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K C Kumara Swamy, Rajnikanth Sunke, and ADULA KALYANI

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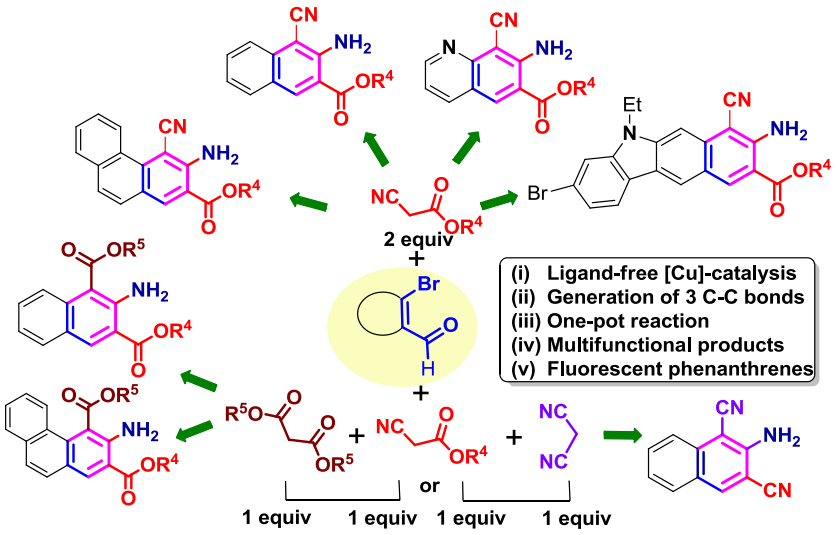
Cu(I)-Catalyzed Ligand-free Tandem One Pot or Sequential Annulation via Knoevenagel Intermediate: An Entry into Multifunctional Naphthalenes, Phenanthrenes, Quinolines and Benzo[*b*]carbazoles

*Rajnikanth Sunke, Adula Kalyani and K. C. Kumara Swamy**

School of Chemistry, University of Hyderabad, Hyderabad 500 046, Telangana, India



ABSTRACT

A simple but efficient one-pot or sequential copper-catalyzed protocol using 2-bromo-aldehydes and active methylene group containing substrates that affords multifunctional naphthalenes, phenanthrenes, quinolines and benzo[*b*]carbazoles via Knoevenagel condensation, C-arylation and decarboxylation followed by aromatization, has been developed. The reaction utilizes the potential of Knoevenagel intermediates and does not require ancillary ligand. The phenanthrene products thus obtained show moderate fluorescence activity. Structural elaboration of the products to obtain dihydrobenzoquinazolines is also highlighted.

INTRODUCTION

The development of new and efficient methodologies for the construction of highly substituted polycyclic arenes and *N*-heteroarenes with flexible substituent patterns is a worthwhile exercise as it allows access to the diversity based chemical space useful for pharmaceuticals and electronic materials.[1] Among polycyclic arenes, multifunctional naphthalenes and phenanthrenes are important classes of organic compounds because they have not only found widespread applications in pharmaceutical chemistry (cf. Figure 1)[2] but also play a significant role in supramolecular chemistry, nanotechnology, electronic materials and the design of chiral catalysts.[3] Therefore, the development of efficient strategies to access such structural motifs from readily accessible starting materials has immense impact and value. Consequently, a number of synthetic strategies toward polysubstituted naphthalenes or phenanthrenes have been developed. The most important avenues include Diels-Alder reaction,[4] annulation reaction,[5] metathesis,[6] rearrangements of strained rings,[7] catalytic cyclization,[8] C-H activation,[9] cyclo-isomerization[10] and cross-coupling protocol.[11] In addition, *N*-heteroarenes such as quinolines and benzocarbazoles also feature prominently among many natural products and drug candidates.[12] As a result, a number of synthetic platforms are used for the construction of such structural systems.[13] While significant progress has been achieved for the construction of naphthalenes, phenanthrenes, quinolines and benzo[*b*]carbazoles with diverse substitutions, the number of approaches based on Cu(I)-catalyzed reactions is rather limited.

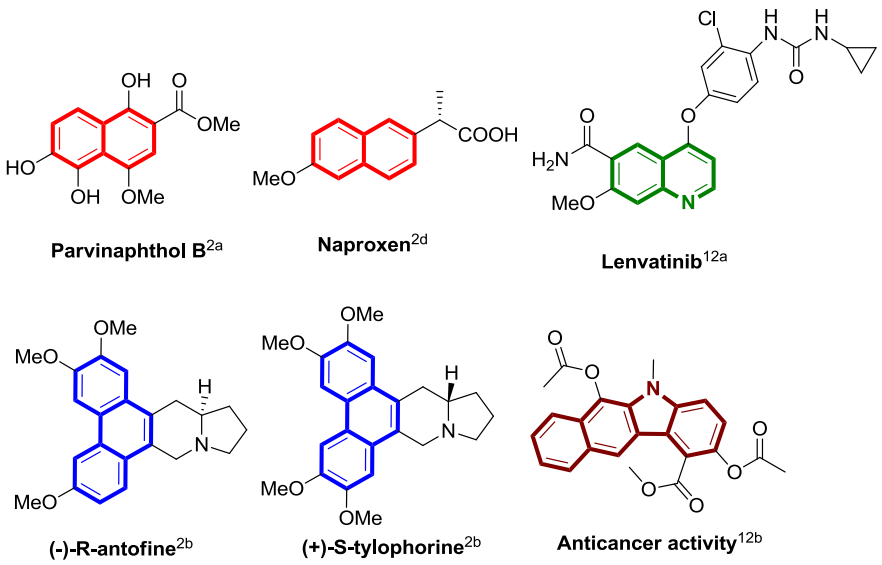
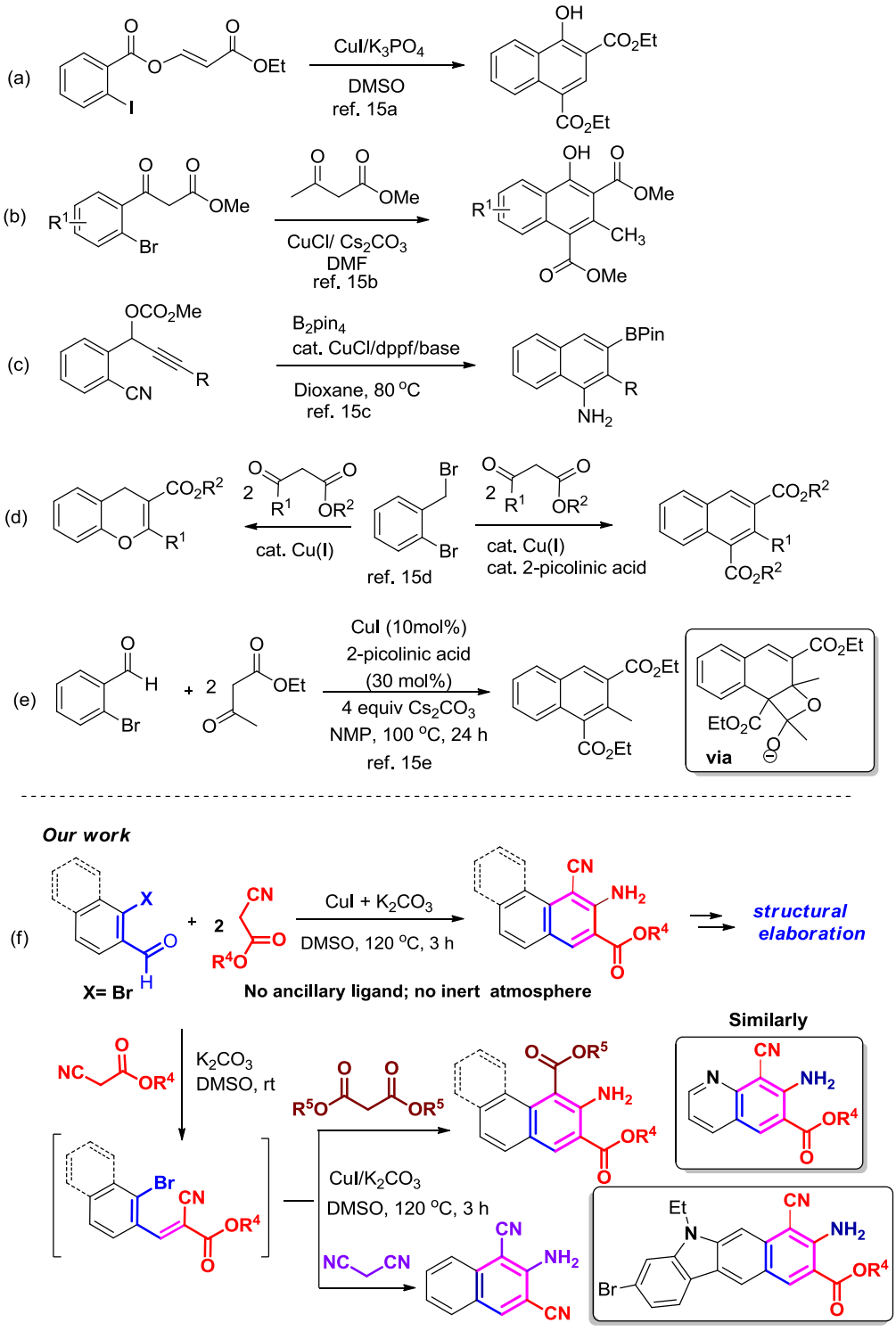


Figure 1. Selected examples of natural products and biologically active molecules containing substituted naphthalenes, phenanthrenes, quinolines and benzo[*b*]carbazoles.

Although Cu(I)-catalyzed cross-coupling reactions are well-studied in domino and multi-component reactions,[14] their application for the construction of polysubstituted naphthalene derivatives is very limited. Panda *et al*. developed an efficient method for the synthesis of polysubstituted *α*-naphthols from simple monocyclic enol esters (Scheme 1a).[15a] Jiang and co-workers disclosed a copper-catalyzed tandem reaction of methyl-3-(2-bromophenyl)-3-oxopropanoate with methyl-3-oxobutanoate for the synthesis of dimethyl-4-hydroxy-2-methylnaphthalene-1,3-dicarboxylate (Scheme 1b),[15b] Liu and co-workers described a copper-catalyzed borylative cyclization strategy to construct 3-boryl-1-naphthylamines from *o*-(cyano)phenyl propargyl carbonates (Scheme 1c).[15c] In the year 2011, Beifuss and coworkers developed an efficient copper-catalyzed domino method for the synthesis of dialkyl-2-alkylnaphthalene-1,3-dicarboxylates via the reaction of *o*-halobenzyl halide with two

molecules of a *β*-ketoester (Scheme 1d).[15d] Later, the same group extended this protocol to *o*-halobenzaldehydes as substrates to access same substituted naphthalenes (Scheme 1e).[15e] Inspite of these outstanding efforts, it is still challenging to prepare polysubstituted aromatic compounds (PACs) possessing diverse substituents directly from readily available building blocks in a single synthetic operation. In this context, we report herein a convenient and efficient copper-catalyzed tandem or sequential synthesis of multifunctional naphthalenes, phenanthrenes, quinolines and benzo[*b*]carbazoles by using commercially available starting materials such as *o*-bromoarylaldehydes, alkyl cyanoacetates, dialkyl malonates and malononitrile (Scheme 1f). Our reaction works under ligand-free conditions and further elaboration of the products can be readily achieved, as shown by the isolation of dihydrobenzoquinazolines. Also, the phenanthrene products are fluorescence active, a property that may be useful in applications.

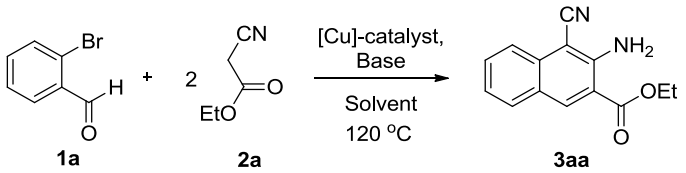
Scheme 1. Selected Related Reports on [Cu]-Mediated Approaches to Polysubstituted Naphthalenes and Our Present Work



RESULTS AND DISCUSSION

Initially, 2-bromobenzaldehyde **1a** was treated with ethyl 2-cyanoacetate **2a** in the presence of CuBr (10 mol%) and K_2CO_3 (3.0 equiv) in DMSO at 120 °C for 3 h. TLC analysis showed that **1a** was consumed completely to give ethyl 3-amino-4-cyano-2-naphthoate **3aa** in 74% yield (Table1, entry1). To identify the best reaction condition, we have varied the catalysts, bases and solvents as shown in Table 1. First, copper catalysts CuBr, CuCl, CuI, $CuCl_2$, $Cu(OAc)_2$ and $Cu(OTf)_2$ (0.1equiv) were checked by using 3.0 equiv of K_2CO_3 as the base and DMSO as the solvent at 120 ºC (Table 1, entries 1-6). CuI provided the highest yield and the target product **3aa** was isolated in 81% yield (entry 4). In the absence of copper catalyst, product **3aa** was not at all observed (entry 7). Lowering of catalyst loading to 5 mol % decreased the yield (entry 8) whereas increasing the catalyst loading to (20 mol %) did not improve yield of the reaction (entry 8). Among the bases K_2CO_3, Cs_2CO_3, Na_2CO_3, K_3PO_4, *t*-BuOK, Et_3N and DBU (entries 4, 9-14) that were checked, K_2CO_3 provided the highest yield. Among the solvents DMSO, *N,N*-dimethylacetamide (DMA), 1,4-dioxane, toluene, and PEG-400 (entries 4, 16-19) that were tested, DMSO was found to be the solvent of choice, although DMF (entry 15) also gave a comparable yield. Conducting the reaction at 70 ^{o}C/10 h or 150 ^{o}C/ 3 h afforded **3aa** in nearly the same yield (entry 20). It was also noteworthy that this reaction protocol required neither an inert atmosphere nor any additional ligand to produce alkyl 3-amino-4-cyano-2-naphthoate **3aa** in good yield (entry 22). Eventually, reaction conditions in entry 4 was determined as optimal [**1a** (1.0 mmol), **2b** (2.0 mmol), CuI (10 mol %), and K_2CO_3 (3.0 mmol) in DMSO at 120 °C/ 3 h].

Table 1. Optimization of the Reaction Conditions[a]



Entry	catalyst	base	solvent	yield of **3aa** (%)[b]
1	CuBr	K_2CO_3	DMSO	74
2	CuCl	K_2CO_3	DMSO	52
3	$CuCl_2$ (anh.)	K_2CO_3	DMSO	47
4	**CuI**	**K_2CO_3**	**DMSO**	**81**[c]
5	$Cu(OAc)_2$ (anh.)	K_2CO_3	DMSO	54
6	$Cu(OTf)_2$	K_2CO_3	DMSO	52
7	-	K_2CO_3	DMSO	-[d]
8	CuI	K_2CO_3	DMSO	54 (80)[e]
9	CuI	Cs_2CO_3	DMSO	76
10	CuI	Na_2CO_3	DMSO	71
11	CuI	K_3PO_4	DMSO	60
12	CuI	*t*-BuOK	DMSO	42
13	CuI	Et_3N	DMSO	14
14	CuI	DBU	DMSO	25
15	CuI	K_2CO_3	DMF	75
16	CuI	K_2CO_3	DMA	37
17	CuI	K_2CO_3	Dioxane	10
18	CuI	K_2CO_3	Toluene	11

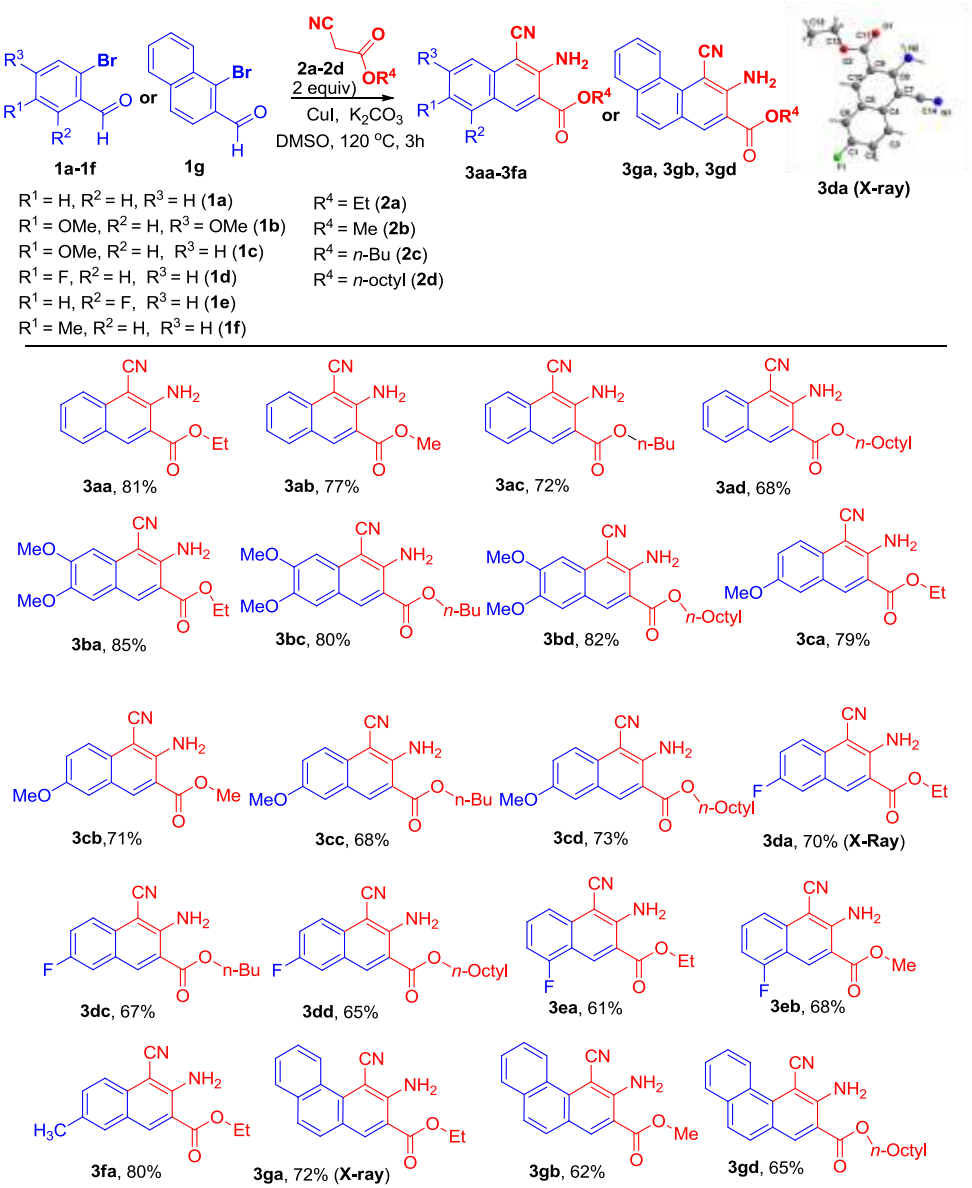
19	CuI	K_2CO_3	PEG-400	7
20	CuI	K_2CO_3	DMSO	77 (80)[f]
21	CuI	-	DMSO	-[g]
22	CuI	K_2CO_3	DMSO	80(77)[h]

[a]Reaction conditions: **1a** (0.54 mmol), **2a** (1.09 mmol), base (1.62 mmol), catalyst (0.054 mmol), solvent (2 mL), 120 ^oC (oil bath) for 3 h in a stoppered Schlenk tube in air. [b]Isolated yield of **3aa**. [c]Reaction performed under nitrogen gave the same yield but under oxygen (balloon), the yield was only 45%. [d]No catalyst was added. [e]5 mol % and 20 mol % of CuI were used. [f]The yields are for the reaction performed at 70 ^oC/10 h (77%) and 150 ^oC/ 3 h (80%). [g]No base was added; only Knoevenagel product (38%) was isolated. [h]10 mol % of L-proline (or 1,10-phenanthroline) was used.

As shown in Table 2, 2-bromobenzaldehydes **1a-1f** possessing electron-neutral, electron rich or electron-withdrawing substituents smoothly converted to the corresponding products **3** in good yields. The nitriles **2a, 2c** and **2d** containing CO_2R^4 [R^4 = Me, Et, *n*-Bu, *n*-octyl) could also be successfully utilized. We were pleased to find that the tandem reaction of 1-bromo-2-naphthaldehyde **1g** with alkyl-2-cyanoacetates **2a-2d** afforded the fluorescence active (vide infra) alkyl 3-amino-4-cyanophenanthrene-2-carboxylates **3ga** (X-ray in Figure S2, SI), **3gb**, and **3gd** in good yields. We subsequently examined the reaction of 2-bromo-3-pyridinecarboxaldehyde **1h** with alkyl cyanoacetates **2a, 2b** and **2d**; satisfyingly, the reaction furnished the desired products **3ha, 3hb and 3hd** in moderate to good yields of 72-52% (Table 3) along with < 17% yield of **3ha'** and **3hd'**. We successfully extended this chemistry to the synthesis of alkyl 7-amino-8-cyano-5-

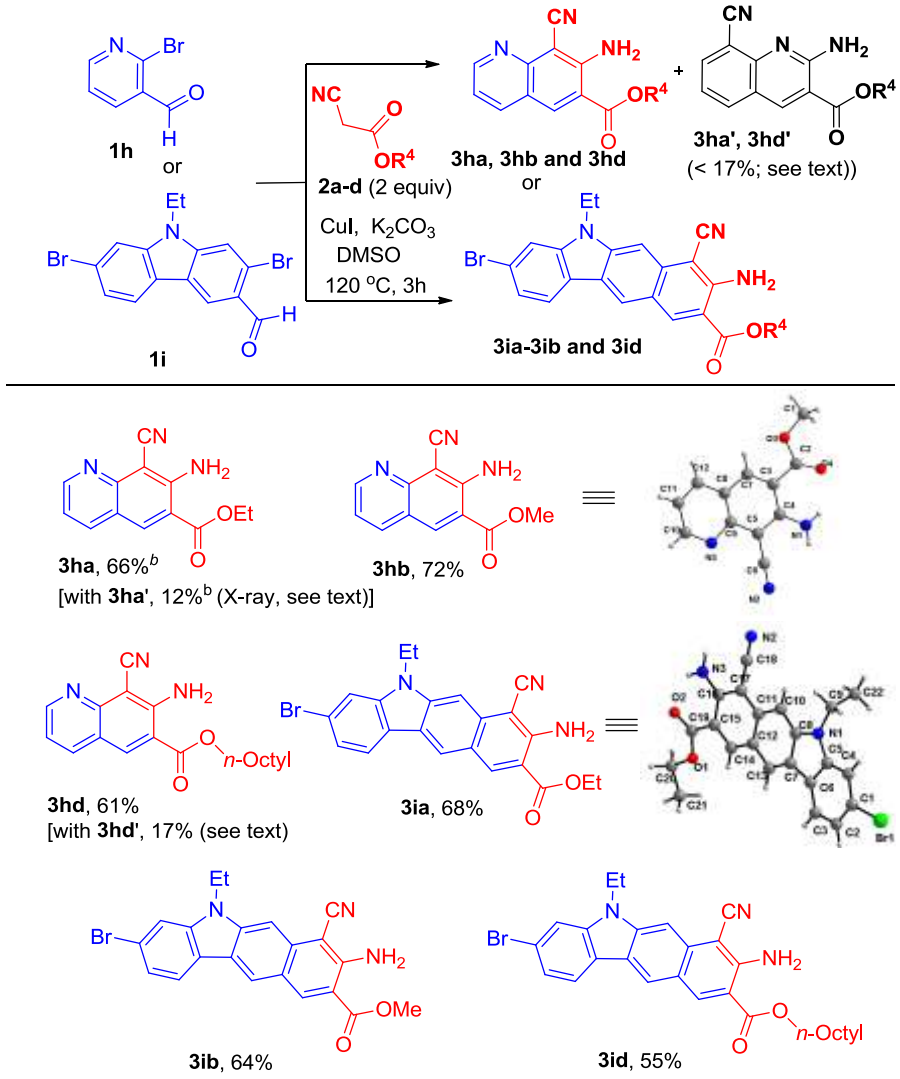
ethyl-5*H*-benzo[*b*]carbazole-9-carboxylate **3ia** (X-ray; Figure S5, SI), **3ib** and **3id** by using precursor **1i**[16] (Table 3)**.**

Table 2. Substrate Scope for [Cu]-Catalyzed Tandem Synthesis of Multifunctional Naphthalenes and Phenanthrenes 3[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), K_2CO_3 (1.6 mmol), CuI (0.05 mmol), DMSO (2 mL) in a stoppered Schlenk tube in air at 120 °C (oil bath) for 3h. [b]Yield of product **3**.

Table 3. Cu(I)-Catalyzed Tandem Synthesis of Multifunctional Quinolines and Benzo[*b*]carbazoles 3[a,b]

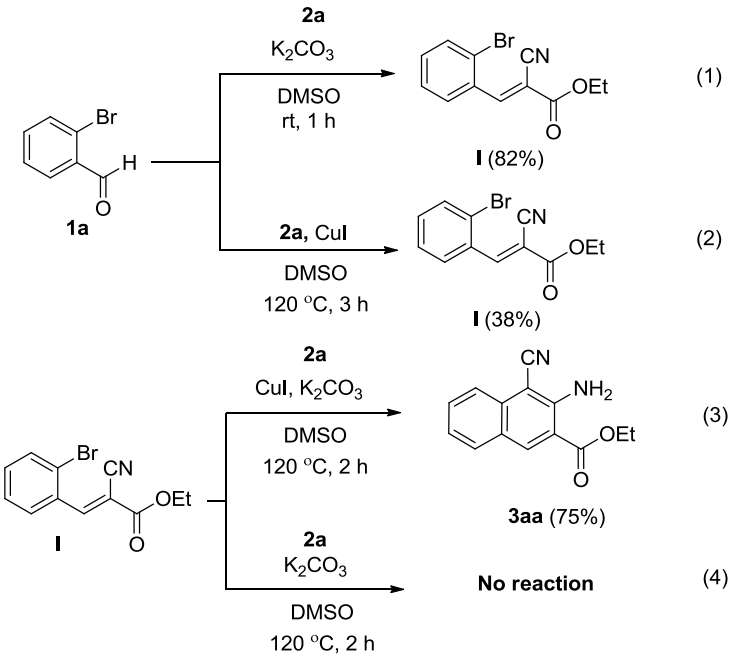


[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), K_2CO_3 (1.6 mmol), CuI (0.05 mmol), DMSO (2 mL), in a stoppered Schlenk tube in air at 120 °C (oil bath) for 3 h. [b]Yield of product **3**.

In order to decipher the reaction pathway, we performed the reaction of 2-bromobenzaldehyde **1a** (1 mmol) with ethyl cyanoacetate **2a** (1 mmol) using K_2CO_3 (1.0

mmol) in DMSO at rt (25 ^{o}C) for 1 h that provided the Knoevenagel adduct **I** in 82% yield (Scheme 2, eq 1). In the absence of K_2CO_3, the Knoevenagel adduct **I** was obtained in only 38% yield, along with unreacted starting material **1a** (Scheme 2, eq 2). When we treated **I** (1 mmol) with ethyl cyanoacetate **2a** (1 mmol), CuI (0.1 mmol), and K_2CO_3 (2.0 mmol) at 120 ºC for 2 h, the desired product **3aa** was obtained in excellent yield (Scheme 2, eq 3). In the absence of CuI, the reaction did not proceed (Scheme 2, eq 4). These simple observations clearly showed that copper mediated C-arylation is the key step in this tandem process.

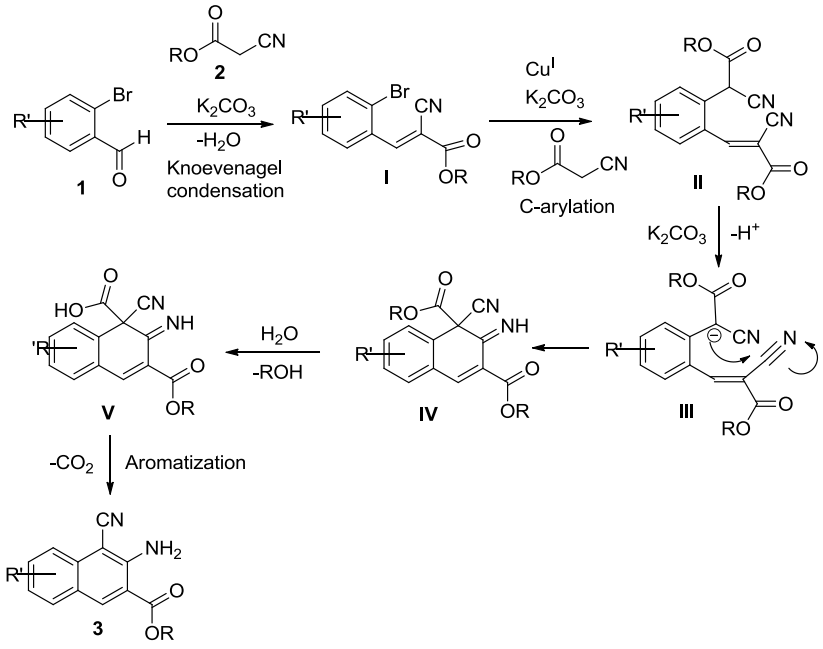
Scheme 2. Control Experiments



On the basis of the above control experiments and literature reports,[17, 15b, 5i] a plausible pathway for the formation of **3aa** is illustrated in Scheme 3. Initially, the reaction of 2-bromobenzaldehyde **1** and alkyl cyanoacetate **2** generated Knoevenagel adduct **I**. Copper-catalyzed coupling of **I** with **2** leads to C-arylation product **II**. Then, the base abstracts a

proton from an active methine carbon of **II** forming the highly nucleophilic carbanion **III** that attacks the nitrile leading to the cyclized intermediate **IV** which undergoes hydrolysis to give **V**. Decarboxylation, followed by aromatization of **V** affords alkyl 3-amino-4-cyano-2-naphthoate (**3**). We wish to emphasize here that (i) the later stages of this reaction pathway as well as the resulting products differ from the one reported using *β*-ketoesters wherein an oxetane intermediate and elimination of carboxylate species is proposed[15e] and (ii) the formation of **3ha'** and **3hd'** albeit in very low yields perhaps offers a different type of mechanism for their formation but currently it is a puzzling observation.

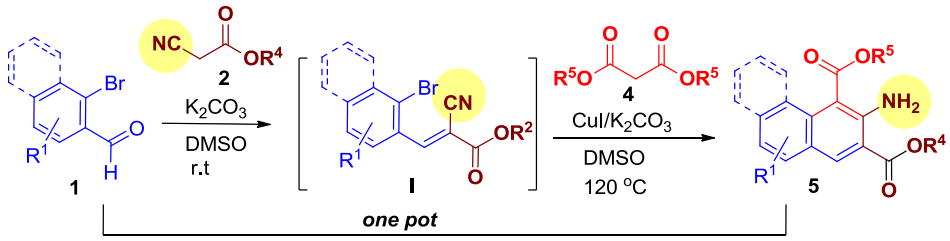
Scheme 3. Plausible Pathway for the Formation of Products 3

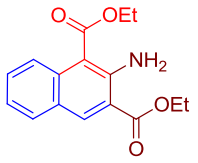


For expanding the scope of substrates, we treated 2-bromobenzaldehyde **1a** (1.0 mmol) with methyl cyanoacetate **2b** (1.0 mmol**)** and K_2CO_3 (1.0 mmol) in DMSO at rt for 1 h to generate intermediate **I**; after consumption of all of **1a** (TLC), CuI (10 mol%), K_2CO_3

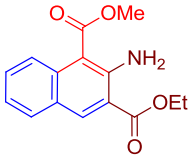
(2.0 mmol) and dimethylmalonate (**4b**, 1.0 mmol) were added and the contents heated at 120 °C for 2 h. The overall reaction proceeded smoothly to afford dimethyl 2-aminonaphthalene-1,3-dicarboxylate **5abb** (X-ray in Figure S6, SI) in 68% yield (Table 4). The scope of this protocol was examined using diverse 2-bromobenzaldehydes (**1a**, **1c, 1d** and **1g**), alkyl 2-cyanoacetates (**2a-b**) and dialkylmalonates (**4a-c**; R^5 = Et, Me, *i*-Pr). The corresponding products **5aaa-5aac**, **5abb**, **5cbb**, and **5dab** were isolated in good yields (Table 4). This new one-pot sequence also allows for the synthesis of polysubstituted phenanthrene **5gaa** in 80% yield (Table 4).

Table 4. Cu(I)-Catalyzed One-Pot Sequential Synthesis of 5[a,b]

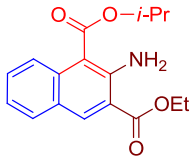




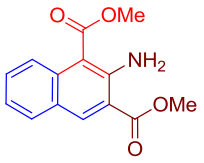
5aaa; 80%



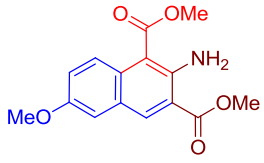
5aab; 79%



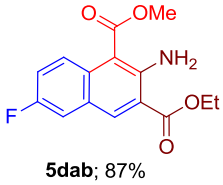
5aac; 74%



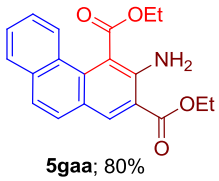
5abb; 68%



5cbb; 87%



5dab; 87%

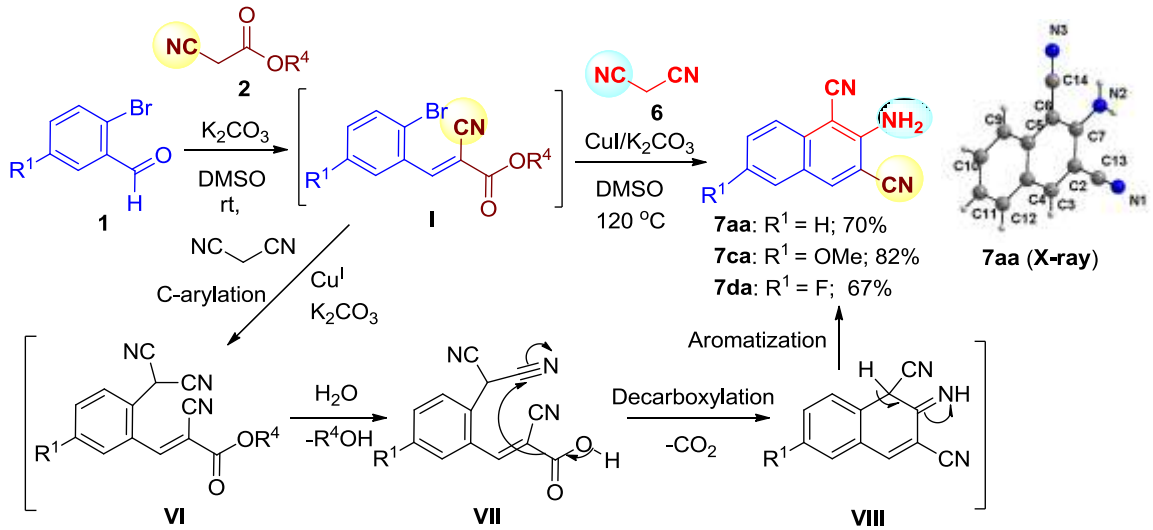


5gaa; 80%

[a]Reaction conditions: **1** (~0.5 mmol), **2** (0.5 mmol), K_2CO_3 (0.5 mmol), DMSO (2 mL), at rt for 1 h in a stoppered Schlenk tube in air; then CuI (0.05 mmol), **4** (0.5 mmol), and K_2CO_3 (1.0 mmol) were added in air and contents heated at 120 ^oC (oil bath) for 2 h. [b]Yield of product **5**.

In order to explore the above one pot sequential method further, malononitrile (**6**; 1 mmol) was used to replace dialkylmalonate **4** in Table 4. Very interestingly, this reaction afforded 2-aminonaphthalene-1,3-dicarbonitriles **7aa, 7ca and 7da** in 67-82% yield (Table 5). Mechanistically, the reaction seems to involve an initial C-arylation via copper-catalyzed coupling of **I** with **6** to give intermediate **VI**. Hydrolysis of ester on **VI** leads to **VII**. Decarboxylation followed by cyclization of **VII** leads to intermediate **VIII**. Finally, aromatization of **VIII** afforded product **7**. Thus the later stages of this pathway appears to be slightly different from that shown in Scheme 3 or the one involving *β*-ketoesters.[15e]

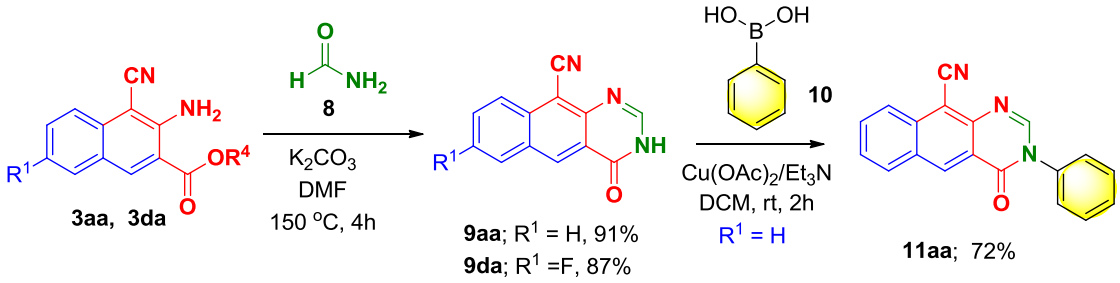
Table 5. Cu(I)-Catalyzed One-Pot Sequential Synthesis of 2-Aminonaphthalene-1,3-dicarbonitrile 7[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), K_2CO_3 (0.5 mmol), DMSO (2 mL), at rt for 1h, in a stoppered Schlenk tube in air; then CuI (0.05 mmol), **6** (0.5 mmol), and K_2CO_3 (1.0 mmol) were added in air and the contents heated at 120 °C (oil bath) for 2h.[b] Yield of product **7**.

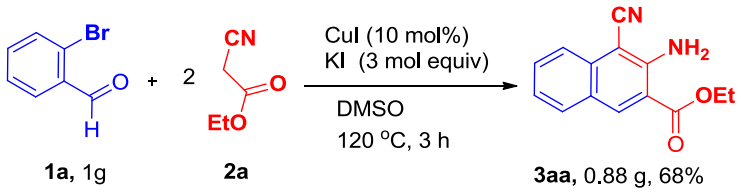
To demonstrate the utility of the present protocol, further structural elaboration of compounds **3aa** and **3da** was performed via the reaction with formamide **8** in the presence of K_2CO_3 to give the corresponding benzo[*g*]quinazoline **9**. Later, the compound **9aa** was converted to 4-oxo-3-phenyl-3,4-dihydrobenzo[*g*]quinazoline-10-carbonitrile **11aa** by using a reported Cu-mediated C-N bond forming reaction (Scheme 4);[18] there was no perceptible reaction when CuI was used in place of $Cu(OAc)_2$ under the conditions given in Table 2.

Scheme 4. Structural Elaboration of 3



To examine the scalability of the optimized method, the tandem reaction between 2-bromobenzaldehyde **1a** and ethyl cyanoacetate **2a** was carried out under standard conditions on a gram scale. The expected product **3aa** could be obtained in 68% isolated yield (Scheme 5).

Scheme 5. Gram-Scale Transformation



Photophysical Properties of Phenanthrenes 3ga, 3gd and 5gaa.

We expected phenanthrene-2-carboxylates **3ga, 3gd** and **5gaa** to be photo chemically active and perhaps could be used later. Hence the UV-visible and fluorescence spectra were recorded. The emission spectra of compounds **3ga**, **3gd**, and **5gaa** were recorded upon excitation at 330 nm. As expected, these compounds show moderate fluorescence emission intensity (cf. Figure 2). The absorption peak wavelengths (λ_{abs}), molar extinction coefficient (Ɛ), emission peak wavelengths (λ_{em}) in solution are summarized in Table 6 and Figure 2.

Table 6. UV−Visible Absorption and Fluorescence Emission Properties of Phenanthrene Carboxylates 3ga, 3gd and 5gaa

entry	compound	λ_{abs} (nm)[a]	Ɛ (10^4 $M^{-1}cm^{-1}$)	λ_{em} (nm)[b]
1	**3ga**	435	1.0	461
2	**3gd**	435	3.3	467
3	**5gaa**	427	1.9	488

[a]UV-visible absorption wavelengths, [b]Emission wavelengths at rt in toluene at concentration of 1×10^{-5}M.

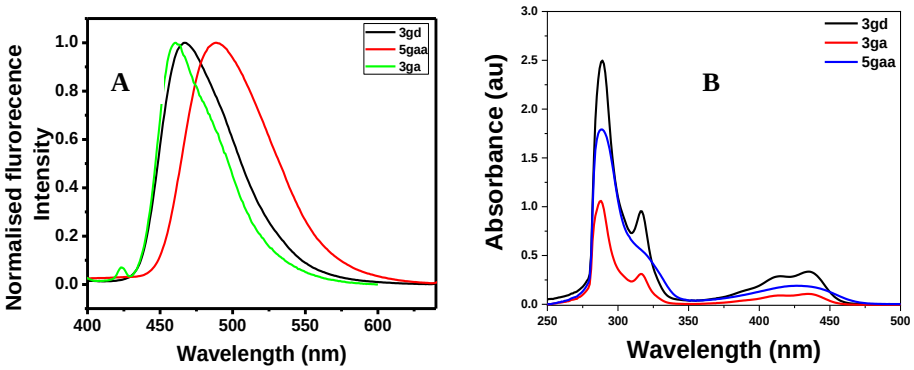


Figure 2. (A) Absorbance and (B) Fluorescence emission spectra of compounds **3ga**, **3gd** and **5gaa** in toluene (10^{-5} M) at rt (25 °C).

CONCLUSIONS

We have developed a simple and highly efficient ligand-free one pot Cu(I)-mediated tandem or sequential protocol for the synthesis of multifunctional naphthalenes, phenanthrenes, quinolines and benzo[*b*]carbazoles. The protocol entails readily available substrates such as *o*-bromoarylaldehydes, alkyl cyanoacetates, dialkylmalonates and active methylene nitriles. The developed methodology was

utilized further for the synthesis of 4-oxo-3-phenyl-3,4-dihydrobenzo[*g*]quinazoline-10-carbonitrile. The photophysical properties of phenanthrene carboxylates reveal possible applications for the highly fluorescent materials.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in air, unless specified otherwise. All required chemicals were procured and used as purchased without further purification, unless noted otherwise. Melting points were determined using a SUPERFIT hot stage apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tubes on a Bruker 400 and 500 MHz NMR spectrometer [field strengths: 400/100 or 500/125 MHz respectively] in $CDCl_3$/DMSO-d_6 solution with shifts referenced to TMS (^{1}H, ^{13}C: ö = 0). All *J* values are in Hz. Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. Crystallographic data were collected at 293 K on an X-ray diffractometer system using Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α (λ = 1.54184 Å) radiation. Structures were solved and refined using standard methods.[19] Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh)/neutral alumina, for column elution process hexane-EtOAc mixture was used as the eluent unless otherwise stated.

o-Bromoarylaldehydes (**1a-1h**) were purchased from Aldrich and used without further purification and **1i** was prepared by using a literature report.[16]

(i). General procedure for the synthesis of compounds 3aa-3ib. To an oven dried Schlenk tube, with a magnetic stirrer bar was added *o*-bromoaryl aldehyde **1** (~0.5 mmol, 1 equiv, individual quantities given below), CuI (0.05 mmol, 10 mol %), K_2CO_3 (1.6 mmol, 3 equiv), alkyl cyanoacetate **2** (1.0 mmol, 2 equiv) and DMSO (2 mL). The tube with the contents was stoppered and heated at 120 °C (oil bath) for 3h. After completion of the reaction as monitored by TLC, the crude reaction mixture was cooled to rt (25 ^oC), diluted with ethyl acetate (20 mL) and passed through a short celite column. The resulting solution was washed with water (2 x 20 mL) and the aqueous part extracted twice with ethyl acetate (20 mL). The combined organic layer was washed with brine solution (2 x 20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was then purified by using silica gel column chromatography using hexane-ethyl acetate (9:1) as eluent to afford the pure desired compounds **3**. Compounds **3aa-3ib** were prepared from the appropriate *o*-bromoaryl aldehyde **1** and alkyl cyanoacetate **2** by using the same procedure using similar molar quantities/ratio.

(ii). Procedure for the Scale-up Reaction. To an oven dried Schlenk tube, with a magnetic stirrer bar was added *o*-bromoaryl aldehyde **1** (1.000 g, 5.40 mmol), CuI (0.103 g, 0.54 mmol), K_2CO_3 (2.200 g, 16.20 mmol), ethyl cyanoacetate **2** (1.15 mL, 10.81 mmol) and DMSO (20 mL). The tube with the contents was stoppered and heated at 120 °C (oil bath) for 3h. After completion of the reaction as monitored by TLC, the crude reaction mixture was cooled to rt (25 ^oC), diluted with ethyl acetate (100 mL) and passed through a short celite (ca 10 g) column. The resulting solution was washed with water and the aqueous part extracted twice with ethyl acetate (2 x 100 mL). The combined organic layer was washed with brine solution (2 x 100 mL), dried over anhydrous

Na_2SO_4, and concentrated in vacuum. The residue was then purified by using silica gel column chromatography using hexane-ethyl acetate (9:1) as eluent to afford the desired compound **3aa** (0.88 g, 68%) as a yellow solid).

*Ethyl 3-amino-4-cyano-2-naphthoate (**3aa**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol) and **2a**. Yellow solid, yield 0.106 g (81%); mp 146-148 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.66-7.63 (m, 1H), 7.34 (t, J = 7.4 Hz, 1H), 6.71 (br s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 151.0, 138.8, 136.1, 131.5, 130.1, 124.8, 123.8, 122.9, 116.9, 114.1, 88.9, 61.6, 14.3; IR (neat) ν_{max} 3427, 3327, 2967, 2926, 2203, 1739, 1613, 1366, 1210, 1072, 1029, 787, 747 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{12}N_2NaO_2$ $[M^+$+Na] *m/z* 263.0796, found 263.0792.

*Methyl 3-amino-4-cyano-2-naphthoate (**3ab**)*: This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol) and **2b**. Yellow solid, yield 0.095 g (77%); mp 152-154 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0Hz, 1H), 7.68-7.64 (m, 1H), 7.36 (t, J = 8.0 Hz, 1H), 6.70 (br s, 2H), 4.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.1, 151.0, 138.9, 136.2, 131.6, 130.1, 124.8, 123.9, 123.0, 116.8, 113.8, 89.0, 52.5; IR (neat) ν_{max} 3440, 3337, 3015, 2962, 2218, 1739, 1625, 1366, 1213, 1076, 790, 744 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2$ $[M^+$+H] *m/z* 227.0821, found 227.0815.

*Butyl 3-amino-4-cyano-2-naphthoate (**3ac**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol) and **2c**. Yellow solid, yield 0.105 g (72%); mp 142-

144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.35-7.31 (m, 1H), 6.70 (br s, 2H), 4.40 (t, *J* = 6.4 Hz, 2H), 1.87-1.80 (m, 2H), 1.58-1.49 (m, 2H), 1.04 (t, *J* = 7.6Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 151.1, 138.7, 136.1, 131.5, 130.1, 124.8, 123.8, 122.9, 116.9, 114.1, 89.0, 65.4, 30.7, 29.7, 19.3, 13.8; IR (neat) ν_{max} 3433, 3330, 2957, 2927, 2864, 2207, 1695, 1613, 1455, 1304, 1210, 1077, 794, 750 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}N_2O_2$ [M^++H] *m/z* 269.1290, found 269.1283.

*Octyl 3-amino-4-cyano-2-naphthoate (**3ad**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol) and **2d**. Yellow solid, yield 0.120 g (68 %); mp 149-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.36-7.32 (m, 1H), 6.71 (br s, 2H), 4.40 (t, *J* = 6.8 Hz, 2H), 1.88-1.81 (m, 2H), 1.53-1.32 (m, 10H), 0.92 (t, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 151.1, 138.8, 136.1, 131.6, 130.1, 124.8, 123.9, 123.0, 116.9, 114.2, 88.9, 65.8, 31.8, 29.3, 29.2, 28.6, 26.1, 22.7, 14.1; IR (neat) ν_{max} 3436, 3334, 2924, 2857, 2208, 1737, 1699, 1616, 1573, 1456, 1367, 1303, 1211, 1170, 1083, 794, 755 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{25}N_2O_2$ [M^++H] *m/z* 325.1916, found 325.1917.

*Ethyl 3-amino-4-cyano-6,7-dimethoxy-2-naphthoate(**3ba**)*. This compound was prepared by using precursors **1b** (100 mg, 0.408 mmol) and **2a**. Yellow solid, yield 0.104 g (85%); mp 161-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.96 (s, 1H), 6.96 (s, 1H), 6.28 (s, 2H), 4.53 (q, *J* = 7.0 Hz, 2H), 4.02 (s, 3H), 3.98 (s, 3H), 1.53 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 153.2, 147.7, 147.3, 137.8, 131.8, 121.6, 117.3, 107.6, 105.1, 104.9, 98.4, 61.2, 55.9, 55.8, 14.5; IR (neat) ν_{max} 3481, 3352, 2924,

2854, 2214, 1673, 1614, 1435, 1323, 1295, 1013, 814 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}N_2O_4$ $[M^+ + H]$: *m/z* 301.1188, found 301.1189.

*Butyl 3-amino-4-cyano-6,7-dimethoxy-2-naphthoate (**3bc**)*. This compound was prepared by using precursors **1b** (100 mg, 0.408 mmol) and **2c**. Yellow solid, yield 0.107 g (80%); mp 157-159 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 6.57 (s, 2H), 4.38 (t, *J* = 6.5 Hz, 2H), 4.07 (s, 3H), 3.99 (s, 3H), 1.85-1.79 (m, 2H), 1.57-1.50 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.0, 154.3, 150.3, 147.9, 136.3, 133.3, 119.9, 117.3, 111.5, 108.2, 102.0, 88.4, 65.0, 56.2, 56.0, 30.7, 19.3, 13.8; IR (neat) ν_{max} 3437, 3336, 2959, 2926, 2873, 2203, 1686, 1614, 1461, 1299, 1094, 1039, 974,752 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}N_2O4$ $[M^+ + H]$ *m/z* 329.1501, found 329.1502.

*Octyl 3-amino-4-cyano-6,7-dimethoxy-2-naphthoate (**3bd**)*. This compound was prepared by using precursors **1b** (100 mg, 0.408 mmol) and **2d**. Yellow solid, yield 0.129 g (82%); mp 149-151 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 6.57 (s, 2H), 4.36 (t, *J* = 6.5 Hz, 2H), 4.07 (s, 3H), 3.99 (s, 3H), 1.85-1.80 (m, 2H), 1.51-1.32 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.0, 154.3, 150.3, 147.9, 136.4, 133.3, 119.9, 117.3, 111.6, 108.3, 102.1, 88.4, 65.4, 56.3, 56.0, 31.8, 29.3, 29.2, 28.7, 26.1, 22.7, 14.1; IR (neat) ν_{max} 3440, 3343, 2955, 2925, 2855, 2204, 1688, 1611, 1509, 1331, 1298, 1039, 1022, 787, 754 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{29}N_2O_4$ $[M^+ + H]$ *m/z* 385.2127, found 385.2128.

*Ethyl 3-amino-4-cyano-7-methoxy-2-naphthoate (**3ca**)*. This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol) and **2a**. Yellow solid, yield 0.100 g (79 %); mp 165-167 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 1H),

7.33 (dd, J = 8.8, 2.4 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 6.54 (s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H). 1.49 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 155.9, 150.1, 137.8, 131.3, 125.5, 124.6, 123.7, 117.2, 114.7, 109.3, 88.0, 61.8, 55.8, 14.5; IR (neat) ν_{max} 3429, 3329, 2979, 2205, 1739, 1614, 1366, 1211, 1074, 1031, 787, 749 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_3$ $[M^+ + H]$ *m/z* 271.1083, found 271.1077.

*Methyl 3-amino-4-cyano-7-methoxy-2-naphthoate (**3cb**)*: This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol) and **2b**. Yellow solid, yield 0.085 g (71 %); mp 170-172 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.33 (dd, J = 9.0, 2.5 Hz, 1H), 7.10 (d, J = 3.0 Hz, 1H), 6.52 (br s, 2H), 3.99 (s, 3H), 3.91 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.2, 156.2, 149.5, 137.3, 131.5, 125.7, 124.5, 124.3, 116.9, 114.2, 108.0, 89.5, 55.4, 52.4; IR (neat) ν_{max} 3446, 3345, 2959, 2922, 2209, 1738, 1704, 1617, 1505, 1374, 1289, 1215, 1142, 1089, 1012, 824, 787 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}N_2O_3$ $[M^+ + H]$ *m/z* 257.0926, found 257.0929.

*Butyl 3-amino-4-cyano-7-methoxy-2-naphthoate (**3cc**).* This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol) and **2c**. Yellow solid, yield 0.095 g (68 %); mp 161-163 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.33 (dd, J = 9.2, 2.4 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 6.53 (br s, 2H), 4.40 (t, J = 6.4 Hz, 2H), 3.92 (s, 3H), 1.87-1.80 (m, 2H), 1.57-1.49 (m, 2H), 1.05 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 156.1, 149.6, 137.1, 131.4, 125.7, 124.4, 124.2, 117.0, 114.5, 107.9, 89.5, 65.3, 55.4, 30.7, 19.3, 13.8; IR (neat) ν_{max} 3437, 3335, 2925, 2858, 2207, 1738, 1691, 1609, 1459, 1375, 1227, 1080, 1024, 799 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{19}N_2O_3$ $[M^+ + H]$ *m/z* 299.1396, found: 299.1390.

*Octyl 3-amino-4-cyano-7-methoxy-2-naphthoate (**3cd**)*. This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol) and **2d**. Yellow solid, yield 0.121 g (73%); mp 153-155 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.33 (dd, J = 8.8, 2.4 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.53 (br s, 2H), 4.39 (t, J = 6.8 Hz, 2H), 3.92 (s, 3H), 1.88-1.81 (m, 2H), 1.53-1.27 (m, 10H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 156.1, 149.6, 137.1, 131.4, 125.6, 124.4, 124.2, 117.0, 114.4, 107.9, 89.4, 65.7, 55.4, 31.8, 29.2_4, 29.1_8, 28.6, 26.0, 22.6, 14.1; IR (neat) ν_{max} 3440, 3337, 2924, 2854, 2207, 1694, 1611, 1505, 1463, 1380, 1296, 1233, 1184, 1170, 1086, 1005, 818, 731 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}N_2O_3$ [M^++H] *m/z* 355.2022, found 355.2019.

*Ethyl 3-amino-4-cyano-7-fluoro-2-naphthoate (**3da**)*. This compound was prepared by using precursors **1d** (100 mg, 0.493 mmol) and **2a**. Yellow solid, yield 0.089 g (70 %); mp 161-163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.90-7.86 (m, 1H), 7.45-7.40 (m, 2H), 6.65 (br s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.4, 159.0 (J = 243.6 Hz), 150.5, 137.6 (J = 5.0 Hz), 132.9, 125.2 (J = 8.3 Hz), 125.1,121.6 (J = 25.2 Hz), 116.6, 115.2, 113.1 (J = 20.8 Hz), 89.2, 61.7, 14.3; IR (neat) ν_{max} 3429, 3330, 2958, 2922, 2858, 2209, 1739, 1696, 1616, 1506, 1372, 1281, 1220, 1162, 1087, 1025, 823, 794 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{11}FN_2NaO_2$ [M^++Na] *m/z* 281.0697, found 281.0696.

*Butyl 3-amino-4-cyano-7-fluoro-2-naphthoate (**3dc**)*. This compound was prepared by using precursors **1d** (100 mg, 0.493 mmol) and **2c**. Yellow solid, yield 0.095 g (67 %); mp 154-156 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.92-7.88 (m, 1H), 7.46-7.41 (m, 2H), 6.67 (s, 2H), 4.41 (t, J = 6.8 Hz, 2H), 1.87-1.80 (m, 2H), 1.56-1.48 (m, 2H),

1.04 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 159.0 (J = 243.7 Hz), 150.5, 137.6 (J = 5.1 Hz), 132.9, 125.2 (J = 8.2 Hz), 125.1 (J = 8.8 Hz), 121.6 (J = 25.3 Hz), 116.7, 115.2, 113.2 (J = 20.1 Hz), 89.2, 65.6, 30.6, 19.3, 13.8; IR (neat) ν_{max} 3440, 3338, 2961, 2208, 1738, 1609, 1506, 1373, 1297, 1225, 1082, 1036, 818, 740 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}FN_2O_2$ (M^+ + H) *m/z* 287.1196, found 287.1183.

*Octyl 3-amino-4-cyano-7-fluoro-2-naphthoate (**3dd**)*. This compound was prepared by using precursors **1d** (100 mg, 0.493 mmol) and **2d**. Yellow solid, yield 0.110 mg (65 %); mp 149-151 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.91-7.88 (m, 1H), 7.45-7.41 (m, 2H), 6.66 (s, 2H), 4.40 (t, J = 6.5 Hz, 2H), 1.87-1.81 (m, 2H), 1.51-1.45 (m, 2H), 1.43-1.31 (m, 8H), 0.92 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 159.0 (J = 243.6 Hz), 150.5, 137.6 (J = 5.0 Hz), 132.9, 125.2 (J = 8.4 Hz), 125.1 (J = 8.8 Hz), 121.6 (J = 25.1 Hz), 116.7, 115.2, 113.2 (J = 20.1 Hz), 89.2, 65.9, 31.8, 29.2_4, 29.2_0, 28.6, 26.0, 22.7, 14.1; IR (neat) ν_{max} 3483, 3363, 2958, 2927, 2856, 2204, 1796, 1693, 1609, 1572, 1376, 1279, 1216, 1157, 1077, 1024, 831, 732 cm^{-1} ; HRMS (ESI) calcd for $C_{20}H_{24}FN_2O_2$ [M^++H] *m/z* 343.1822, found 343.1814.

*Ethyl 3-amino-4-cyano-8-fluoro-2-naphthoate (**3ea**)*. This compound was prepared by using precursors **1e** (100 mg, 0.493 mmol) and **2a**. Yellow solid, yield 0.078 g (61%); mp 160-162 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H),7.61-7.55 (m, 1H), 7.01-6.97 (m, 1H), 6.83 (s, 2H), 4.48 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.5, 160.0 (J = 254.2 Hz), 151.6, 137.3 (J = 3.4 Hz), 132.0 (J = 9.3 Hz), 131.5 (J = 5.6 Hz), 118.8 (J = 4.1 Hz),116.5, 115.1, 114.3, 107.5 (J = 19.6 Hz), 88.9, 61.8, 14.3; IR (neat) ν_{max} 3429, 3327, 2984, 2926, 2207,

1735, 1696, 1616, 1574, 1438, 1376, 1273, 1181, 1122, 1048, 866, 796, 747 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{11}FNaN_2O_2$ [M^++Na] *m/z* 281.0702, found 281.0700.

*Methyl 3-amino-4-cyano-8-fluoro-2-naphthoate (**3eb**)*. This compound was prepared by using precursors **1e** (100 mg, 0.493 mmol) and **2b**. Yellow solid, yield 0.082 g (68 %); mp 165-167 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.61-7.55 (m, 1H), 7.01-6.97 (m, 1H), 6.81 (s, 2H), 4.02 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.9, 160.0 (*J* = 254.5 Hz), 151.5, 137.3, 132.1 (*J* = 9.3 Hz), 131.7 (*J* = 5.8 Hz), 118.8 (*J* = 4.2 Hz),116.5, 115.2 (*J* = 17.2 Hz), 114.0, 107.1 (*J* = 19.6 Hz), 88.9, 52.6; IR (neat) ν_{max} 3440, 3335, 2960, 2922, 2846, 2215, 1710, 1624, 1571, 1443, 1365, 1306, 1208, 1077, 791 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{10}FN_2O_2$ [M^++H] *m/z* 245.0726, found 245.0726.

*Ethyl 3-amino-4-cyano-7-methyl-2-naphthoate (**3fa**)*. This compound was prepared by using precursors **1f** (100 mg, 0.502 mmol) and **2a**. Yellow solid, yield 0.103 g (80 %); mp 140-142 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.69-7.67 (m, 2H), 7.17(dd, *J* = 8.4, 1.6 Hz, 1H), 6.68 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 151.2, 142.4, 138.5, 136.4, 129.9, 126.2, 123.1, 122.2, 117.1, 113.1, 88.4, 61.4, 22.2, 14.3; IR (neat) ν_{max} 3427, 3328, 2974, 2931, 2203, 1739, 1705, 1612, 1572, 1366, 1209, 1151, 1071, 1030, 786, 749 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_2$ [M^++H] *m/z* 255.1134, found 255.1137.

*Ethyl 2-amino-3-cyanophenanthrene-1-carboxylate (**3ga**)*. This compound was prepared by using precursors **1g** (100 mg, 0.425 mmol) and **2a**. Yellow solid, yield 0.089 g (72%); mp 176-180 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.74-9.71 (m, 1H), 8.61 (s, 1H), 7.87-7.85 (m, 1H), 7.70-7.66(m, 2H), 7.59-7.54 (m, 2H), 7.00 (br s, 2H), 4.47 (q, *J* = 7.2 Hz, 2H),

1.49 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 153.1, 138.5, 134.9, 134.3, 128.9, 127.5, 127.3, 126.6, 125.3, 123.2, 119.9, 112.3, 88.7, 61.5, 14.3; IR (neat): ν_{max} 3464, 3316, 2922, 2190, 1731, 1601, 1370, 1215, 1093, 1064, 804, 747 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{14}N_2NaO_2$ $[M^+ + Na]$ *m/z* 313.0953, found: 313.0945.

*Methyl 2-amino-3-cyanophenanthrene-1-carboxylate (**3gb**)*. This compound was prepared by using precursors **1g** (100 mg, 0.425 mmol) and **2b**. Yellow solid, yield 0.073 g (62%); mp 178-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74-9.72 (m, 1H), 8.61 (s, 1H), 7.88-7.86 (m, 1H), 7.71-7.68 (m, 2H), 7.56 (s, 2H), 6.99 (br s, 2H), 4.01 (s, 3H); $^{13}C\{^{1}H\}$ NMR(100 MHz, $CDCl_3$) δ 167.2, 153.0, 138.5, 134.9, 134.3, 128.9_4, 128.9_1, 127.4, 127.2, 126.6, 125.3_4, 125.2_8, 123.2, 120.0, 111.9, 88.7, 52.4; IR (neat) ν_{max} 3447, 3339, 2958, 2921, 2010, 1702, 1610, 1459, 1609, 1459, 1316, 1279, 1260, 1219, 1092, 1026, 909, 803, 748, 563 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{13}N_2O_2$ $[M^+ + H]$ *m/z* 277.0977, found 277.0979.

*Octyl 3-amino-4-cyanophenanthrene-2-carboxylate (**3gd**)*. This compound was prepared by using precursors **1g** (100 mg, 0.425 mmol) and **2d**. Yellow solid, yield 0.104 g (65%); mp 120-124 ^{o}C;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75-9.74 (m, 1H), 8.61 (s, 1H), 7.89-7.87 (m, 1H), 7.71-7.69 (m, 2H), 7.61-7.57 (m, 2H), 7.02 (br s, 2H), 4.41 (t, J = 6.5 Hz, 2H), 1.89-1.83 (m, 2H), 1.54-1.48 (m, 2H), 1.44-1.32 (m, 8H), 0.93 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR(125 MHz, $CDCl_3$) δ 166.8, 153.1, 138.4, 134.9, 134.3, 128.9, 127.4, 127.3, 126.6, 125.3, 123.2, 120.0, 112.3, 88.6, 65.7, 31.8, 29.3, 29.2, 28.7, 26.1, 22.7, 14.1; IR (neat) ν_{max} 3453, 3335, 2923, 2851, 2193, 1737, 1692, 1608, 1581, 1517, 1313, 1282, 1217, 1199, 1122, 1094, 1024, 971, 807, 752, 729, 682, 659 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_2$ $[M^+ + H]$ *m/z* 375.2073, found: 375.2091.

*Ethyl 7-amino-8-cyanoquinoline-6-carboxylate (**3ha**)*. This compound (along with **3ha'**; see below) was prepared by using precursors **1h** (100 mg, 0.537 mmol) and **2a**. R_f 0.3 (ethyl acetate:hexane 1:9).Yellow solid, yield 0.086 g (66%); mp 151-153 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.65 (s, 1H), 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29-7.26 (m, 1H), 6.95 (v br, 2H), 4.48 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.2, 155.0, 153.2, 151.3, 138.1, 137.6, 119.5, 119.4, 116.2, 114.8, 92.0, 61.8, 14.2; IR (neat) ν_{max} 3416, 3325, 3301, 2215, 1738, 1628, 1581, 1565, 1370, 1310, 1206, 1083, 1033, 924, 794, 727, 510 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{12}N_3O_2$ $[M^+ + H]$ *m/z* 242.0930, found 242.0930.

*Ethyl 7-amino-6-cyanoquinoline-8-carboxylate (**3ha'**)***:*** R_f 0.5 (ethyl acetate:hexane 1:9). This compound was prepared by using precursors **1h** and **2a** along with **3ha** as described above. Yield 0.015 g (12%) as yellow solid; mp: 142-145 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.74 (s, 1H), 8.01 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.28 (t, *J* = 6.0 Hz, 1H), 5.88 (s, 2H), 4.46 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 165.9, 157.6, 150.2, 142.5, 137.9, 133.8, 122.4, 121.6, 117.6, 111.8, 109.0, 61.8, 14.2; IR (neat): ν_{max} 3416, 3294, 3183, 2906, 2221, 1696, 1607, 1564, 1478, 1305, 1281, 1203, 1100, 1020, 795, 755 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{12}N_3O_2$ $[M^+ + H]$: m/z 242.0930. Found: 242.0930.

*Methyl 7-amino-8-cyanoquinoline-6-carboxylate (**3hb**)*. This compound was prepared by using precursors **1h** (100 mg, 0.537 mmol) and **2b**. Yellow solid, yield 0.088 g (72%); mp 134-141 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.65 (s, 1H), 8.07 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29-7.26 (m, 1H), 6.94 (v br, 2H), 4.01 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.7, 155.0, 153.2, 151.2, 138.3, 137.7, 119.5,

116.2, 114.5, 91.8, 52.7; IR (neat) ν_{max} 3479, 3410, 3299, 2949, 2210, 1701, 1619, 1581, 1562, 1488, 1428, 1310, 1197, 1071, 1020, 918, 794, 698, 605 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{10}N_3O_2$ $[M^+ + H]$ *m/z* 228.0773, found 228.0774.

*Octyl 7-amino-8-cyanoquinoline-6-carboxylate (**3hd**)*. This compound (along with **3hd'**; see below) was prepared by using precursors **1h** (100 mg, 0.537 mmol) and **2d**. R_f 0.3 (ethyl acetate:hexane 1:9). Yellow solid, yield 0.107 g (61%); mp 162-164 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99-8.98 (m, 1H), 8.63 (s, 1H), 8.10-8.08 (m, 1H), 7.30-7.27 (m, 1H), 6.92 (v br, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 1.88-1.81 (m, 2H), 1.49-1.32 (m, 10H), 0.91 (t, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$) δ 166.3, 155.0, 153.2, 151.3, 138.1, 137.7, 119.5, 119.4, 116.3, 114.8, 91.9, 66.0, 31.8, 29.2_3, 29.1_9, 28.6, 26.0, 22.7, 14.1; IR (neat) ν_{max} 3425, 3310, 3059, 2961, 2227, 1702, 1628, 1566, 1488, 1463, 1439, 1278, 1198, 1015, 966, 755, 691 cm^{-1}; HRMS (ESI), calcd for $C_{19}H_{24}N_3O_2$ $[M^+ + H]$ *m/z* 326.1869, found 326.1869.

*Octyl 7-amino-8-cyanoquinoline-6-carboxylate (**3hd'**)***:*** This compound was prepared by using precursors **1h** and **2d** along with **3hd** as described above. R_f 0.5 (ethyl acetate:hexane 1:9). Yield 0.030 g (17%) as yellow solid; mp: 169-171 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.71 (s, 1H), 8.00 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29-7.26 (m, 1H), 5.95 (s, 2H), 4.38 (t, *J* = 6.5 Hz, 2H), 1.86-1.80 (m, 2H), 1.50-1.45 (m, 2H), 1.40-1.31 (m, 8H), 0.91 (t, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 166.0, 157.6, 150.2, 142.5, 138.0, 133.9, 122.3, 121.6, 117.7, 111.8, 108.9, 66.0, 31.8, 29.2_4, 29.1_9, 28.6, 26.0, 22.7, 14.1; IR (neat): ν_{max} 3426, 3311, 2954, 2919, 2868, 2226, 1701, 1628, 1565, 1458, 1377, 1305, 1278, 1197, 1081, 966, 892, 799, 758, 590 cm^{-1}; HRMS (ESI): Calcd. for $C_{19}H_{24}N_3O_2$ $[M^+ + H]$: m/z 326.1869. Found: 326.1869.

*Ethyl 8-amino-3-bromo-7-cyano-5-ethyl-5H-benzo[b]carbazole-9-carboxylate (**3ia**)*. This compound was prepared by using precursors **1i** (100 mg, 0.262 mmol) and **2a**. Yellow solid, yield 0.078 g (68%); mp 208-210 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H),8.34 (s, 1H),7.86 (d, *J* = 8.0 Hz, 1H),7.52 (s, 1H),7.44 (d, *J* = 1.5 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.68 (br, 2H),4.38 (q, *J* = 7.0 Hz, 2H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 8.0 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.9, 151.3, 143.8, 143.1, 139.9, 135.1, 122.9$_3$, 122.8$_9$, 122.3, 121.7$_0$, 121.6$_6$,121.0, 119.8, 118.0, 111.8, 111.3, 98.5, 86.9, 61.3, 37.9, 14.4, 13.3; IR (neat) ν_{max}3343, 2921, 2852, 2203, 1734, 1682, 1460, 1254, 1084, 799, 582 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{18}{}^{79}BrN_3O_2$ and $C_{22}H_{18}{}^{81}BrN_3O_2$ [M$^+$+H] *m/z* 436.0661 and 438.0661, found 436.0658 and 438.0640.

*Methyl 8-amino-3-bromo-7-cyano-5-ethyl-5H-benzo[b]carbazole-9-carboxylate (**3ib**)*. This compound was prepared by using precursors **1i** (100 mg, 0.262 mmol) and **2b**. Yellow solid, yield 0.071 g (64%); mp 195-197 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.35 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.73 (br, 2H), 4.32 (t, *J* = 7.0 Hz, 2H), 4.01(s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.3, 151.2, 143.8, 143.1, 139.9, 135.2, 128.8, 123.0, 122.2, 121.7, 121.6, 121.1, 119.8, 117.8, 111.8, 111.0, 98.5, 87.0, 52.2, 37.9, 13.2; IR (neat): ν_{max} 3427, 3338, 2921, 2852, 2207, 1707, 1632, 1517, 1433, 1332, 1216, 1187, 1060, 827, 582 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{17}{}^{79}BrN_3O_2$ and $C_{21}H_{17}{}^{81}BrN_3O_2$ [M$^+$+H] *m/z* 422.0504 and 424.04, found 422.0505 and 424.0470.

*Octyl 8-amino-3-bromo-7-cyano-5-ethyl-5H-benzo[b]carbazole-9-carboxylate (**3id**)*. This compound was prepared by using precursors **1i** (100 mg, 0.262 mmol) and **2d**. Yellow solid, yield 0.075 g (55%); mp 229-231 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H),

8.45 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.54 (d, J = 1.0 Hz, 1H), 7.40 (dd, J = 8.0, 1.5 Hz, 1H), 6.77 (s, 2H),4.41-4.35 (m, 4H), 1.89-1.83 (m, 2H), 1.52-1.49 (m, 4H), 1.44-1.27 (m, 9H), 0.93 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 167.0, 151.4, 143.9, 143.2, 139.9, 135.2, 123.0, 122.3, 121.7, 121.0, 119.9, 118.0, 111.8, 111.4, 98.6, 87.0, 65.5, 38.0, 31.8, 29.3, 29.2, 28.7, 26.1, 22.7, 14.1,13.3; IR (neat) ν_{max} 3349, 2923, 2854, 2195, 1699, 1608, 1460, 1332, 1193, 1057, 586 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{31}{}^{79}BrN_3O_2$ and $C_{28}H_{31}{}^{81}BrN_3O_2$ $[M^+ + H]$ *m/z* 520.1600 and 522.1579, found 520.1600 and 522.1585.

(*iii). General procedure for the synthesis of compounds 5aaa-5gaa and 7aa-7da*. To an oven dried Schlenk tube with a magnetic stirrer bar was added *o*-bromo aldehyde **1** (~0.5 mmol, 1 equiv), K_2CO_3 (0.5 mmol, 1 equiv), alkyl cyanoacetate **2** (0.5 mmol, 1 equiv) and DMSO (2 mL). The contents were sealed and heated at rt for 1h. Then CuI (0.05 mmol, 10 mol%), K_2CO_3 (1.0 mmol, 2 equiv) and **4** or **6** (0.5 mmol, 1 equiv) was added and the reaction was performed at 120 °C for 2 h. After completion of the reaction as monitored by TLC, the crude reaction mixture was cooled to rt. The mixture was diluted with ethyl acetate (20 mL) and passed through celite. The resulting solution was washed with water and the aqueous part extracted twice with ethyl acetate (20 mL). The combined organic layer was washed with brine solution (2 x 20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was then purified by using silica gel column chromatography using hexane-ethyl acetate (9:1) as eluent to afford the pure compounds **5** and **7**. A similar molar stoichiometry/ratio was used in all the cases.

*Diethyl 2-aminonaphthalene-1,3-dicarboxylate (**5aaa**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol)**, 2a** and **4a**. Yellow oil, yield 0.125 g (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 7.77 (br s, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.53-7.50 (m, 1H), 7.23 (t, *J* = 7.0 Hz, 1H), 4.52 (q, *J* = 7.0 Hz, 2H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.51-1.45 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 167.4, 149.8, 139.0, 135.7, 130.3, 130.2, 125.1, 124.5, 122.4, 114.9, 105.6, 61.2, 60.8, 14.4, 14.3;IR (neat): ν_{max} 3453, 3352, 2926, 1702, 1621, 1561, 1366, 1264, 1204, 1160, 1074, 1027, 804, 747 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}NO_4$ [M^++H] *m/z* 288.1236, found 288.1238.

*3-Ethyl 1-methyl 2-aminonaphthalene-1,3-dicarboxylate (**5aab**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol), **2a** and **4b**. Yellow oil, yield 0.117 g (79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 7.84 (br s, 2H), 7.71 (d, *J* = 8.0Hz, 1H), 7.54-7.51 (m, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 4.04 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 167.4, 150.1, 139.3, 135.7, 130.4, 130.3, 125.1, 124.5, 122.4, 114.8, 105.0, 61.2, 51.7, 14.3; IR (KBr) ν_{max} 3450, 3347, 2981, 2950, 2203, 1697, 1619, 1601, 1556, 1260, 1201, 1158, 1071, 1018, 802, 744 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}NO_4$ [M^++H] *m/z* 274.1079, found 274.1078.

*3-Ethyl 1-isopropyl 2-aminonaphthalene-1,3-dicarboxylate (**5aac**)***.*** This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol)**, 2a** and **4c**. Yellow oil, yield 0.121 g (74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.31 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.73-7.71 (m, 1H), 7.68 (br s, 2H), 7.53-7.50 (m, 1H), 7.25-7.22 (m, 1H), 5.48-5.43 (m, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 1.50-1.46 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

δ 168.8, 167.5, 149.4, 138.8, 135.6, 130.2, 125.1, 124.3, 122.4, 114.8, 106.1, 68.6, 61.2, 22.2, 14.3; IR (KBr) ν_{max} 2981, 2936, 2203, 1728, 1703, 1622, 1561, 1381, 1204, 1145, 1098, 1018, 805, 750 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}NO_4$ $[M^+ + H]$ *m/z* 302.1392, found 302.1393.

*3-Methyl 1-methyl 2-aminonaphthalene-1,3-dicarboxylate (**5abb**)*: This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol), **2b** and **4b**. Yellow oil, yield 0.096 g (68%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.83 (br s, 2H), 7.72-7.70 (m, 1H), 7.55-7.51 (m, 1H), 7.26-7.23 (m, 1H), 4.04 (s, 3H), 3.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.7, 167.8, 150.0, 139.4, 135.7, 130.5, 130.3, 125.1, 124.5, 122.5, 114.5, 105.1, 52.2, 51.7; IR (KBr) ν_{max} 3337, 2926, 2856, 2216, 1707, 1623, 1572, 1445, 1306, 1207, 1158, 1076, 948, 745 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{14}NO_4$ $[M^+ + H]$ *m/z* 260.0923, found 260.0924.

*Dimethyl 2-amino-6-methoxynaphthalene-1,3-dicarboxylate (**5cbb**)*. This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol), **2b** and **4b**. Yellow oil, yield 0.118 g (87 %); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.22 (d, *J* = 9.5 Hz, 1H), 7.63 (br s, 2H), 7.22 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 167.9, 154.9, 148.5, 137.9, 131.1, 126.3, 126.0, 122.8, 114.9, 108.0, 105.8, 55.3, 52.2, 51.7; IR (KBr) ν_{max} 3391, 3337, 3181, 2918, 2848, 2360, 1692, 1645, 1608, 1560, 1467, 1428, 1259, 1191, 1038, 950, 824. cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}NO_5$ $[M^+ + H]$ *m/z* 290.1028, found 290.1027.

*3-Ethyl 1-methyl 2-amino-6-fluoronaphthalene-1,3-dicarboxylate (**5dab**)*. This compound was prepared by using precursors **1d** (100 mg, 0.493 mmol), **2b** and **4b**.

Yellow oil, yield 0.125 g (87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.30 (dd, *J* = 9.5, 5.0 Hz, 1H), 7.77 (br s, 2H), 7.36 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.32-7.30 (m, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 4.03 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.4, 167.2, 158.1(*J* = 242.3 Hz), 149.5, 138.0 (*J* = 4.8 Hz), 132.5, 127.0 (*J* = 7.5 Hz), 125.5 (*J* = 8.3 Hz), 120.0 (*J* = 24.1 Hz), 116.1, 112.8 (*J* = 20.0 Hz), 105.4, 61.3, 51.7, 14.3;IR (KBr) ν_{max} 3451, 3348, 2923, 2852, 1704, 1612, 1568, 1504, 1462, 1371, 1264, 1222, 1204, 1136, 853, 731; HRMS (ESI) calcd for $C_{15}H_{15}FNO_4$ [M^++H] *m/z* 292.0985, found 292.0982.

*Diethyl 2-aminophenanthrene-1,3-dicarboxylate (**5gaa**)*. This compound was prepared by using precursors **1g** (100 mg, 0.425 mmol), **2a** and **4a**. Yellow oil, yield 0.115 g (80%);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.60-7.58 (m, 2H), 7.53-7.46 (m, 2H), 7.03 (br s, 2H), 4.45 (q, *J* = 7.0 Hz, 2H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 167.5, 147.6, 135.9, 134.7, 134.0, 128.3, 128.2, 127.8, 127.6, 127.0, 125.0, 124.3, 123.4, 113.3, 110.9, 61.5, 61.1, 14.4, 13.8; IR (neat) ν_{max} 3646, 2919, 2850, 1738, 1608, 1367, 1260, 1216, 1023, 799, 750 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{20}NO_4$ [M^++H] *m/z* 338.1392, found 338.1394.

*2-Aminonaphthalene-1,3-dicarbonitrile (**7aa**)*. This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol), **2a** and **6**. Yellow solid, yield 0.073 g (70%); mp 140-142 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.97 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74-7.71 (m, 1H), 7.46-7.43 (m, 1H), 5.30 (br s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 139.9, 135.2, 132.3, 129.3, 125.4, 125.2, 123.6, 115.6_0, 115.5_7, 99.8, 89.5; IR (KBr) ν_{max} 3473, 3359, 3242, 2923, 2853, 2349, 2229, 2208, 1638,

1504, 1220, 770 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_7N_3$ [M^+] *m/z* 193.0640, found 193.0642.

*2-Amino-6-methoxynaphthalene-1,3-dicarbonitrile (**7ca**)*. This compound was prepared by using precursors **1c** (100 mg, 0.465 mmol), **2a** and **6**. Yellow solid, yield 0.085 g (82%); mp 147-149 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.43-7.38 (m, 2H), 6.74 (br s, 2H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.3, 149.2, 140.5, 130.8, 126.0, 124.9, 124.3, 116.5_5, 116.4_6, 108.6, 100.6, 87.7, 55.9; IR (neat) ν_{max} 3450, 3320, 3240, 2923, 2850, 2221, 2217, 1680, 1612, 1243, 1093, 1020, 792 cm^{-1} HRMS (ESI) calcd for $C_{13}H_{10}N_3O$ [M^++H] *m/z* 224.0824, found 224.0826.

*2-Amino-6-fluoronaphthalene-1,3-dicarbonitrile (**7da**)*. This compound was prepared by using precursors **1d** (100 mg, 0.493 mmol), **2a** and **6**. Yellow solid, yield 0.070 g (67%); mp 165-169 ^oC; ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.99-7.96 (m, 1H), 7.53-7.49 (m, 1H),7.44 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.28 (br s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7 (*J* = 246.5 Hz), 148.3, 138.7 (*J* = 5.1 Hz), 132.0, 126.0 (*J* = 8.6 Hz), 125.9 (*J* = 9.3 Hz), 122.5, 122.3, 115.3 (*J* = 11.4 Hz), 112.7 (*J* = 21.6 Hz), 101.2, 89.9; IR (KBr) ν_{max} 3472, 3348, 3247, 3050, 2211, 2207, 2027, 1983, 1601, 1224, 1181, 1147, 967, 816, 721 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_7FN_3$ [M^++H] *m/z* 212.0624, found 212.0624.

(iv). Synthesis of compounds 9aa, 9da, and 11aa. 4-Oxo-3,4-dihydrobenzo[g]quinazoline-10-carbonitrile (9aa). This compound was prepared by using precursors **3aa** (100 mg, 0.416 mmol) and **8**. White solid, yield 0.083 g (91%); mp 176-178 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 12.52 (s, 1H), 9.13 (s, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 8.31(s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.97-7.93 (m, 1H), 7.77-7.74 (m, 1H);

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.7, 149.1, 148.7, 135.9, 133.8, 132.4, 131.2, 130.6, 127.9, 124.7, 121.9, 116.2, 105.2; IR (neat) ν_{max} 3480, 2923, 2853, 2159, 2030, 1976, 1453, 1367, 1228, 1216, 798 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_8N_3O$ $[M^+ + H]$ *m/z* 222.0667, found: 222.0663.

*7-Fluoro-4-oxo-3,4-dihydrobenzo[g]quinazoline-10-carbonitrile (**9da**)*. This compound was prepared by using precursors **3da** (100 mg, 0.418 mmol) and **8**. White solid, yield 0.077 g (87%); mp 185-187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.55 (s, 1H), 9.14-9.08 (m, 1H), 8.31-8.19 (m, 3H), 7.88-7.87 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.0 (*J* = 246.2 Hz), 159.7,148.6, 148.5, 133.0 (*J* = 6.1 Hz), 132.9, 131.4 (*J* = 10.2 Hz), 127.9 (*J* = 9.0 Hz), 122.9 (*J* = 26.4 Hz), 122.7, 116.0, 113.9 (*J* = 21.5 Hz), 105.6; IR (neat) ν_{max} 3390, 3057, 2920, 2222, 1701, 1609, 1482, 1302, 1231, 1166, 1102, 866, 799, 556 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_7FN_3O$ $[M^+ + H]$ *m/z* 240.0568, found 240.0541.

*4-Oxo-3-phenyl-3,4-dihydrobenzo[g]quinazoline-10-carbonitrile (**11aa**)*. This compound was prepared by using precursors **9aa** (100 mg, 0.452 mmol) and **10**. White solid, yield 0.096 g (72%); mp 146-148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.31(s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.92-7.89 (m, 1H),7.75-7.72 (m, 1H), 7.64-7.61(m, 2H), 7.58-7.55 (m, 1H) 7.50-7.48 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.1, 148.2, 147.3, 137.0, 136.3, 134.0, 131.7, 131.2, 130.3, 129.9, 129.5, 127.9, 126.9, 125.6, 120.6, 115.5, 107.2; IR (neat): ν_{max} 3066, 2916, 2214, 1691, 1606, 1581, 1259, 1017, 935, 796 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{12}N_3O$ $[M^+ + H]$ *m/z* 298.0980, found 298.0974.

2,7-Dibromo-9-ethyl-9H-carbazole-3-carbaldehyde (***1i***). White solid, yield 0.081 g (75%); mp 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.69 (s, 1H), 7.99

(d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.61 (d, J = 1.6 Hz, 1H), 7.46 (dd, J = 8.0, 1.6 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 191.5, 143.9, 141.7, 125.5, 124.4, 124.1, 122.7, 122.4, 122.2, 121.9, 121.0, 113.1, 112.5, 38.2, 13.7; IR (neat) ν_{max} 3073, 2974, 2864, 2786, 1670, 1579, 1438, 1339, 1229, 1053, 840, 787 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}Br_2NO$ $[M + H]^+$ *m/z* 379.9286, found 379.9279.

*(E)-Ethyl 3-(2-bromophenyl)-2-cyanoacrylate (**I**).* This compound was prepared by using precursors **1a** (100 mg, 0.540 mmol) and **2a**. Colorless oil, yield 0.113 g (75%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.65 (s, 1H), 8.18 (dd, J = 7.5, 1.0 Hz, 1H), 7.71 (dd, J = 8.0, 1.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.41-7.38 (m, 1H), 4.42 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.7, 153.7, 133.7, 133.6, 131.7, 130.1, 128.1, 126.5, 114.7, 106.4, 62.9, 14.1; IR (KBr): 2995, 2222, 1726, 1609, 1460, 1424, 1283, 1255, 1199, 1119, 1024, 756, 738 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{10}{}^{79}BrNaO_2$ and $C_{12}H_{10}{}^{81}BrNaO_2$ $[M^+ + Na]$ *m/z* 301.9793 and 303.9793, found 301.9795 and 301.9774.

(v). X-ray data and crystals structures of 3da, 3ga, 3hb, 3ia, 5abb, 7aa and 3ha'.

Compound 3da: $C_{14}H_{11}FN_2O_2$, M = 258.25, Monoclinic, Space group *P21/c*, a = 8.2304(11), b = 13.6434(17), c = 10.9178(12) Å, V = 1225.3(30) $Å^3$, β = 91.930(4)°, Z = 4, μ = 0.106 mm^{-1}, data/restraints/parameters: 2145/0/181, R indices (I> 2σ\(I)): R1 = 0.0363, *w*R2 (all data) = 0.1043. CCDC No: 1583383

Compound 3ga: $C_{18}H_{14}N_2O_2$, M = 290.31, Triclinic, Space group *P-1*, a = 7.300(2), b = 9.493(4), c = 10.119(5) Å, V = 707.32(50) $Å^3$, α = 103.93(12)°, β = 98.12(12)°, γ =

97.41(16)°, Z = 2, μ = 0.090 mm^{-1}, data/restraints/parameters 2407/0/208, R indices (I> 2σ\(I)) R1 = 0.0448, *w*R2 (all data) = 0.1591. CCDC No: 1963460.

Compound 3ha': $C_{13}H_{11}N_3O_2$, M = 241.25, triclinic, Space group *P-1*, a = 7.6992(12), b = 8.7622(4), c = 9.7258(6) Å, V = 579.93(11) Å^3, α = 66.365(5)°, β = 74.766(11)°, γ = 84.533(8)°, Z = 2, μ = 0.097 mm^{-1}, data/restraints/parameters: 2033/0/165, R indices (I> 2σ\(I)): R1 = 0.0923, *w*R2 (all data) = 0.3195. CCDC No: 1963461.

Compound 3hb: $C_{12}H_9N_3O_2$, M = 906.87, Monoclinic, Space group *PC*, a = 10.1364 (8), b = 30.3806 (19), c= 7.3026 (5) Å, V= 2159.9 (3) Å^3, , β = 106.248 (7)°, Z = 8, μ= 0.099 mm^{-1}, data/restraints/parameters: 7033/2/617, R indices (I> 2σ\(I)): R1 = 0.0697, *w*R2 (all data) = 0.1606. CCDC No: 1963462.

Compound 3ia: $C_{22}H_{18}BrN_3O_2$, M = 436.30, Orthorhombic, Space group *Pbca*, a = 20.5404(6), b = 8.9927(3), c = 20.6948(6) Å, V = 3822.61(20) Å^3, $\alpha = \beta = \gamma$ = 90°, Z = 8, μ = 2.174 mm^{-1}, data/restraints/parameters 3379/0/255, R indices (I> 2σ\(I)) R1 = 0.0547, *w*R2 (all data) = 0.1170. CCDC No: 1963463.

Compound 5abb: $C_{14}H_{13}NO_4$, M = 259.25, Triclinic, Space group *P-1*, a = 7.7957(2), b = 8.5442(3), c = 10.0862(3) Å, V = 618.81(3) Å^3, α =68.141(3)°, β = 83.048(3)°, γ = 88.471(3)°, Z = 2, μ = 0.102 mm^{-1}, data/restraints/parameters 2177/0/182, R indices (I> 2σ\(I)) R1 = 0.0535, *w*R2 (all data) = 0.1784. CCDC No: 1963464.

Compound 7aa: $C_{12}H_7N_3$, M = 193.21, monoclinic, Space group $P2_1/c$, a = 3.8196(5), b = 16.069(2), c = 15.350(2) Å, V = 941.12(20) Å^3, β = 92.66(1)°, Z = 4, μ = 0.086 mm^{-1}, data/restraints/parameters 1664/0/124, R indices (I> 2σ\(I)) R1 = 0.0433, *w*R2 (all data) = 0.1072. CCDC No: 1963465.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (cif files), ORTEPs of compounds **3da**, **3ga, 3hb**, **3ha'**, **3ia**, **5abb** and **7aa** (Figures S1-S7; CCDC 1583383 and 1963460-1963465), and ^{1}H/ ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

*E-mail: kckssc@uohyd.ac.in; kckssc@yahoo.com.

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