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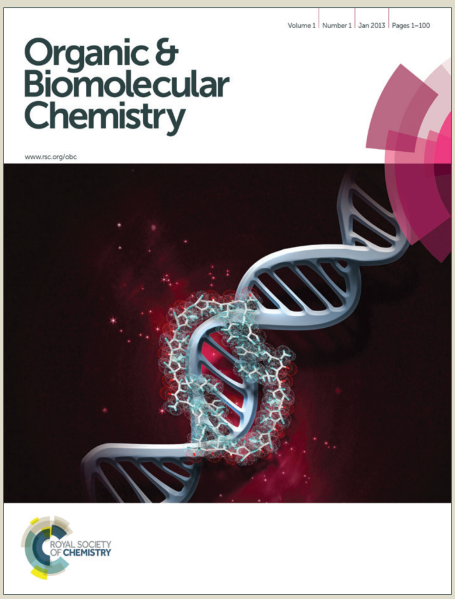

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ARTICLE

Vertically-expanded imidazo[1,2-*a*]pyridines and imidazo[1,5-*a*]pyridine *via* dehydrogenative coupling

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Anion-radical coupling of structurally diverse series of aromatic compounds possessing biaryl linkages led to seven fused, polycyclic heterocycles in reasonable yields. The yield of the key step (K, toluene, O_2) depends on both electronic and steric factors. The whole strategy consists of just two steps starting from unsubstituted imidazo[1,2-*a*]pyridine, giving target compounds in overall yield 4-34%. The same strategy also works for derivative of imidazo[1,5-*a*]pyridine. New process has been discovered for such vertically-expanded imidazo[1,2-*a*]pyridines, consisting of sequential Diels-Alder reaction followed by retro-Diels-Alder reaction. The optical properties of the library of π-expanded imidazo[1,2-*a*]pyridines were for the first time fully characterized, showing that fluorescence quantum yields of are significantly lower that for the singly-linked compounds.

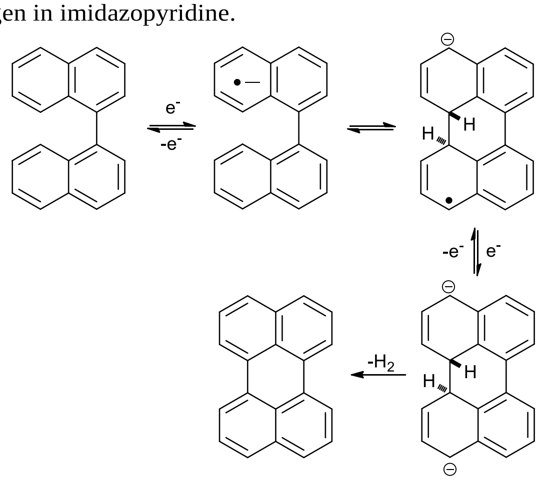
Introduction

The recent renaissance in the chemistry of polycyclic aromatic hydrocarbons is overwhelmingly visible in the literature.[1] New, previously unthinkable architectures were brought to light such as corranulene,[2] sumanene,[3] inherently chiral polycyclic imides,[4] dicyclopenta[*de*,*mn*]tetracenes[5] and cycloparaphenylenes.[6] Synthetic methodology leading to these new carbon-rich compounds is also constantly evolving.[7] On the contrary the chemistry of their heterocyclic counterparts is far less developed. While heterocyclic analogs acenes are known,[8] aza-rylenes are far less ubiquitous.[9]

Recently we revealed that 3-(naphthalen-1-yl)-imidazo[1,2-*a*]pyridine can be synthesized from singly-linked precursor by anion-radical coupling[10] in 63% yield.[11] Since anion-radical coupling is relatively weakly studied reaction (Scheme 1), we wondered if this methodology can be expanded to its analogs possessing other aromatic units instead of naphthalene. This would allow us to study relationship between structure of substrates and efficiency of this reaction. The second aim of this study was to gain further insight into trends in optical properties of such previously unknown fused heterocyclic compounds.

Results and discussion

Given the multiple aims of this investigation, we designed small but diverse library of substrates bearing imidazo[1,2-*a*]pyridine as ‘Northern Half’ of the molecule and analogs of naphthalene at ‘Southern Half’. Electronically similar (phenanthrene and anthracene) as well as structurally similar but electronically different units (naphthalene-imide and benzo[*h*]quinoline) have been chosen as ‘Southern Half’. We also modified the linkage place, shifting it from C3 to C5, as well as the position of nitrogen in imidazopyridine.



Scheme 1 The mechanism of anionic cyclodehydrogenation of 1,1'-binaphthyl as proposed by Scott and co-workers.[10d]

For the construction of necessary substrates we decided to follow the same pathway as before i.e. direct arylation of imidazo[1,2-*a*]pyridine with bromoarenes. Although many conditions were recently published, which allow to carry out this transformation in good yields,[12] the best protocol was revealed by Doucet and co-workers with low loading of simple palladium salts and without any ligand.[13] Direct arylation of unsubstituted imidazo[1,2-*a*]pyridine (**1**)[14] with bromoarenes **2a-d** led to products **3a-3d** in 50-83% (Scheme 2).

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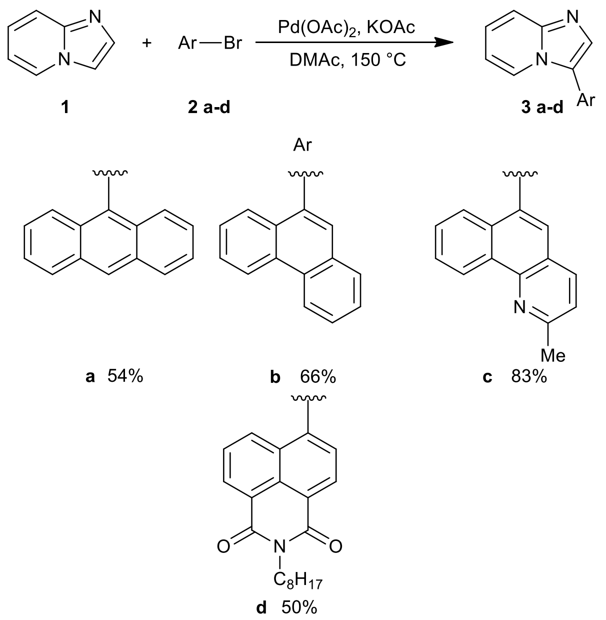
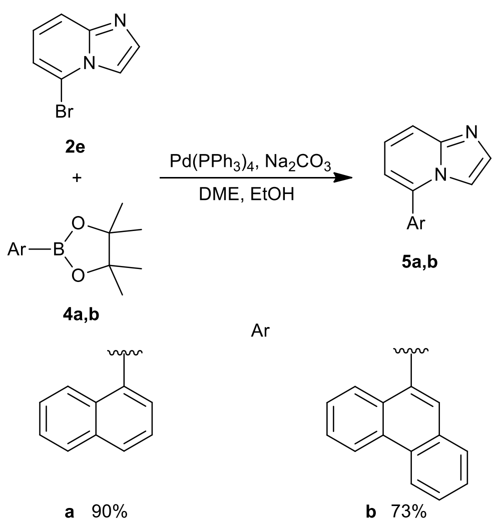


Scheme 2 The synthesis of 3-substituted imidazo[1,2-*a*]pyridines.

Required substrate **2c** was prepared by modified Skraup reaction,[15] while compound **2d** was obtained *via* imidation of anhydride of 4-bromonaphthalene-1,4-dicarboxylic acid with 1-octylamine.[16]

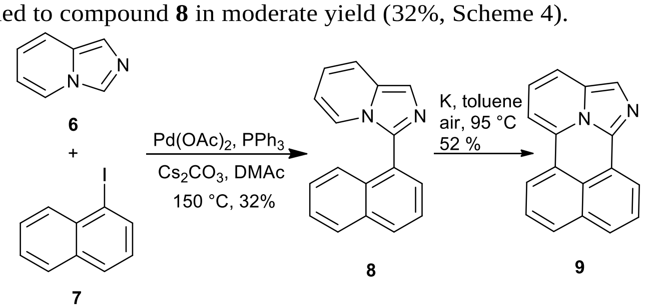


Scheme 3 Suzuki reaction leading to 5-aryl-imidazo[1,2-*a*]pyridines **5a,b**.

Intriguing question was if anion-radical coupling would work if position C-3 of the heterocyclic core (the most electron-rich one) is unsubstituted. Consequently, 5-substituted two imidazo[1,2-*a*]pyridines were prepared *via* Suzuki-Miyaura coupling from boronic acid pinacol esters **4a,b**, derived from naphthalene and phenathrene (Scheme 3).[17] The key substrate i.e. compound **2e**, was obtained *via* condensation of 2-amino-6-bromopyridine and 2-chloroacetaldehyde.[18] Suzuki coupling was conducted following known procedure utilizing palladium catalyst.[19]

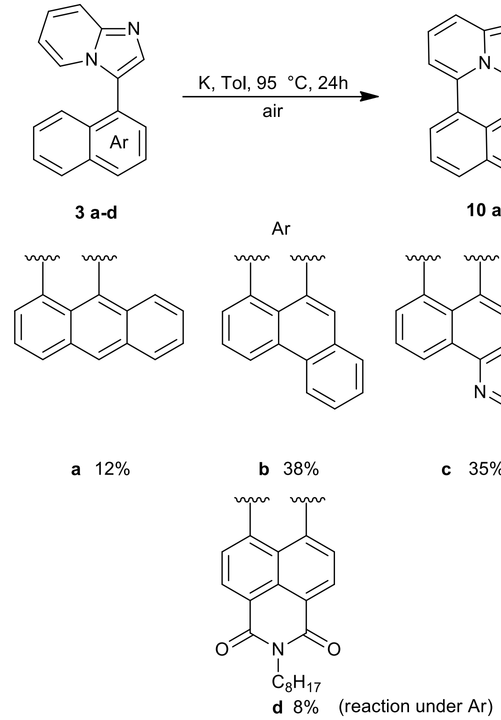
In analogy to imidazo[1,2-*a*]pyridine, C3 at imidazo[1,5-*a*]pyridine (**6**) also possesses the highest reactivity in direct arylation.[20] Murai and co-workers have shown that double direct arylation can take place in case of this heterocyclic compound.[21]

Our attempt to perform direct arylation with 1-iodonaphthalene led to compound **8** in moderate yield (32%, Scheme 4).



Scheme 4 The synthesis of compounds **8** and **9**.

The key difference between 3-(naphthalen-1-yl)-imidazo[1,2-*a*]pyridine and the corresponding anthracenyl compound **3a** is an additional steric hindrance, which has to be overcome during fusion. Consequently, it came with no surprise that anion-radical coupling, performed under previously optimized conditions,[11] led to compound **10a** in 12% yield only (Scheme 5).



Scheme 5 Anion-radical coupling leading to compounds **10a-d**.

Stability of intermediate radical-anions increases when reacting unit is more electron-deficient.[10] As a result, we expected higher yield of coupling in case of compound **3c** vs. substrate **3b**. Yet, structurally analogous derivatives of phenanthrene and benzo[*h*]quinoline (**3b** and **3c**) afforded corresponding products **10b** and **10c** in similar yield (~30%). Yields of fused heterocycles **10b** and **10c** were the same regardless if reactions were performed under air or under oxygen. Unfortunately, despite thorough optimization, the anion-radical coupling of derivative **3d** led to the formation of compound **10d** in a low yield (Scheme 5). Intriguingly, in this particular case, the yield of compound **10d** was higher if the first step of reaction was

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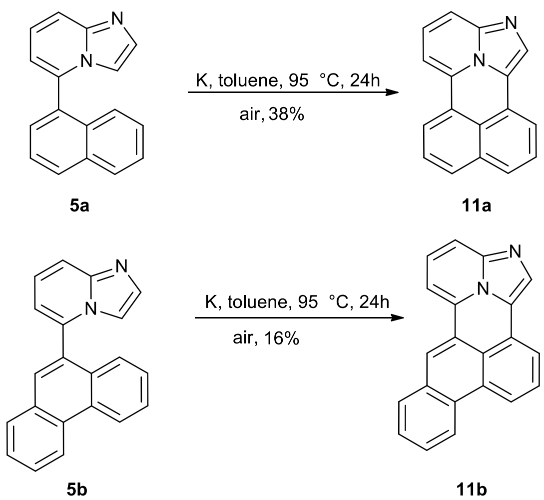
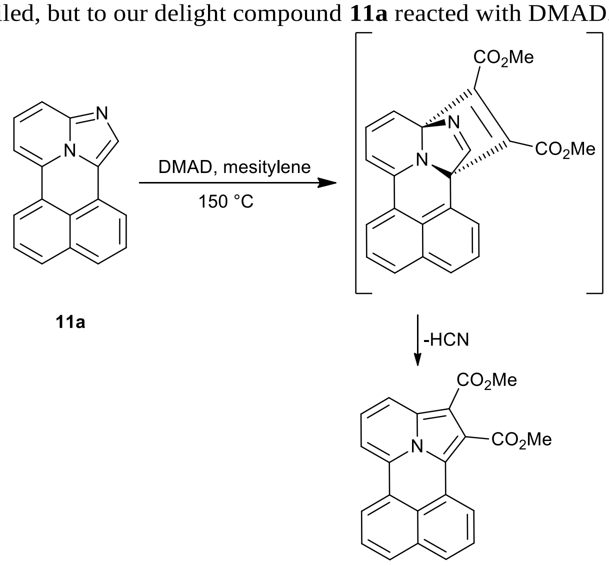
performed under argon. Groups of Müllen and Swager have shown that if naphthalene-1,8-carboxyimide is present in the molecule as one of reacting sites, conditions for dehydrogenative coupling do not have to be so strong and they can include weaker bases such as *i.e.* K_2CO_3 and DBN/*t*-BuONa, still leading to corresponding fused products in good yields.[23,24] Attempts to perform transformation of imide **3d** into **10d** following these alternative procedures,[23,24] failed.

According to our predictions based on relative stability of various anion-radicals, coupling of 5-substituted imidazo[1,2-*a*]pyridines led to expected products **11a** and **11b** in lower yields than in the case of cyclization of their 3-substituted analogs (Scheme 6). Regioisomeric imidazo[1,5-*a*]pyridine **8** has been coupled in the same manner as 3-(naphthalen-1-yl)imidazo[1,2-*a*]pyridine under air to give heterocycle **9** in 52% yield (Scheme 4).



Scheme 6 Anion-radical coupling leading to compounds **11a,b**.

An important phenomenon to be investigated was reactivity of synthesized compounds. It is well-known that perylene undergoes Diels Alder reaction with maleic anhydride or dimethyl acetylenedicarboxylate (DMAD) at its bay region.[25] The initially attempted reaction of **11a** with maleic anhydride failed, but to our delight compound **11a** reacted with DMAD.

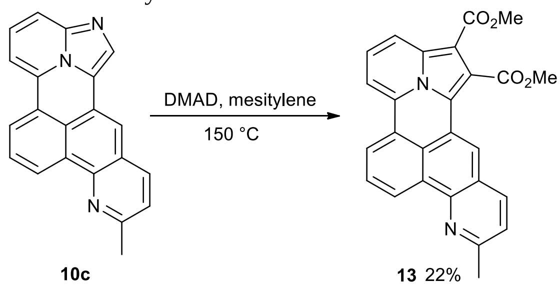


11a

12 47%

Scheme 7 The synthesis of diester **12** *via* Diels-Alder reaction.

Careful analysis of the product revealed that instead of expected Diels-Alder reaction at bay position, process led to π-expanded indolizine **12** (Scheme 7). The only imaginable rationale behind this reaction is Diels-Alder reaction at imidazole moiety followed by retro-Diels-Alder reaction with elimination of HCN. The overall pathway is quite effective leading to ester **12** in 47% yield. It is worth to note that vertically-expanded indolizines are unknown in the literature. Analogous process, albeit in lower yield, was observed in case of compound **10c** (Scheme 8). Diester **13** was obtained in 22% yield. This reaction resembles transformation of *N*-benzoylpyrrole into dimethyl *N*-benzoyl-pyrrole-3,4-dicarboxylate upon reaction with DMAD and elimination of acetylene.[26]



10c

13 22%

Scheme 8 The synthesis of ester **13**.

The successful synthesis of small library of novel aza-heterocycles and their π-expanded analogs gave us an excellent opportunity for measuring their photophysical properties for the first time (Table 1, Fig. 1). While heterocycles **3a-d** and **5a,b** absorb mainly UV-radiation and emit violet light, absorption of fused compounds is bathochromically shifted and they emit green light. The exception is **3d** which has emission maximum at 513 nm (Table 1). In analogy to what has been noticed before,[11] single-linked heterocycles **3a-d** and **5a-d** possess relatively high fluorescence quantum yield (Φ_{fl}) and large Stokes shifts (up to 12300 cm^{-1} for compound **5a**). After intramolecular dehydrogenative coupling, although dyes become flat (i.e. with lower probability for free rotation) Φ_{fl} dropped significantly to 0.08-0.5% (Table 1). Regioisomeric **10b** and **11b** differ significantly in optical properties. Although their absorption and emission maxima are located at the same regions, the Φ_{fl} for compound **11b** is almost ten times higher than for **10b**. π-Expanded indolizine **12** possessed similar properties to that of dyes **10a-d** and **11a,b**. The Stokes shifts for fused compounds **9**, **10a-d**, **11a,b**, **12** and **13** are rather low (400-2400 cm^{-1}). Previous studied clearly showed that imidazo[1,5-*a*]pyridines are less emissive than imidazo[1,2-*a*]pyridines.[27] The same trend is visible for their π-expanded analogs **9** and **11a**. The fluorescence quantum yield of **11a** is 10 times higher than for **9**.

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Table 1 Spectroscopic properties of compounds **3**-**12**.[a]

Compd.	Abs_{max} (nm)	$Emission_{max}$ (exc.)(nm)	Stokes shift (cm^{-1})	Φ_{fl}[b] (%)
3a	369, 388	(387) 449	3500	23
3b	298, 310	(315) 407	7700	45
3c	318, 333, 349	(315) 408	4100	47
3d	406	(408) 513	5100	24
5a	283	(315) 435	12300	22
5b	300	(300) 413	9100	29
8	336	(336) 438	6900	7
9	436, 472, 499	(410) 556	2000	0.5
10a	552	(553) 579	840	0.08
10b	376, 397, 449, 476	(397) 537	2400	0.6
10c	357, 377, 396	(397) 490, 527	4800	8.0
10d	536, 574	(536) 598	700	2.5
11a[c]	396, 418, 450, 479, 511	(435) 522, 562	400	5
11b	407, 432, 457, 486	(407) 506, 535	800	3
12	428, 454, 483, 516	(407) 536	700	2.5
13	391, 415, 455, 485	(417) 544	2200	1.3

[a] measured in DCM. [b] measured with perylene or quinine sulfate in H_2SO_4, as a standard. [c] published data (in cyclohexane).[11]

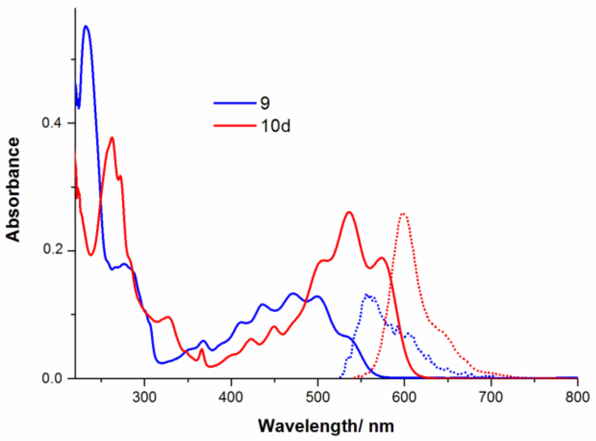

Fig. 1 Absorption (solid line) and normalized fluorescence (dotted line) spectra of **9** (blue) and **10d** (red) measured in DCM.

Conclusions

It was proved that intramolecular anion-radical coupling is a general strategy for the synthesis of heterocyclic analogs of 2a[1]*H*-benzo[*hi*]aceanthrylene possessing imidazo[1,2-*a*]pyridine or imidazo[1,5-*a*]pyridine subunits. The reaction occurs in presence of oxygen from air and yields the previously unknown π-expanded systems in moderate efficiency. If electron density at fusion position is higher the yields of anion-radical coupling are lower. Fusion of imidazo[1,2-*a*]pyridine with naphthalene alters its reactivity against dimethyl acetylenedicarboxylate – imidazole moiety behaves like azabutadiene. Fusion of imidazopyridine moiety in vertical manner leads to green-emitting π-expanded compounds possessing low fluorescence quantum yield.

Experimental section

General synthetic information.

Materials. All commercially available compounds were used as received. All solvents were dried and distilled prior to use. Transformation and oxygen sensitive compounds were performed under argon atmosphere. The reaction progress was monitored by means of thin layer chromatography (TLC) which was performed on aluminum sheets, coated with silica gel 60 F_{254} (Merck) with detection by UV-Lamp. Product purification was performed by column chromatography on silica (flash P 60, 40–63 mm, SiliCycle), and dry column vacuum chromatography (DCVC) on silica (MN-Kieselgel P/UV254) or aluminum oxide (MN-Aluminumoxid G). Identity and purity of prepared compounds were proved by 1D NMR (^{1}H NMR and ^{13}C NMR) and 2D NMR (COSY) (on Varian 500 MHz). High-resolution mass spectra (EI, and ESI) were obtained on MaldiSYNAPT G2-S HDMS/GCT Premier, Waters. Melting points were measured with Ez-Melt, SRS and were given without correction.

General procedure of direct arylation. Imidazo[1,2-*a*]pyridine **1** (1.5 mmol), aryl bromide **2a-e** (1 mmol) and KOAc (2 mmol) were reacted in DMAc (4 mL) in the presence of $Pd(OAc)_2$ (0.224 mg, 0.001 mmol, 0.1 mol%) at 150 °C, overnight under Ar. Upon completion the mixture directly absorbed into celite and purified as follows:

3-(Anthracen-9-yl)imidazo[1,2-*a*]pyridine (3a); Compound **1** (0.15 mL, 1.5 mmol), 9-bromoantracene (**2a**, 257 mg, 1 mmol), KOAc (200 mg, 2 mmol). The resulting mixture was purified by DCVC on SiO_2 (1% MeOH in CH_2Cl_2) to affords off-white solid (173 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.11 (d, J = 8.5 Hz, 2 H), 7.92 (s, 1 H), 7.84 (dd, J_1 = 9.5 Hz, J_2 = 1 Hz, 1 H), 7.55 – 7.49 (m, 4 H), 7.41 – 7.38 (m, 2H), 7.34 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 1 H), 7.26 (dt, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1 H), 6.65 (dt, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1 H). Other properties concur with published data.[13]

3-(Phenanthren-9-yl)imidazo[1,2-*a*]pyridine (3b); Compound **1** (0.15 mL, 1.5 mmol), 9-bromophenanthrene (**2b**, 257 mg, 1 mmol), KOAc (200 mg, 2 mmol). The resulting mixture was purified by DCVC on SiO_2 (60% EtOAc in hexanes) and recrystallized (aceton) to affords white crystal (195 mg, 66%), mp. 180-181°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (d, J = 8.8 Hz, 1 H), 8.77 (d, J = 8.3 Hz, 1 H), 7.93 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1 H), 7.91 (s, 1 H), 7.87 (s, 1 H), 7.78 – 7.65 (m, 5 H), 7.52 (m, 2 H), 7.24 (ddd, J_1 = 9.3 Hz, J_2 = 6.8 Hz, J_3 = 1.4 Hz, 1 H), 6.72 ppm (td, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.0, 134.1, 131.4686, 130.9, 130.9, 130.8, 130.7, 127.8, 127.4, 127.3, 127.3, 126.2, 125.2, 124.5, 124.4, 123.9, 123.4, 123.4, 122.8, 118.2, 112.5 ppm; HRMS (EI): *m/z* (M^+) calcd for $C_{21}H_{14}N_2$: 294.1157; found: 294.1157.

6-(Imidazo[1,2-*a*]pyridin-3-yl)-2-methylbenzo[*h*]quinoline (3c); Compound **1** (0.6 mL, 6 mmol), 6-bromo-2-methylbenzo[*h*]quinoline **2c** (1.09 g, 4 mmol), KOAc (800 mg, 8 mmol). The resulting mixture was purified by DCVC on SiO_2 (1% MeOH in CH_2Cl_2) to afford off-white crystals (1.03 g, 83%), mp. 180-181°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.48 (dd, J_1 = 8.3 Hz, J_2 = 1 Hz, 1 H), 8.08 (d, J = 7.8 Hz, 1 H), 7.86 (s, 1 H), 7.81 (s, 1H), 7.77 – 7.71 (m, 3 H), 7.59 (ddd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, J_3 = 1.4 Hz, 1 H), 7.49 (d, J = 7.8 Hz, 1 H), 7.45 (d, J = 8.3 Hz, 1 H), 7.24 (ddd, J_1 = 9.3 Hz, J_2 = 6.8 Hz, J_3 = 1 Hz, 1 H), 6.71 (td, J_1 = 6.8 Hz, J_2 = 1 Hz, 1 H), 2.88 ppm (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.0, 146.4, 146.1, 136.3, 134.2, 132.3, 131.9, 129.0, 128.7, 127. 4, 125.4, 125.3, 125.1, 124.5, 124.4, 123.7, 122.8, 118.3, 112.5, 25.7 ppm; HRMS (EI): *m/z* (M^+) calcd for $C_{21}H_{15}N_3$: 309.1266; found: 309.1261.

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6-(Imidazo[1,2-*a*]pyridin-3-yl)-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3d); Compound **1** (0.3 mL, 3 mmol), 6-(imidazo[1,2-*a*]pyridin-3-yl)-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione **2d** (776 mg, 2 mmol), KOAc (393 mg, 4 mmol). The resulting mixture was purified by DCVC on Al_2O_3 (CH_2Cl_2) and recrystallized (cyclohexane/EtOAc) to affords yellow crystals (424 mg, 50%), mp. 145-147°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 7.3 Hz, 1 H), 8.67 (dd, J_1 = 7.3 Hz, J_2 = 1 Hz, 1 H), 8.10 (dd, J_1 = 8.6 Hz, J_2 = 1 Hz, 1 H), 7.93 (dd, J_1 = 7.8 Hz, J_2 = 1 Hz, 1 H), 7.90 (d, *J* = 7.3 Hz, 1 H), 7.89 (s, 1 H), 7.80 (dt, J_1 = 9.3 Hz, J_2 = 1 Hz, 1 H), 7.74 (dd, J_1 = 8.3 Hz, J_2 = 7.3 Hz, 1 H), 7.32 (ddd, J_1 = 9.3 Hz, J_2 = 6.9 Hz, J_3 = 1 Hz, 1 H), 6.85 (dd, J_1 = 6.8 Hz, J_2 = 1.4 Hz, 1 H), 4.21 (t, J = 7.8, 2 H), 1.76 (m, 2 H), 1.47 – 1.25 (m, 10 H), 0.88 ppm (t, *J* = 7 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.9, 146.8, 135.4, 133.0, 131.8, 131.7, 131.0, 130.4, 129.1, 128.7, 127.8, 123.8, 123.5, 123.2, 121., 118.6, 113.4, 40.8, 32.0, 29.5, 29.4, 28.3, 27.9, 22.8, 14.2 ppm; HRMS (ESI): *m/z* ([M+H]$^+$) calcd for $C_{27}H_{28}N_3O_2$: 426.2182; found: 426.2185.

5-(Naphthalen-1-yl)imidazo[1,2-*a*]pyridine (5a); 4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (**4a**, 400 mg, 1.56 mmol) and $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) were stirred in DME (6 mL) at rt under Ar. To this mixture compound **2e** (307 mg, 1.56 mmol), EtOH (4 mL), and saturated aqueous Na_2CO_3 (4 mL) were added subsequently. The mixture were refluxed at 110 °C for 17 h, cooled and extracted with CH_2Cl_2/saturated $NaHCO_3$. The organic fraction were collected and solvent evaporated. The resulting mixture were purified by DCVC on Al_2O_3 (15% EtOAc in hexanes) to afford white solid (345 mg, 90%), mp. 149-150°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (dd, J_1 = 6.4 Hz, J_2 = 3.4 Hz, 1 H), 7.97 (d, *J* = 8.3 Hz, 1 H), 7.74 (d, *J* = 8.8 Hz, 1 H), 7.64 – 7.60 (m, 2 H), 7.56 – 7.53 (m, 2 H), 7.41 (m, 1 H), 7.35 – 7.32 (m, 2 H), 6.98, (s, 1 H) 6.89 ppm (d, J = 6.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.1, 137.1, 133.8, 133.5, 131.8, 130.9, 130.5, 128.8, 128.0, 127.3, 126.7, 125.7, 125.0, 124.5, 117. 1, 114.0, 112.0 ppm; HRMS (EI): *m/z* (M$^+$) calcd. for $C_{17}H_{12}N_2$: 244.1000; found: 244.0995.

5-(Phenanthren-9-yl)imidazo[1,2-*a*]pyridine (5b); following procedure of **5a**, 4,4,5,5-tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane **4b** (600 mg, 1.95 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol), DME (7.5 mL), compound **2e** (385 mg, 1.95 mmol), EtOH (5 mL), and saturated Na_2CO_3 (5 mL) were reacted. The resulting mixture was purified by column chromatography on SiO_2 (2% MeOH in CH_2Cl_2) and recrystallized (EtOAc) to afford white crystals (419 mg, 73%), mp. 178.6-179.6°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 8.3 Hz, 1 H), 8.79 (d, *J* = 8.3 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 1 H), 7.91 (s, 1 H), 7.80 – 7.67 (m, 4 H), 7.54 (d, *J* = 1.5 Hz, 1 H), 7.48 (ddd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, J_3 = 1 Hz, 1 H), 7.39 – 7.33 (m, 2 H), 7.01 (s, 1 H), 6.98 ppm (dd, J_1 = 6.8 Hz, J_2 = 1 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.0, 137.2, 133.6, 131.2, 131.1, 130.8, 130.6, 129.5, 129.3, 129.3, 128.2, 127.5, 127.5, 127.4, 125.9, 124.5, 123., 122.9, 117.2, 114.0, 112.1 ppm; HRMS (EI): *m/z* (M$^+$) calcd. for $C_{21}H_{14}N_2$: 294.1157; found: 294.1147.

3-(Naphthalen-1-yl)imidazo[1,5-*a*]pyridine (8); In a pressure reaction tube, Cs_2CO_3 (0.7 g, 2.2 mmol) was heated at 150 °C under Ar flow. Subsequently $Pd(OAc)_2$ (22.4 mg, 5 mol%), PPh_3 (26.4 mg, 5 mol%), imidazo[1,5-*a*]pyridine (**6**, 240 mg, 2 mmol), 1-iodonaphthalene (0.32 mL, 2.2 mmol), and DMAc (4 mL) were added under Ar. The vessel was closed and the reaction was stirred at the same temperature for 21 h. The resulting mixture was absorbed into celite, pre-purified by DCVC on SiO_2 (1% MeOH in CH_2Cl_2) and followed by second DCVC on Al_2O_3 (5% EtOAc in hexanes) to afford off-white solid (159 mg, 32%), mp. 134°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.3 Hz, 1 H), 7.95 (d, *J* = 8.3 Hz, 1 H), 7.75 – 7.67 (m, 4H), 7.61 (dd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, 1 H), 7.56 – 7.52 (m, 2H), 7.46 (m, 1H), 6.75 (m, 1H), 6.46 ppm (td, J_1 = 7.3 Hz, J_2 = 1 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 134.0, 131.9, 131.1, 129.8, 128.5, 127.4, 126.9, 126.9, 126.3, 125.6, 125.3, 121.8, 120.3, 118.8, 118.6, 112.6 ppm; HRMS (ESI): *m/z* ([M+H]$^+$) calcd. for $C_{17}H_{13}N_2$: 245.1075; found: 245.1069.

General procedure for anion radical coupling (9, 10a-d, 11a,b); Imidazopyridine derivative (0.1 mmol) was dissolved in dry toluene (1.5 mL) under argon atmosphere in a Schlenck flask. Potassium was then added and the mixture was degassed backfill with Ar. The reaction mixture then stirred at 95 °C for 30 minutes under Ar flows with condensator attached. Subsequently air/oxygen in a balloon introduced and stirred at the same temperature for one day, quenched by EtOH under Ar, and directly absorbed onto celite. Product was purified as follows:

Imidazo[2,1,5-*de*]naphtho[1,8-*ab*]quinolizine (9); Compound **8** (49.7 mg, 0.2 mmol), K (39 mg, 1 mmol), and toluene (3 mL) were reacted under air. Reaction mixture was pre-purified by DCVC on SiO_2 (1% MeOH in CH_2Cl_2) followed by column chromatography on SiO_2 (1% TEA and 15% EtOAc in cyclohexane) to afford yellowish-red solid (24.8 mg, 52%), mp. 175-179°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.3 Hz, 1 H), 7.73 (d, *J* = 7.3 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.45 (d, *J* = 8.1 Hz, 1 H), 7.40 – 7.32 (m, 3 H), 7.20 (d, *J* = 9.0 Hz, 1 H), 7.02 (d, *J* = 7.0 Hz, 1 H), 6.73 ppm (dd, J_1 = 9.0 Hz, J_2 = 6.9 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.9, 135.2, 133.3, 131.7, 130,0 128.5, 127.6, 126.4, 126.3, 125.8, 122.2, 119.0, 117.9, 117.2, 107.3 ppm; HRMS (ESI): *m/z* ([M+H]$^+$) calcd. for $C_{17}H_{11}N_2$: 243.0922; found: 243.0919.

Anthra[1,9-*ab*]imidazo[5,1,2-*de*]quinolizine (10a); Compound **3a** (59 mg, 0.2 mmol), K (78 mg, 2 mmol) were reacted in toluene (3 mL) under air. Purification using DCVC on SiO_2 (1% TEA in CH_2Cl_2, Et_2O) followed by crystallization (CH_2Cl_2/cyclohexane) afforded red crystal (6.8 mg, 12%), mp. 178-180°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.1 Hz, 1 H), 8.26 (s, 1 H), 7.80 (s, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.59 – 7.58 (m, 2 H), 7.47 (t, *J* = 8.1 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 5.3 Hz, 1 H), 7.22 – 7.18 ppm (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.9, 136.2, 133.5, 132.7, 132.5, 129.1, 129.0, 128.0, 127.4, 126.6, 126.6, 126.0, 125.3, 124.9, 124.7, 124.1, 123.2, 121.9, 117.7, 116.2, 106.7 ppm; HRMS (EI): *m/z* (M$^+$) calcd. for $C_{21}H_{12}N_2$: 292.1000; found: 292.1003.

Imidazo[5,1,2-*de*]phenanthro[1,10-*ab*]quinolizine (10b); Compound **3b** (58.9 mg, 0.2 mmol) and K (78 mg, 2 mmol) were reacted in toluene (3 mL) under air. Purification using DCVC on SiO_2 (2% MeOH in CH_2Cl_2) followed by crystallization (CH_2Cl_2/EtOAc) afforded red crystals (22.6 mg, 38%), mp. 257-259°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 8.2 Hz, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H), 7.91 (s, 1 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.52 – 7.44 (m, 4 H), 7.36 (d, *J* = 8.7 Hz, 1 H), 7.17 (d, *J* = 6.9 Hz, 1 H), 7.11 ppm (dd, J_1 = 8.6 Hz, J_2 = 7.2 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.7, 134.3, 132.3, 132.0, 129.5, 128.1, 127.8, 127. 6, 127.4, 127.0, 126.3, 126.1, 125.8, 124.0, 123.1, 122.6, 122.6, 120.4, 116.8, 115.6, 106.8 ppm; HRMS (EI): *m/z* (M$^+$) calcd. for $C_{21}H_{12}N_2$: 292.1000; found: 292.0993.

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10-Methylimidazo[5,1,2-*de*]pyrido[2',3':5,6]naphtho[1,8-*ab*]quinolizine (10c); Compound **3c** (1.03 g, 3.3 mmol) and K (1.3 g, 33 mmol) were reacted in toluene (50 mL) under O_2. Purification using DCVC on SiO_2 (3% MeOH in CH_2Cl_2) followed by crystallization (CH_2Cl_2/EtOAc) afforded orange solid (314 mg, 31%), mp. 282°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.10 (d, *J* = 8.2 Hz, 1 H), 7.94 (d, *J* = 7.7 Hz, 1 H), 7.92 (s, 1 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 7.58 (t, *J* = 7.7 Hz, 1 H), 7.48 (s, 1 H), 7.40 (d, *J* = 8.7 Hz, 1 H), 7.28 – 7.26 (m, 2 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 2.75 ppm (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.9, 145.6, 143.9, 135.0, 134.3, 132.9, 129.2, 128.9, 127.3, 126.8, 126.1, 125.5, 124.8, 123.2, 122.9, 122.4, 121.7, 116.6, 113.8, 107.1, 25.3 ppm; HRMS (EI): *m/z* (M^+) calcd. for $C_{21}H_{13}N_3$: 307.1109; found: 307.1109.

2-Octyl-1*H*-imidazo[5,1,2-*de*]pyrido[3',4',5':4,5]naphtho[1,8-*ab*]quinolizine-1,3(2*H*)-dione (10d); Compound **3d** (86 mg, 0.2 mmol) and K (39 mg, 1 mmol) were reacted in toluene (3 mL) under Ar atmosphere. DCVC on SiO_2 (1% MeOH in CH_2Cl_2), followed by column chromatography on SiO_2 (50% Et_2OAc in CH_2Cl_2) afforded red solid (7 mg, 8%), mp. 178-180°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 7.9 Hz, 1 H), 8.41 (d, *J* = 7.9 Hz, 1 H), 8.30 (s, 1 H), 7.96 (d, *J* = 7.9 Hz, 1 H), 7.76 (d, *J* = 8.7 Hz, 1 H), 7.71 (d, *J* = 7.3 Hz, 1 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 7.65 (t, *J* = 8.2 Hz, 1 H), 4.16 (t, *J* = 7.6 Hz, 2 H), 1.74 (t, *J* = 7.6 Hz, 2 H), 1.47 – 1.25 (m, 12 H), 0.88 ppm (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.3, 163.3, 134.8, 134.8, 132.7, 132.6, 131.4, 131.1, 130.6, 130.2, 128.0, 126.6, 122.0, 121.3, 119.1, 118.0, 117.6, 115.7, 111.2, 40.6, 31.8, 29. 4, 29.2, 28.0, 27.2, 22.6, 14.1 ppm; HRMS (ESI): *m/z* ($[M+H]^+$) calcd. for $C_{27}H_{26}N_3O_2$: 424.2025; found: 424.2025.

Imidazo[5,1,2-*de*]naphtho[1,8-*ab*]quinolizine (11a). Compound **5a** (49.8 mg, 0.2 mmol) and K (39 mg, 1 mmol) were reacted in toluene (3 mL) under air. Purification by DCVC on Al_2O_3 (1% MeOH in CH_2Cl_2) afforded yellow solid (19.2 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.72 (d, *J* = 7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.46 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.23 (d, J = 7 Hz, 1H), 7.16 (dd, J_1 = 8.8 Hz, J_2 = 7.3 Hz, 1H). Other properties concur with published data.[11]

Imidazo[5,1,2-*de*]phenanthro[10,1-*ab*]quinolizine (11b); Compound **5b** (404 mg, 1.37 mmol) and K (0.53 g, 13.7 mmol) were reacted in toluene (20 mL) under O_2. Purification by DCVC on SiO_2 (3% MeOH in CH_2Cl_2) followed by recrystallization (CH_2Cl_2/EtOAc) afforded orange solid (67.2 mg, 16%), mp. 267-268°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 7.8 Hz, 1 H), 8.16 (d, *J* = 8.2 Hz, 1 H), 7.87 (s, 1 H), 7.82 (s, 1 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.57 – 7.51 (m, 3 H), 7.43 (t, *J* = 7.8 Hz, 1 H), 7.39 (d, *J* = 8.7 Hz, 1 H), 7.25 ppm (d, 1 H), (t, *J* = 7.9 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 134.7, 131.8, 131.5, 129.9, 129.2, 128.9, 127.7, 127.5, 127.4, 126.9, 125.7, 125.5, 124.4, 122.6, 122.5, 120.3, 119.4, 118.3, 116.4, 106.8 ppm; HRMS (EI): *m/z* (M^+) calcd. for $C_{21}H_{12}N_2$: 292.1000; found: 292.0993..

Dimethyl benzo[*de*]indolizino[3,4,5-*ab*]isoquinoline-1,2-dicarboxylate (12); In a dried pressure tube, compound **11a** (50 mg, 0.2 mmol) was dissolved in mesitylene (4 mL) under Ar, and DMAD (244 μL, 2 mmol) was added. The reaction mixture was stirred at 150 °C for 2h. The resulting mixture was directly loaded into DCVC on SiO_2 (CH_2Cl_2) and recrystallized (CH_2Cl_2/hexanes) to afford red crystals (34 mg, 47%), mp. 214-216°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.8 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.29 – 7.21 (m, 4 H), 7.05 ppm (dd, J_1 = 8.8 Hz, J_2 = 7.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.1, 163.8, 136.0, 135.0, 134.7, 128.7, 128.5, 127.4, 126.4, 126.1, 125.9, 125.5, 125.1, 120.5, 119.4, 119.2, 118.9, 116.9, 108.5, 104.0, 53.1, 51.4 ppm; HRMS (EI): *m/z* (M^+) calcd. for $C_{22}H_{15}NO_4$: 357.1001; found: 357.1010..

Dimethyl 5-methylindolizino[5',4',3':1,2,3]isoquinolino[4,5-*gh*]quinoline-9,10-dicarboxylate (13); Following procedure for **12**, compound **10c** (30.5 mg, 0.1 mmol), mesitylene (2 mL), and DMAD (122 μL, 2 mmol). The mixture was stirred at 150 °C for 2h. The resulting mixture was then directly loaded into DCVC on SiO_2 (1% MeOH in CH_2Cl_2) and recrystallized (Et_2O/cyclohexane) to afford red crystals (9.5 mg, 22%), mp. 255-257°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.04 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 7.83 (d, *J* = 8.8 Hz, 1 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.48 (d, *J* = 8.1, Hz, 1 H), 7.30 (s, 1 H), 7.24 (d, *J* = 7.32 Hz, 1 H), 7.21 (d, *J* = 8.1, Hz, 1 H), 7.06 (dd, J_1 = 8.7 Hz, J_2 = 7.3 Hz, 1 H) 4.14 (s, 3 H), 3.92 (s, 3 H), 2.72 ppm (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0, 163.8, 157.0, 136.0, 136.0, 135.9, 135.5, 133.8, 128.3, 127.1, 126.2, 125.9, 124.9, 124.8, 123.1, 123.0, 121.9, 119.6, 119.4, 119.2, 114.9, 108.7, 104.3, 53.1, 51.5, 25.0 ppm; HRMS (ESI): *m/z* ($[M+H]^+$) calcd. for $C_{26}H_{19}N_2O_4$: 423.1345; found: 423.1343.

Optical properties

Absorption and fluorescence spectra of all compounds in liquid solutions of CH_2Cl_2 (spectroscopic grade) at room temperature were measured with the aid of a PerkinElmer UV/VIS Spectrometer Lambda 35, and a Perkin-Elmer 512 Fluorescence Spectrometer, respectively. Fluorescence quantum yield (Φ_{fl}) was determined using perylene in cyclohexane as a standard (Φ_{fl}=0.96). We estimate that the error inherent with the Φ_{fl} estimation does not exceeds 10%.

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Notes and references

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Electronic Supplementary Information (ESI) available: [copies of ^{1}H and ^{13}C NMR spectra for all new compounds]. See DOI: 10.1039/b000000x/

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Table of contents entry:

The intramolecular dehydrogenative coupling mediated by potassium constitutes the general methodology leading to weakly emitting π-expanded heterocycles.