Synlett N. Someshwar et al. Letter

Desymmetrization of Symmetrical Triarylcarbinols: Synthesis of 7-Arylfluorenes and a C_2-Symmetric Chiral BIFOL Phosphoric Acid

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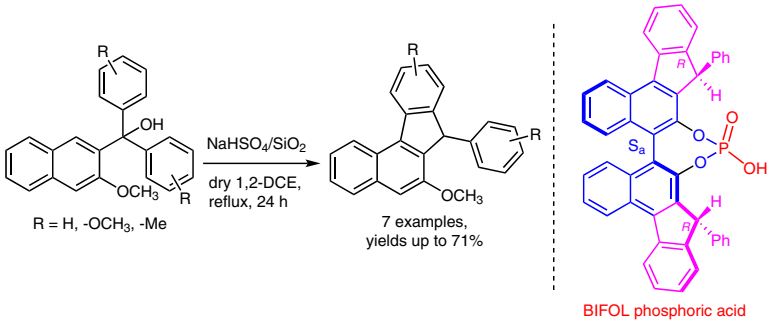
Dedicated to Prof. Takahiko Akiyama for his contribution in chiral phosphoric acid organocatalysis



Received: 27.04.2017
Accepted after revision: 20.06.2017
Published online: 19.07.2017
DOI: 10.1055/s-0036-1589074; Art ID: st-2017-b0297-l

Abstract A simple and an efficient method for the synthesis of 7-arylfluorenes by intramolecular cyclization of the corresponding triarylcarbinols in the presence of the solid-acid catalyst $NaHSO_4/SiO_2$ has been developed. By using this method, a new chiral diol with a C_2-symmetric bisfluorenyl unit, 7,7′-diphenyl-7*H*,7′*H*-5,5′-bibenzo[*c*]fluorene-6,6′-diol (BIFOL), having central chirality was synthesized in an optically active form from (*S*)-(–)-BINOL-3,3′-dicarboxylic acid. The absolute configuration of the chiral bisfluorene derivative BIFOL was ascertained by single-crystal X-ray analysis. Furthermore, a new chiral phosphoric acid was synthesized from BIFOL and evaluated for enantioselective transfer hydrogenation.

Key words benzofluorenes, ligands, asymmetric synthesis, triarylcarbinols, cyclization, transfer hydrogenation

In asymmetric synthesis, effective and selective catalysts are always in demand. By modulating the steric and electronic factors that are used to fine-tune a catalyst, the optimal rate and selectivity can be achieved in a particular reaction.[1] The perfect situation of rationally designed chiral catalysts with predictable chemical reactivities and enantioselectivities is an unachieved goal because of our inability to understand and control the way in which catalysts work. Consequently, continuous efforts have been made to develop new chiral molecules of potential use as chiral discriminators in stereoselective transformations. For example, C_2-symmetric diols have been successfully used as backbones for the preparation of various chiral molecules, such as diamines or diphosphines, that are widely used as ligands for transition metals. Importantly, chiral diols have also been employed as synthetic precursors for the preparation of organocatalysts such as phosphoric acids[2] or phosphoramidites.[3] A tunable dihedral angle capable of satisfying coordination requirements and a rigid C_2-symmetric structure together play a fundamental role in the stereochemical control of chemical transformations, as well as in avoiding the involvement of multiple transition states in stereoselective transformations, permitting reactions to deliver good to excellent stereoselectivities.[4–10,11d] The privileged chiral diols used in asymmetric organic transformations are mainly based on chiral hydrobenzoin **1**,[4] TADDOL **2**,[5] BIPHENOL **3**,[6] BINOL **4**,[7] VAPOL **5**,[9] VANOL **6**,[9] SPINOL **7**,[10] other derivatives (Figure 1).[8,11a–c] Most of these chiral diols possess C_2-symmetry with chiral elements such as axial chirality, central chirality or planar chirality. Chiral diols possessing both axial and central chirality have scarcely been investigated for their use as analogues. Hence, the development of new C_2-symmetric chiral diols is always in demand to realize good selectivity in enantioselective or diastereoselective

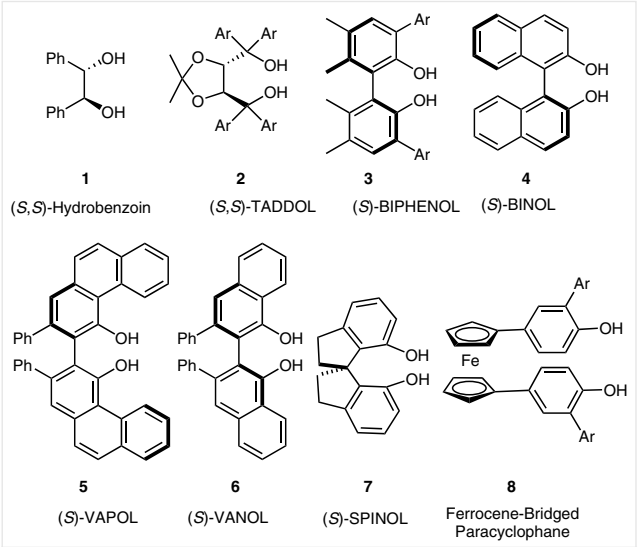
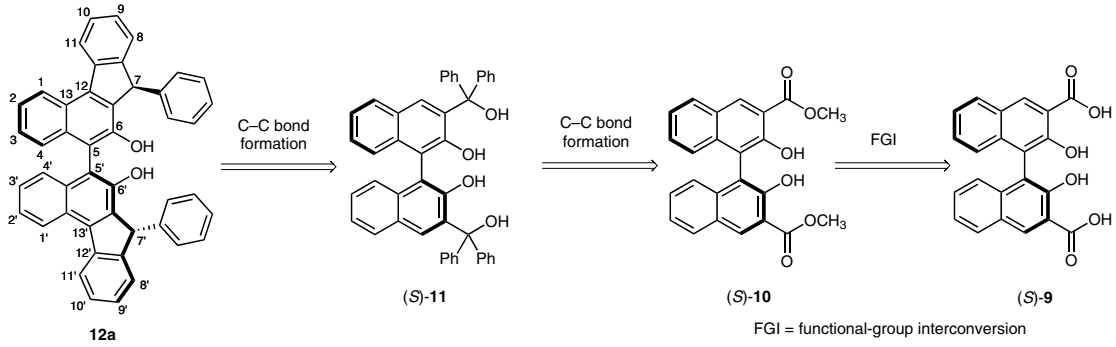


Figure 1 Representative examples of chiral diols



Scheme 1 Retrosynthetic analysis of BIFOL (**12a**)

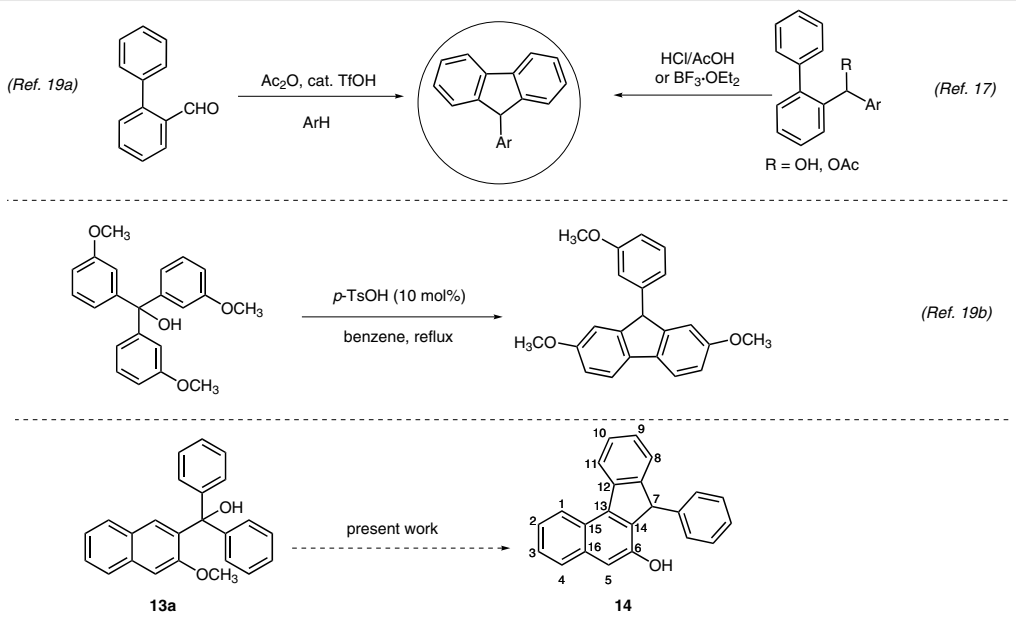
reactions. This prompted us to design and develop a new class of chiral diols having a C_2-symmetric bisfluorenyl unit with integral central chirality.

The design and production of synthetic chiral molecules is an interesting and active field in asymmetric catalysis. Owing to the possibility of preparing both isomers of the catalyst in enantiomerically pure forms, new synthetic chiral diols with the necessary stereochemistry are always attractive. Hence, we conceptually designed a novel chiral molecule BIFOL (**12a**) possessing both axial and central chirality. A retrosynthetic analysis of BIFOL (**12a**) is shown in Scheme 1.

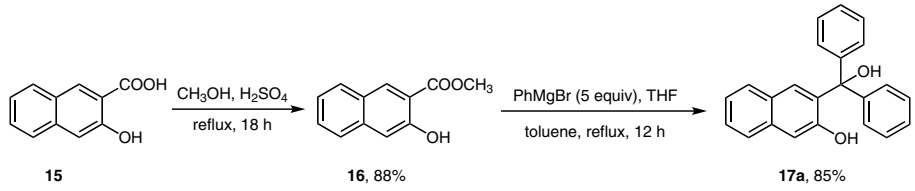
Precursor (*S*)-**11** for the preparation of BIFOL (**12a**) might be generated from diol (*S*)-**10** through addition of PhMgBr. Diol (*S*)-**10** might, in turn, be synthesized from the simple key starting material (*S*)-BINOL-3,3′-dicarboxylic acid [(*S*)-**9**].

Because BIFOL (**12a**) is a dimeric form of the benzofluorenol **14** (Scheme 2), we made a systematic effort to develop a method for assembling the monomeric fluorene skeleton **14** from 3-hydroxy-2-naphthoic acid. There are many reported methods for the synthesis of aryl-substituted fluorene derivatives.[12–19] However, most of these protocols give poor yields and some of them involve multiple steps or have narrow substrate scopes; in some cases, the required 9-arylfluorenes are not even generated. There are few reports in the literature on the preparation of aryl-substituted fluorenes from triarylcarbinols. Because triarylcarbinols are easily accessible from arylcarboxylic acids by Grignard reactions, we intended to develop a method for preparing 7-arylfluorene derivatives by this route.

The symmetrical triarylcarbinol **17a**, required for the synthesis of the 7-arylfluorene **14**, was easily prepared in

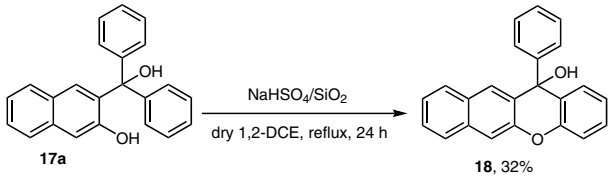


Scheme 2 Syntheses of arylfluorene derivatives from carbinols



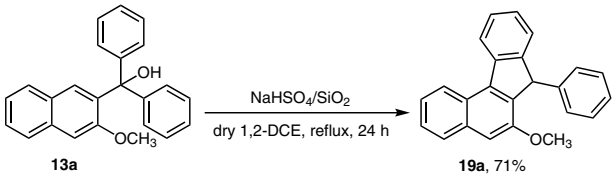
15 16, 88% 17a, 85%

Scheme 3 Synthesis of triarylcarbinol **17a**



17a 18, 32%

Scheme 4 Formation of xanthene **18** from triarylcarbinol **17a**

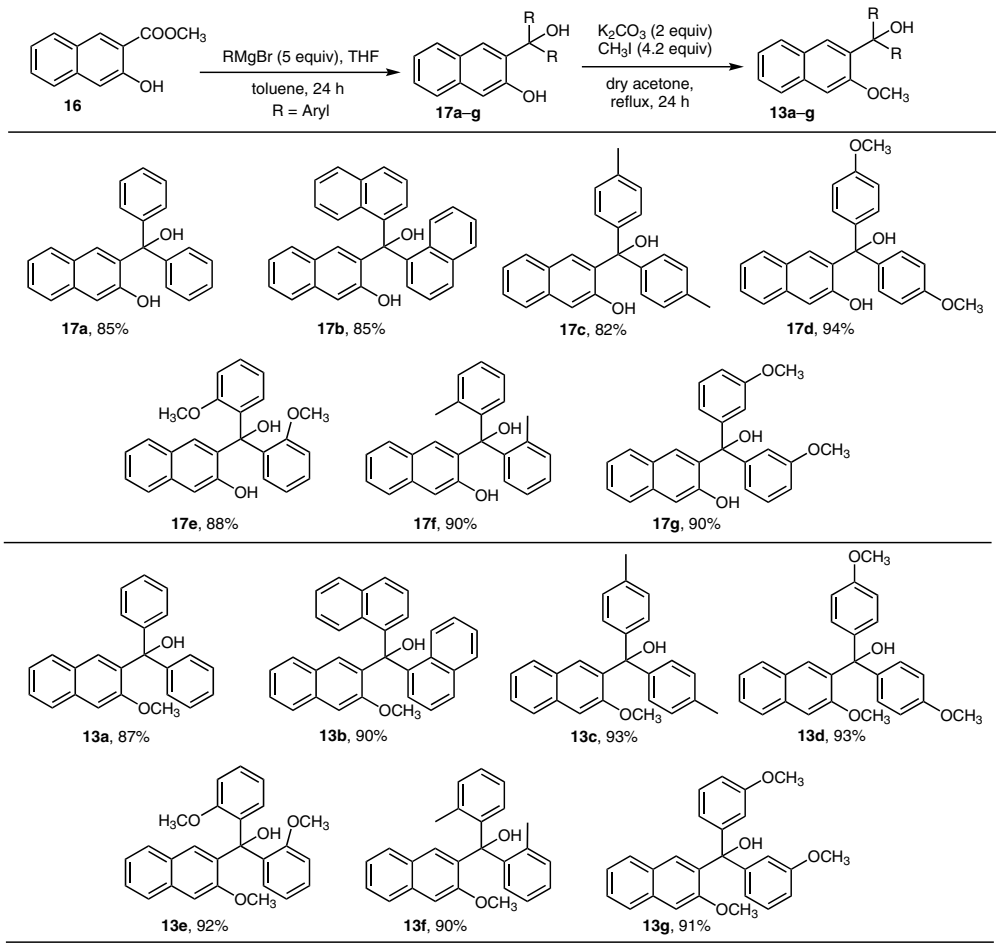


13a 19a, 71%

Scheme 5 Formation of the 7-arylfluorene **19a**

two steps from commercially available 2-hydroxy-3-naphthoic acid (**15**) through esterification followed by a Grignard reaction (Scheme 3).

Attempts were made to synthesize fluorene **14** by various reported methods, but none of them gave the required compound. Recently, the heterogeneous catalyst



Scheme 6 Synthesis of triarylcarbinols **17a–g** and **13a–g**

$NaHSO_4/SiO_2$ has been used in Friedel–Crafts-type reactions to facilitate C–C bond formation to produce tetraaryl methane derivatives.[20] This report encouraged us to attempt the reaction of triarylcarbinol **17a** with $NaHSO_4/SiO_2$ in refluxing 1,2-dichloroethane. After 24 hours, this reaction failed to give the required fluorene moiety; instead, xanthene **18** was isolated in 32% yield, indicating the formation of a carbocation followed by cyclic ether formation from the available free phenolic hydroxy group (Scheme 4).

To avoid the formation of xanthene **18** and to facilitate the formation of the required fluorene derivative, the phenolic hydroxy group was selectively protected as its methyl ether. To our delight, the methyl ether derivative **13a** smoothly delivered the expected stereogenic center-containing fluorene derivative **19a** in 71% yield through desymmetrization in the presence of $NaHSO_4/SiO_2$ in refluxing 1,2-dichloroethane after 24 hours (Scheme 5).

Our successful synthesis of 6-methoxy-7-phenyl-7*H*-benzo[*c*]fluorene (**19a**) from triarylmethanol **13a** by using $NaHSO_4/SiO_2$ encouraged us to try this method for the preparation of various aryl-substituted fluorene derivatives. The required methoxy-protected derivatives of triarylcarbinols **13a–g** were each synthesized in two steps by treatment of methyl 3-hydroxy-2-naphthoate (**16**) with various Grignard reagents. The first step involved the addition of the aryl Grignard reagent; this was followed by selective etherification with iodomethane, and the results are summarized in Scheme 6.

The resulting triarylcarbinols **13a–g** were subjected to cyclization in the presence of $NaHSO_4/SiO_2$. This method was found to be general, as demonstrated by the successful conversion of triarylcarbinols **13a–g** into the corresponding fluorene derivatives **19a–g** in 62–71% yield (Scheme 7). For example, the phenyl- and naphthyl-substituted carbinols **13a** and **13b**, respectively, furnished the corresponding fluorenes **19a** and **19b** in 71% and 66% yield. The position of an electron-donating functional group, for example methoxy, on the phenyl ring did not have any predictable effect on the product yield. For example, the 2-methoxyphenyl- and 4-methoxyphenyl-substituted carbinols **13d** and **13e** gave the corresponding fluorenes **19d** and **19e** in 65% and 70% yield, respectively. Carbinols **13c** and **13f** containing phenyl groups with moderately electron-donating substituents also gave the corresponding fluorenes **19c** and **19f** in 62% and 65% yield, respectively. The *m*-anisyl-group-containing carbinol **13g** gave the corresponding fluorene **19g** in 69% yield.[21]

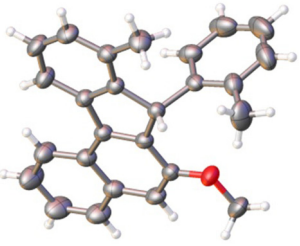
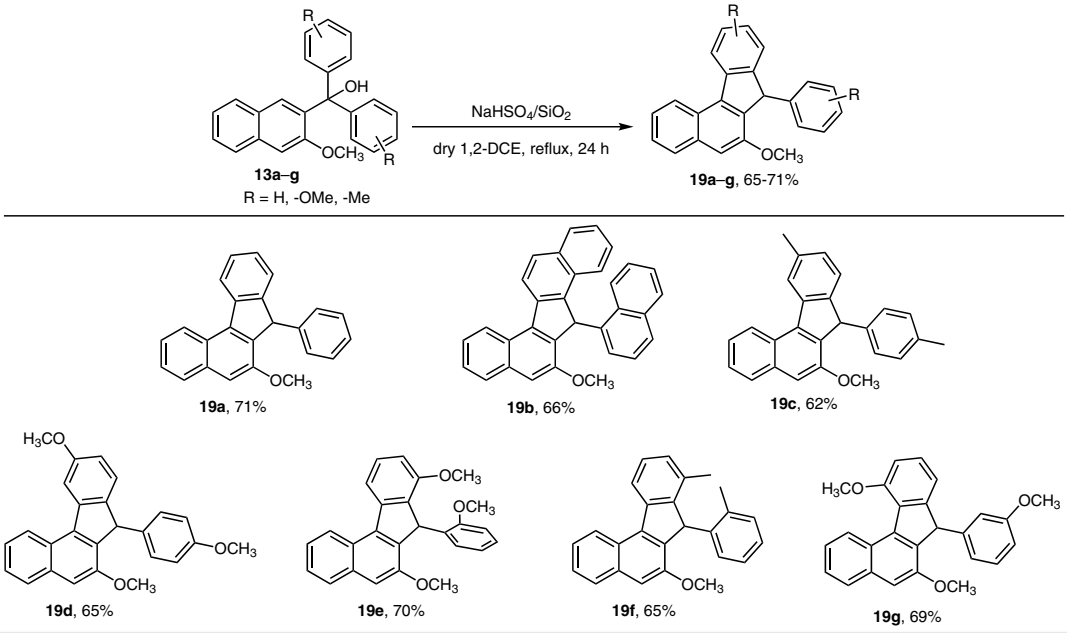
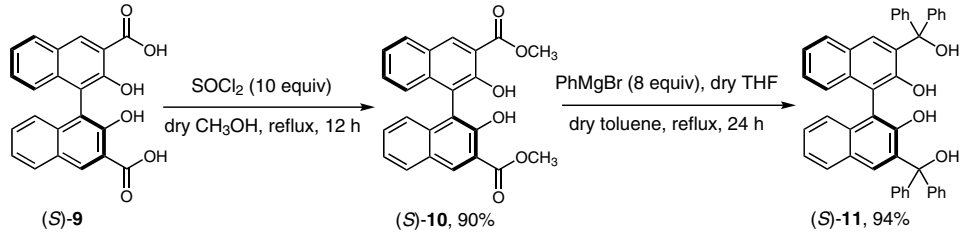


Figure 2 ORTEP diagram of crystal structure of **19f** at the 50% probability level



Scheme 7 Synthesis of aryl-substituted fluorenes **19a–g**. *Reaction conditions*: **13a–g** (1 mmol), $NaHSO_4/SiO_2$ (500 mg), anhyd DCE (10 mL), reflux, 24 h. Isolated yields of products are reported.



Scheme 8 Synthesis of (*S*)-**10** and (*S*)-**11**

Moreover, in this cyclization process, racemic mixtures of the 7-arylfluorenes **13a–g** were generated by desymmetrization through interaction of the methoxynaphthalene with one of the two other identical aryl groups. The structure of the cyclized compound **19f** was confirmed by single-crystal X-ray diffraction analysis (Figure 2).[22]

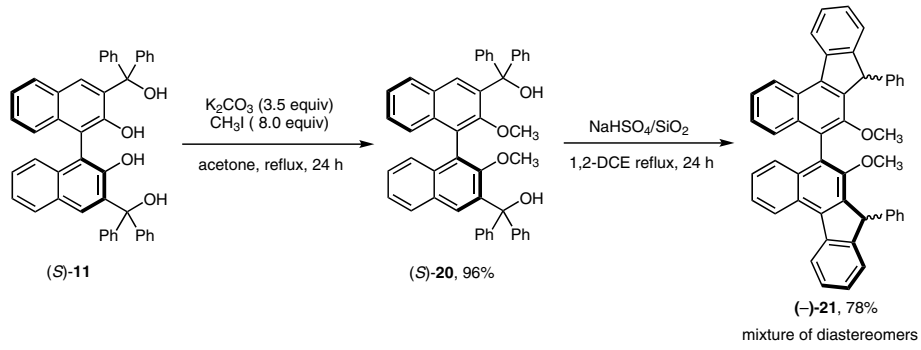
Having successfully synthesized fluorene derivatives **19a–g**, we decided to employ this cyclization strategy to prepare diol (*S*)-**20** from (*S*)-BINOL-3,3′-dicarboxylic acid [(*S*)-**9**]. Accordingly, the starting material (*S*)-**10** and (*S*)-**11** were prepared in optically active form from (*S*)-**9** by following the reported two-step protocol.[23] Esterification of (*S*)-BINOL-3,3′-dicarboxylic acid (*S*)-9 in presence of $SOCl_2$ in MeOH furnished dimethyl (*S*)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate [(*S*)-**10**] in 90% yield (Scheme 8).[24a] Addition of PhMgBr to (*S*)-**10** gave (*S*)-3,3′-bis[hydroxy(diphenyl)methyl]-1,1′-binaphthalene-2,2′-diol [(*S*)-BIMBOL; (*S*)-**11**][24b] in 94% yield (Scheme 8).

To avoid any side reaction in the cyclization process, the phenolic hydroxy group in the bistriarylcarbinol (*S*)-**11** was selectively protected as the methyl ether. Treatment of (*S*)-BIMBOL [(*S*)-**11**] with MeI in the presence of K_2CO_3 in refluxing dry acetone for 24 hours gave the corresponding dimethyl ether (*S*)-**20** in 96% yield (Scheme 9). As in the case of the monomer, the reaction of (*S*)-**20** in the presence of $NaHSO_4/SiO_2$ catalyst in refluxing 1,2-dichloroethane for 24 hours gave the dimethyl ether derivative of chiral BIFOL [(–)-**21**] as a mixture of diastereomers in 78% yield (Scheme 9).

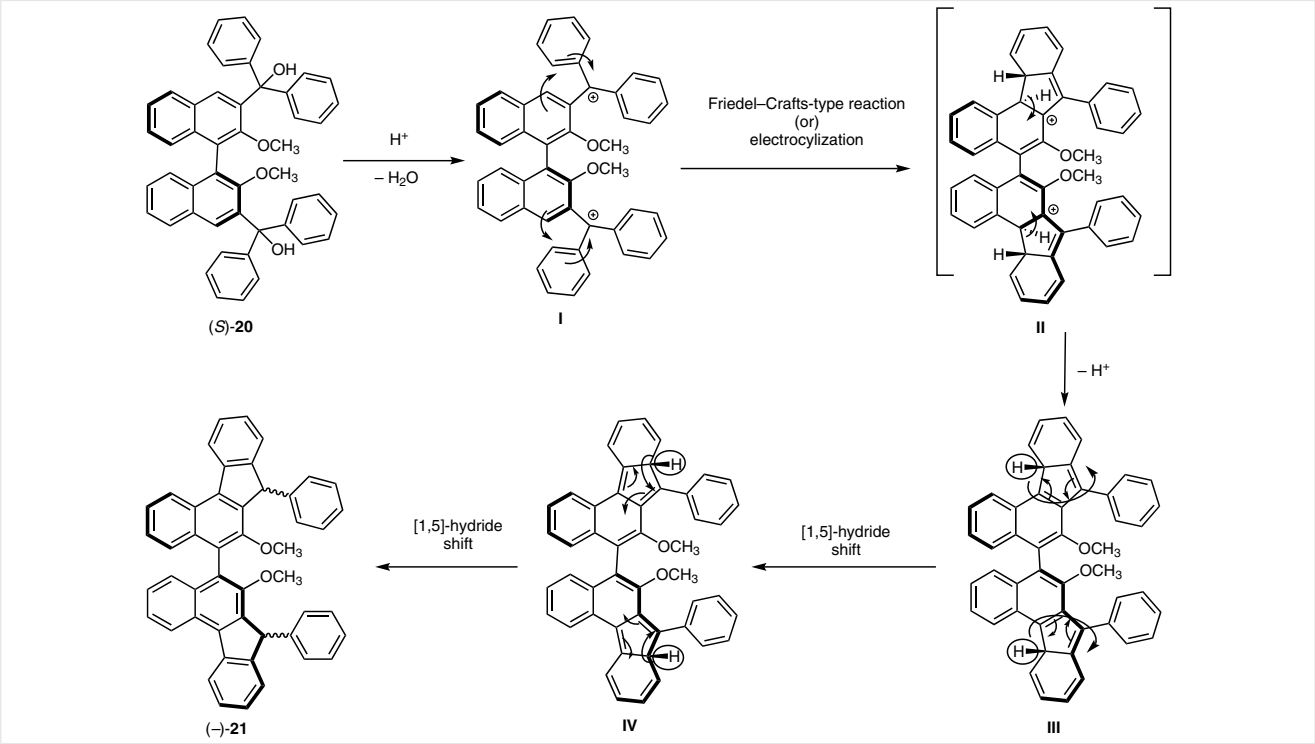
A plausible mechanism for the formation of diastereomeric mixture (–)-**21** is shown in Scheme 10. The first step in the reaction might be the generation of the bistriarylcarbocation **I** from bistriarylcarbinol (*S*)-**20** in the presence of $NaHSO_4/SiO_2$. In the second step, the bistriaryl carbocation intermediate **I** might undergo either a Nazarov-type cyclization or a Friedel–Crafts-type reaction to generate intermediate **II**. Loss of a proton from intermediate **II** generates intermediate **III**, which undergoes two successive [1,5]-hydride shifts to give the chiral BIFOL derivative (–)-**21**. The formation of a diastereomeric mixture of (–)-**21** from (*S*)-**20** indicates the involvement of carbocation generation and a Nazarov-type cyclization or a Friedel–Crafts-type reaction, followed by two successive [1,5]-hydride shifts.

The structure of (–)-**21** clearly indicates the presence of two chiral elements: central chirality at the 7 and 7′ positions and axial chirality of the binaphthyl unit. The presence of two chiral centers and one axial chirality can generate four possible diastereomers for molecule (–)-**21** (Figure 3). The ^1H NMR of (–)-**21** revealed that the reaction mixture contained four diastereomers in a 0.65:1:1:1 ratio. Unfortunately, these isomers were not separable by column chromatography.

We surmised that the generation of free phenolic hydroxy groups in the diastereomeric mixture by ether cleavage might increase the polarity of mixture, thereby permitting the separation of the isomers through column chromatography. Accordingly, demethylation in (–)-**21** was effected



Scheme 9 Preparation of dimethyl ether (–)-**21**



Scheme 10 Plausible mechanism for the formation of (–)-**21**

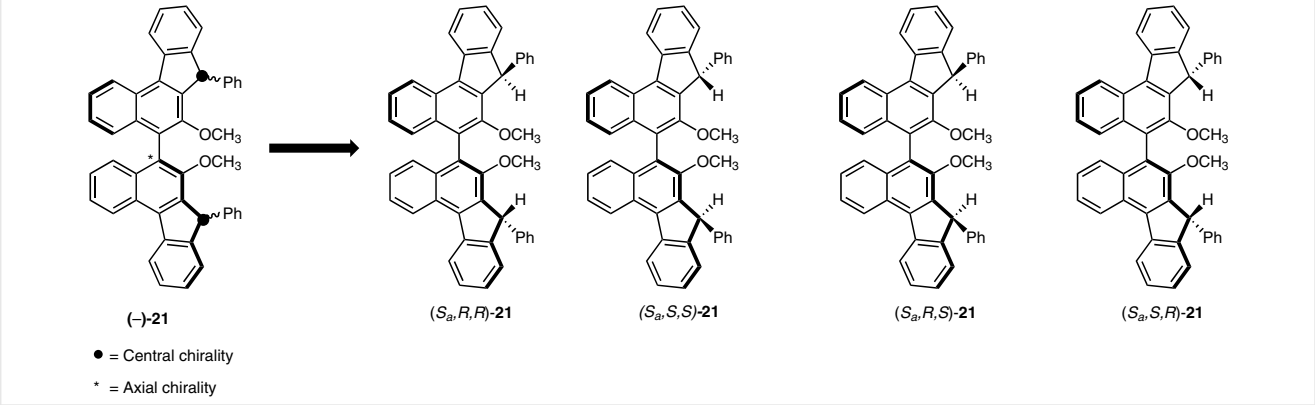


Figure 3 Possible stereoisomers of (–)-**21**

by using excess BBr_3 in dry dichloromethane at 0 °C for 24 hours to furnish the derivatives containing the free hydroxy groups (Scheme 11).

The proton NMR spectrum of the crude mixture of diols **12** displayed eight singlets in the range δ_H = 4.97–5.32 ppm; these were assigned to four benzylic CH protons and four phenolic OH protons indicating the presence of four diastereomers. The crude mixture was purified by silica gel column chromatography to give one *trans*-isomer **12a** with a positive optical rotation in 22% yield. The remaining *trans*-isomer and two *cis*-isomers were not separable (Figure 4).

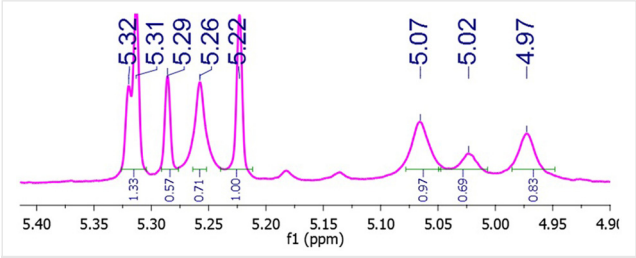
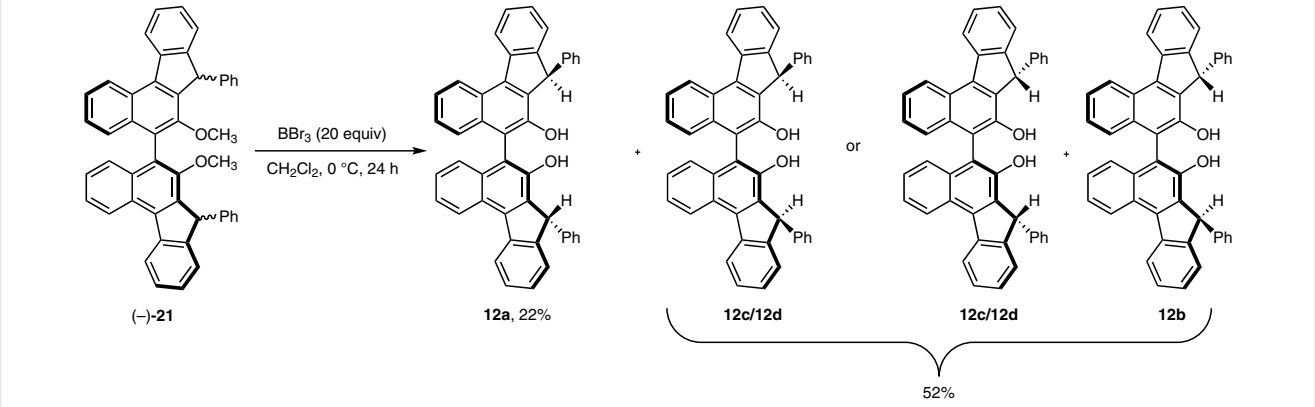


Figure 4 ^{1}H NMR spectra of the crude mixture **12** from δ_H = 4.90 to 5.4 ppm



Scheme 11 Demethylation of (–)-**21**

The structure of the C_2-symmetric *trans*-isomer (+)-**12a** was confirmed by ^{1}H NMR. In the ^{1}H NMR spectrum of (+)-**12a**, the two singlets at δ_H = 5.28 and 5.02 ppm might be due to either the benzylic CH protons at the 7- and 7′-positions or to the phenolic OH protons at the 6- and 6′-positions. The phenolic OH protons in the 6,6′-positions and the benzylic CH protons at the 7,7′-positions were distinguished by deuterium-exchange studies with (+)-**12a**. The addition of D_2O to the NMR sample of (+)-**12a** caused the disappearance of the singlet at δ_H = 5.02 ppm, indicating that the phenolic OH protons appear at δ_H = 5.02 ppm and that the benzylic CH protons appear at δ_H = 5.28 ppm for isomer (+)-**12a** (Figure 4).

Large crystals of the chiral C_2-symmetric *trans*-isomer (+)-**12a** (BIFOL) were easily obtained by dissolving the compound in hot hexane and freely cooling to room temperature. The relative configurations at the 7- and 7′-positions were assigned on basis of the known axial chirality of the starting (*S*)-(–)-BINOL-3,3′-dicarboxylic acid in the crystal structure of BIFOL [(+)-**12a**], and were found to be *R* and *R*, respectively. Therefore, the absolute configuration of the chiral compound in BIFOL, (+)-**12a** is S_a,*R*,*R* (Figure 5).[22]

To examine the stability of BIFOL [(+)-**12a**] under basic and acidic conditions, (+)-**12a** was first treated with five equivalents of NaOH in methanol or in toluene for 24 hours. No racemization was observed in either solvent. A similar result was observed with 6 N HCl (see Supporting Information). Furthermore, BIFOL [(+)-**12a**] isolated after acid or base treatment was converted into the corresponding methyl ether (+)-**21a** through etherification with K_2CO_3/MeI in dry acetone (Scheme 12).

The ^{1}H NMR of (+)-**21a** revealed that the resulting sample of BIFOL [(+)-**12a**] was formed from a 0.65 ratio of isomers in the diastereomeric mixture.

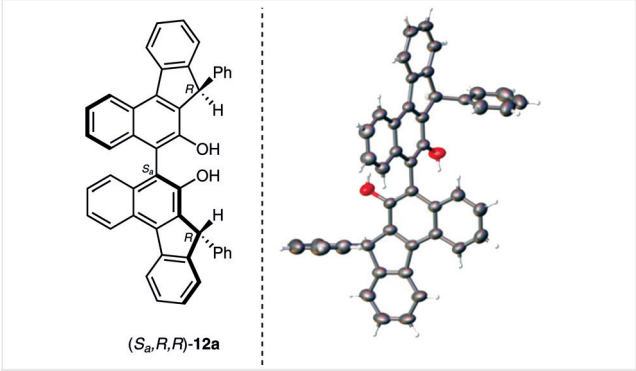
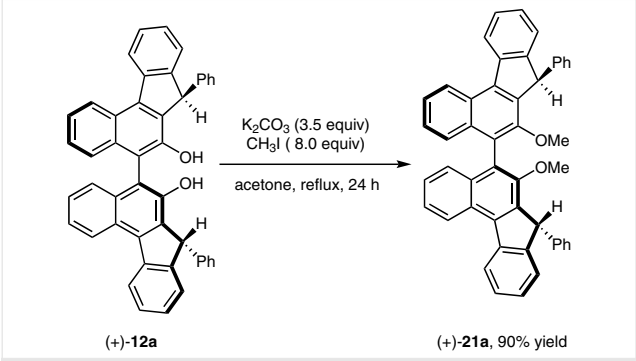
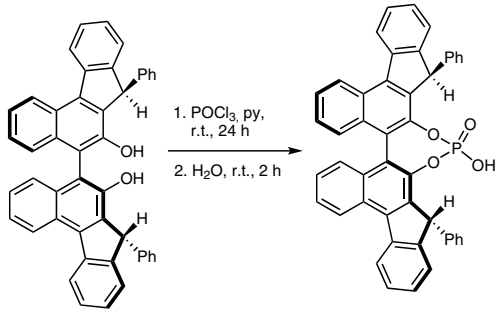


Figure 5 ORTEP diagram of (S_a,*R*,*R*)-**12a**



Scheme 12 Methylation of (+)-**12a**

To examine the possibility of using chiral BIFOL in an asymmetric organic transformation, (+)-**12a** was converted into the corresponding phosphoric acid, (+)-**22** by treatment with $POCl_3$/pyridine and subsequent hydrolysis (Scheme 13).



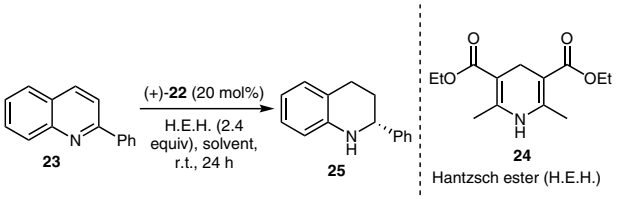
Scheme 13 Synthesis of chiral BIFOL phosphoric acid (+)-**22**

The introduction of new catalyst into the toolbox for chiral organocatalysis requires a preliminary evaluation of the new catalyst with standard reactions. We therefore screened the catalyst BIFOL phosphoric acid (+)-**22** for the enantioselective transfer hydrogenation of 2-phenylquinoline (**23**).[25] The preliminary experiments were carried out by treating 2-phenylquinoline (**23**) with Hantzsch ester **24** as a hydride source in the presence of 20 mol% of catalyst (+)-**22** in various solvents at room temperature (Table 1, entries 1–9). The BIFOL-derived phosphoric acid catalyst (+)-**22** displayed a maximum conversion after 24 hours with low enantioselectivity in various solvents. (2*R*)-2-Phenyl-1,2,3,4-tetrahydroquinoline (**25**) was obtained in 22% ee when toluene was used as a solvent (Table 1, entry 5).

Although our new chiral BIFOL phosphoric acid (+)-**22a** did catalyze the transfer hydrogenation effectively, the selectivity was not promising. Hence, either the isolation of other stereoisomers of BIFOL from the diastereomeric mixture, followed by their conversion into phosphoric acids and evaluation in transfer hydrogenation reactions, and\or the modification of the BIFOL structure is essential to achieve stereoselectivity in transfer hydrogenation reactions.

In conclusion, we have developed a new method for the synthesis of racemic arylfluorenes from the corresponding triarylcarbinols in the presence of $NaHSO_4/SiO_2$. This strategy was successfully employed with the bistriarylcarbinol derived from (*S*)-BINOL-3,3′-dicarboxylic acid to synthesize a new class of biaryl system containing bisfluorenediol moieties. The reaction of the dimethyl derivative of (*S*)-BIMBOL with $NaHSO_4/SiO_2$ generated the corresponding bisfluorene derivative as a diastereomeric mixture in a 0.65:1:1:1 ratio. From the diastereomeric mixture of BIFOL obtained from (*S*)-BINOL-3,3′-dicarboxylic acid, optically active (S_a,*R*,*R*)-**12a** was isolated through simple column chromatography. (S_a,*R*,*R*)-**12a** was converted into the corresponding chiral BIFOL phosphoric acid, (+)-**22** and examined as a catalyst for enantioselective transfer hydrogenation.

Table 1 Effect of the Catalyst and Solvent on the Efficiency and Enantioselectivity of the Hydrogenation of 2-Phenylquinoline[a]



Entry	Solvent	Conversion[b] (%)	ee[c] (%)
1	$CHCl_3$	95	6 (*R*)
2	CH_2Cl_2	94	4 (*R*)
3	DCE	100	10 (*R*)
4	$Cl_2CHCHCl_2$	100	13 (*R*)
5	**toluene**	**90 (88)**[d]	**22** (*R*)
6	benzene	94	15 (*R*)
7	THF	88	17 (*R*)
8	1,4-dioxane	90	15 (*R*)
9	Et_2O	85	8 (*R*)

[a] Reaction conditions: **23** (0.125 mmol, 1 equiv), **24** (0.3 mmol, 2.4 equiv), (+)-**22** (0.025 mmol, 20 mol%), solvent (3 mL), r.t.
[b] Determined by ^1H NMR spectroscopy.
[c] Determined by chiral HPLC analysis.[26]
[d] Isolated yield.

Funding Information

We thank CSIR, New Delhi, and DST, New Delhi, India for financial support. This work has been supported by the Science and Engineering Research Board [Grant Number SR/S1/OC-04/2011(G)] and Council of Scientific and Industrial Research [Grant Number 02(0027)/11/EMR-II]. N.S. thanks the Council of Scientific and Industrial Research, New Delhi, for an SRF. M.K. thanks Pondicherry University for a fellowship.

Acknowledgment

We thank Mr. S. V. Ganesh for solving the crystal data. We are grateful to CIF, Pondicherry University, for NMR/IR data. The assistance of the DST-FIST program and the UGC-Special Assistance Program to the Department of Chemistry, Pondicherry University, is gratefully acknowledged for XRD, HRMS, and HPLC data.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1589074.

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(21) **Arylfluorenes 19a–g; General Procedure**
A mixture of the appropriate (3-methoxy-2-naphthyl)(diaryl)methanol **13a–g** (0.5 mmol) and $NaHSO_4/SiO_2$ (250 mg) in dry DCE (10 mL) was heated at 90 °C with vigorous stirring for 24 hours under N_2. The mixture was then cooled to r.t., filtered, and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexane–EtOAc (99:1)] to give the arylfluorene **19a–g** in pure form.
6-Methoxy-7-phenyl-7*H*-benzo[*c*]fluorene (19a)
White solid; yield: 114 mg (71%); mp 168–170 °C. IR (KBr): 2922, 2846, 1592, 1559, 1457, 824, 735, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 8.0 Hz, 1 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 7.79–7.77 (m, 1 H), 7.46–7.35 (m, 3 H), 7.29–7.27 (m, 1 H), 7.21–7.17 (m, 2 H), 7.14–7.09 (m, 2 H), 7.04–6.98 (m, 3 H), 5.09 (s, 1 H), 3.70 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 150.0, 141.7, 141.0, 137.9, 137.8, 136.0, 129.7, 128.4, 128.3, 128.1, 128.0, 127.3, 126.8, 126.5, 125.9, 125.4, 125.3, 124.4, 124.0, 123.1, 106.0, 55.5, 53.0. HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{24}H_{19}O$: 323.1436; found: 323.1425.
(22) CCDC No. 1537731 and 1537733 contain the supplementary crystallographic data for compounds **19f** and **12a**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.
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(25) **(2*R*)-2-Phenyl-1,2,3,4-tetrahydroquinoline (25); Typical Procedure**
The quinoline **23** (25.6 mg, 0.125 mmol), catalyst (+)-**22** (15.3 mg, 0.025 mmol, 20 mol%), Hantzsch dihydropyridine **24** (76 mg, 0.3 mmol), and toluene (3 mL) were added under N_2 to test tube equipped with a side arm. The resulting yellow solution was stirred at r.t. for 24 h. The solvent was evaporated in vacuo, and the residue was purified by column chromatography (silica gel) to give a colorless oil; yield: 23 mg (88%; 22% ee); IR (neat): 3403, 2922, 1605, 1487, 1112, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.44 (m, 5 H), 7.22–7.18 (m, 2 H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.68 (d, *J* = 7.6 Hz, 1 H), 4.58 (dd, *J* = 9.2, 3.2 Hz, 1 H), 4.14 (s, 1 H), 3.13–3.05 (m, 1 H), 2.93–2.87 (m, 1 H), 2.32–2.25 (m, 1 H), 2.21–2.17 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.85, 144.72, 129.29, 128.56, 127.41, 126.90, 126.56, 120.81, 117.14, 114.00, 56.18, 30.97, 26.34. Chiral HPLC: (Chiralcel OD-H (4.6 × 250 mm); Mobile phase: hexanes–*i*-PrOH), flow rate: 0.6 mL/min, λ = 254 nm: $t_R(S)$ = 20.13 min, $t_R(R)$ = 27.16 min.
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