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# A convenient chromatography-free access to enantiopure 6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol and its 3,3'-dibromo, di-*tert*-butyl and phosphorus derivatives: utility in asymmetric synthesis

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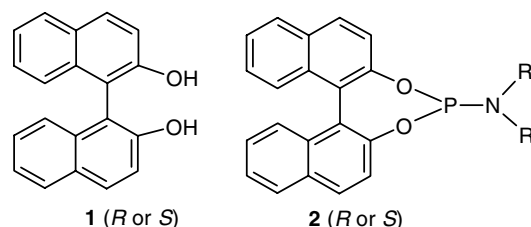
**Abstract**—A simple chromatography-free high-yielding synthesis of the *hexane*-soluble enantiopure 6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol **3** (6,6'-di-*tert*-butyl BINOL) using Friedel–Crafts reaction on 1,1'-binaphthalene-2,2'-diol **1** (BINOL) is described. The enantiomeric purity was fully maintained in the reaction. Compound **3** has been used as an entry point for the convenient chromatography-free synthesis of 3,3',6,6'-tetra-*tert*-butyl BINOL **4** and 3,3'-dibromo-6,6'-di-*tert*-butyl BINOL **5**. A straightforward route to enantiopure bisphosphites [(6,6'-R<sub>2</sub>C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>)P]<sub>2</sub>[O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-6,6'-R<sub>2</sub>] [R = H **15**, *t*-Bu **16**] by simply reacting phosphorochloridite (6,6'-R<sub>2</sub>C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>)PCl [R = H **20**, *t*-Bu **6**] with metallic sodium is highlighted. The identity of **15** and **16** as their selenium-oxidized products **17** and **18** (at phosphorus center) is confirmed by X-ray crystallography (**17** in the enantiopure form and **18** as racemate). Various enantiopure phosphoramidites of the modified BINOL have been synthesized. It is established that even when the phosphoramidites derived from the unsubstituted BINOL **1** fail to give an appreciable optical induction in the asymmetric reduction of acetophenone/phenacyl chloride, those derived from **3** do induce moderate chiral induction (up to 30% ee in the case for acetophenone and 43% ee in the case of phenacyl chloride), thus leaving scope for further improvement in ee for related reactions.

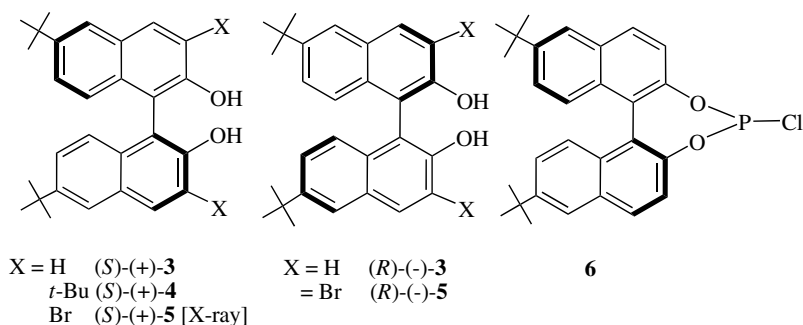
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## 1. Introduction

Asymmetric catalysis is one of the most cost effective and environmentally friendly methods for the production of a large variety of enantiomerically enriched molecules.<sup>1</sup> An important area of research within asymmetric catalysis involves designing enantiopure ligands and transition metal catalysts, which can lead to an efficient and selective transformation. The 2,2'-substituted-1,1'-binaphthyls are well known axially chiral ligands due to their highly stable configuration. The rigid structure and C<sub>2</sub> symmetry of binaphthyl molecules plays a crucial role in chiral induction.<sup>2–7</sup> BINOL **1** often serves as a precursor for obtaining enantiopure binaphthyl compounds. Good resolution methods are now available for BINOL<sup>8</sup> and the price of either of the enantiopure forms has drastically reduced [1 g of either of the enantiomers costs INR ~ 135/- (US\$ ~2.50)].<sup>9</sup> The

2,2'-hydroxyl groups of **1** can be easily converted into other functional groups. In addition, the 3,3'-, and 6,6'-positions can be selectively functionalized, thus leading to a vast array of binaphthyl derivatives.<sup>2a,10</sup> In particular, the phosphoramidites (e.g., **2**) have taken the pride of place among the most sought after ligands in catalytic reactions.<sup>11</sup> Recent literature reports have witnessed numerous applications utilizing BINOL and its phosphoramidites in asymmetric catalysis.<sup>11,12</sup> It is possible that strategic placement of substituents into the BINOL framework may lead to an improvement in the catalytic efficiency.

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Our interest in BINOL based systems is related in part to the continuing work on phosphorane and organophosphate chemistry.<sup>13,14</sup> In this context, we became interested in substituted BINOL systems that are more soluble in non-polar solvents. One way to carry this out is to introduce

*tert*-butyl groups onto the BINOL ring. We also wanted to explore the catalytic activity of its P(III) derivatives vis à vis those of unsubstituted BINOL. Surprisingly, to the best of our knowledge, there is no report on the use of enantiopure 6,6'-di-*tert*-butylated BINOL.<sup>15</sup> We felt that a simple route to enantiopure 6,6'-di-*tert*-butylated BINOL **3** would be a valued addition. Two other useful *enantiopure* BINOL derivatives, 3,3',6,6'-tetra-*tert*-butyl BINOL **4** and 3,3'-dibromo-6,6'-di-*tert*-butyl BINOL **5**, have been obtained using **3** as the precursor. Several phosphoramidite derivatives **7–14** (Chart 1) have been prepared by starting from the phosphorochloridite **6** (of **3**) which could be of practical utility in diverse asymmetric catalytic applications. An alternative route to the enantiopure bisphosphites [(6,6'-R<sub>2</sub>C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>)P]<sub>2</sub>[O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-6,6'-R<sub>2</sub>] [R = H **15**, *t*-Bu (**16**; new)] using the reaction of respective phosphorochloridite with sodium is also discussed herein; their identity is established by X-ray structures of the diseleno derivatives **17–18**. Finally, we demonstrate that the phosphoramidites **7–14** derived from **3** perform moderately well in the asymmetric reduction of acetophenone,<sup>16</sup> when simple BINOL based phosphoramidite derivatives fail, thus leaving scope for the exploitation of this di-*tert*-butyl BINOL **3** in chiral catalysis.

## 2. Results and discussion

### 2.1. Substituted BINOLS

Treatment of BINOL with an excess of *tert*-butyl chloride (eightfold) in the presence of anhydrous aluminum chloride at  $-78^\circ\text{C}$  afforded a mixture that showed two predominant products [ratio ~15:1; HPLC] corresponding to **3** and **4**, respectively, along with only trace amounts of unreacted BINOL. This reaction was conducted using racemic, (S)- or (R)-BINOL. Compound **3** could be readily separated from the others, without using column chromatography, by making use of its high solubility in hexane (Scheme 1); other minor products were relatively insoluble. The CD spectra of the so-crystallized samples of (S)-(+)- and (R)-(-)-**3** depicted in Figure 1 are essentially identical to those of the corresponding enantiomers of BINOL. This feature also shows that there is no loss of enantiomeric purity during the reaction. A simple but critical point to be noted is that the temperature has to be low; if the reaction is conducted at room temperature (or even at  $0^\circ\text{C}$ ), too many tarry products are formed.

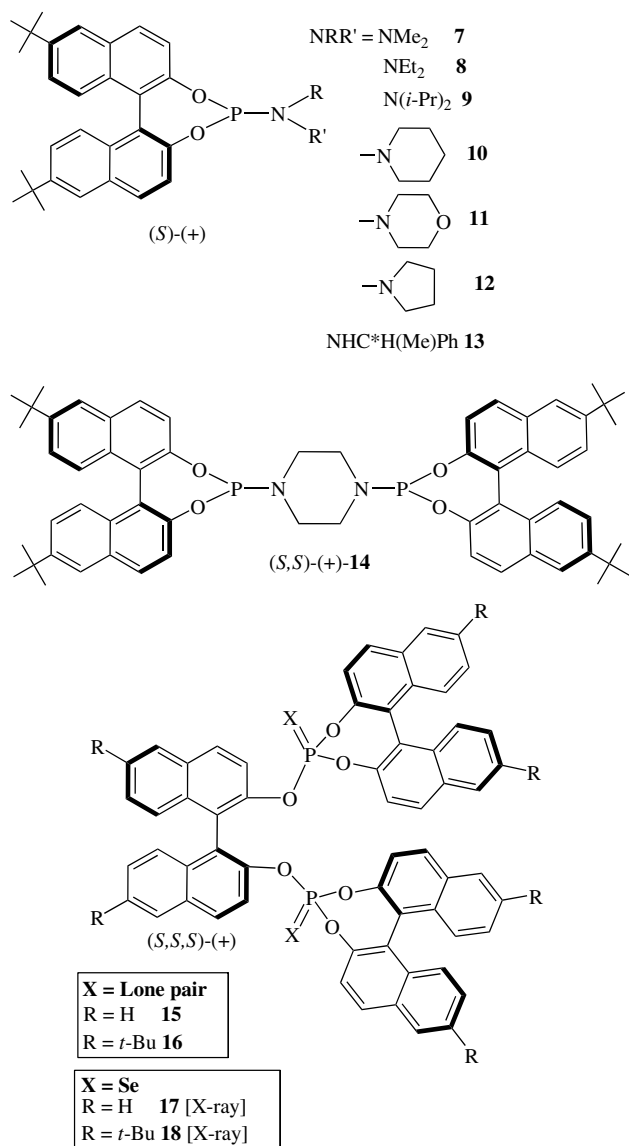
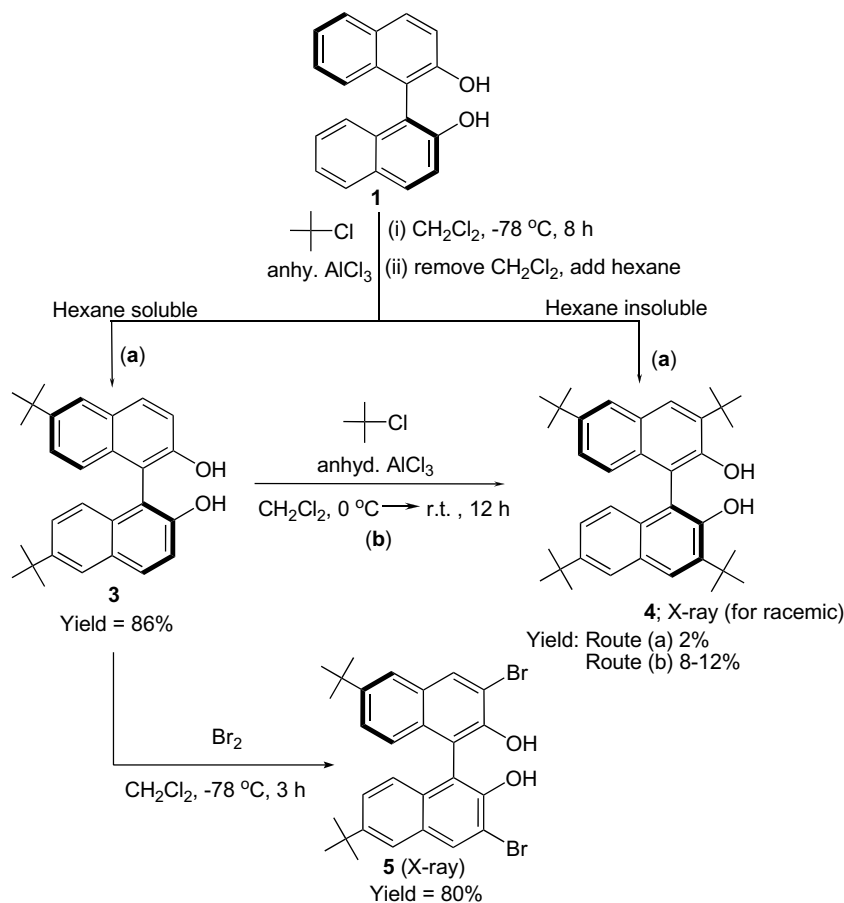
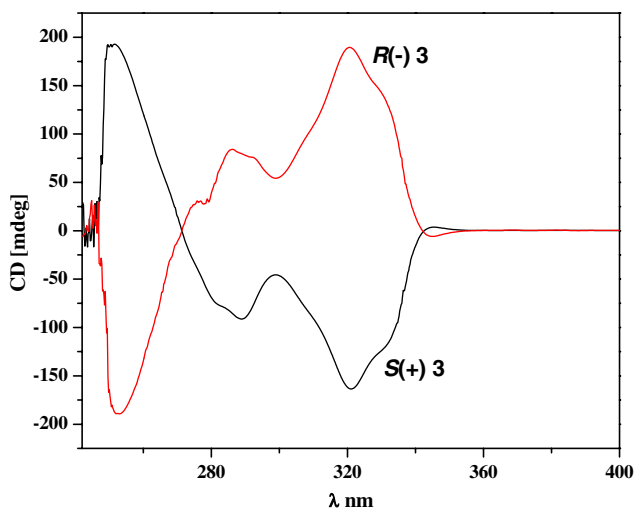


Chart 1.



Scheme 1.

Figure 1. CD spectra of (*R*)-(-)-**3** and (*S*)-(+)-**3**.

We have also checked other methods for the purification of **3**. Bisacetylation to **19** followed by hydrolysis using  $\text{CH}_3\text{O-Na/CH}_3\text{OH}$  (Scheme 2) worked well without any noticeable loss of enantiomeric purity. Although  $\text{LiAlH}_4$  and  $\text{NaBH}_4/\text{I}_2$  could be used for the conversion of **19** back to **3**, (obviously) sodium methoxide is much cheaper.

The second major component in the Friedel–Crafts reaction of BINOL (ca. 5%) was 3,3',6,6'-tetra-*tert*-butyl BINOL **4** (Fig. 2). The racemic form of this compound is known and can be prepared by starting with the corresponding bis-*tert*-butyl-2-naphthol.<sup>17</sup>

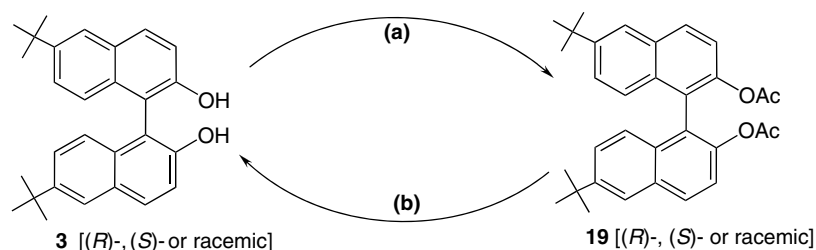
We made an attempt to obtain a better yield of **4** by further Friedel–Crafts reaction of **3**. Although we could only increase the yield up to ca. 12%, we were able to obtain the enantiopure (*S*)-form rather readily (see Scheme 1).

Bromination of **3** leads to 3,3'-dibromo-6,6'-di-*tert*-butylated BINOL **5** in very good (isolated) yields as shown in Scheme 1 (Fig. 3).

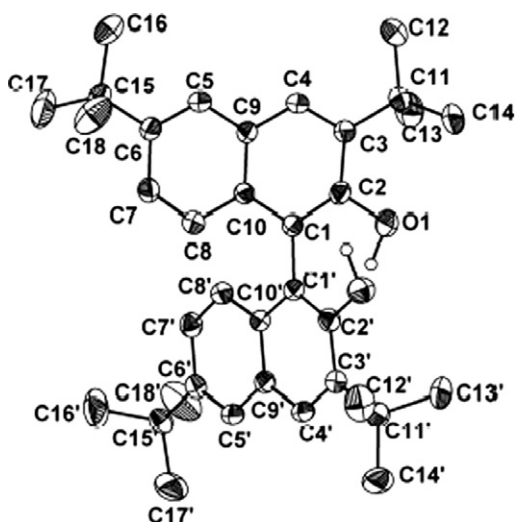
It is important to note that for *ortho*-bromination of BINOL, protection–deprotection and column chromatography are generally required (Scheme 3) while in the synthesis of **5**, no such step is needed.<sup>18</sup> It should also be noted that simple bromination (using  $\text{Br}_2$ ) of BINOL will lead to 6,6'-dibromo-BINOL.<sup>18d</sup>

## 2.2. Phosphoramidites and diphosphites

Phosphoramidites **7–14** were prepared in good yields via the phosphorochloridite **6** by using the general routes (cf. Scheme 4) in this type of chemistry. To prepare the diphos-



**Scheme 2.** Reagents and conditions: (a) (i) remove hexane, add  $\text{CH}_2\text{Cl}_2$ , (ii)  $\text{Ac}_2\text{O}$ /pyridine,  $0\text{ }^\circ\text{C}$ , (iii) crystallize from ether; (b)  $\text{CH}_3\text{ONa}/\text{CH}_3\text{OH}$ ,  $0\text{ }^\circ\text{C}$ , 1 h.

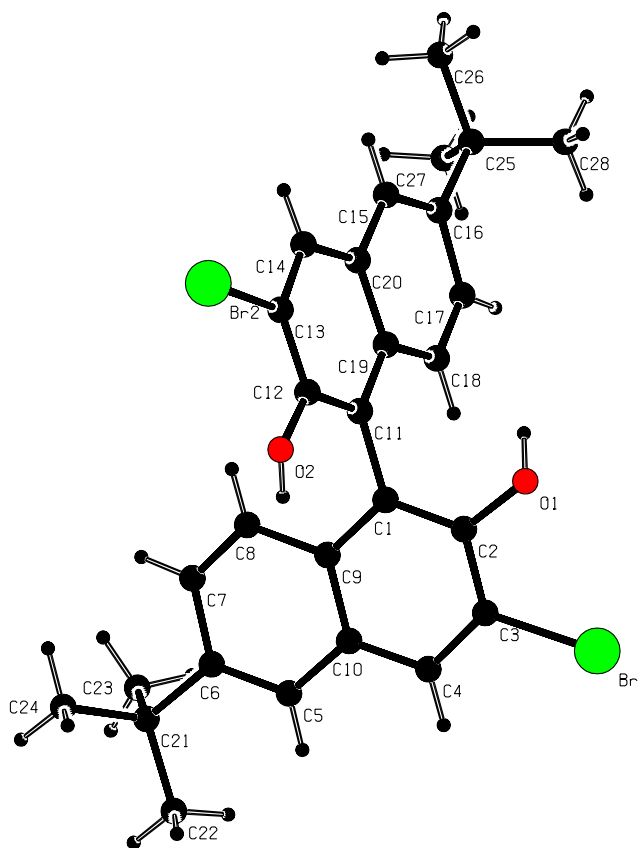


**Figure 2.** An ORTEP drawing of **4**. Intramolecular H-bond parameters:  $\text{O1-H1-O1}'$  1.01(4) Å, 2.86(3) Å, 3.231(4) Å, 103(2) $^\circ$ ; Symm equiv:  $-x+1, -y+1/2, z$ . Dihedral angle between two naphthyl rings is 73.42(3) $^\circ$ .

phites **15** and **16**, we treated the phosphorochloridites with metallic sodium in refluxing toluene (Scheme 5).<sup>19–22</sup> The mechanism of product formation would involve the ring opening and formation of  $\text{NaP}_x$  in addition to  $\text{NaCl}$ ; indeed the insoluble material obtained during these reactions is black, suggesting the formation of a phosphide as well. The identity of compounds **15** and **16** was confirmed by the X-ray structures of their diseleno derivatives **17** and **18** [ORTEP plot for enantiopure **17**, see Fig. 4]. Figure 5 shows the X-ray structure for **18** (racemic form).<sup>23</sup> Chelating diphosphite ligands such as **15** have played an important role in chiral catalysis,<sup>11d,19b,24</sup> hence the addition of new enantiopure diphosphites is likely to be a valuable asset in asymmetric synthesis (Table 1).

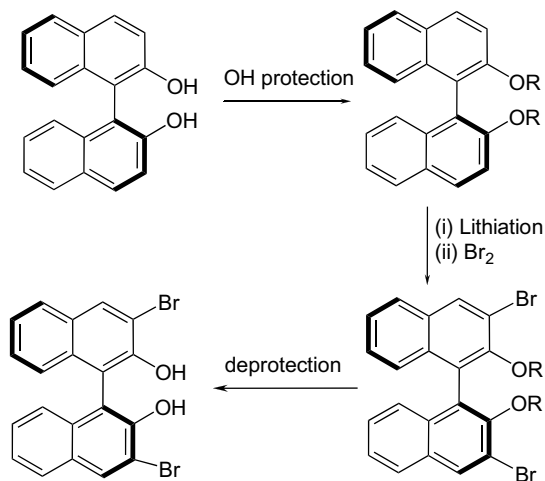
### 2.3. Asymmetric reduction of acetophenone and phenacyl chloride

Asymmetric borane reduction of prochiral ketones to enantiomerically enriched alcohols is a fundamental transformation in synthetic organic chemistry. Phosphinamides containing an  $\text{N-P=O}$  unit, and tricoordinated phospho-



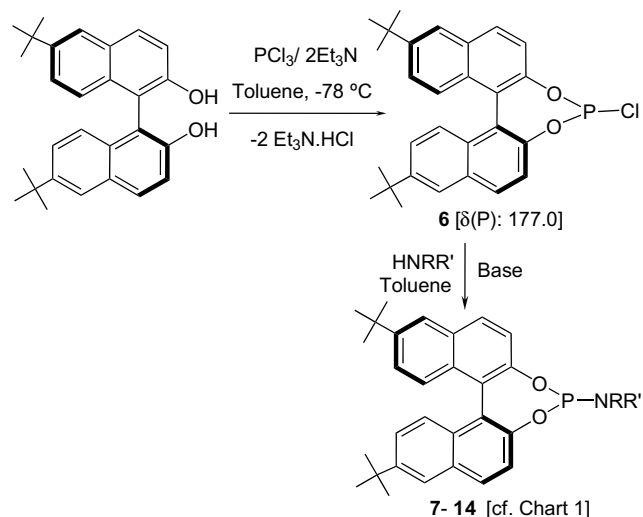
**Figure 3.** A PLATON drawing of **5** (disordered solvent could not be modeled) [orthorhombic, space group  $P2_12_12_1$ ,  $a = 10.1809(6)$ ,  $b = 11.5246(7)$ ,  $c = 31.796(2)$  Å,  $V = 3730.6(4)$  Å<sup>3</sup>,  $Z = 4$ ].

rus–borane complexes are efficient catalysts for the asymmetric reduction of ketones by borane.<sup>25,26</sup> Although there are other efficient catalysts for this purpose, we were curious to examine whether the phosphoramidites prepared in this study would induce enantiopure selectively in the reduction of acetophenone/phenacyl chloride or not. We found that in the reaction shown in Scheme 6, phosphoramidites, for example **8**, based on the di-*tert*-butylated BINOL were significantly more effective than the ones, for example **2b**, using unsubstituted BINOL, although the ee obtained was moderate. Either the (*R*)-enantiomer of **21** or the (*S*)-enantiomer of **22** was the major product. The



Scheme 3.

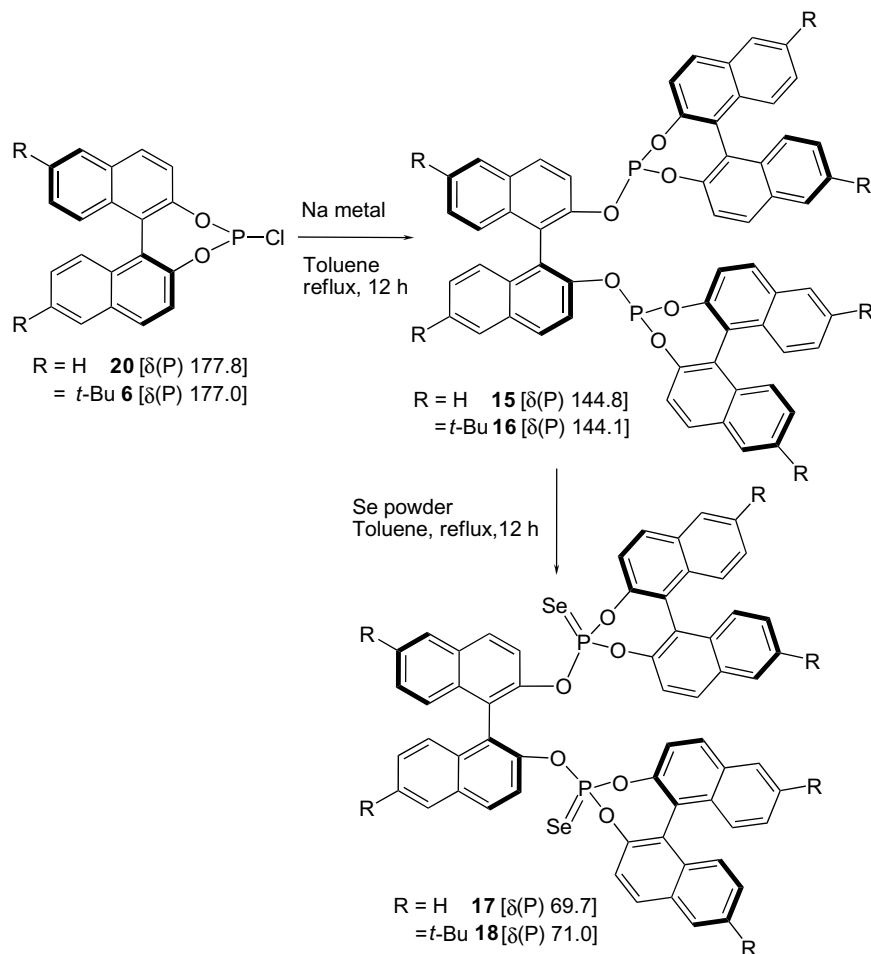
ee in the case of **22** was 43% using the *tert*-butylated derivative **8**, which is substantially higher than 10% using the simple BINOL derivative **2b**. Thus, we believe that there is room for improvement in cases where BINOL based derivatives are moderately efficient in catalytic asymmetric synthesis.<sup>27</sup> Efforts are being made in this direction (Table 2).



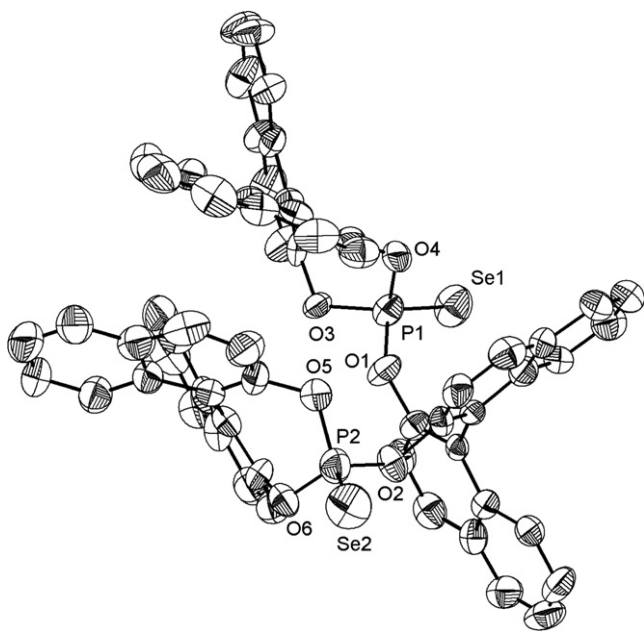
Scheme 4.

### 3. Conclusion

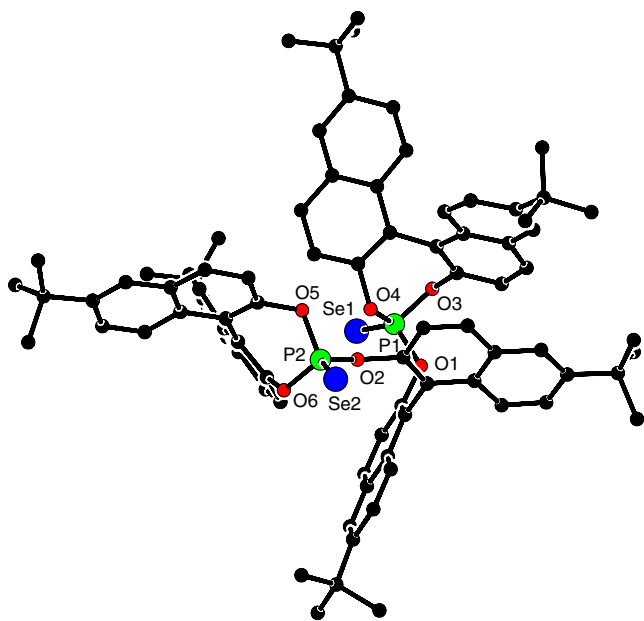
In conclusion, we have synthesized enantiopure *tert*-butylated and *ortho*-substituted bromo BINOLs by simple chromatography-free methods. The high solubility of **3** and its



Scheme 5.



**Figure 4.** An ORTEP drawing of **17**. Dihedral angles between naphthyl rings in each binaphthol residues located (a) between P1 and P2: 87.3(1)°, (b) at P1: 56.6(1)°, and (c) at P(2) 55.4(2)°. Configuration at P2 is *S* by checkcif.



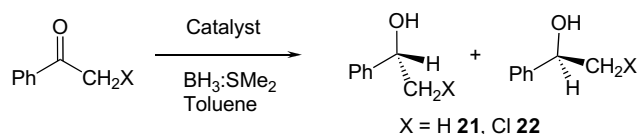
**Figure 5.** A PLATON drawing of **18** (racemic form, the other molecule in the asymmetric unit is not shown). Only selected atoms are labeled. Selected bond distances: P1–O1 1.578(4), P1–O3 1.576(4), P1–O4 1.585(4), P1–Se1 2.0441(16), P2–O2 1.575(3), P2–O5 1.595(3), P2–O6 1.588(3), P2–Se2 2.0432(14) Å. Dihedral angles between naphthyl rings in the binaphthol residue are: (a) 77.6(1)° for those located between P1 and P2, (b) 72.1(1)° for those located at P1, and (c) 59.1(1)° for those located at P(2).

enantiopure phosphorus derivatives may also be gainfully exploited in asymmetric synthesis when the products are less soluble. Enantiopure chelating diphosphite ligands based on BINOL and di-*tert*-butylated BINOL were pre-

**Table 1.** <sup>31</sup>P NMR data and specific rotation values for phosphoramidites **7–14**<sup>a</sup> and **15–18**

| Phosphorus compound | $\delta(\text{P})/\text{ppm}$ | Specific rotation $[\alpha]_{\text{D}}^{\text{c}}$ at 27 °C ( $c$ 0.5, $\text{CHCl}_3$ ) |
|---------------------|-------------------------------|--|
| <b>7</b>            | 148.1                         | +512.0   |
| <b>8</b>            | 149.3                         | +426.0   |
| <b>9</b>            | 151.1                         | +526.2   |
| <b>10</b>           | 149.3                         | +473.1   |
| <b>11</b>           | 144.3                         | +498.0   |
| <b>12</b>           | 149.7                         | +300.1   |
| <b>13</b>           | 151.3                         | +215.8   |
| <b>14</b>           | 144.2                         | +311.4   |
| <b>15</b>           | 144.8                         | +335.0 (Toluene)   |
| <b>16</b>           | 144.1                         | +269.8 (Toluene)   |
| <b>17</b>           | 69.7                          | +535.4 (Toluene)   |
| <b>18</b>           | 71.0                          | +442.3 (Toluene)   |

<sup>a</sup> Yields were essentially quantitative in all the cases.



**Scheme 6.**

**Table 2.** Details of the asymmetric reduction of acetophenone and phenacyl chloride (cf. **Scheme 6**) using phosphoramidites **2b** and **8–13**<sup>a</sup>

| Entry  | Catalyst               | Temperature (°C) | Solvent | Yield (%) | ee <sup>b</sup> (%) |
|--|------------------------|------------------|---------|-----------|---------------------|
| <i>Substrate: Acetophenone</i> <sup>c</sup>      |                        |                  |         |           |                     |
| 1  | <b>2b</b>              | rt               | Toluene | 90        | 2                   |
| 2  | <b>2b</b>              | 110              | Toluene | 86        | 8                   |
| 3  | <b>8</b>               | rt               | THF     | 86        | 15                  |
| 4  | <b>8</b>               | 50               | THF     | 83        | 18                  |
| 5  | <b>8</b>               | rt               | Toluene | 88        | 22                  |
| 6  | <b>8</b>               | 110              | Toluene | 84        | 30                  |
| 7  | <b>9</b>               | 110              | Toluene | 88        | 23                  |
| 8  | <b>10</b>              | 110              | Toluene | 78        | 24                  |
| 9  | <b>11</b>              | 110              | Toluene | 84        | 18                  |
| 10   | <b>12</b>              | 110              | Toluene | 88        | 24                  |
| 11   | <b>13</b> <sup>d</sup> | 110              | Toluene | 81        | 31 <sup>c</sup>     |
| <i>Substrate: Phenacyl chloride</i> <sup>d</sup> |                        |                  |         |           |                     |
| 12   | <b>2b</b>              | 110              | Toluene | 86        | 10 <sup>e</sup>     |
| 13   | <b>8</b>               | 110              | Toluene | 88        | 43 <sup>e</sup>     |
| 14   | <b>13</b> <sup>d</sup> | 110              | Toluene | 85        | 45 <sup>e</sup>     |

<sup>a</sup> 10 mol % of the catalyst was used.

<sup>b</sup> Checked by using both polarimeter and by chiral HPLC (chiralcel OD-H).

<sup>c</sup> In acetophenone reduction, the (*R*)-form of **21** was the dominant product.

<sup>d</sup> Here, we have used phosphoramidite **13** prepared using (*S*)-(+)-**3** and either (*R*)- or (*S*)- $\alpha$ -methylbenzylamine, although the ee and configuration of the product remained essentially the same.

<sup>e</sup> In phenacyl chloride reduction, the (*S*)-form of **22** was the dominant product.

pared by simply reacting sodium with the corresponding phosphorochloridites. Modified BINOL based enantiopure phosphoramidites were more effective than unsubstituted

BINOL based ones in the asymmetric reduction of acetophenone/phenacyl chloride, thus suggesting that an improvement in enantiopure induction is possible using derivatives of enantiopure compound **3**.

#### 4. Experimental

Chemicals were purified when required according to standard procedures.<sup>28</sup> All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{H} NMR spectra were recorded using a 200 or a 400 MHz spectrometer in CDCl<sub>3</sub> (unless stated otherwise) with shifts referenced to SiMe<sub>4</sub> ( $\delta = 0$ ) or 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0$ ). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. For TLC, glass microslides were coated with silica-gel-GF<sub>254</sub> (mesh size 75  $\mu$ m) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100–200 mesh size was used. LC–MS or GC–MS equipment was used to record mass spectra for isolated compounds where appropriate. LC–MS data were obtained using electrospray ionization (positive mode) on a C-18 column at a flow rate of 0.2 mL/min using MeOH–water (90:10) as eluent. GC–MS data were obtained on EI mode using ZB-1 column. Retention time ( $t_R$ ) values for GC–MS (helium flow rate 4 mL/min) and LC–MS are quoted in min. CD spectra were recorded on a Spectropolarimeter. Specific rotation was measured using polarimeter and chiral HPLC using chiralcel OD-H column.

The phosphorochloridite of BINOL **20** and the phosphoramidite **2** (R = R' = Me **2a**, Et **2b**, and *i*-Pr **2c**) were prepared by reported procedures.<sup>29</sup> Compounds **7–14** were synthesized by general procedures as shown.

#### 4.1. Procedure for (R)-(–) or (S)-(+)-6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol **3** [6,6'-di-*tert*-butylated BINOL]

A solution of (R)-(+)- or (S)-(–)-1,1'-bi-2-naphthol (5.0 g, 17.5 mmol) in 150 mL of dry dichloromethane was cooled to  $-78^\circ\text{C}$ , and 16 mL (13.0 g, 139.7 mmol) of *tert*-butyl chloride was added via pipette followed by the portion-wise addition of anhydrous AlCl<sub>3</sub> (3.7 g, 27.9 mmol). The reaction mixture was stirred at the same temperature (monitored by TLC) for 12 h, quenched with ice-cold water, and then extracted with additional dichloromethane (3  $\times$  40 mL). The organic layer was washed with saturated NaHCO<sub>3</sub> solution (3  $\times$  20 mL), dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>), and the solvent evaporated under reduced pressure to give the crude product as a foam. To this material, 140 mL of hexane was added, and the insolubles removed by filtration. Crystals of 6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol (5.9 g) were obtained by slow evaporation of the solvent over a period of 24 h at 25  $^\circ\text{C}$ . The crystallized portion, which constituted as most of the product, was enantiopure in our hands. It is possible that a slight amount of racemization could have occurred in what was remaining in the mother-liquor, but this is difficult to verify

because of traces of other impurities. *Note*: If the temperature is higher, a lot of black material is formed and the yields are lower. The yield of **3** as shown by reverse phase HPLC using C-18 column was  $\sim 80\%$ .

**4.1.1. (S)-(+)-6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol (S)-(+)-**3**.** Yield 5.91 g (86%); white solid; mp 112–114  $^\circ\text{C}$ ; Anal. Calcd for C<sub>28</sub>H<sub>30</sub>O<sub>2</sub>: C, 84.38; H, 7.59. Found: C, 84.36; H, 7.59;  $\nu_{\text{max}}$  (KBr) 3532, 2959, 1597, 1155, 826 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.96 (d, 2H,  $J = 8.8$  Hz), 7.84 (d, 2H,  $J = 1.6$  Hz), 7.42 (dd, 2H,  $J = 8.8$  and 1.6 Hz), 7.38 (d, 2H,  $J = 8.8$  Hz), 7.16 (d, 2H,  $J = 8.8$  Hz), 5.02 (s, 2H, OH), 1.41 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 152.3, 146.7, 131.5, 131.3, 129.4, 126.4, 124.0, 123.5, 117.6, 110.7 (all aromatic-C), 34.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), GC–MS: 398.2 [M]<sup>+</sup>; [ $\alpha_{\text{D}}^{27}$ ] = +48.0 (*c* 1, THF).

**4.1.2. (R)-(–)-6,6'-Di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol (R)-(–)-**3**.** The [ $\alpha_{\text{D}}$ ] value is  $-48.0$  for the (R)-isomer. The yield, mp, IR, and NMR data were identical to that of (S)-(+)-**3**. For the racemic form, the mp was 116  $^\circ\text{C}$ .

**4.1.3. (S)-(+)-3,3',6,6'-Tetra-*tert*-butyl-1,1'-binaphthalene 2,2'-diol **4**.** A solution of (S)-(+)-**3** (1.00 g, 2.5 mmol) in dry dichloromethane (40 mL) was cooled to 0  $^\circ\text{C}$ , and 4.5 mL of *tert*-butyl chloride (0.38 g, 40.2 mmol) was added followed by anhydrous AlCl<sub>3</sub> (0.53 g, 4.1 mmol). The reaction mixture was stirred for 1 h at 0  $^\circ\text{C}$ , brought to room temperature, and stirring continued for 12 h more. It was then quenched with ice-cold water (10 mL), and extracted using dichloromethane (3  $\times$  20 mL). The organic layer was washed with saturated NaHCO<sub>3</sub> solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent evaporated. Hexane (30 mL) was added, upon which (S)-(+)-**4** precipitated out. After filtration, this product was crystallized from dichloromethane.

**4.1.3.1. Compound (S)-(+)-**4**.** Yield 0.11 g (8%); white solid; colorless blocks; mp  $>280^\circ\text{C}$ ; Anal. Calcd for C<sub>36</sub>H<sub>46</sub>O<sub>2</sub>: C, 84.66; H, 9.08. Found: C, 84.62; H, 9.09;  $\nu_{\text{max}}$  (KBr) 3495, 2959, 1599, 1150, 826 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 7.92 (s, 2H); 7.80 (s, 2H), 7.27 (dd, 2H,  $J = 8.8$  and 1.6 Hz), 7.00 (d, 2H,  $J = 8.8$  Hz), 5.32 (s, 2H, OH), 1.56 and 1.39 (2s, 36H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (50 MHz, CDCl<sub>3</sub>) 152.3, 146.5, 138.3, 130.2, 129.1, 127.4, 125.4, 123.5, 111.5 (all aromatic-C); 35.5 and 34.6 (2s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 and 29.8 (2s, C(CH<sub>3</sub>)<sub>3</sub>); [ $\alpha_{\text{D}}^{27}$ ] = +38.2 (*c* 1, THF) for the (S)-isomer. X-ray structural was carried out on a racemic sample **4**.

**4.1.4. 3,3'-Dibromo-6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol **5**.** To a solution of (R)-(–)- or (S)-(+)-**3** (1.00 g, 2.5 mmol) in dichloromethane (30 mL) cooled to  $-78^\circ\text{C}$ , bromine (1.10 g, 6.8 mmol) in dichloromethane (10 mL) was added drop-wise (15 min). The mixture was stirred for 3 h, brought to room temperature, stirred further for 10 min and then quenched with ice-cold water. The mixture was extracted with more dichloromethane (3  $\times$  30 mL), and the organic layer was washed with sodium thiosulfate solution to remove the excess of bromine. Washing with a brine solution, drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and removal of

solvent under reduced pressure gave the crude product. Hexane (25 mL) was added, and the insoluble **5** was collected by filtration and crystallized from ethyl acetate–hexane (1:2) mixture. A partial X-ray structure for (*S*)-(+)-**5** (see Fig. 3) is also available for this compound.

**4.1.4.1. Compound (*S*)-(+)-**5**.** Yield 0.9 g (80%); white solid; colorless blocks; mp 208–210 °C; Anal. Calcd for C<sub>28</sub>H<sub>28</sub>Br<sub>2</sub>O<sub>2</sub> (after drying): C, 60.45; H, 5.07. Found: C, 60.48; H, 5.17;  $\nu_{\max}$  (KBr) 3505, 2957, 2861, 1599, 1148, 826 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.21 (s, 2H), 7.72 (d, 2H,  $J = 1.6$  Hz), 7.39 (dd, 2H,  $J = 8.8$  Hz and 2.0 Hz), 7.06 (d, 2H,  $J = 9.2$  Hz), 5.44 (s, 2H, OH), 1.36 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 147.6, 132.8, 130.9, 129.8, 126.6, 124.4, 122.5, 114.4, 112.0 (all aromatic-C), 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (s, C(CH<sub>3</sub>)<sub>3</sub>); LC–MS 554.0 [M]<sup>+</sup> and 556.0 [M+2]<sup>+</sup> (1:1);  $[\alpha]_{\text{D}}^{27} = -50.0$  ( $c$  1, THF) for the (*R*)-isomer and  $[\alpha]_{\text{D}}^{27} = +50.0$  ( $c$  1, THF) for the (*S*)-isomer at 27 °C. An X-ray structure was determined for the (*S*)-(+)-**5** after crystallization from ethyl acetate–hexane mixture (1:2).

## 4.2. Synthesis of phosphorus(III) derivatives 6–14 and I

**4.2.1. Synthesis of the phosphorochloridite (*S*)-(–)-**6**.** Distilled PCl<sub>3</sub> (0.50 g, 3.6 mmol) in 40 mL of toluene was cooled to –78 °C and triethylamine (1.5 g, 15.1 mmol) was added. To this solution, solid (*S*)-(+)-**1** (1.20 g, 3.0 mmol) was slowly added (30 min). After another 30 min of stirring at –78 °C, the reaction mixture was brought to room temperature and stirred for a further 2 h. Filtration followed by the removal of solvent (and residual PCl<sub>3</sub>) in vacuo afforded **6** as a white solid.

**4.2.1.1. 9,14-Di-*tert*-butyl-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene **6**.** Yield quantitative; pale yellow powder; mp 72–74 °C; Anal. Calcd for C<sub>28</sub>H<sub>28</sub>O<sub>2</sub>ClP: C, 72.64; H, 6.10. Found: C, 76.62; H, 6.11;  $\nu_{\max}$  (KBr) 2963, 1597, 1472, 1155, 1020, 731 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.01 (dd, 2H,  $J = 8.2$  and 2.4 Hz), 7.91 (s, 2H), 7.51 (d, 2H,  $J = 8.2$  Hz), 7.45 (dd ~ t, 4H,  $J = 8.3$  and 2.5 Hz), 1.45 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 148.5, 148.2, 132.0, 131.6, 130.8, 130.0, 126.8, 126.7, 125.7, 125.5, 121.2 (d,  $J = 48.0$  Hz), 123.5, 34.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (s, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{P}}$  (80 MHz, CDCl<sub>3</sub>) 177.0;  $[\alpha]_{\text{D}}^{27} = +835.0$  ( $c$  0.5, toluene).

**4.2.2. Synthesis of phosphoramidite (*S*)-(+)-**7**.** Gaseous dimethylamine (dried over KOH) was bubbled into a stirred solution of **6** in toluene (20 mL) for 2 h at –78 °C. The reaction mixture was kept at 0 °C overnight, filtered, and the filtrate concentrated in vacuo to yield **7** as a white solid.

**4.2.2.1. (9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-dimethyl amine **7**.** Yield quantitative; white solid; mp 126–128 °C; Anal. Calcd for C<sub>30</sub>H<sub>34</sub>NO<sub>2</sub>P: C, 76.41; H, 7.27; N, 2.97. Found: C, 76.36; H, 7.30; N, 3.07;  $\nu_{\max}$  (KBr) 2957, 1589, 1460, 1250, 810 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.83 (d, 1H,  $J = 8.8$  Hz), 7.77 (d, 1H,  $J = 8.8$  Hz), 7.74 (dd, 2H,  $J = 8.8$  and 1.6 Hz), 7.13–7.39 (m, 6H), 2.47 (d, 6H,  $J =$

9.2 Hz, N(CH<sub>3</sub>)<sub>2</sub>), 1.34 and 1.33 (2s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 148.5, 148.4, 147.9, 146.3, 130.3, 129.1, 125.8, 124.6, 123.9, 122.2, 120.7 (all aromatic-C), 34.9 (d,  $J = 21.0$  Hz, N(CH<sub>3</sub>)<sub>2</sub>), 33.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.2 (s, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (160 MHz, CDCl<sub>3</sub>) 148.1;  $[\alpha]_{\text{D}}^{27} = +512.0$  ( $c$  0.5, CHCl<sub>3</sub>).

**4.2.3. Synthesis of phosphoramidites 8–12.** The corresponding amine (2.0 mmol) in toluene (10 mL) was added drop-wise to a stirred solution of phosphorochloridite (*S*)-(+)-**6** (1.0 mmol) in toluene (20 mL) over a period of 5 min at 0 °C. After 15 min, the solution was slowly brought up to room temperature and the stirring continued for 10 h. Filtration followed by removal of solvent in vacuo afforded **8–12** as solids.

**4.2.3.1. (9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-diethyl amine **8**.** Yield quantitative; white solid; mp 132 °C; Anal. Calcd for C<sub>32</sub>H<sub>38</sub>NO<sub>2</sub>P: C, 76.93; H, 7.67; N, 2.80. Found: C, 76.92; H, 7.74; N, 2.81;  $\nu_{\max}$  (KBr) 2963, 1589, 1462, 1235, 1208, 949 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.29–7.98 (m, 8H, all Ar-*H*), 7.23 (d, 2H,  $J = 8.8$  Hz), 3.08 and 2.99 (2m, 4H, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.46 and 1.51 (2s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.07 (t, 6H,  $J = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>),  $\delta_{\text{C}}$  (50 MHz, CDCl<sub>3</sub>) 149.4 (d,  $J = 20.6$  Hz), 149.3, 147.4, 147.0, 130.1, 129.7, 126.9, 124.9, 123.3, 122.1, 121.9 (all aromatic-C), 38.4 (d,  $J = 22.3$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 14.8 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>);  $\delta_{\text{P}}$  (160 MHz, CDCl<sub>3</sub>) 149.3;  $[\alpha]_{\text{D}}^{27} = +426.0$  ( $c$  0.5, CHCl<sub>3</sub>).

**4.2.3.2. (9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-diisopropyl amine **9**.** Yield quantitative; white solid; mp 150–152 °C; Anal. Calcd for C<sub>34</sub>H<sub>42</sub>NO<sub>2</sub>P: C, 77.40; H, 8.02; N, 2.65. Found: C, 77.50; H, 8.08; N, 2.60;  $\nu_{\max}$  (KBr) 2965, 1589, 1464, 1235, 1200, 947 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.97 (d, 1H,  $J = 8.0$  Hz), 7.90 (s, 1H), 7.88 (s, 1H), 7.52 (d, 1H,  $J = 8.0$  Hz), 7.48 (d, 1H,  $J = 8.0$  Hz), 7.43 (dd ~ t, 1H,  $J = 8.0$  Hz and 4.0 Hz), 7.38 (s, 1H), 7.27 (d, 1H,  $J = 8.0$  Hz), 7.23 (d, 2H,  $J = 8.0$  Hz), 3.41–3.51 (2m, 2H, N(CH(CH<sub>3</sub>)<sub>2</sub>)), 1.48 and 1.46 (2s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 and 1.24 (2d, 12H,  $J = 6.7$  Hz, N(CH(CH<sub>3</sub>)<sub>2</sub>));  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 149.8, 146.9 (d,  $J = 20.6$  Hz), 130.1, 129.3, 129.1, 128.3, 127.0, 124.8, 123.3, 122.4 (all aromatic-C), 44.7 (d,  $J = 27.0$  Hz, N(CH(CH<sub>3</sub>)<sub>2</sub>)), 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 19.2 (s, N(CH(CH<sub>3</sub>)<sub>2</sub>)),  $\delta_{\text{P}}$  (160 MHz, CDCl<sub>3</sub>) 151.1;  $[\alpha]_{\text{D}}^{27} = +526.2$  ( $c$  0.5, CHCl<sub>3</sub>).

**4.2.3.3. 1-(9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-piperidine **10**.** Yield quantitative; white solid; mp 172 °C; Anal. Calcd for C<sub>33</sub>H<sub>38</sub>NO<sub>2</sub>P: C, 77.47; H, 7.49; N, 2.74. Found: C, 77.42; H, 7.50; N, 2.70;  $\nu_{\max}$  (KBr) 2963, 1593, 1466, 1209, 1067, 947 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.97 (d, 1H,  $J = 8.0$  Hz), 7.93 (d, 1H,  $J = 8.0$  Hz), 7.84 (br s, 2H), 7.56 (d, 1H,  $J = 8.0$  Hz), 7.46 (d, 1H,  $J = 8.0$  Hz), 7.42 (s, 2H), 7.37 (dd, 1H,  $J = 8.0$  Hz and 1.6 Hz), 7.29 (d, 1H,  $J = 12.0$  Hz), 3.06 (m, 4H, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–)), 1.52 and 1.46 (2m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.42 and 1.39 (2s, 18H C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 148.2, 131.4, 131.1,



130.5, 127.1, 126.9, 125.4, 123.5, 121.2, 120.9 (all aromatic-C), 46.4 (s, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)), 34.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 26.1 (s, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)), 24.3 (s, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)),  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 149.3;  $[\alpha]_D^{27} = +473.1$  (c 0.5, CHCl<sub>3</sub>).

**4.2.3.4. 4-(9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-morpholine 11.** Yield quantitative; white solid; mp 154–156 °C; Anal. Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>O<sub>3</sub>P: C, 74.83; H, 7.06; N, 2.73. Found: C, 74.71; H, 7.07, N, 2.78;  $\nu_{\max}$  (KBr) 2959, 1589, 1462, 1233, 945 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.97 (d, 1H, *J* = 8.7 Hz), 7.92 (d, 1H, *J* = 8.7 Hz), 7.88 (d, 1H, *J* = 8.7 Hz), 7.52 (d, 1H, *J* = 8.7 Hz), 7.38–7.45 (m, 4H), 7.29 (d, 1H, *J* = 6.8 Hz), 7.21 (s, 1H), 3.58 (br s, 4H, N(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-)), 3.12 and 3.02 (2m, 4H, N(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-)), 1.46 and 1.45 (2s, 36H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 148.8, 147.5, 147.3, 130.9, 130.2, 129.9, 129.0, 126.8, 125.1, 123.4, 121.7 (all aromatic-C), 67.9 and 65.3 (2s, N(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-)), 44.8 (s, N(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-)), 44.5, 44.1, 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 144.3;  $[\alpha]_D^{27} = +498.0$  (c 0.5, CHCl<sub>3</sub>).

**4.2.3.5. 1-(9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-pyrrolidine 12.** Yield quantitative; white solid; mp 136–138 °C; Anal. Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>P: C, 77.24; H, 7.29; N, 2.81. Found: C, 77.27; H, 7.29, N, 2.89;  $\nu_{\max}$ (KBr) 2961, 1588, 1462, 1209, 1063, 949 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.96 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 7.51 (d, 1H, *J* = 8.0 Hz), 7.39–7.46 (m, 4H), 7.29 (d, 1H, *J* = 8.0 Hz), 7.22 (d, 1H, *J* = 12.0 Hz), 3.22 and 2.98 (2m, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)), 1.73 (m, 4H, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)), 1.46 and 1.45 (2s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 149.8, 149.4, 147.3, 147.0, 131.4, 131.1, 130.9, 130.7, 130.1, 126.8, 123.3, 121.9, 44.7 (d, *J* = 15.0 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)), 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 25.9 (d, *J* = 4.0 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)),  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 149.7;  $[\alpha]_D^{27} = +300.1$  (c 0.5, CHCl<sub>3</sub>).

**4.2.4. Synthesis of phosphoramidites 13 and 14.** The amine (1.0 mmol) and dry triethylamine (1.0 mmol) in toluene (10 mL) were added drop-wise to a stirred solution of **6** (1.0 mmol) in toluene (20 mL) over a period of 5 min at 0 °C. After 15 min, the solution was slowly brought up to room temperature and the stirring continued for 10 h. The precipitate was filtered off and the solvent removed in vacuo to obtain **13** or **14** as a solid.

**4.2.4.1. (9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-(1-phenyl-ethyl)-amine 13.** Yield quantitative; white solid; mp 102–104 °C; Anal. Calcd for C<sub>36</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>P: C, 78.95; H, 6.99; N, 2.56. Found: C, 79.04; H, 6.97, N, 2.55;  $\nu_{\max}$ (KBr) 3368, 2963, 1588, 1460, 1209, 1065, 947 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.25–7.90 (m, 15H, all Ar-*H*), 4.67 (m, 1H, PNH), 3.48 (dd, 1H, *J* = 12.0 Hz and 4.0 Hz, NHCH(CH<sub>3</sub>)Ph), 1.63 (d, 3H, *J* = 8.0 Hz, CH<sub>3</sub>), 1.51 and 1.50 (2s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 148.9, 147.4, 147.0, 145.8, 131.0, 130.1, 129.3, 128.5, 128.3, 127.0, 126.8, 126.1, 126.0, 125.1, 123.4, 123.3, 122.4, 121.7 (all aromatic-C), 50.5 (d, *J* = 23.0 Hz, NCH(CH<sub>3</sub>)), 34.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3

(s, C(CH<sub>3</sub>)<sub>3</sub>), 26.7 (s, NCH(CH<sub>3</sub>));  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 151.3;  $[\alpha]_D^{27} = +215.8$  (c 0.5, CHCl<sub>3</sub>).

**4.2.4.2. 1,4-Bis-(9,14-Di-*tert*-butyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene-4-yl)-piperazine 14.** Yield quantitative; white solid; mp 246–248 °C; Anal. Calcd for C<sub>60</sub>H<sub>64</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 76.74; H, 6.87. Found: C, 76.73; H, 6.88, N, 2.98;  $\nu_{\max}$ (KBr) 2959, 1588, 1464, 1209, 1067, 941 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.23–7.99 (m, 20H, all Ar-*H*), 2.97 (br s, 8H, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)N), 1.46 and 1.42 (2s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_C$  (400 MHz, CDCl<sub>3</sub>) 147.3, 147.0, 145.7, 145.4, 136.2, 129.7, 129.2, 129.0, 128.9, 128.5, 128.3, 127.3, 126.5, 125.1, 124.8, 123.6, 123.4, 123.3, 122.0, 121.7, 121.6, 120.7, 120.0, 119.9 (all aromatic-C), 43.8 (d, *J* = 22.0 Hz, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)N), 33.0 and 32.9 (2s, C(CH<sub>3</sub>)<sub>3</sub>), 29.5 and 29.4 (2s, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 144.2;  $[\alpha]_D^{27} = +311.4$  (c 0.5, CHCl<sub>3</sub>).

**4.2.5. Synthesis of phosphorochloridite ( $\pm$ ) I given in Ref. 20 of the manuscript.** An excess of PCl<sub>3</sub> (1.50 g, 10.8 mmol) was added to 3,3',6,6'-tetra-*tert*-butyl-1,1'-binaphthalene 2,2'-diol (0.40 g, 0.78 mmol), and the mixture was refluxed for 3 d. Excess PCl<sub>3</sub> was removed by distillation to obtain **I** as a white solid.

**4.2.5.1. 2,6,9,14-Tetra-*tert*-butyl-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene I.** Yield quantitative; white solid; mp 138–140 °C; Anal. Calcd for C<sub>36</sub>H<sub>44</sub>ClO<sub>2</sub>P: C, 75.18; H, 7.71. Found: C, 75.23; H, 7.78;  $\nu_{\max}$ (KBr) 2963, 1597, 1209, 1155, 826 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.94 (s, 2H), 7.84 (s, 2H), 7.34 (d, 2H, *J* = 8.8 Hz), 7.20 (d, 1H, *J* = 7.2 Hz), 7.00 (d, 1H, *J* = 8.8 Hz), 1.58 and 1.41 (2s, 36H, C(CH<sub>3</sub>)<sub>3</sub>);  $\delta_C$  (50 MHz, CDCl<sub>3</sub>) 152.3, 146.5, 138.3, 130.2, 129.0, 127.4, 125.5, 123.5, 123.4, 111.5 (all aromatic-C), 35.5 and 34.6 (2s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 and 29.8 (2s, C(CH<sub>3</sub>)<sub>3</sub>),  $\delta_P$  (80 MHz, CDCl<sub>3</sub>) 172.1.

### 4.3. Reaction of phosphorochloridites with sodium: formation of diphosphites 15 and 16

A mixture of phosphorochloridite (1.0 mmol) **20**, or **6** and sodium metal (35 mg, 1.5 mmol) in dry toluene (30 mL) was heated at reflux for 18 h. The mixture was filtered through a frit and the solvent removed under vacuo. The compound was purified by flash chromatography (dry nitrogen) using dry hexane as the eluent.

**4.3.1. Compound 15 (known compound).** Yield 0.21 g (60%); white powder; mp 186 °C. (lit. 188 °C<sup>19b</sup>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.20–7.93 (many lines, 32H, all Ar-*H*); 6.36 (d, 2H, *J* = 8.8 Hz), 5.99 (d, 2H, *J* = 8.8 Hz);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 147.6, 146.3, 145.6, 133.1, 131.7, 131.4, 131.1, 130.9, 130.4, 129.3, 129.1, 128.3, 128.2, 127.2, 127.0, 126.4, 125.9, 125.6, 121.0, 120.5, 119.7 (all aromatic-C);  $\delta_P$  (160 MHz, CDCl<sub>3</sub>) 144.8 (lit.: 145.2 ppm<sup>19b</sup>);  $[\alpha]_D^{27} = +335$  (c 0.5, toluene) for the (*S*)-isomer.

**4.3.2. Compound 16.** Yield 0.27 g (58%); white powder; mp 148–150 °C; Anal. Calcd for C<sub>84</sub>H<sub>84</sub>O<sub>6</sub>P<sub>2</sub>: C, 80.67;

H, 6.77. Found: C, 80.76; H, 6.74;  $\nu_{\max}$  (KBr) 2961, 1589, 1497, 1462, 1215, 947, 816  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.87 (d, 2H,  $J = 8.8$  Hz), 7.29–7.85 (m, 24H), 7.17 (d, 2H,  $J = 8.8$  Hz), 6.35 (d, 2H,  $J = 8.8$  Hz), 1.39 (s, 54H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 148.2, 147.3, 146.0, 145.4, 131.8, 131.4, 130.7, 130.2, 128.9, 126.9, 126.2, 126.0, 125.1, 124.0, 123.1, 121.1, 120.4, 122.0, 119.6, 34.8 (s,  $\text{C}(\text{CH}_3)_3$ ), 31.4 (s,  $\text{C}(\text{CH}_3)_3$ ),  $\delta_{\text{P}}$  (160 MHz,  $\text{CDCl}_3$ ) 144.1;  $[\alpha]_{\text{D}}^{27} = +269.8$  ( $c$  0.5, toluene) for the (*S*)-isomer.

#### 4.4. Reaction of 15 and 16 with selenium

A mixture of compound **15** or **16** (0.2 mmol) and selenium powder (0.08 g, 1.0 mmol) in dry toluene (20 mL) was heated at reflux for 18 h. Filtration followed by removal of solvent in vacuum, purification by silica-gel column chromatography (hexane) and crystallization from dichloromethane–hexane mixture (1:2) afforded the diselenium products **17** or **18**.

**4.4.1. Compound 17.** Yield 0.16 g (76%); white solid; colorless plates type; mp 280 °C; Anal. Calcd for  $\text{C}_{60}\text{H}_{36}\text{O}_6\text{P}_2\text{Se}_2$ : C, 67.18; H, 3.38. Found: C, 67.23; H, 3.35;  $\nu_{\max}$  (KBr) 2920, 1589, 1507, 1460, 1213, 1069, 959, 876  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.74–7.93 (m, 4H), 7.72 (s, 2H), 7.44–7.66 (m, 12H), 7.36–7.39 (m, 8H), 7.28 (s, 2H), 7.20 (br s, 4H), 6.36 (d, 2H,  $J = 8.8$  Hz), 6.00 (d, 2H,  $J = 8.8$  Hz);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 147.8, 147.6, 146.3, 145.7, 145.6, 133.0, 132.3, 132.0, 131.7, 131.4, 131.1, 130.9, 130.4, 129.2, 129.0, 128.3, 128.2, 127.2, 127.0, 126.3, 125.8, 125.6, 122.5, 122.1, 120.9, 120.4, 119.6 (all aromatic-C);  $\delta_{\text{P}}$  (160 MHz,  $\text{CDCl}_3$ ) 69.7 ( $J_{\text{P-Se}} = 960$  Hz);  $[\alpha]_{\text{D}}^{27} = +535.4$  ( $c$  0.5, toluene) for the (*S*)-isomer; An X-ray structure was determined for the racemic sample after crystallization from dichloromethane–hexane mixture (1:2).

**4.4.2. Compound 18.** Yield 0.23 g (81%); white solid; colorless blocks; mp 268–270 °C; Anal. Calcd for  $\text{C}_{84}\text{H}_{84}\text{O}_6\text{P}_2\text{Se}_2$ : C, 71.58; H, 6.01. Found: C, 71.57; H, 6.04;  $\nu_{\max}$  (KBr) 2957, 1589, 1497, 1462, 1361, 1263, 1120, 954, 822  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.62–7.83 (m, 8H), 7.42–7.49 (m, 8H), 7.26–7.36 (m, 4H), 7.22–7.24 (m, 6H), 6.32 (d, 2H,  $J = 8.8$  Hz), 5.96 (d, 2H,  $J = 8.8$  Hz), 1.48, 1.47, 1.36 (3s, 54H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 148.3, 148.2, 148.1, 147.4, 147.2, 146.0, 145.9, 145.4, 145.3, 131.7, 131.3, 130.8, 130.7, 130.4, 130.2, 128.9, 127.0, 126.9, 126.1, 126.0, 125.1, 124.0, 123.2, 123.0, 121.9, 121.0, 120.6, 120.3, 119.5, 34.8, 34.7, (2s,  $\text{C}(\text{CH}_3)_3$ ), 31.3, 31.1 (2s,  $\text{C}(\text{CH}_3)_3$ );  $\delta_{\text{P}}$  (160 MHz,  $\text{CDCl}_3$ ) 71.0 ( $J_{\text{P-Se}} = 1056$  Hz);  $[\alpha]_{\text{D}}^{27} = +442.3$  ( $c$  0.5, toluene) for the (*S*)-isomer.

An X-ray structure was determined for this sample after crystallization from acetonitrile–dichloromethane mixture (2:1).

#### 4.5. Acetylation of 6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol (*S*)-(+)-**3** and hydrolysis of the acetylated product **19**

Compound **3** as prepared above can be purified by this alternative procedure also. To the crude product mixture (~6.5 g) in dichloromethane (100 mL), pyridine (6.47 g,

63.4 mmol) was added, followed by the drop-wise addition of acetic anhydride (6.21 g, 78.5 mmol) in dichloromethane (20 mL) over a period of 30 min at 0 °C. The contents were stirred for 6 h at the same temperature, quenched with ice-cold water, and extracted using additional dichloromethane (2 × 50 mL). The organic layer was washed with 5 N HCl (2 × 20 mL) followed by a brine solution, dried anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent evaporated. The solid obtained was crystallized using diethyl ether: hexane mixture (4:1) to obtain 6,6'-di-*tert*-butyl-1,1'-binaphthalene-2,2'-diacetate **19** (6.4 g; 84%) after 36 h.

**4.5.1. 6,6'-Di-*tert*-butyl-1,1'-binaphthalene-2,2'-diacetate 19.** Yield 6.4 g (84%); colorless solid; mp 163 °C; Anal. Calcd for  $\text{C}_{32}\text{H}_{34}\text{O}_4$ : C, 79.64; H, 7.10. Found: C, 79.70; H, 7.01;  $\nu_{\max}$  (KBr) 2957, 1761, 1364, 1200, 1013  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.95 (d, 2H,  $J = 8.7$  Hz), 7.86 (s, 2H), 7.39 (dd ~ t, 4H,  $J = 8.7$  and 1.6 Hz), 7.15 (d, 2H,  $J = 8.7$  Hz), 1.40 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.88 (s, 6H,  $\text{C}(\text{O})\text{CH}_3$ ),  $\delta_{\text{C}}$  (50 MHz,  $\text{CDCl}_3$ ) 169.4 (s,  $\text{C}(\text{O})\text{CH}_3$ ), 148.3, 146.4, 131.6, 131.5, 129.3, 126.0, 125.6, 123.2, 123.1, 121.7 (all aromatic-C), 34.7 (s,  $\text{C}(\text{CH}_3)_3$ ), 31.2 (s,  $\text{C}(\text{CH}_3)_3$ ), 20.6 (s,  $\text{C}(\text{O})\text{CH}_3$ ); GC–MS: 482.2  $[\text{M}]^+$ ; LC–MS: 482.0  $[\text{M}]^+$ ;  $[\alpha]_{\text{D}}^{27} = +60.6$  ( $c$  1, THF). The  $[\alpha]_{\text{D}}$  value was  $-60.6$  for the (*R*)-isomer. The racemic form of **19** (mp is 168 °C) was also prepared similarly.

Compound **19** thus obtained was dissolved in dry methanol (200 mL), and sodium methoxide (1.8 g, 3.32 mmol) was added portion-wise (10 min) at 0 °C with stirring. Stirring was continued for 0.5 h, after which ice-cold water was added and the solvent removed under reduced pressure. To the residue, 1 M HCl (10 mL) and hexane (2 × 50 mL) were added and the separated organic layer was washed with brine solution, water, and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was partly removed under reduced pressure (to ~20 mL) to give crystals of (*S*)-(+)-**3** (5.5 g, 80% based on BINOL), mp 112–114 °C. In a similar manner, the (*R*)-form of **3** could also be hydrolyzed and there was no change in the  $[\alpha]_{\text{D}}$  value when compared to the one obtained directly (without acetylation).

#### 4.6. Asymmetric reduction of acetophenone and phenacyl chloride

One molar of  $\text{BH}_3 \cdot \text{SMe}_2$  (2.5 mL) was added to a toluene solution (4 mL) of acetophenone (0.30 g, 2.5 mmol) and the catalyst (0.75 mmol) under nitrogen stream after which the mixture was heated at 110 °C for about 1 h, then it was quenched with 3 mL of saturated  $\text{NH}_4\text{Cl}$  solution. The reaction mixture was extracted with ether (2 × 5 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , evaporated to give the crude product as a pale yellow liquid. This was purified using silica-gel column chromatography using hexane–ethyl acetate mixture as eluent. The isolated product was confirmed by checking with an authentic sample (TLC) and  $^1\text{H}$  NMR.

**4.6.1. X-ray crystallography.** Single crystal X-ray data were collected on an Enraf-Nonius MACH3 or on a Bruker AXS-SMART diffractometer using  $\text{Mo K}_\alpha$

( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The structures were solved by direct methods and refined by full-matrix least squares method using standard procedures.<sup>30</sup> Absorption corrections were carried out using SADABS program, where applicable. In general, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier map and refined isotropically. Compounds **18** showed disordered *tert*-butyl groups and hence the final *R* indices are a bit high; otherwise the structure is fine. PLATON/ORTEP drawings of **4** and **17** are available with the authors. Crystal data are available as CIF files and the CCDC reference numbers are 644354–644356 and 654644.

**4.6.2. Crystal data.** Compound **4**: C<sub>18</sub>H<sub>23</sub>O, *M* = 255.36, tetragonal, space group I4<sub>1</sub>/a, *a* = 20.2083(9), *b* = 20.2083(9), *c* = 15.1515(13) Å, *V* = 6187.5(7) Å<sup>3</sup>, *Z* = 16,  $\mu = 0.066 \text{ mm}^{-1}$ , data/restraints/parameters: 2712/0/198, *R* indices (*I* > 2 $\sigma$ (*I*)): *R*1 = 0.0515, *wR*2 (all data) = 0.1233.

Compound **17**: C<sub>60</sub>H<sub>36</sub>O<sub>6</sub>P<sub>2</sub>Se<sub>2</sub>, *M* = 1072.75, orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 8.9777(12), *b* = 21.311(3), *c* = 25.470(3) Å, *V* = 4873.1(11) Å<sup>3</sup>, *Z* = 4,  $\mu = 1.637 \text{ mm}^{-1}$ , data/restraints/parameters: 8541/0/631, *R* indices (*I* > 2 $\sigma$ (*I*)): *R*1 = 0.0720, *wR*2 (all data) = 0.1164.

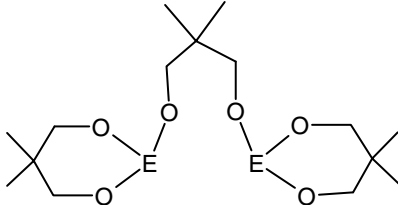
Compound **18**: C<sub>84</sub>H<sub>84</sub>O<sub>6</sub>P<sub>2</sub>Se<sub>2</sub>, *M* = 1409.37, triclinic, space group P $\bar{1}$ , *a* = 16.548(2), *b* = 17.107(2), *c* = 17.531(2) Å,  $\alpha = 85.116(2)^\circ$ ,  $\beta = 63.415(2)^\circ$ ,  $\gamma = 75.709(2)^\circ$ , *V* = 4299.0(9) Å<sup>3</sup>, *Z* = 2,  $\mu = 0.942 \text{ mm}^{-1}$ , data/restraints/parameters: 14974/1/847, *R* indices (*I* > 2 $\sigma$ (*I*)): *R*1 = 0.0726, *wR*2 (all data) = 0.2047.

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