The [2＋2]-Cycloaddition Reaction of Bisallenes: A Dramatic Substituent Effect[†]

Lu, Ping[a](陆平)　　Ma, Shengming*[,a,b](麻生明)

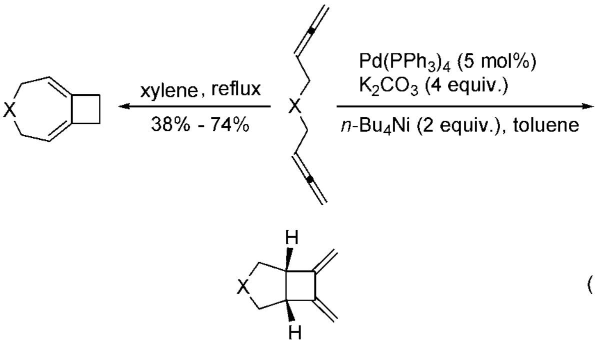
[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Linglin Lu, Shanghai 200032, China
[b] Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

The bisallenes **1** possessing a phenylsulfonyl or *n*-butyl substituent at the internal position of allene moieties could be smoothly transformed to the bicyclo[5.2.0] or bicyclo[6.2.0] derivatives **2** in moderate to excellent yields with good regioselectivity upon refluxing in toluene. This [2＋2]-cycloaddition reaction shows an interesting substituent effect as unveiled by comparing with the results of unsubstituted substrates. However, further attention should be paid to the control of the regioselectivity of the [2＋2]-cycloaddition involving different C＝C bonds.

Keywords　allenes, substituent effects, cycloaddition reaction, cyclobutane, phenylsulfonyl group

Introduction

Cyclobutanes are found as basic structural elements in many biologically active natural products.[1] Their syntheses and applications as synthetic intermediates have flourished in recent years.[2] As one of the reliable preparative methods, the [2＋2] reactions of two allene moieties have been extensively studied for the construction of different cyclobutanes with different regioselectivities.[3] During our further explorations of the chemistry of bisallene,[4,5] we have observed the controllable [2＋2]-reaction of bisallenes, delivering the two different types of cyclobutane derivatives depending on the regioselectivity (Eq. 1).[4e]



(1)

On the other hand, we have also disclosed the switch of the cyclometallation pathway of bisallenes when terminal substituents R^1 were installed with a different catalyst, indicating that the terminal substituent(s) may have some influence on the reaction (Scheme 1).[4a-4c] As a part of further study, we envisioned to install a functional group at the internal position of allene moieties to learn their effect on the [2＋2]-cycloaddition reaction.

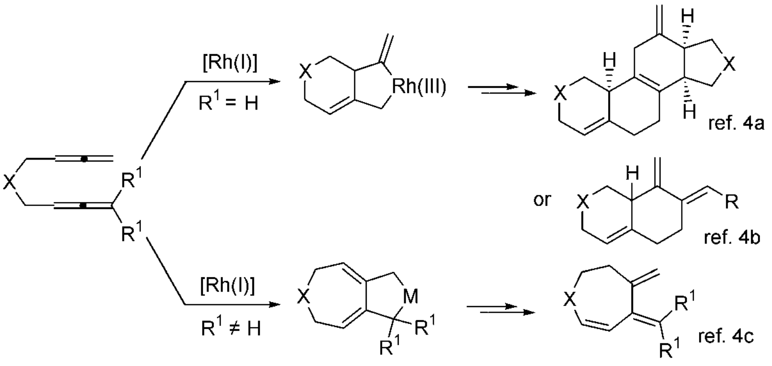
Results and discussion

This study commenced with bisallene **1a** possessing a phenylsulfonyl group[6] at the internal 3-position of one allene moiety. It is found that the reaction of bisallene **1a**, under the catalysis of 2.5 mol% $[RhCl(CO)_2]_2$ in CH_3CN under reflux, afforded no major product as judged from TLC analysis, along with **1a** being recovered in 12% yield (Scheme 2). We then turned to explore other reaction conditions. It is interesting to observe that the reaction of **1a** afforded the bicyclo [5.2.0] derivative **2a** in 89% yield, together with the inseparable regioisomer **2a'** (**2a**∶**2a'**⩾97∶3) when it was simply heated in toluene under reflux (conditions A). As a comparison, the [2＋2]-cycloaddition of non-subtituted bisallene **3** in toluene under reflux for 103 h afforded the cyclobutane derivative **5a** in only 11% yield, with **3** being recovered in 72% yield. Meanwhile the reaction of bisallene **4** with the *n*-butyl group installed instead of the phenylsufonyl group provided the expected bicyclic product **5b** and regioisomer **5b'** in a ratio of 88.5∶11.5, however, the reaction is much slower. These results obviously indicate that the substituent group (phenylsulfonyl or butyl group) here plays an important role in this [2＋2] cycloaddition reaction.[7]

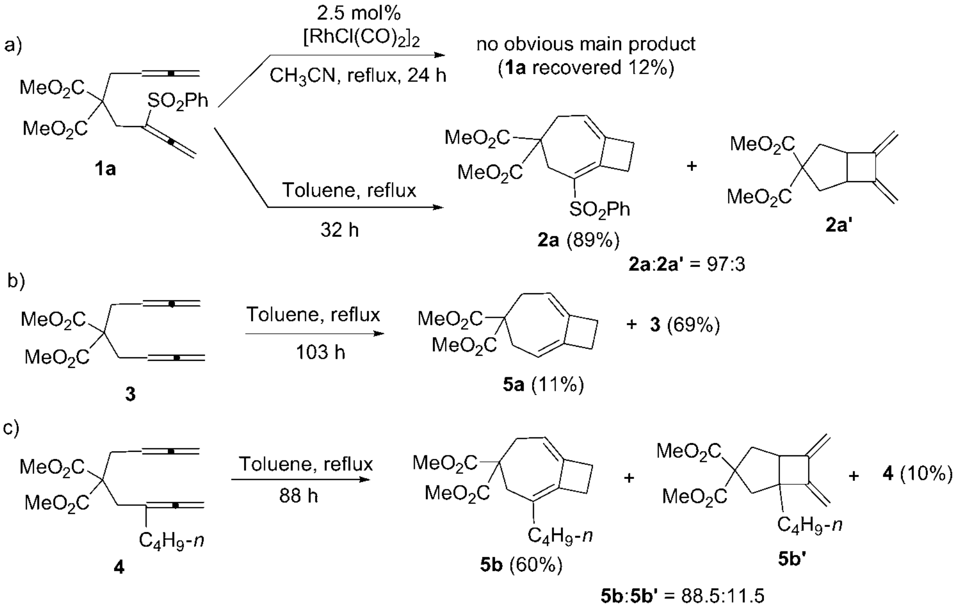
---

* E-mail: masm@sioc.ac.cn
Received June 20, 2010; revised July 13, 2010; accepted July 22, 2010.
Project supported by the National Natural Science Foundation of China (No. 20732005) and the Major State Basic Research Development Program (No. 2009CB825300).
[†] Dedicated to the 60th Anniversary of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Scheme 1



Scheme 2



The substrate scope of the reaction of 1,5-bisallenes with a phenylsulfonyl substituent affording bicyclo[5.2.0] derivatives was then explored (Scheme 3). The substrate **1b** possessing two methyl substituents at the terminal position of allene moiety smoothly transformed to cyclobutane derivative **2b** in 90% yield under conditions A. The substrate **1c** with an extra methyl group at the vicinal position of the allene moiety afforded the bicyclic product **2c** in 71% yield. The structure of this product was unambiguously established by X-ray diffraction studies (Figure 1).[8] The *N*-tethered 1,5-bisallenes **1d** and **1e** afforded the expected bicyclo[5.2.0] products **2d** and **2e** in good yields, together with isomeric bicyclo[3.2.0] products **2d'** and **2e'** as determined by ^{1}H NMR analysis.

Furthermore, the reactions of 1,6-bisallenes **1f**—**1h** afforded the corresponding bicyclo[6.2.0] derivatives **2f**—**2h** in moderate to good yields under conditions A (Scheme 4). It should be noted that the formation of 8-membered ring is not easy.[9,10] Here the structure of **2h** was also unambiguously established by X-ray diffraction studies (Figure 2).[11] Again, the *N*-tether substrate **1i** with two methyl groups installed at the terminal position of allene moiety afforded the bicyclic products **2i** and **2i'** in a combined yield of 76%, with a ratio of **2i**/**2i'** being ≥92∶8.

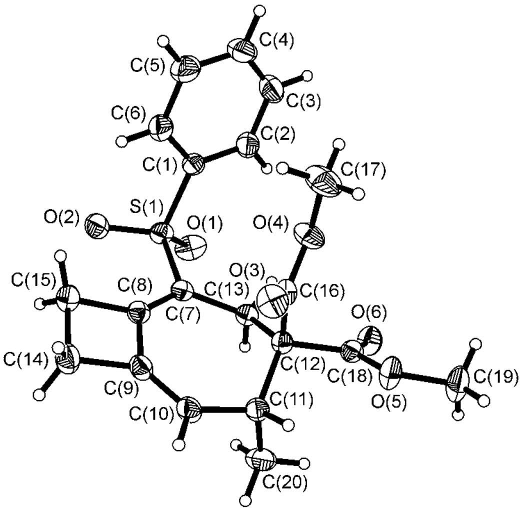
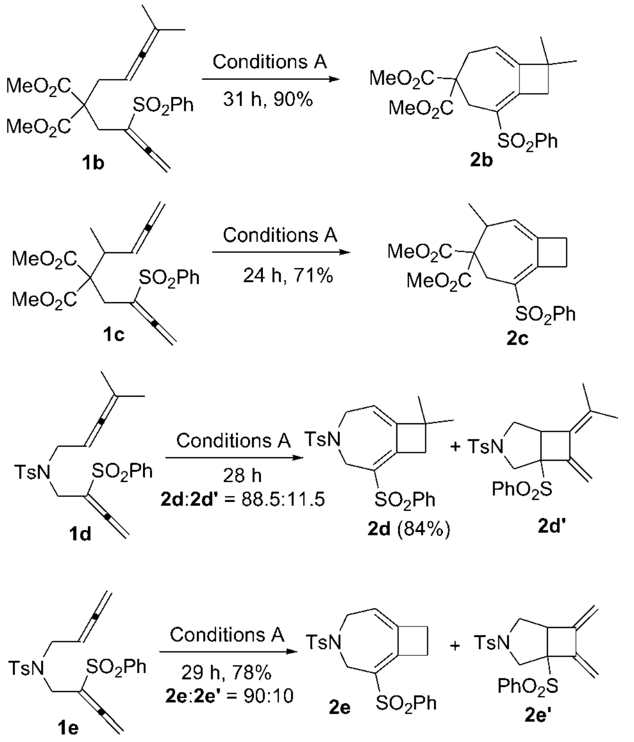


Figure 1 ORTEP representation of **2c**.

Scheme 3 The substrate scope of the cycloaddition of 1,5-bisallene **1**



Conditions A: The bisallene **1** (0.05 mol/L) was heated in toluene under reflux.

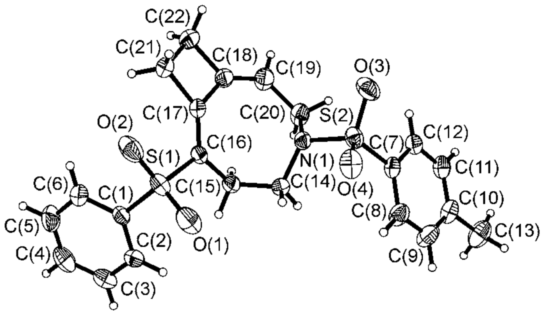
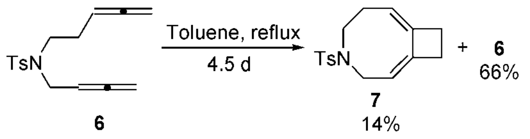


Figure 2 ORTEP representation of **2h**.

We further compared these results with the reactions of 1,6-bisallene without a phenylsulfonyl group. When non-substituted bisallene **6** was heated in toluene under reflux for 4.5 d, the bicyclic product **7** was isolated in only 14% yield and starting material **6** was recovered in 66% yield (Eq. 2).



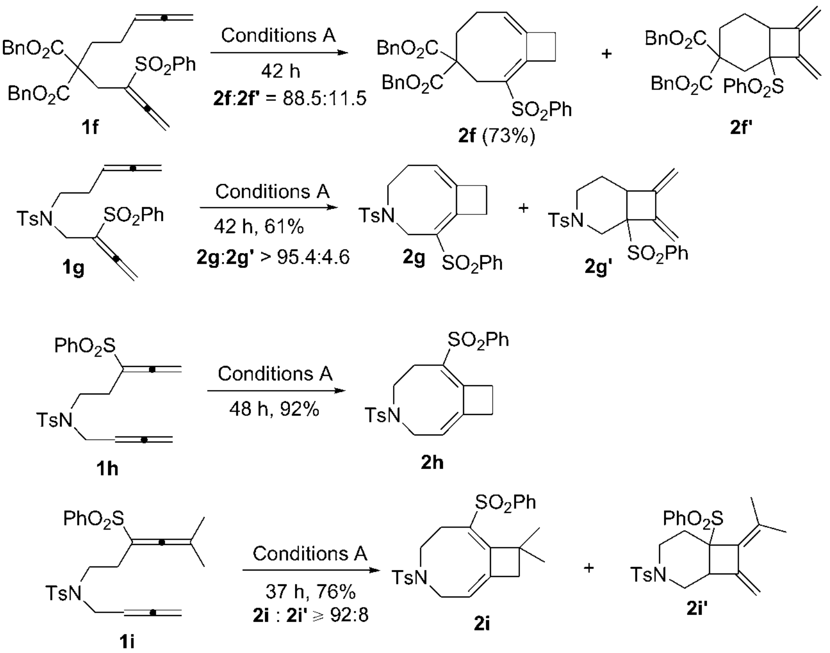
(2)

This [2+2]-cycloaddtion reaction may involve biradical intermediates[12] (Scheme 5). Simply heating bisallene **1** forms a carbon-carbon bond between two center carbon atoms affording the biradical intermediate **M1**, which would lead to the formation of bicylic product **2** via intramolecular radical coupling. The formation of regioisomer **2'** obviously could be attributed to the formation of intermediate **M2**.

Conclusion

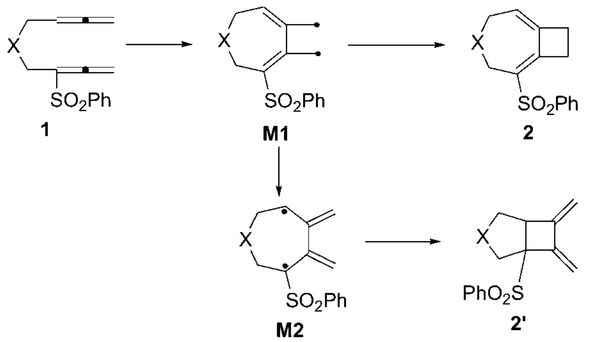
In conclusion, we report here a [2+2]-cycloaddition reaction of bisallenes which is mediated by the presence of substituent(s), affording bicyclo[5.2.0] derivatives or

Scheme 4 The substrate scope of the cycloaddtion of 1,6-bisallene **1**



Conditions A: The bisallene **1** (0.05 mol/L) was heated in toluene under reflux.

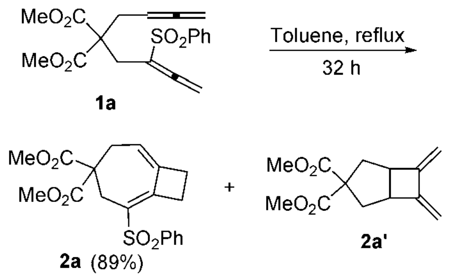
Scheme 5



bicyclo[6.2.0] derivatives in moderate to excellent yields with good regioselectivities. The substituent effect observed here may further be applied to the synthesis of other bicyclic compounds with a four-membered ring. Due to the presence of a conjugated 1,3-diene unit, further elaboration may be conducted to construct more complicated skeleton. Further studies in this area including the real role of the substituent in this type of reaction and the complete control of the regioselectivity of the [2+2]-cycloadditions are being pursued in this laboratory.

Experimental section

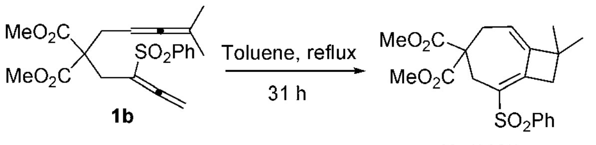
4,4-Bis(methoxycarbonyl)-2-(phenylsulfonyl)-bicyclo[5.2.0]nona-1,6-diene (2a)



2a:**2a'** = 97:3

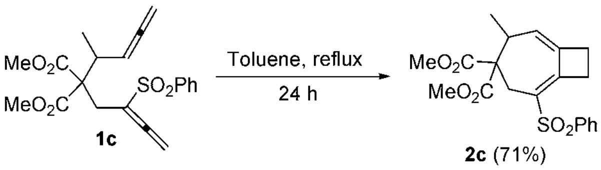
Typical procedure: To a Schlenk tube were added bisallene **1a** (37.6 mg, 0.1 mmol) and toluene (2 mL) under argon. The resulting mixture was heated under reflux for 32 h. Then the reaction mixture was cooled to r.t. and evaporated to afford the residue, which was purified by flash chromatography (eluent: petroleum ether/ethyl acetate=4∶1) on silica gel to afford 33.3 mg (89%) of pure **2a** (the ratio of **2a** to **2a'** was determined by ^{1}H NMR analysis of the crude product before separation): Liquid; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.92—7.85 (m, 2H), 7.66—7.50 (m, 3H), 5.76—5.67 (m, 1H), 3.55 (s, 6H), 3.16—3.04 (m, 4H), 2.85—2.75 (m, 2H), 2.73—2.62 (m, 2H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ: 27.5, 29.1, 35.0, 36.1, 52.8, 54.8, 127.52, 127.55, 127.57, 129.0, 133.1, 139.1, 140.9, 152.8, 170.4; IR (neat) ν: 2954, 2926, 2854, 1736, 1446, 1305, 1253, 1204, 1160, 1141, 1086, 1071 cm^{-1}; MS (ESI) m/z: 399.1 (M+Na$^+$), 394.1 (M+ NH$_4^+$); HRMS calcd for C$_{19}$H$_{21}$O$_6$S (M$^+$+H) 377.1053, found 377.1051.

4,4-Bis(methoxycarbonyl)-2-(phenylsulfonyl)-8-dimethylbicyclo[5.2.0]nona-1,6-diene (2b)



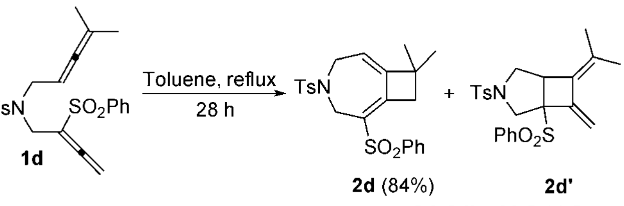
The reaction of **1b** (40 mg, 0.1 mmol) in toluene (2 mL) under reflux afforded 36 mg (90%) of **2b**: Liquid; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.93—7.84 (m, 2H), 7.66—7.51 (m, 3H), 5.70 (t, J=4.7 Hz, 1H), 3.52 (s, 6H), 3.06—3.03 (m, 2H), 2.91—2.87 (m, 2H), 2.79 (d, J=4.7 Hz, 2H), 1.17 (s, 6H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ: 27.0, 35.4, 35.8, 41.0, 44.6, 52.7, 55.0, 124.4, 127.6, 129.0, 129.1, 133.1, 140.8, 149.2, 149.5, 170.3; IR (neat) ν: 2953, 2925, 2860, 1736, 1647, 1446, 1416, 1364, 1305, 1246, 1206, 1180, 1157, 1140, 1085, 1040 cm^{-1}; MS (ESI) m/z: 427.0 (M$^+$+Na), 421.0 (M$^+$+NH$_4$); HRMS calcd for C$_{21}$H$_{24}$O$_6$SNa (M$^+$ + Na) 427.1186, found 427.1196.

4,4-Bis(methoxycarbonyl)-5-methyl-2-(phenylsulfonyl)bicyclo[5.2.0]nona-1,6-diene (2c)



The reaction of **1c** (100.2 mg, 0.26 mmol) in toluene (5.1 mL) under reflux afforded 71.4 mg (71%) of **2c** together with two unknown spots: Solid; m.p.: 139—140 ℃ (petroleum ether/ethyl acetate); ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.90 (d, J=7.2 Hz, 2H), 7.66—7.50 (m, 3H), 5.83 (d, J=6.3 Hz, 1H), 3.66 (s, 3H), 3.35—2.97 (m, 7H), 2.87—2.57 (m, 3H), 0.92 (d, J=6.6 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ: 18.2, 27.4, 29.1, 30.2, 39.0, 52.4, 53.0, 58.8, 127.2, 127.7, 129.1, 133.1, 133.8, 137.0, 140.9, 153.1, 169.1, 170.3; IR (KBr) ν: 2995, 2956, 2929, 2842, 1763, 1740, 1672, 1644, 1587, 1447, 1436, 1413, 1383, 1373, 1347, 1333, 1302, 1293, 1276, 1239, 1201, 1179, 1160, 1142, 1119, 1086, 1065, 1040, 1000 cm^{-1}; MS (ESI) m/z: 413.0 (M$^+$+Na), 391.0 (M$^+$+H). Anal. calcd for C$_{20}$H$_{22}$O$_6$S: C 61.52, H 5.68; found C 61.51, H 5.86.

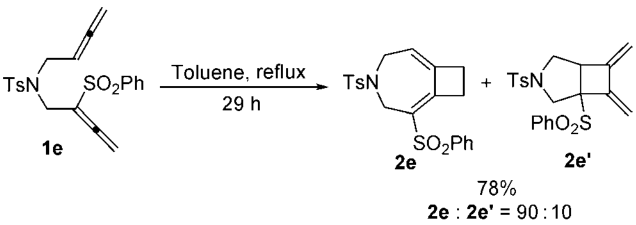
N-Tosyl-2-(phenylsulfonyl)-8-dimethyl-4-azabicyclo[5.2.0]nona-1,6-diene (2d)



2d:**2d'** = 88.5:11.5

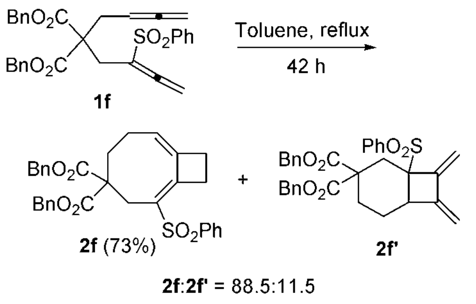
The reaction of **1d** (44 mg, 0.1 mmol) in toluene (2 mL) under reflux afforded 37 mg (84%) of pure **2d** (the ratio of **2d** to **2d'** was determined by ^{1}H NMR analysis of the crude product before separation): Solid; m.p.: 144—145 ℃ (petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.96—7.90 (m, 2H), 7.72—7.57 (m, 3H), 7.34 (d, J=8.1 Hz, 2H), 7.15 (d, J=8.1 Hz, 2H), 5.72—5.63 (m, 1H), 4.31—4.25 (m, 2H), 4.20—4.10 (m, 2H), 2.37 (s, 3H), 2.18 (d, J=2.4 Hz, 2H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.4, 26.5, 42.9, 43.5, 50.0, 50.3, 127.3, 128.2, 129.1, 129.23, 129.24, 130.4, 133.6, 136.95, 137.05, 140.2, 143.2, 160.3; IR (KBr) v: 1598, 1448, 1436, 1380, 1362, 1339, 1331, 1307, 1291, 1186, 1161, 1126, 1095, 1064 cm^{-1}; MS (ESI) m/z: 466.1 ($M^+ + Na$), 444.1 ($M^+ + H$). Anal. calcd for $C_{23}H_{25}NO_4S_2$: C 62.28, H 5.68, N 3.16; found C 62.20, H 5.69, N 2.98.

N-Tosyl-2-(phenylsulfonyl)-4-azabicyclo[5.2.0]nona-1,6-diene (2e)



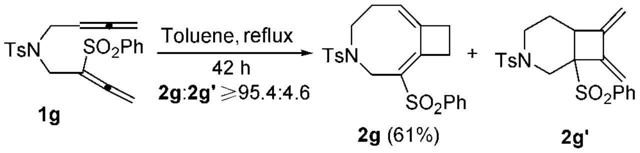
The reaction of **1e** (41.8 mg, 0.1 mmol) in toluene (2 mL) under reflux afforded 32.8 mg (78%) of a mixture of **2e** and **2e'** (the ratio of **2e** to **2e'** was determined to be 90 ∶ 10 by ^{1}H NMR analysis). The pure sample of the major isomer **2e** could be obtained further from recrystallization: Solid; m.p.: 141—142 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.96—7.92 (m, 2H), 7.73—7.59 (m, 3H), 7.34 (d, J=8.1 Hz, 2H), 7.14 (d, J=8.1 Hz, 2H), 5.60—5.54 (m, 1H), 4.42—4.36 (m, 2H), 4.16—4.08 (m, 2H), 2.80 (t, J=7.5 Hz, 2H), 2.45—2.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.5, 27.2, 28.3, 49.8, 50.1, 127.4, 127.7, 128.5, 129.1, 129.3, 133.7, 136.9, 140.5, 140.6, 143.2, 153.6; IR (KBr) v: 2946, 1641, 1447, 1333, 1153, 1092, 1063 cm^{-1}; MS(ESI) m/z: 438.0 ($M^+ + Na$), 470.0 ($M^+ + MeOH + Na$). Anal. calcd for $C_{21}H_{21}NO_4S_2$: C 60.70, H 5.09, N 3.37; found C 60.33, H 5.05, N 3.18.

4,4-Bis(benzyloxycarbonyl)-2-(phenylsulfonyl)bicyclo[6.2.0]deca-1,7-diene (2f)



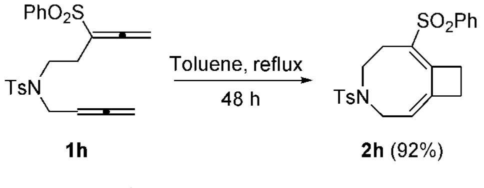
The reaction of **1f** (43.2 mg, 0.08 mmol) in toluene (1.6 mL) under reflux afforded 31.4 mg (73%) of pure **2f** (the ratio of **2f** to **2f'** was determined by ^{1}H NMR analysis of the crude product before separation) (eluent: petroleum ether/ethyl acetate=5 ∶ 1): Liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76 (d, J=7.2 Hz, 2H), 7.56 (t, J=7.4 Hz, 1H), 7.44 (t, J=7.8 Hz, 2H), 7.37—7.19 (m, 10H), 5.53—5.45 (m, 1H), 5.20 (d, J=12.5 Hz, 2H), 5.15 (d, J = 12.5 Hz, 2H), 3.07—3.94 (m, 4H), 2.60—2.47 (m, 4H), 2.15—2.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 24.1, 28.3, 30.6, 31.2, 56.5, 67.4, 125.0, 127.5, 128.1, 128.2, 128.4, 129.1, 129.6, 133.1, 135.5, 138.8, 140.9, 157.8, 170.4; IR (neat) v: 3064, 3033, 2949, 1731, 1632, 1498, 1446, 1375, 1305, 1275, 1244, 1214, 1171, 1145, 1103, 1083, 1060, 1027 cm^{-1}; MS (ESI) m/z: 565.1 ($M^+ + Na$), 1107.4 ($2M^+ + Na$); HRMS calcd for $C_{32}H_{30}O_6SNa$ ($M^+ + Na$) 565.1655, found 565.1650.

N-Tosyl-2-(phenylsulfonyl)-4-azabicyclo[6.2.0]deca-1,7-diene (2g)



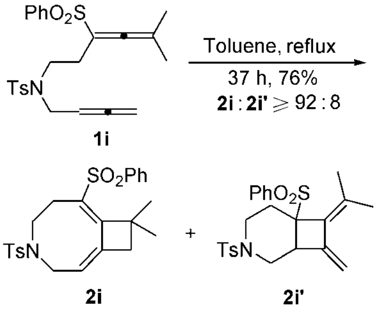
The reaction of **1g** (85.1 mg, 0.2 mmol) in toluene (4 mL) under reflux afforded 51.5 mg (61%) of pure **2g** (eluent: petroleum ether/ethyl acetate=4 ∶ 1—3 ∶ 1) (the ratio of **2g** to **2g'** was determined by ^{1}H NMR analysis of the crude product before separation): Solid; m.p. 127—128 ℃ (petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99—7.93 (m, 2H), 7.74—7.58 (m, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.19 (d, J=8.0 Hz, 2H), 5.46 (t, J=6.9 Hz, 1H), 4.15—4.09 (m, 2H), 3.43 (t, J=5.9 Hz, 2H), 2.99 (t, J=7.5 Hz, 2H), 2.52—2.33 (m, 7H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.4, 27.2, 28.6, 30.3, 46.0, 48.5, 124.6, 125.1, 126.9, 127.7, 129.1, 129.5, 133.5, 136.1, 140.3, 141.7, 143.2, 155.1; IR (KBr) v: 2926, 1637, 1597, 1446, 1336, 1305, 1252, 1151, 1124, 1084, 1049, 1013 cm^{-1}; MS (ESI) m/z: 452.0 ($M^+ + Na$), 484.0 ($M^+ + MeOH + Na$); HRMS calcd for $C_{22}H_{23}NO_4S_2Na$ ($M^+ + Na$) 452.0961, found 452.0960.

N-Tosyl-2-(phenylsulfonyl)-5-azabicyclo[6.2.0]deca-1,7-diene (2h)



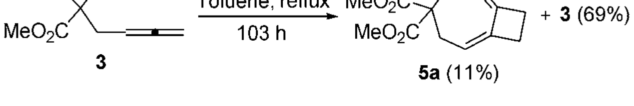
The reaction of **1h** (43.1 mg, 0.1 mmol) in toluene (2 mL) under reflux afforded 39.7 mg (92%) of **2h**: Solid; m.p.: 143—144 ℃ (petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.90 (d, J=7.5 Hz, 2H), 7.68—7.52 (m, 5H), 7.29 (d, J = 8.4 Hz, 2H), 5.35—5.27 (m, 1H), 3.97—3.90 (m, 2H), 3.38 (t, J=5.7 Hz, 2H), 2.81 (t, J=7.5 Hz, 2H), 2.62 (t, J=5.6 Hz, 2H), 2.54—2.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.5, 28.0, 28.2, 30.1, 45.9, 48.9, 122.4, 126.7, 127.1, 127.6, 129.2, 129.5, 133.3, 136.5, 140.7, 140.8, 143.2, 154.8; IR (KBr) v: 2927, 2858, 1645, 1596, 1461, 1444, 1429, 1336, 1306, 1161, 1142, 1120, 1084, 1043 cm^{-1}; MS (ESI) m/z: 452.0 (M^++Na), 484.0 (M^++MeOH+Na). Anal. calcd for $C_{22}H_{23}NO_4S_2$: C 61.51, H 5.40, N 3.26; found C 61.18, H 5.51, N 2.95.

N-Tosyl-2-(phenylsulfonyl)-10-dimethyl-5-azabicyclo[6.2.0]deca-1,7-diene (2i)



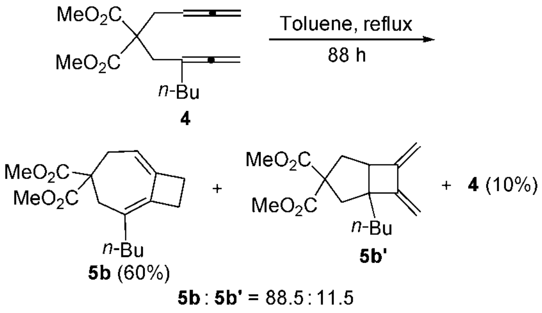
The reaction of **1i** (46 mg, 0.1 mmol) in toluene (2 mL) under reflux afforded 35 mg (76%) of **2i** and **2i'** (inseparable, the ratio of **2i** to **2i'** was determined by ^{1}H NMR analysis): Foam; **2i**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.01—7.89 (m, 2H), 7.67—7.52 (m, 5H), 7.33—7.24 (m, 2H), 5.50—5.42 (m, 1H), 3.87—3.80 (m, 2H), 3.05 (t, J=5.7 Hz, 2H), 2.56 (t, J=6.0 Hz, 2H), 2.46—2.35 (m, 5H), 1.49 (s, 6H); The following data are assigned to **2i'**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.84 (s, 1H), 4.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.5, 26.5, 29.2, 43.6, 45.3, 46.3, 48.5, 125.2, 126.3, 127.0, 128.4, 129.1, 129.7, 133.2, 136.2, 138.1, 140.5, 143.3, 162.7; IR (KBr) v: 2956, 2924, 2866, 1621, 1598, 1495, 1447, 1378, 1339, 1304, 1250, 1158, 1147, 1125, 1086, 1038, 1022 cm^{-1}; MS (ESI) m/z: 475.0 (M^++NH_4), 480.0 (M^++Na); HRMS calcd for $C_{24}H_{28}NO_4S_2$ (M^++H) 458.1454, found 458.1455.

4,4-Bis(methoxycarbonyl)bicyclo[5.2.0]nona-1,6-diene (5a)



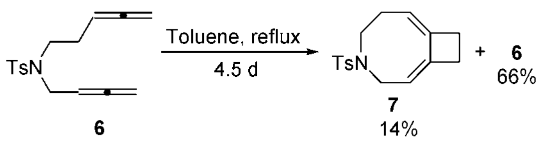
The reaction of **3** (136 mg, 0.58 mmol) in toluene (11 mL) under reflux afforded 15 mg (11%) of **5a** and 94 mg (69%) of recovered **3** (eluent: petroleum ether/ethyl acetate=50 : 1). **5a**: Liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.36—5.28 (m, 2H), 3.70 (s, 6H), 2.81 (d, J=3.9 Hz, 4H), 2.55 (s, 4H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 26.2, 36.2, 52.6, 56.2, 118.4, 141.9, 171.9; IR (neat) v: 2970, 1737, 1436, 1365, 1229, 1217 cm^{-1}; MS (EI) m/z: 236 (M^+, 3.24), 57 (100); HRMS calcd for $C_{13}H_{16}O_4$ (M^+) 236.1049, found 236.1048.

4,4-Bis(methoxycarbonyl)-2-(*n*-butyl)bicyclo[5.2.0]-nona-1,6-diene (5b)



The reaction of **4** (41.2 mg, 0.14 mmol) in toluene (3 mL) under reflux afforded 24.9 mg (60%) of **5b** and 4.1 mg (10%) of recovered **4** (eluent: petroleum ether/ethyl acetate=30 : 1). The ratio of **5b** to **5b'** was determined by ^{1}H NMR analysis of the crude reaction mixture before separation. **5b**: Liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.25—5.19 (m, 1H), 3.69 (s, 6H), 2.75 (s, 4H), 2.48 (s, 4H), 1.94 (t, J=7.5 Hz, 2H), 1.46—1.22 (m, 4H), 0.90 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 14.0, 22.6, 25.2, 25.9, 29.5, 33.6, 35.9, 39.6, 52.5, 55.7, 116.1, 131.2, 135.5, 141.2, 172.1; IR (neat) v: 2955, 2930, 2859, 1737, 1435, 1315, 1243, 1201, 1119, 1084, 1057 cm^{-1}; MS (EI) m/z: 292 (M^+, 42.38), 217 (100); HRMS calcd for $C_{17}H_{24}O_4$ (M^+) 292.1675, found 292.1676.

N-Tosyl-4-azabicyclo[6.2.0]deca-1,7-diene (7)



The reaction of **6** (216.7 mg, 0.75 mmol) in toluene (6 mL) under reflux afforded 31.4 mg (14%) of **7** and 142.7 mg (66%) of recovered **6** (eluent: petroleum ether/ethyl acetate=40 : 1). **7**: Liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.68 (d, J=8.1 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 5.21—5.13 (m, 1H), 4.99—4.92 (m, 1H), 3.81 (d, J=3.0 Hz, 2H), 3.34 (t, J=5.3 Hz, 2H), 2.54—2.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.5, 27.6, 28.0, 29.9, 47.3, 48.8, 114.1, 119.3, 127.5, 129.4, 135.3, 138.8, 140.4, 143.1; IR (neat) v: 3031, 2924, 1597, 1493, 1454, 1423, 1399, 1377, 1336, 1305, 1291, 1230, 1159, 1118, 1097, 1049, 1019 cm^{-1}; MS (EI) m/z: 289 (M^+, 5.09), 106 (100); HRMS calcd for $C_{16}H_{19}NSO_2$ (M^+) 292.1675, found 292.1676.

References and notes

1 (a) Dembitsky, V. M. *J. Nat. Med.* **2008**, *62*, 1.
(b) Ortuno, R. M.; Moglioni, A. G.; Moltrasio, G. Y. *Curr. Org. Chem.* **2005**, *9*, 237.
(c) Hansen, T. V.; Stenstrom, Y. *Organic Synthesis*: *Theor. Appl.* **2001**, *5*, 1.

(d) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797.

2 (a) Rappoport, Z. J.; Liebman, J. F. *The Chemistry of Cyclobutanes*, Wiley, Chichester, **2005**.
(b) Namyslo, J. C.; Kaufmann, D. E. *Chem. Rev.* **2003**, *103*, 1485.
(c) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449.
(d) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

3 For reviews on the [2＋2] cycloaddition involving allenes, see:
(a) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805.
(b) Murakami, M.; Matsuda, T. In *Modern Allene Chemistry*, Vol. 2, Eds.: Krause, N.; Hashmi, A. S. K., Wiley-VCH, Weinheim, **2004**, pp. 727—815.
(c) Ma, S. *Chem. Rev.* **2005**, *105*, 2829.

4 (a) Ma, S.; Lu, P.; Lu, L.; Hou, H.; Wei, J.; He, Q.; Gu, Z.; Jiang, X.; Jin, X. *Angew. Chem., Int. Ed.* **2005**, *44*, 5275.
(b) Lu, P.; Ma, S. *Org. Lett.* **2007**, *9*, 5319.
(c) Lu, P.; Ma, S. *Org. Lett.* **2007**, *9*, 2095.
(d) Ma, S.; Lu, L. *Chem. Asian J.* **2007**, *2*, 199.
(e) Ma, S.; Jiang, X.; Chen, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 8009.

5 (a) Kim, S. M.; Park, J. H.; Kang, Y. K.; Chung, Y. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4532.
(b) Inagaki, F.; Narita, S.; Hasegawa, T.; Kitagaki, S.; Mukai, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 2007.

6 For reports on the reactions involving allenes with phenylsulfonyl functionality, see:
(a) Padwa, A.; Murphree, S. S.; Ni, Z.; Watterson, S. H. *J. Org. Chem.* **1996**, *61*, 3829.
(b) Flick, A. C.; Caballero, M. J. A.; Padwa, A. *Org. Lett.* **2008**, *10*, 1871.
(c) Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.* **2002**, *4*, 1755.
(d) Mukai, C.; Hara, Y.; Miyashita, Y.; Inagaki, F. *J. Org. Chem.* **2007**, *72*, 4454.

7 The Mukai group recently reported some examples of [2＋2]-reaction of bisallenes with phenylsulfonyl substituent as side reaction, see ref. 5b.

8 Crystal data for **2c**: $C_{20}H_{22}O_6S$, $M_r=390.44$, triclinic, space group P-1. Final R indices $[I>2\sigma(I)]$, $R_1=0.0350$, $wR_2=0.0990$, R indices (all data) $R_1=0.0384$, $wR_2=0.1026$, $a=8.2270(3)$ Å, $b=8.8719(3)$ Å, $c=13.4377(5)$ Å, $\alpha=82.0240(10)°$, $\beta=81.2390(10)°$, $\gamma=81.5790(10)°$, $V=952.08(6)$ Å^3, $T=296(2)$ K, $Z=2$. Reflections collected/unique: 11186/3331 ($R_{\text{int}}=0.0156$), number of observations $[>2\sigma(I)]$ 3029; parameters, 244. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center: CCDC 777608.

9 For reviews on synthesis of cyclooctanoids, see:
(a) Sieburth, S. McN.; Cunard, N. T. *Tetrahedron* **1996**, *52*, 6251.
(b) Mehta, G.; Singh, V. *Chem. Rev.* **1999**, *99*, 881.
(c) Yet, L. *Chem. Rev.* **2000**, *100*, 2963.

10 (a) Gilbertson, S. R.; DeBoef, B. *J. Am. Chem. Soc.* **2002**, *124*, 8784.
(b) Evans, P. A.; Robinson, J. E.; Baum, E. W.; Fazal, A. N. *J. Am. Chem. Soc.* **2002**, *124*, 8782.
(c) Wender, P. A.; Ihle, N. C.; Correia, C. R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5904.
(d) Wender, P. A.; Correa, A. G.; Sato, Y.; Sun, R. *J. Am. Chem. Soc.* **2000**, *122*, 7815.
(e) Wender, P. A.; Gamber, G. G.; Hubbard, R. D.; Zhang, L. *J. Am. Chem. Soc.* **2002**, *124*, 2876.
(f) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108.
(g) Snapper, M. L.; Tallarico, J. A.; Randall, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 1478.

11 Crystal data for **2h**: $C_{22}H_{23}NO_4S_2$, $M_r=429.53$, monoclinic, space group $P2(1)/c$. Final R indices $[I>2\sigma(I)]$, $R_1=0.0412$, $wR_2=0.1157$, R indices (all data) $R_1=0.0473$, $wR_2=0.1246$, $a=14.8344(5)$ Å, $b=9.9884(4)$ Å, $c=14.1291(5)$ Å, $\alpha=90.00°$, $\beta=94.5000(10)°$, $\gamma=90.00°$, $V=2087.08(13)$ Å^3, $T=296(2)$ K, $Z=4$. Reflections collected/unique: 23582/3674 ($R_{\text{int}}=0.0187$), number of observations $[>2\sigma(I)]$ 3200; parameters, 262. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center: CCDC 777609.

12 (a) Padwa, A.; Filipkowski, M. A.; Meske, M.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1993**, *115*, 3776.
(b) Padwa, A.; Meske, M.; Murphree, S. S.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1995**, *117*, 7071.

(E1006202 Lu, Y.; Dong, H.)