe$_2$SiCl, imidazole, DMF, 0°C, 24 h, 98%. (b) *t*-BuPh$_2$SiCl, imidazole, DMF, 0°C, 24 h, 94%. (c) H_2, Pd/C, THF, ca. 20°C, 18 h, quant.

3. Conclusion

In summary, a series of C_2-symmetric vicinal diamines derived from L-tartaric acid were generated. The increasing bulkiness of the terminal ether functionalities of the diamines **3b**–**f** make them useful precursors for the preparation of chiral ligands and metal chelates for asymmetric catalysis.[15]

4. Experimental

*4.1. (2S,3S)-1,4-Bis(methoxy)butane-2,3-diol dimethanesulfonate **5b***

Methanesulfonyl chloride (0.218 mL, 2.8 mmol) was slowly added at 0°C to a solution of diol **4b** (0.175 g, 1.17 mmol) and triethylamine (0.49 mL, 3.5 mmol) in anhydrous dichloromethane (6 mL). After stirring for 1 h at 0°C, the reaction mixture was allowed to warm up to ca. 20°C. Water was added and the resulting mixture was extracted three times with ethyl acetate. The combined organic phases were successively washed with brine and water, dried ($MgSO_4$) and concentrated. Chromatography on silica gel (ethyl acetate:petroleum ether 2:3) afforded dimesylate **5b** as a pale yellow oil, which crystallized after storage in the refrigerator yielding cream-colored crystals (0.355 g, 99%, R_f=0.10, ethyl acetate:petroleum ether 2:3, mp 42–44°C); IR (neat, NaCl): ν 3031, 2941, 2824, 1460, 1359, 1176, 1126, 1027, 975, 920, 828, 801, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96–4.91 (m, 2H, C*H*-OMs),[16] 3.76–3.64 (m, 4H, CHC*H*$_2$O),[16] 3.41 (s, 6H, OC*H*$_3$), 3.13 (s, 6H, OMs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 78.72 (dm, 2C, *J*=149.9 Hz, *C*H-OMs), 71.19 (tqd, 2C, *J*=143.8, 5.4, 1.8 Hz, *C*H$_2$O), 59.25 (qt, 2C, *J*=141.9, 3.0 Hz, O*C*H$_3$), 38.72 (q, 2C, *J*=139.6 Hz, OMs); MS (EI, 70 eV) *m/z* (%): 307 (0.05) [M+H]$^+$, 275 (0.2) [M−OMe]$^+$, 165 (74) [M−MsOH−CH$_2$OCH$_3$]$^+$, 87 (80), 79 (29), 59 (69), 45 (100, e.g. base peak); $[\alpha]_D^{23}$ −22.4, $[\alpha]_{578}^{23}$ −23.3, $[\alpha]_{546}^{23}$ −26.4, $[\alpha]_{436}^{23}$ −43.5 (c=3.8, $CHCl_3$).

4.2. (2S,3S)-1,4-Bis(methoxy)-2,3-diazidobutane **6b**

A mixture of dimesylate **5b** (0.355 g, 1.17 mmol) and sodium azide (0.266 g, 4.1 mmol) in DMSO (3.5 mL) was stirred at 80°C for 1 day, cooled to ca. 20°C, and the white suspension was diluted with ca. 15% aq. NaCl (10 mL). The aqueous layer was extracted three times with light petroleum ether and the combined organic extracts were dried ($MgSO_4$). Concentration in vacuo and chromatography of the remaining brown liquid on silica gel (ether:light petroleum ether 5:95) afforded diazide **6b** as a colorless liquid (0.206 g, 88%, R_f=0.24, ethyl acetate:petroleum ether 1:9); IR (neat, NaCl): ν 2992, 2931, 2897, 2835, 2818, 2106, 1458, 1335, 1267, 1197, 1125 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.71–3.65 (m, 2H, C*H*-N_3),[16] 3.62–3.58 (m, 4H, CHC*H*$_2$O),[16] 3.41 (s, 6H, OC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.04 (tm, 2C, *J*=143.1 Hz, *C*H_2O), 60.89 (d sextet, 2C, *J*=143.7, 2.6 Hz, *C*H-N_3), 59.23 (qt, 2C, *J*=141.6, 2.9 Hz, O*C*H_3); MS (EI, 70 eV) *m/z* (%): 100 (7) $[M/2]^+$, 72 (23) $[M/2-N_2]^+$, 45 (100) $[MeOCH_2]^+$, 41 (56), 29 (100); $[\alpha]_D^{24}$ −45.8, $[\alpha]_{578}^{24}$ −47.8, $[\alpha]_{546}^{24}$ −53.7, $[\alpha]_{436}^{24}$ −86.2, $[\alpha]_{365}^{24}$ −119.4 (c=3.4, $CHCl_3$).

4.3. (2S,3S)-1,4-Bis(methoxy)-2,3-diaminobutane **3b**

A solution of diazide **6b** (0.170 g, 0.85 mmol) in methanol (10 mL) in a one-necked flask (250 mL) was stirred during 5 min under a slow stream of nitrogen. Then 10% Pd/C (0.060 g) was suspended into the solution and the flask was rapidly flashed with a strong stream of hydrogen and the mixture was hydrogenated at ca. 20°C and at atmospheric pressure for 18 h. The catalyst was then removed by filtration over Celite and the filtrate was evaporated under vacuum to afford diamine **3b** as a colorless syrup (0.126 g, quant.); IR (neat, NaCl): ν 3369 (broad), 3284, 2982, 2926, 2896, 2822, 1602, 1461, 1194, 1113, 954, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.41 (pseudo dd, 2H, *J*=9.3, 4.3 Hz, C*H*$_2$O),[16] 3.36 (s, 6H, OC*H*$_3$), 3.33 (pseudo dd, 2H, *J*=9.3, 6.5 Hz, C*H*$_2$O),[16] 2.97–2.90 (m, 2H, C*H*-NH_2),[16] 1.54 (broad s, 4H, CH-N*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 74.61 (tm, 2C, *J*=142 Hz, *C*H_2O), 59.08 (qt, 2C, *J*=141.1, 2.7 Hz, O*C*H_3), 52.18 (dm, 2C, *J*=137 Hz, *C*H-NH_2); MS (EI, 70 eV) *m/z* (%): 103 (8) $[M-CH_2OCH_3]^+$, 86 (7) $[M-NH_3-CH_2OCH_3]^+$, 74 (100) $[M/2]^+$, 43 (33) $[M/2-OMe]^+$, 30 (16); $[\alpha]_D^{24}$ +5.6, $[\alpha]_{578}^{24}$ +5.8, $[\alpha]_{546}^{24}$ +6.4, $[\alpha]_{436}^{24}$ +11.1, $[\alpha]_{365}^{24}$ +17.0 (c=2.0, $CHCl_3$).

For analytical purposes, diamine **3b** was converted into its dibenzamide as follows:

Benzoyl chloride (0.14 mL, 1.2 mmol) was slowly added at 0°C to a solution of diamine **3b** (0.06 g, 0.4 mmol) and triethylamine (0.224 mL, 1.6 mmol) in anhydrous dichloromethane (4 mL). After stirring for 1 h at 0°C, the reaction mixture was allowed to warm up to ca. 20°C and stirred for additional 18 h. Water was added and the resulting mixture was extracted three times with ethyl acetate. Combined organic phases were successively washed with brine and water, dried ($MgSO_4$) and concentrated. Short plug chromatography on silica gel (methanol:dichloromethane 1:99) afforded dibenzamide of **3b** as a cream-colored solid [0.124 g, 87%, R_f=0.22, methanol:dichloromethane 2:98, mp 148–149°C (ethyl acetate:petroleum ether)]; IR (Nujol, NaCl): ν 3301 (broad), 1634, 1531, 1192, 1106, 955, 802, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dm, 4H, *J*=8.3 Hz, H *ortho*), 7.44 (ddt, 2H, *J*=8.3, 6.3, 1.4 Hz, H *para*), 7.40–7.34 (m, 4H, H *meta*), 7.25 (broad d, 2H, *J*=7.8 Hz, NH), 4.65–4.56 (m, 2H, C*H*-NH), 3.71 (pseudo dd, 2H, *J*=10.0, 2.9 Hz, C*H*$_2$O), 3.63 (pseudo dd, 2H, *J*=10.0, 3.6 Hz, C*H*$_2$O), 3.40 (s, 6H, OC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.01 (2C, *C*ONH), 134.08 (2C_{ipso}), 131.50 (dddd, 2C_{para}, *J*=161.0, 7.9, 7.2, 1.1 Hz), 128.50 (d pseudo dd, 4C_{meta}, *J*=161.3, 7.7, 1.0 Hz), 127.04 (dm, 4C_{ortho}, *J*=160.4 Hz), 71.61 (tq, 2C, *J*=142.6, 4.9 Hz, O*C*H_2-CH), 59.30 (qt, 2C, *J*=141.2, 2.7 Hz, O*C*H_3), 51.08 (dm, 2C, *J*=140.6 Hz, *C*H-NH); MS (EI, 70 eV) *m/z* (%): 311 (17) $[M-CH_2OCH_3]^+$, 279 (21) $[M-MeOH-CH_2OCH_3]^+$, 203 (12) $[M-MeOH-PhCONH_2]^+$, 190 (22) $[M-CH_2OCH_3-PhCONH_2]^+$, 178 (53) $[M/2]^+$, 147 (48) $[M/2-OCH_3]^+$, 105 (86) $[PhCO]^+$, 85 (100); $[\alpha]_D^{24}$ −49.1, $[\alpha]_{578}^{24}$ −51.4,

$[\alpha]_{546}^{24}$ −59.0 (c=2.2, $CHCl_3$). Anal. calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.55; H, 6.98; N, 7.65.

4.4. (2S,3S)-1,4-Bis(2-naphthylmethoxy)butane-2,3-diol **4c**

In a round-bottomed three-neck flask, equipped with a stirring bar, pressure equalizing drop funnel, a reflux condenser and a stopper, was placed under nitrogen sodium hydride [(0.74 g of a 60% dispersion in oil, 0.44 g, 18.5 mmol); the oil was removed by washing with petroleum ether (3×2.5 mL)] and dry THF (10 mL) was then added under nitrogen. A solution of (+)-2,3-*O*-isopropylidene-L-threitol (1.27 g, 7.8 mmol) in dry THF (5 mL) was then added dropwise with stirring at 0°C, followed by washing of the addition funnel with dry THF (3 mL). Powdered 2-(bromomethyl)naphthalene (3.6 g, 16.3 mmol) was added in one portion. After stirring for 14 h at ca. 20°C, the mixture was heated at reflux for 2 h, cooled in an ice bath and quenched by addition of water until a clear yellow solution resulted. THF was removed under reduced pressure, the residue diluted with water and extracted three times with ethyl acetate. The organic extracts were combined, dried ($MgSO_4$) and, after evaporation of volatile material, the crude ketal (2*S*,3*S*)-2,3-*O*-isopropylidene-1,4-bis(2-naphthylmethoxy)butane **8**[17] was obtained as an oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.73 (m, 6H of 2-naphthyl, $H_{4,5,8}$), 7.73 (broad s, 2H of 2-naphthyl, H_1), 7.47–7.42 (m, 4H arom., $H_{6,7}$, Δδ=0 ppm, J_{56}=J_{78}=8.2 Hz, J_{67}=6.9 Hz, J_{57}=J_{68}=1.2 Hz, J_{58}=0.7 Hz), 7.40 (dd, *J*=8.3, 1.8 Hz, 2H of 2-naphthyl, H_3), 4.71 (d, 2H, *J*=12.4 Hz, C*H*$_2$-2-naphthyl), 4.69 (d, 2H, *J*=12.4 Hz, C*H*$_2$-2-naphthyl), 4.11–4.04 (m, 2H, OCH_2CH),[16] 3.68–3.59 (m, 4H, OCH_2-CH),[16] 1.45 (s, 6H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.40 (2C$_{ipso}$), 133.18 (2C$_{ipso}$), 132.95 (2C$_{ipso}$), 128.16 (2CH), 127.83 (2CH), 127.67 (2CH), 126.41 (2CH), 126.08 (2CH), 125.85 (2CH), 125.60 (2CH), 109.73 (1C, *C*$(CH_3)_2$), 77.48 (2C, OCH_2CH), 73.58 (2C, *C*H$_2$-2-naphthyl), 70.65 (2C, OCH_2CH), 27.03 (2C, $C(CH_3)_2$).

The crude ketal **8** was dissolved in methanol (10 mL), 1.0 N hydrochloric acid (1 mL) and the resulting mixture was heated at reflux. Acetone and methanol were slowly distilled off with a Vigreux column. After 1 h, more methanol (10 mL) was added and the distillation was continued for about 5 h. After cooling to ca. 20°C, a solid material was obtained, which was dissolved in saturated aqueous sodium carbonate solution (25 mL) and extracted four times with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and after evaporation of the solvent the crude reaction product was obtained as a slight yellow oil, which solidified in the refrigerator. This solid was recrystallized in petroleum ether:toluene to provide 2.44 g (78% for two steps) of diol **4c** as pale yellow crystals (R_f=0.22, ethyl acetate:petroleum ether 2:3, mp 115–116°C, NMR-analysis of mother liquor showed the presence of 2-(bromomethyl)naphthalene with less than 5% diol); IR (Nujol, NaCl): ν 3395 (broad), 3051, 1600, 1100, 1060, 1041, 1006, 952, 902, 863, 825, 755, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.78 (m, 6H of 2-naphthyl), 7.74 (broad d, *J*=0.7 Hz, 2H of 2-naphthyl), 7.50–7.44 (m, 4H of 2-naphthyl, $H_{6,7}$, Δδ=0.0057 ppm, J_{56}=J_{78}=8.2 Hz, J_{67}=6.9 Hz, J_{57}=J_{68}=1.2 Hz, J_{58}=0.7 Hz), 7.42 (dd, *J*=8.5, 1.6 Hz, 2H of 2-naphthyl), 4.71 (d, 2H, *J*=12.1 Hz, C*H*$_2$-2-naphthyl), 4.68 (d, 2H, *J*=12.1 Hz, C*H*$_2$-2-naphthyl), 3.91 (dm, 2H, *J*=4.1 Hz, C*H*-OH),[16] 3.66 (pseudo dd, 2H, *J*=9.7, 4.4 Hz, OCH_2-CH),[16] 3.62 (pseudo dd, 2H, *J*=9.7, 5.6 Hz, OCH_2-CH),[16] 2.83 (d, 2H, *J*=4.1 Hz, CH-O*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.14 (C_2 arom.), 133.19 and 133.01 (C_{4a} and C_{8a} arom.), 128.30 (dd, $^1J_{CH}$=159.2 Hz, $^3J_{C4\text{-}H5}$=5.0 Hz, C_4 arom.), 127.87 (dm, $^1J_{CH}$=158.1 Hz, C_8 arom.), 127.70 (dm, $^1J_{CH}$=158.8 Hz, C_5 arom.), 126.64 (ddtd, $^1J_{CH}$=157.8 Hz, $^3J_{C3\text{-}H1}$ ~9 Hz, $^3J_{\text{with } CH2O}$ ~5.5 Hz, $^2J_{C3\text{-}H4}$ ~1 Hz, C_3 arom.), 126.18 (dd, $^1J_{CH}$=159.5 Hz, $^3J_{C6\text{-}H8}$ or $^3J_{C7\text{-}H5}$=8.4 Hz, C_6 or C_7 arom.), 125.99 (dd, $^1J_{CH}$=159.5 Hz, $^3J_{C6\text{-}H8}$ or $^3J_{C7\text{-}H5}$=8.2 Hz, C_6 or C_7 arom.), 125.66 (ddt, $^1J_{CH}$=158.4 Hz, $^3J_{C1\text{-}H3}$=7.2 Hz, $^3J_{\text{with } CH2O}$=4.0 Hz, C_1 arom.), 73.67 (tm, $^1J_{CH}$=142.0 Hz, OCH_2CHOH), 71.95 (pseudo tt, $^1J_{CH}$=141.5 Hz, $^3J_{\text{with } OCH2}$=3.9 Hz, 2-naphthyl-*C*H$_2$O), 70.61 (dm, $^1J_{CH}$=143.1 Hz, *C*HOH); MS (EI, 70 eV) *m/z* (%): 402 (2) $[M]^+$, 262 (16), 157 (47)

[OCH_2-2-naphthyl]$^+$, 141 (100) [CH_2-2-naphthyl]$^+$, 129 (29), 115 (32); $[\alpha]_D^{26}$ −6.4, $[\alpha]_{578}^{26}$ −6.7, $[\alpha]_{546}^{26}$ −7.6, $[\alpha]_{436}^{26}$ −13.2 (c=3.0, $CHCl_3$). Anal. calcd for $C_{26}H_{26}O_4$: C, 77.58; H, 6.52. Found: C, 77.64; H, 6.51.

4.5. (2S,3S)-1,4-Bis(2-naphthylmethoxy)butane-2,3-diol dimethanesulfonate **5c**

Methanesulfonyl chloride (0.093 mL, 1.2 mmol) was slowly added at 0°C to a solution of diol **4c** (0.201 g, 0.5 mmol) and triethylamine (0.209 mL, 1.5 mmol) in anhydrous dichloromethane (2.5 mL). After stirring for 1 h at 0°C, the reaction mixture was allowed to warm up to ca. 20°C. Water was added and the resulting mixture was extracted three times with ethyl acetate. The combined organic phases were successively washed with brine and water, dried ($MgSO_4$) and concentrated. Chromatography on silica gel (ethyl acetate:petroleum ether 1:4) afforded dimesylate **5c** as a white solid (0.28 g, quant., R_f=0.36, ethyl acetate:petroleum ether 2:3, mp 100–102°C); IR (Nujol, NaCl): ν 3022, 1345, 1178, 1123, 1028, 974, 907, 860, 822, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.78 (m, 6H arom.), 7.71 (broad d, J=0.8 Hz, 2H arom.), 7.52–7.46 (m, 4H arom., $H_{6,7}$, Δδ=0.0030 ppm, J_{56}=J_{78}=8.2 Hz, J_{67}=6.9 Hz, J_{57}=J_{68}=1.2 Hz, J_{58}=0.7 Hz), 7.39 (dd, J=8.4, 1.7 Hz, 2H arom.), 5.07–5.01 (m, 2H, C*H*-OMs),[16] 4.70 (d, 2H, J=11.8 Hz, CH_2-2-naphthyl), 4.60 (d, 2H, J=11.8 Hz, CH_2-2-naphthyl), 3.81 (pseudo dd, 2H, J=11.2, 3.7 Hz, OCH_2-CH),[16] 3.78 (pseudo dd, 2H, J=11.2, 5.7 Hz, OCH_2-CH),[16] 3.03 (s, 6H, CH-OMs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.30 (C_{ipso} arom.), 133.16 (C_{ipso} arom.), 133.10 (C_{ipso} arom.), 128.43 (CH arom.), 127.94 (CH arom.), 127.72 (CH arom.), 127.02 (CH arom.), 126.34 (CH arom.), 126.23 (CH arom.), 125.77 (CH arom.), 78.72 (*C*HOMs), 73.77 (*C*H_2-2-naphthyl), 68.64 (O*C*H_2-CH), 38.80 (OMs); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{28}H_{30}O_8S_2$ 558.1382 $[M]^+$, found 558.1371 (3), 157.1 (13) [OCH_2-2-naphthyl]$^+$, 141.1 (100) [CH_2-2-naphthyl]$^+$, 127.1 (20) [2-naphthyl]$^+$; $[\alpha]_D^{26}$ −2.1, $[\alpha]_{578}^{26}$ −2.1, $[\alpha]_{546}^{26}$ −2.2, $[\alpha]_{436}^{26}$ −1.2, $[\alpha]_{365}^{26}$ +5.5 (c=1.9, $CHCl_3$).

4.6. (2S,3S)-1,4-Bis(2-naphthylmethoxy)-2,3-diazidobutane **6c**

A mixture of dimesylate **5c** (0.28 g, 0.5 mmol) and sodium azide (0.114 g, 1.75 mmol) in DMSO (1.5 mL) was stirred at 80°C for 1 day, cooled to ca. 20°C, and the white suspension was diluted with water:brine 1:1 (3.5 mL). The aqueous layer was extracted three times with ethyl acetate and the combined organic extracts were dried ($MgSO_4$). Concentration in vacuo and chromatography of the remaining brown-red liquid on silica gel (ethyl acetate:petroleum ether 5:95) afforded diazide **6c** as a colorless oil, which solidified after storage at ca. −20°C (0.192 g, 85%, R_f=0.21, ethyl acetate:petroleum ether 10:90, mp 37–39°C); IR (neat, NaCl): ν 3056, 3024, 2908, 2864, 2103, 1344, 1271, 1125, 1107, 856, 818, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.77 (m, 6H arom.), 7.74 (broad s, 2H arom.), 7.52–7.44 (m, 4H arom., $H_{6,7}$, Δδ=0.0057 ppm, J_{56}=J_{78}=8.2 Hz, J_{67}=6.9 Hz, J_{57}=J_{68}=1.2 Hz, J_{58}=0.7 Hz), 7.42 (dd, J=8.4, 1.7 Hz, 2H arom.), 4.68 (s, 4H, CH_2-2-naphthyl), 3.79–3.73 (m, 2H, C*H*-N_3),[16] 3.72–3.62 (m, 4H, OCH_2-CH);[16] ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.77 (C_{ipso} arom.), 133.18 (C_{ipso} arom.), 133.07 (C_{ipso} arom.), 128.37 (CH arom.), 127.91 (CH arom.), 127.72 (CH arom.), 126.67 (CH arom.), 126.24 (CH arom.), 126.07 (CH arom.), 125.59 (CH arom.), 73.65 (*C*H_2-2-naphthyl), 69.59 (O*C*H_2-CH), 61.02 (*C*H-N_3); MS (EI, 70 eV) *m/z* (%): 452 (1.3) $[M]^+$, 337 (4.8) $[M-C_9H_7]^+$, 311 (1.8) [M−CH_2-2-naphthyl]$^+$, 226 (13) $[M/2]^+$, 198 (66) $[M/2-N_2]^+$, 168 (27), 155 (68), 141 (100) [CH_2-2-naphthyl]$^+$, 127 (42) [2-naphthyl]$^+$, 115 (94) $[C_9H_7]^+$; HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{26}H_{25}N_6O_2$ $[M+H]^+$ 453.2039, found 453.2022 (4), calcd for $C_{26}H_{25}N_4O_2$ 425.1978 $[M-N_2+H]^+$, found 425.1974 (3), calcd for $C_{26}H_{27}N_4O_2$ 427.2134 $[M-N_2+H_2+H]^+$ (from in situ reduction of one azide function), found 427.2125 (1), 198.0 $[M/2-N_2]^+$ (11), 141.0 [CH_2-

2-naphthyl]$^+$ (100); $[\alpha]_D^{24}$ −38.0, $[\alpha]_{578}^{24}$ −39.6, $[\alpha]_{546}^{24}$ −44.8, $[\alpha]_{436}^{24}$ −74.4, $[\alpha]_{365}^{24}$ −110.9 (c=5.5, $CHCl_3$). Anal. calcd for $C_{26}H_{24}N_6O_2$: C, 69.01; H, 5.35; N, 18.57. Found: C, 68.36; H, 5.36; N, 19.06.

*4.7. (2S,3S)-1,4-Bis(2-naphthylmethoxy)-2,3-diaminobutane **3c***

The same procedure as described for (2*S*,3*S*)-**3b** was followed. To a solution of diazide **6c** (0.192 g, 0.42 mmol) in dry THF (5 mL) in a one-necked flask (100 mL) was added 10% Pd/C (0.03 g). The mixture was hydrogenated at ca. 20°C and at atmospheric pressure for 18 h. The catalyst was then removed by filtration over Celite and the filtrate was evaporated under vacuum to afford diamine **3c** as a colorless oil, which crystallized after prolonged storage at ca. −20°C yielding colorless crystals (0.171 g, quant., mp 100–102°C); IR (Nujol, NaCl): ν 3369, 3052, 1349, 1261, 1102, 863, 821, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.84–7.76 (m, 6H arom.), 7.73 (broad s, 2H arom.), 7.49–7.43 (m, 4H arom., $H_{6,7}$, Δδ=0.0088 ppm, $J_{56}=J_{78}$=8.2 Hz, J_{67}=6.9 Hz, $J_{57}=J_{68}$=1.2 Hz, J_{58}=0.7 Hz), 7.42 (dd, *J*=8.4, 1.5 Hz, 2H arom.), 4.63 (s, 4H, CH_2-2-naphthyl), 3.52 (pseudo dd, 2H, *J*=9.3, 4.4 Hz, OCH_2-CH),[16] 3.43 (pseudo dd, 2H, *J*=9.3, 6.3 Hz, OCH_2-CH),[16] 3.06–3.00 (m, 2H, C*H*-NH_2),[16] 1.69 (s, 4H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.58 (C_{ipso} arom.), 133.18 (C_{ipso} arom.), 132.94 (C_{ipso} arom.), 128.21 (CH arom.), 127.83 (CH arom.), 127.67 (CH arom.), 126.46 (CH arom.), 126.12 (CH arom.), 125.88 (CH arom.), 125.68 (CH arom.), 73.46 (*C*H_2-2-naphthyl), 73.35 (O*C*H_2-CH), 52.64 (*C*H-NH_2); MS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{26}H_{29}N_2O_2$ 401.2 $[M+H]^+$, found 400 (3), 401 (100), 402 (31), 403 (6); $[\alpha]_D^{24}$ −10.7, $[\alpha]_{578}^{24}$ −11.1, $[\alpha]_{546}^{24}$ −12.7, $[\alpha]_{436}^{24}$ −22.3, $[\alpha]_{365}^{24}$ −37.2 (c=2.5, $CHCl_3$).

For analytical purposes, diamine **3c** (0.17 g, 0.42 mmol) was converted into its dibenzamide by reaction with benzoyl chloride (0.146 mL, 1.26 mmol) and triethylamine (0.234 mL, 1.68 mmol) in anhydrous dichloromethane (4.5 mL) as described for diamine **3b**. Short plug chromatography on silica gel (methanol:dichloromethane 1:99) afforded the dibenzamide as a white solid [0.237 g, 92%, R_f=0.11, methanol:dichloromethane 1:99, mp 145–146°C (ethyl acetate:petroleum ether)]; IR (Nujol, NaCl): ν 3310, 3052, 1632, 1579, 1526, 1101, 1030, 853, 820, 724, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85–7.80 (m, 2H of 2-naphthyl), 7.79–7.74 (m, 4H of 2-naphthyl), 7.70 (broad s, 2H of 2-naphthyl), 7.58 (pseudo dd, 4H, *J*=8.4, 1.2 Hz, H *ortho* of COPh), 7.52–7.45 (m, 4H of 2-naphthyl, $H_{6,7}$, Δδ=0.0080 ppm, $J_{56}=J_{78}$=8.2 Hz, J_{67}=6.9 Hz, $J_{57}=J_{68}$=1.2 Hz, J_{58}=0.7 Hz), 7.39 (dd, *J*=8.4, 1.7 Hz, 2H of 2-naphthyl), 7.37 (ddt, 2H, *J*=7.9, 7.0, 1.2 Hz, H *para* of COPh), 7.30 (broad d, 2H, *J*=7.9 Hz, NH), 7.21 (dd pseudo t, 4H, *J*=7.9, 7.4, 1.6 Hz, H *meta* of COPh), 4.76–4.64 (m, 2H, C*H*-NH), 4.62 (s, 4H, CH_2-2-naphthyl), 3.79 (pseudo dd, 2H, *J*=9.7, 3.2 Hz, OCH_2-CH), 3.73 (pseudo dd, 2H, *J*=9.7, 4.6 Hz, OCH_2-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.57 (2C, *C*ONH), 134.89 (2C_{ipso} of 2-naphthyl), 133.89 (2C_{ipso} of COPh), 133.16 (2C_{ipso} of 2-naphthyl), 133.06 (2C_{ipso} of 2-naphthyl), 131.42 (2C_{para} of COPh), 128.41 (4C_{meta} of COPh and 2CH of 2-naphthyl), 127.93 (2CH of 2-naphthyl), 127.72 (2CH of 2-naphthyl), 126.99 (2CH of 2-naphthyl), 126.91 (4C_{ortho} of COPh), 126.28 (2CH of 2-naphthyl), 126.14 (2CH of 2-naphthyl), 125.87 (2CH of 2-naphthyl), 73.67 (2C, *C*H_2-2-naphthyl), 68.98 (2C, O*C*H_2-CH), 51.05 (2C, *C*H-NH); MS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{40}H_{37}N_2O_4$ 609.3 $[M+H]^+$, found 608 (4), 609 (100), 610 (46), 611 (11), 451 (21) $[M-2\text{-naphthylCH}_2O]^+$; $[\alpha]_D^{24}$ −72.6, $[\alpha]_{578}^{24}$ −76.3, $[\alpha]_{546}^{24}$ −86.9, $[\alpha]_{436}^{24}$ −155.1, $[\alpha]_{365}^{24}$ −265.3 (c=1.0, $CHCl_3$). Anal. calcd for $C_{40}H_{36}N_2O_4$: C, 78.92; H, 5.96; N, 4.60. Found: C, 79.02; H, 6.24; N, 4.63.

*4.8. (2S,3S)-1,4-Bis(triphenylmethoxy)-2,3-diazidobutane **6d***

A mixture of diol **7** (0.103 g, 0.6 mmol) and tritylpyridinium tetrafluoroborate (0.589 g, 1.44 mmol) in dry acetonitrile (2.5 mL) was stirred at 65°C for 8 h, cooled to ca. 20°C and the slight yellow solution

was evaporated. The residue was diluted with petroleum ether (6 mL) to precipitate the pyridinium tetrafluoroborate, and ca. 15% aq. NaCl (3 mL). The aqueous layer was extracted three times with ether and the combined organic extracts were dried ($MgSO_4$). Concentration in vacuo and chromatography of the crude product on silica gel (*tert*-butyl methyl ether:petroleum ether 2:98) afforded diazide **6d** as a colorless oil (0.323 g, 82%, R_f=0.16, ethyl acetate:petroleum ether 2:98, mp 53–55°C); IR (neat, NaCl): ν 3087, 3060, 3032, 2928, 2876, 2856, 2099, 1735, 1598, 1491, 1448, 1276, 1087, 1079, 907, 766, 743, 734, 703, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.35 (m, 12H), 7.29–7.20 (m, 18H), 3.52–3.45 (m, 2H, C*H*-N_3),[16] 3.27 (pseudo dd, 2H, *J*=9.9, 4.4 Hz, CH_2O),[16] 3.13 (pseudo dd, 2H, *J*=9.9, 6.8 Hz, CH_2O);[16] ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.37 (6C_{ipso}), 128.53 and 127.93 (12C_{meta} and 12C_{ortho}), 127.22 (6C_{para}), 87.43 (2C, *C*$(Ph)_3$), 63.47 (2C, *C*H_2O), 62.00 (2C, *C*H-N_3); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{42}H_{37}N_6O_2$ 657.2978 $[M+H]^+$, found 657.2923 (0.14), 579.2 (0.15) $[M-Ph]^+$, 243.1 (100) $[Ph_3C]^+$; $[\alpha]_D^{24}$ +8.4, $[\alpha]_{578}^{24}$ +9.0, $[\alpha]_{546}^{24}$ +10.4, $[\alpha]_{436}^{24}$ +22.0, $[\alpha]_{365}^{24}$ +47.1 (c=2.0, $CHCl_3$). Anal. calcd for $C_{42}H_{36}N_6O_2$: C, 76.81; H, 5.52; N, 12.80. Found: C, 76.85; H, 5.81; N, 12.73.

*4.9. (2S,3S)-1,4-Bis(triphenylmethoxy)-2,3-diaminobutane **3d***

The same procedure as described for (2*S*,3*S*)-**3b** was followed. To a solution of diazide **6d** (0.262 g, 0.4 mmol) in dry THF (6 mL) in a one-necked flask (100 mL) was added 20% $Pd(OH)_2$/C (humid: commercial Pearlman's catalyst) (0.035 g). The mixture was hydrogenated at ca. 20°C and at atmospheric pressure for 18 h. The catalyst was mostly removed by filtration over Celite and the filtrate was evaporated in vacuo to afford diamine **3d** as a dark syrup which became a dark foam under vacuum (0.244 g, quant., mp 51–52°C). The compound was contaminated with a small amount of colloidal Pd, which could not be removed by stirring in the presence of activated carbon or by further filtrations over Celite and polymers with pores of 0.5 μm; IR (Nujol, NaCl): ν 3381, 3086, 3057, 3031, 3022, 1961, 1596, 1490, 1449, 1220, 1154, 1071, 899, 764, 746, 706, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.35 (m, 12H), 7.28–7.18 (m, 18H), 3.10 (pseudo dd, 2H, *J*=8.0, 3.4 Hz, CH_2O), 2.98–2.88 (m, 4H, C*H*-NH_2 and CH_2O), 1.41 (broad s, 4H, CH-NH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.00 (6C_{ipso}), 128.63 and 127.80 (12C_{meta} and 12C_{ortho}), 126.97 (6C_{para}), 86.51 (2C, *C*Ph_3), 66.18 (2C, *C*H_2O), 53.26 (2C, *C*H-NH_2); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{42}H_{41}N_2O_2$ 605.3168 $[M+H]^+$, found 605.3174, 243.1 (100) $[Ph_3C]^+$; [α] could not be measured due to traces of colloidal Pd.

For analytical purposes, diamine **3d** (0.091 g, 0.15 mmol) was converted into its dibenzamide by reaction with benzoyl chloride (0.055 mL, 0.47 mmol) and triethylamine (0.085 mL, 0.61 mmol) in anhydrous dichloromethane (2 mL) as described for diamine **3b**. Short plug chromatography on silica gel (ethyl acetate:petroleum ether 1:9) afforded the dibenzamide as a white powder [0.113 g, 93%, R_f=0.15, ethyl acetate:petroleum ether 1:4, mp 225–226°C (toluene:petroleum ether)]; IR (Nujol, NaCl): ν 3312 (broad), 3056, 1703, 1642, 1532, 1487, 1074, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.64 (m, 4H, H *ortho* of COPh), 7.47 (ddt, 2H, *J*=8.2, 6.5, 1.3 Hz, H *para* of COPh), 7.39 (pseudo tt, 4H, *J*=8.1, 1.6 Hz, H *meta* of COPh), 7.38–7.31 (m, 12H of Tr), 7.22–7.14 (m, 18H of Tr and 2H of NH), 4.79–4.71 (m, 2H, C*H*-NH), 3.53 (pseudo dd, 2H, *J*=10.0, 2.2 Hz, CH_2O), 3.26 (pseudo dd, 2H, *J*=10.0, 2.0 Hz, CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.21 (2C, *C*ONH), 144.01 (6C_{ipso} of Tr), 134.06 (2C_{ipso} of COPh), 131.50 (2C_{para} of COPh), 128.51 (4C_{meta} of COPh), 128.46 and 127.97 (12C_{meta} and 12C_{ortho} of Tr), 127.15 (4C_{ortho} of COPh), 127.01 (6C_{para} of Tr), 86.76 (2C, O*C*Ph_3), 61.90 (2C, O*C*H_2CH), 51.71 (2C, *C*H-NH); MS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{56}H_{49}N_2O_4$ 813.4 $[M+H]^+$, found 813 (0.2) $[M+H]^+$, 243 (100) $[Ph_3C]^+$; $[\alpha]_D^{24}$ −3.0, $[\alpha]_{578}^{24}$ −3.2, $[\alpha]_{546}^{24}$ −3.9, $[\alpha]_{436}^{24}$ −6.7 (c=1.7, $CHCl_3$). Anal. calcd for $C_{56}H_{48}N_2O_4$: C, 82.73; H, 5.95; N, 3.45. Found: C, 82.52; H, 6.19; N, 3.43.

4.10. (2S,3S)-1,4-Bis[(t-butyldimethylsilyl)oxy]-2,3-diazidobutane **6e**

tert-Butyldimethylsilyl chloride (0.362 g, 2.4 mmol) was added to a solution of diol **7** (0.172 g, 1.0 mmol) and imidazole (0.350 g, 5.1 mmol) in anhydrous DMF (2 mL) at 0°C. After 24 h of reaction at 0°C in the refrigerator without stirring, water was added. The mixture was extracted three times with petroleum ether and the combined organic extracts were subsequently washed with water and dried (Na_2SO_4). Concentration in vacuo and chromatography of the crude product on silica gel (petroleum ether) afforded diazide **6e** as a colorless oil (0.393 g, 98%, R_f=0.19, ethyl acetate:petroleum ether 1:99); IR (neat, NaCl): ν 2956, 2931, 2886, 2859, 2106, 1472, 1465, 1259, 1114, 1006, 839, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.85–3.80 (m, 4H, C*H*$_2$O), 3.60–3.54 (m, 2H, C*H*-N_3), 0.91 (s, 18H, *t*-Bu), 0.11 (s, 12H, $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.28 (2C, *C*H_2O), 62.33 (2C, *C*H-N_3), 25.76 (6C, C(*C*H_3)$_3$), 18.17 (2C, *C*(CH_3)$_3$), −5.56 (2C, Si-*C*H_3), −5.57 (2C, Si-*C*H_3); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{16}H_{37}N_6O_2Si_2$ 401.2517 $[M+H]^+$, found 401.2517 (3), calcd for $C_{15}H_{33}N_6O_2Si_2$ 385.2204 $[M-Me]^+$, found 385.2211 (11), 343.2 (52) $[M-t\text{-Bu}]^+$, 330.2 (12.5) $[M-N_2-C_3H_6]^+$, 315.2 (45) $[M-N_2-t\text{-Bu}]^+$, 287.1 (7) $[M-2N_2-t\text{-Bu}]^+$, 272.1 (13) $[M-2N_2-t\text{-Bu}-Me]^+$, 230.1 (12) $[M-2N_2-2t\text{-Bu}]^+$, 200.1 (4), $[M/2]^+$, 147.1 (65), 116.1 (54) $[HSiMe_2t\text{-Bu}]^+$, 89.0 (100); $[\alpha]_D^{25}$ −36.5, $[\alpha]_{578}^{25}$ −38.2, $[\alpha]_{546}^{25}$ −43.0, $[\alpha]_{436}^{25}$ −69.8, $[\alpha]_{365}^{25}$ −99.9 (c=5.0, $CHCl_3$). Anal. calcd for $C_{16}H_{36}N_6O_2Si_2$: C, 47.96; H, 9.06; N, 20.97. Found: C, 47.87; H, 8.78; N, 21.34.

4.11. (2S,3S)-1,4-Bis[(t-butyldimethylsilyl)oxy]-2,3-diaminobutane **3e**

The same procedure as described for (2*S*,3*S*)-**3b** was followed. To a solution of diazide **6e** (0.25 g, 0.62 mmol) in dry THF (9 mL) in a one-necked flask (250 mL) was added 10% Pd/C (0.08 g). The mixture was hydrogenated at ca. 20°C and at atmospheric pressure for 18 h. Most catalyst was removed by filtration over Celite and the filtrate was evaporated under vacuum to afford diamine **3e** as a slightly black syrup (0.218 g, quant.). The compound was contaminated with a small amount of colloidal Pd, which could not be removed; IR (neat, NaCl): ν 3379 (broad), 2955, 2931, 2888, 2858, 1588, 1470, 1390, 1361, 1256, 1098, 1006, 838, 777, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.63 (pseudo dd, 2H, *J*=9.9, 4.4 Hz, C*H*$_2$O),[16] 3.55 (pseudo dd, 2H, *J*=9.9, 6.1 Hz, C*H*$_2$O),[16] 2.86–2.78 (m, 2H, C*H*-NH_2),[16] 1.51 (broad s, 4H, CH-N*H*$_2$), 0.90 (s, 18H, *t*-Bu), 0.06 (s, 12H, $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.39 (2C, *C*H_2O), 54.25 (2C, *C*H-NH_2), 25.91 (6C, C(*C*H_3)$_3$), 18.25 (2C, *C*(CH_3)$_3$), −5.39 (2C, Si-*C*H_3), −5.40 (2C, Si-*C*H_3); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{16}H_{41}N_2O_2Si_2$ 349.2707 $[M+H]^+$, found 349.2712 (50) $[M+H]^+$, 291.2 (3) $[M-t\text{-Bu}]^+$, 174.1 (31) $[M/2]^+$, 147.1 (9), 136.1 (21), 116.1 (43) $[HSiMe_2t\text{-Bu}]^+$; [α] could not be measured due to traces of colloidal Pd.

In the HRMS spectrum, the base peak was measured at *m/z*=359.2556 (calcd for $C_{17}H_{39}N_2O_2Si_2$=359.2550) which would fit to $[M'+H]^+$ where M′ is an imidazoline derivative. Although such a compound was not detected by NMR, it might be highly ionizable and present in a small amount in the crude diamine.

For analytical purposes, diamine **3e** (0.070 g, 0.2 mmol) was converted into its dibenzamide [(2*S*,3*S*)-*N*,*N*′-dibenzoyl-1,4-bis[(*t*-butyldimethylsilyl)oxy]-2,3-diaminobutane] by reaction with benzoyl chloride (0.070 mL, 0.60 mmol) and triethylamine (0.110 mL, 0.80 mmol) in anhydrous dichloromethane (2 mL) as described for diamine **3b**. Chromatography on silica gel (gradient elution from petroleum ether to petroleum ether:EtOAc 9:1) afforded dibenzamide as colorless crystals (0.103 g, 93%, R_f=0.26, CH_2Cl_2 (100%), mp 154–155°C); IR (Nujol, NaCl): ν 3285 (broad), 3064, 3032, 1639, 1605, 1538, 1491, 1342, 1254, 1135, 1104, 1013, 837, 779, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.71 (m, 4H, H *ortho* of COPh), 7.46 (ddt, 2H, *J*=8.4, 6.2, 1.3 Hz, H *para* of COPh), 7.42–7.36 (m, 4H, H *meta* of COPh), 7.22 (broad d, 2H, *J*=7.8 Hz, N*H*), 4.58–4.48 (m, 2H, C*H*-NH), 3.96 (pseudo dd, 2H, *J*=10.7, 2.3 Hz,

C*H*$_2$O), 3.92 (pseudo dd, 2H, *J*=10.7, 3.1 Hz, C*H*$_2$O), 0.93 (s, 18H, C(C*H*$_3$)$_3$), 0.10 (s, 6H, Si-C*H*$_3$), 0.08 (s, 6H, Si-C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.87 (2C, *C*ONH), 134.15 (2C$_{ipso}$ of COPh), 131.48 (2C$_{para}$ of COPh), 128.55 (4C$_{meta}$ of COPh), 126.90 (4C$_{ortho}$ of COPh), 62.14 (2C, O*C*H$_2$CH), 52.30 (2C, *C*H-NH), 25.89 (6C, C(*C*H$_3$)$_3$), 18.27 (2C, *C*(CH$_3$)$_3$), −5.42 (2C, Si-*C*H$_3$), −5.45 (2C, Si-*C*H$_3$); MS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{30}H_{49}N_2O_4Si_2$ 557.32 $[M+H]^+$, found 557 (80) $[M+H]^+$, 541 (12) $[M-Me]^+$, 499 (97) $[M-t\text{-}Bu]^+$, 425 (100) $[M-OSiMe_2t\text{-}Bu]^+$, 278 (16) $[M/2]^+$; $[\alpha]_D^{20}$ −91.1, $[\alpha]_{578}^{20}$ −95.2, $[\alpha]_{546}^{20}$ −109.5, $[\alpha]_{436}^{20}$ −199.6 (c=1.99, $CHCl_3$). Anal. calcd for $C_{30}H_{48}N_2O_4Si_2$: C, 64.70; H, 8.69; N, 5.03. Found: C, 65.96; H, 8.75; N, 4.93.

4.12. (2S,3S)-1,4-Bis[(t-butyldiphenylsilyl)oxy]-2,3-diazidobutane ***6f***

tert-Butylchlorodiphenylsilane (600 μL, 0.632 g, 2.3 mmol) was added dropwise to a solution of diol **7** (0.172 g, 1.0 mmol) and imidazole (0.334 g, 4.9 mmol) in anhydrous DMF (2 mL) at 0°C. After 24 h reaction at 0°C in the refrigerator without stirring, water was added. The mixture was extracted three times with petroleum ether and the combined organic extracts were subsequently washed with water and dried (Na_2SO_4). Concentration in vacuo and chromatography of the crude product on silica gel (gradient elution from petroleum ether to *tert*-butyl methyl ether:petroleum ether 2:98) afforded diazide **6f** as a colorless oil (0.610 g, 94%, R_f=0.41, ethyl acetate:petroleum ether 2:98); IR (neat, NaCl): ν 3072, 3051, 2958, 2932, 2859, 2106, 1590, 1471, 1428, 1263, 1112, 823, 740, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 8H, *ortho* of $SiPh_2$), 7.48–7.35 (m, 12H, *para* and *meta* of $SiPh_2$), 3.82–3.77 (m, 4H, C*H*$_2$O), 3.66–3.59 (m, 2H, C*H*-N$_3$), 1.06 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.53 (4C$_{meta}$), 135.50 (4C$_{meta}$), 132.62 (4C$_{ipso}$), 129.97 (4C$_{para}$), 127.87 (8C$_{ortho}$), 63.83 (2C, *C*H$_2$O), 62.42 (2C, *C*H-N$_3$), 26.70 (6C, C(*C*H$_3$)$_3$), 19.12 (2C, *C*(CH$_3$)$_3$); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{36}H_{45}N_6O_2Si_2$ 649.3143 $[M+H]^+$, found 649.3094 (1), calcd for $C_{36}H_{47}N_4O_2Si_2$ 623.3238 $[M-N_2+H_2+H]^+$ (from in situ reduction of one azide function), found 623.3234 (6), calcd for $C_{32}H_{35}N_6O_2Si_2$ 591.2360 $[M-C_4H_9]^+$, found 591.2372 (10), 571.3 (8) $[M-Ph]^+$, 135.1 (100); $[\alpha]_D^{24}$ −14.1, $[\alpha]_{578}^{24}$ −14.7, $[\alpha]_{546}^{24}$ −16.4, $[\alpha]_{436}^{24}$ −26.1, $[\alpha]_{365}^{24}$ −34.0 (c=1.0, $CHCl_3$). Anal. calcd for $C_{38}H_{44}N_6O_2$: C, 66.63; H, 6.83; N, 12.95. Found: C, 66.19; H, 6.75; N, 13.07.

4.13. (2S,3S)-1,4-Bis[(t-butyldiphenylsilyl)oxy]-2,3-diaminobutane ***3f***

The same procedure as described for (2*S*,3*S*)-**3b** was followed. To a solution of diazide **6f** (0.100 g, 0.16 mmol) in dry THF (3 mL) in a one-necked flask (50 mL) was added 10% Pd/C (0.03 g). The mixture was hydrogenated at ca. 20°C and at atmospheric pressure for 18 h. The catalyst was mostly removed by filtration over Celite and the filtrate was evaporated under vacuum to afford diamine **3f** as a slightly black syrup (0.095 g, quant.). The compound was contaminated with a small amount of colloidal Pd, which could not be removed; IR (neat, NaCl): ν 3384 (broad), 3071, 3050, 2959, 2931, 2892, 2858, 1589, 1471, 1428, 1391, 1361, 1262, 1111, 823, 740, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.59 (m, 8H, *ortho* of $SiPh_2$), 7.44–7.31 (m, 12H, *para* and *meta* of $SiPh_2$), 3.62 (pseudo dd, 2H, *J*=10.0, 4.7 Hz, C*H*$_2$O),[16] 3.55 (pseudo dd, 2H, *J*=10.0, 6.1 Hz, C*H*$_2$O),[16] 2.95–2.88 (m, 2H, C*H*-NH$_2$),[16] 1.43 (broad s, 4H, CH-N*H*$_2$), 1.04 (s, 18H, C(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.55 (4C$_{meta}$), 135.54 (4C$_{meta}$), 133.43 (2C$_{ipso}$), 133.40 (2C$_{ipso}$), 129.72 (2C$_{para}$), 129.70 (2C$_{para}$), 127.71 (8C$_{ortho}$), 66.84 (2C, *C*H$_2$O), 53.84 (2C, *C*H-NH$_2$), 26.89 (6C, C(*C*H$_3$)$_3$), 19.25 (2C, *C*(CH$_3$)$_3$); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{36}H_{49}N_2O_2Si_2$ 597.3333 $[M+H]^+$, found 597.3339 (41) $[M+H]^+$, 451.3 (4), 355.1 (4), 327.0 (7) $[M-CH_2OSiPh_2t\text{-}Bu]$, 310.1 (5), 298.2 (6) $[M/2]^+$, 281.1 (25) $[M/2-NH_3]^+$, 240.1 (8) $[HSiPh_2t\text{-}Bu]^+$, 221.1 (14) $[M/2-Ph]^+$, 197.1 (50), 135.1 (100); [α] could not be measured due to traces of colloidal Pd.

As for **3e**, in the HRMS spectrum, an extra peak with an added mass of 10 was visible (*m/z*=607.3161, rel. int.: 34%, calcd for $C_{37}H_{47}N_2O_2Si_2$=607.3176) which would also fit an imidazoline derivative. Such a compound was not detected by NMR and probably present in small amounts in the crude diamine. Moreover, the peak at 607 was always present in the recorded mass spectrum using another matrix (glycerol) with the same intensity relatively to that of the peak at 597.

Diamine **3f** was converted into di(*p*-bromobenzamide) [(2*S*,3*S*)-*N*,*N*′-di(*p*-bromobenzoyl)-1,4-bis[(*t*-butyldiphenylsilyl)oxy]-2,3-diaminobutane]: reaction of diamine (0.036 g, 0.06 mmol) with *p*-bromobenzoyl chloride (0.04 g, 0.18 mmol) and triethylamine (34 μL, 0.24 mmol) in anhydrous dichloromethane (0.48 mL) for 1 h at 0°C and then 3.5 h at ca. 20°C. Chromatography on silica gel (1.6 g, solid transfer of crude product, elution with petroleum ether:EtOAc 95:5) afforded bisamide as a white powder (0.042 g, 72%, R_f=0.35, petroleum ether:EtOAc 4:1, mp 122°C); IR (Nujol, KBr): ν 3275 (broad), 3070, 3048, 1637, 1591, 1534, 1428, 1112, 1012, 740, 702, 608, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.53 (m, 8H arom.), 7.53–7.44 (m, 8H arom.), 7.43–7.35 (m, 4H arom.), 7.35–7.26 (m, 8H arom.), 7.06 (broad dm, 2H, *J*=7.6 Hz, NH), 4.63–4.53 (m, 2H, C*H*-NH), 3.89 (dd, 2H, *J*=11.0, 1.4 Hz, CH_2O), 3.80 (broad dd, 2H, *J*=11.0, 0.8 Hz, CH_2O), 1.06 (s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.93 (2C, *C*ONH), 135.55 (2CH_{ortho} of $SiPh_2$), 135.46 (2CH_{ortho} of $SiPh_2$), 132.83 and 132.70 and 132.56 (2C_{ipso} of $SiPh_2$ and C_{ipso} α to Br), 131.79 (2*C*H β to CONH), 130.06 (*C*H$_{para}$ of $SiPh_2$), 129.99 (*C*H$_{para}$ of $SiPh_2$), 128.48 (2*C*H β to Br), 127.91 (2*C*H$_{meta}$ of $SiPh_2$), 127.89 (2*C*H$_{meta}$ of $SiPh_2$), 126.26 (C_{ipso} α to CONH), 62.49 (2C, O*C*H$_2$CH), 52.28 (2C, *C*H-NH), 26.93 (6C, C(*C*H$_3$)$_3$), 19.30 (2C, *C*(CH$_3$)$_3$); HRMS (FAB, *m*-nitrobenzylic alcohol matrix) *m/z* (%): calcd for $C_{50}H_{55}Br_2N_2O_4Si_2$ 963.2054 $[M+H]^+$, found 963.2091 (6) $[M+H]^+$, 905.1 (32) [M−*t*-Bu], 885.1 (13) [M−Ph], 707.1 (10) [M−OSiPh$_2$*t*-Bu], 199.0 (46) [NHCO*p*-^{81}Br-C$_6$H$_4$], 197.0 (56) [NHCO*p*-^{79}Br-C$_6$H$_4$], 184.9 (66) [CO*p*-^{81}Br-C$_6$H$_4$], 182.9 (70) [CO*p*-^{79}Br-C$_6$H$_4$], 135.0 (100); $[\alpha]_D^{20}$ −30.4, $[\alpha]_{578}^{20}$ −31.8, $[\alpha]_{546}^{20}$ −36.9, $[\alpha]_{436}^{20}$ −68.7, $[\alpha]_{365}^{20}$ −127.6 (c=1.4, $CHCl_3$).

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We would also like to thank Mrs Isabelle Plessis and Mr Hervé Léon for their substantial experimental work and the Centre Régional de Mesures Physiques de l'Ouest for mass spectra.

References

1. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1993.
2. (a) Tomioka, K. *Synthesis* **1990**, 541–549. (b) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 497–526.
3. (a) Whitesell, J. K. *Chem. Rev*. **1989**, *89*, 1581–1590. (b) Nantz, M. H.; Lee, D. A.; Bender, D. M.; Roohi, A. H. *J. Org. Chem*. **1992**, *57*, 6653–6657. (c) Kotsuki, H.; Kuzume, H.; Gohda, T.; Fukuhara, M.; Ochi, M.; Oishi, T.; Hirama, M.; Shiro, M. *Tetrahedron: Asymmetry* **1995**, *6*, 2227–2236.
4. Scheurer, A.; Mosset, P.; Saalfrank, R. W. *Tetrahedron: Asymmetry* **1997**, *8*, 1243–1251 and 3161.
5. Seebach, D.; Kalinowski, H.-O.; Bastani, B.; Crass, G.; Daum, H.; Dörr, H.; DuPreez, N. P.; Ehrig, V.; Langer, W.; Nüssler, C.; Oei, H.-A.; Schmidt, M. *Helv. Chim. Acta* **1977**, *60*, 301–325.
6. Diols **4a** and **4b** are commercially available [for a synthesis of **4a**, see: Mash, E. A.; Nelson, K. A.; Van Deusen, S.; Hemperly, S. B. *Org. Synth., Coll. Vol. VIII* **1993**, 155–161]. Diol **4c** was used for diastereoselective cyclopropanations [see: Mash, E. A.; Hemperly, S. B.; Nelson, K. A.; Heidt, P. C.; Van Deusen, S. *J. Org. Chem*. **1990**, *55*, 2045–2055]. However, the experimental and spectroscopic data of **4c** were not reported. **4c** was prepared from 2,3-*O*-isopropylidene-L-threitol [2,3-*O*-Isopropylidene-L-threitol is readily available from (+)-diethyl tartrate in two steps. We used the procedure described by Holy, A. (*Collect. Czech. Chem. Commun*. **1982**, *47*, 173–189; acetalization by triethyl orthoformate and

acetone followed by reduction of the ethyl ester groups by sodium borohydride in absolute ethanol)] by double alkylation with 2-(bromomethyl)naphthalene followed by acetonide cleavage (see Experimental).
7. Vicinal diazides are interesting compounds in their own right: for reactions of analogous diazides with C_{60} affording chiral bisazafulleroids, see: Shen, C. K.-F.; Chien, K.-M.; Juo, C.-G.; Her, G.-R.; Luh, T.-Y. *J. Org. Chem*. **1996**, *61*, 9242–9244.
8. Although reduction of diazides **6a** and **6b** to diamines **3a** and **3b** was reported with $LiAlH_4$[5] [see also: Oishi, T.; Hirama, M. *Tetrahedron Lett*. **1992**, *33*, 639–642], catalytic hydrogenation was found to be more efficient and convenient. In the case of diazide **6c**, reaction with $LiAlH_4$ resulted in cleavage of β-naphthylmethoxy groups to 2-methylnaphthalene. Use of other reducing agents (ammonium formate, Pd/C, MeOH or sodium borohydride in the presence of copper sulfate) led to complete decomposition.
9. The catalytic hydrogenation of diazide **6c** to afford diamine **3c** was also successful in isopropanol at 45°C, but THF was found to be more convenient. The catalytic hydrogenation of diazide **6a** to diamine **3a** was carried out in methanol, see Ref. 4, but THF is also an excellent solvent.
10. Ditritylation of diol **5d** using standard conditions (excess trityl chloride and Et_3N, cat. DMAP, refluxing THF) only afforded a very low yield of **6d** (14%).
11. Hanessian, S.; Staub, A. P. A. *Tetrahedron Lett*. **1973**, 3555–3558.
12. In this case, palladium on carbon was a totally ineffective catalyst. However, when Pearlman's catalyst was used, diamine **6d** was contaminated by colloidal palladium, which could not be removed.
13. Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc*. **1972**, *94*, 6190–6191.
14. Hanessian, S.; Lavallée, P. *Can. J. Chem*. **1975**, *53*, 2975–2977.
15. Recently, the vicinal diamines **3a–d** were used for the preparation of salen Mn(III) complexes as catalysts for the enantioselective epoxidation of unfunctionalized alkenes: Scheurer, A.; Mosset, P.; Spiegel, M.; Saalfrank, R. W. *Tetrahedron* **1999**, *55*, 1063–1078.
16. For the ^1H NMR spectrum, a symmetrical six spin ABCC′A′B′ system was observed. Simulation afforded the NMR parameters shown in Table 1.

Table 1
Chemical shifts and non equal to zero coupling constants of the ABCC′A′B′ system observed in ^1H NMR spectra of compounds **3b**,**c**,**e**,**f**, **4c**, **5b**,**c**, **6b–d** and **8**

Compound	**5b**	**6b**	**3b**	**4c**[a]	**5c**	**6c**	**3c**	**6d**	**3e**	**3f**	**8**
$\delta_A = \delta_{A'}$ (ppm)	3.708	3.598	3.332	3.619	3.781	3.670	3.435	3.132	3.549	3.556	3.631
$\delta_B = \delta_{B'}$ (ppm)	3.687	3.604	3.418	3.655	3.810	3.686	3.518	3.267	3.633	3.617	3.638
$\delta_C = \delta_{C'}$ (ppm)	4.934	3.682	2.935	3.902	5.040	3.762	3.030	3.489	2.818	2.914	4.075
$J_{AB} = J_{A'B'}$ (Hz)	- 11.2	- [b]	- 9.3	- 9.7	- 11.2	- 9.8	- 9.3	- 9.9	- 9.9	- 10.0	- [b]
$J_{AC} = J_{A'C'}$ (Hz)	6.5	6.5	6.6	5.6	5.8	6.7	6.4	6.8	6.2	6.2	4.6
$J_{BC} = J_{B'C'}$ (Hz)	3.3	5.4	4.2	4.3	3.4	4.6	4.3	4.4	4.4	4.7	4.5
$J_{CC'}$ (Hz)	4.5	4.2	4.8	3.3	5.5	4.9	4.8	5.4	4.8	4.9	8.1

All spectra were recorded in $CDCl_3$.
[a] With addition of D_2O.
[b] Due to closeness of δ_A and δ_B, J_{AB} could not be determined.

17. Crude acetonide **8** was obtained along with residual 2-(bromomethyl)naphthalene and was used as such for the next step. Subsequent acetonide cleavage yielded crystalline diol **4c** which was easily purified.