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A synthesis of bicyclo[*n*.1.0]alkanes having *tert*-butyl carboxylate or acetamide moiety via the intramolecular 1,3-CH insertion of magnesium carbenoids

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ABSTRACT

Treatment of 1-chlorovinyl *p*-tolyl sulfoxides, derived from various cyclic ketones and chloromethyl *p*-tolyl sulfoxide, with lithium enolate of carboxylic acid *tert*-butyl esters or *N*,*N*-dimethylacetamide gave adducts in high yields. The adducts were treated with ether solution of isopropylmagnesium chloride in dry toluene to give bicyclo[*n*.1.0]alkane derivatives having *tert*-butyl carboxylate or acetamide moiety on the bridgehead carbon in high to quantitative yields via magnesium carbenoid 1,3-CH insertion reaction. The 1,3-CH insertion reaction proved to be regioselective and stereospecific. The reaction mechanism and origin of the selectivity and specificity are discussed.

1. Introduction

Carbenes and carbenoids have long been recognized to be highly reactive carbon species and are frequently used as versatile intermediates in organic synthesis.[1] The carbon–hydrogen insertion (CH insertion) is one of the most striking reactions of carbenes and carbenoids.[2] The CH insertion reaction is very interesting and highly useful for construction of molecules, because the reaction enables the formation of a carbon–carbon bond between a carbene (or carbenoid) carbon and a *non-activated carbon*.

Previously, we found that the magnesium carbenoids, generated from aryl 1-chloroalkyl sulfoxides with Grignard reagents via the sulfoxide–magnesium exchange reaction, were stable below −60 °C for at least 30 min.[3] Quite interestingly, when the carbon adjacent to the magnesium carbenoid carbon was quaternary, 1,3-CH insertion took place to afford cyclopropanes in high to quantitative yields upon warming the reaction mixture to 0 °C.[4]

In continuation of our interest in the chemistry of the magnesium carbenoid 1,3-CH insertion reaction, we recently investigated the reaction of 1-chloroalkyl *p*-tolyl sulfoxides **5** with *i*-PrMgCl and found that the reaction resulted in the formation of bicyclo[*n*.1.0]alkane derivatives **7** in high yields (Scheme 1).[5] As shown in Scheme 1, this method is very useful for a synthesis of bicyclo[*n*.1.0]alkane derivatives **7** by assemblage of three components, cyclic ketones **1**, chloromethyl *p*-tolyl sulfoxide **2**, and carboxylic acid derivatives **4**. Thus, 1-chlorovinyl *p*-tolyl sulfoxides **3** were easily synthesized in three steps from cyclic ketones **1** and chloromethyl *p*-tolyl sulfoxide **2** in high overall yields.[6] Conjugate addition of lithium enolate of *tert*-butyl carboxylate or *N*,*N*-dimethylacetamide **4** gave the adducts **5** in high yields.[7] Treatment of the adducts **5** with *i*-PrMgCl afforded bicyclo[*n*.1.0]alkane derivatives **7** in high yields via magnesium carbenoid intermediates **6**. Details of these reactions and some discussions for the mechanism of the reactions are described.

2. Results and discussion

2.1. Synthesis of bicyclo[*n*.1.0]alkane derivatives having *tert*-butyl carboxylate moiety on the bridgehead carbon and some mechanistic studies of the reactions

At first, 1-chlorovinyl *p*-tolyl sulfoxide **8** was synthesized from cyclopentadecanone[6] and was treated with the lithium enolate of *tert*-butyl acetate to give adduct **9** in a quantitative yield (Scheme 2).[7] A solution of the adduct **9** in toluene was added to a solution of *i*-PrMgCl (in ether) in dry toluene at −78 °C dropwise with stirring. The temperature of the reaction mixture was slowly allowed to warm to 0 °C for 2 h to give bicyclo[13.1.0]hexadecane having *tert*-butyl acetate moiety on the bridgehead carbon **11** in 96% yield via magnesium carbenoid intermediate **10**. As reported in the preliminary communication,[5] using *i*-PrMgCl in ether and toluene as the reaction solvent was found to be essential to this reaction.

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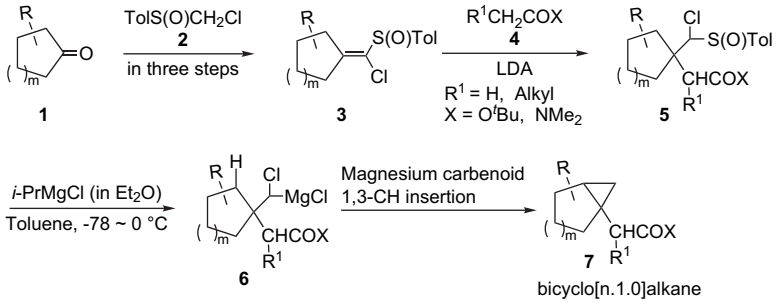
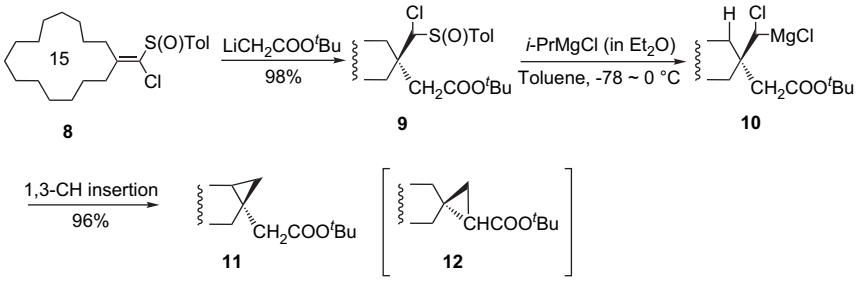


Scheme 1.



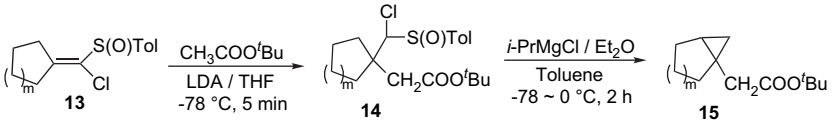
Scheme 2.

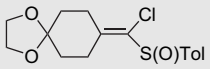
The magnesium carbenoid 1,3-CH insertion reaction was expected to take place between the carbenoid carbon and the methylene carbon on the cyclopentadecane ring (giving cyclopropane **11**) or the methylene carbon adjacent to the carbonyl carbon (giving spiro-type cyclopropane **12**). In this reaction, cyclopropane **11** was obtained as a single product and no spiro-type cyclopropane **12** was observed. Namely, this reaction was highly regioselective. In addition, in the case of cyclopropane **11**, *E*- or *Z*-isomer could be formed. At present, *E*-isomer is anticipated as the product **11**. Stereoselectivity of this reaction was also high. The regioselectivity and the stereoselectivity of this reaction will be discussed later.

We next investigated the generality of this reaction and the results are summarized in Table 1. The reaction starting from 1-chlorovinyl *p*-tolyl sulfoxides derived from cyclopentanone and cyclohexanone (**13a** and **13b**) gave **15a** and **15b**, respectively, in good overall yields via adducts **14a** and **14b**. In the case of 1-chlorovinyl *p*-tolyl sulfoxide derived from cyclohexane-1,4-dione mono ethylene ketal (**13c**), the addition reaction gave **14c** as a mixture of separable two diastereomers (entry 3). These adducts were separately treated with *i*-PrMgCl to afford the same cyclopropane **15c** both in high yields. This procedure starting from medium-sized cycloalkanone (cyclooctanone and cyclodecanone) gave the desired cyclopropanes **15d** and **15e** in good overall yields (entries 4 and 5). Interestingly, all the produced bicyclo[*n*.1.0]alkane derivatives **15** were single isomers, except one case (entry 5). Obviously, the product **15e** is a mixture of *E*- and *Z*-isomers with respect to the configuration of the cyclopropane ring.

The results using *tert*-butyl propionate, *tert*-butyl hexanoate, and *tert*-butyl 4-phenylbutyrate as the ester component are summarized in Table 2. Because the reaction of 1-chlorovinyl *p*-tolyl sulfoxides with lithium enolate of *tert*-butyl carboxylate is highly stereoselective,[8] all the adducts **16** were obtained as a single product in good to quantitative yields. Generation of the magnesium carbenoids from **16** was carried out under the same conditions as described above to give bicyclo[*n*.1.0]alkane derivatives **17** in high yield. Interestingly, when **13a** was used as the starting vinyl

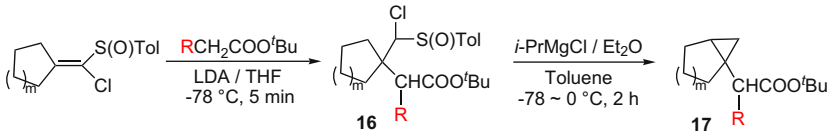
Table 1
Synthesis of bicyclo[*n*.1.0]alkane derivatives having *tert*-butyl acetate moiety **15** from 1-chlorovinyl *p*-tolyl sulfoxides **13** via adducts **14**



Entry	**13**		**14**, Yield %	**15**, Yield %
		m		
1	**13a**	1	98	74
2	**13b**	2	97	89
3	**13c**		(L) 86[a] (P) 14[a]	(L) 95[b] (P) 93[c]
4	**13d**	4	97	90
5	**13e**	6	96	77[d]

[a] The adduct **14c** was obtained as a mixture of separable two diastereomers (less polar adduct (86%) and more polar adduct (14%)).
[b] The yield from the adduct **14c-L**.
[c] The yield from the adduct **14c-P**.
[d] The product **15e** was obtained as a mixture of two inseparable diastereomers (ratio about 2:1).

Table 2
Synthesis of bicyclo[*n*.1.0]alkane derivatives having *tert*-butyl carboxylate moiety **17** from 1-chlorovinyl *p*-tolyl sulfoxides **13** via adducts **16**



Entry	1-Chlorovinyl *p*-tolyl sulfoxide		R	**16**,[a] Yield %	**17**, Yield %
		m			
1	**13a**	1	$PhCH_2CH_2$	**16a**, 60	**17a**, 94[b]
2	**13b**	2	CH_3	**16b**, 99	**17b**, 76[c]
3			$CH_3(CH_2)_3$	**16c**, 99	**17c**, 95[c]
4			$PhCH_2CH_2$	**16d**, 99	**17d**, 89[c]
5	**13d**	4	CH_3	**16e**, 88	**17e**, 96[c]
6			$CH_3(CH_2)_3$	**16f**, 78	**17f**, 89[c]

[a] All adducts **16** were obtained as a single isomer.
[b] About 5:1 mixture of two diastereomers.
[c] Single isomer.

sulfoxide, the product **17a** was obtained as a mixture of two diastereomers (entry 1). All other products **17** were obtained as single product (entries 2–6).

It is already well established that the addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides with the lithium enolate of *tert*-butyl carboxylate is highly stereoselective.[8,9] In the case of the present study, the adduct **16a** has relative stereochemistry as shown in Scheme 3. As the epimerization of the stereogenic center bearing the alkyl substituent is quite unlikely under the conditions, the stereoselectivity of the 1,3-CH insertion reaction of the carbenoid derived from **16a** is thought to be low to afford a mixture of **17A** and **17B** shown in Scheme 3. On the other hand, stereoselectivity of the 1,3-CH insertion reaction of the magnesium carbenoid derived from other adducts **16b**–**16f** proved to be high.

The results of the procedure starting from unsymmetrical ketones are summarized in Table 3. As shown in Table 3, quite interesting specificity was observed. Thus, at first, geometrical isomers of the 1-chlorovinyl *p*-tolyl sulfoxides **18a** and **18b** were synthesized from 2-cyclohexenone in high overall yields.[7c] The *E*-isomer **18a** was treated with the lithium enolate of *tert*-butyl acetate to give adduct **19a**, which was treated with *i*-PrMgCl to afford cyclopropane **20a** in 90% yield (entry 1). Very interestingly, when the adduct **19b**, derived from *Z*-geometrical isomer **18b** with the lithium enolate of *tert*-butyl acetate, was treated with *i*-PrMgCl only a complex mixture was obtained (entry 2). Namely, the magnesium carbenoid 1,3-CH insertion reaction is thought to be highly stereospecific.

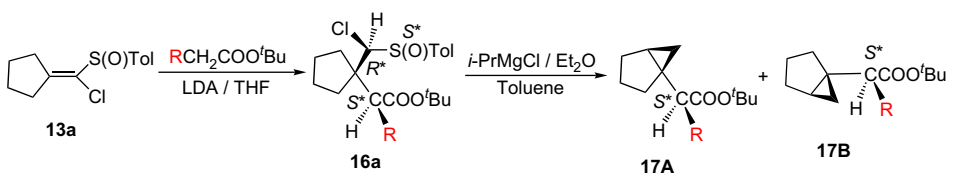
The situation was quite similar in the reactions starting from α-tetralone (entries 3 and 4). Thus, *E*-vinyl sulfoxide **18c** gave the desired cyclopropane **20c** through adduct **19c**. However, the reaction starting from *Z*-vinyl sulfoxide **18d** gave alkylated product **20d**.[3] In addition, the reaction starting from vinyl sulfoxide **18e**, which was derived from 1-indanone, gave one-carbon ring-expanded product **20e** (entry 5).

The specificity of this reaction mentioned above can be explained as follows (Scheme 4). As already mentioned above, the addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides with the lithium enolate of *tert*-butyl carboxylate is highly stereoselective.[8,9] Thus, the adducts **19a** and **19b**, derived from **18a** and **18b**, respectively, have relative stereochemistry as shown in Scheme 4. We propose a six-membered transition state model **A** for the 1,3-CH insertion reaction of the magnesium carbenoid intermediate derived from adduct **19a** with *i*-PrMgCl.[9] In this transition state, C–H bond on the methylene carbon of the cyclohexene ring could attack the chlorine atom from its backside to give smoothly cyclopropane **20a**. On the other hand, magnesium carbenoid intermediate derived from **18b** would form a six-membered transition state **B**. Because the bond placed on backside of the chlorine atom is between olefinic carbon and hydrogen, the CH insertion should not take place and the magnesium carbenoid intermediate would decompose upon warming.

These transition state models also explain the reason why the CH insertion does not take place between the carbenoid carbon and the methylene carbon adjacent to the carbonyl carbon as mentioned before. In these transition states, attack of both the C–H bonds on the methylene carbon adjacent to the carbonyl carbon to the chlorine atom from backside is impossible.

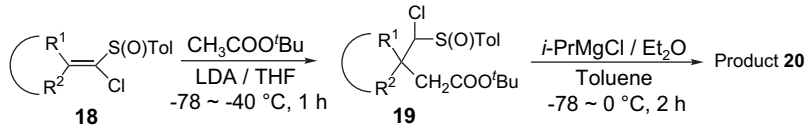
The results were quite similar with the reactions starting from **18c** and **18d** (entries 3 and 4). Treatment of the adduct **19c** derived from *E*-vinyl sulfoxide **18c** with *i*-PrMgCl gave cyclopropane **20c** and the same transition state model can be applied to this reaction. On the other hand, the reaction of the adduct **19d**, derived from *Z*-vinyl sulfoxide **18d**, with *i*-PrMgCl didn't give a cyclopropane but isopropylated product **20d**. The alkylation of the magnesium carbenoid intermediate with *i*-PrMgCl was thought to occur in this particular case.[3]

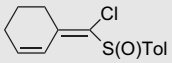
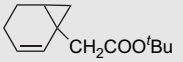
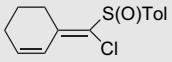
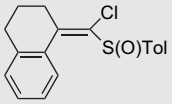
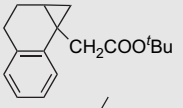
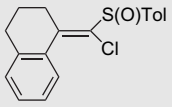
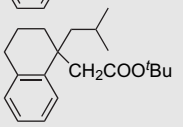
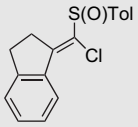
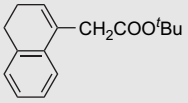
Interesting one-carbon ring-expansion reaction was observed in the reaction starting from 1-chlorovinyl *p*-tolyl sulfoxide derived from 1-indanone (**18e**, entry 5). Thus, treatment of adduct **19e**, derived from **18e** in a quantitative yield, with *i*-PrMgCl gave dihydronaphthalene derivative **20e** in 69% yield. Magnesium carbenoid 1,2-CC insertion reaction is expected to occur in this relatively strained five-membered ring.



Scheme 3.

Table 3
Reaction of 1-chlorovinyl *p*-tolyl sulfoxides **18** derived from unsymmetrical ketones with lithium enolate of *tert*-butyl acetate followed by *i*-PrMgCl

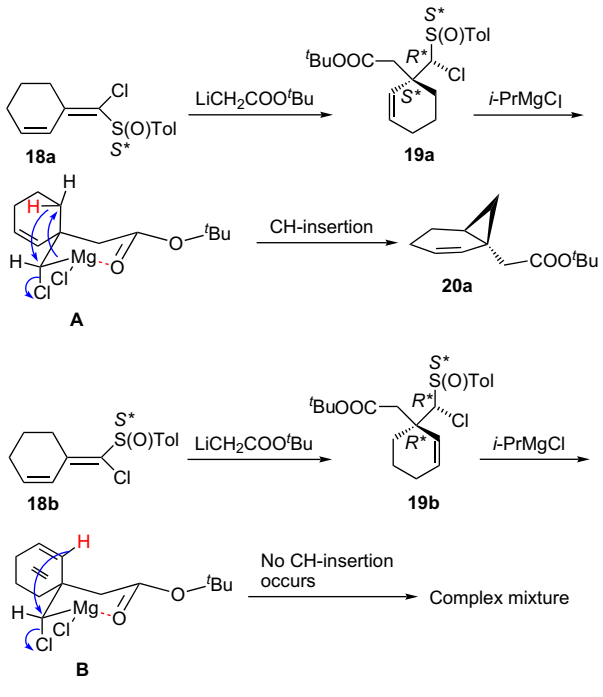


Entry	1-Chlorovinyl *p*-tolyl sulfoxide **18**			**19**, Yield %	Product **20**		Yield %
1	**18a**		(*E*)	**19a**, 96	**20a**		90
2	**18b**		(*Z*)	**19b**, 98		Complete mixture	—
3	**18c**		(*E*)	**19c**, 53	**20c**		57
4	**18d**		(*Z*)	**19d**, 95	**20d**		—[a]
5	**18e**			**19e**, 99	**20e**		69

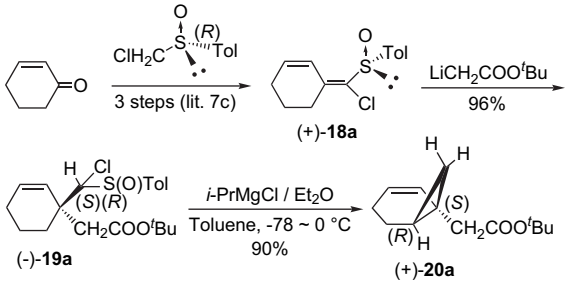
[a] A product containing inseparable unknown compounds.

2.2. Asymmetric synthesis of bicyclo[4.1.0]hept-2-ene having *tert*-butyl acetate moiety

As an application of the presented method, an asymmetric synthesis of optically active bicyclo[4.1.0]hept-2-ene having acetic ester moiety on the bridgehead carbon was investigated as follows (Scheme 5). At first, optically active vinyl sulfoxide (+)-**18a**[7c] was synthesized from 2-cyclohexenone and (*R*)-chloromethyl *p*-tolyl sulfoxide.[10] The vinyl sulfoxide was treated with lithium enolate of *tert*-butyl acetate to afford adduct (−)-**19a** in 96% yield. The absolute configuration and optical purity of (−)-**19a** had been established already.[7c] Finally, (−)-**19a** was treated with *i*-PrMgCl under the same conditions described above to give optically pure (1*S*,6*R*)-bicyclo[4.1.0]hept-2-en-1-ylacetic acid *tert*-butyl ester (+)-**20a** ($[\alpha]_D^{28}$ +137.2 (*c* 0.1, EtOH)) in 90% yield.



Scheme 4.

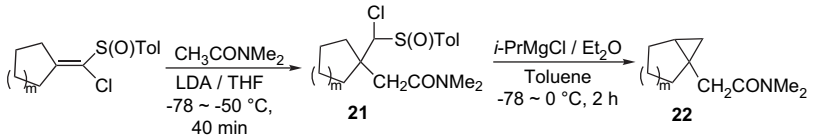


Scheme 5.

2.3. Synthesis of bicyclo[*n*.1.0]alkane derivatives having *N*,*N*-dimethylacetamide moiety on the bridgehead carbon

Finally, as an extension of this synthetic method, we investigated an availability of *N*,*N*-dimethylacetamide, instead of *tert*-butyl carboxylate, in this procedure and the results are summarized in Table 4. At first, 1-chlorovinyl *p*-tolyl sulfoxides having various ring size were synthesized and the reaction with the lithium enolate of *N*,*N*-dimethylacetamide was studied.[7b] As shown in Table 4, the yields for adducts **21** are usually very good except for *m*=1 and 4 (entries 1 and 4). Especially, the addition reaction with 1-chlorovinyl *p*-tolyl sulfoxide derived from cyclooctanone (**13d**) was very low. However, the reason for the low yield is still obscure.

Table 4
Synthesis of bicyclo[*n*.1.0]alkane derivatives having *N*,*N*-dimethylacetamide moiety **22** from 1-chlorovinyl *p*-tolyl sulfoxides via adducts **21**



Entry	1-Chlorovinyl *p*-tolyl sulfoxide		**21**, Yield % (diastereomeric ratio)	**22**, Yield %
		m		
1	**13a**	1	**21a**, 57 (9:1)	**22a**, 93
2	**13b**	2	**21b**, 99 (5:4)	**22b**, 99
3	**13f**	3	**21c**, 99 (19:1)	**22c**, 73
4	**13d**	4	**21d**, 22 (14:1)	**22d**, 92
5	**13g**	8	**21e**, 99(13:1)	**22e**, 84[a]
6	**8**	11	**21f**, 99 (10:1)	**22f**, 88[a]

[a] A 3:1 mixture of two geometrical isomers.

Treatment of the adducts **21** with *i*-PrMgCl was investigated under the same conditions as described above. Fortunately, the 1,3-CH insertion reaction of the generated magnesium carbenoids proceeded smoothly to afford the desired bicyclo[*n*.1.0]alkanes having *N*,*N*-dimethylacetamide moiety on the bridgehead carbon from 73 to 99% yields. Interestingly, the bicyclo[*n*.1.0]alkanes **22** having a large-sized ring (12- and 18-membered ring) were obtained as a mixture of two geometrical isomers (entries 5 and 6).

In conclusion, we have developed a new method for a synthesis of bicyclo[*n*.1.0]alkanes having *tert*-butyl carboxylate or *N*,*N*-dimethylacetamide moiety on the bridgehead carbon by assemblage of three components, cyclic ketones **1**, chloromethyl *p*-tolyl sulfoxide **2**, and carboxylic acid derivatives **4** with magnesium carbenoid 1,3-CH insertion as the key reaction in relatively short step. We believe that the magnesium carbenoid 1,3-CH insertion reaction will be used widely in the synthesis of cyclopropane derivatives.

3. Experimental

3.1. General

All melting points were measured on a Yanaco MP-S3 heated stage apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, 500, BRUKER DPX 400 and AV 600 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion by HITACHI M-80B mass spectrometer. IR spectra were recorded on spectrum One series Fourier transform infrared spectrometer using either NaCl plates or KBr pellets. 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. In experiments requiring dry solvents and reagents, THF and diethyl ether were distilled from diphenylketyl. Diisopropylamine and toluene were distilled from CaH_2. All reactions involving air- or water-sensitive compounds were routinely conducted in glassware, which was flame-dried under a positive pressure of argon. Compounds **13a**,[6b] **13b**,[6b] **13c**,[6a] **13e**,[7b] **14c**,[7a] **14e**,[7a] **18a**,[7c] **18b**,[7c] **18c**,[6b] **19a**,[7c] **19b**,[7c] and **21f**[7b] are previously reported.

3.2. {1-[Chloro(*p*-tolylsulfinyl)methyl]cyclopentadecyl}acetic acid *tert*-butyl ester (9)

tert-Butyl acetate (3.1 mL; 22.8 mmol) was added to a solution of LDA (22.8 mmol) in 40 mL of dry THF at −78 °C with stirring. The solution was stirred for 10 min and then a solution of **8** (1.8 g; 4.56 mmol) in THF (5 mL) was added. The solution was stirred for 5 min and the reaction was quenched by adding satd aq NH_4Cl. The whole mixture was extracted with AcOEt. The product was purified by silica gel column chromatography to afford 2.31 g (99%) of **9** as a colorless oil. IR (neat) 2929, 1721 (CO), 1362, 1146, 1052, 760 cm^{-1}; ^{1}H NMR δ 1.3–1.6 (28H, m), 1.46 (9H, s), 2.41 (3H, s), 2.50, 3.09 (each 1H, d, *J*=15.6 Hz), 5.27 (1H, m), 7.30, 7.74 (each 2H, d, *J*=8.3 Hz). MS *m*/*z* (%) 510 (M$^+$, 0.3), 279 (38), 219 (40), 140 (100), 57 (54). Calcd for $C_{29}H_{47}ClO_3S$: M, 510.2939. Found: *m*/*z* 510.2934.

3.3. Bicyclo[13.1.0]hexadec-1-ylacetic acid *tert*-butyl ester (11)

To a flame-dried flask was added dry toluene (4 mL) followed by *i*-PrMgCl (0.5 mmol; 2.5 equiv) in ether at −78 °C. A solution of adduct **9** (102 mg; 0.2 mmol) in toluene (2.5 mL) was added to the solution of Grignard reagent dropwise with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford 64.5 mg (96%) of cyclopropane **11** as a colorless oil. IR (neat) 2929, 2857, 1735 (CO), 1459, 1391, 1366, 1309, 1250, 1147, 1025, 959, 842 cm^{-1}; ^{1}H NMR δ 0.25 (1H, dd, *J*=5.8, 4.8 Hz), 0.47–0.53 (2H, m), 0.59–0.68 (1H, m), 1.08–1.17 (1H, m), 1.21–1.49 (22H, m), 1.46 (9H, s), 1.54–1.59 (1H, m), 1.76 (1H, d, *J*=15.6 Hz), 1.99–2.15 (1H, m), 2.57 (1H, d, *J*=15.6 Hz); ^{13}C NMR δ 79.93 (4), 37.81 (2), 36.71 (2), 29.10 (2), 28.74 (2), 28.17 (1), 27.86 (2), 27.31 (2), 27.17 (2), 26.86 (2), 26.70 (2), 26.49 (2), 26.47 (2), 26.24 (2), 26.22 (2), 26.14 (2), 22.65 (3), 22.11 (4), 18.71 (2). MS *m*/*z* (%) 336 (M$^+$, 2), 280 (29), 262 (10), 220 (100), 109 (5), 81 (10), 57 (25). Calcd for $C_{22}H_{40}O_2$: M, 336.3028. Found: *m*/*z* 336.3023.

3.4. [Chloro(*p*-tolylsulfinyl)methylene]cyclooctane (13d)

Colorless crystals; mp 72.5–73.0 °C (hexane–AcOEt); IR (KBr) 2931, 2907, 1579, 1471, 1413, 1086, 1054 (SO), 898, 801 cm^{-1}; ^{1}H NMR δ 1.37–1.55 (4H, m), 1.58–1.63 (2H, m), 1.73–1.88 (3H, m), 1.91–1.99 (1H, m), 2.41 (3H, s), 2.48 (2H, dd, *J*=7.0, 4.9 Hz), 2.85 (1H, ddd, *J*=15.0, 7.7, 4.3 Hz), 2.90 (1H, ddd, *J*=15.0, 8.9, 4.0 Hz), 7.31 (2H, d, *J*=8.0 Hz), 7.50 (2H, d, *J*=8.3 Hz). Anal. Calcd for $C_{16}H_{21}ClOS$: C, 64.74; H, 7.13; Cl, 11.94; S, 10.80. Found: C, 64.71; H, 7.09; Cl, 11.85; S, 10.85.

3.5. {1-[Chloro(*p*-tolylsulfinyl)methyl]cyclopentyl}acetic acid *tert*-butyl ester (14a)

Colorless oil; IR (neat) 2961, 1723 (CO), 1597, 1455, 1368, 1218, 1151, 1056, 812 cm^{-1}; ^{1}H NMR δ 1.47 (9H, s), 1.65–1.74 (4H, m), 1.76–1.85 (2H, m), 2.13–2.20 (2H, m), 2.42 (3H, s), 2.57 (1H, d, *J*=15.9 Hz), 3.19 (1H, d, *J*=15.9 Hz), 5.31 (1H, s), 7.31 (2H, d, *J*=8.6 Hz), 7.71 (2H,

d, J=8.0 Hz). MS m/z (%) 370 (M^+, 0.1), 297 (12), 231 (1), 175 (7), 157 (4), 140 (100), 92 (11), 57 (29). Calcd for $C_{19}H_{27}ClO_3S$: M, 370.1369. Found: m/z 370.1371.

3.6. {1-[Chloro(*p*-tolylsulfinyl)methyl]cyclohexyl}acetic acid *tert*-butyl ester (14b)

Colorless oil; IR (neat) 2931, 1716 (CO), 1456, 1368, 1255, 1153, 1083, 1055, 811 cm^{-1}; ^1H NMR δ 1.23–1.37 (1H, m), 1.40–1.58 (2H, m), 1.48 (9H, s), 1.58–1.68 (3H, m), 1.72–1.81 (1H, m), 1.86–1.98 (2H, m), 2.01–2.10 (1H, m), 2.42 (3H, s), 2.71 (1H, d, J=15.6 Hz), 3.20 (1H, d, J=15.5 Hz), 5.29 (1H, s), 7.31 (2H, d, J=7.8 Hz), 7.74 (2H, d, J=7.8 Hz). MS m/z (%) 384 (M^+, 0.1), 311 (11), 276 (2), 189 (14), 140 (100), 91 (11), 57 (29). Calcd for $C_{20}H_{29}ClO_3S$: M, 384.1526. Found: m/z 384.1523.

3.7. {1-[Chloro(*p*-tolylsulfinyl)methyl]cyclooctyl}acetic acid *tert*-butyl ester (14d)

Colorless oil; IR (neat) 2927, 1723 (CO), 1471, 1367, 1254, 1153, 1055, 811 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.47–1.65 (8H, m), 1.71–1.76 (3H, m), 1.90 (1H, ddd, J=15.2, 9.2, 1.9 Hz), 2.17 (1H, dd, J=13.2, 8.9 Hz), 2.31 (1H, ddd, J=15.3, 9.2, 2.7 Hz), 2.42 (3H, s), 2.54 (1H, d, J=15.3 Hz), 3.03 (1H, d, J=15.6 Hz), 5.22 (1H, s), 7.31 (2H, d, J=8.2 Hz), 7.73 (2H, d, J=8.2 Hz). MS m/z (%) 412 (M^+, trace), 356 (1), 339 (10), 297 (1), 217 (12), 181 (20), 140 (100), 121 (35), 92 (8), 57 (25). Calcd for $C_{22}H_{33}ClO_3S$: M, 412.1838. Found: m/z 412.1826.

3.8. Bicyclo[3.1.0]hex-1-ylacetic acid *tert*-butyl ester (15a)

Colorless oil; IR (neat) 2932, 2862, 1732 (CO), 1455, 1392, 1368, 1256, 1141 cm^{-1}; ^1H NMR δ 0.35 (1H, dd, J=8.2, 5.3 Hz), 0.43 (1H, t, J=4.3 Hz), 1.06–1.13 (1H, m), 1.13–1.23 (1H, m), 1.45 (9H, m), 1.57–1.69 (2H, m), 1.71–1.83 (2H, m), 2.30 (1H, d, J=14.6 Hz), 2.37 (1H, d, J=14.7 Hz). MS m/z (%) 183 ($[M-H]^+$, 41), 179 (74), 167 (28), 124 (100), 96 (43), 81 (60), 57 (82).

3.9. Bicyclo[4.1.0]hept-1-ylacetic acid *tert*-butyl ester (15b)

Colorless oil; IR (neat) 2931, 2859, 1732 (CO), 1455, 1368, 1256, 1146 cm^{-1}; ^1H NMR δ 0.26 (1H, t, J=4.8 Hz), 0.47 (1H, dd, J=9.0, 4.6 Hz), 0.81–0.91 (1H, m), 1.10–1.36 (4H, m), 1.46 (9H, s), 1.53–1.62 (1H, m), 1.73 (2H, t, J=6.4 Hz), 1.91 (1H, sextet, J=6.8 Hz), 2.01 (1H, d, J=14.5 Hz), 2.16 (1H, d, J=14.6 Hz). MS m/z (%) 210 (M^+, 0.2), 154 (52), 109 (100), 79 (13), 57 (62). Calcd for $C_{13}H_{22}O_2$: M, 210.1620. Found: m/z 210.1621.

3.10. Cyclopropane (15c)

Colorless oil; IR (neat) 2935, 1728 (CO), 1393, 1368, 1259, 1149, 1075, 948, 841 cm^{-1}; ^1H NMR δ 0.47 (1H, t, J=5.2 Hz), 0.61 (1H, dd, J=9.2, 4.9 Hz), 0.41–0.46 (1H, m), 1.35 (1H, ddd, J=14.6, 9.8, 4.9 Hz), 1.46 (9H, s), 1.54 (1H, ddt, J=13.4, 5.8, 1.8 Hz), 1.74 (1H, d, J=14.4 Hz), 1.99 (1H, d, J=13.1 Hz), 1.94–2.01 (2H, m), 2.06 (1H, d, J=14.4 Hz), 2.20 (1H, d, J=14.4 Hz), 3.85–3.92 (4H, m). MS m/z (%) 268 (M^+, 6), 212 (9), 195 (8), 183 (2), 167 (12), 153 (4), 99 (13), 86 (100), 57 (6). Calcd for $C_{15}H_{24}O_4$: M, 268.1675. Found: m/z 268.1671.

3.11. Bicyclo[6.1.0]non-1-ylacetic acid *tert*-butyl ester (15d)

Colorless oil; IR (neat) 2925, 2856, 1732 (CO), 1456, 1368, 1314, 1257, 1144, 1035, 966, 846 cm^{-1}; ^1H NMR δ −0.02 (1H, dt, J=5.0, 1.2 Hz), 0.39–0.47 (1H, m), 0.69 (1H, dd, J=8.5, 4.6 Hz), 0.91–1.07 (2H, m), 1.26–1.47 (4H, m), 1.50–1.71 (5H, m), 1.45 (9H, s), 2.02 (2H, ddt, J=14.7, 10.7, 3.6 Hz), 2.76 (1H, dd, J=14.1, 1.3 Hz). MS m/z (%) 238 (M^+, 2), 223 (5), 182 (22), 165 (7), 154 (11), 137 (9), 122 (100), 95 (23), 81 (32), 57 (59). Calcd for $C_{15}H_{26}O_2$: M, 238.1933. Found: m/z 238.1936.

3.12. Bicyclo[8.1.0]undec-1-ylacetic acid *tert*-butyl ester (15e)

Colorless oil; IR (neat) 2928, 2861, 1732 (CO), 1455, 1392, 1368, 1300, 1255, 1146, 842 cm^{-1}; ^1H NMR δ −0.20 (0.4H, ddd, J=6.1, 4.7, 1.3 Hz), 0.22 (0.6H, dd, J=6.2, 4.6 Hz), 0.41 (0.6H, ddd, J=8.8, 4.6, 1.5 Hz), 0.50 (0.4H, ddd, J=10.0, 9.5, 6.3 Hz), 0.57–0.67 (0.6H, m), 0.71 (0.4H, dd, J=9.2, 4.8 Hz), 0.94–1.02 (0.6H, m), 1.03–1.12 (0.6H, m), 1.13–1.22 (0.8H, m), 1.23–1.43 (6H, m), 1.45 (3.6H, s), 1.46 (5.4H, s), 1.47–1.65 (6H, m), 1.67–1.90 (1H, m), 1.75 (0.6H, d, J=14.3 Hz), 1.76 (0.4H, d, J=14.4 Hz), 1.95 (0.4H, dt, J=15.0, 4.7 Hz), 2.25 (0.6H, dt, J=14.5, 3.5 Hz), 2.76 (0.4H, d, J=14.3 Hz), 2.76 (0.6H, d, J=14.2 Hz). MS m/z (%) 266 (M^+, 2), 210 (7), 193 (5), 165 (2), 150 (100), 109 (14), 95 (19), 81 (19), 57 (48). Calcd for $C_{17}H_{30}O_2$: M, 266.2246. Found: m/z 266.2248.

3.13. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclopentyl}-4-phenylbutyric acid *tert*-butyl ester (16a)

Colorless crystals; mp 125.0–126.0 °C (hexane–AcOEt); IR (KBr) 2963, 1712 (CO), 1595, 1455, 1365, 1145, 1053, 814, 696 cm^{-1}; ^1H NMR δ 1.51 (9H, s), 1.55–1.65 (2H, m), 1.68–1.80 (2H, m), 1.86 (1H, dddd, J=13.0, 10.4, 6.5, 2.6 Hz), 1.92–2.20 (5H, m), 2.42 (3H, s), 2.56 (1H, ddd, J=13.7, 10.0, 6.6 Hz), 2.68 (1H, ddd, J=14.1, 10.6, 5.0 Hz), 3.21 (1H, dd, J=11.8, 2.7 Hz), 4.61 (1H, m), 7.15–7.24 (3H, m), 7.28–7.33 (2H, m), 7.29 (2H, d, J=7.8 Hz), 7.62 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{27}H_{35}ClO_3S$: C, 68.26; H, 7.43; Cl, 7.46; S, 6.75. Found: C, 68.15; H, 7.24; Cl, 7.43; S, 6.73.

3.14. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclohexyl}-propionic acid *tert*-butyl ester (16b)

Colorless oil; IR (neat) 2930, 1728 (CO), 1456, 1367, 1145, 1056, 811, 760 cm^{-1}; ^1H NMR δ 1.22–1.34 (4H, m), 1.34 (3H, d, J=7.0 Hz), 1.47 (9H, m), 1.60–1.79 (3H, m), 1.84 (1H, ddd, J=13.8, 11.7, 4.6 Hz), 2.08–2.17 (1H, m), 2.43 (3H, s), 2.45–2.52 (1H, m), 3.11 (1H, q, J=7.1 Hz), 4.95 (1H, m), 7.32 (2H, d, J=8.2 Hz), 7.72 (2H, d, J=8.2 Hz). MS (FAB) m/z (%) 399 ($[M+H]^+$, 42), 343 (100), 325 (21), 269 (3), 203 (15), 167 (73), 140 (16), 123 (16), 93 (11), 57 (14). Calcd for $C_{21}H_{32}ClO_3S$: [M+H], 399.1761. Found: m/z 399.1759.

3.15. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclohexyl}hexanoic acid *tert*-butyl ester (16c)

Colorless oil; IR (neat) 2929, 1723 (CO), 1456, 1367, 1144, 1057, 812 cm^{-1}; ^1H NMR δ 0.93 (3H, t, J=7.1 Hz), 1.20–1.47 (8H, m), 1.49 (9H, s), 1.60–1.76 (3H, m), 1.78–1.93 (3H, m), 2.06–2.14 (1H, m), 2.44 (3H, m), 2.49–2.58 (1H, m), 2.94 (1H, dd, J=10.2, 4.3 Hz), 4.98 (1H, s), 7.33 (2H, d, J=8.0 Hz), 7.73 (2H, d, J=8.2 Hz). MS (FAB) m/z (%) 441 ($[M+H]^+$, 50), 385 (100), 367 (36), 245 (27), 209 (80), 140 (21), 93 (14), 57 (20). Calcd for $C_{24}H_{38}ClO_3S$: [M+H], 441.2230. Found: m/z 441.2228.

3.16. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclohexyl}-4-phenylbutyric acid *tert*-butyl ester (16d)

Colorless oil; IR (neat) 2929, 1716 (CO), 1456, 1368, 1253, 1144, 1055, 757 cm^{-1}; ^1H NMR δ 1.15–1.36 (2H, m), 1.36–1.51 (2H, m), 1.54 (9H, s), 1.60–176 (3H, m), 1.77–1.91 (1H, m), 2.05–2.20 (2H, m), 2.22 (1H, dd, J=8.2, 6.9 Hz), 2.43 (3H, s), 2.46–2.56 (1H, m), 2.56 (1H, dd, J=16.4, 8.2 Hz), 2.63–2.79 (1H, m), 3.02 (1H, dd, J=8.4, 6.8 Hz), 4.93 (1H, s), 7.17–7.35 (7H, m), 7.67 (2H, d, J=8.2 Hz). MS (FAB) m/z (%) 489 ($[M+H]^+$, 22), 433 (100), 415 (47), 379 (17), 293 (43), 257 (34),

211 (35), 91 (73), 57 (50). Calcd for $C_{28}H_{38}ClO_3S$: [M+H], 489.2230. Found: *m*/*z* 489.2230.

3.17. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclooctyl}propionic acid *tert*-butyl ester (16e)

Colorless oil; IR (neat) 2926, 1728 (CO), 1597, 1456, 1368, 1255, 1152, 1057, 811 cm^{-1}; ^1H NMR δ 1.35 (3H, d, *J*=7.3 Hz), 1.40–1.88 (10H, m), 1.47 (9H, m), 2.01 (2H, t, *J*=5.3 Hz), 2.07 (1H, ddd, *J*=15.2, 7.7, 2.2 Hz), 2.29 (1H, ddd, *J*=15.2, 9.3, 2.3 Hz), 2.43 (3H, s), 3.00 (1H, q, *J*=7.2 Hz), 4.61 (1H, s), 7.32 (2H, d, *J*=8.1 Hz), 7.71 (2H, d, *J*=8.4 Hz). MS (FAB) *m*/*z* (%) 427 ($[M+H]^+$, 60), 371 (100), 353 (17), 231 (17), 195 (68), 154 (22), 121 (43), 93 (14), 57 (20). Calcd for $C_{23}H_{36}ClO_3S$: [M+H], 427.2074. Found: *m*/*z* 427.2073.

3.18. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclooctyl}hexanoic acid *tert*-butyl ester (16f)

Colorless oil; IR (neat) 2928, 1723 (CO), 1455, 1367, 1254, 1150, 1057, 811 cm^{-1}; ^1H NMR δ 0.85–0.93 (2H, m), 0.92 (3H, t, *J*=7.0 Hz), 1.19–1.72 (10H, m), 1.49 (9H, s), 1.73–1.81 (2H, m), 1.85 (2H, dd, *J*=14.5, 7.7 Hz), 1.92–2.07 (3H, m), 2.33 (1H, ddd, *J*=15.4, 8.6, 3.1 Hz), 2.43 (3H, s), 2.86 (1H, dd, *J*=8.5, 7.4 Hz), 4.58 (1H, m), 7.32 (2H, d, *J*=8.2 Hz), 7.71 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 469 ($[M+H]^+$, 60), 413 (100), 395 (33), 273 (28), 237 (70), 191 (16), 154 (18), 121 (59), 93 (11), 57 (28). Calcd for $C_{26}H_{42}ClO_3S$: [M+H], 469.2543. Found: *m*/*z* 469.2541.

3.19. 2-Bicyclo[3.1.0]hex-1-yl-4-phenylbutyric acid *tert*-butyl ester (17a)

Colorless oil; IR (neat) 2933, 2862, 1728 (CO), 1605, 1497, 1455, 1392, 1367, 1256, 1143, 1020, 851, 699 cm^{-1}; ^1H NMR δ 0.28 (0.2H, dd, *J*=8.1, 5.1 Hz), 0.37 (0.8H, t, *J*=4.7 Hz), 0.41–0.49 (1H, m), 1.04 (0.8H, dt, *J*=8.0, 4.0 Hz), 1.09–1.25 (1.2H, m), 1.46 (1.8H, s), 1.47 (7.2H, s), 1.61–1.79 (6H, m), 1.98–2.13 (2H, m), 2.48–2.68 (2H, m), 7.18 (3H, d, *J*=6.8 Hz), 7.27 (2H, t, *J*=8.3 Hz). MS *m*/*z* (%) 300 (M^+, 3), 280 (2), 244 (50), 199 (12), 140 (54), 117 (30), 104 (100), 91 (50). Calcd for $C_{20}H_{28}O_2$: M, 300.2089. Found: *m*/*z* 300.2087.

3.20. 2-Bicyclo[4.1.0]hept-1-ylpropionicacid *tert*-butyl ester (17b)

Colorless oil; IR (neat) 2979, 2931, 1729 (CO), 1592, 1457, 1368, 1246, 1153, 1118, 852 cm^{-1}; ^1H NMR δ 0.24–0.30 (1H, m), 0.66–0.75 (1H, m), 1.04–1.11 (1H, m), 1.08 (3H, d, *J*=7.2 Hz), 1.12–1.29 (5H, m), 1.44 (9H, s), 1.59–1.69 (2H, m), 1.76–1.89 (2H, m). MS *m*/*z* (%) 224 (M^+, 0.1), 209 (0.3), 181 (0.7), 168 (22), 154 (3), 123(26), 95 (100), 81 (28), 57 (52).

3.21. 2-Bicyclo[4.1.0]hept-1-ylhexanoic acid *tert*-butyl ester (17c)

Colorless oil; IR (neat) 2930, 2860, 1727 (CO), 1455, 1367, 1256, 1151 cm^{-1}; ^1H NMR δ 0.22 (1H, t, *J*=4.8 Hz), 0.65 (1H, dd, *J*=9.3, 4.5 Hz), 0.68–0.76 (1H, m), 0.89 (3H, t, *J*=7.0 Hz), 1.08–1.35 (10H, m), 1.37–1.51 (1H, m), 1.44 (9H, m), 1.63 (1H, dd, *J*=13.2, 6.8 Hz), 1.68–1.79 (1H, m), 1.79–1.90 (2H, m). MS *m*/*z* (%) 266 (M^+, 2), 210 (20), 154 (22), 116 (16), 109 (11), 95 (100), 57 (27). Calcd for $C_{17}H_{30}O_2$: M, 266.2246. Found: *m*/*z* 266.2248.

3.22. 2-Bicyclo[4.1.0]hept-1-yl-4-phenylbutyric acid *tert*-butyl ester (17d)

Colorless oil; IR (neat) 2930, 2859, 1781 (CO), 1604, 1496, 1454, 1367, 1256, 1226, 1144, 1021, 850, 699 cm^{-1}; ^1H NMR δ 0.24 (1H, t, *J*=3.6 Hz), 0.62–0.72 (2H, m), 1.07–1.28 (4H, m), 1.46 (9H, s), 1.47–1.55 (2H, m), 1.58–1.66 (1H, m), 1.72 (1H, dddd, *J*=13.4, 10.3, 6.7, 5.0 Hz), 1.79–1.92 (2H, m), 2.11 (1H, ddt, *J*=13.5, 10.0, 5.2 Hz), 2.54 (1H, ddd, *J*=13.7, 10.0, 6.5 Hz), 2.63 (1H, ddd, *J*=13.6, 10.2, 5.3 Hz), 7.18 (3H, d, *J*=6.8 Hz), 7.27 (2H, dd, *J*=8.4, 7.3 Hz). MS *m*/*z* (%) 314 (M^+, 6), 258 (41), 240 (7), 213 (6), 167 (8), 154 (57), 131 (13), 104 (100), 95 (67), 91 (51), 57 (42). Calcd for $C_{21}H_{30}O_2$: M, 314.2246. Found: *m*/*z* 314.2246.

3.23. 2-Bicyclo[6.1.0]non-1-ylpropionic acid *tert*-butyl ester (17e)

Colorless oil; IR (neat) 2927, 1729 (CO), 1456, 1367, 1252, 1151, 851 cm^{-1}; ^1H NMR δ −0.25 (1H, t, *J*=4.7 Hz), 0.55–0.64 (1H, m), 0.66 (1H, dd, *J*=4.1, 8.9 Hz), 0.95–1.12 (2H, m), 1.08 (3H, d, *J*=6.8 Hz), 1.29–1.41 (4H, m), 1.43 (9H, s), 1.49–1.62 (2H, m), 1.63–1.80 (2H, m), 1.92–2.04 (2H, m), 2.45 (1H, q, *J*=6.7 Hz). MS *m*/*z* (%) 252 (M^+, 3), 237 (5), 196 (27), 151 (12), 123 (100), 109 (11), 81 (41), 67 (25), 57 (77). Calcd for $C_{16}H_{28}O_2$: M, 252.2090. Found: *m*/*z* 252.2097.

3.24. 2-Bicyclo[6.1.0]non-1-ylhexanoic acid *tert*-butyl ester (17f)

Colorless oil; IR (neat) 2926, 2859, 1728 (CO), 1469, 1367, 1256, 1150, 1035, 852 cm^{-1}; ^1H NMR δ −0.26 (1H, t, *J*=4.9 Hz), 0.46–0.56 (1H, m), 0.71 (1H, dd, *J*=9.0, 4.3 Hz), 0.93–1.06 (2H, m), 1.14–1.78 (17H, m), 1.44 (9H, s), 1.92–2.02 (2H, m), 2.61 (1H, dd, *J*=11.2, 2.6 Hz). MS *m*/*z* (%) 294 (M^+, 4), 238 (28), 210 (3), 193 (11), 181 (28), 123 (100), 116 (42), 81 (35), 57 (54). Calcd for $C_{19}H_{34}O_2$: M, 294.2559. Found: *m*/*z* 294.2567.

3.25. (*Z*)-1-[Chloro(*p*-tolylsulfinyl)methylene]-1,2,3,4-tetrahydro-naphthalene (18d)

Colorless crystals; mp 142–143 °C (hexane–AcOEt); IR (KBr) 2968, 1584, 1451, 1435, 1289, 1175, 1086, 1060, 908, 812, 521 cm^{-1}; ^1H NMR δ 1.88–2.05 (1H, m), 2.07–2.22 (1H, m), 2.41 (3H, m), 2.89 (2H, t, *J*=6.5 Hz), 3.06 (1H, ddd, *J*=14.3, 7.5, 5.4 Hz), 3.27 (1H, ddd, *J*=14.3, 8.2, 5.2 Hz), 7.13–7.22 (2H, m), 7.27 (1H, dd, *J*=6.9, 1.7 Hz), 7.33 (2H, d, *J*=7.9 Hz), 7.55 (2H, d, *J*=8.3 Hz), 7.85–7.91 (1H, m). Anal. Calcd for $C_{18}H_{17}ClOS$: C, 68.23; H, 5.41; Cl, 11.19; S, 10.12. Found: C, 68.23; H, 5.42; Cl, 11.09; S, 10.03.

3.26. (*Z*)-1-[Chloro(*p*-tolylsulfinyl)methylene]indane (18e)

Colorless crystals; mp 140–141 °C (hexane–AcOEt); IR (KBr) 2919, 1589, 1492, 1442, 1305, 1085, 1057 (SO), 879, 807, 759, 527 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 3.07–3.23 (2H, m), 3.24 (1H, ddd, *J*=16.4, 8.7, 5.2 Hz), 3.56 (1H, ddd, *J*=16.6, 8.2, 3.9 Hz), 7.24–7.35 (1H, m), 7.32 (2H, d, *J*=8.3 Hz), 7.35–7.42 (2H, m), 7.56 (2H, d, *J*=8.2 Hz), 8.27 (1H, d, *J*=7.96 Hz). Anal. Calcd for $C_{17}H_{15}ClOS$: C, 67.43; H, 4.99; Cl, 11.71; S, 10.59. Found: C, 67.33; H, 4.99; Cl, 11.60; S, 10.60.

3.27. {1-[Chloro(*p*-tolylsulfinyl)methyl]-1,2,3,4-tetrahydro-naphthalen-1-yl}acetic acid *tert*-butyl ester (19c)

Derived from **18c**; colorless crystals; mp 89–91 °C (hexane–AcOEt); IR (KBr) 2952, 1720 (CO), 1494, 1448, 1367, 1213, 1143, 1056, 811 cm^{-1}; ^1H NMR δ 1.34 (9H, s), 1.72–1.89 (1H, m), 1.99 (1H, dt, *J*=13.7, 5.3 Hz), 2.32 (2H, t, *J*=6.5 Hz), 2.41 (3H, s), 2.74–2.84 (2H, m), 2.91 (1H, d, *J*=15.6 Hz), 3.15 (1H, *J*=15.7 Hz), 5.49 (1H, s), 7.11 (1H, dd, *J*=7.0, 1.8 Hz), 7.20 (2H, ddt, *J*=14.0, 7.0, 1.6 Hz), 7.29 (2H, d, *J*=8.2 Hz), 7.59 (1H, dd, *J*=7.1, 2.0 Hz), 7.63 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{24}H_{29}ClO_3S$: C, 66.57; H, 6.75; Cl, 8.19; S, 7.40. Found: C, 66.81; H, 6.78; Cl, 8.06; S, 7.37.

3.28. {1-[Chloro(*p*-tolylsulfinyl)methyl]-1,2,3,4-tetrahydronaphthalen-1-yl}acetic acid *tert*-butyl ester (19d)

Derived from **18d**; colorless crystals; mp 130–133 °C (hexane–AcOEt); IR (KBr) 2938, 1710 (CO), 1494, 1447, 1367, 1225, 1153, 1083, 1054, 815, 741 cm^{-1}; ^1H NMR δ 1.34 (9H, s), 1.77–2.08 (2H, m), 2.42 (3H, s), 2.48 (1H, ddt, J=13.7, 3.8, 0.9 Hz), 2.58 (1H, ddd, J=13.7, 12.2, 3.8 Hz), 2.70–2.93 (2H, m), 3.04 (1H, d, J=15.5 Hz), 3.30 (1H, d, J=15.6 Hz), 5.71 (1H, s), 7.05–7.18 (3H, m), 7.32 (2H, d, J=8.0 Hz), 7.41–7.47 (1H, m), 7.79 (2H, d, J=8.2 Hz). Anal. Calcd for $C_{24}H_{29}ClO_3S$: C, 66.57; H, 6.75; Cl, 8.19; S, 7.40. Found: C, 66.14; H, 6.74; Cl, 8.07; S, 7.33.

3.29. {1-[Chloro(*p*-tolylsulfinyl)methyl]indan-1-yl}acetic acid *tert*-butyl ester (19e)

Colorless crystals; mp 115–116.5 °C (hexane–AcOEt); IR (KBr) 2980, 1718 (CO), 1456, 1367, 1226, 1148, 1057, 814, 506 cm^{-1}; ^1H NMR δ 1.33 (9H, s), 2.42 (3H, s), 2.43 (1H, ddd, J=13.1, 8.7, 4.1 Hz), 2.82 (1H, ddd, J=13.3, 9.7, 7.4 Hz), 2.94 (1H, d, J=15.7 Hz), 3.03 (1H, dd, J=16.1, 8.1 Hz), 3.15 (1H, ddd, J=16.1, 9.8, 4.2 Hz), 3.26 (1H, d, J=15.8 Hz), 5.72 (1H, m), 7.10–7.20 (1H, m), 7.21–7.25 (2H, m), 7.26–7.29 (1H, m), 7.31 (2H, d, J=8.2 Hz), 7.68 (2H, d, J=8.2 Hz). Anal. Calcd for $C_{23}H_{27}ClO_3S$: C, 65.93; H, 6.50; Cl, 8.46; S, 7.65. Found: C, 65.98; H, 6.48; Cl, 8.40; S, 7.70.

3.30. Bicyclo[4.1.0]hept-2-en-1-ylacetic acid *tert*-butyl ester (20a)

Colorless oil; IR (neat) 2979, 2930, 1732 (CO), 1455, 1368, 1256, 1147, 1089, 964, 762 cm^{-1}; ^1H NMR δ 0.65 (1H, dd, J=8.3, 4.6 Hz), 0.79 (1H, t, J=5.2 Hz), 1.26–1.29 (1H, m), 1.44 (9H, s), 1.55–1.64 (1H, m), 1.66–1.74 (1H, m), 1.90–2.00 (2H, m), 2.08 (1H, d, J=14.9 Hz), 2.38 (1H, d, J=14.9 Hz), 5.45 (1H, ddd, J=9.5, 6.8, 1.9 Hz), 5.94 (1H, dd, J=10.1, 2.8 Hz). MS m/z (%) 208 (M^+, 7), 193 (11), 152 (100), 132 (12), 107 (64), 93 (65), 57 (88), 18 (77). Calcd for $C_{13}H_{20}O_2$: M, 208.1463. Found: m/z 208.1470.

3.31. (1,1a,2,3-Tetrahydrocyclopropa[*a*]naphthalen-7b-yl)-acetic acid *tert*-butyl ester (20c)

Colorless oil; IR (neat) 2978, 2929, 1732 (CO), 1495, 1455, 1368, 1280, 1251, 1151, 738 cm^{-1}; ^1H NMR δ 0.82 (1H, dd, J=8.4, 5.3 Hz), 0.98 (1H, t, J=5.5 Hz), 1.32 (9H, s), 1.49–1.56 (1H, m), 1.88 (1H, ddt, J=12.9, 5.2, 3.4 Hz), 2.06 (1H, ddd, J=13.0, 5.8, 2.6 Hz), 2.18 (1H, d, J=16.1 Hz), 2.48 (1H, ddd, J=16.1, 12.6, 6.1 Hz), 2.65 (1H, ddd, J=16.1, 5.3, 2.7 Hz), 3.14 (1H, d, J=16.1 Hz), 7.03 (1H, dd, J=6.7, 1.2 Hz), 7.06–7.17 (2H, m), 7.36 (1H, d, J=7.6 Hz). MS m/z (%) 258 (M^+, 7), 238 (3), 202 (100), 185 (10), 157 (29), 142 (67), 129 (26), 115 (21), 57 (37). Calcd for $C_{17}H_{22}O_2$: M, 258.1619. Found: m/z 258.1620.

3.32. (1-Isobutyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetic acid *tert*-butyl ester (20d)

Colorless oil; IR (neat) 2932, 1723 (CO), 1455, 1392, 1368, 1255, 1147, 750 cm^{-1}; ^1H NMR δ 0.88 (6H, d, J=6.7 Hz), 1.43 (9H, s), 1.64–1.75 (2H, m), 1.82–1.87 (2H, m), 1.90–2.04 (2H, m), 2.71–2.80 (2H, m), 2.82–2.88 (2H, m), 7.05–7.12 (4H, m).

3.33. (3,4-Dihydronaphthalen-1-yl)acetic acid *tert*-butyl ester (20e)

Colorless oil; IR (neat) 2978, 2932, 1732 (CO), 1487, 1456, 1368, 1257, 1143, 754 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 2.34 (2H, t, J=8.3 Hz), 2.84 (2H, t, J=8.3 Hz), 3.11 (2H, s), 6.32 (1H, s), 6.99 (1H, d, J=6.7 Hz), 7.06–7.16 (3H, m). MS m/z (%) 244 (M^+, 20), 188 (79), 143 (93), 128 (76), 115 (23), 57 (100). Calcd for $C_{16}H_{20}O_2$: M, 244.1462. Found: m/z 244.1463.

3.34. [Chloro(*p*-tolylsulfinyl)methylene]cycloheptane (13f)

Colorless crystals; mp 95–95.5 °C (hexane–AcOEt); IR (KBr) 2930, 2854, 1441, 1084 (SO), 1055 (SO), 803, 527 cm^{-1}; ^1H NMR δ 1.44–1.74 (7H, m), 1.83–1.95 (1H, m), 2.41 (3H, s), 2.53 (2H, m), 2.86–3.06 (2H, m), 7.31 (2H, d, J=8.1 Hz), 7.49 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{15}H_{19}ClOS$: C, 63.70; H, 6.77; Cl, 12.53; S, 11.34. Found: C, 63.86; H, 6.71; Cl, 12.54; S, 11.35.

3.35. [Chloro(*p*-tolylsulfinyl)methylene]cyclododecane (13g)

Colorless crystals; mp 104–104.5 °C (hexane–AcOEt); IR (KBr) 2931, 2849, 1470, 1086 (SO), 1052 (SO), 893, 807, 522 cm^{-1}; ^1H NMR δ 1.38–1.78 (18H, m), 2.30–2.46 (2H, m), 2.41 (3H, s), 2.65–2.85 (2H, m), 7.31 (2H, d, J=8.1 Hz), 7.48 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{20}H_{29}ClOS$: C, 68.06; H, 8.28; Cl, 10.04; S, 9.08. Found: C, 68.06; H, 8.21; Cl, 9.95; S, 9.06.

3.36. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclopentyl}-*N*,*N*-dimethylacetamide (21a)

N,*N*-Dimethylacetamide (0.46 mL; 5.0 mmol) was added to a solution of LDA (5.0 mmol) in 15 mL of dry THF at −78 °C with stirring. The solution was stirred for 10 min and then a solution of **13a** (254 mg; 1.0 mmol) in THF (5 mL) was added. The reaction mixture was slowly allowed to warm to −50 °C for 40 min. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to afford 200 mg (57%) of **21a** as a colorless oil (12:1 mixture of two diastereomers). IR (neat) 2954, 1645 (CO), 1398, 1085 (SO), 1052 (SO), 812 cm^{-1}; ^1H NMR δ 1.61–1.74 (4H, m), 1.76–1.86 (2H, m), 2.22–2.30 (2H, m), 2.41 (3H, s), 2.60 (0.9H, d, J=16.6 Hz), 2.82 (0.2H, s), 2.95 (3H, s), 3.02 (2.8H, s), 3.05 (0.2H, s), 3.40 (0.9H, d, J=16.6 Hz), 5.67 (0.1H, s), 5.79 (0.9H, s), 7.29 (1.8H, d, J=7.9 Hz), 7.31 (0.2H, d, J=8.2 Hz), 7.51 (0.2H, d, J=8.2 Hz), 7.68 (1.8H, d, J=7.9 Hz). MS m/z (%) 341 (M^+, 0.5), 204 (18), 202 (54), 166 (62), 139 (48), 121 (28), 91 (32), 72 (100). Calcd for $C_{17}H_{24}ClNO_2S$: M, 341.1216. Found: m/z 341.1216.

3.37. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclohexyl}-*N*,*N*-dimethylacetamide (21b)

Main product: colorless oil; IR (neat) 2929, 1634 (CO), 1456, 1398, 1147, 1051 (SO), 812 cm^{-1}; ^1H NMR δ 1.22–1.75 (5H, m), 1.87–1.96 (1H, m), 1.99–2.19 (4H, m), 2.41 (3H, s), 2.80 (1H, d, J=16.6 Hz), 2.99 (3H, br s), 3.06 (3H, br s), 3.25 (1H, d, J=16.6 Hz), 5.80 (1H, s), 7.29 (2H, d, J=8.1 Hz), 7.70 (2H, d, J=8.1 Hz). MS m/z (%) 355 (M^+, 0.3), 246 (25), 218 (22), 216 (65), 180 (32), 153 (100), 139 (25), 87 (45), 72 (84). Calcd for $C_{18}H_{26}ClNO_2S$: M, 355.1373. Found: m/z 355.1372.

Minor product: colorless oil; IR (neat) 2931, 1634 (CO), 1398, 1089 (SO), 1061 (SO), 811 cm^{-1}; ^1H NMR δ 1.25–1.50 (4H, m), 1.61–1.67 (2H, m), 1.82–2.11 (4H, m), 2.40 (3H, s), 2.88 (1H, d, J=16.8 Hz), 2.90 (1H, d, J=16.8 Hz), 2.96 (3H, s), 3.10 (3H, s), 5.50 (1H, s), 7.31 (2H, d, J=8.2 Hz), 7.51 (2H, d, J=8.2 Hz). MS m/z (%) 355 (M^+, 0.1), 218 (33), 216 (100), 180 (31), 139 (7), 72 (76). Calcd for $C_{18}H_{26}ClNO_2S$: M, 355.1373. Found: m/z 355.1375.

3.38. 2-{1-[Chloro-(*p*-tolylsulfinyl)-methyl]-cyclopentyl}-*N*,*N*-dimethylacetamide (21c)

Main product: colorless oil; IR (neat) 2923, 2858, 1645 (CO), 1398, 1085 (SO), 1052 (SO), 811, 734 cm^{-1}; ^1H NMR δ 1.36–1.42 (1H,

m), 1.49–1.59 (3H, m), 1.63–1.84 (5H, m), 2.06–2.12 (1H, m), 2.19–2.30 (2H, m), 2.41 (3H, s), 2.67 (1H, d, J=16.5 Hz), 2.97 (3H, br s), 3.04 (3H, br s), 3.25 (1H, d, J=16.5 Hz), 5.86 (1H, s), 7.29 (2H, d, J=8.2 Hz), 7.70 (2H, d, J=8.2 Hz). MS m/z (%) 369 (M^+, 1.4), 278 (28), 240 (80), 232 (28), 230 (88), 139 (56), 123 (62), 87 (93), 72 (100). Calcd for $C_{19}H_{28}ClNO_2S$: M, 369.1530. Found: m/z 369.1526.

3.39. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclooctyl}-*N*,*N*-dimethylacetamide (21d)

Main product: colorless oil; IR (neat) 2922, 1646 (CO), 1398, 1266, 1053 (SO), 812 cm^{-1}; ^1H NMR δ 1.39–1.81 (10H, m), 1.84–2.02 (2H, m), 2.18–2.25 (1H, m), 2.32–2.43 (1H, m), 2.41 (3H, s), 2.56 (1H, d, J=16.4 Hz), 2.95 (3H, s), 3.05 (3H, s), 3.15 (1H, J=16.4 Hz), 5.77 (1H, s), 7.29 (2H, d, J=8.0 Hz), 7.71 (2H, d, J=8.0 Hz). MS m/z (%) 383 (M^+, 0.25), 244 (32), 208 (30), 181 (100), 121 (30), 91 (23), 87 (43), 72 (52). Calcd for $C_{20}H_{30}ClNO_2S$: M, 383.1686. Found: m/z 383.1679.

3.40. 2-{1-[Chloro(*p*-tolylsulfinyl)methyl]cyclododecyl}-*N*,*N*-dimethylacetamide (21e)

Main product: colorless, amorphous; IR (KBr) 2929, 2861, 1644 (CO), 1471, 1398, 1084 (SO), 1049 (SO), 810, 732 cm^{-1}; ^1H NMR δ 1.25–1.50 (16H, m), 1.56–1.73 (3H, m), 1.80–1.90 (2H, m), 2.02–2.07 (1H, m), 2.38 (1H, d, J=17.6 Hz), 2.41 (3H, s), 2.96 (3H, br s), 3.03 (3H, s), 3.30 (1H, d, J=17.6 Hz), 5.95 (1H, s), 7.29 (2H, d, J=8.2 Hz), 7.69 (2H, d, J=8.2 Hz). MS m/z (%) 439 (M^+, 0.1), 281 (13), 252 (52), 87 (100), 72 (40). Calcd for $C_{24}H_{38}ClNO_2S$: M, 439.2312. Found: m/z 439.2306.

3.41. 2-Bicyclo[3.1.0]hex-1-yl-*N*,*N*-dimethylacetamide (22a)

To a flame-dried flask was added dry toluene (3.0 mL) followed by *i*-PrMgCl (in ether; 0.5 mmol; 5.0 equiv) at −78 °C. A solution of adduct **21a** (34 mg; 0.1 mmol) in toluene (2.0 mL) was added to the solution of Grignard reagent dropwise with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole mixture was extracted with $CHCl_3$. As the product **22a** and the produced isopropyl *p*-tolyl sulfoxide were very difficult to separate by silica gel chromatography, the sulfoxide was oxidized to sulfone. Thus, $CHCl_3$ was evaporated and the residue was dissolved in THF (1.0 mL) and *m*-CPBA (0.12 mmol; 1.2 equiv) was added to the solution at room temperature. The reaction mixture was stirred for 60 min. The reaction was quenched with satd aq Na_2SO_3 and the whole mixture was extracted with $CHCl_3$ and the organic layer was washed with 5% aq NaOH. The product was purified by silica gel column chromatography to afford 15.8 mg (93%) of **22a** as a colorless oil. IR (neat) 2927, 2859, 1644 (CO), 1452, 1396, 1267, 1132, 1022 cm^{-1}; ^1H NMR δ 0.34 (1H, dd, J=8.0, 5.1 Hz), 0.48 (1H, t, J=4.5 Hz), 1.10 (1H, quintet, J=4.1 Hz), 1.16–1.23 (1H, m), 1.55–1.61 (2H, m), 1.67 (1H, dd, J=12.3, 7.9 Hz), 1.75–1.82 (1H, m), 1.84 (1H, dd, J=11.1, 7.40 Hz), 2.51 (1H, d, J=15.0 Hz), 2.60 (1H, d, J=15.0 Hz), 2.94 (3H, s), 3.00 (3H, s). MS m/z (%) 167 (M^+, 21), 95 (12), 87 (42), 72 (100). Calcd for $C_{10}H_{17}NO$: M, 167.1309. Found: m/z 167.1311.

3.42. 2-Bicyclo[4.1.0]hept-1-yl-*N*,*N*-dimethylacetamide (22b)

Colorless oil; IR (neat) 2924, 1652 (CO), 1452, 1394, 1266, 1137 cm^{-1}; ^1H NMR δ 0.30 (1H, t, J=5.2 Hz), 0.45 (1H, dd, J=9.2, 4.7 Hz), 0.75–0.83 (1H, m), 1.10–1.40 (4H, m), 1.55–1.61 (1H, m), 1.67 (1H, ddd, J=5.4, 7.8, 13.4 Hz), 1.78 (1H, ddd, J=4.8, 6.9, 12.1 Hz), 1.96 (1H, sextet, J=6.6 Hz), 2.24 (1H, d, J=15.4 Hz), 2.38 (1H, d, J=15.4 Hz), 2.94 (3H, s), 2.97 (3H, s). MS m/z (%) 181 (M^+, 28), 138 (18), 109 (12), 87 (93), 72 (100), 45 (29). Calcd for $C_{11}H_{19}NO$: M, 181.1467. Found: m/z 167.1471.

3.43. 2-Bicyclo[5.1.0]oct-1-yl-*N*,*N*-dimethylacetamide (22c)

Colorless oil; IR (neat) 2918, 1651 (CO), 1465, 1393, 1267, 1141, 1026 cm^{-1}; ^1H NMR δ 0.39 (1H, t, J=4.3 Hz), 0.64–0.79 (2H, m), 0.98 (1H, dt, J=13.6, 10.4 Hz), 1.11–1.85 (7H, m), 1.96 (1H, d, J=14.8 Hz), 2.08–2.21 (2H, m), 2.79 (1H, d, J=14.8 Hz), 2.93 (3H, s), 3.01 (3H, s). MS m/z (%) 195 (M^+, 20), 180 (19), 138 (21), 87 (81), 72 (100), 45 (23). Calcd for $C_{12}H_{21}NO$: M, 195.1622. Found: m/z 195.1623.

3.44. 2-Bicyclo[6.1.0]non-1-yl-*N*,*N*-dimethylacetamide (22d)

Colorless oil; IR (neat) 2921, 1651 (CO), 1393, 1138, 1032 cm^{-1}; ^1H NMR δ 0.05 (1H, t, J=5.1 Hz), 0.42–0.52 (1H, m), 0.60 (1H, dd, J=8.7, 4.6 Hz), 0.90–1.15 (2H, m), 1.31–1.62 (8H, m), 1.84 (1H, d, J=15.2 Hz), 2.01 (1H, dq, J=14.3, 3.3 Hz), 2.15 (1H, dt, J=14.9, 3.8 Hz), 2.89 (1H, d, J=15.2 Hz), 2.93 (3H, s), 2.99 (3H, s). MS m/z (%) 209 (M^+, 15), 166 (10), 138 (15), 87 (93), 72 (100), 45 (28). Calcd for $C_{13}H_{23}NO$: M, 209.1777. Found: m/z 209.1770.

3.45. 2-Bicyclo[10.1.0]tridec-1-yl-*N*,*N*-dimethylacetamide (22e)

Colorless oil (3:1 mixture of two diastereomers); IR (neat) 2927, 1652 (CO), 1447, 1393, 1264, 1137 cm^{-1}; ^1H NMR δ 0.05 (0.25H, t, J=5.1 Hz), 0.18 (0.75H, dd, J=5.9, 4.9 Hz), 0.50–0.60 (1H, m), 0.62–0.70 (1H, m), 0.75–0.90 (1H, m), 1.02–1.68 (17.25H, m), 1.83–1.87 (1H, m), 1.91 (0.75H, d, J=15.8 Hz), 1.96 (0.25H, d, J=15.2 Hz), 2.22–2.28 (0.75H, m), 2.77 (0.25H, d, J=15.2 Hz), 2.84 (0.75H, d, J=15.8 Hz), 2.92 (0.75H, s), 2.96 (2.25H, s), 2.97 (0.75H, s), 3.03 (2.25H, s). MS m/z (%) 265 (M^+, 94), 222 (18), 138 (25), 87 (85), 72 (100), 55 (14). Calcd for $C_{17}H_{31}NO$: M, 265.2405. Found: m/z 265.2404.

3.46. 2-Bicyclo[13.1.0]hexadec-1-yl-*N*,*N*-dimethylacetamide (22f)

Colorless oil (3:1 mixture of two diastereomers); IR (neat) 2927, 1651 (CO), 1461, 1393, 1265, 1137, 753 cm^{-1}; ^1H NMR δ 0.06 (0.25H, s), 0.22 (0.75H, s), 0.48–0.68 (3H, m), 1.15–1.76 (24.25H, m), 1.90 (0.75H, d, J=15.0 Hz), 2.04–2.11 (0.75H, m), 2.18 (0.25H, d, J=15.0 Hz), 2.54 (0.25H, d, J=15.0 Hz), 2.77 (0.75H, d, J=15.7 Hz), 2.92 (0.75H, s), 2.96 (2.25H, s), 2.98 (0.75H, s), 3.03 (2.25H, s). MS m/z (%) 307 (M^+, 38), 264 (11), 138 (12), 87 (71), 72 (100), 55 (26), 41 (29). Calcd for $C_{20}H_{37}NO$: M, 307.2873. Found: m/z 307.2880.

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References and notes

1. Some monographs and reviews concerning chemistry of carbenes and carbenoids: (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, NY, 1971; (b) Dorwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999; (c) *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker: New York, NY, 2002; (d) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473; (e) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383; (f) Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361; (g) Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288; (h) Wynberg, H.; Meijer, E. W. *Org. React.* **1982**, *29*, 1; (i) Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751; (j) Oku, A.; Harada, T. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 736; (k) Oku, A. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 710; (l) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765; (m) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223; (n) Zaragoza, F. *Tetrahedron* **1997**, *53*, 3425; (o) Kirmse, W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1164; (p) Braun, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 430; (q) Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477; (r) Muller, P. *Acc. Chem. Res.* **2004**, *37*, 243; (s) Knorr, R. *Chem. Rev.* **2004**, *104*, 3795.

2. Some reviews concerning carbon–hydrogen insertion reaction: (a) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385; (b) Sulikowski, G. A.; Cha, K. L.; Sulikowski, M. M. *Tetrahedron: Asymmetry* **1998**, *9*, 3145; (c) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861; (d) Davies, H. M. L.; Loe, O. *Synthesis* **2004**, 2595; (e) Davies, H. M. L. *Angew. Chem., Int. Ed* **2006**, *45*, 6422.
3. Satoh, T.; Kondo, A.; Musashi, J. *Tetrahedron* **2004**, *60*, 5453.
4. Satoh, T.; Musashi, J.; Kondo, A. *Tetrahedron Lett.* **2005**, *46*, 599.
5. Preliminary results of this study were reported as a communication: Satoh, T.; Ogata, S.; Wakasugi, D. *Tetrahedron Lett.* **2006**, *47*, 7249.
6. (a) Satoh, T.; Takano, K.; Ota, H.; Someya, H.; Matsuda, K.; Koyama, M. *Tetrahedron* **1998**, *54*, 5557; (b) Satoh, T.; Kawashima, T.; Takahashi, S.; Sakai, K. *Tetrahedron* **2003**, *59*, 9599.
7. (a) Satoh, T.; Sugiyama, S.; Kamide, Y.; Ota, H. *Tetrahedron* **2003**, *59*, 4327; (b) Satoh, T.; Kamide, Y.; Sugiyama, S. *Tetrahedron* **2004**, *60*, 11805; (c) Sugiyama, S.; Satoh, T. *Tetrahedron: Asymmetry* **2005**, *16*, 665.
8. Kido, M.; Sugiyama, S.; Satoh, T. *Tetrahedron: Asymmetry* **2007**, *18*, 1934.
9. Ogata, S.; Masaoka, S.; Sakai, K.; Satoh, T. *Tetrahedron Lett.* **2007**, *48*, 5017.
10. Satoh, T.; Oohara, T.; Ueda, Y.; Yamakawa, K. *J. Org. Chem.* **1989**, *54*, 3130.