Superacid-Promoted Synthesis of Imidazole-Containing Spirocycles

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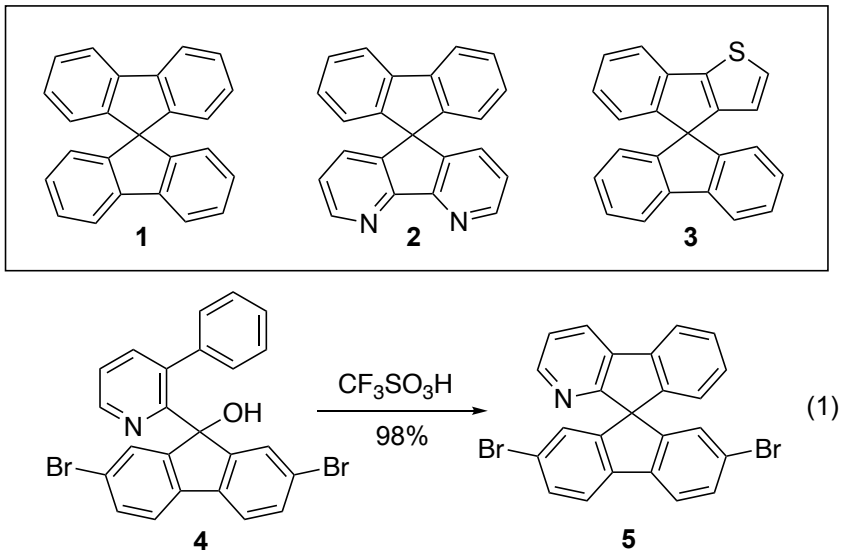
Abstract

A series of imidazole-containing fluorenyl spirocycles have been prepared from 9-fluorenol derivatives. Highly acidic media and superacid media are shown to promote spirocyclization to this new class of spirocycles. A mechanism is proposed involving fluorenyl cationic species, including dicationic ions. Electrochemical and optical experiments were conducted for the calculation of frontier molecular orbital energy levels. Fluorescence spectroscopy showed that select conjugated fluorophores were intensely emissive in the near-UV visible (blue-purple) spectrum range.

Introduction

Aromatic spirocycles have been of great interest in recent years, due in large part to their use in organic-based electronics.[1] For example, 9,9'-spirobifluorene (**1**) and related spirocycles have been used in organic light emitting diodes and other devices.[2] These compounds have high thermal stabilities, amorphous solid phase, and orthogonal π-systems – facilitating the design of hole-carrying, electron-carrying, and emissive layers. Many heteroaromatic derivatives (i.e., **2**-

3) have also been prepared and these often exhibit novel properties due to the effects of the heteroatoms on the systems.[3] The spirocyclic scaffold is most often prepared from the reactions

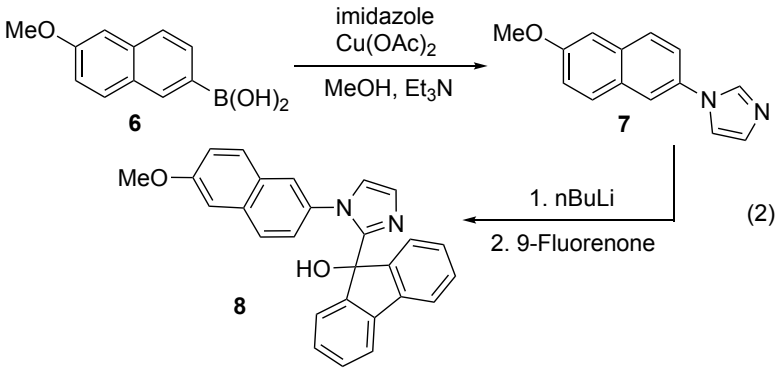


of fluorenols in acidic media (eq 1).[4] Despite considerable effort to incorporate heteroatoms in these aromatic spirocycles, there has yet to be successful syntheses of imidazole-containing fluorenyl spirocycles. A recent patent has described the synthesis of benzimidazole-containing spirocycles.[5] Beyond that intellectual property disclosure, this is largely an unexplored area of chemistry. In the following manuscript, we describe a synthetic route to structurally diverse spirocycles with imidazole ring-substructures.

Results and Discussion

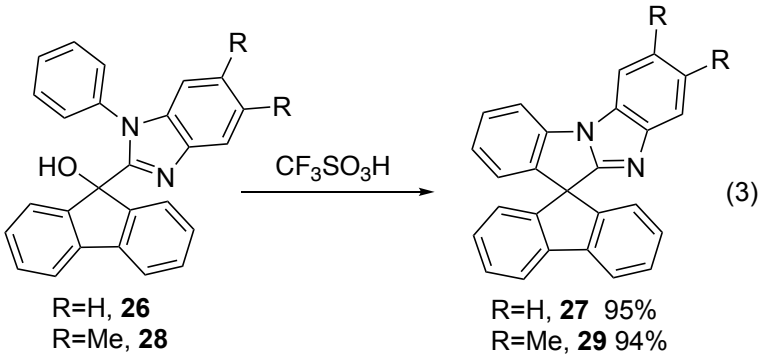
We hypothesized that *N*-arylimidazole groups could undergo cyclizations to the imidazole-containing spirocycles from the appropriately-substituted fluorenol. The 2-position of the

imidazole ring is readily deprotonated, allowing for 1-arylimidazoles to be used to prepare 9-fluorenols by reaction with 9-fluorenone (eq 2). Although 1-phenylimidazole is commercially available, more diverse structures may be prepared by the copper mediate C-N coupling of imidazoles and aryl boronic acids (eq 2).[6] Thus, the naphthyl boronic acid **6** is coupled to imidazole to provide derivative **7** in 27% isolated yield. Upon lithiation and reaction with 9-fluorenone, the 9-fluorenol **8** is obtained in 37% isolated yield. Other 9-fluorenols were obtained from *N*-arylimidazoles in yields ranging from 27-82% (12 examples). Although some coupling reactions were accomplished in good yields, this method typically gave the *N*-aryl-imidazole in less than 50% yield.



With the fluorenol derivatives in hand, cyclizations reactions were done using strongly acidic media (Table 1).[4] For example, fluorenol **9** from *N*-phenylimidazole reacts in excess triflic acid to provide the spirocycle **10** in quantitative yield. Substitution with methyl or methoxy groups likewise provided excellent yields of the imidazole-containing spirocycles **12** and **14**. Starting from 2,7-dibromofluorenone, the fluorenol **15** was prepared which cyclized cleanly to spirocycle **16** in 98% yield from a reaction with triflic acid. Extended aromatic systems can be useful in optimizing redox chemistry or absorption/emission characteristics for spirocycles. In

this regard, several large aryl groups were used. Thus, the naphthyl-substituted fluorenols (**8** and **20**) were prepared and the cyclization provided the spirocycles (**17** and **21**) in excellent yield. In both cases, cyclization occurred regioselectively, despite the potential to generate a pair of regioisomers. Structural assignments were made using DQF-COSY NMR analysis. Other spirocycles prepared include the dibenzofuran derivative (**19**), the phenanthrene derivative (**23**), and the pyrene derivative (**24**). These structural assignments were confirmed by NMR analysis. In all cases, the imidazole-containing fluorenols provided the spirocyclic products in excellent yield. Likewise, the benzimidazole substrates (**24** and **26**) gave the spirocyclic products (**25** and **27**) in almost quantitative yields (eq 5).

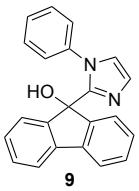
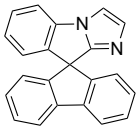
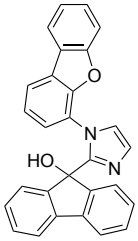
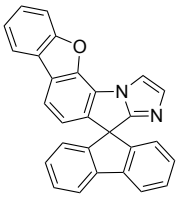
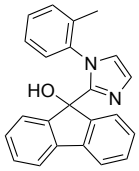
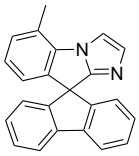
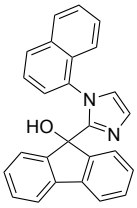
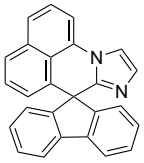
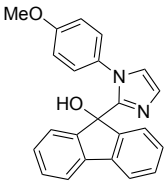
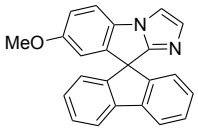
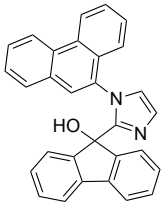
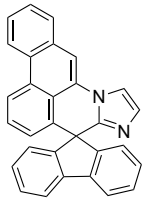
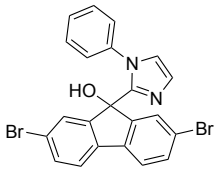
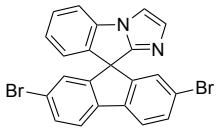
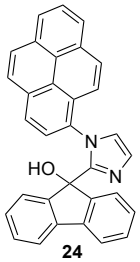
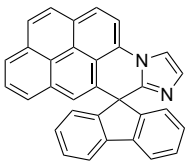
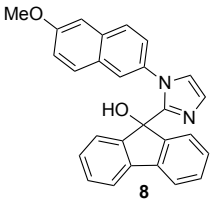
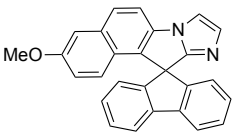


(3)

In addition to the fully unsaturated spirocycles, benzyl imidazole provided excellent yields of the imidazole-containing spirocycles (Table 2). Thus, benzyl imidazole was lithiated with nBuLi and reacted with 9-fluorenone to provide the fluorenol **30**. When this substrate was reacted with triflic acid, the resulting spirocycle **31** was isolated in quantitative yield. The nitro- and bromo-substituted fluorenols (**32** and **34**) also provided the respective spirocycles (**33** and **35**) in very high yields. Other ring systems provide spirocycles from the benzylimidazole, including the 2-oxindole and the xanthene (**36** and **38**). Thus, the spiro 2-oxindole **37** is isolated

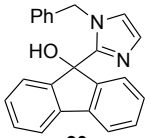
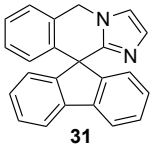
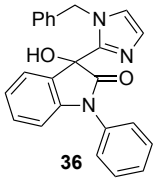
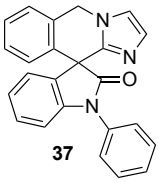
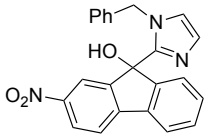
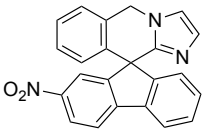
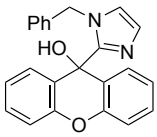
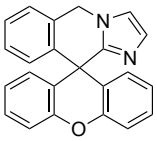
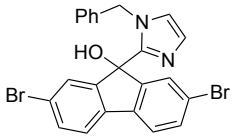
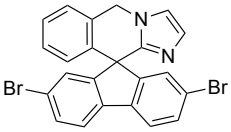
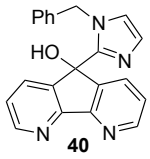
in 83% yield, while the spiro xanthene **39** is isolated in 91% yield. In the later case, xanthydrol **38** did not provide the spirocycle **38** in the reaction with superacidic CF_3SO_3H, but only provided the spirocycle **39** when a weaker acid system was used (HCl, AcOH). Alcohol **40** did not provide the expected spirocycle, but rather the starting material (**40**) was recovered.

Table 1. Products and isolated yields from acid-promoted cyclizations.

Starting Material	Product	Starting Material	Product
 **9**	 **10** 99%[a]	 **18**	 **19** 97%[a]
 **11**	 **12** 99%[a]	 **20**	 **21** 92%[a]
 **13**	 **14** 97%[b]	 **22**	 **23** 99%[a]
 **15**	 **16** 98%[a]	 **24**	 **25** 86%[b]
 **8**	 **17** 99%[b]		

[a]1 mmol fluorenol, 30 mmol CF_3SO_3H, 25°, 12 hrs.
[b]1 mmol fluorenol, 30 mmol CF_3CO_2H:CF_3SO_3H (3:7), 25°, 12 hrs.

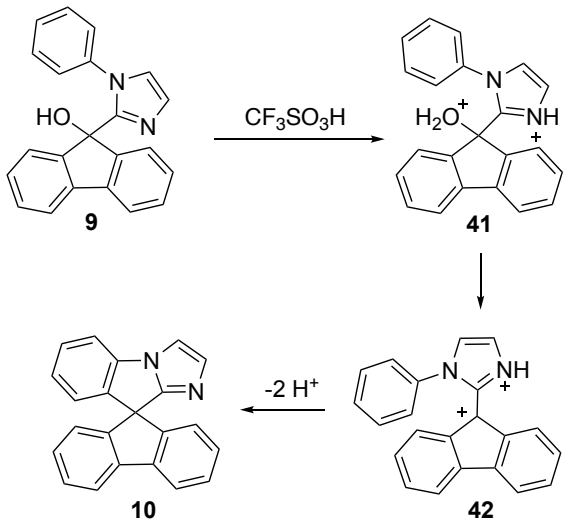
Table 2. Products and isolated yields from acid-promoted cyclizations.

Starting Material	Product	Starting Material	Product
 **30**	 **31** 99%[a]	 **36**	 **37** 83%[a]
 **32**	 **33** 97%[a]	 **38**	 **39** 91%[b]
 **34**	 **35** 99%[a]	 **40**	No Reaction[a,b]

[a]1 mmol substrate, 30 equiv TfOH in $CHCl_3$ [b]2 mmol substrate, 2 mL AcOH, 1 HCl

These superacid promoted reactions to the spirocycles likely involve formation of dicationic electrophilic species.[7] For example, ionization of compound **9** in superacid would involve protonation of the imidazole and then the hydroxy group to form the dication **41** (Scheme 1). Loss of water then gives the fluorenyl dication **42**, which undergoes cyclization to the spirocycle **10**. In the case of substrate **40**, no reaction conditions were found to give the desired spirocyclic product. This suggests that protonation of the nitrogen base sites gives dication **43** and this species is unable to undergo further ionization at the diazafluorenol group, presumably due to the instability of the tricationic intermediate that would form (Scheme 2). Likewise, substrates **8**, **13**, and **24**, required weaker acid (3:7, CF_3CO_2H:CF_3SO_3H) to promote the spiro cyclizations. This may be a consequence of the stronger acid, 100% CF_3SO_3H, protonating the aryl group – rendering it less reactive as an internal nucleophile for the cyclization. Thus for

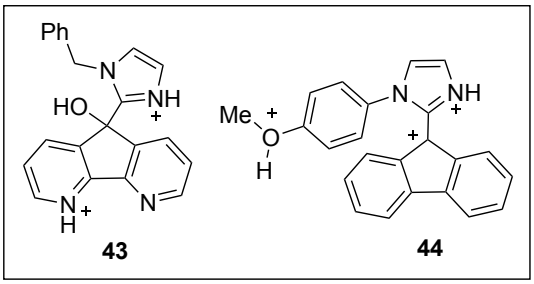
Scheme 1.

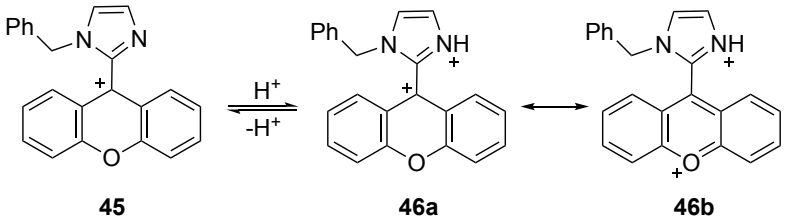


compound **13**, the stronger acid may be generating species such as **44**, which prevents cyclization. The xanthinol **38** only formed the spirocycle **38** in relatively weak acidic media (CH_3CO_2H:HCl). We speculate that this system forms an equilibrium between **45** and **46** – with cyclization occurring only through the monocationic intermediate **45**. In stronger acids, the dicationic species **46** is formed. Through charge-charge repulsive effects, it is likely that the dibenzopyrylium ion **46b** becomes increasingly important compared to the localized carbocation structure **46a**. With **45**, the reverse is true. The localized carbocation structure is important, and consequently the cyclization can occur with the monocation **45**.

Absorption and emission spectroscopy was done on all fully conjugated spirocycle products (**10, 12, 14, 16, 17, 19, 21, 23, and 25**). For each tested compound, spectra showed the emission characteristics of the two distinct chromophores. The fluorenyl chromophores' emission maxima were consistently observed at ~295 nm, and all of the aryl imidazole

Scheme 2.





chromophores were substantially or entirely emissive in the ultraviolet range. However, the aryl imidazole chromophores of compounds **17**, **21**, and **23** exhibited a substantial portion of its emissive characteristics in the purple/near UV portion of the visible region (Figure 1). Furthermore, these three aryl imidazole chromophores exhibited exceptionally large emission peak maxima relative to that of their corresponding fluorenyl chromophores.

Conclusion

Nitrogen-containing spirocycles may be readily prepared using *N*-aryl imidazoles or benzimidazoles and fluorene or aza-fluorene components. With preparation of the fluorenol precursors, spirocyclizations occur efficiently in superacid media. Weaker acids are used in cases where over protonation can occur. Mechanisms are proposed involving dicationic intermediates. Some of the resulting spirocycles show fluorescence in the near-UV and purple region of the visible spectrum.

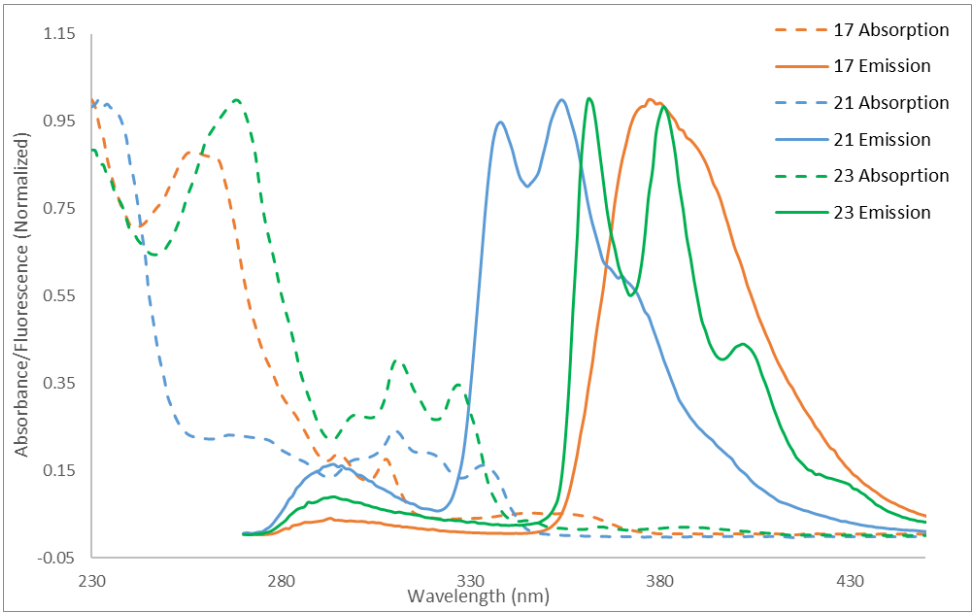


Figure 1. *UV/Vis absorption/emission spectroscopy for select spirocycles.*

Experimental Section

General Experimental Details

All reactions were performed in oven-dried glassware with magnetic stirring. Air and moisture sensitive liquids were transferred by syringe. Purification of the reaction products was carried out by column chromatography using silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm). Reagents and solvents were purchased from commercial suppliers and used as received. Synthetic reactions were done using oven-dried glassware under an inert atmosphere. Low-resolution mass spectra were obtained from an Agilent 6890 gas chromatograph equipped with a 5973 mass-selective detector. High-resolution mass spectra were obtained from a Bruker Maxis Plus Quadrupole Time-of-Flight mass spectrometer. Proton and carbon NMR spectra were obtained from Bruker

Avance III NMR spectrometers (300 or 500 MHz) with solvent resonance as the internal standard. (1H NMR: CDCl3 at 7.26 ppm; 13C NMR: CDCl3 at 77.16 ppm). 1H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet), coupling constant(s) in Hz, and integration. Cyclic Voltammetry (CV) measurements were carried out in a standard 3-electrode electrochemical cell in 0.1 M Bu_4NPF_6 in CH_2Cl_2 as an electrolyte with a 2 mm diameter Pt button working electrode, Pt wire auxiliary electrode, and Ag/Ag^+ reference electrode using Autolab PGSTAT 302 potentiostat from Eco Chemie. The data was corrected by the CV of ferrocene/ferrocene$^+$ under the same conditions immediately before and after the measurements. UV-visible spectra were recorded on Varian Cary 50 UV-Vis spectrophotometer. Fluorescence studies were carried out with a PTA QuantaMaster4/2006SE spectrofluorimeter.

Procedure A: General Procedure for Spirocycle Formation:

The flourenyl alcohol (1 equiv) was added to an oven dried round bottom flask equipped with a magnetic stirbar. The mixture was thoroughly stirred in 10 mL of chloroform or methylene chloride, after which triflic acid (30 equiv) was added dropwise via syringe. The reaction flask was sealed and allowed to stir overnight at room temperature. The reaction mixture was then quenched on ice and made basic with sodium bicarbonate, and 20 mL of additional methylene chloride was added. The organic layer was washed with water and then brine, allowed to dry over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified via silica gel column chromatography, when necessary, to give the spirocyclic product.

Procedure B: General Procedure for Flourenyl Alcohol Formation:

The N-aryl heterocycle (1 equiv) was added to an oven dried side arm round bottom flask equipped with a magnetic stirbar. The starting material was thoroughly stirred in anhydrous tetrahydrofuran (THF), and the flask was evacuated and subsequently flushed with nitrogen three times. The solution was cooled to -78°C, after which a solution of butyllithium (1.3 equiv) was added dropwise via syringe. The reaction flask was allowed to stir at constant temperature for 30 minutes, after which a solution of the carbonyl compound dissolved in anhydrous THF (1 equiv) was added slowly via syringe. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours before being quenched with 10 mL of a concentrated aqueous ammonium chloride solution. The solution was extracted using methylene chloride and water, and the organic layer was subsequently washed with water and then brine, allowed to dry over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified via silica gel column chromatography to give the fluorenyl alcohol.

Procedure C: General Procedure for N-Aryl Heterocycle Formation:

In a pressure tube, a mixture of the N-heterocycle (1 equiv) and the aryl boronic acid (1 equiv) was dissolved in methanol. While stirring, triethylamine (5 equiv) and then cupric acetate (10% mol) was added. The mixture was refluxed for 20 hours in a pressure tube, venting with air every few hours. The crude reaction mixture was concentrated in vacuo and the residue purified via silica gel column chromatography.

9-(1-phenyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (9)

Using procedure B, 1-phenylimidazole (0.11 mL, 0.125 g, 0.87 mmol), 9-flourenone (0.10 g, 0.58 mmol), and *t*-butyllithium (1.00 mmol) provides compound **9** (0.15 g, 0.46 mmol, 79%) as a white solid after silica gel column chromatography. m.p. = 170-173°C; R_f = 0.37 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (t, J = 4.80 Hz, 2H), 7.23-7.14 (m, 7H), 7.00 (t, 7.50 Hz, 1H), 6.86 (s, 1H), 6.78 (t, J = 7.80 Hz, 2H), 6.13 (d, J = 7.50 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 147.1, 140.5, 136.0, 129.2, 128.0, 127.8, 127.0, 126.0, 124.5, 124.3, 119.9, 79.3. HRMS calculated for $C_{22}H_{16}N_2O$ $[M + Na]^+$ m/z = 347.1155, found 347.1152.

Spiro[flourene-9,9'-imidazo[1,2-a]indole] (10)

Using procedure A, 9-(1-phenyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.03 g, 0.09 mmol), and triflic acid (0.2 mL, 0.8 mmol) provides compound **10** (0.028 g, 0.09 mmol, 99%) as a white solid after silica gel column chromatography. m.p. = 205-209°C; R_f = 0.57 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.50 Hz, 2H), 7.47-7.37 (m, 5H), 7.23-7.16 (m, 3H), 7.06 (td, J = 0.90 Hz, J = 7.50 Hz, 1H), 6.88 (d, J = 7.50 Hz, 2H), 6.78 (d, J = 7.50 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 145.8, 141.8, 140.6, 138.6, 134.0, 128.6, 128.1, 125.6, 125.1, 124.0, 120.5, 111.0, 58.2. HRMS calculated for $C_{22}H_{14}N_2$ $[M + Na]^+$ m/z = 329.1049, found 329.1048.

9-(1-(o-tolyl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (11)

Using procedure C, imidazole (0.1 g, 1.5 mmol), and *o*-tolyl boronic acid (0.19 g, 1.5 mmol) provides 1-(*o*-tolyl)imidazole (0.08 g, 0.51 mmol, 36%) as a yellow oil after silica gel column chromatography. R_f = 0.45 (ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.34-7.31

(m, 2H), 7.29-7.26 (m, 1H), 7.21-7.19 (m, 2H), 7.04 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 136.7, 133.9, 131.3, 129.4, 128.8, 126.9, 126.5, 120.5, 17.6. Using procedure B, 1-(o-tolyl)-1H-imidazole (0.08 g, 0.51 mmol), 9-fluorenone (0.09 g, 0.51 mmol), and *n*-butyllithium (0.6 mmol) provides compound **11** (0.13 g, 0.41 mmol, 79%) as a white solid after silica gel column chromatography. m.p. = 162-164°C; R_f = 0.5 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.29 (m, 2H), 7.27-7.13 (m, 7H), 6.94 (td, J = 1.20 Hz, J = 7.50 Hz, 1H), 6.80 (s, 1H), 6.71 (d, J = 7.50 Hz, 1H), 6.56 (t, J = 7.80 Hz, 1H), 5.90 (dd, J = 1.20 Hz, J = 7.80 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 146.0, 140.7, 140.2, 135.2, 134.7, 129.6, 129.3, 129.1, 128.4, 128.0, 127.6, 126.0, 125.4, 124.6, 124.4, 123.8, 120.1, 119.5, 79.4, 17.0. HRMS calculated for $C_{23}H_{18}N_2O$ $[M + H]^+$ m/z = 339.1492, found 339.1507.

5'-methylspiro[fluorene-9,9'-imidazo[1,2-a]indole] (12)

Using procedure A, 9-(1-(o-tolyl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.2 g, 0.59 mmol) and triflic acid (0.25 mL, 3.0 mmol) provides 5'-methylspiro[fluorene-9,9'-imidazo[1,2-a]indole] (0.19 g, 0.59 mmol, 99%) as a white solid after silica gel column chromatography. m.p. = 199-203°C; R_f = 0.5 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.80 Hz, 2H), 7.60 (s, 1H), 7.41 (t, J = 7.50 Hz, 2H), 7.18 (t, J = 8.40 Hz, 4H), 6.99-6.87 (m, 3H), 6.60 (d, J = 7.50 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 146.0, 141.7, 140.4, 137.8, 133.3, 130.9, 128.6, 128.2, 125.5, 124.0, 122.6, 122.1, 120.5, 113.6, 113.5, 58.1, 18.0. HRMS calculated for $C_{23}H_{16}N_2$ $[M + H]^+$ m/z = 321.1386, found 321.1393.

9-(1-(4-methoxyphenyl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (13)

Using procedure B, 1-(4-methoxyphenyl)imidazole (0.2 g, 1.1 mmol), 9-fluorenone (0.13 g, 0.73 mmol), and *t*-butyllithium (1.3 mmol) provides compound **13** (0.21 g, 0.58 mmol, 81%) as a white solid after silica gel column chromatography. m.p. = 180-182°C; R_f = 0.50 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.24-7.19 (m, 6H), 7.11 (d, J = 1.08 Hz, 1H), 6.83 (d, J = 1.08 Hz, 1H), 6.26 (d, J = 8.91 Hz, 2H), 6.03 (d, J = 8.91 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 149.5, 147.3, 140.5, 129.2, 128.7, 128.1, 128.0, 125.9, 124.5, 119.8, 113.0, 79.3, 55.5. HRMS calculated for $C_{23}H_{18}N_2O_2$ $[M + H]^+$ m/z = 355.1441, found 355.1443.

7'-methoxyspiro[fluorene-9,9'-imidazo[1,2-a]indole] (14)

Using a modified version of procedure A, 9-(1-(4-methoxyphenyl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.11 g, 0.31 mmol), trifluoroacetic acid (0.2 mL, 2.8 mmol), and triflic acid (0.6 mL, 6.5 mmol) provides compound **14** (0.101 g, 0.30 mmol, 97%) as a white solid after silica gel column chromatography. m.p. = 182-184°C; R_f = 0.56 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 7.62 Hz, 2H), 7.44-7.36 (m, 4H), 7.19 (qd, J = 1.05 Hz, J = 7.56 Hz, 3H), 6.92-6.88 (m, 3H), 6.32 (d, J = 2.52 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 156.0, 145.9, 142.0, 141.7, 133.5, 132.6, 128.5, 128.1, 124.0, 120.4, 113.4, 111.4, 111.3, 110.8, 58.5, 55.7. HRMS calculated for $C_{23}H_{16}N_2O$ $[M + H]^+$ m/z = 337.1335, found 337.1342.

2,7-dibromo-9-(1-phenyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (15)

Using procedure B, 1-phenylimidazole (0.1 mL, 0.79 mmol), 2,7-dibromofluorenone (0.26 g, 0.79 mmol), and *n*-butyllithium (1.03 mmol) provides compound **15** (0.11 g, 0.23 mmol, 29%) as a white solid after silica gel column chromatography. m.p. = 182-183°C; R_f = 0.33 (hexanes/ethyl acetate = 9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 1.25 Hz, 2H), 7.37 (dd, J = 8.05 Hz, J = 1.70 Hz, 2H), 7.16 (s, 1H), 7.08 (t, J = 2.25 Hz, 1H), 7.03 (d, J = 2.42 Hz, 2H), 6.92 (s, 1H), 6.87 (t, J = 8.10 Hz, 2H), 6.56 (s, 1H), 6.25 (dd, J = 8.40 Hz, J = 1.10 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 147.8, 138.4, 135.8, 132.5, 128.4, 128.2, 128.1, 127.1, 126.4, 124.6, 122.0, 121.3, 78.9. HRMS calculated for $C_{22}H_{14}N_2OBr_2$ $[M + H]^+$ m/z = 482.9531, found 482.9526.

2,7-dibromospiro[fluorene-9,9'-imidazo[1,2-a]indole] (16)

Using procedure A, 2,7-dibromo-9-(1-phenyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.04 g, 0.083 mmol), and triflic acid (0.22 mL, 2.3 mmol) provides compound **16** (0.1 g, 0.082 mmol, 98%) as a white solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.62 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.15 Hz, 2H), 7.54 (dd, J = 1.77 Hz, J = 8.15 Hz, 2H), 7.49-7.43 (m, 3H), 7.24 (d, J = 1.14, 1H), 7.12 (td, J = 1.21 Hz, J = 7.45 Hz, 1H), 6.99 (d, J = 1.66 Hz, 2H), 6.78 (d, J = 7.30 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 147.4, 139.7, 138.9, 138.7, 134.3, 132.0, 129.3, 127.4, 125.9, 125.2, 122.1, 121.8, 111.5, 111.3, 57.7. HRMS calculated for $C_{23}H_{14}N_2Br_2$ $[M + H]^+$ m/z = 464.9425, found 464.9421.

9-(1-(6-methoxynaphthalen-2-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (8)

Using procedure C, imidazole (0.17 g, 2.5 mmol), and 6-methoxy-2-naphthaleneboronic acid (0.5 g, 2.5 mmol) provides 1-(6-methoxynaphthalen-2-yl)-1H-imidazole (0.15 g, 0.67 mmol, 27%) as a brown solid after silica gel column chromatography. R_f = 0.42 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.72 (d, J = 9.05 Hz, 1H), 7.65 (d, J = 9.10 Hz, 1H), 7.60 (d, J = 1.95 Hz, 1H), 7.35 (dd, J = 2.50 Hz, J = 8.95 Hz, 1H), 7.24 (d, J = 9.95 Hz, 1H), 7.17 (d, J = 2.45 Hz, 1H), 7.15 (d, J = 2.50 Hz, 1H), 7.08 (d, J = 1.85 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 135.8, 133.4, 132.8, 130.3, 129.2, 128.8, 128.6, 120.7, 120.3, 119.0, 118.5, 105.7, 55.3. Using procedure B, 1-(6-methoxynaphthalen-2-yl)-1H-imidazole (0.11 g, 0.49 mmol), 9-fluorenone (0.09 g, 0.49 mmol), and *n*-butyllithium (0.65 mmol) provides compound **8** (0.074 g, 0.18 mmol, 37%) as a white solid after silica gel column chromatography. m.p. = 203-205°C; R_f = 0.38 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.40 Hz, 2H), 7.24-7.06 (m, 8H), 6.95-6.93 (m, 2H), 6.87 (d, J = 7.45 Hz, 2H), 6.40 (d, J = 1.30 Hz, 1H), 6.27 (dd, J = 1.95 Hz, J = 8.60 Hz, 1H), 5.95 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 149.4, 147.1, 140.4, 133.5, 131.2, 129.7, 129.1, 127.9, 127.6, 126.3, 126.0, 124.8, 124.4, 119.7, 119.1, 105.1, 79.3, 55.3. HRMS calculated for $C_{27}H_{20}N_2O_2$ $[M + H]^+$ m/z = 405.1598, found 405.1598.

3-methoxyspiro[benzo[e]imidazo[1,2-a]indole-11,9'-fluorene] (17)

Using a modified version of procedure A, 9-(1-(6-methoxynaphthalen-2-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.06 g, 0.15 mmol), triflouroacetic acid (0.1 mL, 1.3 mmol), and triflic acid (0.3 mL, 3.1 mmol) provides compound # (0.058 g, 0.15 mmol, 99%) as a white solid after silica gel column chromatography. m.p. = 220-224°C; R_f = 0.54 (hexanes/ethyl acetate = 7/3); ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.96-7.89 (m, 4H), 7.77 (d, J = 1.40 Hz, 1H), 7.46 (td, J = 0.70 Hz, J = 7.60 Hz, 2H), 7.15-7.10 (m, 3H), 6.77 (dd, J = 2.50 Hz, J = 9.25 Hz, 1H), 6.72 (d, J = 7.60 Hz, 2H), 6.63 (s, 1H), 6.53 (d, J = 9.25 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 155.2, 143.7, 141.5, 134.4, 134.0, 132.0, 129.8, 129.4, 129.0, 128.6, 124.4, 123.9, 123.4, 121.2, 112.5, 112.0, 107.1, 58.8, 55.3. HRMS calculated for $C_{27}H_{18}N_2O$ $[M + H]^+$ m/z = 387.1492, found 387.1493.

9-(1-(dibenzo[b,d]furan-4-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (18)

Using procedure C, imidazole (0.15 g, 2.2 mmol), and 4-dibenzylfuranboronic acid (0.46 g, 2.2 mmol) provides compound 1-(dibenzo[b,d]furan-4-yl)-1H-imidazole (0.087 g, 0.37 mmol, 17%) as a white solid after silica gel column chromatography. R_f = 0.44 (hexanes/ethyl acetate = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.94 (dd, J = 0.50 Hz, J = 7.65 Hz, 1H), 7.86 (dd, J = 1.10 Hz, J = 7.60 Hz, 1H), 7.62-7.57 (m, 2H), 7.50 (td, J = 1.25 Hz, J = 7.30 Hz, 1H), 7.44 (dd, J = 1.10 Hz, J = 7.85 Hz, 1H), 7.40-7.33 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 147.2, 128.1, 126.7, 123.6, 123.5, 121.0, 119.6, 119.3, 112.0. Using procedure B, 1-(dibenzo[b,d]furan-4-yl)-1H-imidazole (0.08 g, 0.34 mmol), 9-fluorenone (0.06 g, 0.34 mmol), and *n*-butyllithium (0.44 mmol) provides 9-(1-(dibenzo[b,d]furan-4-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.107 g, 0.26 mmol, 76%) as a white solid after silica gel column chromatography. m.p. = 195-198°C; R_f = 0.47 (hexanes/ethyl acetate = 7/3); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.65 Hz, 1 H), 7.63 (dd, J = 0.95 Hz, J = 7.70 Hz, 1H), 7.46-7.29 (m, 7H), 7.00-6.80 (m, 6H), 6.74 (t, J = 7.75 Hz, 1H), 6.11 (dd, J = 0.90 Hz, J = 7.70 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 150.5, 149.7, 146.2, 140.0, 128.9, 127.5, 126.6, 126.2, 125.0, 124.5, 124.2, 123.3, 123.0, 122.1, 121.0, 120.6, 120.5, 119.3, 111.9, 79.4. HRMS calculated for $C_{28}H_{18}N_2O_2$ $[M + H]^+$ m/z = 415.1441, found 415.1442.

spiro[benzofuro[3,2-g]imidazo[1,2-a]indole-4,9'-fluorene] (19)

Using procedure A, 9-(1-(dibenzo[b,d]furan-4-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.024 g, 0.06 mmol), and triflic acid (0.25 mL, 0.17 mmol) provides spiro[benzofuro[3,2-g]imidazo[1,2-a]indole-4,9'-fluorene] (0.023 g, 0.06 mmol, 97%) as a white solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.66 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.22 H, 2H), 7.90 (d, J = 7.69 Hz, 2H), 7.77 (t, J = 8.38 Hz, 2H), 7.62 (td, J = 1.20 Hz, J = 7.40 Hz, 1H), 7.51-7.46 (m, 3H), 7.35 (s, 1H), 7.22 (td, J = 0.78 Hz, J = 7.55 Hz, 2H), 6.85 (d, J = 7.62 Hz, 2H), 6.80 (d, J = 8.00 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 154.9, 142.9, 141.9, 141.3, 138.7, 130.6, 129.7, 129.3, 128.6, 127.4, 124.4, 124.0, 123.9, 123.3, 121.1, 119.2, 114.3, 112.3, 59.1. HRMS calculated for $C_{28}H_{16}N_2O$ $[M + H]^+$ m/z = 397.1335, found 397.1334.

9-(1-(naphthalen-1-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (20)

Using procedure C, imidazole (0.2 g, 2.9 mmol), and 1-naphthaleneboronic acid (0.5 g, 2.9 mmol) provides 1-(naphthalen-1-yl)-1H-imidazole (0.25 g, 1.3 mmol, 44%) as a white solid after silica gel column chromatography. R_f = 0.54 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, J = 1.30 Hz, J = 8.40 Hz, 2H), 7.76 (s, 1H), 7.61-7.49 (m, 4H), 7.44 (dd, J = 1.00 Hz, J = 7.25 Hz, 1H), 7.28 (d, J = 29.10 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 134.2, 134.1, 129.6, 129.5, 129.2, 128.3, 127.6, 127.0, 125.2, 123.6, 122.3, 121.7. Using procedure B, 1-(naphthalen-1-yl)-1H-imidazole (0.13 g, 0.67 mmol), 9-fluorenone (0.09 g, 0.5 mmol), and *n*-butyllithium (0.87 mmol) provides 9-(1-(naphthalen-1-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol

(0.156 g, 0.41 mmol, 82%) as a white solid after silica gel column chromatography. m.p. = 189-191°C; R_f = 0.26 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.15, 1H), 7.54 (d, J = 8.30 Hz, 1H), 7.48 (d, J = 3.50 Hz, 1H), 7.32-7.28 (m, 4H), 7.19-7.13 (m, 3H), 6.99 (s, 1H), 6.84 (t, J = 9.05 Hz, 1H), 6.76-6.73 (m, 2H), 6.63-6.57 (m, 2H), 6.12 (d, J = 7.15 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 149.7, 148.0, 145.5, 140.5, 139.4, 133.3, 132.4, 129.6, 129.1, 128.7, 128.1, 127.6, 127.3, 127.2, 126.2, 125.7, 125.3, 124.4, 124.3, 124.1, 124.0, 122.1, 119.9, 118.5, 79.6. HRMS calculated for $C_{26}H_{18}N_2O$ $[M + H]^+$ m/z = 375.1492, found 375.1490.

spiro[benzo[de]imidazo[1,2-a]quinoline-7,9'-fluorene] (21)

Using procedure A, 9-(1-(naphthalen-1-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.08 g, 0.21 mmol), and triflic acid (0.6 mL, 6.4 mmol) provides compound **21** (0.069 g, 0.19 mmol, 92%) as a white solid after silica gel column chromatography. m.p. = 247-249°C; R_f = 0.43 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.78 (m, 6H), 7.67 (t, J = 7.94 Hz, 1H), 7.41 (td, J = 0.61 Hz, J = 7.55 Hz, 2H), 7.31 (t, J = 7.73 Hz, 2H), 7.16 (td, J = 0.73 Hz, J = 7.55 Hz, 2H), 6.95 (d, J = 7.62 Hz, 1H), 6.79 (d, J = 0.67 Hz, 1H), 6.72 (dd, J = 0.43 Hz, J = 7.35 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 145.7, 140.0, 134.0, 133.9, 130.2, 128.7, 128.5, 127.7, 127.2, 126.5, 126.3, 125.4, 124.6, 120.9, 120.6, 114.1, 111.3, 56.6. HRMS calculated for $C_{26}H_{16}N_2$ $[M + H]^+$ m/z = 357.1386, found 357.1387

9-(1-(phenanthren-9-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (22)

Using procedure C, imidazole (0.15 g, 2.1 mmol), and 9-phenanthrene boronic acid (0.47 g, 2.1 mmol) provides 1-(phenanthren-9-yl)-1H-imidazole (0.074 g, 0.32 mmol, 15%) as a white solid

after silica gel column chromatography. R_f = 0.39 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, J = 8.35 Hz, 1H), 8.77 (d, J = 8.30 Hz, 1H), 7.96 (dd, J = 1.25 Hz, J = 8.25 Hz, 2H), 7.81-7.77 (m, 3H), 7.71 (td, J = 1.08 Hz, J = 6.94 Hz, 1H), 7.65 (td, J = 1.04 Hz, J = 8.15 Hz, 1H), 7.60 (dd, J = 0.86 Hz, J = 8.20 Hz, 1H), 7.39 (d, J = 21.26 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 132.6, 131.1, 130.6, 130.2, 129.6, 128.9, 128.6, 127.9, 127.8, 127.7, 127.5, 124.6, 124.5, 123.2, 123.1, 122.8, 121.8. Using procedure B, 1-(phenanthren-9-yl)-1H-imidazole (0.067 g, 0.27 mmol), 9-flourenone (0.05 g, 0.27 mmol), and *n*-butyllithium (0.35 mmol) provides compound # (0.054g, 0.13 mmol, 49%) as a white solid after silica gel column chromatography. m.p. = 193-195°C; R_f = 0.40 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 8.32 Hz, 1H), 8.44 (d, J = 8.26 Hz, 1H), 7.68 (td, J = 1.02 Hz, J = 8.15 Hz, 1H), 7.61 (d, J = 6.96 Hz, 1H), 7.56-7.50 (m, 2H), 7.37-7.32 (m, 3H), 7.25 (d, J = 7.31 Hz, 2H), 7.12 (d, J = 6.62 Hz, 2H), 6.90 (d, J = 7.45 Hz, 1H), 6.83 (d, J = 8.12 Hz, 1H), 6.53-6.47 (m, 2H), 6.40-6.36 (m, 2H); ^{13}C NMR (125 MHz, CH_3OD) δ 149.5, 148.1, 145.0, 140.2, 139.5, 130.8, 130.3, 130.0, 129.2, 128.3, 128.1, 127.8, 127.4, 127.0, 126.7, 126.6, 126.3, 126.1, 124.2, 124.1, 123.1, 122.1, 122.0, 119.9, 118.2, 79.6. HRMS calculated for $C_{30}H_{20}N_2O$ $[M + H]^+$ m/z = 425.1654, found 425.1648.

spiro[dibenzo[de,g]imidazo[1,2-a]quinoline-8,9'-fluorene] (23)

Using procedure A, 9-(1-(phenanthren-9-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.044 g, 0.10 mmol) and triflic acid (0.05 mL, 0.5 mmol) provides compound **23** (0.042 g, 0.10 mmol, 99%) as a white solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.43 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (dd, J = 2.21 Hz, J = 6.86 Hz, 1H), 8.63 (d, J = 8.13 Hz, 1H), 8.02-8.00 (m, 1H), 7.91-7.84 (m, 4H), 7.72-7.68 (m, 2H), 7.50 (t, J = 7.89 Hz, 1H),

7.41 (td, J = 0.64 Hz, J = 7.46 Hz, 2H), 7.19 (td, J = 0.80 Hz, J = 6.76 Hz, 3H), 7.03 (d, J = 7.62 Hz, 2H), 6.90 (dd, J = 0.52 Hz, J = 6.97 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 146.4, 140.3, 135.4, 131.6, 131.3, 131.0, 129.3, 128.8, 128.4, 128.3, 127.8, 126.7, 126.2, 124.6, 123.1, 122.0, 120.7, 120.6, 113.4, 110.1, 57.0. HRMS calculated for $C_{30}H_{18}N_2$ $[M + H]^+$ m/z = 407.1548, found 407.1543.

1-(pyren-1-yl)-1H-imidazole (24a)

Using procedure C, imidazole (0.11 g, 1.6 mmol), and 1-pyreneboronic acid (0.4 g, 1.6 mmol) provides 1-(pyren-1-yl)-1H-imidazole (0.12 g, 0.47 mmol, 29%) as a white solid after silica gel column chromatography. m.p. = 136-138°C; Rf = 0.34 (hexane/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 7.60 Hz, 1H), 8.15 (dd, J = 7.60, J = 10.20 Hz, 2H), 8.09 (d, J = 8.90 Hz, 1H), 8.04-8.01 (m, 3H), 7.87 (d, J = 8.05 H, 2H), 7.76 (d, J = 9.20 Hz, 1H), 7.41 (s, 1H), 7.36 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 131.4, 131.1, 130.9, 130.7, 129.8, 129.3, 128.4, 126.9, 126.7,126.6, 126.1, 125.8, 125.0, 124.8, 124.2, 123.8, 122.2, 121.0. HRMS calculated for $C_{19}H_{12}N_2$ $[M + H]^+$ m/z = 269.1073, found 269.1076.

9-(1-(pyren-1-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (24)

Using procedure B, 1-(naphthalen-1-yl)-1H-imidazole (0.1 g, 0.37 mmol), 9-fluorenone (0.065 g, 0.37 mmol), and *n*-butyllithium (0.48 mmol) provides compound **24** (0.09 g, 0.21 mmol, 56%) as a white solid after silica gel column chromatography. m.p. = 194-197°C; R_f = 0.32 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 7.43 Hz, 1H), 8.13 (d, J = 7.37 Hz, 1H), 8.08 (d, J = 8.92 Hz, 1H), 8.03 (t, J = 7.57 Hz, 1H), 7.92 (d, J = 8.92 Hz, 1H), 7.73 (d, J = 9.15 Hz,

1H), 7.55-7.52 (m, 2H), 7.37-7.31 (m, 2H), 7.26 (t, J = 7.34 Hz, 2H), 7.11 (s, 1H), 6.94-6.90 (m, 2H), 6.68 (d, J = 8.02 Hz, 1H), 6.52 (td, J = 0.66Hz, J = 7.35 Hz, 1H), 6.19 (d, J = 7.37 Hz, 1H), 6.12-6.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 147.6, 145.5, 140.6, 139.3, 131.2, 130.7, 130.3, 129.3, 128.3, 128.1, 128.0, 127.9, 127.5, 126.7, 126.4, 126.2, 125.7, 125.6, 125.2, 124.6, 124.3, 123.9, 123.7, 123.4, 121.3, 119.7, 118.3, 79.5. HRMS calculated for $C_{32}H_{20}N_2O$ $[M + H]^+$ m/z =449.1648, found 449.1647.

spiro[fluorene-9,7'-imidazo[1,2-a]phenaleno[1,9-fg]indole] (25)

Using a modified version of procedure A, 9-(1-(pyren-1-yl)-1H-imidazol-2-yl)-9H-fluoren-9-ol (0.055 g, 0.12 mmol), triflouroacetic acid (0.1 mL, 1.2 mmol), and triflic acid (0.25 mL, 2.8 mmol) provides compound **25** (0.045 g, 0.047 mmol, 86%) as a white solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.40 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 8.45 Hz, 1H), 8.48 (d, J = 2.10 Hz, 1H), 8.44 (d, J = 8.35 Hz, 1H), 8.19 (d, J = 7.35 Hz, 1H), 8.10 (s, 2H), 7.98-7.88 (m, 4H), 7.54-7.50 (m, 3H), 7.45 (s, 1H), 7.20 (t, J = 7.60 Hz, 2H), 7.10 (d, J = 7.70Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 144.8, 140.1, 131.6, 131.1, 130.7, 130.4, 129.3, 129.2, 128.9, 127.4, 127.3, 127.1, 127.0, 126.5, 124.7, 124.5, 123.5, 122.2, 119.0, 117.6, 116.9, 114.1, 55.3. HRMS calculated for $C_{32}H_{18}N_2$ $[M + H]^+$ m/z = 431.1543, found 431.1544.

9-(1-phenyl-1H-benzo[d]imidazol-2-yl)-9H-fluoren-9-ol (26)

Using procedure C, benzimidazole (0.5 g, 4.2 mmol), and phenyl boronic acid (0.51 g, 4.2 mmol) provides 1-phenyl-1H-benzo[d]imidazole (0.19 g, 0.97 mmol, 23%) as a yellow oil after silica gel

column chromatography. R_f = 0.38 (hexanes/ethyl acetate = 2/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.89 (d, J = 7.30 Hz, 1H), 7.53-7.30 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 142.3, 136.3, 133.6, 130.0, 128.0, 123.9, 123.7, 122.8, 120.6, 110.5. Using procedure B, 1-phenyl-1H-benzo[d]imidazole (0.19 g, 0.98 mmol), 9-flourenone (0.18 g, 0.98 mmol), and *n*-butyllithium (1.27 mmol) provides compound **26** (0.13 g, 0.34 mmol, 35%) as a white solid after silica gel column chromatography. m.p. = 159-160°C; R_f = 0.46 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.15 Hz, 1H), 7.41 (d, J = 7.10 Hz, 2H), 7.34 (t, J = 7.35 Hz, 1H), 7.29-7.17 (m, 7H), 7.12 (t, J = 7.50 Hz, 1H), 6.89 (t, J = 7.95 Hz, 2H), 6.76 (d, J = 8.05 Hz, 1H), 6.16 (d, J = 7.45 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 146.7, 140.8, 140.2, 139.3, 134.0, 129.5, 128.4, 128.1, 124.7, 123.4, 122.6, 120.1, 119.3, 110.5, 79.6. HRMS calculated for $C_{26}H_{18}N_2O$ $[M + H]^+$ m/z = 375.1492, found 375.1495.

spiro[benzo[4,5]imidazo[1,2-a]indole-11,9'-fluorene] (27)

Using procedure A, 9-(1-phenyl-1H-benzo[d]imidazol-2-yl)-9H-fluoren-9-ol (0.11 g, 0.29 mmol), and triflic acid (0.8 mL, 0.92 mmol) provides compound **27** (0.10 g, 0.276 mmol, 95%) as a white solid after silica gel column chromatography. m.p. = 220-224°C; R_f = 0.61 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (t, J = 9.85, 3H), 7.78 (t, J = 7.90 Hz, 2H), 7.52-7.44 (m, 4H), 7.36 (td, J = 1.0 Hz, J = 8.20 Hz, 1H), 7.21 (td, J = 0.95 Hz, J = 7.60 Hz, 2H), 7.10 (td, J = 0.80 Hz, J = 7.60 Hz, 1H), 6.95 (d, J = 7.60 Hz, 2H), 6.86 (d, J = 7.50 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 148.4, 145.7, 141.9, 139.3, 139.2, 130.0, 129.0, 128.8, 128.3, 125.2, 125.0, 124.2, 123.4, 122.9, 121.0, 120.6, 110.9, 110.6, 58.4. HRMS calculated for $C_{26}H_{16}N_2$ $[M + H]^+$ m/z =

357.1386, found 357.1386.

9-(5,6-dimethyl-1-phenyl-1H-benzo[d]imidazol-2-yl)-9H-fluoren-9-ol (28)

Using procedure C, 5,6-dimethylbenzimidazole (0.61 g, 4.2 mmol), and phenyl boronic acid (0.51 g, 4.2 mmol) provides the starting aryl imidazole (0.13 g, 0.58 mmol, 14%) as a yellow oil after silica gel column chromatography. R_f = 0.38 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.66 (s, 1H), 7.58-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.46-7.43 (m, 1H), 7.33 (s, 1H), 2.42 (s, 1H), 2.39 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 141.5, 136.7, 132.9, 132.2, 131.7, 130.0, 127.8, 123.9, 120.5, 110.6, 20.6, 20.3. HRMS calculated for $C_{15}H_{14}N_2$ $[M + H]^+$ m/z = 223.1235, found 223.1230. Using procedure B, 5,6-dimethyl-1-phenyl-1H-benzo[d]imidazole (0.12 g, 0.56 mmol), 9-flourenone (0.1 g, 0.56 mmol), and *n*-butyllithium (0.73 mmol) provides compound **28** (0.13 g, 0.32 mmol, 57%) as a white solid after silica gel column chromatography. m.p. = 159-160°C; R_f = 0.44 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.35 (d, J = 7.44 Hz, 2H), 7.26-7.18 (m, 6H), 7.10 (t, J = 7.52 Hz, 1H), 6.86 (t, J = 8.12 Hz, 2H), 6.51 (s, 1H), 6.12 (dd, J = 1.12 Hz, J = 8.36 Hz, 2H), 2.42 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 146.8, 140.8, 138.6, 137.9, 134.3, 132.7, 131.5, 129.4, 128.4, 128.1, 128.0, 124.7, 120.0, 119.4, 119.3, 110.5, 79.5, 20.3. HRMS calculated for $C_{28}H_{23}N_2O$ $[M + H]^+$ m/z = 403.1801, found 403.1805.

7,8-dimethylspiro[benzo[4,5]imidazo[1,2-a]indole-11,9'-fluorene] (29)

Using procedure A, 9-(5,6-dimethyl-1-phenyl-1H-benzo[d]imidazol-2-yl)-9H-fluoren-9-ol (0.04 g, 0.1 mmol), and triflic acid (0.25 mL, 3.0 mmol) provides compound **29** (0.036 g, 0.094 mmol,

94%) as a white solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.78 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 7.65 Hz, 2H), 7.74 (d, J = 7.75 Hz, 1H), 7.69 (s, 1H), 7.51-7.42 (m, 4H), 7.19 (td, J = 0.95 Hz, J = 7.55 Hz, 2H), 7.07 (td, J = 0.80 Hz, J = 7.60 Hz, 1H), 6.92 (d, J = 7.60, 2H), 6.82 (d, J = 7.55 Hz, 1H), 2.52 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 146.9, 145.9, 141.9, 139.4, 139.3, 132.5, 131.7, 128.9, 128.7, 128.4, 128.2, 125.1, 124.7, 124.2, 121.0, 120.6, 110.9, 110.8, 58.3, 20.7, 20.5. HRMS calculated for $C_{28}H_{20}N_2$ $[M + H]^+$ m/z = 385.1705, found 385.1699.

9-(1-benzyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (30)

Using procedure B, 1-benzylimidazole (0.15 g, 0.95 mmol), 9-flourenone (0.17 g, 0.95 mmol), and *t*-butyllithium (1.1 mmol) provides compound **30** (0.20 g, 0.69 mmol, 63%) as a white solid after silica gel column chromatography. m.p. = 145-146°C; R_f = 0.28 (hexanes/ethyl acetate = 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 7.50 Hz, 2H), 7.39-7.33 (m, 4H), 7.26-7.21 (m, 2H), 7.17-7.06 (m, 4H), 6.71 (s, 1H), 6.46 (d, J = 7.20 Hz, 2H), 4.16 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 146.7, 140.2, 135.5, 129.8, 128.6, 128.4, 127.6, 125.0, 122.4, 120.4, 79.2, 49.3. HRMS calculated for $C_{23}H_{18}N_2O$ $[M + H]^+$ m/z = 339.1492, found 339.1496.

5'H-spiro[fluorene-9,10'-imidazo[1,2-b]isoquinoline] (31)

Using procedure A, 9-(1-benzyl-1H-imidazol-2-yl)-9H-fluoren-9-ol (1.0 g, 3.0 mmol), and triflic acid (2.6 mL, 30 mmol) provides compound **31** (0.96 g, 2.96 mmol, 99%) as a white solid without further need for purification. m.p. = 204-205°C; R_f = 0.21 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 7.80 Hz, 2H), 7.39 (m, 2H), 7.28 (m, 2H), 7.21 (td, J = 7.50 Hz, J = 0.90 Hz, 2H), 7.10-7.00 (m, 5H), 6.58 (d, J = 7.80 Hz, 1H), 5.63 (s, 2H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 150.8, 145.6, 140.5, 136.3, 129.1, 128.4, 128.3, 127.9, 127.6, 127.5, 126.3, 124.6, 120.4, 118.5, 55.5, 47.8. HRMS calculated for $C_{23}H_{16}N_2$ $[M + Na]^+$ m/z = 343.1206, found 343.1202.

9-(1-benzyl-1H-imidazol-2-yl)-2,7-dibromo-9H-fluoren-9-ol (32)

Using procedure B, 1-benzylimidazole (0.10 g, 0.63 mmol), 2,7-dibromo-9-flourenone (0.17 g, 0.50 mmol), and *n*-butyllithium (0.82 mmol) provides 9-(1-benzyl-1H-imidazol-2-yl)-2,7-dibromo-9H-fluoren-9-ol (0.12 g, 0.24 mmol, 48%) as a white solid after silica gel column chromatography. m.p. = 117-120°C; R_f = 0.5 (hexanes/ethyl acetate = 4/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.39 (m, 6H), 7.17-7.10 (m, 4H), 6.84 (d, J = 0.90 Hz, 1H), 6.45 (d, J = 6.00 Hz, 2H), 4.25 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 146.7, 138.0, 135.0, 133.0, 128.6, 128.4, 127.8, 126.5, 126.1, 123.4, 122.8, 121.7, 78.8, 49.4. HRMS calculated for $C_{23}H_{16}N_2OBr_2$ $[M + H]^+$ m/z = 496.9683, found 496.9689.

2,7-dibromo-5'H-spiro[fluorene-9,10'-imidazo[1,2-b]isoquinoline] (33)

Using procedure A, 9-(1-benzyl-1H-imidazol-2-yl)-2,7-dibromo-9H-fluoren-9-ol (0.050 g, 0.09 mmol), and triflic acid (0.08 mL, 0.9 mmol) provides compound **33** (0.048 g, 0.09 mmol, 99%) as a yellow solid after silica gel column chromatography. m.p. > 260°C; R_f = 0.17 (hexanes/ethyl acetate = 4/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.10 Hz, 2H), 7.51 (dd, J = 1.50 Hz, J = 8.10 Hz, 2H), 7.43-7.32 (m, 2H), 7.15-7.08 (m, 4H), 7.03 (s, 1H), 6.53 (d, J = 7.80 Hz, 1H), 5.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 144.3, 138.6, 134.8, 131.7, 129.4, 129.0, 128.6, 128.0, 127.9, 126.5, 122.2, 122.0, 118.4, 55.5, 47.5. HRMS calculated for $C_{23}H_{14}N_2Br_2$ $[M + H]^+$ m/z = 478.9577, found 478.9587.

3-(1-benzyl-1H-imidazol-2-yl)-3-hydroxy-1-phenylindolin-2-one (34)

Using procedure B, 1-benzylimidazole (0.15 g, 0.95 mmol), 1-phenylisatin (0.16 g, 0.71 mmol), and *n*-butyllithium (1.2 mmol) provides 3-(1-benzyl-1H-imidazol-2-yl)-3-hydroxy-1-phenylindolin-2-one (0.09 g, 0.25 mmol, 35%) as a white solid after silica gel column chromatography. m.p. = 184-187°C; R_f = 0.5 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.39 (m, 4H), 7.31-7.28 (m, 4H), 7.24 (dd, J = 1.36 Hz, J = 8.72 Hz, 2H), 7.14-7.12 (m, 2H), 6.94 (dd, J = 2.30 Hz, J = 7.15 Hz, 2H), 6.86-6.84 (m, 2H), 5.03 (d, J = 15.56 Hz, 1H), 4.97 (d, J = 15.57 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 144.6, 143.9, 135.2, 133.7, 130.9, 129.7, 129.0, 128.4, 128.3, 127.8, 127.2, 126.2, 126.0, 124.3, 123.0, 122.8, 110.3, 74.5, 50.3. HRMS calculated for $C_{24}H_{19}N_3O_2$ $[M + H]^+$ m/z = 382.1550, found 382.1550.

1'-phenyl-5H-spiro[imidazo[1,2-b]isoquinoline-10,3'-indolin]-2'-one (35)

Using procedure A, 3-(1-benzyl-1H-imidazol-2-yl)-3-hydroxy-1-phenylindolin-2-one (0.09 g, 0.24 mmol), and triflic acid (0.6 mL, 7.1 mmol) provides compound **35** (0.072 g, 0.20 mmol, 83%) as a white/yellow solid after silica gel column chromatography. m.p. = 150-154°C; R_f = 0.26 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, J = 8.04 Hz, 2H), 7.46-7.37 (m, 6H), 7.28-7.22 (m, 3H), 7.15 (dd, J = 0.87 Hz, J = 7.31 Hz, 2H), 7.02 (d, J = 7.97 Hz, 1H), 6.92 (d, J = 7.73 Hz, 1H), 5.76 (d, J = 15.60, 1H), 5.32 (d, J = 15.64 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 144.9, 143.0, 134.4, 134.2, 132.2, 132.0, 129.6, 129.5, 129.3, 128.2, 128.1, 126.9, 126.7, 126.6, 126.1, 124.3, 119.2, 110.1, 55.2, 48.1. HRMS calculated for $C_{24}H_{17}N_3O$ $[M + H]^+$ m/z = 364.1444, found 364.1453.

9-(1-benzyl-1H-imidazol-2-yl)-2-nitro-9H-fluoren-9-ol (36)

Using procedure B, 1-benzylimidazole (0.16 g, 1 mmol), 2-nitroflourenone (0.16 g, 0.7 mmol), and *n*-butyllithium (1.3 mmol) provides 9-(1-benzyl-1H-imidazol-2-yl)-2-nitro-9H-fluoren-9-ol (0.071 g, 0.19 mmol, 27%) as a beige solid after silica gel column chromatography. m.p. = 191-192°C; R_f = 0.34 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, J = 2.11 Hz, J = 8.35 Hz, 1H), 8.02 (d, J = 1.99 Hz, 1H), 7.74 (d, J = 7.55 Hz, 1H), 7.65 (d, J = 8.37 Hz, 1H), 7.50-7.44 (m, 2H), 7.39 (td, J = 0.91 Hz, J = 7.50 Hz, 1H), 7.22 (d, J = 1.02 Hz, 1H), 7.11-7.03 (m, 3H), 6.87 (d, J = 1.25 Hz, 1H), 6.39 (d, J = 7.26 Hz, 2H), 4.37 (d, J = 16.01 Hz, 1H), 4.11 (d, J = 15.99 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 147.7, 147.6, 146.5, 146.2, 137.9, 135.2, 130.7, 130.4, 128.4, 127.6, 126.7, 125.8, 125.7, 125.4, 123.8, 121.6, 120.9, 120.3, 78.8, 49.4. HRMS calculated for $C_{23}H_{17}N_3O_3$ $[M + H]^+$ m/z = 384.1343, found 384.1344.

2-nitro-5'H-spiro[fluorene-9,10'-imidazo[1,2-b]isoquinoline] (37)

Using procedure A, 9-(1-benzyl-1H-imidazol-2-yl)-2-nitro-9H-fluoren-9-ol (0.032 g, 0.084 mmol), and triflic acid (0.2 mL, 0.23 mmol) provides compound **37** (0.0295 g, 0.081 mmol, 97%) as a yellow solid after silica gel column chromatography. m.p. = 249-251°C; R_f = 0.32 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, J = 2.10 Hz, J = 8.45 Hz, 1H), 7.96-7.92 (m, 2H), 7.84 (d, J = 1.98 Hz, 1H), 7.49-7.43 (m, 2H), 7.35 (td, J = 1.09 Hz, J = 7.55 Hz, 2H), 7.14 (d, J = 1.23 Hz, 1H), 7.12-7.05 (m, 3H), 6.53 (dd, J = 0.72 Hz, J = 8.00 Hz, 1H), 5.70 (d, J = 16.67 Hz, 1H), 5.65 (d, J = 16.68 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 152.7, 147.6, 147.2, 144.3, 138.2, 135.0, 130.4, 130.1, 129.5, 128.7, 128.4, 127.9, 127.7, 126.6, 125.0, 124.4, 121.9, 120.8, 120.3,

118.3, 56.0, 47.5. HRMS calculated for $C_{23}H_{15}N_3O_2$ $[M + H]^+$ m/z = 366.1237, found 366.1238.

9-(1-benzyl-1H-imidazol-2-yl)-9H-xanthen-9-ol (38)

Using procedure B, 1-benzylimidazole (0.2 g, 1.26 mmol), xanthone (0.17 g, 0.84 mmol), and *t*-butyllithium (1.43 mmol) provides compound **38** (0.13 g, 0.37 mmol, 44%) as a white solid after silica gel column chromatography. m.p. = 146-147°C; R_f = 0.50 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 7.19-7.06 (m, 8H), 6.71 (d, J = 0.90 Hz, 1H), 6.48 (t, J = 6.90 Hz, 2H), 4.30 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 150.0, 134.9, 129.8, 129.1, 128.5, 127.8, 127.4, 125.6, 123.7, 123.0, 122.3, 116.7, 66.2, 49.8. HRMS calculated for $C_{23}H_{18}N_2O_2$ $[M + H]^+$ m/z = 355.1441, found 355.1446.

5H-spiro[imidazo[1,2-b]isoquinoline-10,9'-xanthene] (39)

Using a modified version of procedure A, 9-(1-benzyl-1H-imidazol-2-yl)-9H-xanthen-9-ol (0.07 g, 0.2 mmol), 2 mL of acetic acid, and 1 mL of hydrochloric acid stirred overnight at 80°C provides compound **39** (0.61 g, 0.18 mmol, 91%) as a white solid after silica gel column chromatography. m.p. > 245-248°C; R_f = 0.22 (hexanes/ethyl acetate = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.25-7.19 (m, 5H), 7.11 (td, J = 1.01 Hz, J = 4.00 Hz, 2H), 7.06 (d, J = 0.93 Hz, 1H), 6.89 (td, J = 1.56 Hz, J = 6.57 Hz, 2H), 6.60 (dd, J = 1.28 Hz, J = 7.80 Hz, 2H), 5.55 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 149.8, 141.5, 131.7, 130.3, 129.3, 128.6, 128.3, 127.9, 127.1, 126.9, 125.4, 123.4, 117.1, 116.8, 47.1, 44.4. HRMS calculated for $C_{23}H_{16}N_2O$ $[M + H]^+$ m/z = 337.1335, found 337.1335.

5-(1-benzyl-1H-imidazol-2-yl)-5H-cyclopenta[1,2-b:5,4-b']dipyridin-5-ol (40)

Using procedure B, 1-benzylimidazole (0.1 g, 0.63 mmol), 4,5-diazaflourenone (0.08 g, 0.42 mmol), and *n*-butyllithium (0.72 mmol) provides compound **42** (0.08 g, 0.26 mmol, 61%) as a white solid after silica gel column chromatography. m.p. = 174-175°C; R_f = 0.28 (methanol/ethyl acetate = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (t, J = 1.50 Hz, 2H), 7.56 (dd, J = 1.50 Hz, J = 7.50 Hz, 2H), 7.12-7.05 (m, 6H), 6.86 (d, J = 1.20 Hz, 1H), 6.44 (dd, J = 1.20 Hz, J = 7.20 Hz, 2H), 4.28 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 151.8, 146.0, 141.7, 135.1, 132.5, 128.6, 127.7, 126.7, 126.0, 124.0, 123.7, 75.9, 49.7. HRMS calculated for $C_{21}H_{16}N_4O$ $[M + H]^+$ m/z = 341.1397, found 341.1397.

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