Efficient routes to alkyl ether linked derivatives of 1,1′-(bi-2-naphthol) bearing 3-*N*,*N*-dialkylamide substituents

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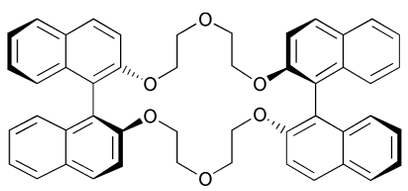
Reaction of (R_a) or (S_a)-2-(*N*,*N*-dialkylcarbamoyloxy)-2′-hydroxy-1,1′-binaphthyls (diethyl and diisopropyl derivatives) with α,ω-I$(CH_2)_n$I (n = 6, 8) in the presence of K_2CO_3 leads to the formation 1,*n*-bis{2′-[2-(*N*,*N*-dialkylcarbamoyloxy)-1,1′-binaphthyl]oxy}alkanes. These diethers when treated with Bu^{s}Li–TMEDA fashion 1,*n*-bis{2′-[2-hydroxy-3-(*N*,*N*-dialkylamido)-1,1′-binaphthyl]oxy}alkanes, the products of double anionic Fries rearrangement.

Introduction

Interesting ligands can be made by linking two 1,1′-binaphthyl units together. There are several examples of such compounds in the literature, some of which are shown in structures **1**–**3**.



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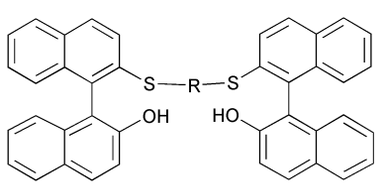
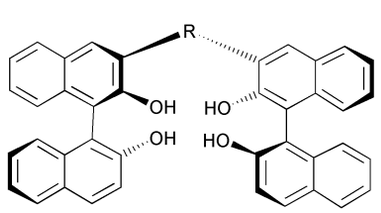


2a R = nothing
2b R = -$(CH_2)_2$-
2c R = -$(CH_2)_3$-



3a R = -CH_2-
3b R = -CH_2CH_2-
3c R = -C(O)-
3d R = -C≡C-

Cram and co-workers prepared **1**,[1] along with numerous other related cyclic polyethers, in the 1970s for use in molecular recognition.[1,2] We have prepared the disulfide **2a**–**c**[3,4] to enable analysis of the enantiopurity of the parent thiol by ^{13}C NMR spectroscopy. The 3,3-position linked 1,1′-binaphthyls **3a**–**c** have been prepared by Shibasaki and co-workers[5] for use in the mechanistic study of asymmetric syntheses involving BINOL and derivatives, as well as for use as ligands in their own right. Li and co-workers[6] prepared **3d** with the aim of using it as a chiral ligand. Other examples include chiral diimine[7] and 4,4-bipyridine[8] linking groups between the 3- or 3,3′- positions. A cyclic compound containing three BINOL units linked by diyne groups through the 3,3′- positions has also been prepared.[9]

Results and discussion

Alkylation studies

We have developed a method allowing very selective preparation of mono carbamoyl derivatives of 1,1′-(bi-2-naphthol), such as **4** and **5** (Scheme 1, just the S_a enantiomers are shown for convenience).[10] The ready availability of these compounds suggested the possibility of linking two of these units *via* the free hydroxy group in the 2′- position. Under basic conditions it seemed likely that α,ω-diiodides would react with the monocarbamates **4** and **5** *via* a double Williamson ether synthesis to give two 1,1′-(bi-2-naphthol)urethane units linked through the 2′-position by an alkyl chain. These products could then be subjected to Fries rearrangement conditions to give the potentially tetradentate ligands.[10] Construction of molecular models indicated that 1,6-diiodohexane and 1,8-diiodooctane would lead to the ligands most likely to encapsulate metal cations in a tetradentate manner; as shown in the schematic structure **A** (Scheme 1).

The enantiopure monocarbamates **4**, **5**, as either the (R_a) or (S_a) series, were treated with 0.5 equivalents of either 1,6-diiodohexane or 1,8-diiodooctane in the presence of excess K_2CO_3 in acetone. The products **6**–**9** were formed in high yield after reflux for approximately one week. The progress of the reaction could be followed by TLC analysis; the reactions were stopped when only small amounts of the starting material remained. Complete disappearance of **4** and **5** is never observed and column chromatography is required to separate these from the products **6**–**9** (Scheme 1). The products are not crystalline. They have low melting points (50–70 °C), and appear to entrain solvent molecules quite effectively; a property we have noted before.[10] It is possible to obtain elemental analyses for some of them; the rest were characterised by HRMS in addition to standard spectroscopic techniques. The bridging ether strap provides some steric hindrance to C–NR_2 rotation in the carbamate groups and only broad ^{1}H NMR signals are observed in compounds **6**–**9**.

When following these reactions by TLC it can be seen that intermediate materials are produced during the reactions. These materials become less prominent as the reaction proceeds but,

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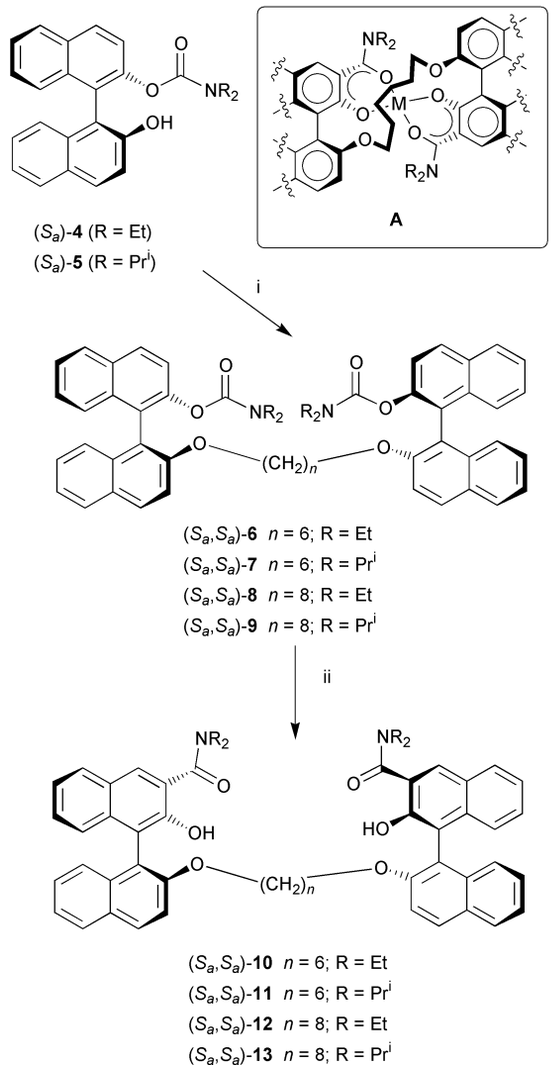
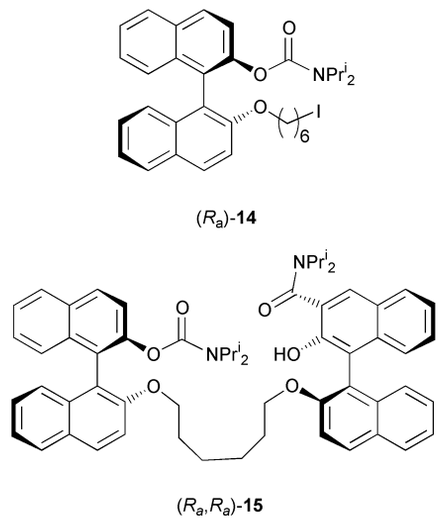


Scheme 1 *Reagents and conditions*: i, K_2CO_3 acetone, reflux 1 week; ii, Bu^sLi–TMEDA, −78 °C to ambient temperature.

like the starting material, they never completely disappear. However, they are easily removed during chromatography. The nature of the intermediate was investigated in the reaction of (R_a)-**5** with one equivalent of 1,6-diiodohexane instead of the normal 0.5 and a reflux time of just 16 hours before work-up and column chromatography. Although a significant amount of (R_a),(R_a)-**7** is isolated (32%), the major product is a colourless viscous oil which contains significant amounts of 1,6-diiodohexane. Repeated chromatography leads to a new 1,1′-binaphthyl derivative as the occluded diiodo compound is gradually released. The spectroscopic properties of the pure compound are consistent with the presence of (R_a)-**14** as required by a two step mechanism.

Anionic Fries rearrangement studies

Preliminary lithiations of (S_a)-**6** with Bu^sLi–TMEDA (5–30 minutes) followed by trapping with MeI indicated clean formation of the dilithio species. Based on these results the preparation of **10**–**13** was performed under standard anionic Fries rearrangement conditions.[10] These conditions are found to be quite adequate and no modifications are required, giving the products in reasonable yields after column chromatography. These materials are also not crystalline and as with the precursors **6**–**9** they are difficult to obtain completely solvent free, often resulting in inadequate combustion analysis. A by-product isolated in 29% yield from a preparation of (R_a), (R_a)-**11** is (R_a),(R_a)-**15**, presumably this results from



either incomplete lithiation of the substrate or only partial rearrangement of the dilithio species. As with their parent carbamates compounds **10**–**13** and **15** show broadened amido resonances in their ^1H NMR spectra due to restricted C–NR_2 rotations.

Complexation and catalysis studies

Reactions of ligands **10**–**13** with either $M(OAc)_2$ (M = Cu and Mn) under a variety of workup conditions failed to lead to tractable products and in all cases the free ligand is recovered in 50–100% yield. In most cases significant colour changes are observed in the reaction mixtures when 1 : 1 mixtures of ligands and M^{2+} sources are combined in the presence of suitable bases. However, the products formed appear to be very sensitive to hydrolysis upon attempted isolation. Attempts to monitor these reactions by UV-vis spectroscopy were hampered by the non-homogeneity of the reaction mixtures. Because of these features ligand (S_a,S_a)-**10** was tested in two catalytic reactions where anhydrous conditions can be assured and that allowed *in situ* catalyst formation. The addition of Bu^tSH to cyclohexene oxide, introduced by Shibasaki,[11] was attempted using bimetallic catalysts derived from deprotonation of **10** by appropriate organometallics. The Li_2, Ca, and Zn derivatives of ligand (S_a,S_a)-**10** (10 mol%) are inactive for even stoichiometric $LiSBu^t$ addition while *in situ* prepared $Ga(SBu^t)$(**10** − $2H^+$) promotes some addition of the thiol (one turnover, 12% ee). Similarly, attempts to use ligand (S_a,S_a)-**10** (10 mol%) in the addition of $ZnEt_2$ to PhCHO lead only to the formation of trace amounts of product (2%) in low ee (26%).

In conclusion, although 2,2′-alkyl-linked derivatives of 1,1′-(bi-2-naphthol) are easily prepared, thus far, the types of metal complexes they provide do not appear to be especially active in benchmark asymmetric catalytic reactions possibly due to a lack of free co-ordination sites. Other applications for this class of easily prepared species are currently being sought, with studies concentrating on titanium promoted reactions.

Experimental

General

Procedures involving moisture sensitive intermediates were carried out under nitrogen atmospheres using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium–benzophenone immediately prior to use. Specific rotations were measured using an Optical Activity AA-10 automatic polarimeter at ambient conditions and are given in 10^{-1} deg cm^2 g^{-1}; *c* is in g 100 cm^{-3} of solvent. Column chromatography and TLC analyses were performed on silica gel, Rhône-Poulenc Sorbsil and Merck Kieselgel 60 $F_{254+366}$ respectively. Infrared spectra

were recorded using a Perkin-Elmer 983 G infrared spectrophotometer and a Perkin-Elmer 882 infrared spectrophotometer. Proton and ^{13}C NMR spectra were recorded on either JEOL (JNM-GX270, JNM-LA400) or Bruker (WH 360) spectrometers using tetramethylsilane as standard; *J* values are given in Hz. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Mass spectra were obtained on a Finnigan-MAT 1020 (electron impact ionisation, EI) machine and a VG-ZAB (fast atom bombardment ionisation, FAB; or liquid scintillation ionisation mass spectrometry, LSIMS) machine (EPSRC Service, Swansea). Elemental analyses were performed using a Fisons instruments EA 1108 CHN elemental analyser. Compounds **4** and **5** were obtained by literature procedures.[10] Additions of Bu^{t}SH to cyclohexene oxide[11] and $ZnEt_2$ to PhCHO[12] were carried out under the reported conditions.

General procedure for the preparation of bis{2[2-(*N*,*N*-dialkylcarbamoyloxy)-1,1′-binaphthyl]oxy} alkanes 6–9

2-(*N*,*N*-Dialkylcarbamoyloxy)-2′-hydroxy-1,1′-binaphthalene **4** or **5** (12.10 mmol) and α,ω-diiodoalkane (6.05 mmol) was added to a slurry of K_2CO_3 (6.68 g, 48.4 mmol) in acetone (100 ml) and the solution refluxed until only a trace of starting material remained by TLC (1 : 9 ethyl acetate–light petroleum). Typical reaction times were 4–8 days. The reaction mixture was cooled and partitioned between water and ethyl acetate. The organic layer was washed with 2 M $HCl_{(aq)}$ (×2), water, brine, and dried over Na_2SO_4. The solvent was removed to give a colourless foam that was purified by column chromatography (ethyl acetate–light petroleum).

1,6-Bis{(S_a)-2′-[2-(*N*,*N*-diethylcarbamoyloxy)-1,1′-binaphthyl]oxy}hexane (S_a,S_a)-6. White foam, 75%; mp 52–53 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 24 °C) −72; ν_{max} (KBr disc)/cm^{-1} 3060 w (Ar C–H), 2940 (alkyl C–H), 1710 vs (C=O), 1625, 1595, 1510, 1475, 1420, 1270 s, 1215 s, 1155 s, 1080, 1050, 985, 805, 780; δ_H (400 MHz; $CDCl_3$) 0.39 (3 H, apparent br s with unresolved splitting, CH_2CH_3), 0.59 (2 H, apparent br s with unresolved splitting, $OCH_2CH_2CH_2$), 0.78 (3 H, apparent br s with unresolved splitting, CH_2CH_3), 1.05–1.18 (2 H, m, $OCH_2CH_2CH_2$), 2.60–2.67 (2 H, m, CH_2CH_3), 2.93–2.99 (1 H, m, $CHHCH_3$), 3.03–3.11 (1 H, m, $CHHCH_3$), 3.70–3.78 (2 H, m, $OCH_2CH_2CH_2$), 7.10–7.12 (1 H, m, Ar), 7.18–7.31 (5 H, m, Ar), 7.33 (1 H, d, *J* 9.0, 3 or 3′-H), 7.55 (1 H, d, *J* 9.0, 3 or 3′-H), 7.75 (1 H, d, *J* 8.0, 5 or 5′-H), 7.81 (1 H, d, *J* 9.0, 4 or 4′-H), 7.82 (1 H, d, *J* 8.3, 5 or 5′-H), 7.92 (1 H, d, *J* 9.0, 4 or 4′-H); δ_C (100.4 MHz; $CDCl_3$) 12.9, 13.1, 24.9, 29.0, 41.1, 41.7, 69.4, 115.4, 119.3, 122.4, 123.6, 124.7, 124.9, 125.6, 126.0 (2 C), 126.3, 127.5, 127.9, 128.4, 129.1, 129.4, 131.2, 133.6, 133.9, 147.4, 153.4, 154.4; *m*/*z* (EI) 852 (M^+, 30%), 468 (44), 385 (100) [found (HRMS) M^+ 852.4146. $C_{56}H_{56}N_2O_6$ requires 852.4138].

1,6-Bis{(R_a)-2′-[2-(*N*,*N*-diisopropylcarbamoyloxy)-1,1′-binaphthyl]oxy}hexane (R_a,R_a)-7. White foam, 73%; mp 62–64 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 24 °C) +72; ν_{max} (KBr disc)/cm^{-1} 3170 w (Ar C–H), 2970 and 2955 (alkyl C–H), 1715 vs (C=O), 1510, 1430, 1310 s, 1225 s, 1155, 1045, 1010, 805, 750; δ_H (400 MHz; $CDCl_3$) 0.51–0.59 [8 H, m, $CH(CH_3)_2$ and $OCH_2CH_2CH_2$], 0.89 [3 H, apparent br s, $CH(CH_3)CH_3$], 1.02 [5 H, m, $CH(CH_3)CH_3$ and $OCH_2CH_2CH_2$], 3.47 (2 H, apparent br s, CH), 3.69–3.78 (2 H, m, $OCH_2CH_2CH_2$), 7.10–7.14 (1 H, m, Ar), 7.18–7.30 (5 H, m, Ar), 7.32 (1 H, d, *J* 9.0, 3 or 3′-H), 7.48 (1 H, d, *J* 8.8, 3 or 3′-H), 7.75 (1 H, d, *J* 8.3, 5 or 5′-H), 7.81 (2 H, apparent d, *J* 8.5, Ar), 7.91 (1 H, d, *J* 9.0, 4 or 4′-H); δ_C (100.4 MHz; $CDCl_3$) 20.4 (4 C), 25.0, 29.1, 45.9, 46.2, 69.4, 115.4, 119.6, 123.0, 123.6, 125.0, 125.1, 125.9, 126.0, 126.1, 126.4, 127.5, 128.0, 128.4, 129.3, 129.5, 131.4, 133.9, 134.1, 147.5, 152.6, 154.5; *m*/*z* (LSIMS) 931 (MNa^+, 10), 909 (MH^+, 8%) [found (HRMS) MH^+ 909.4834. $C_{60}H_{65}N_2O_6$ requires 909.4842].

1,8-Bis{(S_a)-2′-[2-(*N*,*N*-diethylcarbamoyloxy)-1,1′-binaphthyl]oxy}octane (S_a,S_a)-8. White foam, 73%; mp 51–52 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 30 °C) −71 (found: C, 78.8; H, 7.1; N, 3.1. $C_{58}H_{60}N_2O_6$ requires C, 79.1; H, 6.9; N, 3.2%); ν_{max} (KBr disc)/cm^{-1} 3060 w (Ar C–H), 2935 (alkyl C–H), 1720 s (C=O), 1625, 1595, 1510, 1460, 1420, 1275, 1215 s, 1155 s, 1080, 1050, 985, 805, 775; δ_H (400 MHz; $CDCl_3$) 0.41 (3H, apparent br s with unresolved splitting, CH_2CH_3), 0.73–0.80 (7 H, m, CH_2CH_3 + $OCH_2CH_2CH_2CH_2$), 1.27–1.35 (2 H, m, $OCH_2CH_2CH_2CH_2$), 2.61–2.66 (2 H, m, CH_2CH_3), 2.94–3.01 (1 H, m, $CHHCH_3$), 3.03–3.12 (1 H, m, $CHHCH_3$), 7.16–7.35 (6 H, m, Ar), 7.37 (1 H, d, *J* 8.9, 3 or 3′-H), 7.57 (1 H, d, *J* 9.0. 3 or 3′-H), 7.82 (2 H, apparent d, *J* 8.1, 5 and 5′-H), 7.87 (1 H, d, *J* 8.9, 4 or 4′-H), 7.92 (1 H, d, *J* 9.0, 4 or 4′-H); δ_C (100.4 MHz; $CDCl_3$) 12.9, 13.1, 25.3, 28.7, 29.2, 41.2, 41.7, 69.7, 115.5, 119.4, 122.4, 123.6, 124.7, 124.9, 125.7, 126.0, 126.1, 126.4, 127.5, 127.9, 128.4, 129.1, 129.5, 131.3, 133.7, 134.0, 147.4, 153.4, 154.5; *m*/*z* (LSIMS) 903 (MNa^+, 29%), 881 (MH^+, 100).

1,8-Bis{(R_a)-2′-[2-(*N*,*N*-diisopropylcarbamoyloxy)-1,1′-binaphthyl]oxy}octane (R_a,R_a)-9. White foam, 87%; mp 61–63 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 30 °C) +69 (found: C, 79.3; H, 7.6; N, 2.9. $C_{62}H_{68}N_2O_6$ requires C, 79.5; H, 7.3; N, 3.0%); ν_{max} (KBr disc)/cm^{-1} 3060 w (Ar C–H), 2980 w and 2935 (alkyl C–H), 1720 vs (C=O), 1625, 1595, 1510, 1470, 1430, 1310 s, 1225 s, 1150, 1040, 1005, 805, 750; δ_H (400 MHz; $CDCl_3$) 0.52–0.60 [6 H, br m, $CH(CH_3)_2$], 0.73 (4 H, br s with further coupling, $OCH_2CH_2CH_2CH_2$), 0.89 [3 H, apparent br s, $CH(CH_3)CH_3$], 1.02 [3 H, apparent br s, $CH(CH_3)CH_3$], 1.29–1.35 (2 H, br m, $OCH_2CH_2CH_2CH_2$), 3.48 (2 H, br s, CH), 3.87 (2 H, t, *J* 6.3, $OCH_2CH_2CH_2CH_2$), 7.15–7.33 (6 H, m, Ar), 7.36 (1 H, d, *J* 9.0, 3 or 3′-H), 7.51 (1 H, d, *J* 8.8, 3 or 3′-H), 7.80 (1 H, d, *J* 8.0, 5 or 5′-H), 7.81 (1 H, d, *J* 8.3, 5 or 5′-H), 7.87 (1 H, d, *J* 8.8, 4 or 4′-H), 7.90 (1 H, d, *J* 9.0, 4 or 4′-H); δ_C (100.4 MHz; $CDCl_3$) 20.3 (4 C), 25.3, 28.7, 29.2, 45.8, 46.1, 69.6, 115.4, 119.6, 122.9, 123.5, 124.8, 125.0, 125.8, 125.9, 126.0, 126.3, 127.4, 127.9, 128.3, 129.2, 129.4, 131.3, 133.8, 134.0, 147.4, 152.5, 154.5; *m*/*z* (LSIMS) 959 (MNa^+, 5%), 937 (MH^+, 13) [found (HRMS) MH^+ 937.5209. $C_{62}H_{69}N_2O_6$ requires 937.5155].

General procedure for the preparation of bis{2′-[3-(*N*,*N*-dialkylcarbamoyl)-2-hydroxy-1,1′-binaphthyl]oxy}alkanes 10–13

A solution of Bu^{s}Li in hexanes (1.3 M; 3.0 ml, 3.9 mmol) was added dropwise over 8 min to a stirred solution of **6**–**9** (1.76 mmol) and TMEDA (524 µl, 3.52 mmol) in dry THF (15 ml) at −78 °C under an inert atmosphere. The reaction was allowed to warm slowly to ambient temperature over 16 h and worked-up by quenching with saturated $NH_4Cl_{(aq)}$, removing the volatiles with high vacuum, extracting into DCM and drying over $MgSO_4$. Removal of solvent gave the impure products as yellow foams that were purified by column chromatography (ethyl acetate–light petroleum).

1,6-Bis{(S_a)-2′-[3-(*N*,*N*-diethylcarbomyl)-2-hydroxy-1,1′-binaphthyl]oxy}hexane (S_a,S_a)-10. Yellow foam, 82%; mp 96–99 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 30 °C) −50 (found: C, 79.3; H, 6.8; N, 3.3. $C_{56}H_{56}N_2O_6$ requires C, 78.85; H, 6.6; N, 3.3%); ν_{max} (KBr disc)/cm^{-1} 3500–2200 vbr (O–H), 3060 w (Ar C–H), 2940 (alkyl C–H), 1635 s (C=O), 1595, 1510, 1465, 1435, 1330, 1265, 1240, 1145, 1085, 815, 750; δ_H (400 MHz; $CDCl_3$) 0.59 (2 H, apparent br s with unresolved splitting, $OCH_2CH_2CH_2$), 1.09–1.20 (2 H, m, $OCH_2CH_2CH_2$), 1.21 (6 H, t, *J* 7.1, CH_3), 3.49 [4 H, q, *J* 7.1, $N(CH_2CH_3)_2$], 3.70–3.76 (1 H, m, $OCHHCH_2CH_2$), 3.84–3.89 (1 H, $OCHHCH_2CH_2$), 7.01 (1 H, d, *J* 8.3, 8 or 8′-H), 7.14 (1 H, ddd, *J* 8.3, 7.0, 1.4, Ar), 7.17–7.27 (3 H, m, Ar), 7.33 (1 H, ddd, *J* 8.1, 6.7, 1.4, Ar), 7.37–7.39 (2 H,

m, Ar and OH), 7.70 (1 H, d with further unresolved splitting, *J* 7.8, 5 or 5′-H), 7.81 (1 H, s, 4-H), 7.87 (1 H, d, *J* 8.0, 5 or 5′-H), 7.97 (1 H, d, $J_{4',3'}$ 9.0, 4′-H); δ_C (100.4 MHz; $CDCl_3$) 13.5 (2 C), 24.9, 29.0, 41.9 br (2 C), 69.3, 115.5, 117.5, 117.7, 123.4, 123.7, 123.9, 125.0 (2 C), 126.8, 127.2, 127.3, 127.6, 128.1, 128.4, 129.4, 130.2, 133.9, 134.7, 149.8, 154.9, 170.0; *m*/*z* (LSIMS) 875 (MNa^+, 25%), 853 (MH^+, 100), 707 (48) [found (HRMS) MH^+ 853.4239. $C_{56}H_{56}N_2O_6$ requires 853.4216].

1,6-Bis{(*R*$_a$)-2′-[2-hydroxy-3-(*N*,*N*-diisopropylcarbamoyl)-1,1′-binaphthyl]oxy}hexane (*R*$_a$,*R*$_a$)-11. Pale yellow foam, 57%; mp 118–120 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 29 °C) +52; ν_{max} (KBr disc)/cm^{-1} 3700–2800 vbr s (O–H), 3060 w (Ar C–H), 2965 and 2935 (alkyl C–H), 1625 vs (C=O), 1595, 1505, 1460, 1375, 1345 s, 1265, 1245, 1210, 1150, 810, 750; δ_H (400 MHz; $CDCl_3$) 0.60 (2 H, s with unresolved splitting, $OCH_2CH_2CH_2$), 1.05–1.18 (2 H, m, $OCH_2CH_2CH_2$), 1.36 (12 H, apparent br s, CH_3), 3.67–3.74 (1 H, m, $OCHCH_2CH_2$), 3.81–3.87 (3 H, m, 2 × CH + $OCHCH_2CH_2$), 6.60 (1 H, s, OH), 7.01 (1 H, d with further unresolved splitting, *J* 8.3, 8 or 8′-H), 7.14 (1 H, ddd, *J* 8.3, 6.7, 1.6, Ar), 7.17–7.27 (3 H, m, Ar), 7.34 (1 H, ddd, *J* 8.1, 6.7, 1.4, Ar), 7.38 (1 H, d, $J_{3',4'}$ 8.9, 3′-H), 7.69 (1 H, d with further unresolved splitting, *J* 7.9, 5 or 5′-H), 7.73 (1 H, s, 4-H), 7.87 (1 H, d, *J* 8.0, 5 or 5′-H), 7.98 (1 H, d, $J_{4',3'}$ 8.9, 4′-H); δ_C (100.4 MHz; $CDCl_3$) 20.7 (2 C), 20.8 (2 C), 24.9, 29.0, 49 vbr (2 C), 69.3, 115.5, 117.0, 117.2, 123.6, 123.9, 124.9, 126.0, 126.3, 126.9 (2 C), 128.0, 128.3, 129.4, 130.4, 133.8, 134.1, 149.1, 155.1, 169.2; *m*/*z* (LSIMS) 931 (MNa^+, 5%), 909 (MH^+, 19), 707 (27) [found (HRMS) MH^+ 909.4862. $C_{60}H_{65}N_2O_6$ requires 909.4843].

1,8-Bis{(*S*$_a$)-2′-[3-(*N*,*N*-diethylcarbamoyl)-2-hydroxy-1,1′-binaphthyl]oxy}octane (*S*$_a$,*S*$_a$)-12. Yellow foam, 53%; mp 92–95 °C; $[\alpha]_D$ (*c* 2.0 in $CHCl_3$, 30 °C) −42 (found: C, 78.75; H, 7.0; N, 3.2. $C_{58}H_{60}N_2O_6$ requires C, 79.1; H, 6.9; N, 3.2%); ν_{max} (KBr disc)/cm^{-1} 3600–2400 vbr (O–H), 3060 w (Ar C–H), 2940 (alkyl C–H), 1635 vs (C=O), 1595, 1505, 1460 s, 1435, 1335, 1215 s, 1150, 1090, 815, 750; δ_H (400 MHz; $CDCl_3$) 0.75 (4 H, m, $OCH_2CH_2CH_2CH_2$), 1.24 (6 H, t, *J* 6.8, CH_3), 1.30–1.36 (2 H, m, $OCH_2CH_2CH_2CH_2$), 3.53 [4 H, q, *J* 6.8, $N(CH_2CH_3)_2$], 3.85–3.91 (1 H, m, $CHCH_2CH_2CH_2CH_2$), 3.95–4.01 (1 H, m, $CHCH_2CH_2CH_2$), 7.05 (1 H, d, *J* 8.3, 8 or 8′-H), 7.15–7.27 (4 H, m, OH + Ar), 7.34 (1 H, t with further unresolved splitting, *J* 6.9, Ar), 7.43 (1 H, d, $J_{3',4'}$ 9.0, 3′-H), 7.75 (1 H, d, *J* 8.0, 5 or 5′-H), 7.86 (1 H, s, 4-H), 7.87 (1 H, d, *J* 8.0, 5 or 5′-H), 7.98 (1 H, d, *J* 9.0, 4′-H); δ_C (100.4 MHz; $CDCl_3$) 13.5 (2 C), 25.3, 28.7, 29.1, 42 vbr (2 C), 69.6, 115.5, 117.6, 117.7, 123.3, 123.6, 123.9, 125.0 (2 C), 126.8, 127.2, 127.3, 127.6, 128.1, 128.4, 129.4, 130.3, 133.9, 134.7, 149.9, 155.0, 170.1; *m*/*z* (LSIMS) 903 (MNa^+, 28%), 881 (MH^+, 100), 735 (29) [found (HRMS) 882.3461. $C_{58}H_{60}N_2O_6$ requires 880.4451].

1,8-Bis{(*R*$_a$)-2′-[2-hydroxy-3-(*N*,*N*-diisopropylcarbamoyl)-1,1′-binaphthyl]oxy}octane (*R*$_a$,*R*$_a$)-13. Pale yellow foam, 88%; mp 114–118 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 30 °C) +43 (found: C, 79.4; H, 7.6; N, 2.8. $C_{62}H_{68}N_2O_6$ requires C, 79.5; H, 7.3; N, 3.0%); ν_{max} (KBr disc)/cm^{-1} 3600–2800 vbr (O–H), 3060 w (Ar C–H), 2930 (alkyl C–H), 1635 s (C=O), 1595, 1510, 1460 s, 1345 s, 1270, 1240, 1210, 1150, 1050, 810, 750; δ_H (400 MHz; $CDCl_3$) 0.70–0.77 (4 H, m, $OCH_2CH_2CH_2CH_2$), 1.30–1.40 (14 H, br, 2 × $CH(CH_3)_2$ + $OCH_2CH_2CH_2CH_2$), 3.84–3.99 (4 H, m, CH + $OCH_2CH_2CH_2CH_2$), 6.60 (1 H, s, OH), 7.05 (1 H, d, *J* 8.5, 8 or 8′-H), 7.14–7.27 (4 H, m, Ar), 7.34 (1 H, ddd, *J* 8.0, 6.6, 1.4, Ar), 7.42 (1 H, d, $J_{3',4'}$ 9.1, 3′-H), 7.74–7.76 (2 H, m, 4 and 5 or 5′-H), 7.87 (1 H, d, *J* 8.0, 5 or 5′-H), 7.99 (1 H, d, $J_{4',3'}$ 9.1, 4′-H); δ_C (100.4 MHz; $CDCl_3$) 20.8 (2 C), 21.0 (2 C), 25.3, 28.8, 29.2, 49 vbr (2 C), 69.6, 115.6, 117.1, 117.3, 123.6, 124.0, 125.0 (2 C), 125.9, 126.3, 126.9 (2 C), 128.0, 128.1, 128.3, 129.4, 130.5, 133.9, 134.2, 149.2, 155.2, 169.3; *m*/*z* (LSIMS) 959 (MNa^+, 26%), 937 (MH^+, 100), 735 (90) [found (HRMS) M^+ 936.5123. $C_{62}H_{68}N_2O_6$ requires 936.5774].

1-{(*R*$_a$)-2′-[2-(*N*,*N*-Diisopropylcarbamoyloxy)-1,1′-binaphthyl]oxy}-6-iodohexane (*R*$_a$)-14. By-product isolated as colourless oil from reactions of (*R*$_a$)-**5** with 1,6-diiodohexane in the presence of K_2CO_3 under reflux in acetone. 52%; $[\alpha]_D$ (*c* 2.5 in $CHCl_3$, 36 °C) +64; ν_{max} ($CHCl_3$ solution)/cm^{-1} 3061w (Ar C–H), 2935 m and 2872 m (alkyl C–H), 1709 s (C=O), 1622, 1592, 1459, 1369, 1314, 1146, 1082, 1044, 1005, 906; δ_H (400 MHz; $CDCl_3$) 0.56 [6 H, apparent br s, $CH(CH_3)CH_3$], 0.79–1.07 [10 H, m, $CH(CH_3)CH_3$ and $OCH_2CH_2CH_2CH_2CH_2CH_2I$], 1.34–1.53 (4 H, m, $OCH_2CH_2CH_2CH_2CH_2CH_2I$), 2.93 (2 H, t, *J* 7.3, CH_2I), 3.48 (2 H, apparent br s, CH), 3.87–3.94 (2 H, m, OCH_2), 7.19–7.31 (5 H, m, Ar), 7.35 (1 H, d, *J* 9.0, 3 or 3′-H), 7.41 (1 H, ddd, *J* 8.1, 6.0, 1.9, Ar), 7.55 (1 H, d, *J* 8.9, 3 or 3′-H), 7.79 (1 H, d, *J* 8.0, 5 or 5′-H), 7.89 (1 H, d, *J* 8.8, 4 or 4′-H), 7.91 (1 H, d, *J* 8.2, 5 or 5′-H), 7.95 (1 H, d, *J* 8.8, 4 or 4′-H); δ_C (100.6 MHz; $CDCl_3$) 7.2, 20.3 (4 C), 24.6, 29.1, 29.9, 33.4, 45.9, 46.2, 69.6, 115.6, 119.8, 123.0, 123.7, 125.0, 125.1, 125.9, 126.0, 126.1, 126.5, 127.6, 128.0, 128.4, 129.3, 129.6, 131.4, 133.9, 134.1, 147.5, 152.6, 154.5; *m*/*z* (EI) 623 (M^+, 4%), 495 (100, M − HI) [found (HRMS, FAB) M 623.1898. $C_{33}H_{38}INO_3$ requires 623.1896].

1-{(*R*$_a$)-2′-[2-(*N*,*N*-Diisopropylcarbamoyloxy)-1,1′-binaphthyl]oxy}-6-{(*R*$_a$)-2′-[2-hydroxy-3-(*N*,*N*-diisopropylcarbamoyl)-1,1′-binaphthyl]oxy}hexane (*R*$_a$,*R*$_a$)-15. By-product isolated as a pale yellow foam from the preparation of (*R*$_a$,*R*$_a$)-**10**, 29%; mp 87–90 °C; $[\alpha]_D$ (*c* 5.0 in $CHCl_3$, 30 °C) +56; ν_{max} (KBr disc)/cm^{-1} 3600–2800 vbr (O–H), 3060 (Ar C–H), 2970 and 2940 (alkyl C–H), 1710 s (C=O), 1630 (C=O), 1595, 1510, 1465, 1430, 1340, 1310, 1270, 1210 s, 1150, 1045, 805, 750; δ_H (400 MHz; $CDCl_3$) 0.50–0.60 [10 H, m, $CH_2CH_2CH_2CH_2CH_2CH_2$ and 2–OC(O)-$NCH(CH_3)_2$], 0.87 [3 H, apparent br s with unresolved coupling, 2–OC(O)$NCH(CH_3)CH_3$], 0.97–1.16 [7 H, m, CH_2-$CH_2CH_2CH_2CH_2CH_2$, 2–OC(O)$NCH(CH_3)CH_3$], 1.37 [12 H, apparent br s with unresolved coupling, 3–C(O)N{CH-$(CH_3)_2$}$_2$], 3.46 [2 H, br s, 2–OC(O)N{$CH(CH_3)_2$}$_2$], 3.68–3.78 (3 H, m, $CHCH_2CH_2CH_2CH_2CH_2$), 3.81–3.87 [3 H, m, $CHCH_2CH_2$ and 3–C(O)N{$CH(CH_3)_2$}$_2$], 6.57 (1 H, s, OH), 6.97 (1 H, d with further unresolved coupling, *J* 8.6, Ar), 7.08 (1 H, ddd, 8.2, 6.9, *J* 1.2, Ar), 7.14–7.29 (9 H, m, Ar), 7.31 (1 H, d, *J* 9.0, Ar), 7.35 (1 H, ddd, *J* 8.0, 6.7, 1.4, Ar), 7.39 (1 H, d, *J* 9.2, Ar), 7.48 (1 H, d, *J* 8.8, Ar), 7.69–7.74 (3 H, m, Ar), 7.79 (1 H, d, *J* 8.8, Ar), 7.79 (1 H, d, *J* 8.1, Ar), 7.88 (1 H, d, *J* 8.0, Ar), 7.89 (1 H, d, *J* 9.0, Ar), 8.00 (1 H, d, *J* 9.0, Ar) (the 2- and 3-locants refer to the carbamoyloxy and carbamoyl binaphthyl substituents respectively); δ_C (67.8 MHz; $CDCl_3$) 20.3 (2 C), 20.8 (4 C), 21.1 (2 C), 24.9, 25.0, 29.0, 29.1, 45.8, 46.1, 48 br (2 C), 69.2, 69.4, 115.4, 115.5, 117.0, 117.2, 119.5, 122.9, 123.6, 123.7, 124.0, 124.9, 125.0, 125.1, 125.8, 125.9, 126.1, 126.3, 126.4, 127.0, 127.5, 127.9, 128.0, 128.1, 128.3, 129.2, 129.4, 130.5, 131.3, 133.8, 133.9, 134.0, 134.2, 147.5, 149.1, 152.6, 154.4, 155.1, 169.4; *m*/*z* (LSIMS) 931 (MNa^+, 39%), 909 (MH^+, 100), 781 (9), 680 (7) [found (HRMS) MH^+ 909.4910. $C_{60}H_{65}N_2O_6$ requires 909.4843].

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