A simple, efficient Pd-catalyzed synthesis of *N*-sulfonylimines from organoboronic acids and tosylbenzimidoyl chlorides†

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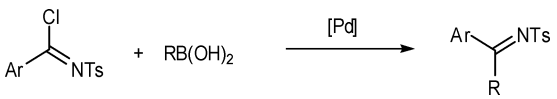
A simple and efficient synthesis of *N*-sulfonyl ketimines through a Pd-catalyzed cross-coupling reaction between organoboronic acids and tosylbenzimidoyl chlorides under mild conditions has been developed.

Introduction

N-Sulfonyl imines are attractive synthetic intermediates because they are highly reactive and configurationally stable. They have been widely used in organic synthesis.[1] For example, they are used as substrates in hetero Diels–Alder reactions[2] and trimethylenemethane cycloadditions,[3] which provide a useful route to nitrogen-containing heterocycles. *N*-Sulfonyl imines are also employed as electrophiles in various addition[4] and reduction reactions.[5] Therefore, many synthetic methods have been developed for their preparation. However, unlike sulfonyl aldimines, *N*-sulfonyl ketimines are relatively difficult to prepare by direct condensation of ketones with sulfonylamines. The most prevalent strategy for *N*-sulfonyl ketimine synthesis relies on the condensation of oximes with sulfinyl chloride[6] or sulfonyl cyanide.[7] However, sulfinyl chlorides are often unstable and very reactive, and the analogous cyanides are quite expensive and generate toxic byproducts. For these reasons, alternative strategies toward the synthesis of *N*-sulfonyl ketimines have been explored. Recently the Ruano group[8] reported a high-yielding method for synthesizing *N*-sulfonyl ketimines through condensation of carbonyl compounds and sulfonamides followed by oxidation with *m*-CPBA. As regards transition-metal-catalyzed methods, so far only two examples have been reported, by Wolfe[9] and Tanaka.[10] In the former case the substrate scope was limited to methyl ketimines, and the latter method used organotin compounds as the starting materials. Therefore, it is apparent that the synthesis of sulfonyl ketimines remains a big challenge. We present herein a simple, efficient procedure for *N*-sulfonyl ketimine synthesis through a Pd-catalyzed cross-coupling reaction between organoboronic acids and tosylbenzimidoyl chlorides (Scheme 1).



Scheme 1

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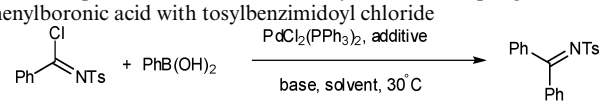
Results and discussion

Initially, we screened various reaction conditions for the reaction of tosylbenzimidoyl chloride with phenylboronic acid, and the results are summarized in Table 1.

$PdCl_2(PPh_3)_2$ was determined to be the most effective catalyst. Among the three additives, Ag_2O gives the highest yield (Table 1, entries 1–3). After several attempts, we were pleased to find that *N*-sulfonyl ketimine **3a** could be obtained in quantitative yield (99% isolated yield) when the reaction was run using Na_2CO_3 as the base, Ag_2O as the additive and toluene as solvent. The reaction proceeded smoothly with $Mg(OH)_2$, $NaHCO_3$ and Na_2CO_3, while $K_3PO_4{\cdot}3H_2O$ and $KHCO_3$ gave low yields. Lower yields also resulted when a smaller number of equivalents of Ag_2O were used or when other solvents were used instead of toluene, indicating that both Ag_2O and the solvent play an important role (Table 1, entries 10–16).

We applied these optimised conditions to other substrates, the results being summarised in Table 2. We found that the

Table 1 Optimization of the Pd-catalyzed cross-coupling reaction of phenylboronic acid with tosylbenzimidoyl chloride

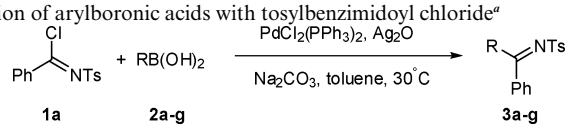


1a **2a** **3a**

Entry	Additive	Base	Solvent	Yield[b] (%)
1	Ag_2O	K_2CO_3	Toluene	41
2	KI	K_2CO_3	Toluene	12
3	Si-Al-supporting	K_2CO_3	Toluene	25
4	Ag_2O	$KHCO_3$	Toluene	14
5	Ag_2O	Cs_2CO_3	Toluene	25
6	Ag_2O	$K_3PO_4{\cdot}3H_2O$	Toluene	41
7	Ag_2O	$Mg(OH)_2$	Toluene	87
8	Ag_2O	$NaHCO_3$	Toluene	89
9	Ag_2O	Na_2CO_3	Toluene	99
10	Ag_2O (0.5 eq.)	Na_2CO_3	Toluene	82
11	Ag_2O (0.2 eq.)	Na_2CO_3	Toluene	76
12	Ag_2O (0.1 eq.)	Na_2CO_3	Toluene	61
13	Ag_2O	Na_2CO_3	CH_2Cl_2	43
14	Ag_2O	Na_2CO_3	CH_3CN	54
15	Ag_2O	Na_2CO_3	DME	39
16	Ag_2O	Na_2CO_3	THF	30

[a] *Reagents and conditions*: tosylbenzimidoyl chloride (1.0 eq.), phenylboronic acid (1.2 equiv.), base (1.5 equiv.), additives (1.1 equiv.) and 1.0 mol% $PdCl_2(PPh_3)_2$. [b] Isolated yield.

Table 2 Pd-catalyzed cross-coupling reaction of arylboronic acids with tosylbenzimidoyl chloride[a]



1a 2a-g 3a-g

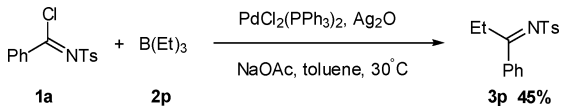
Entry	Arylboronic acid	R	Product	Time/h	Yield[b] (%)
1	**2a**	Ph	**3a**	1	99
2	**2b**	4-Me–C_6H_4	**3b**	1	95
3	**2c**	4-MeO–C_6H_4	**3c**	1	99
4	**2d**	4-CF_3–C_6H_4	**3d**	4	80
5	**2e**	3-CF_3–C_6H_4	**3e**	12	36
6	**2f**	3-Cl–C_6H_4	**3f**	6	65
7	**2g**	2-Cl–C_6H_4	**3g**	12	Not detected

[a] *Reagents and conditions*: tosylbenzimidoyl chloride (1.0 eq.), arylboronic acid (1.2 eq.), Na_2CO_3 (1.5 eq.), Ag_2O (1.1 eq.) and $PdCl_2(PPh_3)_2$ (1.0 mol%). [b] Isolated yield.

reaction works well irrespective of whether the substituents at the 4-position of the phenylboronic acid are electron-donating or electron withdrawing. We were, however, disappointed to find that very low yields resulted when there were substituents at the 3- and 2-positions (Table 2, entries 5–7).

To improve the yield, we carefully checked our reaction conditions, and noted that $K_3PO_4 \cdot 3H_2O$ gives a higher yield than other potassium salts (Table 1, entries 1, 4 and 6). We also found some Suzuki-type cross-coupling reactions that had been carried out in water,[11] and this led us to consider that the water molecules of $K_3PO_4 \cdot 3H_2O$ may be affecting the reaction. To test our hypothesis, we carried out the unsuccessful cases in Table 2 by adding a trace amount of water to the reaction, and were pleased to observe a dramatic improvement of yields (compare entries 5–7 in Table 2 with entries 1–3 in Table 3). Almost all reactions gave good to excellent yields. In fact, reagent-grade toluene could be used rather than dry toluene, giving similarly good results, and making the reaction very simple and convenient.

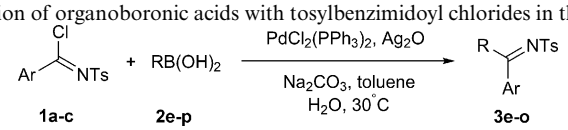
Interestingly, an alkenylboronic acid (Table 3, entry 12) and triethylborane (Scheme 2) also afforded the cross-coupling products, in 48% and 45% yields respectively. The cross-coupling product **3p**, 4-methyl-*N*-(1-phenylpropylidene)benzene sulfonamide, which is prone to enolization and is difficult to prepare by other methods, was synthesized by Suzuki cross-coupling for the first time under our reaction conditions. A single crystal of **3p** was obtained and X-ray diffraction analysis performed†.



1a 2p 3p 45%

Scheme 2

Table 3 Pd-catalyzed cross-coupling reaction of organoboronic acids with tosylbenzimidoyl chlorides in the presence of water[a]



1a-c 2e-p 3e-o

	Tosylbenzimidoyl chloride		Arylboronic acid				
Entry	No.	Ar	No.	R	Product	Time/h	Yield[b] (%)
1	**1a**	Ph	**2e**	3-CF_3–C_6H_4	**3e**	4	88
2	**1a**	Ph	**2f**	3-Cl–C_6H_4	**3f**	3	88
3	**1a**	Ph	**2g**	2-Cl–C_6H_4	**3g**	1	85
4	**1a**	Ph	**2h**	3-MeC(O)–C_6H_4	**3h**	2	94
5	**1a**	Ph	**2i**	3-EtOOC–C_6H_4	**3i**	2	92
6	**1a**	Ph	**2j**	3-Me–C_6H_4	**3j**	8	75
7	**1a**	Ph	**2k**	2-MeO–C_6H_4	**3k**	1	98
8	**1a**	Ph	**2l**	4-F–C_6H_4	**3l**	7	86
9	**1a**	Ph	**2m**	4-Cl–C_6H_4	**3m**	2	88
10	**1b**	2-F–C_6H_4	**2n**	Ph	**3n**	1	94
11[c]	**1c**	2-MeO–C_6H_4	**2n**	Ph	**3k**	12	99
12[d]	**1a**	Ph	**2o**	(*E*)-PhCH=CH	**3o**	12	48

[a] *Reagents and conditions*: tosylbenzimidoyl chloride (1.0 eq.), arylboronic acid (1.2 eq.), Na_2CO_3 (1.5 eq.), Ag_2O (1.1 eq.), $PdCl_2(PPh_3)_2$ (1.0 mol%) solvent (water–toluene = 1 : 1000, v/v). [b] Isolated yield. [c] NaOAc was used as the base. [d] Water was not added.

Conclusions

In summary, we have demonstrated a mild $PdCl_2(PPh_3)_2/Ag_2O$-catalyzed[12] cross-coupling reaction of organoboronic acids with tosylbenzimidoyl chlorides to afford sulfonyl ketimines in moderate to excellent yields. This method offers several advantages including mild reaction conditions and a highly catalytic process. It was found that our catalytic system could also effectively catalyze the cross-coupling reaction of an alkenylboronic acid or triethylborane with *N*-tosylbenzimidoyl chloride, which are difficult to prepare by other methods.

Experimental

All reagents were used as received. All solvents were dried and/or distilled by standard methods. All anaerobic sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer. IR spectra were obtained on a Shimadzu IR-440 infrared spectrophotometer. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Elemental analyses were performed on a Foss-Heraeus Vario EL instrument. HRMS analyses were acquired on an ApexIII Bruker (Daltonions) instrument. The X-ray structure determination for complex **3p** was carried out on a Smart Apex Bruker diffractometer.

Synthesis of *N*-tosylbenzamides

***N*-Tosylbenzamide.** $TsNH_2$ (3.42 g, 0.02 mol) and K_2CO_3 (6.9 g, 0.05 mol) were dissolved in 200 mL THF and stirred for 20 min at rt, then cooled to 0 °C with an ice-bath. Benzene carbonic chloride (36. g, 0.026 mol) in 100 ml THF was syringed into the reaction mixture. After stirring for 48 h, a white precipitate formed, and the reaction mixture was then refluxed for 12 h. The reaction was quenched by 50% H_2SO_4 and was extracted with 100 mL ethyl estacetate twice, washed with water and brine, dried over Na_2SO_4, evaporated *in vacuo*, and crystallized to give colorless crystals of *N*-tosylbenzamide (5.155 g, 0.0187 mol, 94% yield). Colorless crystals; mp 144–146 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.15$ (s, 1H), 8.05 (d, $J = 8.7$ Hz, 2H), 7.80 (d, $J = 8.7$ Hz, 2H), 7.58–7.53 (m, 1H), 7.45–7.34 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 164.37$, 145.22, 133.43, 131.05, 129.59, 128.84, 128.59, 127.83, 21.68; MS: $m/z = 276$, 211, 155, 108, 105, 91, 77; IR(KBr): $\nu = 3262$, 1696, 1598, 1453, 1427, 1168, 1083, 1062, 563, 547; Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09; Found: C, 61.00; H, 4.83; N, 5.00.

2-Fluoro-*N*-tosylbenzamide. Prepared as for *N*-tosylbenzamide. Colorless crystals; mp 131–133 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.70$ (d, $J = 15.0$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 2H), 8.00–7.94 (m, 1H), 7.59–7.51 (m, 1H), 7.36 (d, $J = 9.0$ Hz, 2H), 7.28–7.12 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 162.27$, 160.22, 158.97, 145.20, 135.55, 135.22, 132.12, 129.46, 128.66, 125.19, 125.14, 118.44, 118.30, 116.47, 116.14, 21.57; IR(KBr): $\nu = 3256$, 1699, 1614, 1428, 1169, 754, 571 cm^{-1}; MS: $m/z = 294$, 229, 155, 123, 108, 95, 91; Anal. Calcd for $C_{14}H_{12}F_3NO_3S$: C, 57.33; H, 4.12; N, 4.78; Found: C, 57.46; H, 4.33; N, 4.77.

2-Methoxy-*N*-tosylbenzamide. Prepared as for *N*-tosylbenzamide. Colorless crystals; mp 99–101 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.82$ (s, 1H), 8.04 (d, $J = 8.1$ Hz, 2H), 7.40–7.26 (m, 5H), 7.07–7.04 (m, 1H), 3.74 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 164.46$, 159.70, 145.19, 135.23, 132.18, 129.75, 129.54, 128.47, 120.36, 120.02, 112.02, 55.35, 21.61; IR(KBr): $\nu = 3261$, 2925, 1701, 1599, 1160, 1037, 866, 547 cm^{-1}; MS: $m/z = 304$, 241, 171, 155, 135, 108, 91, 77; Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95; N, 4.59; Found: C, 59.00; H, 4.94; N, 4.40.

Typical procedure for the preparation of *N*-tosylbenzimidoyl chlorides

A typical procedure is given for the synthesis of *N*-tosylbenzimidoyl chloride **1a**. A mixture of *N*-tosylbenzamide (2.40 g, 8.7 mmol) and PCl_5 (1.90 g, 8.8 mmol) was dissolved in benzene (30 ml) at room temperature, and stirred at this temperature for 0.5 h. Then the reaction mixture was refluxed for 6 h, after which time the reaction was complete, as determined by TLC analysis. The solvent was removed *in vacuo*, and the crude product was recrystallized from diethyl ether to afford **1a** (2.34 g, 91%) as a white solid.

Typical procedure for the coupling reaction to prepare *N*-sulfonyl ketimines

N-Tosylbenzimidoyl chloride **1a** (293 mg, 1.0 mmol), phenylboronic acid **2a** (1.2 mmol), Na_2CO_3 (160 mg, 2.1 mmol), Ag_2O (254 mg, 1.1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 1 mol%) and toluene (10 ml) were combined and stirred at 30 °C. The reaction was monitored by TLC. The reaction mixture was filtered and evaporated *in vacuo*, and the residue purified by flash chromatography (pentane–EtOAc 15 : 1) to give a white solid **3a** (332 g, 0.99 mmol, 99% yield).

***N*-(Diphenylmethylene)-4-methylbenzenesulfonamide (3a).** White solid; mp 100–101 °C; R_f 0.48 (hexane–EtOAc = 5:1); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.83$ (d, $J = 8.1$ Hz, 2H), 7.56–7.29 (m, 10H), 7.25 (d, $J = 8.1$ Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 178.70$, 143.31, 143.29, 138.33, 129.32, 128.06, 127.97, 127.24, 21.64; MS: $m/z =$ 228, 157, 129, 113, 91, 77, 55, 43; Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18; Found: C, 71.63; H, 5.20; N, 3.96.

4-Methyl-*N*-(phenyl(*p*-tolyl)methylene)benzenesulfonamide (3b). White solid; mp 127–129 °C; R_f 0.45 (hexane–EtOAc = 5 : 1); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.83$ (d, $J = 8.1$ Hz, 2H), 7.53–7.41 (m, 7H), 7.30–7.23 (m, 4H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 178.77$, 143.14, 138.51, 130.74, 129.25, 128.84, 127.92, 127.17, 21.61, 21.50; MS: $m/z = 349$, 285, 194, 155, 91, 77, 65; Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01; Found: C, 72.02; H, 5.67; N, 3.90.

***N*-((4-Methoxyphenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3c).** White solid; mp. 105–107 °C; R_f 0.26 (hexane–EtOAc = 5 : 1); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 7.80 (d, $J = 7.8$ Hz, 2H), 7.58 (m, $J = 9.0$ Hz, 2H), 7.51–7.39 (m, 5H), 7.25 (d, $J = 7.8$ Hz, 2H), 6.86 (d, $J = 7.8$ Hz, 2H), 3.52 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 177.88$, 142.92, 138.67, 132.76, 132.34, 129.14, 128.01, 127.22,

126.98, 126.19, 113.52, 55.36, 21.35; MS: m/z = 364, 210, 195, 167, 135, 91, 77, 65, 44; E. A. Anal. Calcd: C, 69.02; H, 5.24; N, 3.83; Found: C, 68.99; H, 5.39; N, 3.73.

4-Methyl-*N*-(phenyl(4-(trifluoromethyl)phenyl)methylene)benzenesulfonamide (3d). White solid; mp 129–131 °C; R_f 0.08 (hexane–EtOAc = 2 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.81 (d, J = 8.4 Hz, 2H), 7.70–7.42 (m, 9H), 7.30 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 176.77, 143.70, 137.81, 133.83, 130.47, 129.41, 128.43, 127.27, 125.35, 124.97, 121.73, 21.48; IR(KBr): MS: m/z = 402, 338, 248, 155, 91, 77, 65; Anal. Calcd: $C_{16}H_{21}NF_3O_2S$: C, 62.52; H, 4.00; N, 3.47; Found: C, 62.77; H, 4.05; N, 3.42.

4-Methyl-*N*-(phenyl(3-(trifluoromethyl)phenyl)methylene)benzenesulfonamide (3e). White solid; mp 88–90 °C; R_f 0.08 (hexane–EtOAc = 2 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80–7.73 (m, 4H), 7.57–7.45 (m, 7H), 7.29 (s, J = 7.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 176.87, 143.77, 137.75, 130.57, 129.45, 128.74, 128.39, 127.32, 125.30, 21.55; ^{19}F NMR (75 MHz, $CDCl_3$, 25 °C, TMS): −63.10; IR (KBr): MS: m/z = 338, 248, 155, 91, 77, 65, 51, 44; Anal. Calcd: C, 62.52; H, 4.00; N, 3.47; Found: C, 62.55, H, 3.96, N, 3.25.

***N*-((3-Chlorophenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3f).** White solid; mp 83–85 °C; R_f 0.35 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.79 (d, J = 8.4 Hz, 2H), 7.56–7.41 (m, 9H), 7.28 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 176.90, 143.60, 137.89, 134.25, 139,67, 129.38, 128.27, 109.64, 21,52; MS: m/z = 370, 368, 305, 214, 155, 91, 77, 65, 51; Anal. Calcd: C, 64.95; H, 4.36; N, 3.79; Found: C, 64.90, H, 4.20, N, 3.45.

***N*-((2-Chlorophenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3g).** White solid; mp 94–95 °C; R_f 0.35 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.84 (d, J = 8.4 Hz, 2H), 7.68 (m, 2H), 7.56–7.51 (m, 1H), 7.56–7.51 (m, 1H), 7.45–7.34 (m, 6H), 2.28 (d, J = 8.7 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 174.73, 143.79, 137.36, 135.78, 134.59, 133.83, 131.01, 129.91, 129.38, 129.28, 128.64, 127.60, 1126.51, 21.60; MS: m/z = 333, 214, 155, 111, 91, 77, 65, 51; Anal. Calcd: C, 64.95; H, 4.36; N, 3.79; Found: C, 64.97, H, 4.34, N, 3.60.

***N*-((4-Methoxyphenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3h).** White solid; mp 120–122 °C; R_f 0.26 (hexane–EtOAc = 2 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.10 (d, J = 7.5 Hz, 1H), 8.02 (br, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.73–7.72 (m, 1H), 7.57–7.72 (m, 6H), 7.27 (d, J = 8.1 Hz, 2H), 2.57 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.82, 177.50, 143.48, 137.97, 132.80, 130.47, 129.31, 128.28, 127.15, 26.49, 21.41; IR (KBr): ν = 3063, 2924, 1686, 1598, 1561, 1322, 1154, 1090, 833, 685, 554 cm^{-1}; MS (m/z) 378.2; Anal. Calcld: C, 70.00; H, 5.07; N, 3.71; Found: C, 69.85; H, 5.42; N, 3.62.

Ethyl 3-(phenyl(tosylimino)methyl)benzoate (3i). White solid; mp 104–105 °C; R_f 0.14 (hexane–EtOAc = 2 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.20 (d, J = 7.8 Hz, 1H), 7.82–7.75 (m, 4H), 7.57–7.42 (m, 6H), 7.28 (d, J = 8.1 Hz, 2H), 4.36 (d, q = 6.9 Hz, 2H), 2.41 (s, 1H), 1.36 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 177.50, 165.48, 143.47, 137.99, 130.41, 129.34, 128.22, 127.24, 61.24, 21.46, 14.15; MS: m/z = 407, 343, 252, 224, 155, 104, 91, 77, 65, 44; Anal. Calcd: C, 67.79; H, 5.19; N, 3.44; Found: C, 67.84; H, 5.32; N, 3.18.

4-Methyl-*N*-(phenyl(*m*-tolyl)methylene)benzenesulfonamide (3j). White solid; mp 99–101 °C; R_f 0.46 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.81 (d, J = 7.8 Hz, 2H), 7.53–7.28 (m, 9H), 7.26 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 178.96, 143.18, 138.34, 129.24, 127.94, 127.21, 21.47, 21.28; MS: m/z = 349, 285, 242, 194, 155, 91, 77, 65; Anal. Calcd: C, 72.18; H, 5.48; N, 4.01; Found: C, 72.17; H, 5.53; N, 4.16.

***N*-((2-Methoxyphenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3k).** White solid; mp 89–91 °C; R_f 0.25 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.73 (m, 4H), 7.50–7.19 (m, 7H), 7.06 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 3.58 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 176.51, 155.65, 143.06, 137.49, 136.77, 133.27, 131.32, 131.27, 129.74, 128.91, 128.22, 127.38, 124.15, 119.92, 55.25, 21.42; Anal. Calcd: C, 69.02; H, 5.24; N, 3.83; Found: C, 68.84; H, 5.31; N, 3.46.

***N*-((4-Fluorophenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3l).** Prepared as *N*-(diphenylmethylene)-4-methylbenzenesulfonamide **3a** to give a colorless oil; R_f 0.12 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.83 (d, J = 8.1 Hz, 2H), 7.60–7.51 (m, 7H), 7.29 (d, J = 8.1 Hz, 2H), 7.09 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 177.26, 143.28, 138.17, 133.11, 130.60, 129.22, 127.97, 127.06, 115.29, 21.33; MS: m/z = 270, 238, 223, 152, 104, 76, 43; HRMS Calcd: 353.0880; Found: 353.0874.

***N*-((4-Chlorophenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3m).** White solid; mp 106–108 °C; R_f 0.38 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (d, J = 8.4 Hz, 2H), 7.56–7.41 (m, 9H), 7.28 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 177.29, 143.43, 138.09, 129.31, 128.37, 128.12, 127.18, 21.46; MS: m/z = 371, 369, 305, 214, 155, 111, 91, 77, 65, 51; Anal. Calcd: C, 64.95; H, 4.36; N, 3.79; Found: C, 64.87; H, 4.49; N, 3.68.

***N*-((2-Fluorophenyl)(phenyl)methylene)-4-methylbenzenesulfonamide (3n).** White solid; mp 74–76 °C; R_f 0.10 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.53–7.29 (m, 8H), 7.12 (t, J = 9.1 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 173.10, 143.64, 137.50, 136.31, 133.85, 132.12, 132.03, 129.81, 129.32, 128.53, 127.85, 127.36, 123.80, 115,58, 115,31, 21.47; MS: m/z = 353, 289, 198, 155, 91, 77, 65, 51; Anal. Calcd: C, 67,97; H, 4.56; N, 3.96; Found: C, 67.94; H, 4.54; N, 3.73.

(*E*)-*N*-(1,3-Diphenylallylidene)-4-methylbenzenesulfonamide (3o). White solid; mp 147–149 °C; R_f 0.69 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.12–8.07 (m, 1H), 7.94 (s, J = 6.9 Hz, 2H), 7.65–7.30 (m, 12H), 7.05 (d, J = 15.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 177.52, 148.82, 143.39, 138.56, 134.41, 131.93, 131.12, 129.36, 128.95, 128.65, 127.09, 122.47, 21.50; MS: m/z = 361, 296, 206,103, 91, 77, 65.

4-Methyl-*N*-(1-phenylpropylidene)benzenesulfonamide (3p). White solid; mp 113–115 °C; R_f 0.74 (hexane–EtOAc = 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.97$ (d, $J = 6.6$ Hz, 2H), 7.81 (d, $J = 6.6$ Hz, 2H), 7.55–7.53 (m, 1H), 7.48–7.43 (m, 1H), 7.48–7.43 (m, 2H), 7.32–7.29 (m, 2H), 3.01 (q, $J = 7.2$ Hz, 2H), 2.42 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 2H). A single crystal of **3p** suitable for X-ray diffraction analysis was obtained by recrystallization from pentane–EtOAc (15 : 1).

X-Ray crystal structure determination. Data were collected using a Smart Apex Bruke diffractometer, with graphite monochromated MoKα radiation using standard procedures at 293 K. The structure was solved by direct methods, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. $C_{16}H_{17}NO_2S$: $M = 287.37$, monoclinic, space group $P2_1/c$, $a = 8.6787(9)$, $b = 13.9781(15)$, $c = 12.3242(13)$ Å, $\alpha = 90$, $\beta = 99.664(2)$, $\gamma = 90°$, $V = 1473.9(3)$ Å^3, $Z = 4$, calculated density 1.295 Mg m^{-3}, colourless blocks, crystal dimensions = 0.496 × 0.415 × 0.347 mm^3. Range for data collection: 4.761–53.719°. A total of 8462 unique reflections were measured for $-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-15 \leq l \leq 7$. The final R indices were $R1 = 0.0498$, $wR2 = 0.1359$ [$I > 2\sigma(I)$]. See ESI for further details†.

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