# 4,5-Dihydro-4,4-dimethyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]stannepin as a Precursor of 2,2′-Bis(lithiomethyl)-1,1′-binaphthyl

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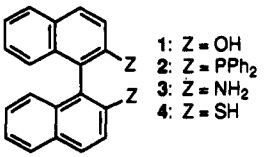
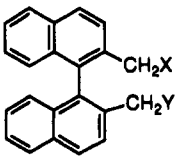
The 1,1′-binaphthyl ring system is a key component of a number of chiral ligands that have been used very successfully for asymmetric synthesis.[1] Most notable are 2,2′-disubstituted systems such as dihydroxy derivative **1**[2] and diphosphine **2**;[3] other heteroatom substituted systems such as **3** (and derivatives thereof)[4] and **4**[5] have also been recently described. Binaphthyl derivatives based on 2,2′-dimethyl-1,1′-binaphthyl (**5**)[6] have been employed far less frequently. Among the compounds based on **5** that have been reported are amine **6**,[7] cyclopentadiene **7**,[8] and phosphine **8**.[9] These compounds have all been prepared using nucleophilic substitution chemistry on dibromide **9**.[6a,b] Other derivatives such as borane **10**,[10] silanes **11**[11] and **12**,[12] and stannane **13**[10] have been prepared via metalation (*n*-BuLi, TMEDA) of **5**.




**1**: Z = OH
**2**: Z = $PPh_2$
**3**: Z = $NH_2$
**4**: Z = SH




**5**: X = Y = H
**6**: X, Y = NH
**7**: X, Y = 1,2-Cp
**8**: X = Y = $PPh_2$
**9**: X = Y = Br
**10**: X, Y = BCl
**11**: X,Y = $SiMe_2$
**12**: X, Y = SiHMe
**13**: X,Y = $SnMe_2$
**14**: X = Y = Li
**15**: X = Y = Cl
**16**: X = Y = MgCl
**17**: X = Y = MgBr
**18**: X = H, Y = $SnMe_3$

We were interested in preparing organometallic derivatives of **5** for use as reagents for asymmetric synthesis and expected that the dilithiobinaphthyl **14** would be a reasonable precursor to a wide range of "2,2′-carbon-based" derivatives. Binaphthyl **14** was first prepared[11] by metalation of the dimethyl species **5** in modest (~50%) yield based on isolation of silepin **11** after reaction with $Me_2SiCl_2$. Subsequent reports[10,12] suggest that this metalation does not proceed to completion and only 30–50% yields of products may be expected. A better approach to **14** might be via transmetalation of the stannane **13**. While benzylstannanes have been used only rarely as precursors of benzyllithiums,[13] it is well known that the former compounds undergo Sn–Li exchange with MeLi very cleanly to afford high yields of the corresponding benzyllithiums.[14] Furthermore, the only byproduct would be $Me_4Sn$ (bp 74 °C) which is very volatile and easily removed. Stannepin **13** (prepared from **5** in 29% yield) has been reported once before[10] but its Sn–Li chemistry does not seem to have been explored. We now report a better route to **13** and that it can serve as the precursor, via Sn–Li exchange and electrophilic quench, to a variety of binaphthyl derivatives.

Treatment of Grignard reagent **16**, prepared from dichloride **15** using magnesium–anthracene,[15] with $Me_2SnCl_2$ cleanly provided stannane **13** (74% from **15**). It was necessary to separate the anthracene byproduct from **16** prior to introduction of $Me_2SnCl_2$ to obtain high isolated yields of **13**. When anthracene was not removed, stannane **13** was formed in >90% yield (based on $^1H$ NMR analysis of the crude product) but could not be efficiently separated from anthracene. Fortunately, the Grignard reagent **16** (along with anthracene) could be precipitated from the reaction mixture (THF) using petroleum ether, and the anthracene could be easily removed by washing of the precipitate with benzene. By using this procedure, the crude product contained essentially only the desired stannane **13**. Use of the Grignard reagent **17**, derived from dibromide **9**, resulted in lower yields (50–60%) of **13**; this result is consistent with the expectation that bromides provide poorer yields of benzylic-type Grignard reagents than chlorides.[15,16]

(1) (a) For a recent review of binaphthyl derivatives as chiral auxiliaries, see: Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) For a review of $C_2$-symmetric chiral auxiliaries, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(2) (a) Noyori, R.; Timino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. (b) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717. (c) Kazlauskas, R. J. *Org. Synth.* **1991**, *70*, 60. (d) Sakai, N.; Nozaki, K.; Mashima, K.; Takaya, H. *Tetrahedron: Asymmetry* **1992**, *3*, 583. (e) Smrcina, M.; Lorenc, M.; Hanus, V.; Sedmera, P.; Kocovsky, P. *J. Org. Chem.* **1992**, *57*, 1917 and references cited therein.

(3) (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (c) Ohta, T.; Miyake, T.; Seido, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *Tetrahedron Lett.* **1992**, *33*, 635.

(4) (a) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171. (b) Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717. (c) Smrcina, M.; Lorenc, M.; Hanus, V.; Kocovsky, P. *Synlett* **1991**, 231. (d) Rosini, C.; Franzini, L.; Iuliano, A.; Pini, D.; Salvadori, P. *Tetrahedron: Asymmetry* **1991**, *2*, 363.

(5) (a) Cram, D. J.; Helgeson, R. C.; Koga, K.; Kyba, E. P.; Madan, K.; Sousa, L. R.; Siegel, M. G.; Moreau, P.; Gokel, G. W.; Timko, J. M.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 2758. (b) Di Furia, F.; Lucini, G.; Modena, G.; De Lucchi, O. *Tetrahedron Lett.* **1989**, *30*, 2575. (c) Cossu, S.; Delogu, G.; De Lucchi, O.; Fabbri, D.; Licini, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 766. (d) Dore, A.; Cossu, S.; De Lucchi, O.; Valle, G. *Tetrahedron Lett.* **1991**, *32*, 4771.

(6) (a) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242. (b) Maigrot, N.; Mazaleyrat, J.-P. *Synthesis* **1985**, 317. (c) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

(7) (a) Hawkins, J. M.; Fu, G. C. *J. Org. Chem.* **1986**, *51*, 2920. (b) Rudolf, K.; Hawkins, J. M.; Loncharich, R. J.; Houk, K. N. *J. Org. Chem.* **1988**, *53*, 3879.

(8) Halterman, R. L.; Coletti, S. L. *Tetrahedron Lett.* **1989**, *30*, 3513.

(9) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, *18*, 1389.

(10) Gross, U.-M.; Bartels, M.; Kaufmann, D. *J. Organomet. Chem.* **1988**, *344*, 277.

(11) Noyori, R.; Sano, N.; Murata, S.; Okamoto, Y.; Yuki, H.; Ito, T. *Tetrahedron Lett.* **1982**, *23*, 2969.

(12) Jung, M. E.; Hogan, K. T. *Tetrahedron Lett.* **1988**, *29*, 6199.

(13) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis, Butterworths*: London, 1987; p 177.

(14) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431.

(15) Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* **1988**, *53*, 3134.

(16) It has been reported[10] that treatment of Grignard reagent **17** with $Me_2SnCl_2$ produced the dimethylbinaphthyl **5**, the unexpected trimethylstannane **18**, and an unidentified compound in a ratio of 19:66:15 (by GC-MS); stannane **13** was not isolated. In our hands the major product of the reaction was stannane **13** and we did not isolate any of the stannane **18**; the causes for the different outcomes are not clear.

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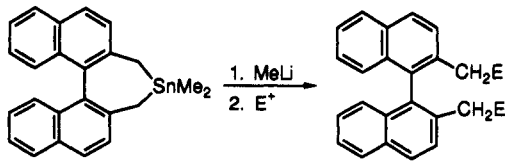
**Table I. Preparation of 2,2′-Disubstituted Binaphthyls from Stannane 13**




13

| entry | $E^+$ | product | yield (%)[a] |
|---|---|---|---|
| 1 | $CH_3OH$ | 5 | 100 |
| 2 | $Me_3SiCl$ | 19 | 93 |
| 3 | $Ph_2SiCl_2$ | 20 | 99 |
| 4 | $Me_2SiCl_2$ | 11 | 97 |
| 5 | $CH_3OCH_2Cl$ | 21 | 90 |
| 6 | $CH_2{=}CHCH_2Cl$ | 22 | 88 |
| 7 | $CH_3CH_2CHO$ | 23 | 78 |
| 8 | MeC(O)Me[b] | 24 | 57 |
| 9 | HCHO[c] | 25 | 55 |

[a] Isolated yields. [b] Dried over $B_2O_3$. [c] Generated by pyrolysis of $(CH_2O)_n$ at 180 °C. Only 5 was isolated when $(CH_2O)_n$ was added directly to the reaction mixture.

The stannane 13 underwent transmetalation (2.2 equiv of MeLi, THF, −78 °C) cleanly and efficiently to generate a dark red solution of dilithiobinaphthyl 14. Subsequent reaction with electrophiles provided substituted binaphthyls in good to excellent yields (Table I). In general, reactions with silylating agents (entries 2–4) and reactive alkylating agents (entries 5, 6) afforded trapped products in excellent yields. Trapping with an aldehyde (entry 7) gave a mixture of diastereomers in good yield, but competing enolization was a problem when acetone (entry 8) was used.

In principle, use of enantiomerically enriched stannane 13 (prepared from 5 which is readily available in high enantiomeric purity[6b,c]) should provide substituted binaphthyls in chiral nonracemic form. (*R*)-Stannane 13 ($[\alpha]_D$ +51° (*c* 0.7, $CCl_4$); lit.[10,17] $[\alpha]_D$ −55.0° (*c* 0.73, $CCl_4$)) was prepared from (*R*)-dichloride 15 ($[\alpha]_D$ +145° (*c* 1.0, $C_6H_6$)), and conversion of (*R*)-13 to the known silepin 11 was carried out via a transmetalation/trapping sequence (MeLi; $Me_2SiCl_2$). Comparison of the optical rotation of the isolated product ($[\alpha]_D$ −310° (*c* 0.088, 1,4-dioxane)) with those previously reported ($[\alpha]_D$ −324° [11] and $[\alpha]_D$ −317° [10]) showed that the reaction proceeded without significant racemization (as expected[4b]). Since it is difficult to detect small degrees of racemization using optical rotation, another means of analysis was sought. Diol 24 was prepared starting from (*R*)-stannane 13 and converted to its bis MTPA ester;[18] no signal for the minor diasteromer was detected by $^{19}F$ NMR spectroscopy. Since a $^{13}C$ satellite (of 0.55% intensity) of the signal for the major diastereomer was clearly visible, we can confidently state that the transmetalation/trapping sequence proceeded with <1% racemization.[19]

(17) The fact that our rotation is opposite to that previously reported was quite perturbing. Since the rotations of our starting dibromide (*R*)-9 and the final product (*R*) silane 11 both suggest that their absolute configuration is *R*, the intermediate stannane 13 should also be *R*. The possibility of a double inversion (i.e., inversions in transformations 15 → 13 and 13 → 11) is unlikely; X-ray crystal structures of (*R*)-15 and a boracycle derived from it both indicate *R* configurations (Chong, J. M.; MacDonald, G. K.; Taylor, N. J. *unpublished results*). The previous literature report[10] includes both (*R*)- and (*S*)-13; perhaps the rotations were inadvertently exchanged.

(18) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(19) Hull, W. E.; Seeholzer, K.; Baumeister, M.; Ugi, I. *Tetrahedron* **1986**, *42*, 547.

Stannane 13 appeared to be quite stable in crystalline form and, in contrast to a previous report,[10] did not decompose significantly in air at rt over a period of several months. Samples stored at 0 °C under argon showed no detectable (TLC, $^1H$ and $^{13}C$ NMR) decomposition after several months. However, samples in ($CDCl_3$) solution showed 50% decomposition within one week.

In summary, we have shown that stannane 13 is a convenient precursor to dilithiobinaphthyl 14. A variety of 2,2′-disubstituted-1,1′-binaphthyls may be prepared in good yields by treatment of 14 with electrophiles.

## Experimental Section

All reactions were carried out in oven- or flame-dried glassware in a glovebox (nitrogen atmosphere) or under argon. Melting points are uncorrected. $^1H$ NMR spectra were recorded at 200 or 250 MHz in $CDCl_3$; $^{13}C$ NMR spectra were recorded at 50 or 63 MHz in $CDCl_3$. $^{19}F$ NMR (188 MHz) signals are reported relative to $CFCl_3$ ($\delta$ 0.0) with positive upfield shifts. Mass spectra were recorded using EI (70 eV) ionization. Microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

**2,2′-Bis(chloromethyl)-1,1′-binaphthyl (15)** was prepared according to the general procedure of Raston[15] for converting benzylic bromides to chlorides. Thus dibromide 9 (12.0 g, 27.3 mmol) was stirred with LiCl (6.94 g, 164 mmol) in DMF (200 mL) at rt for 3 h. Aqueous workup afforded 15 (9.24 g, 97%) as white crystals: mp 140–140.5 °C; IR (KBr) 1440, 1261, 823, 755, 704 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.04 (d, 2 H, $J$ = 8.6 Hz), 7.93 (d, 2 H, $J$ = 8.1 Hz), 7.77 (d, 2 H, $J$ = 8.6 Hz), 7.49 (ddd, 2 H, $J$ = 8.1, 6.9, 1.2 Hz), 7.27 (ddd, 2 H, $J$ = 8.3, 6.9, 1.2 Hz), 7.06 (d, 2 H, $J$ = 8.3 Hz), 4.32 (s, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 134.0, 133.9, 133.2, 132.6, 129.2, 128.0, 127.0, 126.8, 126.6, 126.5, 44.7; MS *m/e* (rel intensity) 350 (13, $M^+$), 316 (22), 279 (19), 191 (45), 179 (78), 135 (21), 43 (100). Anal. Calcd for $C_{22}H_{16}Cl_2$: C, 75.22; H, 4.59. Found: C, 75.35; H, 4.56.

Use of (*R*)-dibromide (*R*)-9 ($[\alpha]_D$ +164 (*c* 1.0, $C_6H_6$); lit.[6b] $[\alpha]_D$ +163.0 (*c* 1.0, $C_6H_6$)) afforded the previously unreported (*R*)-dichloride (*R*)-15: mp 174–175 °C; $[\alpha]_D^{20}$ +145° (*c* 1.0, $C_6H_6$).

**4,5-Dihydro-4,4-dimethyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]stannepin (13).** A solution of dichloride 15 (5.00 g, 14.3 mmol) in THF (95 mL) was added dropwise to an orange slurry of magnesium–anthracene·3THF (11.90 g, 28.6 mmol) in THF (45 mL) at rt over ~1 h. The reaction mixture turned dark green during the addition of 15 and changed sharply to a light yellow-green solution as the last drop of 15 was added. Petroleum ether (bp 100–120 °C, 150 mL) was then added and THF was removed in vacuo. Benzene (330 mL) was added and the slurry was stirred for 4 h. The precipitate was collected on a fine frit and washed with petroleum ether (20 mL of bp 100–120 °C followed by 20 mL of bp 30–60 °C). The solid was then dissolved in THF (300 mL) to provide a solution of the desired Grignard reagent free of anthracene. Dimethyltin dichloride (3.19 g, 14.5 mmol) was then added and the solution was stirred at rt for 45 min. The reaction solution changed from reddish-yellow and to colorless over the course of the reaction. The reaction mixture was diluted with $Et_2O$ (500 mL). The ethereal solution was washed with 1 N HCl (100 mL), water (2 × 200 mL), saturated $Na_2CO_3$ (100 mL), and saturated NaCl (100 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed in vacuo to provide 4.51 g (74% from 15) of the desired product 13 as white crystals: mp 208–215 °C dec [lit.[10] mp 220–232 °C dec]. This material exhibited spectral data ($^1H$ and $^{13}C$ NMR) essentially identical with that previously reported.[10]

When (*R*)-15 was used, (*R*)-13 was produced which exhibited $[\alpha]_D$ +51° (*c* 0.7, $CCl_4$); lit.[10] $[\alpha]_D$ −55.0° (*c* 0.73, $CCl_4$).

**Representative Procedure for Preparation of Binaphthyls from Stannane 13. 2,2′-Bis((trimethylsilyl)methyl)-1,1′-binaphthyl (19).** To a cold (−78 °C) solution of 13 (200 mg, 0.467 mmol) in THF (5 mL) was added MeLi (1.4 M in $Et_2O$, 0.74 mL, 1.03 mmol) dropwise, and the resulting intense, dark red solution was stirred for 30 min. Chlorotrimethylsilane (0.130 mL, 1.03 mmol) was then added dropwise and the reaction mixture

was stirred at −78 °C for 1 h. The yellow solution was diluted with $Et_2O$ (40 mL), washed with $H_2O$ (2 × 10 mL), dried ($MgSO_4$), and concentrated in vacuo to yield a yellow oil. Flash chromatography (6 g silica, hexanes/$CH_2Cl_2$ 100:1) afforded 185 mg (93%) of the desired product as a colorless oil which slowly solidified: mp 70.5–72.5 °C; IR (neat) 3050, 2925, 1506, 1248, 848, 745 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.83 (d, 2 H, $J$ = 7.9 Hz), 7.80 (d, 2 H, $J$ = 8.5 Hz), 7.34 (d, 2 H, $J$ = 8.5 Hz), 7.32 (ddd, 2 H, $J$ = 7.9, 6.8, 1.0 Hz), 7.13 (ddd, 2 H, $J$ = 8.3, 6.8, 1.0 Hz), 7.10 (d, 2 H, $J$ = 8.3 Hz), 2.03 (d, 2 H, $J$ = 13.8 Hz), 1.90 (d, 2 H, $J$ = 13.8 Hz), −0.30 (s, 18 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 137.7, 133.7, 133.4, 131.4, 128.5, 127.6, 127.2, 127.0, 125.6, 124.3, 24.4; MS $m/e$ (rel intensity) 426 ($M^+$, 85), 323 (16), 179 (92), 165 (60), 151 (55), 123 (58), 109 (100). Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found C, 78.67; H, 8.00.

Other compounds were prepared in a similar fashion using the electrophiles shown in Table I.

**4,5-Dihydro-4,4-diphenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepin (20)**: mp 234–238 °C; IR (KBr) 3053, 1506, 1427, 1143, 1110, 908 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.86 (d, 2 H, $J$ = 8.3 Hz), 7.74 (d, 2 H, $J$ = 8.3 Hz), 7.45–7.1 (m, 18 H), 2.49 (s, 4 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 135.71, 134.83, 134.25, 134.16, 132.65, 132.60, 131.89, 129.68, 128.36, 128.03, 127.84, 127.75, 126.39, 125.77, 124.39, 21.52; MS $m/e$ (rel intensity) 462 ($M^+$, 7), 282 (28), 265 (15), 252 (32), 197 (100). Anal. Calcd for $C_{34}H_{26}Si$: C, 88.27; H, 5.66. Found: C, 88.12; H, 5.79.

**2,2′-Bis(2-methoxyethyl)-1,1′-binaphthyl (21)**: IR (neat) 3053, 2888, 1506, 1382, 1110, 817, 750 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.86 (dd, 2 H, $J$ = 8.6, 8.6 Hz), 7.59 (d, 2 H, $J$ = 8.5 Hz), 7.34 (ddd, 2 H, $J$ = 7.8, 7.8, 1.1 Hz), 3.37 (m, 4 H), 3.09 (s, 6 H), 2.45–2.55 (m, 4 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 135.23, 134.94, 133.18, 132.32, 127.78, 127.66, 126.20, 125.91, 125.19, 72.30, 58.17, 33.79; MS $m/e$ (rel intensity) 370 ($M^+$, 8), 338 (100), 306 (4), 293 (48), 279 (43). Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.30; H, 7.07. Found: C, 84.32; H, 7.15.

**2,2′-Bis(3-butenyl)-1,1′-binaphthyl (22)**: IR (neat) 3056, 2927, 1639, 1507, 911, 815, 748 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.81 (dd, 2 H, $J$ = 7, 8.2 Hz), 7.55 (d, 2 H, $J$ = 8.5 Hz), 7.39 (ddd, 2 H, $J$ = 8.1, 6.7, 1.4 Hz), 7.18 (ddd, 2 H, $J$ = 8.3, 6.7, 1.5 Hz), 7.03 (d, 2 H, $J$ = 8.5 Hz), 5.59 (dddd, 2 H, $J$ = 17.7, 9.4, 6.6, 6.6 Hz), 4.85–4.70 (m, 4 H), 2.50–2.35 (m, 4 H), 2.10–2.30 (m, 4 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 138.18, 137.97, 134.53, 133.24, 132.18, 127.78, 127.68, 127.33, 126.43, 125.87, 125.07, 114.67, 34.31, 33.31; MS $m/e$ (rel intensity) 362 ($M^+$, 100), 321 (89), 279 (79), 265 (84). Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.89; H, 7.41.

**2,2′-Bis(2-hydroxybutyl)-1,1′-binaphthyl (23)**: IR (neat) 3053 (br), 3053, 2961, 1557, 1016, 973, 813, 745 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 8.25–8.0 (m, 4 H), 7.86 (m, 2 H), 7.6 (m 2 H), 7.48–7.25 (m, 4 H), 4.1–3.9 (m, 1 H), 3.85–3.6 (m, 3 H), 2.9–2.6 (m, 4 H), 1.6–1.25 (m, 4 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 135.86, 135.81, 135.47, 135.32, 135.14, 134.96, 133.25, 133.10, 132.14, 132.08, 128.35, 128.16, 127.91, 127.81, 127.73, 127.63, 127.60, 126.77, 126.22, 126.05, 125.90, 125.83, 125.26, 125.20, 125.13, 125.01, 72.66, 72.61, 72.48, 41.54, 41.50, 40.85, 40.07, 30.52, 30.03, 29.73, 29.69, 9.81, 9.78, 9.36; MS $m/e$ (rel intensity) 398 ($M^+$, 4), 380 (12), 362 (7), 340 (21), 322 (25), 282 (100). Anal. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.39; H, 7.41.

**2,2′-Bis(2-hydroxy-2-methylpropyl)-1,1′-binaphthyl (24)**: mp 80–81 °C; IR (KBr) 3385 (br), 3057, 2971, 1373, 1130, 825, 760 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.89 (d, 2 H, $J$ = 6.0 Hz), 7.88 (dd, 4 H, $J$ = 9.1, 8.6 Hz), 7.40 (ddd, 2 H, $J$ = 8.1, 6.4, 1.6 Hz), 7.15 (m, 4 H), 2.81 (d, 2 H, $J$ = 14.0 Hz), 2.57 (d, 2 H, $J$ = 14.0 Hz), 0.99 (s, 6 H), 0.85 (s, 6 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 135.75, 135.45, 133.25, 132.19, 129.10, 127.83, 127.57, 127.39, 125.71, 125.23, 71.76, 46.02, 30.73, 29.30; MS $m/e$ (rel intensity) 398 ($M^+$, 1), 380 (4), 340 (21), 322 (83), 307 (10), 282 (100). Anal. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.65; H, 7.40.

(*R*)-**24**: mp 72–74 °C; $[\alpha]_D$ −145° (*c* 1.19, THF). The bis MTPA ester derived from (*R*)-MPTA showed a $^{19}F$ NMR signal at δ 70.135; racemic diol 24 gave diastereomers with signals at δ 70.135 and 70.643.

**2,2′-Bis(2-hydroxyethyl)-1,1′-binaphthyl (25)**: mp 71–72 °C; IR (melt) 3333 (br), 3053, 2913, 1506, 1037, 816, 749 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 7.48 (d, 2 H, $J$ = 8.5 Hz), 7.34 (ddd, 2 H, $J$ = 8.0, 6.7, 1.2 Hz), 7.14 (ddd, 2 H, $J$ = 8.1, 6.8, 1.3 Hz), 3.49 (sym m, 4 H), 2.45–2.55 (m, 4 H); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 135.17, 134.96, 133.20, 132.29, 127.88, 127.12, 126.15, 126.03, 125.32, 61.92, 36.49; MS $m/e$ (rel intensity) 342 ($M^+$, 2), 324 (4), 312 (100), 293 (8), 281 (47), 265 (73). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 83.92; H, 6.65.

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