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Thiophosphonates of 1,1'-Binaphthol as Chiral Equivalents of H_2S. Preparation of 2-Mercaptonorbornanes and 2-Mercaptonorbornenes

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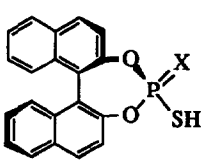
Abstract: Isomerically pure *exo*- and *endo*-2-mercaptonorbornanes and 2-mercaptonorbornenes were prepared by radical addition of the binaphthol-derived thiophosphonates **1a** and **1b** to norbornene and norbornadiene, separation of the *exo* and *endo* isomers by flash-chromatography and reduction with lithium aluminium hydride. The reaction of **1b** with norbornadiene performed with enantiopure 1,1'-binaphthol, produced a 1:1 mixture of the *exo*-diastereoisomers, one of which could be obtained in pure form by fractional crystallization. The latter, upon reduction with lithium aluminium hydride, afforded enantiomerically pure *exo*-2-mercaptonorbornene showing that the binaphthylthiophosphonates can be considered as safe, chiral synthetic equivalents of hydrogen sulfide.

Because of their reactivity and versatility, enantiopure thiols are potentially useful chiral auxiliaries or ligands for catalysts in asymmetric synthesis. So far, enantiopure thiols are almost exclusively derived from chiral natural sources as for example those derived from menthol,[1] borneol,[2] mirthanol,[3] cholesterol,[4] several sugars,[5] etc.[6] Little is available for the synthesis of enantiopure thiols from non-natural sources,[7] despite the fact that the design of new structural architectures could enlarge the possibility of high efficiency in the chiral transmission.[8]

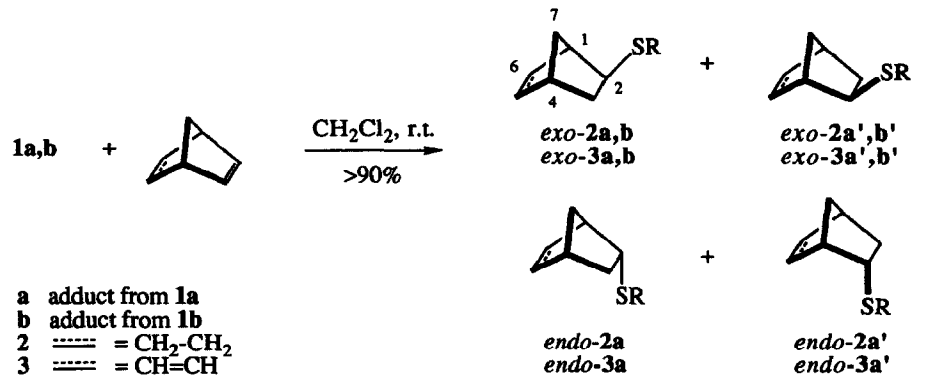
Since a rather general method for the preparation of organic thiols is the addition of hydrogen sulfide to olefins,[9] we thought that a chiral synthetic equivalent of hydrogen sulfide would constitute an useful reagent for this class of compounds. Indeed, the preparation of organic thiols *via* radical addition is often performed with reagents where the mercaptanic function can be generated after the addition. Typical examples are thioacetic acid,[10] *t*-butylmercaptan,[10] 2-tetrahydropyranthiol,[11] *etc.* The approach with these reagents also overcomes the inherent hazard and toxicity of hydrogen sulfide.

Here we report on the ability of the title chiral reagents **1** to react with olefins and the transformation of the adducts into the free mercaptans. Specifically, we have investigated the addition of **1a** and **1b** to norbornene and norbornadiene and we have determined the *endo-exo* selectivity with respect to the norbornyl skeleton and the face selectivity with respect to the binaphthyl residue.

Reagents **1a** and **1b** are crystalline solids, readily available with simple procedures.[12] They are soluble in most solvents, air stable and virtually non odorous. The reactions with norbornene and norbornadiene were carried out in $CHCl_3$ or $CDCl_3$ (NMR tube) at room temperature. The reactions reached completeness within a few minutes as it could be followed by the ^{1}H-NMR analysis. The results of the addition are summarised in equation (1).



1a (X = O)
1b (X = S)

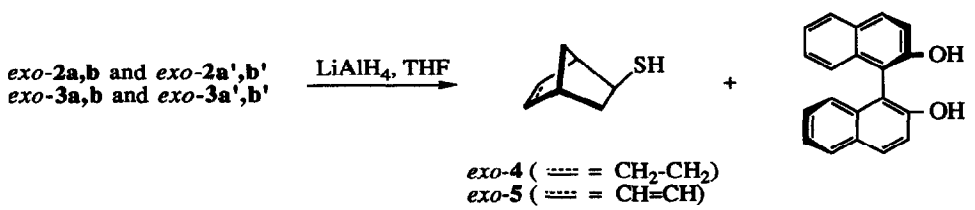


(1)

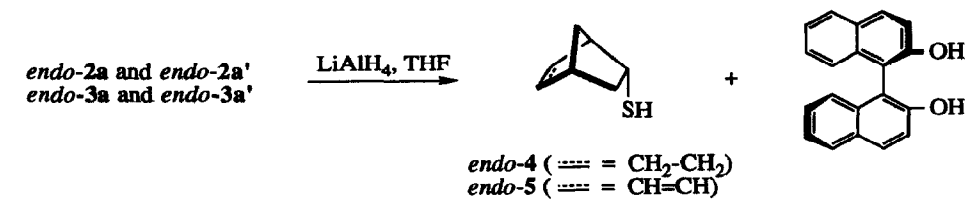
The reaction of **1a** with both norbornene and norbornadiene gave rise to 4.5:1 *exo-endo* ratio of diastereoisomers **2a**, **2a'** (from norbornene) and **3a**, **3a'** (from norbornadiene). The larger formation of the *exo* isomers was expected in view of the well known *exo* selectivity of the norbornenyl double bond.[13] Differently, the reaction of **1b** with the same substrates afforded only the *exo* addition products *exo*-**2b**, *exo*-**2b'** and *exo*-**3b**, *exo*-**3b'**. The stereochemistry of the addition was assigned on the basis of the coupling constants in the ^{1}H-NMR spectrum. In all the reactions so far carried out, the two *exo* and the two *endo* adducts were formed as mixtures of diastereoisomers (*ca.* 1:1 in all cases) with respect to the binaphthyl residue. In other words, **2a,b** and **2a',b'** or **3a,b** and **3a',b'** formed in almost equal amount in all cases. Whereas the *exo* isomers could be readly separated by the *endo* ones by flash-chromatography, the **2a,b** and **2a',b'** or **3a,b** and **3a',b'** diastereoisomers had to be separated by fractional crystallization or, analytically, by chiral GC.

The reaction of enantiopure **1b** with norbornadiene afforded, likewise the racemic mixture, only the adducts *exo*-**3a** and *exo*-**3a'** in high yield. The two diastereoisomers were separated by recrystallization from CH_2Cl_2 and EtOH. After four recrystallizations, one diastereoisomer was obtained pure (^{1}H-NMR and HPLC), while the other, recovered from the mother liquors, was enriched to the extent of *ca.* 3:1.

All adducts were readily transformed into the free thiols[14] by $LiAlH_4$ in THF in virtually quantitative yields [eqs (2) and (3)]. With this method, concomitant recovery of binaphthol was also achieved. In practice, after standard work-up, the reaction mixture was distilled to afford the thiol as the volatile component and the diol as the residue of distillation. The binaphthol recovered from the experiments carried out with enantiopure material did not show any loss of optical purity and could thus be recycled in subsequent experiments.



(2)



(3)

The thiol (+)-*exo*-**5** obtained from diastereomerically pure *exo*-**3b** (or *exo*-**3b'**) displayed an α value of 22 (c = 0.8, $CHCl_3$) and was confirmed to be enantiopure by chiral GC. The other diastereoisomer that was in *ca.* 3:1 mixture with the other epimer, afforded enriched (-)-*exo*-**5** at the expected extent of *ca.* 44% e.e. It should be noted, however, that the pure (-)-enantiomer *exo*-**5** can be obtained starting from the other enantiomer of binaphthol.

The use of binaphthol is in this type of reaction, offers several advantages over other possible chiral C_2-symmetric diols as the high crystallinity, the absence of racemisable carbons and the absence of signals in the aliphatic region of the NMR spectra. 1,1'-Binaphthol can be obtained in enantiomerically pure form with rather inexpensive and rapid methods, one of which has recently been proposed by ourselves.[15] We are currently exploring this diol as chiral auxiliary in the preparation of other reagents that function as chiral equivalents to other small molecules.

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EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectral data were recorded with a Varian VXR 5000 (300 MHz) spectrometer, using TMS as internal standard. Optical activities were measured with a Perkin-Elmer 241 polarimeter. Melting points were determined on a Buchi 510 apparatus. Mass spectra were recorded on a Perkin-Elmer 8310 spectrophotometer with an ion trap detector.

4-Mercapto-4-oxide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin (1a). To a solution of racemic binaphthol (5 g, 17.5 mmol) in pyridine (200 mL), thiophosphorylchloride was added at room temperature with stirring (2.43 mL, 24.0 mmol). The solution was stirred at 85 °C for 3 hours and then cooled to about 40 °C. Water (50 mL) was added, the solution was heated to 90 °C and allowed stirring at this temperature for 2 hours. The reaction mixture was cooled, washed with dilute sulfuric acid and extracted with dichloromethane (2x80 mL). The organic phase was washed with saturated aqueous sodium carbonate (200 mL). The aqueus layer was separated, made acidic with dilute HCl and extracted with dichloromethane (2x80 mL). After drying over sodium sulfate, the solvent was removed to obtain a pale yellow solid (4.2 g) consisting of 4-mercapto-4-oxide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin, dichloromethane and water in approximataly 1:1:1 ratio (^{1}H-NMR analysis): mp: 139-140 °C (with decomposition); ^{1}H-NMR ($CDCl_3$) δ 5.25 (s, 2H, CH_2Cl_2), 6.10 (bs, 2H, H_2O), 7.30 (t, J = 7.8 Hz, Ar, 1H), 7.32 (d, J = 7.5 Hz, Ar, 1H), 7.40 (d, J = 8.7 Hz, Ar, 2H), 7.48 (t, J = 7.5 Hz, Ar, 2H), 7.50 (t, J = 8.7 Hz, Ar, 1H), 7.59 (d, J = 9.0 Hz, Ar, 1H), 7.92 (d, J = 8.4 Hz, Ar, 1H), 7.96 (d, J = 8.4 Hz, Ar, 1H), 7.97 (d, J = 8.7 Hz, Ar, 1H), 8.05 (d, J = 9.0 Hz, Ar, 1H); ^{13}C-NMR ($CDCl_3$) δ 120.95, 121.33, 122.11, 122.41, 125.96, 126.85, 126.90, 127.34, 128.67, 128.74, 131.17, 131.32, 131.92, 132.12, 132.51, 132.60, 146.67, 146.78, 147.94, 198.12. IR (KBr disk): 3050 (w), 1588 (m), 1225 (s), 960 (s), 842 (s), 810 (s), 720 (m). This product was used without further purification.

4-Mercapto-4-sulfide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin (1b). Racemic 4-mercapto-4-sulfide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin **1b** was prepared in 84% yield from racemic binaphthol by the method of Gong *et al.*[12] mp 233-5 °C (lit.[12] 232-4 °C). Optically active (*R*)-(-)-4-mercapto-4-sulfide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin (-)-**1b** was prepared in 85% yield from (*R*)-(+)-binaphthol by the same method: $[\alpha]^{25}_D$ -589.5 (c = 1.0, $CHCl_3$).

Reaction of 1a with Norbornene. To a stirred solution of racemic 4-mercapto-4-oxide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin **1a** (1 g, 2.7 mmol) in dichloromethane (15 mL) was added a solution of norbornene (2.82 g, 30 mmol) in dichloromethane (5 mL). The solution was stirred at room temperature for 120 min. After evaporation of the solvent, the crude product was subjected to flash chromatography using dichloromethane/petroleum ether (1:1) as eluent to separate the two *exo* and the two *endo* isomers which were formed in 4.5:1 ratio as determined by ^{1}H-NMR (1.11 g, 90%). *Exo*-**2a** and *exo*-**2a'** (1:1 mixture): mp 261-3 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$) δ 1.02-1.72 (series of m, 14H), 1.82-2.02 (series of m, 2H), 2.28 (m, $H_{1(4)}$+$H_{1'(4')}$, 2H), 2.49 (d, J = 4.5 Hz, $H_{4(1)}$, 1H), 2.60 (d, J = 4.2 Hz, $H_{4'(1')}$, 1H), 3.50 (m, H_2+$H_{2'}$, 2H), 7.22-7.58 (series of m, Ar, 16H), 7.85-8.10 (series of m, Ar, 8H); ^{13}C-NMR ($CDCl_3$) (aliphatic carbons only) δ 28.20 (d, $^3J_{CP}$ = 44.8 Hz, $C_{3(3')}$), 28.58 (d, $^3J_{CP}$ = 40.2 Hz, $C_{3'(3)}$), 35.50, 35.78, 36.78, 36.82, 40.22, 40.33, 41.02, 41.10, 44.90 (d, $^3J_{CP}$ = 22.3 Hz, $C_{1(1')}$), 45.01 (d, $^3J_{CP}$ = 22.2 Hz, $C_{1'(1)}$), 48.10 (d, $^2J_{CP}$ = 9.9 Hz, $C_{2(2')}$), 48.15 (d, $^2J_{CP}$ = 10.2 Hz, $C_{2'(2)}$); MS, *m/z* 458 (M^+), 364 (100%),

284, 268, 239, 67. Anal. Calcd. for $C_{27}H_{23}O_3PS$: C, 70.80; H, 5.05; Found: C, 71.11; H, 5.09. *Endo*-**2a** and *endo*-**2a'** (1:1 mixture): mp 239-40 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$) δ 1.04-1.84 (series of m, 16H), 2.21 (m, $H_{1(4)}$, 1H), 2.27 (m, $H_{1'(4')}$, 1H), 2.43 (m, $H_{4(1)}$, 1H), 2.60 (m, $H_{4'(1')}$, 1H), 4.79 (m, H_2+$H_{2'}$, 2H), 7.23-7.55 (series of m, Ar, 16H), 7.88-8.02 (series of m, Ar, 8H); ^{13}C-NMR ($CDCl_3$) (aliphatic carbons only) δ 23.66, 23.77, 27.90, 27.92, 31.52, 34.93, 34.98, 35.33, 35.42, 40.10 (d, $^3J_{CP}$ = 21.9 Hz, $C_{3(3')}$), 40.45 (d, $^3J_{CP}$ = 19.8 Hz, $C_{1(1')}$), 42.68 (d, $^3J_{CP}$ = 19.7 Hz, $C_{1'(1)}$), 42.86 (d, $^3J_{CP}$ = 16.2 Hz, $C_{3'(3)}$), 84.43 (d, $^3J_{CP}$ = 20.24 Hz, $C_{2(2')}$), 84.53 (d, $^3J_{CP}$ = 24.0 Hz, $C_{2'(2)}$); MS, *m/z* 458 (M^+), 364 (100%), 284, 268, 239, 67. Anal. Calcd. for $C_{27}H_{23}O_3PS$: C, 70.80; H, 5.05; Found: C, 70.68; H, 5.16.

Reaction of 1b with Norbornene. According to the procedure described above, only the two adducts *exo*-**2b** and *exo*-**2b'** were obtained as a colorless crystalline material that was recrystallised from dichloromethane/ethanol (90% yield). *Exo*-**2b** and *exo*-**2b'** (1:1 mixture): mp 219-20 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$) δ 1.10-1.82 (series of m, 14H), 1.86-2.05 (series of m, 2H), 2.33 (m, H_4+$H_{4'}$, 2H), 2.53 (d, *J* = 3.9 Hz, H_1, 1H), 2.67 (d, *J* = 3.9 Hz, $H_{1'}$, 1H), 3.51 (m, H_2+$H_{2'}$, 2H), 7.21-7.57 (series of m, Ar, 16H), 7.90-8.01 (series of m, Ar, 8H); ^{13}C-NMR ($CDCl_3$) (aliphatic carbons only) δ 28.00 (d, $^3J_{CP}$ = 44.1 Hz, $C_{3(3')}$), 28.61 (d, $^3J_{CP}$ = 38.1 Hz, $C_{3'(3)}$), 35.49, 35.96, 36.59, 36.75, 38.70, 38.86, 40.23, 40.53, 44.59 (d, $^3J_{CP}$ = 21.9 Hz, $C_{1(1')}$), 44.79 (d, $^3J_{CP}$ = 12.0 Hz, $C_{1'(1)}$), 51.31 (d, $^2J_{CP}$ = 10.2 Hz, $C_{2(2')}$), 51.46 (d, $^2J_{CP}$ = 10.2 Hz, $C_{2'(2)}$). Anal. Calcd. for $C_{27}H_{23}O_2PS_2$: C, 68.33; H, 4.88; Found: C, 68.81; H, 4.97.

Reaction of 1a with Norbornadiene. To a stirred solution of racemic 4-mercapto-4-oxide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin **1a** (1 g, 2.7 mmol) in dichloromethane (15 mL) was added a solution of norbornadiene (2.76 g, 30 mmol) in dichloromethane (5 mL). The solution was stirred at room temperature for 120 min. Evaporation of the solvent and flash chromatography using dichloromethane/petroleum ether (1:1) as eluant afforded the two *exo* (*exo*-**3a** and *exo*-**3a'**) and the two *endo* (*endo*-**3a** and *endo*-**3a'**) in 4.5:1 ratio (1.19 g, 95%). *Exo*-**3a** and *exo*-**3a'** (1:1 mixture): mp 262-5 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$) δ 1.53-1.86 (series of m, 8H), 2.90 (bs, $H_{1(4)}$+$H_{1'(4')}$, 2H), 3.13 (bs, $H_{4(1)}$, 1H), 3.23 (bs, $H_{4'(1')}$, 1H), 3.35 (m, H_2+$H_{2'}$, 2H), 6.04 (m, $H_{5(6)}$+$H_{5'(6')}$, 2H), 6.10 (m, $H_{6(5)}$+$H_{6'(5')}$, 2H), 7.21-7.37 (series of m, Ar, 8H), 7.41-7.60 (series of m, Ar, 8H), 7.90-8.01 (series of m, Ar, 8H); ^{13}C-NMR ($CDCl_3$) δ 35.10 (d, $^3J_{CP}$ = 44.1 Hz, $C_{3(3')}$), 35.60 (d, $^3J_{CP}$ = 33.9 Hz, $C_{3'(3)}$), 41.75, 41.82, 43.37 (d, *J* = 9.9 Hz, $C_{1(1')}$), 43.44 (d, *J* = 9.9 Hz, $C_{1'(1)}$), 45.60, 45.79, 49.82 (d, *J* = 14.1 Hz, $H_{2(2')}$), 50.00 (d, *J* = 19.8 Hz, $H_{2'(2)}$), 120.50, 120.52, 125.90, 126.80, 126.85, 127.20, 127.25, 128.00, 130.08, 130.14 130.14, 130.18, 132.00, 132.02, 134.15, 134.16, 138.10, 138.18, 146.15, 146.19. Anal. Calcd. for $C_{27}H_{21}O_3PS$: C, 71.03; H, 4.63; Found: C, 70.96; H, 4.66. *Endo*-**3a** and *endo*-**3a'** (1:1 mixture): mp 257-9 °C (CH_2Cl_2/EtOH); ^{1}H-NMR ($CDCl_3$) δ 1.40-1.85 (series of m, 8H), 2.78 (bs, $H_{1(4)}$, 1H), 2.84 (bs, $H_{1'(4')}$, 1H), 3.01 (bs, $H_{4(1)}$, 1H), 3.18 (bs, $H_{4'(1')}$, 1H), 4.85 (m, H_2+$H_{2'}$, 2H), 5.91 (dd, *J* = 3.42, 5.86 Hz, $H_{5(6)}$, 1H), 5.96 (dd, *J* = 3.42, 5.46 Hz, $H_{5'(6')}$, 1H), 6.23 (m, $H_{6(5)}$+$H_{6'(5')}$, 2H), 7.30-7.57 (series of m, Ar, 16H), 7.86-8.00 (series of m, Ar, 8H); ^{13}C-NMR ($CDCl_3$) δ 35.16 (d, $^3J_{CP}$ = 24.0 Hz, $C_{3(3')}$), 35.50 (d, $^3J_{CP}$ = 24.2 Hz, $C_{3'(3)}$), 40.48, 40.59, 46.05, 46.06, 48.59 (d, $^3J_{CP}$ = 19.5 Hz, $C_{1(1')}$), 48.73 (d, $^3J_{CP}$ = 20.0 Hz, $C_{1'(1)}$), 82.00 (d, $^2J_{CP}$ = 32.4 Hz, $C_{2(2')}$), 83.10 (d, $^2J_{CP}$ = 32.6 Hz, $C_{2'(2)}$), 120.45, 120.49, 121.19, 121.23, 125.61, 125.62, 126.48, 126.57, 126.98, 127.17, 128.28, 128.42, 130.59, 130.96, 130,97, 131.80, 131.98, 132.32, 141.75, 141.95. Anal. Calcd. for $C_{27}H_{21}O_3PS$: C, 71.03; H, 4.63; Found: C, 70.77; H, 4.77.

Reaction of 1b with Norbornadiene. According to the procedure described above, only the two isomers *exo*-**3b** and *exo*-**3b'** (1:1 mixture) were obtained as colorless crystalls (89% yield): mp 206-7 °C (CH_2Cl_2/EtOH). Anal. Calcd. for $C_{27}H_{21}O_2PS_2$: C, 68.23; H, 4.48; Found: C, 68.11; H, 4.50. The two diastereoisomers were separated by fractional crystallization from dichloromethane/ethanol. *Exo*-**3b**: ^{1}H-NMR ($CDCl_3$) δ 1.49-1.76 (series of m, 4H), 2.90 (bs, $H_{1(4)}$, 1H), 3.24 (bs, $H_{4(1)}$, 1H), 3.31 (dt, *J* = 4.2, 9.0 Hz, H_2, 1H), 6.03 (dd, *J* = 3.3, 5.4 Hz, $H_{5(6)}$, 1H), 6.12 (dd, *J* = 2.7, 5.4 Hz, $H_{6(5)}$, 1H), 7.21-7.47 (series of m, Ar, 7H), 7.56 (dd, *J* = 1.2, 8.7 Hz, Ar, 1H), 7.91 (d, *J* = 8.1 Hz, Ar, 1H), 7.97 (d, *J* = 8.7 Hz, Ar, 1H), 7.99 (d, *J* = 9.0 Hz, Ar, 1H); ^{13}C-NMR ($CDCl_3$) δ 34.10 (d, $^3J_{CP}$ = 45.9 Hz, C_3), 41.90, 45.77, 47.10 (d, $^3J_{CP}$ = 6.2 Hz, C_2), 49.92 (d, $^3J_{CP}$ = 12.0 Hz, C_1), 121.26 (d, *J* = 12 Hz), 121.59 (d, *J* = 9.9 Hz), 125.67, 125.74, 126.51, 126.59, 126.96, 127.15, 128.34, 128.46, 130.48 (d, *J* = 5.8 Hz) 130.75 (d, *J* = 6.0 Hz), 131.66, 131.70, 131.87, 132.95, 134.53, 138.27, 146.40 (d, *J* = 44.1 Hz), 147.72 (d, *J* = 56.1 Hz). *Exo*-**3b'**: ^{1}H-NMR ($CDCl_3$) δ 1.49-1.90 (series of m, 4H), 2.90 (bs, $H_{1'(4')}$, 1H), 3.12 (bs, $H_{4'(1')}$, 1H), 3.31 (m, $H_{2'}$, 1H), 6.04 (m, $H_{5'(6')}$, 1H), 6.12 (m, $H_{6'(5')}$, 1H), 7.21-7.57 (series of m, Ar, 8H), 7.91 (d, *J* = 8.1 Hz, Ar, 1H), 7.94-8.05 (series of m, Ar, 4H); ^{13}C-NMR ($CDCl_3$) (aliphatic carbons only) δ 35.50 (d, $^3J_{CP}$ = 32.1 Hz, $C_{3'}$), 42.05, 46.30, 47.27 (d, $^3J_{CP}$ = 8.1 Hz, $C_{1'}$), 49.89 (d, $^2J_{CP}$ = 22.2 Hz, $C_{2'}$).

The adducts obtained from norbornadiene and enantiomerically pure (*R*)-(-)-4-mercapto-4-sulfide-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin (-)-**1b** (1g) were separated by crystallization from dichloromethane (40 mL) and absolute ethanol (20 mL) and afforded colorless needles after 6 h at room temperature. The crystallization was repeated four times to obtain a single pure diastereoisomer (0.20 g): mp: 234-5°C; $[\alpha]^{25}_D$ -249.0 (*c* = 1.1, $CHCl_3$). The other diastereoisomer (0.10 g) was obtained in 43.6 de

(determined by ^{1}H-NMR) from evaporation of the solution and two crystallizations from dichloromethane/petroleum ether 40/30.

Preparation of the Mercaptans. General Procedure. The adduct (0.5 g, 1.05 mmol) in THF (15 mL) was cooled at 0 °C under argon and lithium aluminium hydride (0.4 g, 10.5 mmol) was added in portions under magnetic stirring. After 2 h at 0 °C, water (50 mL) and dilute HCl were added up to a slightly acidic pH. The solution was extracted with dichloromethane (2x50 mL), dried over sodium sulfate and rotoevaporated. The oily residue was purified by distillation to obtain the thiol. The residue of the distillation was purified by flash chromatography (elution with dichloromethane) to recover the binaphthol.

exo-**4** (85% yield): bp 70 °C/18 mm Hg (lit.[16] 67-68 °C/18 mm Hg); ^{1}H-NMR ($CDCl_3$) δ 1.10-1.22 (series of m, H_{5X}+H_{5N}, 2H), 1.26-1.38 (m, H_{3X}, 1H), 1.40-1.62 (series of m, H_{6X}+H_{6N}, 2H), 1.64-1.72 (series of m, H_7+$H_{7'}$, 2H), 1.76-1.85 (m, H_{3N}, 1H), 2.32 (m, H_1, 1H), 2.26 (m, H_4, 1H), 2.84 (m, H_2, 1H); ^{13}C-NMR ($CDCl_3$) δ 27.98, 28.66, 34.68, 36.69, 40.21, 42.18, 46.44; MS, *m/z* 128 (M^+, 20%), 95 (M^+, SH) (100%), 67, 39. Pure binaphthol was recovered in 88% yield.

endo-**4** (80% yield): bp 75 °C/18 mm Hg (lit.[16] 73-4 °C/20 mm Hg); ^{1}H-NMR ($CDCl_3$) δ 0.90-1.62 (series of m, 9H), 2.11 (bs, $H_{1(4)}$, 1H), 2.20 (bs, $H_{4(1)}$, 1H), 3.73 (m, H_2, 1H); ^{13}C-NMR ($CDCl_3$) δ 24.18, 25.31, 27.90, 34.13, 35.15, 41.79, 43.83; MS, *m/z* 95 (M^+, SH, 100%), 79, 67, 39. Pure binaphthol was recovered in 81% yield.

exo-**5** (0.12 g, 92%): bp 60 °C/15 mm Hg; ^{1}H-NMR ($CDCl_3$) δ 1.30-1.82 (series of m, 5H), 2.69 (bs, $H_{1(4)}$, 1H), 2.72 (m, H_2, 1H), 2.85 (bs, $H_{4(1)}$, 1H), 6.08 (m, $H_{5,6}$, 2H); ^{13}C-NMR ($CDCl_3$) δ 35.88, 36.78, 42.06, 45.16, 51.74, 134.94, 137.31; MS, *m/z* 94 (M^+-SH), 66, 63, 40. Binaphthol recovered: 0.27 g, 90%.

Diastereomeric pure *exo*-**3b** (or *exo*-**3b'**) under treatment with lithium aluminium hydride gave enantiopure [by chiral GC, Cyclodex B column (J.&W. Scientific), isotherm 75 °C] *exo*-**5** as colorless oil (0.25 g, 92%): $[\alpha]^{25}_D$ +22.0 (*c* = 0.8, $CHCl_3$). Pure (*R*)-(+)-binaphthol was recovered in 90% yield and optical purity >99%. Similarly, the other diastereoisomer of *exo*-**3b** (71.8/28.2 diastereomeric mixture by ^{1}H-NMR) gave an enantiomeric mixture (e.e. 43.6%, confirmed by chiral GC) of *exo*-**5** as colorless oil (89% yield): $[\alpha]^{25}_D$ -10.0 (*c* = 0.7, $CHCl_3$). Pure (*R*)-(+)-binaphthol was recovered in 93% yield and optical purity >99%.

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