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# Regioselective 6-*endo-dig* Iodocyclization: An accessible approach for Iodo-benzo[*a*]phenazines

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A facile approach for the synthesis of substituted iodo-benzo[*a*]phenazines from 2-aryl-3-(aryl/alkylethynyl)quinoxalines via 6-*endo-dig* ring closure has been described under mild reaction conditions. The iodocyclization proceeds through the iodonium ion intermediate followed by nucleophilic cyclization with the C-H bond of the arene. Further, the resulting 6-iodo-5-aryl/alkyl benzo[*a*]phenazine derivatives were allowed for structural diversification by employing various coupling reactions. The structure of iodo-benzo[*a*]phenazine was confirmed by X-ray crystallographic studies of the compound.

## Introduction

Phenazine derivatives constitute an important class of compounds which show a wide range of biological activities and act as the medicinally important scaffold.[1,2] Significantly, reduced as well as oxidized forms of natural and synthetic phenazines inhibit the growth of malaria[3a] (Figure 1, i), bacteria[3b] (Figure 1, ii) and hepatitis C viral replication.[4] In particular, benzo[a]phenazine derivatives act as potent anticancer agents,[5] fluorescers,[6] inhibitors of topoisomerase I and II of DNA in the cell cycles which are affected by key enzymes,[7] mycobacterium tuberculosis activity,[8] bioreductive antitumor agents[9] (Figure 1, iii) and antifungal activity.[10a] Their derivatives have acted as anti chagas' agent[10b] (Figure 1, iv) and dication DNA-binder (Figure 1, v). Apart from the significant biological activity benzo[*a*]phenazine derivatives are useful in photodynamic therapy (PDT).[11]

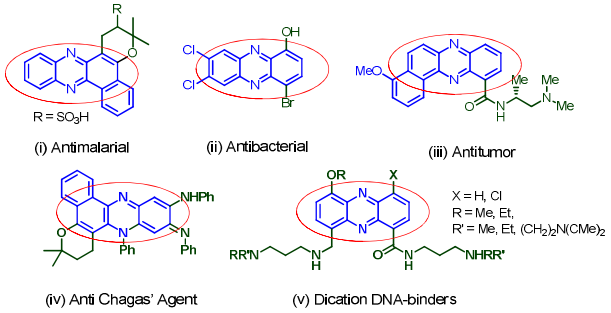


**Figure 1.** Biologically Active Phenazines Cores.

The iodocyclization of alkynes represents a useful method for the construction of important heterocycles.[12a,b] The iodo functionality introduced via electrophilic iodocyclization, provide a useful route for structure elaboration to generate complex molecules. Iodine reagents have attracted much attention by organic chemists due to their eco-friendly and cost effective properties. This developed approach employs molecular iodine which is more economical and convenient to use then the transition-metal catalyst.

Due to the vast biological significance of phenazines an alternative and approachable route for their synthesis is still challenging. Till now, various metal-catalyzed strategies are known for the development of phenazine analogs; however, halogen-induced electrophilic cyclizations remain elusive. During the past decade, iodocyclization has emerged as an efficient tool for the synthesis of functionalized cyclic compounds such as indoles,[12c,d] quinolines,[13] quinolinones,[14] furans,[15] benzo[*b*]thiophenes,[16] selenophene,[17] pyrroles,[18] naphthalenes,[19] isochromenes[20] and other heterocycles.[21] In 2003, Barluenga and co-workers reported the synthesis of fused polycyclic aromatic scaffolds by employing $IPy_2BF_4$-mediated electrophilic cyclization.[22] Later Larock *et al.* have reported the synthesis of polycyclic carbocycles from arene-containing acetylenes via intramolecular electrophilic induced cyclization of alkyne (Scheme 1i).[23] In 2014, Chen and fellow-workers demonstrated the synthesis of iodo-substituted dibenzocyclohepten-5-ones *via* 7-*endo-dig* iodine monochloride mediated electrophilic cyclization of 1-([1,1′-biphenyl]-2-yl)alkynone (Scheme 1ii).[24] Gulevskaya group reported the synthesis of iodophenazines under harsh reaction condition with less substrate scope.[25] Recently, our group accomplished the synthesis of benzo[*a*]phenazines derivatives via palladium-catalyzed intramolecular hydroarylation(Scheme 1iii).[26]

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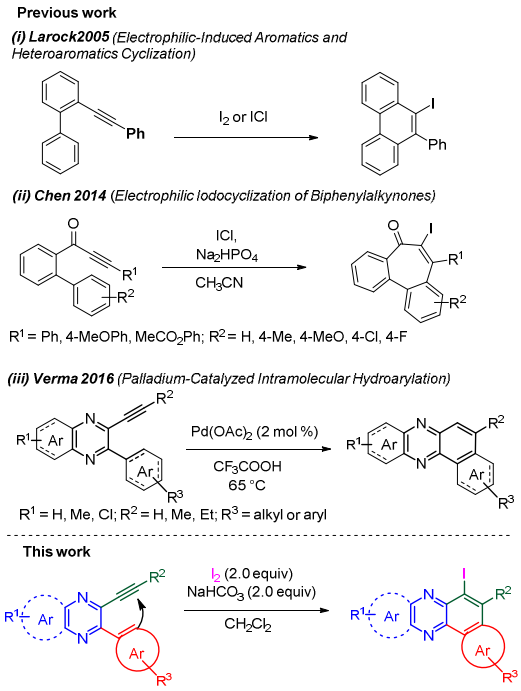
Owing to the great significance of benzophenazines; regioselective, inexpensive and environmental benign strategy for the synthesis of highly functionalized iodo-benzo[*a*]phenazines under mild reaction conditions remains elusive. In continuation of our interest in iodocyclization chemistry[27] here, we reported a versatile and efficient protocol for the construction of diversified iodo benzophenazines using iodine-mediated electrophilic cyclization at room temperature. This provides a variety of functional group variations on the halo benzo[*a*]phenazines which were further elaborated using various palladium-catalyzed coupling reactions.

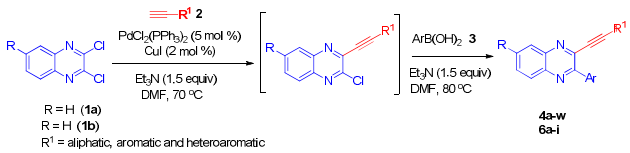
**Scheme 1.** Iodine-mediated Electrophilic Cyclization from Arenes




## Results and discussion

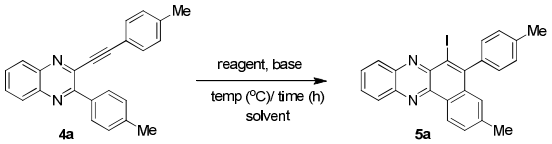
**Synthesis of 2-aryl/alkyl-3-(aryl/alkylethynyl)quinoxaline.** Starting substrates 2-aryl/alkyl-3-(aryl/alkylethynyl)quinoxaline **4a–w** and **6a-i** required for examining the scope and generality of this designed chemistry were readily prepared by the reported Sonogashira and Suzuki coupling of corresponding *o*-dichloroquinoxaline **1a** and **1b** with commercially available terminal alkynes and boronic acids **3** (Scheme 2)[26d].

**Scheme 2.** Synthesis of 2-aryl/alkyl-3-(aryl/alkylethynyl) quinoxaline




To identify the optimal reaction conditions, 2-(*p*-tolyl)-3-(*p*-tolylethynyl)quinoxaline **4a** was chosen as representative substrates along with various electrophile and organic solvents at different reaction temperatures (Table 1). Initially, the reaction was performed with 2-(*p*-tolyl)-3-(*p*-tolylethynyl) quinoxaline **4a**, iodine and $K_2CO_3$ in $CH_2Cl_2$ for 25 h at 25°C to afford the desired product 6-iodo-3-methyl-5-(*p*-tolyl) benzo[*a*]phenazine **5a** in 45% yield (entry 1). Increasing the amount of iodine from 1.0 to 1.5 equiv afforded the desired phenazine product **5a** in 55% yield (entry 2). Further increasing the amount of iodine made no significant improvement in the yield of the product **5a** (entries 3-4). When $NaHCO_3$ was employed, the corresponding iodocyclized product **5a** was obtained in 78% yield in 25 h (entry 5). On running the reaction for a longer time made no improvement in the yield of desired

**Table 1.** Optimization of Reaction Conditions[a]




| entry | reagent (equiv) | (solvent) | base (equiv) | temp (◦C) | time (h) | yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | $I_2$ (1.0) | $CH_2Cl_2$ | $K_2CO_3$ | 25 | 25 | 45 |
| 2 | $I_2$ (1.5) | $CH_2Cl_2$ | $K_2CO_3$ | 25 | 25 | 55 |
| 3 | $I_2$ (2.0) | $CH_2Cl_2$ | $K_2CO_3$ | 25 | 25 | 60 |
| 4 | $I_2$ (2.5) | $CH_2Cl_2$ | $K_2CO_3$ | 25 | 25 | 62 |
| **5** | **$I_2$ (2.0)** | **$CH_2Cl_2$** | **$NaHCO_3$** | **25** | **25** | **78** |
| 6 | $I_2$ (2.0) | $CH_2Cl_2$ | $NaHCO_3$ | 25 | 40 | 75 |
| 7 | $I_2$ (2.0) | $CH_2Cl_2$ | $KHCO_3$ | 25 | 40 | 68 |
| 8 | $I_2$ (2.0) | $CH_2Cl_2$ | $Cs_2CO_3$ | 25 | 25 | 52 |
| 9 | $I_2$ (2.0) | $CH_2Cl_2$ | $KO^tBu$ | 25 | 25 | 65 |
| 10 | $I_2$ (2.0) | $CH_2Cl_2$ | $Et_3N$ | 25 | 25 | 20 |
| 11 | $I_2$ (2.0) | DCE | $NaHCO_3$ | 25 | 25 | 65 |
| 12 | $I_2$ (2.0) | DCE | $NaHCO_3$ | 50 | 25 | 68 |
| 13 | $I_2$ (1.0) | DMF | $NaHCO_3$ | 50 | 25 | 44 |
| 14 | $I_2$ (1.0) | MeCN | $NaHCO_3$ | 50 | 25 | 38 |
| 15 | ICl (2.0) | $CH_2Cl_2$ | $NaHCO_3$ | 0 | 25 | 57 |
| 16 | NIS (2.0) | $CH_2Cl_2$ | $NaHCO_3$ | 25 | 25 | 48 |
| 17[c] | $I_2$ (2.0) | $CH_2Cl_2$ | $NaHCO_3$ | 25 | 25 | 76 |
| 18 | $I_2$ (2.0) | MeOH | $NaHCO_3$ | 25 | 25 | 20 |
| 19 | $I_2$ (2.0) | $H_2O$ | $NaHCO_3$ | 25 | 25 | trace |

[a]All reactions were performed using 0.5 mmol of the 2-(*p*-olyl)-3-(p-tolylethynyl)quinoxaline **4a**, 2.0 equiv. of base, and 2.0 mL of solvent under inert atmosphere conditions. [b]Isolated yields. [c]2.5 equiv. of the base was used

product **5a** (entry 6). Other bases like $KHCO_3$, $Cs_2CO_3$ and $KO^tBu$ afforded the product in 52-68% yield (entries 7-9). However, an organic base such as $Et_3N$ was ineffective (entry 10). When the reaction proceeded in DCE at 25 °C and 50 °C, the desired compound was obtained in 71% and 68% yield, respectively (entries 11-12). When DMF and MeCN were used as solvents lower yield of the desired product **5a** was observed (entries 13-14). Use of other electrophiles like ICl and NIS provided the product in lower yields (entries 15-16). Using 2.5

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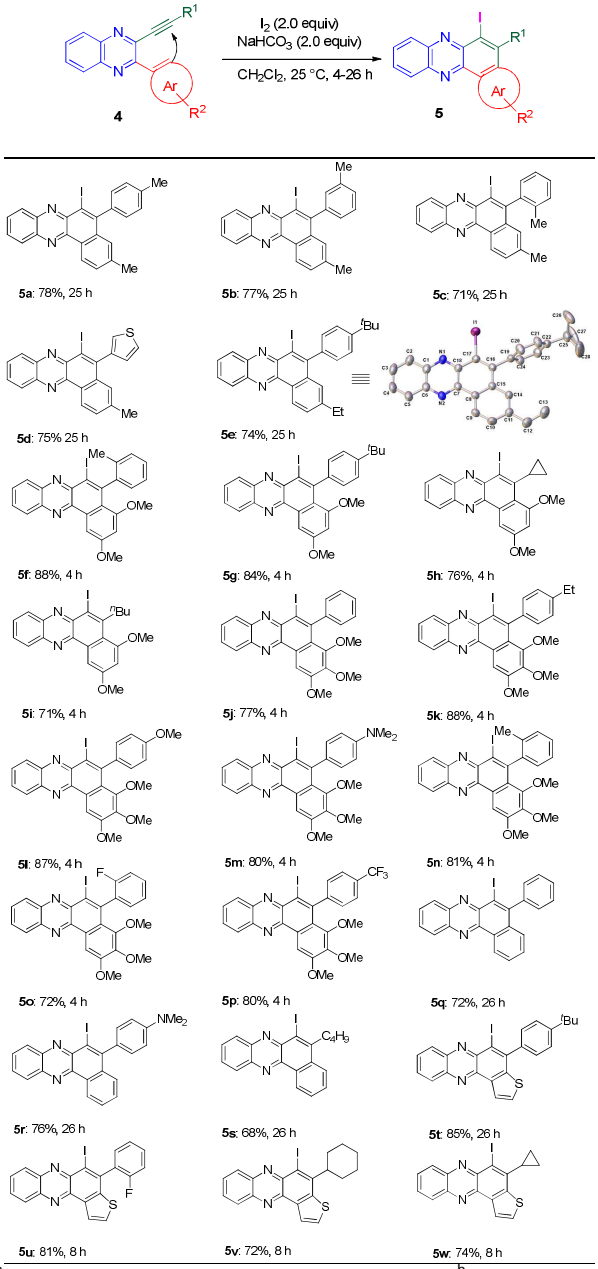
equiv of $NaHCO_3$ made no appreciable amendment in the yield of desired product **5a** (entry 17). Inferior results were obtained on performing the reaction of **4a** with MeOH and $H_2O$ (entries 18-19).

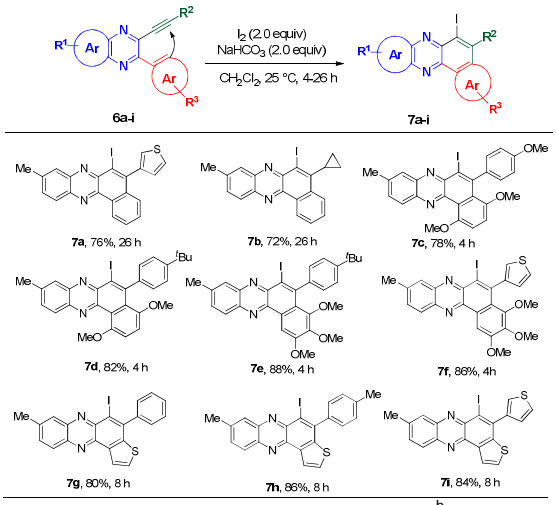
**Scheme 3.** Synthesis of 6-Iodo-5-aryl/alkylbenzo[*a*]phenazine[a]




[a]Using optimized conditions (entry 5, Table 1). [b]Isolated yield. CCDC numbers of **5e** is 1518194.

After optimizing the reaction conditions, scope and generality of the reaction were explored with substituted substrates 2-aryl-3 (aryl/alkylethynyl)quinoxaline **4a–w** for the synthesis of diversified iodo-benzo[*a*]phenazines derivatives **5a–w** (Scheme 3). The reaction was well tolerated with electron-rich quinoxalines having a *para*, *meta* and *ortho* substituted methyl arenes attached to carbon-carbon triple bond (**5a–c**). Substrates **4d** bearing thienyl group afforded the desired iodophenazine **5d** in 75% yield. The reaction of bulky substrate **4e** in the presence of molecular iodine provided the desired product **5e** in 74% yield. The X-ray crystallographic studies further confirmed the formation of product **5e**. The 3,5-dimethoxyphenylethynylquinoxaline **4f–g** were also successful in providing the desired products **5f–g** in 88% and 84% yields respectively. Treatment of cyclopropylethynyl dimethoxyphenylquinoxaline **4h** with $I_2$ provided the iodo phenazine **5h** in 76% yield. The reaction of quinoxaline alkynes **4i** having aliphatic substituents provided the desired iodocyclized product **5i** in 71% yields. Substrates **4j–p** containing trimethoxy group underwent cyclization smoothly to afford the iodo phenazines derivatives **5j–p** in 72-88% yields. Generally, the substrates **4q–r** bearing an electron-neutral phenyl ring neighboring to the carbon-carbon triple bond furnished the desired iodo cyclized product **5q** and **5r** in 72% and 76% yield respectively (Scheme 3). Substrates **4s** bearing aliphatic *n*-butyl group to the carbon-carbon triple bond tolerated the reaction conditions and provided the desired product **5s** in 68% yield. Thienyl substituted substrates **4t-w** provided the cyclized products **5t-w** in good yields (Scheme 3).

**Scheme 4.** Synthesis of 6-Iodo-9-methyl-5-aryl/alkylbenzo[*a*] phenazine[a]




[a]Using optimized conditions (entry 5, Table 1). [b]Isolated yield.

**Synthesis of 6-methyl substituted iodo benzo[*a*]phenazine.** Encouraged by the above results; we further extended the scope of iodocyclization chemistry by using substituted quinoxaline (Scheme 4). The reactions of 6-methyl substituted quinoxalines **6a–b** having thiophene and cyclopropyl ethynyl moieties provided the corresponding iodo benzo[*a*]phenazine **7a–b** in 76% and 72% yields (Scheme 4). We observed that reaction of *p*-methoxyphenyl-substituted quinoxalines **6c** with $I_2$ underwent iodocyclization and afforded the iodo benzo[*a*]phenazine **7c** in 78% yields. Similar electronic effects of substituents were observed with electron-rich quinoxalines **6d-h** and products were obtained in good yield. The presence

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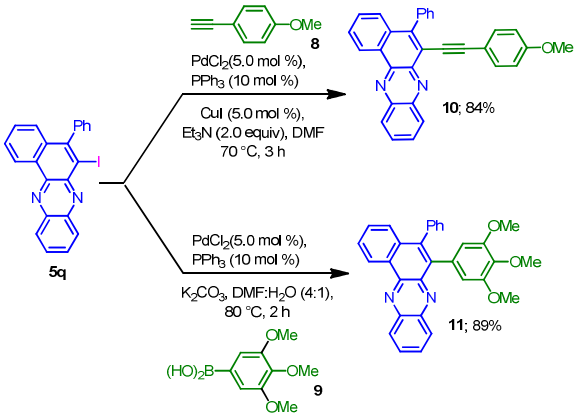
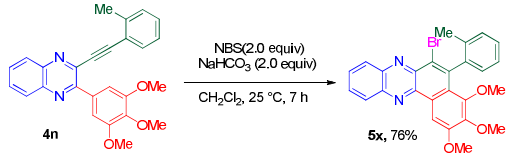
of thiophene ethynyl)quinoxaline **6i** afforded the desired iodocyclized product **7i** in 84 % yield.

**Scheme 5.** Synthetic Elaboration of Iodo-benzophenazine **5q**



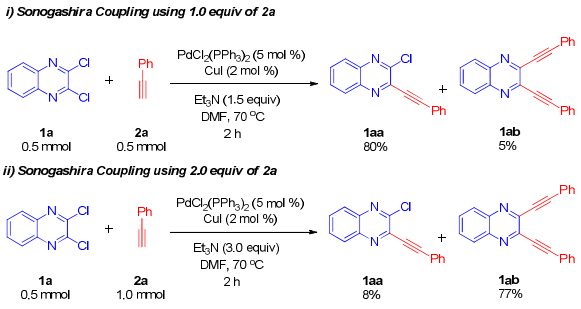

Inspired by these results, we next elaborated the scope of iodo-substituted benzo[*a*]phenazine using palladium-catalyzed Sonogashira and Suzuki cross-coupling reactions (Scheme 5). The reaction of 6-iodo-5-phenylbenzo[*a*]phenazine **5q** with 1-ethynyl-4-methoxybenzene (**8**) and (3,4,5-trimethoxyphenyl) boronic acid (**9**) provide the corresponding coupling product **10** and **11** in 84% and 89% yields respectively.

**Scheme 6.** Synthesis of 6-Bromo-2,3,4-trimethoxy-5-(o-tolyl) benzo[*a*]phenazine




Encouraged by the above results, we explored the Bromo cyclization of 2-(*o*-tolylethynyl)-3-(3,4,5-trimethoxy phenyl) quinoxaline **4n** with *N*-bromosuccinimide; desired product 6-bromo-2,3,4-trimethoxy-5-(*o*-tolyl)benzo[*a*] phenazine **5x** was obtained in 76% yield (Scheme 6).

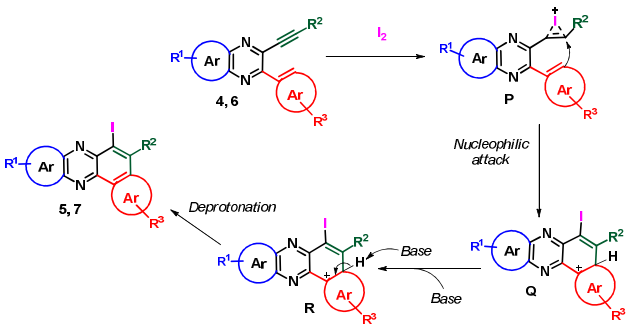
**Scheme 7.** Control Experiment




In order to confirm the reactivity and selectivity of the Sonogashira coupling reaction on **1a,** we performed two sets off an experiment using 0.5 mmol and 1.0 mmol of the alkyne **2a**, in first case mono-alkynyl-mono-chloro product **1aa** was obtained in 80% yield with 5% of di-alkynyl product **1ab** (Scheme 7i). In the second experiment when 1.0 mmol of alkyne was used the di-alkynyl product **1ab** was obtained in 77% with 8% of product **1aa** (Scheme 7ii).

On the basis of previous literature,[21] a plausible mechanism was proposed for this iodine-induced intramolecular cyclization of 2-aryl-3 (aryl/alkylethynyl) quinoxaline in Scheme 8. The reaction initiates with the coordination of iodine with carbon-carbon triple bond to form an electrophilic acetylenic iodonium complex **P**, which then undergoes cyclization triggered through the nucleophilic attack of the neighbouring aromatic ring of the quinoxaline on the carbon-carbon triple bond to generate the intermediate **Q**. After the deprotonation of species **Q,** the desired iodo aryl/alkylbenzo[*a*]phenazine was obtained.

**Scheme 8.** Plausible Mechanism




## Conclusions

In conclusion, we have developed a versatile protocol for the synthesis of iodo benzophenazine derivatives with high functional group tolerance via the molecular iodine induced electrophilic intramolecular regioselective cyclization of 2-aryl-3-(aryl/alkylethynyl)quinoxaline under mild reaction conditions. This methodology accommodates a wide range of 6-iodo-5-aryl/alkylbenzo[*a*]phenazine derivatives in good to excellent yields. The regioselectivity of the cyclic products was confirmed by the X-ray crystallography studies. The cyclized products 6-iodo-5-phenylbenzo[*a*]phenazine having iodo group could be further elaborate for using organopalladium chemistry. Developed approach is general, operationally simple, and expands the synthetic utility of *o*-alkynyl aryl quinoxaline for the synthesis of a variety of iodo benzophenazine which are of great importance in medicinal chemistry as well as in natural products.

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## EXPERIMENTAL SECTION

**General Method**. Nuclear Magnetic Resonance spectra were recorded in $CDCl_3$ $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra at ambient temperature. Chemical shifts ($\delta$) for all protons are reported in parts per million (ppm) and were measured relative to residual $CHCl_3$ and TMS resonance as an internal reference in the deuterated solvent. Chemical shifts for all spectra were reported in ppm relative to deuterochloroform (77.0 ppm) and all were obtained with $^1H$ decoupling. The following abbreviations were used to describe the multiplicities: when appropriate s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Reactions were monitored using thin-layer chromatography on commercially prepared silica gel plates and visualized by either UV irradiation or by staining with $I_2$. Chemical yields are referred to the pure isolated substances. Chromatographic Purification of the label compounds was accomplished by column chromatography using 100-200 mesh size silica gels.

**General Procedure for the Synthesis of Starting Substrate**

**General experimental procedure for sequential Sonogashira/Suzuki coupling reaction and Analytic data of 4a-w and 6a-i**

To a solution of substituted 2,3-dichloroquinoxaline (0.5 mmol) in DMF (2 mL), 2 mol% of $Pd(PPh_3)_2Cl_2$ was added. The reaction vial was then sealed and flushed with nitrogen. Then, 1.5 equiv of $Et_3N$ and 0.51 mmol of alkyne **2** were added to the reaction mixture. The reaction was then stirred at 70 °C until TLC revealed complete conversion of the starting material. After the completion of the first coupling reaction (Monitored by TLC) 3 mol% of $Pd(PPh_3)_2Cl_2$, 0.5 mmol of boronic acid **3**, 1.5 equiv of $Et_3N$ was added under nitrogen atmosphere. The reaction was then stirred at 80 °C until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with $H_2O$ and extracted with EtOAc (3X10 mL). The combined organic layers were dried over $Na_2SO_4$, concentrated under vacuum, and purified by column chromatography using 100−200 mesh size silica gels (hexane: ethylacetate) to afford the corresponding product. The structure and purity of known starting materials **4a, 4d-j, 4l-r, 4t-w, 6b and 6h**, were confirmed by comparison of their physical and spectral data ($^1H$ NMR and $^{13}C$ NMR) with those reported in the literature[26d].

**General experimental Procedure for 6-Iodo-5-aryl/alylbenzo[*a*] Phenazine 5a-w and 7a-i**

In a oven-dried round bottom flask, a solution of *o*-alkynylaryl derivatives **4** and **6** (0.5 mmol) in 2.0 mL of DCM as a solvent and 2.0 equiv of $NaHCO_3$ then added 2.0 equiv of $I_2$. The resulting reaction mixture was stirred at 25°C for 4-26 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of *o*-alkynylaryls the reaction mixture was quenched with saturated aq sodium thiosulfate solution. The resulting mixture was extracted with ethyl acetate (10 mL) and water (15 mL) and then filtered through a plug of Celite. The layers were separated, and the organic layer was washed with aqueous saturated brine solution, dried over $Na_2SO_4$. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (hexane: ethyl acetate) and recrystallization in DCM: hexane. The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data ($^1H$ NMR, $^{13}C$ NMR, and HRMS).

***2-Chloro-3-(phenylethynyl)quinoxaline*** (**1aa**). The product was obtained as a yellow solid; (105.9 mg, 80%): mp 102–106 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.12–8.08 (m, 1H), 8.02–7.99 (m, 1H), 7.81–7.77 (m, 2H), 7.73–7.71 (m, 2H), 7.48–7.40(m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 148.0, 140.7, 140.3, 138.6, 132.5, 131.4, 130.7, 130.1, 128.8, 128.6, 128.2, 121.2, 97.1, 85.4; HRMS (ESI-TOF) Calcd for $C_{16}H_9ClN_2$ requires $[M+H]^+$ 265.0533, found 265.0538.

***2,3-Bis(phenylethynyl)quinoxaline*** (**1ab**). The product was obtained as a yellow oil; (127.2 mg, 77%), $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.09–8.05 (m, 2H), 7.77–7.69 (m, 4H), 7.44–7.36 (m, 5H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.18–7.11(m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.9, 140.3, 132.3, 130.9, 129.8, 128.9, 128.5, 128.2, 128.1, 127.6, 125.6, 121.6, 95.8, 86.7; HRMS (ESI-TOF) Calcd for $C_{24}H_{14}N_2$ requires $[M+H]^+$ 331.1235, found 331.1237.

***2-(p-Tolyl)-3-(m-tolylethynyl)quinoxaline*** **(4b).** The product was obtained as a yellow needles (120.3 mg, 75%): mp 80–84 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.13–8.10 (m, 2H), 8.05–8.02 (m, 2H), 7.74–7.72 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.31–7.29 (m, 2H ), 7.24–7.16 (m, 2H), 2.47 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 154.8, 140.6, 139.8, 138.0, 137.9, 134.5, 132.6, 130.5, 130.4, 130.1, 129.8, 129.6, 129.1, 129.0, 128.8, 128.4, 128.2, 121.4, 115.3, 95.4, 88.0, 21.4, 21.1; HRMS (ESI) calcd for $[C_{24}H_{18}N_2]$ requires $[M+Na]^+$ 357.1368, found 357.1360.

***2-(p-Tolyl)-3-(o-tolylethynyl)quinoxaline*** **(4c).** The product was obtained as a brown needles (125.4 mg, 75%): mp 122–125 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.07–8.01 (m, 2H), 7.88 (d, *J* = 8.56 Hz, 2H), 7.69–7.65 (m, 2H), 7.44 (d, *J* = 7.32 Hz, 1H), 7.25 (d, *J* = 7.96 Hz, 2H), 7.21–7.16 (m, 1H), 7.12–7.06 (m, 2H), 2.37 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.1, 141.2, 141.0, 140.7, 139.7, 138.3, 135.0, 132.8, 130.5, 130.0, 129.54, 129.50, 129.2, 128.9, 128.7, 125.6, 121.6, 94.0, 91.9, 21.4, 20.5; HRMS (ESI) calcd for $[C_{24}H_{18}N_2]$ requires $[M+Na]^+$ 357.1368, found 357.1360.

***2-((4-Ethylphenyl)ethynyl)-3-(3,4,5-trimethoxyphenyl)quinoxaline*** **(4k).** The product was obtained as a yellow needles (157.0 mg, 74%): mp 94–98 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.18–8.15 (m, 2H), 7.82–7.79 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 2H), 7.23 (d, *J* = 7.6 Hz, 2H ), 4.00 (s, 3H), 3.96 (s, 6H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 154.5, 152.8, 146.3, 140.8, 140.3, 139.2, 137.9, 132.8, 132.0, 130.5, 129.0, 128.6, 128.0, 125.9, 118.5, 106.9, 95.7, 87.9, 60.9, 56.1, 28.8, 15.1; HRMS (ESI) calcd for $[C_{26}H_{22}N_2O_3]$ requires $[M+H]^+$ 425.1865, found 425.1862.

***2-(Hex-1-yn-1-yl)-3-phenylquinoxaline*** **(4s).** The product was obtained as a brown oil (97.3 mg, 68%); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.04–7.99 (m, 2H), 7.95–7.93 (m, 1H), 7.67–7.63 (m,

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2H), 7.44–7.41 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H ), 6.79–6.74 (m, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.49–1.41 (m, 2H), 1.30–1.22 (m, 2H), 0.79 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 156.1, 154.9, 140.7, 140.5, 138.4, 137.5, 130.4, 129.5, 129.1, 128.4, 128.0, 120.1, 115.4, 98.0, 79.7, 29.7, 21.9, 19.3, 13.5; HRMS (ESI) calcd for $[C_{20}H_{18}N_2]$ requires $[M+H]^+$ 287.1548, found 287.1552.

***6-Methyl-2-phenyl-3-(thiophen-2-ylethynyl)quinoxaline*** **(6a).** The product was obtained as a brown needles (114.2 mg, 70%): mp 123–127 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.00–7.97 (m, 2H), 7.93-7.90 (m,1H), 7.81–7.79 (m, 1H), 7.50–7.41 (m, 5H), 7.19–7.17 (m,1H), 7.04(d, *J* = 4.8 Hz, 1H), 2.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.1, 141.4, 140.9, 140.7, 139.1, 137.6, 132.9, 132.6, 131.1, 129.6,128.7, 128.0, 127.4, 125.6, 120.9, 90.3, 88.1 ,21.9; HRMS (ESI) calcd for $[C_{21}H_{14}N_2S]$ requires $[M+Na]^+$ 327.0956, found 327.0982.

***2-(2,5-Dimethoxyphenyl)-3-((4-methoxyphenyl)ethynyl)-6-methylquinoxaline*** **(6c).** The product was obtained as a yellow needles (160.0 mg, 78%): mp 108–112 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, *J* = 8.4Hz, 1H), 7.88 (s,1H), 7.60–7.56 (m, 1H), 7.25 (d , *J* = 8.4Hz, 2H), 7.08–7.04 (m, 2H), 7.00–6.98 (m, 1H), 6.81 (d, *J*= 8.4 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 2.60 (s, 3H) ; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.3, 153.8, 153.5, 151.9, 141.1, 140.7, 140.2, 138.8, 133.8, 132.3, 128.7, 128.1, 127.5, 116.1, 115.7, 114.0, 113.8, 112.0, 94.1, 87.1, 56.1, 55.8, 55.2, 21.9; HRMS (ESI) calcd for $[C_{26}H_{22}N_2O_3]$ requires $[M+Na]^+$ 433.1528, found 433.1523.

***3-((4-(tert-Butyl)phenyl)ethynyl)-2-(2,5-dimethoxyphenyl)-6-methylquinoxaline*** **(6d).** The product was obtained as a yellow needles (174.6 mg, 80%): mp 84–88 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 (d, *J*= 9.2 Hz, 1H), 7.87 (s, 1H), 7.57–7.53 (m, 1H), 7.30–7.28 (m , 2H), 7.24–7.21(m, 2H), 7.06–7.01 (m, 2H), 6.98–6.95 (m, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.57 (s, 3H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 153.9, 153.5, 152.7, 151.9, 141.1, 140.7, 140.1, 138.9, 132.4, 131.9, 128.6, 128.2, 127.5, 125.3, 118.8, 116.1, 115.6, 112.0, 94.0, 87.5, 56.1, 55.8, 34.8, 31.0, 21.8; HRMS (ESI) calcd for $[C_{29}H_{28}N_2O_2]$ requires $[M+H]^+$ 437.2229, found 437.2229.

***3-((4-(tert-Butyl)phenyl)ethynyl)-6-methyl-2-(3,4,5-trimethoxyphenyl)quinoxaline*** **(6e).** The product was obtained as a yellow semi-solid (195.9 mg, 84%): $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.91 (d, *J* = 9.2 Hz, 1H), 7.79 (s, 1H), 7.49 (d, *J* = 9.1 Hz, 1H), 7.33–7.31 (m , 1H), 7.28–7.24 (m, 4H), 3.85 (s, 3H), 3.81 (s, 6H), 2.50 (s, 3H), 1.20 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 152.9, 141.4, 140.9, 140.5, 139.4, 138.9, 137.9, 133.1, 132.6, 131.8, 128.6, 128.0, 127.4, 125.5, 118.5, 106.9, 95.5, 88.0, 60.9, 56.2, 34.9, 31.0, 22.0, 21.9; HRMS (EI-TOF) calcd for $[C_{30}H_{30}N_2O_3]$ requires $[M]^+$ 466.2256, found 466.2252.

***6-Methyl-3-(thiophen-3-ylethynyl)-2-(3,4,5-trimethoxyphenyl)quinoxaline*** **(6f).** The product was obtained as a yellow needles (131.4 mg, 82%): mp 89–93 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.95–7.92 (m, 1H), 7.83–7.81 (m, 1H), 7.55–7.51 (m, 2H), 7.28–7.27 (m , 2H), 7.25–7.23(m, 1H), 7.08 (d, *J* = 5.3 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 6H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 152.9, 140.9, 139.2, 139.0, 137.6, 133.1, 132.9, 131.2, 131.1, 129.6, 128.6, 127.4, 125.9, 120.8, 106.9, 104.5, 90.5, 88.2, 61.0, 56.2, 21.9; HRMS (EI-TOF) calcd for $[C_{24}H_{20}N_2O_3S]$ requires $[M]^+$ 416.1195, found 416.1191.

***6-Methyl-3-(phenylethynyl)-2-(thiophen-3-yl)quinoxaline*** **(6g).** The product was obtained as a yellow needles (124.0 mg, 76%): mp 102–106 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.30–8.26 (m, 1H), 7.87–7.84 (m, 1H), 7.81– 7.76 (m, 1H), 7.67–7.65 (m , 1H), 7.48–7.45 (m, 2H), 7.37–7.34 (m, 1H), 7.30–7.28 (m, 1H), 7.24–7.21 (m, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 148.5, 141.2, 140.4, 138.94, 138.86, 136.7, 132.9, 131.9, 129.4, 128.7, 128.4, 127.5, 127.2, 125.0, 121.5, 94.4, 88.6, 21.7; HRMS (ESI) calcd for $[C_{21}H_{14}N_2S]$ requires $[M+H]^+$ 327.0956, found 327.0982.

***6-Methyl-2-(thiophen-3-yl)-3-(thiophen-3 ylethynyl)quinoxaline*** **(6i).** The product was obtained as a yellow needles (121.3 mg, 73%): mp 111–115 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.39–8.36 (m, 1H), 7.97–7.91 (m, 2H), 7.80 (s, 1H), 7.67–7.66 (m , 1H), 7.54–7.51(m, 1H), 7.43–7.40 (m, 1H), 7.32–7.30 (m, 1H), 7.25 (d, *J* = 5.4 Hz, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) $\delta$ 148.6, 140.6, 139.1, 136.9, 133.0, 132.4, 131.2, 131.1, 129.6, 128.8, 128.5, 127.9, 127.6, 127.4, 125.8, 125.2, 120.8, 90.1, 88.4, 21.9; HRMS (EI-TOF) calcd for $[C_{19}H_{12}N_2S_2]$ requires $[M]^+$ 332.0442, found 332.0438.

***6-Iodo-3-methyl-5-(p-tolyl)benzo[a]phenazine*** **(5a).** The product was obtained as a yellow needles (179.5 mg, 78%): mp 271–274 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.26 (d, *J* = 8.2 Hz, 1H), 8.34–8.29 (m, 2H), 7.84–7.77 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* =7.8 Hz, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 151.0, 143.2, 142.4, 141.7, 141.6, 140.8, 140.4, 137.9, 134.2, 130.4, 129.9, 129.64, 129.55, 129.3, 129.2, 129.0, 128.7, 128.3, 125.5, 108.1, 21.9, 21.5; HRMS (ESI) calcd for $[C_{24}H_{17}IN_2]$ requires $[M+H]^+$ 461.0515, found 461.0532.

***6-Iodo-3-methyl-5-(m-tolyl)benzo[a]phenazine*** **(5b).** The product was obtained as a yellow needles (177.2 mg, 77%): mp 239–242 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.14–8.10 (m, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.75–7.72 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 1H), 7.01–6.98 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 151.1, 143.7, 143.2, 142.4, 141.7, 141.6, 140.4, 138.2, 134.2, 130.4, 130.1, 130.0, 129.7, 129.6, 129.0, 128.9, 128.7, 128.4, 128.3, 126.4, 125.5, 107.9, 22.0, 21.7; HRMS (ESI) calcd for $[C_{24}H_{17}IN_2]$ requires $[M+H]^+$ 461.0515, found 461.0531.

***6-Iodo-3-methyl-5-(o-tolyl)benzo[a]phenazine*** **(5c).** The product was obtained as a yellow needles (163.4 mg, 71%): mp 220–224 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.27 (d, *J* = 8.2 Hz, 1H), 8.33–8.28 (m, 2H), 7.82–7.77 (m, 2H), 7.54–7.52 (m, 1H), 7.41–7.31 (m, 3H), 7.13–7.11 (m, 1H), 7.01 (s, 1H), 2.35 (s, 3H), 1.97 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 150.7, 143.2, 142.5, 141.7, 141.6, 140.7, 135.8, 133.7, 130.4, 130.3, 130.0, 129.8, 129.6, 129.2, 129.0, 128.9, 128.5, 127.5, 126.2, 125.6, 108.1, 21.9, 19.6; HRMS (ESI) calcd for $[C_{24}H_{17}IN_2]$ requires $[M+H]^+$ 461.0515, found 461.0531.

***6-Iodo-3-methyl-5-(thiophen-3-yl)benzo[a]phenazine*** **(5d).** The product was obtained as a yellow needles (169.6 mg, 75%): mp 246–250 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.23 (d, *J* = 8.2 Hz, 1H), 8.33–8.27 (m, 2H), 7.83–7.77 (m, 2H), 7.54–7.50 (m, 2H), 7.32–7.31 (m, 1H), 7.19–7.18 (m, 1H), 7.11–7.09 (m,

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1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 146.6, 143.3, 143.1, 142.4, 141.6, 140.5, 134.2, 130.5, 130.0, 129.7, 129.6, 129.0, 128.6, 127.8, 125.9, 125.5, 124.8, 114.1, 108.7, 21.9; HRMS (ESI) calcd for $[C_{21}H_{13}IN_2S]$ requires $[M+H]^+$ 452.9922, found 452.9931.

***5-(4-(tert-Butyl)phenyl)-3-ethyl-6-iodobenzo[a]phenazine*** **(5e).** The product was obtained as a yellow needles (191.0 mg, 74%): mp 210–213 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.31 (d, $J$ = 8.4 Hz, 1H), 8.35–8.31 (m, 2H), 7.85–7.79 (m, 2H), 7.59 (d, $J$ = 7.6 Hz, 1H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.22–7.17 (m, 3H), 2.67 (q, $J$ = 7.6 Hz, 2H), 1.39 (s, 9H), 1.16 (t, $J$ = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 151.3, 151.1, 146.7, 143.2, 142.4, 140.9, 134.4, 130.4, 130.0, 129.6, 129.02, 128.96, 128.4, 127.3, 125.6, 125.44, 125.37, 108.0, 34.8, 31.5, 29.1, 15.5; HRMS (ESI) calcd for $[C_{28}H_{25}IN_2]$ requires $[M+H]^+$ 517.1141, found 517.1140.

***6-Iodo-2,4-dimethoxy-5-(o-tolyl)benzo[a]phenazine*** **(5f).** The product was obtained as a brown needles (222.7 mg, 88%): mp 188–192 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.58 (d, $J$ = 2.7 Hz, 1H), 8.32–8.29 (m, 2H), 7.80–7.77 (m, 2H), 7.24–7.17 (m, 3H), 6.98–6.96 (m, 1H), 6.60 (d, $J$ = 2.2 Hz, 1H), 4.03 (s, 3H), 3.29 (s, 3H), 1.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.4, 157.8, 148.5, 143.8, 142.3, 142.1, 140.7, 134.8, 134.6, 130.3, 130.2, 129.5, 129.1, 128.9, 127.6, 126.9, 125.1, 118.9, 106.5, 102.5, 99.5, 56.1, 55.8, 19.9; HRMS (ESI) calcd for $[C_{25}H_{19}IN_2O_2]$ requires $[M+H]^+$ 507.0569, found 507.0586.

***5-(4-(tert-Butyl)phenyl)-6-iodo-2,4-dimethoxybenzo[a]phenazine*** **(5g).** The product was obtained as a yellow needles (230.3 mg, 84%): mp 201–205 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.629–8.621 (m, 1H), 8.44–8.39 (m, 2H), 7.92–7.89 (m, 2H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.22 (d, $J$ = 8.4 Hz, 2H), 6.67–6.66 (m, 1H), 4.14 (s, 3H), 3.34 (s, 3H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.2, 157.5, 149.4, 148.9, 145.8, 143.7, 142.1, 141.8, 140.6, 134.3, 130.2, 130.0, 129.4, 129.0, 127.6, 124.0, 119.2, 106.6, 102.6, 99.1, 55.9, 55.7, 34.6, 31.5; HRMS (ESI) calcd for $[C_{28}H_{25}IN_2O_2]$ requires $[M+H]^+$ 549.1039, found 549.1039.

***5-Cyclopropyl-6-iodo-2,4-dimethoxybenzo[a]phenazine*** **(5h).** The product was obtained as a yellow needles (173.3 mg, 76%): mp 172–176 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.37–8.26 (m, 3H), 7.79 (s, 2H), 6.72 (s, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 2.51–2.47 (m, 1H), 0.91–0.84 (m, 2H), 0.61–0.54 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.7, 157.6, 149.5, 143.3, 141.7, 140.5, 139.2, 133.9, 130.0, 129.7, 129.3, 120.7, 114.0, 108.5, 101.8, 98.3, 55.7, 55.6, 14.1, 13.5; HRMS (ESI) calcd for $[C_{21}H_{17}IN_2O_2]$ requires $[M+H]^+$ 457.0413, found 457.0405.

***5-Butyl-6-iodo-2,4-dimethoxybenzo[a]phenazine*** **(5i).** The product was obtained as a yellow needles (167.6 mg, 71%): mp 194–198 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.51–8.50 (m, 1H), 8.32–8.28 (m, 2H), 7.82–7.75 (m, 2H), 6.67 (s, 1H), 4.04 (s, 3H), 3.90 (s, 3H), 1.71–1.66 (m, 2H), 1.58–1.53 (m, 2H), 1.26–1.22 (m, 2H), 1.02 (t, $J$ = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.5, 157.9, 149.0, 143.4, 142.1, 141.4, 140.3, 134.6, 130.0, 129.6, 129.1, 128.9, 118.5, 107.3, 102.1, 99.3, 55.7, 55.6, 43.6, 31.8, 23.2, 14.0; HRMS (ESI) calcd for $[C_{22}H_{21}IN_2O_2]$ requires $[M+H]^+$ 473.0726, found 473.0734.

***6-Iodo-2,3,4-trimethoxy-5-phenylbenzo[a]phenazine*** **(5j).** The product was obtained as a yellow needles (201.0 mg, 77%): mp 177–180 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.79 (s, 1H), 8.31–8.28 (m, 2H), 7.82–7.77 (m, 2H), 7.44 (t, $J$ = 6.8 Hz, 2H), 7.38–7.34 (m, 1H), 7.23–7.21 (m, 2H), 4.13 (s, 3H), 3.83 (s, 3H), 3.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.2, 150.4, 148.3, 148.2, 145.0, 143.5, 142.1, 141.6, 140.5, 130.4, 130.1, 129.5, 128.9, 128.5, 128.1, 127.6, 126.8, 123.0, 109.0, 102.8, 60.9, 60.8, 56.2; HRMS (ESI) calcd for $[C_{25}H_{19}IN_2O_3]$ requires $[M+Na]^+$ 545.0338, found 545.0356.

***5-(4-Ethylphenyl)-6-iodo-2,3,4-trimethoxybenzo[a]phenazine*** **(5k).** The product was obtained as a yellow needles (242.1 mg, 88%): mp 281–284 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.89 (s, 1H), 8.40–8.38 (m, 2H), 7.89–7.87 (m, 2H), 7.34 (d, $J$ = 7.6 Hz, 2H), 7.20 (d, $J$ = 7.6 Hz, 2H), 4.21 (s, 3H), 3.91 (s, 3H), 3.27 (s, 3H), 2.82–2.76 (m, 2H), 0.87 (t, $J$ = 5.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.2, 150.5, 148.5, 145.6, 143.5, 142.8, 142.1, 141.7, 140.5, 130.3, 130.1, 129.5, 128.9, 128.5, 128.0, 127.0, 124.1, 123.5, 115.8, 102.8, 60.9, 56.2, 22.7, 15.8; HRMS (ESI) calcd for $[C_{27}H_{23}IN_2O_3]$ requires $[M+H]^+$ 551.0832, found 551.0823.

***6-Iodo-2,3,4-trimethoxy-5-(4 methoxyphenyl)benzo[a]phenazine*** **(5l).** The product was obtained as a brown semisolid (240.2 mg, 87%); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.80 (s, 1H), 8.31–8.29 (m, 2H), 7.81–7.78 (m, 2H), 7.14 (d, $J$ = 8.36 Hz, 2H), 6.97 (d, $J$ = 8.4 Hz, 2H), 4.13 (s, 3H), 3.84 (s, 6H), 3.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 158.5, 154.1, 150.5, 148.1, 145.1, 143.5, 142.1, 141.7, 140.9, 140.5, 130.3, 130.1, 129.5, 129.2, 128.9, 128.4, 123.3, 112.9, 109.9, 102.8, 61.0, 60.9, 56.2, 55.3; HRMS (ESI) calcd for $[C_{26}H_{21}IN_2O_4]$ requires $[M+Na]^+$ 575.0444, found 575.0445.

***4-(6-Iodo-2,3,4-trimethoxybenzo[a]phenazin-5-yl)-N,N-dimethylaniline*** **(5m).** The product was obtained as a orange needles (226.1 mg, 80%): mp 229–233 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.94 (s, 1H), 8.46–8.43 (m, 2H), 7.95–7.90 (m, 2H), 7.22 (d, $J$ = 9.1 Hz, 2H), 6.94 (d, $J$ = 9.1 Hz, 2H), 4.27 (s, 3H), 3.99 (s, 3H), 3.40 (s, 3H), 3.12 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.0, 150.8, 149.4, 148.9, 145.2, 143.5, 142.0, 139.2, 137.1, 130.2, 129.5, 128.9, 128.4, 124.0, 123.6, 115.9, 114.0, 111.4, 110.3, 102.8, 61.2, 60.9, 56.2, 40.7; HRMS (ESI) calcd for $[C_{27}H_{24}IN_3O_3]$ requires $[M+H]^+$ 566.0941, found 566.0930.

***6-Iodo-2,3,4-trimethoxy-5-(o-tolyl)benzo[a]phenazine*** **(5n).** The product was obtained as a yellow needles (217.2 mg, 81%): mp 191–194 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.82 (s, 1H), 8.33–8.30 (m, 2H), 7.81–7.79 (m, 2H), 7.28–7.21 (m, 3H), 7.05 (d, $J$ = 7.0 Hz, 1H), 4.13 (s, 3H), 3.83 (s, 3H), 3.18 (s, 3H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.2, 150.5, 148.0, 147.8, 144.9, 143.5, 142.2, 140.5, 135.2, 130.3, 130.1, 129.5, 129.3, 128.9, 128.5, 127.8, 127.2, 125.3, 122.8, 114.0, 108.6, 102.9, 60.8, 60.6, 56.2, 20.0; HRMS (ESI) calcd for $[C_{26}H_{21}IN_2O_3]$ requires $[M+H]^+$ 537.0675, found 537.0672.

***5-(2-Fluorophenyl)-6-iodo-2,3,4-trimethoxybenzo[a]phenazine*** **(5o).** The product was obtained as a yellow needles (194.5 mg, 72%): mp 170–174 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.79 (s, 1H), 8.32–8.29 (m, 2H), 7.82–7.77 (m, 2H), 7.41–7.35 (m, 1H), 7.24–7.14 (m, 3H), 4.13 (s, 3H), 3.85 (s, 3H), 3.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.2, 157.7, 154.3, 150.1, 144.8, 143.4, 142.4, 142.3, 141.5, 140.6, 135.9, 135.8, 130.5, 130.3 (d, $J$ = 3.8 Hz, 1C), 130.2,

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129.5, 129.0, 128.9, 128.5, 123.5 (d, *J* = 2.8 Hz, 1C), 122.8, 115.0 (d, *J* = 22.0 Hz, 1C), 109.5, 102.9, 60.9, 60.8, 56.3; HRMS (ESI) calcd for $[C_{25}H_{18}FIN_2O_3]$ requires $[M+H]^+$ 541.0424, found 541.0413.

***6-Iodo-2,3,4-trimethoxy-5-(4-(trifluoromethyl)phenyl)benzo[a]phenazine*** **(5p).** The product was obtained as a yellow needles (236.0 mg, 80%): mp 195–198 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.77 (s, 1H), 8.30–8.28 (m, 2H), 7.82–7.77 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.12 (s, 3H), 3.82 (s, 3H), 3.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.4, 151.7, 149.9, 146.6, 144.9, 143.5, 142.3, 141.3, 140.4, 130.6, 130.3, 129.5, 128.9, 128.6, 128.5, 125.8, 124.6 (q, *J* = 19.0 Hz, 1C), 122.5, 108.4, 102.9, 60.9, 60.6, 56.3; HRMS (ESI) calcd for $[C_{26}H_{18}F_3IN_2O_3]$ requires $[M+H]^+$ 591.0392, found 591.0370.

***6-Iodo-5-phenylbenzo[a]phenazine*** **(5q).** The product was obtained as a yellow needles (155.6 mg, 72%): mp 262–264 °C;$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.42 (d, *J* = 7.9 Hz, 1H), 8.36–8.33 (m, 2H), 7.85–7.83 (m, 2H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.55–7.48 (m, 4H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.31–7.29 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CF_3COOD$) $\delta$ 165.0, 145.0, 144.3, 142.1, 138.5, 134.4, 134.3, 133.7, 133.5, 132.6, 131.2, 130.8, 130.6, 130.5, 129.6, 129.3, 128.6, 126.4, 120.6, 90.6; HRMS (ESI) calcd for $[C_{22}H_{13}IN_2]$ requires $[M+H]^+$ 433.0202, found 433.0210.

***4-(6-Iodobenzo[a]phenazin-5-yl)-N, N-dimethylaniline*** **(5r).** The product was obtained as a orange needles (180.6 mg, 76%): mp 292–296 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.39 (d, *J* = 8.3 Hz, 1H), 8.36–8.31 (m, 2H), 7.84–7.80 (m, 2H), 7.73–7.69 (m, 1H), 7.52 (d, *J* = 3.8 Hz, 2H), 7.18–7.15 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.02 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 151.6, 150.1, 143.4, 142.2, 141.6, 134.6, 131.6, 131.0, 130.3, 130.1, 129.9, 129.6, 129.1, 128.8, 128.0, 125.5, 111.8, 108.7, 40.4; HRMS (ESI) calcd for $[C_{24}H_{18}IN_3]$ requires $[M+H]^+$ 476.0624, found 476.0645.

***5-Butyl-6-iodobenzo[a]phenazine*** **(5s).** The product was obtained as a brown semisolid (140.1 mg, 68%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10–8.06 (m, 2H), 7.78–7.76 (m, 1H), 7.73–7.69 (m, 2H), 7.41–7.37 (m, 3H), 2.90–2.82 (m, 1H), 2.61–2.54 (m, 1H), 1.45–1.38 (m, 2H), 1.23–1.14 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.4, 152.5, 141.5, 140.4, 137.8, 130.7, 130.2, 129.6, 129.3, 129.2, 129.1, 128.0, 109.4, 48.9, 29.8, 21.4, 14.0; HRMS (ESI) calcd for $[C_{20}H_{17}IN_2]$ requires $[M+H]^+$ 413.0515, found 413.0503.

***4-(4-(tert-Butyl)phenyl)-5-iodothieno[3,2-a]phenazine*** **(5t).** The product was obtained as a yellow needles (210.1 mg, 85%): mp 248–252 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.41 (d, *J* = 5.3 Hz, 1H), 8.36–8.33 (m, 1H), 8.30–8.27 (m, 1H), 7.84–7.79 (m, 2H), 7.58 (d, *J* = 5.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 152.0, 145.8, 143.21, 143.16, 142.5, 142.1, 140.0, 139.0, 136.6, 130.7, 130.0, 129.8, 128.9, 128.6, 128.4, 125.5, 124.3, 103.1, 34.9, 31.4; HRMS (ESI) calcd for $[C_{24}H_{19}IN_2S]$ requires $[M+H]^+$ 495.0392, found 495.0385.

***4-(2-Fluorophenyl)-5-iodothieno[3,2-a]phenazine*** **(5u).** The product was obtained as a yellow needles (184.7 mg, 81%): mp 190–194 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.42 (d, *J* = 5.3 Hz, 1H), 8.35–8.33 (m, 1H), 8.29–8.27 (m, 1H), 7.85–7.79 (m, 2H), 7.59 (d, *J* = 5.3 Hz, 1H), 7.54–7.48 (m, 1H), 7.41–7.37 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 9.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 158.8 (d, *J* = 248.2 Hz, 1C), 143.2, 142.8, 142.6, 141.7, 140.3, 139.1 (d, *J* = 20.1 Hz, 1C), 136.9, 131.2 (d, *J* = 8.6 Hz, 1C), 130.94, 130.85, 130.82, 130.2, 129.9, 128.9, 128.2, 124.6, 124.53, 124.4, 116.4, (d, *J* = 22.0 Hz, 1C), 114.1, 104.6; HRMS (ESI) calcd for $[C_{20}H_{10}FIN_2S]$ requires $[M+H]^+$ 456.9672, found 456.9680.

***4-Cyclohexyl-5-iodothieno[3,2-a]phenazine*** **(5v).** The product was obtained as a yellow needles (159.9 mg, 72%): mp 211–216 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.07–8.03 (m, 2H), 7.90–7.89 (m, 1H), 7.72–7.68 (m, 1H), 7.67–7.64 (m, 1H), 7.33–7.31 (m, 1H), 2.43–2.36 (m, 1H), 1.79–1.73 (m, 4H), 1.55–1.52 (m, 1H), 1.49–1.38 (m, 3H), 1.21–1.18 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.0, 147.3, 141.4, 140.2, 138.7, 130.6, 129.9, 129.1, 129.04, 129.00, 127.7, 125.2, 118.7, 90.8, 52.6, 32.9, 31.6, 25.5; HRMS (ESI) calcd for $[C_{20}H_{17}IN_2S]$ requires $[M+H]^+$ 445.0235, found 445.0249.

***4-Cyclopropyl-5-iodothieno[3,2-a]phenazine*** **(5w).** The product was obtained as a yellow needles (148.8 mg, 74%): mp 180–184 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.34–8.29 (m, 2H), 8.23–8.19 (m, 1H), 7.78–7.75 (m, 2H), 7.57–7.55 (m, 1H), 2.31–2.24 (m, 1H), 1.37–1.32 (m, 2H), 1.08–1.04 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 143.6, 143.4, 143.0, 142.3, 141.9, 138.6, 136.7, 130.5, 129.9, 129.8, 128.8, 127.1, 124.2, 106.3, 22.7, 10.7; HRMS (ESI) calcd for $[C_{17}H_{11}IN_2S]$ requires $[M+H]^+$ 402.9766, found 402.9760.

***6-Bromo-2,3,4-trimethoxy-5-(o-tolyl)benzo[a]phenazine*** **(5x).** The product was obtained as a yellow needles (185.9 mg, 76%): mp 171–174 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.89 (s, 1H), 8.42–8.38 (m, 2H), 7.92–7.87 (m, 2H), 7.35–7.31 (m, 3H), 7.18–7.17 (m, 1H), 4.22 (s, 3H), 3.91 (s, 3H), 3.26 (s, 3H), 2.14 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.1, 150.8, 145.2, 143.6, 143.04, 143.96, 141.9, 141.2, 140.5, 135.3, 130.5, 130.3, 129.7, 129.2, 128.0, 127.6, 127.1, 125.2, 123.2, 122.5, 102.9, 60.8, 60.7, 56.3, 20.0; HRMS (ESI) calcd for $[C_{26}H_{21}BrN_2O_3]$ requires $[M+H]^+$ 489.0814, found 489.0805.

***6-Iodo-9-methyl-5-(thiophen-3-yl)benzo[a]phenazine*** **(7a).** The product was obtained as a yellow needles (171.8 mg, 76%): mp 209–213 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.32 (d, *J* = 8.3 Hz, 1H), 8.19 (t, *J* = 9.1 Hz, 1H), 8.09–8.05 (m, 1H), 7.70–7.62 (m, 2H), 7.52–7.47 (m, 2H), 7.44–7.42 (m, 1H), 7.31–7.30 (m, 1H), 7.10–7.09 (m, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 146.4, 143.4, 143.3, 141.4, 141.0, 133.9, 133.4, 133.1, 131.0, 129.7, 129.0, 128.5, 128.1, 128.0, 127.98, 127.93, 127.5, 125.8, 125.3, 124.8, 108.8, 22.1; HRMS (ESI) calcd for $[C_{21}H_{13}IN_2S]$ requires $[M+H]^+$ 452.9922, found 452.9917.

***5-Cyclopropyl-6-iodo-9-methylbenzo[a]phenazine*** **(7b).** The product was obtained as a yellow needles (147.6 mg, 72%): mp 189–293 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04–8.00 (m, 1H), 7.92–7.89 (m, 1H), 7.82–7.79 (m, 2H), 7.62–7.59 (m, 1H), 7.46–7.44 (m, 2H), 2.58 (s, 3H), 1.78–1.71 (m, 1H), 0.93–0.79 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.5, 151.5, 141.4, 140.8, 140.6, 140.1, 138.0, 133.0, 132.5, 129.6, 129.2, 128.7, 128.0, 127.9, 114.2, 21.9, 14.1, 11.3, 10.3; HRMS (ESI) calcd for $[C_{20}H_{15}IN_2]$ requires $[M+H]^+$ 411.0358, found 411.0362.

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***6-Iodo-1,4-dimethoxy-5-(4-methoxyphenyl)-9-methylbenzo[a]phenazine* (7c).** The product was obtained as a brown needles (209.1 mg, 78%): mp 194–198 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.30–8.23 (m, 1H), 8.17–8.13 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.17–7.13 (m, 3H), 7.02–7.00 (m, 2H), 4.17 (s, 3H), 3.91 (s, 3H), 3.35 (s, 3H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 158.2, 154.1, 151.0, 148.0, 142.1, 141.5, 141.1, 140.5, 132.8, 129.1, 128.9, 127.9, 127.5, 125.9, 122.1, 115.4, 114.7, 114.5, 113.5, 112.6, 58.1, 57.1, 55.3, 22.1; HRMS (ESI) calcd for $[C_{26}H_{21}IN_2O_3]$ requires $[M+H]^+$ 537.0675, found 537.0679.

***5-(4-(tert-Butyl)phenyl)-6-iodo-1,4-dimethoxy-9-methylbenzo[a]phenazine* (7d).** The product was obtained as a brown needles (230.6 mg, 82%): mp 199–203 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.35 (d, *J* = 9.16 Hz, 1H), 8.19 (s, 1H), 7.78–7.75 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 9.16 Hz, 1H), 4.22 (s, 3H), 3.30 (s, 3H), 2.72 (s, 3H), 1.48 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.2, 151.0, 149.3, 148.5, 146.3, 142.1, 141.5, 141.1, 140.5, 132.8, 128.9, 127.8, 127.5, 126.0, 124.0, 122.1, 115.4, 114.7, 112.7, 58.1, 57.0, 34.6, 31.5, 22.1; HRMS (ESI) calcd for $[C_{29}H_{27}IN_2O_2]$ requires $[M+H]^+$ 563.1195, found 563.1189.

***5-(4-(tert-Butyl)phenyl)-6-iodo-2,3,4-trimethoxy-9-methylbenzo[a]phenazine* (7e).** The product was obtained as a yellow needles (260.6 mg, 88%): mp 226–230 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.85–8.84 (m, 1H), 8.27–8.24 (m, 1H), 8.15–8.13 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.20 (s, 3H), 3.91 (s, 3H), 3.23 (s, 3H), 2.68–2.65 (m, 3H), 1.44 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.0, 150.4, 149.6, 148.2, 145.4, 144.8, 143.5, 142.2, 140.7, 133.0, 128.9, 128.3, 127.9, 127.7, 127.3, 124.3, 123.0, 109.2, 102.5, 60.8, 60.7, 56.2, 34.6, 31.5, 22.0; HRMS (ESI) calcd for $[C_{30}H_{29}IN_2O_3]$ requires $[M+H]^+$ 593.1301, found 593.1301.

***6-Iodo-2,3,4-trimethoxy-9-methyl-5-(thiophen-3-yl)benzo[a]phenazine* (7f).** The product was obtained as a brown semisolid (233.2 mg, 86%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.82–8.81 (m, 1H), 8.26–8.22 (m, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.70–7.66 (m, 1H), 7.46–7.44 (m, 1H), 7.15–7.14 (s, 2H), 4.18 (s, 3H), 3.92 (s, 3H), 3.40 (s, 3H), 2.67–2.65 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.1, 150.3, 147.7, 144.8, 143.6, 141.4, 141.2, 140.9, 140.8, 139.9, 133.2, 132.9, 129.0, 128.3, 127.9, 127.3, 124.0, 121.6, 109.9, 102.5, 61.0, 60.9, 56.2, 20.0; HRMS (ESI) calcd for $[C_{24}H_{19}IN_2O_3S]$ requires $[M+H]^+$ 543.0239, found 543.0247.

***5-Iodo-8-methyl-4-phenylthieno[3,2-a]phenazine* (7g).** The product was obtained as a yellow needles (180.9 mg, 80%): mp 253–257 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10–8.03 (m, 1H), 7.95–7.92 (m, 1H), 7.82–7.81 (m, 1H), 7.65–7.60 (m, 1H), 7.48–7.46 (m, 1H), 7.41–7.32 (m, 4H), 6.78–6.75 (m, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 145.4, 143.3, 143.0, 141.8, 141.3, 140.8, 138.4, 136.7, 133.7, 132.9, 132.4, 130.9, 129.0, 128.7, 128.3, 128.1, 124.2, 103.1, 22.1; HRMS (ESI) calcd for $[C_{21}H_{13}IN_2S]$ requires $[M+H]^+$ 452.9922, found 452.9914.

***5-Iodo-8-methyl-4-(p-tolyl)thieno[3,2-a]phenazine* (7h).** The product was obtained as a brown needles (200.5 mg, 86%): mp 223–227 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.37 (d, *J* = 5.5 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.10 (s, 1H), 7.65–7.61 (m, 1H), 7.56–7.54 (m, 1H), 7.35–7.30 (m, 4H), 2.59 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 145.5, 143.3, 142.6, 141.9, 141.3, 140.7, 140.2, 138.8, 138.4, 136.7, 133.6, 129.4, 128.8, 128.3, 128.1, 124.2, 103.2, 22.1, 21.6; HRMS (ESI) calcd for $[C_{22}H_{15}IN_2S]$ requires $[M+H]^+$ 467.0079, found 467.0095.

***5-Iodo-8-methyl-4-(thiophen-3-yl)thieno[3,2-a]phenazine (7i).*** The product was obtained as a yellow needles (186.4 mg, 84%): mp 212–216 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.46–8.44 (m, 1H), 8.30–8.22 (m, 1H), 8.18 (s, 1H), 7.74–7.70 (m, 1H), 7.66–7.62 (m, 2H), 7.56–7.54 (m, 1H), 7.37–7.34 (m, 1H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 143.3, 142.6, 141.7, 140.9, 138.4, 136.8, 133.7, 133.0, 129.3, 128.6, 128.31, 128.26, 127.1, 125.9, 125.5, 124.3, 114.1, 103.4, 22.1; HRMS (ESI) calcd for $[C_{19}H_{11}IN_2S_2]$ requires $[M+H]^+$ 458.9487, found 458.9482.

**General Procedure for the synthesis of Sonogashira and Suzuki coupled Product 10 and 11.** The products **10** and **11** were synthesized according to the reported protocols[28].

***6-((4-Methoxyphenyl)ethynyl)-5-phenylbenzo[a]phenazine (10).*** The product was obtained as a yellow needles (183.3 mg, 84%): mp 197–201 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.51 (d, *J* = 8.4 Hz, 1H), 8.47–8.44 (m, 1H), 8.42–8.38 (m, 1H), 7.92–7.90 (m, 2H), 7.82–7.77 (m, 1H), 7.69–7.64 (m, 2H), 7.62–7.56 (m, 5H), 7.26 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.6, 147.8, 143.0, 142.5, 142.0, 141.7, 138.7, 133.3, 130.8, 130.3, 130.2, 130.0, 129.8, 129.5, 128.2, 128.1, 127.9, 127.6, 125.5, 120.7, 115.6, 113.8, 99.8, 85.7, 55.3; HRMS (ESI) calcd for $[C_{31}H_{20}IN_2O]$ requires $[M+Na]^+$ 459.1473, found 459.1467.

***5-Phenyl-6-(3,4,5-trimethoxyphenyl)benzo[a]phenazine* (11).** The product was obtained as a yellow needles (210.2 mg, 89%): mp 211–214 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.51 (d, *J* = 8.3 Hz, 1H), 8.32 (d, *J* = 9.1 Hz, 1H), 8.14 (d, *J* = 8.4Hz, 1H), 7.82–7.78 (m, 1H), 7.75–7.71 (m, 1H), 7.60–7.59 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.27–7.22 (m, 3H), 7.19–7.17 (m, 2H), 6.44 (s, 2H), 3.80 (s, 3H), 3.59 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.8, 152.0, 149.1, 147.0, 142.8, 142.1, 141.5, 138.7, 136.9, 133.6, 132.5, 130.9, 130.6, 130.0, 129.6, 129.4, 128.0, 127.6, 127.2, 125.4, 119.1, 114.1, 110.0, 60.8, 56.0; HRMS (ESI) calcd for $[C_{31}H_{24}N_2O_3]$ requires $[M+H]^+$ 473.1865, found 473.1862.

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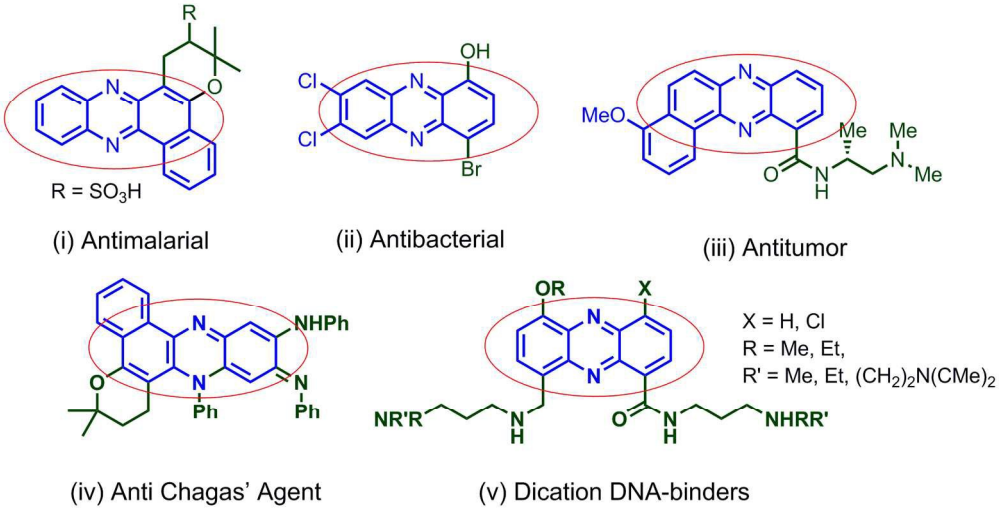


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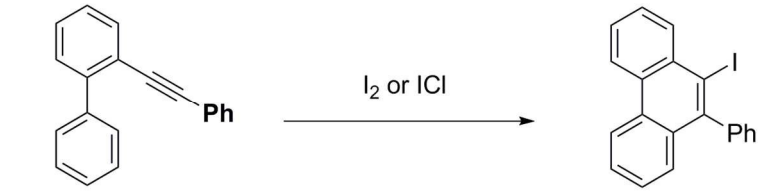
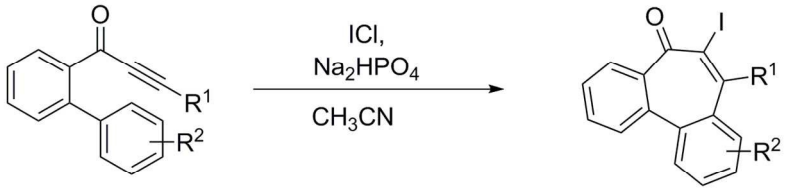
**Previous work**

***(i) Larock2005*** *(Electrophilic-Induced Aromatics and Heteroaromatics Cyclization)*

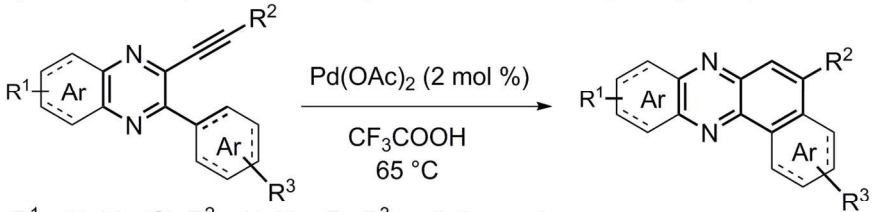



***(ii) Chen 2014*** (*Electrophilic Iodocyclization of Biphenylalkynones)*




$R^1$ = Ph, 4-MeOPh, $MeCO_2Ph$; $R^2$ = H, 4-Me, 4-MeO, 4-Cl, 4-F

***(iii) Verma 2016*** *(Palladium-Catalyzed Intramolecular Hydroarylation)*




$R^1$ = H, Me, Cl; $R^2$ = H, Me, Et; $R^3$ = alkyl or aryl

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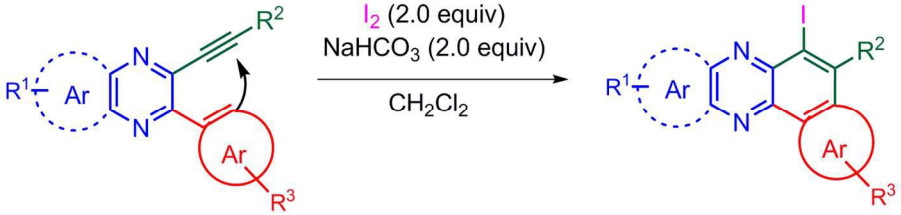
**This work**

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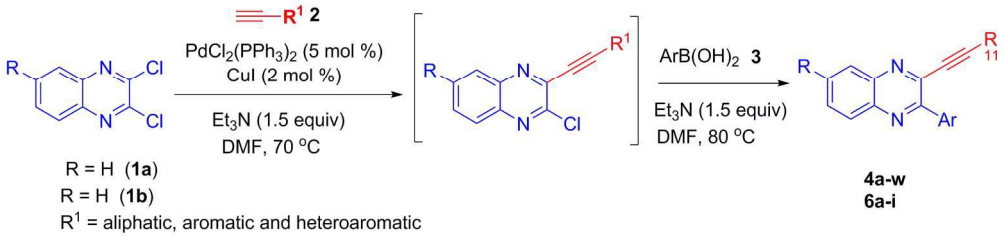


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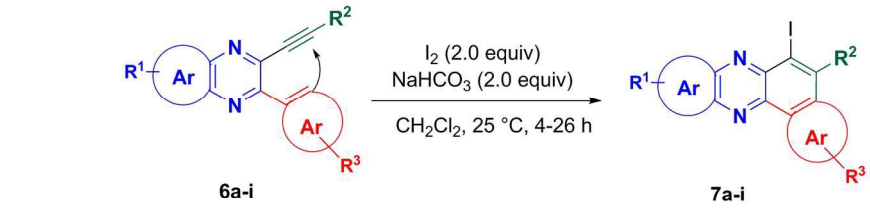


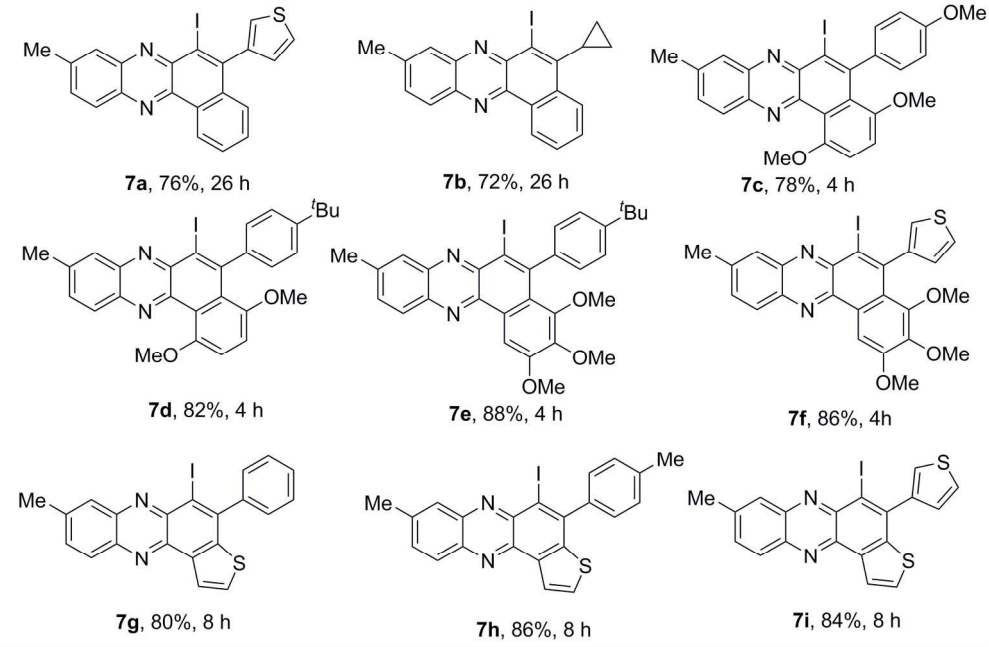


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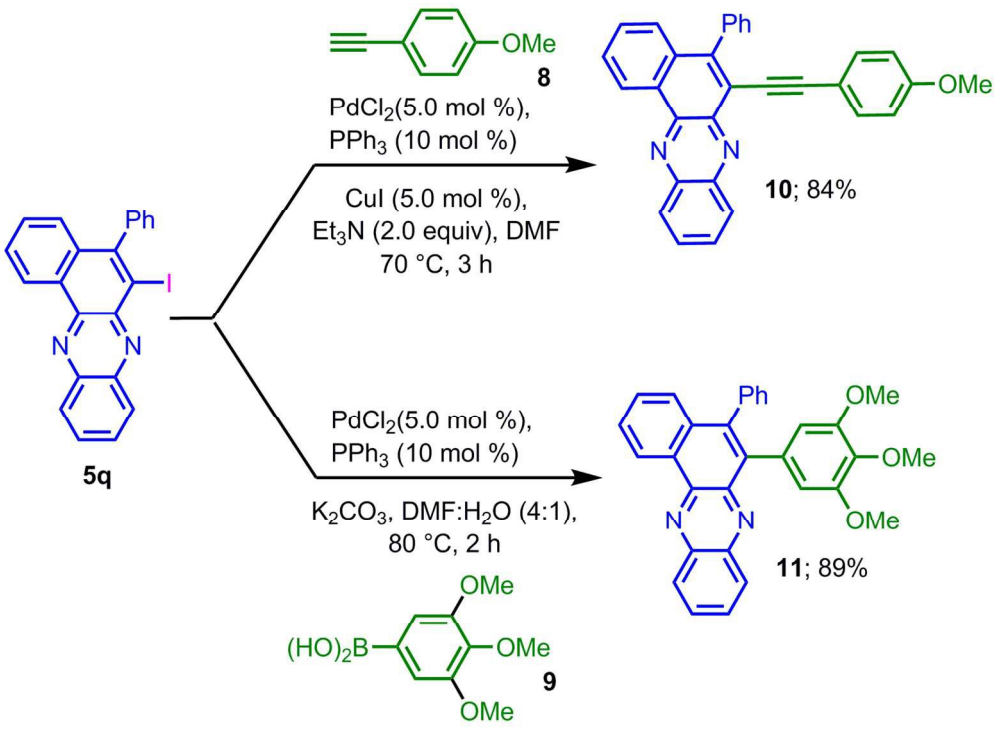


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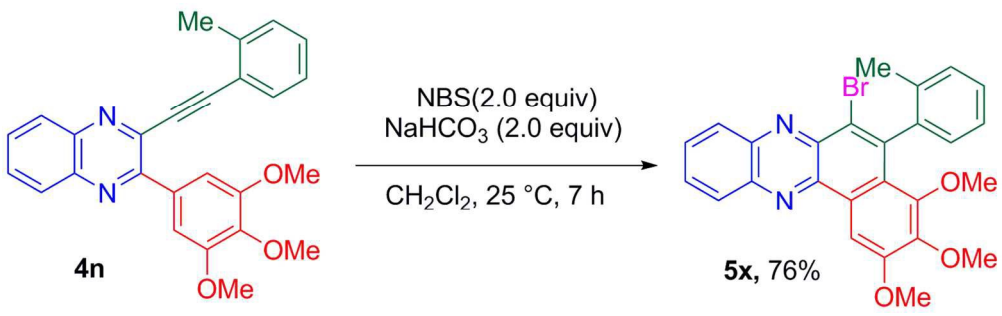


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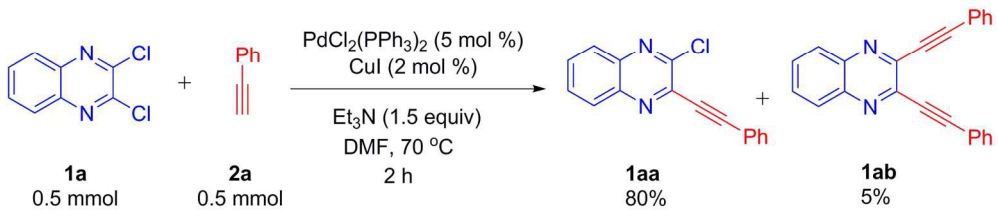
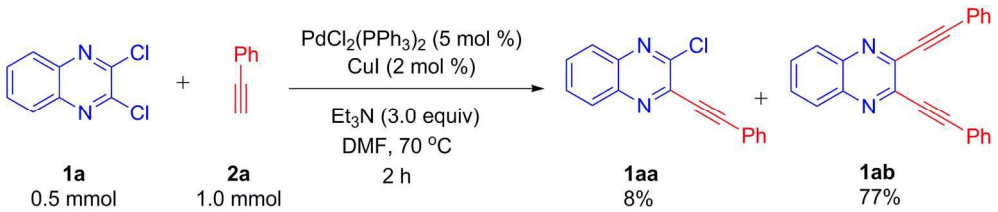
***i) Sonogashira Coupling using 1.0 equiv of 2a***




**1a** 0.5 mmol | **2a** 0.5 mmol | **1aa** 80% | **1ab** 5%

***ii) Sonogashira Coupling using 2.0 equiv of 2a***




**1a** 0.5 mmol | **2a** 1.0 mmol | **1aa** 8% | **1ab** 77%

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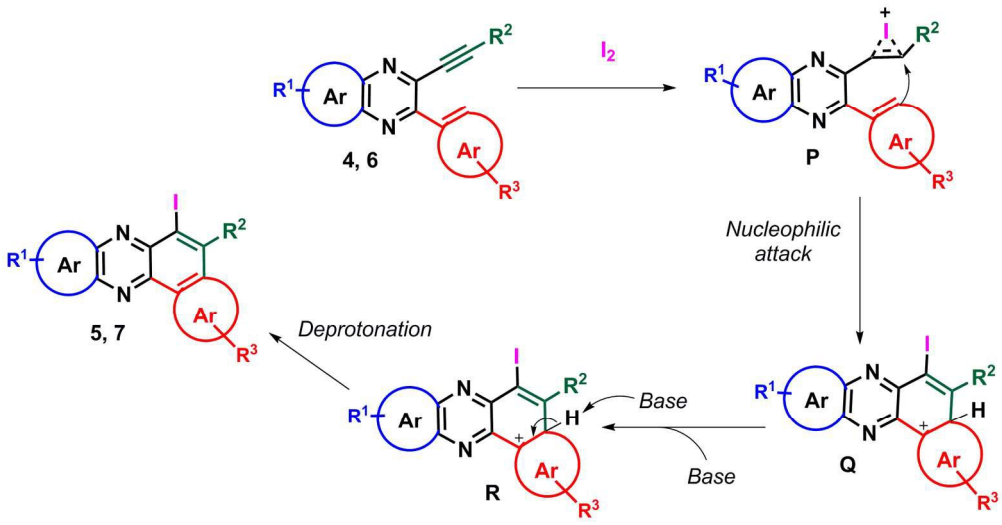


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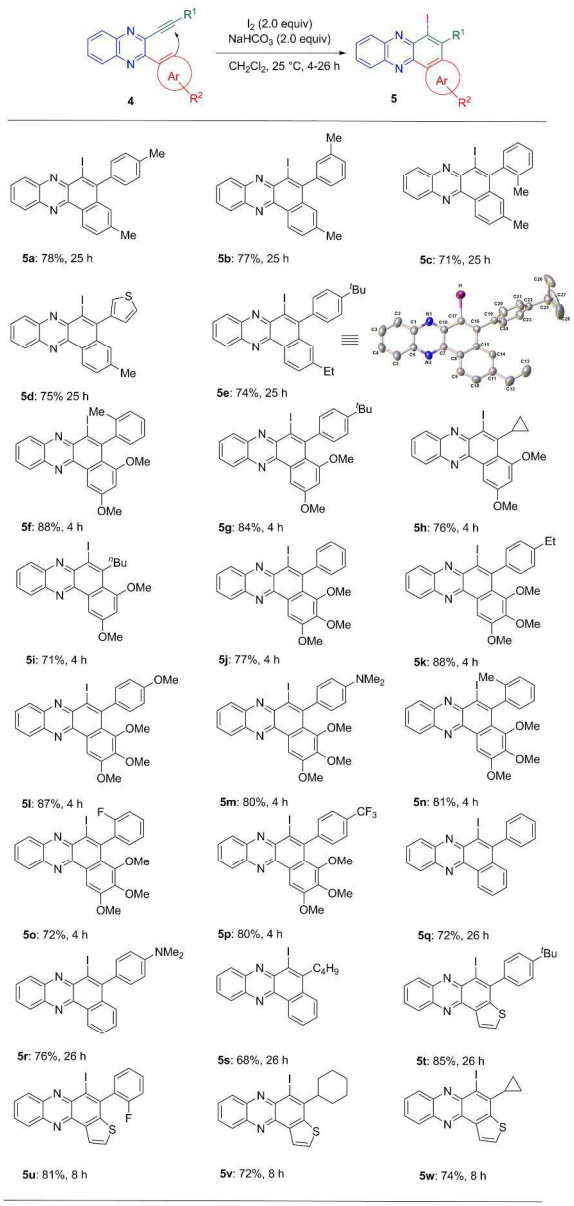


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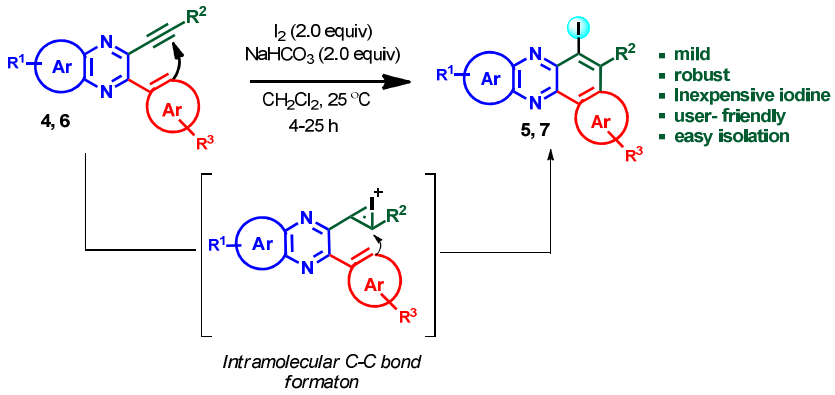
## Graphical Abstract




A tandem approach for the synthesis of iodo benzo[*a*]phenazine derivatives using molecular iodine has been described under the mild reaction conditions.