Supporting Information

A transition metal- and photosensitizer-free approach for site-selective (hetero)arylation of polychlorinated heteroarenes

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1. General Information

Synthesis of the substrates were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. $2b-2h^1$ and $2k^2$ were synthesized according to published procedures. Acetonitrile were purchased from J&K and used without additional purification. All other reagents were purchased from commercial suppliers (TCI, Sigma-Aldrich, Alfa Aesar, Macklin, Bide Pharmatech, Adamasbeta[®], J&K Scientific, etc.) and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, pH = 6.7-7.0). Photochemical reactions were performed in 10 mL Schlenk tubes under an atmosphere of argon and upon irradiation with a 40 W Kessil LED lamp (PR160L, $\lambda_{max} = 427$ nm; commercial supplier: Anhui Kemi Instrument Co. Ltd., website: http://www.ahkemi.com); ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker AM (500 MHz) or Bruker AM (600 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $CDCl_3 = 7.26 \text{ ppm} (^{1}\text{H NMR})$, 77.0 ppm ($^{13}\text{C NMR}$); Acetone- $d_6 = 2.05 \text{ ppm} (^{1}\text{H NMR})$, 29.84 ppm and 206.26 ppm (${}^{13}C$ NMR); DMSO- $d_6 = 2.50$ ppm (${}^{1}H$ NMR), 40.0 ppm (${}^{13}C$ NMR); Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were recorded on an Agilent 1290-G6545XT QTOF instrument using ESI technique. UV-Vis absorption spectra were recorded on a spectraMax M5 in a 1.0 mm quartz cuvette. X-ray diffraction data were recorded on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 100 or 293 K. Melting points were determined by a Swithzerland Buchi M-5600 melting point.

2. Synthesis of the Substrates

2a, **2i**, **2j**, **2l**, **2m**, **2n**, **2o**, **2p**, **2q** were purchased from Bide Pharmatech, Adamas-beta[®], *J&K*, etc. and used without further purification. **2b–2h** and **2k** were prepared by published procedures.¹⁻²

Preparation of substrates 2b-2h.¹



General procedure A: Select a 100 mL circular bottom flask, 1*H* indole (3.8 mmol), phenylboronic acid (7.6 mmol), Pd(AcO)₂ (0.38 mmol, 86.4 mg), and 2,9-dimethyl-1,10-phenanthroline hemihydrate (0.76 mmol, 173 mg) in 1,2-dichloroethane (DCE, 20 mL). Under air, the reaction mixture was stirred at 80 °C in an oil bath until the complete conversion of the starting material on TLC. Then, the reaction mixture was cooled to room temperature, and added water. The resulting mixture was extracted with EtOAc (20 mL × 3), The combined organic layers were dried with Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (eluted with Petroleum Etherpe (PE) : EtOAc = 9:1) to afford the pure products **2b–2h**.

4-methyl-2-phenyl-1*H*-indole (2b)



According to general procedure A, 2b was synthesized as an orange solid (0.58 g, 2.8 mmol, 73% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.27 (s, 1H), 7.69 – 7.59 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.19 (m, 2H), 7.11 – 7.08 (m, 1H), 6.92 (d, *J* = 7.1 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 2.58 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 137.3, 136.6, 132.6, 130.3, 129.3, 129.1, 127.6, 125.1, 122.5, 120.4, 108.5, 98.6, 18.8.

All other data was in agreement with the literature.²

5-methyl-2-phenyl-1*H*-indole (2c)



According to **general procedure A**, **2c** was synthesized as a yellow solid (0.13 g, 0.63 mmol, 17% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.24 (s, 1H), 7.69 – 7.63 (m, 2H), 7.47 – 7.41 (m, 3H), 7.35 – 7.28 (m, 2H), 7.02 – 7.00 (m, 1H), 6.75 – 6.74 (m, 1H), 2.46 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 138.0, 135.2, 132.6, 129.6, 129.5, 129.0, 127.6, 125.1, 124.0, 120.3, 110.5, 99.6, 21.5.

All other data was in agreement with the literature.²

7-methyl-2-phenyl-1*H*-indole (2d)



According to general procedure A, 2d was synthesized as a yellow solid (0.69 g, 3.3 mmol, 87% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.33 (s, 1H), 7.90 – 7.84 (m, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.58 – 7.52 (m, 1H), 7.38 – 7.35 (m, 1H), 7.29 – 7.27 (m, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 2.73 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 137.9, 136.9, 132.9, 129.2, 129.2, 127.9, 125.5, 123.3, 120.8, 120.4, 118.8, 100.9, 16.9.

All other data was in agreement with the literature.²

4-methoxy-2-phenyl-1*H*-indole (2e)



According to **general procedure A**, **2e** was synthesized as a yellow solid (0.21 g, 0.93 mmol, 30% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.28 (s, 1H), 7.56 – 7.52 (m, 2H), 7.35 – 7.32 (m, 2H), 7.26 – 7.21 (m, 1H), 7.09 – 7.06 (m, 1H), 6.96 – 6.92 (m, 2H), 6.51 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 153.4, 138.3, 136.6, 132.4, 129.1, 127.5, 125.1, 123.24, 120.1, 104.6, 100.2, 97.3, 55.5.

All other data was in agreement with the literature.¹

5-methoxy-2-phenyl-1*H*-indole (2f)



According to **general procedure A**, **2f** was synthesized as a chartreuse solid (0.41 g, 1.8 mmol, 54% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.23 (s, 1H), 7.67 – 7.63 (m, 2H), 7.44– 7.41 (m, 2H), 7.34 – 7.29 (m, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.86 – 6.84 (m, 1H), 6.76– 6.75 (m, 1H), 3.87 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.5, 138.6, 132.5, 132.1, 129.8, 129.0, 127.6, 125.1, 112.7, 111.6, 102.3, 99.9, 55.9.

All other data was in agreement with the literature.¹

6-methoxy-2-phenyl-1*H*-indole (2g)



According to general procedure A, 2g was synthesized as a yellow solid (0.33 g, 1.5 mmol, 43% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.24 (s, 1H), 7.65 – 7.60 (m, 2H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.27 (m, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.81– 6.78 (m, 1H), 6.76 – 6.75 (m, 1H), 3.87 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.8, 137.7, 136.9, 132.6, 129.0, 127.3, 124.7, 123.6, 121.3, 110.2, 99.9, 94.6, 55.7.

All other data was in agreement with the literature.³

2-(3,4-dimethoxyphenyl)-1*H*-indole (2h)



According to **general procedure A**, **2h** was synthesized as an orange solid (0.41 g, 1.6 mmol, 42% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.46 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.19 – 7.13 (m, 3H), 7.12 – 7.08 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.4, 149.0, 138.2, 136.8, 129.4, 125.7, 122.0, 120.4, 120.2, 117.7, 111.7, 110.8, 109.0, 99.0, 56.0.

All other data was in agreement with the literature.³

Preparation of substrate 2k.²



A high pressure tube equipped with a magnetic stirring bar was charged with 4-methyl-1*H*-indole (0.50 g, 3.8 mmol, 1.0 equiv.), norbornene (0.72 g, 7.6 mmol, 2.0 equiv.), K_2CO_3 (1.10 g, 7.6 mmol, 2.0 equiv.), and PdCl₂(MeCN)₂ (99.0 mg, 0.38 mmol, 0.10 equiv.). A solution of water (5.0 mL) in DMF (25 mL) was added *via* syringe, and then the 1-ethyl-4-iodobenzene (1.80 g, 7.6 mmol, 2.0 equiv.) was added *via* syringe. The reaction mixture was then placed in a preheated oil bath at 80 °C. Vigorous stirring was applied. The reaction was monitored by TLC. Then, the reaction mixture was cooled to room temperature and added water. The resulting mixture was extracted with EtOAc (20 mL × 3), The combined organic layers were dried with Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (eluted with PE: EtOAc = 9:1) to afford the pure product **2k** as a red solid (0.67 g, 2.9 mmol, 75% yield). Mp: 63.3 – 66.7 °

2-(4-ethylphenyl)-4-methyl-1*H*-indole (2k)



¹H NMR (500 MHz, CDCl₃) δ 8.29 (s, 1H), 7.61 – 7.56 (m, 2H), 7.30 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 7.10 – 7.07 (m, 1H), 6.92 – 6.90 (m, 1H), 6.80 – 6.79 (m, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 143.9, 137.5, 136.4, 130.1, 129.3, 128.5, 125.1, 122.3, 120.3, 108.4, 98.0, 28.6, 18.8, 15.5.

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{18}N^+(M+H)^+$: 236.1434, found: 236.1434.

3. Photochemical Reaction of Polychlorinated Heteroarenes with Electron-enriched Arenes

3.1 Optimization of Reaction Conditions

A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 0.10 mmol, 19.8 mg), 2phenyl-1*H*-indole (**2a**, 0.30 mmol, 58.0 mg), basic additive (0.10 or 0.20 mmol, 1.0 or 2.0 equiv.) and the indicated solvent (1.0 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from LED lamp ($\lambda_{max} = 427$ nm) with a direct current (DC) fan cooling. The reaction was stirred at 30 °C for 6 – 19 h. The residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3aa**) as a yellow solid.





Entry	427 nm LED (power)	basic additive	solvent	T (h)	Yield ^b
1	20 W	none	MeCN	15 h	trace
2	20 W	$K_2CO_3^c$	MeCN	15 h	59%
3	20 W	$K_2CO_3^c$	THF	19 h	trace
4	20 W	$K_2CO_3^c$	DCM	19 h	n.d.
5	20 W	$K_2CO_3^c$	DMF	19 h	trace
6	20 W	$K_2CO_3^c$	DMSO	19 h	trace
7	20 W	$K_2CO_3^c$	CHCl ₃	16 h	n.d.
8	20 W	$K_2CO_3^c$	Acetone	16 h	26%
9	20 W	$K_2CO_3^c$	Toluene	16 h	n.d.
10	20 W	$K_2CO_3^c$	CH ₃ OH	16 h	31%
11	20 W	$K_2CO_3^c$	Ethylene glycol	16 h	n.d.

12	20 W	$K_2CO_3^c$	DME	16 h	n.d.
13	20 W	$K_2CO_3^c$	HFIP	16 h	trace
14	20 W	$K_2CO_3^c$	3-Methyl-1-butanol	16 h	n.d.
15	20 W	$Cs_2CO_3^d$	MeCN	15 h	49%
16	20 W	CH_3COOK^d	MeCN	15 h	37%
17	20 W	$K_3PO_4^{d}$	MeCN	15 h	48%
18	20 W	$Na_2CO_3^d$	MeCN	15 h	42%
19	20 W	$K_2CO_3^d$	MeCN	15 h	59%
20	40 W	$K_2CO_3^d$	MeCN	6 h	17%
21	40 W	$Cs_2CO_3^d$	MeCN	6 h	61%
22	40 W	$Cs_2CO_3^d$	$MeCN + H_2O = 7:3$	6 h	72%
23	none	$Cs_2CO_3^d$	$MeCN + H_2O = 7:3$	6 h	n.d.
24^{e}	40 W	$Cs_2CO_3^d$	$MeCN + H_2O = 7:3$	6 h	n.d.
25 ^f	40 W	none	$MeCN + H_2O = 7:3$	15 h	20%

^{*a*} Reaction conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.30 mmol, 3.0 equiv.), basic additive (0.10 or 0.20 mmol), indicated solvent (1.0 mL), under argon, upon irradiation with a LED lamp ($\lambda_{max} = 427$ nm), at 30 °C. ^{*b*} Isolated yield. ^{*c*} 2.0 equiv.. ^{*d*} 1.0 equiv.. ^{*e*} Reaction in air. n.d. = not detected. ^{*f*} LED lamp ($\lambda_{max} = 400$ nm). THF = tetrahydrofuran, DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide, DME = 1,2-dimethoxy-ethan, DMSO = dimethyl sulfoxide, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

3.2 Substrate Scope



$$R^{1}_{l} \xrightarrow{N}_{R^2} R^3$$

or naphthylamine,naphthol





3-chloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3aa)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 6 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3aa**) as a yellow solid (25.5 mg, 0.072 mmol, 72% yield). The regioisomeric ratio of **3aa** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 216.3 – 217.0 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 11.00 (s, 1H), 7.94 – 7.92 (m, 1H), 7.89 (d, J = 0.9 Hz, 1H), 7.80 (m, 7.81 – 7.79, 1H), 7.68 – 7.64 (m, 1H), 7.55 – 7.57 (m, 1H), 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.24 – 7.16 (m, 4H), 7.07 – 7.04 (m, 1H).

¹³C NMR (126 MHz, Acetone-*d*₆) δ 157.6, 144.9, 138.9, 137.3, 136.4, 132.5, 131.1, 129.6, 128.6, 128.0, 127.8, 127.7, 127.3, 127.2, 126.9, 122.6, 120.3, 119.5, 118.5, 118.3, 111.1.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{16}ClN_2^+$ (M+H)⁺: 355.0997, found: 355.0989.

3-chloro-5-methyl-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ab)



A dried 10 mL Schlenk tube was charged with 1,3-dichloro-5-methylisoquinoline (1b, 21.1 mg, 0.10

mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ab**) as a yellow solid (26.2 mg, 0.071 mmol, 71% yield). The regioisomeric ratio of **3ab** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 243.1 – 245.8 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 11.95 (s, 1H), 8.01 (d, *J* = 0.8 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.36 – 7.31 (m, 2H), 7.28 – 7.25 (m, 3H), 7.24 – 7.20 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.04 – 7.00 (m, 1H), 2.67 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 158.1, 144.8, 138.3, 137.3, 136.4, 133.9, 132.4, 131.9, 129.5, 129.1, 128.3, 127.9, 127.5, 127.1, 126.0, 122.8, 120.6, 119.4, 116.0, 112.1, 110.9, 18.9.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1152

3-chloro-6-methyl-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ac)



A dried 10 mL Schlenk tube was charged with 1,3-dichloro-6-methylisoquinoline (**1c**, 21.2 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ac**) as a yellow solid (22.0 mg, 0.060 mmol, 60% yield). The

regioisomeric ratio of **3ac** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 190.6 – 192.5 °C. ¹H NMR (500 MHz, Acetone- d_6) δ 10.97 (s, 1 H), 7.80 (d, J = 0.9 Hz, 1H), 7.72 (dd, J = 2.0, 1.0 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.46 – 7.39 (m, 2H), 7.32 – 7.30 (m, 1H), 7.26 – 7.19 (m, 5H), 7.07 – 7.04 (m, 1H), 2.47 (d, J = 1.0 Hz, 3H).

¹³C NMR (126 MHz, Acetone-*d*₆) δ 157.1, 145.0, 141.5, 139.3, 137.1, 136.2, 132.5, 129.6, 129.4, 128.5, 127.8, 127.7, 125.4, 125.1, 122.5, 120.2, 119.5, 117.8, 111.4, 111.4, 111.1, 20.9.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1154.

3-chloro-7-methyl-1-(2-phenyl-1*H*-indol-3-yl) isoquinoline (3ad)



A dried 10 mL Schlenk tube was charged with 1,3-dichloro-7-methylisoquinoline (**1d**, 21.2 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ad**) as a yellow solid (21.9 mg, 0.059 mmol, 59% yield). The regioisomeric ratio of **3ad** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 253.1 – 257.8 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 11.93 (s, 1H), 7.96 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.46 (s, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.20 (m, 5H), 7.04 (t, *J* = 7.5 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 156.8, 143.7, 137.5, 137.5, 137.3, 136.5, 133.8, 132.6, 129.4, 129.0, 128.3, 128.0, 126.9, 126.7, 126.6, 122.8, 120.6, 119.5, 118.7, 112.1, 110.7, 21.7. HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1148.

3-chloro-6-fluoro-1-(2-phenyl-1H-indol-3-yl) isoquinoline (3ae)



A dried 10 mL Schlenk tube was charged with 1,3-dichloro-6-fluoroisoquinoline (**1e**, 21.6 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ae**) as a yellow solid (33.9 mg, 0.091 mmol, 91% yield). The regioisomeric ratio of **3ae** was determined as 12:1 *rr* by the crude ¹H NMR. Mp: 175.5 – 176.7 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.64 (s, 1H), 7.84 – 7.87 (m, 1H), 7.70 (s, 1H), 7.50 – .48 (m, 2H), 7.39 – 7.37 (m, 1H), 7.33 – 7.30 (m, 2H), 7.28 – 7.21 (m, 4H), 7.18 – 7.15 (m, 1H), 7.03 – 6.99 (m, 1H). ¹³C NMR (126 MHz, Acetone-*d*₆) δ 161.0 (d, *J* = 869.4 Hz), 162.4, 146.1, 140.7 (d, *J* = 11.3 Hz), 137.6, 136.4, 132.3 (d, *J* = 5.0 Hz), 131.7 (d, *J* = 10.1 Hz), 129.4 (d, *J* = 5.0 Hz), 128.6, 127.9, 124.1, 122.7, 120.4, 119.4, 117.9 (d, *J* = 5.0 Hz), 117.4, 117.2, 111.5 (d, *J* = 6.3 Hz), 109.4 (d, *J* = 22.7 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -106.45.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₅ClFN₂⁺ (M+H)⁺: 373.0902, found: 373.0901.

3-chloro-7-fluoro-1-(2-phenyl-1H-indol-3-yl) isoquinoline (3af)



3af

A dried 10 mL Schlenk tube was charged with 1,3-dichloro-7-fluoroisoquinoline (**1f**, 21.6 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3af**) as a yellow solid (28.0 mg, 0.076 mmol, 76% yield). The regioisomeric ratio of **3af** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 208.3 – 213.3 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.56 (s, 1H), 7.71 – 7.68 (m, 1H), 7.65 (s, 1H), 7.40 – 7.37 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 7.14 – 7.13 (m, 3H), 7.09 – 7.06 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 160.7 (d, J = 869.4 Hz), 156.5 (d, J = 6.0 Hz), 137.3, 136.0, 135.8, 131.9, 129.4, 128.5 (d, J = 9.1 Hz), 128.3, 127.8, 127.6 (d, J = 9.1 Hz), 123.3, 121.9, 121.7, 121.2, 119.9, 118.5, 111.8, 111.6, 111.1.

¹⁹F NMR (565 MHz, CDCl₃) δ -110.72.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₅ClFN₂⁺ (M+H)⁺: 373.0902, found: 373.0900.

4-chloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ag)



A dried 10 mL Schlenk tube was charged with 1,4-dichloroisoquinoline (**1g**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 55 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ag**) as a yellow solid (19.9 mg, 0.056 mmol, 56% yield). The regioisomeric ratio of **3ag** was determined as 10:1 *rr* by the crude ¹H NMR. Mp: 199.7 – 200.8 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.40 (s, 1H), 8.56 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.38 – 7.34 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.02 – 6.98 (m, 4H), 6.90 – 6.87 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 155.8, 141.2, 137.7, 136.1, 134.3, 131.9, 131.3, 129.5, 129.1, 128.9, 128.8, 128.7, 127.9, 127.7, 127.2, 125.2, 123.5, 122.6, 120.5, 119.6, 111.5.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{15}ClN_2Na^+$ (M+Na)⁺: 377.0816, found: 377.0818.

5-chloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ah)



A dried 10 mL Schlenk tube was charged with 1,5-dichloroisoquinoline (**1h**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ah**) as a yellow solid (19.2 mg, 0.054 mmol, 54% yield). The regioisomeric ratio of **3ah** was determined as 10:1 *rr* by the crude ¹H NMR. Mp: 143.1 – 145.3 °C.

¹H NMR (500 MHz, DMSO- d_6) δ 11.92 (s, 1H), 8.76 (d, J = 6.0 Hz, 1H), 8.06 (d, J = 5.9 Hz, 1H), 7.94 - 7.87 (m, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.42 - 7.39 (m, 1H), 7.32 - 7.27 (m, 2H), 7.26 – 7.18 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.03 – 6.97 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 156.8, 137.2, 136.0, 134.7, 132.0, 131.1, 130.2, 129.7, 129.1, 128.9, 128.7, 127.9, 127.6, 127.4, 126.8, 125.2, 122.9, 120.8, 119.8, 116.0, 111.2.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₆ClN₂⁺ (M+H)⁺: 355.0997, found: 355.0998.

6-chloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ai)



A dried 10 mL Schlenk tube was charged with 1,6-dichloroisoquinoline (**1i**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ai**) as a yellow solid (14.9 mg, 0.042 mmol, 42% yield). The regioisomeric ratio of **3ai** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 156.3 – 157.9 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 10.96 (s, 1H), 8.67 (d, J = 5.7 Hz, 1H), 8.05 (d, J = 2.1 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.59 – 7.57 (m, 1H), 7.41 – 7.37 (m, 2H), 7.35 (dd, J = 9.0, 2.2 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.23 – 7.19 (m, 4H), 7.05 – 7.02 (m, 1H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 156.8, 144.0, 137.6, 136.9, 136.5, 135.5, 132.6, 130.0, 129.7, 128.5, 127.6, 127.6, 127.5, 126.4, 125.6, 122.4, 120.1, 119.4, 118.7, 111.8, 111.5.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₆ClN₂⁺ (M+H)⁺: 355.0997, found: 355.0996.

5-chloro-4-(2-phenyl-1*H*-indol-3-yl)quinoline (3aj)



A dried 10 mL Schlenk tube was charged with 4,5-dichloroquinoline (**1j**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3aj**) as a yellow solid (22.0 mg, 0.062 mmol, 62% yield). The regioisomeric ratio of **3aj** was determined as 14:1 *rr* by the crude ¹H NMR. Mp: 204.5 – 205.5 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.90 (d, J = 4.4 Hz, 1H), 8.58 (s, 1H), 8.21 – 8.19 (m, 1H), 7.65 – 7.62 (m, 1H), 7.54 – 7.49 (m, 2H), 7.40 (d, J = 4.4 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.28 – 7.22 (m, 4H), 7.11 – 7.07 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.9, 149.9, 142.5, 135.5, 134.4, 132.0, 131.1, 130.6, 129.6, 129.4, 129.1, 128.8, 127.8, 127.5, 126.6, 126.6, 123.0, 120.7, 119.3, 113.8, 110.9.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₆ClN₂⁺ (M+H)⁺: 355.0997, found: 355.0995.

ethyl 6-chloro-4-(2-phenyl-1*H*-indol-3-yl)quinoline-3-carboxylate (3ak)



A dried 10 mL Schlenk tube was charged with ethyl 4,6-dichloroquinoline-3-carboxylate (1k, 27.0 mg,

0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ak**) as a yellow solid (26.5 mg, 0.062 mmol, 62% yield). The regioisomeric ratio of **3ak** was determined as 14:1 *rr* by the crude ¹H NMR. Mp: 218.7 – 220.9 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.32– 9.28 (m, 2H), 8.44 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.27 – 7.22 (m, 5H), 7.17 – 7.10 (m, 2H), 3.98 (qq, *J* = 10.8, 7.1 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 165.1, 147.6, 137.1, 136.2, 136.0, 134.8, 133.7, 131.2, 129.1, 129.0, 128.8, 128.6, 128.2, 127.5, 127.1, 126.7, 123.5, 121.4, 118.7, 111.6, 111.6, 107.5, 61.9, 13.5.

HRMS (ESI-TOF, m/z) calcd for C₂₆H₂₀ClN₂O₂⁺ (M+H)⁺: 427.1208, found: 427.1205.

3-(6-chloro-3-(trifluoromethyl) pyridin-2-yl)-2-phenyl-1H-indole (3al)



A dried 10 mL Schlenk tube was charged with 2,6-dichloro-3-(trifluoromethyl)pyridine (**1**, 21.6 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3al**) as a yellow solid (33.2 mg, 0.089 mmol, 89% yield). The

regioisomeric ratio of **3al** was determined as 10:1 rr by the crude ¹H NMR. Mp: 144.6 – 145.9 °C.

¹H NMR (500 MHz, DMSO- d_6) δ 11.85 (s, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.35 – 7.26 (m, 5H), 7.20 – 7.17 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.03 – 7.00 (m, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 155.0, 153.7, 139.3, 139.3, 136.3, 135.9, 132.1, 129.5, 129.2, 128.3, 127.4, 126.0 (q, *J* = 30.2, 61.7 Hz), 123.9, 123.7 (d, *J* = 273.4 Hz), 122.7, 120.4, 119.1, 111.9, 110.1.
¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -59.24.

HRMS (ESI-TOF, m/z) calcd for C₂₀H₁₃ClF₃N₂⁺ (M+H)⁺: 373.0714, found: 373.0714.

3-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)-2-phenyl-1H-indole (3am)



A dried 10 mL Schlenk tube was charged with 2,3-dichloro-5-(trifluoromethyl)pyridine (**1m**, 17.6 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3am**) as a colorless solid (32.8 mg, 0.088 mmol, 88% yield). The regioisomeric ratio of **3am** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 175.8 – 177.2 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 11.91 (s, 1H), 9.07 – 9.01 (m, 1H), 8.50 (d, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.32 (m, 6H), 7.22 – 7.19 (m, 1H), 7.10 – 7.03 (m, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 157.8, 145.0, 137.8, 136.4, 135.6, 132.8, 131.9, 129.3, 128.6, 128.3, 127.7, 124.6 (d, *J* = 25.2, 32.8 Hz), 122.8, 122.5, 120.6, 119.7, 112.2.

¹⁹F NMR (471 MHz, DMSO- d_6) δ -60.42.

HRMS (ESI-TOF, m/z) calcd for C₂₀H₁₃ClF₃N₂⁺ (M+H)⁺: 373.0714, found: 373.0713.

3-(2-chloro-5-fluoro-6-methylpyrimidin-4-yl)-2-phenyl-1*H*-indole (3an)



A dried 10 mL Schlenk tube was charged with 2,4-dichloro-5-fluoro-6-methylpyrimidine (**1n**, 18.1 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3an**) as a yellow solid (30.7 mg, 0.091 mmol, 91% yield). The regioisomeric ratio of **3an** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 163.6 – 165.6 °C.

¹H NMR (500 MHz, Acetone-*d*₆) δ 11.16 (s, 1H), 7.95 – 7.93 (m, 1H), 7.61 – 7.58 (m, 2H), 7.55 – 7.53 (m, 1H), 7.47 – 7.42 (m, 3H), 7.28 – 7.25 (m, 1H), 7.21 – 7.18 (m, 1H), 2.38 (d, J = 2.9 Hz, 3H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 157.9 (d, J = 18.9 Hz), 153.9, 153.7 (d, J = 5.0 Hz) 152.7, 152.5, 151.9, 140.7 (d, J = 17.6 Hz), 136.6 (d, J = 18.9 Hz), 128.8, 128.7, 128.0, 127.9 (d, J = 5.0 Hz), 123.0, 121.1, 120.2, 111.6 (d, J = 7.6 Hz), 16.9.

¹⁹F NMR (471 MHz, Acetone- d_6) δ -136.24.

HRMS (ESI-TOF, m/z) calcd for C₁₉H₁₃ClFN₃Na⁺ (M+Na)⁺: 360.0674, found: 360.0673.

tert-butyl 2-chloro-4-(2-phenyl-1H-indol-3-yl)-5,8-dihydropyrido[3,4-d]pyrimidine-7(6H)-carboxylate (3ao)



A dried 10 mL Schlenk tube was charged with *tert*-butyl 2,4-dichloro-5,8-dihydropyrido[3,4-*d*] pyrimidine-7(6*H*)-carboxylate (**1o**, 30.4 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 5:1) to afford the pure product (**3ao**) as a yellow solid (35.5 mg, 0.077 mmol, 77% yield). The regioisomeric ratio of **3ao** was determined as 5:1 *rr* by the crude ¹H NMR. Mp: 305.0 – 306.2 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.68 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 7.15 – 7.11 (m, 1H), 4.53 (s, 2H), 3.22 (s, 2H), 2.03 (s, 2H), 1.37 (s, 9H).

¹³C NMR (151 MHz, DMSO-*d*₆) δ 165.7, 157.8, 154.1, 138.8, 136.7, 132.5, 129.5, 129.2, 128.1, 126.1, 123.1, 121.0, 119.8, 112.3, 108.7, 80.0, 55.4, 48.4, 47.8, 28.4, 25.2.

HRMS (ESI-TOF, m/z) calcd for C₂₆H₂₆ClN₄O₂⁺ (M+H)⁺: 461.1739, found: 461.1733.

2-chloro-6,7-dimethoxy-4-(2-phenyl-1*H*-indol-3-yl)quinazoline (3ap)



A dried 10 mL Schlenk tube was charged with 2,4-dichloro-6,7-dimethoxyquinazoline (**1p**, 25.9 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ap**) as a yellow solid (24.1 mg, 0.058 mmol, 58% yield). The regioisomeric ratio of **3ap** was determined as 6:1 *rr* by the crude ¹H NMR. Mp: 315.3 – 316.7 °C.

¹H NMR (500 MHz, DMSO- d_6) δ 12.18 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.34 – 7.33 (m, 4H), 7.29 – 7.24 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.82 (s, 1H), 3.94 (s, 3H), 3.32 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 164.5, 156.6, 155.3, 150.9, 149.9, 139.6, 137.0, 132.5, 129.3, 129.0, 128.8, 128.7, 123.3, 121.1, 120.3, 117.2, 112.3, 108.9, 106.4, 105.7, 56.7, 55.7.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₃NaO₂⁺ (M+Na)⁺: 438.0980, found: 438.0979.

2,7-dichloro-4-(2-phenyl-1*H*-indol-3-yl)quinoline (3aq)



A dried 10 mL Schlenk tube was charged with 2,4,7-trichloroquinoline (**1q**, 23.2 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3aq**) as a yellow solid (37.0 mg, 0.095 mmol, 95% yield). The regioisomeric ratio of **3aq** was determined as 12:3:1 *rr* by the crude ¹H NMR. Mp: 286.0 – 287.9 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 11.15 (s, 1H), 8.09 – 7.97 (m, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.48 (s, 1H), 7.43 – 7.39 (m, 3H), 7.32 – 7.27 (m, 5H), 7.12 – 7.09 (m, 1H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 151.6, 149.0, 146.9, 137.0, 136.7, 135.9, 131.7, 128.8, 128.8, 128.7, 128.2, 127.9, 127.5, 127.3, 125.2, 124.2, 122.9, 120.6, 118.7, 111.8, 107.9.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{15}Cl_2N_2^+$ (M+H)⁺: 389.0607, found: 389.0605.

3,6-dichloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (3ar)



A dried 10 mL Schlenk tube was charged with 1,3,6-trichloroisoquinoline (**1r**, 23.2 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ar**) as a yellow solid (29.6 mg, 0.076 mmol, 76% yield). The regioisomeric ratio of **3ar** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 229.6 – 230.6 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 11.08 (s, 1H), 8.04 (d, J = 2.1 Hz, 1H), 7.91 (d, J = 0.9 Hz, 1H),

7.82 – 7.80 (m, 1H), 7.59 – 7.57 (m, 1H), 7.44 – 7.37 (m, 3H), 7.34 – 7.32 (m, 1H), 7.29 – 7.21 (m, 4H), 7.10 – 7.07 (m, 1H).

¹³C NMR (126 MHz, Acetone-*d*₆) δ 157.7, 146.1, 139.8, 136.7, 136.4, 136.3, 132.3, 130.3, 129.4, 128.6, 128.0, 127.9, 127.8, 125.1, 125.0, 122.7, 120.4, 119.4, 117.5, 111.5, 111.5.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{15}Cl_2N_2^+$ (M+H)⁺: 389.0607 found: 389.0605.

2-butoxyethyl 2-((3,5-dichloro-6-(2-phenyl-1*H*-indol-3-yl)pyridin-2-yl)oxy)acetate (3as)



A dried 10 mL Schlenk tube was charged with 2-butoxyethyl 2-((3,5,6-trichloropyridin-2-yl)oxy) acetate (**1s**, 35.7 mg, 0.10 mmol), 2-phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3as**) as a brown solid (10.2 mg, 0.020 mmol, 20% yield). The regioisomeric ratio of **3as** was determined as 12.5:1 *rr* by the crude ¹H NMR. Mp: 169.1 – 171.3 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 7.64 (s, 1H), 7.39 – 7.37 (m, 1H), 7.35 – 7.33 (m, 1H), 7.28 – 7.25 (m, 2H), 7.24–7.21 (m, 2H), 7.17 – 7.13 (m, 2H), 7.07 – 7.04 (m, 1H), 4.80 (s, 2H), 4.13 – 4.08 (m, 2H), 3.41 – 3.36 (m, 2H), 3.24 (t, *J* = 6.6 Hz, 2H), 1.26 – 1.18 (m, 2H), 1.25 – 1.20 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 155.7, 147.7, 139.9, 137.1, 135.7, 132.8, 128.9, 128.5, 128.2, 127.3, 124.5, 122.9, 120.7, 120.2, 116.5, 111.0, 110.6, 71.1, 68.2, 64.2, 63.1, 31.6, 19.2, 13.9.

HRMS (ESI-TOF, m/z) calcd for $C_{27}H_{26}Cl_2N_2NaO_4^+$ (M+Na)⁺: 535.1162, found: 535.1164.

3-chloro-1-(4-methyl-2-phenyl-1*H*-indol-3-yl)isoquinoline (3ba)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 4methyl-2-phenyl-1*H*-indole (**2b**, 62.2 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3ba**) as a yellow solid (12.9 mg, 0.035 mmol, 35% yield). The regioisomeric ratio of **3ba** was determined as 5:1 *rr* by the crude ¹H NMR. Mp: 249.6 – 251.1 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 11.87 (s, 1H), 8.10 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.26 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.18 – 7.15 (m, 1H), 7.11 – 7.08 (m, 1H), 6.74 (d, *J* = 7.1 Hz, 1H), 1.63 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.7, 144.0, 138.2, 136.5, 136.0, 132.4, 131.8, 129.6, 129.0, 128.7, 128.5, 128.1, 128.0, 127.8, 127.5, 126.9, 122.8, 121.7, 119.5, 110.8, 110.2, 19.9.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1151

3-chloro-1-(5-methyl-2-phenyl-1*H*-indol-3-yl)isoquinoline (3bb)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 5methyl-2-phenyl-1*H*-indole (**2c**, 62.2 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bb**) as a yellow solid (25.0 mg, 0.068 mmol, 68% yield). The regioisomeric ratio of **3bb** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 235.8 – 236.7 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 10.88 (s, 1H), 7.98 – 7.96 (m, 1H), 7.92 (d, J = 1.0 Hz, 1H), 7.80 – 7.82 (m, 1H), 7.72 – 7.69 (m, 1H), 7.47 – 7.45 (m, 1H), 7.41 – 7.36 (m, 3H), 7.24 – 7.19 (m, 3H), 7.10 – 7.11 (m, 1H), 7.08 – 7.05 (m, 1H), 2.33 (s, 3H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 157.8, 144.9, 138.9, 137.2, 134.8, 132.6, 131.0, 129.9, 129.2, 128.5, 128.0, 127.7, 127.6, 127.2, 127.0, 126.3, 124.2, 118.9, 118.3, 111.2, 110.6, 20.7.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1160.

3-chloro-1-(7-methyl-2-phenyl-1*H*-indol-3-yl)isoquinoline (3bc)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 7methyl-2-phenyl-1*H*-indole (**2d**, 62.2 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bc**) as a yellow solid (23.0 mg, 0.063 mmol, 63% yield). The regioisomeric ratio of **3bc** was determined as 12:1 *rr* by the crude ¹H NMR. Mp: 166.5 - 168.7 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 10.71 (s, 1H), 7.96 – 7.94 (m, 1H), 7.90 (d, J = 1.0 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.70 – 7.67 (m, 1H), 7.44 – 7.41 (m, 2H), 7.38 – 7.34 (m, 1H), 7.24 – 7.19 (m, 3H), 7.18 – 7.16 (m, 1H), 7.05 – 7.03 (m, 1H), 7.00 – 6.97 (m, 1H), 2.66 (s, 3H).

¹³C NMR (126 MHz, Acetone-*d*₆) δ 157.7, 144.8, 138.9, 137.4, 135.9, 132.6, 131.0, 129.3, 128.4, 128.1, 128.0, 127.7, 127.1, 126.9, 126.3, 123.2, 121.0, 120.6, 118.3, 117.2, 111.6, 16.3.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂⁺ (M+H)⁺: 369.1153, found: 369.1153.

3-chloro-1-(4-methoxy-2-phenyl-1*H*-indol-3-yl)isoquinoline (3bd)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 4methoxy-2-phenyl-1*H*-indole (**2e**, 67.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bd**) as a yellow solid (25.0 mg, 0.065 mmol, 65% yield). The regioisomeric ratio of **3bd** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 292.3 – 294.1 °C. ¹H NMR (500 MHz, Acetone-*d*₆) δ 10.93 (s, 1H), 7.97 – 7.95 (m, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.74 – 7.70 (m, 1H), 7.46 – 7.43 (m, 1H), 7.40 – 7.37 (m, 2H), 7.23 – 7.16 (m, 4H), 7.15 – 7.12 (m, 1H), 6.51 – 6.49 (m, 1H), 3.32 (s, 3H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 159.2, 154.0, 144.1, 138.1, 137.5, 132.5, 130.7, 128.7, 128.4, 128.1, 127.4, 127.4, 126.9, 125.9, 123.4, 119.7, 118.3, 110.4, 104.8, 104.7, 100.6, 54.5.
HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂O⁺ (M+H)⁺: 385.1102, found: 385.1100.

3-chloro-1-(5-methoxy-2-phenyl-1*H*-indol-3-yl)isoquinoline (3be)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 5methoxy-2-phenyl-1*H*-indole (**2f**, 67.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3be**) as a yellow solid (13.4 mg, 0.035 mmol, 35% yield). The regioisomeric ratio of **3be** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 243.8 – 245.0 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 10.87 (s, 1H), 7.97 – 7.95 (m, 1H), 7.90 (d, J = 1.0 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.72 – 7.68 (m, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.40 – 7.37 (m, 3H), 7.24 – 7.19 (m, 3H), 6.90 – 6.87 (m, 1H), 6.85 (d, J = 2.5 Hz, 1H), 3.66 (s, 3H).

¹³C NMR (126 MHz, Acetone-*d*₆) δ 157.7, 154.9, 144.9, 139.0, 137.9, 132.6, 131.5, 131.4, 131.0, 130.0, 128.5, 128.0, 127.7, 127.1, 126.8, 126.3, 118.3, 112.9, 112.2, 112.2, 101.0, 54.9.

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{18}ClN_2O^+$ (M+H)⁺: 385.1102, found: 385.1100.

3-chloro-1-(6-methoxy-2-phenyl-1*H*-indol-3-yl)isoquinoline (3bf)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 6methoxy-2-phenyl-1*H*-indole (**2g**, 67.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bf**) as a yellow solid (21.2 mg, 0.055 mmol, 55% yield). The regioisomeric ratio of **3bf** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 227.4 – 229.2 °C.

¹H NMR (500 MHz, DMSO- d_6) δ 11.76 (s, 1H), 8.02 (s, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.39 – 7.36 (m, 1H), 7.29 – 7.26 (m, 2H), 7.24 (t, J = 7.6 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.08 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 2.3 Hz, 1H), 6.71 – 6.69 (m, 1H), 3.83 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 157.7, 156.8, 144.5, 138.9, 137.3, 136.1, 132.5, 131.7, 129.0, 128.0, 127.9, 127.9, 127.6, 126.9, 126.7, 123.9, 120.3, 118.9, 110.9, 110.5, 94.9, 55.8.

HRMS (ESI-TOF, m/z) calcd for C₂₄H₁₈ClN₂O⁺ (M+H)⁺: 385.1102, found: 385.1107.





A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2-(3,4-dimethoxyphenyl)-1*H*-indole (**2h**, 78.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bg**) as a yellow solid (26.1 mg, 0.063 mmol, 63% yield). The regioisomeric ratio of **3bg** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 302.3 - 303.7 °C. ¹H NMR (500 MHz, Acetone-*d*₆) δ 10.94 (s, 1H), 7.98 – 7.97 (m, 1H), 7.93 (d, *J* = 0.9 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.73 – 7.69 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.31 – 7.29 (m, 1H), 7.22 – 7.18 (m, 1H), 7.06 – 7.02 (m, 3H), 6.84 – 6.82 (m, 1H), 3.74 (s, 3H), 3.49 (s, 3H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 158.0, 149.4, 149.2, 144.8, 138.9, 137.2, 136.0, 131.0, 129.7, 128.0, 127.3, 127.1, 126.3, 124.9, 122.2, 120.2, 120.1, 119.2, 118.3, 111.7, 111.6, 111.2, 111.2, 55.1, 54.8.

HRMS (ESI-TOF, m/z) calcd for C₂₅H₁₉ClN₂NaO₂⁺ (M+Na)⁺: 437.1027, found: 437.1030.

3-chloro-1-(2-(4-fluorophenyl)-1*H*-indol-3-yl)isoquinoline (3bh)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2-(4-fluorophenyl)-1*H*-indole (**2i**, 63.4 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.1 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bh**) as a yellow solid (23.0 mg, 0.062 mmol, 62% yield). The regioisomeric ratio of **3bh** was determined as 10:1 *rr* by the crude ¹H NMR. Mp: 256.4 – 258.3 °C.

¹H NMR (500 MHz, Acetone- d_6) δ 11.02 (s, 1H), 7.99 – 7.97 (m, 1H), 7.92 (d, J = 1.0 Hz, 1H), 7.83 – 7.81 (m, 1H), 7.73 – 7.70 (m, 1H), 7.68 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.38 – 7.41 (m, 1H), 7.35 – 7.33 (m, 1H), 7.26 – 7.22 (m, 1H), 7.10 – 7.01 (m, 3H).

¹³C NMR (151 MHz, Acetone- d_6) δ 162.3 (d, J = 246.1 Hz), 157.3, 144.8, 139.0, 136.3(d, J = 3.1 Hz), 131.1, 129.9, 129.9, 129.4, 128.9 (d, J = 4.5 Hz), 127.9, 127.3, 126.8, 126.4, 122.6, 120.3, 119.5, 118.4,

115.5, 115.4, 111.5.

¹⁹F NMR (471 MHz, Acetone- d_6) δ -115.23.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₄ClFN₂Na⁺ (M+Na)⁺: 395.0722, found: 395.0719.

3-chloro-1-(2-(4-chlorophenyl)-1H-indol-3-yl) isoquinoline(3bi)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2-(4-chlorophenyl)-1*H*-indole (**2j**, 68.3 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bi**) as a yellow solid (19.1 mg, 0.049 mmol, 49% yield). The regioisomeric ratio of **3bi** was determined as 10:1 *rr* by the crude ¹H NMR. Mp: 255.3 – 257.8 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 12.01 (s, 1H), 8.05 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.35 – 7.30 (m, 4H), 7.25 – 7.22 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.05 – 7.02 (m, 1H).

¹³C NMR (151 MHz, DMSO-*d*₆) δ 157.2, 144.5, 139.0, 136.5, 136.2, 133.0, 131.8, 131.2, 129.7, 129.2, 129.2, 128.2, 127.8, 127.0, 126.7, 123.1, 120.8, 119.6, 119.1, 112.2, 110.9.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₁₅Cl₂N₂⁺ (M+H)⁺: 389.0607, found: 389.0612.

3-chloro-1-(2-(4-ethylphenyl)-4-methyl-1H-indol-3-yl) isoquinoline(3bj)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2-(4-ethylphenyl)-4-methyl-1*H*-indole (**2k**, 70.6 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp (λ_{max} = 427 nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bj**) as a yellow solid (21.8 mg, 0.055 mmol, 55% yield). The regioisomeric ratio of **3bj** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 186.5 – 191.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.77 – 7.61 (m, 3H), 7.54 – 7.50 (m, 1H), 7.25 – 7.18 (m, 2H), 7.06 – 7.01 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 7.1 Hz, 1H), 2.43 (q, *J* = 7.6 Hz, 2H), 1.69 (s, 3H), 1.05 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 159.4, 144.4, 143.9, 138.0, 136.3, 135.8, 131.1, 130.7, 129.4, 128.7, 128.5, 128.3, 128.2, 127.4, 127.3, 125.9, 122.7, 121.9, 119.1, 111.0, 108.9, 28.4, 20.0, 15.1.

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{22}ClN_2^+$ (M+H)⁺: 397.1466 , found: 397.1463.

3-chloro-1-(2-(naphthalen-2-yl)-1*H*-indol-3-yl)isoquinoline (3bk)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2-(naphthalen-2-yl)-1*H*-indole (**2l**, 73.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol),

MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bk**) as a yellow solid (15.4 mg, 0.038 mmol, 38% yield). The regioisomeric ratio of **3bk** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 195.2 – 197.5 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.61 (s, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.79 – 7.77 (m, 1H), 7.70 – 7.67 (m, 2H), 7.65 – 7.63 (m, 2H), 7.52 – 7.47 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.22 – 7.19 (m, 2H), 7.16 – 7.13 (m, 1H), 7.09 – 7.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.7, 140.2, 139.1, 136.7, 134.8, 133.0, 132.7, 130.5, 129.3, 128.9, 128.4, 128.1, 127.9, 127.7, 127.4, 126.3, 126.3, 126.2, 126.1, 125.6, 123.5, 121.3, 121.0, 120.2, 117.8, 112.7, 96.1.

HRMS (ESI-TOF, m/z) calcd for C₂₇H₁₇ClN₂Na⁺ (M+Na)⁺: 427.0972, found: 427.0974.

3-chloro-1-(1-methyl-2-phenyl-1H-indol-3-yl)isoquinoline (3bl)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 1methyl-2-phenyl-1*H*-indole (**2m**, 62.2 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3bl**) as a yellow solid (12.9 mg, 0.035 mmol, 35% yield). The regioisomeric ratio of **3bl** was determined as 6:1 *rr* by the crude ¹H NMR. Mp: 224.4 - 225.4 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.94 – 7.88 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.35 – 7.26 (m, 8H), 7.14 – 7.11 (m, 1H), 3.80 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 157.1, 144.2, 140.7, 138.7, 137.4, 131.5, 131.3, 130.8, 128.8, 128.7, 128.0, 127.8, 127.7, 126.7, 126.6, 122.8, 121.0, 119.7, 118.6, 111.9, 111.0, 31.7.

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{17}ClN_2Na^+$ (M+Na)⁺: 391.0972, found: 391.0970.

3-chloro-1-(3-phenyl-1H-indol-2-yl)isoquinoline (3bm)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 3chloro-1-(3-phenyl-1*H*-indol-2-yl)isoquinoline (**2n**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pumpthaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp (λ_{max} = 427 nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 19:1) to afford the pure product (**3bm**) as a yellow solid (15.0 mg, 0.042 mmol, 42% yield). The regioisomeric ratio of **3bm** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 160.8 – 162.6 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.50 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.56 – 7.48 (m, 2H), 7.30 – 7.36 (m, 3H), 7.25 – 7.21 (m, 3H), 7.19 – 7.09 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 153.4, 143.9, 139.0, 136.6, 134.9, 131.4, 129.8, 129.7, 128.7, 128.6, 127.6, 127.2, 126.4, 125.7, 124.6, 124.2, 120.7, 120.3, 119.9, 119.8, 111.7.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{16}ClN_2^+$ (M+H)⁺: 355.0997, found: 355.0996.

1-(3-chloroisoquinolin-1-yl)naphthalen-2-amine (3bn)





A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), naphthalen-2-amine (**2o**, 43.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 36 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 5:1) to afford the pure product (**3bn**) as a brown solid (17.1mg, 0.056 mmol, 56% yield). The regioisomeric ratio of **3bn** was determined as >20:1 *rr* by the crude ¹H NMR. Mp: 176.4 – 177.0 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.75 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.64 – 7.60 (m, 1H), 7.48 – 7.46 (m, 1H), 7.32 – 7.29 (m, 1H), 7.16-7.08 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.79 – 6.77 (m, 1H), 3.10 (s, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 159.6, 145.6, 142.6, 138.9, 133.7, 131.6, 130.4, 128.1, 128.0, 127.9, 127.8, 127.3, 126.8, 126.3, 123.8, 122.5, 119.6, 118.7, 115.2.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{14}ClN_2^+$ (M+H)⁺: 305.0840, found: 305.0840.

1-(3-chloroisoquinolin-1-yl)naphthalen-2-ol (3bo)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (1a, 19.8 mg, 0.10 mmol),
naphthalen-2-ol (**2p**, 43.3 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 40 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 5:1) to afford the pure product (**3bo**) as a white solid (10.0 mg, 0.033 mmol, 33% yield). The regioisomeric ratio of **3bo** was determined as 7:1 *rr* by the crude ¹H NMR. Mp: 146.0 – 147.2 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 10.07 (s, 1H), 8.06 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.49 – 7.45 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.24 – 7.20 (m, 1H), 6.81 (d, *J* = 8.3 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.5, 153.2, 144.5, 138.5, 133.8, 132.0, 130.9, 128.6, 128.4, 128.1, 127.5, 127.3, 127.3, 127.0, 123.9, 123.4, 119.6, 118.6, 117.3.

HRMS (ESI-TOF, m/z) calcd for C₁₉H₁₃ClNO⁺ (M+H)⁺: 306.0680, found: 306.0681.

3-chloro-1-(2-methoxynaphthalen-1-yl)isoquinoline (3bp)



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2methoxynaphthalene (**2q**, 47.5 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED lamp ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 40 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 19:1) to afford the pure product (**3bp**) as a yellow solid (8.0 mg, 0.025 mmol, 25% yield). The regioisomeric ratio of **3bp** was determined as 5:1 *rr* by the crude ¹H NMR. Mp: 185.4 – 187.8 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 8.19 (d, J = 9.1 Hz, 1H), 8.15 (s, 1H), 8.08 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.40 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 6.87 (d, J = 8.5 Hz, 1H), 3.76 (s, 3H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.0, 155.0, 144.4, 138.5, 133.3, 132.0, 131.4, 128.8, 128.6, 128.6, 127.6, 127.6, 127.2, 127.0, 124.3, 124.2, 119.9, 119.8, 114.2, 56.7.

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{15}CINO^+$ (M+H)⁺: 320.0837, found: 320.0836.

3.3 Unsuccessful Substrates



Under the standard condition, electronically rich polychlorinated heteroarenes such as 3-(cyclopropylmethoxy)-*N*-(3,5-dichloropyridin-4-yl)-4-(difluoromethoxy)benzamide, (2,6dichloropyridin-4-yl)(piperidin-1-yl)methanone, and *N*-benzyl-2,6-dichloroisonicotinamide, were found to be unreactive substrates.

4. Mechanistic Investigations

4.1 Radical Trapping Experiments



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), ((2-phenylallyl) sulfonyl) benzene (129 mg, 0.50 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The reaction mixture was analyzed by HRMS.

Results:

Compound 4, HRMS (ESI-TOF, m/z) calcd for C₁₈H₁₄ClNNa⁺ (M+Na)⁺: 302.0707, found: 302.0709.





A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), Triethyl phosphite (P(OEt)₃) (166 mg, 1.0 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The reaction mixture was analyzed by HRMS.

Results:





4.2 An EPR Experiment



A dried 10 mL Schlenk tube was charged with 1,3-dichloroisoquinoline (**1a**, 19.8 mg, 0.10 mmol), 2phenyl-1*H*-indole (**2a**, 58.0 mg, 0.30 mmol), cesium carbonate (32.5 mg, 0.10 mmol), *N-tert*-Butyl- α phenylnitrone (PBN) (58.6 mg, 0.50 mmol), MeCN (0.70 mL) and H₂O (0.30 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 15 h. The test solution was drawn through a capillary tube, then the reaction mixture was analyzed by HRMS and analyzed in situ by electron paramagnetic resonance (EPR) in air.

Results:

Compound **6**, HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{20}ClN_2NaO^{+}$ (M+Na)⁺: 362.1156, found: 362.1149.



Obvious signals of the compound 6 of isoquinoline aryl radical to PBN was observed in the EPR spectra.



4.3 UV-Vis Spectra of the Reaction Components

A variety of solutions of **1a** (0.1 M), **2a** (0.3 M), Cs_2CO_3 (0.1 M), **1a** (0.1 M) + Cs_2CO_3 (0.1 M), **2a** (0.1 M) + Cs_2CO_3 (0.1 M), **1a** (0.1 M) + **2a** (0.1 M) and **1a** (0.1 M) + **2a** (0.1 M) + Cs_2CO_3 (0.1 M) in MeCN were prepared. The UV-Vis absorption spectra of a series of solutions were recorded on SpectraMax M5 spectrometer, by measuring 3.0 mL solution into the 1.0 cm path quartz cuvettes.

Results: indicate possible interactions among the two substrates and the basic additive.



4.4 ¹H NMR Analysis on the Reaction Components

The solutions of **1a** (0.05 M), **2a** (0.05 M), **1a** (0.05 M) + **2a** (0.05 M), **1a** (0.05 M) + **2a** (0.05 M) + Cs_2CO_3 (0.05 M) were prepared. The resulting mixture was added into acetonitrile- d_3 (500 µL) and recorded at 500 MHz.

Results: indicate possible hydrogen bonding interactions among the two substrates and the basic additive.



4.5 An Alternative Mechanism



In the presence of hydrogen bonding, 1,3-dichloroisoquinoline (1a), 2-phenylindole (2a), and Cs_2CO_3 in acetonitrile form an EDA complex, specifically an isoquinoline-indole-carbonate anion ternary complex. This EDA complex intermediate absorbs photons and undergoes an intramolecular SET process to produce a radical ion pair. The subsequent cleavage of the C–Cl bond, along with a proton departure and radical-radical combination, results in the formation of the final product (3aa).

5. Synthetic Utility

5.1 A Scale-up Reaction



A dried 100 mL reaction eggplant bottle with gas valve support was charged with 1,3dichloroisoquinoline (**1a**, 0.396 g, 2.0 mmol), 2-phenyl-1*H*-indole (**2a**, 1.16 g, 6.0 mmol), cesium carbonate (0.650 g, 2.0 mmol), MeCN (14 mL) and H₂O (6.0 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 2 cm away from a 40 W LED ($\lambda_{max} = 427$ nm) with a DC fan cooling. The reaction was stirred at 30 °C for 14 h. The organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was concentrated to dryness, the residue was subjected to flash chromatography on silica gel (eluted with PE: EtOAc = 9:1) to afford the pure product (**3aa**) as a yellow solid (0.432 g, 1.2 mmol, 61% yield).

5.2 A Further Transformation of Product 3aa



A dried 25 mL Schlenk tube was charged with 3-chloro-1-(2-phenyl-1*H*-indol-3-yl)isoquinoline (**3aa**, 71.0 mg, 0.20 mmol), (10-phenylanthracen-9-yl)boronic acid (**7**, 72.0 mg, 0.24 mmol),

tetrakis(triphenylphosphine)palladium (46.2 mg, 0.04 mmol), potassium carbonate (55.3 mg, 0.40 mmol), tetrahydrofuran (6.0 mL) and H₂O (2.0 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned in oil bath. After being stirred at 75 °C for 12 h until the complete conversion of the starting material on TLC. Then, the reaction mixture was cooled to room temperature, and added water (5.0 mL). The reaction was quenched with 3 M HCl and keep the solution at pH = 3. The resulting mixture was extracted with EtOAc (5.0 mL × 3), the combined organic layers were dried with Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (eluted with PE: EtOAc = 9:1) to afford the pure product (**8**) as a white solid (50.0 mg, 0.087 mmol, 44% yield). Mp: 288.3 – 301.3 °C.

1-(2-phenyl-1*H*-indol-3-yl)-3-(10-phenylanthracen-9-yl)isoquinoline (8)



¹H NMR (500 MHz, DMSO-*d*₆) δ 11.85 (s, 1H), 8.13 (d, *J* = 9.6 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.69 – 7.62 (m, 3H), 7.61 – 7.53 (m, 6H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.42 – 7.35 (m, 5H), 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.17 (m, 1H), 7.01 – 6.98 (m, 1H).

¹³C NMR (151 MHz, DMSO-*d*₆) δ 157.1, 150.7, 138.6, 137.5, 137.1, 136.9, 136.4, 136.3, 132.6, 131.4, 131.3, 131.2, 129.9, 129.7, 129.7, 129.1, 129.1, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.3, 127.0, 126.8, 126.0, 122.6, 122.4, 120.4, 119.6, 112.1, 112.0.

HRMS (ESI-TOF, m/z) calcd for $C_{43}H_{29}N_2^+$ (M+H)⁺: 573.2325, found: 573.2322.

6. X-Ray Diffraction

6.1 X-Ray Diffraction of Product 3ak

Crystallization procedure. Compound **3ak** was dissolved in a mixture of *n*-hexane (2.0 mL) and dichloromethane (2.0 mL). Single crystals were obtained by slow evaporation of the solvent under ambient condition.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 233.01 (10) K. Data reduction and absorption correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Supplementary Fig. 1.** Crystallographic data for **3ak** was deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2249565.



Supplementary Fig. 1 X-Ray structure of 3ak (CCDC 2249565)

Crystal data and structure refinement for 3ak	
Empirical formula	$C_{26}H_{19}ClN_2O_2$
Formula weight	426.88

Temperature	233K (10)
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	<i>I</i> 2/a
Unit cell dimensions	$a = 23.4970(6) \text{ Å} \qquad \alpha = 90^{\circ}$
	b = 7.6930(2) Å β = 115.156(3)°
	$c = 25.2904(7) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume (Å ³)	4138.0(2)
Ζ	8
Density (g/m ³)	1.370
Absorption coefficient (mm ⁻¹)	1.845
F(000)	1776.0
Crystal size (mm ³)	0.3 x 0.2 x 0.2
Theta range for data collection	7.724 to 148.544
Index ranges	$-28 \leq h \leq 26,$
	$-6 \leq k \leq 9,$
	$-29 \leq 1 \leq 31$
Reflections collected	7981
Independent reflections	4089 [$R_{int} = 0.0383$, $R_{sigma} = 0.0457$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4089/0/282
Goodness-of-fit on F^2	1.102
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0418, wR_2 = 0.1004$
<i>R</i> indices (all data)	$R_1 = 0.0609, wR_2 = 0.1099$
Largest diff. peak and hole	0.24/-0.20

6.2 X-Ray Diffraction of Product 3am

Crystallization procedure. Compound **3am** was dissolved in a mixture of *n*-hexane (2.0 mL) and dichloromethane (2.0 mL). Single crystals were obtained by slow evaporation of the solvent under ambient condition.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 100 K. Data reduction and absorption correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Supplementary Fig. 2**. Crystallographic data for **3am** was deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2270451.



Supplementary Fig. 2 X-Ray structure of 3am (CCDC 2270451)

Crystal data and structure refinement for 3am	
Empirical formula	$C_{40}H_{24}Cl_2F_6N_4$
Formula weight	745.53
Temperature	100 K
Wavelength	1.54184 Å

Crystal system	trigonal
Space group	R3
Unit cell dimensions	$a = 31.8395(3) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 31.8395(3) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 8.58300(10) \text{ Å} \qquad \gamma = 120^{\circ}$
Volume (Å ³)	7535.33(17)
Ζ	9
Density (g/m ³)	1.479
Absorption coefficient (mm ⁻¹)	2.361
F(000)	3420.0
Crystal size (mm ³)	0.8 x 0.6 x 0.4
Theta range for data collection	5.552 to 152.94
Index ranges	$-39 \leq h \leq 39,$
	$-39 \leq k \leq 39,$
	$-10 \leq 1 \leq 9$
Reflections collected	46317
Independent reflections	6667 [$R_{int} = 0.0382$, $R_{sigma} = 0.0172$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6667/1/470
Goodness-of-fit on F^2	1.057
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0425, wR_2 = 0.1127$
<i>R</i> indices (all data)	$R_1 = 0.0430, wR_2 = 0.1133$
Largest diff. peak and hole	0.47/-0.43

6.3 X-Ray Diffraction of Product 3aq

Crystallization procedure. Compound **3aq** was dissolved in a mixture of *n*-hexane (2.0 mL) and dichloromethane (2.0 mL). Single crystals were obtained by slow evaporation of the solvent under ambient condition.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 233.01 (10) K. Data reduction and absorption correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Supplementary Fig. 3**. Crystallographic data for **3aq** was deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2254507.



Supplementary Fig. 3 X-Ray structure of 3aq (CCDC 2254507)

Crystal data and structure refinement for 3aq	
Empirical formula	$C_{23}H_{14}Cl_2N_2$
Formula weight	389.26
Temperature	233K (10)
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	<i>P</i> -1

Unit cell dimensions	$a = 9.3919(5) \text{ Å}$ $\alpha = 84.887(4)^{\circ}$
	b = 10.1672(5) Å β = 64.323(5)°
	$c = 10.7498(5) \text{ Å}$ $\gamma = 82.321(5)^{\circ}$
Volume (Å ³)	916.27(9)
Ζ	2
Density (g/m ³)	1.411
Absorption coefficient (mm ⁻¹)	3.253
F(000)	400.0
Crystal size (mm ³)	0.1 x 0.1 x 0.1
Theta range for data collection	8.782 to 152.136
Index ranges	$-11 \leq h \leq 11,$
	$-12 \leq k \leq 12,$
	$-12 \leq 1 \leq 13$
Reflections collected	6326
Independent reflections	3678 [$R_{int} = 0.0218$, $R_{sigma} = 0.0317$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3678/0/301
Goodness-of-fit on F^2	0.678
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0335, wR_2 = 0.1014$
<i>R</i> indices (all data)	$R_1 = 0.0405, wR_2 = 0.1126$
Largest diff. peak and hole	0.25/-0.23

6.4 X-Ray Diffraction of product 3ba

Crystallization procedure. Compound **3ba** was dissolved in a mixture of *n*-hexane (2.0 mL) and dichloromethane (2.0 mL). Single crystals were obtained by slow evaporation of the solvent under ambient condition.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 293 (2) K. Data reduction and absorption

correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Supplementary Fig. 4.** Crystallographic data for **3ba** was deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2249566.



Supplementary Fig. 4 X-Ray structure of 3ba (CCDC 2249566)

Crystal data and structure refinement for 3ba	
Empirical formula	$C_{24}H_{17}ClN_2$
Formula weight	368.84
Temperature	293 К
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ /n
Unit cell dimensions	$a = 15.0202(6) \text{ Å} \qquad \alpha = 90^{\circ}$
	b = 7.3714(3) Å β = 99.321(3)°
	$c = 16.6190(6) \text{ Å} \qquad \gamma = 90^{\circ}$

Volume (Å ³)	1815.76(12)
Ζ	4
Density (g/m ³)	1.349
Absorption coefficient (mm ⁻¹)	1.929
F(000)	768.0
Crystal size (mm ³)	0.8 x 0.6 x 0.4
Theta range for data collection	7.364 to 141.44
Index ranges	$-15 \leq h \leq 18,$
	$-8 \leq k \leq 8,$
	$-18 \leqslant 1 \leqslant 20$
Reflections collected	6076
Independent reflections	3416 [$R_{int} = 0.0476, R_{sigma} = 0.0535$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3416/0/245
Goodness-of-fit on F^2	1.029
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0651, wR_2 = 0.0.176$
R indices (all data)	$R_1 = 0.0795, wR_2 = 0.2022$
Largest diff. peak and hole	0.50/-0.39

6.5 X-Ray Diffraction of Product 3bl

Crystallization procedure. Compound **3bl** was dissolved in a mixture of *n*-hexane (2.0 mL) and dichloromethane (2.0 mL). Single crystals were obtained by slow evaporation of the solvent under ambient condition.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 233.01 (10) K. Data reduction and absorption correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Supplementary Fig. 5.** Crystallographic data for **3bl** was deposited with the Cambridge



Crystallographic Data Centre as supplementary publication number CCDC 2249557.

Supplementary Fig. 5 X-Ray structure of 3bl (CCDC 2249557)

Crystal data and structure refinement for 3bl	
Empirical formula	$C_{24}H_{17}CIN_2$
Formula weight	368.84
Temperature	233K (10)
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	a = 9.2175(6) Å α = 97.410(5)°
	b = 10.4599(7) Å β = 109.977(6)°
	c = 10.9144(7) Å $\gamma = 103.615(5)^{\circ}$
Volume (Å ³)	1935.60(11)
Ζ	2
Density (g/m ³)	1.309

Absorption coefficient (mm ⁻¹)	1.871
F(000)	384.0
Crystal size (mm ³)	0.6 x 0.3 x 0.1
Theta range for data collection	8.856 to 149.712
Index ranges	$-9 \leq h \leq 11,$
	$-13 \leq k \leq 12,$
	$-13 \leq 1 \leq 12$
Reflections collected	6621
Independent reflections	3712 [$R_{int} = 0.0216$, $R_{sigma} = 0.0258$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3712/0/313
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	$R_1 = 0.0373, wR_2 = 0.0969$
<i>R</i> indices (all data)	$R_1 = 0.0494, wR_2 = 0.1051$
Largest diff. peak and hole	0.18/-0.30

7. ¹H, ¹³C, and ¹⁹F NMR Spectrum



11.0 17.93 17.94 17.95 1









- 8.64 - 8.64 - 8.64 - 7.75 -







13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



$\begin{array}{c} -2.40\\ -2$





~ 877 ~ 878 ~ 878 ~ 878 ~ 878 ~ 878 ~ 877 ~ 779 ~ 779 ~ 779 ~ 772







20 210 200 190 180 170 160 150 f1 (ppm) -10 -2 140 130



7.0000 7.00000 7.0000 7.0000 7.00000 7.00000 7.0000 7.0000 7.000000 7.

9.32 9.32 9.32 9.28 9.28 9.28 9.29 9.20 <li











20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)
$\begin{array}{c} 7.75\\$

-11.16



20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2 f1 (ppm)









S77





13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)

















20 10 0 -10 -20 -30 -40 -50 -60 -70 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)







S90















8. References

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