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Endo- and *Exo*-Configured Cyclopropylidenes Incorporated into the Norbornadiene Skeleton: Generation, Rearrangement to Allenes, and the Effect of Remote Substituents on Carbene Stability

Benan Kílbaş,[†] Akın Azizoğlu,[†,‡] and Metin Balci*[,†]

[†]*Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey, and* [‡]*Department of Chemistry, Balikesir University, 10100 Balikesir, Turkey*

mbalci@metu.edu.tr

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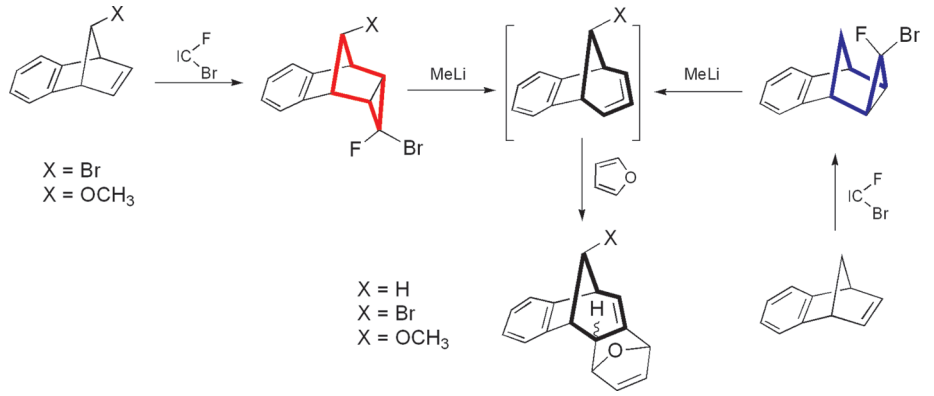

For the synthesis of *endo*-configured cyclopropylidenes annelated to benzonorbornadiene, first the *exo*-bridge hydrogen in benzonorbornadiene was blocked with ethyl, bromine, and methoxy groups. All efforts to add dichloro-, dibromo-, or fluorobromocarbenes to ethylbenzonorbornadiene failed. However, addition of fluorobromocarbene to bromo- or methoxybenzonorbornadiene gave the corresponding cyclopropane derivatives bearing two halogen atoms, which were submitted to the Doering−Moore−Skattebøl reaction. The formed allene intermediates were trapped with furan. The reactivity of the double bonds in substituted benzonorbornadienes was analyzed by determination of the pyramidalization angles. Furthermore, the relative energies of various carbenes and their rearrangement to allene were studied at B3LYP/6-31G(d) level.

Introduction

Carbenes are neutral and highly reactive organic molecules containing a carbon atom with six valence electrons and having the general formula R-*C*-R. Because of the electron deficiency in the outer shell, carbenes react in various ways to complete their valence shells, by intramolecular as well as intermolecular reactions.[1] Carbenes can undergo insertion reactions into C−H bonds, skeletal rearrangements, and additions to double bonds. The reactivity and the mode of the reaction can be strongly influenced by substituents.[2]

Cyclopropylidenes (carbenacyclopropanes) are the carbenes or carbenoids of cyclopropanes and are also known as interesting reactive intermediates.[3] Moore and co-workers[4] and Skatebøl[5] discovered almost simultaneously that allenes

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(2) (a) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263–309. (b) Kirmse, W. *Eur. J. Org. Chem.* **2005**, 237–260. (c) Mieusset, J. L.; Brinker, U. H. *Eur. J. Org. Chem.* **2008**, 3363–3368. (d) Mieusset, J. L.; Brinker, U. H. *J. Org. Chem.* **2008**, *73*, 1553–1558.

(3) (a) De Meijere, A.; Faber, D.; Heinecke, U.; Walsh, R.; Muller, T.; Apeloig, Y. *Eur. J. Org. Chem.* **2001**, *4*, 663–680. (b) Bakkes, J.; Brinker, U. H. *Methoden der Organischen Chemie* (*Houben-Weyl*); Thieme: Stuttgart, 1989; Vol. E19b, p 391. (c) Averina, E. B.; Karimov, R. R.; Sedenkova, K. N.; Grishin, Y. K.; Kuznetzova, T. S.; Zefirov, N. S. *Tetrahedron* **2006**, *62*, 8814–8821.

(4) (a) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1960**, *25*, 2073–2073. (b) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019–2020.

(5) Skattebøl, L. *Tetrahedron Lett.* **1961**, *5*, 167–172.

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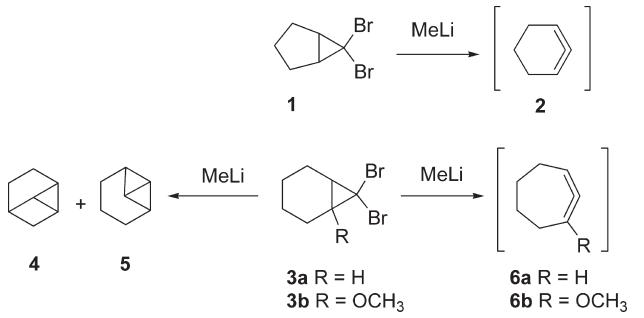
SCHEME 1



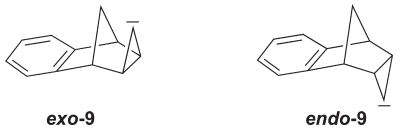
were formed when 1,1-dihalocyclopropanes[6] were exposed to an alkyl lithium reagent at low temperature (−78 °C) (Scheme 1). Doering and LaFlamme obtained allenes[7] in fair yields by treating the same cyclopropanes with pieces of metals (Na, Mg) at elevated temperatures. This reaction is now called the Doering−Moore−Skattebøl reaction.

The reaction involves cyclopropylidene or cyclopropylidene carbenoid intermediates, which usually open very easily to allenes.[4b,8,9] This method is the most efficient for generation of cyclohexa-1,2-diene **2**[10] but, paradoxically, was not successful for the higher homologue **6a**. Köbrich and Goyert[11] isolated a mixture of insertion products **4** and **5** from the reaction of **3a** with MeLi (Scheme 1). Hence, Schleyer et al.[12] have focused on the ring-opening of the carbene derived from **3a** by using density functional theory computations at B3LYP/DZP and TZP level. They found that the ring opening to **6a** has an unusually high activation energy of 14.6 kcal/mol because of the unfavorable conformational changes in the cyclohexane moiety. On the other hand, the activation barriers for intramolecular CH-insertions to yield highly strained hydrocarbons tricyclo[4.1.0.0^{2,7}]heptane (**4**) and tricyclo-[4.1.0.0^{3,7}]heptane (**5**) were found to be 6.4 and 9.1 kcal/mol, respectively. However, it is interesting to note that the Doering−Moore−Skattebøl reaction does successfully give **6b** for the methoxy derivative **3b**.[13] The formation of allenes from *gem*-dihalocyclopropanes competes with the formation of intramolecular CH-insertion products, usually bicyclobutanes. The results of this competition usually depend on the nature of the substituents attached to the cyclopropane ring.

More recently, we have investigated the ring-opening reactions of substituted lithium bromocyclopropylidenoids

SCHEME 2

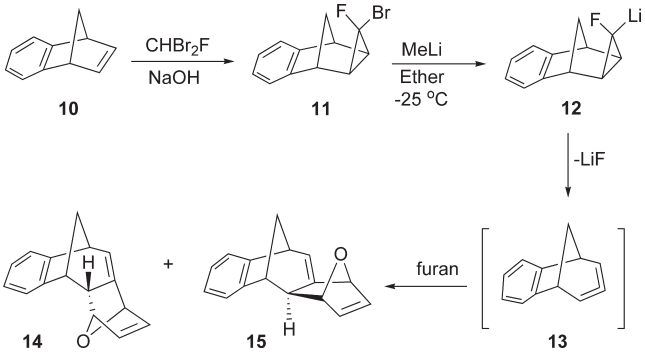
7 to allenes **8** and found that the electron-withdrawing substituents impede the reaction, whereas electron-donating groups lower the barrier to allene formation (Scheme 2).[14] In this paper, we were interested in the ring-opening reaction of the isomeric carbenes ***exo*-9** and ***endo*-9**. Herein, we report the full details of the generation and the ring-opening behavior of ***endo*-9** and computational studies on the ring-opening of carbenoids and free carbenes ***exo*-9** and ***endo*-9** in connection with remote substituents. For the synthesis of *exo*- and *endo*-configured carbenes, norbornadiene skeleton was chosen as a bicyclic alkene. To prevent the addition of the carbenes to two double bonds in norbornadiene, one of these double bonds was protected with the benzene ring.



Results and Discussion

Recently, we reported that the bromofluorocarbene adduct **11** proved to be a reliable precursor for the generation of ***exo*-9**.[15] Treatment of **11** with MeLi in ether at −25 °C in the presence of furan as the trapping reagent afforded two cycloaddition products **14** and **15** in 21% and 24% yield, respectively (Scheme 3).[15]

SCHEME 3



To determine whether free carbene intermediate is initially formed or not, theoretical calculations (B3LYP/6-31(d)) were carried out using density functional theory at both the B3LYP/6-31(d) and B3LYP/ 6-311++G(d,p) levels. We were not able to find any minima for the structure of carbene ***exo*-9**. Isomerization of a carbenoid to an allene may occur readily without the intermediacy of a free carbene.

The double bond in benzonorbornadiene **10** is pyramidalized in the *endo*-direction (*endo* refers to the motion of the vinyl hydrogen to the side of the benzene ring)

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(15) Özen, R.; Balci, M. *Tetrahedron* **2002**, *58*, 3079–3083.

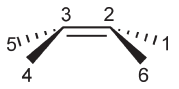
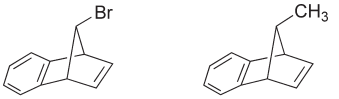


FIGURE 1. Definition of the dihedral angle.

about 5.28°.[16] As the pyramidalization angle, we will use the butterfly angle $\Psi = 180° - |D_1|$.[17] The dihedral angle (D_1) is defined by the bonding sequence 1−2−3−4 (Figure 1).

Benzonorbornadiene (**10**) exclusively undergoes an *exo* attack upon treatment with the electrophiles. This observed *exo*-selectivity[18] in benzonorbornadiene and related compounds such as norbornene and norbornadiene is certainly not surprising, since both electronic and steric factors would be expected to favor attack on the convex face of the pyramidalized double bond. For the generation of ***endo*-9**, the carbene addition (dibromo, dichloro, or bromofluoro carbenes) to the double bond in **10** must occur from the *endo* face of the double bond. To achieve an addition from the *endo* face, the *exo* face of the double bond should be shielded by bulky groups. Therefore, we decided to block the *exo*-face of the double bond with a methyl group. *exo*-Bromobenzonorbornadiene **16**[19] was treated with methyllithium and then with methyl bromide to achieve a substitution reaction.

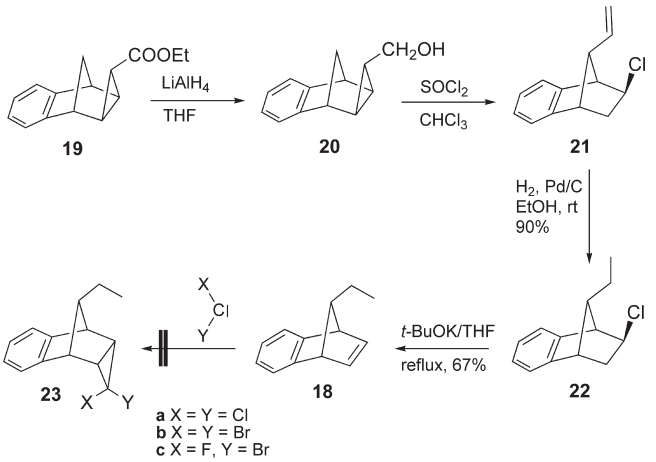


16 **17**

Unfortunately, all efforts to replace the bromine atom in **16** with a methyl group to form **17** failed. Then we synthesized *anti*-ethylbenzonorbornadiene **18** starting from the known ester **19** (Scheme 4).[20] The ester was reduced to alcohol **20** by reaction with $LiAlH_4$ in THF. The alcohol formed was reacted with thionyl chloride in chloroform to give the desired chlorovinyl derivative **21** as described in the literature.[21] Catalytic hydrogenation of **21** with Pd/C in EtOAc gave the reduced product **22** in 90% yield. Dehydrochlorination of **22** with potassium *tert*-butoxide in THF afforded the symmetrical compound **18** in 67% yield.

All efforts to add dichloro-, dibromo-, or fluorobromocarbenes generated under the different conditions to **18** failed to produce either *endo*- or *exo*-addition products. In order to understand the failure of this reaction we calculated the degree of the pyramidalization of the double bond in **18**. Actually, there is no dramatic change in the degree

SCHEME 4



of pyramidalization by going from **10** (butterfly bending angle = 5.20°) to **18** (butterfly bending angle = 4.88°).

After the failure of this reaction we turned our attention to the other substituents, which can decrease the butterfly bending angle of the double bond and block the addition of the carbenes from the *exo*-face of the double bond. The geometries of **24a** and **26** were calculated in order to determine the effect of the bridge substituents on the degree of pyramidalization (see Table 1). The butterfly bending angles of the double bond in **24a** and **26** were found to be 4.07° and 3.83°, respectively. This means that the electron withdrawing groups attached to the bridge carbon atom decrease the degree of pyramidalization and make the double bond more flat. Therefore, we synthesized the bromo derivative **24a** and methoxy derivative **26** and studied the addition of the relevant carbenes to the double bonds.

24a X = Br
24b X = OH

25a X = Br
25b X = OH

First, the monobromide **24a**[22] was prepared by addition of bromine to benzonorbornadiene **10**, followed by the potassium *tert*-butoxide promoted elimination of hydrogen bromide. Wilt and Chenier[23] reported that both *syn*- and *anti*-7-bromobenzonorbornadienes **24a** and **25a** solvolyze in aqueous dioxane with retention of the configuration to yield **24b** and **25b**, respectively. Christol and Nachtigal also reported similar results in the acetolysis of the corresponding chloro derivatives.[24] We tried to solvolyze **24a** in a mixture of methanol and dioxane. The mixture was refluxed for 24 h, but there was no evidence for the formation of **26**. Even in a sealed tube and at elevated temperatures the expected product **26** was not detected. When the solvolysis reaction was performed in the presence of silver nitrate in methanol at 0 °C, the desired product **26** was formed in 48% yield along with the nitrate **27** (Scheme 5).

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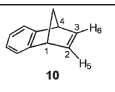
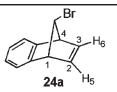
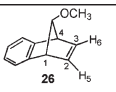
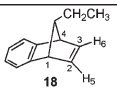
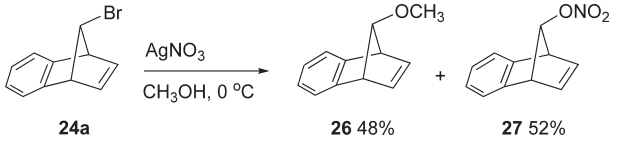
TABLE 1. Pyramidalization Angles of Optimized Molecules at the B3LYP/6-31G(d) and B3LYP/ 6-311++G(d,p) (in Parentheses) Levels

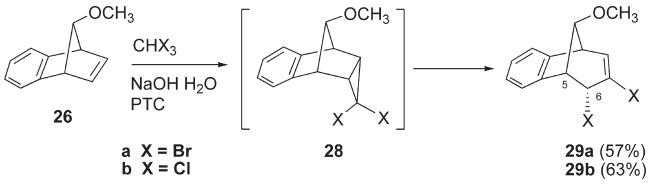
	 10	 24a	 26	 18
Dihedral angle, D_1[a]	-174.80 (-174.73)	-175.93 (-176.10)	-176.17 -(176.32)	-175.12 (-175.18)
Butterfly bending angle, ψ[b]	5.20 (5.27)	4.07 (3.90)	3.83 (3.68)	4.88 (4.82)
Direction of Pyramidalization	*endo*	*endo*	*endo*	*endo*

[a]The dihedral angle (D_1) is defined by the bonding sequence 1−2−3−6. [b]$\Psi = 180° - |D_1|$.

SCHEME 5



SCHEME 6

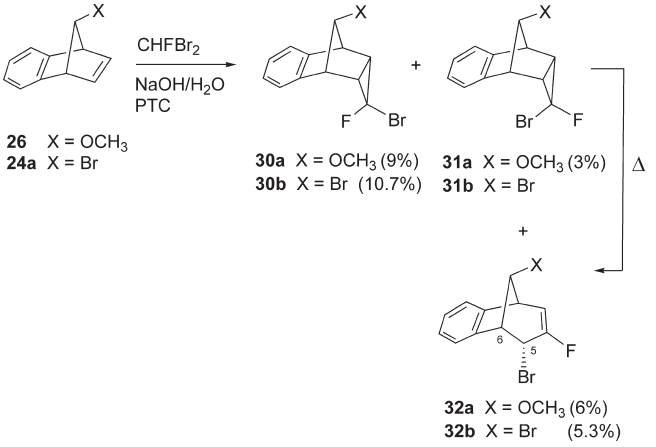


To determine the reactivity of the double bond in **26**, the methoxy derivative was reacted with dibromocarbene, generated from $CHBr_3$ and NaOH under phase-transfer conditions to give **29a** as the only product, with the total yield of 57% (based on unrecovered starting material after two sequential reactions) (Scheme 6).

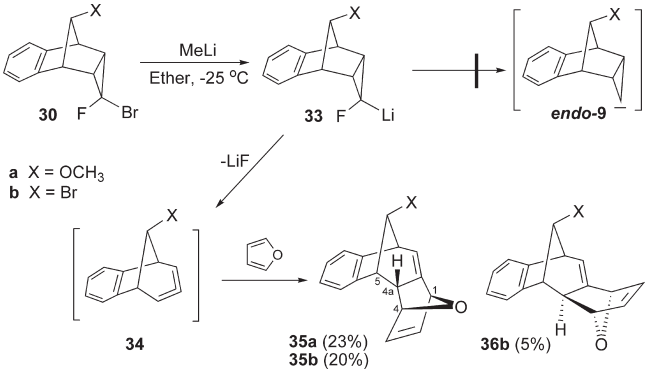
The *endo*-configuration of the allylic bromine atom in **29a** was apparent from the value $J_{5,6} = 4.5$ Hz. The corresponding coupling constant for the *exo*-derivative is about 1.5−2.5 Hz depending on the nature of the halide.[15,25] The *endo*-orientation of the bromine atom implies *endo*-addition of dihalocarbene. The initially formed dibromocyclopropane **28a** undergoes a ring-opening reaction due to the increased strain and steric effects in the molecule, to afford a ring-expanded dihalide **29a**, which has been rationalized in terms of orbital symmetry conservation (Woodward−Hoffmann rules).[26] This reaction involves the cyclopropyl to allyl cation interconversion with participation of cyclopropyl bonding electrons from the face of the cyclopropyl ring opposite that of the departing bromine anion. Collapse of the resulting ion pair then affords the allylic halides **29**. It has been well established that the departing halide is the one in the *endo*-position. Since chlorine is not as good a leaving group as the bromine atom, we decided to add dichloro carbene to **26** which unfortunately also resulted in the formation of the ring-opening product **29b**.

After the failure to isolate halocyclopropane derivatives such as **28a** and **28b** we turned our attention to the addition

SCHEME 7



SCHEME 8



of fluorobromocarbene to **26** to prevent the ring-opening reaction in at least one of the isomers.

Addition of fluorobromocarbene[27] generated from $CHFBr_2$[28] under conditions similar to those for **26** afforded the expected addition products **30a**, **31a**, and the ring-opened product **32a** in a ratio of 3:1:2 and in a total yield of 18% (Scheme 7). When the reaction was carried out with the bromine compound **24a**, similar results were obtained. The isomer **31b** was not observed. We assume that **31b** was isomerized to the ring-opening product **32b** during the distillation process. Compounds **30a** and **30b** were stable at the

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(27) (a) For similar addition, see: Algi, F.; Özen, R.; Balci, M. *Tetrahedron Lett.* **2002**, *43*, 3129–3131.
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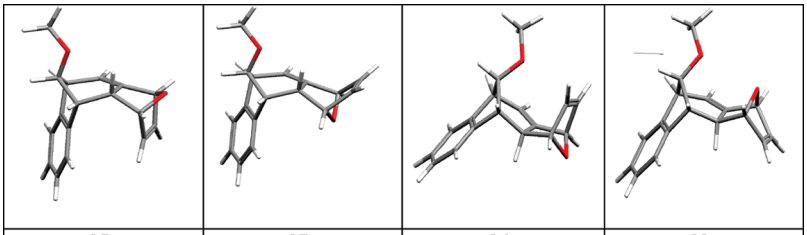


35a	37a	36a	38a
0.00	1.56	4.07	5.30 kcal/mol

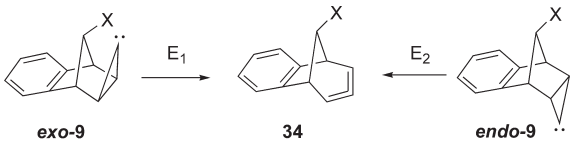
FIGURE 2. Optimized structures of **35a**, **36a**, **37a**, and **38a** at the B3LYP/6-31G(d) level and their relative energies in kcal/mol.

reflux temperature of toluene, whereas the stereoisomer **31a** isomerized to **32a** in quantitative yield.

The symmetrical structures of **30** and **31** were established by the observation of five (six in the case of methoxy derivative) signals in the ^{13}C NMR spectra, as required by the symmetry in the molecule. The *endo*-orientation of allylic bromide in **32** was determined by measuring the coupling constant between the bridgehead proton and the allylic proton as described above.

After successful synthesis and characterization of dihalocyclopropane derivatives **30a** and **30b** they were submitted to the Doering-Moore-Skatebol reaction. Treatment of bromofluorocyclopropanes **30a** and **30b** with MeLi in ether at −25 °C followed by addition of furan at the same temperature as the trapping reagent afforded cycloaddition products **35** and **36** (Scheme 8). In the case of **30a** we isolated a single isomer **35a**, whereas in the case of **30b** two isomers (**35b** and **36b**) were formed. The addition of furan to the initially formed allene may result in the formation of four possible isomers *exo,syn*-**35a** (*endo,exo* refers to the hydrogen, *syn,anti* refers to the oxygen and methylene bridges), *endo,anti*-**36a**, *exo,anti*-**37a**, and *endo,syn*-**38a**. Geometry optimization of the structures **35**−**38** at B3LYP/6-31G(d) level indicate that the dihedral angle between protons H_{4a} and H_5 is 56−59° if the hydrogen H_{4a} has an *exo*-configuration (Figure 2). In case of the *endo*-configuration of the hydrogen atom H_{4a}, the dihedral angle was calculated to be around 89−92°. The measured coupling constant $J_{4a,5}$ = 3.9 and 4.0 Hz clearly indicates the *exo*-configuration of the hydrogen atom H_{4a} in **35a** and **35b**. The configuration of the oxygen bridge was determined by measuring the coupling constant between the hydrogens H_{4a} and H_4. Again, calculations predict that the dihedral angle between the protons H_{4a} and H_4 is around 52−54° in **35** and **36**, whereas this angle is 95−98° in **37** and **38**. The determined coupling constant $J_{4,4a}$ = 3.6 Hz in **35** and **36** supported the suggested configuration of the oxygen bridge. After successful determination of the structures, we propose that furan approaches the double bond of the allene unit mainly from the *endo*-face of the double bond in **34a**. Probably, the methoxyl group hinders the *exo*-addition of the furan ring due to the free rotation of the methoxyl group about the C−C bond. In the case of **34b**, the double bond is attacked from both sides however, the main attack occurs from the *endo*-face. Furthermore, our calculations indicate that the most stable isomer is **35**.

SCHEME 9



a, X=-H
b, X=-F
c, X=-Cl
d, X=-Br
e, X=-OCH_3
f, X=-Me

Computational Methods. All structures were optimized using the density functional theory (DFT)[29] by applying the three-parameter hybrid functional by Becke (B3)[30] and the correlation functional suggested by Lee, Yang, and Parr (LYP).[31] As the basis set we used 6-311++G(d,p) and 6-31G(d) as recommended by Pople et al.,[32] implemented in Gaussian 03.[33] The stationary points were characterized as minima or transition structures by vibrational frequency calculations, and all energies reported here are corrected with unscaled zero-point vibrational energies. Carbenes were considered as singlets because this represents the ground-state of cyclopropylidenes.[34] For molecules that exist in several conformations, the most stable conformer was first determined with conformational analysis at the semiempirical AM1 level by using HyperChem 5.0 program. Natural atomic charges were also calculated within the natural bond orbital (NBO) analysis at the B3LYP/6-311++G(d,p) level.

The geometry optimizations of molecules **10**, **18**, **24a**, and **26** were achieved to understand the effect of substituents on the degree of pyramidalization of fused double bond at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels.

The results in Table 1 indicate that introduction of the electronegative substituents such as bromine and methoxyl group into the bridge carbon (**24a** and **26**) decreases the degree of the double bond from 5.27° to 3.90 and 3.68°, respectively. Probably, the flattening of the double bond about 1.3−1.6° is suitable for addition of the carbene from the *exo*-face of the double bond. These can be investigated effectively at higher level of theory (B3LYP/6-311++G(d,p)).

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TABLE 2. Absolute Energies (*E*, in Hartree/Particle), Number of Imaginary Frequencies (in Brackets), Zero-Point Vibrational Energies (ZPVE, in kcal/mol), and Energies Relative to the Corresponding Carbene Ground State Including Zero-Point Corrections (in kcal/mol) for *exo*-9a−f and *endo*-9a−f and Related Transition States at B3LYP/6-311++G(d,p)

	E	ZPVE	rel energy
***exo*-9a**	[a]		
***endo*-9a**	−463.03943 [0]	111.5	
***exo*-9b**	−562.32830 [0]	107.1	0.0
***endo*-9b**	−562.31880 [0]	106.6	6.0
***exo*-9c**	−922.68585 [0]	106.5	0.0
***endo*-9c**	−922.67430 [0]	105.7	7.3
***exo*-9d**	−3036.60806 [0]	106.1	0.0
***endo*-9d**	−3036.59516 [0]	105.3	8.1
***exo*-9e**	−577.58157 [0]	133.5	
***endo*-9e**	[a]		
***exo*-9f**	−502.35091 [0]	129.2	0.0
***endo*-9f**	−502.33803 [0]	128.8	8.1
TS (*exo*-9a→34a)	[a]		[b]
TS (*endo*-9a→34a)	−463.03955 [1]	111.4	−0.1 [b]
TS (*exo*-9b→34b)	−562.32796 [1]	106.8	0.2 [b]
TS (*endo*-9b→34b)	−562.31892 [1]	106.5	−0.08 [b]
TS (*exo*-9c→34c)	−922.68381 [1]	105.9	1.3 [b]
TS (*endo*-9c→34c)	−922.67430 [1]	105.6	0.0 [b]
TS (*exo*-9d→34d)	−3036.60477 [1]	105.5	2.1 [b]
TS (*endo*-9d→34d)	−3036.59509 [1]	105.2	−0.04 [b]
TS (*exo*-9e→34e)	−577.57216 [1]	131.9	5.9 [b]
TS (*endo*-9e→34e)	[a]		[b]
TS (*exo*-9f→34f)	−502.34953 [1]	129.1	0.9 [b]
TS (*endo*-9f→34f)	−502.33813 [1]	128.7	−0.06 [b]

[a]Isomerization to allene occurs during optimization. [b]Energies relative to ***exo*-9a−f** and ***endo*-9a−f**, respectively.

As discussed above, the ethyl group does not change the pyramidalization very much. Therefore, all efforts to add carbenes to **18** failed.

Initially, we performed B3LYP/6-311++G** calculations on carbenes ***exo*-9a** and ***endo*-9a** and related transition states for their rearrangements to allene **34a** (Scheme 9) and found that the cyclopropylidene structure ***exo*-9a** cannot be found as a minimum (Table 2).

Instead, all attempts to locate a minimum for structure ***exo*-9a** lead directly to the corresponding allene **34a**. Accordingly, no **TS *exo*-9a** structure was found. The carbene ***exo*-9a** has a rigid and boatlike structure and can undergo ring-opening without conformational changes. This finding is in good agreement with the value of 0.2 kcal/mol determined for the ring-opening process of the carbene formed from **1**.[12] However, the structure ***endo*-9a** was minimized and the activation barrier for the ring-opening of ***endo*-9a** to **34a** was determined to be −0.1 kcal/mol relatively low for this type of reaction.

Furthermore, we investigated the influence of various substituents attached at the bridge carbon on these rearrangements. Energy results in Table 2 indicate that all substituents (X = F, −Cl, −Br, $-OCH_3$, and −Me) stabilize the carbene structures ***exo*-9**'s, which have lower energy than ***endo*-9**'s in the range of 6.0−8.1 kcal/mol. The calculated activation barriers for rearrangement of *exo*- and *endo*-carbenes to allene are generally low. However, the methoxy group retards the ring-opening of carbene ***exo*-9e** to **34e** with the activation barrier of 5.9 kcal/mol more effectively than the other groups. The calculated distances between the carbenic center and halogen and oxygen atoms for **exo9b**, ***exo*-9c**, ***exo*-9d**, and ***exo*-9e** are 247, 252, 253, and 173 pm, respectively. The results indicate that there is a strong electronic interaction between the nonbonding electrons of the oxygen atom and the carbene carbon in ***exo*-9e**. However, the minimized structure for the carbene ***endo*-9e** as well as the related transition structure for the rearrangement to allene could not be optimized.

TABLE 3. NBO Charges on the Carbenic Carbon Atoms of *exo*-9b−f, *endo*-9b−f, and Their Transition States for Corresponding Allene Isomerization at the B3LYP/6-311++G(d,p) Level

structure	charge on carbenic carbon	transition structure	charge on carbenic carbon
***exo*-9a**		**TS *exo*-9a**	
***exo*-9b**	0.149	**TS *exo*-9b**	0.029
***exo*-9c**	0.057	**TS *exo*-9c**	−0.017
***exo*-9d**	−0.008	**TS *exo*-9d**	−0.034
***exo*-9e**	−0.023	**TS *exo*-9e**	−0.046
***exo*-9f**	0.046	**TS *exo*-9f**	−0.025
***endo*-9a**	0.195	**TS *endo*-9a**	0.159
***endo*-9b**	0.187	**TS *endo*-9b**	0.149
***endo*-9c**	0.201	**TS *endo*-9c**	0.135
***endo*-9d**	0.202	**TS *endo*-9d**	0.128
***endo*-9e**		**TS *endo*-9e**	
***endo*-9f**	0.182	**TS *endo*-9f**	0.164

NBO is a method for determining the charge distribution in molecules based on creating atomic natural orbitals.[35] Analysis of NBO charges on the carbenic carbon for ***exo*-9a−f**, ***endo*-9a−f**, and their transition states given in Table 3 reveals that substituents attached to the bridge carbon interact with the carbenic carbon of cyclopropylidenes ***exo*-9b−f** and enrich them with electrons. Moreover, the stabilization resulting from electron donation from the oxygen lone pair into the LP* of the carbene occurs more effectively than the other substituents. The bridging interaction of a halogen lone pair with a carbenic site makes an important stabilizing contribution to **34b−d**. However, electrons of carbenic carbon of ***endo*-9a−f** fluctuating with substituents were not observed.

The delocalization can also be tracked by a natural bond orbital (NBO) analysis. For ***exo*-9b−f**, different deviations from the Lewis structure are calculated. All valence carbon atom NBOs are occupied by more than 1.95 e^- with the exception of aromatic ring carbon atoms with occupancy of 1.67 e^-. However, lone pairs (LP) of halogen and oxygen atoms are differently populated for ***exo*-9b**, ***exo*-9c**, ***exo*-9d,** and ***exo*-9e** with occupancies of (1.99, 1.97, 1.94 e^-), (1.99, 1.97, 1.82 e^-), (1.99, 1.97, 1.75 e^-), and (1.96, 1.68 e^-), respectively. Accordingly, the non-Lewis lone pairs NBO (LP*) at the carbenic centers for ***exo*-9b**, ***exo*-9c**, ***exo*-9d**, and ***exo*-9e** are partly filled with occupancies of 0.22, 0.30, 0.36, and 0.35 e^-, respectively. A second-order perturbation analysis of the Fock matrix estimates the orbital interaction energies between the donor NBOs (LPs of halogen and oxygen atoms) and the acceptor NBO (LP* of carbenic centers) for ***exo*-9b**, ***exo*-9c**, ***exo*-9d**, and ***exo*-9e**, to be 6.6, 31.0, 48.4, 150.7 kcal/mol, respectively. The results depict that the strongest donating interaction to the LP* carbene carbon comes from the lone pair of the oxygen atom. In ***exo*-9f**, carbene is mainly stabilized by donating interactions between the C−H bond of methyl group (occupied by 1.87 e^-) and the LP* at the carbenic center (occupied by 0.30 e^-). Their orbital interaction energy is 23.4 kcal/mol. On the contrary, it is

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found that there is no drastic effects of substituents attached to the bridge carbon atom of benzonorbornadiene on the stability of ***endo*-9a−f** carbene by a second-order perturbation theory analysis of the Fock matrix.

Experimental Section

(1*S*,2*R*,4*R*,9*R*)-*rel*-2-Chloro-9-ethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene (22). Into a 50 mL, two-necked, round-bottomed flask were placed Pd/C (10%) (100 mg) catalyst and **21**[20] (1.0 g, 4.88 mmol) in EtOAc (20 mL). One of the necks was attached to hydrogen gas with a three-way stopcock, and the other neck was capped with a rubber septum. The reactants were degassed and flushed with hydrogen gas while stirring magnetically. After 4 h, the solution was decanted from the catalyst. Evaporation of the solvent provided **22** as a colorless liquid (0.9 g, 4.35 mmol, 90%). For analytical purposes the residue was chromatographed on silica gel (20 g) eluting with hexane: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.00 (m, 4H), 3.79 (dd, J = 7.1 and 3.8 Hz, 1H), 3.40 (br s, 1H), 3.22 (br d, J = 3.4 Hz, 1H), 2.30 (dt, A-part of the AB system, J = 13.4, 3.8 Hz, 1H), 2.11−2.02 (m, 2H), 1.87−1.74 (dqui, A-part of the AB system, J = 14.6, 7.3, 1H), 1.74−1.60 (dqui, B-part of the AB system, J = 14.6, 7.3, 1H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 146.4, 126.5, 126.2, 121.4, 121.1, 63.8, 58.7, 54.5, 47.2, 37.3, 22.7, 12.8; IR (KBr, cm^{-1}) 2968, 2872, 1463, 1378, 1296, 1265, 1013, 964, 888, 747. Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.53; H, 7.31. Found: C, 75.86; H, 7.64.

***anti*-9-Ethyl-1,4-dihydro-1,4-methanonaphthalene (18).** To a stirred solution of **22** (0.9 g, 4.35 mmol) in dry THF (35 mL) was added *t*-BuOK (2.44 g, 21.75 mmol) at reflux temperature. The mixture was stirred for 3 days. After evaporation of the solvent, H_2O (40 mL) was added. The mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layer was washed with saturated aq $NaHCO_3$ solution and dried ($CaCl_2$). After evaporation of the solvent, the residue was submitted to column chromatography eluting with hexane. Compound **18** was obtained as a colorless liquid (0.5 g, 2.91 mmol, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−6.84 (AA′BB′ system, 4H), 6.56 (s, 2H), 3.66 (d, J = 1.3 Hz, 2H), 2.56 (t, J = 7.4 Hz, 1H), 1.46 (qui, J = 7.4 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 139.4, 124.0, 121.2, 84.1, 53.7, 21.5, 12.6; IR (KBr, cm^{-1}) 3068, 2960, 1453, 1377, 1318, 1299, 789, 742, 697. Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.96; H, 8.43.

Solvolysis of 7-*anti*-Bromobenzonorbornadiene 24a with Silver Nitrate. To a magnetically stirred solution of $AgNO_3$ (1.8 g, 10.6 mmol) in 100 mL of methanol cooled to 0 °C was added dropwise a solution of **24a** (2.3 g, 10.4 mmol) in 50 mL of methanol over 1 h. After the addition was completed, the solution was allowed to warm to room temperature and stirred for 5 h at that temperature. Then, the silver bromide was filtered off and washed well with ether. Water was added to the filtrate and extracted with ether. The combined organic phases were washed with water, dried, and concentrated. The oily residue was passed through silica gel (75 g) eluting with *n*-hexane. The nitrate (**27**) was isolated as the first fraction. Eluting with hexane−ethyl acetate (10:1) gave the desired compound **26** as colorless liquid (0.86 g, 48%).

Data for *anti*-9-nitrooxy-1,4-dihydro-1,4-methanonaphthalene (27): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.13 (AA′BB′ system, 4H), 6.66 (s, 2H), 4.90 (s, 1H), 4.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 138.1, 126.4, 123.2, 101.7, 52.6; IR (NaCl, cm^{-1}) 3076, 3007, 2898, 1712, 1635, 1455, 1357, 1309, 1284, 1181, 1021, 987, 919, 867, 795, 750, 704, 620. Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.90; H, 4.40; N, 6.67.

Data for *anti*-9-methoxy-1,4-dihydro-1,4-methanonaphthalene (26): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.02 (AA′BB′ system, 4H), 6.63 (s, 2H), 3.98 (s, 2H), 3.74 (s, 1H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 137.8, 125.5, 122.7, 107.4, 57.0, 53.8; IR (KBr, cm^{-1}) 3071, 2985, 2930, 2881, 2826, 1632, 1568, 1455, 1361, 1361, 1310, 1232, 1213, 1003, 899, 829, 789, 745, 693; MS m/z 171 (M − 1)$^+$,73), 155 (19), 141 (100), 129 (100), 115 (79), 102 (56), 77 (47), 63(47), 51(48). Anal. Calcd. for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.51; H, 6.94.

Addition of Dibromocarbene to *anti*-7-Methoxybenzonorbornadiene (26). A mixture of *anti*-7-methoxybenzonorbornadiene **26** (3.1 g, 18 mmol), 15 mL of $CHBr_3$, 50% NaOH solution (20 mL), and benzyltriethylammonium chloride (0.5 g, 2.2 mmol) was vigorously stirred at 50 °C for 5 h. The mixture was diluted with water and extracted with ether, and the combined extracts were washed with water, dried, and evaporated. Unreacted alkene was recovered by distillation (97−99 °C/5 mm), and the distillation residue was saved. The recovered alkene **26** was resubmitted to the same reaction, using the same quantities of $CHBr_3$, NaOH, and phase-transfer catalyst. Workup was as before, and distillation afforded unchanged *anti*-7-methoxybenzonorbornadiene **26** (0.8 g). The combined distillation residues were submitted to rapid silica gel (60 g) filtration eluting with hexane−ethyl acetate (10:1) to yield 2.62 g (57% based on unrecovered starting material) **29a** as the sole product, which was crystallized from hexane−CH_2Cl_2 to give colorless crystals, mp 165−166 °C.

Data for (5*R*,6*R*,9*R*,10*R*)-*rel*-6,7-dibromo-10-methoxy-6,9-dihydro-5,9-methano-5*H*-benzocycloheptene (29a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.44 (m, 1H), 7.21−7.18 (m, 2H), 7.14−7.12 (m, 1H), 6.43 (d, J = 7.0 Hz, 1H), 5.09 (d, J = 4.9 Hz, 1H), 4.04 (t, J = 4.0 Hz, 1H), 3.67 (t, J = 4.6 Hz, 1H), 3.48 (1H, overlapped with -OCH_3 resonance), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 139.2, 132.4, 128.5, 128.3, 127.1, 122.3, 121.9, 86.3, 57.3, 53.7, 51.7, 44.9; IR (KBr) 2957, 2924, 2879, 2825, 1638, 1451, 1338, 1301, 1261, 1202, 1144, 1107, 1019, 993, 963, 946, 843, 795, 755; MS m/z 346/344/342 (M$^+$, 3), 263/265 (79), 219 (39), 184 (100), 169 (48), 140 (83), 115 (53), 88 (19), 75 (29), 62 (31). Anal. Calcd for $C_{13}H_{12}Br_2O$: C, 45.38; H, 3.52. Found: C, 45.26; H, 3.37.

Addition of Dichlorocarbene to *anti*-7-Methoxybenzonorbornadiene (26). A mixture of **26** (3.4 g, 19.8 mmol), chloroform (15 mL), 50% NaOH solution (20 mL), and benzyltriethylammonium chloride (0.5 g, 2.2 mmol) was vigorously stirred at 40 °C for 5 h. The reaction mixture was worked up as described above. Crystallization from hexane/dichloromethane gave **29b** as colorless crystals (3.56 g, 63%, based on unrecovered starting material), mp 128−129 °C.

Data for (5*R*,6*R*,9*R*,10*R*)-*rel*-6,7-dichloro-10-methoxy-6,9-dihydro-5,9-methano-5*H*-benzocycloheptene (29b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 1H), 7.24−7.22 (m, 2H), 7.19−7.16 (m, 1H), 6.22 (d, J = 7.1 Hz, 1H), 4.89 (d, J = 5.1 Hz, 1H), 4.10 (t, J = 4.0 Hz, 1H), 3.66 (t, J = 4.6 Hz, 1H), 3.54 (dd, J = 4.2, 6.6 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 138.3, 130.6, 128.6, 128.5, 128.2, 127.2, 122.3, 86.6, 59.0, 57.3, 50.9, 43.7; IR (KBr, cm^{-1}) 2951, 2932, 2834, 1620, 1466, 1348, 1211, 1117, 1011, 891, 794, 762, 695; MS m/z 254 (M$^+$, 39), 219 (100), 203 (32), 187 (60), 177 (100), 162 (75), 152 (100), 139 (100), 127 (38), 115 (98), 102 (20), 89 (40), 75 (51), 63 (60), 45 (44). Anal. Calcd for $C_{13}H_{12}Cl_2O$: C, 61.20; H, 4.74. Found: C, 61.12; H, 4.71.

Addition of Fluorobromocarbene to *anti*-7-Methoxybenzonorbornadiene (26). To a magnetically stirred solution of *anti*-7-methoxybenzonorbornadiene (**26**) (5.8 g, 33.7 mmol), benzyltributylammonium chloride (1.0 g, 4.4 mmol), and dibromofluoromethane (10 g, 52 mmol) heated to 50 °C was added dropwise a solution of 50% NaOH (20 mL) over 4 h. After the completion of addition, the reaction mixture was stirred for 2 h.

Then, the solution was allowed to cool to room temperature. The mixture was diluted with water and thoroughly extracted with methylene chloride, and the combined extracts were washed with water, dried, and concentrated. Unreacted alkene was recovered by distillation (97−99 °C/5 mm). The recovered alkene **26** was resubmitted again to the same reaction, using the same quantities of $CHBr_2F$, NaOH, and phase-transfer catalyst. Workup was as before and distillation afforded unchanged *anti*-7-methoxybenzonorbornadiene (**26**) (3.9 g). The combined distillation residues were submitted to rapid silica gel filtration (120 g) eluting with hexane−ethyl acetate (10:1). Three products were isolated **30a** (0.28 g, 9%), **31a** (0.094 g, 3%), and **32a** (0.19 g, 6%) in that order from the column chromatography.

Data for (1a*S*,2*S*,7*R*,7a*R*)-1-*exo*-bromo-1-fluoro-8-methoxy-1a,2,7,7a-tetrahydro-2,7-methano-1*H*-cyclopropa[*b*]naphthalene (30a): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.11 (AA′BB′ system, 4H), 3.83 (s, 1H), 3.70 (quasi d, A-part of AA′BB′ system, 2H), 3.37 (s, 3H), 2.57 (quasi t, B-part of AA′BB′ system, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, J_{CF} = 3.4 Hz, 2C), 127.3 (2C), 122.9 (2C), 107.0 (d, J_{CF} = 4.6 Hz), 93.0 (d, J_{CF} = 340 Hz), 56.7 (2C), 48.6 (2C), 37.3 (d, J_{CF} = 13.2 Hz, 2C); IR (NaCl) 2985, 2928, 2826, 1642, 1561, 1458, 1357, 1211, 1106, 1041, 994, 798, 718, 592.; MS *m*/*z* 282/284 (M^+, 7%), 262/264 (23), 247/249 (33), 239 (10), 219/221 (24), 203 (39), 189 (12), 171 (80), 159 (100), 139 (49), 128 (85), 115 (26), 95 (43), 81 (37), 67 (19). Anal. Calcd for $C_{13}H_{12}BrFO$: C, 55.15; H, 4.27. Found: C, 55.09; H, 4.15.

Data for (1a*S*,2*S*,7*R*,7a*R*)-1-*endo*-bromo-1-fluoro-8-methoxy-1a,2,7,7a-tetrahydro-2,7-methano-1*H*-cyclopropa[*b*]naphthalene (31a:). colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.16 (A-part of AA′BB′ system, 2H), 7.09−7.06 (B-part of AA′BB′ system, 2H), 3.81 (s, 2H), 3.20 (s, 3H), 3.19 (s, 1H), 1.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 126.7, 122.4, 97.4 (d, J_{CF} = 351 Hz), 86.6, 56.9, 48.9 (d, J_{CF} = 2 Hz), 42.0 (d, J_{CF} = 16 Hz,); IR (NaCl, cm^{-1}) 3030, 2975, 2927, 2872, 2825, 1642, 1466, 1396, 1371, 1250, 1217, 1195, 1015, 997, 949, 894, 802, 755, 722; MS *m*/*z* 284/282 (M^+, 4) 219 (3), 203 (15), 159 (100), 133 (23), 115 (7). Anal. Calcd for $C_{13}H_{12}BrFO$: C, 55.15; H, 4.27. Found: C, 55.07; H, 4.18.

Data for (5*S*,6*S*,9*S*,10*S*)-*rel*-6-bromo-7-fluoro-10-methoxy-6,9-dihydro-5,9-methano-5*H*-benzocycloheptene (32a): colorless crystals; mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 1H), 7.23−7.14 (m, 3H), 5.63 (dd, J = 12.4 and 7.3 Hz, 1H), 5.07 (d, J = 5.2 Hz, 1H), 3.95 (bs, 1H), 3.64 (dt, J = 11.9 and 5.2 Hz, 1H), 3.49 (ddd, J = 3.5, 7.1, and 10.5 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (d, J_{CF} = 259 Hz), 147.1, 138.2, 127.9, 127.8, 126.4, 121.9, 106.7 (d, J_{CF} = 14.3 Hz), 85.8 (d, J_{CF} = 1.3 Hz), 56.7, 50.0 (d, J_{CF} = 4.3 Hz), 45.1 (d, J_{CF} = 21.3 Hz), 40.6 (d, J_{CF} = 6.3 Hz); IR (KBr, cm^{-1}) 2981, 2922, 2761, 1643, 1504, 1361, 1119, 997, 827, 754, 698; MS *m*/*z* 284/282 (M^+, 56), 237 (9), 219(16), 203 (100), 171 (81), 132 (37), 114 (13), 102 (7). Anal. Calcd for $C_{13}H_{12}BrFO$: C, 55.15; H, 4.27. Found: C, 55.13; H, 4.21.

Addition of Fluorobromocarbene to *anti*-7-Bromobenzonorbornadiene (24a). To a magnetically stirred solution of *anti*-7-bromobenzonorbornadiene (**24a**) (10.0 g, 45.23 mmol), benzyltributylammonium chloride (1.0 g, 2.8 mmol), and dibromofluoromethane (20 g, 104 mmol) heated to 50 °C was added dropwise a solution of 60% NaOH (30 mL) over 4 h. After the completion of addition, the reaction mixture was stirred for 2 h. Workup was carried out as described above. Unreacted alkene was recovered by distillation (110−115 °C/5 mm), which was submitted twice to the same reaction conditions. At the end of three sequential reactions, 6.1 g of the starting material was recovered. The combined distillation residues were submitted to rapid silica filtration using silica gel (120 g) eluting with hexane. Three products were isolated in the order **24a** (700 mg), **30b** (512 mg, 10.7%), and **32b** (250 mg, 5.3%) from the column chromatography.

Data for (1a*S*,2*S*,7*R*,7a*R*)-1-*exo*,8-dibromo-1-fluoro-1a,2,7,7a-tetrahydro-2,7-methano-1*H*-cyclopropa[*b*]naphthalene (30b): colorless crystal; mp 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.02 (AA′BB′ system, 4H), 4.22 (s, 1H), 3.71 (bs, 2H), 2.71 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0 (d, J = 4.1 Hz), 127.5, 122.0, 94.7 (d, J = 339.7 Hz), 72.4 (d, J = 7.5 Hz), 51.9, 37.8 (d, J = 13.3 Hz); IR (KBr, cm^{-1}) 3042, 2996, 1461, 1365, 1230, 1193, 1006, 956, 907, 783, 737. Anal. Calcd for $C_{12}H_9Br_2F$: C, 43.41; H, 2.73. Found: C, 43.43; H, 2.78.

Data for (5*S*,6*S*,9*S*,10*S*)-*rel*-6,10-dibromo-7-fluoro-6,9-dihydro-5,9-methano-5*H*-benzocycloheptene (32b): colorless crystals;, mp 76−78 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.16 (m, 4H), 5.73 (dd, J = 12.0, 7.2 Hz, 1H), 5.20 (d, J = 5.2 Hz, 1H), 4.56 (t, J = 4.0 Hz, 1H), 3.66 (q-like, J = 5.2 Hz, 1H), 3.59 (dt, J = 7.2, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, J = 260.5 Hz), 147.8, 138.5, 128.8, 127.9, 127.2, 121.6, 109.3 (d, J = 15.0 Hz), 54.3, 52.5 (d, J = 7.1 Hz), 45.2, 44.9; IR (KBr) 2947, 1670, 1465, 1357, 1283, 1236, 1132, 1100, 951, 862, 797, 759. Anal. Calcd for $C_{12}H_9Br_2F$: C, 43.41; H, 2.73. Found: C, 43.22; H, 2.69.

Reaction of 30a with MeLi. To a magnetically stirring solution of **30a** (0.83 g, 2.93 mmol) in ether was added dropwise a solution of 1.6 M MeLi (7.20 mmol, 4.5 mL) in ether over 10 min at −25 °C under nitrogen atmosphere. Then, furan (0.2 g, 3 mmol) was added dropwise over 5 min at the same temperature. The reaction mixture was stirred continuously and allowed to warm to room temperature over 4 h. The reaction mixture was quenched carefully with water. The mixture was extracted with ether, and the organic layer was washed with saturated NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The oily residue was submitted to a neutral aluminum oxide column (100 g, grade III) eluting with hexane-ethyl acetate (10:1) to give **35a** as the only product (0.17 g, 23%): colorless crystals; mp 93.5−94.7 °C.

Data for (1*S*,4*R*,4a*R*,5*R*,10*S*,12*R*)-*rel*-1,4-epoxy-5,10-methano-12-methoxy-4,4a,5,10-tetrahydro-1*H*-dibenzo[*a*,*d*]cycloheptene (35a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (bd, J = 6.6 Hz, 1H), 7.14−7.10 (m, 3H), 6.28 (dd, A-part of AB-system, J = 5.6 and 1.5 Hz, 1H), 6.09 (dd, B-part of AB-system, J = 5.6 and 1.3 Hz, 1H), 5.78 (dd, J = 7.1 and 2.3 Hz, 1H), 5.04 (d, J = 3.7 Hz, 1H), 5.02 (bs, 1H), 3.86 (t, J = 3.9 Hz, 1H), 3.57 (dd, J = 7.1 and 4.0 Hz, 1H), 3.16 (bs, 1H), 3.15 (s, 3H), 2.46 (t, J = 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.1, 142.6, 134.7, 130.5, 127.1, 126.7, 123.2, 122.1, 117.3, 84.2, 81.8, 80.3, 55.5, 44.4, 42.7, 41.0; IR (KBr, cm^{-1}) 2975, 2931, 2866, 2732, 1731, 1653, 1501, 1372, 1125, 1009, 833, 778, 748, 704; MS *m*/*z* 252 (M^+, 8), 220 (38), 191 (100), 178 (62), 165 (46), 152 (22), 128 (11), 115 (19), 95 (15), 81 (17), 67 (10). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.81; H 6.28.

Reaction of 30b with MeLi. To a magnetically stirring solution of **30b** (500 mg, 1.51 mmol) in ether was added dropwise a solution of 1.6 M MeLi (5.28 mmol, 3.30 mL) in ether over a period of 10 min at −25 °C under nitrogen atmosphere. Then furan (250 mg, 3.70 mmol) was added dropwise over 5 min at the same temperature. The reaction mixture was stirred continuously and allowed to warm to room temperature over 4 h. The reaction mixture was quenched carefully with water and worked up as described above. The oily residue was submitted to column chromatography (120 g SiO_2) eluting with CH_2Cl_2/hexane (8:92) to give **35b** (85 mg, 20%) and **36b** (29 mg, 5%), consecutively.

Data for (1*S*,4*R*,4a*R*,5*R*,10*S*,12*R*)-*rel*-1,4-epoxy-5,10-methano-12-bromo-4,4a,5,10-tetrahydro-1*H*-dibenzo[*a*,*d*]cycloheptene (35b): colorless crystals from ether; mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.2 Hz, 1H), 7.09 (dt, J = 7.2, 1.2 Hz, lH), 7.0 (dt, J = 7.2, 1.2 Hz, 1H), 6.85 (d, J = v 7.2 Hz, 1H), 5.50 (dd, A-part of AB system J = 5.6, 1.6, 1H), 5.44 (m, 1H), 5.36 (dd, B-part of AB system, J = 5.6, 1.2 Hz, 1H), 5.03 (d,

J = 0.8 Hz, 1H), 4.92 (d, J = v 3.6 Hz, 1H), 4.45 (t, J v = 4.4 Hz, 1H), 3.54 (t, J = 4.4 Hz, 1H), 3.49 (t, J = 4.0 Hz, 1H), 3.27 (q-like, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 138.1, 134.1, 130.3, 130.0, 127.6, 125.6, 125.1, 119.4, 116.9, 80.4, 79.9, 53.0, 48.1, 45.4, 41.2; IR (KBr, cm^{-1}) 3004, 2931, 2895, 1462, 1308, 1283, 1287, 891, 848, 820, 777. Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.35. Found: C, 64.04; H 4.43.

Data for (1*R*,4*S*,4a*S*,5*R*,10*S*,12*R*)-*rel*-1,4-epoxy-5,10-methano-12-bromo-4,4a,5,10-tetrahydro-1*H*-dibenzo[*a*,*d*]cycloheptene (36b): colorless crystals; mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.13 (m, 4H), 6.32 (dd, A-part of AB system, J = 5.6, 1.6 Hz, 1H), 6.30 (dd, B-part of AB system, J = 5.6, 1.2 Hz, 1H), 5.89 (dd, J = 6.8, 2.8, 1H), 5.12 (s, 1H), 5.09 (d, J = 4.0 Hz, 1H), 4.46 (t, J = 3.6, 1H), 3.65 (dd, J = 6.8, 3.6, 1H), 3.33 (d, J = 3.6 Hz, 1H), 2.60 (t, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 143.3, 139.5, 134.1, 130.9, 126.5, 126.3, 121.5, 119.8, 115.9, 80.5, 79.4, 48.55, 44.6, 44.1, 43.3; IR (KBr, cm^{-1}) 2923, 1463, 1378, 1262, 1141, 724. Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.35. Found: C, 64.18; H 4.53.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds and Cartesian coordinates and energy values for all the optimized structures and transition states at the B3LYP/6-311++G (d,p) level. This material is available free of charge via the Internet at http://pubs.acs.org.