Synthesis of Multi-Substituted Cyclobutanes and Alkylidenecyclobutanes by the Reaction of Cyclobutylmagnesium Carbenoids with Nucleophiles

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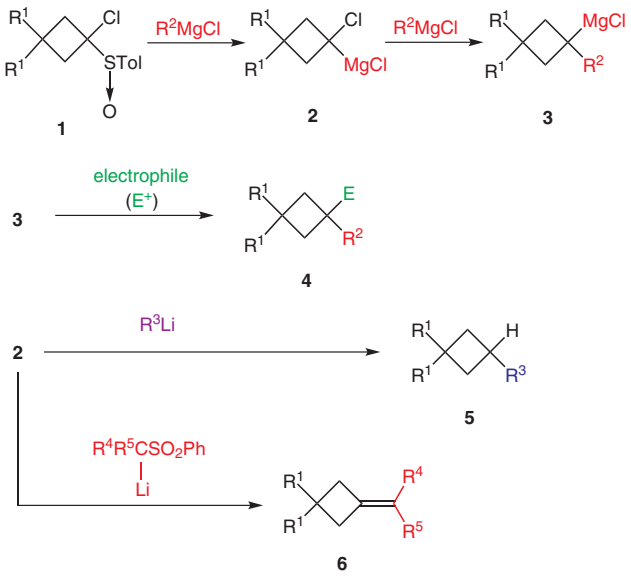
Abstract: Treatment of 1-chlorocyclobutyl *p*-tolyl sulfoxides with Grignard reagents such as ethylmagnesium chloride, isopropylmagnesium chloride, and cyclopentylmagnesium chloride in THF at low temperature gave cyclobutylmagnesium carbenoids in high yields. The generated magnesium carbenoids were found to be stable at –78 °C for at least 30 minutes. The cyclobutylmagnesium carbenoids reacted with several nucleophiles to give multi-substituted cyclobutanes. The reaction of the cyclobutylmagnesium carbenoids with lithium α-sulfonyl carbanions afforded alkylidenecyclobutanes in moderate to good yields.

Key words: cyclobutane, alkylidenecyclobutane, magnesium carbenoid, cyclobutylmagnesium carbenoid, cyclobutylmagnesium chloride

Although cyclobutane skeletal structures are not widely found in natural products, cyclobutane derivatives are quite interesting compounds. Due to high angular and torsional strain, cyclobutanes are fairly reactive under a variety of conditions and often used as versatile intermediates in organic synthesis.[1] Cyclopropanes are another small-ring compounds having inherent ring strain comparable to that of cyclobutanes and have been widely studied in organic chemistry; however, the chemistry of cyclobutanes is not fully investigated even now.

We have been interested in the chemistry of cyclopropanes, especially cyclopropylmagnesium carbenoids (cyclopropanes bearing magnesium and chlorine atoms at the same carbon) generated from 1-chlorocyclopropyl *p*-tolyl sulfoxides with Grignard reagents, and many interesting properties of the carbenoids have been unveiled.[2] In continuation of our interest in the chemistry of small-ring magnesium carbenoids, we recently started to investigate the generation, property, and synthetic uses of cyclobutylmagnesium carbenoids, which delivered quite interesting results.[3]

Thus, as shown in Scheme 1, treatment of 1-chlorocyclobutyl *p*-tolyl sulfoxides **1** with Grignard reagents (R^2MgCl) in THF at low temperature afforded cyclobutylmagnesium carbenoids **2** in high yields via the sulfoxide–magnesium exchange reaction.[4] The generated cyclobutylmagnesium carbenoids **2** were found to be stable at –78 °C for at least 30 minutes. When this reaction was carried out with excess R^2MgCl, carbenoids **2** were alkylated with the Grignard reagents to give the alkylated cyclobutylmagnesium chloride intermediates **3**, which could be trapped with electrophiles to give multi-substituted cyclobutanes **4** in moderate to good yields. Cyclobutylmagnesium carbenoids **2** were proved to be reactive with some alkyllithiums and *N*-lithioarylamines to give cyclobutanes **5**. The reaction of **2** with lithium α-sulfonyl carbanions gave alkylidenecyclobutanes **6** in moderate to good yields. Details of the aforementioned results are reported in this paper.



Scheme 1

Synthesis of 1-Chlorocyclobutyl *p*-Tolyl Sulfoxides

Three 1-chlorocyclobutyl *p*-tolyl sulfoxides **1a–c** were selected, which are the precursors for the generation of cyclobutylmagnesium carbenoids **2**, and synthesized them as follows (Scheme 2). Alkylation of the two hydroxy groups of known diol **7**[5] with 3-phenylpropyl bromide followed by catalytic hydrogenation and oxidation with IBX in DMSO gave cyclobutanone **8** in high overall yields. Reductive thiolation of cyclobutanone **8** with 4-methylbenzenethiol under Fyfe's conditions[6] gave cyclobutyl *p*-tolyl sulfide **9** in quantitative yield. Oxidation of the sulfide **9** with MCPBA followed by chlorination of the re-

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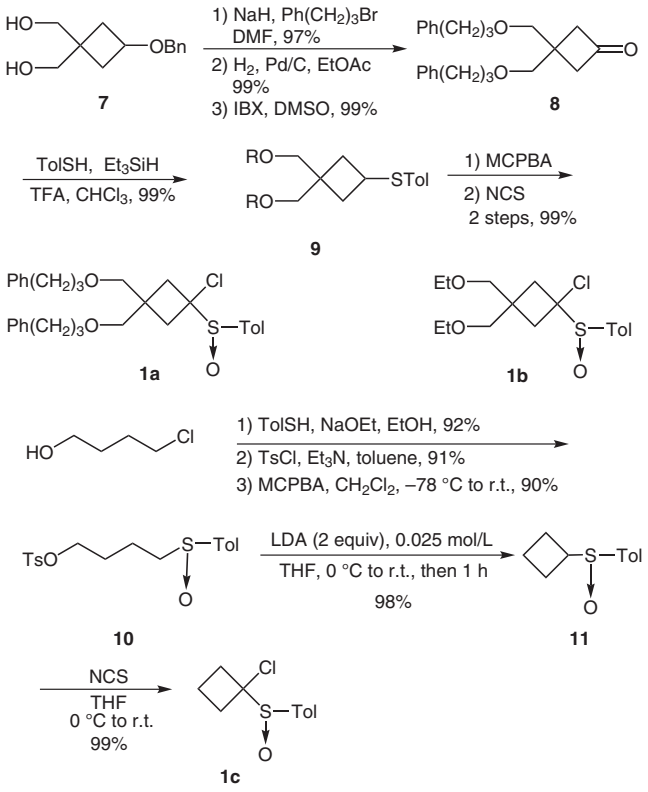
sulting sulfoxide with NCS gave the desired 1-chlorocyclobutyl *p*-tolyl sulfoxide **1a** in quantitative yield. When the alkylation of diol **7** was carried out with iodoethane, 1-chlorocyclobutyl *p*-tolyl sulfoxide **1b** was obtained in a similar overall yield as that of **1a**.

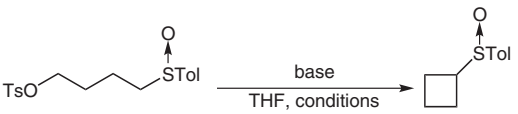


Scheme 2 Synthesis of 1-chlorocyclobutyl *p*-tolyl sulfoxides **1a**–**c**

As cyclobutanone itself is very expensive, the desired 1-chlorocyclobutyl *p*-tolyl sulfoxide (**1c**) was synthesized from much less expensive starting material. Thus, 4-chlorobutan-1-ol was treated with sodium 4-methylbenzenethiolate and the hydroxy group in the resultant sulfide was tosylated[7] to give tosyloxy sulfide in high yield. The sulfur of the sulfide was oxidized with MCPBA to afford tosyloxy sulfoxide **10** in good yield. Next, the conditions for the intramolecular alkylation of **10** were investigated and the results are summarized in Table 1.

At first, **10** was treated with 2 equiv of LDA in THF (concentration of the reaction mixture: 0.2 mol/L) at –78 °C and the temperature of the reaction mixture was allowed to warm to room temperature (Table 1, entry1). Fortunately, the desired cyclobutyl *p*-tolyl sulfoxide **11** was obtained in 68% yield with some unknown by-products. Next, the reaction was conducted in dilute conditions (entries 2–4) and the yield of **11** was improved up to 80%. Reducing the amount of LDA to 1.5 equiv was found to be less effective (entry 5). Sodium hydride and lithium hexamethyldisilazide (LiHMDS) were also found to be less effective in this reaction (entries 6 and 7). Only potassium hexamethyldisilazide (KHMDS) was proved to be effective to give **11** in the same yield as that with LDA

Table 1 Conditions for the Intramolecular Alkylation of **10** to Cyclobutyl *p*-Tolyl Sulfoxide (**11**)



10 **11**

Entry	Base	Concn (mol/L)	Conditions	**11**, Yield (%)
1	LDA (2 equiv)	0.2	–78 °C to r.t.	68
2	LDA (2 equiv)	0.1	–78 °C to r.t.	74
3	LDA (2 equiv)	0.05	–78 °C to r.t.	78
4	LDA (2 equiv)	0.025	–78 °C to r.t.	80
5	LDA (1.5 equiv)	0.025	–78 °C to r.t.	56
6	NaH (2 equiv)	0.025	–78 °C to r.t.	24
7	LiHMDS (2 equiv)	0.025	–78 °C to r.t.	54
8	KHMDS (2 equiv)	0.025	–78 °C to r.t.	80
9	LDA (2 equiv)	0.025	0 °C, 1 h	92
10	LDA (2 equiv)	0.025	0 °C to r.t., 1 h; then r.t. ,1 h	98

(80%; compare the yields in entries 4 and 8). Fortunately, when this reaction was carried out at 0 °C for 1 h, much better yield (92%) was obtained (entry 9). Finally, the conditions shown in entry 10 were selected as the conditions of choice for this reaction. Chlorination of **11** smoothly proceeded with NCS in THF at room temperature to give 1-chlorocyclobutyl *p*-tolyl sulfoxide (**1c**) in quantitative yield.

Generation and Property of Cyclobutylmagnesium Carbenoids

In our previous study,[2h,i] we could generate cyclopropylmagnesium carbenoids from 1-chlorocyclopropyl *p*-tolyl sulfoxides with *i*-PrMgCl via the sulfoxide–magnesium exchange reaction.[4] Based on these experiences, 1-chlorocyclobutyl *p*-tolyl sulfoxide **1a** was treated with 2.5 equivalents of *i*-PrMgCl in THF at –78 °C for 10 minutes and the reaction was quenched with MeOD (Table 2, entry 1). A clean reaction mixture was obtained, in which all the starting material **1a** had disappeared. Deuterated chlorocyclobutane **12** was obtained in 84% yield with perfect deuterium incorporation. This result implied that the sulfoxide–magnesium exchange reaction of **1a** took place instantaneously with *i*-PrMgCl even at –78 °C to afford the desired cyclobutylmagnesium carbenoid **2a** in high yield.

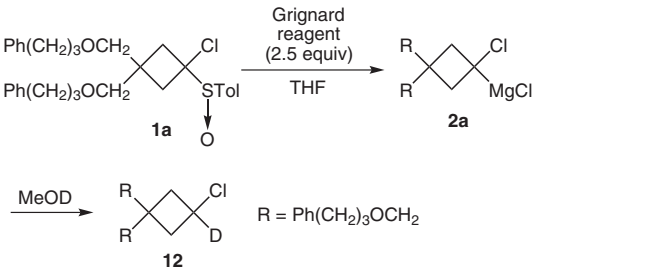
Generation of cyclobutylmagnesium carbenoid **2a** from **1a** was carried out with other Grignard reagents and the results are summarized in Table 2, entries 2 to 5. Interestingly, methylmagnesium chloride was found to be totally ineffective to the sulfoxide–magnesium exchange reaction (entry 2). Ethylmagnesium chloride proved to be the best Grignard reagent (entry 3). Cyclopentylmagnesium

chloride was found to be effective in this reaction; however, phenylmagnesium chloride was not (entries 4 and 5). *tert*-Butylmagnesium chloride also was totally ineffective in this sulfoxide–magnesium exchange reaction.

In order to investigate the stability of cyclobutylmagnesium carbenoid **2a**, the sulfoxide **1a** was treated with ethylmagnesium chloride under various temperature and time, and the reaction was quenched with MeOD. The stability of cyclobutylmagnesium carbenoid **2a** was estimated from the chemical yield and deuterium content of the product **12**. The results are summarized in Table 2, entries 6–16. Entry 6 shows that the sulfoxide–magnesium exchange reaction of **1a** instantaneously proceeds even at –90 °C. From the results in entries 7 and 8, it is implied that the generated cyclobutylmagnesium carbenoid **2a** is stable at lower than –78 °C for at least 30 minutes. It is worth noting that cyclobutylidene derived from 1,1-dibromocyclobutane with methyllithium or diazocyclobutane was reported to be highly reactive and gave rearranged products such as methylenecyclopropane, cyclobutene, and buta-1,3-diene.[8] In contrast to this, cyclobutylmagnesium carbenoid **2a** is proved to be quite stable and the rearranged products were not observed in our cases.

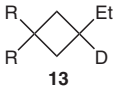
When this reaction was carried out at higher temperature, the yield of **12** was gradually diminished (entries 10–13). Interestingly, when this reaction was carried out at –50 °C or higher, ethylated cyclobutane **13** was obtained as a by-product (entries 14–16). These results implied that magnesium carbenoid **2a** is prone to react with Grignard reagents and the intermediate of this reaction is ethylated cyclobutylmagnesium chloride **14** (R^1 = Et; see Table 3).

Table 2 Generation of Cyclobutylmagnesium Carbenoid **2a** from **1a** and Quenching with MeOD



Entry	Grignard reagent	Temp (°C)	Time (min)	**12**, Yield (%)
1	*i*-PrMgCl	–78	10	84[a]
2	MeMgCl	–78	10	no reaction
3	EtMgCl	–78	10	90[a]
4	*c*-PentMgCl	–78	10	79[a]
5	PhMgCl	–78	10	trace
6	EtMgCl	–90	10	94[a]
7	EtMgCl	–90	30	88[a]
8	EtMgCl	–78	30	86[a]
9	EtMgCl	–78	60	83[a]
10	EtMgCl	–70	10	81[a]
11	EtMgCl	–70	30	78[a]
12	EtMgCl	–60	10	80[a]
13	EtMgCl	–60	30	72[a]
14	EtMgCl	–50	10	57[a,b]
15	EtMgCl	–50	30	48[a,c]
16	EtMgCl	–40	10	40[a,d]

[a] D-content over 99%.
[b] About 20% of ethylated cyclobutane **13** was obtained as a by-product.



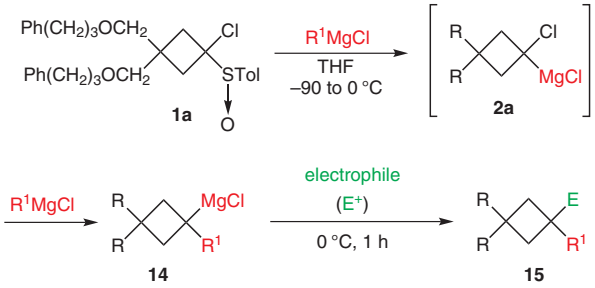
[c] About 30% of **13** was obtained.
[d] About 40% of **13** was obtained

Reaction of 1-Chlorocyclobutyl *p*-Tolyl Sulfoxides with Excess Grignard Reagents Followed by Electrophiles: Synthesis of Multi-Substituted Cyclobutanes with Two Carbon–Carbon Bond Formation in One-Pot

From the viewpoint of organic synthesis, alkylation of cyclobutylmagnesium carbenoids with carbanions is very interesting. As mentioned above, we found that cyclobutylmagnesium carbenoid **2a** reacted with ethylmagnesium chloride to afford ethylated cyclobutane **13** (see Table 2, footnote). The intermediate of this reaction was expected to be the ethylated cyclobutylmagnesium chloride **14** (R^1 = Et; see Table 3). If this intermediate **14** can be trapped with carbon electrophiles, multi-substituted cyclobutane derivatives bearing a quaternary carbon **15** would be synthesized. We brought this plan in practice and the results are summarized in Table 3.

Thus, 1-chlorocyclobutyl *p*-tolyl sulfoxide **1a** was treated with 5 equivalents of ethylmagnesium chloride in THF at –90 °C and the temperature of the reaction mixture was slowly allowed to warm to 0 °C. When this reaction was quenched with water, ethylated cyclobutane **15a** (R^1 = Et, E = H) was produced in 76% yield (Table 3, entry 1). When this reaction was treated with 5 equivalents of iodomethane in the presence of 10 mol% of Cu(I) iodide[2h] at 0 °C for one hour, dialkylated cyclobutane **15b** (R^1 = Et, E = Me) was obtained in 69% yield (entry 2). Allylated product **15c** was obtained in 64% yield by the same treatment with allyl iodide (entry 3). Benzoylation of the intermediate **14** was also found to be successful under the same conditions described above to give cyclobutane bearing a quaternary carbon **15d** in 60% yield (entry 4). The reaction with ethyl chloroformate gave the desired product; however, the yield was moderate (entry 5). The addition reaction of the carbanion intermediate **14** with benzaldehyde did not proceed at all (entry 6).

Table 3 Reaction of 1-Chlorocyclobutyl *p*-Tolyl Sulfoxide **1a** with Excess Grignard Reagent Followed by Electrophiles to Afford Multi-Substituted Cyclobutanes **15**



Entry	R^1MgCl	Electrophile	Additive	**15**, Yield (%)
1	EtMgCl[a]	H_2O	none	**15a**, 76
2	EtMgCl[a]	MeI	CuI[b]	**15b**, 69
3	EtMgCl[a]	$H_2C{=}CHCH_2I$	CuI[b]	**15c**, 64
4	EtMgCl[a]	PhCOCl	CuI[b]	**15d**, 60
5	EtMgCl[a]	EtOCOCl	none	**15e**, 45
6	EtMgCl[a]	PhCHO	CuI[b]	–[c]
7	*i*-PrMgCl[d]	H_2O	none	**15f**, 72
8	*i*-PrMgCl[d]	MeI	CuI[b]	**15g**, 74
9	*i*-PrMgCl[d]	$H_2C{=}CHCH_2I$	CuI[b]	**15h**, 72
10	*i*-PrMgCl[d]	PhCOCl	CuI[b]	**15i**, 33
11	*c*-PentMgCl[d]	H_2O	none	**15j**, 77
12	*c*-PentMgCl[d]	MeI	CuI[b]	**15k**, 70
13	*c*-PentMgCl[d]	$H_2C{=}CHCH_2I$	CuI[b]	**15l**, 75
14	*c*-PentMgCl[d]	PhCOCl	CuI[b]	**15m**, 51

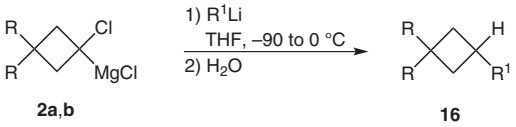
[a] Five equiv of EtMgCl was used.
[b] Ten mol% of CuI was used.
[c] Ethylated cyclobutane **15a** was obtained as the main product.
[d] Grignard reagent used: 7.5 equiv.

A similar reaction was proved to be able to carry out with isopropylmagnesium chloride and cyclopentylmagnesium chloride (entries 7–14); however, in these reactions, 7.5 equivalents of the Grignard reagents were required in order to give good results. As shown in entries 7–10, isopropylated cyclobutanes **15f–i** (R^1 = *i*-Pr) were obtained in similar yields compared with the corresponding ethylated products. Interestingly, the reactions with cyclopentylmagnesium chloride gave somewhat better yields of the desired products **15j–m** (R^1 = cyclopentyl; entries 11–14).

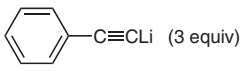
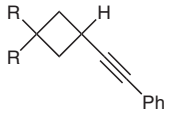
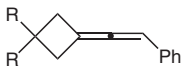
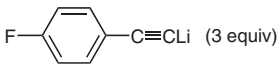
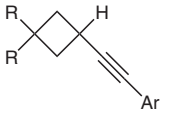
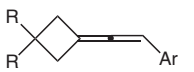
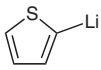
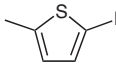
Reaction of Cyclobutylmagnesium Carbenoids with Lithium Acetylides, 2-Lithiothiophenes, *N*-Lithio-*N*-methylarylamines and *N*-Lithiophenothiazine

We have previously reported the reaction of magnesium alkylidenecarbenoids with lithium acetylides.[9] Based on this experience, the reaction of cyclobutylmagnesium carbenoids with lithium acetylides was investigated and the results are summarized in Table 4. Thus, cyclobutylmagnesium carbenoid **2a**, which was generated from **1a** with 2.5 equivalents of EtMgCl in THF at –90 °C, was treated with 3 equivalents of lithium acetylide derived from phenylacetylene with *n*-BuLi and the temperature of the reaction mixture was slowly allowed to warm to 0 °C (Table 4, entry 1). Interestingly, an inseparable mixture of cyclobutylacetylene **16a** and allene **16b** (the ratio of **16a/16b** = 3:10) was obtained in 78% yield. When this reaction was conducted with lithium acetylide derived from 4-fluorophenylacetylene, an inseparable mixture of **16c** and **16d** (the ratio of **16c/16d** = 9:10) was produced in 47% yield (entry 2). In both reactions, allene (**16b** and **16d**, respectively) was the main product. We attempted to obtain allene **16b** as the single product; however, any effort to change the ratio in favor of the allene was fruitless.

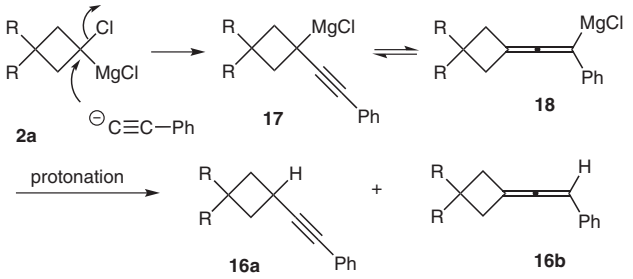
Table 4 Reaction of Cyclobutylmagnesium Carbenoids **2** with Lithium Acetylides and 2-Lithiothiophenes



a: R = $Ph(CH_2)_3OCH_2$
b: R = $EtOCH_2$

Entry	**2**	R^1Li	**16**, Yield (%)
1	**2a**	 (3 equiv)	 **16a**  **16b** **16a/16b** = 3:10 (78)
2	**2a**	 (3 equiv)	 **16c**  **16d** **16c/16d** = 9:10 (47)
3	**2b**	 (5 equiv)	**16e** (34)
4	**2b**	 (5 equiv)	**16f** (22)

The mechanism of this interesting reaction was presumed to be as follows (Scheme 3). Thus, S_N2 like substitution reaction of magnesium carbenoid **2a** with lithium acetylide gave cyclobutylmagnesium chloride intermediate **17**. This propargylic carbanion then rearranged to allenic carbanion **18**.[10] Carbanions **17** and **18** must be present in



Scheme 3 A plausible mechanism for the formation of **16a** and **16b** by the reaction of cyclobutylmagnesium carbenoid **2a** with lithium acetylide derived form phenylacetylene

equilibrium and they are protonated in the reaction medium to afford acetylene **16a** and allene **16b**.

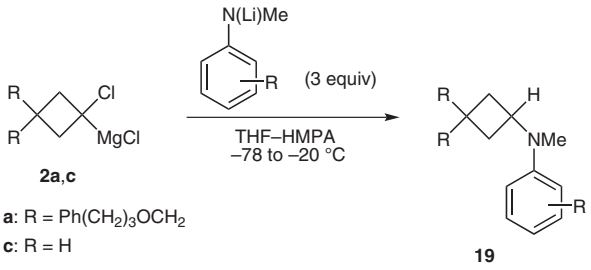
We have also previously reported the reaction of magnesium alkylidenecarbenoids with 2-lithiothiophenes to give 2-alkenylated thiophenes in good yields.[11] Based on this study, the reaction of cyclobutylmagnesium carbenoid **2b** with 2-lithiothiophenes was investigated (Table 4, entries 3 and 4). Thus, carbenoid **2b** generated from **1b** with 2.5 equivalents of EtMgCl in THF at –90 °C was treated with 5 equivalents of 2-lithiothiophenes, which were derived from thiophenes with *n*-BuLi, and the temperature of the reaction mixture was slowly allowed to warm to 0 °C. The desired 2-cyclobutylthiophenes **16e** and **16f** were obtained; however, the yields were very low compared to those from the reaction with magnesium alkylidene carbenoids.[11]

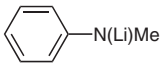
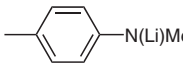
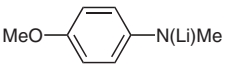
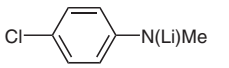
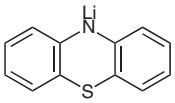
Finally, the reaction of cyclobutylmagnesium carbenoid **2** with nitrogen nucleophiles was investigated (Table 5).[12] Thus, carbenoid **2c** generated from **1c** with 2.5 equivalents of EtMgCl in THF at –78 °C was treated with 3 equivalents of *N*-lithio-*N*-methylaniline, which was generated from *N*-methylaniline with *n*-BuLi, and the temperature of the reaction mixture was slowly allowed to warm to –20 °C. The desired *N*-cyclobutyl-*N*-methylaniline (**19a**) was obtained; however, the yield was only 35%. The results of the reaction with *N*-methyl-4-substituted anilines and *N*-methyl-1-naphthylamine are summarized in entries 2–5. These reactions gave the desired products in up to 34%. The reaction of cyclobutylmagnesium carbenoid **2a** with *N*-lithiophenothiazine gave *N*-cyclobutylphenothiazine **20** in somewhat better yield (entry 6).

Synthesis of Alkylidenecyclobutanes by the Reaction of Cyclobutylmagnesium Carbenoids with Lithium α-Sulfonyl Carbanions

Alkylidenecyclobutanes are quite interesting compounds in synthetic organic chemistry.[13] In our previous studies, we have reported the reaction of magnesium carbenoids, magnesium alkylidenecarbenoids, and cyclopropylmagnesium carbenoids with lithium α-sulfonyl carbanions to give olefins,[14] allenes,[15] and alkylidenecyclopropanes,[2b] respectively. These reactions were applied to the cyclobutylmagnesium carbenoids **2** and indeed we could obtain the desired alkylidenecyclobutanes **6** in moderate to good yields. The results are summarized in Table 6.

Table 5 Reaction of Cyclobutylmagnesium Carbenoids **2** with *N*-Lithio-*N*-methylarylamines and *N*-Lithiophenothiazine

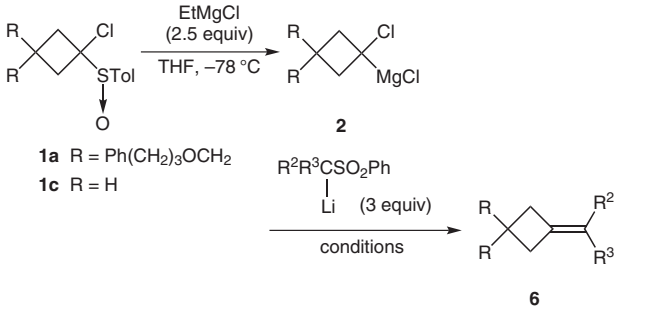


Entry	2	*N*-Lithioarylamine	19	Yield (%)
1	**2c**		**19a**	35
2	**2c**		**19b**	32
3	**2c**		**19c**	31
4	**2c**		**19d**	28
5	**2c**		**19e**	34
6	**2a**		**20**	40

Thus, at first, cyclobutylmagnesium carbenoid **2a** was generated from **1a** with 2.5 equivalents of EtMgCl at –78 °C in THF. In an another flask, a solution of lithium α-sulfonyl carbanion of benzyl phenyl sulfone was prepared from benzyl phenyl sulfone and *n*-BuLi at 0 °C and it was transferred to the solution of **2a** through a cannula and the temperature of the reaction mixture was slowly allowed to warm to –20 °C to afford benzylidenecyclobutane **6a** (Table 6, entry 1) in 83% yield. Other examples for the reaction of **2a** with various lithium α-sulfonyl carbanions are summarized in entries 2 to 8 in Table 6. Generally, the yields were better when the sulfonyl carbanions have an aromatic group or a conjugated unsaturated group (entries 1–5). Alkylidenecyclobutanes bearing a fully substituted olefinic group, **6c** and **6h**, also could be synthesized by this procedure (entries 3 and 8). The reaction starting from 1-chlorocyclobutyl *p*-tolyl sulfoxide (**1c**) via cyclobutylmagnesium carbenoid **2c** gave the desired alkylidenecyclobutanes **6i–k** in similar yields (entries 9–11).

In conclusion, we have found that the reaction of 1-chlorocyclobutyl *p*-tolyl sulfoxides with Grignard reagents, especially EtMgCl, at low temperature gave cyclobutyl-

Table 6 Synthesis of Alkylidenecyclobutanes **6** from 1-Chlorocyclobutyl *p*-Tolyl Sulfoxides **1** and Lithium α-Sulfonyl Carbanions via Cyclobutylmagnesium Carbenoids **2**



Entry	**1**	Sulfone		Conditions	**6**, Yield (%)
		R^2	R^3		
1	**1a**	Ph	H	–78 to –20 °C	**6a**, 83
2	**1a**	1-naphthyl	H	–78 to –20 °C	**6b**, 76
3	**1a**	Ph	Me	–78 to –20 °C	**6c**, 71
4	**1a**	H_2C=CH	H	–78 to –20 °C	**6d**, 77
5	**1a**	MeC≡C	H	–78 to –20 °C	**6e**, 67
6	**1a**	H	H	–78 to –50 °C, then 3 h	**6f**, 56
7	**1a**	Me	H	–78 to –50 °C, then 3 h	**6g**, 47
8	**1a**	Me	Me	–78 to –50 °C, then 3 h	**6h**, 49
9	**1c**	Ph	H	–78 to –20 °C	**6i**, 78
10	**1c**	1-naphthyl	H	–78 to –20 °C	**6j**, 70
11	**1c**	Ph	Me	–78 to –20 °C	**6k**, 64

magnesium carbenoids in high yields. The generated cyclobutylmagnesium carbenoids were found to be stable at –78 °C for at least 30 minutes. Multi-substituted cyclobutanes were synthesized in moderated to good yield based on the reaction of the cyclobutylmagnesium carbenoids with carbanions and *N*-lithioarylamines. Alkylidenecyclobutanes were synthesized by the reaction of cyclobutylmagnesium carbenoids with lithium α-sulfonyl carbanions in moderate to good yields. The chemistry presented here is unprecedented and will contribute to the synthesis of cyclobutane derivatives.[1]

All melting points were measured on Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Jeol JNMLA 500 and Bruker XWIN-600 spectrometers in $CDCl_3$ solution. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion by Hitachi M-80B mass spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument. Silica gel 60N (Kanto Chemical) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. CH_2Cl_2, *i*-Pr_2NH, Et_3N, DMF, and HMPA were distilled from CaH_2 for use in experiments requiring an anhyd reagent. THF was distilled from diphenylketyl and acetone was dried over $CaSO_4$ and distilled before use. Benzaldehyde, benzoyl chloride, and ethyl chloroformate were distilled before use.

3,3-Bis(3-phenylpropoxymethyl)cyclobutanone (8)

A solution of **7** (0.44 g, 2 mmol) in anhyd DMF (3 mL) was added to a suspension of NaH (0.35 g, 8 mmol) in anhyd DMF (17 mL) at 0 °C. After stirring the reaction mixture for 1 h, 3-phenylpropyl bromide (1.2 mL, 8 mmol) was added. The mixture was stirred for 2 h and the reaction was quenched by the addition of sat. aq NH_4Cl (1 mL) at 0 °C. The mixture was extracted with benzene (3 × 100 mL) (***Caution!*** Benzene has been identified as a carcinogen. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required). The combined organic layers were washed with sat. aq NH_4Cl (100 mL) and dried ($MgSO_4$). The solvent was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography (hexane–EtOAc) to give the intermediate ether (0.89 g, 97%) as a colorless oil. To a solution of the intermediate ether (0.80 g, 1.74 mmol) in EtOAc (9 mL) was added 10% Pd/C (0.16 g, 20%wt). The reaction mixture was stirred under H_2 atmosphere for 12 h. The mixture was filtered and the solvent was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography (hexane–EtOAc) to give the intermediate alcohol (0.63 g, 99%) as a colorless oil. IBX (0.58 g, 2.08 mmol) was added to a solution of the alcohol (0.64 g, 1.73 mmol) in DMSO (8 mL) and the reaction mixture was stirred for 2 h at r.t. The mixture was extracted with benzene (2 × 50 mL) (***Caution!*** see above) and the combined organic layers were washed with H_2O (3 × 50 mL) and dried ($MgSO_4$). The solvent was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography (hexane–EtOAc) to give **8** (0.65 g, 99%) as a colorless oil.

IR (neat): 3026, 2930, 2860, 2797, 1785 (C=O), 1603, 1497, 1454, 1376, 1115, 924, 818 cm^{-1}.

^{1}H NMR: δ = 1.88 (4 H, quint, *J* = 6.3 Hz), 2.68 (4 H, t, *J* = 7.7 Hz), 2.91 (4 H, s), 3.47 (4 H, t, *J* = 6.3 Hz), 3.53 (4 H, s), 7.16–7.19 (6 H, m), 7.25–7.29 (4 H, m).

MS: *m*/*z* (%) = 366 (M^+, 8), 248 (8), 118 (98), 91 (100).

HRMS: *m*/*z* calcd for $C_{24}H_{30}O_3$ (M^+): 366.2195; found: 366.2192.

1,1-Bis(3-phenylpropoxymethyl)-3-(*p*-tolylsulfanyl)cyclobutane (9)

TFA (4.1 mL) was added slowly to a stirred solution of cyclobutanone **8** (0.61g, 1.65 mmol) and *p*-toluenethiol (0.23g, 1.82 mmol) in $CHCl_3$ (4.1 mL) keeping at r.t. Et_3SiH (1.3 mL, 8.25 mmol) was then added to the reaction mixture over 5 min, again ensuring that the internal temperature stayed below r.t. The mixture was stirred at r.t. for 6 h and partitioned between $CHCl_3$ (50 mL) and H_2O (50 mL). The aqueous phase was further extracted with $CHCl_3$ (50 mL) and the combined organic extracts were washed with H_2O (80 mL), sat. aq Na_2CO_3 (80 mL) and H_2O (80 mL), and dried ($MgSO_4$). Filtration, solvent removal, and flash chromatography (hexane–EtOAc) furnished the compound **9** (0.80 g, 99%) as a colorless oil.

IR (neat): 3025, 2930, 2858, 2793, 1602, 1494, 1455, 1367, 1113, 923 cm^{-1}.

^{1}H NMR: δ = 1.83–1.92 (4 H, m), 1.96–2.00 (2 H, m), 2.30 (3 H, s), 2.34–2.43 (2 H, m), 2.65–2.70 (4 H, m), 3.35 (2 H, s), 3.40 (2 H, t, *J* = 6.3 Hz), 3.43 (2 H, s), 3.46 (2 H, t, *J* = 6.3 Hz), 3.79 (1 H, quint, *J* = 8.1 Hz), 7.07–7.09 (2 H, m), 7.17–7.19 (8 H, m), 7.25–7.29 (4 H, m).

MS: *m*/*z* (%) = 474 (M^+, 62), 150 (100), 135 (14), 118 (16), 91 (63).

HRMS: *m*/*z* calcd for $C_{31}H_{38}O_2S$ (M^+): 474.2593; found: 474.2593.

1-Chloro-3,3-bis(3-phenylpropoxymethyl)-1-(*p*-tolylsulfinyl)cyclobutane (1a)

A solution of sulfide **9** (4.86 g, 10.2 mmol) in $CHCl_3$ (40 mL) was cooled to –78 °C. To this solution was added *m*-chloroperbenzoic acid (75%, 2.69 g, 11.7 mmol) and the reaction mixture was stirred and slowly allowed to warm to 0 °C. The reaction was quenched with sat. aq Na_2SO_3 (2 mL) and the mixture was diluted with $CHCl_3$ (30 mL). The organic layer was washed with aq 5% NaOH (2 × 60 mL) followed by sat. aq NH_4Cl (60 mL). The organic layer was dried ($MgSO_4$) and the solvent was evaporated. The product was purified by silica gel column chromatography (hexane–EtOAc) to afford 4.96 g (99%) of the sulfoxide as a colorless oil. *N*-Chlorosuccinimide (1.69 g, 12.7 mmol) was added to a solution of the sulfoxide (4.96 g, 10.1 mmol) in anhyd THF (25 mL) and the suspension was stirred at r.t. for 12 h. The solution was concentrated and the precipitate (succinimide) was filtered off and the filtrate was evaporated to give a residue that was then purified by silica gel column chromatography (hexane–EtOAc) to afford 5.3 g (99%) of **1a** as a colorless oil.

IR (neat): 3061, 3026, 2935, 2860, 1599, 1495, 1455, 1407, 1368, 1292, 1178, 1114, 1056, 929 cm^{-1}.

^1H NMR: δ = 1.84–1.91 (4 H, m), 2.00 (1 H, d, *J* = 14.2 Hz), 2.41 (3 H, s), 2.46 (1 H, d, *J* = 14.3 Hz), 2.65–2.70 (4 H, m), 2.87 (1 H, d, *J* = 14.4 Hz), 2.98 (1 H, d, *J* = 14.3 Hz), 3.44–3.49 (6 H, m), 3.59 (2 H, s), 7.15–7.29 (12 H, m), 7.61–7.63 (2 H, m).

MS: *m*/*z* (%) = 524 (M^+, trace), 385 (12), 119 (49), 91(100).

HRMS: *m*/*z* calcd for $C_{31}H_{37}ClO_3S$ (M^+): 524.2152; found: 524.2150.

1-Chloro-3,3-bis(ethoxymethyl)-1-(*p*-tolylsulfinyl)cyclobutane (1b)

Compound **1b** was similarly prepared as above from the corresponding ethoxy-substituted derivative; yield: 98%; colorless oil.

IR (neat): 2975, 2931, 2867, 1597, 1491, 1407, 1377, 1355, 1292, 1178, 1111, 1057, 809 cm^{-1}.

^1H NMR: δ = 1.14–1.21 (6 H, m), 1.91–1.98 (1 H, m), 2.38–2.49 (1 H, m), 2.41 (3 H, s), 2.83–2.89 (1 H, m), 2.92–2.98 (1 H, m), 3.42–3.54 (6 H, m), 3.60 (2 H, s), 7.27–7.31 (2 H, m), 7.59–7.64 (2 H, m).

MS: *m*/*z* (%) = 345 ($[M + H]^+$, 100), 158 (24), 114 (45), 58 (48).

HRMS: *m*/*z* calcd for $C_{17}H_{26}ClO_3S$ (M^+): 345.1291; found: 345.1289.

4-Tosyloxybutyl *p*-Tolyl Sulfoxide (10)

To a stirred solution of 4-chlorobutan-1-ol (1.09 g, 10 mmol) in EtOH (12.5 mL) was added NaOEt (1.09 g, 16 mmol) at 0 °C. A solution of *p*-toluenethiol (1.86 g, 15 mmol) in EtOH (10 mL) was added to the solution and the reaction mixture was stirred at r.t. for 12 h. The reaction was quenched by adding sat. aq NH_4Cl (100 mL) and the mixture was extracted with $CHCl_3$ (3 × 80 mL). The combined organic layers were dried ($MgSO_4$) and the product was purified by silica gel column chromatography to give the sulfanyl alcohol (1.80 g, 92%) as a colorless oil. TsC1 (2.86 g, 15 mmol) in toluene (10 mL) was added to a stirred solution of the sulfanyl alcohol (1.96 g, 10 mmol), Et_3N (3.48 mL, 25 mmol), and $Me_3N{\cdot}HC1$ (95.6 mg, 1.0 mmol) in toluene (10 mL) at 0 °C. The reaction mixture was stirred and slowly allowed to warm to r.t., and stirred for an additional 1 h. H_2O (100 mL) was added to the mixture and it was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with H_2O (60 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–EtOAc) to give the desired tosylate (3.19 g, 91%) as a colorless oil. A solution of the tosylate (3.19 g, 9.1 mmol) in CH_2Cl_2 (36 mL) was cooled to 0 °C. To this solution was added slowly *m*-chloroperbenzoic acid (70%, 2.47 g, 10 mmol) and the mixture was stirred for 2 h. The reaction was quenched with sat. aq Na_2SO_3 (2 mL) and the mixture was diluted with CH_2Cl_2 (20 mL). The mixture was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were washed with 5% NaOH (2 × 60 mL) followed by sat. aq NH_4Cl (100 mL). The organic layer was dried ($MgSO_4$) and the solvent was evaporated. The product was purified by silica gel column chromatography (hexane–EtOAc) to afford 3.20 g (96%) of sulfoxide **10** as colorless crystals; mp 48–49 °C (hexane–EtOAc).

IR (KBr): 2924, 1598, 1495, 1453, 1357, 1189, 1176, 1088, 1044, 1016, 931, 813 cm^{-1}.

^1H NMR: δ = 1.65–1.83 (4 H, m), 2.42 (3 H, s), 2.46 (3 H, s), 2.70–2.75 (2 H, m), 4.00–4.04 (2 H, m), 7.31–7.36 (4 H, m), 7.47 (2 H, d, *J* = 8.2 Hz), 7.76 (2 H, d, *J* = 8.2 Hz).

Anal Calcd for $C_{18}H_{22}O_4S_2$: C, 58.66; H, 6.08; S, 17.27. Found: C, 58.99; H, 6.05; O, 17.46; S, 17.50.

Cyclobutyl *p*-Tolyl Sulfoxide (11)

Sulfoxide **10** (0.73 g; 2.0 mmol) was added dropwise to a solution of LDA (4 mmol) in anhyd THF (80 mL) at 0 °C with stirring under argon atmosphere. The reaction mixture was stirred and slowly allowed to warm to r.t., and stirred additionally for 1 h at r.t. The reaction was quenched with sat. aq NH_4Cl (50 mL). The mixture was extracted with $CHCl_3$ (3 × 50 mL) and the combined organic layers were dried ($MgSO_4$). The product was purified by silica gel column chromatography (hexane–EtOAc) to afford **11** (0.38 g, 98%) as a colorless oil.

IR (neat): 2984, 2943, 1597, 1494, 1266, 1245, 1088, 1046, 811 cm^{-1}.

^1H NMR: δ = 1.72–1.79 (1 H, m), 1.90–1.97 (2 H, m), 2.10–2.17 (1 H, m), 2.39–2.47 (1 H, m), 2.40 (3 H, s), 2.53–2.61 (1 H, m), 3.43 (1 H, quint, *J* = 8.3 Hz), 7.27–7.29 (2 H, m), 7.43–7.45 (2 H, m).

MS: *m*/*z* (%) = 194 (M^+, 53), 140 (87), 92 (41), 91 (28), 55 (100).

HRMS: *m*/*z* calcd for $C_{11}H_{14}OS$ (M^+): 194.0765; found: 194.0763.

1-Chlorocyclobutyl *p*-Tolyl Sulfoxide (1c)

N-Chlorosuccinimide (0.31 g, 2.35 mmol) was added to a solution of sulfoxide **11** (0.38 g, 1.96 mmol) in anhyd THF (10 mL) and the suspension was stirred at r.t. for 12 h. The solvent was evaporated and the precipitate was collected by filtration. The product was purified by silica gel column chromatography (hexane–EtOAc) to afford 0.44 g (99%) of **1c** as colorless crystals; mp 43–44 °C (hexane–EtOAc).

IR (KBr): 2955, 2917, 1593, 1489, 1417, 1298, 1254, 1221, 1084, 1054, 913, 810 cm^{-1}.

^1H NMR: δ = 1.90–2.04 (2 H, m), 2.18–2.30 (1 H, m), 2.42 (3 H, s), 2.40–2.52 (1 H, m), 2.98–3.17 (2 H, m), 7.30 (2 H, d, *J* = 8.1 Hz), 7.63 (2 H, d, *J* = 8.1 Hz).

Anal Calcd for $C_{11}H_{13}ClOS$: C, 57.73; H, 5.68; Cl, 15.37; S, 13.84. Found: C, 57.76; H, 5.68; Cl, 15.50; O, 6.99; S, 14.02.

1-Chloro-1-deuterio-3,3-bis(3-phenylpropoxymethyl)cyclobutane (12)

A solution of EtMgCl (2.0 M solution in THF, 0.25 mL, 0.5 mmol) was added to a solution of **1a** (105 mg, 0.2 mmol) in of THF (2 mL) at –78 °C with stirring under argon atmosphere. The solution was stirred for 10 min and the reaction was quenched with MeOD (0.3 mL) followed by sat. aq NH_4Cl (50 mL). The mixture was extracted with $CHCl_3$ (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane–EtOAc) to afford **12** (69.6 mg, 90%) as a colorless oil.

IR (neat): 3027, 2941, 2859, 1944, 1871, 1803, 1603, 1496, 1455, 1367, 1180, 1112, 921, 820 cm^{-1}.

^1H NMR: δ = 1.84–1.96 (4 H, m), 2.20–2.30 (2 H, m), 2.46–2.58 (2 H, m), 2.62–2.75 (4 H, m), 3.35 (2 H, s), 3.39 (2 H, s), 3.40–3.47 (4 H, m), 7.12–7.32 (10 H, m).

MS: *m*/*z* (%) = 387 (M^+, trace), 118 (100), 91 (58).

HRMS: *m*/*z* calcd for $C_{24}H_{30}DClO_2$ (M^+): 387.20755; found: 387.2076.

1-Deuterio-1-ethyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (13)
This compound was isolated from the reaction of **1a** with EtMgCl conducted as above, but at –40 °C or –50 °C (see, Table 2); colorless oil.

IR (neat): 3026, 2952, 2926, 2854, 1603, 1497, 1455, 1366, 1112, 745, 699 cm^{-1}.

^1H NMR: δ = 0.79 (3 H, t, *J* = 7.4 Hz), 1.39 (2 H, q, *J* = 7.3 Hz), 1.45–1.54 (2 H, m), 1.81–1.97 (6 H, m), 2.68 (4 H, t, *J* = 7.4 Hz), 3.31 (2 H, s), 3.37–3.51 (6 H, m), 7.12–7.34 (10 H, m).

MS: *m*/*z* (%) = 381 (M^+, 8), 118 (100), 91 (80).

HRMS: *m*/*z* calcd for $C_{26}H_{35}DO_2$ (M^+): 381.2778; found: 381.2777.

1-Ethyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15a)
A solution of EtMgCl (2.0 M solution in THF, 0.5 mL, 1.0 mmol) was added to a solution of **1a** (105 mg, 0.2 mmol) in THF (2 mL) at –90 °C with stirring under argon atmosphere. The reaction mixture was stirred and slowly allowed to warm to 0 °C. The reaction was quenched by adding sat. aq NH_4Cl (50 mL) and the mixture was extracted with $CHCl_3$ (3 × 20 mL) The combined organic layers were dried ($MgSO_4$) and concentrated. The product was purified by flash column chromatography (hexane–EtOAc) to give **15a** (57.8 mg, 76%) as a colorless oil.

IR (neat): 2953, 2924, 2854, 1604, 1496, 1455, 1367, 1113 cm^{-1}.

^1H NMR: δ = 0.79 (3 H, t, *J* = 7.4 Hz), 1.40 (2 H, quint, *J* = 7.4 Hz), 1.46–1.53 (2 H, m), 1.83–1.95 (6 H, m), 2.03–2.19 (1 H, m), 2.66–2.71 (4 H, m), 3.25 (2 H, s), 3.38–3.58 (6 H, m), 7.15–7.29 (10 H, m).

MS: *m*/*z* (%) = 380 (M^+, 13), 244 (8), 118 (100), 91 (73).

HRMS: *m*/*z* calcd for $C_{26}H_{36}O_2$ (M^+): 380.2715; found: 380.2714.

1-Ethyl-1-methyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15b); Typical Procedure
A solution of EtMgCl (2.0 M solution in THF, 0.5 mL, 1.0 mmol) was added to a solution of **1a** (105 mg, 0.2 mmol) in THF (2 mL) at –78 °C with stirring under argon atmosphere. The reaction mixture was stirred and slowly allowed to warm to 0 °C. To the mixture were added successively CuI (4 mg, 0.02 mmol) and MeI (0.06 mL, 1 mmol) and the mixture was stirred at 0 °C for 1 h. The reaction was quenched by adding sat. aq NH_4Cl (50 mL) and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The product was purified by flash column chromatography (hexane–EtOAc) to give **15b** (54.5 mg, 69%) as a colorless oil.

IR (neat): 2952, 2924, 2855, 1497, 1455, 1365, 1113 cm^{-1}.

^1H NMR: δ = 0.76–0.81 (3 H, m), 1.08 (3 H, s), 1.44 (2 H, q, *J* = 7.4 Hz), 1.46–1.53 (2 H, m), 1.57–1.70 (2 H, m), 1.83–1.93 (4 H, m), 2.65–2.72 (4 H, m), 3.36–3.48 (8 H, m), 7.15–7.29 (10 H, m).

MS: *m*/*z* (%) = 394 (M^+, 13), 258 (8), 118 (100), 91 (76).

HRMS: *m*/*z* calcd for $C_{27}H_{38}O_2$ (M^+): 394.2871; found: 394.2871.

1-Allyl-1-ethyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15c)
Colorless oil.

IR (neat): 2923, 2855, 1639, 1603, 1496, 1455, 1366, 1112 cm^{-1}.

^1H NMR: δ = 0.76 (3 H, t, *J* = 7.4 Hz), 1.48 (2 H, q, *J* = 7.4 Hz), 1.61 (2 H, d, *J* = 12.6 Hz), 1.68 (2 H, d, *J* = 12.6 Hz), 1.81–1.94 (4 H, m), 2.22 (2 H, d, *J* = 7.2 Hz), 2.62–2.72 (4 H, m), 3.37–3.46 (8 H, m), 4.94–5.06 (2 H, m), 5.65–5.79 (1 H, m), 7.15–7.29 (10 H, m).

MS: *m*/*z* (%) = 420 (M^+, 10), 284 (4), 242 (13), 118 (100), 91 (96).

HRMS: *m*/*z* calcd for $C_{29}H_{40}O_2$ (M^+): 420.3028; found: 420.3027.

[1-Ethyl-3,3-bis(3-phenylpropoxymethyl)cyclobutyl]phenylmethanone (15d)
Colorless oil.

IR (neat): 2932, 2859, 1714, 1674 (C=O), 1455, 1239, 1113, 911 cm^{-1}.

^1H NMR: δ = 0.67 (3 H, t, *J* = 7.4 Hz), 1.74–1.83 (2 H, m), 1.88–1.97 (2 H, m), 2.10–2.17 (4 H, m), 2.56–2.64 (4 H, m), 2.70–2.75 (2 H, m), 3.23 (2 H, s), 3.33 (2 H, t, *J* = 6.3 Hz), 3.42 (2 H, s), 3.49 (2 H, t, *J* = 6.3 Hz), 7.10–7.31 (10 H, m), 7.39–7.44 (2 H, m), 7.48–7.54 (1 H, m), 7.87–7.90 (2 H, m).

MS: *m*/*z* (%) = 484 (M^+, 40), 319 (13), 243 (18), 118 (100), 91 (98), 77 (13).

HRMS: *m*/*z* calcd for $C_{33}H_{40}O_3$ (M^+): 484.2978; found: 484.2985.

1-Ethyl-3,3-bis(3-phenylpropoxymethyl)cyclobutanecarboxylic Acid Ethyl Ester (15e)
Colorless oil.

IR (neat): 2932, 2858, 1727 (C=O), 1456, 1249, 1176, 1114 cm^{-1}.

^1H NMR: δ = 0.78 (3 H, t, *J* = 7.4 Hz), 1.25 (3 H, t, *J* = 7.1 Hz), 1.78–1.94 (8 H, m), 2.28–2.32 (2 H, m), 2.64–2.72 (4 H, m), 3.35–3.46 (8 H, m), 4.14 (2 H, q, *J* = 7.1 Hz), 7.17–7.30 (10 H, m).

MS: *m*/*z* (%) = 452 (M^+, 28), 407 (8), 242 (12), 118 (100), 91 (68).

HRMS: *m*/*z* calcd for $C_{29}H_{40}O_4$ (M^+): 452.2927; found: 452.2923.

1-Isopropyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15f)
A solution of *i*-PrMgCl (2.0 M solution in THF, 0.38 mL, 0.75 mmol) was added to a solution of **1a** (52.5 mg, 0.1 mmol) in THF (1 mL) at –90 °C with stirring under argon atmosphere. The reaction mixture was stirred and slowly allowed to warm to 0 °C. The reaction was quenched by adding sat. aq NH_4Cl (20 mL) and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The product was purified by flash column chromatography (hexane–EtOAc) to give **15f** (28.5 mg, 72%) as a colorless oil.

IR (neat): 2951, 2857, 1603, 1496, 1454, 1364, 1112 cm^{-1}.

^1H NMR: δ = 0.79 (6 H, d, *J* = 6.6 Hz), 1.37–1.50 (1 H, m), 1.50–1.60 (2 H, m), 1.77–1.95 (7 H, m), 2.62–2.74 (4 H, m), 3.29 (2 H, s), 3.38–3.51 (6 H, m), 7.14–7.30 (10 H, m).

MS: *m*/*z* (%) = 394 (M^+, 12), 258 (8), 118 (100), 91 (70).

HRMS: *m*/*z* calcd for $C_{27}H_{38}O_2$ (M^+): 394.2872; found: 394.2869.

1-Isopropyl-1-methyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15g); Typical Procedure
A solution of *i*-PrMgCl (2.0 M solution in THF, 0.38 mL, 0.75 mmol) was added to a solution of **1a** (52.5 mg, 0.1 mmol) in THF (1 mL) at –90 °C with stirring under argon atmosphere. The reaction mixture was stirred and slowly allowed to warm to 0 °C. To the mixture were successively added CuI (2 mg, 0.01 mmol) and MeI (0.06 mL, 1 mmol) and the mixture was stirred at 0 °C for 1 h. The reaction was quenched by adding sat. aq NH_4Cl (20 mL) and the

mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The product was purified by flash column chromatography (hexane–EtOAc) to give **15g** (31.1 mg, 74%) as a colorless oil.

IR (neat): 2954, 2861, 1496, 1454, 1363, 1112 cm^{-1}.

^1H NMR: δ = 0.71–0.84 (7 H, m), 0.97 (2 H, s), 1.49–1.78 (5 H, m), 1.81–1.95 (4 H, m), 2.64–2.74 (4 H, m), 3.29 (1 H, s), 3.34 (1 H, s), 3.37–3.52 (6 H, m), 7.12–7.34 (10 H, m).

MS: *m*/*z* (%) = 408 (M^+, 9), 118 (100), 91 (86).

HRMS: *m*/*z* calcd for $C_{28}H_{40}O_2$ (M^+): 408.3028; found: 408.3028.

1-Allyl-1-isopropyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15h)
Colorless oil.

IR (neat): 2953, 2930, 2858, 1638, 1603, 1496, 1454, 1365, 1113, 911 cm^{-1}.

^1H NMR: δ = 0.78–0.87 (6 H, m), 1.48–1.96 (9 H, m), 2.15–2.54 (2 H, m), 2.64–2.74 (4 H, m), 3.27–3.48 (8 H, m), 4.91–5.09 (2 H, m), 5.71–5.96 (1 H, m), 7.11–7.32 (10 H, m).

MS: *m*/*z* (%) = 434 (M^+, 8), 256 (11), 118 (73), 91 (100), 28 (23).

HRMS: *m*/*z* calcd for $C_{30}H_{42}O_2$ (M^+): 434.3185; found: 434.3186.

[1-Isopropyl-3,3-bis(3-phenylpropoxymethyl)cyclobutyl]phenylmethanone (15i)
Colorless oil.

IR (neat): 2938, 2859, 1721, 1674 (C=O), 1598, 1496, 1453, 1263, 1114, 918 cm^{-1}.

^1H NMR: δ = 0.92 (6 H, d, *J* = 6.6 Hz), 1.70–1.82 (2 H, m), 1.84–1.97 (2 H, m), 2.22–2.39 (3 H, m), 2.45–2.62 (4 H, m), 2.65–2.75 (2 H, m), 3.25 (2 H, s), 3.32 (2 H, t, *J* = 6.3 Hz), 3.37–3.50 (4 H, m), 7.07–7.33 (10 H, m), 7.37–7.46 (2 H, m), 7.46–7.56 (1 H, m), 7.84–7.94 (2 H, m).

MS: *m*/*z* (%) = 498 (M^+, 10), 319 (10), 118 (70), 105 (48), 91 (100).

HRMS: *m*/*z* calcd for $C_{34}H_{42}O_3$ (M^+): 498.3134; found: 498.3135.

1-Cyclopentyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15j)
Colorless oil.

IR (neat): 2945, 2858, 1496, 1453, 1113 cm^{-1}.

^1H NMR: δ = 1.02–1.12 (2 H, m), 1.44–1.60 (6 H, m), 1.60–1.70 (2 H, m), 1.77–1.94 (7 H, m), 1.99–2.10 (1 H, m), 2.64–2.72 (4 H, m), 3.31 (2 H, s), 3.39–3.48 (6 H, m), 7.12–7.30 (10 H, m).

MS: *m*/*z* (%) = 420 (M^+, 12), 284 (6), 118 (100), 91 (70).

HRMS: *m*/*z* calcd for $C_{29}H_{40}O_2$ (M^+): 420.3028; found: 420.3035.

1-Cyclopentyl-1-methyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15k)
Colorless oil.

IR (neat): 2949, 2863, 1603, 1496, 1454, 1372, 1113 cm^{-1}.

^1H NMR: δ = 1.03–1.28 (5 H, m), 1.42–1.72 (8 H, m), 1.73–1.81 (2 H, m), 1.83–1.99 (5 H, m), 2.62–2.74 (4 H, m), 3.37 (2 H, s), 3.40–3.51 (6 H, m), 7.08–7.32 (10 H, m).

MS: *m*/*z* (%) = 434 (M^+, 6), 298 (11), 118 (100), 91 (96).

HRMS: *m*/*z* calcd for $C_{30}H_{42}O_2$ (M^+): 434.3185; found: 434.3180.

1-Allyl-1-cyclopentyl-3,3-bis(3-phenylpropoxymethyl)cyclobutane (15l)
Colorless oil.

IR (neat): 2947, 2861, 1638, 1603, 1496, 1454, 1366, 1113, 911 cm^{-1}.

^1H NMR: δ = 1.09–1.28 (2 H, m), 1.43–1.80 (9 H, m), 1.80–1.99 (6 H, m), 2.28–2.38 (2 H, m), 2.62–2.74 (4 H, m), 3.35–3.51 (8 H, m), 4.92–5.11 (2 H, m), 5.71–5.91 (1 H, m), 7.10–7.32 (10 H, m).

MS: *m*/*z* (%) = 460 (M^+, 18), 282 (19), 147 (22), 118 (89), 91 (100).

HRMS: *m*/*z* calcd for $C_{32}H_{44}O_2$ (M^+): 460.3341; found: 460.3343.

[1-Cyclopentyl-3,3-bis(3-phenylpropoxymethyl)cyclobutyl]phenylmethanone (15m)
Colorless oil.

IR (neat): 2946, 2863, 1722, 1674 (C=O), 1597, 1496, 1454, 1263, 1176, 1115, 910 cm^{-1}.

^1H NMR: δ = 1.28–1.69 (8 H, m), 1.70–1.81 (2 H, m), 1.83–1.97 (2 H, m), 2.20–2.32 (2 H, m), 2.42–2.62 (5 H, m), 2.66–2.75 (2 H, m), 3.23 (2 H, s), 3.31 (2 H, t, *J* = 6.3 Hz), 3.38–3.50 (4 H, m), 7.05–7.33 (10 H, m), 7.37–7.46 (2 H, m), 7.46–7.54 (1 H, m), 7.87–7.97 (2 H, m).

MS: *m*/*z* (%) = 524 (M^+, 15), 147 (28), 118 (52), 105 (43), 91 (100).

HRMS: *m*/*z* calcd for $C_{36}H_{44}O_3$ (M^+): 524.3290; found: 524.3285.

Acetylene 16a and Allene 16b; Typical Procedure
To a solution of phenylacetylene (0.035 mL, 0.3 mmol) in anhyd THF (1 mL) in a flame-dried flask at 0 °C under argon atmosphere were added successively *n*-BuLi (0.19 mL, 0.31 mmol) and HMPA (0.05 mL, 0.3 mmol) to give a clear yellow solution. The mixture was cooled to –90 °C and to this mixture was added a solution of **2a** (56 mg, 0.1 mmol) in THF (1 mL) followed by EtMgCl (2.0 M solution in THF, 0.13 mL, 0.25 mmol) with stirring. The temperature of the reaction mixture was gradually allowed to warm to –40 °C and the stirring was continued at this temperature for 1 h. The temperature of the mixture was then slowly allowed to warm to 0 °C. The reaction was quenched by the addition of sat. aq NH_4Cl (20 mL). The mixture was extracted with $CHCl_3$ (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$). The product was purified by silica gel column chromatography (hexane–EtOAc) to afford an inseparable 3:10 mixture of **16a** and **16b** (34.1 mg, 78%) as a colorless oil.

IR (neat): 3026, 2930, 2858, 2343 (C≡C), 1950 (C=C=C), 1496, 1454, 1112, 746, 699 cm^{-1}.

^1H NMR: δ = 1.82–2.01 (4 H, m), 2.60–2.76 (4 H, m), 2.76–2.84 (4 H, m), 2.84–2.90 (0.23 H, m), 3.32–3.60 (8 H, m), 6.15 (0.77 H, m, C=C=CH), 7.10–7.35 (15 H, m).

MS: *m*/*z* (%) = 452 (M^+, trace), 167 (13), 128 (14), 118 (100), 91 (87).

HRMS: *m*/*z* calcd for $C_{32}H_{36}O_2$ (M^+): 452.2715; found: 452.2714.

Acetylene 16c and Allene 16d
Colorless oil (an inseparable 9:10 mixture of **16c** and **16d**).

IR (neat): 3026, 2928, 2858, 2344 (C≡C), 1949 (C=C=C), 1601, 1508, 1224, 1113 cm^{-1}.

^1H NMR: δ = 1.84–2.02 (4 H, m), 2.64–2.76 (4 H, m), 2.76–2.82 (4 H, m), 2.82–2.88 (0.47 H, m), 3.32–3.60 (8 H, m), 6.12 (0.53 H, m, C=C=CH), 6.92–6.97 (2 H, m), 7.10–7.35 (12 H, m).

MS: *m*/*z* (%) = 470 (M^+, trace), 118 (100), 91 (73).

HRMS: *m*/*z* calcd for $C_{32}H_{35}FO_2$ (M^+): 470.2621; found: 470.2627.

2-[3,3-Bis(ethoxymethylcyclobutyl)]thiophene (16e); Typical Procedure
A solution of EtMgCl (2.0 M solution in THF, 0.125 mL, 0.25 mmol) was added to a solution of **2b** (34.5 mg, 0.1 mmol) in THF (1 mL) at –90 °C with stirring under argon atmosphere. Thiophene

(0.04 mL, 0.5 mmol) was added to a solution of *n*-BuLi (1.65 M solution in *n*-hexane, 0.3 mL, 0.5 mmol) in anhyd THF (1 mL) in an another flame-dried flask at –90 °C under argon atmosphere to give a clear yellow solution. This solution was added to the solution of the carbenoid via a cannula. The reaction mixture was stirred and slowly allowed to warm to 0 °C and the reaction was quenched with sat. aq NH_4Cl (20 mL). The mixture was extracted with $CHCl_3$ (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$). The product was purified by silica gel column chromatography (hexane–EtOAc) to afford **16e** (8.6 mg, 34%) as a colorless oil.

IR (neat): 2974, 2931, 2859, 1731, 1444, 1376, 1354, 1111, 825 cm^{-1}.

^1H NMR: δ = 1.15–1.27 (6 H, m), 2.04–2.16 (2 H, m), 2.28–2.39 (2 H, m), 3.38 (2 H, s), 3.44–3.60 (6 H, m), 3.69 (1 H, quint, *J* = 8.9 Hz), 6.79–6.85 (1 H, m), 6.92 (1 H, dd, *J* = 5.1, 3.4 Hz), 7.11 (1 H, dd, *J* = 5.1, 1.1 Hz).

MS: *m*/*z* (%) = 254 (M^+, 5), 110 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{22}O_2S$ (M^+): 254.1341; found: 254.1345.

2-[3,3-Bis(ethoxymethylcyclobutyl)]-5-methylthiophene (16f)
Colorless oil.

IR (neat): 2974, 2931, 2862, 1445, 1376, 1354, 1170, 1110, 881 cm^{-1}.

^1H NMR: δ = 1.14–1.28 (6 H, m), 1.98–2.12 (2 H, m), 2.24–2.36 (2 H, m), 2.43 (3 H, s), 3.37 (2 H, s), 3.44–3.68 (7 H, m), 6.51–6.62 (2 H, m).

MS: *m*/*z* (%) = 268 (M^+, 5), 124 (100).

HRMS: *m*/*z* calcd for $C_{15}H_{24}O_2S$ (M^+): 268.1497; found: 268.1498.

***N*-Cyclobutyl-*N*-methylaniline (19a)**
To a solution of *N*-methylaniline (0.066 mL, 0.6 mmol) in anhyd THF (2 mL) in a flame-dried flask at 0 °C under argon atmosphere was added *n*-BuLi (1.57 M solution in hexane, 0.38 mL, 0.6 mmol) dropwise with stirring. The reaction mixture was cooled to –78 °C and HMPA (0.1 mL, 0.6 mmol) and a solution of **2c** (45.7 mg, 0.2 mmol) in anhyd THF (2 mL) were added dropwise with stirring. After 5 min, EtMgCl (2.0 M solution in THF, 0.25 mL, 0.5 mmol) was added to the mixture and the temperature of the mixture was slowly allowed to warm to –20 °C. The reaction was quenched by the addition of sat. aq NH_4Cl (20 mL) and the mixture was extracted with $CHCl_3$ (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$). The product was purified by silica gel column chromatography (hexane–EtOAc) to afford **19a** (11.2 mg, 35%) as a light yellow oil.

IR (neat): 2972, 2940, 1599, 1504, 1321 cm^{-1}.

^1H NMR: δ = 1.65–1.75 (2 H, m), 2.02–2.15 (2 H, m), 2.20–2.30 (2 H, m), 2.83 (3 H, s), 3.90–4.01 (1 H, m), 6.73–6.81 (3 H, m), 7.20–7.25 (2 H, m).

MS: *m*/*z* (%) = 161 (M^+, 16), 132 (100), 117 (13), 91 (23), 77 (18).

HRMS: *m*/*z* calcd for $C_{11}H_{15}N$ (M^+): 161.1204; found: 161.1202.

***N*-Cyclobutyl-*N*-methyl-*p*-toluidine (19b)**
Light yellow oil.

IR (neat): 2929, 2859, 1618, 1518, 1316, 806 cm^{-1}.

^1H NMR: δ = 1.74–1.95 (2 H, m), 1.99–2.12 (2 H, m), 2.17–2.26 (2 H, m), 2.25 (3 H, s), 2.77 (3 H, s), 3.80–3.90 (1 H, m), 6.72–6.75 (2 H, m), 7.02–7.05 (2 H, m).

MS: *m*/*z* (%) = 175 (M^+, 21), 147 (93), 146 (100), 132 (16), 106 (26), 91 (24).

HRMS: *m*/*z* calcd for $C_{12}H_{17}N$ (M^+): 175.1361; found: 175.1360.

***N*-Cyclobutyl-*N*-methyl-*p*-anisidine (19c)**
Light yellow oil.

IR (neat): 2938, 2857, 1727, 1511, 1242, 1040, 819 cm^{-1}.

^1H NMR: δ = 1.64–1.73 (2 H, m), 1.95–2.09 (2 H, m), 2.14–2.24 (2 H, m), 2.71 (3 H, s), 3.66–3.76 (1 H, m), 3.76 (3 H, s), 6.82 (4 H, s).

MS: *m*/*z* (%) = 191 (M^+, 22), 163 (100), 148 (18), 122 (32).

HRMS: *m*/*z* calcd for $C_{12}H_{17}NO$ (M^+): 191.1310; found: 191.1308.

4-Chloro-*N*-cyclobutyl-*N*-methylaniline (19d)
Light brown oil.

IR (neat): 2941, 2871, 1598, 1498, 1327, 1248, 1137, 1099, 811 cm^{-1}.

^1H NMR: δ = 1.65–1.75 (2 H, m), 2.00–2.14 (2 H, m), 2.19–2.29 (2 H, m), 2.80 (3 H, s), 3.85–3.96 (1 H, m), 6.67–6.70 (2 H, m), 7.13–7.17 (2 H, m).

MS: *m*/*z* (%) = 195 (M^+, 27), 167 (100), 138 (11), 131 (21), 125 (23), 111 (17).

HRMS: *m*/*z* calcd for $C_{11}H_{14}ClN$ (M^+): 195.0815; found: 195.0823.

***N*-Cyclobutyl-*N*-methyl-1-naphthylamine (19e)**
Light orange oil.

IR (neat): 3047, 2936, 2852, 1576, 1466, 1395, 1343, 1294, 1078, 1056, 801, 775 cm^{-1}.

^1H NMR: δ = 1.65–1.74 (2 H, m), 1.91–2.05 (2 H, m), 2.12–2.22 (2 H, m), 2.73 (3 H, s), 3.78–3.89 (1 H, m), 6.94–6.97 (1 H, m), 7.33–7.38 (1 H, m), 7.43–7.53 (3 H, m), 7.78–7.82 (1 H, m), 8.26–8.29 (1 H, m).

MS: *m*/*z* (%) = 211 (M^+, 19), 183 (100), 168 (13), 142 (54), 127 (18), 90 (10).

HRMS: *m*/*z* calcd for $C_{15}H_{17}N$ (M^+): 211.1361; found: 211.1356.

10-[3,3-Bis(3-phenylpropoxymethyl)cyclobutyl]-10*H*-phenothiazine (20)
Light orange oil.

IR (neat): 2934, 2858, 1593, 1571, 1496, 1459, 1320, 1287, 1258, 1236, 1217, 1111, 754 cm^{-1}.

^1H NMR: δ = 1.75–1.84 (2 H, m), 1.85–1.92 (2 H, m), 1.93–2.01 (2 H, m), 2.56–2.63 (4 H, m), 2.73–2.78 (2 H, m), 3.30–3.35 (4 H, m), 3.50–3.57 (4 H, m), 4.48 (1 H, quint, *J* = 7.0 Hz), 6.56–6.61 (2 H, m), 6.90–6.95 (2 H, m), 7.07–7.32 (14 H, m).

MS: *m*/*z* (%) = 549 (M^+, 30), 225 (100), 198 (15), 91 (19).

HRMS: *m*/*z* calcd for $C_{36}H_{39}NO_2S$ (M^+): 549.2702; found: 549.2700.

3,3-Bis(3-phenylpropoxymethyl)-1-benzylidenecyclobutane (6a); Typical Procedure
A solution of EtMgCl (2.0 M solution in THF, 0.25 mL, 0.5 mmol) was added to a solution of **1a** (105 mg, 0.2 mmol) in THF (2 mL) at –78 °C with stirring under argon atmosphere. In an another flame-dried flask, a solution of benzyl phenyl sulfone (139 mg, 0.6 mmol) in THF (0.5 mL) was added to a solution of *n*-BuLi (1.57 M solution in *n*-hexane, 0.38 mL, 0.6 mmol) in anhyd THF (2 mL) at 0 °C under argon atmosphere to give a clear yellow solution. This solution was cooled to –78 °C and was added to the solution of the cyclobutylmagnesium carbenoid via a cannula. The reaction mixture was stirred and slowly allowed to warm to –20 °C; then the reaction was quenched with sat. aq NH_4Cl (20 mL). The mixture was extracted with $CHCl_3$ (3 × 20 mL) and the solution was dried ($MgSO_4$). The product was purified by silica gel column chromatography (hexane–EtOAc) to afford **6a** (73.1 mg, 83%) as a colorless oil.

IR (neat): 3026, 2942, 2858, 1680, 1601, 1496, 1454, 1112, 910, 742 cm^{-1}.

^1H NMR: δ = 1.84–1.94 (4 H, m), 2.66–2.71 (6 H, m), 2.85 (2 H, s), 3.46 (4 H, t, *J* = 6.3 Hz), 3.48 (4 H, s), 6.19 (1 H, m), 7.13–7.21 (7 H, m), 7.24–7.32 (8 H, m).

MS: *m*/*z* (%) = 440 (M^+, 7), 305 (11), 304 (50), 170 (27), 168 (30), 156 (19), 155 (100), 142 (8), 129 (12), 119 (18), 91 (93).

HRMS: *m*/*z* calcd for $C_{31}H_{36}O_2$ (M^+): 440.2715; found: 440.2708.

3,3-Bis(3-phenylpropoxymethyl)-1-(1-naphthyl)methylidenecyclobutane (6b)
Colorless oil.

IR (neat): 3026, 2942, 2858, 1691, 1603, 1496, 1454, 1113, 909, 782, 733 cm^{-1}.

^1H NMR: δ = 1.86–1.92 (4 H, m), 2.66–2.70 (4 H, m), 2.78 (4 H, s), 3.46 (4 H, t, *J* = 6.3 Hz), 3.50 (4 H, s), 6.90–6.92 (1 H, m), 7.15–7.25 (10 H, m), 7.39–7.50 (4 H, m), 7.69–7.71 (1 H, m), 7.82–7.84 (1 H, m), 8.10–8.12 (1 H, m).

MS: *m*/*z* (%) = 490 (M^+, 46), 354 (30), 218 (23), 206 (20), 205 (100), 203 (10), 179 (17), 165 (25), 119 (8), 91 (51).

HRMS: *m*/*z* calcd for $C_{35}H_{38}O_2$ (M^+): 490.2872; found: 490.2866.

3,3-Bis(3-phenylpropoxymethyl)-1-(1-phenyl)ethylidenecyclobutane (6c)
Colorless oil.

IR (neat): 3026, 2933, 2858, 1600, 1496, 1454, 1114, 910, 760 cm^{-1}.

^1H NMR: δ = 1.84–1.93 (7 H, m), 2.62–2.71 (8 H, m), 3.45 (4 H, t, *J* = 6.3 Hz), 3.46 (4 H, s), 7.14–7.18 (7 H, m), 7.23–7.31 (8 H, m).

MS: *m*/*z* (%) = 454 (M^+, 7), 318 (31), 200 (3), 182 (16), 169 (100), 129 (10), 118 (14), 91 (58).

HRMS: *m*/*z* calcd for $C_{32}H_{38}O_2$ (M^+): 454.2872; found: 454.2879.

3,3-Bis(3-phenylpropoxymethyl)-1-(ethen-1-yl)methylidenecyclobutane (6d)
Colorless oil.

IR (neat): 3026, 2928, 2856, 1676, 1605, 1496, 1454, 1114, 992, 898, 745 cm^{-1}.

^1H NMR: δ = 1.83–1.92 (4 H, m), 2.53 (2 H, s), 2.58 (2 H, s), 2.62–2.70 (4 H, m), 3.44 (4 H, s), 3.45 (4 H, t, *J* = 6.3 Hz), 4.91–4.95 (1 H, m), 5.00–5.06 (1 H, m), 5.87–5.90 (1 H, m), 6.21–6.34 (1 H, m), 7.14–7.19 (6 H, m), 7.24–7.29 (4 H, m).

MS: *m*/*z* (%) = 390 (M^+, trace), 254 (10), 120 (16), 119 (21), 118 (21), 105 (20), 92 (23), 91 (100). HRMS: *m*/*z* calcd for $C_{27}H_{34}O_2$ (M^+): 390.2559; found: 390.2560.

3,3-Bis(3-phenylpropoxymethyl)-1-(2-methylethyn-1-yl)methylidenecyclobutane (6e)
Colorless oil.

IR (neat): 3026, 2915, 2856, 2219 (C≡C), 1666, 1603, 1496, 1455, 1368, 1112, 924, 868, 746 cm^{-1}.

^1H NMR: δ = 1.83–1.92 (4 H, m), 1.95–1.96 (3 H, m), 2.54 (2 H, s), 2.60 (2 H, s), 2.65–2.70 (4 H, m), 3.43 (4 H, s), 3.44 (4 H, t, *J* = 6.3 Hz), 5.28–5.30 (1 H, m), 7.15–7.20 (6 H, m), 7.25–7.30 (4 H, m).

MS: *m*/*z* (%) = 402 (M^+, trace), 266 (28), 132 (67), 118 (30), 117 (78), 91 (100).

HRMS: *m*/*z* calcd for $C_{28}H_{34}O_2$ (M^+): 402.2559; found: 402.2554.

3,3-Bis(3-phenylpropoxymethyl)-1-methylidenecyclobutane (6f)
Colorless oil.

IR (neat): 3026, 2943, 2858, 1678, 1603, 1497, 1455, 1367, 1114, 876, 745, 699 cm^{-1}.

^1H NMR: δ = 1.84–1.93 (4 H, m), 2.50 (4 H, t, *J* = 2.4 Hz), 2.65–2.70 (4 H, m), 3.44 (4 H, s), 3.45 (4 H, t, *J* = 6.3 Hz), 4.81–4.84 (2 H, m), 7.15–7.19 (6 H, m), 7.25–7.29 (4 H, m).

MS: *m*/*z* (%) = 364 (M^+, trace), 228 (5), 119 (25), 118 (61), 91 (100).

HRMS: *m*/*z* calcd for $C_{25}H_{32}O_2$ (M^+): 364.2402; found: 364.2395.

3,3-Bis(3-phenylpropoxymethyl)-1-ethylidenecyclobutane (6g)
Colorless oil.

IR (neat): 3027, 2929, 2856, 1603, 1497, 1455, 1367, 1114, 745 cm^{-1}.

^1H NMR: δ = 1.49–1.52 (3 H, m), 1.84–1.93 (4 H, m), 2.41–2.42 (4 H, m), 2.65–2.70 (4 H, m), 3.44 (4 H, s), 3.45 (4 H, t, *J* = 6.3 Hz), 5.17–5.25 (1 H, m), 7.15–7.19 (6 H, m), 7.25–7.29 (4 H, m).

MS: *m*/*z* (%) = 378 (M^+, trace), 242 (10), 119 (25), 118 (47), 108 (13), 91 (100).

HRMS: *m*/*z* calcd for $C_{26}H_{34}O_2$ (M^+): 378.2559; found: 378.2557.

3,3-Bis(3-phenylpropoxymethyl)-1-isopropylidenecyclobutane (6h)
Colorless oil.

IR (neat): 3027, 2925, 2856, 1603, 1497, 1455, 1370, 1112, 745 cm^{-1}.

^1H NMR: δ = 1.49–1.53 (6 H, m), 1.84–1.93 (4 H, m), 2.37–2.38 (4 H, m), 2.65–2.70 (4 H, m), 3.43 (4 H, s), 3.45 (4 H, t, *J* = 6.3 Hz), 7.15–7.19 (6 H, m), 7.24–7.29 (4 H, m).

MS: *m*/*z* (%) = 392 (M^+, trace), 256 (28), 118 (24), 107 (82), 91 (100).

HRMS: *m*/*z* calcd for $C_{27}H_{36}O_2$ (M^+): 392.2715; found: 392.2718.

Benzylidenecyclobutane (6i)
Colorless oil.

IR (neat): 3024, 2980, 2953, 2911, 1676, 1597, 1498, 1448, 909, 860, 764 cm^{-1}.

^1H NMR: δ = 2.04–2.16 (2 H, m), 2.85–2.91 (2 H, m), 3.01–3.09 (2 H, m), 6.06–6.09 (1 H, m), 7.11–7.31 (5 H, m).

MS: *m*/*z* (%) = 144 (M^+, 49), 139 (10), 129 (100), 128 (26), 116 (39), 115 (72).

HRMS: *m*/*z* calcd for $C_{11}H_{12}$ (M^+): 144.0939; found: 144.0946.

1-Naphthyl-1-methylidenecyclobutane (6j)
Colorless oil.

IR (neat): 3046, 2951, 2913, 1671, 1590, 1508, 1395, 1015, 796, 778 cm^{-1}.

^1H NMR: δ = 2.05–2.15 (2 H, m), 2.93–2.99 (4 H, m), 6.77–6.78 (1 H, m), 7.34–7.51 (4 H, m), 7.67–7.70 (1 H, m), 7.80–7.84 (1 H, m), 8.08–8.11 (1 H, m).

MS: *m*/*z* (%) = 194 (M^+, 67), 179 (71), 165 (100).

HRMS: *m*/*z* calcd for $C_{15}H_{14}$ (M^+): 194.1096; found: 194.1097.

1-Phenyl-1-ethylidenecyclobutane (6k)
Colorless oil.

IR (neat): 2977, 2927, 1599, 1496, 1443, 1375, 1054, 1026 cm^{-1}.

^1H NMR: δ = 1.89 (3 H, s), 1.93–2.04 (2 H, m), 2.81–2.92 (4 H, m), 7.13–7.20 (1 H, m), 7.28–7.33 (4 H, m).

MS: *m*/*z* (%) = 158 (M^+, 55), 143 (100), 129 (64), 115 (48).

HRMS: *m*/*z* calcd for $C_{12}H_{14}$ (M^+): 158.1096; found: 158.1093.

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