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General synthesis of pyrido[1,2-a]indoles via Pd-catalyzed cyclization of *o*-picolylbromoarenes

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Dedicated to Prof. Beletskaya on the occasion of her 85th birthday

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ABSTRACT

An efficient Pd-catalyzed cyclization of *o*-picolylbromoarenes into pyridoindoles has been developed. This novel transformation, which proceeds through a not common for Pd catalysis L-to X-type pyridine ligand swap, provides an efficient route to aryl-, as well as to cyanopyrido[1,2-a]indoles, not easily accessible by existing cyclization methods.

1. Introduction

Pyrido[1,2-a]indole scaffold is an important heterocyclic motif broadly found in organic materials [1] and biologically active molecules [2] (Chart 1). Although, numerous methods toward assembly of this essential core have been developed, synthesis of fully aromatic pyrido[1,2-a]indoles still remains a challenging task [3,4]. One of the methods toward this skeleton relies on annulation of pyridine derivatives with benzynes [4] or alkynes [5] (Scheme 1A,B). While the reaction with benzynes leads to formation of pyridoindoles in moderate yields, employment of alkynes generally results in pyrrolo[2,1-a]isoquinolines or tetrasubstituted pyridoindoles. A presence of an activating group at C-3 position (R) is a requisite for the success of the latter transformation. Klumpp and co-workers [6a] developed an elegant synthesis of the pyridoindole moiety using an acid-mediated aza-Nazarov type cyclization. However, this transformation is limited to substrates possessing hydroxyl- and aryl substituents at C-3 position (Scheme 1C) [6]. Later, Sekar reported Iron catalyzed C–H functionalization process to access the same core (Scheme 1D) [7]. Although appealing, this method operates under harsh acidic conditions and is also limited to substrates possessing aryl substituents at the C-3 position. Herein, we report a novel efficient and general Pd-catalyzed cyclization of *o*-picolyl haloarenes into pyrido[1,2-*a*]indoles (Scheme 1E). Notably, this transformation, which proceeds under basic conditions, offers a practical synthetic route to fully aromatic pyrido[1,2-*a*]indoles possessing aryl, or cyano groups at the C-3 position [8]. Notably, picolyl group in this transformation serves as both L- and X-type ligand, which is not common for Pd-catalyzed intramolecular C–N coupling reactions [9–11].

2. Results & discussion

As a part of our on-going research program toward development of general and efficient methods for synthesis of diverse fused heterocyclic scaffolds [12], we turned our attention to synthesis of pyrido[1,2-*a*]indoles. We thought that upon exposure to Pd(0)/L/Base system, **1** would be converted into a Pd(II) species **3**, where the picolyl group serves as an L-type ligand. Here, we hypothesized that a subsequent deprotonation/–tautomerization would convert the latter into an X- type ligand (**3** → **4**) [9–11], thus setting up a stage

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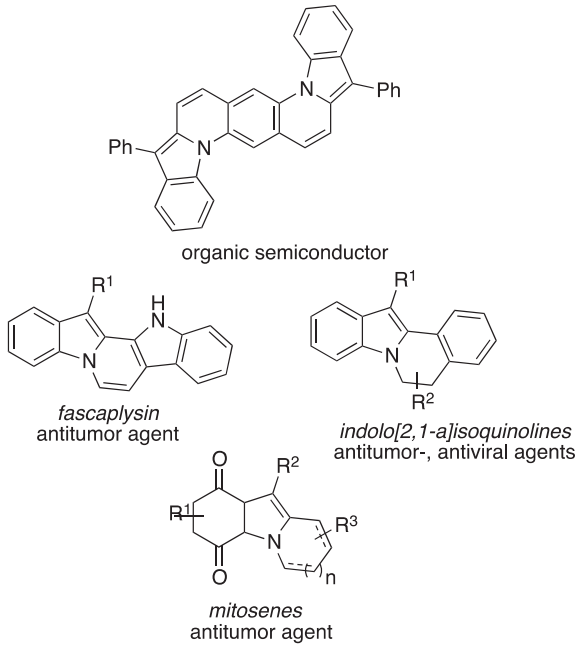
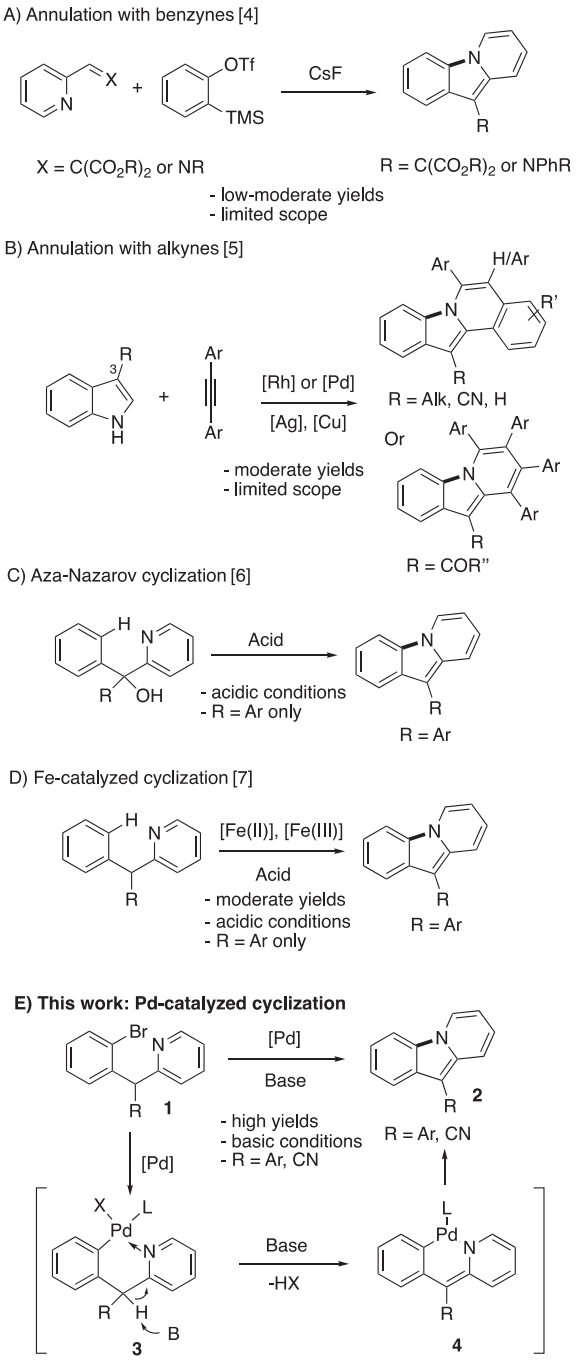


Chart 1. Selected examples of important molecules containing pyrido[1,2-a]indole fragment.

for a reductive elimination into the targeted product **2** (Scheme 1E) [13]. In order to test this hypothesis, *o*-picolyl bromobenzene **1a** was first subjected to the $Pd(PPh_3)_4$ complex and a base, which resulted in the formation of pyrido[1,2-a]indole product **2a** in good yield. (Table 1, entry 1). The combination of palladium(II) catalysts and triphenylphosphine ligand resulted in lower yields (entries 2, 3). DPEphos was found to be the best ligand, providing nearly quantitative yield of **2a**, while dppf was less efficient (entries 4, 5). Further screening indicated potassium phosphate and toluene as the optimal combination of a base and a solvent (entries 6–10). In addition, two transition metal-catalyzed conditions, that were employed for synthesis of pyridoindole by Sekar [7] and pyridobenzimidazoles by Maes [14] were inefficient (entries 11, 12). The control experiment indicated that palladium catalyst is crucial for this transformation (entry 13).

With the optimized conditions in hand, the generality of this method was examined (Table 2). Tolyl-substituted derivative reacted well producing the cyclized product **2b** in good yield. Picolylarenes **1c**,**d**, possessing electron-withdrawing substituents, such as chloride and fluoride at the benzene ring, were competent substrates producing the fused indole products in high yields. Presence of an electron-releasing methoxy substituent (**1e**) did not hamper the reaction, as well. Likewise, substituents at the pyridine ring did not affect the reaction outcome. Thus, fluorine-containing heteroarene, which was previously shown to react inefficiently [7], produced the tricyclic product **2f** in good yield. Cyclization of the methyl-substituted substrate **1g** proceeded uneventfully to produce the corresponding pyridoindole in 96% yield. Notably, not only aryl-substituted reactants, but also a substrate possessing the nitrile group at the benzylic position (**1h**) was a capable reactant for this cyclization reaction, producing **2h** in excellent yield. Importantly, this substitution motif at pyrido[1,2-a]indoles is not easily accessible via existing synthetic methods (*vide supra*). Moreover, *o*-picolyl bromonaphthalene (**1i**), reacted efficiently producing tetracyclic benzopyrido[1,2-a]indole **2i** in nearly quantitative yield. Notably, selective cyclization of unsymmetrical substrates **1e, i** highlights the superiority of this method vs reported protocols leading to the mixtures of the regioisomers (Scheme 1D [7]).



Scheme 1. Synthesis of pyrido[1,2-a]indole.

3. Conclusions

In summary, we have developed a practical synthesis of phenyl- and cyanopyrido[1,2-a]indoles via the Pd-catalyzed cyclization reaction of *o*-picolylbromoarenes. This reaction is quite general with respect to the substitution pattern at both, benzene and pyridine rings. In contrast to the existing transition metal-catalyzed cyclization methods toward this core, which operate under strong acidic conditions, this complementary method proceeds under basic conditions. The reaction underwent efficient cyclization providing this tricyclic scaffold in excellent yields. It is believed that this approach may be extended to other heterocyclic cores, and, thus,

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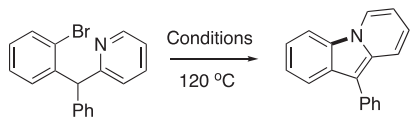
Table 1
Screening of reaction conditions.



1a **2a**

Entry	Catalyst, Ligand	Base/Acid	Solvent	Yield(%)[a]
1	$Pd(PPh_3)_4$	K_3PO_4	CH_3Ph	72
2	$Pd(OAc)_2$, PPh_3	K_3PO_4	CH_3Ph	45
3	$PdCl_2(PPh_3)_2$, PPh_3	K_3PO_4	CH_3Ph	31
4	$Pd(OAc)_2$, dppf	K_3PO_4	CH_3Ph	68
5	**$Pd(OAc)_2$, DPEphos**	**K_3PO_4**	**CH_3Ph**	**96**
6	$Pd(OAc)_2$, DPEphos	Cs_3CO_3	CH_3Ph	22
7	$Pd(OAc)_2$, DPEphos	DIPEA	CH_3Ph	41
8	$Pd(OAc)_2$, DPEphos	K_3PO_4	DMF	19
9	$Pd(OAc)_2$, DPEphos	K_3PO_4	MeCN	51
10	$Pd(OAc)_2$, DPEphos	K_3PO_4	dioxane	21
11	$FeCl_2$, $FeCl_3$	PivOH	xylene	0[b]
12	$Cu(OAc)_2$	3,4,5-TFBA	DMSO	0[c]
13	*No* [*Pd*], DPEphos	K_3PO_4	CH_3Ph	0[b]

[a] GC yields.
[b] No reaction.
[c] Decomposition.

will find broad applications for synthesis of important polycyclic molecules.

4. Experimental section

4.1. Synthesis and characterization of starting materials

4.1.1. 2-((2-bromophenyl)(phenyl)methyl)pyridine (*1a-1f*)

To an argon-charged flask, 0.34 mL of 2-bromopyridine (3.6 mmol) and 10 mL of THF were added under a positive pressure of argon, and cooled at −78 °C for 5 min 1.4 mL of *n*-BuLi solution in hexane (2.5 M, 3.5 mmol) was added. The metal-halogen exchange step completed in 30 min according to TLC. 3.6 mL of corresponding 2-bromobenzaldehyde was added to 2-pyridyl lithium solution at −78 °C. Reaction was kept at this temperature for 2 h, then stirred at an ambient temperature for another 6 h. Afterwards, the reaction was quenched by adding 50 mL of saturated aqueous ammonium chloride solution, then extracted by 30 mL of ethyl acetate. The combined organic extract was dried (anhydrous sodium sulfate), filtered (celite plug), and concentrated under a reduced pressure. The crude alcohol was submitted to next step without purification.

To the crude alcohol, 4 mL benzene (44 mmol) was added under an argon atmosphere, and stirred until the alcohol was completely dissolved. This benzene solution was cooled at 0 °C for 5 min, and 2 mL of trifluoromethanesulfonic acid was added. The flask was removed from ice bath, and reaction mixture was stirred at room temperature for 12 h. The reaction mixture was added to 20 mL of cooled saturated sodium bicarbonate solution, and extracted by 20 mL of ethyl acetate. The combined organic extract was dried (anhydrous sodium sulfate), filtered (celite plug), and concentrated under a reduced pressure. A silica gel column chromatography (20:1 Hexanes/EtOAc) afforded the product **1a-g,i.**

1a, 33% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.62 (d, J = 3.80 Hz, 1 H), 7.68–7.50 (m, 2 H), 7.37–7.28 (m, 2 H), 7.28–7.19 (m, 3 H), 7.19–7.06 (m, 4 H), 7.06–6.92 (m, 2 H), 6.09 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.99, 149.71, 142.12, 141.59, 136.43, 133.08, 131.31, 129.58, 128.50, 128.20, 127.27, 126.70, 125.58, 124.08, 121.50, 58.37. ^{13}C-DEPT 135 NMR (100 MHz, $CDCl_3$) δ ppm 149.71, 136.43, 133.08, 131.31, 129.58, 128.50, 128.20, 127.28, 126.70, 124.08, 121.50, 58.37.

1b, 46% yield over 2 steps: 7: 1, ortho: para; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.62 (d, J = 4.38 Hz, 1H), 7.63–7.56 (m, 2H), 7.28–7.00 (m, 9H), 6.07 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 21.11, 58.07, 121.42, 124.03, 125.59, 127.27, 128.14, 129.25, 129.47, 131.30, 133.07, 136.25, 136.39, 138.60, 142.33, 149.69, 162.28.

1c, 53% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.66–8.57 (m, 1H), 7.66–7.57 (m, 1H), 7.35–6.98 (m, 10H), 6.05(s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 57.77, 121.67, 124.12, 125.70, 126.92, 127.52, 128.62, 129.47, 132.11, 132.56, 133.12, 136.56, 140.88, 149.75, 161.46.

1d, 32% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.64 (d, J = 4.03 Hz, 1H), 7.60 (t, J = 7.70 Hz, 1H), 7.38–7.29 (m, 3H), 7.29–7.22 (m, 1H), 7.20–7.11 (m, 3H), 7.11–7.04 (m, 2H), 6.99–6.92 (m, 1H), 6.09(s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 57.65, 114.35, 120.08, 121.67, 124.13, 125.32, 126.91, 128.66, 129.52, 132.22, 136.58, 138.26, 141.58, 149.78, 160.09, 161.76, 162.07. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −114.6.

1e, 47% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.60 (d, J = 4.97 Hz, 1H), 7.60 (t, J = 7.60 Hz, 1H), 7.32–7.09 (m, 7H), 6.74–6.79 (m, 3H), 5.68(s, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 55.13, 59.37, 111.67, 115.50, 121.45, 121.89, 123.75, 126.57, 128.43, 129.37, 136.44, 142.55, 144.31, 149.54, 159.65, 160.64.

1f, 42% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.73–7.66 (m, 1H), 7.60 (d, J = 7.89 Hz, 1H), 7.37–7.22 (m, 4H), 7.19–7.07 (m, 4H), 6.91–6.97 (m, 1H), 6.83–6.77 (m, 1H), 6.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 57.71, 107.30, 121.42, 125.54, 126.96, 127.42, 128.47, 128.62, 129.56, 131.32, 133.15, 141.00, 141.38, 160.64, 162.00, 164.39. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −66.7.

1g, 39% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.52 (d, J = 5.13 Hz, 1H), 7.61 (d, J = 8.07 Hz, 1H), 7.36–7.30 (m, 2H), 7.27–7.19 (m, 4H), 7.18–7.14 (m, 1H), 7.11–7.06 (m, 1H), 7.00–6.93 (m, 2H), 6.17 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 21.22, 58.36, 122.69, 125.08, 125.69, 126.77, 127.39, 128.29, 128.58, 129.70, 131.54, 133.11, 141.86, 142.35, 147.63, 149.50, 161.79.

1i, 31% yield over 2 steps: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.63 (d, J = 4.97 Hz, 1H), 8.35 (d, J = 8.48 Hz, 1H), 7.79 (d, J = 7.89 Hz, 1H), 7.72 (d, J = 8.77 Hz, 1H), 7.65–7.55 (m, 2H), 7.53–7.47 (m, 1H), 7.34–7.22 (m, 4H), 7.19–7.10 (m, 4H), 6.49 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 59.02, 121.54, 124.24, 125.40, 126.41, 126.70, 127.39, 127.77, 128.06, 128.25, 128.52, 129.57, 132.65, 133.48, 136.47, 149.73, 162.09.

4.1.2. Synthesis of 2-(2-bromophenyl)-2-(pyridin-2-yl)acetonitrile (*1h*)

A 100 mL round bottom flask was evacuated and back-filled by argon 3 times, and charged with 0.84 mL of *o*-bromophenylacetonitrile (6.5 mmol) and 25 mL of toluene under a positive pressure of argon. After being cooled in an ice bath for 5 min, 7.5 mL of a solution of NaHMDS in THF (1 M, 7.5 mmol) was added to this toluene solution, and the ice bath was removed. After 30 min, 0.47 mL of 2-chloropyridine (5.0 mmol) was added, and the mixture was heated in a 70 °C oil bath for 6 h. The progress of reaction was monitored by TLC. Upon completion, reaction was quenched by adding 50 mL of saturated aqueous ammonium chloride solution reaction, then

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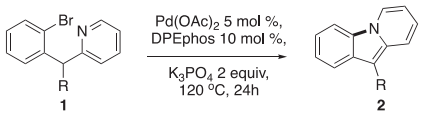
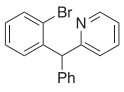
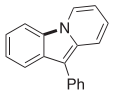
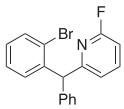
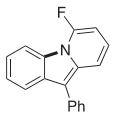
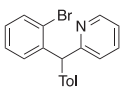
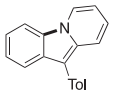
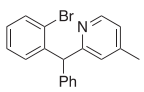
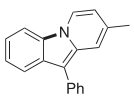
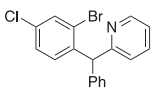
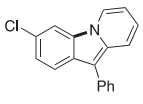
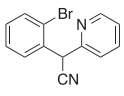
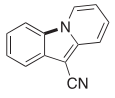
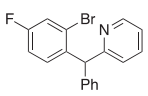
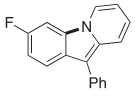
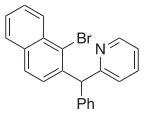
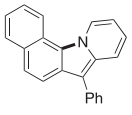
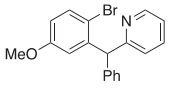
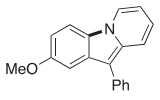
Table 2
Pd-catalyzed synthesis of pyrido[1,2-a]indoles.[a]



Substrate	Product	Substrate	Product
 **1a**	 **2a**, 95%	 **1f**	 **2f**, 78%
 **1b**	 **2b**, 86%	 **1g**	 **2g**, 96%
 **1c**	 **2c**, 76%	 **1h**	 **2h**, 95%
 **1d**	 **2d**, 94%	 **1i**	 **1i**, 98%
 **1e**	 **2e**, 80%[b]		

0.3 mmol **1**, 5 mol % $Pd(OAc)_2$, 10 mol % DPEphos, 2 equiv K_3PO_4, 120 °C 24h. [a] Isolated yields. [b] NMR yield.

extracted by 30 mL of ethyl acetate for three times. The combined organic extract was dried (anhydrous sodium sulfate), filtered (celite plug), and concentrated under a reduced pressure. A silica gel column chromatography purification (9:1 Hexanes/EtOAc) afforded 0.84 g of **1h** in 64% yield.

1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.63–8.62 (1H, m), 7.70–7.59 (m, 3H), 7.59–7.35 (m, 1H), 7.38–7.20 (m, 3H), 5.80 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 153.95, 150.23, 137.38, 134.17, 133.40, 130.44, 130.26, 128.40, 123.70, 123.27, 122.51, 118.53, 44.74. ^{13}C-DEPT 135 NMR (101 MHz, $CDCl_3$) δ ppm 150.23, 137.37, 133.39, 130.43, 130.24, 128.39, 123.26, 122.50, 44.72.

4.2. General procedure for palladium-catalyzed synthesis of pyrido [1,2-a]indole

0.3 mmol of the corresponding *o*-picolylbromobenzene was added to a screw-thread vial, which was evacuated and back-filled by argon three times on a double bank Schlenk manifold. To this vial, 2.5 mL of dry toluene was added under a flow of argon. The vial was closed by a cap, and swirled gently till all solid particles are dissolved. This vial and an oven-dried Wheaton conical vial were transferred into an argon filled glovebox. To this conical vial, a stirring bar, 0.015 mmol of $Pd(OAc)_2$, 0.03 mmol of a ligand, and 0.6 mmol of a designated base were added. The toluene solution of substrate was added to this conical vial using a glass pipette. This conical vial was closed by a cap equipped with a pressure release valve, removed from glovebox, and placed in a metal bath over a stirring plate preheated to designated temperature. The progress of reaction was monitored by TLC and GC-MS. Upon complete, the reaction mixture was cooled down and filtered (celite plug), under a pressure of argon, and rinsed by 10 mL dicholormethane. The filtrate was concentrated under a reduced pressure, and purified by a neutralized (by trimethylamine) silica gel column (20:1 Hexanes/EtOAc) packed under argon.

2b, 86% yield:: 7: 1, ortho: para; ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.34 (d, $J = 7.34$ Hz, 1H), 8.05 (d, $J = 8.44$ Hz, 1H), 7.91 (d, $J = 8.44$ Hz, 1H), 7.72 (d, $J = 9.17$ Hz, 1H), 7.62 (d, $J = 8.07$ Hz, 2H), 7.44 (t, $J = 8.07$ Hz, 1H), 7.39–7.32 (m, 4H), 6.94–6.89 (m, 1H), 6.51 (t, $J = 6.24$ Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 21.28, 108.23, 110.24, 118.18, 119.38, 120.13, 122.60, 123.17, 124.33, 127.64, 128.49, 128.73, 129.27, 129.60, 132.23, 133.85, 135.25. HRMS-(+)EI calcd. for $C_{19}H_{15}N$ $[M]^+$: 257.12045, found: 257.12008.

2c, 76% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.24 (d, $J = 7.02$ Hz, 1H), 7.94–7.90 (m, 2H), 7.71–7.63 (m, 3H), 7.52 (t, $J = 7.31$ Hz, 2H), 7.40–7.30 (m, 2H), 6.95–6.90 (m, 1H), 6.54 (t, $J = 7.02$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 106.20, 108.98, 110.30, 118.30, 120.30, 123.05, 123.96, 125.89, 129.01, 129.45, 133.72, 134.69. HRMS-(+)EI calcd. for $C_{18}H_{12}ClN$ $[M\text{-}H]^+$: 277.06582, found: 277.06622.

2d, 94% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.14 (d, $J = 7.02$ Hz, 1H), 7.97 (dd, $J = 8.77$, 5.26 Hz, 1H), 7.69 (d, $J = 8.18$ Hz,

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3H), 7.59–7.51 (m, 3H), 7.36 (t, $J = 7.31$ Hz, 1H), 7.25–7.18 (m, 1H), 6.90–6.83 (m, 1H), 6.49 (t, $J = 6.43$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 96.41, 106.05, 108.69, 112.31, 112.56, 118.39, 120.37, 122.36, 124.03, 125.89, 128.96, 133.57, 134.91, 157.52, 159.62. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −121.3. HRMS-(+)EI calcd. for $C_{18}H_{12}FN$ $[M\text{-}H]^+$: 261.09537, found: 261.09551.

2f, 78% yield: ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.26 (dd, $J = 8.44$, 3.67 Hz, 1H), 8.02 (d, $J = 8.44$ Hz, 1H), 7.70 (d, $J = 6.97$ Hz, 2H), 7.57–7.44 (m, 4H), 6.93–6.86 (m, 1H), 6.14 (t, $J = 6.97$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 87.92, 107.95, 113.13, 115.21, 117.89, 118.91, 120.99, 123.07, 123.71, 126.14, 128.30, 128.89, 133.69, 134.19, 152.35, 154.45. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −106.7. HRMS-(+) EI calcd. for $C_{18}H_{12}FN$ $[M - H]^+$: 261.09537, found: 261.09552.

2g, 96% yield: ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.24 (d, $J = 7.34$ Hz, 1H), 8.04 (d, $J = 8.07$ Hz, 1H), 7.88 (d, $J = 8.44$ Hz, 1H), 7.74 (d, $J = 8.07$ Hz, 1H), 7.55 (t, $J = 7.70$ Hz, 2H), 7.50–7.48 (m, 1H), 7.43 (t, $J = 6.97$ Hz, 1H), 7.37–7.29 (m, 2H), .6.36 (d, $J = 7.34$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 21.69, 104.48, 110.08, 111.27, 115.52, 118.99, 119.66, 123.14, 123.76, 125.41, 128.04, 128.83, 129.27, 133.52, 133.79, 135.58. HRMS-(+)EI calcd. for $C_{19}H_{15}N$ $[M - H]^+$: 257.12045, found: 257.12062.

2h, 95% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.46 (d, $J = 7.09$ Hz, 1H), 7.91 (d, $J = 8.62$ Hz, 2H), 7.74 (dd, $J = 9.13$, 1.02 Hz, 1H), 7.58–7.48 (m, 1H), 7.46–7.37 (m, 1H), 7.36–7.28 (m, 1H), 6.83 (td, $J = 6.83$, 1.10 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 141.85, 129.37, 128.98, 127.25, 125.49, 125.18, 122.07, 119.66, 118.12, 116.75, 111.16, 110.83, 74.45. ^{13}C NMR DEPT-135 (101 MHz, $CDCl_3$) δ ppm 127.25, 125.49, 125.18, 122.07, 119.66, 118.12, 111.16, 110.83.

2i, 98% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.17 (d, $J = 7.34$ Hz, 1H), 8.66 (d, $J = 8.44$ Hz, 1H), 8.08 (d, $J = 8.80$ Hz, 2H), 7.91 (d, $J = 9.17$ Hz, 1H), 7.81–7.70 (m, 4H), 7.60 (t, $J = 7.34$ Hz, 2H), 7.54 (t, $J = 6.97$ Hz, 1H), 7.43 (t, $J = 7.70$ Hz, 1H), 7.04–6.97 (m, 1H), 6.79 (t, $J = 7.34$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 108.92, 110.43, 118.39, 119.41, 119.71, 120.14, 121.99, 123.21, 123.80, 125.05, 125.80, 126.14, 126.29, 126.60, 128.58, 128.91, 129.77, 129.95, 130.72, 133.17, 134.91. HRMS-(+)EI calcd. for $C_{22}H_{15}N$ $[M]^+$: 293.12045, found: 293. 11987.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.03.003

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