Synthesis K. Skonieczny et al. Special Topic

The Synthesis of Imidazo[1,2-*f*]phenanthridines, Phenanthro-[9,10-*d*]imidazoles, and Phenanthro[9′,10′:4,5]imidazo[1,2-*f*]-phenanthridines via Intramolecular Oxidative Aromatic Coupling

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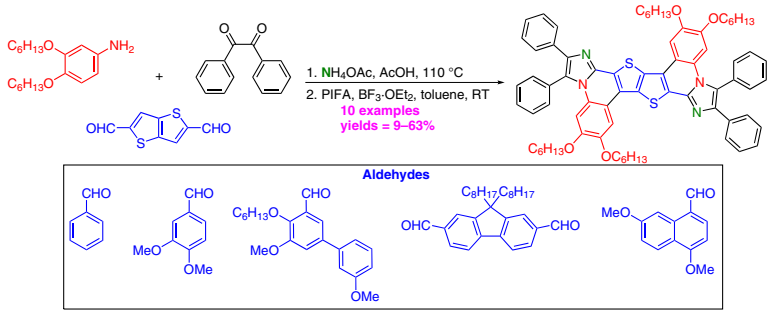

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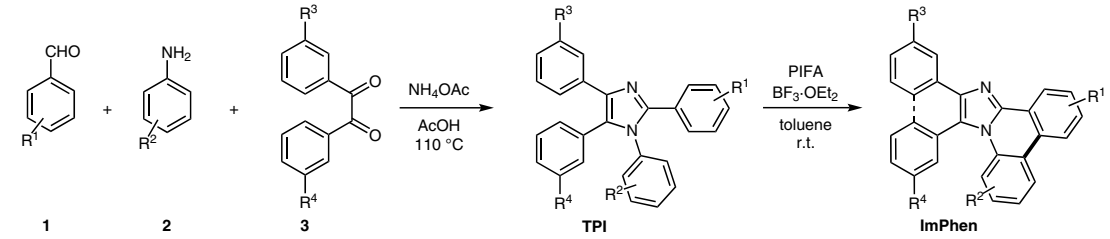
Abstract A short and efficient access to phenanthro[9,10-*d*]imidazoles, imidazo[1,2-*f*]phenanthridines, and phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridines was achieved by the action of [bis(trifluoroacetoxy)iodo]benzene (PIFA) on properly substituted tetraarylimidazoles. By pre-installing suitable electron-donating groups, it is possible to control the site of intramolecular oxidative aromatic coupling. In particular, by placing 3,4-dimethoxyphenyl and 3-methoxyphenyl moieties in close proximity, it was possible to direct the reaction into forming two biaryl linkages leading eventually to the formation of phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridines. Starting from bis-aldehydes that are derivatives of thieno[3,2-*b*]thiophene and fluorene enabled the synthesis of π-expanded imidazoles bearing 8-9 conjugated rings. By placing a dimethoxynaphthalene unit on the imidazole scaffold, we have directed the oxidative coupling reaction towards closing a five-membered ring with concomitant removal of methoxy group leading to formation of an α,β-unsaturated ketone. All resulting π-expanded imidazoles display blue emission, and the fluorescence quantum yields in some cases reaches 0.9.

Key words oxidation, multicomponent reaction, heterocycles, imidazole, fluorescence

While oxidative aromatic coupling[1] was discovered over 150 years ago,[2] it still holds many mysteries and continues to surprise.[3] The breakthrough work of various groups,[4] have proven that the careful design of precursors, based on expected effects of steric hindrance and electron density does not always lead to the expected results. Additionally, the mechanistic aspects are still under discussion,[5] although Waldvogel and co-workers have recently made significant progress.[1m,6] The majority of studies have been performed using polycyclic aromatic hydrocarbons (PAHs),[1,7] although structural diversity is in this case not necessarily easy to implement. In order to gain further insight into intramolecular oxidative aromatic coupling we opted for tetraphenyl-imidazoles (TPI) as suitable precursors.[8] The fundamental advantage of this class of compounds is that they can be synthesized using the Debus–Radziszewski process[9] which allows the transformation of aromatic 1,2-diketones, primary aromatic amines, and aromatic aldehydes into a spectacular variety of imidazoles and phenanthro[9,10-*d*]imidazoles, which in turn have been utilized in various areas of research.[10]

The combinatorial nature of the Debus–Radziszewski reaction allows various aromatic substituents differing in electron density and steric hindrance to be placed within the substrates, enabling the study of the influence of these factors on the direction of dehydrogenative coupling. The key motivation for this research was the hypothesis that local electron density (imparted by the presence of electron-donating substituents at various rings located around the imidazole core) can control the place where intramolecular oxidative aromatic coupling occurs. The additional goal was developing efficient reaction conditions for performing this reaction for the 1,2,4,5-tetraaryl-imidazole series and extending this methodology to build large π-expanded heterocycles. The secondary motivation came from the fact that imidazo[1,2-*f*]phenanthridines (ImPhen), are rather elusive, and there are only a few existing methods for their synthesis.[11,12] Finally, since one can envision the expansion of the imidazole core will significantly alter its optical properties, we planned to investigate photophysical properties of the targeted compounds.

Oxidative aromatic coupling with the use of an imidazole scaffold is not obvious since it is known that these compounds form chromotropic dimers when oxidized.[13] It is well known that oxidative aromatic coupling does not usually proceed when two unsubstituted phenyl rings are present as the oxidation potential is too high.[1a,b,7f] One, or preferably two, electron-donating groups have to be present for this reaction to occur efficiently. Taking advantage of the



1 2 3 TPI ImPhen

Aldehyde	R^1	Amine	R^2	Diketone	R^3-R^4	TPI	Yield (%)	ImPhen	Yield (%)
1a	2-OH-3-OMe	**2a**	3,4-$(OMe)_2$	**3a**	H	**4**	71	-	-
1b	3,4-$(OMe)_2$	**2a**	3,4-$(OMe)_2$	**3a**	H	**5**	51	**6**	73
1c	4-Me	**2b**	3,4,5-$(OMe)_3$	**3a**	H	**7**	51	**8**	36
1b	3,4-$(OMe)_2$	**2a**	3,4-$(OMe)_2$	**3b**	OMe	**9**	61	**10a** (-4H)	50
								10b (-2H)	15

Scheme 1 The synthesis of tetraphenylimidazoles **4**, **5**, **7**, and **9** and their intramolecular oxidative aromatic coupling

'combinatorial' nature of the Debus–Radziszewski reaction, we could easily place various substituted phenyl groups in the desired positions with the imidazole without the need for extensive synthetic manipulations. We turned our attention to derivatives bearing methoxy and hydroxyl substituents. The first substrate was prepared from benzil (**3a**), *o*-vanilin (**1a**), and 3,4-dimethoxyaniline (**2a**); the corresponding imidazole **4** was obtained in 71% yield (Scheme 1).[14]

The all attempts to oxidize this molecule using $FeCl_3$[15] led to the decomposition of the substrate. We turned therefore to Kita's work featuring [bis(trifluoroacetoxy)iodo]benzene (PIFA) as a universal oxidative agent, which often allows for cleaner oxidations without the formation of electrophilic side products.[16] Unfortunately this reaction also failed; there was almost no conversion of substrate **4** and no expected product was formed as judged by MS. The most electron-rich position of an phenyl ring bearing an OH group is located at the *para* position to this group. Apparently, the high overall electron density of the 2-hydroxy-3-methoxyphenyl substituent is not sufficient for intramolecular oxidative aromatic coupling to occur. The fact that the local electron density is located at a geometrically unfavorable place turned out to be critical. Consequently, we turned our attention to imidazole **5**, bearing four methoxy groups in 'classical' arrangement,[1b,17] so that the linking between the most electron-rich positions allows for the formation of a six-membered ring. Imidazole **5** was prepared using the Debus–Radziszewski reaction from aldehyde **1b**, amine **2a**, and benzil (**3a**) in 51% yield (Scheme 1).

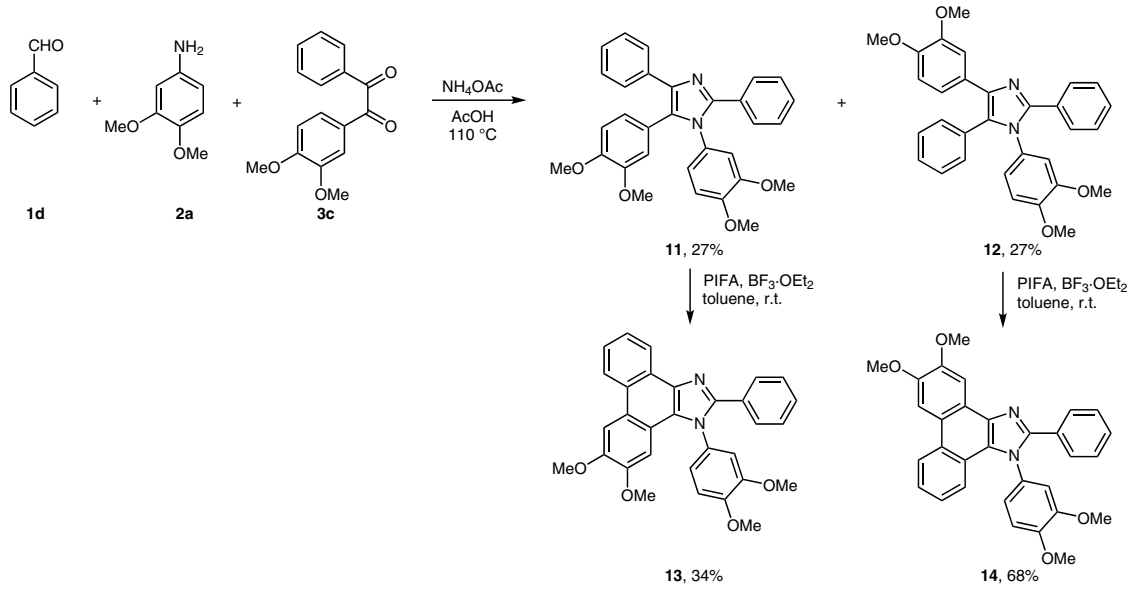
The oxidative coupling was attempted in CH_2Cl_2 (solvent typically used for PIFA)[16] and did not lead to any noticeable conversion within 2 h. The product **6** started to form after longer reaction times and full conversion was observed after 36 h (Table 1, entry 1). The replacement of CH_2Cl_2 with toluene significantly accelerated the reaction rate. Full conversion was reached within 30 minutes and the yield of compound **6** increased to 73% (Table 1, entry 2). In both reactions the amount of oxidizing reagent was double that typically reported in the literature. With smaller amounts of PIFA, no conversion of the substrate was observed or it was not complete.

Table 1 Optimization of the Oxidation of Imidazole **5** Leading to Compound **6**

Entry	Oxidant (equiv)	Solvent	Yield[a] (%) of **6**
1	PIFA (2)	CH_2Cl_2	57
2	PIFA (2)	toluene	73
3	$Fe(ClO_4)_3{\cdot}2H_2O$ (5)	CH_2Cl_2/$MeNO_2$	10
4	iron(III) 2-ethylhexanoate (4)	CH_2Cl_2	0
5	iron(III) 2-ethylhexanoate (4)	toluene	0
6	VOF_3 (3.5)	CH_2Cl_2	55
7	CoF_3 (6)	CH_2Cl_2	75

[a] Isolated yields.

In an attempt to optimize this transformation, we screened various oxidizing agents (Table 1, entries 3–7). Since $FeCl_3$ is known to lead to concomitant chlorination[18] we attempted other iron-based salts like $Fe(ClO_4)_3{\cdot}2H_2O$[19] and lipophilic iron(III) 2-ethylhexanoate (which led to substrate recovery). These unsuccessful transformations prompted the examination of other oxidizing agents such as VOF_3 and CoF_3. While VOF_3 has been successfully used numerous times in oxidative aromatic coupling,[20] CoF_3 is commonly known as a fluorination agent,[21] resulting in few reports on its use in this regard mainly concerning large aromatic hydrocarbons.[22] While both salts mediate the



Scheme 2 The synthesis of tetraphenylimidazoles **11** and **12** and their intramolecular oxidative aromatic coupling leading to phenanthro[9,10-*d*]imidazoles **13** and **14**

desired transformation of imidazole **5** into compound **6**, CoF_3 affords very high yields of the desired transformation (Table 1, entry 7). Surprisingly, CoF_3 which is known to perform not only oxidative aromatic coupling, but also oxidative removal of alkoxy substituents[20] does not promote the latter reaction in our case.

Having established the optimal conditions for the oxidative aromatic coupling for compound **6**, we designed variously substituted 1,2,4,5-tetrasubstituted imidazoles, aiming to probe the role of local electron density. We found that if an electron-rich 3,4,5-trimethoxyphenyl substituent is placed at position 1, the reaction occurs even if other substituents are electron-neutral (Scheme 1). Thus, imidazole **7** was successfully transformed into imidazo[1,2-*f*]phenanthridine **8**. The reaction occurred regioselectively linking benzene rings located at positions 1 and 2.

We wondered if introducing electron-rich substituents at all four positions, would enable parallel oxidative aromatic coupling forming at more than one biaryl linkage. The

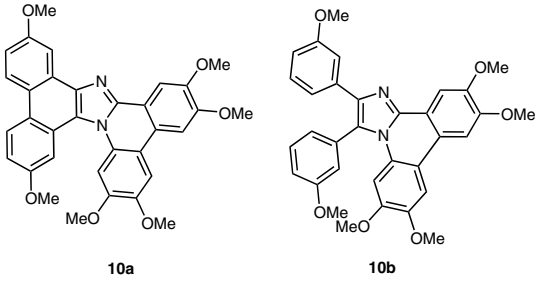


Figure 1 Structures of the products of oxidative aromatic coupling of imidazole **9**

corresponding tetrasubstituted imidazole **9** was prepared starting from analogues substrates, replacing benzil (**3a**) with 3,3′-dimethoxybenzil (**3b**) (Scheme 1). Compound **9** was obtained in 61% yield. Subjecting compound **9** to PIFA gave a mixture of **10a** and **10b** (Figure 1), possessing the phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine and imidazo[1,2-*f*]phenanthridine skeletons, respectively. This constitutes only the third available route leading to the phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine skeleton.[11,23]

In this case, 6 equiv of PIFA had to be used since the number of protons abstracted was 4. After 14 hours at room temperature, two products were obtained possessing very similar polarity, which were eventually separated via chromatography. Analysis proved that entirely fused product **10a** formed in 50% yield while partially fused product **10b** in only 15% yield. The attempts to obtain greater amounts of compound **10b** by lowering the amount of PIFA did not proved successful. This is in agreement with King's study[7f] related to lowering oxidation potential in sequential oxidative coupling in hexaphenylbenzene.

Adding more equivalents of PIFA and using forcing reaction conditions did not lead to the formation of a third C–C bond, linking benzene rings at positions 1 and 5. Since both steric and electronic factors could be responsible for this result, we resolved to eliminate the steric factor by redesigning substrate **9**. For this purpose, we prepared the corresponding unsymmetrical 1,2-diketone **3c** (details in the Supporting Information) possessing two methoxy groups in one of the aromatic ring. Subjecting this building block to 3,4-dimethoxyaniline (**2a**) and benzaldehyde (**1d**), gave a mixture of two imidazoles **11** and **12** (Scheme 2). Despite

the similar polarity, it was possible to separate these compounds with careful chromatography. We expected the intramolecular oxidative coupling of compound **11**, possessing electron-rich aryl rings located at positions 1 and 5 of the imidazole core, should lead to the formation of biaryl linkage between these two rings. Interestingly, the reaction occurred at different sites, linking benzene rings in positions 4 and 5 of substituted imidazole **11**, leading to the formation of phenanthro[9,10-*d*]imidazole **13** (Scheme 2). Derivative **12** with activated rings at positions 1 and 4 also underwent intramolecular oxidative coupling, affording dye **14**, possessing biaryl linkage between benzene rings located at positions 4 and 5.[24] The structure of these two products has been unequivocally established by X-ray analysis (Figure 2).

Imidazole **15** was designed to provide conclusive evidence of the crucial role of orchestrating local electron density in all participating arene units. For this purpose, we designed and synthesized the aldehyde **1e** (details are provided in the Supporting Information), which yielded imidazole **15** in a Debus–Radziszewski reaction (Scheme 3). Imidazole **15** possesses altogether five alkoxy groups enforcing preorganizing higher electron density towards the formation of a triphenylene system. We found that in order to obtain a

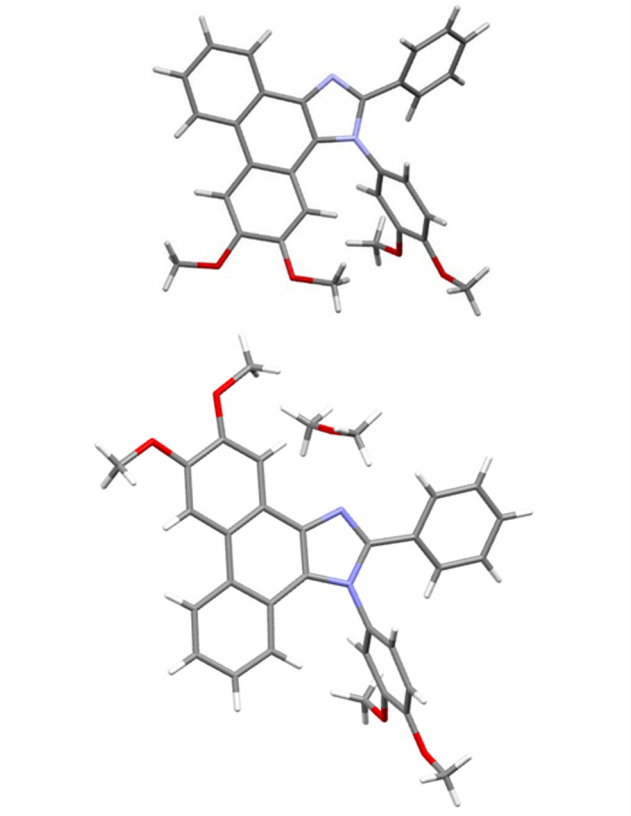
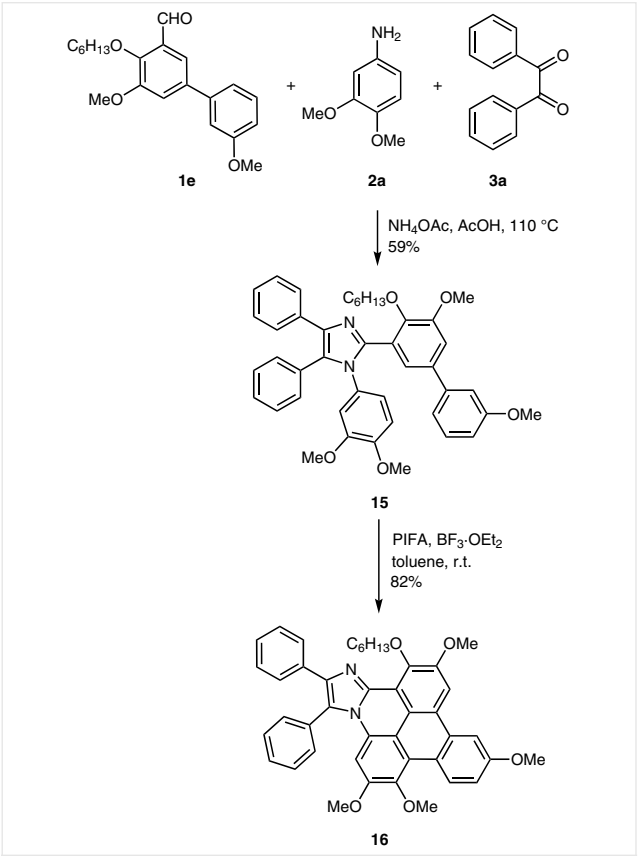


Figure 2 X-ray crystal structures of compound **13** (top) and **14** (bottom)



Scheme 3 The synthesis of imidazole **15** and π-expanded imidazole **16**

fully conjugated product **16**, only 2.5 equiv of oxidant was sufficient. No partially fused products were observed, indicating that the first oxidative coupling facilitated the sequential oxidation, analogously to the transformation of hexaphenylbenzene into hexabenzocoronene.[7f]

Subsequently, we extended this methodology towards the synthesis of larger aromatic systems (Scheme 4). For this purpose, we selected fluorene and thieno[3,2-*b*]thiophene as cores possessing suitably high electron density. Accordingly, 9,9-dioctylfluorene-2,7-dicarbaldehyde (**1f**) and thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde (**1g**) were prepared following literature procedures,[25] and transformed into bis-imidazoles **17** and **19** in 72% and 29% yields, respectively. Initially 3,4-dimethoxyaniline (**2a**) was used in both cases, but we found out that condensation of this compound with thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde (**1g**) and benzil led to material possessing with almost no solubility in organic solvents. Consequently, an analogous aniline **2c** possessing two hexyl chains was utilized in the synthesis of bis-imidazole **19**,[26] which enabled its full spectroscopic characterization.

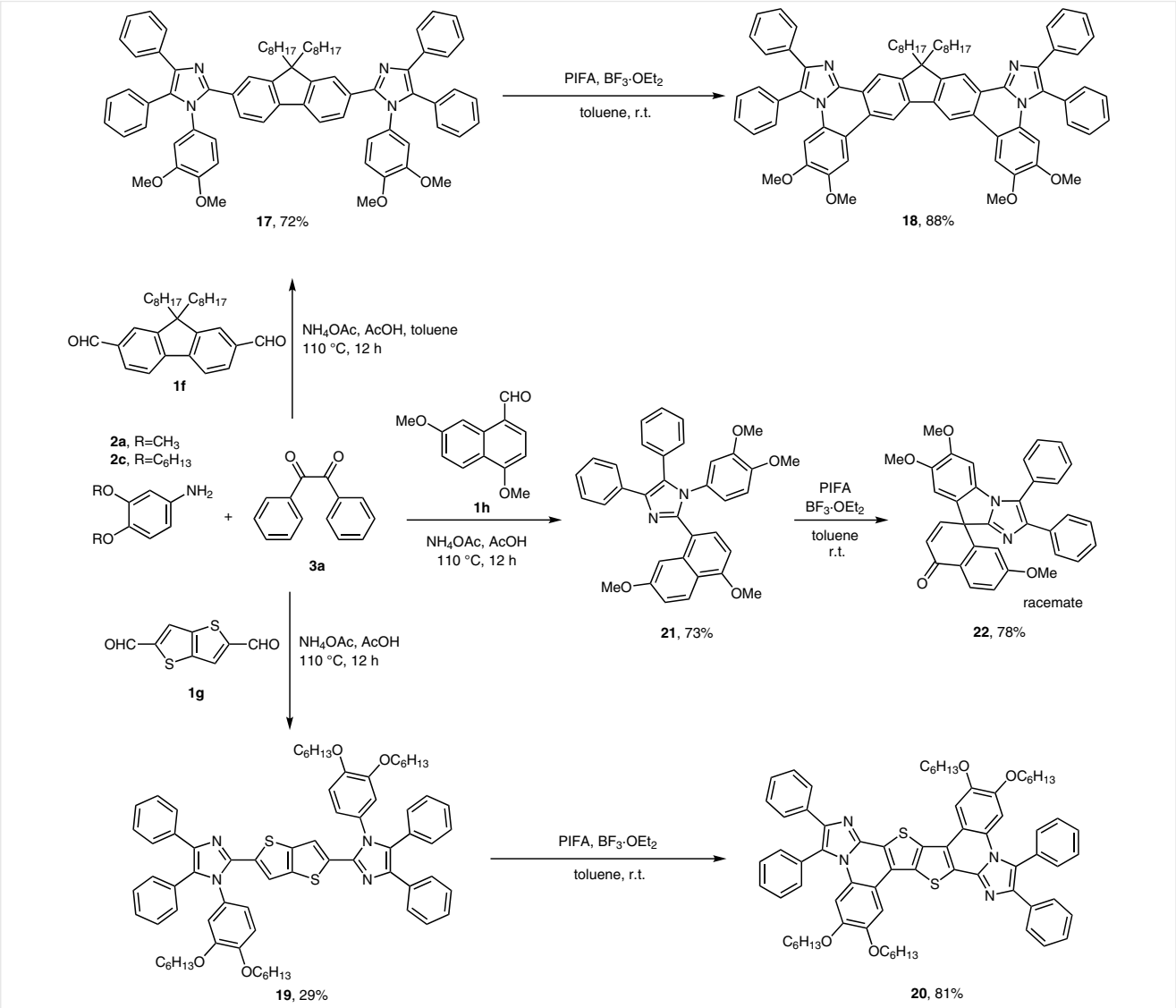
The oxidative aromatic coupling of both **17** and **19** required a large excess of oxidizing agent. The use of 4 equiv of PIFA gave a mixture of starting material with mono- and

diconjugated compounds. Only when we used 5 equiv was full conversion of the pure product of **18** and **20** obtained in 88% and 81% yields, respectively. It is noteworthy that the solubility of the product **20** was not sufficient at room temperature, and the NMR spectra for this compound were performed at an elevated temperature (47 °C).

We wondered if this methodology would be successful in formation of analogous seven-membered rings. The suitably substituted 4,7-dimethoxynaphthalenyl unit was chosen, since it was previously oxidatively coupled with porphyrins at position 8.[19a] The aldehyde **1h**, was condensed with amine **2a** to give compound **21** (Scheme 4). The latter was swiftly oxidized to a non-fluorescent product.

The MS and ^{1}H NMR spectra indicated the presence of four oxygen atoms in a molecule, and three methyl groups. The inspection of the aromatic range of ^{1}H NMR and COSY spectra revealed two spin systems, assigned to two Ph groups: the AMX and AB spin systems and two signals of isolated ^{1}H atoms (singlets). In addition, the ^{13}C NMR spectrum showed two signals of quaternary atoms at δ = 49.7 and 183.2, assigned to Csp^3 and C=O structural moieties. The presence of the C=O group was confirmed by the IR spectrum (band at 1663 cm^{-1}). The number of ^{1}H signals excluded the coupling between two CH groups, suggested the reaction between CH and C^{IV} atoms. All the above findings are satisfied by five spiro structures (Figure 3).

The selection of structures where achieved on the basis of the ^{1}H NMR spectrum. Structures (c), (d), and (e) were excluded due to the presence of one AMX and two AB spin systems. Structure (f) was excluded because of the presence



Scheme 4 The synthesis of compounds **17**–**22**

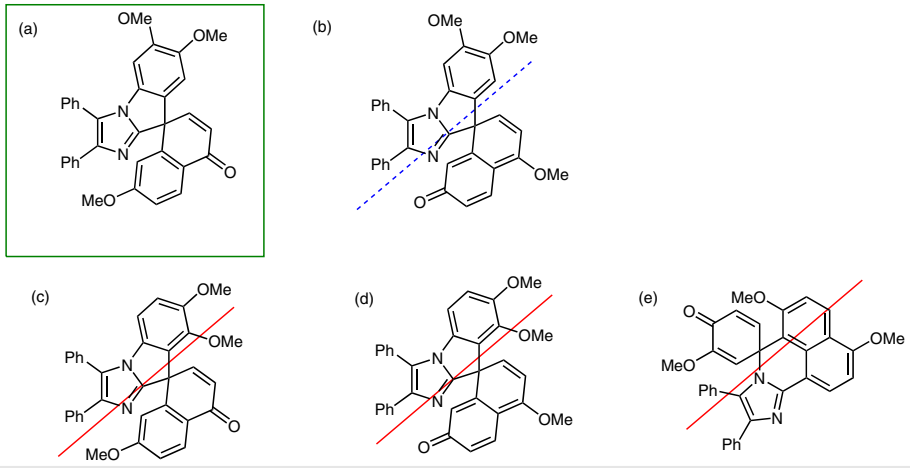


Figure 3 The possible structures of compound **22**

of two AMX spin systems. Only two structures, (a) and (b) were expected to exhibit the signals of AMX and AB systems, and two singlets arising from isolated ^{1}H atoms. Thus, only these compounds agree with the ^{1}H spectrum.

The ^{13}C, ^{1}H HMBC correlation spectrum provided further information. Namely, the signal of the carbonyl carbon atom correlated with the signals of ^{1}H atoms in both AMX and AB spin systems, which is expected for the compound (a). In the case of (b), the AB hydrogens are too far from the C=O carbon atom.

The suggested ^{1}H and ^{13}C signal assignment is presented in the Supporting Information. The assignments were performed on the basis of ^{1}H,^{1}H COSY, ^{13}C,^{1}H HSQS, and ^{13}C,^{1}H HMBC spectra, and in some cases with the help of calculated DFT GIAO NMR chemical shifts. Calculated ^{1}H and ^{13}C chemical shifts correlated satisfactorily with experimental values. We performed also similar analysis on structure (b) obtaining rather bad correlation (see the Supporting Information).

Because the compound under consideration is expected to be chiral and to form racemic mixture, we performed ^{1}H NMR measurements using of dirhodium tetrakis[(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate] dimer as the chiral recognition agent ('dirhodium method').[27] We observed chemical shift changes due the formation of adducts (Δδ parameters) and splitting of some signals originating in the formation of two diastereomers (Δν parameter). Thus, the experiment confirmed the presence of two enantiomers in the mixture.

The spectral characteristics of fused imidazoles **6**, **8**, **10a**, **10b**, **13**, **14**, **16**, **18**, **20**, and **22** were then examined and compared to those of imidazoles **5**, **7**, **9**, **11**, **12**, **15**, **17**, **19**, and **21** (Table 2, Figures 4 and 5). The most notable feature of these compounds is moderate to strong emission of blue light (λ_{em} = 350–480 nm) regardless the degree of fusion. Absorption of fused imidazoles is significantly bathochromically shifted when compared with unexpanded imidazoles (Table 2). In particular, this is evident in the case of compounds **15** → **16**, **17** → **18**, **19** → **20** (Figure 5). The fact that there is no bathochromic shift of emission in all these cases can only be explained by reasoning the excited state geometry of imidazoles **5**, **7**, **9**, **11**, **12**, **15**, **17**, **19**, and **21** is planar. The analogous effect has often been observed for dyes possessing multiple biaryl linkages.[28] A dramatic increase in the fluorescence quantum yield in compounds **10a** and **10b** versus **9** (as well as **11** → **13**, **12** → **14**) can be attributed to a substantial decrease in nonradiative relaxation to the ground state caused by limited possibilities for free rotations. Comparison of optical properties of imidazo[1,2-*f*]phenanthridines **6** and **10b** with phenanthro[9,10-*d*]imidazoles[29] leads to the conclusion that they display similar fluorescence quantum yields (Φ_{fl} ~20–40%), but larger Stokes shifts (3000–6500 vs. ~1000 cm^{-1}).

According to expectations, substantial decrease in the Stokes shift is observed when going from imidazoles **5**, **7**, **9**, **11**, **12**, and **15** (9500–10500 cm^{-1}), to partly fused derivatives **6**, **8**, and **10b** (3000–6500 cm^{-1}), to planar compounds **10a**, **16** (250–750 cm^{-1}). Stokes shift decreases sharply after

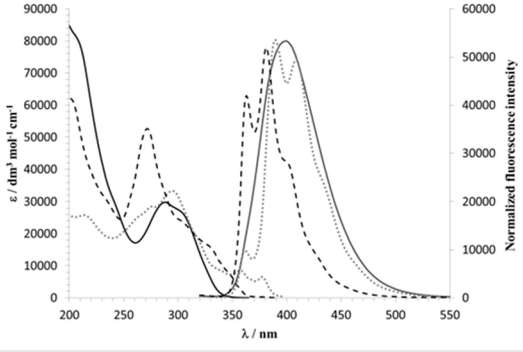


Figure 4 Absorption and emission of compounds **9** (solid line), **10a** (dotted line) and **10b** (dashed line)

Table 2 Spectroscopic Properties

Compound	λ_{abs} (nm)	λ_{em} (nm)	Φ	Stokes shift (cm^{-1})	ε
5	288	395	0.34[a]	9400	30000
6	276 333	396	0.26[a]	4800	71000 17000
7	282	387	0.08[a]	9600	27000
8	269 324	403	0.04[a]	6500	76000 11000
9	288	399	0.20[a]	9700	30000
10a	295 378	389 409	0.39[a]	750	33000 6500
10b	272 327	363 381	0.35[a]	3000	53000 16500
11	284	387 394	0.38[a]	9400	36700
12	288	396 401	0.33[a]	9500	25250
13	362	371 388	0.52[a]	700	5500
14	360	372 387	0.50[a]	900	7500
15	271	379	0.09[a]	10500	43900
16	377 396	400 422 444	0.32[a]	250	10500 14500 500
17	354	426	1.00[b]	4800	56000
18	396 416	411 433	0.98[b]	1000	96300 37500
19	389	438 461	0.79[b]	2900	52900
20	391 414	435 456	0.33[b]	1200	44500 46200
21	285 333	411	0.40[a]	5700	24000 900
22	205	427	0.01[a]	9400	28000

[a] Determined in MeCN using 2-aminopyridine in H_2SO_4 (0.5 M) as a standard.
[b] Determined in MeCN using quinine sulfate in H_2SO_4 (0.5 M) as a standard.

the formation of the phenanthrene-type bond in the part of imidazole derived from diketone unit, **11** and **12** (~9500 cm^{-1}) compared to **13** and **14** (700–900 cm^{-1}).

In conclusion, the first examples of intramolecular oxidative aromatic coupling transforming 1,2,4,5-tetraphenylimidazoles into various fused heterocycles were presented. It was found that only selected reagents such as PIFA/BF_3·Et_2O/toluene or CoF_3 can perform this transformation in high yield. It was also found that the formation of biaryl linkage between rings present at positions 4 and 5 and at 1 and 2 of the imidazole is favored. Even if only one of these substituents is equipped with electron-donating groups, the reaction proceeds easily. On the other hand, the formation of biaryl linkage between rings located at positions 1 and 5 is disfavored. It does not occur even if both substituents present in spatial proximity possess electron-donating substituents. The strategy can be employed for the synthesis of π-expanded heterocycles only if the central unit is electron-rich. When electron-rich naphthalene unit is present at position 2 of the imidazole, oxidation occurs in an unusual way to afford a compound bearing a heretofore unknown skeleton of 4′H-spiro[imidazo[1,2-*a*]indole-9,1′-naphthalen]-4′-one.

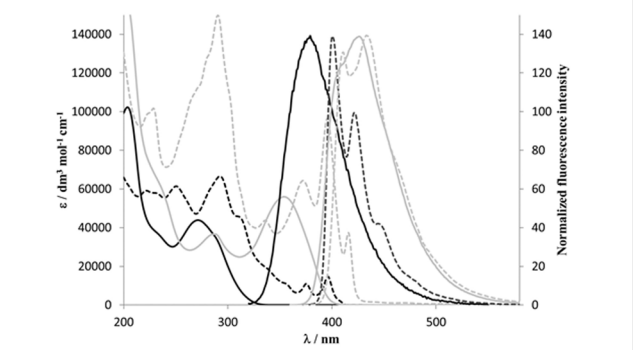


Figure 5 Absorption and emission of compounds **15** (black solid line), **16** (black dotted line), **17** (grey solid line) and **18** (grey dotted line)

This work also shows that various fused systems possessing imidazole core are moderate to good emitters of blue light. The almost identical value of emission (λ_{max} = 390–440 nm) for tetraaryl-substituted imidazoles as well as for fused products is an evidence that their geometry in the excited state is very similar. These results are not only of theoretical significance, providing insight into factors influencing the intramolecular aromatic oxidative coupling, but they may also open doors to practical applications in such diverse areas as molecular electronics and fluorescent imaging.

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. Chromatography was performed on silica (200–400 mesh). All reported NMR spectra were recorded on 400, 500, and 600 MHz spectrometers with TMS as the internal reference. Mass spectra were obtained via EI-MS, ESI-MS, and FD-MS. UV-Vis and fluorescence spectra were recorded in MeCN. For the determination of quantum yields, 2-aminopyridine (or quinine sulfate) in 0.5 M H_2SO_4 was used as a standard. 9,9-Dioctyl-9*H*-fluorene-2,7-dicarbaldehyde (**1f**),[25a] thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde (**1g**),[25b] 3,4-bis(hexyloxy)aniline (**2c**),[26] and TPI **4**[14] were prepared according to procedures from the literature.

Tetraarylimidazoles 5, 7, 9, 11, 12, 15, 17, 19, 21; General Procedure 1 (GP1)

To the solution of benzaldehyde (1 equiv) and aniline (1.5 equiv) in glacial AcOH, benzil (1 equiv) and NH_4OAc (5 equiv) were added. The mixture was stirred at 110 °C for 12 h. The solution was poured into copious amount of water and extracted with CH_2Cl_2. The combined

organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The product was purified by chromatography (silica gel, hexanes/EtOAc).

Phenanthro[9,10-*d*]imidazoles, Imidazo[1,2-*f*]phenanthridines, and Phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridines 6, 8, 10a, 10b, 13, 14, 16, 18, 20, 22; General Procedure 2 (GP2)

To a stirred solution of imidazole (1 equiv) in dry toluene at 0 °C under argon atmosphere, PIFA (2–6 equiv) and $BF_3{\cdot}Et_2O$ (2–10 equiv) were added. The mixture was allowed to warm to r.t. and stirred for ca. 0.5–3 h until complete consumption of the starting material (TLC monitoring). The resulting brown solution was poured into copious amount of water and extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent were removed under reduced pressure. The product was purified by crystallization or chromatography (silica gel, hexanes/EtOAc).

1,2-Bis(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5)

Following GP1 using 3,4-dimethoxybenzaldehyde (665 mg, 4.0 mmol), 3,4-dimethoxyaniline (919 mg, 6.0 mmol), benzil (841 mg, 4.0 mmol), and NH_4OAc (1.54 g, 20.0 mmol) in AcOH (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 2:1). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 1.01 g (51%); mp 157–158 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59–7.62 (m, 2 H), 7.22–7.27 (m, 5 H), 7.17–7.20 (m, 1 H), 7.12–7.17 (m, 3 H), 6.93 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.73 (d, *J* = 8.4 Hz, 2 H), 6.64 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.52 (d, *J* = 2.4 Hz, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.74 (s, 3 H), 3.59 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.2, 149.0, 148.7, 148.4, 146.7, 131.1, 130.7, 130.0, 128.4, 128.1, 128.0, 127.4, 126.6, 121.6, 120.7, 112.1, 111.8, 110.7, 110.6, 56.0, 55.9, 55.8, 55.7.

HRMS (EI): *m*/*z* [M] calcd for $C_{31}H_{28}N_2O_4$: 492.2049; found: 492.2057.

6,7,10,11-Tetramethoxy-2,3-diphenylimidazo[1,2-*f*]phenanthridine (6)

Following GP2 using **5** (148 mg, 0.30 mmol, 1 equiv), PIFA (262 mg, 0.61 mmol, 2 equiv), and $BF_3{\cdot}Et_2O$ (77 µL, 0.61 mmol, 2 equiv) in dry toluene (30 mL). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 0.11 g (73%); mp 229–230 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 7.64–7.55 (m, 7 H), 7.55–7.52 (m, 1 H), 7.51 (s, 1 H), 7.28–7.23 (m, 2 H), 7.22–7.18 (m, 1 H), 6.94 (s, 1 H), 4.14 (s, 3 H), 4.10 (s, 3 H), 4.02 (s, 3 H), 3.28 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.7, 149.8, 148.5, 146.4, 142.1, 133.5, 132.4, 129.5, 129.2, 128.1, 127.9, 127.3, 127.0, 124.0, 121.9, 115.7, 105.6, 105.0, 103.0, 101.0, 56.5, 56.3, 56.1, 55.0.

HRMS (EI): *m*/*z* [M] calcd for $C_{31}H_{26}N_2O_4$: 490.1893; found: 490.1898.

4,5-Diphenyl-2-(*p*-tolyl)-1-(3,4,5-trimethoxyphenyl)-1*H*-imidazole (7)

Following GP1 using *o*-tolualdehyde (360 mg, 3.0 mmol), 3,4,5-trimethoxyaniline (824 mg, 4.5 mmol), benzil (631 mg, 3.0 mmol), and NH_4OAc (1.15 g, 15.0 mmol) in AcOH (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 0.73 g (51%); mp 161–163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.5 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.28–7.14 (m, 8 H), 7.08 (d, *J* = 8.1 Hz, 2 H), 6.19 (s, 2 H), 3.83 (s, 3 H), 3.52 (s, 6 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 146.9, 138.2, 138.0, 137.5, 134.4, 132.5, 131.0, 130.9, 130.4, 129.5, 128.8, 128.7, 128.3, 128.1, 127.9, 127.6, 127.4, 126.5, 125.2, 105.9, 61.1, 56.1, 21.3.

HRMS (FD): *m*/*z* [M] calcd for $C_{31}H_{28}N_2O_3$: 476.2100; found: 476.2083.

6,7,8-Trimethoxy-10-methyl-2,3-diphenylimidazo[1,2-*f*]phenanthridine (8)

Following GP2 using **7** (100 mg, 0.21 mmol, 1 equiv), PIFA (180 mg, 0.42 mmol, 2 equiv), and $BF_3{\cdot}Et_2O$ (106 µL, 0.84 mmol, 4 equiv) in dry toluene (10 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 36 mg (36%); mp 189–192 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.04 (s, 1 H), 8.79 (d, *J* = 8.1 Hz, 1 H), 7.61–7.54 (m, 6 H), 7.53–7.49 (m, 1 H), 7.45 (dd, *J* = 8.1, 0.9 Hz, 1 H), 7.25–7.22 (m, 2 H), 7.21–7.17 (m, 1 H), 6.92 (s, 1 H), 3.98 (s, 3 H), 3.92 (s, 3 H), 3.23 (s, 3 H), 2.58 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3, 152.24, 143.2, 141.2, 140.2, 138.7, 134.4, 133.8, 132.2, 130.6, 129.5, 129.0, 128.6, 128.1, 128.0, 127.9, 127.4, 126.9, 126.2, 124.4, 124.3, 120.8, 110.9, 97.7, 61.2, 60.5, 54.8, 22.4.

HRMS (FD): *m*/*z* [M] calcd for $C_{31}H_{26}N_2O_3$: 474.1943; found: 474.1925.

1,2-Bis(3,4-dimethoxyphenyl)-4,5-bis(3-methoxyphenyl)-1*H*-imidazole (9)

Following GP1 using 3,4-dimethoxybenzaldehyde (125 mg, 0.75 mmol), 3,4-dimethoxyaniline (168 mg, 1.1 mmol), 1,2-bis(3-methoxyphenyl)ethane-1,2-dione (202 mg, 0.75 mmol), and NH_4OAc (289 mg, 3.75 mmol) in AcOH (20 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 2:1 to 3:2). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 253 mg (61%); mp 149–150 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (s, 1 H), 7.21–7.13 (m, 4 H), 6.93 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.82–6.71 (m, 5 H), 6.70–6.68 (m, 1 H), 6.67 (d, *J* = 2.4 Hz, 1 H), 6.56 (d, *J* = 2.3 Hz, 1 H), 3.85 (s, 6 H), 3.74 (s, 3 H), 3.69 (s, 3 H), 3.63 (s, 3 H), 3.62 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 159.3, 149.2, 149.0, 148.7, 148.4, 146.6, 131.9, 130.7, 130.0, 129.4, 129.1, 123.6, 121.6, 120.7, 119.9, 116.4, 114.0, 113.2, 112.1, 111.7, 110.7, 110.6, 56.0, 55.9, 55.8 (2 signals), 55.2, 55.1.

HRMS (EI): *m*/*z* [M] calcd for $C_{33}H_{32}N_2O_6$: 552.2260; found: 552.2279.

2,3,6,7,11,16-Hexamethoxyphenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine (10a) and 6,7,10,11-Tetramethoxy-2,3-bis(3-methoxyphenyl)imidazo[1,2-*f*]phenanthridine (10b)

Following GP2 using **9** (100 mg, 0.18 mmol, 1 equiv), PIFA (467 mg, 1.08 mmol, 6 equiv), and $BF_3{\cdot}Et_2O$ (137 µL, 1.08 mmol, 6 equiv) in dry toluene (20 mL). The mixture of products **10a** and **10b** was isolated by chromatography (silica gel, hexanes/EtOAc, 2:1 to 3:2).

2,3,6,7,11,16-Hexamethoxyphenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine (10a)

Crystallization (EtOAc/pentane) afforded a slightly yellow crystalline solid of **10a**; yield: 50 mg (50%); mp 284–285 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 9.2 Hz, 1 H), 8.51 (d, *J* = 9.1 Hz, 1 H), 8.48–8.34 (m, 2 H), 7.86 (s, 1 H), 7.81 (d, *J* = 2.5 Hz, 1 H), 7.65 (s, 1 H), 7.58 (s, 1 H), 7.29 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.23 (dd, *J* = 9.0, 2.6 Hz, 1 H), 4.22 (s, 3 H), 4.15 (s, 3 H), 4.14 (s, 3 H), 4.13 (s, 3 H), 3.91 (s, 3 H), 3.88 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.5, 156.2, 149.9, 148.0, 126.2, 125.6, 124.2, 123.9, 123.7, 123.4, 123.2, 123.1, 116.2, 113.3, 107.0, 106.6, 105.5, 103.7, 103.1, 56.7, 56.5, 56.2 (2 signals), 55.9, 55.5.

HRMS (EI): *m*/*z* [M] calcd for $C_{33}H_{28}N_2O_6$: 548.1947; found: 548.1935.

6,7,10,11-Tetramethoxy-2,3-bis(3-methoxyphenyl)imidazo[1,2-*f*]phenanthridine (10b)

Crystallization (EtOAc/pentane) afforded a white crystalline solid of **10b**; yield: 15 mg (15%); mp 184–185 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 9.2 Hz, 1 H), 8.49 (d, *J* = 9.2 Hz, 1 H), 8.25 (s, 1 H), 7.34 (s, 1 H), 7.24 (dd, *J* = 9.0, 2.8 Hz, 1 H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.13 (dd, *J* = 8.3, 2.4 Hz, 1 H), 7.10 (dd, *J* = 9.1, 2.6 Hz, 1 H), 7.06 (s, 1 H), 7.05 (d, *J* = 6.4 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.69 (d, *J* = 2.6 Hz, 1 H), 4.09 (s, 3 H), 4.00 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.50 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 157.0, 150.7, 150.1, 149.9, 149.6, 148.5, 137.3, 131.6, 128.3, 127.3, 125.0, 124.3, 123.4, 123.1, 122.7, 122.4, 122.0, 121.7, 116.2, 114.7, 112.4, 112.3, 111.4, 110.7, 102.8, 102.3, 56.3 (2 signals), 55.8 (2 signals), 55.7, 54.7.

HRMS (EI): *m*/*z* [M] calcd for $C_{33}H_{30}N_2O_6$: 550.2103; found: 550.2093.

1,5-Bis(3,4-dimethoxyphenyl)-2,4-diphenyl-1*H*-imidazole (11) and 1,4-Bis(3,4-dimethoxyphenyl)-2,5-diphenyl-1*H*-imidazole (12)

Following GP1 using benzaldehyde (113 μL, 1.11 mmol), 3,4-dimethoxyaniline (255 mg, 1.66 mmol), 1-(3,4-dimethoxyphenyl)-2-phenylethane-1,2-dione (300 mg, 1.11 mmol), and NH_4OAc (428 mg, 5.55 mmol) in AcOH (30 mL). The mixture of products **11** and **12** was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1 to 2:1).

1,5-Bis(3,4-dimethoxyphenyl)-2,4-diphenyl-1*H*-imidazole (11)

Crystallization (EtOAc/hexane) afforded a white crystalline solid of **11**; yield: 150 mg (27%); mp 220–221 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.6 Hz, 2 H), 7.51–7.47 (m, 2 H), 7.29–7.24 (m, 5 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 6.76–6.70 (m, 3 H), 6.65–6.61 (m, 2 H), 6.54 (d, *J* = 1.8 Hz, 1 H), 3.86 (s, 3 H), 3.86 (s, 3 H), 3.60 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.0, 148.7, 148.6, 146.6, 137.5, 130.7, 129.9, 128.9, 128.4, 128.1 (2 signals), 127.4, 126.7, 123.8, 122.9, 120.6, 114.0, 111.7, 110.9, 110.7, 56.0, 55.9, 55.7 (2 signals).

HRMS (EI): *m*/*z* [M] calcd for $C_{31}H_{28}N_2O_4$: 492.2049; found: 492.2056.

1,4-Bis(3,4-dimethoxyphenyl)-2,5-diphenyl-1*H*-imidazole (12)

Crystallization (EtOAc/hexane) afforded a white crystalline solid of **12**; yield: 150 mg (27%); mp 212–213 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 2 H), 7.28–7.24 (m, 6 H), 7.21–7.16 (m, 3 H), 7.13 (d, *J* = 1.7 Hz, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 6.70 (d, *J* = 8.5 Hz, 1 H), 6.61 (dd, *J* = 8.5, 2.3 Hz, 1 H), 6.49 (d, *J* = 2.3 Hz, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.65 (s, 3 H), 3.57 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 148.6, 148.5, 147.8, 146.6, 137.8, 131.2, 131.0, 130.2, 129.8, 128.9, 128.4, 128.3, 128.1, 127.9, 120.6, 119.7, 111.7, 111.0, 110.6, 55.9, 55.8 (2 signals), 55.5.

HRMS (EI): *m*/*z* [M] calcd for $C_{31}H_{28}N_2O_4$: 492.2049; found: 492.2054.

1-(3,4-Dimethoxyphenyl)-9,10-dimethoxy-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (13)

Following GP2 using **11** (125 mg, 0.25 mmol, 1 equiv), PIFA (218 mg, 0.50 mmol, 2 equiv), and $BF_3{\cdot}Et_2O$ (64 μL, 0.50 mmol, 2 equiv) in dry toluene (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1 to 2:1). Crystallization (EtOAc/hexane) afforded a white crystalline solid; yield: 43 mg (34%); mp 214–215 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.84 (dd, *J* = 7.9, 1.0 Hz, 1 H), 8.53 (d, *J* = 8.3 Hz, 1 H), 8.09 (s, 1 H), 7.69–7.66 (m, 3 H), 7.63–7.59 (m, 1 H), 7.33–7.30 (m, 3 H), 7.13 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.05–7.02 (m, 2 H), 6.71 (s, 1 H), 4.08 (s, 3 H), 3.97 (s, 3 H), 3.81 (s, 3 H), 3.48 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 150.1, 149.9, 148.6, 147.6, 136.4, 131.5, 130.7, 129.2, 128.7, 128.3, 127.7, 126.5, 126.3, 125.2, 123.8, 122.9, 122.6, 121.8, 117.5, 112.5, 111.5, 105.3, 102.2, 56.3 (2 signals), 55.9, 55.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{31}H_{26}N_2O_4$: 490.1893; found: 490.1888.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (14)

Following GP2 using **12** (50 mg, 0.10 mmol, 1 equiv), PIFA (87 mg, 0.20 mmol, 2 equiv), and $BF_3{\cdot}Et_2O$ (26 μL, 0.20 mmol, 2 equiv) in dry toluene (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1 to 2:1). Crystallization (EtOAc/hexane) afforded a white crystalline solid; yield: 34 mg (68%); mp 249–250 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.4 Hz, 1 H), 8.24 (s, 1 H), 8.06 (s, 1 H), 7.67–7.62 (m, 2 H), 7.53–7.47 (m, 1 H), 7.35–7.24 (m, 5 H), 7.07 (dd, *J* = 8.4, 2.3 Hz, 1 H), 7.00 (dd, *J* = 12.9, 5.4 Hz, 2 H), 4.18 (s, 3 H), 4.14 (s, 3 H), 4.02 (s, 3 H), 3.81 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.9, 150.0, 149.9, 149.8, 148.4, 137.0, 131.3, 130.7, 129.3, 128.8, 128.6, 128.2, 127.5, 125.3, 124.5, 123.5, 122.3, 122.2, 122.1, 121.3, 121.0, 111.9, 111.4, 104.4, 103.2, 56.3, 56.2, 56.1, 56.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{31}H_{27}N_2O_4$: 491.1971; found: 491.1969.

1-(3,4-Dimethoxyphenyl)-2-[4-(hexyloxy)-3′,5-dimethoxybiphenyl-3-yl]-4,5-diphenyl-1*H*-imidazole (15)

Following GP1 using 4-(hexyloxy)-3′,5-dimethoxybiphenyl-3-carbaldehyde (326 mg, 0.95 mmol), 3,4-dimethoxyaniline (218 mg, 1.43 mmol), benzil (200 mg, 0.95 mmol), and NH_4OAc (367 mg, 4.76 mmol) in AcOH (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1). Crystallization (EtOAc/hexane) afforded a yellow crystalline solid; yield: 375 mg (59%); mp 157–158 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 2 H), 7.47–7.44 (m, 2 H), 7.27–7.22 (m, 6 H), 7.20–7.16 (m, 3 H), 7.05 (d, *J* = 2.1 Hz, 1 H), 6.93 (t, *J* = 5.8 Hz, 2 H), 6.59–6.54 (m, 3 H), 3.94 (t, *J* = 6.4 Hz, 2 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.75 (s, 3 H), 3.51 (s, 3 H), 1.60–1.54 (m, 2 H), 1.29–1.23 (m, 2 H), 1.22–1.16 (m, 4 H), 0.78 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 152.8, 148.1, 148.0, 146.6, 145.3, 137.5, 136.5, 134.7, 133.1, 131.2, 130.9, 129.7, 129.5, 128.4, 128.0 (2 signals), 127.8, 127.4, 126.9, 126.3, 121.9, 119.8, 114.1, 112.0, 111.4, 110.2, 74.2, 55.9, 55.7 (2 signals), 55.3, 31.6, 30.1, 25.6, 22.6, 14.0.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{43}H_{44}N_2O_5$: 668.3250; found: 668.3256.

3-(Hexyloxy)-2,9,10,13-tetramethoxy-5,6-diphenylimidazo[1,2-*f*]naphtho[1,2,3,4-*lmn*]phenanthridine (16)

Following GP2 using **15** (85 mg, 0.13 mmol, 1 equiv), PIFA (136 mg, 0.32 mmol, 2.5 equiv), and $BF_3{\cdot}Et_2O$ (40 µL, 0.32 mmol, 2.5 equiv) in dry toluene (20 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1). Crystallization (EtOAc/hexane) afforded a white crystalline solid; yield: 69 mg (82%); mp 77–78 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.30 (d, *J* = 2.7 Hz, 1 H), 8.50 (d, *J* = 9.2 Hz, 1 H), 8.20 (s, 1 H), 7.73–7.69 (m, 2 H), 7.68–7.61 (m, 4 H), 7.60–7.56 (m, 1 H), 7.34 (s, 1 H), 7.32 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.29–7.24 (m, 2 H), 7.23–7.19 (m, 1 H), 4.44 (t, *J* = 6.9 Hz, 2 H), 4.17 (s, 3 H), 4.00 (s, 3 H), 3.85 (s, 3 H), 3.38 (s, 3 H), 2.26–2.17 (m, 2 H), 1.69–1.62 (m, 2 H), 1.50–1.36 (m, 4 H), 0.94 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 153.0, 150.7, 145.1, 143.8, 141.4, 140.3, 134.8, 134.1, 132.1, 129.9, 129.7, 129.2, 128.6, 127.9, 127.8, 126.8, 125.0, 124.4, 124.3, 124.2, 123.0, 117.2, 117.1, 116.4, 113.4, 110.4, 106.8, 101.3, 73.7, 60.4, 57.0, 55.3, 55.1, 32.0, 30.5, 25.8, 22.8, 14.2.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{43}H_{40}N_2O_5$: 664.2937; found: 664.2941.

2,2′-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(1-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (17)

Following GP1 using 9,9-dioctyl-9*H*-fluorene-2,7-dicarbaldehyde (500 mg, 0.91 mmol), 3,4-dimethoxyaniline (418 mg, 2.73 mmol), benzil (383 mg, 1.82 mmol), and NH_4OAc (702 mg, 9.11 mmol) in AcOH/toluene (4:1, 50 mL. The product was isolated by chromatography (silica gel, hexanes/EtOAc, 4:1). Crystallization (EtOAc/hexane) afforded a yellow crystalline solid; yield: 0.72 g (72%); mp 145–146 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.4 Hz, 4 H), 7.58–7.52 (m, 4 H), 7.36 (s, 2 H), 7.28–7.18 (m, 12 H), 7.16 (dd, *J* = 7.7, 1.6 Hz, 4 H), 6.70 (d, *J* = 8.5 Hz, 2 H), 6.65 (dd, *J* = 8.5, 2.2 Hz, 2 H), 6.52 (d, *J* = 2.3 Hz, 2 H), 3.84 (s, 6 H), 3.56 (s, 6 H), 1.69–1.62 (m, 4 H), 1.24–1.17 (m, 4 H), 1.17–1.05 (m, 8 H), 1.01–0.89 (m, 8 H), 0.82 (t, *J* = 7.2 Hz, 6 H), 0.44–0.36 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.6, 149.0, 148.7, 147.3, 140.6, 138.2, 134.5, 131.1, 130.9, 130.2, 129.4, 128.4, 128.2, 127.9, 127.4, 126.6, 123.0, 120.6, 119.7, 111.8, 110.6, 55.9, 55.8, 55.0, 40.3, 31.9, 30.0, 29.4, 29.3, 23.8, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{75}H_{79}N_4O_4$: 1099.6101; found: 1099.6108.

ImPhen 18

Following GP2 using **17** (100 mg, 0.09 mmol, 1 equiv), PIFA (195 mg, 0.45 mmol, 5 equiv), and $BF_3{\cdot}Et_2O$ (115 µL, 0.90 mmol, 10 equiv) in dry toluene (20 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1 to 2:1). Crystallization (hexane) afforded a white crystalline solid; yield: 88 mg (88%); mp 337–339 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.92 (s, 2 H), 8.79 (s, 2 H), 8.06 (s, 2 H), 7.69–7.65 (m, 4 H), 7.65–7.57 (m, 8 H), 7.57–7.52 (m, 2 H), 7.29 (t, *J* = 7.4 Hz, 4 H), 7.25–7.20 (m, 2 H), 7.02 (s, 2 H), 4.12 (s, 6 H), 3.31 (s, 6 H), 2.39–2.31 (m, 4 H), 1.13–0.99 (m, 16 H), 0.98–0.91 (m, 4 H), 0.74 (t, *J* = 7.1 Hz, 6 H), 0.72–0.65 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.3, 149.3, 146.4, 142.9, 141.5, 134.6, 133.6, 132.3, 129.5, 129.2, 128.2 (2 signals), 128.0, 127.2, 127.0, 124.6, 123.2, 118.9, 116.3, 112.7, 106.5, 101.1, 56.9, 55.8, 55.0, 41.4, 31.8, 30.1, 29.5, 29.2, 24.2, 22.5, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{75}H_{75}N_4O_4$: 1095.5788; found: 1095.5798.

2,5-Bis[1-(3,4-bis(hexyloxy)phenyl]-4,5-diphenyl-1*H*-imidazol-2-yl)thieno[3,2-*b*]thiophene (19)

Following GP1 using thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde (65 mg, 0.33 mmol), 3,4-bis(hexyloxy)aniline (293 mg, 1.00 mmol), benzil (140 mg, 0.66 mmol), and NH_4OAc (256 mg, 3.33 mmol) in AcOH/toluene (2:1, 30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 6:1). Crystallization (EtOAc/hexane) afforded a yellow crystalline solid; yield: 110 mg (29%); mp 263–264 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.2 Hz, 4 H), 7.25–7.14 (m, 16 H), 6.83 (d, *J* = 6.8 Hz, 4 H), 6.79 (dd, *J* = 8.4, 2.1 Hz, 2 H), 6.68 (d, *J* = 1.9 Hz, 2 H), 4.01 (t, *J* = 6.6 Hz, 4 H), 3.81 (t, *J* = 5.7 Hz, 4 H), 1.89–1.80 (m, 4 H), 1.73–1.65 (m, 4 H), 1.55–1.45 (m, 4 H), 1.41–1.26 (m, 20 H), 0.93 (t, *J* = 7.0 Hz, 6 H), 0.89 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 149.1, 142.2, 139.8, 138.4, 135.5, 134.2, 131.7, 130.9, 130.4, 128.8, 128.3, 128.1, 128.0, 127.3, 126.7, 121.3, 117.9, 114.1, 112.8, 69.3, 69.2, 31.6, 31.5, 29.2, 28.9, 25.7, 25.5, 22.6, 22.5, 14.0 (2 signals).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{72}H_{81}N_4O_4S_2$: 1129.5699; found: 1129.5707.

ImPhen 20

Following GP2 using **19** (26 mg, 0.02 mmol, 1 equiv), PIFA (47 mg, 0.11 mmol, 5 equiv), and $BF_3{\cdot}Et_2O$ (28 µL, 0.22 mmol, 10 equiv) in dry toluene (20 mL). Crystallization ($CHCl_3$/hexane) afforded a yellow crystalline solid which is unstable in the presence of strong daylight; yield: 21 mg (81%); mp 302–304 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.61 (m, 8 H), 7.61–7.53 (m, 8 H), 7.29–7.20 (m, 6 H), 6.97 (s, 2 H), 4.20 (t, *J* = 6.3 Hz, 4 H), 3.31 (t, *J* = 6.8 Hz, 4 H), 1.95–1.87 (m, 4 H), 1.69–1.62 (m, 4 H), 1.62–1.54 (m, 4 H), 1.44–1.33 (m, 20 H), 1.00–0.93 (m, 12 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.8, 146.9, 140.1, 134.5, 133.8, 133.6, 132.6, 129.5, 129.2, 128.1 (2 signals), 127.8, 127.0, 124.3, 113.7, 108.0, 102.2, 69.7, 68.3, 31.8, 31.6, 29.3, 28.9, 25.9, 25.5, 22.7, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{72}H_{77}N_4O_4S_2$: 1125.5386; found: 1125.5393.

2-(4,7-Dimethoxynaphthalen-1-yl)-1-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (21)

Following GP1 using 4,7-dimethoxy-1-naphthaldehyde (108 mg, 0.5 mmol), 3,4-dimethoxyaniline (115 mg, 0.75 mmol), benzil (105 mg, 0.5 mmol), and NH_4OAc (193 mg, 2.5 mmol) in AcOH (30 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:1). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 153 mg (73%); mp 181–182 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 9.2 Hz, 1 H), 7.69–7.66 (m, 2 H), 7.52 (d, *J* = 1.7 Hz, 1 H), 7.29–7.22 (m, 8 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 7.10 (dd, *J* = 9.2, 2.5 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 1 H), 6.49 (d, *J* = 8.6 Hz, 1 H), 6.41 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.36 (d, *J* = 2.3 Hz, 1 H), 3.94 (s, 3 H), 3.83 (s, 3 H), 3.72 (s, 3 H), 3.37 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.6, 156.3, 148.3, 148.0, 146.5, 135.2, 131.1, 130.6, 129.5, 128.5, 128.1, 127.9, 127.3, 126.5, 123.8, 120.7, 119.9, 117.0, 111.2, 110.2, 105.1, 101.2, 55.7, 55.6, 55.4, 55.3.

HRMS (EI): *m*/*z* [M] calcd for $C_{35}H_{30}N_2O_4$: 542.2206; found: 542.2210.

6,7,7′-Trimethoxy-2,3-diphenyl-4′*H*-spiro[imidazo[1,2-*a*]indole-9,1′-naphthalen]-4′-one (22)

Following GP2 using **21** (48 mg, 0.09 mmol, 1 equiv), PIFA (76 mg, 0.18 mmol, 2 equiv), and $BF_3{\cdot}Et_2O$ (56 µL, 0.44 mmol, 5 equiv) in dry toluene (20 mL). The product was isolated by chromatography (silica gel, hexanes/EtOAc, 3:2). Crystallization (EtOAc/pentane) afforded a white crystalline solid; yield: 37 mg (78%); mp 280–281 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.8 Hz, 1 H), 7.65 (dd, *J* = 7.6, 1.5 Hz, 2 H), 7.60–7.55 (m, 3 H), 7.54–7.51 (m, 2 H), 7.22–7.18 (m, 2 H), 7.17–7.14 (m, 1 H), 6.97 (dd, *J* = 8.8, 2.5 Hz, 1 H), 6.71 (AB, *J* = 9.6 Hz, 2 H), 6.48 (s, 1 H), 6.43 (s, 1 H), 6.20 (d, *J* = 2.4 Hz, 1 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.62 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 183.8, 163.2, 153.8, 149.7, 147.5, 144.7, 143.6, 142.1, 133.5, 131.7, 130.8, 130.1, 129.9, 129.8, 129.6, 129.4, 129.1, 128.2, 127.0 (2 signals), 125.6, 123.5, 113.5, 113.0, 108.5, 97.2, 56.5, 56.0, 55.4, 49.7.

HRMS (EI): *m*/*z* [M] calcd for $C_{34}H_{26}N_2O_4$: 526.1893; found: 526.1885.

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