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Application of Roof-Shape Amines as Chiral Solvating Agents for Discrimination of Optically Active Acids by NMR Spectroscopy: Study of Match–Mismatch Effect and Crystal Structure of the Diastereomeric Salts

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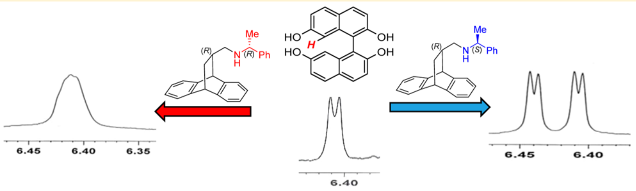
Supporting Information

ABSTRACT: Optically active roof-shape amines were prepared and scanned as chiral solvating agents to study molecular recognition of acids by NMR analysis. Three types of amines were studied to establish a match–mismatch effect for structurally diverse acid analytes. Single-crystal X-ray diffraction analysis was performed on the diastereomeric salts of roof-shape amines and both isomers of mandelic acid to establish molecular conformation and correlate the absolute configuration with the observed NMR shift. The present system also recognizes the two isomers of weakly acidic BINOL and its derivatives.



■ INTRODUCTION

Chiral molecules of different shapes, sizes, and functional groups have found a number of applications in diverse areas of modern chemistry, medicinal chemistry and material science. The relationship of their specific properties and chiral description has also been established by intense study. Because of the different pharmacological properties associated with the enantiomeric pair of the racemic compound the use of its optically pure form is becoming mandatory, particularly when used as drugs or as fragrance materials. Thus, establishing its optical purity by reliable techniques is becoming a vital consideration and a subject of active research in analytical sciences. The ratio of optical isomers of the test sample can be analyzed by different techniques such as chromatography,[1] mass spectrometry,[2] IR, UV and fluorescence spectroscopy,[3] CD, and electrophoresis,[4] etc. Some of these protocols may only succeed if a certain type of structural requirement or specific functional group is present in the analyte. In some cases, additional accessories, such as special chiral columns, are needed for the chromatography.

Nuclear magnetic resonance (NMR) spectroscopy offers an alternative method for fast, accurate, and reliable determination of optical purity of chiral molecules.[5] However, the regular NMR analysis of chiral compounds in an achiral environment (solvent) cannot differentiate the signals of the two enantiomers. The use of chiral solvents in NMR analysis has been explored with limited success.[6] For the NMR discrimination which can be conveniently measured; the enantiomers need to be derivatized to diastereomers, either by covalent bond formation or temporarily by noncovalent interactions. A traditional technique involving in situ preparation of diastereomeric lanthanide chelate complexes is one such widely used procedure.[7] Alternatively, this may also be done by the use of chiral derivatizing agents (CDA)[8] for formation of diastereomeric compounds.[9] The diastereomer formation for NMR analysis may be done by simply mixing the analyte and the chiral solvating agent (CSA) during the spectroscopic analysis.[10] Even though the use of proton NMR is more commonly employed, the focus on targeting other NMR active nuclei for the purpose of determining optical purity is increasingly being studied.[11−15] The two components, the sample under investigation, and the chirally pure CSA in the solution, interact with each other through noncovalent interactions like hydrogen bonding, halogen bonding, π-stacking, van der Waals interactions, etc. The effectiveness of a good CSA to distinguish the two isomers of the analyte primarily depends on combination of these supramolecular forces, and hence, they are quite sensitive and specific in their action. The selectivity of each CSA for specific substrates could be considered its limitation. Hence, there is constant need to design newer derivatives to scan for wider analytes for the NMR analysis.

A novel class of compounds resembling the shape of a roof was introduced and studied by Weber, while searching their applications as clathrate hosts with inclusion properties.[16] Such molecules find few applications in different areas ranging from medicinal chemistry to material science.[17] We have previously presented the synthesis and resolution of roof shape alcohols **I** and **II** and their derivatives (Chart 1).[18,19] The optically pure

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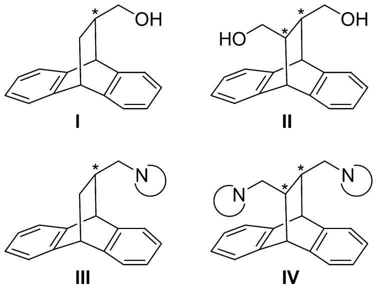
Chart 1. Roof-Shape Chiral Alcohols and Amines

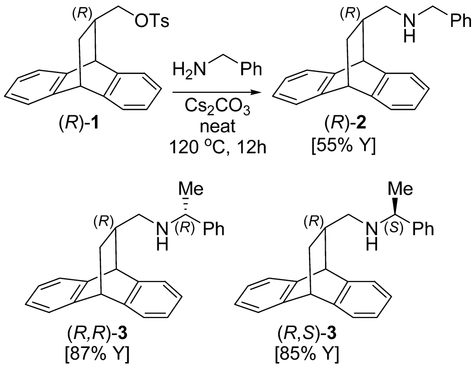


roof-shape alcohols were also converted to amines **III** and **IV** to be scanned as chiral solvating agents for discrimination of the signals of some optically active compounds in NMR spectroscopy,[19] while we also used **I** as a chiral auxiliary for asymmetric synthesis of α-halo acids.[18b]

RESULT AND DISCUSSION

In the present study, we have prepared optically pure roof-shape secondary amines and evaluated them as chiral solvating agents for the discrimination of signals of chiral acids by NMR spectroscopy. In the design, we have explored the possibility of introducing another aromatic system by choosing to attach benzyl amine with the aim of adding an additional supramolecular interaction in the form of π-stacking. With this aim, the chiral alcohol **I** was converted to its monotosylate (*R*)-**1**, and it was then treated with benzylamine to furnish chiral secondary amine (*R*)-**2** (Scheme 1). In order to study the match–mismatch effect by changing the orientation of the aromatic ring of benzyl amine, we further prepared two more derivatives by selecting two enantiomers of the chiral benzyl amine. Roof-shape amine (*R*,*R*)-**3** was prepared by using (*R*)-α-phenylethylamine, and its diastereomer (*R*,*S*)-**3** was obtained by using (*S*)-α-phenylethylamine from (*R*)-**1** by a substitution reaction. One of the two aromatic rings of the rigid bicyclic roof shape portion of the CSA, second aromatic ring of the benzyl unit, and the second chiral center should control the orientation of its diastereomeric complex with acidic analyte for effective chiral discrimination by molecular recognition.

Scheme 1. Synthesis of Roof-Shape Amines



Having prepared the three roof-shape secondary amines (*R*)-**2**, (*R*,*R*)-**3**, and (*R*,*S*)-**3** we examined different acidic substrates for a possible, detectable discrimination of the NMR signals in the analysis. The recognition study was conducted in $CDCl_3$ (400 MHz; 20 mM concentration; ratio of 1:1) with (*R*/*S*)-mandelic acid as the test substrate, targeting the $C_\alpha H$ proton of Ph*CH(OH)COOH. For such study, the degree of induced chemical shift ($\Delta\delta$) and nonequivalence ($\Delta\Delta\delta$) on the complex formation with CSA are measured. In this case, the signal of the $C_\alpha H$ proton shifted toward the upfield region in all three cases, while for (*R*)-**2** and (*R*,*R*)-**3** the signals also separated (Figure 1). However, in the case of (*R*,*S*)-**3** the signals did not resolve, and both $C_\alpha H$ protons of the diastereomeric salt appeared as one singlet (Figure 1 and Table 1).

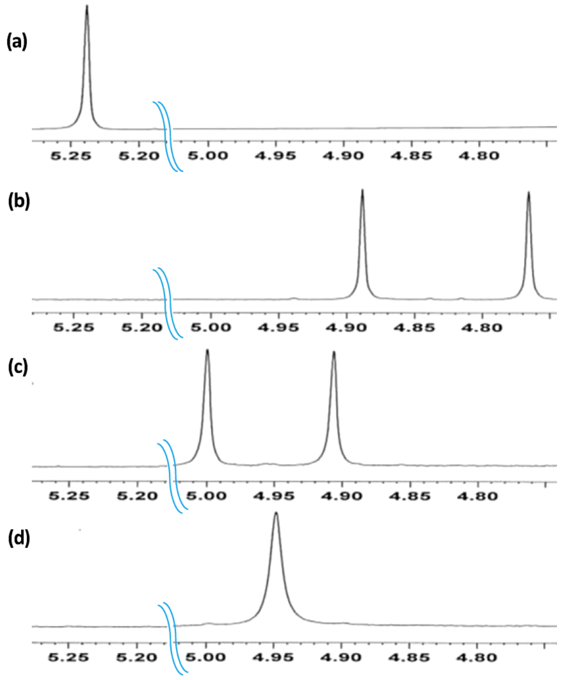


Figure 1. Separation of $C_\alpha H$ signals of (a) (*R*/*S*)-mandelic acid (b) with (*R*)-**2**; (c) with (*R*,*R*)-**3**; (d) with (*R*,*S*)-**3** (20.0 mM, $CDCl_3$, 400 MHz).

The probable mode of action for the recognition of substrates with amino CSA should involve its protonation followed by its complexation with carboxylate. The formation of the carboxylate anion was confirmed when the carbonyl stretch (1716 cm^{-1} for mandelic acid) disappeared in the FT-IR spectra of its mixture with (*R*)-**2** or (*R*,*R*)-**3**, and the new strong peaks appeared at 1624 and 1602 cm^{-1} (the COO^- stretch).[20] However, in the case of (*R*,*S*)-**3** all the three peaks were observed, possibly indicating incomplete complex formation.

In the case of α-chloropropanoic acid, all three roof-shape amines failed to distinguish the signals (entry 2, Table 1). We also examined derivatives of mandelic acid where the hydroxyl group was blocked by introducing suitable protecting groups. In the case of *O*-acetyl mandelic acid and *O*-methyl mandelic acid, we observed a similar pattern of selectivity, although the chemical shift nonequivalence ($\Delta\Delta\delta$) was much reduced (entries 3 and 4, Table 1). Similar selectivity was seen in the case of α-bromo phenylacetic acid (entry 5, Table 1), contrary to α-chloropropanoic acid, indicating the supporting role of aromatic ring in the molecular recognition. It is often advantageous to analyze a sample by targeting more than one nuclei to confirm the optical purity. Application of ^{19}F NMR spectra for structural determination has distinct advantages of fewer and sharper peaks compared to ^1H NMR. We extended our study for 4-trifluoromethylmandelic acid and compared the

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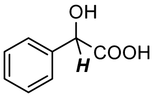
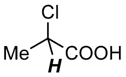
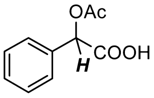
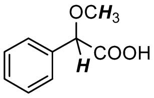
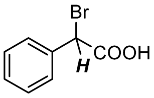
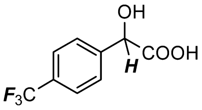
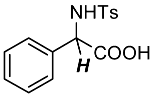
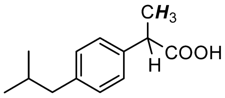
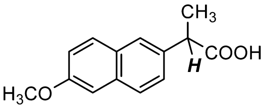
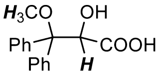
Table 1. Comparison of the Ability of CSA To Discriminate Signals of Chiral Acids

No	Substrates	nmr nucleus	(*R*)-**2**		(*R*,*R*)-**3**		(*R*,*S*)-**3**	
			(Δδ)[a]	(ΔΔδ)[b]	(Δδ)	(ΔΔδ)	(Δδ)	(ΔΔδ)
1		^{1}H	-0.411	0.123	-0.285	0.093	-0.289	--[c]
2		^{1}H	-0.048	--[c]	0.042	--[c]	-0.016	--[c]
3		^{1}H	-0.130	0.050	0.003	0.032	-0.041	--[c]
4		^{1}H (Cα)	-0.179	0.028	-0.055	0.043	-0.104	--[c]
		^{1}H (CH_3)	-0.167	0.003	0.060	0.049	-0.082	--[c]
5		^{1}H	-0.010	0.034	0.128	0.040	0.020	--[c]
6		^{1}H	-0.351	0.077	-0.356	0.062	-0.357	0.017
		^{19}F	-0.127	0.032	-0.094	0.076	-0.099	0.015
7		^{1}H (Cα)	-0.165	0.055	-0.201	0.070	-0.146	0.049
		^{1}H (CH_3)	-0.396	0.079	-0.353	0.074	-0.287	0.031
8		^{1}H	-0.038	0.015	0.007	0.019	-0.004	0.008
9		^{1}H	-0.050	--[c]	0.010	--[c]	-0.074	--[c]
10		^{1}H (Cα)	-0.135	0.039	-0.067	0.146	-0.056	0.006
		^{1}H (OCH_3)	-0.029	0.016	0.020	0.079	0.028	0.013

[a] Induced chemical shift (Δ*δ*). [b] Nonequivalence (ΔΔ*δ*). [c] Signals were not separated; (20.0 mM, $CDCl_3$, 400 MHz for H and 376 MHz for F NMR).

separation of signals in ^{1}H NMR for the $C_\alpha H$ and ^{19}F NMR for CF_3 group (entry 6, Table 1). Although CSA (*R*)-**2** and (*R*,*R*)-**3** were almost equally effective where baseline separation of signals was observed, the CSA (*R*,*S*)-**3** showed relatively poor resolution.

Optically active natural and artificial amino acids have become an integral part of the design and synthesis of several biologically important molecules. Determination of optical purity of amino acids is becoming an important consideration. Recently, few chiral solvating agents have been studied to measure optical purity of amino acids by NMR analysis.[21] We also extended our study of the present CSAs to check the discrimination of the protons of the N-Ts derivative of phenyl glycine (entry 7, Table 1). In this case, the signals of the methyl group of N-Ts and $C_\alpha H$ showed discrimination in ^{1}H NMR analysis. Almost similar selectivity was seen, where CSA (*R*,*S*)-**3** showed comparatively poor separation of both these signals. Next, we examined ibuprofen and naproxen, two commonly studied nonsteroidal anti-inflammatory drugs as substrates. The CSA (*R*)-**2** and (*R*,*R*)-**3** showed the same ability to recognize the isomers of ibuprofen, but the other was quite less effective, while all the three proved incapable of showing separation of signals of naproxen (entries 8 and 9, Table 1). The present system was then examined for relatively bulky 2-hydroxy-3-methoxy-3,3-diphenylpropanoic acid, which is an intermediate for few pharmaceuticals.[22] Signals of $C_\alpha H$ and $C_\beta OCH_3$ of this compound were seen to have been resolved due to the complex formation between this racemic acid and the (*R*,*R*)-**3**, more than the other two derivatives (entry 10, Table 1). At this stage, we conclude that (*R*)-**2** and (*R*,*R*)-**3** were more effective in chiral recognition of mandelic acid and its derivatives compared to (*R*,*S*)-**3**. In most of the cases, we found the present roof-shape amine to be comparable or better than some of the reported chiral amine based CSAs (see Table 1 of the SI for the details). In order to further establish the role of the roof shape part of the secondary amine, we prepared the *N*-methyl derivative of (*R*)-*α*-phenylethylamine and scanned as CSA for the recognition of (±)-mandelic acid. We observed a small shift in signal (induced chemical shift; $\Delta\delta = -0.066$ ppm) but there was no splitting of the signals ($\Delta\Delta\delta = 0$ ppm).

An experiment was designed to determine the difference in binding ability of (*R*,*R*)-**3** with both the isomers of mandelic acid. For a constant concentration of (*R*,*R*)-**3** (20 mM), a varying amount of (*R*)-MA and (*S*)-MA was added in such a way that the molar ratio varied from 0.2, 0.5, 1.0, and 1.5. The change in the chemical shift ($\Delta\delta$) value for *α-H* proton of mandelic acid was plotted against the molar ratio of chiral mandelic acid (Figure 2). The negative values for $\Delta\delta$ suggest an upfield shift of the signal. For both the isomers of MA, a minima is observed at molar ratio of 1.0 indicating maximum shift in δ value. However, the shift with (*R*)-MA is much more than that with (*S*)-MA indicating a stronger association of (*R*,*R*)-**3** with (*R*)-MA as compared to its association with (*S*)-MA.

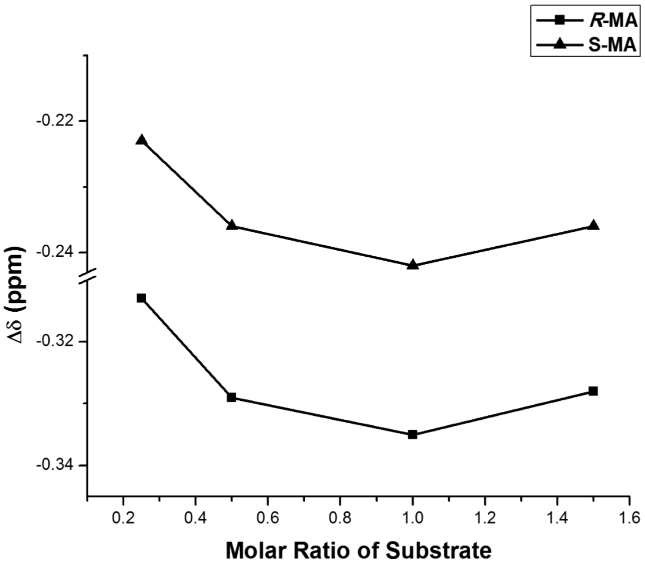


Figure 2. Graph showing the effect of different molar ratios of (*S*)-MA and (*R*)-MA with (*R*,*R*)-**3** upon change in chemical shift for the *α-H* proton of mandelic acid.

The use of optically pure of 1,1′-binaphthyl-2,2′-diol (BINOL) and its derivatives in asymmetric synthesis and catalysis is now a very important subject.[23] There are only a few reports on the use of chiral solvating agents for establishing optical purity of BINOL and its derivatives in the literature. Even in these reports, BINOL and analogues were converted to their alkoxy derivative before being subjected to the CSA analysis.[24a] There is also one other report on the use of quinine as CSA to discriminate signals of isomers of BINOL in ^{1}H NMR.[24b] Since our present secondary amine based roof-shape CSAs were expected to be strongly basic in nature, we investigated them for weakly acidic BINOL or its derivatives. However, for BINOL all three were ineffective in separating the signals (entry 1, Table 2). Structurally similar 2,2′,7,7′-tetrahydroxy-1,1′-binaphthyl possessing a C_2-symmetric axis is also utilized in asymmetric chemistry.[25] The presence of two more easily accessible hydroxyl groups in this molecule may lead to better interactions with the CSA. This was supported by the observation that the CSAs (*R*)-**2** and (*R*,*S*)-**3** were able to separate the signal of the most shielded hydrogen attached to the C8 position while CSA (*R*,*R*)-**3** failed to resolve them (entry 2, Table 2). This hydrogen showed a clear doublet in the most upfield part of the aromatic region (δ 6.4), convenient for easy measurement (Figure 3). This hypothesis was confirmed when poor separations were seen when these two outside hydroxyl groups were either blocked as 7,7′-dimethoxy-2,2′-dihydroxy-1,1′-binaphthyl or in case of 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl (entries 3 and 4, Table 2).

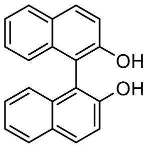
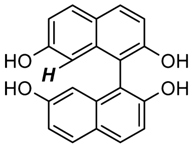
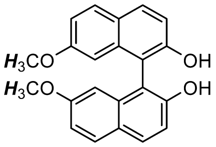
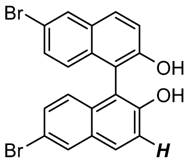
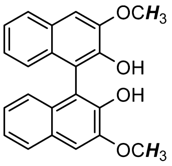
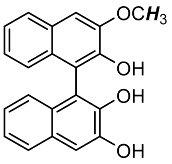
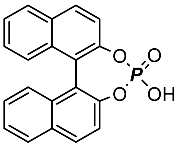
In another set of experiments, we examined 3,3′-dimethoxy-2,2′-dihydroxy-1,1′-binaphthyl and 3-methoxy-2,2,′3′-trihydroxy-1,1′-binaphthyl for the same study. Similar to the above observations, the latter one showed reasonable separation with (*R*,*S*)-**3** as against the other two (entries 5 and 6, Table 2).

Recently, chiral Brønsted acids such as phosphoric acid derivative 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate and its analogues have found wide uses as chiral catalysts.[26] We examined the effect of these CSAs by systematically studying the ^{31}P NMR and concluded the efficiency of (*R*)-**2** and (*R*,*S*)-**3** to be higher as against (*R*,*R*)-**3** (entry 7, Table 2). In all of the examples investigated in this class of compounds, (*R*)-**2** and (*R*,*S*)-**3** were more effective. Between them, the latter one (*R*,*S*)-**3** proved to be slightly superior class of CSA for binaphthyl system, while its diastereomer (*R*,*R*)-**3** was found more effective in the chiral recognition of derivatives of mandelic acid. Such a match−mismatch effect for controlling supramolecular interactions between diastereomeric chiral solvating agents for molecular recognition is noteworthy.

This molecular recognition was further studied to establish the linear relationship between the observed and actual values of % ee for establishing usefulness of the CSA (Figure 4). The observed % ee values were found to be within acceptable level of actual values, which confirms the accuracy of the analysis and possibility of the practical use in determination of sample of unknown purity.

Having established the efficacy of the three CSAs and collected information about the match-mismatch effect, we proceeded to understand the supramolecular interactions in depth. First, the experiments were run with nonracemic sample of mandelic acid with one known isomer excess with optically pure (*R*,*R*)-**3**. The signal of proton attached to the chiral center $C_\alpha H$ of (*R*)-mandelic acid [(*R*,*R*)-**3**·*R*-MA] appeared more upfield. The solution of the equimolar mixture of (*R*,*R*)-**3** with (*R*)-mandelic acid in acetonitrile was left for slow evaporation, and the crystals obtained were subjected to X-ray diffraction study.[27] Similarly, a mixture of (*R*,*R*)-**3** with (*S*)-mandelic acid was allowed to give a crystal of its diastereomeric salt [(*R*,*R*)-**3**·*S*-MA] for the similar analysis. The sample of [(*R*,*R*)-**3**·*R*-MA] crystallized in monoclinic chiral space group $P2_1$. The crystal structure contained one molecule each of (*R*,*R*)-**3** with (*R*)-mandelic acid along with a molecule of acetonitrile in the asymmetric unit (Figure 5). The hydrogen attached to the chiral carbon of (*R*)-mandelic acid appears to be laying on top of one of the aromatic rings of the roof-shape bicyclic framework. The shortest perpendicular distance between the

Table 2. Comparison of the Ability of CSA To Discriminate Signals of Chiral BINOL Derivatives

No	Substrates	nmr nucleus	(*R*)-**2**		(*R*,*R*)-**3**		(*R*,*S*)-**3**	
			(Δδ)[a]	(ΔΔδ)[b]	(Δδ)	(ΔΔδ)	(Δδ)	(ΔΔδ)
1		^{1}H	0.007	--[c]	0.010	--[c]	0.011	--[c]
2		^{1}H	-0.015	0.019	0.005	--[c]	0.017	0.032
3		^{1}H	-0.008	0.004	-0.004	0.005	-0.003	0.002
4		^{1}H	0.005	0.011	0.001	0.018	-0.002	0.005
5		^{1}H	0.002	--[c]	0.001	--[c]	--[d]	--[c]
6		^{1}H	-0.033	--[c]	-0.014	--[c]	-0.014	0.007
7		^{31}P	+0.529	0.205	-0.114	--[c]	-0.739	0.341

[a] Induced chemical shift (Δ*δ*). [b] Nonequivalence (ΔΔ*δ*). [c] Signals were not separated. [d] No shift; (20.0 mM, $CDCl_3$, 400 MHz for H and 161 MHz for P NMR).

plane passing through this ring and the hydrogen is 4.18 Å, and it is observed to be shifting upfield region due its shielding effect in ^{1}H NMR analysis. The C−O bond lengths (∼1.24−1.25 Å) in the COOH group show that proton transfer has occurred from *R*-MA to amine moiety of the (*R*,*R*)-**3**, revealing that the complex is salt (see the SI for a detailed discussion on crystal structure). In general, two molecules of (*R*,*R*)-**3** linked to the two molecules of *R*-MA through N−H···O hydrogen-bonding interactions to generate the tetrameric assembly which formed an extended chain assembly along the *b*-axis. The neighboring chains along the *bc*-diagonal were linked through acetonitrile molecules via C−H···N interactions (H···N = 2.714 Å, N···C = 3.427 Å /C−H···N = 134°) between the N atom of the guest acetonitrile and C−H aromatic proton of the (*R*,*R*)-**3** moiety and other van der Waals forces between the host and the guest molecules. This reveals that acetonitrile molecules play a vital role in fusing the neighboring helical chains, thereby inducing its crystallization.

The complex [(*R*,*R*)-**3**·*S*-MA] also crystallized in monoclinic chiral $P2_1$ space group containing two molecules of each component in the asymmetric unit. The crystal structure of [(*R*,*R*)-**3**·*S*-MA] (Figure 6) is isostructural to the [(*R*,*R*)-**3**·*R*-MA] structure. The C−O bond lengths (∼1.24−1.26 Å) in the COOH group show that proton transfer has occurred from *S*-MA to the amine moiety of the (*R*,*R*)-**3** revealing that the complex is salt. Similar to the crystal structure of [(*R*,*R*)-**3**·*R*-MA], two molecules of each *S*-MA and (*R*,*R*)-**3** constitute a tetrameric structure through hydrogen-bonding interactions,

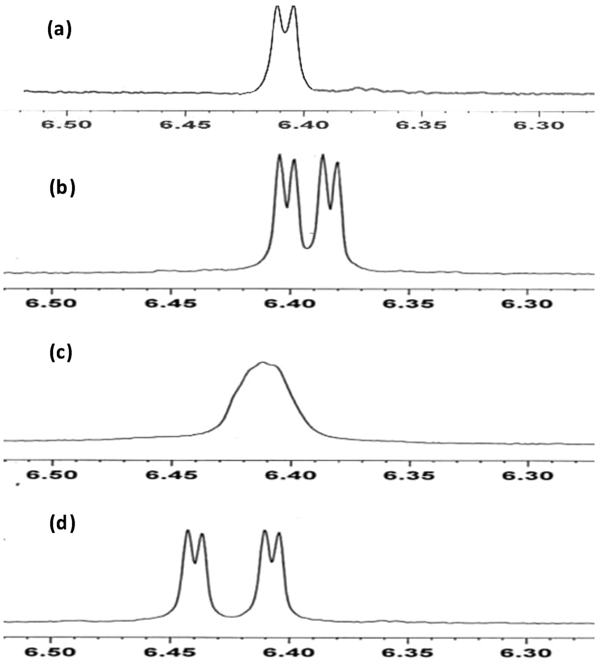


Figure 3. Separation of C_8H signal of (a) 2,2′,7,7′-tetrahydroxy-1,1′-binaphthyl (b) with (*R*)-**2**; (c) with (*R*,*R*)-**3**; (d) with (*R*,*S*)-**3** (20.0 mM, $CDCl_3$, 400 MHz).

which is extended along the *a*-axis to generate the chain structure. The neighboring chains are loosely connected to each other roughly along the *b*-axis via hydrophobic interactions. To the best of our knowledge, there are very few reports on the crystal study of the structure of the salt of test substrate and the CSA to understand the supramolecular interactions.[28] The experimental observations of shielding and deshielding effects in the two pairs in ^{1}H NMR analysis corroborated well with the information obtained from these crystal structures, even though one needs to be cautious in comparing the two.

Hence, in this paper we present preparation of three optically pure roof shape secondary amines, study of their applications for discrimination of signals of chiral acidic compounds by NMR spectroscopy, and evaluation of their match and mismatch effect of the diastereomers on the molecular recognition. We have also investigated the two pairs of diastereomeric salts by single-crystal X-ray diffraction analysis to establish the conformation of the hydrogen attached to the chiral carbon of mandelic acid. In one pair, we observed shielding effect due to its position above the aromatic ring of the bicyclic roof shape moiety, while in other the hydrogen is oriented away resulting in downfield shift in NMR analysis.

■ EXPERIMENTAL SECTION

***N*-Benzyl-1-((12*R*)-9,10-dihydro-9,10-ethanoanthracen-12-yl)methanamine ((*R*)-2).** A mixture of **1** (0.30 g, 7.69 mmol), cesium carbonate (0.54 g, 15.3 mmol), and benzylamine **2** (0.16 g, 15.3 mmol) was taken in a dry round-bottom flask and heated under nitrogen (120 °C, 12 h). After completion of the reaction, cold water was added to the reaction mixture, which was then extracted with ethyl acetate (3 × 25 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to obtain the crude product. The product was purified by column chromatography over silica gel using light petroleum ether and ethyl acetate as eluent to obtain the product (*R*)-**2** as a colorless oil (0.13g, 55%): $[\alpha]_D$ +14.6 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.32 (m, 3H), 7.31−7.29 (m, 3H), 7.28−7.23 (m, 3H), 7.15−7.09 (m, 4H), 4.38−4.37 (d, *J* = 2.0 Hz, 1H), 4.28−4.27 (t, *J* = 2.4 Hz, 1H), 3.81−3.78 (d, *J* = 13.2 Hz, 1H), 3.74−3.70 (d, *J* = 13.2 Hz, 1H), 2.36−2.33 (br s, 1H), 2.33−2.29 (dd, *J* = 11.2 Hz, 5.6 Hz, 1H), 2.22−2.17 (dd, *J* = 11.2, 5.6 Hz, 1H), 2.16−2.11 (m, 1H), 2.04−1.98 (m, 1H), 1.18−1.14 (ddd, *J* = 12.0, 4.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 143.8, 143.7, 140.5, 39.9, 128.4(2C), 128.2(2C),

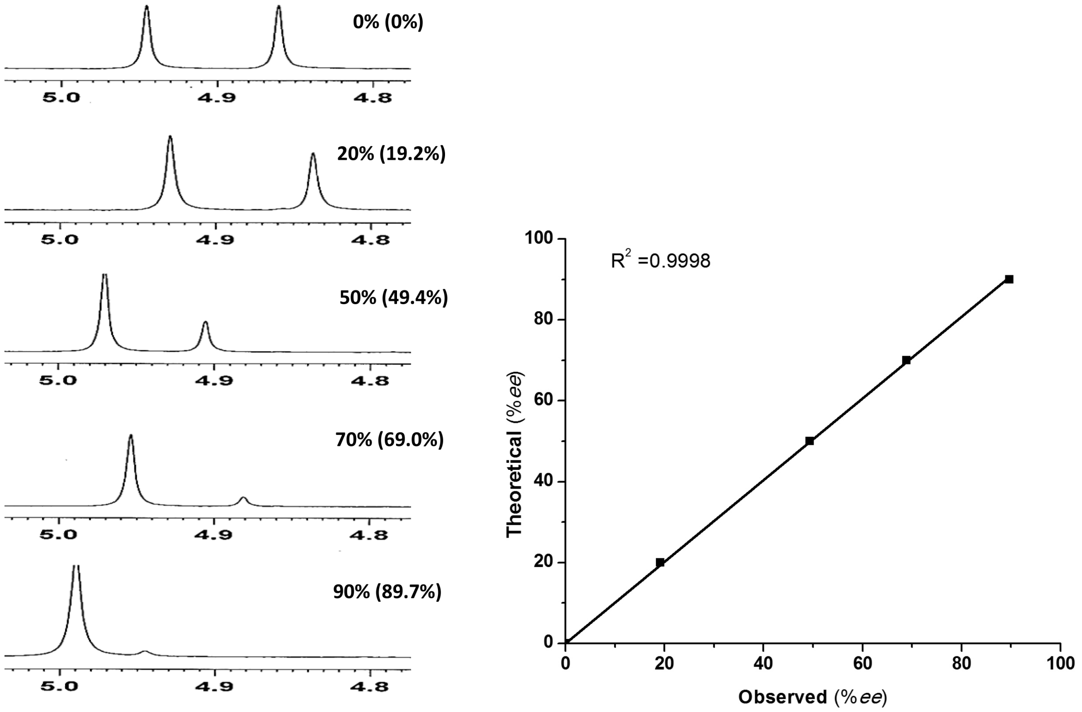


Figure 4. Selected region of ^{1}H NMR spectra of scalemic mixture of mandelic acid in the presence of (*R*,*R*)-**3**; values in parentheses are observed by NMR (left) and its correlation between theoretical and observed % ee values (right).

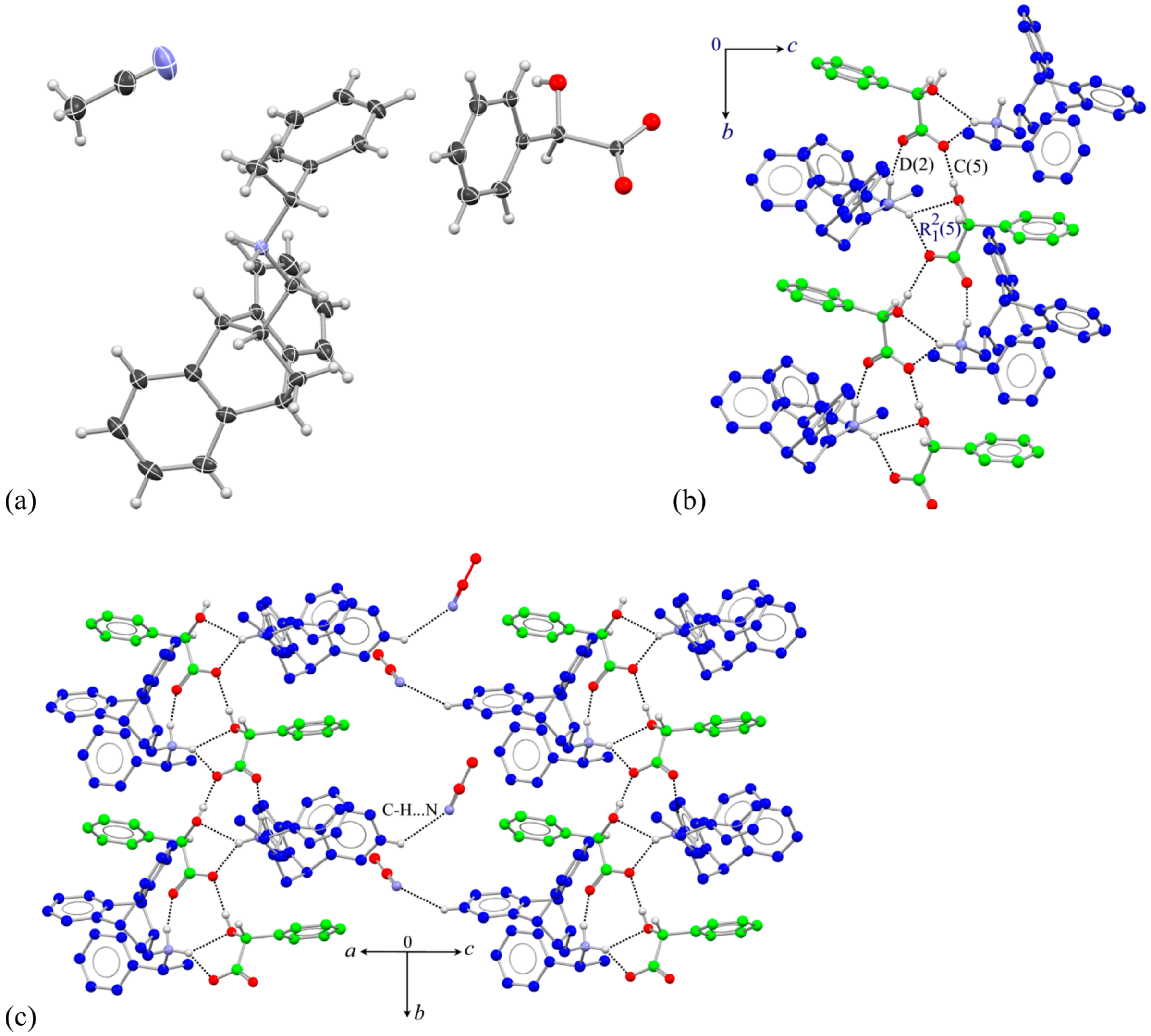


Figure 5. (a) ORTEP view of (*R*,*R*)-**3**·*R*-MA salt. The displacement ellipsoids are drawn at a 30% probability level, and H atoms are shown as small spheres of arbitrary radii. (b) Association of the (*R*,*R*)-**3** (blue) molecules to the O−H···O hydrogen bonded helical chain of *R*-MA (green) through N−H···O hydrogen-bonding interactions generating an extended chain assembly. (c) Linking of the neighboring helical chains through acetonitrile molecules via C−H···N interactions.

127.1, 125.8, 125.6(2C), 125.5, 125.3, 123.5, 123.4, 123.0, 54.0, 53.8, 46.7, 44.1, 38.6, 33.1; IR (neat) ν 3064.9, 3022.4, 2939.1, 2862.8, 2815.3, 1603.4, 1583.8, 1455.2, 1199.9, 1114.2, 747.4, 698.7, 555.7 cm^{-1}; MS (DIP-EI) *m*/*z* 236.3 (9), 325.2 (51), 324.2 (31), 177.9 (100), 119.9 (94), 90.8 (82); HRMS (TOF ES+) *m*/*z* calcd for $C_{24}H_{24}N$ [M + H]$^+$ 326.1903, found 326.1898.

(*R*)-*N*-(((12*R*)-9,10-Dihydro-9,10-ethanoanthracen-12-yl)-methyl)-1-phenylethan-1-amine ((*R*,*R*)-3). The synthetic procedure was similar to the one described above using (*R*)-α-phenylethylamine instead of benzylamine. The product (*R*,*R*)-**3** was obtained as a white solid on purification using column chromatography on silica gel (0.23 g, 87%): mp 102−104 °C; [α]$_D$ +49.1 (*c* = 1 in CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37−7.31 (m, 5H), 7.28−7.25 (m, 2H), 7.22−7.20 (m, 1H), 7.17−7.14 (m, 1H), 7.13−7.09 (m, 2H), 7.08−7.02 (m, 2H), 4.37−4.36 (d, *J* = 2.0 Hz, 1H), 4.24−4.23 (t, *J* = 2.4 Hz, 1H), 3.71−3.66 (q, *J* = 6.4 Hz, 1H), 2.24−2.19 (dd, *J* = 11.2, 5.6 Hz, 1H), 2.08−2.01 (br s, 1H), 1.98−1.92 (m, 2H), 1.38−1.36 (d, *J* = 6.4 Hz, 3H), 1.10−1.06 (ddd, *J* = 11.7, 4.0, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.8, 144.3, 143.8, 140.5, 128.4(2C), 126.8, 126.6(2C), 125.7, 125.6, 125.5, 125.4, 125.3, 123.5, 123.4, 122.9, 58.4, 52.7, 46.6, 44.2, 39.1, 33.1, 24.7; IR (KBr) ν 3065.4, 3017.9, 2957.8, 2891.3, 2819.8, 1598.7, 1489.4, 1465.1, 1172.9, 1129.7, 755.7, 704.7, 590.6, 555.9 cm^{-1}; MS (DIP-EI) *m*/*z* 339.3 (28), 338.4 (21), 323.6 (37), 177.9 (100), 134.2 (39), 104.9 (82); HRMS (ESI) *m*/*z* calcd for $C_{25}H_{26}N$ [M + H]$^+$ 340.2060, found 340.2055.

(*S*)-*N*-(((12*R*)-9,10-Dihydro-9,10-ethanoanthracen-12-yl)-methyl)-1-phenylethan-1-amine ((*R*,*S*)-3). The synthetic procedure is similar to the one described above using (*S*)-α-phenylethylamine instead of benzylamine. The product (*R*,*S*)-**3** was obtained as pale yellow liquid on purification using column chromatography on silica gel (0.22 g, 85%): [α]$_D$ −17.5 (*c* = 1 in CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32−7.24 (m, 9H), 7.12−7.09 (m, 4H), 4.37−4.36 (d, *J* = 1.6 Hz, 1H), 4.24−4.23 (t, *J* = 2.4 Hz, 1H), 3.69−3.64 (q, *J* = 6.8 Hz, 1H), 2.17−2.16 (m, 1H), 2.05−2.03 (m, 2H), 2.02−1.94 (m, 1H), 1.38−1.36 (d, *J* = 6.8 Hz, 3H), 1.09−1.06 (ddd, *J* = 12.0, 4.0, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.6, 144.1, 143.82, 143.80, 140.6, 128.4(2C), 126.9, 126.6(2C), 125.8, 125.6(2C), 125.5, 124.2, 123.5, 123.3, 123.0, 58.3, 52.5, 46.6, 44.2, 38.7, 33.1, 24.1; IR (neat) ν 3065.4, 3022.1, 2936.9, 2863.5, 1602.2, 1461.0, 1123.6, 851.1, 725.2, 704.2, 595.64, 501.4 cm^{-1}; MS (DIP-EI) *m*/*z*) 339.3 (8), 178.1 (25), 97.1 (35), 69.2 (60), 68.6 (100); HRMS (TOF ES+) *m*/*z* calcd for $C_{25}H_{26}N$ [M + H]$^+$ 340.2060, found 340.2060.

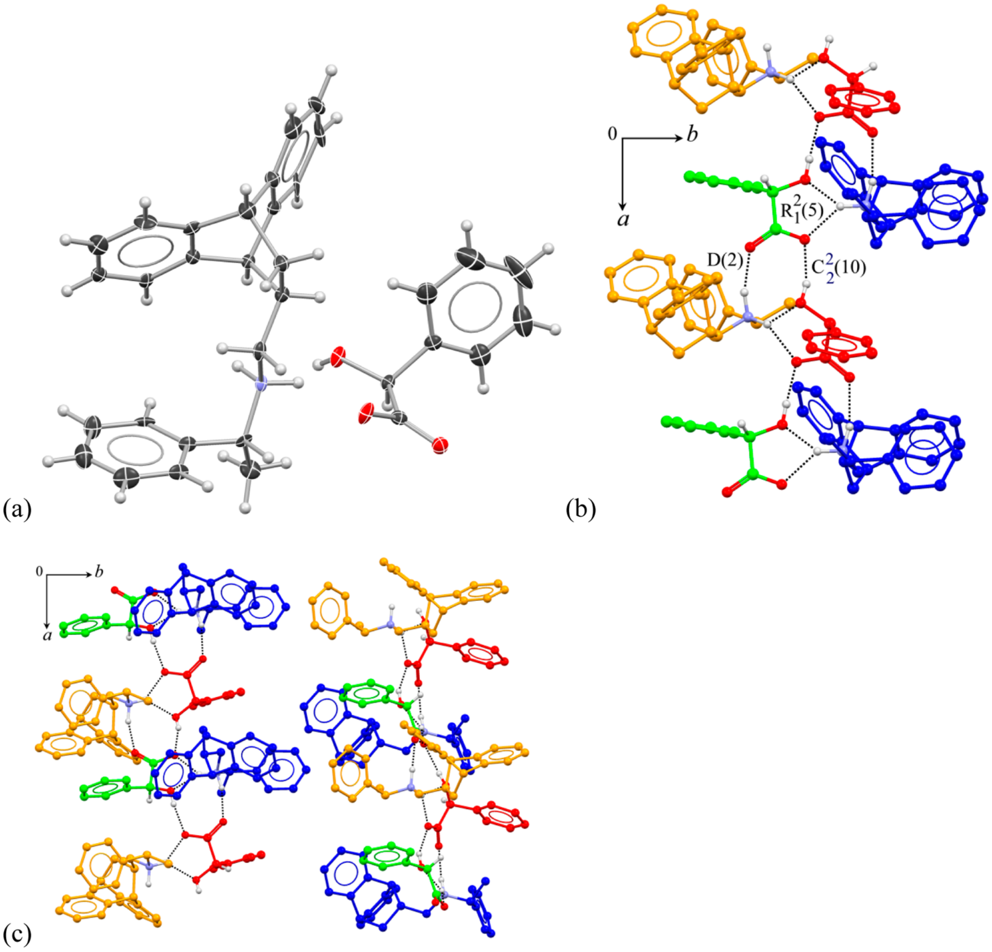


Figure 6. (a) ORTEP view of (*R*,*R*)-**3**·*S*-MA salt. The displacement ellipsoids are drawn at 40% probability level, and H atoms are shown as small spheres of arbitrary radii. (b) Association of the symmetry-independent (*R*,*R*)-**3** molecules to the O−H···O hydrogen-bonded helical chain of *S*-MA (green and red) through N−H···O hydrogen-bonding interactions generating an extended chain assembly. (c) Linking of the neighboring helical chains through van der Waals forces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00935.

X-ray data for (*R*,*R*)-**3**·(*R*)-mandelic acid salt (CIF)

(*R*,*R*)-**3**·(*S*)-mandelic acid salt (CIF)

Details of CSA study, spectral reproductions, and X-ray structure data (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Prof. Vishwakarma Singh on the occasion of his 65th birthday.

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(27) Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre [CCDC No. 1468129 for the salt of (*R*,*R*)-**3**·(*R*)-mandelic acid and CCDC No. 1468131 for the salt of (*R*,*R*)-**3**·(*S*)-mandelic acid]. Copies of the data can be obtained from http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD21EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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Helicenes

Enantiomerically Pure 5,13-Dicyano-9-oxa[7]helicene: Synthesis and Study

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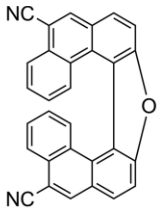
Abstract: Optically pure dicyano oxa[7]helicenes and helicene-like molecules have been prepared and investigated for their optical behavior. The isomers of the intermediate 4,4′-biphenanthrene-3,3′-diol were resolved by physically separating their 1-menthyl carbonate derivatives. In this work a mild method was developed to cleave ArOMe in presence of a cyano group. The optical rotation of atropisomeric diol, helicenes-like compounds and the oxa[7]helicenes was observed to be in increasing order, while the molecules also showed good response to circularly polarized luminescence.

Introduction

Helically shaped molecules have fascinated the organic chemists as they pose exciting challenges for their synthesis as well as structural aspects. This class of compounds are known to exhibit unique properties associated with extended conjugation and show chirality due to the shape created, resulting from the internal twist. The developments in the field of helical molecules is well summarized in many reviews published recently.[1] Although the earlier explorations were focused on carbohelicenes, recently more interesting properties have been observed for the heterohelicenes containing one or more heteroatoms. Compounds with the rigid shape and twisted π-condensed ring systems, with the presence of different functionalities, tunable planarity are potential candidates for the study of their distinct photophysical and chiroptical properties. Several types of helical systems have been investigated with diverse photophysical properties such as luminescence,[2] circularly polarized luminescence,[3] fluorescence,[4] circular dichroism,[1a,5] etc., and the optical properties are discussed in few reviews.[1h,6] The helical compounds have also been used in asymmetric catalysis, self-assembly and biomolecular recognition.[7] Polycyclic aromatic compounds fused with oxygen containing rings, such as furans, are expected to possess high HOMO levels[8] and are used in electronic devices such as organic light-emitting diodes and organic field-effect transistors.[9] Some of these kind of compounds have also been prepared and studied for their photophysical properties.[10]

Due to some interesting properties we have been involved in the synthesis and study of different types of aza[*n*]helicenes.[11] The oxygen analogues, oxa[*n*]helicenes have also been subject of active research and several reports on their synthesis and study are available.[12] In continuation of our work in this area[13] we have undertaken the present work to synthesize optically pure dicyano oxa[7]helicenes **1**, its helicenes like analogue **2** and discuss the findings of their response to circularly polarized luminescence (CPL) and optical rotation.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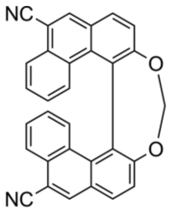
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In our earlier efforts[14] we have explored the conformational aspects of oxa[5]helicenes, where two naphthalene units were attached to furan moiety. We have concluded that the energy barrier for the isomerization of the conformations of oxa[5]helicenes is quite low for practical separation of the enantiomers. Hence, to provide sufficient steric bulk to prepare stable helical isomers we need to introduce additional aromatic rings, or make oxa[7]helicenes. In the present approach we intend to introduce cyano functionality in order to broaden the scope of the study as it is known to influence photophysical response by changing the energy levels of the orbitals[15a] or in some cases directs the crucial supramolecular interactions leading to spontaneous resolution of helical molecules.[15b] Based on these aspects we have designed the present helicenes **1** and helicenes-like molecule **2** and present their synthesis and study of photophysical properties. In these compounds we propose to replace the naphthalene unit by phenanthrene and introduce cyano groups symmetrically situated in the moiety. The latter class of helicene-like compounds diarylated [*d*,*f*][1,3]dioxepine analogues have been subject of similar study by our group and by others.[16]

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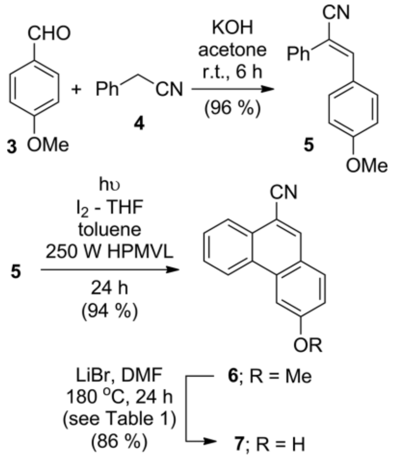
Results and Discussion

The target compound **1** is basically a diarylfuran derivative, which can be accessed by acid catalyzed dehydration of corresponding dihydroxy compound[17] or by palladium mediated cyclization of its activated analogue.[18] The required 9,9′-dicyano-4,4′-biphenanthryl-3,3′-diol **8** can be prepared by oxidative coupling of **7**. Based on this retrosynthetic strategy we began our synthesis by accessing stilbene derivative **5** as a single, *Z* isomer by Knoevenagel condensation of anisaldehyde **3** and benzyl cyanide **4** (Scheme 1). The photo induced oxidative cyclization[19] of **5** gave us the phenanthrene derivative **6** in good conversion. Both the acid sensitive functional groups survived during the reaction, confirmed by usual spectroscopic analysis. In the next part we needed to cleave the methyl ether to access phenol **7**. It was assumed that the usual stronger conditions such as BBr_3 or HBr/AcOH may damage the cyano group. The literature revealed a few methods of selectively cleaving aryl methyl ethers under milder conditions in presence of acid sensitive groups.[20,21] However, our initial attempts to follow some of these protocols for converting **6** to phenol **7**, resulted in decomposition. Use of sodium iodide[21] to cleave methyl ethers of phenol was investigated with some success, but the use of lithium bromide gave us clean reaction, although considerable unreacted **6** was recovered (Table 1, entry 1). Addition of phase-transfer catalyst[20a] with bromide anion marginally affected the cleavage reaction (entry 2). Lower amount of LiBr or conducting reaction at lesser temperature resulted in poor conversion. The use of weakly acidic condition may help the promotion of the ether cleavage; hence reaction was performed with addition of solid materials like Montmorillonite K10 or Molecular Sieves. The presence of these additives considerably improved the cleavage reaction, where the desired product **7** was obtained in clean conversion, while the solid catalysts may be recovered and reused for further applications. Characterization of the product **7** clearly indicated that the acid labile cyano group remains unaffected during this reaction condition, even though the reaction temperature was a bit high.



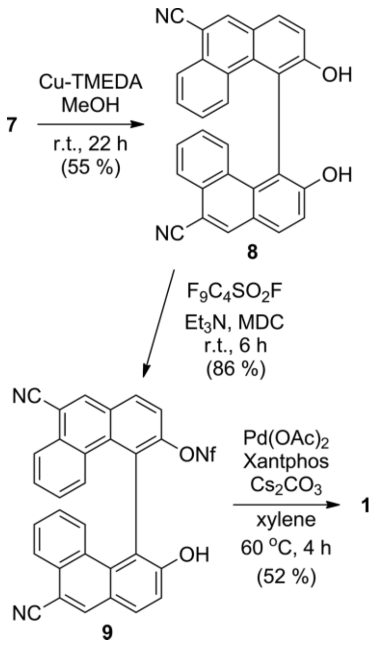
Scheme 1. Synthesis of 6-cyano-2-hydroxy phenanthrene (**7**).

Table 1. Conditions studied for cleavage of methoxy group of **6**.[a]

No	Additive	**7** (% Y)	**6** (% Y)
1	–	37	63
2	TBAB (0.1 equiv.)	51	49
3	Mont-K10 (40 % w/w)	73	25
4	Mont-K10 (100 % w/w)	82	16
5	4A MS (40 % w/w)	65	32
6	4A MS (100 % w/w)	85	12

[a] LiBr (2 equiv.), DMF, 180 °C, 24 h.

Having established a practical method to access adequate quantities of 9-cyano-3-hydroxy phenanthrene **7**, the focus was shifted to its homocoupling method. There are few reports on the oxidative coupling of 3-hydroxy phenanthrene to the corresponding 3,3′-dihydroxy-4,4′-biphenanthryl,[22] analogous to synthesis of BINOL from β-naphthol. The oxidative coupling reaction is known to proceed with copper or vanadium based homogeneous catalysts. Accordingly, we subjected the oxidative coupling of **7** in presence of Cu•TMEDA, prepared from Cu^ICl and tetramethylethylenediamine, in methanol at ambient conditions to afford the single regioisomer of (±)-**8** in medium yield (Scheme 2). Attempts to perform acid catalyzed dehydration reaction on this diol with *p*TsA, conc. H_2SO_4 and solid acidic catalysts like Montmorillonite K10 resulted in either no reaction or formation of decomposed material. Hence, we resorted to the other method of palladium catalytic cyclization[18a] after due activation of the diol. Hence, **8** was converted to its mono nonafluoro sulfonate **9** by the known procedure and subjected to cyclization with palladium acetate-xantphos catalyst system. The cyclized product, the desired target 5,13-dicyano-9-oxa[7]helicenes **1** was isolated in moderate yield. The structure was established by usual spectral analysis, particularly typical shifts in ^1H NMR signals. Hydrogen attached to C1 and C17 fall underneath the last aromatic rings and are observed at much shielded region at 6.47 δ.



Scheme 2. Synthesis of oxa[7]helicenes **1**.

The structure of (±)-**1** was further confirmed by single-crystal X-ray analysis (Figure 1).[23] The molecule shows stable helical conformation, separated on chiral phase HPLC columns at ambient conditions, which is also reflected in observed dihedral angle of 39.64° seen in the X-ray structure. As expected for the helical compounds, the carbon–carbon bond lengths of outside portion were lower than the normal aromatic system while the inside ones were found to be slightly elongated, see supporting information for the details. Comparing the crystal structures, of **1** with oxa[7]helicenes[18a] along with the CH–π and π–π interaction, indicated an additional C–N•••H–Ar interaction (2.74 Å). The sum of five dihedral angles on the inner helical rim was reduced by 2.1° in case of oxa[7]helicenes (78.9°), to 76.8° in **1**. The angle between the planes passing through the two terminal rings in oxa[7]helicene is reported to be 33.63°, whereas it was found to be 39.64° in **1**.

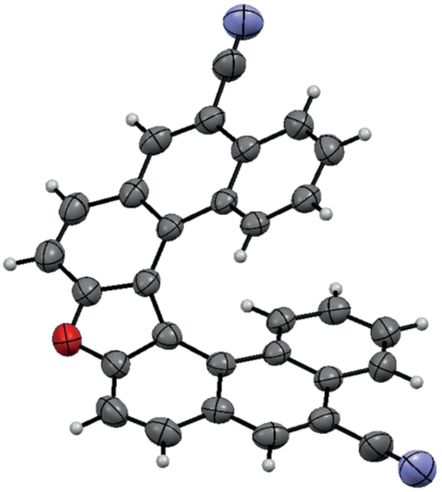
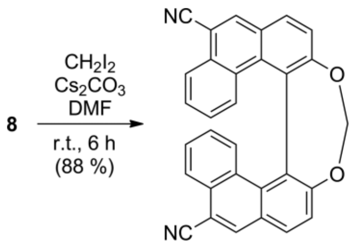


Figure 1. ORTEP diagram of **1**.

As already mentioned the other class of helicene-like compounds diarylated [*d*,*f*][1,3]dioxepine analogues are also subject of the present study. Thus, the diol **8** was subjected to ether formation with diiodomethane and Cs_2CO_3 as base. The dioxepine derivative **2** was obtained as single compound in good yield and isolated for characterization (Scheme 3). Efforts to grow good quality crystals of (±)-**2** for single-crystal X-ray analysis failed.



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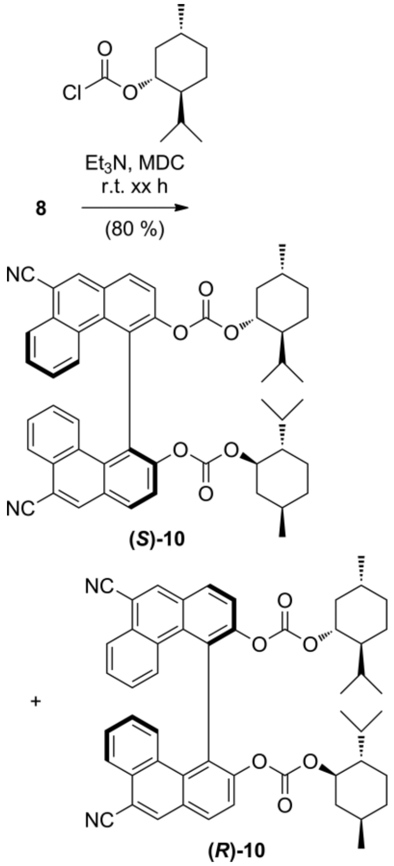
Scheme 3. Synthesis of oxa[7]helicene like **2**.

The other objective is to access optically pure isomers of **1** and **2** and to study optical and chiroptical properties of individual enantiomer. Separating the enantiomers of axially chiral samples of (±)-**8** is a challenging task. Converting helical enantiomers to diastereomers by attaching chiral auxiliary, making it suitable for physical separation and then regenerating the optically pure compounds is one of the standard protocols. Attaching (–)-menthyl chloroformate to hydroxyl group to make such separable diastereomers is often employed for resolution of chiral molecules.[24] The racemic diol **8** was subjected to the bis-carbonate formation with (–)-menthyl chloroformate to obtain the diastereomeric mixture of **10** (Scheme 4). The purified mixture was subjected to crystallization in several solvents and the mixture of chloroform (30 %) in hexane was found suitable for this purpose. The crystals were separated and the ^1H NMR analysis indicated them to be of a single diastereomer of bis-carbonate of (–)-menthyl derivative (> 99 % *de*).



Scheme 4. Separation of isomers of **8** by making diastereomer **10**.

The single-crystal X-ray analysis[23] of the solid compound obtained clearly established the stereochemistry of the chiral axis to be "*S*" of the carbonate (Figure 2). Solvent molecules were also seen trapped in the unit cell (not shown in the Figure), which was identified to be crystallized in P 2_1 2_1 2_1 space group.

The soluble portion after the crystals were separated contains the other diastereomer in 96 % diastereomeric excess as confirmed by ^1H NMR analysis.

The optically pure (*S*)-**10** was then subjected to alkaline hydrolysis to generate chirally enriched diol (*S*)-**8** (Scheme 5). Under the hydrolysis condition there appears to be no loss of optical purity of the atropisomeric diol, as confirmed by HPLC analysis on chiral phase column. Identical treatment was given to the solid obtained from the filtrate containing enriched (*R*)-**10** to regenerate (*R*)-**8**. Optically pure (*S*)-**8** was converted to (*P*)-**1** by

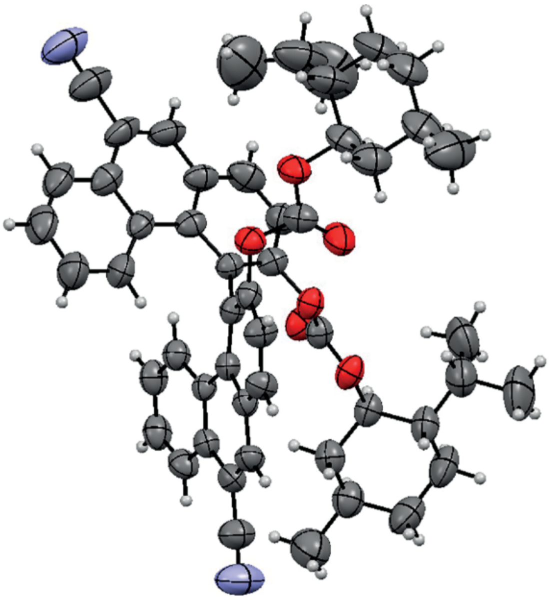
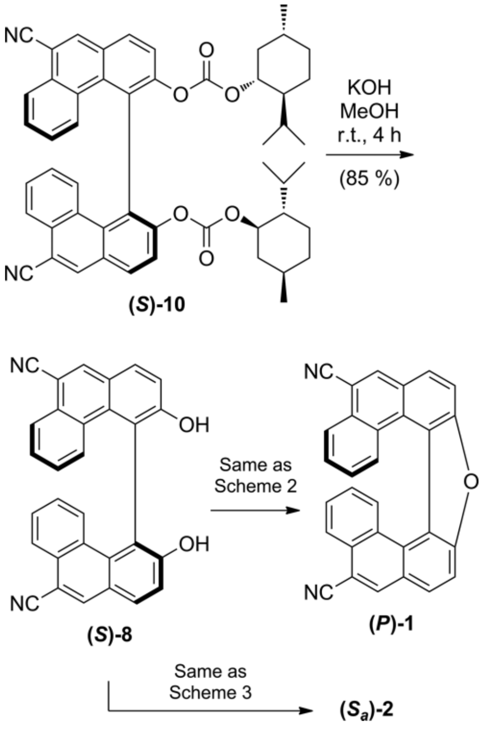


Figure 2. ORTEP of (*S*)-**10**.

step wise procedure as described earlier, while also converted to methylene bridge containing helicenes-like (*Sa*)-**2**. The other set of isomers, (*M*)-**1** and (*Ra*)-**2** were prepared from similar procedure from (*R*)-**8** (Figure 3).



Scheme 5. Regeneration of chiral **8** and synthesis of chiral **1** and **2**.

Optical properties of compounds **1** and **2** were studied by UV/Vis and fluorescence spectroscopy (Table 2). The observed values of absorption and emission bands and the Stokes shift were in the expected range for such types of helical compounds.[25] Helicene-like compound **2** showed marginal red shift in the emission spectra (18 nm) and higher Stokes shift. The lower value of the emission maxima in helicenes is probably attributed to more facile intersystem crossing in such molecules.[25b]

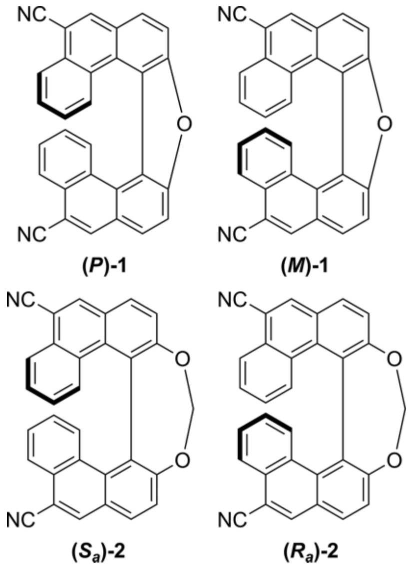


Figure 3. List of optically pure helicenes **1** & helicenes-like compounds **2** prepared.

Table 2. Photophysical properties of **1** and **2**.

Compound	λ_{abs} [nm]	λ_{ems} [nm]	Stokes Shift [nm]
1	323	421	98
2	310	439	129

One of the important properties of optically pure helical compounds is their high optical rotation ($[\alpha]_D$) and molecular optical rotation ($[\phi]_D$). Moreover the helical materials are studied as isotropic planar chiral waveguides as universal chiral sensors.[26] However, the primary requirement for making such sensory devices is to access materials which can show high degree of specific optical rotation. It is known that chiral compounds with chiral center or chiral axis tend to have much lower optical rotations, which tend to change to higher value when converted to helicenes-like molecules, while show further enhanced rotation when converted to helical compounds with continuous delocalization of electrons and high conjugation.[16] The comparison of the present set of compounds also indicate to the similar observation (Table 3). Both the isomers of chirally pure sample of **8** showed much less rotation, which changed considerably when converted to helicenes-like compounds **2**. When the helical compound was synthesized, there was considerable increase in the value of optical rotation as well as molecular rotation. The sample of (*S*)-**8** with OR of +157 and molecular OR of +685 was converted to (*P*)-**1**, the values changed to +790 and +3306, respectively.

A considerable difference was found on comparing the physical properties of oxa[7]helicenes[18a] with our 5,13-dicyano-9-oxa[7]helicene **1**. We found that there was an increase in the

Table 3. Chiroptical properties of isomers of **8**, **2** and **1**.

	(*R*)-**8**	(*S*)-**8**	(R_a)-**2**	(S_a)-**2**	(*M*)-**1**	(*P*)-**1**
[α][a]	–150	+157	–515	+543	–755	+790
[ϕ][b]	–655	+685	–2310	+2433	–3160	+3306

[a] Specific optical rotation, *c* = 0.1, in DMSO. [b] Molecular optical rotation; (*R*)-**8**, (R_a)-**2** and (*M*)-**1** = 96 % *ee*; (*S*)-**8**, (S_a)-**2** and (*P*)-**1** = 99 % *ee*.

melting point and a decrease of solubility in organic solvents. There is also a considerable change in the specific optical rotation value which was reported to be +1430° (*c* = 0.10, $CHCl_3$) for *(P)*-oxa[7]helicene and +790° (*c* = 0.10, DMSO) for *(P)*-**1**. Also a Bathochromic shift of 10 nm was observed in the UV/Vis spectra, λ_{max} for oxa[7]helicene is reported to be around 313 nm whereas for **1** it shifted to 323 nm.

The separated isomers of **1** and **2** were further analyzed by circular dichroism (Figure 4), where two opposite bisignate couplets, were observed. The (*P*) isomer of helical compound **1** shows more pronounced positive signal (Figure 4b) as compared the (*P*) isomer of helicenes like compound **2** (Figure 4a), which is a typical observation for optically pure helicenes.[16b,27]

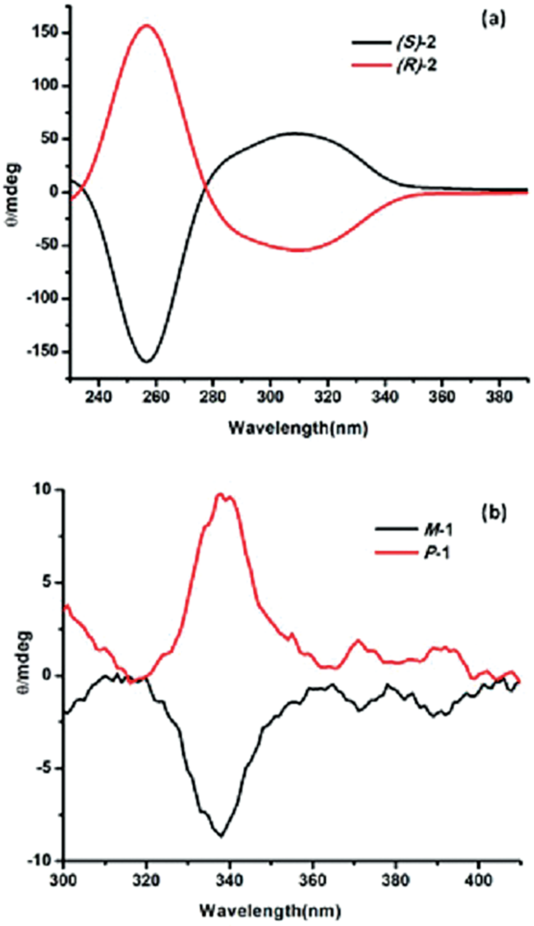


Figure 4. Circular Dichroism spectra of resolved helicene like (a) (Black Line) (*S*)-**2** and (Red Line) (*R*)-**2** at a concentration of 1.0 X 10^{-5} mol in chloroform at 25 °C; helicene (b) (Red Line) (*P*)-**1** and (Black Line) (*M*)-**1** at a concentration of 2.1 X 10^{-4} mol in DMSO at 25 °C.

The CPL activity was another useful chiroptical property to consider for the synthesized optically pure dicyano oxa[7]helicenes **1** and its helicenes-like analogue **2**. It allows to further investigate the influence of the helical-like structure of the compounds of interests on the chiroptical properties. The CPL spectra measured for the two sets of enantiomers (*P*)-/(*M*)-**1** and (*P*)-/(*M*)-**2** in DMSO solutions at 295 K are shown in Figure 5. Both sets of enantiomers, (*P*)-/(*M*)-**1** and (*P*)-/(*M*)-**2**, showed a somewhat mirror-like CPL signal with opposite g_{lum} values around the emission maximum (+0.003/–0.002 and +0.005/–0.002, respectively). These small values are in the typical range of g_{lum} values for most chiral organic molecules.[28] However, these results confirm that the solutions of **1** and **2** in DMSO exhibit active CPL signals, and also that the emitted light is polarized in opposite directions for the two enantiomeric forms for each set of these helicenes-like structures. It is worth noting that **1** and **2** give a relatively similar CPL response, which is in accordance with the slight structural differences between these two compounds resulting delocalization of electrons in helicenes **1** or helicenes-like compounds in **2**. One can conclude from the CPL results (i.e. similar g_{lum} values with a slightly larger value for **2**) that the structural changes are not sufficient to significantly influence in a different manner the chiroptical properties of these two compounds (at least from a CPL standpoint). This is in agreement with the well-established fact that the CPL activity is mainly dependent on the structural properties of the chiral compounds of interest.[28]

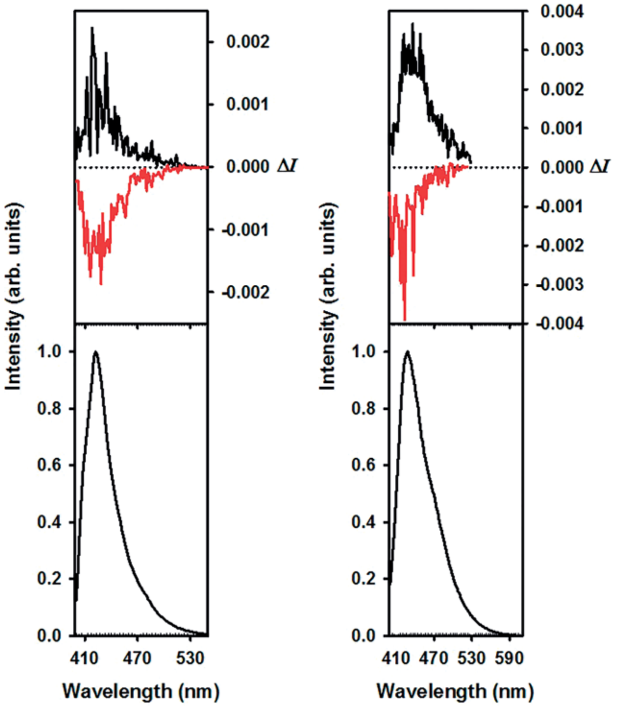


Figure 5. CPL (upper curve) and total luminescence (lower curve) spectra of (*P*)-/(*M*)-**1** (left) and (*P*)-/(*M*)-**2** (right) in 3.2 mM AR grade DMSO at 295 K, upon excitation at 367/388 and 388/395 nm, respectively [black for (*P*) and red for (*M*)].

Conclusions

Dicyano-substituted derivatives of oxa[7]helicenes and helicenes-like compounds have been prepared. During the synthesis, a mild and effective method is also developed to cleave aryl methyl ether, in presence of acid sensitive cyano group. The enantiomers of these compounds were accessed by making physically separable diastereomers of phenolic intermediate, by attaching (*l*)-menthyl chloroformate. The separated enantiomers were characterized by optical rotation, fluorescence and CD spectroscopy and circularly polarized luminescence. Both sets of enantiomers, (*P*)-/(*M*)-**1** and (*P*)-/(*M*)-**2**, showed a mirror-like CPL signal with opposite g_{lum} values around the emission maximum, which correspond to the typical range of similar chiral molecules.

Experimental Section

Reagents were purchased from Sigma–Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited, etc., and were used without further purification. All the glassware was flame dried before the experiment. All solvents used were stored on oven dried molecular sieves (4 Å). Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using SRL silica gel (60–120 mesh). ^{1}H and ^{13}C NMR spectra are recorded on a 400 MHz Bruker Avance 400 spectrometer (100 MHz for ^{13}C) with $CDCl_3$ as a solvent (unless specified) and TMS as an internal standard. Signal multiplicity is denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublet (dd), triplet (t), doublet of triplet (dt), quartet (q) and multiplet (m). Mass spectra were recorded on a Thermo-Fischer DSQ II GC–MS instrument. IR spectra were recorded on a Perkin–Elmer FTIR RXI spectrometer as KBr pallets or neat in the case of liquids. UV/Vis spectra were recorded on Perkin–Elmer Lambda-35. Fluorescence spectra were recorded on a JASCO FP-6300 spectrofluorometer. Specific optical rotations were measured on JACSO P-2000 polarimeter. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

3-(4-Methoxyphenyl)-2-phenylacrylonitrile [5]: A mixture of benzyl cyanide **4** (1.17 g; 10 mmol), finely ground solid KOH (0.65 g; 10 mmol) and 4-methoxybenzaldehyde **3** (0.68 g; 10 mmol) in methanol (30 mL) was stirred at room temperature for 6 hours. The resultant reaction mixture was concentrated under reduced pressure, poured into water and extracted using ethyl acetate (3X50 mL). The combined organic layer was dried with sodium sulfate and concentrated to give crude **5** as pale-yellow solid (2.23 g, 96 %); Melting Point: 96 °C (Lit:[29] 93–95 °C); which is recrystallized from ethyl acetate/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.37–7.41 (m, 1 H), 7.44 (d, *J* = 7.6 Hz, 2 H), 7.48 (s, 1 H), 7.67 (d, *J* = 7.6 Hz, 2 H), 7.91 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 108.5, 114.4 (2 C), 118.6, 125.8 (2 C), 126.5, 128.8, 129.1 (2 C), 131.2 (2 C), 134.8, 141.9, 161.4 ppm. MS (DIP-EI): *m/z* (%) = 235 (21) [[M$^+$]], 234 (17), 190 (100), 165 (91), 164 (57), 139 (25). IR (KBr): $\tilde{\nu}$ = 3013, 2844, 2207, 1596, 1507, 1448, 1304, 1250, 1179, 1026, 905, 828, 756, 693, 533 cm^{-1}.

3-Methoxyphenanthrene-9-carbonitrile [6]: A solution of **5** (0.1 g, 0.42 mmol) and iodine (0.12 g, 0.47 mmol) in toluene (425 mL) and tetrahydrofuran (1.7 mL, 21.3 mmol, 50 equiv.) was irradiated in a standard immersion well photoreactor with 250W high pressure mercury vapor lamp for 24 hours. The reaction mixture was then washed with aqueous sodium thiosulfate and dried with anhydrous sodium sulfate. The concentrated mixture was purified on silica gel column using ethyl acetate and petroleum ether (1:4) to afford **6** as pale-yellow solid (0.093 g, 94 %); Melting Point: 118 °C (Lit:[30] 116–118 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07 (s, 3 H), 7.325 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.75–7.79 (m, 2 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 8.035 (d, *J* = 2.0 Hz, 1 H), 8.21 (s, 1 H), 8.29–8.32 (m, 1 H), 8.63–8.66 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 104.1, 106.6, 117.9, 118.4, 123.1, 124.5, 126.1, 127.7, 128.2, 129.3, 129.4, 131.2, 133.6, 135.5, 160.9 ppm. MS (DIP-EI): *m/z* (%) = 233 (100) [M$^+$], 232 (61), 190 (39), 189 (77), 166 (14), 81 (38), 69 (40), 57 (27). IR (KBr): $\tilde{\nu}$ = 3022, 2966, 2935, 2845, 2217, 1618, 1503, 1453, 1372, 1232, 1144, 1030, 897, 835, 816, 721, 620, 565, 490, 427 cm^{-1}.

3-Hydroxyphenanthrene-9-carbonitrile [7]: To a round-bottomed flask, was added **6** (0.5 g, 2.15 mmol), lithium bromide (0.37 g, 4.30 mmol) in dimethylformamide (30 mL). To this solution was added 4 Å molecular sieves (100 % w/w) and stirred at room temperature for 15 min, followed by heating in an oil bath to 180 °C for 22 h. The reaction mixture was then cooled to room temperature and filtered to remove molecular sieves. Water was added to the reaction mixture and it was allowed to stir till solution becomes clear. It was extracted using ethyl acetate (3X50 mL). The combined organic layer was dried with sodium sulfate and concentrated under reduced pressure. The concentrated mixture was purified on silica gel column using ethyl acetate and petroleum ether (2:3) to afford **7** as pale-yellow solid (0.39 g, 85 %); Melting Point: > 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 (s, 1 H), 7.265 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.73–7.79 (m, 2 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 8.055 (d, *J* = 2.0 Hz, 1 H), 8.22 (s, 1 H), 8.28–8.32 (m, 1 H), 8.58–8.62 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.2, 117.9, 118.3, 123.2, 124.6, 126.1, 127.8, 128.4, 129.2, 129.3, 131.6, 133.9, 135.4, 157.1 ppm. MS (DIP-EI): *m/z* (%) = 219 (59) [M$^+$], 218 (100), 201 (23), 190 (49), 165 (16), 163 (21). IR (KBr): $\tilde{\nu}$ = 3404, 2217, 1628, 1575, 1507, 1450, 1342, 1245, 1203, 899, 856, 810, 753, 621, 564 cm^{-1}.

3,3′-Dihydroxy-[4,4′-biphenanthrene]-9,9′-dicarbonitrile [(±)8]: In a 50 mL round-bottomed flask, a mixture of 3-hydroxyphenanthrene-9-carbonitrile **7** (0.2 g, 0.9 mmol), $CuCl(OH)[(Me_2N)_2CH_2CH_2(NMe_2)_2]$ (0.21 g, 0.9 mmol) in methanol (25 mL) was placed and was sonicated for 10 min. The reaction mixture was stirred at room temperature for 4.5 h under oxygen atmosphere (1 atm). The reaction mixture was concentrated to remove methanol and 1 *m* aqueous HCl was added. The resulting mixture was extracted with ethyl acetate (3X40 mL). The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography with petroleum ether/ethyl acetate (1:1) as an eluent gave the ***rac*-8** as a colorless solid (0.11 g, 55 %); Melting Point: > 220 °C. Chiral HPLC was performed on Chiralpak OD-H in 30 % Isopropanol/hexane, at a flowrate of 1 mL/min and UV 254 nm, t_R 10.4 and 15.8 min. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.03–7.07 (m, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.54–7.58 (m, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.8 Hz, 1 H), 8.17 (d, *J* = 8.8 Hz, 1 H), 8.71 (s, 1 H), 10.01 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 104.9, 118.7, 118.9, 122.2, 125.5 (2 C), 125.8, 127.3, 128.4, 129.9, 130.8, 132.4, 132.8, 137.9, 157.3 ppm. MS (DIP-EI): *m/z* (%) = 436 (70) [M$^+$], 435 (100), 367 (27), 313 (33), 312 (56), 220 (30), 218 (20). IR (KBr): $\tilde{\nu}$ = 3355, 2926, 2221, 1600, 1569, 1493, 1443, 1395, 1250, 1222, 1084, 898, 762, 661, 629, 569 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_{16}N_2O_2Na$ [M + Na] 459.1104, found 459.1109.

9,9′-Dicyano-(4,4′-biphenanthrene)-3,3′-diyl(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexylbiscarbonate [(±)10]: To a solution of **(±)-8** (0.20 g, 0.45 mmol) and triethylamine (0.16 mL, 1.15 mmol) in dichloromethane was added (1*R*,2*S*,5*R*)-(–)-menthyl chloroformate (0.22 mL, 1.01 mmol) drop wise at 0 °C under N_2 atmosphere. After completion of the reaction (tlc), the reaction mixture was poured in ice cold water. The aqueous layer was extracted with dichloromethane (2X50 mL), the extracts were combined, and the organic layer was dried with Na_2SO_4 and evaporated to obtain a crude solid. The crude product was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (13:1) furnishing a pale-yellow solid (0.30 g, 80 %).

(*S*)-9,9′-Dicyano-(4,4′-biphenanthrene)-3,3′-diyl-bis[(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]biscarbonate [(*S*)-10]: Melting Point: > 220 °C. $[\alpha]_D$ = +48 (*c* = 1.0, $CHCl_3$, 99 % *ee*). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.36–0.45 (m, 1 H), 0.585 (d, *J* = 6.8 Hz, 3 H), 0.70–0.74 (m, 1 H), 0.78 (d, *J* = 7.2 Hz, 3 H), 0.80–0.84 (m, 1 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 1.04–1.23 (m, 3 H), 1.45–1.58 (m, 3 H), 4.02 (dt, *J* = 10.8, 4.4 Hz, 1 H), 7.14–7.16 (m, 1 H), 7.61–7.65 (m, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.18 (d, *J* = 8.8 Hz, 1 H), 8.325 (dd, *J* = 8.0, 0.8 Hz, 1 H), 8.44 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 20.6, 21.9, 23.1, 25.7, 31.1, 33.8, 39.5, 46.2, 79.3, 110.4, 117.6, 123.6, 126.1, 126.3, 127.3, 127.9, 128.6, 129.2, 129.9, 130.1, 131.6, 132.1, 135.7, 149.2, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 2956, 2926, 2869, 2223, 1750, 1597, 1491, 1453, 1370, 1270, 1231, 1086, 1030, 954, 759 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{52}H_{52}N_2O_6Na$ [M + Na] 823.3718, found 823.3708.

(*R*)-9,9′-Dicyano-(4,4′-biphenanthrene)-3,3′-diyl-bis[(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]biscarbonate [(*R*)-10]: Melting Point: 98 °C. $[\alpha]_D$ = –175 (*c* = 1.0, $CHCl_3$, 96 %*ee*). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.16 (d, *J* = 7.2 Hz, 3 H), 0.60 (d, *J* = 7.2 Hz, 3 H), 0.70–0.84 (m, 1 H), 0.865 (d, *J* = 6.4 Hz, 3 H), 0.96–0.99 (m, 1 H), 1.04–1.09 (m, 1 H), 1.27–1.28 (m, 2 H), 1.44–1.62 (m, 3 H), 1.72–1.75 (m, 1 H), 4.07 (dt, *J* = 11.2, 4.4 Hz, 1 H), 7.01–7.05 (m, 1 H), 7.51–7.55 (m, 1 H), 7.77 (d, *J* = 8.8 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 8.215 (d, *J* = 8.8 Hz, 1 H), 8.245 (dd, *J* = 8.0, 0.8 Hz, 1 H), 8.42 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9, 20.3, 21.9, 23.2, 23.9, 25.9, 31.2, 33.8, 46.3, 79.4, 110.5, 117.6, 123.5, 126.1, 126.2, 127.3, 127.8, 128.4, 129.5, 129.8, 129.9, 131.7, 131.8, 135.5, 149.7, 151.9 ppm.

Regeneration of Chiral Diol [(*S*)-8]: To solution of KOH (0.042 g, 0.75 mmol) in degassed methanol (20 mL), 0.5 g of ***(S)*-10** (0.63 mmol) was added and the mixture was allowed to stir at room temperature for 4 h after which no starting material remained (TLC). The mixture was concentrated and to it was added 20 mL of water. The aqueous layer was separated and acidified with 6 M HCl, producing a white precipitate that was extracted with ethyl acetate (2X30 mL). The ether layer was dried with Na_2SO_4, filtered off and the solvent evaporated in vacuo to give ***(S)*-8** as white solid (0.27 g, 86 %) ***(S)*-8** $[\alpha]_D$ = +157 (*c* = 0.1, DMSO, 99 %*ee*).

Similar hydrolysis treatment of ***(R)*-10** gave ***(R)*-8** $[\alpha]_D$ = –150 (*c* = 0.1, DMSO, 96 %*ee*).

9,9′-Dicyano-3′-hydroxy-[4,4′-biphenanthren]-3-yl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate [(±)-9]: A mixture of **(±)-8** (0.1 g, 2.3 mmol) and triethylamine (0.035 mL, 2.5 mmol) in CH_2Cl_2 (10 mL) was placed in a round-bottomed flask. To this solution was slowly added nonafluorobutanesulfonyl fluoride (0.045 mL, 2.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h and then concentrated to remove CH_2Cl_2. The resulting mixture was extracted with ethyl acetate (40 mLX3). The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography with petroleum ether/ethyl acetate (70:30) as an eluent gave **(±)9** as a pale yellow solid (0.14 g, 86 %); Melting Point: 106 °C; ***(S)*-9** $[\alpha]_D$ = +59 (*c* = 1.0, $CHCl_3$, 99 %*ee*); ***(R)*-9** $[\alpha]_D$ = –56 (*c* = 1.0, $CHCl_3$, 96 %*ee*). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.61 (br. s, 1 H), 7.04–7.08 (m, 1 H), 7.20–7.25 (m, 1 H), 7.39 (d, *J* = 8.8 Hz, 1 H), 7.57–7.61 (m, 1 H), 7.68–7.72 (m, 1 H), 7.77 (dd, *J* = 8.8 Hz, 1.2 H, 2 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 8.28 (d, *J* = 8.8 Hz, 1 H), 8.32 (dd, *J* = 8.4, 1.2 Hz, 1 H), 8.37–8.40 (m, 2 H); 8.38 (s, 1 H), 8.48 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.9, 112.2, 117.2, 117.9, 118.1, 118.5, 121.9, 125.3, 125.4, 126.4, 126.6 (2 C), 127.4, 128.2, 128.7, 129.3, 129.7, 129.9, 130.0, 130.5, 130.6, 131.0, 132.3, 132.6, 132.8, 133.3, 135.4, 136.1, 147.9, 154.7 ppm. MS (DIP-EI): *m/z* (%) = 734 (39) $[M^+]$; 590 (39), 577 (43), 433 (55), 406 (100), 392 (56), 379 (69), 378 (95). IR (KBr): $\tilde{\nu}$ = 3334, 3076, 2226, 1663, 1607, 1574, 1526, 1498, 1423, 1351, 1239, 1035, 1009, 907, 792, 734, 693, 530, 488 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{34}H_{15}N_2O_4F_9SNa$ [M + Na] 741.0501, found 741.0502.

Diphenanthro[3,4-b:4′,3′-*d*]furan-5,13-dicarbonitrile [(±)1]: A mixture of **(±)-9** (0.17 g, 0.23 mmol), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol), xantphos (27 mg, 0.046 mmol), anhydrous Cs_2CO_3 (0.16 g, 0.46 mmol) in xylene (10 mL) was placed in a 50 mL round-bottomed flask and degassed by sonicating for 10 min. The reaction mixture was stirred at 60 °C for 4 h under nitrogen atmosphere. The reaction mixture was cooled down to ambient temperature and was then diluted with toluene (10 mL). The resulting mixture was washed with water, extracted with toluene, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as an eluent to give **(±)1** as a pale-yellow solid (50 mg, 52 %). Melting Point: > 220 °C; ***(P)*-1** $[\alpha]_D$ = +790 (*c* = 0.1, DMSO, 99 %*ee*); ***(M)*-1** $[\alpha]_D$ = –755 (*c* = 0.1, DMSO, 96 % *ee*). ^1H NMR (400 MHz, $[D_6]$DMSO): δ = 6.45–6.48 (m, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.50–7.54 (m, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.48 (d, *J* = 8.8 Hz, 1 H), 8.55 (d, *J* = 8.8 Hz, 1 H), 9.03 (s, 1 H) ppm. MS (DIP-EI): *m/z* (%) = 418 (45) $[M^+]$, 410 (59), 312 (100), 256 (64), 236 (72), 199 (63), 155 (73), 140 (53). IR (KBr): $\tilde{\nu}$ = 2220, 1584, 1519, 1486, 1446, 1347, 1320, 1271, 1225, 1106, 922, 898, 772, 644 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_{14}N_2ONa$ [M + Na] 441.0998, found 441.0995.

Diphenanthro[3,4-d:4′,3′-*f*][1,3]dioxepine-5,15-dicarbonitrile [(±)2]: A solution of **(±)-8** (0.10 g, 0.23 mmol) and anhydrous Cs_2CO_3 (0.29 g, 1.15 mmol) in dry DMF (5 mL), CH_2I_2 (0.028 mL, 0.34 mmol) was added and the mixture was stirred for 6 h at room temperature under nitrogen atmosphere. After the completion of the reaction (tlc) the reaction mixture was poured in ice cold water. The aqueous layer was extracted with ethyl acetate (3X50 mL), dried with Na_2SO_4 and concentrated under reduced pressure to obtained crude solid. The crude product was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (80:20) furnishing **(±)-2** as white solid (0.09 g, 88 %). Melting Point: > 220 °C; ***(S)*-2** $[\alpha]_D$ = +543 (*c* = 0.1, DMSO, 99 %*ee*); ***(R)*-2** $[\alpha]_D$ = –515 (*c* = 0.1, DMSO, 96 %*ee*). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.89 (s, 1 H), 6.58–6.59 (m, 2 H), 7.19–7.23 (m, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.24 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.1, 109.1, 117.6, 122.2, 124.9, 125.8, 126.1, 127.9, 128.9, 129.0, 129.1 (2 C), 131.8, 131.9, 135.0, 153.5 ppm. MS (DIP-EI): *m/z* (%) = 448 (100) $[M^+]$, 447 (41), 368 (99), 313 (50), 236 (81), 152 (62), 111 (80). IR (KBr): $\tilde{\nu}$ = 3061, 2922, 2853, 2226, 1586, 1519, 1494, 1444, 1391, 1320, 1270, 1198, 1018, 973, 895, 767, 642, 554, 448 cm^{-1}. HRMS (TOF MS EI+) *m/z* calcd. for $C_{31}H_{16}N_2O_2$ $[M^+]$ 448.1212, found 448.1207.

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