Organometallic Reactions in Aqueous Media. Indium- and Zinc-Mediated Allylation of Sulfonimines[1]

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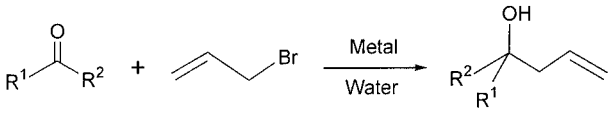
Sulfonimines derived from aryl and nonenolizable aliphatic aldehydes can be effectively allylated to the corresponding homoallylic sulfonamides with allylic bromides promoted by indium or zinc. The solvent used can be water, THF, or a mixed aqueous THF solvent. The regioselectivity and stereoselectivity of the reaction were studied.

Introduction

Allylation of carbonyl compounds and imines, giving the corresponding homoallylic alcohols or amines, is an important synthetic transformation, and a number of reagents have been developed for this purpose.[2] Recently, metal-mediated allylation of carbonyl compounds (Scheme 1) in aqueous media has attracted much interest.[3,4]

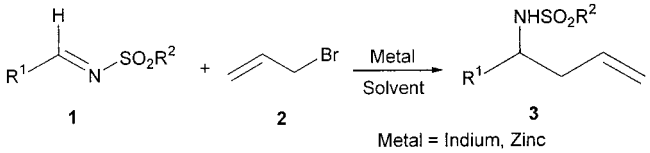
Scheme 1



Various metals have been exploited for the allylation reaction including zinc,[5] tin,[6] bismuth,[7] and indium.[8] Indium has been found to be the metal of choice because the allylation can proceed in water without the need of activation, and the amount of side products due to reduction or coupling of carbonyl compounds is often minimal.[9] However, the indium-mediated allylation reaction has been limited to carbonyl compounds. Extension of the reaction to aldimines to give the corresponding homoallylic amines in aqueous media has not been reported.[10] This could be attributed to the fact that aldimines are less electrophilic than the corresponding carbonyl compounds.[11] Previous attempts of indium-mediated allylation reaction toward aldimines in aqueous media suffered serious side reactions. Many imines are hydrolyzed to the corresponding carbonyl compounds before allylation occurs, thus giving the corresponding homoallylic alcohols instead.[12] Furthermore, it has also been reported that imines can homocouple by indium in aqueous media to give the corresponding 1,2-diamines.[13]

It is our expectation that the difficulties associated with the C=N bond in aqueous media can be overcome by using sulfonimines in place of simple imines.[14] In comparison to aldimines, sulfonimines are more electrophilic due to the strong electron-withdrawing sulfonyl group. Moreover, sulfonimines are more stable to hydrolysis than the aldimines. Sulfonimines offer the additional advantage that the sulfonyl group can be readily removed from the product homoallylic sulfonamides to give the corresponding primary amines.[15] We therefore investigated the metal-mediated allylation of sulfonimines in aqueous media (Scheme 2).

Scheme 2



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(15) For review, see: Davis, F. A.; Zhou, P.; Chen, B. C. *Chem. Soc. Rev.* **1998**, *27*, 13.

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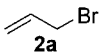
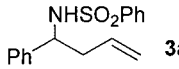
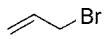
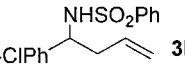
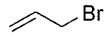
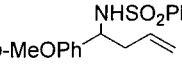
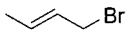
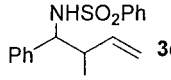
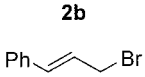
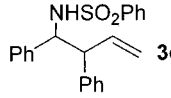
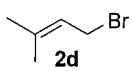
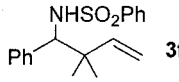
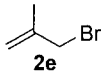
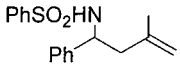
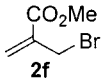
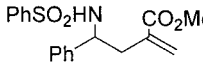
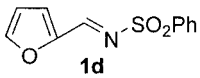
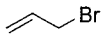
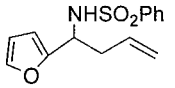
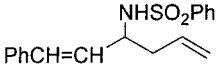
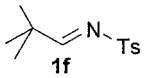
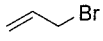
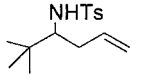
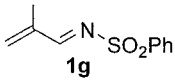
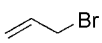
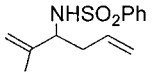
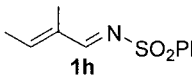
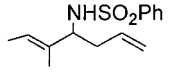
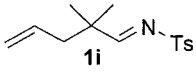
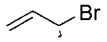
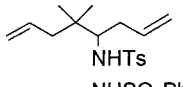
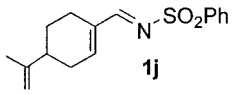
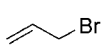
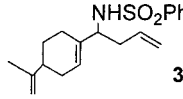
Table 1. Indium-Mediated Allylation Reaction with Sulfonimines

Entry	Sulfonimine	Allyl Bromide	Solvent	Product	Yield%[a]
1	PhCH=NSO$_2$Ph **1a**	 **2a**	THF Dioxane DMF H$_2$O	 **3a**	99[b] 99[b] 99[b] 95
2	*p*-ClPhCH=NSO$_2$Ph **1b**		H$_2$O H$_2$O:THF= 3:1	 **3b**	50[b] 95
3	*p*-MeOPhCH=NSO$_2$Ph **1c**		H$_2$O H$_2$O:THF= 3:1	 **3c**	80[b] 95
4	PhCH=NSO$_2$Ph	 **2b**	H$_2$O	 **3d**	92[c]
5	PhCH=NSO$_2$Ph	 **2c**	H$_2$O H$_2$O:THF= 1:1	 **3e**	50[d] 85[d]
6	PhCH=NSO$_2$Ph	 **2d**	H$_2$O:THF= 1:1	 **3f**	55
7	PhCH=NSO$_2$Ph	 **2e**	H$_2$O:THF= 1:1	 **3g**	95
8	PhCH=NSO$_2$Ph	 **2f**	H$_2$O:THF= 1:1	 **3h**	30
9	 **1d**		H$_2$O:THF= 1:1	 **3i**	97
10	PhCH=CH-CH=NSO$_2$Ph **1e**		H$_2$O:THF= 1:1	 **3j**	90
11	 **1f**		H$_2$O H$_2$O:THF= 1:1	 **3k**	<5 50
12	 **1g**		H$_2$O H$_2$O:THF= 1:1	 **3l**	35[b] 90
13	 **1h**		H$_2$O H$_2$O:THF= 1:1	 **3m**	40[b] 85
14	 **1i**		H$_2$O H$_2$O:THF= 1:1	 **3n**	<5 60
15	 **1j**		H$_2$O H$_2$O:THF= 1:1	 **3o**	36[b] 87

[a] Isolated yield. [b] Yields were determined by ^{1}H NMR spectra. [c] Ratios of syn/anti are shown in Table 3. [d] Only syn isomer was obtained.

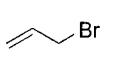
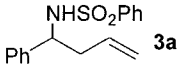
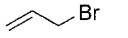
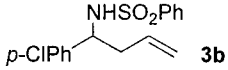
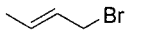
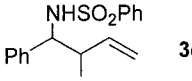
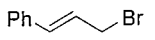
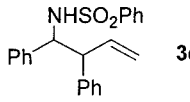
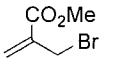
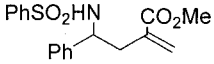
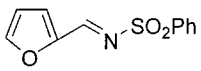
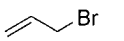
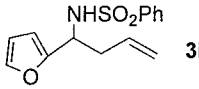
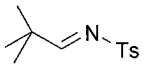
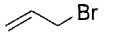
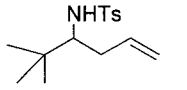
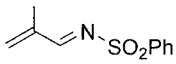
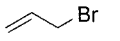
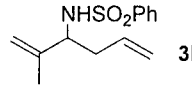
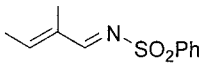
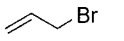
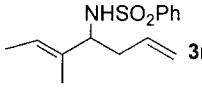
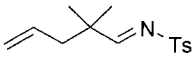
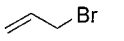
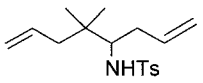
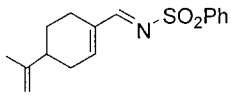
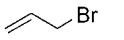
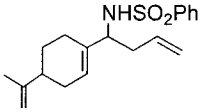
Results and Discussion

(1) Allylation of Sulfonimines Mediated by Indium. Barbier-type allylation reaction of a number of sulfonimines (**1**) mediated by indium was examined (Table 1). Homoallylic sulfonamides (**3**) were obtained in high yields (entries 1−15). The allylation can be smoothly carried out in THF, in pure water (entries 1−4), or in aqueous THF mixtures. In those cases where the solid sulfonimines had low solubility in water, adding some THF to the aqueous media was helpful in increasing the yields. The optimal medium for this allylation reaction seemed to be a 1:1 mixture of THF and water. When α,β-unsaturated sulfonimines were employed, only 1,2-adducts were obtained and no 1,4-allylation was observed (entries 10, 12, 13, and 15). Aliphatic sulfonimines (entries 11−15) were found to be generally less reactive than the aromatic sulfonimines, and the reaction needed longer reaction time with relatively lower yields obtained. Furthermore, it is worth noting that the preparation of aliphatic sulfonimines was restricted to those from non-enolizable aldehydes since sulfonimines bearing α-hydrogen undergo facile isomerization to give the corresponding unsaturated sulfonamides.[16]

(2) Allylation of Sulfonimines Mediated by Zinc. Similar allylation of sulfonimines in aqueous media medi-

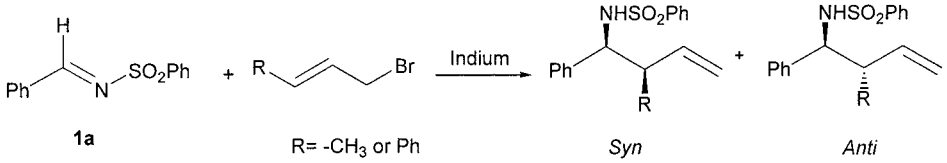
(16) Trost, B. M.; Marrs, C. *J. Org. Chem.* **1991**, *56*, 6468.

Table 2. Zinc Mediated Allylation Reaction with Sulfonimines in Saturated Aqueous NH_4Cl

Entry	Sulfonimine	Allyl Bromide	Product	Yield%[a]
1	PhCH=NSO$_2$Ph		 **3a**	99[b]
2	*p*-ClPhCH=NSO$_2$Ph		 **3b**	95
3	PhCH=NSO$_2$Ph		 **3d**	92[c]
4	PhCH=NSO$_2$Ph		 **3e**	87[d]
5	PhCH=NSO$_2$Ph		 **3h**	96
6			 **3i**	97
7			 **3k**	72
8			 **3l**	90
9			 **3m**	92
10			 **3n**	95
11			 **3o**	80

[a] Isolated yield. [b] Yield was determined by ^{1}H NMR spectra. [c] The ratio of syn/anti was 46:54. [d] Only syn isomer was obtained.

Scheme 3



ated by zinc was also investigated since zinc may mediate the coupling reaction through a mechanism different from that of indium.[17] In conformity with previous work on zinc-mediated allylation of carbonyl compounds, the reaction required the use of saturated aqueous ammonium chloride solution. Under these conditions, the zinc-mediated aqueous allylation reaction was faster than the indium-mediated reaction in water. The reaction was usually completed in 2 h to give high yields of the products (Table 2). Consequently, for the less reactive sulfonimines such as aliphatic sulfonimines or for the less reactive bromides, the zinc-mediated aqueous conditions were preferable to that of indium (Table 2, entries 4−10). An illustrative example was the reaction of the bezenesulfonimine **1a** with methyl 2-(bromomethyl)acrylate. (**2f**). Using indium, this reaction gave only 30% yield of the adduct **3h** (Table 1, entry 8) with formation of the homoallylic alcohol as the main side product. However, when the same reaction was mediated by zinc, the reaction proceeded smoothly in aqueous saturated NH_4Cl solution to give high yield of the product **3h** (Table 2, entry 4).

(3) Regioselectivity. Indium-mediated aqueous allylation reaction of sulfonimines showed excellent regioselectivity when crotyl (**2b**), cinnamyl (**2c**), or γ,γ-dimethylallyl bromide (**2d**) was used (Table 1, entries 4, 5, and 6). The γ-allylation products were obtained exclusively from the allylation, and no α-products were observed (Scheme 3). These results are in accord with the previously known regioselectivity observed for indium-mediated allylation reaction of carbonyl com-

(17) The nature of the allylmetal intermediate in indium-mediated aqueous Barbier-type allylation reaction has been deduced. However, up to now, no allylzinc intermediates have been observed. See: Chan, T. H.; Yang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3228.

Table 3. Reaction of Benzenesulfonimine (1a) with Crotyl Bromide (2b) in Different Solvents

entry	solvent (H_2O/THF)	yield[a] (%)	**3d** syn/anti
1	100:0	98	39:61
2	95:5	98	66:44
3	90:10	98	67:33
4	70:30	98	78:22
5	50:50	98	79:21
6	40:60	98	78:22
7	30:70	98	77:23
8	0:100	98	68:32

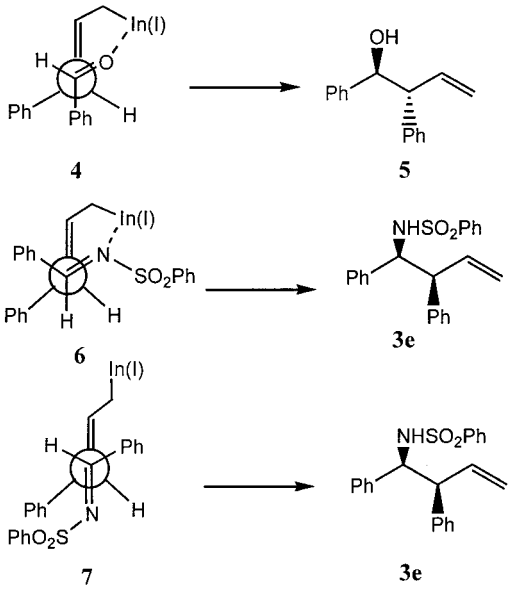
[a] Yields were determined by ^{1}H NMR spectra.

pounds.[18] Similar regioselectivity was observed in the zinc-mediated reaction using crotyl or cinnamyl bromide (Table 2, entries 3 and 10), also in agreement with the previously observed regiochemistry in the zinc-mediated allylation of carbonyl compounds.[19]

(4) Diastereoselectivity. In the allylation of benzenesulfonimine (**1a**) with cinnamyl bromide (**2c**) with indium in 1:1 H_2O/THF, the reaction gave only one crystalline compound **3e** in high yield (Table 1, entry 5). X-ray crystallography showed that the compound had the syn stereochemistry.[20] The same syn stereoisomer was obtained, albeit in lower yield, when the reaction was carried out in water alone. The syn selectivity in this case is to be contrasted with the situation in the indium-mediated allylation of benzaldehyde with cinnamyl bromide in water where an anti stereoselectivity was observed (anti/syn = 96:4).[18] On the other hand, the stereoselectivity in the indium-mediated coupling of benzenesulfonimine (**1a**) with crotyl bromide (**2b**) to give **3d** appeared to be quite solvent sensitive (Table 3). In pure water, the product **3d** was a mixture of anti and syn isomers (anti/syn = 61:39). Their stereochemistries were determined by removal of the sulfonyl groups with sodium in liquid ammonia to give the corresponding primary amines, the ^{1}H NMR of which were compared with the literature data.[21] However, when the reaction was performed in THF or a mixture of THF and water in various ratios, the diastereoselectivity of the reaction was reversed and moderate syn selectivity was obtained (Table 3). In comparison, crotylation of benzaldehyde in water mediated by indium gave a 50:50 mixture of the anti and syn isomers.[18] We have also examined briefly the diastereoselectivity of the zinc-mediated coupling reaction. In the coupling of benzenesulfonimine (**1a**) with cinnamyl bromide by zinc, the same syn isomer **3e** was obtained. With crotyl bromide, the product **3d** was also a mixture of anti and syn isomers with a slight preference for the anti compound (Table 2, entry 3).

(5) Discussion. The present investigation shows that sulfonimines can be effectively allylated with either indium or zinc and allyl bromides to give the corresponding homoallylic sulfonamides. The solvents used can be water, THF, or mixed aqueous THF solvents. Since the sulfonyl group can be readily removed, the reaction may be considered as a viable method for the synthesis of homoallylic primary amines. With unsymmetrical allylic bromides, the reaction showed good regioselectivity in conformity with previous observations on metal-mediated allylation of carbonyl compounds. In the case of indium, it has been suggested that the reaction proceeds through an allylindium(I) intermediate.[17] Furthermore, the allylindium(I) intermediate is postulated to react with the carbonyl compound via a six-membered chair transition state.[18,22] This has been used as the explanation to account for the regio- as well as the diastereoselectivity in the reaction of benzaldehyde with cinnamyl bromide to give compound **5** with anti stereochemistry (Scheme 4, **4** to **5**). If the same mechanism is invoked for the

Scheme 4



reaction between benzenesulfonimine **1a** and cinnamyl bromide with indium, a transition state such as **6** would have to be postulated to accommodate the transoid structure of the sulfonimine **1a**. While this would indeed lead to the formation of the syn product **3e**, there are considerable gauche interactions in **6**. Alternatively, a transition state such as **7** with fewer gauche interactions but with anti attack[23] of the allylindium on the electrophilic carbon center can also lead to the syn product **3e**. Information available at this time is insufficient for us to draw any definite conclusion. In the crotyl bromide case, the sensitivity of the diastereoselectivity to solvent composition (Table 3) does suggest that there may well be more than one possible mechanism operating in the reaction between allylindiums with sulfonimines. There has been no mechanistic studies regarding the zinc-mediated reaction, and reaction occurring at the metal surface cannot be excluded.[24] It is interesting to note, however, that the same syn product **3e** was obtained under the zinc-mediated conditions as in the indium-mediated reaction.

Experimental Section

Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plastic-backed plates and was visualized by dipping into a solution of ammonium molybdate (2.5 g) and

(18) Isaac, M. B.; Chan, T. H. *Tetrahedron Lett.* **1995**, *36*, 9857.
(19) Petrier, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 910.
(20) We thank Dr. C. Pearson and Dr. A. Debuis of Department of Chemistry, McGill University, for X-ray crystallographic structure determination of **3e**.
(21) Hoffmann, R. W.; Endesfelder, A. *Liebigs Ann. Chem.* **1987**, 215.
(22) Marshall, J. A. *Chemtracts—Org. Chem.* **1997**, *10*, 481.
(23) The possibility of anti attack of allylmetal on the electrophilic carbon center has been postulated previously to account for the change in diastereoselectivity. See ref 2.
(24) The mechanism of magnesium-mediated allylation of carbonyl compounds in aqueous media has been discussed. See: Li, C. J.; Zhang, W. C. *J. Am Chem. Soc.* **1998**, *120*, 9102.

ceric sulfate (1 g) in concentrated H_2SO_4/H_2O (10 mL/90 mL) and heated with a heat gun. Solvents were reagent grade unless otherwise specified. Indium and zinc powder were freshly opened for use. Allyl bromide compounds were checked for purity by ^1H NMR and were distillated or recrystallized if impure. Sulfonimines, **1a**−**d**,[25a] **1e**[25b] **1g**,[25b] **1h**,[25b] **1j**,[25b] **1f**,[16] and **1i**[16] were prepared following the method reported in the literature.[25]

General Procedure. (A) Allylation of Sulfonimines Mediated by Indium. To a stirred mixture of the sulfonimine (**1**, 0.5 mmol) and allyl bromide (**2**, 1.5 mmol) in aqueous or organic solvent (4 mL) was added indium (1.5 mmol) powder. The reaction was stirred overnight, quenched by adding 1 N HCl (2 mL), and extracted with ether (2 × 15 mL). The combined organic phase was washed with saturated $NaHCO_3$ solution and brine and dried over anhydrous Na_2SO_4. The crude product, after evaporation of ether, was purified by flash column chromatography on silica gel (eluent: 10−15% ethyl acetate in hexane).

(B) Allylation of Sulfonimine by Zinc. To a vigorously stirred mixture of the sulfonimine (**1**, 0.5 mmol) and allyl bromide (**2**, 1.5 mmol) in saturated NH_4Cl aqueous solution (4 mL) was added zinc (1.5 mmol) powder. The reaction was stirred for 2 h, quenched by adding 1 N HCl (2 mL), and extracted with ether (2 × 15 mL). The combined organic phase was washed with saturated $NaHCO_3$ solution and brine and dried over anhydrous Na_2SO_4. The crude product, after evaporation of ether, was purified by flash column chromatography on silica gel (eluent: 10−15% ethyl acetate in hexane).

***N*-(1-Phenyl-3-butenyl)benzenesulfonamide (3a)** white solid; mp 80−81 °C; IR (neat, cm^{-1}) 3279, 1448, 1323, 1161; ^1H NMR (200 MHz, $CDCl_3$) δ 7.78−7.63 (m, 2H), 7.50−7.25 (m, 4H), 7.18−7.03 (m, 4H), 5.64 (ddt, 1H, J = 17.5, 9.6, 7.1 Hz), 5.15−4.94 (m, 2H), 5.03 (br 1H), 4.42 (dt, 1H, J = 6.7, 6.7 Hz), 2.47 (dd, 2H, J = 7.0, 7.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.6, 140.3, 133.3, 132.5, 129.0, 128.7, 127.8, 127,4, 126,8, 119.7, 58.4, 43.2; MS (CI, NH_3) *m/e* 288 (M + H^+, 1), 246 (100); HRMS c alcd for $C_{16}H_{17}NO_2S + H^+$ 288.1058, found 288.1059. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.77; H, 6.36; N, 4.87.

***N*-[1-(4-Chlorophenyl)-3-butenyl)benzenesulfonamide (3b):** white solid; mp 108−110 °C; IR (neat, cm^{-1}) 3252, 1453,1318, 1162; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65−7.64 (m, 2H), 7.51−7.48 (m, 1H), 7.38−7.35 (m, 2H), 7.12 (d, 2H, J = 8.5 Hz), 7.00 (d, 2H, J = 8.5 Hz), 5.52−5.44 (ddt, 1H, J = 17.0, 10.5, 7.0 Hz), 5.10−5.05 (m, 2H), 4.95 (d, 1H, J = 6.5 Hz), 4.38 (dt, 1H, J = 7.0, 7.0 Hz), 2.41 (dd, 2H, J = 7.0, 7.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.1, 138.5, 133.1, 132.4, 132.3, 128.6, 128.3, 127.8, 126.9, 119.7, 56.3, 41.6; MS (CI, NH_3) *m/e* 322 (M + H^+, 31), 165 (98), 136 (100); HRMS calcd for $C_{16}H_{16}ClNO_2S + H^+$ 322.0669, found 322.0667. Anal. Calcd for $C_{16}H_{16}ClNO_2S$: C, 59.71; H, 5.01; N, 4.35. Found: C, 59.54; H, 5.28; N, 4.31.

***N*-[1-(4-Methoxyphenyl)-3-butenyl)benzenesulfonamide (3c):** white solid; mp 71−73 °C; IR (neat, cm^{-1}) 3279,1612, 1447, 1322,1157; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66−7.47(m, 1H), 7.54−7.32 (m, 3H), 6.97 (d, 2H, J = 8.5 Hz), 6.69 (d, 2H, J = 8.5 Hz), 5.65−5.42 (ddt, 1H, J = 17.4, 9.9, 6.8 Hz), 5.07−5.04 (m, 2H), 4.80 (br, 1H), 4.36 (dt, 1H, J = 6.8, 6.8 Hz), 3.76 (s, 3H), 2.46 (ddd, 2H, J = 6.9, 6.9, 1.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 140.34, 133, 132.1, 132, 128.5, 127.6, 126.9, 119.1, 113.6, 56.5, 55, 41.7; MS (FAB, NaCl) *m/e* 340 (M + Na^+, 4), 276 (82), 161(100); HRMS calcd for $C_{17}H_{19}NO_3S + Na^+$ 340.0983, found 340.0984. Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.53; H, 6.44; N, 4.90.

***N*-(1-Phenyl-2-methyl-3-butenyl)benzenesulfonamide-(3d):** white solid; mp 128−130 °C; IR (neat, cm^{-1}) 3264, 1450, 1319, 1163; ^1H NMR (500 MHz, $CDCl_3$) δ syn isomer 7.60−7.58 (m, 1H), 7.42−7.36 (m, 1H), 7.28−7.24 (m, 3H), 7.13−7.08 (m, 3H), 6.93−6.89(m, 2H), 5.48−5.41 (ddd, 1H, J = 17.5,10.0, 8.0 Hz), 5.40−5.05 (m, 2H), 4.95 (d, 1H, J = 8.0 Hz), 4.30 (dd, 1H, J = 8.0, 5.8 Hz), 2.58−2.50 (m, 1H), 0.93 (d, 3H, J = 7.0 Hz); anti isomer 7.55−7.52 (m, 1H), 7.40−7.36 (m, 1H), 7.28−7.24 (m, 3H), 7.13−7.08 (m, 3H), 7.03−6.99 (m, 2H), 5.62−5.54 (ddd, 1H, J = 17.5, 10.5, 8.5 Hz), 5.18−5.12 (m, 2H), 4.98 (d, 1H, J = 8.0 Hz), 4.10 (dd, 1H, J = 8.0, 5.5 Hz), 2.44−2.38 (m, 1H), 0.83 (d, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 138.4 (anti 139.1), 137.8, 132.0, 131.9, 128.4, 128.3, 127.9, 127.7, 127.2, 127, 126.9, 126.7, 116.9 (117.5), 0.61.4 (61.9), 43.7(44.4), 16.1(16.8); MS (FAB + NaCl) *m/e* 324 (M + Na^+, 9.6), 301 (M, 0.6), 246 (78), 145 (100); HRMS calcd for $C_{17}H_{19}NO_2S + Na^+$ 324.1034, found 324.1033. Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.75; H, 6.84; N, 4.61.

***N*-(1,2-Diphenyl-3-butenyl)benzenesulfonamide (3e):** white solid; mp 140−142 °C; IR (neat, cm^{-1}) 3265, 1450, 1320, 1162; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52−6.82 (m, 15H); 5.85−5.60 (ddd, 1H, J = 18.6, 10.2, 8.3 Hz), 5.06−4.82 (m, 2H), 4.83 (d, 1H, J = 6.0 Hz), 4.58 (dd, 1H, J = 7.5, 6.0 Hz), 3.55 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.2, 139.1, 138.3, 136.5, 132.4, 129.1, 128.8, 128.7, 128.2, 128.1, 127.8, 127.7, 127.7, 127.4, 118.7, 62.7, 57.6; MS (CI, NH_3) *m/e* 364 (M + H^+, 5), 246 (100); HRMS calcd for $C_{22}H_{21}NO_2S + H^+$ 364.1371, found 364.1371. Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found: C, 72.68; H, 6.26; N, 3.84.

***N*-(1-Phenyl-2,2-dimethyl-3-butenyl)benzenesulfonamide (3f):** white solid; mp 119−120 °C; IR (neat, cm^{-1}) 3276, 1446, 1317, 1160; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.52 (m, 2H), 7.40−7.39 (m, 1H), 7.26−7.23 (m, 3H), 7.04−7.01 (m, 2H), 6.86−6.84 (m, 2H), 5.56 (dd, 1H, J = 18.0, 11.0 Hz), 5.17−5.06 (m, 2H), 4.93 (d, 1H, J = 7.5 Hz), 4.07 (d, 1H, J = 7.0 Hz), 1.05 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.84, 142.46, 139.85, 135.84, 132.9, 132.0, 129.5, 128.4, 127.5, 126.8, 123.4, 115.5, 64.8, 40.8, 24.7; MS (CI, NH_3) *m/e* 316 (M + H^+, 4.3), 246 (100); HRMS calcd for $C_{18}H_{21}NO_2S + H^+$ 316.1371, found 316.1371. Anal. Calcd for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.63; H, 7.05; N, 4.46.

***N*-(1-Phenyl-3-methyl-3-butenyl)benzenesulfonamide (3g):** white solid; mp 72−74 °C; IR (neat, cm^{-1}) 3281, 1448, 1323, 1161; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65−7.62 (m, 2H), 7.50−7.25 (m, 3H), 7.20−7.07 (m, 5H), 4.98−4.48 (br 1H), 4.84 (s, 1H), 4,75 (s, 1H), 4.47−4.35 (dt, 1H, J = 7.4, 4.8 Hz), 2.36 (d, 2H, J = 7.4 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 141.2, 140.9, 140.3, 128.9, 128.6, 127.8, 127.5, 126.9, 115.7, 56.8, 48.0, 23.1; MS (CI, NH_3) *m/e* 302 (M + H^+, 0.6), 246 (100), 145 (62); HRMS calcd for $C_{17}H_{19}NO_2S + H^+$ 302.1215, found 302.1216. Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.73; H, 6.81; N, 4.63.

Methyl ester of α-methylene-γ-[(phenylsulfonyl)amino]benzenebutanoic acid (3h): colorless oil; IR (neat, cm^{-1}) 3283, 1716, 1446, 1326, 1160; ^1H NMR (200 MHz, $CDCl_3$) δ 7.70−7.10 (m, 10H), 6.11 (s, 1H), 5.52 (s, 1H), 5.56−5.53 (br, 1H), 4.61−4.50 (dt, 1H, J = 7.3, 7.3 Hz), 3.71 (s, 3H), 2.65 (d, 2H, J = 7.4 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 167.5, 140.7, 136.1, 132.4, 129.4, 128.9, 128.7, 127.8, 127.3, 126.7, 59.0, 53.4, 41.7; MS (CI, NH_3) *m/e* 346 (M + H^+, 4.1), 246 (100); HRMS calcd for $C_{18}H_{19}NO_4S + H^+$ 346.1113, found 346.1112. Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06. Found: C, 62.24; H, 5.45; N, 4.22.

***N*-[1-(2-Furanyl)-3-butenyl]benzenesulfonamide (3i):** white solid; mp 61−63 °C; IR (neat, cm^{-1}) 3276, 1447, 1329, 1162, 1094; ^1H NMR (200 MHz, $CDCl_3$) 7.78−7.73 (m, 2H), 7.74−7.40 (m, 3H), 7.13 (d, 1H, J = 1.8 Hz), 6.13−6.10 (dd, 1H, J = 3.2, 1.8 Hz), 5.94 (d, 1H, J = 3.2 Hz), 5.70−5.48 (ddt, 1H, J = 17.8, 9.3, 6.9 Hz), 5.09−5.01(m, 2H), 5.05 (br, 1H), 4.58−4.46 (dt, 1H, J = 6.7, 6.7 Hz), 2.53(m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 151.5, 141.15, 139.82, 131.94, 131.69, 128.17, 126.36, 118.71, 109.63, 106.81, 51.42, 39.52; MS (EI) *m/e* 278 (M + H^+, 0.8), 236 (100), 141 (44); HRMS calcd for $C_{14}H_{15}NO_3S + H^+$ 278.0851, found 278.0851. Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.96; H, 5.43; N, 4.99.

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***N*-[1-(2-Phenylethenyl)-3-butenyl]benzenesulfonamide (3j):** colorless oil; IR(neat, cm^{-1}) 3278, 1642, 1447, 1326, 1162; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92−7.82 (m, 2H), 7.58−7.40 (m, 3H), 7.40−7.08 (m, 5H), 6.33 (d, 1H, J = 16.0 Hz), 5.83 (dd, 1H, J = 16.0, 6.9 Hz), 5.75−5.54 (m, 1H), 5.12−5.04 (m, 2H), 4.84 (d, 1H, J = 7.3 Hz), 4.14−4.01(m, 1H), 2.33 (dd, 2H, J = 6.9, 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 135.9, 132.6, 132.3, 131.5, 128.8, 128.3, 128.11, 127.6, 127.1, 126.2, 119.3, 55.1, 40.0; MS (FAB, NBA + NaCl) *m/e* 336 (M + Na^+, 3.8), 313 (M^+, 0.8), 77 (100); HRMS calcd for $C_{18}H_{19}NO_2S + Na^+$ 336.1034, found 336.1034. Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47. Found: C, 68,87; H, 6.35; N, 4.93.

***N*-[3-(5, 5-Dimethyl-1-hexenyl)]-*p*-tolylsulfonamide (3k):** white solid; mp 122−124 °C; IR (neat, cm^{-1}) 3287, 2972, 1427, 1323, 1157; ^1H NMR (200 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.2 Hz), 7.26 (d, 2H, J = 8.2 Hz), 5.55−5.34 (m, 1H), 4.88−4.76 (m, 2H), 4.49 (d, 1H, J = 8.0 Hz), 3.19−3.08 (ddd, 1H, J = 8.1, 5.1, 4.4 Hz), 2.42 (s, 3H), 2.32−2.20 (m, 1H), 2.06−1.90 (m, 1H), 0.86 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 143.1, 139.1, 135.3, 129.7, 127.5, 117.9, 63.6, 37.4, 36.6, 28.4, 23.1; MS (CI, NH_3) *m/e* 282 (M + H^+, 60), 240(100); HRMS calcd for $C_{15}H_{23}NO_2S + H^+$ 282.1528, found 282.1527. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24; N, 4.98. Found: C, 64.48; H, 8.59; N, 5.05.

***N*-[3-(2-Methyl-1,5-hexadienyl)]benzenesulfonamide (3l):** white solid; mp 80−82 °C; IR (neat, cm^{-1}) 3275, 1648, 1449, 1308, 1161; ^1H NMR (200 MHz, $CDCl_3$) δ 7.87−7.82 (m, 2H), 7.53−7.48 (m, 3H), 5.62−5.41 (ddt, 1H, J = 15.5, 14.0, 7.0 Hz), 5.08−4.98 (m, 2H), 4.80 (s, 1H), 4.77 (s, 1H), 6.20 (d, 1H, J = 6.8 Hz), 3.83−3.74 (dd, 1H, J = 6.9, 6.9 Hz), 2.36−2.12 (m, 2H), 1.56 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 143.1, 140.8, 133.3, 132.8, 129.1, 127.5, 119.3, 113.9, 59.6, 39.6, 19.8; MS (CI/NH_3) *m/e* 252 (M + H^+, 16), 210 (100); HRMS calcd for $C_{13}H_{17}NO_2S + H^+$ 252.1058, found 252.1059. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.42; H, 7.03; N, 5.64.

***N*-[4-(5-Methyl-1,5-heptadienyl)]benzenesulfonamide (3m):** white solid; mp 71−73 °C; IR (neat, cm^{-1}) 3279, 1448, 1325, 1161; ^1H NMR (200 MHz, $CDCl_3$) δ 7.83−7.78 (m, 2H), 7.58−7.38 (m, 3H), 5.65−5.43 (ddt, 1H, J = 17.5, 9.6, 7.0 Hz), 5.34−5.21 (m, 1H), 5.07−5.05 (m, 2H), 4.69 (d, 1H, J = 6.2 Hz), 3.81−3.71 (m, 1H), 2.34−2.09 (m, 2H), 1.37 (d, 3H, J = 6.7 Hz), 1.26 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 141.0, 133.9, 133.2, 132.5, 128.9, 127.7, 123.5, 118.7, 61.8, 39.7; MS (CI/NH_3) *m/e* 266 (M + H^+, 8.8), 224 (100); HRMS calcd for $C_{14}H_{19}NO_2S + H^+$ 266.1215, found 266.1215. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.69; H, 7.50; N, 5.34.

***N*-[4-(5,5-Dimethyl-1,7-octadienyl)]-*p*-tolylsulfonamide (3n):** white solid; mp 59−60 °C; IR (neat, cm^{-1}) 3288, 2970, 1431, 1323, 1158; ^1H NMR (200 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.1 Hz), 7.27 (d, 2H, J = 8.1 Hz), 5.90−5.69 (ddt, 1H, J = 16.9,14.3,11.4 Hz), 5.53−5.32 (ddt, 1H, J = 17.2, 9.9, 6.9 Hz), 5.07−4.95 (m, 2H), 4.86−4.74 (m, 2H), 4.41 (d, 1H, J = 9.6 Hz), 3.26−3.15 (ddd, 1H, J = 9.2, 5.1, 4.1 Hz), 2.41 (s, 3H), 2.34−2.21 (m, 1H), 2.00 (d, 2H, J = 7.3 Hz), 2.06−1.91 (m, 1H), 0.85 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 143.1, 139.2, 135.2, 134.83, 129.7, 127.5, 118.1, 118.0, 62.7, 45.2, 39.4, 37.1, 26.0, 25.4, 23.1; MS (CI/NH_3) *m/e* 308(M + H^+, 49.4), 266(91), 224 (100); HRMS calcd for $C_{17}H_{25}NO_2S + H^+$ 308.1684, found 308.1686. Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.21; H, 8.61; N, 4.69.

1*R*-*N*-[1-[4*S*-(2-propenyl)cyclohexenyl]-3-butenyl]benzenesulfonamide and 1*S*-*N*-[1-[4*S*-(2-propenyl)cyclohexenyl]-3-butenyl]benzenesulfonamide (3o): white solid; mp 75−76 °C, de = 51% (determined by ^{13}C NMR, the absolute configuration was not assigned); IR (neat, cm^{-1}) 3276, 2921, 1447, 1323, 1160; ^1H NMR (200 MHz, $CDCl_3$) 7.86−7.82 (m, 2H), 7.63−7.41 (m, 3H), 5.66−5.42 (m, 1H), 5.51−5.45 (m, 1H), 5.12−4.86 (m, 2H), 4.86 (br, 1H), 4.70−4.52 (m, 2H), 3.86−3.76 (m, 2H), 2.37−2.10 (m, 2H), 1.65 (s, 3H), 1.48−1.98 (m, 6H), 1.40−1.25 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) (the ^{13}C NMR signals in parentheses are from two diasteroisomers) δ 149.4, 141.2, 134.8, 133.9 (133.7), 132.6 (132.5), 129.0, 127.8 (127.7), 125.2(126.1), 118.8, 109.2, 60.2(60.3), 41.8(42.3), 39.7 (39.3), 31.7 (31.8), 28.4 (28.3), 25.6 (25.3), 22.3; MS (FAB, NBA + NaCl) *m/e* 354 (M + Na^+, 9), 175 (74), 77 (100); HRMS calcd for $C_{19}H_{25}NO_2S + Na^+$ 354.1504, found 354.1504. Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.59; H, 7.91; N, 4.25.

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Supporting Information Available: X-ray crystallographic data of **3e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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