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Water-assisted metal-free catalyzed cyclization of 2-alkynylarylketones: a facile approach to indenones†

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A simple and directed synthetic strategy starting from 2-alkynylarylketones was developed for the construction of various indenones under metal-free and water-assisted conditions. This intramolecular cyclization reaction could well tolerate a wide range of functional groups, and the corresponding functionalized indenones were obtained in moderate to excellent yields (up to 94%). In addition, the possible mechanism of this reaction may involve isobenzofuranium intermediates.

Introduction

Indenones, prevalent in natural products and materials science, have drawn a considerable amount of attention (Fig. 1).[1] Because of the importance of indenones, various synthetic methods for substituted indenones have already been reported. The traditional synthesis of functional indenones included multistep intramolecular Friedel–Crafts acylation or used organometallic reagents.[2,3] The use of transition metal species including Rh,[4] Co,[5] Pd[6] or other metals[7] as a catalyst has been developed by intermolecular or intramolecular cyclization reactions in recent decades. In contrast, metal-free synthetic strategies for constructing indenones have been less elucidated. Methyl trifluoromethanesulfonate (MeOTf)-mediated annulation of arylnitriles or isothiocyanates with aromatic alkynes to synthesize indenones has been demonstrated under mild conditions by Xi and coworkers.[8] An efficient acid catalyzed rearrangement of a tetrahalo-7,7-dimethoxybicyclo[2.2.1] heptenyl system leading to indenones was described by Khan *et al.*[9] Superacid-induced intramolecular cyclization of 1,3-diarylpropynones was described for the synthesis of indenones.[10] An efficient I_2-catalyzed access to the synthesis of indenones from 2-alkynylbenzyl alcohols has been studied by Li *et al.*[11] Benzoyl peroxide (BPO)-promoted radical cyclizations were also reported.[12] Although the above elegant metal-free methods have been made to date, the development of a simple and efficient metal-free synthetic approach to indenones is highly desirable.

2-Alkynylarylketones as an important class of substrates were widely investigated due to their convenient synthesis *via* the Sonogashira reaction[13] and functionalized transformations to corresponding cyclic compounds.[14] Usually, the intramolecular cyclization of 2-alkynylarylketones infer to two active intermediates isobenzopyrylium I and isobenzofuranium II (Scheme 1). Owing to the aromatization of the heterocyclic ring, isobenzopyrylium ions as stable oxonium cations has been extensively studied in both nucleophilic addition reactions and cycloaddition reactions.[15] However, the reactivity of isobenzofuranium intermediates has been less explored.[16] Based on the above studies, great interest has been aroused to further explore isobenzofuranium intermediates involved in the reaction. Herein, we are the first time to report a simple and effective access to various indenones by water-assisted metal-free catalyzed intramolecular cyclization of 2-alkynylaryl-ketones under mild reaction conditions, and the possible path of this reaction may involve in isobenzofuranium intermediates.

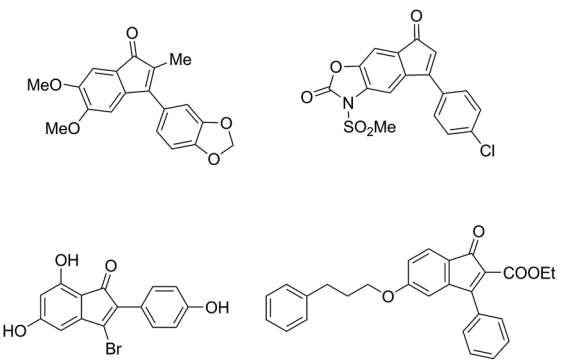

Fig. 1 Representative examples of bioactive and naturally occurring important indenones.

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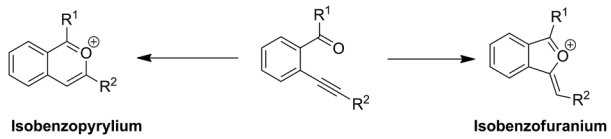
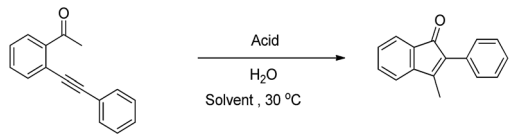
† Electronic supplementary information (ESI) available: X-ray crystallographic data for compound **2n**. Copies of ^{1}H NMR and ^{13}C NMR of products. ESI-HRMS spectrum for detecting the reaction system. CCDC 1510707. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra05487d



Scheme 1 Intramolecular cyclization reactions of 2-alkynylarylketones.

Table 1 Optimization of the reaction conditions for intramolecular cyclization of 2-alkynylarylketones[a]

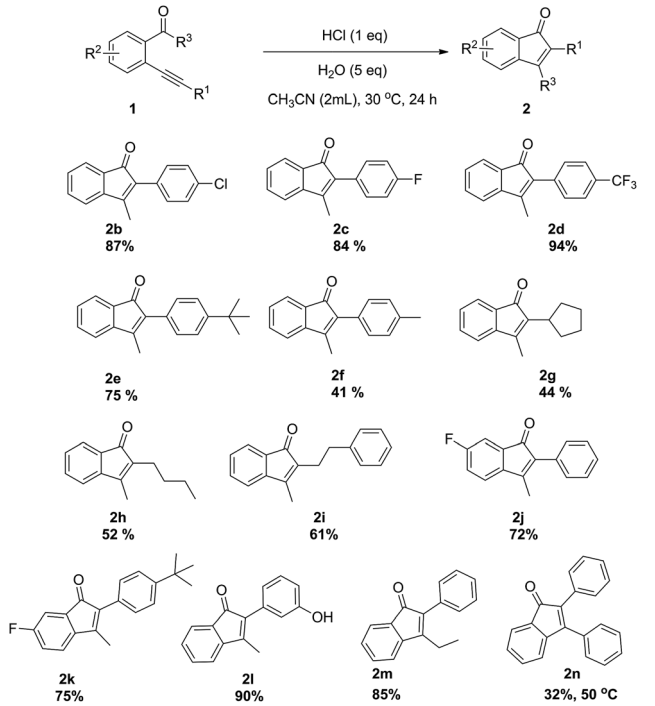


Entry	Acid (X equiv.)	H_2O (X equiv.)	Solvent	Yield[b] (%)
1	CH_3COOH (1)	3	CH_3CN	—
2	CF_3COOH (1)	3	CH_3CN	—
3	p-$CH_3C_6H_4SO_3H$ (1)	3	CH_3CN	18
4	CH_3SO_3H (1)	3	CH_3CN	33
5	CF_3SO_3H (1)	3	CH_3CN	40
6	HCl (1)[c]	3	CH_3CN	85
7	H_2SO_4 (1)	3	CH_3CN	25
8	HCl (1)[c]	3	DMF	—
9	HCl (1)[c]	3	DMSO	—
10	HCl (1)[c]	3	1,4-Dioxane	43
11	HCl (1)[c]	3	THF	36
12	HCl (1)[c]	3	CH_2Cl_2	44
13	HCl (0.5)[c]	3	CH_3CN	80
14	HCl (1)[c]	1	CH_3CN	49
15	HCl (1)[c]	5	CH_3CN	91

[a] General reaction conditions: **1a** (0.3 mmol), catalyst, solvent (2.0 mL), 24 h at 30 °C. [b] Isolated yield. [c] HCl in 1,4-dioxane (4N).

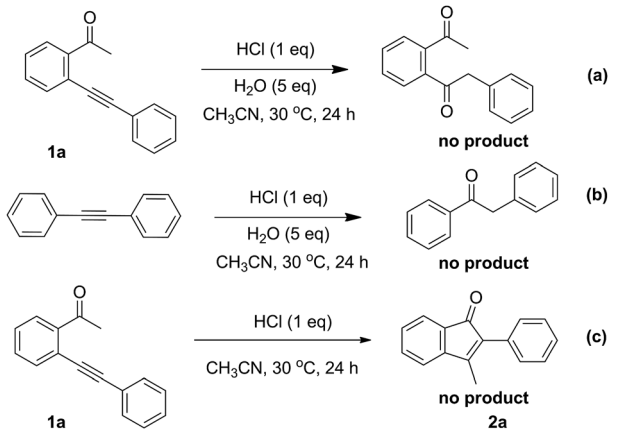
Results and discussion

At the outset of our study, 2-alkynylarylketone **1a** was chosen as a model substrate to optimize the reaction conditions and the experimental results are summarized in Table 1. When the intramolecular cyclization of 2-alkynylarylketones **1a** using one equivalent amount of CH_3COOH or CF_3COOH as catalyst and 3 equiv. H_2O in CH_3CN under 30 °C was attempted, no desired product **2a** was obtained (Table 1, entries 1 and 2). Treatment of **1a** with p-$CH_3C_6H_4SO_3H$, CH_3SO_3H or CF_3SO_3H under same conditions afforded product **2a** in 18%, 33%, or 40% yields, respectively (Table 1, entries 3–5). To our delight, a simple and typical inorganic acid HCl (4N in 1,4-dioxane) was used as catalyst for the intramolecular cyclization of **1a** to give a yield of 85% at 30 °C (Table 1, entry 6). However, using another inorganic acid H_2SO_4 as catalyst led to a highly decreased yield (Table 1, entry 7). These observations clearly indicate that the properties of the acid play an important role in this transformation. Encouraged by the above results, further condition optimization of reaction solvents was conducted. In high polar solvents such as DMF or DMSO, no product **2a** was obtained (Table 1, entries 8 and 9). Other solvents such as 1,4-dioxane, THF and CH_2Cl_2 afforded the product **2a** in 43%, 36% or 44% yield, respectively (Table 1, entries 10–12). A slight decline in the yield of **2a** appeared when the loading of HCl was decreased from 1.0 to 0.5 equiv. (Table 1, entry 13). In addition, the loading of H_2O was decreased from 3.0 to 1.0 equiv. to give an apparent decline in the yield of **2a** (Table 1, entry 14). On the contrary, increasing the loading of H_2O from 3.0 to 5.0 equiv. can accelerate the reaction and a satisfying 91% yield of **2a** was obtained (Table 1, entry 15). Thus, the optimal reaction conditions were obtained as follows: 0.3 mmol **1a**, 1 equiv. HCl, 5 equiv. H_2O in 2.0 mL CH_3CN at 30 °C.

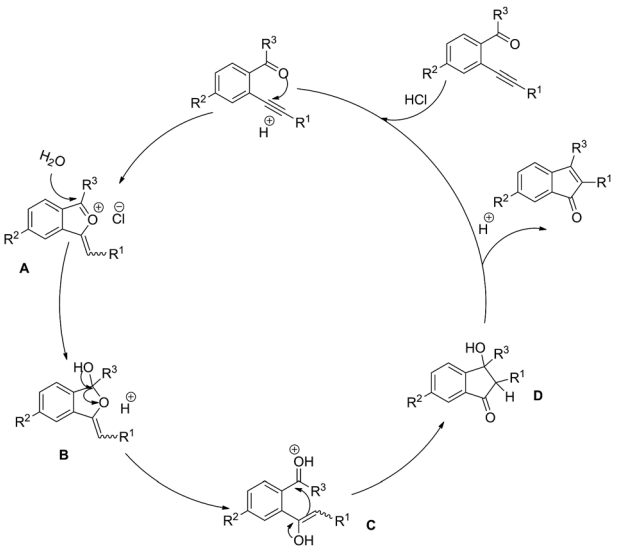


Scheme 2 Intramolecular cyclization of various 2-alkynylarylketones.

With the optimized conditions established, various substituted substrates for this intramolecular cyclization promoted by HCl were investigated and the results were shown in Scheme 2. It is clear that the electronic property of substituents on the phenyl ring in the R^1 group exerts an obvious influence on the product yield. Substrates **1b–d** with electron-withdrawing 4-Cl, 4-F and 4-CF_3 groups showed higher reactivity in comparison with substrates **1e–f** with electron-donating 4-^{t}Bu and 4-Me groups. The corresponding products **2g**, **2h** and **2i** were obtained in middle yields, when the alkyl-substituted alkynes **1g**, **1h** and **1i** were as substrates. The cyclization reactions of substrates having 4-F (**1j** or **1k**) substituents on the phenyl ring in the R^2 group were efficiently catalyzed to give the corresponding products **2j–k** in high yields. In addition, substrate having 3-OH (**1l**) substituent on the phenyl ring in the R^1 group was smoothly transformed into the corresponding product **2l** in excellent yield. The steric effect of the R^3 group on the reaction was also investigated. The reaction of substrate **1m**



Scheme 3 Control experiments.



Scheme 4 Possible mechanism for intramolecular cyclization of 2-alkynylarylketones.

with an ethyl group gave a good yield, whereas that of substrate **1n** with phenyl group gave desired product **2n** in only 35% yield at 50 °C. The structure of **2n** was unambiguously determined by X-ray crystallography (see ESI†).

To understand the mechanistic pathway more clearly, some control experiments were carried out (Scheme 3). To exclude the hydration of the triple of substrates **1**, **1a** and 1,2-diphenylethyne failed to afford the corresponding hydration product under the standard conditions (Scheme 3a and b). Additionally, the experimental result showed that no product **2a** was given under anhydrous conditions (Scheme 3c). This result indicates that the water is necessary to participate in this reaction. On the basis of the above results and previous work,[7f] a possible mechanism was proposed and shown in Scheme 4. When substrate is firstly activated by HCl, a 5-*exo*-dig cyclization takes place to form isobenzofuranium intermediate **A**. Then the new intermediate **B** is produced by the nucleophilic addition of H_2O to **A**. The carbon–oxygen bond cleavage could form enol intermediate **C** by protonation of the oxygen atom of isobenzofuran **B**. Subsequently, the intermediate **D** can be obtained *via* an intramolecular ring-closing reaction of the intermediate **C**. Finally, after elimination of H_2O in the presence of HCl, the product indenone is released together with the regenerated catalyst HCl for finishing a catalyst cycle. Furthermore, ESI-HRMS detection of the reaction mixture using **1a** as substrate with 1 h was conducted to capture the information of reaction intermediates. The species of *m*/*z* 221.0961 ascribed to the intermediate **A** (R^1 = Ph, R^2 = H, R^3 = Me; $[M_A]^+$) and the species of *m*/*z* 239.1067 ascribed to the intermediates **B**, **C** and **D** (R^1 = Ph, R^2 = H, R^3 = Me; $[M_B + H]^+$, $[M_c]^+$ and $[M_D + H]^+$) were observed (see ESI Fig. S1† for details).

Conclusions

In summary, a simple and efficient HCl mediated water-assisted method to the construction of useful indenones by the intramolecular cyclization reaction of 2-alkynylarylketones is described under mild conditions. Various functional substrates could smoothly apply to this cyclization reaction. The reaction process may be initiated by 5-*exo*-dig cyclization of the carbonyl group with the alkyne triple bond, leading to isobenzofuranium intermediates.

Experimental

All chemicals and reagents were purchased from commercial suppliers without further purification unless otherwise stated. NMR spectra were recorded with tetramethylsilane as the internal standard. NMR spectrawere recorded on a Bruker Avance II 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) was measured using a Nicolet NEXUS FT-IR spectrophotometer. Substrates 2-alkynylarylketones were prepared by Sonogashira coupling reaction of corresponding 2-bromoacetophenones with alkyne according to the relate literature.[7f,15m,16e,17]

Representative experimental procedure for the intramolecular cyclization of 2-alkynylarylketones

Taking the intramolecular cyclization of 2-1-(2-(phenylethynyl)-phenyl)ethanone (**1a**) as example: A 10 mL vial was charged with 1-(2-(phenylethynyl)phenyl)ethanone **1a** (66.1 mg, 0.30 mmol) and acetonitrile (2 mL), then H_2O (27.0 mg, 1.5 mmol) and 0.30 mmol HCl (4N in 1,4-dioxane) was sequentially added into above solution. The vial was sealed and the reaction mixture was stirred at 30 °C for 24 h. After cooling to room temperature, the resulting mixture was diluted with ethyl acetate (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (PE/EtOAc) to give **2a** in 91% yield.

3-Methyl-2-phenyl-1*H*-inden-1-one (2a). This compound was obtained as a brown oil (91% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (d, J = 6.8 Hz, 1H), 7.37–7.44 (m, 5H), 7.30–7.34 (m, 1H), 7.21–7.25 (m, 1H), 7.14 (d, J = 7.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.51, 154.79, 145.93, 133.70, 133.43, 131.24, 130.44, 129.62, 128.97, 128.36, 127.76, 122.16, 119.53, 12.67; IR (film, cm^{-1}): 3398, 3056, 2964, 1715, 1600, 1457, 1380, 1262, 1179, 1084, 1028, 916, 854, 804, 757, 699, 660, 597, 514; HRMS (ESI-TOF) calcd for $C_{16}H_{13}O^+$ ([M + H]$^+$): 221.0961, found: 221.0961.

2-(4-Chlorophenyl)-3-methyl-1*H*-inden-1-one (2b). This compound was obtained as an orange solid (87% yield), mp 102.5–103.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, J = 7.2 Hz, 1H), 7.40–7.45 (m, 3H), 7.34–7.37 (m, 2H), 7.28–7.30 (m, 1H), 7.18 (d, J = 7.2 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.23, 155.19, 145.76, 133.86, 133.79, 132.35, 130.93, 130.36, 129.71, 129.22, 128.66, 122.35, 119.71, 12.74; IR (film, cm^{-1}): 3388, 2945, 2924, 1710, 1586, 1491, 1455, 1378, 1329, 1095, 1029, 1011, 860, 823, 750, 708, 514; HRMS (ESI-TOF) calcd for $C_{16}H_{12}ClO^+$ ([M + H]$^+$): 255.0571, found: 255.0569.

2-(4-Fluorophenyl)-3-methyl-1*H*-inden-1-one (2c). This compound was obtained as an orange solid (84% yield), mp 115.1–117.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 (d, J = 7.2 Hz, 1H), 7.38–7.44 (m, 3H), 7.25–7.29 (m, 1H), 7.11–7.18 (m, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.48, 162.41 (d, J_{C-F} = 246.1 Hz), 154.71, 145.86, 133.83, 132.55, 131.39 (d, J_{C-F} = 8.0 Hz), 130.37, 129.10, 127.27 (d, J_{C-F} = 3.3 Hz), 122.30, 119.61, 115.48 (d, J_{C-F} = 21.4 Hz), 12.69; IR (film, cm^{-1}): 3396, 3067, 2927, 1708, 1592, 1507, 1460, 1378, 1331, 1228, 1164, 1090, 1023, 834, 756, 713, 525; HRMS (ESI-TOF) calcd for $C_{16}H_{12}FO^+$ ([M + H]$^+$): 239.0867, found: 239.0866.

3-Methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-inden-1-one (2d). This compound was obtained as an orange solid (94% yield), mp 80.6–82.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, J = 8.4 Hz, 1H), 7.51–7.55 (m, 3H), 7.43–7.47 (m, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.90, 156.37, 145.55, 135.00, 133.97, 132.25, 130.33, 129.94, 129.65 (q, J_{C-F} = 32.2 Hz), 129.55, 125.34 (q, J_{C-F} = 3.8 Hz), 124.30 (q, J_{C-F} = 270.4 Hz), 122.51, 119.98, 12.79; IR (film, cm^{-1}): 3401, 3069, 2924, 2852, 1713, 1615, 1458, 1409, 1381, 1327, 1167, 1117, 1069, 1015, 865, 838, 757, 713, 600, 515; HRMS (ESI-TOF) calcd for $C_{17}H_{12}F_3O^+$ ([M + H]$^+$): 289.0835, found: 289.0830.

2-(4-(*tert*-Butyl)phenyl)-3-methyl-1*H*-inden-1-one (2e). This compound was obtained as an orange solid (75% yield), mp 98.1–99.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45–7.49 (m, 3H), 7.36–7.43 (m, 3H), 7.23–7.27 (m, 1H), 7.16 (d, J = 7.2 Hz, 1H), 2.33 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.82, 154.26, 150.72, 146.17, 133.70, 133.33, 130.56, 129.31, 128.85, 128.32, 125.39, 122.16, 119.41, 34.76, 31.41, 12.74; IR (film, cm^{-1}): 3398, 3041, 2961, 2868, 1708, 1601, 1509, 1462, 1375, 1333, 1273, 1175, 1119, 1084, 1024, 912, 834, 756, 721, 676, 560; HRMS (ESI-TOF) calcd for $C_{20}H_{21}O^+$ ([M + H]$^+$): 277.1587, found: 277.1588.

3-Methyl-2-(*p*-tolyl)-1*H*-inden-1-one (2f). This compound was obtained as an reddish solid (41% yield), mp 94.0–95.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (d, J = 6.8 Hz, 1H), 7.38–7.42 (m, 1H), 7.30–7.32 (m, 2H), 7.22–7.25 (m, 3H), 7.14 (d, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.77, 154.18, 146.15, 137.69, 133.70, 133.48, 130.55, 129.55, 129.15, 128.86, 128.32, 122.17, 119.42, 21.46, 12.70; IR (film, cm^{-1}): 3395, 2963, 2921, 2856, 1706, 1612, 1593, 1511, 1457, 1380, 1332, 1262, 1081, 1032, 861, 820, 794, 756, 711, 680, 585, 518; HRMS (ESI-TOF) calcd for $C_{17}H_{15}O^+$ ([M + H]$^+$): 235.1117, found: 235.1116.

2-Cyclopentyl-3-methyl-1*H*-inden-1-one (2g). This compound was obtained as a yellow solid (44% yield), mp 81.6–82.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29–7.34 (m, 2H), 7.15 (dt, J = 7.2, 0.8 Hz, 1H), 6.99 (d, J = 7.2, 1H), 2.81–2.90 (m, 1H), 2.12 (s, 3H), 1.76–1.87 (m, 6H), 1.60–1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.17, 153.26, 146.28, 137.35, 133.30, 131.07, 128.12, 121.41, 118.54, 35.74, 31.74, 26.39, 11.67; IR (film, cm^{-1}): 3389, 2952, 2868, 1704, 1610, 1455, 1385, 1322, 1283, 1150, 1083, 1022, 952, 755, 716, 649, 546; HRMS (ESI-TOF) calcd for $C_{15}H_{17}O^+$ ([M + H]$^+$): 213.1274, found: 213.1273.

2-Butyl-3-methyl-1*H*-inden-1-one (2h). This compound was obtained as a yellow solid (52% yield), mp 60.2–62.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30–7.36 (m, 2H), 7.15 (dt, J = 7.2, 0.8 Hz, 1H), 7.01 (d, J = 7.2, 1H), 2.27 (t, J = 7.2, 2H), 2.11 (s, 3H), 1.28–1.47 (m, 4H), 0.91 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.35, 153.91, 146.46, 135.31, 133.34, 130.96, 128.14, 121.60, 118.63, 31.33, 22.78, 22.57, 14.04, 11.59; IR (film, cm^{-1}): 3395, 2957, 2930, 2858, 1707, 1609, 1457, 1384, 1287, 1159, 1103, 1083, 1016, 937, 756, 715, 632, 526; HRMS (ESI-TOF) calcd for $C_{14}H_{17}O^+$ ([M + H]$^+$): 201.1274, found: 201.1264.

3-Methyl-2-phenethyl-1*H*-inden-1-one (2i). This compound was obtained as a yellow solid (61% yield), mp 63.1–64.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, J = 7.2 Hz, 1H), 7.28–7.32 (m, 1H), 7.22–7.26 (m, 2H), 7.13–7.18 (m, 4H), 6.94 (d, J = 7.2 Hz, 1H), 2.75 (t, J = 7.2 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.14, 155.04, 146.19, 141.64, 133.68, 133.38, 130.86, 128.74, 128.42, 128.28, 126.02, 121.62, 118.81, 35.13, 25.19, 11.20; IR (film, cm^{-1}): 3392, 3061, 3027, 2926, 2856, 1706, 1603, 1455, 1384, 1351, 1316, 1148, 1083, 1030, 957, 861, 754, 706, 632, 564; HRMS (ESI-TOF) calcd for $C_{18}H_{17}O$ ([M + H]$^+$): 249.1274, found: 249.1274.

5-Fluoro-3-methyl-2-phenyl-1*H*-inden-1-one (2j). This compound was obtained as a reddish brown solid (72% yield), mp 93.4–95.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43–7.46 (m, 2H), 7.38–7.41 (m, 2H), 7.21 (dd, J = 7.2, 2.4 Hz, 1H), 7.04–7.13 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.85, 163.81 (d, J_{C-F} = 248.6 Hz), 154.96 (d, J_{C-F} = 2.0 Hz), 141.37 (d, J_{C-F} = 3.2 Hz), 133.94 (d, J_{C-F} = 4.6 Hz), 132.93 (d, J_{C-F} = 7.1 Hz), 131.02, 129.54, 128.46, 127.93, 120.64 (d, J_{C-F} = 7.8 Hz), 118.86 (d, J_{C-F} = 22.9 Hz), 110.01 (d, J_{C-F} = 24.7 Hz), 12.87; IR (film, cm^{-1}): 3399, 3095, 3061, 2963, 2925, 2853, 1707, 1619, 1477, 1442, 1375, 1311, 1262, 1222, 1098, 1027, 892, 841, 796, 737, 701, 577, 522; HRMS (ESI-TOF) calcd for $C_{16}H_{12}FO^+$ ([M + H]$^+$): 239.0867, found: 239.0867.

2-(4-(*tert*-Butyl)phenyl)-5-fluoro-3-methyl-1*H*-inden-1-one (2k). This compound was obtained as a reddish brown solid (75% yield), mp 106.1–108.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.20

(dd, J = 7.2, 1 Hz, 1H), 7.03–7.13 (m, 2H), 2.32 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.15, 163.76 (d, J_{C-F} = 248.3 Hz), 154.44 (d, J_{C-F} = 2.1 Hz), 150.92, 141.58 (d, J_{C-F} = 3.2 Hz), 133.82 (d, J_{C-F} = 4.6 Hz), 133.01 (d, J_{C-F} = 7.1 Hz), 129.21, 128.08, 125.47, 120.48 (d, J_{C-F} = 7.8 Hz), 118.82 (d, J_{C-F} = 22.8 Hz), 111.00 (d, J_{C-F} = 24.6 Hz), 34.81, 31.42, 12.93; IR (film, cm^{-1}): 3406, 3053, 2963, 2905, 2869, 1713, 1620, 1507, 1474, 1438, 1377, 1331, 1266, 1224, 1204, 1113, 1093, 1028, 1011, 887, 838, 787, 762, 734, 561; HRMS (ESI-TOF) calcd for $C_{20}H_{20}FO^+$ ([M + H]$^+$): 295.1493, found: 295.1493.

2-(3-Hydroxyphenyl)-3-methyl-1*H*-inden-1-one (2l). This compound was obtained as a red solid (90% yield), mp 128.5–129.9; ^{1}H NMR (400 MHz, d^6-DMSO) δ (ppm): 9.52 (s, 1H), 7.53 (td, J = 7.2, 0.8 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.32–7.37 (m, 2H), 7.25 (t, J = 8.0 Hz, 1H), 6.82–6.84 (m, 2H), 6.76–6.79 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO) δ (ppm): 195.79, 157.11, 155.51, 145.29, 134.18, 132.26, 131.99, 129.60, 129.21, 129.20, 121.65, 120.30, 120.20, 116.25, 114.77, 12.58; IR (KBr, cm^{-1}): 3278, 3068, 2923, 2853, 1692, 1596, 1508, 1440, 1381, 1345, 1314, 1285, 1257, 1233, 1167, 1089, 1035, 1000, 917, 875, 841, 812, 778, 758, 704, 668; HRMS (ESI-TOF) calcd for $C_{16}H_{13}O_2^+$ ([M + H]$^+$): 237.0910, found: 237.0910; anal. calcd for $C_{16}H_{12}O_2$ (%); C, 81.34; H, 5.12. Found: C, 81.05; H, 5.07.

3-Ethyl-2-phenyl-1*H*-inden-1-one (2m). This compound was obtained as a yellow solid (85% yield), mp 186.6–188.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, J = 7.2 Hz, 1H), 7.33–7.46 (m, 6H), 7.24–7.28 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 2.74 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.94, 160.05, 144.99, 133.69, 132.94, 131.37, 130.90, 129.45, 128.87, 128.44, 127.88, 122.50, 119.98, 20.12, 12.93; IR (film, cm^{-1}): 3397, 3057, 2973, 2935, 2876, 1712, 1601, 1492, 1459, 1345, 1298, 1173, 1087, 1051, 916, 853, 837, 755, 723, 699, 665, 640, 590, 512; HRMS (ESI-TOF) calcd for $C_{17}H_{15}O^+$ ([M + H]$^+$): 235.1117, found: 235.1121.

2,3-Diphenyl-1*H*-inden-1-one (2n). This compound was obtained as a red solid (32% yield), mp 151.8–153.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (d, J = 7.2 Hz, 1H), 7.35–7.43 (m, 6H), 7.25–7.31 (m, 6H), 7.15 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.64, 155.46, 145.35, 133.57, 132.83, 132.52, 130.87, 130.85, 130.10, 129.42, 129.09, 128.91, 128.63, 128.20, 127.87, 123.11, 121.39; IR (film, cm^{-1}): 3384, 3065, 2923, 2854, 1701, 1601, 1486, 1450, 1348, 1281, 1180, 1076, 1024, 922, 843, 755, 699, 585, 518; HRMS (ESI-TOF) calcd for $C_{21}H_{15}O$ ([M + H]$^+$): 283.1117, found: 283.1119; anal. calcd for $C_{21}H_{14}O$ (%); C, 89.34; H, 5.00. Found: C, 89.09; H, 5.06.

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