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Note

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Palladium-catalyzed annulation of alkynes with *ortho*-halide-containing benzyl alcohols in aqueous medium

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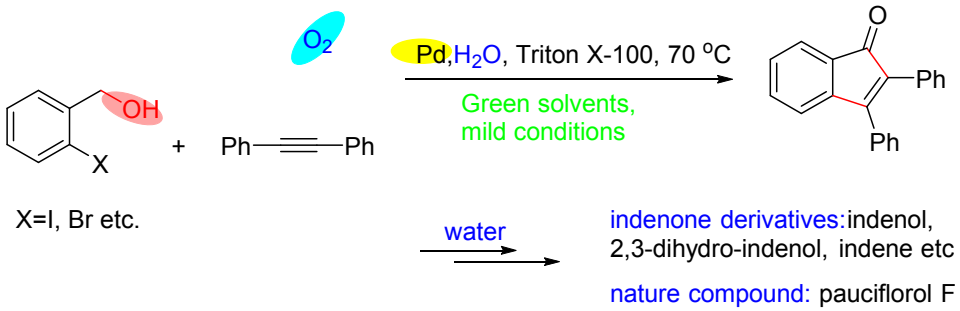
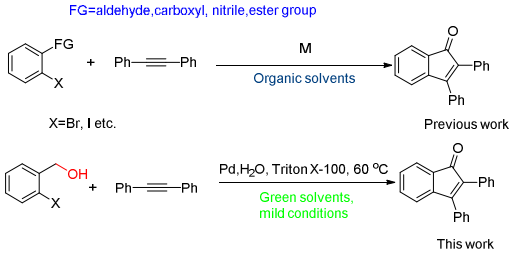


Abstract:

The Pd-catalyzed annulations of *ortho*-halide-containing benzyl alcohols with alkynes for the synthesis of indenones were achieved in aqueous Triton X-100 micelles with good yields and wide substrate scopes. Moreover, the indenones obtained in this procedure can be further functionalized to form some more synthetic useful derivatives *via* an environmental-friendly way.

Indenones are a class of important compounds since they are ubiquitous in synthetic chemistry, biology, pharmacology and material chemistry.[1] Consequently, preparation of indenones and their derivatives has aroused great interest among

synthetic chemists over the past decades.[2] Typically, indenones have been synthesized by transition metal (Pd[3], Co[4], Ru[5] *etc.*)-catalyzed annulations of alkynes with ortho-bifunctionalized arenes (Scheme 1).[6] In recent years, guided by powerful C−H activation technologies, Rh-catalyzed direct annulations of aldehydes with alkynes have appeared.[7] In addition, other approaches such as trimerization, cross couplings and amino transfer reactions have also been developed for the formation of indenones.[8]



Scheme 1 Preparation of indeones via annulation of alkynes.

Despite all these advances, development of greener methods for preparation of indenones is in high demand as the existing methods usually require high reaction temperature, expensive reagents and the use of potential toxic organic solvents.

Water is an ideal green medium for organic synthesis.[9] Meanwhile, nonionic surfactants develop well that enable transition-metal catalyzed cross-couplings to be performed in water. The surfactants may spontaneously self-aggregate to form nanomicelles that serve as nanoreactors for many valued types of couplings.[10]

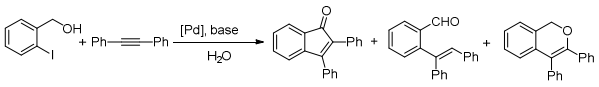
Alone this line, we herein wish to explore a novel approach to synthesize indenones *via* Pd-catalyzed annulation in water under relatively mild conditions. We originally planned to furnish the Pd-catalyzed annulations with *ortho*-halogenated benzaldehydes and alkynes in water. In the course of exploring this reaction, it was

found that *ortho*-halide-containing benzyl achohols could also efficiently convert to indenones. To date, there is no report describing the synthesis of indenones from *ortho*-halide-containing benzyl achohols. In addition, the usage of benzyl achohols may broaden the scope of substrates to prepare indenones. In this regard, the Pd-catalyzed annulations using cheaper benzyl alcohols instead of corresponding aldehydes (for example, 2-iodobenzaldehyde 20 $/g *vs* 2-iodobenzyl alcohol 1 $/g in aldrich) deserved further investigation.

As a representative example, the annulation of 2-iodobenzyl alcohol and diphenylethyne was selected to optimize the reaction (Table 1). The present reaction could not occur in the absence of a palladium catalyst (entry 1). The use of surfactant is crucial for the reaction, and the yield increased from 5% to 69% in the presence of a surfactant (entries 2, 3). Screening ionic and nonionic surfactants revealed that Triton X-100 was still the best choice (entries 3-6). Next, the reaction temperature was examined in a quest to improve the yield. There was a sharply decrease of the reactivity at lower temperature (entries 3, 7-9), but side reactions could be inhibited at the same time. Avoiding the nasty by-products, the reaction was finally conducted at 70 °C. To our delight, satisfactory yield could be obtained when the reaction was extended to 24 hours (entry 10). Considering that the annulation of 2-iodobenzyl alcohol with diphenylethyne may need consumption of molecular oxygen, an oxygen balloon was introduced. As expected, oxygen promoted the reaction with the yield increased to 86% (entry 11). Then some other commercial available palladium complexes were tested (entries 12-14). However, palladium complexes, such as

$Pd(dppf)Cl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(Xphos)Cl_2$ did not give any improvement. Finally, an examination of the bases demonstrated that K_2CO_3 was the most effective base for this transformation, and other bases were not suitable for this reaction (entries 11, 15-17).

Table 1 Optimizations for the preparation of indenone.[a]



1a 2a 3a 4a 5a

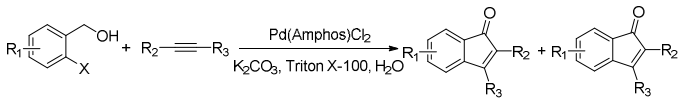
Entry	Catalysts	Additives	Bases	Temp °C	Time h	Yield %[b]
1	-	TX-100[c]	K_2CO_3	110	2	0
2	$Pd(Amphos^{d})Cl_2$	-	K_2CO_3		2	5
3	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	110	2	69 (15[e],10[f])
4	$Pd(Amphos)Cl_2$	TBAC	K_2CO_3	110	2	23
5	$Pd(Amphos)Cl_2$	SDS	K_2CO_3	110	2	50
6	$Pd(Amphos)Cl_2$	Brij L23	K_2CO_3	110	2	55
7	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	90	2	53 (13[e])
8	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	25	2	0
9	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	70	2	31 (2[e])
10	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	70	24	80 (9[e])
11[h]	$Pd(Amphos)Cl_2$	TX-100	K_2CO_3	70	24	86 (6[e])
12[h]	$Pd(dppf)Cl_2$	TX-100	K_2CO_3	70	24	70 (17[e])
13[h]	$Pd(PPh_3)_2Cl_2$	TX-100	K_2CO_3	70	24	17 (10[e], 23[f])
14[h]	$Pd(Xphos)Cl_2$	TX-100	K_2CO_3	70	24	44 (15[e])
15[h]	$Pd(Amphos)Cl_2$	TX-100	NaOAc	70	24	16 (62[e])
16[h]	$Pd(Amphos)Cl_2$	TX-100	$KHCO_3$	70	24	7 (41[e])
17[h]	$Pd(Amphos)Cl_2$	TX-100	*t*-BuOK	70	24	40[f]

[a] reaction conditions: (2-iodobenzyl alcohol 0.5 mmol, 1,2-diphenylethyne 0.55 mmol, palladium complex 0.01 mmol, base 0.5 mmol, 2 wt.% surfactants/H_2O, 2 mL, in air, 24 h. [b] determined by GC. [c] Tx-100 was Triton X-100. [d] Amphos= di-*tert*-butyl(4-dimethylaminophenyl)phosphine. [e] the yield of **5a**. [f] the yield of **4a**. [h] with O_2 balloon.

With the optimized conditions in hand, a series of internal alkynes and 2-halobenzyl alcohols were chosen to establish the scope and generality of the method (Table 2). Symmetric diarylethynes bearing methyl substituent at different positions coupled with 2-iodobenzyl alcohol to afford the indenones in good yields (**3b**, **3c**).

Notably, alkyl-substituted internal alkyne was also tolerated (**3e**), but propargyl chloride failed to provide the desired product (**3d**).

Table 2 Scope of substrates.[a,b]



1 2 3 3'

3a X=I, 86%; X=Br, 75%[c] X=Cl, 7%[c]

3b X=I, 87%; X=Br, 77%[c]

3c X=I, 81%

3d X=I, 0%

3e X=I, 77%

3f X=I, 68%[d](77%[e]); X=Br, 35%[c]

3g X=I, 84%[d](50:50)[g]

3h X=I, 80%

3i X=I, 87%, X=Br, 65%[c]

3j X=I, 90%, X=Br, 78%[c]

3k X=I, 85%

3l X=I, trace

3m X=I, 68%[f](56:44)[g]

3n X=I, 93%[f](50:50)[h]

3o X=I, 82%[f](50:50)[h]

3p X=I, 81%[f](51:49)[g]

3q X=I, 83%[f](75:25)[h]

3r X=I, 73%[f](77:23)[h]

[a] reaction conditions: 2-halobenzyl alcohol 0.5 mmol, alkyne 0.55 mmol, palladium complex 0.01 mmol, base, 0.5 mmol, 2wt.% Triton X-100/H_2O 2 mL, with O_2 balloon, 70°C, 24 h.; [b] isolated yields; [c] the reaction was conducted at 110 °C; [d] the reaction was conducted at 80 °C; [e] 2wt.% Triton X-100/H_2O 2 mL was replaced by 2 wt.% Brij L23/H_2O; [f] yield of all the isomers; [g] the two isomers were separated, and the ratio of two isomers(**3**/**3'**) was determined by isolated yield; [h] the two isomers were un-separated, the ratio of two isomers (**3**/**3'**) was determined by ^1H NMR, and the regioselectivty was not determined.

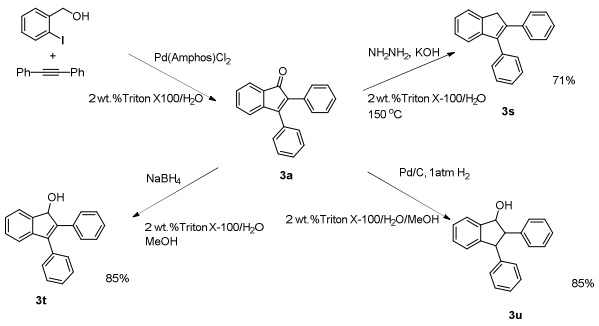
As for asymmetric diarylacetylenes, most of them underwent smooth coupling with two isomers obtained (**3g**, **3n**-**3p**). The electronic effect seems to have little influence on the regioselectivity except for **3q**, while the steric effect plays an important role on the regioselectivity. For example, the usage of but-1-yn-1-ylbenzene only afforded sole product (**3h**). Similarly, regioselective product was obtained when 1-pentyl-4-(phenylethynyl)benzene was used (**3r**). After that, substituted 2-iodobenzyl alcohols were examined. Variation of substituents showed obvious effects on the reaction efficiency. Chloro or fluoro substituted 2-iodobenzyl alcohols survived the reaction with satisfactory yields (**3i**-**3k**). However, 2-iodobenzyl alcohol substituted with an

electron-donating group afforded the corresponding product in only 68% yield even at a higher temperature (**3f**). Gratefully, higher yield could be obtained when Triton X-100 was replaced by Brij L23. 2-Iodo-4-nitrobenzyl alcohol was also subjected to the reaction. But unfortunately, the de-iodination product instead of the desired indenone was observed in this case (**3l**). We further used 2-bromobenzyl alcohol and 2-chlorobenzyl alcohol to replace 2-iodobenzyl alcohol. 2-Bromobenzyl alcohol survived this reaction with moderate to good yields at a higher temperature (110 ^{o}C) (**3a, 3b, 3f, 3i, 3j**). As for 2-chlorobenzyl alcohol, only trace amount of product could be observed at 110 ^{o}C for 24 h **(3a).**

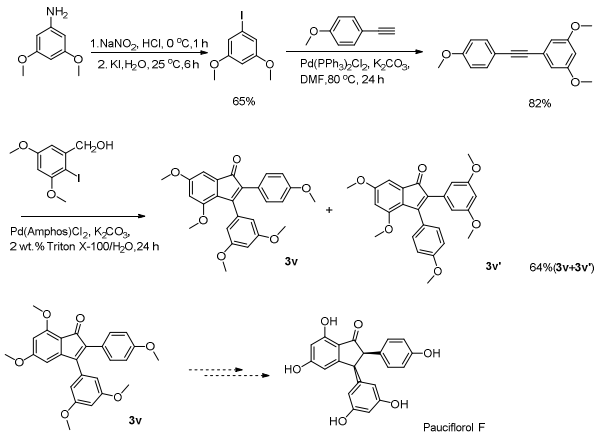
Next, we performed several experiments to explore the sequence reactions of the above-mentioned annulation (Scheme 2). 2,3-Diphenyl-1*H*-inden-1-one (**3a)** could easily convert to 2,3-diphenyl-1*H*-indene (**3s**) with hydrazine in the presence of KOH. When **3a** was treated with $NaBH_4$, the corresponding indenol (**3t**) was obtained, whereas in Pd/C hydrogenation conditions, 2,3-diphenyl-2,3-dihydro-1*H*-inden-1-ol (**3u**) was produced. All the reactions were conducted in Triton X-100/water system (methanol need to be added in some cases) which doesn't need separation of indenones from the original reaction system. Thus these synthetic useful structures (indenol, 2,3-dihydro-indenol, indene *etc.*) can be achieved in one pot *via* an environmental-friendly way.

To further highlight the potential advantage of our methodology, the developed method was utilized for preparation of 2-(3,5-dimethoxyphenyl)-5,7-dimethoxy-3-(4-methoxyphenyl)-1*H*-inden-1-one (**3v**), a key intermediate which can eventually

convert to *Pauciflorol F* (a kind of polyphenolic natural products[1e]) (Scheme 3). 1,3-Dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene was firstly synthesized via iodidation and Sonogashira couplings using 3,5-dimethoxyaniline as the starting material.[11] Next, 1,3-Dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene reacted with (2-iodo-3,5-dimethoxyphenyl)methanol under the developed conditions to obtain two isomers in moderate yields (64% total yields). Indenone **3v** was separated by preparative HPLC. According to the literature[1e], further hydrogenation and demethylation of **3v** can finally yield the *Pauciflorol F*.



Scheme 2 Sequence reactions with indenones in aqueous medium.

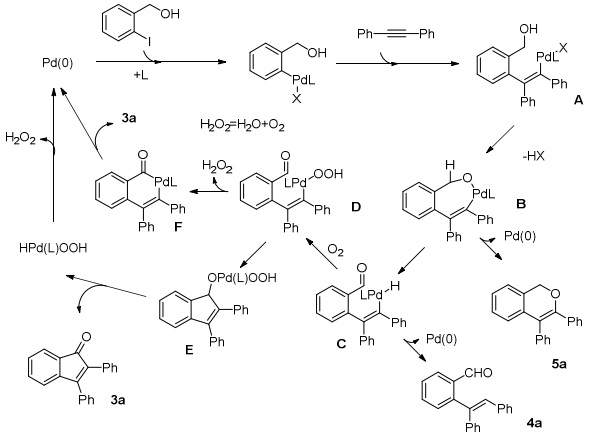


Scheme 3 A potential application of the protocol in total synthesis

Finally, we tried to go through the mechanism of the developed reaction. The reaction could not proceed under argon atmosphere which means oxygen is necessary

for this reaction. To clarify when benzyl alcohol was oxidized, 2-iodobenzyl alcohol was stirred under the optimal conditions. It failed to convert to 2-iodobenzaldehyde under the optimal conditions without adding alkyne. However, the oxidative addition of 2-iodobenzyl alcohol to the active Pd(0) complex occurred with self-coupling product obtained. It indicates that the insertion of alkyne may occur before the oxidation. Although details about the mechanism remain to be ascertained, based on the results above and the well documented annulation of *ortho*-halobenzaldehyde with an alkyne[3a, 6b], a proposed mechanism was outlined in Scheme 4. The palladium complex Pd(Amphos)Cl_2 was a precursors for the active Pd(0) complex. The oxidative addition of 2-iodobenzyl alcohol to the Pd(0) complex firstly took place. Then the alkyne was inserted to the C–Pd bond to form the intermediate **A**. After dehydrohalogenation, intermediate **B** was formed. The intermediate **B** can directly lead to byproduct **5a** via the reductive elimination of palladium. Also, intermediate **B** can convert to intermediate **C** through hydrogen transfer. The formation of intermediate **C** provided a good explanation for the formation of byproduct **4a**. According to the paper reported by Uemura[14], a palladium hydroperoxide intermediate **D** may further formed. Then there may exist two ways to close the ring. Intermediate **D** could transfer to the intermediate **E** via the insertion of the C=O double bond. Then β-H elimination of intermediate **E** would give the indenone and HPdOOH species. The HPdOOH species could further decompose to the Pd(0) complex and H_2O_2 which finished the catalytic cycle. On the other hand, intermediate F was produced via the intramolecular oxidative addition along with the detachment

of H_2O_2. Intermediate F could also form the desired indenone **3a** and Pd(0) species. The H_2O_2 formed in the two paths may produce H_2O and O_2 *in situ*. In this procedure, ligands and Triton X-100 may help to stabilize and improve the reactivity of the Pd(0) species in water (it is possible to form nanomicelles), avoiding the formation of palladium black.



Scheme 4 Proposed mechanism of the Pd-catalyzed annulation

In summary, we have described a novel synthesis of indenones via Pd-catalyzed annulation of *ortho*-halobenzyl alcohol with internal alkynes in aqueous system. This new procedure is environmental-friendly because no toxic solvent is required in the coupling step. In addition, the indenones formed in the procedure can undergo some sequence reactions without any separation process which can decrease the consumption of energy and reagents. The protocol also exhibits good yields and broad substrate scopes, thereby offering considerable potential applications to complex targets (*Pauciflorol F* intermediate) in water.

Experimental Section

Melting points are uncorrected. All commercial materials were used without further purification. Asymmetric diarylacetylenes was synthesized according to the literature[12]; 2-iodo-4,6-dimethoxybenyl alcohol was synthesized according to the literature[13]. The proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained in $CDCl_3$ using a 500 MHz spectrometer referenced to TMS and are reported in δ units. Coupling constants (*J* values) are reported in Hz. Mass spectra was obtained using EI technique. Elemental analysis was performed on a C/H mode. Preparative high performance liquid chromatography was performed on the Column: XDB-C18 9.6×250 mm with methanol/water (70:30) as eluent.

General procedure for synthesis of indenones

A mixture of 2-iodobenzyl alcohol (0.5 mmol), alkyne (0.55 mmol), Pd(Amphos)Cl_2 (0.01 mmol), K_2CO_3 (0.50 mmol) were stirred in 2wt.% Triton X-100 /H_2O (2 mL) in a 5 ml vial with oxygen balloon at 70 ^{o}C for 24 h. The reaction mixture was then cooled, extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to give a crude mixture which was purified by silica gel column chromatography to afford the desired product.

2,3-Diphenyl-1H-inden-1-one (**3a**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 121 mg of product as a red solid (86% yield); mp. 152-153 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.0 Hz, 1H), 7.36 – 7.28 (m, 6H), 7.20 (dt, *J* = 6.5, 5.3 Hz, 6H), 7.08 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 154.4, 144.3, 132.5,

131.8, 131.4, 129.8, 129.0, 128.4, 128.0, 127.8, 127.6, 127.1, 126.8, 122.0, 120.3. GC/MS, m/z: 282 [M^+]; Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.65; H, 5.15.

2,3-Di-p-tolyl-1H-inden-1-one (**3b**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-di-p-tolylethyne 113 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 135 mg of product as a red solid (87% yield); mp. 143-145 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.0 Hz, 1H), 7.36 (s, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.22 (m, 2H), 7.20 – 7.10 (m, 4H), 7.07 (d, J = 12.0 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 154.5, 144.5, 137.4, 136.5, 132.5, 131.8, 129.7, 129.1, 127.9, 127.7, 127.6, 126.9, 126.1, 124.8, 121.9, 120.3, 20.5. GC/MS, m/z: 310 [M^+]; Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.79; H, 5.69.

2,3-Di-m-tolyl-1H-inden-1-one (**3c**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-di-m-tolylethyne 113 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 125 mg of product as a red solid (81% yield); mp 141-143 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.0 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.21 (d, J = 7.8 Hz, 2H), 7.15 (dd, J = 13.7, 7.6 Hz, 3H), 7.07 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 153.8, 144.5, 138.4, 136.6, 132.3, 131.1, 130.0, 128.9, 128.5, 127.9, 127.7, 127.5, 127.0, 121.8, 120.2, 20.5, 20.4. GC/MS, m/z: 310 [M^+]; Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.63; H, 5.71.

2,3-Dipropyl-1H-inden-1-one(**3e**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), dec-5-yne 76 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:20) to give 82 mg of product as a red oil (77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.0 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.27 – 2.20 (m, 2H), 1.61 – 1.54 (m, 2H), 1.48 – 1.38 (m, 4H), 1.33 (dd, J = 14.9, 7.2 Hz, 2H), 0.96 (dd, J = 13.8, 6.5 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 156.7, 144.7, 133.9, 132.1, 130.2, 126.9, 120.7, 118.0, 30.5, 29.0, 25.0, 22.1, 21.8, 21.7, 12.9. GC/MS, m/z: 214 [M^+]; Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.39; H, 8.38.

5,7-Dimethoxy-2,3-diphenyl-1H-inden-1-one(**3f**). Starting material: 2-iodo-4,6-dimethoxy benzyl alcohol 147 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:20) to give 116 mg of product as a red oil (68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 5H), 7.17 (d, J = 7.4 Hz, 3H), 7.11 (d, J = 6.9 Hz, 2H), 6.87 (s, 1H), 6.42 (s, 1H), 3.86 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 161.8, 157.3, 154.0, 134.0, 133.3, 130.2, 130.1, 128.9, 127.7, 127.4, 126.8, 126.5, 126.0, 121.6, 106.2, 103.1, 101.9, 54.9, 54.7. GC-MS, m/z: 342 [M^+]; Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.29; H, 5.45.

2-(4-Chlorophenyl)-3-phenyl-1H-inden-1-one (**3g**) and *3-(4-chlorophenyl)-2-phenyl-1H-inden-1-one* (**3g'**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-chloro-4-(phenylethynyl)benzene 117 mg (0.55 mmol). The crude material was

purified by column chromatography (ethyl acetate: petroleum ether, 1:20) to give 132 mg of product (mixture of **3g**, **3g'**, the ratio is 1:1 which is determined by ^{1}H NMR) as a red oil (84% yield). **3g** and **3g'** was separated by preparative HPLC (methonol:water, 70:30).

2-(4-Chlorophenyl)-3-phenyl-1H-inden-1-one (**3g**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.0 Hz, 1H), 7.41 (d, J = 8.3 Hz, 3H), 7.35 (d, J = 8.5 Hz, 2H), 7.33 – 7.24 (m, 7H), 7.14 (d, J = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 154.8, 144.1, 132.8, 132.6, 131.5, 129.7, 128.6, 128.2, 128.0, 127.4, 122.1, 120.4; GC-MS, m/z: 316 [M^+]; Anal. Calcd for $C_{21}H_{13}ClO$: C, 79.62; H, 4.14. Found: C, 80.01; H, 4.28.

3-(4-Chlorophenyl)-2-phenyl-1H-inden-1-one (**3g'**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 7.0 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.42 – 7.36 (m, 3H), 7.32 (t, J = 7.3 Hz, 1H), 7.24 (q, J = 8.7 Hz, 4H), 7.16 (d, J = 7.2 Hz, 1H);^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 152.9, 143.9, 134.3, 132.6, 131.9, 130.2, 129.6, 129.4, 129.0, 128.2, 127.2, 127.0, 122.2, 120.0. GC-MS, m/z: 316 [M^+]; Anal. Calcd for $C_{21}H_{13}ClO$: C, 79.62; H, 4.14. Found: C, 79.97; H, 4.31;

2-Ethyl-3-phenyl-1H-inden-1-one (**3h**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), but-1-yn-1-ylbenzene 71.5 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:50) to give 94 mg of product as an orange oil (80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.0 Hz, 2H), 7.45 (t, J = 8.6 Hz, 4H), 7.28 (s, 1H), 7.19 (s, 1H), 7.00 (d, J = 7.2 Hz, 1H), 2.35 (q, J = 7.5 Hz, 2H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ

197.2, 153.7, 144.9, 135.7, 132.2, 131.8, 130.1, 128.1, 127.8, 127.2, 126.8, 121.4, 119.6, 76.3, 76.0, 75.8, 15.7, 13.0; GC-MS, m/z: 234 [M^+]; Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.39; H, 5.84.

6-Chloro-2,3-diphenyl-1H-inden-1-one (**3i**). Starting material: 5-chloro-2-iodo benzyl alcohol 134 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 137 mg of product as an orange-red solid (87% yield). mp: 183-184 ^oC ; ^1H NMR (500 MHz, CDCl3) δ 7.54 (d, J = 1.6 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.39 – 7.32 (m, 3H), 7.25 (d, J = 7.6 Hz, 5H), 7.09 (d, J = 7.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 154.1, 142.3, 134.1, 131.7, 131.4, 131.3, 129.4, 129.0, 128.6, 127.9, 127.4, 127.2, 127.0, 122.6, 121.2. GC-MS, m/z: 316 [M^+]; Anal. Calcd for $C_{21}H_{13}ClO$: C, 79.62; H, 4.14. Found: C, 79.89; H, 3.97.

6-Fluoro-2,3-diphenyl-1H-inden-1-one (**3j**). Starting material: 5-fluoro-2-iodo benzyl alcohol 126 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 135 mg of product as an orange-red oil (90% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (ddd, J = 7.0, 5.8, 3.4 Hz, 4H), 7.33 – 7.15 (m, 7H), 7.11 (dd, J = 8.0, 4.5 Hz, 1H), 7.03 (td, J = 8.7, 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 166.5, 152.2, 147.6, 132.7, 131.3, 129.4, 129.0, 128.5, 128.0, 127.4, 127.2, 127.1, 125.6, 123.8, 123.8, 113.5, 113.4, 109.3, 109.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.53. GC-MS, m/z: 300[M^+]; Anal. Calcd for $C_{21}H_{13}FO$: C, 83.98; H, 4.36. Found: C, 83.79; H, 4.53.

5-Fluoro-2,3-diphenyl-1H-inden-1-one (**3k**). Starting material: 4-fluoro-2-iodo benzyl alcohol 126 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 128 mg of product as an orange oil (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.9, 5.2 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.37 (dd, J = 6.6, 3.0 Hz, 2H), 7.27 (d, J = 3.9 Hz, 5H), 6.94 (td, J = 9.0, 2.1 Hz, 1H), 6.87 (dd, J = 8.5, 2.0 Hz, 1H);^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 166.5, 152.2, 147.6, 132.7, 131.3, 129.4, 129.0, 128.5, 128.0, 127.4, 127.2, 127.1, 125.6, 123.8,123.8, 113.5, 113.4, 109.3, 109.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -104.02; GC-MS, m/z: 300 [M^+]; Anal. Calcd for $C_{21}H_{13}FO$: C, 83.98; H, 4.36. Found: C, 83.76; H, 4.47.

2-(2,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-1H-inden-1-one (**3m**) and *3-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-1H-inden-1-one* (**3m'**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene 147 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, from 1:200 to 1:20) to give 126 mg of product (mixture of **3m**, **3m'**, the ratio is 56:44 which is determined by ^{1}H NMR) as a red oil (68% yield). **3m** and **3m'** was separated by preparative HPLC (methonol:water, 70:30).

2-(2,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-1H-inden-1-one (**3m**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 6.8 Hz, 1H), 7.33 (dd, J = 14.5, 7.8 Hz, 3H), 7.23 (s, 2H), 7.05 (d, J = 8.3 Hz, 1H), 6.87 (d, J = 8.2 Hz, 2H), 6.47 (d, J = 8.3 Hz, 1H), 6.39 (s, 1H), 3.80 (m, 6H), 3.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 160.9, 158.0,

157.4, 150.9, 145.1, 132.3, 131.4, 129.8, 129.6, 129.5, 127.2, 123.6, 121.3, 120.1, 114.0, 112.5, 104.0, 98.3, 54.4, 54.3, 54.2; MS, m/z: 372 [M^+]; Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.67; H, 5.49.

3-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (**3m'**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.1 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.24 (m, 2H), 7.20 (s, 1H), 7.15 (d, J = 9.0 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.78 (d, J = 8.4 Hz, 2H), 6.51 (s, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 160.0, 159.2, 157.7, 154.3, 144.4, 131.9, 131.3, 130.7, 129.1, 128.5, 127.4, 125.3, 121.6, 120.0, 112.8, 103.7, 98.1, 54.3, 54.3, 54.2; MS, m/z: 372 [M^+]; Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.73; H, 5.54.

2-(4-Fluorophenyl)-3-phenyl-1H-inden-1-one (**3n)** and *3-(4-Fluorophenyl)-2-phenyl-1H- inden-1-one* (**3n')**. Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-fluoro-4-(phenylethynyl)benzene 108 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 139.5 mg of product (mixture of **3n**, **3n'**, the ratio is 1:1 which is determined by ^{1}H NMR) as a red oil (93% yield). **3n** and **3n'** could hardly be separated.

Mixture of **3n**, **3n'**, the ratio is 1:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.45 – 7.32 (m, 4H), 7.32 – 7.20 (m, 4H), 7.16 – 7.05 (m, 2H), 6.94 (t, J = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 195.2, 170.1, 163.1, 162.3, 161.1, 160.4, 154.3, 153.2, 144.2, 144.0, 132.5, 132.5, 131.6, 130.8, 130.8, 130.4, 129.6, 129.0, 128.8, 128.4, 128.1, 127.9, 127.7, 127.5, 127.2, 126.9, 125.8, 122.1, 120.3, 120.1, 115.2, 115.0, 114.3, 114.1; GC-MS, m/z: 300 [M^+]. Anal.Calcd for $C_{21}H_{13}FO$: C, 83.98; H,

4.36. Found: C, 84.18; H, 4.53.

2-(3-Methylphenyl)-3-phenyl-1H-inden-1-one (**3o)** and *3-(3-methylphenyl)-2-phenyl-1H-inden-1-one* (**3o')**. Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-methyl-4-(phenylethynyl)benzene 106 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, 1:100) to give 121 mg of product (mixture of **3o**, **3o'**, the ratio is 1:1 which is determined by ^{1}H NMR) as a red oil (82% yield). **3o** and **3o'** could hardly be separated.

Mixture of **3o** and **3o'** (50:50); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, 1H), 7.41 – 7.35 (m, 3H), 7.24 (m, 6H), 7.12 (dd, J = 13.7, 6.9 Hz, 2H), 7.04 (d, J = 7.5 Hz, 0.5×1H), 6.99 (d, J = 7.6 Hz, 0.5×1H), 2.34 (s, 0.5×3H), 2.26 (s, 0.5×3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.2, 195.6, 154.2, 144.4, 136.6, 132.4, 131.3, 129.8, 129.6, 129.1, 129.0, 128.2, 127.9, 127.7, 127.6, 127.5, 127.0, 126.9, 126.7, 126.1, 124.7, 121.9, 120.3, 20.5. GC-MS, m/z: 296 [M^+]; Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 88.98; H, 5.52.

3-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (**3p**) and *2-(4-chlorophenyl)-3-(4-methoxyphenyl)-1H-inden-1-one* (**3p'**). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-chloro-4-((4-methoxyphenyl)ethynyl)benzene 133 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, from 1:200 to 1:20) to give 140 mg of product (mixture of **3p**, **3p'**, the ratio is 51:49 which is determined by ^{1}H NMR) as a red oil (81% yield). **3p** and **3p'** was separated by preparative HPLC (methanol: water, 70:30).

3-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (**3p**). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.56 (d, J = 7.0 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 8.6 Hz, 2H), 7.27 (d, J = 7.3 Hz, 1H), 7.20 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 7.3 Hz, 1H), 6.81 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 158.5, 151.3, 144.2, 134.1, 132.5, 131.4, 130.5, 130.3, 129.6, 129.0, 128.2, 127.8, 122.1, 121.8, 119.7, 112.8, 54.2; GC-MS, m/z:346 [M^+]; Anal. Calcd for $C_{22}H_{15}ClO_2$: C, 76.19; H, 4.36. Found: C, 76.38; H, 4.47.

2-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1H-inden-1-one (**3p'**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.0 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.21 (dd, J = 15.8, 7.3 Hz, 4H), 6.93 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 159.7, 154.7, 144.0, 132.6, 132.4, 130.3, 130.0, 129.2, 128.6, 128.1, 127.4, 123.6, 121.9, 120.4, 113.4, 54.4; GC-MS, m/z:346 [M^+]; Anal. Calcd for $C_{22}H_{15}ClO_2$: C, 76.19; H, 4.36. Found: C, 76.39; H, 4.45.

2-(4-Nitrophenyl)-3-phenyl-1H-inden-1-one (**3q)** and *3-(4-nitrophenyl)-2-phenyl-1H-inden-1-one* **(3q').** Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-nitro-4-((4-methoxyphenyl)ethynyl)benzene 123 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, from 1:20 to 1:10) to give 135 mg of product (mixture of **3q**, **3q'**, the ratio is 75:25 which is determined by ^{1}H NMR, but the regioselectivity is not determined.) as a red oil (total yield 83%). **3q** and **3q'** could hardly be separated.

Mixture of **3q** and **3q'** (75:25). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.27 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.7 Hz, 0.75×1H), 8.08 (d, J = 8.7Hz, 0.25×1H), 8.06 (m, 1H), 7.62 (m, 1H), 7.56 (m, 1H), 7.50 – 7.38 (m, 3H), 7.34 (m, 2H), 7.28 (m, 1H),

7.19 (t, J = 6.5 Hz, 0.75×2H), 7.07 (d, J = 7.2 Hz, 0.25×2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 157.4, 145.8, 143.5, 136.8, 132.9, 130.9, 129.7, 129.6, 129.1, 128.9, 128.2, 127.3, 125.2, 122.4, 122.3, 121.1, 111.3; GC-MS, m/z: 327 [M^+]. Anal.Calcd for $C_{21}H_{13}NO_3$: C, 77.05; H, 4.00. Found: C, 76.77; H, 4.25.

2-(4-Pentylphenyl)-3-phenyl-1H-inden-1-one (**3r)** and *3-(4-pentylphenyl)-2-phenyl-1H-inden-1-one* (**3r')** (77:23). Starting material: 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1-pentyl-4-(phenylethynyl)benzene 136 mg (0.55 mmol). The crude material was purified by column chromatography (ethyl acetate: petroleum ether, from 1:200 to 1:10) to give 135 mg of product (mixture of **3r**, **3r'**, the ratio is 77:23 which is determined by ^{1}H NMR, but the regioselectivity is not determined.) as a red oil (73% yield). **3r** and **3r'** could hardly be separated.

Mixture of **3r** and **3r'**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.27 (dd, J = 16.1, 6.7 Hz, 7H), 7.19 (dd, J = 10.8, 8.1 Hz, 3H), 7.09 (dd, J = 24.2, 7.6 Hz, 1H), 2.59 (dt, J = 42.1, 7.8 Hz, 2H), 1.69 – 1.59 (m, 2H), 1.39 – 1.28 (m, 4H), 0.90 (dd, J = 13.7, 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 154.6, 144.3, 143.6, 132.3, 131.1, 130.0, 130.0, 129.0, 128.9, 128.8, 128.2, 127.9, 127.8, 127.5, 127.2, 127.1, 126.6, 121.9, 120.4, 120.1, 34.9, 34.8, 30.6, 29.9, 21.6, 13.1. MS, m/z: 352 [M^+]; Anal. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86. Found: C, 88.27; H, 6.51.

The synthesis of 2, 3-diphenyl-1*H*-indene 3s

A mixture of 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol), $Pd(Amphos)Cl_2$ 8 mg (0.01 mmol), K_2CO_3 69 mg (0.50 mmol) were

stirred in 2 wt.% Triton X-100/H_2O (2 ml) in a 5 ml vial with oxygen balloon at 60 ^oC for 24 h. Then the resulting indenone mixture was transferred to a sealed tube. Then KOH, 31 mg (0.55 mmol), hydrazine 28 mg (0.55 mmol) and H_2O 1 mL was added. The resulting mixture was stirred at 150 ^oC for 24 h. Upon competition, the mixture was cooled, extracted with ethyl acetate (15 mL) and washed with diluted hydrochloric acid (3 × 15 mL), sat. aq. $NaHCO_3$ (3 × 15 mL), and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated in vacuo and the residue was purified by column chromatography on silica gel (pure petroleum ether) to give 95 mg **3s** (71% total yield) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.1 Hz, 1H), 7.44 (d, J = 6.7 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.32 – 7.19 (m, 8H), 3.95 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 141.4, 140.1, 139.0, 135.6, 135.1, 128.4, 127.8, 127.3, 127.2, 126.4, 125.9, 125.5, 124.1, 122.6, 119.4, 40.2. GC-MS, m/z: 268 [M^+] Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.79; H, 5.89.

The synthesis of 2, 3-diphenyl-1*H*-indenol 3t

A mixture of 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol), Pd(Amphos)Cl_2 8 mg (0.01 mmol), K_2CO_3 69 mg (0.50 mmol) were stirred in 2wt.% Triton X-100/H_2O (2 mL) in a 5 mL vial with oxygen balloon at 60 ^oC for 24 h. Then the resulting indenone mixture was added 3 mL methanol and cooled to 0 ^oC, $NaBH_4$ (3 mmol) was then added in portion over 30 min. The resulting mixture was stirred at 0 ^oC for another 3 h. After that the mixture was treated with diluted hydrochloric acid, extracted with ethyl acetate (15 mL), washed with sat. aq.

$NaHCO_3$ (3 × 15 mL), and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated in vacuo and the residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether, 1:10) to give 121 mg **3t** (85% total yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 6.7 Hz, 1H), 7.35 (d, J = 6.9 Hz, 2H), 7.30 (dd, J = 17.2, 9.0 Hz, 5H), 7.24 (t, J = 6.6 Hz, 2H), 7.21 (s, 1H), 7.18 (s, 1H), 7.16 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 6.8 Hz, 1H), 5.65 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 142.9, 142.8, 138.8, 133.8, 133.1, 128.3, 128.1, 127.8, 127.7, 127.3, 127.1, 126.8, 126.4, 125.4, 122.7, 119.7, 76.3; GC-MS, m/z: 284 [M^+] Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.57; H, 5.74.

The synthesis of 2,3-diphenyl-2,3-dihydro-1*H*-inden-1-ol 3u

A mixture of 2-iodobenzyl alcohol 117 mg (0.5 mmol), 1,2-diphenylethyne 97.9 mg (0.55 mmol), Pd(Amphos)Cl_2 8 mg (0.01 mmol), K_2CO_3 69 mg (0.50 mmol) were stirred in 2 wt.% Triton X-100/H_2O (2 mL) in a 5 mL vial with oxygen balloon at 60 ^{o}C for 24 h. Then the resulting indenone mixture was added 10% Pd/C (50 mg), 3 mL methanol and introduced to a pressure reactor. The suspension was stirred at room temperature for 6 h under 5 atm of hydrogen. After the reaction, the pressure was released. The reaction mixture was then extracted with ethyl acetate (15 mL) and filtered through a pad of Celite®. After filtration, the organic layer was concentrated in vacuo and the residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether, 1:4) to give 109 mg **3u** (78% total yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.97 (t, J = 7.4 Hz,

2H), 6.85 (dd, *J* = 6.2, 3.0 Hz, 2H), 6.65 (d, *J* = 7.3 Hz, 2H), 5.45 (t, *J* = 7.0 Hz, 1H), 4.68 (d, *J* = 7.4 Hz, 1H), 4.02 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 142.6, 139.1, 135.5, 129.2, 128.6, 127.3, 127.0, 126.7, 126.5, 126.0, 125.4, 124.5, 122.9, 76.3, 76.0, 75.8, 58.5, 53.2. GC-MS, m/z: 286 [M^+] Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.27; H, 6.19.

The synthesis of *Pauciflorol F* intermediate 3v

A mixture of (2-iodo-3,5-dimethoxyphenyl)methanol 147 mg (0.5 mmol), 1,3-dimethoxy-5-((4-methoxyphenyl)phenylethyne 147 mg (0.55 mmol), Pd(Amphos)Cl_2 8 mg (0.01 mmol), K_2CO_3 69 mg (0.50 mmol) were stirred in 2 wt.% Triton X-100/H_2O (2 mL) in a 5 mL vial with oxygen balloon at 100 ^{o}C for 24 h. The reaction mixture was then cooled to room temperature, extracted with EtOAc (15 mL), washed with sat. aq. $NaHCO_3$ (3 × 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated in vacuo affording a mixture of indenone isomers 138 mg (64% yield). **3v** and **3v'** was separated by preparative HPLC (methanol: water, 70:30). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J*= 1.9 Hz, 1H), 6.75 (d, *J*= 8.7 Hz, 2H), 6.49 (d, *J* = 2.1 Hz, 2H), 6.43 (d, *J* = 2.0 Hz, 2H), 3.86 (s, 3H), 3.76 (s, 3H), 3.70 (s, 6H), 3.60 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 161.5, 159.2, 157.8, 155.6, 153.7, 136.0, 133.1, 130.0, 129.7, 122.6, 121.8, 112.5, 105.6, 103.2, 101.8, 100.0, 54.9, 54.8, 54.4, 54.2. Anal.Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.37; H, 5.44.

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Supporting information

Copies of ^{1}H NMR spectra and ^{13}C NMR spectra. This material is available free of charge via the Internet athttp://pubs.acs.org

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