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(Benz)Imidazole directed cobalt (III) catalysed C-H activation of Arenes: A facile strategy to access polyheteroarenes *via* oxidative annulation

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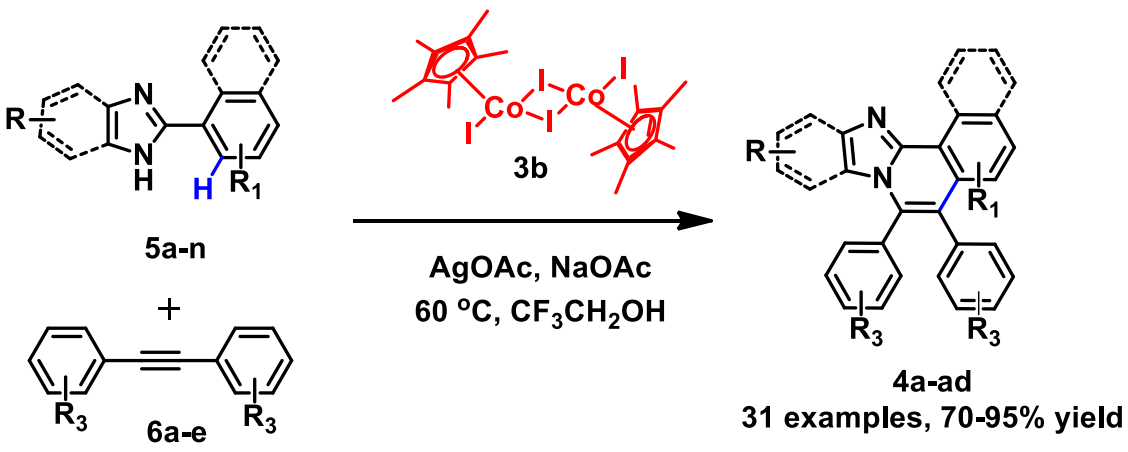
Abstract

A facile cobalt (III) catalysed C-H activation of arenes with substituted ((benz)imidazoles as directing groups (DG) is reported. The strategy was utilized for the synthesis of polyheteroarenes when appropriate substrates were reacted with diarylacetylenes as the coupling partner. The desired compounds were synthesized in moderate to excellent yield. A putative reaction mechanism is proposed. The final compounds revealed photoluminescence properties.

TOC Graphic

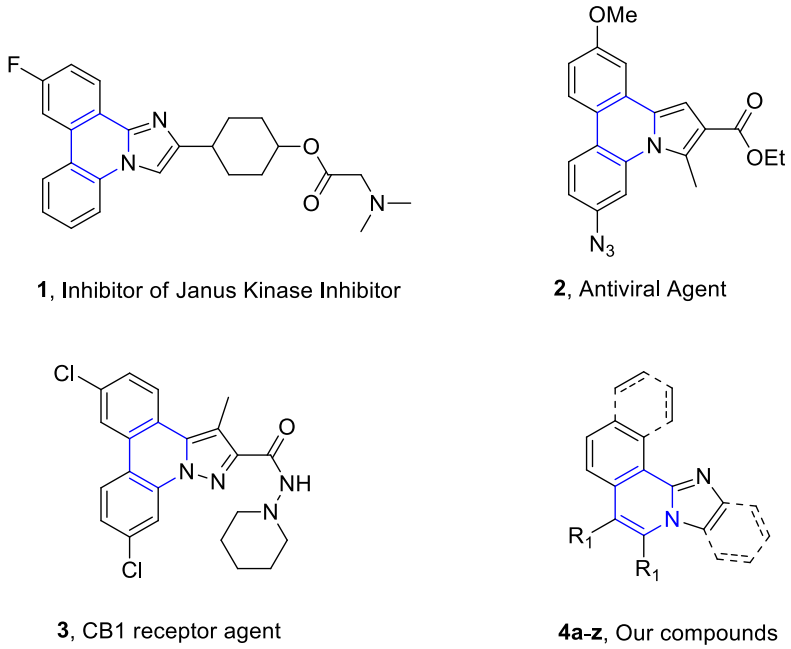


Introduction

By virtue of constructing complex organic molecules in a step economical fashion, functionalization of unreactive C-H bond has inarguably emerged as one of the most important tools in the recent past.[1,2] Accordingly, developing novel catalytic methods to activate the unreactive C-H bonds towards the formation of C-C and C-X (heteroatom) bond is highly desirable. It is noteworthy that along with catalysts, the success of such reactions also depend on careful choice directing groups (DG). In this regard, second row transition metals like ruthenium (Ru) and rhodium (Rh) are well explored as catalysts to activate unreactive C-H bonds in benzene rings along with diverse DGs such as pyrrolidine, N-chloroamides, sulfonamides, carboxylic acids and etc.[3,4] Despite their high catalytic activity and broad reaction scope, their moisture sensitivity and high cost have left chemists in quest for an earth abundant, air stable, cheap metal catalyst to facilitate the similar catalytic activities.[5] Majority of first row transition metals, regardless of exhibiting all these desired qualities, proven to be less effective due to their unwanted strong chelation with heteroatoms *viz.* N and S. Interestingly in the recent years cobalt catalysts are emerging as a promising alternatives devoid of such disadvantages observed in other first row transition metal catalysts, for C-H activation reactions. For example Daugulis *et al*. reported a cobalt acetate (tetrahydrate) catalysed synthesis of polyaryl heterocycles using 8-aminoquinolineas a DG.[6] Later Sundararaju and co-workers demonstrated a facile C(sp^2)-H activation towards alkynes followed by annulation, with a Cp*Co(III) catalyst and carboxylic acid as the directing group.[7]A similar reaction was reported by Zhu and co-workers with the same catalyst but with N-chloroamides as the DG.[8] In addition to these, cobalt has proven to be a successful metal catalyst for C-H activation mediated several other functionalization such as cyanation, halogenation and allylation.[9]

The polycyclic N-heteroaryl molecular framework with fused aromatic core has drawn profound interest owing to their medicinal, electrochemical and optoelectronic properties. They are obtained in alkaloids which display diverse biological activities as janus kinase inhibitors, **1**, anti-viral, **2**, anti-tumor agents **3** (Figure 1) and many more.[10] The densely packed aromatic skeleton of the compounds bring about their enhanced ability to act as a charge carrier and fluorescent emitter in the solid state.[11a] This in turn has opened a new doorway towards the fabrication of devices like organic semiconductor and organic light emitting diodes (OLED).[11b] In spite of the importance of these compounds and a plethora of functional group directed C-H activation and subsequent oxidative annulation of arenes, there are not very many syntheses to afford them.[12] Herein we have demonstrated (benz)imidazole directed cobalt catalysed tandem

functionalization of C-H bond followed by oxidative annulation of benzene rings to afford (benz)imidazoloisoquinoline (representing polycyclic N-heteroaryl class of molecules) **4a-z** and **4aa-ac** in moderate to excellent yield.



1, Inhibitor of Janus Kinase Inhibitor

2, Antiviral Agent

3, CB1 receptor agent

4a-z, Our compounds

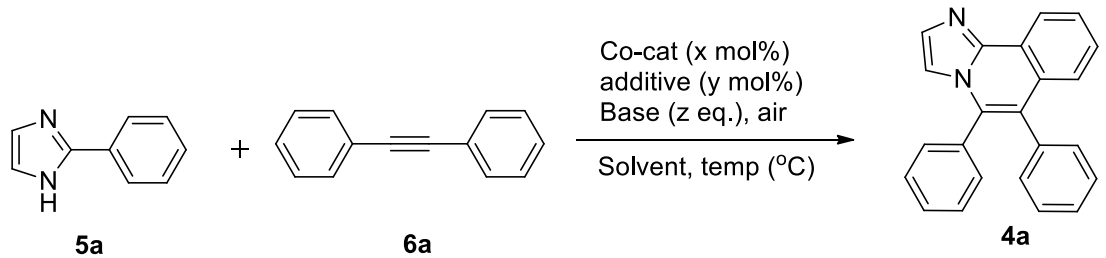
Figure 1. Representative polycyclic N-heteroaryl bearing bioactive compounds

Results and discussion

To investigate the feasibility of our reaction, 2-phenylimidazole and diphenylacetylene were considered as model reaction partners. The reaction was carried in trifluoroethanol (TFE) as solvent under various conditions *viz*. cobalt sources as catalyst (5 mol%), additives and temperature. The details of the exploratory reactions are summarized in table 1. The readily available cobalt sources like $Co(OAc)_2$, $Co(acac)_2$ and $CoBr_2$ did not afford any product (Table 1, entry 1-3), where pivalic acid was used as additive. Applying $Cp^*Co(III)$ based catalyst **3a**, along with silver hexafluoroantimonate, $AgSbF_6$ as the additive, led to the formation of the desired product **4a**, albeit in moderate yield of 54% (Table 1, entry 4). Interestingly, reaction in absence of the additive provided **4a** in 34% yield (Table 1, entry 5). Next we utilized a dimeric Cp*Co(III) complex **3b** as the catalyst for this reaction. To our utmost pleasure the yield drastically enhanced to 78% (Table 1, entry 6). In a bid to incorporate an additive more robust than $AgSbF_6$ (susceptible to air and moisture degradation) trial reaction with AgOAc resulted in slight increase of yield (80%) (Table 1, entry 7). Reaction at lower temperature (60 ^oC) enhanced the yield further (93%) (Table 1, entry 8). However when **5a** was reacted with

6a in presence of catalyst, sodium acetate but in absence of silver acetate (Table 1, entry 9), the yield of **4a** in the reaction deteriorated (~35%). Other additives such as potassium hexafluorophosphate (KPF_6) or sodium tetrafuoroborate ($NaBF_4$) (Table 1, entries 10 and 11) resulted in no further improvement of yield. Interestingly, reaction under inert atmosphere (Table 1, entry 12) generated **4a** in poor yield (~30%), thereby emphasizing the contribution of air in the reaction. Hence the optimized procedure included reaction of 1 equiv. of **5a** with 1 equiv. of diphenyl acetylene **6a** in presence of dimeric Co(III) complex $[Cp^*CoI_2]_2$ as catalyst (10 mol%) with silver acetate (AgOAc) as additive (20 mol%) in 2,2,2-trifluoroethanol (TFE) at 60 °C to afford the desired **4a** in 93% yield.

Table 1. Optimization of reaction condition[b]



Entry	Co-catalyst	Base (equiv.)	Additive (mol %)	Temp. (°C)	Yield (%)[a]
1.	$Co(OAc)_2.4H_2O$	Na_2CO_3 (2)	Pivalic acid (200)	80	0
2.	$Co(acac)_2$	″	Pivalic acid (200)	″	0
3.	$CoBr_2$	″	-	″	0
4.	$Cp^*Co(CO)I_2$	″	$AgSbF_6$ (20)	″	54
5.	″	″	-	″	34[c]
6.	$[Cp^*CoI_2]_2$	K_2CO_3 (2)	$AgSbF_6$ (20)	″	78
7.	″	KOAc (2)	AgOAc (20)	″	80
8.	″	NaOAc (2)	″	60	93
9.	″	″	-	″	35
10.	″	″	KPF_6 (20)	″	22
11.	″	″	$NaBF_4$ (20)	″	0
12.[d]	″	″	AgOAc (20)	″	27

[a] Isolated yield; [b] Reaction scale: 0.7 mmole of **5a** and 0.7 mmole of **6a**, [c]Yield in absence of $AgSbF_6$; [d] Under argon atmosphere

With the optimised protocol in hand, we set out to assess the substrate scope of our catalyst with benzimidazole as DG, for the oxidative annulation reactions between 2-arylbenzimidazoles **5b-n** and symmetrical and unsymmetrical diarylacetylenes **6a-e** (Figure 2).

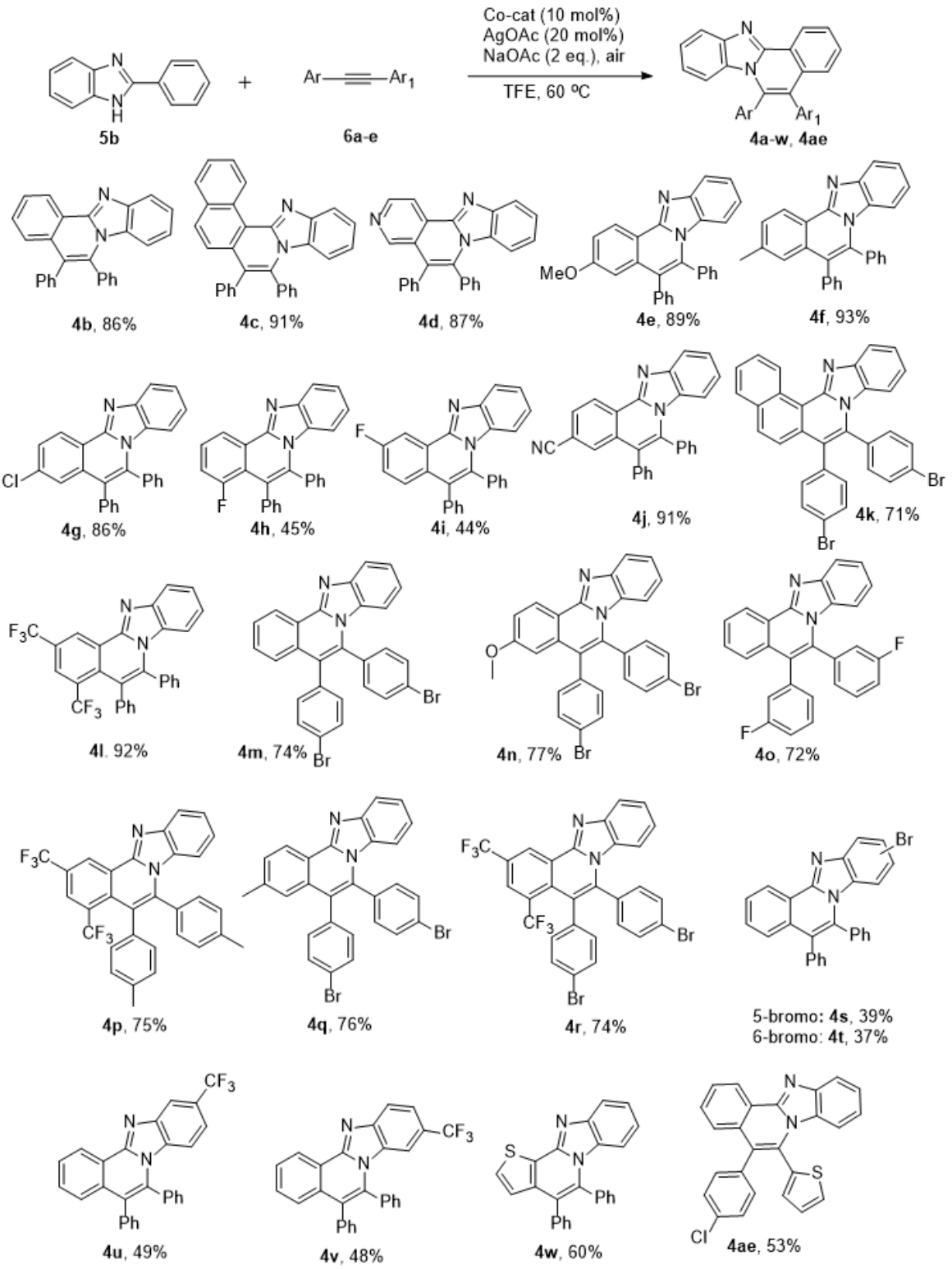


Figure 2. Reactions of various benzimidazoles and diarylacetylenes

To begin with the reaction of **5b-n** with diphenyl acetylene afforded the desired products **4b-j**, **l** and **s-w**, in excellent yield of 85-90%. Interestingly the reaction of **5h** afforded two regiomers, **4h** and **I** (Figure 2). Reaction of **5k** and **m** with diphenyl acetylene, **6a,** also afforded regiomers **4s**/**t** and **u**/**v**, in equimolar mixture with an overall yield of 76% and 97% respectively (Figure 2).

Next, reactions of **5b**, **c**, **e**, **f** and **k** with bis(4-bromophenyl)acetylene, **6b**, bis(3-fluorophenyl)acetylene, **6c** and bis(4-tolyl)acetylene, **6d**, afforded **4k**,**m-r** in moderate to excellent yield (71-83%). It was noteworthy, that the electron withdrawing groups at the benzene ring of the acetylenes favoured the reaction whereas the electron donating groups proved detrimental (Figure 2).

During the reaction of **5b** with 4-chlorophenyl-2-thiophenylacetylene **6e**, only the major diastereomer **4ae** could be isolated. Reaction with phenyl acetylene or with phenyl-2-isoproply acetylene rendered the reaction inactive (Figure 2).

The structures of the desired compounds were confirmed by the single crystal X-ray of the representative molecules **4u** and **4v** (Figure 3).

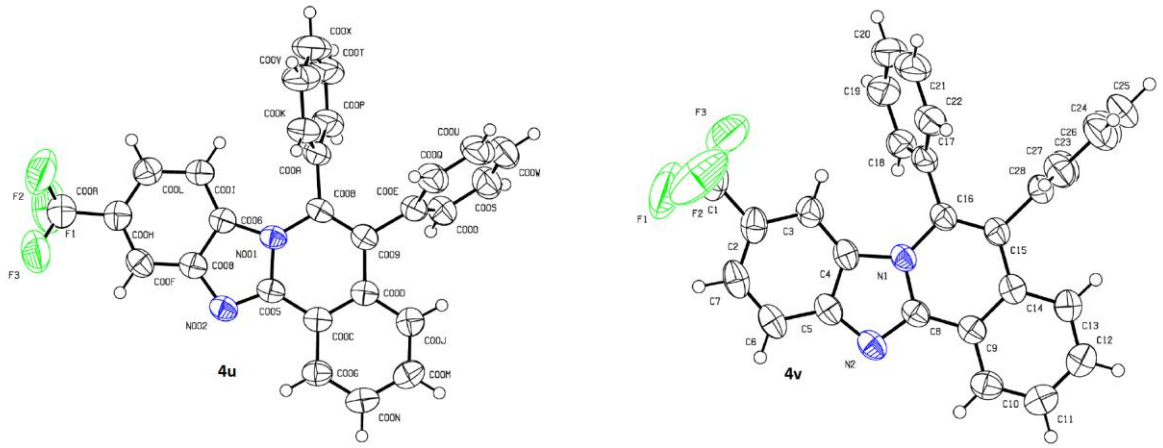


Figure 3. Single crystal X-Ray of **4u** and **v**

Next, imidazoles were screened for their ability to induce the C-H activation and subsequent annulation with our cobalt catalyst. Accordingly, 2-phenylimidazole, **5a** was reacted with **6a-d** to afford the desired compounds **4a** and **4x-z** in decent yield of 81-88% (Figure 4). The corresponding 4-methylimidazole substrate **5l** when reacted with diphenylacetylene, afforded the corresponding product **4aa** in moderate yield of 72% (Figure 4). Interestingly when it was further reacted with bis(2-fluorophenyl)acetylene, **6e**, afforded equimolar mixtures **4ab** and

4ac in 92% over all (Figure 4). Next reaction of **5a** with 4-chlorophenyl-2-thiophenylacetylene afforded the desired compound **4ad** in 39% yield.

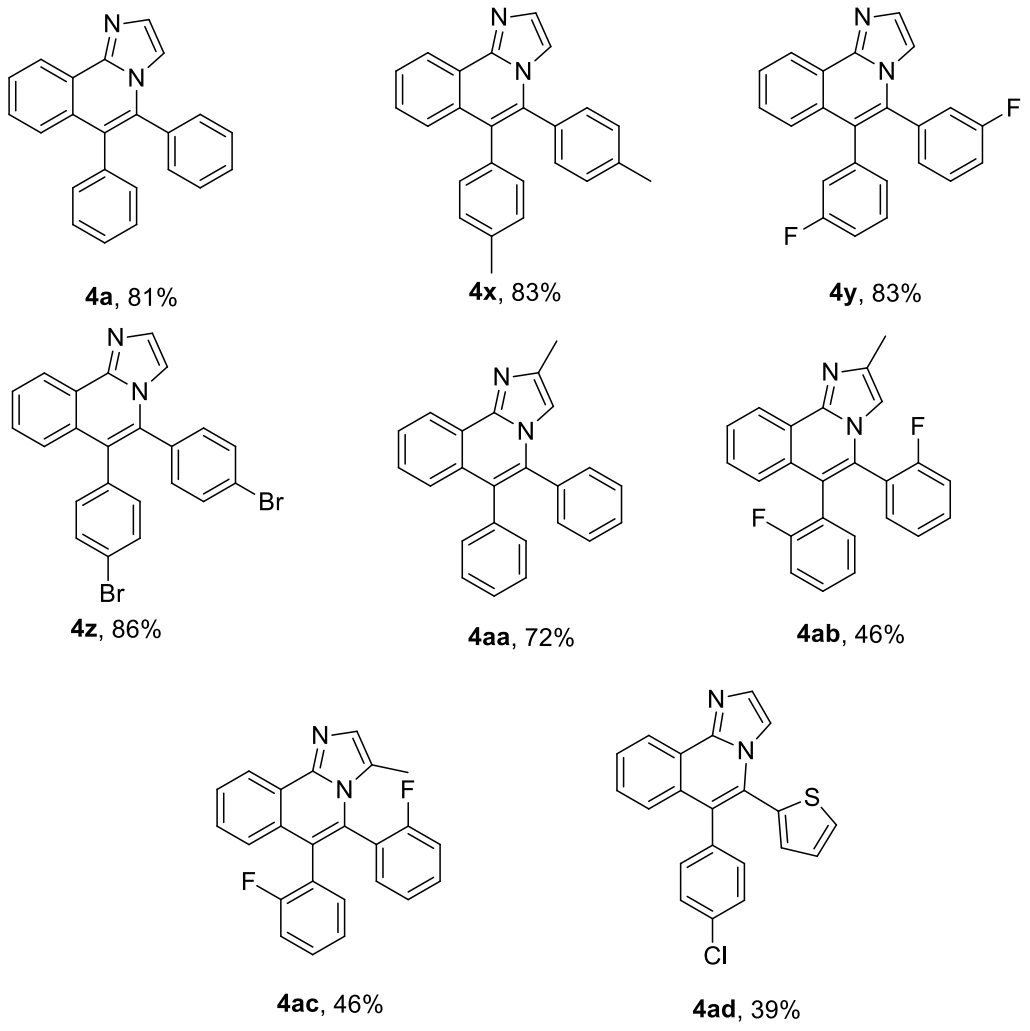
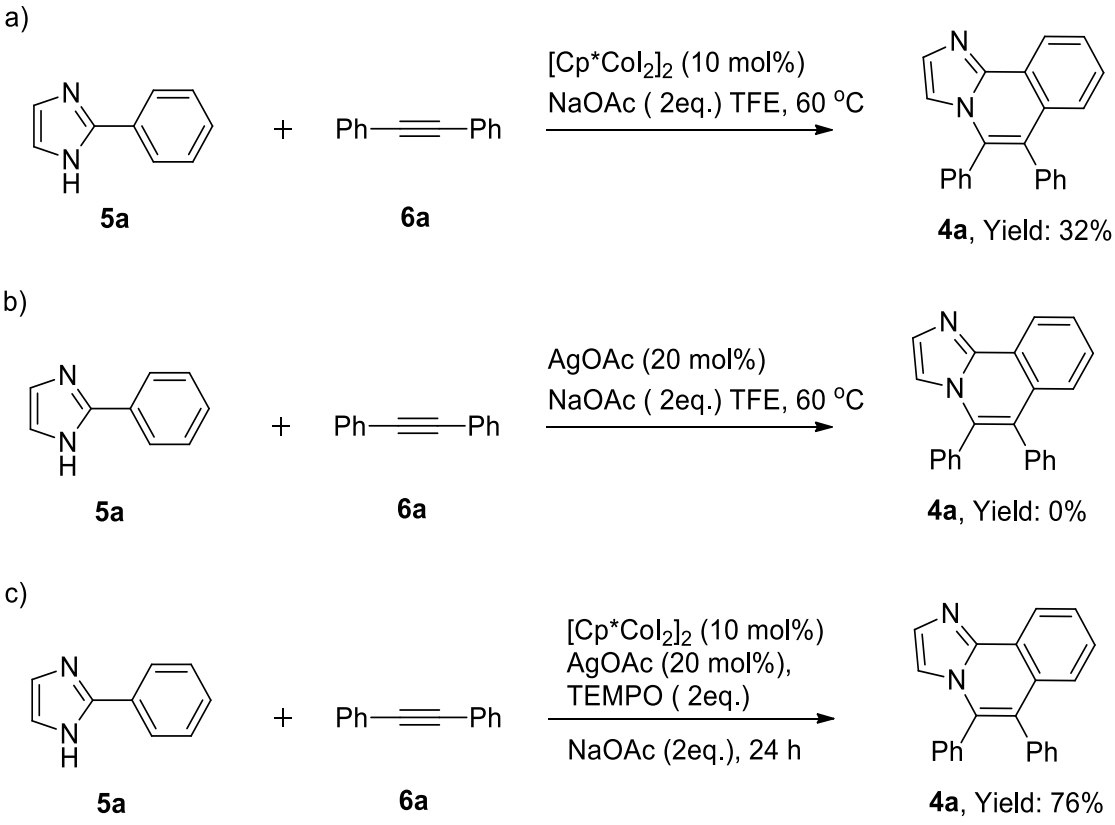


Figure 4. Reactions of various imidazoles and diarylacetylenes

To understand the mechanism of transformation we conducted several control experiments as depicted in Scheme 1. Reaction between **5a** and **6a** in the absence of the catalyst or the oxidant AgOAc (Scheme 1a and b) could not provide the desired compounds, thereby indicating their indispensability in the reaction. When they were reacted in presence of radical scavenger TEMPO (Scheme 1c), the reaction rate remain unchanged, there by indicating that the reaction proceeded through ionic pathway.



Scheme 1. Control experiments to delineate the reaction mechanism

Based on our control experiments and the previously reported similar methodologies, a plausible reaction mechanism is depicted in Scheme 2 with the representative reaction partners **5a** and **6a**.[13] Initial iodide abstraction from the dimeric cobalt complex by AgOAc and subsequent co-ordination of the resulting species with the nitrogen atom of **5a** may result into complex **I**. A concerted metallation-deprotonation (CMD) assisted C-H activation then affords the formation of the cobaltacycle **II**. Co-ordinative unsaturation may induce the complexation of **II** with alkyne which ultimately leads to the seven membered intermediate **IV**. This, in the subsequent step leads to the formation of the desired product **4a** and Cp*Co(I). Ag (I) reoxidize the Co(I) to Co(III) which is the active species for the next catalytic cycle.

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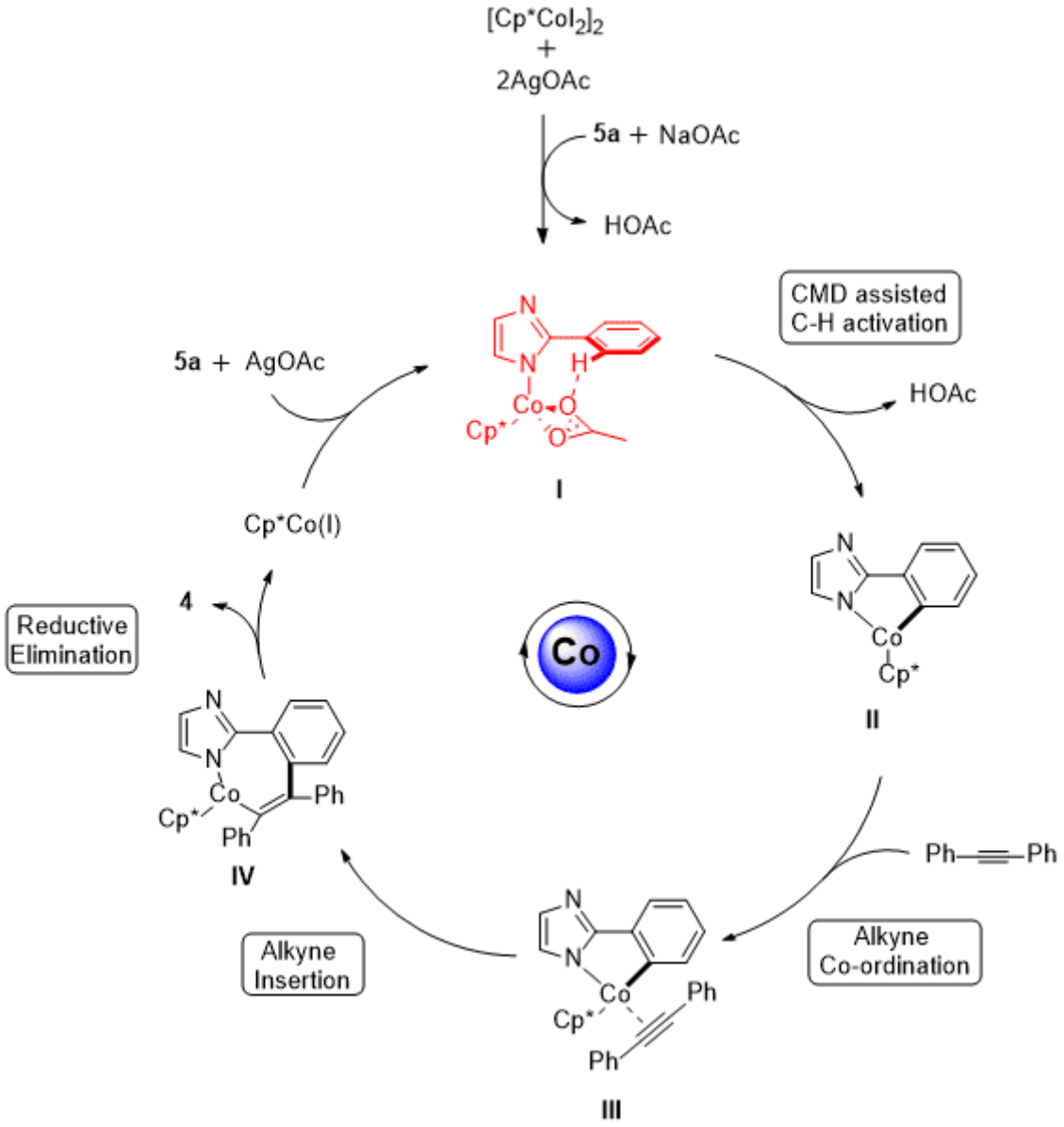

Scheme 2. Plausible mechanism of transformation for $[Cp^*CoI_2]_2$ catalyzed C-H activation and subsequent oxidative annultion of benzene rings toward alkyne

To investigate the utility of our novel polyaryl olefins, the steady state emission and photoluminescence (PL) experiments were executed for compound **4c** (Figure 5) in dichloromethane. Emission at 407 nm with wide PL band in the visible range was observed. The existence of continuous π conjugation in our molecules unambiguously modulates the PL band. We envision that due to their fluorescence properties our molecules may have application as fluorescent labels in macromolecular studies.

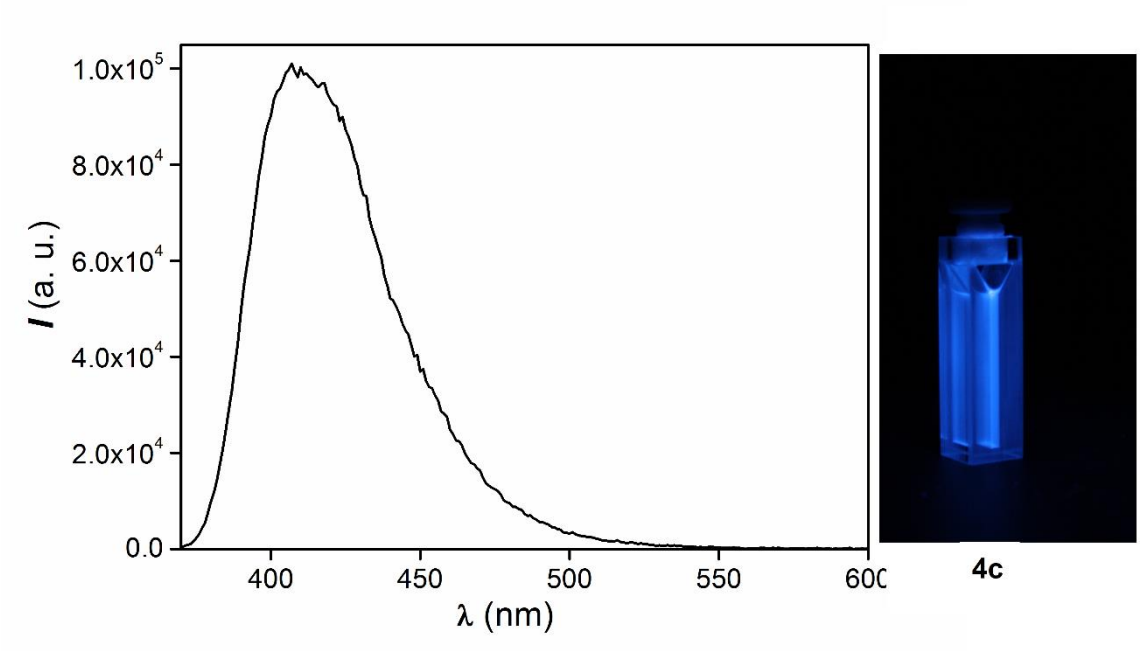

Figure 5. PL-spectra of **4c** in dichloromethane (1 X 10^{-6} M) and picture of **4c** in dichloromethane under the UV lamp

Conclusion

In conclusion, we mention that 2-aryl(benz)imidazole substrates have been used to demonstrate cobalt catalyzed C-H functionalization. The (benz)imidazole functionality on the substrate is harnessed for directing C-H functionalization reactions on the arenes for the construction of polyaryl olefins. Unactivated alkynes as reaction partners provide facile access to the final compounds. The wide substrate scope affords the ability to include diverse range of functionalities as substituents into the final scaffold. Control experiments provided crucial insights to propose a reaction pathway to afford the products. The desired final compounds demonstrated fluorescence properties which in turn makes these potential candidates as fluorescent labels in macromolecular studies. Presently this is being investigated in our lab.

Experimental

General. All reactions were carried out under N_2 atmosphere as specified. Reaction was monitored by thin layer chromatography (TLC, Silica gel 60 F_{254}), using UV light to visualize the course of the reaction. 2-aryl(benz)imidazoles **5a-l** were procured from multiple commercial vendors. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR spectroscopy. Splitting

patterns are designated as singlet (s), broad singlet (br, s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Mass spectrometry analysis was done with a 6540 UHD Accurate-Mass QTOF LC-MS system (Agilent Technologies) equipped with an Agilent 1290 LC system obtained by the Department of Chemistry, School of Natural Sciences, Shiv Nadar University, Uttar Pradesh 201314, India. HPLC experiments were carried out in Agilent Eclipse Plus C18 column.

General protocol for the synthesis of polyheteroarenes **4a**-**4ae**

An oven dried screw capped pressure tube, equipped with magnetic stir bar, was charged with 2-phenylimidazole (100 mg, 0.7 mmole), diphenyl acetylene (123 mg, 0.7 mmole), $[Cp^*CoI_2]_2$ (62 mg, 0.07 mmole), AgOAc (23 mg, 0.14 mmole) and NaOAc (113 mg, 1.38 mmole) in 2, 2, 2-trifluoroethanol and allowed to stir at 60^{o}C under air for 12 hours. The crude reaction mixture was then filtered through a plug of celite and washed with EtOAc. The solvent was removed under reduced pressure and purified by column chromatography using the indicated eluent.

5,6-diphenylimidazo[2,1-a]isoquinoline (4a): EtOAc/*n*-hexane (15%); Yellow crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J*= 8 Hz, 1H), 7.64 (t, *J*= 8 Hz, 1H), 7.55 (s, 1H), 7.48 (t, *J*= 8 Hz, 1H), 7.39 (d, *J*= 8 Hz, 1H), 7.34-7.33 (m, 1H), 7.32 (bs, 2 H), 7.30 (s, 1H), 7.29-7.28 (m, 1H), 7.27-7.26 (m, 2H), 7.25-7.23 (m, 1H), 7.21-7.19 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.08, 135.93, 133.48, 131.42, 13.83, 130.63, 130.22, 128.86, 128.66, 128.06, 127.86, 127.31, 126.45, 124.49, 123.20, 122.63, 113.95. HRMS (EI+) m/z calcd. for$C_{23}H_{16}N_2[M]^+$: 320.1313, found: 320.1316

5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4b): EtOAc/*n*-hexane (7%); Yellow crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8 Hz, 1H), 7.99 (d, *J* = 8 Hz, 1H), 7.69 (t, *J* = 8 Hz, 1H), 7.60-7.56 (m, 1H), 7.45-7.41 (m, 1H), 7.39 (s, 1H), 7.35 (t, *J* = 8 Hz, 4H), 7.31-7.29 (m, 1H), 7.27 (d, *J* = 4 Hz, 2H), 7.24-7.21 (m, 2H), 6.93 (t, *J* = 8 Hz, 1H), 6.01 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.79, 144.31, 135.70, 135.15, 132.67, 131.53, 131.23, 13.66, 129.88, 129.23, 128.75, 128.03, 127.76, 127.27, 126.38, 125.08, 124.12, 123.54, 122.97, 121.24, 119.60, 114.14. HRMS (EI+) m/z calcd. for $C_{27}H_{18}N_2$ $[M]^+$: 370.1470, found: 370.1472

7,8-diphenylbenzo[h]benzo[4,5]imidazo[2,1-a]isoquinoline (4c): EtOAc/*n*-hexane (5 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.93-7.89 (m, 2H), 7.86 (d, *J* = 8 Hz, 1H), 7.65 (t, *J* = 8 Hz, 1H), 7.37-7.33 (m, 5H), 7.30-7.29 (m, 2H), 7.25-7.21 (m, 3H), 7.19-7.17 (m, 3H), 6.91-6.87 (m, 1H), 6.02 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.01, 147.93, 144.72, 136.49, 136.19, 134.09, 132.65, 132.55, 131.81, 130.93, 130.64, 130.29, 129.98, 129.32, 129.24, 128.91, 128.42, 128.35, 128.18, 127.37, 126.95, 124.45, 124.12, 124.09, 121.19, 119.96, 118.16, 114.51, 77.38, 77.13, 76.87. HRMS (EI+) m/z calcd. for$C_{31}H_{20}N_2$ $[M]^+$: 420.1626, found: 420.1619

5,6-diphenylbenzo[4,5]imidazo[2,1-a][2,6]naphthyridine (4d): EtOAc/*n*-hexane (20 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87-8.74 (m, 3H), 8.03 (d, *J* = 8 Hz, 1H), 7.46-7.40 (m, 4H), 7.36-7.35 (m, 2H), 7.30 (t, *J* = 8 Hz, 3H), 7.25-7.23 (m, 2H), 7.01 (t,*J* = 8 Hz, 1H), 6.05 (d, *J* = 12 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.32, 133.98, 133.07, 131.48, 131.23, 130.57, 129.70, 129.03, 128.35, 127.85, 124.87, 122.59, 120.31, 12.29, 114.51, 100.00. . HRMS (EI+) m/z calcd. for$C_{26}H_{17}N_3$ $[M]^+$: 371.1422, found: 371.1421

3-methoxy-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4e): EtOAc/*n*-hexane (12 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d,*J* = 8 Hz, 1H), 7.97 (d,*J* = 8 Hz, 1H), 7.45-7.40 (m, 3H), 7.39-7.35 (m, 3H), 7.33-7.31 (m, 2H), 7.29-7.27 (m, 2H), 7.25-7.23 (m, 2H), 6.92 (t, *J* = 8 Hz, 1H), 6.76 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.02, 148.01, 144.47, 135.71, 135.65, 134.59, 133.82, 133.44, 131.19, 130.59, 129.16, 128.70, 128.06, 127.28, 126.97, 123.96, 123.19, 120.74, 119.23, 116.86, 116.35, 113.95, 108.83, 55.33. . HRMS (EI+) m/z calcd. for$C_{28}H_{20}N_2O$ $[M]^+$: 400.1576, found: 40.1573

3-methyl-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4f): EtOAc/*n*-hexane (5 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8 Hz, 1H), 7.96 (d,*J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 1H), 7.43-7.42 (m, 1H), 7.40-7.38 (m, 2H), 7.37-7.35 (m, 1H), 7.34-7.33 (m, 1H), 7.32-7.30 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.22 (m, 2H), 7.20 (bs, 1H), 7.11 (s,1H), 6.91 (t, *J* = 8 Hz, 1H), 5.99 (d, *J* = 8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.06, 144.41, 140.40, 135.85, 135.24, 133.91, 132.84, 131.62, 131.27, 130.74, 129.46, 129.26, 128.81, 128.09, 127.30, 126.20, 125.11, 124.11, 123.47, 121.08, 120.71, 119.49, 114.16, 22.15. HRMS (EI+) m/z calcd. for$C_{28}H_{20}N_2$ $[M]^+$: 384.1626, found: 384.1625

3-chloro-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4g): EtOAc/*n*-hexane (8 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8 Hz, 1H), 7.97 (d, *J* = 8 Hz, 1H), 7.66-7.63 (m, 1H), 7.45-7.43 (m, 1H), 7.421-7.38 (m, 3H), 7.36-7.32 (m, 3H), 7.31-7.27 (m, 3H), 7.21-7.18 (m, 2H), 6.96-6.92 (m, 1H), 6.00 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.24, 144.35, 136.45, 136.29, 133.46, 131.50, 131.22, 130.53, 129.51, 128.93, 128.37, 128.35, 128.68, 126.73, 125.84,124.48, 122.70, 121.63, 121.37, 114.26. HRMS (EI+) m/z calcd. for$C_{27}H_{17}ClN_2$ $[M]^+$: 404.1080, found: 404.1079

4-fluoro-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4h): EtOAc/*n*-hexane (8 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8 Hz, 1H), 7.98 (d*J* = 8 Hz, 1H), 7.65 (sex, *J* = 4 Hz, 1H), 7.41-7.35 (m, 5H), 7.31-7.30 (m, 1H), 7.29-7.28 (m, 1H), 7.25-7.23 (m, 1H), 7.21-7.20 (m, 3H), 7.19-7.17 (m, 1H), 6.94 (t, *J* = 8 Hz, 1H), 5.91 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.18 157.64, 144.31, 137.60, 136.53, 133.30, 130.69, 130.59 (d, J_F = 3 Hz), 129.22, 128.77, 128.67, 127.31, 126.79, 125.05, 124.41, 121.65, 121.31, 121.27, 121.15, 119.72, 119.37, 117.00, 116.78, 114.21. HRMS (EI+) m/z calcd. for$C_{27}H_{17}FN_2$ $[M]^+$: 388.1376, found: 388.1372.

2-fluoro-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4i): EtOAc/*n*-hexane (8 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ8.76 (d, *J* = 8 Hz, 1H), 7.67 (t, *J* = 8 Hz, 1H), 7.57 (s,1H), 7.52-7.49 (m, 1H), 7.37-7.33 (m, 2H), 7.30-7.28 (m, 1H), 7.18 (s,1H), 7.11-7.08 (m, 1H), 7.07-7.04 (m, 1H), 7.02-6.97 (m, 3H), 6.95-6.91 (t, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.20, 160.72, 144.22, 135.51, 133.54, 131.42, 131.24, 130.67, 129.28, 128.99, 128.95 (d, J_F = 8 Hz), 128.77, 128.10, 127.41, 124.30, 121.57, 119.76, 118.45, 118.22, 114.21, 110.47, 110.23. HRMS (EI+) m/z calcd. form/z calcd. For $C_{27}H_{17}FN_2$ $[M]^+$: 388.1376, found: 388.1378

5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline-3-carbonitrile (4j): EtOAc/*n*-hexane (15 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07(d, *J* = 8 Hz, 1H), 8.01 (d, *J* = 8 Hz, 1H), 7.89-7.87 (m, 1H), 7.66 (s,1H), 7.48-7.44 (m, 1H), 7.44-7.43 (m,1H), 7.42 (bs, 1H), 7.41-7.40 (m,1H), 7.35-7.33 (m, 1H), 7.34-7.32 (m, 2H), 7.31 (bs, 1H), 7.31-7.30 (bs, 1H), 7.20-7.18 (m, 2H), 7.02-6.98 (m, 1H), 6.02 (d, *J* = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.25, 144.40, 137.13, 134.35, 133.07, 132.66, 131.40, 131.25, 131.23, 130.38, 129.75, 129.60, 129.06, 128.57, 128.04, 126.03, 125.69, 124.92, 122.56, 122.48, 120.16, 118.81, 114.43, 113.13, 77.37, 77.11, 76.86. HRMS (EI+) m/z calcd. For $C_{28}H_{17}N_3$[M]$^+$: 395.1422, found: 395.1426

7,8-bis(4-bromophenyl)benzo[h]benzo[4,5]imidazo[2,1-a]isoquinoline (4k): EtOAc/*n*-hexane (12 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (d, d, *J* = 8 Hz, 1H), 8.14 (d, d, *J* = 4 Hz, 1H), 8.01-7.94 (m, 3H), 7.76-7.73 (m, 1H), 7.60-7.58 (m, 2H), 7.50-7.47 (m, 2H), 7.46-7.45 (m, 1H), 7.33 (d, d, *J* = 8 Hz, 1H), 7.25-7.23 9m, 2H), 7.12-7.10 (m, 2H), 7.06-7.02 (m, 1H), 6.18 (d, *J* = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.79, 144.76, 135.24, 134.87, 133.32, 132.74, 132.71, 132.48, 132.17, 131.92, 131.70, 131.19, 130.20, 129.74, 129.28, 128.61, 128.41, 127.22, 124.70, 123.98, 123.62, 123.16, 121.96, 120.24, 118.44, 114.16.HRMS (EI+) m/z calcd. for$C_{31}H_{18}Br_2N_2$ [M]+ : 690.9814, 692.9796, found: 690.9811, 692.9793.

5,6-diphenyl-2,4-bis(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4l):
EtOAc/*n*-hexane (10 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00-8.97 (m, 1H), 7.96 (d, *J* = 4 Hz, 1H), 7.45-7.42 (m, 1H), 7.41-7.40 (m,1H), 7.40 (bs, 1H), 7.39-7.38 (m, 1H), 7.38-7.37 (m,1H), 7.36 (bs, 1H), 7.35-7.34 (m, 1H), 7.34-7.33 (m, 2H), 7.32-7.29 (m, 1H), 7.29-7.27 (m, 1H), 7.21-7.19 (m, 2H), 5.97 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.74, 162.76, 147.42, 144.34, 136.40, 135.20, 134.96, 134.89, 133.50, 131.45, 131.21, 130.53, 129.49, 128.92, 128.33, 127.64, 124.38, 123.00, 122.98, 121.41, 119.60, 116.60, 116.41, 114.21, 111.95, 111.76.HRMS (EI+) m/z calcd. for$C_{29}H_{16}F_6N_2$ [M]+ : 506.1218, found: 506.1216.

5,6-bis(4-bromophenyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4m): EtOAc/*n*-hexane (15 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8 Hz, 1H), 7.99 (d, *J* = 8 Hz, 1H), 7.71 (t, *J* = 8 Hz, 1H), 7.61-7.56 (m,3H), 7.46 (d, *J* = 8 Hz, 2H), 7.40 (t, *J* = 8 Hz, 1H), 7.28 (d, *J* = 8 Hz, 1H), 7.21 (d, *J* = 12 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 7.01 (t, *J* = 8 Hz, 1H), 6.10 (d, *J* = 12 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.62, 144.30, 134.40, 133.94, 133.02, 132.31, 132.16, 132.05, 131.56, 130.97, 130.09, 128.18, 126.10, 125.22, 124.39, 123.90, 123.06, 122.66, 121.87, 121.62, 119.84, 113.79, 77.32, 77.00, 76.68.HRMS (EI+) m/z calcd. for$C_{27}H_{16}Br_2N_2$ [M]+ : 526.9753, 528.9734, found: 526.9756, 528.9731.

5,6-bis(4-bromophenyl)-3-methoxybenzo[4,5]imidazo[2,1-a]isoquinoline (4n): EtOAc/*n*-hexane (5 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8 Hz, 1H), 7.95 (d,*J* = 8 Hz, 1H), 7.56 (d,*J* = 8 Hz, 2H), 7.45 (d,*J* = 8 Hz, 2H), 7.37 (t,*J* = 8 Hz, 1H), 7.31-7.28 (m, 1H), 7.20 (d,*J* = 8 Hz, 2H), 7.07 (d,*J* = 8 Hz, 2H), 6.97 (t, *J* = 8 Hz, 1H), 6.66-6.65 (m, 1H), 6.06 (d,*J* = 8 Hz, 1H), 3.78 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19, 134.48,

133.96, 133.87, 132.96, 132.29, 132.10, 131.61, 127.19, 124.30, 123.87, 122.33, 121.90, 121.17, 119.44, 116.66, 113.64, 108.70, 55.44. HRMS (EI+) m/z calcd. for$C_{28}H_{18}Br_2N_2O$ [M]+ : 556.9859, 558.984, found: 556.9860, 558.9842.

5,6-bis(3-fluorophenyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4o): EtOAc/*n*-hexane (8 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.72 (t, *J* = 8 Hz, 1H), 7.63-7.59 (m, 1H), 7.46-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.20-7.15 (m, 2H), 7.09-7.06(m, 1H), 7.04-6.98 (m, 3H), 6.96-6.92 (m, 1H), 6.09-6.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.67, 144.32, 130.25, 128.34, 127.39, 127.37, 126.59, 126.57, 126.26, 125.27, 124.51, 123.08, 121.73, 119.88, 118.58, 118.56, 118.41,118,.39, 117.93, 117.91, 117.75, 117.74, 116.90, 116.75, 116.73, 114.88, 114.86, 114.72, 114.69, 114.53, 113.83. HRMS (EI+) m/z calcd. for$C_{27}H_{16}F_2N_2$ [M]+ : 407.1354, found 407.1355.

5,6-di-p-tolyl-2,4-bis(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4p): EtOAc/*n*-hexane (10 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97-8.95 (m,1H), 7.95 (d, *J* = 8 Hz, 1H), 7.40-7.35 (m, 2H), 7.20 (s, 3H), 7.11-7.06 (m, 4H), 6.99-6.96 (m, 1H), 6.96-6.92 (m, 1H), 6.02 (d, *J* = 8 Hz, 1H), 2.42 (s, 3H), 2.33 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.71, 162.72, 147.47, 144.32, 139.28, 137.13, 136.51, 135.28, 135.21, 132.23, 131.29, 131.24, 130.67, 130.32, 129.62, 129.04, 127.75, 127.68, 124.27, 122.99, 122.96, 121.28, 119.49, 116.41, 116.22, 114.37, 111.95, 111.77, 77.37, 77.12, 76.86, 21.67, 21.37. HRMS (EI+) m/z calcd. for$C_{31}H_{20}F_6N_2$ [M]+ : 534.1603, found: 534.1603.

5,6-bis(4-bromophenyl)-3-methylbenzo[4,5]imidazo[2,1-a]isoquinoline (4q): EtOAc/*n*-hexane (10 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8 Hz, 1H), 7.97 (d, *J* = 8 Hz, 1H), 7.57-7.53 (m, 3H), 7.46-7.45 (m, 2H), 7.40-7.37 (m, 1H), 7.21-7.19 (m, 1H), 7.07-7.03 (m, 3H), 7.07-6.97 (m, 1H), 6.08 (d, *J* = 8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.90, 144.38, 140.72, 134.57, 134.02, 133.13, 132.51, 132.38, 132.25, 132.24, 131.64, 131.01, 129.88, 125.95, 125.24, 124.40, 123.92, 123.89, 122.61, 121.88, 121.47, 120.78, 119.74, 113.83, 22.14.HRMS (EI+) m/z calcd. for$C_{28}H_{18}Br_2N_2$ [M]+ : 540.991, 542.9891, found: 540.9908, 542.9889.

5,6-bis(4-bromophenyl)-2,4-bis(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4r): EtOAc/*n*-hexane (12 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98-8.95 (m,1H), 7.97 (d, *J* = 8 Hz, 1H), 7.59-7.57 (m,2H), 7.48-7.46 (m, 2H), 7.44-7.39 (m, 2H), 7.22-

7.20 (m, 1H), 7.07-7.04 (m, 2H), 7.03-6.99 (m, 1H), 6.92 (dd, J_1= 4 Hz, J_2= 8 Hz, 1H), 6.09 (d, J = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.80, 162.81, 147.24, 144.32, 135.24, 134.30, 134.23, 133.90, 132.96, 132.50, 132.09, 132.03, 131.88, 130.96, 128.03, 127.96, 124.68, 124.20, 122.28, 122.10, 122.07, 121.81, 119.85, 119.65, 119.64, 117.04, 116.86, 113.89, 111.75, 111.56.HRMS (EI+) m/z calcd. for$C_{29}H_{14}Br_2F_6N_2$ [M]+ : 662.9501, 664.9482, found: 662.9502, 664.9479.

9-bromo-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4s): EtOAc/*n*-hexane (8 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 8 Hz, 1H), 8.03 (s, 1H), 7.63 (t, J = 8 Hz, 1H), 7.52 (t, J = 8 Hz, 1H), 7.38-7.32 (m, 3H), 7.30-7.27 (m, 1H), 7.24-7.20 (m, 3H), 7.19-7.18 (m, 2H), 7.15-7.13 (m, 2H), 6.96-9.93 (m , 1H), 5.76 (d, J = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.58, 144.60, 134.40, 131.77, 13.40, 129.54, 129.23, 128.41, 127.88, 127.07, 126.95, 126.38, 125.47, 124.18, 123.24, 123.06, 121.72, 121.25, 116.42, 114.20. HRMS (EI+) m/z calcd. for$C_{27}H_{17}BrN_2$[M]+ : 449.0648, 451.0631, found: 449.0647, 451.0633.

10-bromo-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4t): EtOAc/*n*-hexane (8 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 8 Hz, 1H), 7.77 (d, J = 8 Hz, 1H), 7.64 (t, J = 8 Hz, 1H), 7.56-7.52 (m, 1H), 7.41-7.40 (m, 1H), 7.39-7.35 (m, 2H), 7.30-7.28 (m, 2H), 7.24 (b, 1H), 7.22-7.21 (m, 2H), 7.20 (s, 2H), 7.17-7.15 (m, 2H), 5.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.31, 142.13, 134.38, 133.84, 132.23, 131.70, 130.99, 130.40, 129.48, 129.20, 128.50, 127.94, 127.08, 126.98, 126.40, 126.36, 125.51, 124.11, 123.00, 121.80, 119.61, 116.27, 113.12. HRMS (EI+) m/z calcd. for$C_{27}H_{17}BrN_2$[M]+ : 449.0648, 451.0631, found: 449.0645, 454.0630.

5,6-diphenyl-9-(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4u): EtOAc/*n*-hexane (5 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 8 Hz, 1H), 8.26 (s, 1H), 7.73 (t,J = 8 Hz, 1H), 7.62 (t, J = 8 Hz, 1H), 7.44-7.40 (m, 3H), 7.38-7.33 (m, 3H), 7.29 (d, J = 8 Hz, 3H), 7.23 (d, J = 8 Hz, 2H), 7.17 (d,J = 8 Hz, 1H), 6.06 (d,J = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.32, 143.79, 135.29, 134.85, 133.35, 132.85, 131.37, 130.59, 130.50, 129.52, 128.95, 128.12, 127.47, 126.57, 125.30, 124.47, 122.91, 122.77, 117.80, 117.09, 114.56. HRMS (EI+) m/z calcd. for$C_{28}H_{17}F_3N_2$ [M]+ : 439.1417, found: 439.1416.

5,6-diphenyl-10-(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinoline (4v): EtOAc/*n*-hexane (5 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 8 Hz, 1H),

8.03(d,*J* = 8 Hz, 1H), 7.73 (t,*J* = 8 Hz, 1H), 7.66-7.59 (m, 2H), 7.48-7.43 (m, 3H), 7.40 (t,*J* = 8 Hz, 1H), 7.36-7.33(m, 2H), 7.31-7.27 (m, 3H), 7.25-7.24 (m, 2H), 6.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.76, 146.29, 135.23, 134.97, 133.09, 133.00, 131.38, 130.58, 130.48, 129.64, 129.10, 128.15, 128.10, 127.52, 126.52, 125.32, 124.33, 122.67, 12.96, 119.80, 112.14. HRMS (EI+) m/z calcd. for $C_{28}H_{17}F_3N_2$[M]+ : 377.1107, found: 377.1105.

4,5-diphenylbenzo[4,5]imidazo[1,2-a]thieno[2,3-c]pyridine (4w): EtOAc/*n*-hexane (10 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8 Hz, 1H), 7.61 (d, *J* = 8 Hz, 1H), 7.46-7.44 (m 2H), 7.42 (s, 1H), 7.42-7.39 (m, 2H), 7.37-7.35 (m, 3H), 7.26-7.23 (m, 4H), 7.05 (d, *J* = 8 Hz, 1H), 6.91 (t, *J* = 8 Hz, 1H), 6.08 (d, *J* = 8 Hz, 1H). ^{13}C NMR 130.23, (100 MHz, $CDCl_3$) δ 144.92, 140.35, 136.14, 134.99, 133.26, 130.84, 130.80, 129.39, 129.19, 128.85, 128.00, 127.28, 125.72, 125.27, 124.53, 121.56, 12.70, 119.45, 114.43. HRMS (EI+) m/z calcd. for $C_{25}H_{16}N_2S$ [M]+ : 439.1417, found: 439.1415.

6-(4-chlorophenyl)-5-(thiophen-2-yl)benzo[4,5]imidazo[2,1-a]isoquinoline (4ae):

EtOAc/*n*-hexane (5 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (t, *J* = 8 Hz, 1H), 8.03-8.01 (m, 1H), 7.77-7.72 (m, 1H), 7.68-7.62 (m, 1H), 7.57-7.52 (m, 1H), 7.48-7.46 (m, 1H), 7.45-7.41 (m, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.36-7.31 (m, 2H), 7.26-7.23 (m, 1H), 7.15-7.13 (m, 1H), 7.09-7.04 (m, 1H), 7.03-6.93 (m, 1H), 6.17-6.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.88, 135.71, 135.66, 133.97, 133.68, 133.44, 132.84, 132.62, 132.48, 131.97, 131.79, 130.89, 130.30, 130.26, 130.14, 129.22, 128.80, 128.39, 128.27, 127.49, 127.14, 126.86, 126.42, 126.22, 125.24, 125.03, 124.57, 124.49, 121.84, 121.75, 119.75, 119.57, 113.89, 113.89, 113.81. HRMS (EI+) m/z calcd. for $C_{25}H_{15}ClN_2S$ [M]+ : 411.0717, found: 411.0729.

5,6-di-p-tolylimidazo[2,1-a]isoquinoline (4x): EtOAc/*n*-hexane (12 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8 Hz, 1H), 7.62 (t, *J* = 8 Hz, 1H), 7.52 (s, 1H), 7.45 (t, *J* = 8 Hz, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.17 (d, *J* = 8 Hz, 3H), 7.14-7.12 (m, 2H), 7.08-7.06 (m, 4H), 2.34 (s 3H), 2.33 (s, 3H). ^{13}C NMR 130.23, (100 MHz, $CDCl_3$) δ 142.12, 137.56, 135.74, 132.47, 132.01, 130.23, 129.89, 129.89, 129.75, 129.71, 129.03, 128.31, 127.75, 126.85, 126.59, 125.44, 123.25, 122.23, 122.09, 112.94, 20.34, 20.22. HRMS (EI+) m/z calcd. for $C_{25}H_{20}N_2$[M]$^+$: 348.1626, found: 348.1624.

5,6-bis(3-fluorophenyl)imidazo[2,1-a]isoquinoline (4y): EtOAc/*n*-hexane (8 %); white crystalline solid , ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8 Hz, 1H), 7.67 (t, *J* = 8 Hz, 1H),

7.57(s, 1H), 7.50 (t, *J* = 8 Hz, 1H), 7.37-7.35 (m, 2H), 7.33- 7.28 (m, 1H), 7.18 (br, s, 1H), 7.11-7.06 (m, 2H), 7.04-6.97(m, 3H), 6.95-6.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77, 163.74, 163.53, 163.51, 161.79, 161.76, 161.57, 161.54, 143.16, 143.16, 137.91, 137.91, 137.85, 137.85, 135.19, 135.12, 132.15, 131.39, 130.81, 130.81, 130.74, 130.74, 130.71, 130.71, 130.64, 130.64, 130.03, 129.94, 129.92, 129.86, 128.40, 127.29, 127.27, 127.25, 126.30, 126.11, 126.08, 123.61, 123.42, 123.41, 118.47, 118.46, 118.30, 118.29, 117.41, 117.24, 116.53, 116.52, 116.37, 116.35, 114.90, 114.88, 114.73, 114.72, 113.87, 100.00, 77.38, 77.12, 76.87, 0.10. HRMS (EI+) m/z calcd. for $C_{23}H_{14}F_2N_2[M]^+$: 357.1198, found: 357.1120.

5,6-bis(4-bromophenyl)imidazo[2,1-a]isoquinoline(4z): EtOAc/*n*-hexane (20 %); white crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d,*J* = 8 Hz, 1H), 7.66 (t,*J* = 8 Hz, 1H), 7.56-7.50 (m, 3H), 7.49-7.44 (m, 3H), 7.33 (d, *J* = 8 Hz, 1H), 7.16 (d, *J* = 8 Hz, 3H), 7.06 (d, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.16, 134.70, 133.03, 132.36, 132.16, 131.85, 131.687, 131.33, 130.13, 128.39, 128.38, 126.25, 123.66, 123.62, 123.44, 123.39, 121.98. HRMS (EI+) m/z calcd. for $C_{23}H_{14}Br_2N_2[M]^+$: 476.9597, 478.9577, found: 476.9595, 478.9578.

2-methyl-5,6-diphenylimidazo[2,1-a]isoquinoline (4aa): EtOAc/*n*-hexane (15%); Yellow crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8 Hz, 1H), 7.52 (t, *J* = 8 Hz, 1H), 7.36 (t, *J* = 8 Hz, 1H), 7.29 (d, *J* = 8 Hz, 1H), 7.24-7.23 (m, 3H), 7.20 (s, 1H), 7.19-7.18 (m, 2H). 7.18-7.15 (m, 3H), 7.11-7.09 (m , 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.55, 139.48, 135.06, 132.72, 132.10, 130.48, 129.47, 129.17, 127.71, 127.56, 126.97, 126.58, 126.18, 125.33,

123.87, 122.78, 122.03, 121.73, 109.83, 13.25. HRMS (EI+) m/z calcd. for $C_{24}H_{18}N_2[M]^+$: 334.1470, found: 334.1472.

5,6-bis(2-fluorophenyl)-2-methylimidazo[2,1-a]isoquinoline (4ab): EtOAc/*n*-hexane (12 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8 Hz, 1H), 7.57 (t,*J* = 8 Hz, 1H), 7.42-7.39 (m, 1H), 7.31-7.28 (m, 1H), 7.23-7.2 (s, 1H), 7.19 (s, 1H), 7.16-7.12 (m, 2H), 7.05-6.99 (m, 3H), 6.97-6.89 (m, 1H), 6.84 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.50, 160.98, 159.55, 159.00, 142.64, 140.96, 132.62, 131.79, 131.73, 130.30, 130.24, 129.69, 128.21, 128.13, 125.80, 124.77, 124.74, 124.25, 124.22, 123.27, 122.95, 119.43, 115.97, 115.80, 115.46, 155.28, 110.70, 100.00, 14.41. HRMS (EI+) m/z calcd. for $C_{24}H_{16}F_2N_2[M]^+$: 371.1354, found: 371.1356.

5,6-bis(2-fluorophenyl)-3-methylimidazo[2,1-a]isoquinoline (4ac): EtOAc/*n*-hexane (15 %); brown crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8 Hz, 1H), 7.64 (t, *J* = 8 Hz, 1H), 7.49-7.46 (m, 1H), 7.37-7.32 (m, 2H), 7.30-7.28 (m ,2H), 7.21 (t, *J* = 8 Hz, 1H), 7.13-7.11 (m, 1H), 7.09-7.08 (m, 1H), 7.06-7.02 (m, 2H), 6.84 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.59, 14.89, 133.37, 132.61, 132.16, 132.14, 131.80, 131.74, 131.63, 131.57, 131.55, 130.31, 129.70, 128.25, 128.24, 128.17, 125.87, 125.80, 124.78, 124.75, 124.25, 124.22, 123.36, 123.32, 115.98, 115.81, 110.77, 110.70, 14.37. HRMS (EI+) m/z calcd. for $C_{24}H_{16}F_2N_2[M]^+$: 371.1354, found: 371.1357.

6-(4-chlorophenyl)-5-(thiophen-2-yl)imidazo[2,1-a]isoquinoline (4ad): EtOAc/*n*-hexane (6 %); yellow crystalline solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8 Hz, 1H), 7.70-7.66 (m, 1H), 7.61-7.59 (m, 1H), 7.57 (br, s, 1H), 7.55-7.52 (m, 1H), 7.38 (d, *J* = 8 Hz, 2H), 7.34-7.30 (m, 3H), 7.16 (br, s, 1H), 7.01-6.99 (m, 1H), 6.93-6.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.89, 135.36, 133.99, 131.31, 130.93, 130.16, 129.17, 128.60, 128.41, 127.12, 126.89, 126.29, 123.27, 113.84. HRMS (EI+) m/z calcd. for $C_{21}H_{13}ClN_2S$ $[M]^+$: 361.0561, found: 361.0578.

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Keywords

Annulation, catalysis, cobalt, fluorescence, polyheteroarenes

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