Tetrahedron: *Asymmetry* 25 (2014) 767–774

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Application of optically active aminonaphthols as NMR solvating agents for chiral discrimination of mandelic acid

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ARTICLE INFO

Article history:
Received 15 February 2014
Accepted 4 April 2014

ABSTRACT

A series of optically active aminonaphthol derivatives were prepared and screened as chiral solvating agents to discriminate the $C^{\alpha}H$ of racemic mandelic acid by ^{1}H NMR analysis. An effort was made to establish a correlation of the structure of aminonaphthol derivatives and the selectivity in this non-covalent interaction. A linear relationship between the experimental and calculated enantiomeric purity was established by indicating the potential use of the system to determine the ee for the samples of mandelic acid of unknown enantiomeric purity.

1. Introduction

The synthesis and applications of aminonaphthol derivatives have been widely studied and summarized by Szatmári and Fülöp in a recently published review.[1] The pioneering work on similar molecules started in the early 20th century when Italian chemist Mario Betti first reported on the synthesis of aminobenzylnaphthol or Betti base.[2] Since then, several derivatives have been prepared with achiral amines and then resolved to access chiral aminonaphthols or chiral derivatives prepared directly utilizing non-racemic amines for Mannich reactions. The reaction of β-naphthol with a chiral primary amine and an aldehyde follows an aromatic Mannich reaction via an initially formed chiral imine. The reaction usually proceeds with considerable stereocontrol due to the chiral amine, and produces the second stereogenic center with good selectivity. Due to this simple synthesis of chiral analogues of Betti base or 1-(α-aminobenzyl)-2-naphthols much attention has been focused on exploring their applications.[1,3] Some of the significant applications of these ligands in asymmetric transformations include enantioselective alkylations of aldehydes,[4] asymmetric reductions of acetophenone,[5] resolution of important chiral molecules such as BINOL and ibuprofen,[6] as chiral auxiliaries for the synthesis of enantiomerically pure products such as 2,5-disubstituted pyrrolidines,[7] piperidines,[8] and α-aminophosphonic acids,[9] and the synthesis of chiral phosphine ligands[10] and chiral calix[4]arenes.[11] In another study, a new macrocyclic compound has been synthesized from a derivative of a bis-aminonaphthyl system and its application as a chiral solvating agent has been investigated.[12] In addition to the chiral analogues, many derivatives of achiral aminonaphthols have been studied for several applications,[3] including our own attempts to use them as phosphine free ligands in palladium catalyzed coupling reactions.[13–16]

The significance of chiral molecules is not restricted to bioactive molecules such as pharmaceuticals, flavoring agents, and fragrances, but has covered many other areas of molecular recognition and material science. Many properties of such molecules are clearly linked to the chirality of the system and hence it is vital to know the composition of the present isomers in a test sample. This has necessitated a need for quick, accurate, and reliable techniques to establish the ratio of enantiomers in chiral samples. More routinely used contemporary techniques for such determinations are based on chromatographic separations such as GC and HPLC, but their success mainly depends on the efficiency and compatibility of the chiral stationary phases of the columns. Among other available methods, NMR spectroscopy has advantages, such as being fast and accurate when determining the ratio of the enantiomers. Two enantiomers of a chiral sample cannot be recognized in an achiral environment by NMR spectroscopy; hence the techniques require some modifications. Enantiomers which show identical NMR need to be converted, temporarily or otherwise, into diastereomers which are expected to show different spectroscopic patterns. Converting the test sample to diastereomers can be carried out in two ways, by forming covalent bonds with chiral derivatizing agents (CDA) or alternatively by forming temporary supramolecular interactions with chiral solvating (or complexing) agents (CSA). The first option is cumbersome and time consuming while the second one is simple, practical and hence has been investigated considerably in recent years.[17] In the case of CSA, the temporary formation of

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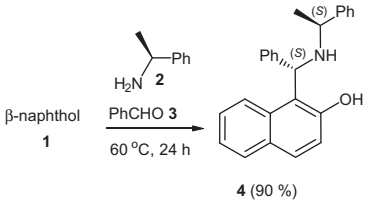
http://dx.doi.org/10.1016/j.tetasy.2014.04.003
0957-4166/

diastereomers with enantiomerically pure reagents results in non-equivalence of the chemical shifts of the protons of the two enantiomers of the analyte. This technique has the distinct advantages of simplicity, more accurate analysis compared to the derivatization process with CDA, and is non-destructive due to weak non-covalent interactions with the CSA. Such intermolecular interactions including dipole–dipole, charge transfer, van der Waals, π–π stacking, and the formation of H-bonding, etc. were then exploited by many researchers in the design and testing of a series of CSAs. A variety of compounds such as amines, amides, lactams, carboxylic acids, cyclodextrins, etc. with suitable coordination cites and orientation have been developed to be effective in recognizing the analytes and function as CSAs.[18] Several chiral crown ethers have also been designed as effective CSAs where the interactions could be of a different nature.[19]

The success of this technique depends on the proper combination of supramolecular interactions between the two partners of the complex. Hence, even though a large number of CSAs are available, there is a need to design more molecules which can be readily prepared in enantiomerically pure form while they may be easily modified to suit a particular requirement. Herein we report on a simple synthesis of a series of chiral derivatives of aminonaphthol and their assessment as CSAs for the test case of mandelic acid.

2. Results and discussion

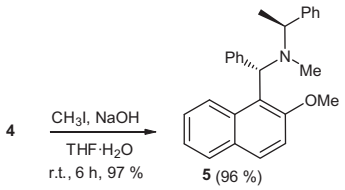
The basic unit 1-(α-aminobenzyl)-2-naphthol **4** was prepared by a three component aromatic Mannich reaction of β-naphthol **1** with the imine formed in situ from (*S*)-1-phenylethylamine **2** and benzaldehyde **3** (Scheme 1).[4b] We chose this system due to the simplicity of its preparation from readily available materials and the juxtaposition of two vital functional groups of a weakly acidic phenolic hydroxyl group and the secondary amine closely situated to the stereogenic center. The two heteroatoms are also separated by three carbons, two being rigid aromatic sp^2 system and the third being a stereogenic sp^3 center.



Scheme 1. Synthesis of enantiopure aminoalkylnaphthol by a solvent free asymmetric Mannich reaction.

Herein we planned to make different derivatives of this enantiomerically pure 1-(α-aminobenzyl)-2-naphthol **4** where the two functional groups could be modified and the molecules generated would be screened as CSAs for chiral discrimination of DL-mandelic acid as the standard test substrate in ^{1}H NMR spectroscopy. Compound (*S*,*S*)-**4** was subjected to alkylation with excess methyl iodide and sodium hydroxide as the base; as expected both the NH and OH were converted into *N*-Me and *O*-Me groups to afford dialkylated aminonaphthol (*S*,*S*)-**5** in good yield (Scheme 2). This compound lacks the hydrogens attached to heteroatoms, which may prevent it forming H-bonds with the hydrogen acceptor atoms of the test substrate in the proposed CSA study. We have also studied its single crystal X-ray diffraction pattern and the ORTEP plot is presented in Figure 1.[20]

We next tried to block the N–H functionality while exposing the acidic OH group of the aminonaphthol to interactions with the analyte. With this aim a sample of (*S*,*S*)-**4** was converted into 1,3-oxazine system **6** by condensing with formaldehyde, which



Scheme 2. Synthesis of a dialkyl derivative of aminonaphthol.

was then selectively reduced with lithium aluminum hydride to give the *N*-Me, OH derivative (*S*,*S*)-**7** with excellent conversion (Scheme 3).[10a]

The fourth combination was prepared whereby the acidic phenolic group was protected by selectively converting it into a

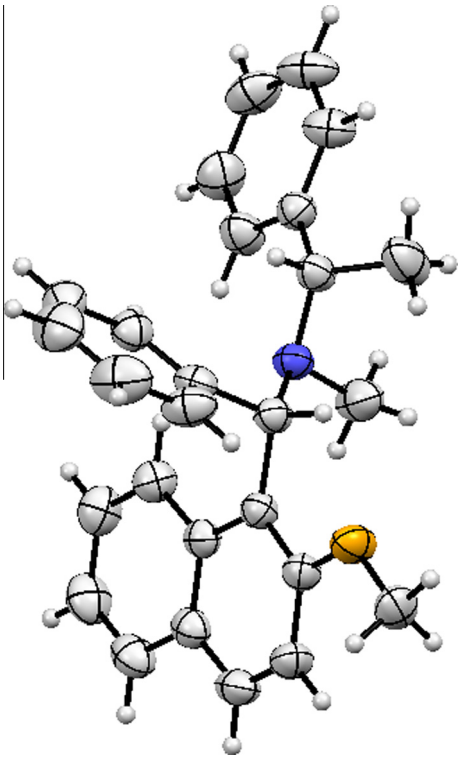
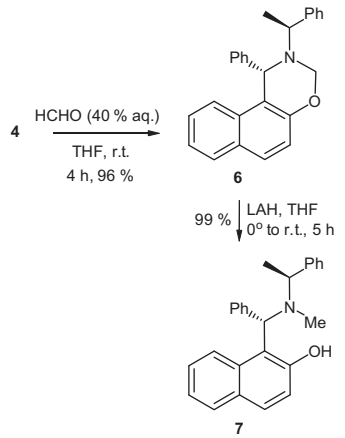
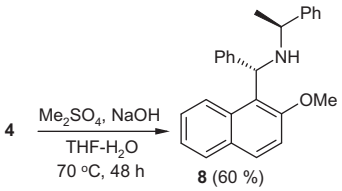


Figure 1. ORTEP plot of (*S*,*S*)-**5**.



Scheme 3. Synthesis of the *N*-Me derivative of aminonaphthol.

methyl ether using dimethyl sulfate in an alkaline medium (Scheme 4) in a one-step reaction.[10b] In this variant of the methoxy derivative (*S*,*S*)-**8**, the NH is free to form H-bonds with the test substrate and may possibly offer a good binding site.



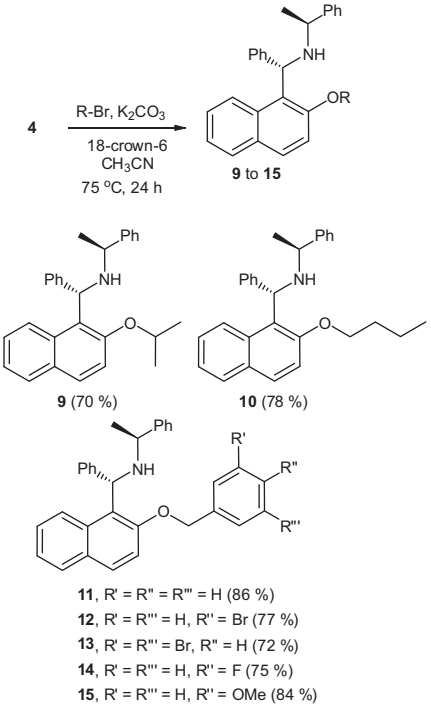
Scheme 4. Synthesis of a methoxy derivative of aminonaphthol.

Having prepared the four derivatives, they were then screened to see their efficacy in binding with a test sample of DL-mandelic acid in ^{1}H NMR analysis. The NMR experiments were run with stoichiometric amounts of mandelic acid and CSA (1:1) (22 mM, $CDCl_3$, 400 MHz). The upfield change in the position of the signal of $C^{\alpha}H$ proton of mandelic acid upon treatment with CSA was measured as chemical shift change ($\Delta\delta$) while the degree of splitting was measured by the differences in the separated peaks in terms of chemical shift non-equivalences ($\Delta\Delta\delta$). The first four entries of Table 1 indicate that the basic unit (*S*,*S*)-**4** with free NH and OH groups showed very poor recognition (entry 1) while the *N*-Me, OH derivative (*S*,*S*)-**7** remained totally ineffective (entry 3). The derivative (*S*,*S*)-**5** with *N*-Me and *O*-Me showed poor selectivity (entry 2) while the one with free NH and OMe (*S*,*S*)-**8** showed promising results (entry 4). Encouraged by this, we decided to vary the substituents on this molecule. Under a slightly alkaline medium, the basic unit of (*S*,*S*)-**4** was treated with several alkyl bromides to perform a selective O-alkylation reaction. A few representative molecules with different types of the *O*-alkyl group were prepared (Scheme 5) and then screened for CSA activity. The single crystal X-ray diffraction analysis of (*S*,*S*)-**10** was also performed (Fig. 2).[20] The aliphatic derivatives (*S*,*S*)-**9** with an isopropyl group and (*S*,*S*)-**10** with an *n*-butyl group did not show much improvement (entries 5 and 6), whereas *O*-benzyl derivative (*S*,*S*)-**11** showed much improvement in the interaction (Fig. 3). In order to further explore the scope of the present derivative and to study the effect of substituents on the aromatic ring of the

Table 1
Effect of aminonaphthyl derivatives as CSAs on the α-proton of racemic mandelic acid. [$\Delta\delta$ = Induced chemical shift;[a] $\Delta\Delta\delta$ = chemical shift non-equivalences.]

No	Aminonaphthyl derivative	Probe signal PhC*H*(OH)COOH	
		$\Delta\delta$ (ppm)	$\Delta\Delta\delta$ (ppm)
1	(*S*,*S*)-**4**	−0.22	0.005
2	(*S*,*S*)-**5**	−0.24	0.012
3	(*S*,*S*)-**7**	−0.09	—[b]
4	(*S*,*S*)-**8**	−0.33	0.021
5	(*S*,*S*)-**9**	−0.28	0.009
6	(*S*,*S*)-**10**	−0.30	0.013
7	(*S*,*S*)-**11**	−0.31	0.025
8	(*S*,*S*)-**12**	−0.28	0.025
9	(*S*,*S*)-**13**	−0.26	0.021
10	(*S*,*S*)-**14**	−0.29	0.022
11	(*S*,*S*)-**15**	−0.31	0.024
12	(*S*,*S*)-**16**	−0.16	0.022
13	(*S*,*S*)-**17**	−0.02	—[b]
14	(*S*,*S*)-**18**	−0.35	0.023
15	(*S*,*S*)-**20**	−0.28	0.016
16	(*S*,*S*)-**22**	−0.02	—[b]

[a] The difference between the signals of DL-mandelic acid in $CDCl_3$ solution and the average of the signals of the two enantiomers after the addition of the CSA.
[b] Not resolved.



Scheme 5. Synthesis of *O*-alkyl/*O*-aryl derivatives of aminonaphthol.

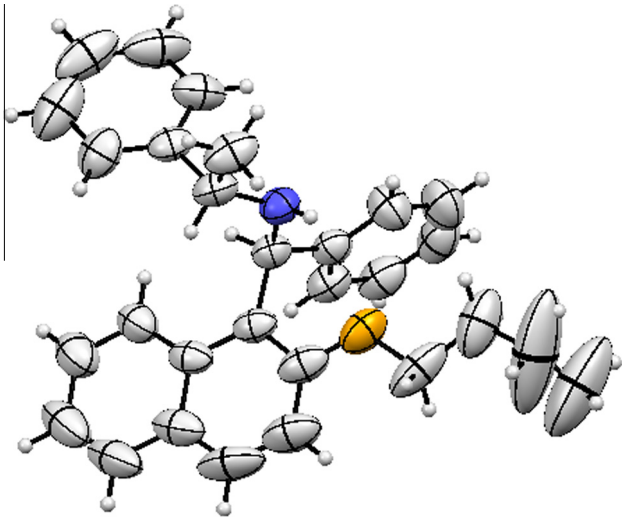


Figure 2. ORTEP plot of (*S*,*S*)-**10**.

O-benzyl, a series of molecules (*S*,*S*)-**12**-(*S*,*S*)-**15** were similarly prepared. These benzyl derivatives with different substitutions on the aromatic ring were scanned for CSA interactions, which showed selectivity in the similar range (entries 8–11). This observation perhaps indicates that the presence of the aromatic system is sufficient to offer a π–π interaction between the aromatic rings of the *O*-benzyl of the CSA and that of mandelic acid.

This possibility was further evaluated by introducing *p*-toluenesulfonyl ester on the aminonaphthyl system, with a free NH in (*S*,*S*)-**16** and by blocking it as an *N*-Me derivative of (*S*,*S*)-**17** (Scheme 6).

Both of these molecules were tested for their interactions in the ^{1}H NMR and the results were as expected; the molecule with the free NH showed good activity **16**, while *N*-Me **17** did not recog-

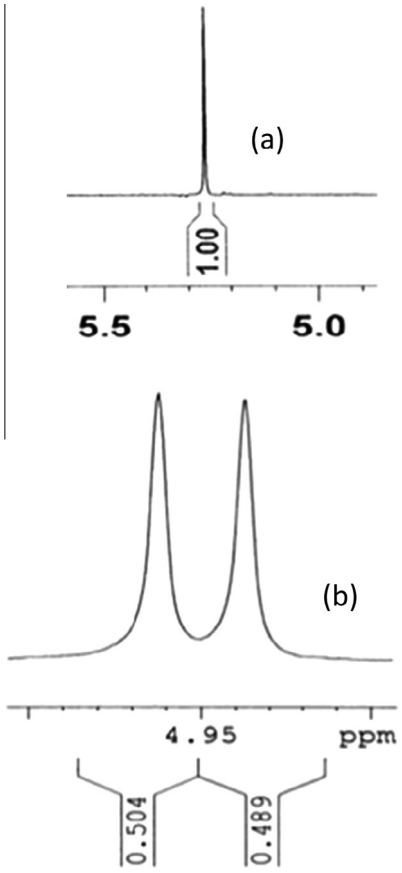
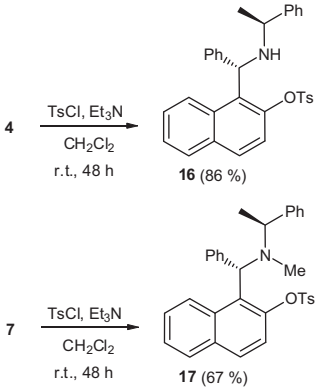
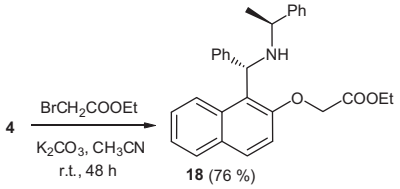


Figure 3. Effect of CSA on the ^{1}H NMR spectra (400 MHz, $CDCl_3$): C$^{\alpha}$H proton of DL-mandelic acid (a), C$^{\alpha}$H proton of DL-mandelic acid + (*S*,*S*)-**11** (1:1 at 22 mM) (b).



Scheme 6. Synthesis of OT derivatives of the aminonaphthyl system.

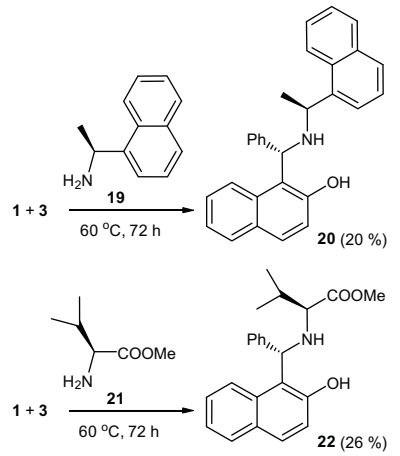
nize mandelic acid (entries 12 and 13, Table 1). This hypothesis was further investigated by introducing a carbonyl system in place of the aromatic ring in the ester of aminonaphthol. Accordingly α-aryloxy acetate (*S*,*S*)-**18** was prepared from (*S*,*S*)-**4** and ethyl bromoacetate (Scheme 7). This molecule showed comparable activity as a CSA for resolution of the signals of mandelic acid (entry 14, Table 1) to that of the *O*-Bn derivative (*S*,*S*)-**11**. This particular case is significant since the presence of a carbonyl of the ester in place of the aromatic ring was also probably providing sufficient binding



Scheme 7. Synthesis of α-aryloxy acetate derivative.

to the mandelic acid unit for the stability of the electrostatic ion pair with the analyte.

Two more derivatives of the chiral aminonaphthol were prepared by changing the primary amine to (*S*)-1-(1-naphthyl)ethylamine **19** and L-methyl valinate **21**, while keeping the two other components the same (Scheme 8). Both of these molecules **20** and **22** were screened as CSAs and the results showed that the former displays a similar range of resolution (entry 15, Table 1) while the latter is not effective (entry 16, Table 1).



Scheme 8. Synthesis of aminonaphthols with other chiral sources.

Having concluded that compound (*S*,*S*)-**11** showed reasonably good CSA activity, samples of different enantiomeric purity of mandelic acid were prepared and evaluated with the same amine. The ratio of the two isomers was experimentally established by CSA analysis with (*S*,*S*)-**11** and compared with the actual values and found to be in good agreement (Fig. 4).

The probable mode of recognition of the isomers of mandelic acid is by complex formation between the carboxylate ion of the acid and the protonated nitrogen of the aminonaphthyl unit. The formation of the carboxylate anion was confirmed when the position of the carbonyl stretch (1716 cm^{-1} for mandelic acid) decreased in the FT-IR spectra of a 1:1 mixture of (*S*,*S*)-**11** and DL-mandelic acid, and strong peaks appeared at 1596 and 1623 cm^{-1} (the COO^- stretch). Similar observations have previously been noted for different CSA systems.[11,12b] This may support the suggestion that the binding of the carboxylate ion of a racemic acid with a chiral CSA provides a diastereomeric complex structure where the aromatic ring of the acid may favor a π–π interaction with the *O*-benzyl ring. This will also corroborate the other experimental observations of the requirement of the N–H and a π-system attached to the hydroxyl group of the naphthyloxy function of this type of solvating agent for effective electrostatic interactions and suitable π–π interactions between the two aromatic rings of the analyte and guest molecules. A schematic

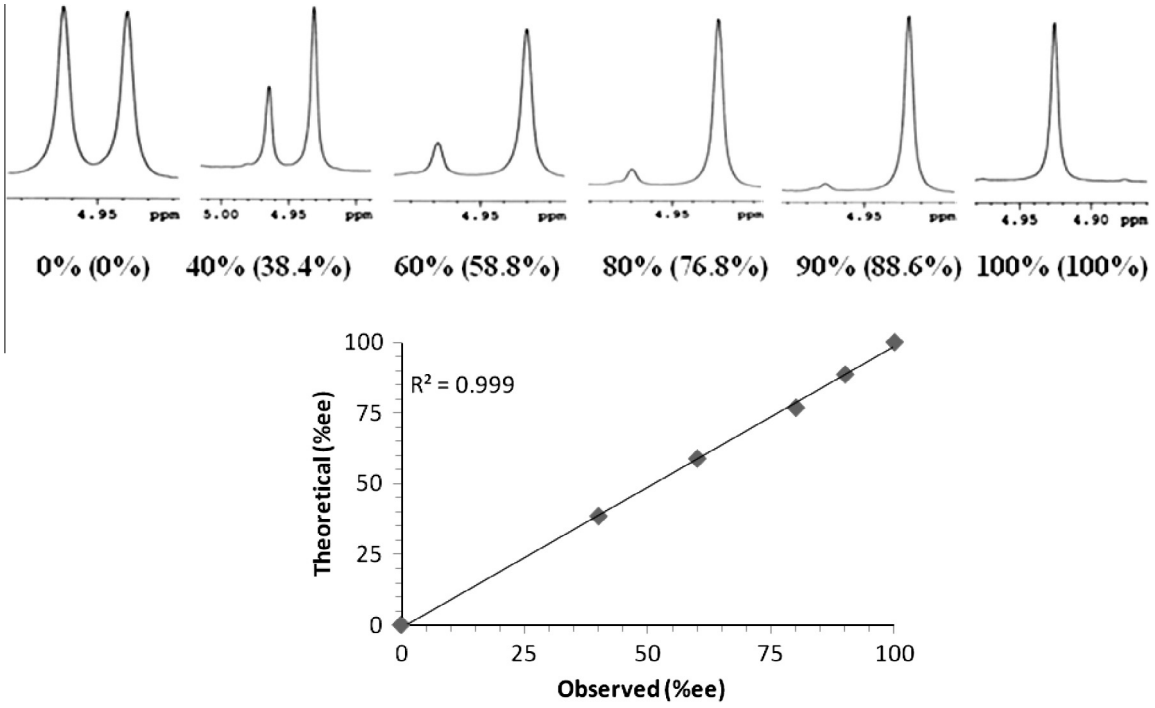
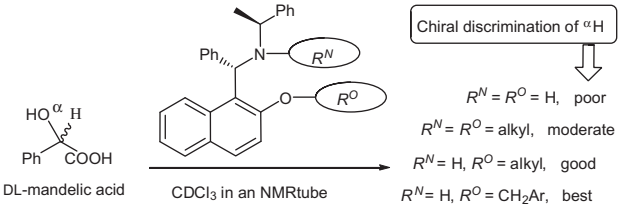


Figure 4. Selected regions of the ^{1}H NMR spectra of (±)-mandelic acid of various ratios of enantiomeric purity in the presence of (*S*,*S*)-**11**. Values in parenthesis are observed purity. [Left] correlation of observed and actual values of ee of a test sample of DL-mandelic acid. R^2 = correlation coefficient [right].

representation of the structure—CSA activity may be made to summarize this conclusion (Scheme 9).



Scheme 9. Summary of the structural features of the chiral aminonaphthols on the efficiency as a CSA.

3. Conclusion

Herein we have prepared a few derivatives of chiral 1-(α-aminobenzyl)-2-naphthol and tested their efficacy as chiral solvating agents or chiral complexing agents in ^{1}H NMR spectroscopy to discriminate the $C^{\alpha}H$ of DL-mandelic acid. A linear relationship has been observed between the experimental and observed values of ee indicating the possible use of these compounds for quick and reliable analysis of enantiomerically enriched samples of mandelic acid. From the experiments performed a preliminary conclusion indicated that the CSA with a free NH group and the benzyl derivative of the phenol of Betti base derivatives or 1-(α-aminobenzyl)-2-naphthols are most effective in the chiral discrimination of mandelic acid in ^{1}H NMR analysis.

4. Experimental

4.1. General

Thin layer chromatography was performed on silica gel plates quoted on aluminum sheets. The spots were visualized under UV light or with iodine vapor. All of the compounds were purified by column chromatography on silica gel (60–120 mesh). All of the reactions were carried out under an inert atmosphere (nitrogen) unless other conditions are specified. NMR Spectra were recorded on a 400 MHz Spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and TMS as the internal standard. Single crystal X-ray diffraction data were collected with an Xcalibur, Eos, Gemini diffractometer. Mass spectra were recorded on a GCMS instrument in direct injection EI-mode. IR Spectra were recorded as KBr pellets. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

4.1.1. 1-[Phenyl(1-phenylethylamino)methyl]naphthalen-2-ol (*S*,*S*)-4

Enantiomerically pure aminonaphthol (*S*,*S*)-**4** was prepared according to the literature.[4b] White solid, 90% yield, mp 152–154 °C (reported mp 155–156 °C).[4b]

4.1.2. [(2-Methoxynaphthalen-1-yl)phenylmethyl]methyl(1-phenylethyl)amine (*S*,*S*)-5

Powdered NaOH (0.28 g, 7.08 mmol) was added to a solution of (*S*,*S*)-**4** (0.5 g, 1,42 mmol) in THF (10 mL). After 10 min CH_3I (0.9 mL, 14.15 mmol) was dropped into the slurry. The mixture was stirred for 6 h and then a solution of saturated NH_4Cl was added. After extraction with ethyl acetate, the organic extracts were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/EtOAc (10:1) as eluent to give a white solid (0.785 g, 97% yield). White solid; mp 120–122 °C, $[\alpha]_D^{25}$ = +61.6 (*c* 0.753, $CHCl_3$). IR (KBr): *ν* 3056, 2847, 1684, 1599, 1509, 1488, 1464, 1419, 1371, 1313, 1260, 1248, 1184, 1148, 1080, 1069, 1048, 1024, 808, 752, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.48–1.5 (d, *J* = 6.8 Hz, 3H), 2.09 (s, 3H), 4.04 (s, 3H), 4.26–4.32 (q, *J* = 6.8 Hz, 1H), 5.88 (s, 1H), 7.1–7.78 (m, 15H), 9.63–9.65 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 13.9, 33.6, 56.6, 56.7, 64.0, 113.6, 123.4, 123.9, 125.9, 126.2,

126.5, 126.6, 127.8, 128.0, 128.2, 128.4, 129.3, 129.6, 133.2, 142.1, 143.5, 154.7. EIMS (*m*/*z*): 380.95 ([M]$^+$, 42%), 365.91 (11.6%), 303.81 (8%), 275.87 (12%), 246.75 (100%), 214.76 (13%), 104.88 (6%), 90.87 (11%). HRMS: 382.5242 (calcd, M+H). Found: 382.2165.

4.1.3. 1-Phenyl-2-(1-phenyl-ethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (*S*,*S*)-6

White solid, 90% yield, mp 124–126 °C (reported mp 125–128 °C).[4b]

4.1.4. 1-{[Methyl(1-phenylethyl)amino]phenylmethyl}naphthalen-2-ol (*S*,*S*)-7

White solid, 99% yield, mp 126–128 °C (reported mp 128–129 °C).[4c]

4.1.5. [(2-Methoxynaphthalen-1-yl)phenylmethyl](1-phenylethyl) amine (*S*,*S*)-8

Powdered NaOH (0.16 g, 3.95 mmol) was added to a solution of (*S*,*S*)-**4** (0.2 g, 0.56 mmol) in THF·H_2O (1:1, 6 mL). After 10 min, Me_2SO_4 (0.27 mL, 2.82 mmol) was added to the slurry. The reaction mixture was then heated at 70 °C for 2 days, after which the reaction mixture was quenched with water and extracted with ethylacetate (2 × 25 mL). The combined organic layer was washed with water, the combined organic extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/EtOAc (10:1) as eluent to give a pale yellow solid (0.125 g, 60% yield), mp 102–104 °C (reported mp 104–106 °C).[10b]

4.1.6. [(2-Benzyloxynaphthalen-1-yl)phenylmethyl](1-phenylethyl)amine (*S*,*S*)-11

To a solution of (*S*,*S*)-**4** (0.1 g, 0.28 mmol), K_2CO_3 (0.06 g, 0.42 mmol), and 18-crown-6 (0.015 g, 0.056 mmol) in acetonitrile (7 mL) was added benzyl chloride (0.072 g, 0.42 mmol). The reaction mixture was heated at 75 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethylacetate (2 × 25 mL). The combined organic layer was washed with water, dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (20:1) as eluent to give a white solid (0.107 g, 86% yield). mp 116–118 °C, $[\alpha]_D^{25}$ = −68.56 (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3348, 3056, 3028, 2968, 2871, 1684, 1623, 1595, 1511, 1492, 1455, 1368, 1352, 1236, 1168, 1123, 1067, 1027, 964, 880, 804, 768, 745, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.25–1.26 (d, *J* = 6.8 Hz, 3H), 3.65–3.70 (q, *J* = 6.4 Hz, 1H), 4.90–4.93 (d, *J* = 12 Hz, 1H), 5.12–5.13 (d, *J* = 11.6 Hz, 1H), 5.71 (s, 1H), 7.05–7.06 (m, 2H), 7.18–7.47 (m, 16H), 7.71–7.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 25.9, 55.1, 55.7, 71.0, 114.9, 123.6, 125.6, 125.9, 126.5, 126.8, 126.8, 127.2, 127.3, 127.8, 128.3, 128.5, 128.6, 129.1, 136.8, 145.1, 146.3, 154.6. EIMS (*m*/*z*): 442.83 ([M]$^+$, 9%), 440.89 (100%), 338.15 (16%). HRMS: 444.5950 (calcd, M+H). Found: 444.2332.

4.1.7. [(2-Isopropoxynaphthalen-1-yl)phenylmethyl](1-phenylethyl)amine (*S*,*S*)-9

The procedure was the same as for (*S*,*S*)-**11**. Mp 128–130 °C, $[\alpha]_D^{25}$ = −71.1 (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3343, 3056, 3027, 2984, 2952, 1620, 1596, 1512, 1493, 1463, 1448, 1332, 1249, 1234, 1111, 1060, 1031, 981, 880, 827, 810, 771, 746, 716, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.82 (br s, 3H), 1.28–1.30 (d, *J* = 6.8 Hz, 6H), 3.06 (br s, 1H), 3.64–3.70 (q, *J* = 6.4 Hz, 1H), 4.60–4.70 (h, 1H), 5.60 (s, 1H), 7.16–7.44 (m, 13H), 7.61–7.63 (d, *J* = 8 Hz, 1H), 7.81–7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 21.3, 22.5, 26.00, 55.0, 55.7, 69.9, 115.1, 123.2, 125.6, 125.8, 126.4, 126.8, 126.8, 127.3, 127.6, 128.2, 128.5, 128.8, 145.5, 146.4, 153.4. EIMS (*m*/*z*): 395.23 ([M]$^+$, 11%), 318.31 (27%), 317.43 (24%), 290.65 (96%), 289.4 (100%), 247.44 (24%). HRMS: 396.5510 (calcd, M+H). Found: 396.2328.

4.1.8. [(2-Butoxynaphthalen-1-yl)phenylmethyl](1-phenylethyl)-amine (*S*,*S*)-10

The procedure was the same as for (*S*,*S*)-**11**. Mp 126–128 °C, $[\alpha]_D^{25}$ = −45.6 (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3339, 3056, 3026, 2961, 2874, 1622, 1596, 1515, 1492, 1460, 1447, 1368, 1351, 1252, 1240, 1171, 1148, 1119, 1083, 1068, 1025, 960, 880, 805, 768, 748, 715, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.84–0.88 (m, 3H), 1.18–1.28 (m, 5H), 1.43–1.5 (m, 2H), 2.30 (br s, 1H), 3.60–3.65 (q, *J* = 6.4 Hz, 1H), 3.72–3.78 (q, *J* = 6.4 Hz, 1H), 4.04–4.09 (q, *J* = 6.8 Hz, 1H), 5.62 (s, 1H), 7.12–7.44 (m, 13H), 7.64–7.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 13.8, 19.1, 25.9, 31.4, 55.1, 55.6, 68.7, 114.6, 123.3, 125.0, 125.7, 126.3, 126.7, 126.7, 127.2, 127.7, 128.2, 128.6, 129.0, 145.3, 146.3, 155.0. EIMS (*m*/*z*): 409.59 ([M]$^+$, 16%), 331.37 (24%), 303.53 (100%), 288.22 (11%), 105.15 (9%). HRMS: 410.5778 (calcd, M+H). Found: 410.2478.

4.1.9. {[2-(4-Bromobenzyloxy)naphthalen-1-yl]phenylmethyl}-(1-phenylethyl)amine (*S*,*S*)-12

The procedure was the same as for (*S*,*S*)-**11**. Oil, $[\alpha]_D^{25}$ = +44.2 (*c* 1.38, $CHCl_3$). IR (neat): *ν* 3349, 3059, 3025, 2959, 1652, 1622, 1596, 1514, 1489, 1456, 1433, 1368, 1351, 1217, 1170, 1147, 1121, 1069, 1012, 960, 880, 841, 805, 760, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.22–1.23 (d, *J* = 6.8 Hz, 1H), 3.60–3.65 (q, *J* = 6.4 Hz, 1H), 4.79–4.82 (d, *J* = 11.6 Hz, 1H), 5.02–5.05 (d, *J* = 12 Hz, 1H), 5.64 (s, 1H), 6.80–6.82 (d, *J* = 8 Hz, 2H), 7.16–7.26 (m, 5H), 7.29–7.43 (m, 10H), 7.68–7.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 26.0, 55.0, 55.7, 70.2, 114.7, 121.7, 123.7, 125.91, 126.6, 126.8, 127.2, 127.9, 128.3, 128.6, 129.0, 129.2, 131.5, 135.7, 154.2. EIMS (*m*/*z*): 523.48 ([M+1]$^+$, 16%), 522 ([M]$^+$, 18%), 521 (22%), 446.07 (46%), 418.36 (100%), 414.93 (92%), 402.71 (85%), 351.97 (66%), 104.84 (70%). HRMS: 523.4911 (calcd, M+H). Found: 523.1464.

4.1.10. {[2-(3,5-Dibromobenzyloxy)naphthalen-1-yl]phenylmethyl}(1-phenylethyl)amine (*S*,*S*)-13

The procedure was the same as for (*S*,*S*)-**11**. Mp 104–106 °C, $[\alpha]_D^{25}$ = +66.1 (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3344, 3080, 3060, 3022, 2956, 1622, 1556, 1513, 1491, 1456, 1425, 1367, 1349, 1282, 1245, 1218, 1200, 1168, 1107, 1088, 1068, 1027, 957, 880, 848, 795, 742, 720, 698, 676, 548, 511 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.24–1.26 (d, *J* = 6.4 Hz, 3H), 2.77 (br s, 1H), 3.60–3.64 (q, *J* = 6.4 Hz, 1H), 4.68–4.71 (d, *J* = 12 Hz, 1H), 4.98–5.01 (d, *J* = 12.4 Hz, 1H), 5.66 (s, 1H), 7.11–7.43 (m, 15H), 7.59–7.6 (t, 1H), 7.71 (br s, 1H), 7.84–7.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 26.0, 54.9, 55.7, 69.7, 114.9, 123.0, 123.7, 124.0, 126.1, 126.4, 126.6, 126.7, 126.9, 127.2, 128.0, 128.3, 128.7, 128.9, 129.3, 129.6, 133.6, 140.7, 144.9, 146.1, 154.0. HRMS: 602.3872 (calcd, M+H). Found: 602.0509.

4.1.11. {[2-(4-Fluorobenzyloxy)naphthalen-1-yl]phenylmethyl}-(1-phenylethyl)amine (*S*,*S*)-14

The procedure was the same as for (*S*,*S*)-**11**. Mp 78–80 °C, $[\alpha]_D^{25}$ = +61.3 (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3344, 3056, 2960, 1623, 1596, 1513, 1492, 1461, 1445, 1368, 1352, 1228, 1156, 1119, 1078, 1067, 1019, 960, 880, 861, 828, 804, 763, 705, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.22–1.23 (d, *J* = 6.4 Hz, 3H), 3.61–3.66 (q, *J* = 6.4 Hz, 1H), 4.81–4.84 (d, *J* = 11.6 Hz, 1H), 5.04–5.07 (d, *J* = 11.2 Hz, 1H), 5.67 (s, 1H), 6.9–6.97 (m, 4H), 7.18–7.43 (m, 13H), 7.84–7.86 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 25.9, 55.0, 55.7, 70.4, 114.9, 115.2, 115.4, 123.7, 125.7, 125.9, 126.5, 126.8, 127.2, 127.9, 128.3, 128.7, 129.2, 129.3, 132.5, 132.5, 145.1, 146.2, 154.4, 161.2, 163.6. EIMS (*m*/*z*): 460.27 (6%), 441.55 (7%), 356.15 (32%), 355.15 (17%), 339.62 (18%), 232.34

(18%), 230.9 (100%), 104.89 (6%). HRMS: 462.5851 (calcd, M+H). Found: 462.2229.

4.1.12. {[2-(4-Methoxybenzyloxy)naphthalen-1-yl]phenylmethyl}-(1-phenylethyl)amine (*S,S*)-15

The procedure was the same as for (*S,S*)-**11**. Mp 116–118 °C, $[\alpha]_D^{25}$ = +59.0 (*c* 1.01, $CHCl_3$). IR (KBr): *ν* 3341, 3053, 2962, 2836, 1616, 1593, 1515, 1491, 1461, 1388, 1370, 1352, 1304, 1248, 1178, 1119, 1076, 1066, 1029, 1014, 960, 880, 859, 805, 761, 745, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.23–1.25 (d, *J* = 6.4 Hz, 3H), 3.63–3.68 (q, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 4.81–4.84 (d, *J* = 11.2 Hz, 1H), 5.04–5.06 (d, *J* = 11.2 Hz, 1H), 5.67 (s, 1H), 6.81–6.83 (m, 2H), 6.94–6.96 (d, *J* = 8 Hz, 2H), 7.17–7.43 (m, 13H), 7.68 (br s, 1H), 7.84–7.86 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 25.8, 55.3, 55.8, 70.8, 113.8, 115.0, 123.5, 125.9, 126.5, 126.8, 126.9, 127.3, 127.8, 128.3, 128.6, 128.8, 129.1, 154.6, 159.3. EIMS (*m/z*): 473.57 ([M^+], 10%), 472.43 (19%), 367.46 (27%), 352.43 (84%), 351.23 (81%), 245.86 (64%), 239.88 (70%), 230.42 (50%), 121.29 (99%), 120.54 (100%), 104.84 (22%). HRMS: 474.6208 (calcd, M+H). Found: 474.2431.

4.1.13. Toluene-4-sulfonic acid-1-[phenyl(1-phenylethylamino)-methyl]naphthalen-2-yl ester (*S,S*)-16

p-Toluenesulfonyl chloride (0.324 g, 1.7 mmol) was slowly added to a solution of (*S,S*)-**4** (0.3 g, 0.85 mmol) and Et_3N (0.24 mL, 1.7 mmol) in CH_2Cl_2 (7 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 days. After removal of the solvent under reduced pressure, the resulting residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (20:1) as eluent to give (*S,S*)-**16** as a light yellow oil (0.37 g, 86% yield). Oil, $[\alpha]_D^{25}$ = +11.15 (*c* 1.01, $CHCl_3$). IR (neat): *ν* 3358, 3057, 3026, 2960, 1684, 1597, 1511, 1492, 1449, 1374, 1306, 1202, 1173, 1093, 1044, 1029, 963, 936, 885, 819, 757, 701, 679 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.18–1.19 (d, *J* = 6.4 Hz, 3H), 2.24 (s, 3H), 3.60–3.62 (q, *J* = 6.4 Hz, 1H), 5.23 (s, 1H), 6.90–6.91 (m, 2H), 7.10–7.47 (m, 14H), 7.61–7.67 (m, 2H), 7.86–7.9 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 21.6, 25.7, 55.1, 56.0, 121.2, 125.7, 126.0, 126.5, 126.9, 126.9, 127.4, 127.7, 127.9, 128.3, 129.2, 129.6, 130.0, 132.7, 143.4, 144.9, 145.7, 146.9. HRMS: 508.6590 (calcd, M+H). Found: 508.1941.

4.1.14. Toluene-4-sulfonic acid-1{[methyl(1-phenylethyl)amino]-phenylmethyl}naphthalen-2-yl ester (*S,S*)-17

The procedure was the same as for (*S,S*)-**16**. Mp 84–86 °C, $[\alpha]_D^{25}$ = +296.81 (*c* 0.44, $CHCl_3$). IR (KBr): *ν* 3086, 3060, 3029, 2975, 1620, 1598, 1508, 1493, 1455, 1372, 1308, 1200, 1174, 1093, 1056, 1028, 955, 880, 834, 818, 752, 700, 680 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.34–1.36 (d, *J* = 6.8 Hz, 3H), 1.94 (s, 3H), 2.50 (s, 3H), 4.23–4.28 (q, *J* = 6.8 Hz, 1H), 5.87 (s, 1H), 7.12–7.8 (m, 17H), 7.92–7.94 (m, 2H), 9.69–9.71 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 10.1, 21.8, 32.7, 56.3, 65.2, 120.3, 125.9, 126.4, 126.4, 126.8, 127.7, 127.7, 128.1, 128.1, 128.4, 128.4, 129.4, 130.1, 130.1, 132.6, 132.7, 133.9, 142.1, 144.1, 145.6, 146.2. HRMS: 522.6858 (calcd, M+H). Found: 522.2097.

4.1.15. {1-[Phenyl-(1-phenylethylamino)methyl]naphthalen-2-yloxy}acetic acid ethyl ester (*S,S*)-18

Ethyl bromoacetate (0.15 mL, 1.36 mmol) was added slowly to a solution of (*S,S*)-**4** (0.2 g, 0.57 mmol) and K_2CO_3 (0.236 g, 1.7 mmol) in acetonitrile (10 mL). The reaction mixture was then stirred for 2 days at room temperature after which the reaction mixture was quenched with water and extracted with ethylacetate (2 × 100 mL). The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/EtOAc (10:1) as eluent to give a colorless oil (0.19 g, 76% yield). Oil, $[\alpha]_D^{25}$ = +185.58 (*c* 0.7, $CHCl_3$). IR (neat): *ν* 3337, 2971, 2921, 1751, 1684, 1623, 1598, 1512, 1492, 1464, 1448, 1381, 1356, 1280, 1203, 1164, 1096, 1044, 1028, 964, 880, 861, 812, 770, 746, 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.30–1.33 (m, 6H), 3.65–3.70 (q, *J* = 6.4 Hz, 1H), 4.23–4.30 (m, 3H), 4.55–4.59 (d, *J* = 16 Hz, 1H), 5.64 (s, 1H), 7.14–7.67 (m, 14H), 7.82–7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.1, 25.7, 55.1, 55.8, 61.4, 66.2, 114.4, 123.6, 124.0, 125.9, 126.2, 126.7, 126.8, 126.9, 127.3, 127.7, 127.9, 128.0, 128.3, 128.6, 129.3, 129.7, 144.8, 146.2, 153.6, 169.0. HRMS: 440.5600 (calcd, M+H). Found: 440.2220.

4.1.16. 1-[(1-Naphthalen-1-yl-ethylamino)-phenyl-methyl]-naphthalen-2-ol (*S,S*)-20

White solid, 20% yield, mp 192–194 °C (literature mp 195–197 °C).[4b]

4.1.17. 2-{[(2-Hydroxynaphthalen-1-yl)phenylmethyl]amino}-3-methylbutyric acid methyl ester (*S,S*)-22

A mixture of β-naphthol (0.44 g, 3.05 mmol), benzaldehyde (0.32 g, 3.05 mmol), and L-valine methyl ester (0.4 g, 3.05 mmol) was stirred at 80 °C for 72 h under nitrogen atmosphere. The reaction mixture was dispersed at room temperature with ethanol and purified by column chromatography on silica gel with hexane/EtOAc (10:1) as eluent to give a white solid (0.285 g, 26% yield). Mp 146–148 °C, $[\alpha]_D^{25}$ = +428.0 (*c* 0.36, $CHCl_3$). IR (KBr): *ν* 3330, 2953, 1730, 1624, 1601, 1520, 1456, 1428, 1369, 1316, 1202, 1071, 1031, 991, 956, 907, 876, 852, 811, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 0.98–1.02 (m, 6H), 2.07–2.15 (m, 1H), 2.70–2.73 (d, *J* = 12.8 Hz, 1H), 3.34–3.39 (q, *J* = 5.2 Hz, 1H), 3. 81 (s, 3H), 5.60 (s, 1H), 7.18–7.21 (d, *J* = 8.8 Hz, 1H), 7.25–7.47 (m, 7H), 7.61–7.63 (d, *J* = 8.4 Hz, 1H), 7.76–7.78 (d, *J* = 8.4 Hz, 2H), 12.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 19.0, 31.7, 51.9, 61.6, 65.4, 112.6, 120.0, 121.0, 122.6, 126.6, 128.0, 128.2, 128.7, 128.9, 129.1, 130.0, 132.9, 140.5, 156.5, 174.5. EIMS (*m/z*): 362.83 ([$M]^+$, 20%), 233.33 (15%), 232.24 (19%), 230.79 (100%), 202.17 (10%). HRMS: 364.4624 (calcd, M+H). Found: 364.1907.

Acknowledgements

We thank Council of Scientific and Industrial Research (CSIR), New Delhi for the award of fellowship to A.R.C. We are also grateful to DST-PURSE for the single crystal X-ray diffraction facility of the Faculty of Science.

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20. Crystallographic data for the structures of compound (*S*,*S*)-**5** and (*S*,*S*)-**10** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 960671 and CCDC 977361, respectively). 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 336 033; e-mail: eposit@ccdc.cam.ac.uk).