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Preparation of (1*R*,1′*R*)-1,1′-(anthracene-9,10-diyl)bis(2,2,2-trifluoroethanamine): a chiral diamine with low basicity

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ABSTRACT

A new chiral diamine with low basicity was synthesized in enantiopure form. (1*R*,1′*R*)-1,1′-(Anthracene-9,10-diyl)bis(2,2,2-trifluoroethanamine) was obtained by means of several stereochemically controlled reactions. The structures of the title compound and several intermediates were studied.

1. Introduction

Chiral compounds able to form non-covalent bonds with appropriate substrates result in sets of association complexes, which display the usual properties of diastereomeric stereoisomers. The main advantage of these diastereomeric association complexes is that they lack the rigidity of covalent bonds between their moieties. This is the objective of preparing compounds with easy associative properties that can be applied to enantiorecognition in a versatile way.[1] Additionally, the same compounds may also be used to form covalent derivatives useful as chiral auxiliaries in stereoselective synthesis.[2]

Common chiral auxiliaries are donor–acceptor compounds that can participate in hydrogen bonds or π interactions. We have previously described the chiral auxiliary capacity of enantiopure α,α′-(bistrifluoromethyl)-9,10-anthracenedimethanol.[3] Some features of its structure make this compound a very effective chiral solvating agent (CSA): (i) the presence of two stereogenic centers, (ii) two acidic groups (OH) that can give hydrogen bonds, (iii) two C–H bonds with a strong α withdrawing group such as trifluoromethyl, and (iv) a large aromatic ring such as anthracene with the corresponding stereo and anisotropic influence and that provides π-stacking stabilization forces. All substituents on each chiral center may participate in several simultaneous soft connections, while in addition the hydroxyl groups can be advantageously used for building covalent stable intermediates under differential stereocontrolled conditions. Other derivatives, also effective as CSAs, can likewise be applied as effective auxiliaries in stereocontrolled reactions.[4] The formation of tweezer structures[5] takes advantage of these properties.

Besides the hydroxyl function, present in all cases discussed so far, a complementary basic center to make the hydrogen bond could be useful. We now present the preparation of a similar molecule in which the OH groups were replaced by two amino groups, namely (1*R*,1′*R*)-1,1′-(anthracene-9,10-diyl)bis(2,2,2-trifluoroethanamine) (**1**), a diamino compound with basic properties that should be capable of forming bonds with acidic centers (Fig. 1). We wish to emphasize the low basic character of these amino groups[6] due to the electron withdrawing character of the trifluoromethyl group. This implies that ionic ammonium salts derived from a complete reaction with weak acids will not be easily formed, since formation of associated species should be more favorable.

Much effort has been spent into asymmetric synthesis of α-trifluoromethylamines, which has resulted in a diversity of methodologies: reduction of an enantiopure imine formed from a ketone and an enantiopure amine;[7] reduction of an imine or oxime using an enantiopure catalyst;[8] and imine reduction by a [1,3] proton shift process.[9] Finally, the trifluoromethylation of a carbon–nitrogen double bond of an enantiopure molecule is the method[10] used in

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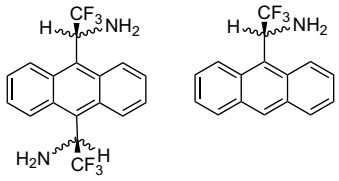

Figure 1. Structure of target compounds **1** and **2**.

the present work to obtain the homochiral enantiomers of 1,1′-(anthracene-9,10-diyl)bis(2,2,2-trifluoroethanamine) (**1**). Both steps, the preparation of an enantiopure sulfinamide[11] and the trifluoromethylation process have been extensively studied and developed.[12]

2. Results and discussion

Enantiomers of the amine 1-(anthracen-9-yl)-2,2,2-trifluoroethanamine (**2**) have been described only once, but as their hydrochloride ammonium salts.[13] Therefore, we began by preparing and studying the monofunctional free amine **2**. Attempted condensation processes between 9-anthraldehyde and one of the enantiomers of *tert*-butanesulfinamide[14] in the presence of $MgSO_4$[15] or $CuSO_4$[16] under heating resulted in decomposition of the corresponding sulfinamide to anthracenenitrile.[17] Only the reaction with $CuSO_4$, after 60 days at room temperature, gave an 85% yield. On the other hand, the described[18] condensation with $Ti(OEt)_4$ was very effective and, when used with (S_S)-*tert*-butanesulfinamide, gave (E,R_S)-*N*-(anthracen-9-ylmethylene)-*tert*-butane-2-sulfinamide (**3S$_S$**) in high yield (95%). The ^{1}H and ^{19}F NMR spectra revealed a single stereoisomer.

The trifluoromethylation of **3S$_S$** was carried out as described, with trifluoromethyltrimethylsilane ($TMSCF_3$) (Ruppert's reagent) using tetrabutylammonium triphenylsilyldifluorosilicate (TBAT),[13] *t*-BuOK[19] or tetramethylammonium fluoride (TMAF)[18,20] as initiators. Only the third initiator resulted in complete conversion to *N*-((*R*,S_S)-1-(anthracen-9-yl)-2,2,2-trifluoroethyl)-*tert*-butane-2-sulfinamide (**4RS$_S$**). Acid (HCl) hydrolysis in methanol followed by neutralization furnished the free amine (*R*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanamine (**2R**) in high yield (80%) and total selectivity. The selectivity was measured by chiral HPLC on Welch-O1 column, which resulted in a single peak. This confirms the enantioselectivity of the method. Using the variation of chemical shift of several protons of **2R** (in CD_3OD) with pD and using HypNMR[21] computer program, we measured the p*K*a of the ammonium salt as 3.21±0.02. The enantiomeric free amine (*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanamine (**2S**) was obtained using (R_S)-*tert*-butanesulfinamide.

The structures of sulfinamide **4** and the free amine **2** were studied using NMR. Both compounds exhibited conformations in which the CF_3 group was pointing away from the anthracene ring in an almost orthogonal orientation (Fig. 2). Thus, rotation around the C_9–C_{11} bond is hindered by the interaction between the CF_3 group and the *peri*-hydrogen atoms H_1 and H_8. NMR spectra (both ^{1}H and ^{13}C) illustrate the lack of symmetry of the anthracene ring, showing separate signals for each individual aromatic proton and carbon atoms. We measured the rotation energy around the C_9–C_{11} bond of **2** by means of ^{1}H NMR at several temperatures. At the coalescence temperature (350 K) we obtained k=1219 s^{-1} and $\Delta G^{\neq}$=15.9 kcal/mole. This value is greater than the value obtained for the corresponding alcohol derivative.[22]

We obtained single crystals of **2S** and determined its structure by X-ray diffraction. The crystal structure is monoclinic with $P2_1$ as space group. The CF_3 group is placed in an orthogonal position to anthracene plane. Molecules are packed in a herring bone arrangement (Fig. 3) forming stacks where anthracenes are parallel and partially overlapped. This overlapping and the distance between anthracene planes, 3.547 Å, point out the existence of π–π interactions. Moreover, molecules are linked by N–H···N and N–H···F three-center hydrogen bonds forming infinite chains. Weaker C_{ar}H···F intermolecular hydrogen bonds are also present.

Although there is no precedent for the double formation of disulfinamides, we used similar conditions to prepare (*E*,*E*,S_S,S_S)-*N*,*N*′-(anthracene-9,10-diylbis(methan-1-yl-1-ylidene))-bis(2-methylpropane-2-sulfinamide) **5S$_S$S$_S$** (Fig. 4). The reaction between anthracene-9,10-dicarbaldehyde and (S_S)-*tert*-butanesulfinamide in the presence of anhydrous $CuSO_4$ gave anthracene-9,10-dicarbonitrile as the only product, although in a very slow reaction even under heating. The best condensation conditions with water elimination were achieved using $Ti(OEt)_4$ in THF, which afforded a high yield (90%) of **5S$_S$S$_S$**. The mono-reacted compound (**6S$_S$**) was also observed.

Attempts to prepare the trifluoromethylated compound **5**, carried out using $TMSCF_3$ and *t*-BuOK as initiator, were unsuccessful. In all tested reaction conditions and for all concentrations of the reactants we observed the degradation to anthracene-9,10-dicarbonitrile. The very high basicity of the initiator possibly induces this decomposition to a much larger extent than for the monofunctional compound **3**.

We obtained monotrifluoromethylation of **5S$_S$S$_S$** (i.e., derivative **7RS$_S$S$_S$**) almost exclusively when $TMSCF_3$ and TBAT were used as a source of fluorine (Fig. 5). TBAT (6 equiv) was used to obtain a quantitative yield of the intermediate compound (**7RS$_S$S$_S$**). A variety of changes in the conditions did not achieve bistrifluoromethyl addition in a useful proportion. Moreover, after isolation of **7RS$_S$S$_S$**, further reaction under the same conditions

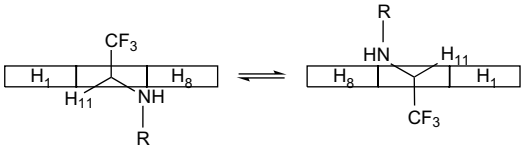

Figure 2. Vertical view of the equilibrium between rotational conformers of compounds **2** (R=H) and **4** (R=SO-*tert*-butyl).

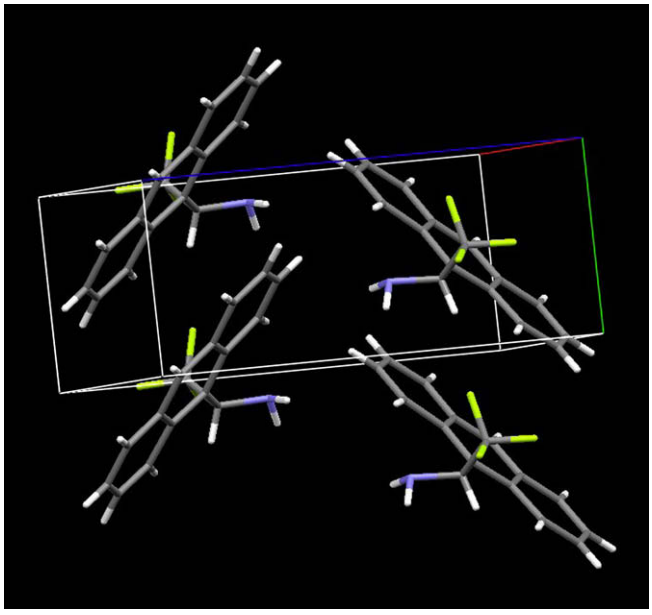

Figure 3. Cell representation of X-ray structure of (*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanamine (**2S**).

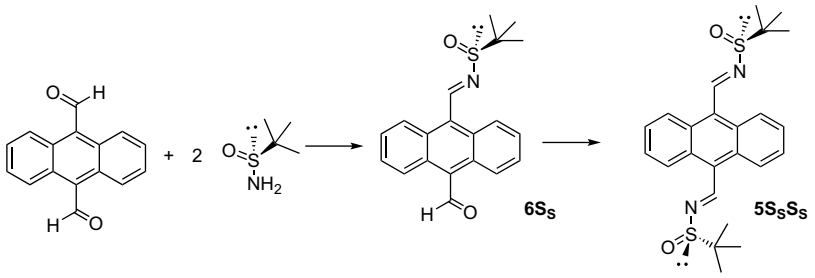

Figure 4. Preparation of (*E*,*E*,S_S,S_S)-*N*,*N*′-(anthracene-9,10-diylbis(methan-1-yl-1-ylidene))bis(2-methylpropane-2-sulfinamide) **5S$_S$S$_S$**.

failed to promote the addition of a second CF_3 group. The first sulfinamide group of **5S$_S$S$_S$** was more reactive than the second one, and also more than that of monofunctionalized compound **4**. The maximum yield obtained when TBAT was used was 5%.

Tetramethylammonium fluoride (TMAF) is a fluoride anion source less sterically hindered than TBAT. Using TMAF in similar conditions we could finally obtain the desired doubly reacted compound. Both trifluoromethyl groups add to the *si* face of the imine *E*-bonds, giving (S_S,S_S)-*N*,*N*′-(1*R*,1′*R*)-1,1′-(anthracene-9,10-diyl)bis(2,2,2-trifluoroethane-1,1-diyl)bis(2-methylpropane-2-sulfinamide) (**8RRS$_S$S$_S$**) as a single isomer, as shown by analysis using NMR and chiral HPLC. Single crystal X-ray diffraction furnished the structure shown in Figure 6 with the *R*,*R* absolute configuration in the new stereogenic carbon atoms.

The crystal structure shows the two CF_3 groups orthogonal to the aromatic ring and on the same side of the anthracene plane. They define a '*cisoid*' conformation. Crystal structure is orthorhombic with $P2_12_12_1$ as space group of symmetry. Molecules are linked by N–H···O=S hydrogen bonds forming layers.

The enantiomer (R_S,R_S)-*N*,*N*′-(1*S*,1′*S*)-1,1′-(anthracene-9,10-diyl)-bis(2,2,2-trifluoroethane-1,1-diyl)bis(2-methylpropane-2-sulfinamide) (**8SSR$_S$R$_S$**) was obtained in the same way beginning with the other enantiomer **5R$_S$R$_S$** ((*E*,*E*,S_S,S_S)-*N*,*N*′-(anthracene-9,10-diyl-bis(methan-1-yl-1-ylidene))bis(2-methylpropane-2-sulfinamide)).

Even at room temperature, solutions of **8** show the presence of two conformers differing in the relative positions of both trifluoromethyl groups with respect to the anthracene ring (Fig. 7), either on the same face (*cisoid* isomer) or on opposite faces (*transoid* isomer) of the aromatic plane. Proton NMR (Fig. 8) gave two groups of signals, namely A and B, that could be assigned to the *transoid* and *cisoid* conformers, respectively.

Full analysis of the ^{1}H NMR spectrum of **8** using NOE results (see Supplementary data) allowed the individual assignment of all protons for both conformers, A and B, as shown on experimental part. From these data, HSQC, and HMBC spectra allowed the ^{13}C NMR assignment of all carbons for both conformers, also shown on experimental part. Finally, taking into account the two different types of C_2 symmetry exhibited by both conformers, isomer B was assigned the *cisoid* conformation on the basis of HMBC results. Thus, the presence of the HMBC cross peaks H_4^B/C_2^B and H_1^B/C_3^B is only compatible with a *cisoid* conformation.

Hydrolysis of **8RRS$_S$S$_S$** (Fig. 9) was carried out in 4 M HCl in methanol/dioxane. This furnished, after neutralization, the enantiomer **1RR** of the target molecule. In this case, the ^{1}H NMR (Fig. 10) shows the presence of the two conformers *cisoid*/*transoid* only after cooling at 250 K (T_c=280 K, K=47.0 s^{-1}, $\Delta G^{\neq}$=14.2 kcal/mol). Similar processes starting with **8SSR$_S$R$_S$** yielded **1SS**.

After assigning all ^{1}H and ^{13}C NMR signals, and considering the presence of H_1^A/C_3^A and H_4^A/C_2^A cross peaks in the HMBC spectrum (only compatible with a *cisoid* situation) (Fig. 11), we assigned the *cisoid* conformation to A signals. Consequently B resonances correspond to the *transoid* conformation.

The two amino groups bear the electron withdrawing trifluoromethyl group in the β position. This reduces the availability of the nitrogen atom electron pair, thus decreasing the basicity of the amine and increasing the acidity of the corresponding ammonium salts. We measured the variation of the chemical shift of several protons with the pD, and using computational methods (HypNMR) we determined the p*K*a's for the two deprotonation processes for the double ammonium salt of **1RR**. The resulting p*K*a values, 3.06±0.04 and 1.36±0.08, correspond to the deprotonation of the monoprotic and diprotic ammonium salts (Fig. 12).

Preliminary studies of the behavior of **1RR** as chiral solvating agent have been carried out with ibuprofen, a chiral carboxylic acid with a high industrial interest. The difference between the chemical shift of two protons (H_2 and H_3) of ibuprofen enantiomers was plotted against the concentration of **1RR** (Fig. 13). The high solubility of **1RR** allows the use of high CSA/substrate ratios. As shown by the tendency of the data, the enantiodifferentiation increases slowly but in a long range, achieving large values for a ratio of 15:1.

Possibly, the very low basicity of the diamine requires high ratios to complex with the substrate. On the other hand, after use of the CSA, recovery of both substrate and CSA is very easy. Simple column chromatography of the contents of the NMR tube leads to a complete separation of the components without loss of material.

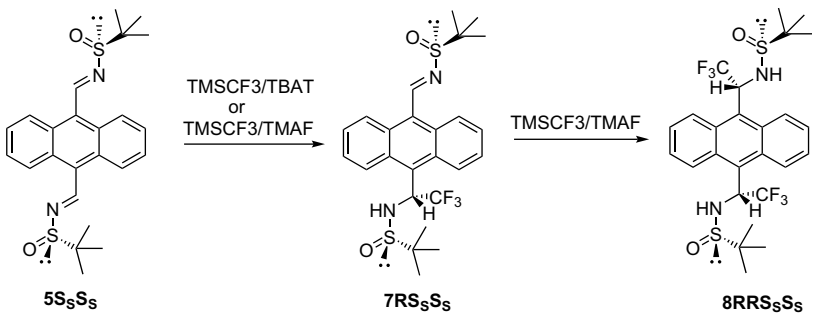

Figure 5. Trifluoromethylation of sulfinamide **5**.

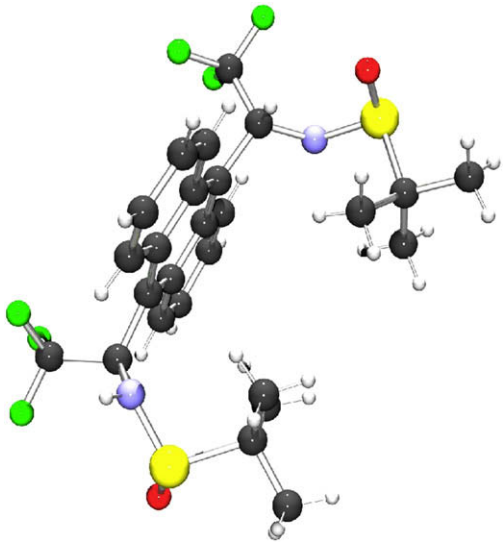

Figure 6. X-ray structure of S_S,S_S-*N*,*N*′-(1*R*,1′*R*)-1,1′-(anthracene-9,10-diyl)bis(2,2,2-trifluoroethane-1,1-diyl)bis(2-methylpropane-2-sulfinamide) (**8RRS$_S$S$_S$**).

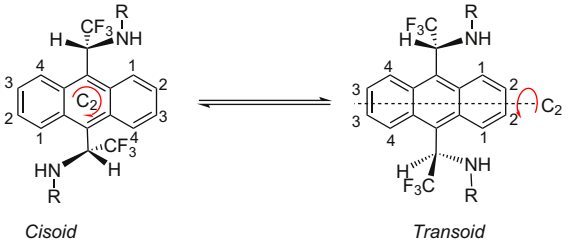

Figure 7. Equilibrium between rotational conformers of compound **8RRS$_S$S$_S$** (R=SOC(CH$_3$)$_3$) and compound **1RR** (R=H). The numbering is shown for identifying symmetry C_2.

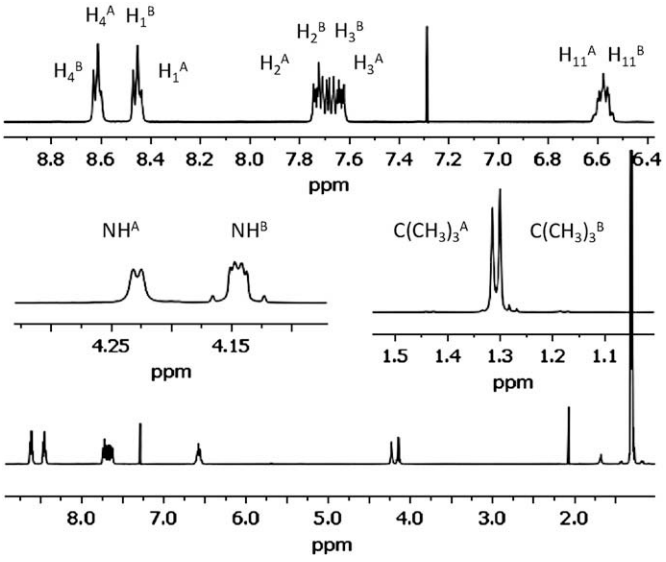

Figure 8. 300 K NMR edited spectrum of **8SSR$_S$R$_S$** where *transoid* and *cisoid* forms are indicated as A and B, respectively.

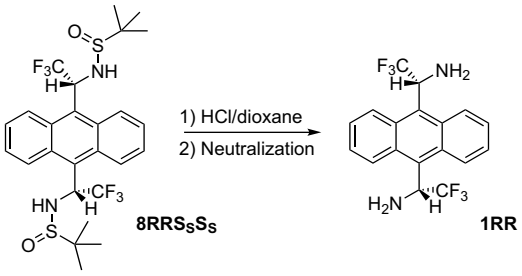

Figure 9. Hydrolysis of disulfinamide **8RRS$_S$S$_S$**.

3. Experimental section

3.1. General

Both enantiomers of compounds **3**, **4** and of hydrochloride of **2** have been previously described. Free amines **2R** and **2S** are fully described here for the first time and were stable at room temperature. All compounds were completely characterized (Supplementary data). The compounds partially reacted are also described in Supplementary data.

NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H. The temperature was controlled to 0.1 °C. The NMR signals were identified completely with the aid of several 1D (NOE) and 2D (COSY, NOESY, HMQC, and HMB) spectra. HRMS were obtained in a Micromass Autospec by EI ionization (70 eV).

3.2. (*E*,*E*,*S*$_S$,*S*$_S$)-*N*,*N*′-(Anthracene-9,10-diylbis(methan-1-yl-1-ylidene))bis(2-methylpropane-2-sulfinamide) (5S$_S$S$_S$)

Under nitrogen 705 mg (5.83 mmol) of (*S*)-(−)-2-methyl-propansulfinamide and 750 mg (3.20 mmol) of 9,10-anthracendicarboxaldehyde were dissolved in 15 mL of anhydrous THF in a 250 mL round-bottom flask. After cooling at 0 °C, 4.90 mL of a freshly prepared 0.5 M solution of Ti(OEt)$_4$ was added (2.45 mmol). It was raised to room temperature and after 15 h the mixture was poured into ice-water (100 mL). After filtration, it was extracted with AcOEt (3×50 mL) and the organic layer dried with MgSO$_4$ anhydrous. After the solvent evaporated the crude was purified by column chromatography (flash) with hexane/CH$_2$Cl$_2$ 95:5 to obtain 1.10 g of **5S$_S$S$_S$** (86% yield). Mp dec; IR (KBr) 2961, 2926, 2865, 1584, 1523, 1444, 1361 (m), 1177, 1074, 758, 736 cm^{-1}; ^{1}H NMR

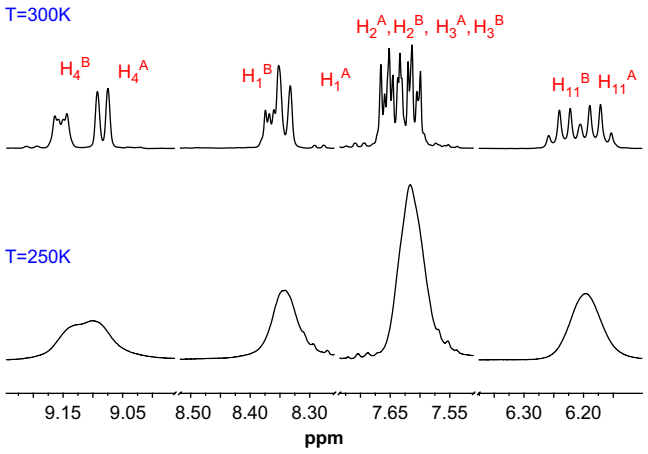

Figure 10. Part of the ^{1}H NMR (CDCl$_3$) spectrum at two temperatures of **1RR**. A and B signals corresponds to *cisoid* and *transoid* conformers, respectively.

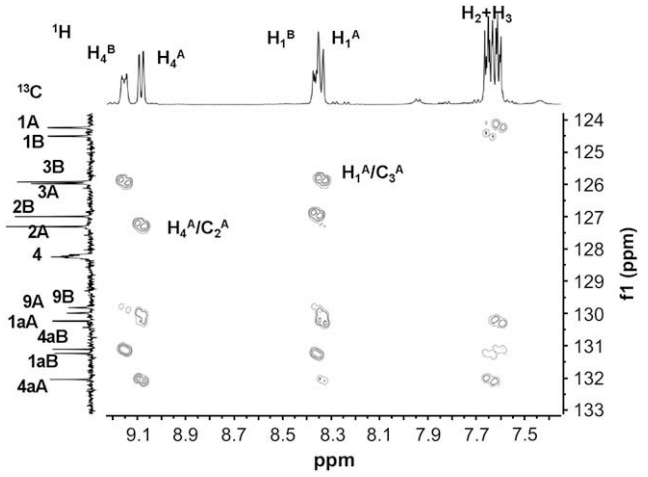

Figure 11. Aromatic part of HMBC spectrum of compound **1RR** at 250 K.

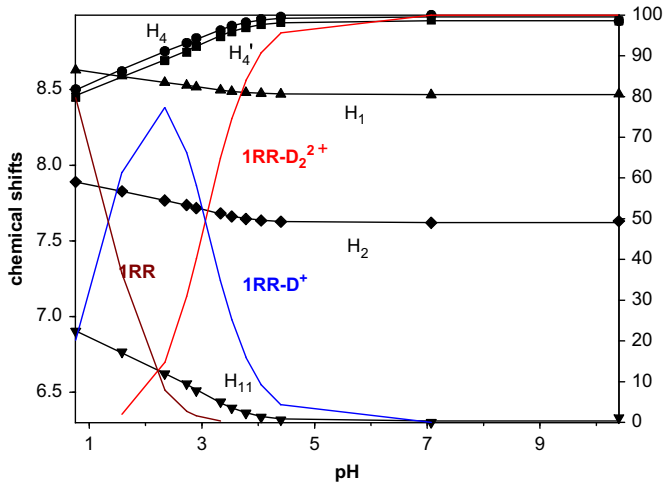

Figure 12. Evolution of chemical shift of several protons of **1RR** with pD (black lines). Red, blue, and brown lines correspond to the speciation of free amine, monoprotic, and diprotic ammonium salts, respectively.

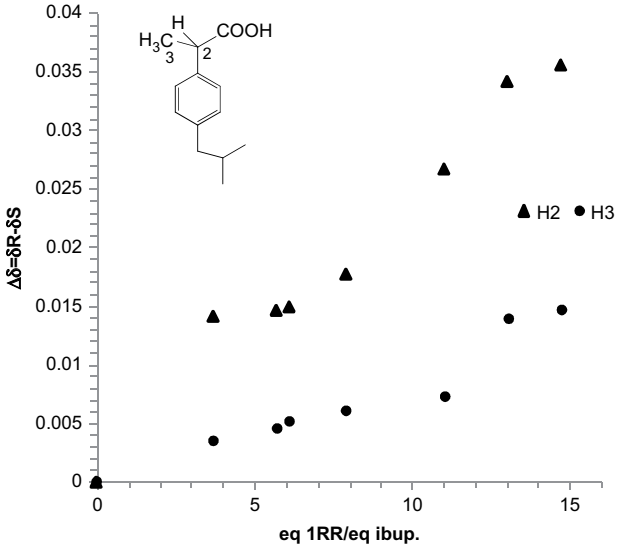

Figure 13. Evolution of enantiodifferentiation of protons H_2 and H_3 of ibuprofen with the ratio eq **1RR**/eq ibuprofen.

(400 MHz, $CDCl_3$) δ 9.86 (H_{11}, s, 2H), 8.69 (H_1, m, 4H), 7.65 (H_2, m, 4H), 1.40 (H_{14}, s, 9H); ^{13}C NMR (100 MHz, CDCl3) δ 162.7 (C_{11}), 129.9 (C_{1a}), 129.6 (C_9), 127.4 (C_2), 125.1 (C_1), 58.0 (C_{13}), 22.7 (C_{14}); MS (ES) (*m/z*, %): 465 ($(MNa+2)^+$, 11), 464 ($(MNa+1)^+$, 27), 463 (MNa^+, 100), 441.1 (MH^+, 6).

3.3. (*S*$_S$,*S*$_S$)-*N*,*N*′-(1*R*,1′*R*)-1,1′-(Anthracene-9,10-diyl)bis(2,2,2-trifluoroethane-1,1-diyl)bis(2-methylpropane-2-sulfinamide) (8RRS$_S$S$_S$)

Under nitrogen 686 mg (1.56 mmol) of (*E*,*E*,*S*$_S$,*S*$_S$)-*N*,*N*′-(anthracene-9,10-diylbis(methan-1-yl-1-ylidene))bis(2-methylpropane-2-sulfinamide) (**5S$_S$S$_S$**) was dissolved in 30 mL of anhydrous THF in a 250 mL round-bottom flask and 872 mg (9.36 mmol) of tetramethylammonium fluoride (TMAF) were added. After cooling at 195 K, 1.85 mL of a freshly prepared solution of 0.35 M of $TMSCF_3$ in anhydrous THF (12.51 mmol) was added. After 4 h the reaction was quenched with NH_4Cl solution, raised to room temperature and extracted with AcOEt. The dried organic phase was evaporated and purified by flash chromatography (hexane/CH_2Cl_2 70:30), which resulted in 796 mg (1.37 mmol, 88%) of **8RRS$_S$S$_S$**. Mp dec; $[\alpha]_{254}^{25}$ +31.0 (*c* 3, CH_3OH); IR (KBr) 3267, 2960, 2922, 2851, 1255, 1164, 1096, 1054, 1008, 765, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ *cisoid* 8.62 (H_4, m, 2H), 8.45 (H_1, m, 2H), 7.69 (H_2, m, 2H), 7.67 (H_3, m, 2H), 6.55 (H_{11}, dq, *J*=8.31, 2.97 Hz, 2H), 4.14 (NH, d, *J*=2.98 Hz, 2H), 1.29 (H_{17}, s, 18H); δ *transoid* 8.60 (H_4, m, 2H), 8.43 (H_1, m, 2H), 7.72 (H_2, m, 2H), 7.63 (H_3, m, 2H), 6.58 (H_{11}, dq, *J*=8.58, 3.94 Hz, 2H), 4.22 (NH, d, *J*=3.41 Hz, 2H), 1.31 (H_{17}, s, 18H); ^{13}C NMR (125 MHz $CDCl_3$) δ *cisoid* 131.5 (C_{4a}), 129.5 (C_{1a}), 128.5–128.6 (C_9), 127.4 (C_2), 126.5 (C_3), 126.0 (C_4), 125.5 (C_{13}, q, *J*=295.6 Hz), 124.4 (C_1), 57.0 (C_{15}), 56.1–56.2 (C_{11}, q, *J*=32.63 Hz), 22.4 (C_{17}); δ *transoid* 129.9 (C_{4a}), 131.1 (C_{1a}), 128.5–128.6 (C_9), 127.7 (C_2), 126.1 (C_3), 126.4 (C_4), 125.5 (C_{13}, q, *J*=295.6 Hz), 123.9 (C_1), 57.2 (C_{15}), 56.1–56.2 (C_{11}, q, *J*=32.63 Hz), 22.4 (C_{17}); ^{19}F NMR (235.37 MHz, $CDCl_3$) δ *cisoid* −69.11 (CF_3, d, *J*=8.6 Hz); δ *transoid* −68.79 (CF_3, d, *J*=9.5 Hz).

3.4. (1*R*,1′*R*)-1,1′-(Anthracene-9,10-diyl)bis(2,2,2-trifluoroethanamine) (1RR)

In a 250 mL round-bottom flask 796 mg (1.37 mmol) of **8RRS$_S$S$_S$** solved in 60 mL of methanol and 15 mL of HCl (4 M in 1,4-dioxane) was added. After 3.5 h the solution was neutralized and extracted with AcOEt. The organic phase was dried, concentrated, and purified by flash chromatography (hexane/CH_2Cl_2 85:15) obtaining 354 mg (70%) of the target compound **1RR**. Mp 114–116 °C; $[\alpha]_{254}^{25}$ −37.0 (*c* 3, CH_3OH); IR (KBr) 3346, 1255, 1155, 1107, 882, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 250 K) δ *cisoid* 9.07 (H_4, d, 2H), 8.33 (H_1, d, 2H), 7.62 (H_2, H_3, m, 4H), 6.17 (H_{11}, q, 2H), 2.20 (NH_2, s, 4H); δ *transoid* 9.14 (H_4, m, 2H), 8.35 (H_1, m, 2H), 7.62 (H_2, H_3, m, 4H), 6.22 (H_{11}, q, 2H), 2.20 (NH_2, s, 4H); ^{13}C RMN (125 MHz, $CDCl_3$, 250 K) δ *cisoid* 132.1 (C_{4a}), 130.3 (C_{1a}), 130.0 (C_9), 128.2 (C_4), 127.3 (C_2), 127.1 (C_{13}, q, *J*=283.7 Hz), 125.9 (C_3), 124.2 (C_1), 53.8 (C_{11}, q, *J*=31.7 Hz); δ *transoid* 131.1 (C_{4a}), 131.3 (C_{1a}), 129.8 (C_9), 128.2 (C_4), 127.0 (C_2), 127.1 (C_{13}, q, *J*=283.7 Hz), 125.9 (C_3), 124.5 (C_1), 54.1 (C_{11}, q, *J*=30.7 Hz); ^{19}F RMN (235.37 MHz, $CDCl_3$) δ *cisoid* −71.2 (CF_3, b), δ *transoid* −71.4 (CF_3, b); MS (ES) (*m/z*, %): 396 ($(MNa+1)^+$, 9), 395 (MNa^+, 43). HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{14}N_2F_6$ [M^+]: 372.10589; found: 372.10612.

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Supplementary data

Characterization NMR data of described compounds **2**, **3**, **4** and intermediates compounds **5, 6**, and **7** (1D-NOE, NOESY, COSY, ^{13}C NMR, HSQC, HMBC, ^{1}H DNMR, X-ray, and p*K*a). Some other edited NMR spectra of compounds **8** and **1**, X-ray data and the HypNMR application. Numerical data for the enantiodifferentiation of ibuprofen.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-702798 (**2S**) and 702799 (**8RRS$_S$S$_S$**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.082.

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