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A New and Regioselective Method for the Synthesis of Aromatic, Heteroaromatic, and Olefinic Sulfonamides by Electrophilic Destannylation

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A mild and effective method for the preparation of aromatic and olefinic sulfonamides is described. The reaction of trialkylaryl- (**4a–f**), heteroaryl- (**4g**), and vinylic stannanes (**4h**) with sulfuryl chloride and secondary amines provides the corresponding sulfonamides in an *ipso*-specific manner.

Sulfur-containing organic compounds, especially sulfonamides, are of common pharmacological and technical interest[2,3]. Although the number of modern and effective synthetic procedures increases, conventional methods for the synthesis of sulfonamides are still used today. For example, aromatic *N,N*-dialkyl sulfonamides are generated from an aromatic sulfonyl chloride and the corresponding amine[4a,b] (eq. 1).

(1)

R = Me, OMe
R^1, R^2 = alkyl, aryl

This synthetical procedure is subject to some general restrictions. The regiospecific synthesis of the aromatic sulfonyl chlorides is limited by the electronic effects of substituents already present in the aromatic compound. Thus, only certain substitution patterns are available. Drastic conditions and aggressive reagents are also often necessary[4a,b], which is especially detrimental to vinylic or sensitive natural compounds.

A method to avoid these problems seemed to be the one-step introduction of the sulfonamido function. *p*-Substituted aromatic sulfonamides were obtained in a Friedel-Crafts-analogous reaction[5], but the method is restricted to activated arenes.

The use of trialkylsilyl-substituted toluenes in this reaction yields aromatic sulfonamides but not in a regiospecific manner[6,7]. The application of trialkylstannanes allows the introduction of electrophiles into an aromatic or a vinylic system in an *ipso*-specific manner[8a–d]. Even the strong directing effects of functional groups already present in the aromatic system are overcompensated by the effectiveness of the trialkylstannyl group as a leaving group. These elegant route to unconventional substitution patterns at an aromatic or a vinylic system, which could not be obtained by conventional electrophilic substitution, is available.

In this paper we present a new method for the preparation aromatic, heteroaromatic, and vinylic sulfonamides by use of aromatic, heteroaromatic, and vinylic trialkylstannanes. The two-step procedure includes the in situ generation of a sulfonyl chloride by the reaction of a stannane **4a–h** with sulfuryl chloride and subsequent formation of the corresponding sulfonamide by the addition of a secondary amine, e.g. morpholine (**1**), piperidine (**2**), or diethylamine (**3**).

Results and Discussion

Trialkylarylstannanes **4a–f** react under mild conditions (0–20°C, no catalyst) within 4 h with SO_2Cl_2 in an *ipso*-specific manner with destannylation to form the corresponding sulfonyl chlorides. The addition of a secondary amine **1**, **2**, or **3** yields the analogous sulfonamides (eq. 2).

$HN[CH_2CH_2]_2O$ **1** $HN[CH_2]_5$ **2** Et_2NH **3**

A comparison of the yields of the sulfonamides **5a–d** and **5f, g** obtained from trimethyl- or tributylstannanes shows that the tributylstannyl group is as effective as leaving group as the trimethylstannyl group. Therefore, it is appropriate to use the toxicologically much less problematic tributylstannyl group in this type of electrophilic aromatic destannylation. The strongly directing forces of the methyl and even the methoxy group is completely overcompensated by the application of the trialkylstannyl moiety as leaving group. So substitution patterns with the sulfonamide function in the 3-position with respect to the methyl or methoxy group are available directly. This is not possible by the

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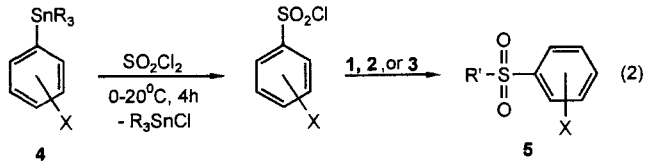
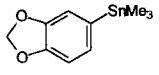
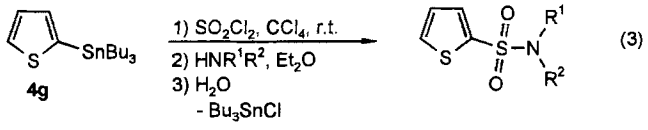


stannane	R	X	R'	yield	product
4a	Bu	3-Me	R^1	53%	5a
4b	Bu	3-OMe	R^1	58%	5b
4c	Me	3-Me	R^1	57%	5a
4d	Me	3-OMe	R^1	46%	5b
4a	Bu	3-Me	R^2	39%	5c
4b	Bu	3-OMe	R^2	41%	5d
4c	Me	3-Me	R^2	45%	5c
4d	Me	4-Me	R^2	55%	5e
4c	Me	3-Me	R^3	41%	5f
4e	Bu	4-OMe	R^3	59%	5g
4f			R^3	44%	5h

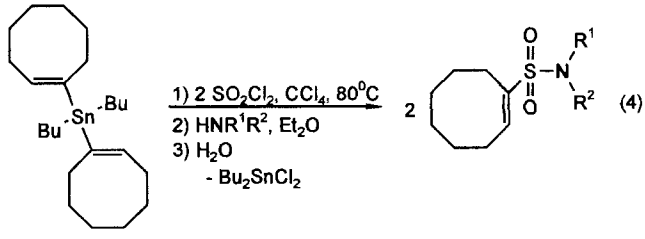
classic aromatic substitution. In comparison with the conventional synthesis of aromatic sulfonyl chlorides[4a,b] the temperatures can be reduced from 120 to 0°C. The use of aggressive Lewis acid catalysts like aluminium trichloride can also be avoided. The two-step procedure allows us to work under non-acidic conditions. Thus, acid-sensitive molecules like the stannylated benzodioxole **4f** could be converted into the till unknown sulfonamide **5h** (eq. 2).

This method for the preparation of sulfonamides can be extended to heterocyclic stannanes (eq. 3). Various sulfonamides of 2-substituted thiophene are available in yields up to 65% by reaction of **4g** with an excess of SO_2Cl_2 followed by aminolysis with a secondary amine (eq. 3).



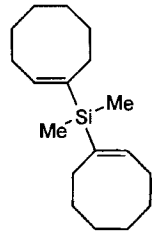
R^1	R^2	yield	product
$-[CH_2]_2-O-[CH_2]_2-$		61%	5i
$-[CH_2]_5-$		65%	5k
Et	Et	51%	5l

Vinylstannanes are of considerable interest in electrophilic destannylation reactions[14a,b] for the synthesis of functionalized α,β-unsaturated compounds. This is e.g. demonstrated by Friedel-Crafts acylations[15], amidations[8d], or the synthesis of sodium sulfonates[1]. Reaction of dibutyldi-1-cycloocten-1-ylstannane for 24 h at 80°C with SO_2Cl_2 and a secondary amine affords the corresponding α,β-unsaturated sulfonamides. Yields above 50% show that both of the cyclooctenyl substituents are liberated by the electrophile. Since the reactivity of the vinylstannanes is much lower than that of the arylstannanes, higher temperatures (80°C) and longer reaction times (48 h) as well as a large excess of SO_2Cl_2 are necessary to carry out a substitution at a vinylic stannane in acceptable yields (eq. 4).



R^1	R^2	yield	product
$-[CH_2]_2-O-[CH_2]_2-$		60%	5m
$-[CH_2]_5-$		56%	5n
Et	Et	68%	5o

The superior leaving ability of the stannyl moiety is demonstrated by the fact that the corresponding silane di-1-cycloocten-1-yldimethylsilane (**6**) does not react under the same conditions as the stannane **4h** with SO_2Cl_2 in the presence of a secondary amine. The silyl group, which was also used in electrophilic demetalation reactions[16], is too unreactive because the Si–C bond is more stable than the Sn–C bond and the coordination ability of the silicon atom is too low to facilitate the reaction with the weak electrophilic sulfuryl chloride.



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Experimental

Melting points: Büchi SMP 20. – IR: Shimadzu 470. – NMR: Varian EM 360 (60 MHz, ^1H), Bruker AM 300 (300 MHz, ^1H; 75.47 MHz, ^{13}C). – MS: Finnigan MAT 8230, 70 eV. – Elemental Analyses: Carlo Erba MOD 1106.

The trialkylarylstannanes and di-1-alkenyldibutylstannanes were prepared according to published procedures[8d,9–12].

General Procedure I: 5.00 mmol of a trialkylarylstannane (**4a–f**) is cooled to 0°C under Ar. Then SO_2Cl_2 is added dropwise and very slowly at this temp. When the addition of SO_2Cl_2 is complete the temp. is allowed to rise to 20°C. After stirring for 4 h, 30 ml of diethyl ether and 30.0 mmol of a secondary amine (**1**, **2**, or **3**) are added. After 1 h of vigorous stirring, the reaction mixture is treated with 6 ml of a saturated aqueous KF solution for 3 h. The precipitated R_3SnF is filtered off, the organic layer is washed twice with 10 ml of water and dried with $MgSO_4$. The solvent is removed in vacuo and the crude product recrystallized twice from *n*-pentane.

4-[(3-Methylphenyl)sulfonyl]morpholine (**5a**): From 1.73 ml (5.00 mmol) of **4a**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 2.61 ml (30.0 mmol) of **1** 0.64 g (53%) of **5a** is obtained according to the general procedure I. From 0.98 ml (5.00 mmol) of **4c**, 0.40 ml (5.00

mmol) of SO_2Cl_2, and 2.61 ml (30.0 mmol) of **1** 0.67 g (57%) of **5a** is obtained according to the general procedure I, m.p. 122°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1345 cm^{-1}, 1169, 1155, 1118. – ^1H NMR ($CDCl_3$): δ = 2.48 (s, 3H, CH_3), 2.95–3.17 (m, 4H, NCH_2), 3.68–3.87 (m, 4H, OCH_2), 7.30–7.63 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.34 (CH_3), 45.98 (NCH_2), 66.07 (OCH_2), 124.95, 128.05, 128.90, 133.70 (all CH), 135.01, 139.29 (all C_q). – MS, *m/z* (%): 241 (72) [M^+], 210 (16) [$M^+ - CH_3O$], 198 (43) [$M^+ - C_2H_3O$], 155 (58) [$C_7H_7SO_2^+$], 91 (86) [$C_7H_7^+$], 86 (99) [$C_4H_8NO^+$], 65 (70) [$C_5H_5^+$], 56 (100) [$C_4H_8^+$]. – $C_{11}H_{15}NO_3S$ (241.3): calcd. C 54.8, H 6.3, N 5.8; found C 54.3, H 6.6, N 5.3.

4-[(3-Methoxyphenyl)sulfonyl]morpholine (**5b**): From 1.77 ml (5.00 mmol) of **4b**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 2.61 ml (30.0 mmol) of **1** 0.75 g (58%) of **5b** is obtained according to the general procedure I. From 0.97 ml (5.00 mmol) of **4d**, 0.40 (5.00 mmol) of SO_2Cl_2, and 2.61 ml (30.0 mmol) of **1** 0.59 g (46%) of **5b** is obtained according to the general procedure I, m.p. 132°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1346 cm^{-1}, 1261, 1165, 1155, 1114. – ^1H NMR ($CDCl_3$): δ = 3.00–3.32 (m, 4H, NCH_2), 3.73–3.90 (m, 4H, OCH_2), 3.97 (s, 3H, OCH_3), 7.08–7.55 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 45.97 (NCH_2), 55.63 (OCH_3), 66.05 (OCH_2), 112.75, 118.99, 119.84, 130.10 (all CH), 136.30, 159.90 (all C_q). – MS, *m/z* (%): 257 (57) [M^+], 226 (6) [$M^+ - CH_3O$], 214 (9) [$M^+ - C_2H_3O$], 171 (45) [$C_7H_7SO_3^+$], 107 (68) [$C_7H_7O^+$], 86 (100) [$C_4H_8NO^+$], 56 (96) [$C_4H_8^+$]. – $C_{11}H_{15}NO_4S$ (257.3): calcd. C 51.4, H 5.9, N 5.4; found C 51.0, H 6.0, N 5.4.

1-[(3-Methylphenyl)sulfonyl]piperidine (**5c**): From 1.73 ml (5.00 mmol) of **4a**, 0.40 (5.00 mmol) of SO_2Cl_2, and 2.50 ml (30.0 mmol) of **2** 0.47 g (39%) of **5c** is obtained according to the general procedure I. From 0.98 ml (5.00 mmol) of **4c**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 2.50 ml (30.0 mmol) of **2** 0.47 g (45%) of **5c** is obtained according to the general procedure I, m.p. 79°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1341 cm^{-1}, 1158. – ^1H NMR ($CDCl_3$): δ = 1.70–1.98 (m, 6H, CH_2), 2.67 (s, 3H, CH_3), 3.13–3.45 (m, 4H, NCH_2), 7.50–7.82 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.30 (CH_3), 23.45 (CH_2), 25.13 (NCH_2CH_2), 46.86 (NCH_2), 124.70, 127.83, 128.65, 133.23 (all CH), 136.20, 138.96 (all C_q). – MS, *m/z* (%): 239 (29) [M^+], 155 (11) [$C_7H_7O_2S^+$], 91 (40) [$C_7H_7^+$], 84 (100) [$NC_4H_{10}^+$], 56 (7) [$C_4H_8^+$]. – $C_{12}H_{17}NO_2S$ (239.3): calcd. C 60.2, H 7.2, N 5.9; found C 60.5, H 7.3, N 6.1.

1-[(3-Methoxyphenyl)sulfonyl]piperidine (**5d**): From 1.77 ml (5.00 mmol) of **4b**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 2.50 ml (30.0 mmol) of **2** 0.50 g (41%) of **5d** is obtained according to the general procedure I, m.p. 119°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1341 cm^{-1}, 1255, 1156. – ^1H NMR ($CDCl_3$): δ = 1.47–1.83 (m, 6H, CH_2), 2.92–3.17 (m, 4H, NCH_2), 3.90 (s, 3H, OCH_3), 7.03–7.53 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 23.46 (CH_2), 25.15 (NCH_2CH_2), 46.89 (NCH_2), 55.58 (OCH_3), 112.51, 118.55, 119.68, 129.87 (all CH), 137.58, 159.76 (all C_q). – MS, *m/z* (%): 255 (46) [M^+], 171 (1) [$M^+ - NC_5H_{10}$], 107 (25) [$C_7H_7O^+$], 92 (9) [$C_6H_4O^+$], 84 (100) [$NC_4H_{10}^+$], 56 (5) [$C_4H_8^+$]. – $C_{12}H_{17}NO_3S$ (255.3): calcd. C 56.5, H 6.7, N 5.5; found C 55.9, H 6.9, N 5.5.

1-[(4-Methylphenyl)sulfonyl]piperidine (**5e**): From 0.98 ml (5.00 mmol) of **4d**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 2.50 ml (30.0 mmol) of **2** 0.66 g (55%) of **5e** is obtained according to the general procedure I, m.p. 98°C (*n*-pentane) (ref.[13] 101°C). – IR (KBr): $\tilde{\nu}$ = 1358 cm^{-1}, 1164.

N,N-Diethyl-3-methylbenzenesulfonamide (**5f**): From 0.98 ml (5.00 mmol) of **4c**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 3.10 ml (30.0 mmol) of **3** 0.46 g (41%) of **5f** is obtained according to the general procedure I, m.p. 38–39°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1136 cm^{-1}, 1201, 1017, 938, 1176. – ^1H NMR ($CDCl_3$): δ = 1.37 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3), 2.68 (s, 3H, CH_3), 3.52 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.52–7.97 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.15 (NCH_2CH_3), 21.30 (CH_3), 42.04 (NCH_2CH_3), 124.03, 127.39, 128.76, 132.91 (all CH), 139.04, 140.21 (all C_q). – MS *m/z* (%): 227 (24) [M^+], 212 (84) [$M^+ - CH_3$], 155 (77) [$C_7H_7SO_2^+$], 91 (100) [$C_7H_7^+$], 72 (8) [$C_4H_{10}N^+$], 65 (34) [$C_5H_5^+$], 56 (20) [$C_4H_8^+$]. – $C_{11}H_{17}NO_2S$ (227.3): calcd. C 58.1, H 7.5, N 6.2; found C 58.6, H 7.7, N 6.2.

N,N-Diethyl-4-methoxybenzenesulfonamide (**5g**): From 0.97 ml (5.00 mmol) of **4e**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 3.10 ml (30.0 mmol) of **3** 0.72 g (59%) of **5g** is obtained according to the general procedure I, m.p. 53–54°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1336 cm^{-1}, 1259, 1203, 1016, 933, 1152. – ^1H NMR ($CDCl_3$): δ = 1.30 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3), 3.37 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 4.02 (s, 3H, OCH_3), 7.03–7.97 (AA'BB', 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.02 (NCH_2CH_3), 41.87 (NCH_2CH_3), 55.45 (OCH_3), 114.01, 128.90 (all CH), 132.10, 162.46 (all C_q). – MS, *m/z* (%): 243 (27) [M^+], 228 (77) [$M^+ - CH_3$], 171 (100) [$M^+ - NEt_2$], 155 (5) [$C_7H_7O_2S^+$], 107 (46) [$C_7H_7O^+$], 92 (14) [$C_6H_4O^+$]. – $C_{11}H_{17}NO_3S$ (243.3): calcd. C 54.3, H 7.0, N 5.8; found C 54.4, H 7.2, N 5.7.

N,N-Diethyl-1,3-benzodioxole-5-sulfonamide (**5h**): From 0.94 ml (5.00 mmol) of **4f**, 0.40 ml (5.00 mmol) of SO_2Cl_2, and 3.10 ml (30.0 mmol) of **3** 0.56 g (44%) of **5h** is obtained according to the general procedure I, m.p. 74°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1297 cm^{-1}, 1198, 1141, 1081, 1014, 933. – ^1H NMR ($CDCl_3$): δ = 1.05 (t, ^3J = 7.0 Hz, 6H, CH_3), 3.32 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 6.17 (s, 2H, OCH_2), 7.47–7.57 (m, 3H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.13 (NCH_2CH_3), 42.02 (NCH_2CH_3), 102.11 (OCH_2), 107.29, 108.12, 122.96 (all CH), 133.89, 148.06, 150.89 (all C_q). – MS, *m/z* (%): 257 (29) [M^+], 242 (52) [$M^+ - CH_3$], 185 (100) [$M^+ - NC_4H_{10}$], 169 (3) [$C_7H_5O_3S^+$], 121 (59) [$C_7H_5O_2^+$], 72 (8) [$C_4H_{10}N^+$], 65 (19) [$C_5H_5^+$], 56 (5) [$C_4H_8^+$]. – $C_{11}H_{15}NO_4S$ (257.3): calcd. C 51.4, H 5.9, N 5.4; found C 51.4, H 5.9, N 5.4.

General Procedure II: 8.00 mmol of SO_2Cl_2 is added to a solution of 8.00 mmol of 2-(Tributylstannyl)thiophene (**4g**) in 10 ml of anhydrous tetrachloromethane under Ar. The mixture is stirred for 6 h. After cooling to 20°C 25 ml of anhydrous ether and 50 mmol of the secondary amine (**1**, **2**, or **3**) are added. The mixture is stirred for 3 h at room temp. and than poured into 50 ml of water and stirred again for 30 min. The organic layer is washed twice with 20 ml of water and dried with $MgSO_4$. The solvent is removed in vacuo and the crude product purified by distillation or recrystallized from an appropriate solvent.

4-(2-Thienylsulfonyl)morpholine (**5i**): From 2.62 ml (8.00 mmol) of **4g**, 0.65 ml (8.00 mmol) of SO_2Cl_2, and 4.36 ml (50.0 mmol) of **1** 1.13 g (61%) of **5i** is obtained according to the general procedure II, m.p. 68°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2940, 2855, 1550, 1320, 1159, 1115, 1070, 763. – ^1H NMR ($CDCl_3$): δ = 3.01 (m, 4H, CH_2N), 3.59 (m, 4H, CH_2O), 6.80 (m, 1H, CH), 6.93 (m, 1H, CH), 7.23 (m, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 45.3 (CH_2N), 67.9 (CH_2O), 122.8, 126.7, 127.5 (all CH), 165.0 (C_q). – MS, *m/z* (%): 233 (38) [M^+], 232 (13) [$M^+ - H$], 150 (31) [$M^+ - C_4H_3S$], 146 (100) [$M^+ - C_4H_8NO$], 86 (63) [$C_4H_8NO^+$], 83 (48) [$C_4H_3S^+$]. – $C_8H_{11}NO_3S_2$ (233.3): calcd. C 41.2, H 4.8, N 6.0; found C 41.0, H 4.5, N 5.8.

1-(2-Thienylsulfonyl)piperidine (**5k**): From 2.62 ml (8.00 mmol) of **4g**, 0.65 ml (8.00 mmol) of SO_2Cl_2, and 4.94 ml (50.0 mmol) of **2** 1.21 g (65%) of **5k** is obtained according to the general procedure II, m.p. 65°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2940, 2865, 1315, 1160, 1120, 1054, 930, 701, 680. – ^1H NMR ($CDCl_3$): δ = 2.98 (m, 10H, CH_2, piperidine), 6.89 (m, 1H, CH), 7.03 (m, 1H,

CH), 7.15 (m, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 26.4, 26.8 (CH_2), 46.9 (CH_2N), 122.8, 125.5, 126.8 (all CH), 165.1 (C_q). – MS, *m/z* (%): 231 (18) [M^+], 230 (37) [M^+ – H], 148 (21) [M^+ – C_4H_3S], 147 (100) [M^+ – $C_5H_{10}N$], 84 (66) [$C_5H_{10}N^+$], 83 (28) [$C_4H_3S^+$]. – $C_9H_{13}NO_2S_2$ (231.3): calcd. C 46.7, H 5.7, N 6.1; found C 46.5, H 5.8, N 6.0.

N,N-Diethyl-2-thiophenesulfonamide (**5l**): From 2.62 ml (8.00 mmol) of **4g**, 0.65 ml (8.00 mmol) of SO_2Cl_2, and 5.18 ml (50.0 mmol) of **3** 0.98 g (51%) of **5l** is obtained according to the general procedure II, b.p. 50°C/0.01 Torr. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2940, 2875, 1380, 1306, 1214, 1134, 1026, 676. – ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, 6H, CH_3, $^3J_{HH}$ = 7.2 Hz), 3.07 (q, 4H, CH_2, $^3J_{HH}$ = 7.2 Hz), 6.76–6.82 (m, 2H, CH), 6.98–7.02 (m, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 13.1 (CH_3), 42.1 (CH_2N), 123.9, 125.8, 126.4 (all CH), 164.8 (C_q). – MS, *m/z* (%): 219 (11) [M^+], 218 (15) [M^+ – H], 147 (100) [M^+ – $N(C_2H_5)_2$], 83 (61) [$C_4H_3S^+$], 72 (48) [$N(C_2H_5)_2^+$]. – $C_8H_{13}NO_2S_2$ (219.3): calcd. C 43.8, H 6.0, N 6.4; found C 43.5, H 6.0, N 6.2.

General Procedure III: 5.00 mmol of SO_2Cl_2 is added to a solution of 5.00 mmol of the di-1-alkenyldibutylstannane **4h** in 20 ml of anhydrous tetrachloromethane under Ar. The mixture is stirred at 70°C for 12 h. Then 5.00 mmol of SO_2Cl_2 is added again, and the mixture is stirred at 70°C for additional 12 h. After cooling to 20°C 50 ml of anhydrous ether and 60.0 mmol of the secondary amine (**1**, **2**, or **3**) are added. The mixture is stirred for 3 h at room temp. and then poured into 50 ml of water and stirred again for 30 min. The organic layer is washed twice with 20 ml of water each and dried with $MgSO_4$. The solvent is removed in vacuo and the crude product purified by distillation or recrystallized from an appropriate solvent.

4-(1-Cycloocten-1-ylsulfonyl)morpholine (**5m**): From 2.20 g (5.00 mmol) of **4h**, 1.30 g (10.0 mmol) of SO_2Cl_2, and 5.30 g (60.0 mmol) of **2** 1.50 g (60%) of **5m** is obtained according to the general procedure III, m.p. 91°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1112 cm^{-1}, 1154, 1361, 1641. – ^{1}H NMR ($CDCl_3$): δ = 1.46 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 2.25 (m, 2H, CH_2, allylic), 2.41 (m, 2H, CH_2, allylic), 3.13 (m, 4H, CH_2), 3.66 (m, 4H, CH_2), 6.71 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = 25.6, 25.7, 25.9, 26.5, 28.1, 29.4 (all CH_2), 46.5 (CH_2N), 66.3 (CH_2O), 138.5 (C_q), 140.1 (CH). – MS, *m/z* (%): 259 (15) [M^+], 173 (100) [M^+ – C_4H_8NO], 109 (21) [cyclooctenyl$^+$], 86 (22) [$C_4H_8NO^+$]. – $C_{12}H_{21}NO_3S$ (259.4): calcd. C 55.6, H 8.2, N 5.4; found C 55.1, H 7.9, N 5.2.

1-(1-Cycloocten-1-ylsulfonyl)piperidine (**5n**): From 2.20 g (5.00 mmol) of **4h**, 1.30 g (10.0 mmol) of SO_2Cl_2, and 5.10 g (60.0 mmol) of **2** 1.50 g (56%) of **5n** is obtained according to the general procedure III, m.p. 77°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1116 cm^{-1}, 1154, 1332, 1640. – ^{1}H NMR ($CDCl_3$): δ = 1.50 (m, 8H, CH_2), 2.21 (m, 2H, CH_2, allylic), 2.35 (m, 2H, CH_2, allylic), 3.09 (m, 10H, CH_2), 6.63 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = 23.7, 25.4, 25.5, 25.6, 25.8, 26.3, 28.1, 29.3 (all CH_2), 47.0 (CH_2N), 139.1 (C_q), 140.1 (CH). – MS, *m/z* (%): 257 (15) [M^+], 256 (44) [M^+ – H], 173 (100) [M^+ – $C_4H_{10}N$], 109 (18) [cyclooctenyl$^+$], 84 (26) [$C_5H_{10}N^+$]. – $C_{13}H_{23}NO_2S$ (257.4): calcd. C 60.7, H 9.0, N 5.4; found C 60.1, H 9.2, N 5.5.

N,N-Diethyl-1-cyclooctene-1-sulfonamide (**5o**): From 2.20 g (5.00 mmol) of **4h**, 1.30 g (10.0 mmol) of SO_2Cl_2, and 4.20 g (60.0 mmol) of **3** 1.60 g (68%) of **5o** is obtained according to the general procedure III, b.p. 90°C/0.01 Torr. – IR (KBr): $\tilde{\nu}$ = 1114 cm^{-1}, 1145, 1352, 1640. – ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 6H, CH_3, $^3J_{HH}$ = 6.6 Hz), 1.36 (m, 4H, CH_2), 1.51 (m, 4H, CH_2), 2.16 (m, 2H, CH_2, allylic), 2.31 (m, 2H, CH_2, allylic), 3.12 (q, 4H, CH_2, $^3J_{HH}$ = 6.6 Hz), 6.56 (t, 1H, CH, $^3J_{HH}$ = 7.7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 24.9, 25.5, 25.7, 26.0, 28.0, 29.2 (all CH_2), 41.3 (CH_2N), 138.7 (CH), 140.1 (C_q). – MS, *m/z* (%): 245 (5) [M^+], 244 (31) [M^+ – H], 229 (100) [M^+ – O], 109 (27) [cyclooctenyl$^+$], 72 (26) [Et_2N^+], 58 (97) [$C_3H_8N^+$], 55 (18) [$C_4H_7^+$], 41 (28) [$C_3H_5^+$]. – $C_{12}H_{23}NO_2S$ (145.4): calcd. C 58.7, H 9.5, N 5.7; found C 58.5, H 9.6, N 5.6.

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