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Direct catalytic C–H arylation of imidazo[1,2-*a*]pyridine with aryl bromides using magnetically recyclable Pd–Fe₃O₄ nanoparticles

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ABSTRACT

The direct C–H arylation of a heteroarene with aryl bromides has been achieved under the catalysis of magnetic nanoparticles. In the presence of bimetallic Pd–Fe₃O₄ heterodimer nanocrystals (1 mol % in palladium), the reaction of imidazo[1,2-*a*]pyridine with various aryl bromides gives the corresponding arylated products with exclusive C3-selectivity. The highly regioselective method is applicable to a wide range of aryl bromides with varying electronic and steric properties. The Pd–Fe₃O₄ nanocrystals can be recoverable by simple magnetic separation and have been recycled ten times without loss of catalytic activity.

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1. Introduction

The aryl-heteroaryl linkage is an important structural motif in a wide array of pharmaceuticals, natural products, and functional materials.¹ Among the methods for the formation of heterobiaryl C-C bonds, transition metal-catalyzed cross-coupling reactions have been most popular, providing numerous applications.² However, traditional cross-couplings, despite their widespread utility, are unfavorable from the vantage point of atom-economy since they require preformation of organometallic reagents and inevitably produce metallic waste of a stoichiometric amount. In this regard, recent approaches based on transition metal-catalyzed C-H functionalization are attractive, as a specific C-H bond of heteroarenes may be directly activated to undergo regioselective arylation.³ Great advances have indeed been made in the last decade for the direct C-H arylation of heteroarenes using various transition metal catalysts, such as Pd, Rh, Cu, Ni, Ir, Ru, and Fe.⁴ Notably, phosphine-free conditions, which presumably involve nanoparticle formations have also made their way to heterobiaryl synthesis with potential advantages from both homogeneous and heterogeneous catalysis.⁵

In conjunction with our studies on the utility of magnetically separable Fe_3O_4 nanoparticles,⁶ we questioned about the ability of the bimetallic Pd—Fe₃O₄ nanocrystals with a unique hetero-dimeric morphology to mediate catalytic reactions.⁷ It was of particular

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interest to examine whether the good catalytic activity displayed by these nanocrystals in Suzuki coupling reactions could be translated into other types of transformations. Recently, a variety of magnetic nanoparticles amenable for easy separation and recovery have been synthesized and applied as catalysts to a range of chemical reactions.⁸ However, their utility in direct C–H functionalization processes remains largely to be established.⁹ Given the importance of heterobiaryl synthesis and the practical benefits associated with using magnetic nanoparticles, it would be of great significance to develop a protocol for the direct C–H arylation of heteroarenes that takes advantage of magnetically recoverable nanocatalysts. Described here are the results of our studies on the C–H arylation of imidazo[1,2-*a*] pyridine with aryl bromides through a catalysis mediated by magnetically separable and hence reusable Pd–Fe₃O₄ nanocrystals.

2. Results and discussion

The Pd–Fe₃O₄ heterodimer nanocrystals were prepared from a solution of Pd(acac)₂, Fe(acac)₂, oleylamine, and oleic acid using a two-step thermal decomposition procedure according to the previous report.⁷ The synthesis could be easily practiced up to a 2 g scale (2.45 wt % Pd), and the obtained nanocrystals were bench stable and could be stored at ambient temperature for several weeks without alteration in shape or reactivity. As shown in the transmission electron microscopy (TEM) images (Fig. 1a and b), nearly all of the nanoparticles were a 1:1 hybrid bimetallic system composed of a single Pd nanosphere (~6 nm in diameter) and a faceted Fe₃O₄ nanocrystal (~30 nm in dimension). All of the peaks in the X-ray





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Fig. 1. (a) TEM image, (b) HRTEM image, (c) XRD pattern, and (d) VSM M-H curve of Pd–Fe₃O₄ measured at 300 K.

diffraction (XRD) pattern could also be assigned to the corresponding lattice planes of face-centered-cubic (fcc) Pd and Fe₃O₄ crystals in accordance with the bimetallic heterodimer structure (Fig. 1c). The M-H curve analysis using a vibrating sample magnetometer (VSM) showed the hybrid nanocrystals to be soft ferrimagnetic with a low coercivity, indicating the suitability for their use in magnetic separation and recovery applications (Fig. 1d).¹⁰

The probe of Pd—Fe₃O₄ nanocrystals for their catalytic activity to mediate a direct C—H arylation was conducted using imidazo[1,2-*a*] pyridine (**1**),¹¹ a key structural component of important pharmaceuticals as exemplified by Zolpidem and Miroprofen. Our exploration began with screening various parameters of the cross-coupling reaction between **1** and 4-bromonitrobenzene (**2a**) employing phosphine-free conditions (Table 1).¹² When a 1.5:1 mixture of **1** and **2a** in *N*,*N*-dimethylacetamide (DMA) was heated

Table 1

8

9

10

DMF

NMP

NMP

Direct arylation of imidazo[1,2-a]pyridine with 4-bromonitrobenzene^a



^a All reactions were carried out with 4-bromonitrobenzene (0.50 mmol), imidazo [1,2-a]pyridine (0.75 mmol), base (1.0 mmol), and Pd-Fe₃O₄ (0.005 mmol, 1 mol % in Pd) at 0.25 M concentrations.
 ^b Isolated yields based on **2a**.

120

166

180

NaOAc

NaOAc

NaOAc

under reflux (166 °C) in the presence of Pd-Fe₃O₄ nanocrystals (1 mol % in Pd) and NaOAc (2 equiv), the reaction was completed in 12 h to give rise to the C3-arylated product **3a** exclusively in 88% yield (Table 1, entry 1). Similarly, the reactions employing KOAc or CsOAc as a base also gave **3a**, but in lower yields (Table 1, entries 2 and 3). In contrast, the use of AgOAc resulted in a low conversion, and **3a** was obtained only in a yield of 5% from a sluggish reaction (Table 1, entry 4). Various carbonate bases were also examined. among, which K₂CO₃ proved to be most effective (Table 1, entries 5-7). It was notable that Na₂CO₃ performed poorly vis-à-vis NaOAc, whereas K₂CO₃ and KOAc gave comparable results (Table 1, entries 1 and 2 vs 5 and 6). In a brief survey of solvents, N-methyl-2pyrrolidone (NMP) was found to be equally effective as DMA while the reaction in N,N-dimethylformamide (DMF) led to a significant decrease in both the reaction rate and yield. It should be noted that in contrast to the report on arene C–H arylation,⁹ the Pd-Fe₃O₄ nanocrystals were absolutely necessary for this heteroarene C-H arylation reaction as verified by a control experiments where no reaction occurred in the absence of Pd-Fe₃O₄ or in the presence of only Fe₃O₄ even at a higher reaction temperature for a prolonged reaction time. The arylation was also performed with chloro and iodo substrates for comparison with 2a. Whereas 4chloronitrobenzene did not undergo the arylation but instead decomposed slowly under the conditions of entry 1, the reaction of 4-iodonitrobenzene was completed in 9 h to produce 3a in 87% yield, indicating the differential reactivity of aryl halides in this process.

Having established the viability of Pd–Fe₃O₄ nanocrystals as the catalyst to effect the direct C–H arylation of imidazol 1.2-alpyridine. we set out to examine the scope of the reaction. It was found that the conditions were general and efficient with a wide range of aryl bromides (Table 2). Under the optimal conditions derived from screening experiments (1.0 mol % Pd catalyst, NaOAc, DMA, 166 °C, 12 h), aryl bromides having differential electronic and steric properties participated well in the cross-coupling reaction with imidazo[1,2-a]pyridine (1) to afford the corresponding C3-arylated products 3. In no case, was detected the formation of other regioisomers including the C2-arylated product. While electronpoor (Table 2, entries 1–4) as well as electron-rich (Table 2, entry 6) aryl bromides underwent the direct C–H arylation, the reaction of the latter was less efficient to give a low yield.¹³ A variety of functional groups, such as nitrile (**3b** and **3h**), aldehyde (**3c** and **3i**), ketone (3d), chloride (3e), and ether (3g), were tolerated. When the reaction was performed with 4-bromochlorobenzene (2e), the desired arylated product 3e was produced in 67% yield with the chloride group unaffected, suggesting the possibility of carrying out an additional cross-coupling process. The C-H arylation reaction was insensitive to the substituent present in aryl bromides as shown by the comparable outcomes from the reactions of para- and meta-substituted aryl bromides (Table 2, entries 1 and 2 vs 7 and 8). Furthermore, polycyclic aryl bromides including ortho-fused substrates 2k and 2l could also be successfully employed for the reaction (Table 2, entries 9-11). In these reactions, both 1- and 2bromonaphthalenes 2j and 2k proved to be equally competent participants of the cross-coupling reaction with 1 to furnish 3j and **3k**, respectively. It was worthy of note that 9-bromoanthracene (**2l**), a substrate with high steric congestion, was also found to be suitable for the reaction, furnishing the anthracenylated product 31 in 58% yield (Table 2, entry 11).

In order to investigate the recoverability and reusability of the $Pd-Fe_3O_4$ nanocrystals, we carried out a set of catalyst recycling experiments (Table 3). Under the standard conditions, the cross-coupling reaction of **1** with 4-bromonitrobenzene (**2a**) was repeated using the nanocrystals that were recovered each time from the previous run. Remarkably, the catalytic activity was found to remain unaltered throughout 10 runs to produce **3a** at the same

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Table 2

Scope of the	direct a	rylation of imic	lazo[1,2-a]pyridine w	ith aryl bromides ^a
N-		+ A * D*	cat. Pd-Fe ₃ O ₄	N—I Ar
	N	+ Ar-Br	NaOAc, DMA	K N − 1
1		2	100 °C, 12 fi	3
Entry		Aryl bromic	le Pro	oduct Yield (%) ^b
1	2b	Br	≻−CN 3b	95
2	2c	Br	⊖ 3 с	82
3	2d	Br	→ Me 3d	94
4	2e	Br	≻−Cl 3e	67
5	2f	Br	-Me 3f	81
6	2g	Br	OMe 3g	42
7	2h	Br	3h CN	94
8	2i	Br	∮ 0 3i H	74
9	2j	Br	3 j	75
10	2k	Br	3k	70
11	21		31	58

^a All reactions were carried out with imidazo[1,2-*a*]pyridine (0.75 mmol), aryl bromide (0.50 mmol), NaOAc (1.0 mmol), and Pd $-Fe_3O_4$ (0.005 mmol, 1 mol % in Pd) in DMA (0.25 M) at 166 °C for 12 h.

Β̈́r

^b Isolated yields based on aryl bromide **2**.

Table 3													
Recycling of the Pd—Fe ₃ O ₄ nanocrystals for the reaction of 1 with 2a													
Run	1	2	3	4	5	6	7	8	9	10			
Yield	88	87	83	85	85	84	85	84	87	86			

level of high efficiency (average yield 85%). In these recycling experiments, more than 98% of the nanocrystals could be recovered through a simple procedure involving separation by an outer magnet and catalyst purification by dispersion–collection cycles.

3. Conclusion

In summary, we have described the direct C–H arylation of a heteroarene via magnetically recoverable palladium nanoparticlemediated catalysis. The Pd nanosphere immobilized on faceted Fe_3O_4 nanocrystals efficiently catalyzes the arylation of imidazo [1,2-*a*]pyridine with a wide variety of aryl bromides to give rise to mono-arylated products in high yield. The reaction is highly regioselective to form only 3-arylated products exclusively. Also noteworthy is that the reaction is carried out under phosphine-free conditions. The Pd—Fe₃O₄ heterodimeric nanocrystals can be easily recovered by using an external permanent magnet, and the catalytic activity remains unaltered even after recycling 10 times. The efficiency, operational simplicity, cost effectiveness, and environmentally benign features of the present Pd—Fe₃O₄ catalyst system lends itself to large-scale applications including industrial processes. Current efforts are aimed at exploring the full potential of the nanoparticle catalyst.

4. Experimental

4.1. General remarks

All the reactions were performed using oven-dried glassware and commercial reagents were used without further purification unless otherwise noted. Solvents were used by passing through activated alumina columns of a solvent purification systems from Glass Contour. Sonication was carried out in a 120 W ultrasonic bath (Branson, B-3210). The progress of reactions was checked on thin layer chromatography (TLC) plates and the spots were visualized under UV light and/or by charring the TLC plate after dipping it into a KMnO₄ solution. Flash column chromatography was performed on silica gel eluting with a mixture of hexanes—ethyl acetate. ¹H and ¹³C NMR spectra were obtained on Agilent MR DD2 (400 MHz) spectrophotometer.

4.2. Preparation of the catalyst

The synthesis of Pd-Fe₃O₄ was performed by two-step thermal decomposition of a mixture composed of iron acetate, palladium acetate, oleylamine, and oleic acid. In a typical experiment, 200 mg of Pd(acac)₂ (0.66 mmol) and 14 g of Fe(acac)₃ (40 mmol) were added into a solution containing 120 mL of oleylamine (350 mmol) and 80 mL of oleic acid (250 mmol), and the mixture was heated to 120 °C in reduced pressure with vigorous stirring for 2 h. The resulting dark brown solution was heated to 220 °C under Ar atmosphere at a heating rate of 2 °C/min and kept at this temperature for 30 min, and then it was further heated to 300 °C at the same heating rate and aged for 30 min. After cooled to ambient temperature, the reaction mixture was treated with 250 mL of ethanol to induce precipitation, and the resultant powdery nanocrystals were retrieved by centrifugation (1700 rpm, 15 min). The nanocrystals were purified by dispersing in 150 mL of hexanes and collecting with a neodymium magnet (3880 G, 50 mm diameter × 10 mm thick). These washing cycles were repeated until the hexane layer showed no color, at which point the Pd-Fe₃O₄ nanocrystals were dried under vacuum (2.8 g).

4.3. Characterization of the catalyst

All transmission electron microscopy (TEM) and high resolution (HRTEM) images were obtained on a JEOL EM-2010 microscope at an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) was performed using a Rigaku D/Max-3C diffractometer (Cu K α radiation, λ =0.15418 nm). The magnetic properties (*M*-*H* curve) were characterized using a vibrating sample magnetometer (Quantum Design PPMS VSM) at 300 K.

4.4. Recycle of the catalyst

After completion of the reaction, $Pd-Fe_3O_4$ nanocrystals were placed on the bottom of the flask by a neodymium magnet, and the supernatant solution was removed. The separated nanocrystal

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catalyst was washed successively with 10 mL of water, ethanol, ethyl acetate, dichloromethane, and hexanes, and then dried. In a typical recycling experiment, more than 98% of $Pd-Fe_3O_4$ could be recovered.

4.5. General procedure for the Pd-catalyzed C-H arylation

In DMA (2 mL) degassed by a stream of argon gas for 10 min were dissolved aryl bromide **2** (0.5 mmol), imidazo[1,2-*a*]pyridine (**1**, 0.0886 g, 0.75 mmol), NaOAc (0.0821 g, 1 mmol), and Pd–Fe₃O₄ (0.0217 g, 0.005 mmol). The resulting suspension was degassed by argon for 10 min, sonicated for 3 min, and stirred at 166 °C for 12 h. After cooled to room temperature, the reaction mixture was filtered with a short silica gel pad and concentrated under reduced pressure. Alternatively, the reaction mixture was concentrated after magnetic separation of Pd–Fe₃O₄. The crude product was purified by flash column chromatography on a silica gel column.

4.6. Characterization of the arylation products

4.6.1. 3-(4-Nitrophenyl)-imidazo[1,2-a]pyridine (**3a**).¹⁴ Yield (88%) from **1** and 4-bromonitrobenzene (**2a**). ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J*=7.0 Hz, 1H), 8.38 (d, *J*=8.7 Hz, 2H), 7.86 (s, 1H), 7.81–7.69 (m, 3H), 7.30 (ddd, *J*=8.6, 6.8, 0.7 Hz, 1H), 6.94 (t, *J*=6.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 147.0, 136.1, 134.9, 127.7, 125.6, 125.0, 123.9, 123.4, 119.0, 113.8.

4.6.2. 4-Imidazo[1,2-a]pyridine-3-ylbenzonitrile (**3b**).¹¹ Yield (95%) from **1** and 4-bromobenzonitrile (**2b**). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (dt, *J*=7.0, 1.1 Hz, 1H), 7.86–7.76 (m, 3H), 7.71 (qt, *J*=2.1, 1.4 Hz, 3H), 7.32–7.23 (m, 1H), 6.90 (td, *J*=6.9, 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 134.4, 134.2, 133.3, 127.9, 125.4, 124.2, 123.3, 118.9, 118.8, 113.6, 111.4.

4.6.3. 4-Imidazo[1,2-a]pyridin-3-ylbenzaldehyde (**3c**).¹¹ Yield (82%) from **1** and 4-bromobenzaldehyde (**2c**). ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H), 8.44 (d, *J*=6.9 Hz, 1H), 8.04 (t, *J*=9.9 Hz, 2H), 7.84 (s, 1H), 7.77 (d, *J*=8.1 Hz, 2H), 7.72 (d, *J*=9.1 Hz, 1H), 7.34–7.21 (m, 1H), 6.91 (t, *J*=6.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 147.2, 135.5, 134.4, 130.8, 127.7, 125.2, 124.7, 123.5, 118.8, 113.4.

4.6.4. 4-Imidazo[1,2-a]pyridin-3-ylacetophenone (**3d**).^{11f} Yield (94%) from **1** and 4-bromoacetophenone (**2d**). ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J*=7.0 Hz, 1H), 8.11 (d, *J*=8.3 Hz, 2H), 7.81 (s, 1H), 7.74–7.65 (m, 3H), 7.29–7.22 (m, 1H), 6.89 (t, *J*=6.8 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 147.0, 136.3, 134.2, 134.0, 129.5, 127.5, 125.0, 124.9, 123.5, 118.7, 113.3, 26.8.

4.6.5. 3-(4-Chlorophenyl)-imidazo[1,2-a]pyridine (**3e**).^{11e} Yield (67%) from **1** and 1-bromo-4-chlorobenzene (**2e**). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J=7.0 Hz, 1H), 7.67 (d, J=10.6 Hz, 2H), 7.49 (s, 4H), 7.21 (ddd, J=9.0, 6.7, 1.1 Hz, 1H), 6.82 (td, J=6.9, 0.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 134.2, 134.2, 133.0, 129.7, 129.4, 128.0, 124.6, 123.3, 118.6, 113.0.

4.6.6. 3-(4-*Methylphenyl*)-*imidazo*[1,2-*a*]*pyridine* (**3***f*).¹⁵ Yield (81%) from **1** and 4-bromotoluene (**2***f*). ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, J=7.0 Hz, 1H), 7.66 (d, J=8.2 Hz, 2H), 7.45 (d, J=7.1 Hz, 2H), 7.32 (d, J=7.7 Hz, 2H), 7.18 (dd, J=8.4, 7.3 Hz, 1H), 6.79 (t, J=6.8 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 138.3, 132.5, 130.1, 128.2, 126.5, 125.9, 124.2, 123.5, 118.4, 112.6, 21.5.

4.6.7. 3-(4-Methoxylphenyl)-imidazo[1,2-a]pyridine (**3g**).¹⁵ Yield (42%) from **1** and 4-bromoanisole (**2g**). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J*=6.9 Hz, 1H), 7.68–7.61 (m, 2H), 7.50–7.44 (m, 2H), 7.17 (ddd, *J*=9.0, 6.7, 1.1 Hz, 1H), 7.09–7.02 (m, 2H), 6.79 (td, *J*=6.8, 0.9 Hz, 1H), 3.88 (s,

3H); ¹³C NMR (100 MHz, CDCl₃) *δ* 159.8, 146.0, 132.2, 129.8, 125.7, 124.1, 123.5, 121.8, 118.4, 114.9, 112.5, 55.6.

4.6.8. 3-Imidazo[1,2-a]pyridine-3-ylbenzonitrile (**3h**).^{11f} Yield (94%) from **1** and 3-bromobenzonitrile (**2h**). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (dd, *J*=6.9, 1.1 Hz, 1H), 7.83 (s, 1H), 7.80–7.75 (m, 1H), 7.72 (s, 1H), 7.70–7.57 (m, 3H), 7.25–7.18 (m, 1H), 6.90–6.83 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 133.7, 132.0, 131.5, 131.0, 130.9, 130.4, 125.1, 123.5, 123.0, 118.7, 118.4, 113.7, 113.4.

4.6.9. 3-*Imidazo*[1,2-*a*]*pyridin*-3-*ylbenzaldehyde* (**3i**).^{11*f*} Yield (74%) from **1** and 3-bromobenzaldehyde (**2i**). ¹H NMR (400 MHz, CDCl₃) δ 10.05 (s, 1H), 8.30 (dd, *J*=6.9, 1.0 Hz, 1H), 8.04 (t, *J*=1.4 Hz, 1H), 7.87 (dt, *J*=7.6, 1.3 Hz, 1H), 7.82–7.75 (m, 1H), 7.72 (s, 1H), 7.68–7.60 (m, 2H), 7.24–7.14 (m, 1H), 6.82 (td, *J*=6.9, 1.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 146.6, 137.3, 133.7, 133.3, 130.5, 130.2, 129.6, 128.3, 124.9, 124.4, 123.2, 118.5, 113.2.

4.6.10. 3-Naphthalene-2-yl-imidazo[1,2-a]pyridine (**3***j*).^{11f} Yield (75%) from **1** and 2-bromonaphthalene (**2***j*). ¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, *J*=7.0 Hz, 1H), 8.03 (s, 1H), 7.98 (d, *J*=8.5 Hz, 1H), 7.93–7.87 (m, 2H), 7.81 (s, 1H), 7.71 (d, *J*=9.1 Hz, 1H), 7.67 (dd, *J*=8.5, 1.7 Hz, 1H), 7.59–7.51 (m, 2H), 7.23 (ddd, *J*=9.1, 6.7, 1.2 Hz, 1H), 6.84 (td, *J*=6.8, 1.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.5, 133.8, 133.2, 133.0, 129.2, 128.2, 128.1, 127.0, 126.89, 126.87, 126.7, 126.0, 124.5, 123.6, 118.6, 112.9.

4.6.11. 3-Naphthalene-1-yl-imidazo[1,2-a]pyridine (**3k**).¹⁵ Yield (70%) from **1** and 1-bromonaphthalene (**2k**). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dt, *J*=16.0, 6.3 Hz, 2H), 7.80 (s, 1H), 7.74 (d, *J*=9.1 Hz, 1H), 7.71 (d, *J*=6.9 Hz, 1H), 7.62–7.56 (m, 2H), 7.55–7.47 (m, 2H), 7.46–7.38 (m, 1H), 7.21 (tt, *J*=17.6, 6.1 Hz, 1H), 6.69 (t, *J*=6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.0, 134.1, 134.0, 132.2, 129.8, 129.3, 128.9, 127.1, 126.6, 126.4, 125.8, 125.4, 124.5, 124.3, 118.2, 112.5.

4.6.12. 3-Anthracen-9-ylimidazo[1,2-a]pyridine (**31**).^{11f} Yield (58%) from **1** and 9-bromoanthracene (**21**). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 1H), 7.96 (d, *J*=8.4 Hz, 2H), 7.80 (s, 1H), 7.71 (d, *J*=9.1 Hz, 1H), 7.42 (d, *J*=8.7 Hz, 2H), 7.39–7.32 (m, 2H), 7.27–7.20 (m, 2H), 7.17 (t, *J*=6.9 Hz, 1H), 7.14–7.06 (m, 1H), 6.47 (t, *J*=6.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 135.6, 133.6, 131.9, 131.6, 129.3, 128.9, 126.9, 125.7, 124.5, 124.2, 122.1, 120.8, 118.1, 112.4.

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Supplementary data

¹H and ¹³C NMR spectra for all compounds. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/ j.tet.2013.04.031.

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