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Shyamal Kanti Bera, Md Toufique Alam, and Prasenjit Mal

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C-N Coupling *via* Antiaromatic Endocyclic Nitrenium Ion

Shyamal Kanti Bera,‡ Md Toufique Alam‡ and Prasenjit Mal *

School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, PO Bhimpur-Padanpur, Via Jatni, District Khurda, Odisha 752050, India,

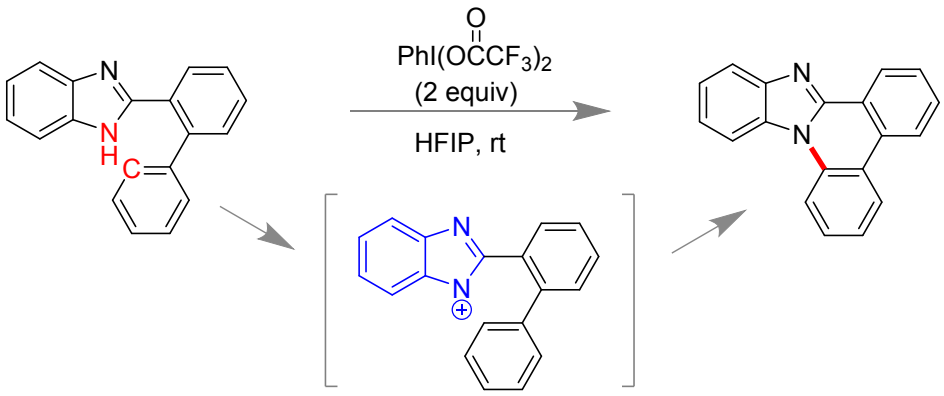
E-mail: pmal@niser.ac.in

‡ Equal Contributing Authors

ABSTRACT:

Herein, we report a C-N coupling reaction *via* antiaromatic endocyclic nitrenium ion. The nitrenium ion intermediate was generated by combination of iodine(III) reagent $PhI(OCOCF_3)_2$ and N-H center of benzimidazole units at ambient laboratory condition. Metal-free synthesis of benzimidazole-fused phenanthridine derivatives were achieved in good to excellent yields.

TOC GRAPHIC



antiaromatic and endocyclic nitrenium ion

INTRODUCTION

The nitrenium ion chemistry rose to prominence among synthetic chemists since beginning.[1] The combinations of amine or amine derivatives with hypervalent iodine(III) reagents[2-8] generally produce nitrenium ion.[9,10] The divalent nitrogen-containing species with six electrons in its valence shell with positive charge on nitrogen is recognized as nitrenium ion (Figure 1a).[11,12] Nitrenium ions are isoelectronic with carbene family having two non-bonding electrons. Nitrenium ion is considered as one of the most important synthetic intermediates in innumerable chemical transformations.[13-18] Depending on the nature and stability of nitrenium ion, many oxidative transformations are reported for the preparation of functional molecules of interests using exocyclic nitrenium ions.[19,20] Due to the electron spin orientation nitrenium ions exist in two different forms *i.e.*, singlet state and triplet state (Figure 1a).[21] In Figure 1b, generation of nitrenium ion is shown from the mixtures of amine or amide with iodine(III) reagents. In general, nitrenium ion is electrophilic and highly reactive intermediate with the formula of $RR'N^{+}$.[22,23]

The Hückel aromatic and antiaromatic systems consist of [4n + 2] or [4n] delocalized circuits electrons, respectively and display ring currents around their perimeters.[24] The antiaromatic compounds are highly reactive and unstable. Therefore the existence of antiaromatic compounds are often found in porphyrinoid systems[25,26] or in large ring macrocycles.[27] However, in case of small molecules the antiaromaticity is demonstrated in acene systems having1,4-diazapentalene core.[28] The mixture of iodine(III) reagent $PhI(OCOCF_3)_2$ (PIFA) and N-H center of benzimidazole scaffold produced endocyclic nitrenium ion which has 4nπ system and is considered to be antiaromatic. The antiaromatic transition state is possibly stabilized *via* resonance. Interestingly, limited reports are available in which endocyclic and antiaromatic nitrenium ions are directly used for synthesis.[23] Falvey and co-workers

demonstrated the existence of endocyclic and antiaromatic nitrenium ions through spectroscopic investigations and theoretical calculations.[23,29] The term endocyclic was documented to demonstrate that nitrenium ions having cationic nitrogen contained inside a ring and possesses antiaromatic character (Figure 1c).[29] Herein, we report the synthesis of phenanthridine derivatives *via* C-N coupling reaction. And, demonstrated the use of antiaromatic and endocyclic nitrenium ions as the intermediate which were directly generated from benzimidazole system using iodine(III) reagent $PhI(OCOCF_3)_2$ (PIFA, Figure 1d).

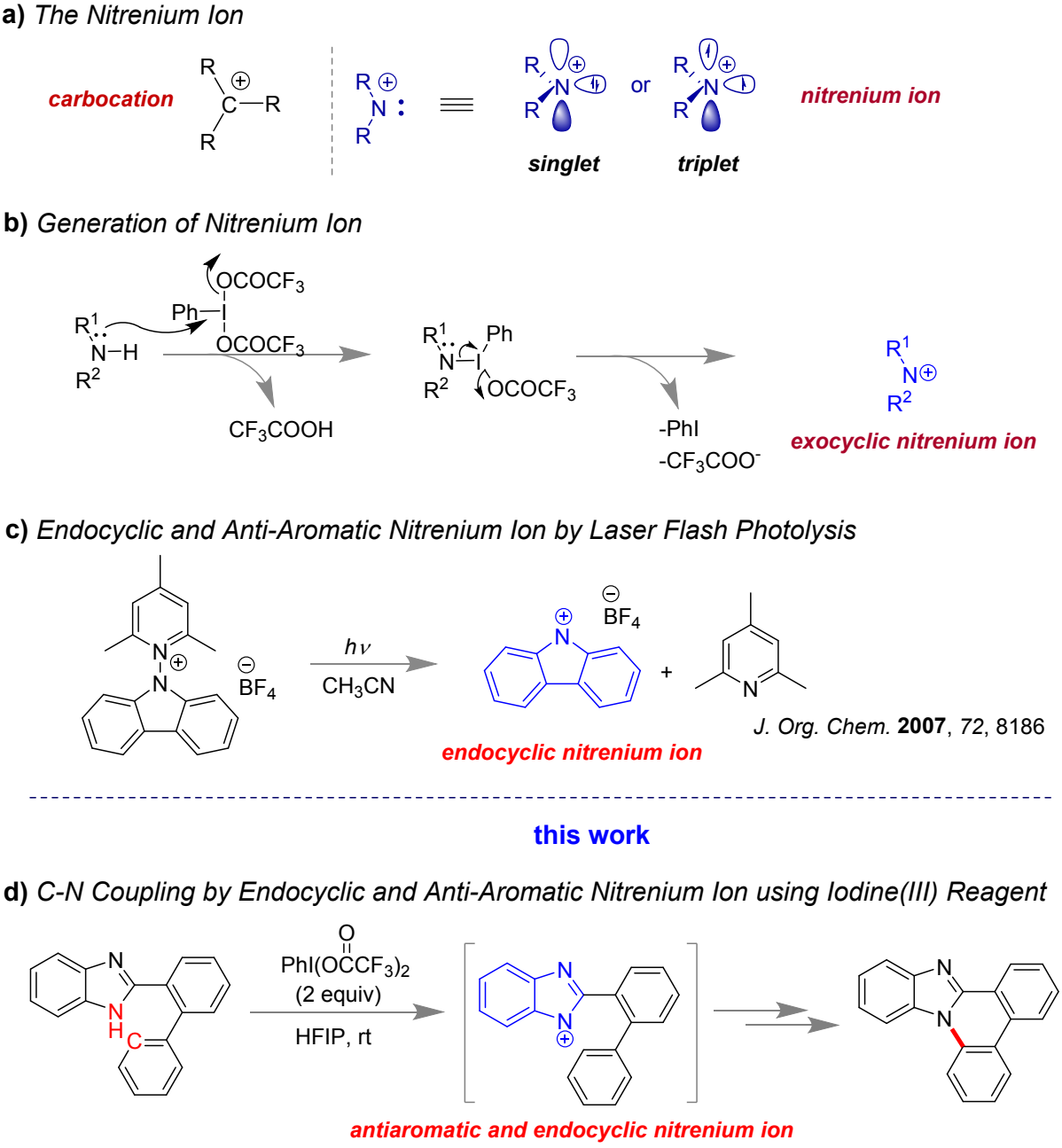


Figure 1. a) The nitrenium ion. b) Generation of nitrenium ion. c) Using laser flash photolysis Falvey and co-workers reported the generation and detection of endocyclic and antiaromatic nitrenium ion.[29] d) Our current work on the C-N coupling reaction based on the generation of endocyclic and antiaromatic nitrenium ion using iodine(III) reagent PIFA.

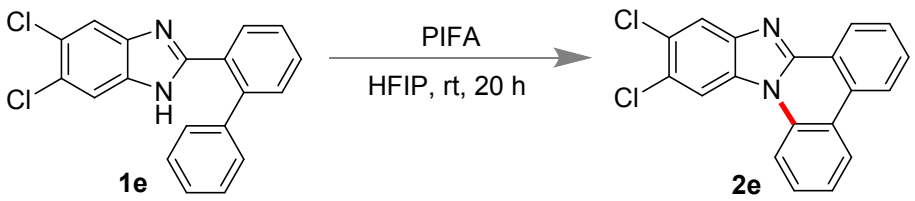
RESULTS AND DISCUSSION

Nitrogen-containing fused heteroaromatic compounds having phenanthridine moiety are ubiquitous in many pharmaceuticals and natural products.[30] Owing to extensive π-conjugation, these type of compounds are utilized as organic semiconductors and luminescent materials.[31] For example, 1,2-disubstituted (hetero)aryl-fused benzimidazoles acts as an electron-transporting and emission functional units.[32,33] Due to the planarity of the system, phenanthridine moiety shows the ability to bind with human telomere derived g-quadruplexes.[34] Considerable efforts have been paid for developing the methods for synthetic transformations of (hetero)aryl-fused phenanthridines using metal catalyst.[31,35,36] Moreover, this type of methodology suffers from disadvantages like metal contamination in products, reusability of metal catalyst, requirements of multistep paths, etc.[37] We anticipate that our current N-H/C-H arylation method (Figure 1c) using PIFA in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for the preparation of benzimidazole-fused phenanthridines can be considered as the easiest approach known in literature.

Towards optimization of the reaction condition, compound 2-([1,1'-biphenyl]-2-yl)-5,6-dichloro-1H-benzo[d]imidazole (**1e**) was chosen as a model substrate (Table 1). When **1e** was treated with 2.0 equiv of PIFA in dichloromethane, the product **2e** was isolated in 57% yield after 20 h of stirring at room temperature (entry 1). However, using polar protic solvent such as ethanol (EtOH) and methanol (MeOH), trace amount of product formation was observed. However, in water no product was obtained (entry 10). When the reaction was carried out in solvents DCE (1,2-dichloroethane), TFE (2,2,2-trifluoroethanol), CH_3CN (acetonitrile) and DMF, yield of the products were found to be poor. Contrastingly, in non-polar solvents like benzene and toluene, 70% and 40% yield of final products were obtained, respectively. In this reaction, HFIP was found to be the best among the solvents examined (entry 7). The reaction

did not proceed in absence of any oxidant (entry 16). Upon lowering the equivalence of PIFA, inferior results were obtained (entries 17-18). Attempts to the use of $PhI(OAc)_2$ (PIDA) instead of PIFA did not make any appreciable change in yield (entry 19). The oxidizing ability of PIDA is much less than that of PIFA. In case of PIDA, under the stander condition 44% yield of final products were obtained and 52% of the starting material was recovered. Use of molecular iodine was also found to be unsuccessful (entry 20). Finally, the most appropriate condition was recognized when the reaction was performed using PIFA (2.0 equiv) in HFIP. Under this optimized condition, the final product 11,12-dichlorobenzo[4,5]imidazo[1,2-f]phenanthridine (**2e**) was isolated in near quantitative (98%) yield within 20 h at room temperature (entry 7). In addition, using PhIO the product **2e** was obtained in 48% yield (entry 21).

Table 1. Condition Optimization.[a]



Entry	Reagent (equiv)	Solvent	Yield (%)[b]
1	PIFA (2)	DCM	57
2	PIFA (2)	DCE	28
3	PIFA (2)	CH_3CN	38
4	PIFA (2)	Benzene	70
5	PIFA (2)	Toluene	40
6	PIFA (2)	TFE	25
7	PIFA (2)	HFIP	98
8	PIFA (2)	DMSO	60
9	PIFA (2)	DMF	35
10	PIFA (2)	H_2O	-[c]

11	PIFA (2)	EtOH	07
12	PIFA (2)	MeOH	06
13	PIFA (2)	Acetone	05
14	PIFA (2)	EtOAc	09
15	PIFA (2)	HFIP:DCM (1:1)	60
16	-[d]	HFIP	-[c]
17	PIFA (1)	HFIP	67
18	PIFA (1.5)	HFIP	80
19	PIDA (2)	HFIP	44
20	I_2 (2)	HFIP	-[c]
21	PhIO (2)	HFIP	48

[a]Reaction conditions: 0.176 mmol of **1e** and 0.353 mmol of PIFA (2 equiv) in 1.0 mL HFIP at room temperature for 20 h. [b]Yield of isolated product after purification through silica-gel column chromatography. [c]No reaction. [d]Without any reagent.

Under standard conditions, the substrate scope was explored for the synthesis of highly substituted fused heterocycles *via* C-N bond formation reaction. Symmetrically substituted or disubstituted benzimidazoles having various neutral, electron rich and electron poor functional groups could be efficiently converted into benzimidazole-fused phenanthridine derivatives (Figure 2). Benzimidazoles bearing ethyl, fluoro, acetyl groups of the 2-aryl moiety afforded **2b**, **2c** and **2d** with 96%, 95% and 94%, respectively. Similarly, the unsubstituted aryl skeleton at the 2-position of benzimidazole produced **2a** with 91% yield of product. Again the substitutions in 2-aryl moiety by electron withdrawing (fluoro, chloro, acetyl, trifluoromethyl), as well as electron donating groups (such as ethyl, ^{t}butyl) of the 5,6-dichloro benzimidazoles, could be successfully converted to corresponding products (**2f- 2k**) in good to excellent yields. However, 5,6-dimethyl benzimidazoles with a variety of substituents (ethyl, ^{t}butyl, fluoro, chloro and acetyl) at the 2-aryl group also afforded the respective product (**2m-2q)** in good

yields. The unsubstituted aryl group at 2-position of 5,6-dichloro and 5,6-dimethyl benzimidazoles gave **2e** and **2I** with 98% and 96% yield, respectively. The incorporation of the electron withdrawing fluoro group in the meta-position of the 2-aryl moiety of 5,6-dichloro and 5,6-dimethyl benzimidazoles correspondingly provided **2r** and **2s** with 95% and 94% yield, respectively. Overall, electron deficient functional group containing substrates took longer time than that of electron rich substrates. Notably, substrate **1e** was prepared by the reaction of commercially available *o*-phenylene diamines and formylbiphenyl derivatives in presence of dimethyl formamide (DMF) as a solvent at 80 ºC (supporting information).

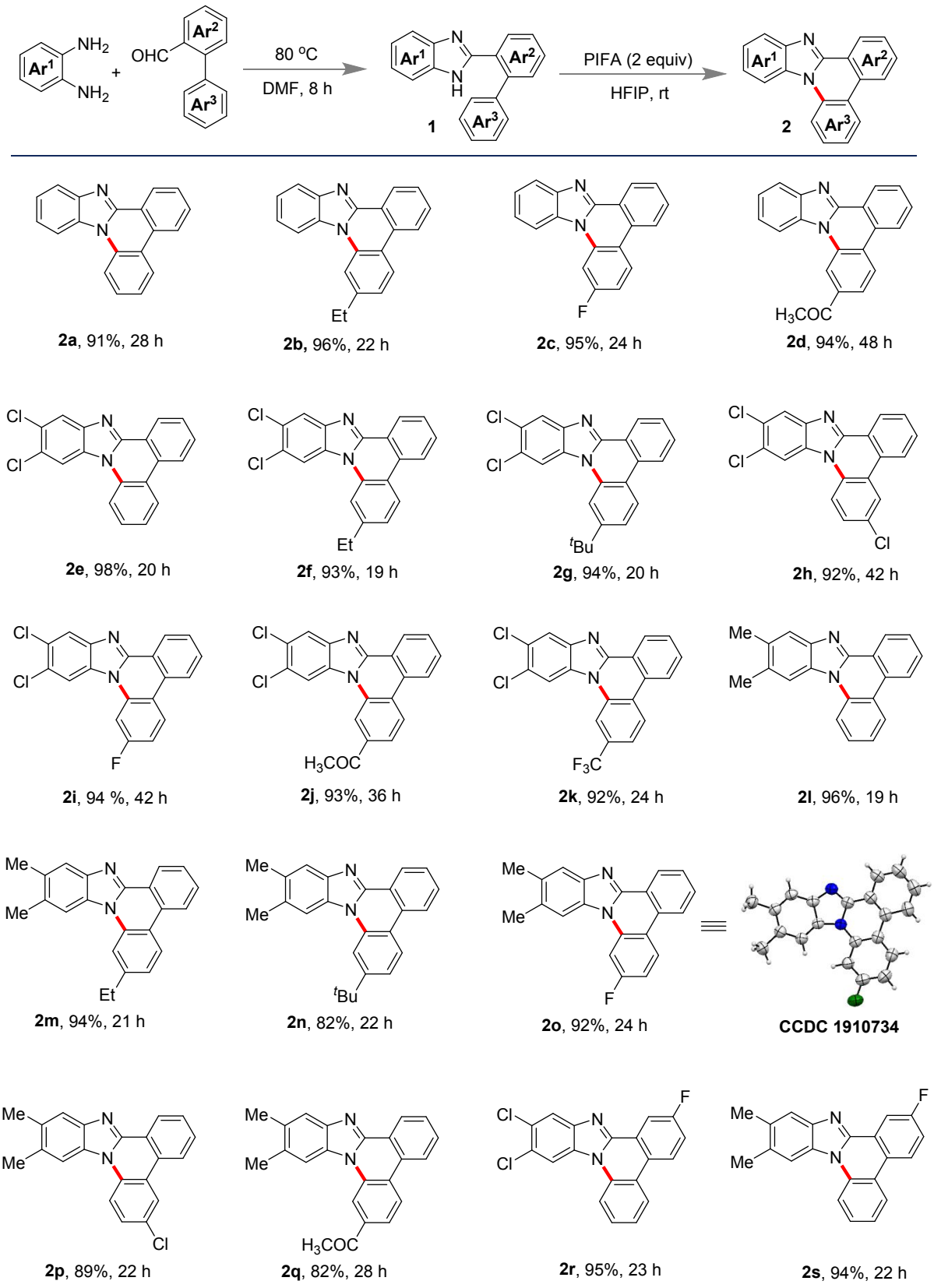


Figure 2. Functional-group tolerance in synthesis of benzimidazole-fused phenanthridines.

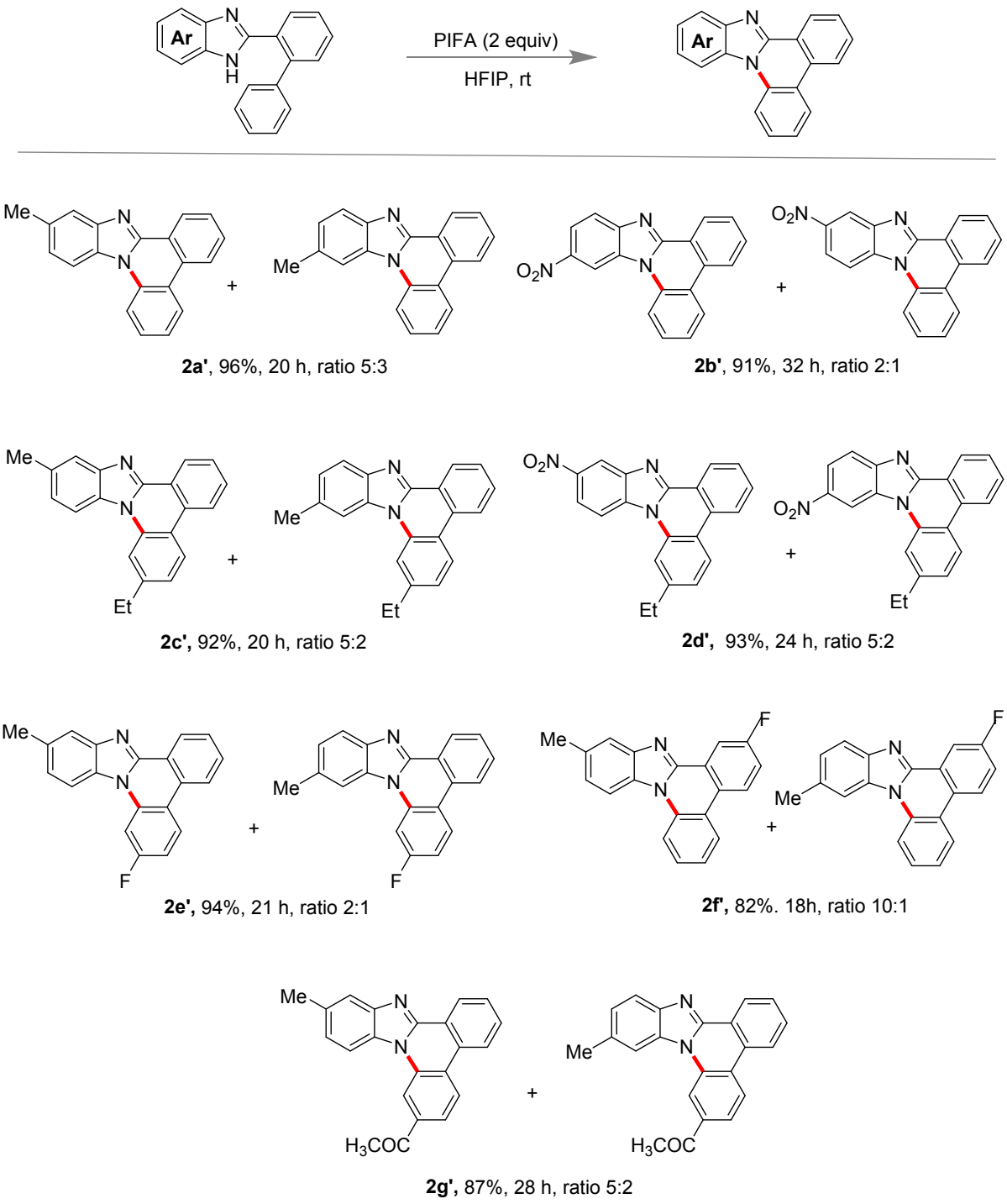


Figure 3. Inseparable mixture of regioisomers.

The substrates scope for this methodology was further extended to unsymmetrically substituted or mono substituted benzimidazoles, which furnished the mixture of regioisomers under

standard reaction condition (Figure 3). Thus, for the mono substituted benzimidazoles, there are two possibilities for the formation of products. One is 11-substituted and another is 12-substituted (hetero)aryl-fused phenanthridines. The aryl group at 2-position of 3-methyl and 3-nitro benzimidazoles led to 5:3 and 2:1 mixture of regioisomers **2a'** and **2b'** with 96% and 91% yield, respectively. Similarly, 3-methyl and 3-nitro benzimidazoles bearing ethyl group in the 2-aryl moiety also afforded 5:2 mixture of regioisomers **2c'** and **2d'** with excellent yield of products. Nevertheless, the electron withdrawing fluoro group in the *meta*-position of 2-aryl moiety of 3-methyl benzimidazole gave 10:1 mixture of regioisomers **2f'**. Again, 3-methyl benzimidazoles bearing fluoro and acetyl group in the 2-aryl moiety also produced 2:1 and 5:2 mixture of regioisomers **2e'** and **2g'** with 94% and 87% yield of products.

To establish the mechanism of the reaction, control experiments were performed which are shown in (Figure 4). In presence of TEMPO[19] at standard condition, reaction proceeded smoothly and giving 98% of the product as isolated (based on recovery yield, Figure 4a). This fact clearly indicates that radical pathway for the reaction was not operative. For the generation of nitrenium ion the presence of N-H group in the benzimidazole core was one of the essential criteria. After the removal of N-H bond in presence of iodine(III) reagent the antiaromatic transition state was created. This hypothesis was further proved when N-Me substituted benzimidazole moiety (**2ab**) was found to be unreactive under standard condition (Figure 4b).

Based on control experiments and literature precedence[38] a plausible mechanism is proposed in Figure 4c. Initially, substrate **1a** was reacted with PIFA to form ammonium ion intermediate **3**,[39] which could undergo proton abstraction by trifluoroacetate ion and followed by elimination of trifluoroacetic acid and iodobenzene to produce nitrenium ion intermediate **4.** Following, the nitrenium ion **4** underwent C-N bond formation *via* cyclization to form the Wheland

intermediate **5** or **6**.[40,41] Finally, the product **2a** was formed after elimination of one hydrogen by trifluoroacetate anion. Trifluoroacetic acid is generated in the reaction mixture as a by-product, which can also protonate the N-H proton that's why higher concentration (2 equiv) of oxidant PIFA was required for the conversion.

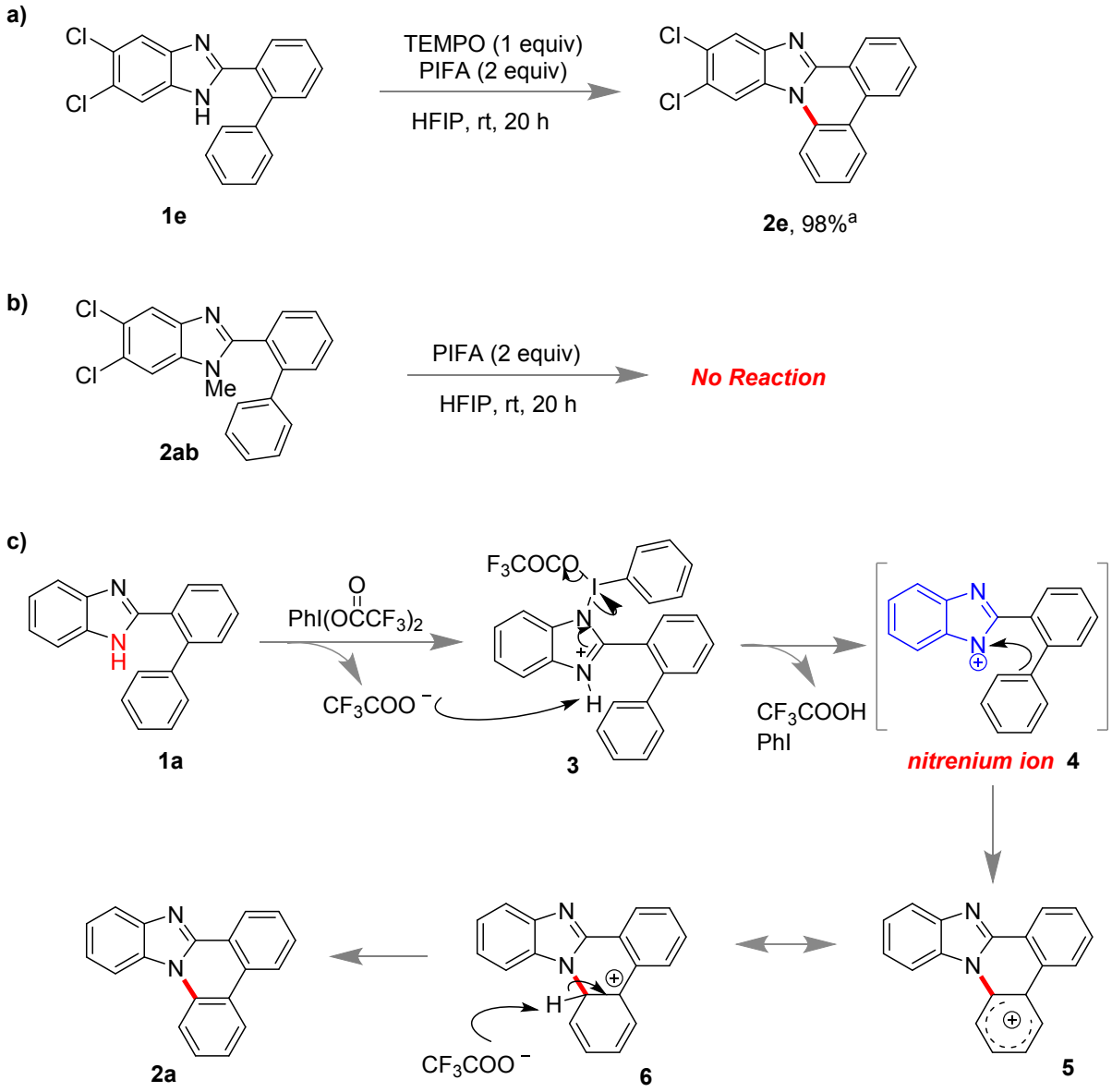


Figure 4. a) and b) Control experiments. c) Plausible mechanism.

Towards exploring the synthetic utility of the method, we have carried out the same transformation using PhI (iodobenzene, 1.0 equiv)-*m*CPBA (1.5 equiv) in HFIP as the

organocatalytic condition[42] and the product **2e** was isolated in 94% (based on recovered starting materials, Figure 5a). It is established in literature that PhIO is the reactive intermediate from PhI-mCPBA combination,[42] however, HFIP stabilizes the iodinium intermediates.[43,44] Similar observation we have also made when PhI was treated with mCPBA in presence of HFIP (supporting information, Figure S107). Furthermore, the efficiency of the method was verified by scaling up the reaction up to ~4.0 mmol of substrate **1c** (gram scale, Figure 5b). Under optimized condition when the reaction was performed with 2-(4'-fluoro-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole **1c**, fluorobenzo[4,5]imidazo[1,2-f]phenanthridine **2c** was isolated in 96% of yield after 20 h of reaction time.

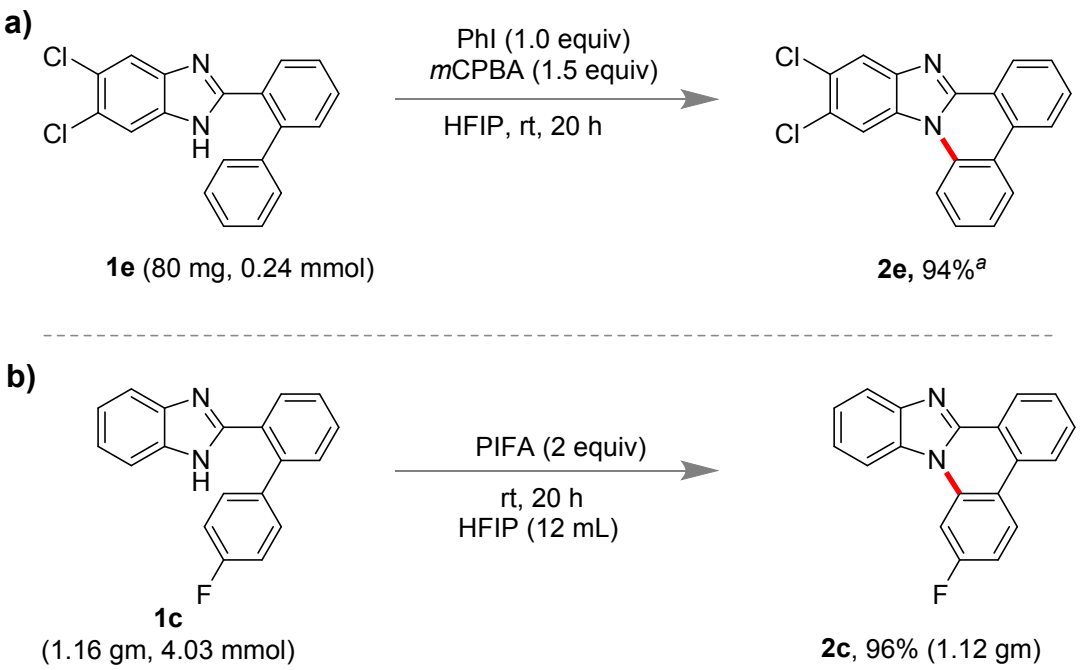


Figure 5. a) Synthesis of benzimidazole-fused phenanthridines in organocatalytic condition. b) Gram scale synthesis of 2-fluorobenzo[4,5]imidazo[1,2-f]phenanthridine (**2c**). [a]Based on recovered starting material.

Due to extended π-conjugation nitrogen-containing fused heteroaromatic compounds become potential fluorophores and shown to have strong luminescence behavior. For selected

benzimidazole-fused phenanthridines (**2f, 2d, 2o, 2r, 2a**) absorption and emission properties are shown in Figure 6. For the acetyl containing benzimidazole-fused phenanthridine **2d**, high bathochromically shifted emission behavior was observed.

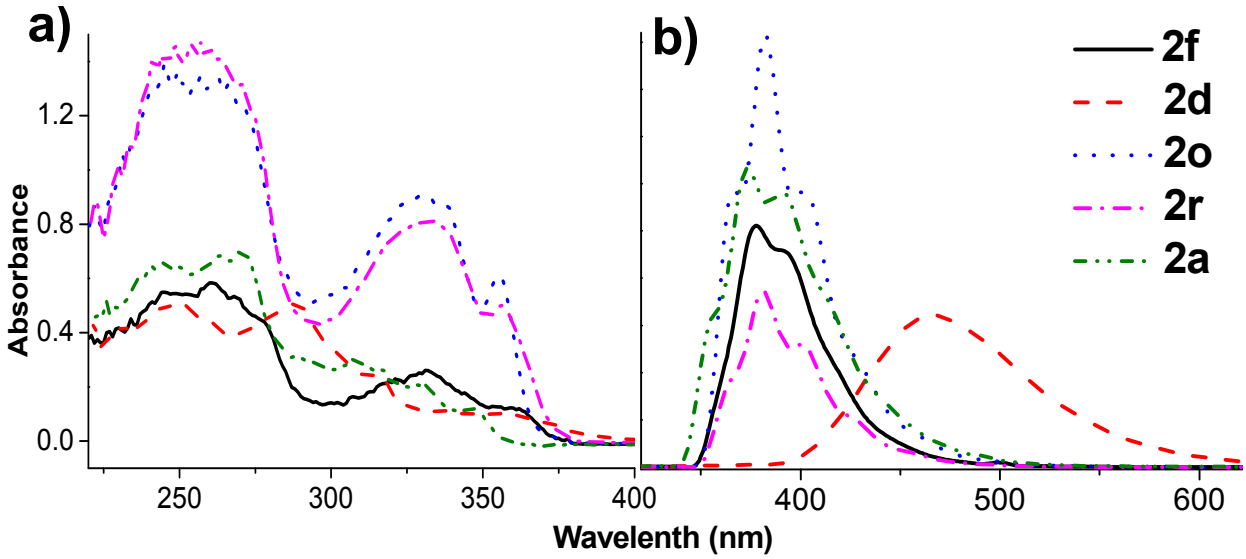


Figure 6. a) Absorption and b) emission spectra for selected compounds. Concentration: 3 × 10^{-5} M in dichloromethane.

CONCLUSION

In summary, we have shown here that direct C-N coupling reaction could be done *via* antiaromatic endocyclic nitrenium ion and subsequently synthesis of fused heterocycles like benzimidazole-fused phenanthridines were achieved under metal free condition. During the synthesis we have avoided the use of any expensive catalyst (mainly metal based), harsh condition and the reactions were performed using PIFA as a sole reagent. Additionally, ambient condition, commercial viability of iodide reagent, made the methodology more synthetically attractive towards construction of heterocycles. We anticipate that this approach can provide

direct access to various heteroaromatic compounds which might be useful in the synthesis of complex structural motifs.

EXPERIMENTAL SECTION

General Information. Commercially available reagents and solvents were used as received. Column chromatographic purifications of the compounds were performed using silica gel (mesh 230–400) and hexane – ethyl acetate solvent mixtures. NMR spectra were recorded on a 400 MHz or 700 MHz instrument at 25 °C. The chemical shift values are reported in parts per million (ppm) with respect to residual trichloromethane (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). The peak patterns are designated as follows: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; dd: doublet of doublets; td: triplet of doublets; br s: broad singlet. The coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HR-MS) were recorded on an ESI-TOF (time of flight) mass spectrometer. Infrared spectral data are reported in wave number (cm-1). FT-IR spectra were recorded after making thin layer of the compounds on the surface of NaCl crystal using dichloromethane. Melting points of the compounds were determined using a digital melting point apparatus and uncorrected.

Representative Procedure for Preparation of 2-([1,1'-biphenyl]-2-yl)-5,6-dichloro-1H-benzo[d]imidazole 1e.[45] A solution of [1,1'-biphenyl]-2-carbaldehyde (500 mg, 2.82 mmol) and the appropriate *o*-phenylenediamine (2.82 mmol) in DMF (5 mL) was heated at 80 °C. The reaction mixture was allowed to stir for 8 h and resulting solution was brought to room temperature and then extracted with ethyl acetate (EtOAc). The organic layer washed with

brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with *n*-Hexane-EtOAc. The compound **1e** was obtained as white solid. (914 mg, 95% yield), R_f = 0.45 (hexane/ethyl acetate 4:1).

Representative Procedure for Preparation of 11,12-Dichlorobenzo[4,5]imidazo[1,2-f]phenanthridine (2e). To a stirred solution of 2-([1,1'-Biphenyl]-2-yl)-5,6-dichloro-1H-benzo[d]imidazole **1e** (60 mg, 0.176 mmol), in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (2.0 mL), PIFA (152 mg, 0.35 mmol) was added slowly at room temperature. The reaction mixture was allowed to stir until completion. Progress of reaction was monitored by TLC using ethyl acetate and hexane as eluent. After the completion of reaction (20 h) resulting solution was evaporated to dryness. The crude residue was purified on silica gel column chromatography (20% EtOAc in hexane) to get the pure product 11, 12-dichlorobenzo[4,5]imidazo[1,2-f]phenanthridine **2e** (59 mg, yield 98%).

2-([1,1'-Biphenyl]-2-yl)-1H-benzo[d]imidazole (1a). R_f = 0.70 (hexane/ethyl acetate 7:3); white solid; yield 71% (440 mg); mp 214−216 °C (lit.[46] mp 212-213 °C); ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.08 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.53 (t, *J* = 8.4 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.25 (d, *J* = 7.7 Hz, 3H), 7.19 (d, *J* = 6.3 Hz, 2H), 7.16 – 7.11 (m, 2H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 152.1, 143.5, 141.0, 140.2, 134.5, 131.1, 130.5, 130.2, 129.9, 128.8, 128.1, 127.4, 127.1, 122.1, 121.2, 118.9, 111.3; IR (KBr) $\tilde{\nu}$ = 3431, 3061, 2981, 2929, 2882, 2733, 1469, 1446, 1432, 1275 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{15}N_2$ $[M + H]^+$ 271.1230, found 271.1247.

2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1b). R_f = 0.45 (hexane/ethyl acetate 4:1); white solid; yield 72% (138 mg); mp 230 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.15 – 7.12 (m, 2H), 7.11-7.08 (m, 4H), 2.55 (q, *J* = 7.7 Hz, 2H), 1.13 (t, *J* = 7.7 Hz, 3H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 152.3, 143.5, 142.5, 140.9, 137.5, 134.5, 131.2, 130.5, 130.1, 129.9, 128.7, 127.6, 127.1, 122.1, 121.2, 118.9, 111.3, 27.7, 15.3; IR (KBr) $\tilde{\nu}$ = 3425, 3058, 2969, 2924, 2857, 1450, 1410, 1282, 1098 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{19}N_2$ $[M + H]^+$ 299.1543, found 299.1530.

2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1c). R_f = 0.60 (hexane/ethyl acetate 7:3); white solid; yield 97% (387 mg); mp 254 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.14 (s, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.7, Hz, 1H), 7.49 – 7.58 (m, 3H), 7.36 (s, 1H), 7.21-7.19 (m, 2H), 7.14 (d, *J* = 4.2 Hz, 2H), 7.09 (t, *J* = 8.4 Hz, 2H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 161.9 (d, $^1J_{C,F}$ = 243.9 Hz), 152.3, 143.9, 140.4, 137.0 (d, $^4J_{C,F}$ = 3.1 Hz), 135.0, 131.5, 131.2 (d, $^3J_{C,F}$ = 8.2 Hz), 131.0, 130.6, 130.4, 128.0, 122.6, 121.8, 119.3, 115.4 (d, $^2J_{C,F}$ = 21.4 Hz), 111.8; IR (KBr) $\tilde{\nu}$ = 3440, 3060, 2922, 1445, 1423, 1279, 1227, 1163 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{14}FN_2$ $[M + H]^+$ 289.1136, found 289.1149.

1-(2'-(1H-Benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (1d). R_f = 0.50 (hexane/ethyl acetate 7:3); white solid; yield 72% (311 mg); mp 276 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.26 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.77 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.65 (td, *J* = 7.7, 1.4 Hz, 1H), 7.59 (td, *J* = 7.7, 1.4 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.16 (m, 2H), 2.53 (s, 3H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 197.6, 151.7, 145.1, 143.5, 139.9, 135.3, 134.6, 131.2, 130.6, 130.2, 130.0, 129.2, 128.1, 128.1, 122.3, 121.4, 118.9, 111.4, 26.7; IR (KBr) $\tilde{\nu}$ = 3418, 2924, 2847, 1678, 1651,

1381, 1269, 1098 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{17}N_2O$ $[M + H]^+$: 313.1335, found 313.1325.

2-([1,1'-Biphenyl]-2-yl)-5,6-dichloro-1H-benzo[d]imidazole (1e). R_f = 0.45 (hexane/ethyl acetate 4:1); white solid; yield 95% (914 mg); mp 249-251 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.85 (s, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.59 (s, 1H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 3H), 7.14 – 7.17 (m, 2H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 154.8, 143.1, 141.1, 139.8, 134.0, 131.0, 130.6, 130.4, 129.2, 128.7, 128.3, 127.5, 127.3, 124.5, 123.9, 120.0, 112.7 ; IR (KBr) $\tilde{\nu}$ = 3095, 2922, 2842, 2364, 2337, 1448, 1428, 1388, 1296, 1101 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{13}Cl_2N_2$ $[M + H]^+$ 339.0450, found 339.0463.

5,6-Dichloro-2-(4'-ethyl-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1f). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 97% (307 mg); mp 285 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.87 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.60 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.07 – 7.12 (m, 4H), 2.55 (q, *J* = 7.7 Hz, 2H), 1.14 (t, *J* = 7.7 Hz, 3H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 154.9, 143.1, 142.7, 140.9, 137.1, 134.0, 131.1, 130.5, 130.4, 129.1, 128.6, 127.7, 127.2, 124.5, 123.9, 120.0, 112.7, 27.7, 15.3; IR (KBr) $\tilde{\nu}$ = 3420, 2966, 2929, 1445, 1428, 1386, 1296, 1096 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{17}Cl_2N_2$ $[M + H]^+$ 367.0763, found 367.0764.

2-(4'-(Tert-butyl)-[1,1'-biphenyl]-2-yl)-5,6-dichloro-1H-benzo[d]imidazole (1g). R_f = 0.45 (hexane/ethyl acetate 4:1); white solid; yield 79% (315 mg); mp 215 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.87 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.54 – 7.50 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 1.23 (s, 9H); $^{13}C\{1H\}$ NMR

(175 MHz, DMSO-d_6) δ 155.0, 149.6, 143.2, 140.8, 136.9, 134.1, 131.2, 130.7, 130.4, 129.1, 128.4, 127.3, 125.1, 124.5, 124.0, 120.1, 112.7, 34.3, 31.1; IR (KBr) $\tilde{\nu}$ = 3417, 2969, 1650, 1445, 1383, 1097 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{20}Cl_2N_2$ $[M + H]^+$ 395.1076, found 395.1084.

5,6-Dichloro-2-(3'-chloro-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1h). R_f = 0.60 (hexane/ethyl acetate 4:1); pale yellow solid; yield 96% (205 mg); mp 226 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.60 (s, 1H), 7.86 (s, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.60 – 7.55 (m, 2H), 7.32 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.29 (s, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 154.4, 143.1, 142.0, 139.6, 134.1, 132.9, 131.1, 130.7, 130.6, 130.0, 129.2, 128.6, 128.2, 127.6, 127.2, 124.7, 124.1, 120.1, 112.8; IR (KBr) $\tilde{\nu}$ = 3418, 3065, 2924, 2857, 1594, 1382, 1296, 1096 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{12}Cl_3N_2$ $[M + H]^+$ 373.0061, found 373.0048.

5,6-Dichloro-2-(4'-fluoro-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1i). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 93% (280 mg); mp 224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.53 (brs, 1H), 7.73 (d, *J* = 7.2 Hz, 3H), 7.67 – 7.59 (m, 2H), 7.54 (dd, *J* = 12.4, 7.2 Hz, 3H), 7.21 – 7.15 (m, 3H), 7.12 – 7.05 (m, 3H); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 161.6 (d, $^1J_{C,F}$ = 244.3 Hz), 154.6 (×2), 142.9, 140.0, 136.2 (d, $^4J_{C,F}$ = 3.2 Hz), 134.1, 131.0, 130.8 (d, $^3J_{C,F}$ = 8.3 Hz), 130.6, 130.4, 129.2, 127.7, 124.3, 120.0, 115.1 (d, $^2J_{C,F}$ = 21.5 Hz), 112.7; IR (KBr) $\tilde{\nu}$ = 3437, 2947, 2855, 1522, 1485, 1455, 1425, 1396, 1304, 1222, 1158, 1106 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{12}Cl_2FN_2$ $[M + H]^+$ 357.0356, found 357.0372.

1-(2'-(5,6-Dichloro-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (1j). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 92% (296 mg); mp 285 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.85 (d, J = 8.4 Hz, 3H), 7.77 (d, J = 7.0 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.55 (m, 3H), 7.30 (d, J = 8.4 Hz, 2H), 2.53 (s, 3H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 197.6, 154.4, 144.7, 143.1, 140.1, 135.4, 134.1, 131.1, 130.7, 130.5, 129.2, 129.1, 128.3, 128.1, 124.7, 124.1, 120.1, 112.8, 26.7; IR (KBr) $\tilde{\nu}$ = 3417, 2924, 2855, 1685, 1653, 1443, 1262, 1096 cm^{-1}; HR-MS (ESI-TOF): m/z calcd for $C_{21}H_{15}Cl_2N_2O$ $[M + H]^+$: 381.0556, found: 381.0570.

5,6-Dichloro-2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1k). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 93% (320 mg); mp 286 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 7.84 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.66 – 7.60 (m, 4H), 7.59 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 154.2, 144.2, 143.1, 139.6, 134.0, 131.1, 130.8, 130.5, 129.6, 129.2, 128.4, 127.8, 127.4, 125.6, 125.0 (q, $^3J_{C,F}$ = 3.9 Hz), 124.7, 124.1, 120.1, 112.8; IR (KBr) $\tilde{\nu}$ = 3440, 2922, 2850, 1653, 1324, 1128, 1078 cm^{-1}; HR-MS (ESI-TOF): m/z calcd for $C_{20}H_{12}N_2Cl_2F_3$ $[M + H]^+$: 407.0324, found: 407.0324.

2-([1,1'-Biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1l). R_f = 0.40 (hexane/ethyl acetate 4:1); orange-red solid; yield 98% (538 mg); mp 248-250 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.68 (dd, J = 7.7, 1.4 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.51 (t, J = 7.0 Hz, 2H), 7.31 (s, 1H), 7.24 (d, J = 7.0 Hz, 3H), 7.18 – 7.14 (m, 2H), 7.08 (s, 1H), 2.27 (s, 6H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 151.1, 142.2, 140.9, 140.2, 133.1, 131.0, 130.6, 130.5, 130.4, 129.7, 129.4, 128.7, 128.1, 127.3, 127.0, 118.9, 111.30, 19.9 (×2); IR (KBr) $\tilde{\nu}$ = 3445,

3057, 2974, 2921, 2696, 1455, 1431, 1402, 1311, 1267, 1165, 1108 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{19}N_2$ $[M + H]^+$ 299.1543, found 299.1548.

2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1m). R_f = 0.50 (hexane/ethyl acetate 4:1); white solid; yield 88% (306 mg); mp 218-220 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 11.80 (s, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.33 (s, 1H), 7.08 (s, 5H), 2.55 (q, *J* = 7.0 Hz, 2H), 2.27 (s, 6H), 1.14 (t, *J* = 7.7 Hz, 3H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 151.3, 142.4, 142.2, 140.8, 137.5, 133.1, 131.1, 130.5, 130.4, 130.4, 129.6, 129.4, 128.6, 127.5, 127.0, 118.9, 111.3, 27.7, 19.9 (×2), 15.3; IR (KBr) $\tilde{\nu}$ = 3438, 2964, 2925, 1633, 1455, 1407, 1312, 1264 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{23}N_2$ $[M + H]^+$ 327.1856, found 327.1861.

2-(4'-(Tert-butyl)-[1,1'-biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1n). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 82% (320 mg); mp 205 °C. ^1H NMR (700 MHz, DMSO-d_6) δ 11.87 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.57 (dd, *J* = 10.8, 4.2 Hz, 1H), 7.48 (dd, *J* = 15.6, 7.8 Hz, 2H), 7.32 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 1H), 2.27 (s, 6H), 1.22 (s, 9H). $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 151.4, 149.4, 142.2, 140.6, 137.3, 133.2, 131.3, 130.7, 130.6, 130.3, 129.7, 129.5, 128.5, 127.1, 125.0, 118.9, 111.3, 34.2, 31.1, 20.0 (×2); IR (KBr) $\tilde{\nu}$ = 3439, 2962, 2924, 2860, 1457, 1405, 1316, 1269, 1111, 1002 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{25}H_{27}N_2$ $[M + H]^+$ 356.2202, found 356.2214.

2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1o). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 96% (337 mg); mp 230 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 11.85 (s, 1H), 7.71 – 7.67 (m, 1H), 7.58 (td, *J* = 7.7, 1.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.32 (s, 1H), 7.18 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.08 (dd, *J* = 16.8, 7.7 Hz, 3H), 2.27 (s, 6H);

$^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 161.4 (d, $^1J_{C,F}$ = 243.7 Hz), 150.9, 142.2, 139.8, 136.6, 133.1, 131.0, 130.8, 130.7, 130.4, 130.4, 129.7, 129.5, 127.5, 119.0, 114.9 (d, $^2J_{C,F}$ = 21.4 Hz), 111.3, 20.0, 19.9 (×2); IR (KBr) $\tilde{\nu}$ = 3048, 2971, 2921, 2857, 2689, 1514, 1462, 1405, 1316, 1227, 1160 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{18}FN_2$ $[M + H]^+$ 317.1448, found 317.1422.

2-(3'-Chloro-[1,1'-biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1p). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 93% (340 mg); mp 232 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 11.95 (s, 1H), 7.72 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 (td, *J* = 7.7, 1.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.34 – 7.25 (m, 3H), 7.22 (t, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.27 (s, 6H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 150.6, 142.5, 142.2, 139.3, 133.0, 132.7, 131.0, 130.5, 130.4, 129.8, 129.7, 128.7, 128.6, 128.1, 128.0, 127.5, 126.9, 118.9, 111.4, 20.0 (×2); IR (KBr) $\tilde{\nu}$ = 3440, 3058, 2969, 2917, 2867, 1601, 1457, 1408, 1319, 1262, 1081 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{18}ClN_2$ $[M + H]^+$ 333.1153, found 333.1164.

1-(2'-(5,6-Dimethyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (1q). R_f = 0.40 (hexane/ethyl acetate 7:3); white solid; yield 73% (272 mg); mp 278 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 12.00 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.62 (td, *J* = 7.7, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 3H), 7.10 (s, 1H), 2.52 (s, 3H), 2.26 (s, 6H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 197.6, 150.8, 145.2, 142.2, 139.9, 135.2, 133.1, 131.1, 130.8, 130.5, 130.4, 129.8, 129.6, 129.1, 128.1, 128.0, 119.0, 111.4, 26.7, 19.9 (×2); IR (KBr) $\tilde{\nu}$ = 3440, 2966, 2924, 2862, 2681, 1681, 1651, 1605, 1403, 1353, 1267, 1009 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{21}N_2O$ $[M + H]^+$ 341.1648, found 341.1660.

5,6-Dichloro-2-(4-fluoro-[1,1'-biphenyl]-2-yl)-1H-benzo[d]imidazole (1r). R_f = 0.50 (hexane/ethyl acetate 4:1); white solid; yield 84% (255 mg); mp 258-260 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.57 (s, 1H), 7.86 (s, 1H), 7.62 (s, 1H), 7.60 – 7.55 (m, 2H), 7.49 (td, J = 8.4, 2.8 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.14 (dd, J = 6.4, 2.8 Hz, 2H). ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 161.1 (d, $^1J_{C,F}$ = 245.5 Hz), 153.4, 142.9, 138.9, 137.6 (d, $^4J_{C,F}$ = 3.0 Hz), 133.9, 132.8 (d, $^3J_{C,F}$ = 8.2 Hz), 131.0 (d, $^3J_{C,F}$ = 8.3 Hz), 128.8, 128.3, 127.3, 124.9, 124.2, 120.2, 117.6 (d, $^2J_{C,F}$ = 23.0 Hz), 117.3 (d, $^2J_{C,F}$ = 21.0 Hz), 112.8; IR (KBr) $\tilde{\nu}$ = 3417, 2927, 2845, 1655, 1477, 1448, 1383, 1200, 1093 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{12}Cl_2FN_2$ $[M + H]^+$ 357.0356, found 357.0368.

2-(4-Fluoro-[1,1'-biphenyl]-2-yl)-5,6-dimethyl-1H-benzo[d]imidazole (1s). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 91% (320 mg); mp 220-222 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 7.57 – 7.49 (m, 2H), 7.43 (td, J = 8.4, 2.8 Hz, 1H), 7.32 (s, 1H), 7.24 – 7.21 (m, 3H), 7.16 – 7.04 (m, 3H), 2.26 (s, 6H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 161.1 (d, $^1J_{C,F}$ = 245.2 Hz), 149.8, 142.0, 139.3, 137.5 (d, $^4J_{C,F}$ = 3.1 Hz), 133.1, 132.7 (d, $^3J_{C,F}$ = 8.3 Hz), 132.3 (d, $^3J_{C,F}$ = 8.3 Hz), 131.1, 129.8, 128.8, 128.2, 127.2, 119.1, 117.4 (d, $^2J_{C,F}$ = 22.6 Hz), 116.6 (d, $^2J_{C,F}$ = 20.9 Hz), 111.5, 19.98 (×2); IR (KBr) $\tilde{\nu}$ = 3438, 2969, 2919, 2857, 1610, 1586, 1460, 1417, 1314, 1200, 1006 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{18}FN_2$ $[M + H]^+$ 317.1449, found 317.1451.

Mixture of 2-([1,1'-Biphenyl]-2-yl)-5-methyl-1H-benzo[d]imidazole and 2-([1,1'-Biphenyl]-2-yl)-6-methyl-1H-benzo[d]imidazole (1a'). R_f = 0.60 (hexane/ethyl acetate 7:3); inseparable white solid (1:1); yield 85% (590 mg); mp 220-222 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 11.97 (s, 1H), 11.92 (s, 1H), 7.69 (d, J = 7.0 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.52 (t, J = 7.0 Hz, 4H), 7.43 (s, 1H), 7.34 (s, 1H), 7.21 – 7.25 (m, 6H), 7.18 (dd, J = 7.0, 1.4 Hz,

5H), 7.10 (s, 1H), 6.95 (d, J = 8.4 Hz, 2H), 2.37 (s, 6H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 152.0, 151.6, 144.8, 141.6, 140.9, 140.2, 134.8, 132.6, 131.4, 131.1, 130.5, 130.3, 130.1, 129.8, 128.8, 128.1, 127.4, 127.1, 123.5, 122.8, 118.5, 118.4, 111.0, 110.8, 21.3; IR (KBr) $\tilde{\nu}$ = 3440, 3057, 2922, 2867, 2664, 2362, 2337, 1455, 1434, 1403, 1311, 1289, 1232, 1148 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{17}N_2$ $[M + H]^+$ 285.1386, found 285.1361.

2-([1,1'-Biphenyl]-2-yl)-5-nitro-1H-benzo[d]imidazole (1b'). R_f = 0.40 (hexane/ethyl acetate 4:1); white solid; yield 81% (332 mg); mp 234-236 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 8.41 (s, 1H), 8.07 (dd, J = 8.8, 2.0 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.2 Hz, 3H), 7.32 – 7.23 (m, 3H), 7.22 – 7.14 (m, 2H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 156.8, 142.6, 141.2, 139.7, 131.1, 130.7(×2), 129.0, 128.8(×2), 128.3(×2), 127.6, 127.4, 117.7, 114.9, 111.9; IR (KBr) $\tilde{\nu}$ = 3418, 3063, 2922, 2850, 2714, 1636, 1519, 1477, 1430, 1338, 1286, 1068 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{14}N_3O_2$ $[M + H]^+$ 316.1081, found 316.1052.

Mixture of 2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-5-methyl-1H-benzo[d]imidazole and 2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-6-methyl-1H-benzo[d]imidazole (1c'). R_f = 0.45 (hexane/ethyl acetate 4:1); Inseparable white solid (1:1.2); yield 92% (355 mg); mp 222 °C; ^1H NMR (700 MHz, DMSO-d_6) δ 11.96 (s, 1H), 11.92 (s, 1H), 7.66 (d, J = 7.7 Hz, 2.2H), 7.61 – 7.56 (m, 2.2H), 7.51 – 7.47 (m 4.8H), 7.44 (d, J = 8.4 Hz, 1.2H), 7.35 (s, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.11 – 7.07 (m 9.6H), 6.95 (d, J = 8.4 Hz, 2.2H), 2.55 (q, J = 7.7 Hz, 4.4H), 2.37 (s, 6.6H), 1.13 (t, J = 7.7 Hz, 6.6H); $^{13}C\{1H\}$ NMR (175 MHz, DMSO-d_6) δ 152.2, 151.7, 143.8, 142.5, 141.6, 140.8, 137.5, 134.8, 132.6, 131.3, 131.1, 130.4, 130.3, 130.1, 129.8, 128.7, 127.6, 127.1, 123.5, 122.7, 118.6, 118.4, 111.0, 110.8, 27.7, 21.3, 15.3; IR (KBr) $\tilde{\nu}$ = 3430, 3057, 2964,

2921, 2872, 2662, 1633, 1446, 1407, 1314, 1282, 1267, 1150, 1054, 1007 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{22}H_{21}N_2$ $[M + H]^+$ 313.1699, found 313.1710.

Mixture of 2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-5-nitro-1H-benzo[d]imidazole and 2-(4'-Ethyl-[1,1'-biphenyl]-2-yl)-6-nitro-1H-benzo[d]imidazole (1d'). R_f = 0.55 (hexane/ethyl acetate 4:1); Inseparable pale yellow solid(1:1); yield 84% (283 mg); mp 228-230 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.81 (s, 1H), 8.49 (s, 1H), 8.22 (s, 1H), 8.10 – 8.05 (m, 2H), 7.79 – 7.72 (m, 3H), 7.65 (t, *J* = 7.0 Hz, 2H), 7.56 – 7.53 (m, 5H), 7.11 (s, 8H), 2.55 (q, *J* = 7.7 Hz, 4H), 1.13 (t, *J* = 7.7 Hz, 6H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 158.1, 156.9, 148.5, 143.3, 143.1, 143.0, 141.5, 139.7, 137.5, 134.2, 131.6, 131.1, 129.4, 129.2, 128.2, 127.8, 119.5, 118.5, 117.7, 115.5, 112.2, 108.3, 28.1, 15.7 ; IR (KBr) $\tilde{\nu}$ = 3403, 2966, 2929, 2850, 2364, 2342, 1625, 1521, 1476, 1339, 1066 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{18}N_3O_2$ $[M + H]^+$ 344.1394, found 344.1410.

Mixture of 2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-5-methyl-1H-benzo[d]imidazole and 2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)-6-methyl-1H-benzo[d]imidazole (1e'). R_f = 0.50 (hexane/ethyl acetate 7:3); Inseparable white solid (1:1.2); yield 86% (319 mg); mp 226-228 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.96 (s, 1H), 7.71 (d, *J* = 7.0 Hz, 2.2H), 7.59 (td, *J* = 7.7, 1.4 Hz, 2.2H), 7.53 (dd, *J* = 7.7, 1.4 Hz, 2.2H), 7.52 – 7.49 (m, 2.2H), 7.43 (s, 1.2H), 7.35 (s, 1H), 7.23 (s, 1H), 7.22 – 7.18 (m, 4.4H), 7.13 (s, 1.2H), 7.09 (t, *J* = 9.1 Hz, 4.4H), 6.96 (d, *J* = 7.0 Hz, 2.2H), 2.38 (s, 6.6H); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 161.5 (d, $^1J_{C,F}$ = 243.9 Hz), 151.8, 151.4, 143.9, 141.6, 139.9, 136.6 (d, $^4J_{C,F}$ = 3.0 Hz), 134.8, 132.6, 131.5, 131.0, 130.8 (d, $^3J_{C,F}$ = 8.2 Hz), 130.5, 130.3, 129.8, 127.5, 123.6, 122.9, 118.7, 118.5, 115.0 (d, $^2J_{C,F}$ = 21.4 Hz), 111.1, 110.9, 21.3; IR (KBr) $\tilde{\nu}$ = 3444, 3057, 2971, 2919, 2855, 2669,

1633, 1605, 1511, 1494, 1446, 1463, 1403, 1309, 1280, 1222, 1158, 1094 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{16}FN_2$ $[M + H]^+$ 303.1292, found 303.1272.

Mixture of 2-(4-Fluoro-[1,1'-biphenyl]-2-yl)-5-methyl-1H-benzo[d]imidazole and 2-(4-Fluoro-[1,1'-biphenyl]-2-yl)-6-methyl-1H-benzo[d]imidazole (1f'). R_f = 0.60 (hexane/ethyl acetate 4:1); Inseparable white solid (1:1.2); yield 85% (154 mg); mp 185 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.04 (s, 1H), 11.98 (s, 1H), 7.56 – 7.50 (m, 4.8), 7.48 – 7.40 (m, 3.6H), 7.35 (s, 1H), 7.27 – 7.21 (m, 7.2H), 7.18 – 7.09 (m, 5.8H), 6.96 (t, J = 7.2 Hz, 2.2H), 2.37 (s, 6.6H); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 161.1 (d, $^1J_{C,F}$ = 245.6 Hz), 150.62, 150.18, 143.7, 141.5, 139.26, 137.5, 134.8, 132.7 (d, $^3J_{C,F}$ = 8.2 Hz), 132.6, 132.1 (d, $^3J_{C,F}$ = 8.9 Hz), 131.8, 130.4, 128.8, 128.2, 127.2, 123.9, 123.0, 118.8, 118.6, 117.5 (d, $^2J_{C,F}$ = 22.5 Hz), 116.7 (d, $^2J_{C,F}$ = 21.2 Hz), 111.2, 111.0, 21.30; IR (KBr) $\tilde{\nu}$ = 3437, 3070, 3023, 2918, 2862, 2778, 1611, 1589, 1509, 1446, 1418, 1284, 1201, 1073 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{16}FN_2$ $[M + H]^+$ 303.1292, found 303.1273.

Mixture of 1-(2'-(5-Methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one and 1-(2'-(6-Methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (1g'). R_f = 0.60 (hexane/ethyl acetate 7:3); Inseparable pale yellow solid (1:1.2); yield 88% (351 mg); mp 265−267 °C; ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.15 (s, 1H), 12.10 (s, 1.2H), 7.82 (d, J = 7.7 Hz, 4.4H), 7.74 (d, J = 7.7 Hz, 2.2H), 7.63 (td, J = 7.7, 1.4 Hz, 2.2H), 7.57 (td, J = 7.7, 1.4 Hz, 2.2H), 7.54 (d, J = 7.7 Hz, 2.2H), 7.42 (d, J = 8.4 Hz, 1.2H), 7.35 – 7.29 (m, 5.6H), 7.23 (d, J = 7.7 Hz, 1H), 7.12 (s, 1H), 6.99 – 6.91 (m, 2.2H), 2.52 (s, 6.6H), 2.36 (s, 6.6H); ^{13}C{1H} NMR (175 MHz, DMSO-d_6) δ 197.7, 151.7, 151.2, 145.2, 143.9, 141.7, 139.9, 135.3, 134.9, 132.6, 131.7, 131.2, 130.6, 130.4, 130.3, 130.0, 129.2, 128.2, 128.1, 123.8, 123.0, 118.7, 118.6, 111.2, 111.0, 26.8, 21.4, 21.3; IR (KBr) $\tilde{\nu}$ = 3351, 3060, 2919, 2857, 1682, 1606, 1405, 1361,

1314, 1269, 1185 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{22}H_{19}N_2O$ $[M + H]^+$ 327.1492, found 327.1475.

Benzo[4,5]imidazo[1,2-f]phenanthridine (2a). R_f = 0.40 (hexane/ethyl acetate 9:1); pale yellow solid; yield 91% (58 mg); mp 144 °C (lit.[36] mp 144−146 °C); ^1H NMR (700 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 7.7 Hz, 1H), 8.47 (d, *J* = 7.0 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.0 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.55 – 7.45 (m, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 147.7, 144.7, 134.6, 132.0, 130.6, 129.7, 129.3, 128.8, 126.2, 124.6, 124.4, 124.3, 123.6, 123.1, 122.4, 121.9, 120.5, 116.2, 114.1; IR (KBr) $\tilde{\nu}$ = 3351, 2364, 2332, 1532, 1453, 1440, 1373 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{13}N_2$ $[M + H]^+$ 269.1073, found 269.1058.

2-Ethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2b). R_f = 0.55 (hexane/ethyl acetate 4:1); pale yellow solid; yield 96% (57 mg); mp 162 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.7 Hz, 1H), 8.38 – 8.26 (m, 4H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.0 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 2.92 (q, *J* = 7.7 Hz, 2H), 1.42 (t, *J* = 7.7 Hz, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 147.7, 146.1, 144.3, 134.6, 131.9, 130.7, 129.9, 128.4, 126.2, 124.7, 124.3(×2), 123.0, 122.9, 122.2, 120.3, 119.6, 115.3, 114.2, 29.29, 15.64; IR (KBr) $\tilde{\nu}$ = 3416, 2961, 2923, 2855, 1614, 1537, 1449, 1428, 1665 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{17}N_2$ $[M + H]^+$ 297.1386, found 297.1372.

2-Fluorobenzo[4,5]imidazo[1,2-f]phenanthridine (2c). R_f = 0.55 (hexane/ethyl acetate (4:1); white solid; yield 95% (55 mg); mp 190 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.7 Hz, 1H), 8.37 – 8.30 (m, 1H), 8.18 (dd, *J* = 12.6, 7.7 Hz, 2H), 8.13 (d, *J* = 9.8 Hz, 1H), 8.01 (d, *J*

= 7.7 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 1H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.87 (d, $^1J_{C,F}$ = 249.0 Hz), 147.6, 144.6, 135.3 (d, ^4J = 10.6 Hz), 131.7, 130.7, 129.1, 128.5, 126.2, 126.1 (d, $^4J_{C,F}$ = 9.7 Hz), 124.6, 123.3, 122.9, 122.1, 120.6, 118.2, 113.6, 112.1 (d, $^3J_{C,F}$ = 22.0 Hz), 103.32 (d, $^2J_{C,F}$ = 26.9 Hz); IR (KBr) $\tilde{\nu}$ = 3422, 2927, 2857, 1618, 1540, 1450, 1432, 1350, 1169 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{12}FN_2$ $[M + H]^+$ 287.0979, found 287.0971.

1-(Benzo[4,5]imidazo[1,2-f]phenanthridin-2-yl)ethan-1-one (2d). R_f = 0.70 (hexane/ethyl acetate 7:3); white solid; yield 94% (56 mg); mp 222 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.80 – 8.73 (m, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.22 – 8.18 (m, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.67 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 2.71 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 147.1, 144.2, 136.7, 134.1, 131.7, 130.7, 129.9, 128.4, 126.2, 125.4, 124.7, 124.3, 124.1, 124.0, 123.8, 123.0, 120.5, 115.5, 114.1, 26.9; IR (KBr) $\tilde{\nu}$ = 3439, 3048, 1682, 1620, 1534, 1450, 1427, 1653, 1264 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{15}N_2O$ $[M + H]^+$ 311.1179, found 311.1168.

11,12-Dichlorobenzo[4,5]imidazo[1,2-f]phenanthridine (2e). R_f = 0.55 (hexane/ethyl acetate 4:1); white solid; yield 98% (59 mg); mp 234 °C (lit.[35] mp 231-232 °C); ^1H NMR (700 MHz, $CDCl_3$) δ 8.65 (d, *J* = 7.7 Hz, 1H), 8.36 (d, *J* = 7.7 Hz, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 8.21 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.71 (t, *J* = 7.0 Hz, 1H), 7.62 (s, 2H), 7.46 (t, *J* = 7.0 Hz, 1H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 149.1, 143.9, 133.6, 131.1, 130.7, 129.7, 129.5, 128.9, 128.2, 126.5, 126.3, 125.1, 124.4, 122.8, 122.4, 121.8, 121.1, 115.7, 115.1;

IR (KBr) $\tilde{\nu}$ = 3444, 2919, 2852, 1651, 1537, 1438, 1364 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{11}Cl_2N_2$ $[M + H]^+$ 337.0294, found 337.0270.

11,12-Dichloro-2-ethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2f). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 93% (55.5 mg); mp 241 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.7 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.26 (t, *J* = 7.7 Hz, 2H), 7.99 (d, *J* = 11.9 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 2.90 (q, *J* = 7.7 Hz, 2H), 1.41 (t, *J* = 7.7 Hz, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 149.3, 146.4, 143.9, 133.8, 131.1, 130.8, 129.9, 128.5, 128.2, 126.3, 126.3, 125.1, 124.5, 122.4, 122.2, 121.0, 119.5, 115.2, 114.8, 29.3, 15.6; IR (KBr) $\tilde{\nu}$ = 3442, 2969, 2924, 2364, 2335, 1440, 1311, 1116 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{15}Cl_2N_2$ $[M + H]^+$ 365.0607, found 365.0594.

2-(Tert-butyl)-11,12-dichlorobenzo[4,5]imidazo[1,2-f]phenanthridine (2g). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 94% (56 mg); mp 234 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.75 (d, J = 7.0 Hz, 1H), 8.39 (t, J = 6.6 Hz, 1H), 8.32 – 8.34 (m, 3H), 8.03 (dd, J = 11.9, 5.6 Hz, 1H), 7.72 – 7.76 (m, 1H), 7.65 (t, J = 7.0 Hz, 1H), 7.62 – 7.58 (m, 1H), 1.54 (s, 9H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 153.4, 149.5, 144.2, 133.8, 131.2, 130.9, 129.9, 128.6, 128.2, 126.4, 126.3, 124.3, 122.9, 122.7, 122.3, 121.2, 119.4, 115.3, 112.5, 35.6, 31.5; IR (KBr) $\tilde{\nu}$ = 3439, 2959, 2867, 2359, 2339, 1615, 1439 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{19}Cl_2N_2$ $[M + H]^+$ 393.0920, found 393.0932.

3,11,12-Trichlorobenzo[4,5]imidazo[1,2-f]phenanthridine (2h). R_f = 0.70 (hexane/ethyl acetate 4:1); white solid; yield 92% (55 mg); mp 260 °C; ^1H NMR (400 MHz, $CDCl_3$ + TFA-D) δ 8.85 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 1.6 Hz, 1H), 8.61 (s, 1H), 8.54 (t, *J* = 9.2 Hz, 2H),

8.23 (s, 1H), 8.12 (t, *J* = 7.6 Hz, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.90 (dd, *J* = 9.2, 1.6 Hz, 1H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$ + TFA-D) δ 146.5, 138.1, 133.2, 132.7, 130.9, 130.5, 130.3, 130.2, 129.2, 128.9, 128.7, 126.7, 124.4, 123.2, 122.8, 119.5, 119.4, 117.4, 115.4; IR (KBr) $\tilde{\nu}$ = 3439, 2922, 2852, 1651, 1542, 1445, 1368, 1106 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{10}Cl_3N_2$ $[M + H]^+$ 370.9904, found 370.9891.

11,12-Dichloro-2-fluorobenzo[4,5]imidazo[1,2-f]phenanthridine (2i). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 94% (56 mg); mp 264 °C; ^1H NMR (700 MHz, $CDCl_3$: TFA-D 15:1) δ 8.81 (dd, J = 9.1, 5.6 Hz, 1H), 8.74 – 8.68 (m, 2H), 8.65 (d, J = 8.4 Hz, 1H), 8.38 (dd, J = 9.1, 1.4 Hz, 1H), 8.21 – 8.16 (m, 2H), 7.98 (t, J = 7.7 Hz, 1H), 7.72 – 7.68 (m, 1H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$: TFA-D 15:1) δ 163.9 (d, $^1J_{C,F}$ = 255.9 Hz), 144.9, 136.5, 134.8, 132.7, 131.9 (d, $^3J_{C,F}$ = 10.3 Hz), 131.7, 131.0, 130.7, 127.9 (d, $^3J_{C,F}$ = 9.0 Hz), 126.3, 123.6, 119.4 (d, $^4J_{C,F}$ = 2.7 Hz), 117.3 (d, $^2J_{C,F}$ = 22.3 Hz), 115.4, 114.7, 113.7, 112.1, 104.9 (d, $^2J_{C,F}$ = 27.7 Hz); IR (KBr) $\tilde{\nu}$ = 3053, 2986, 2305, 1621, 1537, 1447, 1345, 1264, 1196, 1113 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{10}Cl_2FN_2$ $[M + H]^+$ 355.0200, found 355.0213.

1-(11,12-Dichlorobenzo[4,5]imidazo[1,2-f]phenanthridin-2-yl)ethan-1-one (2j). R_f = 0.60 (hexane/ethyl acetate 7:3); white solid; yield 93% (55.6 mg); mp 256 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.27 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 2.77 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.5, 148.8, 143.9, 137.1, 133.6, 131.4, 130.7, 130.1, 128.8, 128.7, 127.2, 126.5, 125.6, 124.8, 124.7, 123.8, 123.2, 121.3, 115.2, 115.1, 26.9; IR (KBr) $\tilde{\nu}$ = 3418, 2919, 1682, 1442, 1353, 1259, 1118 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{13}Cl_2N_2O$ $[M + H]^+$ 379.0399, found 379.0376.

11,12-Dichloro-2-(trifluoromethyl)benzo[4,5]imidazo[1,2-f]phenanthridine (2k). R_f = 0.70 (hexane/ethyl acetate 4:1); white solid; yield 92% (55 mg); mp 275 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.7 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.23 (s, 1H), 8.00 (s, 1H), 7.85 – 7.76 (m, 2H), 7.74 (t, *J* = 7.7 Hz, 1H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 148.8, 143.8, 133.5, 131.6, 131.3 (q, $^2J_{C,F}$ = 33 Hz), 130.5, 130.3, 129.0, 128.6, 127.4, 126.6 (q, $^1J_{C,F}$ = 273 Hz), 125.3, 124.8, 124.5, 123.4, 122.9, 121.7 (q, $^3J_{C,F}$ = 3.5 Hz), 121.5, 114.9, 112.8 (q, $^3J_{C,F}$ = 3.5 Hz); IR (KBr) $\tilde{\nu}$ = 3422, 2922, 2852, 1620, 1537, 1442, 1302, 1285, 1125, 1112, 1081 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{10}Cl_2F_3N_2$ $[M + H]^+$ 405.0168, found 405.0159.

11,12-Dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2l). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 96% (58 mg); mp 164 °C (lit.[35] mp 161-162 ℃); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.84 (d, *J* = 7.7 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 7.7 Hz, 1H), 8.37 (d, *J* = 7.7 Hz, 1H), 8.08 (s, 1H), 7.78 (s, 1H), 7.70 (q, *J* = 7.0 Hz, 2H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 2.53 (s, 3H), 2.47 (s, 3H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 146.3, 142.6, 134.1, 132.8, 131.7, 129.9, 129.6, 128.9, 128.6, 128.1, 125.5, 123.7, 123.7, 123.2, 121.8, 121.2, 119.8, 115.5, 113.8, 20.7, 20.0; IR (KBr) $\tilde{\nu}$ = 3202, 2927, 2855, 2359, 1640, 1535, 1439, 1371 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{17}N_2$ $[M + H]^+$ 297.1386, found 297.1359.

2-Ethyl-11,12-dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2m). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 94% (56 mg); mp 186 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.82 (d, *J* = 7.7 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.31 (s, 2H), 8.04 (s, 1H), 7.77 (s, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.93 (q, *J* = 7.7

Hz, 2H), 2.53 (s, 3H), 2.46 (s, 3H), 1.43 (t, J = 7.7 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.0, 145.9, 142.8, 134.7, 133.4, 132.2, 130.4, 130.3, 129.6, 128.3, 126.1, 124.4, 124.2, 123.1, 122.1, 120.2, 119.5, 115.2, 114.4, 29.3, 21.3, 20.5, 15.6; IR (KBr) $\tilde{\nu}$ = 3404, 2921, 2855, 1686, 1611, 1428 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{21}N_2$ $[M + H]^+$ 325.1699, found 325.1694.

2-(Tert-butyl)-11,12-dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2n). R_f = 0.65 (hexane/ethyl acetate 4:1); white solid; yield 82% (49 mg); mp 208 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.84 (d, J = 8.4 Hz, 1H), 8.58 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.09 (s, 1H), 7.80 (s, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (dd, J = 8.4, 1.4 Hz, 1H), 2.55 (s, 3H), 2.48 (s, 3H), 1.54 (s, 9H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 152.9, 147.3, 143.5, 134.7, 133.2, 131.9, 130.5, 130.1, 129.5, 128.3, 126.0, 124.0, 123.6, 122.2, 121.9, 120.5, 119.3, 114.4, 112.9, 35.5, 31.6, 21.5, 20.6; IR (KBr) $\tilde{\nu}$ = 3417, 2960, 2359, 2340, 1615, 1532, 1463, 1428, 1359 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{25}H_{25}N_2$ $[M + H]^+$ 353.2012, found 353.2025.

2-Fluoro-11,12-dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2o). R_f = 0.60 (hexane/ethyl acetate 4:1); white solid; yield 92% (55 mg); mp 208 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.77 (d, J = 7.7 Hz, 1H), 8.37 (dd, J = 9.1, 6.3 Hz, 1H), 8.23 (d, J = 7.7 Hz, 1H), 8.17 – 8.11 (m, 1H), 7.91 (s, 1H), 7.74 (s, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.21 – 7.14 (m, 1H), 2.51 (s, 3H), 2.45 (s, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.9 (d, $^1J_{C,F}$ = 248.4 Hz), 147.0, 143.2, 135.5 (d, $^3J_{C,F}$ = 10.6 Hz), 133.7, 132.5, 130.3, 130.2, 128.9, 128.5, 126.0, 126.0, 123.2, 122.1, 120.6 , 118.2, 113.9, 111.8 (d, $^2J_{C,F}$ = 22.1 Hz), 103.2 (d, $^2J_{C,F}$ = 26.8 Hz), 21.2, 20.5; IR (KBr) $\tilde{\nu}$ = 3439, 2922, 2847, 1656, 1651, 1541, 1462, 1434, 1178 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}FN_2$ $[M + H]^+$ 315.1292, found 315.1308.

3-Chloro-11,12-dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2p). R_f = 0.65 (hexane/ethyl acetate 4:1); white solid; yield 89% (53 mg); mp 210 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.81 (d, *J* = 7.7 Hz, 1H), 8.41 (d, *J* = 9.1 Hz, 1H), 8.38 (d, *J* = 1.4 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 7.96 (s, 1H), 7.76 (s, 1H), 7.73 – 7.66 (m, 2H), 7.61 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 146.7, 143.2, 133.6, 133.1, 132.6, 130.4, 130.3, 129.9, 129.4, 129.0, 128.3, 126.1, 124.1, 124.1, 123.4, 122.5, 120.6, 117.3, 114.0, 21.2, 20.6; IR (KBr) $\tilde{\nu}$ = 3417, 2917, 2845, 1534, 1452, 1108, 1024 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}ClN_2$ $[M + H]^+$ 331.0997, found 331.1009.

1-(11,12-Dimethylbenzo[4,5]imidazo[1,2-f]phenanthridin-2-yl)ethan-1-one (2q). R_f = 0.70 (hexane/ethyl acetate 7:3); white solid; yield 82% (49 mg); mp 198 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.75 – 8.69 (m, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.23 – 8.19 (m, 1H), 7.94 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.65 (m, 2H), 2.70 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 196.8, 146.4, 143.0, 136.7, 134.3, 133.7, 132.9, 130.3, 130.2, 129.7, 128.3, 126.0, 125.4, 124.4, 124.2, 123.8, 123.1, 120.5, 115.5, 114.2, 26.8, 21.3, 20.6; IR (KBr) $\tilde{\nu}$ = 2929, 2847, 1685, 1604, 1405, 1274, 1215, 1185, 1106 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{23}H_{19}N_2O$ $[M + H]^+$ 339.1492, found 339.1518.

11,12-Dichloro-7-fluorobenzo[4,5]imidazo[1,2-f]phenanthridine (2r). R_f = 0.65 (hexane/ethyl acetate 4:1); white solid; yield 95% (57 mg); mp 280 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + TFA-D 15:1) δ 8.75 (s, 1H), 8.72 – 8.64 (m, 3H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H), 8.04 (t, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$ + TFA-D 15:1)) δ 163.1 (d, *J* = 256.2 Hz), 143.6, 134.4, 132.3, 131.4 (d, *J* = 16.8 Hz), 130.8, 129.0, 128.4 (d, *J* = 2.6 Hz), 128.0, 126.5 (d, *J* = 8.9 Hz), 125.3, 124.6 (d, *J*

= 23.6 Hz), 122.2, 119.1, 117.3, 117.2, 117.1, 113.4, 112.4 (d, J = 25.3 Hz), 110.5; IR (KBr) $\tilde{\nu}$ = 2919, 2845, 1537, 1443, 1361, 1331, 1197, 1116, 1083 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_9Cl_2FN_2$ $[M + H]^+$ 355.0200, found 355.0196.

7-Fluoro-11,12-dimethylbenzo[4,5]imidazo[1,2-f]phenanthridine (2s). R_f = 0.70 (hexane/ethyl acetate 4:1); white solid; yield 94% (56 mg); mp 215 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.48 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 9.1 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.31 (dd, J = 8.4, 4.9 Hz, 1H), 8.04 (s, 1H), 7.75 (s, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.0 Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{C,F}$ = 249.1 Hz), 146.0, 143.1, 134.2, 133.6, 132.7, 130.5, 129.0, 125.8, 125.6 (d, $^3J_{C,F}$ = 9.4 Hz), 124.9 (d, $^3J_{C,F}$ = 8.4 Hz), 124.5, 124.1, 121.2, 120.6, 118.4 (d, $^2J_{C,F}$ = 23.2 Hz), 116.1, 114.3, 111.5 (d, $^2J_{C,F}$ = 23.6 Hz), 21.2, 20.6; IR (KBr) $\tilde{\nu}$ = 3417, 2924, 2852, 1509, 1542, 1457, 1433, 1334, 1252, 1210 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}FN_2$ $[M + H]^+$ 315.1292, found 315.1292.

Mixture of **11-Methylbenzo[4,5]imidazo[1,2-f]phenanthridine** and **12-Methylbenzo[4,5]imidazo[1,2-f]phenanthridine (2a').** R_f = 0.60 (hexane/ethyl acetate 7:3); Inseparable white solid (5:3); yield 96% (57 mg); mp 162 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.73 (d, J = 7.7 Hz, 1.6H), 8.30 – 8.21 (m, 3.2H), 8.17 (d, J = 7.7 Hz, 1.6H), 7.98 (d, J = 8.4 Hz, 1H), 7.91 (s, 0.6H), 7.85 (d, J = 7.7 Hz, 0.6H), 7.74 (s, 1H), 7.63 – 7.56 (m, 3.2H), 7.50 (t, J = 7.0 Hz, 1.6H), 7.31 (dd, J = 14.0, 7.0 Hz, 1.6H), 7.28 – 7.24 (m, 0.6H), 7.17 (d, J = 8.4 Hz, 1H), 2.59 (s, 1.8H), 2.54 (s, 3H). $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 147.2, 146.9, 144.6, 142.4, 134.3, 134.2, 134.0, 132.8, 131.9, 130.2, 130.1, 129.8, 129.3, 129.3, 129.0, 128.9, 128.5, 128.5, 125.9, 125.8, 125.7, 124.4, 124.2, 124.2, 124.0, 123.4, 123.3, 122.2, 122.1, 121.5, 121.4, 119.9, 119.7, 115.8, 115.8, 113.9, 113.4, 22.4, 21.7; IR (KBr) $\tilde{\nu}$ = 3402, 2924, 2852, 2359,

2339, 1539, 1457, 1439, 1376, 1264, 1041 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{15}N_2$ $[M + H]^+$ 283.1230, found 283.1204.

Mixture of **11-Nitrobenzo[4,5]imidazo[1,2-f]phenanthridine** and **12-Nitrobenzo[4,5]imidazo[1,2-f]phenanthridine (2b').** R_f = 0.55 (hexane/ethyl acetate 4:1); Inseparable pale yellow solid (2:1); yield 91% (54 mg); mp 256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 – 9.21 (m, 1H), 8.78 (t, *J* = 8.4 Hz, 2H), 8.45 (t, *J* = 8.8 Hz, 3H), 8.42 – 8.31 (m, 3H), 8.28 (s, 0.5H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.66 (m, 4.5H), 7.61 – 7.52 (m, 1.5H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 151.7, 149.1, 143.0, 135.6, 133.7, 133.5, 131.9, 131.7, 130.9, 130.3, 130.0, 129.7, 129.2, 129.2, 126.7, 126.6, 125.7, 124.7, 124.7, 122.6, 122.6, 122.5, 122.0, 120.1, 120.0, 118.1, 116.4, 116.1, 113.8, 110.9; IR (KBr) $\tilde{\nu}$ = 3420, 2924, 2850, 1537, 1460, 1505, 1435, 1348, 1291 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{12}N_3O_2$ $[M + H]^+$ 314.0924, found 314.0925.

Mixture of **2-Ethyl-11-methylbenzo[4,5]imidazo[1,2-f]phenanthridine** and **2-Ethyl-12-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (2c').** R_f = 0.60 (hexane/ethyl acetate 4:1); Inseparable pale yellow solid (5:2); yield 92% (54 mg); mp 175 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.83 (t, *J* = 8.4 Hz, 1.4H), 8.30 – 8.36 (m, 4.2H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 0.4H), 7.92 (d, *J* = 8.4 Hz, 0.4H), 7.82 (s, 1H), 7.75 – 7.67 (m, 1.4H), 7.64 (t, *J* = 7.0 Hz, 1.4H), 7.34 (d, *J* = 7.7 Hz, 1.8H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.89–2.94 (m, 2.8H), 2.66 (s, 1.2H), 2.58 (s, 3H), 1.42 (t, *J* = 7.7 Hz, 4.2H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 147.5, 147.2, 146.1, 146.0, 134.7, 134.5, 134.3, 133.0, 132.1, 130.6, 130.5, 129.9, 129.8, 129.7, 128.4, 126.2, 126.1, 125.9, 124.6, 124.6, 124.5, 124.3, 124.3, 123.1, 122.8, 122.2, 120.0, 119.7, 119.6, 119.5, 115.3, 115.2, 114.2, 113.7, 29.3, 22.6, 21.8, 15.7, 15.6; IR (KBr) $\tilde{\nu}$ = 2974, 2922, 2855, 1615, 1590,

1538, 1435, 1362, 1261 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{22}H_{19}N_2$ $[M + H]^+$ 311.1543, found 311.1540.

Mixture of **2-Ethyl-11-nitrobenzo[4,5]imidazo[1,2-f]phenanthridine** and **2-Ethyl-12-nitrobenzo[4,5]imidazo[1,2-f]phenanthridine (2d').** R_f = 0.50 (hexane/ethyl acetate 4:1); Inseparable Pale yellow solid (5:2); yield 93% (55.5 mg); mp 242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.73 (dd, *J* = 12.0, 8.0 Hz, 1.8H), 8.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.33 – 8.27 (m, 2.8H), 8.27 – 8.25 (m, 0.4H), 8.24 (s, 0.4H), 8.19 (s, 1H), 8.16 (s, 0.4H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.80 – 7.71 (m, 1.4H), 7.64 (dd, *J* = 15.2, 8.0 Hz, 1.4H), 7.38 (d, *J* = 8.0 Hz, 1.4H), 3.00 – 2.84 (m, 2.8H), 1.39 – 1.46 (m, 4.2H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 151.9, 150.7, 149.1, 146.9, 146.5, 144.4, 144.2, 142.8, 135.5, 133.8, 133.7, 131.8, 131.6, 130.9, 130.4, 130.0, 128.7, 128.6, 126.6, 126.5, 125.7, 124.6, 124.6, 122.3, 122.3, 122.2, 120.0, 119.9, 119.8, 119.6, 117.9, 116.3, 115.1, 115.0, 113.8, 110.9, 29.3, 15.6, 15.5; IR (KBr) $\tilde{\nu}$ = 3442, 2966, 2924, 1619, 1594, 1539, 1450, 1430, 1341, 1294, 1086 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}N_3O_2$ $[M + H]^+$ 342.1237, found 342.1248.

Mixture of 2-Fluoro-11-methylbenzo[4,5]imidazo[1,2-f]phenanthridine and 2-Fluoro-12-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (2e'). R_f = 0.50 (hexane/ethyl acetate 7:3); Inseparable white solid (2:1); yield 94% (56 mg); mp 165 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.81 (t, *J* = 7.7 Hz, 1.5H), 8.45 – 8.36 (m, 1.5H), 8.27 (d, *J* = 7.7 Hz, 1.5H), 8.20 (d, *J* = 9.8 Hz, 0.5H), 8.16 (d, *J* = 9.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.01 (s, 0.5H), 7.91 (d, *J* = 7.7 Hz, 0.5H), 7.81 (s, 1H), 7.67 – 7.73 (m, 1.5H), 7.63 – 7.67 (m, 1.5H), 7.35 (d, *J* = 8.4 Hz, 0.5H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1.5H), 2.66 (s, 1.5H), 2.58 (s, 3H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 163.0 (d, $^1J_{C,F}$ = 248.8 Hz), 162.9 (d, $^1J_{C,F}$ = 248.5 Hz), 147.7, 147.3, 144.9, 142.7, 135.5 (d, $^3J_{C,F}$ = 10.5 Hz), 135.4 (d, $^3J_{C,F}$ = 10.3 Hz), 134.6, 133.5, 132.0,

130.6, 130.6, 129.8, 129.1, 129.0, 128.6, 128.6, 126.2 (d, $^{3}J_{C,F}$ = 6.5 Hz), 126.1 (d, $^{3}J_{C,F}$ = 8.2 Hz), 124.9, 123.1, 123.0, 122.2, 120.4, 120.1, 118.3 (d, $^{4}J_{C,F}$ = 3.0 Hz), 118.2 (d, $^{4}J_{C,F}$ = 2.6 Hz), 113.7, 113.1, 112.0 (d, $^{2}J_{C,F}$ = 22.1 Hz), 103.4 (d, $^{2}J_{C,F}$ = 26.9 Hz), 103.3 (d, $^{2}J_{C,F}$ = 26.8 Hz), 22.5, 21.8; IR (KBr) $\tilde{\nu}$ = 3417, 2922, 2852, 1623, 1534, 1467, 1440, 1384, 1185 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{14}FN_2$ $[M + H]^+$ 301.1136, found 301.1148.

Mixture of **7-Fluoro-11-methylbenzo[4,5]imidazo[1,2-f]phenanthridine** and **7-Fluoro-12-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (2f').** R_f = 0.60 (hexane/ethyl acetate 4:1); Inseparable white solid (10:1); yield 82% (49 mg); mp 170 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.41 – 8.45 (m, 2.2H), 8.31 (d, *J* = 7.7 Hz, 1.1H), 8.28 (dd, *J* = 8.4, 5.6 Hz, 1.1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 0.1H), 7.78 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1.1H), 7.44 (t, *J* = 7.7 Hz, 1.1H), 7.41 – 7.36 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 0.1H), 7.27 (s, 1H), 2.64 (s, 0.3H), 2.57 (s, 3H); ^{13}C{1H} NMR (175 MHz, $CDCl_3$) δ 162.7 (d, $J_{C,F}$ = 249.2 Hz), 146.6, 146.6, 144.8, 142.6, 134.3, 134.0, 133.4, 130.0, 129.1, 129.0, 126.0, 125.9, 125.9, 125.4 (d, $J_{C,F}$ = 9.2 Hz), 124.9, 124.9, 124.8, 124.6, 124.5, 124.1, 121.1, 120.4, 120.1, 118.6 (d, $J_{C,F}$ = 23.1 Hz), 116.1, 116.1, 114.1, 113.6, 111.5 (d, $J_{C,F}$ = 23.5 Hz), 111.5 (d, $J_{C,F}$ = 23.9 Hz), 22.5, 21.8; IR (KBr) $\tilde{\nu}$ = 3417, 2961, 2922, 2850, 2367, 2335, 1626, 1547, 1514, 1480, 1430, 1361, 1339, 1200, 1091 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{20}H_{14}FN_2$ $[M + H]^+$ 301.1136, found 301.1123.

Mixture of **1-(11-Methylbenzo[4,5]imidazo[1,2-f]phenanthridin-2-yl)ethan-1-one** and **1-(12-Methylbenzo[4,5]imidazo[1,2-f]phenanthridin-2-yl)ethan-1-one (2g').** R_f = 0.50 (hexane/ethyl acetate 7:3); Inseparable pale yellow solid (2.5:1); yield 87% (52 mg); mp 198 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.89 (s, 0.4H), 8.86 (s, 1H), 8.73 (dd, *J* = 6.3, 3.5 Hz, 1.4H), 8.35 – 8.24 (m, 1.4H), 8.18 (d, *J* = 3.5 Hz, 1.4H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 0.4H), 7.86

(d, J = 8.4 Hz, 0.4H), 7.81 (t, J = 8.4 Hz, 1.4H), 7.75 (s, 1H), 7.65 (d, J = 3.5 Hz, 2.8H), 7.32 (d, J = 8.4 Hz, 0.4H), 7.27 (s, 1H), 2.69 (s, 4.2H), 2.64 (s, 1.2H), 2.57 (s, 3H); $^{13}C\{1H\}$ NMR (175 MHz, $CDCl_3$) δ 196.8, 196.8, 147.1, 146.8, 144.7, 142.5, 136.7, 134.5, 134.3, 134.2, 133.7, 132.0, 130.5, 130.4, 129.8, 128.4, 128.3, 126.2, 126.1, 126.1, 125.5, 125.3, 125.2, 124.4, 124.3, 124.2, 124.0, 123.9, 123.0, 120.3, 120.0, 115.5, 115.4, 114.0, 113.5, 26.9, 22.6, 21.8; IR (KBr) $\tilde{\nu}$ = 3403, 2922, 2857, 1682, 1590, 1537, 1434, 1355, 1262 cm^{-1}; HR-MS (ESI-TOF) m/z calcd for $C_{22}H_{17}N_2O$ $[M + H]^+$ 325.1335, found 325.1348.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information file contains crystallographic data, NMR spectra and Mass Spectra. This information is available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author: *pmal@niser.ac.in

ORCID

Prasenjit Mal: 0000-0002-7830-9812

NOTES

The authors declare no competing financial interest

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