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Modular Assembly of Ring-Fused and π-Extended Phenanthroimidazoles via C−H Activation and Alkyne Annulation

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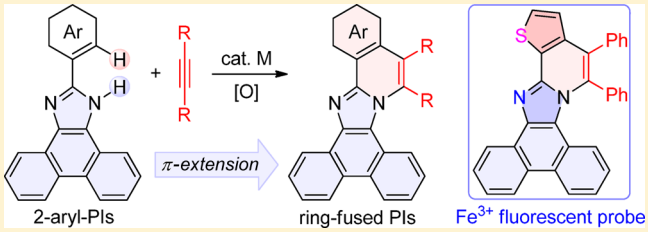
Supporting Information

ABSTRACT: π-Extension of 2-aryl-phenanthroimidazoles via rhodium(III)-catalyzed C−H activation and alkyne annulation is developed. This method enables rapid, practical and modular assembly of diverse ring-fused phenanthroimidazoles, including an unusual rearrangement product using aryl-alkyl asymmetric alkyne and a thiophene fused product which could serve as a Fe^{3+} fluorescent probe. The feasibility of the one-pot synthesis and ruthenium(II)-catalyzed versions of this reaction was also verified.

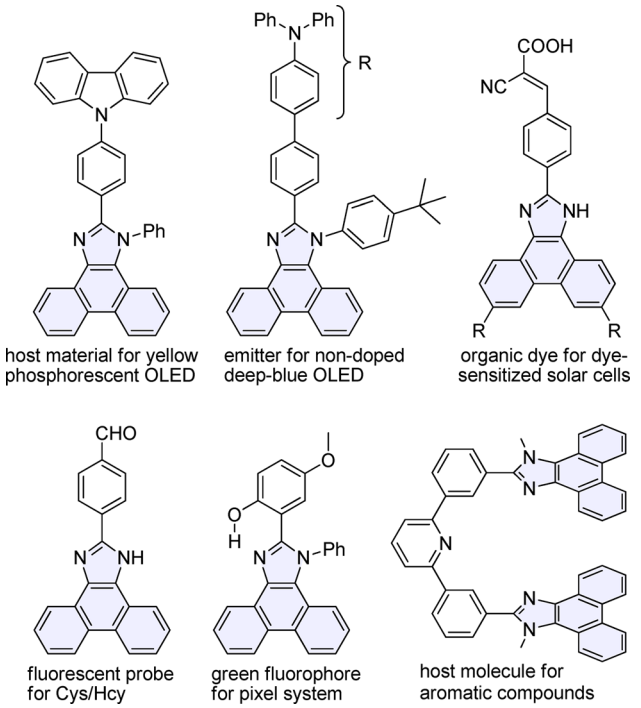


INTRODUCTION

1*H*-Phenanthro[9,10-*d*]imidazole, which is usually called phenanthroimidazole (PI) for short, is a rigid π-conjugated heterocyclic skeleton fused by imidazole and phenanthrene. The PI unit shows excellent electron injection and transport properties and good thermal stability, making it a suitable component for organic semiconductors used in organic light-emitting diodes (OLEDs)[1] and solar cells[2] (Scheme 1). For example, some PI−triphenylamine derivatives were employed in OLEDs as efficient deep-blue emitters,[1a] and some PI−carbazole derivatives are applicable bipolar hosts for green and yellow phosphorescent OLEDs.[1b] PI chromophore were developed for dye-sensitized solar cells which exhibited good efficiencies up to 4.68%.[2a] PI unit has also been widely used in syntheses of useful fluorophores,[3] such as superradiant laser dye,[3a] ratiometric fluorescent probes for cysteine and homocysteine,[3b] fluorescent ionic liquid sensor arrays,[3c] and green component for RGB-emitting molecular pixel system.[3d] In addition, the PI unit has been employed as a component for host molecules,[4] such as a molecular tweezer to host 1,3,5-trinitrobenzene.[4a]

Ring-fusion of a conjugated parent molecule is a robust tool to build a library of π-extended derivatives with tunable π-electron distribution and π−π stacking.[5] The related optical and electrical properties, such as fluorescence, electron mobility, and band gap are shifted and diversified after π-extension, which is crucial for development of new materials. PI derivatives for use are typically substituted with aryls at the 2- and/or 1-position via σ-bonds (Scheme 1).[1−4] Though a few ring-fused PI derivatives are known, they are synthesized from restrictive substrates under harsh conditions,[6] while direct π-extension of the PI parent molecule is still challenging. As alkyne is an ideal C2 synthon to extend a conjugated system with high atom economy and substitution degree, we focused on direct π-extension of the PI parent molecule via alkyne annulation.

Scheme 1. Examples of Phenanthroimidazole Derivatives for Use



In the past decade, C−H activation has emerged as a robust and versatile tool for atom-economical assembly of heterocycles,[7−10] syntheses, and late-stage diversification of functional

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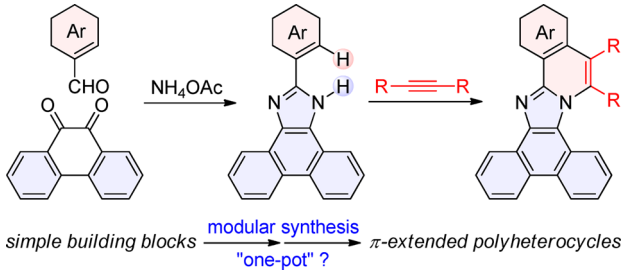
molecules.[11] In 2008, Satoh and Miura[8] disclosed an imidazoisoquinoline synthesis via Rh(III)-catalyzed oxidative coupling of 2-aryl-1*H*-imidazoles and alkynes. This work unveiled a direct strategy for alkyne annulation of arene−azaarene biaryls via C−H/N−H bond cleavage.[8−10] However, only two examples were investigated, and a costly ligand tetraphenylcyclopentadiene ($C_5H_2Ph_4$) was needed to activate the Rh(III) catalyst.

Encouraged by Miura's work[8a] and our continuous efforts[12] on *N*-annulation via C−H activation, we envisioned that 2-aryl-PIs should be suitable substrates for alkyne annulation to form π-extended PIs with a unique phenanthrene/imidazole/isoquinoline fused heterocyclic system (Scheme 2). It should

Scheme 2. Reaction Design



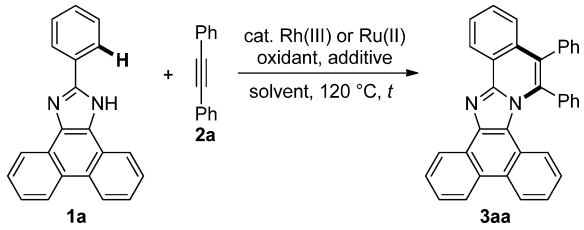
be note that the 2-aryl-PI substrates are readily available via facile multicomponent reaction of 9,10-phenanthraquinone, aryl aldehyde, and ammonium acetate. In addition, this reaction could also be incorporated with the subsequent alkyne annulation in one-pot. Thus, a highly π-extended polyheterocyclic library could be rapid assembled from simple building blocks in a modular fashion.

RESULTS AND DISCUSSION

We commenced our study by employing 2-phenyl-PI (**1a**) and diphenylacetylene (**2a**) as substrates, $[Cp^*RhCl_2]_2$ as catalyst precursor, and stoichiometric $Cu(OAc)_2{\cdot}H_2O$ as oxidant, yet without the $C_5H_2Ph_4$ ligand (Table 1). Ring-fused product **3aa** was obtained as expected. The reaction was sluggish at 80 °C (entry 1), and elevating the temperature to 120 °C gave an improved yield (entry 2). After an extensive survey of solvents, reaction in dioxane (entry 3) or acetone (entry 4) gave nearly full conversion, while using other solvents such as DCE, toluene, and *t*-AmOH gave lower conversion. Due to the low solubility of **1a** and Cu(II) salt in acetone, the reaction was carried out in a dilute solvent and gave an improved yield (entry 5). A satisfactory yield (83%) was obtained under these conditions on a 0.5 mmol scale. The yield was not further improved by either replacing $Cu(OAc)_2{\cdot}H_2O$ with anhydrous $Cu(OAc)_2$ (entry 6) or using a cation form of Rh(III) catalyst $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (entry 7). Reaction carried out without nitrogen protection also proceeded smoothly, with a slightly declined yield (entry 8). However, using catalytic Cu(II) for aerobic oxidative annulation gave an unsatisfactory result in either acetone with an air balloon or *o*-xylene in an open flask.

We then turned our attention to $[Ru(p\text{-cymene})Cl_2]_2$,[7e] a Ru(II) catalyst that has similar structure, similar catalytic activity in many examples, and much lower price with $[Cp^*RhCl_2]_2$. Ru(II) was also found to be active for catalyzing the reaction, though the conversion was much lower even with higher catalyst loading and longer reaction time (entries 9 and

Table 1. Optimization of Conditions[a]

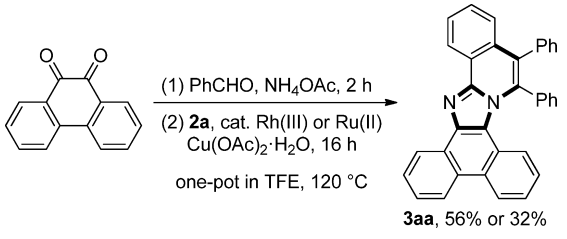


entry	catalyst	additive	solvent	time (h)	yield[b] (%)
1[c]	Rh(III)		DMF[d]	16	30
2	Rh(III)		DMF[d]	12	61
3	Rh(III)		dioxane[d]	12	68
4	Rh(III)		acetone[d]	12	74
5	**Rh(III)**		**acetone**	**12**	**81 (83[e])**
6[f]	Rh(III)		acetone	12	80
7	Rh(III)[g]		acetone	12	78
8[h]	Rh(III)		acetone	12	75
9	Ru(II)		acetone	24	35
10	Ru(II)		DCE	24	37
11	Ru(II)	$AgSbF_6$[i]	DCE	24	42
12	Ru(II)	KPF_6[i]	DCE	24	40
13	Ru(II)	Na_2CO_3[j]	DCE	24	56 (58[e])

[a]Conditions: **1a** (0.20 mmol), **2a** (0.28 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.44 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %) or $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), solvent (2.0 mL). [b]Isolated yield of **3aa**. [c]80 °C. [d]1.0 mL of solvent. [e]0.5 mmol scale. [f]$Cu(OAc)_2$ (0.44 mmol) as oxidant. [g]$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol %) as catalyst. [h]Without N_2 protection. [i]20 mmol %. [j]2.0 equiv.

10) compared to Rh(III)-catalyzed conditions (entry 5). Adding an additive such as $AgSbF_6$ or KPF_6 gave only a slightly improved yield (entries 11 and 12), while adding 2.0 equiv of Na_2CO_3 gave 58% yield on a 0.5 mmol scale (entry 13). With our keen interest in C−H activation and alkyne annulation of in situ ammoniated species,[12,13] we embarked on preparation and π-extension of 2-aryl-PIs in one pot. Trifluoroethanol (TFE) was found to be an optimal medium for its high compatibility in both steps.[14] Though the yield was only moderate [56% using cat. Rh(III); 32% using cat. Ru(II)], this protocol enables assembly of ring-fused PIs from simple building blocks in a step-economic procedure (Scheme 3).

Scheme 3. One-Pot Synthesis of 3aa



Under the optimized conditions (Table 1, entry 5, in 0.5 mmol scale; also "standard conditions" for following studies), we set out to examine the generality of the reaction (Table 2). With **2a** as alkyne substrate, a range of 2-aryl-PI substrates with different *para*-substituents were surveyed. Both alkyl- and aryl-substituted substrates reacted well to afford **3ba** (92%) and **3ca** (85%), respectively. Compound **3ba** has a much better solubility in common organic solvents than **3aa**, which would be beneficial for fabrication of solution-processed devices.

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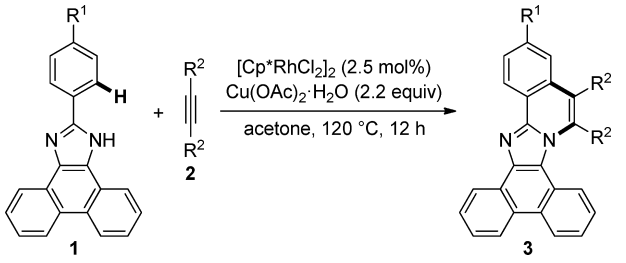
Table 2. General Substituent Scope[a]



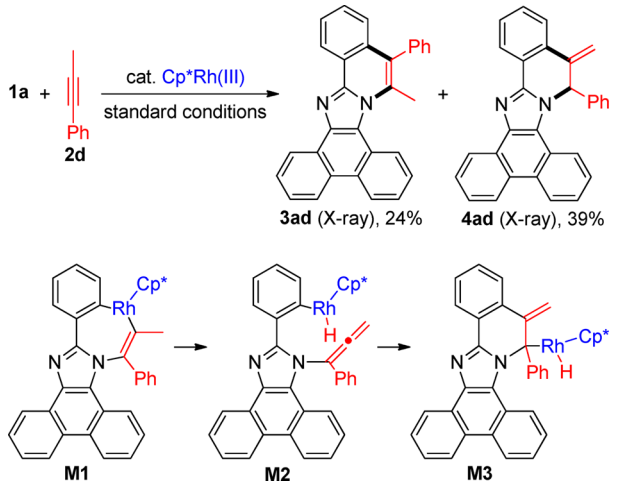
entry	1 (R^1)	2 (R^2)	3	yield (%)
1	**1a** (H)	**2a** (Ph)	**3aa**	83
2	**1b** (*t*-Bu)	**2a**	**3ba**	92
3	**1c** (Ph)	**2a**	**3ca**	85
4	**1d** (OMe)	**2a**	**3da**	42
5	**1e** (NMe_2)	**2a**	**3ea**	67
6	**1f** (F)	**2a**	**3fa**	51
7	**1g** (Cl)	**2a**	**3ga**	90
8	**1h** (Br)	**2a**	**3ha**	93
9	**1a**	**2b** (4-$MeOC_6H_4$)	**3ab**	80
10	**1a**	**2c** (4-ClC_6H_4)	**3ac**	64

[a]Reactions were carried out using **1** (0.50 mmol) and **2** (0.70 mmol) with $[Cp^*RhCl_2]_2$ (2.5 mol %) and $Cu(OAc)_2·H_2O$ (1.1 mmol) in 5.0 mL of acetone at 120 °C for 12 h under N_2.

Substrates bearing an electron-donating group such as OMe and NMe_2, as well as fluorinated substrate, afforded **3da**–**fa** in lower yield. Gratifyingly, substrates with Cl and Br reacted quite well to afford the corresponding halogenated products (**3ga**, 90%; **3ha**, 93%), which would greatly facilitate further derivatization of the fused PI products via functional group transformations or cross-coupling reactions. The reaction proceeded smoothly with diarylalkynes with OMe or Cl as *para*-substituents to afford **3ab** and **3ac**, respectively.

Interestingly, when asymmetric alkyne **2d** was employed, two types of products (**3ad** and **4ad**) were obtained, with the phenyl at different positions (Scheme 4). The rearrangement product **4ad** has a chiral center adjacent to a nitrogen atom and an exocyclic double bond. A possible pathway[8a] to form the rearrangement product **4ad** may be triggered by *β*-elimination of rhodacycle intermediate **M1** to form **M2**, followed by intramolecular allene insertion[15] to form **M3** and then reductive elimination to obtain **4ad**. For a complete proposed mechanism for the formation of **3ad** and **4ad**, see Scheme S1 in the Supporting Information.

Scheme 4. Formation of the Rearrangement Products



As shown in the crystal structure of **4ad** (Figure 1), the phenyl group is almost perpendicular to the PI skeleton. The

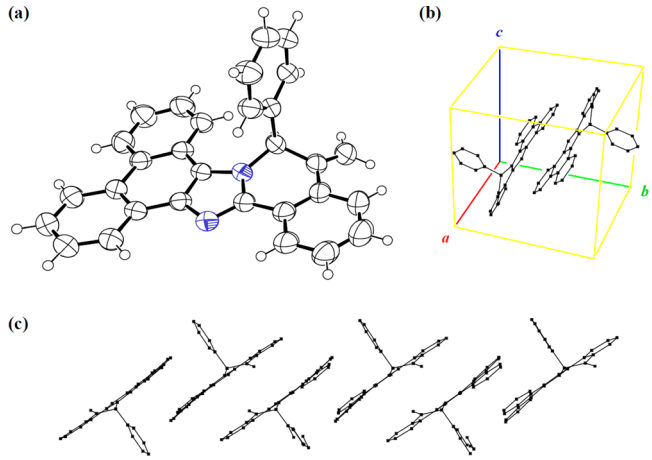


Figure 1. X-ray structural details of **4ad**: (a) ORTEP drawing of **4ad** (one of the enantiomers) with 50% probability ellipsoids; (b) dimer of the two enantiomers in a unit cell; (c) one-dimensional packing of the two enantiomers along the *a* direction.

two enantiomers of **4ad** formed a dimer in the unit cell and packed alternately along the *a* direction. The one-dimensional molecular packing was also observed in crystal structures of **3aa** and **3ad** (see the Supporting Information), indicating *π*–*π* stacking of the PI skeleton.

As replacing benzene to polycyclic arene or heterocyclic arene is a widely used strategy to regulate properties of fluorophores and organic semiconductors, we became interested in extending this method to PI substrates with other 2-aryls. Naphthalene-fused products (**3ia** and **3ja**) and thiophene-fused products (**3ka** and **3la**) were obtained as expected from the corresponding 2-aryl PIs **1i**–**l** (Table 3). The regioselective formation of **3ja** was confirmed with X-ray analysis, and one-dimensional molecular packing was also observed in its crystal structure. Though the yields were not high, these products greatly enriched the diversity of the fused PI library. In particular, we envisioned that **3ka** could be a candidate for a fluorescent ligand for metal ions.

To illustrate the utility of our product, we employed **3ka** as a fluorescent probe for Fe^{3+} detection.[16] As shown in Figure 2a, the fluorescence intensity of acetone solution of **3ka** showed 4.6 times enhancement and slightly blue shift after Fe^{3+} adding. In addition, the fluorescence change could be detected under a UV lamp by naked eye. Almost no change were observed in the fluorescence emission spectra of **3ka** solution by adding other metal ions, such as Li^+, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+}, while only Cr^{3+} gave some interference (Figure 2b).[16] In control experiments, adding Fe^{3+} into solution of **3aa** or **3ia** showed no change in the fluorescence emission spectrum, while adding Fe^{3+} into solution of 2-(2-thienyl)-PI **1k** weakened the fluorescence slightly. We surmised that N in imidazole and S in thiophene in **3ka** could serve as a bidentate ligand for Fe^{3+},[17] while the fused ring could enhance the structural rigidity and change the *π*-electron distribution.

In summary, we have developed a modular approach for rapid access ring-fused phenanthroimidazoles via Rh(III)-

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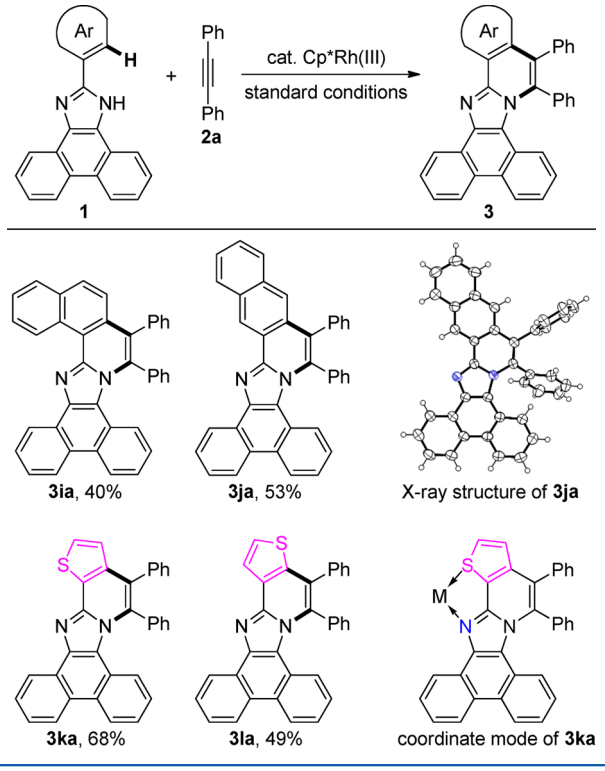
Table 3. Scope of Diverse Fused Products



catalyzed C−H activation and alkyne annulation. This method enables direct π-extension of 2-arylphenanthroimidazoles, which is a class of widely used and readily available parent molecules. One-pot synthesis and Ru(II)-catalyzed C−H activation for the reaction were also explored. One-dimensional molecular packing was observed in the crystal structures of fused product **3** and the unusual rearrangement product **4ad**. The thiophene-fused product **3ka** showed a selective fluorescent response for Fe^{3+}, which gave an illustration for materials development using molecules with novel skeletons that assembled by newly developed synthetic tools such as C−H activation.

EXPERIMENTAL SECTION

General Methods. All organic compounds and metal salts were analytically pure and used directly after purchased. All solvents were used without any particular precautions to extrude moisture. 2-Aryl-1*H*-phenanthro[9,10-*d*]imidazoles **1** were prepared following a literature procedure.[18] 1,2-Bis(4-methoxyphenyl)ethyne **2b** and 1,2-bis(4-chlorophenyl)ethyne **2c** were prepared by a reported procedure[19] with our improvement.[12a] $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3{\cdot}xH_2O$ following a literature procedure.[20] All products are new compounds, which were characterized by ^1H and ^{13}C NMR, HRMS, and melting point. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent at 298 K. ^1H NMR (300 MHz) chemical shifts (δ) were referenced to internal standard TMS (for ^1H, δ = 0.00). ^{13}C NMR (75 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (for ^{13}C, δ = 77.16). In some ^{13}C NMR spectra, the number of distinguishable peaks is less than expected due to overlap. HRMS spectra were obtained on a high-resolution magnetic sector mass spectrometer with electron spray ionization (ESI) source. The melting points were uncorrected.

X-ray Analysis. Single crystals of **3aa**, **3ja**, **3ad**, and **4ad**·MeOH were obtained by slow evaporation of their solution by using a good solvent (acetone or CH_2Cl_2) and a poor solvent (MeOH or hexane) as cosolvent systems. The single-crystal X-ray diffraction data were collected on a diffractometer equipped with graphite-monochromatized Mo Kα radiation at 294 ± 1 K. Raw intensities were corrected for Lorentz and polarization effects. The structures were refined on F^2 by full-matrix least-squares methods.

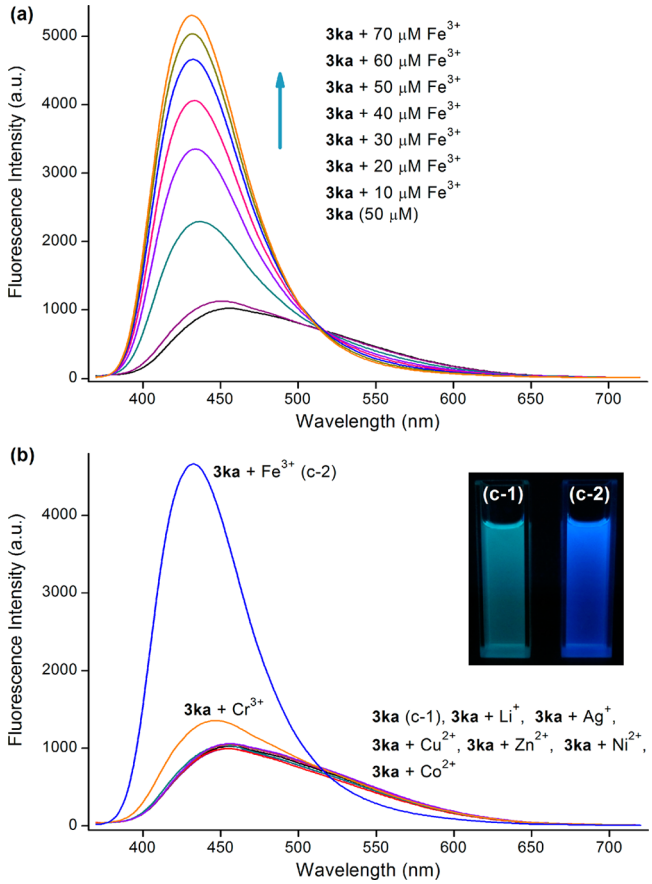


Figure 2. Selective Fe^{3+} detection using **3ka**: (a) fluorescence emission spectra (λ_{ex} = 356 nm) of **3ka** acetone solvent with different concentration of Fe^{3+} (10−70 μM). (b) Fluorescence emission spectra (λ_{ex} = 356 nm) of **3ka** acetone solvent (50 μM) with different metal ions (50 μM). Insert: photo of **3ka** acetone solvent without (c-1) or with (c-2) Fe^{3+} under a UV lamp (λ_{ex} = 365 nm).

Fluorescence Analysis. Fluorescence emission spectra were measured under excitation at 356 nm. Test solutions containing 50 μM **3ka** and 10x μM Fe^{3+} (x = 1, 2, 3, 4, 5, 6, 7) were prepared by adding 100x μL $FeCl_3{\cdot}6H_2O$ acetone solution (0.4 mM) and (2000−100x) μL acetone to 2 mL of **3ka** acetone solution (0.1 mM). Test solutions containing other metal ions (Li^+, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Cr^{3+}) were prepared by using their chlorides (for Li^+, Zn^{2+}, and Co^{2+}) or nitrates (for Ag^+, Ni^{2+}, and Cr^{3+}) instead of $FeCl_3{\cdot}6H_2O$.

General Procedure for Synthesis of 3. To a 25 mL tube equipped with a magnetic stirrer were added sequentially 2-aryl-1*H*-phenanthro[9,10-*d*]imidazole **1** (0.5 mmol), 1,2-diarylacetylene **2** (0.7 mmol), $[Cp^*RhCl_2]_2$ (7.7 mg, 0.0125 mmol, 2.5 mmol %), and $Cu(OAc)_2{\cdot}H_2O$ (220.0 mg, 1.1 mmol). The tube was evacuated and backfilled with nitrogen for three cycles. Acetone (5.0 mL) was added under nitrogen, and the tube was sealed. The tube was immersed in an oil bath (120 °C) and stirred for 12 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/acetone (typically gradient mixture ratio from 100:0 to 80:20) as eluant to afford **3**.

*5,6-Diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]isoquinoline (**3aa**):* pale yellow solid (194.5 mg, 83%); mp 264−266 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 9.11−9.04 (2H, m), 8.66−8.58 (2H, m), 7.80−7.65 (3H, m), 7.53−7.48 (1H, m), 7.38−6.94 (13H, m), 6.83−6.78 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 140.7, 137.1, 135.6, 135.0, 131.8, 130.0, 129.8, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.4, 127.3, 126.64, 126.56, 126.2, 124.7, 124.6, 124.1, 123.8, 123.7,

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123.5, 123.3, 123.0; HRMS (ESI) calcd for $C_{35}H_{23}N_2$ $[M + H]^+$ 471.1856, found 471.1854.

*3-tert-Butyl-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ba**):* off-white solid (242.7 mg, 92%); mp 260−262 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07−8.99 (2H, m), 8.61−8.54 (2H, m), 7.77−7.60 (3H, m), 7.36−7.15 (7H, m), 7.03−6.89 (6H, m), 6.79−6.74 (1H, m), 1.28 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 148.0, 140.7, 137.1, 135.7, 134.7, 131.7, 131.5, 129.9, 129.7, 128.1, 128.0, 127.9, 127.4, 127.3, 127.1, 126.44, 126.39, 126.1, 124.4, 123.9, 123.7, 123.5, 123.4, 123.2, 122.9, 122.5, 121.4, 35.2, 31.3; HRMS (ESI) calcd for $C_{39}H_{31}N_2$ $[M + H]^+$ 527.2482, found 527.2480.

*3,5,6-Triphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]isoquinoline (**3ca**):* pale yellow solid (232.8 mg, 85%); mp 277−279 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09−9.03 (2H, m), 8.60−8.54 (2H, m), 7.88−7.84 (1H, m), 7.75−7.70 (1H, m), 7.64−7.49 (4H, m), 7.40−7.10 (9H, m), 7.05−6.87 (6H, m), 6.78−6.73 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 141.6, 140.9, 140.7, 136.9, 135.5, 135.2, 132.0, 131.7, 130.0, 129.7, 129.0, 128.31, 128.26, 128.2, 127.9, 127.7, 127.42, 127.35, 127.2, 127.1, 126.6, 126.1, 125.2, 124.6, 124.5, 124.1, 123.72, 123.69, 123.4, 123.2, 122.9, 122.6; HRMS (ESI) calcd for $C_{41}H_{27}N_2$ $[M + H]^+$ 547.2169, found 547.2167.

*3-Methoxy-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3da**):* pale yellow solid (104.6 mg, 42%); mp 228−229 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05−8.99 (2H, m), 8.67−8.59 (2H, m), 7.80−7.65 (2H, m), 7.33−7.24 (5H, m), 7.18−7.15 (2H, m), 7.10−6.94 (6H, m), 6.83−6.75 (2H, m), 3.73 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 148.3, 140.7, 137.1, 135.7, 135.6, 133.5, 131.7, 130.0, 129.7, 128.4, 127.99, 127.95, 127.43, 127.38, 127.2, 126.6, 126.5, 125.8, 124.6, 123.9, 123.7, 123.54, 123.49, 123.4, 123.3, 123.0, 117.8, 117.0, 108.7, 55.4; HRMS (ESI) calcd for $C_{36}H_{25}N_2O$ $[M + H]^+$ 501.1961, found 501.1961.

*N,N-Dimethyl-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinolin-3-amine (**3ea**):* yellow solid (172.8 mg, 67%); mp 275−277 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (1H, d, J = 7.9 Hz), 8.89 (1H, d, J = 8.9 Hz), 8.63−8.55 (2H, m), 7.77−7.60 (2H, m), 7.27−6.74 (14H, m), 6.37−6.36 (1H, m), 2.83 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 149.0, 140.7, 137.6, 136.0, 135.0, 133.5, 131.7, 130.0, 129.6, 128.13, 128.08, 127.8, 127.6, 127.4, 127.1, 127.0, 126.2, 126.0, 125.9, 124.4, 123.7, 123.6, 123.2, 123.12, 123.06, 122.9, 114.5, 113.9, 106.8, 40.2; HRMS (ESI) calcd for $C_{37}H_{28}N_3$ $[M + H]^+$ 514.2278, found 514.2274.

*3-Fluoro-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3fa**):* off-white solid (125.1 mg, 51%); mp 283−285 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05−8.97 (2H, m), 8.62−8.55 (2H, m), 7.76−7.62 (2H, m), 7.39−7.22 (5H, m), 7.10−6.89 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{CF}$ = 248.5 Hz), 147.5, 140.7, 136.6, 136.1, 135.3, 133.6 (d, $^3J_{CF}$ = 9.1 Hz), 131.6, 130.7, 129.9, 129.8, 128.6, 128.5, 128.2, 128.0, 127.6, 127.34, 127.25, 126.7, 125.3 (d, $^4J_{CF}$ = 3.3 Hz), 124.6, 124.0, 123.74, 123.67, 123.5, 123.34, 123.26, 123.0, 120.2, 116.7 (d, $^2J_{CF}$ = 23.8 Hz), 111.7 (d, $^2J_{CF}$ = 23.5 Hz); HRMS (ESI) calcd for $C_{35}H_{22}FN_2$ $[M + H]^+$ 489.1762, found 489.1760.

*3-Chloro-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ga**):* pale yellow solid (228.1 mg, 90%); mp 285−287 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00−8.96 (2H, m), 8.64−8.57 (2H, m), 7.78−7.58 (3H, m), 7.34−7.24 (5H, m), 7.13−7.05 (3H, m), 7.02−6.92 (5H, m), 6.82−6.76 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3, 140.8, 136.3, 136.1, 135.2, 135.1, 132.8, 131.6, 129.9, 129.8, 128.6, 128.5, 128.3, 128.0, 127.7, 127.3, 127.2, 126.8, 126.3, 125.8, 125.0, 124.6, 124.1, 123.9, 123.7, 123.3, 123.0, 121.9; HRMS (ESI) calcd for $C_{35}H_{22}ClN_2$ $[M + H]^+$ 505.1466, found 505.1466.

*3-Bromo-5,6-diphenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ha**):* pale yellow solid (256.5 mg, 93%); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01−8.91 (2H, m), 8.66−8.57 (2H, m), 7.79−7.66 (3H, m), 7.49−7.48 (1H, m), 7.36−6.94 (12H, m), 6.83−6.78 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 140.9, 136.3, 136.2, 135.2, 133.1, 131.7, 131.2, 129.94, 129.87, 128.9, 128.7, 128.5, 128.3, 128.1, 127.7, 127.4, 127.2, 126.8, 126.4, 125.0, 124.7, 124.2, 124.0, 123.8, 123.7, 123.6, 123.3, 123.0, 122.3; HRMS (ESI) calcd for $C_{35}H_{22}BrN_2$ $[M + H]^+$ 549.0961, found 549.0958.

*5,6-Bis(4-methoxyphenyl)phenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ab**):* pale yellow solid (212.4 mg, 80%); mp 258−259 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07−9.03 (2H, m), 8.63−8.55 (2H, m), 7.77−7.61 (3H, m), 7.49−7.22 (3H, m), 7.04−6.96 (3H, m), 6.90−6.80 (5H, m), 6.48−6.45 (2H, m), 3.80 (3H, s), 3.61 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 158.7, 148.0, 140.7, 135.1, 132.7, 132.2, 131.2, 129.7, 129.2, 129.0, 128.2, 128.1, 127.7, 127.4, 127.2, 126.5, 126.4, 125.4, 124.60, 124.55, 124.5, 123.7, 123.5, 123.2, 123.0, 113.8, 113.4, 55.3; HRMS (ESI) calcd for $C_{37}H_{27}N_2O_2$ $[M + H]^+$ 531.2067, found 531.2065.

*5,6-Bis(4-chlorophenyl)phenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ac**):* pale yellow solid (173.4 mg, 64%); mp 292−293 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04−8.99 (2H, m), 8.63−8.56 (2H, m), 7.78−7.64 (3H, m), 7.47−7.44 (1H, m), 7.33−7.23 (4H, m), 7.05−6.83 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 140.8, 135.2, 134.6, 133.8, 133.7, 133.0, 131.1, 129.8, 129.2, 128.8, 128.43, 128.35, 128.3, 127.4, 127.2, 126.8, 126.2, 125.1, 124.7, 124.6 124.1, 124.0, 123.72, 123.65, 123.4, 123.3, 123.0; HRMS (ESI) calcd for $C_{35}H_{21}Cl_2N_2$ $[M + H]^+$ 539.1076, found 539.1075.

*7,8-Diphenylbenzo[h]phenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ia**):* yellow solid (104.5 mg, 40%); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.33 (1H, d, J = 8.6 Hz), 9.22 (1H, d, J = 7.6 Hz), 8.67−8.58 (2H, m), 8.03−7.68 (6H, m), 7.45−6.80 (14H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 141.2, 137.7, 135.7, 135.6, 133.0, 132.05, 131.3, 130.1, 130.0, 129.9, 129.8, 129.6, 128.4, 128.33, 128.28, 128.1, 127.9, 127.51, 127.47, 127.3, 127.0, 126.8, 126.7, 124.6, 124.2, 124.1, 123.8, 123.4, 123.3, 123.1, 122.2, 118.8; HRMS (ESI) calcd for $C_{39}H_{25}N_2$ $[M + H]^+$ 521.2012, found 521.2011.

*10,11-Diphenylbenzo[g]phenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ja**):* yellow solid (138.7 mg, 53%); mp 288−290 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.54 (1H, s), 9.07−9.04 (1H, m), 8.64−8.56 (2H, m), 8.16 (1H, d, J = 8.1 Hz), 7.78−7.63 (4H, m), 7.57−7.44 (2H, m), 7.37−7.19 (6H, m), 7.08−6.91 (6H, m), 6.84−6.79 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 140.2, 137.2, 135.5, 134.5, 133.4, 132.6, 131.8, 130.1, 129.8, 129.6, 128.6, 128.4, 128.3, 127.9, 127.5, 127.3, 126.8, 126.5, 126.2, 126.0, 124.6, 124.2, 123.94, 123.88, 123.6, 123.4, 123.3, 123.0, 122.1; HRMS (ESI) calcd for $C_{39}H_{25}N_2$ $[M + H]^+$ 521.2012, found 521.2011.

*4,5-Diphenylphenanthro[9′,10′:4,5]imidazo[1,2-a]thieno[2,3-c]-pyridine (**3ka**):* yellow solid (161.6 mg, 68%); mp 299−301 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04−9.01 (1H, m), 8.67−8.60 (2H, m), 7.79−7.67 (2H, m), 7.53 (1H, d, J = 5.2 Hz), 7.33−6.99 (13H, m), 6.83−6.78 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 141.6, 139.3, 137.7, 135.0, 134.8, 131.0, 130.0, 128.5, 128.3, 128.21, 128.15, 128.0, 127.4, 127.24, 127.21, 126.9, 125.5, 124.6, 124.1, 124.04, 123.97, 123.7, 123.3, 123.0, 122.8; HRMS (ESI) calcd for $C_{33}H_{21}N_2S$ $[M + H]^+$ 477.1420, found 477.1417.

*4,5-Diphenylphenanthro[9′,10′:4,5]imidazo[1,2-a]thieno[3,2-c]-pyridine (**3la**):* pale yellow solid (116.4 mg, 49%); mp 255−257 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02−9.00 (1H, m), 8.67−8.60 (2H, m), 8.26 (1H, d, J = 5.4 Hz), 7.79−7.66 (2H, m), 7.56 (1H, d, J = 5.4 Hz), 7.34−7.11 (7H, m), 7.05−6.98 (5H, m), 6.83−6.78 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 141.8, 141.2, 137.9, 134.8, 133.7, 130.4, 130.1, 129.9, 128.6, 128.2, 128.1, 128.0, 127.5, 127.4, 127.3, 126.8, 124.5, 124.0, 123.8, 123.7, 123.6, 123.5, 123.3, 123.2, 123.0, 122.6; HRMS (ESI) calcd for $C_{33}H_{21}N_2S$ $[M + H]^+$ 477.1420, found 477.1419.

Procedure for Synthesis of 3ad and 4ad. To a 25 mL tube equipped with a magnetic stirrer were added sequentially 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole **1a** (147.2 mg, 0.5 mmol), $[Cp^*RhCl_2]_2$ (7.7 mg, 0.0125 mmol, 2.5 mmol %), and $Cu(OAc)_2{\cdot}H_2O$ (220.0 mg, 1.1 mmol). The tube was evacuated and backfilled with nitrogen for three cycles. 1-Phenyl-1-propyne **2d** (92.9 mg, 0.8 mmol) was dissolved in acetone (5.0 mL) and added under nitrogen. The tube was sealed, immersed in an oil bath (120 °C), and stirred for 12 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/acetone (gradient mixture ratio from 100:0 to 80:20) as eluant to afford **3ad** (49.8 mg, 24%) and **4ad** (79.2 mg, 39%).

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*6-Methyl-5-phenylphenanthro[9′,10′:4,5]imidazo[2,1-a]-isoquinoline (**3ad**):* pale yellow solid (49.8 mg, 24%); mp 228−230 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99−8.95 (2H, m), 8.64−8.61 (2H, m), 7.94−7.92 (1H, m), 7.76−7.20 (12H, m), 2.51 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 141.3, 137.7, 131.84, 131.76, 131.2, 129.7, 129.0, 128.9, 128.5, 128.1, 127.4, 127.2, 126.6, 126.4, 125.6, 125.4, 124.6, 124.42, 124.35, 124.3, 124.2, 123.6, 123.2, 123.0, 22.9; HRMS (ESI) calcd for $C_{30}H_{21}N_2$ $[M + H]^+$ 409.1699, found 409.1699.

*5-Methylene-6-phenyl-5,6-dihydrophenanthro[9′,10′:4,5]-imidazo[2,1-a]isoquinoline (**4ad**):* pale yellow solid (79.2 mg, 39%); mp 209−211 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (1H, dd, J = 8.0, 1.2 Hz), 8.74−8.70 (1H, m), 8.64 (1H, d, J = 8.3 Hz), 8.51−8.49 (1H, m), 8.06−8.03 (1H, m), 7.76−7.70 (1H, m), 7.64−7.04 (11H, m), 6.93 (1H, s), 5.71 (1H, s), 5.70 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 141.9, 138.9, 138.6, 130.6, 129.8, 129.6, 129.2, 129.0, 128.3, 128.1, 127.5, 127.4, 126.8, 126.2, 125.7, 125.4, 125.12, 125.08, 124.9, 124.3, 123.2, 122.9, 122.8, 120.9, 115.6, 64.6; HRMS (ESI) calcd for $C_{30}H_{21}N_2$ $[M + H]^+$ 409.1699, found 409.1697.

One-Pot Procedure for Synthesis of 3aa. To a 25 mL tube equipped with a magnetic stirrer were added 9,10-phenanthraquinone (104.1 mg, 0.5 mmol), NH_4OAc (115.6 mg, 1.5 mmol), benzaldehyde (53.0 mg, 0.5 mmol), and TFE (5.0 mL). The tube was sealed, immersed in an oil bath (120 °C), and stirred for 2 h. After the tube was cooled, 1,2-diphenylacetylene (124.8 mg, 0.7 mmol), $[Cp^*RhCl_2]_2$ (7.7 mg, 0.0125 mmol, 2.5 mmol %), $Cu(OAc)_2{\cdot}H_2O$ (240.0 mg, 1.2 mmol), and an additional 1.0 mL of TFE were added to the reaction mixture. The tube was sealed again, immersed back to the oil bath (120 °C), and stirred for 16 h. Chromatography purification was performed to afford **3aa** (131.1 mg, 56%). Replacing $[Cp^*RhCl_2]_2$ with $[Ru(p\text{-cymene})Cl_2]_2$ (15.3 mg, 0.025 mmol, 5 mol %) also afforded **3aa** (74.8 mg, 32%).

■ ASSOCIATED CONTENT

Supporting Information

Proposed mechanism, copies of ^{1}H and ^{13}C NMR spectra of all products, and X-ray structural details (including CIF) of **3aa**, **3ja**, **3ad**, and **4ad**·MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Zhang, Y.; Lai, S.-L.; Tong, Q.-X.; Lo, M.-F.; Ng, T.-W.; Chan, M.-Y.; Wen, Z.-C.; He, J.; Jeff, K.-S.; Tang, X.-L.; Liu, W.-M.; Ko, C.-C.; Wang, P.-F.; Lee, C.-S. *Chem. Mater.* **2012**, *24*, 61. (b) Huang, H.; Wang, Y.; Zhuang, S.; Yang, X.; Wang, L.; Yang, C. *J. Phys. Chem. C* **2012**, *116*, 19458. (c) Chou, H. H.; Chen, Y. H.; Hsu, H. P.; Chang, W. H.; Cheng, C. H. *Adv. Mater.* **2012**, *24*, 5867. (d) Zhuang, S. Q.; Shangguan, R. G.; Jin, J. J.; Tu, G. L.; Wang, L.; Chen, J. S.; Ma, D. G.; Zhu, X. J. *Org. Electron.* **2012**, *13*, 3050.

(2) (a) Tsai, M.-S.; Hsu, Y.-C.; Lin, J. T.; Chen, H.-C.; Hsu, C.-P. *J. Phys. Chem. C* **2007**, *111*, 18785. (b) Chang, Y.-T.; Hsu, S.-L.; Su, M.-H.; Wei, K.-H. *Adv. Mater.* **2009**, *21*, 2093. (c) Lee, W.; Yang, Y.; Cho, N.; Ko, J.; Hong, J.-I. *Tetrahedron* **2012**, *68*, 5590.

(3) (a) Krebs, F. C.; Lindvold, L. R.; Jørgensen, M. *Tetrahedron Lett.* **2001**, *42*, 6753. (b) Lin, W.; Long, L.; Yuan, L.; Cao, Z.; Chen, B.; Tan, W. *Org. Lett.* **2008**, *10*, 5577. (c) Zhu, W.; Li, W.; Yang, H.; Jiang, Y.; Wang, C.; Chen, Y.; Li, G. *Chem.−Eur. J.* **2013**, *19*, 11603. (d) Kwon, J. E.; Park, S.; Park, S. Y. *J. Am. Chem. Soc.* **2013**, *135*, 11239.

(4) (a) Krebs, F. C.; Jørgensen, M. *J. Org. Chem.* **2001**, *66*, 6169. (b) Botana, E.; Nättinen, K.; Prados, P.; Rissanen, K.; de Mendoza, J. *Org. Lett.* **2004**, *6*, 1091.

(5) For a review, see: (a) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489. For recent examples, see: (b) Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697. (c) Yue, W.; Gao, J.; Li, Y.; Jiang, W.; Di Motta, S.; Negri, F.; Wang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 18054. (d) Fukutomi, Y.; Nakano, M.; Hu, J.-Y.; Osaka, I.; Takimiya, K. *J. Am. Chem. Soc.* **2013**, *135*, 11445. (e) Fukazawa, A.; Kishi, D.; Tanaka, Y.; Seki, S.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 12091.

(6) (a) Quante, H.; Geerts, Y.; Müllen, K. *Chem. Mater.* **1997**, *9*, 495. (b) Mamada, M.; Bolívar, C. P.; Anzenbacher, P., Jr. *Org. Lett.* **2011**, *13*, 4882 Fused PI products were obtained from phenanthrene-9,10-diamine and naphthalene dicarboxylic anhydride at 220 °C or higher temperature..

(7) For recent reviews on heterocycle syntheses via C−H activation, see: (a) Satoh, T.; Miura, M. *Chem.−Eur. J.* **2010**, *16*, 11212. (b) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (c) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31. (d) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (e) Zhu, C.; Wang, R.; Falck, J. R. *Chem.—Asian J.* **2012**, *7*, 1502. (f) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281.

(8) (a) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. For related examples on synthesis of imidazole-fused heterocycles via C−H activation, see: (b) Huang, J.-R.; Dong, L.; Han, B.; Peng, C.; Chen, Y.-C. *Chem.−Eur. J.* **2012**, *18*, 8896. (c) Reddy, V. P.; Iwasaki, T.; Kambe, N. *Org. Biomol. Chem.* **2013**, *11*, 2249. (d) Peng, J.; Shang, G.; Chen, C.; Miao, Z.; L, B. *J. Org. Chem.* **2013**, *78*, 1242.

(9) For other examples using this strategy, see: (a) Morimoto, K.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 2068. (b) Li, X.; Zhao, M. *J. Org. Chem.* **2011**, *76*, 8530. (c) Ackermann, L.; Wang, L.; Lygin, A. V. *Chem. Sci.* **2012**, *3*, 177. (d) Li, B.; Feng, H.; Wang, N.; Ma, J.; Song, H.; Xu, S.; Wang, B. *Chem.−Eur. J.* **2012**, *18*, 12873. (e) Ma, W.; Graczyk, K.; Ackermann, L. *Org. Lett.* **2012**, *14*, 6318.

(10) For another leading work on Rh(III)-catalyzed alkyne annulation via C−H/N−H bond cleavage, see: (a) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474. See also: (b) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326.

(11) For a review, see: (a) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369. For examples of syntheses of functional molecules via Rh(III)-catalyzed C−H activation, see: (b) He, T.; Too, P. C.; Chen, R.; Chiba, S.; Sun, H. *Chem.−Asian J.* **2012**, *7*, 2090. (c) Dong, J.; Long, D.; Song, F.; Wu, N.; Guo, Q.; Lan, J.; You, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 580. (d) Luo, C.-Z.; Gandeepan, P.; Jayakumar, J.; Parthasarathy, K.; Chang, Y.-W.; Cheng, C.-H. *Chem.—Eur. J.* **2013**, *19*, 14181. (e) Lian, Y.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122.

(12) (a) Zheng, L.; Ju, J.; Bin, Y.; Hua, R. *J. Org. Chem.* **2012**, *77*, 5794. (b) Zheng, L.; Hua, R. *Chem.−Eur. J.* **2014**, *20*, 2352.

(13) For examples of other groups, see: (a) Jayakumar, J.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2012**, *51*, 197. (b) Sim, Y.-K.; Lee, H.; Park, J.-W.; Kim, D.-S.; Jun, C.-H. *Chem. Commun.* **2012**, *48*, 11787. (c) Lee, H.; Sim, Y.-K.; Park, J.-W.; Jun, C.-H. *Chem.—Eur. J.* **2014**, *20*, 323.

(14) For catalyst-free synthesis of imidazoles in TFE, see: (a) Khaksar, S.; Alipour, M. *Monatsh. Chem.* **2013**, *144*, 395. For Rh(III)- or Ru(II)-catalyzed reactions in TFE, see: (b) Hyster, T. K.; Rovis, T. *Chem. Commun.* **2011**, *47*, 11846. (c) Li, B.; Ma, J.; Wang, N.; Feng, H.; Xu, S.; Wang, B. *Org. Lett.* **2012**, *14*, 736.

(15) For examples of allene insertion into the C−Rh bond, see: (a) Wang, H.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7318.

(b) Zeng, R.; Fu, C.; Ma, S. *J. Am. Chem. Soc.* **2012**, *134*, 9597. (c) Ye, B.; Cramer, N. *J. Am. Chem. Soc.* **2013**, *135*, 636.
(16) Sahoo, S. K.; Sharma, D.; Bera, R. K.; Crisponi, G.; Callan, J. F. *Chem. Soc. Rev.* **2012**, *41*, 7195. As listed in this review, Cu^{2+} and Cr^{3+} are two of the most common interferents for Fe^{3+} detection.
(17) Qu, X.; Liu, Q.; Ji, X.; Chen, H.; Zhou, Z.; Shen, Z. *Chem. Commun.* **2012**, *48*, 4600.
(18) Behmadi, H.; Roshani, M.; Saadati, S. M. *Chin. Chem. Lett.* **2009**, *20*, 5.
(19) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199.
(20) Fujita, K.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 2785.

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