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

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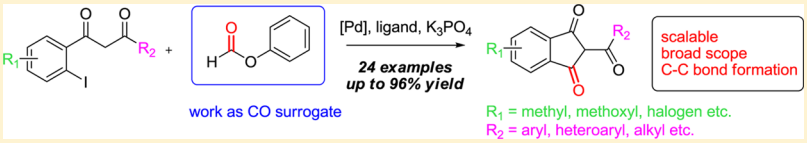
Supporting Information



ABSTRACT: An efficient synthesis of 2-substituted indene-1,3(2*H*)-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 Manabe[5] and Tsuji[6] groups have independently reported the use of aryl formate as a CO surrogate to esterify aryl halides. In addition, 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 bioactive substances via potent cabonylative 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.

Indanones exist ubiquitously in natural products, pharmaceuticals, and pesticides, and could be used for the preparation of organic light emitting materials and 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 microtubules,[15] while **C** is an inhibitor of the GlyT1 glycine transporter.[16] Among all of the indanones, 2-substituted indene-1,3(2*H*)-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 antitumor 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] MOreover, the substrate scope in this method is limited to a small range, which is only confined to groups on the R_2 side (R_2 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(2*H*)-diones has been proven to be applicable to various substituents in the R_2 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 Et_3N 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-1*H*-indene-1,3(2*H*)-dione (**3a**) was isolated in 43% yield (Table 1, entry 3). To our delight, the yield was raised to 80% when inorganic base K_3PO_4 was used (Table1, entry 4). In contrast with K_3PO_4, K_2HPO_4 gave decreased yield even with prolonged

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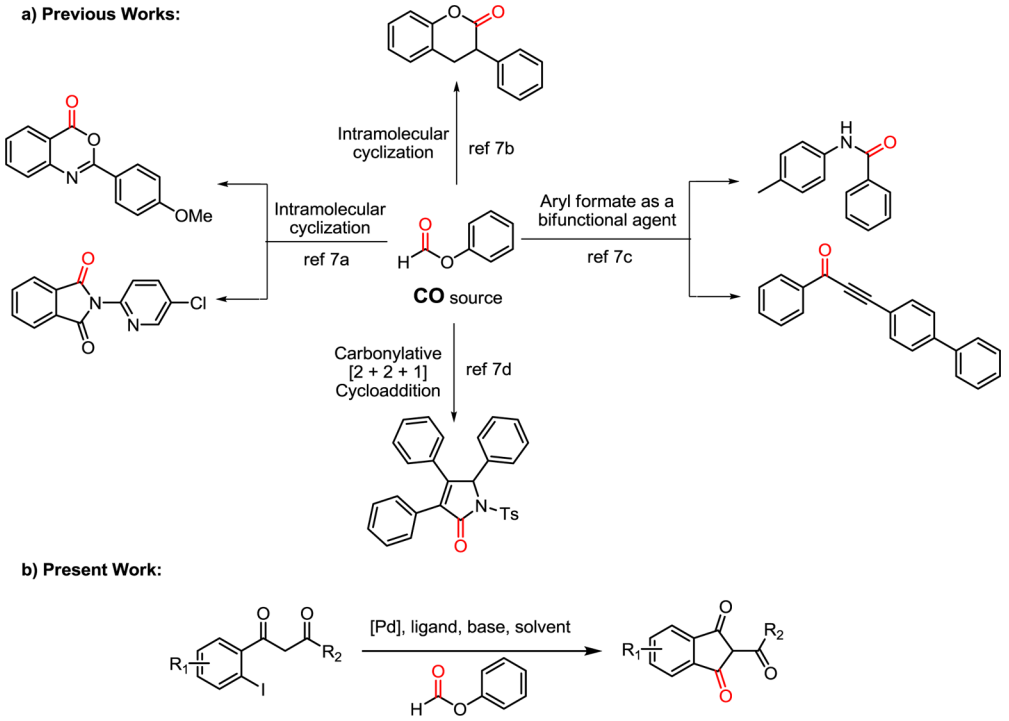
Scheme 1. Synthesis of Various Compounds Using Aryl Formate as a "CO-Free" Source



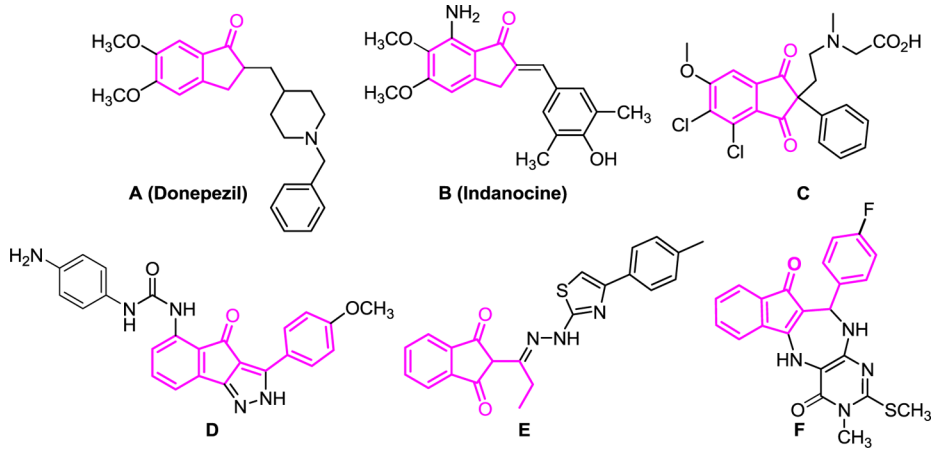


Figure 1. Representative pharmaceuticals or bioactive compounds containing 2-substituted indanone structures.

reaction time (Table 1, entry 5). Other commercially available catalysts were also tested to further improve the yield (Table1, entries 6 and 7). Employment of $PdCl_2(MeCN)_2$ delivered the carbonylative cyclization product in excellent yield (Table 1, entry 7), which was superior to $Pd(OAc)_2$. 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 (Table1, 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 and 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), $PdCl_2(MeCN)_2$ (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(2*H*)-diones in good yields (Table 2, entries 12−16). Compared to the conventional methods known for synthesizing

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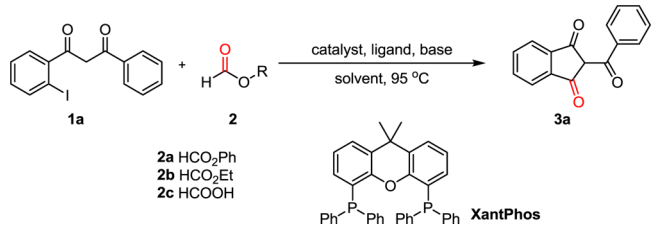
Table 1. Optimization for the Synthesis of 2-Substituted Indene-1,3(2*H*)-diones[a]



entry	2	catalyst	ligand	base	solvent	yield (%)[b]
1	**2a**	$Pd(OAc)_2$	XantPhos	Et_3N	DMSO	0
2	**2a**	$Pd(OAc)_2$	XantPhos	DBU	DMSO	4
3	**2a**	$Pd(OAc)_2$	XantPhos	NaO*t*Bu	DMSO	43
4	**2a**	$Pd(OAc)_2$	XantPhos	K_3PO_4	DMSO	80
5	**2a**	$Pd(OAc)_2$	XantPhos	K_2HPO_4	DMSO	55
6	**2a**	$PdCl_2(PPh_3)_2$	XantPhos	K_3PO_4	DMSO	22
7	**2a**	$PdCl_2(MeCN)_2$	XantPhos	K_3PO_4	DMSO	96
8	**2a**	$PdCl_2(MeCN)_2$	dppp	K_3PO_4	DMSO	78
9	**2a**	$PdCl_2(MeCN)_2$	dppf	K_3PO_4	DMSO	12
10	**2a**	$PdCl_2(MeCN)_2$	*R*-BINAP	K_3PO_4	DMSO	3
11	**2a**	$PdCl_2(MeCN)_2$	PPh_3	K_3PO_4	DMSO	6
12	**2a**	$PdCl_2(MeCN)_2$	XantPhos	K_3PO_4	DMF	69
13	**2a**	$PdCl_2(MeCN)_2$	XantPhos	K_3PO_4	THF	0
14	**2a**	$PdCl_2(MeCN)_2$	XantPhos	K_3PO_4	toluene	0
15	**2b**	$PdCl_2(MeCN)_2$	XantPhos	K_3PO_4	DMSO	0
16	**2c**	$PdCl_2(MeCN)_2$	XantPhos		DMSO	0 (98)[c]

[a]General 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. [b]Isolated yields. [c]Ninety-eight percent of **1a** was isolated.

2-substituted indene-1,3(2*H*)-diones,[21,29] the enolic activation−carbonylative annulation approach presented here is more effective and efficient with a broad scope of substrates.

Next, we explored the flexibility of the method for various R_1 groups (Table 3). Corresponding products **3q**−**3x** were successfully obtained from **1q**−**1x** with different R_1 substituents. Both electron-rich and electron-poor groups were effectively cyclized (Table 3, entries 1−6). When R_1 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 R_1 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**.

We also applied this method with a bromo substrate **1bb′**, and 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, with neither were 2-substituted indene-1,3(2*H*)-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).

Indenopyrazole, a novel system containing two fused five-membered rings, was one of the attractive frameworks for development of kinase inhibitors[22] 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(2*H*)-one with 86% yield. Synthesis of other indenopyrazoles and their biology activity evaluation are underway in our laboratory.

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 species[26] 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**.

■ CONCLUSION

In conclusion, we have demonstrated a novel and convenient palladium-catalyzed carbonylative cyclyzation reaction to generate 2-substituted Indene-1,3(2*H*)-dione derivatives. This methodology showcases the use of aryl fomate 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. In addition, aryl formate is a greener carbonylative surrogate than toxic CO gas. Further applications of aryl formate to construct bioactive materials are under way, and the results will be reported in due course.

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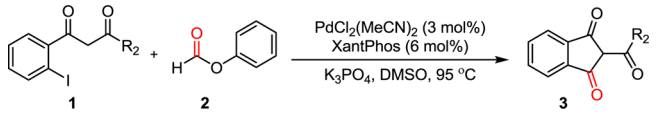
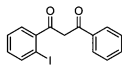
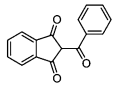
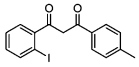
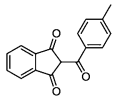
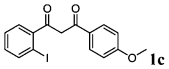
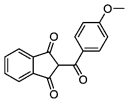
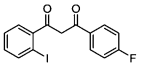
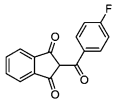
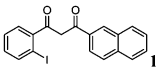
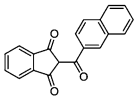
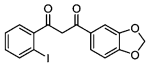
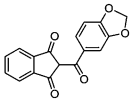
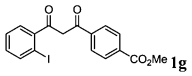
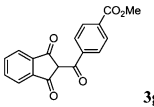
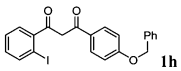
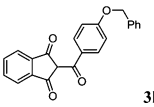
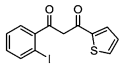
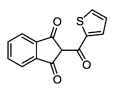
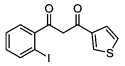
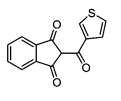
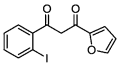
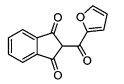
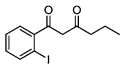
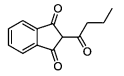
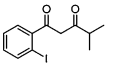
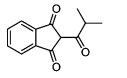
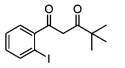
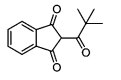
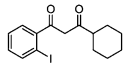
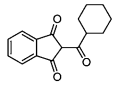
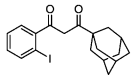
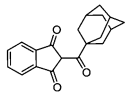
Table 2. Substrate Scope on the R_2 Side of Palladium-Catalyzed Synthesis of 2-Substituted Indene-1,3(2*H*)-dione Derivatives[a]



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	 1g	 3g	81
8	 1h	 3h	83
9	 1i	 3i	83
10	 1j	 3j	68
11	 1k	 3k	81
12	 1l	 3l	75
13	 1m	 3m	66
14	 1n	 3n	60
15	 1o	 3o	58
16	 1p	 3p	64

[a]General conditions: the reactions were run on a 0.4 mmol scale under nitrogen in a sealed tube, using **2** (0.8 mmol), $PdCl_2(MeCN)_2$ (0.012 mmol), XantPhos (0.024 mmol), K_3PO_4 (0.8 mmol) in DMSO (1.0 mL) at 95 °C for 24 h. [b]Isolated yields.

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 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 ($^1H/^{13}C$). 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, 2 g, 8.08 mmol) was placed in a 25 mL round-bottomed flask and the excess thionyl-chloride was added dropwise with stirring. After a refluxing period of about 4 h at 80 °C, 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 a stirring period of 3 h at 0 °C, benzoyl chloride was added and the mixture was continued to react for another 5 h. Then, the solvent was quenched with 20 mL of 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(2*H*)-diones. Substrate **1** (0.4 mmol), $PdCl_2(MeCN)_2$ (0.03 equiv, 3 mg, 0.012 mmol), Xantphos (0.06 equiv, 14 mg, 0.024 mmol), HCO_2Ph (2 equiv, 90 μL, 0.8 mmol), and K_3PO_4 (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 Na_2SO_4. 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, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{11}O_3$ $[M + H]^+$, 251.0708; found, 251.0714.

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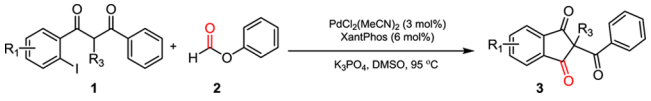
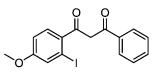
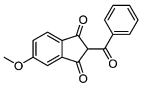
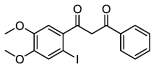
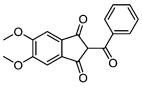
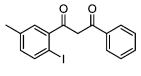
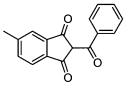
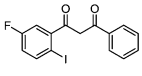
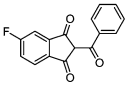
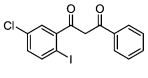
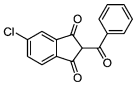
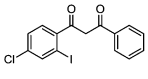
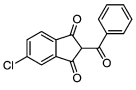
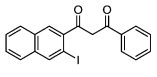
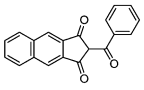
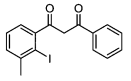
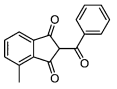
Table 3. Substrate Scope on the R_1 Side of Palladium-Catalyzed Synthesis of 2-Substituted Indene-1,3(2*H*)-dione Derivatives[a]



1 2 3

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

[a]General conditions: the reactions were run on a 0.4 mmol scale under nitrogen in a sealed tube, using **2** (0.8 mmol), $PdCl_2(MeCN)_2$ (0.012 mmol), XantPhos (0.024 mmol), K_3PO_4 (0.8 mmol) in DMSO (1.0 mL) at 95 °C for 24 h. [b]Isolated yields. [c]With $PdCl_2(MeCN)_2$ (0.024 mmol), XantPhos (0.048 mmol).

2-(4-Methylbenzoyl)-1H-indene-1,3(2H)-dione (**3b**).[28] Yellow solid (97 mg, 92%); mp 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{13}O_3$ $[M + H]^+$, 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{13}O_4$ $[M + H]^+$, 281.0814; found, 281.0816.

2-(4-Fluorobenzoyl)-1H-indene-1,3(2H)-dione (**3d**). Yellow solid (91 mg, 85%); mp 176−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{10}FO_3$ $[M + H]^+$, 269.0614; found, 269.0610.

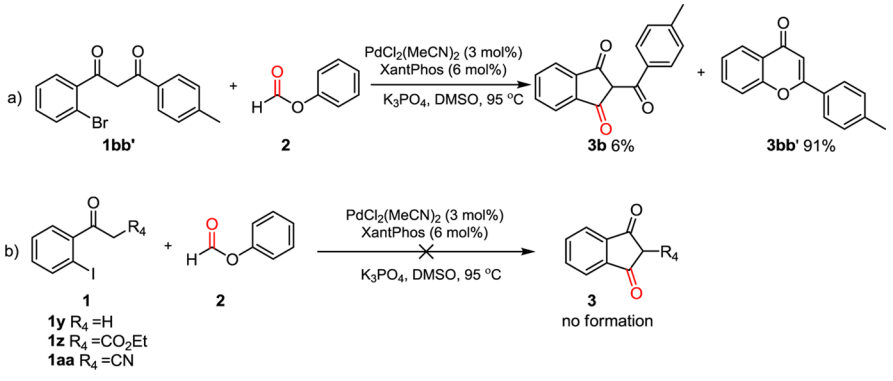
2-(2-Naphthoyl)-1H-indene-1,3(2H)-dione (**3e**).[29] Yellow solid (100 mg, 84%); mp 139−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.97−7.84 (m, 4H), 7.79−7.69 (m, 2H), 7.59 (dt, J = 14.8, 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 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 $C_{20}H_{13}O_3$ $[M + H]^+$, 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{11}O_5$ $[M + H]^+$, 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 °C. ^{1}H 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 $C_{18}H_{13}O_5$ $[M + H]^+$, 309.0763; found, 309.0771.

2-(4-(Benzyloxy)benzoyl)-1H-indene-1,3(2H)-dione (**3h**). Yellow solid (118 mg, 83%); mp 97−99 °C. ^{1}H 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, $CDCl_3$) 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,

Scheme 2. Scope of Other Substrates



DOI: 10.1021/acs.joc.5b01758
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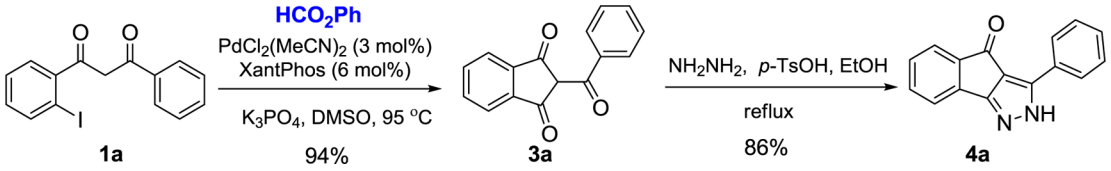
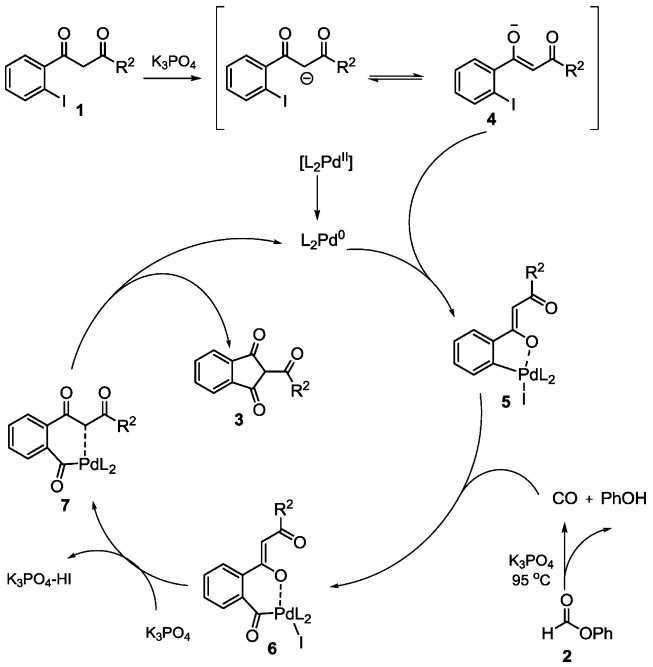
Scheme 3. Scale-Up Application of Carbonylative Annulation of 1a



Scheme 4. Proposed Reaction Mechanism



740 cm^{-1}. HRMS (CI): m/z calcd for $C_{23}H_{17}O_5$ [M + 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 °C. ^{1}H 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 $C_{14}H_9O_3S$ [M + 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 °C. ^{1}H 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 $C_{14}H_9O_3S$ [M + 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. ^{1}H 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 $C_{14}H_9O_4$ [M + H]$^+$, 241.0501; found, 241.0508.

*2-Butyryl-1H-indene-1,3(2H)-dione (**3l**).*[29] Red-brown oil (65 mg, 75%). ^{1}H 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 $C_{13}H_{13}O_3$ [M + 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. ^{1}H 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 $C_{13}H_{13}O_3$ [M + 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. ^{1}H 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 $C_{14}H_{15}O_3$ [M + 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{17}O_3$ [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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{20}H_{21}O_3$ [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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{17}H_{13}O_4$ [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. ^{1}H NMR (400 MHz, $CDCl_3$) 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 $C_{18}H_{15}O_5$ [M + 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. ^{1}H 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 $C_{17}H_{13}O_3$ [M + 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. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.86 (s,

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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 $C_{16}H_{10}FO_3$ $[M + H]^+$, 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{10}ClO_3$ $[M + H]^+$, 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{10}ClO_3$ $[M + H]^+$, 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{20}H_{13}O_3$ $[M + H]^+$, 301.0865; found, 301.0864.

*2-Benzoyl-4-methyl-1H-indene-1,3(2H)-dione (**3x**).* Yellow solid (56 mg, 53%); mp 129−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{13}O_3$ $[M + H]^+$, 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. ^{1}H 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). ^{13}C 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 $C_{16}H_{11}N_2O$ $[M + H]^+$, 247.0871; found, 247.0886.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01758.

^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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