$FeCl_3$ Catalysed Intramolecular Michael Reaction of Styrenes for The Synthesis of Highly Substituted Indenes

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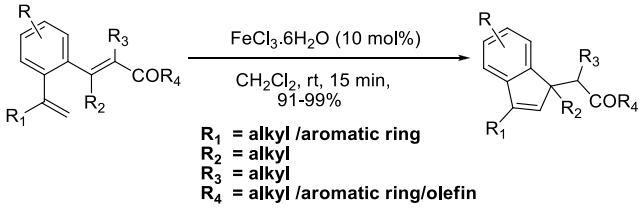
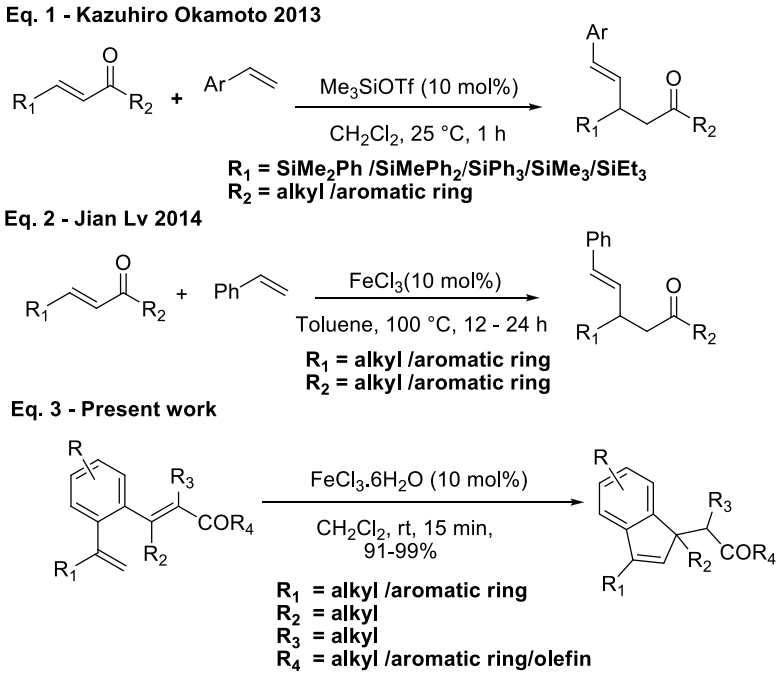


ABSTRACT: An intramolecular $FeCl_3$ catalysed Michael addition reaction of styrene, a poor nucleophile, onto the α-β unsaturated ketones was developed for the synthesis of highly substituted indene derivatives. The method was further applied for the total synthesis of sesquiterpene natural product (±)-jungianol and 1-*epi*-jungianol.

Michael addition reaction is a fundamental carbon-carbon bond forming reaction.[1] Over the decades many variants of this reaction have been developed, intermolecular olefin-Michael addition reaction have been reported by various groups, in 1980 Snider and co-workers reported that a stoichiometric amount of a *Lewis* acid catalyzed the addition of alkenes to α,β-enones.[2a] Okamoto and Ohe described an acid-catalyzed addition of simple alkenes to β-silyl substituted enones (Scheme-1 eq.1).[2b] Recently, Luo *et. al*. reported an anionic ligand strategy to facilitate β-proton elimination by suppressing cationic olefin polymerization, thus enabling the β-vinylation of enones with a variety of simple alkenes (Scheme-1 eq.2).[2c] Although intermolecular Michael reaction is well studied, the analogous intramolecular Michael reaction of olefin (alkene/styrene double bond) has rarely been explored due to the low nucleophilicity



Scheme 1: Olefin-Michael addition reaction.

of olefin carbon, uncontrolled side reactions as well as polymerization reaction in case of styrene derivatives. Variety of naturally occurring molecules contain indene/indane as a basic unit (fig. 1).[3] Indene derivatives have various applications in pharmaceuticals,[4] material chemistry[5] and also used as a ligand for transition metal complexes.[6] Due to the various applications of indene derivatives in diverse area, it is always subject of extensive study in organic synthesis and many methods for their synthesis have

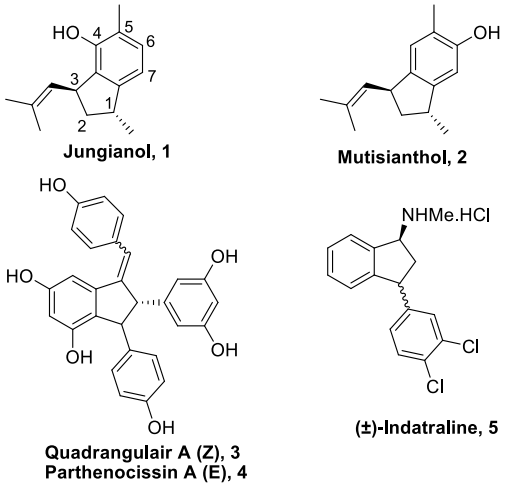
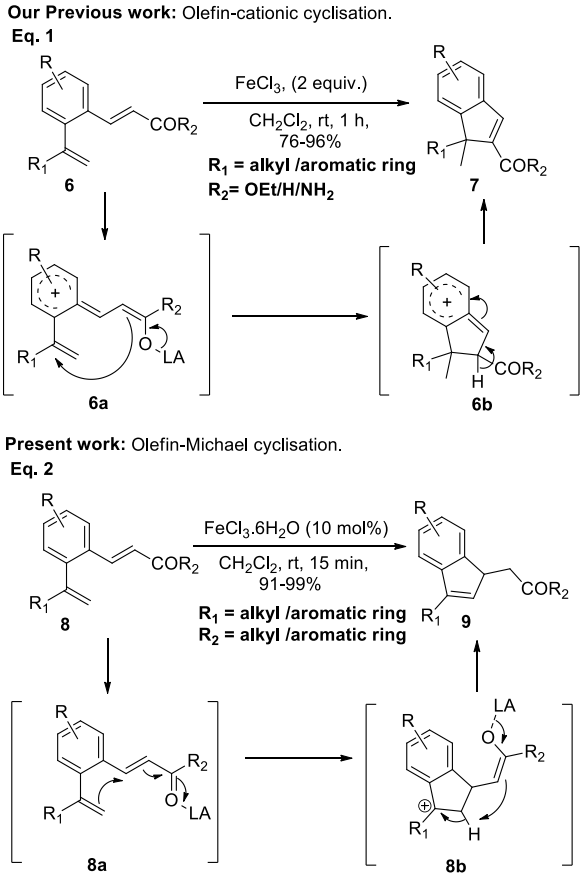


Fig1: Indane Based Natural Products.

been reported.[7] With our ongoing interest in the development of novel methods for the synthesis of indene derivatives and its application in natural product synthesis by C-C bond forming reactions,[8a,b] earlier we tried to construct the indene motif by intramolecular Michael reaction of styrene double bond onto α-β unsaturated ester, surprisingly reaction went in reverse direction than what we had planned and generated indene derivatives by intramolecular olefin cation cyclisation of cinnamates (Scheme 2).[8a]

Scheme 2: Intramolecular Olefin-Cationic Cyclisation and Intramolecular Olefin-Michael Cyclisation.



Scheme 3. Synthesis of α-β Unsaturated Ketone 13a.

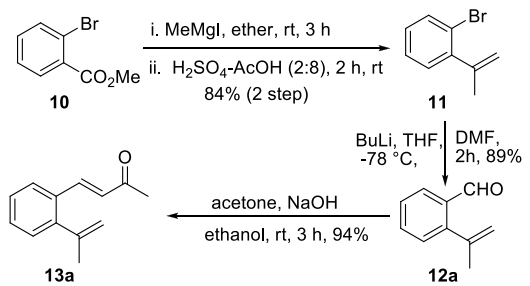
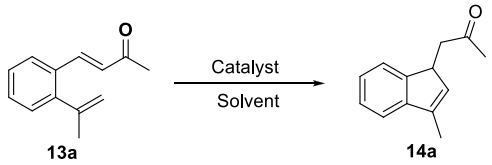


Table 1. Optimization of Olefin-Michael Cyclisation Reaction.



Entry	Catalyst	Equvi.	Solvent	Temp.	Time	Yield %
1	$FeCl_3$	2	CH_2Cl_2	rt	5 min.	C. R. M.
2	$FeCl_3$	1	CH_2Cl_2	rt	5 min.	C. R. M.
3	$FeCl_3$	0.5	CH_2Cl_2	rt	5 min.	13
4	$FeCl_3$	0.25	CH_2Cl_2	rt	5 min.	29
5	$FeCl_3$	0.1	CH_2Cl_2	rt	5 min.	53
6	$FeCl_3$	0.05	CH_2Cl_2	rt	5 min.	45
7	$Sc(OTf)_3$	0.1	CH_2Cl_2	rt	12 h	N. R.
8	$BF_3{\cdot}OEt_2$	0.1	CH_2Cl_2	rt	15 min.	68
9	$Sn(OTf)_2$	0.1	CH_2Cl_2	rt	35 min.	90
10	$SnCl_4$	0.1	CH_2Cl_2	rt	40 min.	50
11	$ZnCl_2$	0.5	CH_2Cl_2	rt	24 h	N. R
12	$FeCl_3{\cdot}6H_2O$	0.1	CH_2Cl_2	rt	15 min.	99
13	$FeCl_3{\cdot}6H_2O$	0.1	THF	rt	12 h	N. R.
14	$FeCl_3{\cdot}6H_2O$	0.1	CH_3CN	rt	12 h	70
15	$FeCl_3{\cdot}6H_2O$	0.1	MeOH	rt	12 h	N. R.
16	AgOTf	0.1	CH_2Cl_2	rt	5 h	N. R.
17	$TiCl_4$	0.1	CH_2Cl_2	rt	5 h	N. R
18	$InCl_3$	0.1	CH_2Cl_2	rt	1 h	79
19	$TiCl_3$	0.1	CH_2Cl_2	rt	5 h	N.R.
20	PTSA	0.5	CH_2Cl_2	rt	12 h	N. R.
21	$BiCl_3$	0.1	CH_2Cl_2	rt	3 h	70
22	$Fe(OTf)_3$	0.2	CH_2Cl_2	rt	30 min.	70
23	$Cu(OTf)_2$	0.1	CH_2Cl_2	rt	24 h	N.R.
24	$AlCl_3$	0.2	CH_2Cl_2	rt	12 h	N. R.
25	$Cu(OTf)_2$	0.5	DCE	80 °C	12 h	32

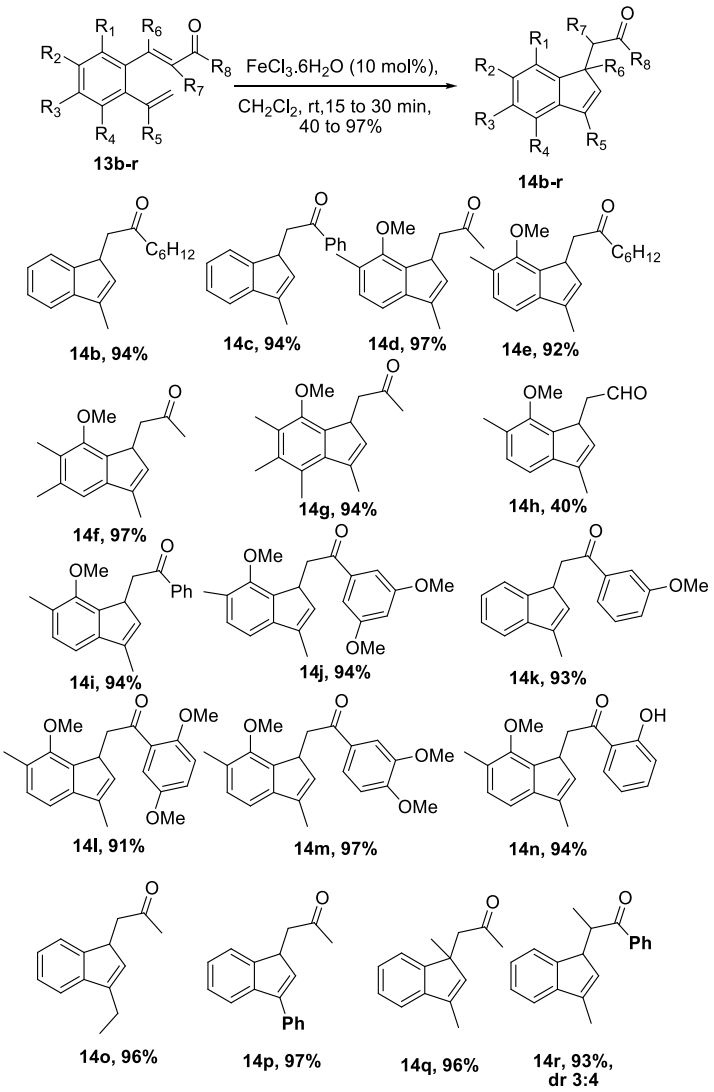
C.R.M. = Complex reaction mixture, N.R. = No reaction

According to proposed mechanism for this reaction, *Lewis* acid activates the ester group of cinnamate to generate intermediate **6a,** which undergoes intramolecular cyclization with olefin, forming intermediate **6b** which on subsequent rearomatization furnishes indene derivative **7** (scheme 2, Eq. 1). After reporting the $FeCl_3$ mediated intramolecular olefin-cation cyclisation of cinnamates, we were interested to extend this method for unsaturated ketones to see that whether reaction will follow the same path and generate the similar type of indene motif.

To begin with, the desired α-β unsaturated ketone **13a** was prepared from commercially available ethyl ortho-bromobenzoate **10**. Treatment of **10** with MeMgI followed by dehydration under acidic conditions generated the styrene derivative **11**.[9a] Compound **11** on treatment with *n*-BuLi followed by quenching with DMF generated the aldehyde **12a**.[9b] Aldol reaction of aldehyde **12a** with acetone in presence of NaOH in ethanol afforded the required ketone **13a** in 94% yield. After having the ketone **13a** in hand, it was treated with 2 equiv. $FeCl_3$ in CH_2Cl_2 as a solvent at room temperature, the best condition found for the olefin-cation cyclisation of cinnamates,[8a] but unfortunately to our disappointment it resulted in complex reaction mixture and we couldn't isolate any compound from this mixture (table 1, entry 1). Same result was obtained when **13a** was treated with 1 equiv. of $FeCl_3$ in CH_2Cl_2 as a solvent at room temperature (table 1, entry 2). Due to decomposition of starting material with stoichiometric amount of $FeCl_3$, it was decided to decrease the catalyst loading and surprisingly, we observed that when **13a** was treated with 50 mol% of $FeCl_3$ it generated olefin Michael addition product **14a** in low yield (13%), instead of olefin-cation cyclisation product as in case of cinnamates and yield of **14a** was improved to 53% when catalyst loading was decreased to 10 mol%, further decrease in catalyst loading also decreased the yield of the product **14a** (entry- 3, 4, 5 and 6, Table 1). We then screened different *Lewis* acids as shown in table 1 for this transformation. Different acid catalyst such as *p*-TSA, $Sc(OTf)_3$, AgOTf, $Cu(OTf)_2$, $AlCl_3$, $TiCl_3$, $TiCl_4$ and $ZnCl_2$ failed to generate any product and starting material **13a** was recovered. $SnCl_4$ generated required cyclised compound **14a** in 50% yield. $Sn(OTf)_2$, $InCl_3$, $BiCl_3$ and $Fe(OTf)_3$ afforded **14a** with improved yield compared to $FeCl_3$ and $SnCl_4$ (entry-9, 18, 21, 22, Table

1). $Cu(OTf)_2$ in DCE at 80 °C afforded the Michael addition product in poor yield (32%) (entry- 25, Table 1). To our delight, ketone **13a** on treatment with catalytic amount of $FeCl_3.6H_2O$ in CH_2Cl_2 as a solvent at room temperature for 15 min. generated indene derivative **14a** in almost quantitative yield (entry-12, Table 1). It is worth mentioning that to effect this transformation only catalytic

Scheme 4: Olefin-Michael Cyclisation for Synthesis of Indene Derivative.

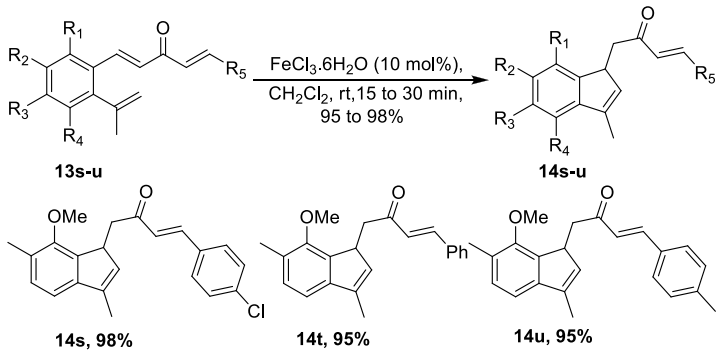


Diastereoselectivities determined from ^1H NMR of the crude reaction mixture.

amount (10 mol%) of $FeCl_3.6H_2O$ was required, unlike in the case of cinnamates derivatives **6**, which required 2 equivalents of $FeCl_3$ for olefin-cationic cyclisation reaction (Scheme 2, eq. (1)). The reaction was also found to be highly dependent on the solvent used, coordinative polar solvents such as THF, CH_3CN and MeOH either generated low yield or proved ineffective in promoting the cyclisation reac-

tion (entry-13, 14, 15, Table 1). The plausible reaction mechanism is depicted in scheme 2 (eq.2). Lewis acid activates the enone of compound **8**, which on Michael reaction with styrene double bond generates intermediate **8b**, subsequent deprotonation furnishes indene derivative. After establishing the reaction conditions, in order to expand the scope of reaction, several chalcone derivatives **13b-g** were subjected to this standard reaction condition and all were converted smoothly into indene derivatives **14b-g** with excellent yields. However in case of α-β unsaturated aldehyde **13h,** indene derivative **14h** was obtained in only 40% yield.

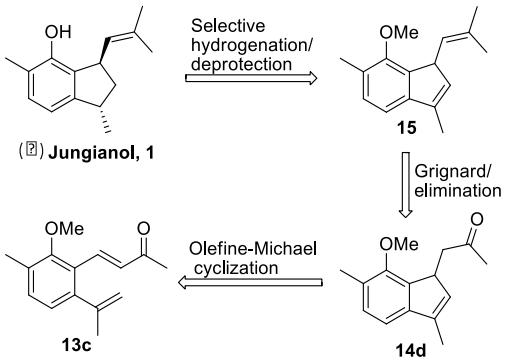
Scheme 5. Olefin-Michael Cyclisation for Synthesis of Indene Derivatives from Keto-dienone.



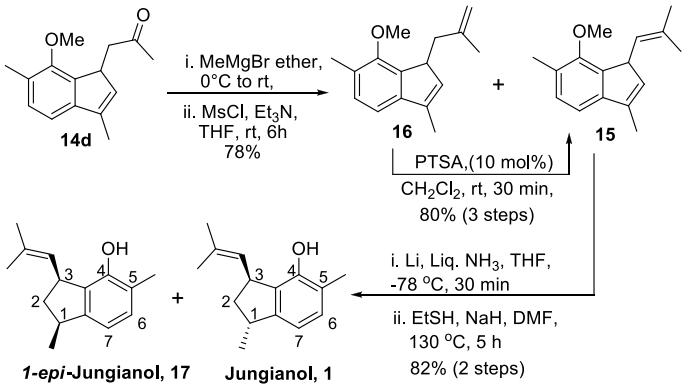
we prepared ketone **13i-n** and dienone **13s-u** having the aromatic ring or electron donating group on aromatic ring, all these compounds smoothly furnished cyclised products **14i-n** and **14s-u** respectively with very good yields (Scheme 3 and 4). Compound **13o** and **13p** containing ethyl and phenyl on α-position of styrene converted into **14o** and **14p** with 96% and 97% yield respectively. Interestingly, **13q** having α- substitution on enone converted into **14q** with 96% yield and **13r** having the β-substitution on enone furnished the compound **14r** in 93% yield with 3:4 diastereomeric mixture (Scheme 3). Next we applied this method in the total synthesis of sesquiterpene jungianol **1**, which was isolated by Bolhmann *et. al*. in 1977 from a South American plant, *Jungia malvaefolia.* Jungianol is a sesquiterpene natural product containing tetrasubstituted indene framework, having methyl and isobutene side chains on the 1 and 3 position of the indane five-member ring respectively.[3a] Initial stereo chemical assignments of side chains by isolation group was later revised by Hashmi *et. al.* unambiguously by first total synthesis of

jungianol **1** and its epimer **17**.[10] Prior to their synthesis Ho *et. al.* reported the total synthesis and revision of another isomeric natural product mutisianthol **2** in 1997[4e] that differs only in the position of the phenolic hydroxyl group from jungianol **1**. Although the biological activity of jungianol **1** is not known, its isomer mutisianthol **2** exhibits moderate antitumor activity.[4k] Our group also reported total synthesis of (±)-jungianol **1** and mutisianthol **2** using Prins-type and Nazarov cyclisation respectively.[8c,b]

Scheme 6. Retro Synthetic Analysis of (±)-Jungianol (1).



Scheme 7. Total Synthesis of (±)-Jungianol (1) and 1-*epi*-jungianol (17).



Retrosynthetic analysis of **1** is shown in Scheme 6. (±)-Jungianol **1** could be obtained from indene derivative **15** by regio- and stereo selective hydrogenation of an endocyclic double bond followed by deprotection of phenolic hydroxyl group. Indene derivative **15** could be synthesized from previously prepared Michael product **14d** (Scheme 3) through Grignard reaction followed by elimination of tertiary alcohol. Accordingly indene derivative **14d** on reaction with MeMgI followed by elimination of resulting tertiary alcohol, furnished mixture of isomers **15** and **16** in 78% yield**.** Inseparable mixture of isomers **15** and **16** on treatment with catalytic amount of *p*-TSA in CH_2Cl_2 at room temperature completely

converted into olefin **15** by isomerisation of geminally disubstituted olefin to more stable trisubstituted double bond. After having the required olefin **15** in hand, it was subjected for the selective hydrogenation of benzylic endocyclic double bond using Li/liq NH_3 at -78 °C in THF followed by deprotection of resultant methyl ether furnished mixture of jungianol **1** and its epimer **17**, which were carefully separated by silica gel column chromatography. The spectral data of jungianol **1** and *epi*-jungianol **17** (IR, ^{1}H, ^{13}C, and HRMS) was in complete agreement with those reported in literature.[3a,10]

In conclusion, after varying Michael acceptor from unsaturated ester/amide/acid to unsaturated ketone/aldehyde on ortho-position of styrene, exclusive intramolecular olefin-Michael cyclisation reaction occurred instead of intramolecular olefin-cationic cyclisation. Various substituted indene derivatives were prepared from ortho substituted unsaturated keto styrenes using $FeCl_3.6H_2O$ catalysed intramolecular olefin-Michael reaction. Further this reaction was utilised for the total synthesis of jungianol **1** (30% overall yield), and its 1-*epi*-jungianol **17** (30% overall yield).

EXPERIMENTAL SECTION

General Aspects. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially and used without further purification. Anhydrous THF and diethyl ether were distilled from sodium benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60F-254) using UV light as a visualizing agent and a p-anisaldehyde or ninhydrine stain, and heat as developing agents. Silica gel (particle size: 100−200 and 230−400 mesh) was used for flash column chromatography. Neat coumpounds were used for recording IR spectra. NMR spectra were recorded on either 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Mass spectrometric data were obtained using Q-Tof-ESI. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet

of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad

Experimental Procedures. A) General procedure for Aldol reaction: A mixture of corresponding aldehyde (1 equiv.) and the corresponding ketone (1 equiv.) in anhydrous ethanol was stirred at room temperature for 5 min. Then NaOH (3 equiv.) was added. The reaction mixture was stirred at room temperature until aldehyde consumed (usually up to 3h). After that, HCl (10%) was added until pH 5 was obtained. Extracted with ethyl acetate (3 x 7 ml). The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel column chromatography using EtOAc-hexane as eluent furnished unsaturated ketone**.**

*(E)-4-(2-(prop-1-en-2-yl)phenyl)but-3-en-2-one (**13a**)*. According to the general procedure **A** for aldol reaction, 2-(prop-1-en-2-yl)benzaldehyde **(12a)** (1 gm, 6.84 mmol), acetone (**18a)** (0.5 ml, 6.84 mmol), and NaOH (820 mg, 20 mmol), in ethanol (7 ml) were used to furnish the product **13a** (1.2 gm, 94%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2924, 2852, 1692, 1672, 1608, 1595, 1463, 1358, 1313, 1254, 1176, 981; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (d, *J* = 0.91 Hz, 3H), 2.36 (s, 3H), 4.88 (s, 1H), 5.36 (s, 1H), 6.65 (d, *J* = 16.3 Hz, 1H), 7.26 - 7.33 (m, 2H), 7.33 - 7.43 (m, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 27.3, 117.6, 126.6, 127.4, 127.9, 128.3, 130.0, 131.7, 142.6, 143.7, 145.1, 198.6; HRMS: m/z calcd for $C_{13}H_{15}O$ $[(M+H)^+]$: 187.1123; Found: 187.1125.

*(E)-1-(2-(prop-1-en-2-yl)phenyl)non-1-en-3-one (**13b**)*. According to the general procedure **A** for aldol reaction, reaction, 2-(prop-1-en-2-yl)benzaldehyde **(12a)** (45 mg, 0.31 mmol), octan-2-one (**18b)** (37 mg, 0.31 mmol), and NaOH (35 mg, 0.92 mmol), in ethanol (2 ml) were used to furnish the product **13b** (66 mg, 86%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 3:97); IR (neat): ν_{max}/cm^{-1} 2956, 2929, 1691, 1667, 1609, 1595, 1480, 1452, 1303, 1174, 1074; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, *J* = 14.0 Hz, 3H), 1.32 (m, 6H), 1.63 - 1.72 (m, 2H), 2.09 (s, 3H), 2.64 (t, *J* = 7.5 Hz, 2H), 4.86 (s, 1H), 5.35 (s, 1H),

6.64 (s, 1H), 7.26 - 7.39 (m, 3H), 7.62 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 15.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 24.5, 24.9, 29.0, 31.6, 40.6, 117.6, 126.5, 127.0, 127.3, 128.3, 129.8, 131.9, 141.5, 143.7, 145.1, 201.0; HRMS: m/z calcd for $C_{18}H_{25}O$ [$(M+H)^+$]: 257.1905; Found: 257.1904.

*(E)-1-phenyl-3-(2-(prop-1-en-2-yl)phenyl)prop-2-en-1-one (**13c**).* According to the general procedure **A** for aldol reaction, 2-(prop-1-en-2-yl)benzaldehyde **(12a)** (50 mg, 0.34 mmol), acetophenone (**18c)** (41 mg, 0.34 mmol), and NaOH (41 mg, 1.03 mmol), in ethanol (2 ml) were used to furnish the product **13c** (70 mg, 82%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 3:97); IR (neat): v_{max}/cm^{-1} 3060, 1662, 1603, 1592, 1479, 1447, 1314, 1212,1016; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 4.90 (s, 1H), 5.35 (d, J = 1.7 Hz, 1 H), 7.27 - 7.41 (m, 3H), 7.46 - 7.53 (m, 3H), 7.55 - 7.62 (m, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.96 - 8.04 (m, 2H), 8.06 (d, J = 15.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.9, 117.7, 122.7, 126.8, 127.3, 128.4, 128.5, 128.6, 130.0, 132.3, 132.7, 138.2, 143.7, 143.9, 143.9, 145.5, 190.6; HRMS: m/z calcd for $C_{18}H_{17}O$ [$(M+H)^+$]: 249.1279; Found: 249.1272.

*(E)-4-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)but-3-en-2-one (**13d**).* According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (1 gm, 5.26 mmol), acetone (**18a)** (0.385 ml, 5.26 mmol), and NaOH (630 mg, 15.77 mmol), in ethanol (7 ml) were used to furnish the product **13d** (1.12 gm, 93%) as a yellow oil. R_f = 0.23 (EtOAc-hexane 5:95); IR (neat): v_{max}/cm^{-1} 2927, 1670, 1456, 1327, 1251, 1093, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.30 (s, 3H), 2.35 (s, 3H), 3.67 (s, 3H), 4.89 (s, 1H), 5.23 - 5.26 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 16.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.6, 27.4, 59.9, 116.8, 124.4, 125.0, 130.5, 131.2, 132.2, 139.0, 144.6, 144.8, 157.8, 199.4; HRMS: m/z calcd for $C_{15}H_{19}O_2$ [$(M+H)^+$]: 231.1385; Found: 231.1380.

(E)-1-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)non-1-en-3-one (13e). According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (45 mg, 0.23 mmol), octan-2-one (**18b)** (28 mg, 0.23 mmol), and NaOH (28 mg, 0.71 mmol), in ethanol (5 ml) were used to furnish the product **13e** (52 mg, 89%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR

(neat): ν_{max}/cm^{-1} 2929, 1690, 1664, 1607, 1591, 1475, 1302, 1218, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 - 0.93 (m, 3H), 1.28 - 1.38 (m, 6H), 1.62 - 1.68 (m, 2H), 1.98 - 2.03 (m, 3H), 2.30 (s, 3H), 2.57 - 2.64 (m, 2H), 3.67 (s, 3H), 4.89 (dd, *J* = 1.8, 1.0 Hz, 1H), 5.24 (t, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 16.5 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 15.9, 22.5, 24.5, 24.6, 29.0, 31.6, 41.1, 59.9, 116.8, 124.4, 125.3, 130.3, 130.4, 132.0, 137.8, 144.6, 144.8, 157.8, 201.7; HRMS: m/z calcd for $C_{20}H_{29}O_2$ $[(M+H)^+]$: 301.2168; Found: 301.2162.

*(E)-4-(2-methoxy-3,4-dimethyl-6-(prop-1-en-2-yl)phenyl)but-3-en-2-one (**13f**)*. According to the general procedure **A** for aldol reaction, 2-methoxy-3,4-dimethyl-6-(prop-1-en-2-yl)benzaldehyde (**12c)** (100 mg, 0.49 mmol), acetone (**18a)** (0.036 ml, 0.49 mmol), and NaOH (59 mg, 1.47 mmol), in ethanol (3 ml) were used to furnish the product **13f** (112 mg, 94%) as a yellow oil. R_f = 0.2 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2927, 1667, 1591, 1446, 1357, 1314, 1251, 1093, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 - 2.06 (m, 3H), 2.21 (s, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 3.65 (s, 3H), 4.85 - 4.92 (m, 1H), 5.15 - 5.32 (m, 1H), 6.82 (s, 1H), 7.00 (d, *J* = 16.7 Hz, 1H), 7.68 (d, *J* = 16.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 20.3, 24.7, 27.4, 60.2, 116.6, 122.4, 126.0, 129.3, 130.4, 139.3, 140.4, 143.9, 145.0, 157.8, 199.6; HRMS: m/z calcd for $C_{16}H_{20}NaO_2$ $[(M+Na)^+]$: 267.1361; Found: 267.1369.

*(E)-4-(2-methoxy-3,4,5-trimethyl-6-(prop-1-en-2-yl)phenyl)but-3-en-2-one (**13g**)*. According to the general procedure **A** for aldol reaction, 2-methoxy-3,4,5-trimethyl-6-(prop-1-en-2-yl)benzaldehyde (**12d)** (90 mg, 0.41 mmol), acetone (**18a)** (0.03 ml, 0.26 mmol), and NaOH (102 mg, 0.26 mmol), in ethanol (3 ml) were used to furnish the product **13g** (96 mg, 94%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2926, 1665, 1600, 1572, 1453, 1358, 1250, 1102; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.18 (s, 3H), 2.23 (s, 3H), 2.25 (s, 3H), 2.32 - 2.34 (m, 3H), 3.61 - 3.64 (m, 3H), 4.81 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 7.08 (d, *J* = 16.6 Hz, 1H), 7.67 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.7, 16.8, 16.9, 25.0, 27.4, 59.9, 116.9, 121.9, 128.9, 129.3, 130.4, 139.6, 140.0, 143.6, 144.4, 155.9, 199.9; HRMS: m/z calcd for $C_{17}H_{23}O_2$ $[(M+H)^+]$: 259.1698; Found: 259.1690.

*(E)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)acrylaldehyde (**13h**).* Step 1: Benzyl chloride (0.72 ml, 6.3 mmol) was added to a stirred solution of the LAH_4 (48 mg, 1.26 mmol) in dry THF (4 ml) at 0 °C and stirred reaction mixture for 30 minute at same temperature then (E)-ethyl 3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)acrylate (**19)** (110 mg, 0.42 mmol) in THF (1 ml) was added to this reaction mixture and resultant reaction mixture was stirred for 3h. The reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Evaporation of the solvent furnished the alcohol, which was used in the oxidation reaction without further purification. Step 2: To a solution of the crude alcohol obtained in above reaction in ethyl acetate (4 ml) was added IBX (208 mg, 0.84 mmol) and refluxed for 3 h. Aq. $NaHCO_3$ was added to the reaction mixture and extracted with ethyl acetate (3 x 15 ml). The organic extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel column chromatography using EtOAc-hexane as eluent furnished aldehyde **13h** (70 mg, 77%) as a yellow oil. R_f = 0.40 (EtOAc-hexane 15:85); IR (neat): ν_{max}/cm^{-1} 2934, 1681, 1616, 1593, 1477, 1303, 1216, 1121, 1017; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.31 (s, 3H), 3.68 (s, 3H), 4.91 (s, 1H), 5.27 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.04 (dd, *J* = 16.3, 8.0 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 16.0 Hz, 1H), 9.66 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.7, 59.9, 117.1, 124.5, 130.6, 132.7, 133.3, 144.5, 144.8, 148.7, 158.0, 195.5; HRMS: m/z calcd for $C_{14}H_{17}O_2$ $[(M+H)^+]$: 217.1229; Found: 217.1223.

*(E)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)-1-phenylprop-2-en-1-one (**13i**).* According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (63 mg, 0.33 mmol), acetophenone (**18c)** (40 mg, 0.33 mmol), and NaOH (40 mg, 1.00 mmol), in ethanol (3 ml) were used to furnish the product **13i** (78 mg, 81%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 15:85); IR (neat): ν_{max}/cm^{-1} 2923, 1612, 1491, 1448, 1254, 1216, 1180, 1156; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.33 (s, 3H), 3.72 (s, 3H), 4.94 (s, 1H), 5.29 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 1.8

Hz, 2H), 8.01 - 8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.8, 60.0, 116.9, 124.4, 125.9, 126.0, 128.5, 128.6, 145.0, 130.5, 132.2, 132.7, 138.3, 140.0, 145.0, 145.0, 158.0, 190.9; HRMS: m/z calcd for $C_{20}H_{21}O_2$ [$(M+H)^+$]: 293.1542; Found: 293.1543.

(E)-1-(3,5-dimethoxyphenyl)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13j)***. According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (70 mg, 0.37 mmol), 1-(3,5-dimethoxyphenyl)ethanone (**18d)** (66 mg, 0.37 mmol), and NaOH (44 mg, 1.10 mmol), in ethanol (3 ml) were used to furnish the product **13j** (99 mg, 76%) as a yellow oil. R_f = 0.40 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2937, 1663, 1589, 1425, 1456, 1351, 1310, 1205, 1156, 1042; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.32 (s, 3H), 3.71 (s, 3H), 3.86 (s, 6H), 4.86 - 5.02 (m, 1H), 5.19 - 5.36 (m, 1H), 6.62 - 6.70 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 7.11 - 7.21 (m, 3H), 7.86 (d, *J* = 15.7 Hz, 1H), 7.96 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.7, 55.5, 60.0, 105.1, 106.1, 106.3, 116.8, 124.5, 125.7, 126.1, 130.5, 132.2, 140.1, 140.3, 144.9, 145.1, 158.0, 160.8, 190.5; HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ [$(M+Na)^+$]: 375.1572; Found: 375.1570.

(E)-1-(3-methoxyphenyl)-3-(2-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13k)***. According to the general procedure **A** for aldol reaction, 2-(prop-1-en-2-yl)benzaldehyde **(12a)** (40 mg, 0.27 mmol), 1-(3-methoxyphenyl) ethanone (**18e)** (41 mg, 0.27 mmol), and NaOH (32 mg, 0.82 mmol), in ethanol (2 ml) were used to furnish the product **13k** (55 mg, 81%) as a yellow oil. R_f = 0.23 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2937, 1661, 1588, 1450, 1429, 1318, 1267, 1195, 1027; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.89 (s, 3H), 4.89 - 4.91 (m, 1H), 5.35 - 5.37 (m, 1H), 7.11 - 7.15 (m, 1H), 7.28 - 7.43 (m, 4H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.55 (s, 1H), 7.59 - 7.62 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.9, 55.5, 112.8, 117.7, 119.2, 121.0, 122.8, 126.8, 127.3, 128.4, 130.0, 132.3, 139.6, 143.7, 144.0, 145.5, 159.9, 190.3; HRMS: m/z calcd for $C_{19}H_{19}O_2$ [$(M+H)^+$]: 279.1385; Found: 279.1388.

(E)-1-(2,5-dimethoxyphenyl)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13l)***. According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (80 mg, 0.42 mmol), 1-(2,5-dimethoxyphenyl)ethanone (**18f)** (76 mg, 0.42 mmol), and NaOH (50 mg, 1.26 mmol), in ethanol (3 ml) were used to furnish the product **13l** (114 mg, 77%) as a yellow oil. R_f = 0.40 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2937, 1654, 1581, 1493, 1463, 1412, 1301, 1276, 1222, 1042, 1022; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.30 (s, 3H), 3.70 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 4.91 (d, *J* = 0.9 Hz, 1H), 5.22 (d, *J* = 1.7 Hz, 1H), 6.87 - 6.93 (m, 2H), 7.01 (dd, *J* = 8.9, 3.1 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 3.1 Hz, 1H), 7.70 (d, *J* = 16.3 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.6, 55.8, 56.3, 60.0, 113.1, 114.3, 116.6, 118.9, 124.4, 125.8, 129.8, 130.4, 130.7, 132.0, 138.9, 144.9, 145.1, 152.5, 153.5, 158.0, 193.3; HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ $[(M+Na)^+]$: 375.1572; Found: 375.1573.

(E)-1-(3,4-dimethoxyphenyl)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13m)***. According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (56 mg, 0.29 mmol), 1-(3,4-dimethoxyphenyl)ethanone (**18g)** (53 mg, 0.29 mmol), and NaOH (35 mg, 0.88 mmol), in ethanol (3 ml) were used to furnish the product **13m** (79 mg, 76%) as a yellow oil. R_f = 0.20 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2935, 1655, 1594, 1580, 1514, 1463, 1417, 1304, 1265, 1162, 1023; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.33 (s, 3H), 3.71 (s, 3H), 3.97 (s, 6H), 4.95 (s, 1H), 5.28 (s, 1H), 6.92 - 6.94 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.63 - 7.71 (m, 2H), 7.94 (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.7, 55.9, 56.0, 60.0, 110.0, 110.7, 116.7, 123.0, 124.5, 125.7, 125.8, 130.4, 131.4, 132.0, 139.1, 144.8, 145.2, 149.1, 153.1, 157.9, 189.1; HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ $[(M+Na)^+]$: 375.1572; Found: 375.1571.

(E)-1-(2-hydroxyphenyl)-3-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13n)***. According to the general procedure **A** for aldol reaction, 2-methoxy-3-methyl-6-(prop-1-en-2-yl)benzaldehyde (**12b)** (100 mg, 0.53 mmol), 1-(2-hydroxyphenyl)ethanone (**18h)** (72 mg, 0.53mmol), and NaOH (63 mg, 1.58 mmol), in ethanol (3 ml) were used to furnish the product **13n** (130 mg, 80%)

as a yellow oil. R_f = 0.30 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 3391, 2935, 1636, 1579, 1486, 1443, 1395, 1360, 1271, 1252, 1218, 1156, 1021; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.34 (s, 3H), 3.73 (s, 3H), 4.95 (s, 1H), 5.33 (s, 1H), 6.91 - 6.96 (m, 2H), 7.03 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.1, 1.8 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.02 - 8.07 (m, 1H), 8.08 - 8.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.8, 60.0, 117.1, 118.5, 118.8, 120.2, 124.2, 124.5, 125.3, 129.7, 130.6, 132.7, 136.2, 140.7, 144.9, 145.3, 158.2, 163.6, 194.7; HRMS: m/z calcd for $C_{20}H_{21}O_3$ [$(M+H)^+$]: 309.1491; Found: 309.1491.

*(E)-4-(2-(but-1-en-2-yl)phenyl)but-3-en-2-one(**13o**)*. According to the general procedure **A** for aldol reaction, 2-(but-1-en-2-yl)benzaldehyde (**12c)** (100 mg, 0.62 mmol), acetone (**18a)** (36 mg, 0.62 mmol), and NaOH (75 mg, 1.87 mmol), in ethanol (3 ml) were used to furnish the product **13o** (100 mg, 80%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2924, 1691, 1565, 1480, 1452, 1315, 1174; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.4 Hz, 3H), 2.33 - 2.36 (m, 3H), 2.36 - 2.45 (m, 2H), 4.88 (s, 1H), 5.33 (s, 1H), 6.64 (d, *J* = 16.3 Hz, 1H), 7.21 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (td, *J* = 7.4, 1.5 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.74 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 27.2, 31.3, 115.2, 126.4, 127.3, 127.8, 128.7, 129.8, 132.1, 142.6, 144.8, 149.7, 198.6; HRMS: m/z calcd for $C_{14}H_{17}O$ [$(M+H)^+$]: 201.1279; Found: 201.1286.

*(E)-4-(2-(1-phenylvinyl)phenyl)but-3-en-2-one (**13p**)*. According to the general procedure **A** for aldol reaction, 2-(1-phenylvinyl)benzaldehyde **(12d)** (104 mg, 0.5 mmol), acetone **(18a)** (29 mg, 0.5 mmol), and NaOH (60 mg, 1.5 mmol), in ethanol (3 ml) were used to furnish the product **13p** (101 mg, 81%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2950, 1695, 1586, 1472, 1215; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 3H), 5.24 (d, *J* = 1.2 Hz, 1H), 5.88 (d, *J* = 1.1 Hz, 1H), 6.50 (d, *J* = 16.4 Hz, 1H), 7.22 - 7.26 (m, 2H), 7.26 - 7.33 (m, 4H), 7.35 - 7.43 (m, 2H), 7.50 (d, *J* = 16.4 Hz, 1H), 7.62 - 7.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 117.1, 126.4, 126.9, 128.0, 128.1, 128.2,

128.5, 130.1, 130.7, 133.1, 140.9, 142.6, 142.9, 147.9, 198.8; HRMS: m/z calcd for $C_{18}H_{17}O$ $[(M+H)^+]$: 249.1279; Found: 249.1280.

(E)-4-(2-(prop-1-en-2-yl)phenyl)pent-3-en-2-one ***(13q)*** Step1: A solution of Diethyl 2-oxopropanephosphonate (242 mg, 1.25 mmol) in THF (2 ml) was slowly added to a suspension of NaH (50 mg, 1.25 mmol) in THF (3 mL) at 0 °C during a period of 30 minutes. The mixture was stirred at room temperature and then became clear. 1-(2-(prop-1-en-2-yl)phenyl)ethanone (**18c**) (100 mg, 0.624 mmol) was added to the mixture at 0 °C, then stirred at room temperature for 30 hours. After confirmation of consumption of starting material, a solution of saturated aqueous $NaHCO_3$ (3 mL) was added. THF was removed under reduced pressure, and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with brine (2 mL) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel furnish the product **13q** (55 mg, 44%) as a yellow oil. R_f = 0.4 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 1655, 1589, 1465, 1314, 1265, 1262, 1023; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.24 (s, 3H), 2.41 (s, 3H), 4.98 (d, J = 1.4 Hz, 1H), 5.11 - 5.16 (m, 1H), 6.30 (d, J = 0.9 Hz, 1H), 7.13 - 7.17 (m, 1H), 7.23 - 7.25 (m, 1H), 7.27 - 7.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 23.9, 32.0, 116.4, 126.7, 127.0, 127.8, 127.9, 128.0, 128.7, 141.5, 142.1, 145.1, 157.1, 198.8; HRMS: m/z calcd for $C_{14}H_{17}O$ $[(M+H)^+]$: 201.1279; Found: 201.1281.

(E)-2-methyl-1-phenyl-3-(2-(prop-1-en-2-yl)phenyl)prop-2-en-1-one ***(13r)***. According to the general procedure **A** for aldol reaction, 2-(prop-1-en-2-yl)benzaldehyde **(12a)** (50 mg, 0.34 mmol), propiophenone **(18b)** (46 mg, 0.34 mmol), and NaOH (41 mg, 1.03 mmol), in ethanol (3 ml) were used to furnish the product **13r** (68 mg, 76%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2924, 1692, 1660, 1595, 1368, 1224,; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H), 2.15 (d, J = 1.4 Hz, 3H), 4.84 (dd, J = 1.9, 1 Hz, 1H), 5.16 - 5.21 (m, 1H), 7.22 - 7.27 (m, 2H), 7.27 - 7.34 (m, 2H), 7.35 - 7.47 (m, 3H), 7.49 - 7.54 (m, 1H), 7.67 - 7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 24.2,

116.8, 126.7, 127.8, 128.1, 128.3, 129.3, 129.4, 131.5, 133.4, 136.8, 138.5, 142.6, 143.9, 144.3, 199.4; HRMS: m/z calcd for $C_{19}H_{19}O$ $[(M+H)^+]$: 263.1436; Found: 263.1439.

*(1E,4E)-1-(4-chlorophenyl)-5-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)penta-1,4-dien-3-one (**13s**).* According to the general procedure **A** for aldol reaction, 4-chlorobenzaldehyde (**20a**) (70 mg, 0.30 mmol), ketone **13d** (43 mg, 0.30 mmol), and NaOH (37 mg, 0.91 mmol), in ethanol (3 ml) were used to furnish the product **13s** (95 mg, 89%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2927, 1656, 1612, 1490, 1406, 1318, 1218, 1090, 1012; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 - 2.04 (m, 3H), 2.32 (s, 3H), 3.70 (s, 3H), 4.92 - 4.93 (m, 1H), 5.28 (t, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.36 - 7.40 (m, 2H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.51 - 7.55 (m, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.7, 60.0, 117.0, 124.4, 125.4, 126.5, 129.0, 129.2, 129.4, 130.5, 132.3, 133.3, 136.2, 139.0, 141.5, 144.8, 144.9, 157.9, 189.5; HRMS: m/z calcd for $C_{22}H_{22}ClO_2$ $[(M+H)^+]$: 353.1308; Found: 353.1309.

*(1E,4E)-1-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)-5-phenylpenta-1,4-dien-3-one (**13t**).* According to the general procedure **A** for aldol reaction, benzaldehyde (**20b**) (90 mg, 0.40 mmol), ketone **13d** (42 mg, 0.40 mmol), and NaOH (47 mg, 1.17 mmol), in ethanol (3 ml) were used to furnish the product **13t** (98 mg, 79%) as a yellow oil. R_f = 0.29 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2931, 1652, 1616, 1475, 1444, 1394, 1332, 1218, 1098; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.33 (s, 3H), 3.71 (s, 3H), 4.94 (s, 1H), 5.29 (t, *J* = 1.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.58 - 7.63 (m, 2H), 7.71 (d, *J* = 16.0 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 24.7, 60.0, 116.9, 124.4, 125.5, 126.2, 128.3, 128.3, 128.9, 129.1, 130.4, 130.5, 132.2, 134.9, 138.8, 143.0, 144.9, 157.9, 189.8; HRMS: m/z calcd for $C_{22}H_{23}O_2$ $[(M+H)^+]$: 319.1698; Found: 319.1690.

*(1E,4E)-1-(2-methoxy-3-methyl-6-(prop-1-en-2-yl)phenyl)-5-p-tolylpenta-1,4-dien-3-one (**13u**).* According to the general procedure **A** for aldol reaction, 4-methylbenzaldehyde (**20c**) (80 mg, 0.35 mmol), ke-

tone **13d** (42 mg, 0.35 mmol), and NaOH (42 mg, 1 mmol), in ethanol (3 ml) were used to furnish the product **13u** (92 mg, 77%) as a yellow oil. R_f = 0.30 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2931, 1651, 1614, 1511, 1448, 1325, 1258, 1179, 1096, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.33 (s, 3H), 2.39 (s, 3H), 3.71 (s, 3H), 4.89 - 4.99 (m, 1H), 5.26 - 5.29 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.19 - 7.25 (m, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 16.5 Hz, 1H), 7.48 - 7.54 (m, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.87 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 21.5, 24.7, 59.9, 116.9, 124.4, 125.3, 125.6, 125.9, 128.3, 129.2, 129.6, 130.4, 132.1, 132.1, 138.5, 140.9, 143.1, 144.8, 144.9, 157.9, 189.9; HRMS: m/z calcd for $C_{23}H_{24}NaO_2$ [$(M+Na)^+$]: 355.1674; Found: 355.1674.

B) General procedure for the olefin-Michael cyclisation reaction: Under argon atmosphere to a magnetically stirred solution of keto in CH_2Cl_2 was added $FeCl_3.6H_2O$ (10 mol %) and stirred for 15 to 30 min. When completion of the reaction was noticed by TLC, added saturated solution of $NaHCO_3$ and resultant reaction mixture was extracted with CH_2Cl_2. The combined organic extract was washed with brine and dried over Na_2SO_4. Evaporation of solvent and purification of residue on a silica gel column using EtOAc-hexane as eluent, afforded cyclised product.

*1-(3-methyl-1H-inden-1-yl)propan-2-one (**14a**).* According to the general procedure of cyclization reaction, compound **13a** (71 mg, 0.381 mmol) and $FeCl_3.6H_2O$ (10.3 mg, 0.038 mmol), in CH_2Cl_2 (4 ml) were used to furnish the product **14a** (70 mg, 99%) as a yellow oil. R_f = 0.29 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2920, 1716, 1463, 1359, 1155; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.18 (s, 3H), 2.52 (dd, *J* = 17.3, 8.6 Hz, 1H), 2.85 (dd, *J* = 17.4, 6.4 Hz, 1H), 3.83 - 3.93 (m, 1H), 6.17 (s, 1H), 7.15 - 7.24 (m, 1H), 7.27 - 7.33 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 30.3, 43.9, 45.3, 119.1, 122.8, 124.9, 126.7, 133.3, 139.4, 145.4, 147.3, 207.7; HRMS: m/z calcd for $C_{13}H_{15}O$ [$(M+H)^+$]: 187.1123; Found: 187.1126.

*1-(3-methyl-1H-inden-1-yl)octan-2-one (**14b**).* According to the general procedure of cyclization reaction, compound **13b** (36 mg, 0.140 mmol) and $FeCl_3.6H_2O$ (3.8 mg, 0.014 mmol), in CH_2Cl_2 (3 ml)

were used to furnish the product **14b** (34 mg, 94%) as a yellow oil. R_f = 0.4 (EtOAc-hexane 5:95); **IR** (neat): v_{max}/cm^{-1} 2956, 2929, 2857, 1712, 1606, 1463, 1405, 1375, 1265, 1126, 1080; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 2H), 1.28 (br. s., 4H), 1.59 (m, 3H), 2.12 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.49 (dd, *J* = 17.2, 8.5 Hz, 1H), 2.80 (dd, *J* = 17.2, 6.5 Hz, 1H), 3.87 - 3.91 (m, 1H), 6.16 (s, 1H), 7.15 - 7.22 (m, 1H), 7.27 - 7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 13.0, 14.0, 22.5, 23.8, 28.9, 29.7, 31.6, 43.2, 43.9, 44.3, 119.0, 122.8, 124.9, 126.6, 133.4, 139.3, 145.4, 147.5, 210.2; HRMS: m/z calcd for $C_{18}H_{25}O$ [$(M+H)^+$]: 257.1905; Found: 257.1903.

*2-(3-methyl-1H-inden-1-yl)-1-phenylethanone (**14c**).* According to the general procedure of cyclization reaction, compound **13c** (36 mg, 0.145 mmol) and $FeCl_3.6H_2O$ (3.9 mg, 0.014 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14c** (34 mg, 94%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): v_{max}/cm^{-1} 2926, 1684, 1597, 1448, 1356, 1276, 1180, 1075; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H), 3.05 (dd, *J* = 17.3, 8.7 Hz, 1H), 3.39 (dd, *J* = 17.3, 6.2 Hz, 1H), 4.09 (br. s., 1H), 6.26 (s, 1H), 7.20 (dt, *J* = 8.0, 4.0 Hz, 1H), 7.29 - 7.34 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 40.6, 44.2, 119.1, 123.0, 124.9, 126.7, 128.1, 128.6, 133.2, 133.7, 136.9, 139.3, 145.5, 147.6, 199.1; HRMS: m/z calcd for $C_{18}H_{17}O$ [$(M+H)^+$]: 249.1279; Found: 249.1272.

*1-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)propan-2-one (**14d**).* According to the general procedure of cyclization reaction, compound **13d** (40 mg, 0.174 mmol) and $FeCl_3.6H_2O$ (4.6 mg, 0.017 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14d** (39 mg, 97%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): v_{max}/cm^{-1} 2927, 1715, 1577, 1477, 1448, 1416, 1359, 1254, 1162, 1025; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (br. s., 3H), 2.17 (s, 3H), 2.23 - 2.28 (m, 1H), 2.31 (s, 3H), 3.39 (dd, *J* = 17.5, 4.3 Hz, 1H), 3.79 (s, 3H), 3.94 - 4.06 (m, 1H), 6.14 (br. s., 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 15.8, 30.3, 42.7, 43.4, 59.8, 114.9, 127.8, 130.1, 132.9, 137.5, 139.1, 145.7, 154.5, 208.1; HRMS: m/z calcd for $C_{15}H_{19}O_2$ [$(M+H)^+$]: 231.1385; Found: 231.1380.

*1-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)octan-2-one (**14e**).* According to the general procedure of cyclization reaction, compound **13e** (40 mg, 0.133 mmol) and $FeCl_3.6H_2O$ (3.6 mg, 0.013 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14e** (37 mg, 92%) as a yellow oil. R_f = 0.33 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2927, 2856, 1714, 1476, 1416, 1243, 1121, 1243, 1121, 1020; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 - 0.91 (m, 3H), 1.27 - 1.35 (m, 6H), 1.59 - 1.64 (m, 2H), 2.08 (br. s., 3H), 2.23 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.31 (s, 3H), 2.33 - 2.41 (m, 1H), 2.41 - 2.50 (m, 1H), 3.35 (dd, *J* = 17.4, 4.3 Hz, 1H), 3.79 (s, 3H), 3.97 - 4.05 (m, 1H), 6.13 (br. s., 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 14.0, 15.8, 22.5, 23.8, 28.9, 31.6, 42.4, 42.7, 43.2, 59.8, 114.9, 127.7, 130.0, 133.0, 137.6, 138.9, 145.7, 154.5, 210.6; HRMS: m/z calcd for $C_{20}H_{28}NaO_2$ $[(M+Na)^+]$: 323.1987; Found: 323.1981.

*1-(7-methoxy-3,5,6-trimethyl-1H-inden-1-yl)propan-2-one (**14f**).* According to the general procedure of cyclization reaction, compound **13f** (30 mg, 0.12 mmol) and $FeCl_3.6H_2O$ (3.3 mg, 0.012 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14f** (29 mg, 97%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2927, 1715, 1475, 1458, 1426, 1244, 1025; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (br. s., 3H), 2.16 (s, 3H), 2.18 - 2.22 (m, 3H), 2.25 (d, *J* = 7.1 Hz, 1H), 2.31 (s, 3H), 3.38 (dd, *J* = 17.4, 4.3 Hz, 1H), 3.76 (s, 3H), 3.92 - 4.01 (m, 1 H), 6.12 (br. s., 1H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 12.9, 20.5, 30.3, 42.7, 43.5, 60.1, 116.7, 126.3, 132.9, 134.9, 137.4, 139.1, 144.7, 154.3, 208.3; HRMS: m/z calcd for $C_{16}H_{21}O_2$ $[(M+H)^+]$: 245.1542; Found: 245.1542.

1-*(7-methoxy-3,4,5,6-tetramethyl-1H-inden-1-yl)propan-2-one (**14g**).* According to the general procedure of cyclization reaction, compound **13g** (35 mg, 0.135 mmol) and $FeCl_3.6H_2O$ (3.66 mg, 0.013 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14g** (33 mg, 94%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2928, 1714, 1576, 1461, 1416, 1360, 1270, 1163, 1091, 1005; ^1H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H), 2.21 (s, 3H), 2.23 (s, 3H), 2.24 (br. s., 1H), 2.30 (s, 3H), 2.44 (s, 3H), 3.41 (dd, *J* = 17.4, 4.3 Hz, 1H), 3.72 (s, 3H), 3.88 (m, 1H), 6.11 (br. s., 1H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 12.7, 15.4, 16.1, 18.5, 30.3, 41.4, 43.8, 60.1, 126.2, 126.5, 134.9, 136.1, 136.3, 140.7, 141.7, 152.4, 208.5; HRMS: m/z calcd for $C_{17}H_{23}O_2$ $[(M+H)^+]$: 259.1698; Found: 259.1696.

*2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)acetaldehyde (**14h**).* According to the general procedure of cyclization reaction, compound **13h** (30 mg, 0.138 mmol) and $FeCl_3.6H_2O$ (3.7 mg, 0.014 mmol), in CH_2Cl_2 (2.5 ml) were used to furnish the product **14h** (12 mg, 40%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2928, 2855, 1722, 1479, 1453, 1416, 1257, 1213, 1174, 1021; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.32 (s, 3H), 2.49 - 2.57 (m, 1H), 3.21 (ddd, *J* = 17.2, 4.5, 1.8 Hz, 1H), 3.81 (s, 3H), 3.97 (td, *J* = 4.3, 1.8 Hz, 1H), 6.04 - 6.27 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 9.68 (t, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 15.9, 41.7, 43.4, 59.8, 115.1, 128.0, 130.4, 132.0, 132.0, 137.0, 139.8, 202.0; HRMS: m/z calcd for $C_{14}H_{17}O_2$ $[(M+H)^+]$: 217.1229; Found: 217.1220.

*2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)-1-phenylethanone (**14i**).* According to the general procedure of cyclization reaction, compound **13i** (40 mg, 0.136 mmol) and $FeCl_3.6H_2O$ (3.7 mg, 0.014 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14i** (37 mg, 92%) as a yellow oil. R_f = 0.25 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2933, 1684, 1579, 1596, 1415, 1448, 1257, 1212, 1019; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.35 (s, 3H), 2.76 (dd, *J* = 17.6, 11.2 Hz, 1H), 3.84 (s, 3 H), 4.03 (dd, *J* = 17.4, 3.7 Hz, 1H), 4.21 (dt, *J* = 11.0, 1.8 Hz, 1H), 6.26 (t, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.44 - 7.49 (m, 2H), 7.54 - 7.59 (m, 1H), 7.98 - 8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 15.8, 38.7, 42.9, 59.9, 114.9, 127.7, 128.1, 128.5, 130.1, 133.0, 133.2, 136.9, 137.7, 139.0, 145.8, 154.6, 199.4; HRMS: m/z calcd for $C_{20}H_{21}O_2$ $[(M+H)^+]$: 293.1542; Found: 293.1541.

*1-(3,5-dimethoxyphenyl)-2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)ethanone (**14j**).* According to the general procedure of cyclization reaction, compound **13j** (34 mg, 0.110 mmol) and $FeCl_3.6H_2O$ (3.0 mg, 0.011 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14j** (32 mg, 94%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2936, 1684, 1593, 1425, 1457, 1355, 1296, 1253, 1205,

1155, 1065; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (br. s., 3H), 2.34 (s, 3H), 2.72 (dd, *J* = 17.4, 11.0 Hz, 1H), 3.82 (s, 6H), 3.83 (s, 3H), 3.97 (dd, *J* = 17.4, 3.7 Hz, 1H), 4.18 (dt, *J* = 11.1, 1.5 Hz, 1H), 6.22 (s, 1H), 6.65 (t, *J* = 2.3 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.09 - 7.14 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 15.8, 38.9, 43.0, 55.6, 59.9, 105.6, 105.8, 114.9, 127.7, 130.1, 133.2, 137.6, 138.8, 139.0, 145.8, 154.6, 160.8, 199.1; HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ $[(M+Na)^+]$: 375.1573; Found: 375.1573.

*1-(3-methoxyphenyl)-2-(3-methyl-1H-inden-1-yl)ethanone (**14k**).* According to the general procedure of cyclization reaction, compound **13k** (55 mg, 0.201 mmol) and $FeCl_3.6H_2O$ (5.4 mg, 0.02 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14k** (52 mg, 93%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): v_{max}/cm^{-1} 2923, 1685, 1583, 1597, 1485, 1463, 1430, 1276, 1256, 1162, 1044, 1071; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 3.04 (dd, *J* = 17.3, 8.7 Hz, 1H), 3.38 (dd, *J* = 17.5, 6.0 Hz, 1H), 3.86 (s, 3H), 4.09 (br. s., 1H), 6.25 (s, 1H), 7.12 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.21 (dt, *J* = 7.5, 3.8 Hz, 1H), 7.30 - 7.34 (m, 2H), 7.34 - 7.38 (m, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.50 - 7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 40.8, 44.2, 55.4, 112.2, 119.1, 119.7, 120.8, 123.0, 124.9, 126.7, 129.6, 133.7, 138.2, 139.3, 145.5, 147.6, 159.8, 198.8; HRMS: m/z calcd for $C_{19}H_{19}O_2$ $[(M+H)^+]$: 279.1385; Found: 279.1381.

*1-(2,5-dimethoxyphenyl)-2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)ethanone (**14l**).* According to the general procedure of cyclization reaction, compound **13l** (44 mg, 0.124 mmol) and $FeCl_3.6H_2O$ (3.4 mg, 0.012 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14l** (40 mg, 91%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 10:90); IR (neat): v_{max}/cm^{-1} 2937, 1672, 1609, 1579, 1495, 1464, 1413, 1278, 1222, 1162, 1021; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.31 (s, 3H), 2.81 (dd, *J* = 18.32, 10.99 Hz, 1H), 3.78 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 3.94 (dd, *J* = 17.9, 3.7 Hz, 1H), 4.18 (ddt, *J* = 10.9, 3.7, 1.8 Hz, 1H), 6.22 (t, *J* = 1.8 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.98 - 7.04 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 15.9, 43.4, 43.7,

55.8, 55.9, 59.8, 113.0, 113.9, 114.7, 154.7, 119.9, 127.6, 128.4, 129.9, 133.7, 138.5, 146.0, 153.2, 153.3, 201.2; HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ [$(M+Na)^+$]: 375.1573; Found: 375.1572.

*1-(3,4-dimethoxyphenyl)-2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)ethanone (**14m**).* According to the general procedure of cyclization reaction, compound **13m** (39 mg, 0.11 mmol) and $FeCl_3.6H_2O$ (3.0 mg, 0.011mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14m** (38 mg, 97%) as a yellow oil. R_f = 0.4 (EtOAc-hexane 20:80); IR (neat): v_{max}/cm^{-1} 2934, 1673, 1586, 1514, 1463, 1417, 1345, 1267, 1153, 1023; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (t, *J* = 1.6 Hz, 3H), 2.34 (s, 3H), 2.73 (dd, *J* = 17.3, 11.31 Hz, 1H), 3.84 (s, 3H), 3.92 - 3.95 (m, 6H), 3.97 (d, *J* = 3.4 Hz, 1H), 6.14 - 6.30 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.52 - 7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 15.8, 38.2, 43.2, 56.0, 56.0, 59.9, 110.0, 110.1, 114.9, 122.8, 127.7, 130.1, 130.1, 133.4, 137.7, 138.9, 145.9, 148.9, 153.2, 154.6, 198.1; HRMS: m/z calcd for $C_{22}H_{25}O_4$ [$(M+H)^+$]: 353.1753; Found: 353.1758.

*1-(2-hydroxyphenyl)-2-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)ethanone (**14n**).* According to the general procedure of cyclization reaction, compound **13n** (50 mg, 0.162 mmol) and $FeCl_3.6H_2O$ (4.2 mg, 0.016 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14n** (47 mg, 94%) as a yellow oil. *Rf* = 0.3 (EtOAc-hexane 10:90); IR (neat): v_{max}/cm^{-1} 3350, 1691, 1638, 1612, 1579, 1485, 1446, 1349, 1255, 1207, 1156, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.34 (s, 3H), 2.76 (dd, *J* = 17.4, 11.0 Hz, 1H), 3.84 (s, 3H), 4.06 (dd, *J* = 17.4, 3.7 Hz, 1H), 4.11 - 4.22 (m, 1H), 6.23 (t, *J* = 1.6 Hz, 1H), 6.86 (td, *J* = 7.7, 1.1 Hz, 1H), 6.97 - 7.04 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 1 H), 7.45 - 7.50 (m, 1H), 7.74 (dd, *J* = 8.0, 1.6 Hz, 1H), 12.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 15.8, 38.5, 42.7, 59.9, 115.0, 118.4, 118.9, 119.4, 127.9, 130.1, 130.3, 132.7, 136.3, 137.3, 139.4, 145.7, 154.6, 162.4, 205.7; HRMS: m/z calcd for $C_{20}H_{21}O_3$ [$(M+H)^+$]: 309.1491; Found: 309.1488.

*1-(3-ethyl-1H-inden-1-yl)propan-2-one (**14o**).* According to the general procedure of cyclization reaction, compound **13o** (25 mg, 0.125 mmol) and $FeCl_3.6H_2O$ (3.37 mg, 0.0125 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14o** (24 mg, 96%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR

(neat): ν_{max}/cm^{-1} 2956, 1712, 1609, 1465, 1265, 1126, 1180; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 - 1.28 (m, 3H), 2.18 (s, 3H), 2.46 - 2.58 (m, 3H), 2.86 (dd, *J* = 17.3, 6.2 Hz, 1H), 3.87 (tt, *J* = 6.3, 2.0 Hz, 1H), 6.17 (q, *J* = 1.7 Hz, 1H), 7.17 - 7.21 (m, 1H), 7.26 - 7.34 (m, 2H), 7.36 (dd, *J* = 7.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 20.6, 30.3, 43.8, 45.4, 119.1, 122.9, 124.9, 126.6, 131.2, 144.8, 145.6, 147.6, 207.7; HRMS: m/z calcd for $C_{14}H_{17}O$ $[(M+H)^+]$: 201.1279; Found: 201.1279.

*1-(3-phenyl-1H-inden-1-yl)propan-2-one(**14p**).* According to the general procedure of cyclization reaction, compound **13p** (42 mg, 0.17 mmol) and $FeCl_3.6H_2O$ (4.6 mg, 0.017 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14p** (41 mg, 97%) as a yellow oil. R_f = 0.24 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2950, 1691, 1658, 1485, 1446, 1349, 1255, 1020; ^1H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.65 (dd, *J* = 17.2, 8.6 Hz, 1H), 2.97 (dd, *J* = 17.7, 6.3 Hz, 1H), 4.01 - 4.11 (m, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 7.24 - 7.28 (m, 1H), 7.30 - 7.35 (m, 1H), 7.35 - 7.40 (m, 1H), 7.42 - 7.47 (m, 3H), 7.52 - 7.61 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.3, 44.2, 45.2, 120.6, 123.3, 125.3, 126.8, 127.7, 127.8, 128.6, 135.3, 135.6, 143.2, 144.4, 147.8, 207.4; HRMS: m/z calcd for $C_{18}H_{17}O$ $[(M+H)^+]$: 249.1279; Found: 249.1285.

*1-(1,3-dimethyl-1H-inden-1-yl)propan-2-one(**14q**)* According to the general procedure of cyclization reaction, compound **13q** (25 mg, 0.124 mmol) and $FeCl_3.6H_2O$ (3.3 mg, 0.0124 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14q** (24 mg, 96%) as a yellow oil. R_f = 0.33 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2942, 1694, 1666, 1580, 1420, 1256, 1020; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 1.90 (s, 3 H), 2.09 (d, *J* = 1.8 Hz, 3H), 2.58 (d, *J* = 14.6 Hz, 1H), 2.89 (d, *J* = 15.1 Hz, 1H), 6.25 (s, 1H), 7.19 - 7.26 (m, 2H), 7.26 - 7.31 (m, 1H), 7.31 - 7.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.8, 22.9, 31.1, 49.7, 51.3, 119.4, 121.3, 125.2, 126.9, 137.2, 138.9, 144.1, 151.9, 207.6; HRMS: m/z calcd for $C_{19}H_{19}O$ $[(M+H)^+]$: 263.1436; Found: 263.1435.

*2-(3-methyl-1H-inden-1-yl)-1-phenylpropan-1-one(**14r**).* According to the general procedure of cyclization reaction, compound **13r** (30 mg, 0.11 mmol) and $FeCl_3.6H_2O$ (3.0 mg, 0.0.011 mmol), in CH_2Cl_2 (3

ml) were used to furnish the product **14r** (28 mg, 93%) as a yellow oil. R_f = 0.4 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2950, 2840, 1693, 1658, 1485, 1545, 1509, 1250, 1020; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H), 2.10 (t, *J* = 1.8 Hz, 3H), 2.15 - 2.17 (m, 2H), 3.60 - 3.66 (m, 1H), 3.72 - 3.97 (m, 3H), 6.08 (s, 1H), 6.23 (s, 1H), 7.11 - 7.22 (m, 2H), 7.26 - 7.31 (m, 4H), 7.31 - 7.36 (m, 1H), 7.42 - 7.51 (m, 5H), 7.52 - 7.63 (m, 2H), 7.93 - 7.97 (m, 2H), 7.99 - 8.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 13.0, 13.9, 14.7, 42.3, 42.8, 50.4, 50.9, 119.0, 119.0, 122.8, 124.4, 124.6, 124.9, 126.7, 128.4, 128.4, 128.6, 128.7, 130.1, 131.1, 132.7, 132.9, 133.0, 134.8, 136.5, 139.5, 140.4, 145.4, 145.9, 146.3, 146.4, 203.4, 203.6; HRMS: m/z calcd for $C_{19}H_{19}O$ $[(M+H)^+]$: 263.1436; Found: 263.1442.

(E)-4-(4-chlorophenyl)-1-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)but-3-en-2-one ***(14s)***. According to the general procedure of cyclization reaction, compound **13s** (40 mg, 0.113 mmol) and $FeCl_3.6H_2O$ (3.0 mg, 0.011 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14s** (39 mg, 98%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); IR (neat): ν_{max}/cm^{-1} 2928, 1691, 1665, 1612, 1490, 1349, 1244, 1198, 1122, 1088; ^1H NMR (500 MHz, $CDCl_3$) δ 2.09 (br. s., 3H), 2.33 (s, 3H), 2.52 (dd, *J* = 17.2, 10.9 Hz, 1H), 3.63 - 3.69 (m, 1H), 3.84 (s, 4H), 4.02 - 4.20 (m, 1H), 6.19 (br. s., 1H), 6.70 (d, *J* = 16.6 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 15.8, 40.6, 42.9, 59.9, 114.9, 126.8, 127.7, 129.2, 129.4, 130.1, 132.9, 136.3, 137.5, 139.1, 141.2, 141.2, 145.8, 154.5, 199.3; HRMS: m/z calcd for $C_{22}H_{21}ClNaO_2$ $[(M+Na)^+]$: 375.1128; Found: 375.1120.

(E)-1-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)-4-phenylbut-3-en-2-one ***(14t)***. According to the general procedure of cyclization reaction, compound **13t** (44 mg, 0.138 mmol) and $FeCl_3.6H_2O$ (3.7 mg, 0.014 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14t** (42 mg, 95%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 10:90); IR (neat): ν_{max}/cm^{-1} 2927, 1661, 1609, 1449, 1250, 1198, 1017; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (br. s., Hz, 3H), 2.34 (s, 3H), 2.52 (dd, *J* = 16.8, 10.9 Hz, 1H), 3.68 (dd, *J* = 17.0, 3.8 Hz, 1H), 3.85 (s, 3H), 4.07 - 4.16 (m, 1H), 6.18 - 6.25 (m, 1H), 6.75 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J*

= 7.7 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.36 - 7.43 (m, 3H), 7.50 - 7.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 15.8, 40.4, 43.0, 59.9, 114.9, 126.4, 127.7, 128.2, 128.9, 130.1, 130.4, 133.1, 134.5, 137.6, 139.0, 142.8, 145.8, 154.5, 199.5; HRMS: m/z calcd for $C_{22}H_{23}O_2$ [$(M+H)^+$]: 319.1698; Found: 319.1691.

*(E)-1-(7-methoxy-3,6-dimethyl-1H-inden-1-yl)-4-p-tolylbut-3-en-2-one (**14u**).* According to the general procedure of cyclization reaction, compound **13u** (42 mg, 0.126 mmol) and $FeCl_3.6H_2O$ (2.42 mg, 0.012 mmol), in CH_2Cl_2 (3 ml) were used to furnish the product **14u** (40mg, 95%) as a yellow oil. R_f = 0.3 (EtOAc-hexane 5:95); **IR** (neat): ν_{max}/cm^{-1} 2922, 1662, 1603, 1512, 1476, 1415, 1349, 1245, 1199, 1093; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.09 (br. s., 3H), 2.33 (s, 3H), 2.38 (s, 3H), 2.47 - 2.55 (m, 1H), 3.67 (dd, *J* = 16.9, 3.7 Hz, 1H), 3.85 (s, 3H), 4.11 (dt, *J* = 10.9, 2.0 Hz, 1H), 6.21 (br. s., 1H), 6.71 (d, *J* = 16.6 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.18 - 7.22 (m, *J* = 8.0 Hz, 2H), 7.41 - 7.44 (m, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 15.8, 21.5, 40.3, 43.0, 59.9, 114.9, 125.5, 127.7, 128.2, 129.7, 130.1, 131.7, 133.1, 137.6, 138.9, 141.0, 142.9, 145.8, 154.5, 199.6; HRMS: m/z calcd for $C_{23}H_{24}NaO_2$ [$(M+Na)^+$]: 355.1674; Found: 355.1677.

*7-methoxy-3,6-dimethyl-1-(2-methylprop-1-enyl)-1H-indene (**15**).* Step 1: To a magnetically stirred solution of methyl magnesium iodide [prepared from magnesium turnings (25 mg, 1.05 mmol), catalytic iodine and methyl iodide (0.09 ml, 139 mmol) in anhydrous diethyl ether], was added slowly to the ketone **13d** (80 mg, 0.35 mmol) in anhydrous diethyl ether. The reaction mixture was stirred for 2 h at RT. It was then quenched with aq. NH_4Cl solution, extracted with ethyl acetate, washed with brine and dried over Na_2SO_4. Evaporation of the solvent furnished the crude tertiary alcohol, which was used in the elimination reaction without further purification. Step 2: To a magnetically stirred solution of crude tertiary alcohol in anhydrous THF (3 ml) at 0 °C triethyl amine (0.24ml, 1.73 mmol) was added and stirred for 5 minute then mesyl chloride (0.08 ml, 1.04 mmol) added slowly. Resultant mixture was allowed to warm to room temperature and reaction mixture was stirred for 6h. It was then quenched with water, extracted with ethyl acetate, washed with brine and dried over Na_2SO_4. Evaporation of the solvent fur-

nished the mixture of crude **15** and **16** eliminated product, was used directly for isomerisation reaction without further purification. Step 3: Under argon atmosphere, to a stirred solution of crude eliminated compound in CH_2Cl_2 catalytic amount of p-TSA (6 mg, 0.035 mmol) was added at 0 °C and stirred for 30 min. at room temperature. The reaction progress was monitored by TLC analysis then reaction was quenched by sodium bisulphate. The reaction mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography using EtOAc-hexane as eluent to furnish the **15** (64 mg, 81% (over 3 steps)) R_f = 0.6 (EtOAc-hexane 2:98) as a yellow oil. IR (neat): ν_{max}/cm^{-1} 2969, 2859, 1575, 1475, 1254, 1226; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.75 (s, 3H), 1.91 (s, 3H), 2.10 (s, 3H), 2.31 (s, 3H), 3.77 (s, 3H), 4.37 (d, *J* = 9.7 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 15.9, 18.3, 25.9, 47.1, 59.8, 114.5, 121.6, 127.7, 129.9, 132.8, 133.5, 138.4, 138.6, 146.3, 154.7; HRMS: m/z calcd for $C_{16}H_{19}O$ [(M-H)+]: 227.1436; Found: 227.1438.

Jungianol, (1) and epi-Jungianol, (17). Step 1: To a 30 ml of anhydrous ammonia at -78 °C, was added (20 mg, 6.6 mmol) lithium metal. A solution of (80 mg, 0.22 mmol) of **15**, in 4 ml THF was then added at the same temperature, followed by stirring for 10 min. Quenching with ammonium chloride was followed by evaporation of the ammonia gave a crude product which was used further reaction without purification. Step 2: Under argon atmosphere, NaH (440 mg, 11 mmol, 60% in mineral oil) was washed with anhydrous hexane (3 times). After a few minutes, anhydrous DMF (4 ml) was added. To this mixture, was slowly added a solution of EtSH (0.47 ml, 6.60 mmol) in anhydrous DMF (1 ml) at 0 °C and the resulting yellow solution was stirred for 20 min at RT. A solution of crude in anhydrous DMF (1 ml) was then added drop wise and the resulting mixture was stirred for 5h at 130 °C. It was becoming slightly brown. The mixture was cooled to RT and the saturated solution of NH_4Cl was added. The mixture was extracted with Et_2O then organic phase was washed with H_2O, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting brown oil was purified by

flash chromatography (EtOAc-hexanes, 3:97 as eluent) to give jungianol (**1**) (31 mg, 41%) as a yellow colour Solid. R_f = 0.3 (EtOAc-hexane 1:99) and *epi*-jungianol (**18**) (31 mg, 41%) as a yellow colour Solid, R_f = 0.3 (EtOAc-hexane 1:99); *Jungianol (1) :* IR (neat): ν_{max}/cm^{-1} 3380, 2910, 1582, 1480, 1443, 1271; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, *J* = 7.2 Hz, 3H), 1.81 (d, *J* = 1.4 Hz, 3H), 1.88 (d, *J* = 1.4 Hz, 3H), 1.94 (ddd, *J* = 3.2, 7.6, 12.7 Hz, 1H), 2.0 (ddd, *J* = 8.1, 8.1, 12.7 Hz, 1H), 2.20 (s, 3H), 3.26 (m, *J* = 2.7, 7.2, 7.7, 3.2 Hz, 1H), 4.18 (dm, *J* = 10.4 Hz, 1H), 5.30 (dm, *J* = 10.4 Hz, 1H), 5.59 (s, 1 H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 18.1, 21.5, 26.0, 38.6, 40.0, 42.0, 115.4, 122.4, 127.4, 129.0, 130.2, 135.0, 148.4, 151.4; HRMS: m/z calcd for $C_{15}H_{21}O$ $[(M+H)^+]$: 217.1592; Found: 217.1598.

*1-epi-jungianol (**17**):* IR (neat): ν_{max}/cm^{-1} 3390, 2920, 1572, 1475, 1453, 1263; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (d, *J* = 6.8 Hz, 3H), 1.35 (ddd, *J* = 10.4, 10.4, 12.2 Hz, 1H), 1.83 (d, *J* = 0.91 Hz, 3H), 1.87 (d, *J* = 0.91 Hz, 3H), 2.19 (s, 3H), 2.19 (s, 3H), 3.06 (dm, *J* = 10.4 Hz, 1H), 4.00 (td, *J* = 7.2, 7.2, 10.4 Hz, 1H), 5.35 (dm, *J* = 10.0 Hz, 1H), 5.92 (s, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 18.7, 19.7, 26.4, 38.8, 41.5, 44.2, 115.1, 122.9, 128.1, 129.7, 130.3, 136.5, 148.2; HRMS: m/z calcd for $C_{15}H_{21}O$ $[(M+H)^+]$: 217.1592; Found: 217.1598.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information

Characterizations of all new compounds, proton and carbon NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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