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Practical and General Entry to *N*-Tosyl Aryl Aldimines Promoted by Sulfamic Acid in Water and Alcohol

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Abstract: A practical, indirect procedure composed of a three-component condensation using aromatic aldehydes, *p*-tosylamide, and sodium *p*-toluenesulfinate in the presence of sulfamic acid in tap water–alcohol solvents to afford amidosulfones, and the subsequent water two-phase basic elimination of the amidosulfones to *N*-tosyl arylimines, was developed. The process has little environmental impact, easy workup, mild reaction conditions, and good yields and is amenable to large-scale preparations.

Keywords: aqueous solvent, condensation, sulfamic acid, sulfonamide, sulfonyl imines

In view of the tremendous versatility of the C═N double bond of imines and imine derivatives in their use in recent organic synthesis,[1] especially the employment of imines in stereoselective reactions,[2] many preparative approaches to *N*-substituted imines have been devised.[3] Sulfonyl imine is one of the few kinds of imines bearing electron-withdrawing *N*-substitutions[4] with appropriate electrophilicity and enough stability to undergo addition reactions. Direct and indirect synthetic routes and various approaches from aldehydes/ketones or their equivalents toward *N*-sulfonyl imines have been

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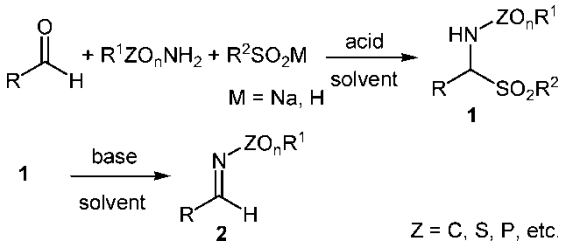
developed.[5] However, there exist some obvious drawbacks in the published methods, such as the difficulties of heat-sensitive aldehydes to undergo direct condensation at elevated temperature, the tendency of many carbonyls in the strong Lewis acid or Brønsted acid catalysis to enolize, the incompatibility of some functional groups with the harsh reaction conditions, the inconvenience of employing unusual apparatus and using special and expensive reagents, and especially the use of hazardous solvents and the tedious purifications. In the course of our work on asymmetric synthesis of special amino acids,[6] we needed to prepare arrays of *N*-substituted imines of diversity structures. α-Amido sulfones[7] emerged recently as versatile and powerful precursors to *N*-activated imines formed in situ or separated as stable intermediates. In the latter category, a two-step approach[8] consisting of the preparation of amidosulfones by a three-component condensation of aldehydes, amides, and sulfinic acid, and the subsequent basic elimination of sulfinate from the intermediate amidosulfones to afford *N*-substituted imines, appeared to be a feasible one. Nevertheless, the scope of the preparations was limited; some aspects of the process needed to be improved, such as the choice of more efficient acid and use of environmentally friendly solvents. Practical, simple, green, and large-scale preparations to *N*-sulfonylimines were our main focus.

Using water or aqueous media for green, sustainable organic synthesis has attracted much attention in the past decade.[9] The research and development of nonhazardous alternatives to conventional organic solvents posed a challenge for academia, industrial, and regulatory bodies.[10] Because of the limited solubility and compatibility of organic compounds in water,[11] performing organic reactions in neat water is not always feasible. Because aqueous media has a lot to be recommended in green chemical preparations, water-mixture solvents and aqueous two-phase systems are highly preferred.[12] Thus employment of tap water as reaction media was another purpose of ours.

Most recently, sulfamic acid has been widely used as a solid catalyst in many organic reactions.[13] It has many prominent properties[14]: it is moderately acidic, nonvolatile, noncorrosive, insoluble in common organic solvents, inexpensive, and readily available and has outstanding physical stability. In contrast to its various applications as a cost-effective Lewis acid catalyst, sulfamic acid was rarely used as a Brønsted acid in current organic synthesis to the best of our knowledge.

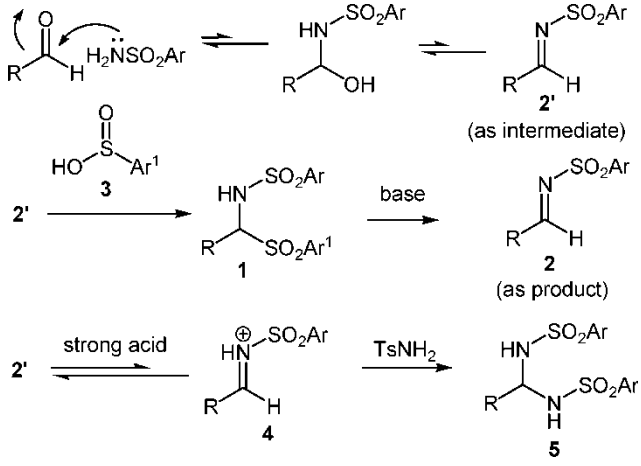
Based on the seminal work of Strating's group[15] on preparation of amidosulfones (compound **1**, Scheme 1) by a three-component condensation involving aldehydes, amide, and sodium sulfinate in acidic solvent and the remarkable jobs of Chemla et al.[8f] and others[8a–d] on the basic elimination of the amidosulfones **1** to afford imines **2**, and in light of these considerations on the two aspects in acid choice and solvent selection, we have first reported a preliminary investigation on a two-step synthetic route to *N*-sulfonyl imines mediated by sulfamic acid in aqueous media.[16] However, the previous



Scheme 1.

communication was focused on green aspects of the process; several types of aldehydes including α,β-unsaturated aliphatic aldehydes, hetero-aromatic aldehydes, and most important, the benzaldehydes bearing electron-donating substitutions remained elusive in the preparations. In continuation of our work in this regard, expanded investigations on the scope and limitation of an array of substituted benzaldehydes in different aqueous media at varied temperatures were carried out.

The screening of an appropriate Brønsted acid was the key in this preparation. Because the precedent methods in the three-component condensations used formic acid (pK_a 3.77) or acetic acid (pK_a 4.76) as proton source and solvent or cosolvent, and the acidity of the sulfinic acid is stronger (pK_a 2.1) than that of the carboxylic acids, the reaction proceeded sluggishly as a result of the low concentration of the active sulfinic acid **3** (Scheme 2) and its partial decomposition in the case of elevated temperature. A catalytic amount of camphorsulfonic acid (pK_a − 2.6) had been employed in one



Scheme 2. Plausible mechanism of the trapping of the intermediate imine **2′** with sulfinic acid **3** and the formation of the undesired *bis*-amide **5**.

occasion,[8e] unfortunately the intermediate **2′** was protonated by the strong acid to afford iminum ion **4**, which was added preferably by sulfonylamide to irreversibly produce the by-product *bis*-amide **5**. Ordinarily, sulfonylimine as intermediate **2′** was formed at quite a low level in the mixture. Sulfinic acid **3** may trap it to form amidosulfone **1** within a favorable pH window. In this context, neither carboxylic acid nor sulfonic acid was ideal for this addition step. In searching for an appropriate acid, sulfamic acid caught our attention because of its moderate acidity[17] (pK_a 1.0) and unique structure.[18] Although free arenesulfinic acid was used in this condensation,[8d,e] the acid decomposed readily on storage and had to be prepared carefully on the spot. Sulfamic acid as a moderate acid produces sulfinic acid in situ, keeps its concentration at a reasonable level, and avoids the possible iminum ion **4** and *bis*-amide **5** formations.

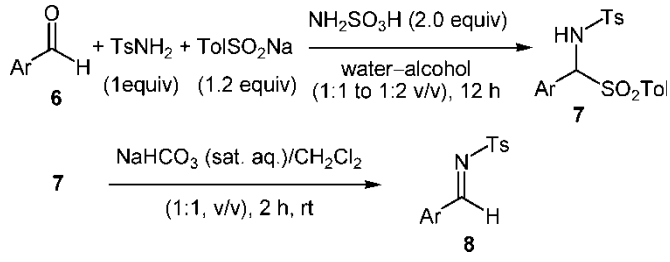
Selection of aqueous solvents was carried out in various aqueous systems (see Table 1). In water-miscible ones, combinations of acetonitrile–water, dioxane–water, DMF–water, DMSO–water, ethanol–water, methanol–water, and *i*-propanol–water were tried and showed promising effects on the condensations. Two-phase water systems composed of water/CH_2Cl_2 and water/dichloroethane were tested without success. Pure water as solvent was excluded because most aldehydes used in the preparation and all amidosulfones **7** formed were not soluble in it. Finally, water–methanol and water–ethanol were chosen for their good performance, benign environmental influence,[12] economy, and adjustability of solvent strength, tunable for different aldehydes. Sulfonamidosulfones **7** (see Scheme 3) precipitated from water–alcohol and pulled the condensations to completion.

More than half of the preparations ran smoothly at ambient temperature, yet several unexpected results were observed as the temperature dropped around 0°C or rose above 35°C in winter or summer, Reaction of piperonal

Table 1. Three-component condensations mediated by NH_2SO_3H[a]

Entry	Solvent (ratio by volume)	Time (h)	Yield (wt %)
1	$CH_3CN–H_2O$ (1 : 1)	24	35
2	Dioxane–H_2O (1 : 1)	24	47
3	DMF–H_2O (1 : 1)	24	29
4	DMSO–H_2O (1 : 1)	24	54
5	EtOH–H_2O (1 : 1)	12	69
6	MeOH–H_2O (1 : 1)	12	74
7	*i*-PrOH–H_2O (1 : 1)	12	65
8	H_2O/CH_2Cl_2 (1 : 1)	12	—
9	H_2O/DCE (1 : 1)	12	—

[a]Benzaldehyde (1 mmol), $TsNH_2$ (1 equiv), $TolSO_2Na$ (1.2 equiv), NH_2SO_3H (2 equiv), in 5 mL of solvent, at rt (ca. 20°C), for 12 h.



Scheme 3.

was an extreme example, which appeared whimsical, and the condensation reactions fluctuated abruptly in yields. Thus the influence of temperature on the first condensation step was investigated (Table 2). For aldehydes with electron-withdrawing substitutions on the phenyl group, the condensations proceeded faster (entries 22–24) even at lower temperature (entry 25) in comparison with benzaldehyde (entries 1–4) as control. On the contrary, electron-donating groups made the condensation slower (entries 11 and 13), but longer reaction time and lower temperature resulted in good yield (entries 12, 14, and 15). The compositions of the water–alcohol were adjusted in such a manner as to keep the aldehyde, amide, sodium sulfinate, and sulfamic acid totally dissolved and a clear solution formed. As the condensation proceeded, the sulfonamidosulfones **7** precipitated as white particles. Pure **7** was obtained by simple filtration. Sulfamic acid remaining in the filtrate can be recovered for large-scale preparations. Sulfonamidosulfones **7** were eliminated in the basic two-phase water systems to afford the imines **8** quantitatively, which remained in the lower organic phase in pure form. The eliminated sulfinate went to the upper water phase and was removed with the basic water. Thus the products of the two steps separated simultaneously as the reactions proceeded, making the preparation quite efficient and the separations remarkably simple.

In conclusion, a practical, mild, convenient, and green synthesis has been developed for the preparation of *N*-tosyl imines of substituted benzaldehydes through a two-step approach (Scheme 3). The first step was sulfamic acid–mediated three-component condensation in tap water–alcohol solvent, and the second step was basic elimination in a two-phase tap water media. Electron-withdrawing substitution(s) on the benzaldehydes facilitated the condensations. For benzaldehydes with electron-donating substitution(s), lower temperatures and longer times gave acceptable condensation yields. Higher temperatures worsen the partial decomposition of the sulfonamidosulfones, which compromised the faster reactions. Methanol–water and ethanol–water were the preferred solvents with benign environmental influence and efficient performance. Sulfamic acid was ideal[19] for the three-component condensations.

Table 2. Preparation of tosylimines by three-component condensations mediated by NH_2SO_3H and subsequent basic elimination

Entry	Aldehyde	Imine[a]	Ar	Solvent (ratio by volume)	Temp[b] (°C)	Time[b] (h)	Yield[c] (wt %)
1[d]	**6a**	**8a**[5e]	C_6H_5	MeOH–H_2O (1:1)	20	12	74
2				EtOH–H_2O (1:1)			69
3				MeOH–H_2O (1:1)	0		72
4				EtOH–H_2O (1:1)			65
5	**6b**	**8b**[5ll]	4-MeC_6H_4	MeOH–H_2O (1:1)			68
6					20		68
7	**6c**	**8c**[5ll]	2-HOC_6H_4				37
8	**6d**	**8d**[5e]	4-HOC_6H_4				44
9	**6e**	**8e**[5dd]	4-$MeOC_6H_4$				68
10					0		70
11	**6f**	**8f**[5d]	3,4-$(MeO)_2C_6H_3$	EtOH–H_2O (4:3)	20		47
12					0		56
13	**6g**	**8g**[5gg]	Piperonyl	EtOH–H_2O (2:1)	20	48	31
14					0		66
15					−10		74
16	**6h**	**8h**[5gg]	2-ClC_6H_4	MeOH–H_2O (4 : 3)	20	12	65
17					0		64
18	**6i**	**8i**[5e]	4-ClC_6H_4		20		76
19					0		75
20	**6j**	**8j**[5ll]	2,4-$Cl_2C_6H_3$	EtOH–H_2O (4 : 3)	20		47
21					35	6	50
22	**6k**	**8k**[5e]	4-$CF_3C_6H_4$		20		81
23	**6l**	**8l**[5dd]	4-$NO_2C_6H_4$				71
24	**6m**	**8m**[5m]	3-$NO_2C_6H_4$	MeOH–H_2O (1 : 1)			68
25					−10		67

[a]All imines gave satisfactory spectroscopic data that agreed with that of the literature.[5]
[b]Of the first three-component condensation step.
[c]Based on **6**, overall separated yield of **8**.
[d]Preparation of **8a** was scaled up to 3 L (1 mol of **6a**); overall separated yield was 75%.

EXPERIMENTAL

All reactants and solvents are commercially available and were used as received without purification. Melting points were determined using a microscope hot-stage apparatus without correction. IR spectra were recorded for KBr pellets on a Thermo Nicolet Nexus 870 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 and 125.5 MHz, respectively, in $CDCl_3$, on a Bruker DRX-500 instrument. Chemical shifts were expressed in parts per million (ppm) using TMS as internal standard for ^{1}H NMR; for ^{13}C NMR spectra, $CDCl_3$ ($\delta = 77.0$ ppm) was used. High-resolution electrospray mass spectra were obtained on a Mariner ESI-TOF spectrometer.

Preparation of Sulfonamidosulfones 7; General Procedure

To a stirred mixture of $TsNH_2$ (342 mg, 2 mmol), $TolSO_2Na$ (428 mg, 2.4 mmol), and H_2NSO_3H (388 mg, 4 mmol) in tap water–alcohol (10 mL, compositions as in Table 2), the corresponding aldehyde **6** (2 mmol) was added in one portion. A clear solution formed within 15 to 30 min. The liquid turned milky, and a white precipitate accumulated. As the reaction completed, the white precipitate product was collected by filtration and washed with water (2 × 3 mL) and hexane (3 mL). Sulfonamidosulfone **7** was obtained as a white solid. The wet sulfonamidosulfones **7** were subjected to the next elimination step immediately because of their instability on drying or further purification.

Preparation of *N*-Tosyl Imines 8; Typical Procedure

The sulfonamidosulfone **7** as wet filtrate cake was dispersed into CH_2Cl_2 (15 mL) (some entries partially dissolved), then saturated aqueous $NaHCO_3$ (15 mL) was added, and the two-phase liquid was stirred for 2 h at rt. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phase was dried (Na_2SO_4), and solvent was vacuum evaporated. The residue was pure imine **8**.

Data

N-Benzylidene-4-methylbenzenesulfonamide (**8a**)[5e]

White solid; mp 113–114°C. IR: 3261, 1652, 1326, 1170 cm^{-1}. ^{1}H NMR: $\delta = 2.45$ (s, 3 H), 7.36 (d, $J = 8.0$ Hz, 2 H), 7.50 (t, $J = 7.5$ Hz, 2 H), 7.64 (t, $J = 7.5$ Hz, 1 H), 7.90–7.95 (q, 4 H), 9.05 (s, 1 H). ^{13}C NMR: $\delta = 21.6$,

128.2, 128.9, 129.2, 130.0, 131.1, 133.8, 135.9, 143.4, 192.4. HRMS: m/z $[M + H]^+$ calcd. for $C_{14}H_{14}NO_2S^+$: 260.0745; found 260.0739.

N-(Benzo[*d*][1,3]dioxol-5-ylmethylene)-4-methylbenzenesulfonamide (**8g**)[5gg]

White solid; mp 119–120°C. IR: 3327, 1658, 1334, 1171 cm^{-1}. ^1H NMR: $\delta = 2.43$ (s, 1 H), 6.06 (s, 2 H), 6.98 (d, $J = 8.2$ Hz, 1 H), 7.10 (m, 1 H), 7.22 (d, $J = 8.5$ Hz, 2 H), 7.58 (d, $J = 1.8$ Hz, 1 H), 7.63 (d, $J = 8.5$ Hz, 2 H), 9.00 (s, 1 H).

4-Methyl-*N*-(3-nitrobenzylidene)benzenesulfonamide (**8m**)[5m]

White solid; mp 141–142°C. IR: 3247, 1675, 1317, 1128 cm^{-1}. ^1H NMR: $\delta = 2.48$ (s, 3H), 7.41 (d, $J = 8.0$ Hz, 2 H), 7.74 (t, $J = 8.0$ Hz, 1 H), 7.93 (d, $J = 8.0$ Hz, 2 H), 8.27 (d, $J = 7.5$ Hz, 2 H), 8.47 (d, $J = 7.5$ Hz, 1 H), 8.79 (s, 1 H), 9.13 (s, 1 H).

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REFERENCES

1. (a) Bloch, R. Additions of organometallic reagents to C=N bonds: Reactivity and selectivity. *Chem. Rev.* **1998**, *98*, 1407; (b) Adams, J. P. Imines, enamines and oximes. *J. Chem. Soc., Perkin Trans. 1* **2000**, 125; (c) Miyabe, H.; Ueda, M.; Naito, T. Carbon–carbon bond construction based on radical addition to C=N bond. *Synlett* **2004**, 1140; (d) Hou, X. L.; Wu, J.; Fan, R. H.; Ding, C. H.; Luo, Z. B.; Dai, L. X. Towards reaction selectivities of imines and aziridines. *Synlett* **2006**, 181.
2. (a) Enders, D.; Reinhold, U. Asymmetric synthesis of amines by nucleophilic 1,2-addition of organometallic reagents to the CN double bond. *Tetrahedron: Asymmetry* **1997**, *8*, 1895; (b) Kobayashi, S.; Ishitani, H. Catalytic enantioselective addition to imines. *Chem. Rev.* **1999**, *99*, 1069; (c) Dai, L.-X.; Lin, Y.-R.; Hou, X.-L.; Zhou, Y.-G. Stereoselective reactions with imines. *Pure Appl. Chem.* **1999**, *71*, 1033; (d) Alvaro, G.; Savoia, G. Addition of organometallic reagents to imines bearing stereogenic *N*-substituents: Stereochemical models explaining the 1,3-asymmetric induction. *Synlett* **2002**, 651.
3. Weinreb, S. M. *N*-Sulfonyl imines—Useful synthons in stereoselective organic synthesis. *Top. Curr. Chem.* **1997**, *190*, 131.
4. (a) Davis, F. A.; Zhou, P.; Chen, B.-C. Asymmetric synthesis of amino acids using sulfinimines (thiooxime S-oxides). *Chem. Soc. Rev.* **1998**, *27*, 13; (b) Ellman, J. A.; Owens, T. D.; Tang, T. P. *N*-tert-Butanesulfinyl imines: Versatile intermediates for

the asymmetric synthesis of amines. *Acc. Chem. Res.* **2002**, *35*, 984; (c) Ellman, J. A. Applications of tert-butanesulfinamide in the asymmetric synthesis of amines. *Pure Appl. Chem.* **2003**, *75*, 39; (d) Zhou, P.; Chen, B.-C.; Davis, F. A. Recent advances in asymmetric reactions using sulfinimines (*N*-sulfinyl imines). *Tetrahedron* **2004**, *60*, 8003; (e) Weinreb, S. M.; Orr, R. K. *N*-phosphinoylimines: An emerging class of reactive intermediates for stereoselective organic synthesis. *Synthesis* **2005**, 1205.

5. For direct condensations of carbonyls with sulfonylamides, see (a) Vishwakarma, L. C.; Strinnger, O. D.; Davis, F. A. (±)-*trans*-2-(Phenylsulfonyl)-3-phenyloxaziridine. *Org. Synth.* **1987**, *66*, 203; (b) Boger, D. L.; Corbett, W. L.; Curran, T. T.; Kasper, A. M. Inverse electron demand Diels–Alder reactions of *N*-sulfonyl α,β-unsaturated imines—A general approach to implementation of the 4-pi participation of 1-aza-1,3-butadienes in Diels–Alder reactions. *J. Am. Chem. Soc.* **1991**, *113*, 1713; (c) Love, B. E.; Ren, J. Synthesis of sterically hindered imines. *J. Org. Chem.* **1993**, *58*, 5556; (d) Love, B. E.; Raje, P. S.; Williams II, T. C. Preparation of *N*-tosylaldimines. *Synlett* **1994**, 493; (e) Wynne, J. H.; Price, S. E.; Rorer, J. R.; Stalick, W. M. Synthesis of novel functionalized *N*-tosylaldimines. *Synth. Commun.* **2003**, *33*, 341; For activation of carbonyls by Lewis acid catalysis or using acetals in place of ketones/aldehydes, see (f) McKay, W. R.; Proctor, G. R. Removal of toluene-*p*-sulfonyl groups from sulfonamides, 4: Synthesis of phenylglyoxal imine monomers. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2435; (g) Jennings, W. B.; Lovely, C. J. An efficient method for the preparation of *N*-phosphinoyl and *N*-sulfonyl imines directly from aromatic aldehydes. *Tetrahedron Lett.* **1988**, *29*, 3725; (h) Davis, F. A.; Thimma Reddy R.; Weismiller, M. C. (-)-α,α-Dichlorocamphorsulfonyloxaziridine: A superior reagent for the asymmetric oxidation of sulfides to sulfoxides. *J. Am. Chem. Soc.* **1989**, *111*, 5964; (i) Jennings, W. B.; Lovely, C. J. The titanium tetrachloride induced synthesis of *N*-phosphinoylimines and *N*-sulphonylimines directly from aromatic aldehydes. *Tetrahedron* **1991**, *47*, 5561; (j) Ram, R. N.; Khan, A. A. A simple method for the preparation of *N*-sulfonylimines by direct condensation of *p*-toluenesulfonamide with diaryl ketones. *Synth. Commun.* **2001**, *31*, 841; (k) Albrecht, R.; Kresze, G. Heterocyclen durch diensynthese—dienophile azomethine und deren dienaddukte. *Chem. Ber.* **1964**, *97*, 490; (l) Davis, F. A.; Kaminski, J. M.; Kluger, E. W.; Freilich, H. S. Chemistry of sulfur–nitrogen bond, 9: Transmission of electronic effects in n-alkylidenearenesulfenamides, *N*-alkylidenearenesulfinamides *N*-alkylidenearenesulfonamides, and arenesulfenanilides. *J. Am. Chem. Soc.* **1975**, *97*, 7085; (m) Davis, F. A.; Lamendola, J., Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R. Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. Chemistry of oxaziridines, 1: Synthesis and structure of 2-arenesulfonyl-3-aryloxaziridines—New class of oxaziridines. *J. Am. Chem. Soc.* **1980**, *102*, 2000, By Kresze reaction and related methods, see; (n) Albrecht, R.; Kreaze, G.; Mlakar, B. Arylsulfonylimine—Darstellung eigenschaften und reaktivitat. *Chem. Ber.* **1964**, *97*, 483; (o) Albrecht, R.; Kresze, G. Heterocyclen durch diensynthese, 2: *N*-[Butyloxycarbonylmenthylen]-*p*-toluolsulfonamid ein neues dienophil zur darstellung von pyridin- piperidein- und piperidin-derivaten durch Diels–Alder-synthese. *Chem. Ber.* **1965**, *98*, 1431; (p) Kresze, G.; Wucherpfennig, W. Organic syntheses with imides of sulfur dioxide. *Angew. Chem. Int. Ed.* **1967**, *6*, 149; (q) Melnick, M. J.; Freyer, A. J.; Weinreb, S. M. Generation and intramolecular cationic cyclizations of *N*-tosylimines derived from enolizable aldehydes. *Tetrahedron Lett.* **1988**, *29*,

3891; (r) Sisko, J.; Weinreb, S. M. A convenient in situ procedure for effecting intermolecular and intramolecular Diels–Alder reactions of *N*-sulfonyl imines. *Tetrahedron Lett.* **1989**, *30*, 3037; (s) Sisko, J.; Weinreb, S. M. Addition of Grignard and organolithium reagents to *N*-sulfonyl aldimines generated in situ from aldehydes and *N*-sulfinyl sulfonamides. *J. Org. Chem.* **1990**, *55*, 393; (t) Hamley, P.; Holmes, A. B.; Kee, A.; Ladduwahetty, T.; Smith, D. F. A convenient synthesis of methyl (*p*-toluenesulphonylimino)acetate—addition reactions with dienes. *Synlett* **1991**, 29. Through Hudson reaction and related methods, see (u) Hudson, B. F.; Record, F. A. F. Preparation and rearrangement of *O*-sulphinyl oxirnes. *J. Chem. Soc., Chem. Commun.* **1976**, 831; (v) Brown, C.; Hudson, R. F.; Record, K. A. F. Complex C.I.D.N.P. effects in the rearrangement of *O*-sulphinylated oxirnes. *J. Chem. Soc., Chem. Commun.* **1977**, 540; (w) Brown, C.; Hudson, R. F.; Record, K. A. F. The reaction between oximes and sulphinyl chlorides: A ready, low temperature radical rearrangement process. *J. Chem. Soc., Perkin Trans. 1* **1978**, 822; (x) Boger, D. L.; Corbett, W. L. A convenient and general preparation of *N*-sulfonylimines. *J. Org. Chem.* **1992**, *57*, 4777; (y) McIntosh, M. C.; Weinreb, S. M. An approach to total synthesis of (+)-lycoricidine. *J. Org. Chem.* **1993**, *58*, 4823; (z) Artman III, G. D.; Bartolozzi, A.; Franck, R. W.; Weinreb, S. M. Preparation of *N*-sulfonylimines bearing easily removable protecting groups via the Hudson reaction of oximes with sulfinyl chlorides. *Synlett* **2001**, 232; Recent indirect methods other than the previously mentioned ones, see (aa) Ruano, J. L. G.; Aleman, J.; Cid, M. B.; Parra, A. A general method for the preparation of *N*-sulfonyl aldimines and ketimines. *Org. Lett.* **2005**, *7*, 179; (bb) Sugihara, Y.; Iimura, S.; Nakayama, J. Aza-pinacol rearrangement: Acid-catalyzed rearrangement of aziridines to imines. *Chem. Commun.* **2002**, 134; (cc) Wolfe, J. P.; Ney, J. E. A new, mild synthesis of *N*-sulfonyl ketimines via the palladium-catalyzed isomerization of aziridines. *Org. Lett.* **2003**, *5*, 4607; (dd) Jian, S. L.; Sharma, V. B.; Sain, B. Ruthenium catalyzed imido-transfer reactions of aldehydes: An easy access to *N*-sulfonyl aldimines under mild reaction conditions. *J. Mol. Catal. A: Chem.* **2005**, *239*, 92; (ee) Sharma, V. B.; Jain, S. L.; Sain, B. Ruthenium catalysed imidation of aldehydes using PhI=NTs as imido transfer reagent. *J. Chem. Res., Synop* **2005**, 182; (ff) Davis, F. A.; Zhou, P.; Lal, G. S. A new synthesis of α-functionalized unsubstituted sulfonamides. *Tetrahedron Lett.* **1990**, *31*, 1653; (gg) Trost, B. M.; Marrs, C. A. convenient synthesis of *N*-tosylimines. *J. Org. Chem.* **1991**, *56*, 6468; (hh) Fujii, T.; Kimura, T.; Furukawa, N. Preparation of *N*-*p*-tosylaldimines by the intramolecular photo-imino group migration of naphtho[1,8-de]dithiin-1-*N*-tosylsulfilimines. *Tetrahedron Lett.* **1995**, *36*, 1075; (i) Georg, G. I.; Harriman, G. C. B.; Peterson, S. A. A facile one-flask conversion of aldehydes and ketones to *N*-sulfonyl imines. *J. Org. Chem.* **1995**, *60*, 7366; (j) Vass, A.; Dudas, J.; Varma, R. S. Solvent-free synthesis of *N*-sulfonylimines using microwave irradiation. *Tetrahedron Lett.* **1999**, *40*, 4951; (k) Lee, K. Y.; Lee, C. G.; Kim, J. N. A practical synthesis of *N*-tosylimines of arylaldehydes. *Tetrahedron Lett.* **2003**, *44*, 1231; (l) Jin, T.; Feng, G.; Yang, M.; Li, T. A solvent-free procedure for synthesis of *N*-sulfonylimines using microwave irradiation catalyzed by $ZrO_2/S_2O_8^{2-}$ solid super acid. *Synth. Commun.* **2004**, *34*, 1277.

6. (a) Li, Z.; Wan, H.; Wei, P.; Shi, Y.; Ouyang, P. Asymmetric synthesis of tailor-made α-amino acids by chiral auxiliaries—Glycine equivalent approach. *Chin. J. Org. Chem.* **2005**, *25*, 881; (b) Qin, W.; Cao, F.; Li, Z.; Zhou, H.; Wan, H.; Wei, P.; Shi, Y.; Ouyang, P. Synthesis and crystal structures of complexes of Ni

(II) to chiral schiff bases of (*R*)-and (*S*)-serine with (*S*)- and (*R*)-2-*N*-(*N*′-benzyl-prolyl)-aminobenzophenone. *J. Chem. Crystallogr* **2006**, *36*, DOI: 10.1007/s10870-005-9025-9.

7. Petrini, M. α-Amido sulfones as stable precursors of reactive *N*-acylimino derivatives. *Chem. Rev.* **2005**, *105*, 3949.
8. (a) Van Leusen, A. M.; Wildeman, J.; Oldenziel, O. H. Base-induced cycloaddition of sulfonylmethyl isocyanides to carbon, nitrogen double bonds: Synthesis of 1,5-disubstituted and 1,4,5-trisubstituted imidazoles from aldimines and imidoyl chlorides. *J. Org. Chem* **1977**, *42*, 1153; (b) McKay, W. R.; Proctor, G. R. Removal of toluene-*p*-sulfonyl groups from sulfonamides, 4: Synthesis of phenylglyoxal imine monomers. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2435; (c) Morton, J.; Rahim, A.; Walker, E. R. H. A new general method of α-amino-alkylation. *Tetrahedron Lett.* **1982**, *23*, 4123; (d) Kanazawa, A. M.; Denis, J.-N.; Greene, A. E. Highly stereocontrolled and efficient preparation of the protected, esterification-ready docetaxel (Taxotere) side chain. *J. Org. Chem.* **1994**, *59*, 1238; (e) Sisko, J.; Mellinger, M.; Sheldrake, P. W.; Baine, N. H. An efficient method for the synthesis of substituted TosMIC precursors. *Tetrahedron Lett.* **1996**, *37*, 8113; (f) Chemla, F.; Hebbe, V.; Normant, J.-F. An easy synthesis of aliphatic and aromatic N-sulfonyl aldimines. *Synthesis* **2000**, *75*.
9. (a) Li, C.-J. Organic reactions in aqueous media—With a focus on carbon–carbon bond formation. *Chem. Rev.* **1993**, *93*, 2023; (b) Lindström, U. M. Stereoselective organic reactions in water. *Chem. Rev.* **2002**, *102*, 2751; (c) Li, C.-J. Organic reactions in aqueous media with a focus on carbon–carbon bond formations: A decade update. *Chem. Rev.* **2005**, *105*, 3095; (d) Li, C.-J.; Chen, L. Organic chemistry in water. *Chem. Soc. Rev.* **2006**, *35*, 68.
10. (a) DeSimone, J. M. Practical approaches to green solvents. *Science* **2002**, *297*, 799; (b) Blaser, H.-U.; Studer, M. Catalysis for fine chemicals—Who needs (will use) new solvents. *Green Chem.* **2003**, *5*, 112; (c) Sheldon, R. A. Green solvents for sustainable organic synthesis—State of the art. *Green Chem.* **2005**, *7*, 267.
11. (a) Lubineau, A.; Auge, J. Water as solvent in organic synthesis. *Top. Curr. Chem* **1999**, *206*, 1; (b) Cornils, B. Modern solvent systems in industrial homogeneous catalysis. *Top. Curr. Chem.* **1999**, *206*, 133.
12. Hellweg, S.; Fischer, U.; Scheringer, M.; Hungerbühler, K. Environmental assessment of chemicals—Methods and application to a case study of organic solvents. *Green Chem.* **2004**, *6*, 418.
13. (a) Singh, P. R.; Singh, D. U.; Samant, S. D. Sulphamic acid—An efficient and cost-effective solid acid catalyst for the Pechmann reaction. *Synlett* **2004**, 1909; (b) Nagarajan, R.; Magesh, C. J.; Perumal, P. T. Inter- and intramolecular imino Diels–Alder reactions catalyzed by sulfamic acid: A mild and efficient catalyst for a one-pot synthesis of tetrahydroquinolines. *Synthesis* **2004**, 69; (c) Wang, B.; Gu, Y.; Luo, C.; Yang, T.; Yang, L.; Suo, J. Sulfamic acid as a cost-effective and recyclable catalyst for liquid Beckmann rearrangement, a green process to produce amides from ketoximes without waste. *Tetrahedron Lett.* **2004**, *45*, 3369; (d) Yadav, J. S.; Rao, P. P.; Sreenu, D.; Rao, R. S.; Kumar, V. N.; Nagaiah, K.; Prasad, A. R. Sulfamic acid: An efficient, cost-effective and recyclable solid acid catalyst for the Friedlander quinoline synthesis. *Tetrahedron Lett.* **2005**, *46*, 7249; (e) Rajitha, B.; Kumar, B. S.; Geddy, Y. T.; Reddy, P. N.; Sreenivasulu, N. Sulfamic acid: A novel and efficient catalyst for the synthesis of aryl-14*H*-dibenzo[a.j]xanthenes under conventional heating and microwave irradiation. *Tetrahedron Lett.* **2005**, *46*, 8691.

14. Wang, B. Sulfamic acid: A very useful catalyst. *Synlett* **2005**, 1342.
15. (a) Engberts, J. B.; Strating, J. Chemistry of α-diazosulfones, 3: Simple preparation of *N*-(sulfonylmethyl)urethanes by mannich condensation. *Recl. Trav. Chim. Pays-B.* **1964**, *83*, 733; (b) Engberts, J. B.; Strating, J. Mannich condensation of sulfinic acids aldehyde and ethyl carbamate, 2: Use of higher aldehydes. *Recl. Trav. Chim. Pays-B.* **1965**, *84*, 942; (c) Engberts, J. B.; Olijnsma, T.; Strating, J. Mannich condensation of sulfinic acids aldehyde and ethyl carbamate, 3: Use of ethyl *N*-monosubstituted carbamates ethyl monothiocarbamated and ethyl dithiocarbamates. *Recl. Trav. Chim. Pays-B.* **1966**, *85*, 1211; (d) Olijnsma, T.; Engberts, J. B.; Strating, J. Mannich condensation of sulfinic acid with aldehydes and carboxamides sulfonamides or lactams, 4. *Recl. Trav. Chim. Pays-B.* **1967**, *86*, 463; (e) Olijnsma, T.; Strating, J.; Engberts, J. B. Mannich-type condensation reactions of sulfinic acids with aldehydes and nitrogen bases, 5: Formamide as amine component in Mannich-type condensation with sulfinic acids and aldehydes. *Recl. Trav. Chim. Pays-B.* **1972**, *91*, 209; (f) Meijer, H.; Tel, R. M.; Strating, J.; Engberts, J. B. Mannich-type condensation reactions of sulfinic acids with aldehydes and nitrogen bases, 6: Use of ureas, thioureas and thiobenzamide. *Recl. Trav. Chim. Pays-B.* **1973**, *92*, 72.
16. Li, Z.; Ren, X.; Wei, P.; Wan, H.; Shi, Y.; Ouyang, P. A convenient preparation of aliphatic and aromatic *N*-sulfonylimines mediated by sulfamic acid in aqueous media. *Green Chem.* **2006**, *8*, 433.
17. Sulfamic acid in industry was regarded as a "strong" acid because of its hydrolysis in water at elevated temperature for a long time. See Benson, G. A.; Spillane, W. J. Sulfamic acid and its *N*-substituted derivatives. *Chem. Rev.* **1980**, *80*, 151.
18. (a) Philip, D.; Eapen, A.; Aruldhas, G. Vibrational surface-enhanced raman-scattering spectra of sulfamic acid. *J. Solid State Chem.* **1995**, *116*, 217; (b) Canagaratna, M.; Ott, M. E.; Leopold, K. R. Determination of the dipole moment of H_3N-SO_3 in the gas phase. *Chem. Phys. Lett.* **1997**, *281*, 63.
19. The structures of $H_2N - SO_3H$ were investigated in gas phase (see Ref. 18b) and in molecular clusters (condensed phase) as zwitterionic units, but the catalysis in crystalline and in solution was not further investigated. See (a) Canagaratna, M.; Phillips, J. A.; Goodfriend, H.; Leopold, K. R. Structure and bonding of the sulfamic acid zwitterion: Microwave spectrum of $^{+}H_3N{-}SO_3^{-}$. *J. Am. Chem. Soc.* **1996**, *118*, 5290; (b) Pawlowski, P. M.; Okimoto, S. R.; Tao, F. M. Structure and stability of sulfur trioxide–ammonia clusters with water: Implications on atmospheric nucleation and condensation. *J. Phys. Chem. A* **2003**, *107*, 5327.