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# An access to C5-alkylated indolines/indoles via Michael-type Friedel-Crafts alkylation using aryl-nitroolefins

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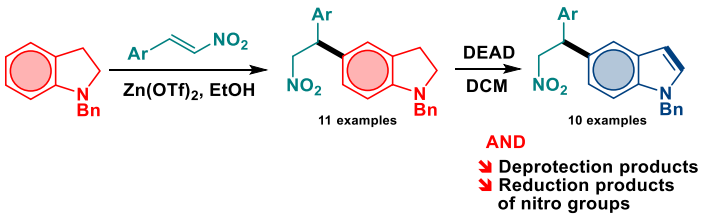
**ABSTRACT:** A straightforward synthetic route toward C5-alkylated indolines/indoles has been developed. The strategy is composed of $Zn(OTf)_2$-catalyzed Friedel–Crafts alkylation of *N*-benzylindolines with nitroolefins, and a series of diverse indolines was first obtained in up to 99% yield. This reaction provides a direct and practical route to a variety of the C5-alkylated indolines which were also utilized for accessing corresponding indoles. Indoline derivatives with free NH groups could be obtained through an *N*-deprotection reaction. Moreover, the primary alkyl nitro groups in both indolines and indoles are amenable to further synthetic elaborations thereby broadening the diversity of the products.

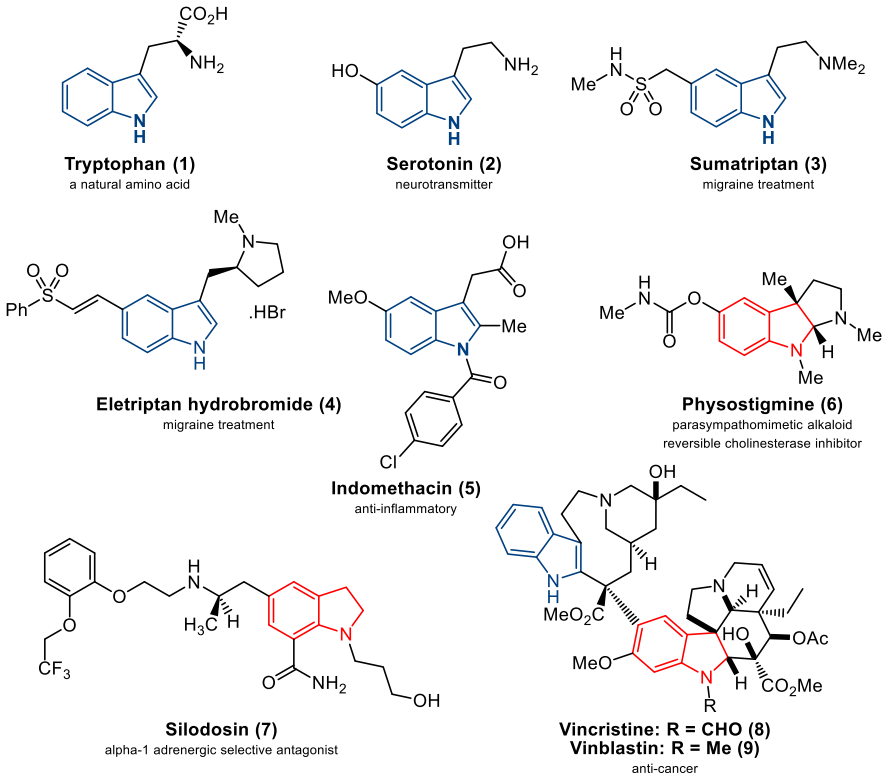



## ■ INTRODUCTION

The indole scaffold is one of the most widely studied organic templates over the past century as it is associated with biologically active compounds and natural products it is and crucial for the discovery of new drugs.[1] The indole motif is a bacterial intercellular signaling molecule and is found in the structure of many natural products such as tryptophan (**1**) (essential amino acid), and serotonin (**2**) (neurotransmitter).[2] In 2014, the indole ring was reported to present in 24 marketed drugs as the fourth most prevalent heteroaromatic ring used for the discovery of drugs.[3] For example, sumatriptan (**3**)[4] and eletriptan hydrobromide (**4**)[5] are two of the triptan class drugs used for the treatment of migraine and cluster headaches. Indomethacin (**5**) is a nonsteroidal anti-inflammatory drug (NSAID) used to treat pain or inflammation caused by many conditions such as arthritis, gout, ankylosing spondylitis, bursitis, or tendinitis.[6] Indoline skeleton is found in the structures of natural products and

biologically active compounds.[7] Their simple or complex structures are responsible for their potent biological activities in a range of molecules. Physostigmine (**6**) is a reversible inhibitor of acetylcholinesterase and used to reverse the effects of certain drugs or substances that interfere with nerve-muscle communication.[8] Silodosin (**7**), a drug that is including indoline ring, is a selective antagonist of alpha-1 adrenoreceptors and is used for the treatment of the signs and symptoms of benign prostatic hyperplasia (BPH).[9] The binary indole–indoline alkaloids such as vincristine (**8**) and vinblastine (**9**) were also isolated from *Catharanthus roseus* and used clinically in the treatment of cancers including various lymphomas and sarcomas, advanced testicular cancer, breast cancer, and acute leukemia (Figure 1).[10]

**Figure 1.** Several examples of alkaloids and drugs containing the indole and indoline motifs.




The indole is one of the most important of the privileged structures not only in the area of medicinal chemistry/drug discovery but also in other research areas such as agrochemistry and material science.[11] Furthermore, indole-based phosphorus ligands are reported to perform in catalytic systems.[12] Accordingly, the development of new methods for the construction of the indole ring has been extensively investigated for more than a century. Access to the functionalized indoles can be broadly categorized into three main strategies.[13] The first approach involves many name reactions wherein the indole ring and embedded functionalities are constructed from benzenoid precursors or other structures through condensation reactions or by metal-catalyzed means.[1a,14,15] Classical

syntheses such as Fischer,[16] Bartoli,[17] and Larock[18] are at the forefront among a multitude of other synthetic protocols. The second and third protocols include the derivatization of the indole nucleus itself, either through halogenation and following cross-coupling methodology or direct C-H activation.[19]

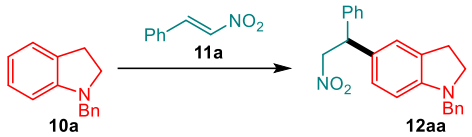
Nitroolefins are important and invaluable building blocks in organic synthesis and have been widely used in a number of carbon-carbon bond-forming reactions.[20] Particularly, the Friedel–Crafts reactions employing nitroolefins as the electrophilic partner are very attractive in indole chemistry, since the nitro groups of the products allow subsequent versatile transformations such as the synthesis of tryptamine and carboline derivatives.[21] While many alkylation methods exist for the functionalization of indoles in a directly or directed C–H and N–H functionalization at N1,[22,23] C2,[24] and C3[25] in chiral and achiral meaning as a result of the inherent reactivity of the pyrrole-type ring, C–H functionalization on the benzenoid ring is limited. Despite this, the directing group-assisted catalytic methods that allow derivatization at the less activated positions, C4–C7, have been recently developed.[26] In fact, the most sparingly observed selectivity in the direct functionalization of the indole benzenoid ring is the access to the C5 position. However, to the best of our knowledge, there has been no previous report on catalytic C–H alkylation at the C5-position of indoles. Herein, we described a facile approach for the C5-selective Friedel–Crafts type C–H alkylation of *N*-benzylindoline with β-aryl-nitroolefins. Notably, the resultant *N*-benzyl-C5-alkylated indolines can be readily converted to C5-alkylated indoles under oxidative conditions and deprotected.

## ■ RESULTS AND DISCUSSIONS

In our previous studies, a series of nitrostyrene derivatives were evaluated to yield *N*-alkylated indolines as electrophilic partners against indoline.[23] To our surprise, we noticed that the reaction between β-nitrostyrene and indoline using $Zn(OTf)_2$ as a catalyst afforded a C5–alkylated product along with an *N*-alkylation product. This observation encouraged us to study this reaction in detail. To prevent the *N*-alkylation, the nitrogen atom of indoline was protected by the benzyl group. The reaction of indoline with benzyl bromide in the conditions reported in the literature led to 1-benzylindoline (**10a**).[27] Using a similar reaction, we also obtained the 1-benzyl-2-methylindoline (**10b**) and ethyl 1-benzylindoline-2-carboxylate (**10c**). The reaction of 1-benzylindoline (**10a**) and β-nitrostyrene (**11a**) was initially tested as a model reaction to optimize the reaction conditions with different catalysts, solvents, and temperature. The optimization results are summarized in Table 1. We found that zinc salts gave the expected reaction. Gratifyingly, the best result was obtained with a catalytic amount of zinc triflate (0.2 equiv) in ethanol at 25 °C (Table 1, entry 16), where the desired

product **12aa** was obtained in 98% yield as the only product. The structure of **12aa** was unequivocally determined by NMR spectroscopy.

**Table 1.** Optimization Conditions for Reaction of 1-Benzylindoline (**10a**) and β-Nitrostyrene (**11a**).




| entry | catalyst | x (mol%) | solvent | *T* (°C) | *t* (h) | yield (%) |
|---|---|---|---|---|---|---|
| 1 | $Bi(NO_3)_3{\cdot}5H_2O$ | 0.5 | $CH_2Cl_2$ | 25 | 2 | - |
| 2 | $Bi(NO_3)_3{\cdot}5H_2O$ | 0.1 | $CH_2Cl_2$ | 25 | 2 | - |
| 3 | $Bi(NO_3)_3{\cdot}5H_2O$ | 0.5 | $CH_2Cl_2$ | 25 | 24 | - |
| 4 | $Bi(NO_3)_3{\cdot}5H_2O$ | 0.5 | $CH_2Cl_2$ | 40 | 2 | - |
| 5 | $Bi(NO_3)_3{\cdot}5H_2O$ | 1 | $CH_2Cl_2$ | 40 | 2 | - |
| 6 | $Bi(NO_3)_3{\cdot}5H_2O$ | 0.2 | EtOH | 25 | 12 | - |
| 7 | $Pb(CH_3COO)_4$ | 0.2 | $CH_2Cl_2$ | 25 | 2 | - |
| 8 | $Mg(OTf)_2$ | 0.1 | $CH_2Cl_2$ | 25 | 24 | - |
| 9 | $Mg(OTf)_2$ | 0.5 | $CH_2Cl_2$ | 25 | 24 | - |
| 10 | $Zn(CF_3CO_2)_2$ | 0.2 | $CH_2Cl_2$ | 25 | 4 | - |
| 11 | $Zn(CF_3CO_2)_2$ | 0.2 | $CH_2Cl_2$ | 25 | 24 | - |
| 12 | $Zn(CF_3CO_2)_2$ | 0.2 | Toluene | 25 | 24 | - |
| 13 | $Zn(CF_3CO_2)_2$ | 0.2 | EtOH | 25 | 5 | 95 |
| 14 | $Zn(OTf)_2$ | 0.2 | $CH_2Cl_2$ | 25 | 5 | - |
| 15 | $Zn(OTf)_2$ | 0.2 | Toluene | 25 | 5 | 90 |
| **16** | **$Zn(OTf)_2$** | **0.2** | **EtOH** | **25** | **5** | **98** |
| 17 | $Cu(OTf)_2$ | 0.2 | EtOH | 25 | 12 | - |

[a]Reaction conditions: **10a** (1.0 equiv), **11a** (1.0 equiv). Isolated yield.

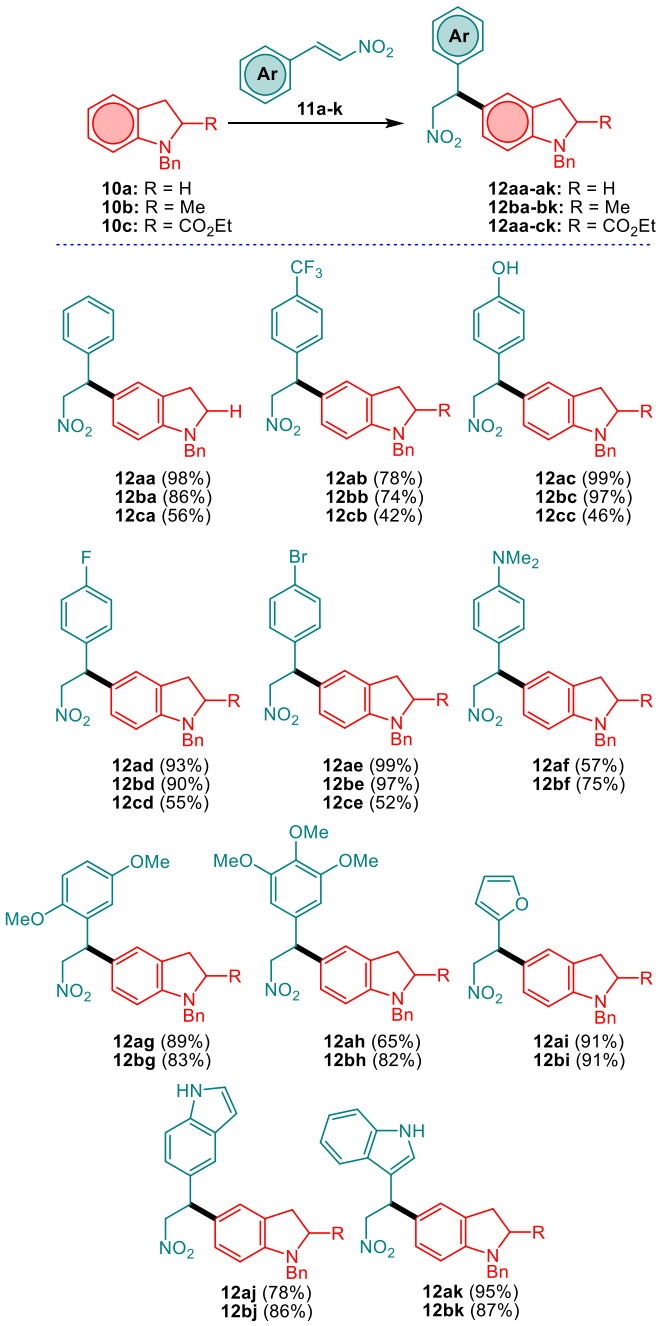
With the optimized conditions in hand, we next examined the scope of nitroolefins (**11a-k**)[28] with 1-benzylindoline (**10a**) to test the feasibility of preparing a variety of 5-alkylated indolines (Scheme 1). The reaction of *N*-benzylindoline (**10a**) could tolerate a wide range of nitroolefins (**11a-k**) bearing electron-withdrawing and donating groups on the aryl ring, and all of the cases delivered the desired products (**12aa–12ak**) in good to excellent yields (57–99% yields). Then, the influence of the electronic nature of the substituent at the 2-position on the saturated ring of indoline was examined. The 2-methyl-*N*-benzylindoline (**10b**) was studied, and the results revealed that the methyl substituent had no impact on the reaction progress and yields (**12ba–bk**, 74–97%). But, indoline (**10c**) with electron-withdrawing ester substituent exhibited lower reactivity, affording the some of the desired products in much lower yields (**12ca-ce**, 42-56%). We postulated that electron donating rings adjacent to olefin system deactivate the nitroolefin by increasing the electron density, whereas the ester substituent on indoline leads to relatively lower reactivity due to both electronic reasons (which can be mesomeric or inductive) and the possible interactions between the catalyst and the ester. On the other hand, in comparison with the electron-donating benzyl group, when *N*-acetylindoline (**10d**) with an electron-withdrawing group was employed as a substrate, no reaction occurred because of the presumably

reduced nucleophilicity. A possible mechanism for the $Zn(OTf)_2$ catalyzed Michael–type Friedel–Crafts reaction between 1-benzylindolines (**10**) and nitroolefins (**11**) is proposed in Scheme 2. The nitroolefin was activated upon chelation to Zn(II) to form a four-membered intermediate **[A]**, which undergoes a nucleophilic addition of indoline from the accessible C5-position to provide the Friedel–Crafts alkylation adduct **[B]**. Subsequently, H–transfer to provide aromatization leads to product formation. We postulate that tertiary nitrogen atom of indoline directs substitution to the *ortho*- and *para*-positions. But an absence of *ortho*-product **13** has been attributed to a steric hindrance between benzyl and the electrophile, which, do not tolerate intermediate **[C]**.

It was hoped that the methodology will provide a facile access to Friedel–Crafts product **12l**, which can be a precursor of silodosin using a medication for the symptomatic treatment of benign prostatic hyperplasia. However, the reaction of indoline **10a** and 2-nitroprop-1-ene (**11l**) failed to give the corresponding product **12l** under the above optimum and other conditions (Table 2, Entries 1-14), the starting materials are recovered in almost quantitative yields. This suggests that both an electron-rich nitroolefin fails to play a role in this type of Friedel-Crafts and a methyl group attached to an alkene prevents the approach of the donor molecule.

Next, we intended to dehydrogenate indolines **12aa-12ak** to give the corresponding indoles. Firstly, **12aa** as a model molecule was subjected to oxidation reaction with oxidizing reagents such as $MnO_2$ and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),[23] and these dehydrogenations resulted in a complex mixture. Our previous study showed that DEAD oxidized protection-free indoline to indole.[23] To our great pleasure, the oxidation of **12aa** with diethyl azodicarboxylate (DEAD) as a milder oxidant in methylene chloride at room temperature for 2 h worked well and the expected product **13aa** was obtained in 55% yield (Scheme 3). Encouraged by this result, the oxidations of other indolines **12ab-aj** under same conditions were studied, and the corresponding 1-benzyl indoles **13ab-13aj** were obtained with good yields (55-90%) (Scheme 3). The oxidation of the indoline **12ai** including furan ring under the same conditions gave inseparable product mixture. Recently, Davis and group reported an oxidation of amines to imines utilizing DEAD.[29] The proposed mechanisms for the oxidation reaction of indoline are shown in Scheme 4. The first has been previously proposed by Davis and group via a triazane intermediate **[D]** for the conversion of seconder amines to imines (Scheme 4, A-pathway). Secondly, the oxidation can occur through an intermolecular hydride transfer (Scheme 4, B-pathway).

**Scheme 1.** Scope of Indolines (**10a-c**) and Nitroolefins (**11a-k**).




[a]Reaction conditions: **10a-c** (1.0 equiv), **11a-k** (1.0 equiv). Isolated yield.

**Scheme 2.** Plausible Reaction Mechanism for C5-Alkylation of 1-Benzylindoline (**10a**).

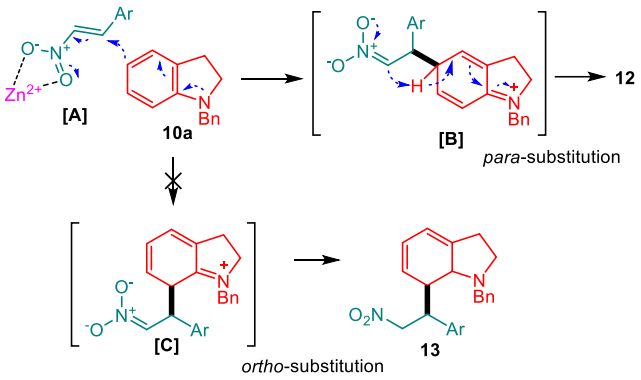
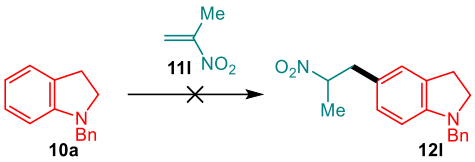


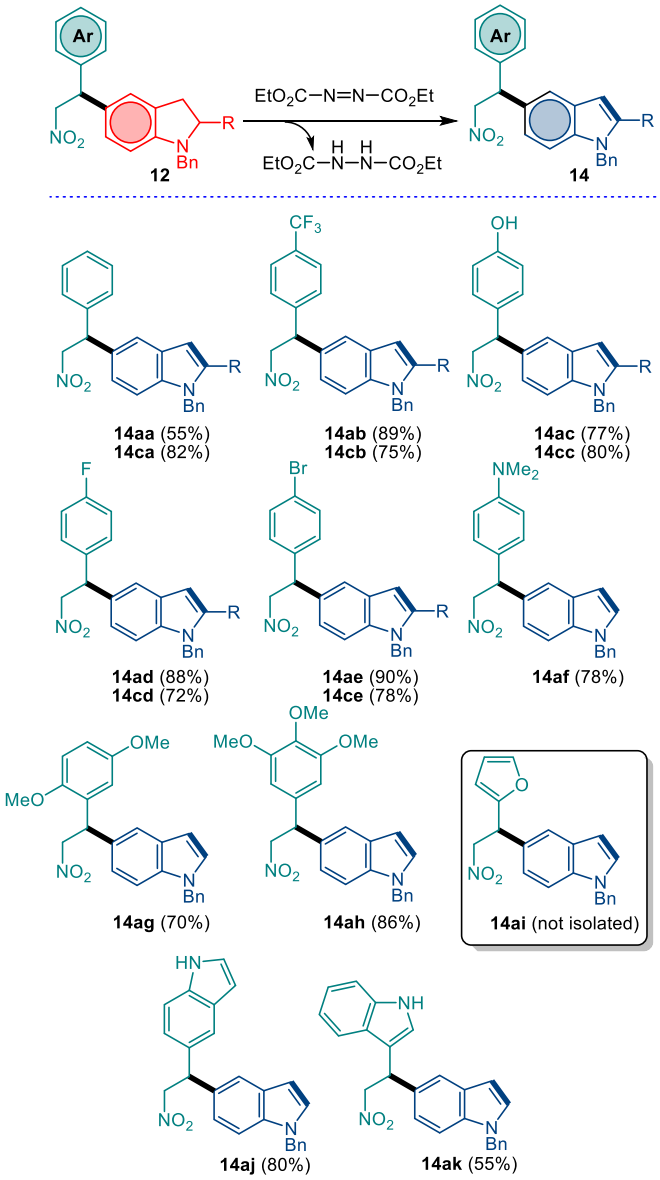

**Table 2.** Reaction between 1-Benzylindoline (**10a**) and 2-Nitroprop-1-ene (**12l**).




| entry | catalyst | x (mol%) | solvent | *T* (°C) | *t* (h) |
|---|---|---|---|---|---|
| 1 | $Zn(CF_3CO_2)_2$ | 0.2 | EtOH | 25 | 5 |
| 2 | $Zn(OTf)_2$ | 0.2 | EtOH | 25 | 5 |
| 3 | $Zn(OTf)_2$ | 0.5 | EtOH | 25 | 5 |
| 4 | $Zn(OTf)_2$ | 0.2 | Toluen | 80-100 | 12 |
| 5 | $Zn(OTf)_2$ | 0.2 | DMF | 25 | 12 |
| 6 | $AuCl_3$ | 0.2 | EtOH | 25 | 5 |
| 7 | $SnCl_2$ | 0.2 | EtOH | 25 | 5 |
| 8 | $AlCl_3$ | 0.2 | EtOH | 25 | 5 |
| 9 | $AlCl_3$ | 0.2 | THF | 25 | 5 |
| 10 | $Zn(OTf)_2$-TFA | 0.2 | EtOH | 25 | 3 |
| 11 | $Zn(OTf)_2$-*p*-TSA | 0.2 | EtOH | 25 | 3 |
| 12 | TFA | 0.2 | EtOH | 25 | 5 |
| 13 | *p*-TSA | 0.2 | EtOH | 25 | 5 |
| 14 | $Zn(OTf)_2$ | 0.2 | 2-nitropropen | 25 | 5 |

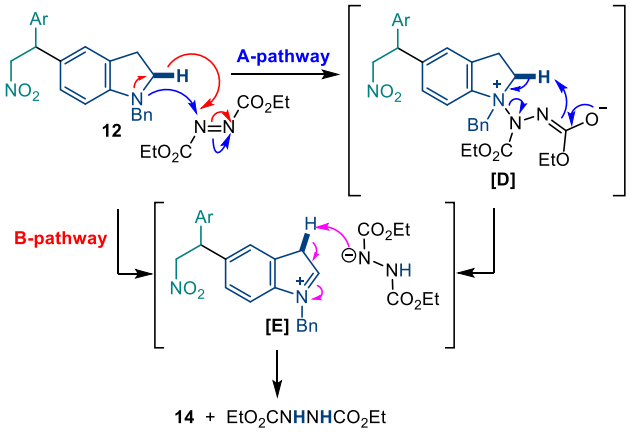
[a]Reaction conditions: **10a** (1.0 equiv), **11l** (1.0 equiv).

**Scheme 3.** Scope of Indolines (**12aa-ak**) to Indoles (**14aa-ak**).



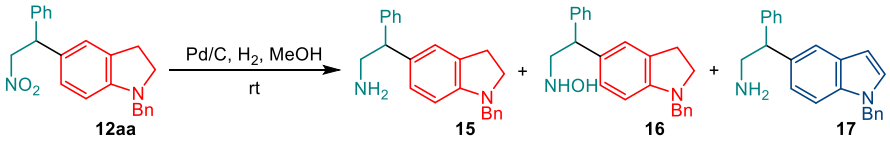

[a]Reaction conditions: **12** (1.0 equiv) and DEAD (1.1 equiv) in DCM were stirred at room temperature for 12 h. Isolated yield.

**Scheme 4.** Proposed Mechanisms for the Oxidation of Indolines (**12**) to Indoles (**14**).

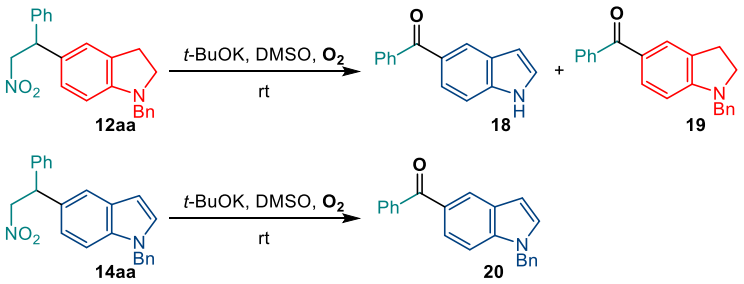


Next, we turned our attention to the removal of the benzyl-protecting group of C5-alkylated indolines **12** and indoles **14** to access main skeletons. The corresponding *N*-benzylindoline **12aa** and indole **14aa** were chosen as representative substrates. To observe its behavior toward catalytic hydrogenation of both benzyl and nitro group, indoline **12aa** was subjected to a Pd-catalyzed hydrogenation reaction. Catalytic hydrogenation gave an inseparable mixture of amine and hydroxylamine derivatives **15-17** via the reduction of the nitro group, whereas no deprotection of benzyl group was observed (Scheme 5). The formation of indole **17** can be attributed to the Pd-catalyzed oxidation of indoline **15**. Furthermore, neither hydrogenolysis catalyzed by palladium hydroxide on carbon ($Pd(OH)_2/C$),[30] nor oxidative debenzylation with cerium (IV) ammonium nitrate (CAN)[31] resulted in any reaction. The starting material was recovered in nearly quantitative yields in both cases. Since three debenzylation attempts were not successful, we decided to investigate whether Deaton-Rewolinski's[32] and Gigg-Conant's[33] debenzylation conditions were viable for our purpose. According to this procedure, while treatment of *N*-benzylindoline **12aa** with potassium *tert*-butoxide/dimethyl sulfoxide (DMSO) and oxygen at room temperature afforded unexpected ketones **18** and **19** in 39 and 43% yield, indole derivative **14aa** gave ketone **20** in 48% yield under the same conditions (Scheme 6). The proposed mechanism for this unexpected transformation is shown in Scheme 7. This mechanism was adapted from a proposed mechanism for the *N*-debenzylation of amides by Gigg and Conant.[33] The resulting benzylic anion **[E]** under basic conditions reacts with oxygen. The peroxy anion intermediate, **[F]**, is easily reduced in the presence of DMSO to afford dimethyl sulfone and an alkoxide, **[G]**, which breaks down to generate ketone **19** and nitromethane. We propose that the formation of ketone **18** involves debenzylation of **19** followed by an oxidation of indoline to indole (Scheme 7).

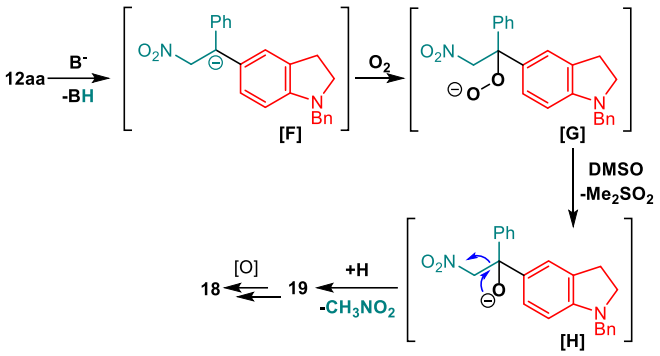
**Scheme 5.** Catalytic hydrogenation of **12aa**.




**Scheme 6.** Reaction of **12aa** and **14aa** with *t*-BuOK/DMSO and Oxygen.

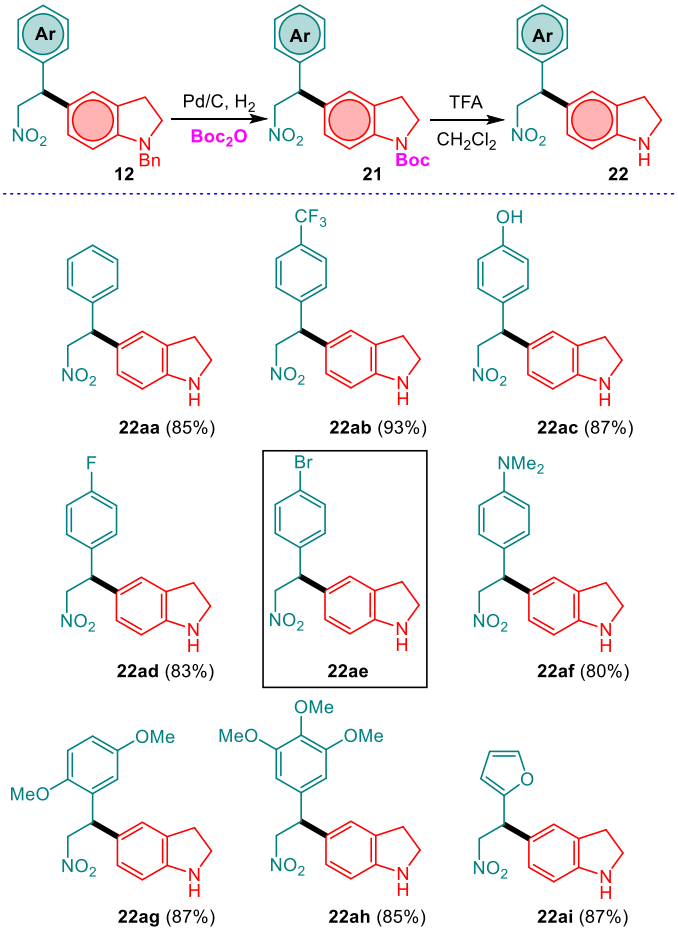



**Scheme 7.** Proposed Mechanism for Formation of Ketones **18/19**.



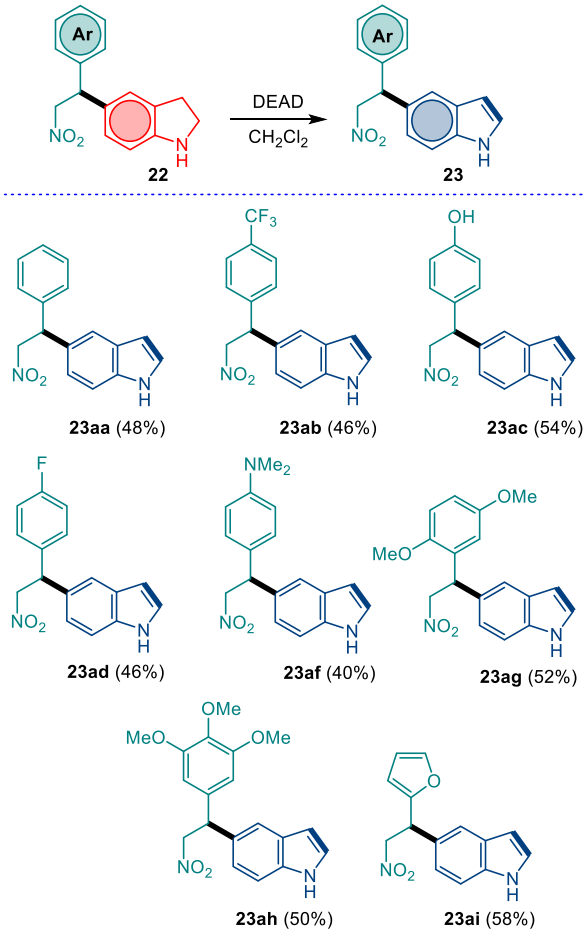

To overcome this problem, we explored a two-step protocol which has been successfully applied for debenzylation of 5-trimethylsilyl-*N*-benzylindoline.[27] The first step of this protocol was the hydrogenolysis in the presence of acetic anhydride so that following the splitting off of the *N*-benzyl group, the amino group was acetylated. In the second step, *N*-acetyl group was hydrolyzed by KOH in diethylene glycol to the corresponding indoline. Catalytic hydrogenolysis in acetic anhydride of indoline **12aa** as a test reaction gave 5-alkylated-*N*-acetylindoline **21aa** in 50% yield. Unfortunately, an alkaline hydrolysis of **21aa** provided a complex product mixture which cannot be separated. Probably, the nitro-alkane structure is not stable under basic conditions, therefore, we decided to use *tert*-butoxycarbonyl (Boc) group as the protecting group, which can be easier deprotected, instead of an acetyl group. Using di-*tert*-butyl dicarbonate ($Boc_2O$), the desired product **22aa** was formed in 93% yield (Scheme 8). In connection with this result, we examined such consecutive debenzylation/Boc-deprotection reaction on other *N*-benzylindolines **12ab-ah** and successfully obtained the corresponding indolines in 80–93% yield (Scheme 8). Unfortunately, the use of **12aj** and **12ak** as substrates failed to give the desired products **22aj** and **22ak** during the deprotection step using such reagents as trifluoroacetic acid (TFA),[34] molecular iodine,[35] tetrabutylammonium fluoride (TBAF),[36] and boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$).[37] It is noteworthy that the reaction of indoline substrate **12ae** bearing a bromine atom on the phenyl ring under the optimized conditions led to an inseparable mixture of the expected product **22ae** and the by-product **22aa** via reduction of the bromine atom. Notably, $Pd(OH)_2$-catalyzed hydrogenation in the presence of $Boc_2O$ followed by deprotection with TFA afforded the debrominated product **22aa**. Furthermore, when we evaluated the debenzylation of *N*-benzylindole derivatives **12aa** as a model compound with both the consecutive debenzylation/Boc-deprotection reaction and Pd/C-catalyzed hydrogenation in MeOH, $Pd(OH)_2$/C-catalyzed hydrogenation in *t*-BuOH/$H_2O$, and oxidative debenzylation with a CAN, no formation of **23aa** occurred and the starting material was recovered in almost quantitative yield. Gratifyingly, the oxidation of the unprotected-indolines with DEAD gave the desired indole **23** in a moderate yield (40-58%), as demonstrated in Scheme 9.

**Scheme 8.** Scope of Debenzylation for Indolines.




[a]Reaction conditions: **12** (1.0 equiv), $Boc_2O$ (1.1 mmol), and Pd/C (0.2 mmol) in MeOH/DCM were stirred under hydrogen atmosphere. To a solution of **21** in DCM was added TFA (1 mL). Isolated yield.

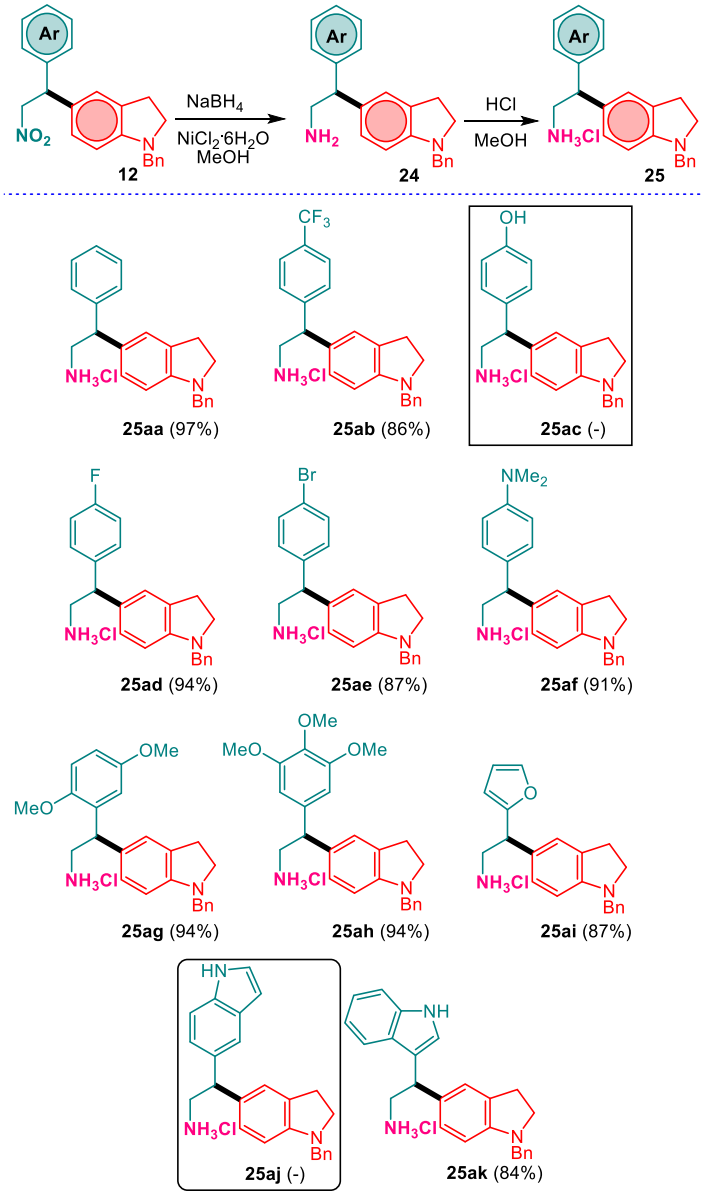
**Scheme 9.** Scope of Unprotected indolines to Indoles.




[a]Reaction conditions: **22** (1.0 equiv) and DEAD (1.1 equiv) in DCM were stirred at room temperature for 12 h. Isolated yield.

To access new silodosin precursors, we also probed the scope of the reduction of the aliphatic nitro groups in the indolines/indoles to amines. *N*-Benzylndoline **12aa** was taken as the model substrate and subjected to reduction with $LiAlH_4$ and Zn-HCl. However, complex mixtures were observed. When $SnCl_2$/AcOH was used reduction was not observed. Using $NaBH_4$-$NiCl_2$ system in methanol as reducing agent, the reaction produced a mixture of the desired amine **24aa** as a major product along with a possible partial reduction product which could not be separated by chromatography and crystallization. Therefore, the crude reduction mixture in methanol was reacted with concentrated HCl to precipitate the amine as its insoluble hydrochloride salt, which could then be recrystallized from ether (Scheme 10). Furthermore, while nine hydrochloride salts **25** were obtained from the corresponding nitro groups in excellent yields (84-97%), only indolines **12ac** and **12aj** did not produce the desired results (Scheme 10). Contrarily, the reduction with the $NaBH_4$-$NiCl_2$ system in methanol was also applied to reduce the aliphatic nitro group of indole derivatives **14** and afforded the corresponding amines **26** in high to excellent yields (78-95%) (Scheme 11). Finally, the reduction of the nitro group in indole **23aa** without *N*-benzyl group as a model compound with $NaBH_4$-$NiCl_2$ system afforded the corresponding amine **27aa** with 92% yield (Scheme 12).

**Scheme 10.** Reduction Scope of Nitro Groups in *N*-Benzylindolines.



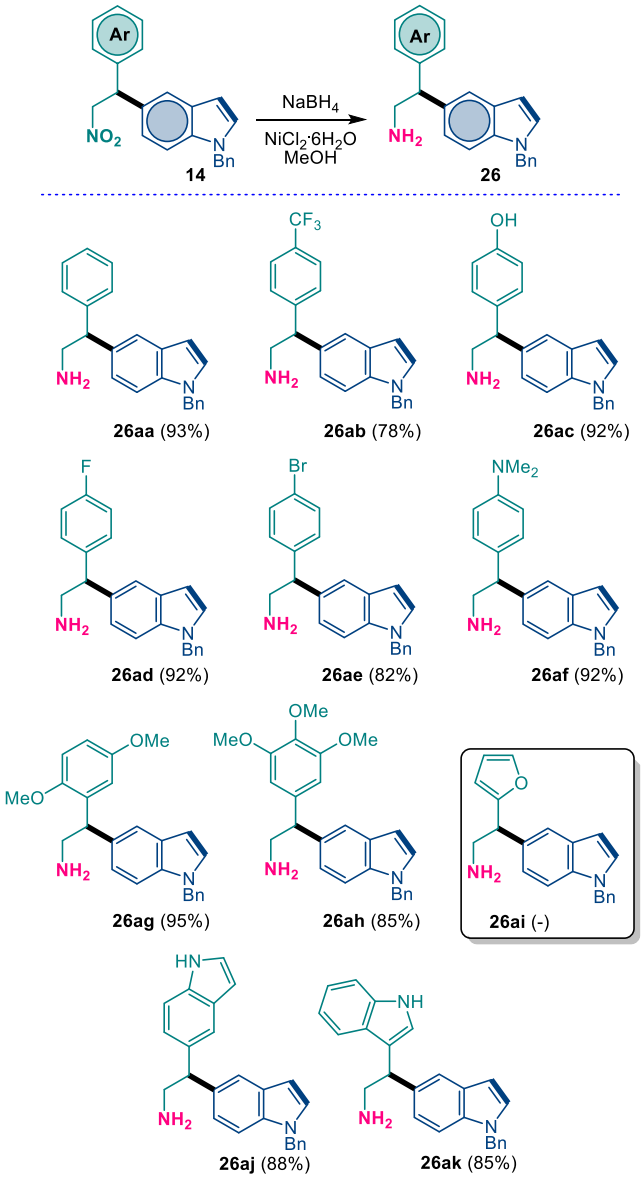

[a]Reaction conditions: **12** (1.0 equiv), $NiCl_2 \cdot 6H_2O$ (1.0 equiv), and $NaBH_4$ (5.0 equiv) in MeOH were stirred at 0 °C for 0.5 h. To a solution of **24** in MeOH (0.5 mL) was added HCl (12 M, 1.2 equiv). Isolated yield.

## ■ CONCLUSION

In summary, we have developed an effective strategy for the synthesis of diverse C5-alkylated indolines by zinc triflate-catalyzed Michael-type Friedel-Crafts reaction of *N*-benzylindolines with nitroolefins. The new approach displays a powerful method for the direct C5-alkylation of indolines. The corresponding indolines were oxidized using diethyl azodicarboxylate to afford a series of C5-alkylated indoles in good to excellent yields. Furthermore, the C5-alkylated *N*-benzylindolines were further functionalized through debenzylation and oxidation reactions. Nitroalkane groups could be

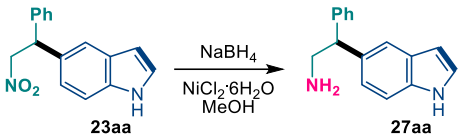
transformed into corresponding amine-hydrochloride salts and amines with sodium borohydride catalyzed by nickel(II) chloride. The present protocol provides a useful synthetic strategy to access various biologically active C5-alkylated indolines/indoles. The asymmetric synthesis of C5-alkylated indolines/indoles, study their bioactivities and synthesis of new silodosin-analogs will be our focus in the future.

**Scheme 11.** Reduction Scope of Nitro Groups in *N*-Benzylindoles.




[a]Reaction conditions: **14** (1.0 equiv), $NiCl_2·6H_2O$ (1.0 equiv), and $NaBH_4$ (5.0 equiv) in MeOH were stirred at 0 °C for 0.5 h. Isolated yield.

**Scheme 12.** Synthesis of Indole **27aa**.




## ■ EXPERIMENTAL SECTION

**General Experimental Methods.** All reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich) and used without further purification. Column chromatography and thin-layer chromatography (TLC) were performed using Silica gel 60 (70-230 Fluka) and Silica gel 60 HF254 (Fluka), respectively. Melting points were determined on Buchi 539 capillary melting apparatus and are uncorrected. Infrared spectra were recorded on a Mattson 1000 FT-IR spectrophotometer. $^{1}$H NMR, $^{13}$C NMR spectra were recorded on 400 (100)-MHz Varian and Bruker spectrometer and are reported in δ units with $SiMe_4$ as the internal standard. Data for $^{1}$H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quarted, p = pentet, m = multiplet, bs = broad singlet, bd = broad doublet) and coupling constant(s) in Hz, integration. Elemental analyses were carried out on a Leco CHNS-932 instrument. High-resolution mass spectrometry measurements were recorded on a Q-TOF mass spectrometer.

**General Procedure 1 (GP1): Preparation of *N*-Protected indolines (10a, 10b)**

*N*-Protected indolines was synthesized according to literature. Indoline (5.0 g, 42 mmol) was added to saturated $NaHCO_3$ in 15 mL of water and the mixture was stirred with heating to 90-95 °C. Benzyl bromide (7.2 g, 42 mmol) was added dropwise during 1.5 hr, and stirring and heating was continued for an additional 3.5 hr. After cooling the layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried over sodium sulfate. Concentration and purification through silica gel column chromatography gave desired *N*-protected indolines.

*1-Benzylindoline (**10a**).*[38] Compound **10a** was obtained using **GP1**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as colourless oil (8.2 g, 93% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, =CH, 4H), 7.34 – 7.26 (m, =CH, 1H), 7.16 – 7.06 (m, =CH, 2H), 6.79 – 6.63 (m, =CH, 1H), 6.56 (d, *J* = 7.8 Hz, =CH, 1H), 4.30 (s, $CH_2$, 2H), 3.36 (t, *J* = 8.3 Hz, $CH_2$, 2H), 3.02 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.5, 138.4, 130.0, 128.4, 127.9, 127.3, 127.1, 124.5, 117.7, 107.0, 53.7, 53.6, 28.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3394, 3026, 2919, 2823, 1875, 1607, 1488, 1471, 1453, 1357, 1269, 1154, 1026, 980, 865, 790. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69; found: C, 86.01; H, 6.92; N, 6.64. Rf = 0.60 (EtOAc/Hexane (1:9), 254 nm).

*1-Benzyl-2-methylindoline (**10b**).*[39] Compound **10b** was obtained using **GP1**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as purple oil (16.7 g, 99% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, =CH, 4H), 7.36 (t, *J* = 7.1 Hz, =CH, 1H), 7.18 (d, *J* = 7.1 Hz, =CH, 1H), 7.11 (t, *J* = 7.1 Hz, =CH, 1H), 6.76 (t, *J* = 7.1 Hz, =CH, 1H), 6.45 (d, *J* = 7.1 Hz, =CH, 1H), 4.48 (d, *J* = 16.1 Hz, A part of AB system, $CH_2$, 1H), 4.31 (d, *J* = 16.1 Hz, B part of AB system, $CH_2$, 1H), 3.88 – 3.80 (m, CH, 1H), 3.29 (dd, *J* = 15.4, 9.0 Hz, A part of AB system, $CH_2$, 1H), 2.80 (dd, *J* = 15.4, 9.0 Hz, B part of AB system, $CH_2$, 1H), 1.42 (d, *J* = 6.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.8, 139.4, 128.9, 128.6, 127.57, 127.52, 127.0, 124.3, 117.6, 107.0, 60.7, 51.3, 37.5, 19.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3026, 2963, 2836, 1606, 1483, 1452, 1352, 1268, 1236, 1145, 1024, 900, 854, 745. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27; found: C, 86.26; H, 7.45; N, 6.03. Rf = 0.64 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}N$ 224.1434; Found 224.1435.

*Ethyl 1-benzylindoline-2-carboxylate (**10c**).*[40] Ethyl 1-benzylindoline-2-carboxylate (**10c**) was synthesized according to literature.[40] A mixture of ethyl indoline-2-carboxylate (1.0 g, 5.23 mmol), $K_2CO_3$ (2.17 g, 15.69 mmol) and benzyl bromide (2.68, 15.69 mmol) in 10 mL DMF was heated with an oil bath to 100 °C. On cooling the reaction mixture was poured into ice water and extracted with ether. The extract was washed with water and dried over sodium sulfate. Concentration and purification through silica gel column chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (1.35 g, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, =CH, 4H), 7.27 – 7.20 (m, =CH, 1H), 7.05 – 7.00 (m, =CH, 2H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 4.51 (d, *J* = 15.5 Hz, A part of AB system, $CH_2$, 1H), 4.30 (d, *J* = 15.5 Hz, B part of AB system, $CH_2$, 1H), 4.23 (dd, *J* = 10.2, 8.3 Hz, CH, 1H), 4.18–4.03 (m, $CH_2$, 2H), 3.37 (dd, *J* = 15.9, 10.2 Hz, A part of AB system, $CH_2$, 1H), 3.19 (dd, *J* = 15.9, 8.3 Hz, B part of AB system, $CH_2$, 1H), 1.20 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.9, 151.5, 137.9, 128.5, 127.9, 127.8, 127.2, 127.0, 124.2, 118.2, 107.2, 65.5, 61.0, 52.2, 33.5, 14.2. IR ($CH_2Cl_2$, $cm^{-1}$): 3556, 3060, 3029, 2980, 2930, 2905, 2855, 1878, 1728, 1607, 1485, 1453, 1328, 1262, 1191, 1162, 1028, 745, 698. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98; found: C, 76.77; H, 6.61; N, 4.91. Rf = 0.48 (EtOAc/Hexane (1:9), 254 nm).

*N-Acetylindoline (10d).*[41] *N*-Acetylindoline (**10d**) was synthesized according to literature.[41] Indoline (2.00 g, 16.78 mmol) is dissolved in acetic anhydride (7.92 mL, 83.92 mmol) at room temperature, followed by addition of pyridine (0.812 mL, 10.07 mmol). The reaction mixture is heated with an oil bath to 120 °C and maintained for 4 h. The reaction is quenched by addition of 2N NaOH (10 mL), and the resulting mixture is diluted with ethyl acetate (2×30 mL). The phases are separated, and the organic phase is washed with saturated aqueous $NaHCO_3$ (20 mL), dried over anhydrous $Na_2SO_4$. Concentration and purification through silica gel column chromatography (EtOAc/Hexane (2:8)) gave the product as white crystals (2.62 g, 96% yield; mp 97-98 °C ($CH_2Cl_2$/hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J*

= 7.7 Hz, =CH, 1H), 7.21 – 7.10 (m, =CH, 2H), 6.99 (t, *J* = 7.7 Hz, =CH, 1H), 4.01 (t, *J* = 8.5 Hz, $CH_2$, 2H), 3.16 (t, *J* = 8.5 Hz, $CH_2$, 2H), 2.19 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.1, 131.3, 127.7, 124.7, 123.7, 117.1, 48.9, 28.1, 24.4. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69; found: C, 74.70; H, 6.99; N, 8.52. Rf = 0.13 (EtOAc/Hexane (3:7), 254 nm).

**General Procedure 2 (GP2): Synthesis of Nitroolefines (11a-k)**

Nitroolefines were synthesized according to literature.[28b] Aldehyde (1.0 equiv), nitromethane (6.0 equiv) and piperidine (0.1 equiv) were added sequentially to a round-bottomed flask containing toluene (3 mL). To this mixture anhydrous $FeCl_3$ (0.1 equiv) was added, and the mixture was heated to reflux slowly for 4 h. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. The excess solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (EtOAc/Hexane (1:9)) to give desired nitroalkenes **11a-k**.

*(E)-1-(2-Nitrovinyl)-4-(trifluoromethyl)benzene (**11b**).*[42] Compound **11b** was obtained using **GP2**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as light yellow crystals (392 mg, 87% yield; mp 76–77 °C ($CH_2Cl_2$/hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 13.7 Hz, A part of AB system, =CH, 1H), 7.74 – 7.72 (m, AA' part of AA'BB' system, =CH, 2H), 7.69 – 7.67 (m, BB' part of AA'BB' system, =CH, 2H), 7.63 (d, *J* = 13.7 Hz, B part of AB system, =CH, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 133.6 – 133.3 (m, 1C), 129.2, 126.36 (q, *J* = 3.7 Hz, 1C), 124.8, 122.1. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 3110, 1925, 1640, 1524, 1416, 1342, 1325, 1165, 1115, 1068, 968, 830. Anal. Calcd for $C_9H_6F_3NO_2$: C, 49.78; H, 2.79; N, 6.45; found: C, 49.99; H, 2.91; N, 6.21. Rf = 0.73 (EtOAc/Hexane (3:7), 254 nm).

*(E)-N,N-Dimethyl-4-(2-nitrovinyl)aniline (**11f**).*[43] Compound **11f** was obtained using **GP2**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as red crystals (216 mg, 82% yield; mp 179–180 °C ($CH_2Cl_2$/hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 13.4 Hz, A part of AB system, =CH, 1H), 7.51 (d, *J* = 13.4 Hz, B part of AB system, =CH, 1H), 7.45 – 7.43 (m, AA' part of AA'BB' system, =CH, 2H), 6.71 – 6.69 (m, BB' part of AA'BB' system, =CH, 2H), 3.10 (s, $CH_3$, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.0, 140.3, 132.0, 131.4, 117.2, 111.9, 40.0. IR ($CH_2Cl_2$, $cm^{-1}$): 2917, 1617, 1555, 1438, 1417, 1327, 1236, 1068, 968, 808, 798. Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57; found: C, 62.28; H, 6.24; N, 14.45. Rf = 0.32 (EtOAc/Hexane (3:7), 254 nm).

*(E)-1,2,3-Trimethoxy-5-(2-nitrovinyl)benzene (**11h**).*[44] Compound **11h** was obtained using **GP2**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as yellow crystals (1.04 g, 85% yield; mp 144–145 °C ($CH_2Cl_2$/hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 13.6 Hz, A part of AB system, =CH, 1H), 7.53 (d, *J* = 13.6 Hz, B part of AB system, =CH, 1H), 6.76 (s, =CH, 2H), 3.91 (s, $CH_3$, 3H), 3.90 (s, $CH_3$, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.9, 142.0, 139.5, 136.6, 125.5, 126.6, 61.3, 56.5. IR ($CH_2Cl_2$, $cm^{-1}$): 2945, 2841, 1625, 1581, 1509, 1491, 1420, 1337, 1249, 1193, 1132, 971, 819. Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86; found: C, 55.45; H, 5.43; N, 5.61. Rf = 0.28 (EtOAc/Hexane (3:7), 254 nm).

*(E)-5-(2-Nitrovinyl)-1H-indole (**11j**).*[45] Compound **11j** was obtained using **GP2**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow crystals (545 mg, 83% yield; mp 154–155 °C (Acetone/hexane)). $^1$H NMR (400 MHz, Acetone-$d_6$) δ 10.67 (bs, NH, 1H), 8.22 (d, *J* = 13.5 Hz, =CH, A part of AB system, =CH 1H), 8.08 (s, =CH, 1H), 7.93 (d, *J* = 13.5 Hz, =CH, B part of AB system, =CH, 1H), 7.61 (dd, *J* = 8.6, 1.6 Hz, A part of AB system, =CH, 1H), 7.56 (d, *J* = 8.6 Hz, B part of AB system, =CH, 1H), 7.49 – 7.44 (m, =CH, 1H), 6.68 – 6.57 (m, =CH, 1H). $^{13}$C NMR (100 MHz, Acetone-$d_6$) δ 142.1, 139.4, 135.5, 129.5, 127.6, 125.4, 122.7, 122.5, 113.3, 103.7. IR (Acetone, $cm^{-1}$): 3376, 2733, 1605, 1494, 1329, 1300, 1285, 1217, 1129, 973, 894, 805, 766. Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.29; N, 14.89; found: C, 63.50; H, 4.53; N, 14.57. Rf = 0.40 (Acetone/Hexane (3:7), 254 nm).

*(E)-3-(2-Nitrovinyl)-1H-indole (**11k**).*[40] Compound **11k** was obtained using **GP2**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow crystals (420 mg, 78% yield; mp 167–168 °C (Acetone/hexane)). $^1$H NMR (400 MHz, Acetone-$d_6$) δ 11.29 (bs, NH, 1H), 8.40 (d, *J* = 13.5 Hz, A part of AB system, =CH, 1H), 8.19 – 8.18 (m, =CH, 1H), 8.02 – 7.96 (m, =CH, 1H), 7.93 (d, *J* = 13.5 Hz, B part of AB system, =CH, 1H), 7.65 – 7.56 (m, =CH, 1H), 7.41 – 7.22 (m, =CH, 2H). $^{13}$C NMR (100 MHz, Acetone-$d_6$) δ 138.2, 135.1, 134.0, 132.1, 125.2, 123.7, 122.2, 120.6, 112.9, 108.9. IR (Acetone, $cm^{-1}$): 3433, 2078, 1638, 1476, 1310, 1237, 1132, 965. Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.29; N, 14.89; found: C, 63.97; H, 4.43; N, 14.66. Rf = 0.27 (Acetone/Hexane (3:7), 254 nm).

*2-Nitroprop-1-ene (**11l**).* 2-Nitroprop-1-ene (**11l**) was synthesized according to literature.[46] 2-Nitro-1-butanol (2.10 g, 20 mmol) and phthalic anhydride (5.92 g, 40 mmol) was added to a round-bottomed flask. The reaction mixture was heated to 150-200 °C and distillated under water aspirator pressure. The desired product distilled over with water into an ice-cooled receiving flask. The aqueous layer was separated and the organic layer was dried over sodium sulfate to give compound **11l**. Compound **11l** was recovered as blue-green oil (890 mg, 52% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.4 (s, =CH, 1H), 5.6 (s, =CH, 1H), 2.2 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2, 118.2, 17.1. IR ($CH_2Cl_2$, $cm^{-1}$): 3363, 2889, 1718, 1556, 1361, 1230, 1002, 849. Anal. Calcd for $C_3H_5NO_2$: C, 41.38; H, 5.79; N, 16.09; found: C, 41.13; H, 5.86; N, 15.72. Rf = 0.43 (EtOAc/Hexane (1:9), 254 nm).

**General Procedure 3 (GP3): Preparation of C5-Alkylated Indolines**

To a solution of β-nitrostyrene derivatives (1.0 equiv.) in ethanol (10 mL) was added $Zn(OTf)_2$ (0.2 equiv.) at room temperature. After stirring for 30 min, a solution of *N*-alkyl indoline (1.0 equiv.) in

ethanol (5 mL) was added dropwise for 5 min to the solution. The mixture was stirred for 12 h at room temperature. After removal of the solvent, the residue was dissolved in $CH_2Cl_2$ (30 mL) and washed with water (2×30 mL). The combined organic layer was dried over $Na_2SO_4$. Concentration and purification through silica gel column chromatography gave desired C5-alkylation products.

*(±)-1-Benzyl-5-(2-nitro-1-phenylethyl)indoline (**12aa**).* Compound **12aa** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as light yellow crystals (2.36 g, 98% yield; mp 77–78 °C ($CH_2Cl_2$/hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, =CH, 10H), 6.94 – 6.87 (m, =CH, 2H), 6.40 (d, *J* = 8.0 Hz, =CH, 1H), 4.94 (dd, *J* = 11.7, 7.4 Hz, A part of AB system, $CH_2$, 1H), 4.89 (dd, *J* = 11.7, 7.4 Hz, B part of AB system, $CH_2$, 1H), 4.78 (t, *J* = 8.2 Hz, CH, 1H), 4.20 (s, $CH_2$, 2H), 3.30 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.91 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.0, 140.1, 138.3, 130.9, 128.9, 128.5, 128.2, 127.9, 127.6, 127.3, 127.2, 126.6, 124.0, 106.9, 79.7, 53.7, 53.6, 48.7, 28.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3430, 3028, 2916, 2827, 1615, 1551, 1496, 1453, 1377, 1271, 1156, 1079, 1029, 890, 809, 734. Anal. Calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19; N, 7.82; found: C, 76.85; H, 6.26; N, 7.70. Rf = 0.64 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O_2$ 359.1760; Found 359.1740.

*(±)-1-Benzyl-5-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)indoline (**12ab**).* Compound **12ab** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as light yellow oil (141 mg, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, AA' part of AA'BB' system, =CH, 2H), 7.28 – 7.26 (m, BB' part of AA'BB' system, =CH, 2H), 7.24 – 7.23 (m, =CH, 4H), 7.20 –7.13 (m, =CH, 1H), 6.80 – 6.76 (m, =CH, 2H), 6.31 (d, *J* = 8.0 Hz, =CH, 1H), 4.90 – 4.80 (m, $CH_2$, 2H), 4.78 – 4.72 (m, CH, 1H), 4.12 (s, $CH_2$, 2H), 3.23 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.83 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.3, 144.2, 138.1, 131.1, 129.7, 129.4, 128.5, 127.9, 127.8, 127.2, 127.11, 126.6, 125.9 (q, *J* = 3.7 Hz), 123.8, 106.9, 79.1, 53.5, 53.4, 48.4, 28.4. IR ($CH_2Cl_2$, $cm^{-1}$): 3439, 1618, 1554, 1497, 1376, 1326, 1266, 1164, 1118, 1069, 736, 701. Anal. Calcd for $C_{24}H_{21}F_3N_2O_2$: C, 67.60; H, 4.96; N, 6.57; found: C, 67.47; H, 4.74; N, 6.29. Rf = 0.32 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}F_3N_2O_2$ 427.1633; Found 427.1661.

*(±)-4-(1-(1-Benzylindolin-5-yl)-2-nitroethyl)phenol (**12ac**).* Compound **12ac** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (2.28 g, 99% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, =CH, 4H), 7.31 – 7.25 (m, =CH, 1H), 7.10 – 7.09 (m, AA' part of AA'BB' system, =CH, 2H), 6.96 – 6.86 (m, =CH, 2H), 6.75 – 6.74 (m, BB' part of AA'BB' system, =CH, 2H), 6.45 (d, *J* = 8.3 Hz, =CH, 1H), 4.90 – 4.89 (m, $CH_2$, 2H), 4.88 (bs, OH, 1H), 4.73 (t, *J* = 8.3 Hz, CH, 1H), 4.23 (s, $CH_2$, 2H), 3.31 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.92 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1, 152.1, 138.4, 132.3, 131.2, 129.0, 128.9, 128.8, 128.2, 127.5, 126.7, 124.2, 116.0, 107.3, 80.2, 53.90,

53.89, 48.2, 28.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3361, 3025, 2823, 1613, 1550, 1513, 1496, 1376, 1265, 1174, 834, 734. Anal. Calcd for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48; found: C, 73.92; H, 5.63; N, 7.27. Rf = 0.31 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O_3$ 375.1709; Found 375.1683.

*(±)-1-Benzyl-5-(1-(4-fluorophenyl)-2-nitroethyl)indoline (**12ad**).* Compound **12ad** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (2.11 g, 93% yield). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.37 (m, =CH, 4H), 7.34 – 7.32 (m, =CH, 1H), 7.28 – 7.25 (m, =CH, 2H), 7.05 (t, *J* = 8.5 Hz, =CH, 2H), 7.00 – 6.88 (m, =CH, 2H), 6.49 – 6.46 (m, =CH, 1H), 4.93 (dd, *J* = 8.3, 2.8 Hz, $CH_2$, 2H), 4.86 – 4.79 (m, CH, 1H), 4.27 (s, $CH_2$, 2H), 3.36 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.97 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.9 Hz), 152.3, 138.4, 136.1, 131.3, 129.4 (d, *J* = 8.1 Hz), 128.8, 128.19, 128.14, 127.5, 126.7, 124.1, 116.1 (d, *J* = 21.4 Hz), 107.1, 79.9, 53.9, 53.7, 48.1, 28.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3029, 2918, 2830, 1889, 1604, 1551, 1508, 1376, 1268, 1228, 1160, 1098, 1015, 943, 890, 837. Anal. Calcd for $C_{23}H_{21}FN_2O_2$: C, 73.39; H, 5.62; N, 7.44; found: C, 73.27; H, 5.57; N, 7.27. Rf = 0.32 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}FN_2O_2$ 377.1665; Found 377.1642.

*(±)-1-Benzyl-5-(1-(4-bromophenyl)-2-nitroethyl)indoline (**12ae**).* Compound **12ae** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (1.90 g, 99% yield). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, AA' part of AA'BB' system, =CH, 2H), 7.35 – 7.23 (m, =CH, 5H), 7.13 – 7.11 (m, BB' part of AA'BB' system, =CH, 2H), 6.89 – 6.83 (m, =CH, 2H), 6.40 (d, *J* = 8.0 Hz, =CH, 1H), 4.91 (dd, *J* = 11.4, 7.0 Hz, A part of AB system, $CH_2$, 1H), 4.86 (dd, *J* = 11.4, 7.0 Hz, B part of AB system, $CH_2$, 1H), 4.78 – 4.71 (m, CH, 1H), 4.21 (s, $CH_2$, 2H), 3.32 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.92 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 152.2, 139.1, 138.2, 132.0, 131.1, 129.3, 128.5, 127.8, 127.5, 127.2, 126.6, 123.8, 121.3, 106.9, 79.4, 53.6, 53.4, 48.1, 28.4. IR ($CH_2Cl_2$, $cm^{-1}$): 3414, 3025, 2806, 1678, 1551, 1488, 1376, 1202, 1071, 1006, 883, 802, 730. Anal. Calcd for $C_{23}H_{21}BrN_2O_2$: C, 63.17; H, 4.84; N, 6.41; found: C, 63.40; H, 4.83; N, 6.32. Rf = 0.30 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}BrN_2O_2$ 437.0859; Found 437.0834.

*(±)-4-(1-(1-Benzylindolin-5-yl)-2-nitroethyl)-N,N-dimethylaniline (**12af**).* Compound **12af** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light green oil (61 mg, 57% yield). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, =CH, 4H), 7.20 – 7.17(m, =CH, 1H), 7.03 – 7.01 (m, AA' part of AA'BB' system, =CH, 2H), 6.89 – 6.77 (m, =CH, 2H), 6.60 – 6.58 (m, BB' part of AA'BB' system, =CH, 2H), 6.32 (d, *J* = 8.2 Hz, =CH, 1H), 4.80 (d, *J* = 8.3 Hz, $CH_2$, 2H), 4.62 (t, *J* = 8.3 Hz, CH, 1H), 4.13 (s, $CH_2$, 2H), 3.21 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.94 – 2.70 (m, $CH_2$, $CH_3$, 8H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 151.8, 149.7, 138.3, 130.8, 129.1, 128.5, 128.2, 127.8, 127.6, 127.1, 126.4, 123.9, 112.7, 106.8, 80.0,

53.7, 53.6, 47.8, 40.5, 28.4. IR ($CH_2Cl_2$, $cm^{-1}$): 2918, 2850, 1734, 1611, 1552, 1521, 1351, 1265, 1078, 881, 737. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47; found: C, 74.85; H, 6.52; N, 10.33. Rf = 0.54 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}N_3O_2$ 402.2182; Found 402.2156.

*(±)-1-Benzyl-5-(1-(2,5-dimethoxyphenyl)-2-nitroethyl)indoline (**12ag**).* Compound **12ag** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as green oil (1.78 g, 89% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, =CH, 4H), 7.33 – 7.24 (m, =CH, 1H), 7.03 – 6.99 (m, =CH, 2H), 6.84 (d, *J* = 8.4 Hz, =CH, 1H), 6.78 – 6.75 (m, =CH, 2H), 6.46 (d, *J* = 8.4 Hz, =CH, 1H), 5.20 – 5.16 (m, CH, 1H), 5.01 (dd, J = 12.7, 8.3 Hz, A part of AB system, $CH_2$, 1H), 4.90 (dd, J = 12.7, 8.3 Hz, B part of AB system, $CH_2$, 1H), 4.24 (s, $CH_2$, 2H), 3.82 (s, $CH_3$, 3H), 3.75 (s, $CH_3$, 3H), 3.33 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.95 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.8, 152.1, 151.3, 138.6, 130.9, 129.8, 128.7, 128.1, 127.8, 127.4, 127.1, 124.5, 115.8, 112.1, 112.0, 107.1, 78.6, 56.3, 55.8, 53.96, 53.95, 43.2, 28.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2953, 2834, 1615, 1551, 1497, 1376, 1226, 1048, 1025, 805, 736. Anal. Calcd for $C_{25}H_{26}N_2O_4$: C, 71.75; H, 6.26; N, 6.69; found: C, 71.78; H, 5.98; N, 6.61. Rf = 0.60 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}N_2O_4$ 419.1971; Found 419.1942.

*(±)-1-Benzyl-5-(2-nitro-1-(3,4,5-trimethoxyphenyl)ethyl)indoline (**12ah**).* Compound **12ah** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as green oil (1.43 g, 65% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, =CH, 5H), 6.97 – 6.88 (m, =CH, 2H), 6.49 – 6.39 (m, =CH, 3H), 4.92 (dd, *J* = 12.4, 8.1 Hz, A part of AB system, $CH_2$, 1H), 4.87 (dd, *J* = 12.4, 8.1 Hz, B part of AB system, $CH_2$, 1H), 4.73 (t, *J* = 8.1 Hz, CH, 1H), 4.22 (s, $CH_2$, 2H), 3.83 (s, $CH_3$, 6H), 3.82 (s, $CH_3$, 3H), 3.33 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.94 (t, *J* = 8.3 Hz, $CH_2$, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.7, 152.3, 138.4, 137.4, 135.8, 131.2, 128.8, 128.2, 128.0, 127.4, 126.6, 124.1, 107.1, 104.9, 79.9, 61.0, 56.4, 53.8, 53.7, 49.1, 28.7. IR ($CH_2Cl_2$, $cm^{-1}$): 2937, 2837, 1614, 1590, 1551, 1495, 1454, 1421, 1377, 1329, 1238, 1127, 1005, 908, 814. Anal. Calcd for $C_{26}H_{28}N_2O_5$: C, 69.63; H, 6.29; N, 6.25; found: C, 69.63; H, 6.43; N, 6.64. Rf = 0.44 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_5$ 449.2076; Found 449.2053.

*(±)-1-Benzyl-5-(1-(furan-2-yl)-2-nitroethyl)indoline (**12ai**).* Compound **12ai** was obtained using **GP3**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (2.29 g, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, =CH, 4H), 7.33 – 7.22 (m, =CH, 2H), 6.99 (s, =CH, 1H), 6.96 – 6.94 (m, AA' part of AA'BB' system, =CH, 1H), 6.45 – 6.43 (m, BB' part of AA'BB' system, =CH, 1H), 6.32 (dd, *J* = 3.2, 2.0 Hz, =CH, 1H), 6.12 (d, *J* = 3.2 Hz, =CH, 1H), 4.97 (dd, *J* = 11.9, 7.6 Hz, A part of AB system, $CH_2$, 1H), 4.85 – 4.79 (m, CH, 1H), 4.75 (dd, *J* = 11.9, 7.6 Hz, B part of AB system, $CH_2$, 1H), 4.24 (s, $CH_2$,

2H), 3.35 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.96 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.2, 152.6, 142.5, 138.4, 131.1, 128.7, 128.0, 127.4, 127.2, 125.9, 124.1, 110.5, 107.1, 107.1, 78.7, 53.8, 53.6, 43.4, 28.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3445, 2845, 1617, 1552, 1497, 1376, 1267, 1146, 1013, 810, 736. Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04; found: C, 72.51; H, 5.72; N, 8.15. Rf = 0.67 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_3$ 349.1552; Found 349.1528.

*(±)-5-(1-(1-Benzylindolin-5-yl)-2-nitroethyl)-1H-indole (**12aj**).* Compound **12aj** was obtained using **GP3**. Column chromatography (Acetone/Hexane (2:8)) gave the product as brown oil (1.85 mg, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, NH, 1H), 7.51 (s, =CH, 1H), 7.37 – 7.23 (m, =CH, 6H), 7.20 – 7.15 (m, =CH, 1H), 7.08 – 7.03 (m, =CH, 1H), 7.00 – 6.93 (m, =CH, 2H), 6.53 – 4.48 (m, =CH, 1H), 6.42 (d, *J* = 7.9 Hz, =CH, 1H), 5.03 – 4.95 (m, $CH_2$, 2H), 4.94 – 4.86 (m, CH, 1H), 4.21 (s, $CH_2$, 2H), 3.29 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.91 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.0, 138.6, 135.1, 131.8, 131.0, 129.5, 128.7, 128.3, 128.1, 127.4, 126.7, 125.0, 124.3, 122.3, 119.5, 111.7, 107.1, 102.9, 80.5, 53.9 (2C), 49.0, 28.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3422, 1614, 1549, 1496, 1377, 1266, 1094, 894, 732. Anal. Calcd for $C_{25}H_{23}N_3O_2$: C, 75.55; H, 5.83; N, 10.57; found: C, 75.29; H, 5.99; N, 10.24. Rf = 0.41 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_2$ 398.1869; Found 398.1854.

*(±)-3-(1-(1-Benzylindolin-5-yl)-2-nitroethyl)-1H-indole (**12ak**).* Compound **12ak** was obtained using **GP3**. Column chromatography (Acetone/Hexane (2:8)) gave the product as brown oil (1.85 mg, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, NH, 1H), 7.49 (d, *J* = 8.0 Hz, =CH, 1H), 7.35 – 7.23 (m, =CH, 6H), 7.21 – 7.15 (m, =CH, 1H), 7.10 – 6.98 (m, =CH, 4H), 6.41 (d, *J* = 8.7 Hz, =CH, 1H), 5.10 – 4.97 (m, $CH_2$, 2H), 4.90 – 4.82 (m, CH, 1H), 4.19 (s, $CH_2$, 2H) 3.31 – 3.24 (m, $CH_2$, 2H), 2.92 – 2.86 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.6, 138.4, 136.5, 130.8, 128.5, 128.3, 127.9, 127.2, 126.8, 126.3, 124.0, 122.6, 121.4, 119.8, 119.2, 115.3, 111.3, 106.9, 80.1, 53.7 (2C), 41.2, 28.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3419, 3047, 2957, 2913, 2829, 1615, 1548, 1495, 1456, 1378, 1265, 1098, 808, 741. Anal. Calcd for $C_{25}H_{23}N_3O_2$: C, 75.55; H, 5.83; N, 10.57; found: C, 75.31; H, 6.00; N, 10.63. Rf = 0.36 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_2$ 398.1869; Found 398.1847.

*(dia)-1-Benzyl-2-methyl-5-(2-nitro-1-phenylethyl)indoline (**12ba**).* Compound **12ba** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (1.08 mg, 86% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.31 (m, =CH, 10H), 7.04 (s, =CH, 1H), 6.98 – 6.93 (m, =CH, 1H), 6.39 – 6.37 (m, =CH, 1H), 5.06 – 4.82 (m, CH, $CH_2$, 3H), 4.45 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 4.28 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.88 – 3.81 (m, $CH_2$, 1H), 3.27 – 3.20 (m, $CH_2$, 1H), 2.75 (dd, *J* = 15.6, 9.4 Hz, $CH_2$, 1H), 1.44 – 1.37 (m, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.5, 140.6, 139.4, 130.0, 129.2, 128.9, 128.4, 127.9, 127.7, 127.6, 127.3, 127.0, 126.9, 124.0, 123.9, 107.0, 79.9, 61.1, 51.5, 49.0, 37.6, 20.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3061, 3028, 2963, 2925, 2839, 1615, 1551,

1494, 1453, 1377, 1354, 1270, 1161, 1109, 1002, 910, 879. Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.50; N, 7.52; found: C, 77.35; H, 6.50; N, 7.61. Rf = 0.68 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_2$ 373.1916; Found 373.1894.

*(dia)-1-Benzyl-2-methyl-5-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)indoline (**12bb**).* Compound **12bb** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (756 mg, 74% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, AA' part of AA'BB' system, =CH, 2H), 7.37 – 7.35 (m, BB' part of AA'BB' system, =CH, 2H), 7.33 – 7.27 (m, =CH, 4H), 7.27 – 7.18 (m, =CH, 1H), 6.84 (s, =CH, 1H), 6.79 (dd, *J* = 8.0, 2.4 Hz, =CH, 1H), 6.21 (dd, *J* = 8.0, 1.2 Hz, =CH, 1H), 5.07 – 4.63 (m, CH, $CH_2$, 3H), 4.32 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.14 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.78 – 3.69 (m, CH, 1H), 3.12 (dd, *J* = 15.7, 9.0 Hz, A part of AB system, $CH_2$, 1H), 2.62 (dd, *J* = 15.7, 9.0 Hz, B part of AB system, $CH_2$, 1H), 1.28 (d, *J* = 6.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.5, 144.3, 139.0, 130.1, 128.7, 128.1, 127.4, 127.2, 127.0, 126.89, 126.84, 126.1 – 126.0 (m, C), 123.7, 123.6, 106.9, 79.3, 60.8, 51.17, 51.16, 48.6, 37.3, 19.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3434, 2963, 1618, 1553, 1494, 1376, 1325, 1163, 1117, 1069, 808, 731, 700. Anal. Calcd for $C_{25}H_{23}F_3N_2O_2$: C, 68.17; H, 5.26; N, 6.36; found: C, 68.41; H, 5.36; N, 6.23. Rf = 0.70 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}F_3N_2O_2$ 441.1790; Found 441.1763.

*(dia)-4-(1-(1-Benzyl-2-methylindolin-5-yl)-2-nitroethyl)phenol (**12bc**).* Compound **12bc** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (1.15 g, 97% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, =CH, 4H), 7.27 – 7.25 (m, =CH, 1H), 7.10 – 7.08 (m, AA' part of AA'BB' system, =CH, 2H), 6.88 (s, =CH, 1H), 6.82 (d, *J* = 8.0 Hz, =CH, 1H), 6.75 – 6.73 (m, BB' part of AA'BB' system, =CH, 2H), 6.24 – 6.22 (m, =CH, 1H), 5.00 (bs, OH, 1H), 4.91 – 4.80 (m, $CH_2$, 2H), 4.71 (t, *J* = 8.2 Hz, CH, 1H), 4.33 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.15 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.80 – 3.62 (m, CH, 1H), 3.12 (dd, *J* = 15.2, 8.6 Hz, A part of AB system, $CH_2$, 1H), 2.63 (dd, *J* = 15.2, 9.5 Hz, B part of AB system, $CH_2$, 1H), 1.29 (d, *J* = 6.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.2, 139.2, 132.4, 129.99, 129.97, 129.0, 128.7, 127.5, 127.2, 126.7, 126.6, 123.8, 123.7, 115.9, 106.9, 80.1, 60.9, 51.3, 48.1, 37.4, 19.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3434, 2964, 2077, 1614, 1550, 1513, 1494, 1377, 1266, 1175, 1103, 835. Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21; found: C, 74.10; H, 6.08; N, 7.16. Rf = 0.44 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_3$ 389.1865; Found 389.1836.

*(dia)-1-Benzyl-5-(1-(4-fluorophenyl)-2-nitroethyl)-2-methylindoline (**12bd**).* Compound **12bd** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (1.05 g, 90% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, =CH, 7H), 7.06 – 6.97 (m, =CH, 2H), 6.87 (s, =CH, 1H), 6.82 (bd, *J* = 8.0 Hz, 1H), 6.24 (bd, *J* = 8.0 Hz, 1H), 5.01 – 4.82 (m, $CH_2$, 2H), 4.80 – 4.72 (m,

CH, 1H), 4.34 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.20 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.84 – 3.71 (m, CH, 1H), 3.17 (dd, *J* = 15.6, 9.0 Hz, A part of AB system, $CH_2$, 1H), 2.65 (dd, *J* = 15.6, 9.0 Hz, B part of AB system, $CH_2$, 1H), 1.33 (d, *J* = 6.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.16 (d, *J* = 246.2 Hz), 152.4, 139.2, 136.1, 130.09, 130.08, 129.43 (d, *J* = 8.0 Hz), 128.7, 127.9, 127.5, 127.2, 126.8, 126.7, 123.79, 123.71, 116.00 (d, *J* = 21.5 Hz), 106.9, 79.9, 60.9, 51.33, 51.32, 48.2, 37.4, 19.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2964, 2925, 2840, 1615, 1604, 1552, 1495, 1377, 1230, 1160, 1100, 838, 813. Anal. Calcd for $C_{24}H_{23}FN_2O_2$: C, 73.83; H, 5.94; N, 7.17; found: C, 73.74; H, 5.87; N, 7.25. Rf = 0.27 (EtOAc/Hexane (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}FN_2O_2$ 391.1822; Found 391.1797.

*(dia)-1-Benzyl-5-(1-(4-bromophenyl)-2-nitroethyl)-2-methylindoline (**12be**).* Compound **12be** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (961 mg, 97% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, AA' part of AA'BB' system, =CH, 2H), 7.34 – 7.23 (m, =CH, 5H), 7.13 – 7.11 (m, BB' part of AA'BB' system, =CH, 2H), 6.84 (s, =CH, 1H), 6.79 (d, *J* = 8.0 Hz, =CH, 1H), 6.22 (d, *J* = 8.0 Hz, =CH, 1H), 4.94 – 4.81 (m, $CH_2$, 2H), 4.77 – 4.68 (m, CH, 1H), 4.33 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.16 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.88 – 3.55 (m, CH, 1H), 3.12 (dd, *J* = 15.7, 9.0 Hz, A part of AB system, $CH_2$, 1H), 2.63 (dd, *J* = 15.7, 9.0 Hz, B part of AB system, $CH_2$, 1H), 1.29 (d, *J* = 6.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.4, 139.3, 139.1, 132.2, 130.0, 129.5, 128.7, 127.4, 127.2, 126.8, 126.7, 123.7, 123.6, 121.4, 106.9, 79.5, 60.9, 51.2, 48.3, 37.4, 19.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3027, 2963, 2923, 2823, 2848, 1616, 1552, 1490, 1376, 1268, 1074, 1010, 811, 733. Anal. Calcd for $C_{24}H_{23}BrN_2O_2$: C, 63.87; H, 5.14; N, 6.21; found: C, 63.75; H, 5.29; N, 6.05. Rf = 0.38 (EtOAc/Hexane (1:9), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}BrN_2O_2$ 451.1021; Found 451.0977.

*(dia)-4-(1-(1-Benzyl-2-methylindolin-5-yl)-2-nitroethyl)-N,N-dimethylaniline (**12bf**).* Compound **12bf** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (814 mg, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, =CH, 3H), 7.27 – 7.21 (m, =CH, 2H), 7.09 (d, *J* = 8.7 Hz, =CH, 2H), 6.88 (s, =CH, 1H), 6.82 (d, *J* = 8.0 Hz, =CH, 1H), 6.69 – 6.67 (m, =CH, 2H), 6.22 – 6.19 (m, =CH, 1H), 4.87 – 4.85 (m, $CH_2$, 2H), 4.67 (t, *J* = 8.2 Hz, CH, 1H), 4.31 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.13 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 3.72 – 3.67 (m, CH, 1H), 3.10 (dd, *J* = 15.5, 9.1 Hz, A part of AB system, $CH_2$, 1H), 2.91 (s, $CH_3$, 6H), 2.61 (dd, *J* = 15.5, 9.1 Hz, A part of AB system, $CH_2$, 1H), 1.27 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.3, 129.8, 128.99, 128.96, 128.6, 128.4, 127.5, 127.1, 126.6, 126.5, 123.8, 123.7, 113.1, 106.8, 80.2, 61.0, 51.4 (2C), 48.1, 37.4, 19.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3411, 2918, 2851, 1614, 1549, 1521, 1493, 1351, 1160, 1060, 733. Anal. Calcd for $C_{26}H_{29}N_3O_2$: C, 75.15; H, 7.03; N, 10.11; found: C, 75.19; H, 7.09; N, 10.20. Rf = 0.56

(EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{30}N_3O_2$ 416.2338; Found 416.2309.

*(dia)-1-Benzyl-5-(1-(2,5-dimethoxyphenyl)-2-nitroethyl)-2-methylindoline (**12bg**).* Compound **12bg** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (862 mg, 83% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, =CH, 4H), 7.27 – 7.23 (m, =CH, 1H), 6.95 (s, =CH, 1H), 6.89 (d, *J* = 8.4 Hz, =CH, 1H), 6.80 (d, *J* = 8.4 Hz, =CH, 1H), 6.76 – 6.67 (m, =CH, 2H), 6.24 – 6.22 (m, =CH, 1H), 5.17 – 5.05 (m, CH, 1H), 5.00 – 4.95 (m, $CH_2$, 1H), 4.90 – 4.81 (m, $CH_2$, 1H), 4.32 (d, *J* = 16.0 Hz, $CH_2$, A part of AB system 1H), 4.16 (d, *J* = 16.0 Hz, B part of AB system $CH_2$, 1H), 3.81 – 3.80 (m, $CH_3$, 3H), 3.74 – 3.73 (m, $CH_3$, CH, 4H), 3.12 (dd, *J* = 15.6, 8.5 Hz, $CH_2$, 1H), 2.64 (m, $CH_2$, 1H), 1.29 (d, *J* = 6.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.7, 152.3, 151.3, 139.4, 129.8, 129.7, 128.6, 127.5, 127.16, 127.14, 127.0, 124.1, 124.0, 115.8, 115.7, 112.05, 112.04, 111.9, 106.9, 78.6, 61.1, 61.0, 56.3, 55.8, 51.58, 51.54, 43.15, 43.13, 37.5, 19.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2962, 2834, 1619, 1551, 1495, 1376, 1225, 1049, 802, 733. Anal. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.53; N, 6.48; found: C, 72.11; H, 6.43; N, 6.64. Rf = 0.62 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_4$ 433.2127; Found 433.2102.

*(dia)-1-Benzyl-2-methyl-5-(2-nitro-1-(3,4,5-trimethoxyphenyl)ethyl)indoline (**12bh**).* Compound **12bh** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as green oil (792 mg, 82% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, =CH, 4H), 7.27 – 7.22 (m, =CH, 1H), 6.88 (s, =CH, 1H), 6.83 (d, *J* = 8.1 Hz, =CH, 1H), 6.44 (s, =CH, 2H), 6.23 (d, *J* = 8.1 Hz, =CH, 1H), 4.98 – 4.76 (m, $CH_2$, 2H), 4.69 (t, *J* = 8.2 Hz, CH, 1H), 4.32 (d, *J* = 16.0 Hz, $CH_2$, 1H), 4.15 (d, *J* = 16.0 Hz, $CH_2$, 1H), 3.82 (s, 6H), 3.80 (s, 3H), 3.75 – 3.70 (m, CH, 1H), 3.12 (dd, *J* = 15.6, 8.6 Hz, A part of AB system, $CH_2$, 1H), 2.63 (dd, *J* = 15.6, 9.4 Hz, B part of AB system, $CH_2$, 1H), 1.28 (d, *J* = 6.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.4, 152.2, 138.9, 137.2, 135.5, 129.7, 128.5, 127.7, 127.3, 127.0, 126.4, 126.3, 123.5, 123.4, 106.6, 104.8, 79.7, 60.8, 60.75, 60.73, 56.1, 51.1, 51.0, 48.9, 37.2, 19.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3424, 2963, 2838, 1590, 1551, 1494, 1454, 1237, 1127, 1005, 733. Anal. Calcd for $C_{27}H_{30}N_2O_5$: C, 70.11; H, 6.54; N, 6.06; found: C, 69.94; H, 6.43; N, 6.17. Rf = 0.25 (EtOAc /Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{31}N_2O_5$ 463.2233; Found 463.2204.

*(dia)-1-Benzyl-5-(1-(furan-2-yl)-2-nitroethyl)-2-methylindoline (**12bi**).* Compound **12bi** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (1.19 mg, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.22 (m, =CH, 6H), 6.96 (s, =CH, 1H), 6.92 – 6.83 (m, =CH, 1H), 6.32 – 6.31 (m, =CH, 1H), 6.26 (d, *J* = 8.0 Hz, =CH, 1H), 6.16 – 6.06 (m, =CH, 1H), 4.96 (dd, *J* = 12.0, 7.6 Hz, A part of AB system, $CH_2$, 1H), 4.85 – 4.77 (m, CH, 1H), 4.73 (dd, *J* = 12.0, 7.6 Hz, B part of AB system, $CH_2$, 1H), 4.36 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.19 (d, *J* = 16.0 Hz, B part of AB

system, $CH_2$, 1H), 3.84 – 3.65 (m, CH, 1H), 3.16 (ddd, *J* = 15.6, 8.5, 1.5 Hz, A part of AB system, $CH_2$, 1H), 2.67 (dd, *J* = 15.6, 9.4 Hz, B part of AB system, $CH_2$, 1H), 1.31 (d, *J* = 6.2 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.2, 152.7, 142.4, 139.2, 129.9, 128.7, 127.5, 127.29, 127.27, 127.23, 125.6, 123.85, 123.83, 110.5, 107.1, 106.9, 78.82, 78.81, 60.9, 51.2, 43.4, 37.4, 19.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3027, 2964, 2925, 2840, 1616, 1553, 1495, 1376, 1274, 1238, 1161, 1146, 1013, 914, 810, 735. Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73; found: C, 72.72; H, 6.09; N, 7.60. Rf = 0.44 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_3$ 363.1709; Found 363.1683.

*(dia)-5-(1-(1-Benzyl-2-methylindolin-5-yl)-2-nitroethyl)-1H-indole (**12bj**).* Compound **12bj** was obtained using **GP3**. Thin layer chromatography (Acetone/Hexane (2:8)) gave the product as yellow oil (18 mg, 86% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, NH, 1H), 7.41 (d, *J* = 8.0 Hz, =CH, 1H), 7.28 – 7.19 (m, =CH, 5H), 7.18 – 7.07 (m, =CH, 2H), 7.02 – 6.92 (m, =CH, 2H), 6.91 – 6.82 (m, =CH, 2H), 6.14 (d, *J* = 8.0 Hz, =CH, 1H), 4.99 – 4.89 (m, $CH_2$, CH, 2H), 4.77 (dd, *J* = 11.8, 7.7 Hz, $CH_2$, 1H), 4.23 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.06 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.71 – 3.50 (m, CH, 1H), 3.05 – 2.97 (m, $CH_2$, 1H), 2.58 – 2.46 (m, $CH_2$, 1H), 1.28 – 1.06 (m, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.1, 139.1, 136.5, 129.5, 128.4, 127.9, 127.3, 126.9, 126.8, 126.6, 126.3, 123.6, 123.5, 122.5, 121.3, 119.7, 119.2, 115.3, 111.2, 106.7, 80.0, 60.84, 60.80, 51.2, 41.1, 37.2, 29.2, 19.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2094, 1635, 1338, 1223, 1079, 1049, 882. Anal. Calcd for $C_{26}H_{25}N_3O_2$: C, 75.89; H, 6.12; N, 10.21; found: C, 75.66; H, 6.15; N, 9.95. Rf = 0.20 (Acetone/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}N_3O_2$ 412.2025; Found 412.1985.

*(dia)-3-(1-(1-Benzyl-2-methylindolin-5-yl)-2-nitroethyl)-1H-indole (**12bk**).* Compound **12bk** was obtained using **GP3**. Thin layer chromatography (Acetone/Hexane (2:8)) gave the product as yellow oil (18.20 mg, 87% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (bs, NH, 1H), 7.41 (d, *J* = 8.1 Hz, =CH, 1H), 7.26 – 7.20 (m, =CH, 4H), 7.17 – 7.15 (m, =CH, 2H), 7.13 – 7.06 (m, =CH, 1H), 7.05 – 6.90 (m, =CH, 2H), 6.91 – 6.78 (m, =CH, 2H), 6.14 (d, *J* = 8.1 Hz, =CH, 1H), 5.02 – 4.83 (m, $CH_2$, 2H), 4.79 – 4.74 (m, CH, 1H), 4.23 (d, *J* = 16.0 Hz, A part of AB system, $CH_2$, 1H), 4.06 (d, *J* = 16.0 Hz, B part of AB system, $CH_2$, 1H), 3.65 – 3.58 (m, CH, 1H), 3.05 – 2.97 (m, $CH_2$, 1H), 2.65 – 2.43 (m, $CH_2$, 1H), 1.34 – 0.96 (m, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.4, 139.3, 136.7, 129.7, 128.9, 128.6, 127.5, 127.1, 126.9, 126.8, 126.2, 123.8, 123.7, 122.7, 121.5, 120.9, 119.9, 119.4, 119.3, 118.9, 115.5, 111.4, 109.7, 106.9, 100.7, 80.4, 80.2, 61.0, 60.9, 51.5, 51.4, 46.8, 41.9, 41.3, 37.4, 19.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3419, 2095, 1634, 1548, 1493, 1455, 1377, 1097, 741. Anal. Calcd for $C_{26}H_{25}N_3O_2$: C, 75.89; H, 6.12; N, 10.21; found: C, 75.96; H, 5.95; N, 10.14. Rf = 0.50 (Acetone/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}N_3O_2$ 412.2025; Found 412.1993.

*(dia)-Ethyl 1-benzyl-5-(2-nitro-1-phenylethyl)indoline-2-carboxylate (**12ca**).* Compound **12ca** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (82 mg, 56% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, =CH, 9H), 7.10 – 7.01 (m, =CH, 1H), 6.92 – 6.87 (m, =CH, 2H), 6.39 – 6.23 (m, =CH, 1H), 4.96 – 4.83 (m, $CH_2$, 2H), 4.79 (t, *J* = 8.2 Hz, CH, 1H), 4.49 (d, *J* = 15.4 Hz, A part of AB system, $CH_2$, 1H), 4.29 (d, *J* = 15.4 Hz, B part of AB system, $CH_2$, 1H), 4.27 – 4.21 (m, CH, 1H), 4.18 – 4.09 (m, $CH_2$, 2H), 3.34 (dd, *J* = 16.0, 10.4 Hz, $CH_2$, 1H), 3.16 (m, $CH_2$, 1H), 1.22 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.9, 162.0, 151.1, 140.1, 139.9, 138.9, 138.3, 137.9, 132.0, 129.2, 129.1, 128.9, 128.83, 128.76, 128.01, 127.9, 127.8, 127.7, 127.6, 127.5, 127.44, 127.39, 127.2, 126.5, 125.6, 124.0, 123.8, 121.4, 111.8, 111.1, 107.3, 79.8, 65.8, 61.4, 60.9, 52.4, 49.2, 48.8, 48.2, 33.6, 29.9, 14.5, 14.4. Rf = 0.34 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}N_2O_4$ 431.1965; Found 431.1942.

*(dia)-Ethyl 1-benzyl-5-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)indoline-2-carboxylate (**12cb**).* Compound **12cb** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (53 mg, 42% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, =CH, 2H), 7.45 – 7.17 (m, =CH, 7H), 6.91 – 6.78 (m, =CH, 2H), 6.36 – 6.32 (m, =CH, 1H), 4.99 – 4.88 (m, $CH_2$, 2H), 4.87 – 4.80 (m, CH, 1H), 4.49 (d, *J* = 15.5 Hz, A part of AB system, $CH_2$, 1H), 4.28 (d, *J* = 15.5 Hz, B part of AB system, $CH_2$, 1H), 4.29 – 4.21 (m, CH, 1H), 4.17 – 4.02 (m, $CH_2$, 2H), 3.34 (dd, *J* = 16.1, 10.4 Hz, $CH_2$, 1H), 3.20 – 3.10 (m, $CH_2$, 1H), 1.21 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.8, 161.9, 151.4, 144.2, 137.7, 128.84, 128.78, 128.38, 128.31, 128.17, 127.9, 127.6, 127.4, 127.3, 126.30 – 125.93 (m), 123.8, 123.7, 107.3, 79.3, 65.6, 61.4, 52.2, 48.5, 33.5, 29.9, 14.3. Rf = 0.28 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}F_3N_2O_4$ 499.1839; Found 499.1825.

*(dia)-Ethyl 1-benzyl-5-(1-(4-hydroxyphenyl)-2-nitroethyl)indoline-2-carboxylate (**12cc**).* Compound **12cc** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (3:7)) gave the product as light yellow oil (62 mg, 46% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) 7.35 – 7.18 (m, =CH, 5H), 7.12 – 7.00 (m, =CH, 2H), 6.89 – 6.83 (m, =CH, 2H), 6.78 – 6.70 (m, =CH, 2H), 6.36 – 6.31 (m, =CH, 1H), 5.34 (bs, OH, 1H), 4.91 – 4.82 (m, $CH_2$, 2H), 4.70 (t, *J* = 8.2 Hz, CH, 1H), 4.46 (d, *J* = 15.4 Hz, A part AB system, $CH_2$, 1H), 4.27 (d, *J* = 15.4 Hz, B part of AB system, $CH_2$, 1H), 4.28 – 4.18 (m, CH, 1H), 4.16 – 4.07 (m, $CH_2$, 2H), 3.33 (dd, *J* = 16.1, 10.5 Hz, $CH_2$, 1H), 3.19 – 3.08 (m, $CH_2$, 1H), 1.21 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.2, 155.2, 155.1, 151.0, 137.8, 132.3, 132.1, 131.8, 129.3, 129.1, 129.0, 128.82, 128.76, 128.0, 127.5, 127.3, 127.0, 126.5, 124.0, 123.7, 115.9, 107.3, 80.1, 65.8, 61.5, 61.0, 52.4, 48.4, 48.0, 33.6, 14.5, 14.3. Rf = 0.02 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}N_2O_5$ 447.1920; Found 447.1890.

*(dia)-Ethyl 1-benzyl-5-(1-(4-fluorophenyl)-2-nitroethyl)indoline-2-carboxylate (**12cd**).* Compound **12cd** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (74 mg, 55% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, =CH, 5H), 7.21 – 7.16 (m, =CH, 2H), 7.04 – 6.97 (m, =CH, 2H), 6.89 – 6.84 (m, =CH, 2H), 6.38 – 6.32 (m, =CH, 1H), 4.91 – 4.84 (m, $CH_2$, 2H), 4.82 – 4.73 (m, CH, 1H), 4.49 (d, *J* = 15.4 Hz, A part of AB system, $CH_2$, 1H), 4.29 (d, *J* = 15.4 Hz, B part of AB system, $CH_2$, 1H), 4.29 – 4.20 (m, CH, 1H), 4.18 – 4.08 (m, $CH_2$, 2H), 3.34 (dd, *J* = 15.9, 10.4 Hz, $CH_2$, 1H), 3.23 – 3.04 (m, $CH_2$, 1H), 1.22 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.8, 162.15 (d, *J* = 246.2 Hz), 151.2, 137.9, 135.91 (d, *J* = 3.4 Hz), 129.40 (d, *J* = 8.1 Hz), 128.8, 128.7, 128.25, 128.23, 128.0, 127.5, 127.3, 127.1, 123.9, 123.7, 116.02 (d, *J* = 21.4 Hz), 107.3, 79.8, 65.7, 61.4, 52.3, 48.0, 33.5, 14.4. IR ($CH_2Cl_2$, $cm^{-1}$): 3452, 3057, 2983, 2925, 2854, 1890, 1737, 1616, 1606, 1554, 1509, 1497, 1376, 1353, 1265, 1226, 1195, 1161, 1099, 1028, 839, 813, 736. Rf = 0.24 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}FN_2O_4$ 449.1877; Found 449.1853.

*(dia)-Ethyl 1-benzyl-5-(1-(4-bromophenyl)-2-nitroethyl)indoline-2-carboxylate (**12ce**).* Compound **12ce** was obtained using **GP3**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (58 mg, 52% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, =CH, 2H), 7.34 – 7.19 (m, =CH, 5H), 7.17 – 7.00 (m, =CH, 2H), 6.87 – 6.81 (m, =CH, 2H), 6.35 – 6.31 (m, =CH, 1H), 4.91 – 4.80 (m, $CH_2$, 2H), 4.76 – 4.67 (m, CH, 1H), 4.48 (d, *J* = 15.5 Hz, A part of AB system, $CH_2$, 1H), 4.27 (d, *J* = 15.5 Hz, B part of AB system, $CH_2$, 1H), 4.26 – 4.24 (m, CH, 1H), 4.16 – 4.08 (m, $CH_2$, 2H), 3.33 (dd, *J* = 16.1, 10.4 Hz, $CH_2$, 1H), 3.19 – 3.10 (m, $CH_2$, 1H), 1.21 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.8, 161.9, 151.3, 139.2, 138.9, 138.1, 137.8, 132.3, 132.2, 131.3, 129.6, 129.5, 128.83, 128.78, 128.3, 128.25, 128.21, 127.9, 127.54, 127.50, 127.3, 127.1, 126.5, 125.3, 123.8, 123.7, 121.7, 121.5, 121.3, 112.0, 111.0, 107.3, 79.5, 65.7, 61.4, 61.0, 52.3, 48.6, 48.3, 48.2, 33.5, 14.5, 14.4. Rf = 0.28 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}BrN_2O_4$ 509.1070; Found 509.1081.

**General Procedure 4 (GP4): Preparation of C5-Alkylated Indoles (14aa-ak)**

To a solution of *N*-benzyl indoline derivatives (1.0 equiv.) in $CH_2Cl_2$ (6 mL), DEAD (1.1 equiv.) was added. The mixture was stirred at the room temperature for 2 h, then concentrated and purified by silica gel chromatography to afford desired C5-alkylated indoles.

*(±)-1-Benzyl-5-(2-nitro-1-phenylethyl)-1H-indole (**14aa**).* Compound **14aa** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light green oil (195 mg, 55% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, =CH, 1H), 7.34 – 7.19 (m, =CH, 9H), 7.14 – 7.07 (m, =CH, 3H), 7.03 – 6.99 (m, =CH, 1H), 6.49 (d, *J* = 3.0 Hz, =CH, 1H), 5.27 (s, $CH_2$, 2H), 5.10 – 4.96 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.1, 137.2, 135.6, 130.4, 129.03, 129.0, 128.9, 128.8, 127.72, 127.7,

127.3, 126.8, 121.7, 119.8, 110.3, 101.8, 79.8, 50.2, 49.1. IR ($CH_2Cl_2$, $cm^{-1}$): 3445, 3029, 2917, 1953, 1603, 1551, 1485, 1453, 1377, 1263, 1183, 1078, 884, 804, 760. Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86; found: C, 77.47; H, 5.77; N, 7.63. Rf = 0.70 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_2O_2$ 357.1603; Found 357.1581.

*(±)-1-Benzyl-5-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)-1H-indole (**14ab**).* Compound **14ab** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light green oil (187 mg, 89% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, =CH, 2H), 7.50 (s, =CH, 1H), 7.42 (d, *J* = 8.1 Hz, =CH, 2H), 7.33 – 7.27 (m, =CH, 2H), 7.28 – 7.23 (m, =CH, 2H), 7.16 (d, *J* = 3.1 Hz, =CH, 1H), 7.12 – 7.11 (m, =CH, 2H), 6.99 (dd, *J* = 8.5, 1.6 Hz, =CH, 1H), 6.53 (d, *J* = 3.1 Hz, =CH, 1H), 5.29 (s, $CH_2$, 2H), 5.11 – 4.99 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.3, 135.9, 129.7, 129.5, 129.3, 129.0, 128.3 (2C), 128.0, 127.08, 127.04, 126.1 – 126.0 (m, 1C), 121.7, 120.0, 110.7, 102.0, 79.5, 50.4, 49.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3434, 2920, 1619, 1553, 1483, 1376, 1326, 1261, 1165, 1116, 1069, 1017, 858, 840, 799. Anal. Calcd for $C_{24}H_{19}F_3N_2O_2$: C, 67.92; H, 4.51; N, 6.60; found: C, 68.03; H, 4.46; N, 6.50. Rf = 0.70 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_3N_2O_2$ 425.1477; Found 425.1454.

*(±)-4-(1-(1-Benzyl-1H-indol-5-yl)-2-nitroethyl)phenol (**14ac**).* Compound **14ac** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as yellow oil (201 mg, 77% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, =CH, 1H), 7.32 – 7.25 (m, =CH, 3H), 7.22 (d, *J* = 8.5 Hz, =CH, 1H), 7.16 – 7.08 (m, =CH, 5H), 7.01 (dd, *J* = 8.5, 1.7 Hz, =CH, 1H), 6.76 – 6.68 (m, =CH, 2H), 6.52 (d, *J* = 3.1 Hz, =CH, 1H), 5.38 (bs, OH, 1H), 5.26 (s, $CH_2$, 2H), 5.06 – 4.85 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0, 137.5, 135.8, 132.4, 130.9, 129.3, 129.1(2C), 129.0, 127.9, 127.0, 121.9, 119.8, 115.9, 110.5, 101.9, 80.2, 50.4, 48.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3391, 3028, 2919, 1884, 1703, 1613, 1550, 1514, 1377, 1264, 1178, 1045, 885, 814, 732. Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52; found: C, 74.29; H, 5.23; N, 7.47. Rf = 0.23 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_2O_3$ 373.1552; Found 373.1528.

*(±)-1-Benzyl-5-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole (**14ad**).* Compound **14ad** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light green oil (721 mg, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, =CH, 1H), 7.37 – 7.23 (m, =CH, 6H), 7.21 – 7.10 (m, =CH, 3H), 7.09 – 6.97 (m, =CH, 3H), 6.60 – 6.52 (m, =CH, 1H), 5.29 (s, $CH_2$, 2H), 5.09 – 4.91 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.19 (d, *J* = 245.9 Hz), 137.5, 136.23 (d, *J* = 3.2 Hz), 135.8, 130.5, 129.57 (d, *J* = 8.2 Hz), 129.51, 129.3, 129.0, 128.0, 127.1, 121.8, 119.9, 116.03 (d, *J* = 21.5 Hz), 110.7, 102.0, 80.0, 50.4, 48.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3674, 3063, 3031, 2922, 2855, 1954, 1889, 1721, 1603, 1551, 1485, 1453, 1376, 1303, 1227, 1201, 1161, 1102, 1077, 1029, 1015, 960, 911, 886, 854, 837, 808. Anal. Calcd for

$C_{23}H_{19}FN_2O_2$: C, 73.78; H, 5.12; N, 7.48; found: C, 73.72; H, 5.05; N, 7.37. Rf = 0.52 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}FN_2O_2$ 375.1509; Found 375.1484.

*(±)-1-Benzyl-5-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole (**14ae**).* Compound **14ae** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as brown oil (320 mg, 90% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, =CH, 2H), 7.33 – 7.06 (m, =CH, 9H), 6.98 – 6.93 (m, =CH, 1H), 6.49 (d, *J* = 3.2 Hz, =CH, 1H), 5.26 (s, $CH_2$, 2H), 5.03 – 4.91 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.2, 135.6, 132.0, 129.8, 129.4, 129.3, 129.0, 128.8, 127.8, 126.8, 121.5, 121.3, 119.7, 110.5, 101.8, 79.5, 50.3, 48.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3434, 2917, 1642, 1551, 1486, 1375, 1262, 1182, 1074, 1010, 729, 701. Anal. Calcd for $C_{23}H_{19}BrN_2O_2$: C, 63.46; H, 4.40; N, 6.44; found: C, 63.32; H, 4.29; N, 6.52 Rf = 0.76 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}BrN_2O_2$ 435.0708; Found 435.0678.

*(±)-4-(1-(1-Benzyl-1H-indol-5-yl)-2-nitroethyl)-N,N-dimethylaniline (**14af**).* Compound **14af** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light green oil (163 mg, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, =CH, 1H), 7.32 – 7.24 (m, =CH, 4H), 7.20 (d, *J* = 8.6 Hz, =CH, 1H), 7.17 – 7.07 (m, =CH, 4H), 7.02 (d, *J* = 8.6 Hz, =CH, 1H), 6.67 (d, *J* = 8.6 Hz, =CH, 2H), 6.49 – 6.47 (m, =CH, 1H), 5.27 (s, $CH_2$, 2H), 4.98 (d, *J* = 7.4 Hz, $CH_2$, 2H), 4.94 – 4.85 (m, CH, 1H), 2.90 (s, $CH_3$, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.5, 131.4, 129.04, 129.0, 128.6, 127.9, 127.8, 127.0, 121.9, 119.7, 117.9, 115.9, 112.9, 110.3, 101.9, 80.4, 50.4, 48.5, 29.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3473, 2919, 2845, 1733, 1337, 1220, 1079, 1042, 970, 884. Anal. Calcd for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52; found: C, 75.03; H, 6.21; N, 10.59. Rf = 0.54 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2025; Found 400.2001.

*(±)-1-Benzyl-5-(1-(2,5-dimethoxyphenyl)-2-nitroethyl)-1H-indole (**14ag**).* Compound **14ag** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light green oil (195 mg, 70% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.60 (m, =CH, 1H), 7.35 – 7.20 (m, =CH, 4H), 7.15 – 7.13 (m, =CH, 4H), 6.84 (d, *J* = 8.6 Hz, =CH, 1H), 6.79 – 6.76 (m, =CH, 2H), 6.54 (d, *J* = 3.1 Hz, 1H), 5.46 – 5.37 (m, CH, 1H), 5.27 (s, $CH_2$, 2H), 5.11 (dd, *J* = 12.9, 8.2 Hz, A part of AB system, $CH_2$, 1H), 5.02 (dd, *J* = 12.9, 8.2 Hz, B part of AB system, $CH_2$, 1H), 3.81 (s, $CH_3$, 3H), 3.73 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.9, 151.4, 137.6, 135.9, 130.0, 129.9, 129.2, 129.08, 129.03, 127.9, 127.1, 122.3, 120.3, 115.9, 112.2, 112.1, 110.3, 102.0, 78.8, 56.3, 55.9, 50.4, 43.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3029, 3002, 2938, 2912, 2835, 2538, 1956, 1708, 1550, 1497, 1453, 1377, 1240, 1225, 1181, 1047, 1026, 880, 804. Anal. Calcd for $C_{25}H_{24}N_2O_4$: C, 72.10; H, 5.81; N, 6.73; found: C, 72.36; H, 5.90; N, 6.61. Rf = 0.60 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}N_2O_4$ 417.1814; Found 417.1789.

*(±)-1-Benzyl-5-(2-nitro-1-(3,4,5-trimethoxyphenyl)ethyl)-1H-indole (**14ah**).* Compound **14ah** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light green oil (556 mg, 86% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, =CH, 1H), 7.30 – 7.24 (m, =CH, 4H), 7.15 – 7.14 (m, =CH, 1H), 7.12 – 7.10 (m, =CH, 2H), 7.07 – 7.05 (m, =CH, 1H), 6.53 (s, =CH, 3H), 5.27 (s, $CH_2$, 2H), 5.04 – 4.97 (m, CH, $CH_2$, 3H), 3.84 (s, $CH_3$, 3H), 3.82 (s, $CH_3$, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.7, 137.50, 137.48, 135.93, 135.90, 130.5, 129.4, 129.2, 129.0, 127.9, 127.0, 121.7, 119.9, 110.5, 105.1, 102.0, 80.0, 61.0, 56.4, 50.4, 49.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3060, 2935, 2839, 1954, 1727, 1590, 1551, 1508, 1485, 1422, 1332, 1238, 1184, 1127, 1004, 910, 805, 732. Anal. Calcd for $C_{26}H_{26}N_2O_5$: C, 69.94; H, 5.87; N, 6.27; found: C, 70.16; H, 6.02; N, 6.09. Rf = 0.47 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}N_2O_5$ 447.1920; Found 447.1890.

*(±)-5-(1-(1H-indol-5-yl)-2-nitroethyl)-1-benzyl-1H-indole (**14aj**).* Compound **14aj** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as green oil (74 mg, 80% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.08 (bs, NH, 1H), 7.56 (s, =CH, 2H), 7.34 – 7.24 (m, =CH, 4H), 7.21 (d, *J* = 8.6 Hz, =CH, 1H), 7.18 – 7.14 (m, =CH, 1H), 7.14 – 7.05 (m, =CH, 5H), 6.51 – 6.50 (m, =CH, 2H), 5.26 (s, $CH_2$, 2H), 5.20 – 4.95 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.6, 135.7, 135.1, 131.8, 131.6, 129.13, 129.10, 129.0, 128.3, 127.9, 127.0, 125.0, 122.4, 122.1, 119.9, 119.6, 111.7, 110.4, 102.9, 102.0, 80.6, 50.4, 49.4. IR ($CH_2Cl_2$, $cm^{-1}$): 3426, 2921, 1633, 1549, 1484, 1377, 1344, 1263, 1183, 1092, 883, 803, 764, 730. Anal. Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63; found: C, 75.84; H, 5.22; N, 10.47. Rf = 0.32 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}N_3O_2$ 396.1712; Found 396.1683.

*(±)-5-(1-(1H-indol-3-yl)-2-nitroethyl)-1-benzyl-1H-indole (**14ak**).* Compound **14ak** was obtained using **GP4**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as light green oil (195 mg, 55% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.02 (bs, NH, 1H), 7.62 (s, =CH, 1H), 7.51 (d, *J* = 7.9 Hz, =CH, 1H), 7.34 – 7.24 (m, =CH, 5H), 7.23 – 7.18 (m, =CH, 2H), 7.16 – 6.99 (m, =CH, 5H), 6.50 – 6.49 (m, =CH, 1H), 5.30 (t, *J* = 8.0 Hz, CH, 1H), 5.26 (s, $CH_2$, 2H), 5.09 (dd, *J* = 12.4, 8.0 Hz, A part of AB system, $CH_2$, 1H), 4.97 (dd, *J* = 12.4, 8.0 Hz, A part of AB system, $CH_2$, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.5, 135.8, 130.4, 129.0, 128.9, 128.8, 127.7, 126.9, 126.4, 122.5, 121.8, 121.5, 120.0, 119.8, 119.2, 115.4, 111.3, 110.1, 101.8, 80.2, 50.2, 41.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3417, 2919, 1698, 1620, 1549, 1485, 1455, 1378, 1263, 1183, 1094, 910, 803, 734. Anal. Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63; found: C, 75.90; H, 5.46; N, 10.58. Rf = 0.22 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}N_3O_2$ 396.1712; Found 396.1683.

*(±)-Ethyl 1-benzyl-5-(2-nitro-1-phenylethyl)-1H-indole-2-carboxylate (**14ca**).* Compound **14ca** was obtained using **GP4**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow

oil (41 mg, 82% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, =CH, 1H), 7.36 – 7.30 (m, =CH, 4H), 7.30 – 7.18 (m, =CH, 6H), 7.17 – 7.13 (m, =CH, 1H), 7.05 (d, J = 6.8 Hz, =CH, 2H), 5.81 – 5.79 (m, $CH_2$, 2H), 5.05 – 5.00 (m, CH, $CH_2$, 3H), 4.33 (q, *J* = 7.1 Hz, $CH_2$, 2H), 1.36 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.0, 139.9, 138.9, 138.3, 132.0, 129.2, 128.8, 128.7, 127.9, 127.7, 127.4, 126.54, 126.50, 125.6, 121.4, 111.8, 111.1, 79.8, 60.9, 49.2, 48.2, 14.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3565, 2917, 2357, 1705, 1552, 1260, 1193, 1096, 730. Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.88; H, 5.65; N, 6.54; found: C, 72.77; H, 5.73; N, 6.43. Rf = 0.02 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_4$ 429.1814; Found 429.1786.

*(±)-Ethyl 1-benzyl-5-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)-1H-indole-2-carboxylate (**14cb**).* Compound **14cb** was obtained using **GP4**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (35 mg, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, AA' part of AA'BB' system, =CH, 2H), 7.54 (s, =CH, 1H), 7.42 – 7.37 (m, BB' part of AA'BB' system, =CH, 2H), 7.35 – 7.28 (m, =CH, 2H), 7.27 – 7.16 (m, =CH, 3H), 7.10 (d, *J* = 8.8 Hz, =CH, 1H), 7.05 – 7.00 (m, =CH, 2H), 5.80 (s, $CH_2$, 2H), 5.10 – 4.91 (m, CH, $CH_2$, 3H), 4.44 – 4.26 (m, $CH_2$, 2H), 1.35 (t, *J* = 6.2 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.7, 143.7, 138.8, 137.9, 130.8, 128.8 (2C), 128.6, 128.1, 127.3, 126.4 (2C), 126.3, 125.98 (q, *J* = 3.7 Hz), 125.0, 121.2, 111.9, 110.8, 79.0, 60.8, 48.7, 48.0, 14.2. IR ($CH_2Cl_2$, $cm^{-1}$): 3328, 2982, 2960, 2727, 2855, 1799, 1711, 1619, 1556, 1524, 1454, 1413, 1376, 1326, 1254, 1191, 1124, 1070, 1018, 752, 703. Anal. Calcd for $C_{27}H_{23}F_3N_2O_4$: C, 65.32; H, 4.67; N, 5.64; found: C, 65.00; H, 4.96; N, 5.56. Rf = 0.41 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}F_3N_2O_4$ 497.1688; Found 497.1656.

*(±)-Ethyl 1-benzyl-5-(1-(4-hydroxyphenyl)-2-nitroethyl)-1H-indole-2-carboxylate (**14cc**).* Compound **14cc** was obtained using **GP4**. Thin layer chromatography (EtOAc/Hexane (3:7)) gave the product as light yellow oil (53 mg, 80% yield). $^1$H NMR (400 MHz, Acetone-*d6*) δ 8.34 (s, =CH, 1H), 7.74 (s, =CH, 1H), 7.46 (d, *J* = 8.7 Hz, =CH, 1H), 7.37 – 7.30 (m, =CH, 2H), 7.27 – 7.16 (m, =CH, 5H), 7.08 (d, *J* = 7.3 Hz, =CH, 2H), 6.80 (d, *J* = 8.5 Hz, =CH, 2H), 5.88 (s, $CH_2$, 2H), 5.23 (dd, *J* = 8.3, 2.0 Hz, $CH_2$, 2H), 4.94 (t, *J* = 8.3 Hz, CH, 1H), 4.31 (q, *J* = 7.1 Hz, $CH_2$, 2H), 1.32 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, Acetone-*d6*) δ 161.7, 156.7, 138.9, 138.8, 133.6, 131.6, 129.1, 128.7, 128.5, 127.3, 126.7, 126.5, 125.7, 121.2, 115.7, 111.8, 110.7, 79.5, 60.6, 48.6, 47.7, 13.9. IR ($CH_2Cl_2$, $cm^{-1}$): 2917, 1706, 1360, 1190. Anal. Calcd for $C_{26}H_{24}N_2O_5$: C, 70.26; H, 5.44; N, 6.30; Found: C, 70.32; H, 5.31; N, 6.23. Rf = 0.12 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_5$ 445.1763; Found 445.1732.

*(±)-Ethyl 1-benzyl-5-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole-2-carboxylate (**14cd**).* Compound **14cd** was obtained using **GP4**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (34 mg, 72% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, =CH, 1H), 7.33 (s, =CH, 1H), 7.29 –

7.17 (m, =CH, 6H), 7.12 – 7.05 (m, =CH, 1H), 7.05 – 6.93 (m, =CH, 4H), 5.78 (s, $CH_2$, 2H), 4.97 (s, CH, $CH_2$, 3H), 4.31 (q, *J* = 7.1 Hz, $CH_2$, 2H), 1.33 (t, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.6 Hz), 160.8, 138.7, 138.0 (2C), 135.44 (d, *J* = 3.1 Hz), 131.6 (2C), 129.3 (d, *J* = 8.1 Hz), 128.6, 127.3, 126.3, 125.2, 121.0, 115.9 (d, *J* = 21.5 Hz), 111.7, 110.8, 79.5, 60.8, 48.2, 48.0, 14.3. IR ($CH_2Cl_2$, $cm^{-1}$): 3338, 3030, 2982, 2929, 2872, 2255, 1884, 1499, 1709, 1604, 1554, 1523, 1509, 1468, 1453, 1411, 1376, 1254, 1192, 1097, 1026, 910, 810, 729. Anal. Calcd for $C_{26}H_{23}FN_2O_4$: C, 69.94; H, 5.19; N, 6.27; found: C, 69.75; H, 5.11; N, 6.34. Rf = 0.25 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}FN_2O_4$ 447.1720; Found 447.1694.

*(±)-Ethyl 1-benzyl-5-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole-2-carboxylate (**14ce**).* Compound **14ce** was obtained using **GP4**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product as light yellow oil (35 mg, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, =CH, 1H), 7.46 – 7.40 (m, AA' part of AA'BB' system, =CH, 2H), 7.33 (s, =CH, 1H), 7.30 – 7.16 (m, =CH, 4H), 7.15 – 7.05 (m, =CH, 3H), 7.05 – 7.00 (m, =CH, 2H), 5.79 (s, $CH_2$, 2H), 5.07 – 4.85 (m, CH, $CH_2$, 3H), 4.32 (q, *J* = 7.0 Hz, $CH_2$, 2H), 1.34 (t, *J* = 7.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.74, 138.70, 137.9, 132.1 (2C), 131.2, 129.4, 128.7, 128.6, 127.3, 126.3, 125.1, 121.5, 121.1, 111.8, 110.8, 79.2, 60.8, 48.4, 48.0, 14.3. IR ($CH_2Cl_2$, $cm^{-1}$): 3386, 2982, 2927, 2254, 1895, 1799, 1708, 1554, 1524, 1489, 1453, 1376, 1254, 1191, 1096, 1011, 909, 731. Anal. Calcd for $C_{26}H_{23}BrN_2O_4$: C, 61.55; H, 4.57; N, 5.52; found: C, 61.39; H, 4.50; N, 5.58. Rf = 0.46 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}BrN_2O_4$ 507.0919; Found 507.0894.

**Catalytic hydrogenation of 12aa:** *(±)*-1-Benzyl-5-(2-nitro-1-phenylethyl)indoline (**12aa**) (50 mg, 0.14 mmol) was dissolved in MeOH (5 mL) and 10% Pd/C (10 mg) was added. The mixture was stirred in $H_2$ atmosphere for 14 h. The Pd/C was removed by filtration and the solvent was evaporated, and the product mixture was not separated by silica gel column chromatography.

**General Procedure 5 (GP5): *N*-Debenzylation with *t*-BuOK/DMSO and Oxygen**

DMSO (5 mL, 24 mmol) was added to a flame dried flask followed by *(±)*-1-benzyl-5-(2-nitro-1-phenylethyl)indoline (428 mg, 1.39 mmol). Then *t*-BuOK (1.10 g, 9.76 mmol) was added to the mixture and oxygen was bubbled into the solution, via a gas dispersion tube, for 10 min. Upon completion (determined by TLC) the reaction was quenched with saturated ammonium chloride solution. The product was extracted three times with EtOAc. The organic layers were combined, dried over $Na_2SO_4$ and concentrated. Products were purified by thin layer chromatography.

*(1H-Indol-5-yl)(phenyl)methanone (**18**).*[47] Compound **18** was obtained using **GP5**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave **18** as first fraction (120 mg, 39% yield; brown crystals, mp

146–147 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.85 (bs, NH, 1H), 8.14 (s, =CH, 1H), 7.86 – 7.77 (m, =CH, 3H), 7.61 – 7.55 (m, =CH, 1H), 7.52 – 7.42 (m, =CH, 3H), 7.31 – 7.29 (m, =CH, 1H), 6.69 – 6.60 (m, =CH, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.7, 139.0, 138.4, 131.7, 130.0, 129.6, 128.2, 127.2, 125.9, 125.4, 124.2, 111.2, 104.2. IR ($CH_2Cl_2$, $cm^{-1}$): 3429, 2916, 2851, 2088, 1637, 1608, 1573, 1445, 1422, 1350, 1326, 1115, 1097, 881, 768. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33; found: C, 81.38; H, 5.08; N, 6.18. Rf = 0.35 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}NO$ 222.0919; Found 222.0896.

*(1-Benzylindoline-5-yl)(phenyl)methanone (**19**).* Compound **19** was obtained using **GP5**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave **19** as second fraction (yellow oil, 55 mg, 42% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, =CH, 2H), 7.68 – 7.66 (m, =CH, 1H), 7.63 – 7.59 (m, =CH, 1H), 7.53 – 7.48 (m, =CH, 1H), 7.47 – 7.41 (m, =CH, 2H), 7.38 – 7.24 (m, =CH, 5H), 6.43 (d, *J* = 8.3 Hz, 1H), 4.40 (s, $CH_2$, 2H), 3.54 (t, *J* = 8.5 Hz, $CH_2$, 2H), 3.07 (t, *J* = 8.5 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.3, 156.3, 139.7, 137.3, 133.6, 131.2, 129.8, 129.6, 128.9, 128.2, 127.8, 127.7, 127.0, 126.6, 104.4, 52.7, 51.7, 27.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3440, 2917, 2845, 2089, 1634, 1602, 1443, 1265, 1093, 739. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47; found: C, 84.22; H, 6.09; N, 4.32. Rf = 0.60 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO$ 314.1545; Found 314.1524.

*(1-Benzyl-1H-indol-5-yl)(phenyl)methanone (**20**).* Compound **20** was obtained using **GP5**. Thin layer chromatography (EtOAc/Hexane (2:8)) gave the product **20** as brown crystals (42 mg, 48% yield; mp 98–99 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.5 Hz, =CH, 1H), 7.78 (ddd, *J* = 10.7, 7.8, 3.4 Hz, =CH, 3H), 7.59 – 7.52 (m, =CH, 1H), 7.50 – 7.43 (m, =CH, 2H), 7.37 – 7.23 (m, =CH, 4H), 7.19 (d, *J* = 3.0 Hz, =CH, 1H), 7.11 (d, *J* = 6.5 Hz, =CH, 2H), 6.63 (d, *J* = 3.0 Hz, =CH, 1H), 5.35 (s, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.2, 139.0, 138.6, 136.9, 131.6, 129.91, 129.86, 129.5, 128.9, 128.1, 127.95, 127.91, 126.8, 125.5, 124.0, 109.6, 103.6, 50.3. IR ($CH_2Cl_2$, $cm^{-1}$): 3429, 2916, 2851, 2088, 1637, 1608, 1573, 1445, 1422, 1350, 1326, 1115, 1097, 881, 768. Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50; found: C, 84.58; H, 5.68; N, 4.40. Rf = 0.36 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}NO$ 312.1388; Found 312.1381.

**General Procedure 6 (GP6): Debenzylation of C5-alkylated *N*-benzyl indolines (22aa-ai)**

To a stirred solution of *N*-benzyl indoline derivative (1 equiv.) in MeOH/$CH_2Cl_2$ (1:1; 6 mL), $Boc_2O$ (1.5 equiv.) and 10% Pd/C (0.4 equiv.) was added. The mixture was stirred on $H_2$ atmosphere for 15h. After the reaction is over, the mixture was filtered and evaporated. The residue was dissolved in $CH_2Cl_2$ (3 mL) and then was added TFA (1 mL). The reaction mixture was stirred for 2 h at ambient temperature, solvent was removed under reduced pressure. The residue was dissolved in EtOAc (40 mL) and washed

with saturated $NaHCO_3$ and brine. The combined organic phase was dried with $Na_2SO_4$ and the solvent was evaporated to afford debenzylation products.

*(±)-5-(2-Nitro-1-phenylethyl)indoline (**22aa**).* Compound **22aa** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as light yellow oil (230 mg, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, =CH, 2H), 7.28 – 7.19 (m, =CH, 3H), 6.97 (s, =CH, 1H), 6.88 (d, *J* = 8.0 Hz, =CH, 1H), 6.56 (d, *J* = 8.0 Hz, =CH, 1H), 5.01 – 4.86 (m, $CH_2$, 2H), 4.80 (t, *J* = 8.2 Hz, CH, 1H), 3.70 (bs, NH, 1H), 3.53 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.98 (t, *J* = 8.4 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 140.3, 130.5, 129.4, 129.1, 127.8, 127.5, 126.8, 124.3, 109.6, 79.9, 48.9, 47.67, 30.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3390, 3059, 3028, 2957, 2923, 2851, 1616, 1549, 1495, 1476, 1433, 1377, 1321, 1254, 1184, 1104, 1055, 1028, 888, 813, 735. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44; found: C, 71.81; H, 6.15; N, 10.31. Rf = 0.28 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_2$ 269.1290; Found 269.1270.

*(±)-5-(2-Nitro-1-(4-(trifluoromethyl)phenyl)ethyl)indoline (**22ab**).* Compound **22ab** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as light green oil (245 mg, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, AA' part of AA'BB' system, =CH, 2H), 7.38 – 7.34 (m, BB' part of AA'BB' system, =CH, 2H), 6.91 (s, =CH, 1H), 6.83 (d, *J* = 8.0 Hz, =CH, 1H), 6.54 (d, *J* = 8.0 Hz, =CH, 1H), 4.99 – 4.89 (m, $CH_2$, 2H), 4.88 – 4.80 (m, CH, 1H), 3.74 (bs, NH, 1H), 3.52 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.96 (t, *J* = 8.4 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.5, 144.2, 130.5, 128.1, 128.0 (2C), 126.6, 125.9 (q, *J* = 3.7 Hz), 125.4, 124.0, 109.4, 79.2, 48.4, 47.4, 29.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3646, 3393, 2922, 2851, 1725, 1618, 1554, 1497, 1165, 1116, 1018, 889. Anal. Calcd for $C_{17}H_{15}F_3N_2O_2$: C, 60.71; H, 4.50; N, 8.33; found: C, 60.94; H, 4.54; N, 8.40. Rf = 0.14 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}F_3N_2O_2$ 337.1164; Found 337.1144.

*(±)-4-(1-(Indolin-5-yl)-2-nitroethyl)phenol (**22ac**).* Compound **22ac** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as brown crystals (198 mg, 87% yield; mp 133–134 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.92 (m, =CH, 3H), 6.83 (d, *J* = 8.0 Hz, =CH, 1H), 6.58 (d, *J* = 8.0 Hz, =CH, 1H), 6.54 (d, *J* = 8.3 Hz, =CH, 2H), 5.54 (bs, NH, OH, 2H), 4.82 (d, *J* = 8.2 Hz, $CH_2$, 2H), 4.68 (t, *J* = 8.2 Hz, CH, 1H), 3.45 – 3.43 (m, $CH_2$, 2H), 2.90 (t, *J* = 8.0 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.8, 131.5, 131.1, 130.1, 128.8, 126.7, 124.3, 115.8, 110.8, 79.9, 47.9, 47.4, 29.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3348, 3021, 2958, 2918, 2850, 2687, 2611, 1886, 1613, 1550, 1514, 1445, 1438, 1378, 1322, 1250, 1176, 1105, 1056, 834. Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; found: C, 67.52; H, 5.59; N, 9.88. Rf = 0.11 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_3$ 285.1239; Found 285.1217.

*(±)-5-(1-(4-Fluorophenyl)-2-nitroethyl)indoline (**22ad**).* Compound **22ad** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (1:9)) gave the product as yellow oil (207 mg, 83% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, =CH, 2H), 7.02 – 6.93 (m, =CH, 2H), 6.92 – 6.87 (m, =CH, 1H), 6.85 – 6.77 (m, =CH, 1H), 6.59 – 6.46 (m, =CH, 1H), 4.93 – 4.80 (m, $CH_2$, 2H), 4.76 (dd, *J* = 13.9, 7.5 Hz, CH, 1H), 3.56 (bs, NH, 1H), 3.51 (m, $CH_2$, 2H), 2.95 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 246.3 Hz), 151.2, 135.8 (d, *J* = 2.9 Hz), 130.3, 129.2 (d, *J* = 8.0 Hz), 128.9, 126.5, 124.0, 115.8 (d, *J* = 21.4 Hz), 109.4, 79.7, 47.9, 47.4, 29.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3392, 3048, 3018, 2958, 2921, 2853, 2741, 2853, 2741, 1890, 1724, 1615, 1604, 1547, 1508, 1477, 1435, 1377, 1321, 1253, 1226, 1161, 1101, 1056, 1025, 890, 835. Anal. Calcd for $C_{16}H_{15}FN_2O_2$: C, 67.12; H, 5.28; N, 9.78; found: C, 67.09; H, 5.12; N, 9.66. Rf = 0.14 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FN_2O_2$ 287.1196; Found 287.1175.

*(±)-4-(1-(Indoline-5-yl)-2-nitroethyl)-N,N-dimethylaniline (**22af**).* Compound **22af** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as brown crystals (350 mg, 80% yield; mp 89–90 °C ($CH_2Cl_2$/Hexane)). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.03 (m, AA' part of AA'BB' system, =CH, 2H), 6.92 (s, =CH, 1H), 6.83 (d, *J* = 7.9 Hz, =CH, 1H), 6.66 – 6.61 (m, AA' part of AA'BB' system, =CH, 2H), 6.48 (d, *J* = 7.9 Hz, =CH, 1H), 4.83 (d, *J* = 8.1 Hz, $CH_2$, 2H), 4.66 (t, *J* = 8.1 Hz, CH, 1H), 3.62 (bs, NH, 1H), 3.44 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.90 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.87 (s, $CH_3$, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.9, 149.7, 130.2, 130.1, 128.3, 127.7, 126.5, 124.1, 112.8, 109.4, 80.1, 47.9, 47.5, 40.6, 29.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3389, 2918, 2851, 1773, 1729, 1614, 1549, 1521, 1496, 1444, 1377, 1254, 1165, 1057, 946, 817. Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49; found: C, 69.38; H, 6.70; N, 13.34. Rf = 0.17 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}N_3O_2$ 312.1712; Found 312.1691.

*(±)-5-(1-(2,5-Dimethoxyphenyl)-2-nitroethyl)indoline (**22ag**).* Compound **22ag** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light brown oil (221 mg, 87% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, =CH, 1H), 6.89 (d, *J* = 8.0 Hz, =CH, 1H), 6.78 (d, *J* = 8.8 Hz, =CH, 1H), 6.73 – 6.69 (m, =CH, 1H), 6.68 – 6.65 (m, =CH, 1H), 6.52 (d, *J* = 8.0 Hz, =CH, 1H), 5.16 – 5.04 (m, CH, 1H), 4.95 (dd, *J* = 12.7, 7.1 Hz, A part of AB system , $CH_2$, 1H), 4.84 (dd, *J* = 12.7, 9.2 Hz, B part of AB system, $CH_2$, 1H), 3.76 (s, $CH_3$, 3H), 3.69 (s, $CH_3$, 3H), 3.62 (bs, NH, 1H), 3.47 (t, *J* = 8.4 Hz, $CH_2$, 2H), 2.94 (t, *J* = 8.4 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 151.1, 151.0, 130.0, 129.6, 128.5, 126.9, 124.4, 115.5, 111.93, 111.87, 109.3, 78.4, 56.1, 55.6, 47.5, 42.9, 29.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3388, 2935, 2837, 2047, 1616, 1588, 1551, 1997, 1446, 1377, 1239, 1228, 1082, 1024, 807. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53; found: C, 65.72; H, 6.10; N, 8.40. Rf = 0.15 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2O_4$ 329.1501; Found 329.1478.

*(±)-5-(2-Nitro-1-(3,4,5-trimethoxyphenyl)ethyl)indoline (**22ah**).* Compound **22ah** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as light green oil (260 mg, 85% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, =CH, 1H), 6.87 (d, *J* = 8.0 Hz, =CH, 1H), 6.54 (d, *J* = 8.0 Hz, =CH, 1H), 6.44 (s, =CH, 2H), 4.96 – 4.78 (m, $CH_2$, 2H), 4.72 (t, *J* = 8.2 Hz, CH, 1H), 3.80 (s, $CH_3$, 9H), 3.69 (bs, NH, 1H), 3.51 (t, *J* = 8.2 Hz, $CH_2$, 2H), 2.96 (t, *J* = 8.2 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.4, 151.2, 137.2, 135.6, 130.3, 128.9, 126.4, 124.0, 109.3, 104.8, 79.7, 60.8, 56.2, 48.9, 47.4, 29.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3442, 2924, 2840, 1620, 1551, 1497, 1462, 1328, 1247, 1126, 1005, 739. Anal. Calcd for $C_{19}H_{22}N_2O_5$: C, 63.68; H, 6.19; N, 7.82; found: C, 63.75; H, 6.10; N, 7.71. Rf = 0.12 (EtOAc/Hexane (4:6), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}N_2O_5$ 359.1607; Found 359.1583.

*(±)-5-(1-(Furan-2-yl)-2-nitroethyl)indoline (**22ai**).* Compound **22ai** was obtained using **GP6**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as dark yellow oil (175 mg, 87% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, =CH, 1H), 7.00 – 6.96 (m, =CH, 1H), 6.90 – 6.85 (m, =CH, 1H), 6.59 – 6.42 (m, =CH, 1H), 6.34 – 6.24 (m, =CH, 1H), 6.10 – 6.05 (m, =CH, 1H), 4.97 – 4.89 (m, CH, 1H), 4.81 – 4.75 (m, $CH_2$, 1H), 4.74 – 4.65 (m, $CH_2$, 1H), 3.73 (bs, NH, 1H), 3.57 – 3.41 (m, $CH_2$, 2H), 3.00 – 2.92 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.0, 151.6, 142.3, 130.2, 127.0, 126.7, 124.1, 110.4, 109.4, 107.0, 78.6, 47.5, 43.2, 29.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3441, 2089, 1633, 1552, 1497, 1377, 1260, 739. Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85; found: C, 65.02; H, 5.38; N, 10.81. Rf = 0.28 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O_3$ 259.1083; Found 259.1062.

**General Procedure 7 (GP7): Preparation of Unprotected Indoles (23aa-ai)**

The C5-substitued indoline derivatives (**22aa**-**ai**) (1equiv.) was dissolved in $CH_2Cl_2$ (6 mL) and then DEAD (1.1 mmol) was added to the solution. The reaction mixture was stirred for 2 h at room temperature. After the reaction is over (monitored by TLC), the solution was concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography to obtain the C5-substitued 1*H*-indole derivatives.

*(±)-5-(2-Nitro-1-phenylethyl)-1H-indole (**23aa**).* Compound **23aa** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as dark yellow oil (100 mg, 48% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, NH, 1H), 7.52 (s, =CH, 1H), 7.35 - 7.26 (m, =CH, 5H), 7.25 – 7.20 (m, =CH, 2H), 7.05 (dd, *J* = 8.4 Hz, 1.4 Hz, =CH, 1H), 6.53 – 6.50 (m, =CH, 1H), 5.05 (s, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.3, 135.2, 130.8, 129.1, 128.3, 127.9, 127.5, 125.3, 122.2, 119.7, 111.9, 102.8, 80.0, 49.3. IR ($CH_2Cl_2$, $cm^{-1}$): 3368, 1794, 1735,1552, 1378, 1265, 1097, 894, 765. Rf=0.26 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1134; Found 267.1124.

*(±)-5-(2-Nitro-1-(4-(trifluoromethyl)phenyl)ethyl)-1H-indole (**23ab**).* Compound **23ab** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as dark yellow crystals (456 mg, 46% yield; mp 92–93 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, NH, 1H), 7.59 (d, *J* = 8.2 Hz, =CH, 2H), 7.52 (m, =CH, 1H), 7.41 (d, *J* = 8.2 Hz, =CH, 2H), 7.32 (d, *J* = 8.4 Hz, =CH, 1H), 7.23 – 7.15 (m, =CH, 2H) 7.03 (dd, *J* = 8.4, 1.8 Hz, =CH, 1H), 6.55 (dd, *J* = 2.6, 1.7 Hz, =CH, 1H), 5.18 – 4.93 (m, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.5, 135.4, 130.0, 129.6, 128.5, 128.3, 126.2 – 126.0 (m, 1C), 125.6, 122.0, 119.8 – 119.7 (m, 1C), 112.2, 102.8, 79.5, 49.1. IR ($CH_2Cl_2$, $cm^{-1}$): 3426, 1554, 1326, 1165, 1115, 1018, 865, 732. Rf=0.13 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}F_3N_2O_2$ 335.1007; Found 335.0995.

*(±)-4-(1-(1H-indole-5-yl)-2-nitroethyl)phenol (**23ac**).* Compound **23ac** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow oil (384 mg, 54% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, NH, 1H), 7.48 (s, =CH, 1H), 7.29 (d, *J* = 8.5 Hz, =CH, 1H), 7.20 – 7.15 (m, =CH, 1H), 7.12 (d, *J* = 8.6 Hz, =CH, 2H), 7.01 (dd, *J* = 8.5, 1.6 Hz, =CH, 1H), 6.72 (d, *J* = 8.6 Hz, =CH, 2H), 6.50 (d, *J* = 2.2 Hz, =CH, 1H), 5.04 – 4.88 (m, CH, OH, $CH_2$, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.9, 135.1, 132.5, 131.1, 129.1, 128.3, 125.2, 122.1, 119.5, 115.9, 111.8, 102.8, 80.2, 48.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3420, 1613, 1548, 1378, 1261, 1177, 814, 733. Rf=0.10 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_3$ 283.1083; Found 283.1083.

*(±)-5-(1-(4-Fluorophenyl)-2-nitroethyl)-1H-indole (**23ad**).* Compound **23ad** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (2:8)) gave the product as dark yellow crystals (285 mg, 46% yield; mp 114–115 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, NH, 1H), 7.49 (s, =CH, 1H), 7.35 – 7.16 (m, =CH, 4H), 7.04 – 6.98 (m, =CH, 3H), 6.54 – 6.51 (m, =CH, 1H), 5.01 (s, CH, $CH_2$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.2 Hz), 136.2 (d, *J* = 3.4 Hz), 135.3, 130.7, 129.5 (d, *J* = 8.0 Hz), 128.4, 125.5, 122.0, 119.6, 116.0 (d, *J* = 21.4 Hz), 112.0, 102.8, 80.0, 48.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3426, 1557, 1377, 1224, 1160, 1015, 811, 731. Rf=0.12 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}FN_2O_2$ 285.1039; Found 285.1028.

*(±)-4-(1-(1H-indole-5-yl)-2-nitroethyl)-N,N-dimethylaniline (**23af**).* Compound **23af** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow oil (374 mg, 40% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, NH, 1H), 7.58 (s, =CH, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.13 – 7.06 (m, =CH, 2H), 6.77 (d, *J* = 8.6 Hz, =CH, 2H), 6.55 (s, =CH, 1H), 5.13 – 4.93 (m, CH, $CH_2$, 3H), 2.96 (s, $CH_3$, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.2, 135.2, 131.6, 128.7, 128.4, 128.3, 125.5, 122.2, 119.5, 113.2, 112.0, 102.6, 80.5, 48.8, 40.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3420, 2914, 1613, 1549, 1347, 1065, 816, 733. Rf=0.15 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}N_3O_2$ 310.1556; Found 310.1549.

*(±)-5-(1-(2,5-Dimethoxyphenyl)-2-nitroethyl)-1H-indole (**23ag**).* Compound **23ag** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light brown crystals (442 mg, 52% yield; mp 158–159 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 (bs, NH, 1H), 7.54 (s, =CH, 1H), 7.31 (d, *J* = 8.4 Hz, =CH, 1H), 7.20 – 7.13 (m, =CH, 1H), 7.10 (dd, *J* = 8.4, 1.7 Hz, =CH, 1H), 6.83 – 6.77 (m, =CH, 1H), 6.75 – 6.70 (m, =CH, 2H), 6.51 – 6.48 (m, =CH, 1H), 5.42 – 5.31 (m, CH, 1H), 5.08 (dd, *J* = 12.9, 8.0 Hz, $CH_2$, 1H), 4.99 (dd, *J* = 12.9, 8.0 Hz, $CH_2$, 1H), 3.79 (s, $CH_3$, 3H), 3.70 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.8, 151.3, 135.3, 130.2, 129.9, 129.3, 124.9, 122.6, 120.0, 115.8, 112.13, 112.10, 111.6, 102.9, 78.7, 56.3, 55.8, 43.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3426, 2835, 1549, 1223, 1047, 1024, 894, 732. Rf = 0.13 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_4$ 327.1345; Found 327.1338.

*(±)-5-(2-Nitro-1-(3,4,5-trimethoxyphenyl)ethyl)-1H-indole (**23ah**).* Compound **23ah** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as white crystals (280 mg, 50% yield; mp 152–153 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, NH, 1H), 7.50 (s, =CH, 1H), 7.34 (d, *J* = 8.4 Hz, =CH, 1H), 7.21 (t, *J* = 2.8 Hz, =CH, 1H), 7.05 (dd, *J* = 8.4, 1.6 Hz, =CH, 1H), 6.54 – 6.51 (m, =CH, 3H), 5.06 – 4.99 (m, CH, $CH_2$, 3H), 3.81 (s, $CH_3$, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 137.4, 135.9, 135.3, 130.7, 128.4, 125.3, 122.0, 119.6, 111.9, 105.1, 102.9, 80.0, 61.0, 56.4, 49.5. IR ($CH_2Cl_2$, $cm^{-1}$): 3368, 2938, 2839, 1591, 1551, 1461, 1126, 733. Rf = 0.11 (EtOAc/Hexane (3:7), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_5$ 357.1450; Found 357.1437.

*(±)-5-(1-(Furan-2-yl)-2-nitroethyl)-1H-indole (**23ai**).* Compound **23ai** was obtained using **GP7**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow oil (532 mg, 58% yield). $^1$H-NMR (400 MHz, $CDCl_3$) δ 8.20 (s, NH, 1H), 7.55 (s, =CH, 1H), 7.41 – 7.32 (m, =CH, 2H), 7.24 – 7.17 (m, =CH, 1H), 7.10 (dd, *J* = 8.4, 1.7 Hz, =CH, 1H), 6.56 – 6.48 (m, =CH, 1H), 6.31 (dd, *J* = 3.2, 1.9 Hz, =CH, 1H), 6.13 (d, *J* = 3.3 Hz, =CH, 1H), 5.15 – 4.97 (m, $CH_2$, 2H), 4.85 (dd, *J* = 11.3, 6.3 Hz, CH, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.3, 135.6, 128.5, 128.4, 125.3, 122.0, 120.3, 111.8, 110.6, 107.3, 104.8, 103.0, 44.0, 29.9. IR ($CH_2Cl_2$, $cm^{-1}$): 3427, 1633, 1552, 1376, 1260, 1013, 805, 734. Rf=0.25 (EtOAc/Hexane (2:8), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_3$ 257.0926; Found 257.0912.

**General Procedure 8 (GP8): Reduction of Nitro Groups in *N*-Benzylindolines (25aa-ak)**

$NaBH_4$ (102.2 mg, 2.70 mmol, 5 equiv.) was added to a suspension of C5-substitued *N*-benzylindoline derivatives (1 equiv.) and $NiCl_2{\cdot}6H_2O$ (1 equiv.) in methanol (4 mL) at 0 °C and the mixture was stirred at 0 °C for 30 min. The reaction mixture was quenched by addition of saturated $NH_4Cl$ solution at 0 °C and extracted with $CH_2Cl_2$ (30 mL). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$. After filtration of the drying agent, the filtrate was concentrated to dryness in

vacuo. The residue was dissolved in 0.5 mL methanol, then HCl (12 M, 1.2 equiv.) was added dropwise to the solution and purified by recrystallization (diethyl ether at 2 °C) to give analytically pure products.

*(±)-2-(1-Benzylindoline-5-yl)-2-phenylethane-1-amine hydrochloride (**25aa**).* Compound **25aa** was obtained using **GP8** and recovered as purple crystals (178 mg, 97% yield; mp 196.6–197.6 °C). $^{1}$H NMR (400 MHz, $CD_3OD$) δ 7.55 (s, =CH, 2H), 7.54 – 7.36 (m, =CH, 10H), 7.37 – 7.23 (m, =CH, 1H), 4.74 (s, $CH_2$, 2H), 4.48 (t, *J* = 8.0 Hz, CH, 1H), 3.91 (t, *J* = 7.5 Hz, $CH_2$, 2H), 3.73 (dd, *J* = 8.0, 2.7 Hz, $CH_2$, 2H), 3.20 (t, *J* = 7.5 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 143.9, 139.9, 139.0, 137.1, 131.3, 130.1, 129.7, 129.2, 129.1, 128.4, 127.9, 127.7, 126.0, 120.4, 60.3, 53.9, 48.8, 43.2, 27.8. Anal. Calcd for $C_{23}H_{25}ClN_2$: C, 75.70; H, 6.91; N, 7.68; found: C, 75.63; H, 7.00; N, 7.53. Rf = 0.76 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2$ 329.2012; Found 329.2002.

*(±)-2-(1-Benzylindoline-5-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1-amine hydrochloride (**25ab**).* Compound **25ab** was obtained using **GP8** and recovered as purple crystals (192 mg, 86% yield; mp 158.2–159.2 °C). $^{1}$H NMR (400 MHz, $CD_3OD$) δ 7.72 – 7.63 (m, =CH, 4H), 7.60 (s, =CH, 1H), 7.55 – 7.38 (m, =CH, 7H), 4.74 (s, $CH_2$, 2H), 4.69 (t, *J* = 8.0 Hz, CH, 1H), 3.89 (t, *J* = 7.4 Hz, $CH_2$, 2H), 3.79 (d, *J* = 8.0 Hz, $CH_2$, 2H), 3.20 (t, *J* = 7.4 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 144.4, 142.8, 139.6, 137.2 (2C), 131.1 (2C), 130.0, 129.9, 129.1, 128.7 (2C), 128.4, 126.0 (m, 1C), 120.2, 60.2, 54.0, 48.6, 42.8, 27.8. Anal. Calcd for $C_{24}H_{24}ClF_3N_2$: C, 66.59; H, 5.59; N, 6.47; found: C, 66.70; H, 5.68; N, 6.29. Rf = 0.20 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}F_3N_2$ 397.1892; Found 397.1868.

*(±)-2-(1-Benzylindoline-5-yl)-2-(4-fluorophenyl)ethane-1-amine hydrochloride (**25ad**).* Compound **25ad** was obtained using **GP8** and recovered as pink crystals (182 mg, 94% yield; mp 72.1–73.1 °C). $^{1}$H NMR (400 MHz, $CD_3OD$) δ 7.63 – 7.33 (m, =CH, 10H), 7.14 – 7.08 (m, =CH, 2H), 4.71 (s, $CH_2$, 2H), 4.50 (t, *J* = 8.1 Hz, CH, 1H), 3.87 (t, *J* = 7.5 Hz, $CH_2$, 2H), 3.69 (d, *J* = 8.1 Hz, $CH_2$, 2H), 3.17 (t, *J* = 7.5 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 162.3 (d, *J* = 245.2 Hz), 143.2, 139.7, 136.9, 135.8 (d, *J* = 3.2 Hz), 131.0, 130.04, 129.98, 129.8 (d, *J* = 8.2 Hz), 129.1, 128.2, 125.7, 119.7, 115.8 (d, *J* = 21.7 Hz), 60.0, 54.0, 48.2, 43.1, 27.7. Anal. Calcd for $C_{23}H_{24}ClFN_2$: C, 72.15; H, 6.32; N, 7.32; found: C, 72.01; H, 6.42; N, 7.45. Rf = 0.63 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}FN_2$ 347.1924; Found 347.1903.

*(±)-2-(1-Benzylindoline-5-yl)-2-(4-bromophenyl)ethane-1-amine hydrochloride (**25ae**).* Compound **25ae** was obtained using **GP8** and recovered as pink crystals (171 mg, 87% yield; mp 115.6–116.6 °C). $^{1}$H NMR (400 MHz, $CD_3OD$) δ 7.70 – 7.19 (m, =CH, 12H), 4.65 (s, $CH_2$, 2H), 4.47 (t, *J* = 7.8 Hz, CH, 1H), 3.79 (t, *J* = 7.0 Hz, $CH_2$, 2H), 3.69 (dd, *J* = 7.8, 4.8 Hz, $CH_2$, 2H), 3.14 (t, *J* = 7.0 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 139.3, 136.5, 136.4, 132.2, 132.1, 130.8, 130.7, 129.8, 129.2, 129.0, 127.8, 125.6, 121.4,

118.5, 59.6, 53.9, 48.3, 42.9, 27.8. Anal. Calcd for $C_{23}H_{24}BrClN_2$: C, 62.25; H, 5.45; N, 6.31; found: C, 62.03; H, 5.13; N, 6.50. Rf = 0.63 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd $C_{23}H_{24}BrN_2$ 407.1123; Found 407.1088.

*(±)-4-(2-Amino-1-(1-benzylindoline-5-yl)ethyl)-N,N-dimethylaniline hydrochloride (**25af**).* Compound **25af** was obtained using **GP8** and recovered as yellow crystals (169 mg, 91% yield; mp 178.6–179.6 °C). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.67 – 7.54 (m, =CH, 4H), 7.37 – 7.24 (m, =CH, 5H), 7.20 – 7.01 (m, =CH, 2H), 6.66 (d, *J* = 8.1 Hz, =CH, 1H), 4.38 (t, *J* = 8.1 Hz, CH, 1H), 4.28 (s, $CH_2$, 2H), 3.64 (d, *J* = 8.1 Hz, $CH_2$, 2H), 3.35 (t, *J* = 8.1 Hz, $CH_2$, 2H), 3.22 (s, $CH_3$, 6H), 2.93 (t, *J* = 8.1 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 142.88, 142.85, 142.4 (2C), 136.8, 132.6, 129.8, 128.5 (2C), 127.6, 127.2, 124.2, 120.7, 109.7, 54.5, 53.5, 48.3, 45.6, 43.2, 28.1. Anal. Calcd for $C_{25}H_{30}ClN_3$: C, 73.60; H, 7.41; N, 10.30; found: C, 73.66; H, 7.32; N, 10.46. Rf = 0.80 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{30}N_3$ 372.2440; Found 372.2425.

*(±)-2-(1-Benzylindoline-5-yl)-2-(2,5-dimethoxyphenyl)ethane-1-amine hydrochloride (**25ag**).* Compound **25ag** was obtained using **GP8** and recovered as purple crystals (175 mg, 94% yield; mp 217.8–218.8 °C). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.52 – 7.34 (m, =CH, 8H), 6.96 – 6.93 (m, =CH, 1H), 6.86 (m, CH, 2H), 4.76 (t, *J* = 8.1 Hz, CH, 1H), 4.70 (s, $CH_2$, 2H), 3.87 (t, *J* = 7.5 Hz, $CH_2$, 2H), 3.78 (s, $CH_3$, 3H), 3.75 (s, $CH_3$, 3H), 3.32 – 3.28 (m, $CH_2$, 2H). 3.15 (t, *J* = 7.5 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 154.3, 151.4, 143.1, 139.2, 136.5, 131.0, 130.0, 129.9, 129.1, 128.5, 128.4, 125.9, 119.4, 114.8, 112.7, 112.2, 60.1, 55.2, 55.0, 54.0, 42.8, 42.2, 27.7. Anal. Calcd for $C_{25}H_{29}ClN_2O_2$: C, 70.66; H, 6.88; N, 6.59; found: C, 70.51; H, 6.75; N, 6.57. Rf = 0.79 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}N_2O_2$ 389.2229; Found 389.2205.

*(±)-2-(1-Benzylindoline-5-yl)-2-(3,4,5-trimethoxyphenyl)ethane-1-amine hydrochloride (**25ah**).* Compound **25ah** was obtained using **GP8** and recovered as light brown crystals (168 mg, 90% yield; mp 162–163 °C). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.53 (s, =CH, 1H), 7.51 – 7.35 (m, =CH, 7H), 6.71 (s, =CH, 2H), 4.68 (s, $CH_2$, 2H), 4.46 – 4.35 (m, CH, 1H), 3.86 – 3.82 (m, $CH_3$, $CH_2$, 8H), 3.73 – 3.65 (m, $CH_3$, $CH_2$, 5H), 3.17 (t, *J* = 7.4 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 153.9, 143.1, 139.9, 137.5, 136.6, 135.6, 130.9, 130.3, 129.90, 129.04, 127.9, 125.6, 119.2, 105.3, 59.8, 55.7, 54.0, 49.2 (2C), 42.9, 27.7. Anal. Calcd for $C_{26}H_{31}ClN_2O_3$: C, 68.64; H, 6.87; N, 6.16; found: C, 68.44; H, 6.78; N, 6.37. Rf = 0.47 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{31}N_2O_3$ 419.2335; Found 419.2309.

*(±)-2-(1-Benzylindoline-5-yl)-2-(furan-2-yl)ethane-1-amine hydrochloride (**25ai**).* Compound **25ai** was obtained using **GP8** and recovered as brown crystals (193 mg, 88% yield; mp 110–111 °C). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.60 – 7.38 (m, =CH, 9H), 6.44 – 6.36 (m, =CH, 2H), 4.76 (s, $CH_2$, 2H), 4.68 – 4.59 (m, CH,

1H), 3.94 - 3.84 (m, $CH_2$, 2H), 3.73 – 3.63 (m, $CH_2$, 1H), 3.56 – 3.45 (m, $CH_2$, 1H), 3.24 – 3.13 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 152.2, 141.4, 139.5, 137.1, 131.2, 130.1, 129.8, 129.1, 128.5, 126.1, 120.3, 110.63, 110.60, 107.9, 60.3, 54.0, 42.9, 42.5, 27.7. Anal. Calcd for $C_{21}H_{23}ClN_2O$: C, 71.08; H, 6.53; N, 7.89; found: C, 71.00; H, 6.58 N, 7.69. Rf = 0.77 ($MeOH/CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O$ 319.1810; Found 319.1788.

*(±)-2-(1-Benzylindoline-5-yl)-2-(1H-indole-3-yl)ethane-1-amine hydrochloride (**25ak**).* Compound **25ak** was obtained using **GP8** and recovered as purple crystals (157 mg, 84% yield; mp 140–141 °C). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.52 – 7.47 (m, =CH, 2H), 7.46 – 7.34 (m, =CH, 9H), 7.11 (t, *J* = 7.5 Hz, =CH, 1H), 6.97 (t, *J* = 7.5 Hz, =CH, 1H), 4.70 (t, *J* = 8.0 Hz, CH, 1H), 4.65 (s, $CH_2$, 2H), 3.83 (t, *J* = 7.6 Hz, $CH_2$, 2H), 3.35 (s, NH, 1H), 3.33 – 3.27 (m, $CH_2$, 2H), 3.11 – 3.04 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 144.0, 139.4, 137.4, 136.5 (2C), 130.9, 130.0, 129.0, 128.3, 126.3, 125.8, 122.4, 121.9, 119.2, 119.0, 118.2, 112.8, 111.5, 60.0, 53.9, 43.4, 41.1, 27.6. Anal. Calcd for $C_{25}H_{26}ClN_3$: C, 74.33; H, 6.49; N, 10.40; found: C, 74.48; H, 6.76; N, 10.55. Rf = 0.22 ($MeOH/CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3$ 368.2127; Found 368.2114.

**General Procedure 9 (GP9): Reduction of Nitro Groups in *N*-Benzylindoles (14aa-ak)**

$NaBH_4$ (102.2 mg, 2.70 mmol, 5 equiv) was added to a suspension of C5-substitued *N*-benzylindole derivatives (1 equiv.) and $NiCl_2{\cdot}6H_2O$ (1 equiv.) in methanol (4 mL) at 0 °C and the mixture was stirred at 0 °C for 30 min. The reaction mixture was quenched by addition of saturated $NH_4Cl$ solution at 0 °C and extracted with $CH_2Cl_2$ (30 mL). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$. After filtration of the drying agent, the filtrate was concentrated to dryness in vacuo. The residue was purified by silica gel column chromatography to obtain the **26aa-26ak**.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-phenylethan-1-amine (**26aa**).* Compound **26aa** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow oil (58 mg, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, =CH, 1H), 7.33 – 7.25 (m, =CH, 7H), 7.24 – 7.15 (m, =CH, 2H), 7.14 – 7.09 (m, =CH, 3H), 7.06 (d, *J* = 8.5 Hz, =CH, 1H), 6.52 (d, *J* = 3.1 Hz, =CH, 1H), 5.28 (s, $CH_2$, 2H), 4.11 (t, *J* = 7.4 Hz, CH, 1H), 3.38 (d, *J* = 7.4 Hz, $CH_2$, 2H), 2.31 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.8, 137.7, 135.5, 133.8, 129.1, 129.0, 128.9, 128.8, 128.3, 127.9, 127.1, 126.5, 122.6, 120.2, 110.2, 101.8, 55.0, 50.4, 47.3. IR ($CH_2Cl_2$, $cm^{-1}$): 3363, 3059, 3027, 2923, 2853, 1950, 1874, 1646, 1601, 1484, 1452, 1355, 1311, 1263, 1182, 1029, 801. Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58; found: C, 84.55; H, 6.73; N, 8.68. Rf = 0.28 ($MeOH/CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd $C_{23}H_{23}N_2$ 327.1861; Found 327.1840.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-amine (**26ab**).* Compound **26ab** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light brown oil (66 mg, 78% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, =CH, 3H), 7.36 (d, *J* = 8.1 Hz, =CH, 2H), 7.33 – 7.22 (m, =CH, 3H), 7.20 (d, *J* = 8.5 Hz, =CH, 1H), 7.16 – 7.04 (m, =CH, 3H), 6.97 (d, *J* = 8.5 Hz, =CH, 1H), 6.50 (d, *J* = 3.1 Hz, =CH, 1H), 5.25 (s, $CH_2$, 2H), 4.31 – 4.24 (m, CH, 1H), 4.25 – 4.10 (m, $CH_2$, 2H), 3.37 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.3, 137.5, 135.7, 132.0, 129.3, 129.1, 129.0, 128.97 (q, *J* = 32.2 Hz), 128.6, 127.9, 127.0, 125.7 (q, *J* = 3.7 Hz), 123.1, 122.3, 120.4, 110.6, 101.9, 52.8, 50.4, 46.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2925, 2089, 1637, 1511, 1484, 1453, 1326, 1264, 1164, 1121, 1068, 1017, 834. Anal. Calcd for $C_{24}H_{21}F_3N_2$: C, 73.08; H, 5.37; N, 7.10; found: C, 73.20; H, 5.45; N, 7.18. Rf = 0.30 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}F_3N_2$ 395.1735; Found 395.1711.

*(±)-4-(2-Amino-1-(1-benzyl-1H-indol-5-yl)ethyl)phenol (**26ac**).* Compound **26ac** was obtained using **GP9**. Column chromatography (MeOH/$CH_2Cl_2$ (2:8)) gave the product as dirty white crystals (161 mg, 92% yield; mp 96.2–97.2 °C ($CH_2Cl_2$/Hexane)). $^{1}$H NMR (400 MHz, $CD_3OD$) δ 7.44 (s, =CH, 1H), 7.22 – 6.87 (m, =CH, 10H), 6.73 – 6.67 (m, =CH, 2H), 6.41 (d, *J* = 3.1 Hz, =CH, 1H), 5.19 (s, $CH_2$, 2H), 3.98 (t, *J* = 7.5 Hz, CH, 1H), 3.25 – 3.15 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 155.9, 138.3, 135.4, 134.1, 133.5, 129.3, 128.9, 128.8, 128.4, 127.2, 126.7, 121.7, 119.5, 115.2, 110.0, 101.1, 52.4, 49.6, 46.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3347, 2925, 1707, 1611, 1514, 1484, 1355, 1264, 1176, 1029, 959, 833, 732. Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18; found: C, 80.88; H, 6.30; N, 8.02. Rf = 0.20 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O$ 343.1810; Found 343.1787.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(4-fluorophenyl)ethan-1-amine (**26ad**).* Compound **26ad** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as dark yellow oil (178 mg, 92% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, =CH, 1H), 7.35 – 7.19 (m, =CH, 6H), 7.15 – 7.09 (m, =CH, 3H), 7.04 – 6.93 (m, =CH, 3H), 6.51 (d, *J* = 3.0 Hz, 1H), 5.28 (s, $CH_2$, 2H), 4.11 – 4.03 (s, CH, 1H), 3.47 – 3.23 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, *J* = 244.3 Hz), 138.7, 137.4, 135.5, 132.6, 129.6 (d, *J* = 7.8 Hz), 129.1, 129.0, 128.9, 127.8, 126.9, 122.2, 120.1, 115.5 (d, *J* = 21.1 Hz), 110.3, 101.7, 50.2, 30.4, 29.8. IR ($CH_2Cl_2$, $cm^{-1}$): 3641, 3371, 3300, 3032, 2924, 2855, 1887, 1727, 1602, 1507, 1484, 1355, 1222, 1159, 1093, 960, 851, 806. Anal. Calcd for $C_{23}H_{21}FN_2$: C, 80.21; H, 6.15; N, 8.13; found: C, 80.09; H, 6.02; N, 8.19. Rf = 0.28 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}FN_2$ 345.1767; Found 345.1741.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(4-bromophenyl)ethan-1-amine (**26ae**).* Compound **26ae** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (3:7)) gave the product as light yellow oil (53 mg, 81% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, =CH, 1H), 7.39 (d, *J* = 8.2, =CH, 2H), 7.31 – 7.24 (m, =CH,

4H), 7.20 (d, *J* = 8.4 Hz, =CH, 1H), 7.12 (m, =CH, 4H), 6.98 (d, *J* = 8.4 Hz, =CH, 1H), 6.50 (d, *J* = 3.0 Hz, =CH, 1H), 5.26 (s, $CH_2$, 2H), 4.09 (t, *J* = 7.3 Hz, CH, 1H), 3.40 – 3.20 (m, $CH_2$, 2H), 3.30 – 3.10 (m, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.6, 135.6, 132.9, 131.8, 130.0, 129.2, 129.1, 129.0, 127.9, 127.1, 122.4, 120.4, 120.2, 110.4, 101.8, 53.6, 50.4, 46.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3025, 2918, 2852, 2358, 1686, 1552, 1486, 1453, 1355, 1260, 1182, 1073, 1009, 726. Anal. Calcd for $C_{23}H_{21}BrN_2$: C, 68.15; H, 5.22; N, 6.91; found: C, 67.98; H, 5.07; N, 6.82 Rf = 0.17 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}BrN_2$ 405.0966; Found 405.0954.

*(±)-4-(2-Amino-1-(1-benzyl-1H-indol-5-yl)ethyl)-N,N-dimethylaniline (**26af**).* Compound **26af** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as light brown oil (178 mg, 92% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, CH, 1H), 7.33 – 7.21 (m, 3H), 7.21 – 6.95 (m, 7H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 2.9 Hz, 1H), 5.25 (s, $CH_2$, 2H), 3.99 (t, *J* = 7.4 Hz, CH, 1H), 3.31 (d, *J* = 7.4 Hz, $CH_2$, 2H), 2.88 (s, $CH_3$, 6H), 1.83 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.8, 135.4, 134.6, 131.7, 129.1, 129.0, 128.9, 128.7, 127.8, 127.1, 122.6, 120.0, 113.2, 110.1, 101.8, 53.9, 50.4, 47.5, 41.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3625, 3365, 3030, 2923, 2802, 1873, 1704, 1613, 1519, 1483, 1352, 1264, 1183, 1132, 1029, 947, 816, 733. Anal. Calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.37; N, 11.37; found: C, 81.16; H, 7.30; N, 11.24. Rf = 0.12 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}N_3$ 370.2283; Found 370.2262.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(2,5-dimethoxyphenyl)ethan-1-amine (**26ag**).* Compound **26ag** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (4:69) gave the product as dark brown oil (178 mg, 92% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, =CH, 1H), 7.37 – 7.19 (m, =CH, 4H), 7.17 – 7.07 (m, =CH, 4H), 6.87 (m, =CH, 1H), 6.80 (d, *J* = 8.8 Hz, =CH, 1H), 6.73 – 6.67 (m, =CH, 1H), 6.52 (d, *J* = 2.7 Hz, =CH, 1H), 5.25 (s, $CH_2$, 2H), 4.58 (s, CH, 1H), 3.76 (s, $CH_3$, 3H), 3.74 (s, $CH_3$, 3H), 3.33 (bs, $CH_2$, , 2H), 2.03 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.9, 151.9, 137.8, 135.5, 133.7, 133.4, 129.1, 129.0, 128.7, 127.8, 127.1, 123.0 120.5, 115.2, 112.0, 110.8, 110.0, 101.8, 56.4 (2C), 55.9, 50.4, 46.7. IR ($CH_2Cl_2$, $cm^{-1}$): 3366, 2932, 1705, 1587, 1496, 1280, 1049, 877, 800, 732. Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25; found: C, 77.58; H, 6.71; N, 7.13. Rf = 0.24 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}N_2O_2$ 387.2073; Found 387.2049.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(3,4,5-trimethoxyphenyl)ethan-1-amine (**26ah**).* Compound **26ah** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as dirty white crystals (88 mg, 86% yield; mp 212–213 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, =CH, 1H), 7.30 – 7.19 (m, =CH, 4H), 7.00 – 7.07 (m, =CH, 4H), 6.50 – 6.54 (m, =CH, 2H), 6.44 (d, *J* = 3.0 Hz, =CH, 1H), 5.20 (s, $CH_2$, 2H), 4.50 – 4.40 (m, CH, 1H), 3.74 (s, $CH_3$, 6H), 3.70 (s, $CH_3$, 3H), 3.65 – 3.50 (m, $CH_2$, $NH_2$, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 137.5, 137.0, 136.5, 135.8, 130.9, 129.22, 129.20,

129.0, 127.9, 127.0, 121.9, 120.0, 110.6, 105.3, 101.9, 60.9, 56.4, 50.4, 49.3, 44.6. IR ($CH_2Cl_2$, $cm^{-1}$): 3435, 2090, 1636, 1509, 1454, 1424, 1353, 1236, 1125, 726. Anal. Calcd for $C_{26}H_{28}N_2O_3$: C, 74.97; H, 6.78; N, 6.73; found: C, 74.90; H, 6.71; N, 6.85. Rf = 0.13 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_3$ 417.2178; Found 417.2151.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(1H-indol-5-yl)ethan-1-amine (**26aj**).* Compound **26aj** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as yellow oil (178 mg, 92% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.71 (bs, NH, 1H), 7.55 - 7.54 (m, =CH, 2H), 7.36 – 6.99 (m, =CH, 11H), 6.48 (dd, *J* = 7.5, 2.8 Hz, 2H), 5.25 (s, $CH_2$, 2H), 4.18 (t, *J* = 7.4 Hz, CH, 1H), 3.44 – 3.36 (m, $CH_2$, 2H), 2.05 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.8, 135.4, 135.0, 134.9, 134.8, 129.1, 129.0, 128.8, 128.3, 127.8, 127.0, 124.9, 122.80, 122.78, 120.0, 119.7, 111.6, 110.1, 102.3, 101.8, 53.8, 50.3, 30.0. Anal. Calcd for $C_{25}H_{23}N_3$: C, 82.16; H, 6.34; N, 11.50; found: C, 82.02; H, 6.27; N, 11.40. IR ($CH_2Cl_2$, $cm^{-1}$): 3413, 2923, 2851, 1641, 1483, 1454, 1343, 1123, 1090, 803, 727.l. Rf = 0.12 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3$ 366.1970; Found 366.1947.

*(±)-2-(1-Benzyl-1H-indol-5-yl)-2-(1H-indol-3-yl)ethan-1-amine (**26ak**)*. Compound **26ak** was obtained using **GP9**. Column chromatography (EtOAc/Hexane (4:6)) gave the product as dirty white crystals (88 mg, 86% yield; mp 212–213 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.17 (bs, NH, 1H), 7.60 (s, =CH, 1H), 7.51 (d, *J* = 7.9 Hz, =CH, 1H), 7.36 – 7.21 (m, =CH, 4H), 7.21 – 7.07 (m, =CH, 5H), 7.07 – 6.94 (m, =CH, 3H), 6.48 (d, *J* = 2.9 Hz, =CH, 1H), 5.24 (s, $CH_2$, 2H), 4.35 – 4.26 (m, CH, 1H), 3.52 – 3.40 (m, $CH_2$, 1H), 3.37 – 3.24 (m, $CH_2$, 1H), 1.73 (bs, $NH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.7, 135.6, 134.19, 134.17, 129.0, 128.9, 128.6, 127.8, 127.4, 127.1, 122.5, 122.2, 121.4, 120.4, 119.8, 119.5, 111.3, 110.0, 101.7, 50.4, 47.9, 47.1. IR ($CH_2Cl_2$, $cm^{-1}$): 3412, 3098, 3053, 2923, 1586, 1484, 1455, 1337, 1264, 1181, 1091, 884, 799. Anal. Calcd for $C_{25}H_{23}N_3$: C, 82.16; H, 6.34; N, 11.50; found: C, 82.04; H, 6.10; N, 11.39. Rf = 0.10 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3$ 366.1970; Found 366.1946.

*(±)-2-(1H-Indol-5-yl)-2-phenylethan-1-amine (**27aa**).* Compound **27aa** was obtained using **GP9**. Column chromatography (MeOH/$CH_2Cl_2$ (2:8)) gave the product as white crystals (160 mg, 92% yield; mp 97–98 °C ($CH_2Cl_2$/Hexane)). $^1$H NMR (400 MHz, $CD_3OD$) δ 7.48 (s, =CH, 1H), 7.34 (d, *J* = 8.3 Hz, =CH, 1H), 7.29 – 7.11 (m, =CH, NH, 7H), 7.15 (bs, =CH, 1H), 7.01 (d, *J* = 6.6 Hz, =CH, 1H), 6.42 (s, =CH, 1H), 4.08 (d, *J* = 4.7 Hz, CH, 1H), 3.34 – 3.22 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 143.7, 135.5, 132.7, 128.6, 128.4, 127.8, 126.2, 125.0, 121.6, 119.1, 111.3, 101.1, 53.6, 46.0. IR ($CH_2Cl_2$, $cm^{-1}$): 3368, 1794, 1735,1552, 1378, 1265, 1097, 894, 765. Rf=0.12 (MeOH/$CH_2Cl_2$ (1:19), 254 nm). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2$ 237.1392; Found 237.1381.

## ■ ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

NMR spectra for all compounds (PDF)

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**Notes**

The authors declare no competing financial interest.

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