

# Enantiopure 3-amido or 3,3'-bisamido substituted 1,1'-bi-2-naphthols by anionic Fries rearrangements

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Mono- or di-carbamates of 1,1'-bi-2-naphthol ortholithiate with  $\text{Bu}^t\text{Li}$ -TMEDA. The resulting anions may either be captured by MeI or allowed to undergo anionic Fries rearrangement. Thus generalised two-step routes to mono- and di-(3-alkyl) or -(3-amido) substituted 2,2'-binaphthols is demonstrated.

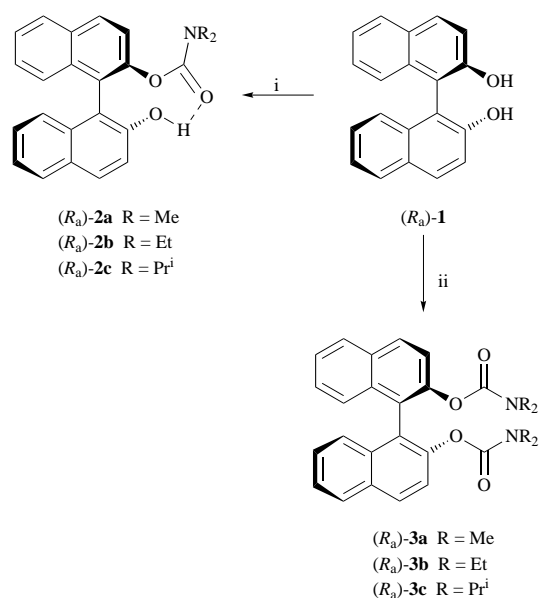
## Introduction

Given the popularity of 1,1'-bi-2-naphthol (BINOL) **1** as a chiral auxiliary in both stoichiometric and catalytic reactions, versatile routes for rapid variation of the 3- and 3'-positions of **1** are desirable.<sup>1,2</sup> These *ortho* sites reside in close proximity to the reactive centres in many asymmetric syntheses using **1**. Changing from an H-atom to a larger functional group can therefore have profound effects on the stereoselectivity of reactions employing 1,1'-bi-2-naphthol **1**.<sup>3-5</sup> In connection with our studies of reactions catalysed by complexes of 1,1'-bi-2-naphthol we had need of simple, *efficient* preparations of BINOL ligands bearing either alkyl or amido functions *ortho* to the naphtholic OH group. While several directed *ortho* metalation procedures are available for the preparation of 3,3'-dialkyl BINOL derivatives<sup>6</sup> (especially the dimethyl compound) only one recent publication by Katsuki and co-workers<sup>7</sup> addresses the preparation of the  $C_2$  symmetrical 3,3'-diamido ligands by multistep synthesis. However, none of these routes were applicable to the synthesis of the  $C_1$  3-amido BINOL ligands we were most interested in.

## Results and discussion

The general reaction of dialkylcarbamoyl chlorides (one equivalent) with 1,1'-bi-2-naphthol **1** under appropriate conditions is entirely chemoselective. Even in the presence of excess electrophile the 4-(dimethylamino)pyridine (DMAP)- $\text{NEt}_3$  promoted reaction yields only the mono acylated species **2a-c** (Scheme 1). We postulate that this high chemoselectivity is due to hydrogen bonding between the naphthol and the carbamate carbonyl moiety effectively raising the  $pK_a$  of the naphtholic OH thus preventing further reaction with  $\text{R}_2\text{NC(O)Cl}$ . Disubstitution is best achieved by alkylation of the sodium dianion of **1** in DMF, this reaction is also entirely chemoselective (Scheme 1), no starting material recovery or monoacylation occurs. While the monocarbamates **2** are all crystalline materials the ( $R_a$ )-dicarbamates **3b-c** are much less tractable, often forming oils. [Interestingly, the racemates ( $\pm$ )-**3** are much more crystalline; presumably they belong to different crystal space groups.] The tendency of compounds **3** to form oils leads to the requirement for their very clean formation. This is achieved with the  $\text{NaH}$ -DMF conditions and the crude products may be used directly.

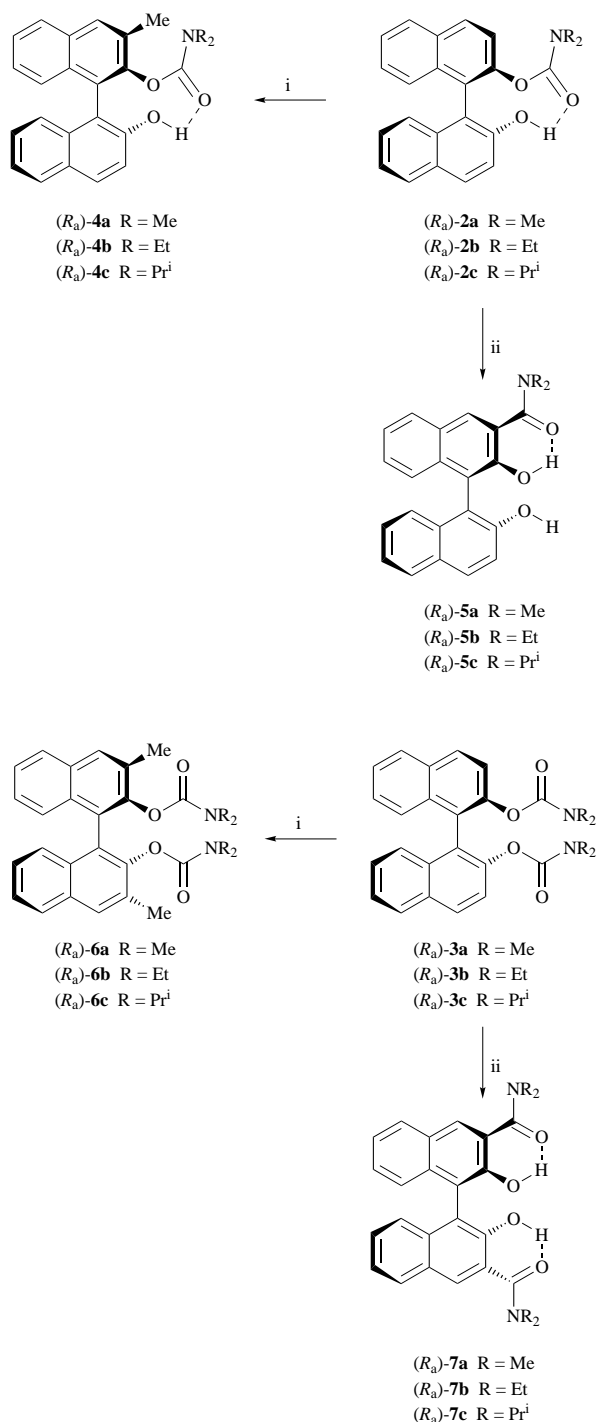
Compounds **2** cleanly lithiate using 2 equiv. of  $\text{Bu}^t\text{Li}$ -TMEDA at  $-80^\circ\text{C}$  ( $-100^\circ\text{C}$  for **2a**). The resulting anion may be intercepted with MeI, for example in the formation of **4a-c** (Scheme 2). As expected the 3-methyl isopropylcarbamate **4c** is resistant to deprotection. Only intractable mixtures (containing some substituted BINOLs) result from use of  $\text{LiAlH}_4$  (20-fold excess,  $80^\circ\text{C}$ ),  $\text{LiBHET}_3$  (7.8-fold excess) or  $\text{KOH}$  (100-fold excess). Problems in the deprotection of aryl diisopropylcarbamates have been noted before.<sup>8</sup> The ethyl derivative **4b** is



Scheme 1 Reagents and conditions: i,  $\text{R}_2\text{NC(O)Cl}$ ,  $\text{NEt}_3$ , DMAP (cat.); ii,  $\text{R}_2\text{NC(O)Cl}$ ,  $\text{NaH}$ , DMF

converted into the free 3-methyl-BINOL with  $\text{LiAlH}_4$  and can conveniently be achieved without isolation of **4b** in a one-pot conversion of **2b** to ( $R_a$ )-3-methyl-BINOL in 46% yield. If the mono anions resulting from **2** are allowed to warm to room temperature then anionic Fries rearrangement takes place and the 3-amino species **5** are formed in fair to good yield (Scheme 2). The only by-product that could be isolated from these reactions were small amounts of the 3- $\text{Bu}^t\text{C(O)}$  derivative, presumably derived from the slight excess of  $\text{Bu}^t\text{Li}$  used in these reactions. This impurity could be removed by flash chromatography. Purification is aided by the high crystallinity of ( $R_a$ )-**4**. No other clean lithiation procedures are available for the synthesis of  $C_1$  3-substituted BINOL compounds. Snieckus and co-workers briefly reported that bisMOM protected **1** can be metallated with  $\text{Bu}^t\text{Li}$  in THF, however, this procedure results in a material which is apparently appreciably contaminated with the dilithio species leading to product mixtures requiring extensive separation on work-up.<sup>6</sup>

The dicarbamates **3** smoothly lithiate using published procedures ( $\text{Bu}^t\text{Li}$ -TMEDA) as demonstrated by the isolation of the dimethylated compounds **6a-c** in good yield.<sup>6</sup> While **6c** is inert to deprotection under all conditions tried, reduction of **6b** is achieved by  $\text{LiAlH}_4$  to fashion 3,3'-dimethyl-BINOL in good yield (73%). Again, this transformation could be carried out in a one pot manner in high efficiency. If the dianions resulting from **3** are allowed to warm to room temperature smooth anionic Fries rearrangement takes place and the diamido



**Scheme 2** Reagents and conditions: i, Bu<sup>t</sup>Li-TMEDA, -80 °C (-100 °C for **2a** and **3a**) then MeI; ii, Bu<sup>t</sup>Li-TMEDA, -80 °C (-100 °C for **2a** and **3a**) then allowed to come to room temp. over 16 h

derivatives **7b-c** are formed in fair yield. The product of the reaction with **3a**, however, is contaminated with significant amounts of a by-product. Spectroscopic data of this material indicate that only one of the carbamate groups has undergone rearrangement. Recently, Katsuki showed that the ligands **7** are useful chiral auxiliaries in Simmons-Smith cyclopropanation reactions and in the catalytic addition of ZnEt<sub>2</sub> to aromatic aldehydes.<sup>7</sup> Several steps were required to prepare the ligands for this chemistry compared with just two in the present case. For example, the published preparation of **7c** has an overall yield of 35% compared to 80% by the present method. Strangely to our knowledge no anionic Fries rearrangements have previously been reported for carbamates of 1,1'-bi-2-naphthol **1** although it is interesting to note that the equivalent chemistry is known in phenolic systems.<sup>9,10</sup>

In conclusion a highly effective simple synthesis of both existing and new ligand types are available by this methodology. Use of these ligands in asymmetric catalysis is of high current interest and is being pursued both in our own and other laboratories.

## 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, while DMF, dichloromethane and TMEDA were dried over 4 Å molecular sieves. Light petroleum refers to the fraction boiling at 40–60 °C. All *N,N*-dialkylcarbamoyl chlorides were used as supplied. Specific rotations were measured using an Optical Activity AA-10 automatic polarimeter at ambient conditions and are given in 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup>; *c* is in g 100 cm<sup>-3</sup> of solvent. Column chromatography and TLC analyses were performed on silica gel, Rhône Poulenc Sorbsil and Merck Kieselgel 60 F<sub>254+366</sub> respectively. Infrared spectra were recorded using a Perkin-Elmer 983 G infrared spectrophotometer and a Perkin-Elmer 882 infrared spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a JEOL JNM-GX270 or JNM-LA400 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) machine (EPSRC Service, Swansea). Elemental analyses were performed using a Fisons Instruments EA 1108 CHN elemental analyser. The following compounds were obtained by literature procedures: (±)-1,1'-bi-2-naphthol **1**,<sup>11</sup> (*R<sub>a</sub>*)-1,1'-bi-2-naphthol (*R<sub>a</sub>*)-**1**.<sup>12</sup>

Difficulties were encountered in attaining complete combustion analyses of these compounds. The use of additives, such as V<sub>2</sub>O<sub>5</sub>, helped though did not always completely remove the problem. Additionally, all the compounds showed a remarkable tendency to retain small amounts of crystallisation solvents. This effect has been noted for compounds **7** before.<sup>7</sup> High resolution mass spectrometry was therefore used to confirm the identity of these products.

### General procedure for the preparation of 2-(*N,N*-dialkylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl **2**

Solid *N,N*-dialkylcarbamoyl chloride (**TOXIC!**) (8.38 mmol) was added to a solution of BINOL **1** (2.00 g, 6.99 mmol), NEt<sub>3</sub> (1.1 cm<sup>3</sup>, 7.9 mmol) and DMAP (0.085 g, 0.7 mmol) in dichloromethane (DCM) (150 cm<sup>3</sup>) under an inert atmosphere. The mixture was stirred at ambient temperature until complete by TLC then worked up by stirring with aqueous NH<sub>4</sub>Cl, separating the layers, and washing the organic layer with aqueous NH<sub>3</sub> (to remove any residual *N,N*-dialkylcarbamoyl chloride), 2 × 2 M HCl, water and brine. After drying and removal of the solvent the crude products were obtained in quantitative yield and could be used as such.

**(*R<sub>a</sub>*)-2-(*N,N*-Dimethylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl **2a**.** 87% Recrystallised, mp 204–205 °C (from MeOH-H<sub>2</sub>O); [*α*]<sub>D</sub> (*c* 5.0 in CHCl<sub>3</sub>, 25 °C) 154 (Found: C, 77.0; H, 5.4; N, 3.9. C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub> requires C, 77.3; H, 5.4; N, 3.9%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3320br (OH), 3060w (Ar CH), 2940w (MeCH), 1700vs (C=O), 1395, 1225s, 1180s, 815, 750; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.41 (3 H, s, Me), 2.72 (3 H, s, Me), 5.92 (1 H, s, OH), 7.05 (1 H, d, *J* 8.6, Ar), 7.21–7.36 (5 H, m, Ar), 7.44–7.49 (2 H, m, Ar), 7.84 (1 H, d, *J* 8.0, Ar), 7.89 (1 H, d, *J* 8.8, Ar), 7.95 (1 H, d, *J* 8.0, Ar), 8.04 (1 H, d, *J* 8.8, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 35.90, 36.54, 115.12, 119.06, 122.12, 123.42, 123.71, 124.71, 125.66, 125.95, 126.47, 127.22, 127.87, 128.19, 129.03, 130.05, 130.49, 132.01, 133.53, 133.74, 148.79, 152.25, 155.64; *m/z* (EI) 357 (M<sup>+</sup>, 9%), 268 (4), 227 (4), 73 (100).

**(R<sub>a</sub>)-2-(N,N-Diethylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl 2b.** 73% Recrystallised, mp 141–142 °C (from MeOH–H<sub>2</sub>O); [α]<sub>D</sub> (c 5.1 in CHCl<sub>3</sub>, 27 °C) 141 (Found: C, 77.8; H, 6.05; N, 3.7. C<sub>25</sub>H<sub>23</sub>NO<sub>3</sub> requires C, 77.9; H, 6.0; N, 3.6%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3350br (OH), 3060w (Ar CH), 2970 and 2930w (Et CH), 1680vs (C=O), 1420, 1270, 1210s, 1160, 980, 750; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.46 (3 H, t, *J* 7.1, Et), 0.92 (3 H, t, *J* 7.1, Et), 2.75 (1 H, dq, *J* 14.1, 7.4, Et), 2.94 (1 H, dq, *J* 14.1, 7.4, Et), 3.05 (1 H, dq, *J* 14.1, 7.4, Et), 3.19 (1 H, dq, *J* 14.1, 7.4, Et), 5.98 (1 H, s, OH), 7.04 (1 H, dd, *J* 8.3, 1.2, Ar), 7.20–7.24 (2 H, m, Ar), 7.28–7.35 (3 H, m, Ar), 7.44–7.52 (2 H, m, Ar), 7.82 (1 H, d, *J* 7.6, Ar), 7.87 (1 H, d, *J* 8.8, Ar), 7.95 (1 H, d, *J* 8.3, Ar), 8.04 (1 H, d, *J* 8.8, Ar); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 13.00, 13.06, 41.71, 42.33, 115.56, 119.37, 122.15, 123.43, 124.04, 124.65, 125.67, 125.91, 126.48, 127.20, 127.87, 128.19, 129.16, 130.02, 130.44, 132.02, 133.62, 133.83, 148.75, 152.32, 155.05; *m/z* (EI) 385 (M<sup>+</sup>, 22%), 268 (8), 239 (10), 226 (10), 100 (100).

**(R<sub>a</sub>)-2-(N,N-Diisopropylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl 2c.** 61% Recrystallised, mp 190–191 °C (from MeOH); [α]<sub>D</sub> (c 5.0 in CHCl<sub>3</sub>, 23 °C) 130 (Found: C, 78.3; H, 6.7; N, 3.3. C<sub>27</sub>H<sub>27</sub>NO<sub>3</sub> requires C, 78.4; H, 6.5; N, 3.4%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3330br s (OH), 3060w (Ar CH), 2980 and 2930w (Pr<sup>i</sup> CH), 1680vs (C=O), 1430, 1315s, 1215s, 1150, 1040, 1010, 820, 750; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.59 (6 H, m, Pr<sup>i</sup>), 1.06 (6 H, m, Pr<sup>i</sup>), 3.47–3.71 (2 H, m, Pr<sup>i</sup>), 6.09 (1 H, s, OH), 7.03 (1 H, d, *J* 7.6, Ar), 7.18–7.35 (5 H, m, Ar), 7.43–7.50 (2 H, m, Ar), 7.81 (1 H, d, *J* 8.1, Ar), 7.86 (1 H, d, *J* 9.0, Ar), 7.95 (1 H, d, *J* 8.3, Ar), 8.05 (1 H, d, *J* 8.8, Ar); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20, 47, 116.08, 119.67, 122.26, 123.41, 124.38, 124.69, 125.67, 125.84, 126.48, 127.13, 127.83, 128.15, 129.21, 129.95, 130.36, 132.00, 133.69, 133.98, 148.66, 152.43, 154.44; *m/z* (EI) 413 (M<sup>+</sup>, 19%), 286 (100), 239 (30), 226 (20), 128 (66), 86 (43).

#### General procedure for the preparation of 2,2'-bis(N,N-dialkylcarbamoyloxy)-1,1'-binaphthyls 3

A solution of BINOL **1** (2.00 g, 6.99 mmol) in dry DMF (100 cm<sup>3</sup>) was added slowly to a stirred suspension of 60% NaH dispersion in mineral oil (0.70 g, 17.5 mmol) in dry DMF at 0 °C under an inert atmosphere, followed by a solution of the appropriate *N,N*-dialkylcarbamoyl chloride (**TOXIC!**) (17.4 mmol) in dry DMF. The mixture was heated to 70 °C for 16 h then allowed to cool. The reaction was worked up by stirring with 10% aqueous KOH, extracting into DCM, washing the organic layer with 5 × 2 M HCl, water and brine, drying the organic with MgSO<sub>4</sub>, and removing the solvent to give quantitative yields of **3** which could be used directly.

**(R<sub>a</sub>)-2,2'-Bis(N,N-dimethylcarbamoyloxy)-1,1'-binaphthyl 3a.** 85% Recrystallised, mp 100–101 °C (from ethyl acetate–light petroleum; [α]<sub>D</sub> (c 5.0 in CHCl<sub>3</sub>, 25 °C) 102 (Found: C, 73.2; H, 5.8; N, 6.5. C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> requires C, 72.9; H, 5.65; N, 6.5%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3060w (Ar CH), 2930w (Me CH), 1720vs (C=O), 1385, 1230s, 1160s, 810, 750; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.19 (6 H, s, Me), 2.67 (6 H, s, Me), 7.30 (4 H, d, *J* 3.7, Ar), 7.39–7.48 (2 H, m, Ar), 7.60 (2 H, d, *J* 9.0, Ar), 7.91 (2 H, d, *J* 8.1, Ar), 7.97 (2 H, d, *J* 9.0, Ar); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 35.60, 36.33, 122.60, 123.68, 125.30, 126.07, 126.43, 127.85, 128.91, 131.19, 133.38, 147.49; 154.16; *m/z* (EI) 428 (M<sup>+</sup>, 9%), 294 (11), 283 (10), 268 (12), 72 (100).

**(R<sub>a</sub>)-2,2'-Bis(N,N-diethylcarbamoyloxy)-1,1'-binaphthyl 3b.** mp 67–68 °C (from MeOH–H<sub>2</sub>O); [α]<sub>D</sub> (c 2.0 in CHCl<sub>3</sub>, 25 °C) 117 (Found: C, 74.6; H, 6.8; N, 5.8. C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub> requires C, 74.4; H, 6.7; N, 5.8%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3060w (Ar CH), 2980 and 2940w (Et CH), 1720s and 1700s (C=O), 1420, 1280, 1210s, 1160s, 985, 769; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.38 (6 H, t, *J* 6.8, Et), 0.84 (6 H, t, *J* 6.8, Et), 2.57–2.75 (4 H, m, Et), 2.94–3.03 (2 H, m, Et), 3.06–3.16 (2 H, m, Et), 7.27–7.34 (4 H, m, Ar), 7.39–7.44 (2 H, m, Ar), 7.59 (2 H, d, *J* 9.0, Ar), 7.89 (2 H, d, *J* 8.0, Ar), 7.94 (2 H, d, *J* 9.0, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 12.91, 41.25, 41.76, 122.51, 123.72, 125.71, 126.07, 126.36, 127.70, 128.79, 131.22, 133.43, 147.51, 153.35; *m/z* (EI)

484 (M<sup>+</sup>, 10%), 412 (38), 296 (84), 268 (42), 239 (40), 226 (30), 100 (100) [Found: (HRMS): M<sup>+</sup>, 484.2362. C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub> requires *M*, 484.2362]. Racemic **3b** has been reported briefly but no data was presented.<sup>6</sup>

**(R<sub>a</sub>)-2,2'-Bis(N,N-diisopropylcarbamoyloxy)-1,1'-binaphthyl 3c.** mp 59–60 °C; [α]<sub>D</sub> (c 5.1 in CHCl<sub>3</sub>, 26 °C) 125 (Found: C, 75.6; H, 7.7; N, 5.1. C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub> requires C, 75.5; H, 7.5; N, 5.2%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3050w (Ar CH), 2980 and 2930w (Pr<sup>i</sup> CH), 1710vs and 1695vs (C=O), 1420, 1310s, 1215, 1150, 1040, 1010, 745; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.55 (12 H, s, Pr<sup>i</sup>), 0.96–1.03 (12 H, m, Pr<sup>i</sup>), 3.42–3.55 (4 H, m, Pr<sup>i</sup>), 7.29 (2 H, d, *J* 7.1, Ar), 7.36–7.42 (4 H, m, Ar), 7.53 (2 H, d, *J* 8.8, Ar), 7.87 (2 H, d, *J* 8.1, Ar), 7.92 (2 H, d, *J* 8.8, Ar); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20.29, 45.91, 46.18, 123.03, 124.18, 125.15, 126.29, 126.36, 127.67, 128.69, 131.37, 133.60, 147.58, 152.57; *m/z* (EI) 540 (M<sup>+</sup>, 8%), 465 (5), 414 (27), 286 (76), 268 (20), 239 (18), 128 (92), 86 (100).

#### General conditions for lithiation of 2-(N,N-dialkylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyls **2** and subsequent reaction with MeI (leading to **4**) or anionic Fries rearrangement (leading to **5**)

A solution of Bu<sup>n</sup>Li in hexanes (1.3 M; 2.2 cm<sup>3</sup>) was added dropwise over 5 min to a stirred solution of 2-(*N,N*-dialkylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl **2** (1.30 mmol) and TMEDA (0.39 cm<sup>3</sup>, 2.6 mmol) in dry THF (10 cm<sup>3</sup>) at –80 °C (–100 °C for **2a**) under an inert atmosphere. This temperature was maintained for a further 10 min then the mixture was either treated with MeI (81 μl, 1.30 mmol) and allowed to warm slowly to –50 °C over 1 h (for **4**), or allowed to warm slowly to ambient temperature 16 h (for **5**). The mixture was then treated with aqueous NH<sub>4</sub>Cl, the product extracted into dichloromethane and isolated in the normal manner. Pure **4** and **5** were obtained by column chromatography (1–2% EtOH in DCM) and/or recrystallisation from MeOH–H<sub>2</sub>O.

**(R<sub>a</sub>)-3-Methyl-2-(N,N-dimethylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl 4a.** 56%, mp 190–191 °C (from dichloromethane–pentane); [α]<sub>D</sub> (c 2.0 in CHCl<sub>3</sub>, 28 °C) 183 (Found: C, 77.35; H, 5.7; N, 3.85. C<sub>24</sub>H<sub>21</sub>NO<sub>3</sub> requires C, 77.6; H, 5.7; N, 3.8%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3320br (OH), 3060w (Ar CH), 2950w and 2920w (CH), 1695vs (C=O), 1390s, 1220s, 1170s, 820, 755s; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.45 (3 H, s, Me), 2.47 (3 H, s, Me), 2.76 (3 H, s, Me), 6.16 (1 H, s, OH), 7.05 (1 H, d, *J* 8.6, Ar), 7.12 (1 H, d, *J* 8.8, Ar), 7.20–7.26 (2 H, m, Ar), 7.29–7.36 (2 H, m, Ar), 7.41–7.45 (1 H, m, Ar), 7.83–7.89 (4 H, m, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 17.08, 35.91, 36.58, 115.36, 119.28br, 123.38, 124.71br, 125.48, 125.94, 126.25, 126.36, 127.38, 127.79, 129.02, 129.88, 130.29, 132.18, 132.38, 133.78, 148.04, 155.5; *m/z* (EI) 371 (M<sup>+</sup>, 6%), 281 (17), 238 (17), 72 (100).

**(R<sub>a</sub>)-3-Methyl-2-(N,N-diethylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl 4b.** 35%, mp 165–167 °C (from dichloromethane–light petroleum); [α]<sub>D</sub> (c 2.0 in CHCl<sub>3</sub>, 25 °C) 147 (Found: C, 78.3; H, 6.5; N, 3.5. C<sub>26</sub>H<sub>25</sub>NO<sub>3</sub> requires C, 78.2; H, 6.3; N, 3.5%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3350br (OH), 3060w (Ar CH), 2980w, 2930w, 1685vs (C=O), 1280, 1170, 750; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.49 (3 H, s, Et), 0.94 (3 H, s, Et), 2.47 (3 H, s, Me), 2.71–2.79 (1 H, m, Et), 2.93–3.07 (2 H, m, Et), 3.18–3.28 (1 H, m, Et), 6.17 (1 H, s, OH), 7.03 (1 H, d, *J* 8.0, Ar), 7.14 (1 H, d, *J* 8.3, Ar), 7.19–7.34 (5 H, m, Ar), 7.43 (1 H, t, *J* 7.1, Ar), 7.80–7.87 (4 H, m, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 13.06, 17.13, 41.71, 42.39, 119.65, 123.33, 124.62, 125.50, 125.89, 126.18, 126.34, 127.36, 127.79, 129.10, 129.83, 130.15, 132.16, 132.38, 133.83, 148; *m/z* (EI) 399 (M<sup>+</sup>, 47%), 282 (11), 239 (14), 100 (100), 72 (54) [Found: (HRMS): M<sup>+</sup>, 399.1834. C<sub>26</sub>H<sub>25</sub>NO<sub>3</sub> requires *M*, 399.1834].

**(R<sub>a</sub>)-3-Methyl-2-(N,N-diisopropylcarbamoyloxy)-2'-hydroxy-1,1'-binaphthyl 4c.** 77%, mp 205–206 °C (from MeOH–H<sub>2</sub>O); [α]<sub>D</sub> (c 2.0 in CHCl<sub>3</sub>, 24 °C) 132 (Found: C, 77.9; H, 7.0; N, 3.2. C<sub>28</sub>H<sub>29</sub>NO<sub>3</sub> requires C, 78.7; H, 6.8; N, 3.3%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3400br (OH), 3060w (Ar CH), 2970w, 2930w, 1695vs

(C=O), 1325s, 1045, 745;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 0.51 (3 H, d,  $J$  6.3, Pr<sup>d</sup>), 0.71 (3 H, d,  $J$  6.1, Pr<sup>d</sup>), 1.07–1.09 (6 H, m, Pr<sup>d</sup>), 2.46 (3 H, s, Me), 3.50 (1 H, m, Pr<sup>d</sup>), 3.81 (1 H, m, Pr<sup>d</sup>), 6.26 (1 H, s, OH), 7.01 (1 H, d,  $J$  8.0, Ar), 7.13–7.34 (5 H, m, Ar), 7.42 (1 H, t, Ar), 7.80 (1 H, d,  $J$  8.0, Ar), 7.83–7.87 (3 H, m, Ar);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 17.23, 20.04, 20.11, 20.27, 20.55, 46.28, 46.82, 116.61, 119.85, 122.22, 123.30, 124.68, 125.53, 125.81, 126.12, 126.33, 127.33, 127.76, 129.15, 129.74, 130.02, 130.58, 132.12, 132.44, 134.10, 148.26, 152.44, 154.40;  $m/z$  (EI) 427 ( $\text{M}^+$ , 18%), 301 (32), 195 (42), 128 (36), 86 (100) [Found: (HRMS):  $\text{M}^+$ , 427.2148.  $\text{C}_{28}\text{H}_{29}\text{NO}_3$  requires  $M$ , 427.2148].

**( $R_a$ )-2,2'-Dihydroxy-3-( $N,N$ -dimethylcarbamoyl)-1,1'-binaphthyl 5a.** 49%, mp 262–264 °C (from  $\text{MeOH-H}_2\text{O}$ );  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in DMSO, 26 °C) 137;  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3520 (OH), 3200br (OH), 2940w (Me CH), 1615vs (C=O), 1345, 830, 755;  $\delta_{\text{H}}$ (400 MHz;  $[\text{D}_6]\text{DMSO}$ ;  $\text{Me}_4\text{Si}$ ) 2.96–3.01 (6 H, m, Me), 6.87 (1 H, d,  $J$  8.3, Ar), 6.92 (1 H, d,  $J$  8.3, Ar), 7.17–7.34 (5 H, m, Ar), 7.85–7.91 (4 H, m, Ar), 8.63 (1 H, br s, OH), 9.40 (1 H, br s, Ar);  $\delta_{\text{C}}$ (400 MHz;  $[\text{D}_6]\text{DMSO}$ ;  $\text{Me}_4\text{Si}$ ) 113.40, 116.57, 118.73, 122.41, 123.10, 123.92, 124.35, 126.16, 126.60, 126.98, 127.27, 127.69, 128.05, 128.21, 128.28, 129.46, 133.92, 134.21, 149.31, 153.80, 169.70;  $m/z$  (EI) 357 ( $\text{M}^+$ , 56%), 339 (52), 312 (30), 283 (84), 267 (100), 255 (73), 239 (82), 225 (84), 114 (77), 72 (38) [Found: (HRMS):  $\text{M}^+$ , 357.1365.  $\text{C}_{23}\text{H}_{19}\text{NO}_3$  requires  $M$ , 357.1365].

**( $R_a$ )-2,2'-Dihydroxy-3-( $N,N$ -diethylcarbamoyl)-1,1'-binaphthyl 5b.** 33%, mp 210 °C (decomp. from dichloromethane–light petroleum);  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in  $\text{CDCl}_3$ , 25 °C) 50;  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3520w (OH), 3160br (OH), 3060w (Ar CH), 2980w and 2940w (Et CH), 1595vs (C=O), 1430, 1345, 1285, 1210, 820, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.31 (6 H, t,  $J$  7.1, Et), 3.60 (4 H, q,  $J$  7.1, Et), 5.28 (1 H, s, OH), 7.12 (1 H, d,  $J$  8.3, Ar), 7.17 (1 H, d,  $J$  8.3, Ar), 7.28–7.41 (5 H, m, Ar), 7.88 (2 H, d,  $J$  8.1, Ar), 7.94 (1 H, d,  $J$  9.0, Ar), 8.00 (1 H, s, Ar), 8.08 (1 H, s, OH);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 13.44, 42.28br, 112.65, 114.00, 117.85, 117.92, 123.08, 123.61, 124.36, 124.58, 126.90, 126.94, 127.83, 128.35, 128.48, 128.84, 128.88, 128.91, 129.30, 130.72, 151.47, 152.07, 169.82;  $m/z$  (EI) 385 ( $\text{M}^+$ , 40%), 367 (42), 312 (52), 283 (49), 268 (100), 255 (46), 239 (61), 226 (62) [Found: (HRMS):  $\text{M}^+$ , 385.1678.  $\text{C}_{25}\text{H}_{23}\text{NO}_3$  requires  $M$ , 385.1678].

**( $R_a$ )-2,2'-Dihydroxy-3-( $N,N$ -diisopropylcarbamoyl)-1,1'-binaphthyl 5c.** 62%, mp 250–253 °C (from dichloromethane–light petroleum);  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in DMSO, 26 °C) 159 (Found: C, 78.7; H, 6.6; N, 3.4.  $\text{C}_{27}\text{H}_{27}\text{NO}_3$  requires C, 78.4; H, 6.6; N, 3.4%);  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3520w (OH), 3060w (Ar CH), 3000br (OH), 2970w (Pr<sup>i</sup> CH), 1590br s (C=O), 1350vs, 1210, 820, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.43 (12 H, s, Pr<sup>i</sup>), 3.92 (2 H, br s, Pr<sup>i</sup>), 5.22 (1 H, br s, OH), 7.12–7.20 (3 H, m, Ar and OH), 7.27–7.41 (5 H, m, Ar), 7.87–7.90 (3 H, m, Ar), 7.95 (1 H, d,  $J$  9.0, Ar);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 20.57, 20.86, 49br, 112.13, 113.49, 117.88, 123.71, 124.31, 124.54, 125.65, 127.05, 128.07, 128.20, 128.24, 128.38, 128.75, 129.36, 130.92, 133.35, 133.94, 150.84, 152.28, 169.04;  $m/z$  (EI) 413 ( $\text{M}^+$ , 29%), 312 (90), 283 (77), 268 (100), 255 (67), 239 (60), 226 (63).

**General conditions for lithiation of 2,2'-bis( $N,N$ -dialkylcarbamoyloxy)-1,1'-binaphthyls 3 and subsequent reaction with MeI (leading to 6) or anionic Fries rearrangement (leading to 7)**

A solution of  $\text{Bu}^i\text{Li}$  in hexanes (1.3 M; 1.8  $\text{cm}^3$ ) was added dropwise over 5 min to a stirred solution of 2,2'-bis( $N,N$ -dialkylcarbamoyloxy)-1,1'-binaphthyl 3 (1.03 mmol) and TMEDA (0.31  $\text{cm}^3$ , 2.1 mmol) in dry THF (10  $\text{cm}^3$ ) at  $-80$  °C ( $-100$  °C for 3a) under an inert atmosphere. This temperature was maintained for a further 10 min then the mixture was either treated with MeI (130  $\mu\text{l}$ , 2.1 mmol) and allowed to warm slowly to  $-50$  °C over 1 h (for 6), or (for 7) allowed to warm slowly to ambient temperature (16 h). The mixture was then treated with aqueous  $\text{NH}_4\text{Cl}$ , the product extracted into dichloromethane and isolated in the normal manner. Pure 6

and 7 were obtained by column chromatography (20–50% ethyl acetate in light petroleum).

**( $R_a$ )-3,3'-Dimethyl-2,2'-bis( $N,N$ -dimethylcarbamoyloxy)-1,1'-binaphthyl 6a.** 50%, mp 69–71 °C;  $[\alpha]_{\text{D}}^{20}$  ( $c$  1.5 in  $\text{CHCl}_3$ , 26 °C) 91 (Found: C, 73.4; H, 6.3; N, 6.0.  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_4$  requires C, 73.7; H, 6.2; N, 6.1%);  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3060w (Ar CH), 2940 (Me CH), 1725vs (C=O), 1390, 1240, 1170s, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 2.26 (6 H, br s, Me), 2.46–2.50 (12 H, m, Me), 7.19–7.25 (4 H, m, Ar), 7.35–7.39 (2 H, m, Ar), 7.79–7.81 (4 H, m, Ar);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 16.38, 34.61, 35.15, 124.05, 124.31, 124.35, 125.33, 125.81, 129.12, 131.28, 131.56, 132.13, 147.48, 153.58;  $m/z$  (EI) 456 ( $\text{M}^+$ , 1%), 309 (2), 295 (4), 252 (3), 239 (5), 72 (100) [Found: (HRMS):  $\text{M}^+$ , 456.2049.  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_4$  requires  $M$ , 456.2049].

**( $R_a$ )-3,3'-Dimethyl-2,2'-bis( $N,N$ -diethylcarbamoyloxy)-1,1'-binaphthyl 6b.** 30%, mp 144–145 °C (from  $\text{MeOH-H}_2\text{O}$ );  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in  $\text{CHCl}_3$ , 25 °C) 17 (Found: C, 75.2; H, 7.2; N, 5.45.  $\text{C}_{32}\text{H}_{36}\text{N}_2\text{O}_4$  requires C, 75.0; H, 7.1; N, 5.5%);  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3060w (Ar CH), 2980, 2930, 1710vs (C=O), 1410, 1280s, 1240, 1160s, 1100, 970, 760;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 0.53–0.80 (12 H, br m, Et), 2.44 (6 H, s, Me), 2.83–2.99 (8 H, br m, Et), 7.17–7.21 (4 H, m, Ar), 7.34–7.38 (2 H, m, Ar), 7.77–7.79 (4 H, m, Ar);  $\delta_{\text{C}}$ (270 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 12.67, 13.44, 17.32, 41.40, 41.80, 125.19, 125.30, 126.75, 129.13, 131.10br, 131.73, 132.31, 147.33, 152.79;  $m/z$  (EI) 512 ( $\text{M}^+$ , 1%), 100 (100), 82 (10), 72 (72). Racemic 6b has been reported briefly but no data was presented.<sup>6</sup>

**( $R_a$ )-3,3'-Dimethyl-2,2'-bis( $N,N$ -diisopropylcarbamoyloxy)-1,1'-binaphthyl 6c.** 35%, mp 80–83 °C (decomp.);  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in  $\text{CHCl}_3$ , 24 °C) 42 (Found: C, 76.3; H, 7.75; N, 4.53.  $\text{C}_{36}\text{H}_{44}\text{N}_2\text{O}_4$  requires C, 76.0; H, 7.8; N, 4.9%);  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  2970, 2925, 1720vs (C=O), 1315s, 1150, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 0.50–1.10 (24 H, br m, Pr<sup>i</sup>), 2.40 (6 H, s, Me), 3.30–3.80 (4 H, br m, Pr<sup>i</sup>), 7.15–7.35 (6 H, m, Ar), 7.74–7.77 (4 H, m, Ar);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 17.27, 20.14, 20.48, 45.75, 46.24, 125.15, 126.04, 126.54, 126.89, 127.15, 128.93, 131br, 131.77, 132.37, 147.29, 151.93;  $m/z$  (EI) 568 ( $\text{M}^+$ , 10%), 441 (47), 314 (100), 296 (49), 269 (42), 253 (54), 239 (82), 128 (33), 86 (100) [Found: (HRMS):  $\text{MH}^+$ , 569.3380.  $\text{C}_{36}\text{H}_{45}\text{N}_2\text{O}_4$  requires  $M$ , 569.3380].

**( $R_a$ )-2,2'-Dihydroxy-3,3'-bis( $N,N$ -dimethylcarbamoyl)-1,1'-binaphthyl 7a.** 25%, mp 171–174 °C;  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in  $\text{CHCl}_3$ , 24 °C) 71;  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3400br (OH), 2920, 1625vs (C=O), 1495s, 1390, 1130, 745;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 3.25 (12 H, s, Me), 7.16 (2 H, d,  $J$  8.4, Ar), 7.28–7.36 (4 H, m, Ar), 7.85 (2 H, d,  $J$  8.0, Ar), 7.99 (2 H, s, Ar), 8.80 (2 H, s, OH);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 38br, 116.39, 120.96, 124.10, 124.86, 127.33, 128.29, 128.85, 129.75, 134.88, 151.80, 171.08; MS (EI)  $m/z$  (EI) 428 ( $\text{M}^+$ , 15%), 383 (35), 338 (33), 295 (48), 72 (100) [Found: (HRMS):  $\text{MH}^+$ , 429.1814.  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_4$  requires  $M$ , 429.1814]. The physical and spectroscopic properties were identical to those reported by Katsuki *et al.*<sup>7</sup>

**( $R_a$ )-2,2'-Dihydroxy-3,3'-bis( $N,N$ -diethylcarbamoyl)-1,1'-binaphthyl 7b.** 42%, mp 185 °C (decomp.);  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.1 in  $\text{CHCl}_3$ , 25 °C) 54;  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3420br (OH), 3060w, 2980w, 1625vs (C=O), 1460, 1385, 1215, 1140, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.32 (12 H, t,  $J$  7.1, Et), 3.52–3.69 (8 H, m, Et), 7.16 (2 H, d,  $J$  8.3, Ar), 7.25–7.37 (4 H, m, Ar), 7.86 (2 H, d,  $J$  7.3, Ar), 7.95 (2 H, s, Ar), 8.25 (2 H, s, OH);  $\delta_{\text{C}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 13.46, 42.23br, 115.90, 122.51, 124.10, 124.78, 127.54, 128.04, 128.27, 128.77, 134.54, 151.14, 170.30;  $m/z$  (EI) 484 ( $\text{M}^+$ , 8%), 466 (10), 367 (12), 312 (42), 283 (31), 254 (64), 226 (83), 113 (30), 72 (100) [Found: (HRMS):  $\text{M}^+$ , 484.2362.  $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_4$  requires  $M$ , 484.2362]. The physical and spectroscopic properties were identical to those reported by Katsuki *et al.*<sup>7</sup>

**( $R_a$ )-2,2'-Dihydroxy-3,3'-bis( $N,N$ -diisopropylcarbamoyl)-1,1'-binaphthyl 7c.** 80%, mp 167–170 °C;  $[\alpha]_{\text{D}}^{20}$  ( $c$  2.0 in  $\text{CHCl}_3$ , 28 °C) 67;  $\nu_{\text{max}}$ (KBr disc)/ $\text{cm}^{-1}$  3420br w (OH), 3060w, 2970, 2940w, 1630br s (C=O), 1460, 1350vs, 1210, 750;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;

Me<sub>4</sub>Si) 1.42 (24 H, s, Pr<sup>d</sup>), 3.95 (4 H, br s, Pr<sup>d</sup>), 7.15 (2 H, d, *J* 8.3, Ar), 7.27–7.40 (6 H, m, Ar + OH), 7.84–7.87 (4 H, m, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20.98, 49.08br, 114.92, 124.17, 124.67, 125.27, 127.58, 127.82, 127.97, 128.65, 133.92, 150.58, 169.42; *m/z* (EI) 540 (M<sup>+</sup>, 83%), 498 (22), 413 (38), 398 (54), 353 (30), 339 (88), 313 (67), 286 (73), 255 (100), 239 (40), 226 (70) [Found: (HRMS): M<sup>+</sup>, 540.2990. C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub> requires *M*, 540.2988]. The physical and spectroscopic properties were identical to those reported by Katsuki *et al.*<sup>7</sup>

#### Preparation of 3-methyl-1,1'-bi-2-naphthol and 3,3'-dimethyl-1,1'-bi-2-naphthol

Crude reaction mixtures containing **4b** or **6b** were allowed to warm to room temperature and a five-fold excess of LiAlH<sub>4</sub> added. The mixtures were refluxed under an inert atmosphere (20 h), allowed to cool and quenched with 5 equiv. of water, 5 equiv. of 15% aqueous KOH and 15 equiv. of water in that order. The mixture was then worked up as above. Alternatively, compounds **4b** and **6b** could be isolated and treated with LiAlH<sub>4</sub> with similar results. Purification was by column chromatography (15–25% ethyl acetate in light petroleum).

**(R<sub>a</sub>)-3-Methyl-1,1'-bi-2-naphthol.** 46%, mp 137–139 °C; [α]<sub>D</sub> (c 1.5 in CDCl<sub>3</sub>, 26 °C) 25 (Found: C, 83.6; H, 6.1. C<sub>21</sub>H<sub>16</sub>O<sub>32</sub> requires C, 84.0; H, 5.4%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3500vs (OH), 3460vs (OH), 3060w (Ar CH), 2960w and 2930w (Me CH), 1220, 1130, 825, 760; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.5 (3 H, s, Me), 5.04 (1 H, s, OH), 5.09 (1 H, s, OH), 7.08 (1 H, d, *J* 8.3, Ar), 7.15 (1 H, d, *J* 8.3, Ar), 7.22–7.40 (5 H, m, Ar), 7.81–7.83 (2 H, m, Ar), 7.90 (1 H, d, *J* 7.8, Ar), 7.98 (1 H, d, *J* 8.8, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 16.96, 110.16, 111.09, 117.68, 123.90, 123.95, 124.23, 126.38, 127.02, 127.40, 127.53, 128.33, 129.37, 129.40, 130.71, 131.29, 132.10, 133.41, 152.00, 152.71; *m/z* (EI) 300 (M<sup>+</sup>, 100%), 239 (33), 126 (45), 113 (42) [Found: (HRMS): M<sup>+</sup>, 300.1150. C<sub>21</sub>H<sub>16</sub>O<sub>2</sub> requires *M*, 300.1150].

**(R<sub>a</sub>)-3,3'-Dimethyl-1,1'-bi-2-naphthol.** 73% (Found: C, 84.1; H, 6.0. C<sub>22</sub>H<sub>18</sub>O<sub>2</sub> requires C, 84.05; H, 5.8%); ν<sub>max</sub>(KBr disc)/cm<sup>-1</sup> 3520s (OH), 3060w (Ar CH), 2980w and 2940w (Me CH), 1390, 1220vs, 1100s, 750s; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.51 (6 H, s, Me), 5.11 (2 H, s, OH), 7.07 (2 H, d, *J* 8.3, Ar), 7.21–

7.23 (2 H, m, Ar), 7.32–7.35 (2 H, m, Ar), 7.81–7.83 (4 H, m, Ar); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 16.98, 110.45, 123.90, 124.03, 126.36, 127.00, 127.54, 129.42, 130.72, 132.14, 152.04; *m/z* (EI) 314 (M<sup>+</sup>, 100%), 252 (23), 239 (29), 226 (18), 125 (88), 113 (70). All other physical and spectroscopic properties were identical to those reported by Cram *et al.*<sup>13</sup>

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