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A synthesis of di- and tri-substituted β,γ-unsaturated esters from aldehydes by the magnesium carbenoid 1,2-CH and 1,2-CC insertion as the key reaction

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ABSTRACT

Addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides, which were derived from aldehydes, with lithium enolate of *tert*-butyl acetate at −78 °C in THF gave adducts in high yields. Treatment of these adducts with Grignard reagents resulted in the formation of magnesium carbenoids via the sulfoxide–magnesium exchange reaction. When the adducts were derived from alkyl aldehydes or electron-deficient aromatic aldehydes, carbenoid 1,2-CH insertion reaction took place from the magnesium carbenoids to afford β,γ-unsaturated butyric esters having a substituent at the β-position. On the other hand, when the adducts were derived from electron-rich aromatic aldehydes, carbenoid 1,2-CC insertion reaction took place from the magnesium carbenoids to give β,γ-unsaturated butyric esters having the aromatic group at the γ-position. Highly stereospecific 1,2-CC insertion reactions were observed in the latter reactions. When the addition reactions were quenched with iodoalkanes, the alkylated adducts were obtained in quantitative yields. Tri-substituted β,γ-unsaturated esters, or in some case γ,δ-unsaturated esters, were obtained by the treatment of the alkylated adducts with EtMgCl. These procedures provide a good way for a new synthesis of di- and tri-substituted β,γ-unsaturated esters from aldehydes with two or three carbon–carbon bond-formations.

1. Introduction

Carboxylic acids and their derivatives are one of the most important and fundamental compounds in organic, synthetic organic,[1] and bioorganic chemistry.[2] In synthetic organic chemistry, α,β-unsaturated and β,γ-unsaturated carboxylic acids are more versatile compounds compared with the saturated ones. α,β-Unsaturated carboxylic acids and their derivatives are usually synthesized from saturated carboxylic acid derivatives by, for example, sulfenylation or selenenylation of the α-carbon followed by oxidation and *syn*-elimination.[3] From aldehydes and ketones, Horner–Wadsworth–Emmons reaction[4] with two-carbon elongation was extensively used. Thus, the synthesis of α,β-unsaturated carboxylic acids and their derivatives is thought to be quite easy.

In contrast to this, no universal method for the synthesis of β,γ-unsaturated carboxylic acid derivatives has been reported. Methods so far reported for the synthesis of β,γ-unsaturated carboxylic acids and their derivatives are as follows. One-carbon elongation of α,β-unsaturated esters or aldehydes.[5] Deconjugative protonation of α,β-unsaturated esters.[6] Photo deconjugation of α,β-unsaturated esters.[7] Deconjugative alkylation of α,β-unsaturated esters.[8] Reductive deconjugation of α-bromo α,β-unsaturated esters.[9] Modified Knoevenagel condensation[10] and others.[11]

Recently, we are interested in the development of new synthetic methods utilizing magnesium carbenoids as the key intermediates.[12] In continuation of the investigation, we found that the reaction of 1-chloroalkyl phenyl sulfoxide having a tertiary carbon next to the carbon bearing a sulfinyl group **1** with *i*-PrMgCl resulted in the formation of olefin **3** by the 1,2-CH insertion of magnesium carbenoid intermediate **2** (Scheme 1).[13] Stimulated by this result, we expected that the reaction of esters having a tertiary carbon at the β-position and chlorine and a sulfinyl group at the γ-position **4** with *i*-PrMgCl results in the formation of β,γ-unsaturated esters **6** via the magnesium carbenoid intermediates **5**.

We studied above-mentioned idea and indeed we could develop a new method for a synthesis of β,γ-unsaturated esters (**11**, **12**, and **15** in Scheme 2) from aldehydes. The essence of this study is as follows. Thus, 1-chlorovinyl *p*-tolyl sulfoxides **7** were derived from aldehydes with chloromethyl *p*-tolyl sulfoxide in two steps in good yields.[14] Addition reaction of **7** with lithium enolate of *tert*-butyl acetate resulted in the formation of α-sulfinyl lithium carbenoid intermediate **8**. Quenching **8** with water gave adducts **9** in high yield.[14b] Quenching **8** with iodoalkanes gave alkylated adducts **13** in quantitative yields.

Treatment of adducts **9** with Grignard reagent gave magnesium carbenoid intermediates **10**, from which β,γ-unsaturated esters **11**

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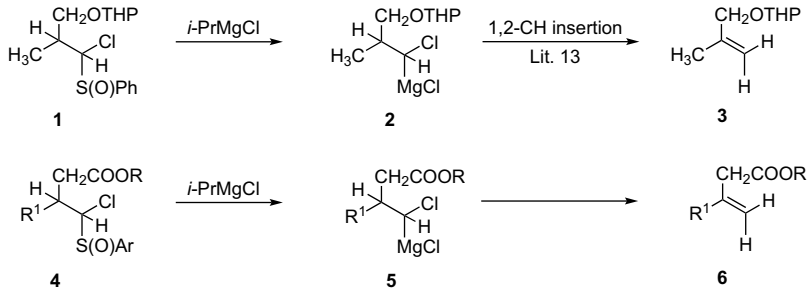
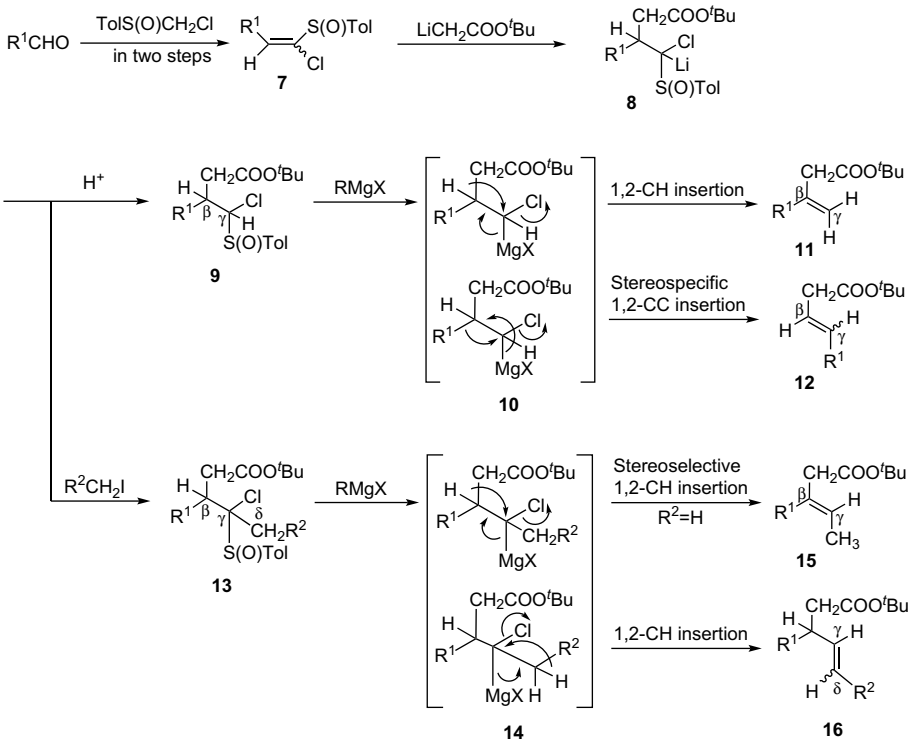


Scheme 1.



Scheme 2.

or **12** were obtained by 1,2-CH insertion or stereospecific 1,2-CC insertion reaction, respectively.[15] On the other hand, treatment of **13** with Grignard reagent afforded magnesium carbenoid intermediates **14**, from which β,γ-unsaturated esters **15**, and γ,δ-unsaturated esters **16** were obtained by 1,2-CH insertion. These procedures offer a novel method for a synthesis of β,γ-unsaturated esters. Details of this study and the mechanisms and stereochemistry of this reaction are described.

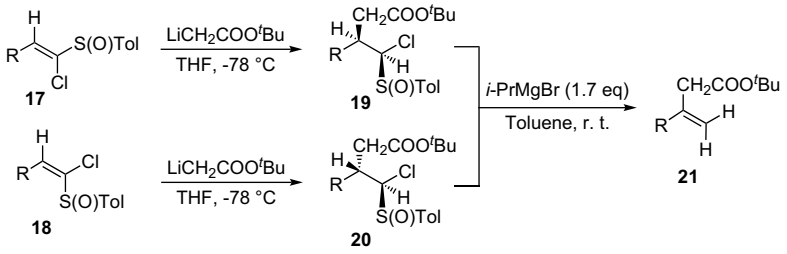
2. Results and discussion

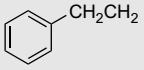
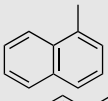
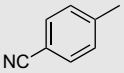
2.1. A synthesis of β,γ-unsaturated esters from aldehydes with chloromethyl *p*-tolyl sulfoxide and *tert*-butyl acetate

At first, 1-chloro-4-phenyl-1-(*p*-tolylsulfinyl)-1-butenes **17a** and **18a** (R=$PhCH_2CH_2$) were synthesized from 3-phenylpropanal and chloromethyl *p*-tolyl sulfoxide in two steps in high overall yield[14b] (see Table 1). The two geometrical isomers were separately treated with lithium enolate of *tert*-butyl acetate to afford the adducts (**19a** and **20a**), each in quantitative yield as a single diastereomer.[14b] The addition reaction proceeded in a highly stereospecific manner, as reported in the previous papers,[14b,16] and the structure of **19a** and **20a** was determined to be (3*S**,4*R**,$_S$*S**)-*tert*-butyl 4-chloro-3-(2-phenylethyl)-4-(*p*-tolylsulfinyl)butyrate and (3*R**,4*R**,$_S$*S**)-isomer, respectively, as shown in Table 1.

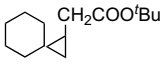
Based on our experiences,[13] the adduct **19a** was first treated with 1.7 equiv of *i*-PrMgCl in toluene at room temperature; however, the treatment gave the expected olefin **21a** in only 5% yield with several unknown products. The treatment of **20a** with *i*-PrMgCl gave only a complex mixture. We tried to find the optimized conditions (Grignard reagent, solvent, temperature) for obtaining the desired **21a** and finally *i*-PrMgBr in toluene at room temperature was the conditions of choice for this reaction. Thus, quite interestingly, treatment of adduct **19a** with *i*-PrMgBr (1.7 equiv) gave the desired β,γ-unsaturated ester **21a** in 85% yield (entry 1). The treatment of **20a** with *i*-PrMgBr also gave the desired β,γ-unsaturated ester **21a** as the main product; however, the yield was worse compared with that from **19a** (entry 2). At present, we still find it difficult to propose the reason why *i*-PrMgBr, not *i*-PrMgCl, gave the good results.

Table 1
Synthesis of β,γ-unsaturated esters **21** from the adducts of 1-chlorovinyl *p*-tolyl sulfoxides with lithium enolate of *tert*-butyl acetate **19** and **20**



Entry	**19** and **20**		**21**	
	R		Yield[a]/%	
1	**19a**		**21a**	85
2	**20a**		**21a**	41
3	**19b**	$CH_3(CH_2)_5$	**21b**	65
4	**20b**	$CH_3(CH_2)_5$	**21b**	50
5	**19c**		**21c**	56[b]
6	**20c**		**21c**	44
7	**19d**	$(CH_3)_3C$	**21d**	70
8	**20d**	$(CH_3)_3C$	**21d**	64
9	**19e**		**21e**	88
10	**20e**		**21e**	50
11	**19f**		**21f**	5
12	**20f**		**21f**	45
13	**19g**		**21g**	47
14	**20g**		**21g**	40

[a] The yield of the reaction of adducts **19** and **20** with *i*-PrMgBr.
[b] Cyclopropane **22** was obtained as an inseparable by-product in 35% yield (calculated from the ^{1}H NMR spectrum).



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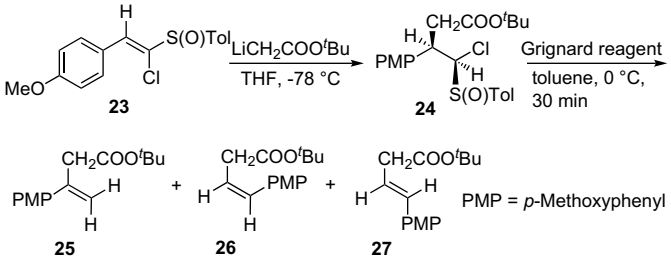
Because we assured that this would become a useful method for a synthesis of β,γ-unsaturated esters, we studied generality of this reaction starting from various aldehydes and the results are summarized in Table 1. *n*-Heptanal, cyclohexanecarboxaldehyde, pivalaldehyde, benzaldehyde, 1-naphthaldehyde, and 4-cyanobenzaldehyde were selected as the representative aldehydes. As mentioned above, 1-chlorovinyl *p*-tolyl sulfoxides **17** and **18** were synthesized from the aldehydes in two steps in high overall yields.[14] Addition reaction of vinyl sulfoxides **17** and **18** with lithium enolate of *tert*-butyl acetate gave almost quantitative yields of adducts **19** and **20**, respectively. Finally, treatment of **19** and **20** with *i*-PrMgBr (1.7 equiv) in toluene at room temperature for 10 min gave moderate to good yields of the desired β,γ-unsaturated esters **21a** to **21g** bearing a substituent R at the β-position except one example (entry 11). Obviously, the products **21** were derived through the 1,2-CH insertion of the magnesium carbenoid intermediates. One example (entry 11) gave quite complex mixture and the desired product **21f** could be obtained in only 5% yield. Only the case of cyclohexyl group as R gave cyclopropane **22** as a by-product by 1,3-CH insertion[17] (entry 5). Although the reason is not clear at present, in all examples, except one case (entries 11 and 12), the yields were better when the reaction was conducted with the isomer **19**. It is worth noting that migration of the double bond at the β,γ-position to the α,β-position under these conditions was never observed throughout this study.

Next, we investigated the above-mentioned reactions with 1-chlorovinyl *p*-tolyl sulfoxide derived from electron-rich aromatic aldehyde, *p*-anisaldehyde (Table 2). The addition reaction of 1-chlorovinyl *p*-tolyl sulfoxide **23** with lithium enolate of *tert*-butyl acetate gave adduct **24** as a single isomer in a quantitative yield. Quite interestingly, treatment of **24** with *i*-PrMgBr gave three β,γ-unsaturated esters **25** (49%, by 1,2-CH insertion), **26**

Table 2
Investigation for the best conditions of the reaction of **24** with Grignard reagent to give (*Z*)-β,γ-unsaturated ester **26** through the magnesium carbenoid 1,2-CC insertion reaction



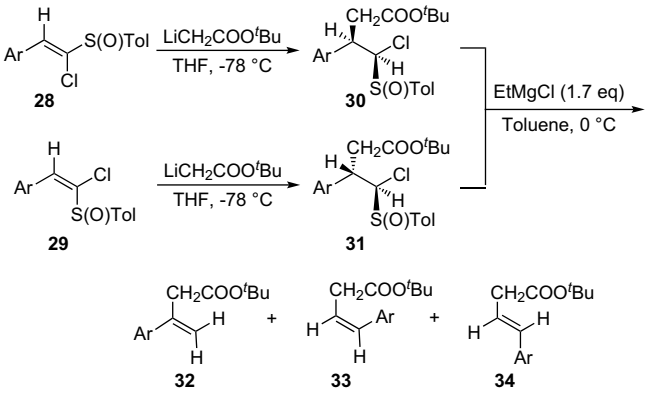
Entry	Grignard reagent	**25**	**26**	**27**
		Yield[a]/%		
1	*i*-PrMgBr	49	21	16
2	*i*-PrMgCl	Trace	64	5
3	MeMgCl	2	46	22
4	EtMgCl	0	80	6

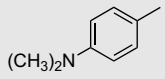
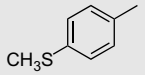
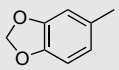
[a] The yield of the reaction of adduct **24** with Grignard reagent.

(21%, by 1,2-CC insertion), and **27** (16%, by 1,2-CC insertion) as shown in entry 1 of Table 2. When *i*-PrMgCl was used in this reaction, β,γ-unsaturated ester **26** became the main product with the geometrical isomer **27** (entry 2). MeMgCl gave the products **26** and **27** through the magnesium carbenoid 1,2-CC insertion reaction; however, the selectivity between them was low (entry 3). Finally, EtMgCl was found to be the best Grignard reagent for this reaction and (*Z*)-β,γ-unsaturated ester **26** was obtained in highly selective manner (entry 4). We still find it very difficult to propose a rational explanation why EtMgCl is the best reagent in this reaction; however, by the discovery mentioned above, we expected that we could obtain β,γ-unsaturated butyl esters bearing an electron-rich aromatic ring at the γ-position from electron-rich aromatic aldehydes.

Examples for the synthesis of β,γ-unsaturated esters **33** and **34** starting from electron-rich aromatic aldehydes (4-(dimethylamino)benzaldehyde, 4-(methylthio)benzaldehyde, piperonal, furfural, and 2-formylthiophene) through 1-chlorovinyl *p*-tolyl sulfoxides (**28** and **29**) and the adducts with lithium enolate of *tert*-butyl acetates (**30** and **31**) are summarized in Table 3. Quite interestingly, as shown in Table 3, adducts **30** derived from (*Z*)-1-chlorovinyl *p*-tolyl sulfoxides **28** gave (*Z*)-β,γ-unsaturated esters bearing an electron-rich aromatic ring at the γ-position **33**. On the other hand, adducts **31** derived from (*E*)-1-chlorovinyl *p*-tolyl sulfoxides **29** gave (*E*)-β,γ-unsaturated esters bearing an electron-rich aromatic ring at the γ-position **34**. From these results, it is obvious that this magnesium carbenoid 1,2-CC insertion reaction is a highly stereospecific reaction. A plausible mechanism for this highly stereospecific magnesium carbenoid 1,2-CC insertion reaction has been proposed in the previous communication.[15] Although the reason is not clear at present, the yields were always better when adducts **30** derived from (*Z*)-1-chlorovinyl *p*-tolyl sulfoxide **28** were used (see entries 2–9).

Table 3
Synthesis of β,γ-unsaturated esters **33** and **34** by treatment of adducts **30** and **31**, derived from electron-rich aromatic aldehydes, with EtMgCl



Entry	**30** and **31** Ar		**32** Yield[a]/%	**33**	**34**
1	**30a**[b]		0	50	0
2	**30b**		3	80	8
3	**31b**		17	8	42
4	**30c**		0	95	0
5	**31c**		12	0	83
6	**30d**		0	92	0
7	**31d**		0	0	75
8	**30e**		0	92	0
9	**31e**		Trace	0	72

[a] The yield of the reaction of **30** and **31** with EtMgCl.
[b] Only *Z*-isomer could be synthesized from 4-(dimethylamino)benzaldehyde.

2.2. A synthesis of β,γ-unsaturated esters from aldehydes with chloromethyl *p*-tolyl sulfoxide, *tert*-butyl acetate, and iodomethane

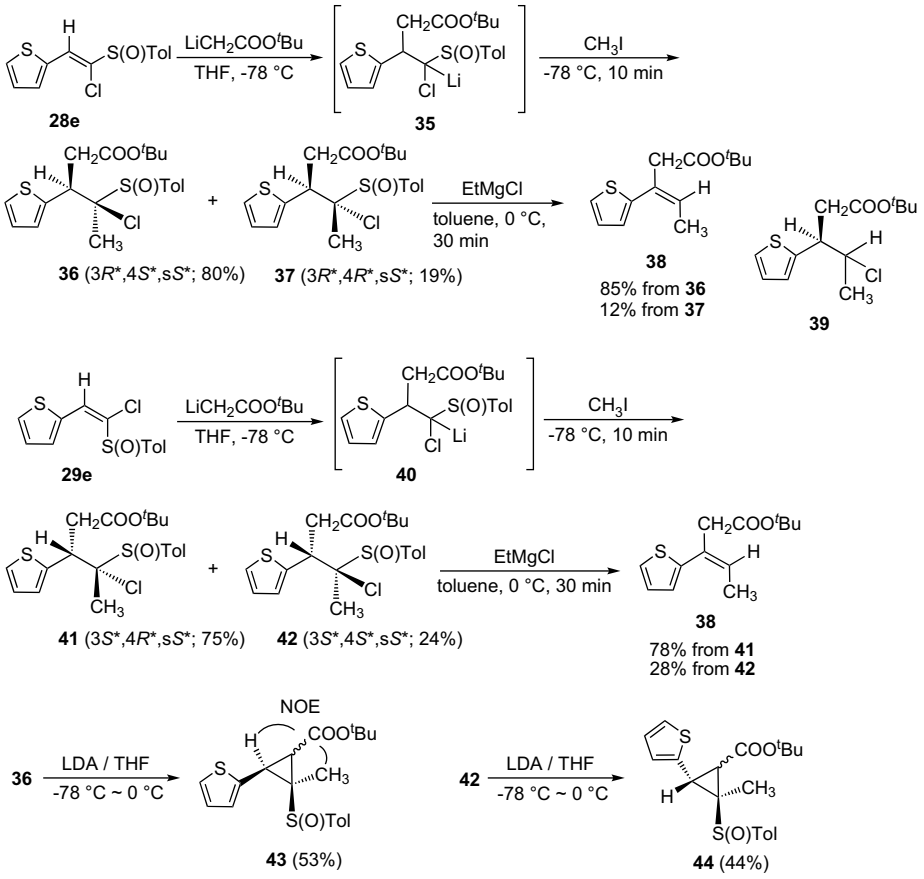
It is well known that the intermediates of the conjugate addition reaction of carbon nucleophiles to α,β-unsaturated sulfoxides are α-sulfinyl carbanions and they can be trapped with several electrophiles.[18] Indeed, in our case, addition reaction of 1-chlorovinyl *p*-tolyl sulfoxide **28e** with lithium enolate of *tert*-butyl acetate followed by treatment of iodomethane gave methylated adducts **36** and **37** in 80% and 19% yields, respectively, via the lithium α-sulfinyl carbanion **35** (Scheme 3). The same treatment of the geometrical isomer **29e** afforded methylated adducts **41** and **42** in 75% and 24% yields, respectively, through the lithium α-sulfinyl carbanion **40**.

Treatment of the main methylated adduct **36** with EtMgCl in toluene at 0 °C for 30 min gave β,γ-unsaturated ester with the thiophene ring at the β-position **38** in 85% yield via the magnesium carbenoid 1,2-CH insertion. No product through the magnesium carbenoid 1,2-CC insertion was obtained. Quite interestingly, only *Z*-isomer was obtained and no *E*-isomer was observed. The same treatment of **37** gave **38** as one of the products. In this case desulfinylated product **39** (45%) was the main product. It is worthy of note that these magnesium carbenoid 1,2-CH insertions are highly selective reactions.

The treatment of **41** with EtMgCl gave β,γ-unsaturated ester with the thiophene ring at the β-position **38** in 78% yield via the magnesium carbenoid 1,2-CH insertion. Very interestingly, the 1,2-CH insertion of the magnesium carbenoid intermediates derived from **36** and **41** gave the same β,γ-unsaturated **38** in highly selective manner. Again the reaction of the minor adduct **42** gave several unknown products with the same β,γ-unsaturated **38** as the main product in only 28% yield.

In order to present a plausible mechanism of these highly stereoselective reactions, we first have to confirm the stereochemistry of the methylated adducts (**36**, **37**, **41**, and **42**). From our cumulative examination, the relative stereochemistry of C-3 and the sulfinyl group is obvious as depicted in Scheme 3.[14b,16] Stereochemistry of the carbons bearing the sulfinyl and the methyl groups was determined from the cyclopropanes derived from the methylated adducts. For example, the methylated adduct **36** was treated with LDA to afford cyclopropane **43** in moderate yield and the stereochemistry was determined from its NOESY spectrum. As the stereochemistry of the methyl group and the hydrogen on the cyclopropane ring was established to be cis, as depicted in Scheme 3, the configuration of methylated adduct **36** is determined to be 3*R**, 4*S**,*sS**. In a similar manner, the stereochemistry of **41** and **42** was determined from the stereochemistry of cyclopropane **44**.

All the stereochemistry of the methylated adducts in hand, we propose the plausible mechanism of this highly stereoselective 1,2-CH insertion as shown in Figure 1. Because the sulfoxide-magnesium exchange reaction is known to take place with retention of the configuration of the carbon bearing the sulfinyl group,[19] treatment of **36**, **37**, **41**, and **42** with EtMgCl gave the magnesium carbenoids having retained configuration (**A**–**D**) as shown in Fig 1. The magnesium and carbonyl oxygen atom of the ester group is supposed to make chair like six-membered conformation **A**–**D**, in which the bulkiest *tert*-butoxy group would occupy the equatorial position.[16] In these intermediates, C–H bond of the carbon bearing the thiophene ring attacks the chlorine atom from its back side to give **38**. This type of reaction is expected to occur smoothly when the chlorine and the hydrogen are in anti periplaner geometry.



Scheme 3.

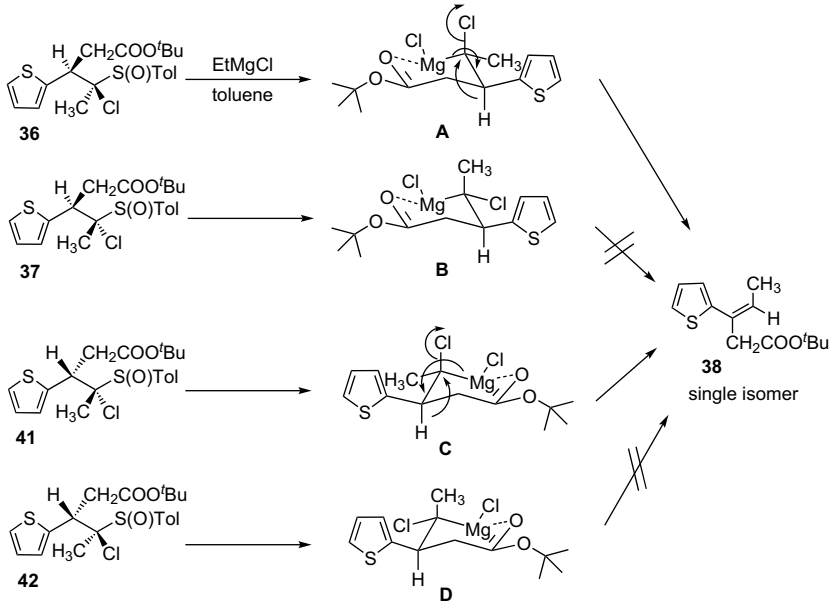
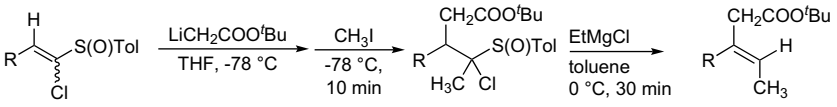
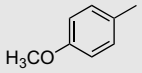
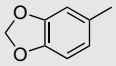
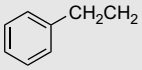


Figure 1.

As mentioned above, compounds **36** and **41** gave smoothly **38** in good yields, respectively. The conformation of the magnesium carbenoid intermediate derived from **36** and **41** is expected to be **A** and **C**, respectively, from which the 1,2-CH insertion takes place smoothly. At the same time, it is explained that why the same (*Z*)-*tert*-butyl 4-methyl-3-thienyl-3-pentenoate **38** was obtained from **36** and **41** in highly stereoselective manner. We can also explain the reason why the magnesium carbenoid intermediates **B** and **D**

Table 4
Synthesis of tri-substituted β,γ-unsaturated esters **46** by treatment of adducts **45**, which were derived from aromatic aldehydes via 1-chlorovinyl *p*-tolyl sulfoxides



Entry	1-Chlorovinyl *p*-tolyl sulfoxide		**45**		**46**	
	R	(Configuration)	Yield[a]/% (diastereomeric ratio)		Yield/%	
1		**23** (*Z*)	**45a**	99 (81:19)	**46a**	77
2		**28c** (*Z*)	**45b**	99 (86:14)	**46b**	76
3		**29c** (*E*)	**45b**	99 (68:32)	**46b**	66
4		**19e** (*Z*)	**45c**	99 (91:9)	**46c**	63
5		**20e** (*E*)	**45c**	99 (69:31)	**46c**	69
6		**19a** (*Z*)	**45d**	99 (61:39)	**46d**	63
7		**20a** (*E*)	**45d**	99 (76:24)	**46d**	42

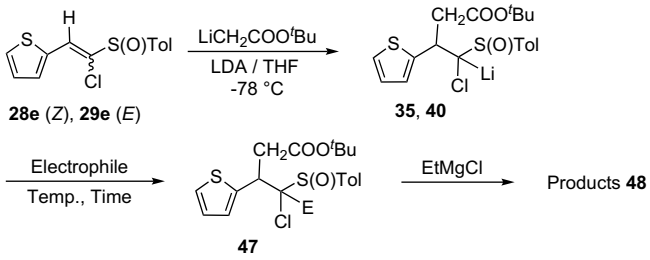
[a] A mixture of two diastereomers was used in the next reaction.

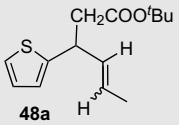
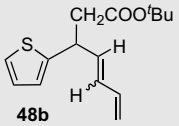
derived from **37** and **42**, respectively, did not give good yield of the olefin but a rather complex mixture from the conformers depicted in Figure 1.

As we recognized that this is a good way for a synthesis of β,γ-unsaturated esters by combination of four components, aldehyde, chloromethyl *p*-tolyl sulfoxide, *tert*-butyl acetate, and iodomethane, generality of this procedure was investigated and the results are summarized in Table 4. Addition reaction of 1-chlorovinyl *p*-tolyl sulfoxides with lithium enolate of *tert*-butyl acetate followed by treatment with iodomethane gave the methylated adduct **45** as a mixture of two diastereomers in quantitative yields. Without separation of the diastereomers, the mixture was treated with EtMgCl in toluene at 0 °C for 30 min to give the desired **46** in moderate to good yields. In this case, again, only *Z*-isomers were obtained.

Finally, this procedure was extended with iodoalkanes other than iodomethane and the results are summarized in Table 5. As shown in Table 5, trapping the intermediates **35** and **40**, derived from **28e** and **29e**, respectively, with iodoethane and allyl iodide gave **47a** and **47b** in high to quantitative yields as a mixture of two diastereomers. Treatment of **47** with EtMgCl smoothly afforded olefins; however, the products were not the expected β,γ-unsaturated esters but γ,δ-unsaturated esters **48**. Moreover, the products were mixture of two geometrical isomers.

Table 5
Synthesis of γ,δ-unsaturated esters **48** from 1-chlorovinyl *p*-tolyl sulfoxide **28e** and **29e** via adduct **47**



Entry	Electrophile		Temp/°C	Time/min	47/Yield %		Product **48**	
					(diastereomeric ratio)		Yield/%	
1[a]	**28e**	CH_3CH_2I	−78 to −0	120	**47a**	83 (79:21)	 **48a**	81[b]
2[a]	**29e**	CH_3CH_2I	−78 to −0	120	**47a**	84 (73:27)		87[c]
3	**28e**		−78	30	**47b**	99 (81:19)	 **48b**	66[d]
4	**29e**		−78	30	**47b**	99 (79:21)		51[e]

[a] equivHMPA (8 equiv) was added as an additive.
[b] A 2:5 mixture of two diastereomers determined from ^{1}H NMR.
[c] A 3:2 mixture of two diastereomers determined from ^{1}H NMR.
[d] A 1:1 mixture of two diastereomers determined from ^{1}H NMR.
[e] A 11:6 mixture of two diastereomers determined from ^{1}H NMR.

In conclusion, we found that magnesium carbenoids **10**, derived from the adduct of 1-chlorovinyl *p*-tolyl sulfoxides **7** with lithium enolate of *tert*-butyl acetate, take place 1,2-CH or 1,2-CC insertion reaction to give β,γ-unsaturated esters **11** or **12** depending on the nature of the substituent R^1. It was also found that the 1,2-CC insertion reaction is highly stereospecific. The intermediate of the reaction of **7** with lithium enolate of *tert*-butyl acetate (**8**) was found to be able to be trapped with iodoalkanes to give **13** in high yields. When R^2=H, treatment of **13** with EtMgCl resulted in the highly stereoselective magnesium carbenoid 1,2-CH insertion to afford β,γ-unsaturated esters **15**. The reactions mentioned in this paper considerably contribute to a synthesis of various β,γ-unsaturated esters.

3. Experimental

3.1. General

All melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H 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 a Perkin–Elmer Spectrum One FTIR instrument. Silica gel 60 N 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 experiment requiring a dry solvent and reagent, HMPA and diisopropylamine and toluene were distilled from CaH_2, and THF was distilled form diphenylketyl. Compounds **17a**,[20] **17e**,[20] **18a**,[20] **18e**,[20] **19a**,[14b] **20a**,[14b] are known.

3.2. (*Z*)-1-Chloro-1-(*p*-tolylsulfinyl)-1-octene (17b)

Colorless oil; IR (neat) 2928, 2857, 1492, 1458, 1089, 1062, 807 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=6.9 Hz), 1.25–1.35 (6H, m), 1.46–1.52 (2H, m), 2.34 (2H, q, *J*=7.3 Hz), 2.42 (3H, s), 6.78 (1H, t, *J*=7.3 Hz), 7.31 (2H, d, *J*=8.1 Hz), 7.56 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 284 (M^+, 22), 267 (24), 236 (23), 158 (29), 140 (100), 123 (49), 92 (33), 91 (23). Calcd for $C_{15}H_{21}ClOS$: M, 284.1002. Found: *m*/*z* 284.0997.

3.3. (*E*)-1-Chloro-1-(*p*-tolylsulfinyl)-1-octene (18b)

Colorless oil; IR (neat) 2928, 2858, 1493, 1458, 1089, 1064, 808 cm^{-1}; ^{1}H NMR δ 0.91 (3H, t, *J*=6.9 Hz), 1.29–1.34 (4H, m), 1.35–1.42 (2H, m), 1.50–1.56 (2H, m), 2.42 (3H, s), 2.60 (1H, dt, *J*=14.5, 7.6 Hz), 2.72 (1H, dt, *J*=14.8, 8.6 Hz), 6.31 (1H, dd, *J*=8.6, 7.6 Hz), 7.32 (2H, d, *J*=8.0 Hz), 7.51 (2H, d, *J*=8.0 Hz). MS *m*/*z* (%) 284 (M^+, 12), 267 (100), 197 (37), 161 (17), 139 (19), 123 (15), 91 (15), 65 (7), 41 (7). Calcd for $C_{15}H_{21}ClOS$: M, 284.1002. Found: *m*/*z* 284.1001.

3.4. (*Z*)-1-Chloro-2-cyclohexyl-1-(*p*-tolylsulfinyl)ethene (17c)

Colorless oil; IR (neat) 2927, 1596, 1493, 1449, 1087, 967, 898, 809 cm^{-1}; ^{1}H NMR δ 1.22–1.33 (5H, m), 1.65–1.78 (5H, m), 2.42 (3H, s), 2.53–2.61 (1H, m), 6.63 (1H, d, *J*=9.2 Hz), 7.31 (2H, d, *J*=8.0 Hz), 7.54 (2H, d, *J*=8.0 Hz). MS *m*/*z* (%) 282 (M^+, 31), 265 (14), 234 (31), 152 (31), 140 (100), 123 (25), 92 (31), 79 (14). Calcd for $C_{15}H_{19}ClOS$: M, 282.0845. Found: *m*/*z* 282.0838.

3.5. (*E*)-1-Chloro-2-cyclohexyl-1-(*p*-tolylsulfinyl)ethene (18c)

Colorless crystals; mp 69.5–70 °C (hexane/AcOEt); IR (KBr) 2921, 1444, 1394, 1089, 1060, 906, 861, 806 cm^{-1}; ^{1}H NMR δ 1.20–1.28 (3H, m), 1.32–1.44 (2H, m), 1.70–1.74 (2H, m), 1.76–1.83 (2H, m), 1.88–1.93 (1H, m), 2.42 (3H, s), 3.06 (1H, tq, *J*=11.0, 3.8 Hz), 6.16 (1H, d, *J*=11.0 Hz), 7.33 (2H, d, *J*=8.3 Hz), 7.50 (2H, d, *J*=8.3 Hz). Anal. Calcd for $C_{15}H_{19}ClOS$: C, 63.70; H, 6.77; Cl, 12.53; S, 11.34. Found: C, 63.79; H, 6.77; Cl, 12.32; S, 11.28.

3.6. (*Z*)-1-Chloro-3,3-dimethyl-1-(*p*-tolylsulfinyl)-1-butene (17d)

Colorless crystals; mp 74.5–75 °C (hexane/AcOEt); IR (KBr) 2959, 1593, 1473, 1363, 1198, 1087, 1056, 869, 804 cm^{-1}; ^{1}H NMR δ 1.25 (9H, s), 2.42 (3H, s), 6.76 (1H, s), 7.31 (2H, d, *J*=8.1 Hz), 7.55 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{13}H_{17}ClOS$: C, 60.80; H, 6.67; Cl, 13.81; S, 12.49. Found: C, 60.67; H, 6.66; Cl, 14.2; S, 12.38.

3.7. (*E*)-1-Chloro-3,3-dimethyl-1-(*p*-tolylsulfinyl)-1-butene (18d)

Colorless oil; IR (neat) 2964, 1597, 1477, 1365, 1250, 1203, 1088, 946, 859, 809, 622 cm^{-1}; ^{1}H NMR δ 1.39 (9H, s), 2.42 (3H, s), 6.45 (1H, s), 7.33 (2H, d, *J*=8.1 Hz), 7.53 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 256 (M^+, 15), 158 (14), 140 (100), 123 (19), 92 (30), 77 (10), 57 (45). Calcd for $C_{13}H_{17}ClOS$: M, 256.0688. Found: *m*/*z* 256.0688.

3.8. (*Z*)-1-Chloro-2-(1-napthyl)-1-(*p*-tolylsulfinyl)ethene (17f)

Colorless crystals; mp 90–90.5 °C (hexane/AcOEt); IR (KBr) 3038, 1591, 1490, 1444, 1393, 1344, 1282, 1087, 1061, 925, 896, 773 cm^{-1}; ^{1}H NMR δ 2.44 (3H, s), 7.36 (2H, d, *J*=8.2 Hz), 7.49 (1H, t, *J*=7.7 Hz), 7.53–7.61 (2H, m), 7.73 (2H, d, *J*=8.2 Hz), 7.81 (1H, d, *J*=7.1 Hz), 7.87–7.89 (2H, m), 8.03 (1H, d, *J*=8.0 Hz), 8.32 (1H, s). Anal. Calcd for $C_{19}H_{15}ClOS$: C, 69.82; H, 4.63; Cl, 10.85; S, 9.81. Found: C, 69.83; H, 4.47; Cl, 10.71; S, 9.72.

3.9. (*E*)-1-Chloro-2-(1-naphethyl)-1-(*p*-tolylsulfinyl)-ethene (18f)

Colorless crystals; mp 154–154.5 °C (hexane/AcOEt); IR (KBr) 3007, 1590, 1491, 1447, 1396, 1083, 1052, 1013, 903, 802, 776 cm^{-1}; ^{1}H NMR δ 2.40 (3H, s), 7.26–7.28 (2H, m), 7.39 (2H, d, *J*=8.3 Hz), 7.54–7.62 (3H, m), 7.67 (1H, d, *J*=7.1 Hz), 7.82 (1H, s), 7.86–7.88 (1H, m), 7.93–7.96 (2H, m). Anal. Calcd for $C_{19}H_{15}ClOS$: C, 69.82; H, 4.63; Cl, 10.85; S, 9.81. Found: C, 69.79; H, 4.48; Cl, 10.85; S, 9.84.

3.10. (*Z*)-1-Chloro-2-(4-cyanophenyl)-1-(*p*-tolylsulfinyl)-ethene (17g)

Colorless crystals; mp 170–170.5 °C (hexane/AcOEt); IR (KBr) 3007, 2226 (CN), 1603, 1492, 1409, 1089, 1060, 920, 832, 808 cm^{-1}; ^{1}H NMR δ 2.43 (3H, s), 7.31 (1H, s), 7.33 (2H, d, *J*=8.3 Hz), 7.45 (2H, d, *J*=8.3 Hz), 7.63 (2H, d, *J*=8.5 Hz), 7.75 (2H, d, *J*=8.5 Hz). Anal. Calcd for $C_{16}H_{12}ClNOS$: C, 63.68; H, 4.01; N, 4.64; Cl, 11.75; S, 10.62. Found: C, 63.58; H, 3.71; N, 4.41; Cl, 11.56; S, 10.60.

3.11. (*E*)-1-Chloro-2-(4-cyanophenyl)-1-(*p*-tolylsulfinyl)-ethene (18g)

Colorless crystals; mp 120.5–121 °C (hexane/AcOEt); IR (KBr) 3014, 2232 (CN), 1604, 1500, 1083, 1069, 900, 822 cm^{-1}; ^{1}H NMR δ 2.43 (3H, s), 7.34 (2H, d, *J*=8.1 Hz), 7.65 (2H, d, *J*=8.1 Hz), 7.66 (1H, s), 7.69 (2H, d, *J*=8.4 Hz), 7.83 (2H, d, *J*=8.4 Hz). Anal. Calcd for $C_{16}H_{12}ClNOS$: C, 63.68; H, 4.01; N, 4.64; Cl, 11.75; S, 10.62. Found: C, 63.63; H, 3.81; N, 4.42; Cl, 11.60; S, 10.60.

3.12. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-hexyl-4-(*p*-tolylsulfinyl)butyrate (19b)

tert-Butyl acetate (0.73 mL, 5.4 mmol) was added to a solution of LDA (5.4 mmol) in 12 mL of dry THF at −78 °C with stirring. The

solution was stirred for 10 min and then a solution of **17b** (300 mg, 1.1 mmol) in THF (3 mL) was added with stirring. The reaction mixture was stirred for 5 min, then the reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The extract was washed with brine and the organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography to afford **19b** (429 mg, 99%) as colorless oil. IR (neat) 2931, 1728 (CO), 1462, 1365, 1219, 1154, 1084, 808 cm^{-1}; ^1H NMR δ 0.90 (3H, t, J=6.9 Hz), 1.30–1.33 (6H, m), 1.40–1.48 (4H, m), 1.44 (9H, s), 2.36 (1H, dd, J=16.0, 9.3 Hz), 2.43 (3H, s), 2.51 (1H, dd, J=16.0, 4.7 Hz), 2.96–3.02 (1H, m), 4.64 (1H, d, J=2.2 Hz), 7.32 (2H, d, J=8.0 Hz), 7.68 (2H, d, J=8.0 Hz). MS (FAB) m/z (%) 401 ($[M+H]^+$, 18), 345 (100), 327 (23), 293 (4), 140 (22), 123 (22), 109 (14), 57 (12). Calcd for $C_{21}H_{34}ClO_3S$: M, 401.1918. Found: m/z 401.1917.

3.13. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-hexyl-4-(*p*-tolylsulfinyl)butyrate (20b)

Colorless oil; IR (neat) 2930, 1732 (CO), 1456, 1368, 1258, 1152, 1057, 812 cm^{-1}; ^1H NMR δ 0.90 (3H, t, J=6.9 Hz), 1.22–1.32 (10H, m), 1.48 (9H, s), 2.31 (1H, dd, J=15.9, 6.4 Hz), 2.44 (3H, s), 2.81 (1H, dd, J=15.9, 3.7 Hz), 2.95–3.02 (1H, m), 4.43 (1H, d, J=2.1 Hz), 7.34 (2H, d, J=8.3 Hz), 7.66 (2H, d, J=8.3 Hz). MS (FAB) m/z (%) 401 ($[M+H]^+$, 17), 345 (100), 327 (39), 293 (4), 140 (20), 123 (18), 109 (11), 57 (10). Calcd for $C_{21}H_{34}ClO_3S$: M, 401.1917. Found: m/z 401.1920.

3.14. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-cyclohexyl-4-(*p*-tolylsulfinyl)butyrate (19c)

Colorless crystals; mp 117.5–118 °C (hexane/AcOEt); IR (KBr) 2931, 1721 (CO), 1447, 1366, 1235, 1154, 1049, 815 cm^{-1}; ^1H NMR δ 1.03 (1H, dq, J=12.4, 3.3 Hz), 1.08–1.18 (1H, m), 1.24–1.36 (3H, m), 1.45 (9H, s), 1.66–1.69 (1H, m), 1.74–1.79 (2H, m), 1.86–1.95 (3H, m), 2.43 (3H, s), 2.48 (1H, dd, J=16.2, 8.7 Hz), 2.56 (1H, dd, J=16.2, 4.9 Hz), 2.79–2.84 (1H, m), 4.68 (1H, d, J=3.6 Hz), 7.33 (2H, d, J=8.3 Hz), 7.69 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{21}H_{31}ClO_3S$: C, 63.22; H, 7.83; Cl, 8.89; S, 8.04. Found: C, 63.35; H, 7.77; Cl, 8.81; S, 8.02.

3.15. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-cyclohexyl-4-(*p*-tolylsulfinyl)butyrate (20c)

Colorless oil; IR (neat) 2928, 1732 (CO), 1450, 1367, 1288, 1152, 1057, 956, 813 cm^{-1}; ^1H NMR δ 1.00–1.27 (6H, m), 1.48 (9H, s), 1.70–1.78 (5H, m), 2.38 (1H, dd, J=16.6, 8.0 Hz), 2.43 (3H, s), 2.69 (1H, dd, J=16.6, 3.6 Hz), 2.91–2.96 (1H, m), 4.48 (1H, d, J=1.8 Hz), 7.33 (2H, d, J=8.1 Hz), 7.66 (2H, d, J=8.1 Hz). MS (FAB) m/z (%) 399 ($[M+H]^+$, 18), 343 (100), 325 (37), 167 (10), 140 (15), 123 (14), 83 (7), 57 (8). Calcd for $C_{21}H_{32}ClO_3S$: M, 399.1761. Found: m/z 399.1763.

3.16. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(1,1-dimethylethyl)-4-(*p*-tolylsulfinyl)butyrate (19d)

Colorless oil; IR (neat) 2969, 1732 (CO), 1480, 1369, 1305, 1258, 1148, 1056, 956, 812 cm^{-1}; ^1H NMR δ 1.17 (9H, s), 1.47 (9H, s), 2.42 (3H, s), 2.47 (1H, dd, J=15.9, 9.9 Hz), 2.54 (1H, dd, J=15.9, 3.5 Hz), 3.00 (1H, ddd, J=9.9, 3.5, 1.7 Hz), 4.62 (1H, d, J=1.7 Hz), 7.31 (2H, d, J=8.1 Hz), 7.69 (2H, d, J=8.1 Hz). MS m/z (%) 372 (M^+, 5), 299 (20), 259 (5), 177 (15), 140 (100), 139 (13), 92 (10), 57 (53). Calcd for $C_{19}H_{29}ClO_3S$: M, 372.1526. Found: m/z 372.1525.

3.17. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(1,1-dimethylethyl)-4-(*p*-tolylsulfinyl)butyrate (20d)

Colorless crystals; mp 79–79.5 °C (hexane/AcOEt); IR (KBr) 2975, 1729 (CO), 1481, 1370, 1294, 1147, 1050, 809, 774 cm^{-1}; ^1H NMR δ 0.95 (9H, s), 1.49 (9H, s), 2.39 (1H, dd, J=16.9, 6.9 Hz), 2.43 (3H, s), 2.51 (1H, dd, J=16.9, 4.4 Hz), 3.06 (1H, ddd, J=6.9, 4.4, 0.8 Hz), 4.57 (1H, d, J=0.8 Hz), 7.32 (2H, d, J=8.1 Hz), 7.67 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{19}H_{29}ClO_3S$: C, 61.19; H, 7.84; Cl, 9.51; S, 8.60. Found: C, 61.33; H, 7.87; Cl, 9.42; S, 8.57.

3.18. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-phenyl-4-(*p*-tolylsulfinyl)butyrate (19e)

Colorless crystals; mp 129.5–130 °C (hexane/AcOEt); IR (KBr) 2979, 1724 (CO), 1455, 1369, 1274, 1243, 1152, 1049, 976, 817, 732 cm^{-1}; ^1H NMR δ 1.30 (9H, s), 2.42 (3H, s), 2.83 (1H, dd, J=15.8, 8.0 Hz), 2.88 (1H, dd, J=15.8, 8.0 Hz), 4.41 (1H, dt, J=8.0, 3.0 Hz), 4.67 (1H, d, J=3.0 Hz), 7.30 (2H, d, J=8.1 Hz), 7.35–7.41 (3H, m), 7.51–7.54 (2H, m), 7.63 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{21}H_{25}ClO_3S$: C, 64.19; H, 6.41; Cl, 9.02; S, 8.16. Found: C, 64.20; H, 6.22; Cl, 8.93; S, 8.34.

3.19. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-phenyl-4-(*p*-tolylsulfinyl)butyrate (20e)

Colorless crystals; mp 75.5–76 °C (hexane/AcOEt); IR (KBr) 2978, 1725 (CO), 1495, 1455, 1369, 1270, 1154, 1041, 965, 809, 702 cm^{-1}; ^1H NMR δ 1.24 (9H, s), 2.42 (3H, s), 3.00 (1H, dd, J=15.9, 10.7 Hz), 3.08 (1H, dd, J=15.9, 4.9 Hz), 4.21 (1H, ddd, J=10.7, 4.9, 3.0 Hz), 4.51 (1H, d, J=3.0 Hz), 7.26–7.36 (7H, m), 7.65 (2H, d, J=8.2 Hz). Anal. Calcd for $C_{21}H_{25}ClO_3S$: C, 64.19; H, 6.41; Cl, 9.02; S, 8.16. Found: C, 64.00; H, 6.22; Cl, 9.00; S, 8.15.

3.20. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(1-naphthyl)-4-(*p*-tolylsulfinyl)butyrate (19f)

Colorless crystals; mp 147–147.5 °C (hexane/AcOEt); IR (KBr) 2978, 1732 (CO), 1597, 1499, 1363, 1267, 1147, 1039, 785 cm^{-1}; ^1H NMR δ 1.12 (9H, s), 2.41 (3H, s), 2.98–3.11 (2H, m), 4.82 (1H, s), 5.22 (1H, s), 7.29 (2H, d, J=8.0 Hz), 7.47–7.53 (2H, m), 7.59–7.63 (3H, m), 7.70 (1H, d, J=7.3 Hz), 7.83–7.88 (2H, m), 8.52 (1H, d, J=8.2 Hz). Anal. Calcd for $C_{25}H_{27}ClO_3S$: C, 67.78; H, 6.14; Cl, 8.00; S, 7.24. Found: C, 67.82; H, 6.05; Cl, 7.90; S, 7.22.

3.21. (3S*,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(1-naphthyl)-4-(*p*-tolylsulfinyl)butyrate (20f)

Colorless oil; IR (neat) 2978, 1732 (CO), 1640, 1598, 1455, 1368, 1287, 1149, 1052, 969, 782 cm^{-1}; ^1H NMR δ 1.09 (9H, s), 2.40 (3H, s), 3.26 (2H, d, J=7.8 Hz), 4.55 (1H, d, J=2.0 Hz), 5.34–5.38 (1H, m), 7.29 (2H, d, J=8.1 Hz), 7.43 (1H, t, J=7.6 Hz), 7.49–7.53 (2H, m), 7.58–7.62 (1H, m), 7.67 (2H, d, J=8.1 Hz), 7.78 (1H, d, J=8.1 Hz), 7.86 (1H, d, J=8.1 Hz), 8.23 (1H, d, J=8.5 Hz). MS m/z (%) 442 (M^+, 4), 369 (13), 302 (5), 247 (44), 229 (46), 211 (73), 165 (86), 140 (100), 139 (16), 92 (14), 57 (78). Calcd for $C_{25}H_{27}ClO_3S$: M, 442.1369. Found: m/z 442.1367.

3.22. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(4-cyanophenyl)-4-(*p*-tolylsulfinyl)butyrate (19g)

Colorless crystals; mp 143.5–144 °C (hexane/AcOEt); IR (KBr) 2985, 2229 (CN), 1722 (CO), 1370, 1268, 1142, 1043, 843, 813 cm^{-1}; ^1H NMR δ 1.31 (9H, s), 2.43 (3H, s), 2.83 (1H, dd, J=16.2, 7.7 Hz), 2.89 (1H, dd, J=16.2, 8.3 Hz), 4.48 (1H, dt, J=7.7, 2.9 Hz), 4.66 (1H, d, J=2.9 Hz), 7.32 (2H, d, J=8.1 Hz), 7.62 (2H, d, J=8.1 Hz), 7.66 (2H, d, J=8.5 Hz), 7.69 (2H, d, J=8.5 Hz). Anal. Calcd for $C_{22}H_{24}ClNO_3S$: C, 63.22; H, 5.79; N, 3.35; Cl, 8.48; S, 7.67. Found: C, 63.30; H, 5.57; N, 3.00; Cl, 8.24; S, 7.63.

3.23. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(4-cyanophenyl)-4-(*p*-tolylsulfinyl)butyrate (20g)

Colorless crystals; mp 132–132.5 °C (hexane/AcOEt); IR (KBr) 2978, 2229 (CN), 1728 (CO), 1368, 1260, 1145, 1049, 845, 818 cm^{-1}; ^1H NMR δ 1.27 (9H, s), 2.42 (3H, s), 3.05 (1H, dd, J=16.3, 10.8 Hz), 3.13 (1H, dd, J=16.3, 4.7 Hz), 4.23 (1H, ddd, J=10.8, 4.7, 2.5 Hz), 4.39 (1H, d, J=2.5 Hz), 7.33 (2H, d, J=8.0 Hz), 7.48 (2H, d, J=8.3 Hz), 7.63 (2H, d, J=8.3 Hz), 7.64 (2H, d, J=8.0 Hz). Anal. Calcd for $C_{22}H_{24}ClNO_3S$: C, 63.22; H, 5.79; N, 3.35; Cl, 8.48; S, 7.67. Found: C, 63.27; H, 5.71; N, 3.24; Cl, 8.39; S, 7.69.

3.24. *tert*-Butyl 3-methylidene-5-phenylpentanoate (21a)

i-PrMgBr (0.76 M solution in THF, 0.27 mL, 0.21 mmol) was added to dry toluene (1.9 mL) in a flame-dried flask at room temperature. A solution of **19a** (50 mg, 0.12 mmol) in toluene (0.5 mL) was added dropwise to the solution of *i*-PrMgBr and the reaction mixture was stirred at room temperature for 10 min. The reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The extract was washed with brine and the organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography to give 24.9 mg (85%) of **21a** as colorless oil. IR (neat) 2979, 1732 (CO), 1455, 1368, 1256, 1146, 899, 699 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 2.39–2.43 (2H, m), 2.76–2.80 (2H, m), 2.99 (2H, s), 4.92 (1H, m), 4.94 (1H, m), 7.16–7.20 (3H, m), 7.26–7.30 (2H, m). MS m/z (%) 246 (M^+, 5), 190 (28), 173 (22), 145 (27), 130 (100), 91 (82), 57 (85). Calcd for $C_{16}H_{22}O_2$: M, 246.1620. Found: m/z 246.1617.

3.25. *tert*-Butyl 3-methylidenenonanoate (21b)

Colorless oil; IR (neat) 2928, 1732 (CO), 1457, 1368, 1256, 1145 cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=6.7 Hz), 1.28–1.31 (8H, m), 1.45 (9H, s), 2.08 (2H, t, J=7.5 Hz), 2.93 (2H, s), 4.86 (1H, m), 4.88 (1H, m). MS m/z (%) 226 (M^+, 2), 211 (14), 170 (14), 110 (31), 69 (13), 57 (100). Calcd for $C_{14}H_{26}O_2$: M, 226.1933. Found: m/z 226.1932.

3.26. *tert*-Butyl 3-cyclohexyl-3-butenoate (21c)

Colorless oil; IR (neat) 2928, 1732 (CO), 1643, 1450, 1368, 1257, 1144, 966, 890, 752 cm^{-1}; ^1H NMR δ 1.10–1.29 (5H, m), 1.45 (9H, s), 1.67–1.69 (1H, m), 1.75–1.82 (4H, m), 1.90–1.96 (1H, m), 2.95 (2H, s), 4.86 (1H, m), 4.89 (1H, m). MS m/z (%) 224 (M^+, 4), 168 (86), 150 (27), 123 (18), 108 (100), 81 (32), 67 (18), 57 (83). Calcd for $C_{14}H_{24}O_2$: M, 224.1776. Found: m/z 224.1776.

3.27. *tert*-Butyl 4,4-dimethyl-3-methylidenepentanoate (21d)

Colorless oil; IR (neat) 2961, 1731 (CO), 1367, 1257, 1137 cm^{-1}; ^1H NMR δ 1.07 (9H, s), 1.45 (9H, s), 2.96 (2H, d, J=1.0 Hz), 4.87 (1H, d, J=0.9 Hz), 5.03 (1H, d, J=0.9 Hz). MS m/z (%) 198 (M^+, 3), 142 (94), 125 (48), 97 (52), 83 (96), 57 (100). Calcd for $C_{12}H_{22}O_2$: M, 198.1620. Found: m/z 198.1622.

3.28. *tert*-Butyl 3-phenyl-3-butenoate (21e)

Colorless oil; IR (neat) 2979, 1732 (CO), 1368, 1258, 1148 cm^{-1}; ^1H NMR δ 1.35 (9H, s), 3.43 (2H, d, J=1.1 Hz), 5.21 (1H, d, J=1.1 Hz), 5.50 (1H, d, J=0.8 Hz), 7.26–7.28 (1H, m), 7.31–7.34 (2H, m), 7.42–7.44 (2H, m). MS m/z (%) 218 (M^+, 2), 162 (79), 145 (15), 134 (31), 117 (35), 91 (18), 57 (100). Calcd for $C_{14}H_{18}O_2$: M, 218.1305. Found: m/z 218.1314.

3.29. *tert*-Butyl 3-(1-naphethyl)-3-butenoate (21f)

Colorless oil; IR (neat) 2978, 1729 (CO), 1638, 1509, 1454, 1368, 1289, 1255, 1150, 964, 779 cm^{-1}; ^1H NMR δ 1.26 (9H, s), 3.45 (2H, s), 5.82 (1H, d, J=1.4 Hz), 5.58 (1H, d, J=1.4 Hz), 7.36 (1H, dd, J=7.1, 1.3 Hz), 7.41–7.45 (1H, m), 7.46–7.49 (2H, m), 7.77 (1H, d, J=8.2 Hz), 7.83–7.86 (1H, m), 8.06–8.09 (1H, m). MS m/z (%) 268 (M^+, 19), 212 (82), 195 (22), 165 (68), 152 (100), 57 (77), 41 (24), 28 (16). Calcd for $C_{18}H_{20}O_2$: M, 268.1462. Found: m/z 268.1464.

3.30. *tert*-Butyl 3-(4-cyanophenyl)-3-butenoate (21g)

Colorless oil; IR (neat) 2979, 2228 (CN), 1729 (CO), 1607, 1369, 1258, 1150, 847 cm^{-1}; ^1H NMR δ 1.35 (9H, s), 3.44 (2H, d, J=1.0 Hz), 5.37 (1H, s), 5.59 (1H, s), 7.52 (2H, d, J=8.7 Hz), 7.62 (2H, d, J=8.7 Hz). MS m/z (%) 243 (M^+, 7), 228 (5), 187 (75), 159 (23), 142 (46), 140 (20), 115 (17), 57 (100). Calcd for $C_{15}H_{17}NO_2$: M, 243.1259. Found: m/z 243.1256.

3.31. (*Z*)-1-Chloro-2-(4-methoxyphenyl)-1-(*p*-tolylsulfinyl)ethene (23)

Colorless crystals; mp 80–80.5 °C (hexane/AcOEt); IR (KBr) 2936, 1605, 1514, 1308, 1256, 1177, 1068, 897, 826, 749 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 3.84 (3H, s), 6.93 (2H, d, J=8.8 Hz), 7.31 (2H, d, J=8.1 Hz), 7.55 (1H, s), 7.62 (2H, d, J=8.1 Hz), 7.75 (2H, d, J=8.8 Hz). Anal. Calcd for $C_{16}H_{15}ClO_2S$: C, 62.64; H, 4.93; Cl, 11.56; S, 10.45. Found: C, 62.57; H, 4.68; Cl, 11.29; S, 10.41.

3.32. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(4-methoxyphenyl)-4-(*p*-tolylsulfinyl)butanoate (24)

tert-Butyl acetate (0.88 mL, 6.52 mmol) was added to a solution of LDA (6.52 mmol) in 28 mL of dry THF at −78 °C with stirring. The solution was stirred for 10 min and then a solution of **23** (500 mg, 1.63 mmol) in THF (5 mL) was added. The reaction mixture was stirred for 5 min and the reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The extract was washed with brine and the organic layer was dried over $MgSO_4$. The solvent was evaporated to give a residue, which was purified by silica gel column chromatography to give 644 mg (93%) of **24** as colorless crystals. Mp 99–99.5 °C (hexane/AcOEt); IR (neat) 2979, 1729 (CO), 1611, 1515, 1456, 1368, 1252, 1149, 1051, 839, 756 cm^{-1}; ^1H NMR δ 1.32 (9H, s), 2.41 (3H, s), 2.78 (1H, dd, J=15.7, 7.8 Hz), 2.83 (1H, dd, J=15.7, 8.0 Hz), 3.83 (3H, s), 4.37 (1H, dt, J=7.8, 2.9 Hz), 4.65 (1H, d, J=2.9 Hz), 6.91 (2H, d, J=8.8 Hz), 7.30 (2H, d, J=8.1 Hz), 7.44 (2H, d, J=8.8 Hz), 7.63 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{22}H_{27}ClO_4S$: C, 62.47; H, 6.43; Cl, 8.38; S, 7.58. Found: C, 62.50; H, 6.38; Cl, 8.32; S, 7.47.

3.33. (*Z*)-*tert*-Butyl 4-(4-Methoxyphenyl)-3-butenoate (26) and *E*-isomer (27)

EtMgCl (2.0 M solution in diethyl ether, 0.1 mL, 0.20 mmol) was added to dry toluene (1.9 mL) at 0 °C, and then a solution of **24** (50 mg 0.118 mmol) in toluene (0.5 mL) was added dropwise to the solution of EtMgCl. The reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$ and the extract was washed with brine and the organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography to give 23.4 mg (80%) of **26** and 1.76 mg (6%) of **27** both as colorless oil. Compound **26**: IR (neat) 2978, 1730 (CO), 1608, 1511, 1459, 1368, 1254 (COC), 1148, 1034, 843 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 3.24 (2H, dd, J=7.3, 1.9 Hz), 3.82 (3H, s), 5.78 (1H, dt, J=11.5, 7.3 Hz), 6.54 (1H, d, J=11.5 Hz), 6.88 (2H, d, J=8.7 Hz), 7.22 (2H, d,

J=8.7 Hz). MS m/z (%) 248 (M^+, 22), 175 (18), 147 (86), 115 (10), 103 (12), 91 (10), 57 (100). Calcd for $C_{15}H_{20}O_3$: M, 248.1412. Found: m/z 248.1412. Compound **27**: IR (neat) 2978, 1730 (CO), 1608, 1513, 1368, 1250 (COC), 1148, 1035, 839 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 3.13 (2H, dd, J=7.2, 5.7 Hz), 3.80 (3H, s), 6.14 (1H, dt, J=16.0, 7.2 Hz), 6.40 (1H, d, J=16.0 Hz), 6.84 (2H, d, J=8.7 Hz), 7.30 (2H, d, J=8.7 Hz). MS m/z (%) 248 (M^+, 31), 192 (20), 147 (100), 131 (10), 103 (13), 91 (10), 57 (70), 41 (12). Calcd for $C_{15}H_{20}O_3$: M, 248.1413. Found: m/z 248.1415.

3.34. *tert*-Butyl 3-(4-methoxyphenyl)-3-butenoate (25)

Colorless oil; IR (neat) 2978, 1725 (CO), 1608, 1513, 1459, 1368, 1249 (COC), 1147, 1034, 836 cm^{-1}; ^1H NMR δ 1.36 (9H, s), 3.40 (2H, d, J=0.9 Hz), 3.81 (3H, s), 5.11 (1H, d, J=0.9 Hz), 5.42 (1H, d, J=0.9 Hz), 6.85 (2H, d, J=8.9 Hz), 7.37 (2H, d, J=8.9 Hz). MS m/z (%) 248 (M^+, 9), 192 (100), 175 (15), 147 (21), 133 (19), 115 (11), 57 (68). Calcd for $C_{15}H_{20}O_3$: M, 248.1410. Found: m/z 248.1401.

3.35. (*Z*)-1-Chloro-2-(4-dimethylaminophenyl)-1-(*p*-tolylsulfinyl)ethene (28a)

Colorless crystals; mp 131.5–132 °C (hexane/AcOEt); IR (KBr) 2917, 1607, 1526, 1374 (CN), 1194, 1085, 1064, 910, 807 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 3.02 (6H, s), 6.68 (2H, d, J=9.0 Hz), 7.30 (2H, d, J=8.1 Hz), 7.48 (1H, s), 7.60 (2H, d, J=8.1 Hz), 7.72 (2H, d, J=9.0 Hz). Anal. Calcd for $C_{17}H_{18}ClNOS$: C, 63.84; H, 5.67; N, 4.38; Cl, 11.08; S, 10.03. Found: C, 63.86; H, 5.56; N, 4.36; Cl, 10.90; S, 9.97.

3.36. (*Z*)-1-Chloro-2-(4-methylthiophenyl)-1-(*p*-tolylsulfinyl)ethene (28b)

Colorless crystals; mp 97.5–98 °C (hexane/AcOEt); IR (KBr) 1592, 1492, 1403, 1326, 1190, 1086, 1069, 895, 884, 823, 810 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 2.50 (3H, s), 7.25 (2H, d, J=8.5 Hz), 7.32 (2H, d, J=8.1 Hz), 7.56 (1H, s), 7.63 (2H, d, J=8.1 Hz), 7.69 (2H, d, J=8.5 Hz). Anal. Calcd for $C_{16}H_{15}ClOS_2$: C, 59.52; H, 4.68; Cl, 10.98; S, 19.86. Found: C, 59.39; H, 4.60; Cl, 10.98; S, 19.66.

3.37. (*E*)-1-Chloro-2-(4-methylthiophenyl)-1-(*p*-tolylsulfinyl)ethene (29b)

Colorless crystals; mp 102.5–103 °C (hexane/AcOEt); IR (KBr) 1589, 1490, 1434, 1401, 1094, 1083, 1052, 890, 826, 808 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 2.53 (3H, s), 7.26 (1H, s), 7.28 (2H, d, J=8.3 Hz), 7.31 (2H, d, J=8.2 Hz), 7.46 (2H, d, J=8.2 Hz), 7.49 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{16}H_{15}ClOS_2$: C, 59.52; H, 4.68; Cl, 10.98; S, 19.86. Found: C, 59.56; H, 4.61; Cl, 10.70; S, 19.94.

3.38. (*Z*)-1-Chloro-2-piperonyl-1-(*p*-tolylsulfinyl)ethene (28c)

Colorless crystals; mp 113–113.5 °C (hexane/AcOEt); IR (KBr) 2900, 1622, 1503, 1448, 1264, 1067, 928, 815 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 6.01 (2H, s), 6.84 (1H, d, J=8.1 Hz), 7.20 (1H, dd, J=8.1, 1.7 Hz), 7.32 (2H, d, J=8.1 Hz), 7.42 (1H, d, J=1.7 Hz), 7.51 (1H, s), 7.62 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08; Cl, 11.05; S, 10.00. Found: C, 59.83; H, 4.02; Cl, 10.87; S, 10.03.

3.39. (*E*)-1-Chloro-2-piperonyl-1-(*p*-tolylsulfinyl)ethene (29c)

Colorless crystals; mp 119.5–120 °C (hexane/AcOEt); IR (KBr) 2917, 1585, 1489, 1447, 1258, 1092, 1031, 924, 885, 811 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 6.05 (2H, s), 6.86 (1H, d, J=8.0 Hz), 7.00 (1H, dd, J=8.0, 1.7 Hz), 7.10 (1H, d, J=1.7 Hz), 7.22 (1H, s), 7.32 (2H, d, J=8.1 Hz), 7.51 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08; Cl, 11.05; S, 10.00. Found: C, 59.84; H, 3.98; Cl, 10.72; S, 9.81.

3.40. (*Z*)-1-Chloro-2-(2-furyl)-1-(*p*-tolylsulfinyl)ethene (28d)

Colorless crystals; mp 100–100.5 °C (hexane/AcOEt); IR (KBr) 3128, 3023, 1610, 1494, 1470, 1397, 1323, 1307, 1085, 1060, 1018, 903, 816, 751 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 6.52 (1H, dd, J=3.4, 1.8 Hz), 7.02 (1H, d, J=3.4 Hz), 7.32 (2H, d, J=8.1 Hz), 7.53 (1H, d, J=1.8 Hz), 7.57 (1H, s), 7.61 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{13}H_{11}ClO_2S$: C, 58.54; H, 4.16; Cl, 13.29; S, 12.02. Found: C, 58.52; H, 3.94; Cl, 13.28; S, 12.20.

3.41. (*E*)-1-Chloro-2-(2-furyl)-1-(*p*-tolylsulfinyl)ethene (29d)

Colorless crystals; mp 103–103.5 °C (hexane/AcOEt); IR (KBr) 3139, 3031, 1621, 1480, 1383, 1275, 1149, 1085, 1063, 1018, 959, 876, 813, 753 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 6.54 (1H, dd, J=3.4, 1.8 Hz), 6.69 (1H, d, J=3.4 Hz), 6.92 (1H, s), 7.30 (2H, d, J=8.1 Hz), 7.60 (1H, s), 7.61 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{13}H_{11}ClO_2S$: C, 58.54; H, 4.16; Cl, 13.29; S, 12.02. Found: C, 58.47; H, 3.93; Cl, 13.10; S, 11.93.

3.42. (*Z*)-1-Chloro-2-(2-thienyl)-1-(*p*-tolylsulfinyl)-ethene (28e)

Colorless crystals; mp 104–104.5 °C (hexane/AcOEt); IR (KBr) 3080, 1595, 1417, 1217, 1018, 1049, 904, 816, 733 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 7.12 (1H, dd, J=5.1, 3.7 Hz), 7.32 (2H, d, J=8.1 Hz), 7.46 (1H, d, J=3.7 Hz), 7.50 (1H, d, J=5.1 Hz), 7.62 (2H, d, J=8.1 Hz), 7.85 (1H, s). Anal. Calcd for $C_{13}H_{11}ClOS_2$: C, 55.21; H, 3.92; Cl, 12.54; S, 22.68. Found: C, 55.24; H, 3.80; Cl, 12.40; S, 22.78.

3.43. (*E*)-1-Chloro-2-(2-thienyl)-1-(*p*-tolylsulfinyl)-ethene (29e)

Colorless crystals; mp 122.5–123 °C (hexane/AcOEt); IR (KBr) 3082, 1587, 1493, 1422, 1211, 1085, 1059, 906, 812, 723 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 7.08 (1H, dd, J=5.2, 3.6 Hz), 7.26 (1H, d, J=3.6 Hz), 7.30 (1H, s), 7.31 (2H, d, J=8.3 Hz), 7.50 (1H, d, J=5.2 Hz), 7.61 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{13}H_{11}ClOS_2$: C, 55.21; H, 3.92; Cl, 12.54; S, 22.68. Found: C, 55.10; H, 3.88; Cl, 12.51; S, 22.81.

3.44. (3*R**,4*R**,*sS**)-*tert*-Butyl 4-chloro-3-(4-dimethylaminophenyl)-4-(*p*-tolylsulfinyl)butanoate (30a)

Colorless crystals; mp 143–143.5 °C (hexane/AcOEt); IR (KBr) 2965, 1707 (CO), 1615, 1523, 1366 (CN), 1296, 1163, 1054, 969, 821 cm^{-1}; ^1H NMR δ 1.33 (9H, s), 2.41 (3H, s), 2.80 (2H, d, J=7.8 Hz), 2.96 (6H, s), 4.32 (1H, dt, J=7.8, 2.8 Hz), 4.67 (1H, d, J=2.8 Hz), 6.72 (2H, d, J=8.0 Hz), 7.29 (2H, d, J=8.9 Hz), 7.37 (2H, d, J=8.9 Hz), 7.63 (2H, d, J=8.0 Hz). Anal. Calcd for $C_{23}H_{30}ClNO_3S$: C, 63.36; H, 6.94; N, 3.21; Cl, 8.13; S, 7.35. Found: C, 63.31; H, 6.94; N, 3.17; Cl, 8.18; S, 7.31.

3.45. (3*R**,4*R**,*sS**)-*tert*-Butyl 4-chloro-3-(4-methylsulfanylphenyl)-4-(*p*-tolylsulfinyl)butanoate (30b)

Colorless oil; IR (neat) 2978, 1728 (CO), 1598, 1495, 1368, 1258, 1150, 1052, 959, 812, 749 cm^{-1}; ^1H NMR δ 1.32 (9H, s), 2.42 (3H, s), 2.77 (3H, s), 2.82 (1H, dd, J=15.8, 7.8 Hz), 2.84 (1H, dd, J=15.8, 7.8 Hz), 4.37 (1H, dt, J=7.8, 2.8 Hz), 4.66 (1H, d, J=2.8 Hz), 7.26 (2H, d, J=8.4 Hz), 7.30 (2H, d, J=8.1 Hz), 7.44 (2H, d, J=8.4 Hz), 7.63 (2H, d, J=8.1 Hz). MS m/z (%) 438 (M^+, 8), 365 (18), 298 (12), 243 (70), 242 (50), 206 (70), 178 (18), 140 (100), 139 (25), 115 (23), 57 (84). Calcd for $C_{22}H_{27}ClO_3S_2$: M, 438.1090. Found: m/z 438.1088.

3.46. (3*S**,4*R**,*sS**)-*tert*-Butyl 4-chloro-3-(4-methylsulfanylphenyl)-4-(*p*-tolylsulfinyl)butanoate (31b)

Colorless oil; IR (neat) 2979, 1728 (CO), 1597, 1495, 1368, 1259, 1151, 1085, 1052, 1016, 956, 812, 756 cm^{-1}; ^1H NMR δ 1.27 (9H, s),

2.42 (3H, s), 2.46 (3H, s), 2.97 (1H, dd, *J*=16.0, 10.8 Hz), 3.07 (1H, dd, *J*=16.0, 4.8 Hz), 4.17 (1H, ddd, *J*=10.8, 4.8, 3.0 Hz), 4.48 (1H, d, *J*=3.0 Hz), 7.20 (2H, d, *J*=8.5 Hz), 7.27 (2H, d, *J*=8.5 Hz), 7.31 (2H, d, *J*=8.1 Hz), 7.64 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 438 (M^+, 5), 365 (25), 299 (14), 243 (100), 242 (37), 206 (50), 184 (18), 140 (94), 115 (22), 57 (90). Calcd for $C_{22}H_{27}ClO_3S_2$: M, 438.1090. Found: *m*/*z* 438.1090.

3.47. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-piperonyl)-4-(*p*-tolylsulfinyl)butanoate (30c)

Colorless amorphous; IR (neat) 2979, 1727 (CO), 1491, 1368, 1253 (COC), 1151, 1042 (SO), 934 cm^{-1}; ^1H NMR δ 1.34 (9H, s), 2.42 (3H, s), 2.78 (1H, dd, *J*=16.0, 8.0 Hz), 2.79 (1H, dd, *J*=16.0, 8.0 Hz), 4.34 (1H, dt, *J*=7.8, 2.9 Hz), 4.63 (1H, d, *J*=3.0 Hz), 5.98 (2H, s), 6.83 (1H, dd, *J*=7.2, 1.4 Hz), 7.01 (1H, s), 7.02 (1H, dd, *J*=7.2, 1.8 Hz), 7.30 (2H, d, *J*=8.2 Hz), 7.63 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 436 (M^+, 12), 363 (12), 241 (40), 240 (36), 204 (42), 140 (100), 139 (22), 91 (13), 57 (79). Calcd for $C_{22}H_{25}ClO_5S$: M, 436.1112. Found: *m*/*z* 436.1107.

3.48. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-piperonyl)-4-(*p*-tolylsulfinyl)butanoate (31c)

Colorless amorphous; IR (neat) 2977, 2929, 1733 (CO), 1504, 1488, 1368, 1242 (COC), 1149, 1040 (SO), 935 cm^{-1}; ^1H NMR δ 1.30 (9H, s), 2.42 (3H, s), 2.92 (1H, dd, *J*=16.0, 10.8 Hz), 3.04 (1H, dd, *J*=16.0, 4.7 Hz), 4.12 (1H, ddd, *J*=7.6, 4.5, 3.1 Hz), 4.48 (1H, d, *J*=2.9 Hz), 5.94 (2H, s), 6.76 (1H, d, *J*=8.0 Hz), 6.81 (1H, dd, *J*=8.1, 1.7 Hz), 6.85 (1H, d, *J*=1.7 Hz), 7.32 (2H, d, *J*=8.3 Hz), 7.64 (2H, d, *J*=8.3 Hz). MS *m*/*z* (%) 436 (M^+, 7), 363 (12), 241 (46), 205 (65), 204 (39), 182 (16), 140 (100), 139 (22), 91 (16), 57 (96). Calcd for $C_{22}H_{25}ClO_5S$: M, 436.1111. Found: *m*/*z* 436.1112.

3.49. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-furyl)-4-(*p*-tolylsulfinyl)butanoate (30d)

Colorless crystals; mp 89–89.5 °C (hexane/AcOEt); IR (KBr) 2979, 1732 (CO), 1596, 1494, 1368, 1291, 1152, 1055, 913, 813, 738 cm^{-1}; ^1H NMR δ 1.39 (9H, s), 2.43 (3H, s), 2.77 (1H, dd, *J*=16.1, 7.7 Hz), 2.91 (1H, dd, *J*=16.1, 7.7 Hz), 4.52 (1H, dt, *J*=7.7, 2.8 Hz), 4.59 (1H, d, *J*=2.8 Hz), 6.40 (1H, dd, *J*=3.2, 1.8 Hz), 6.45 (1H, d, *J*=3.2 Hz), 7.32 (2H, d, *J*=8.1 Hz), 7.46 (1H, d, *J*=1.8 Hz), 7.67 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{19}H_{23}ClO_4S$: C, 59.60; H, 6.05; Cl, 9.26; S, 8.37. Found: C, 59.31; H, 5.69; Cl, 8.95; S, 8.43.

3.50. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-furyl)-4-(*p*-tolylsulfinyl)butanoate (31d)

Colorless oil; IR (neat) 2978, 1739 (CO), 1595, 1501, 1451, 1369, 1264, 1151, 1042, 947, 850, 747 cm^{-1}; ^1H NMR δ 1.37 (9H, s), 2.43 (3H, s), 2.87 (1H, dd, *J*=16.0, 10.8 Hz), 3.02 (1H, dd, *J*=16.0, 4.1 Hz), 4.26 (1H, dt, *J*=10.8, 4.1 Hz), 4.72 (1H, d, *J*=3.7 Hz), 6.26 (1H, d, *J*=3.3 Hz), 6.33 (1H, dd, *J*=3.3, 1.8 Hz), 7.34 (2H, d, *J*=8.2 Hz), 7.36 (1H, d, *J*=1.8 Hz), 7.67 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 382 (M^+, 5), 309 (32), 243 (7), 187 (36), 150 (14), 140 (100), 123 (11), 92 (14), 77 (12), 57 (73), 41 (8). Calcd for $C_{19}H_{23}ClO_4S$: M, 382.1006. Found: *m*/*z* 382.1015.

3.51. (3*R**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)butanoate (30e)

Colorless crystals; mp 105.5–106 °C (hexane/AcOEt); IR (KBr) 2979, 1723 (CO), 1452, 1396, 1368, 1265, 1166, 1043, 851, 815, 717 cm^{-1}; ^1H NMR δ 1.36 (9H, s), 2.42 (3H, s), 2.81 (1H, dd, *J*=16.0, 7.8 Hz), 2.85 (1H, dd, *J*=16.0, 7.8 Hz), 4.67 (1H, d, *J*=2.8 Hz), 4.75 (1H, dt, *J*=7.8, 2.8 Hz), 7.05 (1H, dd, *J*=5.1, 3.5 Hz), 7.26 (1H, d, *J*=3.5 Hz), 7.31 (2H, d, *J*=8.2 Hz), 7.33 (1H, d, *J*=5.1 Hz), 7.65 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{19}H_{23}ClO_3S_2$: C, 57.20; H, 5.81; Cl, 8.89; S, 16.07. Found: C, 57.27; H, 5.76; Cl, 8.77; S, 16.11.

3.52. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)butanoate (31e)

Colorless oil; IR (neat) 2979, 1732 (CO), 1597, 1494, 1456, 1368, 1291, 1258, 1152, 1053, 972, 846, 756, 701 cm^{-1}; ^1H NMR δ 1.33 (9H, s), 2.43 (3H, s), 2.92 (1H, dd, *J*=15.9, 10.5 Hz), 3.10 (1H, dd, *J*=15.9, 4.2 Hz), 4.53 (1H, ddd, *J*=10.5, 4.2, 2.8 Hz), 4.56 (1H, d, *J*=2.8 Hz), 6.96 (1H, dd, *J*=5.1, 1.1 Hz), 7.06 (1H, d, *J*=3.5 Hz), 7.22 (1H, dd, *J*=5.1, 1.1 Hz), 7.33 (2H, d, *J*=8.2 Hz), 7.67 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 398 (M+, 5), 325 (21), 203 (29), 185 (12), 166 (18), 140 (100), 139 (18), 123 (13), 57 (73). Calcd for $C_{19}H_{23}ClO_3S_2$: M, 398.0777. Found: *m*/*z* 398.0780.

3.53. (*Z*)-*tert*-Butyl 4-(4-dimethylaminophenyl)-3-butenoate (33a)

Colorless oil; IR (neat) 2978, 1732 (CO), 1611, 1523, 1446, 1393, 1367 (CN), 1256, 1147, 948, 829 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 2.96 (6H, s), 3.28 (2H, dd, *J*=7.3, 1.9 Hz), 5.69 (1H, dt, *J*=11.6, 7.3 Hz), 6.49 (1H, d, *J*=11.6 Hz), 6.71 (2H, d, *J*=8.5 Hz), 7.20 (2H, d, *J*=8.5 Hz). MS *m*/*z* (%) 261 (M^+, 45), 205 (40), 188 (11), 160 (100), 144 (13), 116 (10), 115 (12), 57 (19). Calcd for $C_{16}H_{23}NO_2$: M, 261.1729. Found: *m*/*z* 261.1726.

3.54. *tert*-Butyl 3-(4-methylsulfanylphenyl)-3-butenoate (32b)

Colorless oil; IR (neat) 2978, 1732 (CO), 1596, 1496, 1368, 1257, 1148, 967, 829 cm^{-1}; ^1H NMR δ 1.36 (9H, s), 2.48 (3H, s), 3.40 (2H, d, *J*=1.0 Hz), 5.17 (1H, d, *J*=1.0 Hz), 5.49 (1H, d, *J*=0.7 Hz), 7.21 (2H, d, *J*=8.6 Hz), 7.36 (2H, d, *J*=8.6 Hz). MS *m*/*z* (%) 264 (M^+, 16), 208 (100), 191 (15), 163 (8), 149 (12), 115 (24), 57 (52). Calcd for $C_{15}H_{20}O_2S$: M, 264.1183. Found: *m*/*z* 264.1183.

3.55. (*Z*)-*tert*-Butyl 4-(4-methylsulfanylphenyl)-3-butenoate (33b)

Colorless oil; IR (neat) 2978, 1729 (CO), 1596, 1494, 1368, 1329, 1257, 1148, 955, 840 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 2.49 (3H, s), 3.24 (2H, dd, *J*=7.4, 1.8 Hz), 5.85 (1H, dt, *J*=11.6, 7.4 Hz), 6.54 (1H, dt, *J*=11.6, 1.8 Hz), 7.21 (2H, d, *J*=8.8 Hz), 7.23 (2H, d, *J*=8.8 Hz). MS *m*/*z* (%) 264 (M^+, 40), 208 (12), 191 (13), 163 (45), 147 (8), 115 (39), 57 (100). Calcd for $C_{15}H_{20}O_2S$: M, 264.1182. Found: *m*/*z* 264.1179.

3.56. (*E*)-*tert*-Butyl 4-(4-methylsulfanylphenyl)-3-butenoate (34b)

Colorless oil; IR (neat) 2978, 1726 (CO), 1596, 1494, 1393, 1368, 1257, 1147, 968, 846 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 2.48 (3H, s), 3.14 (2H, dd, *J*=7.0, 1.4 Hz), 6.25 (1H, dt, *J*=15.9, 7.0 Hz), 6.40 (1H, d, *J*=15.9 Hz), 7.19 (2H, d, *J*=8.4 Hz), 7.29 (2H, d, *J*=8.4 Hz). MS *m*/*z* (%) 264 (M^+, 44), 208 (14), 163 (72), 147 (8), 115 (39), 57 (100). Calcd for $C_{15}H_{20}O_2S$: M, 264.1183. Found: *m*/*z* 264.1190.

3.57. *tert*-Butyl 3-(2-piperonyl)-3-butenoate (32c)

Colorless oil; IR (neat) 2922, 1732 (CO), 1505, 1493, 1445, 1368, 1235 (COC), 1146, 1040, 937, 813 cm^{-1}; ^1H NMR δ 1.38 (9H, s), 3.37 (2H, d, *J*=1.0 Hz), 5.12 (1H, d, *J*=0.9 Hz), 5.40 (1H, d, *J*=0.9 Hz), 5.95 (2H, s), 6.76 (1H, d, *J*=8.1 Hz), 6.90 (1H, dd, *J*=8.1, 1.8 Hz), 6.95 (1H, d, *J*=1.8 Hz). MS *m*/*z* (%) 262 (M^+, 17), 206 (100), 189 (16), 178 (16), 103 (14), 57 (26). Calcd for $C_{15}H_{18}O_4$: M, 262.1205. Found: *m*/*z* 262.1204.

3.58. (*Z*)-*tert*-Butyl 4-(2-piperonyl)-3-butenoate (33c)

Colorless oil; IR (neat) 2978, 1731 (CO), 1490, 1442, 1368, 1237 (COC), 1147, 1040, 846, 820 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 3.23 (2H, dd, J=7.3, 1.9 Hz), 5.79 (1H, dt, J=11.6, 7.3 Hz), 5.96 (2H, s), 6.50 (1H, dt, J=11.5, 1.8 Hz), 6.75 (1H, dd, J=8.1, 1.5 Hz), 6.78 (1H, d, J=7.4 Hz), 6.80 (1H, d, J=1.9 Hz). MS m/z (%) 262 (M^+, 100), 189 (55), 161 (77), 131 (90), 103 (40), 57 (86). Calcd for $C_{15}H_{18}O_4$: M, 262.1205. Found: m/z 262.1207.

3.59. (*E*)-*tert*-Butyl 4-(2-piperonyl)-3-butenoate (34c)

Colorless oil; IR (neat) 2978, 1731 (CO), 1490, 1446, 1368, 1250 (COC), 1147, 1040, 964, 937, 801 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 3.12 (2H, dd, J=7.2, 1.5 Hz), 5.95 (2H, s), 6.11 (1H, dt, J=15.8, 7.2 Hz), 6.37 (1H, d, J=15.8 Hz), 6.73 (1H, d, J=8.0 Hz), 6.78 (1H, dd, J=8.0, 1.6 Hz), 6.92 (1H, d, J=1.6 Hz). MS m/z (%) 262 (M^+, 88), 206 (54), 161 (100), 131 (93), 103 (44), 57 (93). Calcd for $C_{15}H_{18}O_4$: M, 262.1205. Found: m/z 262.1207.

3.60. (*Z*)-*tert*-Butyl 4-(2-furyl)-3-butenoate (33d)

Colorless oil; IR (neat) 2980, 1732 (CO), 1490, 1369, 1277, 1150, 1013, 961, 735 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 3.47 (2H, dd, J=7.0, 1.9 Hz), 5.76 (1H, dt, J=11.6, 7.0 Hz), 6.29 (1H, d, J=3.4 Hz), 6.31 (1H, dt, J=11.6, 1.8 Hz), 6.39 (1H, dd, J=3.4, 1.8 Hz), 7.40 (1H, d, J=1.8 Hz), MS m/z (%) 208 (M^+, 15), 152 (8), 135 (8), 108 (8), 107 (45), 77 (17), 57 (100). Calcd for $C_{12}H_{16}O_3$: M, 208.1098. Found: m/z 208.1098.

3.61. (*E*)-*tert*-Butyl 4-(2-furyl)-3-butenoate (34d)

Colorless oil; IR (neat) 2980, 1732 (CO), 1458, 1393, 1369, 1331, 1257, 1150, 1013, 732 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 3.11 (2H, d, J=6.5 Hz), 6.19 (1H, d, J=3.3 Hz), 6.20 (1H, dt, J=15.8, 6.5 Hz), 6.29 (1H, d, J=15.8 Hz), 6.35 (1H, dd, J=3.3, 1.6 Hz), 7.33 (1H, d, J=1.6 Hz), MS m/z (%) 208 (M^+, 18), 152 (11), 108 (8), 107 (53), 77 (15), 57 (100), 41 (18), 28 (31). Calcd for $C_{12}H_{16}O_3$: M, 208.1099. Found: m/z 208.1108.

3.62. (*Z*)-*tert*-Butyl 4-(2-thienyl)-3-butenoate (33e)

Colorless oil; IR (neat) 2979, 1732 (CO), 1393, 1368, 1330, 1258, 1149, 847, 697 cm^{-1}; ^1H NMR δ 1.48 (9H, s), 3.37 (2H, dd, J=7.0, 2.0 Hz), 5.82 (1H, dt, J=11.6, 7.0 Hz), 6.67 (1H, dt, J=11.6, 2.0 Hz), 7.02 (2H, d, J=3.6 Hz), 7.28 (1H, d, J=3.6 Hz). MS m/z (%) 224 (M^+, 24), 168 (3), 151 (14), 123 (67), 121 (7), 97 (6), 79 (8), 57 (100). Calcd for $C_{12}H_{16}O_2S$: M, 224.0871. Found: m/z 224.0871.

3.63. (*E*)-*tert*-Butyl 4-(2-thienyl)-3-butenoate (34e)

Colorless oil; IR (neat) 2978, 1729 (CO), 1392, 1368, 1336, 1256, 1207, 1147, 955, 851, 696 cm^{-1}; ^1H NMR δ 1.47 (9H, s), 3.12 (2H, dd, J=7.2, 1.4 Hz), 6.12 (1H, dt, J=15.6, 7.2 Hz), 6.58 (1H, d, J=15.6, Hz), 6.91–6.96 (2H, m), 7.13 (1H, d, J=5.0 Hz). MS m/z (%) 224 (M^+, 24), 168 (10), 123 (80), 121 (7), 97 (7), 79 (8), 77 (6), 57 (100). Calcd for $C_{12}H_{16}O_2S$: M, 224.0871. Found: m/z 224.0871.

3.64. (3*R**,4*S**,s*S**)-*tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)pentanoate (36) and (3*R**,4*R**,s*S**)-isomer (37)

tert-Butyl acetate (0.38 mL, 2.83 mmol) was added to a solution of LDA (2.83 mmol) in 12 mL of dry THF at −78 °C with stirring. The solution was stirred for 10 min and then a solution of **28e** (200 mg, 0.71 mmol) in THF (2 mL) was added. The reaction mixture was stirred for 5 min and CH_3I (0.44 mL, 7.07 mmol) was added and stirred for 5 min. The reaction was quenched with satd aq NH_4Cl and the whole was extracted with $CHCl_3$ and the organic layer was dried over $MgSO_4$. The solvent was evaporated to give a residue, which was purified by silica gel column chromatography to give 224 mg (80%) of **36** as colorless crystals and 55 mg (19%) of **37** as colorless crystals. Compound **36**: mp 127.5–128 °C (hexane/AcOEt); IR (KBr) 2975, 1723 (CO), 1432, 1366, 1285, 1157, 1056, 849, 813, 714 cm^{-1}; ^1H NMR δ 1.27 (9H, s), 1.41 (3H, s), 2.44 (3H, s), 2.83 (1H, dd, J=15.3, 11.8 Hz), 3.17 (1H, dd, J=15.3, 3.3 Hz), 4.15 (1H, dd, J=11.8, 3.3 Hz), 6.96 (1H, dd, J=4.8, 3.6 Hz), 7.06 (1H, d, J=3.6 Hz), 7.26 (1H, d, J=4.8 Hz), 7.33 (2H, d, J=8.1 Hz), 7.59 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{20}H_{25}ClO_3S_2$: C, 58.17; H, 6.10; Cl, 8.58; S, 15.53. Found: C, 58.16; H, 6.00; Cl, 8.55; S, 15.57. Compound **37**: mp 111–111.5 °C (hexane/AcOEt); IR (KBr) 2977, 1731 (CO), 1371, 1355, 1251, 1153, 1051, 851, 809 cm^{-1}; ^1H NMR δ 1.27 (9H, s), 1.54 (3H, s), 2.41 (3H, s), 2.84 (1H, dd, J=15.0, 10.0 Hz), 2.88 (1H, dd, J=15.0, 5.2 Hz), 4.34 (1H, dd, J=10.0, 5.2 Hz), 7.01 (1H, dd, J=5.0, 3.5 Hz), 7.26–7.30 (3H, m), 7.32 (1H, d, J=5.0 Hz), 7.59 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{20}H_{25}ClO_3S_2$: C, 58.17; H, 6.10. Found: C, 58.16; H, 6.00.

3.65. (3*S**,4*R**,s*S**)-*tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)pentanoate (41) and (3*S**,4*S**,s*S**)-isomer (42)

Compound **41**: colorless crystals; mp 121–121.5 °C (hexane/AcOEt); IR (KBr) 2976, 1715 (CO), 1478, 1437, 1368, 1292, 1148, 1055, 853, 701 cm^{-1}; ^1H NMR δ 1.25 (3H, s), 1.28 (9H, s), 2.43 (3H, s), 2.95 (1H, dd, J=15.3, 11.6 Hz), 3.34 (1H, dd, J=15.3, 3.6 Hz), 4.33 (1H, dd, J=11.6, 3.6 Hz), 6.96 (1H, dd, J=5.1, 3.6 Hz), 7.04 (1H, dd, J=3.6, 1.0 Hz), 7.23 (1H, dd, J=5.1, 1.0 Hz), 7.33 (2H, d, J=8.3 Hz), 7.66 (2H, d, J=8.3 Hz). Anal. Calcd for $C_{20}H_{25}ClO_3S_2$: C, 58.17; H, 6.10; Cl, 8.58; S, 15.53. Found: C, 58.29; H, 6.11; Cl, 8.51; S, 15.50. Compound **42**: colorless oil; IR (neat) 2979, 1732 (CO), 1597, 1456, 1369, 1287, 1152, 1057, 844, 759, 702 cm^{-1}; ^1H NMR δ 1.24 (9H, s), 1.65 (3H, s), 2.43 (3H, s), 2.84 (1H, dd, J=15.6, 11.7 Hz), 3.37 (1H, dd, J=15.6, 3.4 Hz), 4.00 (1H, dd, J=11.7, 3.4 Hz), 6.96 (1H, dd, J=5.1, 3.6 Hz), 7.01 (1H, dd, J=3.6, 1.0 Hz), 7.25 (1H, dd, J=5.1, 1.0 Hz), 7.33 (2H, d, J=8.1 Hz), 7.61 (2H, d, J=8.1 Hz). MS (FAB) m/z (%) 413 ($[M+H]^+$, 37), 357 (100), 339 (7), 321 (5), 217 (27), 181 (76), 139 (16), 123 (13), 57 (18). Calcd for $C_{20}H_{26}ClO_3S_2$: M, 413.1012. Found: m/z 413.1010.

3.66. (*Z*)-*tert*-Butyl 3-(2-thienyl)-3-pentenoate (38)

EtMgCl (2.0 M solution in diethyl ether, 0.1 mL, 0.2 mmol) was added to dry toluene (1.9 mL) at 0 °C. A solution of **36** (50 mg, 0.12 mmol) in toluene (0.5 mL) was added dropwise to the solution of EtMgCl and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$ and the organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography to give 24.5 mg (85%) of **38** as colorless oil. IR (neat) 2978, 1732 (CO), 1455, 1392, 1368, 1329, 1256, 1146, 843, 696 cm^{-1}; ^1H NMR δ 1.37 (9H, s), 1.89 (3H, d, J=7.1 Hz), 3.30 (2H, t, J=1.0 Hz), 5.74 (1H, q, J=7.1 Hz), 6.99 (1H, dd, J=3.6, 1.3 Hz), 7.01 (1H, dd, J=5.0, 3.6 Hz), 7.26 (1H, dd, J=5.0, 1.0 Hz). MS m/z (%) 238 (M^+, 6), 183 (10), 182 (100), 154 (16), 137 (29), 123 (25), 111 (5), 97 (17), 57 (37). Calcd for $C_{13}H_{18}O_2S$: M, 238.1027. Found: m/z 238.1027.

3.67. *tert*-Butyl 4-chloro-3-(2-thienyl)pentanoate (39)

Colorless oil; IR (neat) 2978, 1732 (CO), 1455, 1368, 1281, 1258, 1150, 846 cm^{-1}; ^1H NMR δ 1.31 (9H, s), 1.43 (3H, d, J=6.6 Hz), 2.62 (1H, dd, J=15.5, 10.1 Hz), 3.04 (1H, dd, J=15.5, 4.7 Hz), 3.61 (1H, ddd, J=10.1, 7.5, 6.6 Hz), 4.15 (1H, dq, J=7.5, 6.6 Hz), 6.91 (1H, dd, J=3.5, 1.2 Hz), 6.94 (1H, dd, J=5.0, 3.5 Hz), 7.19 (1H, dd, J=5.0, 1.2 Hz). MS (ESI) m/z (%) 275 ($[M+H]^+$, 17), 261 (100), 249 (39), 239 (13), 185

(25), 137 (8). Calcd for $C_{13}H_{20}ClO_2S$: M, 275.0870. Found: *m*/*z* 275.0867.

3.68. (*Z*)-*tert*-Butyl 2-methyl-3-(2-thienyl)-2-(*p*-tolylsulfinyl)cyclopropanecarboxylate (43)

A solution of **36** (100 mg, 0.24 mmol) in 1 mL of dry THF was added to a solution of LDA (0.29 mmol) in 4 mL of THF at −78 °C with stirring. The reaction mixture was slowly allowed to warm to 0 °C and the reaction was quenched by adding satd aq NH_4Cl. The whole was extracted with $CHCl_3$ and the organic layer was dried over $MgSO_4$. The solvent was evaporated to give a residue, which was purified by silica gel column chromatography to give 48 mg (53%) of **43** as colorless crystals. Colorless crystals; mp 144.5–145 °C (hexane/AcOEt); IR (KBr) 2978, 1727 (CO), 1455, 1412, 1369, 1215, 1152, 1091, 1052, 809, 703 cm^{-1}; ^1H NMR δ 1.27 (3H, s), 1.40 (9H, s), 2.41 (3H, s), 2.68 (1H, d, *J*=6.3 Hz), 3.12 (1H, dd, *J*=6.3, 0.8 Hz), 7.00 (1H, dd, *J*=5.1, 3.5 Hz), 7.16 (1H, dt, *J*=3.5, 1.1 Hz), 7.27 (1H, dd, *J*=5.1, 1.1 Hz), 7.30 (2H, d, *J*=8.1 Hz), 7.55 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{20}H_{24}O_3S_2$: C, 63.80; H, 6.42; S, 17.03. Found: C, 63.78; H, 6.26; S, 16.95.

3.69. (*E*)-*tert*-Butyl 2-methyl-3-(2-thienyl)-2-(*p*-tolylsulfinyl)-cyclopropanecarboxylate (44)

Colorless crystals; mp 131.5–132 °C (hexane/AcOEt); IR (KBr) 2984, 1716 (CO), 1459, 1412, 1366, 1260, 1153, 1033, 809, 692 cm^{-1}; ^1H NMR δ 0.97 (3H, s), 1.55 (9H, s), 2.30 (1H, d, *J*=6.6 Hz), 2.42 (3H, s), 3.74 (1H, dd, *J*=6.6, 1.0 Hz), 6.91 (1H, dt, *J*=3.5, 1.1 Hz), 6.95 (1H, dd, *J*=5.1, 3.5 Hz), 7.20 (1H, dd, *J*=5.1, 1.1 Hz), 7.31 (2H, d, *J*=8.2 Hz), 7.52 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{20}H_{24}O_3S_2$: C, 63.80; H, 6.42; S, 17.03. Found: C, 63.82; H, 6.42; S, 16.85.

3.70. *tert*-Butyl 4-chloro-3-(4-methoxyphenyl)-4-(*p*-tolylsulfinyl)pentanoate (45a)

Isolable main product: colorless crystals; mp 151–151.5 °C (hexane/AcOEt); IR (KBr) 2973, 1717 (CO), 1610, 1515, 1365, 1290, 1254, 1156, 1055, 811 cm^{-1}; ^1H NMR δ 1.21 (9H, s), 1.31 (3H, s), 2.43 (3H, s), 2.89 (1H, dd, *J*=15.2, 11.8 Hz), 3.10 (1H, dd, *J*=15.2, 3.8 Hz), 3.79 (3H, s), 3.81 (1H, dd, *J*=11.8, 3.8 Hz), 6.85 (2H, d, *J*=8.8 Hz), 7.26 (2H, d, *J*=8.8 Hz), 7.32 (2H, d, *J*=8.1 Hz), 7.58 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{23}H_{29}ClO_4S$: C, 63.22; H, 6.69; Cl, 8.11; S, 7.34. Found: C, 63.24; H, 6.61; Cl, 8.08; S, 7.37.

3.71. *tert*-Butyl 4-chloro-3-(2-piperonyl)-4-(*p*-tolylsulfinyl)-pentanoate (45b)

Isolable main product derived from **28c**: colorless crystals; mp 153.5–154 °C (hexane/AcOEt); IR (KBr) 2974, 1715 (CO), 1492, 1447, 1367, 1291, 1249, 1155, 1054, 933, 811 cm^{-1}; ^1H NMR δ 1.26 (9H, s), 1.31 (3H, s), 2.44 (3H, s), 2.84 (1H, dd, *J*=15.3, 11.8 Hz), 3.07 (1H, dd, *J*=15.3, 3.6 Hz), 3.75 (1H, dd, *J*=11.8, 3.6 Hz), 5.95 (2H, s), 6.74 (1H, d, *J*=8.1 Hz), 6.78 (1H, dd, *J*=8.1, 1.6 Hz), 6.87 (1H, d, *J*=1.6 Hz), 7.33 (2H, d, *J*=8.2 Hz), 7.58 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{23}H_{27}ClO_5S$: C, 61.26; H, 6.03; Cl, 7.86; S, 7.11. Found: C, 61.18; H, 5.95; Cl, 7.82; S, 7.10.

3.72. *tert*-Butyl 4-chloro-3-(2-piperonyl)-4-(*p*-tolylsulfinyl)-pentanoate (45b)

Isolable main product derived from **29c**: colorless crystals; mp 125–125.5 °C (hexane/AcOEt); IR (KBr) 2981, 1708 (CO), 1491, 1445, 1369, 1300, 1237, 1148, 1052, 1034, 929, 806 cm^{-1}; ^1H NMR δ 1.22 (9H, s), 1.56 (3H, s), 2.43 (3H, s), 2.90 (1H, dd, *J*=15.7, 12.1 Hz), 3.38 (1H, dd, *J*=15.7, 3.7 Hz), 3.67 (1H, dd, *J*=12.1, 3.7 Hz), 5.96 (2H, s), 6.75–6.79 (2H, m), 6.83 (1H, d, *J*=1.3 Hz), 7.33 (2H, d, *J*=8.1 Hz), 7.60 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{23}H_{27}ClO_5S$: C, 61.26; H, 6.03; Cl, 7.86; S, 7.11. Found: C, 61.30; H, 6.02.

3.73. *tert*-Butyl 4-chloro-3-phenyl-4-(*p*-tolylsulfinyl)-pentanoate (45c)

Isolable main product derived from **19e**: colorless crystals; mp 159–159.5 °C (hexane/AcOEt); IR (KBr) 2977, 1717 (CO), 1366, 1293, 1155, 1055, 814, 757 cm^{-1}; ^1H NMR δ 1.19 (9H, s), 1.31 (3H, s), 2.44 (3H, s), 2.94 (1H, dd, *J*=15.3, 11.7 Hz), 3.12 (1H, dd, *J*=15.3, 3.7 Hz), 3.83 (1H, dd, *J*=11.7, 3.7 Hz), 7.29–7.35 (7H, m), 7.59 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{22}H_{27}ClO_3S$: C, 64.93; H, 6.69. Found: C, 64.76; H, 6.75.

3.74. *tert*-Butyl 4-chloro-3-phenyl-4-(*p*-tolylsulfinyl)-pentanoate (45c)

Isolable main product derived from **20e**: colorless crystals; mp 126.0–126.5 °C (hexane/AcOEt); IR (KBr) 2980, 1711 (CO), 1370, 1301, 1146, 1087, 1057, 812, 701 cm^{-1}; ^1H NMR δ 1.15 (9H, s), 1.57 (3H, s), 2.43 (3H, s), 3.00 (1H, dd, *J*=15.6, 12.2 Hz), 3.42 (1H, dd, *J*=15.6, 3.8 Hz), 3.77 (1H, dd, *J*=12.2, 3.8 Hz), 7.29–7.34 (7H, m), 7.61 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{22}H_{27}ClO_3S$: C, 64.93; H, 6.69. Found: C, 64.68; H, 6.79.

3.75. *tert*-Butyl 4-chloro-3-(2-phenylethyl)-4-(*p*-tolylsulfinyl)pentanoate (45d)

Isolable main product derived from **19a**: colorless crystals; mp 131–131.5 °C (hexane/AcOEt); IR (KBr) 2972, 1718 (CO), 1597, 1495, 1372, 1281, 1214, 1145, 1061, 811, 702 cm^{-1}; ^1H NMR δ 1.48 (9H, s), 1.49 (3H, s), 1.65–1.72 (1H, m), 2.07–2.14 (1H, m), 2.44 (3H, s), 2.45 (1H, dd, *J*=16.3, 8.3 Hz), 2.51–2.69 (3H, m), 2.96 (1H, dd, *J*=16.3, 3.1 Hz), 7.14 (2H, d, *J*=7.6 Hz), 7.18 (1H, t, *J*=7.3 Hz), 7.24–7.27 (2H, m), 7.33 (2H, d, *J*=8.1 Hz), 7.63 (2H, d, *J*=8.1 Hz). Anal. Calcd for $C_{24}H_{31}ClO_3S$: C, 66.26; H, 7.18; Cl, 8.15; S, 7.37. Found: C, 65.95; H, 7.12.

3.76. *tert*-Butyl 4-chloro-3-(2-phenylethyl)-4-(*p*-tolylsulfinyl)pentanoate (45d)

Isolable main product derived from **20a**: colorless oil; IR (neat) 2978, 1723 (CO), 1598, 1456, 1368, 1259, 1151, 1085, 1049, 754 cm^{-1}; ^1H NMR δ 1.39 (9H, s), 1.51 (3H, s), 1.78–1.91 (1H, m), 2.19–2.30 (1H, m), 2.35–2.48 (2H, m), 2.44 (3H, s), 2.56 (1H, ddd, *J*=13.8, 9.8, 6.8 Hz), 2.73–2.81 (1H, m), 2.83–2.90 (1H, m), 7.20–7.27 (5H, m), 7.31–7.36 (4H, m). MS *m*/*z* (%) 435 (M^+, 33), 379 (78), 361 (5), 325 (10), 239 (7), 203 (100), 143 (53), 140 (21), 91 (25), 57 (23). Calcd for $C_{24}H_{31}ClO_3S$: M, 435.1760. Found: *m*/*z* 435.1763.

3.77. (*Z*)-*tert*-Butyl 3-(4-methoxyphenyl)-3-pentenoate (46a)

Colorless oil; IR (neat) 2979, 1732 (CO), 1610, 1513, 1456, 1367, 1289, 1248, 1148, 1036, 837 cm^{-1}; ^1H NMR δ 1.31 (9H, s), 1.64 (3H, dt, *J*=6.9, 1.1 Hz), 3.23 (2H, t, *J*=1.1 Hz), 3.81 (3H, s), 5.65 (1H, tq, *J*=6.9, 1.1 Hz), 6.86 (2H, d, *J*=8.9 Hz), 7.13 (2H, d, *J*=8.9 Hz). MS *m*/*z* (%) 262 (M^+, 12), 206 (100), 189 (8), 161 (25), 147 (55), 121 (15), 115 (6), 91 (7), 57 (31). Calcd for $C_{16}H_{22}O_3$: M, 262.1569. Found: *m*/*z* 262.1570.

3.78. (*Z*)-*tert*-Butyl 3-(2-piperonyl)-3-pentenoate (46b)

Colorless oil; IR (neat) 2978, 1732 (CO), 1489, 1435, 1367, 1331, 1240, 1155, 1040, 938, 814 cm^{-1}; ^1H NMR δ 1.34 (9H, s), 1.63 (3H, dt, *J*=6.8, 1.1 Hz), 3.20 (2H, t, *J*=1.1 Hz), 5.65 (1H, tq, *J*=6.8, 1.1 Hz), 5.94

(2H, s), 6.66 (1H, dd, *J*=7.8, 1.7 Hz), 6.70 (1H, d, *J*=1.7 Hz), 6.77 (1H, d, *J*=7.8 Hz). MS *m*/*z* (%) 276 (M^+, 15), 220 (100), 203 (13), 175 (14), 161 (27), 145 (13), 131 (23), 115 (11), 103 (5), 57 (31). Calcd for $C_{16}H_{20}O_4$: M, 276.1361. Found: *m*/*z* 276.1361.

3.79. (*Z*)-*tert*-Butyl 3-phenyl-3-pentenoate (46c)

Colorless oil; IR (neat) 2979, 1732 (CO), 1455, 1392, 1368, 1257, 1148, 701 cm^{-1}; ^1H NMR δ 1.30 (9H, s), 1.64 (3H, d, *J*=6.9 Hz), 3.26 (2H, t, *J*=1.1 Hz), 5.69 (1H, tq, *J*=6.9, 1.1 Hz), 7.19–7.25 (3H, m), 7.31–7.34 (2H, m). MS *m*/*z* (%) 232 (M^+, 2), 176 (100), 159 (9), 148 (10), 131 (42), 117 (23), 115 (22), 91 (26), 77 (8), 57 (92). Calcd for $C_{15}H_{20}O_2$: M, 232.1463. Found: *m*/*z* 232.1465.

3.80. (*E*)-*tert*-Butyl 3-(2-phenylethyl)-3-pentenoate (46d)

Colorless oil; IR (neat) 2978, 1732 (CO), 1496, 1455, 1368, 1257, 1148, 747, 699 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.54 (3H, d, *J*=6.7 Hz), 2.40–2.43 (2H, m), 2.66–2.69 (2H, m), 2.92 (2H, s), 5.39 (1H, q, *J*=6.7 Hz), 7.17–7.20 (3H, m), 7.25–7.29 (2H, m). MS *m*/*z* (%) 260 (M^+, 10), 204 (100), 187 (14), 175 (16), 144 (75), 143 (23), 117 (25), 104 (35), 91 (97), 57 (80). Calcd for $C_{17}H_{24}O_2$: M, 260.1777 Found: *m*/*z* 260.1776.

3.81. *tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)-hexanoate (47a)

Isolable main product derived from **28e**: colorless oil; IR (neat) 2978, 1732 (CO), 1597, 1456, 1368, 1255, 1151, 1058, 848, 756, 702 cm^{-1}; ^1H NMR δ 0.90 (3H, t, *J*=7.4 Hz), 1.27 (9H, s), 1.57 (1H, q, *J*=7.5 Hz), 1.98 (1H, q, *J*=7.5 Hz), 2.44 (3H, s), 2.71 (1H, dd, *J*=15.7, 10.0 Hz), 2.77 (1H, dd, *J*=15.7, 4.5 Hz), 4.30 (1H, dd, *J*=10.0, 4.5 Hz), 6.93 (1H, dd, *J*=5.1, 3.5 Hz), 7.00 (1H, dd, *J*=3.5, 0.8 Hz), 7.22 (1H, dd, *J*=5.1, 0.8 Hz), 7.34 (2H, d, *J*=8.1 Hz), 7.70 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 427 ($[M+H]^+$, 22), 371 (43), 353 (7), 317 (7), 263 (11), 231 (57), 195 (100), 194 (22), 140 (19), 139 (17), 57 (29). Calcd for $C_{21}H_{28}ClO_3S_2$: M, 427.1169. Found: *m*/*z* 427.1166.

3.82. *tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)-hexanoate (47a)

Isolable main product derived from **29e**: colorless oil; IR (neat) 2979, 1732 (CO), 1597, 1456, 1368, 1286, 1256, 1154, 1050, 848, 756 cm^{-1}; ^1H NMR δ 1.22 (9H, s), 1.25 (3H, t, *J*=7.6 Hz), 2.01–2.16 (2H, m), 2.45 (3H, s), 2.91 (1H, dd, *J*=16.2, 12.2 Hz), 3.59 (1H, dd, *J*=16.2, 2.9 Hz), 3.91 (1H, dd, *J*=12.2, 2.9 Hz), 6.91–6.96 (2H, m), 7.21 (1H, dd, *J*=4.8, 1.5 Hz), 7.35 (2H, d, *J*=8.1 Hz), 7.70 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 427 ($[M+H]^+$, 44), 371 (80), 353 (8), 317 (7), 231 (48), 195 (100), 154 (14), 140 (17), 123 (12), 57 (20). Calcd for $C_{21}H_{28}ClO_3S_2$: M, 427.1169. Found: *m*/*z* 427.1168.

3.83. *tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)-6-heptenoate (47b)

Isolable main product derived from **28e**: colorless oil; IR (neat) 2979, 1728 (CO), 1641, 1596, 1434, 1393, 1256, 1152, 1044, 845, 756, 703 cm^{-1}; ^1H NMR δ 1.24 (9H, s), 2.42 (3H, s), 2.58–2.80 (2H, m), 2.81 (1H, dd, *J*=14.7, 11.3 Hz), 2.91 (1H, dd, *J*=14.7, 3.9 Hz), 4.54 (1H, dd, *J*=11.3, 3.9 Hz), 5.09 (1H, dd, *J*=17.0, 1.4 Hz), 5.16 (1H, dd, *J*=10.2, 1.4 Hz), 6.08 (1H, dddd, *J*=17.0, 10.2, 8.4, 5.9 Hz), 7.02 (1H, dd, *J*=5.1, 3.9 Hz), 7.29–7.35 (4H, m), 7.65 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 439 ($[M+H]^+$, 49), 383 (100), 365 (10), 263 (29), 243 (69), 207 (95), 161 (29), 159 (48), 140 (36), 123 (21), 57 (53). Calcd for $C_{22}H_{28}ClO_3S_2$: M, 439.1169. Found: *m*/*z* 439.1171.

3.84. *tert*-Butyl 4-chloro-3-(2-thienyl)-4-(*p*-tolylsulfinyl)-6-heptenoate (47b)

Isolable main product derived from **29e**: colorless oil; IR (neat) 2979, 1732 (CO), 1640, 1597, 1429, 1368, 1256, 1153, 1051, 927, 812, 757 cm^{-1}; ^1H NMR δ 1.23 (9H, s), 2.45 (3H, s), 2.68–2.84 (2H, m), 2.91 (1H, dd, *J*=16.1, 12.0 Hz), 3.62 (1H, dd, *J*=16.1, 3.0 Hz), 3.92 (1H, dd, *J*=12.0, 3.0 Hz), 5.33 (1H, dd, *J*=5.5, 1.6 Hz), 5.37 (1H, d, *J*=0.9 Hz), 5.99 (1H, m), 6.94 (1H, dd, *J*=5.0, 3.6 Hz), 6.97 (1H, dd, *J*=3.6, 1.2 Hz), 7.23 (1H, dd, *J*=5.0, 1.2 Hz), 7.35 (2H, d, *J*=8.1 Hz), 7.68 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 439 ($[M+H]^+$, 36), 383 (100), 365 (11), 263 (8), 243 (34), 207 (81), 161 (25), 159 (36), 140 (28), 123 (22), 57 (48). Calcd for $C_{22}H_{28}ClO_3S_2$: M, 439.1168. Found: *m*/*z* 439.1163.

3.85. *tert*-Butyl 3-(2-thienyl)-4-hexenoate (48a)

Colorless oil (5:2 mixture of two diastereomers); IR (neat) 2978, 1732 (CO), 1456, 1393, 1368, 1255, 1151, 964, 848, 764, 695 cm^{-1}; ^1H NMR δ 1.39 (2.6H, s), 1.40 (6.4H, s), 1.67–1.68 (0.9H, m), 1.73 (2.1H, dd, *J*=6.6, 1.5 Hz), 2.53 (0.7H, dd, *J*=14.6, 8.6 Hz), 2.59 (0.3H, dd, *J*=14.7, 8.4 Hz), 2.67 (0.3H, dd, *J*=14.7, 7.0 Hz), 2.72 (0.7H, dd, *J*=14.6, 6.4 Hz), 4.00–4.05 (0.3H, m), 4.37–4.44 (0.7H, m), 5.47–5.62 (2H, m), 6.81 (0.3H, dt, *J*=3.5, 1.0 Hz), 6.83 (0.7H, dt, *J*=3.5, 1.2 Hz), 6.91 (0.7H, dd, *J*=5.1, 3.5 Hz), 6.92 (0.3H, dd, *J*=5.1, 3.5 Hz), 7.13 (0.7H, dd, *J*=5.1, 1.2 Hz), 7.14 (0.3H, dd, *J*=5.1, 1.0 Hz). MS *m*/*z* (%) 252 (M^+, 3), 196 (62), 195 (122), 179 (4), 149 (11), 137 (100), 135 (22), 97 (10), 57 (18). Calcd for $C_{14}H_{20}O_2S$: M, 252.1184. Found: *m*/*z* 252.1187.

3.86. *tert*-Butyl 3-(2-thienyl)-4,6-heptadienoate (48b)

Colorless oil (1:1 mixture of two diastereomers); IR (neat) 2978, 2930, 1729 (CO), 1456, 1368, 1256, 1152, 1040, 847, 699 cm^{-1}; ^1H NMR δ 1.39 (4.5H, s), 1.40 (4.5H, s), 2.56 (0.5H, dd, *J*=14.7, 8.7 Hz), 2.65 (0.5H, dd, *J*=14.8, 8.4 Hz), 2.72 (0.5H, dd, *J*=14.8, 7.0 Hz), 2.77 (0.5H, dd, *J*=14.7, 6.3 Hz), 4.09–4.17 (0.5H, m), 4.52–4.58 (0.5H, m), 5.03–5.29 (2H, m), 5.52 (0.5H, t, *J*=10.4 Hz), 5.81 (0.5H, dd, *J*=15.1, 7.9 Hz), 6.08 (0.5H, t, *J*=10.8 Hz), 6.13 (0.5H, dd, *J*=15.1, 10.4 Hz), 6.39 (0.5H, dt, *J*=16.9, 10.4 Hz), 6.76 (0.5H, dt, *J*=16.8, 10.8 Hz), 6.83–6.84 (1H, m), 6.91–6.94 (1H, m), 7.14–7.17 (1H, m). MS *m*/*z* (%) 264 (M^+, 9), 208 (61), 191 (11), 162 (14), 149 (100), 148 (61), 115 (25), 97 (12), 57 (31). Calcd for $C_{15}H_{20}O_2S$: M, 264.1184. Found: *m*/*z* 264.1185.

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