Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 17 (2006) 1275–1280

[9,9′]Bi[naphtho(2,1-*b*)furanyl]-8,8′-diol, a furo-fused BINOL derivative: synthesis, resolution and determination of absolute configuration

Anil V. Karnik,[a,*] Sunil P. Upadhyay[a] and Manish G. Gangrade[b]

[a]*Department of Chemistry, University of Mumbai, Vidyanagari, Kalina, Mumbai 400 098, India*
[b]*Cipla Ltd, Vikhroli (West), Mumbai 400 083, India*

Received 21 March 2006; accepted 12 April 2006

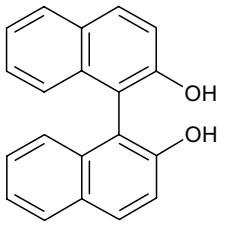
Abstract—A high yielding synthetic protocol was employed in order to achieve the placement of a furan ring at the most sterically crucial position of BINOL to obtain [9,9′]bi[naphtha(2,1-*b*)furanyl]-8,8′-diol. The racemate was resolved and the configuration of one of the enantiomers was found by single crystal X-ray analysis of a Mosher's acid diester derivative. This furo-fused BINOL derivative exhibited modified steric and electronic properties.

1. Introduction

BINOL **1** is one of the best-known representatives of axially chiral C_2-symmetric molecules; BINOL and its derivatives are among the most widely used ligands for a variety of asymmetric reactions.[1]

The outcome of a given asymmetric transformation and a given enantioselective process depends on both the steric and electronic properties of the chiral ligand. Ever since the use[2] of BINOL by Noyori in the asymmetric reduction of prochiral carbonyl compounds, the synthetic chemical community has had undiminished interest in the development of BINOL derivatives[3] with modified electronic and steric properties. Several types of substituents were placed on this ligand, such as electron donating, electron withdrawing, with additional binding sites, etc. in order to prepare modified BINOL ligands with better properties. Efforts to prepare modified BINOL ligands were mainly concentrated on different substituents at the C-3,[4] C-4,[5] C-6[6] and C-7[7] positions with different degrees of success. However there are only a few reports where a substituent at C-8 has been attempted.[8]

Modification of the electronic properties and an increase in dihedral angle were carefully planned after studying the overall substitution patterns and consequent results reported by previous workers. It was realized that the same could be achieved if hetero-aromatic rings could be placed at C-7; C-8 and C-7′; C-8′ positions of the BINOL **1** framework. Furan was considered the most suitable for this purpose as it had sufficient aromatic character while the oxygen lone pair can easily participate in mesomerism. It was decided to fuse the furan ring with C-2; C-3 and C-2′; C-3′ positions at C-7; C-8 and C-7′; C-8′ positions of the BINOL **1** framework; with the oxygen atoms of furan attached at C-7 and C-7′ positions of **1**. Based on this premise, the synthesis of [9,9′]bi[naphtho[2,1-*b*]furanyl]-8,8′-diol **6** was planned (Fig. 1).



1

Figure 1.

* Corresponding author. Tel.: +91 022 26526091; fax: +91 022 26528547; e-mail: avkarnik@chem.mu.ac.in

0957-4166/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2006.04.017

2. Results and discussion

2.1. Synthesis of [9,9′]bi[naphtho(2,1-*b*)furanyl]-8,8′-diol 6

[9,9′]Bi[naphtho(2,1-*b*)furanyl]-8,8′-diol **6** was synthesized from 2,7-naphthalenediol **2** in four steps (Scheme 1). A procedure developed in this laboratory[9] for the preparation of naphthofuranone moiety was followed for the preparation of 1-oxo-1,2-dihydronaphtho[2,1-*b*]furan-8-yl chloroacetate **3**. Hydrolysis of **3** under aqueous acidic conditions gave 8-hydroxynaphtho[2,1-*b*]furan-1(2*H*)-one **4** in high yield while further reduction with sodium borohydride in isopropanol followed by subsequent dehydration in aqueous acidic conditions gave naphtho[2,1-*b*]furan-8-ol **5** in moderate yield. Coupling of **5** by using iron(III) chloride was achieved successfully by modifying the literature procedure[10] to give **6** in excellent yield. Notably this coupling reaction to yield **6** was complete within 5 min, indicating the electronically modified system of **5** when compared to 2-naphthol.

The resolution of racemic **6** was carried out by modifying the literature procedure,[11] using *N*-benzylcinchonidinium chloride as the resolving agent. The enantiomeric purity of the resolved (+)-**6** and (−)-**6** was determined by chiral HPLC.

In order to determine the configuration of the resolved enantiomers of **6**, one of the enantiomers, namely the dextro-rotatory enantiomer of [9,9′]bi[naphtho(2,1-*b*)furanyl]-8,8′-diol **6** was derivatized with a widely used chiral derivatizing agent (CDA), (*S*)-(+)-Mosher's acid chloride, to obtain (−)-diester **7** (Scheme 2). The enantiopurity of the (−)-diester **7** was confirmed by ^{19}F NMR, which gave only a single peak at δ −72.41 ppm for the trifluoromethyl substituents of the (−)-diester **7**. This (−)-diester **7** was further subjected to single crystal X-ray analysis.

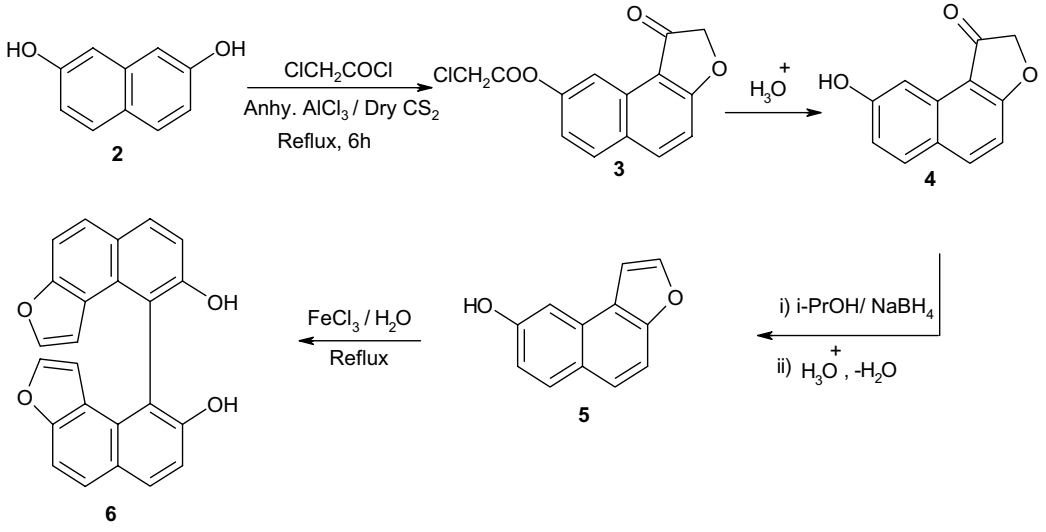
Based on the X-ray analysis (Fig. 2), diester (−)-**7** prepared from enantiopure dextrorotatory **6** was found to have an (*S*)-configuration. On this basis, (+)-**6** was assigned an (*S*)-configuration and accordingly (−)-**6** assigned an (*R*)-configuration. Notably, the same relationship exists between the absolute configuration and the sign of rotation of biphenanthrene.[12] CCDC: 282786 contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK, fax: (+44) 1223 336 033 or deposit@ccdc.cam.ac.uk).

From the X-ray data, it was found that the distances of the C1 and C1′ protons from the centriod of the A and A′ rings [rings with the pivotal bond] were 2.786 Å, and showed the close proximity to these protons from these ring clouds. This was also evident from the ^1H NMR spectrum of **6**, the C-1 and C-1′ protons resonated as doublet (J = 2.1 Hz) at δ 5.15 ppm. In comparison, the C-1 proton of **5** resonated as a doublet (J = 2.0 Hz) at δ 7.15 ppm. A significant anisotropic shielding effect, a large upfield shift by nearly δ 2.05 ppm, was evident for the C-1 and C-1′ protons in **6**. A similar anisotropic shielding effect was seen in case of C-1 and C-1′ protons in **7**.

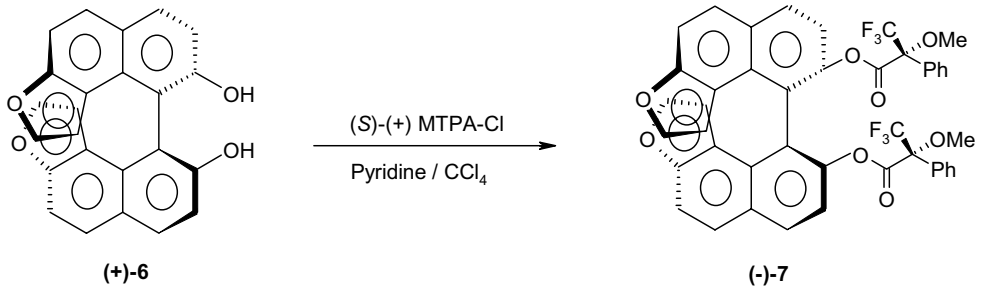
X-ray diffraction studies revealed the dihedral angle θ, of the diester (−)-**7** to be 97°. This is more than the dihedral angle θ of **1**, which is reported[13] to be 77°. $[\alpha]_{589}^{25}$ for compound (+)-**6** was found to be +110 (*c* 1, THF). This is much higher than the reported[14] [α] for (+)-**1** which is $[\alpha]_{589}^{25} = +35.3$ (*c* 1, THF).

2.2. X-ray crystallographic data of diester (−)-7

Suitable X-ray quality crystals of **5** were grown by slow evaporation of CH_2Cl_2–toluene solvent mixtures at room temperature and X-ray diffraction studies were undertaken. X-ray crystallographic data were collected from single crystal samples of ($0.35 \times 0.30 \times 0.30$ mm^3). Unit cell dimensions were obtained using 25 centred reflections in θ range 5.2200–10.1400 mounted on a Nonius MACH 3 dif-



Scheme 1.



Scheme 2.

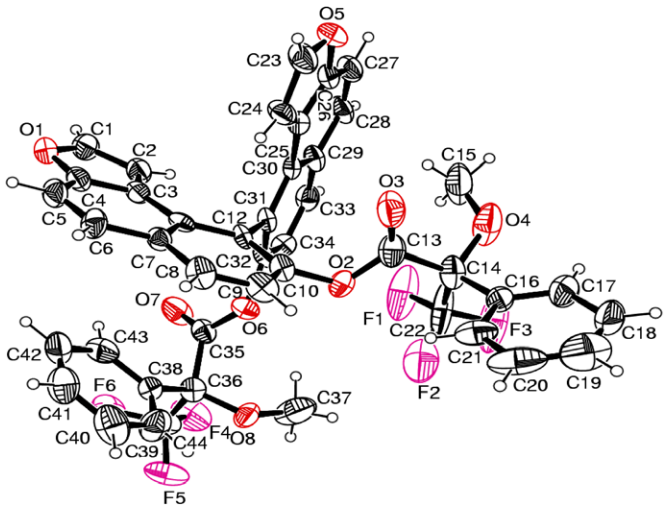


Figure 2. ORTEP representation of the X-ray crystal structure of diester (−)-**7**.

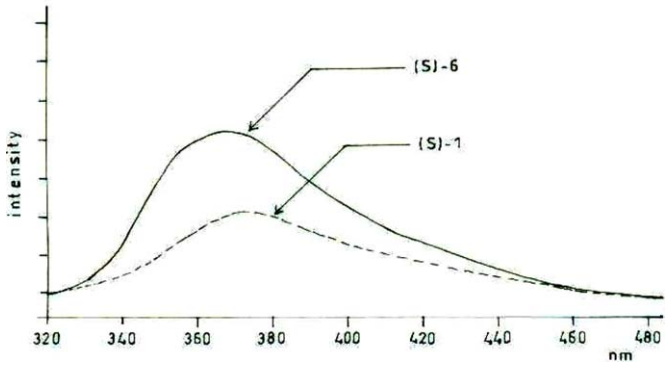


Figure 3. Emission spectrum of compound (*S*)-**1** and (*S*)-**6** at 5.5×10^{-7} M.

fractometer equipped with graphite monochromated Mo Kα radiation (0.710730 Å). The intensity data were collected by ω–2θ scan mode, and corrected by Lorentz Polarization and absorption effects using Psi-Scan (ψ-scan). Three standard reflections were monitored every 200 and three intensity control reflection monitored every hour, and showed no significant changes (<3%). The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F^2 using shelxl97 software. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Crystal data for **4**: $C_{44}H_{28}F_6O_8$, $M = 798.66$, monoclinic, space group; $P21$, $a = 11.098(3)$ Å, $b = 11.5800(16)$ Å, $c = 14.4590(17)$ Å; $\beta = 96.68(3)°$; $U = 1845.6(6)$ Å^3, $D_c = 1.437$ Mg/m^3, $Z = 2$, $F(000) = 820$, $\lambda = 0.71073$ Å, $\mu = 0.118$ mm^{-1}. Total/unique reflections = 3254/3133 [R(int) = 0.0399]. $T = 293(2)$ K θ range = 1.42–24.98°, final $R[I > 2\sigma(I)]$; $R1 = 0.0543$, $wR2 = 0.1150$, R (all data): $R1 = 0.2090$, $wR2 = 0.1578$.

2.3. Photophysical properties

The UV spectrum of **6** at 3.99×10^{-5} M ($\epsilon = 15589$) in $CHCl_3$ showed a red shift in comparison to **1**. The λ_{max} shifting from 285 to 303 nm indicated auxochromic effect of furan unit with naphthalene chromophoric system. The fluorescence spectrum of (*S*)-**6** was compared with that of the parent BINOL **1** molecule, and it was found that the fluorescence intensity of (*S*)-**6** was significantly larger than that of (*S*)-**1**. This enhancement confirmed the effective coupling of the furan moiety with naphthalene chromophoric system. Compound **6** emits at $\lambda_{em} = 367$ nm when excited at 303 nm. Figure 2 shows the fluorescence spectra of **6** (excited at 303 nm, the maximum in its excitation spectrum) and **1** (excited at 285 nm, the maximum in its excitation spectrum) at the same concentration (5.5×10^{-7} M) in chloroform. Only when the concentration of **1** was increased over four times, did its fluorescence intensity become comparable with that of **6** (Fig. 3).

3. Conclusion

In summary, a simple synthetic protocol was employed in order to achieve a new modified BINOL with the introduction of a furan ring fused to the BINOL **1** framework. The configurational assignment of one of the enantiomers was achieved with single-crystal X-ray diffraction studies of derivatized diester **7**. The successful placement of the furan moiety at C-7; C-8 and C-7′; C-8′ positions of **1** resulted in the modification of steric properties and more importantly made available a better fluorescence active molecule. The λ_{max} bathochromic shift in UV, enhancement in fluorescence and higher [α] compared to **1** reflected modification of electronic properties of **6** significantly in comparison to **1**. Thus, a new axially chiral, C_2-symmetric molecule with modified steric and electronic properties, compared

to BINOL, has been made available for a possible variety of asymmetric transformations. Better fluorescence properties offer the exciting possibility of the use of the molecule and macrocycles incorporating this molecules, as enantioselective fluorescent sensors for different classes of compounds. Further results obtained in this regard will be reported soon.

4. Experimental

4.1. General data

Reagents were of LR grade and used without further purification. (−)-*N*-Benzylcinchonidinium chloride and (*S*)-(+)-α-methoxy-α-trifluoromethyl phenyl acetyl chloride (Mosher's acid chloride) were purchased from Fluka Chemical Company, Inc., acetonitrile (AR grade) was obtained from S.D. Fine Chemicals, India. Optical rotations were measured on Jasco DIP-1000 digital polarimeter. Column chromatography was carried out using silica gel (S.D. Fine Chemicals, India) 60–120 mesh. The petroleum ether used, had the boiling range between 40 and 60 °C. Melting points reported are uncorrected. IR spectra were recorded on a Shimadzu FTIR-4200 spectrometer and ^{1}H NMR spectra were recorded on a Varian VR (500 MHz) spectrometers using TMS as an internal standard. Chemical shifts were given in parts per million relative to internal reference for $CDCl_3$ ^{1}H at 7.25 and DMSO-d_6 ^{13}C at 39.22 ppm. Mass spectrum was recorded on GC-MSQP-1000. ^{19}F NMR was recorded on Bruker 400 MHz NMR spectrometer. Elemental analyses were carried on Carlo Enra EA-1108 Elemental analyzer. UV spectra were recorded on a Shimadzu UV–visible Spectrophotometer UV-2100. Fluorescence spectra were recorded on a Shimadzu RF-5301 PC Spectrofluorophotometer. Solvents used for UV and fluorescence studies were of spectral grade. The excitation and emission slits were set at 2.5 and 5.0 nm, respectively. The scan speed was set at 100 nm/min.

4.2. Preparation of 1-oxo-1,2-dihydronaphtho[2,1-*b*]furan-8-yl chloroacetate 3

In a 1 L three-necked round bottom flask fitted with reflux condenser and calcium chloride guard tube were placed a mixture of **2** (6.0 g, 37.5 mmol) and chloroacetyl chloride (6.0 mL, 75.4 mmol) in dry carbon disulfide (700 mL). This mixture was refluxed for 2 h, then cooled to rt and to this mixture was then added slowly (in 3 h) powered anhydrous aluminium chloride (10.0 g, 75.0 mmol). After the complete addition of anhydrous $AlCl_3$, the resulting mixture was refluxed further for 3 h (until the evolution of HCl gas stopped). Carbon disulfide was removed by distillation in an efficient fume cupboard and the reaction mixture was allowed to cool to rt and surrounded by ice. To this mixture, surrounded by ice, approximately 20% HCl (500 mL) solution (ice cold) was added. The solid, which was separated out, was filtered and after a number of aqueous HCl washings, the mixture was finally washed with cold water to remove traces of aqueous HCl and was air-dried. This crude mass was then purified by column chromatography using 60:40 (petroleum ether–chloroform) as an eluent to give **3** (6.76 g, 24.4 mmol, 65%) as a colourless solid. Compound **3**: mp 124–125 °C; FTIR (KBr): 3085, 2960, 1775, 1685, 1630, 1580, 1535, 1150 and 840 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$); δ 4.38 (s, 2H, ring-CH_2), 4.78 (s, 2H, CH_2–Cl), 7.22–7.30 (m, 2H, C5 and C6–Ar), 7.88 (d, $J_{4,5} = 8.8$ Hz, 1H, C4–Ar), 8.10 (d, $J_{7,6} = 8.8$ Hz, 1H, C7–Ar), 8.50 (s, 1H, C9–Ar); MS (70 eV) *m*/*z* (%): 279 ($[M^{+2}]^+$, 31), 277 (M^+, 100), 200 (47), 171 (19), 142 (08), 115 (10). Elemental analyses for $C_{14}H_9ClO_4$: calcd %C (60.78), %H (3.28), %Cl (12.81). Found: %C (60.50), %H (3.25), %Cl (12.65).

4.3. Preparation of 8-hydroxynaphtho[2,1-*b*]furan-1(2*H*)-one 4

In a 500 mL round bottom flask fitted with reflux condenser was taken **3** (5.0 g, 0.018 mmol) in 50% HCl (100 mL) and methanol (200 mL). This mixture was refluxed for 3 h (monitored on TLC). After completion of the reaction, it was then cooled to rt and poured onto ice-cold water. The solid was then separated out, filtered with suction and finally washed with cold water to remove the traces of aqueous HCl and dried. This crude product was crystallized from alcohol. The compound **4** (3.1 g, 15.5 mmol, 85%) was isolated. Mp 219–220 °C; FTIR (KBr): 3200 (broad), 3050, 2980, 1680, 1630, 1685, 1630, 1590, 1560, 1460 and 840 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$); δ 4.37 (s, 2H, ring-CH_2), 6.69 (d, 2H, C5 and C6–Ar), 7.35 (d, $J_{4,5} = 8.8$ Hz, 1H, C4–Ar), 7.35 (d, $J_{7,6} = 8.8$ Hz, 1H, C7–Ar), 7.76 (s, 1H, C9–Ar), 9.48 (s, 1H, OH (D_2O ex)); MS (70 eV) *m*/*z* (%) 200 (100), 186 (50), 171 (30), 158 (32), 142 (55), 115 (22). Elemental analyses for $C_{12}H_8O_3$: calcd %C (72.0), %H (4.03). Found: %C (71.7), %H (4.00).

4.4. Preparation of naphtho[2,1-*b*]furan-8-ol 5

In a 500 mL round bottom flask fitted with calcium chloride guard tube was taken **4** (5.0 g, 0.025 mmol) in a *iso*-propyl alcohol (300 mL). To the stirred ice cold solution was added slowly sodium borohydride (0.35 g, 9.34 mmol) and the mixture then stirred for 1 h. The next portion of sodium borohydride (0.35 g, 9.34 mmol) was further added and this was repeated until all of the sodium borohydride (0.71 g, 18.68 mmol) had been added to the reaction mixture. After the complete addition of sodium borohydride, the flask was fitted with a reflux condenser and the reaction mixture refluxed on a water bath for 4 h (monitored on TLC). After completion of the reaction, it was cooled to rt and then poured into ice (300 g) and HCl (11 M) (100 mL). The resulting suspension was heated on a water bath for 4 h. From this reaction mixture, *iso*-propyl alcohol and water were removed under reduced pressure so as to give crude residue. This residual mass was then purified by column chromatography using 60:40 (petroleum ether–chloroform) as an eluent to give **5** (2.2 g, 45%) as colourless solid. Compound **5**: mp 122–123 °C; FTIR (KBr): 3320 (broad), 3120, 1630, 1585, 1520, 1450, 1140, 830 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$); δ 5.03 (s, 1H, OH (D_2O ex)), 7.05 (dd, $J_{6,9} = 8.8$ and 2 Hz, 1H, C7–Ar), 7.15 (d, $J_{1,2} = 2$ Hz, 1H, C1–Ar), 7.45 (d, $J_{7,9} =$

2 Hz, 1H, C9–Ar), 7.51 (d, $J_{4,5} = 8.8$ Hz, 1H, C5–Ar), 7.64 (d, $J_{5,4} = 8.8$ Hz, 1H, C4–Ar), 7.15 (d, $J_{2,1} = 2$ Hz, 1H, C2–Ar), 7.83 (d, $J_{6,7} = 8.8$ Hz, 1H, C6–Ar); MS (70 eV) *m/z* (%): 184 (M^+, 100), 128 (22), 92 (25), 77 (35), 63 (35), 51 (50). Elemental analyses for $C_{12}H_8O_2$: calcd %C (78.25), %H (4.38). Found: %C (78.00), %H (4.29).

4.5. Synthesis of [9,9′]Bi[naphtho[2,1-*b*]furanyl]-8,8′-diol 6

In a 500 mL three necked round bottom flask, provided with a dropping funnel, a magnetic stirrer and a reflux condenser, was placed **5** (2.0 g, 10.87 mmol) in water (250 mL). The mixture was refluxed until **5** was formed as an oily suspension. To this mixture was added through the dropping funnel and with vigorous stirring, a solution of iron(III) chloride (2.95 g, 10.87 mmol) in water (10 mL) in one portion. The oily drops of **5** disappeared and **6** separated out as flakes within 2 min. The reaction mixture was boiled for a further 3 min. The hot suspension was filtered at the pump through a previously warmed Buchner funnel, washed with boiling water and dried in the air on filter paper. The crude product (1.97 g, 5.38 mmol, 99%) was then isolated. The solid was recrystallized from toluene (about 20 mL); almost colourless crystals, weighed (1.79 g, 4.89 mmol, 90%), mp 200–201 °C were obtained. FTIR (KBr); 3500 (broad), 3100, 1620, 1585, 1520, 1460, 1070, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$); δ 5.05 (d, $J_{1,2} = 2.0$ Hz, 2H, C1 and C1′ Ar), 7.32 (d, $J_{5,4} = 2$H, 5.0 Hz, C5 and C5′ Ar), 7.43 (d, $J_{2,1} = 2.0$ Hz, 2H, C2 and C2′ Ar), 7.49 (d, $J_{6,7} = 9.0$ Hz, 2H, C6 and C6′ Ar), 7.79 (d, $J_{4,5} = 9.0$ Hz, 2H, C4 and C4′ Ar), 8.03 (d, $J_{7,6} = 9.0$ Hz, 2H, C7 and C7′ Ar), 9.31 (s, 2H, OH (D_2O ex)); ^{13}C NMR (DMSO-d_6): δ 106.68 (t), 109.21 (t), 114.87 (q), 115.67 (t), 120.36 (q), 125.23 (t), 125.27 (q), 128.64 (q), 130.29 (t), 142.07 (t), 152.81 (q), 153.57 (q). MS (70 eV) *m/z* (%) 366 (M^+, 100), 337 (22), 250 (20), 183 (28), 155 (26), 131 (65), 113 (43). Elemental analyses for $C_{24}H_{14}O_4$: calcd %C (78.68), %H (3.85). Found: %C (78.42), %H (3.80).

Resolution of [9,9′]bi[naphtho[2,1-*b*]furanyl]-8,8′-diol **6** was carried out using (−)-*N*-benzylcinchonidinium chloride, following and modifying wherever needed, the reported procedure.[11]

4.6. Resolution of [9,9′]bi[naphtho[2,1-*b*]furanyl]-8,8′-diol 6

Racemate **6** (5.0 g, 13.66 mmol) and *N*-benzylcinchonidinium chloride (3.16 g, 7.5 mmol) were taken in acetonitrile (30 mL). The resulting suspension was refluxed for 4h, cooled and stirred at room temperature overnight. The mixture was then cooled to 0–5 °C. The mixture was then kept at that temperature for 2h, and filtered. The residue and the filtrate were then treated separately to recover the separated enantiomer.

The filtrate was concentrated to dryness, the residue obtained was re-dissolved in chloroform (100 mL), and stirred with 0.5 M hydrochloric acid (200 mL) and finally washed with brine (100 mL). The organic layer was dried over sodium sulfate (Na_2SO_4), filtered and concentrated to obtain a light brown solid [2.3 g, mp 199–200 °C, 92% recovery, $[\alpha]_{589}^{25} = +107$ (*c* 1, THF)]. This solid on crystallization gave a very light brown solid 1.0 g, mp 200–201 °C, 40% recovery. 99.1% ee was found on chiral HPLC analysis using a Chiralcel OD-H column and *iso*-propyl alcohol and hexane as eluents. Retention time for *S*-enantiomer was 27.30 min. and $[\alpha]_{589}^{25} = +110$ (*c* 1, THF).

The solid residue obtained in the earlier step, was washed with ice cold acetonitrile (10 mL). This solid complex was suspended in a mixture of chloroform (100 mL) and 0.5 M HCl (200 mL) and stirred until complete dissolution occurred. The solution was then transferred to a separatory funnel, and the organic layer was separated and washed with brine (100 mL). The organic layer was dried over sodium sulfate (Na_2SO_4), filtered and concentrated to a colourless solid [2.25 g, mp 199–200 °C, 90% recovery, $[\alpha]_{589}^{23} = -105$ (*c* 1, THF)]. This solid on crystallization gave white crystalline solid 1.0 g, mp 200–201 °C, 40% recovery, 98.8% ee was found on Chiral HPLC analysis using Chiralcel OD-H column and *iso*-propyl alcohol and hexane as eluents. Retention time for the (*R*)-enantiomer was 12.30 min. and $[\alpha]_{589}^{23} = -107$ (*c* 1, THF).

4.7. Preparation of diester (−)-7

Diester (−)-**7** was prepared from the reaction between (+)-**6** and (*S*)-(+)-α-methoxy-α-trifluoromethyl phenyl acetyl chloride (Mosher's acid chloride) (1:1) in pyridine and carbon tetrachloride by following the literature procedure.[15] The (−)-**7** diester was isolated through column chromatography by using neutral alumina in (50:50) petroleum ether and chloroform as an eluent. The isolated yield of the solid (−)-**7** was 95%. This solid on crystallization gave a colourless crystals, mp 178–179 °C, $[\alpha]_{589}^{25} = -27$ (*c* 1, $CHCl_3$). FTIR (KBr): 3132, 2921, 1766, 1615, 1516, 1466, 1039, 858, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$); δ 3.0 (s, 6H, two OCH_3 groups), 5.14 (d, $J_{1,2} = 2.0$ Hz, 2H, C1 and C1′ Ar), 7.42 (d, $J_{5,4} = 9.0$ Hz, 2H, C5 and C5′ Ar), 7.68 (d, $J_{6,7} = 9.0$ Hz, 2H, C6 and C6′ Ar), 7.81 (d, $J_{4,5} = 9.0$ Hz, 2H, C4 and C4′ Ar), 8.11 (d, $J_{7,6} = 9.0$ Hz, 2H, C7 and C7′ Ar), 6.99–7.30 (m, 12H, C2 and C2′ and Ph and Ph′); ^{13}C NMR (DMSO-d_6): δ 107.30 (t), 113.39 (t), 119.02 (t), 120.67 (q), 121.84 (q), 123.16 (q), 124.78 (q), 125.40 (t), 126.84 (t), 128.09 (1p and 2t), 128.15 (t), 129.27 (t), 129.31 (q), 130.94 (q), 131.09 (t), 143.68 (q), 146.91 (q), 153.47 (t), 164.81 (t). MS (70 eV) *m/z* (%) 799 (M^+, 10), 189 (100). Elemental analyses for $C_{44}H_{28}F_6O_8$: calcd %C (66.17), %H (3.53), %F(14.27). Found: %C (66.00), %H (3.43), %F(14.10). ^{19}F NMR (400 MHz) showed single peak at $\delta - 72.41$ accounting for 100% ee.

Acknowledgements

We are grateful to the National Single Crystal X-ray diffraction facility, IIT, Mumbai, for crystallographic studies. We are also thankful to Professor A. K. Singh, Department of Chemistry, IIT, Mumbai, for his help in the fluorescence studies.

References

1. Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–898.
2. Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129–3131.
3. Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155–3212.
4. Akimoto, H.; Shioiri, T.; Iitaka, Y.; Yamada, S. *Tetrahedron Lett.* **1968**, *9*, 97–102.
5. Belohradsky, M.; Budesýńsky, M.; Guňterová, J.; Hodacova, J.; Holy, P.; Zaýada, J.; Cisarova, I.; Podlaha, J. *J. Org. Chem.* **1996**, *61*, 1205–1210.
6. Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930–1946.
7. Castro, P. P.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 6277–6280.
8. Yudin, A. K.; Martyn, L. J. P.; Pandiaraju, S.; Zheng, J.; Lough, A. *Org. Lett.* **2000**, *2*, 41–44.
9. Karnik, A. V.; Upadhyay, S. P. *Indian J. Chem.* **2004**, *43B*, 1345–1348.
10. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Essex, UK, 1989; pp. 838–839.
11. Cai, D.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Synth.* **2002**, *76*, 1–3.
12. Koike, N.; Hattori, T.; Miyano, S. *Tetrahedron: Asymmetry* **1994**, *5*, 1899–1900.
13. Lorenzo, D. B.; Gennaro, P.; Fabio, M.; Piero, S. *J. Am. Chem. Soc.* **2000**, *122*, 6395–6398.
14. Shan, Z.; Wang, G.; Duan, B.; Zhao, D. *Tetrahedron: Asymmetry* **1996**, *7*, 2847–2850.
15. James, A. D.; Harry, S. M. *J. Am. Chem. Soc.* **1973**, *95*, 512–519.