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Synthesis of highly *N*-substituted indole library via conjugate additions of indoline and their synthetic tool potentials

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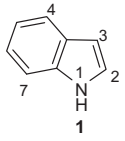
ABSTRACT

A comprehensive library of *N*- or 1-substituted indoles was formed by conjugate additions of indoline with Michael acceptors followed by an oxidation step. Using *N*-substituted indoles as key Michael donors, the synthesis of 1,3-disubstituted indoles was also accomplished.

1. Introduction

The indole (**1**) ring is of great interest and significance since this sub-unit is found in numerous natural alkaloids.[1–7] Therefore, intensive efforts have been devoted to the development of efficient methods for the synthesis of functionalized indoles. While many methods for the functionalization of indole at C3 are well established,[8–11] there is still limited ease of access to *C*2 and *N*-functionalized indoles (Fig. 1). Although *N*-functionalized indoles also represent an important subclass, the derivatization of the indole nitrogen atom is difficult due to its low nucleophilicity.[12–17] Both the alkylation of indoles and the salts of indoles under extreme conditions usually gives N- and C-alkylation products with low regioselectively.[18–22] Michael or conjugate additions are one of the most fundamental indole functionalization reactions.[23–27] Recently, we have been communicating our two-step synthesis results to access new *N*-substituted indoles via the conjugate addition reaction of indoline with Michael acceptors.[28] Herein, we report our detailed results on the synthesis of a highly *N*-substituted indole library.



1

Fig. 1. Indole (**1**).

2. Results and discussions

The Michael addition is the cornerstone of our synthesis. In our synthetic approach, the other cornerstone is the indoline used as a Michael donor. The first step of the method was the conjugate addition of indoline with various acceptors, which provided *N*-alkyl indolines (Scheme 1). Cyclic unsaturated ketones, acyclic unsaturated ketones and esters, nitro alkenes, 1,4-naphthoquinone, 1,1-bis(phenylsulfonyl)ethylene, and *N*-phenyl maleimide were used as Michael acceptors (Table 1, entries 1–17). The results for reaction of the indoline, catalyzed by Lewis acid and base catalysts such as $Bi(NO)_3 \cdot 5H_2O$, KF/Al_2O_3, and 4-dimethylaminopyridine (DMAP) are presented in Table 1. The last step is the oxidation of the alkylated indolines to *N*-alkylated indoles in high yields (Scheme 1).

The Michael reaction of the indoline with 1,4-naphthoquinone (NQ) catalyzed by DMAP or KF/Al_2O_3 provided the indol-1-yl substituted naphthoquinone **5q** after oxidation with MnO_2 (Scheme 2). We also examined the Michael reaction of **3** with indol-1-yl naphthoquinone **5q**. Oxidation of the crude Michael addition product with MnO_2 in situ afforded **6** in 14% yield (Scheme 2). When *p*-benzoquinone (PBQ) was employed as a Michael acceptor, the desired product **7** was obtained in low yield after in situ oxidation with the MnO_2 (Scheme 2).

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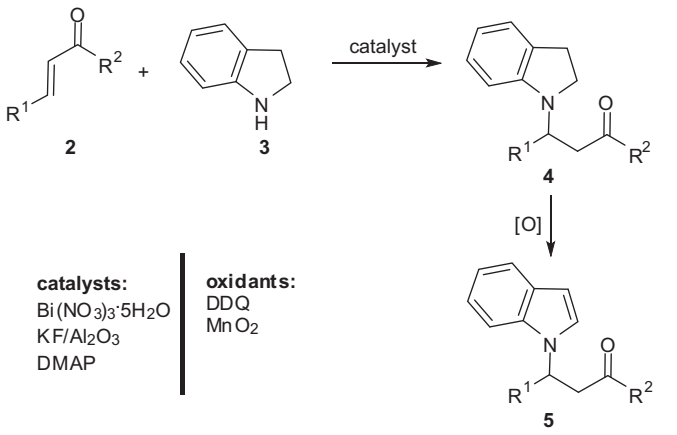


Scheme 1.

When the reaction of indoline with 1,1,2,2-tetracyanoethylene (TCNE, **8**) was carried out in the presence of bismuth nitrate in CH_2Cl_2 at rt for 5 h, the ^1H and ^{13}C NMR spectra of the isolated product **9** with an excellent yield of 95%, indicated that elimination of hydrogen cyanide from the primary Michael adduct resulted in the formation of tricyano compound **9** (Scheme 3). Despite all attempts, oxidation of the indoline ring in **9** to give the indole ring failed. Oxidation was carried out with oxidants such as MnO_2, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), elemental sulfur, Pd/C, and bis(trifluoroacetoxy)iodobenzene (PIFA). When the MnO_2-catalyzed oxidation of **9** was performed in presence of indoline (**3**), we only observed the oxidation of indoline to indole. We proposed that the strong electron-withdrawing CN groups increase the oxidation resistance of **9**.

In addition, an intramolecular Friedel–Crafts ring closure of Michael adduct **4k** obtained from indoline with dimethyl acetylenedicarboxylate (DMAD, **2k**) in CH_2Cl_2 (Table 1, entry 11) was accomplished using polyphosphoric acid (PPA) or Eaton's reagent (P_2O_5/$MeSO_3H$) as a dehydrating agent to provide the corresponding dihydroquinoline **11** (Scheme 4).[29] The Friedel–Crafts product **11** was oxidized with MnO_2 in methylene chloride to give the corresponding tricyclic system **12** (Scheme 4). Under similar reaction conditions, many attempts to perform an intramolecular Friedel–Crafts acylation of *N*-vinyl indole **5k** to **13** under failed, and only polymeric materials were recovered (Scheme 5).

Furthermore, 1-(2-nitro-1-phenylethyl) indoline (**4l**) was easily aromatized with DDQ to afford the corresponding indole **5l** in the 95% yield (Table 1, entry 12). Surprisingly, the use of MnO_2 in this oxidation resulted in an unexpected product mixture (Scheme 6). The reaction mixture was separated by silica gel column to give nitro styrene **14** (64%) and *N*-benzoyl indole (**15**) (31%). We propose a mechanism as depicted in Scheme 7. We assume that the indoline ring, which is very sensitive toward oxidation because of its tendency to be aromatized into an indole, is firstly oxidized with active MnO_2. The mechanism continues via the formation of a benzylic radical intermediate due to the stability of the benzylic radical as in Scheme 7. The decomposition via a six-membered transition state leads to the formation of isomeric nitro styrene **14**. The hydration of nitro olefins undergoes carbon–carbon cleavage to give *N*-benzoyl indole (**15**) and nitro methane. We assumed that MnO_2 acts as a Lewis acid during the addition of water to the olefin. To verify the hydration-bond cleavage, the hydration of olefins was again examined in the presence of MnO_2 and water in CH_2Cl_2. The reaction proceeded smoothly to afford *N*-benzoyl indole (**15**). However, the reaction was carried out in the presence of H_2SO_4/H_2O in CH_2Cl_2 to give the cleavage product **15** as a sole product.

Indoline (**3**) was also reacted with diethyl azodicarboxylate (DEAD; **19**) as a Michael substrate in methylene chloride (Scheme 8). In the presence of bismuth nitrate (0.1 mmol %) as a catalyst, it was found that the reaction afforded a mixture of indole (**1**) and the reduced DEAD **20** instead of the expected Michael adduct **21**. This result indicated that DEAD promoted dehydrogenation of indoline (**3**) to indole (**1**).

To test the developed methodology, we focused our attention on the enantioselective synthesis of *N*-substituted indolines/indoles. We selected the Michael addition of β-nitro styrene with indoline as a model reaction. The chiral catalysts were obtained from commercial sources, and were used in the asymmetric Michael additions. The reaction of β-nitro styrene with indoline in the presence of 0.2–10 mol % of (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate (**22**), L-(+)-tartaric acid (**23**), and (*R*,*R*)-[Al(salen)Cl] (**24**) resulted in excellent yields of the expected Michael product **4l** (93–96%) (Scheme 9). Unfortunately, no enantioselectivity could be detected by ^1H NMR spectroscopy/HPLC in the reactions.

The Michael additions to *N*-alkyl indoles were then carried out with β-nitro styrene (**2l**) to yield 1,3-disubstituted indoles. The results are summarized in Table 2 (entries 1–7). The best results were obtained using zinc triflate (0.1 mmol) as a Lewis acid catalyst. The ^1H and ^{13}C NMR spectra revealed that the products were obtained as a mixture of the expected diastereomers (Table 2, entries 2, 4–7) and enantiomers for both entries 1 and 2. In this manner, the Michael reaction of *N*-vinyl indole derivative **5j** with β-nitro styrene did not occur under the same conditions. The original materials were recovered unchanged (Scheme 10). We assume that the resonance structure **5jR** strongly reduced the reactivity of the indole ring in **5j**. To support this hypothesis, the reaction between *N*-vinyl indoline **4j** and β-nitro styrene was examined under the same conditions (Scheme 11). Interestingly, this reaction afforded an unexpected product **26** as a single product in high yield. The proposed mechanism involves the formation of a zwitterionic enolate **4jR** and the attack of the enolate to the acceptor to give a new α-Michael product **26**. The geometry of the product **26** (*E or Z isomer*) was not determined by NOE ^1H NMR spectroscopy. The reaction of the Michael product **26** with DDQ gave **27** in an 87% yield (Scheme 11). Unlike **4j**, the same product from **5j** was not obtained. We think that both the indole ring and the vinyl group resulted through the resonance structures of **5j** not being prone to give the corresponding Michael adduct. We also examined the enantioselective reaction of the methyl 3-(1*H*-indol-1-yl) propanoate **(5d**) model as a compound with β-nitro styrene in the presence of (*S*,*S*)-2,2′-isopropylidene-bis (4-phenyl-2-oxazoline)–$Zn(OTf)_2$ (Scheme 12). The desired Michael product **29h** was obtained through high chemical yields (85–90%) and low enantioselectivies (15.6–27.6% ee) (Table 3). The enantiomeric excess (ee) for the product was determined by chiral HPLC analysis.

3. Conclusions

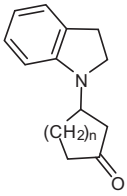
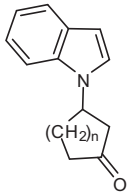
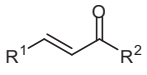
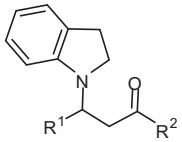
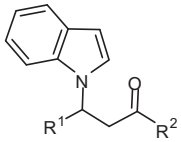
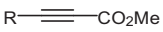
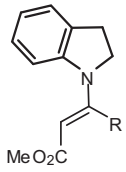
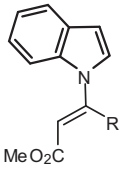
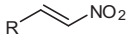
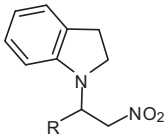
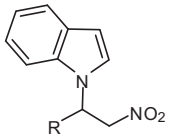
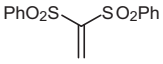
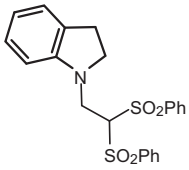
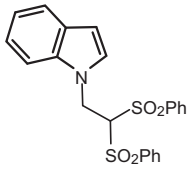
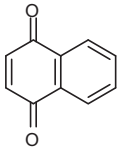
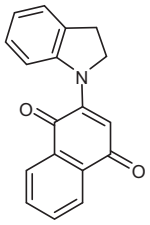
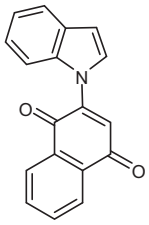
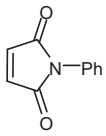
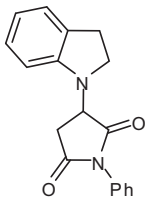
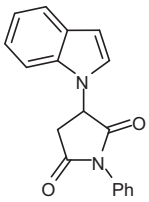
In summary, we have demonstrated that the Lewis acid/base-catalyzed conjugate addition reactions of α,β-unsaturated acceptors with indoline provides a highly *N*-substituted indole library followed by subsequent oxidation. The enantioselective alkylations for the selected model reactions were not observed here. However, we hope that further studies will result in highly enantio- and diastereoselective variants of this reaction.

4. Experimental section

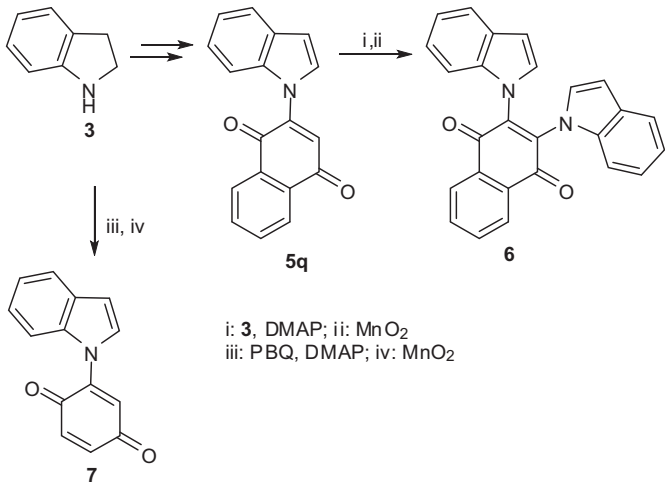
4.1. General

All reagents and solvents were purchased from commercial suppliers (Sigma–Aldrich or Fluka) 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 HF_{254} (Fluka), respectively. Melting points were determined on Buchi 539 capillary melting apparatus and uncorrected. Infrared

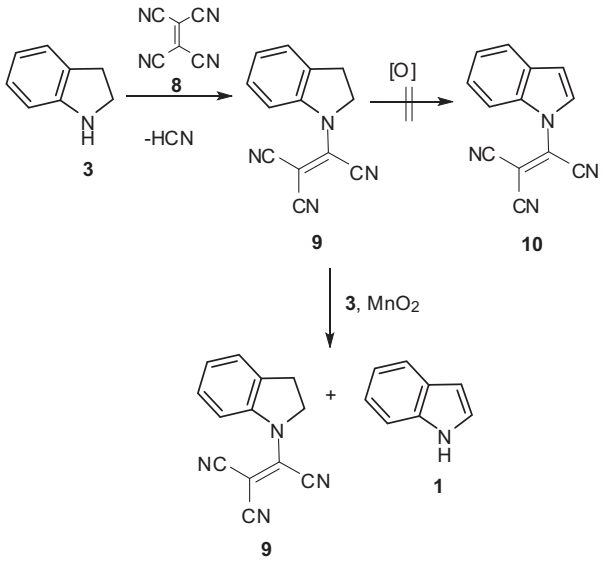
Table 1
The catalysts reagent for the synthesis of new *N*-substituted indolines and indoles

Entry	Acceptor			Product	Yield (%)	Product	Yield (%)
1		**2a**	n=1	 **4a**	NR,[a] 35,[b,f] 90[c,f]	 **5a**	95,[d] 92[e]
2		**2b**	n=2	**4b**	NR,[a] 30,[b] 94[c]	**5b**	92,[d] 90[e]
3		**2c**	n=3	**4c**	NR,[a] 92,[b]96[c]	**5c**	95,[d] 97[e]
4		**2d**	R^1=H, R^2=Me	 **4d**	93,[a] 97,[b] 95[c]	 **5d**	97,[d] 95[e]
5		**2e**	R^1=Me, R^2=Me	**4e**	NR,[a] 92,[b] 90[c]	**5e**	92,[d] 90[e]
6		**2f**	R^1=Ph, R^2=Me	**4f**	NR,[a] 87,[b,f] 86[c,f]	**5f**	87,[d] 85[e]
7		**2g**	R^1=Ph, R^2=Ph	**4g**	NR,[a] 60,[b,f] 58[c,f]	**5g**	60,[d] 65[e]
8		**2h**	R^1=H, R^2=OMe	**4h**	97,[a] 90,[b] 89[c]	**5h**	96,[d] 93[e]
9		**2i**	R^1=Me, R^2=OMe	**4i**	NR,[a] 95,[b] 87[c]	**5i**	95,[d] 92[e]
10		**2j**	R=H	 **4j**	81,[a] 95,[b] 87[c]	 **5j**	97,[d] 95[e]
11		**2k**	R=CO_2Me	**4k**	85,[a] 84,[b] 77[c]	**5k**	85,[d] 84[e]
12		**2l**	R=Ph	 **4l**	95,[a] 94,[b] 87[c]	 **5l**	95,[d] UP[e]
13		**2m**	R=furan	**4m**	96,[a,f] 95,[b,f] 83[c,f]	**5m**	93,[d] 65[e]
14		**2n**	R=thiophen	**4n**	90,[a,f] 87,[b,f] 82[c,f]	**5n**	94,[d] —[e]
15		**2o**		 **4o**	98,[a] 95,[b] 92[c]	 **5o**	98,[d] 56[e]
16		**2p**		 **4p**	NR,[a] 87,[b] 82[c]	 **5p**	47,[d] 51[e]
17		**2q**		 **4q**	91,[a] 85,[b] 81[c]	 **5q**	79,[d] 93[e]

NR: no reaction.
UP: unexpected product.
[a] $Bi(NO_3)_3 \cdot 5H_2O$ (10 mmol %).
[b] KF/Al_2O_3 (10 mmol %).
[c] DMAP (10 mmol %).
[d] DDQ (1 mmol).
[e] MnO_2 (10 mmol).
[f] The yield was determined by ^1H NMR spectroscopy.



Scheme 2.



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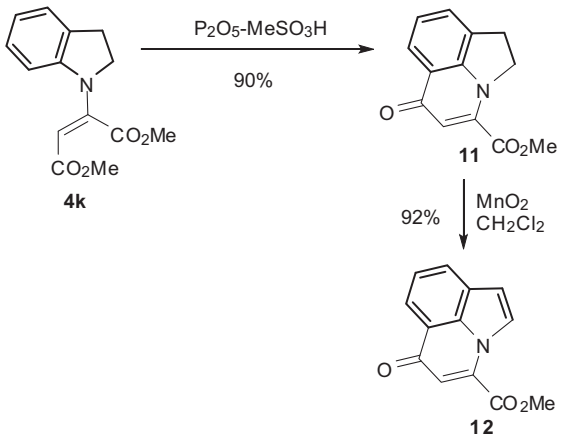

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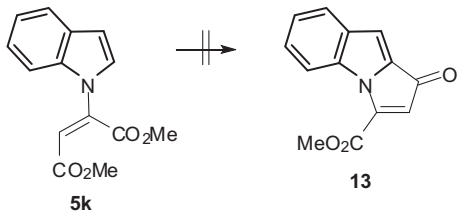

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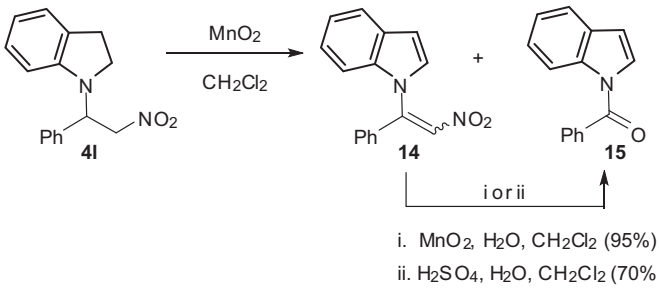
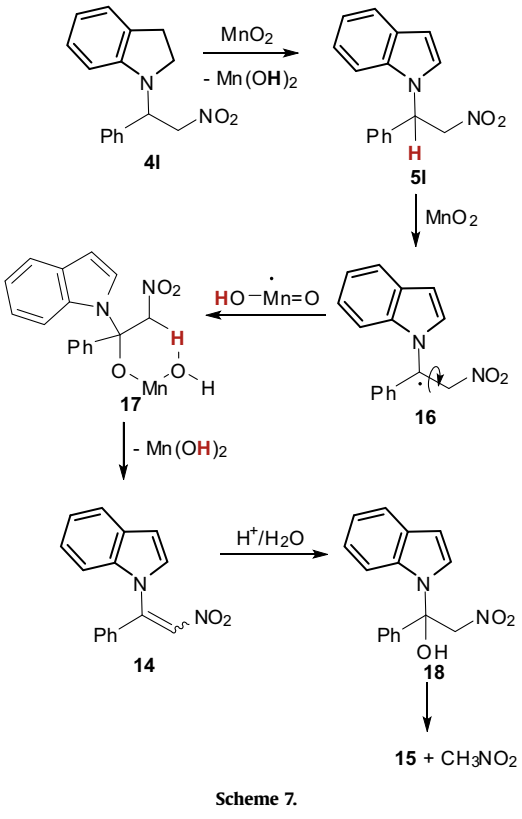
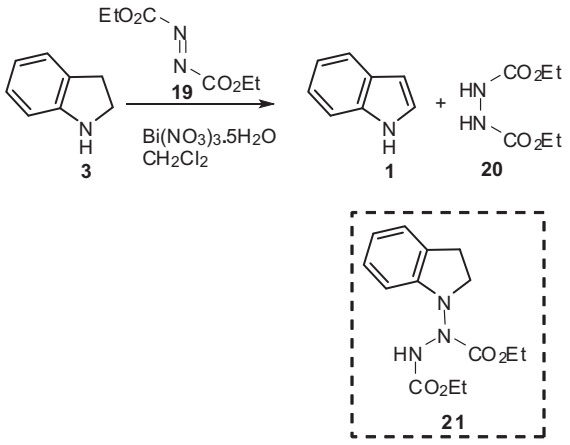


Scheme 6.

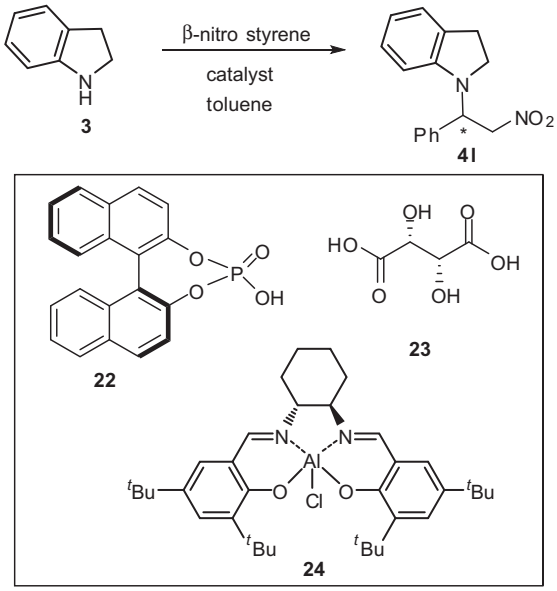


Scheme 7.

spectra were recorded on a Mattson 1000 FT-IR spectrophotometer. ^{1}H NMR and ^{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. Elemental analyses were carried out on a Leco CHNS-932 instrument. Enantiomeric purity for enantioselective syntheses was determined by chiral HPLC (Hewlett Packard 1200) analysis using a enantiopure stationary phase (Daicel Chiralcel OD), eluting with *i*-PrOH/hexane, and using UV detection at 254 nm.



Scheme 8.



Scheme 9.

4.2. General procedure of Lewis acid/base catalyzed Michael addition of indoline with α,β-unsaturated systems

To a solution of indoline (1.0 mmol) and Michael acceptor (1.0 mmol) in CH_2Cl_2 (10 mL) was added Lewis acid/base (0.1 mmol). The mixture was stirred until the starting material disappeared (TLC, hexane/ethyl acetate). After evaporation of the solvent, the crude product was dissolved with EtOAc (40 mL) and the organic phase was washed with water (2×20 mL). The EtOAc extract was dried over Na_2SO_4, filtered, evaporated in vacuo, and the compound was purified by silica gel column chromatography (hexane/ethyl acetate).

*4.2.1. (±)-3-(Indolin-1-yl)cyclohexanone (**4b**).* DMAP catalyzed reaction was performed at rt for 24 h in CH_2Cl_2. (±)-3-(Indolin-1-yl) cyclohexanone was obtained as pale yellow crystals (202 mg, 94%, mp 84–85 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.03 (m, =CH, 2H), 6.64 (t, J=7.6 Hz, =CH, 1H), 6.42 (d, J=7.6 Hz, =CH, 1H), 3.82–3.75 (m, CH, 1H), 3.49–3.43 (m, CH_2, 1H), 3.38–3.31 (m, CH_2, 1H), 2.98 (t, J=8.2 Hz, CH_2, 2H), 2.60–2.57 (m, CH_2, 1H), 2.56–2.50 (m, CH_2, 1H), 2.47–2.41 (m, CH_2, 1H), 2.33–2.25 (m, CH_2, 1H), 2.16–2.07 (m, CH_2, 2H), 1.86–1.70 (m, CH_2, 1H), 1.69–1.60 (m, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 150.2, 130.1, 127.6, 124.8, 117.9, 107.3, 55.0, 46.7, 43.9, 41.3, 28.5, 28.4, 22.9. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.90; H, 8.16; N, 6.69. IR (KBr, cm^{-1}) 3472, 3104, 3052, 2968, 1744, 1611, 1511, 1479, 1462, 1404, 1373, 1313, 1244, 1222, 1175, 1151, 1085, 1014, 979, 888, 848, 744.

*4.2.2. (±)-3-(Indolin-1-yl)cycloheptanone (**4c**).* DMAP catalyzed reaction was performed at rt for 24 h in CH_2Cl_2. (±)-3-(Indolin-1-yl) cycloheptanone was obtained as yellow crystals (220 mg, 96%, mp 73–74 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.06 (m, =CH, 2H), 6.65 (t, J=7.5 Hz, =CH, 1H), 6.46 (d, J=7.5 Hz, =CH, 1H), 3.73–3.67 (m, CH, 1H), 3.44–3.39 (m, CH, 1H), 3.28–3.21 (m, CH_2, 1H), 2.96–2.87 (m, CH_2, 2H), 2.84–2.81 (m, CH_2, 1H), 2.63–2.45 (m, CH_2, 3H), 2.14–1.97 (m, CH_2, 3H), 1.79–1.65 (m, CH_2, 2H), 1.49–1.43 (m, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8, 150.4, 130.5, 127.7, 124.8, 118.1, 107.9, 53.4, 47.1, 46.1, 44.2, 34.7, 28.5, 27.6, 24.5. Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.40; H, 8.46; N, 6.27. IR (KBr, cm^{-1}) 3376, 3046, 3024, 2931, 2855, 1698, 1606, 1488, 1472, 1459, 1392, 1347, 1331, 1304, 1254, 1202, 1162, 1024, 926, 746.

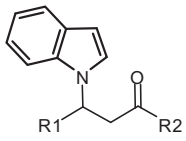
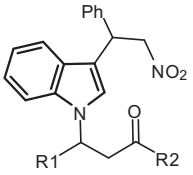
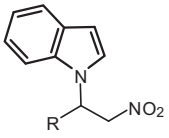
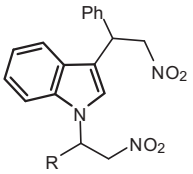
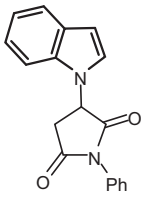
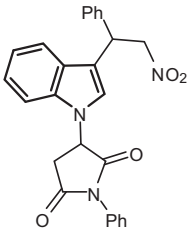
*4.2.3. (±)-4-(Indolin-1-yl)butan-2-one (**4d**).* KF/Al_2O_3 catalyzed reaction was performed at rt for 12 h in CH_2Cl_2. (±)-4-(Indolin-1-yl) butan-2-one was obtained as orange liquid (183 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.05 (m, =CH, 2H), 6.67 (dd, J=7.5, 0.7 Hz, =CH, 1H), 6.49 (d, J=7.5 Hz, =CH, 1H), 3.39 (t, J=7.0 Hz, CH_2, 2H), 3.33 (t, J=7.0 Hz, CH_2, 2H), 2.95 (t, J=7.0 Hz, CH_2, 2H), 2.73 (t, J=7.0 Hz, CH_2, 2H), 2.20 (s, CH_3, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 207.8, 152.1, 130.2, 127.6, 124.7, 118.0, 107.1, 53.5, 44.1, 41.3, 30.5, 28.8. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.45; H, 8.02; N, 7.52. IR (KBr, cm^{-1}) 3048, 2958, 2919, 2846, 1715, 1607, 1489, 1361, 1266, 1165, 747.

*4.2.4. (±)-4-(Indolin-1-yl)pentan-2-one (**4e**).* KF/Al_2O_3 catalyzed reaction was performed at rt for 24 h in CH_2Cl_2. (±)-4-(Indolin-1-yl) pentan-2-one was obtained as yellow liquid (187 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.05 (m, =CH, 2H), 6.64 (t, J=7.7 Hz, =CH, 1H), 6.48 (d, J=7.7 Hz, =CH, 1H), 4.21–4.16 (m, CH, 1H), 3.37 (dd, J=16.7, 8.4 Hz, CH_2, 1H), 3.27 (dd, J=16.7, 8.1 Hz, CH_2, 1H), 2.97–2.91 (m, CH_2, 2H), 2.70 (dd, J=15.7, 5.9 Hz, CH_2, 1H), 2.55 (dd, J=15.7, 8.4 Hz, CH_2, 1H), 2.17 (s, CH_3, 3H), 1.17 (d, J=6.8 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 150.8, 130.5, 127.6, 124.7, 117.8, 107.4, 47.4, 47.3, 46.6, 30.4, 28.4, 16.2. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.83; H, 8.43; N, 6.89. Found: C, 76.67; H, 8.25; N, 6.78. IR (KBr, cm^{-1}) 2968, 2845, 2319, 1713, 1607, 1488, 1460, 1389, 1361, 1259, 1157, 1022, 868, 748, 714, 549.

*4.2.5. Methyl 3-(indolin-1-yl)propanoate (**4h**).* $Bi(NO_3)_3 \cdot 5H_2O$ catalyzed reaction was performed at rt for 3 h in CH_2Cl_2. Methyl 3-(indolin-1-yl) propanoate was obtained as pale green liquid (199 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.06 (m, =CH, 2H), 6.67 (t, J=7.4 Hz, =CH, 1H), 6.52 (d, J=7.4 Hz, =CH, 1H), 3.70 (s, CH_3, 3H), 3.43 (t, J=7.7 Hz, CH_2, 2H), 3.36 (t, J=7.7 Hz, CH_2, 2H), 2.96 (t, J=7.7 Hz, CH_2, 2H), 2.62 (t, J=7.7 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 152.0, 130.1, 127.6, 124.7, 118.1, 107.2, 53.3, 52.0, 45.3, 32.6, 28.8. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.11; H, 7.23; N, 6.98. IR (KBr, cm^{-1}) 2951, 2925, 1737, 1513, 1484, 1464, 1438, 1399, 1368, 1315, 1262, 1208, 1171, 1062, 1014, 988, 841, 764, 743.

*4.2.6. (±)-Methyl 3-(indolin-1-yl)butanoate (**4i**).* KF/Al_2O_3 catalyzed reaction was performed at 80 °C for 4 days in CH_3CN. (±)-Methyl 3-(indolin-1-yl)butanoate was obtained as pale yellow liquid (208 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.05 (m, =CH, 2H), 6.64 (td, J=7.8, 0.7 Hz, =CH, 1H), 6.51 (d, J=7.8 Hz, =CH, 1H), 4.20–4.18 (m, CH, 1H), 3.67 (s, OCH_3, 3H), 3.40–3.35 (m, CH_2,

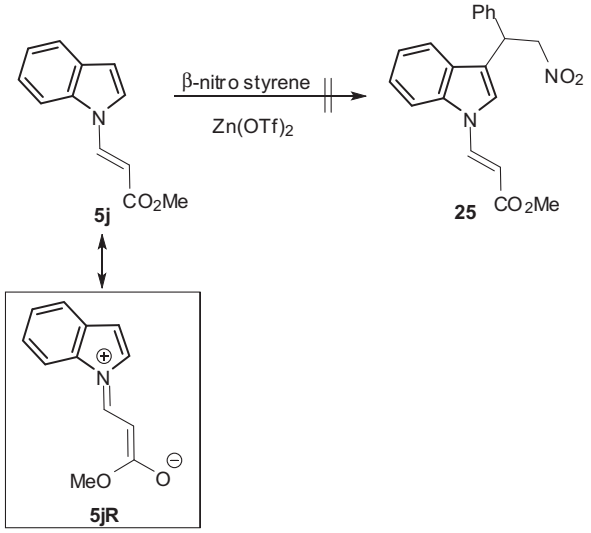
Table 2
The new 1,3-disubstituted indoles

Entry	Reagent		Product		Yield (%)
1		**4d** R_1=H, R_2=Me		**29d**	85
2		**4e** R_1=Me, R_2=Me		**29e**	77
3		**4h** R_1=H, R_2=OMe		**29h**	91
4		**4i** R_1=Me, R_2=OMe		**29i**	71
5		**4l** R=Ph		**29l**	88
6		**4m** R=furanyl		**29m**	82
7		**4q**		**29q**	93

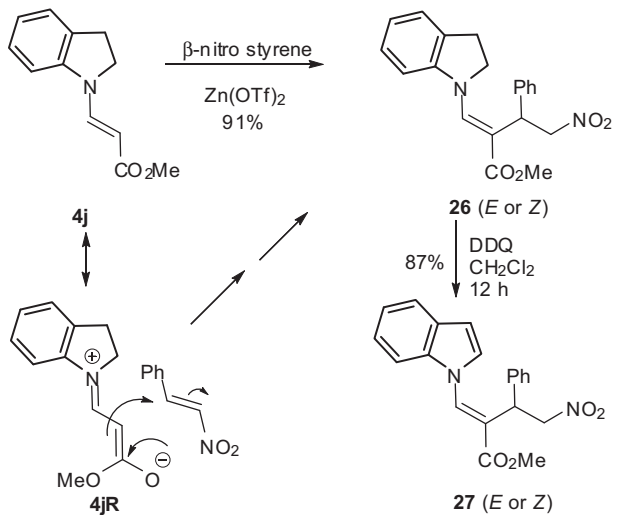
1H), 3.35–3.31 (m, CH_2, 1H), 2.95 (br t, J=8.1 Hz, CH_2, 2H), 2.64 (dd, J=14.5, 6.6 Hz, CH_2, 1H), 2.41 (dd, J=14.5, 8.1 Hz, CH_2, 1H), 1.22 (d, J=6.6 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7 (CO), 150.9, 130.3, 127.6 (=CH), 124.7 (=CH), 117.7 (=CH), 107.5 (=CH), 51.9 (OCH_3), 48.3 (CH), 46.2 (CH_2), 38.3 (CH_2), 28.4 (CH_2), 16.3 (CH_3). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.05; H, 7.83; N, 6.30. IR (KBr, cm^{-1}) 3025, 2963, 2925, 2850, 1736, 1607, 1489, 1436, 1393, 1260, 1160, 1091, 1018, 799, 745.

*4.2.7. (E)-Methyl 3-(indolin-1-yl)acrylate (**4j**).* KF/Al_2O_3 catalyzed reaction was performed at rt for 2 h in CH_2Cl_2. (*E*)-Methyl 3-(indolin-1-yl) acrylate was obtained as yellow crystals (193 mg, 95%, mp 133–134 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J=13.0 Hz, =CH, 1H), 7.19–7.16 (m, =CH, 2H), 6.97 (br d, J=7.5 Hz, =CH, 1H), 6.91 (t, J=7.5 Hz, =CH, 1H), 4.87 (d, J=13.0 Hz, =CH, 1H), 3.78 (t, J=8.5 Hz, CH_2, 2H), 3.73 (s, OCH_3, 3H), 3.21 (t, J=8.5 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 144.3, 140.8 (=CH), 130.7, 128.1 (=CH), 125.7 (=CH), 122.4 (=CH), 108.5 (=CH), 90.0 (=CH), 51.0 (OCH_3), 48.0 (CH_2), 27.8 (CH_2). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.53; H, 6.46; N, 6.95. IR (KBr, cm^{-1}) 3052, 1687, 1633, 1505, 1426, 1310, 1265, 1166, 977, 791, 744.

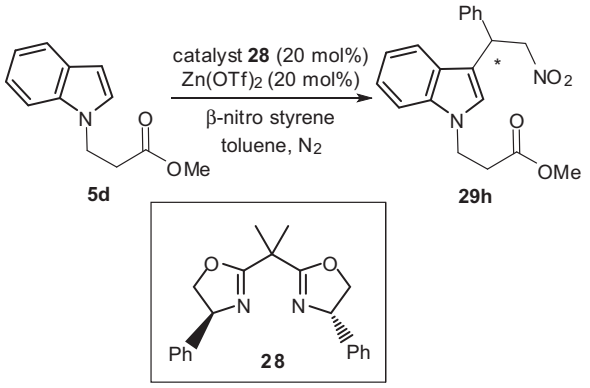
*4.2.8. Dimethyl 2-(indolin-1-yl)maleate (**4k**).* $Bi(NO_3)_3 \cdot 5H_2O$ catalyzed reaction was performed at rt for 3 h in CH_2Cl_2. Dimethyl 2-(indolin-1-yl)maleate was obtained as yellow crystals (222 mg, 85%, mp 134–135 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J=8.1 Hz, =CH, 1H), 7.09 (td, J=8.1, 0.7 Hz, =CH, 1H), 6.93 (br t, J=8.1 Hz, =CH, 1H), 6.81 (d, J=8.1 Hz, =CH, 1H), 5.03 (s, =CH, 1H), 4.04 (s, OCH_3, 3H), 3.86 (t, J=8.4 Hz, CH_2, 2H), 3.69 (s, OCH_3, 3H), 3.16 (t, J=8.4 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8 (CO), 165.6 (CO), 147.4, 142.7, 132.4, 127.9 (=CH), 125.7 (=CH), 123.1 (=CH), 111.5 (=CH), 91.6 (=CH), 53.3 (OCH_3), 51.3



Scheme 10.



Scheme 11.



Scheme 12.

Table 3
Enantioselective Michael reaction of methyl 3-(1*H*-indol-1-yl) propanoate (**5d**) with β-nitro styrene (**2l**) catalyzed by the chiral catalyst (*S*,*S*)-2,2′-isopropylidene-bis (4-phenyl-2-oxazoline) (**28**)

Entry	Time (h)	Temperature (°C)	Yield (%)	ee (%)
1	12	25	90	27.6
2	24	−30	88	19.6
3	24	−70	85	15.6

(OCH_3), 51.3 (CH_2), 27.4 (CH_2). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.33. Found: C, 64.22; H, 5.76; N, 5.26. IR (KBr, cm^{-1}) 2952, 2852, 1734, 1684, 1600, 1575, 1496, 1436, 1415, 1389, 130, 1214, 1171, 974, 867, 793, 746.

*4.2.9. (±)-1-(2-Nitro-1-phenylethyl)indoline (**4l**).* $Bi(NO_3)_3 \cdot 5H_2O$ catalyzed reaction was performed at rt for 1 h in CH_2Cl_2. (±)-1-(2-Nitro-1-phenylethyl)indoline was obtained as orange crystals (255 mg, 95%, mp 125–126 °C) in hexane/ethyl acetate; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.32 (m, =CH, 3H), 7.30–7.26 (m, =CH, 2H), 7.11–7.04 (m, =CH, 2H), 6.70–6.66 (m, =CH, 2H), 5.62 (t, *J*=7.6 Hz, CH, 1H), 5.01 (dd, *J*=12.4, 7.6 Hz, CH_2, 1H), 4.92 (dd, *J*=12.4, 7.6 Hz, CH_2, 1H), 3.46–3.41 (m, CH_2, 1H), 3.17–3.13 (m, CH_2, 1H), 2.96–2.90 (m, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 135.1, 129.8, 129.2 (=CH), 128.8 (=CH), 127.8 (=CH), 127.7 (=CH), 125.0 (=CH), 118.6 (=CH), 107.3 (=CH), 75.6 (CH), 57.7 (CH_2), 47.5 (CH_2), 28.4 (CH_2). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.46; H, 6.00; N, 10.47. IR (KBr, cm^{-1}) 3025, 2913, 2846, 2325, 1608, 1555, 1457, 1373, 1309, 1231, 1194, 1083, 742.

*4.2.10. 1-(2,2-Bis(phenylsulfonyl)ethyl)indoline (**4o**).* $Bi(NO_3)_3 \cdot 5H_2O$ catalyzed reaction was performed at rt for 10 h in CH_2Cl_2. 1-(2,2-Bis(phenylsulfonyl)ethyl)indoline was obtained as white crystals (419 mg, 98%, mp 122–123 °C) in hexane/ethyl acetate; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, =CH, 4H), 7.68 (m, =CH, 2H), 7.50 (m, =CH, 4H), 7.30–7.00 (m, =CH, 2H), 6.69 (t, *J*=8.0 Hz, =CH, 1H), 6.39 (d, *J*=8.0 Hz, =CH, 1H), 4.82 (t, *J*=6.2 Hz, CH, 1H), 3.95 (d, *J*=6.2 Hz, CH_2, 2H), 3.19 (t, *J*=8.4 Hz, CH_2, 2H), 2.71 (t, *J*=8.4 Hz, CH_2, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.6, 138.9, 134.7, 129.6, 129.5, 129.3, 127.6, 124.8, 119.0, 107.3, 82.0, 53.7, 47.7, 28.6. Anal. Calcd for $C_{22}H_{21}NO_4S_2$: C, 61.80; H, 5.95; N, 3.28. Found: C, 61.65; H, 5.78; N, 3.18. IR (KBr, cm^{-1}) 3070, 2930, 2846, 2325, 2297, 1606, 1488, 1446, 1329, 1264, 1153, 1079, 744, 688.

*4.2.11. 2-(Indolin-1-yl)naphthalene-1,4-dione (**4p**).* KF/Al_2O_3 catalyzed reaction was performed at rt for 2 day in CH_2Cl_2. 2-(Indolin-1-yl) naphthalene-1,4-dione was obtained as black crystals (240 mg, 87%, mp 129–130 °C) in hexane/ethyl acetate; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–8.06 (m, =CH, 2H), 7.75–7.71 (m, =CH, 1H), 7.69–7.65 (m, =CH, 1H), 7.26 (br d, *J*=6.6 Hz, =CH, 1H), 7.19–7.18 (m, =CH, 2H), 7.05–6.97 (m, =CH, 1H), 6.70 (s, =CH, 1H), 4.27 (t, *J*=8.0 Hz, CH_2, 2H), 3.15 (t, *J*=8.0 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1, 183.1, 148.5, 144.0, 134.3, 134.1, 132.8, 132.7, 132.5, 127.4, 126.9, 125.8, 125.7, 123.6, 115.5, 112.3, 54.6, 29.3. Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.35; H, 4.81; N, 5.09. IR (KBr, cm^{-1}) 2319, 2297, 1676, 1624, 1547, 1479, 1402, 1339, 1281, 1268, 749, 719.

*4.2.12. (±)-3-(Indolin-1-yl)-1-phenylpyrrolidine-2,5-dione (**4q**).* $Bi(NO_3)_3 \cdot 5H_2O$ catalyzed reaction was performed at rt for 2 h in CH_2Cl_2. (±)-3-(Indolin-1-yl)-1-phenylpyrrolidine-2,5-dione was obtained as pale yellow crystals (266 mg, 91%, mp 114–115 °C) in hexane/ethyl acetate; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51–7.39 (m, =CH, 3H), 7.32 (d, *J*=8.1 Hz, =CH, 2H), 7.14–7.07 (m, =CH, 2H), 6.76 (t, *J*=7.5 Hz, =CH, 1H), 6.48 (d, *J*=8.1 Hz, =CH, 1H), 4.88–4.84 (m, CH, 1H), 3.54–3.45 (m, CH_2, 2H), 3.18 (dd, *J*=18.4, 9.3 Hz, CH_2, 1H), 3.07 (t, *J*=8.2 Hz, CH_2, 2H), 2.94 (dd, *J*=18.4, 5.7 Hz, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 173.8, 131.7, 130.5, 129.5, 129.2, 129.1, 127.7, 126.6, 125.3, 119.6, 107.6, 56.0, 50.0, 31.4, 28.6. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.87; H, 5.40; N, 9.45. IR (KBr, cm^{-1}) 3473, 3048, 2961, 2849, 1777, 1715, 1606, 1500, 1488, 1458, 1382, 1260, 1177, 1063, 1027, 827, 747, 698.

4.3. 2-(Indolin-1-yl)ethene-1,1,2-tricarbonitrile (9)

To a solution of indoline (119 mg, 1.0 mmol) and TCNE (128 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added $Bi(NO_3)_3 \cdot 5H_2O$ (47 mg, 0.1 mmol). After the mixture was stirred at rt for 5 h, the solvent was evaporated under vacuo. The crude product was dissolved with EtOAc (40 mL) and the organic phase was washed with water (2×20 mL). The EtOAc extract was dried over Na_2SO_4, filtered, evaporated in vacuo, and the compound was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1). 2-(Indolin-1-yl)ethene-1,1,2-tricarbonitrile (**9**) was obtained as pale green crystals (209 mg, 95%, mp 143–144 °C) in hexane/ethyl acetate; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J*=8.1 Hz, =CH, 1H), 7.38–7.26 (m, =CH, 3H), 4.51 (t, *J*=7.5 Hz, CH_2, 2H), 3.34 (t, *J*=7.5 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 133.7, 133.6 (2C), 128.7 (=CH), 128.2 (=CH), 126.4 (=CH), 115.5 (=CH), 113.3, 112.9, 110.5, 56.0 (CH_2), 29.0 (CH_2). Anal. Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; N, 25.40. Found: C, 70.67; H, 3.44; N, 25.34. IR (KBr, cm^{-1}) 2922, 2852, 2217, 1550, 1463, 1407, 1329, 1264, 756, 523.

4.4. General procedure for the oxidation of Michael addition products to indole derivatives with MnO_2

To a solution of Michael addition product of indoline (1.0 mmol) in CH_2Cl_2 (10 mL) was added activated MnO_2 (10.0 mmol). The mixture was stirred at rt for 24 h. After filtration, the mixture was evaporated under vacuo and the compound was purified by silica gel column chromatography (hexane/ethyl acetate).

4.5. General procedure for the oxidation of Michael addition products to indole derivatives with DDQ

The Michael addition product (1.0 mmol) and DDQ (1.0 mmol) were dissolved in CH_2Cl_2 (10 mL). The mixture was stirred at rt for 24 h. After completion of the reaction, it was quenched with a saturated aqueous solution of $NaHCO_3$ (5%, 20 mL). CH_2Cl_2 layer was separated and washed with water and brine solution and dried over anhydrous Na_2SO_4 and filtered. The solvent was removed in vacuo and then the compound was purified by silica gel column chromatography (hexane/ethyl acetate).

*4.5.1. (±)-3-(1H-Indol-1-yl)cyclopentanone (**5a**).* (±)-3-(1*H*-Indol-1-yl)cyclopentanone was obtained as yellow oil (189 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J=7.6 Hz, =CH, 1H), 7.40 (d, J=7.6 Hz, =CH, 1H), 7.28 (t, J=7.6 Hz, =CH, 1H), 7.26–7.16 (m, =CH, 2H), 6.59 (d, J=2.9 Hz, =CH, 1H), 5.12–5.09 (m, CH, 1H), 2.87 (dd, J=18.5, 7.4 Hz, CH_2, 1H), 2.65 (dd, J=18.5, 7.4 Hz, CH_2, 1H), 2.61–2.48 (m, CH_2, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0, 136.2, 129.2, 123.8, 122.1, 121.5, 120.2, 109.7, 102.6, 53.3, 44.8, 37.4, 29.8. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.28; H, 6.51; N, 6.87. IR (KBr, cm^{-1}) 3472, 3104, 3052, 2968, 1744, 1611, 1511, 1479, 1462, 1404, 1373, 1313, 1244, 1222, 1175, 1151, 1085, 1014, 979, 888, 848, 744.

*4.5.2. (±)-3-(1H-Indol-1-yl)cyclohexanone (**5b**).* (±)-3-(1*H*-Indol-1-yl)cyclohexanone was obtained as yellow liquid (196 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J=7.8, 2.0 Hz, =CH, 1H), 7.35 (d, J=8.4 Hz, =CH, 1H), 7.26–7.20 (m, =CH, 2H), 7.16–7.12 (m, =CH, 1H), 6.57 (d, J=2.9 Hz, =CH, 1H), 4.72–4.66 (m, CH, 1H), 2.94–2.91 (m, CH_2, 1H), 2.90–2.77 (m, CH_2, 1H), 2.56–2.40 (m, CH_2, 2H), 2.35–2.30 (m, CH_2, 1H), 2.25–2.10 (m, CH_2, 2H), 1.85–1.78 (m, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 135.7, 128.9, 124.0, 122.0, 121.5, 120.1, 109.6, 102.6, 54.4, 48.4, 41.1, 31.6, 22.5. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.75; H, 7.40; N, 6.48. IR (KBr, cm^{-1}) 3048, 3051, 2950, 1713, 1511, 1476, 1461, 1414, 1310, 1216, 1187, 1014, 972, 884, 744.

*4.5.3. (±)-3-(1H-Indol-1-yl)cycloheptanone (**5c**).* (±)-3-(1*H*-Indol-1-yl)cycloheptanone was obtained as pale yellow liquid (220 mg, 97%); ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.55–7.50 (m, =CH, 2H), 7.43 (d, J=2.9 Hz, =CH, 1H), 7.11 (d, J=7.4 Hz, =CH, 1H), 7.00 (d, J=7.4 Hz, =CH, 1H), 6.43 (d, J=2.9 Hz, =CH, 1H), 4.78 (br t, J=11.2 Hz, CH, 1H), 3.36–3.29 (m, CH_2, 1H), 2.68–2.67 (m, CH_2, 1H), 2.64–2.48 (m, CH_2, 2H), 2.13–2.01 (m, CH_2, 2H), 1.95–1.89 (m, CH_2, 2H), 1.73–1.61 (m, CH_2, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 211.1, 135.5, 128.7, 125.8, 121.7, 121.2, 119.8, 110.6, 102.1, 52.7, 50.9, 44.2, 37.9, 27.5, 23.9. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.30; H, 7.40; N, 6.44. IR (KBr, cm^{-1}) 2932, 1701, 1609, 1461, 1411, 1305, 1213, 742.

*4.5.4. 4-(1H-Indol-1-yl)butan-2-one (**5d**).* 4-(1*H*-Indol-1-yl)butan-2-one was obtained as pale green liquid (181 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J=8.2 Hz, =CH, 1H), 7.33 (d, J=8.2 Hz, =CH, 1H), 7.25–7.19 (m, =CH, 1H), 7.13–7.08 (m, =CH, 2H), 6.47 (d, J=2.8 Hz, =CH, 1H), 4.42 (t, J=6.4 Hz, CH_2, 2H), 2.94 (t, J=6.4 Hz, CH_2, 2H), 2.10 (s, CH_3, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 206.4, 135.9, 128.9, 128.3, 121.8, 121.3, 119.7, 109.2, 101.7, 43.7, 40.8, 30.6. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.75; H, 7.01; N, 7.38. IR (KBr, cm^{-1}) 3053, 2908, 2319, 1715, 1464, 1357, 1314, 1164, 743.

*4.5.5. (±)-4-(1H-Indol-1-yl)pentan-2-one (**5e**).* (±)-4-(1*H*-Indol-1-yl)pentan-2-one was obtained as pale green liquid (184 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J=7.4 Hz, =CH, 1H), 7.42 (d, J=7.4 Hz, =CH, 1H), 7.22 (br t, J=7.4 Hz, =CH, 1H), 7.18 (d, J=3.3 Hz, =CH, 1H), 7.11 (br d, J=7.4 Hz, =CH, 1H), 6.53 (d, J=3.3 Hz, =CH, 1H), 5.08–5.03 (m, CH, 1H), 3.04 (dd, J=16.9, 5.5 Hz, CH_2, 1H), 2.90 (dd, J=16.9, 5.5 Hz, CH_2, 1H), 2.07 (s, CH_3, 3H), 1.57 (d, J=6.6 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 135.6, 128.9, 124.4, 121.8, 121.3, 119.8, 109.8, 102.2, 50.6, 47.6, 30.8, 21.1. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.47; H, 7.57; N, 6.97. IR (KBr, cm^{-1}) 3048, 2976, 2928, 1716, 1611, 1510, 1477, 1461, 1412, 1364, 1308, 1219, 1164, 764, 742.

*4.5.6. (±)-4-(1H-Indol-1-yl)-4-phenylbutan-2-one (**5f**).* (±)-4-(1*H*-Indol-1-yl)-4-phenylbutan-2-one was obtained as white crystals (228 mg, 87%, mp 103–104 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (ddd, J=7.7, 1.7, 0.9 Hz, =CH, 1H), 7.34 (dd, J=8.3, 0.9 Hz, =CH, 1H), 7.31–7.20 (m, =CH, 3H), 7.19–7.11 (m, =CH, 4H), 7.09–7.07 (m, =CH, 1H), 6.55 (dd, J=3.3, 0.7 Hz, =CH, 1H), 6.15 (t, J=7.2 Hz, CH, 1H), 3.46 (dd, J=16.9, 7.2 Hz, CH_2, 1H), 3.41 (dd, J=16.9, 7.2 Hz, CH_2, 1H), 2.12 (s, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.0, 140.4, 136.2, 129.03 (=CH), 129.0, 128.1 (=CH), 126.5 (=CH), 125.4 (=CH), 122.0 (=CH), 121.2 (=CH), 120.0 (=CH), 110.3 (=CH), 102.5 (=CH), 55.3 (CH), 48.9 (CH_2), 30.7 (CH_3). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.13; H, 6.51; N, 5.32. Found: C, 82.09; H, 6.43; N, 5.39. IR (KBr, cm^{-1}) 3048, 2913, 2302, 1715, 1459, 1307, 1013, 742.

*4.5.7. (±)-3-(1H-Indol-1-yl)-1,3-diphenylpropan-1-one (**5g**).* (±)-3-(1*H*-Indol-1-yl)-1,3-diphenylpropan-1-one was obtained as white crystals (211 mg, 65%, mp 106–107 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, =CH, 2H), 7.61 (d, J=7.5 Hz, =CH, 1H), 7.56 (d, J=7.5 Hz, =CH, 1H), 7.47–7.37 (m, =CH, 4H), 7.32–7.22 (m, =CH, 5H), 7.17 (td, J=7.5, 1.1 Hz, =CH, 1H), 7.09 (t, J=7.5 Hz, =CH, 1H), 6.53 (d, J=3.3 Hz, =CH, 1H), 6.41 (t, J=7.0 Hz, CH, 1H), 3.98 (d, J=7.0 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 140.6, 136.7, 133.7, 129.0 (2C), 128.6 (2C), 128.3, 128.0, 126.7, 125.6, 122.0, 121.2, 120.0, 110.4, 102.4, 55.4, 44.1. Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.72; H, 5.89; N, 4.10. IR (KBr, cm^{-1}) 2923, 2852, 1685, 1594, 1459, 1306, 1197, 742.

*4.5.8. Methyl 3-(1H-indol-1-yl)propanoate (**5h**).* Methyl 3-(1*H*-Indol-1-yl)propanoate was obtained as pale green liquid (195 mg. 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J=7.7 Hz, =CH, 1H), 7.37 (d, J=8.4 Hz, =CH, 1H), 7.25 (t, J=7.7 Hz, =CH, 1H), 7.16–7.13 (m, =CH, 2H), 6.52 (d, J=3.3 Hz, =CH, 1H), 4.47 (t, J=7.0 Hz, CH_2, 2H), 3.69 (s, OCH_3, 3H), 2.85 (t, J=7.0 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 135.9, 129.0, 128.2, 121.9, 121.3, 119.8, 109.3, 101.9, 52.2, 42.0, 35.0. Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.90; H, 6.40; N, 6.98. IR (KBr, cm^{-1}) 2951, 2925, 1737, 1513, 1484, 1464, 1437, 1368, 1315, 1262, 1208, 1171, 1062, 1014, 988, 841, 764, 743.

*4.5.9. (±)-Methyl 3-(1H-indol-1-yl)butanoate (**5i**).* (±)-Methyl 3-(1*H*-Indol-1-yl)butanoate was obtained as pale yellow liquid (206 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (td, J=7.9, 1.0 Hz, =CH, 1H), 7.47 (br d, J=8.0 Hz, =CH, 1H), 7.29–7.26 (m, =CH, 1H), 7.22 (d, J=3.3, =CH, 1H), 7.18–7.14 (m, =CH, 1H), 6.58 (br d, J=3.3 Hz, =CH, 1H), 5.11–5.03 (m, CH, 1H), 3.64 (s, OCH_3, 3H), 2.95 (dd, J=15.5, 6.6 Hz, CH_2, 1H), 2.80 (dd, J=15.5, 7.6 Hz, CH_2, 1H), 1.64 (d, J=6.8 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 135.8, 128.9, 124.2 (=CH), 121.8 (=CH), 121.3 (=CH), 119.8 (=CH), 109.8 (=CH), 102.4 (=CH), 52.1 (OCH_3), 48.6 (CH), 41.9 (CH_2), 21.0 (CH_3). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.69; N, 6.45. Found: C, 71.72; H, 6.74; N, 6.56. IR (KBr, cm^{-1}) 3053, 2969, 2951, 1736, 1608, 1460, 1410, 1365, 1307, 1217, 1194, 1172, 1088, 1013, 739.

*4.5.10. (E)-Methyl 3-(1H-indol-1-yl)acrylate (**5j**).* (*E*)-Methyl 3-(1*H*-Indol-1-yl)acrylate was obtained as white crystals (195 mg, 97%, mp 80–81 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J=13.9 Hz, =CH, 1H), 7.62–7.58 (m, =CH, 2H), 7.38 (d, J=3.5 Hz, =CH, 1H), 7.34 (td, J=7.5, 1.0 Hz, =CH, 1H), 7.23 (td, J=7.5, 1.0 Hz, =CH, 1H), 6.73 (d, J=3.5 Hz, =CH, 1H), 5.95 (d, J=13.9 Hz, =CH, 1H), 3.82 (s, OCH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1 (CO), 137.6 (=CH), 136.4, 130.1, 124.2 (=CH), 123.8 (=CH), 122.7 (=CH), 121.7 (=CH), 110.3 (=CH), 109.1 (=CH), 100.4 (=CH), 51.8 (OCH_3). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.53; H, 5.31; N, 6.87. IR (KBr, cm^{-1}) 3053, 2969, 2951, 1736, 1608, 1460, 1410, 1365, 1307, 1217, 1194, 1172, 1088, 1013, 739.

*4.5.11. Dimethyl 2-(1H-indol-1-yl)maleate (**5k**).* Dimethyl 2-(1*H*-Indol-1-yl)maleate was obtained as pale yellow oil (220 mg, 85%);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J*=7.1 Hz, =CH, 1H), 7.57 (dd, *J*=8.3, 0.8 Hz, =CH, 1H), 7.29 (dd, *J*=8.3, 1.5 Hz, =CH, 1H), 7.23 (d, *J*=7.1 Hz, =CH, 1H), 7.15 (d, *J*=3.7 Hz, =CH, 1H), 6.69 (dd, *J*=3.7, 0.8 Hz, =CH, 1H), 6.25 (s, =CH, 1H), 4.01 (s, OCH_3, 3H), 3.81 (s, OCH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (CO), 164.7 (CO), 143.7, 135.6, 130.9, 126.4 (=CH), 124.2 (=CH), 122.7 (=CH), 122.0 (=CH), 112.3 (=CH), 108.0 (=CH), 107.1 (=CH), 53.6 (OCH_3), 52.2 (OCH_3). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.63; H, 5.01; N, 5.29. IR (KBr, cm^{-1}) 2952, 2846, 1745, 1717, 1625, 1537, 1458, 1436, 1374, 1292, 1258, 1197, 1166, 1025, 980, 869, 764, 743.

*4.5.12. (±)-1-(2-Nitro-1-phenylethyl)-1H-indole (**5l**).* (±)-1-(2-Nitro-1-phenylethyl)-1*H*-indole was obtained as white crystals (253 mg, 95%, mp 97–98 °C) in hexane/methylene chloride; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J*=6.9, 0.9 Hz, =CH, 1H), 7.38–7.34 (m, =CH, 4H), 7.23–7.15 (m, =CH, 4H), 7.13 (dd, *J*=6.9, 0.9 Hz, =CH, 1H), 6.61 (d, *J*=3.3 Hz, =CH, 1H), 6.44 (dd, *J*=9.0, 6.1 Hz, CH, 1H), 5.23 (dd, *J*=13.3, 9.0 Hz, CH_2, 1H), 5.15 (dd, *J*=13.3, 6.1 Hz, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 135.9, 129.6 (=CH), 129.3 (=CH), 129.1, 126.7 (=CH), 124.6 (=CH), 122.6 (=CH), 121.5 (=CH), 120.6 (=CH), 109.7 (=CH), 103.9 (=CH), 77.4 (CH), 57.3 (CH_2). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.08; H, 5.30; N, 10.40. IR (KBr, cm^{-1}) 3025, 2913, 2846, 2325, 1608, 1555, 1457, 1373, 1309, 1231, 1194, 1083, 742.

*4.5.13. (±)-1-(1-(Furan-2-yl)-2-nitroethyl)-1H-indole (**5m**).* (±)-1-(1-(Furan-2-yl)-2-nitroethyl)-1*H*-indole was obtained as blue oil (238 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J*=7.3 Hz, =CH, 1H), 7.45–7.42 (m, =CH, 2H), 7.26–7.24 (m, =CH, 1H), 7.17–7.13 (m, =CH, 2H), 6.58 (d, *J*=3.3 Hz=CH, 1H), 6.44 (t, *J*=7.5 Hz, CH, 1H), 6.38 (dd, *J*=3.3, 1.8 Hz, =CH, 1H), 6.33 (d, *J*=3.3 Hz, =CH, 1H), 5.18 (dd, *J*=13.4, 7.5 Hz, CH_2, 1H), 5.10 (dd, *J*=13.4, 7.5 Hz, CH_2, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 148.3, 143.7, 135.8, 129.1, 125.3, 122.7, 121.6, 120.7, 111.1, 109.6, 109.3, 104.1, 76.0, 51.8. Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.85; H, 4.66; N, 10.72. IR (KBr, cm^{-1}) 3053, 2913, 1646, 1556, 1458, 1373, 1307, 1236, 1194, 1146, 1014, 742.

*4.5.14. (±)-1-(2-Nitro-1-(thiophen-2-yl)ethyl)-1H-indole (**5n**).* (±)-1-(2-Nitro-1-(thiophen-2-yl)ethyl)-1*H*-indole was obtained as red oil (258 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J*=7.0, 0.8 Hz, =CH, 1H), 7.41 (br d, *J*=8.4 Hz, =CH, 1H), 7.31–7.30 (m, =CH, 1H), 7.25–7.22 (m, =CH, 1H), 7.17–7.13 (m, =CH, 2H), 7.03–6.98 (m, =CH, 2H), 6.64 (t, *J*=7.5 Hz, CH, 1H), 6.60 (d, *J*=3.3 Hz, =CH, 1H), 5.25–5.14 (m, CH_2, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 138.6, 135.9, 129.2, 127.5, 126.8, 126.2, 124.7, 122.8, 121.7, 120.8, 109.5, 104.3, 77.8, 53.5. Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29. Found: C, 62.01; H, 4.40; N, 10.44. IR (KBr, cm^{-1}) 3025, 2913, 2846, 2325, 1608, 1555, 1457, 1373, 1309, 1231, 1194, 1083, 743.

*4.5.15. 1-(2,2-Bis(phenylsulfonyl)ethyl)-1H-indole (**5o**).* 1-(2,2-Bis(phenylsulfonyl)ethyl)-1*H*-indole was obtained as white crystals (417 mg, 98%, mp 150–151 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.93 (m, =CH, 4H), 7.64–7.57 (m, =CH, 2H), 7.56 (d, *J*=0.8 Hz, =CH, 1H), 7.49–7.45 (m, =CH, 4H), 7.24–7.09 (m, =CH, 4H), 6.43 (d, *J*=2.6 Hz, =CH, 1H), 5.07 (d, *J*=5.1 Hz, CH_2, 2H), 4.69 (t, *J*=5.1 Hz, CH, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 138.1, 135.5, 135.0, 129.5, 129.4, 129.3, 129.2, 122.5, 121.5, 120.5, 109.2, 102.9, 82.7, 42.7. Anal. Calcd for $C_{22}H_{19}NO_4S_2$: C, 62.10; H, 4.50; N, 3.29. Found: C, 62.08; H, 4.74; N, 3.26. IR (KBr, cm^{-1}) 3062, 2924, 1580, 1513, 1448, 1401, 1332, 1156, 1079, 998, 815, 736, 686, 620.

*4.5.16. 2-(1H-Indol-1-yl)naphthalene-1,4-dione (**5 p**).* 2-(1*H*-Indol-1-yl)naphthalene-1,4-dione was obtained as red crystals (139 mg, 51%, mp 173–174 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.20 (m, =CH, 1H), 8.17–8.15 (m, =CH, 1H), 7.84–7.80 (m, =CH, 2H), 7.65 (br d, *J*=7.7 Hz, =CH, 1H), 7.60 (br d, *J*=8.4 Hz, =CH, 1H), 7.54 (br d, *J*=3.7 Hz, =CH, 1H), 7.31–7.28 (m, =CH, 1H), 7.26–7.21 (m, =CH, 1H), 7.19 (s, =CH, 1H), 6.75 (d, *J*=3.7 Hz, =CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.7, 181.6, 143.1, 135.9, 134.7, 134.1, 132.0, 131.9, 130.8, 129.4, 127.5, 126.4, 126.0, 123.7, 122.6, 121.8, 112.4, 107.2. Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.04; H, 3.95; N, 5.11. IR (KBr, cm^{-1}) 2924, 1670, 1655, 1593, 1526, 1452, 1365, 1286, 1200, 996, 905, 761, 743, 713.

*4.5.17. (±)-3-(1H-Indol-1-yl)-1-phenylpyrrolidine-2,5-dione (**5q**).* (±)-3-(1*H*-Indol-1-yl)-1-phenylpyrrolidine-2,5-dione was obtained as yellow crystals (270 mg, 93%, mp 130–131 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (br d, *J*=7.7 Hz, =CH, 1H), 7.54–7.51 (m, =CH, 2H), 7.49–7.43 (m, =CH, 2H), 7.27–7.16 (m, =CH, 4H), 7.12 (br d, *J*=3.3 Hz, =CH, 1H), 6.63 (br d, *J*=4.1 Hz, =CH, 1H), 5.57 (t, *J*=4.1 Hz, CH, 1H), 3.51 (dd, *J*=18.6, 9.3 Hz, CH_2, 1H), 3.15 (dd, *J*=18.6, 5.8 Hz, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 172.5, 135.4, 131.4, 129.4, 129.3, 129.2, 126.3, 125.9, 122.7, 121.8, 120.6, 108.9, 104.0, 54.7, 35.8. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.30; H, 4.80; N, 9.44. IR (KBr, cm^{-1}) 3437, 3448, 2961, 2848, 1777, 1715, 1606, 1500, 1488, 1382, 1260, 1177, 827, 748, 699, 627.

4.6. 2,3-Di(1*H*-indol-1-yl)naphthalene-1,4-dione (6)

To a solution of 2-(1*H*-indol-1-yl)naphthalene-1,4-dione (273 mg, 1.0 mmol) and indoline (119 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added DMAP (122 mg, 0.1 mmol). After the mixture was refluxed at 80 °C for 12 h, the reaction mixture was cooled to rt. Then, to a solution of the reaction mixture in CH_2Cl_2 (10 mL) was added activated MnO_2 (870 mg, 10.0 mmol). The mixture was stirred at rt for 12 h. After the filtration, the mixture was evaporated under vacuo and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate, 9:1). The product **6** was obtained as brown crystals (54 mg, 14%, mp 222–223 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (m, 2H), 7.87 (m, 2H), 7.40 (d, *J*=7.7 Hz, =CH, 2H), 7.00 (td, *J*=8.1, 1.5 Hz, =CH, 2H), 6.93–6.86 (m, =CH, 6H), 6.50 (d, *J*=3.3 Hz, =CH, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9, 135.6, 135.2, 134.8 (=CH), 131.5, 129.3, 128.1 (=CH), 127.4 (=CH), 122.9 (=CH), 121.6 (=CH), 121.1 (=CH), 111.4 (=CH), 107.0 (=CH). Anal. Calcd for $C_{26}H_{16}N_2O_2$: C, 80.40; H, 4.15; N, 7.21. Found: C, 80.37; H, 4.12; N, 7.11. IR (KBr, cm^{-1}) 3420, 1672, 1598, 1571, 1451, 1396, 1344, 1270, 1218, 1116, 1102, 1069, 999, 743, 714.

4.7. 2-(1*H*-Indol-1-yl)cyclohexa-2,5-diene-1,4-dione (7)

To a solution of indoline (200 mg, 1.7 mmol) and *p*-benzoquinone (724 mg, 6.7 mmol) in CH_3CN (10 mL) was added $Bi(NO_3)_3 \cdot 5H_2O$ (47 mg, 0.1 mmol). After the mixture was stirred at 100 °C for 2 days, the reaction mixture was cooled to rt and the solvent was removed under vacuo. Then the crude product was dissolved with EtOAc (50 mL) and the activated MnO_2 (1.46 g, 16.8 mmol) was added to the solution. The mixture was stirred at rt for 12 h. After the filtration, the solvent was evaporated under vacuo and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate, 20:1). 2-(1*H*-Indol-1-yl) cyclohexa-2,5-diene-1,4-dione (**7**) was obtained as brown crystals (60 mg, 27%, mp 115–116 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*=8.1 Hz, =CH, 1H), 7.55 (d, *J*=8.4 Hz, =CH, 1H), 7.42 (d, *J*=3.5, =CH, 1H), 7.31–7.21 (m, =CH, 2H), 6.98 (d, *J*=1.8, =CH, 1H), 6.83–6.86 (m, =CH, 2H), 6.73 (dd, *J*=3.5, 0.7 Hz, =CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 183.4, 141.3, 136.9 (=

CH), 135.9 (=CH), 135.7, 130.8, 129.0 (=CH), 123.8 (=CH), 123.3 (=CH), 122.7 (=CH), 121.9 (=CH), 112.2 (=CH), 107.5 (=CH). Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.24; H, 4.20; N, 6.30. IR (KBr, cm^{-1}) 3149, 3098, 3048, 2919, 2852, 1660, 1593, 1454, 1288, 1231, 1088, 895, 750.

4.8. Methyl 6-oxo-2,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinoline-4-carboxylate (11)

Procedure A: Polyphosphoric acid (18.4 g) was added to dimethyl 2-(indolin-1-yl)maleate (801 mg, 3.1 mmol) and the mixture was stirred and maintained at 90 °C for 1 h. The resulting dark blue tar was cooled to 0 °C. After ice water (25 mL) was added, the dark blue solid was dissolved with ethyl acetate (100 mL). The organic phase was washed with $NaHCO_3$ solution (5%, 2×50 mL) and water (50 mL). The organic phase was dried with $NaSO_4$ and the solvent was evaporated. The product **11** was obtained as white crystals (mp 226–227 °C) in methanol (180 mg, 26%). *Procedure B*: Eaton's reagent (5 mL) was added to dimethyl 2-(indolin-1-yl)maleate (499 mg, 1.9 mmol) and the mixture was stirred at 50 °C for 5 h. Then ice water (25 mL) was added to the resulting mixture. The yellow solution was extracted with EtOAc (80 mL) and the organic phase was washed with $NaHCO_3$ solution (5%, 2×40 mL) and water (40 mL). After the ethyl acetate phase was dried with Na_2SO_4, the solvent was evaporated. The product **11** was obtained as white crystals in methanol (395 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J=8.2, 1.1 Hz, =CH, 1H), 7.46 (dd, J=7.2, 1.1 Hz, =CH, 1H), 7.28 (dd, J=8.2, 7.2 Hz, =CH, 1H), 6.99 (s, =CH, 1H), 4.83 (t, J=7.8 Hz, CH_2, 2H), 3.96 (s, CH_3, 3H), 3.49 (t, J=7.3 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.7 (CO), 163.2 (CO), 145.5, 137.0, 133.4, 127.2 (=CH), 125.4 (=CH), 125.0, 122.4 (=CH), 115.2 (=CH), 53.4 (OCH_3), 52.9 (CH_2), 28.3 (CH_2). Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.05; H, 4.76; N, 6.02. IR (KBr, cm^{-1}) 3529, 3468, 3020, 2941, 1732, 1622, 1582, 1514, 1449, 1278, 1256, 775.

4.9. Methyl 6-oxo-6*H*-pyrrolo[3,2,1-*ij*]quinoline-4-carboxylate (12)

To a solution of methyl 6-oxo-2,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinoline-4-carboxylate (229 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added activated MnO_2 (870 mg, 10.0 mmol). The mixture was stirred at rt for 12 h, the product **12** was obtained as pale green crystals (mp 115–116 °C) in hexane/ethyl acetate (209 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J=3.7 Hz, =CH, 1H), 8.16 (d, J=7.5 Hz, =CH, 1H), 7.97 (d, J=7.5 Hz, =CH, 1H), 7.56 (t, J=7.5 Hz, =CH, 1H), 7.15 (s, =CH, 1H), 6.89 (d, J=3.7 Hz, =CH, 1H), 4.04 (s, OCH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9 (CO), 162.8 (CO), 135.7, 134.9, 130.1, 128.2 (=CH), 127.9 (=CH), 125.5 (=CH), 123.2, 122.7 (=CH), 120.0 (=CH), 110.4 (=CH), 53.7 (OCH_3). Anal. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.45; H, 3.73; N, 6.04. IR (KBr, cm^{-1}) 3165, 3120, 2997, 2947, 2852, 2297, 1732, 1635, 1524, 1441, 1378, 1264, 1240, 1137, 822, 772, 741.

4.10. Oxidation of (±)-1-(2-nitro-1-phenylvinyl)-1*H*-indole (4l) with MnO_2

To a solution of (±)-1-(2-nitro-1-phenylethyl)indoline (1.0 mmol, 268 mg) in CH_2Cl_2 (10 mL) was added activated MnO_2 (870 mg, 10.0 mmol). The mixture was stirred at rt for 12 h. The solvent was removed in vacuo and then the compound was purified by silica gel column chromatography (hexane/ethyl acetate, 20:1). Compound **14** was obtained as a mixture of stereo isomers (169 mg, 64%), the product **15** was obtained as a yellow crystals in hexane/ethyl acetate (69 mg, 31% yield).

4.11. (1*H*-Indol-1-yl)(phenyl)methanone (15)

To a solution of (*E*)- and (*Z*)-1-(2-nitro-1-phenylvinyl)-1*H*-indole (**14**) (169 mg, 0.6 mmol) in CH_2Cl_2 (10 mL) was added MnO_2 (577 mg, 6.4 mmol) and H_2O (1–2 drop). The mixture was stirred at rt for 2 h and the product **15** was obtained as a pale yellow crystals (mp 58–59 °C) in hexane/ethyl acetate (210 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (br d, J=7.6 Hz, =CH, 1H), 7.75–7.73 (m, =CH, 2H), 7.63–7.59 (m, =CH, 2H), 7.55–7.51 (m, =CH, 2H), 7.39 (t, J=7.6 Hz, =CH, 1H), 7.34–7.25 (m, =CH, 2H), 6.62 (d, J=3.7 Hz, =CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 136.3, 134.9, 132.1, 131.0, 129.4, 128.8, 127.8, 125.1, 124.1, 121.1, 116.6, 108.8. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.30; H, 4.92; N, 6.44. IR (KBr, cm^{-1}) 2917, 2849, 1731, 1684, 1450, 1376, 1337, 1178, 1055, 937, 884, 749.

4.12. General procedure for reaction of indoline and *trans*-β-nitro styrene with asymmetric catalysts (22–24)

To a flask were added asymmetric catalyst (**22**–**24**) (0.1 mmol) in toluene (2 mL) and the *trans*-β-nitro styrene (1.0 mmol). The mixture was stirred at room temperature for 30 min and indoline (1.0 mmol) was added. The mixture was stirred until the starting material disappeared (TLC, hexane/ethyl acetate, 20:1). After evaporation of the solvent, the crude product was extracted with EtOAc (2×20 mL). The EtOAc extracts were dried over Na_2SO_4, filtered, evaporated in vacuo, and the compound was purified 1-(2-nitro-1-phenylethyl)indoline as orange crystals by silica gel column chromatography (hexane/ethyl acetate, 20:1).

4.13. General procedure for synthesis of 1,3-disubstituted indole derivatives with $Zn(OTf)_2$

To a solution of Michael addition product of indoline (1.0 mmol) and Michael acceptor (1.0 mmol) in CH_2Cl_2 (10 mL) was added $Zn(OTf)_2$ (37 mg, 0.1 mmol). The mixture was stirred until the starting material disappeared (TLC, hexane/ethyl acetate). After evaporation of the solvent, the crude product was extracted with EtOAc (2×20 mL). The EtOAc extracts were dried over Na_2SO_4, filtered, evaporated in vacuo, and the compound was purified by silica gel column chromatography (hexane/ethyl acetate).

*4.13.1. (±)-4-(3-(2-Nitro-1-phenylethyl)-1H-indol-1-yl)butan-2-one (**29d**).* The reaction was performed at rt for 12 h. (±)-4-(3-(2-Nitro-1-phenylethyl)-1*H*-indol-1-yl)butan-2-one was obtained as brown crystals (286 mg, 85%, mp 92–93 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (br d, J=7.6 Hz, =CH, 1H), 7.34–7.20 (m, =CH, 7H), 7.07 (t, J=7.6 Hz, =CH, 1H), 6.99 (s, =CH, 1H), 5.16 (t, J=8.1 Hz, CH, 1H), 5.04 (dd, J=12.4, 7.6 Hz, A part of AB system, CH_2, 1H), 4.93 (dd, J=12.4, 7.6 Hz, B part of AB system, CH_2, 1H), 4.37 (t, J=6.6 Hz, CH_2, 2H), 2.92 (t, J=6.6 Hz, CH_2, 2H), 2.11 (s, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 139.5, 136.4, 129.1, 128.0, 127.7, 127.1, 125.9, 122.6, 119.9, 119.5, 113.4, 109.6, 79.8, 43.5, 41.7, 40.8, 30.6. Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.38; H, 5.80; N, 8.20. IR (KBr, cm^{-1}) 2919, 1716, 1551, 1469, 1454, 1432, 1377, 1165, 745, 702.

*4.13.2. Diastereomeric mixture of 4-(3-(2-nitro-1-phenylethyl)-1H-indol-1-yl)pentan-2-one (**29e**).* The reaction was performed at rt for 24 h. A diastereomeric mixture of 4-(3-(2-nitro-1-phenylethyl)-1*H*-indol-1-yl)pentan-2-one was obtained as orange crystals in hexane/ethyl acetate (270 mg, 77%, mixture of diastereomers A+B, A/B ratio=5.6:4.4, determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$): 7.44–7.38 (m, =CH, 2H), 7.34–7.26 (m, =CH, 3H), 7.24–7.19 (m, =CH, 3H), 7.08–7.02 (m, =CH, 1H), 6.98 (s, =CH, 1H), 5.20–5.15 (m, CH, 1H), 5.08–4.90 (m, CH, 3H), 3.03–2.96 (m, A part of AB system, CH_2, 1H), 2.88 (dd, J=17.0, 7.8 Hz, B part of AB system, CH_2, 1H), 2.07

(s, CH_3, 3H), 2.06 (s, CH_3, 3H), 1.56 (d, J=4.4 Hz, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 139.5, 136.2, 129.2, 128.0, 127.8, 127.0, 122.5, 122.1, 121.8, 120.0, 119.9, 119.4, 113.8, 110.2, 79.9, 79.8, 50.4, 47.8, 41.9, 30.8, 21.1 (Note: diastereoisomeric mixture **29e** must consist in total 38 carbon signals. But 16 carbon signals for **29e** are coincident.). Anal. Calcd for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.84; H, 6.32; N, 7.89. IR (KBr, cm^{-1}) 3422, 3055, 2854, 1717, 1612, 1554, 1463, 1432, 1378, 1314, 1266, 1164, 909, 739, 702.

*4.13.3. (±)-Methyl 3-(3-(2-nitro-1-phenylethyl)-1H-indol-1-yl) propanoate (**29h**).* The reaction was performed at rt for 10 h. Methyl 3-(3-(2-nitro-1-phenylethyl)-1*H*-indol-1-yl)propanoate was obtained as brown crystals (321 mg, 91%, mp 100–101 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (br d, J=8.0 Hz, =CH, 1H), 7.35–7.21 (m, =CH, 7H), 7.08 (t, J=8.0 Hz, =CH, 1H), 6.97 (s, =CH, 1H), 5.17 (t, J=8.1 Hz, CH, 1H), 5.04 (dd, J=12.4, 7.7 Hz, A part of AB system, CH_2, 1H), 4.93 (dd, J=12.4, 7.7 Hz, B part of AB system, CH_2, 1H), 4.42 (t, J=6.8 Hz, CH_2, 2H), 3.66 (s, OCH_3, 3H), 2.80 (t, J=6.8 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 139.5, 136.5, 129.1, 128.0, 127.7, 127.1, 125.7, 122.7, 120.0, 119.5, 113.7, 109.6, 79.7, 52.1, 42.1, 41.7, 35.0. Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.09; H, 5.77; N, 7.88. IR (KBr, cm^{-1}) 3028, 2951, 1735, 1551, 1469, 1454, 1436, 1378, 1334, 1204, 1173, 744, 702.

*4.13.4. Diastereomeric mixture of methyl 3-(3-(2-nitro-1-phenylethyl)-1H-indol-1-yl)butanoate (**29i**).* The reaction was performed at rt for 12 h. A diastereomeric mixture of methyl 3-(3-(2-nitro-1-phenylethyl)-1*H*-indol-1-yl)propanoate was obtained as brown crystals in hexane/ethyl acetate (260 mg, 71%, mixture of diastereomers A+B, A/B ratio=5.6:4.4, determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (br d, J=8.0 Hz, =CH, 1H), 7.35–7.21 (m, =CH, 7H), 7.08 (t, J=8.0 Hz, =CH, 1H), 6.97 (s, =CH, 1H), 5.17 (t, J=8.1 Hz, CH, 1H), 5.04 (dd, J=12.4, 7.7 Hz, A part of AB system, CH_2, 1H), 4.93 (dd, J=12.4, 7.7 Hz, B part of AB system, CH_2, 1H), 4.42 (t, J=6.8 Hz, CH_2, 2H), 3.66 (s, OCH_3, 3H), 2.80 (t, J=6.8 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 139.5, 136.5, 129.1, 128.0, 127.7, 127.1, 125.7, 122.7, 120.0, 119.5, 113.7, 109.6, 79.7, 52.1, 42.1, 41.7, 35.0 (Note: diastereoisomeric mixture **29i** must consist in total 38 carbon signals. But 20 carbon signals for **29i** are coincident.). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.09; H, 5.77; N, 7.88. IR (KBr, cm^{-1}) 3028, 2951, 1735, 1551, 1469, 1454, 1436, 1378, 1334, 1204, 1173, 744, 702.

*4.13.5. Diastereomeric mixture of 1,3-bis(2-nitro-1-phenylethyl)-1H-indole (**29l**).* The reaction was performed at rt for 12 h. A diastereomeric mixture of 1,3-bis(2-nitro-1-phenylethyl)-1*H*-indole was obtained as yellow crystals in hexane/ethyl acetate (366 mg, 88%, mixture of diastereomers A+B, A/B ratio was not determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.24 (m, =CH, 9H), 7.21–7.15 (m, =CH, 3H), 7.10–7.05 (m, =CH, 2H), 7.04 (s, =CH, 1H), 6.37 (t, J=7.7 Hz, CH, 1H), 5.23–5.12 (m, CH, 3H), 5.06–5.01 (m, A part of AB system, CH_2, 1H), 4.96–4.91 (m, B part of AB system, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.9, 135.5, 129.7, 129.4, 129.3, 129.2, 127.9, 127.3, 126.5, 123.4, 122.5, 120.9, 119.8, 115.5, 110.2, 79.8, 79.7, 77.3, 57.6, 57.5, 41.8 (Note: diastereoisomeric mixture **29l** must consist in total 40 carbon signals. But 18 carbon signals for **29l** are coincident.). Anal. Calcd for $C_{24}H_{21}N_3O_4$: C, 69.39; H, 5.10; N, 10.11. Found: C, 69.31; H, 5.14; N, 9.98. IR (KBr, cm^{-1}) 2958, 2918, 2871, 1552, 1494, 1461, 1433, 1378, 1262, 1185, 745, 702.

*4.13.6. Diastereomeric mixture of 1-(1-(furan-2-yl)-2-nitroethyl)-3-(2-nitro-1-phenylethyl)-1H-indole (**29m**).* The reaction was performed at rt for 12 h. A diastereomeric mixture of 1-(1-(furan-2-yl)-2-nitroethyl)-3-(2-nitro-1-phenylethyl)-1*H*-indole was obtained as black crystals in hexane/ethyl acetate (332 mg, 82%, mixture of diastereomers A+B, A/B ratio was not determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, =CH, 1H), 7.40–7.32 (m, =CH, 2H), 7.31–7.27 (m, =CH, 2H), 7.26–7.22 (m, =CH, 5H), 7.09 (t, J=7.5 Hz, =CH, 1H), 7.00 (s, =CH, 1H), 6.41–6.37 (m, =CH, 2H), 6.31 (m,=CH, 1H), 5.19–5.00 (m, CH_2, 3H), 4.99–4.88 (m, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 143.9, 143.8, 138.9, 136.4, 129.2, 128.0, 127.9, 127.4, 123.5, 122.9, 122.7, 120.9, 119.9, 119.8, 115.8, 115.7, 111.2, 109.8, 109.7, 79.7, 76.0, 75.8, 52.1, 52.0, 41.7 (Note: diastereoisomeric mixture **29m** must consist in total 40 carbon signals. But 14 carbon signals for **29m** are coincident.). Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 69.18; H, 4.72; N, 10.37. Found: C, 69.12; H, 4.66; N, 10.15. IR (KBr, cm^{-1}) 3030, 2958, 2923, 1554, 1499, 1461, 1431, 1378, 1189, 1015, 742, 702.

*4.13.7. Diastereomeric mixture of 3-(3-(2-nitro-1-phenylethyl)-1H-indol-1-yl)-1-phenylpyrrolidine-2,5-dione (**29q**).* The reaction was performed at rt for 12 h. A diastereomeric mixture of 3-(3-(2-nitro-1-phenylethyl)-1*H*-indol-1-yl)-1-phenylpyrrolidine-2,5-dione was obtained as pale yellow crystals in hexane/ethyl acetate (409 mg, 93%, mixture of diastereomers A+B, A/B ratio was not determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.43 (m, =CH, 4H), 7.39–7.33 (m, =CH, 5H), 7.30–7.24 (m, =CH, 3H), 7.18–7.11 (m, =CH, 2H), 6.95 (m, =CH, 1H), 5.52–5.47 (m, CH, 1H), 5.20–5.16 (m, CH, 1H), 5.04–5.01 (m, A part of AB system, CH_2, 1H), 4.94 (m, B part of AB system, CH_2, 1H), 3.45 (m, A part of AB system, CH_2, 1H), 3.13 (m, B part of AB system, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 172.4, 138.9, 138.8, 136.3, 136.2, 131.5, 129.6, 129.4, 129.3, 128.0, 127.8, 126.5, 124.0, 123.8, 123.7, 121.0, 120.2, 115.8, 109.5, 109.4, 79.6, 55.1, 41.7, 35.9, 35.8 (Note: diastereoisomeric mixture **29q** must consist in total 44 carbon signals. But 18 carbon signals for **29q** are coincident.). Anal. Calcd for $C_{26}H_{21}N_3O_4$: C, 71.06; H, 4.82; N, 9.56. Found: C, 70.86; H, 4.70; N, 10.03. IR (KBr, cm^{-1}) 3499, 3056, 2956, 2926, 2856, 2305, 1791, 1724, 1598, 1554, 1499, 1463, 1378, 1265, 1182, 1080, 910, 742, 702.

4.14. (±)-(*Z*)- or (*E*)-Methyl 2-(indolin-1-ylmethylene)-4-nitro-3-phenylbutanoate (26)

To a solution of (*E*)-methyl 3-(indolin-1-yl)acrylate (203 mg, 1.0 mmol) and β-nitro styrene (149 mg, 1.0 mmol,) in CH_2Cl_2 (10 mL) was added $Zn(OTf)_2$ (37 mg, 0.1 mmol). The mixture was stirred at rt for 12 h, the product **26** was obtained as orange crystals (321 mg, 91%, mp 134–135 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, =CH, 1H), 7.35–7.31 (m, =CH, 4H), 7.29–7.18 (m, =CH, 3H), 6.99–6.95 (m, =CH, 2H), 5.39–5.33 (m, CH, 1H), 5.18–5.11 (m, CH_2, 2H), 4.37 (dd, J=17.5, 9.0 Hz, CH_2, 1H), 4.18 (dd, J=17.5, 9.0 Hz, CH_2, 1H), 3.69 (s, OCH_3, 3H), 3.25 (t, J=9.0 Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 146.2, 140.7, 140.4, 129.8, 128.9, 128.2, 127.3, 127.2, 125.6, 123.2, 109.9, 99.9, 79.0, 51.5, 50.5, 40.6, 29.1. Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.06; H, 5.95; N, 7.88. IR (KBr, cm^{-1}) 2957, 2925, 2854, 1686, 1620, 1590, 1548, 1488, 1435, 1380, 1348, 1291, 1256, 1187, 1107, 749, 699.

4.15. (±)-(*Z*)- or (*E*)-Methyl 2-(indolin-1-ylmethylene)-4-nitro-3-phenylbutanoate (27)

To a solution of (±)-(*Z*)- or (*E*)-methyl 2-(indolin-1-ylmethylene)-4-nitro-3-phenylbutanoate (352 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added DDQ (870 mg, 1.0 mmol). The mixture was stirred at rt for 12 h, the product **27** was obtained as white crystals (305 mg, 87%, mp 141–142 °C) in hexane/ethyl acetate; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, =CH, 1H), 7.63 (d, J=7.8 Hz, =CH, 1H), 7.50 (d, J=7.8 Hz, =CH, 1H), 7.37–7.25 (m, =CH, 8H), 6.71 (d, J=3.5 Hz, =CH, 1H), 5.36 (dd, J=12.5, 7.2 Hz, CH_2, 1H), 5.27 (t, J=7.2 Hz, CH, 1H), 5.12 (dd, J=12.5, 7.2 Hz, CH_2, 1H), 3.84 (s, OCH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 146.2, 140.4, 136.7, 129.8, 129.4, 128.1, 127.7, 126.2, 124.0, 122.8, 121.6, 110.5, 108.5, 100.0, 78.3, 52.4, 41.9. Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.42; H, 5.02; N,

7.82. IR (KBr, cm^{-1}) 2956, 2925, 2854, 1710, 1632, 1555, 1461, 1377, 1265, 909, 740, 705.

4.16. Reaction of methyl 3-(1*H*-indol-1-yl)propanoate and β-nitro styrene with $Zn(OTf)_2$ and (*S*)-Ph-bisoxazoline (28) at different temperatures

To a dried flask were added $Zn(OTf)_2$ (74 mg, 0.2 mmol) and (*S*)-Ph-bisoxazoline (66 mg, 0.2 mmol) under N_2 atmosphere, followed by addition of the toluene (5 mL). The solution was stirred at room temperature (or −30 °C or −70 °C) for 1 h under N_2 atmosphere, and the *trans*-β-nitro styrene (149 mg, 1.0 mmol) was added. The mixture was stirred for 10 min before the methyl 3-(1*H*-indol-1-yl) propanoate (203 mg, 1.0 mmol) was added. The mixture was stirred until the starting material disappeared (TLC, hexane/ethyl acetate, 20:1). After evaporation of the solvent, the crude product was extracted with EtOAc (2×20 mL). The EtOAc extracts were dried over Na_2SO_4, filtered, evaporated in vacuo, and the compound was purified methyl 3-(3-(2-nitro-1-phenylethyl)-1*H*-indol-1-yl)propanoate (**29h**) as brown crystals by silica gel column chromatography (hexane/ethyl acetate, 20:1).

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Supplementary data

Supplementary data includes some experimental details and ^1H and ^{13}C NMR spectra of compounds. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.066.

References and notes

1. Sundberg, R. J. *Indoles*; Academic: London, 1996.
2. Sundberg, R. J. *The Chemistry of Indoles*; Academic: New York, NY, 1970.
3. Lounasmaa, M.; Tolvanen, A. *Nat. Prod. Rep.* **2000**, *17*, 175–191.
4. O'Connor, S. E.; Maresh, J. J. *Nat. Prod. Rep.* **2006**, *23*, 532–547.
5. Ishikura, M.; Yamada, K. *Nat. Prod. Rep.* **2009**, *26*, 803–852.
6. Neus, N.; Neus, M. N. The Therapeutic use of Bisindole Alkaloids from *Catharanthus* In. *The Alkaloids*; Brossi, A., Suffness, M., Eds.; Academic: New York, NY, 1990; Vol. 37, p 232.
7. Cordell, G. A.; Saxton, J. E. Bisindole Alkaloids In. *The Alkaloids*; Rodrigo, R. G. A., Ed.; Academic: San Diego, CA, 1981; Vol. 20.
8. Praveen, C.; Karthikeyan, K.; Perumal, P. T. *Tetrahedron* **2009**, *65*, 9244–9255.
9. Zhu, J.; Wong, H.; Zhang, Z.; Yin, Z.; Meanwell, N. A.; Kadow, J. F.; Wang, T. *Tetrahedron Lett.* **2006**, *47*, 5653–5656.
10. Miyagi, T.; Hari, Y.; Aoyama, T. *Tetrahedron Lett.* **2004**, *45*, 6303–6305.
11. Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1996**, *61*, 2594–2595.
12. *Physicians Desk Reference*, 51st ed.; Medical Economics: Oradell, NJ, 1997; p 2395.
13. Gupta, R. R. *Heterocyclic Chemistry*; Springer: New York, NY, 1999; Vol. 2; p 192.
14. *Physicians Desk Reference*, 51st ed.; Medical Economics: Oradell, NJ, 1997; p 1521.
15. Sayyed, I. A.; Alex, K.; Tillack, A.; Schwarz, N.; Spannenberg, A.; Michalik, D.; Beller, M. *Tetrahedron* **2008**, *64*, 4590–4595.
16. *Physicians Desk Reference*, 51st ed.; Medical Economics: Oradell, NJ, 1997; p 1723.
17. Antitumor Bisindole Alkaloids from *Catharanthus roseus* (L.) In. *The Alkaloids*; Brossi, A., Suffness, M., Eds.; Academic: San Diego, CA, 1990; Vol. 37, pp 133–204.
18. Robert, M. M.; Ku, Y. Y.; Tuncay, M. S. *Tetrahedron Lett.* **1987**, *28*, 3071–3074.
19. Ernest, W. E.; Charles, A.; Vitor, F. F.; Enrique, L. M.; Serge, R. P.; Jhy, H. S.; Charles, S. S. *J. Org. Chem.* **1986**, *51*, 2343–2351.
20. Rubottom, G. M.; Chabala, J. C. *Synthesis* **1972**, 566–567.
21. Bocchi, V.; Casnati, G.; Dossena, A.; Villani, F. *Synthesis* **1976**, 414–416.
22. Cardillo, B.; Casnati, G.; Pochini, A.; Ricca, A. *Tetrahedron Lett.* **1967**, *23*, 3771–3783.
23. Saracoglu, N. *Top. Heterocycl. Chem.* **2007**, *11*, 1–61.
24. Cavdar, H.; Saracoglu, N. *Tetrahedron* **2005**, *61*, 2401–2405.
25. Cavdar, H.; Saracoglu, N. *J. Org. Chem.* **2006**, *71*, 7793–7799.
26. Sadak, A. E.; Arslan, T.; Celebioglu, N.; Saracoglu, N. *Tetrahedron* **2010**, *66*, 3214–3221.
27. Arslan, T.; Sadak, A. E.; Saracoglu, N. *Tetrahedron* **2010**, *66*, 2936–2939.
28. Bayindir, S.; Erdogan, E.; Kilic, H.; Saracoglu, N. *Synlett* **2010**, *10*, 1455–1458.
29. Zewge, D.; Chen, C.-Y.; Deer, C.; Dormer, P. G.; Hughes, D. L. *J. Org. Chem.* **2007**, *72*, 4276–4279.