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Mg-promoted facile and selective intramolecular cyclization of aromatic δ-ketoesters

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ABSTRACT

Treatment of various types of aromatic δ-ketoesters **2**, **7**, and **9** with Mg-turnings for Grignard reaction at −5 to 0 °C in *N*,*N*-dimethylformamide (DMF) containing trimethylsilyl chloride (TMSCl) brought about selective and reductive intramolecular cyclization to give the corresponding α-aryl-α-hydroxycyclopentanones **5**, **8**, and **10**, respectively, in moderate to good yields. Similar reductive intramolecular cyclization of aromatic δ-ketodiesters **14**, followed by acidic hydrolysis and decarboxylation easily gave the corresponding 2-aryl-2-cyclopenten-1-ones **15**. The present facile coupling may be initiated through electron transfer from Mg metal to the aromatic carbonyl groups of **2**, **7**, **9**, and **14** to generate the corresponding radical anions, followed by their intramolecular nucleophilic attack to the ester groups to give the corresponding five-membered ring compounds **5**, **8**, **10**, and **15**, respectively.

1. Introduction

Selective and facile cross coupling between different electrophiles through electron transfer, mainly promoted by electrochemical or metal-promoted reactions, may provide unique and useful methodology in organic synthesis.[1] Among them, cross coupling involving aromatic carbonyl groups with other electrophilic functional groups has extensively studied to give many types of interesting reactions.[2,6] For example, we have already reported electroreductive coupling of aromatic acid anhydride with aliphatic acid anhydrides,[3] and Mg-promoted coupling of aromatic ketones with aliphatic ketones[4] and acid chloride.[5]

On the other hand, it was reported that intramolecular cyclization of aromatic δ- and ε-ketoesters, 2-alkyl-indanone-2-acetate and/or 2-acyloxymethyl-1-indanones by electrochemical,[6–8] and Sm-promoted reduction.[9,10] These methods may be interesting and noteworthy from the standpoint of organic reactions, although there may be some limitations as organic synthetic methods, especially in a large scale, because of necessity of more than an equivalent mole of expensive SmI_2 and/or some problems regarding inevitable necessity of particular reaction equipments for electroreduction.

In this study, we wish to report selective, facile, effective, and general Mg-promoted intramolecular cyclization of four types of easily available aromatic δ-ketoesters to give 2-aryl-2-hydroxycyclopentan-1-ones or 2-aryl-2-cyclopenten-1-ones in good to moderate yields. Use of inexpensive Mg turning for Grignard reaction and wide generality of the reaction may be emphasized as feature and advantage of the present methods.

2. Results and discussion

2.1. Mg-promoted reductive intramolecular cyclization of aromatic γ-, δ-, and ε-ketoesters, 1, 2a–g, 3, 7a–c, and 9

The starting aromatic γ-, δ-, and ε-ketoesters, **1**, **2a**–**g**, and **3**, were easily prepared by Friedel–Crafts acylation of substituted benzene with succinic, glutaric, and adipic anhydrides, respectively, followed by acid-catalyzed esterification according to the usual procedure.[11]

Treatment of aromatic δ- and ε-ketoesters, **2a** and **3**, with excess of Mg turning for Grignard reaction at −5 to 0 °C in *N*,*N*-dimethylformamide(DMF) containing trimethylsilyl chloride (TMSCl) as an activator of Mg turning,[12] followed by acid-hydrolysis using 5% aqueous H_2SO_4 in methanol, brought about reductive intramolecular cyclization between the keto and the ester groups to give the corresponding cyclization products, α-phenyl-α-hydroxy-cyclopentanones (**5a**)[6] from δ-ketoesters **2a**, and

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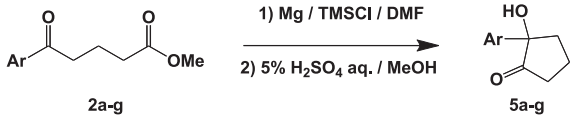
α-phenyl-α-hydroxycyclohexanone (**6**)[6] from ε-ketoesters **3** in 78% and 43% yields, respectively. However, similar treatment of γ-ketoesters, methyl benzoylpropionate (**1**), resulted in simple reduction to give only non-cyclization product, methyl γ-hydroxy-γ-phenylbutyrate (**4**)[13] in a 30% yield.

These phenomena may be considerably attributed to combined effects of ring-strain of the products and proximity between the keto and the ester groups in the cyclization steps.

Furthermore, facile and effective intramolecular cyclization took place to afford 2-aryl-2-hydroxycyclo-pentanones **5b**–**g** in good yields from the corresponding aromatic δ-ketoesters **2b**–**g**[14] according to the similar procedures under the similar reaction conditions, as shown in Table 1.

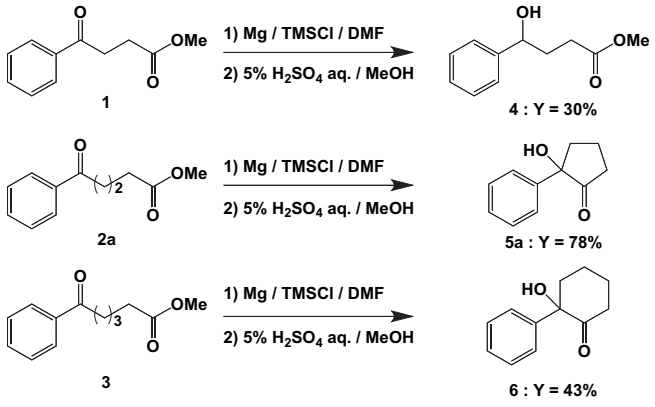
Table 1
Mg-promoted intramolecular cyclization of δ-ketoesters



Ar of δ-ketoesters **2a**–**g**	Yield[a] (%) of products **5a**–**g**
C_6H_5 (**2a**)	78 (**5a**)
3-$CH_3OC_6H_4$ (**2b**)	90 (**5b**)
4-ClC_6H_4 (**2c**)	72 (**5c**)
3-ClC_6H_4 (**2d**)	70 (**5d**)
4-$CH_3C_6H_4$ (**2e**)	67 (**5e**)
2,5-$(CH_3O)_2C_6H_3$ (**2f**)	47 (**5f**)
4-$CH_3OC_6H_4$ (**2g**)	43 (**5g**)

[a] Isolated yields.

In these reactions, the reaction mixtures were usually treated with 5% aqueous H_2SO_4 in methanol to obtain hydrolysis products **5a**–**g** (Scheme 1). Careful attempts for isolation of the trimethylsilylated products before acid-catalyzed hydrolysis of the reaction mixture of **2a** led to successful identification of 1,2-bis(trimethylsilyloxy)-1-methoxy-2-phenylcyclopentane (**5a′**)[6] and 2-trimethylsilyloxy-2-phenylcyclopentanone (**5a″**),[6] as shown in Fig. 1.



Scheme 1. Mg-promoted reductive intramolecular cyclization of γ-, δ-, and aromatic ketoesters **1**, **2a**, and **3**.

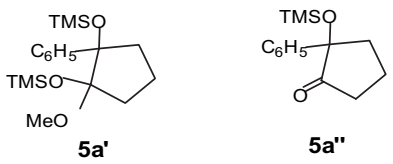


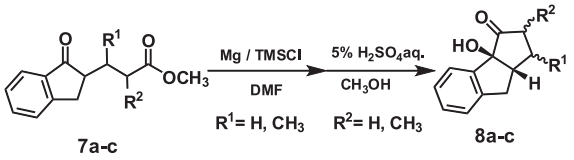
Fig. 1. Trimethylsilylated products.

Also it may be noteworthy that the present Mg-promoted intramolecular cyclization shows rough tendency that an electron-withdrawing group on aromatic ring of **2a**–**g** mostly led to increased yields of the corresponding cyclization products compared with an electron-donating group.

It may be quite interesting and noteworthy that Mg-promoted method, possessing more facility and wider generality, may generally give the better yield of the corresponding same products from the same starting δ-ketoester than electroreduction, promoted by the similar electron-transfer reaction. For instance, the former method gave the corresponding product **5a** from **2a** in a 78% yield while the latter method gave the same product **5a** in a 56% yield.[6]

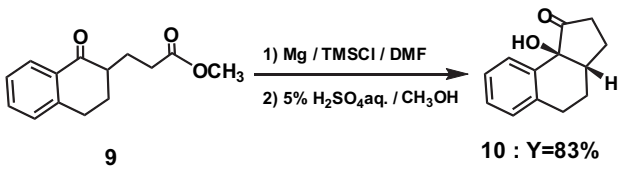
This effective ring-closure may be successfully applied to the related bicyclic systems. Thus, similar Mg-promoted intramolecular ketoester coupling were successfully accomplished in the system of 2-carbomethoxyethyl-α-indanones **7a**–**c**,[15] giving 1-hydroxybicyclo[3.3.0]octan-8-ones **8a**–**c**,[16] as shown in Table 2.

Table 2
Mg-promoted intramolecular cyclization of aromatic ketoester



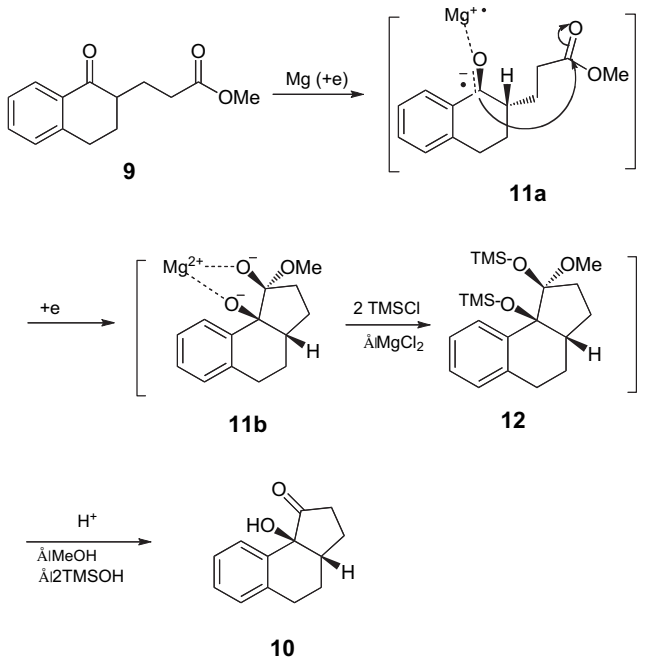
R^2	R^1	Yield (%) of **8a**–**c**	*endo*/*exo*
H	H (**7a**)	64	—
CH_3	H (**7b**)	57	56/44
H	CH_3 (**7c**)	48	65/35

It may be quite noteworthy that use of 2-carbomethoxyethyl-α-tetralone (**9**)[6] as the starting compound in the present Mg-promoted intramolecular ketoester coupling brought about stereoselective and efficient formation of *cis*-1-hydroxybicyclo[4.3.0]nonan-9-one system (**10**)[6] (Scheme 2).



Scheme 2. Mg-promoted intramolecular cyclization of 2-carbomethoxyethyl-α-tetralone (**9**).

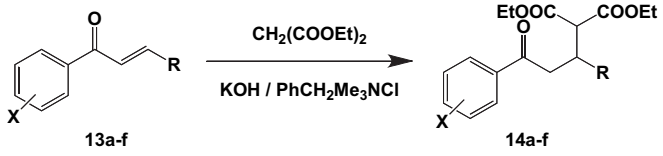
Cyclic voltammetric study[17] of methyl benzoyl pentanoate (**3a**), acetophenone, methyl acetate, and TMSCl showed their reduction potential −2.09 V, −2.20 V, −2.80 V, and no peak up to 3.00 V (vs Ag/AgCl), respectively, indicating that the first electron transfer may take place from Mg metal to the carbonyl group of the benzoyl group of aromatic δ-ketoesters **9** to give the corresponding anion radical **11a**, in which the generated Mg^+•cation radical reasonably makes some of strong participation with the oxygen atom of the keto group of **11a** from the opposite site against the (2-carbomethoxy)ethyl group because of its large steric effect. Furthermore, the anionic α-carbon atom of the anion radical **11a** may attack to the carbonyl carbon atom of the carbomethoxy group, accompanying another electron transfer from Mg^+•cation radical to form the *cis*-condensed bicyclic intermediate **11b**, in which a Mg^{2+}-cation may possess some of ionic bonding with the two oxygen anions. The subsequent electrophilic attack of TMSCl to these oxygen anions of the intermediate may give the bicyclic *cis*-condensed *cis*-bis (trimethylsilyloxy) compound **12**. The following acid-catalyzed hydrolysis may give the product **10** in a stereoselective manner, as shown in the following Scheme 3.



Scheme 3. Proposed reaction mechanism for stereoselective cyclization of δ-ketoesters.

2.2. Novel synthesis of 2-aryl-2-cyclopenten-1-ones 15a–f through Mg-promoted reductive cyclization of aromatic δ-ketodiesters 14a–f followed by acid-catalyzed hydrolysis

The present interesting Mg-promoted reductive cyclization of aromatic δ-ketoesters were successfully applied to development of new synthetic methods of 2-aryl-2-cyclopenten-1-ones **15a**–**f**[18] starting from δ-ketodiesters, diethyl 2-(3-oxo-1,3-diarylpropyl) malonates **14a**–**f**,[19] which were easily prepared through conjugated addition of diethyl malonate anion to the corresponding chalcone derivatives **13a**–**f** according to the usual procedure, as shown in Scheme 4.



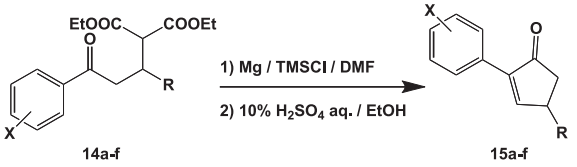
14a (X = H, R = Ph: Y = 37%), **14b** (X = *p*-OMe, R = Ph: Y = 63%),
14c (X = *p*-Cl, R = Ph: Y = 58%), **14d** (X = *p*-Me, R = Ph: Y = 75%),
14e (X = H, R = Me: Y = 77%), **14f** (X = *m*-OMe, R = Ph: Y = 38%)

Scheme 4. Preparation of δ-ketodiesters **14a**–**f**.

Mg-promoted intramolecular coupling of aromatic δ-ketoesters, followed by acid-catalyzed hydrolysis, also smoothly proceeded to give 2-aryl-2-cyclopenten-1-ones **15a**–**f** as the sole products, possibly useful fragrant substances, in 51–14% yields, as shown in Table 3. These conversion of the δ-aryl ketodiesters **14** to 2-aryl-2-cyclopenten-1-ones **15** may be explained by the following Scheme 5, as shown below. The first electron transfer from Mg metal to the benzoyl carbonyl group of δ-aryl ketodiesters **14** gave the corresponding an anion radical **16**, whose anionic carbon may attack to a carbonyl carbon of the ester groups accompanying the second electron transfer from Mg metal to generate a five-membered ring dianion **17**.

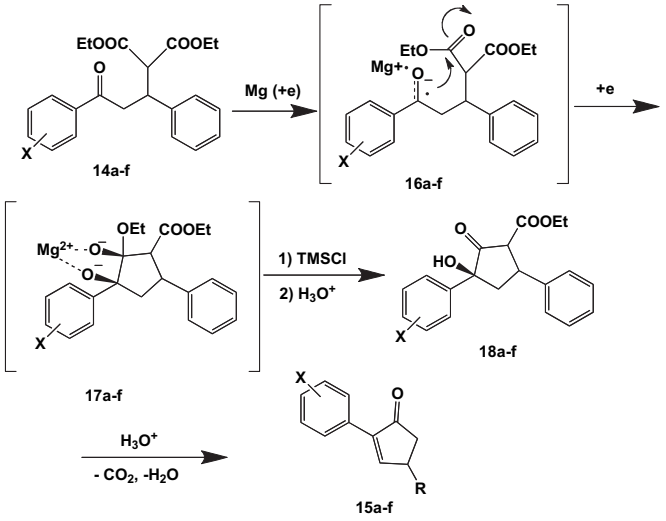
Trapping of the dianion **17a**–**f** with TMSCl followed by acid-catalyzed hydrolysis, decarboxylation, and dehydration may finally give 2-aryl-2-cyclopenten-1-ones **15a**–**f** as the final products.

Table 3
Novel synthesis of 2-aryl-2-cyclopenten-1-ones **15a**–**f** through Mg-promoted reductive cyclization of δ-ketodiesters, followed by acid-catalyzed reactions



Entry	X	R	Isolated yield (%)
1	H	Ph	51 (**15a**)
2	*p*-OMe	Ph	23 (**15b**)
3	*p*-Cl	Ph	31 (**15c**)
4	*p*-Me	Ph	32 (**15d**)
5	H	Me	43 (**15e**)
6	*m*-OMe	Ph	14 (**15f**)

Reaction condition: (First Step) substrate (5 mmol), Mg (10.0 equiv), TMSCl (5.0 equiv), DMF (100 mL): (Second Step) 10% H_2SO_4 (25 mL), EtOH (75 mL), 4 h.



Scheme 5. Proposed reaction mechanism for intramolecular cyclization of ketoesters **14a**–**f**.

In these over-all steps, the substituent effects may be too complex to mention because many steps, such as cyclization, acid-catalyzed hydrolysis, and decarboxylation were involved.

In conclusion, the present Mg-promoted intramolecular cyclization of aromatic δ-ketoesters may be characterized by simple procedure, reasonable yields, and high utility of the products, giving new, important, and useful methodology in organic synthesis. Especially, use of inexpensive and easily available Mg-turnings for Grignard reaction, much facility in a large scale synthesis, and wide generality of the reaction and wide generality of the reaction as well as satisfactory yields and selectivities may be strongly emphasized as features and advantages of the present methods.

3. Experimental section

3.1. Typical procedure for Mg-promoted reductive intramolecular coupling of aromatic δ-ketoesters, 2a–g, 7a–c, 9, 14a–f, and ε-ketoester 3

Into a 50-mL three-necked flask were introduced 30 mL of anhydrous *N*,*N*-dimethylformamide (DMF) as solvent, 10 equiv mol Mg turning for Grignard reaction, and 2.5 equiv of trimethylsilyl chloride (TMSCl) were added under nitrogen atmosphere, and the solution was stirred at room temperature for 0.5 h. Then the mixture of an aromatic δ-ketoesters, **2a**–**g**, **7a**–**c**, **9**, **14a**–**f**, or ε-ketoester **3** (5.0 mmol) and the additional 2.5 equiv of TMSCl

dissolved in 15 mL of anhydrous DMF were added dropwise to the above DMF solution at −5 to 0 °C over 20 min. The reaction mixture was stirred at room temperature for 12 h. After the reaction, the mixture was poured into satd $NaHCO_3$ solution. Organic materials were extracted with three 150-mL portions of ethyl ether. The combined ethereal solution was concentrated under reduced pressure to give the residual oil, which was then treated with 5% sulfuric acid in 50% aqueous methanol at room temperature for 3 h. In the case of the reaction of **14a**–**f**, each of the reaction mixture was found to consist of a complex mixture of several components. Then, the mixture was further treated with 10% aqueous sulfuric acid for another 3 h. The organic components were then extracted with ethyl ether three times, and the combined ethereal solution was dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration and evaporation of the solvent, isolation by column chromatography gave the corresponding cyclization products in satisfactory yield.

In the fivefolded scale reaction of **2a** under the similar reaction conditions, the product **5a** was isolated in a 70% yield.

All the cyclization products, **5a**–**g**, **8a**–**c**, **10**, **15a**–**f**, and **6**, obtained in this study were characterized by spectroscopic and elemental analyses or comparison of spectroscopic and chromatographic behaviors with those of authentic samples.

3.2. Analytical data for new compounds among the products

*3.2.1. 2-Hydroxy-2-(3-methoxyphenyl)cyclopentanone (**5b**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.81–1.89 (m, 1H), 2.03–2.09 (m, 1H), 2.18–2.25 (m, 1H), 2.44–2.52 (m, 3H), 2.99 (br s, 1H), 3.80 (s, 3H), 6.83–6.94 (m, 3H), 7.25–7.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 17.27, 35.75, 37.82, 55.27, 80.56, 111.62, 113.43, 117.84, 129.59, 142.19, 159.66, 218.27. IR (neat, cm^{-1}): 3441 (OH), 3066 (Ar–H), 2965 (C–H), 1742 (C=O), 1265 (C–O–C). MS (EI): *m*/*z* 206 (M^+). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84, found: C, 69.85; H, 6.77.

*3.2.2. 2-Hydroxy-2-(4-chlorophenyl)cyclopentanone (**5c**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.80–1.89 (m, 1H), 2.04–2.13 (m, 1H), 2.19–2.27 (m, 1H), 2.39–2.54 (m, 3H), 2.98 (br s, 1H), 7.26–7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 17.31, 35.75, 37.92, 80.09, 127.17, 128.73, 134.04, 139.13, 217.93. IR (neat, cm^{-1}): 3438 (OH), 3049 (Ar–H), 2974 (C–H), 1745 (C=O). MS (EI): *m*/*z* 210 (M^+). Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26, found: C, 62.78; H, 5.45.

*3.2.3. 2-Hydroxy-2-(3-chlorophenyl)cyclopentanone (**5d**).* ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ 1.81–1.92 (m, 1H), 2.04–2.14 (m, 1H), 2.20–2.28 (m, 1H), 2.39–2.55 (m, 3H), 3.03 (br s, 1H), 7.17–7.36 (m, 4H). ^{13}C NMR (67.5 MHz, $CDCl_3$, ppm): δ 17.38, 35.75, 35.88, 80.14, 123.78, 126.04, 128.22, 129.80, 134.51, 142.83, 217.69. IR (neat, cm^{-1}): 3435 (OH), 3052 (Ar–H), 2972 (C–H), 1743 (C=O). MS (EI): *m*/*z* 210 (M^+). Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26, found: C, 62.82; H, 5.12.

*3.2.4. 2-Hydroxy-2-(4-methylphenyl)cyclopentanone (**5e**).* ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ 1.71–1.88 (m, 1H), 1.96–2.10 (m, 1H), 2.13–2.45 (m, 1H), 2.14 (s, 3H), 2.39–2.53 (m, 3H), 3.15 (br s, 1H), 7.12 (d, *J*=8.5 Hz, 2H) 7.24 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$, ppm): δ 17.17, 21.10, 35.56, 37.57, 80.41, 125.59, 129.18, 137.35, 137.82, 218.45. IR (neat, cm^{-1}): 3435 (OH), 3054 (Ar–H), 2978 (C–H), 1744 (C=O). MS (EI): *m*/*z* 190 (M^+). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42, found: C, 75.86; H, 7.12.

*3.2.5. 2-Hydroxy-2-(2,5-dimethoxyphenyl)cyclopentanone (**5f**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.03–2.14 (m, 3H), 2.31–2.34 (m, 1H), 2.45 (br s, 1H), 2.48–2.50 (m, 1H), 2.55–2.62 (m, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 6.72–6.85 (m, 2H) 7.10–7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 19.69, 36.49, 37.81, 55.70, 55.78, 78.42, 112.44, 112.63, 113.33, 132.62, 148.98, 154.01, 217.92. IR (neat, cm^{-1}): 3425 (OH), 3046 (Ar–H), 2947 (C–H), 1734 (C=O), 1229 (C–O–C), 734. MS (EI): *m*/*z* 236 (M^+). Mp: 99.8102.6 °C. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83, found: C, 66.12; H, 6.86.

*3.2.6. Methyl-3-(1-oxo-2-indanyl) butanoate (**7b**).* Diastereomers ratio=6:4. Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.86 (d, *J*=6.8 Hz, 1.8H), 1.00 (d, *J*=7.1 Hz, 1.2H), 2.29–2.95 (m, 5H), 3.20 (dd, *J*=7.6 , 17.6 Hz, 0.6H), 3.29 (dd, *J*=8.1 , 17.3 Hz, 0.4H), 3.64 (s, 1.2H), 3.69 (s, 1.8H), 7.34–7.38 (m, 1H), 7.46–7.48 (m, 1H), 7.56–7.60 (m, 1H), 7.71–7.75 (m, 1H). IR (neat, cm^{-1}): 3077 (Ar–H), 2953 (C–H), 1735 (ester), 1709 (C=O). MS (EI): *m*/*z* 232 (M^+). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94, found: C, 72.36; H, 7.07.

*3.2.7. Methyl-3-(1-oxo-2-indanyl)-2-methylpropanoate (**7c**).* Diastereomers ratio=1:1. Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.25 (d, *J*=7.1 Hz, 1.5H), 1.26 (d, *J*=7.1 Hz, 1.5H), 1.56–3.70 (m, 5H,), 3.33 (dd, *J*=7.8 , 17.1 Hz, 0.5H), 3.39 (dd, *J*=7.8 , 16.8 Hz, 0.5H), 3.39 (d, *J* = 3.4 Hz , 1.5H), 3.70 (d, *J*=3.4 Hz, 1.5H), 7.34–7.38 (m, 1H), 7.43–7.46 (m, 1H), 7.57–7.60 (m, 1H), 7.73–7.75 (m, 1H). IR (neat, cm^{-1}): 3033 (Ar–H), 2950 (C–H), 1731 (ester). 1711 (C=O). MS (EI): *m*/*z* 232 (M^+). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94, found: C, 72.43; H, 7.16.

3.2.8. (3aS,8aS*)-3a-Hydroxy-1-methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]inden-3-one (**8b**). endo*:*exo*=56:44. Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.02 (d, *J*=6.7 Hz, 1.68H), 1.13 (d, *J*=6.8 Hz, 1.32H), 1.85–3.64 (m, 5H), 3.30 (br s, 1H), 7.21–7.41 (m, 4H). IR (KBr, cm^{-1}): 3443 (OH), 3064 (Ar–H), 2960 (C–H), 1732 (C=O). MS (EI): *m*/*z* 202 (M^+). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98, found: C, 77.16; H, 6.94.

3.2.9. (3aS,8aR*)-3a-Hydroxy-2-methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]inden-3-one (**8c**). endo*:*exo*=65:35. Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.14 (d, *J*=6.8 Hz, 1.05H), 1.22 (d, *J*=6.8 Hz, 1.95H), 1.59–3.45 (m, 5H), 3.09 (br s, 0.65H), 3.28 (br s, 0.35H), 7.21–7.41 (m, 4H). IR (neat, cm^{-1}): 3437 (OH), 3065 (Ar–H), 2931 (C–H), 1740 (C=O). MS (EI): *m*/*z* 202 (M^+). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98, found: C, 77.43; H, 7.08.

*3.2.10. Diethyl-2-[3-(3-methoxyphenyl)-1-phenyl-3-oxopropyl]-malonate (**14f**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (t, *J*=7.3 Hz, 3H), 1.24 (t, *J*=7.3 Hz, 3H), 3.44 (dd, *J*=7.3 , 16.5 Hz, 1H), 3.57 (dd, *J*=4.3 , 16.5 Hz, 1H), 3.81 (d, *J*=9.9 Hz, 1H), 3.82 (s, 3H), 3.95 (q, *J*=7.3 Hz, 2H), 4.14–4.23 (m, 3H), 7.07–7.51 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.73, 14.00, 40.87, 42.75, 55.40, 57.56, 61.32, 61.64, 112.17, 119.86, 120.74, 127.12, 128.23, 128.37, 129.50, 140.39, 159.75, 167.71, 168.32, 197.35. IR (neat, cm^{-1}): 3020 (Ar–H), 2992 (C–H), 1725 (C=O), 1676 (C=O) 1240 (C–O–C). MS (EI): *m*/*z* 398 (M^+). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58, found: C, 69.30; H, 6.51.

*3.2.11. 2-(4-Methoxyphenyl)-4-phenyl-2-cyclopenten-1-one (**15b**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.54 (dd, *J*=1.8 , 18.6 Hz, 1H), 3.10 (dd, *J*=6.8 , 18.6 Hz, 1H), 3.82 (s, 3H), 4.11–4.14 (m, 1H), 6.92–6.94 (m, 2H), 7.18–7.35 (m, 5H), 7.68–7.76 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.58, 45.65, 55.22, 113.86, 123.66, 127.11, 127.20, 128.37, 128.94, 129.09, 142.05, 142.12, 158.67, 207.43. IR (neat, cm^{-1}): 3020 (Ar–H), 2982 (CH), 1733 (C=O), 1246 (C–O–C) cm^{-1}. MS (EI): *m*/*z* 264 (M^+). Anal. Calcd for $C_{18}H_{16}O_2$: C, 86.79; H, 6.10, found: C, 86.80; H, 6.12.

*3.2.12. 2-(4-Chlorophenyl)-4-phenyl-2-cyclopenten-1-one (**15c**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.57 (dd, *J*=4.0 , 16.0 Hz, 1H), 3.12 (dd, *J*=4.0 , 16.0 Hz, 1H), 4.15–4,18 (m, 1H), 7.19–7.38 (m, 7H), 7.71–7.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 43.73, 45.52, 127.23, 127.27, 128.50, 128.69, 129.02, 131.13, 141.90, 142.86, 153.01, 160.51, 207.09. IR (neat, cm^{-1}): 3029 (Ar–H), 2990 (C–H), 1706 (C=

O). MS (EI): *m*/*z* 268 (M^+). Anal. Calcd for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88, found: C, 75.87; H, 4.85.

*3.2.13. 2-(4-Methylphenyl)-4-phenyl-2-cyclopenten-1-one (**15d**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.33 (s, 3H), 3.16 (dd, *J*=3.0 , 18.8 Hz, 1H), 3.57 (dd, *J*=7.6 , 18.8 Hz, 1H), 3.80 (dd, *J*=3.0 , 7.6 Hz, 1H), 7.11–7.64 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.03, 39.24, 51.39, 127.29, 127.57, 127.67, 127.79, 129.58, 131.47, 133.71, 135.61, 136.90, 140.47, 202.93. IR (neat, cm^{-1}): 3030 (Ar–H), 2992 (C–H), 1702 (C=O). MS (EI): *m*/*z* 248 (M^+). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.41, found: C, 87.05; H, 6.33.

*3.2.14. 2-(3-Methoxyphenyl)-4-phenylcyclopentenon (**15f**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.19 (dd, *J*=3.2 , 18.9 Hz, 1H), 3.57 (dd, *J*=8.4 , 18.9 Hz, 1H), 3.79 (s, 3H), 4.25–4,35 (m, 1H), 6.78–7.86 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 39.13, 51.68, 55.20, 112.51, 113.73, 114.94, 119.91, 127.38, 127.67, 128.79, 129.901, 131.52, 140.11, 140.11, 159.88, 204.98. IR (neat, cm^{-1}): 3020 (Ar–H), 2984 (C–H), 1733 (C=O), 1266 (C–O–C). MS (EI): *m*/*z* 264 (M^+). Anal. Calcd for $C_{18}H_{16}O_2$: C, 86.79; H, 6.10, found: C, 86.80; H, 6.12.

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