Synthesis of Spiro[2.6]nonadienones and Spiro[3.6]decadienones by the Reaction of Cyclopropyl- and Cyclobutylmagnesium Carbenoids with Lithium Phenolates and Naphtholates

Tsuyoshi Satoh,* Tsutomu Kimura, Yuki Sasaki, Shinobu Nagamoto

Graduate School of Chemical Sciences and Technology, Tokyo University of Science, Ichigaya-funagawara-machi 12, Shinjuku-ku, Tokyo 162-0826, Japan
Fax +81(3)52614631; E-mail: tsatoh@rs.kagu.tus.ac.jp

Received: 08.03.2012; Accepted after revision: 12.04.2012

Abstract: Treatment of 1-chlorocyclopropyl *p*-tolyl sulfoxides and 1-chlorocyclobutyl *p*-tolyl sulfoxides with a Grignard reagent at low temperature afforded cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids, respectively, via a sulfoxide–magnesium exchange reaction. The reaction of these magnesium carbenoids with lithium phenolates afforded spiro[2.6]nona-6,8-dien-5-ones and spiro[3.6]deca-7,9-dien-6-ones, respectively; however, the yields were rather low. Reaction of the cyclopropylmagnesium carbenoids with lithium 1-naphtholates gave spiro[2.6]nona-5,7-dien-4-ones in moderate to good yields; however, reaction of the cyclobutylmagnesium carbenoids with lithium 1-naphtholates did not give the desired products. Reaction of the cyclopropyl- and cyclobutylmagnesium carbenoids with lithium 2-naphtholates gave spiro[2.6]nona-5,7-dien-4-ones and spiro[3.6]deca-7,9-dien-6-ones, respectively, in moderate to good yields. These unprecedented reactions provide a procedure for the synthesis of spiro[2.6]nona-5,7-dien-4-ones and spiro[3.6]deca-7,9-dien-6-ones from 1-naphthols and 2-naphthols with a one-carbon ring expansion of the phenol ring.

Key words: magnesium carbenoids, lithium phenolates, lithium naphtholates, ring expansion, spirocyclic compounds, dienones

Carbenes and carbenoids are undoubtedly one of the most important sets of highly reactive carbon species and have long been studied for their chemistry, synthesis, and synthetic uses in the territory of organic and synthetic organic chemistry.[1] Carbenes and carbenoids show a variety of reactions, such as addition into a carbon–carbon double bond to give cyclopropanes, dimerization to give olefins, ylide formation, rearrangement, carbon–hydrogen insertion, carbon–carbon insertion, and so on.

Small-ring carbenes and carbenoids, cyclopropylidenes and cyclobutylidenes, are highly reactive carbon species and have been recognized as being too reactive to control. Recently, we have investigated the chemistry of more stable small-ring carbenoid species, cyclopropylmagnesium carbenoids[2] and cyclobutylmagnesium carbenoids,[3] and many new reactions have been described.[2,3]

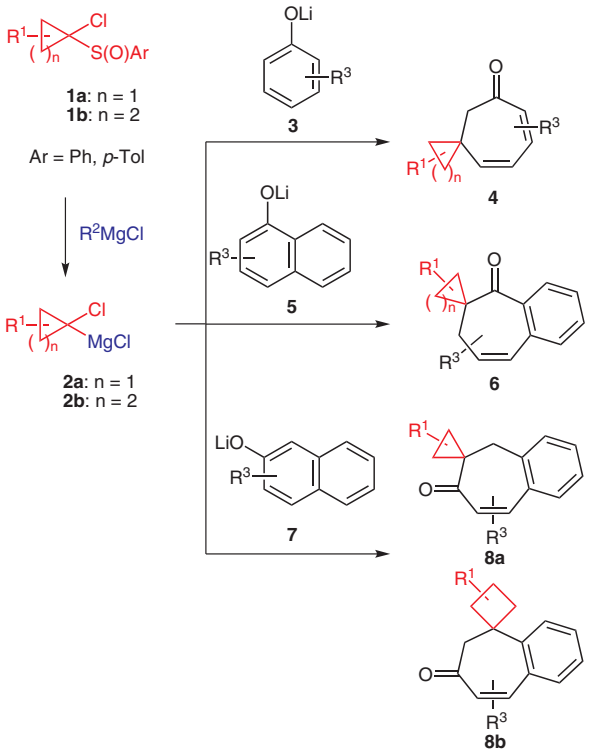
In 2008, we reported the first example for the direct cyclopropylation of arylamines at the 2-position by the reaction of cyclopropylmagnesium carbenoids with *N*-lithio arylamines.[2d,i] In continuation of our efforts to develop new synthetic methods with small-ring magnesium carbenoids, we found that the reaction of cyclopropylmagnesium carbenoids with lithium phenolates and naphtholates resulted in the formation of spiro[2.6]nonadienones in variable yields.[4]

In this paper, we report in detail the reactions of small-ring magnesium carbenoids, cyclopropylmagnesium carbenoids **2a** and cyclobutylmagnesium carbenoids **2b**, which are derived from aryl 1-chlorocyclopropyl sulfoxides **1a** and 1-chlorocyclobutyl *p*-tolyl sulfoxides **1b**, respectively, with a Grignard reagent via a sulfoxide–magnesium exchange reaction,[5] with lithium phenolates **3**, lithium 1-naphtholates **5**, and lithium 2-naphtholates **7** (Scheme 1). Thus, the reaction of magnesium carbenoids **2a** and **2b** with lithium phenolates **3** afforded spiro[2.6]nona-6,8-dien-5-ones **4** (n = 1) and spiro[3.6]deca-7,9-dien-6-ones **4** (n = 2), respectively, in rather low yields. The reaction of magnesium carbenoids **2a** with lithium 1-naphtholates **5** gave spiro[2.6]nona-5,7-dien-4-ones **6** (n = 1), in moderate to good yields; however, the reaction of **2b** with lithium 1-naphtholates **5** did not give the expected products. The reaction of magnesium carbenoids **2a** and **2b** with lithium 2-naphtholates **7** gave spiro[2.6]nona-5,7-dien-4-ones **8a** and spiro[3.6]deca-7,9-dien-6-ones **8b**, respectively, in moderate to good yields. The mechanism of these reactions is also discussed.

As noted above, we reported the first example for the direct cyclopropylation of arylamines at the 2-position by the reaction of cyclopropylmagnesium carbenoids with *N*-lithio arylamines.[2d,i] As an extension of this chemistry, it was expected that the reaction of cyclopropylmagnesium carbenoids with lithium phenolate would result in the formation of 2-cyclopropylphenols in a similar manner. At first, 1-chlorocyclopropyl phenyl sulfoxide (**1aa**)[2i] was treated with isopropylmagnesium chloride (2.5 equiv) in tetrahydrofuran at –78 °C, followed by 5 equivalents of lithium phenolate (Scheme 2).[6,7] This reaction gave a rather complex mixture; however, we obtained the expected 2-cyclopropylphenol (**9**) as an isolable product in 21% yield.

Next, cyclopropylmagnesium carbenoid **2ab** bearing *gem*-methyl groups, derived from **1ab**[2i] with isopropylmagnesium chloride, was reacted with 3 equivalents of lithium phenolate at –78 to –20 °C. This reaction again gave a rather complex mixture; however, we obtained an

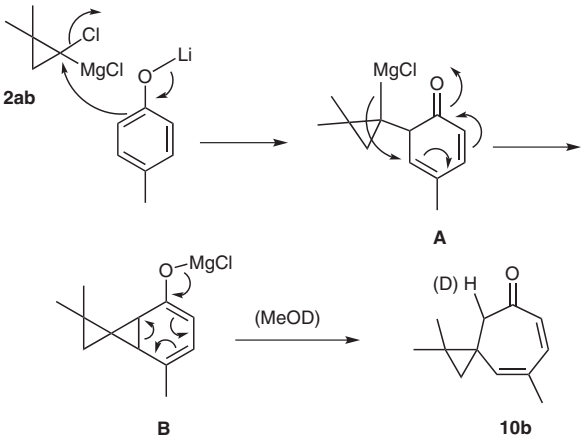
SYNTHESIS 2012, 44, 2091–2101
Advanced online publication: 14.05.2012
DOI: 10.1055/s-0031-1291011; Art ID: SS-2012-F0243-OP



Scheme 1 General scheme for this work

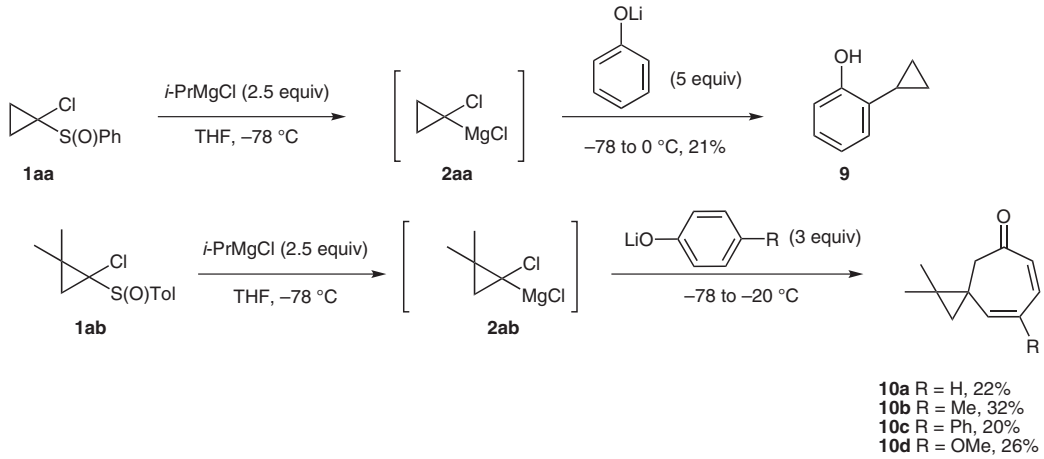
unanticipated product in low yield, without the expected 2-cyclopropylated phenol. The product showed $C_{11}H_{14}O$ as a molecular formula, and the IR spectrum of the product suggested the presence of a conjugated carbonyl group (1659 cm^{-1}), while the ^1H NMR spectrum indicated four olefinic protons. From this evidence, the structure of the product was determined to be one-carbon ring-expanded 1,1-dimethylspiro[2.6]nona-6,8-dien-5-one (**10a**). As we recognized that this is an unprecedented reaction, an investigation for obtaining better yields was carried out; however, all efforts were fruitless. The reactions of **2ab** with lithium 4-methylphenolate, lithium 4-phenylphenolate, and lithium 4-methoxyphenolate were carried out as shown in Scheme 2. The 1,1-dimethylspiro[2.6]nona-6,8-dien-5-ones **10b**–**d** were obtained in up to 32% yield.

A plausible mechanism for this reaction is proposed as follows (Scheme 3). Thus, the substitution reaction of cyclopropylmagnesium carbenoid **2ab** with lithium 4-methylphenolate would take place at the 2-position of the phenolate to give cyclopropylmagnesium chloride intermediate **A**. Conjugate addition of the carbanion to the straight dienone moiety affords highly strained spiro[2.2]pentane alkoxide **B**. The negative charge on the oxygen atom would move to the carbon next to the carbonyl group with cleavage of the highly strained carbon–carbon bond to afford the product **10b**. When this reaction was quenched with methanol-*d* (MeOD), indeed, the hydrogen on the carbon at the 4-position of **10b** was replaced by deuterium.



Scheme 3 A plausible mechanism for the reaction of cyclopropylmagnesium carbenoid **2ab** with lithium 4-methylphenolate giving spiro[2.6]nona-6,8-dien-5-one **10b**

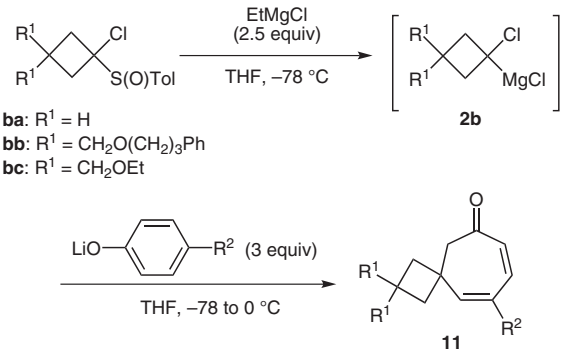
Recently, we have been investigating the chemistry and synthetic uses of cyclobutylmagnesium carbenoids.[3] As a development of the above-described reaction, we carried out the reaction of lithium phenolates with cyclobutylmagnesium carbenoids **2b**, and the results are summarized in Table 1. Thus, 1-chlorocyclobutyl *p*-tolyl sulfoxide (**1ba**)[3c] was treated with ethylmagnesium chloride in the presence of 3 equivalents of lithium phenolate in tetrahy-



Scheme 2 Reaction of cyclopropylmagnesium carbenoids **2aa** and **2ab** with lithium phenolates

drofuran at –78 °C, and the mixture was allowed to slowly warm to 0 °C (entry 1). This reaction gave a rather complex mixture of products from which spiro[3.6]deca-7,9-dien-6-one (**11a**) was obtained as a major product in 30% yield. The expected 2-cyclobutylphenol was not observed at all. The structure of **11a** was proved to be as shown in Table 1 from spectroscopic data. By comparison of the structure of **11a** with that of **10a**, it is expected that the reactions of lithium phenolate with both cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids are governed by the same mechanism.

Table 1 Reaction of Cyclobutylmagnesium Carbenoids **2b** with Lithium Phenolates

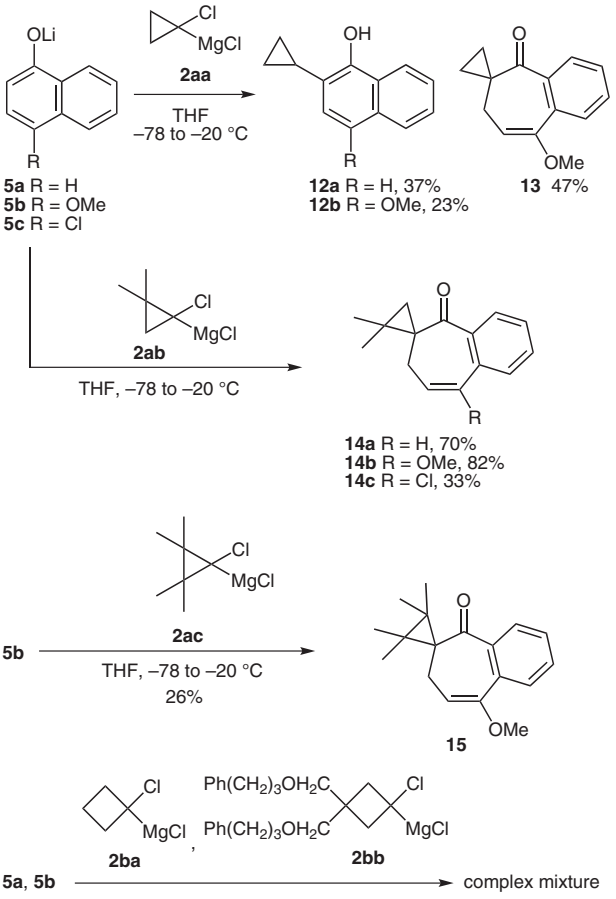


Entry	Sulfoxide	**2b**	R^1	R^2	Yield (%) of **11**
1	**1ba**	**2ba**	H	H	**11a**: 30
2	**1ba**	**2ba**	H	Me	**11b**: 33
3	**1ba**	**2ba**	H	Ph	**11c**: 32
4	**1ba**	**2ba**	H	OMe	**11d**: 37
5	**1bb**	**2bb**	$CH_2O(CH_2)_3Ph$	Ph	**11e**: 24
6	**1bc**	**2bc**	CH_2OEt	Ph	**11f**: 16
7	**1bb**	**2bb**	$CH_2O(CH_2)_3Ph$	OMe	**11g**: 35
8	**1bc**	**2bc**	CH_2OEt	OMe	**11h**: 22

The reaction of magnesium carbenoid **2ba** with lithium 4-methylphenolate, lithium 4-phenylphenolate, and lithium 4-methoxyphenolate gave the corresponding spiro[3.6]deca-7,9-dien-6-ones **11b–d** in 32 to 37% yield (Table 1, entries 2–4). The reactions of cyclobutylmagnesium carbenoids **2bb** and **2bc** bearing substituents at the 3-position with lithium 4-phenylphenolate and lithium 4-methoxyphenolate gave the expected spiro[3.6]deca-7,9-dien-6-ones **11e** to **11h** in somewhat lower yields (Table 1, entries 5–8).

As described above, we found that the reaction of cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids with lithium phenolates gave the unprecedented spiro[2.6]nona-6,8-dien-5-ones **10** and spiro[3.6]deca-7,9-dien-6-ones **11**, respectively; however, the yields proved to be low and they are not promising from the standpoint of synthetic organic chemistry.

Next, we investigated the reaction of cyclopropylmagnesium carbenoids **2a** and cyclobutylmagnesium carbenoids **2b** with lithium 1-naphtholates, and the results are summarized in Scheme 4. Thus, the reaction of cyclopropylmagnesium carbenoid **2aa** with lithium 1-naphtholate (**5a**) gave the anticipated 2-cyclopropyl-1-naphthol (**12a**) in 37% yield, without ring-expanded product. On the other hand, the reaction of lithium 4-methoxy-1-naphtholate (**5b**) with carbenoid **2aa** afforded 2-cyclopropylated product **12b** (23%) and one-carbon ring-expanded spiro[2.6]nona-5,7-dien-4-one **13** (47%) as the major product.

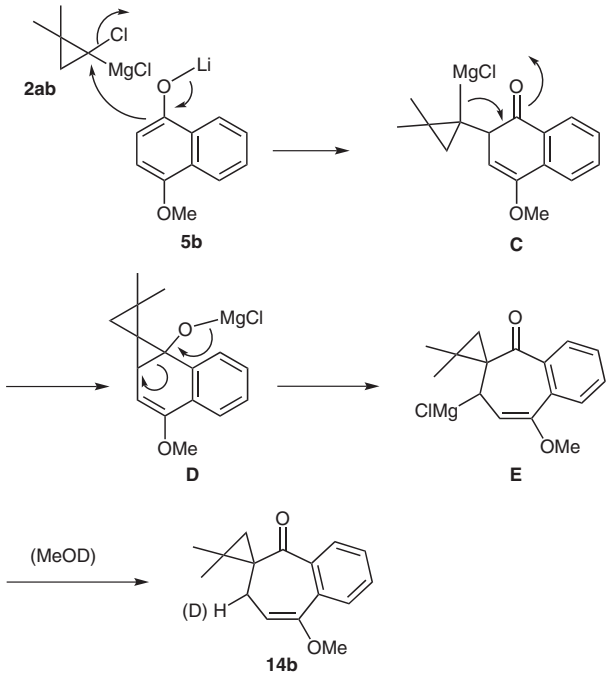


Scheme 4 Reaction of cyclopropylmagnesium carbenoids **2aa**, **2ab**, and **2ac** with lithium 1-naphtholates **5**

The reaction of cyclopropylmagnesium carbenoid **2ab** bearing *gem*-methyl groups with lithium 1-naphtholate (**5a**) gave 1,1-dimethylspiro[2.6]nona-5,7-dien-4-one **14a** in a relatively good yield of 70%. When this reaction was carried out with lithium 4-methoxy-1-naphtholate (**5b**), **14b** was obtained in 82% yield; however, the reaction of carbenoid **2ab** with lithium 4-chloro-1-naphtholate (**5c**) gave the expected product **14c** in only 33% yield (Scheme 4). The reaction of fully substituted cyclopropylmagnesium carbenoid **2ac** with lithium 4-methoxy-1-naphtholate (**5b**) gave the desired product **15**; however, the yield was not satisfactory. The reaction of lithium 1-naphtholates **5a** and **5b** with cyclobutylmagnesium carbenoids **2ba** and **2bb** was carried out. Unfortunately, these reactions gave only complex mixtures.

The structure of the products **13**, **14**, and **15** from the reaction of cyclopropylmagnesium carbenoids **2a** with lithium 1-naphtholates **5** is complementary to that from the reaction with lithium phenolates. As described above, the reaction of cyclopropylmagnesium carbenoid **2ab** with lithium phenolates gives spiro[2.6]nona-6,8-dien-5-ones **10**, in which the cyclopropane ring is placed at the β-position to the carbonyl group (see Scheme 2). On the other hand, the cyclopropane ring is placed at the α-position to the carbonyl group in the products **13**, **14**, and **15** of the reaction of carbenoids **2a** with lithium 1-naphtholates **5**. These results imply that the two reactions must be governed by different mechanisms.

A plausible mechanism for the reaction of cyclopropylmagnesium carbenoid **2ab** with lithium 4-methoxy-1-naphtholate giving **14b** is shown in Scheme 5. Thus, the substitution reaction of cyclopropylmagnesium carbenoid **2ab** with lithium 1-naphtholate **5b** would take place at the 2-position of the naphtholate to give cyclopropylmagnesium chloride intermediate **C**. In the case of the reaction of **2ab** with lithium 4-methylphenolate, as shown in Scheme 3, conjugate addition of the straight dienone intermediate **A** with the carbanion proceeded to give intermediate **B**; however, as one of the double bonds of the straight dienone moiety of intermediate **C** is a component of the aromatic ring, conjugate addition of the magnesium carbanion is thought to be difficult. Intramolecular 1,2-addition of the carbanion to the ketone group would take place to afford the highly strained spiro[2.2]pentane alkoxide **D**, instead of the conjugate addition. The negative charge on the oxygen atom would move to the carbon next to the cyclopropane ring, concomitant with cleavage of the highly strained carbon–carbon bond to afford intermediate **E**, which on protonation would give the product **14b**. When this reaction was quenched with MeOD, the hydrogen on the carbon at the 9-position of **14b** was replaced by deuterium (D content: 99%). This result provides strong evidence for the support of the presented mechanism. The presence of intermediate **E** was further confirmed by trapping experiments using allyl iodide and iodomethane. Spiro[2.6]nona-5,7-dien-4-ones bearing allyl and methyl groups at the 9-position (**14d** and **14e**, see experimental section) were obtained in 30% and 12% yield, respectively.

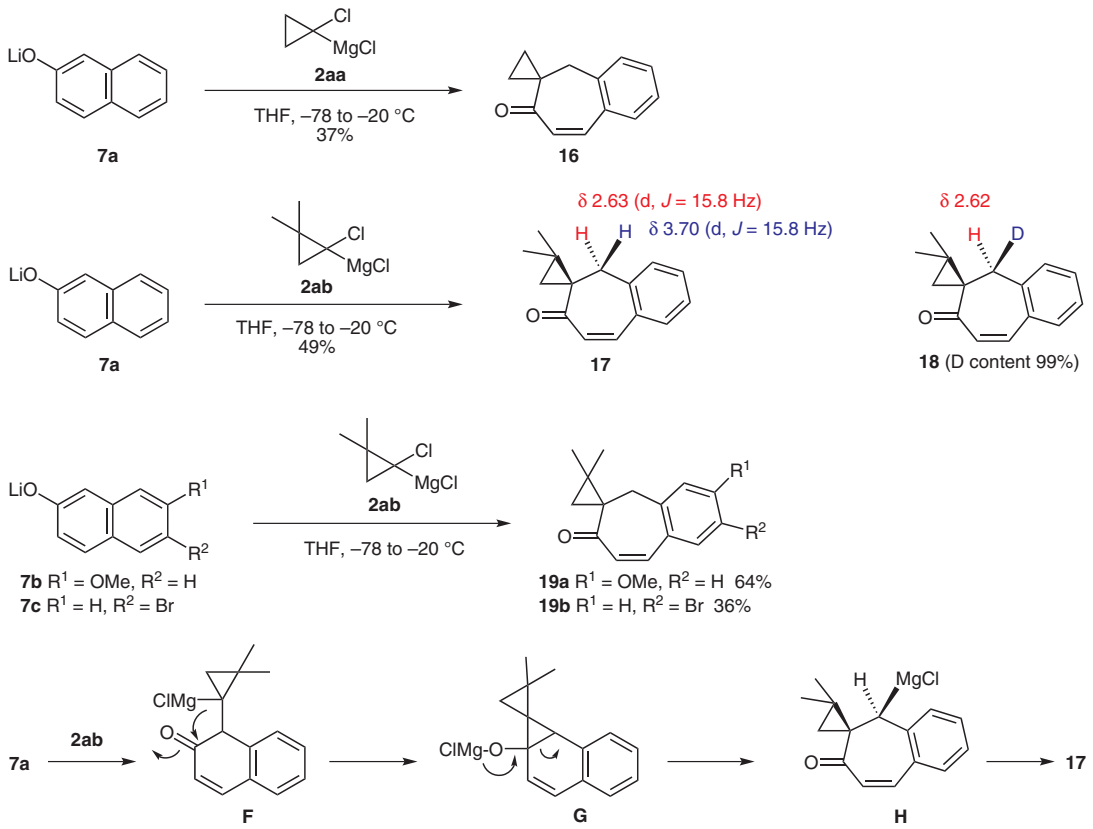


Scheme 5 A plausible mechanism for the reaction of cyclopropylmagnesium carbenoid **2ab** with lithium 4-methoxy-1-naphtholate (**5b**) giving spiro[2.6]nona-5,7-dien-4-one **14b**

The reaction of cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids with lithium 2-naphtholates was investigated next. At first, cyclopropylmagnesium carbenoid **2aa** was treated with 3 equivalents of lithium 2-naphtholate (**7a**) at –78 °C and the temperature of the reaction mixture was allowed to slowly warm to –20 °C (Scheme 6). This reaction gave spiro[2.6]nona-5,7-dien-4-one **16** in 37% yield as an isolable major product. The reaction of cyclopropylmagnesium carbenoid **2ab** bearing *gem*-methyl groups with 2-naphtholate **7a** gave the expected product **17** in a better yield of 49%. The structure of **17** was confirmed by X-ray analysis, which was reported as a preliminary letter of the present study.[2f] The reaction of carbenoid **2ab** with other lithium 2-naphtholates **7b** and **7c** under the same conditions gave the corresponding spiro[2.6]nona-5,7-dien-4-ones **19** in somewhat variable yields.

As shown in Scheme 6, product **17** has two benzylic hydrogens at the 9-position, which appear at δ = 2.63 and 3.70 ppm in its ^{1}H NMR spectrum. When this reaction was quenched with MeOD, the hydrogen observed at 3.70 ppm was completely replaced by deuterium to give **18**. Based on this result, the mechanism of the reaction of **2ab** with **7a** is proposed as shown in Scheme 6. Thus, similar to the reaction of **2ab** with **5b** (shown in Scheme 5), the reaction of **2ab** with lithium 2-naphtholate (**7a**) would give cyclopropylmagnesium chloride intermediate **F**. Intramolecular 1,2-addition of the cyclopropylmagnesium chloride to the ketone group gives the highly strained spiro[2.2]pentane alkoxide **G**. The negative charge on the oxygen atom would move to the benzylic carbon, concomitant with cleavage of the highly strained carbon–carbon bond to afford intermediate **H**, which on protonation would give product **17**. It is noteworthy that the chiral carbon center bearing the magnesium chloride is formed in a stereospecific manner; however, the mechanism of this selectivity is not clearly explained at the present stage.

Finally, the reaction of cyclobutylmagnesium carbenoids **2ba**, **2bb**, and **2bc**, as well as **2bd**, with lithium 2-naphtholates was investigated. 1-Chloro-3,3-dimethylcyclobutyl *p*-tolyl sulfoxide (**1bd**), the precursor of cyclobutylmagnesium carbenoid **2bd**, was synthesized from known compound **20**[8] as shown in Scheme 7. Thus, hydrogenolysis, followed by tosylation, of benzyl ether **20** gave tosylate **21** in high overall yield. Tosylate **21** was treated with potassium *p*-toluenethiolate to afford sulfide **22** in 73% yield. The sulfur group was oxidized to the

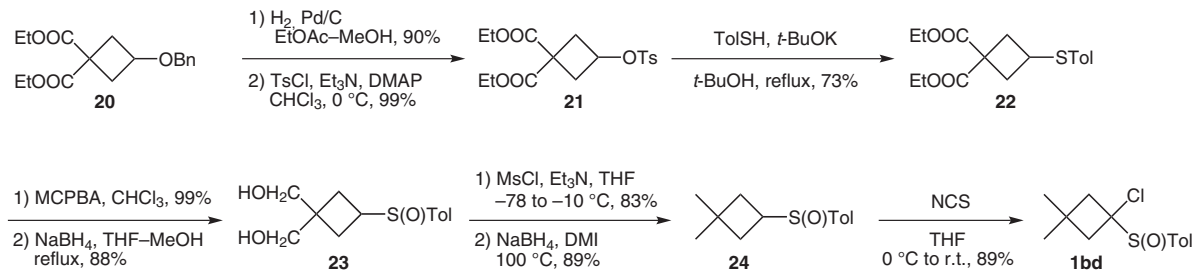


Scheme 6 Reaction of cyclopropylmagnesium carbenoids **2aa** and **2ab** with lithium 2-naphtholates **7**, and a proposed reaction mechanism

sulfoxide group with *m*-chloroperoxybenzoic acid, and the ethyl ester groups were reduced to hydroxymethyl groups with sodium borohydride in tetrahydrofuran–methanol,[9] to give **23**. The hydroxymethyl groups in **23** were reduced to methyl groups in two steps[2i] to give **24**. Finally, sulfoxide **24** was chlorinated with *N*-chlorosuccinimide in tetrahydrofuran to afford **1bd** in good overall yield.

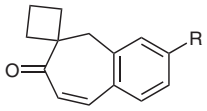
The results for the reaction of cyclobutylmagnesium carbenoids **2ba** to **2bd**, generated from 1-chlorocyclobutyl *p*-tolyl sulfoxides **1ba** to **1bd**, with lithium 2-naphtholate and lithium 7-methoxy-2-naphtholate are summarized in Table 2. As shown in entries 1 and 2, the reaction of cyclobutylmagnesium carbenoid **2ba** bearing no R substituent with lithium 2-naphtholates gave mixtures of spiro[3.6]deca-7,9-dien-6-ones **25a** and **25b** and spiro[3.6]deca-6,8-dien-5-ones **26a** and **26b** (Figure 1). The structures of **25a** and **25b** were determined from their ^{1}H–^{13}C HMBC spectra (see experimental section). In contrast to these results, the reaction of cyclobutylmagnesium carbenoids bearing substituents at the 3-position, **2bb** and **2bc**, with lithium 2-naphtholates gave spiro[3.6]deca-7,9-dien-6-ones **25c**–**f** in good yields (Table 2, entries 3–6).

These results implied that *gem*-disubstituents at the 3-position play some essential role in the reaction. In order to make it clear that the effect belongs to the presence of a substituent itself, rather than the presence of the oxygen atom in the substituent, we synthesized 1-chloro-3,3-dimethylcyclobutyl *p*-tolyl sulfoxide (**1bd**) as described above. Thus, treatment of cyclobutylmagnesium carbenoid **2bd** with lithium 2-naphtholate afforded the expected product **25g** in 69% yield (Table 2, entry 7). The reaction with lithium 7-methoxy-2-naphtholate also gave the desired product **25h** in 65% yield (Table 2, entry 8). On the basis of the regiochemical outcome, the reaction appears to proceed via a mechanism similar to that of the lithium



Scheme 7 Synthesis of 1-chloro-3,3-dimethylcyclobutyl *p*-tolyl sulfoxide (**1bd**) from benzyl ether **20**

phenolates. Although the real reason for the effect of the substituents at the 3-position is unclear at present, this finding is quite important for the uses of the procedure described in this paper.

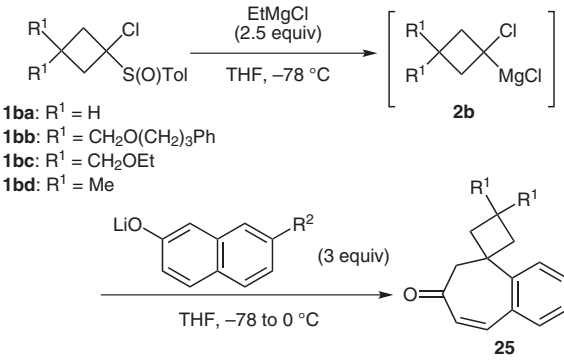


26a R = H
26b R = OMe

Figure 1

In order to elucidate the regioselectivity observed in the reaction of magnesium carbenoids **2a** and **2b** with lithium 1- and 2-naphtholates, geometry optimization and molecular orbital calculation of four model compounds, 1-naphtholate anion (**I**), 2-naphtholate anion (**II**), 2-methylnaphthalen-1(2*H*)-one (**III**), and 1-methylnaphthalen-2(1*H*)-one (**IV**), were performed at the B3LYP/6-311++G(d,p) level with Gaussian software.[10] Selected molecular orbitals of model compounds **I**–**IV** are shown in Figure 2.[11] The HOMO of 1-naphtholate anion is mainly localized on the carbon atoms at the 2- and 4-positions of the naphthol ring, and the reaction at the 2-position would be sterically favorable in comparison with that at the 4-position. 2-Naphtholate anion has a large HOMO coefficient on the carbon atom at the 1-position. Therefore, it is expected that the reaction of magnesium carbenoids with 1-naphtholate anion takes place preferentially at the 2-position to give the intermediate **C** in Scheme 5 and the reaction with 2-naphtholate anion would proceed exclusively at the 1-position to give the intermediate **F** in

Table 2 Reaction of Cyclobutylmagnesium Carbenoids **2b** with Lithium 2-Naphtholates



Entry	Sulfoxide	**2b**	R^1	R^2	Yield (%) of **25**
1	**1ba**	**2ba**	H	H	**25a**: 37[a]
2	**1ba**	**2ba**	H	OMe	**25b**: 31[b]
3	**1bb**	**2bb**	$CH_2O(CH_2)_3Ph$	H	**25c**: 69
4	**1bc**	**2bc**	CH_2OEt	H	**25d**: 70
5	**1bb**	**2bb**	$CH_2O(CH_2)_3Ph$	OMe	**25e**: 69
6	**1bc**	**2bc**	CH_2OEt	OMe	**25f**: 60
7	**1bd**	**2bd**	Me	H	**25g**: 69
8	**1bd**	**2bd**	Me	OMe	**25h**: 65

[a] Compound **26a** was obtained in 24% yield.
[b] Compound **26b** was obtained in 18% yield.

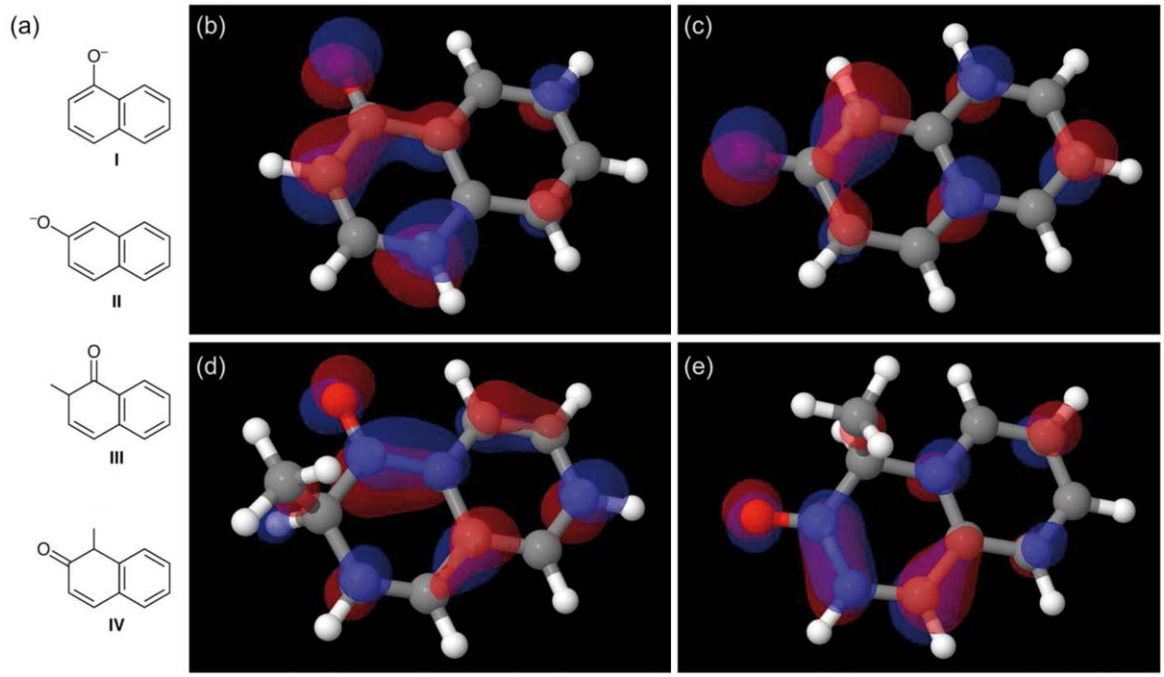


Figure 2 (a) Chemical structures of model compounds **I**–**IV**, (b) HOMO of 1-naphtholate anion (**I**), (c) HOMO of 2-naphtholate anion (**II**), (d) LUMO of 2-methylnaphthalen-1(2*H*)-one (**III**), (e) LUMO of 1-methylnaphthalen-2(1*H*)-one (**IV**).

Scheme 6. In the model compounds **III** and **IV**, the coefficients of the LUMO on the carbonyl carbon atoms are larger than those on the carbon atoms at the δ-position. These results suggest that internal cycloalkylmagnesium chlorides would attack the carbonyl carbon atoms (1,2-addition) rather than the carbon atoms at the δ-position; however, the reaction of cyclobutylmagnesium carbenoids **2b** with lithium 2-naphtholates afforded spiro[3.6]deca-7,9-dien-6-ones **25** (Table 2). Although the precise origin of the regioselectivity remains obscure, it is attributable to steric repulsion between the substituents at the 3-position of the cyclobutyl ring and the hydrogen atom at the 8-position of the naphthalen-2(1*H*)-one ring.

In conclusion, we have outlined a novel reaction of cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids with lithium phenolates, lithium 1-naphtholates, and lithium 2-naphtholates giving ring-expanded spiro[2.6]nonadienones and spiro[3.6]decadienones. Although there are a few reports on the reactions of lithium cyclopropylidenes,[1j,12] there is no previous report on the reaction with phenolates and naphtholates. The results described in this paper are unprecedented for the reactions of cyclopropylmagnesium carbenoids and cyclobutylmagnesium carbenoids, and we believe that they will contribute very much to the chemistry of carbenes and carbenoids.

Melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. NMR spectra were measured in $CDCl_3$ solution with Jeol JNM-LA 300, Jeol JNM-LA 500, Bruker DPX 400, and Bruker AV 600 spectrometers. Assignments in ^{13}C NMR spectra were made using DEPT 90 and 135 experiments. Electron-impact (EI) mass spectra were obtained at 70 eV by direct insertion with a Hitachi M-80B mass spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR instrument. Silica gel 60 N (Kanto Chemical) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiments requiring anhydrous solvents and reagents, THF was distilled from sodium diphenyl ketyl. Et_3N was distilled from CaH_2. All reactions involving air- or water-sensitive compounds were routinely conducted in glassware which had been flame-dried under a positive pressure of argon. Sulfoxides **1aa**,[2b] **1ab**,[2i] 1-chloro-2,2,3,3-tetramethylcyclopropyl *p*-tolyl sulfoxide (**1ac**),[2i] **1ba**,[3c] **1bb**,[3c] and **1bc**[3c] were prepared according to the procedures described in the literature.

2-Cyclopropylphenol (9)[13]

A soln of sulfoxide **1aa** (60.0 mg, 0.30 mmol) in THF (0.8 mL) was added dropwise to a 2.0 M soln of *i*-PrMgCl in THF (0.375 mL, 0.75 mmol) at –78 °C, and the mixture was stirred at that temperature for 10 min. A soln of lithium phenolate, prepared in situ from 1.65 M BuLi in hexane (0.91 mL, 1.5 mmol) and phenol (141 mg, 1.50 mmol) in THF (0.7 mL) at –78 °C, was added via a cannula to the resulting solution at –78 °C, and the mixture was allowed to warm to 0 °C over 1.5 h. The reaction was quenched with sat. aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3 × 7 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.3 (hexane–1,4-dioxane, 10:1)] to give **9** as a yellow oil; yield: 8.5 mg (0.063 mmol, 21%).

IR (neat): 3401 (OH), 3003, 2926, 1754, 1493, 1452, 1214, 1193, 752 cm^{-1}.

^1H NMR (400 MHz): δ = 0.63–0.66 (m, 2 H), 0.96–0.99 (m, 2 H), 1.81 (tt, *J* = 5.3, 8.3 Hz, 1 H), 5.47 (s, 1 H), 6.82–6.87 (m, 2 H), 7.06–7.15 (m, 2 H).

MS (EI): *m*/*z* (%) = 134 (100) $[M]^+$, 119 (41), 91 (37), 77 (21).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{10}O$: 134.0732; found: 134.0726.

1,1-Dimethylspiro[2.6]nona-6,8-dien-5-one (10a); Typical Procedure

The reactions of magnesium carbenoids with lithium phenolates and lithium naphtholates (except the reaction of **2aa** with lithium phenolate) were carried out according to the following procedure. A 1.65 M soln of BuLi in hexane (0.545 mL, 0.90 mmol) was added dropwise to a soln of phenol (84.7 mg, 0.90 mmol) in THF (0.8 mL) at –78 °C, and the mixture was stirred at that temperature for 10 min. A soln of sulfoxide **1ab** (72.6 mg, 0.30 mmol) in THF (0.7 mL) was added to the resulting solution at –78 °C. A 2.0 M soln of *i*-PrMgCl in THF (0.375 mL, 0.75 mmol) was then added to the mixture at –78 °C, and the mixture was allowed to warm to –20 °C over 1.5 h. The reaction was quenched with sat. aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3 × 7 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.4 (hexane–1,4-dioxane, 10:1)] to give **10a** as a yellow oil; yield: 10.7 mg (0.066 mmol, 22%).

IR (neat): 2947, 1659 (C=O), 1626, 1573, 1113, 718 cm^{-1}.

^1H NMR (500 MHz): δ = 0.77 (s, 2 H), 1.06 (s, 3 H), 1.19 (s, 3 H), 2.35 (d, *J* = 15.5 Hz, 1 H), 3.04 (d, *J* = 15.5 Hz, 1 H), 6.04–6.13 (m, 3 H), 6.64 (ddd, *J* = 0.7, 7.2, 12.3 Hz, 1 H).

MS (EI): *m*/*z* (%) = 162 (39) $[M]^+$, 147 (83), 119 (32), 107 (100), 91 (76).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{14}O$: 162.1045; found: 162.1046.

1,1,8-Trimethylspiro[2.6]nona-6,8-dien-5-one (10b)

Yield: 16.9 mg (32%); yellow oil.

IR (neat): 2983, 2945, 1662 (C=O), 1637, 1575, 1455, 1417, 1378, 771 cm^{-1}.

^1H NMR (400 MHz): δ = 0.63 (d, *J* = 4.5 Hz, 1 H), 0.66 (d, *J* = 4.5 Hz, 1 H), 1.02 (s, 3 H), 1.16 (s, 3 H), 1.93 (d, *J* = 1.5 Hz, 3 H), 2.33 (d, *J* = 16.1 Hz, 1 H), 3.00 (d, *J* = 16.1 Hz, 1 H), 5.88 (s, 1 H), 6.06 (d, *J* = 12.5 Hz, 1 H), 6.52 (d, *J* = 12.5 Hz, 1 H).

MS (EI): *m*/*z* (%) = 176 (48) $[M]^+$, 161 (75), 121 (100), 105 (50), 91 (70).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1204.

4-Deuterio-1,1,8-trimethylspiro[2.6]nona-6,8-dien-5-one (10b′)

^1H NMR (500 MHz): δ = 0.62–0.66 (m, 2 H), 1.02 (s, 3 H), 1.16 (s, 3 H), 1.93 (s, 3 H), 2.31 (br s, 0.4 H), 2.99 (br s, 0.4 H), 5.87 (s, 1 H), 6.06 (d, *J* = 12.5 Hz, 1 H), 6.52 (d, *J* = 12.5 Hz, 1 H).

1,1-Dimethyl-8-phenylspiro[2.6]nona-6,8-dien-5-one (10c)

Yield: 14.3 mg (20%); yellow oil.

IR (neat): 2947, 1721, 1660 (C=O), 1601, 1495, 1448, 1418, 1378, 1293, 1269, 1113, 765, 749, 699 cm^{-1}.

^1H NMR (500 MHz): δ = 0.80 (d, *J* = 4.7 Hz, 1 H), 0.81 (d, *J* = 4.7 Hz, 1 H), 1.12 (s, 3 H), 1.23 (s, 3 H), 2.41–2.45 (m, 1 H), 3.15 (d, *J* = 16.3 Hz, 1 H), 6.23–6.26 (m, 1 H), 6.34 (s, 1 H), 6.95 (dd, *J* = 1.2, 12.5 Hz, 1 H), 7.29–7.38 (m, 5 H).

MS (EI): *m*/*z* (%) = 238 (100) $[M]^+$, 223 (44), 183 (84), 165 (36), 155 (55), 115 (36).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1359.

8-Methoxy-1,1-dimethylspiro[2.6]nona-6,8-dien-5-one (10d)
Yield: 15.0 mg (26%); yellow oil.

IR (neat): 2945, 1662 (C=O), 1633, 1594, 1453, 1413, 1269, 1211, 1156 cm^{-1}.

^1H NMR (400 MHz): δ = 0.58 (d, *J* = 4.5 Hz, 1 H), 0.66 (d, *J* = 4.5 Hz, 1 H), 1.05 (s, 3 H), 1.16 (s, 3 H), 2.38 (d, *J* = 16.3 Hz, 1 H), 3.03 (d, *J* = 16.3 Hz, 1 H), 3.54 (s, 3 H), 5.14 (s, 1 H), 6.09 (d, *J* = 12.8 Hz, 1 H), 6.55 (d, *J* = 12.8 Hz, 1 H).

^{13}C NMR (126 MHz): δ = 20.0 (C), 22.9 (CH_3), 23.1 (C), 23.9 (CH_3), 30.1 (CH_2), 49.1 (CH_2), 54.7 (CH_3), 114.1 (CH), 130.2 (CH), 137.9 (CH), 154.0 (C), 199.4 (C).

MS (EI): *m*/*z* (%) = 192 (100) $[M]^+$, 177 (92), 137 (59), 117 (42), 91 (45).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}O_2$: 192.1150; found: 192.1154.

Spiro[3.6]deca-7,9-dien-6-one (11a)
EtMgCl (2.5 equiv) was used; yield: 18.3 mg (30%); pale yellow oil.

IR (neat): 2936, 1658 (C=O), 1630, 1581, 1418, 1303, 706 cm^{-1}.

^1H NMR (300 MHz): δ = 1.95–2.08 (m, 6 H), 2.89 (s, 2 H), 5.87 (dd, *J* = 7.3, 11.2 Hz, 1 H), 6.01 (d, *J* = 12.2 Hz, 1 H), 6.52 (dd, *J* = 7.3, 12.2 Hz, 1 H), 6.57 (d, *J* = 11.2 Hz, 1 H).

MS (EI): *m*/*z* (%) = 148 (3) $[M]^+$, 120 (40), 105 (14), 91 (100), 79 (14).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{10}H_{12}O$: 148.0888; found: 148.0889.

2-Cyclopropyl-1-naphthol (12a)
Yield: 20.4 mg (37%); colorless oil.

IR (neat): 3547 (OH), 3057, 1574, 1509, 1386, 1351, 1267, 1239, 1060, 808, 746 cm^{-1}.

^1H NMR (500 MHz): δ = 0.71–0.74 (m, 2 H), 1.05–1.08 (m, 2 H), 1.92 (tt, *J* = 5.3, 8.2 Hz, 1 H), 6.06 (s, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.42–7.48 (m, 2 H), 7.75 (dd, *J* = 1.8, 7.2 Hz, 1 H), 8.20 (d, *J* = 7.7 Hz, 1 H).

MS (EI): *m*/*z* (%) = 184 (100) $[M]^+$, 169 (19), 155 (14), 141 (28), 128 (25), 115 (18).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{12}O$: 184.0888; found: 184.0893.

2-Cyclopropyl-4-methoxy-1-naphthol (12b)
Yield: 14.8 mg (23%); yellow oil.

IR (neat): 3552 (OH), 3003, 1598, 1459, 1389, 1283, 1223, 1128, 1097, 766 cm^{-1}.

^1H NMR (500 MHz): δ = 0.73 (br s, 2 H), 1.05 (br s, 2 H), 1.95 (br s, 1 H), 3.95 (br s, 3 H), 5.68 (s, 1 H), 6.60 (br s, 1 H), 7.44–7.49 (m, 2 H), 8.13–8.17 (m, 2 H).

MS (EI): *m*/*z* (%) = 214 (100) $[M]^+$, 199 (68), 183 (23), 154 (14), 141 (15), 128 (20), 115 (22).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{14}O_2$: 214.0994; found: 214.0992.

9-Methoxyspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (13)
Yield: 30.2 mg (47%); yellow oil.

IR (neat): 3002, 2939, 2905, 1652 (C=O), 1596, 1439, 1355, 1237, 1211, 1135, 1099, 983, 769 cm^{-1}.

^1H NMR (500 MHz): δ = 0.93 (q, *J* = 3.5 Hz, 2 H), 1.40 (q, *J* = 3.5 Hz, 2 H), 2.20 (d, *J* = 7.4 Hz, 2 H), 3.70 (s, 3 H), 5.24 (t, *J* = 7.4 Hz, 1 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.62 (d, *J* = 7.4 Hz, 1 H), 7.63 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (126 MHz): δ = 20.4 (CH_2), 28.8 (CH_2), 36.6 (C), 55.2 (CH_3), 97.3 (CH), 126.6 (CH), 128.4 (CH), 128.7 (CH), 131.3 (CH), 134.3 (C), 138.5 (C), 155.4 (C), 206.2 (C=O).

MS (EI): *m*/*z* (%) = 214 (100) $[M]^+$, 199 (68), 183 (27), 171 (20), 153 (12), 143 (13), 128 (17), 115 (26).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{14}O_2$: 214.0994; found: 214.0995.

2′,2′-Dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14a)
Yield: 44.6 mg (70%); yellow oil.

IR (neat): 3031, 2950, 1651 (C=O), 1594, 1442, 1376, 1353, 1309, 1244, 1111, 794 cm^{-1}.

^1H NMR (500 MHz): δ = 0.75 (d, *J* = 4.1 Hz, 1 H), 1.03 (s, 3 H), 1.35 (s, 3 H), 1.67 (d, *J* = 4.1 Hz, 1 H), 2.15 (dd, *J* = 7.9, 15.9 Hz, 1 H), 2.87 (ddd, *J* = 1.7, 5.3, 15.9 Hz, 1 H), 6.33 (ddd, *J* = 5.3, 7.9, 10.8 Hz, 1 H), 6.52 (dd, *J* = 1.7, 10.8 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H).

MS (EI): *m*/*z* (%) = 212 (100) $[M]^+$, 197 (48), 179 (21), 169 (21), 157 (79), 129 (41), 128 (78), 115 (38), 102 (11), 89 (7).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1202.

9-Methoxy-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14b)
Yield: 59.6 mg (82%); yellow oil.

IR (neat): 3067, 2991, 2949, 2873, 1652 (C=O), 1596, 1464, 1360, 1267, 1238, 1209, 1137, 1110, 985, 768 cm^{-1}.

^1H NMR (500 MHz): δ = 0.84 (d, *J* = 4.0 Hz, 1 H), 1.19 (s, 3 H), 1.34 (s, 3 H), 1.67 (d, *J* = 4.0 Hz, 1 H), 2.38 (d, *J* = 7.6 Hz, 2 H), 3.69 (s, 3 H), 5.24 (t, *J* = 7.6 Hz, 1 H), 7.36 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.47 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.57 (dd, *J* = 1.4, 7.6 Hz, 1 H), 7.60 (dd, *J* = 1.4, 7.6 Hz, 1 H).

^{13}C NMR (126 MHz): δ = 19.8 (CH_3), 23.4 (CH_3), 26.7 (CH_2), 30.78 (CH_2 or C), 30.83 (CH_2 or C), 46.8 (C), 55.1 (CH_3), 98.1 (CH), 126.1 (Ar), 127.9 (Ar), 128.3 (Ar), 130.7 (Ar), 133.6 (C), 139.6 (C), 155.0 (C), 204.0 (C=O).

MS (EI): *m*/*z* (%) = 242 (100) $[M]^+$, 227 (63), 211 (26), 187 (17), 158 (13), 128 (17), 115 (26), 102 (7), 89 (5).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1307.

7-Deuterio-9-methoxy-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14b′)
^1H NMR (500 MHz): δ = 0.84 (d, *J* = 3.9 Hz, 1 H), 1.19 (s, 3 H), 1.34 (s, 3 H), 1.67 (d, *J* = 3.9 Hz, 1 H), 2.37–2.39 (m, 1 H), 3.68 (s, 3 H), 5.23 (t, *J* = 7.4 Hz, 1 H), 7.36 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.47 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.56 (dd, *J* = 1.4, 7.6 Hz, 1 H), 7.60 (dd, *J* = 1.4, 7.6 Hz, 1 H).

9-Chloro-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14c)
Yield: 24.4 mg (33%); yellow oil.

IR (neat): 3065, 2991, 2928, 2873, 1661 (C=O), 1594, 1468, 1351, 1196, 1105, 975, 764 cm^{-1}.

^1H NMR (500 MHz): δ = 0.88 (d, *J* = 4.1 Hz, 1 H), 1.21 (s, 3 H), 1.35 (s, 3 H), 1.73 (d, *J* = 4.1 Hz, 1 H), 2.43 (d, *J* = 7.8 Hz, 2 H), 6.50 (t, *J* = 7.8 Hz, 1 H), 7.39 (dt, *J* = 1.2, 7.8 Hz, 1 H), 7.52 (dt, *J* = 1.2, 7.8 Hz, 1 H), 7.58 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.69 (dd, *J* = 1.2, 7.8 Hz, 1 H).

MS (EI): *m*/*z* (%) = 246 (24) $[M]^+$, 211 (100), 191 (25), 165 (12), 141 (23), 127 (14), 115 (14).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{15}ClO$: 246.0811; found: 246.0814.

7-Allyl-9-methoxy-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14d)

A 2.0 M soln of *i*-PrMgCl in THF (0.375 mL, 0.75 mmol) was added to a soln of sulfoxide **1ab** (72.8 mg, 0.30 mmol) and lithium 4-methoxy-1-naphtholate (0.90 mmol) in THF–hexane (3:1, 2.0 mL) at –78 °C, and the mixture was allowed to warm to –20 °C over 1.5 h. Allyl iodide (252 mg, 1.50 mmol) was added dropwise to the reaction mixture at –20 °C, and the mixture was allowed to warm to 0 °C over 1 h. The reaction was quenched with sat. aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3 × 7 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.4 (hexane–1,4-dioxane, 10:1)] and preparative thin-layer chromatography (hexane–1,4-dioxane, 30:1) to give **14d** as a yellow oil; yield: 25.4 mg (0.090 mmol, 30%).

IR (neat): 2947, 1650 (C=O), 1593, 1365, 1212, 986, 766 cm^{-1}.

^1H NMR (500 MHz): δ = 0.69 (d, *J* = 4.1 Hz, 1 H), 0.98 (s, 3 H), 1.39 (s, 3 H), 1.76 (d, *J* = 4.1 Hz, 1 H), 2.19–2.21 (m, 3 H), 3.71 (s, 3 H), 4.83 (d, *J* = 17.2 Hz, 1 H), 4.89 (d, *J* = 10.1 Hz, 1 H), 5.52 (d, *J* = 8.0 Hz, 1 H), 5.70–5.78 (m, 1 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 8.11 (d, *J* = 7.6 Hz, 1 H).

MS (EI): *m*/*z* (%) = 282 (0.1) $[M]^+$, 242 (18), 241 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{22}O_2$: 282.1620; found: 282.1614.

9-Methoxy-2′,2′,7-trimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (14e)

Yield: 9.2 mg (12%); yellow oil.

IR (neat): 2927, 1651 (C=O), 1596, 1460, 1388, 1365, 1218, 1100, 987, 765 cm^{-1}.

^1H NMR (300 MHz): δ = 0.63 (d, *J* = 4.1 Hz, 1 H), 0.97 (s, 3 H), 1.07 (d, *J* = 7.4 Hz, 3 H), 1.39 (s, 3 H), 1.67 (d, *J* = 4.1 Hz, 1 H), 2.21–2.32 (m, 1 H), 3.70 (s, 3 H), 5.55 (d, *J* = 9.4 Hz, 1 H), 7.35 (dt, *J* = 1.3, 8.0 Hz, 1 H), 7.51 (dt, *J* = 1.5, 8.0 Hz, 1 H), 7.86 (dd, *J* = 1.3, 8.0 Hz, 1 H), 8.09 (dd, *J* = 1.5, 8.0 Hz, 1 H).

MS (EI): *m*/*z* (%) = 256 (18) $[M]^+$, 241 (100), 225 (17), 211 (18), 186 (17).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}O_2$: 256.1463; found: 256.1461.

9-Methoxy-2′,2′,3′,3′-tetramethylspiro[benzo[7]annulene-6,1′-cyclopropan]-5(7*H*)-one (15)

Yield: 21.1 mg (26%); yellow oil.

IR (neat): 3017, 2938, 2835, 1646 (C=O), 1594, 1463, 1375, 1361, 1283, 1201, 1101, 979, 768 cm^{-1}.

^1H NMR (500 MHz): δ = 1.26 (s, 6 H), 1.32 (s, 6 H), 2.40 (d, *J* = 7.7 Hz, 2 H), 3.68 (s, 3 H), 5.12 (t, *J* = 7.7 Hz, 1 H), 7.31–7.34 (m, 1 H), 7.40–7.43 (m, 2 H), 7.52 (d, *J* = 7.7 Hz, 1 H).

MS (EI): *m*/*z* (%) = 270 (52) $[M]^+$, 239 (3), 227 (14), 213 (15), 199 (13), 186 (100), 165 (5), 152 (5), 141 (4), 128 (6), 115 (9).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{22}O_2$: 270.1620; found: 270.1618.

Spiro[benzo[7]annulene-6,1′-cyclopropan]-7(5*H*)-one (16)

Yield: 20.4 mg (37%); colorless crystals; mp 45.0–46.0 °C (hexane).

IR (KBr): 3005, 1649 (C=O), 1570, 1404, 1363, 1204, 1115, 1097, 820, 748 cm^{-1}.

^1H NMR (500 MHz): δ = 0.85 (d, *J* = 3.4 Hz, 2 H), 1.29 (br s, 2 H), 2.93 (br s, 2 H), 6.29 (d, *J* = 12.5 Hz, 1 H), 7.12–7.15 (m, 2 H), 7.29–7.35 (m, 3 H).

^{13}C NMR (126 MHz): δ = 19.3 (CH_2), 32.4 (C), 39.0 (CH_2), 127.0 (CH), 129.1 (CH), 129.6 (CH), 130.67 (CH), 130.75 (CH), 134.3 (C), 139.2 (C), 140.5 (CH), 202.0 (C=O).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.58; H, 6.64.

2′,2′-Dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-7(5*H*)-one (17)

Yield: 31.2 mg (49%); colorless crystals; mp 39.5–40.5 °C (hexane).

IR (KBr): 2951, 1643 (C=O), 1408, 1361, 1314, 1281, 1099, 831, 801, 748 cm^{-1}.

^1H NMR (500 MHz): δ = 0.68 (d, *J* = 4.0 Hz, 1 H), 0.89 (s, 3 H), 1.08 (s, 3 H), 1.65 (d, *J* = 4.0 Hz, 1 H), 2.63 (d, *J* = 15.8 Hz, 1 H), 3.70 (d, *J* = 15.8 Hz, 1 H), 6.25 (d, *J* = 12.7 Hz, 1 H), 7.07 (d, *J* = 12.7 Hz, 1 H), 7.18–7.20 (m, 1 H), 7.27–7.30 (m, 2 H), 7.34–7.36 (m, 1 H).

^{13}C NMR (126 MHz): δ = 20.1 (CH_3), 23.8 (CH_3), 28.3 (CH_2), 28.9 (C), 37.4 (CH_2), 39.1 (C), 126.8 (CH), 129.5 (CH), 130.2 (CH), 130.8 (CH), 132.0 (CH), 133.7 (C), 140.5 (C), 141.1 (CH), 199.9 (C=O).

MS (EI): *m*/*z* (%) = 212 (76) $[M]^+$, 197 (20), 169 (17), 157 (100), 141 (33), 128 (67), 115 (39), 102 (8), 89 (9), 77 (11).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1197.

5-Deuterio-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-7(5*H*)-one (18)

^1H NMR (500 MHz): δ = 0.68 (d, *J* = 4.0 Hz, 1 H), 0.89 (s, 3 H), 1.09 (s, 3 H), 1.65 (d, *J* = 4.0 Hz, 1 H), 2.62 (t, *J* = 1.9 Hz, 1 H), 6.25 (d, *J* = 12.7 Hz, 1 H), 7.07 (d, *J* = 12.7 Hz, 1 H), 7.18–7.20 (m, 1 H), 7.27–7.30 (m, 2 H), 7.34–7.36 (m, 1 H).

3-Methoxy-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-7(5*H*)-one (19a)

Yield: 46.5 mg (64%); yellow oil.

IR (neat): 3066, 2991, 2950, 2838, 1635 (C=O), 1603, 1564, 1505, 1456, 1433, 1334, 1286, 1251, 1107, 1037, 839, 817, 734 cm^{-1}.

^1H NMR (500 MHz): δ = 0.63 (d, *J* = 4.1 Hz, 1 H), 0.89 (s, 3 H), 1.10 (s, 3 H), 1.65 (d, *J* = 4.1 Hz, 1 H), 2.57 (d, *J* = 15.8 Hz, 1 H), 3.68 (d, *J* = 15.8 Hz, 1 H), 3.83 (s, 3 H), 6.14 (d, *J* = 12.7 Hz, 1 H), 6.71 (d, *J* = 2.6 Hz, 1 H), 6.80 (dd, *J* = 2.6, 8.5 Hz, 1 H), 7.02 (d, *J* = 12.7 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 1 H).

MS (EI): *m*/*z* (%) = 242 (94) $[M]^+$, 227 (18), 199 (12), 187 (100), 158 (24), 144 (13), 128 (17), 115 (29), 102 (7), 89 (6), 77 (8), 63 (5).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1309.

2-Bromo-2′,2′-dimethylspiro[benzo[7]annulene-6,1′-cyclopropan]-7(5*H*)-one (19b)

Yield: 31.4 mg (36%); yellow oil.

IR (neat): 3024, 2991, 2951, 2872, 1646 (C=O), 1587, 1559, 1485, 1455, 1376, 1360, 1105, 891, 834, 732 cm^{-1}.

^1H NMR (500 MHz): δ = 0.69 (d, *J* = 4.1 Hz, 1 H), 0.89 (s, 3 H), 1.09 (s, 3 H), 1.65 (d, *J* = 4.1 Hz, 1 H), 2.61 (d, *J* = 15.8 Hz, 1 H), 3.62 (d, *J* = 15.8 Hz, 1 H), 6.28 (d, *J* = 12.7 Hz, 1 H), 6.97 (d, *J* = 12.7 Hz, 1 H), 7.08 (d, *J* = 8.1 Hz, 1 H), 7.40 (dd, *J* = 1.8, 8.1 Hz, 1 H), 7.49 (d, *J* = 1.8 Hz, 1 H).

MS (EI): *m*/*z* (%) = 290 (77) $[M]^+$, 275 (12), 235 (100), 208 (23), 196 (24), 181 (22), 168 (22), 152 (24), 141 (21), 139 (17), 128 (47), 115 (28).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{15}BrO$: 290.0306; found: 290.0305.

Spiro[benzo[7]annulene-5,1′-cyclobutan]-7(6*H*)-one (25a)
A combination of NMR techniques including ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and DEPT 90 and 135 were applied to elucidate the structures of regioisomers **25a** and **26a**. In the ^{1}H–^{13}C HMBC spectrum of **26a**, correlation between the resonances associated with ^{1}H at the 2′-position (δ_H 1.76) and ^{13}C of the carbonyl group (δ_C 203.1) was observed. In addition, ^{1}H at the 8-position (δ_H 6.11) correlated with secondary ^{13}C (δ_C 53.9) in the ^{1}H–^{13}C HMBC spectrum of **25a**, and that of **26a** (δ_H 6.13) correlated with quaternary ^{13}C (δ_C 51.0). The structure of **25a** was further confirmed by deuteration experiments (see **25a′**).

EtMgCl (2.5 equiv) was used; yield: 22.0 mg (37%); pale yellow oil.

IR (neat): 2979, 2939, 1658 (C=O), 1617, 1311, 1279 cm^{-1}.

^{1}H NMR (600 MHz): δ = 1.82–1.85 (m, 1 H), 1.98–2.08 (m, 1 H), 2.21 (br s, 4 H), 3.05 (s, 2 H), 6.11 (d, *J* = 12.3 Hz, 1 H), 7.11 (d, *J* = 12.3 Hz, 1 H), 7.28 (dt, *J* = 1.4, 7.4 Hz, 1 H), 7.32 (dd, *J* = 1.4, 7.4 Hz, 1 H), 7.38 (dt, *J* = 1.4, 7.4 Hz, 1 H), 7.43 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (126 MHz): δ = 15.7 (CH_2), 31.4 (CH_2), 41.8 (C), 53.9 (CH_2), 124.6 (CH), 126.6 (CH), 129.2 (CH), 130.0 (CH), 132.8 (C), 133.1 (CH), 143.3 (CH), 147.8 (C), 200.9 (C=O).

MS (EI): *m*/*z* (%) = 198 (18) [M]$^+$, 170 (33), 142 (100), 128 (21), 115 (27).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1042.

Spiro[benzo[7]annulene-6,1′-cyclobutan]-7(5*H*)-one (26a)
Yield: 14.3 mg (24%); yellow oil.

IR (neat): 2985, 2936, 1652 (C=O), 1617, 1318, 1204, 1099, 839, 748 cm^{-1}.

^{1}H NMR (600 MHz): δ = 1.74–1.78 (m, 2 H), 1.83–1.94 (m, 2 H), 2.30–2.34 (m, 2 H), 3.19 (s, 2 H), 6.13 (d, *J* = 12.6 Hz, 1 H), 7.01 (d, *J* = 12.6 Hz, 1 H), 7.29–7.30 (m, 2 H), 7.31–7.33 (m, 2 H).

^{13}C NMR (126 MHz): δ = 14.9 (CH_2), 28.9 (CH_2), 41.3 (CH_2), 51.0 (C), 127.1 (CH), 128.1 (CH), 129.8 (CH), 130.9 (CH), 131.9 (CH), 133.7 (C), 138.9 (C), 141.3 (CH), 203.1 (C=O).

MS (EI): *m*/*z* (%) = 198 (25) [M]$^+$, 170 (11), 157 (70), 141 (100), 128 (24), 115 (46), 102 (4), 89 (7).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1046.

6,6-Dideuteriospiro[benzo[7]annulene-5,1′-cyclobutan]-7(6*H*)-one (25a′)
A soln of **25a** (61.3 mg, 0.309 mmol) in THF (1.2 mL) was added to a soln of K_2CO_3 (0.8 mg, 0.006 mmol) in D_2O (0.6 mL) and MeOD (1.2 mL) at r.t., and the mixture was stirred at that temperature for 36 h. The reaction mixture was extracted with $CHCl_3$ (3 × 15 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.3 (hexane–EtOAc, 15:1)] to give **25a′** as a pale yellow oil; yield: 59.4 mg (0.297 mmol, 96%; D content: 96%).

^{1}H NMR (300 MHz): δ = 1.75–1.88 (m, 1 H), 1.97–2.11 (m, 1 H), 2.21 (br s, 4 H), 6.11 (d, *J* = 12.4 Hz, 1 H), 7.11 (d, *J* = 12.4 Hz, 1 H), 7.25–7.44 (m, 4 H).

Calculation
Density functional theory (DFT) calculations were performed with Gaussian 03 software,[10] and the geometries were fully optimized in the gas phase without any symmetry constraints at the B3LYP/6-311++G(d,p) level. Frequency calculations at the same level were performed to determine if the structures corresponded to energy minima (no imaginary frequencies). The Jmol program[11] was used to draw the molecular structures and molecular orbitals.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research No. 19590018 and 22590021 from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and a TUS Grant for Research Promotion from the Tokyo University of Science, which are gratefully acknowledged. High-performance computing resources were provided by the Tokyo University of Science. We also thank Mr. Masaya Watanabe for outstanding research assistance.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

References

(1) For some monographs and reviews on the chemistry of carbenes and carbenoids, see: (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, **1971**. (b) Dorwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, **1999**. (c) *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker: New York, **2002**. (d) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473. (e) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (f) Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361. (g) Schaefer, H. F. III *Acc. Chem. Res.* **1979**, *12*, 288. (h) Wynberg, H.; Meijer, E. W. *Org. React.* **1982**, *29*, 1. (i) Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751. (j) Oku, A. *J. Synth. Org. Chem., Jpn.* **1990**, *48*, 710. (k) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765. (l) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (m) Zaragoza, F. *Tetrahedron* **1997**, *53*, 3425. (n) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1164. (o) Braun, M. *Angew. Chem. Int. Ed.* **1998**, *37*, 430. (p) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (q) Boche, G.; Lohrenz, J. C. W. *Chem. Rev.* **2001**, *101*, 697. (r) Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477. (s) Muller, P. *Acc. Chem. Res.* **2004**, *37*, 243. (t) Knorr, R. *Chem. Rev.* **2004**, *104*, 3795. (u) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577.

(2) For papers from our laboratories on the chemistry and synthetic uses of cyclopropylmagnesium carbenoids, see: (a) Satoh, T.; Kurihara, T.; Fujita, K. *Tetrahedron* **2001**, *57*, 5369. (b) Satoh, T.; Saito, S. *Tetrahedron Lett.* **2004**, *45*, 347. (c) Satoh, T.; Miura, M.; Sakai, K.; Yokoyama, Y. *Tetrahedron* **2006**, *62*, 4253. (d) Yamada, Y.; Miura, M.; Satoh, T. *Tetrahedron Lett.* **2008**, *49*, 169. (e) Miyagawa, T.; Tatenuma, T.; Tadokoro, M.; Satoh, T. *Tetrahedron* **2008**, *64*, 5279. (f) Satoh, T.; Nagamoto, S.; Yajima, M.; Yamada, Y.; Ohata, Y.; Tadokoro, M. *Tetrahedron Lett.* **2008**, *49*, 5431. (g) Satoh, T.; Noguchi, T.; Miyagawa, T. *Tetrahedron Lett.* **2008**, *49*, 5689. (h) Yajima, M.; Nonaka, R.; Yamashita, H.; Satoh, T. *Tetrahedron Lett.* **2009**, *50*, 4754. (i) Yamada, Y.; Mizuno, M.; Nagamoto, S.; Satoh, T. *Tetrahedron* **2009**, *65*, 10025. (j) Satoh, T.; Ikeda, S.; Miyagawa, T.; Noguchi, T. *Tetrahedron Lett.* **2010**, *51*, 1955. (k) Momochi, H.; Noguchi, T.; Miyagawa, T.; Ogawa, N.; Tadokoro, M.; Satoh, T. *Tetrahedron Lett.* **2011**, *52*, 3016. (l) Satoh, T.; Kashiwamura, G.; Nagamoto, S.; Sasaki, Y.; Sugiyama, S. *Tetrahedron Lett.* **2011**, *52*, 4468. (m) Satoh, T.; Tsuru, T.; Ikeda, S.; Miyagawa, T.; Momochi, H.; Kimura, T. *Tetrahedron* **2012**, *68*, 1071.

(3) For papers from our laboratories on the chemistry and synthetic uses of cyclobutylmagnesium carbenoids, see: (a) Nakaya, N.; Sugiyama, S.; Satoh, T. *Tetrahedron Lett.* **2009**, *50*, 4212. (b) Satoh, T.; Kasuya, T.; Miyagawa, T.; Nakaya, N. *Synlett* **2010**, 286. (c) Satoh, T.; Kasuya, T.; Ishigaki, M.; Inumaru, M.; Miyagawa, T.; Nakaya, N.;

Sugiyama, S. *Synthesis* **2011**, 397. (d) Ishigaki, M.; Inumaru, M.; Satoh, T. *Tetrahedron Lett.* **2011**, *52*, 5563.

(4) Preliminary results of this investigation were reported as a Letter; see ref. 2f.

(5) (a) Satoh, T. *Chem. Soc. Rev.* **2007**, *36*, 1561. (b) Satoh, T. In *The Chemistry of Organomagnesium Compounds*; Rappoport, Z.; Marek, I., Eds.; John Wiley & Sons: Chichester, **2008**, 717–769. (c) Satoh, T. *Yakugaku Zasshi* **2009**, *129*, 1013. (d) Satoh, T. *Heterocycles* **2012**, *85*, 1.

(6) Hoffmann, R. W.; Hölzer, B.; Knopff, O.; Harms, K. *Angew. Chem. Int. Ed.* **2000**, *39*, 3072.

(7) Excess lithium phenolates and naphtholates were used throughout the study. Otherwise, the desired ring-expanded products were obtained in very low yields. The major byproducts in the reactions were 1-chlorocycloalkanes, which were formed by protonation of unreacted magnesium carbenoids **2**, and ethyl- or isopropyl-substituted cycloalkanes; see ref. 3c.

(8) Michejda, C. J.; Comnick, R. W. *J. Org. Chem.* **1975**, *40*, 1046.

(9) Soai, K.; Oyamada, H.; Takase, M.; Ookawa, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1948.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc: Wallingford (CT, USA), **2004**.

(11) Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/.

(12) For some papers on the chemistry of lithium cyclopropylidenes, see: (a) Oku, A.; Harada, T. *J. Synth. Org. Chem., Jpn.* **1986**, *44*, 736. (b) Harada, T.; Yamaura, Y.; Oku, A. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1715. (c) Creary, X.; Jiang, Z.; Butchko, M.; McLean, K. *Tetrahedron Lett.* **1996**, *37*, 579. (d) Tverezovsky, V. V.; Baird, M. S.; Bolesov, I. G. *Tetrahedron* **1997**, *53*, 14773. (e) Azizoglu, A.; Ozen, R.; Hokelek, T.; Balci, M. *J. Org. Chem.* **2004**, *69*, 1202. (f) Thomas, E.; Kasatkin, A. N.; Whitby, R. J. *Tetrahedron Lett.* **2006**, *47*, 9181.

(13) Barluenga, J.; Fañanás, F. J.; Sanz, R.; Marcos, C.; Trabada, M. *Org. Lett.* **2002**, *4*, 1587.