Rhodium-Catalyzed Oxidative Decarboxylation Annulation Reactions of Mandelic Acids and Alkynes: An Efficient Synthetic Method for Indenones

Xiaobo Yu,^{†,‡,||}[®] Yulian Duan,^{†,||} Weijie Guo,^{†,||} Tao Wang,[†] Qingxiao Xie,[†] Shutao Wu,[†] Chenggong Jiang,[†] Zixiong Fan,[†] Jianhui Wang,^{*,†,||} and Guiyan Liu^{*,§}

[†]Department of Chemistry, College of Science, Tianjin University, Tianjin 300072, People's Republic of China

[‡]College of Materials Science and Engineering, Jilin Institute of Chemical Technology, Jilin City 132022, People's Republic of China

[§]Tianjin Key Laboratory of Structure and Performance for Functional Molecules; Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry; Ministry of Education; College of Chemistry, Tianjin Normal University, Tianjin 300387, People's Republic of China

^{II}Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, People's Republic of China

S Supporting Information



ABSTRACT: Efficient rhodium-catalyzed oxidative decarboxylation annulation reactions between mandelic acids and alkyne derivatives are described. The desired indenone products were obtained in medium to good yields under the optimized reaction conditions, which were a $[RhCp*Cl_2]_2$ catalyst (10.0 mol %) in combination with a PCy_3 ligand (10.0 mol %) and $AgSbF_6$ (10 mol %) and $Cu(OAc)_2$ (20 mol %) additives. Many functional groups are compatible with the reaction under the optimized reaction conditions. This strategy provides a promising method for the construction of indenones from cheap and commercially available starting materials.

INTRODUCTION

Indenones are useful intermediates in organic synthesis because they play important roles in the chemical, biological, and material fields.¹ Traditionally, indenones are usually synthesized by Friedel-Crafts cyclizations.² This method requires the use of electron-rich aromatic reagents as the starting materials, and therefore the scope of the reactions is limited. In addition, the reaction conditions are relatively harsh and hazardous byproducts are often generated during the reactions. So, the search for more effective methods with broader scopes for the preparation of indenones has been a pursuit of chemists over the past few decades. To this end, transition-metal-catalyzed annulations of ortho-bifunctionalized arenes and alkynes have been used to prepare indenones.³ The ortho-substitution group usually includes halide, 3a,d-f boronic acid, 3b-e or nitrile groups.^{3a,b} These methods are not limited to electronic-rich aromatic substrates, and many electron-deficient compounds have been successfully used in these reactions. However, orthobifunctionalized arenes are rare and expensive compounds that are usually not readily available, and complicated prefunctionalization processes are often required to obtain these arenes, which is both time-consuming and costly.

Recently, transition-metal-catalyzed atom-economic C–H bond activations have attracted much attention.^{4,5} Utilization of the proximate effect by coordinating a functional group to a metal center is often used as a strategy to achieve region-selective ortho C–H bond activations. The annulation of arenes with alkynes using a functional group directed ortho C–H bond activation has been developed as a powerful synthetic method for the construction of cyclic molecular structures.^{6–8} This method does not require ortho-bifunctionalized arenes as substrates and therefore is more economical than traditional cyclization reactions.

Various catalytic processes for the preparation of novel cyclic compounds have been developed using directed C–H bond activation, and some of these have successfully afforded indenones.^{6–8} Kuninobu et al. were the first to report annulations of imines with alkynes via C–H bond activation.⁶ This work inspired expansions of the annulation strategy for various synthetic targets.^{7,8} For example, Kokubo et al. reported a rhodium-catalyzed reaction of aroyl chlorides and alkynes to give indenones.⁸



Received: January 4, 2017

indenones via the annulation of benzimides and alkynes through a rhodium-catalyzed C–H activation process.^{8b} Subsequently, the annulation of aldehydes,^{8c} azomethine ylides,^{8d} and arylnitrones^{8e} with alkynes via rhodium-catalyzed C–H activations have all produced indenones (Scheme 1 A).

Scheme 1. Rhodium-Catalyzed Synthesis of Indenones via the Annulation of Ortho Arene C-H Bonds with Alkynes



However, there are still some drawbacks in this synthesis strategy, for example, the prior activation of the substrates or multistep synthesis. The choice of a proper directing group to achieve the designed annulation reactions via C–H activations is still a challenge that needs to be overcome in order to expand the scope of arene substrates.

Organic compounds containing carboxylic acid functional groups are used in various organic reactions. In recent years, decarboxylative cross-coupling reactions have developed rapidly.⁹ Mandelic acid and its derivatives are readily accessible starting materials that can undergo decarboxylative cross-coupling reactions to regioselectively construct new C–C bonds in place of the carboxylate carbon when CO or CO₂ is extruded. In these reactions, the carboxylate group acts as a temporary directing group for C–H activation.¹⁰ On the basis of these results, we envisage that a decarboxylative annulation reaction of mandelic acids and alkynes could occur through directed ortho C–H activation as shown in Scheme 1B. Herein, the decarboxylative annulation reaction of mandelic acids and alkynes for the one-pot synthesis of indenones is reported.

RESULTS AND DISCUSSION

To achieve this reaction, mandelic acid (1a) and 1,2diphenylethyne (2a) were first used as the model substrates to optimize the reaction conditions. First, different transitionmetal catalysts were tested, and the results are shown in Table 1 (entries 1–9). No desired products were obtained in toluene at 120 °C for 20 h with Pd(OAc)₂, Pd(PPh₃)₄, Pd(dba)₂, (PPh₃)₃RhCl, [Rh(COD)Cl]₂, [IrCp*Cl₂]₂, [Ru(COD)Cl₂]_n, and [RuCl₂(*p*-cymene)]₂ (entries 1–8). When [RhCp*Cl₂]₂ was used as the catalyst under these same conditions, the desired decarboxylative annulation product **3a** was obtained in low yield (23%) (entry 9).

Adding $AgSbF_6$ to the reaction system improved the yield to 32% (entry 10). In order to further increase the yield, copper

toluene

toluene

toluene

toluene

toluene

toluene

toluene

toluene

xylene

32

63

37

40

38

25

0

63

60

Table 1. Optimization of Reaction Conditions for the Reaction of Mandelic Acids with Alkynes a

OH COOH + COOH + COOH - Catalyst, additive					
1a		2a		3a	Ph
1a		2a		3a	
entry	catalyst	additive ^b		solvent	yield (%) ^e
1	$Pd(OAc)_2$			toluene	0
2	$Pd(PPh_3)_4$			toluene	0
3	$Pd(dba)_2$			toluene	0
4	(PPh ₃) ₃ RhCl			toluene	0
5	$[Rh(COD)Cl]_2$			toluene	0
6	$[IrCp*Cl_2]_2$			toluene	0
7	$[Ru(COD)Cl_2]_n$			toluene	0
8	[RuCl ₂ (p- cymene)] ₂			toluene	0
9	$[RhCp*Cl_2]_2$			toluene	23

AgSbF₆

AgSbF₆

AgSbF₆

AgSbF₆

AgSbF₆

AgSbF₆

AgSbF₆

AgSbF₆

 $Cu(OAc)_2$

CuCl

CuI

CuCl

 $Cu(OAc)_2$

 $Cu(OAc)_2$

Cu(OAc)₂

 $Cu(OAc)_2$

10

11

12

13

14

15

16

17

18

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

[RhCp*Cl₂]₂

19^d [RhCp*Cl₂]₂ AgSbF₆ $Cu(OAc)_2$ CH₃CN 0 20^{*d*} [RhCp*Cl₂]₂ AgSbF₆ $Cu(OAc)_2$ DCE 0 21^d [RhCp*Cl₂]₂ AgSbF₆ $Cu(OAc)_2$ Dioxane 0 ^aReaction conditions: 1a (0.1 mmol), 2a (0.12 mmol), catalyst (10 mol %) in 1 mL of toluene in air at 120 °C for 20 h. ^bAdditive (silver salt: 10 mol %, copper salt: 20 mol %). ^cReaction time: 30 h. ^dReaction temperature: 100 °C. ^eIsolated yields.

salts were tested as additives. When 10 mol % AgSbF₆ and 20 mol % Cu(OAc)₂ were used, the yield of **3a** increased to 63% (entry 11). Other copper salts, such as CuCl, CuI, or CuCl₂, did not improve the reaction efficiency (entries 12–14). Further experiments showed that [RhCp*Cl₂]₂, AgSbF₆, and Cu(OAc)₂ are all indispensable for the reaction. In the absence of AgSbF₆, **3a** was obtained in only 25% yield (entry 15) and the reaction did not proceed when AgSbF₆ and Cu(OAc)₂ were used in the absence of [RhCp*Cl₂]₂ (entry16).

Prolonging the reaction time to 30 h, with $[RhCp*Cl_2]_{2\nu}$ AgSbF₆, and Cu(OAc)₂, did not result in an increase in the yield (entry17). Several other solvents, such as xylene, CH₃CN, dichloroethene (DCE), and dioxane, were also tested for this oxidative decarboxylative annulation reaction. Xylene gave a similar yield (60%) to toluene (entry 18). When CH₃CN, DCE, or dioxane was used as the solvent at different temperatures, no products were observed (entries 19–21). So, 10 mol % [RhCp*Cl₂]₂ in combination with 10 mol % AgSbF₆ and 20 mol % Cu(OAc)₂ in toluene was selected as the optimal catalyst system for this oxidative decarboxylation annulation reaction.

Given the importance of phosphine ligands,¹¹ a series of phosphine ligands were examined for the oxidative decarboxylation annulation reaction (Table 2). Initially, some bidentate chelate phosphine ligands, such as 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), rac-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (rac-

Table 2. Optimization of Reaction Conditions for Ligands^a



^{*a*}Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $[RhCp*Cl_2]_2$ (10 mol %), AgSbF₆ (10 mol %), and Cu(OAc)₂ (20 mol %) in 1 mL of toluene in air at 120 °C for 20 h. ^{*b*}Phoshine ligand: 10 mol %. ^{*c*}Isolated yields.

BINAP), and 1,1'-bis(diphenylphosphino)ferrocene (DPPF), were examined for the reaction. The product yields of the reactions with these ligands increased slightly (64–68%, entries 1–4, Table 3). The use of PPh₃ as a ligand also slightly improved the reaction yield to 66% (entry 5). The electron-deficient phosphine ligand P(C_6F_5)₃ gave a yield of 70% (entry

6), and the electron-rich phosphine ligand $(CH_3OC_6H_4)_3P$ improved the reaction yield to 76% (entry 7). The most favorable ligand was PCy₃, which gave the desired product in 85% yield (entry 8). Therefore, the combination of $[RhCp*Cl_2]_2$ and PCy₃ ligand in the presence of AgSbF₆ and Cu(OAc)₂ was selected as the optimized catalytic system for the current transformation.

Next, the reactions of 1a with various 1,2-diphenylethynes bearing electron-donating or electron-withdrawing groups were investigated under the optimized reaction conditions, and the results are shown in Table 3. When 1a reacted with 1,2diphenylethyne (2a), the desired product 3a was obtained in 85% yield. The 1,2-diphenylethynes with methyl substituents in different positions were well-tolerated and afforded the corresponding products 3b-d in good yields (90%, 80%, and 76%, respectively). As a result of the regioselectivity of the reaction, 3c is the major product (ratio of 3c and 3c': 4:1). Various alkoxy-substituted 1,2-diphenylethynes were also tested in the reaction, and they gave 3e-g in good yields (83%, 86%, and 85%, respectively). The regioselective ratio of 3e and 3e' was 3:2. The reaction of 1a with the 1,2-diphenylethyne bearing a tertiary-butyl group proceeded smoothly to give 3h in 87% yield. The corresponding products 3i-m were obtained in 79-83% yields when 1a was reacted with 1,2-diphenylethynes bearing -F, -Cl, or -Br groups. The major products were 3i,

Table 3. Decarboxylative Coupling and Annulation Reactions of Mandelic Acids with Alkynes^a



"Reaction conditions: 1 (0.1 mmol), 2 (0.12 mmol), $[RhCp*Cl_2]_2$ (10 mol %), $AgSbF_6$ (10 mol %), $PCy_3(10 \text{ mol }\%)$, and $Cu(OAc)_2$ (20 mol %) in 1 mL of toluene at 120 °C under air for 20 h; isolated yields. Numbers in parentheses are the ratio of regioisomers (3:3').

3j, and **3k** with regioselective ratios of 7:2, 3:1, and 4:1, respectively. These halide-substituted products can be further modified to give complex useful products.¹²

The 1,2-diphenylethynes with an electron-withdrawing group, such as $-CF_3$ or $-OCF_3$, also gave the desired products **3n** and **3o** in 77% and 75% yields, respectively. However, the yield for the 1,2-diphenylethyne bearing an ester group in the para-position decreased slightly to 60% (**3p**). The 1,2-diphenylethynes with an ester group in the ortho-position also had a lower yield (55% for product **3q**). The lower yields for these substrates may be due to the side reactions that can occur from the competitive complexion of the ester groups to the rhodium metal centers. Other types of alkynes, such as 1,2-di(naphthalen-1-yl)ethyne, also gave the corresponding product **3r** in 72% yield.

The effects of substituents on mandelic acid were also studied (Table 3). Mandelic acid with a methyl group reacted with alkyne 2a to give 3s in 80% yield. A –Ph- or a 1-naphthyl-group-substituted mandelic acid reacted with alkyne 2a and afforded the desired product 3t or 3u in 75% or 72% yield. Mandelic acid bearing a methoxy or a –Br group also reacted to give the desired product 3v or 3w in 65% and 70% yields, respectively.

On the basis of these experimental results and previous reports,¹³ a plausible mechanism for the decarboxylative annulation reactions of mandelic acids with alkynes is proposed in Figure 1. First, the catalytically active species [LRhCp*-



Figure 1. Mechanism for the decarboxylative annulation reactions of mandelic acids with alkynes.

 $(OAc)_2$] is generated from the reaction of $[RhCp*Cl_2]_2$ and $AgSbF_6$ in the presence of $Cu(OAc)_2$ and the PCy_3 ligand. The reaction then begins with the oxidation of 1a to 2-oxo-2-phenylacetic acid (A) by O_2 from the air in the presence of $Cu(OAc)_2$. Next, the ligand exchange of $[LRhCp*(OAc)_2]$ with A generates intermediate B. The intramolecular C–H bond activation in B followed by the release of HOAc then

gives rhodacyclic intermediate C. The decarboxylation of intermediate C gives the four-membered rhodacyclic intermediate D and CO₂. The replacement of the ligand by the alkyne produces intermediate E, and further intramolecular insertion of the alkyne into the Rh–C bond generates intermediate F. Subsequently a reductive elimination occurs to give the Rh(I) species and the product 3. Finally, the Rh(I) species is oxidized by O₂ in the presence of copper(II) to regenerate the catalytically active species [LRhCp*(OAc)₂], which then is used in another catalytic cycle.

CONCLUSION

In summary, a rhodium-catalyzed oxidative decarboxylative annulation of mandelic acids with alkynes has been developed. Various substituted indenones were obtained in medium to good yields under the optimized reaction conditions. A plausible catalytic mechanism involving intramolecular C-H activation, decarboxylation, and annulation has been proposed. The current method opens up a straightforward one-step synthetic pathway for various indenones from mandelic acids and alkynes.

EXPERIMENTAL SECTION

General Information. ¹H NMR, ¹⁹F NMR, and ¹³C NMR were obtained on a 400 MHz spectrometer with CDCl₃ as solvent. The chemical shifts are reported in ppm relative to CDCl₃ (δ = 7.26) for ¹H NMR and relative to the central CDCl₃ resonance (δ = 77.0) for ¹³C NMR. For ¹⁹F NMR, (trifluoromethyl)benzene was used as an external standard. NMR data of known compounds are in agreement with literature values. Coupling constants (*J*) are quoted in Hz at 400 MHz for ¹H. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Infrared spectra were recorded on a PerkinElmer 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.

Materials and Methods. Unless otherwise noted, all reactions were performed under an atmosphere of air with oven-dried glassware and anhydrous solvents. Reactions were monitored by analytical thinlayer chromatography on 0.20 mm silica gel plates, and spots were detected by UV absorption. Silica gel (200–300 mesh) (from Yantai Huagong Chem. Company, Ltd.) was used for flash chromatography. The starting materials, various mandelic acids and 1,2-diphenylethynes, were synthesized and purified according to the literature procedures.¹⁴ Other chemicals or reagents were obtained from commercial sources.

Experimental Procedure for the Rh-Catalyzed Synthesis of Indenones via Mandelic Acids and Alkynes. To an oven-dried screw-top vial were added substituted mandelic acid (0.1 mmol), substituted alkyne (0.12 mmol), $[RhCp*Cl_2]_2$ (0.01 mmol, 6.18 mg), PCy_3 (0.01 mmol, 2.80 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-Oxo-2-phenylacetic acid (A): Mandelic acid (0.1 mmol, 15.2 mg), [RhCp*Cl₂]₂ (0.01 mmol, 6.18 mg), AgSbF₆ (0.01 mmol, 3.44 mg), Cu(OAc)₂ (0.02 mmol, 3.99 mg), and toluene (1 mL) were used. The mixture was stirred at 120 °C for 10 h under air. Organic solvents were removed *in vacuo*, and then the residue was purified by a silica gel column chromatography to give a white solid (13.8 mg, yield 92%). ¹H NMR (C₂D₆SO, 400 MHz): δ 7.88 (d, *J* = 7.12 Hz, 2H), 7.70 (t, *J* = 7.40 Hz, 1H), 7.57 (t, *J* = 7.60 Hz, 2H). ¹³C NMR (C₂D₆SO, 100 MHz): δ 191.98, 168.24, 134.71, 133.27, 129.71, 129.43. IR (KBr): ν 3441, 3060, 2463, 1683, 1591, 1229, 983, 712, 679 cm⁻¹. Anal. Found (calcd) for C₈H₆O₃: C, 64.01 (64.00); H, 4.02 (4.03).

2,3-Diphenyl-1H-inden-1-one (3a): This was purified by column chromatography to provide a red solid (24.0 mg, yield 85%). The compound 3a is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report. ¹⁵ ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, J = 6.97 Hz, 1H), 7.44–7.37 (m, 6H), 7.33–7.27 (m, 6H), 7.17 (d, J = 7.21 Hz, 1H). ¹³C NMR (CDCl₃, 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 3741, 3438, 3064, 2920, 2357, 1707, 1612, 1453, 1351, 1182, 1071, 914, 842, 701 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₄O: C, 89.35 (89.34); H, 5.00 (5.00).

2,3-Di-p-tolyl-1H-inden-1-one (**3b**): This was purified by column chromatography to provide a red solid (27.9 mg, yield 90%). The compound **3b** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report. ¹⁵ ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (d, J = 6.98 Hz, 1H), 7.37–7.28 (m, 4H), 7.25–7.16 (m, 5H), 7.11 (d, J = 7.78 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.67, 154.71, 145.38, 139.27, 137.44, 133.23, 131.97, 130.86, 129.83, 129.79, 129.40, 129.34, 128.77, 128.65, 128.42, 127.92, 122.71, 121.06, 21.46, 21.29. IR (KBr): ν 3621, 2923, 1710, 1603, 1508, 1496, 1349, 1190, 1070, 1021, 819, 742 cm⁻¹. Anal. Found (calcd) for C₂₃H₁₈O: C, 88.98 (89.00); H, 5.84 (5.85).

2-(2,6-Dimethylphenyl)-3-phenyl-1H-inden-1-one (3c): This was purified by column chromatography to provide a red solid (19.8 mg, yield 64%). Mp: 128–130 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.62 (d, *J* = 6.86 Hz, 1H), 7.37 (d, *J* = 6.49 Hz, 3H), 7.32–7.27 (m, 4H), 7.22–7.13 (m, 3H), 6.86 (d, *J* = 7.04 Hz, 1H), 2.39 (s, 3H), 2.05 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.68, 156.08, 146.01, 135.63, 133.63, 132.43, 131.26, 130.73, 130.36, 129.62, 129.02, 128.82, 128.04, 127.67, 122.64, 121.23, 20.99, 19.35. IR (KBr): ν 3451, 2924, 2857, 1708, 1603, 1494, 1457, 1343, 1265, 1173, 1080, 1027, 813, 756, 685 cm⁻¹. HRMS calcd for C₂₃H₁₈O: 310.1358, found 310.1357. Anal. Found (calcd) for C₂₃H₁₈O: C, 89.01 (89.00); H, 5.84 (5.85).

3-(2,6-Dimethylphenyl)-2-phenyl-1H-inden-1-one (3c'): This was purified by column chromatography to provide a red solid (5.0 mg, yield 16%). Mp: 128–130 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.60 (d, J = 6.82 Hz, 1H), 7.38–7.33 (m, 3H), 7.31–7.24 (m, 4H), 7.18–7.11 (m, 3H), 6.84 (d, J = 7.78 Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.70, 156.10, 146.04, 135.64, 133.64, 132.50, 132.45, 132.29, 131.28, 130.73, 130.38, 129.62, 129.03, 128.83, 128.15, 128.04, 127.68, 122.65, 121.24, 21.00, 19.35. IR (KBr): ν 3451, 2924, 2857, 1708, 1603, 1494, 1457, 1343, 1265, 1173, 1080, 1027, 813, 756, 685 cm⁻¹. Anal. Found (calcd) for C₂₃H₁₈O: C, 89.02 (89.00); H, 5.85 (5.85).

2,3-Di-m-tolyl-1H-inden-1-one (**3d**): This was purified by column chromatography to provide a red solid (23.6 mg, yield 76%). The compound **3d** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report. ¹⁶ ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (d, J = 7.78 Hz, 1H), 7.38–7.34 (m, 1H), 7.31–7.27 (m, 2H), 7.22–7.06 (m, 6H), 6.95 (d, J = 7.53 Hz, 1H), 6.89 (d, J = 7.14 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.20, 157.55, 145.88, 137.06, 135.92, 135.79, 133.47, 132.25, 130.97, 130.69, 130.53, 130.23, 128.85, 128.82, 128.10, 125.77, 125.35, 122.84, 121.45, 20.62, 20.14. IR (KBr): ν 3566, 2923, 1709, 1607, 1456, 1337, 1258, 1175, 1068, 1036, 926, 851, 743 cm⁻¹. Anal. Found (calcd) for C₂₃H₁₈O C, 89.02 (89.00); H, 5.84 (5.85).

2-(3-Methoxyphenyl)-3-phenyl-1H-inden-1-one (**3e**): This was purified by column chromatography to provide a red solid (15.6 mg, yield 50%). Mp: 154–156 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, J = 6.72 Hz, 1H), 7.44–7.33 (m, 3H), 7.31–7.28 (m, 5H), 7.21 (d, J = 6.78 Hz, 1H), 7.01–6.96 (m, 2H), 6.93–6.92 (m, 1H), 3.74 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.44, 159.72, 155.14, 145.18, 133.97, 133.44, 132.49, 130.74, 130.71, 129.93, 129.91, 128.93, 128.04, 127.75, 122.95, 121.29, 120.82, 115.13, 113.73, 55.20. IR (KBr): ν 3676, 3058, 2933, 2838, 2362, 1710, 1595, 1453, 1344, 1286, 1249, 1175, 1043, 752, 698 cm⁻¹. HRMS: calcd for C₂₂H₁₆O₂ C, 84.57 (84.59); H, 5.16 (5.16).

3-(3-Methoxyphenyl)-2-phenyl-1H-inden-1-one (3e'): This was purified by column chromatography to provide a red solid (10.3 mg,

yield 33%). Mp: 154–156 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (d, *J* = 7.01 Hz, 1H), 7.43–7.36 (m, 6H), 7.31–7.27 (m, 1H), 7.19–7.13 (m, 2H), 6.88 (d, *J* = 7.69 Hz, 1H), 6.81–6.79 (m, 2H), 3.64 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.32, 159.09, 155.55, 145.16, 133.43, 132.74, 132.18, 131.93, 130.71, 129.27, 129.04, 128.98, 128.77, 128.44, 122.95, 122.47, 121.27, 114.88, 114.08, 54.99. IR (KBr): ν 3676, 3058, 2933, 2838, 2362, 1710, 1595, 1453, 1344, 1286, 1249, 1175, 1043, 752, 698 cm⁻¹. Anal. Found (calcd) for C₂₂H₁₆O₂: C, 84.58 (84.59); H, 5.17 (5.16).

2,3-Bis(4-methoxyphenyl)-1H-inden-1-one (**3f**): This was purified by column chromatography to provide a red solid (29.4 mg, yield 86%). The compound **3f** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁵ ¹H NMR (CDCl₃, 400 MHz): δ 7.58 (d, J = 6.89 Hz, 1H), 7.40–7.37 (m, 3H), 7.31–7.27 (m, 3H), 7.20 (d, J = 7.25 Hz, 1H), 6.97 (d, J = 8.71 Hz, 2H), 6.85 (d, J = 8.81 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.95, 160.29, 159.09, 153.75, 145.49, 133.22, 131.50, 131.26, 131.03, 130.16, 128.58, 127.12, 125.13, 123.43, 122.68, 120.92, 114.20, 113.67, 55.17. IR (KBr): ν3451, 2924, 2363, 1703, 1607, 1506, 1458, 1293, 1249, 1177, 1028, 789 cm⁻¹. Anal. Found (calcd) for C₂₃H₁₈O₃: C, 80.69 (80.68); H, 5.31 (5.30).

2,3-Bis(4-ethoxyphenyl)-1H-inden-1-one (**3g**): This was purified by column chromatography to provide a red solid (31.5 mg, yield 85%). The compound **3g** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁶ ¹H NMR (CDCl₃, 400 MHz): δ 7.58–7.56 (m, 1H), 7.39–7.35 (m, 3H), 7.29–7.24 (m, 3H), 7.19 (d, *J* = 7.22 Hz, 1H), 6.95–6.91 (m, 2H), 6.83–6.81 (m, 2H), 4.12–4.02 (m, 4H), 1.49–1.41 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.96, 159.69, 158.47, 153.73, 153.73, 145.52, 133.18, 131.24, 131.06, 130.15, 128.53, 124.97, 123.29, 122.63, 120.91, 114.65, 114.16, 63.51, 63.32, 14.82, 14.79. IR (KBr): ν 3577, 2976, 2928, 2365, 1706, 1607, 1464, 1343, 1292, 1176, 1078, 1041, 920, 825, 767, 665 cm⁻¹. Anal. Found (calcd) for C₂₅H₂₂O₃: C, 81.06); H, 6.00 (5.99).

2,3-Bis(4-tert-butylphenyl)-1H-inden-1-one (**3h**): This was purified by column chromatography to provide a red solid (34.3 mg, yield 87%). The compound **3h** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.60 (d, J = 7.06 Hz, 1H), 7.47 (d, J = 8.49 Hz, 2H), 7.40–7.33 (m, 4H), 7.32–7.28 (m, 4H), 7.19 (d, J = 7.21 Hz, 1H), 1.41 (s, 9H), 1.35 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.86, 154.63, 152.36, 150.46, 145.55, 133.21, 131.74, 130.87, 129.84, 129.53, 128.59, 128.24, 127.87, 125.54, 124.93, 122.66, 121.21, 34.81, 34.55, 31.23, 31.16. IR (KBr): ν 3455, 2527, 1638, 1412, 1389, 1168, 1107, 1055, 1025, 947, 894, 756 cm⁻¹. Anal. Found (calcd) for C₂₉H₃₀O: C, 88.29 (88.28); H, 7.65 (7.66).

2-(4-Fluorophenyl)-3-phenyl-1H-inden-1-one (**3i**): This was purified by column chromatography to provide a red solid (18.6 mg, yield 62%). The compound **3i** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁸ ¹H NMR (CDCl₃, 400 MHz): δ 7.62 (d, *J* = 7.01 Hz, 1H), 7.43–7.38 (m, 3H), 7.34–7.27 (m, 6H), 7.16–7.11 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.20, 163.08 (d, J = 248 Hz), 154.16, 145.00, 133.45, 132.60, 131.76, 130.58, 130.50, 129.92, 129.05, 128.40, 128.16, 127.87, 123.05, 121.02, 116.02 (d, *J* = 22 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ –110.74 (s, 1F). IR (KBr): ν 3694, 3059, 2925, 2362, 1708, 1603, 1508, 1455, 1345, 1230, 1158, 1072, 850, 756, 703 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃FO: C, 83.96 (83.98); H, 4.37 (4.36).

3-(4-Fluorophenyl)-2-phenyl-1H-inden-1-one (**3i**'): This was purified by column chromatography to provide a red solid (5.4 mg, yield 18%). The compound **3i**' is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁸ ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, J = 6.99 Hz, 1H), 7.47–7.44 (m, 3H), 7.42–7.38 (m, 3H), 7.33–7.27 (m, 3H), 7.16 (d, J= 7.21 Hz, 1H), 7.00–6.96 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.39, 162.31 (d, J = 246 Hz), 155.24, 145.14, 133.51, 132.56, 131.77, 131.69, 131.33, 130.61, 129.40, 129.02, 128.88, 128.41, 123.02, 121.28, 115.19 (d, J = 21 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ –113.36 (s, 1F). IR (KBr): ν 3694, 3059, 2925, 2362, 1708, 1603, 1508, 1455, 1345, 1230, 1158, 1072, 850, 756, 703 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃FO: C, 83.97 (83.98); H, 4.37 (4.36).

2-(4-Chlorophenyl)-3-phenyl-1H-inden-1-one (**3***j*): This was purified by column chromatography to provide a red solid (19.6 mg, yield 62%). The compound **3***j* is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁸ ¹H NMR (CDCl₃, 400 MHz): δ 7.62 (d, *J* = 6.93 Hz, 1H), 7.43–7.39 (m, 3H), 7.36–7.24 (m, 8H), 7.14 (d, *J* = 7.19 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.10, 153.82, 144.78, 135.19, 133.50, 132.75, 131.09, 130.36, 129.92, 129.88, 129.14, 129.09, 128.35, 128.18, 127.94, 123.13, 120.98. IR (KBr): ν 3676, 2923, 2363, 1710, 1489, 1346, 1180, 1091, 1016, 848, 759 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃CIO: C, 79.64 (79.62); H, 4.13 (4.14).

3-(4-Chlorophenyl)-2-phenyl-1H-inden-1-one (**3***j*'): This was purified by column chromatography to provide a red solid (6.6 mg, yield 21%). The compound **3***j*' is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁸ ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, *J* = 6.98 Hz, 1H), 7.47–7.45 (m, 3H), 7.42–7.38 (m, 3H), 7.34–7.30 (m, 1H), 7.28– 7.22 (m, 4H), 7.17 (d, *J* = 7.18 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.12, 155.73, 144.97, 133.70, 133.53, 132.38, 131.21, 131.07, 130.58, 129.50, 129.17, 129.13, 128.91, 128.35, 123.05, 121.39. IR (KBr): ν 3676, 2923, 2363, 1710, 1489, 1346, 1180, 1091, 1016, 848, 759 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃ClO: C, 79.63 (79.62); H, 4.13 (4.14).

2-(4-Bromophenyl)-3-phenyl-1H-inden-1-one (**3k**): This was purified by column chromatography to provide a red solid (23.8 mg, yield 66%). The compound **3k** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁹ ¹H NMR (CDCl₃, 400 MHz): δ 7.60 (d, J = 6.98 Hz, 1H), 7.56 (d, J = 8.46 Hz, 2H), 7.42–7.39 (m, 2H), 7.32–7.27 (m, 7H), 7.13 (d, J = 7.23 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.10, 153.84, 144.76, 133.51, 132.79, 132.10, 131.61, 130.57, 130.37, 130.15, 129.89, 129.11, 128.20, 127.97, 123.48, 123.15, 120.99. IR (KBr): ν3060, 2924, 2360, 1709, 1597, 1487, 1455, 1346, 1182, 1071, 1013, 917, 845, 697 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃BrO: C, 69.84 (69.82); H, 3.62 (3.63).

3-(4-Bromophenyl)-2-phenyl-1H-inden-1-one (**3**k'): This was purified by column chromatography to provide a red solid (6.1 mg, yield 17%). The compound **3**k' is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁹ ¹H NMR (CDCl₃, 400 MHz): δ 7.58 (d, *J* = 8.14 Hz, 1H), 7.44–7.42 (m, 3H), 7.40–7.36 (m, 5H), 7.32–7.28 (m, 1H), 7.15 (d, *J* = 8.50 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.03, 155.79, 145.00, 133.55, 132.40, 131.50, 131.30, 131.13, 130.60, 129.66, 129.51, 129.16, 128.93, 128.34, 123.07, 122.07, 121.41. IR (KBr): ν 3060, 2924, 2360, 1709, 1597, 1487, 1455, 1346, 1182, 1071, 1013, 917, 845, 697 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃BrO: C, 69.83 (69.82); H, 3.62 (3.63).

2,3-Bis(4-chlorophenyl)-1H-inden-1-one (3l): This was purified by column chromatography to provide a red solid (27.7 mg, yield 79%). The compound 3l is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, J = 6.93 Hz, 1H), 7.45–7.39 (m, 3H), 7.35–7.31 (m, 3H), 7.29–7.27 (m, 2H), 7.23–7.20 (m, 2H), 7.14 (d, J = 7.21 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.76, 154.27, 144.63, 135.51, 134.03, 133.67, 133.64, 131.52, 131.18, 130.84, 130.47, 129.83, 129.33, 129.31, 128.53, 123.26, 121.16. IR (KBr): ν 3531, 2963, 2872, 2360, 1725, 1604, 1462, 1391, 1288, 1120, 1084, 1016, 965, 863, 725, 658 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₂Cl₂O: C, 71.82 (71.81); H, 3.44 (3.44).

2,3-Bis(4-bromophenyl)-1H-inden-1-one (**3m**): This was purified by column chromatography to provide a red solid (35.0 mg, yield 80%). The compound **3m** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.62–7.58 (m, 2H), 7.47–7.38 (m, 4H), 7.35–7.27 (m, 4H), 7.18–7.12 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.61, 154.28, 144.52, 133.63, 132.27, 132.08,

131.45, 131.42, 130.42, 130.00, 129.88, 129.79, 129.32, 123.77, 123.24, 122.35, 121.14. IR (KBr): ν 3062, 2924, 2852, 1711, 1605, 1458, 1342, 1265, 1182, 1068, 1010, 922, 831, 766, 677 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₂Br₂O: C, 57.29 (57.31); H, 2.76 (2.75).

2,3-Bis(4-(trifluoromethyl)phenyl)-1H-inden-1-one (**3***n*): This was purified by column chromatography to provide a red solid (32.2 mg, yield 77%). The compound **3n** is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.72 (d, *J* = 8.04 Hz, 2H), 7.64 (d, *J* = 6.98 Hz, 1H), 7.55–7.50 (m, 4H), 7.45–7.41 (m, 1H), 7.37–7.34 (m, 3H), 7.12 (d, *J* = 7.17 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.28, 155.01, 144.30, 135.93, 133.89, 133.80, 131.54 (q, *J* = 32 Hz), 130.20, 130.15, 129.77, 128.82, 126.09 (q, *J* = 3.70 Hz), 125.21 (q, *J* = 3.70 Hz), 123.97 (q, *J* = 269 Hz), 123.72 (q, *J* = 271 Hz), 123.61, 121.44. ¹⁹F NMR (376 MHz, CDCl₃): δ –62.77 (s, 3F), –62.86 (s, 3F). IR (KBr): ν 3624, 2920, 2362, 1710, 1603, 1457, 1340, 1273, 1182, 1071, 1027, 914, 846, 757, 692 cm⁻¹. Anal. Found (calcd) for C₂₃H₁₂F₆O: C, 66.02 (66.04); H, 2.88 (2.89).

2,3-Bis(4-(trifluoromethoxy)phenyl)-1H-inden-1-one (**30**): This was purified by column chromatography to provide a red solid (33.8 mg, yield 75%). Mp: 95–97 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, *J* = 7.02 Hz, 1H), 7.44–7.39 (m, 3H), 7.35–7.27 (m, 5H), 7.15–7.12 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.76, 154.26, 149.34 (q, *J* = 101 Hz), 144.58, 133.72, 131.45, 131.36, 130.85, 130.35, 130.13, 129.43, 128.93, 123.36, 121.25, 120.59, 120.37 (q, *J* = 256 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ –57.73 (s, 6F). IR (KBr): ν 3567, 2920, 2362, 1713, 1612, 1410, 1347, 1262, 1171, 1019, 922, 830, 743, 696 cm⁻¹. HRMS: calcd for C₂₃H₁₂F₆O₃ 450.0691, found 450.0687. Anal. Found (calcd) for C₂₃H₁₂F₆O₃: C, 61.35 (61.34); H, 2.68 (2.69).

Diethyl 4,4'-(1-oxo-1H-indene-2,3-diyl)dibenzoate (**3***p*). This was purified by column chromatography to provide a red solid (25.6 mg, yield 60%). Mp: 131–133 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.11– 8.09 (m, 2H), 7.95–7.92 (m, 2H), 7.63 (d, *J* = 6.82 Hz, 1H), 7.45– 7.39 (m, 3H), 7.36–7.30 (m, 3H), 7.13 (d, *J* = 7.21 Hz, 1H), 4.44– 4.33 (m, 4H), 1.43–1.36 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 194.35, 165.87, 155.49, 144.54, 140.78, 136.91, 134.93, 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 3579, 2926, 2367, 1717, 1605, 1458, 1367, 1276, 1182, 1073, 1021, 925, 833, 768, 708 cm⁻¹. HRMS: calcd for C₂₇H₂₂O₅ 426.1467, found 426.1461. Anal. Found (calcd) for C₂₇H₂₂O₅: C, 76.06 (76.04); H, 5.19 (5.20).

Dimethyl 2,2'-(1-oxo-1H-indene-2,3-diyl)dibenzoate (**3q**): This was purified by column chromatography to provide a red solid (21.9 mg, yield 55%). Mp: 180–182 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.09–8.06 (m, 1H), 8.00–7.97 (m, 1H), 7.58–7.56 (m, 1H), 7.45–7.42 (m, 2H), 7.33–7.28 (m, 3H), 7.25–7.22 (m, 2H), 7.06–7.04 (m, 1H), 6.72 (d, J = 7.17 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.14, 167.59, 167.14, 155.01, 146.25, 134.79, 134.12, 133.43, 132.71, 132.26, 131.69, 131.41, 131.14, 130.38, 130.24, 130.00, 128.82, 128.33, 127.81, 123.03, 119.95, 52.25, 52.13. IR (KBr): ν 3667, 2950, 2362, 1721, 1669, 1436, 1345, 1271, 1187, 1075, 1040, 925, 853, 760, 681 cm⁻¹. HRMS: calcd for C₂₅H₁₈O₅ 398.1154, found 398.1152. Anal. Found (calcd) for C₂₅H₁₈O₅: C, 75.35 (75.37); H, 4.56 (4.55).

2,3-Di(naphthalen-1-yl)-1H-inden-1-one (**3r**): This was purified by column chromatography to provide a red solid (27.5 mg, yield 72%). Mp: 252–254 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.97 (d, *J* = 8.31 Hz, 1H), 7.89–7.70 (m, 6H), 7.57–7.42 (m, 3H), 7.38–7.28 (m, 5H), 7.22–7.07 (m, 2H), 6.86–6.76 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.17, 146.19, 141.26, 137.00, 135.03, 133.64, 133.49, 133.49, 130.49, 129.39, 129.06, 128.52, 128.19, 127.75, 126.20, 126.18, 126.09, 126.04, 126.01, 125.96, 125.93, 125.87, 125.80, 125.77, 125.76, 125.57, 125.52, 125.48, 123.03, 122.16. IR (KBr): *ν* 3534, 2927, 1710, 1597, 1456, 1328, 1259, 1178, 1080, 1021, 967, 775, 695 cm⁻¹. HRMS: calcd for C₂₉H₁₈O 382.1358, found 382.1355. Anal. Found (calcd) for C₂₉H₁₈O: C, 91.05 (91.07); H, 4.75 (4.74).

5-Methyl-2,3-diphenyl-1H-inden-1-one (3s): This was purified by column chromatography to provide a red solid (23.7 mg, yield 80%). Mp: 174–176 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.51 (d, J = 7.27 Hz, 1H), 7.45–7.43 (m, 3H), 7.41–7.38 (m, 2H), 7.29–7.27 (m, 5H),

7.10 (d, J = 7.29 Hz, 1H), 6.96 (s, 1H), 2.38 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.16, 154.92, 145.71, 144.37, 132.89, 132.80, 130.87, 129.96, 129.13, 128.91, 128.76, 128.50, 128.37, 128.00, 127.64, 123.04, 122.51, 22.08. IR (KBr): ν 3572, 2921, 2360, 1703, 1602, 1468, 1357, 1274, 1187, 1070, 1034, 921, 837, 733, 695 cm⁻¹. Anal. Found (calcd) for C₂₂H₁₆O: C, 89.17 (89.16); H, 5.44 (5.44).

2,3,6-Triphenyl-1H-inden-1-one (**3***t*): This was purified by column chromatography to provide a red solid (26.9 mg, yield 75%). Mp: 181–183 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.89 (d, *J* = 1.72 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.45–7.38 (m, 7H), 7.33–7.21 (m, 8H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.28, 155.38, 143.99, 142.25, 139.91, 132.80, 131.66, 131.56, 130.78, 129.96, 129.35, 128.93, 128.81, 128.50, 128.09, 127.89, 127.77, 126.77, 121.94, 121.60. IR (KBr): ν 3361, 2925, 1707, 1603, 1464, 1345, 1260, 1078, 967, 844, 767, 728, 697 cm⁻¹. HRMS: calcd for C₂₇H₁₈O 358.1358, found 358.1365. Anal. Found (calcd) for C₂₇H₁₈O: *C*, 90.46 (90.47); H, 5.07 (5.06).

6-(Naphthalen-1-yl)-2,3-diphenyl-1H-inden-1-one (**3***u*): This was purified by column chromatography to provide a red solid (29.4 mg, yield 72%). Mp: 194–196 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.91–7.86 (m, 3H), 7.75–7.70 (m, 1H), 7.52–7.37 (m, 7H), 7.35–7.23 (m, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.11, 154.98, 146.40, 145.50, 139.28, 133.71, 133.11, 132.56, 131.20, 130.75, 130.44, 129.99, 129.64, 129.26, 128.79, 128.50, 128.48, 128.39, 128.08, 127.79, 126.61, 126.39, 125.99, 125.52, 125.26, 123.25, 122.90. IR (KBr): ν 2926, 2845, 1727, 1601, 1464, 1377, 1262, 1160, 1033, 809, 780, 753 cm⁻¹. HRMS: calcd for C₃₁H₂₀O 408.1514, found 408.1521. Anal. Found (calcd) for C₃₁H₂₀O: C, 91.17 (91.15); H, 4.93 (4.94).

5-Methoxy-2,3-diphenyl-1H-inden-1-one (**3**ν): This was purified by column chromatography to provide a red solid (20.3 mg, yield 65%). The compound **3**v is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.54 (d, J = 7.24 Hz, 1H), 7.41–7.36 (m, 5H), 7.25–7.22 (m, 5H), 6.81–6.79 (m, 2H), 3.86 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.21, 164.70, 153.39, 148.31, 130.62, 129.28, 128.72, 128.44, 128.02, 127.82, 125.99, 123.16, 110.70, 110.59, 55.83. IR (KBr): ν 3568, 2957, 2856, 2362, 1706, 1610, 1478, 1349, 1273, 1222, 1071, 1023, 791, 738, 698 cm⁻¹. Anal. Found (calcd) for C₂₂H₁₆O₂: C, 84.61 (84.59); H, 5.15 (5.16).

5-Bromo-2,3-diphenyl-1H-inden-1-one (**3***w*): This was purified by column chromatography to provide a red solid (25.2 mg, yield 70%). The compound **3***w* is known, and the ¹H NMR and the ¹³C NMR spectra of the compound are in agreement with a previous report.¹⁷ ¹H NMR (CDCl₃, 400 MHz): δ 7.46–7.42 (m, 5H), 7.37–7.34 (m, 2H), 7.27–7.26 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 195.18, 154.14, 147.28, 133.40, 132.18, 131.62, 129.97, 129.56, 129.34, 128.99, 128.36, 128.13, 128.07, 124.69, 124.07. IR (KBr): *ν* 3558, 3060, 2957, 2925, 2853, 1712, 1602, 1485, 1443, 1351, 1262, 1064, 1028, 785 cm⁻¹. Anal. Found (calcd) for C₂₁H₁₃BrO: C, 69.83 (69.82); H, 3.63 (3.63).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00004.

NMR spectra of products (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail (J. Wang): wjh@tju.edu.cn. *E-mail (G. Liu): guiyanliu2013@163.com.

ORCID 🔍

Xiaobo Yu: 0000-0002-0168-1165

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the NSFC (21572155, 21372175).

REFERENCES

 (1) (a) Larock, R. C.; Doty, M. J. J. Org. Chem. 1993, 58, 4579-4583.
 (b) Harada, Y.; Nakanishi, J.; Fujihara, H.; Tobisu, M.; Fukumoto, Y.; Chatani, N. J. Am. Chem. Soc. 2007, 129, 5766-5771. (c) Irvine, S.; Kerr, W. J.; McPherson, A. R.; Pearson, C. M. Tetrahedron 2008, 64, 926-935. (d) Hussain, M.; Hung, N. T.; Khera, R. A.; Villinger, A.; Langer, P. Tetrahedron Lett. 2011, 52, 184-187. (e) Zhang, J.-L.; Yang, F.; Wu, Y.-J. Appl. Organomet. Chem. 2011, 25, 675-679.

(2) Sartori, G.; Maggi, R. Advances in Friedel-Crafts Acylation Reactions; CRC Press: Boca Raton, FL, 2010.

(3) (a) Pletnev, A. A.; Tian, Q.-P.; Larock, R. C. J. Org. Chem. 2002, 67, 9276–9287. (b) Miura, T.; Murakami, M. Org. Lett. 2005, 7, 3339–3341. (c) Tsukamoto, H.; Kondo, Y. Org. Lett. 2007, 9, 4227– 4230. (d) Morimoto, T.; Yamasaki, K.; Hirano, A.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K.; Harada, Y.; Fukumoto, Y.; Chatani, N.; Nishioka, T. Org. Lett. 2009, 11, 1777–1780. (e) Harada, Y.; Nakanishi, J.; Fujihara, H.; Tobisu, M.; Fukumoto, Y.; Chatani, N. J. Am. Chem. Soc. 2007, 129, 5766–5771. (f) Larock, R. C.; Doty, M. J. J. Org. Chem. 1993, 58, 4579–4583. (g) Liu, C.-C.; Korivi, R. P.; Cheng, C.-H. Chem. - Eur. J. 2008, 14, 9503–9506.

(4) Yu, J.-Q.; Shi, Z.-J. *Topics in Current Chemistry*; Springer-Verlag: New York, 2010.

(5) For selected reviews on C-H activation reactions, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. Acc. Chem. Res. 2001, 34, 633-639. (b) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. Acc. Chem. Res. 2008, 41, 1013-1025. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. Chem. Rev. 2010, 110, 624-655. (d) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. Chem. Soc. Rev. 2011, 40, 5068-5083. (e) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. Chem. Soc. Rev. 2011, 40, 4740-4761. (f) Song, G.-Y.; Wang, F.; Li, X.-W. Chem. Soc. Rev. 2012, 41, 3651-3678. (g) Hashiguchi, B. G.; Bischof, S. M.; Konnick, M. M.; Periana, R. A. Acc. Chem. Res. 2012, 45, 885-898. (h) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. Acc. Chem. Res. 2012, 45, 778-187. (i) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. Chem. Rev. 2012, 112, 5879-5918. (j) Johnson, K. R. D.; Hayes, P. G. Chem. Soc. Rev. 2013, 42, 1947-1960. (k) Li, B.; Dixneuf, P. H. Chem. Soc. Rev. 2013, 42, 5744-5767. (1) Baillie, R. A.; Legzdins, P. Acc. Chem. Res. 2014, 47, 330-340. (m) Arnold, P. L.; McMullon, M. W.; Rieb, J.; Kühn, F. E. Angew. Chem., Int. Ed. 2015, 54, 82-100. (n) Segawa, Y.; Maekawa, T.; Itami, K. Angew. Chem., Int. Ed. 2015, 54, 66-81. (o) Lobana, T. S. RSC Adv. 2015, 5, 37231-37274. (p) Wu, X.-F. Chem. - Eur. J. 2015, 21, 12252-12265. (q) Topczewski, J. J.; Sanford, M. S. Chem. Sci. 2015, 6, 70-76.

(6) (a) Kuninobu, Y.; Kawata, A.; Takai, K. J. Am. Chem. Soc. 2005, 127, 13498–13499. (b) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. J. Am. Chem. Soc. 2006, 128, 202–209.

(7) (a) Seoane, A.; Casanova, N.; Quiñones, N.; Mascareñas, J. L.; Gulías, M. J. Am. Chem. Soc. 2014, 136, 7607–7610. (b) Sun, Z.-M.; Chen, S.-P.; Zhao, P.-J. Chem. - Eur. J. 2010, 16, 2619-2627. (c) Tran, D. N.; Cramer, N. Angew. Chem., Int. Ed. 2010, 49, 8181-8184. (d) Tran, D. N.; Cramer, N. Angew. Chem., Int. Ed. 2011, 50, 11098-11102. (e) Patureau, F. W.; Besset, T.; Kuhl, N.; Glorius, F. J. Am. Chem. Soc. 2011, 133, 2154-2156. (f) Jayakumar, J.; Parthasarathy, K.; Cheng, C.-H. Angew. Chem., Int. Ed. 2012, 51, 197-200. (g) Chinnagolla, R. K.; Jeganmohan, M. Eur. J. Org. Chem. 2012, 2012, 417–423. (h) Fukutani, T.; Umeda, N.; Hirano, K.; Satoh, T.; Miura, M. Chem. Commun. 2009, 5141-5143. (i) Zhao, P.; Wang, F.; Han, K.; Li, X.-W. Org. Lett. 2012, 14, 5506-5509. (j) Wang, H.; Wang, Y.-Y.; Yang, H.-J.; Tan, C.-Y.; Jiang, Y.-Y.; Zhao, Y.-F.; Fu, H. Adv. Synth. Catal. 2015, 357, 489-499. (k) Ueura, K.; Satoh, T.; Miura, M. Org. Lett. 2007, 9, 1407-1409. (1) Ueura, K.; Satoh, T.; Miura, M. J. Org. Chem. 2007, 72, 5362-5367.

(8) (a) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. J. Org. Chem. **1996**, 61, 6941–6946. (b) Li, B.-J.; Wang, H.-Y.; Zhu, Q.-L.;

Shi, Z.-J. Angew. Chem., Int. Ed. 2012, 51, 3948–3952. (c) Chen, S.-Y.;
Yu, J.-T.; Jiang, Y.; Chen, F.; Cheng, J. Org. Lett. 2013, 15, 4754–4757.
(d) Chen, Y.-Y.; Wang, F.; Zhen, W.-C.; Li, X.-W. Adv. Synth. Catal.
2013, 355, 353–359. (e) Qi, Z.-S.; Wang, M.; Li, X.-W. Org. Lett.
2013, 15, 5440–5443.

(9) (a) Baudoin, O. Angew. Chem., Int. Ed. 2007, 46, 1373-1375.
(b) Goossen, L. J.; Rodriguez, N.; Goossen, K. Angew. Chem., Int. Ed. 2008, 47, 3100-3120. (c) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. Chem. Commun. 2008, 6312-6314. (d) Wang, C.-Y.; Piel, I.; Glorius, F. J. Am. Chem. Soc. 2009, 131, 4194-4195. (e) Cornella, J.; Lu, P.-F.; Larrosa, I. Org. Lett. 2009, 11, 5506-5509. (f) Xie, K.; Yang, Z.-Y.; Zhou, X.-J.; Li, X.-J.; Wang, S.-Z.; Tan, Z.; An, X.-Y.; Guo, C.-C. Org. Lett. 2010, 12, 1564-1567. (g) Zhang, F.-Z.; Greaney, M.-F. Angew. Chem., Int. Ed. 2010, 49, 2768-2771. (h) Wang, S.-S.; Chen, X.-Z.; Ao, Q.-Q.; Wang, H.-F.; Zhai, H.-B. Chem. Commun. 2016, 52, 9454-9457. (i) Cruz, F. A.; Chen, Z.-W.; Kurtoic, S. I.; Dong, V. M. Chem. Commun. 2016, 52, 5836-5839. (j) Liu, Z.-J.; Lu, X.; Wang, G.; Lei, L.; Jiang, W.-T.; Wang, Y.-D.; Xiao, B.; Fu, Y. J. Am. Chem. Soc. 2016, 138, 9714-9719.

(10) (a) Fang, P.; Li, M.-Z.; Ge, H.-B. J. Am. Chem. Soc. 2010, 132, 11898–11899. (b) Li, M.-Z.; Ge, H.-B. Org. Lett. 2010, 12, 3464–3467. (c) Wang, H.; Guo, L.-N.; Duan, X.-H. Org. Lett. 2012, 14, 4358–4361. (d) Li, Z.-Y.; Li, D.-D.; Wang, G.-W. J. Org. Chem. 2013, 78, 10414–10420. (e) Yang, Z.-Y.; Chen, X.; Liu, J.-D.; Gui, Q.-W.; Xie, K.; Li, M.-M.; Tan, Z. Chem. Commun. 2013, 49, 1560–1562. (f) Park, J.; Kim, M.; Sharma, S.; Park, E.; Kim, A.; Lee, S. H.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. Chem. Commun. 2013, 49, 1654–1656. (g) Li, H.-J.; Li, P.-H.; Zhao, Q.; Wang, L. Chem. Commun. 2013, 49, 9170–9172. (h) Yao, J.-Z.; Feng, R.-K.; Wu, Z.-H.; Liu, Z.-X.; Zhang, Y.-H. Adv. Synth. Catal. 2013, 355, 1517–1522.

(11) (a) Xu, T.; Dong, G.-B. Angew. Chem., Int. Ed. 2012, 51, 7567– 7571. (b) Xu, T.; Ko, H. M.; Savage, N. A.; Dong, G.-B. J. Am. Chem. Soc. 2012, 134, 20005–20008.

(12) (a) Wang, J.-J.; Liu, B.-W.; Zhao, H.-T.; Wang, J.-H. Organometallics **2012**, *31*, 8598–8607. (b) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. Acc. Chem. Res. **2010**, *43*, 1486–1495.

(13) Rodríguez, N.; Goossen, L. J. Chem. Soc. Rev. 2011, 40, 5030– 5048.

(14) (a) Lee, D. G.; Chen, T. J. Am. Chem. Soc. **1993**, 115, 11231–11236. (b) Mio, M.; Lucas, C. K.; Julia, B. B.; Tendai, L. G.; Kami, L. H.; Ronald, G. B.; Christopher, J. M.; Paul, A. G. Org. Lett. **2002**, 4, 3199–3202.

(15) Hussain, M.; Hung, N. T.; Khera, R. A.; Villinger, A.; Langer, P. Tetrahedron Lett. 2011, 52, 184–187.

(16) Li, B.-J.; Wang, H.-Y.; Zhu, Q.-L.; Shi, Z.-J. Angew. Chem., Int. Ed. 2012, 51, 3948–3952.

(17) Qi, Z.-S.; Wang, M.; Li, X.-W. Org. Lett. 2013, 15, 5440-5443.
(18) Feng, J.; Lu, G.-P.; Lv, M.-F; Cai, C. J. Org. Chem. 2014, 79, 10561-10567.

(19) Manning, C.; McClory, M. R.; McCullough, J. J. J. Org. Chem. 1981, 46, 919–930.