DOI: 10.1002/ejoc.200900548

BINBAM – A New Motif for Strong and Chiral Brønsted Acids

Marcel Treskow,[a] Jörg Neudörfl,[a] and Ralf Giernoth*[a]

Keywords: Chirality / Acidity / Sulfonamides / Organocatalysis

We are reporting the first synthesis of the new chiral Brønsted acid BINBAM [(*R*)-1,1′-binaphthyl-2,2′-bis(sulfon)-amide, **2**], which can be obtained in four steps from commercially available BINOL (**5**). The compound is expected to be an alternative for established catalysts like phosphoric acids of BINOL **4** or TRIP and to show stronger Brønsted acidity.

Introduction

Among the more challenging topics in organic chemistry is the development of new chiral catalysts for asymmetric synthesis. These days, so-called organocatalysts[1] (which are in fact small metal-free organic molecules) are often used in their anionic form for asymmetric counteranion-directed catalysis ("ACDC").[2] Other applications include asymmetric transfer hydrogenation[3–5] and hydrogen bond or Brønsted acid catalysis.[6–8] One of the more dominating families of catalysts is the binaphthyls, which evolved into more efficient systems following two routes: first, by creating more steric demand to gain more selectivity, and second, by creating stronger acids for higher activity. This way, various BINOL-derived chiral phosphoric acids have been developed and used in manifold enantioselective transformations.[6] Nonetheless, the systems with the strongest acidities are still based on phosphoric acid – so far without alternative. Cheon and Yamamoto were able to obtain an even stronger system by introducing the *N*-trifluoromethanesulfonyl (NTf) group into a phosphoric acid based molecule.[9] With this, the authors could demonstrate the activation of various carbonyl compounds.

Our aim was to develop chiral catalysts of even higher acidity and thus higher activation potential in organocatalytic reactions, for example, to be able to activate C–C double bonds. We decided on the proven chiral binaphthyl backbone in combination with a known stronger acid – bis(sulfon)amide **1** (Figure 1). This combination directly leads to our target structure BINBAM (**2**). The N–*H* acidity of *N*-bis(trifluoromethanesulfone)amide (**1**) has already been determined to be very strong (pK_a 2.4 in DMSO).[10] Although no pK_a values for BINOL phosphoric acid **4** and its R–NH–Tf derivative **3** can be found in the literature, we expect the acidity to follow an order like that shown in Figure 1.

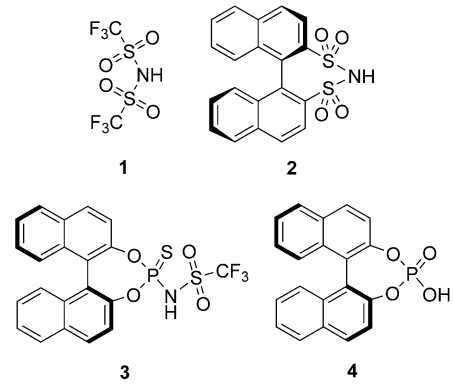

Figure 1. Established Brønsted acids, shown from left to right in decreasing order of acidity.

Results and Discussion

Our synthetic route started with commercially available (*R*)-BINOL (**5**), which when treated with *N*,*N*-dimethylthiocarbamoyl chloride gave 2,2′-bis-*O*-(*N*,*N*-dimethylthiocarbamato)-1,1′-binaphthalene (**6**). After a Newman–Kwart rearrangement followed by oxidation with *N*-chlorosuccinimide, (*R*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (**8**) was obtained. This could subsequently be converted directly into the target molecule BINBAM (**2**) by using gaseous ammonia (Figure 2).

The access to 2,2′-sulfur derivatives of binaphthyl is rather limited. Only one method can be found in the literature that gives access to derivatives of this type directly and selectively starting from the binaphthyl backbone, called the "Newman–Kwart rearrangement",[11,12] which has subsequently been applied by Smith[13] and Ishihara.[14] By applying the procedure of Ishihara for microwave-assisted

[a] University of Cologne, Chemistry Department, Greinstr. 4, 50939 Köln, Germany
E-mail: Ralf.Giernoth@uni-koeln.de
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900548.

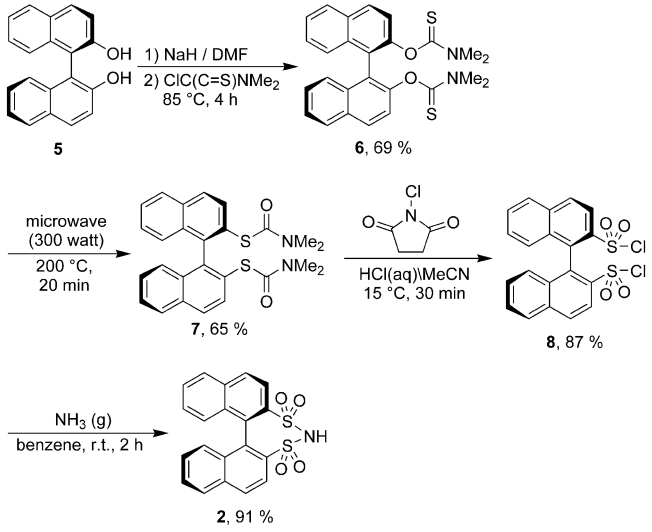

Figure 2. Synthetic pathway for (*R*)-BINBAM (**2**).

synthesis, we hardly achieved reproducible yields, which ranged from 40–55% with 65% in just one case. The major side product in this reaction was binaphthothiophene (**9**), which stems from carbamoyl **7**[13] (Figure 3).

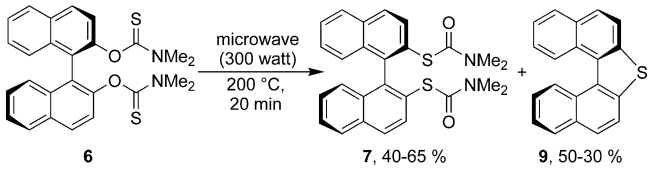

Figure 3. Newman–Kwart rearrangement of **6** with side product binaphthothiophene (**9**).

The synthesis of Ishihara would lead to the disulfonyl chloride in three steps with an overall yield of 70%: reduction with $LiAlH_4$ (95% yield), oxidation with KOH/O_2 (82%),[14] and chlorination with PCl_5 (89.5%).[15] From our own experience in the synthesis of chiral sulfonic acids, we believed that oxychlorination by chlorine gas in water[16] or by *N*-chlorosuccinimide (NCS) in HCl/MeCN[17] would be advantageous, as this reaction directly leads to the corresponding sulfonyl chloride in very good yields with excellent purity (Figure 4).

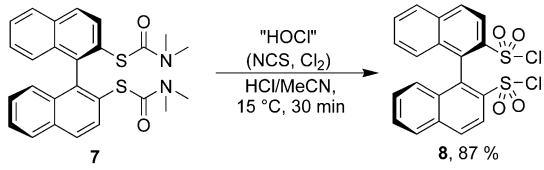

Figure 4. Synthesis of the sulfonyl chloride by oxychlorination of **8** with NCS.

For the conversion of the sulfonyl chloride into the corresponding bis(sulfon)amide, the major challenge was selectivity, as both sulfonyl chloride groups needed to react with one single amine. Unfortunately, even under very high dilution conditions the reaction to unwanted disulfonamide **10** was highly preferred – to an extent that 50% of our sulfonyl chloride could be reisolated. To our own surprise, however, this limitation could easily be solved by using gaseous ammonia instead of amines (as described by Farrar[18] in 1960 in model studies on arenesulfonamides): the reaction led directly to our target molecule BINBAM (**2**) in excellent yield (Figure 5).

For the chemical analysis of BINBAM (**2**) we had to rely mostly on X-ray crystallography, as the ^1H and ^{13}C NMR spectra give no clue as to whether the bis(sulfon)amide had been formed or not (Supporting Information available). As one can see from Figure 6, coordination of one molecule of diethyl ether seems necessary to stabilize the highly acidic proton through hydrogen bonding.

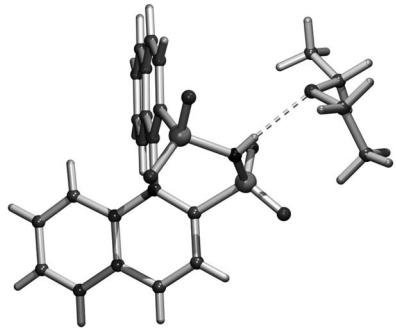

Figure 6. X-ray structure of BINBAM·Et_2O (**2**; visualizing the hydrogen bond).

In this form, the material is not hygroscopic and can be easily handled and stored in air. Even under reduced pressure (0.001 mbar) the ether molecule is not removed from the crystal structure, presumably because it is shielded by a

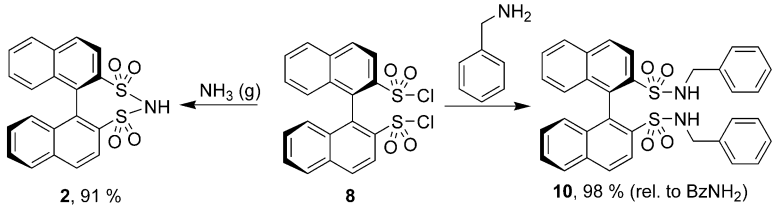

Figure 5. Reaction of sulfonyl chloride **8** with amines.

helical sphere of three BINBAM molecules (Figure 7). However, if necessary the ether molecule can be removed completely by dissolving the product in DMSO and evaporating the solvent under vacuum at room temperature, yielding a highly hygroscopic product that requires storage and handling under a dry atmosphere.

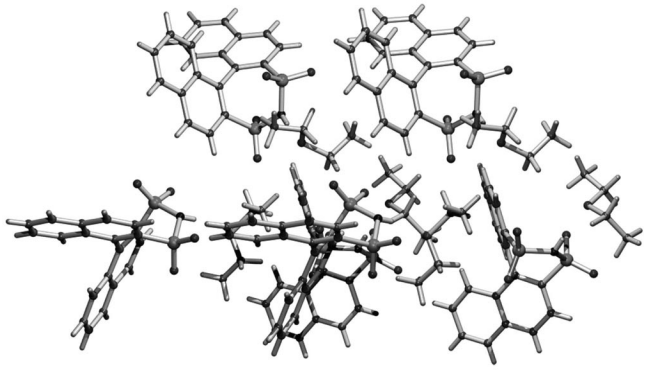

Figure 7. X-ray structures of BINBAM·Et_2O (**2**; visualizing the helical sphere).

Conclusions

In conclusion, we have made available a new class of strong and chiral Brønsted acids, with BINBAM (**2**) as its first member, through an efficient and straightforward four-step synthesis starting from commercially available materials. Currently, we are working on its application in organocatalysis and on the synthesis of various derivatives.[19]

Experimental Section

General Remarks: If not stated otherwise, all chemicals and dry solvents (water content <50 ppm) were bought from Acros Ltd. Int. and used without further purification. TLC aluminum sheets were bought from Macherey–Nagel, coated with 0.2 mm silica gel and containing a fluorescent indicator. Spots were visualized by UV light (354 and 386 nm). ^1H and ^{13}C NMR spectra were measured at ambient temperature and are referenced to the solvent as internal standard relative to TMS. ^{15}N NMR was recorded with a Bruker Avance DRX500 spectrometer by $^1J_{H,N}$–HMQC (90 Hz coupling). Melting points were determined by DSC analysis. Optical rotations were measured with a Perkin–Elmer 343 Plus polarimeter. All reactions were magnetically stirred.

(*R*)-2,2′-Bis-*O*-(*N*-dimethylthiocarbamato)-1,1′-binaphthalene (6): The synthesis of **6** generally followed the procedure by Smith et al.[13] Under an atmosphere of argon a flame-dried, 500-mL flask was charged with (*R*)-(+)-1,1′-binaphthalene-2,2′-diol (**5**; 47.48 g, 165.85 mmol, 1 equiv.). The solid was dissolved in dry *N*,*N*-dimethylformamide (DMF, 310 mL, 24 equiv.) by vigorous stirring, which resulted in a gray-brown solution. After cooling to 0 °C, sodium hydride (15.92 g of 60%, mineral oil dispersion; effective dose: 9.5 g, 398 mmol, 2.4 equiv.) was added over a period of 2 h in small portions. Finally, *N*,*N*-dimethylthiocarbamoyl chloride (41.0 g, 331.7 mmol, 2 equiv.) was added in one portion. The solution was stirred for 4 h at 85 °C [reaction monitored by TLC: CH_2Cl_2, R_f(binol) ≈ 0.5–0.6; R_f(product) ≈ 0.8] and cooled to room temperature. The product was precipitated by slowly adding the solution into 1% aqueous KOH (1.4 L) under vigorous stirring. The precipitate was filtered under reduced pressure and dried in air. The purity of crude **6** was determined by ^1H NMR spectroscopy. Starting material or trace amounts of impurities were easily removed by column chromatography [CH_2Cl_2; R_f(product) ≈ 0.8, first spot]. Usually, the crude product was already pure enough for recrystallization from boiling ethanol. Product **6** (105.1 g, 228.2 mmol, 69%) crystallized as colorless prisms. M.p. 154.5 °C (EtOH). $[\alpha]_D^{20}$ (589 nm) = 118.5 (*c* = 1.0, THF). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.52 (s, 6 H, NCH_3), 3.07 (s, 6 H, NCH_3), 7.24–7.38 (m, 2 H, Ar), 7.40–7.49 (m, 4 H, Ar), 7.62 [d, ^3J(H,H) = 8.8 Hz, 2 H, Ar], 7.90 [d, ^3J(H,H) = 8.8 Hz, 2 H, Ar], 7.96 [d, ^3J(H,H) = 8.8 Hz, 2 H, Ar] ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 37.9 (2 C, CH_3), 42.6 (2 C, CH_3), 123.5 (2 C, *C*H), 123.8 (2 C, *C*), 125.5 (2 C, *C*H), 126.1 (2 C, *C*H), 126.6 (2 C, *C*H), 127.6 (2 C, *C*H), 128.1 (2 C, *C*H), 131.2 (2 C, *C*), 133.1 (2 C, *C*), 149.3 (2 C, *C*-O-C=S), 185.9 (2 C, C-O-*C*=S) ppm. $C_{26}H_{24}N_2O_2S_2$ (460.61): calcd. C 67.80, H 5.25, N 6.08; found C 67.76, H 5.20, N 6.03. IR: $\tilde{\nu}$ = 2932 (w), 1535 (m), 1395 (s), 1286 (s), 1213 (s), 1138 (s), 1118 (m), 812 (m), 750 (m) cm^{-1}.

(*R*)-2,2′-Bis-*S*-(*N*-dimethylthiocarbamato)-1,1′-binaphthalene (7; μ-wave): The synthesis followed the procedure of Ishihara et al.[14] A sealed 10-mL microwave reactor was charged with **6** (6 g, 13 mmol) without solvent. Under microwave irradiation (300 W) the temperature was kept at 200 °C for 20 min. (At 200 °C the irradiation power was about 20–40 W to hold this temperature.) The crude product was scraped out of the reactor and analyzed by ^1H NMR spectroscopy. The residue was dissolved in boiling CH_2Cl_2. Upon cooling, byproduct 1,1′-binaphthothiophene (**9**) separated as thin shiny plates. The remaining solution was purified by column chromatography (silica gel, CH_2Cl_2). Isolated starting material as well as monorearranged product may be reused as starting material in further experiments. [Usually four spots: R_f(thiophene) ≈ 0.98, R_f(starting material) ≈ 0.6–0.8, R_f(mono rearranged product) ≈ 0.4, RF(product) ≈ 0.2.] In the case of complete conversion of **6**, Et_2O was used as eluent and the product was coated on 2 equiv. of silica gel due to its poor solubility [R_f(thiophene) ≈ 0.99, R_f(mono rearranged product) ≈ 0.8, R_f(product) ≈ 0.5]. After evaporating the solvent, the product residue was recrystallized from ethanol to obtain (*R*)-2,2′-bis-*S*-(*N*,*N*-dimethylthiocarbamato)-1,1′-binaphthalene (**7**; 3.9 g, 8.5 mmol, 65%). M.p. 92.5 °C. $[\alpha]_D^{20}$ (589 nm) = 33.8 (*c* = 1.0, THF). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.6–3.0 (br. s, 12 H, NCH_3), 7.08 [d, ^3J(H,H) = 8.5 Hz, 2 H, Ar], 7.21 (m, 2 H, Ar), 7.4–7.5 (m, 2 H, Ar), 7.79 [d, ^3J(H,H) = 8.5 Hz, 2 H, Ar], 7.91 [d, ^3J(H,H) = 7.9 Hz, 2 H, Ar], 7.97 [d, ^3J(H,H) = 8.5 Hz, 2 H, Ar] ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 36.7 (4 C, CH_3), 126.3 (2 C, *C*H), 126.6 (2 C), 126.9 (2 C), 127.8 (2 C), 128.2 (2 C), 128.4 (2 C), 133.1 (4 C), 133.2 (2 C), 140.9 (2 C), 166.2 (2 C, *C*=O) ppm. $C_{26}H_{24}N_2O_2S_2$ (460.61): calcd. C 67.80, H 5.25, N 6.08; found C 67.54, H 5.57, N 5.84. IR: $\tilde{\nu}$ = 2924 (w), 1659 (s), 1356 (m), 1255 (m), 1089 (s), 906 (w), 858 (w), 810 (m), 732 (m), 686 (m), 651 (m) cm^{-1}.

(*R*)-1,1′-Binaphthyl-2,2′-disulfonyl Dichloride (8): The synthesis was based on the sulfonyl chloride formation of sulfur derivatives shown by Nishiguchi et al.[17] (*R*)-2,2′-Bis-*S*-(*N*-dimethylthiocarbamato)-1,1′-binaphthalene (**7**; 1.4 g 3 mmol) was partially dissolved in 2 M HCl(aq)/MeCN (1:5, 10 mL). After cooling to 0 °C, *N*-chlorosuccinimide (3.25 g, 24.3 mmol) was added in small portions, and the mixture became slightly green-yellow. The mixture was warmed to 10–20 °C and kept at this temperature for 30 min. During this the suspension became a solution and later a colorless solid separated. The mixture was extracted with Et_2O (2 × 15 mL), and the

organic phase was washed with brine (5 mL). After evaporating the solvent the residue was purified by column chromatography [silica gel, CH_2Cl_2, R_f(product) ≈ 0.8, first spot]. Pure product **8** was recrystallized from boiling glacial acid [solubility product: acetic acid (118 °C) ≈ 76 mg mL^{-1}, acetic acid (25 °C) ≈ 34 mg mL^{-1}] to obtain finally 1.2 g (2.66 mmol, 87%) of fine colorless needles. Crystallization by evaporation at ambient pressure from glacial acid with 5% acetic anhydride led to a different modification with crystals of better quality. M.p. 244.3 °C (ref.[15] 248–249 °C). $[\alpha]_D^{20}$ (589 nm) = –43.8 (c = 1.0, THF). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.15 [d, ^3J(H,H) = 8.5 Hz, 2 H, Ar], 7.4–7.48 (m, 2 H, Ar), 7.67–7.75 (m, 2 H, Ar), 8.06 [d, ^3J(H,H) = 8.5 Hz, 2 H, Ar], 8.23–8.35 (m, 4 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 123.4 (2 C, *C*H), 128.0 (2 C, *C*H), 128.5 (2 C, *C*H), 128.7 (2 C, *C*H), 130.2 (2 C, *C*H), 131.1 (2 C, *C*), 132.0 (2 C, *C*), 133.7 (2 C, *C*), 135.4 (2 C, *C*), 140.8 (2 C, *C*) ppm. $C_{20}H_{12}Cl_2O_4S_2$ (451.34): calcd. C 53.22, H 2.68, N 0.00; found C 53.22, H 2.67, N 0.01. IR: $\tilde{\nu}$ = 1558 (m), 1506 (m), 1375 (s), 1302 (w), 1262 (w), 1181 (s), 1022 (w), 968 (w), 869 (m), 813 (s), 744 (s), 693 (s), 677 (s), 654 (m) cm^{-1}.

(*R*)-1,1′-Binaphthyl-2,2′-bis(sulfon)amide·Et$_2$O (2): The basis for this synthesis was described by Farrar[18] and was slightly modified. Sulfonyl chloride **8** (0.18 g, 0.4 mmol) was dissolved in benzene (40 mL), stirred, and treated for 2 h with gaseous ammonia. Hereby a white slimy solid separated. After full conversion of the starting material (monitored by TLC) the benzene was removed under reduced pressure. The residue was purified twice by column chromatography on silica gel, first with MeCN/DCM (1:2) to remove trace amounts of diaminated byproduct (R_f ≈ 0.95) and to obtain the ammonia salt in pure form, and second with acidic diethyl ether (1 M HCl) to obtain BINBAM in protonated form. Herefore the ammonia salt needed to be dissolved in a small amount of hot EtOH or coated on silica. Diethyl ether was acidified with concentrated hydrochloric acid, either by saturating with HCl gas or by extracting 1 equiv. concentrated acid with 10 equiv. diethyl ether, followed by drying over $MgSO_4$ and filtration. Also, it is possible to elute first the diaminated byproduct with MeCN/DCM (1:2) and chance then the solvent without isolating the product to elute BINBAM in one column. By eluting with acidic Et_2O the product crystallized with 1 equiv. Et_2O by evaporating the solvent at ambient pressure. After drying at 20 mbar product **2** could be obtained in 91% yield (150 mg, 0.36 mmol). M.p. 113.2 °C. $[\alpha]_D^{20}$ (589 nm) = –185.5 (c = 1.0, THF). MS (ESI): m/z = 393.9. HRMS (ESI–): calcd. for $C_{20}H_{12}NO_4S_2$ (anion) 394.0203; found 394.020 (error: <2 ppm). ^{1}H NMR (600 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 1.16 [t, ^3J(H,H) = 5.5 Hz, 6 H, OCH$_2$C*H*$_3$], 3.46 [q, ^3J(H,H) = 5.5 Hz, 4 H, OC*H*$_2$CH$_3$], 6.76 [t, ^3J(H,H) = 7.3 Hz, 2 H, Ar], 7.03 [t, ^3J(H,H) = 7.3 Hz, 2 H, Ar], 7.10–7.20 (m, 2 H, Ar), 7.39 [d, ^3J(H,H) = 8.3 Hz, 2 H, Ar], 7.48 [d, ^3J(H,H) = 8.3 Hz, 2 H, Ar], 8.16 [d, ^3J(H,H) = 8.3 Hz, 2 H, Ar] (N-H, undetectable due do fast exchange) ppm. ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 1.07 [t, ^3J(H,H) = 6.3 Hz, 6 H, OCH$_2$C*H*$_3$], 3.46 [q, ^3J(H,H) = 6.3 Hz, 4 H, OC*H*$_2$CH$_3$], 7.02 [d, ^3J(H,H) = 7.3 Hz, 2 H, Ar], 7.32 [t, ^3J(H,H) = 6.3 Hz, 2 H, Ar], 7.58 [t, ^3J(H,H) = 6.3 Hz, 2 H, Ar], 8.01 [d, ^3J(H,H) = 7.6 Hz, 2 H, Ar], 8.10 [d, ^3J(H,H) = 7.6 Hz, 2 H, Ar], 8.16 [d, ^3J(H,H) = 7.6 Hz, 2 H, Ar], 10.92 (br. s, 1 H, N*H*) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 15.2 (2 C, *C*H$_3$), 64.9 (2 C, *C*H$_2$), 122.6 (2 C, *C*H), 126.8 (2 C, *C*H), 127.1 (2 C, *C*H), 127.4 (2 C, *C*H), 128.4 (2 C, *C*H), 128.7 (2 C, *C*H), 131.5 (2 C, *C*), 132.4 (2 C, *C*), 133.9 (2 C, *C*), 140.3 (2 C, *C*) ppm. $C_{24}H_{23}NO_5S_2$ (469.57): calcd. C 61.39, H 4.94, N 2.98; found C 61.07, H 4.97, N 2.90. IR: $\tilde{\nu}$ = 2971 (w), 1582 (w), 1337 (s), 1178 (s), 1135 (s), 1117 (s), 948 (w), 816 (s), 747 (m), 697 (w), 671 (m), 654 (m), 616 (m) cm^{-1}. X-ray structural data (Figure 6): $C_{24}H_{23}NO_5S_2$, formula weight 469.55 g/mol, crystal size 0.5 × 0.4 × 0.4 mm, crystal system trigonal, space group $P3_2$, unit cell dimensions a = 14.2808(4) Å, α = 90°, b = 14.2808(4) Å, β = 90°, c = 9.7038(3) Å, γ = 120°, Z = 3, $D_{calcd.}$ 1.365 Mg m^{-3}, absorption coefficient 0.269 mm^{-1}, wavelength 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 26.99°, reflections collected/unique 8487/4740 [R(int) = 0.0322], final R indices [$I > 2\sigma(I)$] R = 0.0412, wR = 0.0919, largest diff. peak and hole 0.582 and –0.331 e Å^{-3}, data collected with a Nonius Kappa CCD diffractometer, structure solved with SHELX97 and refined with SHELX97/SHELX99.

(*R*)-1,1′-Binaphthyl-2,2′-(*N*,*N*′-dibenzyl)disulfonamide (10): To a solution of sulfonyl chloride **8** (200 mg) dissolved in dry THF (40 mL) under an argon atmosphere was added benzylamine (48 μL, 0.44 mmol) by a Hamilton pipette. The solution was stirred for 72 h at room temperature with Na_2CO_3 (47.0 mg, 0.44 mmol, 1 equiv.). After evaporating the solvent, the residue was extracted with boiling CH_2Cl_2 (10 mL) and purified by column chromatography on silica gel. Starting material **8** (85 mg) could be reisolated and 90 mg of dibenzylated product **10** were obtained. M.p. 73.9 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.09 [d, ^3J(H,H) = 6.3 Hz, 4 H, NH-C*H*$_2$-C$_6$H$_5$], 4.67 [t, ^3J(H,H) = 6.3 Hz, 2 H, N*H*-CH$_2$-C$_6$H$_5$], 7.03 [d, ^3J(H,H) = 8.6 Hz, 4 H, NH-C*H*$_2$-C$_6$H$_5$], 7.11–7.20 (m, 4 H, NH-CH$_2$-C$_6$H$_5$), 7.20–7.30 (m, 6 H, NH-CH$_2$-C$_6$H$_5$, 4 H, Ar), 7.50–7.60 (m, 2 H, Ar), 7.98 [d, ^3J(H,H) = 8.2 Hz, 2 H, Ar], 8.1–8.22 (m, 4 H, Ar) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 47.4 (2 C, *C*H$_2$), 124.8 (2 C), 127.1 (2 C), 127.8 (2 C), 127.9 (4 C, Bz), 128.4 (2 C), 128.6 (4 C, Bz), 129.6 (2 C), 133.7 (2 C), 134.6 (2 C), 134.8 (2 C), 136.3 (2 C), 136.4 (2 C) ppm. ^{15}N NMR [50 MHz, $CDCl_3$, 25 °C, NH_3(l)]: δ = 102 ppm. $C_{34}H_{28}N_2O_4S_2$ (592.73): C 68.90, H 4.76, N 4.73; found C 68.66, H 5.15, N 4.64. IR: $\tilde{\nu}$ = 3275 (w), 1698 (w), 1556 (w), 1503 (m), 1453 (m), 1326 (s), 1170 (s), 1135 (m), 1060 (m), 1026 (w), 908 (m), 880 (m), 816 (m), 729 (s), 697 (s), 682 (s), 645 (m), 607 (m) cm^{-1}.

CCDC-721090 (for **6**), -721091 (for **8**), -721092 (for **8**, different polymorph), and -721093 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds **2** and **8**.

Acknowledgments

We sincerely thank the Deutsche Forschungsgemeinschaft (DFG) for funding, Prof. Dr. Hans-Günther Schmalz for giving us access to a microwave reactor, Dr. Mathias Schäfer for measuring the mass spectra, and Prof. Dr. Albrecht Berkessel for generous support throughout.

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[19] Note added in proof: While preparing the final version of this manuscript, the first application of this new class of chiral Brønsted acids was published by List: P. García-García, F. Lay, P. García-García, C. Rabalakos, B. List, *Angew. Chem.* **2009**, *121*, 4427–4430; *Angew. Chem. Int. Ed.* **2009**, *48*, 4363–4366.

Received: March 3, 2009
Revised: May 14, 2009
Published Online: June 17, 2009

