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Article

Synthesis of Blue Emissive Quaternary 9,9-Disubstituted *N*-Methyl-7-azaindole-Appended (Phenylethynyl)-fluorene Derivatives

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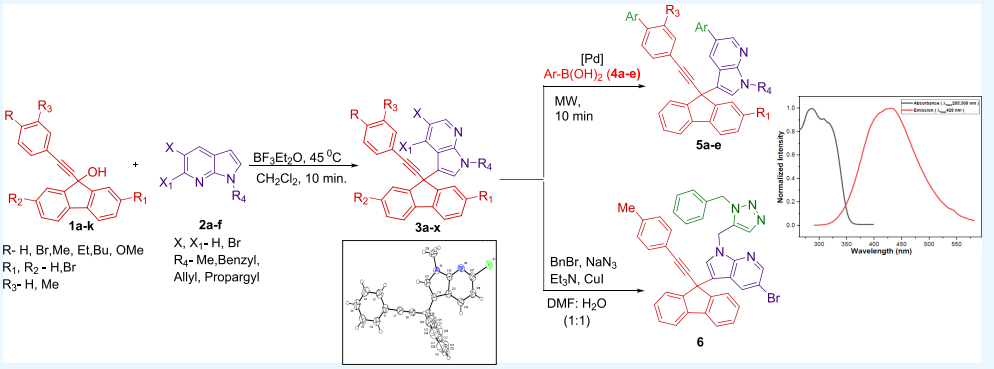

ABSTRACT: A highly functionalized 9,9-disubstituted (phenylethynyl)-fluorene-appended *N*-methyl-7-azaindole derivatives has been synthesized from various fluorene propargylic alcohols and substituted-7-azaindoles using BF_3OEt_2 as a catalyst. The scope of the reaction was demonstrated by selecting a range of fluorene propargylic alcohols and substituting 7-azaindoles. A plausible reaction mechanism for forming title compounds via propargylic carbocation is postulated. The synthetic transformation of the products has been demonstrated by the Suzuki coupling and Click reaction. The Suzuki coupled compounds **5a−5e** were evaluated for photophysical properties such as absorption, solvatochromism, emission, and Stokes shift and found blue emissive in nature.

INTRODUCTION

7-Azaindoles substituted at 3- or 5-positions have been identified as an important nitrogen heterocycle that possesses various biological activities and are used for the treatment of various diseases.[1] For example, variolin B (**I**) isolated from an extremely rare Antarctic sponge is a promising anti-cancer agent,[2] PLX5622 (**II**), a brain-penetrant CSF1R inhibitor, has been used in Alzheimer's disease (AD),[3] and pimodivir (**III**)[4] and AZD6738 (**IV**) are a potent and selective ATR kinase inhibitor.[5] On the other hand, fluorene-based compounds (**V**−**VII**) are essential structural frameworks in natural products,[6] biological activity,[7] light-emitting devices,[8] solar cells, and[9] optoelectronics[10] (Figure 1). A number of reports are available for the preparation of 9,9-disubstituted fluorenes.[11] Thus, developing synthetic methods for the hybrid 7-azaindole and fluorene-based compounds is highly warranted. The propargylic alcohols and their derivatives are extremely useful synthons for organic synthesis.[12] Various propargylic alcohols are highly reactive with Lewis acid reagents[13] and undergo nucleophilic substitution reactions with various nucleophiles to produce diverse and functionalized products.[14−19] The synthesis of 3,4-dihydrocyclopenta[*b*]indole and 1,4-dihydrocyclopenta[*b*]indole and propargylic alcohol in the

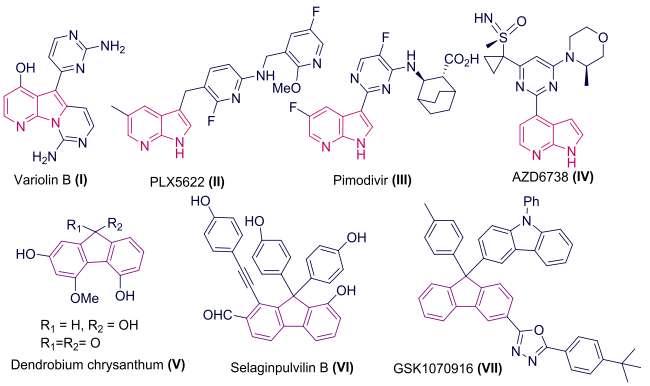

Figure 1. Biologically important molecules containing 7-azaindole and a 9,9-disubstitutedfluorene-based core structure.

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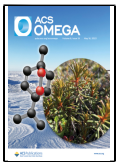


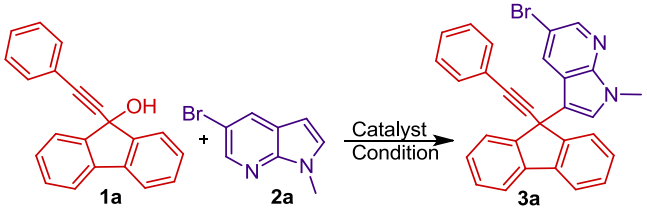
presence of different catalysts are known.[20] We have been working on the chemistry of fluorene propargylic alcohol and diverse nucleophiles under Lewis acid conditions.[21] The reaction of substituted phenyl propargylic alcohol such as 9-(phenylethynyl)-9*H*-fluoren-9-ol with an *N*-methyl-7-azaindole nucleophile is unknown. Thus, we explored the reaction of substituted 9-(phenylethynyl)-9*H*-fluoren-9-ol with many 7-azaindoles using $BF_3{\cdot}Et_2O$ as a Lewis acid catalyst and is reported.

In addition, the biphenyl-fluorene-7-azaindole hybrid products thus obtained via Suzuki coupling reaction were evaluated for photophysical properties and found to be blue emissive materials. The details of the study are presented in this manuscript.

RESULTS AND DISCUSSION

Our initial study was focused on the reaction of fluorene propargylic alcohol **1a** and *N*-methyl-5-bromo-7-azaindole **2a** in the presence of 0.2 equiv of $BF_3{\cdot}OEt_2$ in dichloromethane at 45 °C for 45 min. The reaction afforded the compound, namely, 1-methyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-pyrrolo[2,3-*b*] pyridine **3a** in 53% yield (Table 1, entry 1).

Table 1. Optimization of Synthesis of Compound 3a



entry	catalyst	solvent	catalyst (equiv)	time (min)	% yield of 3a[a]
1	$BF_3{\cdot}OEt_2$	DCM	0.2	45	53
2	$BF_3{\cdot}OEt_2$	DCM	0.6	30	61
3	$BF_3{\cdot}OEt_2$	DCM	1	10	83[b]
4	$BF_3{\cdot}OEt_2$	DCM	1.2	10	78
5	$BF_3{\cdot}OEt_2$	DCM	1	1 h	75
6	$BF_3{\cdot}OEt_2$	DCM	1	3 h	42[c]
7	$BF_3{\cdot}OEt_2$	DCE	1	10	60
8	$BF_3{\cdot}OEt_2$	ACN	1	30	75
9	$BF_3{\cdot}OEt_2$	MeOH	1	10	41
10	$BF_3{\cdot}OEt_2$	toluene	1	10	35
11	$FeCl_3$	DCM	1	60	25
12	$InBr_3$	DCM	1	45	59
13	$In(OTf)_3$	DCM	1	15	43
14	$Cu(OTf)_3$	DCM	1	20	46
15	HOTf	DCE	1	10	44

[a]Isolated yield after column purification. [b]Optimized condition. [c]Reaction was done at RT.

The structure of compound **3a** was established by spectroscopic methods such as ^{1}H NMR, ^{13}C NMR, DEPT-135, and HRMS (see the Supporting Information, Figures S5−S9), and the representative product structure **3b** was established by single-crystal XRD analysis[22] (Figure 2).

To improve the yield of compound **3a**, an optimization study was conducted by varying the reaction parameters such as Lewis acids (LA), solvent, equivalent of catalysts, and reaction time. Decreasing the mole equivalent of catalyst did not improve the yield and took more than 10 min to complete the reaction (Table 1, entries 1 and 2). However, the reaction

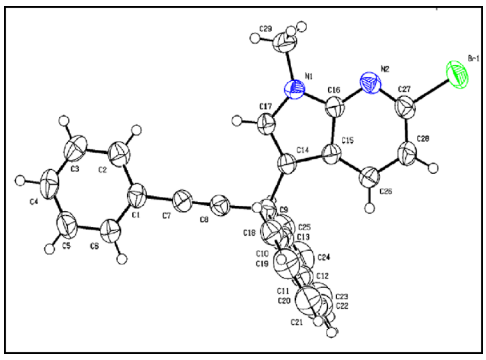
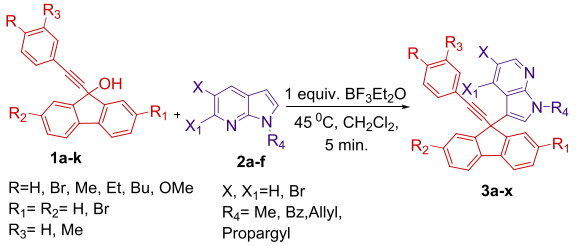


Figure 2. ORTEP diagram of compound **3b** (CCDC 2133015) showing atom labeling drawn at a 50% probability level.

of **1a** with 1 equiv of substituted 7-azaindole **2a** and $BF_3{\cdot}OEt_2$ in 2 mL of DCM at 45 °C (Table 1, entry 3) was completed in 10 min to afford compound **3a** in 83% yield and later found as the optimized condition. Increasing the mole equivalent of the catalyst did not improve the yield (Table 1, entry 4). When the reaction time was extended to 1 h, it showed no improvement in the yield (entry 5). The reaction was carried out at room temperature for 3 h using 1 equiv of $BF_3{\cdot}OEt_2$ and provided only 42% of the yield of the desired product (Table1, entry 6). A change of solvents, such as DCE (1,2-Dichloroethane), ACN (acetonitrile), CH_3OH (methanol), and toluene, did not improve the yield (Table 1, entries 7−10). Of all solvents tested, DCM (dichloromethane) was the most effective solvent to produce the desired compound **3a**. Next, we screened the catalyst using different Lewis acids, such as $FeCl_3$, which showed no remarkable improvement in the reaction yield (Table 1, entry 11). In $InBr_3$, some improvement in the yield was observed (Table 1, entry 12). Then, we continued the reaction by using catalysts like $In(OTf)_3$, $Cu(OTf)_3$, and HOTf and afforded compound **3a** in lower yield (Table 1, entries 13−15). Based on these results, we found that $BF_3{\cdot}OEt_2$ is the most effective LA for the formation of compound **3a**.

Having established an optimal protocol, we next investigated the generality and scope of the transformation utilizing a number of propargylic alcohols **1a−1k** and substituted 7-azaindoles **2a−2f** (Scheme 1).

Scheme 1. Synthesis of 3-Alkylated 7-Aza-indoles (3a−3x)



As illustrated in Figures 3 and 4, the under-optimized reaction conditions described above are effective for the transformation of a number of propargylic alcohols **1a−1k**, and substituted 7-azaindoles **2a−2f** produced corresponding 3-alkylated 7-azaindoles **3a−3x** in good-to-excellent yields (Table 2). Thus, the fluorene propargylic alcohol **1a** reacted with substituted 7-azaindoles **2a**, **2b**, and **2e−2f** provided indole derivatives **3a−3d** in good yields, and the best yield was

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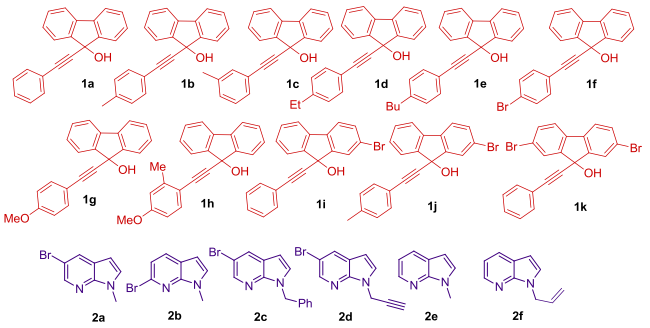


Figure 3. Various fluorene propargylic alcohols **1a**−**1g** and 7-azaindoles **2a**−**2d**.

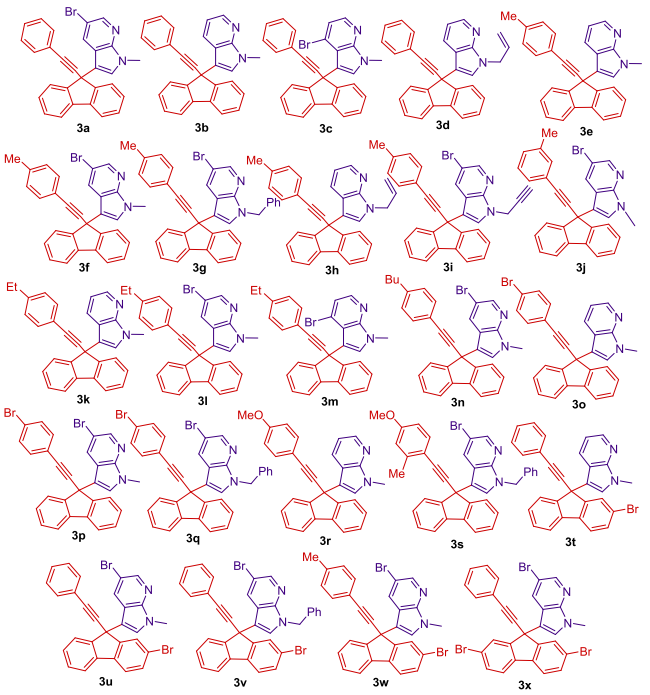


Figure 4. Synthesized compounds **3a**−**3x**.

found for product **3a** (Table 2, entries 1−4). The methyl substitution fluorene propargylic alcohol **1b** reacted with substituted 7-azaindole **2a** and **2c**−**2f** provided 7-azaindole derivatives **3e**−**3i** (Table 2, entries 5−9). The methyl substitution on the meta position **1c** was chosen to react with azaindole **2a** to provide corresponding product **3j** in 76% yield (entry 10). Then, we examined the reaction of substituted 7-azaindoles **2a**, **2b**, and **2e** with different ethyl and *n*-butyl-substituted propargylic alcohols **1d** and **1e** and furnished corresponding products **3k**−**3m** and **3n** in 69, 60, 72, and 70% yields, respectively (entries 11−14). Then, the reaction was carried out with bromo-substituted propargylic alcohol **1f** with substituted 7-azaindoles **2a** and **2c**−**2d**, and the respective products were formed **3o**−**3q** in 75, 71, and 82% yields, respectively (entries 15−17). The propargylic alcohol bearing −OMe substitution **1g** with **2e** afforded product **3r** in 70% yield (entry 18). The reaction was further demonstrated by the propargylic alcohol **1h** bearing 4-methoxy and 2-methyl groups and provided the corresponding product **3s** in 67% yield (entry 19). In addition, the propargylic alcohol having mono bromo substitution **1i** and **1j** also generated the respective compounds **3t**−**3w** in 72, 42, 73, and 65% yields,

Table 2. Scope of the Reaction[a]

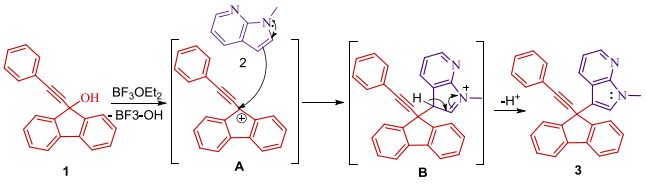
entry	propargylic alcohol **1**	7-azaindole **2**	product **3**	% yield[b]
1	**1a**	**2b**	**3a**	83
2	**1a**	**2a**	**3b**	73
3	**1a**	**2c**	**3c**	64
4	**1a**	**2f**	**3d**	39
5	**1b**	**2a**	**3e**	77
6	**1b**	**2b**	**3f**	79
7	**1b**	**2d**	**3g**	56
8	**1b**	**2f**	**3h**	76
9	**1b**	**2e**	**3i**	78
10	**1c**	**2b**	**3j**	76
11	**1d**	**2a**	**3k**	72
12	**1d**	**2b**	**3l**	69
13	**1d**	**2c**	**3m**	60
14	**1e**	**2b**	**3n**	70
15	**1f**	**2a**	**3o**	82
16	**1f**	**2b**	**3p**	75
17	**1f**	**2d**	**3q**	71
18	**1g**	**2a**	**3r**	70
19	**1h**	**2d**	**3s**	67
20	**1i**	**2a**	**3t**	73
21	**1i**	**2b**	**3u**	72
22	**1i**	**2d**	**3v**	42
23	**1j**	**2b**	**3w**	65
24	**1k**	**2b**	**3x**	44

[a]All the reactions were carried out using 1 equiv of $BF_3{\cdot}OEt_2$ and 3 mL of DCM at 45 °C for 10 min. [b]Isolated yield.

respectively (Table 2, entries 20−23). The 2,7-dibromo-9*H*-fluorene propargylic alcohol **1k** with 5-bromo-*N*-methyl-7-azaindole **2b** afforded compound **3x** in 44% yield (Table 2, entry 24).

Based on the structure of products, a plausible mechanism postulated for the formation of product **3** is provided in Scheme 2. Accordingly, at first, the propargylic alcohol **1a**

Scheme 2. Plausible Mechanism for the Formation of 3



reacts with $BF_3{\cdot}OEt_2$, which forms an electron-deficient alkyne carbocation **A**. The reaction followed by a nucleophilic attack of *N*-methyl-7-azaindole onto the carbocation produces the observed 3-alkylated substituted 7-azaindoles **3**.

To demonstrate the synthetic utility of products thus obtained, the Suzuki coupling[23] of product **3** having halogen substitution was demonstrated (Scheme 3). Thus, a reaction between **3** and aryl boronic acids **4a**−**4d** using $Pd(dppf)Cl_2{\cdot}$DCM as the catalyst and K_2CO_3 as the base in a dioxane:MeOH (3:1) solvent system was microwave (MWs) irradiated (100 W) for 10 min. The reaction afforded biaryl-tethered compounds **5a**−**5e** in very good combined yield (Table 3). Spectroscopic methods established the structure of the products.

The further synthetic transformation was achieved through the Click reaction[24] of *N*-propargylated derivative **3i** with 1

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Scheme 3. Synthesis of Biaryl Derivatives 5a−5e via Suzuki Coupling

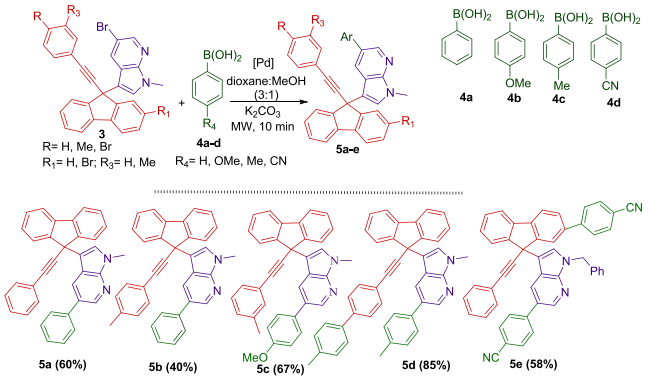


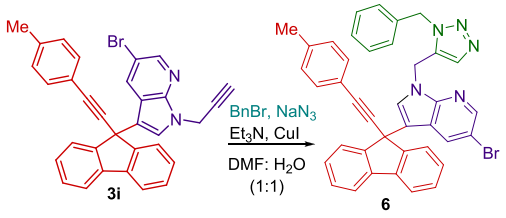
Table 3. Synthetic Transformation of 3 via Suzuki Coupling Reaction

entry	compound 3 (equiv)	boronic acid 4 (equiv)	product 5	% yield
1	3a(1)	4a(1)	5a	60
2	3f(1)	4a(1)	5b	40
3	3j(1)	4b(1)	5c	67
4	3p(1)	4c(2)[a]	5d	85
5	3u(1)	4d(2)[a]	5e	58

[a]2 equiv of boronic acid.

equiv of each BnBr, NaN_3, and Cu(I) catalyst and Et_3N as a base to give rise to triazole derivative **6** in 60% yield (Scheme 4).

Scheme 4. Synthetic Transformation of 3i via "Click" Reaction



Photophysical Studies. The 7-azaindole and their derivatives displayed significant photophysical properties. They were based on the luminescent properties of many materials applications that have been studied.[25] Notably, the 7-azaindole emits a weak $\pi^*-\pi$ transition-based fluorescence, with λ_{max} 350−360 nm in solution and the solid state. At the same time, its anion is a bright blue luminophore in solution and the solid state.[25] Encouraged by this property, our final compounds **5a−5e** possess a 7-azaindole, fluorene, aryl propargyl, and biaryl core group system that envisaged us to probe their photophysical properties. Based on the structural perspective, compound **5e** was selected to evaluate photophysical properties. Thus, the UV absorption and emission spectrum for compound **5e** in ACN showed two absorption maxima, measured at 285 and 308 nm, and emission maxima at 428 nm, observed in the blue region, respectively (Figure 5). A solvatochromism study was undertaken to determine the influence of the polarity solvent effect on compound **5e**. Hence, solvents such as hexane, DCM, EtOAc, dioxane, $CHCl_3$, and ACN in the increasing order of polarity were used

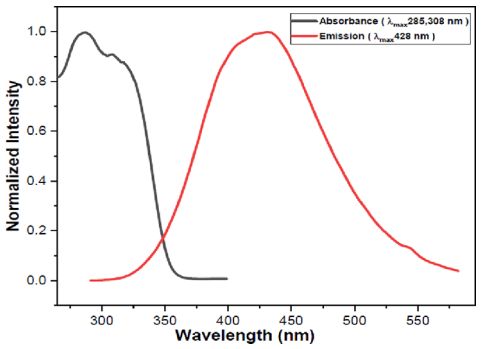


Figure 5. Normalized absorption and emission spectra of compound **5e**.

for the study. The results revealed that a red shift in the emission maxima from 374 to 428 nm was observed as the polarity of the solvent was increased and found to have the highest emission wavelength at 428 nm in ACN (Table 4, Figure 6). Furthermore, compound **5e** showed stokes shifts $\Delta\overline{\upsilon}$ = 11723 cm^{-1} (Table 5, entry 5).

Table 4. Absorption and Emission Maxima of Compound 5e in Various Polarity of Solvents

entry	solvent	absorption[a] $\lambda_{max,abs}$ (nm)	emission[b] $\lambda_{max,emi}$ (nm)
1	hexane	283, 308	374
2	DCM	287, 310	395
3	EtOAc	287, 310	408
4	dioxane	284, 309	387
5	$CHCl_3$	286, 310	382
6	ACN	285, 308	428

[a]Recorded at $C = 10^{-4}$ M at 298 K. [b]Excited at the longest wavelength of the absorption maxima.

Similarly, photophysical characteristics such as absorption ($\lambda_{max,abs}$), emission ($\lambda_{max,emi}$), and Stokes shift ($\Delta\overline{\upsilon}$) of all the synthesized biaryl compounds **5a−5e** were evaluated, and the results are summarized in Table 5. Normalized absorption and emission spectra of compounds **5a−5e** are shown in Figure 7. Compounds **5a−5e** exhibited absorption and emission maxima in 257−285 and 358−428 nm, respectively. All the synthesized biaryl compound Stokes shifts were calculated and showed large Stokes shifts; particularly, compound **5a** has the highest Stokes shift value of 12936 cm^{-1}, while compound **5d** has the lowest Stocks shifts value of 9241 cm^{-1}.

In summary, a number of highly functionalized 7-aza-*N*-methyl indole appended 9-(phenylethynyl)-fluorene derivatives **3a−3x** have been synthesized. The scope of the reaction has been demonstrated by selecting a range of fluorene propargyl alcohols and substituting 7-aza indoles. A plausible reaction mechanism has been explained. Synthetic transformation of the products has been demonstrated by the Suzuki coupling reaction of **5a−5e** and the Click reaction of **6**. The photophysical properties of the Suzuki coupling reaction were evaluated, and luminescence was found in the blue region.

EXPERIMENTAL SECTION

General Remarks. All the reactions were carried out in oven-dried glassware. Progress of reactions was monitored by thin-layer chromatography (TLC), while purification of crude

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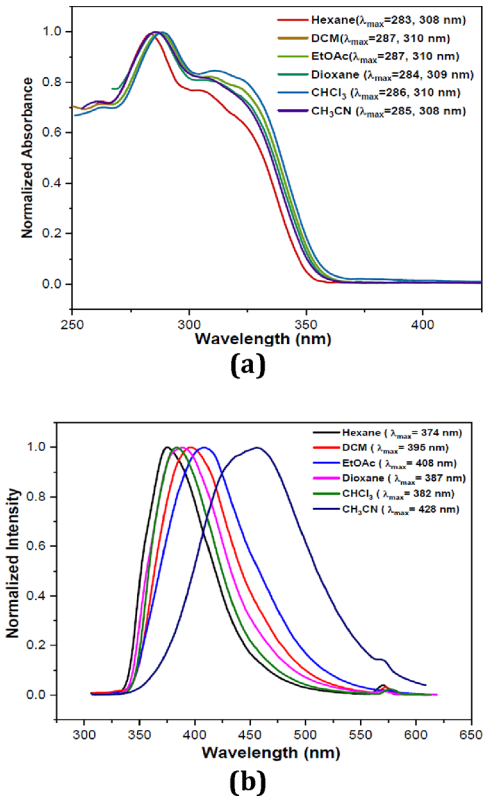

Figure 6. Solvatochromism for compound **5e** recorded at C = 10^{-4} M at 298 K: (a) normalized absorption spectra and (b) normalized emission spectra.

Table 5. Photophysical Properties of Compounds 5a−5e

entry	product	absorption[a] $\lambda_{max,abs}$ (nm)	emission $\lambda_{max,emi.}$ (nm)	Stokes shift (cm^{-1})[b]
1	**5a**	257	385	12936
2	**5b**	261	379	11928
3	**5c**	259	371	11655
4	**5d**	269	358	9241
5	**5e**	285	428	11723

[a]Recorded in CH_3CN at 298 K. [b]Stokes shift = $\lambda_{max,abs} - \lambda_{max,emi}$ [cm^{-1}].

compounds was done by column chromatography using silica gel (mesh size 100−200). The NMR spectra were recorded on a Bruker-400 MHz NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) with $CDCl_3$or $(CD_3)_2SO$ as the solvent and TMS as an internal reference. Integrals are by assignments; coupling constants were reported in hertz (Hz). All ^{13}C spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). HRMS analyses were recorded using Q-T of a micro mass spectrometer (different mass analyses based on the availability of instruments). Yields refer to quantities obtained after chromatography.

Experimental Procedures. *(a) General Procedures for the Preparation of Compounds **3a−3x**.* To a solution of propargylic alcohol derivatives of fluorenones **1a−1k** (1 equiv) and substituted 7-aza indoles **2a−2f** (1 equiv) in DCM (2 mL) was added $BF_3{\cdot}OEt_2$ (1 equiv), and the reaction mixture was stirred at 45 °C for 10 min. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with

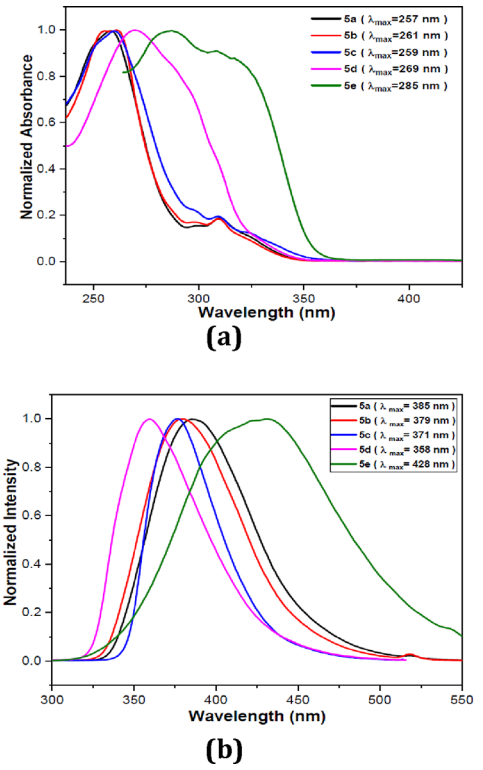

Figure 7. (a) Normalized absorption spectra of compounds **5a−5e** recorded in CH_3CN at C = 10^{-4} M at 298 K; (b) normalized emission spectra of compounds **5a−5e** recorded in CH_3CN at C = 10^{-4} M at 298 K.

DCM, washed with saturated brine and distilled water, and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column to pure compound **3a−3x** in excellent yield (eluent: *n*-hexane/EtOAc).

*(b) General Procedures for the Suzuki Coupling of Compounds **5a−5e**.* A mixture of compound **3a** (1 equiv), aryl boronic acids **4a−4d** (1 equiv), Pd(dppf)Cl_2·DCM (0.2 equiv), and K_2CO_3 (1.5 equiv) in 4 mL of dioxane-MeOH (3:1) was microwave irradiated (power mode) at 100 W for 10 min. After the reaction (TLC) was completed, the solvent was removed *in vacuo*, and the residue was extracted with EtOAc and washed with HCl (0.25 M, 20 mL) followed by saturated brine. The organic layer was dried over anhydrous Na_2SO_4 and purified through a silica gel column chromatography by gradient elution using EtOAc:hexane to afford compounds **5a−5e** in very good yields.

*(c) General Procedures for the Click Reaction of Compound **6**.* A mixture of compound **3i** (1 equiv), NaN_3 (1.2 equiv), benzyl bromide (1 equiv), triethylamine (1 equiv), and CuI (2.5 mol %) in 2 mL of DMF: water (1: 1) was stirred at room temperature for 30 min. Upon completion of the reaction, the catalyst was filtered, and the crude mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum; the crude product was purified using silica gel column chromatography to afford pure triazole derivative **6**.

*5-Bromo-1-methyl-3-(9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3a**).* Nature: yellow liquid; 210 mg, yield: 83%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR-($CDCl_3$/TMS, 400 MHz,): δ 8.26−8.18 (m, 1H), 7.81 (d, *J* =

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7.5 Hz, 2H), 7.54 (s, 2H), 7.48−7.37 (m, 5H), 7.33−7.19 (m, 6H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.8, 146.8, 143.5, 139.5, 131.9, 130.2, 128.9, 128.5, 128.4, 128.3, 128.2, 125.1, 123.2, 120.4, 119.3, 114.5, 111.4, 90.2, 81.9, 49.2, 31.4; HRMS-ESI: Calcd. for $C_{29}H_{20}BrN_2$ $[M + H]^+$ m/z: 475.0810; Found 475.0805.

*4-Bromo-1-methyl-3-(9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3b**).* Nature: white powder; 76 mg, yield: 64%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 7.80 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.46−7.37 (m, 5H), 7.30−7.23 (m, 5H), 6.87−6.81 (m, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.9, 148.0, 139.5, 134.9, 131.9, 130.1, 128.5, 128.4, 128.3, 127.7, 125.2, 123.2, 120.3, 119.0, 116.4, 115.4, 90.1, 81.9, 49.3, 31.5; HRMS-ESI: Calcd. for $C_{29}H_{22}BrN_2$ $[M + 2]^+$ m/z: 477.081; Found 477.0770.

*1-Methyl-3-(9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3c**).* Nature: yellow liquid; 103 mg, yield: 73%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (dd, J = 4.6, 1.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.47−7.45 (m, 2H), 7.40 (dt, J = 7.5, 3.7 Hz, 2H), 7.30−7.25 (m, 5H), 7.04 (d, J = 7.9 Hz, 5H), 6.73 (dd, J = 8.0, 4.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.2, 148.5, 142.9, 139.6, 132.2, 131.9, 128.4, 128.3, 128.2, 128.1, 127.6, 125.3, 123.3, 120.2, 117.9, 115.3, 114.7, 90.5, 81.7, 49.4, 31.3; HRMS-ESI: Calcd. for $C_{29}H_{21}N_2$ $[M + H]^+$ m/z: 397.1705; Found 397.1696.

*1-Allyl-3-(9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo-[2,3-b]pyridine (**3d**).* Nature: brown liquid; 58 mg, yield: 39%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.16 (dd, J = 4.7, 1.5 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.55−7.49 (m, 2H), 7.46−7.37 (m, 4H), 7.30−7.25 (m, 5H), 6.98−6.93 (m, 1H), 6.71 (dd, J = 8.0, 4.7 Hz, 1H), 6.13−6.01 (m, 1H), 5.22 (dd, J = 10.2, 1.3 Hz, 1H), 5.12 (dd, J = 17.0, 1.3 Hz, 1H), 4.93−4.87 (m, 2H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.2, 148.1, 142.9, 139.6, 133.9, 131.9, 128.9, 128.4, 128.3, 128.2, 128.1, 12.9, 127.7, 126.5, 125.3, 123.4, 120.2, 117.8, 117.4, 117.3, 115.8, 115.6, 115.1, 90.5, 81.7, 49.5, 46.7; MS-ESI: Calcd. for $C_{13}H_{22}N_2$ $[M + H]^+$ m/z: 422.17; Found 422.15.

*5-Bromo-1-methyl-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3e**).* Nature: yellow powder; 197 mg, yield: 79%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.13 (d, J = 2.1 Hz, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.39−7.31 (m, 3H), 7.29−7.25 (m, 2H), 7.22 (td, J = 7.5, 1.1 Hz, 2H), 7.12 (d, J = 2.1 Hz, 1H), 7.02 (d, J = 7.9 Hz, 2H), 3.74 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.9, 146.9, 143.5, 139.5, 138.4, 131.8, 130.2, 129.1, 128.9, 128.5, 128.4, 125.2, 120.4, 120.1, 119.3, 114.7, 111.4, 89.3, 82.1, 49.2, 31.5, 21.6; HRMS-ESI: Calcd. for $C_{30}H_{24}BrN$ $[M + 2]^+$ m/z: 491.0966; Found 491.0946.

*1-Benzyl-5-bromo-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3f**).* Nature: brown liquid; 108 mg, yield: 56%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.10 (d, J = 2.2 Hz, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.44 (s, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.29 (td, J = 7.5, 1.1 Hz, 2H), 7.21−7.13 (m, 7H), 7.10−7.05 (m, 2H), 7.02 (d, J = 2.1 Hz, 1H), 6.94 (d, J = 7.9 Hz, 2H), 5.30 (s, 2H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.8, 146.8, 143.7, 139.5, 138.3, 137.4, 131.7, 130.2, 129.0, 128.9, 128.5, 128.4128.0, 127.8, 127.4, 25.1, 120.4, 120.0, 119.2, 115.4, 111.6, 89.3, 82.1, 49.3, 48.2, 21.5; HRMS-ESI: Calcd. for $C_{36}H_{26}BrN_2$ $[M + H]^+$ m/z: 565.1279; Found 565.1278.

*5-Bromo-1-(prop-2-yn-1-yl)-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3g**).* Nature: yellow powder; 136 mg, yield: 78%; R_f (10% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.20 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.71 (s, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.37−7.22 (m, 5H), 7.10 (dd, J = 4.9, 2.7 Hz, 3H), 5.02 (d, J = 2.5 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.7, 146.2, 143.7, 139.6, 138.4, 131.8, 130.4, 129.1, 128.6, 128.5, 127.1, 125.2, 120.4, 120.1, 119.6, 115.9, 111.9, 89.2, 82.2, 73.7, 49.3, 33.9, 21.6; MS-ESI: Calcd. for $C_{32}H_{21}BrN_2$ $[M + H]^+$ m/z: 512.08; Found 512.05.

*1-Methyl-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3h**).* Nature: yellow powder; 107 mg, yield: 77%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (d, J = 4.4 Hz, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.3 Hz, 2H), 7.48 (s, 1H), 7.39 (td, J = 7.5, 0.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.29−7.22 (m, 2H), 7.06 (dd, J = 16.1, 8.1 Hz, 3H), 6.72 (ddd, J = 8.0, 4.7, 0.5 Hz, 1H), 3.85 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.3, 148.5, 142.8, 139.6, 138.3, 131.8, 129.1, 128.3, 128.2, 127.7, 125.3, 120.3, 120.2, 117.9, 115.3, 114.8, 89.7, 81.8, 49.4, 31.3, 21.6; HRMS-ESI: Calcd. for $C_{30}H_{23}N_2$ $[M + H]^+$ m/z: 411.1861; Found 411.1862.

*1-Allyl-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo-[2,3-b]pyridine (**3i**).* Nature: brown liquid; 113 mg, yield: 76%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.08 (dd, J = 4.7, 1.4 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.49 (s, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.33 (td, J = 7.5, 1.0 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.23−7.16 (m, 2H), 7.01 (d, J = 7.9 Hz, 2H), 6.88 (dd, J = 7.9, 1.3 Hz, 1H), 6.63 (dd, J = 8.0, 4.7 Hz, 1H), 6.06−5.93 (m, 1H), 5.14 (dd, J = 10.2, 1.3 Hz, 1H), 5.04 (dd, J = 17.1, 1.3 Hz, 1H), 4.82 (d, J = 5.5 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.3, 148.1, 142.9, 139.6, 138.3, 133.9, 131.8, 129.1, 128.4, 128.3, 128.1, 126.5, 125.3, 120.3, 120.2, 117.8, 117.4, 115.6, 115.2, 89.7, 81.8, 49.5, 46.7, 21.5; MS-ESI: Calcd. for $C_{32}H_{24}N_2$ $[M + H]^+$ m/z: 436.19; Found 436.21.

*5-Bromo-1-methyl-3-(9-(m-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3j**).* Nature: yellow powder; 125 mg, yield: 76%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.21 (d, J = 2.1 Hz, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.45−7.38 (m, 3H), 7.32−7.22 (m, 5H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 3.80 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.8, 146.8, 143.5, 139.5, 138.0, 132.5, 130.2, 129.2, 128.9, 128.5, 128.4, 128.3, 125.1, 122.9, 120.4, 119.3, 114.6, 111.4, 89.8, 82.2, 49.2, 31.4, 21.3; HRMS-ESI: Calcd. for $C_{30}H_{24}BrN_2$ $[M + 2]^+$ m/z: 491.0966; Found 491.0946.

*5-Bromo-3-(9-((4-ethylphenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3k**).* Nature: yellow liquid; 79 mg, yield: 69%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.21 (d, J = 2.2 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.44−7.34 (m, 5H), 7.28 (td, J = 7.5, 1.1 Hz, 2H), 7.21 (d, J = 2.6 Hz, 1H), 7.11 (d, J = 8.3 Hz, 2H), 3.79 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.9, 146.8, 144.7, 143.5, 139.5, 131.9, 130.2, 128.9, 128.5, 128.4, 127.9, 125.2, 120.4, 119.3, 114.7, 111.4, 89.4, 82.2, 49.2, 31.4, 28.9, 15.5; HRMS-ESI: Calcd. for $C_{31}H_{24}BrN_2$ $[M + H]^+$ m/z: 503.1123; Found 503.1114.

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*4-Bromo-3-(9-((4-ethylphenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3l**).* Nature: white powder; 68 mg, yield: 60%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 7.80 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.39 (ddd, J = 12.8, 9.6, 4.6 Hz, 4H), 7.30−7.24 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.88−6.82 (m, 2H), 3.82 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 1.61 (s, 1H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.0, 148.0, 144.7, 139.5, 134.9, 131.9, 130.2, 128.5, 128.4, 127.9, 127.7, 125.2, 120.4, 120.3, 119.0, 116.5, 115.6, 89.3, 82.1, 49.3, 31.6, 28.9, 15.5; HRMS-ESI: Calcd. for $C_{31}H_{24}BrN_2$ $[M + H]^+$ m/z: 503.1123; Found 503.139.

*3-(9-((4-Ethylphenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3m**).* Nature: white powder; 69 mg, yield: 72%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (dd, J = 4.7, 1.4 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.53 (dd, J = 7.6, 0.4 Hz, 2H), 7.48 (s, 1H), 7.39 (ddd, J = 8.1, 5.6, 1.8 Hz, 4H), 7.27 (td, J = 7.5, 1.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 1H), 6.72 (dd, J = 8.0, 4.7 Hz, 1H), 3.85 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.3, 148.5, 144.6, 142.8, 139.6, 131.9, 128.3, 128.1, 127.9, 127.6, 125.3, 120.5, 120.2, 117.9, 115.3, 114.8, 89.7, 81.9, 49.4, 31.3, 29.9, 15.5; HRMS-ESI: Calcd. for $C_{31}H_{25}N_2$ $[M + H]^+$ m/z: 425.2018; Found 425.2009.

*5-Bromo-3-(9-((4-butylphenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3n**).* Nature: white powder; 78 mg, yield: 70%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.13 (d, J = 2.2 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.38−7.31 (m, 3H), 7.28 (d, J = 8.2 Hz, 2H), 7.21 (td, J = 7.5, 1.1 Hz, 2H), 7.12 (d, J = 2.1 Hz, 1H), 7.02 (d, J = 8.2 Hz, 2H), 3.73 (s, 3H), 2.54−2.46 (m, 2H), 1.48 (ddd, J = 15.4, 11.0, 7.5 Hz, 2H), 1.30−1.16 (m, 3H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.9, 146.9, 143.5, 143.4, 139.5, 131.8, 130.2, 128.9, 128.5, 128.4, 125.2, 120.4, 120.3, 119.3, 114.7, 111.4, 89.4, 82.1, 49.2, 35.7, 33.5, 31.5, 22.4, 14.0; MS-ESI: Calcd. for $C_{33}H_{27}BrN_2$ $[M + H]^+$ m/z: 530.13; Found 530.10.

*5-Bromo-3-(9-((4-bromophenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3o**).* Nature: white powder; 145 mg, yield: 75%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.26 (d, J = 2.1 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.47 (dd, J = 10.7, 7.9 Hz, 5H), 7.37−7.31 (m, 4H), 7.24 (d, J = 2.1 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.5, 146.8, 143.6, 139.5, 133.4, 131.6, 130.1, 128.8, 128.7, 128.5, 125.1, 122.5, 122.1, 120.5, 119.3, 114.3, 111.4, 91.4, 80.9, 49.2, 31.5; HRMS-ESI: Calcd. for $C_{29}H_{19}Br_2N_2$ $[M + H]^+$ m/z: 552.9915; Found 552.9897.

*1-Benzyl-5-bromo-3-(9-((4-bromophenyl)ethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3p**).* Nature: yellow liquid; 124 mg, yield: 71%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.21 (d, J = 2.1 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.51−7.45 (m, 3H), 7.42−7.34 (m, 4H), 7.32−7.24 (m, 5H), 7.23−7.21 (m, 1H), 7.19 (dt, J = 11.3, 4.2 Hz, 3H), 7.10 (d, J = 2.1 Hz, 1H), 5.41 (s, 2H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.4, 146.8, 143.8, 139.5, 137.3, 133.3, 131.5, 130.2, 128.8, 128.6, 128.5, 127.9, 127.8, 127.5, 125.1, 122.5, 122.0, 120.5, 119.1, 114.9, 111.7, 91.4, 80.9, 49.3, 48.2; MS-ESI: Calcd. for $C_{35}H_{22}Br_2N_2$ $[M + H]^+$ m/z: 628.01; Found 628.03.

*3-(9-((4-Bromophenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3q**).* Nature: yellow liquid; 108 mg, yield: 82%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (dd, J = 4.7, 1.5 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.43−7.38 (m, 4H), 7.32−7.25 (m, 4H), 7.03 (dd, J = 8.0, 1.5 Hz, 1H), 6.73 (dd, J = 8.0, 4.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.9, 148.4, 142.9, 139.6, 133.4, 131.6, 128.5, 1284, 128.1, 127.5, 125.2, 122.4, 122.3, 120.3, 117.8, 115.4, 114.4, 91.8, 80.7, 49.4, 31.4; HRMS-ESI: Calcd. for $C_{29}H_{20}BrN_2$ $[M + H]^+$ m/z: 475.0810; Found 475.0788.

*3-(9-((4-Methoxyphenyl)ethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3r**).* Nature: yellow liquid; 48 mg, yield: 70%; R_f (25% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (dd, J = 4.7, 1.5 Hz, 1H), 7.84−7.78 (m, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.48 (s, 1H), 7.39 (ddd, J = 6.8, 5.0, 1.2 Hz, 4H), 7.31−7.22 (m, 2H), 7.07−7.00 (m, 1H), 6.84−6.77 (m, 2H), 6.72 (dd, J = 8.0, 4.7 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 159.6, 149.4, 148.5, 142.9, 142.8, 139.6, 133.3, 129.9, 128.3, 128.2, 128.1, 127.6, 125.3, 120.2, 117.9, 115.6, 115.5, 115.3, 114.9, 113.9, 99.4, 88.9, 81.6, 55.4, 31.3; MS-ESI: Calcd. for $C_{30}H_{22}N_2O$ $[M + H]^+$ m/z: 426.17; Found 426.14.

*1-Benzyl-5-bromo-3-(9-((4-methoxy-2-methylphenyl)-ethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3s**).* Nature: yellow powder; 61 mg, yield: 67%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.34 (d, J = 2.1 Hz, 1H), 7.96 (d, J = 2.2 Hz, 1H), 7.72 (d, J = 7.5 Hz, 2H), 7.29 (td, J = 7.5, 1.1 Hz, 2H), 7.24 (d, J = 1.6 Hz, 1H), 7.23−7.20 (m, 3H), 7.17−7.10 (m, 4H), 6.96 (d, J = 7.5 Hz, 2H), 6.46−6.43 (m, 1H), 6.00 (d, J = 2.4 Hz, 1H), 5.98 (s, 1H), 5.44 (s, 2H), 3.51 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 158.8, 151.4, 146.2, 145.9, 144.2, 142.0, 138.6, 137.9, 137.4, 135.4, 132.4, 130.4, 128.9, 128.0, 127.9, 127.8, 127.7, 127.6, 123.9, 122.4, 120.3, 112.6, 112.2, 111.4, 107.0, 66.9, 55.4, 48.2, 19.8; MS-ESI: Calcd. for $C_{37}H_{27}BrN_2O$ $[M + H]^+$ m/z: 594.13; Found 594.10.

*3-(2-Bromo-9-(phenylethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3t**).* Nature: colorless liquid; 69 mg, yield: 73%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.18 (dd, J = 4.7, 1.5 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.43−7.38 (m, 4H), 7.32−7.25 (m, 4H), 7.03 (dd, J = 8.0, 1.5 Hz, 1H), 6.73 (dd, J = 8.0, 4.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.2, 147.1, 142.6, 138.2, 138.1, 132.7, 132.0, 129.9, 129.2, 129.1, 129.0, 128.8, 128.3, 128.0, 124.6, 122.2, 122.1, 121.6, 120.4, 115.5, 99.4, 88.5, 83.7, 75.0, 31.5; HRMS-ESI: Calcd. for $C_{29}H_{20}BrN_2$ $[M + H]^+$ m/z: 475.0810; Found 475.0805.

*5-Bromo-3-(2-bromo-9-(phenylethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3u**).* Nature: yellow liquid; 78 mg, yield: 72%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.14 (d, J = 2.1 Hz, 1H), 7.74−7.70 (m, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 1.8 Hz, 1H), 7.46 (dd, J = 8.1, 1.8 Hz, 1H), 7.42 (d, J = 3.5 Hz, 1H), 7.41−7.37 (m, 3H), 7.35 (dd, J = 7.5, 1.1 Hz, 1H), 7.26−7.20 (m, 4H), 7.00 (d, J = 2.1 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 150.7, 148.6, 146.8, 143.7, 138.5, 138.4, 131.9, 131.7, 129.5, 129.2, 128.9, 128.8, 128.5, 128.4, 125.2, 122.9, 122.0, 121.8, 120.5, 119.0, 113.6, 111.5, 89.2, 82.5, 49.2, 31.5; HRMS-ESI: Calcd. for $C_{29}H_{19}Br_2N_2$ $[M + H]^+$ m/z: 552.9915; Found 552.9901.

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*1-Benzyl-5-bromo-3-(2-bromo-9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**3v**).* Nature: yellow liquid; 73 mg, yield: 42%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.12 (d, J = 2.1 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.54−7.49 (m, 3H), 7.41−7.33 (m, 2H), 7.31−7.25 (m, 3H), 7.23−7.12 (m, 7H), 7.09 (dd, J = 9.3, 2.6 Hz, 2H), 6.91 (d, J = 2.1 Hz, 1H), 5.32 (s, 2H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 150.6, 148.4, 146.8, 143.9, 138.5, 138.4, 137.2, 131.9, 131.7, 129.9, 128.9, 128.8, 128.4, 120.3, 128.2, 127.9, 127.5, 125.2, 122.8, 122.0, 121.7, 120.5, 118.9, 114.3, 111.8, 89.2, 82.5, 49.3, 48.2; HRMS-ESI: Calcd. for $C_{29}H_{20}BrN_2$ $[M + H]^+$ m/z: 475.0810; Found 475.0805.

*5-Bromo-3-(2-bromo-9-(p-tolylethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3w**).* Nature: yellow powder; 79 mg, yield: 65%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.14 (d, J = 2.1 Hz, 1H), 7.75−7.70 (m, 1H), 7.62−7.58 (m, 1H), 7.53 (d, J = 1.5 Hz, 1H), 7.46 (dd, J = 8.1, 1.8 Hz, 1H), 7.43−7.34 (m, 3H), 7.31−7.21 (m, 3H), 7.06−6.98 (m, 3H), 3.77 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 150.9, 148.7, 146.9, 143.7, 138.7, 138.5, 138.4, 131.8, 131.7, 129.9, 129.2, 129.1, 128.9, 128.7, 128.5, 125.2, 122.0, 121.8, 120.5, 119.8, 119.0, 113.8, 111.5, 88.4, 82.6, 49.3, 31.5, 21.6; MS-ESI: Calcd. for $C_{30}H_{20}Br_2N_2$ $[M + H]^+$ m/z: 565.99; Found 565.96.

*5-Bromo-3-(2,7-dibromo-9-(phenylethynyl)-9H-fluoren-9-yl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (**3x**).* Nature: yellow powder; 63 mg, yield: 44%; R_f (15% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.24 (d, J = 2.1 Hz, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.57 (dd, J = 3.5, 1.5 Hz, 3H), 7.55 (d, J = 2.0 Hz, 2H), 7.50−7.46 (m, 2H), 7.37−7.30 (m, 3H), 7.01 (d, J = 2.1 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 150.5, 146.9, 143.9, 137.4, 132.1, 132.0, 129.6, 129.4, 128.7, 128.5, 122.6, 122.5, 121.8, 118.8, 112.7, 111.7, 88.3, 83.0, 49.2, 31.6; MS-ESI: Calcd. for $C_{29}H_{17}Br_3N_2$ $[M + H]^+$ m/z: 629.89; Found 629.91.

*1-Methyl-5-phenyl-3-(9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**5a**).* Nature: colorless liquid; 36 mg, yield: 60%; R_f (25% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.47 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.53−7.43 (m, 6H), 7.41−7.35 (m, 3H), 7.33 (dd, J = 3.9, 2.3 Hz, 7H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.1, 148.1, 142.3, 139.6, 132.0, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 127.4, 127.2, 127.0, 126.8, 126.6, 125.5, 125.3, 123.4, 120.3, 117.9, 115.2, 90.6, 81.9, 60.5, 49.4, 31.4; MS-ESI: Calcd. for $C_{35}H_{24}N_2$ $[M + H]^+$ m/z: 472.19; Found 472.15.

*1-Methyl-5-phenyl-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**5b**).* Nature: white powder; 16 mg, yield: 40%; R_f (30% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.36 (d, J = 2.1 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.40 (s, 1H), 7.34 (td, J = 7.5, 1.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 4H), 7.24−7.18 (m, 6H), 7.02 (d, J = 7.9 Hz, 2H), 3.80 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.3, 148.0, 142.2, 139.6, 138.3, 131.8, 129.1, 128.9, 128.8, 128.4, 128.3, 128.2, 127.2, 126.8, 126.6, 125.3, 120.3, 120.2, 117.9, 115.3, 89.7, 82.0, 49.5, 31.5, 21.6; HRMS-ESI: Calcd. for $C_{36}H_{27}N_2$ $[M + H]^+$ m/z: 487.2174; Found 487.2154.

*5-(4-Methoxyphenyl)-1-methyl-3-(9-(m-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**5c**).* Nature: yellow liquid; 56 mg, yield: 67%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.47 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.48 (dd, J = 16.4, 9.0 Hz, 3H), 7.36 (dd, J = 9.8, 5.1 Hz, 5H), 7.31−7.26 (m, 2H), 7.22 (dd, J = 13.1, 5.5 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 158.9, 149.2, 147.8, 142.9, 142.0, 139.6, 138.0, 132.5, 132.1, 129.1, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 126.2, 125.3, 123.1, 120.3, 117.9, 115.6, 115.0, 114.4, 99.4, 90.2, 82.0, 55.4, 49.4, 31.4, 21.2; MS-ESI: Calcd. for $C_{37}H_{28}N_2O$ $[M + H]^+$ m/z: 516.22; Found 516.25.

*1-Methyl-3-(9-((4′-methyl-[1,1′-biphenyl]-4-yl)ethynyl)-9H-fluoren-9-yl)-5-(p-tolyl)-1H-pyrrolo[2,3-b]pyridine (**5d**).* Nature: yellow powder; 34 mg, yield: 85%; R_f (20% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.35 (d, J = 2.1 Hz, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 4.8 Hz, 4H), 7.39 (d, J = 8.9 Hz, 3H), 7.33 (td, J = 7.5, 1.0 Hz, 2H), 7.22 (td, J = 7.5, 1.0 Hz, 2H), 7.18−7.13 (m, 3H), 7.12−7.06 (m, 4H), 3.80 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 149.2, 147.8, 142.1, 140.9, 139.6, 137.6, 136.6, 132.3, 129.7, 129.6, 128.8, 128.4, 128.2, 127.1, 126.9, 126.8, 126.5, 125.3, 121.9, 120.3, 118.0, 115.1, 91.1, 81.8, 49.5, 31.5, 21.2, 21.1; HRMS-ESI: Calcd. for $C_{43}H_{33}N_2$ $[M + H]^+$ m/z: 577.2644; Found 577.2629.

*4-(1-Benzyl-3-(2-(4-cyanophenyl)-9-(phenylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridin-5-yl)benzonitrile (**5e**).* Nature: yellow liquid; 37 mg, yield: 58%; R_f (30% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.34 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 16.2, 7.8 Hz, 2H), 7.68−7.62 (m, 2H), 7.59 (d, J = 8.8 Hz, 3H), 7.54 (dd, J = 8.5, 3.2 Hz, 4H), 7.48 (d, J = 7.5 Hz, 1H), 7.41 (dd, J = 10.8, 4.2 Hz, 1H), 7.35−7.31 (m, 2H), 7.27 (dd, J = 11.2, 4.1 Hz, 4H), 7.24−7.18 (m, 6H), 6.93 (d, J = 1.7 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 150.0, 149.4, 148.5, 145.3, 144.0, 142.4, 140.2, 139.3, 138.9, 137.5, 132.7, 132.6, 131.9, 129.0, 128.9, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 127.5, 127.3, 126.5, 125.5, 124.0, 121.0, 120.6, 119.0, 117.5, 115.8, 111.0, 110.5, 82.4, 49.5, 48.2; MS-ESI: Calcd. for $C_{49}H_{30}N_4$ $[M + H]^+$ m/z: 674.24; Found 674.22.

*1-((1-Benzyl-1H-1,2,3-triazol-5-yl)methyl)-5-bromo-3-(9-(p-tolylethynyl)-9H-fluoren-9-yl)-1H-pyrrolo[2,3-b]pyridine (**6**).* Nature: yellow liquid; 53 mg, yield: 60%; R_f (30% EtOAc-hexane): 0.40; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz,): δ 8.16 (t, J = 1.9 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 3.2 Hz, 1H), 7.49−7.43 (m, 2H), 7.42−7.36 (m, 3H), 7.33−7.29 (m, 5H), 7.24 (d, J = 6.6 Hz, 2H), 7.20 (dd, J = 6.6, 2.9 Hz, 2H), 7.13 (t, J = 2.4 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 5.47 (s, 2H), 5.42 (s, 2H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 148.7, 146.2, 144.3, 143.4, 139.4, 138.3, 134.4, 131.8, 130.3, 129.2, 129.0, 128.8, 128.5, 128.4, 128.1, 128.0, 125.1, 122.8, 120.3, 119.9, 119.5, 115.4, 111.7, 89.0, 82.2, 54.3, 49.2, 39.9, 25.5; MS-ESI: Calcd. for $C_{39}H_{28}BrN_5$ $[M + H]^+$ m/z: 645.15; Found 645.18.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01255.

Copies of FTIR, ^{1}H NMR, ^{13}C NMR, and HRMS data for all of the new compounds and basic crystallographic data of compound **3b** (PDF)

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Notes

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