Regioselective Intramolecular [3+2] Annulation of Allene-Nitrones

Fuyuhiko Inagaki, Harumi Kobayashi, and Chisato Mukai*

Division of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University; Kakuma-machi, Kanazawa 920–1192, Japan.

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The regioselective intramolecular 1,3-dipolar cycloaddition of the phenylsulfonylallene-nitrone derivatives has been developed. This reaction showed that the distal double bond of the allene exclusively reacted with the nitrone group to produce the bicyclic isoxazolidine derivatives regardless of the substitution pattern on the allenyl moiety.

Key words allene; nitrone; 1,3-dipolar cycloaddition

Allene serves as a unique and powerful π-component in various types of cycloaddtions with an additional π-counterpart.[1—4] It has been clarified that the intermolecular 1,3-dipolar cycloaddition of substituted-allenes with nitrones tends to undergo the regioselective ring closure to produce the corresponding methylene-substituted isoxazolidine derivatives. The thus formed initial products sometimes collapsed into secondary products *via* the N–O bond fission depending on the property of the substituent on the allenyl moiety and/or reaction conditions.[5—15] In contrast to the intermolecular reaction, there are very few examples of the intramolecular 1,3-diploar cycloaddition between the nitrone and allene groups.[16—22] Of particular interest among them is the reaction of the nitrone **1**[16] derived from the reaction of 5,6-heptadien-2-one with *N*-methylhydroxylamine (Chart 1). The *in situ* formed **1** (n=1) furnished the bicyclic isoxazolidine **2** in 45% yield *via* the cycloaddition with the distal double bond of the allenyl group, while the nonselective formation of the two bicyclic cycloadducts **3** (36%, two diastereoisomers in a ratio of 26 to 10) and **4** (29%) was observed when the one carbon-elongated nitrone **1** (n=2) was employed. The production of **3** could be rationalized in terms of the initial formation of compound **3′**, which must have been derived by the participation of the proximal double bond of the allene. On the other hand, we have previously reported that the phenylsulfonylallene-azido derivative **5** was susceptible to the intramolecular 1,3-dipolar cycloaddition to exclusively produce the triazabicyclo[m.3.0]ring system **6** (m=3—5),[23] in which the distal double bond of the allene of **5** consistently took part in the ring-closing process unlike the case of compound **1** (n=2) (Chart 2). We describe here the highly regioselective intramolecular 1,3-dipolar cycloaddition of a series of phenylsulfonylallene-nitrone derivatives **7** with different substitution patterns on the allenyl moiety.

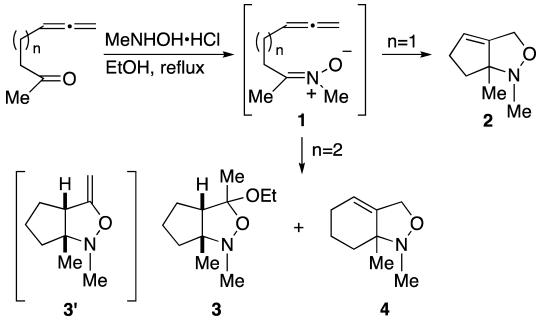


Chart 1. Intramolecular 1,3-Dipolar Cycloaddition of Monosubstituted Allene-Nitrone

Treatment of a 0.1 M solution of the aldehyde **8a**[24] in EtOH with 3 eq of MeNHOH·HCl and $NaHCO_3$ at 0°C for 2 h effected the formation of the nitrone derivative **7a**, followed by the 1,3-dipolar cycloaddition to give the 2-phenylsulfonyl-8-oxa-7-azabicyclo[4.3.0]non-1-ene (**9a**) in 54% yield (Table 1, entry 1). The ring closure exclusively occurred at the distal double bond of the allenyl moiety. This is in good accordance with the behavior of the phenylsulfonylallene-azido derivative **5**[23] (Chart 2). A better yield (63%) was obtained when the reaction was performed at room temperature (entry 2). It was found that 1.3 eq of MeNHOH·HCl and $NaHCO_3$ were enough to get satisfactory yields (entries 3—6). Dimethyl sulfoxide (DMSO) was superior to EtOH or CH_3CN as the solvent (entries 4—6). Thus, the best result was obtained as follows. Upon exposure to MeNHOH·HCl and $NaHCO_3$ (1.3 eq) in DMSO (0.05 M) at room temperature for 0.5 h, **8a** produced **9a** in 96% yield (entry 6).

Since the 1,1-disubstituted allene **8a** exclusively afforded

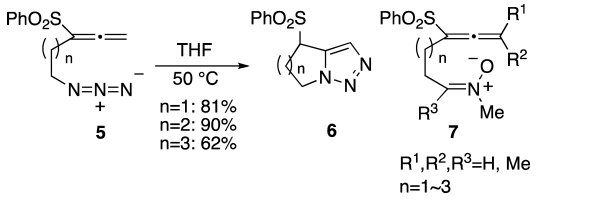
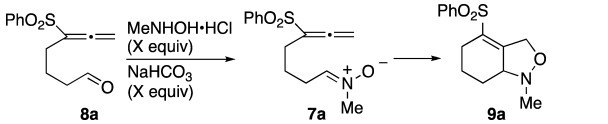


Chart 2. Intramolecular 1,3-Dipolar Cycloaddition of 1,1-Disubstituted Allene-Azide

Table 1. Intramolecular 1,3-Dipolar Cycloaddition of 1,1-Disubstituted Allene-Nitrone **7a**



Entry	X (eq)	Temp.	Solvent (M)	Time (h)	Yield (%)
1	3	0°C	EtOH (0.1)	2	54
2	3	rt	EtOH (0.1)	0.1	63
3	1.3	rt	EtOH (0.1)	1	70
4	1.3	rt	EtOH (0.05)	4	85[a)]
5	1.3	rt	CH_3CN (0.05)	48	75
6	1.3	rt	DMSO (0.05)	0.5	96

a) Starting material **8a** was recovered in 6% yield.

* To whom correspondence should be addressed. e-mail: mukai@p.kanazawa-u.ac.jp

the 8-oxa-7-azabicyclo[4.3.0]nonene **9a** *via* the regioselective reaction with the distal double bond of the allenyl moiety, we next investigated the regioselectivity regarding the distal *versus* proximal double bonds of the 1,1,3-trisubstituted- and 1,1,3,3-tetrasubstituted allene-nitrones (Chart 3). Based on the optimal conditions described in Table 1, entry 6, the 1,1,3-trisubstituted allene **8b**[25] was treated with MeNHOH·HCl in DMSO to provide the 8-oxa-7-azabicyclo[4.3.0] derivative **9b** in 87% yield as a mixture of two diastereoisomers in a ratio of 3 to 2. The distal double bond of the allene again exclusively took part in the ring-closing step. The preparation of the 1,1,3,3-tetrasubstituted allene-aldehyde **8c** was unexpectedly troublesome. The oxidation of the primary alcohol **10c**[26] with Dess–Martin periodinane afforded a mixture of several compounds that involves the desired aldehyde **8c**, which was found to be unstable and partially decompose during the work-up process. The alcohol **10c** was oxidized with IBX (3 eq) in DMSO (the formation of the aldehyde **8c** was monitored by TLC) and the resulting reaction mixture was directly treated with MeNHOH·HCl and $NaHCO_3$ to furnish **9c** in 37% yield. We assumed that the unreacted oxidant might mainly cause the low yield (37%). After carefully screening several conditions, we finally developed the following consecutive procedure. The oxidation of **10c** with IBX (3 eq) in DMSO at room temperature for 3 h was followed by the addition of 2-propanol (5 eq) for complete consumption of the excess IBX. The resulting reaction mixture was subsequently exposed to MeNHOH·HCl and $NaHCO_3$ to produce **9c** in 74% yield in a highly regioselective manner. Thus, it became obvious that the intramolecular 1,3-diploar cycloaddition of the phenylsulfonylallene-nitrone derivatives **7** consistently provided the corresponding bicyclo[4.3.0] skeletons irrespective of the substitution pattern on the allenyl moiety.

The one-pot procedure was then applied to the other two primary alcohols **10a**, **b** to afford **9a** and **b** in 80% and 69% yields, respectively (Chart 4). It should be mentioned that the methylallene-alcohol **11**[27] did not provide the cycloadducts under these conditions in spite of the fact that the formation of the corresponding methylallene-aldehyde was unambiguously confirmed by the ^{1}H-NMR spectrum.

The one-carbon shortened allene-aldehyde **12**[25] under the standard conditions produced a mixture of **13** and its isomer **13'** in 67% yield in the ratio of 2 to 1.[28] In addition, the one-carbon larger-sized 9-oxa-8-azabicyclo[5.3.0] derivative **15** could also be formed from the allene-aldehyde **14**[24] in 74% yield[29] (Chart 5).

As already shown in Chart 1, the nitrone group of the allene-nitrone **1** (n=2) nonselectively reacted with both the distal and proximal double bonds of the allene. This is in sharp contrast to the results obtained for the 1,3-diploar cycloaddition of the phenylsulfonylallene-nitrone derivatives **7**, where the distal double bond exclusively participated in the reaction. Thus, our interests became directed toward the 1,3-diploar cycloaddition of the phenylsulfonylallene-nitrone derivative **17** (Chart 6). Treatment of the allene-ketone **16** with MeNHOH·HCl and $NaHCO_3$ (1 eq) in DMSO at room temperature for 2 d did not give any cycloadducts. Heating the reaction mixture at 80°C provided the 6,7-dimethyl-2-phenylsulfonyl-8-oxa-7-azabicyclo[4.3.0]non-1-ene (**18**) in 29% yield. Several experiments indicated that the formation of the ketonitrone must be the rate-determining step in this transformation (monitored by ^{1}H-NMR spectrum). It was reported[30] that a Lewis acid accelerates the formation of the ketonitrones in the reaction between the ketone and hydroxylamines groups. Thus, we examined some Lewis acids and finally found that the combination of $ZnCl_2$ and $MgSO_4$[30] is suitable for our purpose. In fact, **16** was exposed to MeNHOH·HCl in the presence of $ZnCl_2$ and $MgSO_4$[30] in CH_2Cl_2/DMSO at 30°C for 28.5 h to give the desired product **18** in 73% yield as the sole isolatable product. Introduction of a phenylsulfonyl group on the allenyl moiety of **1** (n=2) led to the highly regioselective construction of the oxa-azabicyclo[m.3.0] frameworks (m=3—5).

In summary, we have developed the intramolecular 1,3-dipolar cycloaddition of phenylsulfonylallene-nitrones for the highly regioselective formation of bicyclo[m.3.0] derivatives (m=3—5). The distal double bond of the phenylsulfonylallene

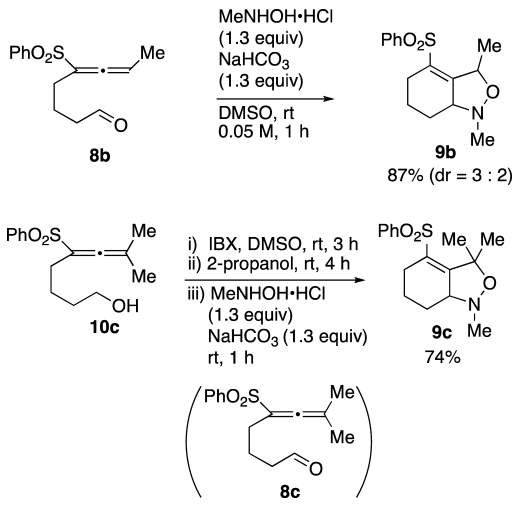


Chart 3. Intramolecular 1,3-Dipolar Cycloaddition of 1,1,3-Tri- and 1,1,3,3-Tetrasubstituted Allene-Nitrones

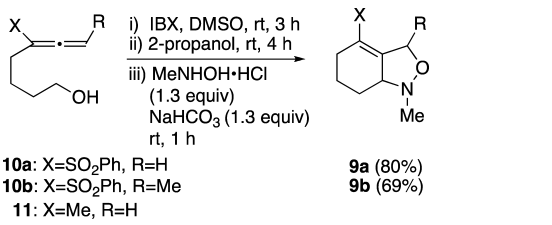


Chart 4. One-Pot Oxidation and 1,3-Dipolar Cycloaddition of Allene-Alcohols

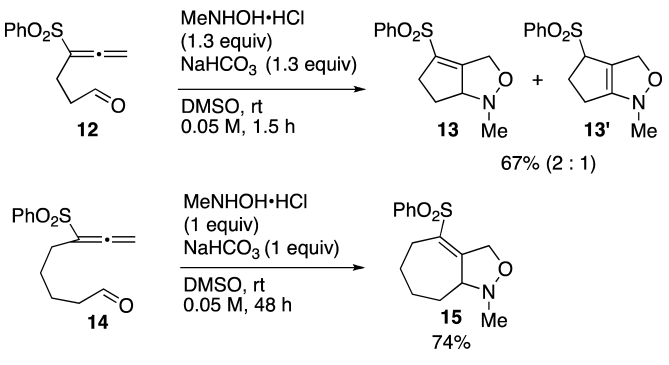


Chart 5. Intramolecular 1,3-Dipolar Cycloaddition with **12** and **14**

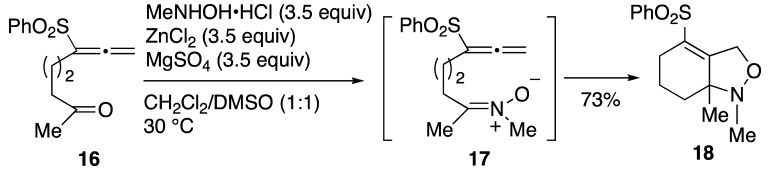


Chart 6. Intramolecular 1,3-Dipolar Cycloaddition of Allene-Ketonitrone **16**

regioselectively reacted with the nitrone moiety. No cycloadducts derived from the reaction between the proximal double bond could be isolated.

Experimental

General Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^{1}H-NMR spectra were taken in $CDCl_3$ unless otherwise indicated. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C-NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard unless otherwise stated. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230—400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

General Procedure for 1,3-Dipolar Cycloaddition with Aldehydes (A) To a solution of aldehyde derivative (0.10 mmol) in DMSO (2 mL) were added MeNHOH·HCl (11 mg, 0.13 mmol) and $NaHCO_3$ (11 mg, 0.13 mmol) at room temperature. After stirring until the complete disappearance of the starting material as indicated by TLC, the reaction mixture was quenched by addition of water, extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt to afford oxa-azabicyclo[*m*.3.0] derivative (*m*=3—5).

General Procedure for One-Pot Oxidation and 1,3-Dipolar Cycloaddition from Alcohols (B) To a solution of alcohol derivative (0.10 mmol) in DMSO (2 mL) was added IBX (84 mg, 0.30 mmol) at room temperature. After stirring for 3 h at the same temperature, 2-propanol (40 μL, 0.52 mmol) was added to the mixture, which was further stirred for 3 h. Then, MeNHOH·HCl (11 mg, 0.13 mmol) and $NaHCO_3$ (11 mg, 0.13 mmol) were added to the mixture at room temperature. After stirring until the complete disappearance of the starting material as indicated by TLC, the reaction mixture was quenched by addition of water, extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford oxa-azabicyclo[*m*.3.0] derivative (*m*=3, 4).

7-Methyl-2-phenylsulfonyl-8-oxa-7-azabicyclo[4.3.0]non-1-ene (9a) Colorless oil; IR 1655 cm^{-1}; ^{1}H-NMR δ: 7.97—7.95 (m, 2H), 7.71—7.66 (m, 1H), 7.56 (t, 2H, *J*=7.8 Hz), 4.60 (d, 1H, *J*=2.7 Hz), 4.35 (d, 1H, *J*=2.7 Hz), 3.70 (br s, 1H), 2.64—2.54 (m, 4H), 2.13—2.08 (m, 1H), 1.93—1.79 (m, 4H); ^{13}C-NMR δ: 157.7, 135.6, 134.2, 130.8, 128.6, 87.5, 85.1, 75.2, 45.1, 35.1, 32.5, 24.7; MS *m/z* 279 (M$^+$, 100.0); high resolution (HR)-MS Calcd for $C_{14}H_{17}NO_3S$ 279.0929, Found 279.0926.

(6*R,9*R**)- and (6*R**,9*S**)-7,9-Dimethyl-2-phenylsulfonyl-8-oxa-7-azabicyclo[4.3.0]non-1-ene (9b)** A mixture of (6*R**,9*R**)-**9b** and (6*R**,9*S**)-**9b** in the ratio of 3 to 2 was obtained as pale yellow powder, mp 108.5—109.5°C (AcOEt/hexane); IR 1684 cm^{-1}; ^{1}H-NMR δ: 7.90—7.87 (m, 2H), 7.67—7.64 (m, 1H), 7.56—7.52 (m, 2H), 5.21 (q, 1Hx3/5, *J*=7.9 Hz), 4.73 (q, 1Hx2/5, *J*=7.2 Hz), 3.66 (d, 1Hx2/5, *J*=4.1 Hz), 3.60 (d, 1Hx3/5, *J*=4.8 Hz), 2.61—2.51 (m, 4Hx2/5, 1Hx3/5), 2.45—2.38 (m, 4Hx3/5), 2.07—2.04 (m, 1Hx2/5), 1.97—1.76 (m, 4Hx3/5, 2Hx2/5), 1.81 (d, 3Hx3/5, *J*=7.9 Hz), 1.70—1.66 (m, 2Hx2/5), 1.60 (d, 3Hx2/5, *J*=7.2 Hz); ^{13}C-NMR δ: 150.6, 149.7, 136.11, 136.08, 134.00, 139.95, 130.5, 130.2, 128.82, 128.75, 102.6, 100.1, 84.8, 84.6, 78.0, 75.6, 45.1, 44.6, 34.2, 32.5, 31.3, 30.8, 25.5, 25.0, 11.3, 11.1; MS *m/z* 293 (M$^+$, 36.6); HR-MS Calcd for $C_{15}H_{19}NO_3S$ 293.1086, Found 293.1088.

7,9,9-Trimethyl-2-phenylsulfonyl-8-oxa-7-azabicyclo-[4.3.0]non-1-ene (9c) Colorless plates, mp 110—111.5°C (AcOEt/hexane); IR 1688 cm^{-1}; ^{1}H-NMR δ: 7.82—7.81 (m, 2H), 7.65 (t, 1H, *J*=7.6 Hz), 7.53 (t, 2H, *J*=7.6 Hz), 3.62 (d, 1H, *J*=4.5 Hz), 2.61—2.56 (m, 1H), 2.46 (s, 3H), 2.41 (dd, 1H, *J*=13.4, 6.5 Hz), 1.99—1.89 (m, 2H), 1.88 (s, 3H), 1.84—1.77 (m, 1H), 1.69—1.67 (m, 1H), 1.62 (s, 3H); ^{13}C-NMR δ: 143.4, 136.2, 133.9, 130.0, 128.5, 112.3, 85.1, 78.7, 44.3, 31.4, 30.5, 25.7, 19.0, 18.7; MS *m/z* 307 (M$^+$, 100.0); HR-MS Calcd for $C_{16}H_{21}NO_3S$ 307.1242, Found 307.1238.

2-Methyl-6-phenylsulfonyl-3-oxa-2-azabicyclo[3.3.0]-oct-5-ene (13), 2-Methyl-6-phenylsulfonyl-3-oxa-2-azabicyclo[3.3.0]oct-1(5)-ene (13′) A 2 : 1 mixture of **13** and **13′** was obtained as a colorless oil. The ratio was determined by ^{1}H-NMR analysis of both the crude and purified product. Analytically pure **13** and **13′** were obtained by column chromatography. Compound **13**: colorless oil; IR 1647 cm^{-1}; ^{1}H-NMR (50°C) δ: 7.94 (d, 2H, *J*=7.6 Hz), 7.68 (t, 1H, *J*=7.6 Hz), 7.57 (t, 2H, *J*=7.6 Hz), 4.57 (br s, 1H), 4.28 (t, 1H, *J*=7.2 Hz), 4.03 (br s, 1H), 2.97 (q, 1H, *J*=10.3 Hz), 2.53 (s, 3H), 2.39—2.31 (m, 1H), 2.28—2.22 (m, 1H), 2.05—2.01 (m, 1H); ^{13}C-NMR (50°C) δ: 158.7, 136.5, 134.3, 130.3, 129.3, 129.1, 85.4, 76.5, 68.0, 26.7, 19.6; MS *m/z* 265 (M$^+$, 100); HR-MS Calcd for $C_{13}H_{15}NO_3S$ 265.0773, Found 265.0776. Compound **13′**: colorless oil; IR 1684 cm^{-1}; ^{1}H-NMR (45°C) δ: 7.90—7.88 (m, 2H), 7.66 (t, 1H, *J*=7.6 Hz), 7.57 (t, 2H, *J*=7.6 Hz), 4.72 and 4.68 (ABq, 2H, J_{AB}=15.5 Hz), 3.83 (t, 1H, *J*=6.9 Hz), 3.13—3.07 (m, 1H), 2.79 (dd, 1H, *J*=15.1, 8.9 Hz), 2.70 (s, 3H), 2.12—2.07 (m, 1H), 1.86—1.79 (m, 1H); ^{13}C-NMR (45°C) δ: 163.9, 139.3, 133.8, 131.5, 129.4, 127.7, 80.2, 65.5, 44.3, 37.6, 28.2; MS *m/z* 265 (M$^+$, 100); HR-MS Calcd for $C_{13}H_{15}NO_3S$ 265.0773, Found 265.0775.

8-Methyl-2-phenylsulfonyl-9-oxa-8-azabicyclo[5.3.0]dec-1-ene (15) To a solution of **14**[25] (26 mg, 0.10 mmol) in DMSO (2 mL) were added MeNHOH·HCl (8.4 mg, 0.10 mmol) and $NaHCO_3$ (8.4 mg, 0.10 mmol) at room temperature. After stirring for 48 h at the same temperature, the reaction mixture was quenched by addition of water, extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (2 : 1) to afford **15** (22 mg, 74%) as colorless plates: mp 87—88°C (AcOEt/hexane); IR 1651 cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ: 7.89—7.87 (m, 2H), 7.76 (t, 1H, *J*=7.6 Hz),

7.63 (t, 2H, J=7.6 Hz), 4.39 (d, 1H, J=2.4 Hz), 4.24 (d, 1H, J=2.4 Hz), 3.26 (br s, 1H), 2.49 (s, 3H), 2.39—2.33 (m, 1H), 1.91—1.87 (m, 1H), 1.79—1.66 (m, 2H), 1.62—1.59 (m, 1H), 1.50—1.37 (m, 3H); ^{13}C-NMR (DMSO-d_6) δ: 156.5, 135.5, 133.8, 130.3, 128.3, 83.1, 74.3, 65.3, 41.9, 27.1, 21.1, 19.2, 17.8; MS m/z 293 (M^+, 100); HR-MS Calcd for $C_{15}H_{19}NO_3S$ 293.1086, Found 293.1090.

6-(Phenylsulfonyl)octa-6,7-dien-2-one (16) To a solution of 2-methyl-2-(6-hydroxy-4-hexynyl)-1,3-dioxolane[31] (61 mg, 0.33 mmol) and Et_3N (0.14 mL, 1.0 mmol) in tetrahydrofuran (THF) (3 mL) was gradually added PhSCl (0.11 mL, 0.99 mmol) in THF (0.2 mL) at −78°C. After stirring for 2 h at the same temperature, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ at −78°C, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (2 : 1) to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH_2Cl_2 (2 mL) was added m-chloroperbenzoic acid (mCPBA) (44 mg, 0.25 mmol) at 0°C. After stirring for 1 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ and $NaHCO_3$, extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (2 : 1) to afford crude sulfone. To a solution of the crude sulfone in MeOH (2 mL) was added 3 drops of 10% HCl at room temperature. After stirring for 1 h at the same temperature, the reaction mixture was diluted with water, extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (2 : 1) to afford **16** (38 mg, 43%) as a colorless oil: IR 1969, 1938, 1715 cm^{-1}; ^{1}H-NMR δ: 7.90—7.88 (m, 2H), 7.64 (tt, 1H, J=7.3, 0.9 Hz), 7.57—7.53 (m, 2H), 5.40 (t, 2H, J=3.7 Hz), 2.44 (t, 2H, J=7.3 Hz), 2.25 (tt, 2H, J=7.3, 3.7 Hz), 2.10 (s, 3H), 1.72 (quin, 2H, J=7.3 Hz); ^{13}C-NMR δ: 207.8, 207.6, 139.9, 133.5, 129.0, 128.0, 112.7, 84.7, 42.1, 29.9, 25.9, 21.3; MS m/z 264 (M^+, 3.5); HR-MS Calcd for $C_{14}H_{16}O_3S$ 264.0820, Found 264.0825.

6,7-Dimethyl-2-phenylsulfonyl-8-oxa-7-azabicyclo[4.3.0]-non-1-ene (18) To a solution of **16** (26 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) were added $ZnCl_2$ (48 mg, 0.35 mmol), MeNHOH·HCl (29 mg, 0.35 mmol), $MgSO_4$ (42 mg, 0.35 mmol) at room temperature. After stirring for 13 h at the same temperature, the reaction mixture was filtered through a short pad of Celite and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (3 : 2) to afford **18** (21 mg, 73%) as a colorless oil: IR 1639 cm^{-1}; ^{1}H-NMR δ: 7.93—7.91 (m, 2H), 7.63 (t, 1H, J=7.3 Hz), 7.51 (t, 2H, J=7.3 Hz), 4.41 (d, 1H, J=2.3 Hz), 3.60 (br s, 1H), 2.88 (dt, 1H, J=12.8, 8.2 Hz), 2.64 (s, 3H), 2.14—2.02 (m, 2H), 1.86 (quin, 2H, J=8.2 Hz), 1.63 (s, 3H), 1.54 (br s, 1H); ^{13}C-NMR δ: 158.9, 138.4, 133.6, 131.0, 128.2, 84.4, 83.5, 78.2, 38.3, 34.9, 29.7, 21.0, 19.0; MS m/z 293 (M^+, 100); HR-MS Calcd for $C_{15}H_{19}NO_3S$ 293.1086, Found 293.1084.

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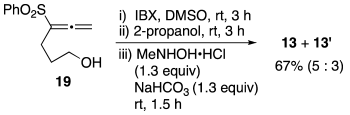
28) One-pot reaction of **19** provided a mixture of **13** and **13′** (5 : 3) in 67% yield.



29) The 1,3-dipolar cycloaddition of **14** under the standard condition (1.3 eq of MeNHOH·HCl and $NaHCO_3$) for 21 h gave **15** in a lower yield (41%). Decrease of MeNHOH·HCl and $NaHCO_3$ (1 eq) would prevent some side reactions, because the formation of another type of nitrone by the reaction of sulfonylallene and methylhydroxylamine was reported (see ref. 18).
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