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Metal-free Radical Oxidative Annulation of Ynones with Alkanes to Access Indenones

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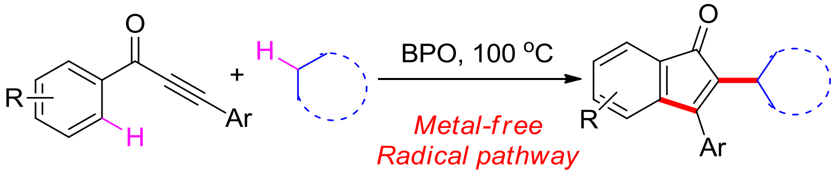
ABSTRACT

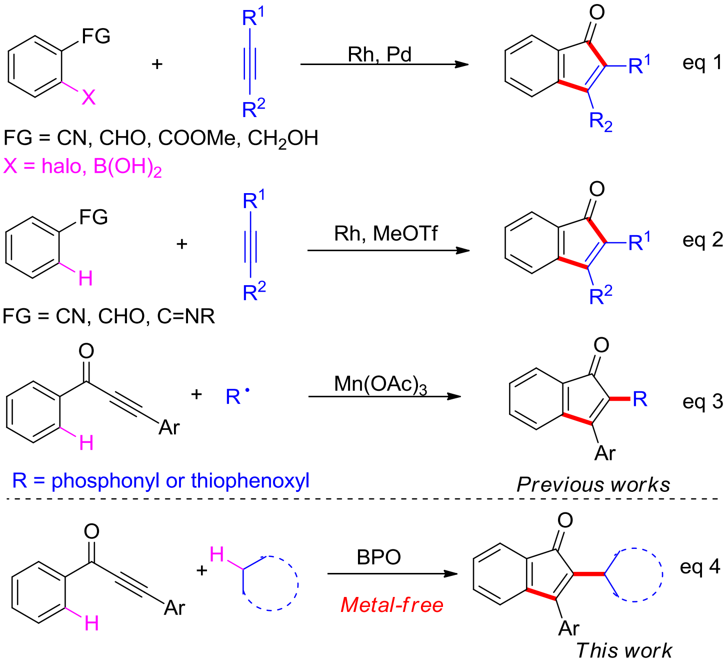


The benzoyl peroxide (BPO)-promoted carboannulation of ynones with alkanes is developed, affording a series of 2-alkyl-3-aryl indenones in moderate to good yields. The procedure undergoes direct functionalization of alkane C(sp^3)–H and arene C(sp^2)–H bonds under metal-free conditions, providing a favorable approach for indenones synthesis.

INTRODUCTION

Indenones are significant carbocycles that are prevalent in bioactive molecules and natural products.[1] Consequently, plenty of methods have been well established in the construction of indenone frameworks.[2-5] Among them, transition-metal catalyzed approaches have been proved with superexcellent advances in recent decades.[2-4] For example, the annulation reactions between alkynes and *ortho*-bifunctionalized aryl aldehydes, esters, nitriles or alcohols have well been developed as efficient synthetic strategies towards a variety of indenones[3] (Scheme 1, eq 1). However, those prefunctionalizated substrates are not commercially available, and their syntheses are always time and cost consuming tasks. Delightfully, the direct C-H activation/annulation of aryl aldehydes, nitriles or amides with internal alkynes catalyzed by rhodium[4] or MeOTf[5] arose as efficient and atom-economic options (Scheme 1, eq 2). Ynones are important structural motifs and synthetic intermediates in organic chemistry that can be conveniently prepared by the Sonogashira coupling of acyl chlorides with terminal alkynes.[6] Using 1,3-diarylpropynones as substrates, Pale and Sommer developed the synthesis of 3-aryl indenone derivatives *via* superacids-promoted intramolecular cyclization. However, the substrate scope is limited due to harsh reaction conditions.[7] In 2011, Zou and Zhang successfully generated the 3-phosphonylated and thiolated indenones by manganese(III)-mediated radical addition of phosphorus- and sulfur-centered radicals to 1,3-diarylpropynones.[8] Although significant achievements have been made, new protocols for the synthesis of diverse indenones with readily available substrates under mild and metal-free conditions are still highly desired.

Scheme 1. Construction of Indenones.

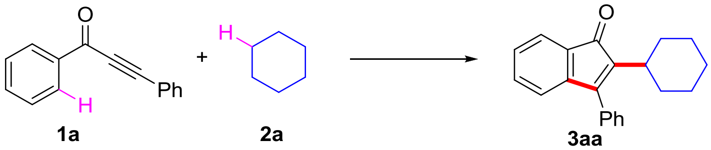


Construction of carbon-carbon bonds through direct C-H functionalization has drawn great attention during recent decades owing to its step- and atom-economy with environmental sustainability.[9] Compared with C(sp^2)-H bond, the activation of C(sp^3)-H bond is more challenging for its relatively strong bond dissociation energy (BDE) with low polarity. Fortunately, radical reaction has demonstrated as an effective tool in organic synthesis[10] and provides promising avenue to the direct functionalization of C(sp^3)-H bond.[11] In view of the abundance and easily availability of alkanes, the direct functionalization of inert C(sp^3)–H bonds of alkanes through radical pathway has attracted considerable attentions.[12] In addition, the alkyl radical induced annulation has been successfully utilized to construct heterocyclic compounds.[13] To our knowledge, synthesis of indenones through radical C(sp^3)-H bond activation of alkanes has not been reported. Herein, we describe the benzoyl peroxide (BPO) induced radical annulation of ynones with alkanes to afford 2,3-difunctionalized indenone derivatives under metal-free conditions (Scheme 1, eq 4).

RESULTS AND DISCUSSION

Initially, 1,3-diphenyl-2-propyn-1-one (**1a**) was chosen as the model substrate to obtain the optimal reaction conditions. To our delight, when *tert*-butyl peroxide (DTBP) was used as the oxidant in cyclohexane (**2a**) under 120 ^{o}C, the desired product 2-cyclohexyl-3-phenyl-indenone (**3aa**) was obtained in 39% isolated yield (Table 1, entry 1). An increase in temperature turned out futile to get higher yields (Table 1, entry 2). Next, other common oxidants, such as TBHP, BPO and DCP were tested, and BPO gave the best result with a yield of 56% (Table 1, entry 4). Further optimization showed that the reaction performed the best efficiency at 100 ^{o}C, providing a 69% yield of the product (Table 1, entry 6). The reaction became sluggish if the amount of oxidant was decreased and no reaction occurred in the absence of any oxidant (Table 1, entries 8-9).

Table 1. Selected Results for Screening the Optimized Reaction Conditions.[a]

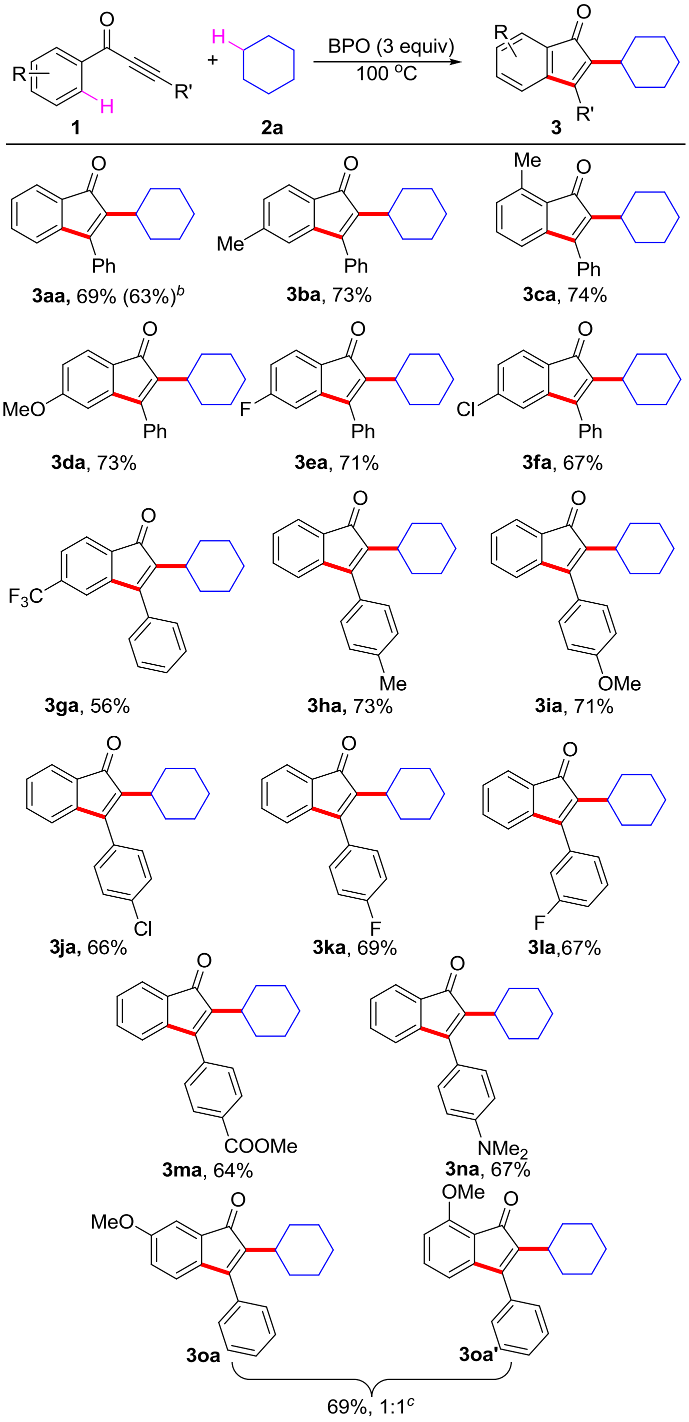


Entry	Oxidant	T (^{o}C)	Yield (%)
1	DTBP	120	39
2	DTBP	140	37
3	TBHP	120	12
4	BPO	120	56
5	DCP	120	trace
6	**BPO**	**100**	**69**
7	BPO	80	51
8	BPO	100	46[b]
9	--	100	0

[a] Reaction conditions: **1a** (0.2 mmol), oxidant (3 equiv) in **2a** (2 mL) at indicated temperature under air, 24 h. [b] BPO (2 equiv). DTBP = *tert*-Butyl peroxide, TBHP = *tert*-butyl hydroperoxide, BPO = benzoyl peroxide, DCP = dicumyl peroxide.

Next, we explored the scopes and limitations of this radical oxidative annulation process. Firstly, ynones with different substituents on 1- or 3- aryls were applied as substrates to react with cyclohexane **2a**, as shown in Figure 1. As expected, substrates with methyl, halogen, methoxy or trifluoromethyl on either phenyl ring of the 1,3-diaryl-2-propynones all proceeded well and afforded the corresponding 3-aryl-2-cyclohexyl indenones in moderate to good yields (**3aa–3la**, Figure 1). The reaction is insensitive to the steric hindrance, for substrate with *ortho*-substituent resulted in similar yield with the *para*-substituted one (**3ca** *vs* **3ba**). This phenomenon was further confirmed by regioselectivity study using aryl ynone bearing a *meta*-methoxy substituted

Figure 1. Scope of the Ynones.[a]

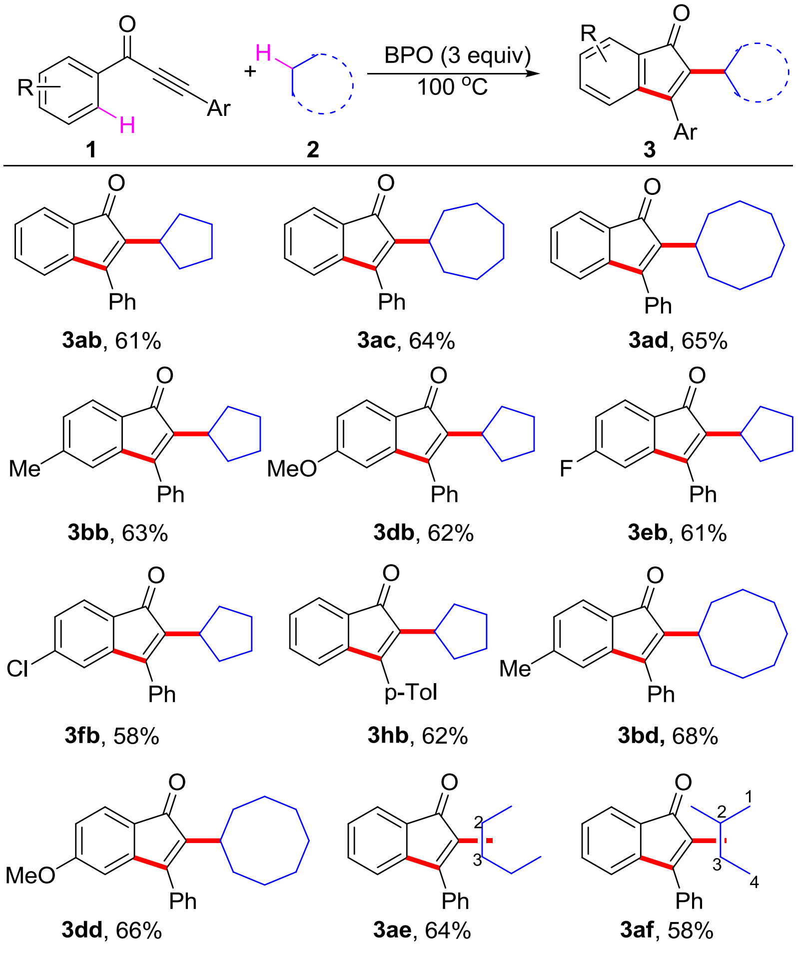


[a] Reaction conditions: **1** (0.2 mmol), BPO (3 equiv) in **2a** (2 mL) at 100 °C under air, 24 h. [b] 1 mmol scale. [c] The ratio of the isomers was determined by ^{1}H NMR.

phenyl, with the generation of two isomers in a 1:1 ratio (**3oa** & **3oa'**). Delightly, the procedure was mild enough to tolerate amine and ester groups (**3ma** & **3na**). Notably, the tolerance of halide substituents such as F and Cl, provides possibilities for further functionalizations (**3ea**, **3fa**, **3ja-3la**). A slightly decreased reactivity was observed for the reaction of ynone with strong electron deficient trifluoromethyl group (**3ga**). The practicability of this procedure was further evaluated by conducting the reaction on a 1 mmol scale, and the product **3aa** was obtained in a comparable 63% yield. Unfortunately, only trace of products were detected when ynones with 3-alkyl substituents, such as 4,4-dimethyl-1-phenylpent-2-yn-1-one (R' = *t*-Bu) and 1-phenylhept-2-yn-1-one (R' = *n*-Bu) were subjected to the procedure.

Afterwards, the reactions of 1,3-diaryl-2-propynones with various alkanes were examined. As shown in Figure 2, cyclopentane, cycloheptane and cyclooctane all worked well, providing the corresponding indenones in moderate to good yields. Particularly, when acyclic alkanes, such as pentane and 2-methylbutane were subjected to the reaction, isomeric mixtures were generated in moderate yields with a preference of 3° > 2° >> 1° carbons was observed (**3ae**, & **3af**).

Figure 2. Substrate Scope of the Reaction.[a]



3ab, 61% **3ac**, 64% **3ad**, 65%

3bb, 63% **3db**, 62% **3eb**, 61%

3fb, 58% **3hb**, 62% **3bd,** 68%

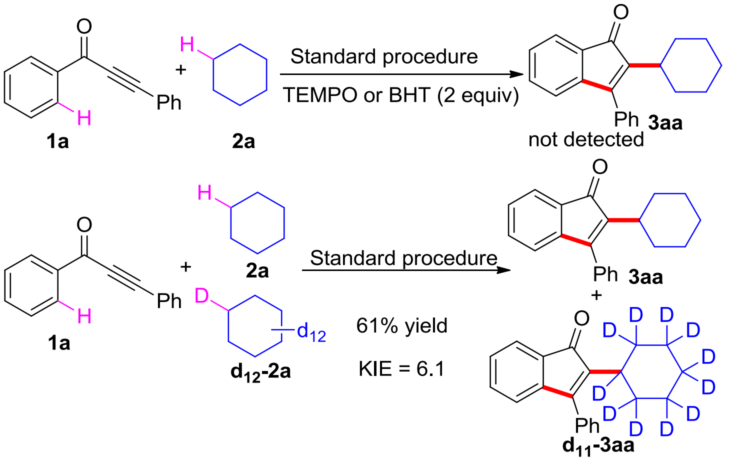
3dd, 66% **3ae**, 64% **3af**, 58%

C2:C3 = 3 : 2[b] C1:C2:C3:C4 = 3:12:8:3[b]

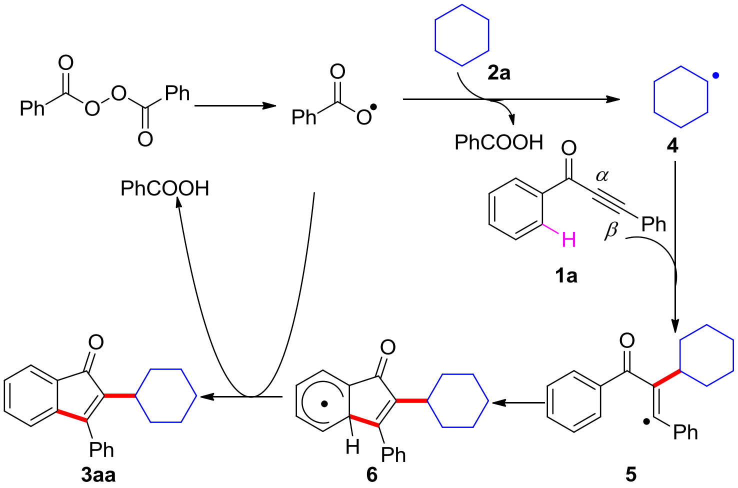
[a] Reaction conditions: **1** (0.2 mmol), BPO (3 equiv) in **2a** (2 mL) at 100 °C under air, 24 h. [b] The ratios of the isomers were determined by ^{1}H NMR.

In order to understand the reaction mechanism of this radical annulation process, control experiments were carried out as shown in Scheme 2. When the radical scavenger 2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added under the standard conditions, the reaction was completely inhibited, which strongly suggests a radical intermediate is involved. Moreover, a large kinetic isotope effect (k_H/k_D = 6.1) was observed, which reveals the C(sp^3)-H bond cleavage of cyclohexane is the rate-determining step (Scheme 2, see Supporting Information for details).

Scheme 2. Mechanism Studies.



Scheme 3. The Proposed Mechanism.



Based on the above mentioned experimental results, the proposed mechanism is outlined in Scheme 3. Initially, thermal homolytic cleavage of BPO produces the benzoyl radical, which abstracts a hydrogen atom of cyclohexane to form a cyclohexanyl radical **4** as well as benzoic acid. This is the rate-determining step as confirmed by the large KIE.

Next, selective addition of the cyclohexanyl radical to the *α*-position of the C=O bond in ynone **1a** produces vinyl radical **5**. Immediately, **5** undergoes intramolecular radical addition to arene and generates another radical intermediate **6**. Finally, after releasing of a H atom, indenone **3aa** is formed along with one equivalent of benzoic acid. Moreover, benzoic acid was detected by GCMS to confirm the above mechanism (see Supporting Information).

CONCLUSION

In conclusion, we have developed a versatile BPO-promoted radical oxidative annulation of ynones with alkanes under metal-free conditions. The reaction tolerates a series of functional groups such as halogen, methoxy, trifluoromethyl, amine and ester group well, giving 2-alkyl-3-aryl indenones in moderate to good yields. Additionally, this transformation is insensitive to the steric hindrance as well as the electro nature of the substituents on either phenyl ring of the 1,3-diaryl-2-propynones. The procedure undergoes direct functionalization of alkane $C(sp^3)$–H and arene $C(sp^2)$–H bonds under metal-free conditions, providing a favorable approach for indenones synthesis.

EXPERIMENTAL SECTION

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode. IR spectra were recorded on a spectrometer using KBr discs.

Experimental Procedure for the Synthesis of Ynones:[6c] To a 50 mL round-bottom flask were added $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), and triethylamine (10 mL). The flask was flushed with nitrogen and the terminal acetylene (5.0 mmol) was added to the stirred suspension, followed by immediate drop-wise addition of acyl chloride (6.5 mmol). After stirring at 25 ^{o}C for 12 h, water (10 mL) was added. The resulting solution was extracted with diethyl ether (3 × 20 mL) and the organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel.

Experimental Procedure for the Oxidative Annulation of Ynone with Alkane to access Indenones: Under air, ynone **1** (0.2 mmol), BPO (0.6 mmol, 144 mg) and alkane **2** (2 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 100 ^{o}C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC or flash column chromatography to afford the desired products.

2-Cyclohexyl-3-phenyl-1*H*-inden-1-one (3aa): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (39.7 mg, 69%). $R_f = 0.38$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55-7.51 (m, 2H), 7.49-7.44 (m, 2H), 7.41-7.39 (m, 2H), 7.29-7.26 (m, 1H), 7.21-7.17 (m, 1H), 6.90 (d, J = 7.1 Hz, 1H), 2.52-2.46 (m, 1H), 1.91-1.82 (m, 2H), 1.77-1.74 (m, 2H), 1.67-1.58 (m, 3H), 1.33-1.14 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 198.2, 154.6, 145.7, 139.0, 133.1, 133.0, 130.9, 128.9, 128.7, 128.2, 127.9, 122.2, 120.4, 35.9, 31.1, 26.5, 25.7. IR (cm^{-1}) v 3058, 2925, 2852, 1703, 1609, 1595, 1454, 1361, 1330, 1166, 1080, 1002. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O$ $(M+H)^+$ 289.1587, found 289.1585.

2-Cyclohexyl-5-methyl-3-phenyl-1*H*-inden-1-one (3ba): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (44.1 mg, 73%). $R_f = 0.38$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55-7.52 (m, 2H), 7.49-7.45 (m, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.70 (s, 1H), 2.51-2.44 (m, 1H), 2.29 (s, 3H), 1.90-1.81 (m, 2H), 1.76-1.73 (m, 2H), 1.67-1.57 (m, 3H), 1.32-1.14 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 197.9, 154.1, 146.2, 144.0, 139.4, 133.2, 128.8, 128.7, 128.5, 128.1, 127.9, 122.3, 121.7, 35.9, 31.1, 26.6, 25.7, 22.0. IR (cm^{-1}) v 3054, 2925, 2852, 1702, 1603, 1491, 1449, 1356, 1327, 1277, 1189, 1096, 1006. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O$ $(M+H)^+$ 303.1743, found 303.1744.

2-Cyclohexyl-7-methyl-3-phenyl-1*H*-inden-1-one (3ca): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (44.7 mg, 74%). $R_f = 0.35$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.54-7.41 (m, 3H), 7.37-7.33 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 7.1 Hz, 1H), 2.54 (s, 3H), 2.50-2.40 (m, 1H), 1.92-1.71 (m, 4H), 1.65-1.55 (m, 3H), 1.27-1.10 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 199.6, 153.6, 146.2, 138.9, 137.2, 133.3, 132.3, 131.5, 128.7, 128.6, 128.0, 127.1, 118.4, 35.9, 31.1, 26.6, 25.8, 17.1. IR (cm^{-1}) v 3059, 2920, 2851, 1704, 1609, 1492, 1455, 1362, 1275, 1188, 1026. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O$ $(M+H)^+$ 303.1743, found 303.1745.

2-Cyclohexyl-5-methoxy-3-phenyl-1*H*-inden-1-one (3da): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 30:1) gives a yellow oil (46.4 mg, 73%). $R_f = 0.32$ (Silica gel, petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54-7.50 (m, 2H), 7.48-7.44 (m, 1H), 7.42-7.36 (m, 3H), 6.58 (d, J = 7.9 Hz, 1H), 6.46 (s, 1H), 3.80 (s, 3H), 2.52-2.45 (m, 1H), 1.91-1.81 (m, 2H), 1.76-1.73 (m, 2H), 1.66-1.57 (m, 3H), 1.32-1.14 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 196.7, 164.2, 152.4, 148.5, 140.6, 133.0, 128.8, 128.7, 128.0, 124.0, 123.7, 109.7, 109.4, 55.6, 36.1, 31.1, 26.5, 25.7. IR (cm^{-1}) v 3028, 2976, 2921, 1702, 1657, 1450, 1427, 1382, 1330, 1220, 1089, 1047. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_2$ $(M+H)^+$ 319.1693, found 319.1691.

2-Cyclohexyl-5-fluoro-3-phenyl-1*H*-inden-1-one (3ea): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (43.4 mg, 71%). R_f = 0.37 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.46 (m, 3H), 7.44-7.41 (m, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 6.84-6.80 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 2.53-2.47 (m, 1H), 1.89-1.74 (m, 4H), 1.61-1.58 (m, 2H), 1.32-1.14 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 196.3, 166.3 (d, *J* = 251.9 Hz), 152.5, 149.1 (d, *J* = 10.9 Hz), 140.5, 132.5, 129.1, 128.9, 127.8, 126.7 (d, *J* = 3.0 Hz), 123.9 (d, *J* = 9.8 Hz), 113.5 (d, *J* = 22.9 Hz), 109.4 (d, *J* = 25.4 Hz), 36.0, 31.0, 26.5, 25.7. IR (cm^{-1}) *ν* 3069, 2926, 2853, 1706, 1597, 1492, 1470, 1449, 1353, 1331, 1202, 1115, 1078, 1006. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}FO$ $(M+H)^+$ 307.1493, found 307.1495.

5-Chloro-2-cyclohexyl-3-phenyl-1*H*-inden-1-one (3fa): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (43.1 mg, 67%). R_f = 0.37 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.47 (m, 3H), 7.38-7.36 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 2.52-2.46 (m, 1H), 1.88-1.74 (m, 4H), 1.64-1.57 (m, 2H), 1.32-1.14 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 196.0, 153.5, 147.7, 140.3, 139.3, 132.4, 129.2, 129.0, 128.9, 127.8, 127.7, 123.1, 121.2, 36.0, 31.0, 26.4, 25.7. IR (cm^{-1}) *ν* 3068, 2926, 2852, 1706, 1604, 1593, 1449, 1350, 1323, 1166, 1066, 1006. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}ClO$ $(M+H)^+$ 323.1197, found 323.1193.

2-Cyclohexyl-3-phenyl-5-(trifluoromethyl)-1*H*-inden-1-one (3ga): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (39.9 mg, 56%). R_f = 0.34 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59-7.56 (m, 1H), 7.55-7.48 (m, 4H), 7.40-7.37 (m, 2H), 7.10 (s, 1H), 2.55-2.45 (m, 1H), 1.91-1.73 (m, 4H), 1.63-1.56 (m, 2H), 1.30-1.12 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 196.7, 154.3, 146.5, 134.7 (q, *J* = 31.9 Hz), 133.6, 132.2, 129.4, 129.0, 127.8, 125.8 (q, *J* = 4.2 Hz), 123.6 (q, *J* = 270.0 Hz), 122.0, 116.9 (q, *J* = 3.6 Hz), 36.0, 30.9, 26.4, 25.7. IR (cm^{-1}) *ν* 3058, 2928, 2854, 1708, 1610, 1492, 1449, 1427, 1374, 1316, 1261, 1162, 1130, 1054, 1007. HRMS (ESI) *m/z* calcd for $C_{22}H_{20}F_3O$ $(M+H)^+$ 357.1461, found 357.1465.

2-Cyclohexyl-3-(*p*-tolyl)-1*H*-inden-1-one (3ha): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (44.1 mg, 73%). R_f = 0.35 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, *J* = 7.0 Hz, 1H), 7.35-7.25 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 2.53-2.46 (m, 4H), 1.93-1.84 (m, 2H), 1.77-1.74 (m, 2H), 1.68-1.57 (m, 3H), 1.31-1.18 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 198.3, 154.8, 145.7, 138.9, 138.7, 133.0, 131.0, 130.0, 129.4, 128.1, 127.8, 122.0, 120.4, 35.9, 31.0, 26.6, 25.8, 21.5. IR (cm^{-1}) *ν* 3025, 2925, 2852, 1702, 1601, 1509, 1451, 1329, 1276, 1183, 1111, 1002. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O$ $(M+H)^+$ 303.1743, found 303.1744.

2-Cyclohexyl-3-(4-methoxyphenyl)-1*H*-inden-1-one (3ia): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (45.1 mg, 71%). $R_f = 0.31$ (Silica gel, petroleum ether/ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.30-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 7.1 Hz, 1H), 3.91 (s, 3H), 2.53-2.47 (m, 1H), 1.94-1.85 (m, 2H), 1.78-1.75 (m, 2H), 1.67-1.57 (m, 2H), 1.35-1.15 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 198.2, 160.1, 154.5, 145.8, 138.4, 132.9, 131.1, 129.4, 128.1, 125.2, 122.0, 120.4, 114.1, 55.3, 36.0, 31.1, 26.6, 25.8. IR (cm^{-1}) *ν* 3034, 2924, 2851, 1701, 1607, 1509, 1453, 1330, 1250, 1176, 1032, 1001. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_2$ $(M+H)^+$ 319.1693, found 319.1692.

3-(4-Chlorophenyl)-2-cyclohexyl-1*H*-inden-1-one (3ja): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (42.5 mg, 66%). $R_f = 0.35$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 6.8 Hz, 1H), 7.34-7.27 (m, 3H), 7.22-7.18 (m, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 2.48-2.40 (m, 1H), 1.89-1.74 (m, 4H), 1.65-1.56 (m, 3H), 1.30-1.17 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 197.8, 153.3, 145.4, 139.4, 134.8, 133.2, 131.5, 130.7, 129.3, 129.1, 128.3, 122.4, 120.2, 36.0, 31.1, 26.5, 25.7. IR (cm^{-1}) *ν* 3064, 2926, 2852, 1704, 1605, 1489, 1450, 1329, 1277, 1166, 1091, 1014, 1001. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}ClO$ $(M+H)^+$ 323.1197, found 323.1193.

2-Cyclohexyl-3-(4-fluorophenyl)-1*H*-inden-1-one (3ka): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (42.2 mg, 69%). $R_f = 0.35$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.42 (m, 1H), 7.40-7.34 (m, 2H), 7.30-7.16 (m, 4H), 6.86 (d, *J* = 7.1 Hz, 1H), 2.48-2.38 (m, 1H), 1.91-1.72 (m, 4H), 1.66-1.54 (m, 3H), 1.33-1.11 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 197.9, 162.9 (d, *J* = 247.3 Hz), 153.6, 145.5, 139.2, 133.2, 130.8, 129.9 (d, *J* = 8.1 Hz), 129.0 (d, *J* = 3.4 Hz), 128.3, 122.3, 120.3, 115.9 (d, *J* = 21.4 Hz), 35.9, 31.1, 26.5, 25.7. IR (cm^{-1}) *ν* 3069, 2926, 2852, 1704, 1600, 1507, 1451, 1329, 1227, 1156, 1002. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}FO$ $(M+H)^+$ 307.1493, found 307.1495.

2-Cyclohexyl-3-(3-fluorophenyl)-1*H*-inden-1-one (3la): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (41.0 mg, 67%). $R_f = 0.34$ (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52-7.42 (m, 2H), 7.31-7.06 (m, 5H), 6.87 (d, *J* = 7.1 Hz, 1H), 2.50-2.39 (m, 1H), 1.90-1.72 (m, 4H), 1.63-1.55 (m, 3H), 1.34-1.11 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 197.8, 162.8 (d, *J* = 245.7 Hz), 153.1 (d, *J* = 2.0 Hz), 145.4, 139.5, 135.2 (d, *J* = 7.8 Hz), 133.3, 130.6, 129.9 (d, *J* = 8.3 Hz), 128.4, 123.7 (d, *J* = 3.0 Hz), 122.4, 120.3, 115.9 (d, *J* = 20.9 Hz), 115.0 (d, *J* = 21.8 Hz), 35.9, 31.0, 26.5, 25.7. IR (cm^{-1}) *ν* 3069, 2926, 2853, 1706, 1601, 1580, 1485, 1452, 1363, 1330, 1264, 1219, 1143, 1003. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}FO$ $(M+H)^+$ 307.1493, found 307.1495.

Methyl 4-(2-cyclohexyl-1-oxo-1H-inden-3-yl)benzoate (3ma): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 10:1) gives a yellow oil (44.3 mg, 64%). R_f = 0.52 (Silica gel, petroleum ether/ethyl acetate = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 3H), 7.31-7.25 (m, 1H), 7.22-7.17 (m, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 3.97 (s, 3H), 2.48-2.38 (m, 1H), 1.88-1.73 (m, 4H), 1.66-1.55 (m, 2H), 1.28-1.09 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 197.7, 166.6, 153.4, 145.4, 139.8, 137.8, 133.3, 130.6, 130.4, 130.0, 128.4, 128.0, 122.5, 120.3, 52.3, 36.0, 31.1, 26.5, 25.7. IR (cm^{-1}) *v* 3062, 2932, 2856, 1708, 1591, 1473, 1448, 1360, 1267, 1222, 1146, 1021. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}O_3$ $(M+H)^+$ 347.1642, found 347.1647.

2-Cyclohexyl-3-(4-(dimethylamino)phenyl)-1*H*-inden-1-one (3na): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 10:1) gives a red oil (44.3 mg, 67%). R_f = 0.42 (Silica gel, petroleum ether/ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39 (d, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.28-7.23 (m, 1H), 7.18-7.13 (m, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 3.05 (s, 6H), 2.61-2.51 (m, 1H), 2.01-1.88 (m, 2H), 1.78-1.73 (m, 2H), 1.60-1.56 (m, 2H), 1.33-1.13 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 198.4, 155.1, 150.7, 145.6, 137.1, 132.6, 131.7, 129.3, 127.9, 121.7, 120.6, 120.3, 111.7, 40.2, 36.0, 31.0, 26.6, 25.8. IR (cm^{-1}) *v* 3047, 2925, 2848, 1705, 1473, 1451, 1356, 1276, 1180, 1021. HRMS (ESI) *m/z* calcd for $C_{23}H_{26}NO$ $(M+H)^+$ 332.2009, found 332.2017.

2-Cyclohexyl-6-methoxy-3-phenyl-1*H*-inden-1-one (3oa) and 2-cyclohexyl-7-methoxy-3-phenyl-1*H*-inden-1-one (3oa'): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 30:1) gives a yellow oil (43.8 mg, 69%). R_f = 0.32 (Silica gel, petroleum ether/ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$, 300 MHz), for **3oa**: δ 7.54-7.30 (m, 5H), 7.18-7.09 (m, 1H), 7.05-7.04 (m, 1H), 6.80-6.77 (m, 1H), 3.50 (s, 3H), 2.47-2.37 (m, 1H), 1.90-1.71 (m, 4H), 1.61-1.48 (m, 2H), 1.28-1.04 (m, 4H); for **3oa'**: δ 7.54-7.30 (m, 5H), 7.18-7.09 (m, 1H), 6.90-6.87 (m, 1H), 6.70-6.67 (m, 1H), 3.80 (s, 3H), 2.34-2.23 (m, 1H), 1.90-1.71 (m, 4H), 1.61-1.48 (m, 2H), 1.28-1.04 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 198.2, 197.9, 160.5, 155.9, 155.5, 153.2, 138.4, 137.9, 137.5, 135.3, 133.2, 133.0, 130.1, 128.9, 128.7, 128.0, 127.9, 127.8, 127.5, 121.2, 119.4, 115.7, 115.4, 110.1, 55.8, 55.7, 35.9, 35.6, 31.1, 31.0, 26.6, 26.5, 25.7. IR (cm^{-1}) *v* 3025, 2972, 2923, 1698, 1452, 1424, 1378, 1325, 1222, 1094, 1042. MS (EI): 318 (M^+).

2-Cyclopentyl-3-phenyl-1*H*-inden-1-one (3ab): Flash column chromatography on a silica gel (petroleum ether /ethyl acetate = 50:1) gives a yellow oil (33.4 mg, 61%). R_f = 0.37 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H

NMR ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 2H), 7.48-7.41 (m, 4H), 7.30-7.26 (m, 1H), 7.21-7.17 (m, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 2.89-2.81 (m, 1H), 1.98-1.83 (m, 4H), 1.79-1.72 (m, 2H), 1.58-1.55 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 197.8, 155.1, 145.6, 137.7, 133.1, 133.0, 131.2, 128.9, 128.1, 128.0, 122.2, 120.3, 36.3, 32.2, 26.4. IR (cm^{-1}) *v* 3052, 2920, 2850, 1703, 1632, 1609, 1470, 1455, 1361, 1173, 1028. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O$ $(M+H)^+$ 275.1430, found 275.1432.

2-Cycloheptyl-3-phenyl-1*H*-inden-1-one (3ac): Flash column chromatography on a silica gel (petroleum ether /ethyl acetate = 50:1) gives a yellow oil (38.6 mg, 64%). R_f = 0.36 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 2H), 7.48-7.43 (m, 2H), 7.41-7.39 (m, 2H), 7.29-7.26 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 2.65-2.60 (m, 1H), 2.02-1.89 (m, 2H), 1.79-1.75 (m, 2H), 1.68-1.53 (m, 5H), 1.41-1.27 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 198.2, 152.9, 145.9, 140.7, 133.1, 133.0, 130.9, 128.9, 128.7, 128.1, 127.9, 122.2, 120.5, 37.3, 33.4, 27.9, 27.7. IR (cm^{-1}) *v* 3058, 2921, 2854, 1704, 1608, 1596, 1456, 1443, 1361, 1273, 1175, 1113, 1028. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O$ $(M+H)^+$ 303.1743, found 303.1744.

2-Cyclooctyl-3-phenyl-1*H*-inden-1-one (3ad): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (41.1 mg, 65%). R_f = 0.37 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.38 (m, 6H), 7.29-7.23 (m, 1H), 7.19-7.14 (m, 2H), 6.91 (d, *J* = 7.1 Hz, 1H), 6.72 (s, 1H), 2.78-2.69 (m, 1H), 2.02-1.89 (m, 2H), 1.75-1.67 (m, 2H), 1.63-1.38 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 198.3, 152.8, 145.9, 141.5, 133.1, 130.8, 129.5, 128.9, 128.6, 128.1, 127.9, 122.2, 120.5, 34.6, 32.3, 26.4, 26.2. IR (cm^{-1}) *v* 3055, 2925, 2851, 1696, 1592, 1466, 1449, 1377, 1327, 1177, 1158, 1025. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}O$ $(M+H)^+$ 317.1900, found 317.1906.

2-Cyclopentyl-5-methyl-3-phenyl-1*H*-inden-1-one (3bb): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (36.3 mg, 63%). R_f = 0.36 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 2H), 7.48-7.40 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.73 (s, 1H), 2.87-2.79 (m, 1H), 2.30 (s, 3H), 1.95-1.82 (m, 4H), 1.77-1.73 (m, 2H), 1.57-1.54 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 197.7, 154.6, 146.0, 144.0, 138.1, 133.1, 129.4, 128.85, 128.80, 128.7, 128.0, 122.2, 121.6, 36.3, 32.1, 26.4, 22.0. IR (cm^{-1}) *v* 3061, 2952, 2867, 1702, 1603, 1470, 1448, 1358, 1274, 1175, 1113, 1027. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O$ $(M+H)^+$ 289.1587, found 289.1589.

2-Cyclopentyl-5-methoxy-3-phenyl-1*H*-inden-1-one (3db): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 30:1) gives a yellow oil (37.8 mg, 62%). R_f = 0.31 (Silica gel, petroleum ether/ethyl acetate = 30:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.39 (m, 6H), 6.59-6.56 (m, 1H), 6.50 (s, 1H), 3.81 (s, 3H), 2.89-2.80 (m, 1H), 1.97-1.81 (m, 4H), 1.77-1.71 (m, 2H), 1.57-1.54 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 196.6, 164.2, 152.8, 148.2, 139.3, 132.9, 128.8, 128.7, 128.1, 124.1, 123.9, 109.6, 106.3, 55.6, 36.4, 32.2, 26.4. IR (cm^{-1}) *v* 3066, 2953, 2867, 1700, 1612, 1597, 1474, 1448, 1365, 1284, 1221, 1178, 1092, 1026. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_2$ $(M+H)^+$ 305.1536, found 305.1539.

2-Cyclopentyl-5-fluoro-3-phenyl-1*H*-inden-1-one (3eb): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (35.6 mg, 61%). R_f = 0.35 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.39 (m, 6H), 6.85-6.80 (m, 1H), 6.67-6.64 (m, 1H), 2.90-2.81 (m, 1H), 1.96-1.82 (m, 4H), 1.79-1.74 (m, 2H), 1.58-1.53 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 196.2, 166.3 (d, *J* = 251.9 Hz), 152.9 (d, *J* = 2.3 Hz), 148.9 (d, *J* = 9.3 Hz), 139.3, 132.4, 129.2, 128.8, 127.9, 126.9 (d, *J* = 3.0 Hz), 123.9 (d, *J* = 9.7 Hz), 113.5 (d, *J* = 22.8 Hz), 109.3 (d, *J* = 25.5 Hz), 36.4, 32.2, 26.4. IR (cm^{-1}) *v* 3056, 2953, 2867, 1706, 1596, 1469, 1443, 1364, 1203, 1115, 1079, 1027. HRMS (ESI) *m/z* calcd for C20H18FO $(M+H)^+$ 293.1336, found 293.1338.

5-Chloro-2-cyclopentyl-3-phenyl-1*H*-inden-1-one (3fb): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (35.7 mg, 58%). R_f = 0.34 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.52 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.36 (m, 1H), 7.19-7.16 (m, 1H), 6.91 (s, 1H), 2.89-2.81 (m, 1H), 1.96-1.82 (m, 4H), 1.79-1.74 (m, 2H), 1.57-1.56 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 196.5, 154.9, 147.4, 139.3, 139.1, 132.4, 129.3, 129.2, 128.9, 127.9, 127.7, 123.1, 121.1, 36.3, 32.2, 26.4. IR (cm^{-1}) *v* 3052, 2920, 2867, 1706, 1604, 1593, 1456, 1409, 1354, 1164, 1066, 1028. HRMS (ESI) *m/z* calcd for C20H18ClO $(M+H)^+$ 309.1041, found 309.1045.

2-Cyclopentyl-3-(*p*-tolyl)-1*H*-inden-1-one (3hb): Flash column chromatography on a silica gel (petroleum ether /ethyl acetate = 50:1) gives a yellow oil (35.7 mg, 62%). R_f = 0.36 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.33-7.26 (m, 5H), 7.20-7.16 (m, 1H), 6.95 (d, *J* = 7.0 Hz, 2H), 2.90-2.82 (m, 1H), 2.46 (s, 3H), 1.98-1.83 (m, 4H), 1.78-1.72 (m, 2H), 1.58-1.52 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 198.1, 155.2, 145.5, 139.0, 137.3, 133.0, 131.3, 130.0, 129.4, 128.1, 127.9, 122.1, 120.3, 36.3, 32.1, 26.4, 21.5. IR (cm^{-1}) *v* 3025, 2952, 2867, 1703, 1601, 1509, 1456, 1454, 1356, 1275, 1173, 1112, 1020. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O$ $(M+H)^+$ 289.1587, found 289.1588.

2-Cyclooctyl-5-methyl-3-phenyl-1*H*-inden-1-one (3bd): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (44.9 mg, 68%). R_f = 0.33 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.52 (m, 2H), 7.49-7.45 (m, 1H), 7.42-7.39 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 2.77-2.70 (m, 1H), 2.30 (s, 3 H), 2.02-1.93 (m, 2H), 1.77-1.70 (m, 2H), 1.66-1.57 (m, 4H), 1.54-1.41 (m, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 198.0, 152.4, 146.4, 144.0, 141.9, 133.2, 129.5, 128.8, 128.6, 128.5, 128.0, 122.2, 121.8, 34.7, 32.3, 26.4, 26.2, 22.0. IR (cm^{-1}) ν 3036, 2920, 2851, 1702, 1604, 1471, 1444, 1356, 1275, 1183, 1098, 1026. HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O$ (M+H)$^+$ 331.2056, found 331.2061.

2-Cyclooctyl-5-methoxy-3-phenyl-1*H*-inden-1-one (3dd): Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 30:1) gives a yellow oil (45.6 mg, 66%). R_f = 0.29 (Silica gel, petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54-7.50 (m, 2H), 7.47-7.43 (m, 1H), 7.41-7.38 (m, 3H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.49 (s, 1H), 3.80 (s, 3 H), 2.77-2.71 (m, 1H), 2.02-1.93 (m, 2H), 1.75-1.69 (m, 2H), 1.65-1.40 (m, 10H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 191.9, 164.2, 150.5, 148.7, 143.1, 133.0, 128.7, 128.6, 128.0, 124.0, 123.7, 109.8, 109.3, 55.6, 34.8, 32.3, 26.42, 26.40, 24.2. IR (cm^{-1}) ν 3046, 2920, 2850, 1699, 1611, 1598, 1473, 1445, 1364, 1284, 1219, 1180, 1093, 1027. HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_2$ (M+H)$^+$ 347.2006, found 347.2002.

3ae: 2-(Pentan-2-yl)-3-phenyl-1*H*-inden-1-one (C2) & 2-(pentan-3-yl)-3-phenyl-1*H*-inden-1-one (C3) (ratio **C2 : C3 =** 3:2**):** Preparative TLC (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (35.3 mg, 64%). R_f = 0.42 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.54-7.50 (m, 2H), 7.48-7.43 (m, 2H), 7.40-7.39 (m, 2H), 7.31-7.28 (m, 1H), 7.22-7.19 (m, 1H), 6.91-6.86 (m, 1H), 2.72-2.67 (m, 0.6H), 2.39-2.35 (m, 0.4H), 1.81-1.47 (m, 3H), 1.27-1.22 (m, 3H), 0.85-0.76 (m, 4H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 198.2, 157.3, 155.4, 145.9, 145.8, 138.8, 137.1, 133.2, 133.16, 131.13, 133.0, 130.9, 130.8, 128.9, 128.7, 128.68, 128.65, 128.2, 127.9, 127.8, 122.2, 120.4, 120.3, 40.2, 37.3, 30.6, 26.7, 21.3, 19.9, 13.9, 12.8. IR (cm^{-1}) ν 3059, 2958, 2928, 2870, 1703, 1608, 1596, 1456, 1443, 1361, 1279, 1169, 1068, 1027. MS (EI): 276 (M$^+$).

3af: 2-(2-methylbutyl)-3-phenyl-1*H*-inden-1-one (C1), 2-*tert*-Pentyl-3-phenyl-1*H*-inden-1-one (C2), 2-(3-methylbutan-2-yl)-3-phenyl-1*H*-inden-1-one (C3) and **2-isopentyl-3-phenyl-1*H*-inden-1-one (C4) (**ratio **C1:C2:C3:C4 =** 3:12:8:3**):** Preparative TLC (petroleum ether/ethyl acetate = 50:1) gives a yellow oil (32.0 mg, 58%). R_f = 0.41 (Silica gel, petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54-7.50 (m, 1H), 7.48-7.38 (m, 4H), 7.31-7.15 (m, 3H), 6.89-6.87 (m, 0.4H), 6.49-6.47 (m, 0.56H), 2.30-2.25 (m. 0.3H), 2.15-2.13 (m, 0.3H), 1.98-1.91 (m, 0.4H), 1.77-1.71 (m, 1.2H), 1.26-1.24 (m, 0.9H), 1.06 (s, 3.3H), 1.01-0.97 (m, 0.9H), 0.92-0.90 (m, 1H), 0.83-0.77 (m, 2.7H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz), δ 198.7, 155.8, 147.9, 145.9, 140.2, 139.2, 135.4, 133.5, 133.2, 130.8, 129.8, 129.4, 128.8, 128.7, 128.3, 128.2, 128.1, 127.9, 127.8, 122.2, 121.9, 120.4, 120.3, 38.3, 37.7, 34.4, 33.8, 31.5, 28.7, 25.7, 22.3, 21.1, 18.1, 9.8, 8.4. IR (cm^{-1}) ν 3056, 2953, 2925, 2872, 1701, 1602, 1592, 1453, 1444, 1363, 1272, 1162, 1031. MS (EI): 276 (M$^+$).

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Supporting Information:

Mechanism studies, ^{1}H and ^{13}C NMR spectra of compounds **3aa-3oa, 3ab-3af**. This material is available free of charge via the Internet at http://pubs.acs.org.

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