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Palladium-Catalyzed Carbonylative Annulation Reactions using Aryl Formate as a CO Source: Synthesis of 2-Substituted Indene-1,3(2H)-dione Derivatives

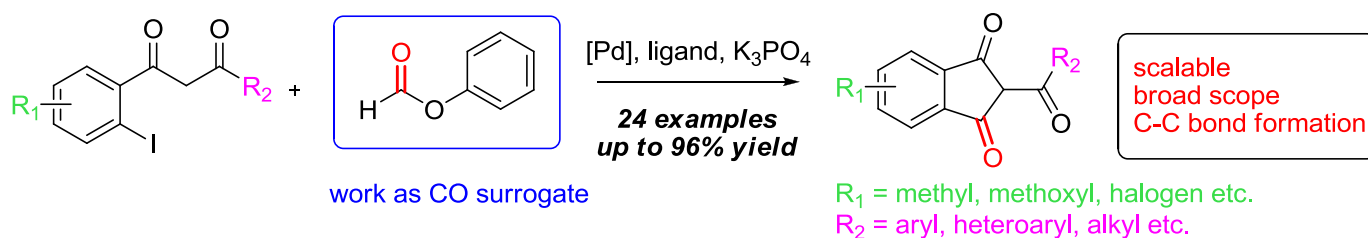
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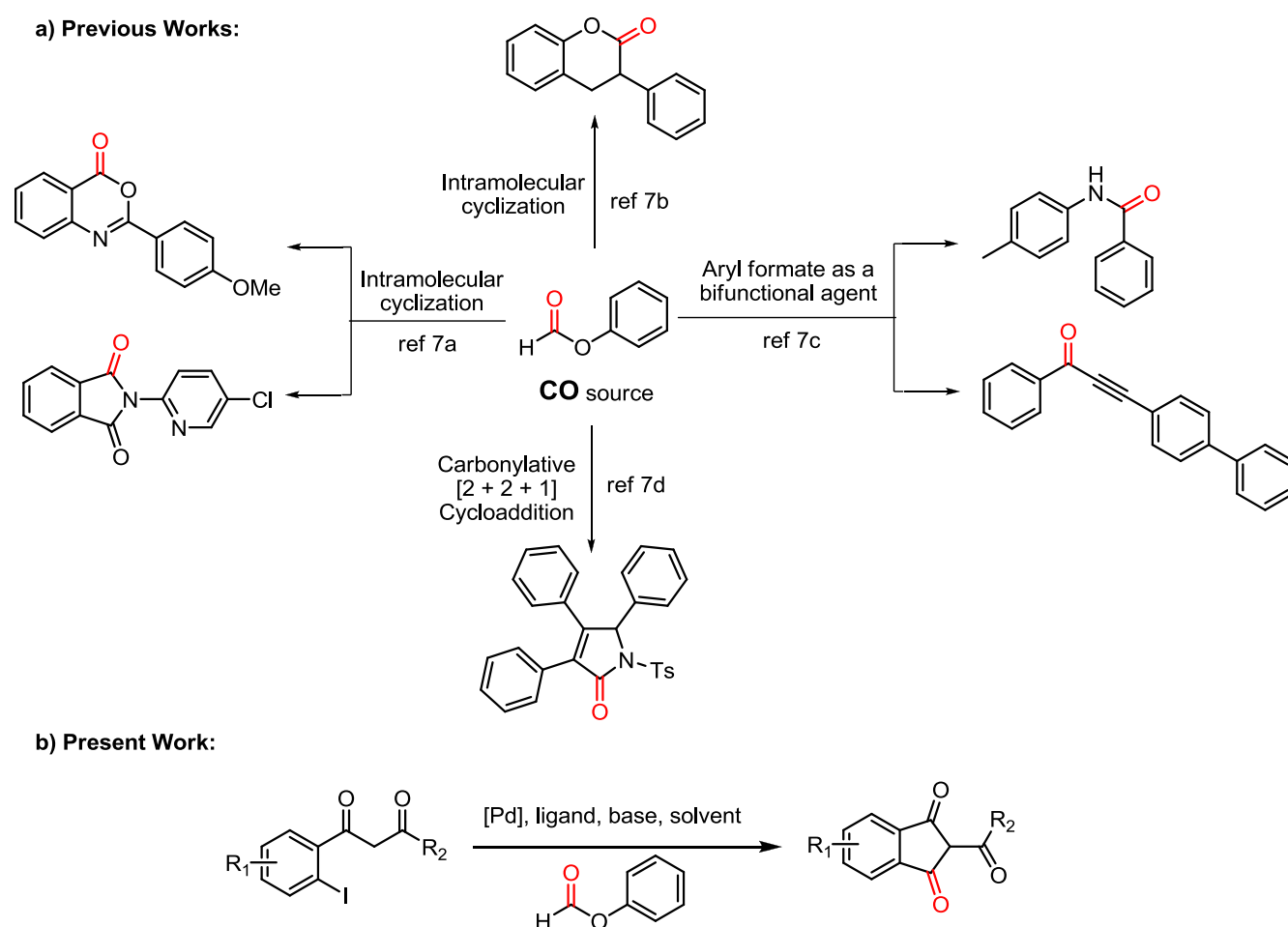
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ABSTRACT: An efficient synthesis of 2-substituted indene-1,3(2H)-diones from stable and readily available 1-(2-halophenyl)-1,3-diones by employing phenyl formate as a CO source has been developed. The reaction occurred via palladium-catalyzed intramolecular carbonylative annulation using K_3PO_4 as a base and DMSO as a solvent at 95 °C. In this protocol, the reaction showed a broad substrate scope with good to excellent yields.

INTRODUCTION

Palladium-catalyzed carbonylative transformations of aryl halides have undergone impressive developments since the pioneering work of Heck and Schoenberg in 1974.¹ In the last four decades, various chemicals such as aldehydes, esters, heterocyclic compounds, etc. have been achieved under CO atmosphere.² In recent years, many researchers intended to introduce versatile CO surrogates in carbonylation processes to displace the use of high toxic and flammable CO.³ Aryl formate was reported to generate CO in the presence of base under milder reaction conditions.⁴ The Manabe⁵ and Tsuji⁶ groups have independently reported the use of aryl formate as a CO surrogate to esterify aryl



Scheme 1. Synthesis of Various Compounds using Aryl Formate as a “CO-free” Source

halides. Besides, several groups also reported the utility of aryl formate in the construction of different compounds including phthalimides,^{7a} lactones,^{7b} alkynones,^{7c} and γ -Lactams^{7d} (route a in Scheme 1). Our group has been aimed at constructing bio-active substances via potent carbonylative resources as alternative to harmful CO for a long time.⁸ As part of our ongoing research, we are making an effort to investigate other molecules that could be gained by employing aryl formate as a “CO-free” source.

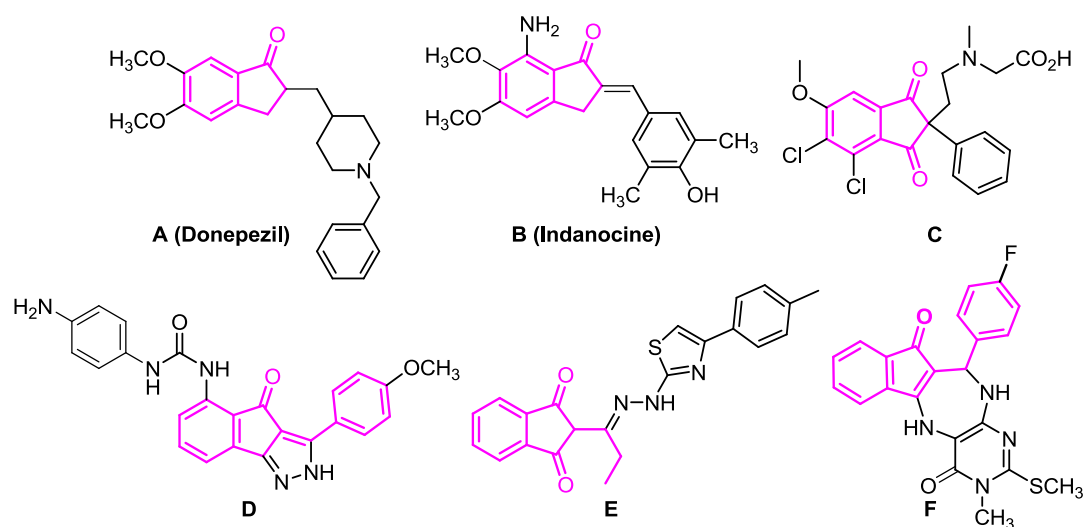


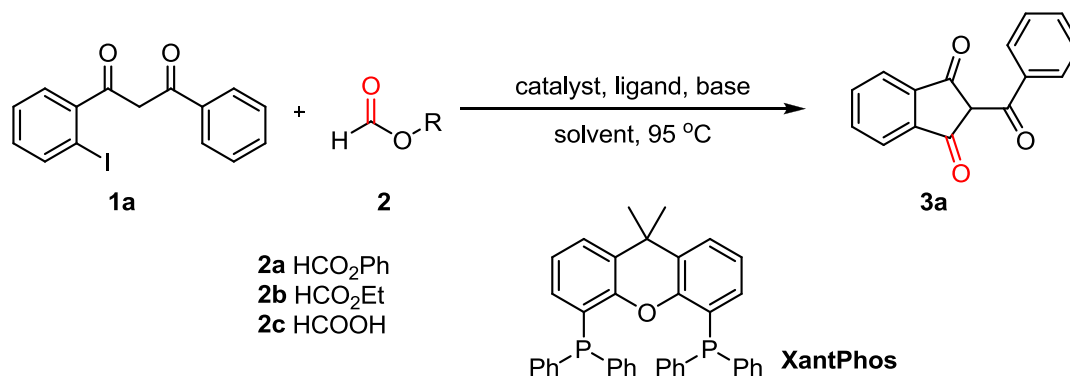
Figure 1. Representative Pharmaceuticals or Bio-active Compounds Containing 2-Substituted Indanone Structures

Indanones exist ubiquitously in natural products, pharmaceuticals, pesticides, and could be used for the preparation of organic light emitting materials, photochromics as well as dyestuff.⁹⁻¹³ For instance (Figure 1), AChE inhibitor Donepezil (**A**) has been approved by FDA and EMEA for the symptomatic treatment of Alzheimer's disease (AD).¹⁴ Indanocine (**B**) demonstrates significant binding affinity for microtubules¹⁵ while **C** is an inhibitor of the GlyT1 glycine transporter.¹⁶ Among all of the indanones, 2-substituted indene-1,3(2H)-diones can be used for synthesizing different types

of important compounds, some of which act as inhibitors of CDK,¹⁷ VEGFR-2 inhibitors (**D**),¹⁸ antimicrobial components (**E**),¹⁹ and potent anti-tumor drugs (**F**).²⁰ Useful as this kind of structural moieties is, approaches for their preparation remain limited by the lack of diversity in starting materials.²¹ The most widely used traditional method to obtain them lies in condensing ethyl phthalate with different ketones using a solution of sodium ethoxide in alcohol as the condensing agent, but products are usually isolated in low yields by this method.²⁹ Besides, the substrate scope in this method is limited to a small range, which is only confined to groups on the R₂ side (R₂ is group as shown in route b in Scheme 1). In contrast, the palladium-catalyzed carbonylative cyclyzation using in situ generated CO from aryl formate to produce 2-substituted indene-1,3(2H)-diones has been proven to be applicable to various substituents in the R₂ part, with good to excellent yields. Thus we report herein a practical and convenient reaction for preparing this skeleton that employs aryl formate as an environmentally friendly CO source (route b in Scheme 1).

RESULTS AND DISCUSSION

Initial studies were focused on the reaction of **1a** with aryl formate **2** in the presence of Pd(OAc)₂ and XantPhos with DMSO as a solvent under nitrogen. As shown in Table 1, no products were observed using Et₃N as a base (Table 1, entry 1). DBU also seemed to be ineffective in this reaction (Table 1, entry 2). Gratifyingly, when a strong base sodium *tert*-butoxide was added instead, the desired product 2-benzoyl-1H-indene-1,3(2H)-dione (**3a**) was isolated in 43% yield (Table 1, entry 3). To our delight, the yield was raised to 80% when inorganic base K₃PO₄ was used (Table 1, entry 4). In contrast with K₃PO₄, K₂HPO₄ gave decreased yield even with prolonged reaction time (Table 1, entry 5). Other commercially available catalysts were also tested to further improve the

Table 1. Optimization for the Synthesis of 2-Substituted Indene-1,3(2H)-diones^a

Entry	2	catalyst	ligand	base	solvent	yield ^b (%)
1	2a	Pd(OAc) ₂	XantPhos	Et ₃ N	DMSO	0
2	2a	Pd(OAc) ₂	XantPhos	DBU	DMSO	4
3	2a	Pd(OAc) ₂	XantPhos	NaOtBu	DMSO	43
4	2a	Pd(OAc) ₂	XantPhos	K ₃ PO ₄	DMSO	80
5	2a	Pd(OAc) ₂	XantPhos	K ₂ HPO ₄	DMSO	55
6	2a	PdCl ₂ (PPh ₃) ₂	XantPhos	K ₃ PO ₄	DMSO	22
7	2a	PdCl ₂ (MeCN) ₂	XantPhos	K ₃ PO ₄	DMSO	96
8	2a	PdCl ₂ (MeCN) ₂	dppp	K ₃ PO ₄	DMSO	78
9	2a	PdCl ₂ (MeCN) ₂	dppf	K ₃ PO ₄	DMSO	12
10	2a	PdCl ₂ (MeCN) ₂	<i>R</i> -BINAP	K ₃ PO ₄	DMSO	3
11	2a	PdCl ₂ (MeCN) ₂	PPh ₃	K ₃ PO ₄	DMSO	6
12	2a	PdCl ₂ (MeCN) ₂	XantPhos	K ₃ PO ₄	DMF	69
13	2a	PdCl ₂ (MeCN) ₂	XantPhos	K ₃ PO ₄	THF	0
14	2a	PdCl ₂ (MeCN) ₂	XantPhos	K ₃ PO ₄	toluene	0
15	2b	PdCl ₂ (MeCN) ₂	XantPhos	K ₃ PO ₄	DMSO	0
16	2c	PdCl ₂ (MeCN) ₂	XantPhos		DMSO	0 (98) ^c

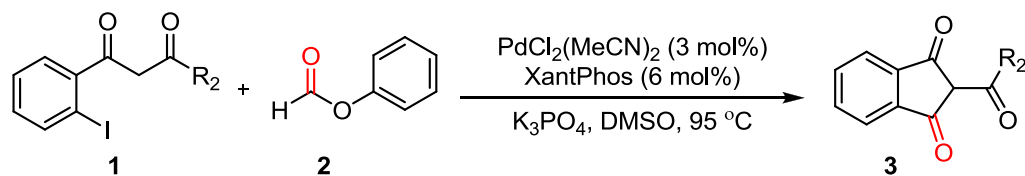
^aGeneral conditions: the reactions were run on a 0.4 mmol scale in solvent (1.0 mL), **2** (0.8 mmol), catalyst (0.012 mmol), ligand (0.024 mmol), base (0.8 mmol) under nitrogen in a sealed tube for 24 h. ^bIsolated yields. ^c98 % of substrate **1a** was isolated.

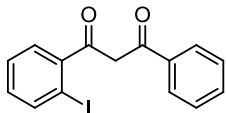
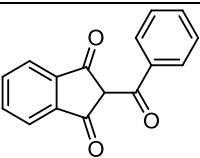
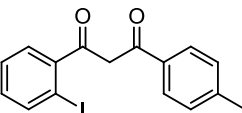
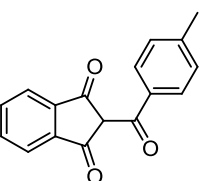
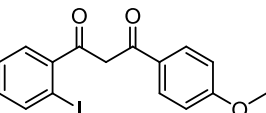
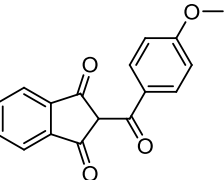
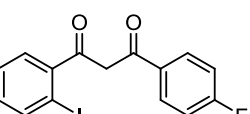
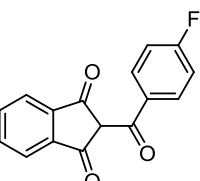
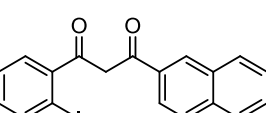
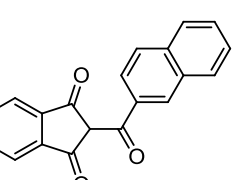
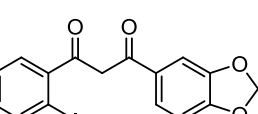
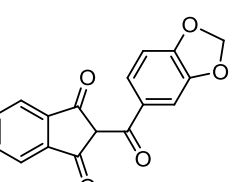
yield (Table 1, entries 6–7). Employment of $\text{PdCl}_2(\text{MeCN})_2$ delivered the carbonylative cyclization product in excellent yield (Table 1, entry 7), which was superior to $\text{Pd}(\text{OAc})_2$. Among other mono- and bidentate ligands examined, none of them were found to compete with XantPhos (Table 1, entries 8–11). Screening of other solvents including DMF, THF and toluene did not give better results (Table 1, entries 12–14). The results indicated that a polar solvent played an important role in the carbonylative cyclization process. Furthermore, few corresponding products were observed using formic acid or one of its derivatives, HCO_2Et , as CO source (Table 1, entries 15–16). Aryl formate is, as a result, a much higher active CO donor than HCO_2H and HCO_2Et in this system. Thus, the best conditions for this reaction were aryl formate (2 equiv), $\text{PdCl}_2(\text{MeCN})_2$ (3 mol %) and XantPhos (6 mol %) as the catalyst system, with K_3PO_4 (2 equiv) as the base and DMSO as the solvent under nitrogen atmosphere at 95 °C.

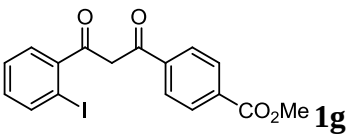
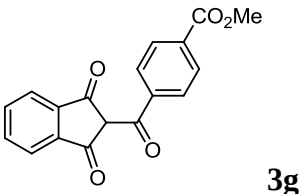
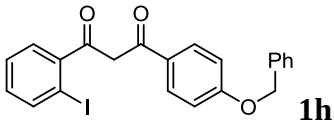
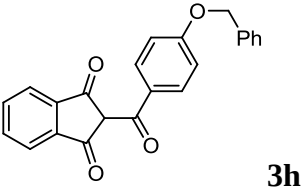
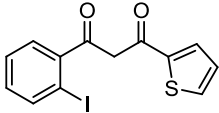
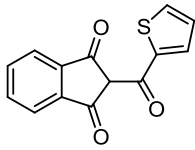
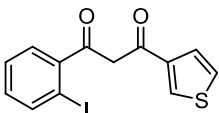
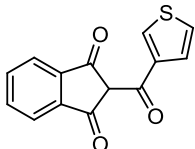
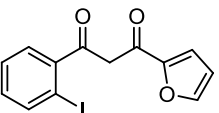
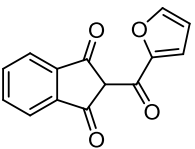
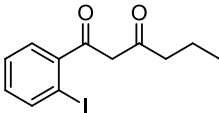
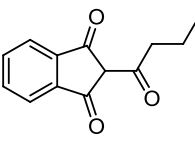
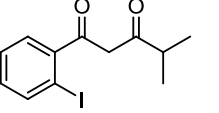
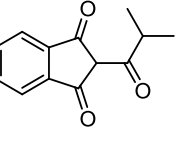
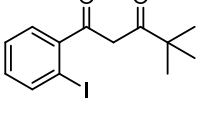
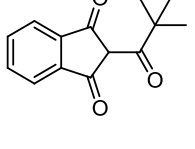
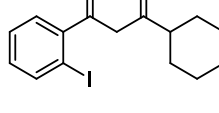
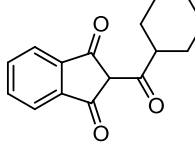
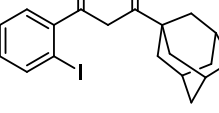
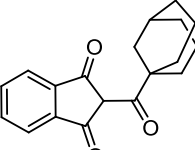
With the optimized reaction conditions in hand, the substrate scope of this palladium-catalyzed carbonylative reaction was investigated. As illustrated in Table 2, a wide variety of reactants bearing either electron-withdrawing or electron-donating substituents on the aryl ring could be transformed into the corresponding compounds **3** in moderate to excellent yields. Halogens, methyl, methoxyl, ester and naphthyl groups were well-tolerated in this system, and yielded desired products over 80% (Table 2, entries 1–8). Other enolizable motif-containing heteroaryl scaffolds, bearing thienyl, furyl on the R^2 side also provided targeted products in 68–83% yields under standard conditions (Table 2, entries 9–11). Substrates with R_2 ranging from simple aliphatic to cyclic groups also underwent carbonylative annulation smoothly and afforded 2-substituted indene-1,3(2H)-diones in good yields (Table 2, entries 12–16). Compared to the conventional methods known for synthesizing 2-substituted indene-1,3(2H)-diones,^{21,29} the enolic activation-carbonylative annulation approach

presented here is more effective and efficient with a broad scope of substrates.

Table 2. Substrate Scope on the R₂ Side of Palladium-Catalyzed Synthesis of 2-Substituted Indene-1,3(2H)-dione Derivatives^a



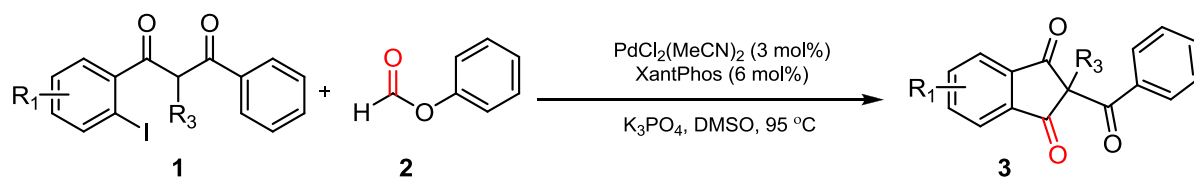
entry	substrate	product	yield ^b (%)
1	 1a	 3a	96
2	 1b	 3b	92
3	 1c	 3c	92
4	 1d	 3d	85
5	 1e	 3e	84
6	 1f	 3f	80

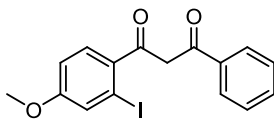
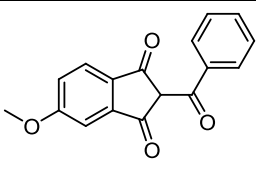
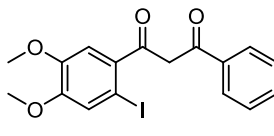
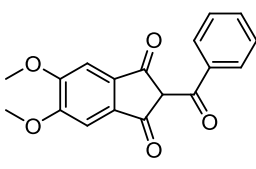
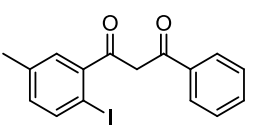
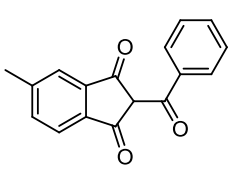
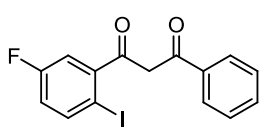
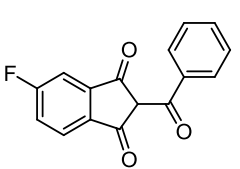
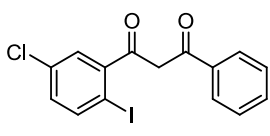
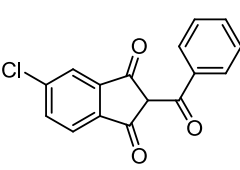
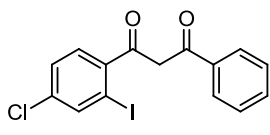
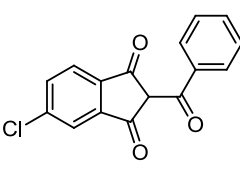
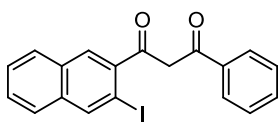
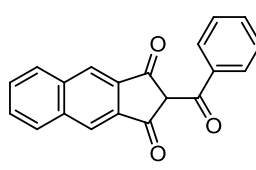
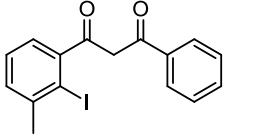
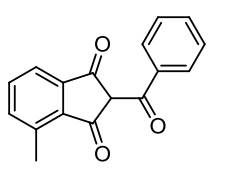
7			81
8			83
9			83
10			68
11			81
12			75
13			66
14			60
15			58
16			64

^aGeneral conditions: the reactions were run on a 0.4 mmol scale under nitrogen in a sealed tube, using **2** (0.8 mmol), PdCl₂(MeCN)₂ (0.012 mmol), XantPhos (0.024 mmol), K₃PO₄ (0.8 mmol) in DMSO (1.0 mL) at 95 °C for 24 h. ^bIsolated yields.

Next, we explored the flexibility of the method for various R₁ groups (Table 3). Corresponding products **3q–3x** were successfully obtained from **1q–1x** with different R₁ substituents. Both electron-rich and electron-poor groups were effectively cyclized (Table 3, entries 1–6). When R₁ was 3-iodonaphthalen-2-yl, the catalyst/ligand loading should be doubled owing to its weak aromaticity (Table 3, entry 7). Additionally, to learn about the steric effect on the R₁ side, 1-(2-iodo-3-methylphenyl)-3-phenylpropane-1,3-dione was subjected to the reaction, and a lower yield of the product was obtained (Table 3, entry 8). Notably, a ketone-enol isomerization phenomenon was observed from the NMR spectra of compounds **3a–3x**.

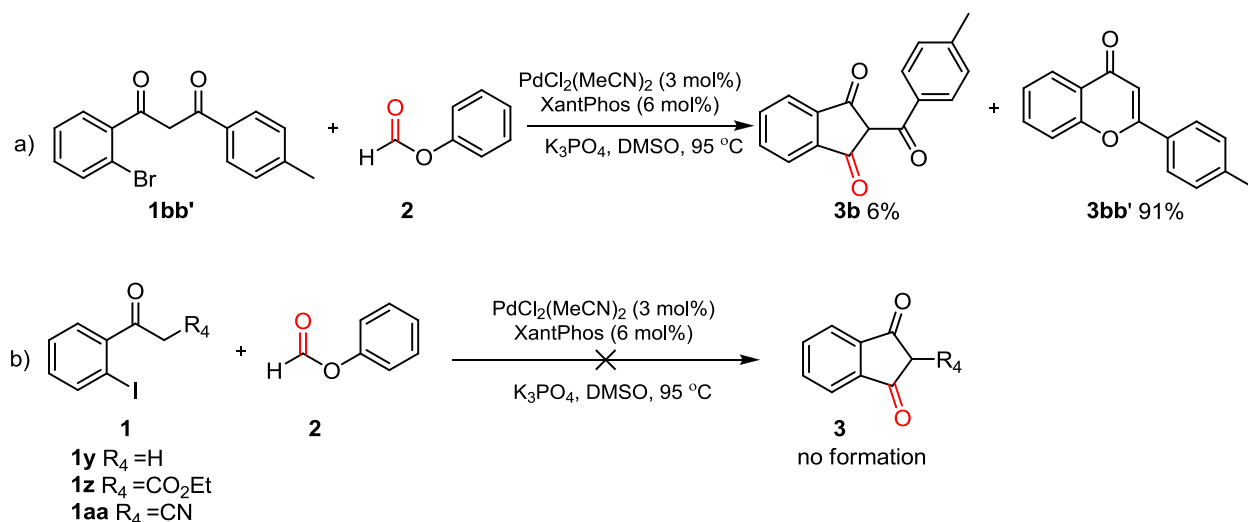
Table 3. Substrate Scope on the R¹ Side of Palladium-Catalyzed Synthesis of 2-Substituted Indene-1,3(2H)-dione Derivatives^a



entry	substrate	product	yield ^b (%)
1	 1q	 3q	80
2	 1r	 3r	87
3	 1s	 3s	90
4	 1t	 3t	80
5	 1u	 3u	78
6	 1v	 3v	56
7 ^c	 1w	 3w	82
8 ^c	 1x	 3x	53

^aGeneral conditions: the reactions were run on a 0.4 mmol scale under nitrogen in a sealed tube, using **2** (0.8 mmol), PdCl₂(MeCN)₂ (0.012 mmol), XantPhos (0.024 mmol), K₃PO₄ (0.8 mmol) in DMSO (1.0 mL) at 95 °C for 24 h. ^bIsolated yields. ^cwith PdCl₂(MeCN)₂ (0.024 mmol), XantPhos (0.048 mmol).

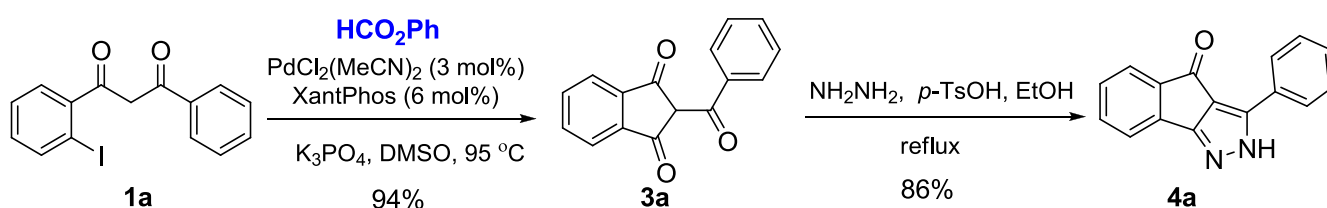
We also applied this method with a bromo substrate **1bb'**, only 6% of desired product **3b**, however, was isolated, and 91% of flavone (**3bb'**) was formed under the same reaction conditions (route a in Scheme 2). It suggested that aryl bromide did not react as actively as aryl iodide in this system. Besides, when using **1y-1aa** as substrates, neither were 2-substituted indene-1,3(2H)-diones observed nor any remaining substrates were isolated, even though these starting materials are supposed to be applicable under these conditions (route b in Scheme 2).



Scheme 2. Scope of other substrates

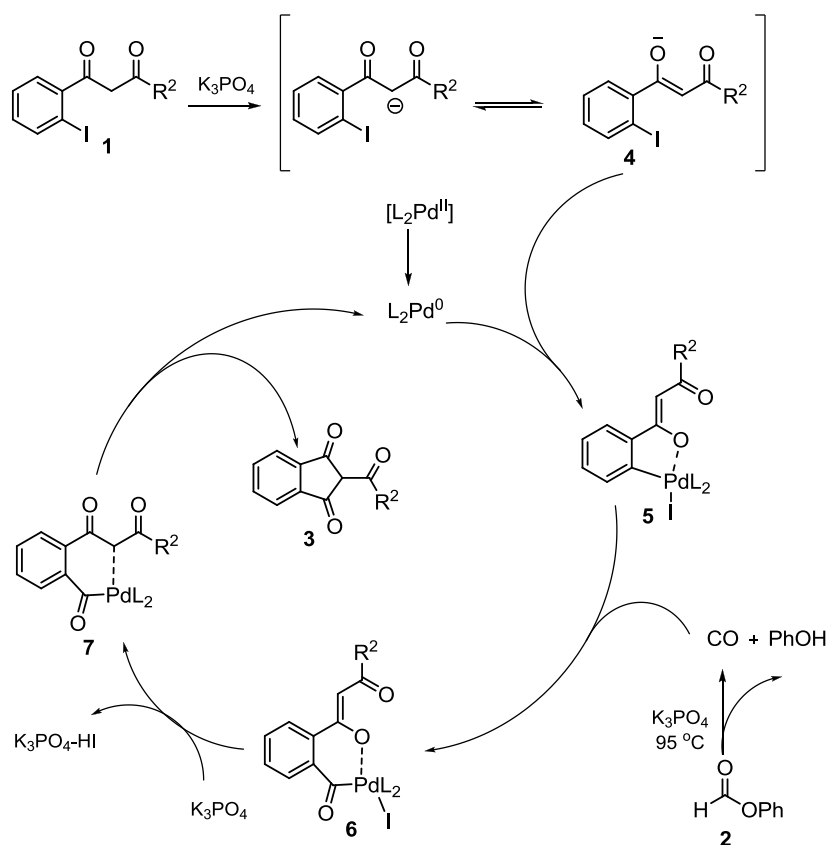
Indenopyrazole, a novel system containing two fused five-membered rings, was one of the attractive frameworks for development of kinase inhibitors²² in medicinal chemistry, such as inhibitors of CDK,^{17,23} PDGFR tyrosine kinase,²⁴ and EGFR.²⁵ These substances are usually derived from the corresponding indanones.^{17,18,23-25} To explore the synthetic utility of our methodology, carbonylative annulation of 1-(2-iodophenyl)-3-phenylpropane-1,3-dione (**1a**) was conducted on

gram scale under standard conditions (Scheme 3). A yield (94%) comparable to that of the small-scale experiment was furnished (Table 2, entry 1). Then, **3a** was treated with hydrazine hydrate to give 3-(4-methoxyphenyl)indeno[1,2-c]pyrazol-4(2H)-one with 86% yield. Synthesis of other indenopyrazoles and their biology activity evaluation are underway in our laboratory.



Scheme 3. Scale-Up Application of Carbonylative Annulation of 1a

With respect to a plausible reaction mechanism (Scheme 4), we assumed that, initially, substrate **1** is enolic activated into **4**, while the aryl formate decomposes into one molecule of CO^5 and phenol. Then, the in situ generated Pd^0 species²⁶ undergoes an oxidative addition to give intermediate **5**. After that, intermediate **5** is transformed into acyl palladium species **6** via CO insertion. At last, product **3** is generated through an intramolecular attack of the nucleophile on acyl palladium species **6**.



Scheme 4. Proposed Reaction Mechanism

CONCLUSION

In conclusion, we have demonstrated a novel and convenient palladium-catalyzed carbonylative cyclization reaction to generate 2-substituted Indene-1,3(2H)-dione derivatives. This methodology showcases the use of aryl formate as a CO source to form C-C bond in the presence of an inorganic base K_3PO_4 , and $PdCl_2(MeCN)_2/XantPhos$ catalytic system. Such a method is operationally simple and more effective than previously reported methods. Besides, aryl formate is a greener carbonylative surrogate than toxic CO gas. Further applications of aryl formate to construct bio-active materials are under way, and the results will be reported in due course.

EXPERIMENTAL SECTION

General Information. Reactants and reagents were purchased from commercial suppliers and used without further purification. All anhydrous solvents used in the reactions were dried and freshly distilled. TLC was performed on silica HSGF254 plates. Melting points were determined with a digital melting-point apparatus. NMR spectra were run in a solution of CDCl_3 or $\text{DMSO}-d_6$ with tetramethylsilane (TMS) as internal standard and were reported in parts per million (ppm). ^1H and ^{13}C NMR spectra were obtained at 400/101 MHz ($^1\text{H}/^{13}\text{C}$). High-resolution mass spectra (HRMS) analyses were carried out on a chemical ionization (CI) apparatus using time-of-flight (TOF) mass spectrometry. Infrared (IR) obtained using KBr tablets and wavenumbers in cm^{-1} .

General Experimental Procedure for the Synthesis of substrates 1a–1x. 2-Iodobenzoic acid (1.01 equiv, 2g, 8.08 mmol) was placed in a 25 mL round-bottomed flask and the excess thionyl-chlorid was added dropwise with stirring. After refluxing at 80 °C for about 4 h, thionyl-chloride was distilled in vacuo to give the corresponding benzoyl chloride and was stored under toluene (5 mL) until use. LiHMDS (Lithium Hexamethyldisilazide, 1.4 equiv, 11.2 mL, 11.2 mmol) was injected into a toluene solution (10 mL) of acetophenone (1.0 equiv, 0.96 g, 8.0 mmol) under nitrogen at 0 °C. After stirring at 0 °C for 3 h, benzoyl chloride was added and the mixture was continued to react for another 5 h. Then the solvent was quenched with 20 mL 1 N HCl and was extracted with EtOAc (20×3 mL). The organic phase was dried over Na_2SO_4 . After the removal of the solvent in vacuo, the residue was purified on a silica gel column using petroleum ether/EtOAc as the eluent to give the substrate **1a** (2.33 g, 83%).

Typical Experimental Procedure for the Synthesis of 2-Substituted Indene-1,3(2H)-diones.

Substrate **1** (0.4 mmol), PdCl₂(MeCN)₂ (0.03 equiv, 3 mg, 0.012 mmol), Xantphos (0.06 equiv, 14 mg, 0.024 mmol), HCO₂Ph (2 equiv, 90 μL, 0.8 mmol) and K₃PO₄ (2 equiv, 109 mg, 0.8 mmol) were successively added into a 15 mL sealed tube, using anhydrous DMSO (1.0 mL) as solvent. The mixture was stirred at 95 °C under nitrogen for 24 h. Upon completion of the reaction as indicated by TLC, the mixture was diluted with water (5 mL) and extracted with EtOAc (3 mL). The aqueous phase was separated and acidified to pH 3 with 1 N HCl, and extracted with EtOAc (10×2 mL). The combined organic layers were dried over Na₂SO₄. Filtrates were concentrated on a rotary evaporator and purified on a silica gel column using petroleum ether/EtOAc as the eluent to give the pure target product.

Characterization Data for Products (3a–3x). *2-Benzoyl-1H-indene-1,3(2H)-dione (3a)*.²⁷ Yellow solid (96 mg, 96%); mp 109–111 °C. ¹H NMR (400 MHz, CDCl₃) δ 14.64 (s, 1H), 8.17–8.11 (m, 2H), 7.84 (t, *J* = 7.3 Hz, 2H), 7.71 (p, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.9, 186.8, 179.7, 140.3, 138.0, 135.3, 134.2, 133.7, 131.4, 130.3, 128.1, 122.97, 123.0, 107.6. HRMS (CI): *m/z* calcd for C₁₆H₁₁O₃ [M + H]⁺, 251.0708; found, 251.0714.

2-(4-Methylbenzoyl)-1H-indene-1,3(2H)-dione (3b).²⁸ Yellow solid (97 mg, 92%); mp 115–117 °C. ¹H NMR (400 MHz, CDCl₃) δ 15.06 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 6.1 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.1, 187.1, 180.0, 145.0, 140.3, 138.0, 135.2, 134.1, 130.5, 129.0, 128.8, 123.0, 122.4, 107.4, 22.0. HRMS (CI): *m/z* calcd for C₁₇H₁₃O₃ [M + H]⁺, 265.0865; found, 265.0860.

2-(4-Methoxybenzoyl)-1H-indene-1,3(2H)-dione (**3c**).^{17a} Yellow solid (103 mg, 92%); mp 120–122 °C. ¹H NMR (400 MHz, CDCl₃) δ 15.23 (s, 1H), 8.31 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 6.5 Hz, 2H), 7.71 (p, *J* = 7.1 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 187.3, 179.5, 164.4, 140.2, 138.0, 135.1, 134.0, 133.1, 124.0, 122.9, 122.2, 113.7, 107.0, 55.7. HRMS (CI): *m/z* calcd for C₁₇H₁₃O₄ [M + H]⁺, 281.0814; found, 281.0816.

2-(4-Fluorobenzoyl)-1H-indene-1,3(2H)-dione (**3d**). Yellow solid (91 mg, 85%); mp 176–178 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.87 (t, *J* = 7.6 Hz, 2H), 7.74 (m, 2H), 7.20 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 187.0, 178.5, 166.1 (d, *J* = 256.2 Hz), 140.3, 138.0, 135.5, 134.3, 133.2 (d, *J* = 9.4 Hz), 127.7 (d, *J* = 3.0 Hz), 123.1, 122.5, 115.6 (d, *J* = 21.9 Hz), 107.6. IR (KBr): ν 2920, 1714, 1692, 1645, 1604, 1572, 1509, 1290, 1240, 1168, 919, 748 cm⁻¹. HRMS (CI): *m/z* calcd for C₁₆H₁₀FO₃ [M + H]⁺, 269.0614; found, 269.0610.

2-(2-Naphthoyl)-1H-indene-1,3(2H)-dione (**3e**).²⁹ Yellow solid (100 mg, 84%); mp 139–141 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.89 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.97–7.84 (m, 4H), 7.79–7.69 (m, 2H), 7.59 (dt, *J* = 14.8, 7.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.1, 187.0, 179.8, 140.3, 138.1, 136.0, 135.4, 134.2, 132.8, 132.3, 130.0, 129.0, 128.8, 127.9, 127.8, 126.8, 125.4, 123.0, 122.4, 107.9. HRMS (CI): *m/z* calcd for C₂₀H₁₃O₃ [M + H]⁺, 301.0865; found, 301.0852.

2-(Benzo[d][1,3]dioxole-5-carbonyl)-1H-indene-1,3(2H)-dione (**3f**). Yellow solid (94 mg, 80%); mp 143–145 °C. ¹H NMR (400 MHz, CDCl₃) δ 15.32(s), 8.02 (s, 1H), 7.84 (d, *J* = 5.1 Hz, 2H), 7.72 (d, *J* = 10.2 Hz, 3H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.08 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 187.2, 179.1, 152.7, 147.8, 140.2, 137.9, 135.2, 134.1, 129.7, 127.5, 122.9, 122.3, 110.2, 108.2, 107.1,

102.1. IR (KBr): ν 3009, 2916, 2865, 1705, 1646, 1595, 1559, 1485, 1262, 1130, 1004, 744 cm^{-1} .

HRMS (CI): m/z calcd for $\text{C}_{17}\text{H}_{11}\text{O}_5$ $[\text{M} + \text{H}]^+$, 295.0606; found, 295.0605.

methyl 4-(1,3-dioxo-2,3-dihydro-1H-indene-2-carbonyl)benzoate (3g) Yellow solid (100 mg, 81%);

mp 160–161 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 14.94 (s, 1H), 8.18 (s, 4H), 7.89 (dd, J = 11.6, 7.1

Hz, 2H), 7.77 (t, J = 6.1 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.9, 186.7, 178.2,

166.4, 140.5, 138.2, 135.7, 135.3, 134.5, 134.2, 130.3, 129.3, 123.3, 122.7, 108.4, 52.6. IR (KBr): ν

1717, 1647, 1618, 1591, 1560, 1541, 1506, 1426, 1134, 880, 776 cm^{-1} . HRMS (CI): m/z calcd for

$\text{C}_{18}\text{H}_{13}\text{O}_5$ $[\text{M} + \text{H}]^+$, 309.0763; found, 309.0771.

2-(4-(benzyloxy)benzoyl)-1H-indene-1,3(2H)-dione (3h) Yellow solid (118 mg, 83%); mp 97–99 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 15.23 (s, 1H), 8.33–8.29 (m, 2H), 7.87–7.82 (m, 2H), 7.71 (td, J = 6.6,

1.2 Hz, 2H), 7.40 (m, 6H), 7.09 (d, J = 7.1 Hz, 2H), 5.18 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 13C

NMR (101 MHz, CDCl_3) δ 199.2, 187.3, 179.4, 163.6, 140.1, 138.0, 136.2, 135.1, 134.0, 133.1,

128.9, 128.4, 127.7, 124.1, 122.9, 122.3, 114.5, 107.0, 70.4. IR (KBr): ν 3033, 2919, 2850, 1704,

1680, 1638, 1579, 1557, 1505, 1464, 1250, 1121, 740 cm^{-1} . HRMS (CI): m/z calcd for $\text{C}_{23}\text{H}_{17}\text{O}_5$ $[\text{M}$

$+ \text{H}]^+$, 357.1127; found, 357.1137.

2-(Thiophene-2-carbonyl)-1H-indene-1,3(2H)-dione (3i).³⁰ Yellow solid (85 mg, 83%); mp

148–150 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 15.26 (s, 1H), 9.20 (d, J = 3.4 Hz, 1H), 7.84–7.80 (dd, J

= 11.4, 6.9 Hz, 3H), 7.73–7.65 (m, 2H), 7.28–7.24 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.9,

187.3, 171.5, 140.2, 137.9, 137.9, 136.2, 135.7, 135.2, 134.0, 128.9, 122.8, 122.3, 105.9. HRMS (CI):

m/z calcd for $\text{C}_{14}\text{H}_9\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$, 257.0272; found, 257.0269.

2-(Thiophene-3-carbonyl)-1H-indene-1,3(2H)-dione (3j).³¹ Yellow solid (70 mg, 68%); mp

134–136 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 15.32 (s, 1H), 9.51 (s, 1H), 7.96 (d, J = 4.9 Hz, 1H),

7.80 (t, $J = 8.1$ Hz, 2H), 7.71–7.63 (m, 2H), 7.36 (d, $J = 2.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 199.3, 187.4, 173.1, 140.2, 137.8, 137.7, 135.1, 134.4, 134.0, 128.4, 125.4, 122.8, 122.2, 106.8.

HRMS (CI): m/z calcd for $\text{C}_{14}\text{H}_9\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$, 257.0272; found, 257.0274.

2-(Furan-2-carbonyl)-1H-indene-1,3(2H)-dione (3k).³² Yellow solid (79 mg, 81%); mp 152–154 °C.

^1H NMR (400 MHz, CDCl_3) δ 15.15 (s, 1H), 8.85 (d, $J = 3.7$ Hz, 1H), 7.80 (dd, $J = 11.7, 4.7$ Hz, 3H), 7.73–7.64 (m, 2H), 6.70 (dd, $J = 3.7, 1.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 199.0, 186.6, 166.0, 148.6, 146.1, 140.3, 137.9, 135.2, 134.0, 125.4, 122.8, 122.3, 113.7, 105.3. HRMS (CI): m/z calcd for $\text{C}_{14}\text{H}_9\text{O}_4$ $[\text{M} + \text{H}]^+$, 241.0501; found, 241.0508.

2-Butyryl-1H-indene-1,3(2H)-dione (3l).²⁹ Red-brown oil (65 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ 13.01 (s, 1H), 7.81 (s, 2H), 7.69 (t, $J = 6.6$ Hz, 2H), 2.94 (t, $J = 7.2$ Hz, 2H), 1.76 (dd, $J = 14.2, 7.0$ Hz, 2H), 1.03 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.3, 188.7, 187.86, 140.8, 138.2, 135.1, 134.2, 122.8, 122.5, 108.6, 34.2, 20.0, 13.9. HRMS (CI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3$ $[\text{M} + \text{H}]^+$, 217.0865; found, 217.0868.

2-Isobutyryl-1H-indene-1,3(2H)-dione (3m).²⁹ Yellow solid (57 mg, 66%); mp 94–96 °C. ^1H NMR (400 MHz, CDCl_3) δ 13.90 (s, 1H), 7.83 (t, $J = 5.8$ Hz, 2H), 7.75–7.66 (m, 2H), 3.89 (dt, $J = 13.9, 6.9$ Hz, 1H), 1.27 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.8, 192.3, 188.5, 140.8, 138.2, 135.1, 134.1, 122.8, 122.5, 107.1, 30.7, 19.0. HRMS (CI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3$ $[\text{M} + \text{H}]^+$, 217.0865; found, 217.0867.

2-Pivaloyl-1H-indene-1,3(2H)-dione (3n).³³ Yellow solid (55 mg, 60%); mp 112–114 °C. ^1H NMR (400 MHz, CDCl_3) δ 16.08 (s, 1H), 7.81–7.77 (m, 2H), 7.72–7.64 (tdd, 2H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.8, 198.0, 186.7, 139.3, 136.9, 134.5, 133.2, 122.2, 121.7, 106.7, 39.3, 25.74. HRMS (CI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3$ $[\text{M} + \text{H}]^+$, 231.1021; found, 231.1028.

2-(Cyclohexanecarbonyl)-1H-indene-1,3(2H)-dione (**3o**).²⁹ Red-brown solid (59 mg, 58%); mp 81–83 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 6.2 Hz, 2H), 7.70 (dd, *J* = 15.0, 7.3 Hz, 2H), 3.59 (t, *J* = 11.7 Hz, 1H), 1.84 (d, *J* = 10.4 Hz, 4H), 1.66–1.53 (m, 2H), 1.46–1.37 (m, 2H), 1.31–1.22 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 191.7, 188.6, 140.8, 138.3, 135.0, 134.1, 122.8, 122.5, 107.2, 40.6, 29.1, 25.8, 25.7. HRMS (CI): *m/z* calcd for C₁₆H₁₇O₃ [M + H]⁺, 257.1178; found, 257.1177.

2-(Adamantanecarbonyl)-1H-indene-1,3(2H)-dione (**3p**). Yellow solid (79 mg, 64%); mp 131–133 °C. ¹H NMR (400 MHz, CDCl₃) δ 16.08 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.67 (m, 2H), 2.16 (s, 6H), 2.09 (s, 3H), 1.86 (d, *J* = 11.9 Hz, 3H), 1.77 (d, *J* = 12.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.6, 198.2, 187.5, 139.9, 137.6, 135.1, 133.8, 122.7, 122.3, 107.4, 42.3, 36.8, 36.5, 28.2. IR (KBr): ν 2916, 2900, 2849, 1701, 1635, 1593, 1555, 1464, 1291, 1137, 976, 742, 696 cm⁻¹. HRMS (CI): *m/z* calcd for C₂₀H₂₁O₃ [M + H]⁺, 309.1491; found, 309.1490.

2-Benzoyl-5-methoxy-1H-indene-1,3(2H)-dione (**3q**). Yellow solid (90 mg, 80%); mp 125–127 °C. ¹H NMR (400 MHz, CDCl₃) δ 14.90 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 7.79 (t, *J* = 9.0 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 5.9 Hz, 1H), 7.24–7.16 (m, 1H), 3.94 (d, *J* = 3.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.6, 198.0, 186.7, 186.1, 178.5, 178.4, 166.0, 165.0, 143.5, 140.8, 133.5, 133.4, 133.4, 131.7, 131.5, 130.8, 130.4, 130.2, 128.2, 124.8, 124.4, 122.3, 121.2, 108.3, 108.0, 106.6, 105.7, 56.2. IR (KBr): ν 2923, 2815, 1706, 1640, 1607, 1585, 1487, 1289, 1128, 998, 764, 698 cm⁻¹. HRMS (CI): *m/z* calcd for C₁₇H₁₃O₄ [M + H]⁺, 281.0814; found, 281.0819.

2-Benzoyl-5,6-dimethoxy-1H-indene-1,3(2H)-dione (**3r**). Yellow solid (108 mg, 87%); mp 188–190 °C. ¹H NMR (400 MHz, CDCl₃) δ 14.45 (s, 1H), 8.08 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 6.9

Hz, 1H), 7.50 (t, $J = 7.3$ Hz, 2H), 7.28 (d, $J = 5.0$ Hz, 2H), 4.00 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.1, 186.5, 176.4, 155.4, 154.5, 135.4, 133.1, 132.3, 131.6, 130.2, 128.1, 107.6, 104.4, 103.67, 56.8. IR (KBr): ν 3063, 3015, 2943, 2835, 1701, 1611, 1583, 1567, 1494, 1304, 1287, 1221, 1082, 988, 766, 698 cm^{-1} . HRMS (CI): m/z calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5$ $[\text{M} + \text{H}]^+$, 311.0919; found, 311.0920.

2-Benzoyl-5-methyl-1H-indene-1,3(2H)-dione (3s). Yellow solid (95 mg, 90%); mp 109–111 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (t, $J = 8.5$ Hz, 2H), 7.75 (t, $J = 7.0$ Hz, 1H), 7.63 (dd, $J = 19.2, 8.1$ Hz, 2H), 7.52 (t, $J = 8.0$ Hz, 3H), 7.22 (t, $J = 7.6$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.1, 198.8, 187.0, 186.8, 179.2 (d, $J = 3.4$ Hz), 146.9, 145.5, 140.8, 138.4, 138.1, 136.1, 135.7, 135.0, 133.7, 133.5, 131.5 (d, $J = 8.2$ Hz), 130.3 (d, $J = 7.1$ Hz), 128.6, 128.1, 123.4, 122.9, 122.8, 122.4, 108.0 (d, $J = 16.9$ Hz), 22.3, 22.1. IR (KBr): ν 3053, 2921, 2852, 1702, 1642, 1601, 1589, 1570, 1489, 1291, 1127, 960, 891, 756, 681 cm^{-1} . HRMS (CI): m/z calcd for $\text{C}_{17}\text{H}_{13}\text{O}_3$ $[\text{M} + \text{H}]^+$, 265.0865; found, 265.0864.

2-Benzoyl-5-fluoro-1H-indene-1,3(2H)-dione (3t). Yellow solid (86 mg, 80%); mp 167–169 °C. ^1H NMR (400 MHz, CDCl_3) δ 14.86 (s, 1H), 8.13 (d, $J = 7.4$ Hz, 2H), 7.90–7.83 (m, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (m, 3H), 7.39 (td, $J = 9.8, 1.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.5, 197.4 (d, $J = 2.2$ Hz), 185.5, 185.4 (d, $J = 2.1$ Hz), 180.1, 180.0, 167.5 (d, $J = 258.8$ Hz), 166.6 (d, $J = 257.2$ Hz), 143.4 (d, $J = 8.7$ Hz), 140.8 (d, $J = 9.0$ Hz), 136.2 (d, $J = 2.6$ Hz), 133.9, 131.3, 131.2, 130.5, 130.4, 128.3, 128.2, 125.4 (d, $J = 9.3$ Hz), 125.0 (d, $J = 9.4$ Hz), 122.4 (d, $J = 23.6$ Hz), 121.4 (d, $J = 23.9$ Hz), 110.4 (d, $J = 23.6$ Hz), 109.6 (d, $J = 23.8$ Hz), 108.0, 107.8 (d, $J = 17.3$ Hz). IR (KBr): ν 2924, 1705, 1645, 1591, 1568, 1490, 1294, 1121, 962, 759, 683 cm^{-1} . HRMS (CI): m/z calcd for $\text{C}_{16}\text{H}_{10}\text{FO}_3$ $[\text{M} + \text{H}]^+$, 269.0614; found, 269.0619.

2-Benzoyl-5-chloro-1H-indene-1,3(2H)-dione (**3u**). Yellow solid (89 mg, 78%); mp 179–181 °C. ¹H NMR (400 MHz, CDCl₃) δ 14.89 (s, 1H), 8.14 (s, 2H), 7.80 (d, *J* = 6.5 Hz, 2H), 7.66 (t, *J* = 14.3, 6.4 Hz, 2H), 7.54 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.8, 197.6, 185.6, 185.4, 180.45, 180.4, 142.1, 141.8, 140.8, 139.5, 138.3, 136.1, 135.3, 134.3, 134.0, 131.3, 131.2, 130.4, 130.3, 128.9, 128.7, 124.4, 123.7, 123.4, 122.7, 107.7, 107.6. IR (KBr): ν 2922, 1702, 1647, 1605, 1587, 1563, 1490, 1292, 1140, 962, 760, 682 cm⁻¹. HRMS (CI): *m/z* calcd for C₁₆H₁₀ClO₃ [M + H]⁺, 285.0318; found, 285.0320.

2-Benzoyl-5-chloro-1H-indene-1,3(2H)-dione (**3v**). Yellow solid (64 mg, 56%); mp 179–180 °C. ¹H NMR (400 MHz, CDCl₃) δ 14.98 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 7.81 (m, 2H), 7.80 (t, *J* = 10.8 Hz, 1H), 7.72–7.61 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.77, 197.57, 185.67, 185.44, 180.53, 180.46, 142.07, 141.80, 140.84, 139.53, 138.35, 136.10, 135.30, 134.28, 134.00, 131.29, 131.22, 130.43, 130.37, 128.29, 128.27, 124.38, 123.75, 123.45, 122.70, 107.75, 107.62. IR (KBr): ν 2922, 1703, 1647, 1586, 1564, 1490, 1292, 1140, 962, 760, 682 cm⁻¹. HRMS (CI): *m/z* calcd for C₁₆H₁₀ClO₃ [M + H]⁺, 285.0318; found, 285.0324.

2-Benzoyl-1H-cyclopenta[*b*]naphthalene-1,3(2H)-dione (**3w**). Yellow solid (99 mg, 82%); mp 168–170 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 17.9 Hz, 2H), 8.23 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.05 (s, 2H), 7.66 (d, *J* = 5.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 198.36, 186.45, 182.16, 136.72, 135.90, 135.72, 133.96, 133.88, 133.63, 131.81, 130.49, 130.56, 130.54, 130.52, 129.33, 129.02, 128.62, 128.24, 123.87, 123.65, 110.31. IR (KBr): ν 2922, 2851, 1686, 1599, 1585, 1559, 1510, 1290, 1142, 958, 760, 685 cm⁻¹. HRMS (CI): *m/z* calcd for C₂₀H₁₃O₃ [M + H]⁺, 301.0865; found, 301.0864.

2-Benzoyl-4-methyl-1H-indene-1,3(2H)-dione (3x). Yellow solid (56mg, 53%); mp 129–132 °C. ¹H NMR (400 MHz, CDCl₃) δ 15.26 (s, 1H), 8.17–8.08 (m, 2H), 7.75–7.68 (m, 1H), 7.54 (m, 5H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 2.74 (d, *J* = 18.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.6, 198.9, 188.6, 187.2, 179.7, 179.6, 138.1, 137.9, 136.6, 134.8, 133.6, 133.6, 133.4, 131.7, 131.6, 130.3, 130.2, 129.7, 128.7, 128.5, 128.2, 120.8, 120.6, 120.2, 115.4, 108.0, 107.8, 18.5, 18.4. IR (KBr): ν 2924, 2853, 1703, 1599, 1585, 1564, 1488, 1290, 1139, 923, 753, 691 cm⁻¹. HRMS (CI): *m/z* calcd for C₁₇H₁₃O₃ [M + H]⁺, 265.0865; found, 265.0867.

*3-Bhenylindeno[1,2-*c*]pyrazol-4(2H)-one (4a)*.³⁴ White solid (550 mg, 86%); mp 259–262 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.81 (s, 1H), 8.21 (d, *J* = 7.7 Hz, 2H), 7.61–7.47 (m, 6H), 7.40–7.34 (m, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) 184.0, 164.2, 141.9, 140.8, 136.0, 134.0, 130.5, 129.3, 129.2, 126.9, 126.6, 123.9, 119.9, 116.6. HRMS (CI): *m/z* calcd for C₁₆H₁₁N₂O [M + H]⁺, 247.0871; found, 247.0886.

ASSOCIATED CONTENT

Supporting Information Figures giving ¹H and ¹³C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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