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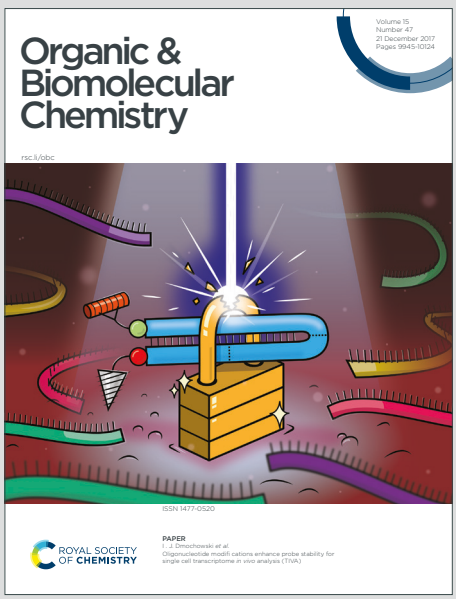

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Synthesis of Phenanthridines by I_2-Mediated sp^3 C–H Amination

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Abstract: An I_2-mediated synthesis of phenanthridines *via* intramolecular sp^3 C–H amination of readily accessible aniline precursors is reported. The present synthetic process is straightforward and applicable to a broad variety of unprotected aniline substrates, and provides facile and efficient access to phenanthridine derivatives. This C–H amination protocol does not use transition metals, is operationally simple, and can be achieved on a gram scale.

▪ Introduction

Phenanthridine is a privileged scaffold widely distributed in natural products[1] and synthetic compounds with diverse pharmacologically important properties,[2] including anticancer,[3] antibacterial,[4] antituberculosis,[5] and topoisomerase inhibitory[6] activities. Consequently, the synthesis of phenanthridine derivatives has drawn considerable attention from organic chemists. Besides classical methods[7] such as the Pictet-Hubert reaction, several new synthetic pathways have been developed to access phenanthridines.[8] These include oxidative cyclization of 2-isocyanobiphenyls[9] with bromides, hydrazines, anilines, 1,4-dioxane or acyl peroxides, cross-ring (5+1) annulation between 2-aminobiphenyls and alkene derivatives,[10] cascade addition and cyclization of biaryl-2-carbonitriles[11] with Grignard or organolithium reagents, and C–H amination reactions involving azide compounds.[12] One of the most straightforward synthetic strategies, intramolecular C–H animation of corresponding aniline precursors was reported for the synthesis of 6-aryl phenanthridines by Alabugin *et al.*,[13] who used $FeCl_3$-DDQ and ^{t}BuOK-O_2-DMF systems (Scheme 1a). Despite these achievements, the search for facile and efficient approaches toward to phenanthridines is still significant for industry and academia.

Direct sp^3 C−H amination is a valuable but challenging transformation in organic synthesis,[14] especially in the construction of nitrogen-containing heterocyclic frameworks. However, most of the current synthetic methods using this strategy involve transition metals, and to date, only a few transition-metal-free protocols,[13b, 15] such as the Hofmann-Loffler-Freytag reaction[16] have been developed. As a continuation of our studies on oxidative C−N bond construction employing molecular iodine,[15e-f, 17] we report herein the I_2-mediated intramolecular sp^3 C−H amination reaction of readily accessible aniline substrates, producing phenanthridines under

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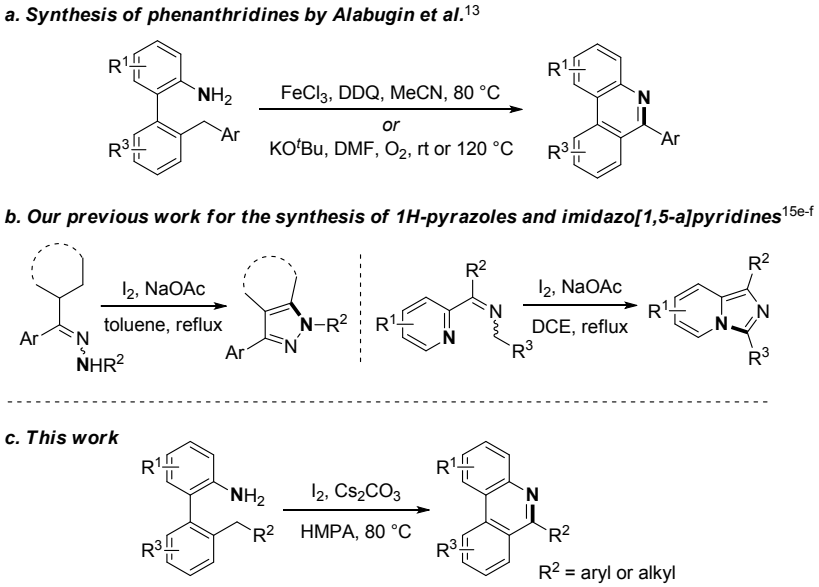
transition-metal-free conditions (Scheme 1).



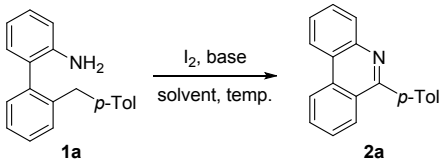
Scheme 1 Synthesis of nitrogen-containing heterocycles by *sp*^{3} C–H aminations

▪ Results and Discussion

The required aniline substrates can be readily prepared according to literature procedures.[13a, 18] Initially, 2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (**1a**) was selected as the model substrate for investigation (Table 1). Solvent screening showed that the I_2-promoted *sp*^{3} C−H amination reaction with **1a** proceeds well at room temperature in hexamethylphosphoramide (HMPA) (entry 10) or pyridine (entry 14) to form the phenanthridine product, 6-(4-methylbenzyl)phenanthridine (**2a**). With HMPA as the solvent, the conversion was incomplete and 15% of **1a** was recovered at room temperature (entry 10). The yield increased with the rising reaction temperature (entries 15–17), and HMPA was therefore selected for further optimization of the reaction conditions. The optimal temperature was found to be 80 °C (entry 16 *vs* entries 15 and 17) and Cs_2CO_3 was found to be the most effective base (entry 16 *vs* entries 18–25) for this transformation. This C−H amination reaction requires at least 2.2 equiv of iodine (entry 16 *vs* entries 26–27) and pre-stirring of iodine and base in

HMPA favors the formation of the product (**2a**) by diminishing the secondary iodination reactions.[19] The reaction was not affected when performed under an atmosphere of nitrogen (entry 28). No expected product was observed when 2,6-di-*tert*-butyl-4-methylphenol (BHT), a free radical scavenger, was added to the reaction system (entry 29). This result suggested that the present reaction might undergo a radical pathway.

Table 1 Optimization of reaction conditions[a]



1a **2a**

entry	I_2 (equiv)	base	solvent	temp.	time (h)	yield (%)[b]
1	2.2	Cs_2CO_3	toluene	rt	2	23
2	2.2	Cs_2CO_3	CH_2Cl_2	rt	2	12
3	2.2	Cs_2CO_3	DCE	rt	2	25
4	2.2	Cs_2CO_3	THF	rt	4	37
5	2.2	Cs_2CO_3	1,4-dioxane	rt	7	49
6	2.2	Cs_2CO_3	MeCN	rt	2	25
7	2.2	Cs_2CO_3	DMF	rt	7	45
8	2.2	Cs_2CO_3	DMA	rt	8	55
9	2.2	Cs_2CO_3	NMP	rt	8	45
10	2.2	Cs_2CO_3	HMPA	rt	12	65[c]
11	2.2	Cs_2CO_3	DMSO	rt	7	48
12	2.2	Cs_2CO_3	MeOH	rt	2	21
13	2.2	Cs_2CO_3	EtOH	rt	2	22
14	2.2	Cs_2CO_3	pyridine	rt	10	65
15	2.2	Cs_2CO_3	HMPA	60 °C	2	75
16	**2.2**	**Cs_2CO_3**	**HMPA**	**80 °C**	**2**	**80**
17	2.2	Cs_2CO_3	HMPA	100 °C	1	74
18	2.2	$NaHCO_3$	HMPA	80 °C	2	0
19	2.2	Na_2CO_3	HMPA	80 °C	2	28
20	2.2	K_2CO_3	HMPA	80 °C	2	40
21	2.2	K_3PO_4	HMPA	80 °C	2	33
22	2.2	KOH	HMPA	80 °C	2	19
23	2.2	NaOAc	HMPA	80 °C	2	73
24	2.2	Et_3N	HMPA	80 °C	2	21
25	2.2	DBU	HMPA	80 °C	5	43

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26	2.0	Cs_2CO_3	HMPA	80 °C	5	75[d]
27	2.4	Cs_2CO_3	HMPA	80 °C	2	80
28[e]	2.2	Cs_2CO_3	HMPA	80 °C	2	80
29[f]	2.2	Cs_2CO_3	HMPA	80 °C	2	0

[a] Optimal reaction conditions (entry 16): A well-stirred mixture of I_2 (1.1 mmol) and Cs_2CO_3 (2.5 mmol) in HMPA (5 mL) was treated with **1a** (0.5 mmol) and then maintained at 80 °C for 2 h. [b] Isolated yields. [c] With 15% of **1a** recovered. [d] With 6% of **1a** recovered. [e] Under N_2 atmosphere. [f] With 2.5 equiv of BHT.

Having established the optimized reaction conditions, we examined the scope and generality of this methodology. As shown in Scheme 2, this synthetic process is compatible with a variety of substrates bearing electron-donating groups (EDG) or electron-withdrawing groups (EWG) at the R^1, R^3 or R^4 positions. The presence of EWGs, especially at the *ortho*- and/or *para*- position of the aniline moiety (**2d**–**2h** & **2j**–**2k**), favors the formation of the phenanthridine products. The structure of the phenanthridine (**2d**) was confirmed by X-ray crystallography.[20] The reaction leading to the product **2f** can be successfully conducted on a gram scale. Replacement of the aromatic R^2 group with hydrogen or an aliphatic group also led to the corresponding phenanthridines (**2u**–**2w**) but in decreased yields. The quinoline product (**2ag**) was synthesized from the corresponding precursor in a satisfactory yield as well.

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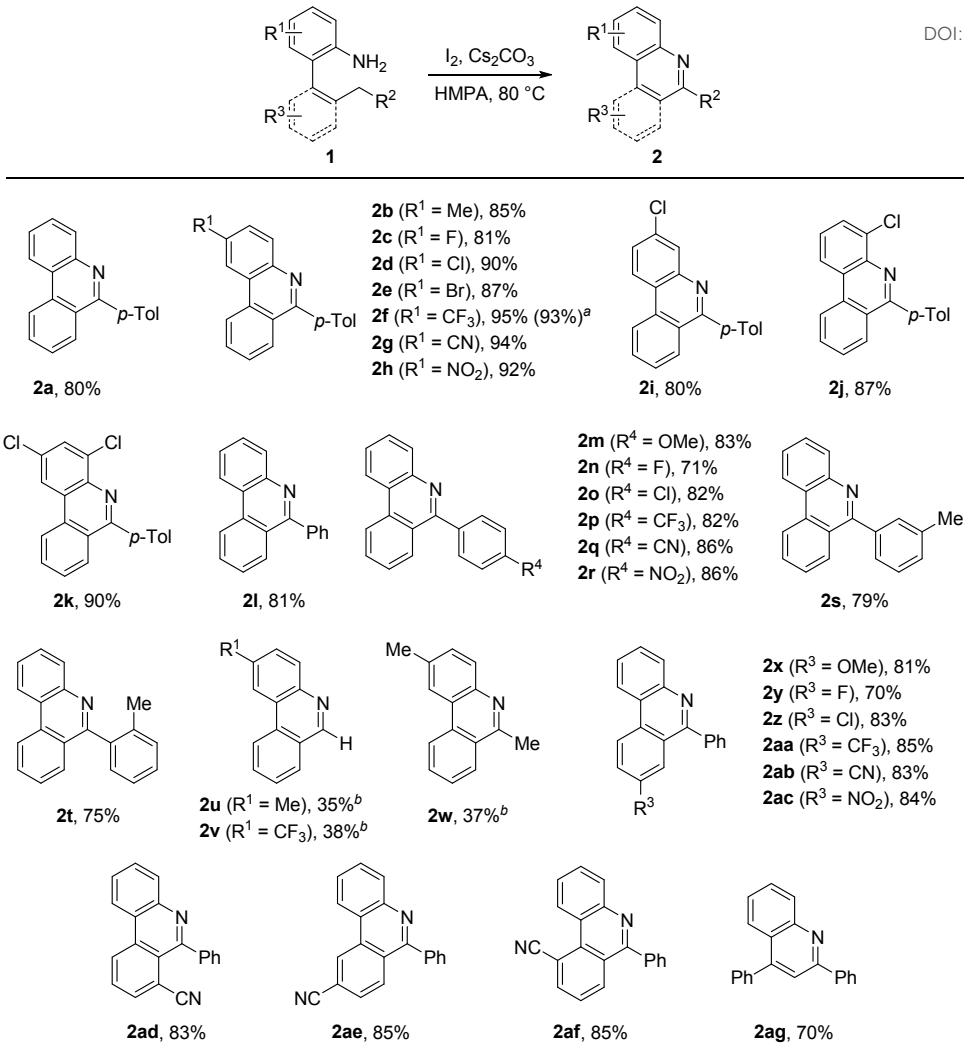

Scheme 2 **Substrate scope.** Reaction conditions: A well-stirred mixture of I_2 (1.1 mmol) and Cs_2CO_3 (2.5 mmol) in HMPA (5 mL) was treated with **1** (0.5 mmol) and then maintained at 80 °C (Isolated yields are given). [a] Yield of a gram-scale reaction (5 mmol). [b] At room temperature.

On the basis of the above experimental results and pioneering works,[13] a tentative mechanism is proposed for this I_2-mediated sp^3 C−H amination reaction and is shown in Scheme 3. Initially, deprotonation of substrate **1a** by base gives a plausible N-centered anion **A**, which reacts with iodine to produce an *N*-iodo intermediate **B**. Then, homolytic cleavage of the N–I bond in **B** under heating generates an N-centered radical species **C**, which may abstract the benzylic C–H intramolecularly to form a

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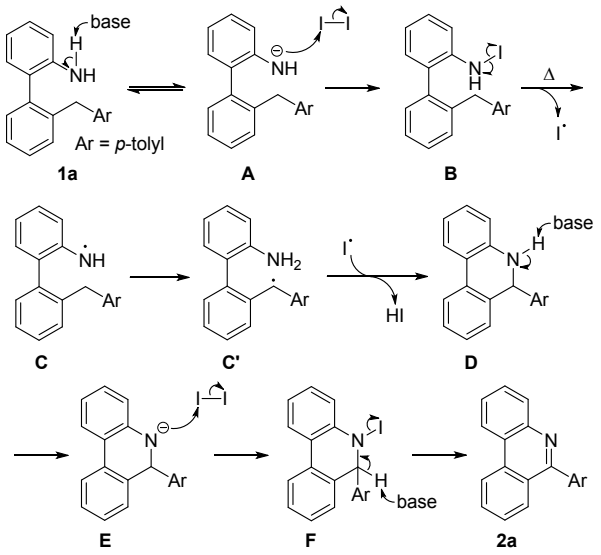
C-center radical **C'**. Reaction of **C'** with iodine radical (I•) leads to the dihydrophenanthridine **D**. The resulting hydrogen iodie (HI) is neutralized by base. Finally, further deprotonation of compound **D** and subsequent oxidative aromatization by iodine under basic conditions affords the phenanthridine product (**2a**).



Scheme 3 Proposed mechanism

▪ Conclusions

We have developed a new and practical intramolecular sp^3 C−H amination reaction of aniline substrates, employing iodine as the oxidant under transition-metal-free conditions, to synthesize phenanthridines. This straightforward synthetic approach is operationally simple and applicable to a broad range of unprotected aniline derivatives to afford various phenanthridine products in an efficient and scalable fashion.

▪ Experimental Section

1. General Information. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz

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(100 MHz for $^{13}C\{^1H\}$ NMR) spectrometer. Chemical shift values are reported in ppm (parts per million) with tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublet of doublets; td, triplet of doublets. The coupling constants (*J*) are reported in hertz (Hz). Melting points were determined on a micromelting point apparatus without corrections. High-resolution mass spectra (HRMS) were obtained on a Q-TOF Mass Spectrometer equipped with an electrospray ion source (ESI), operated in the positive mode. Flash column chromatography was performed over silica gel 200–300 mesh and the solvents were distilled prior to use. THF was dried over Na/benzophenone and then distilled, and HMPA was dried over 4 Å molecular sieves before use. Toluene and EtOH were analytical reagent grade and used without any pretreatment.

2. General Procedure for the Preparation of Substrates 1a, 1l–1t, and 1x–1af. The required aryl bromides were prepared according to literature procedures.[18a, 18b] A mixture of the corresponding bromide (2 mmol), (2-aminophenyl)boronic acid (2.4 mmol), K_2CO_3 (6 mmol) in toluene (15 mL)/EtOH (6 mL)/H_2O (3 mL) was stirred at room temperature under N_2 atmosphere for 0.5 h, and then treated with $Pd(PPh_3)_4$ (0.1 mmol).[13a] The reaction was heated to reflux under N_2 atmosphere for 12 h (TLC indicated the total consumption of the aryl bromide). After cooling to room temperature, it was diluted with H_2O (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to give the substrate **1**.

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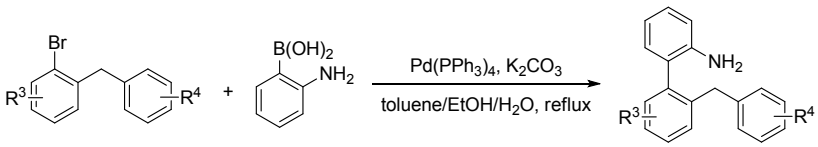
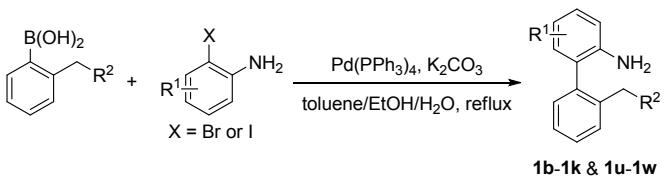


1a, **1l-1t** & **1x-1af**

3. General Procedure for the Preparation of Substrates 1b–1k and 1u−1w. The required aryl boronic acids are commercially available or were prepared according to a literature procedure.[18c] A mixture of the corresponding boronic acid (2 mmol), the substituted 2-bromo/iodo aniline (2.4 mmol), K_2CO_3 (6 mmol), toluene (15 mL)/EtOH (6 mL)/H_2O (3 mL) was stirred at room temperature under N_2 atmosphere for 0.5 h, and then treated with $Pd(PPh_3)_4$ (0.1 mmol).[13a] The reaction was heated to reflux under N_2 atmosphere for 12 h (TLC indicated the total consumption of the boronic acid). After cooling to room temperature, it was diluted with H_2O (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to give the substrate **1**.



1b-1k & **1u-1w**

4. Preparation of Substrate 1ag. A solution of (2-aminophenyl)(phenyl)methanone (3 mmol) in dry THF (10 mL) was treated with phenethylmagnesium bromide (1 M in THF, 10 mL) under N_2 atmosphere,[21] and then heated to 50 °C for 12 h (TLC indicated the total consumption of the ketone). After cooling to room temperature, the reaction was quenched with aqueous HCl solution (2 M, 5 mL), stirred for 0.5 h, diluted with brine (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (2 x 10 mL), dried over anhydrous Na_2SO_4, and concentrated to give the tertiary alcohol intermediate. A reaction mixture of the above

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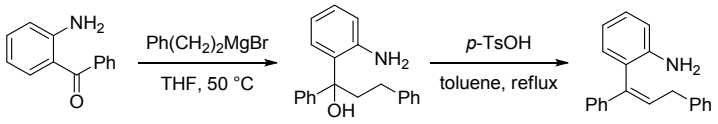
crude tertiary alcohol and *p*-TsOH (0.6 mmol) in toluene (15 mL) was refluxed for 24 h (TLC indicated the total consumption of the alcohol). After cooling to room temperature, it was washed with H_2O (3 x 15 mL) and brine (2 x 15 mL) in sequence, and then extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to afford substrate **1ag**.



1ag

2'-(4-Methylbenzyl)-[1,1'-biphenyl]-2-amine (1a).[13b] EtOAc/petroleum ether (PE) (eluent) 2:98; 388 mg, 71% yield; white solid, mp 66–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 4H, overlapped with the peak of chloroform), 7.18–7.14 (m, 1H), 7.00–6.96 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.77 (td, *J* = 7.6, 1.2 Hz, 1H), 6.74–6.72 (m, 1H), 3.85–3.74 (m, 2H), 3.37 (s, 2H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 140.6, 138.5, 138.1, 135.3, 130.54, 130.53, 130.2, 129.04, 128.99, 128.6, 128.0, 127.2, 126.7, 118.3, 115.3, 38.7, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590, found 274.1589.

5-Methyl-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1b). EtOAc/PE (eluent) 2:98; 482 mg, 84% yield; white solid, mp 68–69 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.19 (m, 4H, overlapped with the peak of chloroform), 7.01–6.96 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.85–3.73 (m, 2H), 3.26 (s, 2H), 2.28 (s, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.4, 140.6, 138.8, 138.2, 135.3, 131.1, 130.5, 130.1, 129.10, 129.05, 128.9, 127.9, 127.5, 127.3, 126.6, 115.4, 38.8, 21.1, 20.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{22}N$ 288.1747, found 288.1748.

5-Fluoro-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1c). CH_2Cl_2/PE (eluent)

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20:80; 495 mg, 85% yield; white solid, mp 49–51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.24 (m, 3H, overlapped with the peak of chloroform), 7.19–7.17 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.90–6.84 (m, 3H), 6.71–6.64 (m, 2H), 3.85–3.74 (m, 2H), 3.23 (s, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.1 (d, $J_{C–F}$ = 234.9 Hz), 140.4, 140.2 (d, $J_{C–F}$ = 2.1 Hz), 137.8, 137.6 (d, $J_{C–F}$ = 1.3 Hz), 135.5, 130.4, 130.3, 129.04, 128.96, 128.4, 128.3 (d, $J_{C–F}$ = 7.2 Hz), 126.8, 116.9 (d, $J_{C–F}$ = 22.0 Hz), 116.1 (d, $J_{C–F}$ = 7.8 Hz), 115.0 (d, $J_{C–F}$ = 22.1 Hz), 38.8, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}FN$ 292.1496, found 292.1498.

5-Chloro-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1d). CH_2Cl_2/PE (eluent) 11:89; 480 mg, 78% yield; white solid; mp 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 3H, overlapped with the peak of chloroform), 7.17–7.15 (m, 1H), 7.10 (dd, J = 8.4, 2.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 2.4 Hz, 1H), 6.84 (d, J = 7.6 Hz, 2H), 6.64 (d, J = 8.8 Hz, 1H), 3.84–3.72 (m, 2H), 3.34 (s, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.7, 140.5, 137.7, 137.3, 135.5, 130.4, 130.1, 129.1, 129.0, 128.53, 128.46, 128.3, 126.9, 122.8, 116.3, 38.8, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}ClN$ 308.1201, found 308.1204.

5-Bromo-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1e). CH_2Cl_2/PE (eluent) 20:80; 610 mg, 87% yield; white solid, mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.22 (m, 4H, overlapped with the peak of chloroform), 7.17–7.15 (m, 1H), 7.02–6.99 (m, 3H), 6.84 (d, J = 7.6 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 3.84–3.72 (m, 2H), 3.36 (s, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 140.5, 137.7, 137.2, 135.5, 133.0, 131.2, 130.38, 130.37, 129.1, 129.03, 128.99, 128.5, 126.9, 116.7, 109.9, 38.9, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}BrN$ 352.0695, found 352.0696.

2'-(4-Methylbenzyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1f). EtOAc/PE

(eluent) 2:98; 550 mg, 81% yield; white solid, mp 63–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 1H), 7.34–7.28 (m, 3H), 7.20–7.18 (m, 1H), 7.13 (s, 1H), 6.98 (d, J = 7.6 Hz, 2H), 6.80 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.4 Hz, 1H), 3.83–3.68 (m, 4H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.1, 140.7, 137.6, 137.1, 135.6, 130.6, 130.5, 129.1, 128.9, 128.6, 127.9 (q, $J_{C–F}$ = 3.8 Hz), 127.0, 126.5, 125.8 (q, $J_{C–F}$ = 3.7 Hz), 124.9 (d, $J_{C–F}$ = 269.1 Hz), 120.0 (q, $J_{C–F}$ = 32.4 Hz), 114.5, 39.0, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{19}F_3N$ 342.1464, found 342.1465.

6-Amino-2'-(4-methylbenzyl)-[1,1'-biphenyl]-3-carbonitrile (1g). EtOAc/PE (eluent) 27:73; 560 mg, 94% yield; white solid, mp 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41(dd, J = 8.4, 2.0 Hz, 1H), 7.37–7.28 (m, 3H), 7.15–7.13 (m, 2H), 6.99 (d, J = 7.6 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 8.4 Hz, 1H), 3.87 (s, 2H), 3.80–3.68 (m, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 140.5, 137.4, 136.1, 135.7, 134.7, 132.9, 130.7, 130.4, 129.1, 128.9, 128.8, 127.2, 126.9, 120.2, 114.7, 100.1, 39.0, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{19}N_2$ 299.1543, found 299.1547.

2'-(4-Methylbenzyl)-5-nitro-[1,1'-biphenyl]-2-amine (1h). EtOAc/PE (eluent) 8:92; 513 mg, 80% yield; light yellow solid, mp 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.8, 2.4 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.38–7.29 (m, 3H), 7.19–7.17 (m, 1H), 6.97 (d, J = 7.6 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.8 Hz, 1H), 4.09 (s, 2H), 3.83–3.70 (m, 2H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 140.6, 138.9, 137.3, 135.9, 135.7, 130.8, 130.5, 129.10, 129.07, 128.8, 127.23, 127.18, 125.8, 125.4, 113.6, 39.0, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_2$ 319.1441, found 319.1442.

4-Chloro-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1i). EtOAc/PE (eluent) 2:98; 345 mg, 56% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m,

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3H, overlapped with the peak of chloroform), 7.18–7.15 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.86–6.83 (m, 3H), 6.74–6.71 (m, 2H), 3.82–3.71 (m, 2H), 3.43 (s, 2H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.3, 140.6, 137.8, 137.4, 135.5, 133.9, 131.6, 130.5, 130.4, 129.0, 128.9, 128.4, 126.8, 125.5, 118.2, 114.8, 38.7, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}ClN$ 308.1201, found 308.1202.

3-Chloro-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1j). EtOAc/PE (eluent) 1:99; 530 mg, 86% yield; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.24 (m, 4H, overlapped with the peak of chloroform), 7.20–7.18 (m, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.88–6.86 (m, 1H), 6.81 (d, J = 8.0 Hz, 2H), 6.69 (t, J = 7.6 Hz, 1H), 3.82–3.71 (m, 4H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 140.5, 137.8, 137.7, 135.4, 130.42, 130.38, 129.01, 128.97, 128.9, 128.6, 128.4, 128.1, 126.9, 119.3, 118.2, 38.8, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}ClN$ 308.1201, found 308.1202.

3,5-Dichloro-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1k). EtOAc/PE (eluent) 1:99; 534 mg, 78% yield; white solid; mp 104–106 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 4H, overlapped with the peak of chloroform), 7.16–7.14 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.82–6.79 (m, 3H), 3.81–3.68 (m, 4H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.5, 139.9, 137.4, 136.6, 135.6, 130.6, 130.2, 129.1, 128.9, 128.8, 128.7, 128.0, 127.0, 122.1, 119.5, 39.0, 21.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{18}Cl_2N$ 342.0811, found 342.0813.

2'-Benzyl-[1,1'-biphenyl]-2-amine (1l).[13b] EtOAc/PE (eluent) 5:95; 369 mg, 71% yield; white solid, mp 67–69 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 4H, overlapped with the peak of chloroform), 7.19–7.10 (m, 4H), 6.96–6.94 (m, 3H), 6.77 (td, J = 7.6, 1.2 Hz, 1H), 6.72 (dd, J = 8.0, 0.8 Hz, 1H), 3.89–3.78 (m, 2H), 3.34 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 141.1, 140.4, 138.6, 130.6, 130.5, 130.3, 129.2, 128.6, 128.3, 128.0, 127.1, 126.8, 125.9, 118.3, 115.3, 39.3; HRMS

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(m/z) $[M + H]^+$ calcd for $C_{19}H_{18}N$ 260.1434, found 260.1436.

2'-(4-Methoxybenzyl)-[1,1'-biphenyl]-2-amine (1m). EtOAc/PE (eluent) 5:95; 313 mg, 54% yield; white solid, mp 65–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 4H, overlapped with the peak of chloroform), 7.19–7.15 (m, 1H), 6.98–6.96 (m, 1H), 6.89–6.87 (m, 2H), 6.80–6.72 (m, 4H), 3.84–3.73 (m, 5H), 3.37 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 144.0, 140.8, 138.5, 133.3, 130.6, 130.5, 130.2, 130.1, 128.6, 128.1, 127.2, 126.7, 118.4, 115.3, 113.7, 55.4, 38.4; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1541.

2'-(4-Fluorobenzyl)-[1,1'-biphenyl]-2-amine (1n).[13b] EtOAc/PE (eluent) 5:95; 477 mg, 86% yield; white solid, mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 4H, overlapped with the peak of chloroform), 7.15 (t, J = 8.0 Hz, 1H), 6.92–6.82 (m, 5H), 6.78–6.71 (m, 2H), 3.86–3.75 (m, 2H), 3.32 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4 (d, $J_{C–F}$ = 242.0 Hz), 144.0, 140.3, 138.7, 136.8 (d, $J_{C–F}$ = 3.2 Hz), 130.7, 130.5 (d, $J_{C–F}$ = 1.1 Hz), 130.4, 130.2, 128.7, 128.1, 127.00, 126.97, 118.4, 115.3, 115.0 (d, $J_{C–F}$ = 21.0 Hz); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}FN$ 278.1340, found 278.1342.

2'-(4-Chlorobenzyl)-[1,1'-biphenyl]-2-amine (1o). CH_2Cl_2/PE (eluent) 25:75; 480 mg, 82% yield; white solid, mp 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H, overlapped with the peak of chloroform), 7.25–7.21 (m, 2H), 7.18–7.12 (m, 3H), 6.91 (dd, J = 7.6, 1.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.78–6.72 (m, 2H), 3.86–3.75 (m, 2H), 3.37 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 139.9, 139.6, 138.7, 131.6, 130.7, 130.5, 130.4, 130.2, 128.7, 128.3, 128.2, 127.1, 126.9, 118.4, 115.3, 38.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}ClN$ 294.1044, found 294.1045.

2'-(4-(Trifluoromethyl)benzyl)-[1,1'-biphenyl]-2-amine (1p). EtOAc/PE (eluent)

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5:95; 342 mg, 52% yield; white solid, mp 60–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.34–7.28 (m, 2H), 7.25–7.23 (m, 2H, overlapped with the peak of chloroform), 7.18–7.14 (m, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.90 (dd, J = 7.2, 1.2 Hz, 1H), 6.77–6.72 (m, 2H), 3.96–3.85 (m, 2H), 3.38 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.3, 143.9, 139.4, 138.8, 130.8, 130.5, 130.3, 129.4, 128.8, 128.23, 128.20 (q, $J_{C–F}$ = 32.0 Hz), 127.3, 126.8, 125.1 (q, $J_{C–F}$ = 3.8 Hz), 124.5 (q, $J_{C–F}$ = 270.1 Hz), 118.4, 115.3, 39.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}F_3N$ 328.1308, found 328.1311.

4-((2'-Amino-[1,1'-biphenyl]-2-yl)methyl)benzonitrile (1q).[13b] EtOAc/PE (eluent) 9:91; 551 mg, 97% yield; white solid, mp 69–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.35–7.31 (m, 2H), 7.26–7.23 (m, 2H, overlapped with the peak of chloroform), 7.16 (td, J = 8.0, 1.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.85–6.82 (m, 1H), 6.75–6.71 (m, 2H), 3.96–3.86 (m, 2H), 3.37 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.8, 143.8, 138.9, 138.8, 132.0, 130.9, 130.41, 130.38, 129.7, 128.8, 128.3, 127.5, 126.6, 119.3, 118.4, 115.3, 109.6, 39.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2$ 285.1386, found 285.1387.

2'-(4-Nitrobenzyl)-[1,1'-biphenyl]-2-amine (1r). CH_2Cl_2/PE (eluent) 50:50; 547 mg, 90% yield; light yellow solid, mp 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 7.36–7.31 (m, 2H), 7.29–7.23 (m, 2H, overlapped with the peak of chloroform), 7.18–7.14 (m, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.84 (dd, J = 8.0, 1.6 Hz, 1H), 6.74–6.71 (m, 2H), 4.01–3.91 (m, 2H), 3.39 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.0, 146.3, 143.8, 138.9, 138.8, 130.9, 130.41, 130.40, 129.7, 128.9, 128.3, 127.6, 126.5, 123.4, 118.4, 115.3, 39.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}N_2O_2$ 305.1285, found 305.1288.

2'-(3-Methylbenzyl)-[1,1'-biphenyl]-2-amine (1s). EtOAc/PE (eluent) 9:91; 410 mg,

75% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 4H, overlapped with the peak of chloroform), 7.18–7.14 (m, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.97–6.92 (m, 2H), 6.80–6.71 (m, 4H), 3.85–3.74 (m, 2H), 3.34 (s, 2H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 141.0, 140.5, 138.6, 137.8, 130.6, 130.5, 130.3, 130.0, 128.6, 128.1, 128.0, 127.2, 126.7, 126.6, 126.2, 118.3, 115.3, 39.3, 21.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590, found 274.1593.

2'-(2-Methylbenzyl)-[1,1'-biphenyl]-2-amine (1t). EtOAc/PE (eluent) 5:95; 350 mg, 64% yield; white solid, mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 3H, overlapped with the peak of chloroform), 7.16 (t, J = 7.6 Hz, 1H), 7.12–7.05 (m, 3H), 7.01–6.96 (m, 3H), 6.80–6.74 (m, 2H), 3.88–3.75 (m, 2H), 3.24 (s, 2H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 139.7, 139.0, 138.7, 136.8, 130.4, 130.3, 130.2, 129.5, 128.6, 128.0, 127.2, 126.6, 126.3, 125.9, 118.5, 115.4, 36.6, 19.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590, found 274.1588.

2',5-Dimethyl-[1,1'-biphenyl]-2-amine (1u).[12a] CH_2Cl_2/PE (eluent) 20:80; 355 mg, 90% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 4H, overlapped with the peak of chloroform), 6.98 (d, J = 8.0 Hz, 1H), 6.83 (s, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.31 (s, 2H), 2.27 (s, 3H), 2.18 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.2, 138.9, 137.0, 130.7, 130.3, 130.2, 129.0, 127.7, 127.5, 126.2, 115.3, 20.6, 19.9; HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{16}N$ 198.1277, found 198.1279.

2'-Methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1v).[12a] EtOAc/PE (eluent) 5:95; 455 mg, 91% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 1H), 7.32–7.24 (m, 4H, overlapped with the peak of chloroform), 7.19–7.17 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.79 (s, 2H), 2.16–2.15 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.8, 137.2, 137.1, 130.6, 130.1, 128.4, 127.4 (q, J_{C-F} = 3.8 Hz), 126.8,

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126.5, 125.7 (q, $J_{C–F}$ = 3.8 Hz), 125.0 (q, $J_{C–F}$ = 268.9 Hz), 119.9 (q, $J_{C–F}$ = 32.3 Hz), 114.3, 19.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{13}F_3N$ 252.0995, found 252.0996.

2'-Ethyl-5-methyl-[1,1'-biphenyl]-2-amine (1w).[12a] CH_2Cl_2/PE (eluent) 17:83; 262 mg, 62% yield; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.26–7.22 (m, 1H, overlapped with the peak of chloroform), 7.18–7.16 (m, 1H), 6.98 (dd, J = 8.0, 1.6 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.30 (s, 2H), 2.58–2.42 (m, 2H), 2.27 (s, 3H), 1.08 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.1, 141.3, 138.3, 130.9, 130.3, 128.9, 128.7, 128.0, 127.5, 127.4, 126.2, 115.3, 26.2, 20.6, 15.4; HRMS (m/z) $[M + H]^+$ calcd for $C_{15}H_{18}N$ 212.1434, found 212.1437.

2'-Benzyl-4'-methoxy-[1,1'-biphenyl]-2-amine (1x). EtOAc/PE (eluent) 9:91; 470 mg, 81% yield; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.10 (m, 5H), 6.97–6.94 (m, 3H), 6.84–6.71 (m, 4H), 3.86–3.75 (m, 5H), 3.37 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 144.4, 141.8, 140.9, 131.6, 131.0, 129.1, 128.5, 128.3, 126.8, 125.9, 118.3, 116.0, 115.2, 111.8, 55.3, 39.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1540.

2'-Benzyl-4'-fluoro-[1,1'-biphenyl]-2-amine (1y). EtOAc/PE (eluent) 9:91; 380 mg, 69% yield; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 7H, overlapped with the peak of chloroform), 6.95–6.91 (m, 3H), 6.77 (td, J = 7.6, 1.2 Hz, 1H), 6.72 (dd, J = 8.0, 0.4 Hz, 1H), 3.85–3.75 (m, 2H), 3.34 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (d, $J_{C–F}$ = 244.5 Hz), 144.2, 143.0 (d, $J_{C–F}$ = 7.2 Hz), 140.3, 134.4 (d, $J_{C–F}$ = 3.2 Hz), 132.1 (d, $J_{C–F}$ = 8.1 Hz), 130.7, 129.2, 128.8, 128.4, 126.2, 126.0, 118.4, 116.9 (d, $J_{C–F}$ = 21.3 Hz), 115.3, 113.7 (d, $J_{C–F}$ = 20.9 Hz), 39.2 (d, $J_{C–F}$ = 1.4 Hz); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}FN$ 278.1340, found 278.1338.

2'-Benzyl-4'-chloro-[1,1'-biphenyl]-2-amine (1z). EtOAc/PE (eluent) 9:91; 420 mg,

71% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.12 (m, 7H, overlapped with the peak of chloroform), 6.95–6.91 (m, 3H), 6.77 (td, *J* = 7.6, 1.2 Hz, 1H), 6.74–6.71 (m, 1H), 3.86–3.75 (m, 2H), 3.35 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 142.5, 140.2, 137.1, 133.8, 131.9, 130.5, 130.2, 129.2, 128.9, 128.4, 127.0, 126.2, 125.8, 118.5, 115.4, 39.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}ClN$ 294.1044, found 294.1045.

2'-Benzyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1aa). EtOAc/PE (eluent) 9:91; 540 mg, 83% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.21–7.12 (m, 4H), 6.93–6.90 (m, 3H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.95–3.84 (m, 2H), 3.32 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.7, 142.6, 141.5, 140.0, 131.2, 130.24 (q, J_{C-F} = 32.1 Hz), 130.17, 129.2, 129.1, 128.5, 127.0 (q, J_{C-F} = 3.7 Hz), 126.3, 125.7, 124.3 (q, J_{C-F} = 270.7 Hz), 123.7 (q, J_{C-F} = 3.8 Hz), 118.6, 115.6, 39.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}F_3N$ 328.1308, found 328.1309.

2'-Amino-2-benzyl-[1,1'-biphenyl]-4-carbonitrile (1ab). EtOAc/PE (eluent) 9:91; 307 mg, 54% yield; white solid, mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.24–7.15 (m, 4H), 6.94–6.90 (m, 3H), 6.80 (td, *J* = 7.6, 1.2 Hz, 1H), 6.75 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.92–3.81 (m, 2H), 3.35 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 143.5, 142.3, 139.4, 133.7, 131.6, 130.4, 129.9, 129.5, 129.1, 128.6, 126.5, 125.1, 119.0, 118.6, 115.7, 111.9, 38.9; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2$ 285.1386, found 285.1387.

2'-Benzyl-4'-nitro-[1,1'-biphenyl]-2-amine (1ac). CH_2Cl_2/PE (eluent) 33:67; 368 mg, 61% yield; yellow solid, mp 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 7.42–7.40 (m, 1H), 7.24–7.15 (m, 4H), 6.95–6.91 (m, 3H),

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6.84–6.80 (m, 1H), 6.77–6.75 (m, 1H), 3.99–3.88 (m, 2H), 3.34 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.8, 145.8, 143.4, 142.8, 139.4, 131.8, 129.9, 129.6, 129.1, 128.7, 126.6, 125.1, 124.9, 121.9, 118.7, 115.8, 39.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}N_2O_2$ 305.1285, found 305.1287.

2'-Amino-2-benzyl-[1,1'-biphenyl]-3-carbonitrile (1ad). EtOAc/PE (eluent) 17:83; 384 mg, 68% yield; white solid, mp 99–101 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.20–7.15 (m, 1H), 7.13–7.08 (m, 3H), 6.84–6.81 (m, 3H), 6.74 (td, *J* = 7.2, 1.2 Hz, 1H), 6.69 (dd, *J* = 8.0, 0.8 Hz, 1H), 4.20–4.10 (m, 2H), 3.18 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.1, 143.8, 140.7, 138.9, 135.8, 132.9, 130.4, 129.4, 128.8, 128.3, 127.7, 126.3, 125.0, 118.8, 118.6, 115.7, 114.4, 37.8; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2$ 285.1386, found 285.1388.

2'-Amino-6-benzyl-[1,1'-biphenyl]-3-carbonitrile (1ae). EtOAc/PE (eluent) 9:91; 370 mg, 65% yield; white solid, mp 86–87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.25–7.14 (m, 4H), 6.94–6.90 (m, 3H), 6.82–6.78 (m, 1H), 6.76–6.74 (m, 1H), 3.94–3.83 (m, 2H), 3.35 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.5, 143.7, 140.0, 139.5, 134.3, 131.6, 131.0, 130.3, 129.5, 129.2, 128.6, 126.5, 124.6, 118.9, 118.7, 115.7, 110.8, 39.4; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2$ 285.1386, found 285.1389.

2'-Amino-6-benzyl-[1,1'-biphenyl]-2-carbonitrile (1af). EtOAc/PE (eluent) 20:80; 517 mg, 91% yield; white solid, mp 95–96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.26–7.16 (m, 4H), 6.96–6.93 (m, 3H), 6.84 (td, *J* = 7.2, 1.2 Hz, 1H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.89–3.79 (m, 2H), 3.33 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.7, 142.6, 142.2, 139.7, 134.5, 131.5, 130.2, 130.1, 129.2, 128.5, 126.4, 122.7,

119.0, 118.1, 116.0, 114.6, 39.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2$ 285.1386, found 285.1389.

(*E*)-2-(1,3-Diphenylprop-1-en-1-yl)aniline (1ag).[21] The *E* configuration was assigned on the basis of NOE correlations between protons of CH_2 and NH_2 groups. EtOAc/PE (eluent) 2:98; 477 mg, 56% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.16 (m, 11H, overlapped with the peak of chloroform), 7.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.82 (td, *J* = 7.6, 1.2 Hz, 1H), 6.78–6.76 (m, 1H), 6.45 (t, *J* = 7.6 Hz, 1H), 3.59 (s, 2H), 3.40 (d, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 140.8, 140.4, 138.7, 131.0, 129.9, 128.7, 128.64, 128.61, 128.59, 127.5, 126.5, 126.1, 124.8, 118.5, 115.6, 36.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{20}N$ 286.1590, found 286.1592.

5. General Procedure for the Synthesis of Products 2. A mixture of I_2 (1.1 mmol) and Cs_2CO_3 (2.5 mmol) in HMPA (5 mL) was stirred at room temperature for 10 min, and then treated with substrate **1** (0.5 mmol). The reaction was heated to 80 °C until TLC indicated the disappearance of the substrate. After cooling to room temperature, it was quenched with 5% $Na_2S_2O_3$ (5 mL), followed by the addition of brine (10 mL), and extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with H_2O (20 mL) and brine (20 mL) in sequence, dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to give the product **2**.

6-(*p*-Tolyl)phenanthridine (2a). 2 h; CH_2Cl_2/PE (eluent) 33:67; 108 mg, 80% yield; white solid, mp 80–82 °C (lit[11d] 80–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.61–8.58 (m, 1H), 8.24 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.14–8.12 (m, 1H), 7.83 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.69–7.63 (m, 3H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.38–7.35 (m, 2H), 2.47 (s, 3H); ^{13}C{^{1}H}

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NMR (100 MHz, $CDCl_3$) δ 161.4, 144.0, 138.7, 137.0, 133.5, 130.6, 130.4, 129.8, 129.2, 129.1, 128.9, 127.2, 126.9, 125.4, 123.8, 122.3, 122.0, 21.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}N$ 270.1277, found 270.1279.

2-Methyl-6-(*p*-tolyl)phenanthridine (2b). 2 h; EtOAc/PE (eluent) 4:96; 121 mg, 85% yield; white solid, mp 144–146 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.0 Hz, 1H), 8.38–8.37 (m, 1H), 8.13–8.10 (m, 2H), 7.81 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.64–7.61 (m, 2H), 7.60–7.55 (m, 2H), 7.37–7.35 (m, 2H), 2.64 (s, 3H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5, 142.3, 138.5, 137.1, 136.8, 133.3, 130.6, 130.4, 130.1, 129.8, 129.2, 129.0, 127.0, 125.5, 123.6, 122.2, 121.6, 22.2, 21.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{18}N$ 284.1434, found 284.1437.

2-Fluoro-6-(*p*-tolyl)phenanthridine (2c). 1 h; EtOAc/PE (eluent) 4:96; 115 mg, 81% yield; white solid, mp 134–135 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.4 Hz, 1H), 8.22–8.13 (m, 3H), 7.85–7.81 (m, 1H), 7.65–7.61 (m, 3H), 7.47 (td, J = 8.8, 2.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3 (d, $J_{C–F}$ = 245.1 Hz), 160.7 (d, $J_{C–F}$ = 2.7 Hz), 140.8 (d, $J_{C–F}$ = 1.4 Hz), 138.8, 136.7, 133.0 (d, $J_{C–F}$ = 4.2 Hz), 132.6 (d, $J_{C–F}$ = 9.0 Hz), 130.6, 129.8, 129.3, 129.1, 127.8, 125.4, 125.1 (d, $J_{C–F}$ = 9.0 Hz), 122.4, 117.8 (d, $J_{C–F}$ = 24.0 Hz), 107.0 (d, $J_{C–F}$ = 23.0 Hz), 21.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}FN$ 288.1183, found 288.1186.

2-Chloro-6-(*p*-tolyl)phenanthridine (2d). 3 h; EtOAc/PE (eluent) 4:96; 137 mg, 90% yield; white solid, mp 171–173 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 8.0 Hz, 1H), 8.55 (s, 1H), 8.15 (d, J = 8.8 Hz, 2H), 7.86 (t, J = 8.0 Hz, 1H), 7.69–7.62 (m, 4H), 7.37 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 142.4, 139.0, 136.7, 132.8, 132.6, 131.9, 130.9, 129.8, 129.4, 129.3, 129.2, 127.9,

125.6, 124.9, 122.3, 121.7, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}ClN$ 304.0888, found 304.0890.

2-Bromo-6-(*p*-tolyl)phenanthridine (2e). 4 h; EtOAc/PE (eluent) 10:90; 151 mg, 87% yield; white solid, mp 185–187 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.81 (dd, J = 8.8, 1.6 Hz, 1H), 7.66–7.62 (m, 3H), 7.37 (d, J = 7.6 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8, 142.7, 139.0, 136.7, 132.5, 132.12, 132.09, 130.9, 129.8, 129.3, 129.2, 127.9, 125.5, 125.3, 124.9, 122.3, 120.9, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}BrN$ 348.0382, found 348.0383.

6-(*p*-Tolyl)-2-(trifluoromethyl)phenanthridine (2f). 3 h; EtOAc/PE (eluent) 5:95; 161 mg, 95% yield (0.5 mmol scale); 1.58 g, 93% (5 mmol scale); white solid, mp 255–257 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.95–7.89 (m, 2H), 7.70–7.64 (m, 3H), 7.39 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 145.5, 139.3, 136.5, 133.3, 131.31, 131.27, 129.8, 129.4, 129.3, 128.5, (q, $J_{C–F}$ = 32.2 Hz), 128.1, 125.7, 124.9 (q, $J_{C–F}$ = 3.3 Hz), 124.5 (q, $J_{C–F}$ = 270.6 Hz), 123.4, 122.4, 119.9 (q, $J_{C–F}$ = 4.3 Hz), 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{15}F_3N$ 338.1151, found 338.1153.

6-(*p*-Tolyl)phenanthridine-2-carbonitrile (2g). 2 h; EtOAc/PE (eluent) 5:95; 138 mg, 94% yield; white solid, mp 235–236 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 1.2 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.96–7.90 (m, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.5, 145.7, 139.6, 136.2, 132.6, 131.7, 131.5, 130.5, 129.8, 129.5, 129.4, 128.5, 127.9, 125.7, 123.9,

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122.3, 119.3, 110.1, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{15}N_2$ 295.1230, found 295.1232.

2-Nitro-6-(*p*-tolyl)phenanthridine (2h). 3 h; EtOAc/CH_2Cl_2/PE (eluent) 1:1:98; 144 mg, 92% yield; Light yellow solid, mp 255–256 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 2.4 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.50 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1, 147.0, 145.8, 139.7, 136.2, 133.5, 131.8, 131.7, 129.9, 129.7, 129.4, 128.7, 125.7, 123.6, 122.8, 122.6, 118.9, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}N_2O_2$ 315.1128, found 315.1131.

3-Chloro-6-(*p*-tolyl)phenanthridine (2i). 2 h; EtOAc/PE (eluent) 1:99; 122 mg, 80% yield; white solid, mp 126–127 °C (lit[11d] 128–129 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 2.0 Hz, 1H), 8.16–8.14 (m, 1H), 7.86 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.65–7.61 (m, 4H), 7.38 (d, *J* = 7.6 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 144.7, 139.0, 136.7, 134.5, 133.2, 131.0, 129.8, 129.6, 129.3, 127.5, 127.4, 125.4, 123.5, 122.3, 122.2, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}ClN$ 304.0888, found 304.0889.

4-Chloro-6-(*p*-tolyl)phenanthridine (2j). 2 h; EtOAc/PE (eluent) 0.5:99.5; 132 mg, 87% yield; white solid, mp 159–160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.51 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.24 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.88–7.83 (m, 2H), 7.75–7.73 (m, 2H), 7.65 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 140.3, 139.1, 136.7, 134.7, 133.5, 130.8, 130.4, 129.3, 129.21, 129.18, 127.7, 126.6, 125.4, 125.3, 122.6, 120.9, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}ClN$ 304.0888, found 304.0889.

2,4-Dichloro-6-(*p*-tolyl)phenanthridine (2k). 4 h; CH_2Cl_2/PE (eluent) 1:99; 152 mg, 90% yield; white solid, mp 246–247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.27–8.24 (m, 1H), 7.88 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.74–7.67 (m, 3H), 7.39–7.37 (m, 2H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8, 139.4, 139.0, 136.5, 135.8, 132.6, 132.0, 131.1, 130.4, 129.4, 129.32, 129.26, 128.4, 125.9, 125.5, 122.7, 120.7, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{14}Cl_2N$ 338.0498, found 338.0501.

6-Phenylphenanthridine (2l). 2 h; CH_2Cl_2/PE (eluent) 20:80; 104 mg, 81% yield; white solid, mp 100–102 °C (lit[11d] 99–101 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.62 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.25 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.10 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.85 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.78–7.73 (m, 3H), 7.69 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.63–7.52 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 143.9, 139.9, 133.5, 130.7, 130.5, 129.8, 129.04, 128.97, 128.8, 128.6, 127.2, 127.1, 125.4, 123.9, 122.3, 122.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{14}N$ 256.1121, found 256.1123.

6-(4-Methoxyphenyl)phenanthridine (2m). 2 h; CH_2Cl_2/PE (eluent) 67:33; 119 mg, 83% yield; white solid, mp 147–148 °C (lit[11d] 144–146 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.23 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.87–7.83 (m, 1H), 7.77–7.60 (m, 5H), 7.10–7.08 (m, 2H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.0, 160.2, 143.9, 133.6, 132.3, 131.3, 130.6, 130.3, 129.1, 128.9, 127.2, 126.9, 125.4, 123.7, 122.3, 122.0, 114.0, 55.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}NO$ 286.1226, found 286.1228.

6-(4-Fluorophenyl)phenanthridine (2n).[13b] 1 h; CH_2Cl_2/PE (eluent) 33:67; 97 mg, 71% yield; white solid, mp 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.07 (dd, *J*

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= 8.4, 0.4 Hz, 1H), 7.86 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.78–7.67 (m, 4H), 7.63 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.29–7.23 (m, 2H, overlapped with the peak of chloroform); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (d, $J_{C–F}$ = 246.5 Hz), 160.3, 143.8, 135.9 (d, $J_{C–F}$ = 3.3 Hz), 133.6, 131.7 (d, $J_{C–F}$ = 8.3 Hz), 130.8, 130.4, 129.1, 128.7, 127.4, 127.2, 125.2, 123.8, 122.4, 122.1, 115.6 (d, $J_{C–F}$ = 21.5 Hz); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}FN$ 274.1027, found 274.1028.

6-(4-Chlorophenyl)phenanthridine (2o).[11d] 2 h; EtOAc/PE (eluent) 5:95; 119 mg, 82% yield; white solid, mp 159–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.71–7.68 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 143.9, 138.3, 135.0, 133.6, 131.3, 130.8, 130.5, 129.1, 128.8, 128.6, 127.4, 127.3, 125.1, 123.9, 122.5, 122.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}ClN$ 290.0731, found 290.0730.

6-(4-(Trifluoromethyl)phenyl)phenanthridine (2p). 2 h; EtOAc/PE (eluent) 1:99; 133 mg, 82% yield; white solid, mp 173–175 °C (lit[8d] 171–173 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.01 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.89–7.82 (m, 5H), 7.77 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.73–7.69 (m, 1H), 7.63 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.8, 143.8, 143.5, 133.6, 131.0, 130.9 (q, $J_{C–F}$ = 32.3 Hz), 130.5, 130.3, 129.2, 128.4, 127.5, 125.6 (q, $J_{C–F}$ = 3.8 Hz), 124.9, 124.3 (q, $J_{C–F}$ = 270.5 Hz), 124.0, 122.5, 122.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}F_3N$ 324.0995, found 324.0996.

4-(Phenanthridin-6-yl)benzonitrile (2q). 2 h; EtOAc/PE (eluent) 9:91; 120 mg, 86% yield; white solid, mp 176–177 °C (lit[8d] 179–181 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.74 (d, J = 8.4 Hz, 1H), 8.64 (dd, J = 8.0, 0.8 Hz, 1H), 8.23 (dd, J = 8.0, 1.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.92–7.87 (m, 5H), 7.81–7.77 (m, 1H), 7.75–7.71 (m, 1H), 7.65 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 144.4, 143.7, 133.7, 132.4, 131.1, 130.7, 130.5, 129.3, 128.1, 127.7, 127.6, 124.7, 124.0, 122.7, 122.2, 118.8, 112.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}N_2$ 281.1073, found 281.1074.

6-(4-Nitrophenyl)phenanthridine (2r). 2 h; EtOAc/PE (eluent) 17:83; 129 mg, 86% yield; light yellow solid, mp 192–193 °C (lit[22] 192–193 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.4 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.8 Hz, 2H), 8.25–8.23(m, 1H), 8.00–7.89 (m, 4H), 7.82–7.73 (m, 2H), 7.66 (t, J = 8.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 148.1, 146.2, 143.7, 133.6, 131.2, 131.0, 130.5, 129.3, 128.0, 127.8, 127.7, 124.7, 124.0, 123.8, 122.7, 122.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}N_2O_2$ 301.0972, found 301.0973.

6-(*m*-Tolyl)phenanthridine (2s).[9e] 2 h; CH_2Cl_2/PE (eluent) 33:67; 107 mg, 79% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.4 Hz, 1H), 8.62 (dd, J = 8.0, 1.6 Hz, 1H), 8.26–8.24 (m, 1H), 8.12–8.10 (m, 1H), 7.85 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.76 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.69 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.61 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.56 (m, 1H), 7.52–7.50 (m, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.35–7.33 (m, 1H), 2.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 143.9, 139.8, 138.4, 133.5, 130.6, 130.5, 130.4, 129.6, 129.1, 128.9, 128.3, 127.2, 126.99, 126.96, 125.4, 123.8, 122.3, 122.1, 21.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}N$ 270.1277, found 270.1279.

6-(*o*-Tolyl)phenanthridine (2t).[11a] 2 h; EtOAc/PE (eluent) 5:95; 101 mg, 75% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.4 Hz, 1H), 8.65 (dd, J = 8.0, 1.2 Hz, 1H), 8.25 (dd, J = 8.0, 1.2 Hz, 1H), 7.86 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H),

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7.80–7.76 (m, 1H), 7.74–7.70 (m, 2H), 7.58 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.44–7.34 (m, 4H), 2.12 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 144.0, 139.3, 136.6, 133.2, 130.8, 130.51, 130.47, 129.4, 129.0, 128.8, 128.7, 127.5, 127.1, 126.0, 124.0, 122.3, 122.1, 20.0; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}N$ 270.1277, found 270.1279.

2-Methylphenanthridine (2u). 2 h; EtOAc/PE (eluent) 17:83; 34 mg, 35% yield; white solid, mp 89–90 °C (lit[23] 90.1–91.1 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.58 (d, J = 8.4 Hz, 1H), 8.34 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.02 (dd, J = 8.0, 0.8 Hz, 1H), 7.83 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.68 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.58–7.55 (m, 1H), 2.63 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.8, 142.9, 137.1, 132.4, 130.9, 130.5, 129.9, 128.8, 127.4, 126.6, 124.0, 121.9, 22.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{12}N$ 194.0964, found 194.0965.

2-(Trifluoromethyl)phenanthridine (2v). 2 h; EtOAc/PE (eluent) 9:91; 47 mg, 38% yield; white solid, mp 100–102 °C (lit[11c] 98–100 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.86 (s, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.11 (dd, J = 8.0, 0.8 Hz, 1H), 7.97–7.93 (m, 2H), 7.80 (ddd, J = 8.0, 7.2, 0.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.8, 146.0, 132.3, 131.9, 131.2, 129.2, 128.9 (d, $J_{C–F}$ = 32.2 Hz), 128.6, 126.7, 124.8 (q, $J_{C–F}$ = 3.3 Hz), 124.4 (d, $J_{C–F}$ = 270.6 Hz), 123.9, 122.1, 120.2 (q, $J_{C–F}$ = 4.2 Hz); HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_9F_3N$ 248.0682, found 248.0683.

2,6-Dimethylphenanthridine (2w). 2 h; CH_2Cl_2/PE (eluent) 33:67; 38 mg, 37% yield; light yellow solid, mp 65–67 °C (lit[24] 69–71 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.4 Hz, 1H), 8.31 (s, 1H), 8.20 (dd, J = 8.4, 0.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.82 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.68 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.53 (dd, J = 8.0, 1.6 Hz, 1H), 3.03 (s, 3H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ

158.0, 142.1, 136.2, 132.5, 130.44, 130.39, 129.2, 127.3, 126.6, 126.1, 123.7, 122.4, 121.7, 23.5, 22.1; HRMS (m/z) $[M + H]^+$ calcd for $C_{15}H_{14}N$ 208.1121, found 208.1120.

8-Methoxy-6-phenylphenanthridine (2x). 2 h; CH_2Cl_2/PE (eluent) 33:67; 116 mg, 81% yield; light yellow solid, mp 128–129 °C (lit[25] 127–129 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 9.2 Hz, 1H), 8.51 (dd, J = 8.4, 1.6 Hz, 1H), 8.21 (dd, J = 8.0, 1.6 Hz, 1H), 7.76–7.74 (m, 2H), 7.71–7.62 (m, 2H), 7.58–7.46 (m, 5H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5, 158.5, 143.1, 140.0, 130.4, 129.6, 128.8, 128.6, 127.95, 127.91, 127.1, 126.6, 124.01, 123.95, 121.6, 121.1, 109.1, 55.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}NO$ 286.1226, found 286.1227.

8-Fluoro-6-phenylphenanthridine (2y).[25] 1 h; CH_2Cl_2/PE (eluent) 34:66; 96 mg, 70% yield; white solid, mp 134–135 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71–8.68 (m, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.26–8.24 (m, 1H), 7.78–7.68 (m, 5H), 7.63–7.54 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3 (d, $J_{C–F}$ = 246.4 Hz), 160.5 (d, $J_{C–F}$ = 3.8 Hz), 143.6 (d, $J_{C–F}$ = 1.3 Hz), 139.4, 130.6, 130.3 (d, $J_{C–F}$ = 1.9 Hz), 129.7, 129.1, 128.9, 128.8, 127.5, 126.7 (d, $J_{C–F}$ = 7.9 Hz), 124.9 (d, $J_{C–F}$ = 8.3 Hz), 123.4 (d, $J_{C–F}$ = 0.8 Hz), 121.9, 119.9 (d, $J_{C–F}$ = 23.8 Hz), 113.4 (d, $J_{C–F}$ = 22.0 Hz); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}FN$ 274.1027, found 274.1026.

8-Chloro-6-phenylphenanthridine (2z). 2 h; CH_2Cl_2/PE (eluent) 33:67; 122 mg, 83% yield; white solid, mp 123–125 °C (lit[8d] 120–122 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J = 8.8, 2.0 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.24 (dd, J = 8.4, 1.2 Hz, 1H), 8.07 (d, J = 2.0 Hz, 1H), 7.81–7.75 (m, 2H), 7.73–7.67 (m, 3H), 7.61–7.53 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 143.8, 139.2, 133.2, 132.0, 131.3, 130.6, 129.7, 129.3, 129.1, 128.8, 128.0, 127.5, 126.3, 124.2, 123.3, 122.0; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}ClN$ 290.0731, found 290.0733.

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6-Phenyl-8-(trifluoromethyl)phenanthridine (2aa).[9b] 2 h; CH_2Cl_2/PE (eluent) 33:67; 137 mg, 85% yield; white solid, mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.8 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.41 (s, 1H), 8.28 (dd, J = 8.4, 1.2 Hz, 1H), 8.05 (dd, J = 8.8, 1.2 Hz, 1H), 7.86–7.82 (m, 1H), 7.76–7.73 (m, 3H), 7.63–7.55 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2, 144.6, 139.0, 135.8, 130.7, 130.2, 129.8, 129.4, 129.1 (q, $J_{C–F}$ = 32.8 Hz), 128.9, 127.7, 126.5 (q, $J_{C–F}$ = 3.2 Hz), 126.4 (q, $J_{C–F}$ = 4.3 Hz), 124.6, 124.1 (q, $J_{C–F}$ = 270.7 Hz), 123.5, 122.9, 122.4; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}F_3N$ 324.0995, found 324.0994.

6-Phenylphenanthridine-8-carbonitrile (2ab). 2 h; CH_2Cl_2/PE (eluent) 33:67; 116 mg, 83% yield; white solid, mp 193–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.4 Hz, 1H), 8.59 (dd, J = 8.4, 1.2 Hz, 1H), 8.46 (d, J = 1.6 Hz, 1H), 8.28 (dd, J = 8.4, 0.8 Hz, 1H), 8.01 (dd, J = 8.8, 1.6 Hz, 1H), 7.86 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.75 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.72–7.69 (m, 2H), 7.64–7.58 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 144.8, 138.5, 136.1, 134.4, 131.8, 130.8, 129.8, 129.5, 128.9, 127.9, 124.8, 123.7, 122.6, 122.5, 118.7, 110.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}N_2$ 281.1073, found 281.1074.

8-Nitro-6-phenylphenanthridine (2ac). 3 h; CH_2Cl_2/PE (eluent) 50:50; 126 mg, 84% yield; yellow solid, mp 234–236 °C (lit[8d] 230–232 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.4 Hz, 1H), 8.83 (d, J = 9.2 Hz, 1H), 8.65–8.62 (m, 2H), 8.30 (dd, J = 8.4, 0.8 Hz, 1H), 7.91–7.87 (m, 1H), 7.80–7.74 (m, 3H), 7.65–7.58 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 146.2, 145.1, 138.5, 137.6, 131.1, 130.9, 129.9, 129.7, 129.0, 128.1, 125.1, 124.7, 124.3, 124.2, 122.9, 122.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{13}N_2O_2$ 301.0972, found 301.0973.

6-Phenylphenanthridine-7-carbonitrile (2ad). 2 h; EtOAc/CH_2Cl_2/PE (eluent) 4:8:88; 116 mg, 83% yield; yellow solid, mp 196–198 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.98 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.64–8.61 (m, 1H), 8.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.95–7.91 (m, 1H), 7.85 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.77 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.65–7.57 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.1, 143.7, 140.0, 136.4, 134.7, 130.7, 130.2, 130.0, 129.9, 129.7, 128.8, 128.0, 127.2, 124.5, 122.7, 122.1, 116.9, 112.0; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}N_2$ 281.1073, found 281.1077.

6-Phenylphenanthridine-9-carbonitrile (2ae). 2 h; EtOAc/PE (eluent) 4:96; 119 mg, 85% yield; white solid, mp 203–208 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.29–8.27 (m, 1H), 8.23–8.21 (m, 1H), 7.87–7.83 (m, 1H), 7.81–7.75 (m, 2H), 7.73–7.69 (m, 2H), 7.62–7.54 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.6, 144.3, 138.8, 133.4, 130.8, 130.3, 130.1, 129.8, 129.4, 128.8, 128.6, 128.1, 127.8, 126.6, 122.3, 122.0, 118.6, 114.1; HRMS (m/z) [M + H]+ calcd for $C_{20}H_{13}N_2$ 281.1073, found 281.1077.

6-Phenylphenanthridine-10-carbonitrile (2af). 2 h; EtOAc/PE (eluent) 5:95; 119 mg, 85% yield; white solid, mp 195–196 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.31–8.26 (m, 2H), 7.91–7.87 (m, 1H), 7.80 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.71–7.67 (m, 3H), 7.61–7.55 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0, 144.8, 139.5, 139.2, 134.5, 133.3, 131.0, 130.7, 129.8, 129.3, 128.8, 127.8, 126.5, 126.1, 124.0, 122.0, 120.8, 107.4; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{13}N_2$ 281.1073, found 281.1075.

2,4-diphenylquinoline (2ag).[26] 2 h; EtOAc/PE (eluent) 2:98; 99 mg, 70% yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.4, 0.4 Hz, 1H), 8.20–8.18 (m, 2H), 7.91 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.82 (s, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.57–7.44 (m, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.0, 149.3, 148.9,

139.8, 138.5, 130.2, 129.7, 129.6, 129.5, 129.0, 128.7, 128.5, 127.7, 126.5, 125.9, 125.8, 119.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{16}N$ 282.1277, found 282.1278.

5-Iodo-2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine (1a'). EtOAc /PE (eluent) 2:98; colorless oil; ^1H NMR (400 MHz, $CDCl_3$), δ 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 7.32–7.24 (m, 3H, overlapped with the peak of chloroform), 7.17–7.14 (m, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 8.0 Hz, 1H), 3.83–3.71 (m, 2H), 3.40 (s, 2H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.8, 140.5, 138.7, 137.7, 137.08, 137.06, 135.5, 130.4, 129.6, 129.1, 129.0, 128.5, 126.9, 117.2, 79.1, 38.9, 21.2; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}IN$ 400.0557, found 400.0559.

2-Iodo-6-(*p*-tolyl)phenanthridine (2a'). EtOAc /PE (eluent) 2:98; white solid; mp 201–203 °C; ^1H NMR (400 MHz, $CDCl_3$), δ 8.93 (d, J = 1.6 Hz, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.14 (dd, J = 8.4, 0.8 Hz, 1H), 7.99 (dd, J = 8.8, 2.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.85 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.65–7.61 (m, 3H), 7.37 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 143.1, 139.0, 137.7, 136.7, 132.2, 132.1, 131.3, 130.9, 129.8, 129.3, 129.2, 127.8, 125.7, 125.5, 122.3, 92.6, 21.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}IN$ 396.0244, found 396.0247.

▪Electronic Supplementary Information (ESI) available: Copies of ^1H and ^{13}C NMR spectra of isolated compounds. See DOI: 10.1039/x0xx00000x

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▪ Conflicts of interest

There are no conflicts to declare.

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▪ Notes and References

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19. Without pre-stirring of iodine and base in HMPA, iodinated substrate (**1a'**) and product (**2a'**) were formed. For their characterization data and NMR spectra, see the Experimental section and Electronic Supplementary Information (ESI).
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