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FULL PAPER

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# Palladium-catalyzed cyclocarbonylation of cyclic diaryliodoniums: Synthesis of fluorenones

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An efficient approach to the synthesis of fluorenones via the palladium-catalyzed cyclocarbonylation of cyclic diaryliodoniums was developed. Our route enables facile access to fluorenones with various substituents in modest to high yields.

**KEYWORDS**
cyclic diaryliodoniums, cyclocarbonylation, fluorenones

## 1 | INTRODUCTION

Linear diaryliodonium salts have received much attention due to their unique properties as electrophilic arylating reagents in modern organic synthesis,[1–7] but all these reactions were characterized by poor atom economy with generating one equivalent of an iodoarene as waste. Cyclic diaryliodoniums can avoid this problem because the iodoarenes remains as a part of the arylated product.[8] Moreover, the iodoarenes could go further transformation to provide more complicated molecules under the same reaction conditions.[9–11] Recently, Detert, Nachtsheim and their coworkers disclosed Pd catalyzed reaction of cyclic diphenyleneiodoniums with anilines to synthesis of carbazole derivatives.[12,13] In 2014, the group of Huang and Wen reported an atom and step economical three-component reaction involving cyclic diphenyleneiodoniums.[14] In 2015, the Liu group developed palladium-catalyzed double-Suzuki-Miyaura couplings between cyclic dibenziodoniums and arylboronic acids.[15] Very recently, Shimizu reported that dibenziodolium triflates smoothly react with potassium thioacetate in the presence of $CuCl_2$ to afford the corresponding dibenzothiophenes in good yields.[16]

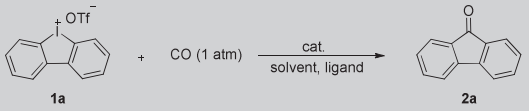
Due to their unique biological properties, fluorenones have gained considerable attention in agricultural science and medicinal chemistry.[17–19] They can be accessible from the oxidation of fluorenes,[20,21] intramolecular acylation of biarylcarboxylic acids,[22] cyclization of benzophenone,[23–27] biphenyl-2-carbonitriles[28] and benzoic anhydrides.[29,30] The Larock group developed a direct route to fluorenones by palladium-catalyzed cyclocarbonylation of *o*-halobiaryls, which $Pd(PCy_3)_2$ and anhydrous cesium picalate were employed.[31,32] We wish to report at this time a palladium-catalyzed cyclocarbonylation of cyclic diaryliodoniums which offers a highly efficient, atom-economical route to the fluoren-9-one skeleton.

## 2 | RESULTS AND DISCUSSION

We first carried out a cyclocarbonylation reaction with cyclic diaryliodoniums **1a** and carbon monoxide in the presence of 2 mol % of $Pd(OAc)_2$ in DCE at 100°C for 8 h. As shown in Table 1, the target product **2a** was obtained in 47% yield without ligand (entry 1). Other copper species including $Cu(OTf)_2$, $CuCl_2$ and CuI were examined (entries 2-4), they all provided low yields. It seemed that ligand favored the reaction, the desired product **2a** was obtained in the presence of 5 mol % of **L1** ($PPh_3$). Then, a screening of ligands was carried out (entries 6-14), and the results indicated that **L5** (1,10-phenanthroline) was the most effective ligand and gave **2a** in a 79% isolated yield (entry 11). Our further studies indicated that heating at 120°C gave the best yield 97% (entry 18). Finally, the effect of solvents was investigated (entries 19-23), different solvents including DMSO, MeCN, THF, $CH_3OH$ and toluene were employed, DCE was chosen as solvent. Thus, our final optimal reaction conditions used 2 mol% $Pd(OAc)_2$ and 5 mol % **L5** in DCE at 120°C for 8 h.

With the optimal reaction conditions in hand, we first explored the scope of cyclic iodoniums **1** (Table 2). Under the reaction conditions, all the cyclic diaryliodoniums provided the expected products at modest to good yields. Use of cyclic diaryliodoniums bearing electron-withdrawing groups such as F and $CF_3$ at the 3-position afforded the corresponding fluorenones **2b** and **2d** in high yields, respectively (Table 2). Substrates with electron-donating groups such as Me, OMe and Et in the 3-position gave lower yields (**2e**, **2f**, **2g**). Substrates with 4-position substituents **1h**, **1i** and **lj** also reacted smoothly to afford **2h**, **2i** and **2j** in modest yields, respectively. The scope of the reaction was further extended to di-substituted diaryliodoniums. The salts bearing two functional groups in the same side or different side were also converted into the desired products smoothly (**2k**-**2n**). Next, we investigated whether heterocyclic cyclic diaryliodoniums could be reacted in the cyclocarbonylation. To our delight, cyclic diaryliodoniums bearing thiophene also gave the expected fluorenones in modest yields (**2o** and **2p**).

**TABLE 1** Optimization of reaction conditions[a]

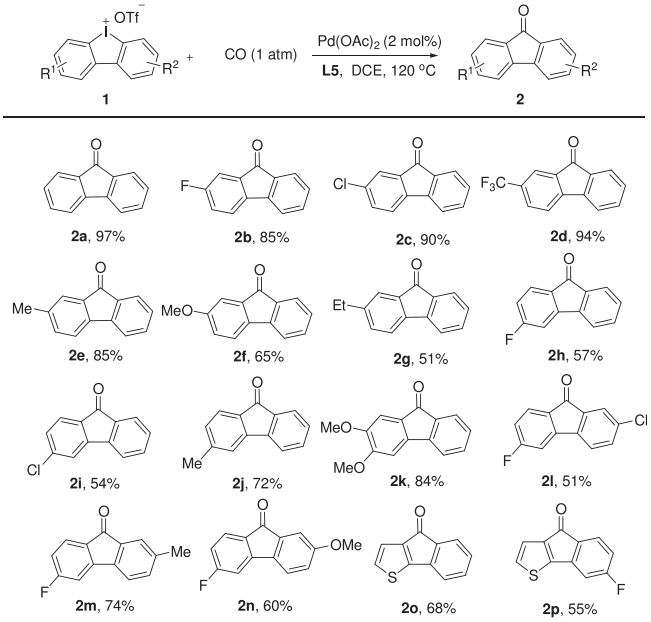



| entry | catalyst | ligand | solvent | temp (°C) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | none | DCE | 100 | 47 |
| 2 | $Cu(OTf)_2$ | none | DCE | 100 | 12 |
| 3 | $CuCl_2$ | none | DCE | 100 | 1 |
| 4 | CuI | none | DCE | 100 | 9 |
| 5 | $FeCl_3$ | none | DCE | 100 | 5 |
| 6 | $Pd(OAc)_2$ | **L1** | DCE | 100 | 46 |
| 7 | $Pd(OAc)_2$ | **L2** | DCE | 100 | 62 |
| 9 | $Pd(OAc)_2$ | **L3** | DCE | 100 | 59 |
| 10 | $Pd(OAc)_2$ | **L4** | DCE | 100 | 68 |
| 11 | $Pd(OAc)_2$ | **L5** | DCE | 100 | 79 |
| 12 | $Pd(OAc)_2$ | **L6** | DCE | 100 | 74 |
| 13 | $Pd(OAc)_2$ | **L7** | DCE | 100 | 35 |
| 14 | $Pd(OAc)_2$ | **L8** | DCE | 100 | 25 |
| 15 | $Pd(OAc)_2$ | **L5** | DCE | 25 | 5 |
| 16 | $Pd(OAc)_2$ | **L5** | DCE | 80 | 32 |
| 17 | $Pd(OAc)_2$ | **L5** | DCE | 100 | 79 |
| **18** | **$Pd(OAc)_2$** | **L5** | **DCE** | **120** | **97** |
| 19 | $Pd(OAc)_2$ | **L5** | DMSO | 120 | 32 |
| 20 | $Pd(OAc)_2$ | **L5** | MeCN | 120 | 40 |
| 21 | $Pd(OAc)_2$ | **L5** | THF | 120 | 87 |
| 22 | $Pd(OAc)_2$ | **L5** | $CH_3OH$ | 120 | 68 |
| 23 | $Pd(OAc)_2$ | **L5** | Toluene | 120 | 91 |

[a]Reaction conditions: **1a** (0.2 mmol), CO (1 atm), catalyst (2 mol%), ligand (5 mol%) in solvents (2 mL), 8 h.

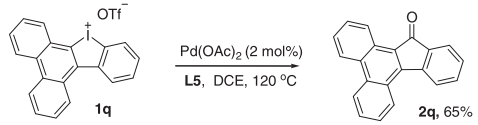
[b]Isolated yields.

**TABLE 2** Palladium-catalyzed cyclocarbonylation of cyclic diaryliodoniums[a,b]

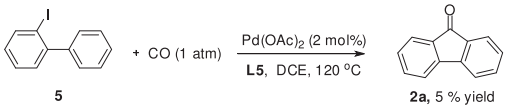



[a]Reaction conditions: **1** (0.2 mmol), CO (1 atm), $Pd(OAc)_2$ (2 mol%), **L5** (5 mol%) in DCE (2 mL), 120 °C, 8 h.

[b]Isolated yields.

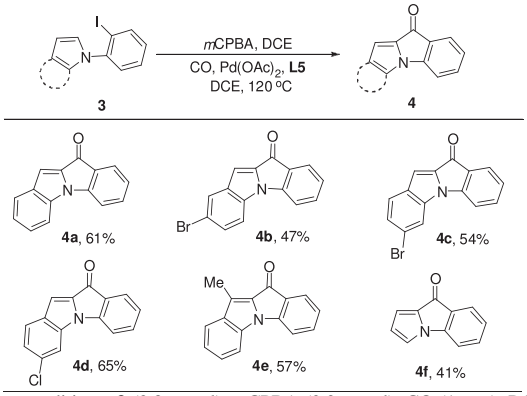



**SCHEME 1** Cyclocarbonylation of phenanthrene skeleton diaryliodonium



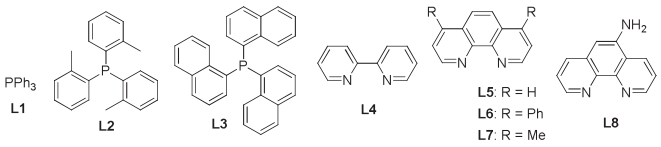

**SCHEME 2** Cyclocarbonylation of 2-Iodobiphenyl

**TABLE 3** One-pot strategy of cyclocarbonylation of *o*-iodobiaryls[a,b]




[a]Reaction conditions: **3** (0.2 mmol), *m*CPBA (0.3 mmol), CO (1 atm), $Pd(OAc)_2$ (2 mol%), **L5** (5 mol%) in DCE (2 mL), 120 °C, 8 h.

[b]Isolated yields.




It is notable that complicated cyclic diaryliodonium including phenanthrene skeleton was well tolerated in the reaction, providing **2q** in 65% yield (Scheme 1), which could be utilized in the synthesis of optoelectronic materials.

Furthermore, the cyclocarbonylation of 2-Iodobiphenyl under the optimal reaction conditions was also investigated, the reaction provided fluorenone in only 5% yield (Scheme 2).

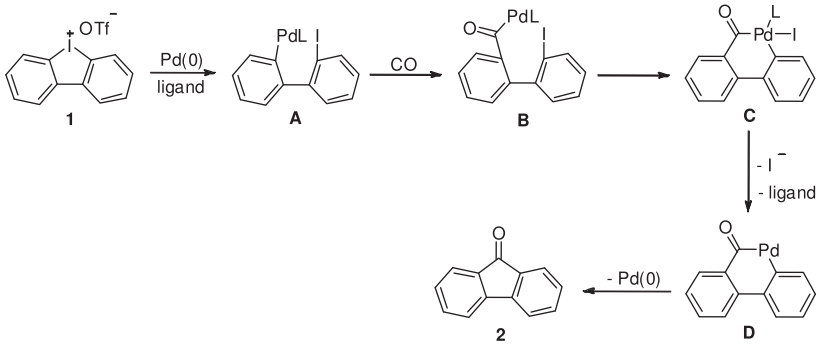
To further explore the synthetic versatility of the cyclocarbonylation reaction, we examined the scope of indole cyclic diaryliodonium.

It is regretful that indole cyclic diaryliodoniums were not obtained from 1-(2-iodophenyl)-1*H*-indole **3a** under traditional synthesis procedure.[33] However, to our satisfaction, combining the cyclic diaryliodonium syntheses and cyclocarbonylation, one pot strategy was used, the corresponding product 10*H*-indolo[1,2-*a*]indol-10-one **4a** was obtained in 61% yield. To explore the general utility of this method, a variety of nitrogenous heterocyclic compounds were investigated for this transformation. It appears that all the substrates were found to perform well in the reaction (Table 3).

Finally, we proposed a possible reaction mechanism for this palladium-catalyzed cyclocarbonylation of cyclic diaryliodoniums (Scheme 3). Initially, oxidative addition of the cyclic diaryliodonium to Pd (0) to form palladium species A, CO insertion to generate the palladium intermediate **B**. A further oxidative addition of the neighboring aryl C-I to the palladium to formation of a Pd(IV) intermediate **C** and subsequent elimination of ligand and iodine anion to generate intermediate **D**, and the final product fluorenone is obtained from reductive elimination of the ketone with simultaneous regeneration of the Pd(0) catalyst.[31,32]

## 3 | CONCLUSION

In summary, we developed a direct route to fluorenones by palladium-catalyzed cyclocarbonylation of cyclic




**SCHEME 3** Proposed mechanism

diaryliodoniums with CO. The reaction outcomes provide straightforward access to synthetically and medicinally fluorenone derivatives in up to 97% yield. In addition, one pot strategy was developed from 1-(2-iodophenyl)-1*H*-indole to syntheses indolo fluorenones in modest yields via the formation of cyclic diaryliodoniums. Further studies to extend the scope and synthetic utility for synthesis of substituted fluorenones are in progress in our laboratory.

## 4 | EXPERIMENTAL

### 4.1 | General procedure

Various reagents were purchased from Aldrich, Acros or Alfa. The cyclic diaryliodonium **1**,[34] iodophenyl-1H-indole **3**[35] were prepared according to literature procedure. Flash column chromatography was performed using silica gel (200–300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). $^{1}$H NMR and $^{13}$C NMR spectra were recorded on Bruker 300 (300 MHz) or 500 (500 MHz) spectrometer, using $CDCl_3$ as solvent and TMS as an internal reference.

### 4.2 | Typical procedure for cyclocarbonylation of cyclic diaryliodoniums

In the pressure tube, a solution of cyclic diaryliodonium **1** (0.2 mmol), $Pd(OAc)_2$ (0.004 mmol) and ligand (0.01 mmol) in solvent (2 ml) was stirred at 120°C for 8 h under 1 atm of CO. After completion of the reaction (observed on TLC), the solvent was evaporated under reduced pressure to obtain the crude mixture. The residues was purified by silica-gel column chromatography (Ethyl acetate / Petroleum ether = 1/50 - 1/10) to afford the pure product **2**. The obtained product was analyzed by $^{1}$H NMR and $^{13}$C NMR.

#### 4.2.1 | 9H-fluoren-9-one 2a

yellow solid; (35.0 mg, 97%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.66 (dt, $J$ = 7.4, 1.0 Hz, 2H), 7.55 – 7.45 (m, 4H), 7.29 (td, $J$ = 7.2, 1.7 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 194.0, 144.4, 134.7, 134.1, 129.1, 124.3, 120.3.

#### 4.2.2 | 2-fluoro-9H-fluoren-9-one 2b

yellow solid; (33.7 mg, 85%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.56 (d, $J$ = 7.2 Hz, 1H), 7.46 – 7.32 (m, 3H), 7.29 – 7.15 (m, 2H), 7.07 (ddd, $J$ = 8.9, 8.1, 2.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 192.5, 163.5 (d, $J$ = 245.2 Hz), 161.9, 143.9, 140.1, 135.1, 128.7 (d, $J$ = 32.2 Hz), 124.6, 121.7, 121.0, 120.7, 120.1, 111.8 (d, $J$ = 21.2 Hz).

#### 4.2.3 | 2-chloro-9H-fluoren-9-one 2c

yellow solid; (38.5 mg, 90%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.69 – 7.59 (m, 2H), 7.56 – 7.41 (m, 4H), 7.39 – 7.28 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 192.5, 143.6, 142.6, 135.6, 135.1, 134.2, 129.3, 124.7, 121.4, 120.4.

#### 4.2.4 | 2-(trifluoromethyl)-9H-fluoren-9-one 2d

yellow solid; (46.6 mg, 94%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.96 – 7.85 (m, 1H), 7.74 (ddt, $J$ = 13.2, 7.4, 0.9 Hz, 2H), 7.68 – 7.52 (m, 3H), 7.39 (td, $J$ = 7.3, 1.4 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 191.8, 147.4, 142.9, 135.0, 134.2, 131.5, 130.1, 124.4, 121.1, 120.5, 53.6.

#### 4.2.5 | 2-methyl-9H-fluoren-9-one 2e

yellow solid; (33.0 mg, 85%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 (dt, $J$ = 7.3, 1.0 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.31 – 7.21 (m, 2H), 2.37 (s, 3H, -$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 194.3, 144.6, 141.8, 139.3, 135.1, 134.6, 134.3, 128.6, 125.0, 124.2, 120.1, 21.5.

#### 4.2.6 | 2-methoxy-9H-fluoren-9-one 2f

yellow solid; (27.3 mg, 65%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.60 (t, $J$ = 7.5 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.24 – 7.16 (m, 2 H), 6.98 (dd, $J$ = 8.2, 2.5 Hz, 1H), 3.86 (s, 3H, -$OCH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 193.9, 160.8, 144.9, 136.9, 135.8, 134.9, 124.3, 121.4, 120.3, 119.6, 109.3, 55.7.

#### 4.2.7 | 2-ethyl-9H-fluoren-9-one 2g

yellow solid; (21.2 mg, 51%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.64 (dt, $J$ = 7.3, 1.0 Hz, 1H), 7.54 – 7.38 (m, 4H), 7.34 – 7.29 (m, 1H), 7.28 – 7.23 (m, 1H), 2.67 (t, $J$ = 7.6 Hz, 2H, -$CH_2$-), 1.26 (t, $J$ = 7.6 Hz, 3H, -$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 194.3, 145.7, 144.6, 142.1, 134.6, 134.1, 128.6, 124.3, 123.9, 120.0, 28.8, 15.4.

#### 4.2.8 | 3-fluoro-9H-fluoren-9-one 2h

yellow solid; (22.6 mg, 57%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.71 – 7.58 (m, 2H), 7.54 – 7.43 (m, 2H), 7.32 (ddd, $J$ = 7.3, 6.6, 1.9 Hz, 1H), 7.17 (dd, $J$ = 8.3, 2.2 Hz, 1H), 6.94 (ddd, $J$ = 9.0, 8.1, 2.2 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 192.1, 168.9, 165.6, 147.5, 142.8, 134.7, 130.2, 129.8, 126.5, 124.3, 120.6, 115.4, 108.3.

#### 4.2.9 | 3-chloro-9H-fluoren-9-one 2i

yellow solid; (23.1 mg, 54%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68 (d, $J$ = 7.2 Hz, 1H), 7.59 (d, $J$ = 7.9 Hz, 1H), 7.51

(ddd, $J$ = 5.6, 2.4, 1.3 Hz, 3H), 7.34 (ddd, $J$ = 7.3, 5.4, 3.2 Hz, 1H), 7.30 – 7.26 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 192.5, 146.1, 143.1, 141.0, 134.8, 134.3, 132.4, 129.8, 129.0, 125.4, 124.6, 121.0, 120.0.

#### 4.2.10 | 3-methyl-9H-fluoren-9-one 2j

yellow solid; (27.9 mg, 72%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.64 (dd, $J$ = 7.3, 1.0 Hz, 1H), 7.55 (d, $J$ = 7.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.36 – 7.26 (m, 2H), 7.09 (d, $J$ = 7.5 Hz, 1H), 2.43 (s, 3H, -$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 187.4, 159.1, 142.0, 138.8, 136.5, 133.9, 129.1, 128.6, 123.7, 121.5, 119.4.

#### 4.2.11 | 2,3-dimethoxy-9H-fluoren-9-one 2k

yellow solid; (40.3 mg, 84%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.52 (d, $J$ = 8.0, 1H), 7.37 (dd, $J$ = 8.0, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.17 (m, 2H), 6.96 (s, 1H), 3.99 ( s, 3H, -$OCH_3$), 3.90 (s, 3H, -$OCH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 193.2, 154.5, 149.7, 143.9, 139.4, 134.7, 134.2, 128.1, 126.8, 123.7, 119.1, 107.1, 103.4, 56.3, 56.2.

#### 4.2.12 | 2-chloro-6-fluoro-9H-fluoren-9-one 2l

yellow solid; (23.7 mg, 51%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.52 (d, $J$ = 7.2, 1.2, 0.7 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.22 – 7.09 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 187.4, 159.1, 142.0, 138.8, 136.5, 133.9, 129.1, 128.6, 123.7, 121.5, 119.4.

#### 4.2.13 | 6-fluoro-2-methyl-9H-fluoren-9-one 2m

yellow solid; (31.4 mg, 74%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62-7.60 (m, 2H), 7.45 (s, 1H), 7.35 (d, $J$ = 7.8 Hz, 1H), 7.29 (d, $J$ = 7.8 Hz, 1H), 7.13 (d, $J$ = 8.4 Hz, 1H), 6.90 (m, 1H), 2.38 (s, 3H, -$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 192.3, 168.6, 166.0, 147.7, 147.6, 140.1, 140.1, 135.1, 134.9, 130.3, 126.3, 125.0, 120.4, 115.1, 114.8, 108.2, 108.0, 21.4.

#### 4.2.14 | 6-fluoro-2-methoxy-9H-fluoren-9-one 2n

yellow solid; (27.4 mg, 60%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.57 (ddd, $J$ = 7.2, 1.2, 0.7 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.16 (m, 1H), 7.04 – 6.82 (m, 3H), 3.83 (s, 3H, -$OCH_3$) . $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 191.9, 168.7, 166.1, 161.3, 147.9, 136.4, 135.1, 130.2, 126.3, 121.5, 120.0, 114.2, 114.0, 109.3, 107.8, 107.5.

#### 4.2.15 | 4H-indeno[1,2-b]thiophen-4-one 2o

yellow solid; (25.3 mg, 68%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45 (ddd, $J$ = 7.2, 1.2, 0.7 Hz, 1H), 7.37-7.31 (m, 1H), 7.22 – 7.09 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 187.4, 159.1, 142.0, 138.8, 136.5, 133.9, 129.1, 128.6, 123.7, 121.5, 119.4.

#### 4.2.16 | 7-fluoro-4H-indeno[1,2-b]thiophen-4-one 2p

yellow solid; (22.4 mg, 55%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (dd, $J$ = 8.0, 5.1 Hz, 1H), 7.26 (d, $J$ = 3.1 Hz, 1H), 7.14 (d, $J$ = 4.9 Hz, 1H), 6.90 – 6.77 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 185.7, 167.7, 165.7, 156.5, 143.2, 141.5, 132.3, 130.1, 125.5, 121.6, 114.1, 108.4.

#### 4.2.17 | 9H-indeno[1,2-l]phenanthren-9-one 2q

yellow solid; (36.4 mg, 65%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.25 (d, $J$ = 7.5 Hz, 1H), 8.74 (d, $J$ = 9.6 Hz, 1H), 8.64 (dd, $J$ = 13.6, 7.8 Hz, 2H), 8.06 (d, $J$ = 7.6 Hz, 1H), 7.83 – 7.59 (m, 5H), 7.54 – 7.45 (m, 1H), 7.32 (t, $J$ = 7.0 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 196.0, 144.7, 143.9, 137.7, 134.4, 134.0, 131.0, 129.3, 128.9, 128.4, 127.7, 127.4, 127.3, 126.1, 125.8, 125.3, 124.0, 123.6, 123.4, 122.7.

### 4.3 | Typical procedure for one-pot strategy of cyclocarbonylation of o-iodobiaryls

In the pressure tube, a solution of *o*-iodobiaryls **3** (0.2 mmol), *m*CPBA (0.3 mmol), $Pd(OAc)_2$ (0.004 mmol) and ligand (0.01 mmol) in solvent (2 ml) was stirred at 120°C for 8 h under 1 atm of CO. After completion of the reaction (observed on TLC), the solvent was evaporated under reduced pressure to obtain the crude mixture. The residues was purified by silica-gel column chromatography (Ethyl acetate / Petroleum ether = 1/50 - 1/10) to afford the pure product **4**. The obtained product was analyzed by $^1$H NMR, $^{13}$C NMR.

#### 4.3.1 | 10H-indolo[1,2-a]indol-10-one 4a

dark yellow solid; (26.7 mg, 61%); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.58 - 7.49 (m, 2H), 7.48 – 7.35 (m, 2H), 7.19 – 7.05 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 181.7, 145.6, 135.8, 135.6, 134.3, 132.6, 129.4, 128.1, 125.2, 123.9, 122.0, 111.4, 108.1.

#### 4.3.2 | 2-bromo-10H-indolo[1,2-a]indol-10-one 4b

dark yellow solid; (27.9 mg, 47%); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 1.9 Hz, 1H), 7.69 (dt, $J$ = 7.5, 0.9 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.47 – 7.35 (m, 2H), 7.18 – 7.07 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 181.1,

145.3, 136.6, 135.7, 134.1, 132.7, 130.9, 129.2, 127.4, 125.4, 124.3, 115.0, 112.5, 111.4, 106.7.

### 4.3.3 | 3-bromo-10H-indolo[1,2-a]indol-10-one 4c

yellow solid; (32.1 mg, 54%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.66 – 7.58 (m, 2H), 7.51 – 7.43 (m, 2H), 7.31 (dt, $J$ = 8.0, 0.8 Hz, 1H), 7.22 -7.16 (m, 1H), 7.12 – 7.02 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 181.2, 145.1, 136.2, 135.7, 134.6, 131.4, 130.1, 129.3, 126.0, 125.5, 124.4, 122.1, 114.2, 111.5, 107.7.

### 4.3.4 | 3-chloro-10H-indolo[1,2-a]indol-10-one 4d

dark yellow solid; (32.9 mg, 65%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 – 7.59 (m, 1H), 7.54 – 7.46 (m, 3H), 7.30 (dt, $J$ = 7.9, 0.8 Hz, 1H), 7.10 – 7.02 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 181.2,145.1, 136.4, 135.6, 134.3, 134.2, 131.1, 129.4, 125.7, 125.4, 124.4, 122.9, 111.4, 107.7.

### 4.3.5 | 7- methyl -10H-indolo[1,2-a]indol-10-one 4e

white solid; (26.6 mg, 57%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.85 – 7.83 (m, 1H), 7.77 – 7.75 (m, 1H), 7.71 – 7.69 (m, 1H), 7.62 – 7.60 (m, 1H), 7.59 – 7.56 (m, 1H), 7.47 – 7.45 (m, 1H), 7.16-7.13 (m, 1H), 7.13 – 7.10 (m, 1H), 2.50 (s, 3H, -$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 178.1, 140.1, 135.8, 133.3, 132.6, 131.7, 128.6, 128.5, 124.1, 123.4, 122.8, 121.5, 121.3, 111.7, 110.6, 9.6.

### 4.3.6 | 9H-pyrrolo[1,2-a]indol-9-one 4f

dark yellow solid; (13.9 mg, 41%); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.58-7.56 (m, 1H), 7.43 (td, $J$ = 7.7, 1.3 Hz, 1H), 7.19 – 7.05 (m, 3H), 6.78 (dd, $J$ = 3.8, 0.9 Hz, 1H), 6.31 (dd, $J$ = 3.8, 2.6 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 179.7, 143.8, 134.1, 132.0, 130.3, 125.5, 124.5, 119.4, 115.9, 114.0, 110.3.

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