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Chirochromic triggers: 3,3′-Disubstituted-2,2′-binaphthalene-1,1′-diols and 2-methylindoline derived phosphoramidates

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Abstract

Diastereomeric binaphthalenes with an appropriate barrier to atropisomerization were sought in an effort to develop possible chirochromic switches that photochemically control the pitch magnitude and sense in an induced cholesteric liquid crystal.

Keywords: Photoisomerization; Phototrigger; Liquid crystal; Binaphthyl; Photochromic

1. Introduction

The development of photoresponsive materials remains the pursuit of intense research [1–5]. In one approach, a chirochromic additive is incorporated into a nematic liquid crystal and can be switched between states that have different induced cholesteric twisting power [6–9]. A chirochromic switch has two diastereomerically related states (D_1, D_2) accessed by irradiation with light of differing wavelength (λ). The switch has some photo-invertible chirality an optical excess of which is largely responsible for the twist sense and magnitude of an induced cholesteric phase. Circularly polarized light is not required to perform switching since diastereomers are chemically distinct and may possess different absorption spectra. The photostationary state composition is wavelength dependent and determined by the difference in extinction coefficient (ε) between the two switch states and also by the difference in quantum efficiencies (ϕ) for switching from each state (Eq. (1)). In the limit of equal quantum efficiencies, the photostationary state composition (de′) is determined solely by the UV absorption spectra of the two switch states (Eq. (2)):

$$\mathrm{de}_{\lambda,\mathrm{pss}} = \frac{([D_1]-[D_2])}{([D1]+[D2])} = \frac{(\varepsilon_{1,\lambda}\phi_{12}-\varepsilon_{2,\lambda}\phi_{21})}{(\varepsilon_{1,\lambda}\phi_{12}+\varepsilon_{2,\lambda}\phi_{21})} \quad (1)$$

$$\mathrm{de}'_{\lambda,\mathrm{pss}} = \frac{(\varepsilon_{1,\lambda}-\varepsilon_{2,\lambda})}{(\varepsilon_{1,\lambda}+\varepsilon_{2,\lambda})} \quad (2)$$

de is the diastereomeric excess, ϕ_{ij} are the quantum efficiencies for isomerization from the *i* to *j* state.

1,1′-Binaphthalene compounds have shown some promise toward a chirochromic liquid crystal switch [8] with the major shortcoming being the high barrier to inter-naphthyl rotation. In an effort to construct a switch with the same high twisting power as 1,1′-binaphthalenes but with a useful barrier to atropisomerism, a series of 2,2′-binaphthalene derivatives was pursued with hopes that substitution at the 3 and 3′ positions would tune the facility of binaphthyl isomerism.

2. Results and discussion

2.1. Design and synthesis

Compounds **1**–**5** (Fig. 1) were synthesized from the corresponding diols by cyclization with $POCl_3$ followed by

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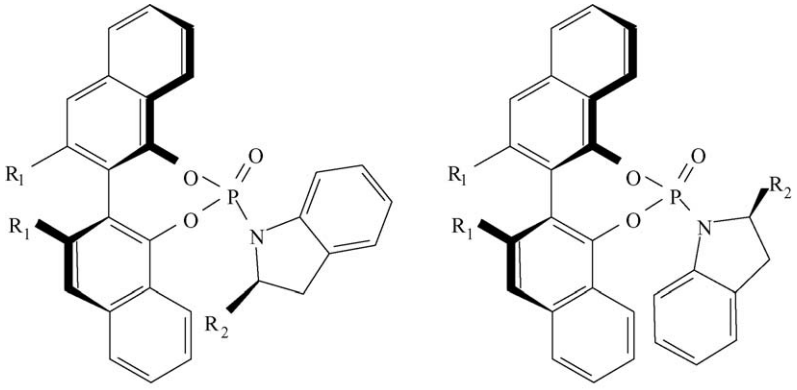


1a: R_1 = Ph, R_2 = CH_3
2a: R_1 = $C_{10}H_{21}$, R_2 = CH_3
3a: R_1 = CH_3, R_2 = CH_3

1b: R_1 = Ph, R_2 = CH_3
2b: R_1 = $C_{10}H_{21}$, R_2 = CH_3
3b: R_1 = CH_3, R_2 = CH_3

4: R_1 = H, R_2 = CH_3
5: R_1 = H, R_2 = H

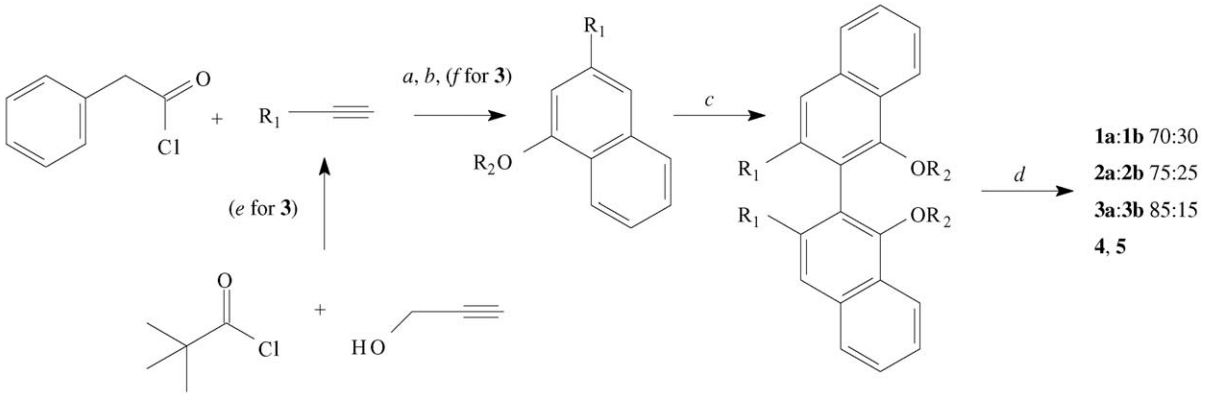
Fig. 1. Phosphoramidate structures. In this study, all syntheses were racemic. For **4** and **5**, binaphthalene interconversion renders the relative stereochemistry dynamic.

addition of the appropriate indoline as the lithium salt. For **1**–**3**, the parent diols were prepared by oxidative coupling of the corresponding naphthols [10]. The functionalized naphthols were prepared using a modification to Wulff's cyclization procedure [11]. Reaction conditions were not optimized (Scheme 1). For **4** and **5**, the 2,2′-binaphthalene-1,1′-diol was commercially available.

Thermal isomerizations of the binaphthyls were attempted by refluxing dilute toluene solutions for several days under inert atmosphere. Photoisomerizations were attempted by irradiating oxygen-free THF solutions for several hours under inert atmosphere using a 250 W mercury lamp optically filtered to wavelengths longer than ∼270 nm.

2.2. Phenyl derivative *1*

The diastereomers (**a** and **b**, in elution order) of **1** were separable by silica gel chromatography. Crystals of **1a** and **1b** were grown and X-ray analyses allowed the assignments of relative stereochemistry (Fig. 2). In addition, the X-ray structures make clear the conformational differences between **1a** and **1b** with each having the alternate face of the indoline aromatic ring presented to the proximal naphthalene. Large chemical shift differences revealed in the ^{1}H NMR spectra (especially of the indoline ring protons) suggest that the conformational differences in the crystal state may extend to solution (Fig. 3). In spite of such conformational changes,



Scheme 1. Synthesis. For **1**, R_1 = –Ph for **2,** R_1 = $–C_{10}H_{21}$: (*a*) 190 °C, 16 h; (*b*) R_2 = $–COCH_2Ph$, LAH; (*c*) R_2 = –H, O_2, 140 °C, 20 h, alumina/$CuSO_4$; (*d*) $POCl_3$, Et_3N, isolate then lithium 2-methylindolinide. For **3** (*e*) imidazole, 12 h, (*a*) R_1 = $(CH_3)_3(CO)OCH_2–$, 200 °C, 24 h, (*b*) R_2 = $–COCH_2Ph$, LAH, (*f*) R_1 = $–CH_2OH$, R_2 = –H, TsCl, NaH isolate then LAH, (*c*) R_1 = $–CH_3$, R_2 = –H, air, 90 °C, 3.5 h, alumina/$CuSO_4$, (*d*) $POCl_3$, Et_3N, isolate then lithium 2-methylindolinide. For **4** (*d*) R_1, R_2 = –H, $POCl_3$, Et_3N, isolate then lithium 2-methylindolinide. For **5** (*d*) R_1, R_2 = –H, $POCl_3$, Et_3N, isolate then lithium indolinide.

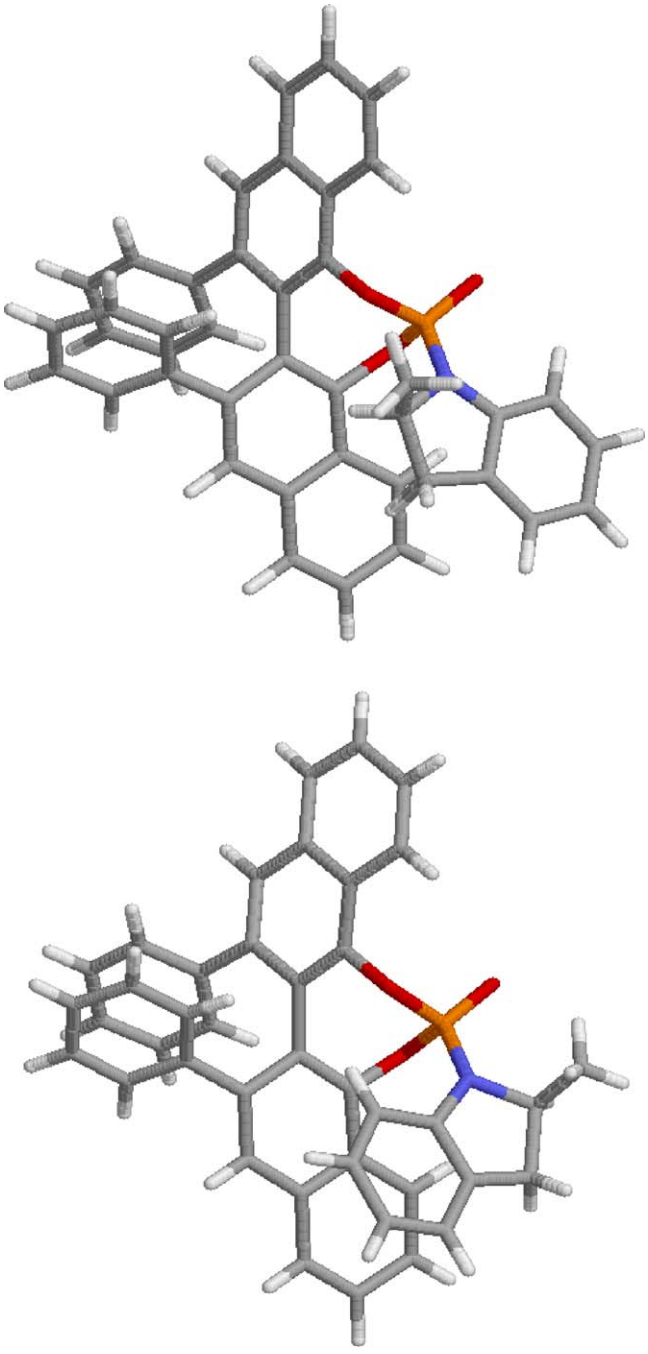


Fig. 2. X-ray crystal structures. **1a** (*top*) and **1b** (*bottom*). The crystal unit structure was a pair of racemates spanning a center of inversion.

the UV absorption spectra of **1a** and **1b** are disappointingly similar (Fig. 4).

The enantiomers of each diastereomer of **1** were separable by chiral HPLC such that all four stereoisomers could be simultaneously resolved. Samples of (optically pure) **1a** and **1b** were treated with the thermal and photochemical isomerization conditions. Neither treatment resulted in detectable isomerization. Evidently, the phenyl groups prevent any rotation about the inter-naphthyl bond.

2.3. Decyl derivative 2

Differences in the absorption spectra of the diastereomers of compounds like **1**–**4** could result from through space electronic interactions which have different qualities in the two states due to changes in the distance or orientation between the binaphthyl and indoline π systems. Large changes in relative orientation of the indoline were indeed observed for **1**. However, since neither π system is perturbed electronically in **1**, donor–acceptor interactions are expected to be weak [12]. Moreover, structural differences between the stereoisomers might include the inter-aryl dihedral angle that would alter the extent of electronic delocalization between the naphthyl subsystems and create spectral variations. Nonetheless, an upper limit is imposed on the inter-aryl dihedral angle by the cyclic phosphoramidate linkage while the phenyl groups of **1** impose a lower limit. Together, such elements may restrict the inter-aryl dihedral angle to similar values in both diastereomers reducing the likelihood of that mechanism for generating spectral differences. These factors might explain the very similar UV absorption spectra of **1a** and **1b**.

Diastereomers of **2** (**a** and **b**) were also separable on silica gel. Compound **2** possesses the more flexible and sterically forgiving decyl groups in place of the phenyl groups of **1**. In addition, unlike the phenyl groups of **1**, alkyl groups contribute no absorption that could overlap and occlude spectral details in the binaphthyl band. These properties may be responsible for the more pronounced absorption spectral differences between **2a** and **2b** (Fig. 5) compared to **1a** and **1b**. Compound **2** was a waxy solid and X-ray quality crystals could not be grown. ^{1}H NMR spectra of the diastereomers of **2** depict large chemical shift differences similar to those found for **1**.

All four stereoisomers of **2** were separable on a chiral HPLC column. Single enantiomers were subjected to thermal treatment and irradiation. No isomerization was detected in either case (vide infra).

2.4. Methyl derivative 3

To exclude the possibility that isomerization of **2** was somehow prevented by the long decyl groups of **2** (either through mutual entanglement or some local viscosity effect) dimethyl substituted **3** was prepared. The ^{1}H NMR spectra of diastereomers **3a** and **3b** reveal similar indoline ring proton chemical shift changes to those between **1a** and **1b** or **2a** and **2b**. The X-ray crystal structure of **3a** indicates a conformation much like that of **1a**, but X-ray quality crystals of **3b** could not be grown. Significant absorption spectral differences exist between **3a** and **3b** (Fig. 6).

All four stereoisomers of **3** were separable with chiral HPLC. Optically pure **3a** showed no isomerization after refluxing in toluene for several days (Fig. 7). To insure that **3a** was not coincidentally the much more stable isomer predominating in an equilibrium mixture, **3b** was also thermally treated. Using chiral HPLC, neither (optically pure) **3a** nor **3b**

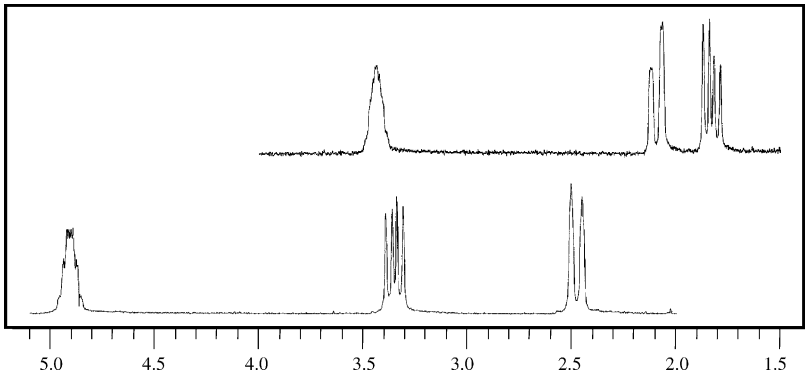


Fig. 3. 300 MHz ^{1}H NMR spectra of **1a** (*top*) and **1b** (*bottom*) in $CDCl_3$ referenced to TMS. Only the indoline ring protons are shown.

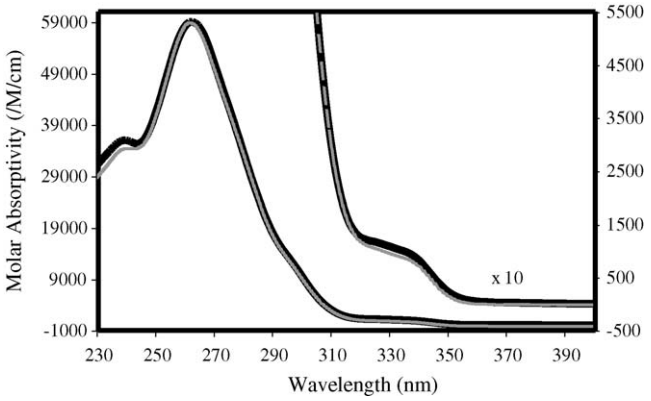


Fig. 4. Absorption spectra of **1a** (*solid*, heavy curve) and **1b** (*light*, dashed curve) in hexane with 10% isopropanol.

showed any isomerization, which would have been revealed as the appearance of a peak matching one of the enantiomers of the alternate diastereomer. Irradiating an optically pure enantiomer of **3a** resulted in no apparent isomerization after 3 h. Evidently, the presence of even a methyl group prevents rotation about the inter-naphthyl bond. As the optical filter cutoff wavelength was lowered, eventually decomposition reactions became evident while epimerization remained unseen.

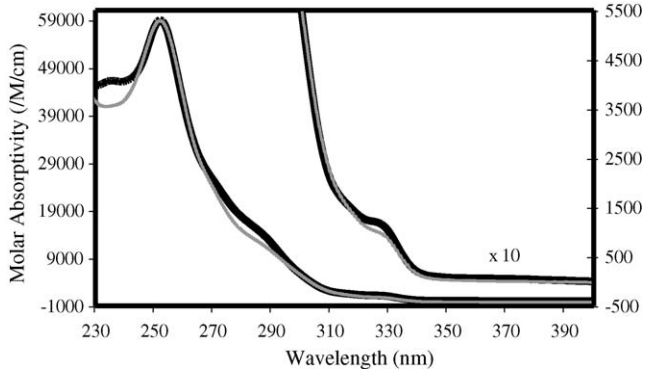


Fig. 5. Absorption spectra of **2a** (*solid*, heavy curve) and **2b** (*light*, dashed curve) in hexane with 10% isopropanol.

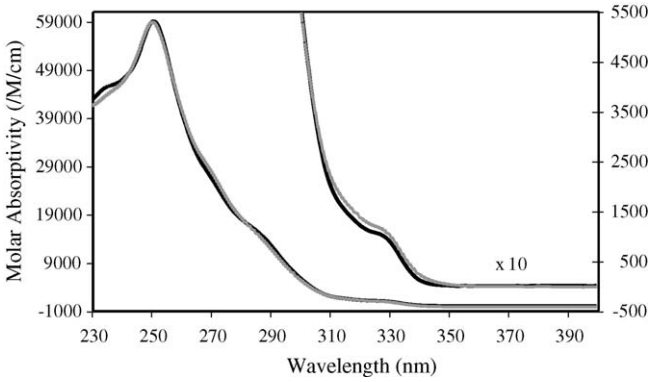


Fig. 6. Absorption spectra of **3a** (*solid*, heavy curve) and **3b** (*light*, dashed curve) in hexane with 10% isopropanol.

2.5. Unsubstituted *4*

Only one (racemic) isomer from the synthesis of **4** was isolated by silica gel chromatography. That this compound was resolved into enantiomers using chiral HPLC was verified by the mirror image CD spectra obtained from the collected

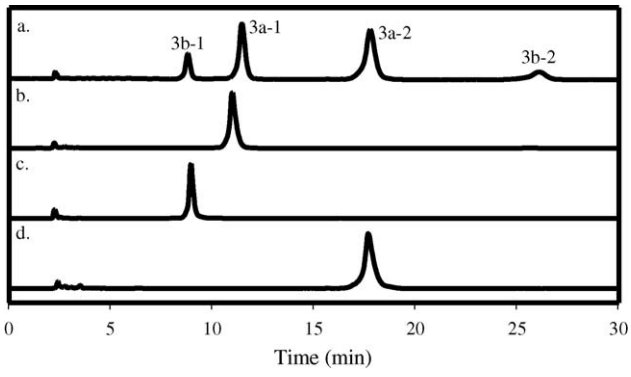


Fig. 7. Attempted stereochemical inversions (example with **3**). Separations were done with chiral HPLC in hexane with 10% isopropanol so that enantiomers (**1** and **2**, indicating elution order) as well as diastereomers (**a** and **b**) were resolved. (a) Mixture of racemic **3a** and racemic **3b** in unequal amounts. (b) Thermally treated single enantiomer **3a**–**1**. (c) Thermally treated single enantiomer **3b**–**1**. (d) Irradiated single enantiomer **3a**–**2**.

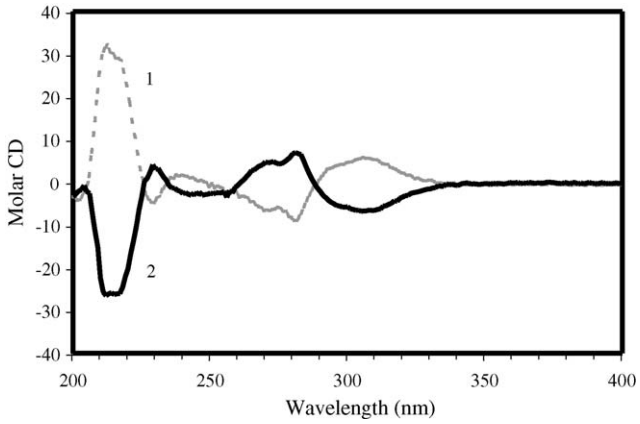


Fig. 8. Circular dichroism spectra for HPLC-separated isomers (**1** and **2**, signifying elution order) of **4** in hexane with 10% isopropanol.

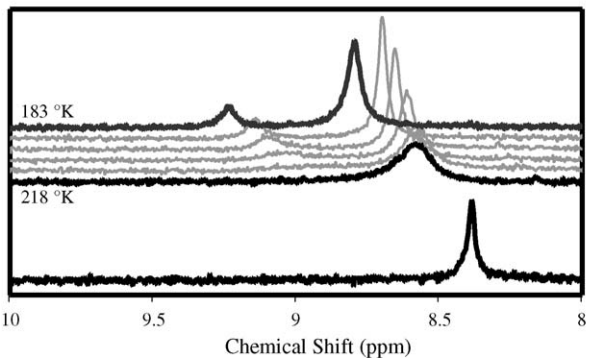


Fig. 10. 162 MHz ^{31}P NMR variable temperature spectra. (*top*) Racemic **4** at 218, 208, 203, 198, 193, 183 K. (*bottom*) "Achiral" **5** at 183 K. All were measured in CD_2Cl_2 and referenced to H_3PO_4 at room temperature.

fractions (Fig. 8). Note the poor HPLC resolution compared to that found for isomers of either **3a** or **3b**. The X-ray crystal structure of **4** revealed a conformation similar to that found with **1a** (Fig. 9).

There are at least three explanations for isolating only one diastereomer of **4**. First, the diastereoselectivity in the phosphoramidate formation reaction was nearly 100% while being only about 75% for **1**–**3**. This could not be dismissed since there is an apparent gradual increase in diastereoselectivity for the series **3** > **2** > **1** (Scheme 1). Second, the other of the diastereomers was "lost" during work-up. Third, both diastereomers interchange rapidly on the laboratory time scale (presumably through binaphthyl inversion while the indoline configuration stays fixed), and the mixture behaves as a single substance with one time-averaged (racemic) structure. In this third scenario, crystals contain only the most thermodynamically stable form.

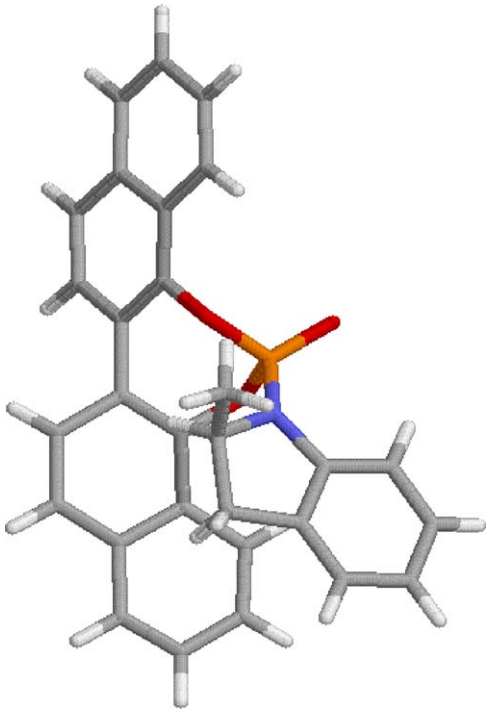


Fig. 9. X-ray crystal structure of **4**. The crystal unit structure was a pair of racemates spanning a center of inversion.

Variable low temperature ^{31}P NMR spectrometry of **4** indeed revealed that some dynamic conformational exchange occurred at room temperature but was frozen out when cooled below 198 K (Fig. 10). The dynamic process was likely to be rotation about the inter-naphthyl bond or rotation of the indoline subunit about the P–N bond since the only other degree of freedom belongs to the freely rotating indolinyl methyl group which is not as likely to affect the phosphorous chemical shift. If the motion was indoline rotation, then similar freezing out would likely occur and be visible in the ^{31}P NMR spectrum of compound **5** that was derived from achiral indoline. Freezing of a putative binaphthyl inversion in **5** would result in a static racemic composition containing enantiomers (since the binaphthyl subunit is the only source of chirality for this material) and hence would have been invisible to an NMR experiment. The ^{31}P NMR spectrum of **5** at 183 K (15 K lower than the temperature required to see decoalescence in **4**) showed only a single sharp peak (Fig. 10). The ^{31}P NMR experiments strongly suggest that compound **4** exists as a rapidly interchanging mixture of diastereomers (through inversion of binaphthyl configuration) at temperatures above 200 K. Worth mention is the fact that refluxing an "isomer" of **4** in toluene for 12 h led to no "isomerization" detectable by chiral HPLC which is consistent with the notion that the material was a mixture of isomers already in dynamic interchange. Also, HPLC analysis of **5** showed only a single sharp peak using the same conditions that resolved **4** (not shown).

3. Conclusions

This study indicates that 2-methylindoline phosphoramidate cyclized 2,2′-binaphthalene-1,1′-diols are inappropriate

for use in situations requiring thermal or photochemical activation of binaphthyl isomerization. The addition of even a single carbon bearing (methyl) substituent at the 3 and 3′ positions prevents atropisomerism of the binaphthalene substructure while lack of any substitution leads to facile interconversion at temperatures above 200 K.

4. Experimental methods

4.1. Instrumentation

All 300 MHz ^{1}H NMR were recorded on a Varian Gemini 2000. All 162 MHz ^{31}P NMR spectra were recorded on a Bruker 500AMX. Unless noted otherwise, ^{1}H NMR measurements were recorded in $CDCl_3$ at 300 MHz referenced to TMS. UV–vis spectra were measured using an HP 8435 Spectrometer. Chiral HPLC separations were performed on an Hitachi L-6200A pump equipped with a Regis Whelk O,1 Pirkle type [13] column and coupled to an Hitachi L-4500A diode array detector. Mass spectra were recorded on a VG Analytical Model 70-SE mass spectrometer using direct probe analysis (exact mass spectra at a high resolution of 5000). Elemental analyses were done at "Atlantic Microlabs" in Norcross, GA. Single crystal X-Ray analysis was performed on a Bruker (Siemens) 1 K CCD diffractometer.

4.2. Thermal isomerizations

The thermal isomerization experiments were performed in refluxing toluene. First, the starting material was purified by chiral HPLC. The chromatography solvent (hexane and isopropyl alcohol) was removed by evaporation. Then the sample (∼10 μmol) was dried by removing anhydrous toluene three times by evaporation (3 × 3 mL). After several hours drying under vacuum, dry toluene was added (∼3 mL) and the sample was heated under argon to reflux and left for 16–24 h. Toluene was removed from the resulting samples by evaporation and oil pump evacuation.

4.3. Photochemical isomerizations

Photochemical experiments were performed in anhydrous THF. The concentrations were $\sim 10^{-3}$ M. The 1 cm cells had path length and were equipped with micro stir bars and stopped with rubber septa. Before irradiation, the solutions were saturated with argon, and argon back pressure was applied during the irradiations. The output from a 250 W mercury vapor lamp was directed to the sample through an aperture fitted with the appropriate optical filter. Small aliquots were tested by HPLC during the experiment by syringe withdrawal. It was noteworthy that allowing light of wavelengths down to ∼220 nm resulted in observable sample decomposition in the course of a few minutes but no observable epimerization.

4.4. 3-Phenyl-1-naphthol (**6**)

Phenylacetylene (2.45 g, 24.0 mmol) was added to decalin (4 mL) in a three-necked flask equipped with a reflux condenser and heated in a sand bath while saturating with nitrogen using plastic HPLC tubing. When the bath temperature reached ∼100 °C, phenylacetyl chloride (4.76 mL, 36 mmol) was added. After refluxing for 16 h at 190 °C (bath) and cooling in ice, lithium aluminum hydride (1.5 g, 40 mmol) was added slowly in diethyl ether (100 mL) to cleave the ester group of the resulting *O*-phenylacetyl-3-phenyl-1-naphthol. The reaction was stirred for 1 h then acidified with 2 M H_2SO_4 and stirred until clear. The organic layer was extracted with 3NKOH until re-extraction into ether after acidification showed no product by TLC (EtOAc in hexane, 10% (v/v), I_2 visualization). This required about 10 × 30 mL of 3NKOH. The extracts were acidified with concentrated HCl, and extracted with ether. The ether extract was washed with 3 × 30 mL saturated $NaHCO_3$, then brine, and dried over Na_2SO_4. Solvent was removed by rotary evaporation. Recrystallization from $CHCl_3$ with hexane gave **6** in 73% yield (F.W. 220.27 g/mol, 3.86 g, 17.5 mmol) as a waxy solid (mp 96–97.5 °C). ^{1}H NMR δ 8.18 (dd, J = 7.2 Hz, 1.5 Hz, 1H), 7.87 (dd, J = 6.6 Hz, 1.8 Hz, 1H), 7.69 (td, J = 8.4 Hz, 1.8 Hz, 3H), 7.57–7.45 (m, 4H), 7.38 (td, J = 7.2 Hz, 0.9 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 5.47 (s, 1H). *m/z* 220 (M+, 100%) 191 (33.8%) 165 (11.5%).

4.5. 3,3′-Diphenyl-2,2′-binaphthyl-1,1′-diol (**7**)

3-Phenyl-1-naphthol (**6**) (3.10 g, 14.1 mmol) was dissolved in chlorobenzene (120 mL) in a 250 mL round bottom flask. Alumina supported $CuSO_4$ (10 g) was added (vide infra). A reflux condenser was attached and was left open to the atmosphere. The reaction was stirred and heated to 140 °C while oxygen was bubbled through. The reaction was monitored by TLC (EtOAc in hexane, 10% (v/v), I_2 visualization). After 20 h the reaction was complete. The coupled product travels farther on silica than the starting material (**6** R_f = 0.17, **7** R_f = 0.29). The warm mixture was filtered and the filter cake washed with ether, then CH_2Cl_2, then acetone. The filtrate solution was concentrated using rotary evaporation. Recrystallization from $CHCl_3$ with hexane (mp 224–224.5 °C) gave **7** in 85% yield (F.W. 438.52 g/mol, 2.6 g, 5.9 mmol). ^{1}H NMR δ 8.36 (m, 2H), 7.80 (m, 2H), 7.57 (m, 4H), 7.33 (s, 2H), 7.09 (t, J = 7.3 Hz, 2H), 6.97 (t, J = 8.3 Hz, 4H), 6.64 (d, J = 8.3 Hz, 4H), 5.89 (s, 2H). *m/z* 438.3 (M+, 100%), 419.3 (3.8%), 361.3 (5.7%), 219.2 (13.5%), 191.2 (7.3%). Catalyst/oxidant: a slurry was made of aluminum oxide (50 g) in water (200 mL). $CuSO_4 \cdot 10H_2O$ (10 g) was added. The mixture was stirred for 2 h, concentrated with rotary evaporation and then poured into a wide evaporation dish. After 48 h, the moist paste was dried in an oven at 150 °C overnight.

4.6. Phosphorylchloride (**8**)

Diol **7** (0.21 g, 0.48 mmol) was dissolved in dry THF (10 mL) by stirring under nitrogen. $POCl_3$ was added at once via syringe (75 μL, 0.57 mmol). Formation of phosphoryl chloride **8** was not observed until triethylamine (147 μL, 1.05 mmol) was added drop wise. The reaction was stirred for 15 min. Absence of **7** was confirmed by TLC (EtOAc in hexane, 10% (v/v), I_2 visualization, **8** $R_f = 0.20$). In cases where starting material remained, $POCl_3$ was added drop wise until none was left. The chloride **8** can be isolated in 98% yield after column chromatography, but this was generally not done. ^{1}H NMR δ 8.44 (d, $J = 7.7$ Hz, 1H), 8.37 (d, $J = 7.7$ Hz, 1H), 7.86 (t, $J = 7.7$ Hz, 2H), 7.75–7.60 (m, 4H), 7.57 (d, $J = 3.3$ Hz, 2H), 7.16–7.08 (m, 2H), 6.94 (td, $J = 7.7$ Hz, 3.3 Hz, 4H), 6.47 (t, $J = 7.7$ Hz, 4H).

4.7. Diphenylphosphoramidates (**1**)

Chloride **8** was washed in ether versus 2 M HCl then saturated $NaHCO_3$ solution. After drying on Na_2SO_4 followed by co-evaporation from benzene and addition of dry THF, lithium 2-methylindolinide in THF (vide infra) was added drop wise until **8** disappeared by TLC (EtOAc in hexane, 20% (v/v), UV visualization, **8** $R_f = 0.40$). Two spots with lower R_f than **8** appeared blue under UV which were the diastereomers **1a** ($R_f = 0.30$) and **1b** ($R_f = 0.15$). Chromatography (EtOAc in hexane, 20% v/v) gave **1a** (F.W. 615.66 g/mol, 0.11 g, 0.18 mmol) and **1b** (34 mg, 55 μmol) in 50% combined yield. The ratio **1a**:**1b** was 70:30. Each diastereomer was recrystallized from toluene with methylcyclohexane (50%, v/v) to give X-ray quality crystals. **1a**—Elemental analysis: measured (calculated) C = 79.86% (79.99%), H = 5.12% (4.91%), N = 2.28% (2.28%), O = 7.93% (7.80%). ^{1}H NMR δ 8.52 (d, $J = 8.2$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.72–7.60 (m, 2H), 7.47–7.54 (m, 4H), 7.07–7.21 (m, 4H), 6.95 (p, $J = 7.7$ Hz, 6H), 6.53 (d, $J = 7.7$ Hz, 2H), 6.49 (d, $J = 7.7$ Hz, 2H), 3.44 (m, 1H), 2.10 (dd, $J = 15.4$ Hz, 2.2 Hz, 1H), 1.83 (dd, $J = 15.9$ Hz, 9.9 Hz, 1H), 1.22 (d, $J = 6.6$ Hz, 3H). *m/z* 616.2 (M + H, 100%), 600.0 (45.7%), 421.1 (15%), 315.1 (10.4%). **1b**—Elemental analysis: measured (calculated) C = 79.13% (79.99%), H = 5.21% (4.91%), N = 2.19% (2.28%), O = 7.97% (7.80%). ^{1}H NMR δ 8.54 (d, $J = 8.0$ Hz, 1H), 8.21 (d, $J = 6.6$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.72–7.53 (m, 4H), 7.42–7.34 (m, 2H), 7.31 (s, 1H), 7.18–7.05 (m, 2H), 6.99 (t, $J = 7.8$ Hz, 2H), 6.91 (t, $J = 7.6$ Hz, 2H), 6.73 (d, $J = 6.7$ Hz, 1H), 6.60–6.34 (m, 7H), 4.93 (m, 1H), 3.35 (dd, $J = 15.6$ Hz, 9.2 Hz, 1H), 2.49 (d, $J = 15.2$ Hz, 1H), 1.2 ppm (d, $J = 6.9$ Hz, 3H). *m/z* 615.3 (M+, 100%), 600.3 (40.7%), 421.3 (13.0%), 315.1 (9.0%). Lithium 2-methylindolinide: *t*-butyl lithium (2.3 mL, 1.7 M in pentane) was added slowly and with ice cooling to 0.5 mL of freshly vacuum distilled 2-methylindoline in dry THF (5 mL) under nitrogen. This was done while stirring the solution and addition of *t*-butyl lithium was not counted until after the persistence of a bright yellow color.

4.8. 3-Decyl-O-phenylacetyl-1-naphthol (**9**)

The procedure performed on 1-dodecyne (0.54 mL, 1.4 mmol) was analogous to that for phenylacetylene above except for the following modifications to the purification. Initial attempts at extraction of 3-decyl-1-napthol (**10**) from ether using KOH failed and resulted in stubborn emulsion-like mixtures. For this reason, its precursor **9** was purified by column chromatography (EtOAc in hexane, 10% (v/v)). Often, some of the naphthol **10** was already present (**9** $R_f = 0.41$, **10** $R_f = 0.30$). The combined yield was 81% (**9** F.W. 402.57 g/mol, 0.90 g, 2.2 mmol, **10** F.W. 284.44 g/mol, 5 mg, 18 μmol). ^{1}H NMR δ 7.72 (d, $J = 8.1$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.47–7.28 (m, 8H), 7.09 (d, $J = 1.5$ Hz, 1H), 3.97 (s, 2H), 2.71 (t, $J = 7.8$ Hz, 2H), 1.65 (p, $J = 7.2$ Hz, 2H), 1.36–1.22 (m, 14H), 0.87 (t, $J = 6.6$ Hz, 3H). MS exact mass 402.25892 (402.25588 calculated). *m/z* 402 (M+, 5.8%), 284 (100%), 266 (5.3%), 181 (7.2%), 158 (59.8%), 91 (35.1%).

4.9. 3-Decyl-1-naphthol (**10**)

Decylnaphthol **10** was prepared in analogy to **7** starting by LAH cleavage of **9** (1.51 g, 3.75 mmol). Because of its high solubility in organic solvents, recrystallization of **10** was not successful. Instead, column chromatography was performed (EtOAc in hexane, 6.25% (v/v), **10** $R_f = 0.26$) to give 75% yield (F.W. 284.44 g/mol, 0.80 g, 2.8 mmol). ^{1}H NMR δ 8.10 (d, $J = 7.7$ Hz, 1H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.43 (m, 2H), 7.22 (s, 1H), 6.67 (s, 1H), 5.19 (s, 1H), 2.68 (t, $J = 7.1$ Hz, 2H), 1.67 (p, $J = 7.7$ Hz, 2H), 1.36–1.20 (m, 14H), 0.88 (t, $J = 7.1$ Hz, 3H). MS exact mass 284.21572 (284.21402 calculated). *m/z* 284 (M+, 50.3%), 173 (12.4%), 171 (14.8%), 158 (100%), 128 (10.6%).

4.10. 3,3′-Didecyl-2,2′-binaphthyl-1,1′-diol (**11**)

Coupling of **10** (1.14 g, 4.0 mmol) was performed in analogy to **6** and was followed by TLC (EtOAc in hexane, 10% (v/v), I_2 visualization, **10** $R_f = 0.30$, **11** $R_f = 0.52$). Chromatography (EtOAc in hexane, 6.25% v/v, **11** $R_f = 0.36$) gave 70% yield (F.W. 566.86 g/mol, 0.79 g, 1.4 mmol). ^{1}H NMR δ 8.24 (d, $J = 7.7$ Hz, 2H), 7.82 (d, $J = 7.7$ Hz, 2H), 7.58–7.44 (m, 6H), 5.27 (s, 2H), 2.56–2.29 (m, 4H), 1.56–1.43 (m, 4H), 1.31–1.05 (m, 28H), 0.86 (t, $J = 6.6$ Hz, 6H). MS exact mass 566.41326 (566.41238 calculated). *m/z* 566 (M+, 100%), 425 (12.7%), 281 (7.3%), 157 (10.9%). The occasional presence of 2-phenylethanol (from the reductive cleavage of **9**) in the starting material **10** did not interfere with its oxidative coupling or purification of **11**.

4.11. Didecylphosphoramidates (**2**)

Diastereomers of **2** were made as those of **1** in comparable yield and diastereoselectivity (47%, **2a**:**2b** 75:25) from **11** (744.00 g/mol, 110 mg, 0.194 mmol) after chromatography (EtOAc in hexane, 20% (v/v)). Another example of this

procedure was done while cooling the reaction on ice during the indolinide addition—the diastereoselectivity changes (**2a**:**2b** 95:5). **2a**—Elemental analysis: measured (calculated) C = 79.09% (79.10%), H = 8.26% (8.40%), N = 1.88% (1.88%), O = 6.56% (6.45%). ^{1}H NMR δ 8.38 (m, 1H), 7.90–7.80 (m, 2H), 7.75–7.70 (m, 3H), 7.62–7.56 (m, 2H), 7.49–7.38 (m, 2H), 7.15 (t, J = 7.1 Hz, 2H), 6.96–6.87 (m, 2H), 3.13 (m, 1H), 2.87–2.56 (m, 4H), 2.04 (dd, J = 15.4 Hz, 2.2 Hz, 1H), 1.72 (dd, J = 15.4 Hz, 8.8 Hz, 1H), 1.40–0.77 (m, 41H). **2b**—^{1}H–NMR δ 8.37 (m, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.87 (m, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.71 (s, 1H), 7.66 (s, 1H), 7.63–7.57 (m, 2H), 7.46 (t, J = 7.14 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 6.97 (q, J = 8.1 Hz, 2H), 6.83 (t, J = 7.1 Hz, 1H), 5.83 (d, J = 15.4 Hz, 1H), 5.61 (dq, J = 8.4 Hz, 6.6 Hz, 1H), 5.08 (d, J = 8.2 Hz, 1H), 2.83–2.52 (m, 4H), 1.62 (d, J = 6.6 Hz, 3H), 1.29–0.80 (m, 38H). MS exact mass 743.43995 (743.44673 calculated). *m/z* 743 (M+, 100%), 602 (17.0%), 295 (6.5%), 281 (8.1%).

*4.12. Propargyl pivaloate (**12**)*

Propargyl alcohol (4.3 g, 77 mmol) was stirred in CH_2Cl_2 (25 mL) under nitrogen and imidazole (5.76 g, 84.6 mmol) was added. Trimethylacetyl chloride was added drop wise (10.4 mL) from a dropping funnel over 10 min. After stirring for 12 h, the solution was washed with 3 × 25 mL of 2 M HCl. Then the solution was washed with 3 × 25 mL of saturated $NaHCO_3$. After reduction to one third volume, the liquid was filtered through a plug of silica. Removal of solvent by rotary evaporation gave propargyl pivaloate **12** as a clear colorless oil (140.18 g/mol, 10.3 g, 71.3 mmol) in 95% yield. ^{1}H NMR δ 4.66 (d, J = 2.8 Hz, 2H), 2.44 (t, J = 2.5 Hz, 1H), 1.33 (s, 9H).

*4.13. 1-Phenylacetyloxy-3-trimethylacetyloxymethylnaphthalene (**13**)*

Ester **12** was added to the same reactor as before (9.4 g, 67 mmol). After argon purge, the bath temperature was raised to 200 °C. Phenylacetyl chloride was injected over the course of 5 min (15.1 mL, 114 mmol). Unlike before, no decalin was added. After 23 h, ^{1}H NMR showed about 50% conversion of alkyne and no remaining chloride. Using vacuum distillation, 40% of **12** (3.6 g) was recovered. The remaining thick brown oil could be purified by silica chromatography (EtOAc in hexane, 6.25% (v/v)), but generally this was not done. ^{1}H NMR δ 7.81 (d, J = 8.1 Hz, 1H) 7.67 (s, 1H) 7.56 (d, J = 8.4 Hz, 1H) 7.50–7.29 (m, 7H) 7.21 (d, J = 1.8 Hz, 1H) 5.23 (s, 2H) 4.02 (s, 2H) 1.23 (s, 9H). *m/z* 376 (M+, 0.8%) 275 (5.9%) 258 (100%) 174 (30.1%) 157 (42.8%) 128 (16.1%) 91 (80.0%) 57 (50.0%).

*4.14. 3-Hydroxymethyl-1-naphthol (**14**)*

The crude reaction mixture containing **13** was transferred to a 2 L round bottom flask using 130 mL THF. To cleave the esters of **13**, LAH was added slowly in increments of ~0.5 g (4 g, 105 mmol). After stirring for 12 h, 100 mL ether was added and ice water was added drop wise until frothing subsided. Sulfuric acid (2 M) was added while stirring until the aqueous layer tested acidic with litmus. The organic phase was washed with $NaHCO_3$ until re-acidification of the separated aqueous layer results in no cloudiness and its ether extract showed no spot on a TLC plate (UV visualization). The original organic layer was then extracted with 2 M KOH until pink coloration was absent in the aqueous phase. The combined aqueous phase was acidified with concentrated HCl to give a turbid pale yellow mixture. The acidified mixture was extracted with ether until the aqueous phase was colorless and *completely* clear. Solvent was removed by rotary evaporation and column chromatography performed (EtOAc in hexane, 50% (v/v), I_2 visualization—not UV, **14** R_f = 0.21). After solvent removal, recrystallization in CH_2Cl_2 (mp 103 °C, sharp) gave **14** (174.19 g/mol, 2.57 g, 14.8 mmol) in 20% yield from **12**. ^{1}H NMR (d^6-acetone) δ 8.95 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.3Hz, 1H), 7.42 (pd, J = 6.8 Hz, 2.2 Hz, 2H), 7.34 (s, 1H), 6.95 (d, J = 1.1 Hz, 1H), 4.70 (d, J = 4.7 Hz, 2H), 4.21 (t, J = 5.2 Hz, 1H). *m/z* 174 (M+, 100%) 172 (16.7%) 157 (19.7%) 145 (44.2%) 128 (39.4%) 115 (48.1%).

*4.15. 3-Hydroxymethyl-1-naphthol-O,O′-ditosylate (**15**)*

Diol **14** (0.729 g, 4.2 mmol) was dried by rotary evaporation from anhydrous benzene (3 × 5 mL) after heating to dissolve. To **14** in 50 mL hot benzene, NaH was added (0.2 g, 8.3 mmol) and the mixture stirred for 15 min. *p*-Toluenesulfonyl chloride (1.7 g, 8.9 mmol) was added. The reaction was monitored by TLC (EtOAc in hexane, 50% (v/v)). A complicated mixture of tosylates developed. More NaH was added until no more **14** remained by TLC. The solvent was removed by rotary evaporation. The mixture could be purified by silica chromatography (EtOAc in hexane, 20% (v/v)), but generally this was not done. On standing, the column fractions containing **15** developed crystals (mp 119–120 °C). ^{1}H NMR δ 7.88–7.82 (m, 1H) 7.77–7.69 (m, 5H) 7.57 (s, 1H) 7.45 (m, 2H) 7.28 (dd, J = 8.7 Hz, 3.3 Hz, 4H) 7.00 (d, J = 1.8Hz, 1H) 5.09 (s, 2H) 2.41 (s, 3H) 2.37 (s, 3H). The major side product (presumably the $HOCH_2$– monotosylate) gave distinctive NMR signals at δ 4.65 (s, 2H) and 2.41 (s, 3H). MS exact mass (**15**) 482.08655 (482.08578 calculated). *m/z* 482.1 (M+, 49.8%) 402.1 (5.4%) 312.1 (16.4%) 247.1 (76.6%) 229.1 (20.1%) 169 (10.0%) 156 (45.9%) 128 (45.7%) 91 (100%).

*4.16. 3-Methyl-1-naphthol (**16**)*

After tosylation, the crude residue containing **15** (and the monotosylate) was dissolved in THF (30 mL) and, to cleave the arylsulfonate and displace the methylenesulfonate, LAH was slowly added (1.5 g, 40 mmol) and the reaction was refluxed overnight (reaction unsuccessful in benzene). The next day, ether was added (80 mL) and the reaction

was quenched by the addition of 2 M H_2SO_4 until the mixture was acidic followed by stirring for 30 min. The ether layer was washed with $NaHCO_3$. The ether solution was dried with brine (3 × 50 mL) and then $NaSO_4$. The NMR showed that this material was still monotosylated (aryloxy) as evidenced by the (naphthyl and tosyl) CH_3 signals δ 2.43 (s, 3H) and 2.40 (s, 3H). The LAH treatment and work-up was repeated in ether to give **16** (158.19 g/mol, 0.35 g, 2.2 mmol) after chromatography (EtOAc in hexane, 20% (v/v)) in 50% yield from **14**. ^{1}H NMR δ 8.10 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.42 (pd, J = 7.3 Hz, 1.6 Hz, 2H), 7.21 (s, 1H), 6.63 (s, 1H), 5.20 (br s, 1H), 2.43 (s, 3H). MS exact mass 158.07339 (158.07317 calculated). *m/z* 158.1 (M+, 100%), 129.1 (32.7%), 115.1 (21.2%). Using hexane, **16** could be recrystallized (mp 89–90 °C).

4.17. 3,3′-Dimethyl-2,2′-binaphthyl-1,1′-diol (*17*)

Naphthol **16** (0.495 g, 3.13 mmol) was dissolved in chlorobenzene (20 mL) and the alumina supported $CuSO_4$ (4 g) was added (vide supra). The slurry was stirred under an open air condenser at 90 °C (without oxygen treatment) and the reaction was done in 3.5 h by TLC. The yield of **17** was 40% (314.38 g/mol, 0.21 g, 0.67 mmol) after chromatography (EtOAc in hexane, 10% v/v). ^{1}H NMR δ 8.24 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 7.59–7.46 (m, 6H), 5.29 (s, 2H), 2.14 (s, 6H). MS exact mass 314.13033 (314.13068 calculated). *m/z* 314.1 (M+ 100%), 299.1 (23.0%), 281.1 (27.6%), 252.1 (10.6%).

4.18. Dimethylphosphoramidates (*3*)

Phosphoramidates **3** were prepared from **17** (100 mg, 0.318 μmol) following the procedure for **1**. Chromatography (EtOAc in hexane, 20% v/v) yielded **3a** (491.52 g/mol, 25 mg, 51 μmol) and **3b** (5 mg, 10 μmol). The diastereoselectivity as similar to that for **1** and **2** (**3a**:**3b** 85:15). X-ray quality crystals of **3a** appeared after 2 days of open-air evaporation from the collected column fractions. **3a**—Elemental analysis: measured (calculated) C = 75.68% (75.75%), H = 5.49% (5.33%), N = 2.79% (2.85%). ^{1}H NMR δ 8.36 (m, 1H), 7.86 (m, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.74–7.68 (m, 3H), 7.6 (m, 2H), 7.50–7.41 (m, 2H), 2.17–7.07 (m, 2H), 6.96–6.88 (m, 2H), 3.14 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.04 (dd, J = 14.8 Hz, 3 Hz, 1H), 1.70 (dd, J = 15.7 Hz, 8.8 Hz, 1H), 1.12 (d, J = 6.2 Hz, 3H). **3b**—^{1}H NMR δ 8.39 (m, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.85 (m, 1H), 7.72 (s, 1H), 7.59 (m, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.47 (s, 1H), 7.32 (m, 2H), 6.71 (m, 1H), 6.48 (m, 2H), 6.35 (m, 1H), 4.78 (m, 1H), 3.25 (dd, J = 9.3 Hz, 5.7 Hz, 1H), 2.42 (d, $J \sim$ 8.2 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.10 (d, J = 6.3 Hz, 3H). MS exact mass 492.17191 (M + H, 492.17286 calculated). *m/z* 492.1 (M + H, 100%), 476.1 (10.8%), 447 (2.6%), 296 (6.8%), 282 (6.6%), 252 (3.9%).

4.19. Phosphoramidate (*4*)

Un-substituted **4** was prepared from 2,2′-binaphthyl-1,1′-diol (286.32 g/mol, 44 mg, 0.15 mmol) using the same procedures as above. The yield of **4** was 30% (463.47 g/mol, 20 mg, 43 μmol). Only one diastereomer was obtained from column chromatography. ^{1}H NMR δ 8.35 (d, J = 7.1 Hz, 1H), 8.06 ppm (d, J = 8.2 Hz, 1H), 7.93–7.83 (m, 4H), 7.73 (dd, J = 11.0 Hz, 8.8 Hz, 2H), 7.51–7.61 (m, 3H), 7.39 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 6.93 (q, J = 7.7 Hz, 2H), 6.80 (t, J = 7.4 Hz, 1H), 4.06 (m, 1H), 2.59 (dd, J = 15.4 Hz, 9.1 Hz, 1H), 2.31 (d, J = 15.4 Hz, 1H), 1.18 (d, J = 6.6 Hz, 3H). MS exact mass 463.13463 (463.13373 calculated). *m/z* 463 (M+, 100%), 448 (88.0%), 332 (17.0%), 268 (41.5%), 239 (14.9%), 226 (7.0%), 130 (8.1%).

4.20. Phosphoramidate (*5*)

In analogy to the other procedures, **5** was made from 2,2′-binaphthyl-1,1′-diol (286.32 g/mol, 10 mg, 35 μmol) but indoline was substituted for 2-methylindoline. The yield after chromatography was 30% (449.44g/mol, 5.0 mg, 11 μmol). ^{1}H NMR δ 8.28 (d, J = 8.1 Hz, 2H), 7.90 (t, J = 8.6 Hz, 4H), 7.74 (d, J = 8.6 Hz, 2H), 7.55 (m, 3H), 7.43 (d, J = 8.2 Hz, 1H), 7.04 (m, 2H), 6.85 (t, J = 7.7 Hz, 2H), 3.56 (td, J = 8.6 Hz, 1.9 Hz, 2H), 2.72 (t, J = 8.5 Hz, 2H).

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