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Expeditious Approach to Pyrrolophenanthridones, Phenanthridines, and Benzo[*c*]phenanthridines *via* Organocatalytic Direct Biaryl-Coupling Promoted by Potassium *tert*-Butoxide[£]

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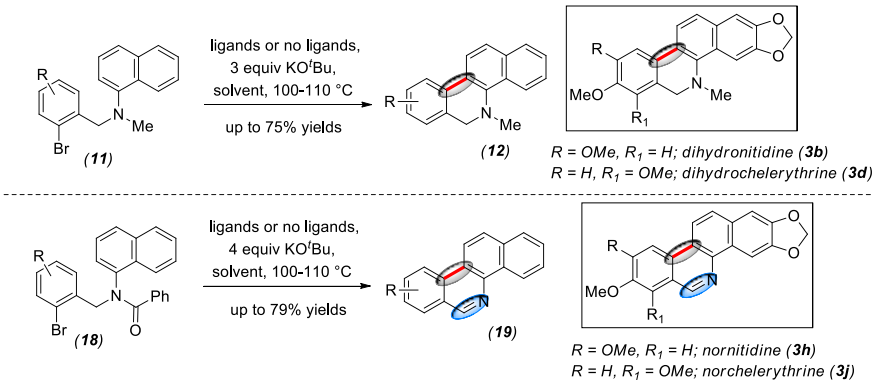
[£]This article is dedicated to Professor Satinder V. Kessar, Punjab University, India, on the occasion of his 80th birthday.

TOC GRAPHIC



ABSTRACT

A methodology involving a *'transition metal-free'* intramolecular biaryl-coupling of *ortho*-halo-*N*-aryl-benzylamines has been developed in the presence of potassium *tert*-butoxide and an organic molecule as catalyst. The reaction appears to proceed through KO^{t}Bu-promoted intramolecular homolytic aromatic substitution (HAS). Interestingly, this biaryl-coupling also works in the presence of just potassium *tert*-butoxide as sole promoter. On extending our approach further, we found that *N*-acyl 2-bromo-*N*-arylbenzylamines undergo a one-pot *N*-deprotection, biaryl-coupling followed by oxidation thus offering an expeditious route to the

phenanthridine and benzo[*c*]phenanthridine skeletons. The strategy has been applied to a concise synthesis of *Amaryllidaceae* alkaloids *viz*. oxoassoanine (**1b**), anhydrolycorinone (**1d**), 5,6-dihydrobicolorine (**2d**), trispheridine (**2b**) and benzo[*c*]phenanthridines alkaloids dihydronitidine (**3b**), dihydrochelerythidine (**3d**), dihydroavicine (**3f**), nornitidine (**3h**), and norchelerythrine (**3j**).

INTRODUCTION

Carbon-carbon (C-C) bond-forming reactions[1] through selective functionalization of aromatic compounds *via* C–H bond activation have emerged as an extremely attractive tool in contemporary organic synthesis for atom- and step-economical pathways.[2, 3, 4] Significant efforts have already been made for the direct C–H bond transformation through traditional demetalhalide cross-coupling utilizing transition metal catalysts. Direct cross-coupling methods such as demetal hydride,[5] demetal hydroxide,[6] dehydrative,[7] dehydrohalide,[8] and dehydrogenative cross-couplings,[9] have received considerable attention to accomplish this target. In fact, these new strategies facilitate the C–C bond formations *via* activation of either C–H or C–OH[7] bond by replacing one, or in some cases both,[9] of the expensive unstable coupling partners (C–X or C–M) with inexpensive and unreactive molecules.

The synthesis of biaryls through direct C-H bond functionalization is particularly of significant interest because of their wider abundance in natural products, pharmaceuticals, and materials and thus requires an extensive study. In this regard, the transition metal catalysis has played a vital role to make use of ArX for substitution reactions. Especially, palladium catalysis is found to be versatile for the coupling reaction of ArX with nucleophiles such as arenes.[10] However, one of the straightforward methods to construct biphenyl frameworks is the homolytic aromatic substitution (HAS) with aryl radicals, which is defined as replacement of a leaving group (in general halogen) by an aryl radicals on an aromatic ring

followed by elimination of a hydrogen radical.[11] But, its utility has been hampered by laborious procedure involved in the generation of aryl radicals. Aromatic compounds such as arenediazonium salts and diaroyl peroxides having an Ar-X bond that readily undergoes homolytic cleavage are although efficient precursors, but are not always easily accessible.[12] Use of readily available aryl halides as precursors of aryl radicals, requires a stoichiometric amount of a radical source such as Bu_3SnH[13a] and $(Me_3Si)_3SiH$[13b] or special conditions such as irradiation.[13c]

A major breakthrough came in the field when Itami and co-workers for the first time described an unprecedented account on KO^{t}Bu-mediated biaryl-coupling of aryl halides and electron deficient heterocyclic substrates in the absence of any transition metal catalyst.[14] Although the scope of their methodology was strictly limited to the electron-deficient 6-membered *N*-heteroarenes such as pyrazine and microwave irradiation was required for high yields, but the work is of significant interest because of the C(sp^2)-C(sp^2) coupling taking place without the aid of transition metals. In 2010, independently, Lei-Kwong et al,[15a] Shi et al,[15b] and Shirakawa-Hayashi et al[15c] revealed that the biaryl-couplings could be promoted in the presence of KO^{t}Bu and a bidentate ligand. While Lei-Kwong and Shi reported biaryl-coupling promoted by KO^{t}Bu in combination with DMEDA (*N*,*N*′-dimethyl ethylenediamine)[15a] and 1,10-phenanthroline derivatives,[15a] respectively, Shirakawa-Hayashi reported NaO^{t}Bu-1,10-phenanthroline-mediated biaryl-coupling at 155 °C.[15c] In these reports, it has been shown that aryl and heteroaryl halides of various electronic character reacted with benzene and other arenes to give biaryls in moderate to high yields. Following these reports, few other reports also revealed that KO^{t}Bu-could efficiently promote the biaryl-coupling in the absence of any transition-metal.[16] In fact, the combination of an inorganic base and a catalytic amount of an organic molecule, preferably a diamine, under heating is enough to synthesize a wide range of biaryls. These pairs presumably initiate single electron transfer

(SET) to a C-X bond at elevated temperatures,[17a] initially providing a radical anion that gives rise to a radical species for further propagation.[17b] The preliminary experimental data from aforementioned reports strongly suggest the involvement of radical intermediate, as their propagation chains were essentially terminated by the addition of common radical scavengers.[17b]

The impetus for syntheses of biaryl compounds lies in their exhaustive use as building blocks of many alkaloids and natural products. In this regard, the indole based alkaloids of *Amaryllidaceae* family having a biaryl connection drew our attention. In general phenanthridinone derivatives (Figure 1) are common structural motifs of several bioactive nitrogen containing natural products.[18] Especially, those containing the pyrrolophenanthridinone core (Figure 1) have been the subject of many synthetic endeavors due to their interesting biological activities, such as cytotoxicity and inhibition of male fertility.[19]

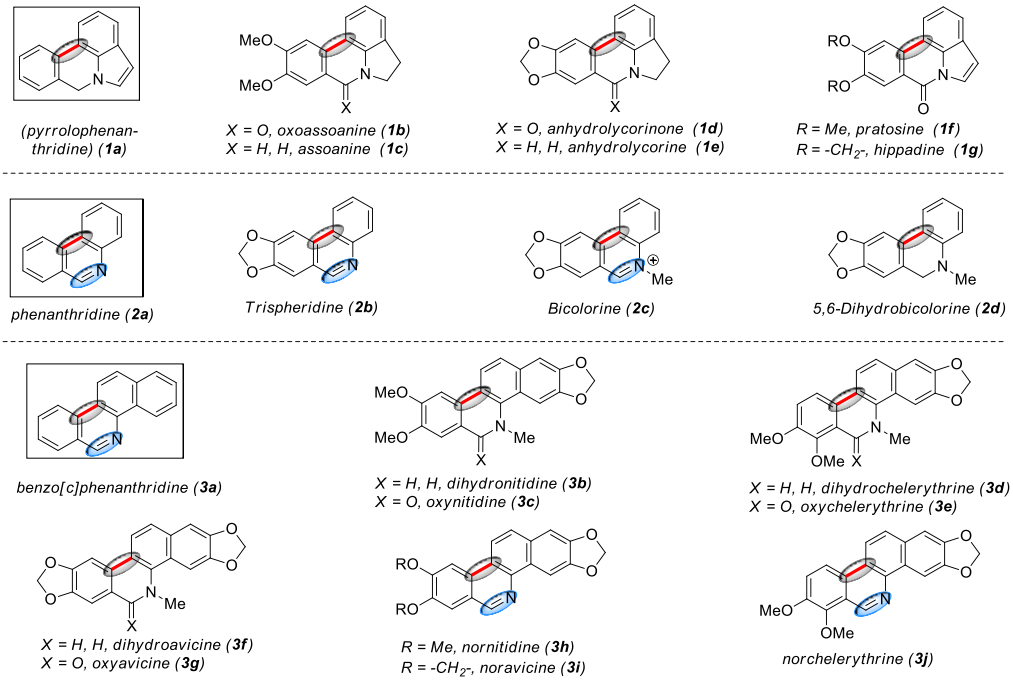


Figure 1: Alkaloids sharing pyrrolophenanthridine, phenanthridine, and benzo[*c*]phenanthridine structures.

On the other hand, phenanthridines represent an important substructure of a variety of natural products, particularly those having benzo[*c*]phenanthridine skeleton (**3a-j**, Figure 1).

Members of this family possess antimicrobial and antiviral properties.[20] In addition, few members of this class are considered as potential antitumor drugs inhibiting DNA topoisomerase I.[20,21] Owing to their interesting architecture and important biological activities, this family of alkaloids gained considerable synthetic interest in contemporary organic synthesis. Traditional methods known so far, either involve longer synthetic routes or suffer from limited substrate generality and functional group tolerance.[22] Alternative methods using palladium-catalyzed approaches are comparatively popular in recent years, due to relatively mild reaction conditions and high functional group tolerance involved.[23] Direct arylation[24] methods allow the use of simplified starting materials and offer a atom economical approach[25] compared to traditional metal-catalyzed cross-coupling reactions. In present perspective, it would be challenging to realize these transformations under '*transition metal-free*' conditions.

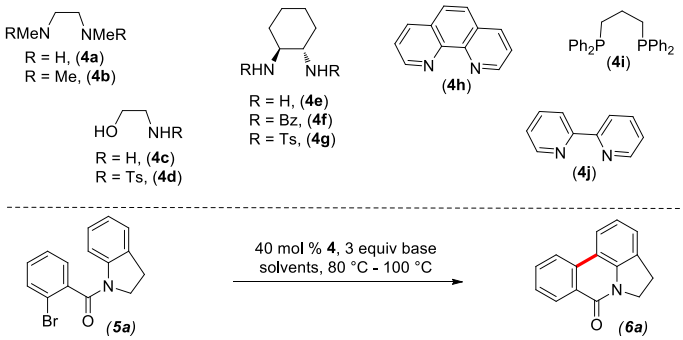
Recently, our group demonstrated organocatalytic biaryl-coupling *via* a homolytic aromatic substitution (HAS)[11] using KO^{t}Bu as sole coupling promoter in the absence or presence of catalytic amount of organic molecules.[26] We have used *N*-dihydroindolyl/ benzyl amine derivatives having a halogen at the *ortho*-position for intramolecular biaryl-coupling. Employing our strategy, we were able to synthesize several pyrrolo- and dihydrophenanthridines comprising vital building blocks of several alkaloids of *Amaryllidaceae* family. In this article, we disclose the scope and limitations of organocatalytic biaryl-coupling as well as our investigations towards the utility of organocatalytic biaryl-coupling for the synthesis of natural products sharing benzo[*c*]phenanthridine based structures. Applying this methodology, recently we accomplished the total synthesis of *Amaryllidaceae* alkaloids oxoasoanine (**1b**), anhydrolycorinone (**1d**) sharing pyrrolophenanthridone structure, 5,6-dihydrobicolorine (**2d**), trispheridine (**2b**) sharing a phenanthridine core, various dihydrobenzo[*c*]phenanthridines *viz*

dihydronitidine (**3b**), dihydrochelerythrine (**3d**), dihydroavicine (**3f**), and benzo[*c*]phenanthridines such as nornitidine (**3h**), norchelerythrine (**3j**) through the intramolecular direct arylation strategy of unactivated arenes.

RESULTS AND DISSCUSION

Initially, we chose 2-bromobenzoylindoline (**5a**) as substrate in the presence of **4a-j** and potassium *tert*-butoxide to access corresponding pyrrolophenanthridine **6a**. After extensive optimization (table 1), we found that 40 mol% of DMEDA **4a** in the presence of 3 equiv. of KO^{t}Bu in mesitylene (condition **A**) as solvent afforded the required product in 63% yield (entry 3, table 1). We found that mesitylene was comparatively better solvent than toluene and benzene, and thus, mesitylene was chosen for further optimization studies (entries 1-3). Under similar condition ligand **4c** afforded products in 52% yields (entry 5). However, ligands **4b** and **4d-g** afforded products in the range of 21-36% yields (entries 4 and 6-9). The reaction could be performed with almost similar efficiency using 40 mol% of 1,10-phenanthroline **4h** (condition **B**) and bipyridine **4j** (entries 10 and 13, respectively). However, dppp **4i** was found to be inferior to **4a** and **4h** in terms of catalytic activity (entry 12). It was found that more basic KO^{t}Bu is superior as compared to NaO^{t}Bu (entries 15-17), whereas the reaction was much more sluggish by use of less basic LiO^{t}Bu. It was also observed that the reactions were associated with 18-20% of indoline probably due to the cleavage of amide linkage of the substrate in the presence of potassium *tert*-butoxide. An interesting and noteworthy observation made here was that, the reaction could also be done just in presence of potassium *tert*-butoxide (condition **C**) without using any organic ligand to afford products in almost similar efficiency (67% yields, entry 18). This clearly demonstrated that KO^{t}Bu is solely responsible for the biaryl-coupling facilitating the reaction through homolytic aromatic substitution (HAS) with aryl radical generated in the presence of KO^{t}Bu.

Table 1. Optimization of organocatalytic biaryl-coupling.

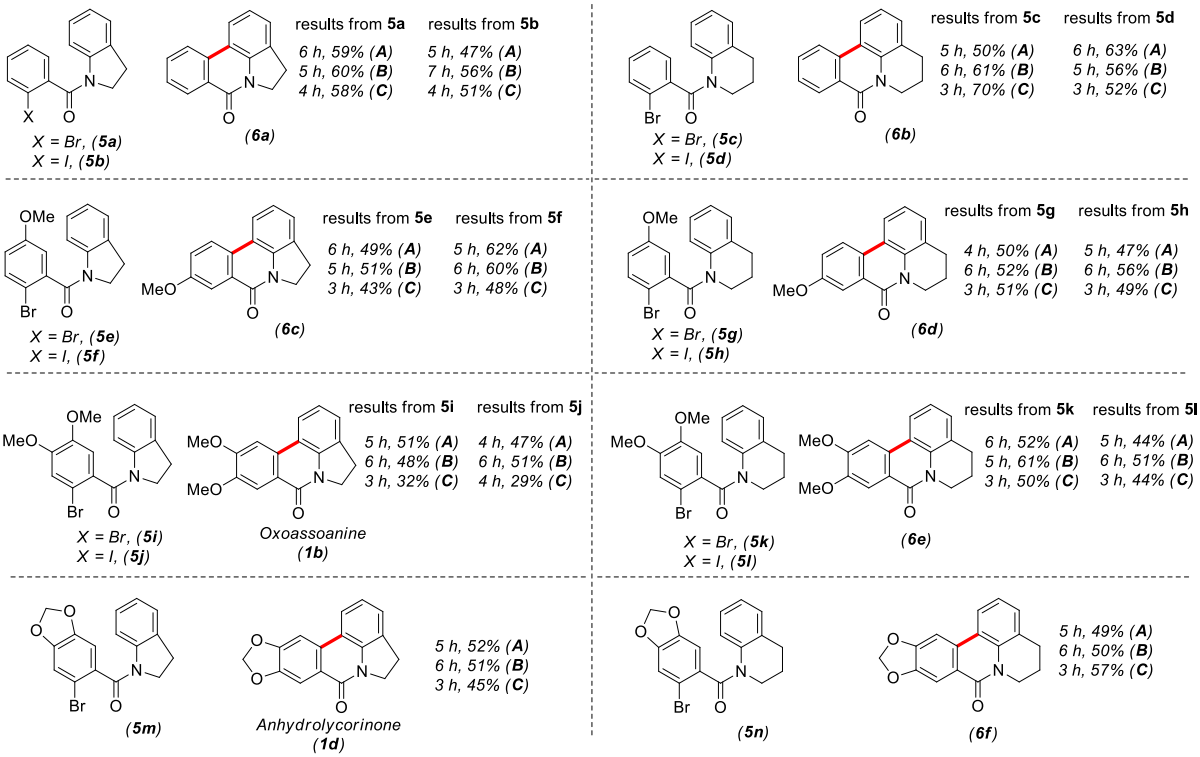


entry[a]	catalyst	base	solvent	temp	time	yield (%)[b]
1	**4a** (40 mol %)	KO^{t}Bu	toluene	100 °C	6 h	45
2	**4a** (40 mol %)	KO^{t}Bu	benzene	80 °C	7 h	51
3	**4a** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	6 h	**63**[c]
4	**4b** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	9 h	21
5	**4c** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	8 h	52
6	**4d** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	6 h	30
7	**4e** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	7 h	36
8	**4f** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	9 h	23
9	**4g** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	7 h	21
10	**4h** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	6 h	**64**[d]
11	**4h** (40 mol %)	KO^{t}Bu	benzene	80 °C	8 h	53
12	**4i** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	8 h	23
13	**4j** (40 mol %)	KO^{t}Bu	mesitylene	100 °C	7 h	58
14	**4j** (40 mol %)	KO^{t}Bu	benzene	80 °C	9 h	45
15	**4a** (40 mol %)	NaO^{t}Bu	mesitylene	100 °C	8 h	trace
16	**4h** (40 mol %)	NaO^{t}Bu	mesitylene	100 °C	7 h	trace
17	no catalyst	NaO^{t}Bu	mesitylene	80 °C	9 h	trace
18	no catalyst	KO^{t}Bu	mesitylene	100 °C	6 h	**67**[e]
19	no catalyst	KO^{t}Bu	benzene	80 °C	6 h	62

[a]Reactions were carried out on a 0.25 mmol of **5a** in presence of 0.10 mmol of catalyst and 0.75 mmol of KO^{t}Bu in 2 mL of solvent in a sealed tube at 80 °C- 100 °C for specified time, unless otherwise stated. [b]In most of the cases the reactions were associated with the cleavage of amides, yielding 18-20% of indoline. [c]Condition **A**. [d]Condition **B**. [e]Condition **C**.

With the optimized conditions in hand (table 1), we then examined the reaction scope. A set of three reaction conditions were chosen *viz*. KO^{t}Bu in the presence of **4a** (condition **A**) and **4h** (condition **B**) as well as KO^{t}Bu alone (condition **C**) in mesitylene and the results are summarized in figure 2. It was gratifying to see that all the three conditions facilitated intramolecular biaryl-coupling in moderate to good yields. Noticeably, 2-haloarylamides prepared from indoline (**5a-b**, **5e-f**, **5i-j**, and **5m**) and 1,2,3,4-tetrahydroquinoline (**5c-d**, **5g-h**, **5k-l**, and **5n**) underwent smooth reactions to afford a wide range of products (figure 2).

Notably, the biaryl-coupling with aromatic bromides and iodides (**5a-n**) were equally efficient. In order to make our strategy practically viable, one of the reactions was conducted with 8 mmol. of **5a** in the presence of 40 mol% of 1,10-phenanthroline and 3 equivalent of KO^{t}Bu (condition **B**), which afforded **6a** in 55% yields along with 20% of indoline as by product due to the cleavage of *N*-arylamide in the presence of KO^{t}Bu under elevated temperature.

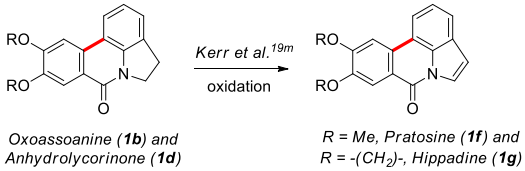


[a]Reactions were carried out on a 1.0 mmol of **5a-n** in presence of 0.40 mmol of **4a** (condition **A**), **4h** (condition **B**) and 3.0 mmol of KO^{t}Bu in 6 mL of solvent in a sealed tube at 100 °C for specified time. Condition **C** = 3.0 mmol of KO^{t}Bu only.

Figure 2: Initial exploration of the substrate scope.

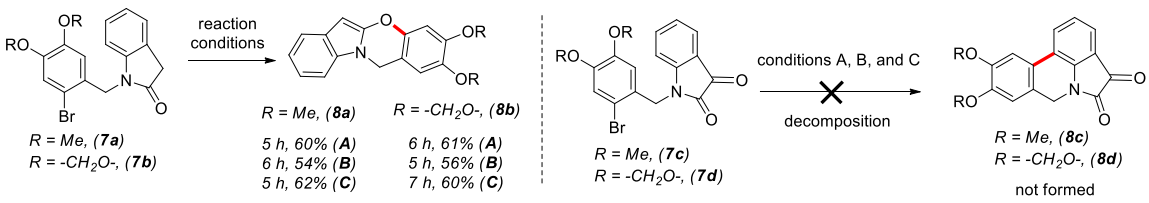
As a preview of the usefulness of this methodology, we could successfully carry out the total syntheses of oxoassoanine (**1b**) starting from 2-halobenzoylindolines **5i-j** and anhydrolycorinone (**1d**) from **5m** (Figure 2). The naturally occurring dihydrophenanthridones oxoassoanine (**1b**) and anhydrolycorinone (**1d**) are in fact the advanced intermediates for the synthesis of pratosine (**1f**) and hippadine (**1g**), respectively (Scheme 1).[19m] Thus, the

methodology presented here offers an opportunity to further explore its applicability in the context of complex alkaloids of *Amaryllidaceae* family after further synthetic elaborations.



Scheme 1: Formal synthesis of pratosine (**1f**) and hippadine (**1g**).[19m]

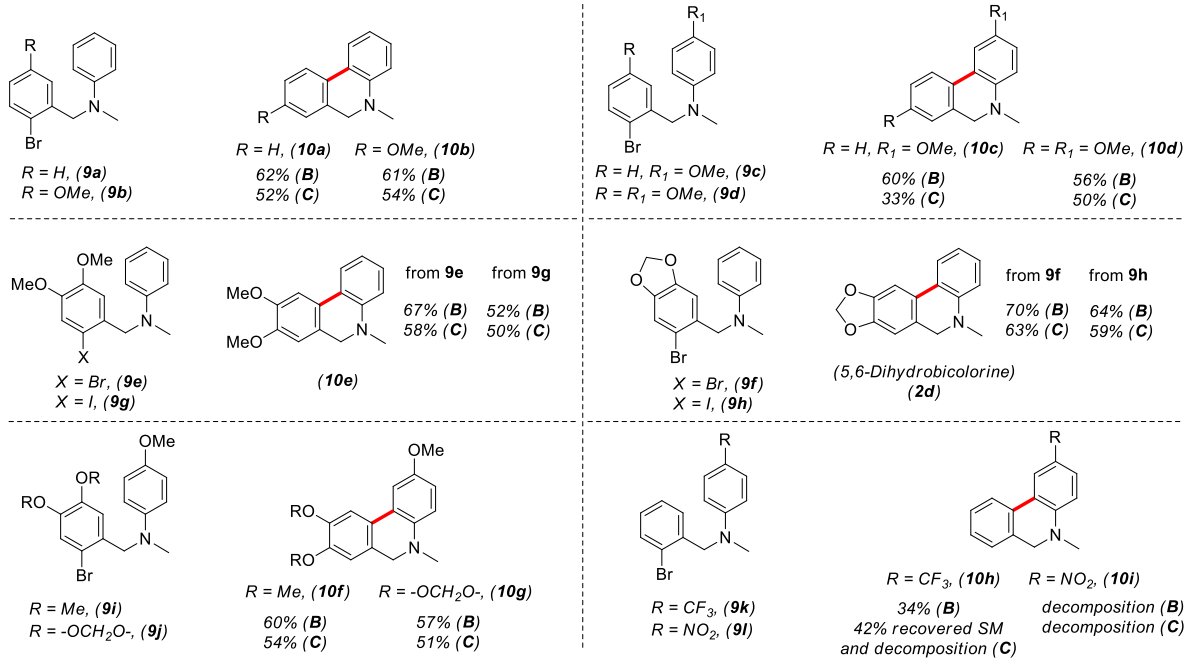
In search for an advanced intermediate aiming to the total synthesis of other pyrrolophenanthridones (figure 1), the methodology was further explored. For this purpose, few *N*-(2-bromobenzyl) 2-oxindoles **7a-b** and *N*-(2-bromobenzyl) isatins **7c-d** were subjected to the optimized conditions to carry out the biaryl-coupling as shown in scheme 2. However, contrary to our assumption, **7a-b** afforded tetracyclic *O*-arylated products **8a-b** in moderate to good yields instead of C-arylated products. In these cases, *O*-arylation took place presumably due to the presence of sufficiently acidic proton at the 3-position of 2-oxindole substrates **7a-b**. The X-ray crystal structure of tetracyclic compound **8a** (see, Supporting Information for ORTEP) provided us an unambiguous proof for this unusual *O*-arylation process. This clearly demonstrates that an organocatalytic *O*-arylation could be realized depending upon the substrate structures, which should, in principle, leads to the formation of various phenol derivatives. To our surprise, under optimized conditions A, B, and C, compounds **7c** and **7d** yielded a mixture of products, from where neither products nor starting materials were isolated.



[a]Reactions were carried out on a 1.0 mmol of **7a-d** in presence of 0.40 mmol of **4a** (condition **A**), **4h** (condition **B**) and 3.0 mmol of KO^{t}Bu in 6 mL of solvent in a sealed tube at 100 °C for specified time. Condition **C** = 3.0 mmol of KO^{t}Bu only.

Scheme 2: Substrate scope of organocatalytic biaryls syntheses.

The organocatalytic biaryl-coupling reaction was further extended to a variety of substrates 2-halo-*N*-aryl-benzylamines **9a-l** for the synthesis of dihydrophenanthridines, which are structurally similar to a number of *Amaryllidaceae* alkaloids (see, **2b-d**; Figure 1). Under the optimized conditions, 2-bromo-*N*-phenyl-benzylamine **9a** afforded products **10a** in 24% (condition **A**), 62% (condition **B**), and 52% (condition **C**) yields, and thus conditions **B** and **C** were chosen for further substrate studies.



[a]Reactions were carried out on a 1.0 mmol of **9a-l** in presence of 0.50 mmol of **4h** (condition **B**) and 3.0 mmol of KO^{t}Bu in 6 mL of solvent in a sealed tube at 100 °C for 24 h. Condition **C** = 3.0 mmol of KO^{t}Bu only.

Figure 3: Substrate scope of dihydrophenanthridine synthesis.

To our delight, under optimized conditions **B** and **C**, the *N*-aryl-2-bromobenzylamines (**9a-l**) afforded various dihydrophenanthridines (**10a-h**) in moderate to good yields (up to 70% yield) as shown in figure 3. Interestingly, just the presence of KO^{t}Bu was sufficient to affect this coupling (condition **C**; figure 3) in these cases as well. The strategy provides one step total synthesis of 5,6-dihydrobicolorine (**2d**, figure 1) in 59-70% yield starting from 2-halo-*N*-(3,4-methylenedioxyphenyl) benzylamines **9f** and **9h**. The reaction was applied to the

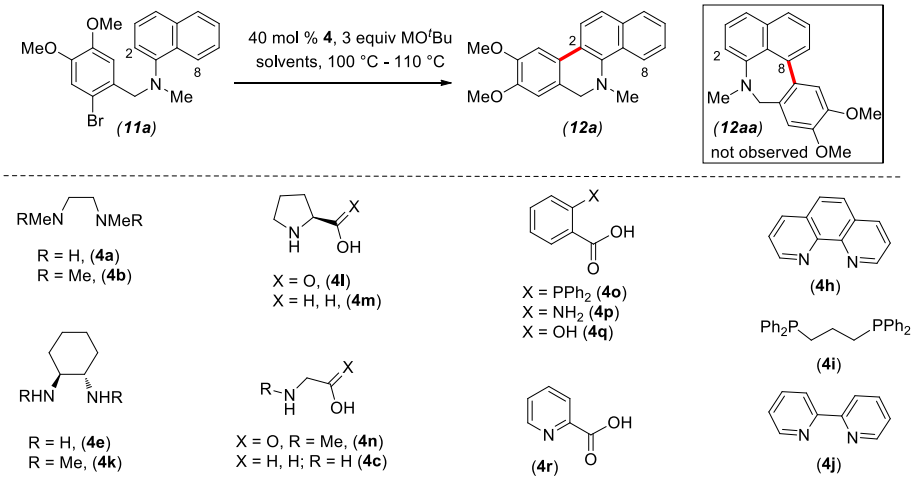
substrates containing an electron-withdrawing group, such as **9k** and **9l** (figure 3). We found that **9k** afforded product **10h** in 34% yield under condition **B**. However, condition **C** was found not suitable, where 42% of starting material **9k** was isolated along with decomposition of the rest of the mass balance. Surprisingly, compound **9l** simply leads to decomposition under optimized conditions **B** and **C** (figure 3), indicating the process might be facilitated by the presence of electron-donating groups.

We then set forth to investigate the utility of organocatalytic biaryl-coupling by applying it to the synthesis of natural products sharing benzo[*c*]phenanthridine structures. We were especially interested to check the regioselective outcome of benzo[*c*]phenanthridines. The substrate of the type 2-bromo-*N*-(α-naphthyl)benzylamine **11a** (Table 2) is challenging in the sense that it could lead to two possible regioisomeric products depending upon two different C-H activation pathways. In one pathway, it could react at C-2 position to afford more stable dihydrophenanthridine **12a** or alternatively it could also react at the C-8 position to afford naphthobenzazepine structures **12aa** (Table 2).[27] Thus, we thought substrates of the type **11a** would provide us an interesting platform to check the regioselectivity issues in the homolytic aromatic substitutions (HAS). So, we performed our studies with *N*-(2-bromo-4,5-dimethoxybenzyl) α-naphthyl-*N*-methylamine **11a** in presence of 3 equiv of KO^{t}Bu and 40 mol% of bidentate ligands **4** (Table 2) in mesitylene at 110 ˚C in a sealed tube.[26]

Optimization studies revealed that when the reactions were carried out in presence of 40 mol% of **4h** (condition **B**) and **4j** (condition **D**), the biaryl-coupling product dihydrobenzo[*c*]phenanthridine **12a** could be achieved in 75% and 72% yield (entries 13 and 15), respectively. The coupling can also be promoted in 66% yield only in the presence of KO^{t}Bu (condition **C**) in benzene and without using any organic ligands (entry 23). Noticeably, no naphthobenzazepine was formed under our optimized conditions. It was also found that 40 mol% of DMEDA **4a** (condition **A**) afforded **12a** in just 22% of yields (entry

1). Thus, based on our studies, three sets of reaction conditions were chosen *viz* KO^{t}Bu in presence of **4h** (condition **B**) and **4j** (condition **D**) in mesitylene as well as KO^{t}Bu as sole promoter in benzene (condition **C**) for further studies and the results so obtained are summarized in Figure 4.

Table 2. Optimization of '*transition metal-free*' biaryl-couplings.



entry[a]	catalyst	base	solvent	temp	time	yield (%)[b]
1	**4a** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	36 h	**22**[c]
2	**4b** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	30 h	16
3	**4e** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	37
4	**4k** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	50
5	**4l** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	54
6	**4m** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	28 h	47
7	**4n** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	30
8	**4c** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	9 h	32
9	**4o** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	30 h	51
10	**4p** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	36 h	35
11	**4q** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	30 h	40
12	**4r** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	37
13	**4h** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	**75**[d]
14	**4i** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	30 h	34
15	**4j** (40 mol %)	KO^{t}Bu	mesitylene	110 °C	24 h	**72**[e]
16	**4h** (20 mol %)	KO^{t}Bu	mesitylene	110 °C	36 h	66
17	**4h** (40 mol %)	KO^{t}Bu	toluene	100 °C	24 h	62
18	**4h** (40 mol %)	KO^{t}Bu	benzene	100 °C	24 h	56
19	**4h** (40 mol %)	NaO^{t}Bu	mesitylene	110 °C	24 h	00[f]
20	no ligand	KO^{t}Bu	mesitylene	110 °C	30 h	57
21	no ligand	NaO^{t}Bu	mesitylene	110 °C	36 h	00[f]
22	no ligand	KO^{t}Bu	toluene	100 °C	28 h	50
23	no ligand	KO^{t}Bu	benzene	100 °C	30 h	**66**[g]

[a]Reactions were carried out on a 0.50 mmol of **11a** in presence of 0.20 mmol of organic ligands **4** and 1.5 mmol of KO^{t}Bu in 3 mL of solvent in a sealed tube at 100 °C-110 °C for specified time. [b]Isolated yield after column chromatography. [c]**Condition A**. [d]**Condition B**. [e]**Condition D**. [f]Starting material was isolated in 88-92%. [g]**Condition C**.

Under the optimized conditions B, C, and D, we then explored the substrate scope using various *N*-2-bromo-*N*-(α-naphthyl)benzylamines **11b-e** (Table 2). In all cases, the biaryl-coupling was found to be quite general and proceeds without event to afford dihydrobenzo[*c*]phenanthridines **12b-e** in moderate to high yields (45-75% yields, see: Figure 4).[27] Further, the X-ray crystal structure of **12a** unambiguously proved the formation of dihydrobenzo[*c*]phenanthridine structure (see, Supporting Information for ORTEP).

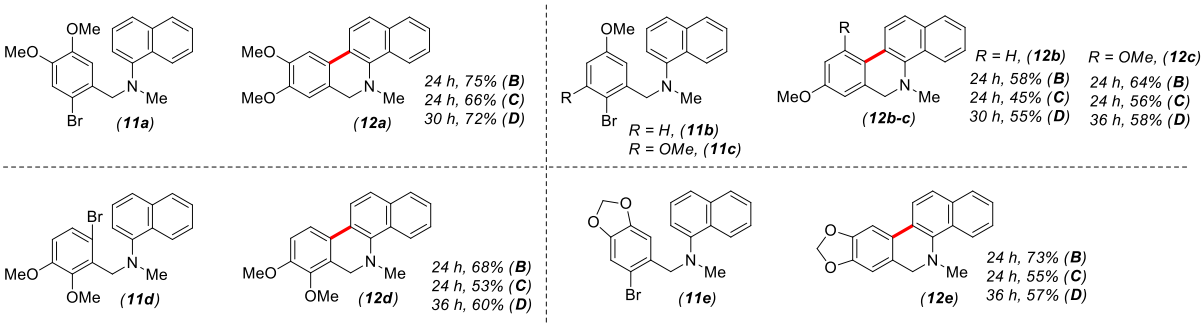
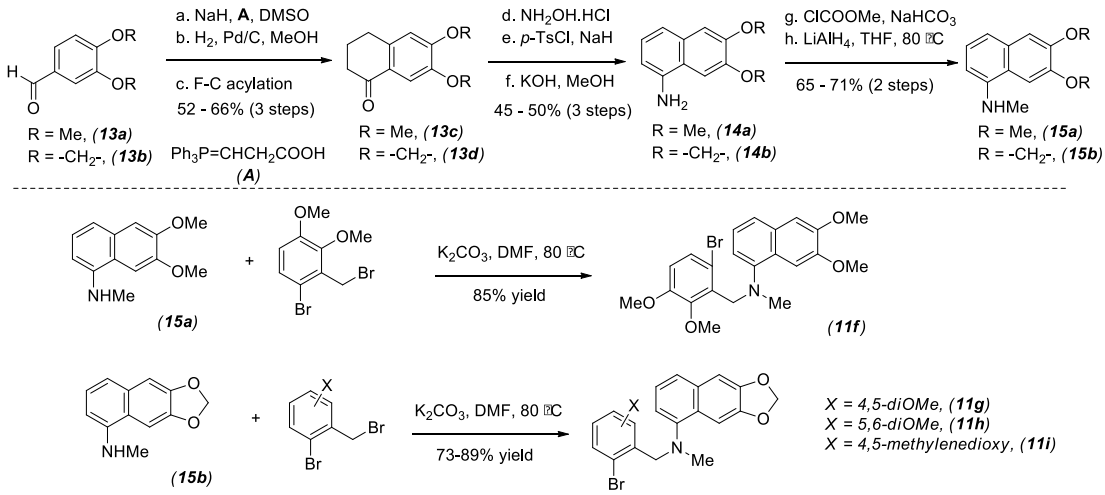


Figure 4: Substrates scope of dihydrobenzo[*c*]phenanthridine synthesis.

Next, we sought-after the synthetic viability of this protocol by applying it to the synthesis of diversely substituted dihydrobenzo[*c*]phenanthridines. In order to materialize this, we prepared α-tetralones **13c-d** starting from aldehydes **13a-b** *via* Wittig olefination, hydrogenation followed by Friedel-Crafts acylations (Scheme 3). α-Tetralones **13c-d** were then converted into α-naphthylamines **14a-b** in three step procedure (*viz* formation of oxime, tosylation followed by detosylation/aromatization sequence). The latter were then converted into **15a-b** in two step sequence involving reaction with chloromethylformate followed by reduction using $LiAlH_4$ (Scheme 3). Few 2-bromo-*N*-(α-naphthyl)benzylamines **11f-i** were prepared from **15a-b** following a simple *N*-benzylation (Scheme 3) and tested in organocatalytic biaryl-coupling reaction.



Scheme 3: Synthesis of 2-bromo-*N*-(α-naphthyl)amines **11f-i**.

Interestingly, conditions **B**, **C**, and **D** afforded dihydrobenzo[*c*]phenanthridines **12f**, **3b**, **3d**, and **3f** in 30-68% yields (Figure 5), thus accomplishing the total synthesis of alkaloids dihydronitidine (**3b**), dihydrochelerythrine (**3d**), and dihydroavicine (**3f**).

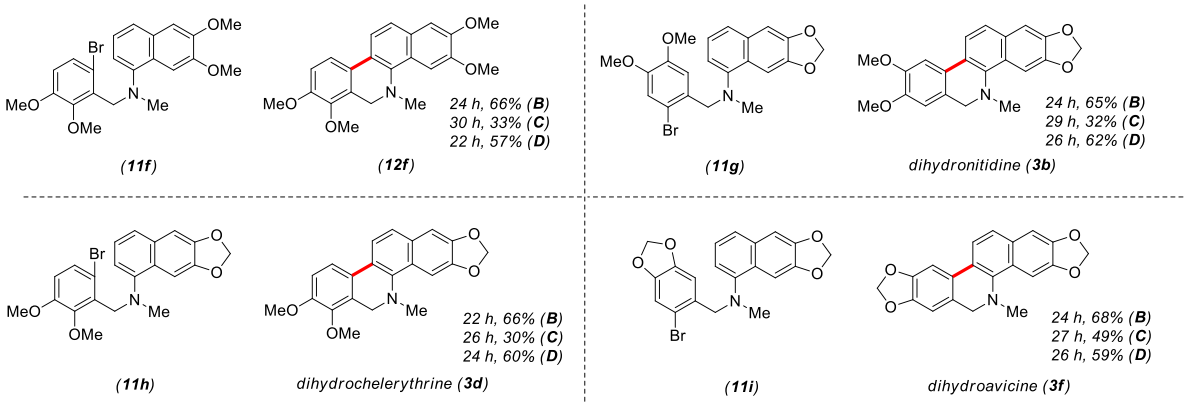
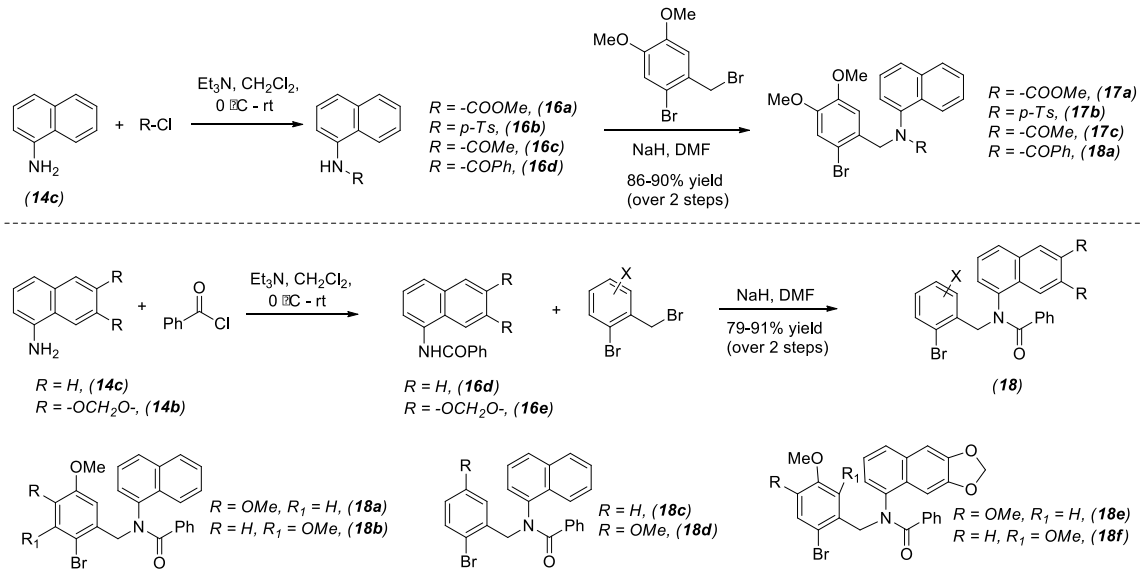


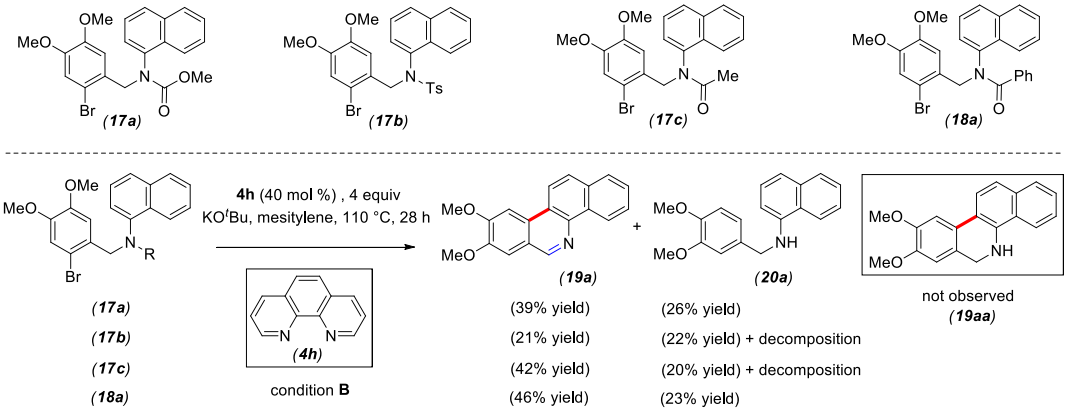
Figure 5: Synthesis of dihydro-nitidine, avicine, and chelerythrine.

We then looked into the substrate scope of biaryl-coupling reactions with the substrates having different protecting group on nitrogen such as *N*-acyl or *N*-tosyl-2-bromo-*N*-(α-naphthyl)benzylamines. A series of *N*-protected-2-bromo-*N*-(α-naphthyl)benzylamines **17a-c** and **18a-f** were synthesized in two steps *viz* *N*-protection in the presence of Et_3N from α-naphthylamines **14b-c** followed by *N*-benzylations with 2-bromobenzyl bromides in the presence of NaH (Scheme 4).



Scheme 4. Synthesis of α-naphthyl-*N*-protected-benzylamines (**18a-f**).

In case of dihydropyrrolophenanthridone synthesis (Figure 2), we observed that the yields were typically in the range of 45-55% because of the *N*-arylamide cleavage in the presence of KO^{t}Bu at elevated temperature. This led us to think for sequential *N*-deprotection followed by biaryl-coupling to afford 5,6-dihydrobenzo[*c*]phenanthridine having secondary amine (Scheme 5). Interestingly, when **17a-c** and **18a** were reacted in the presence of 40 mol% of **4h** in combination with 4 equivalent of KO^{t}Bu (condition B), benzo[*c*]phenanthridine **19a** was achieved in 39%, 21%, 42%, and 46%, respectively, along with 20-26% of debrominated compound **20a** (Scheme 5). No traces of 5,6-dihydrobenzo[*c*]phenanthridine **19aa** was observed which indicated that the reaction might be following a one-pot *N*-deprotection, organocatalytic biaryl-coupling in presence of KO^{t}Bu, and concomitant oxidation.[28] In fact, this result is interesting in the context of the synthesis of benzo[*c*]phenanthridine alkaloids (Figure 1). The results of biaryl-coupling from substrates **17a-c** and **18a** led us to choose *N*-benzoyl substrates of the type **18a** for further studies.



Scheme 5. Optimization of one-pot *N*-deprotection, biaryl-coupling followed by oxidation sequence.

Under optimized conditions **B**, **C**, and **D**, *N*-benzoyl-2-bromo-*N*-(α-naphthyl)benzylamine **18a** afforded **19a** in the range of 40-51% yields along with debrominated secondary amine **20a** in 16-27% yields (Figure 6). The one-pot methodology was further applied to various *N*-benzoyl substrates **18b-f** and found that the one-pot deprotection, biaryl-coupling, and oxidation sequence is quite general and benzo[*c*]phenanthridines **19b-c**, **3h**, and **3j** were synthesized in up to 60% yields (Figure 6), thus accomplishing one-pot total synthesis of nornitidine (**3h**) and norchelerythrine (**3j**) starting from **18e** and **18f**, respectively. The X-ray structure of norchelerythrine **3j** unambiguously proved the formation of benzo[*c*]phenanthridine structure (see, Supporting Information for ORTEP).

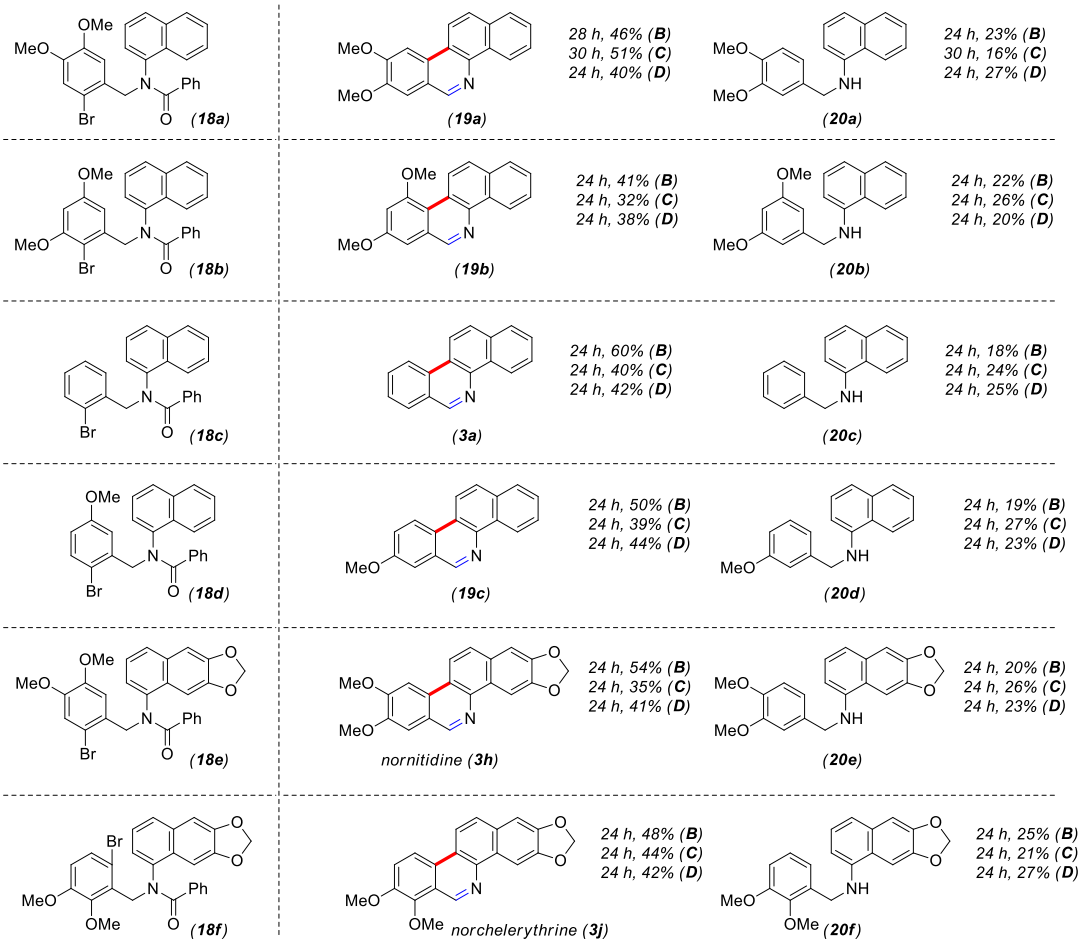
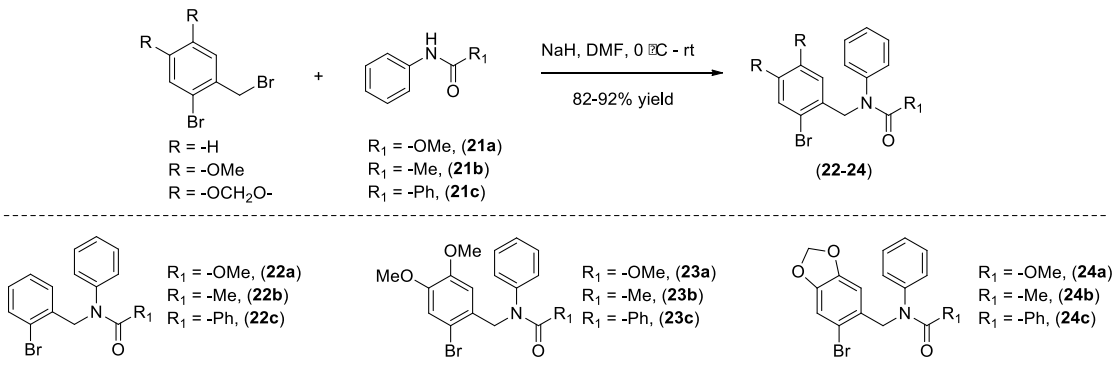


Figure 6. One-pot debenzoylation, biaryl-coupling followed by oxidation sequence.

Further, in search for a straightforward approach to various phenanthridines such as *Amarylidaceae* alkaloid trispheridine **2b** and related structures, a variety of *N*-protected-2-bromo-*N*-arylbenzylamines such as **22a-c**, **23a-c**, and **24a-c** were synthesized *via* *N*-benzylations of three different *N*-acylanilines **21a-c** (Scheme 6).



Scheme 6. Synthesis of *N*-phenylbenzylamines (**22a-c**, **23a-c** and **24a-c**).

Delightfully, our organocatalytic one-pot sequence was quite efficient to afford phenanthridines **2a** and **25** in high yields (up to 79%, see: figure 7) without observing the debrominated products in most of the cases. We also achieved the total synthesis of trispheridine **2b** in up to 77% yields. The phenanthridine skeleton was further confirmed by the X-ray crystal structure of trispheridine **2b** (see, Supporting Information of ORTEP).

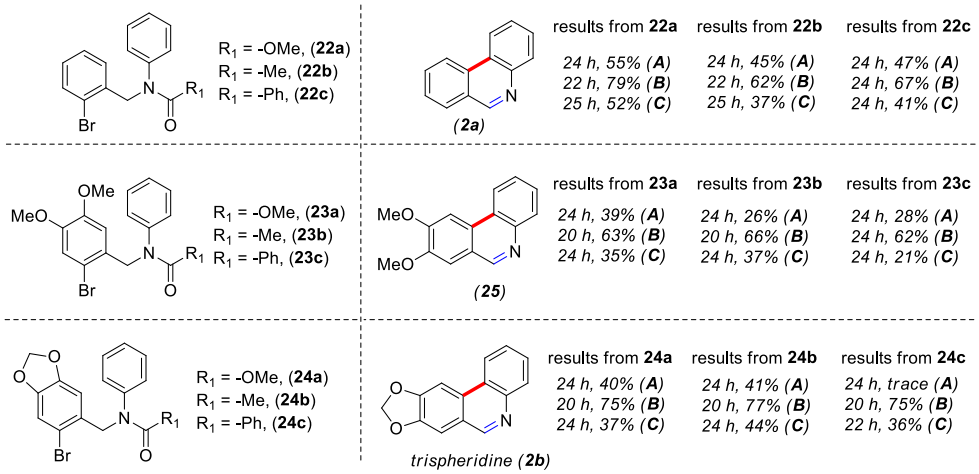
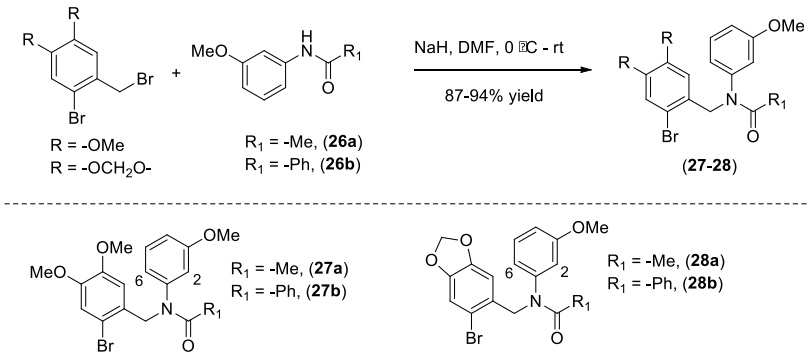


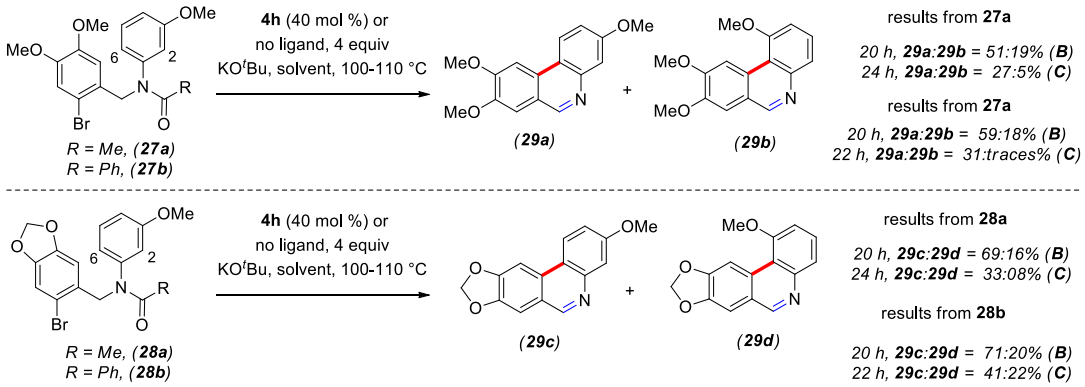
Figure 7. One-pot deprotection, biaryl-coupling followed by oxidation.

To further check the regioselective outcome of the organocatalytic biaryl-coupling, few *N*-acyl-2-bromo-*N*-(*m*-methoxyaryl)benzylamines such as **27a-b** and **28a-b** were synthesized from **26a-b** (Scheme 7). These compounds could provide a regioisomeric mixture, where it could form a biaryl product either reacting at C-2 or C-6 position of *m*-anisidine derivative (Scheme 8). We hypothesized that, the major product from the biaryl-coupling would be possible at C-6 rather than C-2 in the HAS process, as position C-6 is comparatively more electron-rich than C-2. In fact, our results also supported this hypothesis.



Scheme 7. Synthesis of 2-bromo-*N*-(3-methoxyphenyl)benzylamines (**27a-b**, and **28a-b**).

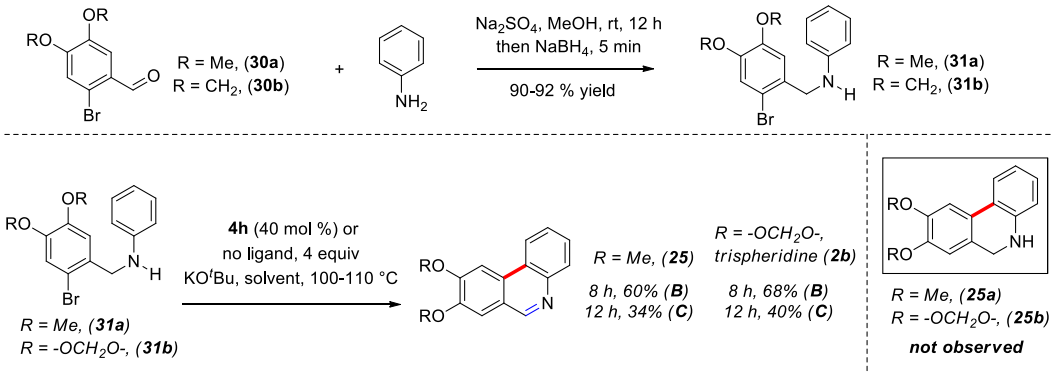
As shown in scheme 9, under the optimized conditions **B** and **C**, **27a-b** and **28a-b** undergo an organocatalytic one-pot *N*-deprotection, biaryl-coupling followed by oxidation to afford products **29a-b** and **29c-d**, where **29a** and **29c** were found to be the major products, presumably arising from the coupling at the more electron-rich C-6 position of *m*-anisidine derivatives.



Scheme 8: Regioselective one-pot deprotection, biaryl-coupling followed by oxidation.

In our hypothesis, we thought that the one-pot organocatalytic approach to phenanthridines and benzo[*c*]phenanthridines undergoes a *N*-deprotection, biaryl-coupling followed by oxidation events. If this is true, then secondaryamines **31a-b** would also lead to the phenanthridines **25** and trispheridine **2b**. We were happy to find that, under optimized conditions **B** and **C**, secondary amines **31a-b** afforded only phenanthridines **25** and **2b** in up

to 68% yields and no biaryl-coupling products having secondary amines such as **25a-b** were isolated (Scheme 9). This might be due to the high stability of the phenanthridines with a fully aromatic structure.



Scheme 9: One-pot biaryl-coupling followed by oxidation.

Previously, we proposed a tentative mechanism[26] based on mechanistic proposals by Shirakawa-Hayashi, where after the initiation step in the presence of **32a (**or KO^{t}Bu), an electron transfer (ET) takes place prior to proton transfer (PT).[17b] However, according to Studer and Curran hypothesis[17b] (which is well accepted by Shirakawa-Hayashi[29]), because of powerful reducing nature of a radical anion as compared to radical, a direct electron transfer (ET) from the intermediate radical anion is quite reasonable than the radical. Therefore, a base promoted HAS must follow a proton transfer (PT) prior to the electron transfer (ET).

In general, the mechanism of base promoted HAS follows a chain reaction mainly involving three steps, *viz* the addition of aryl radical to arenes to form arylcyclohexadienyl radical (step 1), which then gets deprotonated by a very strong base (potassium *tert*-butoxide) to form a radical anion (step 2). The biaryl radical anion being highly conjugated, could act as a powerful reducing agent[30] and, thus, transfers an electron to the starting aromatic halide[31] to provide biaryl-coupling product, potassium halide, and the regeneration of aryl radical (step 3). As shown in figure 8, an initial single electron transfer (SET) from **32a (**or KO^{t}Bu) onto **5**

provides a radical anion intermediate **33a**, which is the initiation step of biaryl-coupling reaction. The radical anion **33a** is then converted into aryl radical **33b**, which could then undergo propagation steps, to add intramolecularly at the 7th position of indoline derivatives, providing cyclohexadienyl radical **33c** (step 1). At this point, a proton transfer (PT) from **33c** in the presence of **32a (**or KO^{t}Bu) leads to the formation of radical anion **33d**, ^{t}BuOH and K^+ (step 2). The intermediate radical anion, **33d** then transfers an electron to the starting aryl halide **5** (step 3) to afford pyrrolophenanthridones **6** or **1**, potassium halide and a new arylradical **33b** (*via* the intermediacy of **33a**), which then continues the catalytic cycle (Figure 8).

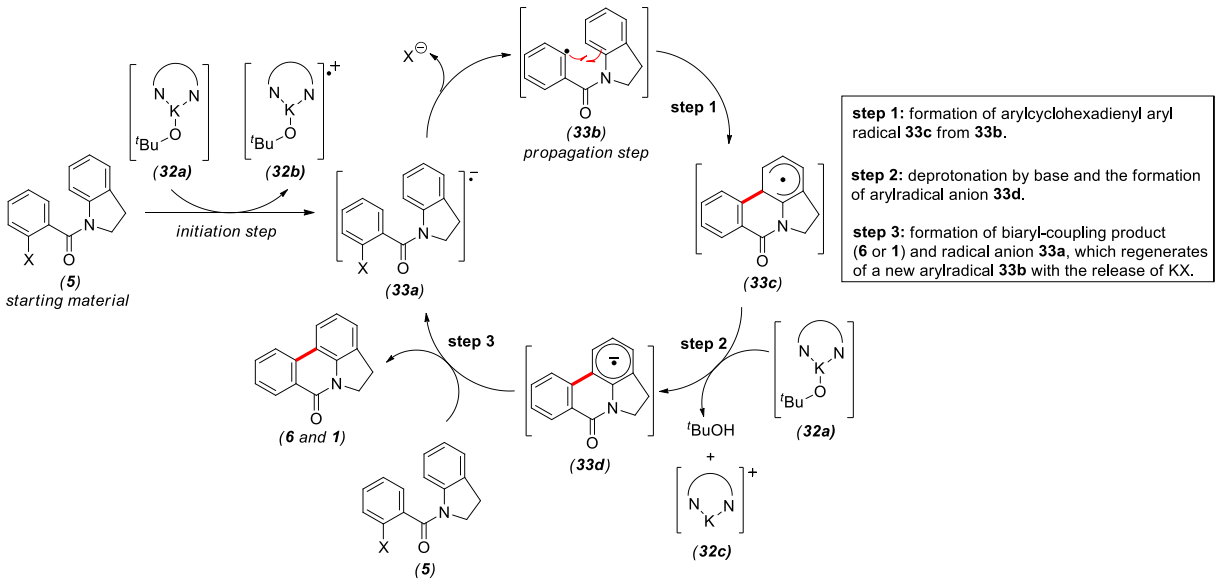


Figure 8: Revised mechanism of the sysnthesis of pyrrolophenanthridines.

On the other hand, a single electron transfer (SET) from **32a (**or KO^{t}Bu) onto **7a-b** (Figure 9) provides a radical **34b** through the intermediacy of radical anion **34a**, which is the initiation step of *O*-arylation. The latter then subsequently follows a *O*-arylation (**8a-b**, scheme 2) with neighbouring carbonyl group to form radical **34c** (step 1). At this point, a proton transfer (PT) from **34c** in presence of **32a (**or KO^{t}Bu) leads to the formation of radical anion **34d**, ^{t}BuOH and K^+ (step 2). Finally, a radical anion transfer from **34d** to the starting

material **7a-b** affords *O*-arylated product **8a-b** and radical anion **34a** (step 3), which then continues the catalytic cycle (Figure 9).

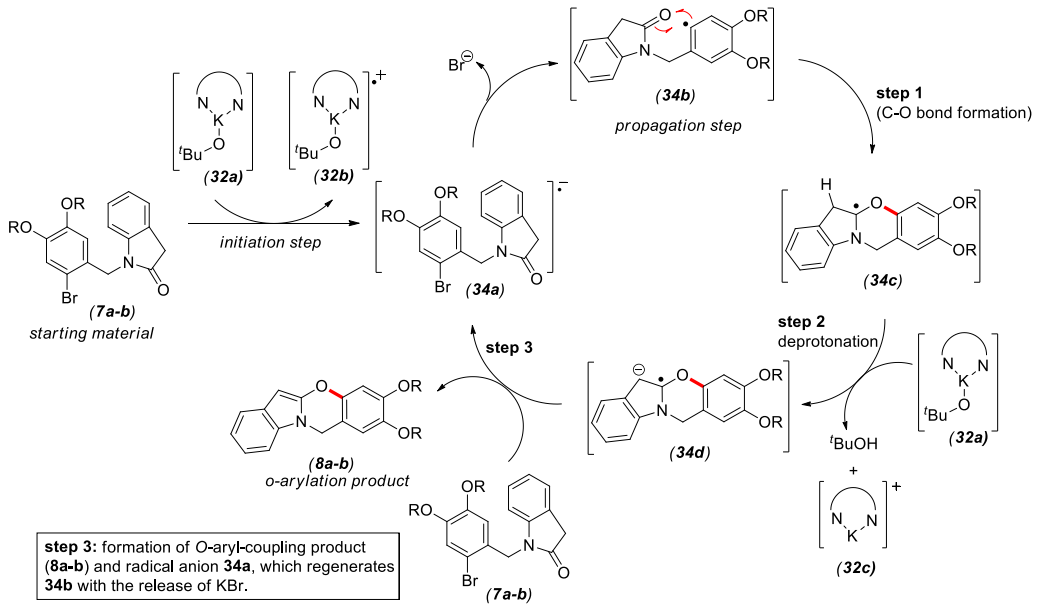


Figure 9: Revised mechanism of intramolecular *O*-arylation of **7a-b**.

A similar SET from **32a (**or KO^{t}Bu) onto **11a-i** (Figure 10) provides a radical **35b** through the intermediacy of radical anion **35a**, which could then follow a propagation step providing arene annulated cyclohexadienyl radical **35c** (step 1). A similar proton transfer (PT) from **35c** in presence of **32a (**or KO^{t}Bu) leads to the formation of radical anion **35d**, ^{t}BuOH and K^+ (step 2). Eventually, a radical anion transfer from **35d** to the starting material **11a-i** to afford dihydrobenzo[*c*]phenanthridines **12** or **3** and the radical anion **35a** (step 3), thus continuing the catalytic cycle (Figure 10). A similar mechanism could also operate in the case of dihydrophenanthridines **10a-h** and **2d** (see: figure 3).

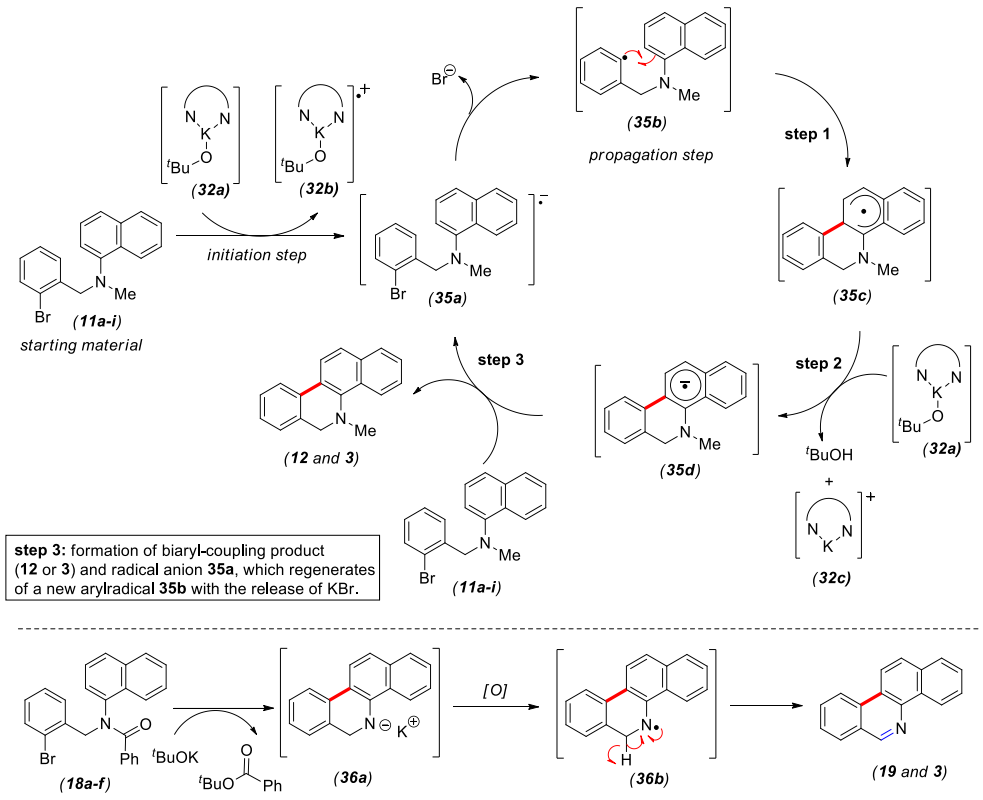
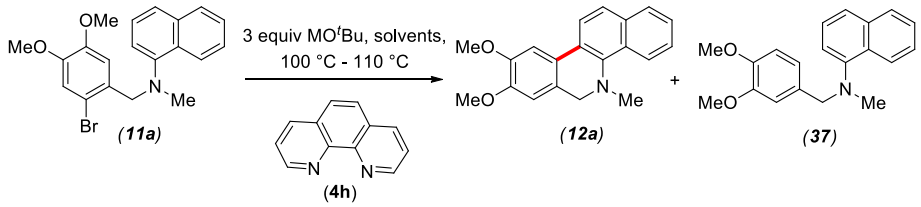


Figure 10: Proposed mechanism of the synthesis of benzo[*c*]phenanthridines.

In case of *N*-benzoyl substrate **18a-f** (Scheme 5 and figure 6), we believe that cleavage of benzoyl group in the presence of KO^{t}Bu forms potassium amide, which undergoes a biaryl-coupling to afford intermediate **36a** (Figure 10). The latter upon oxidation[28] may form nitrogen centered radical[32] **36b** (Figure 10), which in turn could afford final benzo[*c*]phenanthridines **19a-c**, **3h** and **3j** after α-elimination reaction. Similar kind of mechanism might also be operating in case of the synthesis of phenanthridines (Figure 7, Schemes 8-9). The possible reason for a smooth one electron oxidation of **36a**.K^+ to afford benzo[*c*]phenanthridine **19a** (Scheme 5) might be the formation of highly stable aromatic structure. In addition, the very high stabilty of benzo[*c*]phenanthridine could easily be visualized from the crystal packing of natural product norchelerythrine **3j** (see, Supporting Information), clearly depicting the intermolecular H-bonding and π-π stacking.[33]

It is well accepted that single electron reduction of aryl halides enable them to the aromatic nucleophilic substitution ($S_{RN}1$) with various nucleophiles. In a similar fashion, base promoted aromatic homolytic substitution (HAS) requires an initial SET from **32a (**or KO^{t}Bu) onto halo arene of the type **11a** providing a radical anion intermediate **35a** under elevated temperature, which is then converted into an aryl radical **35b** (initiation step of biaryl-coupling). Thus, it can be assumed that a small amount of reducing agent (such as Na metal) could facilitate the first electron transfer step than **32a** (or KO^{t}Bu) alone. In order to provide additional experimental support, we carried out the intramolecular biaryl-coupling of **11a** in the presence of Na-metal and the results are summarized in scheme 10.



entry[a]	MO^{t}Bu	catalyst	additive	solvent	time	% yield (**12a**)[b]	% yield (**37**)[b]
1	KO^{t}Bu	**4h** (40 mol %)	none	mesitylene	24 h	75%	00%
2	KO^{t}Bu	**4h** (40 mol %)	0.5 equiv Na	mesitylene	8 h	62%	20%
3	KO^{t}Bu	**4h** (40 mol %)	0.5 equiv Na	benzene	8 h	57%	19%
4	none	**4h** (40 mol %)	2.0 equiv Na	mesitylene	10 h	58%	15%
5	none	**4h** (40 mol %)	2.0 equiv Na	benzene	10 h	45%	31%
6	none	none	2.0 equiv Na	mesitylene	24 h	traces	51% + 36% **11a**
7	none	none	2.0 equiv Na	benzene	24 h	traces	47% + 41% **11a**

[a]Reactions were carried out on a 0.50 mmol of **11a** in presence of 0.20 mmol of organic ligands **4h** and 1.5 mmol of KO^{t}Bu in 3 mL of solvent in a sealed tube at 100 °C-110 °C. [b]Isolated yield after column chromatography.

Scheme 10: Biaryl-coupling in presence of Na-metal as a reducing agent.

In fact, when biaryl-coupling was done by KO^{t}Bu-40 mol% **4h** in combination with 0.5 equiv. of Na metal (entries 2 and 3), it afforded biaryl-coupling **12a** in 57-62% yields only in 8 h, thereby indicating a reducing agent facilitated the biaryl-coupling.[34] However, these reactions were also associated with debrominated product **37** in 15-19% yields (entries 2 and 3). Interestingly, when reactions were conducted only in the presence of 2.0 equiv. of

Na-metal in combination with 40 mol% **4h**, we obtained **12a** in 45-58% along with debrominated product **37** in 15-31% (entries 4 and 5). On the other hand, if these reactions were carried out only in the presence of 2.0 equiv. of Na-metal under elevated temperature, it provided 47-51% yields of debrominated product **37**, in addition to the 36-41% of starting material **11a** due to incomplete reactions. These results shown in entries 2 and 3 clearly depicted the biaryl-coupling would be facile in the presence of reducing agent which could undergo the first electron transfer step faster.[34]

CONCLUSIONS

In summary, we have demonstrated an operationally simple, inexpensive and environmentally friendly KO^{t}Bu mediated intramolecular homolytic aromatic substitution (HAS) reaction with the aid of a catalytic amount of bidentate organic ligands. Interestingly, the method also works just in the presence of KO^{t}Bu, without the use of organic molecule as ligand. A mechanism has been proposed for the biaryl-coupling reaction where an aryl radical intermediate seems to be involved in homolytic aromatic substitution (HAS). The methodology provides a concise and straightforward total synthesis of *Amaryllidaceae* alkaloids *viz*. oxoassoanine (**1b**), anhydrolycorinone (**1d**), 5,6-dihydrobicolorine (**2d**), and dihydrobenzo[*c*]phenanthridines alkaloids such as dihydronitidine (**3b**), dihydrochelerythidine (**3d**), dihydroavicine (**3f**). Extending further, we have also shown a short total synthesis of phenanthridine alkaloid such as trispheridine (**2b**), benzo[*c*]phenanthridines *viz.* nornitidine (**3h**), and norchelerythrine (**3j**) following a one-pot biaryl-coupling, deprotection followed by oxidation. Thus, it is reasonable to assume that the rapid one-pot construction of molecular complexity using the straightforward biaryl-coupling strategy will soon find more applications in complex natural product synthesis.

EXPERIMENTAL SECTION

Material. Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O) was distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents such as DMF, mesitylene, 1,2-dimethoxyethane, acetonitrile, chloroform, methanol, ethanol, and reagents were used as received. Thin layer chromatography was performed using silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel of particle size 100-200 mesh was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

General Procedure for the synthesis of *N*-(2-bromobenzyl)-*N*-methylnaphthylamine derivatives (11a-e): In an oven-dried sealed tube, *N*-methyl-α-naphthylamine (3.00 mmol; 1.0 equiv) was taken in *N*, *N*-dimethylformamide (10 mL) under argon atmosphere. To this reaction mixture was added K_2CO_3 (4.50 mmol; 1.5 equiv) and 2-bromobenzylbromides (3.30 mmol; 1.1 equiv) at room temperature. The reaction mixture was stirred for 10 h at 80 ºC. Upon completion of the reactions, (TLC showed complete consumption of starting

material) the reaction mixture was quenched with ice-water (5 mL) and then diluted with 20 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford **11a-e**.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-methylnaphthalen-1-amine** (**11a**): The product was obtained as yellow gel (950 mg, 82%), R_f= 0.27 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.28-8.26 (m, 1H), 7.85-7.83 (m, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.89-7.45 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 7.02 (s, 1H), 4.35 (s, 2H), 3.86 (s, 3H), 3.71 (s, 3H), 2.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 148.4, 148.39, 134.9, 129.7, 129.2, 128.5, 125.8, 125.7, 125.5, 123.5, 123.4, 115.9, 115.4, 113.6, 112.3, 59.9, 56.1, 55.9, 42.3; **IR** (film) υ_{max} 2998, 2935, 2845, 1577, 1507, 1459, 1439, 1396, 1380, 1260, 1208, 1159, 1032, 961, 928, 799, 775 cm^{-1}; **LRMS** (ESI) m/z 386.0792 $[M + H]^+$; calculated for $[C_{20}H_{20}BrNO_2 + H]^+$: 386.0750.

***N*-(2-Bromo-5-methoxybenzyl)-*N*-methylnaphthalen-1-amine** (**11b**): The product was obtained as yellow color gel (823 mg, 77%), R_f= 0.61 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.3 Hz, 1H), 7.76-7.74 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.37-7.30 (m, 4H), 7.25 (d, *J* = 2.7 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.30 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.25 (s, 2H), 3.65 (s, 3H), 2.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 159.2, 149.8, 138.9, 134.9, 133.2, 129.1, 128.4, 125.8, 125.7, 125.5, 123.6, 123.4, 115.5, 114.9, 114.3, 114.1, 60.9, 55.4, 42.2; **IR** (film) υ_{max} 3046, 2937, 2835, 1594, 1576, 1509, 1471, 1437, 1397, 1292, 1272, 1238, 1160, 1121, 1045, 1016, 800, 775 cm^{-1}; **HRMS** (ESI) m/z 356.0648 $[M + H]^+$; calculated for $[C_{19}H_{18}BrNO + H]^+$: 356.0645.

***N*-(2-Bromo-3,5-dimethoxybenzyl)-*N*-methylnaphthalen-1-amine** (**11c**): The product was obtained as yellow gel (996 mg, 86%), R_f= 0.4 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ: 8.23 (d, *J* = 8.0 Hz, 1H), 7.84-7.82 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47-7.38 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 4.38 (s, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 2.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 159.0, 156.7, 149.9, 140.0, 134.9, 129.1, 128.5, 125.8, 125.7, 125.4, 123.6, 123.3, 115.4, 105.5, 103.9, 98.4, 61.2, 56.3, 55.5, 42.2; **IR** (film) υ_{max} 2958, 2922, 2848, 1621, 1520, 1463, 1404, 1384, 1253, 1202, 1169, 1141, 1086, 1048, 1027, 812, 790, 771, 755 cm^{-1}; **HRMS** (ESI) m/z 386.0746 $[M + H]^+$; calculated for $[C_{20}H_{20}BrNO_2 + H]^+$: 386.0750.

***N*-(6-Bromo-2,3-dimethoxybenzyl)-*N*-methylnaphthalen-1-amine** (**11d**): The product was obtained as colorless gel (938 mg, 81%), R_f = 0.53 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.41-8.38 (m, 1H), 7.82-7.80 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.45-7.43 (m, 3H), 7.30-7.27 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 4.47 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.2, 151.1, 149.4, 134.8, 131.9, 129.7, 128.1, 128.07, 125.9, 125.7, 125.0, 124.7, 123.3, 117.1, 116.3, 112.7, 61.4, 55.9, 53.7, 43.1; **IR** (film) υ_{max} 2934, 2853, 1731, 1575, 1471, 1396, 1292, 1271, 1232, 1079, 1024, 801, 776 cm^{-1}; **HRMS** (ESI) m/z 386.0770 $[M + H]^+$; calculated for $[C_{20}H_{20}BrNO_2 + H]^+$: 386.0750.

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-methylnaphthalen-1-amine** (**11e**): The product was obtained as colorless solid (944 mg, 85%), R_f = 0.58 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.23-8.22 (m, 1H), 7.85-7.83 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.48-7.45 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 5.98 (s, 2H), 4.28 (s, 2H), 2.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.8, 147.6, 147.2, 134.9, 131.2, 129.1, 128.4, 125.8, 125.7, 125.4, 123.6, 123.4, 115.5, 113.9, 112.7, 109.4, 101.6, 60.5, 42.2; **IR** (film) υ_{max} 3049, 2892, 2852, 1594, 1576, 1503, 1477, 1397, 1369, 1240, 1106, 1074, 1039, 963, 935, 867, 832, 774 cm^{-1}; **HRMS** (ESI) m/z 370.0464 $[M + H]^+$; calculated for $[C_{19}H_{16}BrNO_2 + H]^+$: 370.0437, **MP** 105–107 ºC.

General procedure for organocatalytic biaryl-coupling: In an oven-dried Schlenk flask, *N*-bromobenzyl-*N*-methylnaphthylamines (0.50 mmol; 1.0 equiv.) and DMEDA (0.20 mmol; 40 mol %) [**Condition A**] or 1, 10-phenanthroline (0.20 mmol; 40 mol %) [**Condition B**] or 2, 2'-bipyridine (0.20 mmol; 40 mol %) [**Condition D**] were taken in mesitylene (5 mL) under argon atmosphere. Potassium tert-Butoxide (1.5 mmol; 3.0 equiv) or in some cases (2.0 mmol; 4.0 equiv) was added to the reaction mixture and the Schlenk flask was closed and heated at 100-110 ºC for indicated time. Then the reaction mixture was allowed to cool at room temperature then filtered through celite and washed with dichloromethane (2 x 5 mL). The combined organic layers were concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (2:1 hexanes/EtOAc) to afford biaryl-coupling products (**2**, **3**, **12**, **19** and **25**). [**Condition C**]: In absence of any organic ligands and dry benzene as a solvent.

8,9-Dimethoxy-5-methyl-5,6-dihydrobenzo[*c*]phenanthridine (**12a**): The product was obtained as yellow crystalline solid [115 mg, 75% (condition B)], R_f = 0.17 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 1H), 7.87-7.83 (m, 2H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.45 (m, 1H), 7.36 (s, 1H), 6.83 (s, 1H), 4.20 (s, 2H), 4.02 (s, 3H), 3.97 (s, 3H), 2.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.1, 148.6, 143.2, 133.8 129.4, 128.2, 126.1, 125.7, 125.3, 124.9, 124.6, 124.6, 123.9, 121.5, 110.2, 106.6, 56.2, 56.1, 54.7, 41.4; **IR** (film) υ_{max} 3055, 2937, 2835, 1607, 1520, 1503, 1367, 1353, 1328, 1284, 1253, 1246, 1212, 1152, 1142, 1042, 1021, 815, 764 cm^{-1}; **HRMS** (ESI) m/z 306.1495 $[M + H]^+$; calculated for $[C_{20}H_{19}NO_2 + H]^+$: 306.1489; **MP** 143–145 ºC.

8-Methoxy-5-methyl-5,6-dihydrobenzo[*c*]phenanthridine (**12b**): The product was obtained as yellow gel [80 mg, 58% (condition B)], R_f = 0.30 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.55-7.52 (m, 1H), 7.47-7.44 (m, 1H), 6.95

(dd, *J* = 8.5, 2.6 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 4.22 (s, 2H), 3.89 (s, 3H), 2.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 159.6, 142.9, 133.8, 133.7, 129.4, 128.2, 126.1, 125.6, 125.3, 125.2, 124.7, 124.1, 123.9, 121.6, 113.1, 112.4, 55.4, 55.3, 41.5; **IR** (film) υ_{max} 3057, 2939, 2836, 1614, 1494, 1463, 1371, 1304, 1275, 1243, 1162, 1137, 1094, 1045, 1032, 925, 808, 764 cm^{-1}; **HRMS** (ESI) m/z 276.1384 $[M + H]^+$; calculated for $[C_{19}H_{17}NO + H]^+$: 276.1383.

8,10-Dimethoxy-5-methyl-5,6-dihydrobenzo[*c*]phenanthridine (**12c**): The product was obtained as yellow gel [98 mg, 64% (condition B)], R_f = 0.39 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.52-7.48 (m, 1H), 7.45-7.42 (m, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.49 (d, *J* = 2.19 Hz, 1H), 4.12 (s, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 2.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 160.2, 157.8, 136.5, 133.2, 129.1, 127.9, 126.2, 125.6, 125.4, 124.8, 123.7, 123.5, 114.1, 111.9, 103.9, 98.3, 56.1, 55.6, 55.4, 40.6; **IR** (film) υ_{max} 3002, 2935, 2838, 1598, 1455, 1430, 1371, 1329, 1204, 1156, 1056, 825, 783, 770 cm^{-1}; **HRMS** (ESI) m/z 306.1488 $[M + H]^+$; calculated for $[C_{20}H_{19}NO_2 + H]^+$: 306.1489.

7,8-Dimethoxy-5-methyl-5,6-dihydrobenzo[*c*]phenanthridine (**12d**): The product was obtained as light yellow gel [104 mg, 68% (condition B)], R_f = 0.23 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.87-7.82 (m, 3H), 7.70-7.65 (m, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 4.39 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 2.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.6, 146.2, 133.8, 128.5, 128.2, 125.8, 125.7, 125.2, 124.8, 123.9, 121.6, 120.8, 119.0, 118.9, 111.1, 109.7, 61.1, 55.8, 48.8, 41.6; **IR** (film) υ_{max} 2956, 2924, 2856, 1744, 1592, 1464, 1394, 1366, 1260, 1086, 1032, 1016, 802, 776 cm^{-1}; **HRMS** (ESI) m/z 306.1499 $[M + H]^+$; calculated for $[C_{20}H_{19}NO_2 + H]^+$: 306.1489.

5-Methyl-5,6-dihydrobenzo[*c*][1,3]dioxolo[4,5-j]phenanthridine (**12e**): The product was obtained as yellow gel [106 mg, 73% (condition B)], yellow color, R_f = 0.39 (5% EtOAc in

hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.45 (m, 1H), 7.33 (s, 1H), 6.80 (s, 1H), 6.01 (s, 2H), 4.16 (s, 2H), 2.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.6, 147.3, 143.1, 133.8, 129.2, 128.2, 126.3, 126.2, 126.0, 125.8, 125.4, 124.8, 124.0, 121.6 , 107.5, 103.7, 101.1, 55.1, 41.1; **IR** (film) υ_{max} 3050, 2936, 2886, 1500, 1481, 1441, 1362, 1327, 1257, 1233, 1165, 1110, 1039, 935, 862, 814, 773, 753 cm^{-1}; **HRMS** (ESI) m/z 290.1182 $[M + H]^+$; calculated for $[C_{19}H_{15}NO_2 + H]^+$: 290.1176.

Synthesis of substituted α-tetralones 13c and 13d: General procedure for the synthesis of substituted but-3-enoic acid: An oven-dried round-bottom flask was charged with 3-bromopropionic acid triphenylphosphonium salt (50 gm; 149.5 mmol; 1.0 equiv) in a mixture (1:1) of tetrahydrofuran and dimethyl sulfoxide (2 mL per mmol) and cooled to 0 ºC on an ice-bath. To this reaction mixture NaH (373.75 mmol; 2.5 equiv) was added portion-wise and it was stirred for another 10 min. Then a solution of veratraldehyde (**13a**) or piperonaldehyde (**13b**) in a mixture (1:1) of tetrahydrofuran and dimethyl sulfoxide (10 mL) was added dropwise to the reaction mixture at 0 ºC. Then it was warmed to room temperature and continued for 20 hours. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched and acidified with 4(*N*) HCl solution and then diluted with 100 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 100 mL of water; again it was extracted with EtOAc (50 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum.

General procedure for the synthesis of substituted butanoic acid: In an oven-dried round-bottom flask, the crude but-3-enoic acid derivative (67.5 mmol; 1.0 equiv) was taken in methanol (150 mL) under argon atmosphere. To this reaction mixture Pd on C (13.5 mmol; 0.2 equiv) was added portion-wise and it was stirred for another 10 min at room temperature

under argon atmosphere. Then the reaction mixture was stirred for 4 h under H_2 (g) balloon. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was filtered through celite and concentrated in a rotary evaporator under vacuum. The crude products were directly charged for next step without isolation.

Synthesis of 6,7-dimethoxy-3,4-dihydronaphthalen-1(2H)-one (**13c**): The crude 4-(3,4-dimethoxyphenyl)butanoic acid (5 gm; 22.3 mmol; 1.0 equiv) and polyphosphoric acid (25 g) were dissolved in 20 mL dichloromethane and the mixture was heated under reflux for 4 h. Upon completion of the reactions, the reaction mixture was quenched and basified by saturated $NaHCO_3$ solution. The whole reaction mixture was taken in a separatory funnel and extracted with 20 mL of water; again it was extracted with DCM (20 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (2:1 hexanes/EtOAc) to afford **13c** (3.035 gm) in 66% overall yield in 3 steps as colorless solid, R_f = 0.54 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.51 (s, 1H), 6.66 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.89 (t, *J* = 6.1 Hz, 2H), 2.59 (t, *J* = 6.3 Hz, 2H), 2.11 (p, *J* = 6.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 197.3, 153.5, 147.9, 139.4, 125.9, 110.2, 108.5, 56.05, 56.02, 38.5, 29.5, 23.6; **IR** (film) υ_{max} 2940, 2840, 1668, 1599, 1512, 1464, 1455, 1363, 1270, 1222, 1151, 1031, 795 cm^{-1}; **HRMS** (ESI) m/z 207.1022 $[M + H]^+$; calculated for $[C_{12}H_{14}O_3 + H]^+$: 207.1016; **MP** 95–96 ºC, [lit. (Beugelmans, R.; Chastanet, J.; Ginsburg, H.; Quintero-Cortes, L.; Roussi, G. *J. Org. Chem.* **1985**, *50*, 4933): 96 ºC].

Synthesis of 7,8-dihydronaphtho[2,3-d][1,3]dioxol-5(6H)-one (13d): The crude 4-(benzo[d][1,3]dioxol-5-yl)butanoic acid (2 gm; 9.6 mmol; 1.0 equiv) and cyanuric chloride (19.2 mmol; 2.0 equiv) were dissolved in 30 mL dichloromethane at room temperature. This reaction mixture was treated with pyridine (10.08 mmol; 1.05 equiv) and stirred it vigorously for 1 h. $AlCl_3$ (11.52 mmol; 1.2 equiv) was added portion-wise at room temperature and then

refluxed it for overnight. Upon completion of the reactions, the reaction mixture was filtered through celite and the organic phase was washed with cooled water two times. The organic layer was dried over anhydrous Na_2SO_4, and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford **13d** in (949 mg) 52% overall yield in 3 steps as colorless solid, R_f= 0.44 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.44 (s, 1H), 6.64 (s, 1H), 5.98 (s, 2H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 6.1 Hz, 2H), 2.07 (p, *J* = 6.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 196.7, 152.0, 146.9, 141.4, 127.4, 107.9, 106.2, 101.6, 38.6, 30.0, 23.5; **IR** (film) υ_{max} 2926, 1731, 1668, 1503, 1483, 1440, 1385, 1248, 1038, 935 cm^{-1}; **HRMS** (ESI) m/z 191.0715 $[M + H]^+$; calculated for $[C_{11}H_{10}O_3 + H]^+$: 191.0703; **MP** 76–78 ºC, [lit. (Beugelmans, R.; Chastanet, J.; Ginsburg, H.; Quintero-Cortes, L.; Roussi, G. *J. Org. Chem.* **1985**, *50*, 4933): 75 ºC].

Synthesis of 6,7-dimethoxynaphthalen-1-amine (14a): In an oven-dried round-bottom flask, 6,7-Dimethoxy-1-tetralone (**13c**) (2 gm; 9.70 mmol; 1.0 equiv) was taken in pyridine (2.5 mL per mmol) under argon atmosphere. To this reaction mixture hydroxylamine hydrochloride (14.55 mmol; 1.5 equiv) was added and it was stirred for another 4 h at room temperature. After completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched by 2(*N*) HCl solution and the reaction mixture was diluted by 20 mL diethyl ether. The whole reaction mixture was taken in a separatory funnel and extracted with 20 mL of water; again the aqueous part was extracted with diethyl ether (10 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were directly charged for next step without isolation.

In an oven-dried round-bottom flask, the crude material (9.70 mmol; 1.0 equiv) was taken in 1, 2-dimethoxyethane (5 mL per mmol) under argon atmosphere and the reaction

vessel was cooled to 0 ºC. To this reaction mixture NaH (48.5 mmol; 5.0 equiv) was added portion-wise and it was stirred for another 5 min. Then *p*-TsCl (29.1 mmol; 3.0 equiv) was added to the reaction mixture at 0 ºC and it was warmed to room temperature and placed on an oil-bath maintaining the temperature to 70 ºC and stirring continued another 24 h at same temperature. Upon completion of the reaction (monitoring by TLC), it was cooled to the reaction mixture. The reaction mixture was quenched with ice-water and extracted with 30 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were directly charged for next step without isolated.

An oven-dried 100 mL round-bottom flask was charged with *O*-tosyl oxime (9.70 mmol; 1.0 equiv), KOH (4 mL per mmol, 1M solution in MeOH) and methanol (10 mL per mmol). The deep red reaction mixture was heated at reflux with stirring for 6 h. The resulting brown solution was allowed to cool to room temperature, poured into water 20 mL, and extracted with EtOAc (10 mL X 2). The combined organic extracts were washed with saturated aq. NaCl (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified by flash chromatography (3:1 hexanes/EtOAc) to afford pure α-naphthylamine **14a** in (887 mg) 45% overall yield in 3 steps as brown color gel, R_f= 0.25 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.20-7.13 (m, 2H), 7.08 (s, 1H), 7.04 (s, 1H), 6.68 (d, *J* = 7.0 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.4, 148.8, 140.9, 130.3, 124.7, 119.1, 118.0, 109.3, 107.1, 100.2 55.8, 55.7; **IR** (film) υ_{max} 3368(br), 2934, 2836, 1600, 1513, 1489, 1465, 1455, 1436, 1373, 1257, 1219, 1156, 1029, 847, 811, 734 cm^{-1}; **HRMS** (ESI) m/z 204.1030 $[M + H]^+$; calculated for $[C_{12}H_{13}NO_2 + H]^+$: 204.1019.

Synthesis of naphtho[2,3-d][1,3]dioxol-5-amine (**14b**)**:** In a round-bottom flask, 6,7-(methylenedioxy)-1-tetralone (**13d**) (2 gm; 10.5 mmol; 1.0 equiv), hydroxylamine hydrochloride (26.25 mmol; 2.5 equiv) and sodium acetate (15.75 mmol; 1.5 equiv) was taken in 3 mL ethanol and 4 mL water mixture. Then this reaction mixture was heated at reflux with stirring for 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was diluted by 20 mL EtOAc and the whole reaction mixture was taken in a separatory funnel and extracted with 20 mL of water; the organic layer was separated out and the aqueous part was extracted with EtOAc (10 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were then *O*-tosylated followed by aromatization (as discussed for the synthesis of **14a**) to afford crude **14b**. The crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford pure α-naphthylamine **14b** in (982 mg) 50% overall yield in 3 steps as black color solid, R_f = 0.27 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.17-7.14 (m, 2H), 7.12 (s, 1H), 7.09 (s, 1H), 6.68 (dd, *J* = 6.2, 2.2 Hz, 1H), 6.02 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.5, 147.1, 141.5, 131.5, 124.8, 120.1, 118.7, 109.5, 104.6, 101.0, 97.7; **IR** (film) υ_{max} 3376(br), 2905, 1633, 1470, 1360, 1330, 1250, 1163, 1122, 1092, 1039, 945, 848, 748, 739 cm^{-1}; **HRMS** (ESI) m/z 188.0704 $[M + H]^+$; calculated for $[C_{11}H_9NO_2 + H]^+$: 188.0706; **MP** 155 ºC, [lit. (Kessar, S. V.; Gupta, Y. P.; Balakrishnan, P.; Sawal, K. K.; Mohammad, T.; Dutt, M. *J. Org. Chem.* **1988**, *53*, 1708): 152–155ºC].

General Procedure for the synthesis of *N*-methylnaphthylamines (**15a** and **15b**)**:** A round-bottom flask was charged with α-naphthylamine derivative (15.0 mmol; 1.0 equiv) in toluene:$NaHCO_3$ (1:1) (20 mL). To this reaction mixture methyl chloroformate (30.0 mmol; 2.0 equiv) was added dropwise and it was stirred for 4 h at room temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 30 mL EtOAc. The whole

reaction mixture was taken in a separatory funnel and extracted with 25 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude material was directly treated for next step without isolation.

The crude material (15.0 mmol; 1.0 equiv) was taken in dry THF (30 mL) under argon atmosphere and the reaction vessel was cooled to 0 ºC. To this reaction mixture $LiAlH_4$ (30.0 mmol; 2.0 equiv) was added portion-wise over 10 mins. After stirring at 0 ºC for 5 minutes, the reaction mixture was warmed to 23 ºC and stirring continued for another 10 minutes. Then, the reaction mixture was refluxed on an oil-bath maintaining the temperature to 80 ºC and stirring continued for 6 h. Upon completion of the reaction (monitoring by TLC), it was cooled to room temperature and then to 0 ºC and quenched with EtOAc, basified with 4(*N*) NaOH solution and extracted with EtOAc (2 X 25 mL). The combined organic extracts were washed with saturated aq. NaCl (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure.The crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford pure *N*-methyl-α-naphthylamine (**15a** and **15b**).

6,7-Dimethoxy-*N*-methylnaphthalen-1-amine (**15a**)**:** The product was obtained as yellow color solid (2.313 gm, 71% overall yield in 2 steps), R_f = 0.39 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.27-7.24 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 1H) 7.09 (s, 1H), 7.02 (s, 1H), 6.55 (d, *J* = 7.5 Hz, 1H) 3.98 (s, 3H), 3.97 (s, 3H) , 2.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.2, 148.7, 143.6, 129.9, 125.0, 118.6, 116.6, 107.4, 103.4, 99.6, 55.9, 55.8, 31.2; **IR** (film) υ_{max} 3437(br), 2932, 1627, 1589, 1496, 1436, 1376, 1255, 1220, 1157, 1105, 1024, 841, 805, 777, 735 cm^{-1}; **HRMS** (ESI) m/z 218.1179 $[M + H]^+$; calculated for $[C_{13}H_{15}NO_2 + H]^+$: 218.1176; **MP** 171–173 ºC, [lit. (Harayama, T.; Sato, T.; Y.; Hori, A.; Abe, H.; Takeuchi, Y. *Synthesis* **2004**, 1446): 168–170 ºC].

***N*-Methylnaphtho[2,3-d][1,3]dioxol-5-amine** (**15b**): The product was obtained as light yellow solid (1.962 gm, 65% overall yield in 2 steps), R_f = 0.50 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.29 (t, *J* = 7.8 Hz, 1H), 7.16-7.13 (m, 3H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.05 (s, 2H) 3.97 (brs, 1H), 3.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.3, 147.1, 144.2, 131.2, 125.1, 119.7, 117.3, 104.8, 103.8, 101.0, 97.1, 31.2; **IR** (film) υ_{max} 3418(br), 3072, 2980, 2917, 2811, 1614, 1538, 1471, 1368, 1288, 1250, 1226, 1171, 1135, 1039, 940, 835, 783, 742 cm^{-1}; **LRMS** (ESI) m/z 202.0894 $[M + H]^+$; calculated for $[C_{12}H_{11}NO_2 + H]^+$: 202.0863; **MP** 104–105 ºC, [lit. (Hergueta, A. R.; Moore, H. W. *J. Org. Chem.* **1999,** *64*, 5979): 103–104 ºC].

General Procedure for the synthesis of *N*-(2-bromobenzyl)-*N*-methylnaphthylamine derivatives (11f-i): The procedure is same as for the synthesis of *N*-(2-bromobenzyl)-*N*-methylnaphthylamine derivatives **11a-e**.

***N*-(6-Bromo-2,3-dimethoxybenzyl)-6,7-dimethoxy-*N*-methylnaphthalen-1-amine** (**11f**): The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford **11f** as yellow color solid (1.138 gm, 85%), R_f = 0.38 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33-7.25 (m, 3H), 7.04 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 4.39 (s, 2H), 3.98 (s, 3H), 3.97 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 2.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.1, 149.9, 149.3, 149.27, 148.9, 123.0, 130.4, 128.0, 125.9, 124.3, 122.3, 117.0, 115.9, 112.5, 106.7, 103.7, 61.2, 55.9, 55.8, 55.7, 53.9, 43.9; **IR** (film) υ_{max} 2940, 2839, 1576, 1509, 1472, 1437, 1414, 1268, 1230, 1157, 1079, 1010, 803 cm^{-1}; **HRMS** (ESI) m/z 446.0964 $[M + H]^+$; calculated for $[C_{22}H_{24}BrNO_4 + H]^+$: 446.0961; **MP** 113 ºC, [lit. (Harayama, T.; Sato, T.; Y.; Hori, A.; Abe, H.; Takeuchi, Y. *Synthesis* **2004**, 1446): 111–112 ºC].

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-methylnaphtho[2,3-d][1,3]dioxol-5-amine** (**11g**): The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford

11g as colorless solid (1.149 gm, 89%), R_f = 0.43 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.53 (s, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.17-7.13 (m, 1H), 7.01 (s, 1H), 6.96 (d, *J* =8.0 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 5.91 (s, 2H), 4.18 (s, 2H), 3.75 (s, 3H), 3.63 (s, 3H), 2.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.1, 148.41, 148.39, 147.7, 147.4, 131.9, 129.7, 126.4, 124.4, 123.0, 115.5, 115.3, 113.8, 112.6, 104.4, 100.9, 100.3, 59.7, 56.1, 55.9, 42.5; **IR** (film) υ_{max} 3059, 3002, 2934, 1660, 1596, 1506, 1464, 1440, 1401, 1382, 1261, 1210, 1164, 1031, 987, 802, 779, 738 cm^{-1}; **HRMS** (ESI) m/z 430.0677 $[M + H]^+$; calculated for $[C_{21}H_{20}BrNO_4 + H]^+$: 430.0648; **MP 5**8–60 ºC.

***N*-(6-Bromo-2,3-dimethoxybenzyl)-*N*-methylnaphtho[2,3-d][1,3]dioxol-5-amine** (**11h**): The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford **11h** as light yellow color solid (1.045 gm, 81%), R_f = 0.59 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.78 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.23-7.21 (m, 1H), 7.10 (s, 1H), 6.75 (d, *J* =8.8 Hz, 1H), 6.01 (s, 2H), 4.39 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.1, 150.6, 149.3, 147.4, 131.9, 131.8, 128.0, 126.9, 124.4, 122.9, 117.1, 115.7, 112.7, 104.0, 101.4, 100.8, 100.0, 61.3, 55.9, 53.8, 42.9; **IR** (film) υ_{max} 2936, 2853, 1462, 1415, 1290, 1268, 1242, 1163, 1079, 1039, 1011, 937, 851, 799, 748 cm^{-1}; **HRMS** (ESI) m/z 430.0654 $[M + H]^+$; calculated for $[C_{21}H_{20}BrNO_4 + H]^+$: 430.0648; **MP** 97–99 ºC. [lit. (Harayama, T.; Sato, T.; Y.; Hori, A.; Abe, H.; Takeuchi, Y. *Synthesis* **2004**, 1446): 97–98 ºC].

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-methylnaphtho[2,3-d][1,3]dioxol-5-amine** (**11i**): The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford **11i** as colorless gel (907 mg, 73%), R_f = 0.42 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.27-7.23 (m, 1H), 7.15 (s, 1H), 7.09-7.07 (m, 2H), 6.99 (s, 1H), 6.01 (s, 2H), 5.94 (s, 2H), 4.19 (s, 2H), 2.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.6, 147.5, 147.4, 147.2, 131.9, 131.1, 126.4,

124.4, 122.9, 115.1, 114.1, 112.7, 110.3, 109.5, 104.4, 101.6, 100.9, 100.4, 60.2, 42.5; **IR** (film) υ_{max} 2898, 2791, 1727, 1618, 1601, 1470, 1409, 1361, 1242, 1160, 1107, 1040, 950, 934, 910, 851, 739 cm^{-1}; **LRMS** (ESI) m/z 414.0370 $[M + H]^+$; calculated for $[C_{20}H_{16}BrNO_4 + H]^+$: 414.0335.

2,3,7,8-Tetramethoxy-5-methyl-5,6-dihydrobenzo[*c*]phenanthridine (**12f**): The product was obtained as yellow crystalline solid [120 mg, 66% (condition B)], R_f= 0.33 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.31 (s, 2H), 4.10 (s, 3H), 4.00 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H), 2.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.2, 149.7, 149.4, 146.1, 142.1, 129.6, 126.4, 126.1, 124.8, 123.9, 123.1, 120.0, 118.6, 111.0, 106.9, 102.9, 61.1, 56.0, 55.9, 55.8, 48.8, 41.5; **IR** (film) υ_{max} 2924, 2854, 1728, 1463, 1728, 1258, 1160, 1081, 1036, 966, 854 cm^{-1}; **HRMS** (ESI) m/z 366.1705 $[M + H]^+$; calculated for $[C_{22}H_{23}NO_4 + H]^+$: 366.1700; **MP** 184–186 °C, [lit. (Harayama, T.; Sato, T.; Y.; Hori, A.; Abe, H.; Takeuchi, Y. *Synthesis* **2004**, 1446): 180–183 °C].

2,3-Dimethoxy-12-methyl-12,13-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]phenanthridine (**3b**): The product was obtained as light yellow color solid [114 mg, 65% (condition B)], R_f= 0.25 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.32 (s, 1H), 7.11 (s, 1H), 6.80 (s, 1H), 6.04 (s, 2H), 4.14 (s, 2H), 3.99 (s, 3H), 3.95 (s, 3H), 2.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.9, 148.6, 148.1, 147.5, 142.6, 130.8, 126.4, 124.9, 124.4, 124.37, 123.9, 119.9, 110.2, 106.4, 104.4, 101.0, 100.6, 56.2, 56.0, 54.8, 41.0; **IR** (film) υ_{max} 2921, 2851, 1500, 1463, 1455, 1350, 1281, 1239, 1213, 1174, 1145, 1028, 858 cm^{-1}; **HRMS** (ESI) m/z 350.1390 $[M + H]^+$; calculated for $[C_{21}H_{19}NO_4 + H]^+$: 350.1387; **MP** 223–225 ºC, [lit. (Arthur, H. R.; Hui, W. H.; Ng, Y. L. *J. Chem. Soc.* **1959**, 1840): 221–223 ºC].

1,2-Dimethoxy-12-methyl-12,13-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]phenanthridine (**3d**): The product was obtained as yellow color solid [116 mg, 66% (condition B)], R_f = 0.32 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.11 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.04 (s, 2H), 4.29 (s, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 2.60 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.3, 148.1, 147.5, 146.1, 142.7, 130.8, 126.4, 126.3, 126.3, 123.8, 120.1, 118.7, 111.0, 104.3, 101.0, 100.7, 100.0, 61.1, 55.8, 48.7, 41.3; **IR** (film) υ_{max} 2928, 2848, 2791, 1601, 1493, 1463, 1421, 1360, 1270, 1242, 1224, 1189, 1080, 1040, 1014, 943, 866, 819, 734 cm^{-1}; **HRMS** (ESI) m/z 350.1414 $[M + H]^+$; calculated for $[C_{21}H_{19}NO_4 + H]^+$: 350.1387; **MP** 199–201 ºC, [lit. (Oechsling, S. M.; Konig, M.; Oechslin-Merkeal, K.; Wright, D.; Kinghorn, A. D.; Sticher, O. *J. Nat. Prod.* **1991**, *54,* 519): 200.7 ºC].

5-Methyl-5,6-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*][1,3]dioxolo[4,5-*j*]phenanthridine (**3f**): The product was obtained as yellow color solid [113 mg, 68% (condition B)], R_f = 0.31 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 1H), 7.11 (s, 1H), 6.77 (s, 1H), 6.05 (s, 2H), 5.99 (s, 2H), 4.10 (s, 2H), 2.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.1, 147.5, 147.4, 147.0, 138.9, 130.8, 126.4, 125.8, 124.5, 123.9, 120.1, 107.4, 104.3, 103.6, 101.04, 101.0, 100.9, 100.7, 55.1, 40.7; **IR** (film) υ_{max} 2922, 2851, 1652, 1500, 1469, 1455, 1350, 1281, 1240, 1213, 1162, 1112, 1039, 885, 855 cm^{-1}; **HRMS** (ESI) m/z 334.1068 $[M + H]^+$; calculated for $[C_{20}H_{15}NO_4 + H]^+$: 334.1074; **MP** 220–222 ºC, [lit. (Ninomiya, I.; Naito, T.; Ishii, H.; Ishida, T.; Ueda, M.; Harada, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, *8*, 762): 212–213 ºC].

Synthesis of methyl 2-bromo-4,5-dimethoxybenzyl(naphthalen-1-yl)carbamate (**17a**): A round-bottom flask was charged with α-naphthylamine (2.0 mmol; 1.0 equiv) in 10 mL of toluene:$NaHCO_3$ (1:1) at room temperature. To this reaction mixture methyl chloroformate

(4.0 mmol; 2.0 equiv) was added dropwise and it was stirred for 4 h at room temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 10 mL EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. Without isolation the crude material was directly treated for next step.

In an oven-dried round-bottom flask, the crude carbamate (2.0 mmol; 1.0 equiv) was taken in *N*, *N*-dimethylformamide (5 mL) under argon atmosphere and the reaction vessel was cooled to 0 ºC. To this reaction mixture NaH (2.40 mmol; 1.2 equiv) was added portionwise and it was stirred for another 5 min. A solution of 3, 4-dimethoxy-2-bromobenzylbromides (2.20 mmol; 1.1 equiv) in *N*, *N*-dimethylformamide (2 mL) was added dropwise to the reaction mixture at 0 ºC. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH_4Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (3:1 hexanes/EtOAc) to afford **17a** (765 mg) in 89% overall yield in two steps as yellow color solid, R_f = 0.53 (25% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (approximately 3:2 rotameric mixture) δ: 7.87-7.85 (m, 1H for major rotamer), 7.79-7.77 (m, 1H for major + 2H minor rotameric mixture), 7.50-7.48 (m, 1H for major + 2H minor rotameric mixture), 7.34 (t, *J* = 7.7 Hz, 1H for major rotamer), 7.04-7.02 (m, 3H for major + 3H minor rotameric mixture), 6.93 (brs, 1H for major + 1H minor rotameric mixture), 6.84 (brs, 1H for major + 1H minor rotameric mixture), 5.33-5.29 (m, 1H for minor rotamer), 4.77-4.73 (m, 1H for major rotamer), 4.62 (s, 1H for major + 1H minor rotameric mixture), 3.87 (brs, 6H, for major rotamer), 3.80 (brs, 1H for major + 3H minor rotameric

mixture), 3.72 (brs, 1H for major + 3H minor rotameric mixture), 3.62 (brs, 1H for major + 3H minor rotameric mixture); **^{13}C NMR** (100 MHz, $CDCl_3$) (approximately 3:2 rotameric mixture) δ: 157.1, 149.0, 148.9, 148.5, 148.3, 137.1, 134.4, 130.7, 129.4, 128.8, 128.5, 128.2, 126.7, 126.11, 126.1, 125.4, 122.5, 115.4, 115.1, 114.6, 113.63, 113.61, 113.5, 113.2, 112.4, 71.7, 69.2, 56.2, 56.1, 56.0, 55.9, 53.3, 53.2,; **IR** (film) υ_{max} 3059, 3002, 2843, 1704, 1598, 1506, 1446, 1402, 1378, 1338, 1290, 1262, 1210, 1164, 1141, 1107, 1032, 959, 802, 778, 735 cm^{-1}; **HRMS** (ESI) m/z 430.0646 $[M + H]^+$; calculated for $[C_{21}H_{20}BrNO_4 + H]^+$: 430.0648; **MP** 131–133 ºC.

Synthesis of methyl *N*-(2-bromo-4,5-dimethoxybenzyl)-4-methyl-*N*-(naphthalen-1-yl)benzenesulfonamide (**17b**): An oven-dried round-bottom flask was charged with α-naphthylamine (2.0 mmol; 1.0 equiv) in pyridine (5 mL) under argon atmosphere and the reaction vessel was cooled to 0 ºC. To this reaction mixture *p*-TsCl (4.0 mmol; 2.0 equiv) was added portion-wise and it was stirred for overnight. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with 2(*N*) HCl (10 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. Without isolation the crude material was directly treated for next step.

In an oven-dried round-bottom flask, the crude benzenesulfonamide (2.0 mmol; 1.0 equiv) was taken in *N*, *N*-dimethylformamide (5 mL) under argon atmosphere and the reaction vessel was cooled to 0 ºC. To this reaction mixture NaH (2.40 mmol; 1.2 equiv) was added portion-wise and it was stirred for another 5 min. A solution of 3, 4-dimethoxy-2-bromobenzylbromides (2.20 mmol; 1.1 equiv) in *N*, *N*-dimethylformamide (2 mL) was added dropwise to the reaction mixture at 0 ºC. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, the reaction mixture was quenched with

saturated NH_4Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (3:1 hexanes/EtOAc) to afford **17b** (905 mg) in 86% overall yield in 2 steps as colorless solid, R_f = 0.32 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.10-8.08 (m, 1H), 7.74-7.72 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.42-7.37 (m, 2H), 7.29-7.22 (m, 3H), 6.95 (s, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 5.13 (d, *J* = 14.0 Hz, 1H), 4.74 (d, *J* = 14.0 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.9, 148.2, 143.7, 135.7, 135.3, 134.5, 133.2, 129.6, 129.0, 128.2, 127.9, 126.8, 126.5, 126.47, 126.3, 124.7, 124.2, 114.9, 114.3, 113.5, 55.9, 55.8, 55.0, 21.6; **IR** (film) υ_{max} 3055, 3006, 2844, 1598, 1506, 1463, 1439, 1384, 1347, 1261, 1212, 1091, 1071, 1034, 883, 812, 802, 775, 736, 706 cm^{-1}; **HRMS** (ESI) m/z 526.0682 $[M + H]^+$; calculated for $[C_{26}H_{24}BrNSO_4 + H]^+$: 526.0682; **MP** 158–161 ºC.

Synthesis of methyl *N*-(2-bromo-4,5-dimethoxybenzyl)-*N*-(naphthalen-1-yl)acetamide (**17c**): An oven-dried round-bottom flask was charged with α-naphthylamine (2.0 mmol; 1.0 equiv) and triethylamine (6.0 mmol; 3.0 equiv) in dichloromethane (20 mL) and cooled to 0 ºC on an ice-bath. After 5 minutes of stirring at same temperature, acetyl chloride (2.4 mmol; 1.2 equiv) was added drop wise to the reaction mixture by a glass syringe and allowed to warm to room temperature. The stirring was continued till TLC showed complete consumption of starting materials. The reaction mixture was washed with water (10 mL) and stirred with 2(*N*) HCl solution. The aqueous layer was further extracted with CH_2Cl_2 (5 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was directly treated for next step without further isolation.

In an oven-dried round-bottom flask, the crude acetamide (2.0 mmol; 1.0 equiv) was taken in *N*, *N*-dimethylformamide (5 mL) under argon atmosphere and the reaction vessel

was cooled to 0 ºC. To this reaction mixture NaH (2.40 mmol; 1.2 equiv) was added portion wise and it was stirred for another 5 min. A solution of 3,4-dimethoxy-2-bromobenzylbromides (2.20 mmol; 1.1 equiv) in *N*, *N*-dimethylformamide (2 mL) was added drop wise to the reaction mixture at 0 ºC. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH_4Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (1:1 hexanes/EtOAc) to afford **17c** (721 mg) in 87% overall yield in 2 steps as light yellow solid, R_f = 0.54 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86-7.84 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.74-7.72 (m, 1H), 7.52-7.47 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 5.54 (d, *J* = 14.1 Hz, 1H), 4.60 (d, *J* = 14.2 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.3, 148.9, 148.4, 138.1, 134.6, 130.6, 128.9, 128.8, 128.6, 127.3, 126.7, 126.5, 125.5, 122.2, 114.94, 114.9, 114.0, 56.05, 56.04, 51.0, 22.3; **IR** (film) υ_{max} 3002, 2935, 1660, 1596, 1505, 1464, 1440, 1401, 1382, 1261, 1210, 1164, 1031, 872, 802, 779, 738 cm^{-1}; **HRMS** (ESI) m/z 414.0714 $[M + H]^+$; calculated for $[C_{21}H_{20}BrNO_3 + H]^+$: 414.0699; **MP** 122–125 ºC.

General Procedure for the synthesis of *N*-aryl-*N*-(naphthalen-1-yl) benzamides (18a-f): An oven-dried round-bottom flask was charged with α-naphthylamine (**14b** and **14c**) (2.0 mmol; 1.0 equiv) and triethylamine (6.0 mmol; 3.0 equiv) in dichloromethane (5 mL per mmol) and cooled to 0 ºC on an ice-bath. After 5 minutes of stirring at same temperature, benzoyl chloride (2.4 mmol; 1.2 equiv) was added drop wise to the reaction mixture by a glass syringe and allowed to warm to RT. The stirring was continued till TLC showed

complete consumption of starting materials. The reaction mixture was poured into a separatory funnel and washed with water (10 mL). The aqueous layer was further extracted with CH_2Cl_2 (5 mL X 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was directly treated for next step (without isolation).

In an oven-dried round-bottom flask, the crude benzamide (2.0 mmol; 1.0 equiv) was taken in *N*, *N*-dimethylformamide (5 mL) under argon atmosphere and the reaction vessel was cooled to 0 ºC. To this reaction mixture NaH (2.40 mmol; 1.2 equiv.) was added portionwise and it was stirred for another 5 min. A solution of 2-bromobenzylbromides (2.20 mmol; 1.1 equiv.) in *N*, *N*-dimethylformamide (2 mL) was added dropwise to the reaction mixture at 0 ºC. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, the reaction mixture was quenched with saturated NH_4Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (2:1 hexanes/EtOAc) to afford **18a-f**.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-(naphthalen-1-yl)benzamide** (**18a**): The product was obtained as white color solid (857 mg, 90% overall yield in 2 steps), R_f = 0.24 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 7.05-6.97 (m, 2H), 6.93-6.88 (m, 2H), 6.74 (s, 1H), 6.68 (d, *J* = 7.3 Hz, 1H), 5.78 (d, *J* = 14.2 Hz, 1H), 4.67 (d, *J* = 14.2 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.7, 148.9, 148.4, 138.2, 136.1, 134.3, 130.7, 129.5, 128.8, 128.6, 128.3, 128.0, 127.5, 127.2, 126.2, 125.1, 122.5, 115.4, 115.0, 114.9, 113.9, 56.0, 56.16, 51.8; **IR** (film) υ_{max} 3003, 2934, 2844, 1644, 1599, 1506, 1465, 1440, 1403,

1380, 1262, 1213, 1164, 1031, 974, 864, 777, 735 cm^{-1}; **HRMS** (ESI) m/z 476.0863 $[M + H]^+$; calculated for $[C_{26}H_{22}BrNO_3 + H]^+$: 476.0856; **MP** 139–141 ºC.

***N*-(2-Bromo-3, 5-dimethoxybenzyl)-*N*-(naphthalen-1-yl)benzamide** (**18b**): The product was obtained as yellow solid (867 mg, 91% overall yield in 2 steps), R_f = 0.37 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.59-7.56 (m, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7. 5 Hz, 2H), 7.14-7.06 (m, 2H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 5.90 (d, *J* = 14.8 Hz, 1H), 4.79 (d, *J* = 14.8 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.7, 159.6, 156.6, 138.6, 138.5, 136.0, 134.4, 130.5, 129.6, 128.7, 128.4, 127.7, 127.6, 127.5, 127.2 , 126.3, 125.1, 122.5, 106.7, 104.9, 99.0, 56.3, 55.5, 53.0; **IR** (film) υ_{max} 3059, 2938, 2844, 1645, 1591, 1456, 1402, 1383, 1327, 1305, 1201, 1163, 1084, 1024, 980, 922, 805, 777, 735, 699 cm^{-1}; **HRMS** (ESI) m/z 476.0856 $[M + H]^+$; calculated for $[C_{26}H_{22}BrNO_3 + H]^+$: 476.0856; **MP** 93–95 ºC.

***N*-(2-Bromobenzyl)-*N*-(naphthalen-1-yl)benzamide** (**18c**): The product was obtained as colorless solid (691 mg, 83% overall yield in 2 steps), R_f = 0.51 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.60-7.56 (m, 2H), 7.51-7.47 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30-7.24 (m, 3H), 7.14-7.07 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 5.89 (d, *J* = 14.9 Hz, 1H), 4.80 (d, *J* = 14.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.7, 138.6, 136.6, 135.9, 134.4, 132.7, 130.8, 130.6, 129.6, 129.0, 128.7, 128.4, 127.8, 127.6, 127.52, 127.50, 127.3, 126.3, 125.1, 124.3, 122.5, 52.7; **IR** (film) υ_{max} 3060, 2926, 1645, 1596, 1575, 1471, 1445, 1402, 1383, 1305, 1151, 1027, 966, 776, 757, 698 cm^{-1}; **HRMS** (ESI) m/z 416.0645 $[M + H]^+$; calculated for $[C_{24}H_{18}BrNO + H]^+$: 416.0645; **MP** 91–93 ºC.

***N*-(2-Bromo-5-methoxybenzyl)-*N*-(naphthalen-1-yl)benzamide** (**18d**): The product was obtained as yellow solid (723 mg, 81% overall yield in 2 steps), R_f = 0.40 (20% EtOAc in

hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.4 Hz, 1H), 8.72 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.58-7.48 (m, 1H), 7.43-7.39 (m, 1H), 7.23-7.18 (m, 3H), 7.11-6.99 (m, 3H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.9 Hz, 1H), 5.78 (d, *J* = 14.8 Hz, 1H), 4.66 (d, *J* = 14.8 Hz, 1H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.7, 159.0, 138.6, 137.5, 135.9 134.4, 133.2, 130.5, 129.6, 128.7, 128.4, 127.7, 127.6, 127.5, 127.3, 126.3, 125.1, 122.5, 116.1, 115.1, 114.7, 55.5, 52.8; **IR** (film) υ_{max} 3059, 2932, 2848, 1648, 1597, 1399, 1377, 1300, 1239, 1165, 1053, 1018, 981, 803, 776, 698 cm^{-1}; **HRMS** (ESI) m/z 446.0744 $[M + H]^+$; calculated for $[C_{25}H_{20}BrNO_2 + H]^+$: 446.0750; **MP** 142–145 ºC.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-(naphtho[2,3-d][1,3]dioxol-5-yl)benzamide** (**18e**): The product was obtained as yellow gel (895 mg, 86% overall yield in 2 steps), R_f = 0.46 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.2 Hz, 1H), 7.28-7.26 (m, 3H), 7.22 (s, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.05 (s, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.06 (s, 2H), 5.80 (d, *J* = 14.2 Hz, 1H), 4.70 (d, *J* = 14.2 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.6, 149.0, 148.9, 148.4, 147.8, 137.5, 136.0, 131.6, 129.6, 128.8, 128.0, 127.5, 127.47, 127.2, 126.7, 123.7, 115.0, 114.9, 113.9, 104.5, 101.4, 98.9, 56.1, 56.0, 51.5; **IR** (film) υ_{max} 3059, 2931, 2848, 1644, 1601, 1505, 1464, 1380, 1342, 1249, 1214, 1164, 1037, 958, 857, 792, 748, 699 cm^{-1}; **HRMS** (ESI) m/z 520.0752 $[M + H]^+$; calculated for $[C_{27}H_{22}BrNO_5 + H]^+$: 520.0754.

***N*-(6-Bromo-2,3-dimethoxybenzyl)-*N*-(naphtho[2,3-d][1,3]dioxol-5-yl)benzamide** (**18f**): The product was obtained as yellow gel (822 mg, 79% overall yield in 2 steps), R_f = 0.42 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36-7.28 (m, 4H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.08-7.04 (m, 1H), 7.00-6.95 (m, 3H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.69-6.64 (m, 2H), 6.05 (s, 2H), 5.95 (d, *J* = 13.6 Hz, 1H), 4.86 (d, *J* = 13.6 Hz, 1H), 3.75 (s, 3H), 3.16 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 152.0, 149.8, 148.9, 147.6, 136.6, 136.5, 131.4, 130.2, 129.1, 129.0, 127.5, 127.49, 127.3, 127.2, 127.0, 123.3, 116.4, 113.3, 104.2, 101.3, 99.0, 60.3, 55.9, 45.5; **IR** (film) υ_{max} 3059, 2926, 2853, 1651, 1644, 1577, 1469, 1468, 1379, 1301, 1281, 1249, 1163, 1132, 1078, 1039, 1010, 965, 937, 855, 799 cm^{-1}; **HRMS** (ESI) m/z 520.0772 $[M + H]^+$; calculated for $[C_{27}H_{22}BrNO_5 + H]^+$: 520.0754.

8,9-Dimethoxybenzo[*c*]phenanthridine (**19a**): The product was obtained as colorless solid [74 mg, 51% (condition C)], R_f= 0.22 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.34 (d, *J* = 8.4 Hz, 1H), 9.25 (s, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 7.92 (t, *J* = 9.1 Hz, 2H), 7.79 (s, 1H), 7.76-7.72 (m, 1H), 7.67-7.63 (m, 1H), 7.32 (s, 1H), 4.11 (s, 3H), 4.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.0, 149.9, 149.8, 140.7, 132.8, 132.1, 128.7, 127.6, 127.3, 127.1, 126.9, 124.5, 122.6, 120.6, 119.7, 107.1, 101.6, 56.1, 56.0; **IR** (film) υ_{max} 2932, 2848, 1606, 1515, 1507, 1464, 1263, 1211, 1161, 1030, 822 cm^{-1}; **HRMS** (ESI) m/z 290.1179 $[M + H]^+$; calculated for $[C_{19}H_{15}NO_2 + H]^+$: 290.1176; **MP** 233–234 ºC, [lit. (Stermitz, F. R.; Gillespie, J. P.; Amoros, L. G.; Romero, R.; Stermitz, T. A. *J. Med. Chem.* **1975**, *18*, 708): 233 ºC].

8,10-Dimethoxybenzo[*c*]phenanthridine (**19b**): The product was obtained as yellow solid [59 mg, 41% (condition B)], R_f= 0.40 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.41 (d, *J* = 9.3 Hz, 2H), 9.34 (s, 1H), 7.96 (s, 1H), 7.76-7.73 (m, 1H), 7.69-7.65 (m, 1H), 7.56-7.53 (m, 1H), 7.06 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 4.13 (s, 3H), 4.0 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 159.2, 158.9, 150.9, 132.3, 129.9, 128.9, 127.3, 127.2, 126.9, 126.6, 124.9, 124.7, 121.8, 120.6, 119.3, 103.4, 99.9, 55.9, 55.6; **IR** (film) υ_{max} 2925, 2851, 1614, 1593, 1519, 1455, 1416, 1389, 1372, 1302, 1271, 1203, 1161, 1067, 1038, 947, 836, 800, 762 cm^{-1}; **HRMS** (ESI) m/z 290.1164 $[M + H]^+$; calculated for $[C_{19}H_{15}NO_2 + H]^+$: 290.1176; **MP** 159–161 ºC.

Benzo[*c*]phenanthridine (**3a**): The product was obtained as colorless solid [69 mg, 60% (condition B)], R_f = 0.53 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.48 (s, 1H), 9.42 (d, *J* = 8.3 Hz, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.52 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.03-7.97 (m, 2H), 7.87 (t, *J* = 7.9 Hz, 1H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.73-7.69 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.0, 141.5, 133.3, 132.9, 132.1, 130.8, 128.7, 127.9, 127.7, 127.4, 127.2, 127.0, 126.9, 124.8, 122.2, 121.1, 119.9; **IR** (film) υ_{max} 3060, 2925, 2854, 1583, 1463, 1408, 1279, 1115, 1028, 767 cm^{-1}; **HRMS** (ESI) m/z 230.0956 $[M + H]^+$; calculated for $[C_{17}H_{11}N + H]^+$: 230.0964; **MP** 132–133 ºC, [lit. (Kock, I.; Clement, B. *Synthesis* **2005**, 1052): 130 ºC].

8-Methoxybenzo[*c*]phenanthridine (**19c**): The product was obtained as colorless solid [65 mg, 50% (condition B)], R_f = 0.39 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.42 (s, 1H), 9.37 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 9.1 Hz, 1H), 8.50 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.78-7.74 (m, 1H), 7.69-7.66 (m, 1H), 7.54 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 4.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.7, 151.0, 140.5, 132.8, 132.1, 128.3, 127.9, 127.7, 127.6,127.03, 127.01, 124.4, 124.0, 122.6, 121.3, 119.8, 107.1, 55.6; **IR** (film) υ_{max} 3050, 2958, 2922, 2848, 1621, 1579, 1520, 1463, 1404, 1384, 1253, 1202, 1169, 1141, 1086, 1049, 1027, 935, 840, 812, 790, 771, 755 cm^{-1}; **HRMS** (ESI) m/z 260.1067 $[M + H]^+$; calculated for $[C_{18}H_{13}NO + H]^+$: 260.1070; **MP** 115–117 ºC.

2,3-Dimethoxy-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]phenanthridine (**3h**): The product was obtained as white color solid [90 mg, 54% (condition B)], R_f = 0.33 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.24 (s, 1H), 8.71 (s, 1H), 8.28 (d, *J* = 8.9 Hz, 1H), 7.89 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.40 (s, 1H), 7.26 (s, 1H), 6.13 (s, 2H), 4.16 (s, 3H), 4.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.0, 149.8, 149.7, 148.4, 148.3, 134.4, 129.6, 128.9, 127.5, 126.6, 122.2, 119.9, 118.1, 107.3, 104.4, 102.2, 101.7, 101.3, 56.2, 56.1; **IR** (film)

υ_{max} 2915, 2875, 1612, 1469, 1255, 1223, 1200, 1158, 1112, 1077, 1041, 1019, 940, 872, 840, 800 cm^{-1}; **HRMS** (ESI) m/z 334.1083 $[M + H]^+$; calculated for $[C_{20}H_{15}NO_4 + H]^+$: 334.1074; **MP** 278–280 ºC, [lit. (Kohno, K.; Azuma, S.; Choshi, T.; Nobuhiro, J.; Hibino, S. *Tetrahedron Lett.* **2009**, *50*, 590): 278–281 ºC].

1,2-Dimethoxy-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]phenanthridine (**3j**): The product was obtained as brown color solid [80 mg, 48% (condition B)], R_f= 0.44 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.74 (s, 1H), 8.70 (s, 1H), 8.31 (dd, *J* = 9.1, 1.9 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 9.1 Hz, 1H), 7.24 (s, 1H), 6.12 (s, 2H), 4.12 (s, 3H), 4.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.4. 148.4, 148.2, 146.5, 145.2, 139.9, 129.7, 129.1, 128.0, 127.0, 121.8, 120.0, 118.7, 118.3, 118.2, 104.4, 102.1, 101.3, 61.9, 56.8; **IR** (film) υ_{max} 2919, 2851, 1463, 1274, 1250, 1197, 1164, 1037, 939, 800 cm^{-1}; **HRMS** (ESI) m/z 334.1085 $[M + H]^+$; calculated for $[C_{20}H_{15}NO_4 + H]^+$: 334.1074; **MP** 220–221 ºC, [lit. (Scheuer, P. J.; Changa, M. Y.; Swanholm, C. E. *J. Org. Chem.* **1961**, *27*, 1472): 221.5–222.5 ºC].

***N*-(3,4-Dimethoxybenzyl)naphthalen-1-amine** (**20a**): The product was obtained as liquid [40 mg, 27% (condition B)], R_f= 0.44 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.83-7.81 (m, 2H), 7.49-7.41 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.29-7.27 (m, 1H), 7.01-6.99 (m, 2H), 6.89-6.87 (m, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 4.65 (brs, 1H), 4.43 (s, 2H), 3.90 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.3. 148.3, 143.3, 134.3, 131.6, 128.7, 126.6, 125.8, 124.8, 123.4, 120.0, 119.9, 117.7, 111.3, 111.1, 104.7, 56.0, 55.9, 48.6; **IR** (film) υ_{max} 3424(br), 3050, 2931, 2853, 1582, 1515, 1463, 1408, 1264, 1237, 1154, 1139, 1117, 1028, 786, 770 cm^{-1}; **LRMS** (ESI) m/z 292.1293 $[M - H]^+$; calculated for $[C_{19}H_{19}NO_2 - H]^+$: 292.1332, [lit. (Moreno, I.; Tellitu, I.; Etayo, J.; SanMartin, R.; Dominguez, E. *Tetrahedron* **2001**, *57*, 5403)].

***N*-(3,5-Dimethoxybenzyl)naphthalen-1-amine** (**20b**): The product was obtained as colorless liquid [38 mg, 26% (condition C)], R_f = 0.40 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92-7.88 (m, 1H), 7.82-7.80 (m, 1H), 7.48-7.45 (m, 3H), 7.32 (d, *J* = 4.5 Hz, 2H), 6.73 (bs, 1H), 6.60 (d, *J* = 1.9 Hz, 2H), 6.39 (s, 1H), 4.46 (s, 2H), 3.77 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 161.2, 143.3, 141.8, 134.3, 128.7, 128.6, 126.7, 125.8, 124.8, 123.4, 119.9, 117.7, 109.7, 105.6, 104.8, 99.3, 55.4 (2-OMe ^{13}C), 48.9; **IR** (film) υ_{max} 3446(br), 2952, 2854, 1732, 1597, 1531, 1470, 1463, 1430, 1321, 1204, 1155, 1066, 833, 771, 695 cm^{-1}; **HRMS** (ESI) m/z 294.1505 $[M + H]^+$; calculated for $[C_{19}H_{19}NO_2 + H]^+$: 294.1489.

***N*-Benzylnaphthalen-1-amine** (**20c**)**:** The product was obtained as light yellow solid [29 mg, 25% (condition D)], R_f = 0.67 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86-7.82 (m, 2H), 7.50-7.45 (m, 4H), 7.42-7.37 (m, 2H), 7.35-7.32 (m, 2H), 7.30-7.28 (m, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 4.81 (brs, 1H), 4.52 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.1, 139.0, 134.3, 128.8, 128.7, 127.8, 127.4, 126.6, 125.8, 124.8, 123.4, 119.9, 117.8, 104.9; **IR** (film) υ_{max} 3393(br), 3046, 2923, 2853, 1619, 1583, 1513, 1421, 1397, 1299, 1266, 1246, 1134, 1022, 957, 889, 799, 762 cm^{-1}; **HRMS** (ESI) m/z 234.1275 $[M + H]^+$; calculated for $[C_{17}H_{15}N + H]^+$: 234.1277; **MP** 69–71 ºC, [lit. (Meadows, R. E.; Woodward, S. *Tetrahedron* **2008**, *64*, 1218): 66–68 ºC].

***N*-(3-Methoxybenzyl)naphthalen-1-amine** (**20d**): The product was obtained as colorless liquid [35 mg, 27% (condition C)], R_f = 0.61 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.83 (t, *J* = 7.7 Hz, 2H), 7.50-7.43 (m, 2H), 7.37-7.27 (m, 3H), 7.07-7.04 (m, 2H), 6.88 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 4.72 (brs, 1H), 4.49 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 160.0, 143.2, 140.8, 134.3, 129.8, 128.7, 126.6, 125.8, 124.8, 123.4, 120.0, 119.9, 117.7, 113.3, 112.8, 104.8, 55.3, 48.6; **IR** (film) υ_{max} 3444(br), 3055, 3006, 2926, 1584, 1526, 1488, 1465, 1434, 1408, 1339, 1279, 1264, 1154, 1117, 1084,

1049, 786, 769, 693 cm^{-1}; **HRMS** (ESI) m/z 264.1402 $[M + H]^+$; calculated for $[C_{18}H_{17}NO + H]^+$: 264.1383.

***N*-(3,4-Dimethoxybenzyl)naphtho[2,3-d][1,3]dioxol-5-amine** (**20e**): The product was obtained as colorless solid [44 mg, 26% (condition C)], R_f = 0.55 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.21 (t, *J* = 7.7 Hz, 1H), 7.16-7.13 (m, 2H), 7.10 (s, 1H), 6.99-6.98 (m, 2H), 6.88-6.86 (m, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.01 (s, 2H), 4.38 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.2, 148.4, 147.3,147.2, 143.0, 131.7, 131.2, 125.1, 120.0, 119.7, 117.6, 111.3, 111.1, 104.9, 104.7, 101.0, 97.2, 56.0, 55.9, 48.8; **IR** (film) υ_{max} 3393(br), 2924, 2853, 1537, 1515, 1504, 1470, 1463, 1369, 1245, 1156, 1139, 1128, 1039, 946, 860, 779 cm^{-1}; **HRMS** (ESI) m/z 338.1355 $[M + H]^+$; calculated for $[C_{20}H_{19}NO_4 + H]^+$: 338.1387; **MP** 71–73 ºC.

***N*-(2,3-Dimethoxybenzyl)naphtho[2,3-d][1,3]dioxol-5-amine** (**20f**): The product was obtained as light yellow gel [46 mg, 27% (condition D)], R_f = 0.57 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.22-7.18 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.08 (s, 1H), 7.04-6.99 (m, 2H), 6.89 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.01 (s, 2H), 4.49 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.8, 147.34, 147.31, 147.2, 146.4, 132.5, 131.3, 125.0, 124.2, 121.3, 120.0, 117.9, 117.8, 111.8, 104.8, 101.0, 97.4, 60.9, 55.8, 44.1; **IR** (film) υ_{max} 3415(br), 2923, 2853, 1728, 1500, 1465, 1270, 1246, 1167, 1079, 1040, 1007, 943, 860, 748 cm^{-1}; **HRMS** (ESI) m/z 338.1403 $[M + H]^+$; calculated for $[C_{20}H_{19}NO_4 + H]^+$: 338.1387.

Methyl 2-bromobenzyl(phenyl)carbamate (**22a**): The product was obtained as colorless solid (525 mg, 82%), R_f = 0.35 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.50 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.31-7.25 (m, 3H), 7.20-7.16 (m, 3H), 7.10 (dt, *J* = 7.9, 1.7 Hz, 1H), 4.97 (s, 2H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 141.9, 141.8, 136.7, 132.8, 128.9, 128.7, 127.5, 126.5, 126.3, 122.9, 54.3, 53.2; **IR**

(film) υ_{max} 3059, 2954, 1714, 1598, 1494, 1443, 1383, 1300, 1278, 1233, 1196, 1148, 1027, 751, 698 cm^{-1}; **HRMS** (ESI) m/z 320.0282 $[M + H]^+$; calculated for $[C_{15}H_{14}BrNO_2 + H]^+$: 320.0281; **MP** 70–72 ºC.

***N*-(2-Bromobenzyl)-*N*-phenylacetamide** (**22b**): The product was obtained as yellow gel (517 mg, 87%), R_f = 0.54 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 7.7 Hz, 1.31 Hz, 1H), 7.35-7.24 (m, 4H), 7.12-7.07 (m, 3H), 5.07 (s, 2H), 1.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 142.6, 136.3, 132.7, 130.2, 129.6, 128.8, 128.0, 127.5, 123.8, 121.1, 52.4, 22.7; **IR** (film) υ_{max} 3062, 2923, 1662, 1595, 1495, 1391, 1299, 1277, 1231, 1025, 779, 738, 700 cm^{-1}; **HRMS** (ESI) m/z 304.0347 $[M + H]^+$; calculated for $[C_{15}H_{14}BrNO + H]^+$: 304.0332.

***N*-(2-Bromobenzyl)-*N*-phenylbenzamide** (**22c**): The product was obtained as colorless solid (659 mg, 90%), R_f = 0.4 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.40-7.38 (m, 2H), 7.28-7.21 (m, 2H), 7.18-7.14 (m, 2H), 7.12-7.03 (m, 4H), 6.97-6.495 (m, 2H), 5.27 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 143.3, 136.4, 135.7, 132.8, 129.8, 129.2, 129.0, 128.8, 128.7, 127.8, 127.6, 127.4, 126.7, 123.4, 53.7; **IR** (film) υ_{max} 3055, 2927, 1644, 1594, 1496, 1384, 1303, 1281, 1228, 1151, 1026, 746, 698 cm^{-1}; **HRMS** (ESI) m/z 366.0515 $[M + H]^+$; calculated for $[C_{20}H_{16}BrNO + H]^+$: 366.0488; **MP** 105–108 ºC.

Methyl 2-bromo-4,5-dimethoxybenzyl(phenyl)carbamate (**23a**): The product was obtained as colorless solid (700 mg, 92%), R_f = 0.50 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.29-7.25 (m, 2H), 7.30-7.17 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.92 (s, 1H), 6.84 (s, 1H), 4.91 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 148.8, 148.5, 141.5, 141.46, 128.9, 128.8, 126.9, 126.8, 126.7, 115.4, 56.1, 56.06, 53.5, 53.2; **IR** (film) υ_{max} 2954, 2930, 2852, 1710, 1599, 1505, 1444, 1378, 1260, 1227,

1208, 1164, 1139, 1030, 858, 767, 701 cm^{-1}; **HRMS** (ESI) m/z 380.0507 $[M + H]^+$; calculated for $[C_{17}H_{18}BrNO_4 + H]^+$: 380.0492; **MP** 116–118 ºC.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-phenylacetamide** (**23b**): The product was obtained as colorless solid (634 mg, 87%), R_f = 0.43 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35-7.30 (m, 3H), 7.02-6.99 (m, 2H), 6.96 (s, 1H), 6.89 (s, 1H), 5.01 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 148.8, 148.5, 142.3, 129.5, 128.6, 128.3, 128.0, 115.0, 114.4, 113.5, 56.1, 56.06, 51.5, 22.7; **IR** (film) υ_{max} 2935, 1659, 1596, 1506, 1439, 1381, 1258, 1223, 1206, 1162, 1030, 801, 700 cm^{-1}; **HRMS** (ESI) m/z 364.0560 $[M + H]^+$; calculated for $[C_{17}H_{18}BrNO_3 + H]^+$: 364.0543; **MP** 111–112 ºC.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-phenylbenzamide** (**23c**): The product was obtained as colorless solid (776 mg, 91%), R_f = 0.42 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26-7.24 (m, 2H), 7.14-7.10 (m, 1H), 7.08-6.96 (m, 6H), 6.84-6.81 (m, 3H), 5.12 (s, 2H), 3.72 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 148.8, 148.6, 142.9, 135.9, 129.7, 128.9, 128.7, 128.6, 127.8, 126.8, 115.3, 113.8, 112.7, 112.4, 56.1, 56.06, 52.7; **IR** (film) υ_{max} 3061, 3004, 2955, 2935, 2842, 1634, 1600, 1504, 1493, 1385, 1258, 1209, 1163, 1076, 1031, 986, 914, 867, 803, 732, 698, 637 cm^{-1}; **HRMS** (ESI) m/z 426.0717 $[M + H]^+$; calculated for $[C_{22}H_{20}BrNO_3 + H]^+$: 426.0699; **MP** 112–114 ºC.

Methyl ((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)(phenyl)carbamate (**24a**): The product was obtained as yellow crystalline solid (626 mg, 86%), R_f = 0.41 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.30-7.26 (m, 2H), 7.21-7.17 (m, 1H), 7.17-7.13 (m, 2H), 6.92 (s, 1H), 6.87 (s, 1H), 5.93 (s, 2H), 4.87 (s, 2H), 3.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 147.6, 147.5, 141.6, 130.0, 129.0, 128.9, 126.6, 112.7, 108.9, 108.86, 101.8, 53.9, 53.2; **IR** (film) υ_{max} 2956, 2923, 1713, 1598, 1501, 1480, 1447, 1383, 1295, 1242, 1108, 1038, 932, 763, 699 cm^{-1}; **HRMS** (ESI) m/z 364.0174 $[M + H]^+$; calculated for $[C_{16}H_{14}BrNO_4 + H]^+$: 364.0179; **MP** 70–73 ºC.

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-phenylacetamide** (**24b**): The product was obtained as colorless solid (627 mg, 90%), R_f = 0.65 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36-7.31 (m, 3H), 7.06 (d, *J* = 6.6 Hz, 2H), 6.94 (s, 1H), 6.89 (s, 1H), 5.96 (s, 2H), 4.97 (s, 2H), 1.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 147.6, 147.57, 142.4, 129.7, 129.6, 128.1, 128.0, 114.4, 112.4, 110.0, 101.7, 52.0, 22.6; **IR** (film) υ_{max} 2926, 1661, 1595, 1495, 1479, 1396, 1242, 1112, 1038, 931, 699 cm^{-1}; **HRMS** (ESI) m/z 348.0247 $[M + H]^+$; calculated for $[C_{16}H_{14}BrNO_3 + H]^+$: 348.0230; **MP** 83–84 ºC.

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-phenylbenzamide** (**24c**): The product was obtained as colorless solid (755 mg, 92%), R_f = 0.53 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26-7.24 (m, 2H), 7.14-7.11 (m, 1H), 7.07-6.96 (m, 5H), 6.94 (s, 1H), 6.86-6.84 (m, 2H), 6.82 (s, 1H), 5.81 (s, 2H), 5.09 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 147.7, 147.6, 143.0, 135.7, 129.8, 129.7, 129.0, 128.8, 127.8, 127.6, 126.8, 113.9, 112.6, 109.3, 101.8, 53.2; **IR** (film) υ_{max} 3060, 2901, 1645, 1595, 1485, 1385, 1242, 1147, 1110, 1038, 932, 735, 699 cm^{-1}; **LRMS** (ESI) m/z 410.0417 $[M + H]^+$; calculated for $[C_{21}H_{16}BrNO_3 + H]^+$: 410.0386; **MP** 96–99 ºC.

Phenanthridine (**2a**): The product was obtained as colorless solid [71 mg, 79% (condition B)], R_f = 0.35 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.27 (s, 1H), 8.60-8.54 (m, 2H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86-7.82 (m, 1H), 7.75-7.64 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 144.4, 132.6, 131.1, 130.1, 128.8, 128.7, 127.5, 127.1, 126.4, 124.1, 122.2, 121.9; **IR** (film) υ_{max} 2923, 2844, 1237, 1033, 957, 889, 773, 747, 722 cm^{-1}; **HRMS** (ESI) m/z 180.0819 $[M + H]^+$; calculated for $[C_{13}H_9N + H]^+$: 180.0808, **MP** 102–105 ºC, [lit. (Kessar, S. V.; Gupta, Y. P.; Balakrishnan, P.; Sawal, K. K.; Mohammad, T.; Dutt, M. *J. Org. Chem.* **1988**, *53*, 1708): 104–105 ºC].

8,9-Dimethoxyphenanthridine (**25**): The product was obtained as colorless crystalline solid [79 mg, 66% (condition B)], R_f = 0.25 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$)

δ: 9.13 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.68-7.59 (m, 2H), 7.31 (s, 1H), 4.10 (s, 3H), 4.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 151.6, 150.0, 143.6, 137.2, 129.8, 128.3, 127.8, 126.7, 123.8, 121.7, 107.8, 101.8, 56.2, 56.1; **IR** (film) υ_{max} 3008, 2935, 2868, 1701, 1614, 1594, 1505, 1470, 1442, 1394, 1293, 1266, 1222, 1202, 1159, 1037, 1023, 847, 811, 762, 733 cm^{-1}; **HRMS** (ESI) m/z 240.1027 $[M + H]^+$; calculated for $[C_{15}H_{13}NO_2 + H]^+$: 240.1019; **MP** 163–165 ºC, [lit. (Narasimhan, N. S.; Chandrachood, P. S.; Shete, N. R.; *Tetrahedron* **1981**, *37*, 825): 164 ºC].

[1,3]Dioxolo[4,5-j]phenanthridine (**2b**): The product was obtained as colorless crystalline solid [86 mg, 77% (condition B)], R_f = 0.29 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H), 8.35 (d, *J* = 8.03 Hz, 1H), 8.13 (d, *J* = 8. 0 Hz, 1H), 7. 98 (s, 1H), 7.70-7.65 (m, 1H), 7.63-7.59 (m, 1H), 7.32 (s, 1H), 6.15 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 151.5, 148.2, 144.0, 130.3, 130.0, 128.0, 126.7, 124.3, 123.0, 122.0, 105.5, 101.9, 100.0; **IR** (film) υ_{max} 2921, 1485, 1464, 1395, 1256, 1226, 1198, 1095, 1036, 940, 857, 755 cm^{-1}; **HRMS** (ESI) m/z 224.0732 $[M + H]^+$; calculated for $[C_{14}H_9NO_2 + H]^+$: 224.0706; **MP** 121–123 ºC, [lit. (Banwell, Martin G.; Lupton, David W.; Ma, Xinghua; Renner, Jens; Sydnes, Magne O. *Org. Lett.* **2004**, *6*, 2741): 111–125 ºC].

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-(3-methoxyphenyl)acetamide** (**27a**): The product was obtained as colorless solid (686 mg, 87%), R_f = 0.47 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.22 (t, *J* = 8.1 Hz, 1H), 6.96 (s, 1H), 6.90 (s, 1H), 6.84 (dd, *J* = 8.3 Hz, 2.07 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 4.99 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H) , 3.75 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 160.3, 148.8, 148.5, 143.4, 130.1, 128.7, 120.5, 115.0, 114.4, 114.1, 113.4, 56.1, 55.4, 51.4, 22.6; **IR** (film) υ_{max} 2934, 2839, 1660, 1652, 1601, 1505, 1455, 1381, 1260, 1213, 1163, 1030, 800, 698 cm^{-1}; **HRMS** (ESI) m/z 394.0646 $[M + H]^+$; calculated for $[C_{18}H_{20}BrNO_4 + H]^+$: 394.0648; **MP** 109–111ºC.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-*N*-(3-methoxyphenyl)benzamide** (**27b**): The product was obtained as colorless gel (822 mg, 90%), R_f = 0.19 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.30-7.28 (m, 2H), 7.19-7.16 (m, 1H), 7.12-7.09 (m, 2H), 6.99 (s, 1H), 6.95-6.90 (m, 1H), 6.87 (s, 1H), 6.56-6.53 (m, 1H), 6.41-6.40 (m, 2H), 5.13 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 159.8, 148.7, 148.6, 144.1, 135.9, 129.8, 129.5, 128.7, 128.5, 127.9, 120.1, 115.3, 113.7, 113.5, 112.6, 112.4, 56.13, 56.06, 55.3, 52.7; **IR** (film) υ_{max} 3005, 2931, 2845, 1650, 1645, 1601, 1505, 1488, 1455, 1378, 1316, 1284, 1260, 1214, 1164, 1031, 986, 856, 799, 699 cm^{-1}; **HRMS** (ESI) m/z 456.0821 $[M + H]^+$; calculated for $[C_{23}H_{22}BrNO_4 + H]^+$: 456.0805.

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-(3-methoxyphenyl)acetamide** (**28a**): The product was obtained as colorless solid (711 mg, 94%), R_f = 0.65 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.23 (t, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 6.89 (s, 1H), 6.84 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 5.95 (s, 2H), 4.94 (s, 2H), 3.76 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 160.3, 147.60, 147.56, 143.6, 130.2, 129.7, 120.4, 114.3, 113.9, 113.4, 112.4, 110.0, 101.7, 55.4, 51.9, 22.6; **IR** (film) υ_{max} 2916, 1660, 1601, 1480, 1393, 1284, 1231, 1164, 1112, 1037, 931, 871, 786, 697 cm^{-1}; **HRMS** (ESI) m/z 378.0364 $[M + H]^+$; calculated for $[C_{17}H_{16}BrNO_4 + H]^+$: 378.0335; **MP** 120–122 ºC.

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-(3-methoxyphenyl)benzamide** (**28b**): The product was obtained as colorless gel (775 mg, 88%), R_f = 0.38 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37-7.35 (m, 2H), 7.24-7.21 (m, 1H), 7.17-7.14 (m, 2H), 7.01-6.97 (m, 2H), 6.91 (s, 1H), 6.60 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.52-6.49 (m, 2H), 5.90 (s, 2H), 5.14 (s, 2H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 159.9, 147.7, 147.6, 144.2, 135.8, 129.9, 129.8, 129.6, 128.7, 127.8, 119.9, 113.9, 113.3, 112.6, 112.4, 109.2, 101.8, 55.3, 53.2; **IR** (film) υ_{max} 3060, 2905, 1651, 1645, 1601, 1503, 1480, 1386, 1362,

1284, 1234, 1204, 1165, 1110, 1037, 986, 931, 854, 783, 724, 699 cm^{-1}; **HRMS** (ESI) m/z 440.0508 $[M + H]^+$; calculated for $[C_{22}H_8BrNO_4 + H]^+$: 440.0492.

3,8,9-Trimethoxyphenanthridine (**29a**): The product was obtained as yellow gel [79 mg, 59% (condition B)], R_f = 0.16 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H), 8.30 (d, *J* = 9.1 Hz, 1H), 7.75 (s, 1H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.31 (s, 1H), 7.27 (s, 1H), 4.12 (s, 3H), 4.05 (s, 3H), 3.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 153.4, 151.6, 149.3, 144.9, 128.8, 122.9, 120.7, 118.1, 118.0, 109.1, 107.8, 101.3, 56.2, 56.1, 55.6; **IR** (film) υ_{max} 2925, 2854, 1616, 1505, 1470, 1391, 1267, 1204, 1165, 1039, 1020, 828, 806 cm^{-1}; **HRMS** (ESI) m/z 270.1143 $[M + H]^+$; calculated for $[C_{16}H_{15}NO_3 + H]^+$: 270.1125.

1,8,9-Trimethoxyphenanthridine (**29b**): The product was obtained as yellow gel [26 mg, 19% (condition B)], R_f = 0.36 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.19 (s, 1H), 9.04 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 4.16 (s, 3H), 4.14 (s, 3H), 4.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 152.8, 151.5, 149.2, 128.6, 127.7, 122.2, 121.7, 115.1, 110.0, 108.4, 108.0, 107.8, 56.05, 56.0, 55.9; **IR** (film) υ_{max} 2925, 2855, 1599, 1505, 1470, 1393, 1264, 1245, 1211, 1158, 1081, 1023, 970, 867, 812, 758 cm^{-1}; **HRMS** (ESI) m/z 270.1142 $[M + H]^+$; calculated for $[C_{16}H_{15}NO_3 + H]^+$: 270.1125.

3-Methoxy-[1,3]dioxolo[4,5-j]phenanthridine (**29c**): The product was obtained as light yellow solid [90 mg, 71% (condition B)], R_f = 0.33 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.03 (s, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 7. 78 (s, 1H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.28 (s, 1H), 7.26-7.24 (m, 1H), 6.13 (s, 2H), 3.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 152.0, 151.6, 147.4, 145.6, 130.6, 123.2, 122.0, 118.5, 118.1, 109.3, 105.4, 101.8, 99.4, 55.5; **IR** (film) υ_{max} 2925, 2858, 1610, 1469, 1267, 1181, 1080, 1034, 936, 814 cm^{-1}; **HRMS** (ESI) m/z 254.0826 $[M + H]^+$; calculated for $[C_{15}H_{11}NO_3 + H]^+$: 254.0812; **MP** 192

ºC, [lit. (Rosa, A. M.; Lobo, A. M.; Branco, P. S.; Prabhakar, S.; Pereira, A. M. D. L. *Tetrahedron* **1997**, *53*, 269): 193–195 ºC].

1-Methoxy-[1,3]dioxolo[4,5-j]phenanthridine (**29d**): The product was obtained as yellow solid [28 mg, 22% (condition C)], R_f = 0.5 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.08 (s, 1H), 8.96 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7. 27 (t, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 2H), 4.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 152.2, 151.1, 147.1, 145.9, 129.9, 127.5, 123.7, 122.5, 115.4, 107.5, 106.2, 105.4, 101.8, 55.8; **IR** (film) υ_{max} 2924, 2852, 1587, 1464, 1263, 1241, 1228, 1106, 1077, 1039, 934, 868, 814, 761 cm^{-1}; **HRMS** (ESI) m/z 254.0827 $[M + H]^+$; calculated for $[C_{15}H_{11}NO_3 + H]^+$: 254.0812; **MP** 188 ºC, [lit. (Rosa, A. M.; Lobo, A. M.; Branco, P. S.; Prabhakar, S.; Pereira, A. M. D. L. *Tetrahedron* **1997**, *53*, 269): 185–188 ºC].

***N*-(2-Bromo-4,5-dimethoxybenzyl)aniline** (**31a**): The product was obtained as colorless solid (580 mg, 90%), R_f = 0.25 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.17 (t, *J* = 7.9 Hz, 2H), 7.03 (s, 1H), 6.94 (s, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.31 (s, 2H), 3.85 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 148.6, 147.9, 130.3, 129.3, 117.9, 115.7, 113.2, 113.1, 112.3, 56.2, 56.1, 48.4; **IR** (film) υ_{max} 3408, 2934, 2840, 1603, 1505, 1464, 1436, 1386, 1326, 1260, 1208, 1156, 1030, 955, 861, 799, 751, 694 cm^{-1}; **LRMS** (ESI) m/z 322.0477 $[M + H]^+$; calculated for $[C_{15}H_{16}BrNO_2 + H]^+$: 322.0437; **MP** 85 ºC, [lit. (Gaertzen, O.; Buchwald, S. L. *J. Org. Chem.* **2002**, *67*, 465): 86 ºC].

***N*-((6-Bromobenzo[d][1,3]dioxol-5-yl)methyl)aniline** (**31b**): The product was obtained as light yellow solid (563 mg, 92%), R_f = 0.5 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.18 (t, *J* = 7.6 Hz, 2H), 7.02 (s, 1H), 6.92 (s, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 2H), 4.29 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.63, 147.57, 147.49, 131.6, 129.3, 117.9,113.3, 113.1, 112.8, 109.2, 101.7, 48.4; **IR** (film) υ_{max}

3420, 2900, 1603, 1505, 1480, 1366, 1329, 1240, 1114, 1039, 932, 864, 830, 751, 693 cm^{-1}; **HRMS** (ESI) m/z 306.0136 $[M + H]^+$; calculated for $[C_{14}H_{12}BrNO_2 + H]^+$: 306.0124; **MP** 97 ºC, [lit. (Buden, M. E.; Dorn, V. B.; Gamba, M.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **2010**, *75*, 2206): 96–97 ºC].

***N*-(3,4-Dimethoxybenzyl)-*N*-methylnaphthalen-1-amine** (**37**): The product was obtained as light yellow solid (78 mg, 51%, scheme 10, entry 6), R_f = 0.4 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.36-8.34 (m, 1H), 7.85-7.82 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.50-7.44 (m, 2H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.94-6.93 (m, 1H), 6.88-6.83 (m, 2H), 4.24 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 2.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 148.9, 148.1, 134.9, 131.3, 129.2, 128.4, 125.8, 125.7, 125.3, 123.8, 123.2, 120.4, 115.8, 111.4, 110.9, 61.0, 55.9, 55.8, 41.6; **IR** (film) υ_{max} 3052, 2957, 2934, 2833, 1593, 1575, 1515, 1463, 1454, 1397, 1263, 1236, 1153, 1139, 1030, 802, 776 cm^{-1}; **HRMS** (ESI) m/z 308.1636 $[M + H]^+$; calculated for $[C_{20}H_{21}NO_2 + H]^+$: 308.1645; **MP** 64-66 ºC.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C, and mass spectrum of all new compounds, including CIF file of compounds **2b**, **3j**, and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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