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Ring-Opening Reactions of MCPs with Sulfonamides Promoted by Metal Triflate Lewis Acids

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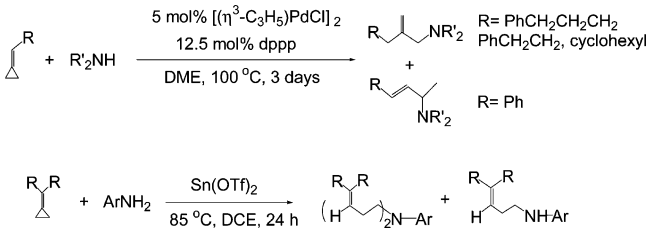
The reaction of aromatic MCPs with sulfonamides catalyzed by Lewis acids affords the corresponding ring-opened homoallylic sulfonamides in good yields and the reaction of aliphatic MCPs with sulfonamides gives the corresponding pyrrolidine derivatives under the same conditions. Through deuterium-labeling experiments, we found that the reaction process is involved with the rearrangement of a cyclopropylcarbinyl cation and a nonclassic carbonium ion.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis. MCPs **1** undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1] Recently, transition-metal catalysts such as palladium complexes[2] or Lewis acids[3] such as metal triflate catalyzed transformations of methylenecyclopropanes (MCPs) have been widely investigated. For example, Yamamoto previously reported the Pd(II)-catalyzed hydroamination of MCPs in a Markovnikov-type addition to give allylic amines in good yields at 100 °C for 3 days (Scheme 1).[2j] In addition, we found that Lewis acids such as $Sn(OTf)_2$, $Yb(OTf)_3$, and $BF_3{\cdot}Et_2O$ can efficiently catalyze the reaction of MCPs **1** with aromatic amines to produce various homoallylic amines (Scheme 1).[3b] In this Lewis acid-mediated reaction, both aromatic and aliphatic MCPs **1** showed high reactivities toward aromatic amines to give the corresponding ring-opened homoallylic aromatic amines in good to quantitative yields under milder conditions (85 °C, 24 h). Since the Lewis acid-mediated addition of amines to MCPs **1** offered a convenient method to furnish novel products having carbon−nitrogen bonds[4] which are different from those derived from Pd-catalyzed reactions, it is necessary to disclose further the scope and limitations of this Lewis acid-mediated ring-opening reaction. Herein we wish to report the new results in our continuing studies on the ring-opening reaction of MCPs with sulfonamides mediated by Lewis acids. Moreover, the plausible reaction mechanism is disclosed based on the deuterium-labeling experiments.

SCHEME 1. The Reaction of MCPs with Amine Catalyzed by Pd or Lewis Acid



Results and Discussion

At first, we used diphenylmethylenecyclopropane (MCP (**1a**); 3.0 equiv) and $TsNH_2$ (**2a**; 1.0 equiv) as the substrates to seek out a suitable Lewis acid catalyst (10 mol %) for this reaction in 1,2-dichloroethane (DCE) at 85 °C. Various $M(OTf)_x$ (M = Sn, Yb, Cu, Sc, Zr, and Zn) type of Lewis acids were tested in this reaction. The

(1) For synthesis of MCPs see: Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 598. For reviews on the reaction of MCPs, please see: (a) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, *344*, 111. (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213.

(2) For Pd(0)- or Pd(II)-catalyzed ring-opening reactions of MCPs please see: (a) Nüske, H.; Notlemeyer, M.; de Meijere, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3411. (b) Nakamura, I.; Oh, B.-H.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1298. (c) Oh, B.-H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6203. (d) Fournet, G.; Balme, G.; Goré, J. *Tetrahedron* **1988**, *44*, 5809. (e) Bräse, S.; de Meijere A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2545. (f) Lautens, M.; Meyer, C.; Lorenz, A. *J. Am. Chem. Soc.* **1996**, *118*, 10676. (g) Tsukada, N.; Shibuya, A.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123. (h) Tsukada, N.; Shibuya, A.; Nakamura, I.; Kitahara, H.; Yamamoto, Y. *Tetrahedron* **1999**, *55*, 8833. (i) Nakamura, I.; Saito, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2661. (j) Nakamura, I.; Itagaki, H.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 6458. (k) Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3365. (l) Suginome, M.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 11015. (m) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. (n) Ohta, T.; Takaya, H. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press, Oxford, UK, 1991; Vol. 5, pp 1185−1205. (o) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (p) Zuber, R.; Carlens, G.; Haag, R.; de Meijere, A. *Synlett* **1996**, 542.

(3) (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145. (b) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019.

(4) (a) Gase, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703. (b) Savoia, D. In *Methods of Organic Chemistry (Houben-Weyl)*; Helmchen, G., Hoffmann, R. W., Wulzer, J., Schaumann, E., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1995; Vol. E21e, p 5356. (c) Muller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.

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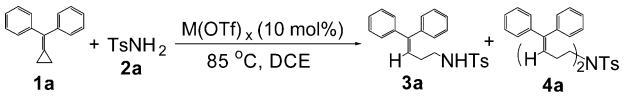
TABLE 1. The Effect of Various M(OTf)$_x$ Lewis Acids on the Reaction of 1a (3.0 equiv) with TsNH$_2$ (2a; 1.0 equiv)



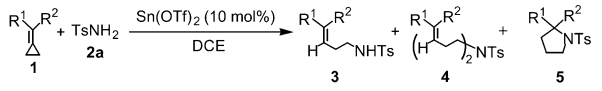
entry	M(OTf)$_x$	time (h)	yields (%)[a] 3a	4a
1	Sn(OTf)$_2$	19	28	72
2	Yb(OTf)$_3$	19	30	65
3	Cu(OTf)$_2$	15	44	54
4	Sc(OTf)$_3$	15	75	24
5	Zr(OTf)$_4$	15	65	35
6	Zn(OTf)$_2$	48	50	9
7	HOTf	24	60	15

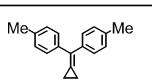
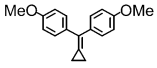
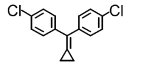
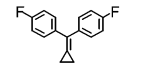
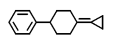
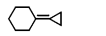
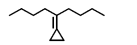
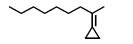
[a] Isolated yields.

results were summarized in Table 1. Except for Zn(OTf)$_2$, many M(OTf)$_x$ (M = Sn, Yb, Cu, Sc, and Zr) Lewis acids can efficiently catalyze this ring-opening reaction to give the two corresponding homoallylic sulfonamide products **3a** and **4a** in high to quantitative yields based on the employed TsNH$_2$ (**2a**) within 19 h at 85 °C (Table 1, entries 1−6). Sc(OTf)$_3$ is the best Lewis acid catalyst for the formation of **3a**. Sn(OTf)$_2$ is the best Lewis acid catalyst for the formation of **4a** (Table 1, entries 1 and 4). In addition, the reaction also can take place in the presence of Brönsted acid CF_3SO_3H (HOTf) (15 mol %) to give **3a** in 60% and **4a** in 15%, respectively (Table 1, entry 7). We confirmed that M(OTf)$_x$ (M = Sn, Yb, Cu, Sc, Zr, and Zn) does not decompose to give CF_3SO_3H upon heating at 80 °C. Thus, as a result of using M(OTf)$_x$ as a Lewis acid, this novel ring-opening reaction does not involve CF_3SO_3H at all.

Then, we utilized Sn(OTf)$_2$ as a Lewis acid to carry out the reaction of various MCPs **1** with TsNH$_2$ (**2a**) in DCE under the same conditions. We found that the substituents on the benzene ring for aromatic MCPs **1** significantly affected the outcome of this reaction. In the case of di(*p*-tolyl)methylenecyclopropane (**1b**), which has an electron-donating group on the benzene ring, **1b** was completely consumed to afford the corresponding *N*-monoalkylated sulfonamide product **3b** at lower temperature (40 °C) in 50% yield along with some unidentified byproducts (Table 2, entry 1). None of the *N*,*N*-dialkylated product was formed even if extending the reaction time. The reaction of **1c** having a methoxy group on the benzene ring even proceeded at room temperature (17 °C). Only **1c** showed such high reactivity to give the corresponding homoallylic sulfonamide **3c**, albeit in moderate yield along with some unidentified byproducts (Table 2, entry 2). At higher reaction temperature, many side reactions take place because of the high reactivities of **1b** and **1c** to give **3b** and **3c** in lower yields, respectively. On the other hand, if MCPs **1** have electron-withdrawing groups on the benzene ring, the reaction rate was slowed, but the ring-opened reaction products were obtained in higher yields at 85 °C within 2 days. For example, with di(*p*-chlorophenyl)methylenecyclopropane (**1d**), prolonged reaction time is required to produce homoallylic sulfonamides **3d** and **4d** in 55% and 38% yield, respectively, based on **2a** (Table 2, entry 3). Di(*p*-fluorophenyl)methylenecyclopropane (**1e**) gives similar results (Table 2, entry 4). The less reactive aliphatic

TABLE 2. The Reaction of MCPs 1 (3.0 equiv) with TsNH$_2$ (2a; 1.0 equiv) Catalyzed by Sn(OTf)$_2$



entry	MCPs		temp. (°C)	time (d)	yield (%)[a] 3	4	5
1[b]		**1b**	40	1	**3b** (50)	–	–
2[b]		**1c**	17	1	**3c** (35)	–	–
3		**1d**	85	2	**3d** (55)	**4d** (38)	–
4		**1e**	85	2	**3e** (39)	**4e** (61)	–
5[c]		**1f**	100	3	–	–	**5f** (51) **5f** (27)[d]
6[c]		**1g**	100	3	–	–	**5g** (46)
7[c]		**1h**	100	3	–	–	**5h** (44)
8[c]		**1i**	100	3	–	–	**5i** (40)

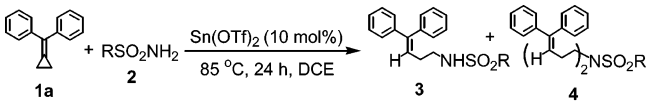
[a] Isolated yields on TsNH$_2$ **2a**. [b] Due to the high reactivity, many side reactions occurred, and we found the MCP was completely consumed in this reaction under the above conditions. [c] For entries 5 to 8, the reactions were carried out with 1.2 equiv of MCPs and 1.0 equiv of TsNH$_2$. [d] Using HOTf (10 mol %) as a catalyst.

MCPs **1f**−**i** (1.2 equiv) with **2a** (1.0 equiv) produced the corresponding pyrrolidine derivatives **5**[5] in moderate yields at 100 °C rather than homoallylic sulfonamides along with some unidentified byproducts (Table 2, entries 5, 6, 7, and 8). With use of HOTf (10 mol %) as a catalyst under the same conditions, **5f** was obtained in 27% (Table 2, entry 5). It should be emphasized here that pyrrolidine derivatives **5** were obtained in lower yields (10−20%) under conditions similar to those described above (3.0 equiv of **2a**, 50−85 °C, 2 days). We believe that **5** is derived from the intramolecular nucleophilic attack of the formed corresponding *N*-monoalkylated sulfonamide product **3** to the double bond,[6] which should be a fast reaction process at 100 °C, therefore, **3** was immediately transformed into **5** as soon as it was formed. Increasing the amount of employed MCPs **1f**−**i** to 3.0 equiv, similar results were obtained. Consequently, we came to the conclusion that the *N*-monoalkylated sulfonamide products **3** derived from the reaction of aromatic MCPs with sulfonamide have a trend to undergo the intermolecular reaction producing *N*,*N*-dialkylated product **4**, while those derived from the reaction of aliphatic MCPs with sulfonamide prefer the intramolecular reaction to form pyrrolidine derivatives **5**. The structures of **3**, **4**, and **5** were determined by ^{1}H NMR and ^{13}C NMR spectroscopic data and HRMS. In addition, the structure of **5f** was

(5) From cyclopropyl ketones to pyrrolidines: (a) Alper, P. B.; Meyers, C.; Lerchner, A.; Siegel, D. R.; Carreira, E. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3186. (b) Lautens, M.; Han, W. *J. Am. Chem. Soc.* **2002**, *124*, 6312. (c) Bertozzi, F.; Gustafsson, M.; Olsson, R. *Org. Lett.* **2002**, *4*, 3147.

(6) For cyclization of homoallylic sulfonamides, please see: Haskins, C. M.; Knight, D. W. *Chem. Commun.* **2002**, 2724.

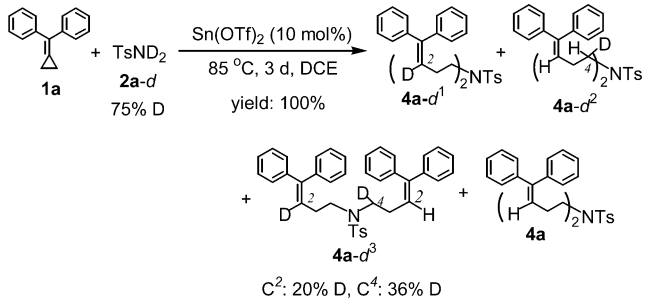
TABLE 3. The Reaction of 1a (3.0 equiv) with RSO_2NH_2 (2; 1.0 equiv) Catalyzed by $Sn(OTf)_2$



entry	RSO_2NH_2[b]		yields (%)[a] 3	4
1	O_2N-C$_6$H$_4$-SO_2NH_2	**2b**	**3j** (62)	-
2	O_2N-C$_6$H$_4$-SO_2NH_2	**2c**	**3k** (54)	-
3	$CH_3SO_2NH_2$	**2d**	**3l** (64)	**4l** (22)
4	NHTs	**2e**	**3m** (88)	

[a] Isolated yields.

SCHEME 2. The Reaction of $TsND_2$ with 1a in the Presence of $Sn(OTf)_2$



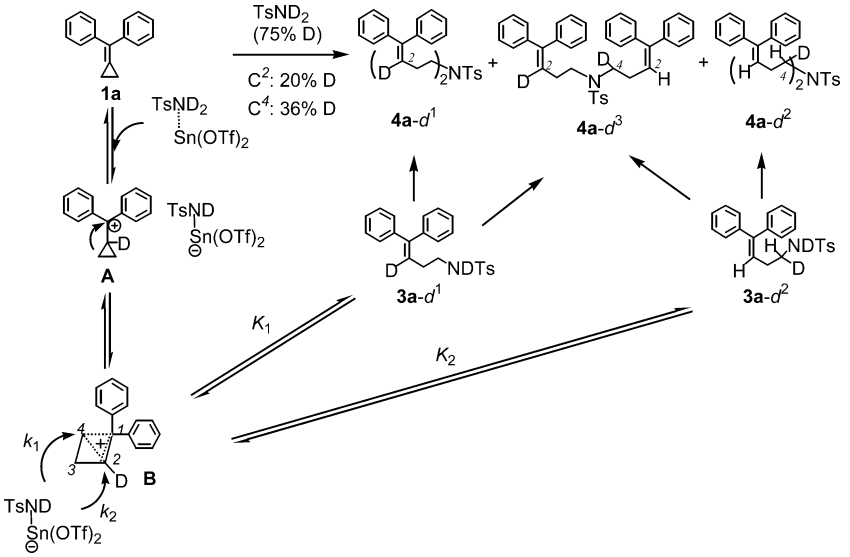
unambiguously disclosed by X-ray diffraction. The ORTEP drawing of **5f** is shown in the Supporting Information.[7]

The reactions of MCP **1a** with sulfonamides **2b**−**e** were also examined (Table 3). For *p*- or *m*-nitrobenzenesulfonamides **2b** and **2c**, only the corresponding *N*-monoalkylated sulfonamide products **3j** and **3k** were formed in 62% and 54% yields, respectively, under the same conditions (Table 3, entries 1 and 2). This may be because nitro substitution reduced the nucleophilicity of sulfonamides **2**. Aliphatic sulfonamides **2d** and **2e** proved more reactive toward **1a**, giving the corresponding homoallylic sulfonamide products **3l**, **4l**, and **3m** in high yields, respectively (Table 3, entries 3 and 4).

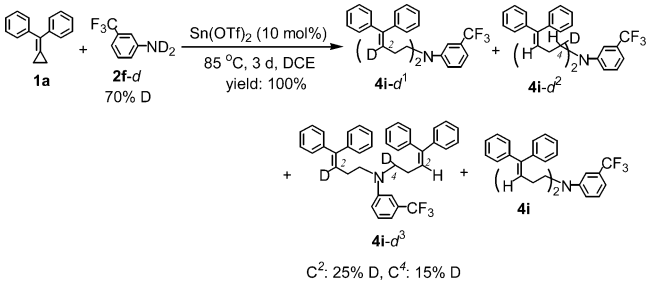
To clarify the reaction mechanism for this ring-opening reaction of MCPs with sulfonamide **2**, the reaction of deuterated sulfonamide:$TsND_2$ (**2a**-*d*)[8] (D content 75%) with **1a** was carried out in the presence of Lewis acid (Scheme 2). On the basis of ^{1}H NMR spectroscopic data, we confirmed that besides olefinic carbon C_2 (D content 20%), deuterium incorporation also occurred at homoallylic carbon C_4 (D content 36%).[9] This result suggests that the ring opening involves addition across a bicyclobutonium ion **B**, probably formed from the collapse of an initially cyclopropylcarbinyl cation **A** (Scheme 3).

A plausible mechanism was shown in Scheme 3. In the presence of Lewis acid, MCPs first formed a cyclopropylcarbinyl cation **A** after seizing D^+ from $TsND_2$ in the presence of $Sn(OTf)_2$. Due to the neighboring-group participation by the cyclopropyl ring, the nonclassic carbocation:bicyclobutonium ion **B**[10,11] would be formed. If the sulfonamide nucleophilic attack took place at C_4 of **B** (k_1), *N*-monoalkylated sulfonamide product **3a**-d^1 with deuterium incorporation exclusively at the carbinyl carbon would result. Product **3a**-d^1 would repeat the cycle with another molecule of **1a**, affording the corresponding doubly deuterated *N*,*N*-dialkylated sulfonamide **4a**-d^1 and **4a**-d^3. Nucleophilic attack at C_2 of **B** (k_2) would afford **3a**-d^2 with deuterium incorporation exclusively at the homoallylic carbon; reaction with a second equivalent of **1a** produces **4a**-d^2 and **4a**-d^3. There is a competition between the two processes (k_1 and k_2). However, at the present stage, it is difficult to determine the exact values of k_1 and k_2 in the reaction of **1a** with $TsND_2$. In the meantime, we also examined the deuterium-labeling experiments in the reactions of MCPs **1** with aromatic amines.[3] The result is shown in Scheme 4. We found that in the reaction of **1a** with deuterated 3-trifluoromethylaniline **2f**-*d* (D content 70%), the deuterium incorporation also occurred at the homoallylic carbon (15% D

SCHEME 3. The Plausible Reaction Mechanism for the Ring-Opening Reaction of MCPs with Deuterated *p*-Toluenesulfonamide



SCHEME 4. The Reaction of Deuterated Aromatic Amine with 1a in the Presence of $Sn(OTf)_2$



content). Thus, we believe that this is a general phenomenon in such ring-opening reactions catalyzed by Lewis acids.

In conclusion, upon investigation of the reactions of MCPs **1** with sulfonamides **2** in the presence of Lewis acid, we found that the corresponding homoallylic sulfonamides **3** and **4** can be produced in moderate to good yields in the reaction of aromatic MCPs **1a**−**e** with sulfonamides **2**.[12] The pyrrolidine derivatives **5** (some of them are spiro-heterocyclic compounds) were formed when aliphatic MCPs **1** were used as the substrates under the same conditions. The deuterium-labeling experiment disclosed that the reaction process is involved with the rearrangement of a cyclopropylcarbinyl cation and a bicyclobutonium ion. Except for deuterated sulfonamide, deuterated aromatic amine was also tested in this reaction. Efforts are underway to elucidate the mechanistic details of this reaction and to disclose its scope and limitations. Work along this line is currently in progress.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were measured by a spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra and HRMS were recorded by EI methods. The organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC silica gel coated plates. Flash column chromatography was carried out with 300−400 mesh silica gel at increased pressure.

General Procedure for the Preparation of Homoallylic Sulfonamides 3 and 4. To a mixture of aromatic MCPs **1** (0.9 mmol), sulfonamide **2** (0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the reaction mixture was stirred at the corresponding temperature under argon atmosphere until the starting materials were completely consumed. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane as the eluent, to yield **3** and **4**.

General Procedure for the Preparation of Pyrrolidine Derivatives 5. To a mixture of aliphatic MCPs **1** (0.36 mmol), sulfonamide **2** (0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 100 °C with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane as the eluent, to yield **5**.

General Procedure for the Reaction of MCP 1a with Deuterated Nucleophiles. To a mixture of MCP **1a** (0.9 mmol), deuterated nucleophile (0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane as the eluent, to yield the corresponding deuterated products.

***N*-(1,1-Diphenyl-1-butenyl)-*p*-toluenesulfonamide (3a) and *N*,*N*-Bis(1,1-diphenyl-1-butenyl)-*p*-toluenesulfonamide (4a).** To a mixture of diphenylmethylenecyclopropane (**1a**; 0.185 g, 0.9 mmol), *p*-toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 19 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by a flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **3a** (0.032 g, 28%) and **4a** (0.126, 72%), respectively, as a colorless liquid. **3a**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.24−2.31 (m, 2H), 2.41 (s, 3H), 3.01−3.08 (m, 2H), 4.39 (t, 1H, J = 6.0 Hz), 5.90 (t, 1H, J = 7.5 Hz), 7.08−7.34 (m, 12H), 7.69 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 30.1, 43.3, 124.8, 127.3, 127.3, 127.5, 127.5, 128.4, 128.6, 129.9, 123.0, 137.0, 139.7, 142.2, 143.6, 144.8; MS (EI) m/z 193 ([M − $C_8H_{10}NSO_2$]$^+$, 44.05), 155 (18.26), 115 (42.51), 91 (27.83), 84 (100); HRMS (EI) calcd for $C_{23}H_{23}NSO_2$ 377.1449, found 377.1432; IR (neat) υ 3283, 3056, 3029, 2984, 2927, 1642, 1598, 1494 cm^{-1}. **4a**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.16−2.24 (m, 4H), 2.35 (s, 3H), 3.13 (t, 4H, J = 7.5 Hz), 5.92 (t, 2H, J = 7.2 Hz), 7.04−7.35 (m, 22H), 7.56 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 28.7, 47.4, 125.1, 127.3, 127.5, 128.4, 128.5, 128.5, 128.6, 128.9, 129.9, 137.4, 139.9, 142.3, 143.2, 144.2; MS (EI) m/z 583 (M$^+$, 2.03), 390 (46.73), 193 (16.80), 167 (100), 91 (44.13); HRMS (EI) calcd for $C_{24}H_{24}NSO_2$ 390.1528, found 390.1478; IR (neat) υ 3055, 3029, 2986, 1655, 1598, 1494 cm^{-1}.

***N*-[1,1-Di-(*p*-tolyl)-1-butenyl]-*p*-toluenesulfonamide (3b).** To a mixture of di(*p*-tolyl)methylenecyclopropane (**1b**; 0.211 g, 0.9 mmol), *p*-toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 40 °C for 24 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **3b** (0.060 g, 50%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.21−2.28 (m, 2H), 2.30 (s, 3H), 2.37 (s, 3H), 2.40 (s, 3H), 2.98−3.04 (m, 2H), 4.64 (t, 1H, J = 6.0 Hz), 5.82 (t, 1H, J = 7.2 Hz), 6.97 (d, 2H, J = 7.8 Hz), 7.03 (s, 4H), 7.14 (d, 2H, J = 7.8 Hz), 7.23 (d, 2H, J = 7.8 Hz), 7.70 (d, 2H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 21.5, 21.8, 30.0, 43.4, 123.7, 127.4, 129.0, 129.2, 129.8, 129.9, 129.9, 136.8, 137.1, 137.3, 137.5, 139.2, 143.5, 144.2; MS (EI) m/z 405 (M$^+$, 5.67), 221 (100), 184 (14.59), 155 (31.01), 91 (46.24); HRMS

(7) The X-ray data of **5f** have been deposited in CCDC, number 213673. Empirical formula: $C_{22}H_{27}O_2NS$. Formula weight: 369.51. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.510 × 0.248 × 0.217 mm^3. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 5.9875(5) Å, b = 19.9377(18) Å, c = 15.8348(14) Å, α = 90°, β = 94.585(2)°, γ = 90°, V = 1884.3(3) Å^3. Space group: $P2(1)/n$; Z value = 4; D_{calc} = 1.303 g/cm^3; F_{000} = 792; μ(Mo Kα) = 1.98 cm^{-1}. Diffractometer: Rigaku AFC7R. Residuals: R, R_w 0.0500, 0.1150.

(8) Deuterated sulfonamide and aromatic amine were prepared according to the literature: (a) Smith, J. K.; Bergbreiter, D. E.; Newcomb, M. *J. Org. Chem*. **1985**, *50*, 4549. (b) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc*. **1981**, *103*, 1048. (c) Guha, A. K.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1999**, 765.

(9) We believe that the low D content is due to the partially D−H exchange of ambient water with $TsND_2$ during a prolonged reaction time.

(10) Mazur, R. H.; White, W. W.; Semenoe, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc*. **1959**, *81*, 4390.

(11) The formation of a four-membered cyclic compound through bicyclobutonium ion **B** has been reported. Please see: Hiroi, K.; Nakamura, H.; Anzai, T. *J. Am. Chem. Soc*. **1987**, *109*, 1249.

(12) Previously, we reported Pd(II)- and Pd(0)-cocatalyzed reactions of sulfonamides with MCPs **1** to give allylic amines in good yields. Shi, M.; Chen, Y.; Xu, B. *Org. Lett*. **2003**, *5*, 1225.

(EI) calcd for $C_{25}H_{27}NSO_2$ 405.1762, found 405.1743; IR (neat) ν 3283, 2923, 1649, 1599, 1511 cm^{-1}.

***N*-[1,1-Di-(*p*-Methoxyphenyl)-1-butenyl]-*p*-toluenesulfonamide (3c).** To a mixture of di(*p*-methoxylphenyl)-methylenecyclopropane (**1c**; 0.240 g, 0.9 mmol), *p*-toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was stirred at 17 °C for 24 h under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/4) as the eluent, to yield **3c** (0.046 g, 35%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.23−2.30 (m, 2H), 2.42 (s, 3H), 3.00−3.06 (m, 2H), 3.79 (s, 3H), 3.84 (s, 3H), 4.34 (t, 1H, J = 6.0 Hz), 5.74 (t, 1H, J = 7.5 Hz), 6.78 (d, 2H, J = 8.7 Hz), 6.88 (d, 2H, J = 8.7 Hz), 7.01 (d, 2H, J = 8.7 Hz), 7.06 (d, 2H, J = 8.7 Hz), 7.25 (d, 2H, J = 8.6 Hz), 7.68 (d, 2H, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 30.0, 43.4, 55.7, 55.7, 113.6, 113.7, 122.7, 127.3, 128.5, 128.6, 129.9, 132.1, 135.3, 137.1, 143.5, 144.0, 158.9, 159.2; MS (EI) *m*/*z* 437 (M^+, 4.77), 253 (100), 184 (3.38), 155 (15.69), 91 (42.66); HRMS (EI) calcd for $C_{23}H_{22}NSO_2Cl$ 437.1661, found 437.1692; IR (neat) ν 3283, 2955, 2836, 1606, 1505, 1463 cm^{-1}.

***N*-[1,1-Di(*p*-chlorophenyl)-1-butenyl]-*p*-toluenesulfonamide (3d) and *N*,*N*-Bis[1,1-di(*p*-chlorophenyl)-1-butenyl]-*p*-toluenesulfonamide (4d).** To a mixture of di(*p*-chlorophenyl)methylenecyclopropane (**1d**; 0.246 g, 0.9 mmol), *p*-toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 48 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluant, to yield **3d** (0.073 g, 55%) and **4d** (0.082 g, 38%), respectively, as a colorless liquid. **3d**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.21−2.28 (m, 2H), 2.42 (s, 3H), 3.01−3.08 (m, 2H), 4.65 (t, 1H, J = 6.6 Hz), 5.92 (t, 1H, J = 7.2 Hz), 7.01 (d, 2H, J = 8.4 Hz), 7.05 (d, 2H, J = 8.4 Hz), 7.21 (d, 2H, J = 8.4 Hz), 7.25 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 29.9, 42.8, 125.7, 126.9, 128.3, 128.4, 128.6, 129.7, 131.0, 133.3, 133.3, 136.7, 137.3, 140.0, 142.3, 143.5; MS (EI) *m*/*z* 445 (M^+, 5.76), 226 (9.63), 184 (100), 155 (68.61), 91 (30.67), 84 (70.59); HRMS (EI) calcd for $C_{23}H_{21}Cl_2NO_2S$ 445.0670, found 445.0665; IR (neat) ν 3278, 3031, 2926, 1597, 1492 cm^{-1}. **4d**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.15−2.22 (m, 4H), 2.40 (s, 3H), 3.13 (t, 4H, J = 7.5 Hz), 5.93 (t, 2H, J = 7.5 Hz), 6.99 (d, 4H, J = 8.4 Hz), 7.07 (d, 4H, J = 8.4 Hz), 7.22 (d, 4H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.4 Hz), 7.33 (d, 4H, J = 8.4 Hz), 7.57 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 28.6, 47.2, 125.8, 126.9, 128.3, 128.4, 128.6, 129.6, 131.0, 133.3, 133.3, 136.8, 137.5, 140.0, 141.7, 143.2; MS (EI) *m*/*z* 719 (M^+, 0.70), 458 (82.82), 261 (14.95), 235 (100), 91 (36.89); HRMS (MALDI) calcd for $[C_{39}H_{33}Cl_4NO_2S]^+$ 719.0986, found 720.1059 $[C_{39}H_{33}Cl_4NO_2S + H]^+$; IR (neat) ν 3031, 2925, 1593, 1492 cm^{-1}.

***N*-[1,1-Di(*p*-fluorophenyl)-1-butenyl]-*p*-toluenesulfonamide (3e) and *N*,*N*-Bis[1,1-di(*p*-fluorophenyl)-1-butenyl]-*p*-toluenesulfonamide (4e).** To a mixture of di(*p*-fluorophenyl)methylenecyclopropane (**1e**; 0.218 g, 0.9 mmol), *p*-toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 48 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluant, to yield **3e** (0.048 g, 39%) and **4e** (0.120 g, 61%), respectively, as a colorless liquid. **3e**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.22−2.29 (m, 2H, CH_2), 2.42 (s, 3H), 3.02−3.08 (m, 2H), 4.39 (t, 1H, J = 6.0 Hz), 5.85 (t, 1H, J = 7.5 Hz), 6.92−7.13 (m, 8H), 7.27 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 29.8, 42.9, 114.9 (d, J_{C-F} = 21.5 Hz), 115.3 (d, J_{C-F} = 21.1 Hz), 124.8, 127.0, 128.7 (d, J_{C-F} = 7.7 Hz), 129.6, 131.2 (d, J_{C-F} = 8.0 Hz), 135.0 (d, J_{C-F} = 3.1 Hz), 136.7, 137.9 (d, J_{C-F} = 3.3 Hz), 142.5, 143.4, 160.4 (d, $^1J_{C-F}$ = 245.9 Hz), 163.7 (d, $^1J_{C-F}$ = 245.9 Hz); MS (EI) *m*/*z* 413 (M^+, 11.26), 229 (22.64), 184 (100), 155 (81.84), 91 (41.67); HRMS (EI) calcd for $C_{23}H_{21}F_2NO_2S$ 413.1261, found 413.1217; IR (neat) ν 3274, 3047, 2927, 1601, 1509, 1223, 1159 cm^{-1}. **4e**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.17−2.23 (m, 4H), 2.39 (s, 3H), 3.16 (t, 4H, J = 7.5 Hz), 5.89 (t, 2H, J = 7.5 Hz), 6.91−7.15 (m, 16H), 7.20 (d, 2H, J = 8.4 Hz), 7.60 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 28.6, 47.3, 115.0 (d, J = 21.3 Hz), 115.3 (d, J = 21.9 Hz), 125.1, 126.9, 128.8 (d, J = 8.0 Hz), 129.6, 131.21 (d, J = 7.9 Hz), 135.3 (d, J = 3.2 Hz), 136.9, 138.1 (d, J = 2.9 Hz), 141.9, 143.1, 160.4 (d, $^1J_{C-F}$ = 245.9 Hz), 163.7 (d, $^1J_{C-F}$ = 245.9 Hz); MS (EI) *m*/*z* 655 (M^+, 1.41), 426 (75.93), 203 (100), 91 (18.92); HRMS (MALDI) calcd for $[C_{39}H_{33}F_4NO_2S]^+$ 655.2168, found 656.2241 $[C_{39}H_{33}F_4NO_2S + H]^+$; IR (neat) ν 3044, 2927, 2871, 1602, 1509, 1224, 1158 cm^{-1}.

***N*-(1,1-Diphenyl-1-butenyl)-*p*-nitrobenzenesulfonamide (3j).** To a mixture of diphenylmethylenecyclopropane (**1a**; 0.185 g, 0.9 mmol), *p*-nitrobenzenesulfonamide (**2b**; 0.061 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 24 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/4) as the eluent, to yield **3j** (0.076 g, 62%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.23−2.30 (m, 2H), 3.12−3.19 (s, 2H), 4.65 (t, 1H, J = 6.0 Hz), 5.86 (t, 1H, J = 7.5 Hz), 7.07−7.37 (m, 10H), 7.81 (dd, 2H, J = 2.1, 6.6 Hz), 8.25 (dd, 2H, J = 2.1, 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.2, 43.5, 124.2, 124.6, 127.4, 127.6, 127.8, 128.4, 128.4, 128.7, 129.8, 139.5, 141.9, 145.2, 146.2, 150.1; MS (EI) *m*/*z* 408 (M^+, 2.19), 215 (7.39), 193 (100), 186 (19.45), 91 (25.26); HRMS (EI) calcd for $C_{22}H_{20}N_2O_4S$ 408.1144, found 408.1140; IR (neat) ν 3296, 3075, 3051, 1606, 1533, 1494 cm^{-1}.

***N*-(1,1-Diphenyl-1-butenyl)-*m*-nitrobenzenesulfonamide (3k).** To a mixture of diphenylmethylenecyclopropane (**1a**; 0.185 g, 0.9 mmol), *m*-nitrobenzenesulfonamide (**2c**; 0.061 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 24 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/4) as the eluent, to yield **3k** (0.066 g, 54%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.26−2.33 (m, 2H), 3.12−3.18 (m, 2H), 4.65 (t, 1H, J = 6.0 Hz), 5.88 (t, 1H, J = 7.5 Hz), 7.07−7.38 (m, 10H), 7.64 (t, 1H, J = 8.1 Hz), 8.11 (dd, 1H, J = 1.8, 8.1 Hz), 8.35 (dd, 1H, J = 1.8, 8.1 Hz), 8.66 (t, 1H, J = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.2, 43.5, 122.4, 124.2, 127.3, 127.4, 127.6, 127.7, 128.4, 128.6, 129.8, 130.7, 132.7, 139.5, 141.9, 142.5, 145.2, 148.4; MS (EI) *m*/*z* 408 (M^+, 3.56), 215 (8.78), 193 (100), 186 (20.99), 91 (31.35); HRMS (EI) calcd for $C_{22}H_{20}N_2O_4S$ 408.1144, found 408.1174; IR (neat) ν 3296, 3080, 3056, 1606, 1533, 1494 cm^{-1}.

***N*-(1,1-Diphenyl-1-butenyl)methanesulfonamide (3l) and *N*,*N*-Bis(1,1-diphenyl-1-butenyl)methanesulfonamide (4l).** To a mixture of diphenylmethylenecyclopropane (**1a**; 0.185 g, 0.9 mmol), methanesulfonamide (**2d**; 0.029 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 24 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **3l** (0.058 g, 64%) and **4l** (0.033 g, 22%), respectively, as a colorless liquid. **3l**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.34−2.41 (m, 2H), 2.82 (s, 3H), 3.16−3.23 (m, 2H), 4.63 (t, 1H, J = 6.0 Hz), 6.04 (t, 1H, J = 7.5 Hz), 7.15−7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 40.5, 43.3, 124.8, 127.5, 127.6, 127.6, 128.5, 128.7, 130.0, 139.7, 142.2, 145.0; MS (EI) *m*/*z* 301 (M^+, 13.93), 193 (100), 108 (9.15), 91 (19.22), 79 (7.24); HRMS (EI) calcd for $C_{17}H_{19}NO_2S$ 301.1136, found 301.1143; IR (neat) ν 3291, 3055, 3025, 2918, 1653, 1599, 1494, 1444 cm^{-1}. **4l**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.26−

2.33 (m, 4H), 2.68 (s, 3H), 3.17 (t, 4H, J = 7.5 Hz), 5.99 (t, 2H, J = 7.5 Hz), 7.10−7.36 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0, 39.2, 47.1, 124.9, 127.4, 127.5, 127.6, 128.4, 128.6, 129.9, 139.8, 142.2, 144.4; MS (EI) m/z 507 (M^+, 1.26), 428 (0.83), 314 (6.13), 193 (23.49), 91 (21.41), 77 (60.36); HRMS (EI) calcd for $C_{37}H_{33}N\,O_2S$ 507.2232, found 507.2214; IR (neat) υ 3052, 3028, 2915, 1645, 1599, 1494, 1445 cm^{-1}.

***N*-(1,1-Diphenyl-1-butenyl)-*N*-propargyl-*p*-toluenesulfonamide (3m).** To a mixture of diphenylmethylenecyclopropane (**1a**; 0.185 g, 0.9 mmol), *N*-propargyl-*p*-toluenesulfonamide (**2e**; 0.062 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 85 °C for 24 h with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/4) as the eluent, to yield **3m** (0.109 g, 88%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.97 (t, 1H, J = 2.4 Hz), 2.35−2.42 (m, 2H), 2.40 (s, 3H), 3.31 (t, 2H, J = 7.5 Hz), 4.01 (d, 2H, J = 2.1 Hz), 6.05 (t, 1H, J = 7.5 Hz), 7.14−7.37 (m, 12H), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 28.0, 36.1, 46.0, 73.8, 76.5, 124.9, 127.2, 127.3, 127.6, 128.1, 128.3, 129.1, 129.5, 129.7, 136.0, 139.6, 142.2, 143.4, 144.1; MS (EI) m/z 415 (M^+, 1.12), 222 (100), 193 (9.01), 179 (2.46), 155 (59.84), 91 (63.89); HRMS (EI) calcd for $C_{26}H_{25}NO_2S$ 415.1606, found 415.1568; IR (neat) υ 3306, 3028, 2926, 2257, 2138, 1599, 1495 cm^{-1}.

1-(Toluene-4-sulfonyl)-7-phenyl-1-aza-spiro[4.5]-decane (5f). To a mixture of *p*-phenylcyclohexylidenecyclopropane (**1f**; 0.071 g, 0.36 mmol), toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 100 °C for 3 d with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **5f** (0.057 g, 51%) as a colorless solid. Mp 149−150 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.43−1.97 (m, 10H), 2.41 (s, 3H), 2.53−2.70 (m, 3H), 3.41 (t, 2H, J = 6.6 Hz), 7.16−7.31 (m, 7H), 7.76 (d, 2H, J = 9.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 23.0, 30.0, 32.5, 36.6, 37.0, 43.2, 49.4, 69.3, 126.3, 126.9, 127.3, 128.6, 129.6, 139.3, 142.8, 146.9; MS (EI) m/z 369 (M^+, 1.26), 250 (100), 155 (14.00), 91 (24.85); IR (neat) υ 2976, 2924, 2867, 1600, 1494, 1343, 1154 cm^{-1}. Anal. Calcd for $C_{22}H_{27}NO_2S$: C, 71.51; H, 7.37; N, 3.79. Found: C, 71.42; H, 7.40; N, 3.61.

1-(Toluene-4-sulfonyl)-1-aza-spiro[4.5]decane (5g). To a mixture of cyclohexylidenecyclopropane (**1g**; 0.044 g, 0.36 mmol), toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 100 °C for 3 d with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **5g** (0.041 g, 46%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.20−1.86 (m, 12H), 2.33 (dt, 2H, J = 3.6, 12.0 Hz), 2.41 (s, 3H), 3.38 (t, 2H, J = 6.0 Hz), 7.26 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22.7, 24.6, 25.0, 29.3, 36.4, 49.1, 69.6, 127.0, 126.3, 139.1, 142.3; MS (EI) m/z 293 (M^+, 23.74), 250 (71.02), 173 (100), 155 (44.66), 138 (23.05), 91 (79.16); HRMS (EI) calcd for $C_{16}H_{23}NO_2S$ 293.1449, found 250.0894 $[C_{16}H_{23}NO_2S - C_3H_7]^+$; IR (neat) υ 2928, 2862, 1598, 1494, 1330, 1152 cm^{-1}.

1-(Toluene-4-sulfonyl)-2,2-dibutylpyrrolidine (5h). To a mixture of dibutylmethylenecyclopropane (**1h**; 0.060 g, 0.36 mmol), toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 100 °C for 3 d with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **5h** (0.045 g, 44%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.86 (t, 3H, J = 6.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 1.16−1.96 (m, 16H), 2.41 (s, 3H), 3.35 (t, 2H, J = 6.6 Hz), 7.26 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.4, 23.1, 23.3, 26.9, 36.0, 40.0, 49.8, 71.9, 126.9, 129.2, 138.8, 142.3; MS (EI) m/z 294 [$(M - C_3H_7)^+$, 3.84], 280 (100), 155 (24.04), 91 (36.48), 57 (8.08); HRMS (EI) calcd for $C_{19}H_{31}NO_2S$ 337.2075, found 337.2076; IR (neat) υ 2956, 2930, 2871, 1599, 1495, 1337, 1157 cm^{-1}.

1-(Toluene-4-sulfonyl)-2-methyl-2-heptylpyrrolidine (5i). To a mixture of methylheptylmethylenecyclopropane (**1i**; 0.060 g, 0.36 mmol), toluenesulfonamide (**2a**; 0.051 g, 0.3 mmol), and $Sn(OTf)_2$ (0.013 g, 10 mol %) was added anhydrous DCE (2.0 mL), and the resulting mixture was heated at 100 °C for 3 d with stirring under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using EtOAc/hexane (1/10) as the eluent, to yield **5i** (0.040 g, 40%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.86−0.91 (t, 3H, J = 6.9 Hz), 0.89 (s, 3H), 1.18−1.93 (m, 16H), 2.41 (s, 3H), 3.35 (dt, 2H, J = 2.1, 6.6 Hz), 7.26 (d, 2H, J = 8.1 Hz), 7.73 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.4, 22.6, 22.8, 25.2, 26.4, 29.3, 30.0, 31.8, 39.3, 41.0, 49.4, 68.5, 127.1, 129.2, 138.7, 142.4; MS (EI) m/z 322 [$(M - CH_3)^+$, 3.16], 238 (100), 155 (22.61), 91 (34.31); HRMS (EI) calcd for $C_{19}H_{31}NO_2S$ 337.2075, found 322.1855 $[C_{19}H_{31}NO_2S - CH_3]^+$. IR (neat) υ 2956, 2927, 2856, 1599, 1495, 1339, 1157 cm^{-1}.

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Supporting Information Available: ^{1}H NMR spectra for all new compounds reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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