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Synthesis of *E*-Aryl Ethenesulfonamides: A Simple One-Pot, Two-Step Procedure from 1-Hydroxy-1-arylalkanes

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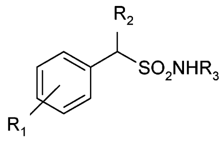
Abstract: The unusual reactivity of 1-phenyl-1-ethanesulfonic acid in thionyl chloride was investigated. Mechanistic considerations led us to set up a new and efficient synthesis of *E*-arylethenesulfonamides starting from 1-hydroxy-1-arylalkanes. The easy availability of the starting materials and the straightforward, one-pot procedure make this process an attractive method for the preparation of these compounds currently largely employed in chemical and pharmaceutical fields.

Sulfonamides are widely employed molecules in pharmaceutical research.[1,2] We have recently described[3] a novel class of acylmethanesulfonamides derived from (*S*) and (*R*) 2-arylpropionic acids showing the ability to inhibit IL-8 biological activities mediated by the cognate receptors CXCR1 and CXCR2.

In connection with our interest in Structure Activity Relationships within the novel class of IL-8 inhibitors we engaged the synthesis of α-substituted benzylsulfonamides (**A**) as potential new isosteres.[4] It is a general concern that α-alkylbenzylsulfonamides cannot be directly obtained from corresponding sulfonyl chlorides due to the tendency of these intermediates to give, by rapid desulfonylation, 1-phenyl-1-chloroalkanes. The formation of 1-chloro-1-phenylethane from 1-phenyl-1-ethanesulfonic acid by treatment with the chlorinating agent PCl_5 was described for the first time in 1938,[5] but,up to date detailed studies investigating the reactivity of these compounds are not known.



A

FIGURE 1.

TABLE 1. Percentage of Detected Compounds at Different Reaction Times[a,b]

entry	time[c] (h)	**2**	**4**	**5**	**7**
1	1	90	<2	<2	<2
2	5	66	15	<2	17
3	8	40	34	<2	24
4	12	7	80	<2	7

[a] Conversion of the starting material is complete after 1 h. [b] Yields calculated on isolated product. [c] Refluxing time of **1** in $SOCl_2$; After removal of $SOCl_2$ the residue was treated with ammonia (see the Experimental Section).

To solve this synthetic problem an alternative "dianion" based strategy has been set up[6] but, actually, very few examples of this class of molecules are known.[7a−d,8a] In our hands, 1-(4-isobutylphenyl)ethanesulfonic acid **1** undergoes the described desulfonylation reaction when heated at reflux in $CHCl_3$ with 3 equiv of thionyl chloride ($SOCl_2$); surprisingly, besides the main product **2**, small amounts of the rearranged ethenesulfonyl chloride **3** were also detected in the reaction mixture. Final treatment with ammonia affords the corresponding ethenesulfonamide **4** in low yields (Scheme 1).

Further experiments have shown that the reaction time and the amount of $SOCl_2$ favorably affect the yield of unsaturated compound **4**. Hence we decided to follow and isolate the reaction intermediates treating **1** at reflux in $SOCl_2$ for different reaction times.

The overall proposed synthetic pathway is depicted in Scheme 2. After 1 h the sulfonic acid **1** is transformed into the halide **2** and only traces of unsaturated compounds (Table 1; entry 1) are detectable. After 12 h and treatment with ammonia the unsaturated sulfonamide **4** was recovered from the reaction mixture in 80% yield. Moreover, 2-(4-Isobutylphenyl)-2-chloro-1-ethanesulfonamide **7** was isolated from the same reaction mixture (entry 4).

The formation of **4** and **7** accounts for the presence of the corresponding intermediate sulfonyl chlorides **3** and **6**. The mixture composition at intermediate times (entries 2 and 3) suggests that **6**, formed on charge of **2**, is the key intermediate to **3**. An E2 elimination pathway is in agreement with the observed stereochemistry of **4**.

Ammonia has been shown not to play a role in the rearrangement to the final product. In fact, direct analysis of the mixture before ammonia addition ($t = 8$ h) has revealed, by GC-MS and ^{1}H NMR analysis, the presence of sulfonyl chloride intermediates **3** and **6** in the same ratio as reported for the corresponding isolated amides (Table 1; entry 3).

Our hypothesis is that **6** is formed through the styrene intermediate **5**, even if only traces of **5** are detectable at any reaction time; the high reactivity of **5** could justify the observed low yield. The conversion of **5** to **6**, under our reaction conditions, is not easily understandable. In

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(1) Chazalette, C.; Riviere-Baudet, M.; Supuran, C. T.; Scozzafava, A. *J. Enzyme Inhib.* **2001**, *16* (6), 475−89.

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(4) Nagai, T.; Shingaki, T.; Inagaki, M.; Ohshima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52* (4), 1102−1106.

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(7) (a) Chazalette, C.; Riviere-Baudet, M.; Supuran, C. T.; Scozzafava, A. *J. Enzymol. Inhib.* **2001**, *16*, 475−489. (b) Davis, A. F.; Zhou, P. *J. Org. Chem.* **1993**, *58*, 4890−4896. (c) Nazarov, A. M.; Komissarov, V. D.; Tolstikov, G. A. *Zh. Org. Khim.* **1991**, *27* (4), 884−885. (d) Hartig, S. *J. Prakt. Chem.* **1966**, *Band 33*, 215−222.

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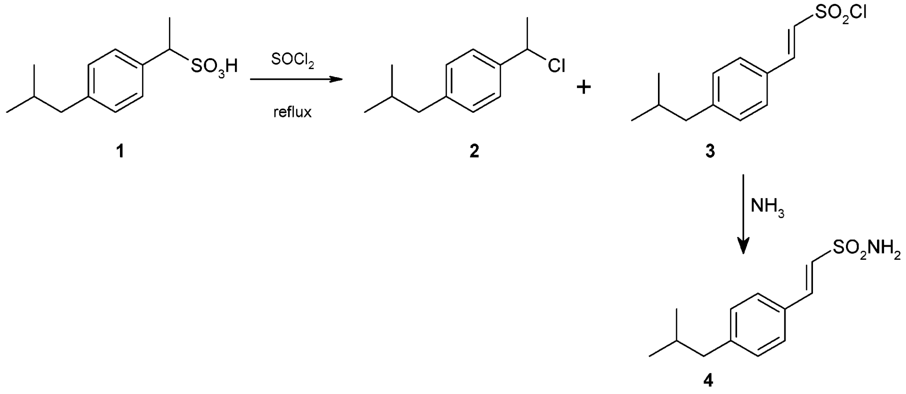
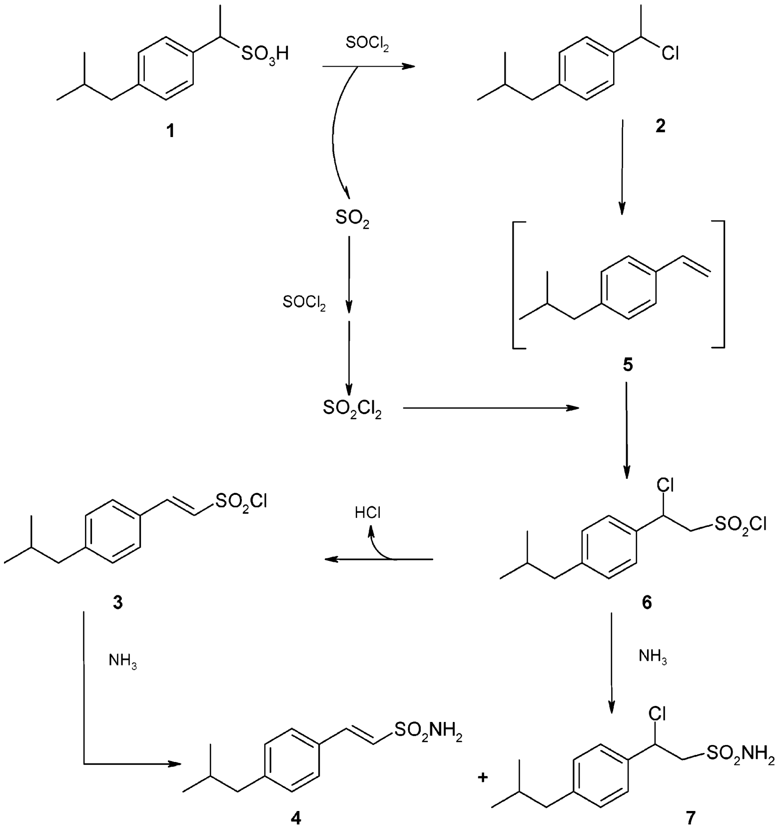
10.1021/jo034770f CCC: \$25.00

SCHEME 1



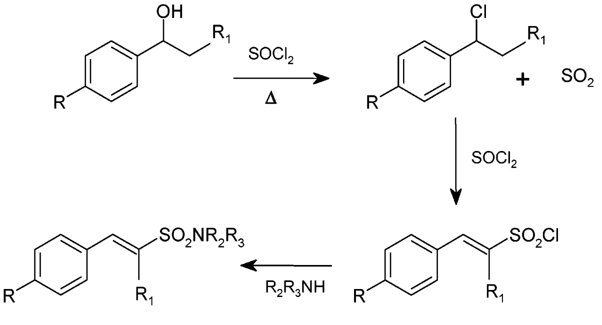
SCHEME 2



fact, as expected, reaction of 4-isobutylstyrene in thionyl chloride does not afford the corresponding ethenesulfonyl chloride. This observation suggests that a sulfur reactive species is generated during the first reaction step on charge of the sulfonic acid **1**. The presence of sulfuryl chloride (SO_2Cl_2) could account for the observed reactivity; in fact, the reaction of SO_2Cl_2 with styrenes is known from the literature[8a,b] to lead to ethenesulfonyl chlorides through an addition−elimination mechanism.

On the basis of these observations we hypothesize that sulfur dioxide (SO_2) formed during the first step is not taken away from the mixture, but reacts with excess $SOCl_2$ to give either SO_2Cl_2 or another species with similar reactivity. In agreement with this hypothesis the intermediate **2**, in the presence of only 1 equiv of $SOCl_2$, does not evolve.

SCHEME 3. Synthetic Pathway to *E*-arylethenesulfonamides



From a practical point of view 1-(aryl)alkanesulfonic acids cannot be considered suitable starting materials due to their low availability and synthetic difficulties. On

SCHEME 4

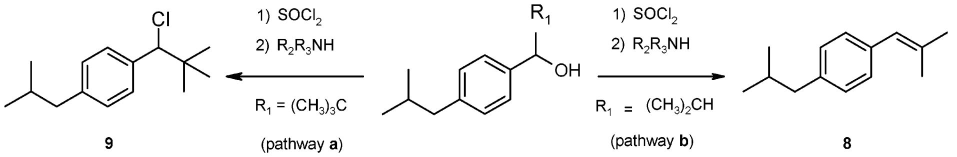


TABLE 2. Reactivity of 1-Hydroxy-1-arylalkanes to *E*-Arylethenesulfonamides

entry	R	R$_1$	R$_2$, R$_3$	yield (%)[a]
a	4-(CH$_3$)$_2$CHCH$_2$	H	H, H	80
b	4-(CH$_3$)$_2$CHCH$_2$	H	H, CH$_2$Ph	75
c	4-(CH$_3$)$_2$CHCH$_2$	H	CH$_3$, CH$_3$	78
d	4-(CH$_3$)$_2$CHCH$_2$	H	H, (CH$_2$)$_3$N(CH$_3$)$_2$	68
e	4-(CH$_3$)$_2$CHCH$_2$	CH$_3$	H, H	75
f	4-(CH$_3$)$_2$CHCH$_2$	CH$_2$CH$_3$	H, H	67
g	H	H	H, H	70
h	3-(CH$_3$)$_2$CH	H	H, H	70
i	4-C$_6$H$_5$CH$_2$	H	H, H	58
j	4-Cl	H	H, H	8
k	4-Br	CH$_3$	H, H	

[a] Isolated yield.

the other hand, based on the described mechanistic hypothesis, it is conceivable that 1-hydroxy-1-arylalkanes should be useful synthetic equivalents because the same intermediates, SO$_2$ and 1-chloro-1-arylalkanes, are generated in the reaction with SOCl$_2$. Hence, an optimized procedure for the direct conversion of 1-hydroxy-1-arylalkanes to *E*-arylethenesulfonamides has been set up. The synthetic pathway is based on a simple one-pot, two-step procedure and *E*-arylethenesulfonamides have been obtained in good yields from readily available starting materials (Scheme 3; Table 2).

Looking at the results listed in Table 2, we can conclude that the described procedure can be considered a suitable process to prepare highly substituted styrene derivatives in good yields starting from the corresponding hydroxyalkanes. This procedure also seems to be an attractive method for the synthesis of *E*-aryl ethenesulfonamides with the R$_1$ group other than hydrogen (entries e and f). Starting from the 4-bromo derivative (entry k), the corresponding ethenesulfonamide is not obtained; the main isolated reaction products, 1-chloro-(4-bromophenyl)propane and 1-(4-bromo)-2-methylstyrene, do not evolve to the final addition products. An unfavorable effect of electron-withdrawing groups on double bond reactivity seems confirmed by the low reactivity of the 4-chloro derivative (entry j).

In the Scheme 4 the behavior of branched 1-hydroxy-1-arylalkanes in the same reaction conditions is depicted. When R$_1$ is *tert*-butyl (pathway a) only the formation of *tert*-butylbenzyl chloride derivative **9** is, obviously, possible. Moreover, when R$_1$ is isopropyl (pathway b), the high percentage of recovered 1-(4-isobutyl)-2,2-dimethylstyrene **8** can be attributed to the unfavorable steric effect of the methyl group on the addition to the double bond.

In conclusion we have described a straightforward, one-pot, simple procedure for the synthesis of *E*-arylethenesulfonamides starting from 1-hydroxy-1-arylalkanes in good yields. The easy availability of the starting materials and the simple synthetic strategy make this process an attractive alternative method for the preparation of these substrates currently largely employed in chemical and pharmaceutical fields.

Experimental Section

1-(4-Isobutylphenyl)ethanesulfonic Acid (1). Sodium borohydride (0.16 g, 4.26 mmol) was added portionwise to a stirred solution of 4-isobutylacetophenone (0.5 g, 2.84 mmol) in methanol (7 mL). After 1 h of refluxing, the mixture was cooled at room temperature and 1 M HCl (5 mL) was added and the solvent distilled off. The resulting aqueous acid phase was extracted with EtOAc (3 × 5 mL) and the combined extract was washed with brine (2 × 15 mL) and dried over Na$_2$SO$_4$. Removal of the solvent under reduced pressure afforded the pure 1-hydroxy-1-(4-isobutylphenyl)ethane (0.495 g, 98%) as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 7.38 (d, 2H, $J = 7$ Hz), 7.18 (d, 2H, $J = 7$ Hz), 4.95 (q, 1H, $J = 7$ Hz), 4.52 (br s, 1H, O*H*), 2.50 (d, 2H, $J = 7$ Hz), 1.95 (m, 1H), 1.55 (d, 3H, $J = 7$ Hz), 1.02 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3345, 2980, 1500, 1380,1130; EI-MS *m*/*z* 178 (M$^+$).

Treatment of 1-hydroxy-1-(4-isobutylphenyl)ethane (0.4 g, 2.24 mmol) with thiolacetic acid and zinc iodide was performed as described.[9] The crude was purified by column chromatography (*n*-hexane/EtOAc 95:5) to give 1-[(4-isobutylphenyl)ethyl]thioacetate (0.43 g, 80%) as a yellow oil: ^{1}H NMR (CDCl$_3$) δ 7.35 (d, 2H, $J = 7$ Hz), 7.20 (d, 2H, $J = 7$ Hz), 4.75 (q, 1H, $J = 7$ Hz), 2.50 (d, 2H, $J = 7$ Hz), 2.35 (s, 3H), 1.85 (m, 1H), 1.65 (d, 3H, $J = 7$ Hz), 0.95 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 2900, 1700, 726, 628; EI-MS *m*/*z* 236 (M$^+$).

Treatment of 1-[(4-isobutylphenyl)ethyl]thioacetate (0.36 g, 1.52 mmol) with 30% H$_2$O$_2$ and acetic acid was performed as described[10] to give **1** (0.38 g, 95%) isolated as sodium salt: ^{1}H NMR (DMSO-d_6) δ 7.28 (d, 2H, $J = 7$ Hz), 7.05 (d, 2H, $J = 7$ Hz), 3.60 (q, 1H, $J = 7$ Hz), 2.45 (d, 2H, $J = 7$ Hz), 1.85 (m, 1H), 1.47 (d, 3H, $J = 7$ Hz), 0.90 (d, 6H, $J = 7$ Hz); IR (Nujol, cm^{-1}) ν 3400, 2950, 2750, 1220, 1200, 1170; EI-MS *m*/*z* 242 (M$^+$) (performed on isolated free acid).

Analytical Data for Compounds Listed in Table 1. All compounds listed in Table 1 have been obtained by purification of the crude from **4** preparation by column chromatography with *n*-hexane/EtOAc (gradient from 98:2 to 7:3) as eluent.

***E*-2-(4-Isobutylphenyl)ethenesulfonamide (4) (Table 2, entry a).** **1** sodium salt (0.27 g, 1.03 mmol) was dissolved in SOCl$_2$ (5 mL, excess). The solution was refluxed overnight and then cooled at room temperature. After SOCl$_2$ removal in vacuo the residue was diluted with dry THF (5 mL) and cooled at $T = 0-5$ °C in an ice/water bath. Ammonia (2 M solution in ethanol, 2.06 mmol) was added and the solution was left to rise to room temperature. After 1 h solvents were evaporated in vacuo and the residue was diluted with CHCl$_3$ (10 mL) and washed with water (2 × 10 mL). The organic layer was dried over Na$_2$SO$_4$. Purification, according to the above-described procedure, afforded the product **4** as a pale yellow oil (0.20 g, yield 80%): ^{1}H NMR (CDCl$_3$) δ 7.55 (d, 1H, $J = 14$ Hz), 7.38 (d, 2H, $J = 7$ Hz), 7.18 (d, 2H, $J = 7$ Hz), 6.88 (d, 1H, $J = 14$ Hz), 4.75 (br s, 2H, SO$_2$N*H*$_2$), 2.55 (d, 2H, $J = 7$ Hz), 1.94 (m, 1H), 1.02 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3250, 2980, 1322, 1160; EI-MS *m*/*z* 239 (M$^+$).

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(10) Corey, E. J.; Cimprich, K. A. *Tetrahedron Lett.* **1992**, *33* (29), 4099−4102.

1-Chloro-1-(4-isobutylphenyl)ethane (2): colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.25 (d, 2H, $J = 7$ Hz), 7.05 (d, 2H, $J = 7$ Hz), 5.05 (q, 1H, $J = 7$ Hz), 2.42 (d, 2H, $J = 7$ Hz), 1.80 (m, 1H, d, 3H, $J = 7$ Hz), 0.85 (d, 6H, $J = 7$ Hz); EI-MS m/z 196/198 ([$^{35/37}$Cl] M$^+$).

4-Isobutylstyrene (5): colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.30 (d, 2H, $J = 7$ Hz), 7.10 (d, 2H, $J = 7$ Hz), 6.75 (d, 1H, $J = 12$ Hz), 6.50 (d, 2H, $J = 12$ Hz), 2.40 (d, 2H, $J = 7$ Hz), 1.80 (m, 1H), 0.85 (d, 6H, $J = 7$ Hz); EI-MS m/z 160 (M$^+$).

2-(4-Isobutylphenyl)-2-chloro-1-ethanesulfonamide (7): yellow oil; ^{1}H NMR (CDCl$_3$) δ 7.35 (d, 2H, $J = 7$ Hz), 7.18 (d, 2H, $J = 7$ Hz), 5.20 (t, 1H, $J = 7$ Hz), 4.50 (br s, 2H, SO$_2$NH_2), 4.15 (d, 2H, $J = 7$ Hz), 2.35 (d, 2H, $J = 7$ Hz), 1.65 (m, 1H), 0.90 (d, 6H, $J = 7$ Hz); EI-MS m/z 275/277 ([$^{35/37}$Cl] M$^+$).

General Procedure for Preparation of *E*-Arylethenesulfonamides (Table 2). 1-Hydroxy-1-arylalkane (1.03 mmol) was dissolved in SOCl$_2$ (5 mL, excess). The solution was refluxed overnight and then cooled at room temperature. SOCl$_2$ was removed in vacuo, and the residue was diluted with dry THF (5 mL) and cooled at $T = 0-5$ °C in an ice/water bath. The selected amine (2.06 mmol) was added and the solution was allowed to rise to room temperature. After 1 h solvents were evaporated in vacuo and the residue diluted with CHCl$_3$ (10 mL), washed with water (2 × 10 mL), and dried over Na$_2$SO$_4$. Solvent removal under reduced pressure afforded a crude residue purified by flash chromatography to give pure products characterized by NMR, IR, and MS analysis.

***E*-2-(4-Isobutylphenyl)ethene-*N*-benzylsulfonamide (entry b):** white solid (eluent mixture: *n*-hexane/EtOAc 7:3); mp 118−121 °C; yield 75%; ^{1}H NMR (CDCl$_3$) δ 7.40 (d, 1H, $J = 14$ Hz), 7.25 (d, 2H, $J = 7$ Hz), 7.10 (d, 2H, $J = 7$ Hz), 6.58 (d, 1H, $J = 14$ Hz), 4.45 (br s, 1H, SO$_2$NH), 4.20 (d, 2H, $J = 5$ Hz), 2.45 (d, 2H, $J = 7$ Hz), 1.80 (m, 1H), 0.85 (d, 6H, $J = 7$ Hz); IR (Nujol, cm^{-1}) ν 3415, 2950, 1150, 1322; EI-MS m/z 329 (M$^+$).

***E*-2-(4-Isobutylphenyl)ethene-*N*,*N*-dimethylsulfonamide (entry c):** yellow oil (eluent mixture: *n*-hexane/EtOAc 8:2); yield 78%; ^{1}H NMR (CDCl$_3$) δ 7.45 (m, 3H), 7.21 (d, 2H, $J = 7$ Hz), 6.65 (d, 1H, $J = 14$ Hz), 2.85 (s, 6H), 2.55 (d, 2H, $J = 7$ Hz), 1.90 (m, 1H), 0.92 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3400, 2950, 1180, 990, 780; EI-MS m/z 267 (M$^+$).

***E*-2-(4-Isobutylphenyl)ethene-*N*-[3-(*N*,*N*-dimethylamino)propyl]sulfonamide (entry d):** yellow oil (eluent mixture: 5% TEA in CHCl$_3$/CH$_3$OH 8:2); yield 68%; ^{1}H NMR (CDCl$_3$) δ 7.45 (m, 3H), 7.20 (d, 2H, $J = 7$ Hz), 6.70 (d, 1H, $J = 14$ Hz), 3.18 (m, 2H), 2.50 (d, 2H, $J = 5$ Hz), 2.45 (m, 2H + SO$_2$NH), 2.30 (s, 6H), 1.92 (m, 1H), 1.75 (m, 2H), 0.92 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3414, 2900, 1148, 780; EI-MS m/z 324 (M$^+$).

***E*-2-(4-Isobutylphenyl)-1-methylethenesulfonamide (entry e):** yellow oil (eluent mixture: *n*-hexane/EtOAc 8:2); yield 75%; ^{1}H NMR (CDCl$_3$) δ 7.60 (s, 1H), 7.32 (d, 2H, $J = 7$ Hz), 7.15 (d, 2H, $J = 7$ Hz), 4.56 (br s, 2H, SO$_2$NH_2), 2.50 (d, 2H, $J = 7$ Hz), 2.35 (s, 3H), 1.88 (m, 1H), 0.97 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3300, 3250, 2950, 1322, 1159; EI-MS m/z 253 (M$^+$).

***E*-2-(4-Isobutylphenyl)-1-ethylethenesulfonamide (entry f):** yellow oil (eluent mixture: *n*-hexane/EtOAc 7:3); yield 67%; ^{1}H NMR (CDCl$_3$) δ 7.58 (s, 1H), 7.30 (d, 2H, $J = 7$ Hz), 7.18 (d, 2H, $J = 7$ Hz), 4.60 (br s, 2H, SO$_2$NH_2), 2.55 (d, 2H, $J = 7$ Hz), 2.45 (q, 2H, $J = 8$ Hz), 1.90 (m, 1H), 1.10 (t, 3H, $J = 8$ Hz), 0.97 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3260, 2950, 1322, 1159; EI-MS m/z 267 (M$^+$).

***E*-2-Phenylethenesulfonamide (entry g):** yellow oil (eluent mixture: *n*-hexane/EtOAc 7:3); yield 70%; ^{1}H NMR (CDCl$_3$) δ 7.55 (d, 1H, $J = 13$ Hz), 7.35 (m, 5H), 6.85 (d, 1H, $J = 13$ Hz), 4.72 (br s, 2H, SO$_2$NH_2); IR (neat, cm^{-1}) ν 3250, 2970, 1330, 1160; EI-MS m/z 183 (M$^+$).

***E*-2-(3-Isopropylphenyl)ethenesulfonamide (entry h):** yellow oil (eluent mixture: *n*-hexane/EtOAc 7:3); yield 70%; ^{1}H NMR (CDCl$_3$) δ 7.50 (d, 1H, $J = 13$ Hz), 7.20 (d, 1H, $J = 7$ Hz), 7.10 (m, 3H), 6.80 (d, 1H, $J = 13$ Hz), 4.72 (br s, 2H, SO$_2$NH_2), 2.90 (m, 1H), 1.02 (d, 6H, $J = 7$ Hz); IR (neat, cm^{-1}) ν 3220, 2910, 1340, 1110; EI-MS m/z 225 (M$^+$).

***E*-2-(4-Benzylphenyl)ethenesulfonamide (entry i):** yellow oil (eluent mixture: *n*-hexane/EtOAc 8:2); yield 58%; ^{1}H NMR (CDCl$_3$) δ 7.55 (d, 1H, $J = 13$ Hz), 7.35−7.10 (m, 9H), 6.80 (d, 1H, $J = 13$ Hz), 4.72 (br s, 2H, SO$_2$NH_2), 3.98 (s, 2H); IR (neat, cm^{-1}) ν 3300, 2900, 1290, 1160; EI-MS m/z 273 (M$^+$).

***E*-2-(4-Chlorophenyl)ethenesulfonamide (entry j):** yellow oil (eluent mixture: *n*-hexane/EtOAc 7:3); yield 8%; ^{1}H NMR (CDCl$_3$) δ 7.60 (d, 1H, $J = 13$ Hz); 7.30−7.20 (m, 4H), 6.65 (d, 1H, $J = 13$ Hz), 4.75 (br s, 2H, SO$_2$NH_2); IR (neat, cm^{-1}) ν 3300, 2970, 1330, 1160; EI-MS m/z 217/219 ([$^{35/37}$Cl] M$^+$).

Analytical Data for Compounds in Scheme 4. 1-(4-Isobutyl)-2,2-dimethylstyrene (8): colorless oil (eluent mixture: *n*-hexane/EtOAc 95:5); yield 80%; ^{1}H NMR (CDCl$_3$) δ 7.05 (m, 4H), 6.15 (s, 1H), 2.40 (d, 2H, $J = 7$ Hz), 1.80 (d, 6H, $J = 7$ Hz + m, 1H), 0.85 (d, 6H, $J = 7$ Hz); EI-MS m/z 188 (M$^+$).

1-(4-Isobutylphenyl)-1-chloro-2,2-dimethylpropane (9): colorless oil (eluent mixture: *n*-hexane/EtOAc 95:5); yield 80%; ^{1}H NMR (CDCl$_3$) δ 7.30 (d, 2H, $J = 7$ Hz), 7.12 (d, 2H, $J = 7$ Hz), 5.35 (s, 1H), 2.52 (d, 2H, $J = 7$ Hz), 1.95 (m, 1H), 1.08 (s, 9H), 0.95 (d, 6H, $J = 7$ Hz); EI-MS m/z 238/240 ([$^{35/37}$Cl] M$^+$).

Supporting Information Available: Elemental analysis data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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