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$FeCl_3$ Catalyzed Regioselective *C*-Alkylation of Indolylnitroalkenes with Amino Group Substituted Arenes

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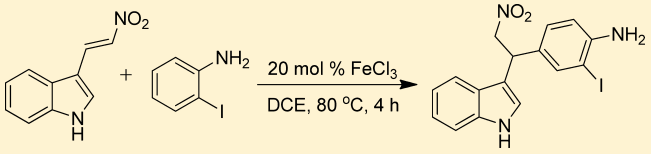
Supporting Information

ABSTRACT: An efficient $FeCl_3$ catalyzed protocol for the synthesis of amino functionalized indolylnitroalkanes from easily available precursor indolylnitroalkenes and substituted amines has been developed. Regioselective *C*-alkylation in the presence of free amino substituted arenes occurred. The scope of this methodology shows good functional group tolerance, and further, this protocol was used to prepare indolylquinoline derivatives.



Indole and its derivatives are important bioactive compounds which possess biological and pharmacological activity.[1] In particular, indolylaminoalkane compounds which are derived from indolylnitroalkane show antimigraine, psychoactive, neurotransmitter, and antifungal activities (Figure 1).[2] Besides these, indolylnitroalkane derivatives are key intermediates to many natural products.[3]

Owing to the importance of the indolylnitroalkanes, various synthetic methods have been developed. Among them, *C*-alkylation of indoles with nitroalkenes, catalyzed by both Lewis and Bronsted acids, is one of the most well-established procedures for achieving both racemic[4] and enantioselective indolylnitroalkanes.[5] Recently, Liao and co-workers reported the rhodium-catalyzed asymmetric addition of arylboronic acids to indolylnitroalkenes (Scheme 1).[6] Moreover, only a few reports are available for the direct *C*-alkylation of aryl substituted nitroalkene with *N,N*-disubstituted amino-arenes.[7] However, the direct *C*-alkylation of either unsubstituted amino arenes to indolylnitroalkenes or indoles to 2-aminonitroalkenes to synthesize the amino substituted indolylnitroalkanes has not been reported in the literature. The reason for the latter may be due to the difficulties in the preparation of amino group substituted nitroalkene from amino benzaldehyde. On the other hand, in the presence of a nucleophilic amino group there is the probability of Michael addition rather than *C*-alkylation.[8] The amino group containing compounds are widely used in industry for the synthesis of additives, dyes, and agrochemicals,[9] and compounds possessing an amino group can be used for the synthesis of various heterocycles.[10] Hence, the development of a novel route for the synthesis of an amino group substituted indolylnitroalkane *via* direct *C*-alkylation of indolylnitroalkenes using efficient processes is an important area of research.

In continuation of our research dealing with the utility of nitroalkenes in organic synthesis,[11] we wish to report, herein, a new approach for the synthesis of amino functionalized indolylnitroalkane derivatives *via* direct *C*-alkylation of amino group substituted arenes to indolylnitroalkenes in the presence of a catalytic amount of $FeCl_3$.

RESULTS AND DISCUSSION

We previously reported the arylation of nitroalkenes with various arenes and heteroarenes using 1 equiv of $AlCl_3$ as the catalyst at −78 °C to obtain arylated products in quantitative yield.[12] When amino group substituted arenes were used as substrates in the presence of $AlCl_3$, we obtained a complex mixture of products. Keeping the importance of amino group substituted indolylnitroalkanes in mind, we focused our attention toward screening this reaction with other catalysts. In this regard, we initially conducted the reaction of 7-ethylindolylnitroalkene with 2-iodoaniline in the presence of 20 mol % $FeCl_3$ as the catalyst at room temperature. To our delight, the reaction furnished a 7-ethylindolylnitroalkane product in 59% isolated yield after 14 h (Scheme 2). The structure of the product was investigated by ^1H and ^{13}C NMR studies and further confirmed by single crystal X-ray analysis (Figure 2).

After establishing the structure of the product, we focused our attention on optimization of the reaction by using different catalysts, solvents, and varying temperature. Initially, to know the effect of temperature, we conducted the reaction of indolylnitroalkene and 2-iodoaniline in the presence of $FeCl_3$ in dichloroethane (DCE) at 60 °C. The reaction under these conditions provided 62% of the desired product in 6 h (Table 1, entry 2). A slight improvement in the yield of the desired product was observed, when the reaction was carried out at 80 °C in 4 h (entry 4). Further, an increase in the temperature to 100 °C did not show any noticeable improvement in the reaction yield. Next, we screened various solvents for this reaction including $CHCl_3$, acetonitrile, THF, methanol, 1,4-dioxane, and DMF. The reaction produced a moderate yield of

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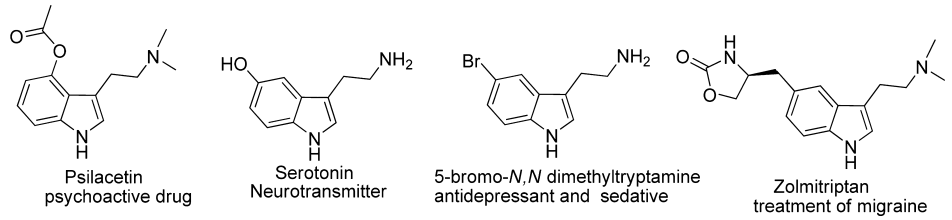
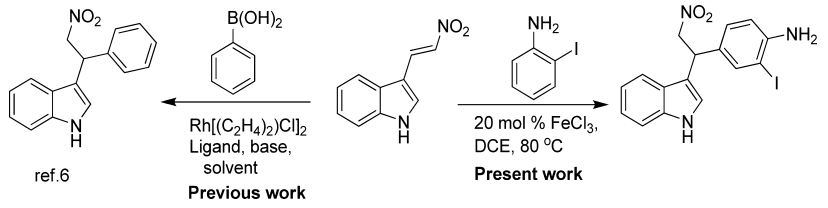
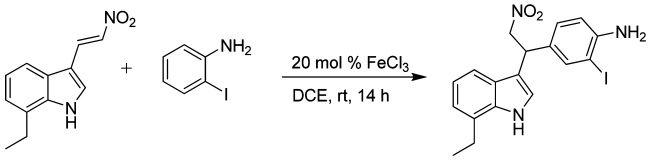


Figure 1. Biologically active indolylaminoalkane derivatives.[2]

Scheme 1. Synthesis of Indolylnitroalkane



Scheme 2. Reaction of 7-Ethyl Indolylnitroalkene and 2-Iodoaniline



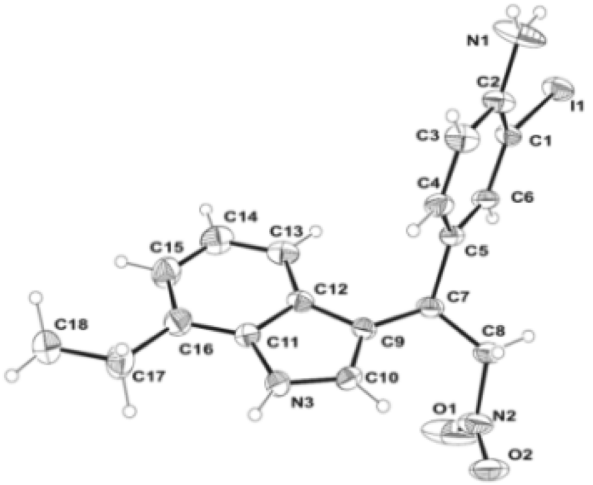
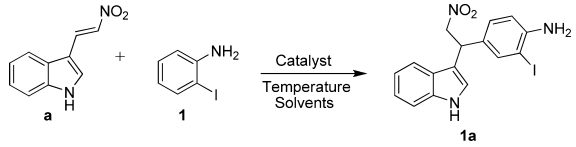


Figure 2. X-ray crystal structure of **1c** (ORTEP diagram).

Table 1. Optimization of Reaction Conditions



sr. no.	solvent	catalyst	temp (°C)	time (h)	result[a,b]
1	DCE	$FeCl_3$	rt	14	59
2	DCE	$FeCl_3$	60	6	62
3	DCE	$FeCl_3$	70	5	66
4	**DCE**	**$FeCl_3$**	**80**	**4**	**68**
5	$CHCl_3$	$FeCl_3$	80	6	56
6	CH_3CN	$FeCl_3$	80	25	31
7	THF	$FeCl_3$	70	10	26
8	MeOH	$FeCl_3$	80	24	mixture of products
9	1,4-dioxane	$FeCl_3$	80	24	42
10	DMF	$FeCl_3$	80	13	NR
11	DCE	–	80	12	NR
12	DCE	I_2	80	8	61
13	DCE	$InCl_3$	80	25	54
14	DCE	$BF_3.OEt_2$	80	4	38
15	DCE	$ZnCl_2$	80	20	mixture of products
16	DCE	$TiCl_4$	80	8	21

[a]All reactions were performed on a 1 mmol scale with 20 mol % catalyst and 4 mL of solvent unless otherwise noted. [b]Yields refers to isolated yields of the purified compound.

the desired product, when $CHCl_3$ used as a solvent (entry 5). Further, when CH_3CN, THF, and 1,4-dioxane were used as solvents, the yields dropped to 31%, 26%, and 42% respectively with a longer reaction time (entries 6, 7, and 9). However, we observed a mixture of products in the case of MeOH (entry 8) while in DMF no conversion to the desired product occurred (entry 10). Furthermore, we screened the reaction in the presence of different Lewis acids. When the reaction was performed in the absence of catalyst, we did not observe any product (entry 11). The reaction in the presence of I_2 and $InCl_3$ furnished moderate yields of the expected product (entries 12 and 13). The lower yields of the product were obtained in the case of $BF_3{\cdot}OEt_2$ and $TiCl_4$ catalysts (entries 14 and 16). Whereas in the presence of $ZnCl_2$, the reaction produced a mixture of products (entry 15). From the optimization studies, the ideal reaction conditions were found to be 20 mol % $FeCl_3$ catalyst, in DCE as solvent at 80 °C.

Having established the optimum reaction conditions, the scope and generality of this reaction were explored by treating different indolylnitroalkenes and amino substituted arenes to generate various substituted indolylnitroalkane products. As shown in Table 2, when unsubstituted indolylnitroalkene was treated with 2-iodoaniline, the expected product was formed in 68% yield (Table 2, **1a**). Then, the reactions of indolylnitroalkene containing methyl and ethyl groups at the seventh position proceeded well with 2-iodoaniline to give products **1b** and **1c** in 64% and 63% yields respectively. Further, the introduction of an electron withdrawing group at the fifth

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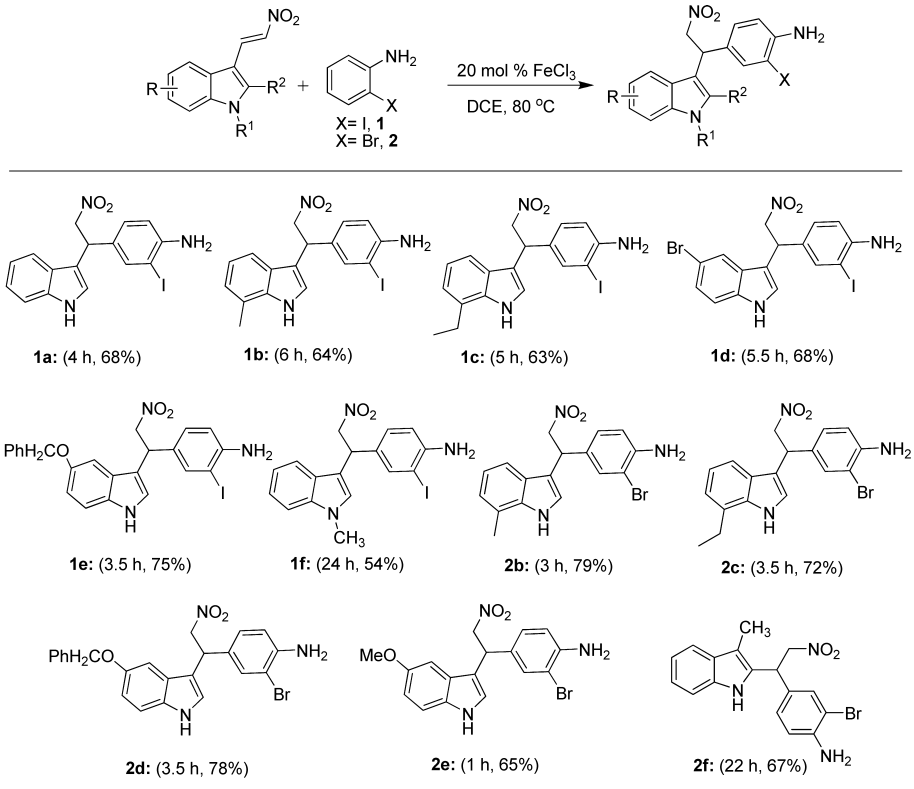
Table 2. Reaction of Substituted Indolylnitroalkene with Substituted Aniline[a,b]



[a]All reactions were performed on a 2 mmol scale. [b]Yields refer to isolated and purified compounds.

position of indolylnitroalkene provided the desired product in 68% yield in 5.5 h (**1d**). Whereas a strong electron-donating group at the same position on indolylnitroalkene produced the expected product in 75% yield in 3.5 h (**1e**). Moreover, when *N*-methylindolylnitroalkene and 2-iodoaniline were used as substrates in this reaction, the reaction took a longer time to produce the desired product in 54% yield (**1f**). On the other hand, the reactions of 7-methyl-, 7-ethyl-, 5-benzoloxy-, and 5-methoxyindolylnitroalkenes with 2-bromoaniline provided the corresponding indolylnitroalkane products (**2b**, **2c**, **2d**, and **2e**) in good yields. Interestingly, the reaction also works well when 3-methyl-2-(2-nitrovinyl)-1*H*-indole is treated with 2-bromoaniline to produce the desired product (**2f**) in 67% yield.

After the successful reaction of various indolylnitroalkenes with 2-iodo and 2-bromoaniline, we wish to investigate the scope of this reaction with respect to different aromatic amines having various electronic properties. The reaction in the presence of electron withdrawing groups such as −Cl, −Br, and −COMe provided good yields of the desired products (**2a**, **3a**, and **4a**; Table 3). Electron-donating substitutions at the *ortho* position of aniline gave a slightly lower yield of the expected products compared to the substrate with electron-withdrawing groups (**5a** and **6a**). When indolylnitroalkene was treated with 3-chloroaniline, the reaction offered the product (**7a**) in 71% yield. Whereas in the case of 3-iodoaniline and anthranilic acid, the yield of the products dropped to 51% and 44% respectively (**8a** and **9a**). When *N*-methyl aniline was used as the substrate the reaction gave a 78% yield of the desired product (**10a**) in 12 h, while in the case of *N*,*N*-dimethylaniline and *N*-methyl-*N*-ethylaniline a longer reaction time was required to afford the desired products in 83% (33 h) and 66% (44 h) yields respectively (**11a** and **12a**). When sterically hindered anilines such as 2,6-dimethylaniline, 2,6-diethylaniline, and 2,6-diisopropylaniline were treated with indolylnitroalkene, it undergoes an efficient reaction that generates the corresponding products in 77%, 78%, and 84% yields respectively (**13a**, **14a**, and **15a**).

After the successful investigations into the scope and limitations of the *C*-alkylation of various aniline derivatives and indolylnitroalkenes, we explored the utility of these newly synthesized indolylnitroalkanes. It is a well-known fact that many indolylquinoline derivatives show a broad range of biological activity such as potent KDR kinase inhibitors, antimicrobial activity, and male contraceptive activity in adult rats.[13] The syntheses of indolylquinoline derivatives were accomplished by following the procedure described by Singh and co-workers.[14] The reaction of a 1-(5-(1-(1*H*-indol-3-yl)-2-nitroethyl)-2-aminophenyl)ethanone derivative (**4a**) with acetophenone in the presence of the $InCl_3$ catalyst furnished the corresponding indolylquinoline derivative (**4af**) in 86% yield in 22 h (Scheme 3) which was confirmed by single-crystal X-ray analysis

Further, the reaction of **4a** and 5,5-dimethylcyclohexane-1,3-dione was conducted in the presence of the same catalyst to obtain the corresponding indolylacridone derivative (**4ag**) in 83% yield.

■ CONCLUSIONS

In summary, we have developed a new and efficient $FeCl_3$ catalyzed regioselective *C*-alkylation of various indolylnitroalkenes with amino substituted arenes under mild reaction conditions. This procedure provides a novel approach toward the synthesis of various amino functionalized indolylnitroalkane derivatives in good to excellent yields. Further, this method-

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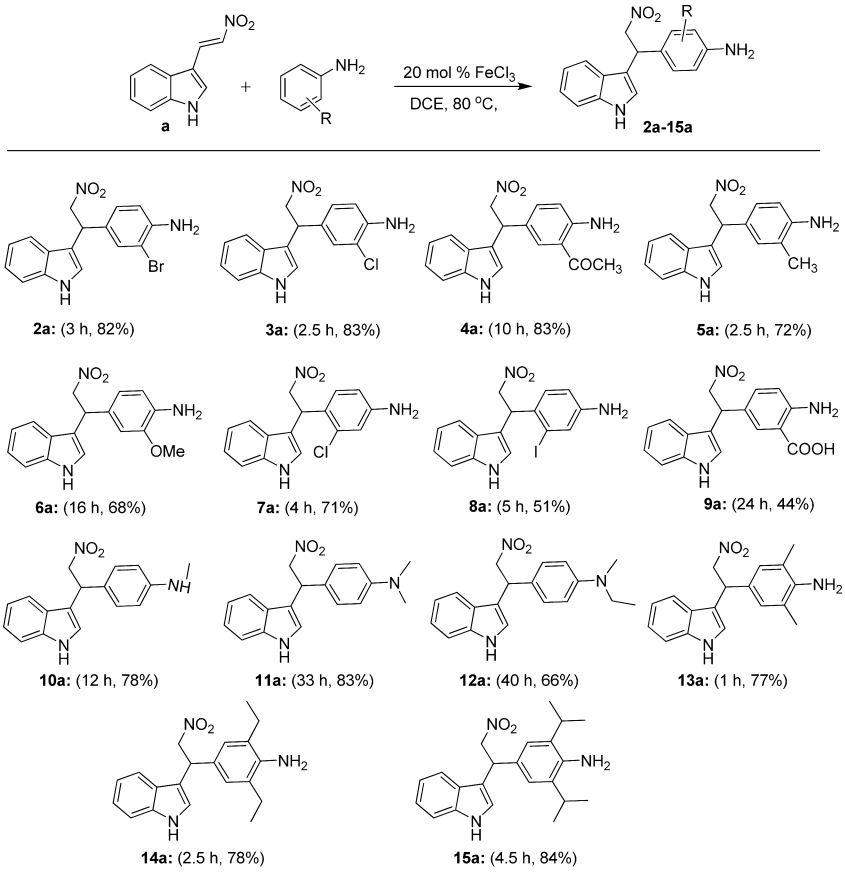
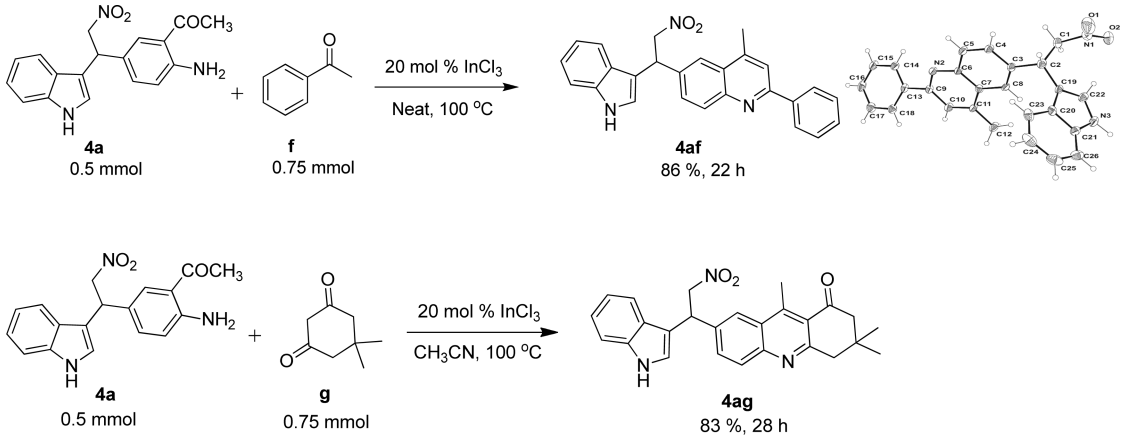
Table 3. Reaction of Indolylnitroalkene with Substituted Aniline[a,b]



[a]All reactions were performed on a 2 mmol scale. [b]Yields refer to isolated and purified compounds.

Scheme 3. Synthesis of Indolylquinoline Derivatives



ology was used to prepare biologically active indolylquinoline derivatives.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from various sources and were used directly without further purification. Analytical thin-layer chromatography was performed using silica gel 60F glass plates, and silica gel 60 (230−400 mesh) was used in flash chromatographic separations. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane and chloroform as the internal standards for ^1H NMR (400 MHz) and $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 MHz). Coupling constants were expressed in hertz. HRMS spectra were recorded using ESI or EI^+ mode. Melting points were recorded using an electrothermal capillary melting point apparatus and are uncorrected.

General Procedure for Preparation of Indolylnitroalkane Derivatives. To a stirred solution of indolylnitroalkene (2 mmol) and 2-iodoaniline (2 mmol) in dichloroethane (6 mL) was added $FeCl_3$ (20 mol %). The reaction mixture was heated at 80 °C, and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated to give the crude product. The resulting

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residue was further purified by flash column chromatography (ethyl acetate/hexane) on silica gel.

Spectral Data. *4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-iodoaniline (**1a**).* Compound **1a** was eluted with 20% EtOAc/Hex as a brown solid (552 mg, 68%); mp: 82−84 °C; FT-IR (KBr) ν/cm^{-1} 3501, 3425, 1616, 1547, 1493, 1373; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (brs, 1H), 7.58 (s, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.4 Hz, 2H), 7.02 (s, 1H), 6.67 (d, J = 8.3 Hz, 1H), 5.05−4.97 (m, 2H), 4.88−4.82 (m, 1H), 4.07 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 138.2, 136.7, 130.9, 129.0, 126.2, 122.9, 121.6, 120.2, 119.1, 115.0, 114.6, 111.6, 84.5, 79.8, 40.5; LRMS (EI) (m/z) (relative intensity) 407 (M$^+$, 86), 361 (42), 347 (100), 299 (27), 233 (26); HRMS (EI) calcd for $C_{16}H_{14}O_2N_3I$ (M$^+$): 407.0131, found 407.0135.

*2-Iodo-4-(1-(7-methyl-1H-indol-3-yl)-2-nitroethyl)aniline (**1b**).* Compound **1b** was eluted with 20% EtOAc/Hex as a dark brown solid (540 mg, 64%); mp: 86−88 °C; FT-IR (KBr) ν/cm^{-1} 3400, 3364, 2921, 1612, 1539, 1492, 1373, 779; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (brs, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.30−7.28 (m, 1H), 7.08 (dd, J = 8.2, 2.0 Hz, 1H), 7.03−7.00 (m, 3H), 6.66 (d, J = 8.2 Hz, 1H), 5.04−4.97 (m, 2H), 4.87−4.81 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 138.2, 136.3, 131.0, 129.0, 125.8, 123.5, 121.3, 120.8, 120.4, 116.9, 115.2, 115.0, 84.5, 79.8, 40.6, 16.7; LRMS (ESI) (m/z) (relative intensity) 422 (M$^+$ + 1, 16), 292 (35), 263 (100), 102 (29); HRMS (ESI) calcd for $C_{17}H_{17}O_2N_3I$ (M$^+$ + H): 422.0366, found 422.0365.

*4-(1-(7-Ethyl-1H-indol-3-yl)-2-nitroethyl)-2-iodoaniline (**1c**).* Compound **1c** was eluted with 15% EtOAc/Hex as a dark brown solid (549 mg, 63%); mp: 154−156 °C; FT-IR (KBr) ν/cm^{-1} 3415, 2958, 1631, 1543, 1488, 1370, 788; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (brs, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.32−7.30 (m, 1H), 7.08 (dd, J = 8.3, 2.0 Hz, 1H), 7.06−7.04 (m, 2H), 6.97 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 5.04−4.97 (m, 2H), 4.87−4.80 (m, 1H), 3.74 (brs, 2H), 2.83 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 138.2, 135.6, 130.9, 129.0, 127.0, 126.0, 121.4, 121.3, 120.5, 116.8, 115.0, 115.0, 84.5, 79.8, 40.6, 24.1, 13.9; LRMS (ESI negative) (m/z) (relative intensity) 434 (M$^+$ − H, 16), 390 (12), 360 (36), 312 (48); HRMS (ESI negative) calcd for $C_{18}H_{17}O_2N_3I$ (M − H)$^-$: 434.0366, found 434.0373.

*4-(1-(5-Bromo-1H-indol-3-yl)-2-nitroethyl)-2-iodoaniline (**1d**).* Compound **1d** was eluted with 20% EtOAc/Hex as a dark brown solid (662 mg, 68%); dark brown solid; mp: 80−82 °C; FT-IR (KBr) ν/cm^{-1} 3424, 3358, 2917, 1611, 1545, 1490, 1376, 885, 793; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (brs, 1H), 7.55−7.53 (m, 2H), 7.26 (dd, J = 8.6, 1.8 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.07−7.02 (m, 2H), 6.66 (d, J = 8.2 Hz, 1H), 4.98−4.91 (m, 2H), 4.84−4.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 138.1, 135.3, 130.3, 128.9, 128.0, 125.9, 122.8, 121.6, 115.0, 114.2, 113.4, 113.1, 84.6, 79.7, 40.2; LRMS (ESI negative) (m/z) (relative intensity) 483 (M$^+$ − H, 65), 381 (34), 379 (44), 265 (45), 126 (58); HRMS (ESI negative) calcd for $C_{16}H_{12}O_2N_3BrI$ (M − H)$^-$: 483.9158, found 483.9149.

*4-(1-(5-(Benzyloxy)-1H-indol-3-yl)-2-nitroethyl)-2-iodoaniline (**1e**).* Compound **1e** was eluted with 20% EtOAc/Hex as a dark brown gummy liquid (763 mg, 75%); FT-IR (KBr) ν/cm^{-1} 3419, 3363, 3024, 1613, 1545, 1489, 1372, 1017; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (brs, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.44 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.1 Hz, 1H), 7.23 (d, J = 9.6 Hz, 1H), 7.05 (dd, J = 8.2, 1.7 Hz, 1H), 6.97−6.92 (m, 3H), 6.66 (d, J = 8.2 Hz, 1H), 5.04 (s, 2H), 4.97−4.90 (m, 2H), 4.83−4.77 (m, 1H), 4.01 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 146.3, 138.2, 137.7, 132.0, 130.8, 129.0, 128.7, 128.0, 127.8, 126.7, 122.4, 115.1, 114.4, 113.8, 112.3, 102.8, 84.6, 79.7, 71.2, 40.5; LRMS (ESI) (m/z) (relative intensity) 514 (M$^+$ + 1, 74), 325 (15), 152 (35), 144 (100); HRMS (ESI) calcd for $C_{23}H_{21}O_3N_3I$ (M$^+$ + H): 514.0628, found 514.0627.

*2-Iodo-4-(1-(1-methyl-1H-indol-3-yl)-2-nitroethyl)aniline (**1f**).* Compound **1f** was eluted with 10% EtOAc/Hex as a brown gummy liquid (454 mg, 54%); FT-IR (KBr) ν/cm^{-1} 3504, 3425, 1614, 1547, 1494, 1372, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.25−7.22 (m, 1H), 7.11−7.07 (m, 2H), 6.84 (s, 1H), 6.65 (d, J = 8.2 Hz, 1H), 5.04−4.95 (m, 2H), 4.82 (dd, J = 11.9, 8.0 Hz, 1H), 3.80 (brs, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 138.1, 137.4, 131.0, 128.9, 126.6, 126.3, 122.4, 119.6, 119.1, 115.0, 112.8, 109.7, 84.5, 79.7, 40.4, 33.0; LRMS (EI) (m/z) (relative intensity) 421 (M$^+$, 53), 361 (100), 233 (16); HRMS (EI) calcd for $C_{17}H_{16}O_2N_3I$ (M$^+$): 421.0287, found 421.0292.

*2-Bromo-4-(1-(7-methyl-1H-indol-3-yl)-2-nitroethyl)aniline (**2b**).* Compound **2b** was eluted with 20% EtOAc/Hex as a dark brown gummy liquid (592 mg, 79%); FT-IR (KBr) ν/cm^{-1} 3413, 3036, 1613, 1543, 1495, 1429, 1374, 880; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (brs, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.29 (t, J = 8.2 Hz, 1H), 7.07−7.03 (m, 1H), 7.01−7.00 (m, 3H), 6.69 (d, J = 8.2 Hz, 1H), 5.06−4.97 (m, 2H), 4.83 (dd, J = 11.2, 7.4 Hz, 1H), 3.73 (brs, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.2, 131.8, 130.5, 127.9, 125.7, 123.3, 121.3, 120.8, 120.3, 116.7, 116.1, 114.8, 109.6, 79.7, 40.7, 16.6; LRMS (EI) (m/z) (relative intensity) 375 (M$^+$ + 2, 48), 373 (M$^+$, 48), 313 (100), 247 (19); HRMS (EI) calcd for $C_{17}H_{16}O_2N_3Br$ (M$^+$): 373.0426, found 373.0421.

*2-Bromo-4-(1-(7-ethyl-1H-indol-3-yl)-2-nitroethyl)aniline (**2c**).* Compound **2c** was eluted with 20% EtOAc/Hex as a brown solid (564 mg, 72%); mp: 149−151 °C; FT-IR (KBr) ν/cm^{-1} 3402, 3374, 2962, 1607, 1545, 1496, 1430; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (brs, 1H), 7.36 (d, J = 1.9 Hz, 1H), 7.31−7.29 (m, 1H), 7.08−7.03 (m, 3H), 6.99 (d, J = 2.3 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 5.06−4.98 (m, 2H), 4.84 (dd, J = 11.4, 7.6 Hz, 1H), 3.92 (brs, 2H), 2.83 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 135.6, 131.9, 130.6, 128.0, 127.0, 126.0, 121.4, 121.2, 120.5, 116.8, 116.2, 115.0, 109.7, 79.8, 40.8, 24.1, 13.9; LRMS (ESI) (m/z) (relative intensity) 388 (M$^+$ + 1, 15), 329 (24), 327 (27), 181 (61), 143 (100); HRMS (ESI) calcd for $C_{18}H_{19}O_2N_3Br$ (M$^+$ + H): 388.0661, found 388.0657.

*4-(1-(5-(Benzyloxy)-1H-indol-3-yl)-2-nitroethyl)-2-bromoaniline (**2d**).* Compound **2d** was eluted with 20% EtOAc/Hex as a brown gummy liquid (728 mg, 78%); FT-IR (KBr) ν/cm^{-1} 3431, 3380, 3028, 1615, 1545, 1479, 1373, 794; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (brs, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.39−7.26 (m, 4H), 7.24 (t, J = 9.0 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 6.98−6.92 (m, 3H), 6.70 (d, J = 8.2 Hz, 1H), 5.03 (s, 2H), 4.99−4.91 (m, 2H), 4.84−4.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.6, 137.6, 131.9, 131.8, 130.3, 128.7, 128.0, 127.9, 127.8, 126.6, 122.4, 116.1, 114.0, 113.6, 112.3, 109.6, 102.8, 79.6, 71.1, 40.6; LRMS (ESI) (m/z) (relative intensity) 466 (M$^+$ + 1, 8), 297 (12), 236 (34), 181 (100); HRMS (ESI) calcd for $C_{23}H_{21}O_3N_3Br$ (M$^+$ + H): 466.0766, found 466.0757.

*2-Bromo-4-(1-(5-methoxy-1H-indol-3-yl)-2-nitroethyl)aniline (**2e**).* Compound **2e** was eluted with 20% EtOAc/Hex as a brown gummy liquid (508 mg, 65%); FT-IR (KBr) ν/cm^{-1} 3429, 2830, 1621, 1585, 1547, 1454, 913; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (brs, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.23 (s, 1H), 7.07 (dd, J = 8.2, 1.7 Hz, 1H), 6.99 (s, 1H), 6.87−6.84 (m, 2H), 6.70 (d, J = 8.2 Hz, 1H), 5.00−4.95 (m, 2H), 4.87−4.82 (m, 1H), 4.05 (brs, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.6, 131.9, 131.8, 130.3, 128.0, 126.7, 122.3, 116.1, 114.2, 113.0, 112.3, 109.7, 101.0, 99.7, 56.1, 40.6; LRMS (EI) (m/z) (relative intensity) 391 (M$^+$ + 2, 49), 389 (M$^+$, 47), 329 (100), 263 (18); HRMS (EI) calcd for $C_{17}H_{16}O_3N_3Br$ (M$^+$): 389.0375, found 389.0375.

*2-Bromo-4-(1-(3-methyl-1H-indol-2-yl)-2-nitroethyl)aniline (**2f**).* Compound **2f** was eluted with 10% EtOAc/Hex as a brown solid (505 mg, 67%); mp: 62−64 °C; FT-IR (KBr) ν/cm^{-1} 3439, 1621, 1545, 1437, 1307, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (brs, 1H), 7.37−7.33 (m, 2H), 7.23 (s, 1H), 7.11−7.04 (m, 3H), 6.66 (d, J = 7.9 Hz, 1H), 5.14−5.05 (m, 3H), 4.04 (brs, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 135.6, 133.0, 131.5, 130.7, 127.5, 126.9, 121.5, 120.0, 118.7, 116.0, 110.9, 109.6, 108.8, 78.9, 39.6, 12.2; LRMS (EI) (m/z) (relative intensity) 375 (M$^+$ + 2, 31), 373 (M$^+$, 33), 313 (80), 202 (100); HRMS (EI) calcd for $C_{17}H_{16}O_2N_3Br$ (M$^+$): 373.0426, found 373.0431.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-bromoaniline (**2a**).* Compound **2a** was eluted with 20% EtOAc/Hex as a brown gummy liquid (592 mg, 82%); FT-IR (KBr) ν/cm^{-1} 3471, 3416, 2921, 1626, 1540, 1493; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (brs, 1H), 7.44 (d, J

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= 7.9 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.10−7.04 (m, 2H), 7.00 (d, J = 2.1 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 5.07−4.97 (m, 2H), 4.84 (dd, J = 11.8, 8.0 Hz, 1H), 3.51 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 138.1, 136.6, 130.8, 128.9, 126.1, 122.8, 121.7, 120.1, 119.0, 115.0, 114.4, 111.6, 84.5, 79.7, 40.4; LRMS (EI) (m/z) (relative intensity) 361 (M^++2, 26), 359 (M^+, 94), 347 (100), 233 (24); HRMS (EI) calcd for $C_{16}H_{14}O_2N_3Br$ (M^+): 359.0269, found 359.0276.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-chloroaniline (**3a**).* Compound **3a** was eluted with 20% EtOAc/Hex as a brown gummy liquid (521 mg, 83%); FT-IR (KBr) ν/cm^{-1} 3479, 3420, 2925, 1612, 1543, 1500, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (brs, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.22−7.19 (m, 2H), 7.08 (t, J = 7.5 Hz, 1H), 7.04−7.01 (m, 2H), 6.69 (d, J = 8.2 Hz, 1H), 5.07−4.98 (m, 2H), 4.84 (dd, J = 11.7, 7.9 Hz, 1H), 3.97 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 136.7, 130.1, 128.8, 127.3, 126.2, 122.9, 121.6, 120.1, 119.7, 119.1, 116.3, 114.5, 111.6, 79.8, 40.8; LRMS (EI) (m/z) (relative intensity) 315 (M^+, 46), 268 (67), 255 (100), 233 (17); HRMS (EI) calcd for $C_{16}H_{14}O_2N_3Cl$ (M^+): 315.0775, found 315.0776.

*1-(5-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-aminophenyl)ethanone (**4a**).* Compound **4a** was eluted with 20% EtOAc/Hex as a yellow solid (541 mg, 83%); mp: 157−159 °C; FT-IR (KBr) ν/cm^{-1} 3496, 3429, 2913, 1635, 1543, 1418; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (brs, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.23−7.19 (m, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 6.25 (brs, 2H), 5.11−5.02 (m, 2H), 4.88 (dd, J = 11.4, 8.0 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 149.8, 136.8, 133.8, 131.3, 126.3, 126.2, 123.0, 121.7, 120.2, 119.1, 118.3, 118.2, 114.7, 111.7, 79.8, 41.1, 28.0; LRMS (ESI) (m/z) (relative intensity) 324 (M^+ + 1, 100), 275 (39), 158 (26), 122 (30); HRMS (ESI) calcd for $C_{18}H_{18}O_3N_3$ (M^+ + H): 324.1348, found 324.1351.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-methylaniline (**5a**).* Compound **5a** was eluted with 25% EtOAc/Hex as a brown solid (428 mg, 72%); mp: 112−114 °C; FT-IR (KBr) ν/cm^{-1} 3429, 3407, 3050, 1624, 1544, 1504, 1376; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (brs, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.0 Hz, 3H), 6.60 (d, J = 7.8 Hz, 1H), 5.08−5.00 (m, 2H), 4.86 (dd, J = 11.7, 7.9 Hz, 1H), 3.41 (brs, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.7, 130.1, 129.3, 126.4, 126.3, 123.0, 122.7, 121.6, 120.0, 119.2, 115.4, 115.2, 111.5, 80.1, 41.1, 17.6; LRMS (ESI) (m/z) (relative intensity) 296 (M^+ + 1, 44), 199 (17); HRMS (ESI) calcd for $C_{17}H_{18}O_2N_3$ (M^+ + H): 296.1399, found 296.1392.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-methoxyaniline (**6a**).* Compound **6a** was eluted with 25% EtOAc/Hex as a brown solid (422 mg, 68%); mp: 128−130 °C; FT-IR (KBr) ν/cm^{-1} 3459, 3372, 2915, 1616, 1551, 1518, 1377, 1265, 736; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (brs, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.01 (s, 1H), 6.74 (d, J = 9.6 Hz, 2H), 6.64 (d, J = 7.7 Hz, 1H), 5.10−5.00 (m, 2H), 4.88 (dd, J = 11.9, 8.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 136.7, 135.7, 129.4, 126.4, 122.8, 121.8, 120.2, 120.1, 119.3, 115.3, 115.2, 111.5, 110.5, 80.1, 55.7, 41.6; LRMS (EI) (m/z) (relative intensity) 311 (M^+, 67), 251 (100), 219 (11), 144 (12); HRMS (EI) calcd for $C_{17}H_{17}O_3N_3$ (M^+): 311.1270, found 311.1277.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-3-chloroaniline (**7a**).* Compound **7a** was eluted with 25% EtOAc/Hex as a brown solid (448 mg, 71%); mp: 82−84 °C; FT-IR (KBr) ν/cm^{-1} 3467, 3418, 2915, 1638, 1547; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (brs, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 2.3 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 6.44 (dd, J = 8.4, 2.4 Hz, 1H), 5.60 (t, J = 7.4 Hz, 1H), 4.99−4.87 (m, 2H), 3.69 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 136.7, 134.4, 129.8, 126.5, 125.9, 122.8, 121.9, 120.1, 119.3, 116.1, 114.2, 114.1, 111.5, 78.3, 37.5; LRMS (EI) (m/z) (relative intensity) 315 (M^+, 68), 255 (100), 233 (55), 219 (24); HRMS (EI) calcd for $C_{16}H_{14}O_2N_3Cl$ (M^+): 315.0775, found 315.0774.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-3-iodoaniline (**8a**).* Compound **8a** was eluted with 20% EtOAc/Hex as a brown gummy liquid (414 mg, 51%); FT-IR (KBr) ν/cm^{-1} 3439, 3406, 2915, 1623, 1543; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (brs, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.09−7.05 (m, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.51 (dd, J = 8.4, 2.4 Hz, 1H), 5.46 (dd, J = 9.0, 6.8 Hz, 1H), 4.92−4.79 (m, 2H), 3.64 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 136.7, 130.7, 128.9, 126.5, 126.0, 122.9, 121.8, 120.1, 119.6, 115.7, 114.7, 111.5, 101.5, 78.5, 45.0; LRMS (EI) (m/z) (relative intensity) 407 (M^+, 100), 360 (78), 347 (50), 233 (79), 220 (43); HRMS (EI) calcd for $C_{16}H_{14}O_2N_3I$ (M^+): 407.0131, found 407.0132.

*5-(1-(1H-Indol-3-yl)-2-nitroethyl)-2-aminobenzoic acid (**9a**).* Compound **9a** was eluted with 30% EtOAc/Hex as a yellow solid (288 mg, 44%); mp: 217−219 °C; FT-IR (KBr) ν/cm^{-1} 3400, 3374, 1664, 1541, 1418, 1234, 740; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.99 (brs, 1H), 8.47 (brs, 2H), 7.67 (d, J = 2.2 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.37−7.28 (m, 3H), 7.05 (t, J = 7.3 Hz, 1H), 6.95−6.91 (m, 1H), 6.66 (d, J = 8.6 Hz, 1H), 5.23 (dd, J = 12.8, 7.8 Hz, 1H), 5.15 (dd, J = 12.8, 8.7 Hz, 1H), 4.87 (t, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 150.5, 136.2, 133.4, 130.1, 126.3, 126.0, 122.1, 121.3, 118.6, 118.4, 116.6, 113.6, 111.5, 109.3, 79.5; LRMS (EI) (m/z) (relative intensity) 325 (M^+, 65), 278 (78), 265 (100), 247 (25); HRMS (EI) calcd for $C_{17}H_{15}O_4N_3$ (M^+): 325.1063, found 325.1069.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-N-methylaniline (**10a**).* Compound **10a** was eluted with 20% EtOAc/Hex as a brown solid (464 mg, 78%); mp: 104−106 °C; FT-IR (KBr) ν/cm^{-1} 3402, 2924, 1647, 1547, 1513, 1376, 742; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (brs, 1H), 7.48−7.45 (m, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.56−6.53 (m, 2H), 5.10−4.99 (m, 2H), 4.87 (dd, J = 11.8, 8.0 Hz, 1H), 3.51 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.7, 128.8, 127.8, 126.5, 122.7, 121.7, 120.0, 119.3, 115.4, 112.9, 111.5, 80.2, 41.1, 30.9; LRMS (EI) (m/z) (relative intensity) 295 (M^+, 46), 235 (100), 124 (8); HRMS (EI) calcd for $C_{17}H_{17}O_2N_3$ (M^+): 295.1321, found 295.1329.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-N,N-dimethylaniline (**11a**).* Compound **11a** was eluted with 15% EtOAc/Hex as a green solid (516 mg, 83%); mp: 132−134 °C; FT-IR (KBr) ν/cm^{-1} 3412, 3384, 2913, 1642, 1611, 1544, 1520; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (brs, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.20−7.17 (m, 3H), 7.07 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.68 (d, J = 8.6 Hz, 2H), 5.12−5.00 (m, 2H), 4.88 (dd, J = 12.0, 8.0 Hz, 1H), 2.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 136.8, 128.6, 127.1, 126.5, 122.7, 121.7, 120.0, 119.3, 115.4, 113.1, 111.5, 80.1, 41.0, 40.8; LRMS (ESI) (m/z) (relative intensity) 310 (M^+ + 1, 100); HRMS (ESI) calcd for $C_{18}H_{20}O_2N_3$ (M^+ + H): 310.1556, found 310.1554.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-N-ethyl-N-methylaniline (**12a**).* Compound **12a** was eluted with 15% EtOAc/Hex as a brown solid (424 mg, 66%); mp: 161−163 °C; FT-IR (KBr) ν/cm^{-1} 3429, 3414, 2958, 1604, 1541, 1508, 1373; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (brs, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.21−7.16 (m, 3H), 7.08 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 1.0 Hz, 1H), 6.65 (d, J = 8.6 Hz, 2H), 5.11−5.00 (m, 2H), 4.89 (dd, J = 12.0, 8.0 Hz, 1H), 3.36 (q, J = 7.0 Hz, 2H), 2.88 (s, 3H), 1.10 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 136.7, 128.7, 126.5, 126.4, 122.7, 121.7, 120.0, 119.3, 115.4, 112.7, 111.5, 80.1, 47.0, 41.0, 37.6, 11.5; LRMS (EI) (m/z) (relative intensity) 323 (M^+, 52), 263 (100), 261 (17), 131 (8); HRMS (EI) calcd for $C_{19}H_{21}O_2N_3$ (M^+): 323.1634, found 323.1627.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2,6-dimethylaniline (**13a**).* Compound **13a** was eluted with 20% EtOAc/Hex as a brown solid (484 mg, 77%); mp: 136−138 °C; FT-IR (KBr) ν/cm^{-1} 3440, 3404, 2908, 1628, 1543, 1490, 1373, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (brs, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 1.8 Hz, 1H), 6.90 (s, 2H), 5.05−4.98 (m, 2H), 4.87 (dd, J = 11.2, 7.3 Hz, 1H), 3.51 (brs, 2H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

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142.1, 136.6, 128.6, 127.7, 126.4, 122.6, 122.3, 121.6, 119.9, 119.2, 115.3, 111.5, 80.2, 41.1, 17.9; LRMS (EI) (*m*/*z*) (relative intensity) 309 (M^+, 50), 262 (41), 249 (100); HRMS (EI) calcd for $C_{18}H_{19}O_2N_3$ (M^+): 309.1477, found 309.1471.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2,6-diethylaniline (**14a**).* Compound **14a** was eluted with 15% EtOAc/Hex as a brown gummy liquid (528 mg, 78%); FT-IR (KBr) ν/cm^{-1} 3402, 2954, 1617, 1547, 1454, 1373, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (brs, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.93 (s, 2H), 5.11−5.01 (m, 2H), 4.90 (dd, *J* = 11.9, 7.8 Hz, 1H), 3.69 (brs, 2H), 2.49 (q, *J* = 7.5 Hz, 4H), 1.22 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 136.7, 128.8, 128.3, 126.5, 125.6, 122.6, 121.8, 119.9, 119.2, 115.4, 111.5, 80.2, 41.4, 24.6, 13.2; LRMS (EI) (*m*/*z*) (relative intensity) 337 (M^+, 31), 290 (43), 277 (100), 261 (17), 141 (18); HRMS (EI) calcd for $C_{20}H_{23}O_2N_3$ (M^+): 337.1790, found 337.1798.

*4-(1-(1H-Indol-3-yl)-2-nitroethyl)-2,6-diisopropylaniline (**15a**).* Compound **15a** was eluted with 15% EtOAc/Hex as a brown gummy liquid (624 mg, 84%); FT-IR (KBr) ν/cm^{-1} 3403, 2956, 1620, 1546, 1461, 1376; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (brs, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.99−6.98 (m, 3H), 5.12−5.02 (m, 2H), 4.91 (dd, *J* = 12.0, 7.9 Hz, 1H), 3.76 (brs, 2H), 2.93−2.86 (m, 2H), 1.24−1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 136.7, 133.0, 128.9, 126.5, 122.6, 122.4, 122.0, 119.9, 119.3, 115.5, 111.5, 80.2, 41.8, 28.2, 22.6, 22.6; LRMS (EI) (*m*/*z*) (relative intensity) 365 (M^+, 35), 305 (100), 276 (7); HRMS (EI) calcd for $C_{22}H_{27}O_2N_3$ (M^+): 365.2103, found 365.2104.

*6-(1-(1H-Indol-3-yl)-2-nitroethyl)-4-methyl-2-phenylquinoline (**4af**).* Compound **4af** was eluted with 20% EtOAc/Hex as a white solid (174 mg, 86%); mp: 231−233 °C; FT-IR (KBr) ν/cm^{-1} 3402, 2915, 2332, 1627, 1402, 1115, 665; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (brs, 1H), 8.16−8.11 (m, 3H), 7.98 (d, *J* = 1.8 Hz, 1H), 7.17 (s, 1H), 7.66 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.53−7.43 (m, 4H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10−7.05 (m, 2H), 5.42 (t, *J* = 7.9 Hz, 1H), 5.17 (dd, *J* = 12.7, 7.2 Hz, 1H), 5.08 (dd, *J* = 12.6, 8.8 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 145.2, 139.7, 137.2, 136.8, 131.1, 129.6, 129.3, 129.0, 127.8, 127.5, 126.3, 123.1, 122.7, 122.1, 120.5, 120.3, 119.0, 114.4, 111.7, 79.6, 42.1, 29.9, 19.3; LRMS (EI) (*m*/*z*) (relative intensity) 407 (M^+, 36), 360 (100), 347 (71); HRMS (EI) calcd for $C_{26}H_{21}O_2N_3$ (M^+): 407.1634, found 407.1637.

*7-(1-(1H-Indol-3-yl)-2-nitroethyl)-3,3,9-trimethyl-3,4-dihydroacridin-1(2H)-one (**4ag**).* Compound **4ag** was eluted with 30% EtOAc/Hex as a yellow solid (178 mg, 83%); m.p.: 207−209 °C; FT-IR (KBr) ν/cm^{-1} 2937, 2346, 1686, 1605, 1550, 1373, 1218, 1096, 842, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.37 (brs, 1H), 8.20 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.22−7.18 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 2H), 5.41 (t, *J* = 8.0 Hz, 1H), 5.17 (dd, *J* = 12.6, 7.0 Hz, 1H), 5.07 (dd, *J* = 12.5, 8.9 Hz, 1H), 3.17 (s, 2H), 3.04 (s, 3H), 2.65 (s, 2H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 161.5, 147.8, 137.6, 136.8, 131.4, 130.1, 127.9, 126.1, 124.7, 124.4, 123.2, 121.9, 120.4, 118.9, 114.1, 111.8, 79.5, 76.9, 55.0, 48.6, 42.1, 32.3, 29.9, 28.5, 16.2; LRMS (EI) (*m*/*z*) (relative intensity) 427 (M^+, 37), 380 (100), 367 (55); HRMS (EI) calcd for $C_{26}H_{25}O_3N_3$ (M^+): 427.1896, found 427.1899.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic structures and information; ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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