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Efficient indenones synthesis via iridium-catalyzed decarboxylative annulation between 2-oxo-2-phenylacetic acids and alkynes

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ABSTRACT

Efficient iridium-catalyzed decarboxylative annulation reactions between 2-oxo-2-phenylacetic acids and alkyne derivatives has been achieved. $[IrCp^*Cl_2]_2$ with a $(CH_3OC_6H_4)_3P$ ligand, $AgSbF_6$ and $Cu(OAc)_2$ additives was the most efficient catalytic system for this transformation. This reaction is suitable for a broad range of alkynes and 2-oxo-2-phenylacetic acids and a variety of indenone derivatives were obtained in medium to high yields. This work provides an efficient approach for the construction of indenones by iridium–catalyzed decarboxylative annulation.

1. Introduction

Transition metal-catalyzed C–H bond activations is a versatile and efficient method of creating organic molecules and many appealing results have been produced [1,2]. Although the activation of C–H bond has made significant progress, the selectivity activation of a designated C–H bond is difficult, which restricts the development of C–H bond activation. To circumvent this problem, a directing group usually needs to be introduced. It is clear that the substance with the directing group itself has the advantage of the activation of C-H bonds. The carboxylic acid containing a removable type oriented group is prone to decarboxylation to selectively construct a new C-C bond, which replace the original carboxylate carbon and extrude CO or CO_2 [3].

Based on the above reasons, in recent years decarboxylation cross-coupling reaction developed rapidly [4]. We demonstrated efficient decarboxylation annulation reactions between mandelic acids and alkyne derivatives to obtain indenones via rhodium catalyzed [5]. In the process of studying the mechanism, we found that mandelic acid was first oxidized to 2-oxo-2-phenylacetic acid in the reaction conditions, and then it reacted with alkynes to produce products. 2-oxo-2-phenylacetic acid is also a commercially available material, for this reason, we next turn our attention to the reaction of 2-oxo-2-phenylacetic acids and alkyne derivatives.

2. Results and discussion

On the basis of previous research work, we further discussed the reaction conditions for the preparation of indenone with 2-oxo-2-phenylacetic acids and 1,2-diphenylacetylene. The results are shown in Table 1. When $[RhCp^*Cl_2]_2$ with $AgSbF_6$ and $Cu(OAc)_2$ was used, the desired annulation product **3aa** was obtained in 52% yield (entry 1). The catalyst was changed to $[IrCp^*Cl_2]_2$, combined with $AgSbF_6$ and $Cu(OAc)_2$, as a result, product **3aa** was obtained in 55% yield (entry 2). If there was no $Cu(OAc)_2$, or NaOAc was used instead of $Cu(OAc)_2$, the reaction did not occur (entries 3,4).

In order to further improve the yield of the product, the effects of several phosphine ligands were studied. Phosphine ligands PCy_3 and $(CH_3OC_6H_4)_3P$ significantly improved the reaction efficiency and afforded the product **3aa** in yields of 83% and 85%, respectively (entries 5,6). Phosphine ligand $P(C_6F_5)_3$ and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) gave lower yields of 64% and 61%, respectively (entries 7,8). This catalytic reaction was also examined under a nitrogen atmosphere. When $(CH_3OC_6H_4)_3P$ was phosphine ligand, the reaction can only provide trace of product **3aa** (entry 9).

According to these results, we used $[IrCp^*Cl_2]_2$ as catalyst, $AgSbF_6$ and $Cu(OAc)_2$ as additive, and $(CH_3OC_6H_4)_3P$ as the best

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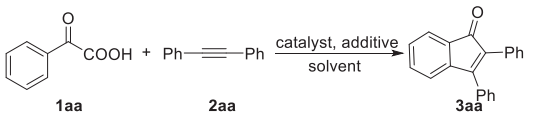
0022-328X/

Table 1
Optimization of Reaction Conditions for the Reaction of 2-oxo-2-phenylacetic acid with Alkyne [a]



Entry	catalyst	additive[b]		ligand[c]	yield (%)[d]
1	**[RhCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**		52%
2	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**		55%
3	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**			0
4	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**NaOAc**		0
5	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**	**PCy$_3$**	83%
6	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**	**(CH$_3$OC$_6$H$_4$)$_3$P**	85%
7	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**	**P(C$_6$F$_5$)$_3$**	64%
8	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**	**DPPF**	61%
9[e]	**[IrCp*Cl$_2$]$_2$**	**AgSbF$_6$**	**Cu(OAc)$_2$**	**(CH$_3$OC$_6$H$_4$)$_3$P**	trace

[a] Reaction conditions: **1aa** (0.1 mmol), **2aa** (0.11 mmol), catalyst (10 moi %) in 1 mL of tolune in air at 120 °C for 20 h.
[b] Additive (silver salt: 10 mol %, copper salt 20 mol %).
[c] Phosphine ligand: 10 mol %.
[d] Isolated yields.
[e] Under nitrogen conditions.

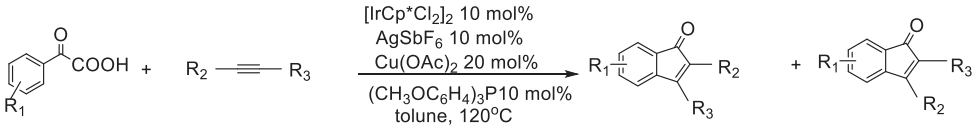
ligand to produce indenone under air.

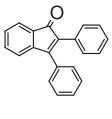
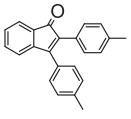
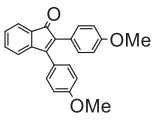
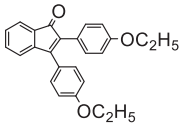
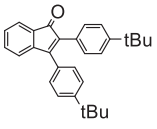
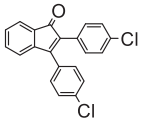
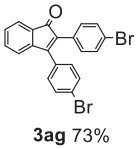
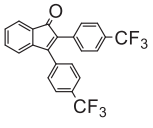
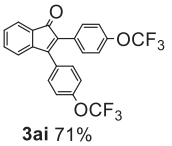
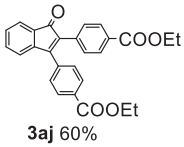
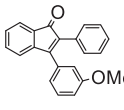
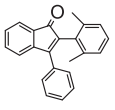
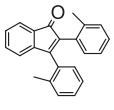
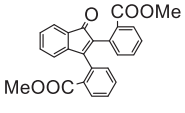
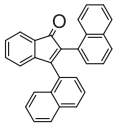
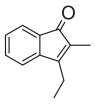
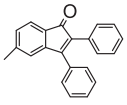
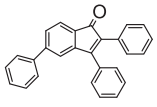
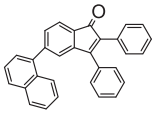
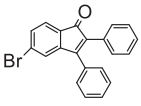
With the optimized reaction conditions in hand, the scope of the iridium-catalyzed decarboxylative annulation was investigated and the results are shown in Table 2. When **1aa** reacted with 1,2-diphenylethyne (**2aa**), the desired product **3aa** was obtained in 85% yield. The 1,2-diphenylethyne with methyl group at *para*-position was readily converted into the corresponding product (**3ab**) in 87% yields. When 2-oxo-2-phenylacetic acid was reacted with 1,2-diphenylethynes bearing methoxy or ethoxy groups at *para*-position, the desired products **3ac** and **3ad** were also obtained in 81% and 80% yields, respectively. The 1,2-diphenylethyne with a *tert*-butyl group also gave the desired product **3ae** in 86% yield.

The 1,2-diphenylethynes with electron withdrawing groups also were applied to the catalytic reaction. 1,2-diphenylethynes bearing -Cl or -Br groups can smoothly reacted with 2-oxo-2-phenylacetic acid to obtain the desired products **3af** and **3ag** in 76% and 73% yields, respectively. The 1,2-diphenylethynes with -CF_3 or -OCF_3 groups also gave the desired products **3ah** and **3ai** in 75% and 71% yields, respectively. These results indicate that electron donating groups are more advantageous for the reaction than electron withdrawing groups. When **1aa** reacted with 1,2-diphenylethyne bearing —COOEt group, the yield of desired product **3aj** was decreased to 60%. Since the ester group may act as a directing group to induce other C-H activation, the yield of the main reaction was affected.

In addition, 1,2-diphenylethyne bearing one methoxy group at *meta*-position gave the corresponding products **3ak** in 79% yields (the ratio of **3ak** and **3ak'** is 5:4). Next, the 1,2-diphenylethynes with groups at ortho-position were applied to the annulation reaction. 1,2-diphenylethynes bearing methyl groups gave the corresponding products **3al** and **3am** in 68% (the ratio of **3al** and **3al'** is 5:6) and 62% yields, respectively. The reaction was also compatible with 1,2-diphenylethynes with —COOMe group to afford the

Table 2
Decarboxylative Annulation Reactions of 2-Oxo-2-phenylacetic acids with Alkynes.[a]



1	2		3	3'
 **3aa** 85%	 **3ab** 87%	 **3ac** 81%	 **3ad** 80%	 **3ae** 86%
 **3af** 76%	 **3ag** 73%	 **3ah** 75%	 **3ai** 71%	 **3aj** 60%
 **3ak** 79%(5:4)	 **3al** 68%(5:6)	 **3am** 62%	 **3an** 55%	 **3ao** 57%
 **3ap** 46%(6:7)	 **3ba** 73%	 **3ca** 70%	 **3da** 66%	 **3ea** 63%

desired product **3an** in 55% yield. When 1,2-di(naphthalen-1-yl) ethyne was used the catalytic reaction can also afford the desired product **3ao** in 57% yield. These results indicate that the catalytic reaction is slightly sensitive to steric effects of functional group.

In addition to diaryl alkynes, we have also studied the reaction of alkyl substituted alkyne under this reaction condition. 2-pentyne was used in this reaction, and as a result, the corresponding product in 46% yield was afforded, and the ratio of the two isomers was 6:7. The reaction has no significant selectivity for the product isomer. The above results also indicate that diaryl alkynes are more favorable to the reaction than alkyl substituted alkynes.

The reactivities of substituted 2-oxo-2-phenylacetic acids were also investigated. The 2-oxo-2-phenylacetic acids bearing a methyl group reacted with 1,2-diphenylethyne can afford the product **3ba** in 73% yield. A phenyl group, or 1-naphthenyl group substituted 2-oxo-2-phenylacetic acids reacted smoothly to obtain **3ca** and **3da** in 70% and 66% yields, respectively. In addition, 2-oxo-2-phenylacetic acid bearing a -Br group also reacted in the catalytic reaction to providing 63% yield of the desired product **3ea**.

The mechanism of the reaction in Fig. 1 is similar to that of the previous studies, the reaction is subjected to a mechanism involving intramolecular C-H activation, decarboxylation, and annulation to afford the desired product [5].

3. Conclusion

In summary, we have developed an iridium-catalyzed decarboxylative annulation of 2-oxo-2-phenylacetic acids with alkynes. Various substituted indenones were obtained in medium to high yields under the standard reaction conditions. The catalytic method provide a straight-forward synthetic pathway for various indenones from 2-oxo-2-phenylacetic acids and alkynes.

4. Experimental section

General information: ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on Bruker AV 400 spectrometers with $CDCl_3$ as the solvent. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer and Nicolet Magna 550 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303 instrument. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

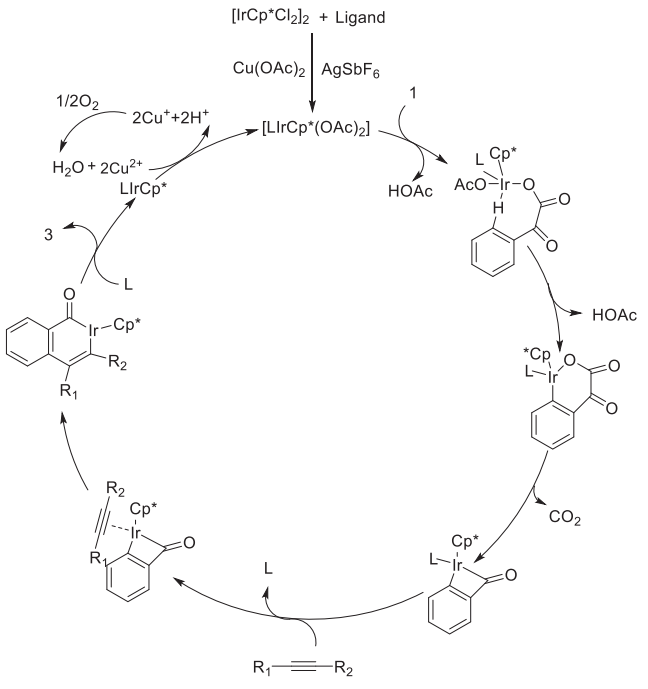


Fig. 1. Mechanism for the Decarboxylative Annulation Reactions of 2-Oxo-2-phenylacetic acids with Alkynes.

Materials and Methods: Unless otherwise noted, all reactions were performed under an atmosphere of air with oven-dried glassware. Reactions were monitored by analytical thin layer chromatography on 0.20 mm silica gel plates, spots were detected by flash chromatography through UV-absorption. Silica gel (200–300 mesh) (from Yantai Huagong Chem. Company, Ltd.). The starting materials various 2-oxo-2-phenylacetic acids and 1,2-diphenylethynes were synthesized and purified according to the literature procedures [5,6]. Other chemicals or reagents were obtained from commercial sources.

4.1. General experimental procedure for the preparation of indenones

To an oven-dried screwed vial were added substituted 2-oxo-2-phenylacetic acid (0.1 mmol), substituted alkyne (0.11 mmol), $[IrCp^*Cl_2]_2$ (0.01 mmol, 7.97 mg), $(CH_3OC_6H_4)_3P$ (0.01 mmol, 3.52 mg), $AgSbF_6$ (0.01 mmol, 3.44 mg), $Cu(OAc)_2$ (0.02 mmol, 3.99 mg), and toluene (1 mL). The mixture was vigorously stirred at 120 °C under air to the end of the reaction. Organic solvents were removed in *vacuo*, and then the residue was purified by a silica gel column chromatography to give the desired product.

2,3-diphenyl-1H-inden-1-one (3aa): Purified by column chromatography to provide a red solid (24.0 mg, yield: 85%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.61 (d, J = 6.96 Hz, 1H), 7.46–7.37 (m, 6H), 7.33–7.27 (m, 6H), 7.17 (d, J = 7.20 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.37, 155.23, 145.11, 133.36, 132.61, 132.27, 131.51, 130.65, 129.90, 129.22, 128.87, 128.71, 128.42, 127.99, 127.66, 122.87, 121.18; **IR (KBr):** ν 3739, 3446, 3062, 2921, 2360, 1708, 1609, 1450, 1349, 1183, 1075, 919, 840, 734, 695 cm^{-1}; Analytical Data. Found (calcd) for: $C_{21}H_{14}O$ C, 89.35 (89.34); H, 5.00 (5.00).

2,3-dip-tolyl-1H-inden-1-one (3ab): Purified by column chromatography to provide a red solid (27.0 mg, yield: 87%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (d, J = 7.00 Hz, 1H), 7.39–7.30 (m, 4H), 7.25–7.18 (m, 5H), 7.12 (d, J = 7.80 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.67, 154.71, 145.38, 139.26, 137.44, 133.23, 131.96, 130.86, 129.83, 129.78, 129.74, 129.39, 129.34, 128.76, 128.65, 128.42, 127.91, 123.83, 122.70, 121.06, 120.94, 21.45, 21.28; **IR (KBr):** ν 3620, 2925, 1709, 1604, 1507, 1460, 1346, 1186, 1071, 1018, 818, 736 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{18}O$ C, 89.01 (89.00); H, 5.84 (5.85).

2,3-bis(4-methoxyphenyl)-1H-inden-1-one (3ac): Purified by column chromatography to provide a red solid (27.7 mg, yield: 81%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 (d, J = 6.92 Hz, 1H), 7.48–7.37 (m, 3H), 7.30–7.25 (m, 3H), 7.19 (d, J = 7.24 Hz, 1H), 6.96 (d, J = 8.76 Hz, 2H), 6.84 (d, J = 8.76 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.91, 160.29, 159.09, 153.75, 145.49, 133.22, 131.25, 131.03, 130.15, 128.58, 127.11, 125.13, 123.43, 122.68, 120.92, 114.20, 113.66, 55.29, 55.17; **IR (KBr):** ν 3450, 2925, 2360, 1703, 1606, 1507, 1459, 1403, 1294, 1249, 1175, 1029, 788 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{18}O_3$ C, 80.69 (80.68); H, 5.30 (5.30).

2,3-bis(4-ethoxyphenyl)-1H-inden-1-one (3ad): Purified by column chromatography to provide a red solid (29.6 mg, yield: 80%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 (d, J = 7.48 Hz, 1H), 7.36 (d, J = 8.64 Hz, 3H), 7.29–7.24 (m, 3H), 7.19 (d, J = 7.20 Hz, 1H), 6.94 (d, J = 8.76 Hz, 2H), 6.82 (d, J = 8.84 Hz, 2H), 4.12–4.02 (m, 4H), 1.49–1.41 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.97, 159.70, 158.47, 153.73, 153.73, 145.52, 133.18, 131.24, 131.06, 130.15, 128.53, 124.98, 123.29, 122.64, 120.92, 114.65, 114.17, 63.52, 63.33, 14.82,

14.79; **IR (KBr):** ν 3579, 2977, 2925, 2360, 1701, 1604, 1468, 1346, 1289, 1178, 1075, 1042, 919, 823, 764, 667 cm^{-1}; Analytical Data. Found (calcd) for: $C_{25}H_{22}O_3$ C, 81.07 (81.06); H, 5.98 (5.99).

2,3-bis(4-*tert*-butylphenyl)-1H-inden-1-one (3ae): Purified by column chromatography to provide a red solid (33.9 mg, yield: 86%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, J = 7.20 Hz, 1H), 7.47 (d, J = 8.52 Hz, 2H), 7.40–7.33 (m, 4H), 7.32–7.28 (m, 4H), 7.19 (d, J = 7.24 Hz, 1H), 1.41 (s, 9H), 1.35 (s, 9H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.86, 154.63, 152.37, 150.47, 145.55, 133.21, 131.74, 130.87, 129.85, 129.53, 128.60, 128.24, 127.87, 125.54, 124.93, 122.67, 121.21, 34.81, 34.55, 31.23, 31.17; **IR (KBr):** ν 3456, 2525, 1634, 1415, 1390, 1167, 1106, 1054, 1026, 945, 891, 750 cm^{-1}; Analytical Data. Found (calcd) for: $C_{29}H_{30}O$ C, 88.29 (88.28); H, 7.66 (7.66).

2,3-bis(4-chlorophenyl)-1H-inden-1-one (3af): Purified by column chromatography to provide a red solid (26.6 mg, yield: 76%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.61 (d, J = 7.00 Hz, 1H), 7.45–7.40 (m, 3H), 7.34 (d, J = 8.28 Hz, 3H), 7.29–7.27 (m, 2H), 7.22 (d, J = 7.56 Hz, 2H), 7.14 (d, J = 8.64 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.77, 154.28, 144.63, 135.52, 134.03, 133.67, 133.65, 131.52, 131.18, 130.85, 130.48, 129.83, 129.34, 129.32, 128.53, 123.27, 121.16; **IR (KBr):** ν 3535, 2962, 2871, 2354, 1723, 1607, 1457, 1389, 1283, 1120, 1082, 1013, 960, 866, 721, 661 cm^{-1}; Analytical Data. Found (calcd) for: $C_{21}H_{12}Cl_2O$ C, 71.80 (71.81); H, 3.45 (3.44).

2,3-bis(4-bromophenyl)-1H-inden-1-one (3ag): Purified by column chromatography to provide a red solid (31.9 mg, yield: 73%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.62–7.56 (m, 2H), 7.46–7.39 (m, 4H), 7.35–7.27 (m, 4H), 7.16–7.12 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.61, 154.28, 144.52, 133.63, 132.27, 132.09, 131.46, 131.43, 130.43, 130.01, 129.88, 129.80, 129.32, 123.78, 123.25, 122.35, 121.15; **IR (KBr):** ν 3059, 2925, 2851, 1709, 1602, 1456, 1342, 1263, 1179, 1069, 1010, 921, 827, 760, 673 cm^{-1}; Analytical Data. Found (calcd) for: $C_{21}H_{12}Br_2O$ C, 57.31 (57.31); H, 2.74 (2.75).

2,3-bis(4-(trifluoromethyl)phenyl)-1H-inden-1-one (3ah): Purified by column chromatography to provide a red solid (31.4 mg, yield: 75%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.75 (d, J = 8.08 Hz, 2H), 7.66 (d, J = 6.92 Hz, 1H), 7.55 (dd, J = 7.44, 6.68 Hz, 4H), 7.45 (t, J = 7.68 Hz, 1H), 7.40–7.37 (m, 3H), 7.14 (d, J = 7.52 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.28, 155.01, 144.30, 135.92, 133.89, 133.80, 131.55 (q, J = 32 Hz), 130.20, 129.76, 128.81, 126.09 (q, J = 3.72 Hz), 125.21 (q, J = 3.72 Hz), 123.97 (q, J = 271 Hz), 123.73 (q, J = 272 Hz), 123.61, 121.43; **^{19}F NMR (376 MHz, $CDCl_3$):** δ − 62.77 (s, 3F), −62.86 (s, 3F); **IR (KBr):** ν 3626, 2921, 2363, 1712, 1603, 1459, 1343, 1272, 1183, 1072, 1026, 915, 849, 757, 694 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{12}F_6O$ C, 66.06 (66.04); H, 2.88 (2.89).

2,3-bis(4-(trifluoromethoxy)phenyl)-1H-inden-1-one (3ai): Purified by column chromatography to provide a red solid (31.9 mg, yield: 71%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.63 (d, J = 6.92 Hz, 1H), 7.46–7.41 (m, 3H), 7.37–7.30 (m, 5H), 7.17–7.14 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.76, 154.26, 149.34 (q, J = 102 Hz), 144.59, 133.73, 131.45, 131.37, 130.85, 130.35, 130.13, 129.44, 128.93, 123.36, 121.66, 120.59, 120.38 (q, J = 258 Hz); **^{19}F NMR (376 MHz, $CDCl_3$):** δ − 57.73 (s, 6F); **IR (KBr):** ν 3567, 2922, 2361, 1715, 1611, 1408, 1346, 1267, 1173, 1021, 926, 837, 744, 692 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{12}F_6O_3$ C, 61.36 (61.34); H, 2.68 (2.69).

diethyl 4,4'-(1-oxo-1H-indene-2,3-diyl)dibenzoate (3aj): Purified by column chromatography to provide a red solid (25.6 mg, yield: 60%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.12 (d, J = 8.44 Hz, 2H), 7.96 (d, J = 8.52 Hz, 2H), 7.65 (d, J = 7.0 Hz, 1H), 7.47–7.42 (m, 3H), 7.38–7.33 (m, 3H), 7.15 (d, J = 8.28 Hz, 1H), 4.46–4.35 (m, 4H), 1.46–1.38 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 194.35, 165.87, 155.49, 151.20, 144.54, 140.78, 136.91, 134.94, 133.78, 131.43, 130.15, 129.83, 129.58, 129.34, 128.44, 123.45, 121.43, 61.29, 60.98, 14.31; **IR (KBr):** ν 3578, 2928, 2367, 1718, 1606, 1459, 1368, 1277, 1180, 1070, 1021, 927, 836, 771, 711 cm^{-1}; Analytical Data. Found (calcd) for: $C_{27}H_{22}O_5$ C, 76.02 (76.04); H, 5.21 (5.20).

2-(3-methoxyphenyl)-3-phenyl-1H-inden-1-one (3ak): Purified by column chromatography to provide a red solid (13.7 mg, yield: 44%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.61 (d, J = 6.72 Hz, 1H), 7.42–7.33 (m, 3H), 7.31–7.28 (m, 5H), 7.21 (d, J = 6.76 Hz, 1H), 7.01–6.96 (m, 2H), 6.93–6.92 (m, 1H), 3.74 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.43, 159.71, 155.14, 145.17, 133.97, 133.43, 132.48, 130.73, 130.70, 129.92, 129.90, 128.92, 128.03, 127.74, 122.94, 121.28, 120.81, 115.12, 113.72, 55.19; **IR (KBr):** ν 3678, 3060, 2933, 2836, 2361, 1711, 1596, 1456, 1345, 1284, 1249, 1176, 1042, 755, 696 cm^{-1}; Analytical Data. Found (calcd) for: $C_{22}H_{16}O_2$ C, 84.56 (84.59); H, 5.17 (5.16).

3-(3-methoxyphenyl)-2-phenyl-1H-inden-1-one (3ak'): Purified by column chromatography to provide a red solid (11.0 mg, yield: 35%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (d, J = 7.04 Hz, 1H), 7.42–7.36 (m, 6H), 7.31–7.27 (m, 1H), 7.19–7.13 (m, 2H), 6.89 (d, J = 7.68 Hz, 1H), 6.81–6.79 (m, 2H), 3.64 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.31, 159.08, 155.54, 145.16, 133.42, 132.74, 132.17, 131.93, 130.71, 129.26, 129.04, 128.98, 128.77, 128.44, 122.94, 122.47, 121.27, 114.87, 114.08, 54.99; **IR (KBr):** ν 3678, 3060, 2933, 2836, 2361, 1711, 1596, 1456, 1345, 1284, 1249, 1176, 1042, 755, 696 cm^{-1}.

2-(2,6-dimethylphenyl)-3-phenyl-1H-inden-1-one (3al): Purified by column chromatography to provide a red solid (12.3 mg, yield: 40%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.62 (d, J = 5.76 Hz, 1H), 7.37 (d, J = 6.48 Hz, 3H), 7.32–7.27 (m, 4H), 7.19–7.13 (m, 3H), 6.86 (d, J = 7.04 Hz, 1H), 2.39 (s, 3H), 2.05 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.68, 156.09, 146.02, 135.63, 133.63, 132.43, 131.27, 130.73, 130.36, 129.62, 129.02, 128.83, 128.04, 127.67, 122.64, 121.23, 21.00, 19.35; **IR (KBr):** ν 3453, 2926, 2857, 1712, 1598, 1493, 1456, 1343, 1264, 1174, 1081, 1028, 815, 759, 697 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{18}O$ C, 89.01 (89.00); H, 5.84 (5.85).

3-(2,6-dimethylphenyl)-2-phenyl-1H-inden-1-one (3al'): Purified by column chromatography to provide a red solid (8.8 mg, yield: 28%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, J = 6.84 Hz, 1H), 7.38–7.33 (m, 3H), 7.31–7.27 (m, 2H), 7.25–7.24 (m, 2H), 7.20–7.11 (m, 3H), 6.84 (d, J = 7.80 Hz, 1H), 2.37 (s, 3H), 2.02 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.71, 156.11, 146.04, 135.65, 133.64, 132.51, 132.45, 132.29, 131.28, 130.74, 130.38, 129.63, 129.03, 128.83, 128.16, 128.05, 127.68, 122.66, 121.24, 21.00, 19.35; **IR (KBr):** ν 3453, 2926, 2857, 1712, 1598, 1493, 1456, 1343, 1264, 1174, 1081, 1028, 815, 759, 697cm^{-1}.

2,3-dim-tolyl-1H-inden-1-one (3am): Purified by column chromatography to provide a red solid (19.2 mg, yield: 62%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, J = 7.76 Hz, 1H), 7.39–7.35 (m, 1H), 7.32–7.27 (m, 2H), 7.23–7.06 (m, 6H), 6.96 (d, J = 7.56 Hz, 1H), 6.90 (d, J = 7.12 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.20, 157.57, 157.51, 145.87, 137.06, 135.91, 135.78, 133.47, 132.27, 130.97, 130.69, 130.53, 130.22, 128.84, 128.10, 125.77, 125.35, 122.84, 121.44, 20.62, 20.13; **IR (KBr):** ν 3563, 2920, 1711, 1606, 1457, 1341, 1261, 1176, 1070, 1033, 925, 849, 752 cm^{-1}; Analytical Data. Found (calcd) for: $C_{23}H_{18}O$ C, 88.98 (89.00); H, 5.86 (5.85).

dimethyl 2,2'-(1-oxo-1H-indene-2,3-diyl)dibenzoate (3an): Purified by column chromatography to provide a red solid (21.9 mg, yield: 55%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.09–8.06 (m, 1H), 8.00–7.97 (m, 1H), 7.57 (d, J = 8.48 Hz, 1H), 7.45–7.42 (m, 2H), 7.33–7.28 (m, 3H), 7.25–7.23 (m, 2H), 7.06–7.04 (m, 1H), 6.72 (d, J = 7.16 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.14, 167.60, 167.15, 155.02, 146.26, 134.80, 134.13, 133.44, 132.71, 132.26, 131.70, 131.42, 131.15, 130.39, 130.24, 130.00, 128.83, 128.34, 127.81, 123.04, 119.95, 52.26, 52.14; **IR (KBr):** ν 3667, 2951, 2363, 1721, 1668, 1437, 1344, 1269, 1187, 1074, 1042, 927, 853, 761, 681 cm^{-1}; Analytical Data. Found (calcd) for: $C_{25}H_{18}O_5$ C, 75.34 (75.37); H, 4.56 (4.55).

2,3-di(naphthalen-1-yl)-1H-inden-1-one (3ao): Purified by column chromatography to provide a red solid (21.8 mg, yield:

57%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.97 (d, J = 8.32 Hz, 1H), 7.89–7.70 (m, 6H), 7.57–7.34 (m, 7H), 7.28–7.07 (m, 3H), 6.86–6.76 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.18, 146.20, 141.27, 137.01, 135.04, 133.65, 133.50, 133.50, 130.49, 129.40, 129.07, 128.53, 128.20, 127.76, 126.21, 126.19, 126.10, 126.05, 126.01, 125.97, 125.94, 125.88, 125.81, 125.77, 125.76, 125.57, 125.53, 125.49, 123.03, 122.17; **IR (KBr):** ν 3534, 2925, 1709, 1596, 1458, 1326, 1258, 1176, 1082, 1018, 964, 773, 697 cm^{-1}; Analytical Data. Found (calcd) for: $C_{29}H_{18}O$ C, 91.08 (91.07); H, 4.73 (4.74).

3-ethyl-2-methyl-1H-inden-1-one (3ap): Purified by column chromatography to provide a white yellow solid (3.6 mg, yield: 21%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37–7.30 (m, 2H), 7.17–7.14 (m, 1H), 7.01 (d, J = 7.16 Hz, 1H), 2.29–2.23 (m, 2H), 2.11 (s, 3H), 0.93–0.89 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 198.17, 146.35, 144.71, 139.85, 135.21, 133.18, 128.00, 121.48, 118.47, 31.18, 14.18, 13.89; **IR (KBr):** ν 2916, 1685, 1590, 1443, 1213, 1057, 909, 746, 702 cm^{-1}; Analytical Data. Found (calcd) for: $C_{12}H_{12}O$ C, 83.67 (83.69); H, 7.03 (7.02).

2-ethyl-3-methyl-1H-inden-1-one (3ap'): Purified by column chromatography to provide a white yellow solid (4.3 mg, yield: 25%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37 (d, J = 7.04 Hz, 1H), 7.32–7.28 (m, 1H), 7.16–7.12 (m, 1H), 7.02 (d, J = 7.16 Hz, 1H), 2.55–2.49 (m, 2H), 1.81 (s, 3H), 0.98–0.94 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.66, 153.51, 141.77, 140.71, 134.97, 128.05, 127.79, 121.71, 118.75, 25.96, 14.19, 13.91.

5-methyl-2,3-diphenyl-1H-inden-1-one (3ba): Purified by column chromatography to provide a red solid (21.6 mg, yield: 73%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51 (d, J = 7.24 Hz, 1H), 7.45–7.44 (m, 3H), 7.41–7.38 (m, 2H), 7.29–7.27 (m, 5H), 7.10 (d, J = 7.28 Hz, 1H), 6.96 (s, 1H), 2.38 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.16, 154.93, 145.72, 144.38, 132.90, 132.81, 130.88, 129.97, 129.14, 128.91, 128.77, 128.51, 128.38, 128.01, 127.65, 123.05, 122.51, 22.08; **IR (KBr):** ν 3572, 2920, 2361, 1704, 1603, 1469, 1357, 1275, 1188, 1070, 1031, 922, 839, 732, 695 cm^{-1}; Analytical Data. Found (calcd) for: $C_{22}H_{16}O$ C, 89.13 (89.16); H, 5.45 (5.44).

2,3,6-triphenyl-1H-inden-1-one (3ca): Purified by column chromatography to provide a red solid (25.1 mg, yield: 70%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.89 (d, J = 1.72 Hz, 1H), 7.67–7.63 (m, 3H), 7.52–7.41 (m, 7H), 7.36–7.29 (m, 7H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.29, 155.39, 144.00, 142.26, 139.92, 132.81, 131.67, 131.57, 130.79, 129.97, 129.35, 128.94, 128.82, 128.51, 128.10, 127.90, 127.78, 126.78, 121.95, 121.61; **IR (KBr):** ν 3362, 2925, 1707, 1605, 1466, 1346, 1260, 1077, 969, 846, 768, 730, 696 cm^{-1}; Analytical Data. Found (calcd) for: $C_{27}H_{18}O$ C, 90.44 (90.47); H, 5.07 (5.06).

6-(naphthalen-1-yl)-2,3-diphenyl-1H-inden-1-one (3da): Purified by column chromatography to provide a red solid (26.9 mg, yield: 66%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.94–7.88 (m, 3H), 7.77 (d, J = 1.12 Hz, 1H), 7.56–7.53 (m, 3H), 7.51–7.44 (m, 7H), 7.34–7.28 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 196.35, 155.34, 144.12, 141.86, 138.94, 134.74, 133.84, 132.77, 132.68, 131.28, 130.98, 130.76, 129.97, 129.44, 129.36, 128.84, 128.61, 128.51, 128.43, 128.21, 128.10, 127.78, 126.74, 126.35, 125.97, 125.56, 125.37, 124.87, 121.23; **IR (KBr):** ν 2926, 2847, 1728, 1602, 1460, 1378, 1260, 1162, 1033, 808, 781, 749 cm^{-1}; Analytical Data. Found (calcd) for $C_{31}H_{20}O$: 91.13 (91.15); H, 4.95 (4.94).

5-bromo-2,3-diphenyl-1H-inden-1-one (3ea): Purified by column chromatography to provide a red solid (22.7 mg, yield: 63%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.46–7.42 (m, 5H), 7.37–7.34 (m, 2H), 7.27–7.26 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 195.18, 154.15, 147.28, 133.40, 132.19, 131.62, 130.27, 129.98, 129.56, 129.35, 129.00, 128.36, 128.14, 128.08, 124.69, 124.07; **IR (KBr):** ν 3561, 3059, 2957, 2926, 2852, 1713, 1601, 1485, 1445, 1350, 1262, 1063, 1029, 786 cm^{-1}; Analytical Data. Found (calcd) for: $C_{21}H_{13}BrO$, C 69.80 (69.82); H, 3.64 (3.63).

Notes

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.09.011.

References

[1] J.-Q. Yu, Z.-J. Shi, Topics in Current Chemistry, Springer-Verlag, New York, 2010.
[2] (Selected reviews on C-H activation reactions, see:). (a) S.H. Cho, J.Y. Kim, J. Kwak, S. Chang, Chem. Soc. Rev. 40 (2011) 5068–5083;
(b) J.C. Lewis, R.G. Bergman, J.A. Ellman, Acc. Chem. Res. 41 (2008) 1013–1025;
(c) D.A. Colby, R.G. Bergman, J.A. Ellman, Chem. Rev. 110 (2010) 624–655;
(d) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, Chem. Soc. Rev. 40 (2011) 4740–4761;
(e) B.G. Hashiguchi, S.M. Bischof, M.M. Konnick, R.A. Periana, Acc. Chem. Res. 45 (2012) 885–898;
(f) G.-Y. Song, F. Wang, X.-W. Li, Chem. Soc. Rev. 41 (2012) 3651–3678;
(g) S. Gaillard, C.S.J. Cazin, S.P. Nolan, Acc. Chem. Res. 45 (2012), 778–187;
(h) P.B. Arockiam, C. Bruneau, P.H. Dixneuf, Chem. Rev. 112 (2012) 5879–5918;
(i) B. Li, P.H. Dixneuf, Chem. Soc. Rev. 42 (2013) 5744–5767;
(j) K.R.D. Johnson, P.G. Hayes, Chem. Soc. Rev. 42 (2013) 1947–1960;
(k) R.A. Baillie, P. Legzdins, Acc. Chem. Res. 47 (2014) 330–340;
(l) X.-F. Wu, Chem. Eur J. 21 (2015) 12252–12265;
(m) P.L. Arnold, M.W. McMullon, J. Rieb, F.E. Kühn, Angew. Chem. Int. Ed. 54 (2015) 82–100;
(n) Y. Segawa, T. Maekawa, K. Itami, Angew. Chem. Int. Ed. 54 (2015) 66–81;
(o) J.J. Topczewski, M.S. Sanford, Chem. Sci. 6 (2015) 70–76;
(p) T.S. Lobana, RSC Adv. 5 (2015) 37231–37274;
(q) Y.-Y. Hu, B.-W. Zhou, C.-Y. Wang, Acc. Chem. Res. 51 (2018) 816–827.
[3] (a) M.-Z. Li, H.-B. Ge, Org. Lett. 12 (2010) 3464–3467;
(b) P. Fang, M.-Z. Li, H.-B. Ge, J. Am. Chem. Soc. 132 (2010) 11898–11899;
(c) Z.-Y. Yang, X. Chen, J.-D. Liu, Q.-W. Gui, K. Xie, M.-M. Li, Z. Tan, Chem. Commun. 49 (2013) 1560–1562;
(d) H. Wang, L.-N. Guo, X.-H. Duan, Org. Lett. 14 (2012) 4358–4361;
(e) Z.-Y. Li, D.-D. Li, G.-W. Wang, J. Org. Chem. 78 (2013) 10414–10420;
(f) J. Park, M. Kim, S. Sharma, E. Park, A. Kim, S.H. Lee, J.H. Kwak, Y.H. Jung, I.S. Kim, Chem. Commun. 49 (2013) 1654–1656;
(g) J.-Z. Yao, R.-K. Feng, Z.-H. Wu, Z.-X. Liu, Y.-H. Zhang, Adv. Synth. Catal. 355 (2013) 1517–1522;
(h) H.-J. Li, P.-H. Li, Q. Zhao, L. Wang, Chem. Commun. 49 (2013) 9170–9172.
[4] (a) A. Voutchkova, A. Coplin, N.E. Leadbeater, R.H. Crabtree, Chem. Commun. (2008) 6312–6314;
(b) L.J. Goossen, N. Rodriguez, K. Goossen, Angew. Chem. Int. Ed. 47 (2008) 3100–3120;
(c) J. Cornella, P.-F. Lu, I. Larrosa, Org. Lett. 11 (2009) 5506–5509;
(d) C.-Y. Wang, I. Piel, F. Glorius, J. Am. Chem. Soc. 131 (2009) 4194–4195;
(e) F.-Z. Zhang, M.-F. Greaney, Angew. Chem. Int. Ed. 49 (2010) 2768–2771;
(f) K. Xie, Z.-Y. Yang, X.-J. Zhou, X.-J. Li, S.-Z. Wang, Z. Tan, X.-Y. An, C.-C. Guo, Org. Lett. 12 (2010) 1564–1567;
(g) S.-S. Wang, X.-Z. Chen, Q.-Q. Ao, H.-F. Wang, H.-B. Zhai, Chem. Commun. 52 (2016) 9454–9457;
(h) Z.-J. Liu, X. Lu, G. Wang, L. Lei, W.-T. Jiang, Y.-D. Wang, B. Xiao, Y. Fu, J. Am. Chem. Soc. 138 (2016) 9714–9719;
(i) F.A. Cruz, Z.-W. Chen, S.I. Kurtoic, V.M. Dong, Chem. Commun. 52 (2016) 5836–5839;
(j) C.-Y. Wang, S. Rakshit, F. Glorius, J. Am. Chem. Soc. 132 (2010) 14006–14008.
[5] X.–B. Yu, Y.–L. Duan, W.–J. Guo, T. Wang, Q.–X. Xie, S.–T. Wu, C.–G. Jiang, Z.–X. Fan, J.–H. Wang, G.–Y. Liu, Organometallics 36 (2017) 1027–1034.
[6] K. Heuzé, D. Méry, D. Gauss, J.C. Blais, D. Astruc, Chem. Eur J. 10 (2004) 3936–3944.