Synthesis of *N*-Sulfonylamidines by Catalyst-Free Hydroamination of Ynamides and Amines

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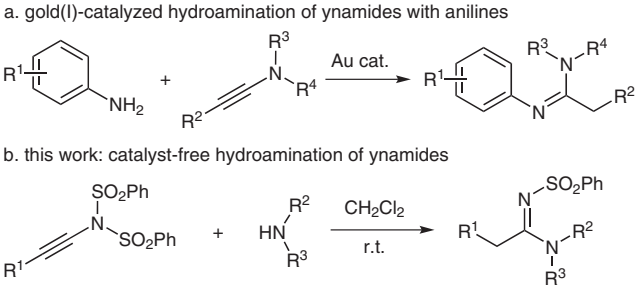
Abstract: A novel synthesis of *N*-sulfonylamidines by catalyst-free hydroamination of *N*,*N*-disulfonyl ynamides with amines was developed. Alkyl amines react with *N*,*N*-disulfonyl ynamides under mild conditions, whereas aryl amines require higher temperatures. Plausible mechanisms are proposed to explain this reaction.

Key words: amines, sulfonamides, aminations

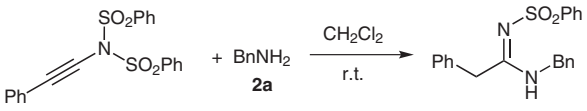
The amidine group is a fundamental motif of various bioactive natural products,[1] and amidines can serve as efficient coordinating ligands and important synthetic intermediates.[2] Although many methods have been established for the synthesis of amidines,[3] more-efficient strategies are still needed. The intermolecular hydroamination of alkynes is an efficient method for preparing substituted amines and imines or ketones.[4,5] Ynamides, an important subclass of alkynes, have emerged as important synthons in modern organic synthesis,[6–8] and a variety of synthetic targets, including amidines,[8a] have been constructed from ynamides. Recently, Skrydstrup and co-workers developed an elegant synthesis of amidines by gold(I)-catalyzed hydroamination of ynamides with anilines (Scheme 1, a).[9] However, there are few reports on catalyst-free hydroaminations of ynamides.[10] In the course of a study on hydroamination reactions of ynamides, we found that *N*,*N*-disulfonyl ynamides[11] react spontaneously with amines without any catalyst (Scheme 1, b). Here, we report this novel catalyst-free hydroamination reaction of ynamides that provides ready access to *N*-sulfonylamidines.

We began our studies by examining the reaction of equimolar ratios of ynamide **1a** and benzylamine (**2a**) in dichloromethane at room temperature. The expected *N*-sulfonylamidine **3a** was obtained in 27% yield in the absence of a catalyst (Table 1, entry 1). Increasing the quantity of amine **2a** to four equivalents significantly improved the yield of **3a** to 89% (entries 2 and 3). Subsequent screening of solvents showed that dichloromethane gave the best results, and that the use of other common solvents, such as toluene or tetrahydrofuran, did not improve the yield (entries 4–7). We therefore chose the following conditions as optimized conditions for all subsequent reactions: 0.5 mmol of **1** and 2.0 mmol of **2** in dichloromethane at room temperature for four hours with stirring.



Scheme 1 Synthesis of amidines from ynamides

Table 1 Optimization of the Reaction Conditions



Entry[a]	Solvent	Ratio **1a**/**2a**	Yield (%) of **3a**
1	CH_2Cl_2	1:1	27
2	CH_2Cl_2	1:2	55
3	CH_2Cl_2	1:4	89
4	THF	1:4	44
5	MeCN	1:4	70
6	toluene	1:4	64
7	DMF	1:4	76

[a] Unless otherwise specified, the reaction was carried out by using **1a** (0.5 mmol) and **2a** (0.5–2.0 mmol) in solvent (4 mL) at r.t. for 4 h.

By using these optimized conditions, we examined the scope of this catalyst-free hydroamination reaction. The reaction was successful for various *N*,*N*-disulfonyl ynamides **1**. The R^1 group of ynamide **1** can be a phenyl group optionally substituted with either an electron-donating or an electron-withdrawing group (Table 2, entries 1–5). A variety of amines, including primary, secondary, acyclic, and cyclic amines, were all efficiently coupled to give the corresponding *N*-sulfonylamidines (entries 1 and 5–8). The reaction was also successful when bulky *tert*-butylamine (**2e**) was used, albeit with a low yield (entry

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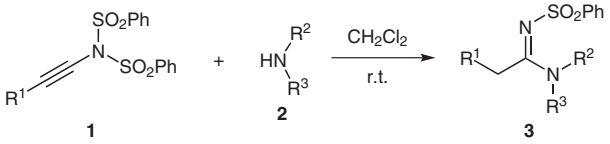
9). However, the presence of a free hydroxy group was not tolerated in this reaction (entry 10).

Aryl amines did not undergo the hydroamination reaction under these mild conditions. However, under modified conditions (1,4-dioxane solvent, 100 °C), anilines **2g–i** also reacted smoothly with ynamides **1a** to give the corresponding amidines **3j–l** (Scheme 2).

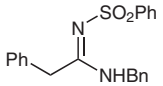
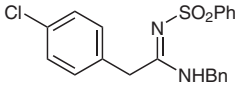
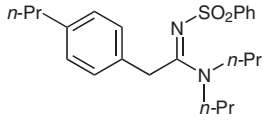
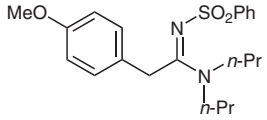
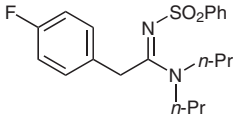
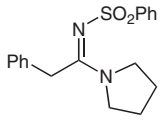
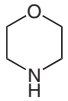
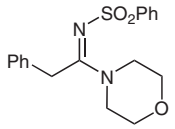
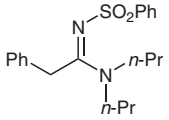
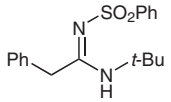
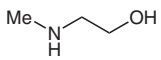
Note, however, that *N*-monosulfonyl ynamides **1f** and **1g** did not undergo this hydroamination reaction, even at 100 °C in 1,4-dioxane for 24 hours; in these cases, the starting material was recovered (Scheme 3).

In every case where reaction did occur, the sulfonamide $PhSO_2NR^2R^3$ was obtained as a byproduct; we therefore suggest the mechanism shown in Scheme 4. Ynamide **1** and amine **2** undergoes a spontaneous hydroamination reaction to form intermediate **A**, which is desulfonylated by a second molecule of amine **2** to give the *N*-sulfonylamidine product **3** (route a). Another elimination–addition

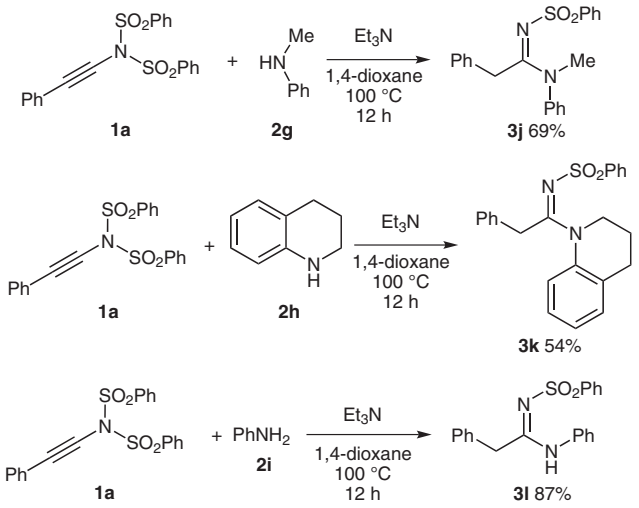
Table 2 Synthesis of *N*-Sulfonylamidines **3**[a]



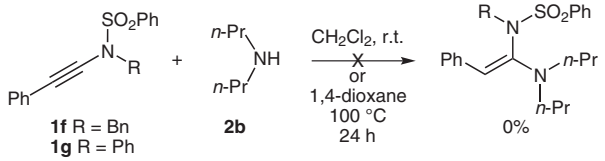
1 2 3

Entry	Ynamide (R^1)		Amine		Product		Yield (%)
1	**1a**	Ph	**2a**	$BnNH_2$	**3a**		89
2	**1b**	4-ClC_6H_4	**2a**	$BnNH_2$	**3b**		65
3	**1c**	4-PrC_6H_4	**2b**	Pr_2NH	**3c**		92
4	**1d**	4-$MeOC_6H_4$	**2b**	Pr_2NH	**3d**		88
5	**1e**	4-FC_6H_4	**2b**	Pr_2NH	**3e**		95
6	**1a**	Ph	**2c**		**3f**		65
7	**1a**	Ph	**2d**		**3g**		58
8	**1a**	Ph	**2b**	Pr_2NH	**3h**		66
9[b]	**1a**	Ph	**2e**	*t*-$BuNH_2$	**3i**		22
10	**1a**	Ph	**2f**			unidentified mixture	–

[a] Unless otherwise specified, the reaction was carried out by using **1** (0.5 mmol) and **2** (2.0 mmol) in CH_2Cl_2 (4 mL) at r.t. for 4 h.
[b] The reaction time was 24 h.



Scheme 2 Synthesis of amidines from aryl amines



Scheme 3 Attempted reaction with *N*-monosulfonyl ynamides

mechanism via the intermediate ketenimine **B** (route b) cannot be ruled out. Neither **A** nor **B** was detected.

In conclusion, we have described a novel synthesis of *N*-sulfonylamidines by a catalyst-free hydroamination of ynamides with amines. Alkyl amines react with *N*,*N*-disulfonyl ynamides under very mild conditions, whereas aryl amines require higher temperatures. Plausible mechanisms are proposed to explain this reaction, and further investigations on the mechanistic details and applications of this reaction are ongoing in our laboratory.

All commercially available chemicals and reagents were used without any further purification. Flash column chromatography was carried out by using 300–400 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer with TMS as the internal standard and $CDCl_3$ as solvent. High-resolution mass spectra were recorded on a Waters Micromass GCT mass spectrometer operating in the ESI-TOF mode. IR spectra were recorded on a Bruker Vector 22 spectrophotometer.

Ynamides were prepared by Muñiz's method.[11] The properties of previously unreported ynamides are listed below.

***N*-[(4-Chlorophenyl)ethynyl]-*N*-(phenylsulfonyl)benzenesulfonamide (1b)**

Pale-yellow solid; yield: 526.9 mg (61%); mp 139–141 °C (CH_2Cl_2).

IR (KBr): 3065, 2237, 1448, 1371, 1170, 1083, 823 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 4 H), 7.69–7.74 (m, 2 H), 7.56–7.60 (m, 4 H), 7.29–7.37 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 135.1, 135.0, 133.3, 129.4, 128.8, 128.6, 120.1, 77.0, 76.3.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{14}ClNNaO_4S_2$: 453.9945; found: 453.9946.

***N*-(Phenylsulfonyl)-*N*-[(4-propylphenyl)ethynyl]benzenesulfonamide (1c)**

Brown oil; yield: 606.5 mg (69%).

IR (neat): 2927, 2239, 1393, 1173, 1083, 841, 681 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 4 H), 7.71–7.73 (m, 2 H), 7.57–7.59 (m, 4 H), 7. 36 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 2.59 (t, *J* = 8.0 Hz, 2 H), 1.60–1.67 (m, 2 H), 0.94 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 137.9, 134.8, 132.3, 129.2, 128.61, 128.58, 118.7, 78.2, 74.7, 38.0, 24.3, 13.8.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{21}NNaO_4S_2$: 462.0804; found: 462.0810.

***N*-[(4-Methoxyphenyl)ethynyl]-*N*-(phenylsulfonyl)benzenesulfonamide (1d)**

Pale-yellow solid; yield: 607.0 mg (71%); mp 119–121 °C (CH_2Cl_2).

IR (KBr): 2935, 1604, 1569, 1392, 1264, 1173, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 4 H), 7.71–7.72 (m, 2 H), 7.57–7.59 (m, 4 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 3.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 137.9, 134.7, 134.3, 129.2, 128.6, 114.0, 113.5, 78.1, 74.1, 55.4.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{17}NNaO_5S_2$: 450.0440; found: 450.0438.

***N*-[(4-Fluorophenyl)ethynyl]-*N*-(phenylsulfonyl)benzenesulfonamide (1e)**

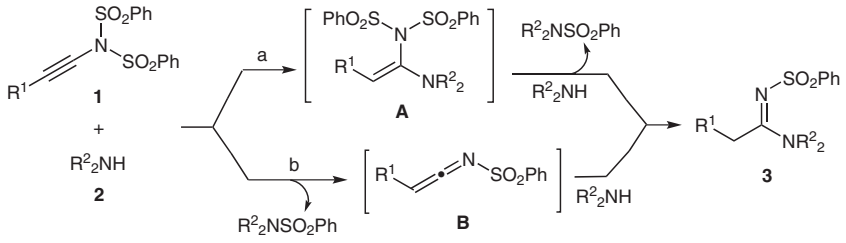
Light-gray solid; yield: 481.9 mg (58%); mp 126–128 °C (CH_2Cl_2).

IR (KBr): 3066, 2241, 1449, 1392, 1175, 1083, 834 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.06 (m, 4 H), 7.71–7.75 (m, 2 H), 7.58–7.60 (m, 4 H), 7.41–7.43 (m, 2 H), 7.01–7.04 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 161.8, 137.9, 134.9, 134.4, 134.3, 129.3, 128.6, 117.7, 115.9, 115.7, 75.0.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{14}FNNaO_4S_2$: 438.0240; found: 438.0245.



Scheme 4 Proposed reaction mechanisms

_N_-Benzyl-2-phenyl-_N′_-(phenylsulfonyl)ethanimidamide (3a); Typical Procedure

$BuNH_2$ (**2a**; 2.0 mmol, 214.4 mg, 4.0 equiv) was added to a solution of disulfonamide **1a** (0.5 mmol, 198.8 mg) in CH_2Cl_2 (4 mL), and the mixture was stirred at r.t. for 4 h until **1a** was consumed [TLC, hexane–EtOAc (6:1)]. The mixture was then concentrated and the residue was purified by flash chromatography [silica gel, hexane–EtOAc (6:1 to 4:1)] to give a pale-tan solid; yield: 162.4 mg (89%); mp 99–101 °C (CH_2Cl_2).

IR (KBr): 2922, 1552, 1265, 1140, 1090, 731, 688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.40–7.51 (m, 3 H), 7.18–7.33 (m, 8 H), 7.04–7.06 (m, 2 H), 5.96 (br s, 1 H), 4.40 (d, *J* = 5.6 Hz, 2 H), 4.29 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 143.4, 136.5, 133.1, 131.7, 130.0, 129.4, 128.7, 128.6, 128.1, 127.7, 127.6, 126.3, 45.9, 39.7.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{21}H_{20}N_2NaO_2S$: 387.1138; found: 387.1152.

_N_-Benzyl-2-(4-chlorophenyl)-_N′_-(phenylsulfonyl)ethanimidamide (3b)

Light-gray solid; yield: 130.4 mg (65%); mp 126–128 °C (CH_2Cl_2).

IR (KBr): 2924, 1551, 1270, 1138, 1089, 733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.38–7.49 (m, 3 H), 7.22–7.25 (m, 5 H), 7.06–7.13 (m, 4 H), 6.12 (br s, 1 H), 4.40 (d, *J* = 5.2 Hz, 2 H), 4.21 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 143.2, 136.4, 133.9, 131.7, 131.1, 129.4, 128.7, 128.6, 127.8, 127.7, 126.2, 46.0, 38.9.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{21}H_{19}ClN_2NaO_2S$: 421.0748; found: 421.0758.

_N′_-(Phenylsulfonyl)-_N_,_N_-dipropyl-2-(4-propylphenyl)ethanimidamide (3c)

Brown oil; yield: 185.2 mg (92%).

IR (neat): 2961, 1541, 1468, 1271, 1140, 1086, 727 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 2 H), 7.32–7.40 (m, 3 H), 7.01 (m, 4 H), 4.31 (s, 2 H), 3.34 (t, *J* = 8.0 Hz, 2 H), 3.05 (t, *J* = 8.0 Hz, 2 H), 2.49 (t, *J* = 8.0 Hz, 2 H), 1.53–1.58 (m, 4 H), 1.26–1.30 (m, 2 H), 0.87 (t, *J* = 8.0 Hz, 3 H), 0.79 (t, *J* = 8.0 Hz, 3 H), 0.68 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 144.3, 141.1, 131.5, 131.2, 128.9, 128.3, 127.8, 126.1, 50.8, 50.6, 37.5, 36.4, 24.5, 21.6, 20.0, 13.7, 11.4, 11.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{23}H_{32}N_2NaO_2S$: 423.2077; found: 423.2091.

2-(4-Methoxyphenyl)-_N′_-(phenylsulfonyl)-_N_,_N_-dipropylethanimidamide (3d)

Brown oil; yield: 170.6 mg (88%).

IR (neat): 2963, 1541, 1246, 1139, 1086, 833 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.86 (m, 2 H), 7.33–7.41 (m, 3 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 4.27 (s, 2 H), 3.70 (s, 3 H), 3.33 (t, *J* = 8.0 Hz, 2 H), 3.06 (t, *J* = 8.0 Hz, 2 H), 1.50–1.57 (m, 2 H), 1.28–1.34 (m, 2 H), 0.78 (t, *J* = 8.0 Hz, 3 H), 0.70 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 158.4, 144.2, 131.2, 129.0, 128.4, 126.3, 126.0, 114.2, 55.2, 50.8, 50.6, 36.0, 21.6, 20.0, 11.4, 11.1.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{21}H_{28}N_2NaO_3S$: 411.1713; found: 411.1730.

2-(4-Fluorophenyl)-_N′_-(phenylsulfonyl)-_N_,_N_-dipropylethanimidamide (3e)

Brown oil; yield: 178.4 mg (95%).

IR (neat): 2965, 1542, 1270, 1139, 1085, 834 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 6.4 Hz, 2 H), 7.34–7.37 (m, 3 H), 7.05–7.15 (m, 2 H), 6.86–6.90 (m, 2 H), 4.30 (s, 2 H), 3.32 (t, *J* = 5.6 Hz, 2 H), 3.03 (t, *J* = 5.6 Hz, 2 H), 1.51–1.53 (m, 2 H), 1.28–1.30 (m, 2 H), 0.76 (t, *J* = 8.0 Hz, 3 H), 0.68 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 162.3, 160.4, 144.1, 131.3, 130.20, 130.17, 129.64, 129.56, 128.4, 126.0, 115.8, 115.6, 50.8, 50.6, 36.0, 21.6, 20.0, 11.3, 11.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{25}FN_2NaO_2S$: 399.1513; found: 399.1522.

_N_-(2-Phenyl-1-pyrrolidin-1-ylethylidene)benzenesulfonamide (3f)

Pale-tan solid; yield: 106.6 mg (65%); mp 119–121 °C (CH_2Cl_2).

IR (KBr): 2977, 1539, 1195, 1136, 1086, 815, 727cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 2 H), 7.36–7.41 (m, 3 H), 7.13–7.24 (m, 5 H), 4.33 (s, 2 H), 3.54–3.60 (m, 2 H), 3.17–3.26 (m, 2 H), 1.75–1.83 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 144.2, 133.6, 131.3, 128.8, 128.5, 128.2, 126.8, 126.3, 49.0, 47.7, 38.3, 25.7, 24.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{20}N_2NaO_2S$: 351.1138; found: 351.1144.

_N_-(1-Morpholino-2-phenylethylidene)benzenesulfonamide (3g)

Light-gray solid; yield: 99.8 mg (58%); mp 121–123 °C (CH_2Cl_2).

IR (KBr): 2856, 1536, 1443, 1268, 1140, 1086, 720 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.93 (m, 2 H), 7.42–7.49 (m, 3 H), 7.21–7.30 (m, 3 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 4.45 (s, 2 H), 3.79–3.80 (m, 2 H), 3.62–3.63 (m, 2 H), 3.32–3.34 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 143.6, 134.0, 131.6, 129.1, 128.6, 127.9, 127.1, 126.4, 66.2, 66.1, 46.9, 45.0, 36.9.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{20}N_2NaO_3S$: 367.1087; found: 367.1086.

2-Phenyl-_N′_-(phenylsulfonyl)-_N_,_N_-dipropylethanimidamide (3h)

Pale-yellow solid; yield: 118.1 mg (66%); mp 110–112 °C (CH_2Cl_2).

IR (KBr): 2965, 1543, 1432, 1273, 1141, 1087, 727 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.88 (m, 2 H), 7.34–7.43 (m, 3 H), 7.17–7.25 (m, 3 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 4.37 (s, 2 H), 3.37 (t, *J* = 7.6 Hz, 2 H), 3.06 (t, *J* = 7.6 Hz, 2 H), 1.55–1.59 (m, 2 H), 1.31–1.35 (m, 2 H), 0.81 (t, *J* = 7.6 Hz, 3 H), 0.71 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 144.2, 134.4, 131.3, 128.9, 128.4, 127.9, 126.9, 126.1, 50.8, 50.6, 36.8, 21.6, 20.0, 11.4, 11.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{26}N_2NaO_2S$: 381.1607; found: 381.1611.

_N_-(*tert*-Butyl)-2-phenyl-_N′_-(phenylsulfonyl)ethanimidamide (3i)

Light-gray solid; yield: 36.3 mg (22%); mp 161–163 °C (CH_2Cl_2).

IR (KBr): 3309, 2917, 1546, 1273, 1138, 1088, 683 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.98 (m, 2 H), 7.45–7.52 (m, 3 H), 7.33–7.37 (m, 3 H), 7.20–7.22 (m, 2 H), 5.09 (br s, 1 H), 4.27 (s, 2 H), 1.22 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 143.8, 133.5, 131.5, 130.0, 129.4, 128.6, 128.1, 126.1, 53.4, 40.6, 28.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{22}N_2NaO_2S$: 353.1294; found: 353.1290.

_N_-Methyl-_N_,2-diphenyl-_N′_-(phenylsulfonyl)ethanimidamide (3j); Typical Procedure

PhNHMe (**2g**; 2.0 mmol, 214.4 mg, 4.0 equiv) was added to a solution of disulfonamide **1a** (0.5 mmol, 198.8 mg) in 1,4-dioxane (4 mL) containing Et_3N (0.5 mL), and the mixture was stirred at 100 °C for 12 h until **1a** was consumed [TLC, hexane–EtOAc (6:1)]. The mixture was then concentrated, and the residue was purified by flash chromatography [silica gel, hexane–EtOAc (6:1 to 4:1)] to give a brown oil; yield: 126.5 mg (69%).

IR (neat): 3062, 1530, 1277, 1143, 1088, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.0 Hz, 2 H), 7.45–7.48 (m, 3 H), 7.19–7.26 (m, 3 H), 7.06 (d, *J* = 4.0 Hz, 3 H), 6.77–6.79 (m, 4 H), 4.24 (s, 2 H), 3.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 143.9, 142.5, 134.6, 131.6, 129.6, 128.6, 128.5, 128.4, 128.3, 127.2, 126.5, 126.4, 41.2, 37.8.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{21}H_{20}N_2NaO_2S$: 387.1138; found: 387.1138.

_N_-[1-(3,4-Dihydroquinolin-1(2*H*)-yl)-2-phenylethylidene]benzenesulfonamide (3k)

Pale-yellow solid; yield: 104.9 mg (54%); mp 154–156 °C (CH_2Cl_2).

IR (KBr): 2951, 1522, 1492, 1278, 1142, 1085, 744 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.0 Hz, 2 H), 7.45–7.51 (m, 3 H), 7.10–7.18 (m, 6 H), 6.90–6.96 (m, 3 H), 4.59 (s, 2 H), 3.80–3.82 (m, 2 H), 2.21–2.23 (m, 2 H), 1.76–1.81 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 143.7, 138.4, 134.4, 131.7, 128.6, 128.4, 128.3, 127.0, 126.6, 126.4, 126.3, 124.9, 46.3, 37.6, 25.7, 23.5.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{23}H_{22}N_2NaO_2S$: 413.1294; found: 413.1299.

_N_,2-Diphenyl-_N′_-(phenylsulfonyl)ethanimidamide (3l)

Pale-tan solid; yield: 152.9 mg (87%); mp 160–162 °C (CH_2Cl_2).

IR (KBr): 3302, 3148, 1537, 1444, 1274, 1138, 1084 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.97 (br s, 0.38 H), 7.94–7.99 (m, 2 H), 6.86–7.54 (m, 14 H), 4.50 (s, 1.21 H), 3.58 (s, 0.8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 163.8, 143.2, 142.0, 136.7, 136.1, 134.4, 132.9, 132.4, 131.9, 130.2, 129.6, 129.5, 128.8, 128.7, 128.4, 127.1, 126.4, 125.8, 121.6, 40.6, 40.2.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{18}N_2NaO_2S$: 373.0981; found: 373.0989.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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