Gold-Catalyzed Skeletal Rearrangement of 1-[2-(1*H*-Isochromen-3-yl)aryl]-ethanones with Alcohols

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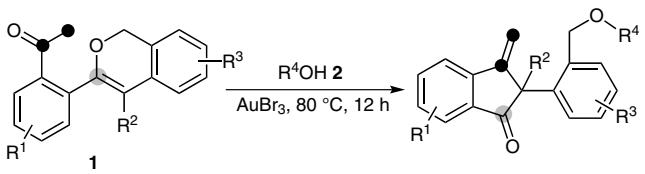
Received: 07.03.2012; Accepted after revision: 19.04.2012

Abstract: A novel gold-catalyzed skeletal rearrangement of 1-[2-(1*H*-isochromen-3-yl)aryl]ethanones with alcohols to construct a five-membered carbocycle ring onto aromatic systems has been developed. This method serves as the first example of synthesizing inden-1-ones by a gold-catalyzed skeletal rearrangement strategy.

Key words: gold, skeletal rearrangement, 1-[2-(1*H*-isochromen-3-yl)aryl]ethanones, alcohols, inden-1-ones

Inden-1-one and its derivatives are commonly found in natural compounds, pharmaceuticals, and functional materials, as well as being versatile synthetic blocks and catalysts in organic synthesis.[1] Most often, the intramolecular Friedel–Crafts acylation of 3-arylpropanoic acids and their derivatives is the most direct method for their construction.[2,3] However, the classical Friedel–Crafts transformation generally require the use of at least an equivalent amount of either a Lewis or Brønsted acid.[3] Thus, it is desirable to develop a catalytic system for these purposes. Recently, many catalytic methods have been disclosed,[3–7] including the Friedel–Crafts reaction,[3] Nazarov cyclization,[4] transition-metal-catalyzed annulation,[5] and ring-closing metathesis.[6] Here, we report a novel route to prepare polysubstituted inden-1-ones by gold-catalyzed skeletal rearrangement of 1-[2-(1*H*-isochromen-3-yl)aryl]ethanones with alcohols (Scheme 1).



Scheme 1 Gold-catalyzed skeletal rearrangement

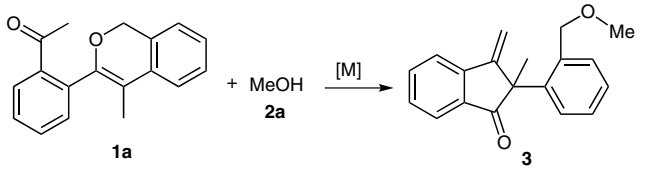
Gold is one of the most important transition metal catalysts in organic synthesis, and has been widely used in organic synthesis for constructing numerous chemical bonds.[8,9] Particularly, gold-catalyzed rearrangement reactions have attracted significant interest because of their synthetic utility and concept: these transformations are highly efficient and atom-economical and provide opportunities to rapidly construct complex molecules and discover new reactions.[8,9] Interestingly, this strategy was applied to construct various carbocycles,[8] including indene derivatives.[9] To the best of our knowledge, however, skeletal rearrangement of 1-[2-(1*H*-isochromen-3-yl)aryl]ethanones with alcohols for the synthesis of inden-1-ones has not been reported.

Our study began with the reaction of 1-[2-(4-methyl-1*H*-isochromen-3-yl)phenyl]ethanone (**1a**) with 5 mol% $AuBr_3$ in THF at 80 °C; however, no reaction was observed (Table 1, entry 1). Gratifyingly, an unexpected skeletal rearrangement reaction took place in the presence of MeOH (**2a**): the desired rearrangement product, 2-[2-(methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (**3**), was obtained in 10% yield at a loading of 10 equivalents of MeOH (entry 2).[10] In light of the results, MeOH was employed as the solvent, and the yield of product **3** was enhanced sharply to 78% (entry 3). The amount of $AuBr_3$ was subsequently investigated (entries 3–5): 10 mol% $AuBr_3$ gave identical results to those of 5 mol% $AuBr_3$ (entry 4), whereas the yield was lowered to 59% when 2 mol% $AuBr_3$ was used (entry 5). Notably, the reaction cannot take place without gold catalysts (entry 6). Screening revealed that gold catalysts, such as $AuCl_3$, $HAuCl_4$, AuCl, or AuI, have reactivity for the reaction, but they were less effective than $AuBr_3$ (entries 7–10). Among the reaction temperature examined, it turned out the reaction at 80 °C gave the best results (entries 3, 11, and 12). However, other metal catalysts, $PtBr_2$ and $PdBr_2$, had no effect on the reaction (entries 13 and 14).

With the optimal reaction conditions in hand, the scope of both 1-[2-(1*H*-isochromen-3-yl)aryl]ethanones **1** and alcohols **2** was explored (Table 2).[10] Initially, a number of alcohols **2b**–**f** were investigated for the reaction with 1-[2-(4-methyl-1*H*-isochromen-3-yl)phenyl]ethanone (**1a**) and $AuBr_3$ (Table 2, entries 1–5). The results disclosed that both primary and secondary alcohols were suitable for the reaction (entries 1–4), but tertiary alcohol (*t*-BuOH) could not furnish the desired product **8** (entry 5). It was found that BnOH (**2g**) was also less reactive for the reaction (entry 6). Subsequently, a variety of 1-[2-(1*H*-isochromen-3-

SYNTHESIS 2012, 44, 2049–2057
Advanced online publication: 01.06.2012
DOI: 10.1055/s-0031-1291152; Art ID: SS-2012-H0240-OP

Table 1 Screening Conditions for Gold-Catalyzed Skeletal Rearrangement[a]



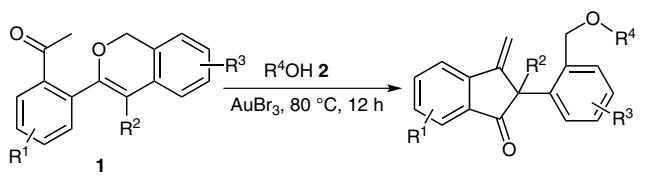
Entry	[M] (mol%)	Solvent	Temp (°C)	Yield (%)[b]
1	$AuBr_3$ (5)	THF	80	0
2[c]	$AuBr_3$ (5)	MeOH–THF	80	10
3	$AuBr_3$ (5)	MeOH	80	78
4	$AuBr_3$ (10)	MeOH	80	79
5	$AuBr_3$ (2)	MeOH	80	59
6	–	MeOH	80	0
7	$AuCl_3$ (5)	MeOH	80	20
8	$HAuCl_4$ (5)	MeOH	80	41
9	AuCl (5)	MeOH	80	30
10	AuI (5)	MeOH	80	33
11	$AuBr_3$ (5)	MeOH	100	78
12	$AuBr_3$ (5)	MeOH	60	40
13	$PtBr_2$ (5)	MeOH	80	trace
14	$PdBr_2$ (5)	MeOH	80	trace

[a] Reaction conditions: **1a** (0.3 mmol), [M], and solvent (2 mL) for 12 h under argon atmosphere.
[b] Isolated yield.
[c] Amount of MeOH added: 10 equiv.

yl)aryl]ethanones **1b–l** were treated with MeOH (**2a**) and $AuBr_3$ (entries 7–17). The results disclosed that 1-[2-(1*H*-isochromen-3-yl)phenyl]ethanone (**1b**) smoothly underwent the rearrangement reaction to afford the corresponding 2-[2-(methoxymethyl)phenyl]-3-methylene-2,3-dihydro-1*H*-inden-1-one (**10**) in 41% yield (entry 7). Interestingly, substrates **1c–l** with a methyl group on the 4-position of the 1*H*-isochromene moiety were also successful in the rearrangement reaction (entries 8–17). Moreover, screening revealed that several functional groups, including Me, MeO, OCH_2O, F, Cl, and NO_2 on the aromatic ring of substrates **1** were tolerated well under the optimal conditions. For example, substrates with three Me groups on different aryl rings smoothly underwent the reaction with MeOH and $AuBr_3$, providing the corresponding products **11** and **12** in good yields (entries 8 and 9). MeO-substituted substrates were also consistent with the optimal conditions: Substrate with two MeO group formed the target product **14** in 86% yield (entry 11), and four MeO-substituted substrate still gave a moderate yield (entry 12). Gratifyingly, a heterocycle and a protected diol, which were introduced into this system, also make this methodology more useful for the preparation of pharmaceuticals and natural products (entry 13). Importantly, substituents, Cl and F, were found to be compatible with the optimal conditions, thereby facilitating additional modifications at the halogenated positions (entries 14–16). Interestingly, substrate **1l** with two electron-withdrawing NO_2 groups could also react with MeOH and $AuBr_3$ to give the desired product in moderate yield (entry 17).

As shown in Scheme 2, the reactions some other isochromenes **1** were also investigated in the presence of $AuBr_3$ and MeOH (**2a**). The results demonstrated that 2-(1*H*-isochromen-3-yl)benzaldehyde (**1m**) was not a suitable substrate for the rearrangement reaction: only <5% yield of the desired product **21** was observed by GC-MS analysis (Scheme 2, equation 1). It is noteworthy that a carbonyl group on the 2-position of the 3-phenyl ring in 1*H*-isochromenes is the key for the occurrence of the reaction; no reaction takes place using 3-phenyl-1*H*-isochromene (**1n**) (Scheme 2, equation 2).

Table 2 Gold-Catalyzed Rearrangement of 1-[2-(1*H*-Isochromen-3-yl)aryl]ethanones **1** with Alcohols **2**[a]



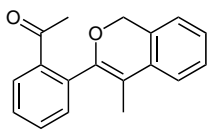
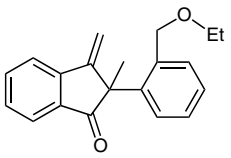
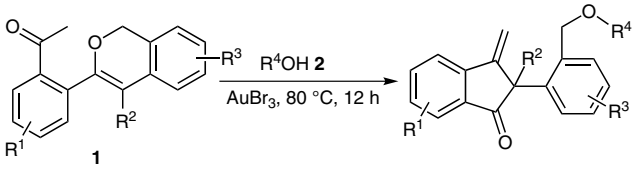
Entry	Substrate **1**	R^4OH **2**	Product (Yield, %)[b]
1	 **1a**	EtOH (**2b**)	 **4** (60)

Table 2 Gold-Catalyzed Rearrangement of 1-[2-(1*H*-Isochromen-3-yl)aryl]ethanones **1** with Alcohols **2**[a] (continued)



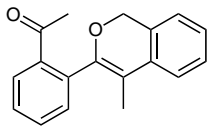
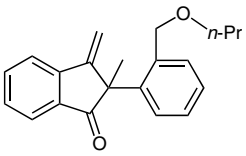
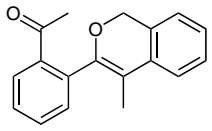
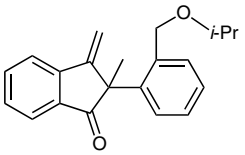
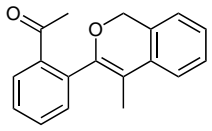
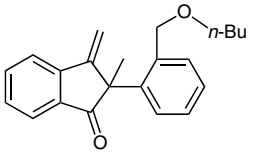
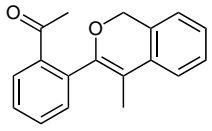
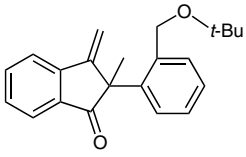
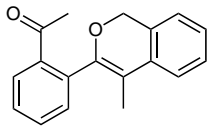
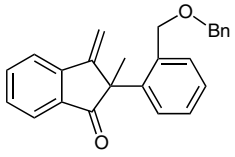
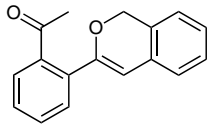
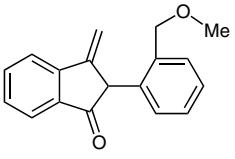
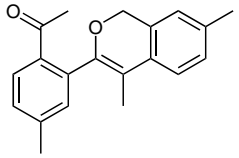
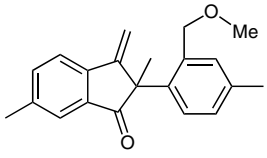
Entry	Substrate **1**	R^4OH **2**	Product (Yield, %)[b]
2	 **1a**	*n*-PrOH (**2c**)	 **5** (72)
3	 **1a**	*i*-PrOH (**2d**)	 **6** (40)
4	 **1a**	*n*-BuOH (**2e**)	 **7** (70)
5	 **1a**	*t*-BuOH (**2f**)	 **8** (0)
6	 **1a**	BnOH (**2g**)	 **9** (12)
7	 **1b**	MeOH (**2a**)	 **10** (41)
8	 **1c**	MeOH (**2a**)	 **11** (87)

Table 2 Gold-Catalyzed Rearrangement of 1-[2-(1*H*-Isochromen-3-yl)aryl]ethanones **1** with Alcohols **2**[a] (continued)

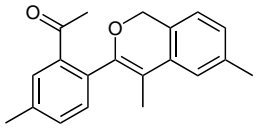
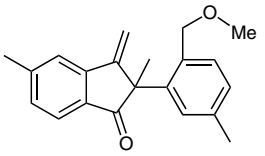
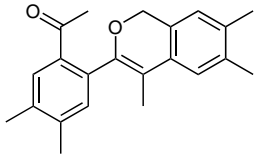
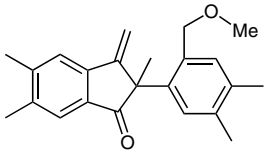
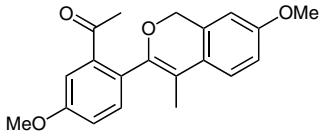
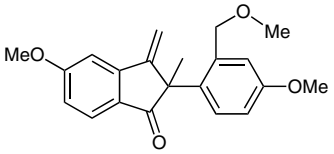
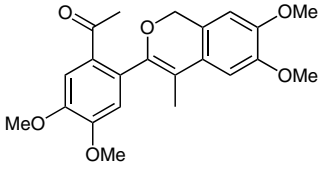
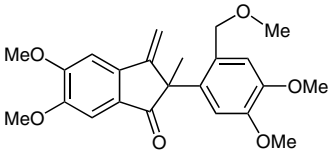
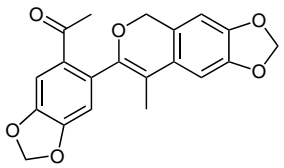
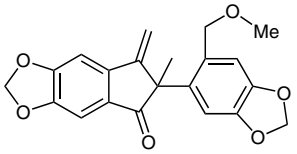
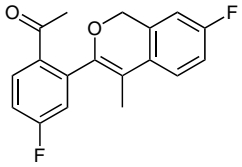
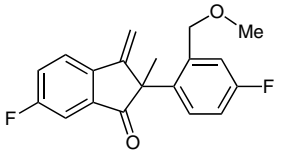
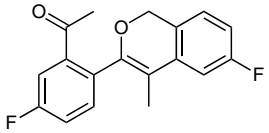
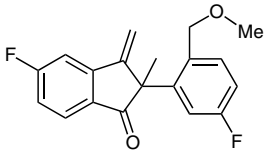
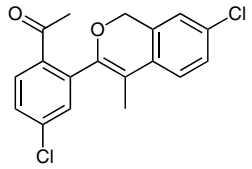
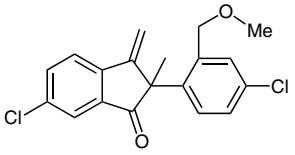
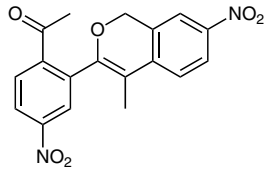
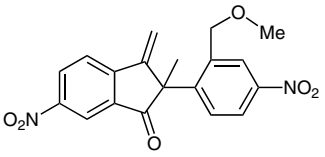
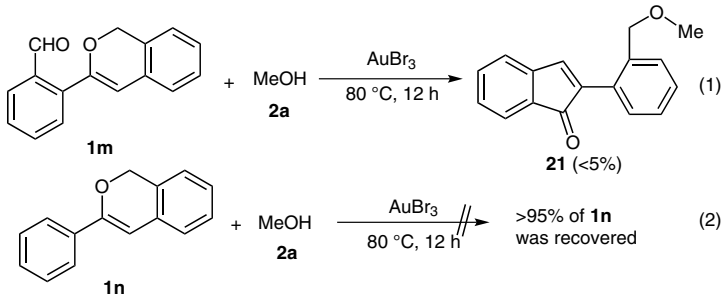
Entry	Substrate **1**	R^4OH **2**	Product (Yield, %)[b]
9	 **1d**	MeOH (**2a**)	 **12** (80)
10	 **1e**	MeOH (**2a**)	 **13** (46)
11	 **1f**	MeOH (**2a**)	 **14** (86)
12	 **1g**	MeOH (**2a**)	 **15** (51)
13	 **1h**	MeOH (**2a**)	 **16** (89)
14	 **1i**	MeOH (**2a**)	 **17** (75)
15	 **1j**	MeOH (**2a**)	 **18** (81)

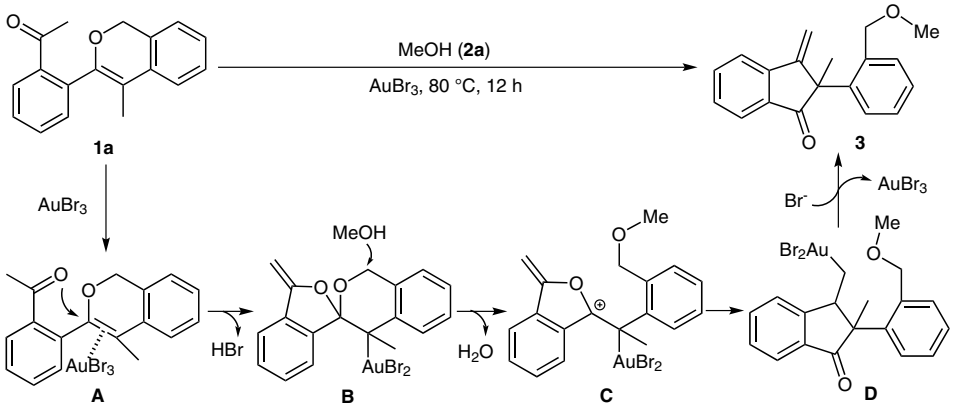
Table 2 Gold-Catalyzed Rearrangement of 1-[2-(1*H*-Isochromen-3-yl)aryl]ethanones **1** with Alcohols **2**[a] (continued)

Entry	Substrate **1**	R^4OH **2**	Product (Yield, %)[b]
16	 **1k**	MeOH (**2a**)	 **19** (60)
17	 **1l**	MeOH (**2a**)	 **20** (60)

[a] Reaction conditions: **1** (0.3 mmol), alcohol **2** (2 mL), and $AuBr_3$ (5 mol%) at 80 °C for 12 h under argon atmosphere.
[b] Isolated yield.



Scheme 2 $AuBr_3$-catalyzed rearrangement reactions of other isochromenes **1m**,**n** with MeOH (**2a**)



Scheme 3 Possible mechanism for the gold-catalyzed skeletal rearrangement

A possible mechanism as outlined in Scheme 3 is proposed.[8,9] Complexation of substrate **1a** with $AuBr_3$ yields intermediate **A**, in which the C=C bond is activated by the $AuBr_3$ Lewis acid catalyst. Subsequently, the addition of the oxygen atom of the carbonyl group to the C=C bond takes place to offer intermediate **B**, followed by addition of methanol to intermediate **B** to form a six-membered oxocycle intermediate **C**.[9e] Intermediate **C** undergoes the oxygen-migration-ring-opening-cyclization sequence to afford intermediate **D**. Finally, the desired product **3** is obtained from intermediate **D** together with the regeneration of the active gold species.

In summary, we have described a novel and general method for the construction of 2,3-dihydro-1*H*-inden-1-ones by alcohol-induced gold-catalyzed skeletal rearrangement. Importantly, this rearrangement method provides a new synthetic utility for gold catalysts. Further study of the detailed mechanism and applications of this gold-catalyzed rearrangement transformation in organic synthesis are currently underway in our laboratory.

NMR spectroscopy was performed on a Bruker Avance spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Mass spectrometric analysis was performed using GC-MS technique (Shimadzu GCMS-QP2010) and ESI-Q-TOF (Bruker Micro-QTOF-II. All melting points are uncorrected.

All starting materials were synthesized according to the literature procedure.[9e] The analytical and spectral data for **1a** are given below.

1-[2-(4-Methyl-1*H*-isochromen-3-yl)phenyl]ethanone (1a)
IR (KBr): 2925, 1768 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.5 Hz, 1 H), 7.49–7.46 (m, 1 H), 7.44–7.41 (m, 2 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.22–7.20 (m, 2 H), 7.05 (d, *J* = 7.5 Hz, 1 H), 5.07 (s, 2 H), 2.52 (s, 3 H), 1.99 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.5, 149.6, 141.4, 133.6, 133.5, 131.3, 130.3, 128.8, 128.7, 128.0, 127.5, 126.7, 123.6, 121.0, 109.8, 69.2, 29.4, 13.6.

LRMS (EI, 70 eV): *m*/*z* (%): 265 (M^+ + 1, 19), 264 (100), 115 (44).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{16}O_2$ (M^+): 264.1223; found: 264.1226.

Gold-Catalyzed Skeletal Rearrangement Reaction; General Procedure
To a Schlenk tube were added 1-[2-(4-methyl-1*H*-isochromen-3-yl)phenyl]ethanone **1** (0.3 mmol), $AuBr_3$ (5 mol%), and alcohol **2** (2 mL). Then, the tube was charged with argon and the mixture was stirred at 80 °C (oil bath temperature) for 12 h until complete consumption of starting material as monitored by TLC (eluent: hexane–EtOAc, 10:1) and GC-MS analysis. After completion of the reaction, the mixture was cooled to r.t., diluted with EtOAc (10 mL), and the EtOAc layer was washed with brine (3 × 3 mL). The aqueous phase was re-extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane–EtOAc, 5:1) to afford the desired product.

2-[2-(Methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (3)
Yield: 65.9 mg (79%); colorless oil.

IR (KBr): 2928, 1748 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 3 H), 7.32–7.28 (m, 2 H), 7.18 (d, *J* = 7.5 Hz, 1 H), 7.10–7.07 (m, 1 H), 6.88 (d, *J* = 7.0 Hz, 1 H), 5.64 (s, 1 H), 5.27 (s, 1 H), 4.90 (d, *J* = 14.5 Hz, 1 H), 4.70 (d, *J* = 15.0 Hz, 1 H), 3.35 (s, 3 H), 1.59 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.5, 153.1, 140.5, 140.1, 138.7, 132.9, 129.5, 127.6, 127.0, 125.9, 124.8, 123.7, 121.9, 107.5, 105.2, 64.9, 52.6, 50.4, 21.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 278 (M^+, 4), 231 (100), 202 (40).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{18}O_2$ (M^+): 278.1307; found: 278.1311.

2-[2-(Ethoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (4)
Yield: 52.6 mg (60%); colorless oil.

IR (KBr): 2926, 1747 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 3 H), 7.23–7.21 (m, 2 H), 7.12 (s, 1 H), 7.02 (s, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 5.56 (s, 1 H), 5.15 (s, 1 H), 4.78 (d, *J* = 14.5 Hz, 1 H), 4.61 (d, *J* = 14.5 Hz, 1 H), 3.78–3.75 (m, 1 H), 3.33–3.30 (m, 1 H), 1.52 (s, 3 H), 1.05 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.3, 153.0, 140.5, 140.0, 138.7, 132.8, 129.5, 127.6, 127.0, 125.9, 124.8, 123.7, 121.9, 107.5, 105.2, 64.9, 52.6, 50.4, 21.8, 14.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 292 (M^+, 8), 247 (40), 157 (82).

HRMS (EI): *m*/*z* for $C_{20}H_{20}O_2$ (M^+): 292.1463; found: 292.1467.

2-Methyl-3-methylene-2-[2-(propoxymethyl)phenyl]-2,3-dihydro-1*H*-inden-1-one (5)
Yield: 66.1 mg (72%); colorless oil.

IR (KBr): 2931, 1692 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 3 H), 7.21–7.20 (m, 2 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 7.00 (t, *J* = 7.0 Hz, 1 H), 6.81 (d, *J* = 7.5 Hz, 1 H), 5.54 (s, 1 H), 5.17 (s, 1 H), 4.80 (d, *J* = 14.5 Hz, 1 H), 4.62 (d, *J* = 14.5 Hz, 1 H), 3.68 (t, *J* = 7.5 Hz, 1 H), 3.22 (t, *J* = 7.5 Hz, 1 H), 1.52 (s, 3 H), 1.46–1.41 (m, 2 H), 0.77 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.8, 153.4, 140.5, 140.2, 133.1, 129.3, 127.6, 127.0, 126.9, 125.8, 124.7, 123.7, 121.7, 107.1, 105.0, 64.8, 64.0, 52.7, 23.1, 22.0, 10.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 4), 231 (100), 217 (22).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{22}O_2$ (M^+): 306.1620; found: 306.1624.

2-[2-(Isopropoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (6)
Yield: 36.7 mg (40%); colorless oil.

IR (KBr): 2919, 1684 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.5 Hz, 1 H), 7.42 (t, *J* = 8.5 Hz, 2 H), 7.28 (t, *J* = 4.5 Hz, 1 H), 7.22 (t, *J* = 6.0 Hz, 1 H), 7.09 (t, *J* = 8.5 Hz, 1 H), 6.88 (d, *J* = 2.5 Hz, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 5.54 (s, 1H), 5.14 (s, 1 H), 4.84 (d, *J* = 11.0 Hz, 1 H), 4.62 (d, *J* = 13.0 Hz, 1 H), 3.28–3.23 (m, 1 H), 1.51 (s, 3 H), 1.49 (d, *J* = 7.0 Hz, 3 H), 1.46 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2, 153.1, 140.5, 140.1, 138.8, 132.9, 129.5, 127.6, 127.0, 125.9, 124.8, 123.7, 121.9, 107.5, 105.2, 71.5, 64.9, 52.6, 21.8, 21.3, 20.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 16), 247 (28), 231 (100).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{22}O_2$ (M^+): 306.1620; found: 306.1624.

2-[2-(Butoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (7)
Yield: 67.2 mg (70%); colorless oil.

IR (KBr): 2925, 1740 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.57–7.55 (m, 1 H), 7.50–7.48 (m, 2 H), 7.33–7.31 (m, 2 H), 7.17 (s, 1 H), 7.09–7.07 (m, 1 H), 6.93 (d, *J* = 7.5 Hz, 1 H), 5.70 (s, 1 H), 5.36 (s, 1 H), 4.88 (d, *J* = 15.0 Hz, 1 H), 4.60 (d, *J* = 15.0 Hz, 1 H), 3.79 (d, *J* = 9.0 Hz, 1 H), 3.21 (d, *J* = 9.5 Hz, 1 H), 1.48 (s, 3 H), 1.36–1.32 (m, 2 H), 1.24–1.20 (m, 2 H), 0.77 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 202.9, 153.1, 140.6, 140.4, 139.3, 133.2, 130.1, 128.2, 127.5, 127.4, 126.5, 125.3, 124.3, 107.0, 106.2, 64.5, 61.6, 52.7, 31.9, 22.2, 19.4, 14.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 320 (M^+, 1), 246 (6), 40 (100).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{24}O_2$ (M^+): 320.1776; found: 320.1780.

2-[2-(Methoxymethyl)phenyl]-3-methylene-2,3-dihydro-1*H*-inden-1-one (10)
Yield: 32.5 mg (41%); yellow oil.

IR (KBr): 2927, 1752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 3 H), 7.32–7.28 (m, 2 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 7.10–7.07 (m, 1 H), 6.88 (d, *J* = 7.0 Hz, 1 H), 5.64 (s, 1 H), 5.27 (s, 1 H), 4.89 (d, *J* = 14.5 Hz, 1 H), 4.71 (d, *J* = 15.0 Hz, 1 H), 4.41 (s, 1 H), 3.11 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.5, 153.1, 140.5, 140.1, 138.7, 132.9, 129.5, 127.6, 127.0, 125.9, 124.8, 123.7, 121.9, 107.5, 105.2, 59.0, 52.6, 50.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 264 (M^+, 27), 246 (100), 176 (11).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{16}O_2$ (M^+): 264.1150; found: 264.1154.

2-[2-(Methoxymethyl)-4-methylphenyl]-2,6-dimethyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (11)
Yield: 79.9 mg (87%); yellow oil.

IR (KBr): 2931, 1745 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 1 H), 7.31–7.29 (m, 1 H), 7.23 (s, 1 H), 7.03 (s, 1 H), 6.95–6.88 (m, 2 H), 5.47 (s, 1 H), 5.10 (s, 1 H), 4.75 (d, *J* = 14.5 Hz, 1 H), 4.60 (d, *J* = 11.0 Hz, 1 H), 3.27 (s, 3 H), 2.30 (s, 3 H), 2.16 (s, 3 H), 1.48 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.9, 153.2, 142.8, 139.4, 137.6, 135.5, 132.7, 130.5, 127.8, 126.8, 125.1, 124.1, 121.6, 107.6, 104.0, 64.9, 52.5, 50.5, 21.8, 21.6, 20.9.

LRMS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 22), 171 (100), 40 (82).

HRMS (EI): *m*/*z* for $C_{21}H_{22}O_2$ (M^+): 306.1620; found: 306.1624.

2-[2-(Methoxymethyl)-5-methylphenyl]-2,5-dimethyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (12)
Yield: 73.4 mg (80%); colorless oil.

IR (KBr): 2930, 1744 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.40–7.35 (m, 2 H), 7.27–7.22 (m, 2 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 5.64 (s, 1 H), 5.34 (s, 1 H), 4.84 (d, *J* = 15.0 Hz, 1 H), 4.55 (d, *J* = 16.0 Hz, 1 H), 3.19 (s, 3 H), 2.27 (s, 3 H), 2.21 (s, 3 H), 1.43 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 200.4, 153.1, 140.9, 140.4, 139.8, 136.4, 130.1, 129.0, 127.9, 127.4, 125.3, 124.2, 122.9, 107.3, 106.0, 64.6, 52.8, 50.2, 22.1, 21.6, 21.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 2), 273 (14), 40 (100).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{22}O_2$ (M^+): 306.1620; found: 306.1624.

2-[2-(Methoxymethyl)-4,5-dimethylphenyl]-2,5,6-trimethyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (13)
Yield: 46.1 mg (46%); colorless oil.

IR (KBr): 2945, 1746 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (s, 1 H), 7.39 (s, 1 H), 7.07 (s, 1 H), 7.00 (s, 1 H), 5.42 (s, 1 H), 5.17 (s, 1 H), 5.05 (d, *J* = 11.5 Hz, 1 H), 4.75 (d, *J* = 13.5 Hz, 1 H), 3.40 (s, 3 H), 2.29 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H), 2.20 (s, 3 H), 1.53 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.5, 155.4, 153.5, 143.5, 139.1, 137.4, 136.7, 136.1, 136.0, 135.8, 135.5, 134.8, 133.9, 106.9, 103.7, 64.8, 52.5, 50.4, 20.2, 20.1, 20.0, 19.8, 19.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 334 (M^+, 9), 297 (100), 149 (21).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{26}O_2$ (M^+): 334.1933; found: 334.1937.

6-Methoxy-2-[4-methoxy-2-(methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (14)
Yield: 87.2 mg (86%); yellow oil.

IR (KBr): 2922, 1697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.46 (d, *J* = 8.5 Hz, 1 H), 7.37 (d, *J* = 8.5 Hz, 1 H), 7.02 (d, *J* = 2.0 Hz, 1 H), 6.93–6.91 (m, 1 H), 6.75–6.73 (m, 1 H), 6.51 (d, *J* = 2.5 Hz, 1 H), 5.49 (s, 1 H), 5.18 (s, 1 H), 4.84 (d, *J* = 15.0 Hz, 1 H), 4.61 (d, *J* = 15.0 Hz, 1 H), 3.80 (s, 3 H), 3.64 (s, 3 H), 3.23 (s, 3 H), 1.41 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 202.2, 159.7, 157.8, 152.8, 140.4, 134.3, 133.2, 132.4, 128.8, 123.6, 116.9, 114.1, 110.0, 108.5, 107.3, 64.8, 56.1, 55.6, 52.4, 50.4, 22.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 338 (M^+, 19), 291 (88), 166 (42).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{22}O_4$ (M^+): 338.1518; found: 338.1522.

2-[4,5-Dimethoxy-2-(methoxymethyl)phenyl]-5,6-dimethoxy-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (15)
Yield: 60.9 mg (51%); white solid; mp 99.6–100.7 °C.

IR (KBr): 2928, 1701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (s, 1 H), 7.10 (s, 1 H), 7.09 (s, 1 H), 6.90 (s, 1 H), 5.51 (s, 1 H), 5.23 (s, 1 H), 5.01 (d, *J* = 6.5 Hz, 1 H), 4.78 (d, *J* = 6.5 Hz, 1 H), 3.98 (s, 3 H), 3.91 (s, 3 H), 3.90 (s, 3 H), 3.81 (s, 3 H), 2.88 (s, 3 H), 1.60 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.6, 155.7, 152.2, 151.6, 148.1, 147.6, 142.0, 130.6, 129.6, 127.4, 112.6, 112.2, 105.5, 104.6, 102.2, 60.4, 57.6, 56.8, 56.3, 56.1, 55.9, 50.9, 22.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 398 (M^+, 12), 217 (100), 40 (72).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{26}O_6$ (M^+): 398.1729; found: 398.1733.

6-[4-(Methoxymethyl)benzo[*d*][1,3]dioxol-5-yl]-6-methyl-7-methylene-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (16)
Yield: 97.7 mg (89%); white solid; mp 102.5–103.4 °C.

IR (KBr): 2930, 1752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (s, 1 H), 7.07 (s, 1 H), 7.06 (s, 1 H), 6.85 (s, 1 H), 6.07 (d, *J* = 2.5 Hz, 2 H), 5.92 (d, *J* = 1.5 Hz, 1 H), 5.89 (d, *J* = 1.0 Hz, 1 H), 5.46 (s, 1 H), 4.79 (s, 1 H), 3.79 (d, *J* = 13.0 Hz, 1 H), 3.73 (d, *J* = 13.0 Hz, 1 H), 2.88 (s, 3 H), 1.54 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.6, 154.6, 151.7, 150.2, 146.9, 146.8, 144.3, 131.8, 131.0, 129.3, 114.7, 109.2, 106.0, 102.7, 102.5, 101.2, 100.7, 71.7, 57.5, 57.2, 26.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 366 (M^+, 7), 335 (42), 40 (52).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{18}O_6$ (M^+): 366.1103; found: 366.1107.

6-Fluoro-2-[4-fluoro-2-(methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (17)
Yield: 70.7 mg (75%); light yellow oil.

IR (KBr): 2920, 1715 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.63–7.61 (m, 1 H), 7.53–7.50 (m, 1 H), 7.40–7.38 (m, 1 H), 7.22–7.18 (m, 1 H), 7.03–7.00 (m, 1

H), 6.84–6.82 (m, 1 H), 5.67 (s, 1 H), 5.35 (s, 1 H), 4.89 (d, *J* = 15.5 Hz, 1 H), 4.61 (d, *J* = 15.5 Hz, 1 H), 3.24 (s, 3 H), 1.44 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 202.3, 151.8, 141.0, 136.7, 136.1, 135.5 (d, *J* = 7.0 Hz, 1 C), 129.9 (d, *J* = 8.0 Hz, 1 C), 124.5 (d, *J* = 9.0 Hz, 1 C), 117.8 (d, *J* = 23.0 Hz, 1 C), 114.7 (d, *J* = 21.0 Hz, 1 C), 112.5 (d, *J* = 23.0 Hz, 1 C), 110.9, 110.7, 106.9, 106.5, 64.3, 52.7, 50.5, 22.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 314 (M^+, 4), 267 (18), 40 (100).

HRMS (EI): *m*/*z* for $C_{19}H_{16}F_2O_2$ (M^+): 314.1118; found: 314.1122.

5-Fluoro-2-[5-fluoro-2-(methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (18)
Yield: 76.3 mg (81%); colorless oil.

IR (KBr): 2919, 1716 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.63–7.61 (m, 1 H), 7.53–7.50 (m, 1 H), 7.40–7.38 (m, 1 H), 7.20–7.18 (m, 1 H), 7.03–6.99 (m, 1 H), 6.84–6.82 (m, 1 H), 5.67 (s, 1 H), 5.35 (s, 1 H), 4.90 (d, *J* = 15.5 Hz, 1 H), 4.61 (d, *J* = 15.5 Hz, 1 H), 3.24 (s, 3 H), 1.44 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 201.2, 151.7, 140.9, 136.7 (d, *J* = 77.0 Hz, 1 C), 135.5, 135.4, 130.0, 124.5 (d, *J* = 9.0 Hz, 1 C), 117.8 (d, *J* = 23.0 Hz, 1 C), 114.7 (d, *J* = 21.5 Hz, 1 C), 112.5 (d, *J* = 23.0 Hz, 1 C), 110.9, 110.7, 106.9, 106.5, 64.3, 52.7, 50.5, 22.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 314 (M^+, 6), 267 (22), 40 (100).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{16}F_2O_2$ (M^+): 314.1118; found: 314.1122.

6-Chloro-2-[4-chloro-2-(methoxymethyl)phenyl]-2-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-one (19)
Yield: 62.5 mg (60%); light yellow oil.

IR (KBr): 2919, 1720 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23–8.17 (m, 2 H), 8.08 (d, *J* = 17.5 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 5.65 (s, 1 H), 5.17 (s, 1 H), 5.13 (d, *J* = 16.0 Hz, 1 H), 5.06 (d, *J* = 13.0 Hz, 1 H), 3.00 (s, 3 H), 1.67 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2, 153.1, 140.5, 140.1, 138.8, 132.9, 129.5, 127.6, 127.0, 126.9, 125.9, 124.8, 123.7, 121.9, 105.2, 64.9, 52.6, 50.4, 21.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 346 (M^+, 25), 316 (100), 276 (22).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{16}Cl_2O_2$ (M^+): 346.0527; found: 346.0531.

2-[2-(Methoxymethyl)-4-nitrophenyl]-2-methyl-3-methylene-6-nitro-2,3-dihydro-1*H*-inden-1-one (20)
Yield: 66.2 mg (60%); yellow oil.

IR (KBr): 2925, 1745 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29–8.23 (m, 2 H), 8.15 (d, *J* = 17.0 Hz, 2 H), 7.57 (d, *J* = 8.5 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 5.65 (s, 1 H), 5.23 (s, 1 H), 5.20 (d, *J* = 16.0 Hz, 1 H), 5.13 (d, *J* = 13.5 Hz, 1 H), 3.06 (s, 3 H), 1.73 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.3, 149.5, 149.0, 146.0, 142.4, 142.3, 141.5, 132.1, 124.0, 123.9, 123.8, 123.2, 116.9, 110.7, 110.6, 60.4, 51.1, 50.2, 21.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 368 (M^+, 9), 202 (23), 40 (100).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{16}N_2O_6$ (M^+): 368.1008; found: 368.1012.

Acknowledgment

The authors thank the National Natural Science Foundation of China (No. 21172060) and Fundamental Research Funds for the Central Universities (Hunan University) for financial support.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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(10) The X-ray single-crystal diffraction analysis of **16** is given in the Supporting Information.