Tetrahedron 69 (2013) 3961–3970

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of small ring-containing conjugated dienes via the coupling reaction of cyclopropyl- and cyclobutylmagnesium carbenoids with α-sulfonylallyllithiums

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ARTICLE INFO

Article history:
Received 9 February 2013
Received in revised form 27 February 2013
Accepted 5 March 2013
Available online 13 March 2013

Keywords:
Allylidenecycloalkane
Conjugated diene
Coupling reaction
[4+2] Cycloaddition
Magnesium carbenoid
DFT calculation

ABSTRACT

A variety of allylidenecyclopropanes and allylidenecyclobutanes were synthesized via the coupling reaction of cyclopropyl- and cyclobutylmagnesium carbenoids with α-sulfonylallyllithiums. Small ring cycloalkylmagnesium carbenoids were generated from aryl 1-chlorocycloalkyl sulfoxides and a Grignard reagent, and the resultant magnesium carbenoids were reacted with α-sulfonylallyllithiums, which were prepared via the deprotonation of *p*-tolyl vinyl sulfones or allyl *p*-tolyl sulfones. Allylidenecycloalkanes were obtained in moderate to good yields, and the Diels–Alder reaction of allylidenecycloalkanes with tetracyanoethylene afforded spirocyclic compounds. The coupling reaction of acyclic alkylmagnesium carbenoids with α-sulfonylallyllithiums provided conjugated dienes as mixtures of geometric isomers. The results from DFT calculations showed that small ring cycloalkylmagnesium carbenoids have a long C–Cl bond and expanded bond angles on the backside of the C–Cl bond relative to those of the corresponding chlorocycloalkanes.

1. Introduction

Small ring hydrocarbons play an important role in organic synthesis.[1] Among these compounds, conjugated dienes bearing a small ring at the terminal position, such as allylidenecyclopropanes and allylidenecyclobutanes, are versatile synthetic intermediates, especially as strain-activated dienes in the Diels–Alder reaction.[2,3] Although several synthetic methods, such as the Wittig or Peterson olefination-based approaches, have previously been reported,[2–7] small ring-containing conjugated dienes are still not readily accessible. The preparation of small ring cycloalkylphosphonium halides from cycloalkyl halides and phosphines is difficult because of the poor reactivity of secondary small ring cycloalkyl halides.[8] In addition, the reaction of small ring cycloalkylidene phosphoranes with carbonyl compounds often proceeds with low efficiency.[5,9] Multi-functionalized small ring cycloalkanes are necessary for the generation of α-silylcycloalkyl anions via the Peterson olefination.[6]

We have developed an efficient method for the generation of magnesium carbenoids **5**–**8** using α-chloro-substituted sulfoxides **1**–**4** as key precursors (Scheme 1), and various types of synthetic transformations have been achieved taking advantage of the diverse reactivity of magnesium carbenoids.[10] In particular, small ring cycloalkylmagnesium carbenoids **6** and **7** can be used as electrophiles,[11,12] whereas small ring cycloalkyl halides are less reactive toward nucleophilic substitution.[13] In addition, we found that magnesium carbenoids **5**–**8** can be coupled with carbon nucleophiles, which have a leaving group on the carbanion center, through a C=C double bond.[11a,b,12b,14] For example, the reaction of magnesium alkylidene carbenoids **5** with α-sulfonylallyllithiums yielded a variety of vinylallenes **9** in good yields (Scheme 1).[14d] Because general methods for the synthesis of sulfoxides **2** and **3** have been establised[11,12] and both *p*-tolyl vinyl sulfones **13** and allyl *p*-tolyl sulfones **14** can be used as α-sulfonylallyl anion sources,[14d] the coupling reaction of small ring cycloalkylmagnesium carbenoids **6** and **7** with α-sulfonylallyllithiums will provide a novel route for the synthesis of small ring-containing conjugated dienes. Herein, we report the synthesis of allylidenecyclobutanes **10** and allylidenecyclopropanes **11** via the coupling reaction of cyclobutyl-**6** and cyclopropylmagnesium carbenoids **7** with α-sulfonylallyllithiums.

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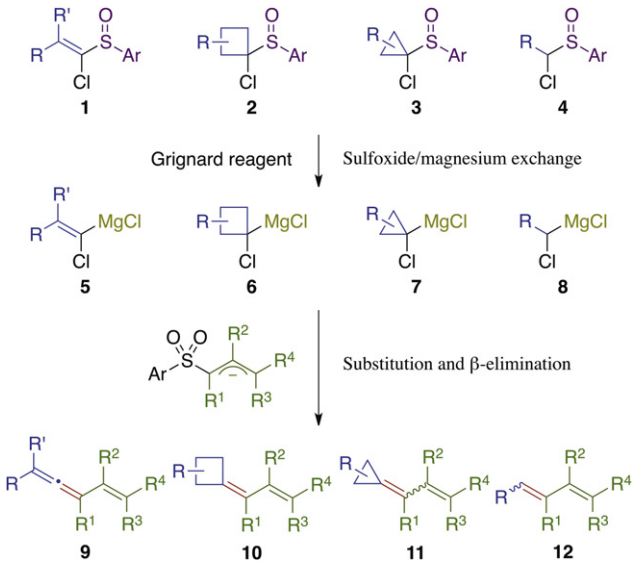
http://dx.doi.org/10.1016/j.tet.2013.03.019



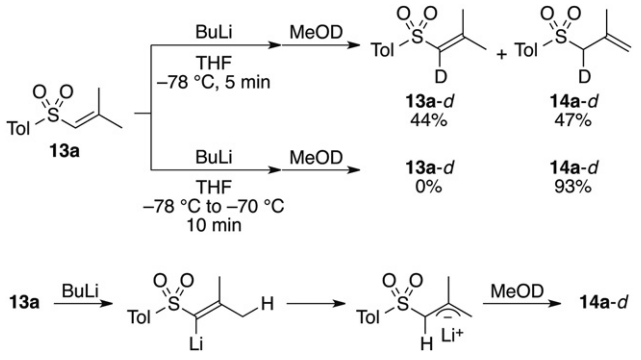
Scheme 1. Coupling reaction of magnesium carbenoids with α-sulfonylallyl anions.

The reaction of acyclic alkylmagnesium carbenoid **8** with α-sulfonylallyllithiums leading to the formation of conjugated dienes **12** is also described.

2. Results and discussion

2.1. Synthesis of allylidenecyclobutanes

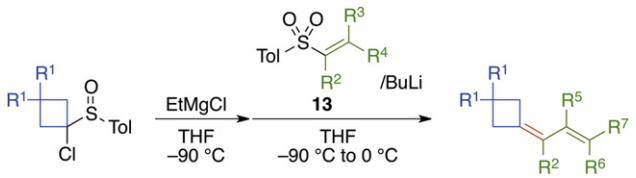
First, we investigated the generation of α-sulfonylallyllithiums from *p*-tolyl vinyl sulfones **13** (Scheme 2). When isocrotyl *p*-tolyl sulfone **13a** was treated with BuLi at −78 °C for 5 min followed by quenching with MeOD, a mixture of α-deuterated *p*-tolyl vinyl sulfone **13a**-*d* and α-deuterated allyl *p*-tolyl sulfone **14a**-*d* was obtained. On the other hand, when the reaction mixture was warmed to −70 °C over a period of 10 min after treatment of sulfone **13a** with BuLi, α-deuterated allyl *p*-tolyl sulfone **14a**-*d* was formed as the sole product. These results indicated that the α-hydrogen atom of sulfone **13a** was initially abstracted by BuLi, and the resultant vinyllithium isomerized to allyllithium at an elevated temperature.[15] We used this deprotonation–isomerization procedure for the generation of α-sulfonylallyllithiums from *p*-tolyl vinyl sulfones **13**.



Scheme 2. Generation of α-sulfonylallyllithium from *p*-tolyl vinyl sulfone **13a**.

The synthesis of methallylidenecyclobutane **10a** was performed using 3,3-bis(ethoxymethyl)-substituted 1-chlorocyclobutyl *p*-tolyl sulfoxide **2a** and sulfone **13a** (Table 1, entry 1).[11b] Cyclobutylmagnesium carbenoid was generated in situ from sulfoxide **2a** and EtMgCl at −90 °C.[16] α-Sulfonylallyllithium (3 equiv) was

Table 1
Synthesis of allylidenecyclobutanes **10** from sulfoxides **2** and *p*-tolyl vinyl sulfones **13**



2a: R^1 = $EtOCH_2$
2b: R^1 = $Ph(CH_2)_3OCH_2$
2c: R^1 = H

Entry	2	13	10	Yield (%)
1	**2a**	**13a**	**10a**	69
2	**2a**	**13b**	**10b**	39
3	**2a**	**13c**	**10c**	49
4	**2a**	**13d**	**10d**	64
5[a]	**2a**	**13e**	**10e**	44
6[a,b]	**2a**	**13e**	**10e**	83
7	**2a**	**13f**	**10f**	70
8	**2a**	**13g**	**10g**	78
9	**2a**	**13h**	**10h**	20
10[c]	**2a**	**13i**	**10i**	32
11[d]	**2a**	**13j**	**10j**	21
12[d,e]	**2a**	**13j**	**10j**	43
13	**2b**	**13g**	**10k**	70
14	**2c**	**13g**	**10l**	49

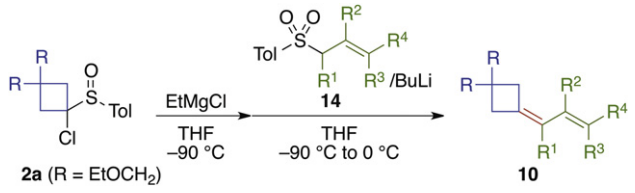
[a] Sulfone **13e** was treated with LDA at 0 °C for 1.5 h.
[b] 5 equiv of sulfone **13e** and LDA were used.
[c] Sulfone **13i** was treated with LDA at 0 °C for 30 min.
[d] Sulfone **13j** was treated with KHMDS at 0 °C for 10 min.
[e] 5 equiv of sulfone **13j** and KHMDS were used.

concurrently generated by deprotonating sulfone **13a** with BuLi at −78 °C followed by warming of the reaction mixture to −70 °C. The resulting solution containing α-sulfonylallyllithium was added to the solution containing magnesium carbenoid through a cannula at −90 °C, and the reaction mixture was allowed to warm to 0 °C. The desired coupling product **10a** was obtained in 69% yield.

We further investigated the scope and generality of this reaction with various sulfones **13** and sulfoxides **2** (Table 1, entries 2–14). The reaction with sulfone **13b** bearing methyl and phenyl groups at the β-position yielded (2-phenylallylidene)cyclobutane **10b** in 39% yield (entry 2). Allylidenecyclobutanes **10c**–**e**, which have an internal alkene unit, were obtained from sulfoxide **2a** and acyclic and cyclic sulfones **13c**–**e** in 44–64% yield (entries 3–5). When α-substituted sulfones **13f**–**j** were used as α-sulfonylallyl anion sources, coupling products **10f**–**j** with a tetrasubstituted alkene unit were formed in variable yields (entries 7–11). The delocalization of the negative charge over the phenyl or carbonyl group at the α-position resulted in the low nucleophilicity of α-sulfonylallyl anions in the reaction with sulfones **13h** and **13i** (entries 9 and 10). The generation of α-sulfonylallyllithiums from sulfones **13e** and **13j** was performed at 0 °C because the isomerization or deprotonation did not proceed at low temperatures (entries 5 and 11). The anionic species generated from sulfones **13e** and **13j** appeared to be unstable at 0 °C, and their degradation resulted in low efficiency. The use of 5 equiv of sulfones **13e** and **13j** improved the yield of products **10e** and **10j** (entries 6 and 12). 3,3-Bis(3-phenylpropoxymethyl)-substituted sulfoxide **2b** and unsubstituted sulfoxide **2c** could also be used as coupling partners (entries 13 and 14).

Next, we investigated the coupling reaction using sulfoxide **2a** and a range of allyl *p*-tolyl sulfones **14**, which do not require an isomerization process (Table 2). α-Sulfonylallyllithiums generated from unsubstituted and γ,γ-disubstituted sulfones **14b**–**d** could be coupled with cyclobutylmagnesium carbenoid to afford the corresponding allylidenecyclobutanes **10m**–**o** in 67–87% yield (entries 1–3). The reaction with sulfones (*E*)-**14e** and (*Z*)-**14e** bearing a (*E*)- and (*Z*)-cinnamyl group, respectively, proceeded without geometric isomerization of the cinnamyl group to yield coupling products (*E*)-**10p** and (*Z*)-**10p**, respectively (entries 4 and 5). Allylidenecyclobutanes **10a** and **10e**, which were prepared from *p*-tolyl vinyl sulfones **13a** and **13e**, respectively, were also obtained from allyl *p*-tolyl sulfones **14a** and **14f** (entries 6 and 7), and the reaction with allyl *p*-tolyl sulfone **14f** was more efficient than that with *p*-tolyl vinyl sulfone **13e** (Table 1, entry 5 and Table 2, entry 7). However, α-methyl-substituted sulfone **14g** was not suitable for the coupling reaction because sulfone **14g** could not be deprotonated using strong bases, such as *t*-BuLi and alkali metal amides (entry 8). Allylidenecyclobutanes **10a**, **10d**, and **10e** could be converted to spirocyclic compounds **15** using the Diels–Alder reaction with tetracyanoethylene (Table 3). The reaction occurred smoothly in diethyl ether at room temperature within 15 min to afford [4+2] cycloadducts **15a**–**c** in 84–89% yield.

Table 2
Synthesis of allylidenecyclobutanes **10** from sulfoxide **2a** and allyl *p*-tolyl sulfones **14**



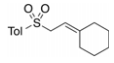
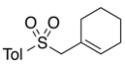
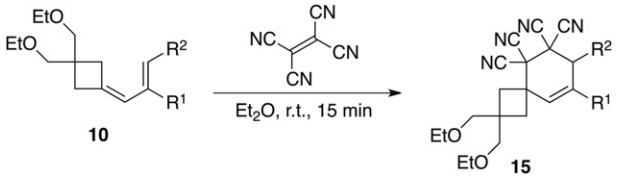
Entry	14	R^1	R^2	R^3	R^4	10	Yield (%)
1	**14b**	H	H	H	H	**10m**	87
2	**14c**					**10n**	84
3	**14d**	H	H	Ph	Ph	**10o**	67
4	(*E*)-**14e**	H	H	H	Ph	(*E*)-**10p**	85
5	(*Z*)-**14e**	H	H	Ph	H	(*Z*)-**10p**	78
6	**14a**	H	Me	H	H	**10a**	71
7	**14f**					**10e**	82
8	**14g**	Me	Me	Me	Me	**10q**	0

Table 3
[4+2] cycloaddition of allylidenecyclobutanes **10** with tetracyanoethylene



Entry	10	R^1	R^2	15	Yield (%)
1	**10a**	Me	H	**15a**	89
2	**10d**	−$(CH_2)_3$−		**15b**	86
3	**10e**	−$(CH_2)_4$−		**15c**	84

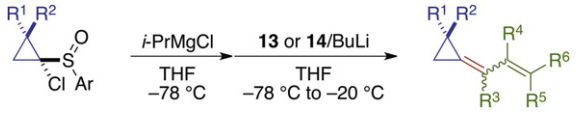
2.2. Synthesis of allylidenecyclopropanes

Encouraged by the successful synthesis of allylidenecyclobutanes **10**, we attempted the coupling reaction of cyclopropylmagnesium carbenoids **7** with α-sulfonylallyllithiums (Table 4). Aryl 1-chlorocyclopropyl sulfoxides **3** were treated with *i*-PrMgCl at −78 °C,[16] and a solution containing α-sulfonylallyllithiums (2 equiv) was added to the solution containing the cyclopropylmagnesium carbenoids. Allylidenecyclopropanes **11a**–**d** were obtained in 42–95% yield (entries 1–4), and the geometric ratio of the products was dependent on the substituents on the cyclopropane ring (entries 1–3). Allylidenecyclopropanes **11** were more or less unstable at room temperature, especially in the neat state, and gradually degraded. For example, allylidenecyclopropanes **11e** and **11f** appeared to be included in the crude products. However, these compounds decomposed during silica gel purification (entries 5 and 6). To confirm the formation of allylidenecyclopropane **11f**, the crude product was immediately trapped by tetracyanoethylene (Scheme 3). The [4+2] cycloaddition proceeded with the degradation of diene **11f** to yield spiro[2.5]oct-4-ene **16** as a mixture of diastereomers in low yield.

2.3. Synthesis of acyclic conjugated dienes

The coupling reaction was also applied to the synthesis of acyclic conjugated dienes (Table 5). Alkylmagnesium carbenoid was

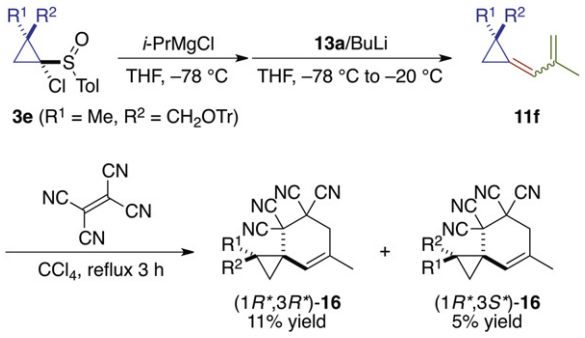
Table 4
Synthesis of allylidenecyclopropanes **11** from sulfoxides **3** and sulfones **13** and **14**



3 **11**

Entry	3	R^1	R^2	Ar	13	11	R^3	R^4	R^5	R^6	Yield (%)	Geometric ratio
1	**3a**	CH_2OTr	H	Tol	**13a**	**11a**	H	Me	H	H	79	10:1
2	**3b**	CH_2OTBS	H	Tol	**13a**	**11b**	H	Me	H	H	56	4:1
3	**3c**	CH_2Bn	Me	Tol	**13a**	**11c**	H	Me	H	H	95	—[a]
4[b]	**3d**	H	H	Ph	**13g**	**11d**	CH_2 PMB	Me	H	H	42	—
5	**3d**	H	H	Ph	**14d**	**11e**	H	H	Ph	Ph	0	—
6	**3e**	Me	CH_2OTr	Tol	**13a**	**11f**	H	Me	H	H	0	—

[a] Diene **11c** was obtained as a single isomer.
[b] The reaction mixture was allowed to warm to −50 °C and stirred at that temperature for 3 h.



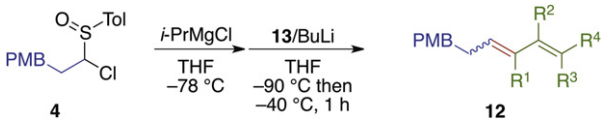
Scheme 3. Synthesis of allylidenecyclopropane **11f** and [4+2] cycloaddition of **11f** with tetracyanoethylene.

generated from 3-(4-methoxyphenyl)propyl *p*-tolyl sulfoxide **4** and *i*-PrMgCl,[16,17] and the resulting alkylmagnesium carbenoid was reacted with α-sulfonylallyllithiums generated from sulfones **13a**, **13d**, and **13f** in a similar manner to the synthesis of allylidenecycloalkanes. Conjugated dienes **12a**–**c** were formed in 60–85% yield with low geometric selectivity.

2.4. Reaction mechanism

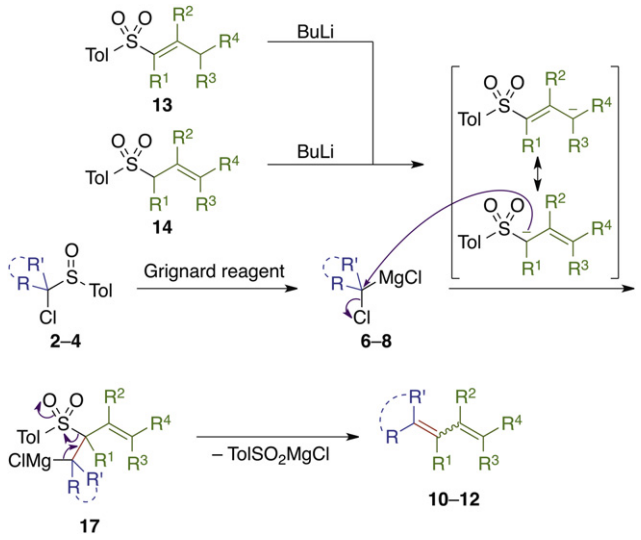
The mechanism of the coupling reaction is described below (Scheme 4). The sulfoxide–magnesium exchange reaction of

Table 5
Synthesis of conjugated dienes **12** from sulfoxide **4** and *p*-tolyl vinyl sulfones **13**



4 **12**

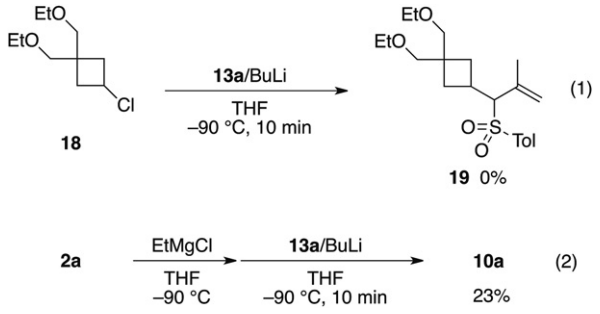
Entry	13	12		Yield (%)	*E*/*Z* ratio
1	**13a**	**12a**	PMB	85	1:3
2	**13d**	**12b**	PMB	60	1:3
3	**13f**	**12c**	PMB	78	1:2.4



Scheme 4. Proposed mechanism for the coupling reaction of magnesium carbenoids with α-sulfonylallyl anions.

sulfoxides **2**–**4** with a Grignard reagent generates magnesium carbenoids **6**–**8**, and the deprotonation of vinyl *p*-tolyl sulfones **13** or allyl *p*-tolyl sulfones **14** with BuLi provides α-sulfonylallyl anions. The nucleophilic substitution of α-sulfonylallyl anions with magnesium carbenoids **6**–**8** primarily occurs at the α-position on the α-sulfonylallyl anions to afford intermediates **17**.[18] The β-elimination of magnesium 4-methylbenzenesulfinate chloride from intermediates **17** affords conjugated dienes **10**–**12**.

As mentioned above, small ring cycloalkyl halides undergo nucleophilic substitution reactions with very low efficiency.[13] Indeed, the reaction of chlorocyclobutane **18** with α-sulfonylallyllithium did not occur at −90 °C (Scheme 5, Eq. 1).



Scheme 5. Reaction of chlorocyclobutanes with α-sulfonylallyllithium.

The difficulty with the nucleophilic substitution at the carbon atom of small ring cycloalkyl halides is primarily due to the inaccessibility of the backside of carbon–halogen bond to nucleophiles and the increased internal ring strain in the transition state.[13] However, the reaction of cyclobutylmagnesium carbenoid with α-sulfonylallyllithium occurred at −90 °C to yield allylidenecyclobutane **10a** (Scheme 5, Eq. 2). To elucidate the curious reactivity of small ring cycloalkylmagnesium carbenoids, DFT calculations of chlorocyclobutane **18′** and bis(dimethyl ether)-solvated 1-chlorocyclobutylmagnesium chloride **6′**·2(OMe_2) were performed using the 6-311++G(d,p) basis set at the B3LYP level with the Gaussian software program (Fig. 1).[19–21] Selected structural parameters of model compounds **18′** and **6′**·2(OMe_2) are listed in Table 6 along with those of cyclopropane analogues **20′** and **7′**·2(OMe_2) in the previous report.[22] Small ring cycloalkylmagnesium carbenoids

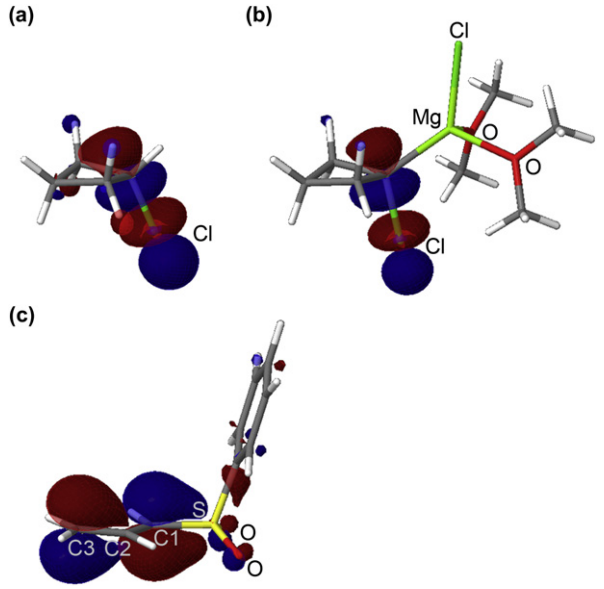
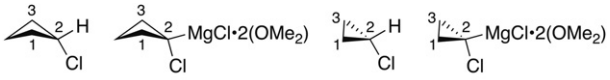


Fig. 1. C–Cl anti-bonding orbital of model compounds: (a) chlorocyclobutane **18′**; and (b) 1-chlorocyclobutylmagnesium chloride **6′**·2(OMe_2). (c) HOMO of the α-(phenylsulfonyl)allyl anion.

Table 6
Selected parameters of model compounds



Compound	H_{C-Cl}[a]	C2–Cl (Å)	B–C2–Cl (°)[b]	B–C2–E (°)[c]	A (°)[d]
18′	$sp^{4.6}$	1.83	123.1	131.9	326.2
6′·2(OMe_2)	$sp^{5.7}$	1.94	112.3	139.5	334.0
20′	$sp^{3.7}$	1.79	124.8	124.9	300.1
7′·2(OMe_2)	$sp^{4.1}$	1.88	114.4	131.6	309.9

[a] Hybridization of carbon atom in the C–Cl bond.
[b] An angle between the bisector of the C1–C2–C3 angle and the C2–Cl bond.
[c] An angle between the bisector of the C1–C2–C3 angle and the C2–E bond (E=H or Mg).
[d] Sum of the C1–C2–E, E–C2–C3, and C3–C2–C1 angles (E=H or Mg).

6′·2(OMe_2) and **7′**·2(OMe_2) have a weakened C–Cl bond and expanded bond angles on the backside of C–Cl bond compared to those of the corresponding chlorocycloalkanes **18′** and **20′**. The difference in geometry between cycloalkylmagnesium carbenoids and chlorocycloalkanes are attributed to the enhanced *p*-character of the carbenoid carbon atom in the C–Cl bond relative to that of chlorocycloalkanes. These structural changes provide a favorable environment for the nucleophilic substitution because the reaction center is more accessible and the structures of the reactants approach to the transition state structures.

Another important point in the reaction mechanism is the regioselectivity of the nucleophilic substitution of α-sulfonylallyllithiums.[23] In all of the cases, the reaction occurred at the α-position of the α-sulfonylallyllithiums. The HOMO of the α-(phenylsulfonyl)allyl anion is localized on the carbon atoms at the α- and γ-positions, and the coefficient of the HOMO at the α-position was larger than that at the γ-position (Fig. 1c).

3. Conclusion

We developed a useful method for the synthesis of multisubstituted conjugated dienes bearing a small ring at the terminal position via the coupling reaction of cyclopropyl- and cyclobutylmagnesium carbenoids with α-sulfonylallyllithiums. The present synthetic method utilizes the electrophilicity of small ring cycloalkylmagnesium carbenoids and is complementary to the conventional synthetic methods using the chemistry of cycloalkyl anions. Allylidenecyclopropane and allylidenecyclobutanes underwent [4+2] cycloaddition with tetracyanoethylene to afford spiro[2.5]oct-4-ene and spiro[3.5]non-5-enes, respectively. The results from DFT calculations of small ring cycloalkylmagnesium carbenoids revealed that the presence of the magnesium atom on the carbon atom bearing the chloro group results in enhanced *p*-character of the carbon atom in the C–Cl bond and facilitates the nucleophilic substitution on the small carbon ring framework. Further synthetic applications of small ring cycloalkylmagnesium carbenoids as electrophiles are ongoing and will be reported in due course.

4. Experimental

4.1. General method

The melting points were measured using a Yanaco MP-S3 apparatus and are uncorrected. The NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, JEOL JNM-LA 500, Bruker AVANCE DPX 300, Bruker AVANCE DPX 400, and Bruker AVANCE 600 spectrometers. The stereochemistry of allylidenecyclobutane **10c**, sulfone **13b**, and [4+2] cycloadducts **16** was assigned based on their NOESY spectra. The assignments of the ^{13}C NMR spectra were made by DEPT 45, 90, and 135. The mass spectra (MS) were obtained at 70 eV by direct injection with a HITACHI M-80B mass spectrometer. The 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 in the column chromatography, and the products that absorbed UV light were detected by UV irradiation. Anhydrous THF was purchased from Kanto Chemical and used as supplied. All of the reactions involving air- or water-sensitive compounds were routinely conducted in glassware that had been flame-dried under a positive pressure of argon. Sulfoxides **2**–**4**,[11,12,17] *p*-tolyl vinyl sulfones **13**,[14d] and allyl *p*-tolyl sulfones **14**[14d] were prepared according to previously published protocols.

*4.1.1. 1,1-Bis(ethoxymethyl)-3-(2-methylallylidene)cyclobutane (**10a**).* A 2.0 M solution of EtMgCl in THF (0.125 mL, 0.25 mmol) was added dropwise to a solution of **2a** (34.5 mg, 0.100 mmol) in THF (1.0 mL) at −90 °C, and the mixture was stirred at that temperature for 1 min. In another flask, a 1.62 M solution of BuLi in hexane (0.185 mL, 0.299 mmol) was added dropwise to a solution of **13a** (63.1 mg, 0.300 mmol) in THF (1.0 mL) at −78 °C, and the mixture was allowed to warm to −70 °C over a period of 10 min. The resultant solution of α-sulfonylallyllithium in THF was transferred to a solution of magnesium carbenoid in THF through a cannula at −90 °C, and the reaction mixture was allowed to warm to 0 °C over a period of 80 min. The reaction was quenched with satd aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3×5 mL). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–EtOAc, 20:1) to yield **10a** (15.5 mg, 0.0691 mmol, 69%) as a colorless oil. When the reaction was conducted on a 1 mmol scale, diene **10a** was obtained in 59% yield (133 mg, 0.592 mmol). IR (neat) 2975, 2931, 2866, 1669, 1608, 1456, 1409, 1376, 1354, 1176, 1112, 1070, 875 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 1.85 (br s, 3H), 2.52 (br s, 2H), 2.75 (br s, 2H), 3.44 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 4.74 (br s, 2H), 5.81–5.85 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3×2), 21.0 (CH_3), 37.4 (CH_2), 37.6 (CH_2), 39.4 (C), 66.7 (CH_2×2), 73.5

(CH_2×2), 113.2 (CH_2), 126.0 (CH), 138.3 (C), 142.6 (C); MS (EI) *m*/*z* (%) 224 (M^+, 6), 119 (100), 117 (30), 105 (18), 93 (18), 91 (33), 79 (23), 59 (17); HRMS (EI) calcd for $C_{14}H_{24}O_2$: 224.1776, found: 224.1774.

*4.1.2. 1,1-Bis(ethoxymethyl)-3-(2-phenylallylidene)cyclobutane (**10b**).* Colorless oil; IR (neat) 2975, 2931, 2866, 1670, 1596, 1445, 1376, 1355, 1175, 1111, 1071, 1027, 888, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J*=7.0 Hz, 6H), 2.26 (br s, 2H), 2.57 (br s, 2H), 3.39 (s, 4H), 3.48 (q, *J*=7.0 Hz, 4H), 5.08 (br s, 1H), 5.18 (br s, 1H), 6.02 (br quint, *J*=2.3 Hz, 1H), 7.21–7.36 (m, 5H); MS (EI) *m*/*z* (%) 286 (M^+, 7), 194 (28), 181 (100), 178 (20), 167 (18), 155 (19), 141 (20), 91 (18); HRMS (EI) calcd for $C_{19}H_{26}O_2$: 286.1933, found: 286.1934.

*4.1.3. (Z)-1,1-Bis(ethoxymethyl)-3-(2-ethylbut-2-en-1-ylidene)cyclobutane (**10c**).* Colorless oil; IR (neat) 2974, 2932, 2867, 1664, 1464, 1445, 1375, 1354, 1175, 1112, 1070, 881 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, *J*=7.5 Hz, 3H), 1.19 (t, *J*=7.0 Hz, 6H), 1.65 (d, *J*=6.9 Hz, 3H), 2.11 (q, *J*=7.5 Hz, 2H), 2.55 (br s, 2H), 2.64 (br s, 2H), 3.45 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 5.22 (q, *J*=6.9 Hz, 1H), 5.98–6.02 (m, 1H); MS (EI) *m*/*z* (%) 252 (M^+, 115), 147 (100), 131 (17), 119 (22), 105 (23), 93 (18), 91 (19); HRMS (EI) calcd for $C_{16}H_{28}O_2$: 252.2089, found: 252.2091.

*4.1.4. 1-{[3,3-Bis(ethoxymethyl)cyclobutylidene]methyl}cyclopent-1-ene (**10d**).* Colorless oil; IR (neat) 2974, 2931, 2865, 1674, 1376, 1354, 1175, 1111, 1070, 816 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 1.86 (quint, *J*=7.5 Hz, 2H), 2.32 (br t, *J*=7.5 Hz, 2H), 2.41–2.54 (m, 4H), 2.71 (br s, 2H), 3.44 (s, 4H), 3.50 (q, *J*=7.0 Hz, 4H), 5.44–5.52 (m, 1H), 5.92–6.00 (m, 1H); MS (EI) *m*/*z* (%) 250 (M^+, 15), 145 (100), 117 (17), 91 (22); HRMS (EI) calcd for $C_{16}H_{26}O_2$: 250.1933, found: 250.1930.

*4.1.5. 1-{[3,3-Bis(ethoxymethyl)cyclobutylidene]methyl}cyclohex-1-ene (**10e**).* Colorless oil; IR (neat) 2975, 2931, 2858, 1671, 1445, 1376, 1354, 1111, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 1.49–1.66 (m, 4H), 2.07 (br s, 2H), 2.18 (br s, 2H), 2.49 (br s, 2H), 2.72 (br s, 2H), 3.43 (s, 4H), 3.50 (q, *J*=7.0 Hz, 4H), 5.50–5.56 (m, 1H), 5.70 (br t, *J*=2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3×2), 22.2 (CH_2), 22.8 (CH_2), 25.7 (CH_2), 26.7 (CH_2), 37.4 (CH_2), 37.8 (CH_2), 39.4 (C), 66.6 (CH_2×2), 73.5 (CH_2×2), 125.8 (CH), 126.7 (CH), 134.3 (C), 136.3 (C); MS (EI) *m*/*z* (%) 264 (M^+, 17), 159 (100), 131 (17), 117 (14), 91 (23), 79 (18), 59 (15); HRMS (EI) calcd for $C_{17}H_{28}O_2$: 264.2089, found: 264.2086.

*4.1.6. 1,1-Bis(ethoxymethyl)-3-(3-methylbut-3-en-2-ylidene)cyclobutane (**10f**).* Colorless oil; IR (neat) 2975, 2931, 2865, 1661, 1606, 1445, 1375, 1173, 1112, 1071, 877 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 1.62–1.66 (m, 3H), 1.90 (br s, 3H), 2.51 (br s, 2H), 2.71 (br s, 2H), 3.43 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 4.77 (br s, 1H), 4.82 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3×2), 15.5 (CH_3), 22.8 (CH_3), 36.7 (CH_2), 38.0 (C), 38.3 (CH_2), 66.6 (CH_2×2), 73.6 (CH_2×2), 110.8 (CH_2), 129.1 (C), 133.7 (C), 144.4 (C); MS (EI) *m*/*z* (%) 238 (M^+, 13), 133 (100), 131 (18), 105 (17), 93 (14), 91 (15); HRMS (EI) calcd for $C_{15}H_{26}O_2$: 238.1933, found: 238.1935.

*4.1.7. 1-{3-[3,3-Bis(ethoxymethyl)cyclobutylidene]-4-methylpent-4-en-1-yl}-4-methoxybenzene (**10g**).* Colorless oil; IR (neat) 2973, 2932, 2901, 2863, 1652, 1612, 1512, 1464, 1444, 1375, 1300, 1246, 1176, 1110, 1039, 880, 819 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J*=7.0 Hz, 6H), 1.88 (br s, 3H), 2.22–2.34 (m, 4H), 2.52–2.65 (m, 4H), 3.34 (s, 4H), 3.48 (q, *J*=7.0 Hz, 4H), 3.78 (s, 3H), 4.89 (br s, 2H), 6.76–6.85 (m, 2H), 7.01–7.10 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3×2), 22.9 (CH_3), 32.0 (CH_2), 33.8 (CH_2), 36.2 (CH_2), 37.900 (CH_2), 37.904 (C), 55.2 (CH_3), 66.609 (CH_2), 66.611 (CH_2), 73.5 (CH_2×2), 111.6 (CH_2), 113.5 (CH), 129.4 (CH), 133.2 (C), 134.1 (C), 134.7 (C), 142.7 (C), 157.7 (C); MS (EI) *m*/*z* (%) 358 (M^+, 3), 253 (17), 155 (13), 121 (100); HRMS (EI) calcd for $C_{23}H_{34}O_3$: 358.2508, found: 358.2507.

*4.1.8. {1-[3,3-Bis(ethoxymethyl)cyclobutylidene]-2-methylallyl}benzene (**10h**).* Colorless oil; IR (neat) 2974, 2931, 2866, 1601, 1444, 1375, 1111, 1070, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 1.87 (br s, 3H), 2.49 (br s, 2H), 2.77 (br s, 2H), 3.44 (s, 4H), 3.52 (q, *J*=7.0 Hz, 4H), 4.65 (br d, *J*=1.7 Hz, 1H), 4.97 (br quint, *J*=1.7 Hz, 1H), 7.14–7.23 (m, 3H), 7.23–7.36 (m, 2H); MS (EI) *m*/*z* (%) 300 (M^+, 13), 195 (100); HRMS (EI) calcd for $C_{20}H_{28}O_2$: 300.2089, found: 300.2088.

*4.1.9. tert-Butyl 2-[3,3-bis(ethoxymethyl)cyclobutylidene]-3-methylbut-3-enoate (**10i**).* Colorless oil; IR (neat) 2976, 2931, 2867, 1706 (C=O), 1662, 1638, 1368, 1321, 1253, 1177, 1156, 1113, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 1.48 (s, 9H), 1.86 (br s, 3H), 2.61 (br s, 2H), 2.83 (br s, 2H), 3.43 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 4.74–4.78 (m, 1H), 4.98–5.03 (m, 1H); MS (FAB+) *m*/*z* (%) 325 ($[M+H]^+$, 17), 269 (72), 268 (47), 251 (100), 177 (57), 147 (23), 131 (32), 59 (20); HRMS (FAB+) calcd for $C_{19}H_{32}O_4$: 325.2379, found: 325.2377.

*4.1.10. 3-[3,3-Bis(ethoxymethyl)cyclobutylidene]cyclohex-1-ene (**10j**).* Colorless oil; IR (neat) 2975, 2931, 2864, 1682, 1611, 1376, 1354, 1175, 1111, 1069, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 1.66 (quint, *J*=6.2 Hz, 2H), 2.06–2.18 (m, 4H), 2.44 (br s, 2H), 2.48 (br s, 2H), 3.43 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 5.68 (td, *J*=4.0, 9.9 Hz, 1H), 6.06 (td, *J*=1.9, 9.9 Hz, 1H); MS (EI) *m*/*z* (%) 250 (M^+, 9), 145 (100), 91 (17); HRMS (EI) calcd for $C_{16}H_{26}O_2$: 250.1933, found: 250.1935.

*4.1.11. 1-{3-[3,3-Bis(3-phenylpropoxymethyl)cyclobutylidene]-4-methylpent-4-en-1-yl}-4-methoxybenzene (**10k**).* Colorless oil; IR (neat) 3027, 2933, 2857, 1611, 1512, 1497, 1454, 1246, 1177, 1112, 1039, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.80–1.94 (m, 7H), 2.26–2.36 (m, 4H), 2.54–2.72 (m, 8H), 3.35 (s, 4H), 3.42 (t, *J*=6.4 Hz, 4H), 3.75 (s, 3H), 4.90 (br s, 2H), 6.76–6.84 (m, 2H), 7.03–7.10 (m, 2H), 7.12–7.22 (m, 6H), 7.22–7.31 (m, 4H); MS (EI) *m*/*z* (%) 538 (M^+, 1.6), 402 (8), 253 (36), 147 (21), 121 (100), 91 (78); HRMS (EI) calcd for $C_{37}H_{46}O_3$: 538.3447, found: 538.3452.

*4.1.12. 1-(3-Cyclobutylidene-4-methylpent-4-en-1-yl)-4-methoxybenzene (**10l**).* Colorless oil; IR (neat) 2947, 2859, 2834, 1648, 1612, 1512, 1464, 1455, 1443, 1300, 1246, 1176, 1040, 880, 820 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.79–1.95 (m, 5H), 2.22–2.33 (m, 2H), 2.51–2.62 (m, 4H), 2.85 (br t, *J*=7.2 Hz, 2H), 3.79 (s, 3H), 4.86 (br s, 1H), 4.88 (br s, 1H), 6.82 (d, *J*=8.7 Hz, 2H), 7.08 (d, *J*=8.7 Hz, 2H); MS (EI) *m*/*z* (%) 242 (M^+, 13), 121 (100); HRMS (EI) calcd for $C_{17}H_{22}O$: 242.1671, found: 242.1673.

*4.1.13. 3-Allylidene-1,1-bis(ethoxymethyl)cyclobutane (**10m**).* Colorless oil; IR (neat) 2976, 2932, 2866, 1677, 1608, 1412, 1377, 1354, 1175, 1112, 1071, 992, 894 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 2.51 (br s, 2H), 2.56 (br s, 2H), 3.43 (s, 4H), 3.50 (q, *J*=7.0 Hz, 4H), 4.92 (br dd, *J*=0.9, 10.5 Hz, 1H), 5.02 (br dd, *J*=0.9, 16.9 Hz, 1H), 5.87 (d of quintets, *J*=2.2, 10.5 Hz, 1H), 6.26 (td, *J*=10.5, 16.9 Hz, 1H); MS (EI) *m*/*z* (%) 210 (M^+, 11), 117 (34), 105 (100), 91 (49), 79 (46), 59 (38); HRMS (EI) calcd for $C_{13}H_{22}O_2$: 210.1620, found: 210.1617.

*4.1.14. {2-[3,3-Bis(ethoxymethyl)cyclobutylidene]ethylidene}cyclohexane (**10n**).* Colorless oil; IR (neat) 2974, 2929, 2854, 1633, 1446, 1376, 1354, 1175, 1111, 1070, 879 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J*=7.0 Hz, 6H), 1.47–1.58 (m, 6H), 2.13 (br s, 2H), 2.20–2.27 (m, 2H), 2.50 (br s, 2H), 2.53 (br s, 2H), 3.43 (s, 4H), 3.50 (q, *J*=7.0 Hz, 4H), 5.64 (d, *J*=11.3 Hz, 1H), 6.07 (d of quintets, *J*=2.3, 11.3 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 ($CH_3\times2$), 26.8 (CH_2), 27.7 (CH_2), 28.6 (CH_2), 29.0 (CH_2), 35.0 (CH_2), 36.5 (CH_2), 37.3 (CH_2), 39.1 (C), 66.6 ($CH_2\times2$), 73.5 ($CH_2\times2$), 117.7 (CH), 118.9 (CH), 137.1 (C), 139.9 (C); MS (EI) *m*/*z* (%) 278 (M^+, 18), 232 (16), 173 (100), 131 (13), 105 (12), 91 (17); HRMS (EI) calcd for $C_{18}H_{30}O_2$: 278.2246, found: 278.2245.

*4.1.15. 1,1-Bis(ethoxymethyl)-3-(3,3-diphenylallylidene)cyclobutane (**10o**).* Colorless oil; IR (neat) 2974, 2931, 2866, 1661, 1597, 1494, 1445, 1376, 1355, 1175, 1111, 1072, 1029, 764, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 2.50 (br s, 2H), 2.67 (br s, 2H), 3.45 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 5.95 (d of quintets, *J*=2.3, 11.4 Hz, 1H), 6.59 (d, *J*=11.4 Hz, 1H), 7.17–7.42 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 ($CH_3\times2$), 35.4 (CH_2), 36.9 (CH_2), 39.2 (C), 66.7 ($CH_2\times2$), 73.5 ($CH_2\times2$), 121.5 (CH), 124.1 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 128.1 (CH), 130.5 (CH), 138.9 (C), 140.0 (C), 142.7 (C), 142.9 (C) (1 signals overlapping); MS (EI) *m*/*z* (%) 362 (M^+, 37), 316 (26), 257 (100), 217 (17), 191 (25), 179 (18), 105 (23), 91 (17); HRMS (EI) calcd for $C_{25}H_{30}O_2$: 362.2246, found: 362.2247.

*4.1.16. (E)-1,1-Bis(ethoxymethyl)-3-(3-phenylallylidene)cyclobutane [(E)-**10p**].* Colorless oil; IR (neat) 3023, 2974, 2931, 2866, 1667, 1595, 1488, 1448, 1376, 1355, 1175, 1111, 1071, 965, 745, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 2.57 (br s, 2H), 2.65 (br s, 2H), 3.46 (s, 4H), 3.52 (q, *J*=7.0 Hz, 4H), 6.02 (d of quintets, *J*=2.2, 10.8 Hz, 1H), 6.37 (d, *J*=15.7 Hz, 1H), 6.69 (dd, *J*=10.8, 15.7 Hz, 1H), 7.14–7.21 (m, 1H), 7.24–7.33 (m, 2H), 7.33–7.40 (m, 2H); MS (EI) *m*/*z* (%) 286 (M^+, 19), 240 (18), 181 (100), 166 (14), 141 (17), 115 (15), 91 (16); HRMS (EI) calcd for $C_{19}H_{26}O_2$: 286.1933, found: 286.1930.

*4.1.17. (Z)-1,1-Bis(ethoxymethyl)-3-(3-phenylallylidene)cyclobutane [(Z)-**10p**].* Colorless oil; IR (neat) 2975, 2931, 2866, 1664, 1598, 1492, 1447, 1409, 1376, 1355, 1175, 1111, 1071, 769, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 6H), 2.55 (br s, 2H), 2.62 (br s, 2H), 3.45 (s, 4H), 3.51 (q, *J*=7.0 Hz, 4H), 6.13 (t, *J*=11.6 Hz, 1H), 6.28 (d, *J*=11.6 Hz, 1H), 6.40–6.46 (m, 1H), 7.16–7.24 (m, 1H), 7.31–7.34 (m, 4H); MS (EI) *m*/*z* (%) 286 (M^+, 19), 240 (18), 181 (100), 141 (16), 115 (14), 91 (14); HRMS (EI) calcd for $C_{19}H_{26}O_2$: 289.1933, found: 286.1932.

*4.1.18. 2-(2-Methylallylidene)-1-(trityloxymethyl)cyclopropane (**11a**).* A 2.0 M solution of *i*-PrMgCl in THF (0.125 mL, 0.25 mmol) was added dropwise to a solution of **3a** (50.1 mg, 0.100 mmol) in THF (1.0 mL) at −78 °C, and the mixture was stirred at that temperature for 1 min. In another flask, a 1.62 M solution of BuLi in hexane (0.125 mL, 0.202 mmol) was added dropwise to a solution of **13a** (42.1 mg, 0.200 mmol) in THF (1.0 mL) at −78 °C, and the mixture was allowed to warm to −70 °C over a period of 10 min. The resulting solution of α-sulfonylallyllithium in THF was transferred to a solution of magnesium carbenoid in THF through a cannula at −78 °C, and the reaction mixture was allowed to warm to 0 °C over a period of 60 min. The reaction was quenched with satd aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3×5 mL). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–$CHCl_3$, 4:1) to afford **11a** (28.9 mg, 0.0789 mmol, 79%, a 10:1 mixture of geometric isomers) as a colorless oil. IR (neat) 3085, 3059, 3033, 2973, 2918, 1617, 1597, 1491, 1449, 1219, 1153, 1062, 1033, 909, 885, 762, 746, 734, 706, 633 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, major: M, minor: m) δ 0.91–0.98 (m, $1H_M$), 1.03–1.13 (m, $1H_m$), 1.23–1.31 (m, $1H_M$, $1H_m$), 1.80 (br s, $3H_M$), 1.82–1.90 (m, $1H_M$, $1H_m$), 1.93 (br s, $3H_m$), 2.89 (dd, *J*=7.7, 9.5 Hz, $1H_M$), 2.92 (dd, *J*=7.4, 9.8 Hz, $1H_m$), 3.33 (dd, *J*=5.3, 9.8 Hz, $1H_m$), 3.36 (dd, *J*=5.0, 9.5 Hz, $1H_M$), 4.87 (br s, $1H_M$), 4.92 (br s, $1H_M$, $1H_m$), 4.94 (br s, $1H_m$), 6.46 (br s, $1H_M$), 6.54 (br s, $1H_m$), 7.16–7.33 (m, $9H_M$, $9H_m$), 7.40–7.52 (m, $6H_M$, $6H_m$); MS (EI) *m*/*z* (%) 366 (M^+, 0.3), 243 (100), 165 (48), 105 (29), 83 (32); HRMS (EI) calcd for $C_{27}H_{26}O$: 366.1984, found: 366.1984.

*4.1.19. tert-Butyldimethyl{[2-(2-methylallylidene)cyclopropyl]methoxy}silane (**11b**).* A 4:1 mixture of geometric isomers; colorless oil; IR (neat) 2956, 2930, 2896, 2858, 1618, 1472, 1464, 1257, 1144, 1089, 1006, 881, 836, 815, 776 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, major: M, minor: m) δ 0.06 (s, $6H_M$, $6H_m$), 0.84–0.96 (m, $10H_M$, $10H_m$), 1.21–1.30 (m, $2H_M$, $2H_m$), 1.92 (br s, $3H_M$), 1.96 (br s, $3H_m$), 3.30 (dd, *J*=8.2, 10.7 Hz, $1H_M$), 3.43 (dd, *J*=7.5, 10.8 Hz, $1H_m$), 3.68 (br dd, *J*=6.0, 10.8 Hz, $1H_m$), 3.93 (ddd, *J*=0.6, 5.0, 10.7 Hz, $1H_M$), 4.92 (br s, $1H_M$, $1H_m$), 4.95 (br s, $1H_M$, $1H_m$), 6.49 (br q, *J*=1.7 Hz, $1H_M$), 6.51 (br q, *J*=1.9 Hz, $1H_m$); MS (EI) *m*/*z* (%) 238 (M^+, 0.4), 181 (159), 163 (29), 127 (32), 115 (121), 93 (48), 75 (100), 73 (97), 59 (21); HRMS (EI) calcd for $C_{14}H_{26}OSi$: 238.1753, found: 238.1754.

*4.1.20. {2-[1-Methyl-2-(2-methylallylidene)cyclopropyl]ethyl}benzene (**11c**).* Single isomer; colorless oil; IR (neat) 3084, 3064, 3028, 2963, 2924, 2861, 1617, 1604, 1497, 1455, 1435, 1374, 881, 752, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (d, *J*=8.7 Hz, 1H), 1.02 (d, *J*=8.7 Hz, 1H), 1.28 (s, 3H), 1.46 (ddd, *J*=5.2, 12.3, 13.4 Hz, 1H), 1.88 (br s, 3H), 1.98–2.14 (m, 1H), 2.57 (ddd, *J*=5.1, 11.5, 13.4 Hz, 1H), 2.64–2.80 (m, 1H), 4.89 (br s, 1H), 4.93 (br s, 1H), 6.40 (br s, 1H), 7.10–7.35 (m, 5H); MS (EI) *m*/*z* (%) 212 (M^+, 1.4), 121 (100), 108 (76), 93 (82), 91 (71); HRMS (EI) calcd for $C_{16}H_{20}$: 212.1565, found: 212.1569.

*4.1.21. 1-(3-Cyclopropylidene-4-methylpent-4-en-1-yl)-4-methoxybenzene (**11d**).* Colorless oil; IR (neat) 2950, 1612, 1512, 1454, 1246, 1177, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77–0.87 (m, 2H), 1.23–1.33 (m, 2H), 2.03 (br s, 3H), 2.61–2.80 (m, 4H), 3.78 (s, 3H), 4.97 (br s, 1H), 5.10 (br s, 1H), 6.77–6.84 (m, 2H), 7.04–7.11 (m, 2H); MS (EI) *m*/*z* (%) 228 (M^+, 10), 121 (100); HRMS (EI) calcd for $C_{16}H_{20}O$: 228.1514, found: 228.1512.

*4.1.22. 1-Methoxy-4-(5-methylhexa-3,5-dien-1-yl)benzene (**12a**).* A 1.02 M solution of *t*-BuMgCl in THF (0.098 mL, 0.100 mmol) was added to a solution of **4** (30.9 mg, 0.100 mmol) in THF (1.0 mL) at −78 °C to remove a trace amount of water in the reaction media, and the mixture was stirred at that temperature for 10 min. A 2.0 M solution of *i*-PrMgCl in THF (0.14 mL, 0.28 mmol) was then added to the solution at −78 °C, and the mixture was stirred at that temperature for 1 min. In another flask, a 1.62 M solution of BuLi in hexane (0.185 mL, 0.299 mmol) was added dropwise to a solution of **13a** (63.1 mg, 0.300 mmol) in THF (1.0 mL) at −78 °C, and the mixture was allowed to warm to −70 °C over a period of 10 min. The resulting solution of α-sulfonylallyllithium in THF was transferred to a solution of magnesium carbenoid in THF through a cannula at −78 °C. The reaction mixture was allowed to warm to −40 °C over a period of 50 min and stirred at −40 °C for 1 h. The reaction was quenched with satd aq NH_4Cl (1.5 mL), and the mixture was extracted with $CHCl_3$ (3×5 mL). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–EtOAc, 20:1) to afford **12a** (17.2 mg, 0.0851 mmol, 85%, a mixture of geometric isomers, *E*:*Z*=1:3) as a colorless oil. IR (neat) 3002, 2934, 1612, 1513, 1464, 1455, 1442, 1300, 1247, 1178, 1039, 890, 825 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83 (br t, *J*=1.0 Hz, $3H_E$), 1.85 (br t, *J*=1.0 Hz, $3H_Z$), 2.33–2.71 (m, $4H_E$, $4H_Z$), 3.786 (s, $3H_Z$), 3.790 (s, $3H_E$), 4.79–4.96 (m, $2H_E$, $2H_Z$), 5.43 (td, *J*=7.0, 11.8 Hz, $1H_Z$), 5.69 (br td, *J*=6.9, 15.6 Hz, $1H_E$), 5.85 (br qd, *J*=1.2, 11.8 Hz, $1H_Z$), 6.17 (br td, *J*=1.2, 15.6 Hz, $1H_E$), 6.78–6.87 (m, $2H_E$, $2H_Z$), 7.06–7.15 (m, $2H_E$, $2H_Z$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.7, 23.3, 30.7, 34.9, 35.0, 35.4, 55.3, 113.7, 114.5, 115.2, 129.3, 130.0, 130.7, 131.3, 133.2, 134.0, 141.8, 157.8 (6 signals overlapping);

MS (EI) *m*/*z* (%) 202 (M^+, 17), 121 (100); HRMS (EI) calcd for $C_{14}H_{18}O$: 202.1358, found: 202.1357.

*4.1.23. 1-[4-(Cyclopent-1-en-1-yl)but-3-en-1-yl]-4-methoxybenzene (**12b**).* A mixture of geometric isomers (*E*:*Z*=1:3); colorless oil; IR (neat) 2951, 2932, 2842, 1612, 1512, 1464, 1442, 1300, 1246, 1177, 1038, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90 (quint, *J*=7.4 Hz, $2H_Z$), 2.00–2.10 (m, $2H_E$), 2.29–2.44 (m, $3H_E$, $3H_Z$), 2.49–2.76 (m, $5H_E$, $5H_Z$), 3.79 (br s, $3H_E$, $3H_Z$), 5.38 (td, *J*=7.0, 11.7 Hz, $1H_Z$), 5.52–5.69 (m, $2H_E$, $1H_Z$), 6.03 (br d, *J*=11.7 Hz, $1H_Z$), 6.30 (br d, *J*=15.6 Hz, $1H_E$), 6.79–6.87 (m, $2H_E$, $2H_Z$), 7.07–7.15 (m, $2H_E$, $2H_Z$); MS (EI) *m*/*z* (%) 228 (M^+, 9), 121 (100); HRMS (EI) calcd for $C_{16}H_{20}O$: 228.1514, found: 228.1515.

*4.1.24. 1-(4,5-Dimethylhexa-3,5-dien-1-yl)-4-methoxybenzene (**12c**).* A 1:2.4 mixture of geometric isomers; colorless oil; IR (neat) 3030, 2994, 2932, 2855, 2834, 1611, 1584, 1512, 1464, 1441, 1374, 1300, 1246, 1177, 1039, 885, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, major: M, minor: m) δ 1.74 (br t, *J*=1.1 Hz, $3H_m$), 1.76 (br s, $3H_M$, $3H_m$), 1.89 (br d, *J*=0.7 Hz, $3H_M$), 2.27–2.37 (m, $2H_m$), 2.42 (br q, *J*=7.4 Hz, $2H_M$), 2.53–2.60 (m, $2H_m$), 2.60–2.69 (m, $2H_M$), 3.78 (br s, $3H_m$), 3.79 (br s, $3H_M$), 4.60–4.63 (m, $1H_m$), 4.86–4.90 (m, $1H_M$, $1H_m$), 4.96–4.99 (m, $1H_M$), 5.19 (qt, *J*=1.5, 7.2 Hz, $1H_m$), 5.63 (br t, *J*=7.4 Hz, $1H_M$), 6.78–6.87 (m, $2H_M$, $2H_m$), 7.05–7.15 (m, $2H_M$, $2H_m$); MS (EI) *m*/*z* (%) 216 (M^+, 12), 121 (100); HRMS (EI) calcd for $C_{15}H_{20}O$: 216.1514, found: 216.1516.

*4.1.25. 1-Methyl-4-[(2-methylprop-1-en-1-yl)sulfonyl]benzene (**13a**).* Colorless crystals (hexane–EtOAc); mp 64.5–65.0 °C; IR (KBr) 3041, 2978, 1634, 1597, 1496, 1443, 1375, 1320, 1285, 1180, 1141, 1087, 874, 812, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.88 (d, *J*=1.3 Hz, 3H), 2.14 (d, *J*=1.3 Hz, 3H), 2.43 (s, 3H), 6.17 (septet, *J*=1.3 Hz, 1H), 7.29–7.37 (m, 2H), 7.75–7.83 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0 (CH_3), 21.5 (CH_3), 26.9 (CH_3), 126.4 (CH), 127.0 (CH), 129.6 (CH), 139.4 (C), 143.8 (C), 153.6 (C); Anal. Calcd for $C_{11}H_{14}O_2S$: C 62.83, H 6.71, S 15.25; found C 62.58, H 6.59, S 15.30.

*4.1.26. (E)-1-Methyl-4-[(2-phenylprop-1-en-1-yl)sulfonyl]benzene (**13b**).* Colorless crystals (hexane–EtOAc); mp 96.5–97.0 °C; IR (KBr) 3055, 1595, 1443, 1311, 1300, 1289, 1141, 1082, 828, 813, 791, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.52 (d, *J*=1.2 Hz, 3H), 6.59 (q, *J*=1.2 Hz, 1H), 7.31–7.42 (m, 7H), 7.81–7.88 (m, 2H); Anal. Calcd for $C_{16}H_{16}O_2S$: C 70.56, H 5.92, S 11.77; found C 70.52, H 5.96, S 11.76.

*4.1.27. 1-[(Cyclohexylidenemethyl)sulfonyl]-4-methylbenzene (**13e**).* Colorless crystals (hexane–EtOAc); mp 37.0–37.6 °C; IR (KBr) 2945, 2936, 2855, 1620, 1443, 1310, 1297, 1288, 1141, 1085, 813, 792 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–1.66 (m, 6H), 2.14 (br t, *J*=5.7 Hz, 2H), 2.41 (s, 3H), 2.71 (br t, *J*=5.7 Hz, 2H), 6.10–6.13 (m, 1H), 7.30 (d, *J*=8.1 Hz, 2H), 7.76 (d, *J*=8.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 25.7, 27.3, 28.3, 29.3, 37.5, 123.7, 127.0, 129.7, 139.9, 143.7, 160.9; Anal. Calcd for $C_{14}H_{18}O_2S$: C 67.16, H 7.25, S 12.81; found C 66.83, H 7.21, S 12.78.

*4.1.28. 1-Methoxy-4-(4-methyl-3-tosylpent-3-en-1-yl)benzene (**13g**).* Colorless crystals (hexane–EtOAc); mp 90.5–91.1 °C; IR (KBr) 2937, 1633, 1610, 1512, 1457, 1444, 1299, 1245, 1172, 1137, 1085, 1029, 814, 692, 601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.13 (s, 3H), 2.42 (s, 3H), 2.64–2.70 (m, 2H), 2.72–2.78 (m, 2H), 3.79 (s, 3H), 6.82 (d, *J*=8.5 Hz, 2H), 7.10 (d, *J*=8.5 Hz, 2H), 7.31 (d, *J*=8.3 Hz, 2H), 7.77 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5 (CH_3), 22.2 (CH_3), 23.8 (CH_3), 32.7 (CH_2), 34.8 (CH_2), 55.2 (CH_3), 113.8 (CH), 127.0 (CH), 129.4 (CH), 129.5 (CH), 133.2 (C), 135.7 (C), 139.7 (C), 143.5 (C), 148.1 (C), 157.9 (C); MS (EI) *m*/*z* (%) 344 (M^+, 16), 121 (100); HRMS (EI) calcd for $C_{20}H_{24}O_3S$: 344.1446, found: 344.1447.

*4.1.29. 1-Methyl-4-[(2-methyl-1-phenylprop-1-en-1-yl)sulfonyl]benzene (**13h**).* Colorless crystals (hexane–EtOAc); mp 100.0–100.5 °C; IR (KBr) 2926, 1618, 1594, 1492, 1443, 1308, 1301, 1287, 1252, 1143, 1087, 1073, 933, 903, 815, 765, 706, 687 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3H), 2.39 (br s, 3H), 2.42 (s, 3H), 6.95–7.02 (m, 2H), 7.15–7.32 (m, 5H), 7.47–7.54 (m, 2H); Anal. Calcd for $C_{17}H_{18}O_2S$: C 71.30, H 6.34, S 11.20; found C 71.23, H 6.32, S 11.23.

*4.1.30. 1-[(2-Cyclohexylideneethyl)sulfonyl]-4-methylbenzene (**14c**).* Colorless crystals (hexane–EtOAc); mp 69.5–70.0 °C; IR (KBr) 2934, 2846, 1448, 1315, 1302, 1291, 1161, 1141, 1124, 1087, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13–1.25 (m, 2H), 1.39–1.51 (m, 4H), 1.81 (br dt, *J*=0.9, 6.2 Hz, 2H), 2.03–2.12 (m, 2H), 2.44 (s, 3H), 3.79 (d, *J*=8.0 Hz, 2H), 5.13 (br tt, *J*=0.9, 8.0 Hz, 1H), 7.29–7.35 (m, 2H), 7.70–7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 28.0 (CH_2), 28.7 (CH_2), 37.1 (CH_2), 55.3 (CH_2), 107.2 (CH), 128.6 (CH), 129.5 (CH), 135.8 (C), 144.3 (C), 150.1 (C); Anal. Calcd for $C_{15}H_{20}O_2S$: C 68.14, H 7.62, S 12.13; found C 68.38, H 7.45, S 12.28.

*4.1.31. (3-Tosylprop-1-ene-1,1-diyl)dibenzene (**14d**).* Colorless crystals (hexane–EtOAc); mp 128.1–128.9 °C; IR (KBr) 2967, 2923, 1595, 1490, 1445, 1314, 1290, 1226, 1167, 1133, 1084, 888, 774, 749, 709, 700, 640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.90 (d, *J*=7.9 Hz, 2H), 6.13 (t, *J*=7.9 Hz, 1H), 6.67–6.73 (m, 2H), 7.14–7.32 (m, 10H), 7.66 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6, 57.5, 114.2, 127.3, 127.7, 128.1, 128.21, 128.24, 128.4, 129.2, 129.6135.7, 137.8, 140.8, 144.5, 149.5; MS (EI) *m*/*z* (%) 348 (M^+, 1), 193 (100), 178 (15), 115 (36), 91 (14); HRMS (EI) calcd for $C_{22}H_{20}O_2S$: 348.1184, found: 348.1181.

*4.1.32. 2,2-Bis(ethoxymethyl)-8-methylspiro[3.5]non-8-ene-5,5,6,6-tetracarbonitrile (**15a**).* Tetracyanoethylene (21.5 mg, 0.168 mmol) was added to a solution of **10a** (25.1 mg, 0.112 mmol) in Et_2O (2.0 mL) at room temperature, and the mixture was stirred at that temperature for 15 min. The mixture was filtered through a bed of Celite® and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–EtOAc, 10:1) to give **15a** (35.1 mg, 0.0997 mmol, 89%) as a yellow oil. IR (neat) 2978, 2934, 2873, 2256 (CN), 1445, 1379, 1356, 1174, 1113, 1074, 913, 879, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J*=7.0 Hz, 3H), 1.26 (t, *J*=7.0 Hz, 3H), 1.84 (br s, 3H), 2.38 (dd, *J*=1.6, 12.9 Hz, 2H), 2.59 (dd, *J*=1.6, 12.9 Hz, 2H), 2.93 (br s, 2H), 3.44 (s, 2H), 3.50 (s, 2H), 3.51 (q, *J*=7.0 Hz, 2H), 3.57 (q, *J*=7.0 Hz, 2H), 6.31 (br sextet, *J*=1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.9 (CH_3), 15.1 (CH_3), 22.6 (CH_3), 36.5 (CH_2), 36.75 (C), 36.77 (C), 37.3 ($CH_2\times2$), 39.2 (C), 48.2 (C), 66.9 ($CH_2\times2$), 73.6 (CH_2), 74.3 (CH_2), 110.7 (C×2), 110.9 (C×2), 124.6 (C), 127.7 (CH); MS (EI) *m*/*z* (%) 352 (M^+, 2), 306 (36), 251 (34), 222 (26), 98 (47), 85 (22), 72 (25), 59 (100); HRMS (EI) calcd for $C_{20}H_{24}N_4O_2$: 352.1899, found: 352.1898.

*4.1.33. 3,3-Bis(ethoxymethyl)-1′,2′,3′,7a′-tetrahydrospiro[cyclobutane-1,5′-indene]-6′,6′,7′,7′-tetracarbonitrile (**15b**).* Yellow oil; IR (neat) 2977, 2934, 2874, 2256 (CN), 1378, 1356, 1165, 1112, 1073, 912, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, *J*=7.0 Hz, 3H), 1.25 (t, *J*=7.0 Hz, 3H), 1.65–1.89 (m, 2H), 1.91–2.08 (m, 1H), 2.27–2.62 (m, 6H), 2.74 (br d, *J*=13.7 Hz, 1H), 3.10–3.21 (m, 1H), 3.38–3.61 (m, 8H), 6.32 (br q, *J*=2.2 Hz, 1H); MS (EI) *m*/*z* (%) 378 (M^+, 20), 332 (26), 248 (24), 221 (21), 98 (44), 85 (31), 59 (100); HRMS (EI) calcd for $C_{22}H_{26}N_4O_2$: 378.2056, found: 378.2056.

*4.1.34. 3,3-Bis(ethoxymethyl)-5′,6′,7′,8′-tetrahydro-3′H-spiro[cyclobutane-1,2′-naphthalene]-3′,3′,4′,4′(4a′H)-tetracarbonitrile (**15c**).* Yellow

oil; IR (neat) 2977, 2940, 2867, 2255 (CN), 1449, 1378, 1163, 1112, 1073, 913, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, J=7.0 Hz, 3H), 1.26 (t, J=7.0 Hz, 3H), 1.30–1.68 (m, 3H), 1.80–1.94 (m, 1H), 1.96–2.21 (m, 2H), 2.24–2.48 (m, 5H), 2.75 (br d, J=14.1 Hz, 1H), 2.86–2.97 (m, 1H), 3.39–3.63 (m, 8H), 6.20 (br septet, J=2.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.9 (CH_3), 15.2 (CH_3), 24.7 (CH_2), 25.4 (CH_2), 29.7 (CH_2), 34.0 (CH_2), 36.8 (C), 37.5 ($CH_2\times2$), 39.1 (C), 42.4 (CH), 43.4 (C), 48.9 (C), 66.9 ($CH_2\times2$), 73.6 (CH_2), 74.3 (CH_2), 109.2 (C), 110.0 (C), 111.7 (C), 111.8 (C), 125.9 (CH), 131.2 (C); MS (EI) m/z (%) 392 (M^+, 6), 364 (50), 346 (36), 291 (32), 262 (27), 235 (26), 98 (63), 85 (39), 59 (100); HRMS (EI) calcd for $C_{23}H_{28}N_4O_2$: 392.2212, found: 392.2205.

4.1.35. (1R,3R*)-1,7-Dimethyl-1-[(trityloxy)methyl]spiro[2.5]oct-7-ene-4,4,5,5-tetracarbonitrile [(1R*,3R*)-**16**].* Colorless crystals; mp 216.5–217.0 °C; IR (KBr) 3059, 2918, 2868, 2256 (CN), 1491, 1449, 1076, 994, 904, 779, 770, 749, 733, 706, 633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, J=7.1 Hz, 1H), 1.62 (d, J=7.1 Hz, 1H), 1.69 (br s, 3H), 1.84 (s, 3H), 2.78 (d, J=10.2 Hz, 1H), 2.87 (d, J=17.9 Hz, 1H), 3.16 (br d, J=17.9 Hz, 1H), 3.53 (d, J=10.2 Hz, 1H), 4.75 (br s, 1H), 7.21–7.37 (m, 9H), 7.38–7.47 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.2 (CH_3), 22.7 (CH_3), 25.5 (CH_2), 28.1 (C), 29.4 (C), 36.1 (CH_2), 40.6 (C), 44.0 (C), 67.2 (CH_2), 86.4 (C), 110.2 (C), 110.4 (C), 111.4 (C), 111.8 (C), 122.6 (CH), 126.7 (C), 127.3 (CH), 127.9 (CH), 128.622 (CH), 128.624 (CH), 143.2 (C) (7 signals overlapping); MS (FAB+) m/z (%) 531 ([M+Na]$^+$, 9), 243 (100), 165 (31), 154 (25), 115 (67), 93 (23); HRMS (FAB+) calcd for $C_{34}H_{28}N_4ONa$: 531.2161, found: 531.2162.

4.1.36. (1R,3S*)-1,7-Dimethyl-1-[(trityloxy)methyl]spiro[2.5]oct-7-ene-4,4,5,5-tetracarbonitrile [(1R*,3S*)-**16**].* Colorless crystals; mp 65.0–65.5 °C; IR (KBr) 3059, 3034, 2940, 2254 (CN), 1491, 1449, 1221, 1070, 1032, 1001, 902, 777, 768, 750, 707, 633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (d, J=7.1 Hz, 1H), 1.45 (s, 3H), 1.68 (d, J=7.1 Hz, 1H), 1.89 (br s, 3H), 2.89 (d, J=17.9 Hz, 1H), 3.11 (br d, J=17.9 Hz, 1H), 3.51 (d, J=10.6 Hz, 1H), 3.66 (d, J=10.6 Hz, 1H), 5.35–5.40 (m, 1H), 7.22–7.37 (m, 9H), 7.45–7.53 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.9 (CH_3), 23.1 (CH_3), 26.8 (CH_2), 28.7 (C), 29.9 (C), 36.1 (CH_2), 41.1 (C), 44.9 (C), 65.7 (CH_2), 87.3 (C), 110.0 (C), 110.4 (C), 110.8 (C), 111.3 (C), 122.0 (CH), 127.3 (CH), 127.8 (CH), 127.9 (CH), 128.1 (C), 128.7 (CH), 128.8 (CH), 143.3 (C) (6 signals overlapping); MS (FAB+) m/z (%) 531 ([M+Na]$^+$, 14), 243 (100), 165 (39), 115 (16), 105 (14); HRMS (FAB+) calcd for $C_{34}H_{28}N_4ONa$: 531.2161, found: 531.2158.

4.2. DFT calculations

The DFT calculations were performed with Gaussian 03 software. The geometries were fully optimized in the gas phase without symmetry constraints at the B3LYP/6-311++G(d,p) level. The frequency calculations at the same level of theory were performed to determine whether the structures corresponded to energy minima (no imaginary frequencies). Natural bond orbital (NBO) analysis was performed at the B3LYP/6-311++G(d,p) level using NBO version 3.1, which is a program contained in the Gaussian 03 package.[22]

Acknowledgements

We wish to acknowledge support from a Grant-in-Aid for Scientific Research No. 22590021 from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and a TUS Grant for Research Promotion from Tokyo University of Science. High performance computing resources were provided by the Tokyo University of Science.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.03.019.

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