Radical Addition of *p*-Toluenesulfonyl Bromide and *p*-Toluenesulfonyl Iodide to Allenic Alcohols and Sulfonamides in the Presence of AIBN: Synthesis of Heterocyclic Compounds

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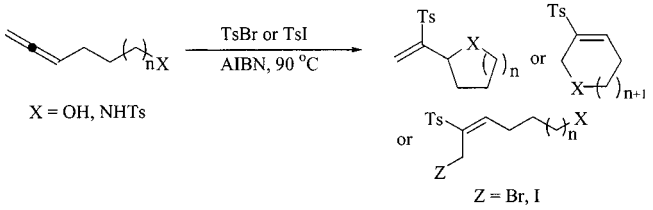
Although the radical chemistry of sulfonyl halides has been extensively investigated and has concentrated on the readily available tosyl chlorides with alkenes and alkynes,[1] much less work has been done with the relatively stable, but less readily available, tosyl bromides and relatively highly reactive and unstable *p*-tosyl iodides with alkenes or alkynes.[2] The radical addition reaction of TsBr and TsI to allenes is rare,[3] and only the light-initiated addition of TsI to allenes[4] and cyclization of eneallenes with TsBr are known.[3a] In the photoinduced addition of sulfonyl iodides to allenes a mixture of adducts resulting from the attack of sulfonyl radical or iodide radical to the central carbon atom or terminal carbon atom was obtained, and the product distribution is highly dependent on the substituents attached to the allene and the reaction conditions, even if in some cases the formation of the products derived from central attack of sulfonyl radical on allenes bearing one or more alkyl or aryl substituent was reported.[4] To the best of our knowledge the stereoselectivity of (*E*)- and (*Z*)- was not specified in the radical addition of TsI to allenes. The use of TsBr and TsI to the substituted allenes under thermal conditions has not been known. Here we wish to report the highly regioselective addition of TsBr and TsI to allenic alcohols and sulfonamides in the presence of a catalytic amount of AIBN under thermal conditions to afford heterocyclic vinyl sulfones directly or acyclic vinyl sulfonyl-substituted allylic bromides or iodides depending on the substrates and cyclization of the acyclic adducts from allenic amines (Scheme 1).

Scheme 1



The results of the radical addition of TsBr[5] and TsI[4b] to hydroxyallenes to form tosyl-substituted bromo allylic alcohols or cyclic ethers are summarized in Table 1. The α-hydroxyallene **1a** reacted with TsBr in the presence of a catalytic amount of AIBN in toluene at 90 °C for 3 h to afford the (*E*)-adduct as a sole product **2a**[8] in 75% yield (entry 1 in Table 1). The use of the pressure tube with Teflon screw is preferred to simple heating.[6] For the *β*-hydroxyallene **1b** treatment with TsBr under the same conditions gave the (*E*)-tosyl-substituted alcohol **2b** in 67% yield (entry 2). The stereochemistry of **2b** was unambiguously determined by the observation of a NOE effect between two allylic protons in ^{1}H NMR.[8] However the radical addition reaction of TsBr with *γ*-hydroxyallene provided the cyclized 1-(2-tetrahydrofuranyl)vinyl sulfone **3a** in 72% yield as the only product resulting from nucleophilic allylic substitution (S_N2') (entry 3). The *δ*-hydroxyallene **1d** was treated with TsBr in the presence of AIBN gave the eight-membered cyclic ether **4a** (52%) along with (*E*)-adduct **2d**[8] (33%) in 85% combined yield (entry 4). This method was applied to TsI with hydroxyallenes. When α-hydroxyallene **1a** was coupled with under the same radical conditions using TsI (2 equiv), unexpectedly bis(tosyl)alcohol **5** was afforded as the sole product. Presumably the sulfonyl-substituted allylic radical the initially formed and/or from sulfonyl-substituted allylic iodide undergoes further radical substitution reaction with another TsI to afford bis(tosyl) compound **5**.[7,8] The reaction of *γ*-hydroxyallene **1c** with TsI in the presence of AIBN furnished the cyclic ether **3a** in 70% yield (entry 6). The *δ*-hydroxyallene **1d** was coupled with TsI under the same conditions to give six-membered cyclic ether **3b** in 53% yield (entry 7).

The radical addition reaction of TsBr was extended to allenic toluenesulfonamides, and the cyclization of the

(1) Review: Bertrand, M. P. *Org. Prepn. Proced. Int.* **1994**, *26*, 257−290.

(2) Simpkins, N. S. In *Sulphones in Organic Sythesis*, Pergamon Press: 1993.

(3) Hatem et al. reported the radical cyclization of the allylallenes: (a) Gueddari, F. E.; Grimaldi, J. R.; Hatem, J. M. *Tetrahedron Lett.* **1995**, *36*, 6685−6688. Caddick et al. also reported the cyclization of 1,5-diynes with TsBr and AIBN: (b) Caddick, S.; Shering, D. L.; Wadman, S. N. *Chem. Commun.* **1997**, 171−172. Surzur et al. investigated the photoinduced radical addition of TsBr to the tethered 1,6-dienes to form heterocycles: (c) De Riggi, E.; Surzur, J.-M.; Bertrand, M. P. *Tetrahedron* **1988**, *44*, 7119−7125. (d) Cristol, S.; Davies, D. I. *J. Org. Chem.* **1964**, *29*, 1282−1284. (e) Nouguier, R.; Lesueur, C.; De Riggi, E.; Bertrand, M. P.; Virgili, A. *Tetrahedron Lett.* **1990**, *31*, 3541−3544.

(4) (a) Byrd, L. R.; Caserio, M. C. *J. Org. Chem.* **1972**, *37*, 3881−3891. (b) Truce, W. E.; Heuring, D. L.; Wolf, G. C. *J. Org. Chem.* **1974**, *39*, 238−244. (c) Truce, W. E.; Heuring, D. L. *J. Org. Chem.* **1974**, *39*, 245−246.

(5) Poshkus, A. C.; Herrweh, J. E.; Magnotta, F. A. *J. Org. Chem.* **1963**, *28*, 2766−2769.

(6) The pressure tube (made of borosilicate glass) was purchased from Aldrich Chem. Co., Inc. (Catalog number Z18, 109−9 type B).

(7) The use of 1 equiv of TsI afforded a mixture of tosyl-substituted allylic iodide (12%) and bis(tosylate) **5** (35%).

(8) The (*E*)-stereochemistry of **2a**, **2b**, **2d**, **5**, **7a**, **7b**, **7c**, and **7d** was determined by NOE experiments in ^{1}H NMR.

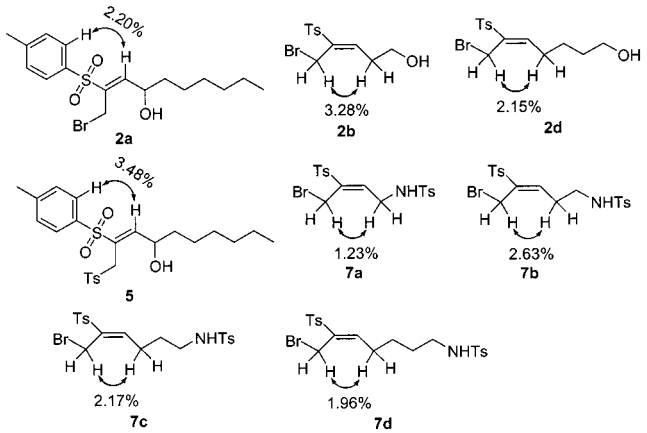


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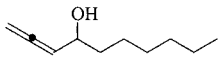
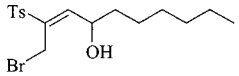
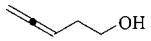
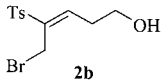
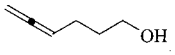
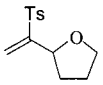
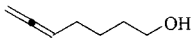
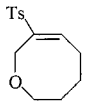
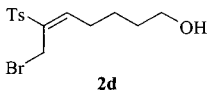
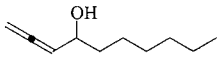
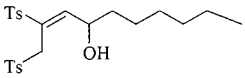
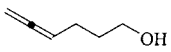
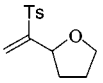
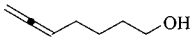
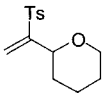
Table 1. Radical Addition of TsBr and TsI to Allenic Alcohols[a]

Entry	Substrate	Radical Source	Product	Isolated Yield (%)
1	 **1a**	TsBr	 **2a**	75
2	 **1b**	TsBr	 **2b**	67
3	 **1c**	TsBr	 **3a**	72
4	 **1d**	TsBr	 **4a** +  **2d**	52 33
5	 **1a**	TsI[b]	 **5**	60
6	 **1c**	TsI	 **3a**	70
7	 **1d**	TsI	 **3b**	53

[a] The reactions were run with allene (1.0 equiv) and TsBr or TsI (1.2 equiv) in the presence of AIBN (0.2 equiv) in toluene at 90 °C for 3 h. [b] Two equivalents of TsI were used.

adducts was accomplished, which was summarized in Table 2. The α-allenic sulfonamide **6a** was allowed to react with TsBr in the presence of AIBN at 90 °C for 3 h, and the simple (*E*)-adduct **7a**[8] was obtained in 70% yield (entry 1 in Table 2). The bromosulfonamide **7a** was inert to the cyclization. For the *β*-allenic sulfonamide **6b**, the radical addition gave the bromotosyl sulfonamide (*E*)-**7b** in 65% yield, and the cyclization of **7b** was accomplished with K_2CO_3 in DMF at room temperature for 30 min to afford the six-membered ring **8a** in 63% yield (entry 2). The stereochemistry of **7b** was deduced by the observation of a NOE effect between two allylic protons.[8] The *γ*-allenic sulfonamide was treated with TsBr to give (*E*)-**7c**,[8] which was cyclized to give five-membered (pyrrolidinyl)vinyl sulfone **9a** in 76% yield (entry 3). *δ*-Allenic sulfonamide **6d** was coupled to afford tosyl-substituted bromosulfonamide **7d**,[8] which readily underwent the cyclization to provide piperidinyl vinyl sulfone **9b** in 78% yield (entry 4).

In summary, the radical addition reaction of allenic alcohols and sulfonamides with TsBr or TsI in the presence of AIBN to afford the simple (*E*)-adducts and/or the cyclized products was accomplished regioselectively and stereoselectively.

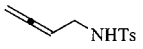
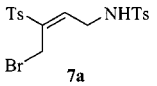
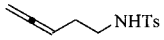
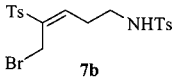
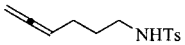
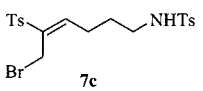
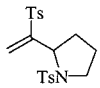
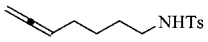
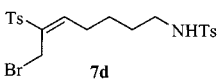
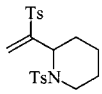
Experimental Section

All solvents for reactions were purified before use. IR spectra were recorded on a FT-IR spectrometer. ^{1}H NMR were conducted at 500 MHz in $CDCl_3$, and chemical shifts are reported in *δ* units relative to the tetramethylsilane (TMS) signal at 0.00 ppm. Coupling constants (*J*) are reported in hertz. Melting points were determined in unsealed capillary tubes and are uncorrected. For thin-layer chromatography (TLC), Merck precoated plates (silica gel 60 F_{254}, 0.25 mm) were used. Silica gel 60 (9385, 230−400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products.

General Procedure for the Radical Addition of TsBr to Allenic Alcohol 1a. A solution of allenic alcohol **1a** (150 mg, 0.97 mmol) and AIBN (32 mg, 0.19 mmol) in toluene (4 mL) was added TsBr (275 mg, 1.17 mmol) and heated in a pressure tube (30 mL) capped with a Teflon screw at 90 °C for 3 h. Toluene was evaporated in vacuo, and the crude product was separated by SiO_2 column chromatography (hexanes:ethyl acetate = 1:1) to afford product **2a** (283 mg, 75%).

(*E*)-1-Bromo-2-(toluene-4-sulfonyl)dec-2-en-4-ol (2a): white solid, mp 64 °C, R_f 0.54 (hexanes:ethyl acetate = 1:1); ^{1}H NMR

Table 2. Radical Addition of TsBr to Allenic Sulfonamides and Cyclization of the Adducts[a]

Entry	Substrate	Product	Isolated Yield(%)	Cyclized Product[b]	Yield (%)
1	 **6a**	 **7a**	70	Not Cyclized	
2	 **6b**	 **7b**	65	 **8a**	63
3	 **6c**	 **7c**	67	 **9a**	76
4	 **6d**	 **7d**	51	 **9b**	78

[a] The reactions were run with allene (1.0 equiv) and TsBr (1.2 equiv) in the presence of AIBN (0.2 equiv) in toluene at 90 °C for 3 h. [b] The cyclization was carried out with K_2CO_3 (1.2 equiv) in DMF at room temperature.

(500 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.29 (m, 7H), 1.43 (m, 1H), 1.66 (m, 2H), 2.30 (d, J = 4.4 Hz, 1H), 2.45 (s, 3H), 4.22 (d, J = 11.4 Hz, 1H), 4.26 (d, J = 11.4 Hz, 1H), 4.55 (m, 1H), 7.02 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 21.3, 22.3, 23.2, 25.6, 29.7, 32.3, 36.7, 69.5, 129.2, 130.6, 137.1, 140.1, 145.6, 147.9; IR (KBr, cm^{-1}) 3500, 2929, 2858, 1313, 1144, 1085, 732, 678; HRMS (EI) m/z 388.0729 (calcd for $C_{17}H_{25}BrO_3S$ 388.0708).

(*E*)-5-Bromo-3-(toluene-4-sulfonyl)but-2-en-1-ol (2b): colorless oil, R_f 0.23 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 1H), 2.44 (s, 3H), 2.57 (td, J = 6.2, 7.6 Hz, 2H), 3.86 (t, J = 6.2 Hz, 2H), 4.17 (s, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 22.4, 33.0, 60.8, 129.1, 130.7, 137.1, 141.0, 145.3, 145.6; IR (neat, cm^{-1}) 3507, 2930, 2860, 1301, 1143, 1085, 1051, 911, 814; HRMS (EI) m/z 317.9922 (calcd for $C_{12}H_{15}BrO_6S$ 317.9925).

2-[1-(Toluene-4-sulfonyl)vinyl]tetrahydrofuran (3a): colorless oil, R_f 0.63 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (m, 3H), 2.19 (m, 1H), 2.43 (s, 3H), 3.75 (m, 1H), 3.91 (m, 1H), 4.51 (dd, J = 6.6, 6.8 Hz, 1H), 6.05 (d, J = 1.2 Hz, 1H), 6.34 (d, J = 1.2 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 26.3, 33.7, 69.3, 76.4, 123.6, 128.8, 130.5, 137.3, 145.3, 153.4; IR (neat, cm^{-1}) 2981, 2952, 2932, 2876, 1597, 1312, 1164, 1139, 1061, 958, 912, 814; HRMS (EI) m/z 252.0806 (calcd for $C_{13}H_{16}O_3S$ 252.0820).

7-(Toluene-4-sulfonyl)-3,4,5,8-tetrahydro-2*H*-oxocine (4a): colorless oil, R_f 0.63 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (m, 4H), 2.34 (m, 2H), 2.45 (s, 3H), 4.09 (dd, J = 5.9, 6.2 Hz, 2H), 4.13(s, 2H), 7.12(dd, J = 7.3, 7.6 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.78(d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 23.5, 25.5, 32.5, 69.1, 74.4, 124.5, 128.2, 129.7, 136.8, 144.4, 152.6; IR (neat, cm^{-1}) 2952, 1635, 1597, 1452, 1390, 1367, 1314, 1243, 1144, 1086, 1042, 815; HRMS (EI) m/z 266.0997 (calcd for $C_{14}H_{18}O_3S$ 266.0977).

(*E*)-7-Bromo-6-(toluene-4-sulfonyl)hept-5-en-1-ol (2d): colorless oil, R_f 0.25 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64 (m, 4H), 1.82 (s, 1H), 2.34 (td, J = 7.3, 7.6 Hz, 2H), 2.44 (s, 3H), 3.67 (t, J = 6.2 Hz, 2H), 4.14 (s, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 22.4, 24.9, 29.5, 32.8, 63.0, 129.6, 130.5, 137.4, 139.5, 145.4, 148.2; IR (neat, cm^{-1}) 3390, 2935, 2867, 1635, 1597, 1462, 1311, 1143, 1085, 1047, 815; HRMS (EI) m/z 346.0218 (calcd for $C_{14}H_{19}BrO_3S$ 346.0238).

General Procedure for the Radical Addition of TsI to Allenic Alcohol 1c. To a solution of allenic alcohol **1c** (150 mg, 1.53 mmol) and AIBN (50 mg, 0.31 mmol) in toluene (4 mL) was added TsI (518 mg, 1.84 mmol), and the mixture was heated in a pressure tube (30 mL) capped with a Teflon screw at 90 °C for 3 h. Toluene was evaporated in vacuo, and the crude product was separated by SiO_2 column chromatography (hexanes:ethyl acetate = 1:1) to afford product **3a** (270 mg, 70%).

(*E*)-1,2-Bis(toluene-4-sulfonyl)dec-2-en-4-ol (5): colorless oil, R_f 0.47 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.29 (m, 7H), 1.47 (m, 1H), 1.64 (m, 2H), 2.43 (s, 3H), 2.47 (s, 3H), 3.52 (d, J = 5.0 Hz, 1H), 4.29 (d, J = 14.7 Hz, 1H), 4.44 (d, J = 14.7 Hz, 1H), 4.54 (m, 1H), 7.16 (d, J = 6.8 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 21.7, 22.6, 25.2, 29.2, 31.0, 31.7, 36.0, 53.3, 69.7, 128.4, 128.6, 130.0, 130.1, 131.9, 135.5, 136.4, 144.9, 145.7, 151.7; IR (neat, cm^{-1}) 3395, 3367, 2929, 2859, 1657, 1598, 1420, 1320, 1267, 1149, 1083, 1060, 1045; HRMS (EI) m/z 464.1683 (calcd for $C_{24}H_{32}O_5S_2$ 464.1691).

2-[1-(Toluene-4-sulfonyl)vinyl]tetrahydropyran (3b): colorless oil, R_f 0.67 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (m, 4H), 1.87 (m, 2H), 2.44 (s, 3H), 3.37 (ddd, J = 10.0, 10.1, 2.6 Hz, 1H), 3.90 (ddd, J = 10.1, 2.6, 2.4 Hz, 1H), 4.06 (dd, J = 10.2, 2.4 Hz, 1H), 6.09 (d, J = 0.9 Hz, 1H), 6.42 (d, J = 0.9 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 23.5, 25.5, 32.6, 69.1, 74.4, 124.5, 128.3, 129.7, 136.8, 144.4, 152.6; IR (neat, cm^{-1}) 3055, 2987, 2946, 2306, 1438, 1423, 1314, 1266, 1139, 897; HRMS (EI) m/z 266.0993 (calcd for $C_{14}H_{18}O_3S$ 266.0977).

General Procedure for the Radical Addition of TsBr Allenic Sulfonamide 6a. To a solution of allenic sulfonamide **6a** (150 mg, 0.67 mmol) and AIBN (22 mg, 0.13 mmol) in toluene (4 mL) was added TsBr (190 mg, 0.81 mmol), and the mixture was heated in a pressure tube (30 mL) capped with a Teflon screw at 90 °C for 3 h. Toluene was evaporated in vacuo, and the crude product was separated by SiO_2 column chromatography (hexanes:ethyl acetate = 1:1) to afford product **7a** (215 mg, 70%).

(*E*)-*N*-[4-Bromo-3-(toluene-4-sulfonyl)but-2-enyl]-4-methylbenzene sulfonamide (7a): white solid, mp 111 °C, R_f 0.41 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.46 (s, 3H), 3.86 (dd, J = 6.8, 6.5 Hz, 2H), 4.03 (s, 2H), 4.82 (t, J = 6.5 Hz, 1H), 6.90 (t, J = 6.8 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 21.7, 29.7, 40.9, 127.2, 128.6, 129.8, 130.1, 135.8. 136.4, 140.8, 141.4, 144.3, 145.3; IR (KBr, cm^{-1}) 3292, 3056, 2986, 2931, 1637, 1598, 1422, 1321, 1266, 1160, 1088, 1042, 895, 815; HRMS (EI) m/z 457.0022 (calcd for $C_{18}H_{20}BrNO_4S_2$ 457.0017).

(*E*)-*N*-[5-Bromo-4-(toluene-4-sulfonyl)pent-3-enyl]-4-methylbenzenesulfonamide (7b): white solid, mp 124 °C, R_f 0.43 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$)

δ 2.44 (s, 3H), 2.45 (s, 3H), 2.51 (td, J = 6.8, 7.6 Hz, 2H), 3.17 (td, J = 6.8, 6.5 Hz, 2H), 4.06 (s, 2H), 4.88 (t, J = 6.5 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 21.6, 21.7, 29.7, 41.0, 127.1, 128.5, 129.9, 130.0, 136.3, 136.7, 141.2, 142.9, 143.8, 145.0; IR (KBr, cm^{-1}) 3289, 3057, 2985, 2930, 1637, 1598, 1423, 1320, 1266, 1160, 1147, 1088, 895, 815;HRMS (EI) *m*/*z* 471.0137 (calcd for $C_{19}H_{22}BrNO_4S_2$ 471.0174).

(*E*)-*N*-[6-Bromo-5-(toluene-4-sulfonyl)hex-4-enyl]-4-methylbenzene sulfonamide (7c): white solid, mp 104 °C, R_f 0.45 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.72 (m, 2H), 2.31 (td, J = 7.7, 7.6 Hz, 2H), 2.42 (s, 3H), 2.43 (s, 3H), 2.95 (td, J = 6.8, 6.5 Hz, 2H), 4.07 (s, 2H), 5.24 (t, J = 6.5 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.4, 21.5, 26.0, 27.6, 42.4, 126.9, 128.2, 129.7, 129.9, 136.4, 136.7, 139.2, 143.4, 144.7, 146.3; IR (KBr, cm^{-1}) 3288, 3058, 2933, 2873, 1636, 1598, 1426, 1320, 1268, 1214, 1154, 1088, 891, 815; HRMS (EI) *m*/*z* 485.0376 (calcd for $C_{20}H_{24}BrNO_4S_2$ 485.0330).

(*E*)-*N*-[7-Bromo-6-(toluene-4-sulfonyl)hept-5-enyl]-4-methylbenzenesulfonamide (7d): colorless oil, R_f 0.43 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (m, 4H), 2.24 (td, J = 7.3, 7.6 Hz, 2H), 2.42 (s, 3H), 2.43 (s, 3H), 2.93 (td, J = 6.5, 6.2 Hz, 2H), 4.08 (s, 2H), 5.08 (t, J = 6.2 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.4, 21.5, 24.5, 28.3, 28.9, 42.5, 126.9, 128.2, 129.6, 129.8, 136.5, 136.8, 138.8, 143.3, 144.6, 147.0; IR (neat, cm^{-1}) 3446, 3057, 2987, 2934, 1733, 1636, 1423, 1375, 1318, 1266, 1158, 1089, 1047, 814; HRMS (EI) *m*/*z* 499.0481 (calcd for $C_{21}H_{26}BrNO_4S_2$ 499.0487).

General Procedure for the Cyclization of Compound 7b. A solution of compound **7b** (50 mg, 0.11 mmol) and K_2CO_3 (18 mg, 0.13 mmol) in DMF (4 mL) was stirred at room temperature for 3 h. The reaction solution was poured into saturated ammonium chloride solution (20 mL), extracted with diethyl ether (three times), and washed with water (two times). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (hexanes:ethyl acetate = 1:1) to afford product **8a** (27 mg, 63%).

1,5-Bis(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (8a): colorless oil, R_f 0.35 (hexanes:ethyl acetate = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (m, 2H), 2.43 (s, 3H), 2.47 (s, 3H), 3.18 (t, J = 5.6 Hz, 2H), 3.79 (s, 2H), 6.99 (t, J = 2.1 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 21.7, 25.2, 41.4, 42.8, 127.6, 128.0, 129.9, 130.2, 133.3, 135.5, 136.0, 137.4, 144.2, 145.0; IR (neat, cm^{-1}) 3056, 2967, 1423, 1349, 1313, 1266, 1164, 1082, 896; HRMS (EI) *m*/*z* 391.0916 (calcd for $C_{19}H_{21}NO_4S_2$ 391.0912).

1-(Toluene-4-sulfonyl)-2-[1-(toluene-4-sulfonyl)vinyl]pyrrolidine (9a): colorless oil, R_f 0.38 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (m, 1H), 1.79 (m, 2H), 2.02 (m, 1H), 2.41 (s, 3H), 2.51(s, 3H), 3.13 (m, 1H), 3.58 (m, 1H), 4.05 (dd, J = 6.6, 2.9 Hz, 1H), 6.20 (d, J = 0.6 Hz, 1H), 6.45 (d, J = 0.6 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 22.5, 24.1, 34.2, 50.3, 58.9, 125.5, 128.1, 129.3, 130.3, 130.5, 133.9, 136.5, 144.5, 145.5, 152.2; IR (neat, cm^{-1}) 3056, 2987, 1598, 1442, 1423, 1349, 1313, 1266, 1164, 1139, 1082, 1006, 896, 814; HRMS (EI) *m*/*z* 405.1058 (calcd for $C_{20}H_{23}NO_4S_2$ 405.1068).

1-(Toluene-4-sulfonyl)-2-[1-(toluene-4-sulfonyl)vinyl]piperidine (9b): colorless oil, R_f 0.40 (hexanes:ethyl acetate = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (m, 1H), 1.42 (m, 1H), 1.50 (m, 2H), 2.24 (m, 1H), 2.41 (s, 3H), 2.47 (s, 3H), 3.04 (m, 1H), 3.75 (m, 1H), 4.90 (dd, J = 4.1, 1.8 Hz, 1H), 5.90 (d, J = 1.2 Hz, 1H), 6.30 (d, J = 1.2 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.0, 22.2, 22.4, 24.7, 28.5, 42.7, 53.7, 127.3, 127.6, 129.1, 130.4, 130.6, 136.8, 138.1, 144.1, 145.5, 150.1; IR (neat, cm^{-1}) 3058, 2987, 2929, 1654, 1598, 1494, 1448, 1422, 1345, 1323, 1301, 1267, 1157, 1111, 1087, 1042, 1020, 995, 968, 908; HRMS (EI) *m*/*z* 419.1296 (calcd for $C_{21}H_{25}NO_4S_2$ 419.1225).

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