Electronic Supporting Information

Synthesis and photophysical properties of novel fluorescent materials containing 2,4,6-triphenylpyridine and 1,8-naphthalimide units using suzuki reaction

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Experimental Section

General information:

All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially available and used without further purification. All reactions were monitored using thin layer chromatography (TLC) on pre-coated silica gel 60 F_{254} (mesh); spots were observed under UV light. Melting points were recorded on electrothermal digital melting point apparatus and were uncorrected. Nuclear Magnetic Resonance (NMR) spectra was recorded at 295 K on a Bruker Avance DPX-400 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. UV-vis spectra were recorded on a Shimadzu UV-2501PC

spectrometer. Fluorescence spectra were obtained on a Hitachi FL-4500 spectrofluorometer. High resolution mass spectroscopy (HRMS) data were measured using micro TOF-Q(APCI) instrument. Cyclic voltammetry measurements were carried out under an inert nitrogen atmosphere with an Autolab potentiostat PGSTAT 10 using a three-electrode cell (platinum was used as the working electrode and as a counter electrode, and scanning calomel electrode as a reference electrode). The rate scan was 100 mV/s and the supporting electrolyte was a Bu_4NPF_6 (0.1 mol/L) solution in CH_2Cl_2. TGA and DSC measurements were carried out on SDT 2960 and DSC 2010 instruments. The thermal analyses were carried out under a nitrogen flow and with a heating rate of 10 °C/min.

Theory for calculation of dipole moment

The solute experiences an electric field due to induced polarization by the electric dipole moment of solute itself on solvent. It is proportional to dipole moment of solute in the ground and excited state, such relationships for the difference and sum of absorption, $\bar{\upsilon}_a$, and fluorescence, $\bar{\upsilon}_f$, maxima in cm^{-1} have been explained by Lippert's equations:

According to the Lippert's equation the difference of absorption, $\bar{\upsilon}_a$, and fluorescence, $\bar{\upsilon}_f$, maxima is given by

$$\bar{\upsilon}_a - \bar{\upsilon}_f = mf(\varepsilon,\eta) + Constant \quad (1)$$

Here, is Lippert's polarity function and is defined as:

$$f(\varepsilon,\eta) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\eta^2 - 1}{2\eta^2 + 1} \quad (2)$$

and m is the slope of the graph obtained by plotting $f(\varepsilon,\eta)$versus Stokes shift ($\bar{\upsilon}_a$ - $\bar{\upsilon}_f$).

Similarly, difference of absorption, $\bar{\upsilon}_a$, and fluorescence, $\bar{\upsilon}_f$, maxima is given by Bakhshiev is as follows

$$\bar{\upsilon}_a - \bar{\upsilon}_f = m_1 f_1(\varepsilon,\eta) + Constant \quad (3)$$

Here, $f_1(\varepsilon,\eta)$is Bakhshiev's polarity function and $m_1$is the slope of the graph obtained by Plotting $f_1(\varepsilon,\eta)$ versus Stokes shift ($\bar{\upsilon}_a - \bar{\upsilon}_f$), which are expressed as follows:

$$f_1(\varepsilon,\eta) = \frac{2\eta^2 + 1}{\eta^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\eta^2 - 1}{\eta^2 + 2}\right] \quad (4)$$

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (5)$$

Here, μ_g and μ_e are the dipole moments in ground state and excited state respectively, h is Planck's constant, c is the velocity of light in vacuum, ε is the solvent dielectric constant and η is the solvent refractive index, a_0 is the Onsager cavity radius.

Table S1 Optical properties of the compounds **8**

Compounds	$\lambda_{Abs.}$ (nm)			λ_{em} (nm)		Φ^a
	CH_2Cl_2	n-Heptane	Toluene	CH_2Cl_2	DMF	
8a	358	404	429	433	445	0.93
8b	358	405	432	434	445	0.64
8c	356	405	435	437	448	0.60
8d	357	402	433	435	446	0.20
8e	357	390	422	441	445	0.57
8f	356	404	421	439	444	0.001
8g	358	408	438	439	448	0.001

[a]The fluorescence quantum yields (Φ) were measured in CH_2Cl_2 using quinine sulfate (Φ = 0.55) as standard.

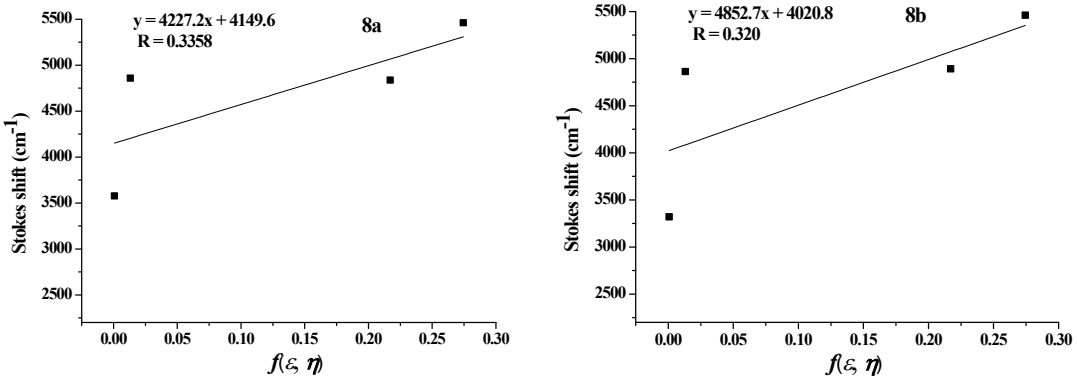
Table S2. Values of solvent polarity functions using different correlation methods.

Solvent	$F(\varepsilon, \eta)$[1]	$F_1(\varepsilon, \eta)$[2]	E_T^{N3}
n-Heptane	0.0007	−0.00131	0.012
Toluene	0.01323	0.02907	0.099
DCM	0.21713	0.59033	0.321
DMF	0.27438	0.83556	0.386

[1] Lippert–Mataga bulk solvent polarity function.

[2] Bakhshiev bulk solvent polarity function.

[3] Reichardt microscopic solvent polarity function.



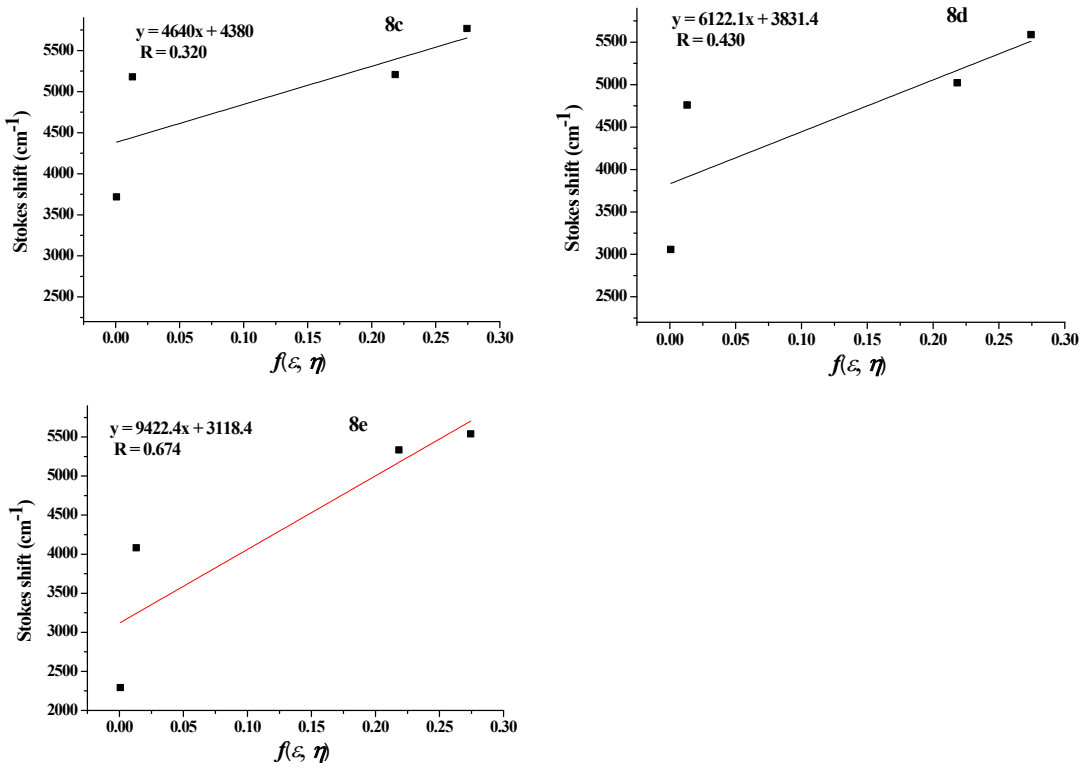


Figure S1. Plot of Stokes shift ($\Delta\nu$) with Lippert's polarity parameter $f(\varepsilon,\eta)$ for compounds **8a-e.**

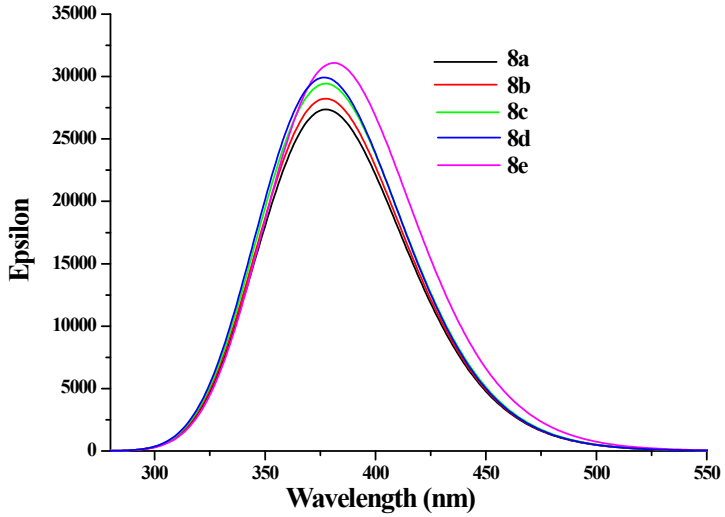


Figure S2. Absorption spectra of **8a-e** in CH_2Cl_2 by theoretical studies using the TDDFT method in the Gaussian 09 W software programme.

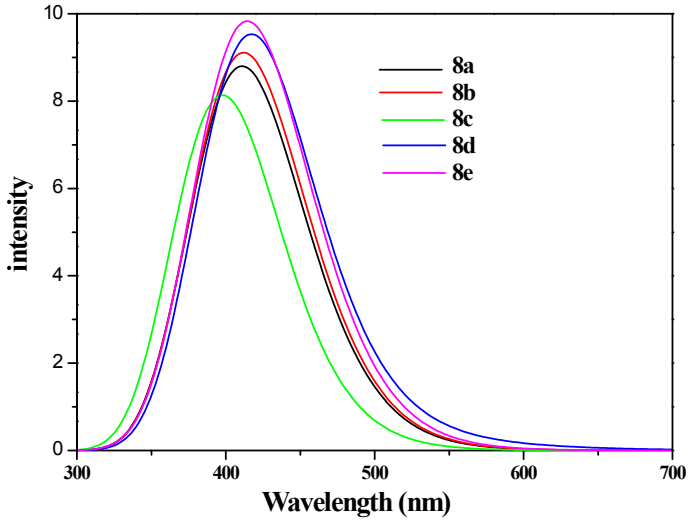


Figure S3. Emission spectra of **8a-e** in CH_2Cl_2 by theoretical studies using the TDDFT method in the Gaussian 09 W software programme.

The procedure for the synthesis of compounds 3

Compound **3** were synthesized according to literature method.[7] A solution of 4-bromobenzaldehyde (10.0 mmol), phenyl methyl ketone (20.0 mmol), ammonium acetate (100 mmol) in ethanol (150 mL) was refluxed at 80 ^{o}C for 24 h. After the finish, filtered the mixture and recrystallized the precipitate with ethanol to give the pure compound **3**.

4-(4-bromophenyl)-2,6-diphenylpyridine (**3**): Yield 30%, white powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.1 Hz, 4H), 7.84 (s, 2H), 7.64 (q, J = 8.6 Hz, 4H), 7.52 (t, J = 7.4 Hz, 4H), 7.46 (t, J = 6.7 Hz, 2H).

The procedure for the preparation of compound 4

Compound **3** (5 mmol), bis(pinacolato)diboron (5 mmol), cesiumcarbonate (7.5 mmol), $Pd(PPh_3)_4$ (0.2 mmol) and dioxane (25 mL) were added into a 50 mL branch-pipe round bottom flask. The mixture was degassed by gently bubbling nitrogen for 30 min and then heated in an oil bath at 85 °C until completion (72 h). After cooling, the product was extracted with DCM, washed with water, dried over Na_2SO_4, filtered, concentrated and further purified by column chromatography (silica gel, hexane/ethyl acetate, 50/1, v/v) to afford compound **4**.

2,6-diphenyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (**4**): Yield

75%, white powder, Mp: 165-168 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 4H), 7.98 (d, J = 7.6 Hz, 2H), 7.92 (s, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 4H), 7.46 (t, J = 7.1 Hz, 2H), 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 135.6, 129.3, 128.7, 127.4, 126.5, 117.6, 84.0, 24.9. HRMS (APCI) m/z:calcd for $C_{29}H_{29}BNO_2$, $(M+H)^+$: 434.2291, Found: 434.2351.

General procedure for the synthesis of compounds 7

Compounds **7** were synthesized according to literature method.[4h] A solution of 4-bromo-1,8-naphthalic anhydride **5** (5 mmol), alkyl amine **6** (or aromatic amine) (6 mmol) in acetic acid (30 mL) was refluxed at 95 ^{o}C for 24 h. After the finish, filtered the mixture and recrystallized the precipitate with ethanol (or acetic acid) to give the pure compounds **7**.

6-Bromo-2-methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7a**): Yield 70%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 7.2 Hz, 1H), 8.57 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.85 (t, J = 7.9 Hz, 1H), 3.56 (s, 3H).

6-Bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7b**): Yield 72%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 7.2 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 7.7 Hz, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.85 (t, J = 7.8 Hz, 1H), 4.18 (t, J = 7.4 Hz, 2H), 1.74 ~ 1.65 (m, 2H), 1.45 (dd, J = 14.8, 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

6-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7c**): Yield 69%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 7.3 Hz, 1H), 8.64 (d, J = 8.5 Hz, 1H), 8.47 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.90 (t, J = 7.9 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 7.8 Hz, 2H).

6-Bromo-2-p-tolyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7d**): Yield 70%, yellow powder,^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 7.3 Hz, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.46 (d, J = 7.7Hz, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 7.4 Hz, 2H), 2.45 (s, 3H).

6-Bromo-2-(naphthalen-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7e**): Yield 65%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 7.3 Hz, 1H), 8.69 (d, J = 8.5 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.98 - 7.89 (m, 2H), 7.63 (m, 2H), 7.51 (t, J = 8.6 Hz, 2H), 7.47 - 7.40 (m, 1H).

6-bromo-2-(naphthalen-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7f**): Yield 65%,

yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.5 Hz, 1H), 8.49 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.95 - 7.84 (m, 4H), 7.54 (m, 2H), 7.39 (m, 1H).

Methyl 4-(6-bromo-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)benzoate (**7g**): Yield 65%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 7.3 Hz, 1H), 8.66 (d, J = 8.5 Hz, 1H), 8.46 (d, J = 7.9 Hz, 1H), 8.23 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 7.9 Hz, 1H), 7.91 (t, J = 7.9 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 3.97 (s, 3H).

General procedure for the synthesis of compounds 8

Compounds **7a-g** (1 mmol), **4** (1.2 mmol), Cesiumcarbonate (1.5 mmol), $Pd(PPh_3)_4$ catalyst (0.04 mmol) and dioxane (5 mL) were added into a 50 mL branch-pipe round bottom flask. The mixture was degassed by gently bubbling nitrogen for 30 min and then heated in an oil bath at 85 °C until completion (72 h). After cooling, the product was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, filtered, concentrated and further purified by recrystallizing from dichloromethane and ethanol to obtain compounds **8a-g**. The seven starburst compounds synthesized are easily soluble in common organic solvents such as chloroform, toluene, ethyl acetate and DMF.

6-(4-(2,6-Diphenylpyridin-4-yl)phenyl)-2-methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8a**): Yield 65%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (t, J = 8.3 Hz, 2H), 8.34 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 7.7 Hz, 4H), 8.00 (s, 2H), 7.96 (d, J = 7.8 Hz, 2H), 7.76 (m, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.5 Hz, 4H), 7.49 (t, J = 7.1 Hz, 2H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 157.7, 149.4, 146.0, 139.5, 139.2, 132.5, 131.3, 130.8, 130.0, 129.3, 128.7, 127.9, 127.5, 127.1, 122.8, 121.9, 117.1, 27.1. HRMS (APCI) m/z: calcd for $C_{36}H_{25}N_2O_2$ $[M+H]^+$: 517.1916, Found: 517.1916.

2-Butyl-6-(4-(2,6-diphenylpyridin-4-yl)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8b**): Yield 63%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (t, J = 8.1 Hz, 2H), 8.33 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 7.4 Hz, 4H), 8.04-7.94 (m, 4H), 7.80-7.70 (m, 4H), 7.60-7.50 (m, 6H), 4.26-4.20 (m, 2H), 1.76 (t, J = 6.5 Hz, 2H), 1.51-1.46 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.4, 139.9, 132.3, 131.3, 130.8, 129.9, 129.6, 128.8, 127.9, 127.5, 127.1, 123.0, 117.70, 40.3, 30.2, 20.4, 13.8. HRMS (APCI) m/z: calcd for $C_{39}H_{31}N_2O_2$ $[M+H]^+$: 559.2386, Found: 559.2350.

6-(4-(2,6-Diphenylpyridin-4-yl)phenyl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8c**): Yield 60%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (t, J = 8.0 Hz, 2H), 8.39 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 7.5 Hz, 4H), 8.05-7.97 (m, 4H), 7.84-7.73 (m, 4H), 7.57 (m, 9H), 7.37 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.2, 157.6, 146.3, 139.5, 139.1, 135.3, 132.7, 131.7, 131.2, 130.7, 130.1, 129.4, 129.1, 128.7, 128.0, 127.6, 127.2, 123.1, 122.2, 117.2. HRMS (APCI) m/z: calcd for $C_{41}H_{27}N_2O_2$ $[M+H]^+$: 579.2073, Found: 579.2071.

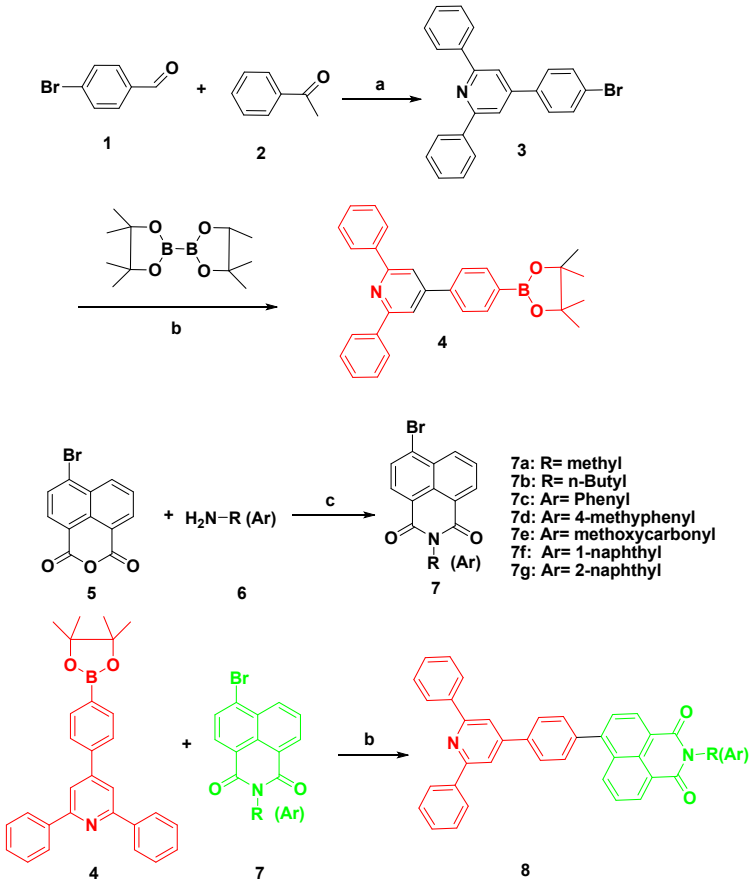
6-(4-(2,6-Diphenylpyridin-4-yl)phenyl)-2-ptolyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8d**): Yield 60%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (t, J = 8.2 Hz, 2H), 8.38 (d, J = 9.1 Hz, 1H), 8.25 (d, J = 6.8 Hz, 4H), 8.07-7.94 (m, 4H), 7.83-7.71 (m, 4H), 7.53 (m, 6H), 7.38 (d, J = 7.2 Hz, 2H), 7.23 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 157.4, 146.1, 138.7, 132.6, 131.7, 131.2, 130.8, 130.1, 129.7, 129.4, 128.8, 128.2, 128.2, 127.5, 127.1, 123.2, 117.7, 21.3. HRMS (APCI) m/z: calcd for $C_{42}H_{29}N_2O_2$ $[M+H]^+$: 593.2229, Found: 593.2214.

6-(4-(2,6-Diphenylpyridin-4-yl)phenyl)-2-(naphthalen-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8e**): Yield 60%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (t, J = 8.3 Hz, 2H), 8.43 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 6.7 Hz, 4H), 8.09 - 7.96 (m, 6H), 7.82 (m, 4H), 7.68 (d, J = 7.5 Hz, 2H), 7.56 (m, 8H), 7.46 (t, J = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.5, 146.4, 139.7, 138.8, 134.5, 132.9, 132.2, 131.9, 131.4, 130.8, 130.2, 129.4, 128.8, 128.0, 127.7, 127.6, 127.1, 126.7, 125.6, 122.2, 121.8, 117.5. HRMS (APCI) m/z: calcd for $C_{45}H_{29}N_2O_2$ $[M+H]^+$: 629.2229, Found: 629.2220.

6-(4-(2,6-Diphenylpyridin-4-yl)phenyl)-2-(naphthalen-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8f**): Yield 65%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (t, J = 8.1 Hz, 2H), 8.44 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 7.3 Hz, 4H), 8.08 - 7.90 (m, 8H), 7.84 (m, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.61 - 7.45 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 157.7, 149.3, 146.4, 139.4, 133.6, 133.2, 132.8, 131.7, 131.2, 130.7, 130.2, 129.2, 128.7, 128.2, 127.8, 127.2, 126.7, 126.4, 126.1, 123.2, 122.1, 117.0. HRMS (APCI) m/z: calcd for $C_{45}H_{29}N_2O_2$ $[M+H]^+$: 629.2229, Found: 629.2220.

Methyl-4-(6-(4-(2,6-diphenylpyridin-4-yl)phenyl)-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)benzoate (**8g**): Yield 65%, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (t,

J = 8.1 Hz, 2H), 8.42 (d, J = 8.5 Hz, 1H), 8.26 (d, J = 7.9 Hz, 5H), 8.02 - 7.94 (m, 4H), 7.81 (m, 2H), 7.69 (m, 3H), 7.55 (t, J = 7.3 Hz, 4H), 7.47 (m, 4H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.7, 139.5, 139.2, 133.0, 131.8, 131.3, 130.7, 129.5, 128.7, 128.0, 127.6, 127.2, 117.1, 52.3. HRMS (APCI) m/z: calcd for $C_{43}H_{29}N_2O_4$ $[M+H]^+$: 637.2127 Found: 637.2290.



Scheme 1 Synthetic routines for compound **3**, **4**, **7** and **8**. *Reagents and conditions:* (a) NH_4OAc, EtOH, 80 °C; (b) cat. $Pd(PPh_3)_4$, Cs_2CO_3, dioxane, 80 °C; (c) acetic acid, 95 °C.