DOI: 10.1002/ejoc.201000810

Synthesis and Structural Characterization of a New Class of Strong Chiral Brønsted Acids: 1,1′-Binaphthyl-2,2′-bis(sulfuryl)imides (JINGLEs)

Albrecht Berkessel,*[a] Philipp Christ,[a] Nicolas Leconte,[a] Jörg-M. Neudörfl,[a][‡] and Mathias Schäfer[a][‡‡]

Keywords: Brønsted acids / Organocatalysis / Chirality / Sulfonamides / Biaryls

We herein present the first synthesis of 1,1′-binaphthyl-2,2′-bis(sulfuryl)imides (JINGLEs). This new class of chiral Brønsted acids was synthesized in one step from the corresponding BINOLs and imidobis(sulfuryl chloride). A total of six enantiopure 1,1′-binaphthyl-2,2′-bis(sulfuryl)imides, carrying different 3,3′-substituents, were synthesized and characterized, inter alia, by X-ray crystallography.

Introduction

Over the past decade, organocatalysis has emerged as a rapidly growing area of organic chemistry.[1] Organocatalysts are small organic molecules that do not contain (catalytically active) metals. Among those, chiral phosphoric acids play a particularly important role as efficient and selective chiral Brønsted acid catalysts.[2] In a number of cases, highly enantioselective transformations were achieved at low catalyst loading. The "first generation" of these catalysts, introduced by Akiyama[3] and Terada,[4] consist of a chiral BINOL backbone esterified with phosphoric acid (e.g., **1**; Figure 1). The introduction of bulky substituents in the 3,3′-positions proved crucial for achieving high enantioselectivities. Typically, chiral Brønsted acids of this type are being used for the activation of relatively basic substrates, such as imines.[3,4] Aiming at enhanced acidity, Yamamoto et al. introduced *N*-triflyl phosphoric amides of general structure **2** (Figure 1).[5] *N*-Triflyl phosphoric amides such as **2** allow the catalytic activation of less basic substrates, such as ketones.[6a,6b] Recently, Jacobsen and co-workers demonstrated the catalytic and inductive power of combinations of strong and achiral Brønsted acids with chiral (thio)ureas.[7]

In 2009, Giernoth et al.[8] and List et al.[9] described the synthesis of the first 1,1′-binaphthyl-2,2′-bis(sulfon)imide (**3**, "BINBAM"; Figure 1), which combines the structural elements of 1,1′-binaphthyls with those of a bis(sulfon)imide. In their synthesis, commercially available BINOL served as the starting point. The overall yield of their four-step synthesis is ca. 30%. Applying this synthetic sequence to the corresponding BINOL derivatives, List et al. were also able to prepare BINBAM catalysts carrying substituents in the 3,3′-positions.[9]

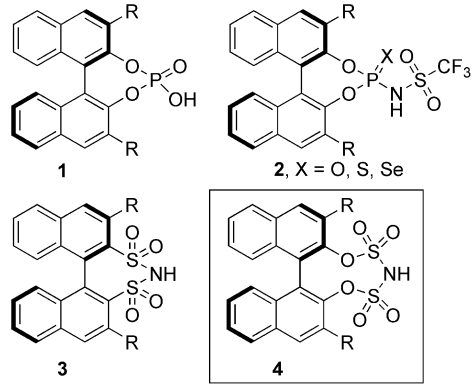


Figure 1. Chiral Brønsted acid organocatalysts, based on phosphoric esters **1**, *N*-triflyl phosphoric (thio, seleno) amides **2**, bis(sulfon)imides **3**, and bis(sulfuryl)imides **4** (this work).

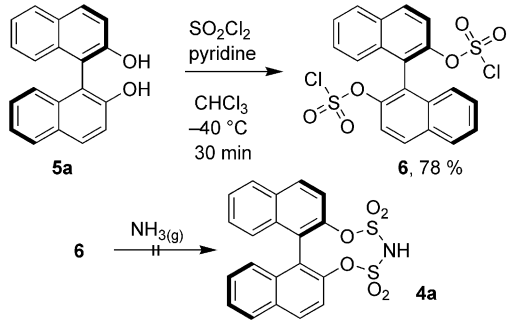
Our aim was the development of yet another class of strong chiral Brønsted acids based on BINOL. We reasoned that novel bis(sulfuryl)imides **4** − due to the fact that they are sulfuric acid derivatives − should show comparable or even increased acidity relative to bis(sulfonyl)imides **3**. In addition, the synthesis of **4** from BINOL does not require O/S exchange (by Newman–Kwart rearrangement) and no oxidative thiol/sulfonyl conversion.

Consequently, the synthesis of bis(sulfuryl)imides **4** from BINOL should require significantly less steps. We herein describe the synthesis of six representatives of this novel class of chiral Brønsted acids. In analogy to bis(sulfon)imide BINBAM (**3**), we dubbed bis(sulfuryl)imides **4** JINGLEs.

[a] University of Cologne, Chemistry Department,
Greinstraße 4, 50939 Köln, Germany
Fax: +49-221-470-5102
E-mail: berkessel@uni-koeln.de
[‡] X-ray structural analyses
[‡‡] HRMS (ESI) measurements

Results and Discussion

Our first synthetic approach towards parent JINGLE **4a** (R = H) is summarized in Scheme 1. The addition of sulfuryl chloride and pyridine to a solution of (*R*)-BINOL (**5a**) in chloroform at –40 °C smoothly afforded (*R*)-1,1′-binaphthyl-2,2′-diyl disulfochloridate (**6**). The X-ray crystal structure of **6** is shown in Figure 2. Unfortunately, treatment of intermediate **6** with gaseous ammonia did not result in the formation of (*R*)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**). Various other amines and solvents were examined, but no evidence for the formation of **4a** could be obtained. Consequently, this approach to bis(sulfuryl)-imides had to be abandoned.



Scheme 1. Sequential approach to the synthesis of (*R*)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**).

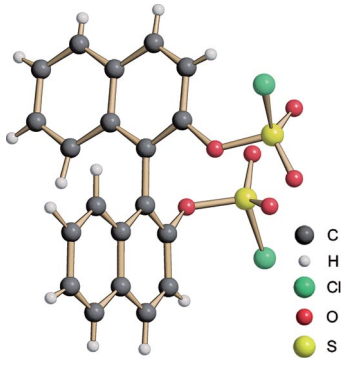
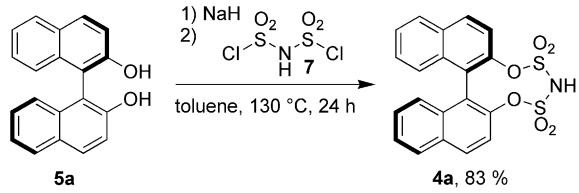


Figure 2. X-ray structure of (*R*)-1,1′-binaphthyl-2,2′-diyl disulfochloridate (**6**).

Our second, successful, and even simpler approach to the synthesis of (*R*)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**) is shown in Scheme 2. BINOL itself and a number of 3,3′-disubstituted BINOLs were readily converted into the corresponding bis(sulfuryl)imides in one single step, simply by treating the disodium salts of the BINOLs with imidobis(sulfuryl chloride) (**7**). For example, parent BINOL (**5a**, *ent*-**5a**) was efficiently converted into the bis(sulfuryl)imide (**4a**, *ent*-**4a**) in 70–80% yield. Imidobis(sulfuryl chloride) (**7**) can easily be prepared according to Beran et al. by heating amidosulfonic acid, thionyl chloride, and chlorosulfonic acid for 24 h under reflux.[10]



Scheme 2. One-step synthesis of (*R*)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**).

For the optimization of the general method, various reaction conditions were examined. The utilization of organic bases such as triethylamine and pyridine was explored, but both tend to decompose when in contact with imidobis(sulfuryl chloride) (**7**). The use of THF as solvent led to a vigorous reaction with **7**, giving a highly viscous and presumably polymeric decomposition product. Chloroform as solvent afforded the desired product in low yield, even after prolonged reaction times. The best results were achieved when (*R*)-BINOL (**5a**) was deprotonated with sodium hydride in dry toluene under an argon atmosphere, and imidobis(sulfuryl chloride) (**7**) was added slowly. The resulting sodium salt of acid **4a** was converted into free acid **4a** by passing it through a silica gel column, eluting with diethyl ether saturated with gaseous hydrogen chloride. Removal of the solvent furnished the product as a slightly yellow foam. Bis(sulfuryl)imide **4a** is soluble in halogenated solvents such as DCM and chloroform, as well as in aromatic solvents like benzene and toluene, and in both DMSO and water.

For future catalytic experiments, we synthesized six different 1,1′-binaphthyl-2,2′-bis(sulfuryl)imides **4**. Besides enantiomers **4a** and *ent*-**4a** derived from (*R*)-/(*S*)-BINOL (**5a**, *ent*-**5a**), respectively, we prepared the bis(sulfuryl)-imides derived from (*S*)-3,3′-dimethyl-1,1′-binaphthyl-2,2′-diol (*ent*-**5b**), (*S*)-3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diol (*ent*-**5c**), (*R*)-3,3′-bis(2-naphthyl)-1,1′-binaphthyl-2,2′-diol (**5d**), and (*R*)-H_8-1,1′-binaphthyl-2,2′-diol (**5e**). All 3,3′-disubstituted 1,1′-binaphthyl-2,2′-diols mentioned were synthesized according to known procedures.[11–14] The structures and yields of the bis(sulfuryl)-imides obtained are summarized in Figure 3.

Besides X-ray crystallography (see below), MS (ESI) proved to be an excellent method for the detection and characterization of JINGLEs **4**. All mass spectra were taken in the negative polarity mode and confirmed the elemental composition of substances **4a**–**e**.

For X-ray crystallographic characterization, we converted 1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**) into imidazolium salt **8**. The latter was crystallized from methanol. Under the crystallization conditions used, two different types of crystals formed (monoclinic and orthorhombic). The results of both X-ray structural analyses are shown in Figures 4 and 5. Interestingly, the two crystal types show different hydrogen-bonding modes of the bis(sulfuryl)imide anion present in salt **8**.

Both solid-state structures result from endless hydrogen-bonded aggregates of methanol–bis(sulfuryl)imide anion–imidazolium cation. In the monoclinic crystal modification

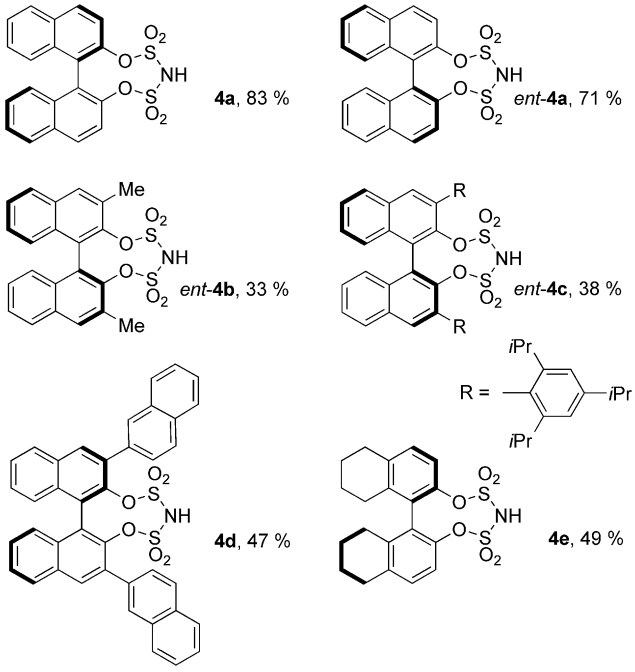


Figure 3. Structures and yields of bis(sulfuryl)imides **4a**–**e**.

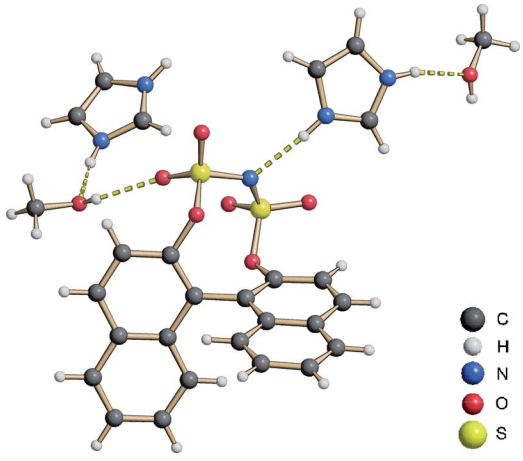


Figure 4. X-ray structure of **8** (monoclinic crystals), showing H-bond networks involving both the N and O atoms of **4a**-H$^+$, the imidazolium cation, and methanol.

(Figure 4), there is a hydrogen bond between the methanol OH group and one of the oxygen atoms of the bis(sulfuryl)-imide anion. A second hydrogen bond exists between the N atom of the bis(sulfuryl)imide anion and the imidazolium cation [d = 2.00(2) Å; d_{NN} = 2.856(4) Å, ∢ = 164(3)°]. In the orthorhombic crystal modification (Figure 5), the hydrogen bonding of the bis(sulfuryl)imide anion occurs exclusively through its oxygen atoms. For example, the length of the hydrogen bond to the imidazolium cation is 1.93(4) Å [d_{NO} = 2.770(4) Å, ∢ = 165(4)°]. The observation of hydrogen bonding to both the O and N atoms of the bis(sulfuryl) imide anion in **8** indicates significant electron density on

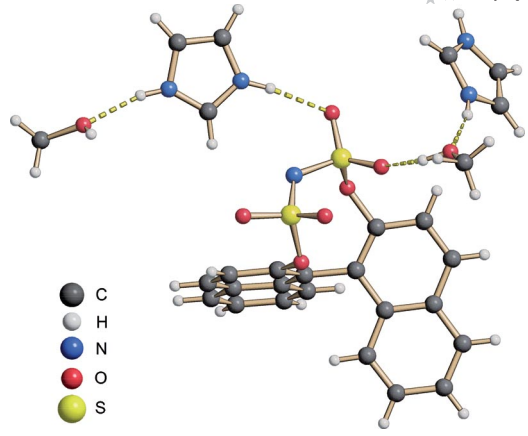


Figure 5. X-ray structure of **8** (orthorhombic crystals), showing H-bond networks, involving the O atoms of **4a**-H$^+$, the imidazolium cation, and methanol.

both atom types. Similarly, metal coordination by oxygen atoms of the Tf_2N^- anion was observed in a Yb^{II} complex.[15]

Similarly, we were able to crystallize (*R*)-H_8-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4e**) as imidazolium salt **9**. The X-ray structure (Figure 6) reveals the presence of stoichiometric (1 equiv.) solvent, that is, acetonitrile, which was used for crystallization. Once again, there is a hydrogen-bonding interaction between the nitrogen atom of the bis(sulfuryl)imide anion and one of the NH groups of the imidazolium cation. This hydrogen bond is not shown in Figure 6, as the determination of its precise geometry proved difficult due to disorder of the imidazolium ion in the crystal.

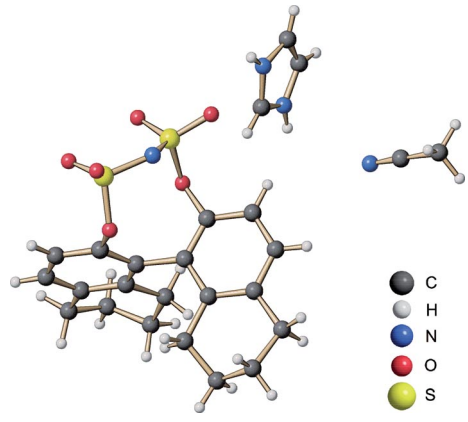


Figure 6. X-ray structure of imidazolium salt **9**.

In the case of *ent*-**4b**, we were able to crystallize the "native", protonated form of the bis(sulfuryl)imide. The X-ray crystal structure of (*S*)-3,3′-dimethyl-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (*ent*-**4b**) is shown in Figure 7. This structure nicely reflects the orthogonal arrangement of the two naphthyl moieties and the protrusion of one of the methyl groups present in the 3′-position of the molecule.

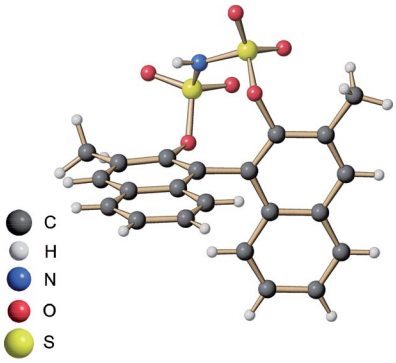


Figure 7. X-ray crystal structure of (*S*)-3,3′-dimethyl-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (*ent*-**4b**).

Conclusions

We have established a versatile one-step synthesis for a new class of chiral, enantiopure Brønsted-acids, namely, 1,1′-binaphthyl-2,2′-bis(sulfuryl)imides (JINGLEs). Readily available (*R*)-/(*S*)-BINOL or 3,3′-disubstituted derivatives thereof served as the starting materials. X-ray crystal structures confirmed the constitution of these new entities, together with their acidic character (salt formation). Furthermore, the modes of hydrogen bonding found in the salts derived from the bis(sulfuryl)imides point to considerable charge density on both the O and the N atoms of the anions. Future studies in our laboratory will be devoted to potential applications of this new class of chiral Brønsted acids/chiral anions.

Experimental Section

General Remarks: All chemicals were purchased from commercial sources and used without further purification. Solvents were dried according to general procedures.[16] TLC aluminum sheets were from Macherey–Nagel, coated with 0.2 mm silica and containing a fluorescent indicator. Spots were visualized by UV light. Flash chromatography was performed on silica gel (Acros Silicagel, 0.035–0.070 mm, 60 Å). ^{1}H and ^{13}C NMR spectra were measured with a DPX 300 spectrometer (Bruker) at ambient temperature and are referenced to the solvent used. Melting points were determined with a Büchi apparatus. IR spectra were measured with a Shimadzu IRAffinity-1 instrument. Optical rotations were measured with a Perkin–Elmer 343 Plus polarimeter.

HRMS (ESI): Exact ion mass measurements were conducted with an LTQ Orbitrap XL hybrid FTMS Mass Spectrometer (ThermoFisher, Bremen, Germany) equipped with an electrospray ion source (ThermoFisher). Optimized electrospray (ESI) conditions: negative spray voltage: 3.0 kV; transfer capillary temperature: 275 °C; sheath and sweep gas: nitrogen; flow rate: 3 μL min^{-1}. Mass accuracy of the linear ion trap LTQ and the Orbitrap FTMS analyzer were both freshly calibrated prior to the exact ion mass determination experiments by standard procedures. The resolution of the Orbitrap FTMS Analyzer was ≥60000 (FWHM). All exact ion mass measurements were conducted with negative ESI polarity and were repeated three times, each in full scan mode and in SIM mode. The taurocholate sulfate anion was used as reference ion for internal standardization. For that purpose, a methanol stock solution of sodium taurocholate ($NaC_{26}H_{44}NSO_7$) was prepared (conc. 10^{-6} M). All compounds and solvents were used as purchased (Sigma Aldrich, Hamburg, Germany). For exact ion mass measurements with internal calibration, a small aliquot of the reference compound stock solution was added to the respective sample solution prior to negative MS (ESI) measurements; the $[C_{26}H_{44}NSO_7]^-$ reference ion at m/z = 514.28329 was used as internal lock mass.

X-ray Crystallography: All crystal structure data were collected with a Nonius Kappa CCD diffractometer at the temperatures stated below. The structures were solved by using SHELXS97 and refined with SHELXL97.

(*R*)-1,1′-Binaphthyl-2,2′-diyl Disulfochloridate (6): To a solution of (*R*)-BINOL (**5a**; 0.5 g, 1.74 mmol) in dry chloroform (5 mL) was added pyridine (0.28 g, 3.5 mmol). After cooling to –40 °C under an argon atmosphere, sulfuryl chloride (0.28 mL, 3.5 mmol) in dry chloroform (5 mL) was added. The solution was stirred at this temperature for 30 min and then 60 min at room temperature. DCM (20 mL) was added, and the solution was washed with water and brine. The organic phase was dried with sodium sulfate, and the solvent was removed under reduced pressure. The remaining solid was recrystallized from ethanol to yield colorless crystals (0.74 g, 1.5 mmol, 88%). M.p. 133 °C. $[\alpha]_D^{20}$ = –225.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (d, ^3J = 8.5 Hz, 2 H, Ar), 7.39 (dt, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 2 H, Ar), 7.58 (dt, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 2 H, Ar), 7.86 (d, ^3J = 9.1 Hz, 2 H, Ar), 8.00 (d, ^3J = 8.4 Hz, 2 H, Ar), 8.16 (d, ^3J = 9.1 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 119.2, 123.2, 127.1, 127.3, 127.9, 128.4, 131.9, 132.4, 133.1, 146.4 ppm. $C_{20}H_{12}Cl_2O_6S_2$ (483.34): calcd. C 49.70, H 2.50; found C 49.71, H 2.55. IR: $\tilde{\nu}$ = 2359 (w), 1508 (m), 1408 (s), 1198 (m), 1169 (s), 1065 (m), 959 (s), 939 (s), 822 (s), 810 (s), 745 (m), 706 (m) cm^{-1}. X-ray structural data: $C_{20}H_{12}Cl_2O_6S_2$, formula weight 483.32 g mol^{-1}, crystal size 0.4 × 0.3 × 0.3 mm, crystal system monoclinic, space group $P2_1$, unit cell dimensions a = 8.4527(5) Å, b = 23.4305(8) Å, c = 10.4435(6) Å, β = 104.293(2)°, Z = 4, $D_{calcd.}$ 1.602 Mg m^{-3}, absorption coefficient 0.569 mm^{-1}, wavelength 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 26.99°, reflections collected/unique 7826/7826, final R indices [$I > 2\sigma(I)$] R = 0.0435, wR = 0.0873, largest diff. peak and hole 0.472 and –0.442 e Å^{-3}.

Imidobis(sulfuryl chloride) (7): This reagent was prepared according to Beran et al.[10] Amidosulfonic acid (24.3 g, 0.25 mol), thionyl chloride (50 mL, 0.69 mol), and chlorosulfonic acid (16.5 mL, 0.25 mol) were heated under reflux for 24 h under exclusion of moisture. The product was fractionally distilled at 5.5 × 10^{-1} mbar. In the temperature interval 75–77 °C, a colorless oil (47.76 g, 223 mmol, 89%) was collected, which crystallized immediately upon cooling to room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.33 (s, 1 H, NH) ppm.

General Procedure for the Preparation of 1,1′-Binaphthyl-2,2′-bis(sulfuryl)imides 4 (JINGLEs): To a stirred solution of BINOL or its derivatives (**5**, 1.74 mmol, 1 equiv.) in dry toluene (20 mL) was added sodium hydride (60% in mineral oil, 5.48 mmol, 3.15 equiv.) under an argon atmosphere. The suspension was heated to 130 °C, and imidobis(sulfuryl chloride) (**7**; 428 mg, 2.00 mmol, 1.15 equiv.) in dry toluene (10 mL) was added over a period of 30 min. The solution was stirred at 130 °C for 24 h. After cooling, the solution was poured into water (10 mL), and all volatile components were removed under reduced pressure. The greenish, semisolid residue was purified by column chromatography on silica gel (DCM/MeOH, 10:1). The resulting solid was passed

through a second silica gel column (eluting with diethyl ether saturated with gaseous HCl). Protonated bis(sulfuryl)imides **4** (JINGLEs) were obtained after removal of the eluent under reduced pressure.

(*R*)-1,1′-Binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (4a): Yield: 649 mg (1.4 mmol, 83%), yellowish foam, m.p. 129–131 °C (dec.). $[a]_D^{20}$ = –129.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 6.85 (d, ^3J = 6.5 Hz, 2 H, Ar), 7.18 (t, ^3J = 7.0 Hz, 2 H, Ar), 7.40 (t, ^3J = 8.1 Hz, 2 H, Ar), 7.73 (d, ^3J = 9.0 Hz, 2 H, Ar), 7.93 (d, ^3J = 8.1 Hz, 2 H, Ar), 8.01 (d, ^3J = 9.0 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 123.4, 125.8, 126.9, 127.0, 127.9, 129.3, 131.0, 133.3, 134.7, 149.3 ppm. $C_{20}H_{13}NO_6S_2$·1/2Et$_2$O (464.51): calcd. C 56.88, H 3.91, N 3.02; found C 56.79, H 3.70, N 3.19. HRMS (ESI–): calcd. for $C_{20}H_{12}NO_6S_2$ (anion) 426.01005; found 426.01020 (error <1 ppm). IR: $\tilde{\nu}$ = 2361 (w), 1242 (w), 1425 (m), 1200 (m), 1175 (s), 1067 (m), 957 (s), 872 (m), 818 (s) 694 (s) cm^{-1}.

(*S*)-1,1′-Binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (*ent*-4a): Yield: 556 mg (1.2 mmol, 71%), yellowish foam, m.p. 129–131 °C (dec.). $[a]_D^{20}$ = +136.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 6.85 (d, ^3J = 6.5 Hz, 2 H, Ar), 7.18 (t, ^3J = 7.0 Hz, 2 H, Ar), 7.40 (t, ^3J = 8.1 Hz, 2 H, Ar), 7.73 (d, ^3J = 9.0 Hz, 2 H, Ar), 7.93 (d, ^3J = 8.1 Hz, 2 H, Ar), 8.01 (d, ^3J = 9.0 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 123.4, 125.8, 126.9, 127.0, 127.9, 129.3, 131.0, 133.3, 134.7, 149.3 ppm. $C_{20}H_{13}NO_6S_2$·1/2Et$_2$O (464.51): calcd. C 56.88, H 3.91, N 3.02; found C 56.72, H 3.67, N 3.07. HRMS (ESI–): calcd. for $C_{20}H_{12}NO_6S_2$ (anion) 426.01005; found 426.01020 (error <1 ppm). IR: $\tilde{\nu}$ = 2361 (w), 1242 (w), 1425 (m), 1200 (m), 1175 (s), 1067 (m), 957 (s), 872 (m), 818 (s) 694 (s) cm^{-1}.

(*S*)-3,3′-Dimethyl-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (*ent*-4b): Yield: 127 mg (0.26 mmol, 33%), greenish foam, m.p. 197–198 °C (dec.). $[a]_D^{20}$ = +9.4 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 2.60 (s, 6 H, CH_3), 6.64 (d, ^3J = 8.5 Hz, 2 H, Ar), 7.07 (t, ^3J = 7.2 Hz, 2 H, Ar), 7.31 (t, ^3J = 7.1 Hz, 2 H, Ar), 7.78 (d, ^3J = 8.2 Hz, 2 H, Ar), 7.82 (s, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 18.4, 126.4, 126.9, 127.0, 128.4, 130.6, 131.6, 132.8, 133.6, 133.7, 149.3 ppm. HRMS (ESI–): calcd. for $C_{22}H_{16}NO_6S_2$ (anion) 454.04136; found 454.04132 (error <1 ppm). IR: $\tilde{\nu}$ = 3144 (w), 1499 (w), 1429 (s), 1221 (m), 1200 (m), 1184 (s), 1167 (s), 1090 (m), 920 (s), 893 (m), 750 (s) cm^{-1}. X-ray structural data: $C_{23}H_{18}Cl_3NO_6S_2$, formula weight 574.85 g mol^{-1}, crystal size 0.3 × 0.15 × 0.05 mm, crystal system monoclinic, space group $P2_1$, unit cell dimensions *a* = 11.0224(10) Å, *b* = 8.5386(5) Å, *c* = 13.6770(10) Å, β = 112.988(3)°, *Z* = 2, $D_{calcd.}$ 1.611 Mg m^{-3}, absorption coefficient 0.606 mm^{-1}, wavelength 0.71072 Å, *T* = 100(2) K, $2\theta_{max}$ = 27.00°, reflections collected/unique 6292/4846 [*R*(int) = 0. 0286], final *R* indices [$I > 2\sigma(I)$] *R* = 0.0461, *wR* = 0.0868, largest diff. peak and hole 0.324 and –0.444 e Å^{-3}.

(*S*)-3,3′-Bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (*ent*-4c): Yield: 243 mg (0.28 mmol, 38%), greenish foam, m.p. 162 °C (dec.). $[a]_D^{20}$ = +25.5 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, MeOD, 25 °C): δ = 0.76–1.34 [m, 34 H, $CH(CH_3)_2$], 2.64–3.03 [m, 4 H, $CH(CH_3)_2$], 3.24–3.28 [m, 4 H, $CH(CH_3)_2$], 6.95–7.30 (m, 8 H, Ar), 7.32–7.42 (m, 2 H, Ar), 7.51–7.76 (m, 2 H, Ar), 7.83–7.93 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 14.1, 20.2, 21.5, 22.0, 22.9, 23.2, 24.2, 119.2, 120.8, 121.3, 126.5, 127.6, 129.5, 130.8, 131.6, 131.9, 132.5, 132.7, 132.9, 135.7, 145.2, 145.8, 147.7 ppm. HRMS (ESI–): calcd. for $C_{50}H_{56}NO_6S_2$ (anion) 830.35436; found 830.35243 (error <2.5 ppm). IR: $\tilde{\nu}$ = 2961 (m), 2870 (w), 1412 (m), 1383 (m), 1171 (s), 1146 (m), 966 (w), 849 (s), 825 (s), 800 (s), 750 (s) cm^{-1}.

(*R*)-3,3′-Bis(2-naphthyl)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (4d): Yield: 150 mg (0.21 mmol, 47%), greenish foam, m.p. 209–211 °C (dec.). $[a]_D^{20}$ = +72.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 7.08 (d, ^3J = 8.3 Hz, 2 H, Ar), 7.31 (t, ^3J = 7.5 Hz, 2 H, Ar), 7.38–7.49 (m, 6 H, Ar), 7.78–7.87 (m, 8 H, Ar), 7.99–8.02 (m, 2 H, Ar), 8.15–8.18 (m, 4 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 126.4, 126.9, 127.6, 128.2, 128.5, 128.6, 129.1, 129.2, 129.4, 129.5, 129.6, 132.8, 133.8, 134.1, 134.3, 135.0, 137.1, 137.8, 147.3 ppm. HRMS (ESI–): calcd. for $C_{40}H_{24}NO_6S_2$ (anion) 678.10396; found: 678.10288 (error <2.5 ppm). IR: $\tilde{\nu}$ = 1974 (w), 1429 (s), 1188 (m), 1174 (s), 894 (s), 854 (m), 817 (m), 794 (s), 742 (s) cm^{-1}.

(*R*)-*H*$_8$-1,1′-Binaphthyl-2,2′-bis(sulfuryl)imide·1/2Et$_2$O (4e): Yield: 396 mg (0.84 mmol, 49%), yellowish foam, m.p. 116–118 °C (dec.). $[a]_D^{20}$ = –118.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 1.53–1.65 (m, 8 H, CH_2), 2.01 (t, ^3J = 6.0 Hz, 4 H, CH_2), 2.71 (t, ^3J = 6.0 Hz, 4 H, CH_2), 7.03 (d, ^3J = 8.6 Hz, 2 H, Ar), 7.13 (d, ^3J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 23.9, 24.0, 28.3, 30.5, 121.5, 130.5, 130.8, 137.3, 137.7, 148.0 ppm. $C_{20}H_{21}NO_6S_2$·1/2Et$_2$O (475.57): calcd. C 55.91, H 5.55, N 2.96; found C 55.60, H 5.59, N 2.94. HRMS (ESI–): calcd. for $C_{20}H_{20}NO_6S_2$ (anion) 434.07266; found 434.07276 (error <1 ppm). IR: $\tilde{\nu}$ = 2934 (w), 1425 (s), 1188 (s), 1175 (s), 1051 (w), 943 (s), 866 (s), 816 (m), 712 (m) cm^{-1}.

Imidazolium (*R*)-1,1′-Binaphthyl-2,2′-bis(sulfuryl)imidate (8): To a solution of (*R*)-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4a**; 50 mg, 0.12 mmol) in dry DCM (2 mL) was added imidazole (10.5 mg, 0.15 mmol). A precipitate formed instantaneously, which was filtered off and recrystallized from methanol to yield colorless crystals (63 mg, 0.12 mmol, quant.). M.p. 255–258 °C (dec.). $[a]_D^{20}$ = +105.0 (*c* = 0.9, MeOH). ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 6.86 (d, ^3J = 8.5 Hz, 2 H, Ar), 7.20 (t, ^3J = 7.3 Hz, 2 H, Ar), 7.39–7.44 (m, 4 H, Ar), 7.74 (d, ^3J = 9.0 Hz, 2 H, Ar), 7.93 (d, ^3J = 8.2 Hz, 2 H, Ar), 8.01 (d, ^3J = 9.0 Hz, 2 H, Ar), 8.64 (s, 1 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 105.2, 120.6, 123.4, 125.8, 127.0, 127.9, 129.3, 131.0, 133.3, 134.7, 144.7, 149.3 ppm. $C_{24}H_{21}N_3O_7S_2$ (527.57): calcd. C 54.64, H 4.01, N 7.96; found C 54.50, H 4.01, N 7.87. IR: $\tilde{\nu}$ = 3155 (w), 2361 (s), 2342 (s), 1346 (m), 1173 (m), 1142 (m), 1069 (w), 957 (m), 835 (m), 689 (m) cm^{-1}. The crystals obtained from methanol consisted of both monoclinic and orthorhombic crystals. X-ray structural data of the monoclinic modification (Figure 4): $C_{24}H_{21}N_3O_7S_2$, formula weight 527.56 g mol^{-1}, crystal size 0.3 × 0.3 × 0.2 mm, space group $P2_1$, unit cell dimensions *a* = 9.6138(8) Å, *b* = 11.0950(8) Å, *c* = 11.0986(8) Å, β = 99.232(4)°, *Z* = 2, $D_{calcd.}$ 1.499 Mg m^{-3}, absorption coefficient 0.281 mm^{-1}, wavelength 0.71073 Å, *T* = 100(2) K, $2\theta_{max}$ = 27.00°, reflections collected/unique 5635/4597 [*R*(int) = 0.0212], final *R* indices [$I > 2\sigma(I)$] *R* = 0.0422, *wR* = 0.0848, largest diff. peak and hole 0.504 and –0.437 e Å^{-3}. X-ray structural data of the orthorhombic modification (Figure 5): $C_{24}H_{21}N_3O_7S_2$, formula weight 527.56 g mol^{-1}, crystal size 0.3 × 0.3 × 0.2 mm, space group $P2_12_12_1$, unit cell dimensions *a* = 9.3341(4) Å, *b* = 10.4322(7) Å, *c* = 23.648(2) Å, *Z* = 4, $D_{calcd.}$ 1.522 Mg m^{-3}, absorption coefficient 0.285 mm^{-1}, wavelength 0.71073 Å, *T* = 100(2) K, $2\theta_{max}$ = 27.00°, reflections collected/unique 4896/4896, final *R* indices [$I > 2\sigma(I)$] *R* = 0.0535, *wR* = 0.1115, largest diff. peak and hole 0.362 and –0.413 e Å^{-3}.

Imidazolium (*R*)-*H*$_8$-1,1′-Binaphthyl-2,2′-bis(sulfuryl)imidate (9): To a solution of (*R*)-*H*$_8$-1,1′-binaphthyl-2,2′-bis(sulfuryl)imide (**4e**; 50 mg, 0.11 mmol) in dry DCM (2 mL) was added imidazole (10.5 mg, 0.15 mmol). A precipitate formed instantaneously, which was filtered off and recrystallized from acetonitrile to yield color-

less crystals (60 mg, 0.11 mmol, quant.). M.p. 155 °C (dec.). $[a]_D^{20}$ = –86.1 (c = 0.9, MeOH).^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 1.57–1.75 (m, 8 H, CH_2), 2.08 (t, ^3J = 6.0 Hz, 4 H, CH_2), 2.76 (t, ^3J = 6.0 Hz, 4 H, CH_2), 7.06 (d, ^3J = 8.4 Hz, 2 H, Ar), 7.28 (d, ^3J = 8.4 Hz, 2 H, Ar), 7.43 (s, 2 H, Ar), 8.63 (s, 1 H, Ar) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 23.9, 24.0, 28.3, 30.5, 120.8, 121.6, 130.6, 130.8, 136.9, 137.5, 145.7, 148.2 ppm. IR: $\tilde{\nu}$ = 3155 (w), 2361 (s), 2342 (s), 1340 (m), 1177 (m), 1146 (m), 943 (m) cm^{-1}. X-ray structural data: $C_{25}H_{28}N_4O_6S_2$, formula weight 544.63 g mol^{-1}, crystal size 0.2 × 0.15 × 0.07 mm, crystal system monoclinic, space group $P2_1$, unit cell dimensions a = 8.0333(3) Å, b = 12.6871(10) Å, c = 12.440(8) Å, β = 94.563(4)°, Z = 2, $D_{calcd.}$ 1.431 Mg m^{-3}, absorption coefficient 0.260 mm^{-1}, wavelength 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 27.00°, reflections collected/unique 6580/4795 [R(int) = 0.0274], final R indices [$I > 2\sigma(I)$] R = 0.0407, wR = 0.0836, largest diff. peak and hole 0.496 and –0.321 e Å^{-3}.

CCDC-776581 (for **6**), -776582 (for **8**, monoclinic), -776583 (for **8**, orthorhombic), -776584 (for *ent*-**4b**), and -776585 (for **9**) 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.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SPP 1179, "Organocatalysis"). P.C. thanks the Fonds der Chemischen Industrie for a Kekulé fellowship.

[1] a) A. Berkessel, H. Gröger, *Asymmetric Organocatalysis: From Biomimetic Concepts to Applications in Asymmetric Synthesis*, Wiley-VCH, Weinheim, **2005**; b) P. I. Dalko (Ed.), *Enantioselective Organocatalysis: Reactions and Experimental Procedures*, Wiley-VCH, Weinheim, **2007**; c) special issue on organocatalysis: B. List (Ed.), *Chem. Rev.* **2007**, *107*, 5413–5883.
[2] T. Akiyama, *Chem. Rev.* **2007**, *107*, 5744–5758.
[3] T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe, *Angew. Chem. Int. Ed.* **2004**, *43*, 1566–1568.
[4] D. Uraguchi, M. Terada, *J. Am. Chem. Soc.* **2004**, *126*, 5356–5357.
[5] a) D. Nakashima, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 9626–9627; b) C. H. Cheon, H. Yamamoto, *J. Am. Chem. Soc.* **2008**, *130*, 9246–9247; c) C. H. Cheon, H. Yamamoto, *Org. Lett.* **2010**, *12*, 2476–2479.
[6] a) M. Rueping, W. Ieawsuwan, A. P. Antonchick, B. J. Nachtsheim, *Angew. Chem. Int. Ed.* **2007**, *46*, 2097–2100; b) P. Jiao, D. Nakashima, H. Yamamoto, *Angew. Chem. Int. Ed.* **2008**, *47*, 2411–2413.
[7] H. Xu, S. J. Zuend, M. G. Woll, Y. Tao, E. N. Jacobsen, *Science* **2010**, *327*, 986–990.
[8] M. Treskow, J. Neudörfl, R. Giernoth, *Eur. J. Org. Chem.* **2009**, 3693–3697.
[9] P. García-García, F. Lay, P. García-García, C. Rabalakos, B. List, *Angew. Chem. Int. Ed.* **2009**, *48*, 4363–4366.
[10] M. Beran, J. Příhoda, *Z. Anorg. Allg. Chem.* **2005**, *631*, 55–59.
[11] K. B. Simonsen, K. V. Gothelf, K. A. Jørgensen, *J. Org. Chem.* **1998**, *63*, 7536–7538.
[12] A. Korostylev, V. Tararov, C. Fischer, A. Monsees, A. Börner, *J. Org. Chem.* **2004**, *69*, 3220–3221.
[13] L. A. Arnold, R. Imbos, A. Mandolino, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865–2878.
[14] S. S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davis, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 8251–8259.
[15] A.-V. Mudring, A. Babai, S. Arenz, R. Giernoth, *Angew. Chem.* **2005**, *117*, 5621–5624.
[16] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth Heinemann, Burlington, **2003**.

Please note: Minor changes have been made to this manuscript Since its publication in the *European Journal of Organic Chemistry* Early View.

The Editor

Received: June 6, 2010
Published Online: August 17, 2010

