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Synthesis of 3-arylindole derivatives from nitroalkane precursors†

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3-Arylindole derivatives were synthesized by Cu(I) catalysed intramolecular Ullmann coupling of 2-bromoarylaminoalkanes. 2-Bromoarylaminoalkanes were synthesized from 2-bromoarylnitroalkanes, which in turn prepared through $AlCl_3$-mediated Friedel–Crafts alkylation of bromo-substituted β-nitrostyrenes and arenes.

Introduction

The indole skeleton is a key structural component in various natural products, pharmaceutical compounds, dyes, agricultural compounds, cosmetics, nutraceuticals, and flavourings.[1] 3-Aryl indole, a derivative of indole also exhibit various interesting activities as shown in Fig. 1. For example, 4-fluoro-3-phenylindole can inhibit brassinin glucosyltransferase, a kind of phytoalexin detoxification enzyme which comes from fungus *Sclerotinia sclerotiorum*.[2] Another example is murrapanine, it was isolated from the root bark of *Murraya paniculata* var. *omphalocarpa* and used for the treatments for lymphocytic leukaemia, lung adenocarcinoma and colon adenocarcinoma.[3]

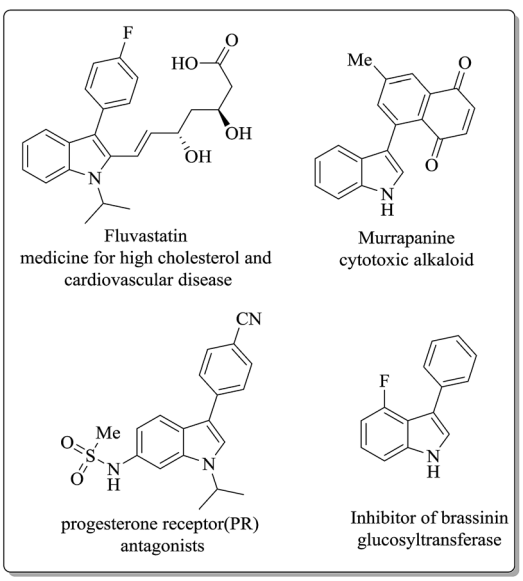

Fig. 1 Pharmaceutically active 3-arylindole derivatives.

Fluvastatin, a multi-purpose medicine for high cholesterol and cardiovascular disease prevention, also found to have antiviral activity against hepatitis C.[4] Also, 3-arylindoles acts as a potent and efficacious progesterone receptor (PR) antagonists and can be used for the treatment of uterine fibroids.[5]

In the light of the importance of these bioactive molecules, several synthetic protocols have been reported.[6] Various methods known for the exclusive synthesis of 3-arylindoles are conventional Fischer indole synthesis,[7] transition-metal-catalyzed coupling of indoles with coupling partners such as aryl halides,[8] diaryl-iodine(III) reagent,[9] carboxylic acids,[10] aryl-hydrazine/amine,[11] other miscellaneous methods.[12] In 2010, Siva Murru *et al.* reported Au and Cu versions of annulation of nitrosoarenes and alkynes for the synthesis of 3-arylindoles.[13] Recently, Kumar *et al.* reported the *t*-BuOK-mediated transition metal free synthesis of 3-(2/4-nitroaryl)-indoles through inter-molecular oxidative coupling of indole with nitroarenes.[14] Most of the developed methodologies requires *N*-protection or C-2 substitution of indoles or requires costly additives/ligands and harsh reaction conditions to obtain exclusively 3-arylindoles. Hence there is a need to develop an alternative and direct method to access the valuable 3-arylindoles.

Results and discussion

In 1991, Russell and Yao *et al.* reported the synthesis of 3-aryl-derivatives from α-phenyl-β-nitrostyrenes in the presence of triethylphosphite[15] (Scheme 1). Since the starting material α-phenyl-β-nitrostyrenes are very tedious to prepare, the same protocol is applied on easily available starting material β-nitrostyrenes. But didn't find any desired 3-arylindole product and end up with a mixture of products.[16] As a part of our interest in developing fascinating methodologies for the synthesis of

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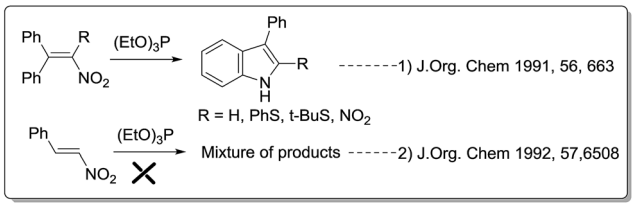
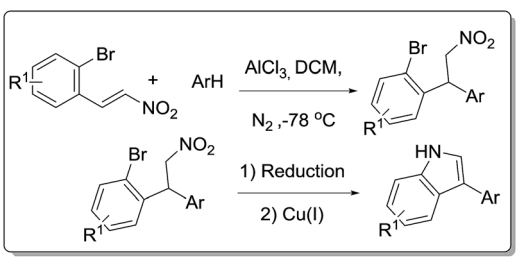
‡ Equal contribution.



Scheme 1 Earlier synthetic approaches from nitrostyrenes.

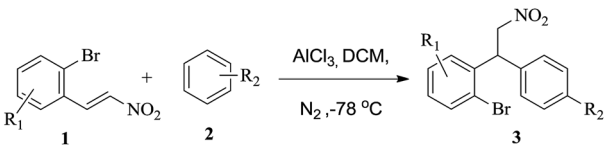
biologically active heterocycles[17] using easily available starting materials, we envisioned that 3-arylindoles can be synthesized from Cu catalyzed intramolecular Ullmann coupling of 2-bromoarylamino alkanes. The required aminoalkanes prepared from racemic 2-bromoarylnitroalkanes, which in turn prepared from our reported method[18] using $AlCl_3$-mediated Friedel–Crafts alkylation of bromo-substituted β-nitrostyrenes and arenes as shown in Scheme 2. 2-Bromoarylnitroalkanes may undergo reduction to form 2-bromoarylaminoalkanes followed by Cu catalyzed intramolecular coupling may afford the desired 3-arylindole product.

In order to check the validity of our hypothesis we initially synthesized various 2-bromo-β-nitrostyrene derivatives (**1**) from nitromethane and corresponding 2-bromobenzaldehydes through Knoevenagel condensation followed by Friedel–Crafts alkylation with $AlCl_3$ to obtain the corresponding nitroalkane derivatives (**3a–3i**) (Table 1). Most of the substrates produced nitroalkanes in moderate to good yields. Starting from simple 2-bromo-β-nitrostyrene various substituents such as OMe, OCH_2O, OPr, naphthyl afford the corresponding nitroalkane derivatives **3a–3f** in good yield with its coupling partner anisole. Its noteworthy that the current protocol not only works well with strong donating groups like OMe on aryl ring but also works well with Me, i-Pr, H substituents (**3g**, **3h** and **3i**) with simple 2-bromo-β-nitrostyrene. In all these entries, the insertion of bromo group on β-nitrostyrene was needed which confined the versatility of our method. For this reason, we attempted to develop another synthetic route, using 3-bromoanisole as substrate in the Friedel–Crafts alkylation. We synthesized another series of nitroalkanes (**3j–3r**) Table 2 as precursors from the same Friedel–Crafts alkylation procedure. The reactions took longer times compared to its former entries due to both steric hindrance and electron-withdrawing effect of bromo group. Most of the substrates produced nitroalkanes in moderate to good yields, while few substrates like 2-methyl, 1-naphthyl and 3-chloro substituted β-nitrostyrene produced poor yields of corresponding nitroalkanes (**3k**, **3o**, **3p**) as shown in Table 2.



Scheme 2 Synthetic strategy for 3-aryl indoles.

Table 1 Synthesis of 2-bromoarylnitroalkane derivatives[a,b]

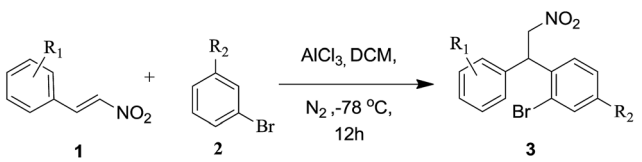


Entry	R_1	R_2	3	Time	Yield%
1	H	OMe	**3a**	3 h	98%
2	5-OMe	OMe	**3b**	3 h	70%
3	4,5-DiOMe	OMe	**3c**	3 h	71%
4	4,5-OCH_2O–	OMe	**3d**	5 h	64%
5	5-OPr	OMe	**3e**	5 h	64%
6	3,4-(CH_4)	OMe	**3f**	1 h	76%
7	H	H	**3g**	5 h	89%
8	H	Me	**3h**	4 h	72%
9	H	^{i}Pr	**3i**	2 h	67%

[a] Reaction conditions: **1** (5 mmol), **2** arene (10 mmol), $AlCl_3$ (10 mmol), DCM (20 mL), −78 °C, under N_2. [b] Isolated yields.

After the preparation of various nitroalkane derivatives, 1-bromo-2-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (**3a**) was taken as the model substrate and reduced with reagents Fe/AcOH and $NaBH_4/BF_3 \cdot THF$. A mixture of 2-(2-bromophenyl)-2-(4-methoxyphenyl)ethan-1-amine (**4a**) and debromonated amine was observed. If we use LAH as reducing reagent, the reaction produced the desired 2-(2-bromophenyl)-2-(4-methoxyphenyl)ethan-1-amine as sole product in quantitative

Table 2 Synthesis of 4-methoxy-2-bromoarylnitroalkane derivatives[a,b]

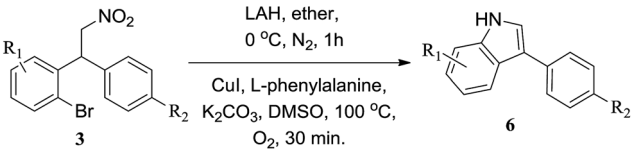


Entry	R_1	R_2	3	Yield%
1	H	OMe	**3j**	97%
2	2-Me	OMe	**3k**	27%
3	4-Me	OMe	**3l**	80%
4	4-*t*-Bu	OMe	**3m**	90%
5	3-OMe	OMe	**3n**	61%
6	2,3-$(CH)_4$	OMe	**3o**	36%
7	3-Cl	OMe	**3p**	34%
8	4-Cl	OMe	**3q**	70%
9	2-NO_2	OMe	**3r**	94%

[a] Reaction conditions: **1** (5 mmol), **2** arene (10 mmol), $AlCl_3$ (10 mmol), DCM (20 mL), −78 °C, under N_2. [b] Isolated yields.

yield, as a result, we utilized the 2-bromoarylamine **4a** for the coupling reactions without further purification. Initially we conducted the reaction of 2-bromoarylamine **4a** with 10 mol% of CuI, 20 mol% of L-proline and 2 eq. of K_2CO_3 in DMSO at 80 °C as the model reaction (Entry 1, Table 3). The reaction produced 49% of indoline (**5a**) and 16% of desired indole product (**6a**). We then focused on variation of other reaction parameters in order to increase the yield of indole product as presented in Table 3. In the ligand tuning, except L-phenylalanine other ligands resulted in lower yields (Entries 2–6). Using L-phenylalanine as ligand, showed better result as the temperature raised from 80 °C to 100 °C (Entries 4, 5). In the solvent tuning, DMSO prevailed other solvents. In 1986, Speier *et al.* reported a kinetics and mechanism research about Cu-catalyzed oxidation of indolines to indoles, the experiments showed that there is a positive correlation between the oxidant's concentration and the oxidation rate in the presence of Cu(I) catalysts.[19] Based on this, we ran a reaction under O_2 atmosphere, and the yield of indole (**6a**) improved to 72%, and the reaction time was shortened from 1 h to 30 min (Entry 9), showing that O_2 indeed assisted the oxidation process of indoline in the reaction. As a result, the following optimizations were conducted under O_2 atmosphere. We further tested different copper catalysts including Cu(I), Cu(II) and Cu(I)/Cu(II) as co-catalyst, but did not receive good result (Entries 10–14). Interestingly, if the reaction was conducted under microwave irradiation, bromoamine was consumed within 5 min and produced 60% of indoline **5a** and 13% of indole **6a** (Entry 15). Whereas, as we prolonged the reaction time, indoline experienced decomposition without any yield increase of desired indole. Finally, after a series of tunings, we found the coupling of bromoamine **4a** had best performance when treated with 10 mol% of CuI, 20 mol% of L-phenylalanine and 2 eq. of K_2CO_3 in DMSO at 100 °C under O_2 atmosphere. The other bromoamine derivatives were also directly subjected

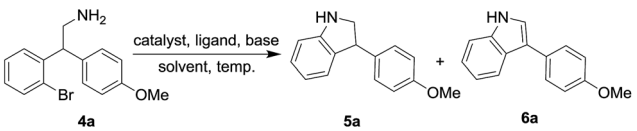
Table 4 Synthesis of 3-arylindole derivatives from 2-bromonitroalkane precursors[a,b]



Entry	R_1	R_2	6	Yield%
1	H	OMe	**6a**	70%
2	5-OMe	OMe	**6b**	72%
3	4,5-DiOMe	OMe	**6c**	57%
4	4,5-OCH_2O–	OMe	**6d**	23%
5	5-OPr	OMe	**6e**	28%
6	3,4-(CH_4)	OMe	**6f**	24%
7	H	H	**6g**	84%
8	H	Me	**6h**	63%
9	H	^{i}Pr	**6i**	67%

[a] Reaction conditions: (i) **3** (1 mmol), LAH (4 mmol), ether (10 mL), 0 °C, N_2, 1 h. (ii) CuI (0.1 mmol), L-phenylalanine (0.2 mmol), K_2CO_3 (2 mmol), DMSO (1 mL), 100 °C, under O_2, 30 min. [b] Isoated yields.

Table 3 Optimization of indolization of amine



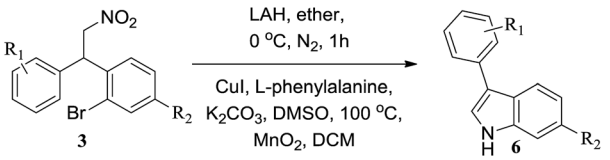
Entry[a]	Ligand	Base	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%) 5a[e]	6a[e]
1	L-Proline	K_2CO_3	CuI	DMSO	80	3	49	16
2	4-Hydroxyproline	K_2CO_3	CuI	DMSO	80	3	30	17
3	1,10-Phenanthroline	K_2CO_3	CuI	DMSO	80	3	8	30
4	L-Phenylalanine	K_2CO_3	CuI	DMSO	80	3	—	54
5	L-Phenylalanine	K_2CO_3	CuI	DMSO	100	1	—	60
6	L-Phenylalanine	K_2CO_3	CuI	DMSO	100	1	—	64
7	L-Phenylalanine	K_2CO_3	CuI	DMF	100	1	—	54
8	L-Phenylalanine	K_2CO_3	CuI	1,4-Dioxane	100	1	—	49
9[b]	**L-Phenylalanine**	**K_2CO_3**	**CuI**	**DMSO**	**100**	**0.5**	**—**	**72**
10[b]	L-Phenylalanine	K_2CO_3	CuCl	DMSO	100	2	—	50
11[b]	L-Phenylalanine	K_2CO_3	CuBr	DMSO	100	3	—	58
12[b]	L-Phenylalanine	K_2CO_3	$Cu(OAc)_2$	DMSO	100	1	—	49
13[bc]	L-Phenylalanine	K_2CO_3	$CuSO_4$	DMSO	100	2.5	—	34
14[b]	L-Phenylalanine	K_2CO_3	CuI/$Cu(OAc)_2$	DMSO	100	2.5	—	39
15[d]	**L-Phenylalanine**	**K_2CO_3**	**CuI**	**DMSO**	**100**	**0.083**	**60**	**13**

[a] Reaction conditions: **4a** (1 mmol), catalyst (10 mol%), ligand (20 mol%), K_2CO_3 (2 eq.), solvent (1 mL). [b] Under O_2. [c] CuI : $Cu(OAc)_2$ = 5 mol% : 5 mol%. [d] Microwave 100 W. [e] NMR yields.

to the coupling reactions without further purification under optimized reaction conditions as shown in Table 4. In the case of 5-methoxy-substituted bromoamine (Table 4, Entry 2), the reaction yielded desired indole derivative in 72% yield. The current protocol works with other strong electron donating groups in obtaining the desired product in low to moderate yields (Table 4, Entries 3, 4 and 5). In case of naphthyl derivative also the desired indole product was obtained in low yield (Table 3, Entry 6). There is a significant enhancement in the yield of the desired indole product in case of substituents like Me, i-Pr and unsubstituted derivatives (Table 4, Entries 7, 8 and 9).

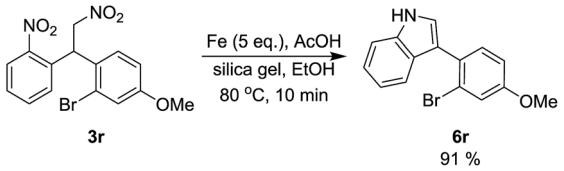
Latter the scope of the current protocol was examined on other nitroalkane derivatives derived from 3-bromoanisole and subjected to optimized reaction conditions. But we found that under optimized reaction conditions along with the formation of desired 3-arylindole derivatives, 10–20% of indolines were observed which was difficult to separate by column chromatography. Subsequently we treated the crude mixtures with MnO_2 as oxidant and it oxidized the indolines to the corresponding indole products without decomposition. Therefore, for the synthesis of these 3-arylindoles (**6j–6q**), we conducted additional oxidation process of crude products after Ullmann reaction, and achieved 3-arylindole derivatives with moderate to good yields as shown in Table 5. The present method works well with various substituents such as Me, OMe, Cl and naphthyl in delivering the desired indole derivatives in good yield. But in the presence of *t*-butyl substituent desired indole product (**6m**) obtained in low yield. Interestingly, as we trying to reduce nitroalkane (**3r**) with LAH, the reaction did not produce the expected bromoamine, but the mixture of indoline and indole (**6r**) was observed in poor yield. Latter nitroalkane **3r** treated with SiO_2-supported with Fe in refluxing AcOH/EtOH for 10 minutes and got excellent yield of 3-arylindole (**6r**) as sole product (Scheme 3).

Table 5 Synthesis of 3-arylindole derivatives from 4-methoxy-2-bromonitroalkane precursors[a,b,c]



Entry	R_1	R_2	6	Yield%
1	H	OMe	**6j**	62%
2	2-Me	OMe	**6k**	65%
3	4-Me	OMe	**6l**	74%
4	4-*t*-Bu	OMe	**6m**	21%
5	3-OMe	OMe	**6n**	62%
6	2,3-$(CH)_4$	OMe	**6o**	80%
7	3-Cl	OMe	**6p**	56%
8	4-Cl	OMe	**6q**	60%
9	2-NO_2	OMe	**6r**	00%

[a] Reaction conditions: (i) **3** (1 mmol), LAH (4 mmol), ether (10 mL), 0 °C, N_2, 1 h. (ii) CuI (0.1 mmol), L-phenylalanine (0.2 mmol), K_2CO_3 (2 mmol), DMSO (1 mL), 100 °C, under O_2, 30 min. [b] Isoated yields. [c] MnO_2 (10 eq.), DCM (5 mL), silica gel (0.25 g), reflux, 12 h.



Scheme 3 Synthesis of 3-arylindole **6r**.

Experimental section

General information

Reagents and solvents were purchased from various commercial sources and were used directly without any further purification, unless otherwise stated. Column chromatography was performed with 63–200 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, or 500 and 125 MHz, respectively. Chemical shifts are reported in parts per million (δ) using TMS and chloroform as internal standards and coupling constants are expressed in Hertz. Melting points were recorded using an electro thermal capillary melting point apparatus and are uncorrected. HRMS spectra were recorded using ESI-TOF or EI^+ mode. The starting material β-nitrostyrene derivatives **1** were synthesized from functionalized benzaldehydes and nitromethane followed by the reported literatures.

General procedure for nitroalkanes 3. β-Nitrostyrene derivative **1** (5 mmol) and granular $AlCl_3$ (1.334 g, 10 mmol) were placed in an oven-dried round bottom flask and thoroughly filled it with N_2. Dry DCM (20 mL) was then added to the flask, and the mixture was stirred at −78 °C for 10 min. The arene (6 mmol) was then added dropwise to the flask *via* a syringe, and the reaction was monitored by TLC. After the reaction was finished, the reaction was quenched with ice-cold brine. The reaction mixture was extracted with DCM and water, and the DCM layer was separated, dried over anhydrous $MgSO_4$ and concentrated under vacuum to give the crude product. The crude product was furthered purified by column chromatography using EA/hexane as eluent to yield the desired product **3**.

General procedure for indole 6a–6i. An oven-dried 50 mL round bottom flask with dropping funnel was added LAH (0.1518 g, 4 mmol) and filled with N_2. The flask was cooled to 0 °C and added dry ether/THF (4 mL), and the nitroalkane derivative **3** (1 mmol) in ether/THF (6 mL) was slowly added to the flask, and stirred for 1 h. After that, the reaction was carefully quenched with H_2O (1.5 mL) and the precipitate was filtered. The filtrate was dried over anhydrous $MgSO_4$, concentrated at low temperature and dried under vacuum to give the amine **4**.

The amine **4** was then dissolved in DMSO (1 mL) and added CuI (0.019 g, 0.1 mmol) and L-phenylalanine (0.033 g, 0.2 mmol), which was then heated to 100 °C for 2–5 min before K_2CO_3 (0.2764 g, 2 mmol) was added. After that, the reaction was stirred with an O_2 balloon for 30 min, and then quenched with water. The reaction mixture was extracted with EA and

water, the EA layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated under vacuum to give the crude product. The crude product was furthered purified by column chromatography using EA/hexane as eluent to yield the desired product **6a–6j**. For indole **6b**, the crude product was dissolved in DCM and treated with DDQ (0.227 g, 1 mmol) for 1 h before purification.

General procedure for indole 6k–6r. The general procedure was as same as the procedure for **6a–6i.** The crude product **6k–6r** was dissolved in DCM (5 mL) and added MnO_2 (0.87 g, 10 mmol), SiO_2 (0.25 g), and heated to reflux for 12 h. After the indoline was consumed, the solvent was dried and the cruRepublic of Chinade was purified by column chromatography using EA/hexane as eluent to yield the desired product **6k–6r.**

General procedure for indole 6r. A mixture of nitroalkane **3r** (0.381 g, 1 mmol), iron powder (0.28 g, 5 mmol) and SiO_2 (0.25 g) in EtOH (1.25 mL) was added AcOH (1.25 mL) and heated to 80 °C for 10 min. The reaction was filtered through celite and washed with EA, the filtrate was then concentrated under vacuum to give the crude product. The crude product was furthered purified by column chromatography using EA/hexane as eluent to yield the desired product **3r.**

Spectral data of compounds

1-Bromo-2-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (3a). Yield: 329 mg, 98%. Colorless solid. Mp: 78–80 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.9 Hz, 1H), 7.30 (td, J = 8.0, 1.0 Hz, 1H), 7.23–7.16 (m, 3H), 7.16–7.10 (td, J = 7.1, 1.6 Hz, 1H), 6.86 (d, J = 4.4 Hz, 2H), 5.38 (t, J = 8.1 Hz, 1H), 4.97 (dd, J = 13.2, 7.5 Hz, 1H), 4.89 (dd, J = 13.2, 8.8 Hz, 1H), 3.78 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.3, 138.7, 134.0, 129.8, 129.3, 129.3, 128.4, 128.1, 125.1, 114.6, 78.3, 55.5, 47.2; HRMS (EI) m/z calcd for $C_{15}H_{14}NO_3Br$ (M^+) 335.0157, found 335.0158.

1-Bromo-4-methoxy-2-(1-(4-methoxyphenyl)-2-nitroethyl) benzene (3b). Yield: 256 mg, 70%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 2.5 Hz, 1H), 6.68 (dd, J = 8.8, 2.6 Hz, 1H), 5.32 (t, J = 8.0 Hz, 1H), 5.00–4.83 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.3, 159.2, 139.6, 134.4, 129.6, 129.3, 115.3, 115.2, 114.6, 113.9, 78.2, 55.6, 55.4, 47.2. HRMS (EI) m/z calcd for $C_{16}H_{16}NO_4Br$ (M^+) 365.0263, found 365.0255.

1-Bromo-4,5-dimethoxy-2-(1-(4-methoxyphenyl)-2-nitroethyl) benzene (3c). Yield: 281 mg, 71%. Yellow solid. Mp: 71–72 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.6 Hz, 2H), 7.03 (s, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.66 (s, 1H), 5.29 (t, J = 8.3 Hz, 1H), 4.97–4.84 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.1, 149.0, 148.8, 130.3, 130.0, 128.9, 116.3, 114.8, 114.5, 111.3, 78.2, 56.2, 55.3, 46.8; HRMS (ESI) m/z calcd for $C_{17}H_{18}NO_5BrNa$ (M^+ + Na) 418.0260, found 418.0252.

5-Bromo-6-(1-(4-methoxyphenyl)-2-nitroethyl)benzo[*d*][1,3] dioxole (3d). Yield: 243 mg, 64%. Yellow solid. Mp: 106–107 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.7 Hz, 2H), 7.03 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 6.67 (s, 1H), 5.93 (dd, J = 6.6, 1.1 Hz, 2H), 5.32 (t, J = 8.2 Hz, 1H), 4.84 (d, J = 8.2 Hz, 2H), 3.77 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.1, 148.0, 147.8, 131.7, 129.9, 128.9, 115.1, 114.6, 113.5, 108.2, 102.2, 78.1, 55.4, 46.9; HRMS (EI) m/z calcd for $C_{16}H_{14}NO_5Br$ (M^+) 379.0048, found 379.0055.

1-Bromo-2-(1-(4-methoxyphenyl)-2-nitroethyl)-4-propoxybenzene (3e). Yield: 315 mg, 64%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.7 Hz, 1H), 7.20 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 2.9 Hz, 1H), 6.67 (dd, J = 8.7, 2.9 Hz, 1H), 5.31 (t, J = 8.2 Hz, 1H), 4.98–4.82 (m, 2H), 3.84 (t, J = 6.6 Hz, 2H) 3.77 (s, 3H), 1.83–1.73 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.2, 158.9, 139.5, 134.3, 129.7, 129.3, 115.7, 114.9, 114.5, 78.2, 70.0, 55.4, 47.2, 22.6, 10.6; HRMS (EI) m/z calcd for $C_{19}H_{22}NO_4Br$ (M^+) 393.0576, found 393.0585.

1-Bromo-2-(1-(4-methoxyphenyl)-2-nitroethyl)naphthalene (3f). Yield: 294 mg, 76%. Red oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 6.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.35–7.28 (m, 3H), 6.94 (d, J = 8.6 Hz, 2H), 5.85 (t, J = 8.1 Hz, 1H), 5.07 (d, J = 8.1 Hz, 2H) 3.80 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.1, 136.5, 133.8, 132.8, 130.1, 129.1, 128.6, 128.3, 128.1, 128.0, 127.1, 125.1, 124.9, 114.6, 78.1, 55.4, 47.9; HRMS (EI) m/z calcd for $C_{19}H_{16}NO_3Br$ (M^+) 385.0314, found 385.0314.

1-Bromo-2-(2-nitro-1-phenylethyl)benzene (3g). Yield: 272 mg, 89%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 1H), 7.40–7.34 (m, 2H), 7.34–7.28 (m, 4H), 7.28–7.23 (m, 1H), 7.20–7.14 (m, 1H), 5.49 (t, J = 8.1 Hz, 1H), 5.06–4.93 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.3, 137.9, 134.0, 129.3, 129.2, 128.5, 128.2, 128.1, 127.9, 125.1, 78.1, 47.8; HRMS (EI) m/z calcd for $C_{14}H_{12}NO_2Br$ (M^+) 305.0051, found 305.0053.

1-Bromo-2-(2-nitro-1-(*p*-tolyl)ethyl)benzene (3h). Yield: 231 mg, 72%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.32.7.25 (m, 1H), 7.24–7.20 (m, 1H), 7.19–7.11 (m, 5H), 5.42 (t, J = 8.1 Hz, 1H), 5.01–4.88 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.6, 137.7, 134.8, 134.0, 129.9, 129.2, 128.5, 128.1, 125.1, 78.2, 47.5, 21.2; HRMS (EI) m/z calcd for $C_{15}H_{14}NO_2Br$ (M^+) 319.0208, found 319.0208.

1-Bromo-2-(1-(4-isopropylphenyl)-2-nitroethyl)benzene (3i). Yield: 233 mg, 67%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.33–7.25 (m, 1H), 7.25–7.20 (m, 1H), 7.18 (s, 4H), 7.16–7.10 (m, 1H), 5.42 (t, J = 8.1 Hz, 1H), 5.01–4.88 (m, 2H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.6, 138.6, 135.1, 134.0, 129.2, 128.6, 128.1, 127.3, 125.1, 78.2, 47.5, 33.9, 24.1; HRMS (EI) m/z calcd for $C_{17}H_{18}NO_2Br$ (M^+) 347.0521, found 347.0519.

2-Bromo-4-methox-1-(2-nitro-1-phenylethyl)benzene (3j). Yield: 326 mg, 97%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.31–7.24 (m, 3H), 7.16 (d, J = 2.5 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 6.85 (dd, J = 8.6, 2.5 Hz, 1H), 5.39 (t, J = 8.2 Hz, 1H), 4.96 (dd, J = 13.4, 7.7 Hz, 1H), 4.92 (dd, J = 13.2, 8.6 Hz, 1H), 3.77 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.4, 138.3, 130.2, 129.1, 128.9, 128.0, 127.8, 125.2, 119.1, 114.1, 78.2, 55.7, 47.1; HRMS (EI) m/z calcd for $C_{15}H_{14}NO_3Br$ (M^+) 335.0157, found 335.0151.

2-Bromo-4-methoxy-1-(2-nitro-1-(*o*-tolyl)ethyl)benzene (3k). Yield: 95 mg, 27%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 4H), 7.21 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 8.7 Hz, 1H), 6.80 (dd, J = 8.7, 2.6 Hz, 1H), 5.51 (dd, J = 9.1, 7.1 Hz, 1H), 4.95–4.82 (m, 2H), 3.79 (s, 3H), 2.31 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.5, 137.1, 136.3, 131.5, 129.8, 129.4, 127.8, 126.4,

125.9, 125.2, 118.8, 114.0, 76.6, 55.7, 44.0, 19.6; HRMS (EI) *m*/*z* calcd for $C_{16}H_{16}NO_3Br$ (M^+) 349.0314, found 349.0308.

2-Bromo-4-methoxy-1-(2-nitro-1-(*p*-tolyl)ethyl)benzene (3l). Yield: 280 mg, 80%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16–7.13 (m, 5H), 7.11 (d, J = 8.7 Hz, 1H), 6.84 (dd, J = 8.7, 2.6 Hz, 1H), 5.34 (t, J = 8.2 Hz, 1H), 4.96–4.86 (m, 2H), 3.77 (s, 3H), 2.32 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.2, 137.2, 135.2, 130.3, 129.6, 128.7, 127.7, 125.0, 118.8, 113.8, 78.1, 55.4, 46.6, 20.9; HRMS (EI) *m*/*z* calcd for $C_{16}H_{16}NO_3Br$ (M^+) 349.0315, found 349.0308.

2-Bromo-1-(1-(4-isobutylphenyl)-2-nitroethyl)-4-methoxybenzene (3m). Yield: 353 mg, 90%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17–7.09 (m, 6H), 6.84 (dd, J = 8.6, 2.6 Hz, 1H), 5.35 (t, J = 8.2 Hz, 1H), 4.97–4.87 (m, 2H), 3.77 (s, 3H), 2.44 (d, J = 7.2 Hz, 2H), 1.88–1.78 (m, 1H), 0.89 (d, J = 6.6 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.4, 141.3, 135.6, 130.5, 129.9, 129.0, 127.7, 125.3, 119.0, 114.1, 78.4, 55.7, 46.8, 45.2, 30.3, 22.6; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{22}NO_3Br$ (M^+ + Na) 414.0675, found 414.0683.

2-Bromo-4-methoxy-1-(1-(3-methoxyphenyl)-2-nitroethyl) benzene (3n). Yield: 223 mg, 61%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 1H), 7.15 (d, J = 2.7 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 6.86–6.80 (m, 4H), 5.36 (t, J = 8.2 Hz, 1H), 4.96–4.87 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.1, 159.4, 139.9, 130.1, 128.9, 125.2, 120.1, 119.0, 114.3, 114.0, 112.7, 78.1, 55.6, 55.3, 47.0, 29.8; HRMS (EI) *m*/*z* calcd for $C_{16}H_{16}NO_4Br$ (M^+) 365.0263, found 365.0268.

1-(1-(2-Bromo-4-methoxyphenyl)-2-nitroethyl)naphthalene (3o). Yield: 139 mg, 36%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.58–7.43 (m, 4H), 7.26 (d, J = 2.8, 1H), 7.00 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.7, 2.6 Hz, 1H), 6.20 (dd, J = 8.8, 7.2 Hz, 1H), 5.09 (dd, J = 13.7, 9.2 Hz, 1H), 4.97 (dd, J = 13.7, 9.2 Hz, 1H), 3.71 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.5, 134.3, 134.0, 131.4, 129.7, 129.7, 129.1, 128.7, 127.0, 126.1, 125.2, 124.9, 124.0, 123.2, 119.0, 114.0, 76.6, 55.5, 43.5; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{16}NO_3Br$ (M + Na^+) 408.0205, found 408.0206.

2-Bromo-1-(1-(3-chlorophenyl)-2-nitroethyl)-4-methoxybenzene (3p). Yield: 126 mg, 34%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 3H), 7.21–7.19 (m, 2H), 7.12 (d, J = 8.6 Hz, 1H), 6.89 (dd, J = 8.6, 2.6 Hz, 1H), 5.4 (t, J = 8.1 Hz, 1H), 4.97–4.91 (m, 2H), 3.81 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.6, 140.4, 135.0, 130.4, 129.4, 128.8, 128.3, 128.1, 126.2, 125.2, 119.2, 114.2, 77.9, 55.7, 46.8; HRMS (EI) *m*/*z* calcd for $C_{15}H_{13}NO_3ClBr$ (M^+) 368.9767, found 368.9775.

2-Bromo-1-(1-(4-chlorophenyl)-2-nitroethyl)-4-methoxybenzene (3q). Yield: 259 mg, 70%. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 2.6 Hz, 1H), 7.07 (d, J = 8.7 Hz, 1H), 6.85 (dd, J = 8.7, 2.6 Hz, 1H), 5.34 (t, J = 16.3 Hz, 1H), 4.96–4.85 (m, 2H), 3.78 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.6, 136.9, 133.8, 129.7, 129.5, 129.3, 128.8, 125.2, 119.2, 114.2, 78.1, 55.8, 46.6; HRMS (EI) *m*/*z* calcd for $C_{15}H_{13}NO_3ClBr$ (M^+) 368.9767, found 368.9775.

2-Bromo-4-methoxy-1-(2-nitro-1-(2-nitrophenyl)ethyl)benzene (3r). Yield: 358 mg, 94%. Yellow solid. Mp: 115–116 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.1, 1.2 Hz, 1H), 7.57–7.53 (m, 1H), 7.47–7.42 (m, 1H), 7.26–7.24 (m, 1H), 7.16 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H), 6.85 (dd, J = 8.6, 2.6 Hz, 1H), 5.86 (dd, J = 8.6, 7.3 Hz, 1H), 5.09–4.97 (m, 2H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.9, 150.0, 133.5, 132.8, 130.0, 128.9, 128.6, 128.3, 125.9, 125.5, 119.7, 113.8, 76.2, 55.8, 43.1; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O_5Br$ (M + Na^+) 402.9900, found 402.9915.

2-(2-Bromophenyl)-2-(4-methoxyphenyl)ethanamine (4a). Yield: 306 mg, 99%. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 1H), 7.35–7.25 (m, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.08 (ddd, J = 7.8, 6.6, 2.2 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 4.48 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), 3.30 (dd, J = 12.9, 7.2 Hz, 1H), 3.27 (dd, J = 13.2, 7.9 Hz, 1H), 1.28 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.5, 142.4, 133.6, 133.5, 129.6, 128.7, 128.1, 127.9, 125.9, 114.2, 55.4, 53.0, 47.0; HRMS (EI) *m*/*z* calcd for $C_{15}H_{16}NOBr$ (M^+) 305.0415, found 305.0421.

3-(4-Methoxyphenyl)indoline (5a). Colorless solid. Mp: 67–69 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.5 Hz, 2H), 7.11–7.04 (m, 1H), 6.91 (d, J = 7.0 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.68–6.75 (m, 2H), 4.45 (t, J = 9.2 Hz, 1H), 3.91 (t, J = 9.0 Hz, 1H), 3.80 (s, 3H), 3.46 (t, J = 9.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.7, 151.7, 135.9, 132.9, 139.3, 127.9, 125.2, 119.3, 114.2, 110.0, 57.0, 55.5, 48.2. HRMS (EI) *m*/*z* calcd for $C_{15}H_{15}NO$ (M^+) 225.1154, found 225.1156.

3-(4-Methoxyphenyl)-1*H*-indole (6a). Yield: 156 mg, 70%. Colorless solid. Mp: 133–134 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.34–7.21 (m, 3H), 7.06 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 136.8, 128.8, 128.3, 126.1, 122.5, 121.4, 120.3, 119.9, 118.2, 114.5, 111.6, 55.6. HRMS (EI) *m*/*z* calcd for $C_{15}H_{13}NO$ (M^+) 223.0997, found 223.1002.

5-Methoxy-3-(4-methoxyphenyl)-1*H*-indole (6b). Yield: 182 mg, 72%. Colorless solid. Mp: 193–194 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.24 (s, 1H), 6.98 (d, J = 8.7 Hz, 2H), 6.94 (dd, J = 8.9, 2.3 Hz, 1H), 6.31 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.5, 155.3, 132.0, 128.9, 127.9, 127.7, 124.8, 118.6, 114.6, 113.1, 110.4, 102.6, 56.2, 55.6. HRMS (EI) *m*/*z* calcd for $C_{16}H_{15}NO_2$ (M^+) 253.1103, found 253.1106.

5,6-Dimethoxy-3-(4-methoxyphenyl)-1*H*-indole (6c). Yield: 161 mg, 57%. Colorless solid. Mp: 207–208 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.56 (d, J = 8.7 Hz, 2H), 7.30 (s, 1H), 7.16 (d, J = 2.3 Hz, 1H), 7.01 (d, J = 8.7 Hz, 2H), 6.92 (s, 1H), 3.93 (s, 6H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 147.6, 145.7, 131.2, 128.7, 128.6, 119.9, 119.0, 118.2, 114.5, 101.8, 94.9, 56.7, 56.4, 55.6. HRMS (EI) *m*/*z* calcd for $C_{17}H_{17}NO_3$ (M^+) 283.1208, found 283.1213.

7-(4-Methoxyphenyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (6d). Yield: 61 mg, 23%. Colorless solid. Mp: 169–170 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.54–7.50 (m, 2H), 7.25 (s, 1H), 7.16 (d, J = 2.5 Hz, 1H), 7.01–6.97 (m, 2H), 6.87 (s, 1H), 5.95 (s, 2H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 145.3, 143.7, 131.7, 128.7, 128.3, 120.1, 120.0, 118.6, 114.5, 100.9, 98.6, 92.3, 55.6. HRMS (EI) *m*/*z* calcd for $C_{16}H_{13}NO_3$ (M^+) 267.0895, found 267.0898.

3-(4-Methoxyphenyl)-5-propoxy-1*H*-indole (6e). Yield: 79 mg, 28%. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.56 (d, J = 7.9 Hz, 2H), 7.34–7.26 (m, 3H), 7.01 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 1H), 3.97 (t, J = 6.6 Hz, 2H), 3.87 (s, 3H), 1.88–1.81 (m, 2H), 1.06 (t, J = 4.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 154.3, 132.0, 128.7, 128.5, 126.6, 122.1, 118.1, 114.5, 113.3, 112.1, 103.1, 70.8, 55.6, 23.0, 10.8. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_2$ (M^+) 281.1416, found 281.1412.

3-(4-Methoxyphenyl)-1*H*-benzo[*g*]indole (6f). Yield: 66 mg, 24%. Gray solid. Mp: 251–252 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.59–7.53 (m, 2H), 7.47–7.44 (m, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.03 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.5, 131.4, 130.8, 129.1, 128.3, 125.8, 124.3, 122.0, 122.0, 121.2, 120.2, 119.9, 119.5, 119.5, 114.5, 55.6. HRMS (EI) m/z calcd for $C_{19}H_{15}NO$ (M^+) 273.1154, found 273.1149.

3-Phenyl-1*H*-indole (6g). Yield: 162 mg, 84%. Colorless solid. Mp: 85–87 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 7.8 Hz, 2H), 7.49–7.42 (m, 3H), 7.38 (d, J = 2.6 Hz, 1H), 7.33–7.18 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.9, 135.8, 129.0, 127.7, 126.2, 126.0, 122.6, 121.9, 120.5, 120.0, 118.6, 111.6. HRMS (EI) m/z calcd for $C_{14}H_{11}N$ (M^+) 193.0891, found 193.0891.

3-(*p*-Tolyl)-1*H*-indole (6h). Yield: 130 mg, 63%. Colorless solid. Mp: 88–90 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 1.2 Hz, 1H), 7.33–7.20 (m, 4H), 2.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.8, 135.8, 132.8, 129.7, 127.6, 126.0, 122.5, 121.7, 120.4, 120.1, 118.5, 111.5, 21.4. HRMS (EI) m/z calcd for $C_{15}H_{13}N$ (M^+) 207.1048, found 207.1049.

3-(4-Isopropylphenyl)-1*H*-indole (6i). Yield: 157 mg, 63%. Colorless solid. Mp: 163–165 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.95 (d, J = 7.88 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 2.5 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.28–7.16 (m, 2H), 3.00–2.94 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.8, 136.9, 133.2, 127.7, 127.0, 126.1, 122.5, 121.7, 120.4, 120.1, 118.6, 111.5, 34.1, 24.3. HRMS (EI) m/z calcd for $C_{17}H_{17}N$ (M^+) 235.1361, found 235.1361.

6-Methoxy-3-phenyl-1*H*-indole (6j). Yield: 138 mg, 62%. Colorless solid. Mp: 147–148 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 7.3 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.30–7.24 (m, 2H), 6.90 (d, J = 2.1 Hz, 1H), 6.87 (dd, J = 8.8, 2.1 Hz, 1H), 3.87 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.9, 137.7, 135.8, 128.9, 127.5, 126.1, 120.7, 120.7, 120.4, 118.6, 110.5, 95.0, 55.9. HRMS (EI) m/z calcd for $C_{15}H_{13}NO$ (M^+) 223.0997, found 223.1001.

6-Methoxy-3-(*o*-tolyl)-1*H*-indole (6k). Yield: 154 mg, 65%. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.43–7.38 (m, 2H), 7.33–7.31 (m, 1H), 7.27–7.24 (m, 2H), 7.08 (s, 1H), 6.92 (s, 1H), 6.82 (d, J = 8.7 Hz, 1H), 3.87 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.8, 137.0, 136.9, 134.8, 131.0, 130.5, 126.9, 125.8, 121.9, 121.7, 121.0, 117.7, 110.1, 94.9, 55.9, 20.9. HRMS (EI) m/z calcd for $C_{16}H_{15}NO$ (M^+) 237.1154, found 237.1148.

6-Methoxy-3-(*p*-tolyl)-1*H*-indole (6l). Yield: 176 mg, 74%. Colorless solid. Mp: 110–111 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.24–7.23 (m, 2H), 6.91 (d, J = 2.2 Hz, 1H), 6.86 (dd, J = 8.8, 2.2 Hz, 1H), 3.87 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.9, 137.7, 135.7, 132.9, 129.6, 127.4, 120.7, 120.5, 120.4, 118.5, 110.3, 95.0, 55.9, 21.3. HRMS (EI) m/z calcd for $C_{16}H_{15}NO$ (M^+) 237.1154, found 237.1151.

3-(4-Isobutylphenyl)-6-methoxy-1*H*-indole (6m). Yield: 59 mg, 21%. Colorless solid. Mp: 77–78 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 2.3 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 2.2 Hz, 1H), 6.85 (dd, J = 8.8, 2.3 Hz, 1H), 3.87 (s, 3H), 2.51 (d, J = 7.1 Hz, 2H), 1.96–1.86 (m, 1H), 0.95 (d, J = 6.6 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.9, 139.6, 137.7, 133.1, 129.7, 127.2, 120.8, 120.6, 120.4, 118.6, 110.3, 95.0, 55.9, 45.4, 30.5, 22.6. HRMS (EI) m/z calcd for $C_{19}H_{21}NO$ (M^+) 279.1623, found 279.1629.

6-Methoxy-3-(3-methoxyphenyl)-1*H*-indole (6n). Yield: 157 mg, 62%. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.37–7.33 (m, 1H), 7.27 (d, J = 2.1 Hz, 1H), 7.23–7.20 (m, 1H), 6.91–6.83 (m, 3H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.2, 157.0, 137.7, 137.2, 129.9, 120.8, 120.8, 120.4, 120.1, 118.5, 113.2, 111.6, 110.5, 95.0, 55.9, 55.5. HRMS (EI) m/z calcd for $C_{16}H_{15}NO_2$ (M^+) 253.1103, found 253.1105.

6-Methoxy-3-(naphthalen-1-yl)-1*H*-indole (6o). Yield: 219 mg, 80%. Red oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.60–7.48 (m, 3H), 7.43–7.36 (m, 2H), 7.27–7.26 (m, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.80 (dd, J = 8.8, 2.1 Hz, 1H), 3.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.0, 137.0, 134.2, 133.3, 132.8, 128.5, 127.8, 127.3, 126.8, 125.9, 125.9, 125.8, 122.5, 122.4, 121.2, 116.8, 110.3, 94.9, 56.0. HRMS (EI) m/z calcd for $C_{19}H_{15}NO$ (M^+) 273.1154, found 273.1151.

3-(3-Chlorophenyl)-6-methoxy-1*H*-indole (6p). Yield: 144 mg, 56%. Colorless solid. Mp: 195–196 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.7 Hz, 1H), 7.60–7.59 (m, 1H), 7.51–7.48 (m, 1H), 7.38–7.34 (m, 1H), 7.28–7.25 (m, 2H), 6.98 (d, J = 2.1 Hz, 2H), 6.92 (dd, J = 8.8, 2.2 Hz, 1H), 6.31 (s, 1H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.5, 137.7, 136.9, 134.8, 130.2, 127.5, 126.5, 125.7, 123.6, 121.2, 121.1, 118.2, 110.8, 93.8, 55.9. HRMS (EI) m/z calcd for $C_{15}H_{12}NOCl$ (M^+) 257.0607, found 257.0601.

3-(4-Chlorophenyl)-6-methoxy-1*H*-indene (6q). Yield: 155 mg, 60%. Yellow solid. Mp: 154–155 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.59–7.55 (m, 2H), 7.41–7.38 (m, 2H), 7.24 (d, J = 2.5 Hz, 1H), 6.91 (d, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.7, 2.2 Hz, 1H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.0, 137.7, 134.3, 131.7, 129.1, 128.6, 120.8, 120.5, 120.1, 117.3, 110.7, 95.1, 55.9. HRMS (EI) m/z calcd for $C_{15}H_{12}NOCl$ (M^+) 257.0607, found 257.0602.

3-(2-Bromo-4-methoxyphenyl)-1*H*-indole (6r). Yield: 275 mg, 91%. Yellow solid. Mp: 122–123 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 4.2 Hz, 2H), 7.36 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 2.5 Hz, 1H), 7.26–7.22 (m,

1H), 7.18–7.14 (m, 1H), 6.95 (dd, J = 8.5, 2.6 Hz, 1H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.0, 135.9, 132.7, 128.3, 127.1, 124.5, 123.9, 122.5, 120.3, 120.2, 118.6, 116.6, 113.7, 111.4, 55.8. HRMS (EI) m/z calcd for $C_{15}H_{12}NOBr$ (M^+) 301.0102, found 301.0109.

Conclusions

In summary, we successfully synthesized unprotected NH 3-arylindole derivatives *via* Cu catalysed intramolecular Ullmann reaction of bromoamines starting from easily available nitrostyrene starting materials. The substructures on both indole and 3-aryl groups can be flexible based on the choices of β-nitrostyrenes and arenes.

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