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Synthesis and separation of the atropisomers of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl and related compounds

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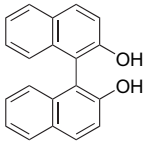
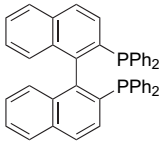
Abstract—Several *syn* and *anti* atropisomers of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl and related compounds were synthesized from 1,1′-binaphthyl-2,2′-diol (BINOL). It was possible to separate the *syn* and *anti* atropisomers by silica gel column chromatography. The *syn* atropisomers are potential hetero-bidentate ligands for complex formation with metals. By starting from enantiomerically pure (*R*)-(+)-BINOL and (*S*)-(−)-BINOL, four optically active *syn* atropisomers and two *anti* atropisomers with high enantiomeric purity were obtained. The structures of two *syn* atropisomers and one *anti* atropisomer were established by X-ray structure analyses.

1. Introduction

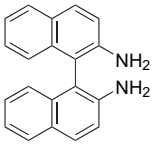
The use of 1,1′-binaphthyl-2,2′-diol (BINOL, **1**) as a chiral reagent for asymmetric synthesis has been extensively investigated.[1–5] The design and synthesis of modified BINOLs as ligands in asymmetric catalysis continue to be an area of intense current interest.[6,7] Conversion of both hydroxyl groups of BINOL to two other identical functional groups capable of coordinating with metals has led to the discovery of many useful C_2-symmetrical homo-bidentate ligands, including BINAP (**2**),[8–10] BINAM (**3**),[11] and 2,2′-bis(2-indenyl)-binaphthyl (**4**).[12]



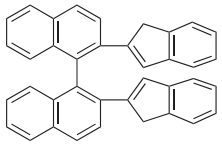
BINOL, **1**



BINAP, **2**



BINAM, **3**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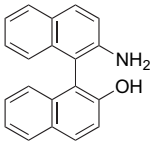
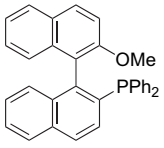
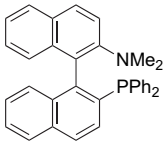
Conversion of only one of the two hydroxyl groups to a different functional group or conversion of both hydroxyl groups to two different functional groups to form hetero-bidentate binaphthyls, such as NOBIN (**5**),[13–17] MOP (**6**),[18–20] and MAP (**7**),[21] has also been investigated.[22] The barriers of rotation around the carbon–carbon single bond connecting the two C1 carbons of these 2,2′-di-substituted binaphthyls are high,[1–5,23,24] giving stability to the chiral configuration even at high temperature and allowing the molecules to be used in a variety of synthetic applications.



NOBIN, **5**



MOP, **6**



MAP, **7**

We recently reported an efficient synthetic pathway using ethynylarenes to produce the benzannulated enediynyl alcohols for subsequent cascade transformations to 5-aryl-11*H*-benzo[*b*]fluorenes.[25] This synthetic method was adopted for the preparation of structurally distorted 4,5-diarylphenanthrenes[26,27] and the atropisomers of 1,2-bis[5-(11*H*-benzo-[*b*]fluorenyl)]benzenes and related compounds.[28] We now report an additional application of this synthetic method using 2-ethynyl-2′-methoxy-1,1′-binaphthyl (**13**), prepared from BINOL (Scheme 1), as the starting ethynylarene for the synthesis of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl and related compounds.

Keywords: 2-(5-Benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyls; Atropisomers; Benzannulated enyne-allenes; Cascade biradical cyclization.
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† To whom correspondence concerning the X-ray structures should be addressed. Tel.: +1 304 293 3435x6423; fax: +1 304 293 4904; e-mail: jeffrey.petersen@mail.wvu.edu.

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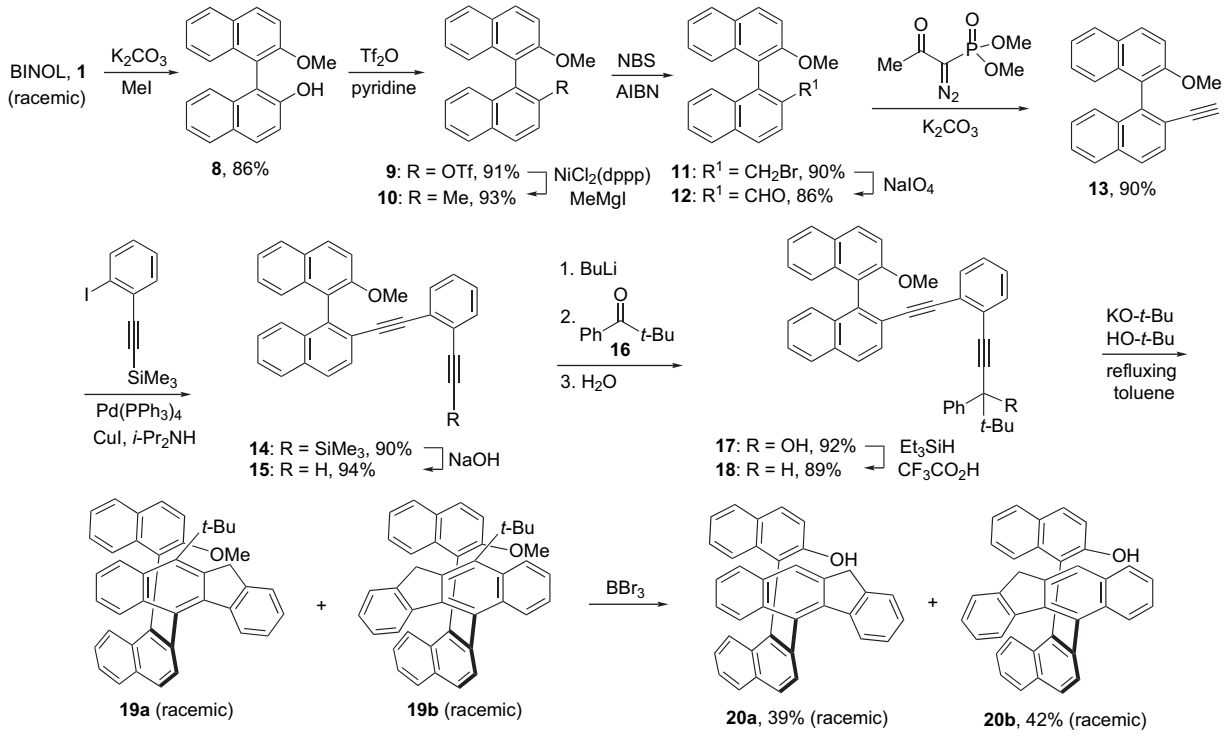


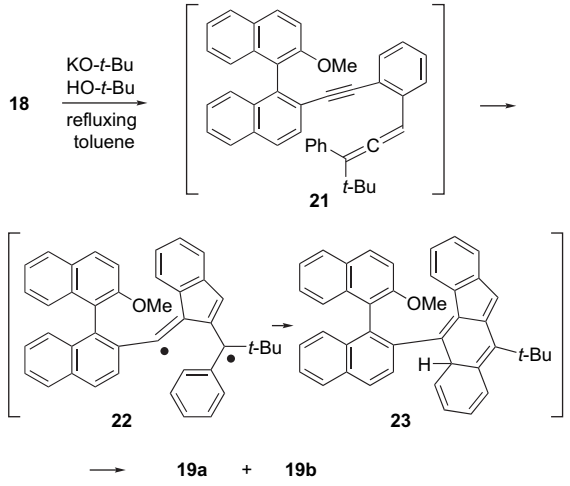
Scheme 1.

2. Results and discussion

Racemic BINOL was converted to 2-hydroxy-2′-methoxy-1,1′-binaphthyl (**8**)[29] for the subsequent transformation to the corresponding triflate **9**[30] as reported previously. The $NiCl_2$(dppp)-catalyzed (dppp=$Ph_2PCH_2CH_2CH_2PPh_2$) cross-coupling reaction[31,32] between **9** and methylmagnesium iodide led to 2-methoxy-2′-methyl-1,1′-binaphthyl (**10**),[33] which was brominated to give 2-(bromomethyl)-2′-methoxy-1,1′-binaphthyl (**11**).[34,35] Oxidation of **11** with $NaIO_4$[36] then produced 2-formyl-2′-methoxy-1,1′-binaphthyl (**12**).[37,38] Treatment of **12** with dimethyl (1-diazo-2-oxopropyl)phosphonate in the presence of potassium carbonate[39] then gave the requisite 2-ethynyl-2′-methoxy-1,1′-binaphthyl (**13**). Attempts to convert **9** to **13** directly by the Sonogashira reaction with (trimethylsilyl)ethyne followed by desilylation were unsuccessful. However, the Sonogashira reaction between **13** and 1-iodo-2-[(trimethylsilyl)ethynyl]benzene[40] furnished **14**, which was then desilylated to produce the benzannulated enediyne **15**.

Condensation between **15** and pivalophenone (**16**) gave the benzannulated enediynyl alcohol **17** as an essentially 1:1 mixture of two diastereomers. Reduction of **17** with triethylsilane in the presence of trifluoroacetic acid then led to the benzannulated enediyne **18**. Treatment of **18** with potassium *tert*-butoxide in refluxing toluene for 5 h then produced an essentially 1:1 mixture of the two atropisomers of 2-(5-benzo[*b*]fluorenyl)-2′-methoxy-1,1′-binaphthyl, the *syn* atropisomer **19a** (racemic) with the methoxyl group and the five-membered ring of the benzo[*b*]fluorenyl moiety *syn* to each other and the corresponding *anti* atropisomer **19b** (racemic). An AB quartet ^{1}H NMR signals attributable to the methylene hydrogens of **19a** occurred at δ 4.44 (J=21.7 Hz) and 4.36 (J=21.8 Hz), whereas those attributable to **19b** occurred upfield at δ 4.00 (J=21.0 Hz) and 3.89 (J=21.0 Hz). On the other hand, the ^{1}H NMR signal of the methoxyl group of **19b** at δ 3.20 is downfield from that of **19a** at δ 2.58.

Presumably, the transformation from **18** to **19a** and **19b** involved an initial 1,3-prototropic rearrangement to form the benzannulated enyne-allene **21** as proposed previously (Scheme 2).[25] A subsequent Schmittel cyclization reaction[41–44] then generated biradical **22** for an intramolecular radical–radical coupling to produce **23** and, after a second prototropic rearrangement, **19a** and **19b**.



Scheme 2.

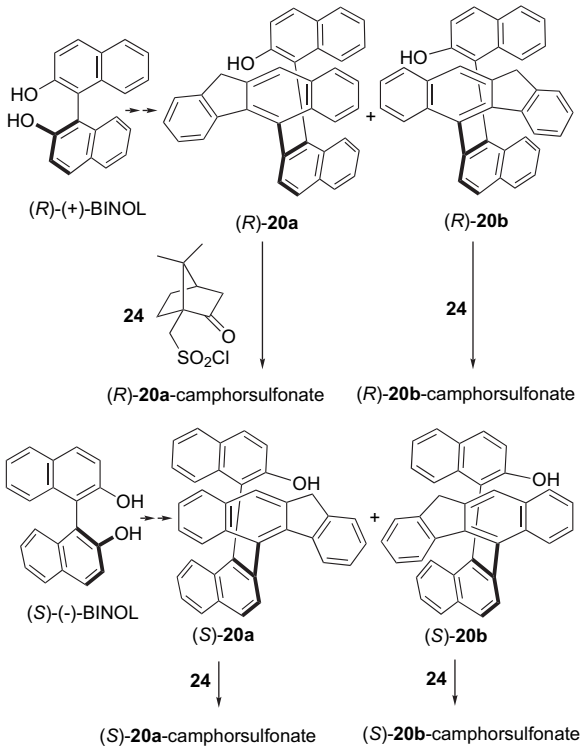
Compared to the dianion of **4** in which the indenyl anions possess a C_2 symmetry and the two faces are homotopic, the 5-benzo[*b*]fluorenyl substituent in **19a** and **19b** lacks

such a symmetry element and its two faces are heterotopic, making it possible to form the two atropisomers **19a** and **19b**. Treatment of the mixture of **19a** and **19b** with BBr_3 for demethylation then produced the corresponding *syn* atropisomer of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl (**20a**, racemic) and the corresponding *anti* atropisomer **20b** (racemic) also as a 1:1 mixture. The *tert*-butyl group was also removed under the reaction conditions. Presumably, the loss of the *tert*-butyl group occurred because of the presence of trace amount of acid in the reaction mixture, which protonated the C10 carbon of the benzofluorenyl substituent followed by the loss of a *tert*-butyl cation as observed in other aromatic systems.[45–48] It was possible to separate **20a** and **20b** by silica gel chromatography and to obtain single crystals of these two atropisomers for X-ray structure analyses.

The X-ray structures of **20a** and **20b** (Fig. 1) revealed that the benzofluorenyl substituent is essentially perpendicular to the central naphthyl ring onto which it is attached, and the other naphthyl ring bearing the hydroxyl group is also essentially perpendicular to the central naphthyl ring. The fact that **20a** and **20b** could be separated as atropisomers indicates that the rates of rotation around the carbon–carbon single bond connecting the C2 carbon of the binaphthyl system and the C5 carbon of the benzo[*b*]fluorenyl substituent and around the C1–C1′ single bond are slow at room temperature. Heating **20a** and **20b** in refluxing toluene (110 °C) for 5 h showed no interconversion between the two atropisomers. The AB quartet ^{1}H NMR signals of the methylene hydrogens of **20a** occurred at δ 4.14 (J=22.2 Hz) and 4.08 (J=21.6 Hz), downfield from those of **20b** at δ 3.87 (J=21.6 Hz) and 3.68 (J=21.6 Hz).

By starting from enantiomerically pure (*R*)-(+)-BINOL with $[\alpha]_D^{25}$ +36.1 (*c* 1, THF) to prepare (*R*)-(+)-**15** with $[\alpha]_D^{25}$ +102 (*c* 0.90, THF) for condensation with **16**, the synthetic sequence led to (*R*)-**20a** and (*R*)-**20b**, which were separated by silica gel chromatography and were found to exhibit specific rotations of $[\alpha]_D^{25}$ +124 (*c* 0.53, THF) and $[\alpha]_D^{25}$ +44.4 (*c* 0.49, THF), respectively (Scheme 3). Similarly, by starting from (*S*)-(−)-BINOL with $[\alpha]_D^{25}$ −36.8 (*c* 1, THF) to prepare (*S*)-(−)-**15** with $[\alpha]_D^{25}$ −102 (*c* 1.1, THF), (*S*)-**20a** with $[\alpha]_D^{25}$ −126 (*c* 0.76, THF), and (*S*)-**20b** with $[\alpha]_D^{25}$ −44.9 (*c* 0.72, THF) were produced.

The four corresponding sulfonic esters, derived from the reactions of (*R*)-**20a**, (*R*)-**20b**, (*S*)-**20a**, and (*S*)-**20b** with



Scheme 3.

(1*S*)-(+)-10-camphorsulfonyl chloride (**24**), were found to be of high diastereomeric purity (>99% de) by ^{1}H NMR analysis of the methyl signals recorded on a 600 MHz NMR spectrometer. The ^{1}H NMR signals of the two methyl groups in (*R*)-**20a**-camphorsulfonate occurred at δ 0.82 and 0.51, clearly separated from those of (*S*)-**20a**-camphorsulfonate at δ 0.84 and 0.49, from those of (*R*)-**20b**-camphorsulfonate at δ 0.88 and 0.57, and from those of (*S*)-**20b**-camphorsulfonate at δ 0.85 and 0.66. The noise levels of the ^{1}H NMR spectra of these four camphorsulfonates were low, allowing the ^{13}C-satellites (0.55% each) of the methyl signals to be clearly discerned. As a result, it was possible to detect the presence of minute quantities (0.55%) of the three other isomers. For example, in the case of (*R*)-**20a**-camphorsulfonate, the ^{13}C-satellites of the most upfield shift methyl signal occurred at δ 0.62 and 0.41 with peak heights significantly taller than any other signals that could be attributed to the methyl groups of the three other isomers at δ 0.49, 0.57, and 0.66. The ability to

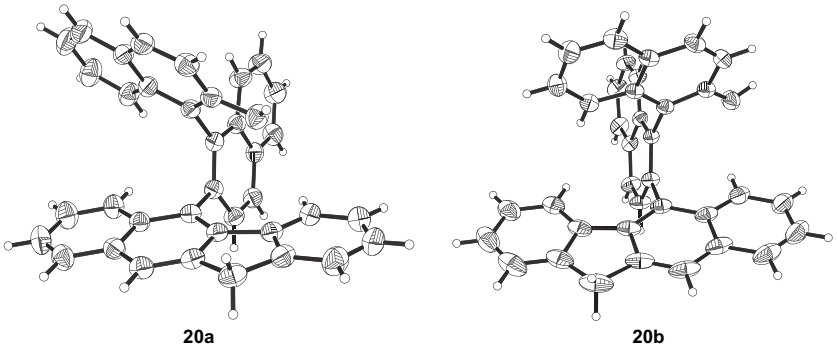
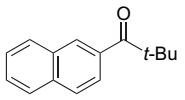
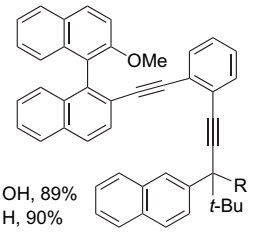
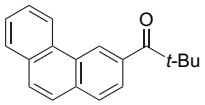
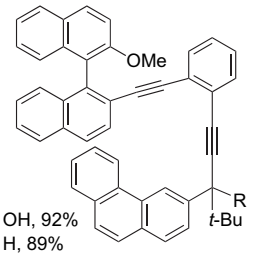


Figure 1. X-ray structures of the *syn* atropisomer **20a** and the *anti* atropisomer **20b**.

Table 1. Synthesis of benzannulated enediynyl alcohols and enediynes

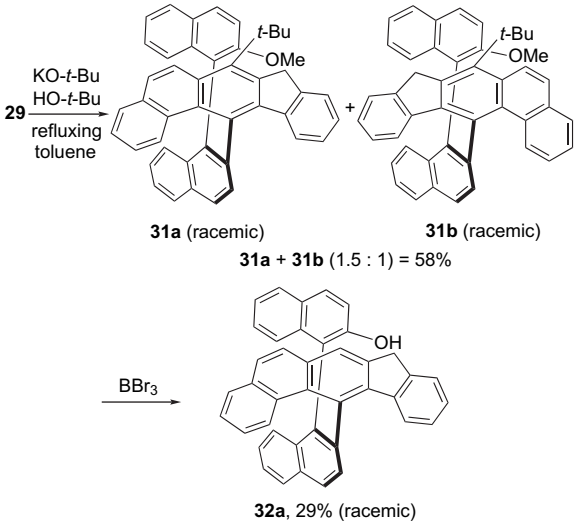
Aryl ketones	Enediynyl alcohols and enediynes
 **25**	 **27**: R = OH, 89% **29**: R = H, 90%
 **26**	 **28**: R = OH, 92% **30**: R = H, 89%

achieve high optical purity also suggests that no rotation occurred around the C1–C1′ single bond during the entire synthetic sequence.

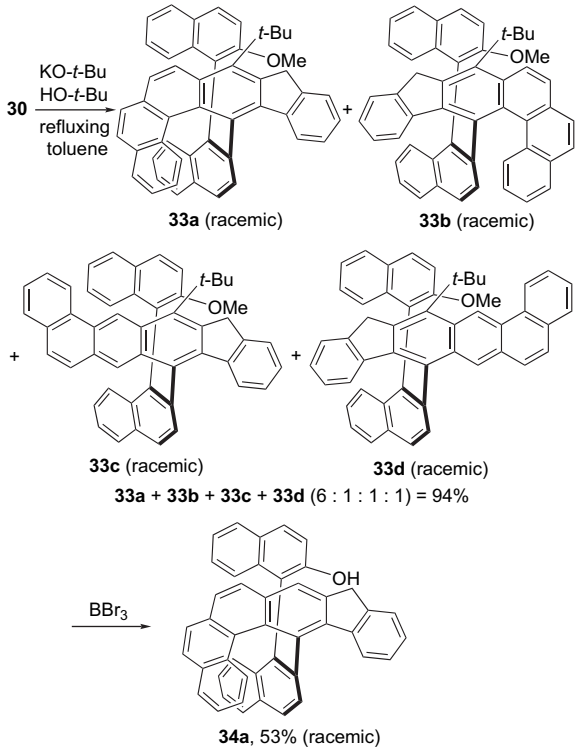
Similarly, the use of aryl ketone **25**, readily prepared from coupling between 2-naphthoyl chloride and *tert*-butylcopper in quantitative yield,[28,49] for condensation with **15** produced enediynyl alcohol **27** (Table 1). The use of aryl ketone **26**, likewise prepared by treatment of 3-phenanthrenecarboxylic acid[50] with thionyl chloride followed by *tert*-butylcopper (95% yield), for condensation with **15** produced **28**. Subsequent reduction of **27** and **28** with triethylsilane in the presence of trifluoroacetic acid then provided the benzannulated enediynes **29** and **30**, respectively. Treatment of **29** with potassium *tert*-butoxide in refluxing toluene for 5 h furnished the *syn* atropisomer **31a** and the *anti* atropisomer **31b** in a 1.5:1 ratio (Scheme 4). It is worth noting that the intramolecular radical–radical coupling reaction of the biradical derived from **29** involved only the α-position of the naphthyl ring originated from aryl ketone **25** to produce **31a** and **31b** as observed previously.[28] Attacking the β-position to form the corresponding indeno-fused anthracene derivatives did not appear to occur. The higher reactivity of the α-position than the β-position of naphthalene in the homolytic addition may be responsible for the regioselectivity.[51,52]

The ^{1}H NMR signals of the methylene hydrogens of **31a** occurred as an overlapping singlet at δ 4.40, whereas those of **31b** occurred upfield as an AB quartet at δ 3.83 (J=20.5 Hz) and 3.54 (J=21.3 Hz), similar to those of **19b**. On the other hand, the ^{1}H NMR signal of the methoxyl hydrogens of **31b** occurred at δ 2.44, downfield from that of **31a** at δ 2.29. A single crystal of **31a** suitable for X-ray structure analysis was obtained by recrystallization of the mixture from a mixture of methylene chloride/hexanes solution. Because of non-bonded steric interactions, the indeno-fused phenanthrene moiety in **31a** is non-planar with the phenanthrene unit showing a bend in the direction away from the 2-methoxynaphthyl ring system. Treatment of a mixture of **31a** and **31b** with BBr_3 for demethylation allowed the separation of **32a** from the resulting mixture by silica gel chromatography.

Treatment of **30** with potassium *tert*-butoxide in refluxing toluene for 5 h produced a more complex mixture of products with the ^{1}H NMR spectrum showing four sets of methylene AB quartets in an approximately 6:1:1:1 ratio with the major AB quartet signals attributable to **33a** occurred at δ 4.51 (J=21.5 Hz) and 4.42 (J=21.0 Hz) (Scheme 5). The other three methylene AB quartets occurred between δ 4.60 and 3.91 could be tentatively attributed to **33b**, **33c**, and **33d**. As in the case of **31a** and **31b**, attacking the C4 carbon of the phenanthryl system originated from aryl ketone



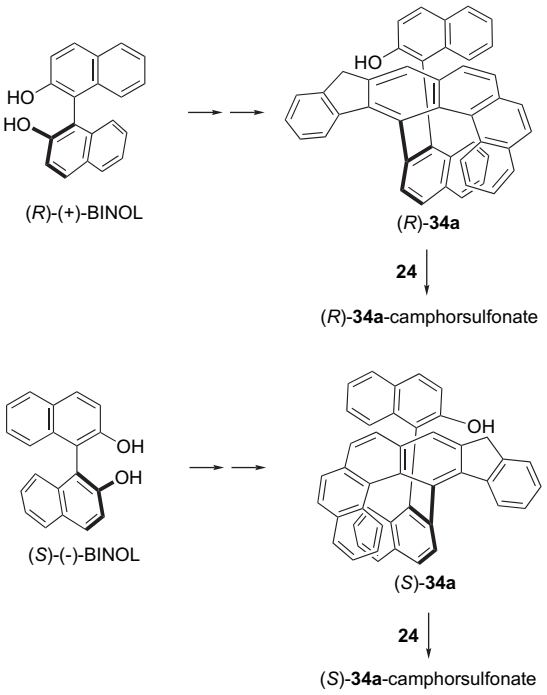
Scheme 4.



Scheme 5.

26 during the intramolecular radical–radical coupling reaction could lead to **33a** and **33b**, whereas attacking the C2 carbon of the phenanthryl system could account for the formation of **33c** and **33d**. Treatment of the mixture with BBr_3 allowed the isolation of the *syn* atropisomer **34a** by silica gel chromatography.

Optically active (*R*)-**34a** with $[\alpha]_D^{20}$ −735 (*c* 1.2, THF) and (*S*)-**34a** with $[\alpha]_D^{20}$ +722 (*c* 0.92, THF) were also prepared from (*R*)-(+)-BINOL and (*S*)-(−)-BINOL, respectively (Scheme 6). The ^1H NMR spectra of the corresponding sulfonic esters, (*R*)-**34a**-camphorsulfonate and (*S*)-**34a**-camphorsulfonate, showed that these two binaphthyl derivatives were also of high diastereomeric purity (>97% de).



Scheme 6.

3. Conclusion

A synthetic pathway leading to the atropisomers of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl and related compounds was developed. The structures of *syn* atropisomers **20a** and **31a** and *anti* atropisomer **20b** were established by X-ray structure analyses. The presence of a hydroxyl group and a benzo[*b*]fluorenyl or a related group in these 2,2′-disubstituted 1,1′-binaphthyls could allow the formation of useful complexes with metals. The enantiomerically pure *syn* atropisomers, (*R*)-**20a**, (*S*)-**20a**, (*R*)-**34a**, and (*S*)-**34a**, hold potential as hetero-bidentate ligands for asymmetric catalysis.

4. Experimental

4.1. General

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. (*R*)-(+)-BINOL with $[\alpha]_D^{25}$ +36.1 (*c* 1, THF), (*S*)-(−)-BINOL with $[\alpha]_D^{25}$ −36.8 (*c* 1, THF), *n*-butyllithium (1.6 M) in hexanes, *tert*-butyllithium (1.7 M) in pentane, triethylsilane, trifluoroacetic acid, potassium *tert*-butoxide (1.0 M) in 2-methyl-2-propanol, 1-bromo-2-[(trimethylsilyl)ethynyl]benzene, $Pd(PPh_3)_4$, copper(I) iodide, $CuBr\cdot SMe_2$, diisopropylamine, pivalophenone (**16**), 2-naphthoyl chloride, boron tribromide, and (1*S*)-(+)-10-camphorsulfonyl chloride (**24**) with $[\alpha]_D^{22}$ +33 (*c* 1, $CHCl_3$) were purchased from chemical suppliers and were used as received. Compounds **8**[29] and **9**[30] were prepared according to the reported procedures. The $NiCl_2$(dppp)-catalyzed (dppp=$Ph_2PCH_2CH_2CH_2PPh_2$) cross-coupling reaction[31,32] between **9** and methylmagnesium iodide was employed for the synthesis of **10**[33] in 93% yield. Bromination of **10** with NBS produced **11**[34,35] in 90% yield. The subsequent oxidation of **11** with $NaIO_4$[36] then furnished **12**[37,38] in 86% yield. 1-Iodo-2-[(trimethylsilyl)ethynyl]benzene[40] was prepared by treatment of 1-bromo-2-[(trimethylsilyl)-ethynyl]benzene in THF with *n*-butyllithium at −78° C followed by iodine. Aryl ketone **25** was prepared in quantitative yield by coupling of 2-naphthoyl chloride with *tert*-butylcopper as described previously.[28,49] Aryl ketone **26** (95% yield) was likewise prepared by treatment of 3-phenanthrenecarboxylic acid with thionyl chloride followed by *tert*-butylcopper. 3-Phenanthrenecarboxylic acid was prepared from commercially available 3-acetylphenanthrene as reported previously.[50] ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^1H δ 7.26) and $CDCl_3$ (^{13}C δ 77.0) as internal standards unless otherwise indicated for those recorded on a 600 MHz NMR spectrometer.

4.1.1. 2-Ethynyl-2′-methoxy-1,1′-binaphthyl (13). To a solution of 0.420 g (1.35 mmol) of **12** and 0.373 g of potassium carbonate in 20 mL of anhydrous methanol was added 0.311 g (1.62 mmol) of dimethyl (1-diazo-2-oxopropyl)-phosphonate,[39] and the reaction mixture was stirred at room temperature for 24 h. The analysis of the reaction mixture by TLC indicated that **12** was completely consumed at this stage. The reaction mixture was then diluted with diethyl ether, washed with a 5% aqueous sodium bicarbonate solution, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/25% CH_2Cl_2 in hexanes) afforded 0.376 g of **13** (1.22 mmol, 90%) as a white solid: IR 3282, 1508, 1262, 1082 cm^{-1}; ^1H δ 8.01 (1H, d, *J*=8.9 Hz), 7.93–7.86 (3H, m), 7.72 (1H, d, *J*=8.4 Hz), 7.51–7.44 (2H, m), 7.37–7.19 (4H, m), 7.02 (1H, d, *J*=8.7 Hz), 3.80 (3H, s), 2.76 (1H, s); ^{13}C δ 154.8, 138.8, 133.6, 133.3, 132.7, 129.8, 129.0, 128.0, 127.9, 127.7, 126.59, 126.54, 126.48, 125.0, 123.6, 121.5, 120.6, 114.0, 83.3, 79.8, 57.0; MS *m*/*z* 331 (MNa^+), 239, 204; HRMS calcd for $C_{23}H_{16}ONa$ (MNa^+) 331.1099, found 331.1096.

Enantiomerically pure (*R*)-**13** with $[\alpha]_D^{25}$ +48.6 (*c* 1.2, THF) and (*S*)-**13** with $[\alpha]_D^{25}$ −49.5 (*c* 1.3, THF) were prepared from (*R*)-(+)-BINOL and (*S*)-(−)-BINOL, respectively.

4.1.2. 2-Methoxy-2′-[2-[(trimethylsilyl)ethynyl]phenyl]-ethynyl-1,1′-binaphthyl (14). To a mixture of 1-iodo-2-[(trimethylsilyl)ethynyl]benzene (0.126 g, 0.813 mmol),[40]

$Pd(PPh_3)_4$ (0.104 g, 0.090 mmol), and copper(I) iodide (0.052 g, 0.272 mmol) in 10 mL of toluene was added via cannula a solution of 0.209 g of **13** (0.679 mmol) in 3 mL of diisopropylamine. After 13 h of stirring at 70 °C, 20 mL of a saturated ammonium chloride solution and 20 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/25% methylene chloride in hexanes) afforded 0.292 g of **14** (0.608 mmol, 90%) as a white solid: IR 2157, 1249, 865 cm^{-1}; ^1H δ 8.04 (1H, d, J=9.1 Hz), 7.96–7.89 (3H, m), 7.80 (1H, d, J=8.4 Hz), 7.52–7.45 (2H, m), 7.37–7.27 (4H, m), 7.23 (1H, td, J=6.7, 1.2 Hz), 7.13 (1H, d, J=7.9 Hz), 7.07 (1H, td, J=7.3, 1.2 Hz), 6.98 (1H, td, J=7.7, 1.4 Hz), 6.24 (1H, dd, J=7.9, 1.4 Hz), 3.80 (3H, s), 0.32 (9H, s); ^{13}C δ 155.0, 138.3, 133.8, 133.1, 132.8, 131.92, 131.85, 129.7, 129.0, 128.5, 128.1, 127.84, 127.77, 127.63, 127.3, 126.5, 126.4, 126.1, 125.4, 124.6, 123.6, 121.92, 121.85, 103.5, 98.2, 93.8, 91.5, 57.0, 0.1.

4.1.3. 2-(2-Ethynylphenyl)ethynyl-2′-methoxy-1,1′-binaphthyl (15). To 0.292 g (0.608 mmol) of **14** in 10 mL of diethyl ether were added 4 mL of a 10% sodium hydroxide solution and 10 mL of methanol. After 30 min of stirring at room temperature, the organic solvent was removed in vacuo, and 20 mL of water and 20 mL of diethyl ether were added to the residue. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/25% methylene chloride in hexanes) afforded 0.232 g of **15** (0.569 mmol, 94%) as a white solid: IR 3282, 2205, 1507, 1267, 1082 cm^{-1}; ^1H δ 8.02 (1H, d, J=8.9 Hz), 7.95–7.88 (3H, m), 7.82 (1H, d, J=8.4 Hz), 7.50–7.43 (2H, m), 7.38–7.20 (5H, m), 7.15–7.08 (3H, m), 6.82–6.78 (1H, m), 3.77 (3H, s), 2.67 (1H, s); ^{13}C δ 155.0, 138.1, 134.1, 133.2, 132.9, 132.1, 131.9, 129.7, 129.06, 128.96, 128.1, 127.8, 127.7, 127.4, 126.5, 125.5, 123.9, 123.5, 121.9, 121.7, 114.2, 93.7, 90.9, 81.5, 80.8, 57.0; MS m/z 431 (MNa^+), 381; HRMS calcd for $C_{31}H_{20}ONa$ (MNa^+) 431.1412, found 431.1409.

Enantiomerically pure (*R*)-**15** with $[\alpha]_D^{25}$ +102 (*c* 0.90, THF) and (*S*)-**15** with $[\alpha]_D^{25}$ −102 (*c* 1.1, THF) were prepared from (*R*)-(+)-BINOL and (*S*)-(−)-BINOL, respectively.

4.1.4. Benzannulated enediynyl alcohol 17. To 0.125 g (0.306 mmol) of **15** in 10 mL of anhydrous diethyl ether under a nitrogen atmosphere at 0 °C was added 0.20 mL of a 1.6 M solution of *n*-butyllithium (0.32 mmol) in hexanes. After 30 min of stirring, a solution of 0.055 g of **16** (0.340 mmol) in 4 mL of diethyl ether was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 15 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% diethyl ether in hexanes) provided 0.160 g (0.281 mmol, 92%) of **17** (essentially a 1:1 mixture of two diastereomers) as a yellow liquid: IR 3568, 1265 cm^{-1}; ^1H δ 8.03 (2H, dd, J=8.9, 1.5 Hz), 7.93–7.74 (8H, m), 7.59 (1H, d, J=7.2 Hz), 7.56 (1H, d, J=6.9 Hz), 7.51–7.44 (4H, m), 7.36–7.20 (16H, m), 7.17–7.06 (4H, m), 6.99 (2H, dt, J=7.6, 1.8 Hz), 6.26 (1H, dd, J=7.7, 0.7 Hz), 6.21 (1H, dd, J=7.7, 0.7 Hz), 3.78 and 3.76 (6H, two singlets), 2.46 and 2.43 (2H, two singlets), 1.13 (18H, s); ^{13}C δ 154.9, 142.1, 138.61, 138.57, 133.8, 133.1, 132.8, 132.2, 131.81, 131.77, 129.7, 129.1, 128.26, 128.20, 128.1, 127.84, 127.78, 127.68, 127.61, 127.4, 127.3, 127.1, 126.51, 125.9, 125.3, 124.2, 123.6, 122.1, 122.0, 121.6, 114.14, 114.07, 96.0, 93.6, 91.8, 91.7, 84.5, 79.5, 57.0, 56.9, 39.7, 25.6; MS m/z 593 (MNa^+), 437, 381; HRMS calcd for $C_{42}H_{34}O_2Na$ (MNa^+) 593.2457, found 593.2454.

4.1.5. Benzannulated enediyne 18. To a mixture of **17** (0.162 g, 0.284 mmol) and triethylsilane (0.102 g, 0.875 mmol) in 15 mL of methylene chloride was added 0.20 mL of trifluoroacetic acid (0.309 g, 2.69 mmol). After 5 min of stirring at room temperature, 0.480 g of sodium carbonate (4.6 mmol) was added followed by 10 mL of water and 40 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/10% CH_2Cl_2 in hexanes) provided 0.140 g (0.253 mmol, 89%) of **18** (essentially a 1:1 mixture of two diastereomers) as a yellow liquid: IR 2226, 1248, 726 cm^{-1}; ^1H δ 8.03 (2H, d, J=9.2 Hz), 7.92 (4H, d, J=7.9 Hz), 7.85 (2H, d, J=8.4 Hz), 7.55 (2H, d, J=8.4 Hz), 7.52–7.44 (9H, m), 7.37–7.20 (15H, m), 7.16–7.11 (2H, m), 7.07 (2H, td, J=7.7, 1.5 Hz), 6.95 (2H, t, J=7.7 Hz), 6.21 (2H, t, J=6.9 Hz), 3.79 (3H, s), 3.76 (3H, s), 3.70 (1H, s), 3.69 (1H, s), 1.09 (18H, s); ^{13}C δ 155.0, 139.2, 138.4, 133.8, 133.1, 132.8, 132.2, 131.8, 131.7, 129.8, 129.7, 129.1, 128.4, 128.0, 127.8, 127.6, 127.5, 127.3, 127.0, 126.7, 126.5, 126.4, 125.7, 125.4, 123.6, 122.1, 121.9, 114.1, 95.3, 93.2, 92.1, 82.4, 57.0, 50.6, 35.5, 27.8; MS m/z 577 (MNa^+), 437, 381; HRMS calcd for $C_{42}H_{34}ONa$ (MNa^+) 577.2507, found 577.2506. The sample of **18** contains about 3% of residual hexanes as determined by the ^1H NMR spectrum.

4.1.6. *syn* and *anti* Atropisomers of 2-(5-benzo[*b*]fluorenyl)-2′-hydroxy-1,1′-binaphthyl (20a and 20b). To 0.089 g of **18** (0.161 mmol) in 5 mL of anhydrous toluene under a nitrogen atmosphere was added 0.2 mL of a 1.0 M solution of potassium *tert*-butoxide (0.2 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 5 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 30 mL of methylene chloride were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% methylene chloride in hexanes) to provide 0.070 g of a 1:1 mixture of **19a** and **19b** (0.126 mmol, 78%) as a pale yellow solid. The AB quartet ^1H NMR signals of the methylene hydrogens of **19a** occurred at δ 4.44 (J=21.7 Hz) and 4.36 (J=21.8 Hz), whereas those of **19b** occurred at δ 4.00 (J=21.0 Hz) and 3.89 (J=21.0 Hz). The signal of the methoxyl hydrogens of **19a** occurred at δ 2.58 and that of **19b** occurred at δ 3.20.

To a mixture of **19a** and **19b** (0.073 g, 0.13 mmol) in 10 mL of methylene chloride was added dropwise 0.2 mL of boron

tribromide at 0 °C. The reaction mixture was stirred at 0 °C for 4 h before 10 mL of water and 20 mL of methylene chloride were introduced. The organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/5% ethyl acetate in hexanes) to provide 0.024 g (0.050 mmol, 39%) of **20a** and 0.026 g (0.054 mmol, 42%) of **20b** as yellow solids. **20a**: ^{1}H (600 MHz) δ 8.28 (1H, d, J=8.4 Hz), 8.16 (1H, d, J=7.8 Hz), 7.79 (1H, d, J=7.8 Hz), 7.77 (1H, s), 7.64 (1H, ddd, J=7.8, 6.6, 1.2 Hz), 7.57 (1H, d, J=7.2 Hz), 7.55 (1H, d, J=7.8 Hz), 7.52–7.50 (2H, m), 7.40–7.38 (2H, m), 7.35 (1H, d, J=7.8 Hz), 7.26 (1H, t, J=7.2 Hz), 7.20–7.14 (3H, m), 7.08 (1H, ddd, J=8.4, 6.6, 1.2 Hz), 7.03 (1H, t, J=7.8 Hz), 6.75 (1H, ddd, J=8.4, 6.6, 1.2 Hz), 6.69 (1H, d, J=9.0 Hz), 6.51 (1H, d, J=7.8 Hz), 4.82 (1H, s), 4.14 (1H, d, J=22.2 Hz), 4.08 (1H, d, J=21.6 Hz); ^{13}C (150 MHz) δ 151.6, 144.5, 141.5, 140.5, 138.5, 137.3, 134.5, 133.54, 133.45, 132.3, 132.1, 131.6, 131.1, 130.0, 129.8, 129.5, 128.5, 128.4, 127.7, 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 126.7, 126.3, 125.9, 125.5, 125.1, 124.2, 123.0, 122.7, 121.5, 117.2, 116.6, 36.4; MS m/z 484 (M^+), 313; HRMS calcd for $C_{37}H_{24}O$ 484.1827, found 484.1829. Recrystallization from a mixture of ethanol and methylene chloride produced a crystal suitable for X-ray structure analysis. **20b**: ^{1}H (600 Hz) δ 8.29 (1H, d, J=8.4 Hz), 8.18 (1H, J=8.4 Hz), 7.92 (1H, dd, J=8.4, 0.6 Hz), 7.67 (1H, t, J=7.2 Hz), 7.59 (1H, d, J=7.8 Hz), 7.57 (1H, d, J=8.0 Hz), 7.56 (1H, s), 7.54 (1H, d, J=8.4 Hz), 7.47 (1H, t, J=7.2 Hz), 7.43 (1H, d, J=7.2 Hz), 7.36 (2H, t, J=7.8 Hz), 7.30 (1H, t, J=7.5 Hz), 7.25–7.23 (2H, m), 7.16 (1H, d, J=8.4 Hz), 7.10 (1H, t, J=7.8 Hz), 6.98 (1H, d, J=8.4 Hz), 6.84 (1H, t, J=7.5 Hz), 6.79 (1H, dd, J=9.0, 1.2 Hz), 6.22 (1H, t, J=7.5 Hz), 4.78 (1H, s), 3.87 (1H, d, J=21.6 Hz), 3.68 (1H, d, J=21.6 Hz); ^{13}C (150 MHz) δ 150.6, 144.0, 141.6, 140.5, 138.7, 137.8, 133.6, 133.4, 133.1, 132.3, 132.2, 131.9, 131.6, 130.3, 129.3 (two carbons), 128.7, 128.1, 127.5, 127.3, 126.91, 126.86, 126.79, 126.5, 126.24, 126.21, 125.9, 125.0, 124.7, 124.5, 124.34, 124.32, 122.7, 122.5, 117.4, 117.1, 36.0; MS m/z 484 (M^+), 215; HRMS calcd for $C_{37}H_{24}O$ 484.1827, found 484.1821. Recrystallization from a mixture of ethanol and methylene chloride produced a crystal suitable for X-ray structure analysis. The sample of **20b** contains about 5% of residual hexanes as determined by the ^{1}H NMR spectrum.

Enantiomerically pure (*R*)-**20a** with $[\alpha]_D^{25}$ +124 (*c* 0.53, THF) and (*R*)-**20b** with $[\alpha]_D^{25}$ +44.4 (*c* 0.49, THF) were prepared from (*R*)-(+)-BINOL, whereas (*S*)-**20a** with $[\alpha]_D^{25}$ −126 (*c* 0.76, THF) and (*S*)-**20b** with $[\alpha]_D^{25}$ −44.9 (*c* 0.72, THF) were also prepared from (*S*)-(−)-BINOL.

4.1.7. (*R*)-20a-Camphorsulfonate. To 0.011 g of (*R*)-**20a** (0.023 mmol) and triethylamine (0.05 mL, 0.09 mmol) in 3 mL of anhydrous methylene chloride at 0 °C under a nitrogen atmosphere was added 0.031 g of (1*S*)-(+)-10-camphorsulfonyl chloride (**24**, 0.12 mmol). The reaction mixture was stirred at 0 °C for 3 h before 2 mL of a 10% aqueous sodium hydroxide solution was added. The reaction mixture was stirred for an additional 2 h. Water was added, and the reaction mixture was extracted with methylene chloride. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/25% methylene chloride in hexanes) afforded 0.015 g of (*R*)-**20a**-camphorsulfonate (0.021 mmol, 91%) as a light yellow solid: IR 1739, 1366, 1218 cm^{-1}; ^{1}H (600 Hz) δ 8.27 (1H, d, J=8.4 Hz), 8.15 (1H, d, J=8.4 Hz), 7.84 (1H, dd, J=8.4, 2.4 Hz), 7.71 (1H, s), 7.59 (1H, t, J=7.5 Hz), 7.55 (1H, d, J=8.4 Hz), 7.53–7.50 (2H, m), 7.48 (1H, d, J=8.4 Hz), 7.44 (1H, dd, J=9.0, 2.4 Hz), 7.39 (1H, t, J=7.5 Hz), 7.36 (1H, d, J=9.0 Hz), 7.29–7.26 (2H, m), 7.23 (1H, t, J=7.2 Hz), 7.20 (1H, t, J=8.4 Hz), 7.11 (1H, t, J=7.2 Hz), 7.02 (1H, td, J=8.4, 3.0 Hz), 6.99 (1H, d, J=8.4 Hz), 6.92 (1H, d, J=7.2 Hz), 6.58 (1H, t, J=7.8 Hz), 4.13 (1H, d, J=21.6 Hz), 4.03 (1H, d, J=21.0 Hz), 2.91 (1H, d, J=14.4 Hz), 2.22 (1H, d, J=18.0 Hz), 2.10 (1H, t, J=12.6 Hz), 1.97 (1H, d, J=14.4 Hz), 1.94 (1H, br t), 1.88–1.83 (1H, m), 1.79 (1H, d, J=18.6 Hz), 1.42–1.36 (1H, m), 0.82 (3H, s), 0.51 (3H, s); ^{13}C (150 MHz) δ 213.5, 145.1, 144.0, 141.6, 140.9, 138.3, 137.8, 133.9, 133.11, 133.06, 132.7, 132.0, 131.9, 131.2, 130.9, 129.5, 129.2, 129.0, 128.4, 127.9, 127.7, 127.3, 127.1, 126.98, 126.96, 126.93, 126.73, 126.65, 126.3, 125.7, 125.3, 125.2, 124.7, 124.6, 123.7, 122.6, 121.1, 57.8, 48.7, 47.5, 42.7, 42.3, 36.4, 26.7, 24.9, 19.5, 19.4.

4.1.8. (*S*)-20a-Camphorsulfonate. The same procedure was repeated as described for (*R*)-**20a**-camphorsulfonate except that 0.014 g of (*S*)-**20a** (0.029 mmol) was used to afford 0.018 g of (*S*)-**20a**-camphorsulfonate (0.026 mmol, 90%) as a light yellow solid: IR 1739, 1366, 1217 cm^{-1}; ^{1}H (600 MHz) δ 8.25 (1H, d, J=8.4 Hz), 8.14 (1H, d, J=8.4 Hz), 7.82 (1H, dd, J=7.8, 1.8 Hz), 7.72 (1H, s), 7.60–7.54 (3H, m), 7.52 (1H, d, J=7.2 Hz), 7.48 (1H, d, J=8.4 Hz), 7.44 (1H, d, J=8.4 Hz), 7.39 (1H, t, J=7.2 Hz), 7.36 (1H, d, J=8.4 Hz), 7.32 (1H, t, J=7.5 Hz), 7.26–7.19 (3H, m), 7.02 (1H, t, J=7.5 Hz), 7.00–6.95 (2H, m), 6.85 (1H, d, J=7.8 Hz), 6.49 (1H, t, J=7.5 Hz), 4.14 (1H, d, J=22.2 Hz), 4.05 (1H, d, J=21.6 Hz), 2.71 (1H, dd, J=15.0, 1.2 Hz), 2.31 (1H, dd, J=15.0, 1.2 Hz), 2.21 (1H, d, J=18.0 Hz), 1.97–1.92 (2H, m), 1.82 (1H, t, J=11 Hz), 1.76 (1H, d, J=18.6 Hz), 1.26–1.11 (2H, m), 0.84 (3H, s), 0.49 (3H, s); ^{13}C (150 MHz) δ 213.3, 145.1, 144.1, 141.7, 140.9, 138.4, 137.8, 133.9, 133.2, 133.0, 132.6, 132.1, 131.8, 131.4, 130.7, 129.6, 129.2 (two carbons), 128.3, 127.9, 127.8, 127.6, 127.4, 127.0, 126.84, 126.81, 126.62, 126.60, 126.3, 125.8, 125.4, 125.0, 124.7, 124.6, 123.6, 122.6, 121.2, 57.8, 48.3, 47.3, 42.9, 42.2, 36.4, 26.7, 25.2, 19.7, 19.4.

4.1.9. 1,1′-Binaphthyl 31a. The same procedure was repeated as described for **19a** and **19b** except that 0.121 g (0.200 mmol) of **29** in 8 mL of anhydrous toluene was treated with 0.42 mL of a 1.0 M solution of potassium *tert*-butoxide (0.42 mmol) in 2-methyl-2-propanol, and the reaction mixture was heated under reflux for 5 h to afford 0.070 g of a mixture of **31a** and **31b** (**31a**:**31b**=1.5:1, 0.116 mmol, 58%) as a pale yellow solid. Recrystallization from a mixture of hexanes and methylene chloride produced a crystal of **31a** suitable for X-ray structure analysis. **31a**: ^{1}H δ 8.41 (1H, d, J=8.7 Hz), 8.29 (1H, d, J=8.9 Hz), 8.13 (1H, d, J=8.2 Hz), 8.11 (1H, d, J=8.9 Hz), 7.70 (1H, d, J=9.7 Hz), 7.56–7.45 (2H, m), 7.34 (1H, d, J=8.6 Hz), 7.23–7.10 (5H, m), 6.95 (1H, t, J=8.4 Hz), 6.90–6.82 (2H, m), 6.75 (1H, d, J=9.4 Hz), 6.58 (1H, d, J=8.2 Hz), 6.48 (1H, d, J=9.2 Hz),

6.31 (1H, ddd, J=8.2, 6.7, 1.5 Hz), 5.94 (1H, d, J=8.7 Hz), 4.40 (2H, s), 2.29 (3H, s), 1.71 (9H, s); MS m/z 604 (M^+), 547; HRMS calcd for $C_{46}H_{36}O$ 604.2766, found 604.2766.

The ^{1}H NMR spectrum of the 1.5:1 mixture of **31a** and **31b** exhibited a set of AB quartet signals at δ 3.83 (J=20.5 Hz) and 3.54 (J=21.3 Hz) and a singlet at δ 2.44 attributable to the methylene hydrogens and methoxyl hydrogens of **31b**, respectively.

4.1.10. 1,1′-Binaphthyl 32a. To a mixture of **31a** and **31b** (0.058 g, 0.096 mmol) in 10 mL of methylene chloride was added dropwise 0.2 mL of boron tribromide at 0 °C. The reaction mixture was stirred at 0 °C for 6 h before 10 mL of water and 20 mL of methylene chloride were introduced. The organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/5% ethyl acetate in hexanes) to provide 0.015 g (0.028 mmol, 29%) of **32a** as a yellow solid: ^{1}H (600 MHz) δ 8.48 (2H, s), 8.25 (1H, d, J=8.4 Hz), 8.22 (1H, d, J=7.8 Hz), 7.74 (1H, s), 7.63 (1H, ddd, J=8.4, 7.2, 1.2 Hz), 7.60 (1H, d, J=7.2 Hz), 7.41 (1H, d, J=7.8 Hz), 7.31–7.24 (6H, m), 7.23 (1H, d, J=9.0 Hz), 7.173 (1H, d, J=8.4 Hz), 7.169 (1H, d, J=9.0 Hz), 7.06 (1H, ddd, J=8.4, 7.2, 1.2 Hz), 7.04 (1H, t, J=7.2 Hz), 6.78 (1H, ddd, J=7.8, 6.0, 1.8 Hz), 6.67 (1H, d, J=8.4 Hz), 6.52 (1H, d, J=9.0 Hz), 6.26–6.21 (2H, m), 4.32 (1H, s), 4.14 (1H, d, J=21.6 Hz), 4.06 (1H, d, J=21.0 Hz); MS m/z 534 (M^+), 265; HRMS calcd for $C_{41}H_{26}O$ 534.1984, found 534.1970.

4.1.11. 1,1′-Binaphthyl 34a. The same procedure was repeated as described for **19a** and **19b** except that 0.087 g (0.133 mmol) of **30** in 5 mL of anhydrous toluene was treated with 0.30 mL of a 1.0 M solution of potassium *tert*-butoxide (0.30 mmol) in 2-methyl-2-propanol, and the reaction mixture was heated under reflux for 5 h to afford 0.082 g of a mixture of **33a**, **33b**, **33c**, and **33d** (**33a**:**33b**:**33c**:**33d**=6:1:1:1, 0.125 mmol, 94%) as a yellow solid. A dominant set of AB quartet ^{1}H NMR signals at δ 4.51 (J=21.5 Hz) and 4.42 (J=21.0 Hz) attributable to **33a** along with three minor sets of AB quartet signals between δ 4.60 and 3.91 attributable to **33b–d** were also observed.

To a mixture of **33a**, **33b**, **33c**, and **33d** (0.039 g, 0.060 mmol) in 5 mL of methylene chloride was added dropwise 0.1 mL of boron tribromide at 0 °C. The reaction mixture was stirred at 0 °C for 2 h before 10 mL of water and 20 mL of methylene chloride were introduced. The organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/5% ethyl acetate in hexanes) to provide 0.019 g (0.032 mmol, 53%) of **34a** as a yellow solid: IR 3541, 1517, 1141 cm^{-1}; ^{1}H (600 MHz) δ 8.84 (1H, d, J=9.0 Hz), 8.60 (1H, d, J=8.4 Hz), 8.15 (1H, d, J=8.4 Hz), 7.93 (1H, d, J=8.4 Hz), 7.87 (1H, s), 7.61 (2H, t, J=6.9 Hz), 7.47 (1H, d, J=8.4 Hz), 7.43 (1H, d, J=7.8 Hz), 7.40 (1H, t, J=7.8 Hz), 7.39 (1H, d, J=7.8 Hz), 7.31 (1H, d, J=7.8 Hz), 7.29–7.27 (2H, m), 7.21 (1H, d, J=9.0 Hz), 7.04–6.99 (3H, m), 6.97 (1H, d, J=8.4 Hz), 6.96 (1H, d, J=8.4 Hz), 6.79 (1H, d, J=7.8 Hz), 6.73 (1H, d, J=8.4 Hz), 6.61 (1H, t, J=7.8 Hz), 6.37 (1H, d, J=8.4 Hz), 5.19 (1H, d, J=8.4 Hz), 4.24 (1H, d, J=21.6 Hz), 4.20 (1H, d, J=21.0 Hz), 3.98 (1H, s); ^{13}C (150 MHz) δ 149.9, 145.0, 141.9, 141.4, 139.8, 139.5, 134.5, 134.0, 133.7, 133.1, 132.65, 132.63, 131.6, 131.5, 131.4, 130.9, 129.2, 128.6, 128.5, 128.0, 127.85, 127.80, 127.5, 127.30, 127.26, 127.22, 127.21, 127.0, 126.41, 126.38, 126.17, 126.10, 125.92, 125.84, 125.75, 125.4, 125.1, 124.5, 124.2, 123.3, 122.5, 121.7, 116.05, 116.01, 36.6; MS m/z 584 (M^+), 315; HRMS calcd for $C_{45}H_{28}O$ 584.2140, found 584.2150. The sample of **34a** contains about 5–10% of residual hexanes as determined by the ^{1}H NMR spectrum.

Enantiomerically pure (*R*)-**34a** with $[\alpha]_D^{20}$ −735 (*c* 1.2, THF) and (*S*)-**34a** with $[\alpha]_D^{20}$ +722 (*c* 0.92, THF) were prepared from (*R*)-(+)-BINOL and (*S*)-(−)-BINOL, respectively.

5. Supplementary information

Experimental procedures and spectroscopic data for (*R*)-**20b**-camphorsulfonate, (*S*)-**20b**-camphorsulfonate, **27–30**, (*R*)-**34a**-camphorsulfonate, and (*S*)-**34a**-camphorsulfonate; ^{1}H and/or ^{13}C NMR spectra of compounds **13–15**, **17**, **18**, **20a**, **20b**, (*R*)-**20a**-camphorsulfonate, (*R*)-**20b**-camphorsulfonate, (*S*)-**20a**-camphorsulfonate, (*S*)-**20b**-camphorsulfonate, **27–30**, **31a**, **32a**, **34a**, (*R*)-**34a**-camphorsulfonate, and (*S*)-**34a**-camphorsulfonate; the ORTEP drawings of the crystal structures of **20a**, **20b**, and **31a**; Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC nos. 292506, 292507, and 292508 have been assigned for the compounds **20a**, **20b**, and **31a**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.06.004.

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