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Enantioselective synthesis of *N*-Boc-1-naphthylglycine

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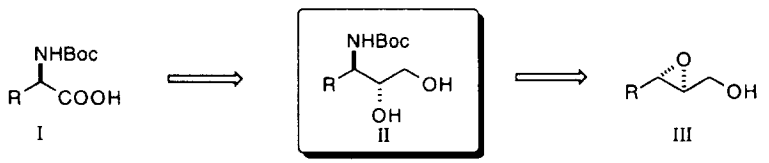
Abstract: A new stereoselective synthesis of enantiomerically pure 1-naphthylglycine has been developed. The source of chirality is the catalytic Sharpless epoxidation. Regioselective and stereospecific ring-opening of the corresponding epoxy alcohol is performed either with sodium azide or with benzhydrylamine as ammonia synthetic equivalents. Subsequent hydrogenation in the presence of $(Boc)_2O$ affords crystalline *N*-Boc-3-(1-naphthyl)propane-1,2-diol which is enantiomerically enriched up to 100% ee and oxidized to the α-amino acid. © 1997 Elsevier Science Ltd

1-Naphthylglycine is a representative example of the arylglycines, an important class of non-proteinogenic amino acids.[1] Arylglycines are present in many biologically active compounds such as cephalosporins[2] or nocardicins.[3] Moreover, they have potential interest as chiral building blocks or as precursors of chiral ligands for asymmetric synthesis. To the best of our knowledge, all syntheses of naphthylglycine described so far are either not stereoselective[4] or based on a chiral auxiliary approach in which the chiral inductor can not be recovered.[5] We report here a practical catalytic enantioselective synthesis of *N*-Boc-1-naphthylglycine using a modification of our methodology based on the catalytic Sharpless epoxidation.[6]

The key intermediates in our approach to the synthesis of α-amino acids **I** are *N*-Boc-3-amino-1,2-diols **II**. These versatile chiral synthons can be prepared from epoxy alcohols **III** through a regio and stereospecific ring-opening by an appropriate ammonia equivalent (Scheme 1) and we have demonstrated their usefulness in the preparation of several biologically active compounds.[7] There are two interesting properties of these intermediates that are worth mentioning: a) they are usually crystalline compounds thus allowing the possibility of enantioenrichment and b) the amino group has a widely used protecting group whose presence can be also useful in the final product.



Scheme 1.

In the present synthesis of *N*-Boc-1-naphthylglycine the starting material was the known[8] allyl alcohol **1** which was prepared in good yield from commercial aldehyde **2** according to the conventional procedure of Wittig olefination followed by DIBAL-H reduction. The catalytic Sharpless asymmetric epoxidation[9] of allyl alcohol **1** afforded the corresponding epoxy alcohol **3** in 73% yield and with an enantiomeric excess of 86%, as determined by HPLC (Scheme 2).

Complete regioselective and stereospecific ring-opening of epoxy alcohol **3** was achieved by treatment with sodium azide under Crotti's conditions,[10] the intermediate 3-azido-1,2-diol being immediately reduced and *in situ* protected to give *N*-Boc-3-amino-3-naphthyl-1,2-propanediol **4** with

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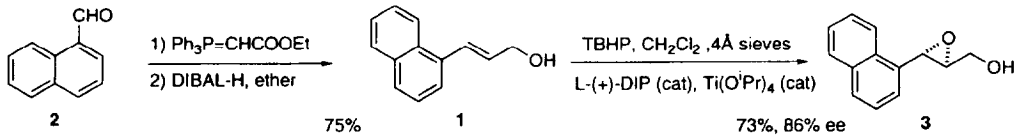
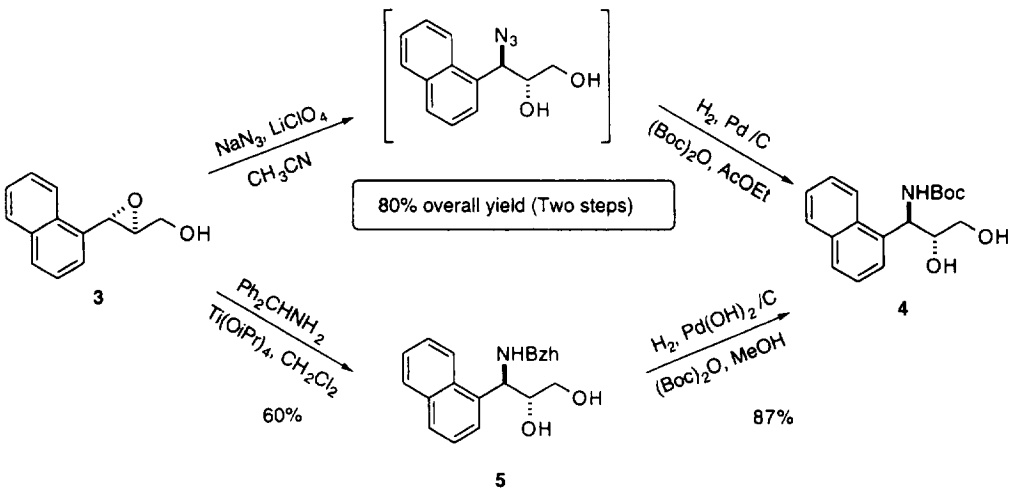


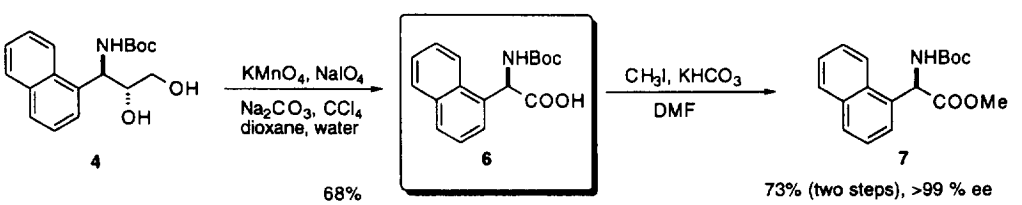
Scheme 2.

an 80% overall yield. An alternative procedure that avoids the preparation of organic azides (more suited for large scale work) involves the use of benzhydrylamine (diphenylmethylamine) as the $-NH_2$ source.[11] The ring-opening of epoxide **3** mediated by titanium tetraisopropoxide afforded the desired 3-benzhydrylamino-3-naphthyl-1,2-propanediol **5** in 60% yield after removal of the C-2 ring-opening product (10%). Conversion of **5** into the corresponding *N*-Boc derivative **4** was conveniently performed by catalytic hydrogenation (Pearlman's catalyst) in the presence of $(Boc)_2O$ in methanol (Scheme 3).



Scheme 3.

N-Boc-3-amino-3-naphthyl-1,2-propanediol **4** was, according to our expectations, a nicely crystalline compound which, on crystallization from chloroform, underwent enantiomeric enrichment as evidenced by polarimetry. Oxidation of **4** was initially performed with $RuCl_3/NaIO_4$ in $CH_3CN/CCl_4/H_2O$[12] but, somewhat surprisingly, very low yields of *N*-Boc-naphthylglycine were obtained. This problem could be overcome by changing the oxidation conditions. When compound **4** was submitted to oxidation with $KMnO_4/NaIO_4/Na_2CO_3$ in dioxane/water[13] *N*-Boc-D-naphthylglycine was obtained in good yield. In order to check its enantiomeric excess the oxidation crude was converted into the corresponding methyl ester which was enantiomerically pure according to HPLC analysis on a chiral stationary phase (Chiralcel® ODR) (Scheme 4).



Scheme 4.

In summary we have developed an efficient procedure for the preparation of enantiopure *N*-Boc-naphthylglycine, an important non proteinogenic amino acid. The source of chirality in our approach is a catalytic Sharpless epoxidation. Although the epoxy alcohol **3** was obtained in 85% ee, the crystallinity of the *N*-Boc-3-naphthyl-1,2-propanediol intermediate allowed enantioenrichment so the final product could be obtained in enantiomerically pure form. Due to the broad scope of the reactions involved, the present methodology should be of general applicability in the synthesis of arylglycines. The use of naphthylglycine as a precursor of chiral ligands for asymmetric synthesis is under study in our laboratories and will be described in due course.

Experimental section

General methods

Optical rotations were measured at room temperature (23°C) on a Perkin–Elmer 241 MC automatic polarimeter (Concentration in g/100 mL). Melting points were determined on a Gallenkamp apparatus and have not been corrected. Infrared spectra were recorded on a Perkin–Elmer 681, or on a Nicolet 510 FT-IR instrument using NaCl film or KBr pellet techniques. NMR spectra were acquired on Varian XL-200 or Varian-Unity-300 instruments. ^{1}H-NMR were obtained at 200 or 300 MHz (s=singlet, d=doublet, t=triplet, q=quartet, dt=double triplet, m=multiplet, b=broad and bd=broad doublet). ^{13}C-NMR were obtained at 50.3 MHz or 75.4 MHz. Carbon multiplicities have been assigned by distortionless enhancement by polarization transfer (DEPT) experiments. Mass spectra were recorded on a Hewlett–Packard 5890 instrument. Elemental analyses were performed by the "Servei d'Anàlisis Elementals del CSIC de Barcelona". Chromatographic separations were carried out using NEt_3 pre-treated (2.5% v/v) SiO_2 (70–230 mesh). Chromatographic analyses were performed on a Helwett–Packard 1050 HPLC instrument equipped with Chiralcel® ODR (25 cm) column.

(E)-3-(1-Naphthyl)-2-propen-1-ol, 1

To a solution of ethyl triphenylphosphoranylacetate (32.75 g, 94 mmol) in dichloromethane (100 mL) 1-naphthaldehyde (13.28 g, 85 mmol) in dichloromethane (50 mL) was added. The mixture was stirred at reflux for 90 minutes. The solvent was removed *in vacuo* and the residual oil was extracted with hexanes (10×25 mL). The hexane solution was concentrated yielding 25.1 g of ethyl 3-(1-naphthyl)acrylate (slightly impurified with triphenylphosphine oxide) as an oil. This oil was solved in diethyl ether (100 mL) and cooled to 0°C. To this solution, 1 M DIBALH (170 mL, 170 mmol) in hexanes was added. After 2 hours of stirring at room temperature, the reaction mixture was diluted with diethyl ether (200 mL), cooled to 0°C and quenched with a careful addition of brine (200 mL). Then, 4 M HCl (200 mL) was added dropwise. The aqueous layer was extracted with diethyl ether (3×150 mL) and the combined organic phases were washed with brine, dried (sodium sulfate) and evaporated. The residue was chromatographed eluting with hexane/ethyl acetate mixtures yielding 117 g of **1** (75%) as an oil that was distilled before its use in the Sharpless epoxidation (172–175; lit. 209–210°C/18 torr[8]). IR (film) ν 3334, 3047, 2863, 1653 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.05 (broad s, 2H), 4.39 (dd, J=1.4, 5.4 Hz, 2H), 6.35 (dt, J=5.4, 15.8 Hz, 1H), 7.21–8.12 (m, 8H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 63.7 (CH_2), 123.7 (CH), 123.8 (CH), 125.5 (CH), 125.7 (CH), 126.0 (CH), 127.9 (CH), 128.0 (CH), 128.4 (CH), 131.0 (CH), 131.7 (C), 133.5 (C), 134.3 (C) ppm. MS (EI) m/e 218 (M^+, 43%), 173 (100%).

(2S,3S)-3-(1-Naphthyl)-2,3-epoxy propanol, 3

Into a 500 mL flask were introduced dry powdered 4 Å molecular sieves (1.35 g) and anhydrous dichloromethane (180 mL) under nitrogen. After cooling to −20°C (CO_2/CCl_4 bath) the following reagents were introduced sequentially *via cannula* under stirring: L-(+)-diisopropyltartrate (0.44 g, 1.89 mmol) in dichloromethane (20 mL), titanium tetraisopropoxide (0.38 mL, 1.29 mmol) and 5.4 M solution of *tert*-butyl hydroperoxide in isooctane (9.3 mL, 50.2 mmol). The mixture was stirred 1 hour at −20°C and a solution of (*E*)-3-naphthyl-2-propen-1-ol **1** (6.02 g, 32.66 mmol) (previously distilled

and stored 24 h with 4 Å molecular sieves) in dichloromethane (10 mL) was added. After 8 h of stirring at the same temperature the reaction was quenched by addition of 10% NaOH solution saturated with NaCl (2.2 mL) and diethyl ether (27 mL). The mixture was allowed to warm to 10°C, and anhydrous $MgSO_4$ (2.61 g) and Celite® (0.33 g) were added. After 15 min stirring at room temperature the mixture was filtered through a short Celite® pad. The solvents were evaporated *in vacuo* and the excess of *tert*-butyl hydroperoxide removed by azeotropic distillation with toluene (3×125 mL). The crude was then chromatographed eluting with hexanes/ethyl acetate mixtures yielding 3.70 g of **3** (73% yield). The enantiomeric excess was determined to be 86% ee by HPLC (Chiralcel® ODR, 0.5 mL/min $NaClO_4$ aq. 0.5 M/MeOH 1/9; t_R (2*R*,3*R*) 13.1 min; t_R (2*S*,3*S*) 19.0 min). $[\alpha]_D$ +50.3 (*c* 1, $CHCl_3$). IR (film) ν 3417, 3058, 2925, 2867, 1598, 1510, 1452, 1084 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.24 (broad s, 1H), 3.21 (m, 1H,), 3.97 (ddd, J=13.5, 5.7, 3.6 Hz, 1H), 4.15 (ddd, J=13.5, 1.0, 1.0 Hz, 1H), 4.57 (d, J=2.4 Hz, 1H), 7.44–8.09 (m, 7H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 53.8 (CH), 61.6 (CH) 61.6 (CH_2), 122.2 (CH), 122.7 (CH), 125.4 (CH), 125.9 (CH), 126.4 (CH), 128.2 (CH), 128.7 (CH), 131.1 (C), 132.7 (C), 133.2 (C) ppm. MS (CI−NH_3) *m/e*: 201 ($M+1^+$, 1%), 218 ($M+18^+$, 100%).

(2R,3R)-3-Diphenylmethylamino-3-(1-naphthyl)-1,2-propanediol, 5

To a solution of (2*S*,3*S*)-3-(1-naphthyl)-2,3-epoxypropanol **3** (0.72 g, 3.6 mmol) in dichloromethane (30 mL) were added *via cannula* benzhydrilamine (0.95 mL, 5.43 mmol) in dichloromethane (7 mL) and titanium tetraisopropoxide (1.65 mL, 5.43 mmol) in dichloromethane (7 mL). After 3 hours of stirring at room temperature the reaction was quenched with 10% NaOH solution saturated with NaCl. The mixture was stirred 15 hours, filtered through a short Celite® pad and washed throughly with dichloromethane. The aqueous layer was extracted with dichloromethane (3×20 mL) and the combined organic phases were dried ($MgSO_4$) and evaporated. The crude was chromatographed eluting with hexanes/ethyl acetate mixtures to afford 0.82 g of **5** (60%) and 0.14 g of (2*R*,3*S*)-2-diphenylmethylamino-3-(1-naphthyl)-1,3-propanediol (10.5%). **5** m.p. 55–57°C. $[\alpha]_D$ −11.2 (*c* 1, $CHCl_3$). IR (KBr) ν 3409, 3060, 2950, 1597, 1510, 1493, 1028 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.89 (broad, 3H), 3.4–3.7 (m, 2H), 3.9 (b, 1H), 4.6 (b, 1H), 4.65 (s, 1H), 7.1–8.1 (m, 7H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 58.0 (CH), 63.7 (CH), 64.6 (CH_2), 73.1 (CH), 122.7 (CH), 125.5 (CH), 125.7 (CH), 126.1 (CH), 126.9 (CH), 127,1 (CH), 127.3 (CH), 127.8 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 142.1 (C), 144.0 (C) ppm. MS (CI−NH_3) *m/e*: 384 ($M+1^+$, 100%), 322 ($M-61^+$, 1%). Anal. Calcd for $C_{26}H_{25}O_2N$: C, 81.43; H 6.57; N, 3.65. Found: C, 81.43; H, 6.59; N, 3.45.

*(2R,3R)-3-(*tert*-Butoxycarbonylamino)-3-(1-naphthyl)-1,2-propanediol, 4*

Method A (from 5)

A suspension of (2*R*,3*R*)-3-diphenylmethylamino-3-(1-naphthyl)-1,2 propanediol **5** (0.25 g, 0.652 mmol), di-*tert*-butyl dicarbonate (0.192 g, 0.848 mmol) and $Pd(OH)_2/C$ (15%, 37 mg) in MeOH (0.8 mL) (two drops of ethyl acetate were added to increase the solubility of **5**) was hydrogenated at room temperature and atmospheric pressure until no starting material could be observed by TLC (approx. 2 days). The reaction mixture was filtered and the solvents evaporated *in vacuo*. The residue was chromatographed eluting with hexanes/ethyl acetate mixtures yielding 0.18 g of **4** (87%).

Method B (from 3)

To a solution of (2*S*,3*S*)-3-(1-naphthyl)-2,3-epoxypropanol **3** (1 g, 5 mmol) in CH_3CN (25 mL), were added 13.1 g of lithium perchlorate. After 10 minutes stirring, sodium azide (1.62 g, 24.8 mmol) was added and the mixture was heated at 65°C for 24 hours under nitrogen. The reaction was treated with water (300 mL) and extracted with diethyl ether (3×190 mL). The combined organic phases were dried ($MgSO_4$) and evaporated. The residue, composed by 1.2 g of (2*R*,3*R*)-3-azido-3-(1-naphthyl)-1,2-propanediol was immediately solved in ethyl acetate (11 mL). This solution was added to a suspension

of di-*tert*-butyl dicarbonate (1.55 g, 6.9 mmol) and Pd/C (10%, 0.121 g) in ethyl acetate (2 mL) and hydrogenated at atmospheric pressure until no starting material could be observed by TLC (approx. 24 hours). The reaction mixture was filtered and the solvents evaporated *in vacuo*. The residue was chromatographed eluting with hexanes/ethyl acetate mixtures yielding 1.27 g of **4** (80% yield) as a white solid that was recrystallized from diethyl ether. m.p. 108–109°C. $[\alpha]_D$ −16.0 (*c* 1, $CHCl_3$). IR (KBr) ν: 3401, 2977, 1686, 1507, 1393, 1368, 1067 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.6 (d, J=8 Hz, 1H), 3.4–4.2 (m, 4H), 5.15 (bd, 1H), 5.6 (t, J=8.5 Hz, 1H), 7.2–8.1 (m, 7H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.8 (CH_3), 52.4 (CH), 63.5 (CH_2), 73.3 (CH), 81.1 (C), 123.4 (CH), 124.4 (CH), 125.8 (CH), 126.3 (CH), 127,1 (CH), 129.1 (CH), 129.4 (CH), 131.9 (C), 134.1 (C), 136 (C), 157.9 (C) ppm. MS (CI−NH_3) *m/e*: 318 ($M+1^+$, 32%), 335 ($M+18^+$, 100%), 352 ($M+35^+$, 3%). Anal. Calcd for: ($C_{18}H_{23}O_4N$): C, 68.11; H, 7.30; N, 4.41. Found: C, 68.04; H, 7.39; N, 4.34.

N-*Boc-D-1-Naphthylglycine, 6*

A mixture of (2*R*,3*R*)-3-(*tert*-butoxycarbonylamino)-3-(1-naphthyl)-1,2-propanediol **4** (0.45 g, 1.41 mmol), Na_2CO_3 (75 mg, 0.7 mmol), $NaIO_4$ (1.2 g, 5.65 mmol), $KMnO_4$ (45 mg, 0.28 mmol) in dioxane (3 mL) and water (1.3 mL) was vigorously stirred at room temperature until no starting material could be observed by TLC (approx. 10 hours). Ethyl acetate (30 mL) was added and the mixture was acidified by addition of 2 M HCl. The organic phase was washed with brine, dried and evaporated yielding 0.4 g of an oil that was disgregated in hexane (95%). The crude can be purified by chromatography (SiO_2, CH_2Cl_2/methanol 0–1%) yielding 0.27 g (64% yield) of pure **6**. An alternative non-chromatographic procedure can also be used. The crude was solved in $NaHCO_3$ solution and the aqueous phase was washed with ethyl acetate, acidified and extracted again with ethyl acetate. The organic phase was then dried and evaporated yielding a solid that was recrystallized from hexane/ether to yield 0.29 g (68% yield) of **6**. m.p. 182–183° $[\alpha]_D$ −147.7 (*c* 1, MeOH). IR (KBr) ν 3299, 2979, 1723, 1686, 1396, 1369, 1163 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$/MeOD, 55°C) δ 1.6 (s, 9H), 4.7 (b, 2H), 6.1 (s, 1H), 7.2–8.1 (m, 7H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$/MeOD, 55°C) δ 28.8 (CH_3), 56.1 (CH), 81.0 (C), 124.5 (CH), 126.3 (CH), 126.5 (CH), 126.9 (CH), 127.6 (CH), 128.6 (CH), 130.0 (CH), 132.6, (C), 134.7 (C), 135.5 (C), 174.6 (C), ppm. MS (CI−NH_3) *m/e*: 302 ($M+1^+$, 3%), 319 ($M+18^+$, 100%).

N-*Boc-D-1-Naphthylglycine methyl ester, 7*

Compound **4** (0.12 g, 0.37 mmol) was oxidized under the previously described conditions. The crude reaction was solved in dimethylformamide (0.77 mL) and $KHCO_3$ (93 mg, 0.93 mmol) was added. The flask was purged with nitrogen and methyl iodide (0.062 mL, 0.74 mmol) was added *via* syringe. The mixture was stirred 16 h at room temperature and quenched by addition of water (2 mL). The product was extracted with 1:1 benzene/ethyl acetate mixtures (3×3mL). The combined organic phases were washed with water, 5% Na_2SO_3 and brine, dried ($MgSO_4$) and evaporated. The crude was chromatographed eluting with hexane/ethyl acetate mixtures yielding 87 mg of **7** (73% from **4**, two steps). Starting from crystalline **4** only the *R* enantiomer could be detected by HPLC analysis (>99% ee) (Chiralcel® ODR, $NaClO_4$ aq. 0.5 M/MeOH 25/75) (t_R (*S*)-**7**, 23.34 min, t_R(*R*)-**7**, 26.26 min). $[\alpha]_D$ −144 (*c* 1, $CHCl_3$). IR (KBr) ν: 3378, 3060, 2979, 1750, 1713, 1497, 1165 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.4 (s, 9H), 3.7 (s, 3H), 5.5 (b, 1H), 6.1 (d, J=9 Hz, 1H), 7.2–8.1 (m, 7H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.2 (CH_3), 52.6 (CH_3), 54.6 (CH), 80.3 (C), 123.2 (CH), 125.2 (CH), 125.3 (CH), 125.9 (CH), 126.8 (CH), 128.8 (CH), 129.2 (CH), 130.9 (C), 133.3 (C), 133.9 (C), 155.1 (C), 171.8 (C) ppm. MS (CI−NH_3) *m/e*: 316 ($M+1^+$, 9%), 333 ($M+18^+$, 100%).

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