JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 22 Jan 2019

Just Accepted

ACS Publications

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Copper Catalyzed Oxidative C−C bond Cleavage of 1,2-Diketones: A Divergent Approach to 1,8-Naphthalimides, Biphenyl-2,2'-dicarboxamides and *N*-Heterocyclic amides

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Supporting Information

Abstract:

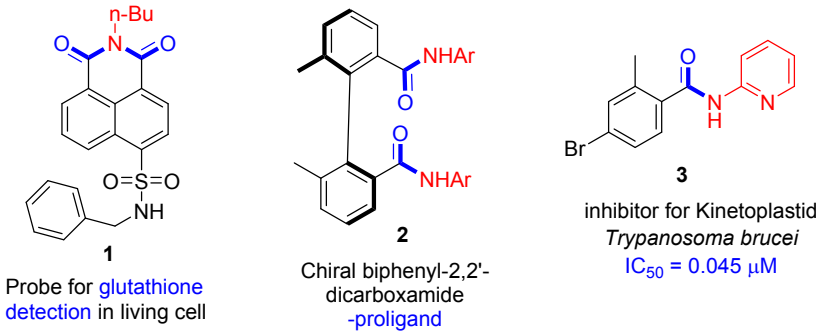
We report here a simple and efficient copper catalyzed oxidative C-C bond cleavage of stable aromatic cyclic-fused and acyclic 1,2-diketones to deliver amides and imides in high yields. This newly developed protocol provides an excellent tool to transform structurally different 1,2-diketones into different products under the same reaction conditions. The key synthetic features of this methodology are the formation of 1,8-naphthalimides and biphenyl-2,2'-dicarboxamide motifs in high yields. The fluorescent studies of 1,8-naphthalimide derivatives were also carried out in order to show potential application of these scaffolds.

Introduction:

The selective cleavage of inherently inert C─C bond followed by their functionalization became an attractive subject for chemists to reassemble molecular architecture into useful compounds.[1,2] Remarkably, strategies developed by using noble transition metals such as iridium,[3] rhodium,[4] ruthenium[5] and palladium[6] for C─C bond cleavage have made an immense contribution, however, inexpensive 3d-transition metal catalysts has received attention only in recent years.[7] Nonetheless, oxidative C─C bond cleavage by means of 3d-transition metal is a popular choice to construct important scafolds.[8] Recently our group has also disclosed a copper-catalyzed oxidative C–C bond cleavage of methyl ketones to form *N*-heterocyclic amides.[9] Although, the reports on selective C–C bond cleavage of highly stable functionalities are increasing, to the best of our knowledge cleavage of 1,2-diketone by means of copper catalysis is not known in the

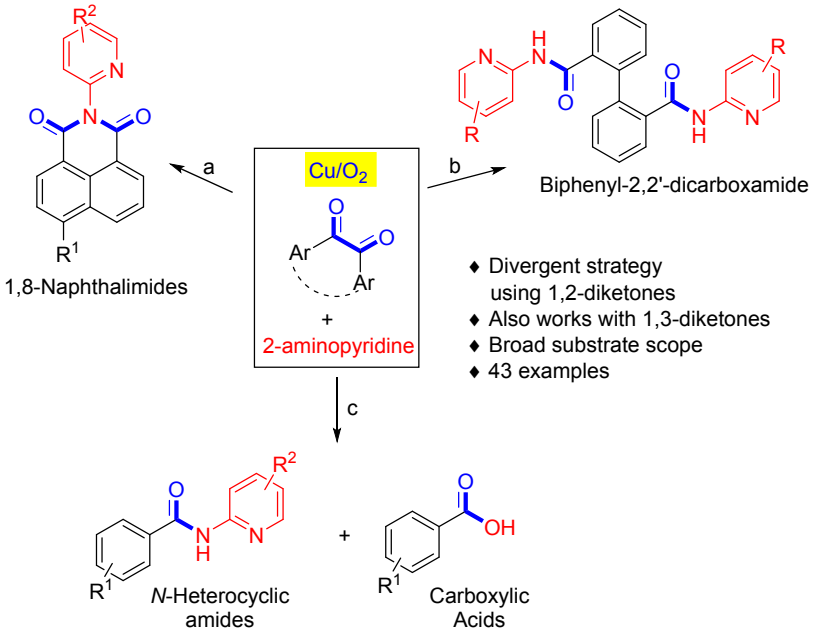
literature.[10] The 1,2-diketone is a versatile motif, used as starting materials in various organic transformations.[11] Furthermore, the selective synthesis of different products from similar substrates by using transition metal catalysis is often considered as an excellent tool to access important motifs.[8a,12] Therefore, we became interested in developing a divergent approach in copper-catalyzed C─C bond functionalization of 1,2-diketones to useful compounds.

Figure 1. Representative amides.



Further, amides are privileged feedstock present in many natural products, medicinally important molecules, and agro-chemicals.[13] The arene-fused cyclic-imides and biphenyl-2,2'-dicarboxamides are special class of amides known for their signature applications (Figure 1). The arene-fused cyclic imides are found in organic semiconductors, fungicides, organic photovoltaics, polymers and pharmaceuticals.[14] Among them, 1,8-naphthalimides are in huge demand due to their inherent photo-physical properties.[15] However, these 1,8-naphthalimides are

Scheme 1. Present work.



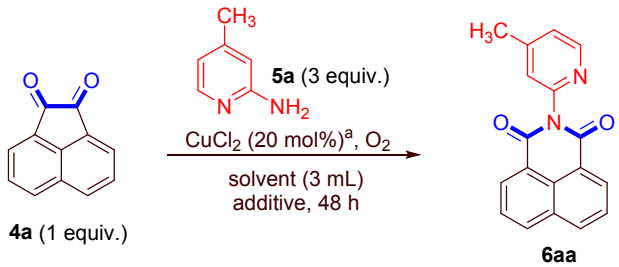
generally synthesized by following a traditional condensation reaction between carboxylic acid derivatives with amines and mostly follow multiple reaction sequence.[15,16] Biphenyl-2,2'-dicarboxamides are another class of amides, having axial chirality, used as proligands and source of chirality for the remote chiral induction in asymmetric catalysis.[17] Despite these impressive applications, sequential reactions such as acid-amine coupling followed by transition metal catalyzed intramolecular aryl-aryl coupling are primarily relied upon for their preparations.[18] In order to overcome these multi-step sequential reactions, we intend to design a divergent cascade approach to synthesize these molecules. Thus, herein, we disclose a copper catalyzed oxidative C–C bond cleavage of various 1,2-diketones with 2-amino heterocycles towards the formation of cyclic-imides, biphenyl-2,2'-dicarboxamides and *N*- heterocyclic amides. Our first strategy involves a copper catalyzed oxidative C–C bond functionalization between various acenaphthoquinones and 2-aminopyridines to 1,8-naphthalimides (Scheme 1; **a**). The second strategy discusses the synthesis of useful biphenyl-2,2'-dicarboxamides from 9,10-

phenanthrenequinone and 2-aminopyridines (**b**). The third strategy deals with the synthesis of *N*-heterocyclic amides and carboxylic acids from acyclic 1,2-diketones (**c**).

Results and Discussion:

Our investigation of proposed C─C bond cleavage strategy began with the exposure of acenaphthoquinone **4a** and 4-methyl-2-aminopyridine **5a** to a series of copper catalytic reaction conditions. When model substrates **4a** and **5a** were subjected in the presence of $CuCl_2$ (20 mol%) in DMF at 80 °C under O_2 atmosphere, we were delighted to observe the formation of the *N*-pyridyl 1,8-naphthalimide **6aa** in 59% yield as sole product (Table 1, entry 1). Further addition of additives was useful in order to improve the yield of the product. However, reaction was sluggish when pyridine was used as an additive (refer Table 1, entry 7–10). After the extensive screening of reaction conditions, the desire product **6aa** was isolated in 98% in the presence of $CuCl_2$ (20 mol%) and *t*-BuOH:*m*-xylene (1:2) solvent system along with 0.1 equiv. of pivalic acid as an additive (Table 1, entry 15).

Table 1. Optimization for 1,8-naphthalimide



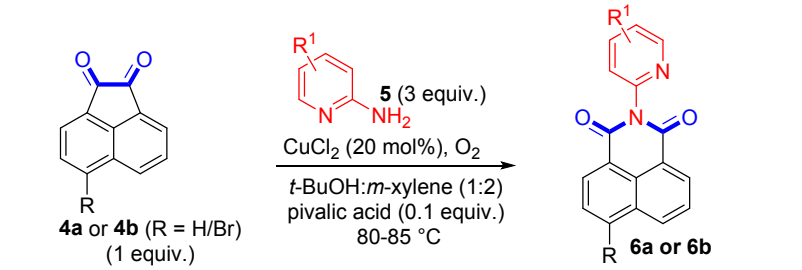
Entry	Solvent	Additive	Isolated Yield (%)
1	DMF	-	59
2	DMSO	-	61

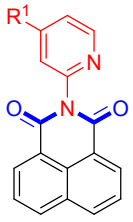
3	*t*-BuOH	-	66
4	*m*-Xylene	-	61
5	*t*-BuOH	Pivalic acid (0.1 equiv.)	81
6	*m*-Xylene	Pivalic acid (0.1 equiv.)	71
7[b]	*t*-BuOH	Pyridine (1.0 equiv.)	87
8[b]	DMF	Pyridine (1.0 equiv.)	72
9[b]	*m*-Xylene	Pyridine (1.0 equiv.)	84
10[b]	Isopropanol	Pyridine (1.0 equiv.)	91
11	CH_3CN	Pyridine (1.0 equiv.)	94
12	NMP: *t*-BuOH (1:2)	Pyridine (1.0 equiv.)	74
13	NMP: *t*-BuOH (1:2)	-	42
14	*t*-BuOH: *m*-Xylene (1:2)	-	70
15	***t*-BuOH: *m*-Xylene (1:2)**	**Pivalic acid (0.1 equiv.)**	**98**

a- our earlier work on copper catalyzed C–C bond cleavage route to amide synthesis was successful using 20 mol% $CuCl_2$.[9] b-reaction time is 72 h.

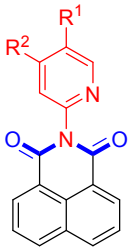
With optimized conditions in hand, the substrate scope for the synthesis of different 1,8-naphthalimides were explored by using a range of 2-aminopyridines **5**. We were pleased to isolate the respective products **6aa–6aj** (Scheme 2) in good to excellent yields under the set reaction condition. Both the electron-donating and -withdrawing substituents on 2-aminopyridines were well tolerated under the reaction conditions. Remarkably, the halogen substituents remain unaffected, proving its explicit selectivity towards the oxidative C─C bond cleavage reaction. Further extension of this protocol with 5-bromoacenaphthylene-1,2-dione **4b** gave corresponding 1,8-napthalimdes under the optimized reaction conditions in good to excellent yields (Scheme 2, **6ba-6bi**). These 4-bromo-1,8-naphthalimides **6b** further could be easily elaborated to useful push-pull fluorescent dyes by using coupling reactions. Notably, the oxidative C–C bond functionalization of 5-bromoacenaphthylene-1,2-dione **4b** took shorter reaction time than the model compound **4a**.

Scheme 2. Scope for 1,8-naphthalimide.



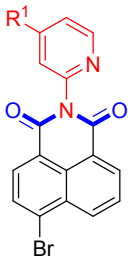


6aa R^1 = Me, 98%, 48 h
6ab R^1 = Cl, 88%, 48 h
6ac R^1 = OMe, quant. 24 h
6ad R^1 = H, 68%, 48 h

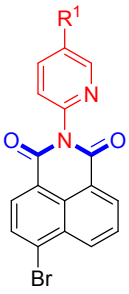


6ae R^1 = OMe, R^2 = H, 86%, 48 h
6af R^1 = Me, R^2 = H, 91%, 48 h
6ag R^1 = CF_3, R^2 = H, 79%. 48 h
6ah R^1 = Br, R^2 = H, 64%, 72 h
6ai R^1 = Br, R^2 = Me, 64%. 72 h

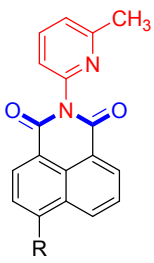
X-ray crystal structure of **6ag**



6ba R^1 = Me, 87%, 6 h
6bb R^1 = Cl, 74%,12 h
6bc R^1 = OMe, 96%, 4 h
6bd R^1 = H, 87%, 6 h



6be R^1 = CF_3, 71%, 12 h
6bf R^1 = Me, 69%, 6 h
6bg R^1 = I, 47%, 24 h
6bh R^1 = Br, 39%, 24 h

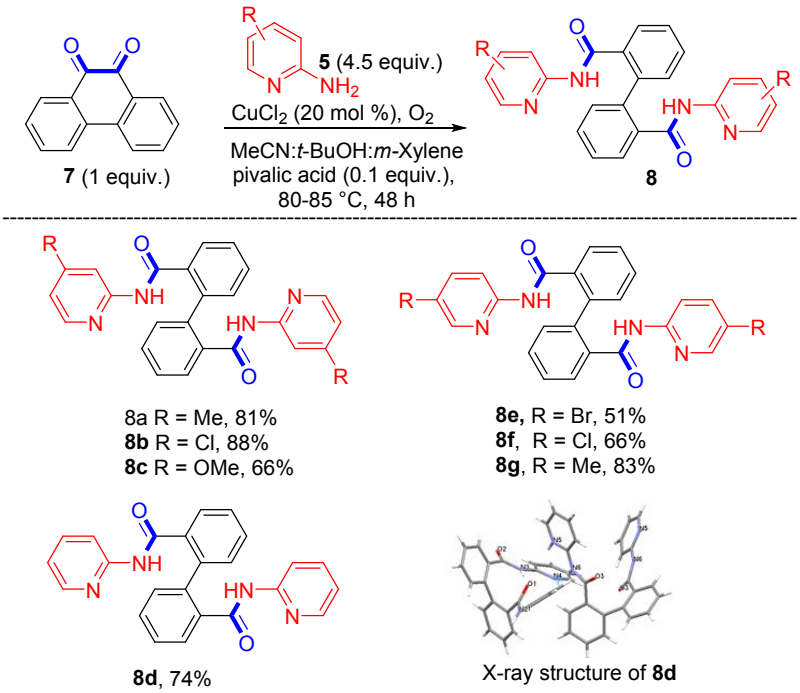


6aj R = H, 94%, 48 h
6bi R = Br, 76%, 6 h

To demonstrate the potential application of this method, we next employed six-membered cyclic 1,2-diketones under the aforementioned conditions in Scheme 2. Interestingly, the reaction of 9,10-phenanthrenequinone **7** with 2-aminopyridine under these conditions offered biphenyl-2,2'-dicarboxamide **8a** in 66% instead of corresponding cyclic-imide along with recovery of some starting material (Scheme 3). Nevertheless, biphenyl-2,2'-dicarboxamide **8a** is a versatile compound used for various purposes including in asymmetric catalysis. As well, to the best of our knowledge, this method would be a shortest and single step protocol for accessing biphenyl-2,2'-dicarboxamides. Hence, we planned to optimize the reaction conditions further to improve the yield of the product. After the solvent modification, we isolated 74% of the desired product **8a** under $CuCl_2$ (20 mol%) in a mixture of MeCN:*t*-BuOH:*m*-xylene (1:1:1). These revised conditions were then applied to various 2-aminopyridines and the corresponding biphenyl -2,2'-

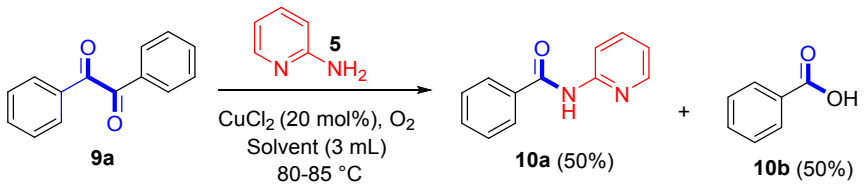
dicarboxamides were isolated in excellent yields (Scheme 3). However, the strong electron withdrawing substituents (-NO_2, and –CN) on 2-aminopyridines have failed to provide the expected products.

Scheme 3. Scope for biphenyl-2,2'-dicarboxyamide.



After successfully developing a simple and efficient process for cleaving the cyclic 1,2-diketones, we focused our attention to extend this strategy to acyclic 1,2-diketones (Scheme 4a). Based on our earlier observations (Scheme 1 & 2) that 2 moles of amide formation was expected from 1 mole of acyclic 1,2- diketones. However, the initial reaction of benzil 9a with 2-aminopyridine 5d under optimized conditions (refer Table 2, entry 7) afforded corresponding *N*-pyridyl amide 10aa in low yield (Scheme 4a). Although a further increase in the amine

Table 2: Optimization for *N*-Heterocyclic Amide

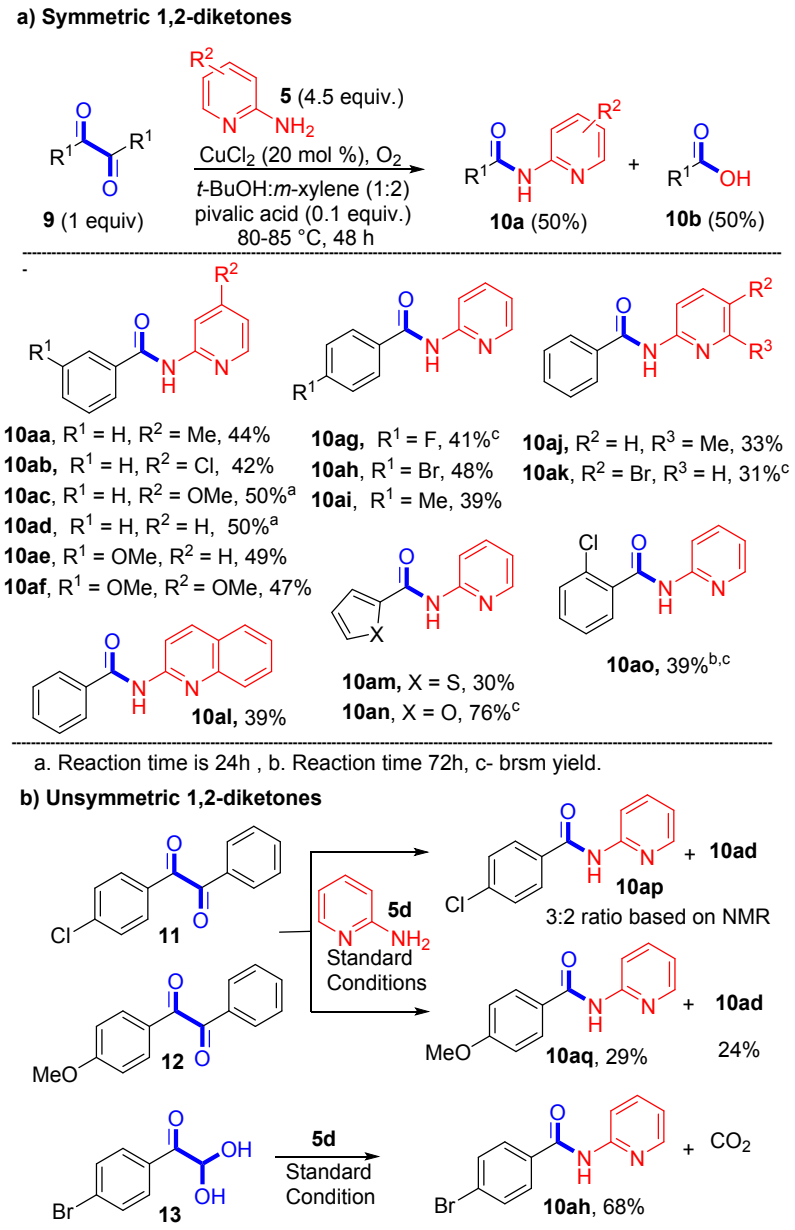


Entry	2-aminopyridine (equiv.)	Solvent	Additive (equiv.)	Time (h)	Isolated Yield for 50%
1	3	DCE	-	48	-
2	3	DMSO	-	48	20
3	3	DMF	-	48	10
4	3	*n*-hexanol	-	48	-
5	3	*n*-pentanol	-	48	-
6	3	*i*-PrOH	-	72	33
7	3	*t*-BuOH:*m*-xylene (1:2)	-	48	39
8	3	NMP:*t*-BuOH (1:2)	-	>72	45
9	3	1,4-dioxane:MeCN (1:2)	-	48	Trace
10	3	NMP	pyridine (1.0)	48	25
11	3	*t*-BuOH	pyridine (1.0)	48	44
12[a]	3+1.5	*t*-BuOH	pyridine (1.0)	72	30
13	3	*m*-xylene	pyridine (1.0)	48	34
14	4.5	*m*-xylene	pyridine (1.0)	72	40
15	5	NMP:*m*-xylene (1:2)	pyridine (1.0)	72	46
16	5	*t*-BuOH:*m*-xylene (1:2)	pyridine (1.0)	72	35
17	3	*t*-BuOH	pivalic acid (0.1)	>72	35
18	3	*m*-xylene	pivalic acid (0.1)	>72	38
19	4.5	*t*-BuOH:*m*-xylene (1:2)	formic acid (1.0)	48	44
20	3	NMP:*t*-BuOH (1:2)	AcOH (0.1)	48	36
21	3	*m*-xylene	2,6-lutidine	48	14
22[b]	**4.5**	***t*-BuOH:*m*-xylene (1:2)**	**pivalic acid (0.1)**	48	**50**

a -1.5 equiv. of 2-aminopyridine was added after 24 h, b – benzoic acid isolated in 30% yield.

equivalence slightly improved the yield, mass imbalance suggested the formation of side product. After careful observations, corresponding benzoic acid 10ba was isolated from the aqueous medium in good yield as another product of the reaction.

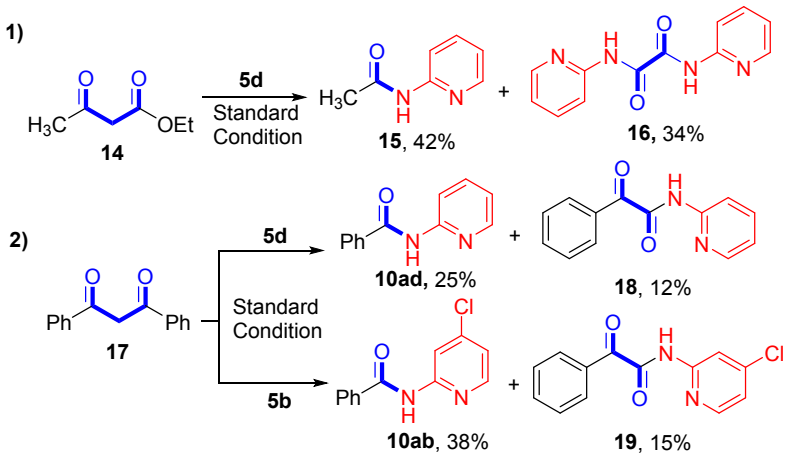
Scheme 4. Substrate scope with acyclic 1,2-diketones.



The reaction scope was examined further with a range of acyclic 1,2-diketones and 2-aminopyridines. Subsequently, the corresponding products, amides **10a** and acids **10b** were isolated in good to excellent yields (Scheme 4a, for acid refer SI). Further, a few unsymmetrical

1,2-diketones[8f] have also been subjected to oxidative C–C bond cleavage reactions and the results are described in Scheme 4b. Finally, the applicability of this catalytic system was tested on other functionalities such as *β*-keto ester and 1,3-diketone. Thus, ethyl acetoacetate **14** with 2-aminopyridine afforded acetamide **15** and N^1,N^2-di(pyridin-2-yl)oxalamide **16** in good yields (Scheme 5, eq. 1), whereas, 1,3-diphenylpropane-1,3-dione **17** delivered the corresponding amides (**10ad** & **10ab**) along with alpha-keto amides in low yields (Scheme 5, eq.2).[8f,9]

Scheme 5. Substrate scope with *β*-keto ester and 1,3-diketone.

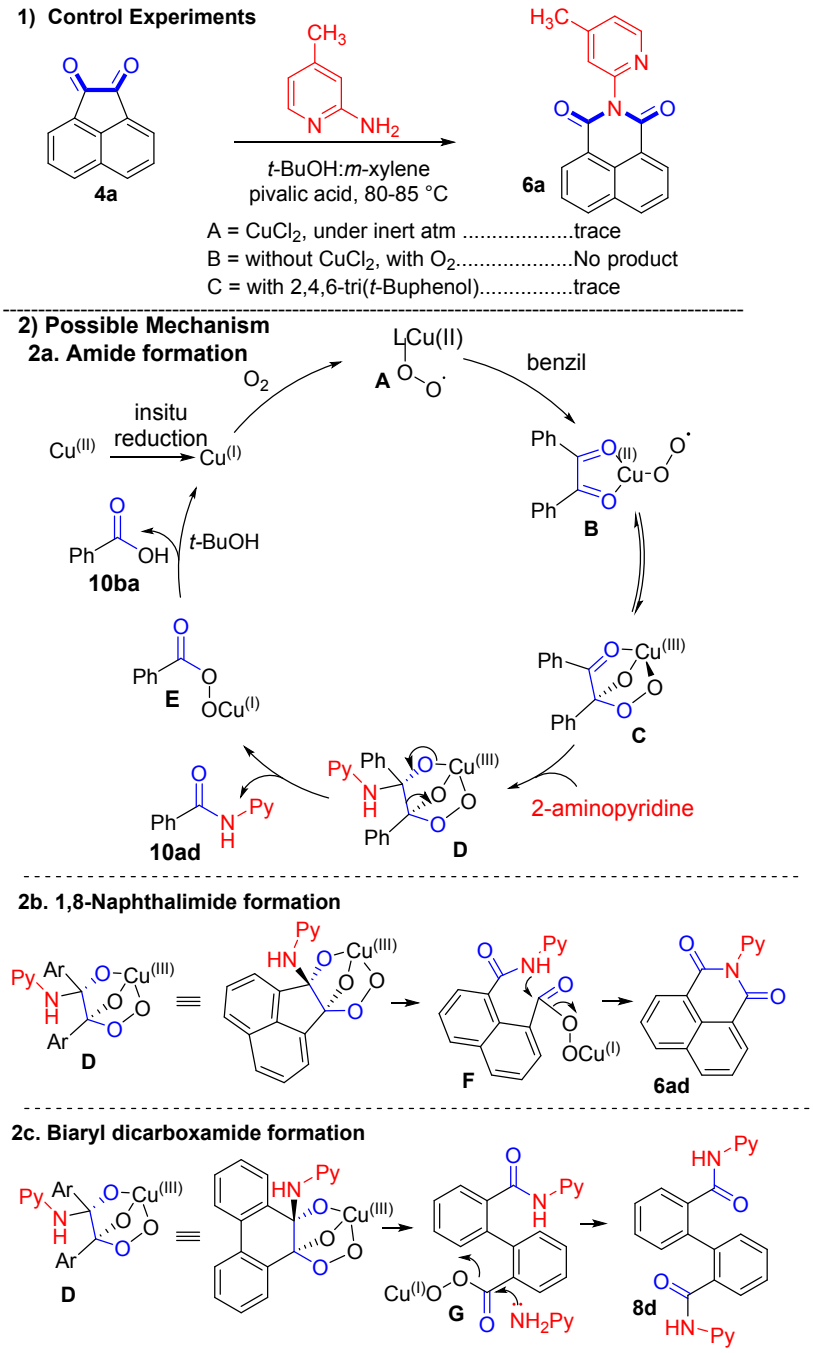


To gain insight into the reaction mechanism, several control experiments were carried out (refer experimental section). When the standard reaction was carried out under an inert atmosphere, only 1,8-naphthalimide **6aa** was obtained in traces, suggesting the necessity of oxygen for the formation of required product (Scheme 6, 1). Further, the reaction didn't give the anticipated product in the absence of copper catalyst. Following our earlier studies,[9] we believed that the mechanistic cycle commences with the formation of the copper-peroxy radical species. Thus, the radical-trapping experiment was conducted using 2,4,6-tri(*t*-Bu)phenol as radical scavenger under the standard conditions. The product formation was significantly inhibited, suggesting radical processes being involved in this oxidative cleavage (Scheme 6). The *in situ* generation of active catalytic species Cu(I) under the reaction medium was supported by XPS analysis (refer SI).[19]

Based on the above control experiments and the literature reports[1a] a plausible mechanism for this oxidative C–C bond cleavage is outlined in Scheme 6, 2a. The catalytic cycle is initiated by the *in situ* generation of active catalyst Cu(I) which upon reaction with molecular O_2 to form

copper-peroxy radical **A**.[9] Subsequent chelation with substrate, 1,2-diketone to **B** followed by SET oxidation to provide Cu(III)-intermediate **C**.[20] It is speculated that the more electrophilic chelation of Cu(III) in intermediate **C** facilitates the nucleophilic addition of 2-aminopyridine to ketone to provide the reactive intermediate **D**.[21] Further, the reductive cleavage of intermediate **D**

Scheme 6. 1) Control Experiments. 2) Possible Mechanism.

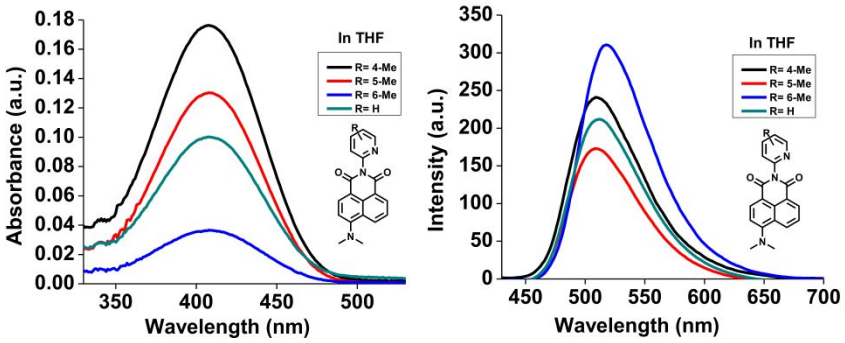


delivers the desired *N*-pyridyl amide and copper benzoyl peroxide **E**. Finally, the ligand exchange or decomposition of copper benzoyl peroxide **E** in the presence of polar solvent regenerate the active catalytic species Cu(I) and by-product, carboxylic acid **10ba**. This mechanism explains the oxidative C–C bond cleavage of acyclic 1,2-diketones. The oxidative C–C bond cleavage of cyclic 1,2-diketone, acenaphthoquinone could be explained from the reactive intermediate **D** (Scheme 6, 2b). The reductive cleavage of **D** offers the desired amide

and copper peroxide moieties in the same compound. The proximity facilitated intramolecular amidation of **F** affords the cyclic-imides and regenerates Cu(I)-species. However, 6-membered cyclic ketone underwent for the intermolecular amidation reaction to obtain corresponding biphenyl-2,2'-dicarboxamide **8d** (Scheme 6, 2c).

In view of their impressive medicinal chemistry application of 1,8-naphthalimides including as fluorescent probes, we envisioned to study the photo-physical properties of our newly synthesized 1,8-naphthalimides. Thus, the chosen compounds were designed as push-pull fluorophore system by attaching the electron donating motif on 4th position of 1,8-naphthalimides (push-pull system) (Figure 2).. Subsequently, we studied extensively the photo-physical properties our push-pull 1,8-naphthalimides by using various solvents. These compounds showed high fluoresce even at 3μM concentration in non-polar solvent like chloroform, dichloromethane whereas in polar solvents like methanol fluorescence is getting quenched (Figure 2).. Also, substituents on pyridine ring did not affect much the absorption or emission frequency in UV-vis and fluorescence spectra respectively (refer SI for details), Thus, for further applications of these compounds as fluorescent dye or sensor, the fluoresces property could be tuned by varying substitutions on naphthalimide core than on pyridyl ring.

Figure 2. Application of 1,8-naphthalimides



Conclusion:

In summary, an efficient strategy for oxidative cleavage of C-C bond of 1,2-diketones has been successfully developed using inexpensive copper-catalyst. The reaction is very mild, simple and a high yielding protocol to access 1,8-naphthalimides, biphenyl-2,2'-dicarboxamides and *N*-heterocyclic amides which are important structural motifs. Our work provides future scope for the utility of different acyclic and cyclic 1,2 or 1,3-diketones towards the synthesis of diverse scaffolds under similar reaction conditions which may find applications in synthetic, applied and material sciences.

Experimental Section:

General Information: All starting materials and reagents were obtained from commercial suppliers and used after further purification as detailed below. The required solvents for isolation of products and chromatography were reagent grade and glass distilled. Toluene and tetrahydrofuran purified using solvent purification system by M-Braun (MB-SPS 5). The reaction flasks were dried in an oven at 150 °C for 12 h. Air and moisture-sensitive reactions were performed under UHP nitrogen atmosphere. Flash column chromatography was performed using silica gel (230-400 mesh, Acma). Thin-layer chromatography (TLC) was conducted with Merck silica gel 60 F_{254} percolated plates (0.25 mm) and visualized with UV. IR spectra were recorded with Perkin Elmer Spectrum One and JASCO V-570 spectrophotometers. Mass spectra were obtained with a Bruker ESI-QTOF spectrometer (maXIS impact 282001.00081). ^{1}H NMR spectra were recorded on a Bruker 400 MHz and a Bruker 500 MHz spectrometer and reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, d^6-DMSO, at 2.50 ppm). Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker 400 MHz and a Bruker 500 MHz spectrometer and have been reported using solvent as an internal standard ($CDCl_3$ at 77.2 ppm, d^6-DMSO at 39.51 ppm). The GC-MS analyses were done by an Agilent 7890A GC system connected with a 5975C inert XL EI/CI MSD (with a triple axis detector). All the UV experiments were carried out using Varian CARY 100 Bio UV-Visible Spectrophotometer. The fluorescent studies were carried out by using Varian CARY Eclipse Fluorescence

Spectrophotometer. The X-Ray studies were carried using Rigaku R-axis 724^+ single crystal x-ray diffraction.

General Procedure A for Synthesis of 1,8-naphthalimide:

To a solution of 1,2-diketone (0.25 mmol/0.5 mmol, 1 equiv.) and 2-aminopyridine (0.75 mmol/1.5 mmol, 3 equiv.) in *t*-BuOH:*m*-xylene (1:2, 3 mL) in a reaction tube, anhydrous $CuCl_2$ (20 mol%) was added at r.t. along with pivalic acid (10 mol%). The reaction mixture was stirred at 80-85 °C for 6-48 h under the oxygen atmosphere and then quenched with H_2O after monitoring by TLC. The aqueous layer was extracted by dichloromethane (DCM, 3 × 20 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude product, which was further purified using flash column chromatography on silica gel (230-400 mesh) column (eluent ethyl acetate-petroleum ether).

2-(4-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6aa):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 4-methyl-2-aminopyridine (162 mg, 1.5 mmol) for 48 h provided corresponding product **6aa** as a pale yellow solid (141 mg, 98%). R_f = 0.1 (100% DCM); m.p. = >260 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.62 (d, J = 7.2 Hz, 2H), 8.57 (d, J = 4.9 Hz, 1H), 8.26 (d, J = 8.2 Hz, 2H), 7.77 (t, J = 7.6 Hz, 2H), 7.25 (s,1H), 7.22 (s, 1H), 2.46 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.4, 150.3, 149.7, 149.7, 134.6, 131.9, 131.7, 128.8, 127.1, 125.3, 124.9, 122.8, 21.2; **IR** υ (KBr, cm^{-1}): 3429, 2921, 1713,

1682, 1668, 1605, 1592, 1405, 1379, 1354, 1244, 781, 772; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}N_2NaO_2$ $[M+Na]^+$ 311.0791, found 311.0792.

2-(4-chloropyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ab):

Following the general procedure **A**, the reaction between acenaphthoquinone (91mg, 0.5 mmol) and 4-chloro-2-aminopyridine (192 mg, 1.5 mmol) for 48 h provided corresponding product **6ab** as a white solid (135 mg, 88%). R_f = 0.19 (20% EtOAc/petroleum ether); m.p. = 257-260 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.66–8.63 (m, 3H), 8.30 (d, J = 8.2 Hz, 2H), 7.81 (t, J = 8.0 Hz, 2H), 7.48–7.44 (m, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.1, 150.7, 150.6, 146.1, 134.8, 131.9, 131.8, 128.7, 127.2, 125.0, 124.7, 122.5; **IR** υ (KBr, cm^{-1}): 3438, 3064, 2922, 1706, 1666, 1574, 1556, 1392, 1374, 1351, 1239, 1197, 837, 775, 743, 720; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_9ClN_2NaO_2$ $[M+Na]^+$ 331.0245, found 331.0247.

2-(4-methoxypyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ac):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 4-methoxy-2-aminopyridine (186 mg, 1.5 mmol) for 24 h provided corresponding product **6ac** as a yellow solid (152 mg, quantitative yield). R_f = 0.4 (100% EtOAc); m.p. = 218-220 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.62 (d, J = 10.0 Hz, 2H), 8.53 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 10.0 Hz, 2H), 7.77 (m, 2H), 6.96 (d, J = 5.0 Hz, 1H), 6.93 (s, 1H), 3.90 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 167.9, 164.2, 151.1, 150.7, 134.6, 131.9, 131.7, 128.7, 127.1, 122.8, 110.9, 110.2, 55.7; **IR** υ (KBr, cm^{-1}):

3363, 3069, 2921, 1708, 1681, 1665, 1600, 1567, 1376, 1357, 1242, 1226, 1195, 1035, 848, 782, 773; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}N_2NaO_3$ $[M+Na]^+$ 327.0740, found 327.0741.

2-(pyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ad):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 2-aminopyridine (141 mg, 1.5 mmol) for 48 h provided corresponding product **6ad** as a yellow solid (125 mg, 68%). R_f = 0.35 (40% EtOAc/petroleum ether); m.p. = 240-243 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.74 (d, J = 4.0 Hz, 1H), 8.64 (d, J = 7.6 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 7.95 (td, J = 7.6, 1.2 Hz, 1H), 7.79 (t, J = 7.6 Hz, 2H), 7.47–7.44 (m, 1H), 7.42 (d, J = 8.4 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 164.4, 150.2, 149.7, 138.7, 134.6, 131.9, 131.7, 128.8, 127.2, 124.3, 124.2, 122.8; **IR** υ (KBr, cm^{-1}): 3433, 3079, 2922, 1704, 1664, 1631, 1589, 1464, 1436, 1375, 1291, 1240, 1198, 1116, 998, 845, 775, 742, 671; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_{10}N_2NaO_2$ $[M+Na]^+$ 297.0634, found 297.0633.

2-(5-methoxypyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ae):

Following the general procedure **A**, the reaction between acenaphthoquinone (45 mg, 0.25 mmol) and 5-methoxy-2-aminopyridine (93 mg, 0.75 mmol) for 48 h provided corresponding product **6ae** as a yellow solid (65 mg, 86%). R_f = 0.10 (40% EtOAc/petroleum ether); m.p. = decomposed >260 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.60 (d, J = 7.2 Hz, 2H), 8.38 (d, J = 2.7 Hz, 1H), 8.25 (d, J = 8.1 Hz, 2H), 7.76 (t, J =

7.7 Hz, 2H), 7.41 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 164.5, 156.0, 142.0, 137.2, 134.5, 131.8, 131.6, 128.7, 127.1, 124.3, 123.1, 122.8, 56.0; **IR** υ (KBr, cm^{-1}): 3438, 3080, 1709, 1680, 1666, 1600, 1588, 1571, 1478, 1391, 1357, 1295, 1259, 1238, 1196, 1126, 1024, 850, 826, 785, 777; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}N_2NaO_3$ $[M+Na]^+$ 327.0740, found 327.0737.

2-(5-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6af):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 5-methyl-2-aminopyridine (162 mg, 1.5 mmol) for 48 h provided corresponding product **6af** as a yellow solid (132 mg, 91%). R_f = 0.12 (40% EtOAc/petroleum ether); m.p. = decomposed >260 °C; **^1H NMR (500 MHz, $CDCl_3$)**: *δ* 8.62 (d, *J* = 5.0 Hz, 2H), 8.55 (s, 1H), 8.26 (d, *J* = 10.0 Hz, 2H), 7.79–7.74 (m, 2H), 7.72 (d, *J* = 5.0 Hz, 1H), 7.29 (d, *J* = 5.0 Hz, 1H), 2.45 (s, 3H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 164.4, 150.5, 147.2, 139.2, 134.5, 134.0, 131.9, 131.6, 128.8, 127.1, 123.5, 122.8, 18.3; **IR** υ (KBr, cm^{-1}): 3427, 1710, 1660, 1646, 1588, 1376, 1353, 1239, 1199, 775; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}N_2NaO_2$ $[M+Na]^+$ 311.0791, found 311.0793.

2-(5-(trifloromethyl)pyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ag):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 5-(trifluoromethyl)-2-aminopyridine (243 mg, 1.5 mmol) for 48 h provided

corresponding product **6ag** as an off white solid (135 mg, 79%). R_f = 0.7 (100% DCM); m.p. = 198-221 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.01 (s, 1H), 8.64 (d, J = 7.1 Hz, 2H), 8.30 (d, J = 8.1 Hz, 2H), 8.18 (d, J = 6.9 Hz, 1H), 7.80 (t, J = 7.6 Hz, 2H), 7.56 (d, J = 8.1 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 164.1, 152.8, 147.3 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 136.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 134.9, 131.9, 128.8, 127.3 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 127.2, 124.6,123.5 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 122.4; **^{19}F NMR (470 MHz, $CDCl_3$)** δ = -62.3 (s, 3F); **IR** υ (KBr, cm^{-1}): 3434, 1709, 1679, 1588, 1376, 1355, 1332, 1240, 1164, 1131, 1079, 779; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_9F_3N_2NaO_2$ $[M+Na]^+$ 365.0508, found 365.0500.

2-(5-bromopyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ah):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 5-bromo-2-aminopyridine (258 mg, 1.5 mmol) for 72 h provided corresponding product **6ah** as a pale orange solid [91 mg, 52% (64% brsm)]. R_f = 0.66 (100% DCM); m.p. = 234-237 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.78 (d, J = 2.1 Hz, 1H), 8.63 (d, J = 7.2 Hz, 2H), 8.28 (d, J = 8.2 Hz, 2H), 8.03 (dd, J = 8.3, 2.3 Hz, 1H), 7.79 (t, J = 7.7 Hz, 2H), 7.31 (d, J = 8.3 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.2, 151.3, 148.3, 141.3, 134.8, 131.9, 131.8, 128.8, 127.2, 125.6, 122.6, 121.2; **IR** υ (KBr, cm^{-1}): 3415, 2924, 1703, 1665, 1589, 1464, 1373, 1353, 1236, 1193, 1010, 826, 778; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_9BrN_2NaO_2$ $[M+Na]^+$ 374.9740, found 374.9738.

2-(5-bromo-4-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ai):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 4-methyl-5-(trifluoromethyl)-2-aminopyridine (280 mg, 1.5 mmol) for 72 h provided corresponding product **6ai** as a off white solid [92 mg, 50% (64% brsm)]. R_f = 0.65 (100% DCM); m.p. = 183-186 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.74 (s, 1H), 8.64-8.61 (m, 2H), 8.29-8.26 (m, 2H), 7.77 (dt, J = 8, 3, 2.3 Hz, 2H), 7.29 (s, 1H), 2.48 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.3, 151.6, 149.9, 148.5, 134.8, 131.9, 131.8, 128.7, 127.2, 126.3, 124.1, 122.6, 22.6; **IR** υ (KBr, cm^{-1}): 3432, 2924, 2169, 1714, 1682, 1669, 1588, 1457, 1376, 1369, 1343, 1239, 1032, 990, 781, 773; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{11}BrN_2NaO_2$ $[M+Na]^+$ 388.9896, found 388.9897.

2-(6-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6aj):

Following the general procedure **A**, the reaction between acenaphthoquinone (91 mg, 0.5 mmol) and 6-methyl-2-aminopyridine (162 mg, 1.5 mmol) for 48 h provided corresponding product **6aj** as a pale yellow solid (135 mg, 94%). R_f = 0.5 (0.2% MeOH : DCM); m.p. = 251-253 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.61 (d, J = 7.2 Hz, 2H), 8.25 (d, J = 8.2 Hz, 2H), 7.81(t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.7 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 2.64 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.4, 159.5, 149.0, 138.8, 134.5, 131.8, 131.6, 128.8, 127.1, 123.9, 122.9, 121.0, 24.4; **IR** υ (KBr,cm^{-1}): 3432, 1714, 1679, 1659, 1591, 1461, 1376, 1355, 1243, 1201, 773, 760; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}N_2NaO_2$ $[M+Na]^+$ 311.0791, found 311.0798.

6-bromo-2-(4-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6ba):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 4-methyl-2-aminopyridine (81 mg, 0.75 mmol) for 6 h provided corresponding product **6ba** as a off white solid (80 mg, 87%). R_f = 0.25 (100% DCM); m.p. = 240-244 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.70 (d, J = 4.0 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 4.0 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.22 (s, 1H), 2.47 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 163.9, 163.8, 150.5, 149.8, 149.3, 133.9, 132.5, 131.6, 131.4, 131.0, 131.0, 129.6, 128.3, 125.5, 124.9, 123.3, 122.4, 21.2; **IR** υ (KBr, cm^{-1}): 3434, 2922, 1710, 1669, 1605, 1588, 1570, 1399, 1359, 1346, 1242, 1193, 779, 773; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}BrN_2O_2$ $[M+H]^+$ 367.0077, found 367.0078.

6-bromo-2-(4-chloropyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bb):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 4-chloro-2-aminopyridine (96 mg, 0.75 mmol) for 12 h provided corresponding product **6bb** as a white solid (53 mg, 74%). R_f = 0.13 (20% EtOAc/petroleum ether)); m.p. = 252-256 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.69 (qd, J = 7.8, 1.0 Hz, 2H), 8.64 (d, J = 5.3 Hz, 1H), 8.46 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.90 (t, J = 7.3 Hz, 1H), 7.47 (dd, J = 5.3, 1.8 Hz, 1H), 7.44 (d, J = 1.6 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 163.6, 163.5, 150.7, 150.3, 146.2, 134.2, 132.7, 131.8, 131.4, 131.3, 131.0, 129.6, 128.4, 125.0, 124.9, 123.0, 122.1; **IR** υ (KBr, cm^{-1}):

2920, 1709, 1679, 1575, 1458, 1390, 1361, 1346, 1240, 1195, 1101, 1077, 778; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_8BrClN_2NaO_2$ $[M+Na]^+$ 408.9350, found 408.9349.

6-bromo-2-(4-methoxypyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bc):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (32 mg, 0.125 mmol) and 4-methoxy-2-aminopyridine (46 mg, 0.375 mmol) for 4 h provided corresponding product **6bc** as a yellow solid (46 mg, 96%). R_f = 0.15 (100% DCM); m.p. = 249-252 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.70 (d, J = 7.8 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 5.7 Hz, 1H), 8.46 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 8 Hz, 1H), 7.89 (t, J = 7.5 Hz, 1H), 6.98 (dd, J = 5.7, 2.2 Hz, 1H), 6.92 (d, J = 2.1 Hz, 1H), 3.91 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 167.9, 163.7, 163.6, 150.9, 150..8, 133.9, 132.5, 131.6, 131.4, 131.0, 129.6, 128.6, 128.3, 123.3, 122.4, 111.0, 110.2, 55.7; **IR** υ (KBr, cm^{-1}): 3438, 2923, 1709, 1666, 1597, 1567, 1558, 1358, 1346, 1242, 1226, 1194, 1017, 994, 838, 778, 746; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}BrN_2O_3$ $[M+H]^+$ 383.0026, found 383.0020.

6-bromo-2-(pyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bd):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 2-aminopyridine (70 mg, 0.75 mmol) for 6 h provided corresponding product **6bd** as a white solid (77 mg, 87%). R_f = 0.11 (20% EtOAc/petroleum ether)); m.p. = 253-256 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.74 (bs, 1H), 8.69 (t, J = 4.3 Hz, 1H), 8.64 (t, J = 8.2 Hz, 1H), 8.45 (t, J = 8.2 Hz, 1H), 8.08 (t, J

= 8.0 Hz, 1H), 7.97 (t, *J* = 4.1 Hz, 1H), 7.94-7.86 (m, 1H), 7.47 (t, *J* = 4.1 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)**: δ 163.8, 163.7, 150.2, 149.3, 138.8, 134.0, 132.5, 131.7, 131.4, 131.1, 130.9, 129.6, 128.3, 124.3, 124.3, 123.2, 122.3; **IR** υ (KBr, cm^{-1}): 3433, 2920, 1712, 1672, 1589, 1568, 1437, 1383, 1369, 1349, 1244, 1197, 1045, 778, 743; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_9BrN_2NaO_2$ $[M+Na]^+$ 374.9740, found 374.9735.

6-bromo-2-(5-(trifluoromethyl)pyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6be):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 5-(trifluoromethyl)-2-aminopyridine (121 mg, 0.75 mmol) for 12 h provided corresponding product **6be** as a off white solid (74 mg, 71%). R_f = 0.7 (100% DCM); m.p. = 219-222 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: 9.00 (s, 1H), 8.71 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)**: δ 163.6, 163.5, 152.4, 147.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 136.1 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 134.2, 132.7, 131.8, 131.4, 130.9, 129.5, 128.3, 127.3 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 124.5,123.5 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz) 122.8, 121.9; **^{19}F NMR (470 MHz, $CDCl_3$)**: δ -62.3 (s, 3F); **IR** υ (KBr, cm^{-1}): 3088, 2921, 1712, 1680, 1587, 1363, 1349, 1331, 1244, 1162, 1124, 1087, 781; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_8BrF_3N_2NaO_2$ $[M+Na]^+$ 442.9613, found 442.9608.

6-bromo-2-(5-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bf):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 5-methyl-2-aminopyridine (81 mg, 0.75 mmol) for 6 h provided corresponding product **6bf** as a pale yellow solid (63 mg, 69%). R_f = 0.13 (20% EtOAc/petroleum ether)); m.p. = 230-234 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.69 (d, J = 4.1 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.55 (s, 1H), 8.45 (d, J = 8.0 Hz, 1H) 8.08 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 8.1 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 163.9, 163.9, 150.5, 146.8, 139.3, 134.3, 133.9, 132.5, 131.7, 131.4, 131.0, 131.0, 129.6, 128.3, 123.5, 123.3, 122.4, 18.4; **IR** υ (KBr, cm^{-1}): 3429, 2929, 1712, 1670, 1589, 1571, 1480, 1364, 1244, 1195, 1023, 779, 754; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{12}BrN_2O_2$ $[M+H]^+$ 367.0077, found 367.0075.

6-bromo-2-(5-iodopyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bg):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (32 mg, 0.125 mmol) and 5-iodo-2-aminopyridine (82 mg, 0.375 mmol) for 24 h provided corresponding product **6bg** as a off white solid (28 mg, 47%). R_f = 0.24 (20% EtOAc/petroleum ether)); m.p. = 239-242 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.93 (s, 1H), 8.70 (d, J = 8 Hz, 1H), 8.66 (d, J = 8 Hz, 1H), 8.46 (d, J = 8 Hz, 1H), 8.23 (dd, J = 8.2, 4.1 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 7.90 (t, J = 8.1 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 163.6, 163.6, 156.4, 148.6, 147.0, 134.2, 132.7,

131.8, 131.4, 131.3, 131.0, 129.6, 128.4, 126.0, 123.0, 122.1, 93.9; **IR** υ (KBr, cm^{-1}): 3430, 2928, 1712, 1674, 1588, 1457, 1402, 1365, 1347, 1241, 1217, 1195, 1045, 971, 819; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_8BrIN_2NaO_2$ $[M+Na]^+$ 500.8706, found 500.8693.

6-bromo-2-(5-bromopyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bh):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 5-bromo-2-aminopyridine (129 mg, 0.75 mmol) for 24 h provided corresponding product **6bh** as a pale yellow solid (42 mg, 39%). R_f = 0.52 (20% ethyl acetate/petroleum ether); m.p. = 232-235 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.78 (d, J = 5.2 Hz, 1H), 8.70 (d, J = 5.2 Hz, 1H), 8.66 (d, J = 5.2 Hz, 1H), 8.45 (d, J = 5.1 Hz, 1H), 8.09 (d, J = 5.0 Hz, 1H), 8.06 (dd, J = 9.8, 5.2 Hz, 1H), 7.89 (t, J = 10.1 Hz, 1H), 7.31 (d, J = 5.0 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 163.6, 163.6, 151.4, 148..0, 141.4, 134.2, 132.8, 131.7, 131.4, 131.3, 131.0, 129.6, 128.4, 125.6, 123.0, 122.1, 121.4; **IR** υ (KBr, cm^{-1}): 3434, 2928, 1714, 1674, 1597, 1588, 1573, 1460, 1367, 1241, 1103, 1092, 779, 755; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{17}H_9Br_2N_2O_2$, $[M+H]^+$ 430.9025 found 430.9029.

6-bromo-2-(6-methylpyridin-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6bi):

Following the general procedure **A**, the reaction between 5-bromo-acenaphthoquinone (65 mg, 0.25 mmol) and 6-methyl-2-aminopyridine (81 mg, 0.75 mmol) for 6 h provided corresponding product **6bi** as a pale yellow solid (70 mg, 76%). R_f = 0.12 (20%

EtOAc/petroleum ether)); m.p. = 239-243 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.68 (d, J = 7.2 Hz, 1H), 8.62 (d, J = 8.5 Hz, 1H), 8.44 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 8 Hz, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 2.60 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 163.8, 163.8, 159.6, 148.6, 138.9, 133.9, 132.5, 131.6, 131.3, 131.0, 130.9, 129.6, 128.3, 124.1, 122.5, 123.3, 121.0, 24.4; **IR** υ (KBr, cm^{-1}): 2935, 1711, 1672, 1588, 1567, 1456, 1363, 1244, 1046, 760; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{18}H_{11}BrN_2NaO_2$ $[M+Na]^+$ 388.9898, found 388.9896.

General Procedure B for biphenyl-2,2'-dicarboxamide synthesis:

To a solution of 1,2-diketone (0.25 mmol/0.5 mmol, 1 equiv.) and 2-aminopyridine (1.125 mmol/2.25 mmol, 4.5 equiv.) in *t*-BuOH:*m*-xylene (1:2, 3 mL) in a reaction tube, anhydrous $CuCl_2$ (20 mol%) was added at RT along with pivalic acid (10 mol%). The reaction mixture was stirred at 80-85 ˚C for 48-72 h under the oxygen atmosphere and then quenched with H_2O after monitoring by TLC. The aqueous layer was extracted by dichloromethane (3 × 20 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude product, which was further purified using flash column chromatography on silica gel (230-400 mesh) column (eluent ethyl acetate-petroleum ether).

***N*2,*N*2'-bis(4-methylpyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8a):**

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (52 mg, 0.25 mmol) and 4-methyl-2-aminopyridine (121 mg, 1.125 mmol) for 48 h delivered the product **8a** as a yellow solid (85 mg, 81%). R_f = 0.16 (40% EtOAc/petroleum ether); m.p.= 233-237 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 10.18 (bs, 2H), 7.99 (s, 2H), 7.66 (d, J = 8.0 Hz, 4H), 7.39–7.31 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 6.67 (t, J = 4.0 Hz, 2H), 2.25 (s, 6H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 168.7, 151.7, 149.8, 147.3, 139.1, 136.1, 130.4, 129.8, 128.1, 127.8, 120.9, 115.0, 21.4; **IR** υ (KBr, cm^{-1}): 3493, 3238, 1659, 1609, 1539, 1411, 1350, 1301, 1278, 1278, 1238, 1167, 891, 828, 760, 710, 610; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{26}H_{22}N_4NaO_2$ $[M+Na]^+$ 445.1635, found 445.1633.

***N*2,*N*2'-bis(4-chloropyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8b):**

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and 4-chloro-2-aminopyridine (288 mg, 2.25 mmol) for 48 h delivered the product **8b** as a off white solid (203 mg, 88%). R_f = 0.24 (40% EtOAc/petroleum ether); m.p.= >260 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.31 (s, 2H), 8.25 (s, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.73–7.70 (m, 2H), 7.46-7.44 (m, 4H), 7.24–7.22 (m, 2H), 6.99–6.97 (m, 2H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 168.6, 152.4, 148.6, 145.8, 139.2, 135.5, 130.9, 130.1, 128.4, 127.6, 120.4, 114.0; **IR** υ (neat, cm^{-1}): 3440, , 1696, 1572, 1519, 1402, 1383, 1291, 1093, 711; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{24}H_{17}Cl_2N_4O_2$ $[M+H]^+$ 463.0723, found 463.0729.

N2,N2'-bis(4-methoxypyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8c):

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (52 mg, 0.25 mmol) and 4-methoxy-2-aminopyridine (139 mg, 1.125 mmol) for 48 h delivered the product **8c** as a semi solid [62 mg, 66% (94% brsm)]. R_f = 0.62 (5% MeOH in DCM); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 10.09 (s, 2H), 7.77 (s, 2H), 7.67–7.63 (m, 4H), 7.42–7.35 (m, 4H), 7.22 (dd, J = 7.4, 0.9 Hz, 2H), 6.41 (dd, J = 5.8, 2.3 Hz 2H), 3.78 (s, 6H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 168.8, 167.3, 153.4, 148.5, 139.1, 136.1, 130.5, 130.1, 128.1, 127.7, 107.6, 99.2, 55.4; **IR** υ (neat, cm^{-1}): 3430, 3225, 2923, 1678, 1606, 1575, 1532, 1467, 1445, 1415, 1305, 1272, 1242, 1199, 1170,1038, 755; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{26}H_{23}N_4O_4$ $[M+H]^+$ 455.1714, found 455.1712.

N2-phenyl-N2'-(pyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicaroxiamide (8d):

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (52 mg, 0.25 mmol) and 2-aminopyridine (105 mg, 1.125 mmol) for 48 h delivered the product **8d** as a white solid (73 mg, 74%). R_f = 0.19 (40% EtOAc : pet ether); m.p.= decomposed at 220 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.74 (bs, 2H), 8.16 (d, J = 8.0 Hz, 2H), 8.02 (s, 2H), 7.71 (d, J = 4.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 2H), 7.40–7.37 (m, 4H), 7.23–7.21 (m, 2H), 6.93 (t, J = 5.6 Hz, 2H); **^{13}C{^{1}H} NMR (100 MHz, d^6-DMSO)**: δ 168.3, 151.4, 148.0, 138.7, 138.1, 135.6, 130.1, 129.1, 128.0, 127.7, 119.9, 113.7; **IR** υ (KBr, cm^{-1}): 3456, 3224, 3066, 1665, 1591, 1531, 1467, 1429, 1353, 1307, 1272,

1150,1042, 891, 779, 763, 751; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{24}H_{18}N_4NaO_2$ $[M+Na]^+$ 417.1322, found 417.1322.

***N*2,*N*2'-bis(5-bromopyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8e):**

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and 5-bromo-2-aminopyridine (387 mg, 2.25 mmol) for 72 h delivered the product **8e** as a yellow solid (140 mg, 51%). R_f = 0.45 (20% EtOAc/petroleum ether); m.p.= 137-140 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.48 (s, 2H), 8.11–8.07 (m, 4H), 7.71–7.68 (m, 4H), 7.44–7.42 (m, 4H), 7.22–7.20 (m, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 168.5, 150.1, 148.8, 140.7, 139.2, 135.5, 130.9, 130.0, 128.4, 127.5, 115.5, 114.9; **IR** υ (KBr, cm^{-1}): 3467, 3224, 1683, 1569, 1519, 1371, 1301, 1222, 1132, 1092, 834, 755 **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{24}H_{16}Br_2N_4NaO_2$ $[M+Na]^+$ 572.9527, found 572.9532.

***N*2,*N*2'-bis(5-chloropyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8f):**

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and 5-chloro-2-aminopyridine (288 mg, 2.25 mmol) for 72 h delivered the product **8f** as a off white solid (152 mg, 66%)). R_f = 0.53 (20% EtOAc/petroleum ether); m.p.= 252-255 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 9.66 (s, 2H), 8.15 (d, J = 10.0 Hz, 2H), 7.88 (d, J = 5.0 Hz, 2H), 7.69–7.67 (m, 2H), 7.55 (dd, J = 10, 5.0 Hz, 2H), 7.44–7.39 (m, 4H), 7.21–7.20 (m, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ = 168.5, 149.8, 146.6, 139.1, 137.9, 135.6, 130.8, 130.0, 128.3, 127.6, 126.9, 115.0;

IR υ (KBr, cm^{-1}): 3452, **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{24}H_{16}Cl_2N_4NaO_2$ $[M+Na]^+$ 485.0543, found 485.0553.

***N*2,*N*2'-bis(5-methylpyridin-2-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide (8g):**

Following the general procedure **B**, the reaction between 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and 5-chloro-2-aminopyridine (243 mg, 2.25 mmol) for 48 h delivered the product **8g** as a white solid (182 mg, 83%). R_f = 0.14 (40% EtOAc/petroleum ether); m.p = 199-202 °C **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 10.08 (bs, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.67–7.65 (m, 2H), 7.61 (s, 2H), 7.39–7.34 (m, 6H), 7.19–7.17 (m, 2H), 2.14 (s, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 168.5, 149.6, 147.7, 139.1, 138.7, 136.3, 130.2, 129.8, 129.0, 128.1, 127.7, 114.0, 17.9; **IR** υ (KBr, cm^{-1}): 3515, 3223, 2924, 1722, 1677, 1590, 1528, 1383, 1310, 1284, 1138, 1030, 834, 756; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{26}H_{22}N_4NaO_2$ $[M+Na]^+$ 445.1635, found 445.1636.

b) General Procedure C for Synthesis of N-Heterocyclic Amide and Acid:

To a solution of 1,2-diketone (0.5 mmol, 1 equiv.) and 2-aminopyridine (2.25 mmol, 4.5 equiv.) in *t*-BuOH:*m*-xylene (1:2, 3 mL) in a reaction tube, anhydrous $CuCl_2$ (20 mol%) was added at RT along with catalytic amount of pivalic acid (10 mol%). The reaction mixture was stirred at 80-85 °C for 24-72 h under an oxygen atmosphere. After completion of the reaction, dichloromethane (DCM, 5 mL) was added to the reaction mixture and it was first washed with 2N $NaHCO_3$ to separate acid. The dichloromethane (DCM) layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated

under vacuum to get the crude amide product, which was then purified by silica gel (230-400 mesh) by flash column chromatography using ethyl acetate-petroleum ether (EtOAc/petroleum ether) as solvent.

_N_-(4-methylpyridin-2-yl)benzamide (10aa):

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 4-methyl-2-aminopyridine (243 mg, 2.25 mmol) for 48 h furnished the product **10aa** as a white solid (95 mg, 44%). R_f = 0.31 (20% EtOAc : petroleum ether); m.p. = 99-103 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.78 (bs, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 4.1 Hz, 1H), 7.96–7.93 (m, 2H), 7.62–7.55 (m, 2H), 7.52–7.48 (m, 2H), 2.32 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 165.8, 149.5, 147.8, 139.2, 134.5, 132.2, 129.4, 128.9, 127.3, 113.9; 18.0; **IR** υ (KBr, cm^{-1}): 3445, 3222, 1681, 1667, 1602, 1588, 1522, 1494, 1385, 1308, 1268, 702; **HRMS** (ESI- QTOF): *m/z* calcd. for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1022, found 213.1021.

The acidification of 2N $NaHCO_3$ layer by dilute HCl and extraction with ethyl acetate provided benzoic acid **10ba** in 36 mg (30%) yield.

_N_-(4-chloropyridin-2-yl)benzamide (10ab):

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 4-chloro-2-aminopyridine (288 mg, 2.25 mmol) for 48 h furnished the product **10ab** as a off-white solid (97 mg, 42%). R_f = 0.31 (20% EtOAc/petroleum ether); m.p. = 62-64 °C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (bs, 1H), 8.50 (m, 1H), 7.99 (d, J = 5.0, 1H), 7.91–7.89 (m, 2H), 7.58–7.54 (m, 1H), 7.49–7.45 (m, 2H), 7.02 (dd, J = 5.0, 2.5 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 166.1, 152.7, 148.5, 146.2, 134.0, 132.6, 128.9, 127.4, 120.4, 114.6; **IR** υ (KBr, cm^{-1}): 3319, 3062, 1682, 1568, 1403, 1285, 1095, 821, 711; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_9ClN_2NaO$ $[M+Na]^+$ 255.0296, found 255.0296.

The benzoic acid **10ba** was isolated in 33 mg (31%) yield from 2N $NaHCO_3$ aqueous layer.

***N*-(4-methoxypyridin-2-yl)benzamide (10ac):**

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 4-methoxy-2-aminopyridine (279 mg, 2.25 mmol) for 24 h furnished the product **10ac** as a white solid (114 mg, 50%). R_f = 0.22 (20% EtOAc/petroleum ether); m.p. = 81-84 °C **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.38 (bs, 1H), 8.06 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 7.8 Hz, 3H), 7.57–7.53 (m, 1H), 7.48–7.45 (m, 2H), 6.57 (s, 1H), 3.89 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 167.7, 166.3, 153.5, 148.4, 134.5, 132.3, 128.9, 127.5, 108.0, 99.0, 55.5; **IR** υ (neat, cm^{-1}): 3483, 3175, 2978, 1676, 1607, 1577, 1530, 1459, 1426, 1311, 1283, 1253, 1198, 1168, 1045, 861, 798, 696, 809 ; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{12}N_2NaO_2$ $[M+Na]^+$ 251.0791, found 251.0798.

The benzoic acid **10ba** was isolated in 48 mg (39%) yield from 2N $NaHCO_3$ layer.

_N_-(pyridin-2-yl)benzamide (10ad):

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10ad** as a off-white solid (99 mg, 50%). R_f = 0.4 (20% EtOAc/ petroleum ether); m.p. = 79-82 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.27 (bs, 1H), 8.41 (d, J = 10.0 Hz, 1H), 8.12 (s, 1H), 7.92 (d, J = 5.0 Hz, 2H), 7.74–7.71 (m, 1H), 7.53 (t, J = 10.0 Hz,, 1H), 7.45 (t, J = 10.0 Hz,, 2H), 7.01 (t, J = 5.0 Hz,, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 166.0, 151.8, 147.9, 138.6, 134.4, 132.3, 128.9, 127.4, 120.0, 114.4; **IR** υ (KBr, cm^{-1}): 3472, 3219, 3021, 1674, 1598, 1579, 1435, 1488, 1435, 1354, 1305, 1278, 1241, 1153, 927, 878, 789, 776, 721, 694, 677; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_{10}N_2NaO$ $[M+Na]^+$ 221.0685, found 221.0683.

The benzoic acid **10bd** was isolated in 36 mg (30%) yield 2N $NaHCO_3$ layer.

3-methoxy-_N_-(pyridin-2-yl)benzamide (10ae):

Following the general procedure **C**, the reaction between 3,3'-dimethoxybenzil (135 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10ae** as a viscous liquid (113 mg, 49%). R_f = 0.24 (20% EtOAc/petroleum ether); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.10 (bs, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.20–8.18 (m, 1H), 7.76–7.72 (m 1H), 7.49–7.45 (m, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.09–7.06 (m, 1H), 7.05–7.02 (m, 1H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 166.1, 159.8, 151.9, 147.4, 138.4, 135.9, 129.6, 119.7, 119.3, 118.4, 114.5, 112.5, 55.3; **IR** υ (neat, cm^{-1}):

3247, 3072, 2940, 1676, 1595, 1579, 1433, 1308, 1274, 1224, 1043, 995, 876, 778, 687,; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{12}N_2NaO_2$ $[M+Na]^+$ 251.0791, found 251.0794.

The 3-methoxy benzoic acid **10be** was isolated in 18 mg (24%) yield from 2N $NaHCO_3$ layer.

3-methoxy-*N*-(4-methoxypyridin-2-yl)benzamide (10af):

Following the general procedure **C**, the reaction between 3,3'-dimethoxybenzil (135 mg, 0.5 mmol) and 4-methoxy-2-aminopyridine (279 mg, 2.25 mmol) for 48 h furnished the product **10af** as a viscous liquid (122 mg, 47%). R_f = 0.19 (20% EtOAc/petroleum ether); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.99 (bs, 1H), 8.04 (d, J = 2.3 Hz, 1H), 8.00–7.97 (m, 1H), 7.47–7.44 (m, 2H), 7.39–7.36 (m, 1H), 7.09 (d, J = 2.3 Hz, 1H), 6.61–6.59 (m, 1H), 3.91 (s, 3H), 3.85 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 167.7, 166.0, 160.1, 153.5, 148.6, 135.9, 129.9, 119.2, 118.8, 112.4, 108.1, 98.9, 55.6, 55.5; **IR** υ (neat, cm^{-1}): 3373, 2940, 1677, 1603, 1437, 1292, 1167, 1040, 856, 816, 748; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{14}H_{14}N_2NaO_3$ $[M+Na]^+$ 281.0897, found 281.0893.

The 3-methoxy benzoic acid **10be** was isolated in 32 mg (21%) yield from 2N $NaHCO_3$ layer.

4-fluoro-*N*-(pyridin-2-yl)benzamide (10ag):

Following the general procedure **C**, the reaction between 4,4'difluorobenzil (123 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10ag** as a white solid [80 mg, 37% (41% brsm)]. R_f = 0.28 (20% EtOAc/petroleum ether); m.p. = 123-126 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.78 (bs, 1H), 8.36 (d, J = 8.5 Hz, 1H), 8.25 (s, 1H), 7.96–7.93 (m, 2H), 7.76 (t, J = 8 Hz, 1H), 7.17 (t, J = 8.0 Hz, 2H), 7.08–7.06 (m, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 165.2 (d, $^1J_{C\text{-}F}$= 251.0 Hz), 165.0, 151.7, 147.9, 138.7, 130.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 120.1, 116.1 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 114.5; **^{19}F NMR (470 MHz, $CDCl_3$)**: δ -106.71 (m, 1F); **IR** υ (KBr, cm^{-1}): 3465, 3175, 2983, 1675, 1584, 1538, 1504, 1438, 353, 1314, 1295, 1223, 1151, 1093, 805, 782, 764; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_9FN_2NaO$ $[M+Na]^+$ 239.0591, found 239.0590.

The 4-fluoro benzoic acid **10bg** was isolated in 20mg [12% (16% brsm)] from 2N $NaHCO_3$ layer.

4-bromo-*N*-(pyridin-2-yl)benzamide (10ah):

Following the general procedure **C**, the reaction between 4,4'-dibromobenzil (184 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10ah** as an off-white solid (128 mg, 48%). R_f = 0.27 (20% EtOAc/petroleum ether); m.p. = 135-138 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.07 (bs, 1H), 8.41 (d, J = 7.5 Hz, 1H), 8.25 (s,1H), 7.84–7.79 (m, 3H), 7.63 (d, J = 7.5 Hz, 2H), 7.10 (m, 1H)); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 165.0, 151.4, 147.3, 139.2, 133.0, 132.2, 129.1, 127.4, 120.2, 114.7; **IR**

υ (KBr, cm^{-1}): 3483, 3237, 3050, 1676, 1579, 1539, 1436, 1310, 820, 782; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_9BrN_2NaO$ $[M+Na]^+$ 298.9790, found 298.9790.

The 4-bromo benzoic acid **10bh** was isolated in 74 mg (39%) from 2N $NaHCO_3$ layer.

4-methyl-*N*-(pyridin-2-yl)benzamide (10ai):

Following the general procedure **C**, the reaction between 4,4'-dimethylbenzil (119 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10ai** as a white solid (83 mg, 39%)). R_f = 0.32 (20% EtOAc/petroleum ether); m.p. = 106-109 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.41 (bs, 1H), 8.54 (d, J = 8.5 Hz, 1H), 8.27 (d, J = 4.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.87 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.14 (td, J = 5.5, 1.5 Hz, 1H), 2.43 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 166.0, 151.4, 145.5, 143.5, 140.3, 130.9, 129.7, 127.7, 119.8, 115.1, 21.7; **IR** υ (KBr, cm^{-1}): 3496, 3233, 3039, 1672, 1611, 1580, 1436, 1355, 1311, 1240, 1155, 890, 777, 748; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{12}N_2NaO$ $[M+Na]^+$ 235.0825, found 235.0823.

The 4-methyl benzoic acid **10bi** was isolated in 22mg (16%) yield from 2N $NaHCO_3$ layer.

***N*-(6-methylpyridin-2-yl)benzamide (10aj)** :

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 6-methyl-2-aminopyridine (243 mg, 2.25 mmol) for 48 h furnished the product **10aj** as a white solid (70 mg, 33%). R_f = 0.35 (20% EtOAc/petroleum ether); m.p. = 82-86 °C; **^{1}H**

NMR (500 MHz, $CDCl_3$): δ 8.78 (bs, 1H), 8.22 (d, J = 8 Hz, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.68–7.64 (m, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 8 Hz, 2H), 6.93 (d, J = 7.5 Hz, 1H), 2.47 (s, 3H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: δ 165.8, 156.7, 150.9, 139.3, 134.3, 132.4, 128.9, 127.4, 119.6, 111.2, 23.9; **IR** υ (KBr, cm^{-1}): 3456, 3194, 1673, 1630, 1600, 1578, 1526, 1455, 1395, 1352 1304, 1276, 1129, 882, 788, 719, 758, 695; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{12}N_2NaO$ $[M+Na]^+$ 235.0842, found 235.0839.

The benzoic acid **10ad** was isolated in 28 mg (23%) yield from 2N $NaHCO_3$ layer.

***N*-(5-bromopyridin-2-yl)benzamide (10ak)**:

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 5-bromo-2-aminopyridine (389 mg, 2.25 mmol) for 48 h furnished the product **10ak** as an off-white solid [58 mg, 21% (31% brsm)]. R_f = 0.31 (20% EtOAc/petroleum ether); m.p. = 114-117 °C; **^1H NMR (400 MHz, $CDCl_3$)**: δ 9.10 (bs, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.34 (d, J = 2.4 Hz, 1H), 7.96 (d, J = 7.2 H, 2H), 7.92 (dd, J = 8.8, 2.4 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: δ 165.8, 150.3, 148.1, 141.6, 133.8, 132.7, 129.1, 127.5, 115.7, 114.8; **IR** υ (KBr, cm^{-1}): 3446, 3231, 1678, 1630, 1581, 1530, 1375, 1304, 1004, 839, 715, 696; **HRMS** (ESI- QTOF): *m/z* calcd. for $C_{12}H_9BrN_2NaO$ $[M+Na]^+$ 298.9790, found 298.9795.

The benzoic acid **10ad** was isolated in 12mg (16% brsm) yield from 2N $NaHCO_3$ layer.

4-(quinolin-2-yl)benzamide (10al):

Following the general procedure **C**, the reaction between benzil (105 mg, 0.5 mmol) and 2-aminoquinoline (324 mg, 2.25 mmol) for 48 h furnished the product **10al** as a white solid (97 mg, 39%). R_f = 0.22 (20% EtOAc/petroleum ether); m.p. = 122-124 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.96 (bs, 1H), 8.60 (d, J = 8. 9 Hz, 1H), 8.23 (d, J = 9 Hz, 1H), 7.99 (d, J = 10.0 Hz, 2H), 7.84 (d, J = 10.0 Hz, 1H),), 7.81 (d, J = 10.0 Hz, 1H),), 7.69–7.66 (m, 1H), 7.59 (t, J = 10.0 Hz, 1H), 7.51 (d, J = 10.0 Hz, 2H), 7.47 (d, J = 10.0 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 151.3, 146.5, 138.9, 134.2, 132.6, 130.2, 129.0, 127.8, 127.5, 127.3, 126.5, 125.4, 114.6; **IR** υ (neat, cm^{-1}): 3465, 3227, 3056, 1678, 1594, 1575, 1498, 1425, 1322, 1289, 832, 703, 688; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{16}H_{13}N_2O$ $[M+H]^+$ 249.1022, found 249.1022.

The benzoic acid **10bd** was isolated in 38 mg (31%) from 2N $NaHCO_3$ layer.

***N*-(pyridin-2-yl)thiophene-2-carboxamibe (10am):**

Following the general procedure **C**, the reaction between 2,2'-thenil (111 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10am** as a white solid (61 mg, 30%). R_f = 0.28 (20% EtOAc/petroleum ether); m.p. = 81-84 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.87 (bs, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 4.2 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 4.8 Hz, 1H), 7.57 (d, J = 4.8 Hz, 1H), 7.13 (t, J = 4.5 Hz, 1H), 7.08–7.05 (m, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 160.2, 151.5, 147.8, 139.0, 138.9, 131.8, 129.2, 128.1. 120.1, 114.9; **IR** υ (KBr, cm^{-1}): 3477, 3346, 3092, 3073, 1645, 1572, 1526, 1508, 1430, 1414, 1304, 1240, 1148, 1074, 1041, 888,

866, 808, 775, 665, 644, 621; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{10}H_9N_2OS$ $[M+H]^+$ 205.0430, found 205.0436.

The thiophene-2-carboxylic acid **10bm** was isolated in 53mg (41%) yield from 2N $NaHCO_3$ layer.

***N*-(pyridin-2-yl)furan-2-carboxamibe (10an):**

Following the general procedure **C**, the reaction between furil (95 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **10an** as a white solid [127 mg, 68% (76% brsm)]. R_f = 0.25 (20% EtOAc/petroleum ether); m.p. = 123-127 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.78 (bs, 1H), 8.33–8.31(m, 2H), 7.73 (t, J = 8.5 Hz, 1H), 7.52 (s, 1H), 7.27 (t, J = 3.5 Hz, 1H), 7.08–7.05 (m, 1H), 6.56 (d, J = 3.5 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 156.3 151.1, 148.2, 147.5, 144.9, 138.5, 120.1, 116.0, 114.3, 112.8; **IR** υ (KBr, cm^{-1}): 3456, 3204, 1672, 1582, 1458, 1439, 1353, 1316, 1172, 1009, 998, 883, 767, 612 ; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{10}H_9N_2O_2$ $[M+H]^+$ 189.0659, found 189.0662.

The furan-2-carboxylic acid **10bn** was isolated in 6 mg (5%) yield from 2N $NaHCO_3$ layer.

2-chloro-*N*-(pyridin-2-yl)benzamide (10ao):

Following the general procedure **C**, the reaction between 2,2'-dichlorobenzil (139 mg, 0.5 mmol) and 2-aminopyridine 211 mg, (2.25 mmol) for 72 h furnished the product

10ao as a white solid [41 mg, 19% (39% brsm)]. R_f = 0.23 (20% EtOAc : pet ether); m.p. = 139-142 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.24 (bs, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.01 (s, 1H), 7.77–7.73 (m, 1H), 7.72–7.70 (m, 1H), 7.45–7.40 (m, 2H), 7.38–7.35 (m, 1H), 7.02–7.00 (m, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 168.3, 151.4, 147.9, 138.7, 135.3, 131.9, 131.1, 130.6, 130.1, 127.3, 120.3, 114.6; **IR** υ (KBr, cm^{-1}): 3457, 3230, 3176, 2987, 1680, 1593, 1578, 1536, 1434, 1310, 1281, 1138, 1050, 889, 774, 763, 750; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_9ClN_2NaO$ $[M+Na]^+$ 255.0296, found 255.0296.

The 2-chloro benzoic acid **10bo** was isolated in 21mg 13% (28% brsm)) from 2N $NaHCO_3$ layer.

4-chloro-*N*-(pyridin-2-yl)benzamide (10ap):

Following the general procedure **C**, the reaction between 4-chlorobenzil (300 mg, 1.2 mmol) and 2-aminopyridine (250 mg, 5.4 mmol) for 48 h furnished the product **10ap** as a white solid (3:2 ratio along with compound **10ad** (106 mg mixture with **10ad**)). R_f = 0.38 (20% EtOAc : pet ether); m.p. = 135-138 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.76 (bs, 1H), 8.37 (d, J = 5.5 Hz, 1H), 8.29 (s, 1H), 7.88 (d, J = 5.3 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.09 (t, d, J = 5.3 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.8, 151.5, 147.9, 138.9, 138.8, 132.7, 129.3, 128.8, 120.3, 114.5; **IR** υ (neat, cm^{-1}): 3343, 1676, 1584, 1537, 1485, 1436, 1315, 1091, 897, 776; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_{10}ClN_2O$ $[M+H]^+$ 233.0476, found 233.0479.

4-methoxy-*N*-(pyridin-2-yl)benzamide (10aq):

Following the general procedure **C**, the reaction between 4-methoxybenzil (112 mg, 0.46 mmol) and 2-aminopyridine (197 mg, 2.09 mmol) for 48 h furnished the product **10aq** as an off-white solid (31 mg, 29%). R_f = 0.20 (20% EtOAc : pet ether); m.p. = 81--84 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.77 (bs, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 4.8 Hz, 1H), 7.92 (dt, J = 5.0, 2.9 Hz, 2H), 7.78–7.74 (m, 1H), 7.07–7.05 (m, 1H), 6.98 (td, J = 5.0, 2.9 Hz, 2H), 3.87 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 165.3, 163.0, 151.8, 147.6, 138.8, 129.4, 126.4, 119.8, 114.4, 114.2, 55.6; **IR** υ (KBr, cm^{-1}): 3304, 2929, 2851, 1675, 1607, 1578, 1529, 1506, 1433, 1304, 1256, 1238, 1176, 1029, 842, 778, 524; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{12}N_2NaO_2$ $[M+Na]^+$ 251.0791, found 251.0793.

N-(pyridin-2-yl)acetamide (15):

Following the general procedure **C**, the reaction between ethyl acetoacetate (63.6 mL, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **15** as a sticky liquid (29 mg, 42%). R_f = 0.26 (20% EtOAc : pet ether); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.90 (bs, 1H), 8.24 (s, 2H), 7.76–7.72 (m, 1H), 7.07–7.04 (m,1H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 169.2, 151.9, 147.4, 138.7, 119.7, 114.6, 24.7; **IR** υ (cm^{-1}): 3256, 1686, 1578, 1534, 1435, 1371, 1302, 1240, 1091, 897, 779; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_7H_9N_2O$ $[M+H]^+$ 137.0715, found 137.0714.

***N*1,*N*2-di(pyridin-2-yl)oxalamide (16):**

Following the general procedure **C**, the reaction between ethyl acetoacetate (63.6 mL, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **16** as a white solid (38mg, 34%). R_f = 0.47 (20% EtOAc : pet ether); m.p. = 135-138 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.82 (bs, 2H), 8.39 (d, J = 4 Hz, 2H), 8.27 (d, J = 8 Hz, 2H), 7.78 (t, J = 8 Hz, 2H), 7.15–7.13 (m, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 157.5, 149.9, 148.6, 138.7, 121.1, 114.3; **IR** υ (KBr, cm^{-1}): 3166, 3073, 1683, 1593, 1575, 1497, 1459, 1431, 1302, 1148, 1097, 1050, 994, 866, 778; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{12}H_{10}N_4NaO_2$ $[M+Na]^+$ 265.0695, found 265.0695.

2-oxo-2-phenyl-N-(pyridin-2-yl)acetamide (18):

Following the general procedure **C**, the reaction between dibenzoylmethane (112 mg, 0.5 mmol) and 2-aminopyridine (211 mg, 2.25 mmol) for 48 h furnished the product **18** as a white solid (15 mg, 12%). R_f = 0.25 (20% EtOAc : pet ether); m.p. = 123-127 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.97 (bs, 1H), 8.42 (d, J = 8 Hz, 1H), 8.23 (s, 1H), 7.94 (d, J = 8 Hz, 2H), 7.52 (t, J = 8 Hz, 1H), 7.27 (dt, J = 8, 16 Hz, 3H), 7.05 (t J = 4 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 186.8, 159.5 150.4, 148.6, 138.6, 134.6, 133.1, 131.5,128.8, 128.8, 127.3, 120.9, 114.3; **IR** υ (KBr, cm^{-1}): 3373, 2923, 1677, 1596, 1578, 1524, 1437, 1281, 776, 761; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{11}N_2O_2$ $[M+H]^+$ 227.0815, found 227.0816.

N-(4-chloropyridin-2-yl)-2-oxo-2-phenylacetamide (19):

Following the general procedure **C**, the reaction between dibenzoylmethane (112 mg, 0.5 mmol) and 4-chloro-2-aminopyridine (288 mg, 2.25 mmol) for 48 h furnished the product **19** as a white solid (20 mg, 15%). R_f = 0.25 (20% EtOAc : pet ether); m.p. = 131-134 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 9.62 (bs, 1H), 8.43 (s, 1H), 8.38 (d, J = 7.6 Hz, 2H), 8.28 (s, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 3.6 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 186.3, 159.6, 151.3, 149.2, 146.2, 135.0, 132.9, 131.5, 128.8, 127.3, 126.9, 121.2, 114.5; **IR** υ (KBr, cm^{-1}): 3448, 3195, 1695, 1677, 1597, 1583, 1570, 1504, 1402, 1385, 1282, 1250, 1234, 1158, 1106, 823, 805, 713, 684; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{13}H_{10}ClN_2O_2$ $[M+H]^+$ 261.0425, found 261.0424.

Control Experiments:

Reaction under the inert atmosphere:

The starting materials acenaphthoquinone **4a** (0.5 mmol) and 4-methyl-2-aminopyridine **5a** (1.5 mmol) were taken in a sealed tube under inert atmosphere (glove box) followed by addition of degassed solvents *t*-BuOH and *m*-xylene (1:2, 3 mL), anhydrous $CuCl_2$ (20 mol%) and a catalytic amount of pivalic acid (10 mol%) the reaction mixture was stirred at 80-85 °C for 48 h under inert atmosphere. After cooling reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude product. Further column chromatographic purification using 100% dichloromethane as a solvent system gave trace amount of product with recovery of most of the starting material.

Reaction in the absence of catalyst $CuCl_2$:

To a solution of acenaphthoquinone **4a** (0.5 mmol) and 4-methyl-2-aminopyridine **5a** (1.5 mmol) in *t*- BuOH:*m*-xylene (1:2, 3 mL) in a reaction tube catalytic amount of pivalic acid (10 mol%) was added at RT. The reaction mixture was stirred at 80-85 °C for 48 h under oxygen

atmosphere. After completion of reaction, the reaction mixture was extracted using dichloromethane and purified. The starting material was fully recovered with no traces of the product.

Radical trapping Experiments:

To a solution of acenaphthoquinone **4a** (0.5 mmol) and 4-methyl-2-aminopyridine **5a** (1.5 mmol) in *t*- BuOH:*m*-xylene (1:2, 3 mL) in reaction tube, anhydrous $CuCl_2$ (20 mol%) was added at RT along with catalytic amount of pivalic acid (0.1 equiv.). After addition of 3 equiv of radical scavenger 2,4,6-*tri*(*t*-Buphenol), the reaction mixture was stirred at 80-85 °C for 48 h under oxygen atmosphere. After completion of reaction, the crude product was extracted using dichloromethane. The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude product, which was then purified by silica gel (230–400 mesh) by flash column chromatography using ethyl acetate–petroleum ether as a solvent system. The reaction gave only traces of the product **6aa**

General Procedure D for fluorescent amine compounds synthesis (20 to 23)[22]:

In a 25 mL round bottom flask containing 50 mg of corresponding 4-bromo-1,8-naphthalimide compound (**6ba, 6bd, 6bf, 6bi**), 3 mL of dimethyl amine (40% water solution) and 5 mL DMF was added and reaction mixture was reflux for overnight. After cooling the water is added in the reaction mixture and the product was extracted with ethyl acetate. The organic layers washed with brine and dried over $NaSO_4$ and evaporated to give the crude product. Pure product obtained from 2-3 times extractions with ethyl acetate from water.

6-(dimethylamino)-2-(4-methylpyridin-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (20):

Following the general procedure **D**, the reaction between corresponding 4-bromo-1,8-naphthalimide **6ba** (50 mg) and dimethylamine (3 mL, (40% in H_2O)) provided corresponding product **20** as a yellow solid (12 h, 36 mg, 80%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.61-8.57 (m, 2H), 8.52-8.48 (m, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.25-7.22 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 3.14 (s, 6H), 2.46 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 164.9, 164.2, 157.5, 150.0, 149.6, 133.1, 131.8, 131.5, 131.0, 125.5, 125.1, 125.1, 125.0, 123.3, 115.0, 113.5, 44.9, 21.2; **IR** υ (KBr, cm^{-1}): 1694, 1585, 1571, 1406, 1363, 1243, 1192, 1076, 817, 780, 773; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{20}H_{18}N_3O_2$ $[M+H]^+$ 332.1384, found 332.1384.

6-(dimethylamino)-2-(5-methylpyridin-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (21):

Following the general procedure **D**, the reaction between corresponding 4-bromo-1,8-naphthalimide **6bf** (50 mg) and dimethylamine (3 mL,40% in H_2O) provided corresponding product **21** as a yellow solid (12 h, 31 mg, 68%). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.57 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 8.46 (t, J = 8.0 Hz, 2H), 7.70-7.63 (m, 2H), 7.25 (d, J = 8 Hz, 1H), 7.11 (d, J = 8 Hz, 1H), 3.11 (s, 6H), 2.41 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 164.9, 164.3, 157.4, 150.4, 147.6, 139.1, 133.8, 133.1, 131.8, 131.5, 131.0, 125.5, 125.0, 123.6, 123.3, 115.0, 113.4, 44.9, 18.3; **IR** υ (KBr, cm^{-1}): 2921, 1701, 1664, 1651, 1586, 1572, 1365, 1335, 1246, 1130, 1016, 836, 786, 776; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{20}H_{18}N_3O_2$ $[M+H]^+$ 332.1394, found 332.1389.

6-(dimethylamino)-2-(6-methylpyridin-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (22):

Following the general procedure **D**, the reaction between corresponding 4-bromo-1,8-naphthalimide **6bi** (50 mg) and dimethylamine (3 mL,40% in H_2O) provided corresponding product **22** as a yellow solid (12 h, 36 mg, 80%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.59 (d, J = 8.0 Hz, 1H), 8.49 (t, J = 8.1 Hz, 2H), 7.80 (t, J = 8 Hz, 1H), 7.67 (t, J = 8 Hz, 1H), 7.28 (d, J = 8 Hz, 1H), 7.19 (d, J = 8 Hz, 1H), 7.13 (d, J = 8 Hz, 1H), 3.14 (s, 6H), 2.64 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 164.9, 164.3, 159.4, 157.4, 149.3, 138.7, 133.1, 131.8, 131.4, 131.0, 125.5, 125.0, 123.7, 123.4, 121.1, 115.0, 113.4, 44.9, 24.5; **IR** υ (KBr, cm^{-1}):1697, 1651, 1598, 1586, 1573, 1454, 1365, 1244, 1188, 1136, 1077, 1020, 804, 796, 770, 753; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{20}H_{18}N_3O_2$ $[M+H]^+$ 332.1394, found 332.1396.

6-(dimethylamino)-2-(pyridin-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (23):

Following the general procedure **D**, the reaction between corresponding 4-bromo-1,8-naphthalimide **6bd** (50 mg) and dimethylamine (3 mL,40% in H_2O) provided corresponding product **23** as a yellow solid (12 h, 29 mg, 64%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.73 (d, J = 4.1 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.50 (t, J = 8.0 Hz, 2H), 7.93 (t, J = 8.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.49-7.39 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 3.14 (s, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 164.8, 164.2, 157.5, 150.1, 150.0, 138.6, 133.1, 131.9, 131.5, 131.0, 125.5, 125.0, 124.4, 124.0, 123.3, 114.9, 113.5, 44.9;

IR υ (KBr, cm^{-1}): 2923, 1705, 1660, 1588, 1449, 1394, 1366, 1240, 1193, 1136, 1013, 943, 841, 757; **HRMS** (ESI-QTOF): *m/z* calcd. for $C_{19}H_{15}N_3O_2$ $[M+Na]^+$ 340.1056, found 340.1052.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^1H, ^{13}C NMR spectra, XPS data, X-ray crystal data, UV-Visible spectra and Fluorescence spectra. (PDF)

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support (EMR/2017/000578) from Science and Engineering Research Board, India, and Indian Institute of Technology Bombay for fellowships to P.R.S and P.S. We also thank the XRD facility of Department of Chemistry, IIT Bombay and ESCA Lab, IIT Bombay for XPS studies.

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