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Rhodium(I)-Catalyzed Intramolecular Carbonylative [2+2+1] Cycloadditions and Cycloisomerizations of Bis(sulfonylallene)s

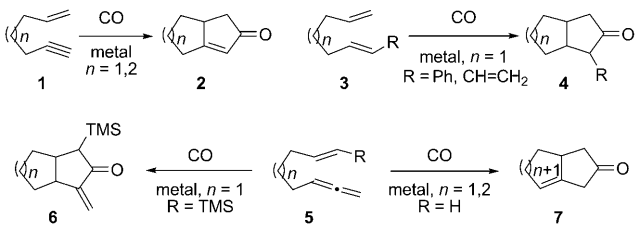
Takamasa Kawamura, Fuyuhiko Inagaki, Syu Narita, Yasuhito Takahashi, Shuichi Hirata, Shinji Kitagaki, and Chisato Mukai*[a]

Abstract: Novel [{RhCl(CO)dppp}$_2$]-catalyzed intramolecular carbonylative [2+2+1] cycloadditions of bis(phenylsulfonylallene) derivatives under CO, leading to the facile formation of bis(phenylsulfonyl)bicyclo[*n*.3.0] frameworks (n=4–6), have been developed. The terminal double bonds of both allenyl moieties served exclusively as the two π-components. In particular, this newly developed method was shown to be a powerful tool for the construction of bicyclo[6.3.0]undecadienones, which have hardly been prepared by the known Pauson–Khand (-type) reactions. The bicyclo[7.3.0]dodecadienone homologue (one extra carbon) could be formed in rather low yields. Alternatively, novel cycloisomerizations of bis(phenylsulfonylallene) derivatives with catalysis by the same Rh^I complex under N_2 readily produced the 3,4-dimethylene-2,5-bis(phenylsulfonyl)cyclononene and the corresponding cyclooctene and cycloheptene frameworks.

Keywords: allenes · cycloaddition · cycloisomerization · medium-ring compounds · rhodium

Introduction

The $Co_2(CO)_8$-mediated [2+2+1] cycloaddition of three components—an alkyne π-bond, an alkene π-bond, and carbon monoxide (CO)—is known as the Pauson–Khand reaction,[1] and its intramolecular version provides both the most straightforward and the most powerful methodology for the construction of cyclopentenone-fused bicyclic frameworks (Scheme 1, conversion of **1** into **2**). Several transition metals, such as Rh, Ir, Mo, Zr, Ti, and so on, have now been found to be useful catalysts for carbonylative [2+2+1] cycloadditions of this type.[2] These ring-closing reactions have been limited almost exclusively to the use of alkyne π-bonds as one of the two π-bond components, although there have been several reported Pauson–Khand-type [2+2+1] cycloadditions based on an alternative π-component instead of the alkyne π-bond. The stepwise stoichiometric conversion of 1-phenylhepta-1,6-diene into the bicyclo[3.3.0] compound via a zirconacyclopentane derivative was reported (Scheme 1, conversion of **3** into **4**, R=Ph).[3] Wender[4] developed [{RhCl(CO)$_2$}$_2$]-catalyzed [2+2+1] cycloadditions of 1,3-dienes, alkenes, and CO, in which the 1,3-diene moiety served as the alkene π-bond[5] instead of the alkyne π-component (Scheme 1, conversion of **3** into **4**, R=vinyl). Itoh described an example of [{RhCl(CO)$_2$}$_2$]-catalyzed [2+2+1] cycloaddition between the internal double bond of the allenyl moiety and a vinylsilane (Scheme 1, conversion of **5** into **6**).[6] We have also developed a new procedure[7] for the formation of bicyclo[5.3.0] and bicyclo[4.3.0] ring systems based on [{RhCl(CO)$_2$}$_2$]-catalyzed [2+2+1] cycloadditions of the terminal double bond of an allene and an alkene (Scheme 1, conversion of **5** into **7**).



Scheme 1. Intramolecular carbonylative [2+2+1] cycloadditions of two π-components and CO.

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On the other hand, the synthetic versatility of bis(allene)s has recently been demonstrated by the Ma group,[8–11] who have found that the thermal and Pd-catalyzed [2+2] cycloadditions of 1,5-bis(allene) compounds give rise to the formation of bicyclo[5.2.0] and bicyclo[3.2.0] frameworks, respectively.[8] Interestingly, they also disclosed that 1,5-bis(allene)s underwent bimolecular cyclization to afford steroid-like skeletons with the aid of *trans*-[RhCl(CO)(PPh$_3$)$_2$],[9] whereas 1,5-bis(allene) derivatives with substituents at the allenic terminus gave seven-membered cross-conjugated trienes through cycloisomerization when treated with [{RhCl(CO)$_2$}$_2$].[10] Chung and Kang also reported intriguing cycloisomerizations and carbonylative [2+2+1] cycloadditions of 1,5-bis(allene)s.[12] Our contiguous interest in the fields of [{RhCl(CO)$_2$}$_2$]- or [{RhCl(CO)dppp}$_2$]-catalyzed allenic cycloadditions[7,13] prompted us to investigate carbonylative [2+2+1] cycloadditions between two allenic π-bonds. We also investigated cycloisomerizations of the bis(allene)s under N_2 instead of CO. This paper describes the Rh^I-catalyzed carbonylative and non-carbonylative ring-closing reactions of bis(sulfonylallene)s to effect the easy preparation of medium-sized bicyclo[*n*.3.0] skeletons and monocyclic rings containing two vicinal *exo*-methylene moieties, respectively.[14]

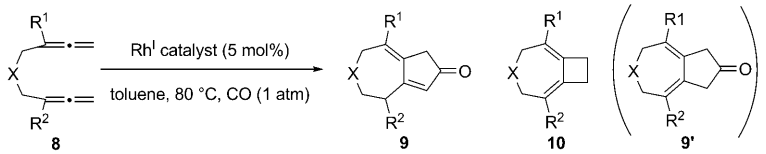
Results and Discussion

Rhodium(I)-catalyzed intramolecular carbonylative [2+2+1] cycloadditions of bis(sulfonylallene)s: Intramolecular Pauson–Khand reactions of enynes (alkyne/alkene derivatives) can generally be applied to the formation of bicyclo[3.3.0]octenones and bicyclo[4.3.0]nonenones in good to high yields. However, the application of this protocol to the construction of larger-sized bicyclo[5.3.0]decenone systems could not be achieved except in the cases of a few specific substrates, possessing, for example, an aromatic ring as the template.[15] Rh^I-catalyzed carbonylative [2+2+1] cycloadditions[16] of allenynes (alkyne/allene derivatives)[13,17,18] or allenenes (alkene/allene)[7] has, however, been reported, by ourselves[7,13] and by Brummond et al.,[17] to afford the corresponding bicyclo[5.3.0] compounds in satisfactory yields.[19] On these grounds, our initial evaluation of a Rh^I-catalyzed carbonylative [2+2+1] cycloaddition of a bis(allene) focused on the preparation of a bicyclo[5.3.0]decadienone from the bis(phenylsulfonylallene) compound **8a**.

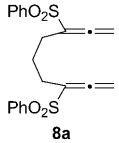
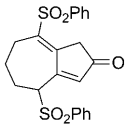
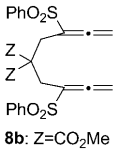
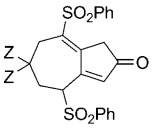
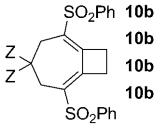
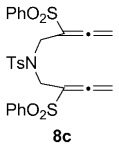
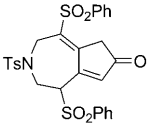
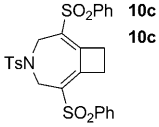
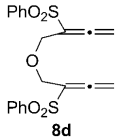
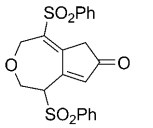
A solution of **8a** in toluene was thus heated at 80 °C under CO in the presence of [{RhCl(CO)dppp}$_2$] (5 mol %) for 1 h to afford 2,6-bis(phenylsulfonyl)bicyclo[5.3.0]deca-1,7-dien-9-one (**9a**) in quantitative yield (Table 1, entry 1). The formation of **9a** can be interpreted in terms of the intermediacy of the initially formed 1,3-diene derivative **9a′** and its subsequent isomerization to the α,β-unsaturated ketone **9a**. The alternative catalyst [{RhCl(CO)$_2$}$_2$] also gave the ring-closing products **9a** in 85 % yield, although a longer reaction time (6 h) was necessary (Table 1, entry 2). Increasing the amount of [{RhCl(CO)$_2$}$_2$] from 5 to 10 mol % provided **9a** in a better yield and in a shorter reaction time (Table 1, entry 3). It should be mentioned that a rather lower reaction temperature (80 °C) than in the cases of allenynes and allenenes, which required toluene or xylene at reflux,[7,13] was sufficient to complete this ring-closing reaction. No [2+2] cycloaddition products could be detected under either set of reaction conditions, presumably because of the low reaction temperature.[20]

The malonate derivative **8b** in the presence of [{RhCl(CO)dppp}$_2$] (5 mol %), however, unexpectedly fur-

Table 1. Rhodium(I)-catalyzed synthesis of bicyclo[5.3.0] compounds through carbonylative [2+2+1] cycloadditions of bis(allene)s.[a]



8 **9** **10** **9'**

Entry	Bis(allene)	Rh^I catalyst	*t* [h]	Products (yield)[b]
1	 **8a**	[{RhCl(CO)dppp}$_2$]	1	 **9a** (quant.)
2		[{RhCl(CO)$_2$}$_2$]	6	**9a** (85%)
3		[{RhCl(CO)$_2$}$_2$][c]	3	**9a** (93%)
4	 **8b**: Z=CO$_2$Me	[{RhCl(CO)dppp}$_2$]	2	 **9b** (20%)  **10b** (70%)
5		[{RhCl(CO)dppp}$_2$][c]	2	**9b** (31%) **10b** (65%)
6		[{RhCl(CO)$_2$}$_2$]	1	**9b** (83%) **10b** (16%)
7		[{RhCl(CO)$_2$}$_2$][c]	1	**9b** (89%) **10b** (7%)
8	 **8c**	[{RhCl(CO)dppp}$_2$]	1	 **9c** (98%)  **10c** (–)
9		[{RhCl(CO)$_2$}$_2$]	3	**9c** (44%) **10c** (34%)
10	 **8d**	[{RhCl(CO)dppp}$_2$]	0.5	 **9d** (92%)
11		[{RhCl(CO)$_2$}$_2$]	20	**9d** (28%)
12		[{RhCl(CO)$_2$}$_2$][c]	4	**9d** (54%)

[a] Reaction conditions: a solution of the bis(allene) **8** (0.1 mmol) and the Rh^I catalyst (5 mol %) in toluene (1 mL) was stirred under CO at 80 °C. [b] Yields of isolated products. [c] 10 mol % of the catalyst. Ts = *p*-toluenesulfonyl; dppp = 1,3-bis(diphenylphosphino)propane.

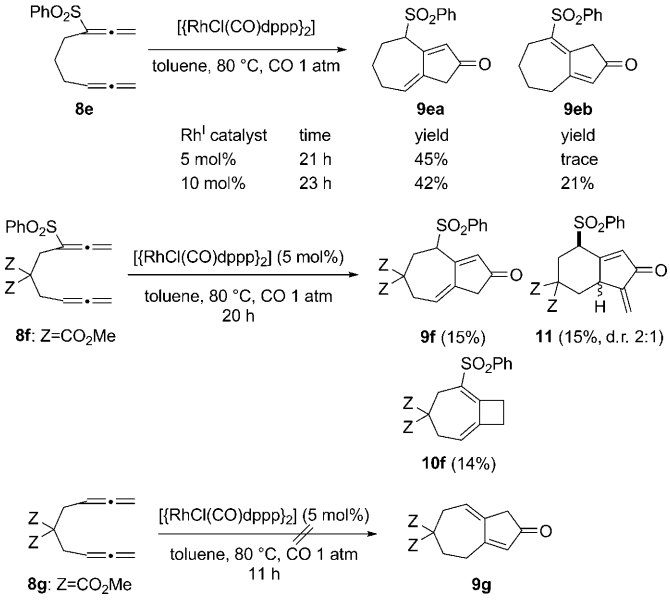
nished **9b** only in low yield, along with the predominant [2+2] cycloaddition product **10b** in 70% yield (Table 1, entry 4). An increase in the amount of [{RhCl(CO)dppp}$_2$] used did not improve the yield of **9b** (Table 1, entry 5). Although the rhodium catalyst had not necessarily been essential for the production of **10b**, it might have accelerated the [2+2] cycloaddition reaction, probably through the intermediacy of a rhodacycle (vide infra).[21,22] Indeed, when **8b** was heated in toluene in the absence of catalyst at 80°C for 6 h, **10b** was obtained in 98% yield. Satisfactory yields (83 or 89%) of **9b** were achieved through the use of [{RhCl(CO)$_2$}$_2$] in place of [{RhCl(CO)dppp}$_2$] (Table 1, entries 6 and 7).

The substrate **8c**, containing a nitrogen atom, reacted in the presence of [{RhCl(CO)dppp}$_2$] to afford the corresponding azabicyclo[5.3.0]decadienone **9c** in 98% yield (Table 1, entry 8). When **8c** was treated with [{RhCl(CO)$_2$}$_2$], however, **9c** was formed only in a low yield (44%) and the [2+2] cycloaddition product **10c** was obtained as a by-product (Table 1, entry 9).

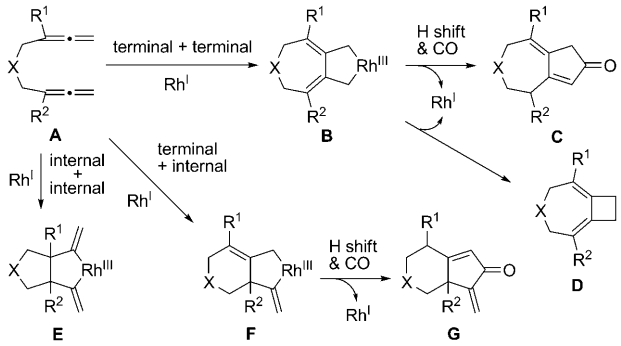
The oxa congener **9d** could also be synthesized in a satisfactory yield from **8d** in the presence of [{RhCl(CO)dppp}$_2$] (Table 1, entry 10). Again, [{RhCl(CO)$_2$}$_2$] provided **9d** in a rather low yield (Table 1, entries 11 and 12). The results in Table 1 therefore indicate that [{RhCl(CO)dppp}$_2$] is superior to [{RhCl(CO)$_2$}$_2$] for carbonylative [2+2+1] cycloadditions of the bis(allene) derivatives **8**, except in the case of the malonate derivative **8b** (Table 1, entries 4–7).

The mono-phenylsulfonyl derivative **8e** (Scheme 2), upon treatment with [{RhCl(CO)dppp}$_2$] (5 mol%), also produced the corresponding bicyclo[5.3.0] derivative **9ea** in 45% yield. An increase in the amount of the catalyst used led to an increase in the total yield of the [2+2+1] cycloadducts (63%), this time including the isomer **9eb**.[23] The malonate derivative **8f** (Scheme 2) underwent the ring-closing reaction to produce the two carbonylative [2+2+1] cycloaddition products **9f** and **11**, each in 15% yield, along with the [2+2] cycloaddition product **10f** (14% yield). The bicyclo[4.3.0] derivative **11**, containing the exomethylene moiety, must have been obtained through the reaction between the terminal and internal double bonds of the two allenyl groups. This observation differs from those mentioned previously, in which the ring-closing reactions consistently involved the participation of the two terminal double bonds of the allenyl functionalities. Furthermore, the non-sulfonylated derivative **8g** (Scheme 2) provided only intractable mixtures under several sets of conditions.

These results, in combination with those shown in Table 1, imply that the introduction of two phenylsulfonyl groups on the two allenyl functionalities makes intramolecular carbonylative [2+2+1] cycloadditions between the terminal double bonds of the two allenyl groups extremely smooth (Scheme 3, **A**→**B**→**C**). The bulky phenylsulfonyl groups might not only suppress cyclometallation between the two internal double bonds (Scheme 3, **A**→**E**)[8] or between one terminal and one internal double bond of two allenyl groups (Scheme 3, **A**→**F**),[9] but might also orient the two terminal



Scheme 2. Intramolecular carbonylative [2+2+1] cycloadditions of mono- or non-sulfonylated bis(allene)s.

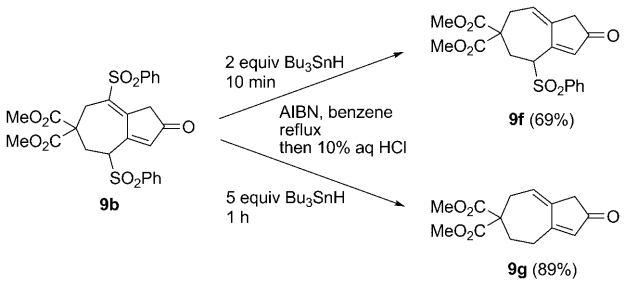


Scheme 3. Formation and reactions of rhodacycle intermediates from bis(allene)s **A**.

double bonds of the allenyl moieties such that they can react.

A phenylsulfonyl group can be regarded as a hydrogen surrogate and can easily be replaced by a hydrogen atom by conventional means.[24] We indeed examined the selective removal of one of the two phenylsulfonyl groups in a [2+2+1] cycloaddition product (Scheme 4). The removal of the vinylic sulfone in **9b** in a highly selective manner was achieved by use of tributyltin hydride (2 equiv) in the presence of AIBN[25] and subsequent acidic workup. Treatment of **9b** with further tributyltin hydride (excess) led to desulfonylation both at the vinylic and at the allylic positions.[26]

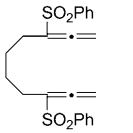
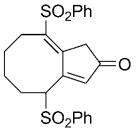
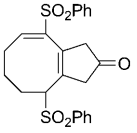
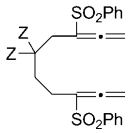
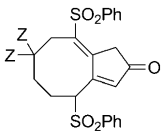
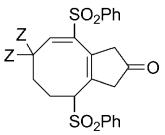
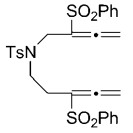
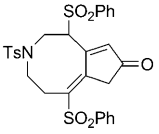
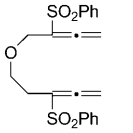
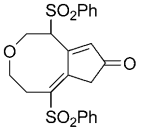
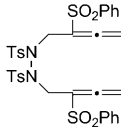
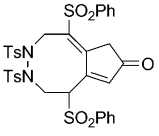
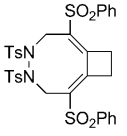
The unexpectedly easy formation of the bicyclo[5.3.0]decadienone framework from the bis(allene)s, particularly from bis(phenylsulfonylallene) derivatives, under mild conditions [{RhCl(CO)dppp}$_2$] (5 mol%), CO (1 atm), toluene 80°C, 1 h} encouraged us to apply this new method to the construction of the bicyclo[6.3.0] skeleton. The prepara-



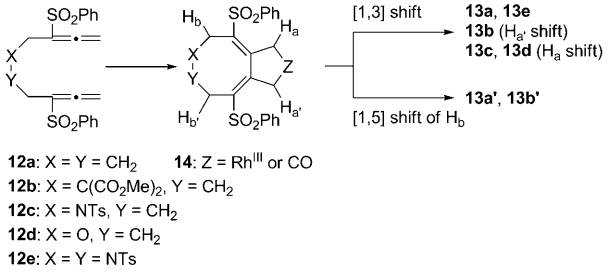
Scheme 4. Desulfonylation of **9b**. AIBN = 2,2′-azobis(isobutyronitrile).

tion of a bicyclo[6.3.0] ring system through a Pauson–Khand-type [2+2+1] cycloaddition, in which allenynes were used as substrates and a template effect was necessary to attain high yields, had been reported by us previously.[13e] Treatment of 3,8-bis(phenylsulfonyl)deca-1,2,8,9-tetraene (**12a**, Table 2) under the standard ring-closing conditions {[{RhCl(CO)dppp}$_2$] (5 mol%), CO (1 atm), 80°C in toluene} for 3 h afforded the bicyclo[6.3.0]undecenone derivative **13a** in 70% yield together with its isomer **13a′** in 23% yield (Table 2, entry 1). No interconversion between **13a** and **13a′** could be observed under the standard conditions, so the production of these two eight-membered ring products could be interpreted in terms of the common intermediate **14a** (Scheme 5): **14a** could undergo either a 1,3-hydrogen shift ($H_{a'}$) to provide **13a**, or a 1,5-hydrogen shift (H_b)[27] to give **13a′** (Scheme 5). Under similar conditions, the malonate derivative **12b** afforded a mixture of **13b** and **13b′** in 75% yield in a ratio of 1:6 (Table 2, entry 2). Interestingly, the carbonylative [2+2+1] cycloadditions of the nitrogen congener **12c** and the oxygen congener **12d** led to the formation of the eight-membered ring products **13c** (87% yield) and **13d** (86% yield), respectively, through exclusive 1,3-hydrogen (H_a) shifts on the side nearest to the heteroatom X in **14c** or **14d** (Table 2, entries 3 and 4). In the case of the diaza derivative **12e**, the desired carbonylative [2+2+1] cycloaddition product **13e** was formed in 27% yield as a minor product after a prolonged reaction time. Instead, the corresponding [2+2] cycloaddition product **15e** was obtained as a major product (Table 2, entry 5). The data in entry 6 of Table 2 indicate a significant improvement in the yield of **13e** with use of 10 mol% of the catalyst.

Table 2. Rhodium(I)-catalyzed synthesis of bicyclo[6.3.0] compounds through carbonylative [2+2+1] cycloadditions of bis(allene)s.[a]

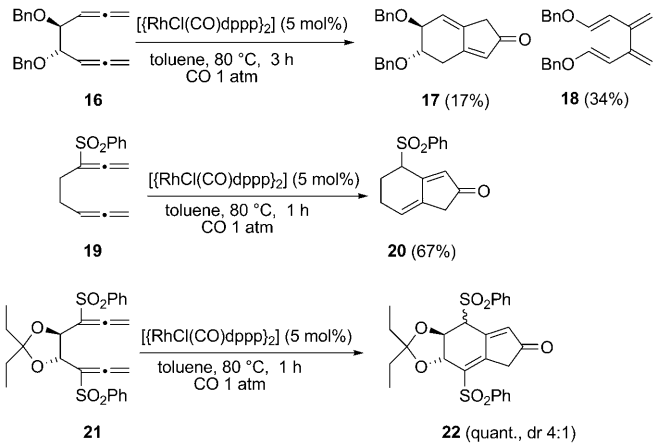
Entry	Bis(allene)	t [h]	Products (yield)[b]	
1	 **12a**	3	 **13a** (70%)	 **13a′** (23%)
2	 **12b**: Z=CO_2Me	5	 **13b**	 **13b′**
			75% (1:6)	
3	 **12c**	1	 **13c** (87%)	
4	 **12d**	1	 **13d** (86%)	
5	 **12e**	22	 **13e** (27%)	 **15e** (39%)
6[c]	**12e**	18	**13e** (54%)	**15e** (22%)

[a] Reaction conditions: a solution of the bis(allene) **12** (0.1 mmol) and [{RhCl(CO)dppp}$_2$] (5 mol%) in toluene (1 mL) was stirred at 80°C under CO. [b] Yields of isolated products. [c] Catalyst (10 mol%) was used.



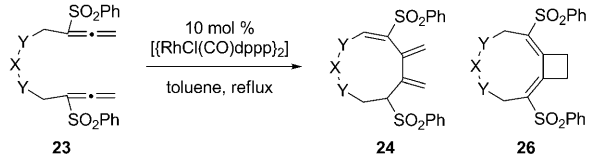
Scheme 5. Hydrogen shifts in intermediates **14**.

To extend the scope of this method, we examined some bis(allene)s that would be expected to lead to bicyclo[4.3.0]nonadienone derivatives. The bis(allene) **16** (Scheme 6), prepared from L-tartrate, was subjected to the standard reaction conditions to give the carbonylative product **17** in 17% yield, together with the tetraene derivative **18** (34% yield); **18** may have arisen from a thermal [3,3]-sigmatropic rearrangement of the starting material.[28] The monophenylsulfonyl substrate **19** afforded the desired product **20** in 67% yield. These results are in good agreement with predictions based on the previously discussed results shown in Table 1 and Scheme 2. Upon treatment with [{RhCl(CO)dppp}$_2$] (5 mol%) in toluene under CO, the bis(phenylsulfonylallene) derivative **21** produced **22** in a quantitative yield as expected. It might thus be concluded that the carbonylative [2+2+1] cycloaddition reactions of bis(allene) derivatives can consistently and efficiently be applied to the preparation of bicyclo[n.3.0]alkadienone skeletons (n = 4–6), although the origins of the regioselectivities



Scheme 6. Formation of bicyclo[4.3.0]nonadienones through rhodium(I)-catalyzed carbonylative [2+2+1] cycloadditions of the bis(phenylsulfonylallene) derivatives **16**, **19**, and **21**.

Table 3. Rhodium(I)-catalyzed cycloisomerizations of undecatetraenes **23**.[a]

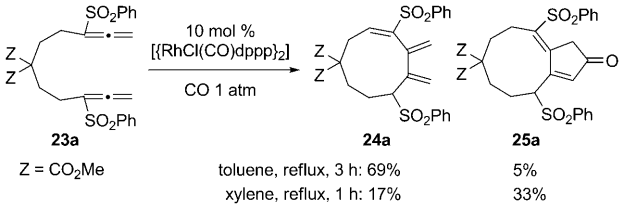


Entry	Substrate	X	Y	t [h]	Product (% yield)[b]
1[c]	**23a**	$C(CO_2Me)_2$	CH_2	2	**24a** (96)
2	**23b**	CH_2	CH_2	1	**24b** (71)
3	**23c**	NNs	CH_2	1	**24c** (70)
4	**23d**	NTs	CH_2	1	**24d** (67), **26d** (7)
5	**23e**	NCO_2Me	CH_2	1	**24e** (67), **26e** (8)
6	**23f**	CH_2	$C(CO_2Me)_2$	38	**24f** (49), **26f** (26)

[a] Reaction conditions: a solution of **23** in toluene (0.1 M or 0.05 M) was heated at reflux in the presence of [{RhCl(CO)dppp}$_2$] under N_2. [b] Yields of isolated products. [c] Catalyst (5 mol %) was used. Ns = *o*-nitrobenzenesulfonyl.

of the observed hydrogen shifts have not yet been determined.

Rhodium(I)-catalyzed cycloisomerizations of bis(sulfonylallene)s: The preparation of larger-sized bicyclo[7.3.0]dodecadienones through Rh^I-catalyzed carbonylative [2+2+1] cycloadditions of bis(allene)s was next examined. Dimethyl bis(3-phenylsulfonylpenta-3,4-dienyl)malonate (**23a**, Scheme 7) was exposed to [{RhCl(CO)dppp}$_2$] (10 mol %) under CO in toluene at reflux for 3 h by the established procedure to produce the nine-membered monocyclic compound **24a** in 69 % yield along with a small amount of the carbonylative product **25a** (5 % yield). A better yield (33 %) of **25a** was recorded in xylene at reflux (1 h), but **24a** was still formed in 17 % yield (Scheme 7).

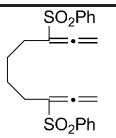
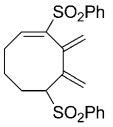
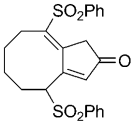
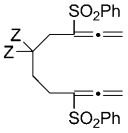
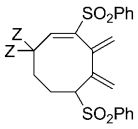
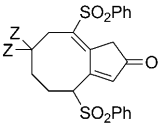
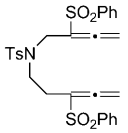
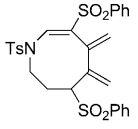
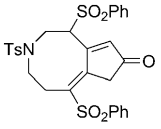
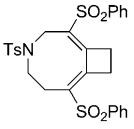
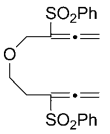
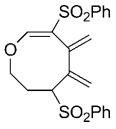
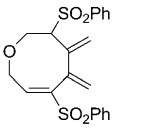
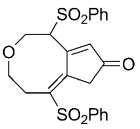


Scheme 7. Formation of **24a** and **25a** under the conditions of rhodium(I)-catalyzed carbonylative [2+2+1] cycloaddition of **23a**.

It is obvious that CO was not involved in the formation of **24a**, so **23a** was treated with [{RhCl(CO)dppp}$_2$] (5 mol %) in toluene at reflux under N_2, instead of CO, to afford **24a** in 96 % yield (Table 3, entry 1). The simpler undecatetraene derivative **23b**, without any substituents on its carbon tether, also gave the corresponding compound **24b** in good yield (Table 3, entry 2). The lower yield of **24b** relative to that of **24a** can be attributed to loss of the geminal disubstituted effect. The N-nosylated substrate **23c** also produced the nine-membered-ring triene **24c** in 70 % yield as the sole isolable product (Table 3, entry 3). The two additional nitrogen analogues **24d** and **24e** were prepared in reasonable yields (67 %) accompanied by the formation of small amounts of the bicyclo[7.2.0] derivatives **26d** and **26e** (Table 3, entries 4 and 5). In the case of the fairly bulky bis(malonate) derivative **23f** a prolonged reaction time was necessary for consumption of the starting material to go to completion and the desired product **24f** was obtained in 49 % yield (Table 3, entry 6) along with **26f** (26 % yield). It should be emphasized that these ring-closing reactions of acyclic substrates **23** to afford the monocyclic nine-membered ring products **24** proceeded smoothly under the standard conditions with normal concentrations (0.05 or 0.1 M solutions).[29–31] We did not need to use a high-dilution technique, although this would usually be used for forming medium- and larger-sized rings to avoid oligomerization.

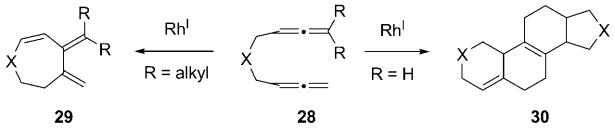
We next focused our efforts on the scope of this transformation. Treatment of the decatetraene derivatives **12** under similar conditions effected cycloisomerizations (Table 4), resulting in the easy formation of the cyclooctene derivatives **27** (**27′**) in high yields along with small yields of by-products such as the carbonylative products **13** and the [2+2] cycloaddition product **15c**. The formation of compounds **13** can be explained in terms of the participation of CO with the rhodium catalyst. The cycloisomerizations of compounds **12** consistently occurred in satisfactory yields under milder conditions (80 °C) than those required for compounds **23** (reflux temperature), which can be attributed to the entropy effect (eight-membered versus nine-membered ring formation). The malonate derivative **12b** and the N-tosylated derivative **12c** produced **27b** and **27c**, respectively, in a highly selective manner and the corresponding regioisomers **27b′** and **27c′** were not formed (Table 4, entries 2 and 3). The oxygen congener **12d**, however, unselectively afforded the two possible regioisomers **27d** and **27d′** in a ratio of 57:43 in 92 % yield (Table 4, entry 4). In the exceptional case of **12c**, the [2+2] cycloaddition product **15c** was obtained in 10 % yield (Table 4, entry 3).

Table 4. Rhodium(I)-catalyzed cycloisomerizations of decatetraenes **12**.[a]

Entry	Substrate	*t* [h]	Products (yield)[b]		
1	 **12a**	3	 **27a** (92%)	 **13a** (6%)	
2	 **12b**	1	 **27b** (89%)	 **13b** (9%)	Z=CO_2Me
3	 **12c**	2.5	 **27c** (71%)	 **13c** (10%)	 **15c** (10%)
4	 **12d**	4.5	 **27d** (52%)	 **27d'**	 **13d**
			27d'+13d (47%)[c]		

[a] Reaction conditions: a solution of **12** in toluene (0.1 M) was heated at 80 °C in the presence of [{RhCl(CO)dppp}$_2$] (5 mol%) under N_2. [b] Yields of isolated products. [c] An inseparable mixture of **27d′** and **13d** in a ratio of 6:1 was obtained.

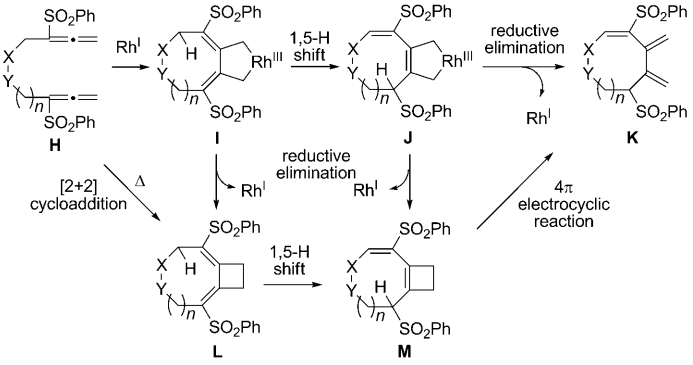
Ma et al. reported the Rh^I-catalyzed cycloisomerizations of the nonatetraene derivatives **28** (R = alkyl) resulting in the cycloheptenes **29** with *exo*-methylene groups,[10] whereas compound **28** (R = H) produced the steroidal skeleton **30** rather than **29** (Scheme 8).[9] Interestingly, the tendencies of



29 **28** **30**

Scheme 8. Rhodium(I)-catalyzed cycloisomerizations of nonatetraenes **28**.

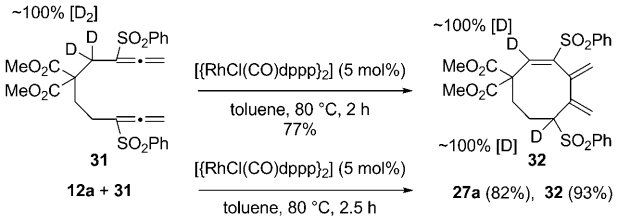
compounds **23** (Table 3) and compounds **12** (Table 4), with bis(terminal allene) functionality, in Rh^I-catalyzed cycloisomerizations were obviously distinct from that of **28** (R = H). The formation of compounds **24** and compounds **27** (compounds **K**, Scheme 9) from compounds **23** and compounds **12** (compounds **H**), respectively, can be tentatively interpreted on the basis of the assumption that the first oxidative insertion of the Rh^I catalyst into the two terminal double bonds of the bis(allene) groups leads to the rhodacycle intermediates **I**,[10,12b,32] which might be susceptible to thermal [1,5]-H shifts (Scheme 9). The resulting compounds



Scheme 9. A plausible mechanism for the formation of compounds **K** from compounds **H**.

J could then collapse to **K** in a reductive elimination process.[33,34]

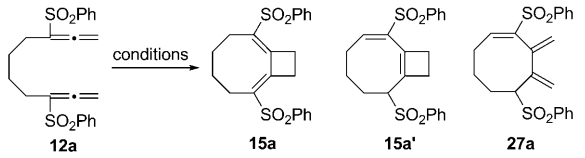
In order to clarify the plausible mechanism, the 4,4-dideuterated decatetraene **31** was prepared and treated in the presence of [{RhCl(CO)dppp}$_2$] (5 mol%) in toluene at 80 °C for 2 h to give **32** in 77% yield (Scheme 10). In addition, the following cross-over experiment was performed. A mixture of **12a** and **31** in toluene was treated in the presence of [{RhCl(CO)dppp}$_2$] to afford **27a** and **32** in 82% and 93% yields, respectively, and no cross-over product was obtained; accordingly, intermolecular hydrogen transfer mechanism was ruled out.



Scheme 10. Transformation of deuterated **31** into the cyclooctene **32**.

The following experiments were performed to investigate an alternative mechanism involving the intermediacy of cyclobutenes **L**,[21,22] as well as the possibility of a simpler thermal reaction pathway (**H**→**L**→**M**→**K**) in which the Rh^I catalyst would not participate. A solution of the undecatetraene **23a** in toluene in the absence of the Rh^I catalyst was heated at reflux for 20 h, but no reaction occurred and **23a** was fully recovered. When heated at reflux in xylene, compound **23a** gradually decomposed. Although compound **23e** was converted into the [2+2] cycloadduct **26e** in 52% yield on treatment in toluene at reflux for a prolonged time (36 h), no interconversion between the bicyclic compound **26e** and the monocyclic compound **24e** was observed in the presence of Rh^I catalyst in toluene at reflux. Furthermore, the decatetraene **12a** was also inactive when heated in toluene at 80 °C for 5 h in the absence of the Rh^I catalyst (Table 5, entry 1). These experiments therefore indicate not

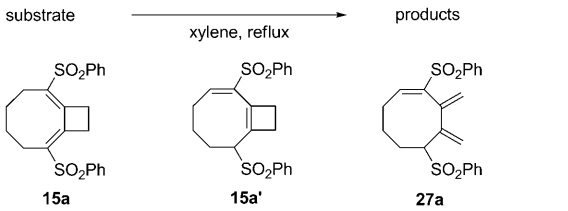
Table 5. Cycloaddition and cycloisomerization of the decatetraene **12a**.[a]



Entry	Solvent	T	t [h]	Results (yield)[b]
1	toluene	80 °C	5	no reaction
2	toluene	reflux	72	**15a** (37 %), **12a**+**15a′**+**27a** (43 %)[c,d]
3	xylene	reflux	24	**15a** (trace),[e] **15a′**+**27a** (70 %)[d,f]

[a] Reaction conditions: a solution of **12a** was heated in toluene or xylene in the absence of [{RhCl(CO)dppp}$_2$] under N_2. [b] Yields of products. [c] A mixture of **12a**, **15a′**, and **27a** in a ratio of 2:5:2 was obtained. [d] The ratio was determined by ^{1}H NMR. [e] Determined by TLC. [f] A mixture of **15a′** and **27a** in a ratio of 5:6 was obtained.

Table 6. Interconversion of **15a**, **15a′**, and **27a** in xylene at reflux.[a]



Entry	Substrate	t [h]	Yield [%][b]	Product ratio[c]
1	**15a**	12	93	**15a**/**15a′**/**27a** 2:5:5
2	**15a**	17	45	**15a′**/**27a** 1:2
3	**15a′**	12	94	**15a′**/**27a** 9:5
4	**15a′**	17	68	**15a′**/**27a** 4:5
5	**27a**	12	46	**15a′**/**27a** 1:2
6	**27a**	17	33	**15a′**/**27a** 2:5

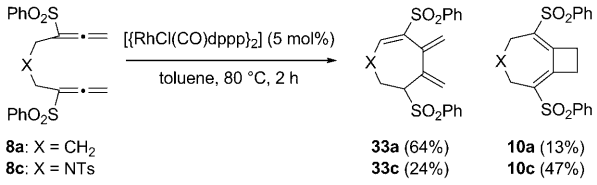
[a] Reaction conditions: a solution of **15a**, **15a′**, or **27a** in xylene was heated at reflux under N_2. [b] Yield of products. [c] The ratio was determined by ^{1}H NMR.

only that [{RhCl(CO)dppp}$_2$] is essential for the transformations of **23** and **12** into **24** and **27**, respectively, but also support the mechanism (**H**→**I**→**J**→**K**) depicted in Scheme 9 as a major pathway.[35]

Cycloaddition and/or cycloisomerization of **12a** did occur, however, after prolonged reaction times at higher reaction temperatures. The solution of **12a** in toluene was heated at reflux for 3 days to produce the [2+2] cycloaddition product **15a** in 37 % yield together with a mixture of **12a**, [1,5]-H shifted **15a′**, and **27a** (43 % yield) in a ratio of 2:5:2 (Table 5, entry 2). Compounds **15a′** and **27a** were major products (70 % yield, **15a′**/**27a** 5:6) after treatment at reflux in xylene for 1 day (Table 5, entry 3). The fact that compound **15a** was present only in trace amounts after treatment at a higher reaction temperature (Table 5, entry 3) suggests that **15a** must be an initial product of **12a**.

When **15a** was heated at reflux in xylene for 12 h, **15a**, **15a′**, and **27a** were obtained in a ratio of 2:5:5 (93 % yield, Table 6, entry 1). Use of a longer reaction time afforded **15a′** and **27a** in a ratio of 1:2 in low yield, probably because of instability of **27a** at higher reaction temperatures (Table 6, entry 2). At reflux in xylene, compounds **15a′** and **27a** independently provided mixtures of **15a′** and **27a**, but never produced **15a** (Table 6, entries 3–6). On the basis of these interconversion experiments, we can interpret the thermal transformation of **12a** into **15a**, **15a′**, and **27a** as the following consecutive three-step process: 1) thermal [2+2] cycloaddition of bis(allene) **12a** (**H**), producing the four-membered ring product **15a** (**L**), 2) [1,5]-H shift of an allylic proton of **15a** (**L**), and 3) thermal 4π electrocyclic ring-opening of the cyclobutene of **15a′** (**M**) to give **27a** (**K**)[36] [**15a′** (**M**) and **27a** (**K**) exist in equilibrium in xylene at reflux] (Scheme 9). This thermal cycloaddition and/or cycloisomerization of **12a** described in Table 5 cannot compete with the Rh^I-catalyzed cycloaddition and/or cycloisomerization of **12**, because the latter reaction proceeded easily at lower reaction temperatures.[37]

Finally we examined the formation of seven-membered-ring triene derivatives. The nonatetraene **8a** was treated in the presence of [{RhCl(CO)dppp}$_2$] (5 mol %) in toluene at 80 °C for 2 h to give **33a** in 64 % yield along with the bicyclo[5.2.0] derivative **10a** (13 % yield, Scheme 11). Similar treatment of the nitrogen congener **8c** gave **33c** in only 24 % yield, with the bicyclo[5.2.0] compound **10c** as the major product (47 % yield) of this cycloisomerization. These relatively low yields in the Rh^I-catalyzed transformations of nonatetraenes into seven-membered-ring trienes may reflect some limitations in the flexibilities of the rhodabicyclo[5.3.0] intermediates **I** leading to **J**, relative to those of the rhodabicyclo[6.3.0] and rhodabicyclo[7.3.0] derivatives shown in Scheme 9.



Scheme 11. Rhodium(I)-catalyzed cycloisomerizations of compounds **8**.

Conclusion

In summary, we have developed novel [{RhCl(CO)dppp}$_2$]-catalyzed intramolecular [2+2+1] cycloadditions of bis(phenylsulfonylallene) derivatives under mild conditions leading to the facile formation of the 2,7-bis(phenylsulfonyl)bicyclo[6.3.0]undecadien-10-one framework, in which the terminal double bonds of both allenyl moieties exclusively served as the two π-components. This method is superior to that previously reported, which took advantage of carbonylative [2+2+1] cycloadditions of allenynes possessing a suitable template functionality. The newly developed method was also shown to be applicable to the construction of 2,6-bis(phenylsulfonyl)bicyclo[5.3.0]decadien-9-one and 2,5-bis(phenylsulfonyl)bicyclo[4.3.0]nonadien-8-one skeletons in high yields. We also developed novel

[{RhCl(CO)dppp}$_2$]-catalyzed easy transformations of 3,9-bis(phenylsulfonyl)undeca-1,2,9,10-tetraene derivatives into the corresponding 3,4-dimethylene-2,5-bis(phenylsulfonyl)-cyclononene framework. The newly developed procedure proceeded under conditions with normal concentrations (0.05 or 0.1 M solution) and is applicable to the construction of one- and two-carbon shortened eight- and seven-membered monocyclic skeletons in reasonable yields. The plausible mechanism behind this transformation of bis(allene)s into the medium-sized monocyclic derivatives was investigated through several additional experiments. The additional scope and limitations of these methods, as well as their application to the synthesis of natural products, are currently under investigation.

Experimental Section

General methods: Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^{1}H NMR spectra were measured in $CDCl_3$. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards unless otherwise stated. ^{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 nitrogen unless otherwise stated. Silica gel (silica gel 60, 230–400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

General procedure for carbonylative [2+2+1] cycloadditions under CO: The rhodium(I) catalyst (5~10 mol%) was added to a solution of the bis(allene) (0.1 mmol) in toluene (1 mL). The reaction mixture was heated at 80 °C under CO until the complete disappearance of the starting material (monitored by TLC). Toluene was evaporated off, and the residual oil was chromatographed with hexane/AcOEt or CH_2Cl_2/AcOEt to afford the cyclized product. Chemical yields are summarized in Tables 1 and 2 and in Scheme 2 and Scheme 6. Characterization data for the products are given in the Supporting Information of ref. [14].

(*E*)-8,8-Bis(methoxycarbonyl)-3,4-dimethylene-2,5-bis(phenylsulfonyl)cyclononene (24a) and 5,5-bis(methoxycarbonyl)-2,8-bis(phenylsulfonyl)-bicyclo[7.3.0]dodeca-1(12),8-dien-11-one (25a): [{RhCl(CO)dppp}$_2$] (4.9 mg, 4.2×10^{-3} mmol) was added to a solution of **23a** (23.0 mg, 4.22×10^{-2} mmol) in xylene (1.0 mL). The reaction mixture was heated at reflux for 1 h under CO. Xylene was evaporated off, and the residual oil was chromatographed with CH_2Cl_2/AcOEt (20:1 to 8:1) to afford **24a** (4.0 mg, 17%) and **25a** (7.9 mg, 33%).

Compound 24a: White powder; m.p. 136–137.5 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): $\delta=7.79$–7.41 (m, 10H), 6.93 (dd, $J=13.9$, 4.0 Hz, 1H), 5.71 (s, 1H), 5.60 (s, 1H), 5.06 (s, 1H), 4.83 (s, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.41 (t, $J=13.9$ Hz, 1H), 3.11 (d, $J=9.8$ Hz, 1H), 2.69–2.56 (m, 3H), 1.71–1.52 ppm (m, 2H); ^{13}C NMR (126 MHz): $\delta=170.7$, 170.1, 145.4, 141.1, 139.3, 139.1, 138.4, 137.1, 133.8, 133.4, 129.6, 129.4, 128.8, 128.6, 122.1, 121.3, 68.0, 57.0, 53.2, 53.1, 32.6, 31.9, 26.4 ppm; IR: $\tilde{\nu}=1732$ cm^{-1}; LRMS (EI): *m/z* (%): 544 (39.2) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{27}H_{28}O_8S_2$: 544.1226, found: 544.1227; elemental analysis calcd (%) for $C_{27}H_{28}O_8S_2$: C 59.54, H 5.18; found: C 59.38, H 5.18.

Compound 25a: White powder; m.p. 210–212 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): $\delta=7.83$–7.78 (m, 4H), 7.70–7.67 (m, 2H), 7.60–7.57 (m, 4H), 7.24 (s, 1H), 4.49 (dd, $J=9.5$, 2.9 Hz, 1H), 3.72–3.67 (m, 4H), 3.49 (s, 3H), 3.10 (d, $J=21.5$ Hz, 1H), 3.02–2.98 (m, 2H), 2.51–2.39 (m, 3H), 2.14–2.09 (m, 1H), 2.02–1.96 (m, 1H), 1.66–1.58 ppm (m, 1H); ^{13}C NMR (67.8 MHz): $\delta=200.5$, 171.6, 170.9, 162.5, 145.4, 139.8, 139.7, 139.6, 137.3, 134.4, 134.1, 129.61, 129.59, 128.8, 127.7, 65.0, 56.9, 53.2, 52.5, 41.5, 34.8, 29.7, 27.0, 24.1 ppm; IR: $\tilde{\nu}=1728$ cm^{-1}; LRMS (EI): *m/z* (%): 572 (34.5) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{28}H_{28}O_9S_2$: 572.1175, found: 572.1170; elemental analysis calcd (%) for $C_{28}H_{28}O_9S_2$: C 58.73, H 4.93; found: C 58.36, H 4.87.

General procedure for cycloisomerization: [{RhCl(CO)dppp}$_2$] (5 or 10 mol%) was added to a solution of the bis(allene) (0.1 mmol) in toluene (1 mL). The reaction mixture was heated under N_2 at 80 °C or at reflux temperature until the complete disappearance of the starting material (monitored by TLC). Toluene was evaporated off, and the residual oil was chromatographed with hexane/AcOEt or CH_2Cl_2/AcOEt to afford the cyclized product. Chemical yields are summarized in Tables 3 and 4 and in Schemes 10 and 11.

(*E*)-3,4-Dimethylene-2,5-bis(phenylsulfonyl)cyclononene (24b): Compound **24b** was obtained as colorless crystals; m.p. 192–193 °C (AcOEt); ^{1}H NMR (500 MHz): $\delta=7.85$–7.40 (m, 10H), 7.09 (dd, $J=12.5$, 5.9 Hz, 1H), 5.69 (s, 1H), 5.47 (s, 1H), 4.91 (s, 1H), 4.63 (s, 1H), 3.26–3.23 (m, 1H), 2.76 (qd, $J=12.9$, 5.2 Hz, 1H), 2.64 (dd, $J=14.2$, 9.5 Hz, 1H), 2.17–2.11 (m, 1H), 1.98–1.92 (m, 1H), 1.84–1.76 (m, 1H), 1.65–1.55 (m, 2H), 1.33–1.25 ppm (m, 1H); ^{13}C NMR (126 MHz): $\delta=145.9$, 144.8, 140.0, 138.9, 138.8, 137.5, 133.6, 133.2, 129.6, 129.3, 128.7, 128.6, 121.3, 120.5, 68.7, 30.3, 27.4, 26.63, 26.57 ppm; LRMS (EI): *m/z* (%): 428 (0.3) $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{24}O_4S_2$: C 64.46, H 5.64; found: C 64.37, H 5.69.

(*E*)-5,6-Dimethylene-1-(2-nitrophenylsulfonyl)-4,7-bis(phenylsulfonyl)-2,3,4,5,6,9-hexahydro-1*H*-azonine (24c): Compound **24c** was a white powder; m.p. 94.5–96.5 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): $\delta=$ 8.00–7.99 (m, 1H), 7.84–7.82 (m, 2H), 7.76–7.58 (m, 9H), 7.51 (t, $J=$ 7.8 Hz, 2H), 7.00 (dd, $J=10.5$, 6.3 Hz, 1H), 5.64 (d, $J=1.2$ Hz, 1H), 5.59 (s, 1H), 5.19 (s, 1H), 4.97 (s, 1H), 4.13 (dd, $J=14.6$, 6.3 Hz, 1H), 3.96 (dd, $J=14.6$, 10.5 Hz, 1H), 3.62–3.56 (m, 2H), 3.31–3.26 (m, 1H), 2.53–2.47 (m, 1H), 2.04–1.96 ppm (m, 1H); ^{13}C NMR (67.8 MHz): $\delta=148.0$, 144.8, 142.2, 138.6, 137.6, 137.1, 135.4, 134.2, 134.1, 133.7, 131.9, 131.8, 131.2, 129.6, 129.4, 129.2, 128.9, 124.4, 122.8, 121.6, 65.6, 47.2, 45.7, 31.3 ppm; LRMS (FAB+): *m/z* (%): 615 (7.9) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{28}H_{27}N_2O_8S_3$: 615.0929; found: 615.0924.

(*E*)-5,6-Dimethylene-1-(4-methylphenylsulfonyl)-4,7-bis(phenylsulfonyl)-2,3,4,5,6,9-hexahydro-1*H*-azonine (24d): Compound **24d** was a white powder; m.p. 97.5–98.5 °C (hexane/Et_2O); ^{1}H NMR (500 MHz): $\delta=7.84$–7.83 (m, 2H), 7.72–7.50 (m, 10H), 7.31 (d, $J=8.1$ Hz, 2H), 6.98 (dd, $J=$ 9.0, 6.1 Hz, 1H), 5.53 (d, $J=1.2$ Hz, 1H), 5.41 (s, 1H), 5.25 (s, 1H), 5.06 (s, 1H), 3.99 (dd, $J=15.1$, 6.1 Hz, 1H), 3.70 (dd, $J=11.5$, 2.7 Hz, 1H), 3.58 (dd, $J=15.1$, 9.0 Hz, 1H), 3.32–3.23 (m, 2H), 2.44 (s, 3H), 2.40–2.34 (m, 1H), 1.99–1.92 ppm (m, 1H); ^{13}C NMR (126 MHz): $\delta=144.3$, 144.1, 141.6, 138.8, 137.9, 137.4, 136.0, 135.0, 133.9, 133.7, 130.0, 129.5, 129.3, 129.2, 128.9, 127.2, 122.4, 121.2, 65.7, 48.1, 47.0, 30.7, 21.5 ppm; LRMS (FAB+): *m/z* (%): 584 (30.0) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{29}H_{30}NO_6S_3$: 584.1235; found: 584.1243.

(1*E*,8*E*)-5-(4-Methylphenylsulfonyl)-2,8-bis(phenylsulfonyl)-5-azabicyclo-[7.2.0]undeca-1,8-diene (26d): Compound **26d** was obtained as colorless crystals; m.p. 255–256 °C (AcOEt); ^{1}H NMR (500 MHz): $\delta=7.95$–7.94 (m, 4H), 7.68–7.65 (m, 2H), 7.60–7.57 (m, 4H), 7.41 (d, $J=8.2$ Hz, 2H), 7.24 (d, $J=8.2$ Hz, 2H), 3.20 (t, $J=6.0$ Hz, 4H), 3.16 (s, 4H), 2.91 (t, $J=$ 6.0 Hz, 4H), 2.40 ppm (s, 3H); ^{13}C NMR (67.8 MHz): $\delta=154.2$, 143.4, 140.2, 136.5, 133.6, 132.1, 129.7, 129.3, 128.1, 126.8, 49.8, 31.0, 29.5, 21.5 ppm; LRMS (FAB+): *m/z* (%): 584 (3.0) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{29}H_{30}NO_6S_3$: 584.1235; found: 584.1239.

(*E*)-1-(Methoxycarbonyl)-5,6-dimethylene-4,7-bis(phenylsulfonyl)-2,3,4,5,6,9-hexahydro-1*H*-azonine (24e): Compound **24e** was a white powder; m.p. 87–89 °C (hexane/AcOEt); ^{1}H NMR (270 MHz, [D$_6$]DMSO, 120 °C): $\delta=7.80$–7.71 (m, 6H), 7.66–7.59 (m, 4H), 6.95 (t, $J=5.9$ Hz, 1H), 5.40 (s, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 4.94 (s, 1H), 3.92–3.77 (m, 3H), 3.52 (s, 3H), 3.39 (ddd, $J=14.8$, 6.4, 4.6 Hz, 1H), 3.25 (ddd, $J=14.8$, 7.3, 4.6 Hz, 1H), 2.28–2.09 ppm (m, 2H); ^{13}C NMR (126 Hz, [D$_6$]DMSO, 120 °C): $\delta=155.0$, 142.9, 139.9, 138.1, 137.7, 137.5, 137.4, 133.3, 133.2, 128.8, 128.5, 128.2, 127.9, 120.8, 119.7, 66.9, 51.8, 47.1, 27.4, 13.4 ppm; IR: $\tilde{\nu}=1701$ cm^{-1}; LRMS (FAB+): *m/z* (%): 488 (56.1) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{24}H_{26}NO_6S_2$: 488.1202; found: 488.1209.

(1*E*,8*E*)-5-(Methoxycarbonyl)-2,8-bis(phenylsulfonyl)-5-azabicyclo[7.2.0]-undeca-1,8-diene (26e): Compound **26e** was a white powder; m.p. 85–

87 °C (hexane/AcOEt); ^{1}H NMR (270 MHz): δ = 7.96 (d, J = 6.7 Hz, 2H), 7.87 (d, J = 7.0 Hz, 2H), 7.69–7.55 (m, 6H), 3.69 (s, 3H), 3.69–3.62 (m, 2H), 3.35–3.32 (m, 2H), 3.23–3.16 (m, 4H), 2.83–2.81 ppm (m, 4H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 150 °C): δ = 155.4, 150.9, 140.3, 133.1, 132.8, 128.6, 126.6, 51.5, 46.1, 29.8, 29.0 ppm; IR: $\tilde{\nu}$ = 1695 cm^{-1}; LRMS (FAB+): *m/z* (%): 488 (32.0) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{24}H_{26}NO_6S_2$: 488.1202; found: 488.1208.

(*E*)-7,7,9,9-Tetrakis(methoxycarbonyl)-3,4-dimethylene-2,5-bis(phenylsulfonyl)cyclononene (24f): Compound **24f** was obtained as colorless needles; m.p. 221–222.5 °C (AcOEt); ^{1}H NMR (270 MHz): δ = 8.10–8.07 (m, 2H), 7.87–7.84 (m, 2H), 7.69–7.51 (m, 7H), 5.97 (s, 1H), 5.85 (s, 1H), 5.44 (s, 1H), 4.55 (d, J = 12.2 Hz, 1H), 3.99 (br s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.52 (s, 3H), 3.47 (s, 3H), 3.460 (s, 1H), 3.456 (s, 1H), 2.74 (dd, J = 13.5, 1.6 Hz, 1H), 2.15 ppm (dd, J = 13.5, 12.2 Hz, 1H); ^{13}C NMR (126 MHz): δ = 171.5, 169.8, 169.3, 167.3, 142.9, 139.9, 139.4, 137.9, 137.8, 136.8, 134.0, 133.5, 129.8, 129.7, 129.0, 128.7, 121.4, 120.2, 61.8, 56.2, 54.4, 54.0, 53.6, 53.4, 53.0, 38.8, 34.8 ppm; IR: $\tilde{\nu}$ = 1744 cm^{-1}; LRMS (EI): *m/z* (%): 660 (0.1) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{31}H_{32}O_{12}S_2$: 660.1336; found: 660.1336.

(1*E*,8*E*)-4,4,6,6-Tetrakis(methoxycarbonyl)-2,8-bis(phenylsulfonyl)-bicyclo[7.2.0]undeca-1,8-diene (26f): Compound **26f** was a white powder; m.p. 75–76 °C (*i*Pr$_2$O/hexane); ^{1}H NMR (500 MHz): δ = 7.83–7.81 (m, 4H), 7.65–7.62 (m, 2H), 7.56–7.53 (m, 4H), 3.77 (s, 6H), 3.68 (s, 6H), 3.51 (d, J = 17.1 Hz, 2H), 3.10 (d, J = 17.1 Hz, 2H), 3.023 (s, 1H), 3.020 (s, 1H), 2.96–2.93 (m, 2H), 2.76–2.73 ppm (m, 2H); ^{13}C NMR (67.8 MHz): δ = 170.7, 169.8, 154.4, 140.6, 134.8, 133.7, 129.3, 127.8, 57.2, 53.4, 53.0, 31.7, 31.2, 30.5 ppm; IR: $\tilde{\nu}$ = 1740 cm^{-1}; LRMS (EI): *m/z* (%): 660 (0.2) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{31}H_{32}O_{12}S_2$: 660.1336; found: 660.1337.

(*E*)-3,4-Dimethylene-2,5-bis(phenylsulfonyl)cyclooctene (27a): Compound **27a** was a white solid; m.p. 133–134 °C (AcOEt); ^{1}H NMR (500 MHz): δ = 7.78 (d, J = 7.6 Hz, 2H), 7.73 (t, J = 7.3 Hz, 1H), 7.65–7.62 (m, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.35–7.23 (m, 5H), 5.63 (s, 2H), 5.46 (s, 1H), 4.80 (s, 1H), 3.23 (d, J = 12.0 Hz, 1H), 2.61–2.54 (m, 2H), 2.42–2.37 (m, 1H), 2.20–2.17 (m, 1H), 2.00–1.92 (m, 1H), 1.56–1.52 ppm (m, 1H); ^{13}C NMR (67.8 MHz): δ = 145.7, 144.5, 139.4, 138.3, 137.6, 137.1, 133.3, 133.1, 129.3, 129.0, 128.6, 128.1, 120.8, 120.7, 66.0, 29.5, 25.4, 24.0 ppm; LRMS (EI): *m/z* (%): 414 (5.9) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{22}O_4S_2$: C 63.74, H 5.35; found: C 63.42, H 5.38.

(*E*)-3,3-Bis(methoxycarbonyl)-7,8-dimethylene-1,6-bis(phenylsulfonyl)cyclooctene (27b): Compound **27b** was a colorless solid; ^{1}H NMR (400 MHz): δ = 7.81–7.79 (m, 2H), 7.67–7.62 (m, 4H), 7.60–7.52 (m, 4H), 7.45 (s, 1H), 5.71 (s, 1H), 5.55 (s, 1H), 5.51 (s, 1H), 5.19 (s, 1H), 3.72 (s, 3H), 3.59 (dd, J = 12.2, 3.7 Hz, 1H), 3.45 (s, 3H), 2.84–2.77 (m, 1H), 2.21–2.05 (m, 2H), 1.73–1.64 ppm (m, 1H); ^{13}C NMR (126 MHz): δ = 169.2, 167.6, 142.0, 138.12, 138.10, 138.0, 137.4, 136.3, 133.9, 133.5, 129.4, 129.0, 128.7, 128.6, 122.3, 117.9, 62.9, 60.0, 53.5, 53.2, 26.9, 26.5 ppm; IR: $\tilde{\nu}$ = 1736 cm^{-1}; LRMS (EI): *m/z* (%): 530 (0.7) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{26}H_{26}O_8S_2$: 530.1069; found: 530.1067.

(*E*)-5,6-Dimethylene-1-(4-methylphenylsulfonyl)-4,7-bis(phenylsulfonyl)-1,2,3,4,5,6-hexahydroazocine (27c): Compound **27c** was a white powder; m.p. 184–185 °C (acetone); ^{1}H NMR (270 MHz): δ = 8.29 (s, 1H), 7.78–7.46 (m, 12H), 7.36 (d, J = 8.4 Hz, 2H), 5.58 (s, 1H), 5.40 (s, 1H), 5.31 (s, 1H), 5.12 (s, 1H), 4.05–3.94 (m, 1H), 3.74–3.62 (m, 2H), 2.46 (s, 3H), 2.16–2.09 ppm (m, 2H); ^{13}C NMR (67.8 MHz): δ = 145.5, 139.6, 138.3, 137.9, 136.9, 136.6, 134.5, 133.9, 133.2, 130.4, 129.2, 129.1, 128.3, 128.1, 127.3, 124.0, 118.2, 117.9, 63.6, 42.4, 30.9, 21.7 ppm; LRMS (FAB+): *m/z* (%): 570 (34.7) $[M+H]^+$; HRMS (FAB+): *m/z*: calcd for $C_{28}H_{28}NO_6S_3$: 570.1079; found: 570.1077.

(1*E*,7*E*)-4-(4-Methylphenylsulfonyl)-2,7-bis(phenylsulfonyl)-4-azabicyclo-[6.2.0]deca-1,7-diene (15c): Compound **15c** was obtained as colorless plates; m.p. 229–230 °C (AcOEt); ^{1}H NMR (500 MHz): δ = 7.96 (d, J = 7.3 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H), 7.78–7.75 (m, 1H), 7.69–7.64 (m, 3H), 7.59–7.56 (m, 2H), 7.19–7.14 (m, 4H), 4.14 (s, 2H), 3.43 (t, J = 5.9 Hz, 2H), 3.00 (t, J = 8.3 Hz, 2H), 2.77 (t, J = 8.3 Hz, 2H), 2.61 (t, J = 5.9 Hz, 2H), 2.40 ppm (s, 3H); ^{13}C NMR (126 MHz): δ = 151.8, 151.5, 143.5, 139.9, 139.2, 136.6, 134.2, 133.9, 132.2, 131.8, 129.7, 129.5, 129.4, 128.1, 128.0, 126.8, 49.3, 46.0, 31.1, 30.8, 27.9, 21.5 ppm; LRMS (FAB+): *m/z* (%): 570 (27.6) $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{27}NO_6S_3$: C 59.03, H 4.78, N 2.46; found: C 58.95, H 4.73, N 2.25.

(*E*)-5,6-Dimethylene-4,7-bis(phenylsulfonyl)-3,4,5,6-tetrahydro-2*H*-oxocine (27d): Compound **27d** was a white solid; ^{1}H NMR (500 MHz): δ = 7.76 (d, J = 7.8 Hz, 2H), 7.70 (s, 1H), 7.66–7.60 (m, 4H), 7.53–7.48 (m, 4H), 5.48 (s, 1H), 5.47 (s, 1H), 5.39 (s, 1H), 5.32 (s, 1H), 4.83–4.78 (m, 1H), 4.13–4.09 (m, 1H), 3.75 (dd, J = 10.5, 4.2 Hz, 1H), 2.42–2.28 ppm (m, 2H); ^{13}C NMR (126 MHz): δ = 155.6, 140.1, 139.3, 137.9, 136.5, 133.7, 133.1, 129.14, 129.11, 128.6, 128.0, 122.7, 119.9, 118.3, 66.4, 63.6, 31.2 ppm; LRMS (EI): *m/z* (%): 416 (0.9) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{21}H_{20}O_5S_2$: 416.0752; found: 416.0753.

(*E*)-4,5-Dimethylene-3,6-bis(phenylsulfonyl)-3,4,5,8-tetrahydro-2*H*-oxocine (27d′): Compound **27d′** was a white solid; ^{1}H NMR (500 MHz): δ = 7.80–7.79 (m, 2H), 7.68–7.53 (m, 6H), 7.46–7.43 (m, 2H), 7.15 (t, J = 5.0 Hz, 1H), 5.37 (s, 1H), 5.33 (s, 1H), 5.10 (s, 1H), 5.09 (s, 1H), 4.51 (dd, J = 16.6, 5.1 Hz, 1H), 4.27 (dd, J = 11.7, 6.8 Hz, 1H), 4.23 (dd, J = 16.6, 5.1 Hz, 1H), 4.05 (dd, J = 11.7, 3.2 Hz, 1H), 3.69 ppm (dd, J = 6.8, 3.2 Hz, 1H); ^{13}C NMR (126 MHz): δ = 141.4, 140.0, 138.4, 138.2, 138.1, 137.8, 133.7, 133.6, 129.1, 129.0, 128.9, 128.8, 122.3, 122.1, 69.6, 68.1, 67.3 ppm; LRMS (EI): *m/z* (%): 416 (0.5) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{21}H_{20}O_5S_2$: 416.0752; found: 416.0750.

3,4-Dimethylene-2,5-bis(phenylsulfonyl)cycloheptene (33a): Compound **33a** was obtained as colorless needles; m.p. 170–172 °C (AcOEt); ^{1}H NMR (500 MHz): δ = 7.78–7.74 (m, 4H), 7.64–7.61 (m, 1H), 7.58–7.56 (m, 1H), 7.53–7.46 (m, 4H), 7.17–7.15 (m, 1H), 5.93 (s, 1H), 5.05 (s, 1H), 4.72 (s, 1H), 4.23 (s, 1H), 3.77 (dd, J = 11.7, 4.2 Hz, 1H), 2.87–2.81 (m, 1H), 2.42–2.23 ppm (m, 3H); ^{13}C NMR (126 MHz): δ = 142.1, 140.0, 139.9, 139.2, 137.0, 136.3, 133.9, 133.1, 129.4, 129.0, 128.7, 128.5, 123.8, 122.0, 69.6, 28.1, 23.2 ppm; LRMS (EI): *m/z* (%): 400 (0.2) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{21}H_{20}O_4S_2$: 400.0803; found: 400.0799.

2,6-Bis(phenylsulfonyl)bicyclo[5.2.0]nona-1,6-diene (10a): Compound **10a** was obtained as colorless needles; m.p. 185–187 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): δ = 7.86–7.84 (m, 4H), 7.65–7.63 (m, 2H), 7.57–7.54 (m, 4H), 3.25 (s, 4H), 2.48 (t, J = 5.4 Hz, 4H), 1.80–1.76 ppm (m, 2H); ^{13}C NMR (67.8 MHz): δ = 148.9, 140.0, 138.4, 133.7, 129.3, 127.6, 30.5, 30.4, 22.7 ppm; LRMS (EI): *m/z* (%): 400 (4.6) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{20}O_4S_2$: C 62.98, H 5.03; found: C 63.12, H 5.10.

4,5-Dimethylene-1-(4-methylphenylsulfonyl)-3,6-bis(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-azepine (33c): Compound **33c** was a white powder; 158–162 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): δ = 8.11 (s, 1H), 7.77–7.74 (m, 4H), 7.71–7.66 (m, 3H), 7.56–7.53 (m, 3H), 7.47–7.44 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 5.91 (s, 1H), 5.00 (s, 1H), 4.54 (s, 1H), 4.21 (s, 1H), 4.21–4.17 (m, 2H), 3.78 (dd, J = 14.6, 13.0 Hz, 1H), 2.49 ppm (s, 3H); ^{13}C NMR (67.8 MHz): δ = 145.9, 140.1, 139.3, 137.2, 136.2, 134.7, 134.4, 133.7, 133.0, 130.6, 129.4, 129.2, 128.7, 128.1, 127.4, 123.4, 123.1, 119.5, 69.2, 45.1, 21.7 ppm; LRMS (EI): *m/z* (%): 555 (0.1) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{27}H_{25}NO_6S_3$: 555.0844; found: 555.0848.

Crossover experiment: [{RhCl(CO)dppp}$_2$] (3.3 mg, 3.3×10^{-3} mmol) was added at room temperature to a solution of bis(allene) **12a** (13.6 mg, 3.28×10^{-2} mmol) and bis(allene) **31** (17.4 mg, 3.28×10^{-2} mmol) in toluene (1.2 mL). After stirring for 2.5 h at 80 °C, the reaction mixture was concentrated to dryness. The residue was chromatographed with CHCl$_3$/AcOEt (40:1) to afford **27a** (11.1 mg, 82%) as a white solid and **32** (16.1 mg, 93%) as a white solid.

(*E*)-[2,6-^{2}H$_2$]-3,3-Bis(methoxycarbonyl)-7,8-dimethylene-1,6-bis(phenylsulfonyl)cyclooctene (32): Compound **32** was a white solid; ^{1}H NMR (400 MHz): δ = 7.81–7.80 (m, 2H), 7.70–7.62 (m, 4H), 7.60–7.52 (m, 4H), 5.70 (s, 1H), 5.55 (s, 1H), 5.52 (s, 1H), 5.19 (s, 1H), 3.72 (s, 3H), 3.45 (s, 3H), 2.84–2.76 (m, 1H), 2.21–2.15 (m, 1H), 2.10–2.05 (m, 1H), 1.72–1.65 ppm (m, 1H); IR: $\tilde{\nu}$ = 1736 cm^{-1}; LRMS (EI): *m/z* (%): 532 (1.6) $[M]^+$; HRMS (EI): *m/z*: calcd for $C_{26}H_{24}D_2O_8S_2$: 532.1195; found: 532.1193.

General procedure for thermal reaction: A solution of bis(allene) in toluene or xylene was heated at reflux under N_2 for the given period of time (see Tables 5 and 6). The solvent was evaporated off, and the residual oil was chromatographed with hexane/AcOEt or CH_2Cl_2/AcOEt to afford the cyclized product. Chemical yields are summarized in Tables 5 and 6.

(1*E*,7*E*)-2,7-Bis(phenylsulfonyl)bicyclo[6.2.0]deca-1,7-diene (15a): Compound **15a** was obtained as colorless needles; m.p. 164.5–165.5 °C (AcOEt); ^{1}H NMR (500 MHz): δ = 7.86 (d, J = 7.3 Hz, 4H), 7.64 (d, J = 7.3 Hz, 2H), 7.57–7.54 (m, 4H), 3.18 (s, 4H), 2.44 (brs, 4H), 1.65–1.64 ppm (m, 4H); ^{13}C NMR (67.8 MHz): δ = 150.4, 140.0, 135.4, 133.7, 129.3, 127.7, 31.3, 26.9, 24.4 ppm; LRMS (EI): *m/z* (%): 414 (3.8) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{22}O_4S_2$: C 63.74, H 5.35; found: C 63.37, H 5.37.

(*E*)-2,7-Bis(phenylsulfonyl)bicyclo[6.2.0]deca-1(8),2-diene (15a′): Compound **15a′** was obtained as colorless needles; m.p. 151.5–152.5 °C (hexane/AcOEt); ^{1}H NMR (500 MHz): δ = 7.77 (d, J = 7.3 Hz, 2H), 7.73 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.51–7.46 (m, 4H), 7.00 (t, J = 8.3 Hz, 1H), 3.88 (d, J = 8.8 Hz, 1H), 2.72–2.69 (m, 1H), 2.54–2.33 (m, 5H), 2.07–2.03 (m, 1H), 1.94–1.86 (m, 1H), 1.78–1.61 ppm (m, 2H); ^{13}C NMR (126 Hz): δ = 141.5, 141.4, 141.1, 140.5, 137.7, 136.4, 133.8, 133.3, 129.14, 129.13, 128.5, 127.5, 67.7, 31.3, 30.1, 26.7, 24.9, 23.0 ppm; LRMS (EI): *m/z* (%): 414 (6.3) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{22}O_4S_2$: C 63.74, H 5.35; found: C 63.67, H 5.38.

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