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RHODIUM-CATALYZED INTRAMOLECULAR CYCLOADDITION OF CYCLOPROPENE-YNES TRIGGERED BY CABON-CARBON BOND CLEAVAGE

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Dedicated to Prof. R. Noyori on the occasion of his 70th birthday

Abstract – In the presence of a catalytic amount of $RhCl(PPh_3)_3$, an intramolecular cycloaddition of cyclopropene-yne proceeded along with carbon-carbon bond cleavage of cyclopropene ring to give various bicyclic cyclopentadiene derivatives in good to high yield.

INTRODUCTION

Generally, carbon-carbon single bond is stable and difficult to cleave under the mild reaction conditions, however, in the case of compounds with small ring systems, the bond cleavage can be possible using release of strain energy as driving force. From a organic synthetic point of view, three-membered carbocycles are fascinating building blocks and many researchers have focused on the development of unique and synthetically valuable transformations.[1] Actually, oxidative addition of transition metal complexes to cyclopropane and cyclopropene rings along with carbon-carbon single bond cleavage has been reported[2] and it was applied for various transition metal-catalyzed transformations.[3]

Also in the cycloaddition, cyclopropane ring is an important C3 unit along with the bond cleavage. For examples, Wender comprehensively studied the reaction of vinylcyclopropane with alkynes and realized Rh-catalyzed intra- and intermolecular [5+2] cycloaddition.[4] Murakami reported an Ir-catalyzed [5+1] cycloaddition of allenylcyclopropane with carbon monoxide,[5] Saito did a Ni-catalyzed intermolecular [3+2+2] cycloaddition of methylenecyclopropanes with two alkynes,[6] and Lauten and Mascareñas independently did a Pd- or Ru-catalyzed intramolecular [3+2] cycloaddition of methylenecyclopropane-ynes.[7] In all these reactions, however, conjugated or adjacent carbon-carbon

double bond to cyclopropane facilitated the ring cleavage. The catalytic cycloaddition including the cleavage of isolated cyclopropane ring has been scarce: Narasaka achieved a Rh-catalyzed [3+2+1] cycloaddition of carbon-tethered cyclopropane-ynes with carbon monoxide in relatively harsh reaction conditions.[8]

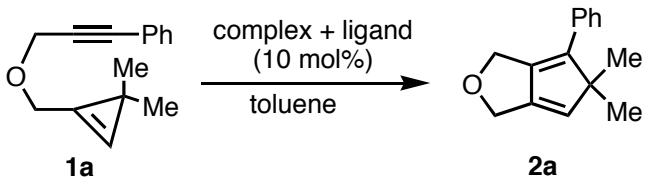
Compared with cyclopropanes, cyclopropenes are unexplored in cycloaddition. For example, the photo-irradiated [3+2] cycloaddition with alkynes was reported, however, it was considered that [2+2] cycloaddition and the following ring expansion proceeded along with the cleavage of cyclopropane ring.[9] Thermal [3+2] cycloaddition of functionalized cyclopropenes, such cyclopropenone acetals[10] and ferrocenyl cyclopropenes, was disclosed.[11] As for transition metal-catalyzed reaction, a Ni-catalyzed [3+2] cycloadditions of a cyclopropenone with a diphenylketene[12] and an unfunctionalized cyclopropene with tolane[13] were reported, but the yield was low and substrates were limited. A Rh-catalyzed carbonylation of cyclopropenyl esters and 3-vinylcyclopropenes is a more practical example, which proceeded under an atmospheric pressure of carbon monoxide to give α-pyrones and phenols, respectively ([5+1] cycloaddition).[14] A Ru-catalyzed reaction of cyclopropenones with alkynes under pressurized conditions of carbon monoxide is also a successful example.[15]

We here disclosed a Rh-catalyzed intramolecular reaction of cyclopropene-ynes. This is a rare example of catalytic cycloaddition including the cleavage of unfunctionalized cyclopropene ring.

RESULTS AND DISCUSSION

As a model substrate, we chose oxygen-tethered 3,3-dimethylcyclopropene-yne **1a** and submitted it to various reaction conditions (Table 1). In the presence of $[RhCl(cod)]_2$ as a catalyst, cyclopropene-yne **1a** was consumed under the reflux condition in toluene to give complex mixture (entry 1). When triphenylphosphine was added as a ligand, it was completely consumed even at 60 °C within 3 h and bicyclic cyclopentadiene **2a** was obtained but in low yield (entry 2). Electron-deficient triarylphosphine gave the comparable results to those of triphenylphosphine (entry 3). Electron-rich triarylphosphine decreased the catalytic activity of the rhodium complex and cyclopentadiene **2a** was obtained in lower yield at higher reaction temperature (entry 4). Bidentate ligand was inappropriate for the present reaction and it took longer reaction time at higher temperature to consume cyclopropene-yne **1a** (entry 5). Cationic rhodium complex shortened the reaction time but the yield did not increase (entry 6). When $RhCl(PPh_3)_3$ was used, the best yield of 74% was achieved in short reaction time (entry 7). Halogenated nor ether type solvent did not improve the yield (entries 8 and 9). The reaction proceeded even at room temperature but the substrate was not completely consumed after 3 days (entry 10). At the elevated temperature, it was promptly consumed but the yield was drastically diminished along with the formation of many unidentified products (entry 11).

Table 1. Screening of various reaction conditions



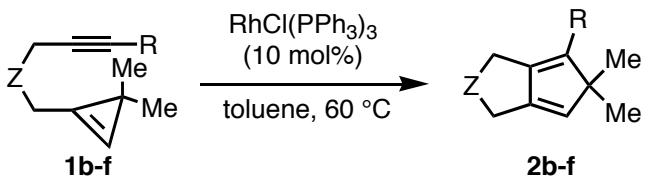
1a **2a**

Entry	Complex	Ligand	Temp./°C	Time/h	Yield/%
1	1/2[RhCl(cod)]$_2$	none	reflux	3	C.M.[a]
2	1/2[RhCl(cod)]$_2$	2PPh$_3$	60	3	36
3	1/2[RhCl(cod)]$_2$	2P(*p*-FC$_6$H$_4$)$_3$	60	2	34
4	1/2[RhCl(cod)]$_2$	2P(*p*-MeOC$_6$H$_4$)$_3$	60-100	9	19
5	1/2[RhCl(cod)]$_2$	DPPP[b]	80	10	22
6[c]	[Rh(cod)$_2$]BF$_4$	2PPh$_3$	60	1	28
7	RhCl(PPh$_3$)$_3$		60	2	74
8[c]	RhCl(PPh$_3$)$_3$		60	2	60
9[d]	RhCl(PPh$_3$)$_3$		60	2	62
10	RhCl(PPh$_3$)$_3$		rt	72	29
11	RhCl(PPh$_3$)$_3$		reflux	0.25	33

[a] Complex mixture. [b] 1,2-Bis(diphenylphosphino)propane. [c] 1,2-Dichloroethane was used as a solvent. [d] 1,4-Dioxane was used as a solvent.

Other cyclopropene-ynes were submitted to the reaction in toluene using RhCl(PPh$_3$)$_3$ as a catalyst (Table 2). Cyclopropene-yne **1b** with alkyl substituent at its alkyne terminus was also transformed into the corre-

Table 2. Intramolecular cycloaddition of various cyclopropene-ynes



1b-f **2b-f**

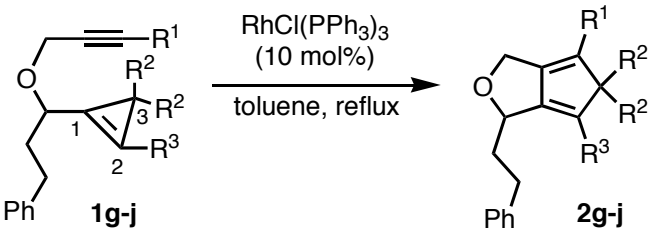
Entry	R	Z		Time/h	Yield/%
1	Ph(CH$_2$)$_3$	O	**1b**	6	60 (**2b**)
2	Ph	NTs	**1c**	4	69 (**2c**)
3[a]	Me	NTs	**1d**	2	64 (**2d**)
4	Ph	C(CO$_2$Et)$_2$	**1e**	9	85 (**2e**)
5[a]	Ph(CH$_2$)$_3$	C(CO$_2$Et)$_2$	**1f**	24	69 (**2f**)

[a] The reaction was examined under reflux condition.

sponding product **2b** (entry 1). Nitrogen-tethered cyclopropene-ynes **1c** and **1d** were also appropriate substrates and intramolecular reaction proceeded in acceptable yields (entries 2 and 3). Carbon-tethered cyclopropene-ynes required longer reaction time than the corresponding heteroatom-tethered ones but good yield was achieved (entries 4 and 5).

Introduction of alkyl substituent at the α-position of cyclopropenyl group significantly diminished the formation of unidentified products and the corresponding bicyclic diene **2g** was obtained in the best yield of 90% (Table 3, entry 1). Even the bulky *tert*-butyl group at the alkyne terminus did not deter the intramolecular reaction and comparable yield was achieved (entry 2). Also in the reaction of cyclopropene-yne **1i** with a methyl group at 2-position of cyclopropene ring, the desired product **2i** was provided in high yield after being stirred for prolonged reaction time (entry 3). On the contrary, in the case of cyclopropene-yne **1j** without methyl group at the 3-position, it was completely consumed within 2 h and the disappearance of cyclopropenyl moiety was ascertained by the NMR analyses of crude products but expected cyclized product **2j** was not detected (entry 4). These results imply that the methyl groups at the 3-position are essential for the efficient cyclization.

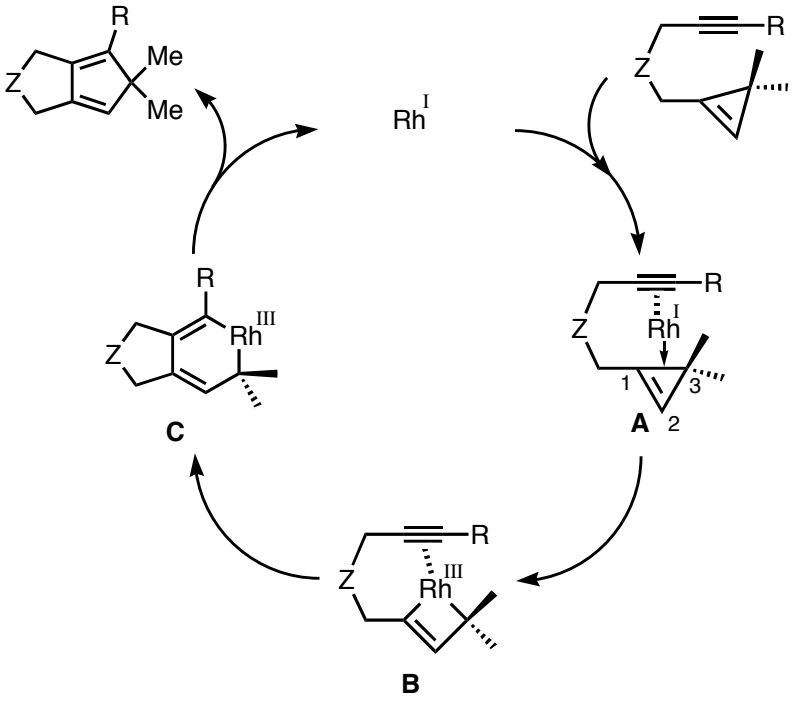
Table 3. Intramolecular cycloaddition of α-substituted cyclopropene-ynes



Entry	R^1	R^2	R^3		Time/h	Yield/%
1[a]	Ph	Me	H	**1g**	1	90 (**2g**)
2	*tert*-Bu	Me	H	**1h**	2	88 (**2h**)
3	Ph	Me	Me	**1i**	8	90 (**2i**)
4	Ph	H	Me	**1j**	2	N.D.[b]

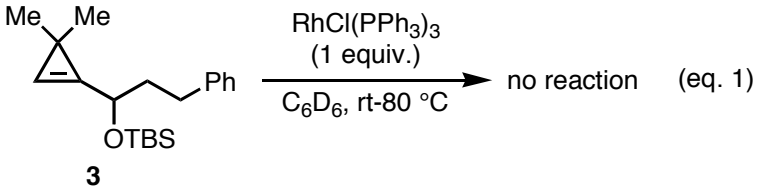
[a] The reaction was examined at 60 °C. [b] Not detected.

The proposed reaction mechanism was depicted in Scheme 1. The coordination of alkynyl group realizes selective approach of the metal center to C1-C3 single bond of the cyclopropene ring. The oxidative addition of metal center along with the bond cleavage affords metallacyclobutene intermediate **B**. The intramolecular alkyne insertion gives the bicyclic metallacyclohexadiene **C** and the following reductive elimination regenerates the catalyst and the bicyclic cyclopentadiene is formed.

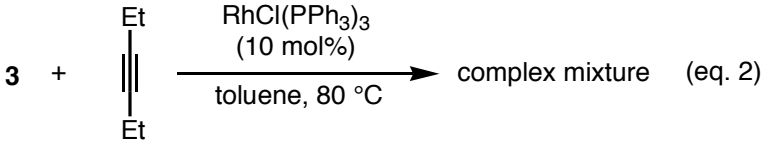


Scheme 1

The alkyne coordination to the metal center would be critical for the bond cleavage of cyclopropene. Actually, the bond cleavage of cyclopropene **3** was not observed at all even in the presence of a stoichiometric amount of $RhCl(PPh_3)_3$ at 80 °C (eq. 1).



When cyclopropene **3** was submitted to the reaction with hex-3-yne, it was completely consumed at 80 °C but no cross-coupled products were detected (eq. 2). These results imply that intramolecular coordination of alkyne to metal center would be important for effective insertion to metallacyclobutene.



In conclusion, we developed Rh-catalyzed cycloaddition of various cyclopropene-ynes. The reaction was initiated by carbon-carbon bond cleavage of cyclopropene ring and gave bicyclic cyclopentadienes. The

alkyne coordination would facilitate the bond cleavage and intramolecular insertion realized the present transformation.

EXPERIMENTAL

Anhydrous toluene, 1,2-dichloroethane, and 1,4-dioxane are commercially available. They were dried over molecular sieves 4A (MS 4A) and degassed by argon bubbling before use. All reactions were examined under an argon atmosphere. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 and Lambda500 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin Elmer PE2400II.

Typical experimental procedure (Table 1, entry 7): $RhCl(PPh_3)_3$ (9.3 mg, 0.0101 mmol) was placed in a flask and a toluene solution (2 mL) of cyclopropene-yne **1a** (21.7 mg, 0.102 mmol) was added. The reaction mixture was stirred at 60 °C for 2 h. The solvent was removed under reduced pressure and the resulting crude products were purified by thin-layer chromatography to give pure bicyclic cyclopentadiene **2a** (16.0 mg, 0.0754 mmol, 74% yield).

(3,3-Dimethylcycloprop-1-enyl)methyl 3-phenylprop-2-ynyl ether (1a). Colorless oil; IR (neat) 1757, 1092, 692 cm^{-1}; ^{1}H-NMR δ 1.20 (s, 6H), 4.47 (s, 2H), 4.65 (d, *J*= 1.6 Hz, 2H), 7.15 (brs, 1H), 7.31-7.32 (m, 3H), 7.44-7.47 (m, 2H); ^{13}C-NMR δ 20.0, 27.3, 58.0, 64.2, 84.6, 86.5, 116.1, 122.5, 128.2, 128.4, 131.2, 131.7; HRMS (EI^+) for M found m/z 212.1208, calcd for $C_{15}H_{16}O$: 212.1201.

(3,3-Dimethylcycloprop-1-enyl)methyl 6-phenylhex-2-ynyl ether (1b). Colorless oil; IR (neat) 1757, 1088, 700 cm^{-1}; ^{1}H-NMR δ 1.18 (s, 6H), 1.81-1.88 (m, 2H), 2.23-2.26 (m, 2H), 2.72 (t, *J*= 7.6 Hz, 2H), 4.23 (t, *J*= 1.8 Hz, 2H), 4.57 (d, *J*= 1.2 Hz, 2H), 7.11 (brs, 1H), 7.17-7.19 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C-NMR δ 18.3, 19.9, 27.3, 30.2, 34.8, 57.8, 63.9, 76.1, 86.8, 115.9, 125.8, 128.3, 128.4, 131.4, 141.4; HRMS (FAB^+) for M found m/z 254.1651, calcd for $C_{18}H_{22}O$: 254.1671.

***N*-[(3,3-Dimethylcycloprop-1-enyl)methyl]-*N*-(3-phenylprop-2-ynyl)-4-methylphenylsulfonylamide (1c).** White solid; mp 79 °C; IR (CH_2Cl_2) 1757, 1163, 814, 692 cm^{-1}; ^{1}H-NMR δ 1.13 (s, 6H), 2.35 (s, 3H), 4.39 (s, 2H), 4.42 (d, *J*= 0.8 Hz, 2H), 6.98 (brs, 1H), 7.09-7.12 (m, 2H), 7.22-7.28 (m, 5H), 7.77 (d, *J*= 8.4 Hz, 2H); ^{13}C-NMR δ 20.1, 21.5, 27.1, 37.3, 42.9, 81.5, 85.8, 117.3, 122.1, 127.8, 128.1, 128.4, 129.4, 129.5, 131.5, 135.7, 143.5; HRMS (FAB^+) for M+1 found m/z 366.1544, calcd for $C_{22}H_{24}NO_2S$: 366.1527.

***N*-But-2-ynyl-*N*-[(3,3-Dimethylcycloprop-1-enyl)methyl]-4-methylphenylsulfonylamide (1d).** Yellow oil; IR (neat) 1757, 1163, 816 cm^{-1}; ^{1}H-NMR δ 1.09 (s, 6H), 1.59 (t, *J*= 2.5 Hz, 3H), 2.42 (s, 3H), 4.09 (d, *J*= 2.5 Hz, 2H), 4.35 (s, 2H), 6.88 (s, 1H), 7.29 (d, *J*= 8.4 Hz, 2H), 7.73 (d, *J*= 8.4 Hz, 2H); ^{13}C-NMR δ

3.3, 20.0, 21.5, 27.0, 36.9, 42.6, 71.6, 81.7, 117.0, 127.8, 129.2, 129.5, 136.1, 143.2; HRMS (FAB^+) for M+1 found m/z 304.1371, calcd for $C_{17}H_{22}NO_2S$: 304.1371.

Diethyl 5-(3,3-Dimethylcycloprop-1-enyl)-1-phenylpent-1-yne-4,4-dicarboxylate (1e). Colorless oil; IR (neat) 1739, 692 cm^{-1}; ^{1}H-NMR δ 1.10 (s, 6H), 1.26 (t, *J*= 7.2 Hz, 6H), 3.13 (s, 2H), 3.30 (d, *J*= 0.8 Hz, 2H), 4.19-4.26 (m, 4H), 6.95 (brs, 1H), 7.27-7.28 (m, 3H), 7.34-7.37 (m, 2H); ^{13}C-NMR δ 14.2, 18.3, 23.8, 27.4, 28.9, 56.2, 61.8, 83.4, 84.3, 116.0, 123.1, 127.8, 128.0, 130.0, 131.5, 169.3; HRMS (FAB^+) for M found m/z 354.1823, calcd for $C_{22}H_{26}O_4$: 354.1831.

Diethyl 8-(3,3-dimethylcycloprop-1-enyl)-1-phenyloct-4-yne-7,7-dicarboxylate (1f). Colorless oil; IR (neat) 1738, 700 cm^{-1}; ^{1}H-NMR δ 1.09 (s, 6H), 1.26 (t, *J*= 7.2 Hz, 6H), 1.72-1.79 (m, 2H), 2.11-2.16 (m, 2H), 2.68 (t, *J*= 7.6 Hz, 2H), 2.90 (t, *J*= 2.2 Hz, 2H), 3.25 (d, *J*= 1.2 Hz, 2H), 4.17-4.22 (m, 4H), 6.92 (brs, 1H), 7.18-7.20 (m, 3H), 7.28-7.30 (m, 2H); ^{13}C-NMR δ 14.2, 18.2, 18.3, 23.2, 27.4, 28.7, 30.6, 34.7, 56.2, 61.6, 74.9, 83.0, 115.9, 125.7, 128.2, 128.4, 130.1, 141.6, 169.5; HRMS (FAB^+) for M found m/z 396.2323, calcd for $C_{25}H_{32}O_4$: 396.2301.

1-(3,3-Dimethylcycloprop-1-enyl)-3-phenylpropyl 3-phenylprop-2-ynyl ether (1g). Yellow oil; IR (neat) 1749, 1085, 694 cm^{-1}; ^{1}H-NMR δ 1.21 (s, 3H), 1.24 (s, 3H), 1.96-2.11 (m, 2H), 2.74-2.88 (m, 2H), 4.37 (d, *J*= 15.6 Hz, 1H), 4.53 (d, *J*= 15.6 Hz, 1H), 4.66 (dd, *J*= 6.4, 6.4 Hz, 1H), 7.14 (s, 1H), 7.17-7.44 (m, 10H); ^{13}C-NMR δ 20.1, 27.8, 27.9, 31.6, 35.9, 56.8, 73.6, 85.3, 86.0, 116.5, 122.6, 125.7, 128.2, 128.3, 128.3, 128.5, 131.7, 133.7, 141.7; HRMS (FAB^+) for M found m/z 316.1841, calcd for $C_{23}H_{24}O$: 316.1827.

1-(3,3-Dimethylcycloprop-1-enyl)-3-phenylpropyl 4,4-dimethylpent-2-ynyl ether (1h). Colorless oil; IR (neat) 1749, 1095, 700 cm^{-1}; ^{1}H-NMR δ 1.19 (s, 6H), 1.21 (s, 9H), 1.94-2.05 (m, 2H), 2.70-2.85 (m, 2H), 4.13 (d, *J*= 15.4 Hz, 1H), 4.29 (d, *J*= 15.4 Hz, 1H), 4.57 (dd, *J*= 6.2, 6.2 Hz, 1H), 7.09 (s, 1H), 7.17-7.23 (m, 3H), 7.27-7.31 (m, 2H); ^{13}C-NMR δ 19.9, 27.5, 27.8, 27.9, 31.0, 31.8, 35.9, 56.6, 73.1, 74.4, 95.1, 116.1, 125.7, 128.3, 128.4, 133.8, 141.9; HRMS (FAB^+) for M found m/z 296.2153, calcd for $C_{21}H_{28}O$: 296.2140.

3-Phenylprop-2-ynyl 3-phenyl-1-(2,3,3-trimethylcycloprop-1-enyl)propyl ether (1i). Yellow oil; IR (neat) 1851, 1088, 694 cm^{-1}; ^{1}H-NMR δ 1.15 (s, 3H), 1.16 (s, 3H), 1.94-2.10 (m, 2H), 2.05 (s, 3H), 2.74-2.85 (m, 2H), 4.32 (d, *J*= 15.6 Hz, 1H), 4.50 (d, *J*= 15.6 Hz, 1H), 4.59 (dd, *J*= 6.4, 6.4 Hz, 1H), 7.17-7.32 (m, 8H), 7.42-7.44 (m, 2H); ^{13}C-NMR δ 9.2, 21.0, 26.0, 26.1, 31.8, 36.2, 56.7, 73.4, 85.6, 85.9, 122.4, 122.7, 124.1, 125.7, 128.2, 128.3, 128.5, 131.7, 142.0; HRMS (FAB^+) for M found m/z 330.1990, calcd for $C_{24}H_{26}O$: 330.1984.

3,3-Dimethyl-2-phenyl-7-oxabicyclo[3.3.0]octa-1,4-diene (2a). White solid; mp 94 °C; IR (CH_2Cl_2) 1595, 1462, 1028, 768, 698 cm^{-1}; ^{1}H-NMR δ 1.43 (s, 6H), 4.55 (d, *J*= 2.0 Hz, 2H), 4.78 (s, 2H), 5.85 (brs,

1H), 7.19-7.39 (m, 5H); ^{13}C-NMR δ 23.2, 62.4, 65.4, 67.1, 125.9, 126.7, 128.4, 133.4, 134.8, 140.1, 144.4, 145.0; HRMS (FAB$^+$) for M found m/z 212.1215, calcd for $C_{15}H_{16}O$: 212.1201.

3,3-Dimethyl-2-(3-phenylpropyl)-7-oxabicyclo[3.3.0]octa-1,4-diene (2b). Colorless oil; IR (neat) 1603, 1456, 1014, 746, 700 cm^{-1}; ^{1}H-NMR δ 1.12 (s, 6H), 1.80-1.85 (m, 2H), 2.12-2.14 (m, 2H), 2.65 (t, *J*= 7.5 Hz, 2H), 4.43 (s, 2H), 4.49 (s, 2H), 5.66 (s, 1H), 7.18-7.21 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C-NMR δ 22.3, 25.5, 29.3, 36.1, 62.5, 65.3, 65.6, 125.7, 128.3, 128.3, 128.9, 139.6, 142.0, 142.9, 145.8; HRMS (FAB$^+$) for M-1 found m/z 253.1591, calcd for $C_{19}H_{21}O$: 253.1593.

3,3-Dimethyl-7-[(4-methylphenyl)sulfonyl]-2-phenyl-7-azabicyclo[3.3.0]octa-1,4-diene (2c). White solid; mp 125 °C; IR (CH_2Cl_2) 1597, 1460, 1165, 814, 762, 696 cm^{-1}; ^{1}H-NMR δ 1.32 (s, 6H), 2.42 (s, 3H), 4.10 (d, *J*= 1.6 Hz, 2H), 4.32 (s, 2H), 5.85 (brs, 1H), 7.23-7.39 (m, 7H), 7.77 (d, *J*= 8.4 Hz, 2H); ^{13}C-NMR δ 21.6, 22.8, 46.6, 48.4, 60.8, 126.5, 126.8, 127.5, 128.5, 129.7, 133.9, 134.5, 135.8, 139.0, 140.5, 142.8, 143.5; HRMS (FAB$^+$) for M+1 found m/z 366.1528, calcd for $C_{22}H_{24}NO_2S$: 366.1527.

3,3-Dimethyl-2-methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[3.3.0]octa-1,4-diene (2d). White solid; mp 75 °C; IR (CH_2Cl_2) 1596, 1458, 1165, 817, 785 cm^{-1}; ^{1}H-NMR δ 1.02 (s, 6H), 1.66 (s, 3H), 2.42 (s, 3H), 3.96 (s, 2H), 4.01 (d, *J*= 2.0 Hz, 2H), 5.70 (brs, 1H), 7.32 (d, *J*= 7.8 Hz, 2H), 7.74 (d, *J*= 7.8 Hz, 2H); ^{13}C-NMR δ 10.4, 21.6, 21.8, 46.1, 47.1, 60.4, 127.5, 129.6, 131.7, 133.9, 135.4, 140.7, 141.4, 143.3; HRMS (FAB$^+$) for M+1 found m/z 304.1371, calcd for $C_{17}H_{22}NO_2S$: 304.1371.

Diethyl 7,7-dimethyl-6-phenylbicyclo[3.3.0]octa-5,8-diene-3,3-dicarboxylate (2e). Yellow oil; IR (neat) 1732, 1597, 1462, 796, 762 cm^{-1}; ^{1}H-NMR δ 1.25 (t, *J*= 7.2 Hz, 6H), 1.34 (s, 6H), 3.05 (d, *J*= 2.0 Hz, 2H), 3.29 (s, 2H), 4.17-4.23 (m, 4H), 5.83 (brs, 1H), 7.18-7.22 (m, 1H), 7.26-7.38 (m, 2H), 7.41-7.44 (m, 2H); ^{13}C-NMR δ 14.2, 23.4, 33.3, 35.4, 60.2, 61.7, 65.1, 125.7, 126.9, 128.1, 135.8, 135.9, 142.3, 143.3, 144.2, 171.2; HRMS (FAB$^+$) for M found m/z 354.1829, calcd for $C_{22}H_{26}O_4$: 354.1831.

Diethyl 7,7-dimethyl-6-(3-phenylpropyl)bicyclo[3.3.0]octa-5,8-diene-3,3-dicarboxylate (2f). Colorless oil; IR (neat) 1734, 1458, 746, 700 cm^{-1}; ^{1}H-NMR δ 1.05 (s, 6H), 1.23 (t, *J*= 7.2 Hz, 6H), 1.86-1.94 (m, 2H), 2.13-2.16 (m, 2H), 2.64 (t, *J*= 7.8 Hz, 2H), 2.96 (d, *J*= 1.6 Hz, 2H), 3.00 (s, 2H), 4.15-4.21 (m, 4H), 5.64 (brs, 1H), 7.16-7.21 (m, 3H), 7.28-7.30 (m, 2H); ^{13}C-NMR δ 14.2, 22.7, 25.8, 29.7, 33.4, 33.6, 36.3, 60.2, 61.5, 65.1, 125.5, 128.1, 128.3, 131.7, 138.6, 142.3, 144.5, 144.6, 171.3; HRMS (FAB$^+$) for M-1 found m/z 395.2232, calcd for $C_{25}H_{31}O_4$: 395.2223.

3,3-Dimethyl-2-phenyl-6-(2-phenylethyl)-7-oxabicyclo[3.3.0]octa-1,4-diene (2g). Yellow oil; IR (neat) 1601, 1456, 1028, 766, 694 cm^{-1}; ^{1}H-NMR δ 1.42 (s, 3H), 1.44 (s, 3H), 1.99-2.05 (m, 2H), 2.77-2.81 (m, 2H), 4.71 (ddd, *J*= 1.7, 6.1, 6.1 Hz, 1H), 4.79 (d, *J*= 14.2 Hz, 1H), 4.86 (d, *J*= 14.2 Hz, 1H), 5.85 (d, *J*= 1.7 Hz, 1H), 7.17-7.31 (m, 8H), 7.36-7.40 (m, 2H); ^{13}C-NMR δ 23.0, 23.4, 31.5, 37.1, 62.0, 66.7, 75.3, 125.7, 125.9, 126.7, 128.3, 128.4, 128.5, 133.9, 134.8, 140.1, 141.8, 144.7, 148.3; HRMS (FAB$^+$) for M found m/z 316.1801, calcd for $C_{23}H_{24}O$: 316.1827.

2-*tert*-Butyl-3,3-dimethyl-6-(2-phenylethyl)-7-oxabicyclo[3.3.0]octa-1,4-diene (2h). Colorless oil; IR (neat) 1603, 1456, 1030, 748, 700 cm^{-1}; ^{1}H-NMR δ 1.18 (s, 9H), 1.70 (s, 6H), 1.91-1.96 (m, 2H), 2.72-2.77 (m, 2H), 4.51-4.55 (m, 2H), 4.61 (d, *J*= 13.2 Hz, 1H), 5.46 (d, *J*= 1.2 Hz, 1H), 7.16-7.22 (m, 3H), 7.28-7.30 (m, 2H); ^{13}C-NMR δ 23.2, 23.6, 30.8, 31.6, 34.8, 37.1, 63.4, 66.3, 74.7, 125.6, 128.2, 128.4, 131.3, 140.8, 142.0, 147.1, 149.8; HRMS (FAB$^+$) for M found m/z 296.2159, calcd for $C_{21}H_{28}O$: 296.2140.

2-Phenyl-6-(2-phenylethyl)-3,3,4-trimethyl-7-oxabicyclo[3.3.0]octa-1,4-diene (2i). Yellow oil; IR (neat) 1597, 1456, 1030, 746, 694 cm^{-1}; ^{1}H-NMR δ 1.30 (s, 3H), 1.32 (s, 3H), 1.84 (s, 3H), 1.92-2.04 (m, 1H), 2.07-2.17 (m, 1H), 2.70-2.82 (m, 2H), 4.78-4.88 (m, 3H), 7.16-7.30 (m, 8H), 7.34-7.38 (m, 2H); ^{13}C-NMR δ 10.3, 22.6, 23.1, 31.4, 36.7, 62.3, 66.9, 75.2, 125.4, 125.7, 126.2, 128.3, 128.4, 128.4, 135.3, 138.6, 140.9, 142.2, 142.7, 144.9; HRMS (FAB$^+$) for M found m/z 330.1981, calcd for $C_{24}H_{26}O$: 330.1984.

1-(*tert*-Butyldimethylsiloxy)-1-(3,3-dimethylcyclopropene-1-yl)-3-phenylpropane (3). Colorless oil. IR (neat) 1757, 1458, 1254, 1095, 837, 775, 698 cm^{-1}, ^{1}H-NMR δ 0.07 (s, 3H), 0.07 (s, 3H), 0.92 (s, 9H), 1.18 (s, 3H), 1.19 (s, 3H), 1.86-2.02 (m, 2H), 2.64-2.81 (m, 2H), 4.71 (t, *J*= 6.0 Hz, 1H), 6.95 (s, 1H), 7.17-7.21 (m, 3H), 7.25-7.32 (m, 2H); ^{13}C-NMR δ -5.09, -4.47, 18.3, 20.9, 25.8, 27.6, 27.9, 31.8, 38.6, 69.1, 114.0, 125.8, 128.4, 128.4, 136.9, 142.3; HRMS (EI$^+$) for M found m/z 316.2186, calcd for $C_{20}H_{32}OSi$: 316.2222.

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