Special Collection of Papers

This article is dedicated to Professor Satoshi Ōmura in celebration of his 2015 Nobel Prize.

Regular Article

Construction of Azabicyclo[6.4.0]dodecatrienes Based on Rhodium(I)-Catalyzed Intramolecular [6+2] Cycloaddition between Azetidine, Allene, and Alkynes

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Treatment of the allenylazetidine–alkynes with a catalytic amount of $[RhCl(CO)dppp]_2$ (dppp: 1,3-bis(diphenylphosphino)propane) effected the intramolecular hetero-[6+2]-type ring-closing reaction *via* the C–C bond cleavage of the azetidine ring to produce azabicyclo[6.4.0]dodecatriene derivatives in good to excellent yields. The formation of the oxa analogue could also be achieved.

Key words allene; azetidine; [6+2] cycloaddition; bicyclic compound; alkyne; rhodium

Small-sized cycloalkanes are often of significant use from synthetic points of view.[1–5] We recently disclosed that the rhodium(I)-catalyzed cycloaddition of allenylcyclopropane–alkynes **1** (n=0) afforded the bicyclo[5.4.0]undecatrienes **2** (n=0)[6] in the [5+2] ring-closing manner (Chart 1). The reaction must have proceeded *via* cleavage of the cyclopropane ring due to the relief of its high strain energy (27.5 kcal/mol).[7] A similar ring construction was realized using allenylcyclobutane–alkynes **1** (n=1) producing the eight-membered bicyclic compounds **2** (n=1)[8] in high yields ([6+2] cycloaddition). The unfunctionalized simple cyclobutane ring is generally known not to open, let alone being used as a C_4-building block.[1–5] We tentatively interpreted that the production of **2** (n=1) would initiate the formation of the rhodabicyclo[4.3.0] intermediate **3** (n=1),[8–10] which should be susceptible to β-carbon elimination,[1–5] with release of the ring strain energy (26.3 kcal/mol)[11] giving rise to the nine-membered rhodabicyclic species **4**. Reductive elimination would occur to provide the final products. The successful application of this methodology to the cyclopentane derivative **1** (n=2) afforded the nine-membered bicyclic compounds **2** (n=2).[9] This novel [7+2] cycloaddition involves the unprecedented cleavage of the normal-sized cyclopentane ring by releasing its strain energy (6.3 kcal/mol)[11] *via* the intermediate **3** (n=2),[8,9] similar to that of the cyclobutane derivatives.

We now report the application of a newly developed eight-membered ring formation method for the preparation of the bicyclic azocine derivatives as well as the oxa analogue (Chart 2). The polycyclic skeleton containing an eight-membered heterocycle has been found as the core structure in various natural products and biologically-active compounds.[12–14]

Results and Discussion

Our initial study employed the phenylsulfonylallene–alkyne **5a** having the *N*-tosyl-3-azetidine ring[15] at the allenic terminus. After careful screening, we found that the use of $[RhCl(CO)dppp]_2$ (dppp: 1,3-bis(diphenylphosphino)propane) in toluene at 80°C was suitable for our purpose to provide the expected azabicyclo[6.4.0]dodecatriene derivative **6a** (90% yield; Table 1, entry 1). The optimized reaction conditions [5 mol% $[RhCl(CO)dppp]_2$ in toluene at 80°C] were applied to several other allenylazetidine–alkyne species **5**. The substrate **5b**, having a methyl group at the allenic position, afforded the desired azabicyclo[6.4.0] product **6b**[16] in 99% yield (entry 2). This ring-closing reaction was found to be applicable to the internal alkyne species. Indeed, the 2-butynyl derivative **5c** gave the bicyclic product **6c** in 96% yield, although a higher reaction temperature was needed (entry 3). The oxygen congener **5d** produced the corresponding oxa compound **6d** in 85% yield (entry 4). We next examined the ring-closing reaction of the substrates having a *gem*-disubstituent (*gem*: geminal).[17] The reactions of the malonate derivative **5e** and the bis(phenylsulfonyl) derivative **5g** with 10 mol% $[RhCl(CO)dppp]_2$ afforded the corresponding cycloadducts **6e** (91% yield)

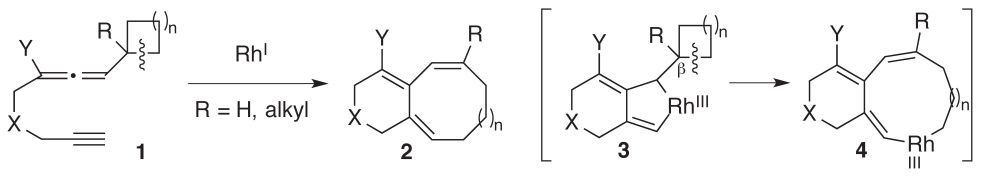

Chart 1. Previous Study: Rhodium(I)-Catalyzed Intramolecular [m+2] Cycloaddition of Allenylcycloalkane–Alkynes (m=5–7)

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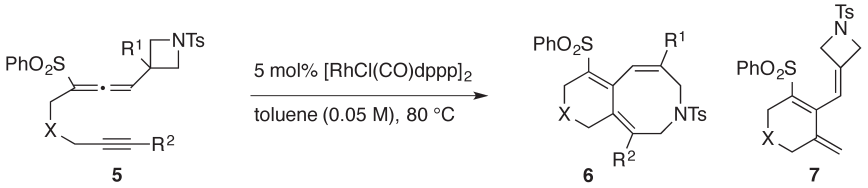
Table 1. $[RhCl(CO)dppp]_2$-Catalyzed Hetero-[6+2] Cycloaddition of Allenylazacyclobutane–Alkynes **5**



Entry	Substrate	R^1	R^2	X	Time (h)	Product and yield (%)[a]
1[b]	**5a**	H	H	NTs	0.2	**6a**: 90
2	**5b**	Me	H	NTs	0.2	**6b**: 99
3[c]	**5c**	Me	Me	NTs	0.2	**6c**: 96
4	**5d**	H	H	O	0.2	**6d**: 85
5[d]	**5e**	H	H	$C(CO_2Me)_2$	0.3	**6e**: 91
6[c]	**5f**	Me	H	$C(CO_2Me)_2$	0.2	**6f**: 82
7[d]	**5g**	H	H	$C(SO_2Ph)_2$	0.5	**6g**: 66
8	**5h**	H	H	$C(CH_2O)_2CMe_2$	0.2	**6h**: 91
9	**5i**	Me	H	CH_2	1	**6i**: 87[e]

a) Isolated yield. *b*) 0.10 M solution was used. *c*) Reaction was heated to reflux. *d*) 10 mol% $[RhCl(CO)dppp]_2$ was used. *e*) Yield was determined by ^{1}H-NMR analysis with $(CHCl_2)_2$ as the internal standard.

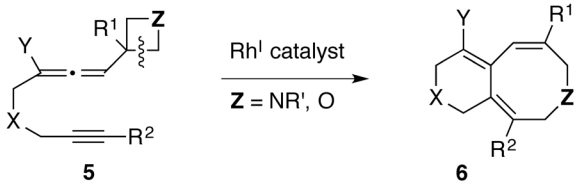


Chart 2. This Study: Rhodium(I)-Catalyzed Intramolecular Hetero-[6+2] Cycloaddition of Allenylheterocyclobutane–Alkynes

and **6g** (66% yield), respectively (entries 5, 7). The malonate derivative **5f**, having a methyl group at the allenic position, gave **6f** in 82% yield under reflux conditions (entry 6). The cyclic ketal derivative **5h** was also successfully converted into the bicyclic adduct **6h** in 91% yield (entry 8). The reaction of the simple carbon tether analogue **5i** without the *gem*-disubstituent was completed within 1 h to provide the corresponding cycloadduct **6i** in 87% NMR yield (entry 9).[18] Thus, it is obvious that the *gem*-disubstituent effect is not mandatory for this efficient transformation.[17] In the cases of the substrates without a substituent at the allenic position (entries 1, 4, 5, 7, 8), the by-production of **7** was detected by ^{1}H-NMR analysis of the crude product.[19]

The formation of **6** and **7** is rationalized to be in line with the previously proposed mechanism for the ring cleavage of the allenylcyclobutane[8] and allenylcyclopentane.[9] The initial coordination of **5** with Rh^I would occur between an allenic distal double bond and an alkyne to form the intermediate **A**, which should immediately collapse into the bicyclic rhodacyclopentene intermediate **B** *via* the oxidative ring-closing reaction (Chart 3). This intermediate **B** would undergo *β*-carbon elimination, presumably assisted by release of the azetidine ring strain,[20] resulting in formation of the nine-membered bicyclic rhodacycle **C**. Finally, the reductive elimination would then give the product **6** and regenerate the active Rh^I catalyst. For the substrates without a substituent at the allenic position, the *β*-hydride elimination instead of the *β*-carbon elimination of the common intermediate **B** (R^1=H) might proceed. Thus, the formation of **7** would be regarded as the *β*-hydride elimination of the common intermediate **B** (R^1=H). A higher yield of **6b** (99%) than that of **6a** (90%) must be due to the complete suppression of the undesired *β*-hydride elimination process.[21]

The substrate scope of this newly developed reaction was evaluated (Chart 4). It should be mentioned that a phenylsulfonyl substituent on the allenyl moiety was not mandatory for this transformation. In fact, the hetero-[6+2] cycloaddition of the methyl derivative **8a** and phenyl derivative **8b** proceeded in refluxing toluene without any problems to provide **9a** (99% yield) and **9b** (88% yield). A phenylsulfonyl group on the allenyl moiety can be regarded as a surrogate of hydrogen and be easily converted into a hydrogen atom by conventional means.[22–25] Upon exposure to the standard reaction conditions, the hetero-[6+2] cycloaddition of the substrate **10** possessing *N*-nosyl-3-azetidine easily occurred to afford the desired azabicyclo[6.4.0] product **11** in 92% yield. Furthermore, the allenyloxacyclobutane **12**[26] was found to be employed for the ring-closing reaction to give the oxa congener **13** in 81% yield.

In summary, we developed the rhodium(I)-catalyzed intramolecular hetero-[6+2] cycloaddition between alkyne, allene, and heterocyclobutanes under mild conditions leading to the efficient formation of the corresponding aza- and oxabicyclo[6.4.0]dodecatriene frameworks, in which the azetidine and oxetane served as a heteroatom-containing four-atom component. The further scope and limitations of this method as well as application to the synthesis of natural products are now in progress.

Experimental

General Melting points were measured with YANAGIMOTO micro melting point apparatus, and are uncorrected. IR spectra were measured with a SHIMADZU FTIR-8700 spectrometer for samples in $CHCl_3$ or with a Thermo Scientific Nicolet iS5 FT-IR spectrometer. ^{1}H-NMR spectra were measured with JNM-ECS400 or JNM-ECA600 spectrometers for samples in chloroform-*d* ($CDCl_3$). Tetramethylsilane (0.00 ppm) for compounds with a phenyl group or $CHCl_3$ (7.26 ppm) were used as an internal reference.

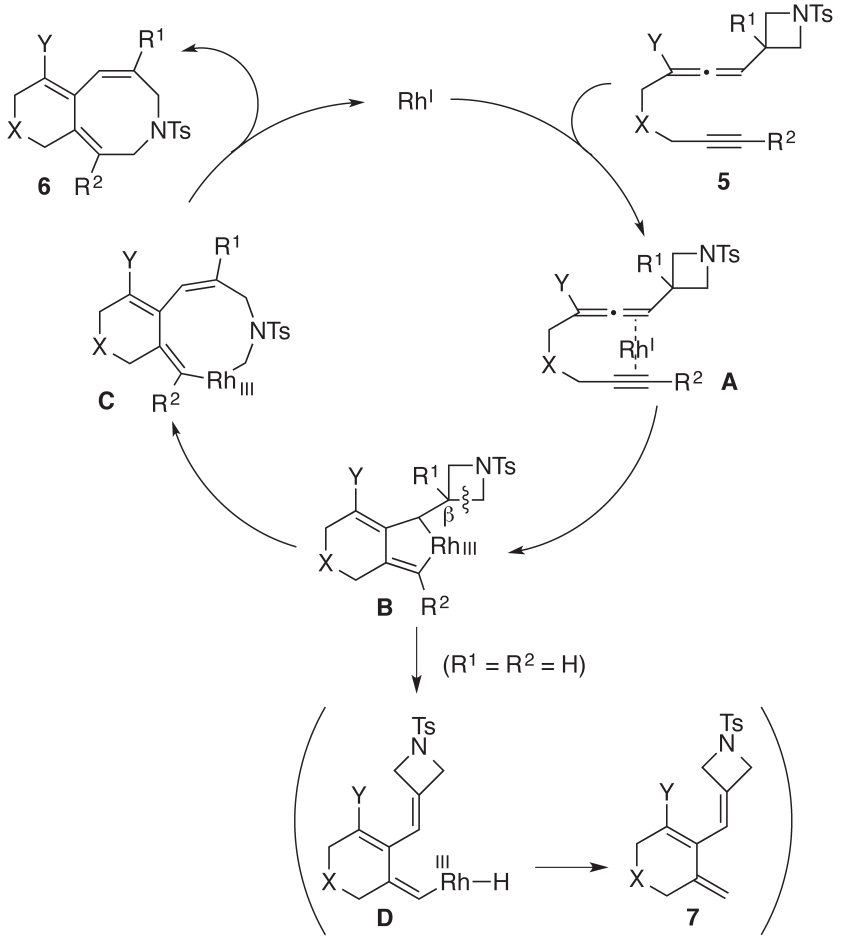


Chart 3. Plausible Mechanism for Intramolecular [6+2] Cycloaddition of **5**

^{13}C-NMR spectra were measured with JNM-ECS400 or JNM-ECA600 spectrometers for samples in $CDCl_3$. $CDCl_3$ (77.0 ppm) was used as an internal reference. High-resolution mass spectra (HR-MS) and MS were measured with JMS-T100TD (Direct Analysis in Real Time; DART) mass spectrometers. Single-crystal X-ray diffraction was measured with R-AXIS RAPID II. Commercially available anhydrous toluene (Kanto Chemical Co.) was employed for reactions. $[RhCl(CO)dppp]_2$[27] was prepared according to the literature procedure. Silica gel (Silica gel 60 N, 40–50 μm, Kanto Chemical Co.) was used for chromatography. All reactions were carried out under N_2 atmosphere. Organic extracts were dried over anhydrous Na_2SO_4.

General Procedure for Rh(I)-Catalyzed Intramolecular [6+2] Cycloaddition To a solution of allenylheterocyclobutane–alkyne (**5**, **8**, **10**, **12**,[28] 0.015–0.10 mmol) in solvent (1.0–2.0 mL) was added 5 mol% or 10 mol% $[RhCl(CO)dppp]_2$ under N_2 atmosphere. Then the reaction mixture was stirred at an appropriate temperature until complete disappearance of the starting material was confirmed by TLC analysis. The solvent was evaporated off, and the residue was chromatographed with hexane– ethyl acetate (AcOEt) or toluene–AcOEt to afford the corresponding cyclized product. Chemical yields are summarized in Table 1 and Chart 4.

***N*,*N*′-Bis(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4,11-diazabicyclo[6.4.0]dode-ca-1,6,8-triene (6a)** Yellow amorphous solid: IR 3030, 1447, 1350, 1163, 1088 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J=7.2 Hz, 2H), 7.66 (t, J=7.2 Hz, 1H), 7.62 (d, J=8.2 Hz, 2H), 7.54 (dd, J=7.2, 7.2 Hz, 2H), 7.48 (d, J=7.9 Hz, 2H), 7.31 (d, J=8.2 Hz, 2H), 7.21 (d, J=7.9 Hz, 2H), 7.07 (d, J=11.3 Hz, 1H), 5.46 (t, J=8.9 Hz, 1H), 5.28 (dt, J=11.3, 8.9 Hz, 1H), 4.21 (s, 2H), 3.74 (d, J=8.9 Hz, 2H), 3.66 (s, 2H), 3.47 (d, J=8.9 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 144.3, 144.1, 140.0, 137.6, 136.1, 136.0, 134.9, 134.1, 133.6, 130.1, 130.0, 129.8, 129.4, 127.7, 127.5, 127.2, 127.1, 126.3, 51.1, 46.8, 41.3, 40.5, 21.6, 21.5; DART MS *m*/*z* 611 (M^++1, 10.4); DART HR-MS Calcd for $C_{30}H_{31}N_2O_6S_3$ 611.1344. Found 611.1338.

6-Methyl-*N*,*N*′-bis(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4,11-diazabicyclo[6.4.0]dodeca-1,6,8-triene (6b) White solid: mp 130–133°C (AcOEt); IR 3030, 1352, 1159 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.75 (d, J=7.2 Hz, 2H), 7.64 (t, J=7.6 Hz, 1H), 7.60 (d, J=8.2 Hz, 2H), 7.55–7.51 (m, 4H), 7.30 (d, J=8.2 Hz, 2H), 7.26–7.25 (m, 2H), 6.58–6.57 (m, 1H), 5.28 (t, J=8.9 Hz, 1H), 4.21 (s, 2H), 3.77 (d, J=8.9 Hz, 2H), 3.55 (s, 2H), 3.20 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 1.65 (d, J=1.4 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 144.3, 144.0, 140.3, 138.5, 136.7, 136.3, 135.3, 134.6, 133.8, 133.3, 129.9, 129.8, 129.0, 127.7, 127.4, 127.0, 126.3, 124.8, 51.1, 46.6, 45.7, 40.3, 22.9, 21.53, 21.52; DART MS *m*/*z* 625 (M^++1, 100); DART HR-MS Calcd for $C_{31}H_{33}N_2O_6S_3$ 625.1501. Found 625.1504.

2,6-Dimethyl-*N*,*N*′-bis(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4,11-diazabicyclo[6.4.0]dodeca-1,6,8-triene

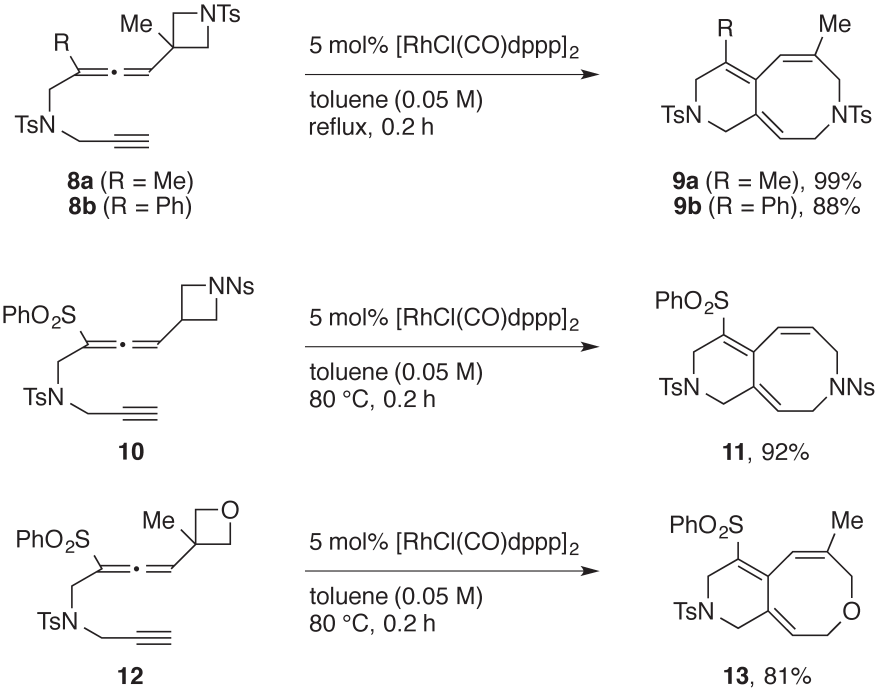


Chart 4. $[RhCl(CO)dppp]_2$-Catalyzed Hetero-[6+2] Cycloaddition of **8**, **10**, and **12**

(6c) White amorphous solid: IR 3060, 1597, 1333, 1150 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, J=7.6 Hz, 2H), 7.64–7.58 (m, 5H), 7.50 (dd, J=7.9, 7.6 Hz, 2H), 7.30–7.28 (m, 4H), 6.851–6.849 (m, 1H), 4.18 (s, 2H), 3.80 (s, 2H), 3.74 (s, 2H), 3.40 (s, 2H), 2.425 (s, 3H), 2.418 (s, 3H), 1.73 (s, 3H), 1.53 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 144.1, 143.8, 141.9, 141.1, 136.8, 135.7, 135.6, 133.6, 133.5, 129.8, 129.7, 129.1, 128.7, 127.6, 127.1, 127.0, 124.5, 48.1, 46.1, 46.0, 45.8, 24.8, 21.52, 21.50, 20.5; DART MS m/z 639 (M^++1, 27.7); DART HR-MS Calcd for $C_{32}H_{35}N_2O_6S_3$ 639.1657. Found 639.1656.

***N*-(4-Methylbenzenesulfonyl)-9-phenylsulfonyl-11-oxa-4-azabicyclo[6.4.0]dodeca-1,6,8-triene (6d)** Yellow powder: mp 173–176°C (AcOEt); IR 3026, 1348, 1163 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, J=7.6 Hz, 2H), 7.66 (d, J=8.2 Hz, 2H), 7.63 (t, J=7.6 Hz, 1H), 7.53 (dd, J=7.6, 7.6 Hz, 2H), 7.33–7.30 (m, 3H), 5.42 (t, J=9.3 Hz, 1H), 5.37 (dt, J=11.7, 8.9 Hz, 1H), 4.54 (s, 2H), 4.00 (s, 2H), 3.93 (d, J=9.3 Hz, 2H), 3.72 (d, J=8.9 Hz, 2H), 2.44 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 143.9, 140.4, 138.0, 137.3, 136.7, 136.3, 133.9, 130.6, 129.9, 129.2, 127.3, 127.1, 126.2, 124.5, 71.0, 66.8, 41.4, 40.5, 21.5; DART MS m/z 458 (M^++1, 52.8); DART HR-MS Calcd for $C_{23}H_{24}NO_5S_2$ 458.1096. Found 458.1089.

11,11-Bis(methoxycarbonyl)-*N*-(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4-aza-bicyclo[6.4.0]-dodeca-1,6,8-triene (6e) White amorphous powder: IR 2957, 1736, 1445, 1261, 1161, 814 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.86 (d, J=7.8 Hz, 2H), 7.64–7.59 (m, 3H), 7.52 (dd, J=7.8, 7.3 Hz, 2H), 7.29 (d, J=8.2 Hz, 2H), 7.15 (d, J=11.9 Hz, 1H), 5.50 (t, J=9.2 Hz, 1H), 5.22 (dt, J=11.9, 9.2 Hz, 1H), 3.81 (d, J=9.2 Hz, 2H), 3.66 (d, J=9.2 Hz, 2H), 3.64 (s, 6H), 3.13 (brs, 2H), 2.71 (brs, 2H), 2.43 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 169.7, 143.8, 140.6, 138.2, 137.8, 137.7, 136.3, 133.5, 130.8, 129.9, 129.0, 127.7, 127.2, 127.0, 125.2, 53.11, 53.07, 41.4, 40.9, 39.2, 33.5, 21.5; DART MS m/z 572 (M^++1, 12.0); DART HR-MS Calcd for $C_{28}H_{30}NO_8S_2$ 572.1413. Found 572.1410.

6-Methyl-11,11-bis(methoxycarbonyl)-*N*-(4-methylbenzenesulfonyl)-9-phenylsulfo-nyl-4-azabicyclo[6.4.0]dodeca-1,6,8-triene (6f) Yellow amorphous solid: IR 1736, 1342, 1153 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.86 (d, J=7.2 Hz, 2H), 7.62–7.59 (m, 3H), 7.52 (dd, J=8.2, 7.2 Hz, 2H), 7.28 (d, J=7.9 Hz, 2H), 6.673–6.671 (m, 1H), 5.37 (t, J=8.9 Hz, 1H), 3.82 (d, J=8.9 Hz, 2H), 3.65 (s, 6H), 3.28 (s, 2H), 3.20 (s, 2H), 2.64 (s, 2H), 2.42 (s, 3H), 1.60 (d, J=1.4 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 169.9, 143.7, 141.1, 139.3, 137.3, 137.0, 136.8, 135.3, 133.4, 129.8, 128.8, 127.5, 127.3, 127.1, 125.8, 53.1, 53.0, 45.7, 40.5, 39.5, 33.3, 22.9, 21.5; DART MS m/z 586 (M^++1, 59.5); DART HR-MS Calcd for $C_{29}H_{32}NO_8S_2$ 586.1569. Found 586.1560.

***N*-(4-Methylbenzenesulfonyl)-9,11,11-tris-(phenylsulfonyl)-4-azabicyclo[6.4.0]dode-ca-1,6,8-triene (6g)** White amorphous powder: IR 3030, 1313, 1151 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.94 (d, J=7.6 Hz, 4H), 7.84 (d, J=7.6 Hz, 2H), 7.74 (t, J=7.6 Hz, 2H), 7.64–7.58 (m, 7H), 7.51 (dd, J=7.9, 7.6 Hz, 2H), 7.29 (d, J=7.9 Hz, 2H), 7.03 (d, J=11.7 Hz, 1H), 5.38 (t, J=8.9 Hz, 1H), 5.21 (dt, J=11.7, 8.9 Hz, 1H), 3.77 (d, J=8.9 Hz, 2H), 3.66 (d, J=8.9 Hz, 2H), 3.45 (s, 2H), 2.98 (s, 2H), 2.43 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 143.9, 140.2, 138.5, 136.2, 135.8, 135.4, 135.1, 134.9, 133.8, 131.3, 129.93, 129.90, 129.1, 129.04, 128.96, 127.4, 127.0, 126.1, 85.1, 41.5, 40.8, 34.9, 29.2, 21.5; DART MS m/z 736 (M^++1, 8.04); DART HR-MS Calcd for $C_{36}H_{34}NO_8S_4$ 736.1167. Found 736.1166.

***N*-(4-Methylbenzenesulfonyl)-9-phenylsulfonyl-4-aza-bicyclo[6.4.0]dodeca-1,6,8-tri-ene-11-spiro-5′-(2′,2′-dimethyl-1′,3′-dioxane) (6h)** Colorless amorphous powder: IR 3028, 1348, 1161, 1086 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J=7.3 Hz, 2H), 7.65–7.58 (m, 3H), 7.50 (dd, J=7.8, 7.3 Hz, 2H), 7.35 (d, J=11.9 Hz, 1H), 7.29 (d, J=8.2 Hz, 2H), 5.46 (t, J=8.7 Hz, 1H), 5.26 (dt, J=11.9, 9.2 Hz, 1H), 3.85 (d,

J=8.7 Hz, 2H), 3.67 (d, J=9.2 Hz, 2H), 3.42 (d, J=11.4 Hz, 2H), 3.37 (d, J=11.4 Hz, 2H), 2.47 (s, 2H), 2.43 (s, 3H), 2.16 (s, 2H), 1.36 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 143.8, 140.6, 138.7, 138.4, 136.3, 133.5, 130.9, 129.9, 129.12, 129.07, 127.3, 127.1, 126.8, 125.2, 98.3, 67.4, 41.6, 41.2, 39.7, 34.2, 32.4, 24.1, 23.0, 21.6; DART MS m/z 556 (M^++1, 3.12); DART HR-MS Calcd for $C_{29}H_{34}NO_6S_2$ 556.1828. Found 556.1827.

6-Methyl-*N*-(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4-azabicyclo[6.4.0]dodeca-1,6,8-triene (6i) Yellow amorphous solid: IR 2938, 1446, 1145 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, J=7.6 Hz, 2H), 7.61 (d, J=8.2 Hz, 2H), 7.58 (t, J=7.6 Hz, 1H), 7.49 (dd, J=7.6, 7.6 Hz, 2H), 7.27 (d, J=8.2 Hz, 2H), 6.789–6.786 (m, 1H), 5.15 (t, J=8.9 Hz, 1H), 3.85 (d, J=8.9 Hz, 2H), 3.30 (s, 2H), 2.64 (t, J=6.2 Hz, 2H), 2.41 (s, 3H), 2.06 (t, J=6.2 Hz, 2H), 1.65–1.61 (m, 5H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 143.5, 141.4, 141.1, 140.3, 139.2, 136.6, 134.9, 133.1, 129.6, 128.7, 127.1, 126.7, 123.7, 45.9, 41.0, 34.6, 28.1, 23.1, 22.4, 21.5; DART MS m/z 470 (M^++1, 100); DART HR-MS Calcd for $C_{25}H_{28}NO_4S_2$ 470.1460. Found 470.1460.

6,9-Dimethyl-*N*,*N*′-bis(4-methylbenzenesulfonyl)-4,11-diazabicyclo[6.4.0]dodeca-1,6,8-triene (9a) Yellow powder: mp 132–145°C (hexane–AcOEt); IR 3030, 1599, 1348, 1159 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.67 (d, J=8.2 Hz, 2H), 7.58 (d, J=7.9 Hz, 2H), 7.31 (d, J=8.2 Hz, 2H), 7.28 (d, J=7.9 Hz, 2H), 6.07 (brs, 1H), 4.78 (t, J=8.9 Hz, 1H), 3.88 (d, J=8.9 Hz, 2H), 3.62 (s, 4H), 3.42 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 1.764–1.762 (m, 3H), 1.63 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 143.8, 143.5, 136.7, 136.4, 133.4, 133.2, 131.3, 129.7, 129.5, 128.0, 127.7, 127.2, 126.0, 116.5, 51.6, 50.5, 46.2, 40.7, 23.2, 21.54, 21.51, 17.6; DART MS m/z 499 (M^++1, 19.5); DART HR-MS Calcd for $C_{26}H_{31}N_2O_4S_2$ 499.1725. Found 499.1723.

6-Methyl-*N*,*N*′-bis(4-methylbenzenesulfonyl)-9-phenyl-4,11-diazabicyclo[6.4.0]do-deca-1,6,8-triene (9b) Colorless crystal: mp 168–170°C (AcOEt); IR 3055, 1597, 1342, 1155 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.69 (d, J=8.2 Hz, 2H), 7.59 (d, J=8.2 Hz, 2H), 7.34–7.26 (m, 7H), 7.08–7.07 (m, 2H), 5.78 (s, 1H), 4.96 (t, J=8.9 Hz, 1H), 3.93 (brs, 2H), 3.91 (d, J=8.9 Hz, 2H), 3.72 (s, 2H), 3.57 (s, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 1.59 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 143.9, 143.5, 137.9, 137.3, 136.7, 136.4, 133.2, 130.5, 130.0, 129.7, 129.5, 128.9, 128.4, 128.2, 127.7, 127.3, 127.1, 119.0, 51.6, 50.5, 46.2, 40.9, 23.4, 21.51, 21.47; DART MS m/z 561 (M^++1, 29.9); DART HR-MS Calcd for $C_{31}H_{33}N_2O_4S_2$ 561.1882. Found 561.1883.

11*N*-(4-Methylbenzenesulfonyl)-4*N*-(2-nitrobenzenesulfonyl)-9-phenylsulfonyl-4,11-diazabicyclo[6.4.0]dodeca-1,6,8-triene (11) White amorphous solid: IR 1543, 1348, 1161 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.98–7.97 (m, 1H), 7.82 (d, J=7.9 Hz, 2H), 7.74–7.63 (m, 4H), 7.56 (dd, J=7.9, 7.9 Hz, 2H), 7.49 (d, J=8.2 Hz, 2H), 7.22–7.18 (m, 3H), 5.70 (t, J=8.9 Hz, 1H), 5.56 (dt, J=11.7, 8.9 Hz, 1H), 4.27 (s, 2H), 3.81–3.80 (m, 4H), 3.53 (d, J=8.9 Hz, 2H), 2.39 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 147.7, 144.4, 139.9, 137.3, 136.4, 135.3, 134.1, 134.0, 133.6, 132.6, 132.0, 130.6, 130.5, 129.8, 129.4, 127.6, 127.4, 126.9, 126.1, 124.3, 51.1, 46.8, 41.2, 40.3, 21.5; DART MS m/z 642 (M^++1, 12.5); DART HR-MS Calcd for $C_{29}H_{28}N_3O_8S_3$ 642.1039. Found 642.1039.

6-Methyl-*N*-(4-methylbenzenesulfonyl)-9-phenylsulfonyl-4-oxa-11-azabicyclo[6.4.0]dodeca-1,6,8-triene (13) White powder: mp 142–145°C (AcOEt); IR 1596, 1351, 1158 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.79 (d, J=7.6 Hz, 2H), 7.64–7.60 (m, 3H), 7.52 (dd, J=7.9, 7.6 Hz, 2H), 7.26 (d, J=7.9 Hz, 2H), 6.70 (s, 1H), 5.73 (t, J=8.2 Hz, 1H), 4.30 (s, 2H), 3.93 (d, J=8.2 Hz, 2H), 3.84 (s, 2H), 3.48 (s, 2H), 2.42 (s, 3H), 1.73 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 144.1, 140.5, 139.8, 137.4, 136.0, 133.9, 133.63, 133.57, 129.7, 129.0, 128.3, 127.8, 127.4, 124.8, 64.3, 58.9, 51.3, 46.6, 23.2, 21.5; DART MS m/z 472 (M^++1, 100); DART HR-MS Calcd for $C_{24}H_{26}NO_5S_2$ 472.1252. Found 472.1251.

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Conflict of Interest The authors declare no conflict of interest.

Supplementary Materials The online version of this article contains supplementary materials.

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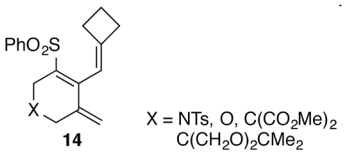
19) Compound **7** was deduced by comparison between the ^{1}H-NMR data of the obtained crude products and that of the previously reported **14**, which is structurally similar to **7** (see ref. 8)



14

20) It was reported that the strain energy of the unsubstituted azetidine was estimated to be 26.3 kcal/mol, being almost identical to that of cyclobutane, based on density functional theory (DFT) calculations, see Smith S. A., Hand K. E., Love M. L., Hill G., Magers D. H., *J. Comput. Chem.*, **34**, 558–565 (2013).
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