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Synthesis, including asymmetric synthesis, of 1-substituted cyclopentenes from cyclobutanones with one-carbon ring-expansion by 1,2-carbon-carbon insertion of magnesium carbenoids

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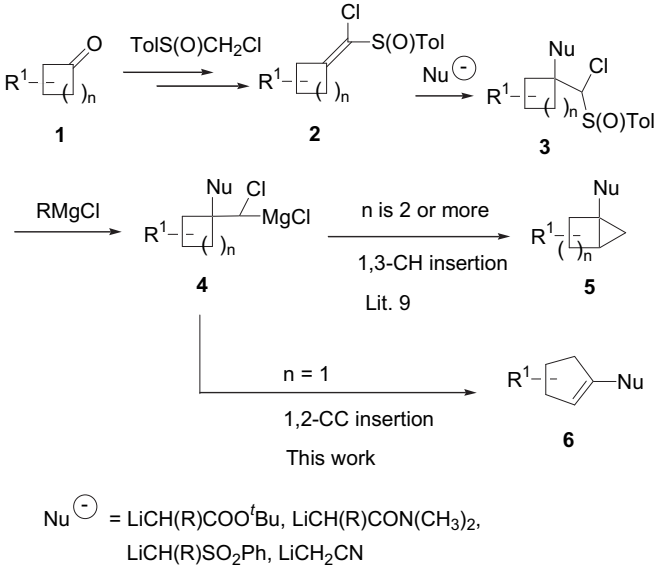
ABSTRACT

Treatment of 1-chlorovinyl *p*-tolyl sulfoxides, which were derived from cyclobutanones and chloromethyl *p*-tolyl sulfoxide, with lithium enolate of *tert*-butyl carboxylates, amides, lithium α-sulfonyl carbanions, and lithium α-carbanion of acetonitrile gave adducts in high to quantitative yields. The adducts were treated with Grignard regents, such as *i*-PrMgCl and EtMgCl in toluene to afford 1-substituted cyclopentenes in good to high yields with one-carbon ring-expansion via 1,2-carbon–carbon (1,2-CC) insertion reaction of the generated magnesium carbenoid intermediates. The magnesium carbenoid 1,2-CC insertion was found to be highly stereospecific. When optically pure chloromethyl *p*-tolyl sulfoxide was used in this procedure, optically active 1-substituted cyclopentenes were obtained in high optical purity.

1. Introduction

Ring enlargement of carbocyclic compounds is one of the most useful and important methods for obtaining the desired carbocycles from lower carbocycles with carbon homologation.[1] One-carbon ring-expansion of cyclic ketones by the rearrangement of β-oxido carbenoid as the key reaction has long been investigated by Normant,[2] Kobrich,[3] Yamamoto,[4] Hiyama,[5] and Cohen.[6] We also have been interested in homologation of carbonyl compounds, including one-carbon ring-expansion of cyclic ketones, by the rearrangement of magnesium β-oxido carbenoids as the key reaction.[7]

In keeping with our ongoing interest in the chemistry and synthetic uses of magnesium carbenoids,[8] we recently reported the synthesis of bicyclo[n.1.0]alkanes **5** (n is 2 or more) from cycloalkanones **1** (*n* is 2 or more) by 1,3-carbon–hydrogen (1,3-CH) insertion of magnesium carbenoid intermediates **4** (*n* is 2 or more),[9] which were generated from the adducts **3** with a Grignard reagent via sulfoxide–magnesium exchange reaction (Scheme 1).[8] Quite interestingly, when this reaction was carried out with the adducts **3** (*n*=1), which were derived from cyclobutanones **1** (*n*=1) via 1-chlorovinyl *p*-tolyl sulfoxides **2** (*n*=1), we obtained 1-substituted cyclopentenes **6**, instead of the expected bicyclo[2.1.0]pentane derivatives **5** (*n*=1), in good to high yields.



Scheme 1.

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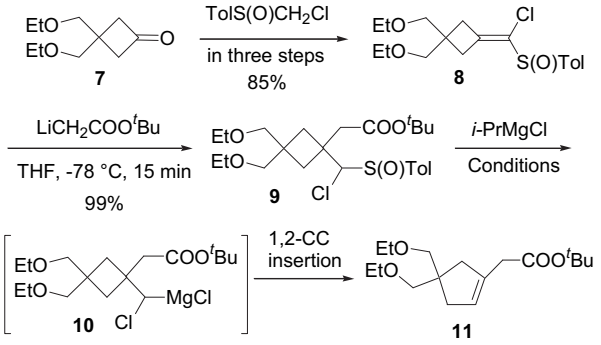
Obviously, instead of the expected 1,3-CH insertion, 1,2-carbon–carbon (1,2-CC) insertion of the generated magnesium carbenoid intermediates **4** took place to afford one-carbon ring-expanded cyclic olefins **6**. Release of the ring-strains of cyclobutanes is presumed to be the driving force of this reaction. As we recognized that this reaction is very useful for the synthesis of 1-substituted cyclopentenes **6** by assemblage of three components, cyclobutanones, chloromethyl *p*-tolyl sulfoxide, and nucleophiles, we further investigated this reaction. Moreover, the synthesis of optically active 1-substituted cyclopentenes would be expected if optically active chloromethyl *p*-tolyl sulfoxide was used in this procedure. We report here, in detail, a synthesis, including asymmetric synthesis, of cyclopentenes bearing esters, amides, sulfones, and nitriles at 1-position **6** from cyclobutanones with one-carbon ring-expansion via 1-chlorovinyl *p*-tolyl sulfoxides **2** and magnesium carbenoids **4** by the 1,2-CC insertion as the key reaction.[10]

2. Results and discussion

2.1. Synthesis of cyclopentenes bearing a *tert*-butyl carboxylate moiety at the 1-position

Representative example of this study starting from cyclobutanone **7** is reported (see Table 1). Thus, 3,3-bis(ethoxymethyl)-1-[chloro(*p*-tolylsulfinyl)methylidene]cyclobutane **8** was synthesized from **7** in three steps in good overall yield.[11] Treatment of **8** with lithium enolate of *tert*-butyl acetate at −78 °C afforded adduct **9** in quantitative yield.[12] In expecting of the formation of bicyclo[2.1.0]pentane derivative by 1,3-CH insertion of the generated magnesium carbenoid intermediate **10**, as described above,[9] a solution of the adduct **9** was added to a solution of 2 equiv of *i*-PrMgCl in toluene at −78 °C and the temperature of the reaction mixture was slowly allowed to warm to 0 °C for 2 h (entry 1, Table 1).

Table 1
Synthesis of cyclopentene bearing a *tert*-butyl acetate moiety at 1-position **11** from cyclobutanone **7** with one-carbon ring-expansion via 1,2-CC insertion of magnesium carbenoid intermediate **10**



Entry	*i*-PrMgCl	Conditions			**11**
	equiv	Temp/°C	Time/h	Solvent	Yield/%
1	2	−78–0	2	Toluene	35[a]
2	3	−78–0	2	Toluene	54[a]
3	5	−78–0	2	Toluene	73
4	5	−40–0	1	Toluene	51
5	5	0	0.5	Toluene	54
6	5	−78–0	2	THF	70
7	5	−78–0	2	CH_2Cl_2	45

[a] Some amount of the starting material **9** was recovered.

Although significant amount of the starting material remained, the reaction mixture was rather clean and a product was obtained. Very interestingly, the product had an olefinic hydrogen (^{1}H NMR spectrum; δ 5.38, 1H, br s) and no hydrogen on the cyclopropane ring was observed. Finally, the structure of the product was determined to be a cyclopentene bearing a *tert*-butyl acetate moiety at the 1-position **11** on the bases of IR, NMR, and MS spectral data. Obviously, the product was produced by magnesium carbenoid 1,2-CC insertion reaction, instead of the expected 1,3-CH insertion. To the best of our knowledge, this is the first example of one-carbon ring-expansion by the magnesium carbenoid 1,2-CC insertion reaction.

Next, we investigated the optimum conditions of this reaction and the results are summarized in Table 1. Using 3 equiv of *i*-PrMgCl in this reaction resulted in better yield (54%); however, some amount of the starting material **9** still remained (entry 2). When 5 equiv of *i*-PrMgCl was used, all the starting material disappeared and the yield of product **11** was improved (entry 3). Worse results were obtained when this reaction was started with higher reaction temperature (−40 or 0 °C) (entries 4 and 5). Selection of THF as a solvent gave a similar result (compare the results in entry 3 and 6). Dichloromethane was proved to be unsuitable solvent (entry 7). We concluded that the conditions in entry 3 are suitable for the reaction.

In order to investigate the generality of these reactions, we further studied this procedure starting with 1-chlorovinyl *p*-tolyl sulfoxides (**8**, **12**, and **13**) and a few *tert*-butyl carboxylates under the conditions described above, and the results are summarized in Table 2. The addition reaction of vinyl sulfoxide **8** with lithium enolate of *tert*-butyl propionate and *tert*-butyl 4-phenylbutyrate proceeded smoothly to give adducts **14a** and **14b**, respectively, in up to 99% yield (entries 1 and 2). Treatment of these adducts **14a** and **14b** with 5 equiv of *i*-PrMgCl resulted in the formation of the desired cyclopentenes **15a** and **15b**, respectively, in high to quantitative yields.

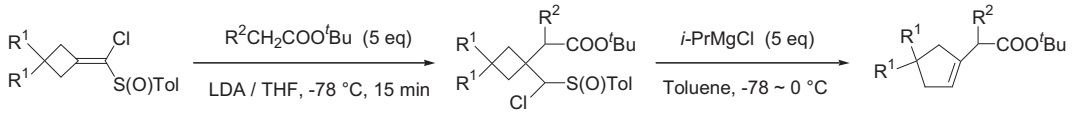
The addition reaction of **12** with *tert*-butyl carboxylates again gave adducts **14c**–**e** in up to 99% yield (entries 3–5). The key reaction was conducted smoothly to give the desired cyclopentenes **15c**–**e** in up to 91% yield without any problem. Entries 6–9 show the results starting from cyclobutanone itself. Addition reaction of vinyl sulfoxide **13** with lithium enolate of *tert*-butyl carboxylates including *tert*-butyl (4-methylphenyl)acetate gave adducts **14f**–**i** all in quantitative yields. Treatment of these four adducts with *i*-PrMgCl resulted in the formation of the desired cyclopentenes **15f**–**i** in somewhat variable yields. It is worth noting that the aromatic ring at the α-position of the ester group did not affect the key reaction, 1,2-CC insertion (entry 9). From these results, generality of this procedure was verified.

Later, we found that the *tert*-butyl carboxylate group was not essential in the 1,2-CC insertion reaction (see Scheme 2). Thus, ether **16** was derived from adduct **9** by treatment with diisobutylaluminum hydride followed by *p*-methoxybenzyl chloride. Ether **16** was treated with *i*-PrMgCl in the same conditions as described above to afford the desired cyclopentene **17** in a similar yield without any problem.

Next, we investigated this procedure starting from an unsymmetrical cyclobutanone and observed very interesting stereospecificity of the 1,2-CC insertion (Scheme 3). Thus, unsymmetrical cyclobutanone **18** was synthesized from cyclopropyl phenyl sulfide,[13] which was converted into 1-chlorovinyl *p*-tolyl sulfoxide **19** in three steps in 42% overall yield as a mixture of two geometrical isomers. The geometrical isomers of the vinyl sulfoxides were separated by silica gel column chromatography to give *E*-isomer **19a** and *Z*-isomer **19b** in a ratio of 21:79. Determination of the stereochemistry of the vinyl sulfoxides was reported previously.[10]

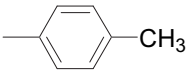
Treatment of both vinyl sulfoxides **19a** and **19b** with lithium enolate of *tert*-butyl acetate afforded adducts **20a** and **20b**, respectively, both as a single isomer with high stereospecificity in good yields. Relative stereochemistry of the adducts was determined to be as shown in Scheme 3 based on our previous study.[14] At first, the sulfoxide–magnesium exchange reaction of **20a** was conducted with *i*-PrMgCl; however, no reaction was observed. Steric hindrance by the 2-phenylethyl group on the cyclobutane ring was thought to be the reason for this difficulty. Fortunately, **20a** reacted smoothly with EtMgCl to afford the desired cyclopentene bearing a *tert*-butyl acetate moiety **22a** in 40% yield as a single product. The same treatment of

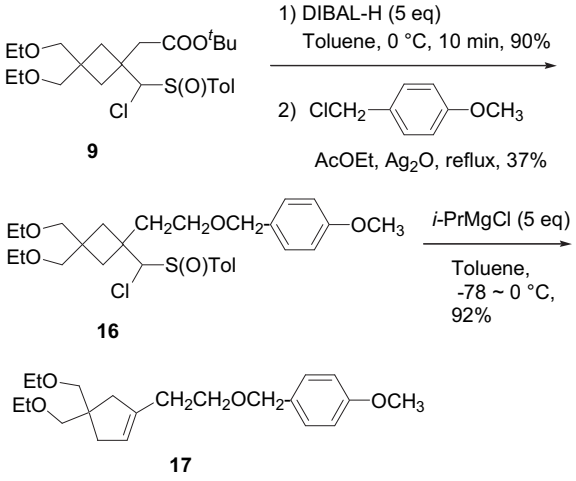
Table 2
Synthesis of cyclopentenes bearing a *tert*-butyl carboxylate moiety at 1-position **15** from 1-chlorovinyl *p*-tolyl sulfoxides **8**, **12**, and **13** via adducts **14** with one-carbon ring-expansion by 1,2-CC insertion of magnesium carbenoid intermediates



8 $R^1 = CH_2OC_2H_5$
12 $R^1 = CH_2O(CH_2)_3Ph$
13 $R^1 = H$

14 **15**

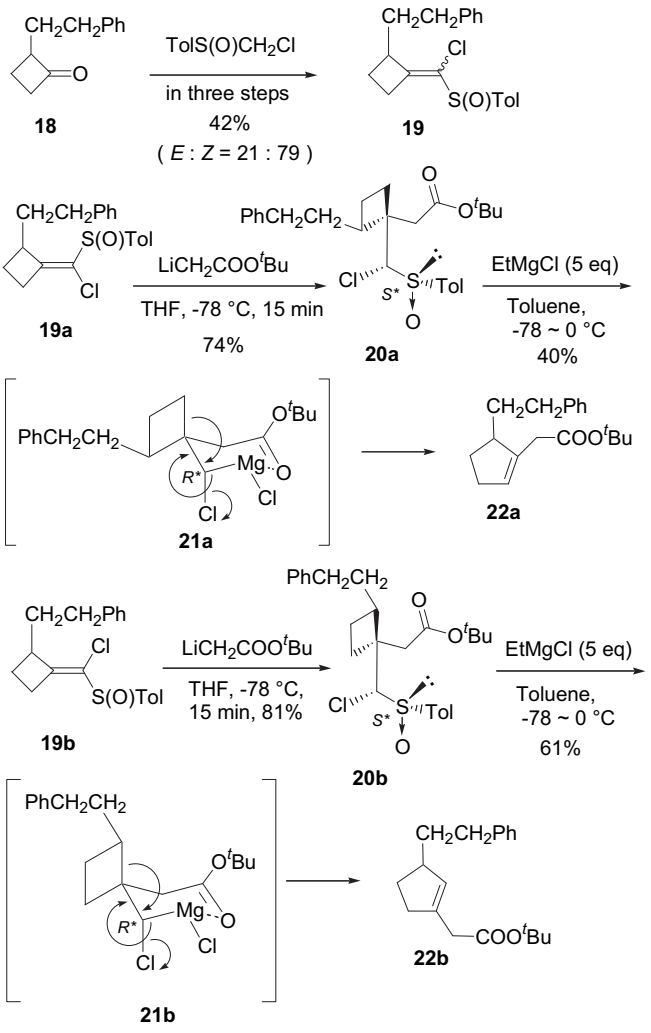
Entry	1-Chlorovinyl *p*-tolyl sulfoxide		**14**			**15**	
		R^1		R^2	Yield/%		Yield/%
1	**8**	$CH_2OC_2H_5$	**14a**	CH_3	86	**15a**	97
2	**8**	$CH_2OC_2H_5$	**14b**	CH_2CH_2Ph	99	**15b**	89
3	**12**	$CH_2O(CH_2)_3Ph$	**14c**	H	94	**15c**	75
4	**12**	$CH_2O(CH_2)_3Ph$	**14d**	CH_3	99	**15d**	84
5	**12**	$CH_2O(CH_2)_3Ph$	**14e**	CH_2CH_2Ph	89	**15e**	91
6	**13**	H	**14f**	H	99	**15f**	77
7	**13**	H	**14g**	CH_3	99	**15g**	70
8	**13**	H	**14h**	CH_2CH_2Ph	99	**15h**	98
9	**13**	H	**14i**		99	**15i**	92



Scheme 2.

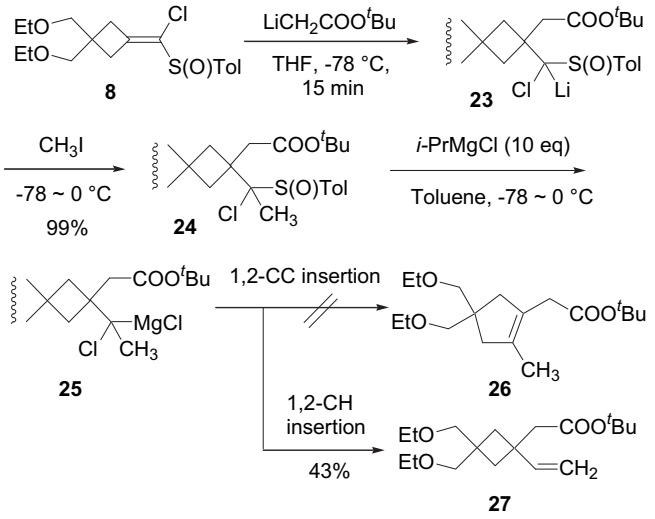
the diastereomer **20b** with EtMgCl gave the structural isomer **22b** in 61% again as a single product. Quite interestingly, these reactions are highly stereospecific. Determination of the structure of the two products (**22a** and **22b**) was reported in the preliminary letter.[10]

The mechanism of this interesting and highly stereospecific magnesium carbenoid 1,2-CC insertion reaction can be explained as follows. As the sulfoxide–magnesium exchange reaction is known to proceed with retention of the configuration of the carbon bearing the sulfinyl group,[15] treatment of **20a** with EtMgCl gives magnesium carbenoid having *R**-configuration at the carbon bearing the magnesium atom. The magnesium and carbonyl oxygen atom of the *tert*-butyl ester group must make six-membered intermediate **21a**,[14] in which the bulkiest *tert*-butoxy group would occupy the equatorial-like position. From this intermediate, the 1,2-CC insertion takes place from behind of the carbon–chlorine bond to give the product **22a**. The situation of the reaction of **20b** with EtMgCl is thought to be similar. The magnesium carbenoid intermediate derived from **20b** must make the six-membered intermediate **21b** and again the 1,2-CC insertion reaction proceeds from behind of the carbon–chlorine bond to afford **22b**.



Scheme 3.

Finally, we attempted to synthesize 1,2-disubstituted cyclopentenes based on the procedure described above and the result is shown in Scheme 4. Thus, treatment of vinyl sulfoxide **8** with lithium enolate of *tert*-butyl acetate at −78 °C afforded adduct, lithium α-sulfinyl carbanion **23**. Addition of excess iodomethane to a solution of this anion gave methylated compound **24** in quantitative yield.[16] In expectation of 1,2-disubstituted cyclopentene **26**, methylated compound **24** was treated with excess *i*-PrMgCl in toluene. Quite interestingly only olefin **27**, which was produced by 1,2-CH insertion reaction between the methyl hydrogen and the carbon of the generated magnesium carbenoid **25**, was obtained as a single isolable product. From this result, we recognized that 1,2-CC insertion and 1,2-CH insertion of magnesium carbenoid, such as **25** are on the delicate balance of the structure and we could hardly deduce the results at present.



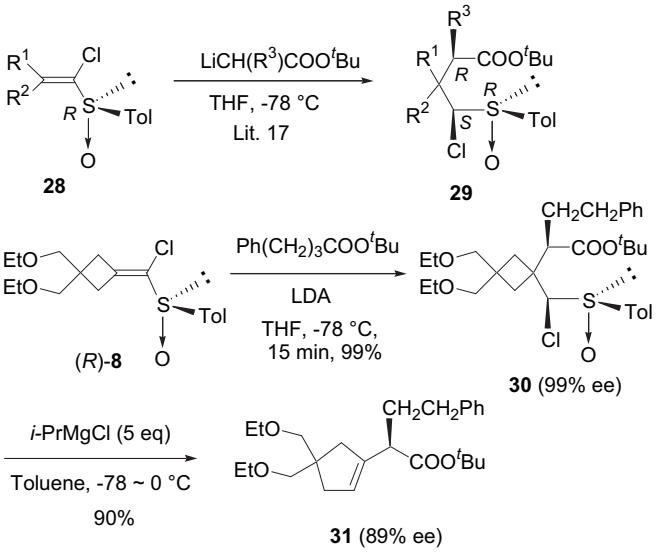
Scheme 4.

2.2. Asymmetric synthesis of cyclopentenes bearing a *tert*-butyl carboxylate moiety at the 1-position starting from optically pure (*R*)-chloromethyl *p*-tolyl sulfoxide

Previously, we reported quite interesting 1,4-asymmetric induction reaction from the sulfoxide stereogenic center. Thus, as shown in Scheme 5, addition reaction of (*R*)-vinyl sulfoxides **28** with lithium enolate of *tert*-butyl carboxylates resulted in the formation of adducts **29** bearing a substituent R^3 at the α-carbon of the ester group as a single product with perfect 1,4-asymmetric induction from the sulfur stereogenic center. The absolute stereochemistry of the α-carbon was proved to be *R* configuration.[17]

In order to extend the procedure described above to the asymmetric synthesis of cyclopentenes bearing a *tert*-butyl carboxylate moiety at the 1-position, we studied our process starting from optically pure vinyl sulfoxide (*R*)-**8** (Scheme 5). At first, (*R*)-**8** was synthesized from cyclobutanone **7** with optically pure (*R*)-chloromethyl *p*-tolyl sulfoxide.[18] The addition reaction of (*R*)-**8** with lithium enolate of *tert*-butyl 4-phenylbutyrate gave adduct **30** in quantitative yield as a single product. Optical purity of **30** was determined by HPLC with chiral column (CHIRALCEL OD) and was proved to be over 99%. Finally, a solution of **30** in toluene was added to a solution of 5 equiv of *i*-PrMgCl in toluene to afford **31** in 90% yield. Optical purity, however, was found to be 89%ee. As the hydrogen on the carbon at the α-position is present in between the carbonyl and olefinic groups, its acidity is thought to be increased. Excess *i*-PrMgCl is presumed to act as a base to result in a slight racemization.

After some investigations, improvement of the optical purity of **31** was successful and the results are summarized in the table in



Entry	*i*-PrMgCl (eq)	**31**	
		Yield / %[a]	ee / %
1	(3)[b]	47 (67)	97
2	(5)[c]	78	95
3	(4)[c]	71 (74)	96
4	(3)[c]	51 (71)	99

[a] The yield in parenthesis refers to the yield calculated from the consumed starting material. [b] Sulfoxide **30** was added to a solution of *i*-PrMgCl. [c] A solution of *i*-PrMgCl was added to a solution of **30** in toluene.

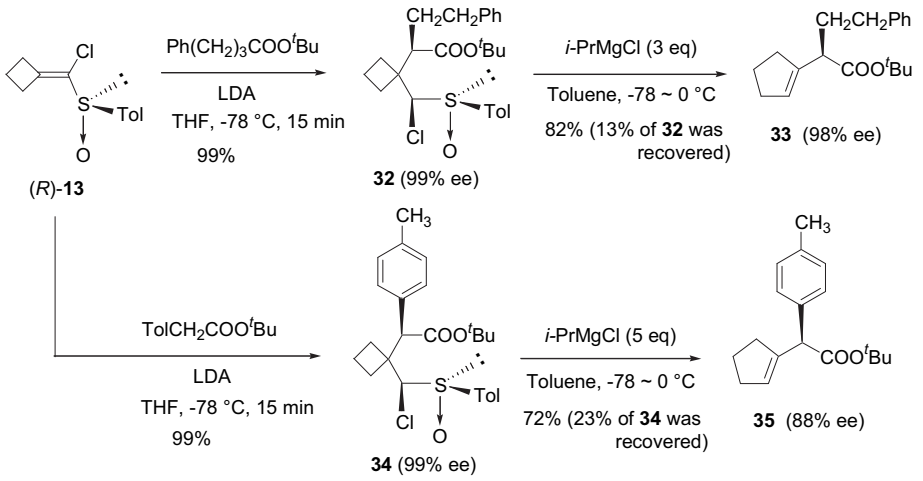
Scheme 5.

Scheme 5. Thus, when the treatment was conducted with 3 equiv of *i*-PrMgCl, the ee was improved to 97%; however, the chemical yield of **31** was only 47% (entry 1). When 5 equiv of *i*-PrMgCl was added to a solution of **30**, olefin **31** was obtained in 78% with 95% ee (entry 2). In cases of using lower amount of *i*-PrMgCl, especially 3 equiv, the ee was improved to 99% and the chemical yield was 51%. In this case, significant amount of **30** was recovered without losing the optical purity and the chemical yield calculated based on the consumed starting material was found to be 71% (entry 4).

Two other examples for the asymmetric synthesis of 1-substituted cyclopentenes are shown in Scheme 6. The addition reaction of vinyl sulfoxide (*R*)-**13** with lithium enolate of *tert*-butyl 4-phenylbutyrate and *tert*-butyl (4-methylphenyl)acetate gave adduct **32** and **34**, respectively, in quantitative yields with high ee. The adduct **32** was treated with *i*-PrMgCl under the same conditions as described above to give the desired **33** in 82% yield with 98% ee. Compared to this, the sulfoxide–magnesium exchange reaction of **34** required 5 equiv of *i*-PrMgCl and, as a result, the enantiopurity of **35** was decreased to 88% ee.

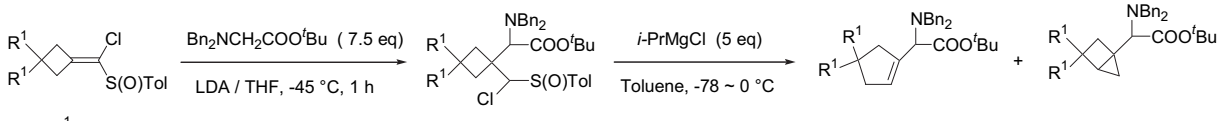
2.3. Synthesis, including asymmetric synthesis, of α-amino acid derivatives bearing a 1-cyclopentene moiety at the α-position

When above-mentioned procedure was conducted with glycine derivative, a synthesis of α-amino acid derivatives bearing a 1-cyclopentene moiety at the α-position was realized (Table 3). Thus,



Scheme 6.

Table 3
Synthesis of α-amino acid derivatives bearing a cyclopentene moiety at the α-position

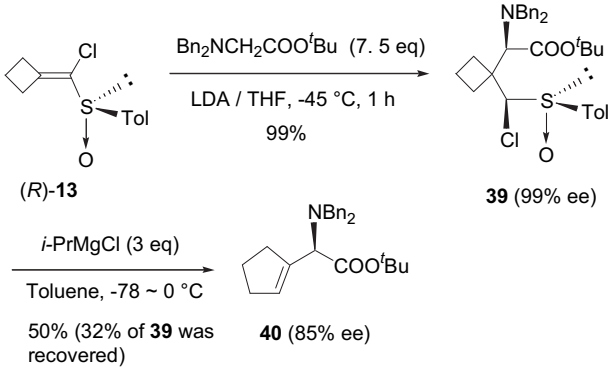


8 $R^1 = CH_2OC_2H_5$
12 $R^1 = CH_2O(CH_2)_3Ph$
13 $R^1 = H$

Entry	1-Chlorovinyl *p*-tolyl sulfoxide		**36**		**37**		**38**	
		R^1		Yield/%		Yield/%		Yield/%
1	**8**	$CH_2OC_2H_5$	**36a**	88	**37a**	56	**38a**	24
2	**12**	$CH_2O(CH_2)_3Ph$	**36b**	90	**37b**	56	**38b**	23
3	**13**	H	**36c**	99	**37c**	78		0

the addition reaction of vinyl sulfoxides **8**, **12**, and **13** with 7.5 equiv of lithium enolate of *N*,*N*-dibenzylglycine *tert*-butyl ester afforded adducts **36a**–**c**, respectively, in good to quantitative yields.[17a] At first, adduct **36a** was treated with 5 equiv of *i*-PrMgCl in toluene. Somewhat surprisingly, this reaction gave the expected ring-expanded product **37a** in 56% yield with bicyclo[2.1.0]pentane derivative **38a** (24%) as a byproduct (entry 1). Obviously, **38a** was derived from the 1,3-CH insertion reaction of the derived magnesium carbenoid intermediate.[9] As shown in entry 2, almost the same result was obtained from the reaction of **36b** with *i*-PrMgCl. Quite interestingly, no bicyclo[2.1.0]pentane derivative was obtained from the reaction of **36c** with *i*-PrMgCl. We still find it very difficult to propose a rational explanation why bicyclo[2.1.0] pentane derivatives **38a** and **38b** were obtained only when adducts **36** have ethereal functional groups on the cyclobutane ring.

Scheme 7 shows the result for the asymmetric synthesis of α-amino acid derivative **40** starting from (*R*)-**13**. Thus, adduct **39** was derived from (*R*)-**13** with 7.5 equiv of lithium enolate of *N*,*N*-dibenzylglycine *tert*-butyl ester with 99%ee. Treatment of **39** with 3 equiv of *i*-PrMgCl was conducted in the same conditions as described above (see Scheme 5) to give the desired product **40** in 50% yield; however, again some racemization was observed.



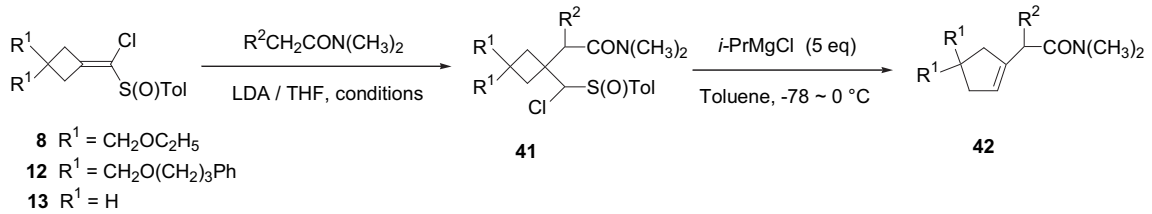
Scheme 7.

2.4. Synthesis of cyclopentenes bearing a carboxylic amide, an alkylsulfonyl, and acetonitrile moiety at the 1-position

The procedure described above was carried out with carboxylic amides and the results are summarized in Table 4. The addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides **8**, **12**, and **13** with lithium enolate of carboxylic acid *N*,*N*-dimethylamides[19] gave adducts **41a**–**d** in up to 99% yields. Treatment of **41a**–**d** with 5 equiv of *i*-PrMgCl in toluene resulted in the formation of cyclopentenes bearing an amide moiety at the 1-position **42** around 80% yields.

The procedure described above was carried out with sulfones and the results are summarized in Table 5. The addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides **8**, **12**, and **13** with lithium α-sulfonyl carbanions afforded the expected adducts **43a**–**d** in somewhat lower yields. Treatment of these adducts with 5 equiv of *i*-PrMgCl resulted in the formation of the desired cyclopentenes bearing an alkylsulfonyl moiety at the 1-position **44** in moderate to quantitative yield via the 1,2-CC insertion reaction of the magnesium carbenoid intermediates.

Table 4
Synthesis of cyclopentenes bearing a carboxylic amide moiety at the 1-position



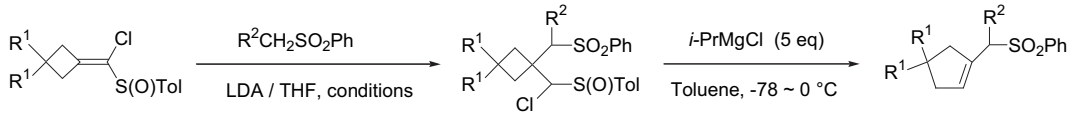
8 $R^1 = CH_2OC_2H_5$
12 $R^1 = CH_2O(CH_2)_3Ph$
13 $R^1 = H$

41 **42**

Entry	1-Chlorovinyl *p*-tolyl sulfoxide		$R^2CH_2CON(CH_3)_2$		Conditions	**41**		**42**	
		R^1	R^2	(equiv)			Yield/%		Yield/%
1	**8**	$CH_2OC_2H_5$	H	(5)	−65 °C, 2 h	**41a**[a]	80	**42a**	76
2	**12**	$CH_2O(CH_2)_3Ph$	H	(5)	−65 °C, 2 h	**41b**[a]	84	**42b**	76
3	**13**	H	H	(5)	−78 °C, 15 min	**41c**[b]	99	**42c**	77
4	**13**	H	CH_3	(10)	−78 °C, 15 min	**41d**[c]	99	**42d**	81

[a] A 4:1 mixture of two diastereomers.
[b] A 15:1 mixture of two diastereomers.
[c] A 2:1 mixture of two diastereomers.

Table 5
Synthesis of cyclopentenes bearing an alkylsulfonyl moiety at the 1-position



8 $R^1 = CH_2OC_2H_5$
12 $R^1 = CH_2O(CH_2)_3Ph$
13 $R^1 = H$

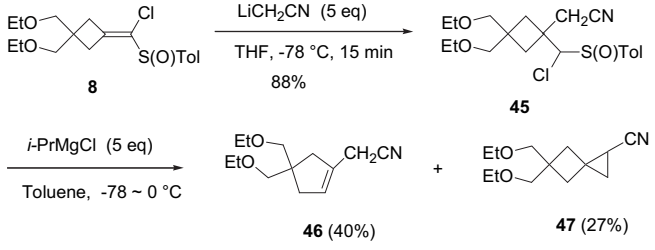
43 **44**

Entry	1-Chlorovinyl *p*-tolyl sulfoxide		$R^2CH_2SO_2Ph$		Conditions	**43**		**44**	
		R^1	R^2	(equiv)			Yield/%		Yield/%
1	**8**	$CH_2OC_2H_5$	H	(5)	−65 °C, 2 h	**43a**	44	**44a**	67
2	**12**	$CH_2O(CH_2)_3Ph$	H	(5)	−65 °C, 2 h	**43b**	33	**44b**	65
3	**13**	H	H	(5)	−78 °C, 15 min	**43c**	87	**44c**	78
4	**13**	H	CH_3	(10)	−78 °C, 15 min	**43d**[a]	60	**44d**	96

[a] A 15:1 mixture of two diastereomers.

Finally, this procedure was carried out with acetonitrile and the result is shown in Scheme 8. Thus, the treatment of vinyl sulfoxide **8** with lithium carbanion of acetonitrile generated from acetonitrile with LDA gave adduct **45** as 2:1 mixture of two diastereomers in 88% yield.[20] Treatment of the mixture of **45** with 5 equiv of *i*-PrMgCl in toluene resulted in the formation of the expected cyclopentene bearing acetonitrile moiety at the 1-position **46** in 40% yield. Quite interestingly, this reaction gave highly strained spirocyclic compound **47** as a byproduct in 27% yield.[21]

In conclusion, we have developed a new method for a synthesis, including asymmetric synthesis, of cyclopentenes bearing a *tert*-butyl carboxylate, a carboxylic acid *N*,*N*-dimethyl amide, and an alkylsulfonyl moiety at the 1-position by assemblage of three components, cyclobutanones, chloromethyl *p*-tolyl sulfoxide, and



Scheme 8.

carboxylic acid derivatives and sulfones with magnesium carbenoid 1,2-CC insertion reaction as the key reaction. We believe that the magnesium carbenoid 1,2-CC insertion reaction presented herein will be used widely in the one-carbon ring-expansion of cyclobutane derivatives to cyclopentenes.

3. Experimental

3.1. General

Melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, 500, BRUKER UltraShield 300, 400, and 600 spectrometer. IR spectra were recorded on a Perkin–Elmer spectrum one FT-IR instrument. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion with JEOL JMS-SX102A. Silica gel 60 N (KANTO CHEMICAL) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent and reagent, THF was distilled from diphenylketyl. Toluene, dichloromethane, and diisopropylamine were distilled from CaH_2. *tert*-Butyl acetate, *tert*-butyl propionate and acetonitrile were distilled from anhydrous $CaSO_4$. Compounds **7**[11], **8**[11], **13**[11], **18**[22], **44c**[23], and **44d**[24] are known.

*3.1.1. (Rs)-3,3-Bis(ethoxymethyl)-1-[chloro(p-tolylsulfinyl)methylidene]cyclobutane ((R)-**8**).* Colorless oil; $[\alpha]_D^{30}$ +162.8 (*c* 0.49, EtOH)

*3.1.2. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}acetate (**9**).* *tert*-Butyl acetate (0.14 mL; 1.0 mmol) was added to a solution of LDA (1.0 mmol) in 3 mL of dry THF at −78 °C under argon atmosphere with stirring. After the solution was stirred for 10 min, a solution of vinyl sulfoxide **8** (71 mg; 0.2 mmol) in THF (1 mL) was added. The reaction mixture was stirred for 15 min and then reaction was quenched by adding saturated aq. NH_4Cl. The whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford adduct **9** (94 mg; 99%) as colorless oil. IR (neat) 2976, 2932, 2870, 1723 (CO), 1368, 1256, 1154, 1107 (COC), 1055 (SO), 811, 755 cm^{-1}; ^1H NMR δ 1.12 (3H, t, *J*=7.1 Hz), 1.19 (3H, t, *J*=7.0 Hz), 1.49 (9H, s), 2.20–2.29 (3H, m), 2.42 (3H, s), 2.66 (1H, d, *J*=13.8 Hz), 2.96 (1H, d, *J*=15.0 Hz), 3.05 (1H, d, *J*=15.0 Hz), 3.36–3.41 (4H, m), 3.46–3.50 (4H, m), 5.42 (1H, s), 7.31 (2H, d, *J*=8.3 Hz), 7.71 (2H, d, *J*=8.3 Hz). MS *m*/*z* (%) 472 (M^+, 0.7), 399 (34), 277 (59), 241 (15), 195 (47), 185 (27), 149 (32), 137 (100), 91 (28). Calcd for $C_{24}H_{37}ClO_5S$: M, 472.2050. Found: *m*/*z* 472.2050.

*3.1.3. tert-Butyl [4,4-bis(ethoxymethyl)cyclopent-1-enyl]acetate (**11**).* To a flame-dried flask was added dry toluene (0.2 mL) followed by *i*-PrMgCl (in ether; 0.39 mmol; 5 equiv) at −78 °C under argon atmosphere. A solution of adduct **9** (37 mg; 0.078 mmol) in toluene (0.2 mL) was added to the solution of the Grignard reagent dropwise with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched by adding saturated aq. NH_4Cl and the whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford cyclopentene **11** (17 mg; 73%) as colorless oil. IR (neat) 2977, 2853, 1731 (CO), 1369, 1256, 1146, 1111 (COC) cm^{-1}; ^1H NMR δ 1.17 (6H, t, *J*=7.0 Hz), 1.44 (9H, s), 2.20 (4H, s), 2.97 (2H, s), 3.33 (4H, s), 3.49 (4H, q, *J*=7.0 Hz), 5.38 (1H, br s). MS *m*/*z* (%) 298 (M^+, 0.9), 242 (15), 196 (16), 183 (12), 152 (10), 150 (55), 137 (48), 105 (43), 91 (55), 57 (100). Calcd for $C_{17}H_{30}O_4$: M, 298.2144. Found: *m*/*z* 298.2148.

*3.1.4. 3,3-Bis(3-phenylpropoxymethyl)-1-[chloro(p-tolylsulfinyl)methylidene]cyclobutane (**12**).* Colorless oil; IR (neat) 2924, 2860, 1496, 1454, 1115 (COC), 1088, 1061 (SO), 749, 700 cm^{-1}; ^1H NMR δ 1.86–1.96 (4H, m), 2.38 (3H, s), 2.65–2.72 (6H, m), 3.00–3.03 (2H, m), 3.43–3.50 (8H, m), 7.15–7.22 (6H, m), 7.25–7.32 (6H, m), 7.50 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 536 (M^+, 8), 235 (11), 119 (28), 91 (100). Calcd for $C_{32}H_{37}ClO_3S$: M, 536.2152. Found: *m*/*z* 536.2148.

*3.1.5. (Rs)-1-[chloro(p-tolylsulfinyl)methylidene]cyclobutane ((R)-**13**).* Colorless oil; $[\alpha]_D^{33}$ +192.4 (*c* 0.53, EtOH).

*3.1.6. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}propionate (**14a**).* Colorless oil; IR (neat) 2976, 2870, 1725 (CO), 1456, 1368, 1152, 1108 (COC), 1055 (SO), 811, 757 cm^{-1}; ^1H NMR δ 1.08 (3H, t, *J*=7.0 Hz), 1.15 (3H, t, *J*=7.0 Hz), 1.44 (3H, d, *J*=7.0 Hz), 1.47 (9H, s), 2.23 (1H, d, *J*=13.9 Hz), 2.34 (1H, d, *J*=13.9 Hz), 2.35 (1H, d, *J*=13.9 Hz), 2.43 (3H, s), 2.67 (1H, d, *J*=13.9 Hz), 3.15 (1H, q, *J*=7.0 Hz), 3.33 (1H, d, *J*=9.2 Hz), 3.34 (2H, s), 3.41 (1H, d, *J*=9.4 Hz), 3.45 (2H, q, *J*=7.0 Hz), 3.45–3.57 (2H, m), 5.67 (1H, s), 7.31 (2H, d, *J*=8.1 Hz), 7.75 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 486 (M^+, 0.1), 413 (19), 291 (29), 209 (36), 151 (100), 140 (52), 57 (54). Calcd for $C_{25}H_{39}ClO_5S$: M, 486.2207. Found: *m*/*z* 486.2210.

*3.1.7. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}-4-phenylbutyrate (**14b**).* Colorless oil; IR (neat) 2975, 2868, 1723 (CO), 1455, 1367, 1147, 1107 (COC), 1053 (SO), 812, 753, 700 cm^{-1}; ^1H NMR δ 1.10 (3H, t, *J*=7.0 Hz), 1.11 (3H, t, *J*=7.0 Hz), 1.52 (9H, s), 2.12–2.39 (5H, m), 2.42 (3H, s), 2.56–2.80 (3H, m), 3.03 (1H, dd, *J*=11.5, 2.7 Hz), 3.27 (1H, d, *J*=9.2 Hz), 3.31 (2H, s), 3.36 (1H, d, *J*=9.2 Hz), 3.40 (2H, q, *J*=7.0 Hz), 3.42–3.59 (2H, m), 5.55 (1H, s), 7.17–7.35 (7H, m), 7.69 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 576 (M^+, 0.1), 503 (15), 381 (30), 253 (34), 241 (96), 195 (43), 139 (52), 117 (42), 91 (95), 59 (100). Calcd for $C_{32}H_{45}ClO_5S$: M, 576.2676. Found: *m*/*z* 576.2677.

*3.1.8. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}acetate (**14c**).* Colorless oil; IR (neat) 2934, 2860, 1723 (CO), 1496, 1455, 1368, 1153, 1111 (COC), 1055 (SO), 812, 749, 700 cm^{-1}; ^1H NMR δ 1.48 (9H, s), 1.76–1.95 (4H, m), 2.34 (3H, s), 2.23–2.37 (3H, m), 2.48–2.76 (5H, m), 2.99 (1H, d, *J*=14.8 Hz), 3.08 (1H, d, *J*=14.8 Hz), 3.32–3.55 (8H, m), 5.44 (1H, s), 7.04–7.09 (2H, m), 7.14–7.31 (10H, m), 7.70 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 652 (M^+, 0.2), 579 (4), 457 (13), 285 (11), 137 (27), 119 (55), 91 (100), 57 (18). Calcd for $C_{38}H_{49}ClO_5S$: M, 652.2989. Found: *m*/*z* 652.2984.

*3.1.9. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}propionate (**14d**).* Colorless oil; IR (neat) 2944, 2861, 1724 (CO), 1496, 1455, 1368, 1152, 1114 (COC), 1054 (SO), 811, 747, 700 cm^{-1}; ^1H NMR δ 1.46 (3H, d, *J*=7.0 Hz), 1.47 (9H, s), 1.71–1.91 (4H, m), 2.31 (3H, s), 2.27–2.61 (5H, m), 2.62–2.74 (3H, m), 3.18 (1H, q, *J*=7.0 Hz), 3.32–3.44 (7H, m), 3.50–3.60 (1H, m), 5.70 (1H, s), 6.98–7.04 (2H, m), 7.13–7.31 (10H, m), 7.72 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 667 ($[M+H]^+$, 27), 611 (30), 185 (21), 151 (32), 119 (59), 91 (100), 57 (20). Calcd for $C_{39}H_{52}ClO_5S$: M+H, 667.3224. Found: *m*/*z* 667.3228.

*3.1.10. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}-4-phenylbutyrate (**14e**).* Colorless oil; IR (neat) 2944, 2860, 1722 (CO), 1496, 1455, 1367, 1147, 1111 (COC), 1052 (SO), 811, 751, 700 cm^{-1}; ^1H NMR δ 1.52 (9H, s), 1.74–1.87 (4H, m), 2.31 (3H, s), 2.14–2.80 (12H, m), 3.05 (1H, dd, *J*=11.3, 2.6 Hz), 3.25–3.44 (7H, m), 3.49–3.59 (1H, m), 5.58 (1H, s), 6.99–7.05 (2H, m), 7.13–7.33 (15H, m), 7.67 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 757 ($[M+H]^+$, 4), 701 (11), 241 (17), 119 (43), 91 (100), 57 (14). Calcd for $C_{46}H_{58}ClO_5S$: M+H, 757.3693. Found: *m*/*z* 757.3691.

*3.1.11. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]cyclobutyl}acetate (**14f**).* Colorless oil; IR (neat) 2978, 1724 (CO), 1368, 1154, 1083, 1056 (SO), 812, 756 cm^{-1}; ^1H NMR δ 1.49 (9H, s), 1.90–2.06 (2H, m), 2.12–2.26 (2H, m), 2.43 (3H, s), 2.38–2.49 (1H, m), 2.55–2.68 (1H, m), 2.84 (1H, d, *J*=15.2 Hz), 3.10 (1H, d, *J*=15.2 Hz), 4.92 (1H, s), 7.33 (2H, d, *J*=8.0 Hz), 7.71 (2H, d, *J*=8.0 Hz). MS (FAB) *m*/*z* (%) 357 ($[M+H]^+$, 32), 301 (100), 283 (14), 123 (19). Calcd for $C_{18}H_{26}ClO_3S$: M+H, 357.1291. Found: *m*/*z* 357.1291.

*3.1.12. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]cyclobutyl}propionate (**14g**).* Colorless oil; IR (neat) 2976, 2929, 1724 (CO), 1368, 1151, 1084, 1058 (SO), 811 cm^{-1}; ^1H NMR δ 1.36 (3H, d, *J*=7.0 Hz), 1.47 (9H, s), 1.76–2.06 (2H, m), 2.44 (3H, s), 2.27–2.50 (4H, m), 3.06 (1H, q, *J*=7.0 Hz), 4.74 (1H, s), 7.33 (2H, d, *J*=8.2 Hz), 7.71 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 371 ($[M+H]^+$, 37), 315 (100), 297 (15), 139 (26), 123 (24), 93 (15), 57 (20). Calcd for $C_{19}H_{28}ClO_3S$: M+H, 371.1448. Found: *m*/*z* 371.1447.

*3.1.13. tert-Butyl 2-{1-[chloro(p-tolylsulfinyl)methyl]cyclobutyl}-4-phenylbutyrate (**14h**).* Colorless crystals; mp 110.1–110.5 °C (hexane); IR (KBr) 2971, 1713 (CO), 1495, 1456, 1364, 1147, 1056 (SO), 812, 699 cm^{-1}; ^1H NMR δ 1.52 (9H, s), 1.72–2.08 (3H, m), 2.15–2.33 (3H, m), 2.43 (3H, s), 2.38–2.50 (2H, m), 2.54–2.80 (2H, m), 2.98 (1H, dd, *J*=11.5, 2.8 Hz), 4.67 (1H, s), 7.18–7.35 (7H, m), 7.66 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{26}H_{33}ClO_3S$: C, 67.73; H, 7.21; Cl, 7.69; S, 6.95. Found: C, 67.91; H, 7.18; Cl, 7.71; S, 6.96.

*3.1.14. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]cyclobutyl}-p-tolylacetate (**14i**).* Colorless oil; IR (neat) 2978, 1727 (CO), 1513, 1368,

1142, 1082, 1056 (SO), 811, 752 cm^{-1}; ^1H NMR δ 1.44 (9H, s), 1.39–1.56 (1H, m), 1.78–1.94 (1H, m), 2.36 (3H, s), 2.42 (3H, s), 2.37–2.50 (1H, m), 2.51–2.66 (3H, m), 4.28 (1H, s), 4.69 (1H, s), 7.17 (2H, d, J=8.0 Hz), 7.30 (2H, d, J=8.1 Hz), 7.42 (2H, d, J=8.1 Hz), 7.67 (2H, d, J=8.2 Hz). MS (FAB) m/z (%) 447 ([M+H]$^+$, 49), 391 (100), 373 (23), 215 (42), 187 (30), 149 (48), 139 (32), 105 (23), 57 (33). Calcd for $C_{25}H_{32}ClO_3S$: M+H, 447.1761. Found: m/z 447.1766.

*3.1.15. tert-Butyl 2-[4,4-bis(ethoxymethyl)cyclopent-1-enyl]propionate (**15a**).* Colorless oil; IR (neat) 2977, 2852, 1732 (CO), 1459, 1368, 1252, 1151, 1112 (COC) cm^{-1}; ^1H NMR δ 1.17 (6H, t, J=7.0 Hz), 1.22 (3H, d, J=7.0 Hz), 1.44 (9H, s), 2.11–2.26 (4H, m), 3.08 (1H, q, J=7.0 Hz), 3.32 (4H, s), 3.48 (4H, q, J=7.0 Hz), 5.36 (1H, br s). MS m/z (%) 312 (M$^+$, 4), 256 (21), 211 (23), 197 (22), 164 (78), 151 (81), 119 (52), 105 (100), 91 (85), 57 (100). Calcd for $C_{18}H_{32}O_4$: M, 312.2301. Found: m/z 312.2303.

*3.1.16. tert-Butyl 2-[4,4-bis(ethoxymethyl)cyclopent-1-enyl]-4-phenylbutyrate (**15b**).* Colorless oil; IR (neat) 2976, 2852, 1728 (CO), 1455, 1368, 1256, 1143, 1112 (COC), 700 cm^{-1}; ^1H NMR δ 1.17 (6H, t, J=7.0 Hz), 1.45 (9H, s), 1.78–1.91 (1H, m), 2.00–2.13 (1H, m), 2.22 (4H, s), 2.57 (2H, t, J=7.9 Hz), 3.02 (1H, t, J=7.5 Hz), 3.31 (2H, s), 3.32 (2H, s), 3.47 (2H, q, J=7.0 Hz), 3.48 (2H, q, J=7.0 Hz), 5.41 (1H, br s), 7.14–7.21 (3H, m), 7.24–7.31 (2H, m). MS m/z (%) 402 (M$^+$, 1), 241 (58), 195 (36), 150 (80), 136 (62), 117 (72), 105 (40), 91 (100), 57 (52). Calcd for $C_{25}H_{38}O_4$: M, 402.2770. Found: m/z 402.2762.

*3.1.17. tert-Butyl [4,4-bis(3-phenylpropoxymethyl)cyclopent-1-enyl] acetate (**15c**).* Colorless oil; IR (neat) 2930, 2854, 1732 (CO), 1497, 1455, 1367, 1255, 1145, 1115 (COC), 746, 700 cm^{-1}; ^1H NMR δ 1.44 (9H, s), 1.82–1.93 (4H, m), 2.22 (4H, s), 2.67 (4H, t, J=7.7 Hz), 2.98 (2H, br s), 3.35 (4H, s), 3.43 (4H, t, J=6.4 Hz), 5.40 (1H, br s), 7.14–7.20 (6H, m), 7.23–7.30 (4H, m). MS m/z (%) 478 (M$^+$, 0.2), 422 (3), 286 (17), 150 (40), 118 (58), 91 (100), 57 (27). Calcd for $C_{31}H_{42}O_4$: M, 478.3083. Found: m/z 478.3086.

*3.1.18. tert-Butyl 2-[4,4-bis(3-phenylpropoxymethyl)cyclopent-1-enyl]propionate (**15d**).* Colorless oil; IR (neat) 2934, 2853, 1729 (CO), 1497, 1455, 1367, 1252, 1150, 1114 (COC), 746, 699 cm^{-1}; ^1H NMR δ 1.23 (3H, d, J=7.1 Hz), 1.43 (9H, s), 1.82–1.95 (4H, m), 2.21 (4H, br s), 2.67 (4H, t, J=7.6 Hz), 3.09 (1H, q, J=7.0 Hz), 3.34 (4H, s), 3.43 (4H, t, J=6.3 Hz), 5.37 (1H, br s), 7.14–7.21 (6H, m), 7.23–7.31 (4H, m). MS m/z (%) 492 (M$^+$, 0.6), 436 (4), 391 (4), 300 (22), 164 (44), 151 (17), 118 (69), 91 (100), 57 (26). Calcd for $C_{32}H_{44}O_4$: M, 492.3240. Found: m/z 492.3242.

*3.1.19. tert-Butyl 2-[4,4-bis(3-phenylpropoxymethyl)cyclopent-1-enyl]-4-phenylbutyrate (**15e**).* Colorless oil; IR (neat) 2931, 2855, 1727 (CO), 1496, 1455, 1367, 1256, 1142, 1114 (COC), 746, 699 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.81–1.92 (5H, m), 2.00–2.15 (1H, m), 2.22 (4H, br s), 2.58 (2H, t, J=7.8 Hz), 2.67 (4H, t, J=7.6 Hz), 3.03 (1H, t, J=7.5 Hz), 3.33 (2H, s), 3.34 (2H, s), 3.42 (2H, t, J=6.3 Hz), 3.43 (2H, t, J=6.3 Hz), 5.42 (1H, br s), 7.13–7.31 (15H, m). MS m/z (%) 582 (M$^+$, 0.6), 390 (23), 254 (25), 241 (28), 150 (55), 136 (24), 118 (55), 105 (19), 91 (100), 57 (22). Calcd for $C_{39}H_{50}O_4$: M, 582.3709. Found: m/z 582.3716.

*3.1.20. tert-Butyl cyclopent-1-enylacetate (**15f**).* Colorless oil; IR (neat) 2978, 2849, 1735 (CO), 1368, 1254, 1149 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.89 (2H, q, J=7.5 Hz), 2.28–2.37 (4H, m), 3.02 (2H, s), 5.52 (1H, br s). MS m/z (%) 182 (M$^+$, 1), 126 (15), 109 (10), 81 (30), 57 (100), 41 (32). Calcd for $C_{11}H_{18}O_2$: M, 182.1307. Found: m/z 182.1311.

*3.1.21. tert-Butyl 2-cyclopent-1-enylpropionate (**15g**).* Colorless oil; IR (neat) 2978, 2929, 1732 (CO), 1368, 1255, 1151 cm^{-1}; ^1H NMR δ 1.24 (3H, d, J=7.1 Hz), 1.44 (9H, s), 1.86 (2H, q, J=7.5 Hz), 2.27–2.34 (4H, m), 3.13 (1H, q, J=7.0 Hz), 5.48–5.52 (1H, m). MS m/z (%) 196 (M$^+$, 7), 140 (31), 95 (60), 67 (26), 57 (100). Calcd for $C_{12}H_{20}O_2$: M, 196.1463. Found: m/z 196.1461.

*3.1.22. tert-Butyl 2-cyclopent-1-enyl-4-phenylbutyrate (**15h**).* Colorless oil; IR (neat) 2977, 2932, 1728 (CO), 1455, 1367, 1143, 699 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.79–1.93 (3H, m), 2.03–2.18 (1H, m), 2.24–2.37 (4H, m), 2.50–2.66 (2H, m), 3.08 (1H, t, J=7.5 Hz), 5.54 (1H, br s), 7.15–7.22 (3H, m), 7.25–7.32 (2H, m). MS m/z (%) 286 (M$^+$, 3), 230 (57), 185 (34), 126 (36), 104 (100), 91 (67), 57 (81). Calcd for $C_{19}H_{26}O_2$: M, 286.1933. Found: m/z 286.1936.

*3.1.23. tert-Butyl cyclopent-1-enyl-p-tolylacetate (**15i**).* Colorless oil; IR (neat) 2929, 1731 (CO), 1514, 1368, 1144 cm^{-1}; ^1H NMR δ 1.43 (9H, s), 1.80–1.91 (2H, m), 2.21–2.28 (2H, m), 2.33 (3H, s), 2.29–2.38 (2H, m), 4.22 (1H, s), 5.48–5.52 (1H, m), 7.11 (2H, d, J=8.1 Hz), 7.18 (2H, d, J=8.1 Hz). MS m/z (%) 272 (M$^+$, 3), 216 (16), 171 (100), 143 (23), 129 (12), 105 (16), 57 (32). Calcd for $C_{18}H_{24}O_2$: M, 272.1776. Found: m/z 272.1775.

*3.1.24. 1-{2-{1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl) cyclobutyl}ethoxymethyl}-p-methoxybenzene (**16**).* DIBAL-H (in hexane; 12.5 mmol) was added to a solution of adduct **9** (1.19g; 2.5 mmol) in dry toluene (25 mL) at 0 °C with stirring under argon atmosphere. The reaction mixture was stirred for 10 min and the reaction was quenched by 4% HCl at 0 °C. The whole was extracted with $CHCl_3$. The product was purified by flash column chromatography to afford an alcohol (0.91 g; 90%) as colorless oil.

A solution of the alcohol (0.2 g; 0.5 mmol) in EtOAc (2.5 mL) was added Ag_2O (0.35 g; 1.5 mmol) and *p*-methoxybenzyl chloride (0.2 mL; 1.5 mmol). The reaction mixture was refluxed for 12 h. The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography to afford **16** (98 mg; 37%) as colorless oil. IR (neat) 2974, 2932, 2866, 1770, 1738, 1614, 1514, 1248, 1174, 1107(COC), 1054 (SO), 912, 811, 733 cm^{-1}; ^1H NMR δ 1.11 (3H, t, J=7.0 Hz), 1.16 (3H, t, J=7.0 Hz), 2.02 (1H, d, J=14.1 Hz), 2.08 (1H, d, J=14.1 Hz), 2.17 (1H, d, J=13.0 Hz), 2.24–2.40 (2H, m), 2.43 (3H, s), 2.67 (1H, d, J=13.2 Hz), 3.29 (2H, s), 3.32 (2H, d, J=4.0 Hz), 3.43 (2H, q, J=7.0 Hz), 3.45–3.54 (2H, m), 3.71–3.86 (2H, m), 3.81 (3H, s), 4.50 (2H, s), 5.31 (1H, s), 5.89 (2H, d, J=8.5 Hz), 7.30 (4H, d, J=8.5 Hz), 7.71 (2H, d, J=8.0 Hz). MS m/z (%) 522 (M$^+$, trace), 505 (trace), 121 (100). Calcd for $C_{28}H_{39}ClO_5S$: M, 522.2207. Found: m/z 522.2203.

*3.1.25. 1-{2-[4,4-Bis(ethoxymethyl)cyclopent-1-enyl]ethoxy}-p-methoxybenzene (**17**).* Colorless oil; IR (neat) 2973, 2930, 2851, 1613, 1513, 1464, 1442, 1374, 1355, 1248, 1172, 1106 (COC), 1037, 819 cm^{-1}; ^1H NMR δ 1.17 (6H, t, J=7.0 Hz), 2.13 (2H, br s), 2.15–2.19 (2H, m), 2.33 (2H, t, J=6.8 Hz), 3.32 (4H, s), 3.49 (4H, q, J=7.0 Hz), 3.53 (2H, t, J=7.0 Hz), 3.80 (3H, s), 4.44 (2H, s), 5.25 (1H, br s), 6.87 (2H, d, J=8.6 Hz), 7.26 (2H, d, J=8.6 Hz). MS m/z (%) 348 (M$^+$, 8), 121 (100), 105 (12). Calcd for $C_{21}H_{32}O_4$: M, 348.2301. Found: m/z 348.2301.

*3.1.26. (E)-2-phenethyl-1-[chloro(p-tolylsulfinyl)methylidene]cyclobutane (**19a**).* Colorless oil; IR (neat) 3025, 2922, 2856, 1493, 1454, 1087, 1059 (SO), 886, 808, 750, 700 cm^{-1}; ^1H NMR δ 1.80–1.89 (1H, m), 1.97–2.06 (1H, m), 2.23–2.34 (2H, m), 2.40 (3H, s), 2.60–2.68 (1H, m), 2.72–2.78 (1H, m), 2.78–2.86 (2H, m), 3.42–3.52 (1H, m), 7.18–7.23 (3H, m), 7.29–7.32 (4H, m), 7.49 (2H, d, J=8.2 Hz). MS m/z (%) 344 (M$^+$, 7), 327 (22), 253 (14), 240 (23), 223 (56), 204 (13), 169 (15), 140 (40), 105 (16), 91 (100). Calcd for $C_{20}H_{21}ClOS$: M, 344.1002. Found: m/z 344.1001.

*3.1.27. (Z)-2-phenethyl-1-[chloro(p-tolylsulfinyl)methylidene]cyclobutane (**19b**).* Colorless oil; IR (neat) 2951, 2927, 1492, 1454, 1085, 1056 (SO), 888, 808, 752, 702 cm^{-1}; ^1H NMR δ 1.83–1.95 (2H, m), 2.21–2.33 (2H, m), 2.40 (3H, s), 2.52–2.63 (1H, m), 2.67–2.76 (1H,

m), 2.94–3.04 (1H, m), 3.08–3.27 (2H, m), 7.14–7.20 (3H, m), 7.24–7.33 (4H, m), 7.49 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 344 (M^+, 43), 327 (12), 237 (13), 223 (12), 169 (14), 140 (35), 91 (100). Calcd for $C_{20}H_{21}ClOS$: M, 344.1002. Found: *m*/*z* 344.1001.

*3.1.28. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-2-phenethylcyclobutyl}acetate (**20a**).* Colorless oil; IR (neat) 2977, 1723 (CO), 1495, 1455, 1368, 1154, 1083, 1057 (SO), 812, 750, 699 cm^{-1}; ^1H NMR δ 1.49 (9H, s), 1.64–1.77 (2H, m), 2.05–2.22 (2H, m), 2.42 (3H, s), 2.36–2.48 (2H, m), 2.55–2.68 (2H, m), 2.72–2.80 (1H, m), 2.82 (1H, d, *J*=13.8 Hz), 2.92 (1H, d, *J*=13.8 Hz), 4.72 (1H, s), 7.12–7.18 (3H, m), 7.22–7.27 (2H, m), 7.31 (2H, d, *J*=8.0 Hz), 7.68 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 461 ($[M+H]^+$, 35), 405 (100), 169 (70), 140 (25), 91 (44), 57 (24). Calcd for $C_{26}H_{34}ClO_3S$: M+H, 461.1917. Found: *m*/*z* 461.1916.

*3.1.29. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-2-phenethylcyclobutyl}acetate (**20b**).* Colorless oil; IR (neat) 2977, 2933, 1728 (CO), 1495, 1455, 1368, 1156, 1083, 1055 (SO), 812, 753, 699 cm^{-1}; ^1H NMR δ 1.43 (9H, s), 1.57–1.73 (2H, m), 1.95–2.15 (3H, m), 2.42 (3H, s), 2.45–2.65 (3H, m), 2.83 (1H, d, *J*=16.0 Hz), 2.80–2.92 (1H, m), 2.99 (1H, d, *J*=16.0 Hz), 5.11 (1H, s), 7.14–7.21 (3H, m), 7.24–7.33 (4H, m), 7.68 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 460 (M^+, trace), 229 (22), 169 (74), 140 (100), 91 (54), 57 (34). Calcd for $C_{26}H_{33}ClO_3S$: M, 460.1839. Found: *m*/*z* 460.1836.

*3.1.30. tert-Butyl (5-phenethylcyclopent-1-enyl)acetate (**22a**).* Colorless oil; IR (neat) 2928, 1731 (CO), 1455, 1368, 1256, 1148, 699 cm^{-1}; ^1H NMR δ 1.42 (9H, s), 1.38–1.47 (1H, m), 1.58–1.63 (1H, m), 1.91–1.97 (1H, m), 2.14–2.19 (1H, m), 2.27–2.33 (2H, m), 2.51–2.56 (1H, m), 2.66–2.70 (2H, m), 2.93 (1H, d, *J*=15.6 Hz), 3.03 (1H, d, *J*=15.6 Hz), 5.56 (1H, br s), 7.14–7.19 (3H, m), 7.26–7.29 (2H, m). ^{13}C NMR δ 28.0, 29.9, 31.0, 33.8, 35.3, 36.5, 46.4, 80.5, 125.7, 128.0, 128.3, 128.4, 140.0, 142.7, 170.9. MS *m*/*z* (%) 286 (M^+, 1.0), 230 (96), 213 (13), 185 (14), 169 (87), 139 (25), 104 (55), 91 (91), 79 (32), 57 (100). Calcd for $C_{19}H_{26}O_2$: M, 286.1933. Found: *m*/*z* 286.1930.

*3.1.31. tert-Butyl (3-phenethylcyclopent-1-enyl)acetate (**22b**).* Colorless oil; IR (neat) 2929, 1732 (CO), 1455, 1368, 1254, 1149, 699 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.42–1.55 (1H, m), 1.55–1.75 (2H, m), 2.10–2.16 (1H, m), 2.23–2.38 (2H, m), 2.62 (2H, t, *J*=8.0 Hz), 2.64–2.70 (1H, m), 3.01 (2H, s), 5.50 (1H, br s), 7.15–7.19 (3H, m), 7.25–7.29 (2H, m). ^{13}C NMR δ 28.0, 30.4, 34.2, 34.6, 37.8, 38.5, 45.1, 80.5, 125.6, 128.3, 128.4, 131.8, 137.2, 142.7, 170.8. MS *m*/*z* (%) 286 (M^+, 1), 230 (47), 185 (15), 170 (38), 125 (23), 104 (17), 91 (77), 79 (25), 57 (100). Calcd for $C_{19}H_{26}O_2$: M, 286.1932. Found: *m*/*z* 286.1931.

*3.1.32. tert-Butyl {1-[1-chloro-1-(p-tolylsulfinyl)ethyl]-3,3-bis(ethoxymethyl)cyclobutyl}acetate (**24**).* *tert*-Butyl acetate (0.51 mL; 3.8 mmol) was added to a solution of LDA (3.8 mmol) in 13 mL of dry THF at −78 °C under argon atmosphere with stirring. After the solution was stirred for 10 min, a solution of vinyl sulfoxide **8** (268 mg; 0.75 mmol) in THF (2 mL) was added. The reaction mixture was stirred for 15 min and CH_3I (0.47 mL, 7.5 mmol) was added. The reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched by adding saturated aq. NH_4Cl and the whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford adduct **24** (365 mg; 99%) as a 5:1 mixture of two diastereomers. Main product: colorless oil; IR (neat) 2976, 2933, 2869, 1728 (CO), 1369, 1251, 1153, 1108 (COC), 1066 (SO), 813, 755 cm^{-1}; ^1H NMR δ 1.15 (3H, t, *J*=7.0 Hz), 1.21 (3H, t, *J*=7.0 Hz), 1.36 (3H, s), 1.49 (9H, s), 2.12 (1H, d, *J*=13.7 Hz), 2.29 (1H, d, *J*=13.1 Hz), 2.37 (1H, d, *J*=13.1 Hz), 2.42 (3H, s), 2.67 (1H, d, *J*=13.7 Hz), 3.19 (1H, d, *J*=15.3 Hz), 3.27 (1H, d, *J*=15.3 Hz), 3.40–3.45 (3H, m), 3.45 (2H, q, *J*=7.0 Hz), 3.54 (2H, q, *J*=7.0 Hz), 3.53–3.57 (1H, m), 7.30 (2H, d, *J*=8.3 Hz), 7.60 (2H, d, *J*=8.3 Hz). MS (FAB) *m*/*z* (%) 487 ($[M+H]^+$, 18), 431 (19), 291 (15), 255 (14), 211 (30), 151 (100), 119 (13), 105 (14), 57 (13). Calcd for $C_{25}H_{40}ClO_5S$: M+H, 487.2285. Found: *m*/*z* 487.2287.

*3.1.33. tert-Butyl [1-ethenyl-3,3-bis(ethoxymethyl)cyclobutyl]acetate (**27**).* Colorless oil; IR (neat) 2976, 2932, 2866, 1731 (CO), 1368, 1155, 1111 (COC) cm^{-1}; ^1H NMR δ 1.16 (3H, t, *J*=7.0 Hz), 1.20 (3H, t, *J*=7.0 Hz), 1.40 (9H, s), 1.96 (2H, d, *J*=12.5 Hz), 2.02 (2H, d, *J*=12.5 Hz), 2.49 (2H, s), 3.36 (2H, s), 3.36 (2H, s), 3.46 (2H, q, *J*=7.0 Hz), 3.51 (2H, q, *J*=7.0 Hz), 5.04 (1H, dd, *J*=10.3, 1.1 Hz), 5.05 (1H, dd, *J*=17.5, 1.1 Hz), 6.02 (1H, dd, *J*=17.5, 10.3 Hz). MS *m*/*z* (%) 312 (M^+, 0.5), 210 (38), 164 (96), 151 (73), 119 (54), 112 (52), 105 (100), 91 (33), 85 (54), 57 (90). Calcd for $C_{18}H_{32}O_4$: M, 312.2301. Found: *m*/*z* 312.2306.

*3.1.34. Compound (**30**).* Colorless oil; $[\alpha]_D^{30}$ −81.0 (*c* 0.52, EtOH).

*3.1.35. Compound (**31**).* Adduct **30** (58 mg; 0.1 mmol) in toluene (5 mL) was added to a flame-dried flask at −78 °C under argon atmosphere with stirring. *i*-PrMgCl (in ether; 0.3 mmol; 3 equiv) was added dropwise with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched by adding saturated aq. NH_4Cl and the whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford cyclopentene **31** (21 mg; 51%, 99%ee) and starting material **30** (16 mg; 28%). Colorless oil; $[\alpha]_D^{29}$ −16.7 (*c* 0.53, EtOH).

*3.1.36. Compound (**32**).* Colorless crystals; $[\alpha]_D^{30}$ −65.8 (*c* 0.48, EtOH).

*3.1.37. Compound (**33**).* Colorless oil; $[\alpha]_D^{29}$ −17.2 (*c* 0.53, EtOH).

*3.1.38. Compound (**34**).* Colorless oil; $[\alpha]_D^{32}$ −69.5 (*c* 0.52, EtOH).

*3.1.39. Compound (**35**).* Colorless oil; $[\alpha]_D^{31}$ +0.7 (*c* 0.27, EtOH).

*3.1.40. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}-N,N-dibenzylaminoacetate (**36a**).* Colorless oil; IR (neat) 2976, 2868, 1722 (CO), 1495, 1455, 1369, 1152, 1108 (COC), 1051 (SO), 755, 699 cm^{-1}; ^1H NMR δ 1.05 (3H, t, *J*=7.0 Hz), 1.11 (3H, t, *J*=7.0 Hz), 1.64 (9H, s), 1.90 (1H, d, *J*=13.8 Hz), 2.08 (1H, d, *J*=13.8 Hz), 2.42 (3H, s), 3.01 (1H, d, *J*=13.6 Hz), 3.12 (1H, d, *J*=13.6 Hz), 3.24–3.61 (10H, m), 3.92 (1H, s), 4.33 (2H, d, *J*=13.3 Hz), 5.63 (1H, s), 7.18–7.36 (8H, m), 7.55 (4H, d, *J*=7.4 Hz), 7.69 (2H, d, *J*=8.0 Hz). MS (FAB) *m*/*z* (%) 668 ($[M+H]^+$, 28), 576 (24), 426 (15), 392 (17), 254 (40), 196 (18), 91 (100). Calcd for $C_{38}H_{51}ClNO_5S$: M+H, 668.3176. Found: *m*/*z* 668.3176.

*3.1.41. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}-N,N-dibenzylaminoacetate (**36b**).* Colorless oil; IR (neat) 2946, 2860, 1722 (CO), 1496, 1455, 1368, 1218, 1151, 1111 (COC), 1049 (SO), 756, 699 cm^{-1}; ^1H NMR δ 1.63 (9H, s), 1.68–1.86 (4H, m), 1.91 (1H, d, *J*=13.9 Hz), 2.14 (1H, d, *J*=13.9 Hz), 2.31 (3H, s), 2.39–2.51 (2H, m), 2.56–2.68 (2H, m), 3.04 (1H, d, *J*=13.7 Hz), 3.16 (1H, d, *J*=13.7 Hz), 3.28–3.38 (6H, m), 3.46 (1H, d, *J*=9.0 Hz), 3.49–3.59 (3H, m), 3.94 (1H, s), 4.33 (2H, d, *J*=12.9 Hz), 5.66 (1H, s), 6.99 (2H, d, *J*=7.3 Hz), 7.11–7.34 (16H, m), 7.55 (4H, d, *J*=7.5 Hz), 7.67 (2H, d, *J*=7.9 Hz). MS (FAB) *m*/*z* (%) 848 ($[M+H]^+$, 10), 756 (7), 254 (28), 196 (12), 91 (100). Calcd for $C_{52}H_{63}ClNO_5S$: M+H, 848.4115. Found: *m*/*z* 848.4121.

*3.1.42. tert-Butyl {1-[chloro(p-tolylsulfinyl)methyl]cyclobutyl}-N,N-dibenzylaminoacetate (**36c**).* Colorless oil; IR (neat) 2977, 1723 (CO), 1495, 1455, 1368, 1148, 1082, 1054 (SO), 750, 699 cm^{-1}; ^1H NMR δ 1.64 (9H, s), 1.65–1.94 (4H, m), 2.39 (3H, s), 2.40–2.52 (1H, m),

2.89–3.02 (1H, m), 3.71 (2H, d, *J*=13.8 Hz), 3.79 (1H, s), 4.05 (2H, d, *J*=13.8 Hz), 5.13 (1H, s), 7.14–7.40 (10H, m), 7.47 (4H, d, *J*=7.1 Hz). MS (FAB) *m*/*z* (%) 552 ([M+H]$^+$, 27), 460 (12), 450 (13), 310 (17), 276 (22), 254 (32), 196 (12), 91 (100). Calcd for $C_{32}H_{39}ClNO_3S$: M+H, 552.2339. Found: *m*/*z* 552.2340.

*3.1.43. tert-Butyl [4,4-bis(ethoxymethyl)cyclopent-1-enyl]-N,N-dibenzylaminoacetate (**37a**).* Colorless oil; IR (neat) 2976, 2851, 1729 (CO), 1495, 1455, 1368, 1113 (COC), 756, 698 cm^{-1}; ^{1}H NMR δ 1.07 (3H, t, *J*=7.0 Hz), 1.16 (3H, t, *J*=7.0 Hz), 1.52 (9H, s), 2.06–2.30 (3H, m), 2.61 (1H, d, *J*=16.8 Hz), 3.19–3.39 (6H, m), 3.47 (2H, q, *J*=7.0 Hz), 3.63 (2H, d, *J*=14.2 Hz), 3.83 (1H, br s), 3.96 (2H, d, *J*=14.2 Hz), 5.52 (1H, br s), 7.18–7.34 (6H, m), 7.38 (4H, d, *J*=7.1 Hz). MS *m*/*z* (%) 493 (M$^+$, 0.1), 392 (100), 91 (33). Calcd for $C_{31}H_{43}NO_4$: M, 493.3192. Found: *m*/*z* 493.3186.

*3.1.44. tert-Butyl [4,4-bis(3-phenylpropoxymethyl)cyclopent-1-enyl]-N,N-dibenzylaminoacetate (**37b**).* Colorless oil; IR (neat) 2930, 2852, 1729 (CO), 1496, 1455, 1367, 1120 (COC), 745, 698 cm^{-1}; ^{1}H NMR δ 1.52 (9H, s), 1.71–1.92 (4H, m), 2.11 (1H, d, *J*=16.5 Hz), 2.30 (2H, br s), 2.54–2.69 (5H, m), 3.22–3.37 (6H, m), 3.41 (2H, t, *J*=6.4 Hz), 3.64 (2H, d, *J*=14.2 Hz), 3.84 (1H, br s), 3.96 (2H, d, *J*=14.2 Hz), 5.53 (1H, br s), 7.09–7.32 (16H, m), 7.39 (4H, d, *J*=7.0 Hz). MS *m*/*z* (%) 673 (M$^+$, 0.2), 572 (100), 91 (30). Calcd for $C_{45}H_{55}NO_4$: M, 673.4131. Found: *m*/*z* 673.4127.

*3.1.45. tert-Butyl (cyclopent-1-enyl)-N,N-dibenzylaminoacetate (**37c**).* Colorless oil; IR (neat) 2976, 2931, 2848, 1729 (CO), 1494, 1455, 1367, 1251, 1131, 745, 698 cm^{-1}; ^{1}H NMR δ 1.53 (9H, s), 1.83 (2H, q, *J*=7.5 Hz), 2.14–2.29 (1H, m), 2.29–3.38 (2H, m), 2.54–2.68 (1H, m), 3.65 (2H, d, *J*=14.3 Hz), 3.89 (1H, br s), 3.96 (2H, d, *J*=14.3 Hz), 5.63–5.68 (1H, m), 7.19–7.28 (2H, m), 7.29–7.34 (4H, m), 7.36–7.42 (4H, m). MS *m*/*z* (%) 377 (M$^+$, 0.6), 276 (100), 91 (40). Calcd for $C_{25}H_{31}NO_2$: M, 377.2355. Found: *m*/*z* 377.2350.

*3.1.46. tert-Butyl [3,3-bis(ethoxymethyl)bicyclo[2.1.0]pent-1-yl]-N,N-dibenzylaminoacetate (**38a**).* Colorless oil; IR (neat) 2976, 2931, 2861, 1728 (CO), 1495, 1455, 1368, 1134, 1109 (COC), 746, 699 cm^{-1}; ^{1}H NMR δ 0.85–0.90 (1H, m), 1.09 (3H, t, *J*=7.0 Hz), 1.11 (1H, d, *J*=5.1 Hz), 1.14 (3H, t, *J*=7.0 Hz), 1.43 (9H, s), 1.41–1.47 (1H, m), 1.52–1.58 (1H, m), 1.72 (1H, dd, *J*=11.3, 1.8 Hz), 3.12 (1H, d, *J*=9.5 Hz), 3.24 (1H, d, *J*=9.5 Hz), 3.33–3.50 (6H, m), 3.74 (1H, s), 3.75 (2H, d, *J*=14.2 Hz), 4.13 (2H, d, *J*=14.2 Hz), 7.19–7.24 (2H, m), 7.26–7.32 (4H, m), 7.37 (4H, d, *J*=7.2 Hz). MS *m*/*z* (%) 493 (M$^+$, 0.3), 392 (100), 254 (33), 91 (76). Calcd for $C_{31}H_{43}NO_4$: M, 493.3192. Found: *m*/*z* 493.3196.

*3.1.47. tert-Butyl [3,3-bis(3-phenylpropoxymethyl)bicyclo[2.1.0]pent-1-yl]-N,N-dibenzylaminoacetate (**38b**).* Colorless oil; IR (neat) 2930, 2857, 1727 (CO), 1495, 1455, 1367, 1133 (COC), 745, 699 cm^{-1}; ^{1}H NMR δ 0.87–0.93 (1H, m), 1.02 (1H, d, *J*=5.0 Hz), 1.42 (9H, s), 1.44–1.57 (2H, m), 1.71–1.90 (5H, m), 2.55–2.68 (4H, m), 3.13 (1H, d, *J*=9.5 Hz), 3.25 (1H, d, *J*=9.5 Hz), 3.32–3.53 (6H, m), 3.77 (2H, d, *J*=14.2 Hz), 3.78 (1H, s), 4.13 (2H, d, *J*=14.2 Hz), 7.10–7.31 (16H, m), 7.38 (4H, d, *J*=7.0 Hz). MS *m*/*z* (%) 673 (M$^+$, 1), 572 (100), 254 (34), 91 (68). Calcd for $C_{45}H_{55}NO_4$: M, 673.4131. Found: *m*/*z* 673.4122.

*3.1.48. Compound (**39**).* Colorless oil; $[\alpha]_D^{29}$ −24.1 (*c* 0.48, EtOH).

*3.1.49. Compound (**40**).* Colorless oil; $[\alpha]_D^{30}$ −5.6 (*c* 0.35, EtOH).

*3.1.50. {1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}-N,N-dimethylacetamide (**41a**).* Colorless oil (about 4:1 mixture of two diastereomers); IR (neat) 2975, 2933, 2869, 1645 (CO), 1494, 1398, 1107 (COC), 1054 (SO), 812, 753 cm^{-1}; ^{1}H NMR δ 1.10 (2.4H, t, *J*=7.0 Hz), 1.13 (0.6H, t, *J*=7.0 Hz), 1.18 (2.4H, t, *J*=7.0 Hz), 1.21 (0.6H, t, *J*=7.0 Hz), 2.09 (0.2H, d, *J*=13.0 Hz), 2.14 (0.8H, d, *J*=13.6 Hz), 2.20 (0.2H, d, *J*=13.3 Hz), 2.22 (0.8H, d, *J*=13.1 Hz), 2.33 (0.8H, d, *J*=13.1 Hz), 2.41 (0.6H, s), 2.42 (2.4H, s), 2.38–2.42 (0.2H, m), 2.50 (0.2H, d, *J*=13.3 Hz), 2.62 (0.8H, d, *J*=13.6 Hz), 2.97 (0.6H, s), 2.99 (2.4H, s), 3.07 (0.6H, s), 3.09 (0.8H, d, *J*=15.2 Hz), 3.10 (2.4H, s), 3.06–3.12 (0.2H, m), 3.20 (0.2H, d, *J*=16.2 Hz), 3.31 (0.8H, d, *J*=15.2 Hz), 3.34–3.56 (8.0H, m), 5.50 (0.2H, s), 5.61 (0.8H, s), 7.30 (2.0H, d, *J*=8.2 Hz), 7.49 (0.4H, d, *J*=8.3 Hz), 7.70 (1.6H, d, *J*=8.3 Hz). MS *m*/*z* (%) 443 (M$^+$, 0.2), 304 (40), 256 (18), 220 (20), 176 (33), 164 (44), 72 (100). Calcd for $C_{22}H_{34}ClNO_4S$: M, 443.1897. Found: *m*/*z* 443.1900.

*3.1.51. {1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}-N,N-dimethylacetamide (**41b**).* Colorless oil (about 4:1 mixture of two diastereomers); IR (neat) 2941, 2860, 1645 (CO), 1496, 1455, 1397, 1111 (COC), 1053 (SO), 750, 700 cm^{-1}; ^{1}H NMR δ 1.74–1.97 (4.0H, m), 2.12 (0.2H, d, *J*=13.4 Hz), 2.20 (0.8H, d, *J*=13.5 Hz), 2.27 (1.0H, d, *J*=13.3 Hz), 2.34 (2.4H, s), 2.36 (0.6H, s), 2.36 (0.8H, d, *J*=13.5 Hz), 2.44 (0.2H, d, *J*=13.3 Hz), 2.48–2.74 (5.0H, m), 2.94 (0.6H, s), 2.96 (2.4H, s), 3.02 (0.6H, s), 3.04 (0.8H, d, *J*=15.0 Hz), 3.08 (2.4H, s), 3.08 (0.2H, d, *J*=15.2 Hz), 3.17 (0.2H, d, *J*=15.2 Hz), 3.30 (0.8H, d, *J*=15.0 Hz), 3.34–3.53 (8.0H, m), 5.47 (0.2H, s), 5.60 (0.8H, s), 7.04–7.12 (2.0H, m), 7.14–7.31 (10.0H, m), 7.48 (0.4H, d, *J*=8.3 Hz), 7.68 (1.6H, d, *J*=8.3 Hz). MS (FAB) *m*/*z* (%) 624 ([M+H]$^+$, 48), 484 (27), 164 (26), 119 (25), 91 (100), 72 (49). Calcd for $C_{36}H_{47}ClNO_4S$: M+H, 624.2914. Found: *m*/*z* 624.2913.

*3.1.52. {1-[Chloro(p-tolylsulfinyl)methyl]cyclobutyl}-N,N-dimethylacetamide (**41c**).* Main product: colorless oil; IR (neat) 2946, 1797, 1644 (CO), 1494, 1400, 1085, 1054 (SO) cm^{-1}; ^{1}H NMR δ 1.92–2.04 (2H, m), 2.06–2.18 (2H, m), 2.42 (3H, s), 2.53–2.72 (2H, m), 2.90 (1H, d, *J*=16.2 Hz), 2.96 (3H, s), 3.07 (3H, s), 3.40 (1H, d, *J*=16.1 Hz), 5.27 (1H, s), 7,30 (2H, d, *J*=7.8 Hz), 7.68 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 327 (M$^+$, 0.7), 188 (60), 152 (43), 139 (14), 72 (100). Calcd for $C_{16}H_{22}ClNO_2S$: M, 327.1060. Found: *m*/*z* 327.1057.

*3.1.53. 2-{1-[Chloro(p-tolylsulfinyl)methyl]cyclobutyl}-N,N-dimethylpropionamide (**41d**).* Colorless oil (about 2:1 mixture of two diastereomers); IR (neat) 2945, 1634 (CO), 1494, 1399, 1083, 1055 (SO) cm^{-1}; ^{1}H NMR δ 1.32 (1.0H, d, *J*=6.8 Hz), 1.41 (2.0H, d, *J*=7.0 Hz), 1.79–2.08 (2.0H, m), 2.42 (2.0H, s), 2.43 (1.0H, s), 2.32–2.61 (4.0H, m), 2.86 (1.0H, s), 2.96 (2.0H, s), 3.12 (1.0H, s), 3.18 (2.0H, s), 3.55 (0.33H, q, *J*=6.8 Hz), 3.75 (0.67H, q, *J*=7.0 Hz), 4.72 (0.33H, s), 4.83 (0.67H, s), 7.28–7.34 (2.0H, m), 7.63 (1.33H, d, *J*=8.2 Hz), 7.74 (0.67H, d, *J*=8.2 Hz). MS *m*/*z* (%) 341 (M$^+$, 0.1), 202 (40), 166 (49), 139 (22), 123 (12), 91 (17), 72 (100). Calcd for $C_{17}H_{24}ClNO_2S$: M, 341.1216. Found: *m*/*z* 341.1216.

*3.1.54. [4,4-Bis(ethoxymethyl)cyclopent-1-enyl]-N,N-dimethylacetamide (**42a**).* Colorless oil; IR (neat) 2975, 2852, 1646 (CO), 1395, 1111 (COC) cm^{-1}; ^{1}H NMR δ 1.16 (6H, t, *J*=7.0 Hz), 2.17–2.24 (4H, m), 2.95 (3H, s), 2.99 (3H, s), 3.10 (2H, s), 3.33 (4H, s), 3.48 (4H, q, *J*=7.0 Hz), 5.28–5.32 (1H, m). MS *m*/*z* (%) 269 (M$^+$, 10), 177 (28), 164 (88), 91 (12), 72 (100). Calcd for $C_{15}H_{27}NO_3$: M, 269.1991. Found: *m*/*z* 269.1989.

*3.1.55. [4,4-Bis(3-phenylpropoxymethyl)cyclopent-1-enyl]-N,N-dimethylacetamide (**42b**).* Colorless oil; IR (neat) 2928, 2854, 1646 (CO), 1497, 1455, 1395, 1112 (COC), 748, 700 cm^{-1}; ^{1}H NMR δ 1.87 (4H, tt, *J*=7.6, 6.4 Hz), 2.19–2.28 (4H, m), 2.67 (4H, t, *J*=7.6 Hz), 2.94 (3H, s), 2.99 (3H, s), 3.11 (2H, s), 3.35 (4H, s), 3.43 (4H, t, *J*=6.4 Hz), 5.32 (1H, br s), 7.14–7.22 (6H, m), 7.23–7.31 (4H, m). MS *m*/*z* (%) 449 (M$^+$, 38), 313 (10), 177 (60), 164 (100), 91 (68), 72 (61). Calcd for $C_{29}H_{39}NO_3$: M, 449.2930. Found: *m*/*z* 449.2935.

*3.1.56. Cyclopent-1-enyl-N,N-dimethylacetamide (**42c**).* Colorless oil; IR (neat) 2931, 2846, 1651 (CO), 1398 cm^{-1}; ^{1}H NMR δ 1.85–1.94

(2H, m), 2.27–2.38 (4H, m), 2.95 (3H, s), 3.00 (3H, s), 3.15 (2H, s), 5.43–5.46 (1H, m). MS *m*/*z* (%) 153 (M^+, 46), 72 (100). Calcd for $C_9H_{15}NO$: M, 153.1154. Found: *m*/*z* 153.1149.

*3.1.57. 2-Cyclopent-1-enyl-N,N-dimethylpropionamide (**42d**).* Colorless oil; IR (neat) 2933, 2852, 1651 (CO), 1396, 1144, 1075 cm^{-1}; ^1H NMR δ 1.24 (3H, d, *J*=6.8 Hz), 1.86 (2H, q, *J*=7.5 Hz), 2.24–2.34 (4H, m), 2.95 (3H, s), 2.99 (3H, s), 3.47 (1H, q, *J*=6.8 Hz), 5.42–5.44 (1H, m). MS *m*/*z* (%) 167 (M^+, 49), 95 (20), 72 (100). Calcd for $C_{10}H_{17}NO$: M, 167.1310. Found: *m*/*z* 167.1310.

*3.1.58. {1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}methyl phenyl sulfone (**43a**).* Colorless oil; IR (neat) 2975, 2932, 2870, 1447, 1308 (SO_2), 1147, 1107 (COC), 1086, 1054 (SO), 754 cm^{-1}; ^1H NMR δ 1.13 (6H, t, *J*=7.0 Hz), 2.37 (1H, d, *J*=13.7 Hz), 2.44 (3H, s), 2.55 (1H, d, *J*=13.6 Hz), 2.57 (1H, d, *J*=13.6 Hz), 2.77 (1H, d, *J*=13.7 Hz), 3.38–3.57 (8H, m), 4.22 (1H, d, *J*=14.0 Hz), 4.42 (1H, d, *J*=14.0 Hz), 5.84 (1H, s), 7.34 (2H, d, *J*=8.1 Hz), 7.54–7.69 (3H, m), 7.82 (2H, d, *J*=8.1 Hz), 7.98–8.04 (2H, m). MS (FAB) *m*/*z* (%) 513 ($[M+H]^+$, 100), 233 (15), 185 (12), 139 (47), 91 (42), 59 (21). Calcd for $C_{25}H_{34}ClO_5S_2$: M+H, 513.1536. Found: *m*/*z* 513.1537.

*3.1.59. {1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(3-phenylpropoxymethyl)cyclobutyl}methyl phenyl sulfone (**43b**).* Colorless oil; IR (neat) 2933, 2861, 1496, 1447, 1308 (SO_2), 1147, 1111 (COC), 1086, 1054 (SO), 751 cm^{-1}; ^1H NMR δ 1.77–1.91 (4H, m), 2.40 (3H, s), 2.40–2.49 (1H, m), 2.62 (4H, t, *J*=7.8 Hz), 2.54–2.66 (2H, m), 2.84 (1H, d, *J*=13.4 Hz), 3.35–3.56 (8H, m), 4.17 (1H, d, *J*=13.8 Hz), 4.41 (1H, d, *J*=13.8 Hz), 5.87 (1H, s), 7.09–7.33 (12H, m), 7.41–7.49 (2H, m), 7.53–7.61 (1H, m), 7.81 (2H, d, *J*=8.2 Hz), 7.93–7.99 (2H, m). MS (FAB) *m*/*z* (%) 693 ($[M+H]^+$, 33), 143 (12), 139 (18), 119 (41), 105 (13), 91 (100). Calcd for $C_{39}H_{46}ClO_5S_2$: M+H, 693.2475. Found: *m*/*z* 693.2475.

*3.1.60. {1-[Chloro(p-tolylsulfinyl)methyl]cyclobutyl}methyl phenyl sulfone (**43c**).* Colorless oil; IR (neat) 2978, 1447, 1309 (SO_2), 1145, 1085, 1051 (SO), 755 cm^{-1}; ^1H NMR δ 1.99–2.29 (4H, m), 2.44 (3H, s), 2.66–2.78 (2H, m), 3.62 (1H, d, *J*=14.2 Hz), 4.52 (1H, d, *J*=14.1 Hz), 5.57 (1H, s), 7.35 (2H, d, *J*=8.3 Hz), 7.56–7.69 (3H, m), 7.80 (2H, d, *J*=8.0 Hz), 8.03 (2H, d, *J*=8.0 Hz). MS (FAB) *m*/*z* (%) 397 ($[M+H]^+$, 100), 143 (76), 139 (28), 79 (69), 55 (34). Calcd for $C_{19}H_{22}ClO_3S_2$: M+H, 397.0699. Found: *m*/*z* 397.0694.

*3.1.61. 1-{1-[Chloro(p-tolylsulfinyl)methyl]cyclobutyl}ethyl phenyl sulfone (**43d**).* Main product: colorless oil; IR (neat) 2942, 1447, 1305 (SO_2), 1141, 1083, 1048 (SO), 761 cm^{-1}; ^1H NMR δ 1.53 (3H, d, *J*=7.0 Hz), 1.92–2.11 (2H, m), 2.36–2.43 (1H, m), 2.45 (3H, s), 2.59–2.68 (1H, m), 2.71–2.80 (1H, m), 2.89–2.97 (1H, m), 4.86 (1H, q, *J*=7.0 Hz), 6.26 (1H, s), 7.36 (2H, d, *J*=7.8 Hz), 7.55–7.67 (3H, m), 7.85 (2H, d, *J*=8.2 Hz), 7.98–8.01 (2H, m). MS (FAB) *m*/*z* (%) 411 ($[M+H]^+$, 100), 271 (12), 241 (10), 149 (41), 143 (36), 93 (57). Calcd for $C_{20}H_{24}ClO_3S_2$: M+H, 411.0855. Found: *m*/*z* 411.0853.

*3.1.62. [4,4-Bis(ethoxymethyl)cyclopent-1-enyl]methyl phenyl sulfone (**44a**).* Colorless oil; IR (neat) 2975, 2854, 1447, 1309 (SO_2), 1153, 1111 (COC), 1087, 742 cm^{-1}; ^1H NMR δ 1.17 (6H, t, *J*=7.0 Hz), 2.17 (2H, br s), 2.27 (2H, br s), 3.25 (4H, s), 3.47 (4H, q, *J*=7.0 Hz), 3.85 (2H, s), 5.34 (1H, br s), 7.50–7.58 (2H, m), 7.61–7.67 (1H, m), 7.85–7.90 (2H, m). MS *m*/*z* (%) 338 (M^+, 0.8), 197 (28), 151 (24), 105 (100), 93 (32), 91 (46), 77 (32), 59 (29). Calcd for $C_{18}H_{26}O_4S$: M, 338.1552. Found: *m*/*z* 338.1552.

*3.1.63. [4,4-Bis(3-phenylpropoxymethyl)cyclopent-1-enyl]methyl phenyl sulfone (**44b**).* Colorless oil; IR (neat) 2929, 2856, 1447, 1309 (SO_2), 1152, 1115 (COC), 1087, 747 cm^{-1}; ^1H NMR δ 1.81–1.93 (4H, m), 2.18 (2H, br s), 2.29 (2H, br s), 2.67 (4H, t, *J*=7.6 Hz), 3.27 (4H, s), 3.41 (4H, t, *J*=6.4 Hz), 3.86 (2H, s), 5.36 (1H, br s), 7.14–7.21 (6H, m), 7.24–7.31 (4H, m), 7.47–7.55 (2H, m), 7.57–7.64 (1H, m), 7.84–7.91 (2H, m). MS *m*/*z* (%) 518 (M^+, 1), 377 (26), 241 (13), 105 (29), 91 (100). Calcd for $C_{32}H_{38}O_4S$: M, 518.2491. Found: *m*/*z* 518.2487.

*3.1.64. {1-[Chloro(p-tolylsulfinyl)methyl]-3,3-bis(ethoxymethyl)cyclobutyl}acetonitrile (**45**).* Colorless oil (about 2:1 mixture of two diastereomers); IR (neat) 2975, 2933, 2870, 2244 (CN), 1378, 1106 (COC), 1057 (SO), 812 cm^{-1}; ^1H NMR δ 1.11 (2.0H, t, *J*=7.0 Hz), 1.13 (1.0H, t, *J*=7.0 Hz), 1.20 (3.0H, t, *J*=7.0 Hz), 2.14 (0.33H, d, *J*=13.5 Hz), 2.20 (0.67H, d, *J*=13.4 Hz), 2.23 (0.67H, d, *J*=13.8 Hz), 2.36 (0.67H, d, *J*=13.4 Hz), 2.29–2.39 (0.67H, m), 2.43 (1.0H, s), 2.44 (2.0H, s), 2.55 (0.33H, d, *J*=13.5 Hz), 2.78 (0.67H, d, *J*=13.8 Hz), 2.99 (0.33 H, d, *J*=17.4 Hz), 3.08 (0.67H, d, *J*=17.0 Hz), 3.16 (0.33H, d, *J*=17.4 Hz), 3.23 (0.67H, d, *J*=17.0 Hz), 3.32 (1.3H, s), 3.28–3.32 (0.33H, m), 3.38–3.60 (6.3H, m), 5.30 (0.33H, s), 5.38 (0.67H, s), 7.34 (2.0H, d, *J*=8.1 Hz), 7.48 (0.66H, d, *J*=8.1 Hz), 7.72 (1.3H, d, *J*=8.1 Hz). MS *m*/*z* (%) 397 (M^+, 1), 258 (47), 212 (19), 176 (47), 140 (100), 132 (55), 118 (94), 91 (49), 59 (95). Calcd for $C_{20}H_{28}ClNO_3S$: M, 397.1478. Found: *m*/*z* 397.1485.

*3.1.65. [4,4-Bis(ethoxymethyl)cyclopent-1-enyl]acetonitrile (**46**).* Colorless oil; IR (neat) 2975, 2852, 2251 (CN), 1376, 1111 (COC) cm^{-1}; ^1H NMR δ 1.17 (6H, t, *J*=7.0 Hz), 2.20–2.27 (4H, m), 3.08 (2H, br s), 3.33 (4H, s), 3.49 (4H, q, *J*=7.0 Hz), 5.60–5.65 (1H, m). MS *m*/*z* (%) 223 (M^+, 2), 177 (19), 131 (51), 117 (55), 91 (73), 79 (37), 59 (100). Calcd for $C_{13}H_{21}NO_2$: M, 223.1572. Found: *m*/*z* 223.1574.

*3.1.66. 5,5-Bis(ethoxymethyl)spiro[2.3]hexane-1-carbonitrile (**47**).* Colorless oil; IR (neat) 2975, 2931, 2858, 2235 (CN), 1378, 1109 (COC) cm^{-1}; ^1H NMR δ 1.06 (1H, t, *J*=5.6 Hz), 1.12 (1H, dd, *J*=8.8, 5.6 Hz), 1.20 (3H, t, *J*=7.0 Hz), 1.21 (3H, t, *J*=7.0 Hz), 1.32 (1H, dd, *J*=8.8, 5.7 Hz), 1.99 (1H, d, *J*=12.1 Hz), 2.06 (1H, d, *J*=12.1 Hz), 2.08 (1H, d, *J*=12.4 Hz), 2.23 (1H, d, *J*=12.4 Hz), 3.46 (2H, s), 3.48 (2H, s), 3.52 (2H, q, *J*=7.0 Hz), 3.53 (2H, q, *J*=7.0 Hz). MS *m*/*z* (%) 223 (M^+, 2), 164 (22), 149 (27), 129 (40), 118 (25), 109 (33), 93 (41), 79 (31), 59 (100). Calcd for $C_{13}H_{21}NO_2$: M, 223.1572. Found: *m*/*z* 223.1574.

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