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SYNTHESIS OF INDOLINES VIA A PHOTOCATALYTIC INTRAMOLECULAR REDUCTIVE CYCLIZATION REACTION

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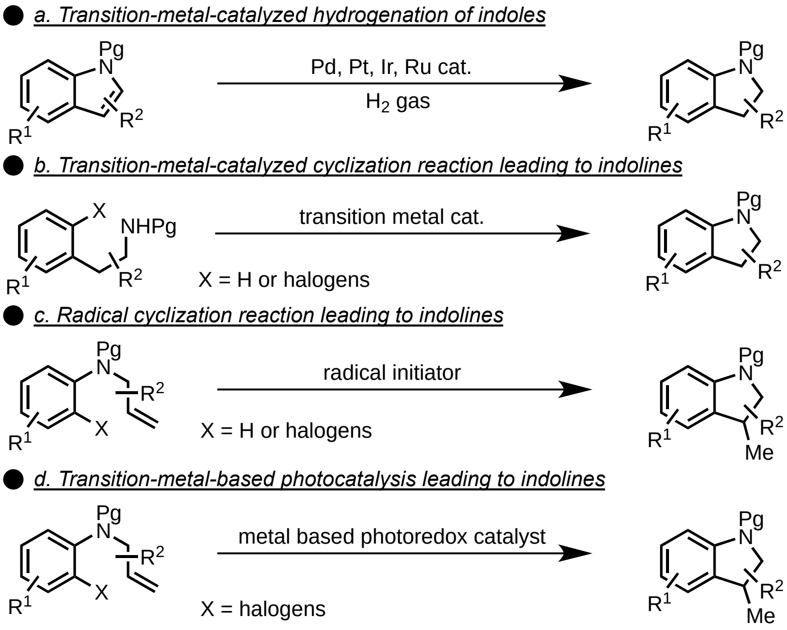
Abstract – Herein, we synthesized a series of indolines using a photocatalytic intramolecular reductive cyclization reaction. This reaction uses several *N*-allyl-2-iodoanilines in the presence of 10-phenylphenothiazine (Ph-PTZ) as an organic photocatalyst. Further, the corresponding aryl radical is generated through the reductive cleavage of the C–I bond, generating 5-*exo* cyclization products.

INTRODUCTION

The nitrogen-containing heterocyclic compounds are an important motif for several biologically active compounds, including agrochemicals, pharmaceuticals, and the naturally occurring products.[1] Further, several materials that are used in organic photo and electronic devices comprise *N*-heteroarenes.[2]

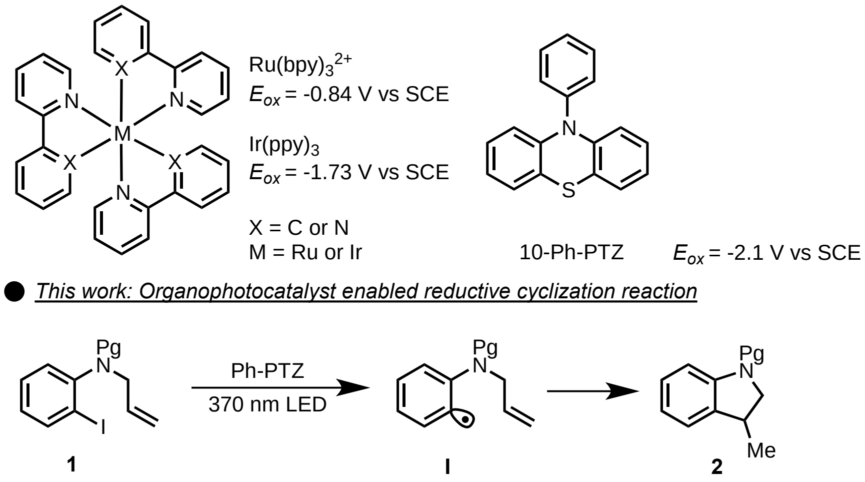
Indolines have received considerable attention from the synthetic chemistry community because of their important properties.[3] In general, indolines have been synthesized by hydrogenating indoles via homogeneous or heterogeneous transition-metal catalysts (Scheme 1a).[4] The transition-metal-catalyzed intramolecular cyclization reactions, which enable the synthesis of polyfunctionalized indolines, have also been previously studied (Scheme 1b).[5] In addition, indolines are synthesized from the corresponding haloanilines through the mediation of a radical cyclization reaction by a radical initiator (Scheme 1c).[6] Although these reactions are highly reliable and versatile, they require expensive transition-metal complexes and a stoichiometric amount of an oxidant or a radical initiator. Therefore, a cost-effective and environment-friendly transformation is of interest.

In contrast, the transition-metal-based photocatalysts have recently been developed because of their unique activation modes for organic molecules when compared with those of the transition-metal-based thermal catalysts.[7] In this context, the usage of metal-based photoredox catalysts has been reported for synthesizing indolines (Scheme 1d).[8] Photoredox catalysis leading to indolines was initiated by the single-electron reduction of a carbon–halogen (C–X) bond to form aryl radicals, which underwent cyclization to form the product. Although the metal-based photoredox methodology was a suitable alternative to the aforementioned methodology for developing indolines, a reaction should be developed without any metal complexes because of their toxicity.



Scheme 1. Synthetic method for producing indolines

From this perspective, tremendous efforts have been devoted to the development of small organic molecule-based photoredox catalysts as alternatives to the metal-based photocatalysts.[9] We have also developed organic photocatalysts as alternatives to the metal-based photocatalysts.[10] In our investigations, we focused on 10-phenylphenothiazine (Ph-PTZ), which is electron-rich and acts as a strong reductant in the excited state (Scheme 2, e.g., *Eox* Ph-PTZ is stronger than the Ru or Ir complex).



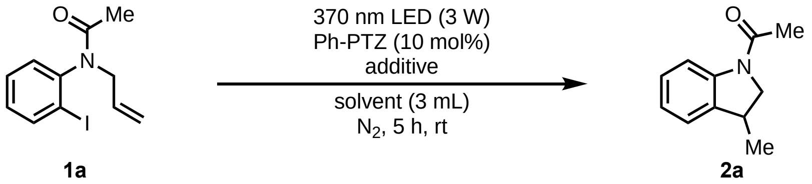
Scheme 2. Organophotoredox-catalyzed reductive cyclization leading to indolines

For instance, Hawker et al. utilized Ph-PTZ in the hydrogenation of organic halides.[11] This reaction was initiated through the single-electron reduction of a carbon–halogen bond by the excited state of Ph-PTZ to generate the corresponding aryl radicals. Also, they attempted cyclization of 2-allyloxybromobenzene in their study for reaction mechanism.[11b] On the basis of this reaction, we hypothesized that the reaction of *N*-allyl-iodoanilines in the presence of a Ph-PTZ photocatalyst generated the aryl radical intermediate **I** through the reductive cleavage of the C–X bond; further, **I** underwent *5-exo-trig* cyclization to produce indolines (Scheme 2). In this study, we report a photocatalytic intramolecular reductive cyclization reaction that produces indolines.

RESULTS AND DISCUSSION

We began our study by optimizing the reaction conditions using **1a** as the model substrate (Table 1). On the basis of the previously reported intermolecular reaction,[12] we have attempted to use a similar reaction condition for the intramolecular reaction comprising **1a**, NBu_3 (10 equiv.), and Ph-PTZ (10 mol%) in MeCN irradiated with a 370-nm light-emitting diode (entry 1).[11b] We exclusively attempted our study in N_2 atmosphere prevent from oxidation at benzylic position of the corresponding product.[11b] The addition of formic acid (10 equiv.) improved the reaction yield to 59% (entry 2). The role of formic acid is thought to contribute regenerating NBu_3 according to the previous report.[11b] High yields of the reductive cyclization product were obtained in polar solvents, such as DMF and DMSO (entries 2–4), with lower yields in the ethereal solvent (entry 5) and minimal reactivity in aromatic hydrocarbons such as toluene

Table 1. Optimization study of the photocatalytic reductive cyclization reaction



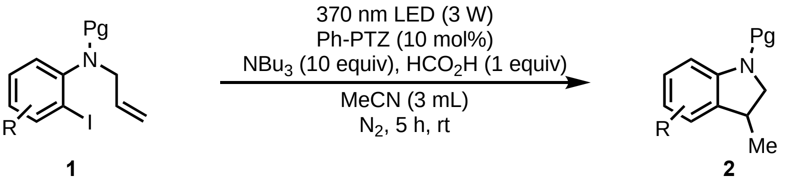
Entry	Additives	Solvent	Yield (%)[a]
1	NBu_3 (10 equiv)	MeCN	11
2	NBu_3 (10 equiv), HCO_2H (10 equiv)	MeCN	59
3	NBu_3 (10 equiv), HCO_2H (10 equiv)	DMF	58
4	NBu_3 (10 equiv), HCO_2H (10 equiv)	DMSO	52
5	NBu_3 (10 equiv), HCO_2H (10 equiv)	Et_2O	18
6	NBu_3 (10 equiv), HCO_2H (10 equiv)	toluene	11
7	NBu_3 (10 equiv), HCO_2H (1 equiv)	MeCN	(57)
8	HCO_2H (10 equiv)	MeCN	0
9[b]	NBu_3 (10 equiv), HCO_2H (1 equiv)	MeCN	0

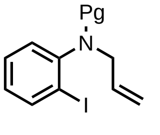
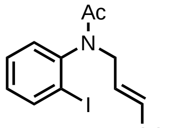
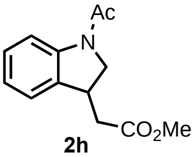
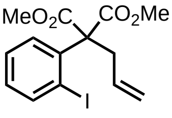
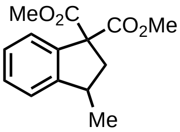
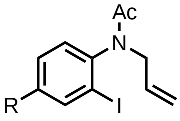
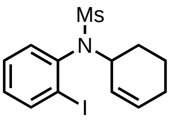
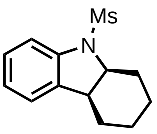
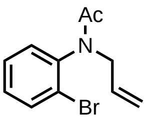
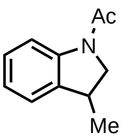
[a] Yields were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. Numbers in parentheses are the isolated yields.
[b] Reaction performed under a dark condition.

(entry 6). Finally, varying the amount of formic acid to 1 equiv. resulted in an isolated yield of 57%; therefore, we selected a reaction with the optimized conditions (entry 7). To investigate the reaction, several control experiments were conducted. The reaction without amine resulted in the suppression of the reaction (entry 8). Further, it is worth noting that the developed reductive cyclization did not proceed in dark conditions, even under optimum conditions (entry 9). These results strongly provide evidence of the essential role played by light and amines during photocatalysis.

With the optimized conditions consisting of 10 mol% of Ph-PTZ, *N*-allylanilines **1** (0.3 mmol), NBu_3 (10 equiv.), and HCO_2H (1 equiv.), we examined the reductive cyclization reaction of various substrates (Table 2). The reaction of *N*-allylanilines containing various protecting groups was performed (entries 1–5). Further, the substrate-bearing electron-withdrawing group (**1a–c**) tended to accelerate the reaction to generate the indolines rather than the substrate-bearing electron-rich group (**1d–e**). The substrate using the malonate derivatives **1f** instead of anilines also produced the product, albeit in a low yield (entry 6). Cyclic compound, such as **1g**, was compatible with the optimized conditions and produced the corresponding product in a yield of 35% (entry 7). Furthermore, the aniline bearing α,β-conjugated ester reacted to produce the indoline **2h** in a moderate yield (entry 8). In general, *N*-allyl-2-iodoanilines bearing halogens or alkyl groups on the aromatic ring were also tolerated under the reaction conditions,

Table 2. Substrate scope of the photocatalytic reductive cyclization reaction



Entry	1	2	Yield[a]	Entry	1	2	Yield[a]
1	 **1a-e**	Pg = Ac (**2a**)	57%	8	 **1h**	 **2h**	49%
2		Ms (**2b**)	49%				
3		Boc (**2c**)	43%				
4		Bn (**2d**)	8%				
5		Me (**2e**)	17%				
6	 **1f**	 **2f**	30%	9	 **1i-l**	R = Br (**2i**)	40%
				10		F (**2j**)	47%
				11		Cl (**2k**)	34%
				12		ⁿBu (**2l**)	26%
7	 **1g**	 **2g**	35%	13[b]	 **1m**	 **2a**	44%

[a] Isolated yield.

[b] Reaction performed for 48 h.

generating products **2i–l** (entries 9–12). Employing 2-bromoaniline derivative for the reaction instead of iodide resulted in a product yield of 44% even though the reaction time was prolonged (entry 13). We found the main by-product of these reactions was reductive product of which C–I bond is only reduced to C–H bond; however, unfortunately, we could not improve their product yields.

In conclusion, we have developed Ph-PTZ photocatalytic reductive intramolecular cyclization reaction leading to indolines in one step. The protocol allowed the simple and efficient preparation of functionalized indolines from easily synthesized starting materials. Mechanistic investigations by intermediate analysis and as well as studies on expanding this reductive cyclization to asymmetric variants are currently underway in our laboratory.

EXPERIMENTAL

GENERAL INFORMATION

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 mm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and phosphomolybdic acid or basic potassium permanganate stain. NMR spectra were recorded on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR,125 MHz for ^{13}C NMR and 470 MHz for ^{19}F NMR), and are internally referenced to residual protio solvent signals or TMS (note: $CDCl_3$ referenced at δ 7.26 and 77.0 ppm respectively, TMS referenced at δ 0 and 0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and reported as *m/z* ($M+H^+$, relative intensity). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured on a Yanagimoto micro melting point apparatus without correlation.

PREPARATION OF CATALYST

To a round-bottom flask with a magnetic stirrer was added K_2CO_3 (2.76 g, 20 mmol, 1 equiv.), benzoic acid (1.22 g, 10 mmol, 0.5 equiv.), $Cu(OAc)_2$ (0.72 g, 4 mmol, 20 mol%), and EtOAc (200 mL), followed by added phenothiazine (3.98 g, 20 mmol) and phenylboronic acid (7.32 g, 60 mmol, 3 equiv.). The reaction mixture was stirred at 80 °C for 72 h. The reaction was filtered through Celite and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (^{n}hexane : EtOAc = 20:1) to give 10-phenylphenothiazine in 37% yield (2.0 g, 7.26 mmol) as a pale yellow solid.[11]

GENERAL PROCEDURE FOR INTRAMOLECULAR CYCLIZATION

To a pyrex test tube equipped rubber septum were added substrate (0.3 mmol), 10-phenylphenothiazine (8.3 mg, 0.03 mmol, 10 mol%), tributylamine (0.56 g, 3 mmol, 10 equiv), formic acid (13.8 mg, 0.3 mmol, 1 equiv), and dry MeCN (3 mL). The mixture was degassed with three freeze-pump-thaw cycles, then backfilled with N_2 and stirred for 5 h at rt with irradiation using 370 nm LED (3 W). The reaction was added 1M HCl to remove tributylamine, extracted with Et_2O, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by flash column chromatography to give product **2**.

1-(3-Methylindolin-1-yl)ethanone (2a)[8a]

57% yield, 30.2 mg; pale yellow solid; **TLC (SiO$_2$)**: R_f = 0.17 (^{n}hexane : EtOAc = 2:1); **^{1}H NMR**: (500 MHz, CDCl$_3$): δ 8.19 (d, J = 8.1 Hz, 1H), 7.22-7.15 (m, 2H), 7.04 (t, J = 7.4 Hz, 1H), 4.21 (t, J = 9.7 Hz, 1H), 3.58 (dd, J = 9.7, 6.3 Hz, 1H), 3.54-3.47 (m, 1H), 2.22 (s, 3H), 1.35 (d, J = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, CDCl$_3$): δ 168.6, 142.3, 136.3, 127.7, 123.7, 123.3, 116.9, 56.9, 34.7, 24.2, 20.3.

3-Methyl-1-(methylsulfonyl)indoline (2b)[13]

49% yield, 31.2 mg; yellow oil; **TLC (SiO$_2$)**: R_f = 0.40 (^{n}hexane : EtOAc = 2:1); **^{1}H NMR**: (500 MHz, CDCl$_3$): δ 7.39 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.0, 7.7 Hz, 1H), 7.09 (d, J = 7.0 Hz, 1H), 7.06 (dd, J = 7.7, 7.0 Hz, 1H), 4.17-4.12 (m, 1H), 3.50-3.45 (m, 2H), 2.87 (s, 3H), 1.35 (d, J = 6.0 Hz, 3H); **^{13}C NMR**: (125 MHz, CDCl$_3$): δ 141.5, 136.3, 128.1, 124.2, 123.7, 113.5, 58.0, 34.7, 34.2, 19.4.

***tert*-Butyl 3-methylindoline-1-carboxylate (2c)**[13]

43% yield, 30.1 mg; pale yellow oil; **TLC (SiO$_2$)**: R_f = 0.25 (^{n}hexane : EtOAc = 20:1); **^{1}H NMR**: (500 MHz, CDCl$_3$): δ 7.85-7.46 (br, 1H), 7.18-7.12 (m, 2H), 6.95 (td, J = 1.0, 7.4 Hz, 2H), 4.14 (m, 1H), 3.50 (br, 1H), 3.43-3.35 (m, 1H), 1.56 (s, 9H), 1.31 (d, J = 6.8 Hz, 3H); **^{13}C NMR**: (125 MHz, CDCl$_3$): δ 152.5, 142.4 (broad), 136.1 (broad), 127.5, 123.5, 122.2, 114.6, 80.3 (broad), 55.6, 34.0, 28.4 (3C), 20.2.

3-Methyl-1-(phenylmethyl)indoline (2d)[14]

8% yield, 5.5 mg; pale yellow oil; **TLC (SiO$_2$)**: R_f = 0.26 (^{n}hexane : EtOAc = 100:1); **^{1}H NMR**: (500 MHz, CDCl$_3$): δ 7.37-7.32 (m, 4H), 7.28-7.25 (m, 1H), 7.06 (t, J = 7.5 Hz, 2H), 6.70 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 4.35 (d, J = 14.3 Hz, 1H), 4.10 (d, J = 14.9 Hz, 1H), 3.51 (t, J = 8.6 Hz, 1H), 3.33-3.26 (m, 1H), 2.83 (t, J = 8.6 Hz, 1H), 1.29 (d, J = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, CDCl$_3$): δ 128.7, 128.5, 127.9, 127.4, 127.1, 126.8, 125.8, 123.2, 121.6, 118.7, 61.6, 35.2, 21.1, 18.6.

1,3-Dimethylindoline (2e)[14]

17% yield, 7.3 mg, pale yellow oil; **TLC (SiO$_2$)**: R_f = 0.26 (^{n}hexane : EtOAc = 100:1); **^{1}H NMR**: (500

MHz, $CDCl_3$): δ 7.11-7.05 (m, 2H), 6.70 (td, J = 1.2, 7.5 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 3.52 (t, J = 8.6 Hz, 1H), 3.31-3.24 (m, 1H), 2.79 (t, J = 8.6 Hz, 1H), 2.74 (s, 3H), 1.30 (d, J = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 153.0, 135.3, 127.4, 122.9, 117.8, 107.3, 64.2, 36.2, 35.3, 18.2.

1,1-Dimethoxycarbonyl-3-methylindane (2f)[8b]

30% yield, 22.7 mg, yellow oil; **TLC (SiO_2)**: R_f = 0.13 (^{n}hexane : EtOAc = 20:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.31 (d, J = 7.5 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.40-3.33 (m, 1H), 3.02 (dd, J = 7.6, 13.2 Hz, 1H), 2.15 (dd, J = 8.7, 13.2 Hz, 1H), 1.32 (d, J = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 171.4, 171.0, 148.7, 138.7, 128.8, 126.8, 126.5, 123.4, 64.6, 52.88, 53.82, 43.1, 37.3, 19.5.

9-(Methylsulfonyl)-5,6,7,8,8a,9-hexahydro-4b*H*-carbazole (2g)[13]

35% yield, 26.4 mg, yellow oil; **TLC (SiO_2)**: R_f = 0.10 (^{n}hexane : EtOAc = 20:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.7 Hz, 1H), 7.24-7.17 (m, 2H), 7.09 (t, J = 7.7 Hz, 1H), 4.42-4.36 (m, 1H), 3.53 (m, 1H), 2.93 (s, 3H), 2.22-2.18 (m, 1H), 2.09-2.06 (m, 1H), 1.88-1.80 (m, 1H), 1.63 (m, 1H), 1.57-1.52 (m, 2H), 1.32-1.19 (m, 2H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 141.2, 134.5, 127.8, 124.0, 123.4, 115.3, 63.9, 40.3, 38.4, 28.5, 24.5, 22.1, 20.7.

Methyl 1-acetylindoline-3-acetate (2h)[13]

49% yield, 34.4 mg, yellow oil; **TLC (SiO_2)**: R_f = 0.23 (^{n}hexane : EtOAc = 1:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.1 Hz, 1H), 7.23 (t, J = 8.1 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 7.04 (td, J = 1.0, 7.5 Hz, 1H), 4.32 (t, J = 10.2 Hz, 1H), 3.88-3.81 (m, 1H), 3.77-3.73 (m, 1H), 3.74 (s, 3H), 2.84 (dd, J = 4.4, 16.6 Hz, 1H), 2.57 (dd, J = 9.8, 16.6 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 172.2, 168.7, 142.6, 132.9, 128.4, 123.7, 123.5, 117.1, 55.1, 51.9, 39.6, 36.5, 24.2.

1-(5-Bromo-3-methylindolin-1-yl)ethanone (2i)[8a]

46% yield, 35.0 mg, pale yellow solid; **TLC (SiO_2)**: R_f = 0.37 (^{n}hexane : EtOAc = 1:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.6 Hz, 1H), 7.31-7.26 (m, 2H), 4.21 (t, J = 10.0 Hz, 1H), 3.59 (dd, J = 6.8, 10.0 Hz, 1H), 3.52-3.45 (m, 1H), 2.21 (s, 3H), 1.34 (d, J = 10.4 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 168.7, 141.5, 138.6, 130.5, 126.5, 118.2, 116.0, 56.9, 34.6, 24.1, 20.1.

1-(5-Fluoro-3-methylindolin-1-yl)ethanone (2j)[15]

47% yield, 27.4 mg, pale yellow solid; **TLC (SiO_2)**: R_f = 0.13 (^{n}hexane : EtOAc = 2:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 8.14 (dd, J = 5.0, 8.7 Hz, 1H), 6.90-6.84 (m, 2H), 4.24 (t, J = 9.5 Hz, 1H), 3.60 (dd, J = 6.9, 9.5 Hz, 1H), 3.54-3.44 (m, 1H), 2.21 (s, 3H), 1.37 (d, J = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 168.4, 160.6, 158.2, 138.3, 117.6 (d, J = 7.7 Hz), 113.7 (d, J = 22.2 Hz), 110.5 (d, J = 24.1 Hz), 57.1, 34.7, 23.9, 20.0; **^{19}F NMR**: (470 MHz, $CDCl_3$): δ -119.1.

1-(5-Chloro-3-methylindolin-1-yl)ethanone (2k)[15]

34% yield, 21.6 mg, pale yellow solid; **TLC (SiO_2)**: R_f = 0.15 (^{n}hexane : EtOAc = 2:1); **^{1}H NMR**: (500

MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.17-7.14 (m, 1H), 7.11 (m, 1H), 4.22 (t, *J* = 9.8 Hz, 1H), 3.59 (dd, *J* = 6.4, 9.8 Hz, 1H), 3.53-3.44 (m, 1H), 2.21 (s, 3H), 1.37 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 168.6, 141.0, 138.2, 128.5, 127.6, 123.6, 117.7, 57.0, 34.6, 24.0, 20.1.

1-(5-Butyl-3-methylindolin-1-yl)ethanone (2l)

26% yield, 18.0 mg, pale yellow solid; **TLC (SiO_2)**: R_f = 0.20 (^{n}hexane : EtOAc = 2:1); **^{1}H NMR**: (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.03-6.97 (m, 2H), 4.19 (t, *J* = 10.0 Hz, 1H), 3.55 (dd, *J* = 6.9, 10.0 Hz, 1H), 3.50-3.43 (m, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.20 (s, 3H), 1.60-1.54 (m, 2H), 1.38-1.31 (m, 5H), 0.92 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR**: (125 MHz, $CDCl_3$): δ 168.2, 140.2, 138.5, 136.3, 127.6, 123.2, 116.5, 57.1, 35.3, 34.7, 33.9, 24.1, 22.3, 20.2, 13.9; **HRMS**: *m/z* (DART) calcd for $C_{15}H_{22}NO^+$ $(M+H)^+$: 232.1701, found 232.1700; **FTIR**: (neat): 3019, 2957, 2932, 2917, 1915, 1653, 1587, 1458, 1442, 1242, 735 cm^{-1}; mp 115-117 °C.

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