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Asymmetric Friedel–Crafts alkylation of indoles with β-nitrostyrenes catalyzed by a chiral Ni^{II} complex based on (*S*)-(2-aminomethyl)pyrrolidine and 3,5-di-*tert*-butylsalicylaldehyde

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General information

All solvents purchased from commercial suppliers were used without further purification (CH_2Cl_2, PhCl, EtOAc, MeCN, 1,4-dioxane, MeOH, THF, MTBE, toluene, $CDCl_3$). Chemicals purchased from commercial suppliers were used without further purification. Complexes **4** and **5** were available from our previous work.[S1,S2] Unless otherwise stated, flash column chromatography was performed on silica gel 60 M from Macherey-Nagel.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 or Bruker Avance 300 spectrometers operating at 400/300 MHz (^{1}H) and 101/75 MHz (^{13}C{1H}). Chemical shifts are reported in ppm relative to the residual solvent peak ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR, δ = 77.1 for ^{13}C NMR). NMR data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constant, integration, and nucleus. Optical rotations were measured on Krüss P3000 Automatic polarimeter in a 10 cm cell. Chiral HPLC was performed on Stayer HPLC systems (Akvilon, Russia) using Chiralpak AS-H, Kromasil 3-Amycoat and Kromasil 5-BBT.

Procedure for the synthesis of Ni^{II} complex 6

To a solution of (*S*)-(2-aminomethyl)pyrrolidine (100 mg, 1.0 mmol, 1.0 equiv.) in 20 mL of methanol was added 3,5-di-*tert*-butylsalicylaldehyde (234.3 mg, 1.0 mmol, 1.0 equiv.), and this was stirred until the solution turned dark yellow. Salt $Ni(OAc)_2{\times}4H_2O$ (248.6 mg, 1 mmol, 1.0 equiv.) was then added to this solution, and the reaction mixture was stirred under reflux for 4 h, then cooled to room temperature. The solvent was evaporated on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOH = 30/1 → 20/1) to give the Ni^{II} complex **6** as a red powder (128.4 mg, 0.296 mmol, 30% yield).

HRMS (ESI, m/z) calcd. for $C_{20}H_{31}N_2NiO$ $[M]^+$: 373.1790, found: 373.1784.

$[\alpha]_D^{26}$ +133 (*c* = 0.03, MeOH).

General procedure for the catalytic enantioselective Friedel-Crafts reaction 1

β-Nitroalkene **2** (0.1 mmol, 1.0 equiv.) and catalyst (5 mol%) were loaded into a vial (1.5 mL) and then dissolved in 0.5 mL of toluene. Then, indole **1** (0.2 mmol, 2.0 equiv.) is added to this mixture and the vial was filled with argon and the reaction mixture was stirred for 24 hours. Conversions and yields were determined by ^{1}H NMR using HMDSO as an internal standard.

Table S1. Concentration and temperature effect on Friedel–Crafts alkylation of indole **1a** with β-nitrostyrene **2a** catalyzed by Ni^{II} complex **6**.[a]

Entry	Conc. of β-nitrostyrene (mmol/mL)	Conv. (%)[b]	*ee* (%)[c]
1	0.1	86	63 (*R*)
2	**0.2**	**99**	**69 (*R*)**
3[d]	0.2	67	56 (*R*)
4	0.333	67	45 (*R*)

[a]Reaction conditions: β-nitrostyrene **2a** (14.9 mg, 0.1 mmol, 1.0 equiv.), catalyst (5 mol%) and indole **1a** (23.4 mg, 0.2 mmol, 2 equiv.) were stirred in toluene under argon atmosphere for 24 h at room temperature. [b]Conversion was determined by ^{1}H NMR analysis. [c]Enantiomeric purity was determined by chiral HPLC analysis using the Chiralpak AS-H column. [d]The reaction was run for 96 h at 5 °C.

Table S2. Screening the effect of the catalyst loading on Friedel–Crafts alkylation reaction of indole **1a** with β-nitrostyrene **2a** catalyzed by Ni^{II} complex **6**.[a]

Entry	Catalyst loading (mol%)	Conv. (%)[b]	*ee* (%)[c]
1	0.5	24	37 (*R*)
2[d]	0.5	48	38 (*R*)
3	1	20	48 (*R*)
4[d]	1	53	46 (*R*)
5	2	87	64 (*R*)
6	**5**	**99**	**69 (*R*)**
7	10	99	61 (*R*)
8	15	99	61 (*R*)

[a]Reaction conditions: β-nitrostyrene **2a** (14.9 mg, 0.1 mmol, 1.0 equiv.), catalyst (0.5–15 mol%) and indole **1a** (23.4 mg, 0.2 mmol, 2 equiv.) were stirred in 0.5 mL of toluene for 24 h under argon atmosphere at room temperature. [b]Conversion was determined by ^{1}H NMR analysis. [c]Enantiomeric purity was determined by chiral HPLC analysis using the Chiralpak AS-H column. [d]The reaction was run for 72 h.

Table S3. Screening the effect of components ratio on Friedel–Crafts alkylation reaction of indole **1a** with β-nitrostyrene **2a** catalyzed by Ni^{II} complex **6**.[a]

Entry	Indole **1a** (equiv.)	β-Nitrostyrene **2a** (equiv.)	Conv. (%)[b]	*ee* (%)[c]
1	**2**	**1**	**99**	**69 (*R*)**
2	1.5	1	67	64 (*R*)
3	1	1.5	30	61 (*R*)
4	1	1	25	21 (*R*)

[a]Reaction conditions: β-nitrostyrene **2a**, catalyst (5 mol%) and indole **1a** were stirred in 0.5 mL of toluene for 24 h under argon atmosphere at room temperature. [b]Conversion was determined by ^{1}H NMR analysis. [c]Enantiomeric purity was determined by chiral HPLC analysis using the Chiralpak AS-H column.

Table S4. Screening the effect of the additives on Friedel–Crafts alkylation reaction of indole **1a** with β-nitrostyrene **2a** catalyzed by Ni^{II} complex **6**.[a]

Entry	Additive	Conv. (%)[b]	*ee* (%)[c]
1	L-Proline	55	49 (*R*)
2	Catechol	16	9 (*R*)
3	L-Valinol	99	63 (*R*)
4	(*R*)-TADDOL	99	68 (*R*)
5	(*S*)-(2-Anilinomethyl)pyrrolidine	99	68 (*R*)

[a]Reaction conditions: β-nitrostyrene **2a** (14.9 mg, 0.1 mmol, 1.0 equiv.), catalyst (5 mol%) and indole **1a** (23.4 mg, 0.2 mmol, 2 equiv.), additive (5 mol%) were stirred in 0.5 mL of toluene for 24 h under argon atmosphere at room temperature. [b]Conversion was determined by ^{1}H NMR analysis. [c]Enantiomeric purity was determined by chiral HPLC analysis using the Chiralpak AS-H column.

Characterization of the products 3

(*R*)-3-(2-Nitro-1-phenylethyl)-1*H*-indole (3a)

Prepared according to the general procedure starting from indole **1a** (23.4 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13 (br. s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.41–7.24 (m, 6H), 7.21 (t, J = 7.7 Hz, 1H), 7.13–6.99 (m, 2H), 5.20 (t, J = 8.0 Hz, 1H), 5.07 (ddd, J = 12.4, 7.6, 1.4 Hz, 1H), 4.94 (ddd, J = 12.4, 8.4, 1.4 Hz, 1H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Chiralpak AS-H column, *ee* = 69% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 26.6 min, t_R = 29.8 min). The absolute configuration of the product was assigned by comparison of the HPLC traces with the literature data.[S3]

All spectroscopic data were in agreement with the literature.[S3]

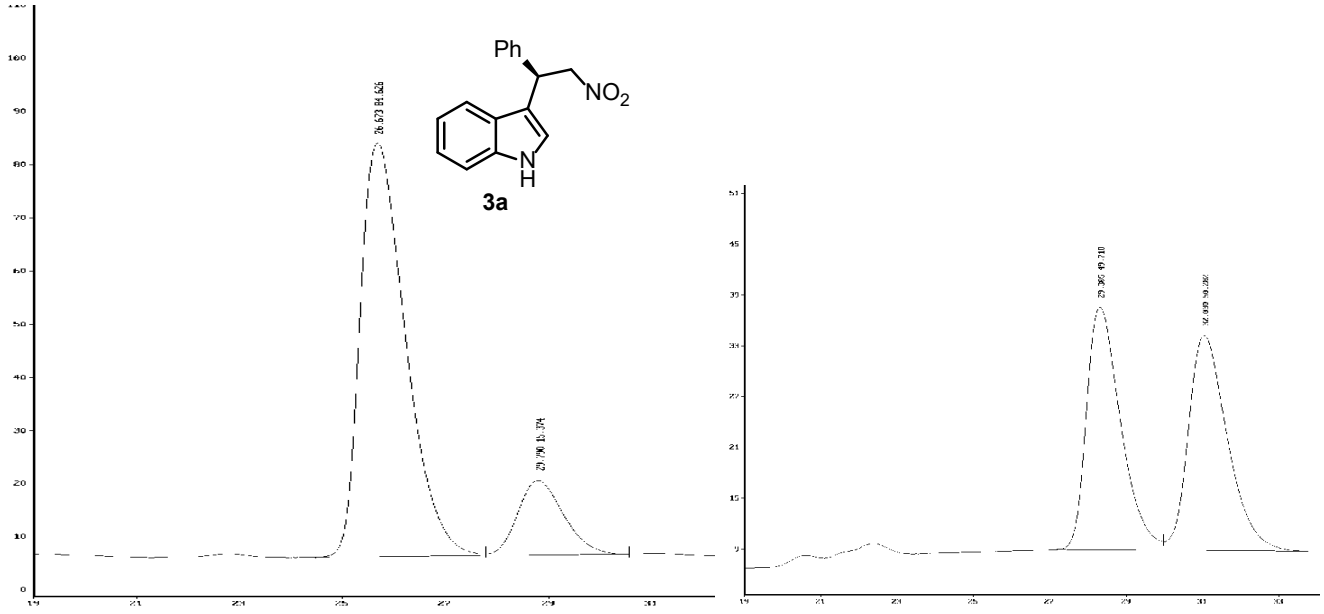

Figure S1. HPLC traces of the enantioenriched (*R*)-**3a** (69% *ee*) and the racemic sample (*reference*).

(*R*)-5-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3b)

Prepared according to the general procedure starting from indole **1b** (26.2 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.02 (br. s, 1H), 7.40–7.24 (m, 7H), 7.06 (dd, J = 8.4, 1.5 Hz, 1H), 7.01–6.97 (m, 1H), 5.24–5.15 (m, 1H), 5.08 (dd, J = 12.4, 7.4 Hz, 1H), 4.96 (dd, J = 12.4, 8.6 Hz, 1H), 2.44 (s, 3H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 66% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 8.6 min, t_R = 11.3 min).

All spectroscopic data were in agreement with the literature.[S4]

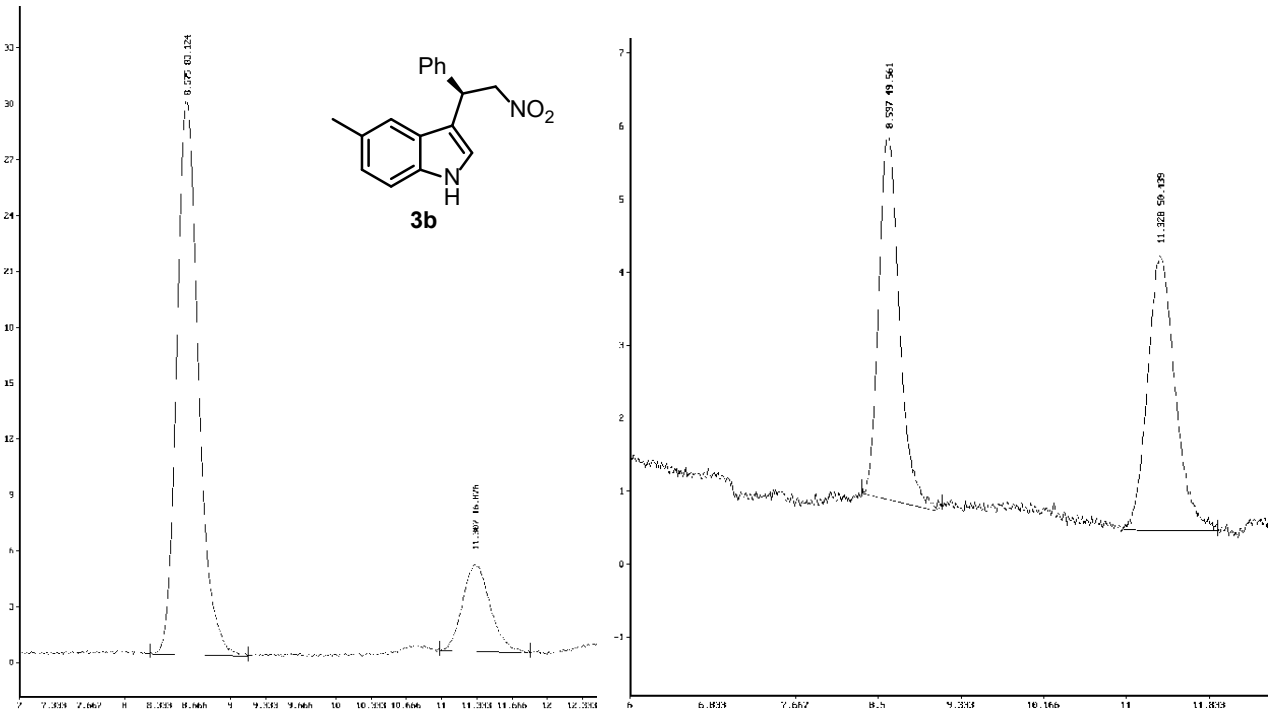

Figure S2. HPLC traces of the enantioenriched (*R*)-**3b** (66% *ee*) and the racemic sample (*reference*).

(*R*)-7-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3c)

Prepared according to the general procedure starting from indole **1c** (26.2 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.04 (br. s, 1H), 7.43–7.25 (m, 6H), 7.07–6.98 (m, 3H), 5.22 (t, J = 7.9 Hz, 1H), 5.10 (dd, J = 12.4, 7.6 Hz, 1H), 4.97 (dd, J = 12.4, 8.3 Hz, 1H), 2.49 (s, 3H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 15% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R = 7.9 min, t_R (major) = 9.4 min).

All spectroscopic data were in agreement with the literature.[S4]

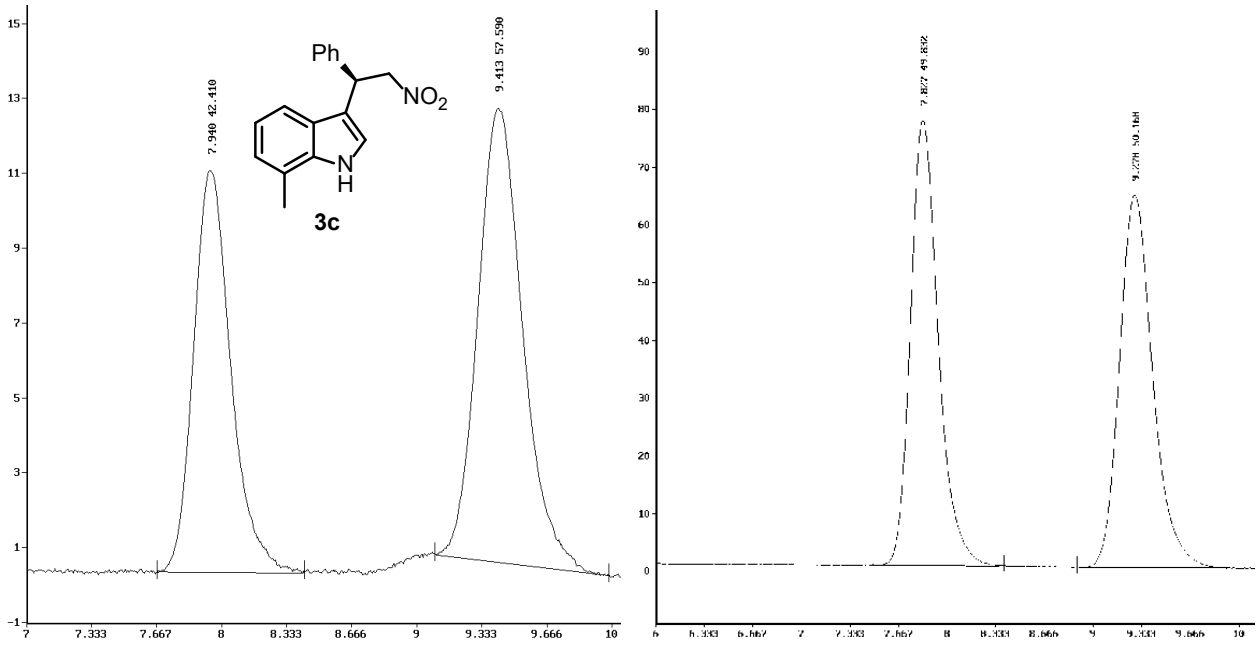

Figure S3. HPLC traces of the enantioenriched (*R*)-**3c** (15% *ee*) and the racemic sample (*reference*).

(*R*)-5-Bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3d)

Prepared according to the general procedure starting from indole **1d** (39.2 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni(II) complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.23 (br. s, 1H), 7.62 (d, J = 1.7 Hz, 1H), 7.45–7.27 (m, 7H), 7.12 (d, J = 2.4 Hz, 1H), 5.19 (t, J = 8.0 Hz, 1H), 5.09 (dd, J = 12.4, 7.9 Hz, 1H), 4.98 (dd, J = 12.4, 8.0 Hz, 1H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 68% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 9.3 min, t_R =10.5 min).

All spectroscopic data were in agreement with the literature.[S4]

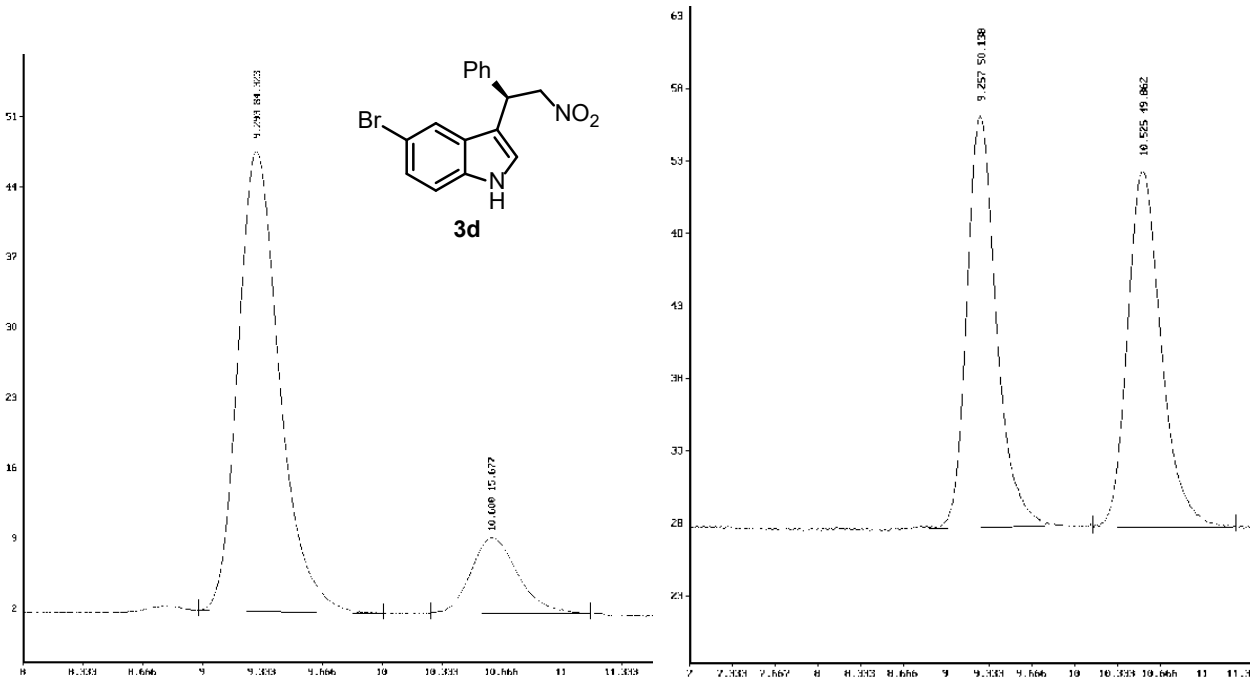

Figure S4. HPLC traces of the enantioenriched (*R*)-**3d** (68% *ee*) and the racemic sample (*reference*).

(*R*)-6-Chloro-3-(2-nitro-1-phenylethyl)-1*H*-indole (3e)

Prepared according to the general procedure starting from indole **1e** (30.3 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13 (br. s, 1H), 7.41–7.24 (m, 7H), 7.10–7.00 (m, 2H), 5.17 (t, J = 7.9 Hz, 1H), 5.06 (dd, J = 12.3, 7.9 Hz, 1H), 4.94 (dd, J = 12.3, 8.0 Hz, 1H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 67% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R = 13.3 min, t_R (major) =15.1 min).

All spectroscopic data were in agreement with the literature.[S5]

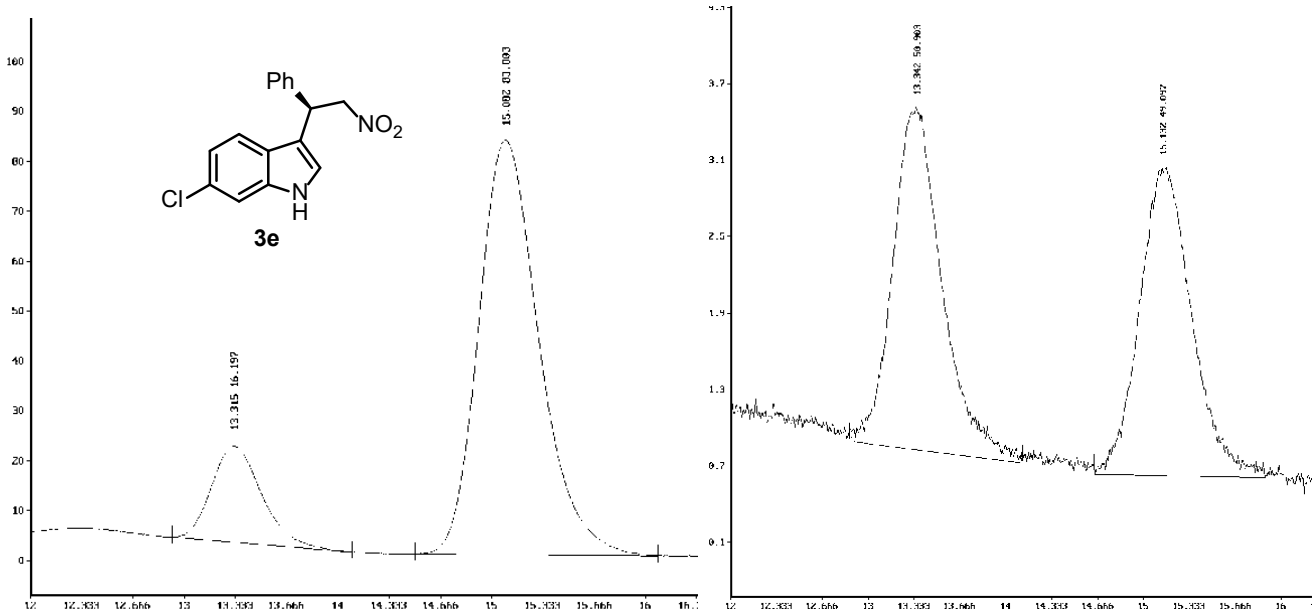

Figure S5. HPLC traces of the enantioenriched (*R*)-**3e** (67% *ee*) and the racemic sample (*reference*).

(*R*)-4-Methoxy-3-(2-nitro-1-phenylethyl)-1*H*-indole (3f)

Prepared according to the general procedure starting from indole **1f** (29.5 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.03 (br. s, 1H), 7.44–7.24 (m, 5H), 7.15 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 5.54 (dd, J = 9.8, 6.0 Hz, 1H), 5.34–5.24 (m, 1H), 4.94 (dd, J = 12.7, 9.8 Hz, 1H), 3.93 (s, 3H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 5-BBT column, *ee* = 65% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 9.0 min, t_R = 9.7 min).

All spectroscopic data were in agreement with the literature.[S6]

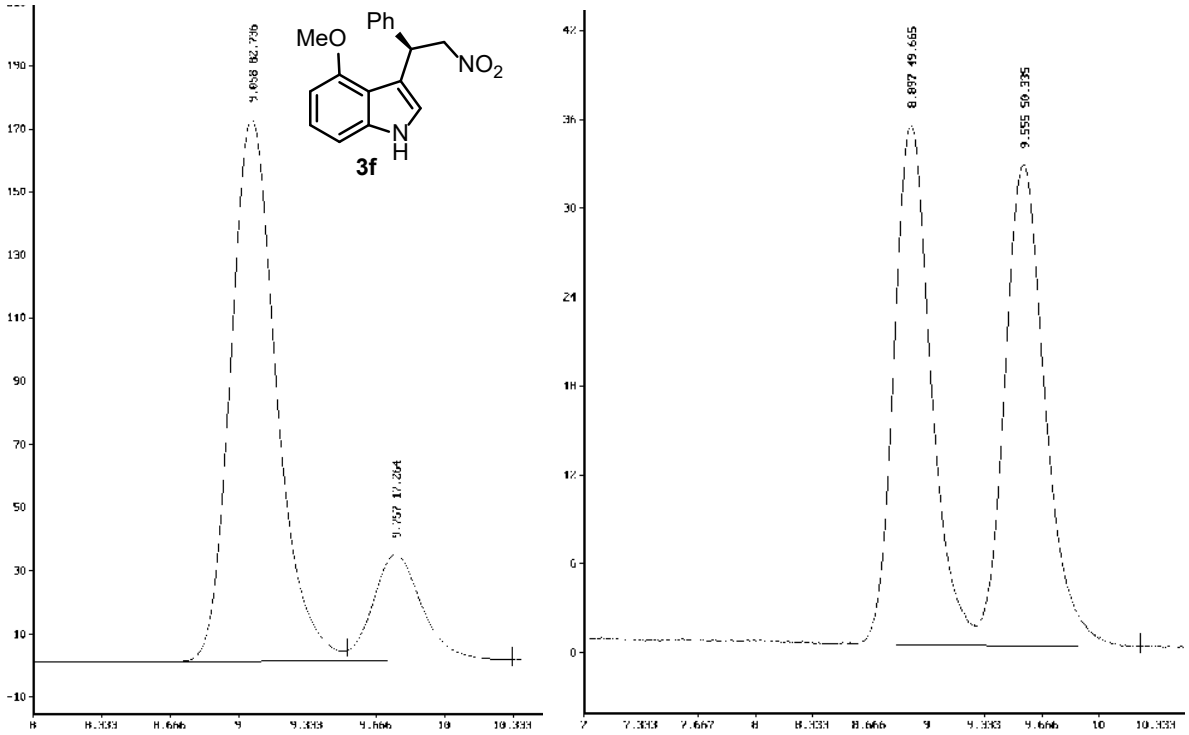

Figure S6. HPLC traces of the enantioenriched (*R*)-**3f** (65% *ee*) and the racemic sample (*reference*).

(*R*)-3-(2-Nitro-1-phenylethyl)indole-4-carboxylic acid methyl ester (3g)

Prepared according to the general procedure starting from indole **1g** (35.0 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.50 (br. s, 1H), 7.61 (dd, J = 7.5, 1.1 Hz, 1H), 7.51 (dd, J = 8.2, 1.1 Hz, 1H), 7.35–7.16 (m, 6H), 7.06 (d, J = 2.7 Hz, 1H), 5.84 (t, J = 7.9 Hz, 1H), 5.12–5.00 (m, 1H), 4.86 (dd, J = 12.9, 8.5 Hz, 1H), 3.87 (s, 3H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 5-BBT column, *ee* = 59% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R = 24.0 min, t_R (major) = 28.0 min).

All spectroscopic data were in agreement with the literature.[S7]

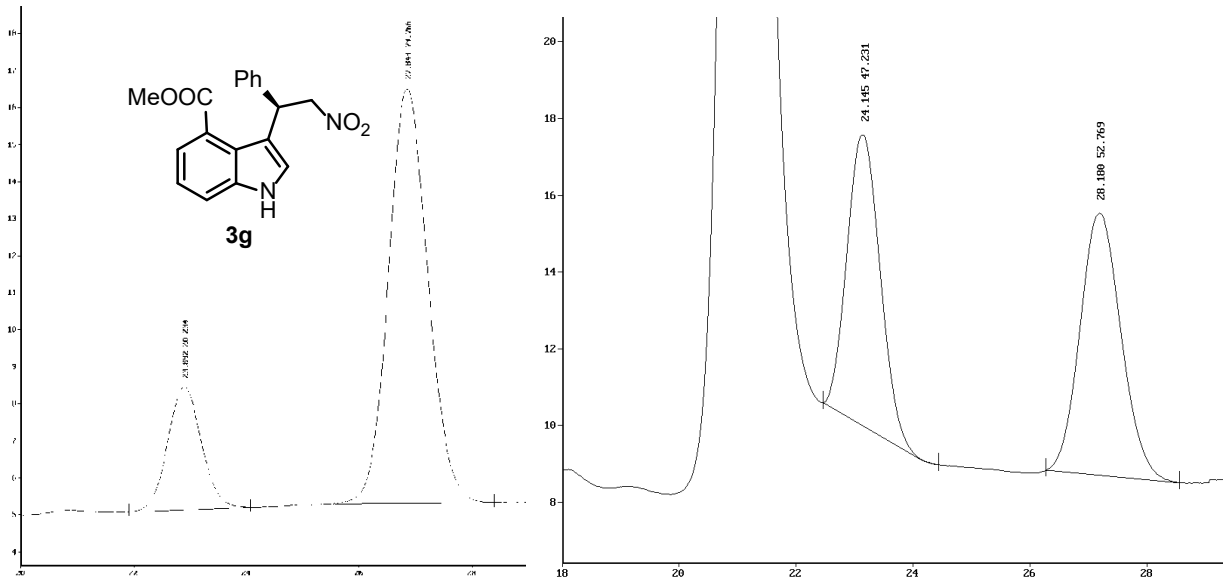

Figure S7. HPLC traces of the enantioenriched (*R*)-**3g** (59% *ee*) and the racemic sample (*reference*).

(*R*)-3-(2-Nitro-1-phenylethyl)indole-5-carboxylic acid methyl ester (3h)

Prepared according to the general procedure starting from indole **1h** (35.0 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni(II) complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.56 (br. s, 1H), 8.26 (s, 1H), 7.92 (dd, J = 8.6, 1.6 Hz, 1H), 7.41–7.21 (m, 6H), 7.13 (d, J = 2.5 Hz, 1H), 5.25 (t, J = 8.1 Hz, 1H), 5.13–4.92 (m, 2H), 3.93 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1, 139.2, 138.9, 129.1, 127.9, 127.8, 125.9, 124.2, 123.2, 122.1, 122.0, 115.8, 111.3, 79.5, 52.1, 41.3 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{17}N_2O_4^+$ $[M+H]^+$: 325.1183, found: 325.1180.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 5-BBT column, *ee* = 62% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R = 28.5 min, t_R (major) = 32.8 min).

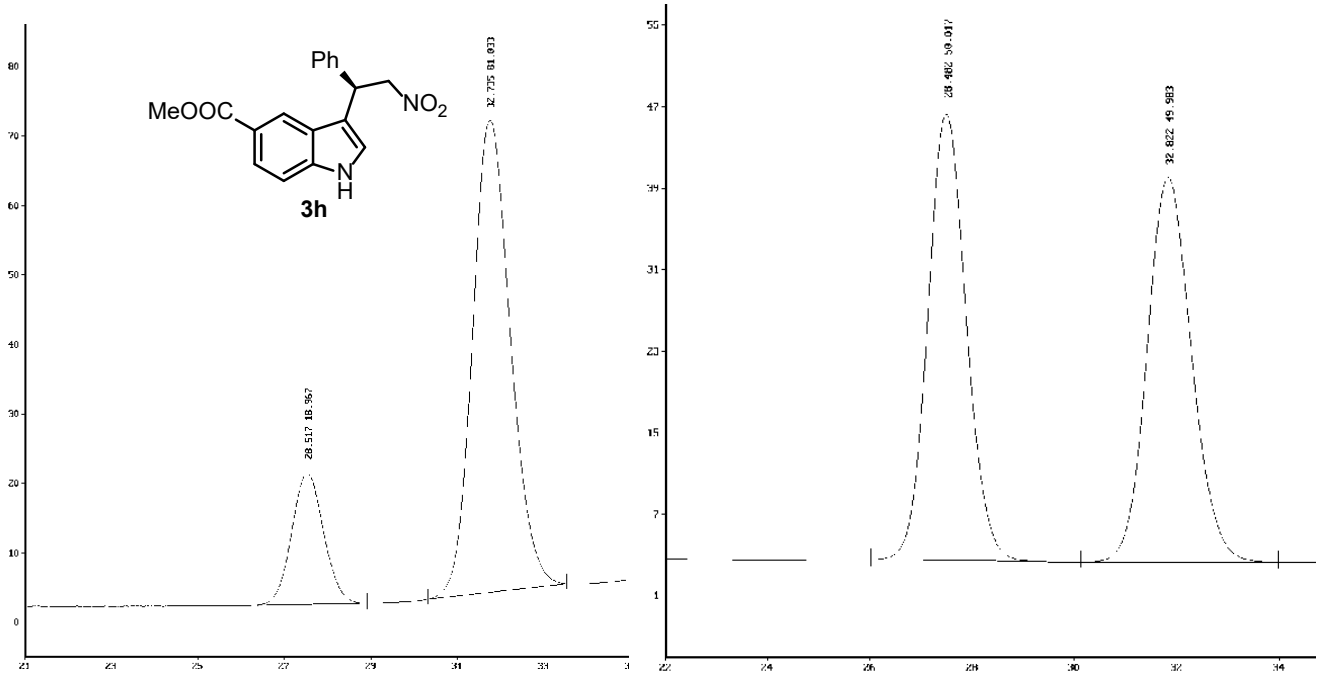

Figure S8. HPLC traces of the enantioenriched (*R*)-**3h** (59% *ee*) and the racemic sample (*reference*).

(*R*)-2-Methyl-5-methoxy-3-(2-nitro-1-phenylethyl)-1*H*-indole (3i)

Prepared according to the general procedure starting from indole **1i** (32.2 mg, 0.2 mmol) and β-nitrostyrene **2a** (14.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.81 (br. s, 1H), 7.38–7.22 (m, 5H), 7.16 (d, J = 8.5 Hz, 1H), 6.84–6.75 (m, 2H), 5.29–5.03 (m, 3H), 3.79 (s, 3H), 2.38 (s, 3H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Chiralpak AS-H column, *ee* = 22% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R = 24.1 min, t_R (major) = 30.2 min).

All spectroscopic data were in agreement with the literature.[S8]

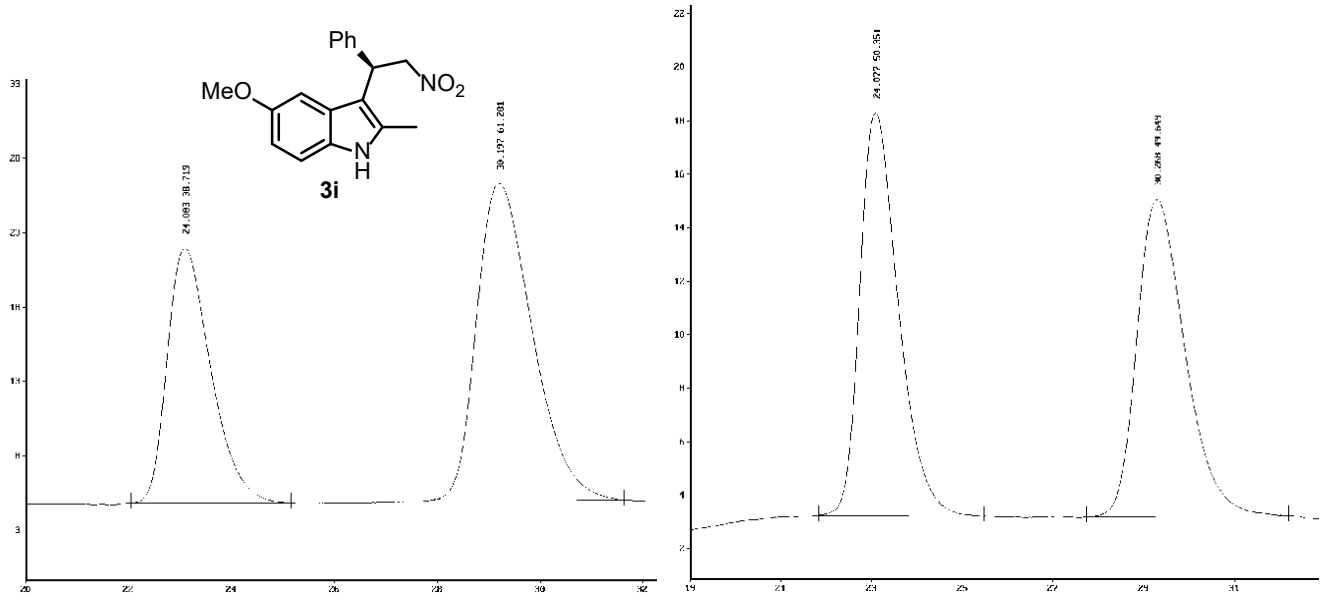

Figure S9. HPLC traces of the enantioenriched (*R*)-**3i** (22% *ee*) and the racemic sample (*reference*).

(*S*)-3-(1-(2-Nitro)-2-nitroethyl)-1*H*-indole (3j)

Prepared according to the general procedure starting from indole **1a** (23.4 mg, 0.2 mmol) and (*E*)-1-nitro-2-(2-nitrovinyl)benzene **2b** (19.4 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.20 (br. s, 1H), 7.93 (dd, J = 8.0, 1.4 Hz, 1H), 7.56–7.30 (m, 5H), 7.25–7.14 (m, 2H), 7.11–7.02 (m, 1H), 5.90 (t, J = 7.7 Hz, 1H), 5.19–5.03 (m, 2H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 15% for the (*S*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 24.2 min, t_R = 32.7 min). (*S*)-configuration due to a change in the precedence of substituents according to the Cahn–Ingold–Prelog (CIP) rules.

All spectroscopic data were in agreement with the literature.[S9]

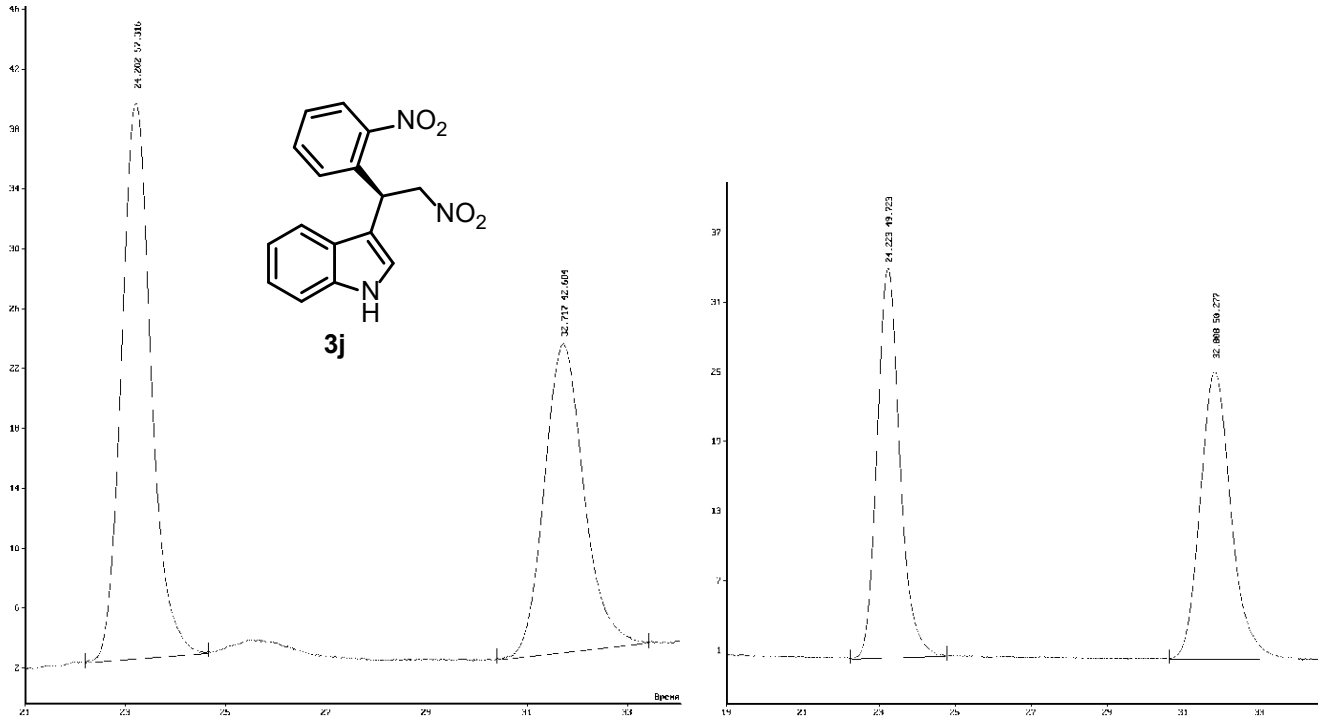

Figure S10. HPLC traces of the enantioenriched (*S*)-**3j** (15% *ee*) and the racemic sample (*reference*).

(*R*)-3-(1-(3-Nitro)-2-nitroethyl)-1*H*-indole (3k)

Prepared according to the general procedure starting from indole **1a** (23.4 mg, 0.2 mmol) and (*E*)-1-nitro-3-(2-nitrovinyl)benzene **2c** (19.4 mg, 0.1 mmol), Ni(II) complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.27 (br. s, 1H), 8.25–8.20 (m, 1H), 8.18–8.11 (m, 1H), 7.78–7.68 (m, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.46–7.36 (m, 2H), 7.31–7.18 (m, 1H), 7.16–7.08 (m, 2H), 5.37–5.27 (m, 1H), 5.13 (dd, J = 12.8, 7.0 Hz, 1H), 5.01 (dd, J = 12.8, 8.9 Hz, 1H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 69% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 21.2 min, t_R = 25.9 min).

All spectroscopic data were in agreement with the literature.[S9]

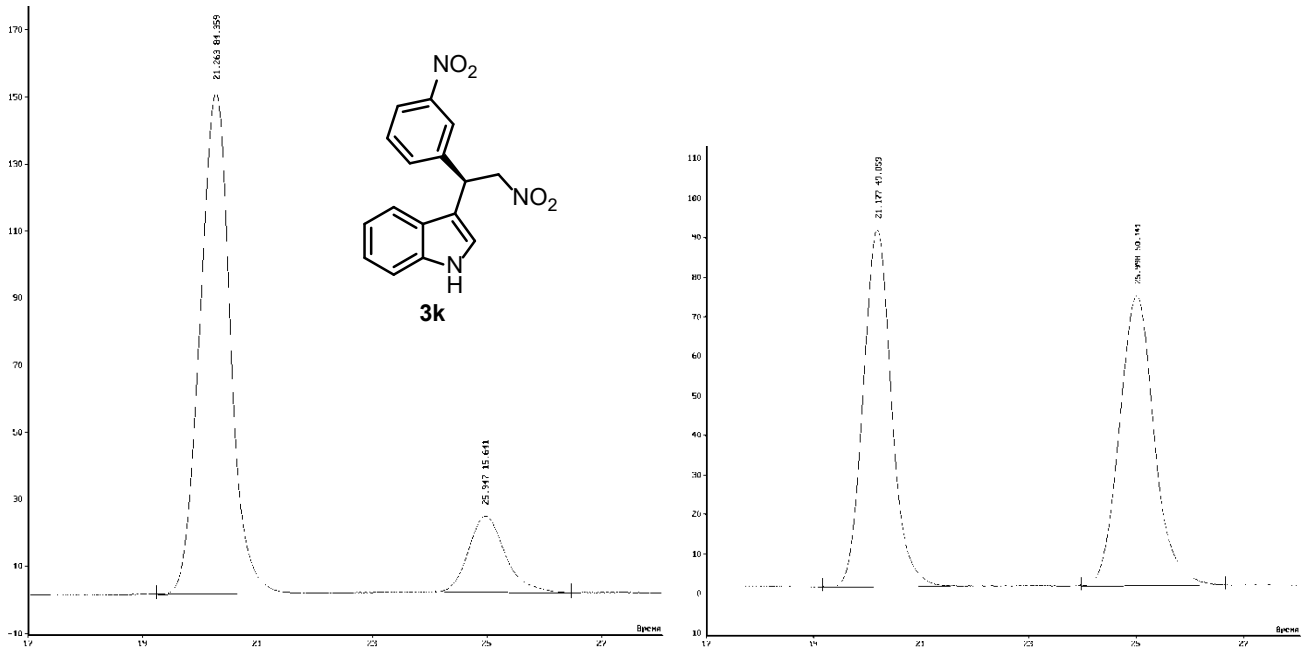

Figure S11. HPLC traces of the enantioenriched (*R*)-**3k** (69% *ee*) and the racemic sample (*reference*).

(*R*)-3-(1-(4-Nitro)-2-nitroethyl)-1*H*-indole (3l)

Prepared according to the general procedure starting from indole **1a** (23.4 mg, 0.2 mmol) and (*E*)-1-nitro-4-(2-nitrovinyl)benzene **2d** (19.4 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.27 (br. s, 1H), 8.25–8.11 (m, 2H), 7.59–7.50 (m, 2H), 7.47–7.34 (m, 2H), 7.33–7.20 (m, 1H), 7.18–7.03 (m, 2H), 5.38–5.26 (m, 1H), 5.13 (dd, J = 12.8, 7.0 Hz, 1H), 5.01 (dd, J = 12.8, 8.9 Hz, 1H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Kromasil 3-Amycoat column, *ee* = 69% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 32.6 min, t_R = 40.7 min).

All spectroscopic data were in agreement with the literature.[S9]

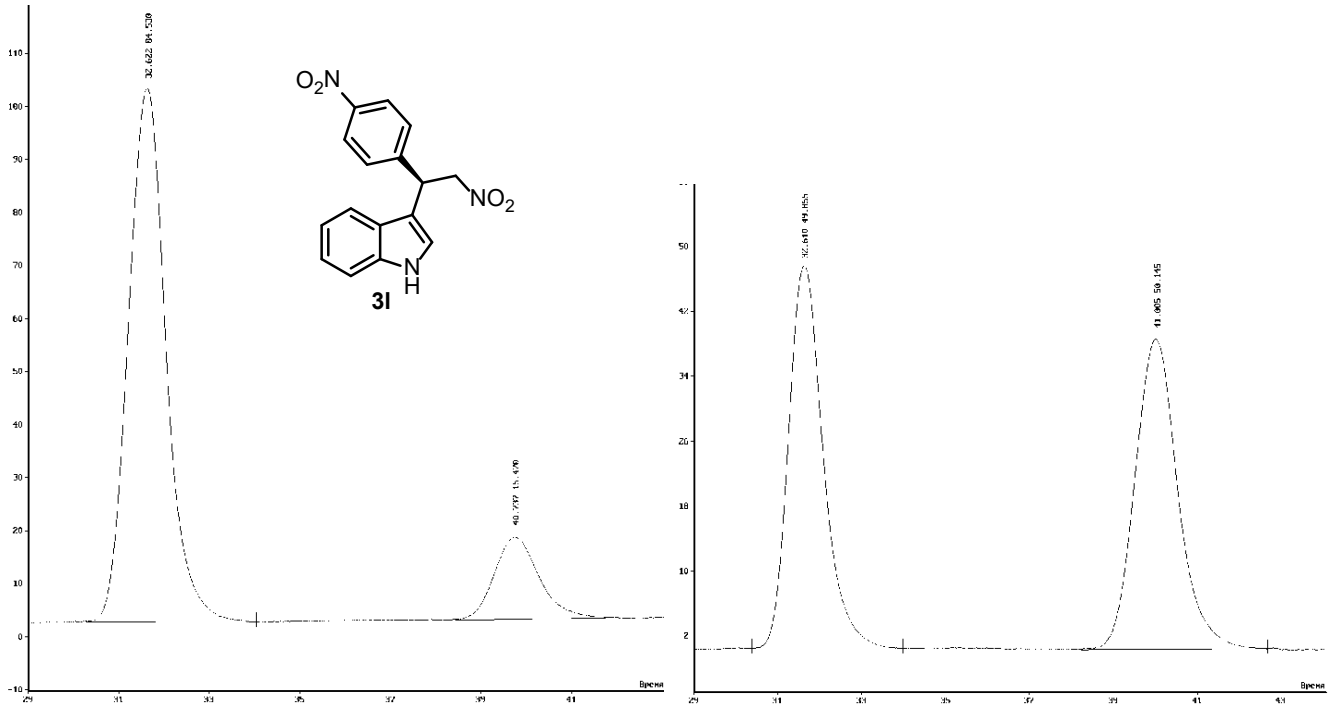

Figure S12. HPLC traces of the enantioenriched (*R*)-**3l** (69% *ee*) and the racemic sample (*reference*).

(*R*)-3-(1-Naphth-2-yl-2-nitroethyl)-1*H*-indole (3m)

Prepared according to the general procedure starting from indole **1a** (23.4 mg, 0.2 mmol) and (*E*)-2-(2-nitrovinyl)naphthalene **2e** (19.9 mg, 0.1 mmol), Ni^{II} complex **6** (2.2 mg, 5 mol%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.08 (s, 1H), 7.83 (dd, *J* = 7.4, 2.8 Hz, 4H), 7.57–7.42 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.27–7.18 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 5.40 (t, *J* = 7.9 Hz, 1H), 5.11 (qd, *J* = 12.5, 7.9 Hz, 2H) ppm.

The enantiomeric excess was determined by HPLC analysis using a Chiralpak AS-H column, *ee* = 52% for the (*R*)-enantiomer of the product (conditions: hexane/isopropanol = 90:10, flow rate: 1 mL/min, 254 nm, 25 °C, t_R (major) = 32.0 min, t_R = 35.4 min).

All spectroscopic data were in agreement with the literature.[S10]

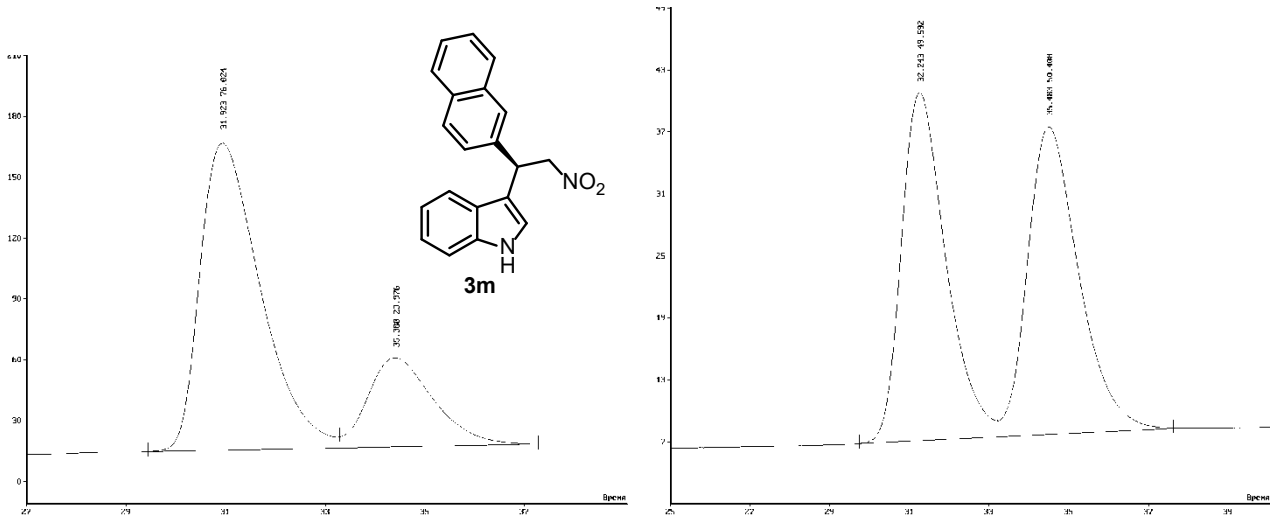

Figure S13. HPLC traces of the enantioenriched (*R*)-**3m** (52% *ee*) and the racemic sample (*reference*).

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NMR spectra

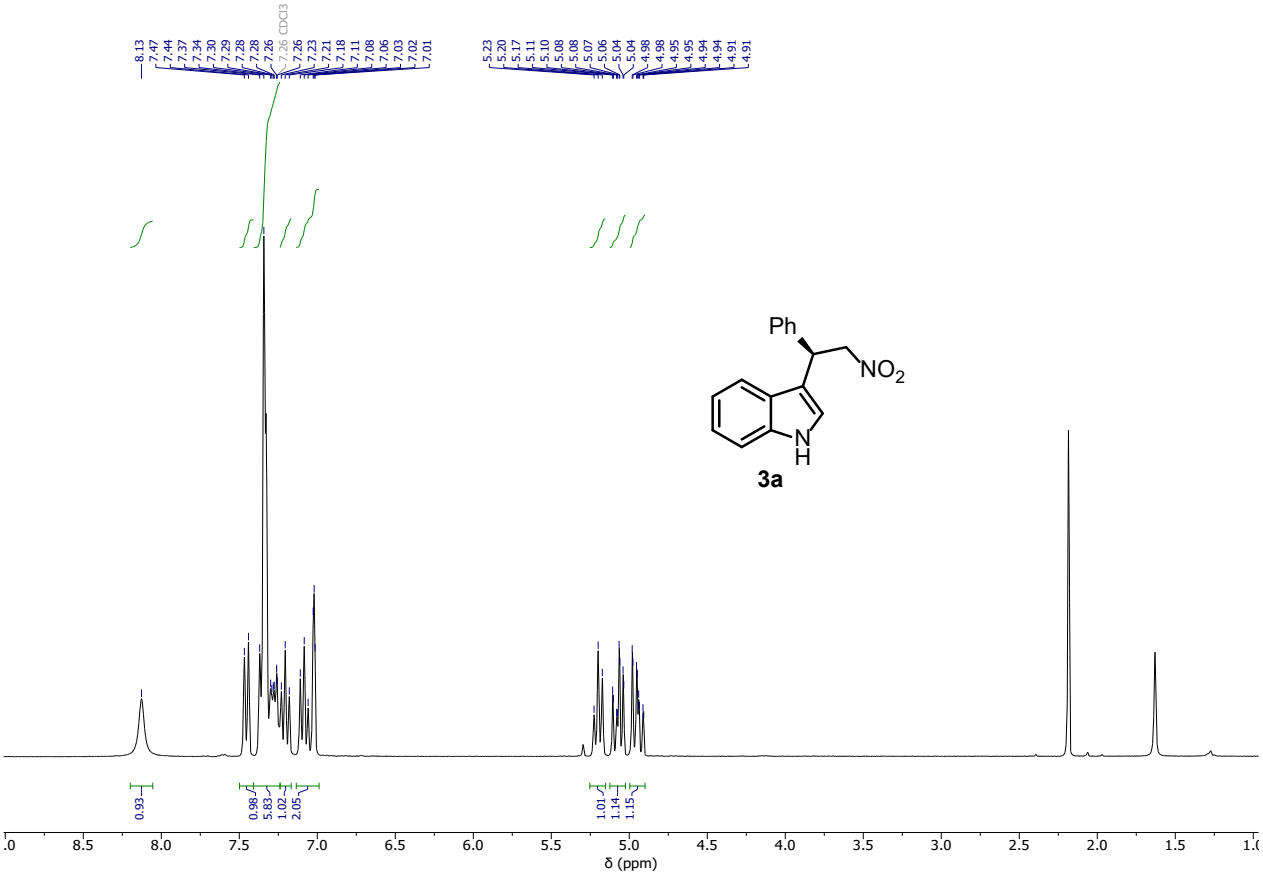

Figure S14. ^{1}H NMR spectrum of **3a** in $CDCl_3$

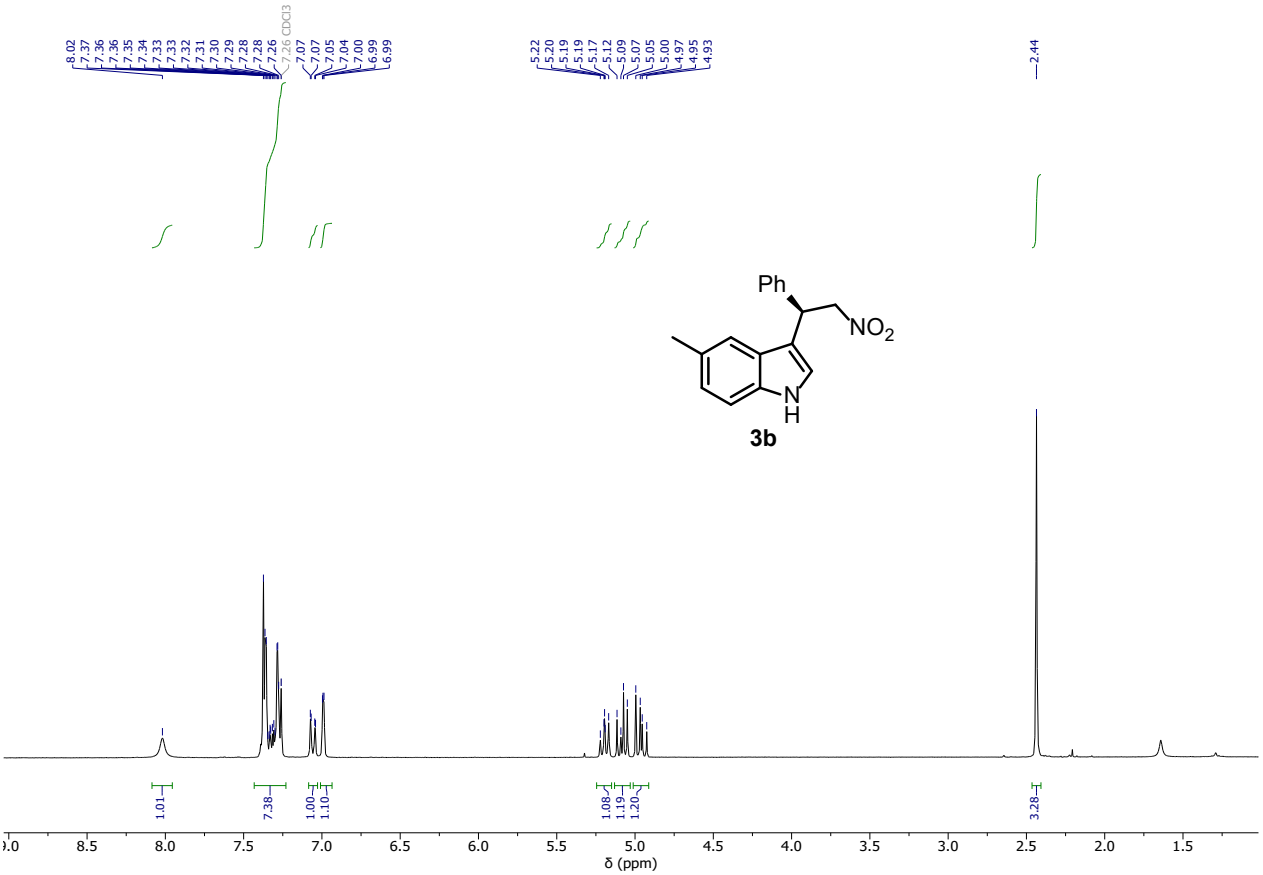

Figure S15. ^{1}H NMR spectrum of **3b** in $CDCl_3$

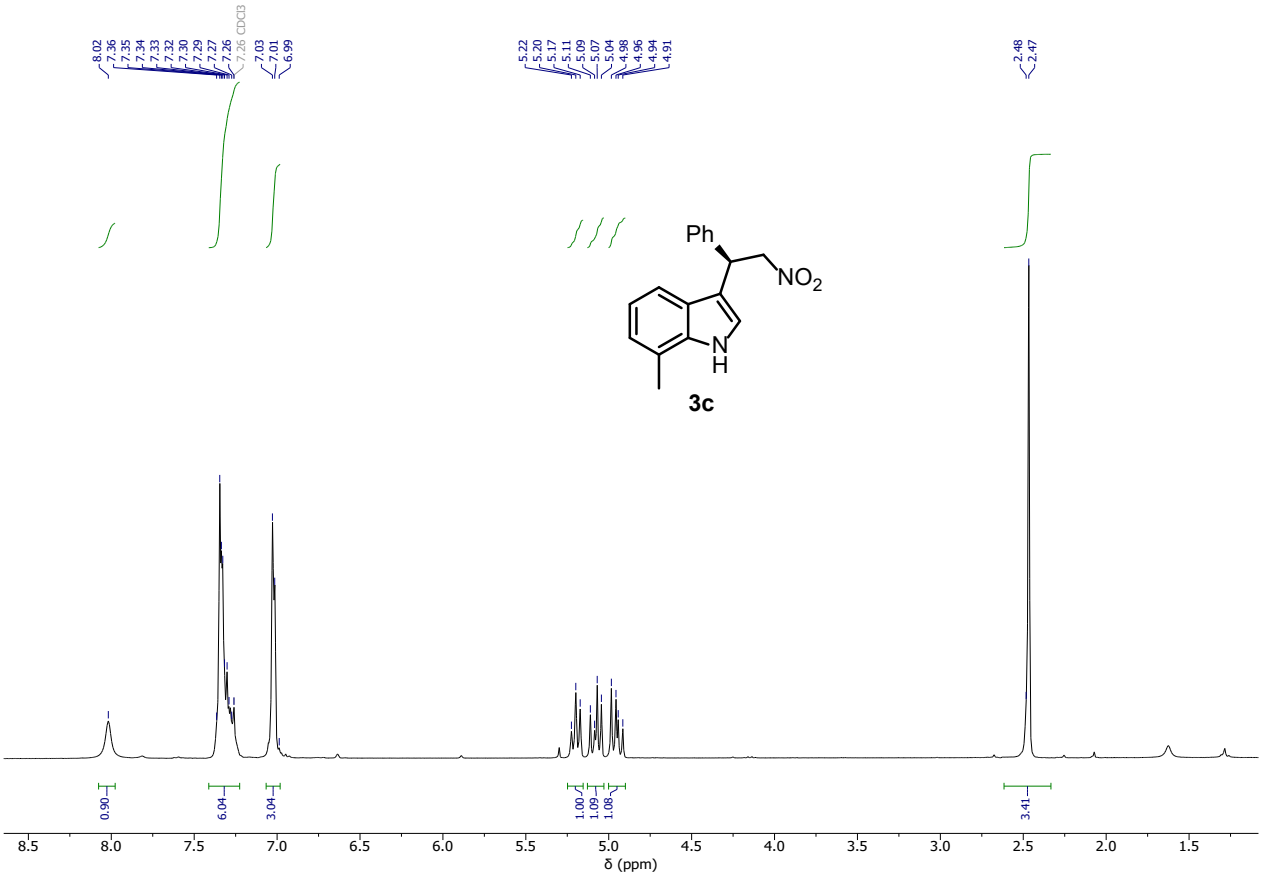

Figure S16. ^{1}H NMR spectrum of **3c** in $CDCl_3$

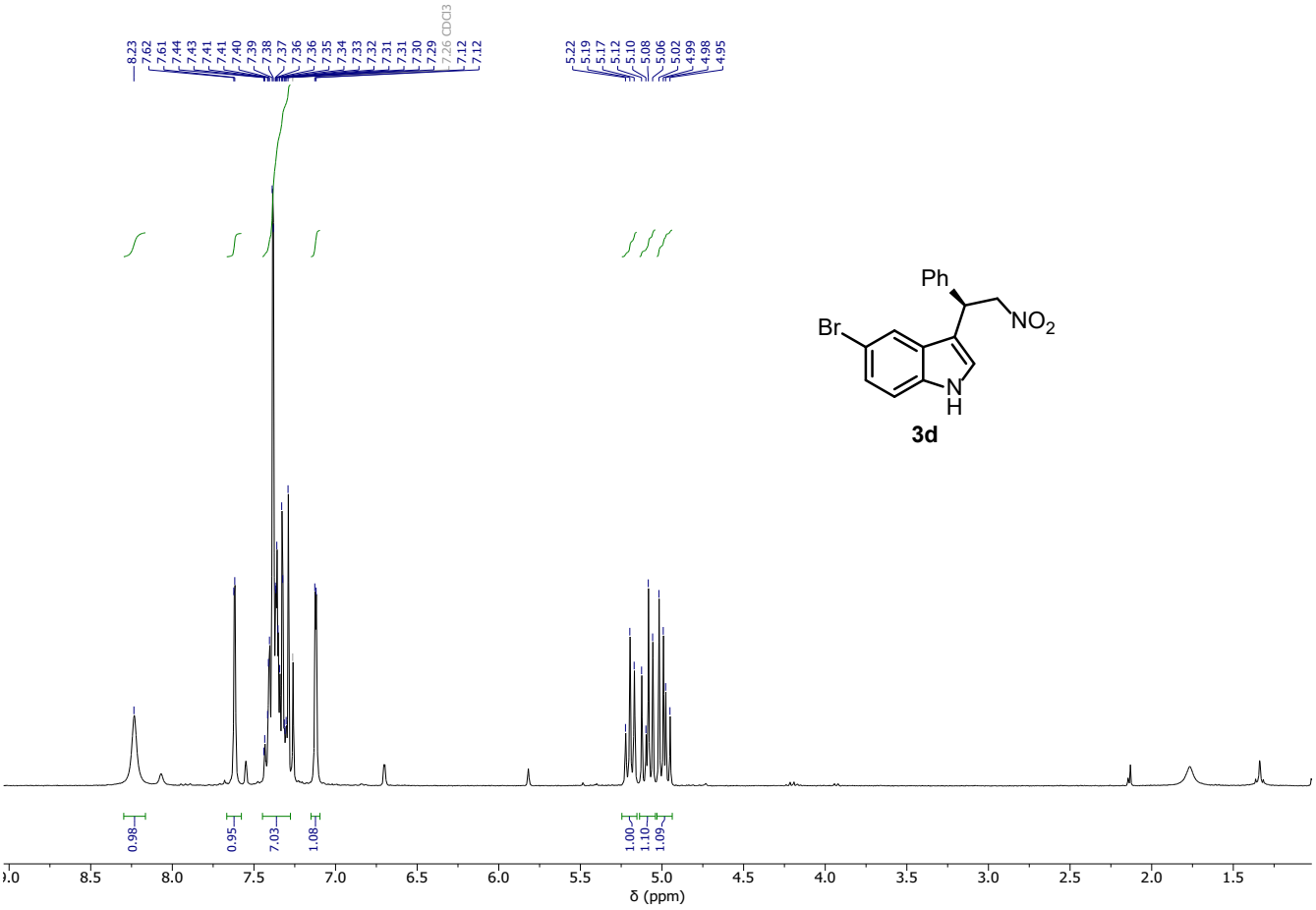

Figure S17. ^{1}H NMR spectrum of **3d** in $CDCl_3$

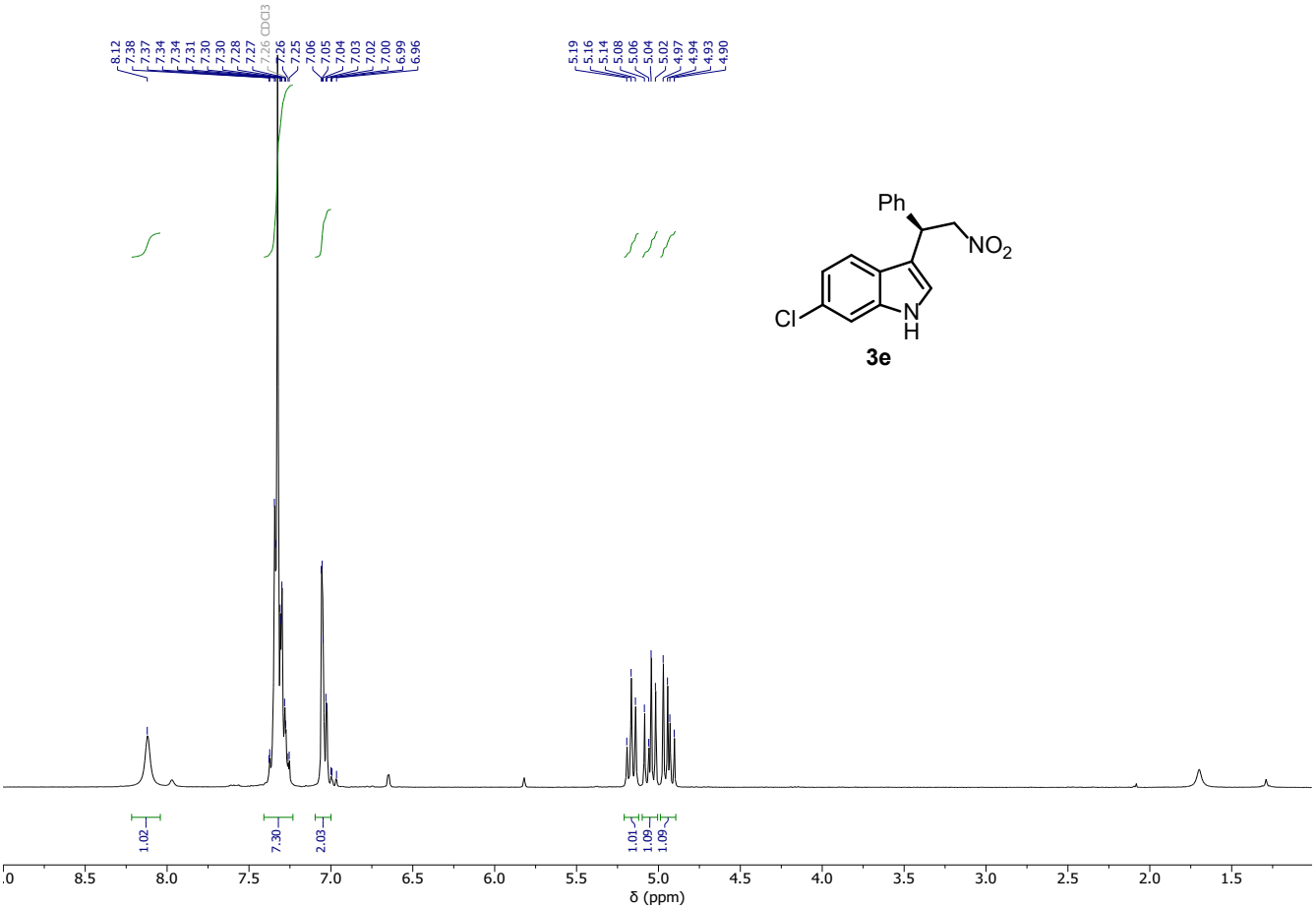

Figure S18. ^{1}H NMR spectrum of **3e** in $CDCl_3$

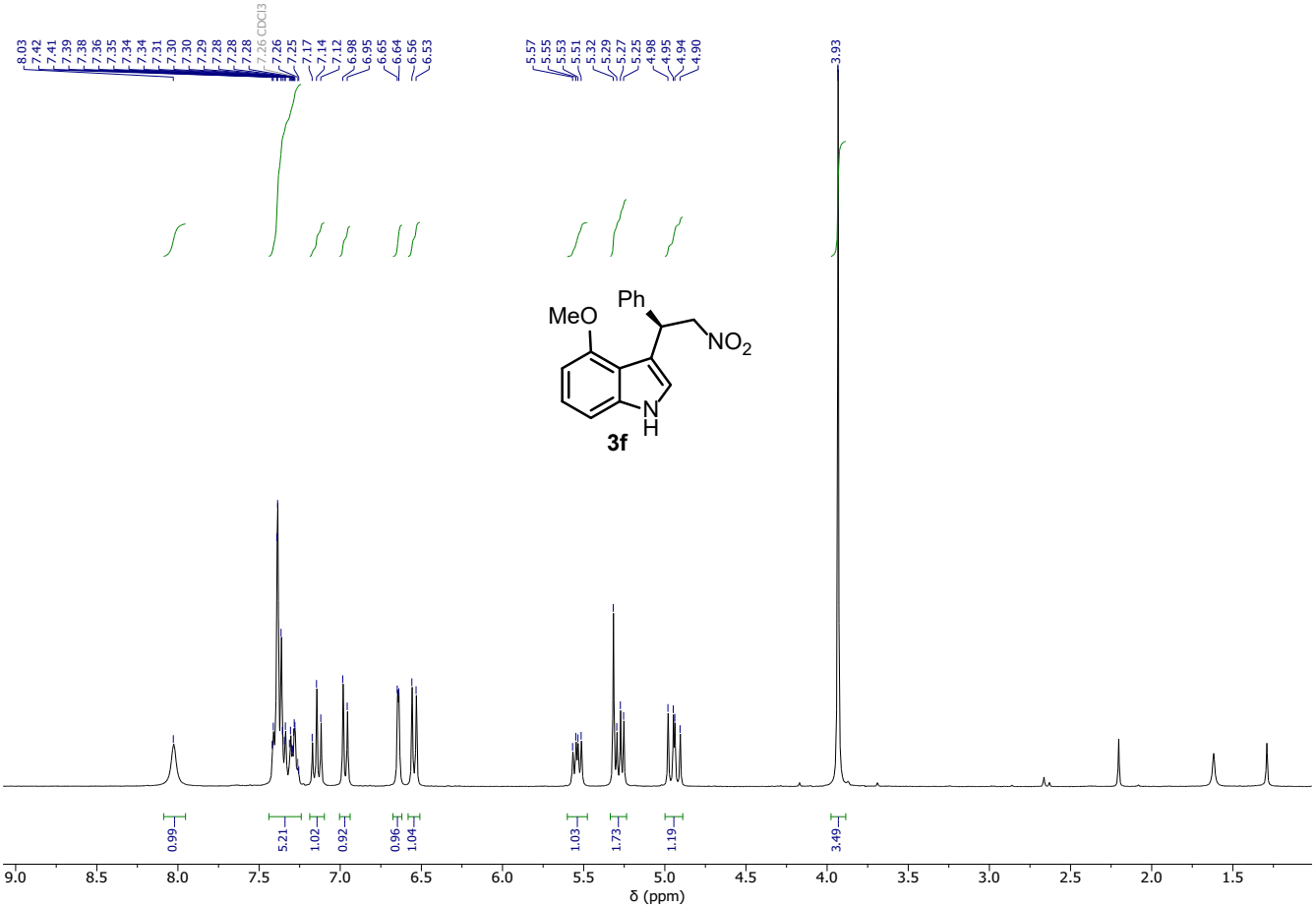

Figure S19. ^{1}H NMR spectrum of **3f** in $CDCl_3$

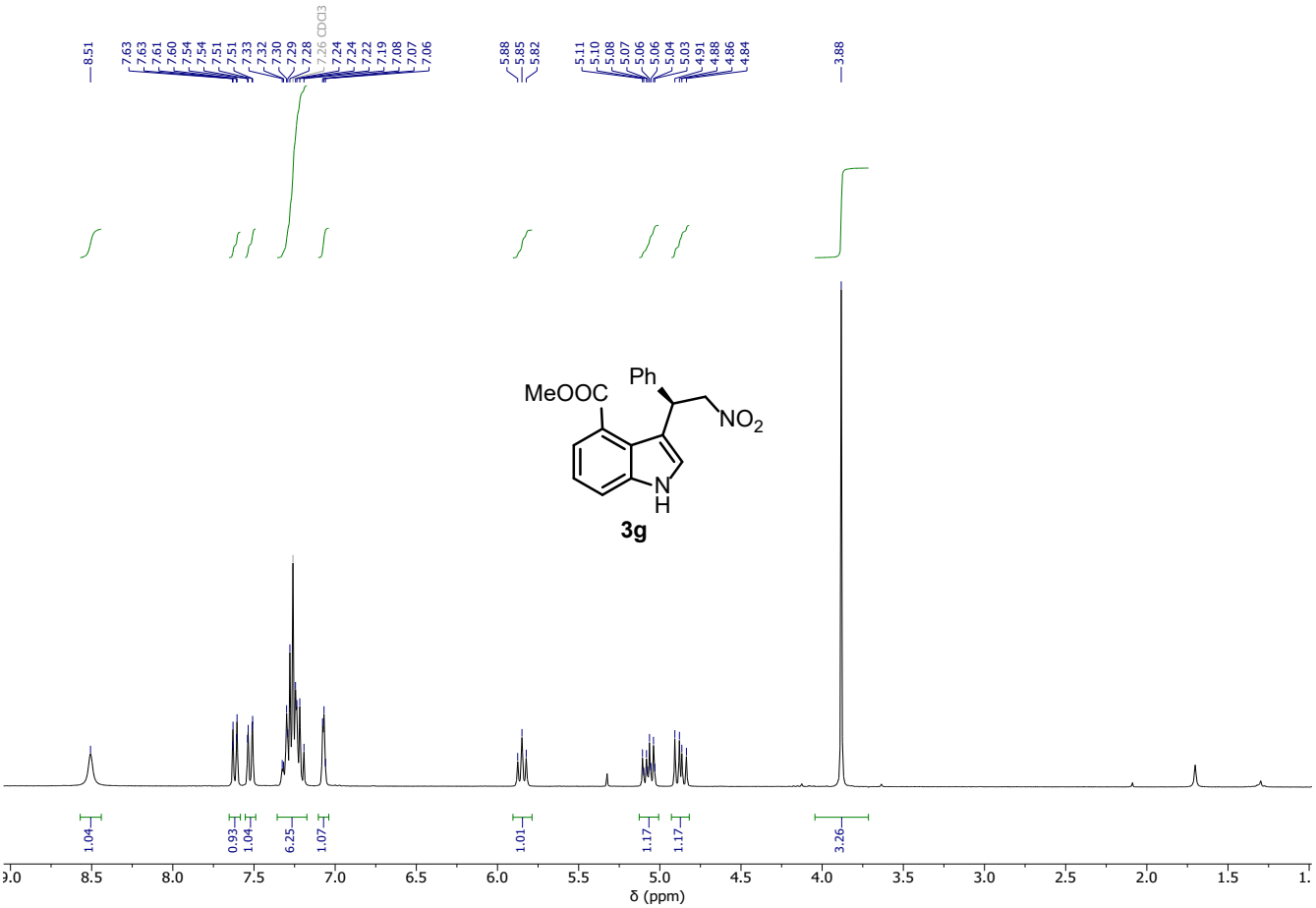

Figure S20. ^{1}H NMR spectrum of **3g** in $CDCl_3$

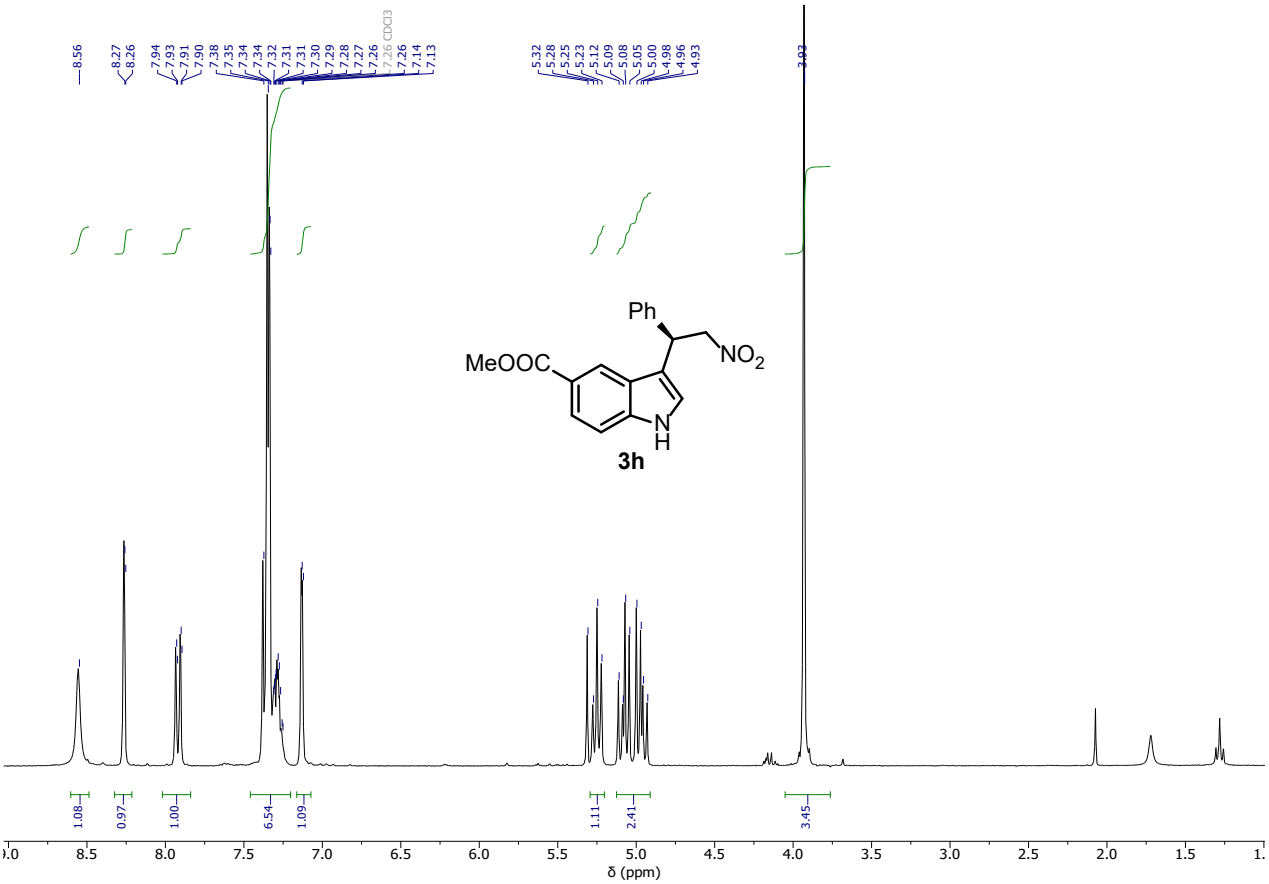

Figure S21. ^{1}H NMR spectrum of **3h** in $CDCl_3$

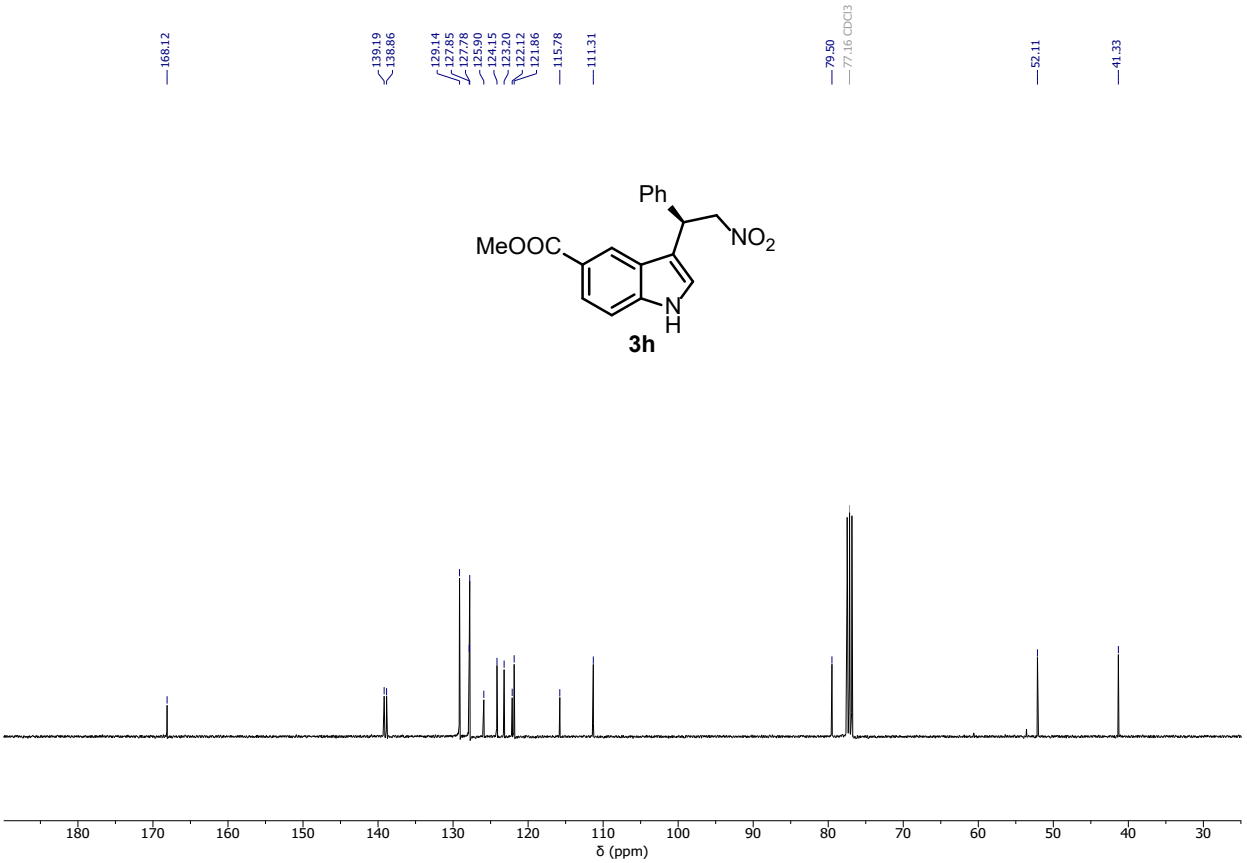

Figure S22. ^{13}C NMR spectrum of **3h** in $CDCl_3$

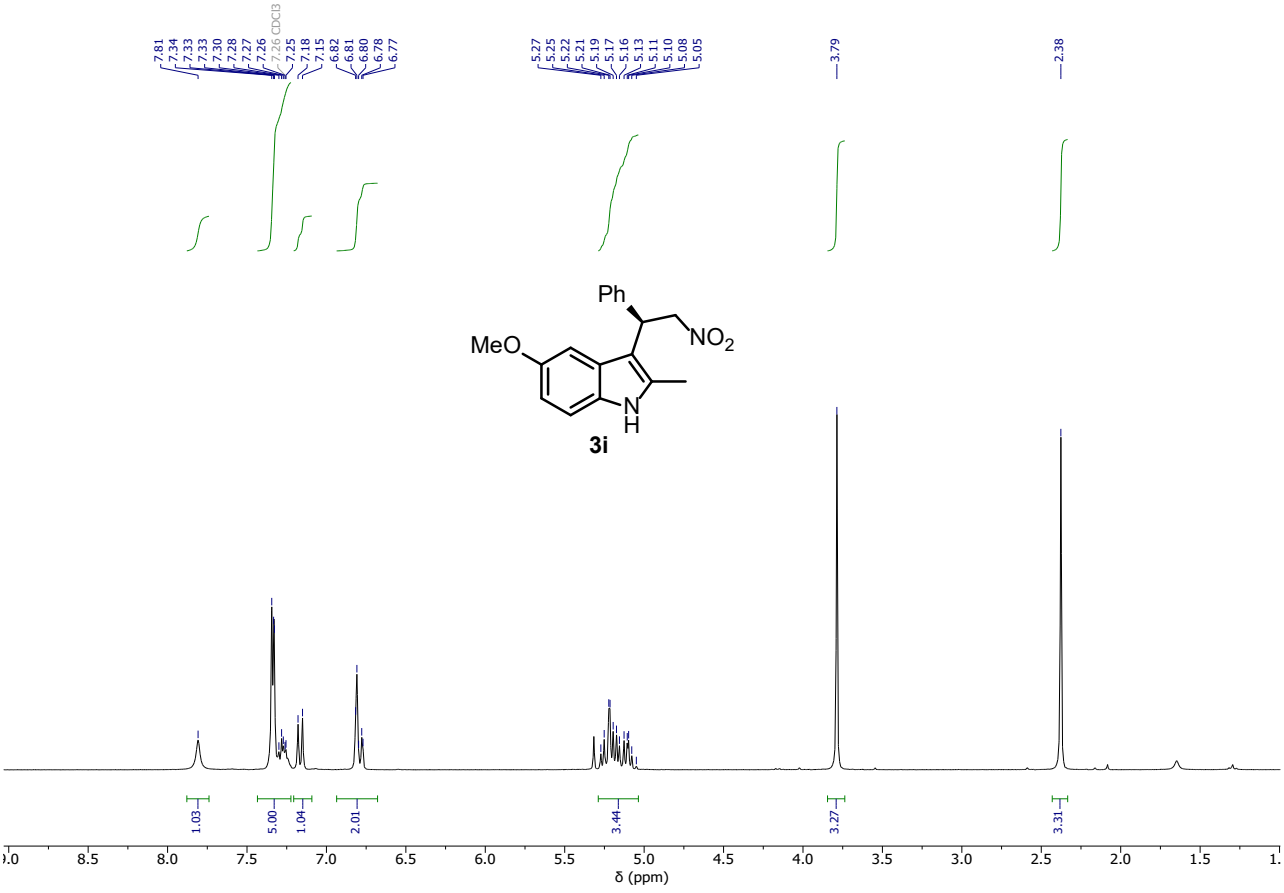

Figure S23. ^{1}H NMR spectrum of **3i** in $CDCl_3$

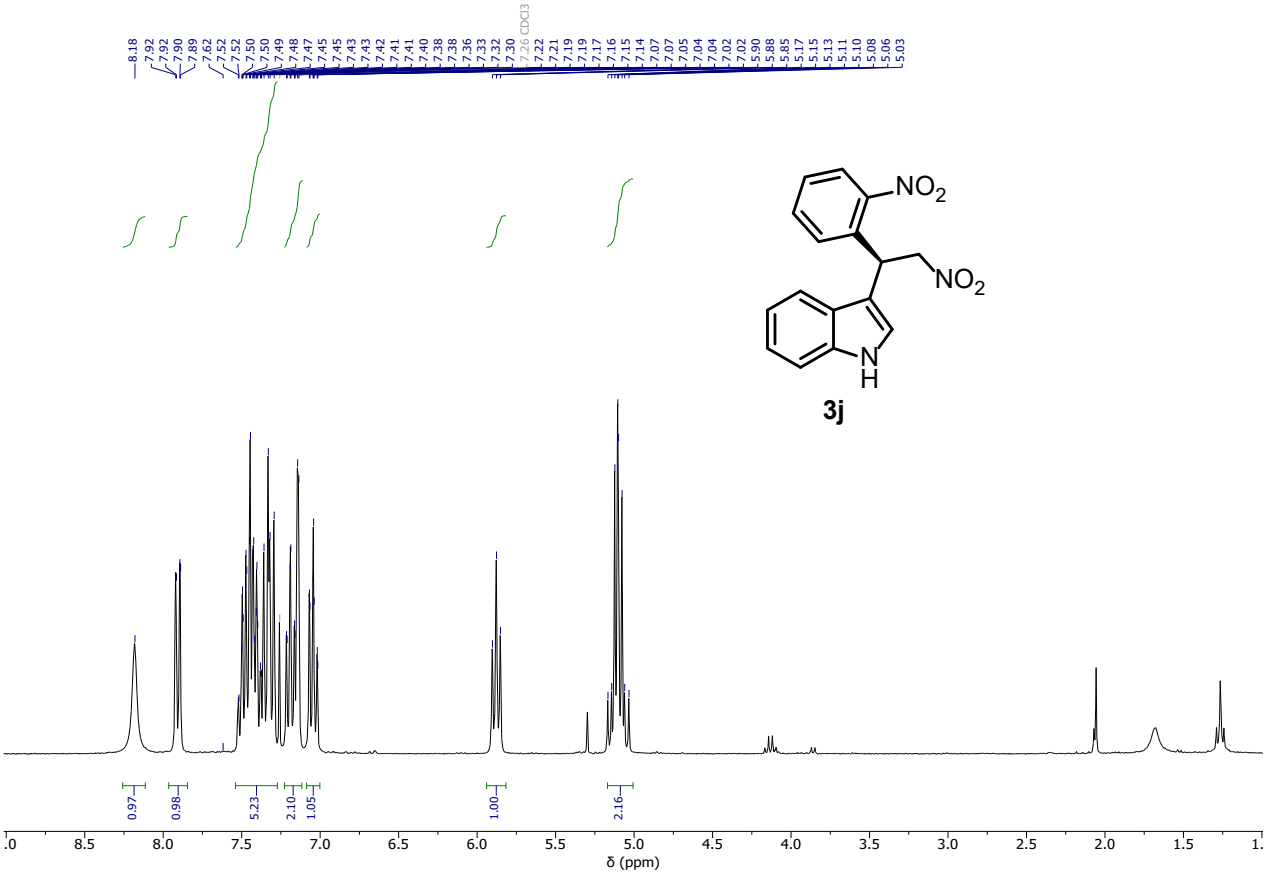

Figure S24. ^{1}H NMR spectrum of **3j** in $CDCl_3$

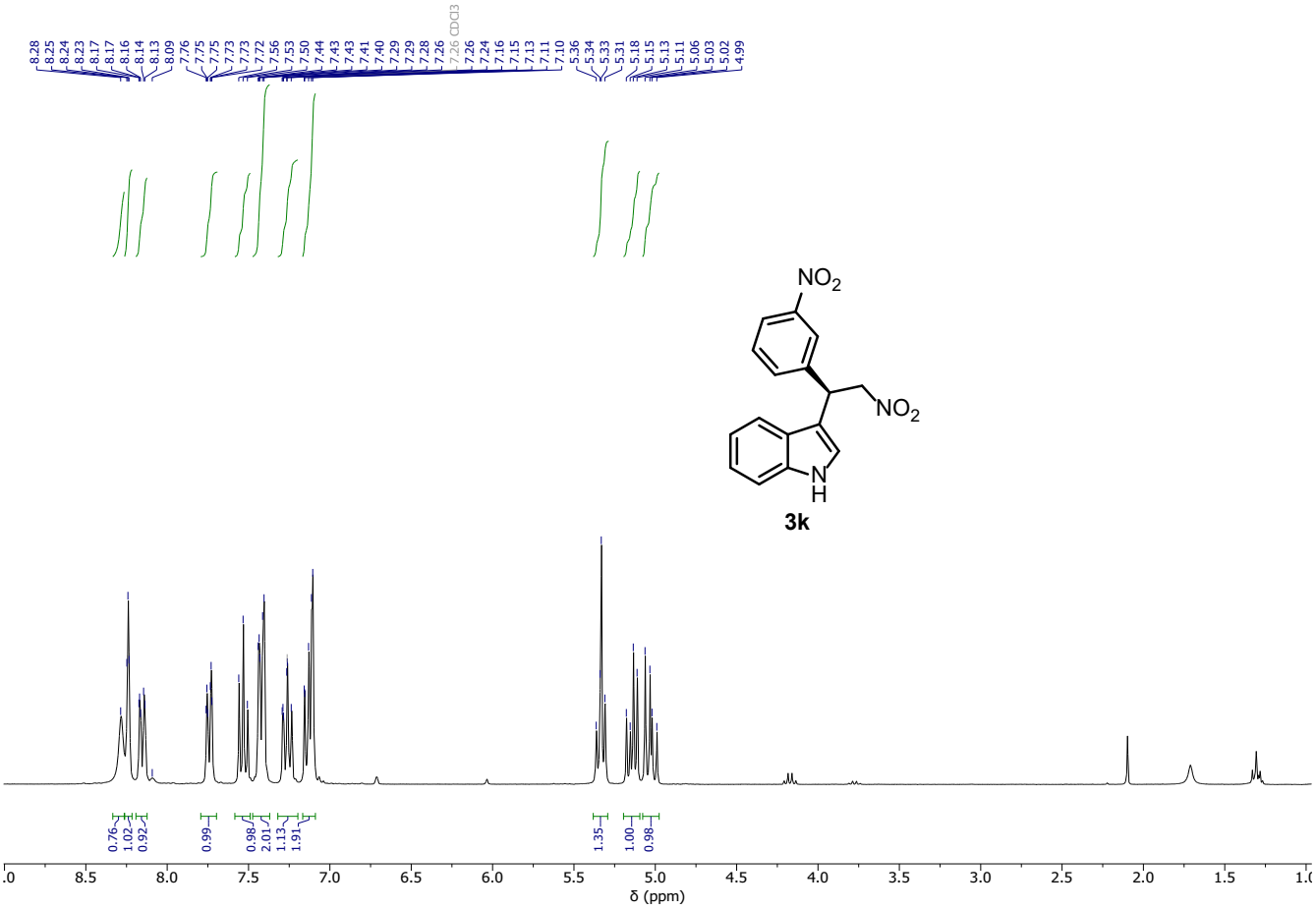

Figure S25. ^{1}H NMR spectrum of **3k** in $CDCl_3$

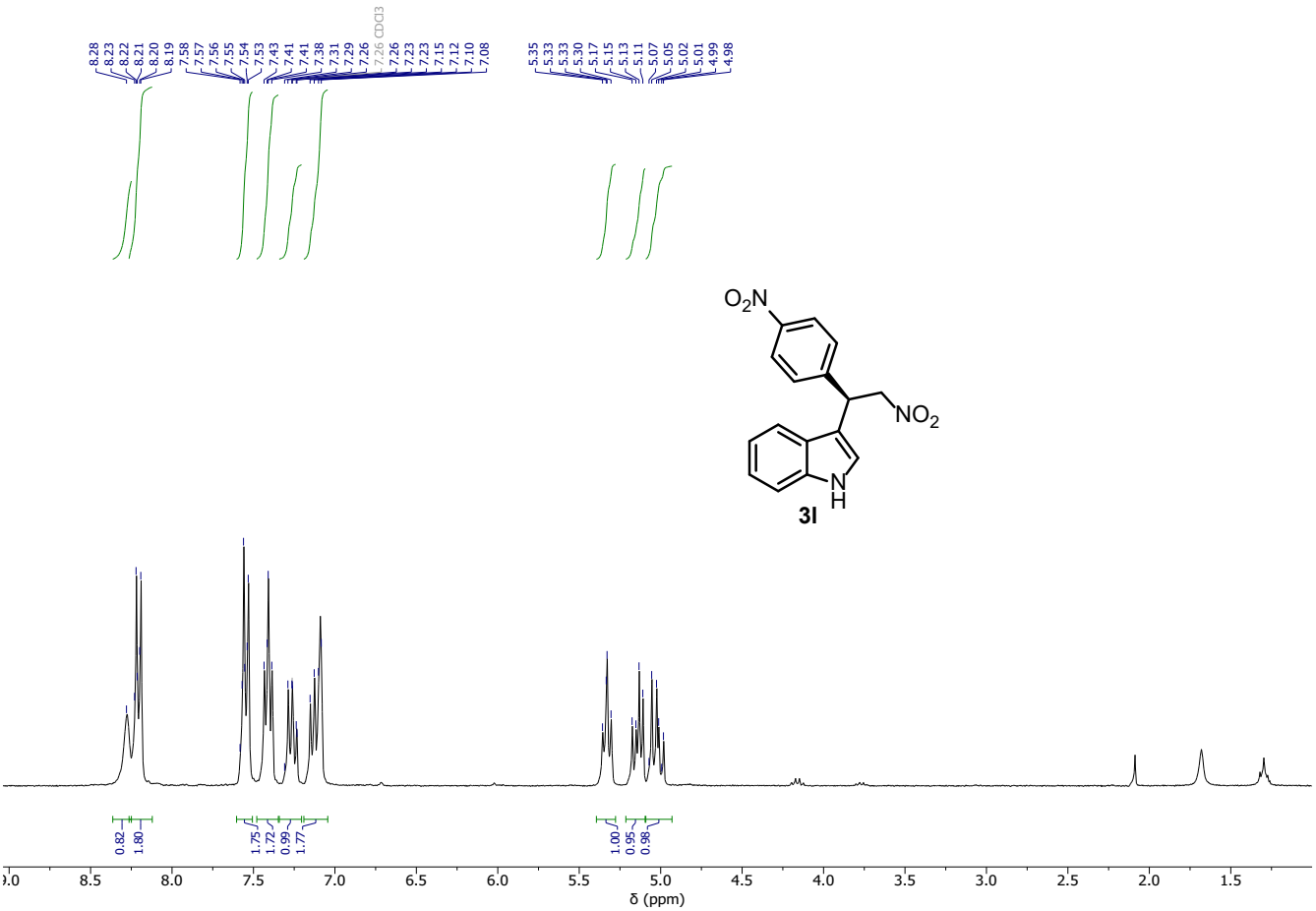

Figure S26. ^{1}H NMR spectrum of **3l** in $CDCl_3$

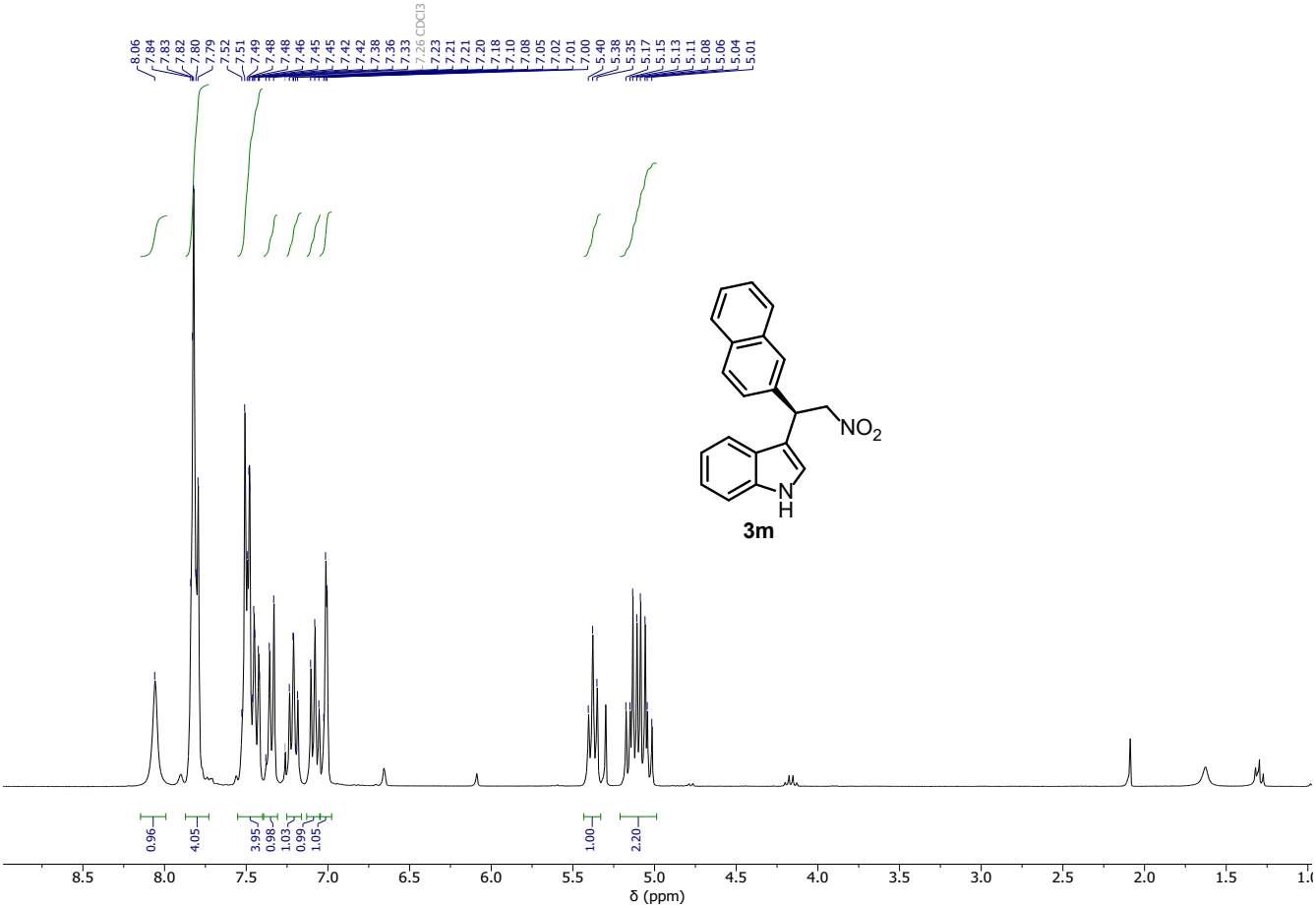

Figure S27. ^{1}H NMR spectrum of **3m** in $CDCl_3$