Tetrahedron 69 (2013) 1994–2003

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

Baylis–Hillman acetates in carbocyclic synthesis: a convenient protocol for synthesis of densely substituted indenes

Deevi Basavaiah *, Bhavanam Sekhara Reddy, Harathi Lingam

School of Chemistry, University of Hyderabad, Central University (PO), Gachibowli, Hyderabad 500 046, India

ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form 20 December 2012
Accepted 26 December 2012
Available online 3 January 2013

Keywords:
Baylis–Hillman reaction
Friedel–Crafts reaction
Chemo selectivity
Indene derivatives
Keto-diesters

ABSTRACT

A simple and facile strategy for synthesis of densely substituted indenes have been developed from Baylis–Hillman acetates in a two step protocol, that is, (1) via treatment with DABCO and then reaction with alkyl 3-oxobutanoates in the presence of K_2CO_3 (2) followed by the intramolecular Friedel–Crafts cyclization of the resulting keto-diesters using titanium tetrachloride.

1. Introduction

Friedel–Crafts reaction is one of the important and useful reactions for construction of carbon–carbon bonds and has been extensively used in various organic synthetic processes.[1] Intramolecular Friedel–Crafts reaction is one of the methods of choice for synthesis of many carbocyclic and heterocyclic molecules.[1,2] Indene/indane derivatives occupy an important place in the carbocyclic frameworks because of the presence of these moieties in various natural products (**1**–**3**, Fig. 1)[3] and bioactive compounds (**4**–**8**, Fig. 1).[4] Therefore, there has been increasing interest in the development of simple and facile procedures for synthesis of indene/indane derivatives via intramolecular Friedel–Crafts cyclization strategies.[5] In continuation of our interest in the synthesis of carbocyclic compounds,[6] we herein report a facile two-step methodology for obtaining highly substituted indene derivatives starting from the Baylis–Hillman acetates using the intramolecular Friedel–Crafts reaction as the key step.

2. Results and discussion

The Baylis–Hillman reaction has been and continues to attract the attention of synthetic chemists as it provides densely functionalized molecules via an interesting atom economy coupling of activated alkenes with electrophiles under the influence of a catalyst.[7] Synthetic and medicinal chemists have used these densely functionalized molecules, which are generally known as the Baylis–Hillman adducts, in developing a number of useful organic transformation protocols.[7,8]

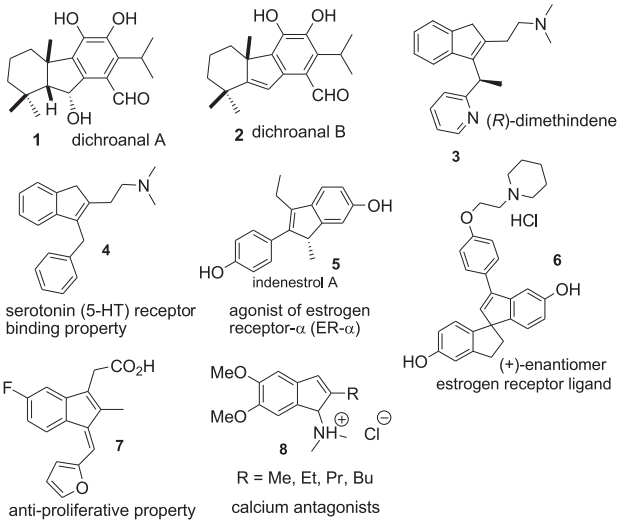
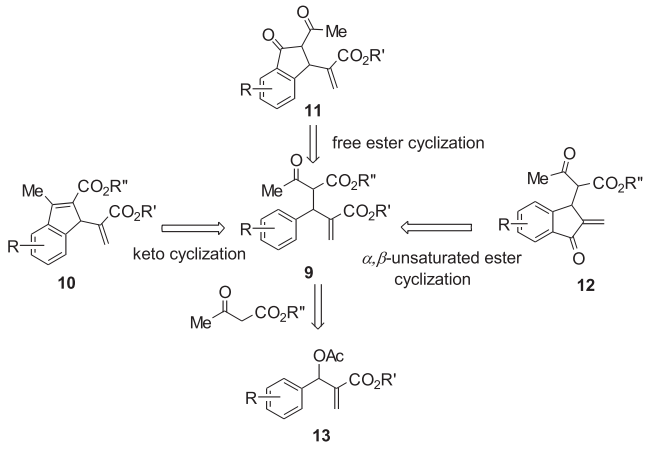


Fig. 1. Natural products and bioactive molecules with ind(a)ene framework.

* Corresponding author. Tel.: +91 040 23134812; fax: +91 40 23012460; e-mail address: dbsc@uohyd.ernet.in (D. Basavaiah).

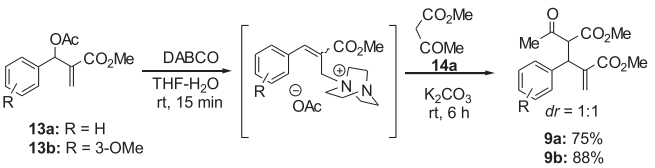
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.12.069

Several years ago we demonstrated the application of various Baylis–Hillman adducts and their derivatives as substrates in a number of Friedel–Crafts reactions.[9] On the basis of this experience it occurred to us that it would be interesting to examine the intramolecular Friedel–Crafts (F–C) reaction of aromatic substrates (**9**) containing one keto and two ester functionalities, as such study will not only provide densely substituted indene or (and) indanone derivatives but will also throw some light on the mechanism and chemoselectivities of these intramolecular Friedel–Crafts (F–C) reactions. Theoretically there is a possibility of formation of three products, that is, (1) keto cyclization product (**10**) (2) free ester cyclization product (**11**) (3) α,β-unsaturated ester cyclization product (**12**) (Scheme 1). We also felt that such aromatic substrates (**9**) containing one keto and two ester functionalities would easily be obtained from the Baylis–Hillman acetates (**13**) via the reaction with suitable nucleophiles as shown in retro-synthetic sequence (Scheme 1).



Scheme 1. Retro-synthetic strategy.

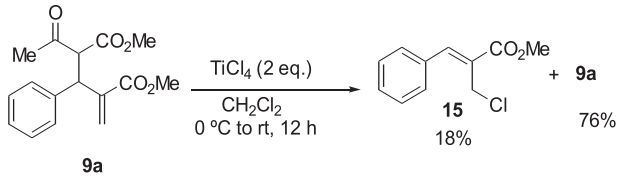
Accordingly we have first selected methyl 3-acetoxy-2-methylene-3-phenylpropanoate (**13a**) and methyl acetoacetate (**14a**) as reaction partners. Thus the treatment of **13a** (10 mmol) with DABCO (10 mmol) followed by the reaction with **14a** (11 mmol) in the presence of K_2CO_3 (11 mmol) in THF–H_2O (1:1) provided the desired keto-diester **9a** in 75% isolated yield as a mixture of diastereomers (1:1) (R=H, Scheme 2).[10]



Scheme 2. Synthesis of **9a** and **9b**.

We have then examined the intramolecular Friedel–Crafts reaction of **9a** under different conditions and our attempts were not successful for obtaining any cyclized product (**10a**, **11a** or **12a** R=H, R′=R″=Me). We also noticed the formation of methyl (2*Z*)-2-(chloromethyl)-3-phenylprop-2-enoate (**15**) in 18% yield along with un-reacted starting material **9a** (76% recovered yield) when $TiCl_4$ was used to perform the intramolecular Friedel–Crafts reaction (Scheme 3).[11]

We have attributed the failure of intramolecular Friedel–Crafts reaction of **9a** to the less nucleophilicity of aromatic carbon(s) for cyclization. At this stage, it occurred to us that electron donating group on aromatic ring at appropriate position may enhance the nucleophilicity of (*para* and/or *ortho*) carbon on the aromatic ring to facilitate the intramolecular Friedel–Crafts cyclization. Accordingly we selected methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-

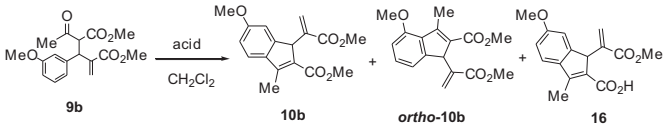


Scheme 3. Reaction of **9a** with titanium tetrachloride.

methylene-5-oxohexanoate (**9b**) as a substrate to examine the intramolecular Friedel–Crafts reaction. The required keto-diester **9b** was prepared from methyl 3-acetoxy-3-(3-methoxyphenyl)-2-methylenepropanoate (**13b**) according to the reaction followed for synthesis of keto-diester **9a**. Thus the treatment of allyl acetate **13b** (5 mmol) with DABCO (5 mmol) for 15 min at room temperature in THF–H_2O (1:1) followed by reaction with methyl acetoacetate (**14a**) (5.5 mmol), in the presence of K_2CO_3 (5.5 mmol) at room temperature for 6 h provided **9b** in 88% isolated yield (dr ≈ 1:1) (*R*=3-OMe, Scheme 2).

For initial studies we have treated **9b** (1 mmol), with methanesulfonic acid (2 mmol) in anhydrous dichloromethane (2 mL), at room temperature for 1 h (addition at 0 °C), which provided *para* cyclization product **10b** and *ortho*-cyclization product *ortho*-**10b** in 19% and 2% isolated yields, respectively (entry 1, Table 1) along with 65% un-reacted starting material **9b**. With a view to confirm the structures of molecules **10b** and *ortho*-**10b**, we also obtained single crystal for these compounds and established their structures by X-ray data analysis (Figs. 2 and 3).[12]

Table 1
Optimization: intramolecular Friedel–Crafts cyclization of **9b**[a]



Entry	Condition(s)	Product yields[b] [%]		
		10b	*ortho*-**10b**	**16**
1	$MeSO_3H$ (2 equiv), 0 °C to rt, 1 h	19	2	—
2	H_2SO_4 (2 equiv), 0 °C to rt, 1 h	46	10	35
3	H_2SO_4 (1 equiv), 0 °C to rt, 1 h	61	10	7
4	$BF_3.OEt_2$ (2 equiv), 0 °C to rt, 1 h	60	7	—
5	**$TiCl_4$ (2 equiv), 0 °C to rt, 1 h**	**76**	**20**	—
6	$TiCl_4$ (1 equiv), 0 °C to rt, 4 h	61	8	—

Bold value indicates highest yield (optimized condition).
[a] All reactions were carried out on a 1 mmol scale of keto-diester **9b** with acid in CH_2Cl_2 (2 mL).
[b] Yields were based on keto-diester **9b**.

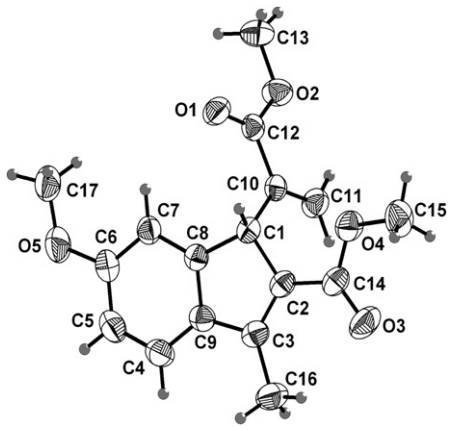


Fig. 2. ORTEP diagram of compound **10b**.

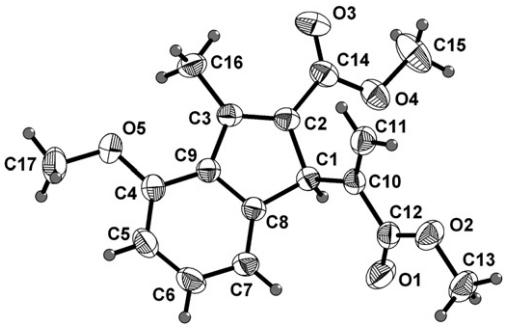
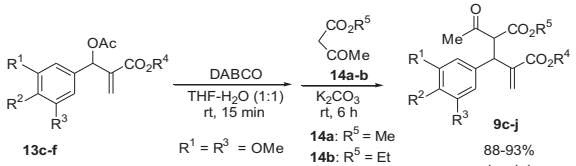


Fig. 3. ORTEP diagram of compound *ortho*-**10b**.

This reaction is indeed encouraging and clearly indicates that ketone functionality takes part in Friedel–Crafts cyclization in preference over ester function even in the presence of two ester functionalities.[13] With a view to increase the yield of the indene derivatives in this reaction strategy, we have examined applicability of various Bronsted and Lewis acids. In this direction we realized that $TiCl_4$ afforded better yields (entry 5, Table 1). Thus, treatment of **9b** (1 mmol) with $TiCl_4$ (2 mmol, 2 M solution in DCM) as a Lewis acid in dichloromethane (DCM) at room temperature for 1 h (addition at 0 °C), provided **10b** (*para* cyclization product) in 76% and *ortho*-**10b** (*ortho*-cyclization product) in 20% isolated yields after usual work-up followed by column chromatography. When H_2SO_4 was used as a reagent for cyclization, ester group at C-3 position underwent hydrolysis and provided 6-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylic acid (**16**) in 35% isolated yield along with expected indene esters **10b** & *ortho*-**10b** in 46 & 10% yields, respectively.

With a view to understand the generality of this reaction we have prepared representative keto-diesters **9c–j** in 88–93% isolated yields (dr ≈ 1:1) via the reaction of selected Baylis–Hillman acetates **13c–f** with DABCO followed by treatment with alkyl acetoacetates (**14a**/**14b**) under similar conditions as in the case of **13a** (or **13b**) (Table 2). Subsequent treatment of these keto-diesters **9c–j** with $TiCl_4$ at room temperature (addition at 0 °C) provided the resulting indene derivatives (**10c–j**) in 91–95% isolated yields (Table 3). Structures of the molecules **10c**, **10e**, and **10h** were further confirmed by single crystal X-ray data analysis (See SD) [for ORTEP diagram of **10h** (see Fig. 4)].[12]

Table 2
Synthesis of keto-diesters **9c–j**[a]



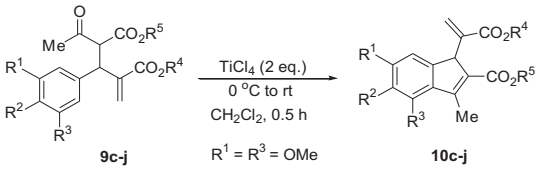
Entry	Acetate	R^2	R^4	Keto-ester	Product[b]	Yield[c] [%]
1	**13c**	H	Me	**14a**	**9c**	93
2	**13d**	OMe	Me	**14a**	**9d**	88
3	**13e**	H	Et	**14a**	**9e**	94
4	**13f**	OMe	Et	**14a**	**9f**	89
5	**13c**	H	Me	**14b**	**9g**	91
6	**13d**	OMe	Me	**14b**	**9h**	93
7	**13e**	H	Et	**14b**	**9i**	92
8	**13f**	OMe	Et	**14b**	**9j**	90

[a] All reactions were carried out on a 5 mmol scale of Baylis–Hillman acetates (**13c–f**) with 5 mmol of DABCO in THF–H_2O (5+5 mL) at rt for 15 min followed by addition of 5.5 mmol of keto ester (**14a** or **14b**) under influence of K_2CO_3 (5.5 mmol) and stirred at room temperature for 6 h.

[b] The diastereomeric ratio was determined by the integration ratio of diastereomeric acetyl methyl protons.

[c] Yields are based on B–H acetates.

Table 3
Synthesis of highly substituted indene derivatives (**10c–j**)[a]



Entry	Keto-diester	R^2	R^4	R^5	Product	Yield[b] [%]
1	**9c**	H	Me	Me	**10c**[c]	94
2	**9d**	OMe	Me	Me	**10d**	92
3	**9e**	H	Et	Me	**10e**[c]	90
4	**9f**	OMe	Et	Me	**10f**	93
5	**9g**	H	Me	Et	**10g**	95
6	**9h**	OMe	Me	Et	**10h**[c]	91
7	**9i**	H	Et	Et	**10i**	94
8	**9j**	OMe	Et	Et	**10j**	93

[a] All reactions were carried out on 1.0 mmol scale of keto-diesters (**9c–j**) with 2 mmol of $TiCl_4$ (1 mL, 2 M solution in CH_2Cl_2) in CH_2Cl_2 (2 mL) at room temperature for 0.5 h.

[b] Yields are based on keto-diesters.

[c] Compound **10c**, **10e**, and **10h** were further characterized by single crystal X-ray data analysis (see SD).[12]

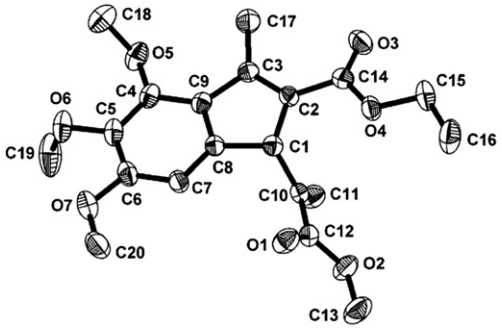
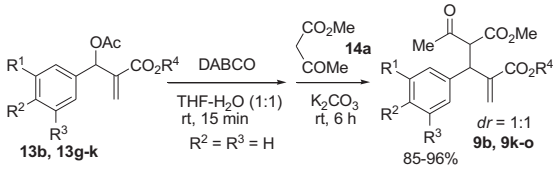


Fig. 4. ORTEP diagram of compound **10h**.

After successful transformations of keto-diesters into highly substituted indene derivatives we also investigated the *ortho–para* selectivity in intramolecular Friedel–Crafts reactions. In this direction we have prepared selected Baylis–Hillman acetates **13g–k** and transformed them into keto-diesters (**9k–o**) in 85–96% isolated yields (in 1:1 diastereomeric ratio) (Table 4). Subsequent

Table 4
Synthesis of keto-diesters (**9b**, **9k–o**)[a]



Entry	Acetate	R^1	R^4	Product[b]	Yield[c] [%]
1	**13b**	OMe	Me	**9b**	88
2	**13g**	OEt	Me	**9k**	92
3	**13h**	OPr	Me	**9l**	96
4	**13i**	OMe	Et	**9m**	85
5	**13j**	OEt	Et	**9n**	86
6	**13k**	OPr	Et	**9o**	91

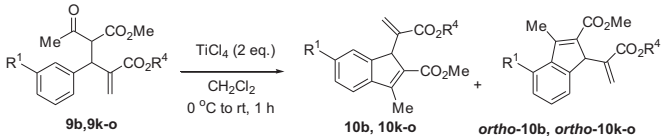
[a] All reactions were carried out on 5 mmol scale of Baylis–Hillman acetates (**13b**, **13g–k**) with 5 mmol of DABCO in THF–H_2O (5+5 mL) at rt for 15 min followed by addition of 5.5 mmol of methyl acetoacetate (**14a**) under influence of K_2CO_3 (5.5 mmol) and stirred at room temperature for 6 h.

[b] The diastereomeric ratio was determined by the integration ratio of diastereomeric acetyl methyl protons.

[c] Yields are based on B–H acetates.

treatment with $TiCl_4$ under similar conditions as in the case of **10b**–**j** gave the *para* cyclized products in major amounts along with *ortho* cyclized products in minor amounts (Table 5). The structures of the molecules **10k**, *ortho*-**10k**, and **10m** were also established by single crystal X-ray data analysis (see SD).[12]

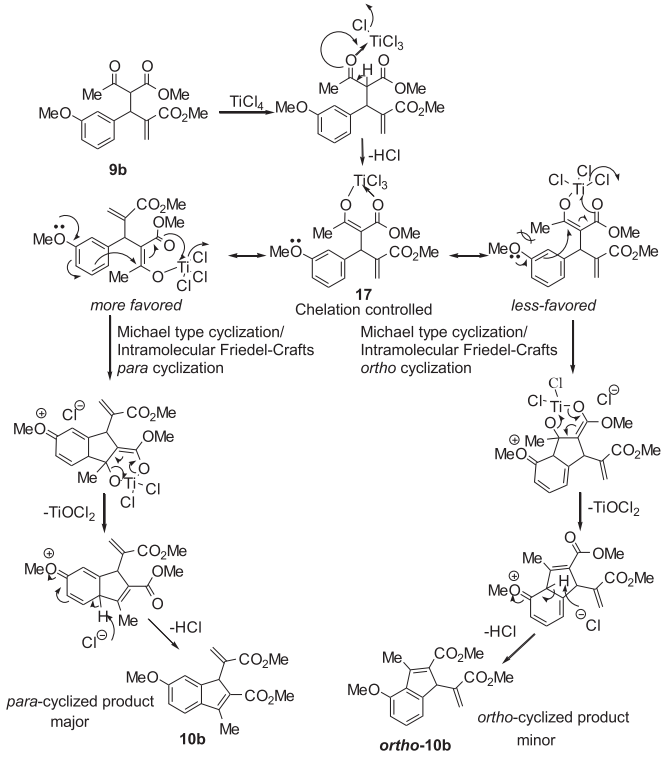
Table 5
Synthesis of indene derivatives (**10b**, **10k**–**o**, *ortho*-**10b** & *ortho*-**10k**–**o**)[a]



Entry	Keto-diester	R^1	R^4	Product	Yield[b] [%]
1	**9b**	OMe	Me	**10b**/*ortho* **10b**	76/20
2	**9k**	OEt	Me	**10k**[c]/*ortho*-**10k**[c]	73/21
3	**9l**	OPr	Me	**10l**/*ortho*-**10l**	75/19
4	**9m**	OMe	Et	**10m**[c]/*ortho*-**10m**	74/20
5	**9n**	OEt	Et	**10n**/*ortho*-**10n**	76/18
6	**9o**	OPr	Et	**10o**/*ortho*-**10o**	72/17

[a] All reactions were carried out on a 1.0 mmol scale of keto-diesters (**9b**, **9k**–**o**) with 2 mmol of $TiCl_4$ (1 mL, 2 M solution in CH_2Cl_2) in CH_2Cl_2 (2 mL) at room temperature for 1 h.
[b] Yields are based on keto-diesters.
[c] Compounds **10k**, *ortho*-**10k**, and **10m** were further characterized by single crystal X-ray data (see SD).[12]

Mechanism for the formation of highly substituted indene derivatives from the keto-diesters is presented in Scheme 4, by taking reaction between methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9b**) and $TiCl_4$ as a model case.[13] Treatment of keto-diester with $TiCl_4$ would generate titanium enolate intermediate (**17**) that might undergo further intramolecular Michael/Friedel–Crafts reactions leading to the formation of the indene derivatives, **10b** & *ortho*-**10b**. It is believed that chelation controlled titanium enolate species directs the mode of cyclization.



Scheme 4. Plausible mechanism.

3. Conclusion

In conclusion we have developed a convenient, operationally simple synthesis of highly substituted indene derivatives from the acetates of the Baylis–Hillman adducts in a two step protocol. This study also throws some light on the competition between keto cyclization and ester cyclization for intramolecular Friedel–Crafts reaction in the substrates alkyl 4-alkoxycarbonyl-3-(alkoxyphenyl)-2-methylene-5-oxohexanoates (**9**) containing two ester groups and one keto group in a similar environment. In all these reactions keto cyclization is preferred over ester cyclization even in the presence of two ester groups. Thus this investigation has demonstrated the importance of the Baylis–Hillman acetates for designing probes to understanding the chemoselectivity[13] profile in intramolecular Friedel–Crafts reactions.

4. Experimental section

4.1. General remarks

Melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer, solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker-AVANCE-400 spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS, δ=0) as an internal standard for ^{1}H NMR and chloroform-*d* middle peak of the triplet (δ=77.10 ppm) as an internal standard for ^{13}C NMR. HRMS spectra were recorded on Bruker maXis ESI-TOF spectrometer. The X-ray diffraction measurements were carried out at 298 K on a Bruker SMART APEX CCD area detector system or Oxford Diffraction Xcalibur Eos Gemini diffractometer equipped with a graphite-mono-chromated Mo-Kα radiation with the wavelength of 0.71073 Å.

4.2. Representative procedure

*4.2.1. Synthesis of methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-phenylhexanoate (**9a**).* To a stirred solution of methyl 3-acetoxy-2-methylene-3-phenylpropanoate (**13a**) (10 mmol, 2.342 g) in THF–H_2O (20 mL, 1:1) was added DABCO (10 mmol, 1.121 g) at room temperature and reaction mixture was stirred at the same temperature for 15 min (until complete formation of salt monitored by TLC). Methyl acetoacetate (**14a**) (11 mmol, 1.277 g) and K_2CO_3 (11 mmol, 1.520 g) were added and stirring was continued for further 6 h at room temperature. Reaction mixture was quenched by adding 2 N HCl (10 mL), and extracted with diethyl ether (3×40 mL). Combined organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated and crude product obtained was purified by column chromatography (5% ethyl acetate in hexanes, silica gel) to provide the title compound as a colorless viscous liquid in 75% (2.180 g) isolated yield. This compound is known in the literature. Spectral data of our compound are in agreement with the known data.[10]

Reaction time: 15 min+6 h; yield: 75%; R_f (20% EtOAc in hexanes) 0.41; colorless viscous liquid; IR (neat): ν 1743, 1716, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.96 & 2.27 (2s, 3H), 3.47, 3.67, 3.68 & 3.70 (4s, 6H), 4.38 & 4.41 (2d, 1H, J=12.4 Hz), 4.71 & 4.73 (2d, 1H, J=12.4 Hz), 5.70 & 5.76 (2s, 1H), 6.27 & 6.29 (2s, 1H), 7.17–7.32 (m, 5H); ^{13}C NMR (100 MHz): δ 28.96, 30.55, 46.01, 46.13, 51.96, 52.01, 52.42, 52.65, 63.28, 64.38, 124.23, 125.16, 127.21, 127.30, 128.18, 128.39, 128.42, 128.60, 138.42, 138.77, 140.59, 141.23, 166.23, 166.38, 167.92, 167.99, 201.21, 201.33; HRMS (ESI) exact mass calcd for $C_{16}H_{18}O_5Na^+$ $(M+Na)^+$: 313.1052, found: 313.1049.

^{1}H & ^{13}C NMR spectra clearly indicate that it is a mixture of two diastereomers almost in 1:1 ratio. The diastereomeric ratio was determined by the integration ratio of diastereomeric acetyl methyl protons.

Methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9b**) (dr ≈ 1:1) was prepared in 88% isolated yield via the treatment of allyl acetate **13b** (5 mmol) with DABCO (5 mmol) for 15 min at room temperature in THF–H_2O (1:1) followed by reaction with methyl acetoacetate (**14a**) (5.5 mmol), in the presence of K_2CO_3 (5.5 mmol) at room temperature for 6 h. Similarly all the remaining keto-diesters **9c**–**o** were prepared in the similar manner from the corresponding BH acetates (**13c**–**k**) (5 mmol) and alkyl acetoacetates (**14a**, **b**) (5.5 mmol). The compounds **9c**–**o** were also obtained as a mixture of two diastereomers almost in 1:1 ratio. The diastereomeric ratio was determined by the integration ratio of diastereomeric acetyl methyl protons.

*4.2.2. Methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9b**).* Reaction time: 15 min+6 h; yield: 88%; R_f (20% EtOAc in hexanes) 0.25; colorless viscous liquid; IR (neat): ν 1745, 1724, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.99 & 2.27 (2s, 3H), 3.50, 3.68, 3.69 & 3.70 (4s, 6H), 3.76 & 3.77 (2s, 3H), 4.38 & 4.39 (2d, 1H, J=12.4 Hz), 4.68 & 4.71 (2d, 1H, J=12.4 Hz), 5.69 & 5.74 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.71–6.88 (m, 3H), 7.15–7.22 (m, 1H); ^{13}C NMR (100 MHz): δ 28.92, 30.51, 45.94, 46.06, 51.90, 51.96, 52.39, 52.55, 55.04, 63.21, 64.31, 112.42, 114.08, 114.43, 120.41, 120.57, 124.33, 125.27, 129.35, 129.53, 140.08, 140.44, 140.55, 141.18, 159.50, 159.59, 166.20, 166.36, 167.86, 167.92, 201.07, 201.18; HRMS (ESI) exact mass calcd for $C_{17}H_{20}O_6Na^+$ (M+Na)$^+$: 343.1158, found: 343.1153.

*4.2.3. Methyl 3-(3,5-dimethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9c**).* Reaction time: 15 min+6 h; yield: 93%; R_f (40% EtOAc in hexanes) 0.38; colorless solid; mp: 76–79 °C; IR (KBr): ν 1747, 1714, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.02 & 2.26 (2s, 3H), 3.54, 3.69, 3.700 & 3.706 (4s, 6H), 3.750 & 3.753 (2s, 6H), 4.36 & 4.37 (2d, 1H, J=12.4 Hz), 4.64 & 4.67 (2d, 1H, J=12.4 Hz), 5.67 & 5.72 (2s, 1H), 6.25–6.33 (m, 2H), 6.39 (d, 1H, J=2.4 Hz), 6. 41 (d, 1H, J=2.0 Hz), ^{13}C NMR (100 MHz): δ 29.05, 30.81, 46.08, 46.21, 52.07, 52.13, 52.60, 52.71, 55.26, 63.23, 64.38, 98.95, 99.00, 106.34, 106.65, 124.55, 125.58, 140.43, 140.92, 141.08, 141.29, 160.65, 160.77, 166.31, 166.47, 167.94, 201.28, 201.41; HRMS (ESI) exact mass calcd for $C_{18}H_{22}O_7Na^+$ (M+Na)$^+$: 373.1263, found: 373.1266.

*4.2.4. Methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3,4,5-trimethoxyphenyl)hexanoate (**9d**).* Reaction time: (15 min+6 h); yield: 88%; R_f (50% EtOAc in hexanes) 0.48; colorless solid; mp: 64–65 °C; IR (KBr): ν 1747, 1718, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.01 & 2.27 (2s, 3H), 3.53, 3.70, 3.71 & 3.72 (4s, 6H), 3.79 & 3.80 (2s, 3H), 3.824 & 3.827 (2s, 6H), 4.39 & 4.40 (2d, 1H, J=12.4 Hz), 4.64 & 4.66 (2d, 1H, J=12.4 Hz), 5.69 & 5.74 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.46 & 6.48 (2s, 2H); ^{13}C NMR (100 MHz): δ 28.97, 30.75, 46.32, 46.46, 52.05, 52.10, 52.56, 52.68, 56.00, 56.05, 60.70, 63.23, 64.35, 105.16, 105.43, 124.36, 125.39, 133.96, 134.36, 136.93, 137.03, 140.45, 141.07, 152.94, 153.09, 166.30, 166.47, 167.87, 167.94, 201.17, 201.45; HRMS (ESI) exact mass calcd for $C_{19}H_{24}O_8Na^+$ (M+Na)$^+$: 403.1369, found: 403.1366.

*4.2.5. Ethyl 3-(3,5-dimethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9e**).* Reaction time: (15 min+6 h); yield: 94%; R_f (40% EtOAc in hexanes) 0.46; colorless viscous liquid; IR (neat): ν 1745, 1718, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.23 & 1.24 (2t, 3H, J=7.2 Hz), 2.01 & 2.26 (2s, 3H), 3.54 & 3.69 (2s, 3H), 3.74 & 3.75 (2s, 6H), 4.07–4.22 (m, 2H), 4.36 (d, 1H, J=12.4 Hz), 4.60–4.70 (m, 1H), 5.65 & 5.70 (2s, 1H), 6.25–6.32 (m, 2H), 6.39 (d, 1H, J=2.0 Hz), 6.41 (d, 1H, J=2.0 Hz); ^{13}C NMR (100 MHz): δ 14.02, 29.01, 30.81, 46.09, 46.23, 52.54, 52.65, 55.22, 60.97, 61.04, 63.21, 64.35, 98.93, 98.98, 106.35, 106.67, 124.24, 125.30, 140.66, 141.00, 141.30, 141.38, 160.61, 160.72, 165.82, 165.99, 167.96, 201.28, 201.46; HRMS (ESI) exact mass calcd for $C_{19}H_{24}O_7Na^+$ (M+Na)$^+$: 387.1420, found: 387.1417.

*4.2.6. Ethyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3,4,5-trimethoxyphenyl)hexanoate (**9f**).* Reaction time: (15 min+6 h); yield: 89%; R_f (50% EtOAc in hexanes) 0.55; colorless viscous liquid; IR (neat): ν 1745, 1716, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.24 & 1.25 (2t, 3H, J=6.8 Hz), 2.00 & 2.27 (2s, 3H), 3.53 & 3.70 (2s, 3H), 3.79, 3.80 & 3.82 (3s, 9H), 4.07–4.26 (m, 2H), 4.38 (d, 1H, J=12.4 Hz), 4.64 & 4.65 (2d, 1H, J=12.0 Hz), 5.66 & 5.71 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.46 & 6.48 (2s, 2H); ^{13}C NMR (100 MHz): δ 14.02, 28.97, 30.81, 46.38, 46.52, 52.55, 52.67, 56.01, 56.06, 60.73, 61.00, 61.06, 63.27, 64.39, 105.22, 105.50, 124.09, 125.15, 134.10, 134.50, 136.95, 137.05, 140.72, 141.34, 152.94, 153.09, 165.87, 166.04, 167.90, 168.00, 201.21, 201.54; HRMS (ESI) exact mass calcd for $C_{20}H_{26}O_8Na^+$ (M+Na)$^+$: 417.1525, found: 417.1528.

*4.2.7. Methyl 3-(3,5-dimethoxyphenyl)-4-ethoxycarbonyl-2-methylene-5-oxohexanoate (**9g**).* Reaction time: (15 min+6 h); yield: 91%; R_f (40% EtOAc in hexanes) 0.46; colorless solid, mp: 59–61 °C; IR (KBr): ν 1741, 1712, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.04 & 1.22 (2t, 3H, J=7.2 Hz), 2.03 & 2.26 (2s, 3H), 3.701 & 3.707 (2s, 3H), 3.75 (s, 6H), 3.98 & 4.15 (2q, 2H, J=7.2 Hz), 4.34 & 4.35 (2d, 1H, J=12.0 Hz), 4.65 (d, 1H, J=12.4 Hz), 5.67 & 5.74 (2s, 1H), 6.23–6.35 (m, 2H), 6.37–6.46 (m, 2H); ^{13}C NMR (100 MHz): δ 13.80, 14.00, 28.98, 30.70, 46.04, 46.09, 52.04, 52.10, 55.26, 61.55, 61.67, 63.48, 64.53, 98.95, 99.03, 106.51, 106.63, 124.59, 125.40, 140.60, 141.09, 141.14, 141.31, 160.63, 160.76, 166.34, 166.51, 167.47, 201.36, 201.42; HRMS (ESI) exact mass calcd for $C_{19}H_{24}O_7Na^+$ (M+Na)$^+$: 387.1420, found: 387.1418.

*4.2.8. Methyl 4-ethoxycarbonyl-2-methylene-5-oxo-3-(3,4,5-trimethoxyphenyl)hexanoate (**9h**).* Reaction time: (15 min+6 h); yield: 93%; R_f (50% EtOAc in hexanes) 0.56; colorless low melting solid; mp: 48–50 °C; IR (neat): ν 1747, 1718, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.02 & 1.23 (2t, 3H, J=7.2 Hz), 2.02 & 2.27 (2s, 3H), 3.71 & 3.72 (2s, 3H), 3.79 & 3.82 (2s, 9H), 3.97 & 4.16 (2q, 2H, J=7.2 Hz), 4.37 & 4.38 (2d, 1H, J=12.4 Hz), 4.65 (d, 1H, J=12.4 Hz), 5.69 & 5.75 (2s, 1H), 6.26 & 6.29 (2s, 1H), 6.47 & 6.49 (2s, 2H); ^{13}C NMR (100 MHz): δ 13.82, 14.00, 28.94, 30.70, 46.36, 46.39, 52.08, 52.13, 56.07, 56.10, 60.76, 61.54, 61.70, 63.55, 64.55, 105.40, 105.48, 124.43, 125.24, 134.16, 134.44, 137.04, 140.64, 141.19, 152.96, 153.13, 166.37, 166.54, 167.40, 167.55, 201.30, 201.51; HRMS (ESI) exact mass calcd for $C_{20}H_{26}O_8Na^+$ (M+Na)$^+$: 417.1525, found: 417.1527.

*4.2.9. Ethyl 3-(3,5-dimethoxyphenyl)-4-ethoxycarbonyl-2-methylene-5-oxohexanoate (**9i**).* Reaction time: (15 min+6 h); yield: 92%; R_f (40% EtOAc in hexanes) 0.37; colorless viscous liquid; IR (neat): ν 1741, 1716, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ [1.03 (t, J=7.2 Hz) & 1.19–1.29 (m) (6H)], 2.02 & 2.27 (2s, 3H), 3.74 (s, 6H), 3.98 (q, 1H, J=7.2 Hz), 4.07–4.22 (m, 3H), 4.33 & 4.35 (2d, 1H, J=12.0 Hz), 4.64 & 4.65 (2d, 1H, J=12.0 Hz), 5.65 & 5.71 (2s, 1H), 6.24–6.33 (m, 2H), 6.40 & 6.42 (2d, 2H, J=2.0 Hz); ^{13}C NMR (100 MHz): δ 13.76, 13.96, 14.02, 28.93, 30.70, 46.03, 46.10, 55.21, 60.93, 61.01, 61.49, 61.60, 63.44, 64.48, 98.91, 98.98, 106.50, 106.64, 124.26, 125.10, 140.80, 141.14, 141.36, 160.57, 160.70, 165.82, 166.00, 167.44, 167.48, 201.35, 201.46; HRMS (ESI) exact mass calcd for $C_{20}H_{26}O_7Na^+$ (M+Na)$^+$: 401.1576, found: 401.1578.

*4.2.10. Ethyl 4-ethoxycarbonyl-2-methylene-5-oxo-3-(3,4,5-trimethoxyphenyl)hexanoate (**9j**).* Reaction time: (15 min+6 h); yield: 90%; R_f (50% EtOAc in hexanes) 0.51; colorless low melting solid; mp: 45–47 °C; IR (neat): ν 1743, 1716, 1630 cm^{-1}; ^{1}H NMR

(400 MHz): δ [1.01 (t, J=6.8 Hz) & 1.19–1.31 (m) (6H)], 2.01 & 2.27 (2s, 3H), 3.79, 3.821 & 3.825 (3s, 9H), 3.97 (q, 1H, J=6.8 Hz), 4.08–4.25 (m, 3H), 4.36 & 4.37 (2d, 1H, J=12.4 Hz), 4.62 (d, 1H, J=12.4 Hz), 5.66 & 5.73 (2s, 1H), 6.26 & 6.29 (2s, 1H), 6.46 & 6.49 (2s, 2H); ^{13}C NMR (100 MHz): δ 13.75, 13.92, 14.00, 28.87, 30.68, 46.30, 46.35, 55.99, 60.67, 60.93, 61.00, 61.44, 61.60, 63.48, 64.47, 105.37, 105.46, 124.08, 124.89, 134.22, 134.51, 136.95, 140.83, 141.36, 152.87, 153.03, 165.84, 166.01, 167.34, 167.52, 201.23, 201.52; HRMS (ESI) exact mass calcd for $C_{21}H_{28}O_8Na^+$ $(M+Na)^+$: 431.1682, found: 431.1684.

*4.2.11. Methyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9k**).* Reaction time: (15 min+6 h); yield: 92%; R_f (20% EtOAc in hexanes) 0.35; colorless solid; mp: 64–66 °C; IR (KBr): ν 1753, 1716, 1631 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.39 (t, 3H, J=7.2 Hz), 1.98 & 2.27 (2s, 3H), 3.50, 3.68, 3.694 & 3.699 (4s, 6H), 3.98 & 3.99 (2q, 2H, J=6.8 Hz), 4.37 & 4.38 (2d, 1H, J=12.4 Hz), 4.67 & 4.70 (2d, 1H, J=12.4 Hz), 5.68 & 5.73 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.69–6.87 (m, 3H), 7.12–7.21 (m, 1H); ^{13}C NMR (100 MHz): δ 14.80, 29.02, 30.71, 46.05, 46.16, 52.06, 52.11, 52.55, 52.71, 63.36, 64.50, 113.15, 114.60, 114.94, 120.44, 120.61, 124.38, 125.40, 129.44, 129.63, 140.04, 140.41, 140.60, 141.24, 158.94, 159.05, 166.33, 166.49, 167.99, 168.06, 201.33, 201.44; HRMS (ESI) exact mass calcd for $C_{18}H_{22}O_6Na^+$ $(M+Na)^+$: 357.1314, found: 357.1318.

*4.2.12. Methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9l**).* Reaction time: (15 min+6 h); yield: 96%; R_f (20% EtOAc in hexanes) 0.36; colorless viscous liquid; IR (neat): ν 1741, 1722, 1635 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.02 (t, 3H, J=7.2 Hz), 1.73–1.84 (m, 2H), 1.98 & 2.27 (2s, 3H), 3.50, 3.68, 3.694 & 3.698 (4s, 6H), 3.86 & 3.87 (2t, 2H, J=6.4 Hz), 4.37 & 4.39 (2d, 1H, J=12.4 Hz), 4.67 & 4.70 (2d, 1H, J=12.4 Hz), 5.68 & 5.74 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.70–6.87 (m, 3H), 7.12–7.20 (m, 1H); ^{13}C NMR (100 MHz): δ 10.54, 22.57, 29.03, 30.74, 46.01, 46.14, 52.07, 52.12, 52.56, 52.73, 63.35, 64.50, 69.37, 113.17, 114.57, 114.88, 120.34, 120.52, 124.39, 125.41, 129.42, 129.60, 139.98, 140.35, 140.56, 141.21, 159.12, 159.22, 166.33, 166.48, 167.98, 168.05, 201.37, 201.49; HRMS (ESI) exact mass calcd for $C_{19}H_{24}O_6Na^+$ $(M+Na)^+$: 371.1471, found: 371.1472.

*4.2.13. Ethyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9m**).* Reaction time: (15 min+6 h); yield: 85%; R_f (20% EtOAc in hexanes) 0.37; colorless viscous liquid; IR (neat): ν 1747, 1718, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.22 & 1.23 (2t, 3H, J=7.2 Hz), 1.98 & 2.27 (2s, 3H), 3.50 & 3.70 (2s, 3H), 3.76 & 3.77 (2s, 3H), 4.05–4.21 (m, 2H), 4.37 & 4.39 (2d, 1H, J=12.4 Hz), 4.67 & 4.70 (2d, 1H, J=12.0 Hz), 5.66 & 5.72 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.69–6.88 (m, 3H), 7.13–7.22 (m, 1H); ^{13}C NMR (100 MHz): δ 14.00, 29.02, 30.74, 46.01, 46.13, 52.52, 52.69, 55.12, 60.98, 61.05, 63.27, 64.41, 112.45, 114.09, 114.46, 120.52, 120.70, 124.12, 125.15, 129.39, 129.56, 140.15, 140.51, 140.73, 141.37, 159.48, 159.58, 165.80, 165.96, 167.97, 168.01, 201.33, 201.48; HRMS (ESI) exact mass calcd for $C_{18}H_{22}O_6Na^+$ $(M+Na)^+$: 357.1314, found: 357.1316.

*4.2.14. Ethyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9n**).* Reaction time: (15 min+6 h); yield: 86%; R_f (20% EtOAc in hexanes) 0.38; colorless viscous liquid; IR (neat): ν 1743, 1718, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.221 & 1.229 (2t, 3H, J=7.2 Hz), 1.39 (t, 3H, J=6.8 Hz), 1.97 & 2.27 (2s, 3H), 3.50 & 3.70 (2s, 3H), 3.94–4.04 (m, 2H), 4.07–4.21 (m, 2H), 4.36 & 4.37 (2d, 1H, J=12.4 Hz), 4.66 & 4.69 (2d, 1H, J=12.0 Hz), 5.66 & 5.71 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.69–6.87 (m, 3H), 7.12–7.21 (m, 1H); ^{13}C NMR (100 MHz): δ 13.99, 14.74, 28.99, 30.74, 45.98, 46.11, 52.49, 52.66, 60.95, 61.01, 63.26, 64.42, 113.04, 114.52, 114.87, 120.43, 120.62, 124.03, 125.08, 129.34, 129.52, 140.04, 140.41, 140.74, 141.38, 158.84, 158.94, 165.79, 165.95, 167.96, 168.01, 201.33, 201.51; HRMS (ESI) exact mass calcd for $C_{19}H_{24}O_6Na^+$ $(M+Na)^+$: 371.1471, found: 371.1481.

*4.2.15. Ethyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9o**).* Reaction time: (15 min+6 h); yield: 91%; R_f (20% EtOAc in hexanes) 0.50; colorless viscous liquid; IR (neat): ν 1747, 1718, 1625 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.02 (t, 3H, J=7.6 Hz), 1.22 & 1.23 (2t, 3H, J=7.2 Hz), 1.72–1.84 (m, 2H), 1.97 & 2.27 (2s, 3H), 3.50 & 3.70 (2s, 3H), 3.86 & 3.87 (2t, 2H, J=6.4 Hz), 4.05–4.20 (m, 2H), 4.37 & 4.38 (2d, 1H, J=12.0 Hz), 4.62–4.73 (m, 1H), 5.66 & 5.71 (2s, 1H), 6.27 & 6.29 (2s, 1H), 6.68–6.86 (m, 3H), 7.12–7.20 (m, 1H); ^{13}C NMR (100 MHz): δ 10.49, 14.00, 22.53, 28.99, 30.75, 46.00, 46.13, 52.50, 52.66, 60.97, 61.03, 63.29, 64.44, 69.31, 113.10, 114.55, 114.88, 120.35, 120.55, 124.06, 125.11, 129.32, 129.51, 140.02, 140.39, 140.75, 141.40, 159.05, 159.15, 165.82, 165.98, 167.98, 168.03, 201.37, 201.54; HRMS (ESI) exact mass calcd for $C_{20}H_{26}O_6Na^+$ $(M+Na)^+$: 385.1627, found: 385.1630.

*4.2.16. Methyl (2Z)-2-(chloromethyl)-3-phenylprop-2-enoate (**15**).* To a stirred solution of methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-phenylhexanoate (**9a**) (1 mmol, 0.290 g), in anhydrous dichloromethane (2 mL), $TiCl_4$ (2 mmol, 1 mL, 2 M solution in dichloromethane) was added at 0 °C. Reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was cooled to 0 °C and quenched with water (2 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue thus obtained on purification by column chromatography (5% ethyl acetate in hexanes, silica gel) provided methyl (2Z)-2-(chloromethyl)-3-phenylprop-2-enoate (**15**) in (0.038 g) 18% isolated yield as a colorless liquid along with un-reacted starting material **9a** in (0.220 g) 76% recovered yield. This compound (**15**) is known in the literature. Spectral data of our compound are in agreement with the known data.[9d]

Reaction time: 12 h; yield: 18%; R_f (10% EtOAc in hexanes) 0.44; colorless liquid; IR (neat): ν 1718, 1630 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.80 (s, 3H), 4.39 (s, 2H), 7.29–7.43 (m, 3H), 7.47 (d, 2H, J=7.2 Hz), 7.80 (s, 1H); ^{13}C NMR (100 MHz): δ 39.22, 52.56, 128.42, 128.95, 129.70, 129.80, 134.19, 143.89, 166.82.

*4.2.17. Intramolecular Friedel–Crafts reaction of methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxo-hexanoate (**9b**) with $TiCl_4$.* To a stirred solution of methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxo-hexanoate (**9b**) (1 mmol, 0.320 g), in anhydrous dichloromethane (2 mL), $TiCl_4$ (2 mmol, 1 mL, 2 M solution in dichloromethane) was added at 0 °C. After stirring at room temperature for 1 h, reaction mixture was cooled to 0 °C and quenched with water (2 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated. Residue thus obtained was purified by column chromatography (5% EtOAc in hexanes, silica gel) to provide methyl 4-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (*ortho*-**10b**) (minor product) and methyl 6-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (**10b**) (major product) in 20% (0.060 g) and 76% (0.230 g) isolated yields, respectively. *ortho*-Cyclization product (*ortho*-**10b**) eluted first (less polar) and *para* cyclized product (**10b**) eluted later (more polar).

*4.2.17.1. Methyl 6-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10b**).* Reaction time: 1 h; yield: 76%; R_f (20% EtOAc in hexanes) 0.39; colorless solid; mp: 88–90 °C; IR (KBr): ν 1708, 1693, 1630, 1602 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.54 (d, 3H, J=2.0 Hz), 3.74 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 4.85 (s, 1H), 5.39 (s, 1H), 6.11 (s, 1H), 6.89 (dd, 1H, J=2.0 & 8.4 Hz), 6.93 (d, 1H, J=2.0 Hz), 7.37 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 12.68, 50.88,

51.09, 52.16, 55.54, 109.39, 113.19, 122.28, 124.72, 130.62, 136.71, 139.09, 149.68, 152.91, 160.73, 165.66, 167.38; HRMS (ESI) exact mass calcd for $C_{17}H_{18}O_5Na^+$ $(M+Na)^+$: 325.1052, found: 325.1054.

Crystal data for **10b**: empirical formula, $C_{17}H_{18}O_5$; formula weight, 302.31; crystal color, colorless; habit, block; crystal dimensions, 0.52×0.40×0.28 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a=9.6539(10) Å, b=9.7867(10) Å, c=10.5569(11) Å, α=68.543(2), β=64.2280(10), γ=61.3790(10); V=772.63(14) Å^3; space group, $p-1$; Z=2; D_{calcd}=1.299 g/cm^3; F_{000}=320; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0473, wR^2=0.1276. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10b** CCDC # 903059).

*4.2.17.2. Methyl 4-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (ortho-**10b**).* Yield: 20%; R_f (20% EtOAc in hexanes) 0.45; pale yellow solid; mp: 76–77 °C; IR (KBr): ν 1720, 1703, 1620, 1599 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.77 (d, 3H, J=2.4 Hz), 3.73 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 4.86 (d, 1H, J=2.0 Hz unresolved quartet), 5.38 (s, 1H), 6.09 (s, 1H), 6.80 (d, 1H, J=8.0 Hz), 6.94 (d, 1H, J=7.2 Hz), 7.22–7.30 (m, 1H); ^{13}C NMR (100 MHz): δ 15.81, 51.08, 51.14, 52.15, 55.31, 109.52, 116.12, 124.59, 129.87, 130.88, 131.11, 139.15, 149.88, 154.33, 156.45, 165.79, 167.38; HRMS (ESI) exact mass calcd for $C_{17}H_{18}O_5Na^+$ $(M+Na)^+$: 325.1052, found: 325.1047.

*Crystal data for ortho-***10b**: empirical formula, $C_{17}H_{18}O_5$; formula weight, 302.31; crystal color, pale yellow; habit, block; crystal dimensions, 0.60×0.38×0.20 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a=8.9453(10) Å, b=9.4121(11) Å, c=10.5433(12) Å, α=106.120(2), β=108.691(2), γ=103.365(2); V=756.17(15) Å^3; space group, $p-1$; Z=2; D_{calcd}=1.328 g/cm^3; F_{000}=320; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0456, wR^2=0.1249. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound *ortho*-**10b** CCDC #903062).

*4.2.18. Treatment of methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxo-hexanoate (**9b**) with H_2SO_4.* To a stirred solution of methyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9b**) (1 mmol, 0.320 g), in anhydrous dichloromethane (2 mL), H_2SO_4 (2 mmol, 0.196 g) was added at 0 °C. After stirring at room temperature for 1 h, reaction mixture was cooled to 0 °C, quenched with water (2 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated, residue thus obtained was subjected to column chromatography (5% EtOAc in hexanes, silica gel) to furnish methyl 4-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (*ortho*-**10b**) in 10%, (0.032 g), methyl 6-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (**10b**) in 46% (0.139 g) and 6-methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylic acid (**16**) in 35% (0.100 g) isolated yields.

Spectral data (IR, ^{1}H, ^{13}C NMR) and mp of the compound **10b** & *ortho*-**10b** are in complete agreement with that prepared via the treatment of **9b** with methanesulfonic acid.

*4.2.18.1. 6-Methoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylic acid (**16**).* Yield: 35%; R_f (50% EtOAc in hexanes) 0.30; pale yellow solid; mp: 176–178 °C; IR (KBr): ν 2800–3200 (b), 1718, 1657, 1601 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.58 (d, 3H, J=2.0 Hz), 3.80 (s, 3H), 3.82 (s, 3H), 4.85 (s, 1H), 5.47 (s, 1H), 6.15 (s, 1H), 6.90 (dd, 1H, J=2.4 & 8.4 Hz), 6.94 (s, 1H, unresolved doublet), 7.40 (d, 1H, J=8.4 Hz), 12.08 (br s, 1H); ^{13}C NMR (100 MHz): δ 12.96, 50.91, 52.18, 55.56, 109.36, 113.42, 122.66, 125.05, 129.95, 136.53, 138.73, 150.19, 155.72, 161.09, 167.28, 170.82; HRMS (ESI) exact mass calcd for $C_{16}H_{16}O_5Na^+$ $(M+Na)^+$: 311.0895, found: 311.0898.

*4.2.19. Methyl 4,6-dimethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10c**).* Reaction time: 0.5 h; yield: 94%; R_f (20% EtOAc in hexanes) 0.34; colorless solid; mp: 130–132 °C; IR (KBr): ν 1715, 1697, 1625, 1597 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.73 (d, 3H, J=2.4 Hz), 3.71 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 4.81 (s, 1H), 5.37 (s, 1H), 6.09 (s, 1H), 6.36 (d, 1H, J=1.6 Hz), 6.51 (s, 1H); ^{13}C NMR (100 MHz): δ 15.64, 50.91, 51.15, 52.16, 55.30, 55.59, 97.63, 100.57, 124.52, 124.69, 128.80, 139.43, 151.69, 154.72, 157.16, 162.09, 165.75, 167.54; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_6Na^+$ $(M+Na)^+$: 355.1158, found: 355.1155.

Crystal data for **10c**: empirical formula, $C_{18}H_{20}O_6$; formula weight, 332.34; crystal color, colorless; habit, block; crystal dimensions, 0.36×0.32×0.28 mm^3; crystal system, monoclinic; lattice type, C centered; lattice parameters, a=19.345(3) Å, b=9.5690(11) Å, c=21.222(4) Å, α=90.00, β=122.10(2), γ=90.00; V=3327.8(9) Å^3; space group, C 1 2/c 1; Z=8; D_{calcd}=1.327 g/cm^3; F_{000}=1408; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0472, wR^2=0.1304. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10c** CCDC # 903060).

*4.2.20. Methyl 1-(1-methoxycarbonylethenyl)-3-methyl-4,5,6-trimethoxy-1H-indene-2-carboxylate (**10d**).* Reaction time: 0.5 h; yield: 92%; R_f (20% EtOAc in hexanes) 0.36; pale yellow solid; mp: 80–83 °C; IR (KBr): ν 1710, 1699, 1625, 1599 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.73 (d, 3H, J=2.4 Hz), 3.72 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 3.95 (s, 3H), 4.79 (d, 1H, J=2.4 Hz, unresolved quartet), 5.38 (s, 1H), 6.10 (s, 1H), 6.70 (s, 1H); ^{13}C NMR (100 MHz): δ 14.71, 50.97, 51.07, 52.11, 56.14, 60.87, 61.42, 103.12, 124.62, 128.59, 130.51, 139.25, 141.61, 144.47, 150.10, 153.73, 154.78, 165.49, 167.50; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_7Na^+$ $(M+Na)^+$: 385.1263, found: 385.1261.

*4.2.21. Methyl 4,6-dimethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10e**).* Reaction time: 0.5 h; yield: 90%; R_f (20% EtOAc in hexanes) 0.38; colorless solid; mp: 70–72 °C; IR (KBr): ν 1714, 1697, 1625, 1599 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.28 (t, 3H, J=7.2 Hz), 2.72 (d, 3H, J=2.4 Hz), 3.71 (s, 3H), 3.79 (s, 3H), 3.84 (s, 3H), 4.19–4.29 (m, 2H), 4.80 (m, 1H, unresolved quartet), 5.38 (s, 1H), 6.11 (s, 1H), 6.36 (d, 1H, J=2.0 Hz), 6.52 (s, 1H); ^{13}C NMR (100 MHz): δ 14.11, 15.50, 50.75, 51.22, 55.18, 55.43, 60.79, 97.51, 100.42, 124.48, 128.70, 139.61, 151.59, 154.50, 157.05, 161.98, 165.63, 166.89; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_6Na^+$ $(M+Na)^+$: 369.1314, found: 369.1316.

Crystal data for **10e**: empirical formula, $C_{19}H_{22}O_6$; formula weight, 346.37; crystal color, colorless; habit, block; crystal dimensions, 0.44×0.36×0.20 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a=12.2022(12) Å, b=8.4746(9) Å, c=17.6407(18) Å, α=90.00, β=102.136(2), γ=90.00; V=1783.4(3) Å^3; space group, $P2(1)/c$; Z=4; D_{calcd}=1.290 g/cm^3; F_{000}=736; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0616, wR^2=0.1635. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10e** CCDC # 903061).

*4.2.22. Methyl 1-(1-ethoxycarbonylethenyl)-3-methyl-4,5,6-trimethoxy-1H-indene-2-carboxylate (**10f**).* Reaction time: 0.5 h; yield: 93%; R_f (20% EtOAc in hexanes) 0.31; colorless solid; mp: 100–103 °C; IR (KBr): ν 1706, 1615, 1599 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.28 (t, 3H, J=7.2 Hz), 2.73 (d, 3H, J=2.4 Hz), 3.73 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 3.95 (s, 3H), 4.23 (q, 2H, J=7.2 Hz), 4.78 (s, 1H), 5.41 (s, 1H), 6.13 (s, 1H), 6.71 (s, 1H); ^{13}C NMR (100 MHz): δ 14.17, 14.71, 50.97, 51.30, 56.15, 60.90, 61.44, 103.11, 124.72, 128.66, 130.52,

139.47, 141.62, 144.47, 150.11, 153.66, 154.76, 165.54, 166.98; HRMS (ESI) exact mass calcd for $C_{20}H_{24}O_7Na^+$ $(M+Na)^+$: 399.1420, found: 399.1422.

*4.2.23. Ethyl 4,6-dimethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10g**).* Reaction time: 0.5 h; yield: 95%; R_f (20% EtOAc in hexanes) 0.37; brick red color solid; mp: 74–76 °C; IR (KBr): ν 1728, 1678, 1620, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 1.25 (t, 3H, J=6.8 Hz), 2.73 (s, 3H), 3.801 (s, 3H), 3.807 (s, 3H), 3.84 (s, 3H), 4.07–4.28 (m, 2H), 4.81 (s, 1H), 5.36 (s, 1H), 6.10 (s, 1H), 6.36 (s, 1H), 6.49 (s, 1H); ^{13}C NMR (100 MHz): δ 14.25, 15.52, 51.04, 52.07, 55.25, 55.54, 59.55, 97.57, 100.50, 124.61, 124.72, 129.18, 139.56, 151.76, 154.38, 157.08, 162.00, 165.24, 167.49; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_6Na^+$ $(M+Na)^+$: 369.1314, found: 369.1317.

*4.2.24. Ethyl 1-(1-methoxycarbonylethenyl)-3-methyl-4,5,6-trimethoxy-1H-indene-2-carboxylate (**10h**).* Reaction time: 0.5 h; yield: 91%; R_f (20% EtOAc in hexanes) 0.39; colorless solid; mp: 72–74 °C; IR (KBr): ν 1720, 1691, 1615, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 1.25 (t, 3H, J=7.2 Hz), 2.73 (d, 3H, J=2.4 Hz), 3.81 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 3.95 (s, 3H), 4.10–4.29 (m, 2H), 4.80 (d, 1H, J=2.0 Hz, unresolved quartet), 5.37 (s, 1H), 6.11 (s, 1H), 6.69 (s, 1H); ^{13}C NMR (100 MHz): δ 14.19, 14.63, 50.97, 52.05, 56.11, 59.68, 60.84, 61.39, 103.07, 124.70, 128.70, 130.90, 139.36, 141.57, 144.56, 150.02, 153.40, 154.70, 165.00, 167.46; HRMS (ESI) exact mass calcd for $C_{20}H_{24}O_7Na^+$ $(M+Na)^+$: 399.1420, found: 399.1422.

Crystal data for **10h**: empirical formula, $C_{20}H_{24}O_7$; formula weight, 376.39; crystal color, colorless; habit, block; crystal dimensions, 0.52×0.40×0.28 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a=10.0264(11) Å, b=16.1212(17) Å, c=12.7802(13) Å, α=90.00, β=107.732(2), γ=90.00; V=1967.6(4) $Å^3$; space group, $P2(1)/c$; Z=4; D_{calcd}=1.271 g/cm^3; F_{000}=800; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0852, wR^2=0.1666 Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10h** CCDC # 903070).

*4.2.25. Ethyl 4,6-dimethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10i**).* Reaction time: 0.5 h; yield: 94%; R_f (20% EtOAc in hexanes) 0.41; brick red color solid; mp: 56–58 °C; IR (KBr): ν 1716, 1689, 1620, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 1.25 (t, 3H, J=7.2 Hz), 1.28 (t, 3H, J=7.2 Hz), 2.73 (d, 3H, J=2.0 Hz), 3.79 (s, 3H), 3.84 (s, 3H), 4.08–4.30 (m, 4H), 4.80 (s, 1H), 5.38 (s, 1H), 6.12 (s, 1H), 6.36 (s, 1H), 6.50 (s, 1H); ^{13}C NMR (100 MHz): δ 14.19, 14.28, 15.53, 51.27, 55.30, 55.56, 59.56, 60.86, 97.61, 100.48, 124.69, 129.17, 139.77, 151.78, 154.35, 157.10, 161.99, 165.30, 167.01; HRMS (ESI) exact mass calcd for $C_{20}H_{24}O_6Na^+$ $(M+Na)^+$: 383.1471, found: 383.1473.

*4.2.26. Ethyl 1-(1-ethoxycarbonylethenyl)-3-methyl-4,5,6-trimethoxy-1H-indene-2-carboxylate (**10j**).* Reaction time: 0.5 h; yield: 93%; R_f (20% EtOAc in hexanes) 0.39; pale yellow solid; mp: 39–40 °C; IR (KBr): ν 1709, 1697, 1616, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 1.26 (t, 3H, J=7.2 Hz), 1.27 (t, 3H, J=7.2 Hz), 2.73 (d, 3H, J=2.4 Hz), 3.85 (s, 3H), 3.86 (s, 3H), 3.95 (s, 3H), 4.10–4.31 (m, 4H), 4.77 (d, 1H, J=2.4 Hz, unresolved quartet), 5.40 (s, 1H), 6.14 (d, 1H, J=0.8 Hz), 6.70 (d, 1H, J=0.4 Hz); ^{13}C NMR (100 MHz): δ 14.10, 14.18, 14.59, 51.24, 56.08, 59.63, 60.79, 60.82, 61.37, 103.03, 124.73, 128.71, 130.82, 139.53, 141.55, 144.49, 150.00, 153.30, 154.65, 165.01, 166.91; HRMS (ESI) exact mass calcd for $C_{21}H_{26}O_7Na^+$ $(M+Na)^+$: 413.1576, found: 413.1574.

*4.2.27. Reaction of methyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9k**) with $TiCl_4$.* Treatment of methyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9k**) with $TiCl_4$ in dichloromethane following the similar procedure described for obtaining **10b** and *ortho*-**10b** (from **9b**), provided methyl 6-ethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (**10k**) (major product) and methyl 4-ethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (*ortho*-**10k**) (minor product) in 73% and 21% isolated yields, respectively, after purification through column chromatography (5% EtOAc in hexanes, silica gel). *ortho*-Cyclization product (*ortho*-**10k**) eluted first (less polar) and *para* cyclized product (**10k**) eluted later (more polar).

*4.2.27.1. Methyl 6-ethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10k**).* Reaction time: 1 h; yield: 73%; R_f (20% EtOAc in hexanes) 0.49; colorless solid; mp: 77–79 °C; IR (KBr): ν 1724, 1685, 1620, 1602 cm^{-1}; ^1H NMR (400 MHz): δ 1.41 (t, 3H, J=7.2 Hz), 2.54 (d, 3H, J=2.0 Hz), 3.74 (s, 3H), 3.80 (s, 3H), 4.03 (q, 2H, J=7.2 Hz), 4.84 (s, 1H), 5.38 (s, 1H), 6.10 (s, 1H), 6.87 (dd, 1H, J=2.4 & 8.4 Hz), 6.92 (d, 1H, J=1.2 Hz), 7.36 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 12.71, 14.85, 50.88, 51.11, 52.19, 63.77, 110.00, 113.63, 122.30, 124.72, 130.53, 136.58, 139.13, 149.70, 153.03, 160.14, 165.73, 167.41; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_5Na^+$ $(M+Na)^+$: 339.1208, found: 339.1217.

Crystal data for **10k**: empirical formula, $C_{18}H_{20}O_5$; formula weight, 316.34; crystal color, pale yellow; habit, plate; crystal dimensions, 0.60×0.28×0.08 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a=5.7636(8) Å, b=9.3432(13) Å, c=15.310(2) Å, α=91.482(2), β=92.853(3), γ=91.267(2); V=822.9(2) $Å^3$; space group, $P-1$; Z=2; D_{calcd}=1.277 g/cm^3; F_{000}=336; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0622, wR^2=0.1638. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10k** CCDC # 903071).

*4.2.27.2. Methyl 4-ethoxy-1-(1-methoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (ortho-**10k**).* Yield: 21%; R_f (20% EtOAc in hexanes) 0.56; pale yellow solid; mp: 75–76 °C; IR (KBr): ν 1722, 1697, 1620, 1597 cm^{-1}; ^1H NMR (400 MHz): δ 1.47 (t, 3H, J=6.8 Hz), 2.78 (d, 3H, J=2.0 Hz), 3.73 (s, 3H), 3.80 (s, 3H), 4.09 (q, 2H, J=6.8 Hz), 4.86 (s, 1H), 5.37 (s, 1H), 6.08 (s, 1H), 6.77 (d, 1H, J=8.4 Hz), 6.92 (d, 1H, J=7.6 Hz), 7.19–7.26 (m, 1H); ^{13}C NMR (100 MHz): δ 14.84, 15.80, 51.06, 52.15, 63.72, 110.26, 115.95, 124.53, 129.84, 130.79, 131.04, 139.20, 149.88, 154.54, 155.84, 165.82, 167.40; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_5Na^+$ $(M+Na)^+$: 339.1208, found: 339.1204.

*Crystal data for ortho-***10k**: empirical formula, $C_{18}H_{20}O_5$; formula weight, 316.34; crystal color, pale yellow; habit, block; crystal dimensions, 0.36×0.32×0.32 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a=6.965(4) Å, b=7.746(4) Å, c=15.540(8) Å, α=78.010(9), β=89.915(10), γ=80.114(9); V=807.4(7) $Å^3$; space group, $P-1$; Z=2; D_{calcd}=1.301 g/cm^3; F_{000}=336; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$= 0.0499, wR^2=0.1372. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound *ortho*-**10k** CCDC # 903073).

*4.2.28. Treatment of methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9l**) with $TiCl_4$.* Reaction of methyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9l**) with $TiCl_4$ in dichloromethane following the similar procedure described for obtaining **10b** and *ortho*-**10b** (from **9b**), gave methyl 1-(1-methoxycarbonylethenyl)-3-methyl-6-propoxy-1*H*-indene-2-carboxylate (**10l**) (major product) and methyl 1-(1-methoxycarbonylethenyl)-3-methyl-4-propoxy-1*H*-indene-2-carboxylate (*ortho*-**10l**) (minor product) in 75% and 19% isolated yields, respectively, after purification through column chromatography (5% EtOAc in hexanes, silica gel). *ortho*-Cyclization

product (*ortho*-**10l**) eluted first (less polar) and *para* cyclized product (**10l**) eluted later (more polar).

*4.2.28.1. Methyl 1-(1-methoxycarbonylethenyl)-3-methyl-6-propoxy-1H-indene-2-carboxylate (**10l**).* Reaction time: 1 h; yield: 75%; R_f (20% EtOAc in hexanes) 0.44; pale yellow solid; mp: 74–76 °C; IR (KBr): ν 1722, 1685, 1620, 1602 cm^{-1}; ^1H NMR (400 MHz): δ 1.03 (t, 3H, J=7.2 Hz), 1.75–1.86 (m, 2H), 2.54 (d, 3H, J=2.4 Hz), 3.74 (s, 3H), 3.80 (s, 3H), 3.92 (t, 2H, J=6.4 Hz), 4.84 (d, 1H, J=2.0 Hz, unresolved quartet), 5.38 (s, 1H), 6.10 (s, 1H), 6.88 (dd, 1H, J=2.4 & 8.4 Hz), 6.92 (d, 1H, J=2.4 Hz), 7.36 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 10.54, 12.65, 22.59, 50.82, 51.04, 52.13, 69.73, 109.97, 113.59, 122.23, 124.65, 130.46, 136.47, 139.11, 149.64, 152.97, 160.31, 165.66, 167.37; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_5Na^+$ $(M+Na)^+$: 353.1365, found: 353.1373.

*4.2.28.2. Methyl 1-(1-methoxycarbonylethenyl)-3-methyl-4-propoxy-1H-indene-2-carboxylate (ortho-**10l**).* Yield: 19%; R_f (20% EtOAc in hexanes) 0.53; pale yellow solid; mp: 79–80 °C; IR (KBr): ν 1718, 1697, 1610, 1597 cm^{-1}; ^1H NMR (400 MHz): δ 1.09 (t, 3H, J=7.2 Hz), 1.82–1.93 (m, 2H), 2.79 (d, 3H, J=2.4 Hz), 3.73 (s, 3H), 3.80 (s, 3H), 3.99 (t, 2H, J=6.0 Hz), 4.86 (d, 1H, J=2.0 Hz, unresolved quartet), 5.38 (s, 1H), 6.08 (s, 1H), 6.78 (d, 1H, J=8.4 Hz), 6.92 (d, 1H, J=7.6 Hz), 7.19–7.26 (m, 1H); ^{13}C NMR (100 MHz): δ 10.88, 15.83, 22.67, 51.00, 51.14, 52.09, 69.65, 110.16, 115.90, 124.46, 129.83, 130.83, 131.08, 139.27, 149.89, 154.40, 156.00, 165.78, 167.38; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_5Na^+$ $(M+Na)^+$: 353.1365, found: 353.1367.

*4.2.29. Treatment of ethyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9m**) with $TiCl_4$.* Reaction of ethyl 4-methoxycarbonyl-3-(3-methoxyphenyl)-2-methylene-5-oxohexanoate (**9m**) with $TiCl_4$ in dichloromethane following the similar procedure described for obtaining **10b** and *ortho*-**10b** (from **9b**), furnished methyl 1-(1-ethoxycarbonylethenyl)-6-methoxy-3-methyl-1*H*-indene-2-carboxylate (**10m**) (major product) and methyl 1-(1-ethoxycarbonylethenyl)-4-methoxy-3-methyl-1*H*-indene-2-carboxylate (*ortho*-**10m**) (minor product) in 74% and 20% isolated yields, respectively, after purification through column chromatography (5% EtOAc in hexanes, silica gel). *ortho*-Cyclization product (*ortho*-**10m**) eluted first (less polar) and *para* cyclized product (**10m**) eluted later (more polar).

*4.2.29.1. Methyl 1-(1-ethoxycarbonylethenyl)-6-methoxy-3-methyl-1H-indene-2-carboxylate (**10m**).* Reaction time: 1 h; yield: 74%; R_f (20% EtOAc in hexanes) 0.50; pale yellow solid; mp: 60–62 °C; IR (KBr): ν 1709, 1695, 1620, 1602 cm^{-1}; ^1H NMR (400 MHz): δ 1.27 (t, 3H, J=7.2 Hz), 2.54 (d, 3H, J=2.0 Hz), 3.74 (s, 3H), 3.81 (s, 3H), 4.18–4.28 (m, 2H), 4.83 (s, 1H), 5.41 (s, 1H), 6.13 (s, 1H), 6.88 (dd, 1H, J=2.0 & 8.4 Hz), 6.93 (d, 1H, J=1.6 Hz, not properly resolved), 7.37 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 12.60, 14.13, 51.00, 55.47, 60.87, 109.26, 113.19, 122.17, 124.65, 130.61, 136.71, 139.30, 149.64, 152.76, 160.69, 165.62, 166.81; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_5Na^+$ $(M+Na)^+$: 339.1208, found: 339.1213.

Crystal data for **10m**: empirical formula, $C_{18}H_{20}O_5$; formula weight, 316.34; crystal color, pale yellow; habit, block; crystal dimensions, 0.40×0.36×0.32 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a=8.4689(13) Å, b=9.7195(15) Å, c=10.6243(16) Å, α=81.293(3), β=88.068(3), γ=72.963(3); V=826.5(2) $Å^3$; space group, $P\bar{1}$; Z=2; D_{calcd}=1.271 g/cm^3; F_{000}=336; λ (Mo-Kα)=0.71073 Å; $R(I\geq 2\sigma_1)$=0.0500, wR^2=0.1288. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **10m** CCDC # 903072).

*4.2.29.2. Methyl 1-(1-ethoxycarbonylethenyl)-4-methoxy-3-methyl-1H-indene-2-carboxylate (ortho-**10m**).* Yield: 20%; R_f (20% EtOAc in hexanes) 0.58; pale yellow solid; mp: 44–46 °C; IR (KBr): ν 1716, 1697, 1625, 1601 cm^{-1}; ^1H NMR (400 MHz): δ 1.27 (t, 3H, J=7.2 Hz), 2.76 (d, 3H, J=2.4 Hz), 3.73 (s, 3H), 3.87 (s, 3H), 4.22 (q, 2H, J=7.2 Hz), 4.85 (d, 1H, J=2.0 Hz, unresolved quartet), 5.39 (s, 1H), 6.11 (s, 1H), 6.80 (d, 1H, J=8.4 Hz), 6.95 (d, 1H, J=7.6 Hz), 7.22–7.28 (m, 1H); ^{13}C NMR (100 MHz): δ 14.15, 15.77, 51.03, 51.28, 55.30, 60.89, 109.47, 116.09, 124.59, 129.80, 130.93, 131.16, 139.37, 149.89, 154.19, 156.42, 165.79, 166.85; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_5Na^+$ $(M+Na)^+$: 339.1208, found: 339.1205.

*4.2.30. Treatment of ethyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9n**) with $TiCl_4$.* Reaction of ethyl 3-(3-ethoxyphenyl)-4-methoxycarbonyl-2-methylene-5-oxohexanoate (**9n**) with $TiCl_4$ in dichloromethane following the similar procedure described for obtaining **10b** and *ortho*-**10b** (from **9b**), provided methyl 6-ethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (**10n**) (major product) and methyl 4-ethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1*H*-indene-2-carboxylate (*ortho*-**10n**) (minor product) in 76% and 18% isolated yields, respectively, after purification through column chromatography (5% EtOAc in hexanes, silica gel). *ortho*-Cyclization product (*ortho*-**10n**) eluted first (less polar) and *para* cyclized product (**10n**) eluted later (more polar).

*4.2.30.1. Methyl 6-ethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (**10n**).* Reaction time: 1 h; yield: 76%; R_f (20% EtOAc in hexanes) 0.40; pale yellow solid; mp: 58–60 °C; IR (KBr): ν 1718, 1685, 1615, 1604 cm^{-1}; ^1H NMR (400 MHz): δ 1.26 (t, 3H, J=7.2 Hz), 1.40 (t, 3H, J=7.2 Hz), 2.53 (d, 3H, J=2.0 Hz), 3.74 (s, 3H), 4.03 (q, 2H, J=7.2 Hz), 4.18–4.27 (m, 2H), 4.82 (d, 1H, J=2.0 Hz, unresolved quartet), 5.40 (s, 1H), 6.12 (s, 1H), 6.87 (dd, 1H, J=2.0 & 8.4 Hz), 6.92 (d, 1H, J=2.0 Hz), 7.36 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 12.62, 14.14, 14.79, 51.01, 60.87, 63.69, 109.86, 113.64, 122.18, 124.65, 130.54, 136.58, 139.35, 149.66, 152.84, 160.08, 165.66, 166.83; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_5Na^+$ $(M+Na)^+$: 353.1365, found: 353.1369.

*4.2.30.2. Methyl 4-ethoxy-1-(1-ethoxycarbonylethenyl)-3-methyl-1H-indene-2-carboxylate (ortho-**10n**).* Yield: 18%; R_f (20% EtOAc in hexanes) 0.48; pale yellow solid; mp: 43–45 °C; IR (KBr): ν 1712, 1630, 1597 cm^{-1}; ^1H NMR (400 MHz): δ 1.27 (t, 3H, J=7.2 Hz), 1.46 (t, 3H, J=6.8 Hz), 2.78 (d, 3H, J=2.4 Hz), 3.73 (s, 3H), 4.09 (q, 2H, J=7.2 Hz), 4.22 (q, 2H, J=6.8 Hz, unresolved two quartets), 4.84 (d, 1H, J=2.0 Hz, unresolved quartet), 5.39 (s, 1H), 6.10 (s, 1H), 6.77 (d, 1H, J=8.4 Hz), 6.93 (d, 1H, J=7.6 Hz), 7.19–7.26 (m, 1H); ^{13}C NMR (100 MHz): δ 14.19, 14.85, 15.78, 51.04, 51.22, 60.91, 63.75, 110.25, 115.97, 124.53, 129.79, 130.89, 131.15, 139.46, 149.93, 154.41, 155.84, 165.85, 166.91; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_5Na^+$ $(M+Na)^+$: 353.1365, found: 353.1363.

*4.2.31. Reaction of ethyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9o**) with $TiCl_4$.* Ethyl 4-methoxycarbonyl-2-methylene-5-oxo-3-(3-propoxyphenyl)hexanoate (**9o**) on treatment with $TiCl_4$ in dichloromethane following the similar procedure described for obtaining **10b** and *ortho*-**10b** (from **9b**), provided methyl 1-(1-ethoxycarbonylethenyl)-3-methyl-6-propoxy-1*H*-indene-2-carboxylate (**10o**) (major product) and methyl 1-(1-ethoxycarbonylethenyl)-3-methyl-4-propoxy-1*H*-indene-2-carboxylate (*ortho*-**10o**) (minor product) in 72% and 17% isolated yields, respectively, after purification through column chromatography (5% EtOAc in hexanes, silica gel). *ortho*-Cyclization product

(*ortho*-**10o**) eluted first (less polar) and *para* cyclized product (**10o**) eluted later (more polar).

*4.2.31.1. Methyl 1-(1-ethoxycarbonylethenyl)-3-methyl-6-propoxy-1H-indene-2-carboxylate (**10o**).* Reaction time: 1 h; yield: 72%; R_f (20% EtOAc in hexanes) 0.43; pale yellow solid; mp: 41–43 °C; IR (KBr): ν 1716, 1685, 1620, 1601 cm^{-1}; ^1H NMR (400 MHz): δ 1.03 (t, 3H, J=7.6 Hz), 1.26 (t, 3H, J=7.2 Hz), 1.75–1.86 (m, 2H), 2.53 (d, 3H, J=2.4 Hz), 3.74 (s, 3H), 3.92 (t, 2H, J=6.8 Hz), 4.225 & 4.230 (2q, 2H, J=7.2 Hz), 4.82 (d, 1H, J=2.0 Hz, unresolved quartet), 5.40 (s, 1H), 6.12 (s, 1H), 6.88 (dd, 1H, J=2.4 & 8.4 Hz), 6.93 (d, 1H, J=2.0 Hz, not properly resolved), 7.35 (d, 1H, J=8.4 Hz); ^{13}C NMR (100 MHz): δ 10.53, 12.63, 14.15, 22.59, 51.02, 60.89, 69.75, 109.90, 113.68, 122.18, 124.68, 130.53, 136.56, 139.37, 149.67, 152.87, 160.31, 165.70, 166.88; HRMS (ESI) exact mass calcd for $C_{20}H_{24}O_5Na^+$ $(M+Na)^+$: 367.1521, found: 367.1523.

*4.2.31.2. Methyl 1-(1-ethoxycarbonylethenyl)-3-methyl-4-propoxy-1H-indene-2-carboxylate (ortho-**10o**).* Yield: 17%; R_f (20% EtOAc in hexanes) 0.52; pale yellow solid; mp: 50–51 °C; IR (KBr): ν 1714, 1695, 1615, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 1.09 (t, 3H, J=7.6 Hz), 1.27 (t, 3H, J=7.2 Hz), 1.83–1.93 (m, 2H), 2.79 (d, 3H, J=2.4 Hz), 3.74 (s, 3H), 3.99 (t, 2H, J=6.4 Hz), 4.230 & 4.233 (2q, 2H, J=7.2 Hz), 4.85 (d, 1H, J=2.4 Hz, unresolved quartet), 5.40 (s, 1H), 6.11 (s, 1H), 6.78 (d, 1H, J=8.0 Hz), 6.93 (d, 1H, J=7.6 Hz), 7.20–7.26 (m, 1H); ^{13}C NMR (100 MHz): δ 10.85, 14.11, 15.79, 22.62, 50.96, 51.22, 60.84, 69.57, 110.03, 115.82, 124.47, 129.75, 130.80, 131.06, 139.42, 149.85, 154.29, 155.93, 165.77, 166.84; HRMS (ESI) exact mass calcd for $C_{20}H_{24}O_5Na^+$ $(M+Na)^+$: 367.1521, found: 367.1525.

Acknowledgements

We thank DST (New Delhi) for funding this project. B.S.R. thanks CSIR and DST (New Delhi) for research fellowships. H.L. thanks CSIR for her research fellowship. We thank UGC (New Delhi) for support and for providing some instrumental facilities. We thank the National Single-Crystal X-ray facility funded by DST. We also thank Professor S. Pal, School of Chemistry, University of Hyderabad, for helpful discussions regarding X-ray data analysis.

Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.12.069.

References and notes

1. (a) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley-Interscience: New York, NY, 1973; (b) Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry*; Marcel Dekker: New York, NY, 1984; (c) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. Friedel–Crafts alkylations In*Trost, B. M., Fleming, I., Eds.. Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991; Vol. 3, pp 293–339; (d) Sartori, G.; Maggi, R. *Chem. Rev.* **2011**, *111*, PR181–PR214; (e) Sartori, G.; Maggi, R. *Friedel–Crafts Acylation Reactions*; CRC: New York, NY, 2010; (f) Terrasson, V.; de Figueiredo, R. M.; Campagne, J. M. *Eur. J. Org. Chem.* **2010**, 2635–2655; (g) Rueping, M.; Nachtsheim, B. J. *Beilstein. J. Org. Chem.* **2010**, *6*, 1–24; (h) You, S.-L.; Cai, Q.; Zeng, M. *Chem. Soc. Rev.* **2009**, *38*, 2190–2201; (i) Poulsen, T. B.; Jorgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903–2915; (j) Sartori, G.; Maggi, R. *Chem. Rev.* **2006**, *106*, 1077–1104.
2. (a) Xu, Q.-L.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 2579–2581; (b) Suzuki, Y.; Nemoto, T.; Kakugawa, K.; Hamajima, A.; Hamada, Y. *Org. Lett.* **2012**, *14*, 2350–2353; (c) Liebert, C.; Brinks, M. K.; Capacci, A. G.; Fleming, M. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 3000–3003; (d) Ying, W.; Barnes, C. L.; Harmata, M. *Tetrahedron Lett.* **2011**, *52*, 177–180; (e) Womack, G. B.; Angeles, J. G.; Fanelli, V. E.; Indradas, B.; Snowden, R. L.; Sonnay, P. *J. Org. Chem.* **2009**, *74*, 5738–5741; (f) Cai, Q.; Zhao, Z.-A.; You, S.-L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7428–7431; (g) Hayashi, R.; Cook, G. R. *Org. Lett.* **2007**, *9*, 1311–1314; (h) Angeli, M.; Bandini, M.; Garelli, A.; Piccinelli, F.; Tommasi, S.; Umani-Ronchi, A. *Org. Biomol. Chem.* **2006**, *4*, 3291–3296; (i) Fillion, E.; Fishlock, D. *J. Am. Chem. Soc.* **2005**, *127*, 13144–13145.
3. (a) Kawazoe, K.; Yamamoto, M.; Takaishi, Y.; Honda, G.; Fujita, T.; Sezik, E.; Yesilada, E. *Phytochemistry* **1999**, *50*, 493–497; (b) Nicholson, A. N.; Pascoe, P. A.; Turner, C.; Ganellin, C. R.; Greengrass, P. M.; Casy, A. F.; Mercer, A. D. *Br. J. Pharmacol.* **1991**, *104*, 270–276; (c) Saxena, D. B. *Phytochemistry* **1986**, *25*, 553–555.
4. (a) Kolanos, R.; Siripurapu, U.; Pullagurla, M.; Riaz, M.; Setola, V.; Roth, B. L.; Dukat, M.; Glennon, R. A. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1987–1991; (b) Clegg, N. J.; Paruthiyil, S.; Leitman, D. C.; Scanlan, T. S. *J. Med. Chem.* **2005**, *48*, 5989–6003; (c) Oda, T.; So, Y.; Sato, Y.; Shimizu, N.; Handa, H.; Yasukochi, Y.; Kasahara, T. *Mutat. Res.* **2003**, *534*, 187–195; (d) Watanabe, N.; Ikeno, A.; Minato, H.; Nakagawa, H.; Kohayakawa, C.; Tsuji, J.-i *J. Med. Chem.* **2003**, *46*, 3961–3964; (e) Karaguni, I.-M.; Glusenkamp, K.-H.; Langerak, A.; Geisen, C.; Ullrich, V.; Winde, G.; Moroy, T.; Muller, O. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 709–713; (f) Schneider, M. R.; Ball, H. *J. Med. Chem.* **1986**, *29*, 75–79; (g) Witiak, D. T.; Kakodkar, S. V.; Brunst, G. E.; Baldwin, J. R.; Rahwan, R. G. *J. Med. Chem.* **1978**, *21*, 1313–1315.
5. (a) Kurouchi, H.; Sugimoto, H.; Otani, Y.; Ohwada, T. *J. Am. Chem. Soc.* **2010**, *132*, 807–815; (b) Wang, J.; Zhang, L.; Jing, Y.; Huang, W.; Zhou, X. *Tetrahedron Lett.* **2009**, *50*, 4978–4982; (c) Zhou, X.; Zhang, H.; Xie, X.; Li, Y. *J. Org. Chem.* **2008**, *73*, 3958–3960; (d) Nakamura, S.; Sugimoto, H.; Ohwada, T. *J. Org. Chem.* **2008**, *73*, 4219–4224; (e) Hu, B.; Xing, S.; Wang, Z. *Org. Lett.* **2008**, *10*, 5481–5484; (f) Basavaiah, D.; Reddy, K. R. *Org. Lett.* **2007**, *9*, 57–60; (g) Womack, G. B.; Angeles, J. G.; Fanelli, V. E.; Heyer, C. A. *J. Org. Chem.* **2007**, *72*, 7046–7049; (h) Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312–2317.
6. (a) Basavaiah, D.; Lenin, D. V. *Eur. J. Org. Chem.* **2010**, 5650–5658; (b) Basavaiah, D.; Aravindu, K.; Kumar, K. S.; Reddy, K. R. *Eur. J. Org. Chem.* **2010**, 1843–1848; (c) Basavaiah, D.; Bakthadoss, M.; Reddy, G. J. *Synthesis* **2001**, 919–923; (d) Basavaiah, D.; Pandiaraju, S.; Sarma, P. K. S. *Tetrahedron Lett.* **1994**, *35*, 4227–4230.
7. For reviews see: (a) Liu, T. Y.; Xie, M.; Chen, Y. C. *Chem. Soc. Rev.* **2012**, *41*, 4101–4112; (b) Basavaiah, D.; Veeraraghavaiah, G. *Chem. Soc. Rev.* **2012**, *41*, 68–78; (c) Basavaiah, D.; Reddy, B. S.; Badsara, S. S. *Chem. Rev.* **2010**, *110*, 5447–5674; (d) Wei, Y.; Shi, M. *Acc. Chem. Res.* **2010**, *43*, 1005–1018; (e) Declerck, V.; Martinez, J.; Lamaty, F. *Chem. Rev.* **2009**, *109*, 1–48; (f) Singh, V.; Batra, S. *Tetrahedron* **2008**, *64*, 4511–4574; (g) Masson, G.; Housseman, C.; Zhu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 4614–4628; (h) Basavaiah, D.; Rao, K. V.; Reddy, R. J. *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; (i) Kataoka, T.; Kinoshita, H. *Eur. J. Org. Chem.* **2005**, 45–58; (j) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–891; (k) Langer, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049–3052; (l) Ciganek, E. In *Oranic Reactions*; Paquette, L. A., Ed.; Wiley: New York, NY, 1997; Vol. 51, pp 201–350; (m) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001–8062; (n) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653–4670.
8. (a) Nair, D. K.; Mobin, S. M.; Namboothiri, I. N. N. *Org. Lett.* **2012**, *14*, 4580–4583; (b) Ressault, B.; Jaunet, A.; Geoffroy, P.; Goudedranche, S.; Miesch, M. *Org. Lett.* **2012**, *14*, 366–369; (c) Reddy, Y. S.; Kadigachalam, P.; Basak, R. K.; Pal, A. P. J.; Vankar, Y. D. *Tetrahedron Lett.* **2012**, *53*, 132–136; (d) Batchu, H.; Batra, S. *Eur. J. Org. Chem.* **2012**, 2935–2944; (e) Lee, H. S.; Kim, K. H.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2012**, *53*, 497–501; (f) Huang, L.; Shi, M. *Chem. Commun.* **2012**, 4501–4503; (g) Peng, J.; Huang, X.; Jiang, L.; Cui, H.-L.; Chen, Y.-C. *Org. Lett.* **2011**, *13*, 4584–4587; (h) de Luna Freire, K. R.; Tormena, C. F.; Coelho, F. *Synlett* **2011**, 2059–2063; (i) Basavaiah, D.; Devendar, B.; Aravindu, K.; Veerendhar, A. *Chem.—Eur. J.* **2010**, *16*, 2031–2035; (j) Rodrigues, M. T., Jr.; Gomes, J. C.; Smith, J.; Coelho, F. *Tetrahedron Lett.* **2010**, *51*, 4988–4990; (k) Kitulagoda, J. E.; Palmelund, A.; Aggarwal, V. K. *Tetrahedron* **2010**, *66*, 6293–6299; (l) Kim, S. H.; Lee, S.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 6305–6309; (m) Jonnalagadda, S. C.; Verga, S. R.; Patel, P. D.; Reddy, A. V.; Srinivas, T.; Scott, P. M.; Mereddy, V. R. *Appl. Organomet. Chem.* **2010**, *24*, 294–300; (n) Baidya, M.; Remennikov, G. Y.; Mayer, P.; Mayr, H. *Chem.—Eur. J.* **2010**, *16*, 1365–1371; (o) Bakthadoss, M.; Sivakumar, G.; Kannan, D. *Org. Lett.* **2009**, *11*, 4466–4469; (p) Basavaiah, D.; Reddy, R. J. *Org. Biomol. Chem.* **2008**, *6*, 1034–1039; (q) Basavaiah, D.; Kumaragurubaran, N.; Sharada, D. S. *Tetrahedron Lett.* **2001**, *42*, 85–87.
9. (a) Basavaiah, D.; Reddy, R. M. *Tetrahedron Lett.* **2001**, *42*, 3025–3027; (b) Basavaiah, D.; Bakthadoss, M.; Pandiaraju, S. *Chem. Commun.* **1998**, 1639–1640; (c) Basavaiah, D.; Krishnamacharyulu, M.; Hyma, R. S.; Pandiaraju, S. *Tetrahedron Lett.* **1997**, *38*, 2141–2144; (d) Basavaiah, D.; Pandiaraju, S.; Padmaja, K. *Synlett* **1996**, 393–395.
10. The compound **9a** is known in the literature and prepared via the reaction of **13a** with **14a** in the presence of DABCO (1.5 equiv) (see Ref: Singh, V.; Madapa, S.; Batra, S. *Synth. Commun.* **2008**, *38*, 2113–2124). We have prepared this compound **9a** using a similar procedure with some modification.
11. It has been well documented in the literature that treatment of Baylis–Hillman acetates with Lewis acid like $AlCl_3$ provides the corresponding allyl chlorides (see Ref. 9d).
12. Detailed X-ray crystallographic data is available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK for compounds **10b** (CCDC # 903059), *ortho*-**10b** (CCDC # 903062), **10c** (CCDC # 903060), **10e** (CCDC # 903061), **10h** (CCDC # 903070), **10k** (CCDC # 903071), *ortho*-**10k** (CCDC # 903073), and **10m** (CCDC # 903072).
13. For recent references on chemoselective intramolecular Friedel–Crafts reactions see **5a** and **5d**.