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Supporting Information

Asymmetric Aza-Henry Reaction to Provide Oxindoles with Quaternary Carbon Stereocenter Catalyzed by a Metal-Templated Chiral Brønsted Base

Ying Hu, Zijun Zhou, Lei Gong, and Eric Meggers

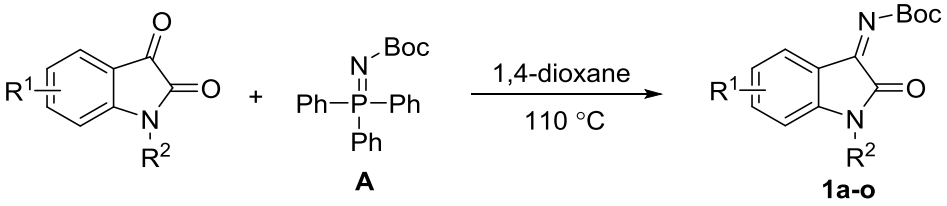
Contents

1. General Information

Solvents preparation: Acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) were distilled under argon from calcium hydride while tetrahydrofuran (THF) and toluene from sodium/benzophenone; anhydrous 1-butoxybutane (*n*Bu_2O, stored under argon), 2-methoxy-2-methyl-propane (MTBE, stored under argon) and 2-isopropoxypropane (*i*Pr_2O, 99+% purity, stabilized with BHT) were purchased from Acros and used directly. All other reagents were purchased from commercial suppliers (Aldrich, Alfa and J&K) and used without further purification. Aryl nitromethanes[1,2] and *N*-alkoxycarbonyl ketimines[3] were prepared according to published procedures. Flash column chromatography was performed with silica gel (300-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM (400 MHz) or Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $CDCl_3$ = 7.26 ppm (^1H NMR) and 77.0 ppm (^{13}C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. The optical rotations were measured on a Anton Paar MCP 500 polarimeter with $[\alpha]_D^{20}$ values reported in degrees at concentrations of 1.0 g/100 mL. The ee and dr values of products were determined by chiral HPLC and absolute configurations were assigned based on a crystal structure of **3k'**.

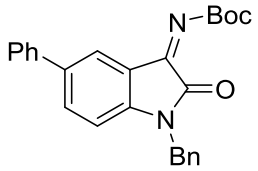
2. Synthesis of Substrates and Racemic References

2.1 Synthesis of *N*-BOC Ketimines



General Procedure: *N*-Alkoxycarbonyl ketimines (**1a-o**) were prepared by a published method with modifications.[3] Accordingly, in an oven-dried Schlenk flask under argon atmosphere, isatin (1.0 mmol) and compound **A** (1.1 mmol) were placed. After an addition of anhydrous 1,4-dioxane (1.0 mL), the mixture was heated at 110 °C until complete disappearance of the starting materials detected by TLC. Then, the reaction was cooled to room temperature. After an evaporation of the volatile organic solvents, the crude residue was purified by flash chromatography (silica gel, *n*hexane/ethyl acetate) and afforded the ketimines **1a-o**, which have been reported except for **1m**.[3]

***tert*-butyl (*Z*)-(1-benzyl-2-oxo-5-phenylindolin-3-ylidene)carbamate (1m)**



Following the general procedure, the chromatography (eluent: EtOAc/*n*hexane = 1/10, v/v) afforded the title compound as a red foam (380 mg, 0.921 mmol, 92% yield).

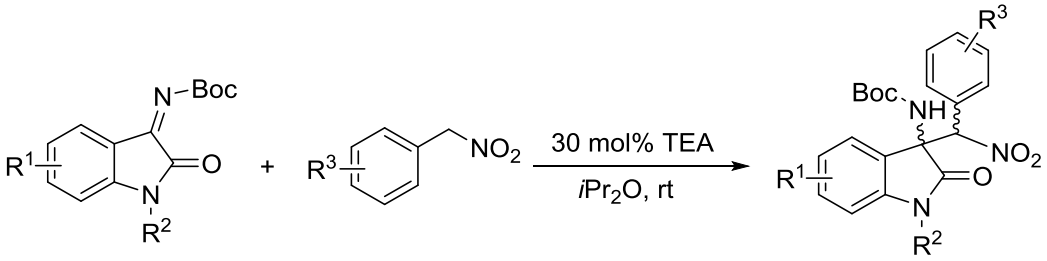
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.90 (s, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.51-7.39 (m, 4H), 7.38-7.28 (m, 6H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.93 (s, 2H), 1.66 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 160.35, 157.39, 153.10, 146.40, 139.42, 136.97, 134.58, 133.84, 128.95, 128.93, 128.05, 127.58, 127.39, 126.53, 122.86, 119.90, 110.58, 83.65, 44.05, 28.02.

IR (film): ν (cm^{-1}) 3064, 3033, 2979, 2931, 1739, 1680, 1621, 1597, 1478, 1369, 1340, 1268, 1251, 1150, 1127, 762, 698.

HRMS calcd for $C_{26}H_{24}N_2NaO_3$ $(M+Na)^+$ 435.1679, found: 435.1675.

2.2 Synthesis of Mixtures of Stereoisomers as HPLC References



General Procedure*:* To a stirred solution of aryl nitromethane (0.15 mmol) in *i*Pr_2O (1.0 mL) was added the ketimine (0.10 mmol) in one portion, followed by Et_3N (0.030 mmol). The reaction mixture was stirred at room temperature until complete disappearance of the starting materials detected by TLC. After an evaporation of the volatile organic solvents, the crude residue was purified by flash chromatography (silica gel, *n*hexane/ethyl acetate). The samples were used as references to determine enantiomeric excess and diastereomer ratio in the asymmetric aza-Henry reactions.

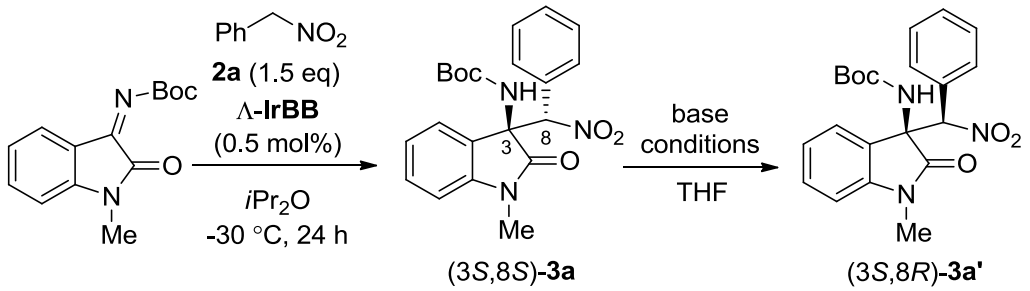
3. Optimization of Reaction Conditions Providing the Kinetic Diastereomer

An oven-dried 3 mL vial was charged with ketimine **1a** (13.0 mg, 0.050 mmol), iridium catalyst Λ-**IrBB** (0.5-3.0 mol%) and the indicated solvent (0.40 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene **2a** (10.3 mg, 0.075 mmol) in the indicated solvent (50.0 μL) was added by syringe in one portion, then the same solvent (50.0 μL) used for rinsing was added in one portion as well. The reaction mixture was stirred at -30 °C for the indicated time. After evaporation of the solvent, the crude product was used directly for a determination of the conversion by ^{1}H NMR as well as ee and dr values by chiral HPLC analysis.

Table S1. Optimization of reaction conditions.

entry	conditions	*t* (h)	conv. (%)	ee	dr (**3a:3a'**)
1	toluene (3 mol% cat)	9	99	90%	51:1
2	toluene (1 mol% cat)	23	>99	89%	51:1
3	*n*Bu_2O (1 mol% cat)	13	100	86%	60:1
4	MTBE (1 mol% cat)	13	100	91%	79:1
5	*i*Pr_2O (1 mol% cat)	13	100	96%	90:1
6	*i*Pr_2O (0.5 mol% cat)	24	100	96%	86:1

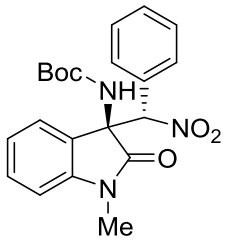
4. Optimization of the Conversion of Kinetic to Thermodynamic Diastereomer



(3*S*,8*S*)-**3a** (3*S*,8*R*)-**3a'**

An oven-dried 3 mL vial was charged with ketimine **1a** (26.0 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr$_2$O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr$_2$O (50.0 μL) was added by syringe in one portion and another indicated solvent (50.0 μL) used to rinse the vial was added in one portion. Then, the reaction was stirred at -30 °C for 24 hours. Upon completion, the precipitate was purified by centrifugation and washing with toluene/*n*hexane (0.7 mL, 1/2, v/v) until the filtrate layer was almost colorless to afford a white solid (**3a**, 32.2 mg, 81% yield, >99% ee, 1:138 dr).

***tert*-butyl ((*S*)-1-methyl-3-((*S*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3a)**



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.51 (s, 1H), 7.37-7.31 (m, 3H), 7.30-7.22 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.65 (d, J = 7.7 Hz, 1H), 6.15 (brs, 1H), 5.75 (s, 1H), 3.14 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 171.87, 154.00, 143.35, 130.20, 130.08, 129.44, 128.24, 127.89, 126.51, 125.10, 123.02, 108.31, 91.39, 81.14, 63.28, 28.03, 26.53.

HRMS calcd for $C_{21}H_{23}N_3NaO_5$ $(M+Na)^+$ 420.1530, found: 420.1526.

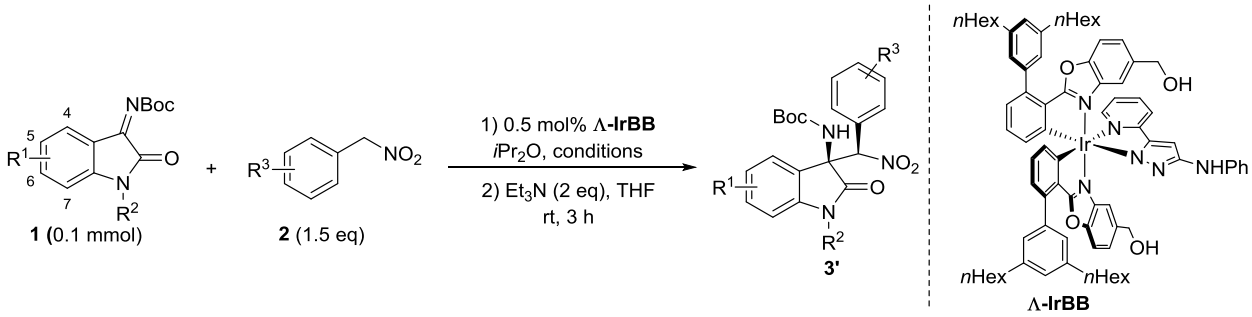
Subsequently, the product (8.0 mg, 0.020 mmol) was dissolved in THF, to which different organic bases (2 equiv.) as shown below were added. Then, the reaction was stirred at room temperature for

3 hours, at which point the reaction solution was diluted with dichloromethane and injected directly to chiral HPLC. The obtained ee and dr values are listed in Table S2.

Table S2. Effect of the base and concentration on the epimerization.

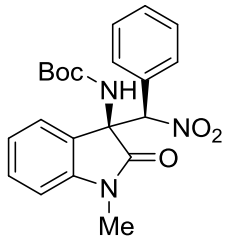
Entry	Base	pK_a (in MeCN)	conc. (mM)	t (h)	ee of **3a'**	dr (**3a'**/**3a**)
1	pyrrolidine (2 eq)	19.56	50	3	>99%	5.7:1
2	TEA (2 eq)	18.82	50	3.5 23	>99% 99%	7.5:1 7.6:1
3	DMAP (2 eq)	17.95	50	3	>99%	7.0:1
4	benzylamine (2 eq)	16.91	50	5	>99%	5.2:1
5	2,4,6-trimethylpyridine (2 eq)	14.98	50	3	>99%	1:14.9
6	**TEA (2 eq)**	**18.82**	**200**	**3**	**>99%**	**8.5:1**
7	TEA (2 eq)	18.82	500	3	>99%	8.3:1
8	TEA (10 eq)	18.82	200	3	>99%	8.4:1

5. Substrate Scope for the Formation of the Thermodynamic Diastereomer



3a' (R^1 = H, R^2 = Me, R^3 =H), 99% yield, 10:1 dr, 96% ee.
3b' (R^1 = H, R^2 = Et, R^3 = H), 98% yield, 15:1 dr, 98% ee.
3c' (R^1 = H, R^2 = Allyl, R^3 = H), 97% yield, 14:1 dr, 97% ee.
3d' (R^1 = H, R^2 = Bn, R^3 = H), 99% yield, 14:1 dr, 98% ee.
3e' (R^1 = H, R^2 = Ac, R^3 = H), 92% yield, 9:1 dr, 98% ee.
3f' (R^1 = H, R^2 = H, R^3 = H), 96% yield, 8:1 dr, 92% ee.
3g' (R^1 = 5-Me, R^2 = Me, R^3 = H), 99% yield, 9:1 dr, 98% ee.
3h' (R^1 = 5-OMe, R^2 = Me, R^3 = H), 98% yield, 9:1 dr, 94% ee.
3i' (R^1 = 5-F, R^2 = Me, R^3 = H), 99% yield, 19:1 dr, 92% ee.
3j' (R^1 = 5-Cl, R^2 = Me, R^3 = H), 99% yield, 11:1 dr, 93% ee.
3k' (R^1 = 5-Br, R^2 = Me, R^3 = H), 99% yield, 10:1 dr, 93% ee.
3l' (R^1 = 5-I, R^2 = Bn, R^3 = H), 97% yield, 16:1 dr, 97% ee.
3m' (R^1 = 5-Ph, R^2 = Bn, R^3 = H), 97% yield, 11:1 dr, 98% ee.
3n' (R^1 = 6-Cl, R^2 = Me, R^3 = H), 98% yield, 10:1 dr, 92% ee.
3o' (R^1 = 7-F, R^2 = Me, R^3 = H),98% yield, 16:1 dr, 90% ee.
3p' (R^1 = H, R^2 = Bn, R^3 = 3-Et), 98% yield, 23:1 dr, 98% ee.
3q' (R^1 = H, R^2 = Bn, R^3 = 4-Me), 99% yield, 18:1 dr, 98% ee.
3r' (R^1 = H, R^2 = Bn, R^3 = 4-OMe), 95% yield, 20:1 dr, 97% ee.
3s' (R^1 = H, R^2 = Bn, R^3 = 4-Cl), 99% yield, 9:1 dr, 97% ee.
3t' (R^1 = H, R^2 = Bn, R^3 = 4-Br), 98% yield, 10:1 dr, 96% ee.

tert-butyl ((*S*)-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3a')



An oven-dried 3 mL vial was charged with ketimine **1a** (26.0 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. The reaction mixture was stirred at -30 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (39.2 mg, 0.099 mmol, 99%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using

a Chiralpak IC column, ee = 96%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/ isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; t_r (**3a'**, major) = 9.2 min, t_r (**3a'**, minor) = 15.7 min, t_r (**3a**, major) = 19.6 min, t_r (**3a**, minor) = 22.8 min). $[\alpha]_D^{20}$ = 5.7° (*c* 0.5, $CHCl_3$).

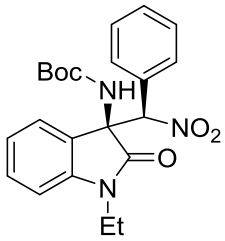
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.4 Hz, 1H), 7.39-7.29 (m, 2H), 7.21-7.11 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), 5.92 (s, 1H), 2.83 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.38, 153.51, 144.21, 130.34, 130.30, 129.47, 128.25, 127.89, 125.41, 124.72, 122.99, 108.20, 92.77, 81.08, 64.18, 28.02, 26.17.

IR (film): ν (cm^{-1}) 3438, 3361, 2978,2928, 1716, 1615, 1558, 1495, 1471, 1456, 1366, 1255, 1168, 752, 728, 699, 624, 542.

HRMS calcd for $C_{21}H_{23}N_3NaO_5$ $(M+Na)^+$ 420.1530, found: 420.1532.

***tert*-butyl ((*S*)-1-ethyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')**



An oven-dried 3 mL vial was charged with ketimine **1b** (27.4 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used to rinse the vial was added in one portion. The reaction mixture was stirred at -30 °C for 25 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel

(eluent: EtOAc/*n*hexane = 1/5, v/v) to afford the title compound (40.2 mg, 0.098 mmol, 98%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 15:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; t_r (**3b'**, major) = 8.7 min, t_r (**3b**, minor) = 13.4 min, t_r (**3b**,major) = 16.8 min, t_r (**3b'**, minor) = 26.6 min). $[\alpha]_D^{20}$ = -7.1° (*c* 0.5, $CHCl_3$).

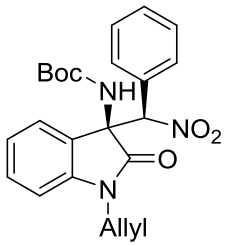
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.4 Hz, 1H), 7.39-7.27 (m, 2H), 7.19-7.10 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.98 (s, 1H), 3.67 (dq, *J* = 14.6, 7.3 Hz, 1H), 3.20 (m, 1H), 1.27 (s, 9H), 0.60 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.81, 153.35, 143.46, 130.33, 130.29, 129.85, 127.97, 127.76, 125.5, 124.69, 122.77, 108.25, 92.82, 80.99, 63.93, 34.72, 27.98, 11.43.

IR (film): ν (cm^{-1}) 3427, 3315, 2979, 2934, 1725, 1613, 1559, 1489, 1468, 1456, 1368, 1349, 1253, 1162, 1134, 750, 699.

HRMS calcd for $C_{22}H_{25}N_3NaO_5$ $(M+Na)^+$ 434.1686, found: 434.1691.

***tert*-butyl ((*S*)-1-allyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3c')**



An oven-dried 3 mL vial was charged with ketimine **1c** (28.6 mg, 0.10 mmol), iridium catalyst Λ**-IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then addition *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 23 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which

TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5, v/v) to afford the title compound (41.0 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 14:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3c'**, major) = 9.5 min, t_r (**3c**, minor) = 15.2 min, t_r (**3c**, major) = 16.9 min, t_r (**3c'**, minor) = 18.9 min). $[\alpha]_D^{20}$ = -20.9° (*c* 1.0, $CHCl_3$).

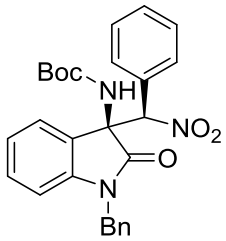
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 7.4 Hz, 1H), 7.36-7.30 (m, 2H), 7.21-7.11 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.02 (s, 1H), 5.92 (s, 1H), 5.14-5.00 (m, 1H), 4.96-4.91(m, 1H), 4.83 (d, *J* = 17.1 Hz, 1H), 4.28-4.19 (m, 1H), 3.82 (dd, *J* = 16.1, 5.5 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.15, 153.40, 143.65, 130.62, 130.38, 130.24, 129.84, 128.11, 127.83, 125.42, 124.59, 122.95, 117.75, 109.21, 92.89, 81.08, 64.05, 42.73, 28.06.

IR (film): ν (cm^{-1}) 3423, 3329, 2978, 2927, 1726, 1613, 1559, 1488, 1468, 1456, 1368, 1274, 1253, 1162, 753, 733, 699.

HRMS calcd for $C_{23}H_{25}N_3NaO_5$ $(M+Na)^+$ 446.1686, found: 446.1692.

tert-butyl ((*S*)-1-benzyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3d')



An oven-dried 3 mL vial was charged with ketimine **1d** (33.6 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one

portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 12 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10~1/5, v/v) to afford the title compound (46.8 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 14:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80/20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3d'**, major) = 9.3 min, t_r (**3d'**, minor) = 12.5 min, t_r (**3d**, minor) = 16.1 min, t_r (**3d**, major) = 19.8 min). $[\alpha]_D^{20}$ = -36.7° (*c* 0.5, $CHCl_3$).

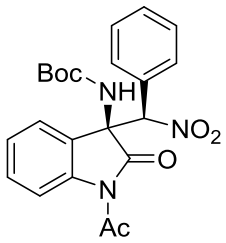
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55 (d, *J* = 7.4 Hz, 1H), 7.42-7.35 (m, 1H), 7.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.21-7.09 (m, 6H), 7.07-7.02 (m, 2H), 6.70 (d, *J* = 7.0 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 6.08 (s, 1H), 5.97 (s, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.85, 153.44, 143.85, 134.81, 130.50, 130.29, 129.95, 128.60, 128.31, 127.83, 127.31, 126.76, 125.49, 124.66, 123.02, 109.52, 92.97, 81.12, 63.93, 44.43, 28.09.

IR (film): ν (cm^{-1}) 3422, 3323, 3062, 3033, 2978, 2929, 2855, 1717, 1613, 1559, 1487, 1468, 1456, 1368, 1270, 1253, 1163, 1081, 1002, 753, 737, 698.

HRMS calcd for $C_{27}H_{27}N_3NaO_5$ $(M+Na)^+$ 496.1843, found: 496.1849.

tert-butyl ((*S*)-1-acetyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3e')



An oven-dried 3 mL vial was charged with ketimine **1e** (28.8 mg, 0.10 mmol), iridium catalyst

Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 20 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10, v/v) to afford the title compound (39.2 mg, 0.092 mmol, 92%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 85/15, flow rate = 1.0 mL/min, T = 25 °C; t_r (**3e'**, major) = 9.2 min, t_r (**3e'**, minor) = 16.8 min, t_r (**3e**, major) = 12.4 min, t_r (**3e**, minor) = 22.9 min). $[\alpha]_D^{20}$ = -26.4° (*c* 1.0, $CHCl_3$).

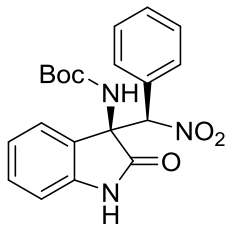
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 8.2 Hz, 1H), 7.47-7.39 (m, 2H), 7.37-7.33 (m, 1H), 7.31-7.27 (m, 1H), 7.22-7.17 (m, 2H), 6.93-6.88 (m, 2H), 6.32 (s, 1H), 5.90 (s, 1H), 2.32 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 173.64, 169.56, 140.91, 130.97, 130.80, 129.76, 128.29, 126.86, 125.55, 124.22, 116.48, 92.57, 81.82, 64.67, 27.91, 25.91.

IR (film): ν (cm^{-1}) 3417, 2977, 2926, 1770, 1716, 1605, 1562, 1477, 1466, 1371, 1337, 1310, 1270, 1173, 1016, 760, 700, 581.

HRMS calcd for $C_{27}H_{27}N_3NaO_5$ $(M+Na)^+$ 448.1479, found: 448.1485.

***tert*-butyl ((*S*)-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')**



An oven-dried 3 mL vial was charged with ketimine **1f** (24.6 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -10 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -10 °C for 30 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (36.8 mg, 0.096 mmol, 96%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 8:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/ isopropanol = 70:30, flow rate = 0.20 mL/min, T = 25 °C; t_r (**3f'**, major) = 27.3 min, t_r (**3f'**, minor) = 29.6 min, t_r (**3f**, major) = 31.3 min, t_r (**3f**, minor) = 35.4 min). $[\alpha]_D^{20}$ = -33.4° (*c* 0.5, $CHCl_3$).

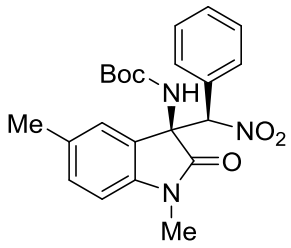
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.72 (brs, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30-7.25 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.10 (s, 1H), 5.96 (s, 1H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 173.99, 153.68, 141.41, 130.41, 130.35, 129.74, 128.13, 127.73, 125.62, 124.97, 122.97, 110.17, 92.61, 81.39, 64.23, 28.03.

IR (film): ν (cm^{-1}) 3401, 3347, 2921, 2850, 1746, 1712, 1558, 1471, 1455, 1368, 1252, 1165, 1048, 757, 744, 729, 698.

HRMS calcd for $C_{20}H_{21}N_3NaO_5$ $(M+Na)^+$ 406.1373, found: 406.1381.

***tert*-butyl ((*S*)-1,5-dimethyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3g')**



An oven-dried 3 mL vial was charged with ketimine **1g** (27.4 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 16 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (40.6 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 85:15, flow rate = 0.80 mL/min, T = 25°C; t_r (**3g'**, major) = 10.2 min, t_r (**3g**, minor) = 20.3 min, t_r (**3g'**, minor) = 22.1 min, t_r (**3g**, major) = 26.2 min). $[\alpha]_D^{20}$ = -24.2° (*c* 1.0, $CHCl_3$).

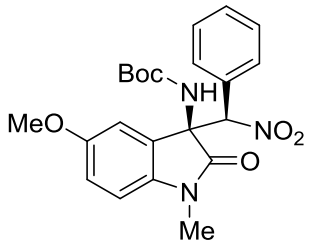
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.28 (m, 2H), 7.22-7.12 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 1H), 5.93 (s, 1H), 2.80 (s, 3H), 2.38 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.25, 153.52, 141.84, 132.61, 130.63, 130.25, 129.56, 127.92, 127.84, 126.00, 124.65, 107.95, 92.75, 80.98, 64.21, 28.03, 26.16, 21.17.

IR (film): ν (cm^{-1}) 3417, 3314, 2977, 2928, 1726, 1622, 1605, 1559, 1500, 1456, 1367, 1253, 1164, 811, 746, 699, 553.

HRMS calcd for $C_{22}H_{25}N_3NaO_5$ $(M+Na)^+$ 434.1686, found: 434.1684.

***tert*-butyl ((*S*)-5-methoxy-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3h')**



An oven-dried 3 mL vial was charged with ketimine **1h** (29.0 mg, 0.10 mmol), iridium catalyst **Λ-IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to 0 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at 0 °C for 22 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (41.9 mg, 0.098 mmol, 98%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 94%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, T = 25 °C; t_r (**3h'**, major) = 8.4 min, t_r (**3h**, minor) = 17.6 min, t_r (**3h'**, minor) = 21.3 min, t_r (**3h**, major) = 23.8 min). $[\alpha]_D^{20}$ = -20.3° (*c* 1.0, $CHCl_3$).

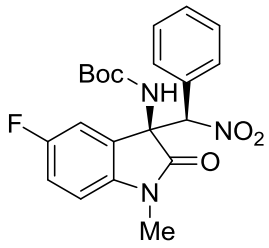
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.28 (m, 1H), 7.22-7.11 (m, 3H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 5.99 (s, 1H), 5.93 (s, 1H), 3.82 (s, 3H), 2.80 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.05, 156.15, 153.50, 137.63, 130.29, 129.49, 127.89, 127.85, 125.81, 115.18, 112.32, 108.67, 92.75, 81.10, 64.47, 55.90, 28.03, 26.24.

IR (film): ν (cm^{-1}) 3411, 3315, 2977, 2931, 1722, 1603, 1558, 1498, 1471, 1456, 1436, 1367, 1298, 1254, 1236, 1209, 1163, 1129, 1071, 1041, 739, 699.

HRMS calcd for $C_{22}H_{25}N_3NaO_6$ $(M+Na)^+$ 450.1636, found: 450.1639.

***tert*-butyl ((*S*)-5-fluoro-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3i')**



An oven-dried 3 mL vial was charged with ketimine **1i** (27.8 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 17 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to wich TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (41.1 mg, 0.099 mmol, 99%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 19:1 ((HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3i'**, major) = 8.8 min, t_r (**3i'**, minor) = 11.0 min, t_r (**3i**, major) = 15.9 min, t_r (**3i**, minor) = 24.5 min; $[\alpha]_D^{20}$ = 29.8° (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37 (dd, *J* = 8.0, 2.6 Hz, 1H), 7.35-7.30 (m, 1H), 7.22-7.16 (m, 2H), 7.09-6.99 (m, 3H), 6.55 (dd, *J* = 8.5, 4.1 Hz, 1H), 6.00 (s, 1H), 5.82 (s, 1H), 2.84 (s, 3H), 1.32 (s, 9H).

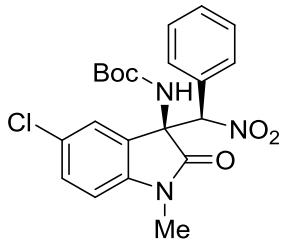
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.19, 159.23 (d, *J* = 242.0 Hz), 153.49, 140.22, 130.44,

129.22, 128.04, 127.69, 116.63 (d, *J* = 23.5 Hz), 113.98 (d, *J* = 25.9 Hz), 108.72 (d, *J* = 7.9 Hz), 92.66, 81.38, 64.33, 28.04, 26.34.

IR (film): ν (cm^{-1}) 3411, 3321, 2961, 2925, 2854, 1716, 1623, 1557, 1495, 1470, 1456, 1393, 1368, 1274, 1259, 1162, 1122, 1070, 1020, 974, 873, 812, 740, 699, 631, 559.

HRMS calcd for $C_{21}H_{22}FN_3NaO_5$ $(M+Na)^+$ 438.1436, found: 438.1435.

***tert*-butyl ((*S*)-5-chloro-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')**



An oven-dried 3 mL vial was charged with ketimine **1j** (29.5 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40°C for 20 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (42.8 mg, 0.099 mmol, 99%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 93%, dr = 11:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3j'**, major) = 8.5 min, t_r (**3j'**, minor) = 10.5 min, t_r (**3j**, major) = 14.8 min, t_r (**3j**, minor) = 24.7 min). $[\alpha]_D^{20}$ = -19.3° (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 2.1 Hz, 1H), 7.36-7.29 (m, 2H), 7.23-7.17(m, 2H),

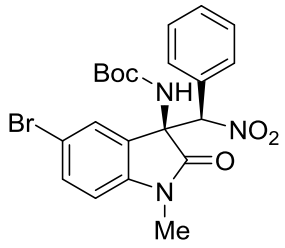
7.04-6.99 (m, 2H), 6.55 (d, *J* = 8.3 Hz, 1H), 5.98 (s, 1H), 5.88 (s, 1H), 2.82 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 172.05, 153.47, 142.80, 130.49, 130.27, 129.24, 128.47, 128.08, 127.63, 126.43, 126.04, 109.13, 92.61, 81.46, 64.20, 28.06, 26.31.

IR (film): ν (cm^{-1}) 3417, 3325, 2978, 2929, 1732, 1611, 1561, 1490, 1456, 1367, 1270, 1252, 1162, 1133, 1108, 1069, 816, 741, 699, 546.

HRMS calcd for $C_{21}H_{22}ClN_3NaO_5$ $(M+Na)^+$ 454.1140, found: 454.1141.

tert-butyl ((*S*)-5-bromo-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')



An oven-dried 3 mL vial was charged with ketimine **1k** (33.9 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5~1/3, v/v) to afford the title compound (47.6 mg, 0.100 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 93%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3k'**, major) = 8.8 min, t_r (**3k'**, major) = 11.1 min, t_r (**3k**, major) = 15.4 min, t_r (**3k**, minor) = 26.3 min). $[\alpha]_D^{20}$ = -26.1° (*c* 1.0, $CHCl_3$).

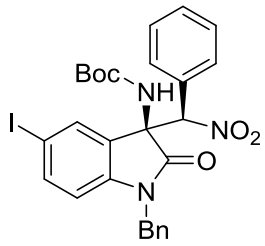
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 (d, *J* = 1.9 Hz, 1H), 7.48 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.36-7.30 (m, 1H), 7.23-7.17 (m, 2H), 7.09-6.94 (m, 2H), 6.50 (d, *J* = 8.3 Hz, 1H), 5.97 (s, 1H), 5.86 (s, 1H), 2.82 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.94, 153.45, 143.26, 133.17, 130.48, 129.22, 128.69, 128.07, 127.59, 126.74, 115.63, 109.61, 92.59, 81.46, 64.14, 28.04, 26.28.

IR (film): ν (cm^{-1}) 3408, 3326, 2978, 2931, 1733, 1609, 1562, 1487, 1456, 1423, 1393, 1367, 1270, 1252, 1162, 1134, 1110, 1067, 813, 740, 699, 535.

HRMS calcd for $C_{21}H_{22}BrN_3NaO_5$ $(M+Na)^+$ 498.0635, found: 498.0634.

***tert*-butyl ((*S*)-1-benzyl-5-iodo-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')**



An oven-dried 3 mL vial was charged with ketimine **1l** (46.2 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 19 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10~1/5, v/v) to afford the title compound (58.1 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 16:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.60 mL/min, T = 25 °C; t_r (**3l'**, major) = 9.2

min, t_r (**3l'**, minor) = 10.4 min, t_r (**3l**, major) = 13.9 min, t_r (**3l**, minor) = 16.9 min). $[\alpha]_D^{20}$ = -59.7° (*c* 1.0, $CHCl_3$).

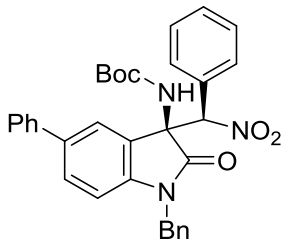
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, *J* = 1.7 Hz, 1H), 7.54 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.43-7.37 (m, 1H), 7.25-7.10 (m, 5H), 7.09-7.04 (m, 2H), 6.68 (d, *J* = 7.1 Hz, 2H), 6.23 (d, *J* = 8.3 Hz, 1H), 6.01 (s, 1H), 5.93 (s, 1H), 4.75 (d, *J* = 16.0 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.20, 153.38, 143.55, 139.08, 134.28, 134.17, 130.63, 129.73, 128.66, 128.46, 127.57, 127.46, 126.98, 126.67, 111.50, 92.75, 85.45, 81.46, 63.73, 44.39, 28.09.

IR (film): ν (cm^{-1}) 3412, 3329, 2978, 2929, 1733, 1604, 1562, 1480, 1455, 1421, 1393, 1254, 1161, 1030, 1001, 875, 811, 740, 698, 528.

HRMS calcd for $C_{27}H_{26}IN_3NaO_5$ $(M+Na)^+$ 622.0809, found: 622.0808.

***tert*-butyl ((*S*)-1-benzyl-3-((*R*)-nitro(phenyl)methyl)-2-oxo-5-phenylindolin-3-yl)carbamate (3m')**



An oven-dried 3 mL vial was charged with ketimine **1m** (41.2 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 22 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction

mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10~1/5, v/v) to afford the title compound (53.3 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 11:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3m'**, major) = 9.3 min, t_r (**3m'**, minor) = 12.6 min, t_r (**3m**, major) = 16.5 min, t_r (**3m**, minor) = 18.8 min). $[\alpha]_D^{20}$ = -81.9° (*c* 1.0, $CHCl_3$).

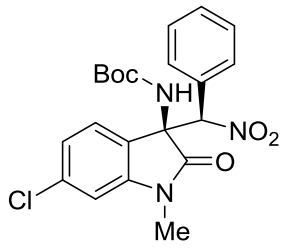
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 1.7 Hz, 1H), 7.60-7.54 (m, 2H), 7.51-7.32 (m, 5H), 7.24-7.13 (m, 5H), 7.12-7.07 (m, 2H), 6.73 (d, *J* = 6.8 Hz, 2H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.10 (s, 1H), 6.04 (s, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 4.51 (d, *J* = 15.9 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.89, 153.46, 143.07, 140.33, 136.29, 134.75, 130.56, 129.98, 129.01, 128.85, 128.64, 128.37, 127.75, 127.38, 127.21, 126.84, 126.79, 125.21, 124.15, 109.74, 92.92, 81.22, 64.05, 44.51, 28.10.

IR (film): ν (cm^{-1}) 3419, 3308, 2978, 2927, 1725, 1616, 1557, 1483, 1456, 1367, 1253, 1161, 764, 739, 698.

HRMS calcd for $C_{33}H_{31}N_3NaO_5$ $(M+Na)^+$ 572.2156, found: 572.2167.

tert-butyl ((*S*)-6-chloro-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3n')



An oven-dried 3 mL vial was charged with ketimine **1n** (29.5 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one

portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 17 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane, 1/5, v/v) to afford the title compound (42.3 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3n'**, major) = 7.8 min, t_r (**3n'**, minor) = 10.5 min, t_r (**3n**, major) = 15.4 min, t_r (**3n**, minor) = 23.4 min). $[\alpha]_D^{20}$ = -9.3° (*c* 1.0, $CHCl_3$).

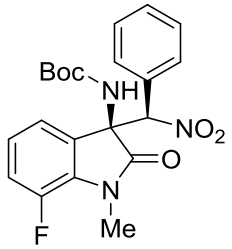
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 1H), 5.98 (s, 1H), 5.87 (s, 1H), 2.82 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 172.41, 153.48, 145.39, 136.25, 130.51, 129.27, 128.11, 127.58, 126.51, 123.09, 122.90, 109.01, 92.56, 81.38, 63.86, 28.04, 26.32.

IR (film): ν (cm^{-1}) 3414, 3331, 2978, 2918, 1731, 1610, 1560, 1495, 1456, 1369, 1248, 1162, 1076, 740, 699.

HRMS calcd for $C_{21}H_{22}ClN_3NaO_5$ $(M+Na)^+$ 454.1140, found: 454.1146.

tert-butyl ((*S*)-7-fluoro-1-methyl-3-((*R*)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3o')



An oven-dried 3 mL vial was charged with ketimine **1o** (27.8 mg, 0.10 mmol), iridium catalyst

Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (**2a**) (20.6 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5, v/v) to afford the title compound (40.7 mg, 0.098 mmol, 98%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 90%, dr = 16:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.70 mL/min, T = 25 °C; t_r (**3o'**, major) = 8.9 min, t_r (**3o'**, minor) = 13.6 min, t_r (**3o**, major) = 20.6 min, t_r (**3o**, minor) = 23.7 min). $[\alpha]_D^{20}$ = -16.1° (*c* 1.0, $CHCl_3$).

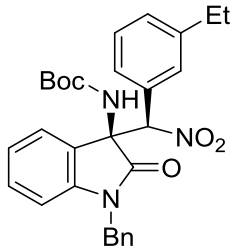
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.29 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.12-7.04 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 5.98 (s, 1H), 5.96 (s, 1H), 3.02 (d, *J* = 2.7 Hz, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.16, 153.45, 148.81, 146.38, 131.01 (d, *J* = 8.0 Hz), 130.55, 129.38, 128.04, 127.54, 123.49 (d, *J* = 6.1 Hz), 121.19 (d, *J* = 3.3 Hz), 118.30 (d, *J* = 19.2 Hz), 92.65, 81.35, 64.32, 28.75 (d, *J* = 5.8 Hz), 28.03.

IR (film): ν (cm^{-1}) 3434, 3352, 2978, 2928, 1729, 1713, 1632, 1561, 1481, 1456, 1366, 1279, 1246, 1168, 1058, 768, 728, 701, 736, 564.

HRMS calcd for $C_{21}H_{22}FN_3NaO_6$ $(M+Na)^+$ 438.1436, found: 438.1441.

***tert*-butyl ((*S*)-1-benzyl-3-((*R*)-(3-ethylphenyl)(nitro)methyl)-2-oxoindolin-3-yl)carbamate (3p')**



An oven-dried 3 mL vial was charged with ketimine **1d** (33.6 mg, 0.10 mmol), iridium catalyst **Λ-IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane **2b** (24.8 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 15 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10, v/v) to afford the title compound (49.4 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak AD-H column, ee = 98%, dr = 23:1 (HPLC conditions: AD-H column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; t_r (**3p'**, major) = 7.1 min, t_r (**3p'**, minor) = 16.5 min, t_r (**3p**, minor) = 22.1 min, t_r (**3p**, major) = 33.1 min). $[\alpha]_D^{20}$ = -40.5° (*c* 1.0, $CHCl_3$).

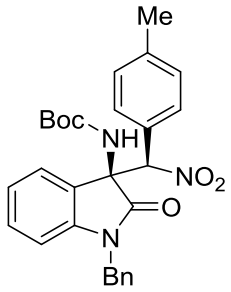
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.26-7.07 (m, 7H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.78-6.75 (m, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 6.47 (d, *J* = 7.7 Hz, 1H), 6.03 (s, 1H), 5.99 (s, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.40 (d, *J* = 16.0 Hz, 1H), 2.41 (q, *J* = 7.6 Hz, 2H), 1.31 (s, 9H), 0.93 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.86, 153.38, 144.36, 143.95, 134.83, 130.20, 130.18, 129.14, 128.58, 128.25, 127.67, 127.57, 127.23, 126.64, 125.48, 124.75, 122.97, 109.50, 93.07, 81.08, 64.06, 44.42, 28.50, 28.08, 15.04.

IR (film): ν (cm^{-1}) 3424, 3329, 2970, 2931, 1727, 1613, 1560, 1487, 1468, 1456, 1368, 1271, 1253, 1163, 753, 733, 703.

HRMS calcd for $C_{29}H_{31}N_3NaO_5$ $(M+Na)^+$ 524.2156, found: 524.2157.

***tert*-butyl (*S*)-1-benzyl-3-((*R*)-nitro(*p*-tolyl)methyl)-2-oxoindolin-3-yl)carbamate (3q')**



An oven-dried 3 mL vial was charged with ketimine **1d** (33.6 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane **2c** (22.7 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 14 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10~1/5, v/v) to afford the title compound (48.1 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 18:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.70 mL/min, T = 25 °C; t_r (**3q'**, major) = 9.3 min, t_r (**3q**, major) = 14.0 min, t_r (**3q'**, minor) = 23.2 min, t_r (**3q**, minor) = 26.4 min). $[\alpha]_D^{20}$ = -53.2° (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.25-7.09 (m, 5H), 6.99-6.88 (m, 4H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 6.02 (s, 1H), 5.96 (s, 1H), 4.90 (d, *J* = 15.9 Hz,

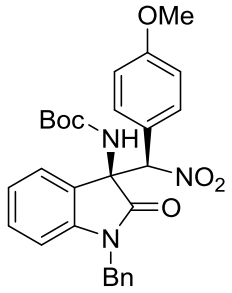
1H), 4.42 (d, *J* = 15.9 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, CDCl3) δ (ppm) 172.92, 153.41, 143.91, 140.67, 134.88, 130.22, 129.84, 129.01, 128.44, 127.27, 126.89, 125.44, 124.89, 124.78, 122.97, 109.46, 92.87, 81.05, 63.89, 44.47, 28.08, 21.34.

IR (film): ν (cm^{-1}) 3423, 3326, 2979, 2927, 1726, 1613, 1559, 1487, 1468, 1456, 1368, 1269, 1253, 1163, 1003, 878, 786, 753, 735, 697, 553.

HRMS calcd for $C_{28}H_{29}N_3NaO_5$ $(M+Na)^+$ 510.1999, found: 510.2003.

***tert*-butyl ((*S*)-1-benzyl-3-((*R*)-(4-methoxyphenyl)(nitro)methyl)-2-oxoindolin-3-yl)carbamate (3r')**



An oven-dried 3 mL vial was charged with ketimine **1d** (33.6 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to 0 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane **2d** (25.1 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at 0 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10~1/5, v/v) to afford the title compound (47.8 mg, 0.095 mmol, 95%) as a yellow foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 97%, dr = 20:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol =

80:20, flow rate = 0.75 mL/min, T = 25 °C; t_r (**3r'**, major) = 9.7 min, t_r (**3r**, major) = 15.8 min, t_r (**3r'**, minor) = 26.4 min, t_r (**3r**, minor) = 29.3 min). $[\alpha]_D^{20}$ = -75.4° (*c* 1.0, $CHCl_3$).

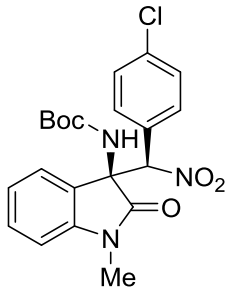
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 7.1 Hz, 1H), 7.28-7.22 (m, 1H), 7.20-7.09 (m, 4H), 6.94-6.89 (m, 2H), 6.69- 6.63 (m, 4H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.00 (brs, 1H), 5.99 (s, 1H), 4.94 (d, *J* = 15.9 Hz, 1H), 4.39 (d, *J* = 15.9 Hz, 1H), 3.76 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.96, 161.29, 153.37, 143.98, 134.84, 131.49, 130.28, 128.45, 127.33, 126.85, 125.31, 124.72, 122.98, 119.74, 113.69, 109.50, 92.63, 81.07, 64.01, 55.16, 44.45, 28.10.

IR (film): ν (cm^{-1}) 3422, 3332, 3061, 2978, 2932, 2840, 1716, 1612, 1583, 1557, 1514, 1489, 1368, 1308, 1255, 1181, 1031, 1002, 878, 836, 798, 754, 736, 698, 553, 539.

HRMS calcd for $C_{28}H_{29}N_3NaO_6$ $(M+Na)^+$ 526.1949, found: 526.1947.

***tert*-butyl ((*S*)-3-((*R*)-(4-chlorophenyl)(nitro)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3s')**



An oven-dried 3 mL vial was charged with ketimine **1a** (26.0 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane **2e** (25.7 mg, 0.15 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 5 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was

directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/5, v/v) to afford the title compound (42.8 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 9:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/isopropanol = 80:20, flow rate = 0.90 mL/min, T = 25 °C; t_r (**3s'**, major) = 8.2 min, t_r (**3s'**, minor) = 15.7 min, t_r (**3s**, major) = 19.0 min, t_r (**3s**, minor) = 25.4 min). $[\alpha]_D^{20}$ = -31.1° (*c* 1.0, $CHCl_3$).

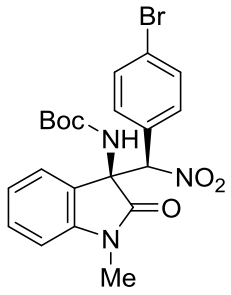
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 7.4 Hz, 1H), 7.41-7.35 (m, 1H), 7.20-7.11 (m, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.04 (s, 1H), 5.87 (s, 1H), 2.89 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.24, 153.50, 144.15, 136.65, 130.90, 130.57, 128.18, 126.37, 125.44, 124.46, 123.18, 108.40, 91.90, 81.21, 63.92, 28.02, 26.29.

IR (film): ν (cm^{-1}) 3414, 3321, 2978, 2932, 1727, 1613, 1562, 1493, 1471, 1369, 1354, 1254, 1161, 1127, 1094, 1017, 791, 753, 539.

HRMS calcd for $C_{21}H_{22}ClN_3NaO_5$ $(M+Na)^+$ 454.1140, found: 454.1145.

tert-butyl ((*S*)-3-((*R*)-(4-bromophenyl)(nitro)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3t')



An oven-dried 3 mL vial was charged with ketimine **1a** (26.0 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.60 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane **2f** (32.4 mg, 0.15 mmol) in *i*Pr_2O (0.30 mL) was added by syringe in one portion, then additional *i*Pr_2O (0.10 mL) used for rinse was added in one portion. Then the reaction was stirred at

-30 °C for 6 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μl, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/*n*hexane = 1/10~1/5, v/v) to afford the title compound (46.8 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 96%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: *n*hexane/ isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (**3t'**, major) = 9.5 min, t_r (**3t'**, minor) = 18.3 min, t_r (**3t**, major) = 21.9 min, t_r (**3t**, minor) = 27.7 min). $[\alpha]_D^{20}$ = -34.7° (*c* 1.0, $CHCl_3$).

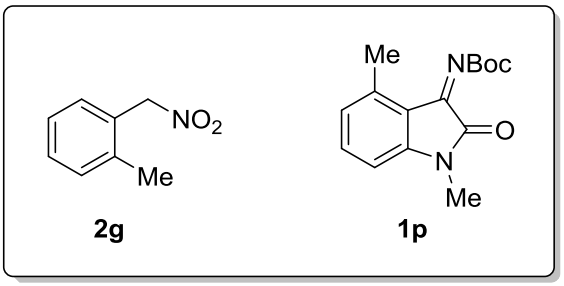
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 7.5 Hz, 1H), 7.41-7.30 (m, 3H), 7.18-7.12 (m, 1H), 6.92-6.86 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.04 (s, 1H), 5.85 (s, 1H), 2.89 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.20, 153.49, 144.12, 131.15, 131.09, 130.57, 126.85, 125.43, 124.97, 124.42, 123.19, 108.42, 91.92, 81.21, 63.83, 28.01, 26.30.

IR (film): ν (cm^{-1}) 3414, 3323, 2978, 2929, 1729, 1614, 1559, 1490, 1472, 1369, 1354, 1254, 1161, 1127, 1075, 1013, 790, 754, 736, 540.

HRMS calcd for $C_{21}H_{22}BrN_3NaO_5$ $(M+Na)^+$ 498.0635, found: 498.0635.

Substrates which didn't work:



Attempted reaction with substrate 2g: An oven-dried 3 mL vial was charged with ketimine **1d** (33.6 mg, 0.10 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and *i*Pr_2O (0.90 mL). Then, a solution of aryl nitromethane **2g** (22.7 mg, 0.15 mmol) in *i*Pr_2O (0.10 mL) was added by syringe in one portion. The reaction was stirred at 20 °C for 24 hours. No product could be

detected by TLC analysis.

Attempted reaction with substrate 1p: An oven-dried 3 mL vial was charged with ketimine **1p** (13.7 mg, 0.050 mmol), iridium catalyst Λ-**IrBB** (0.68 mg, 0.50 μmol, 1.0 mol%) and *i*Pr_2O (0.40 mL). Then, a solution of (nitromethyl)benzene (**2a**) (10.3 mg, 0.075 mmol) in *i*Pr_2O (0.10 mL) was added by syringe in one portion. The reaction was stirred at 20 °C for 19 hours. No product could be detected by TLC analysis.

6. Control Experiments

An oven-dried 3 mL vial was charged with ketimine or isatin (0.050 mmol), iridium catalyst Λ-**IrBB** or Λ-**IrBB'** and *i*Pr_2O (0.40 mL). The resulting suspension was stirred at 20 °C. A solution of (nitromethyl)benzene (**2a**) (0.075 mmol) in *i*Pr_2O (50.0 μL) was added by syringe in one portion, then additional *i*Pr_2O (50.0 μL) used for rinse was added in one portion. The stirring was kept for the indicated time shown in Table S3. Upon completion, the ee and dr values were directly determined by chiral HPLC analysis.

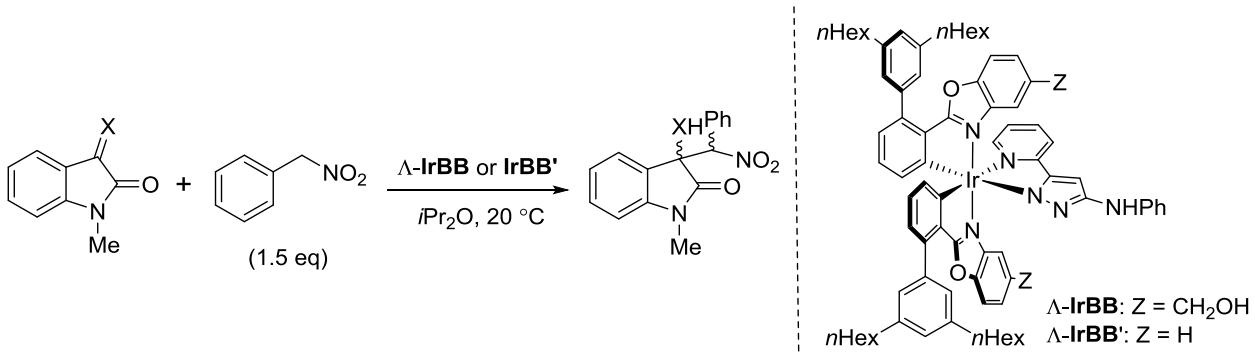


Table S3. Control experiments.

entry	cat.	X	loading (%)	*t* (h)	conv. (%)	ee (%)	dr
1	-	NBoc	-	8	0	-	-
2	Λ-**IrBB'**	NBoc	4.0	8	98	76	1:1.7
3	Λ-**IrBB**	O	1.5	8	0	-	-
4	Λ-**IrBB**	NPMP	1.5	8	0	-	-
5	Λ-**IrBB**	NCbz	1.5	1	100	86	1:22
6	Λ-**IrBB**	NBoc	1.5	1	100	96	1:26
7	Λ-**IrBB**	NBoc	0.5	1.5	100	96	1:23

7. ^{1}H NMR and ^{13}C NMR Spectra

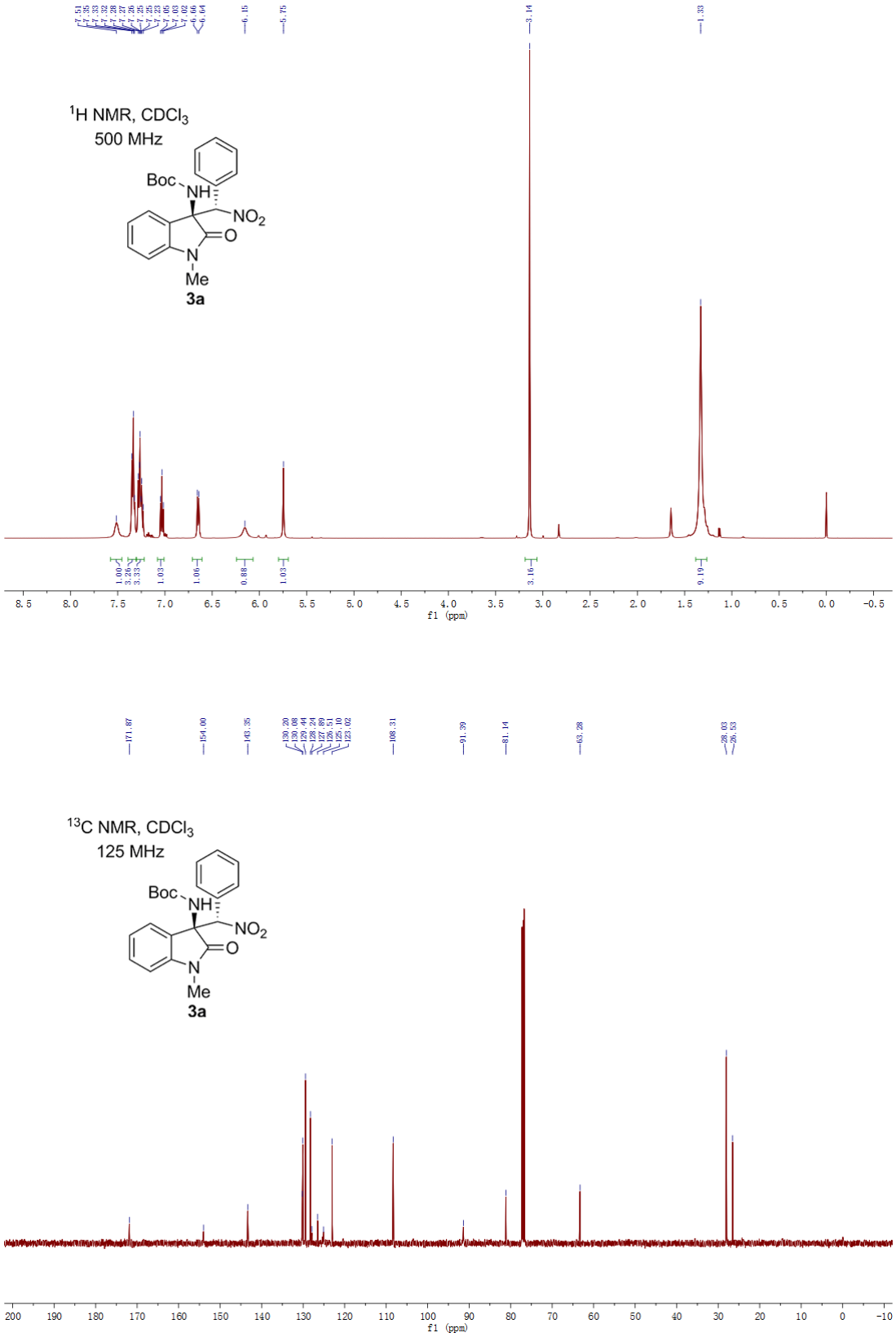


Figure S1. ^{1}H and ^{13}C NMR spectra of **3a**.

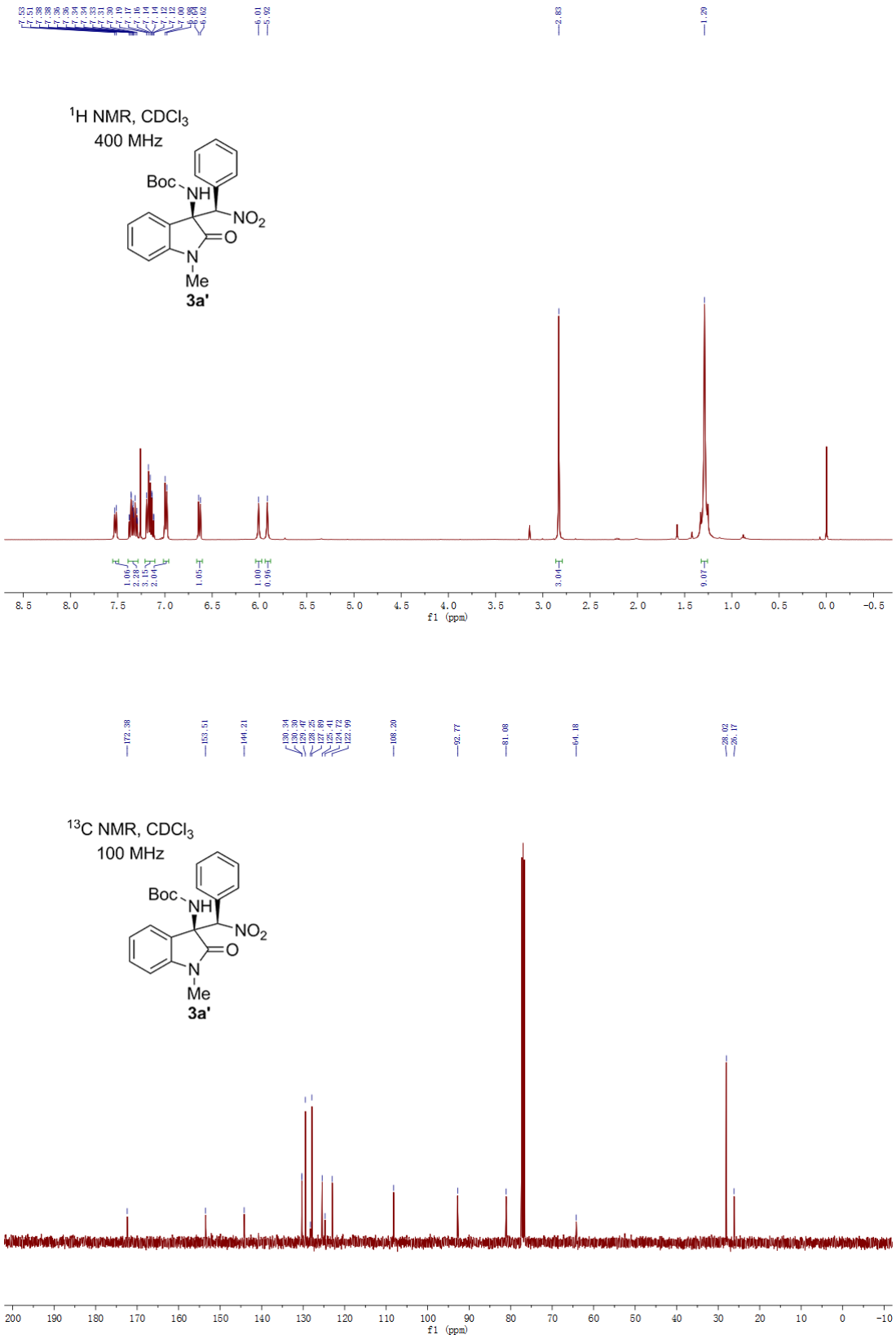


Figure S2. ^{1}H and ^{13}C NMR spectra of **3a'**.

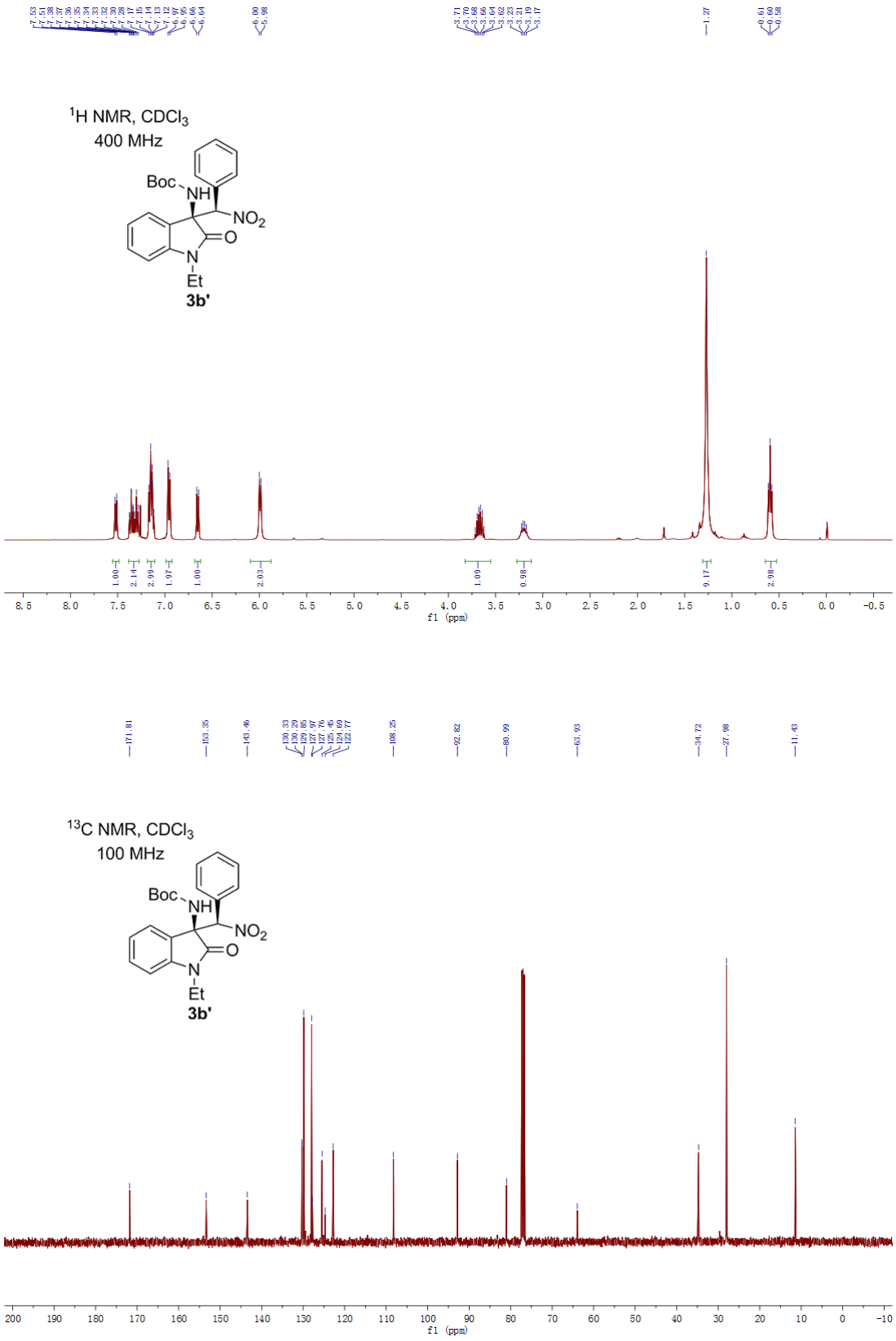


Figure S3. ^{1}H and ^{13}C NMR spectra of **3b'**.

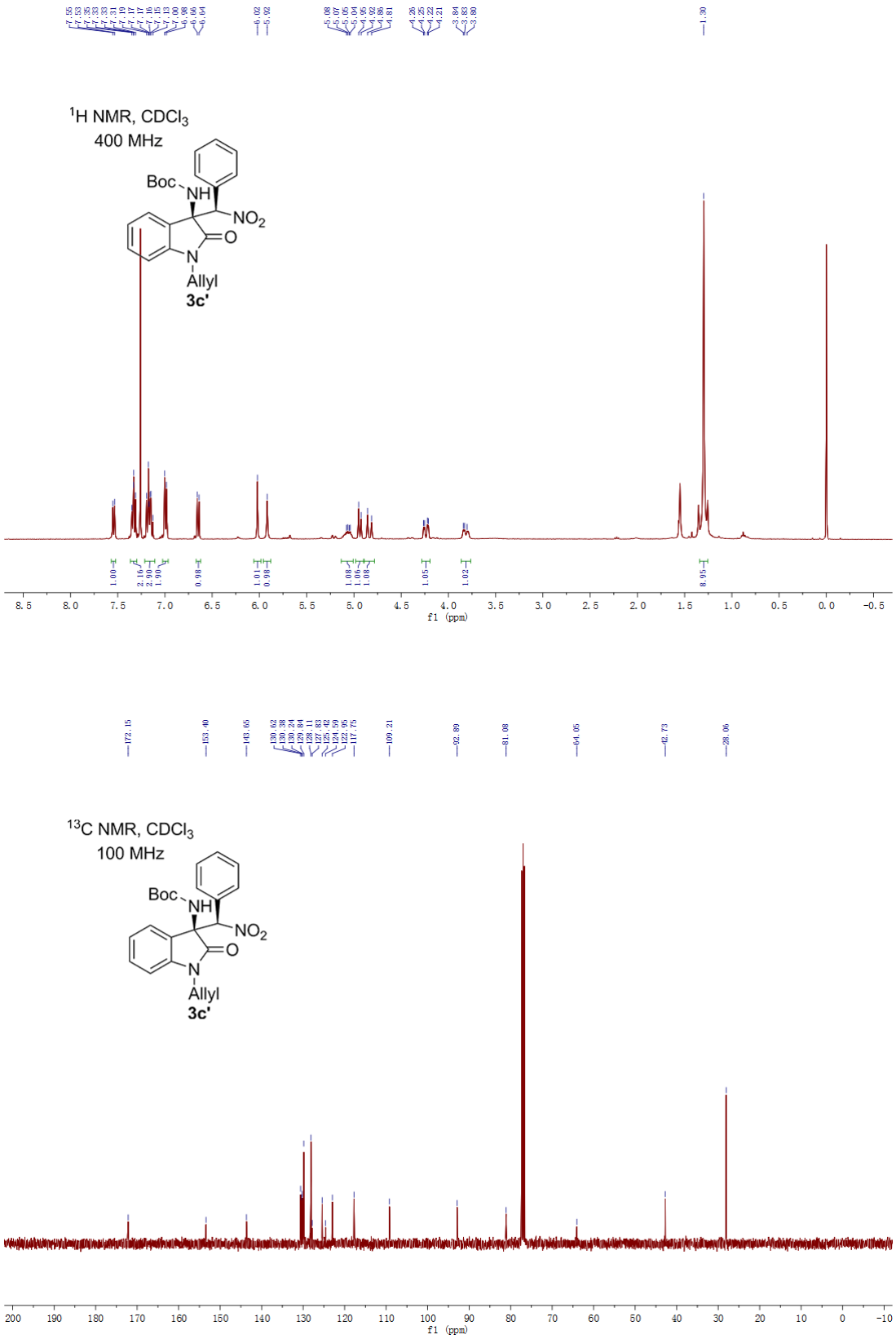


Figure S4. ^{1}H and ^{13}C NMR spectra of **3c'**.

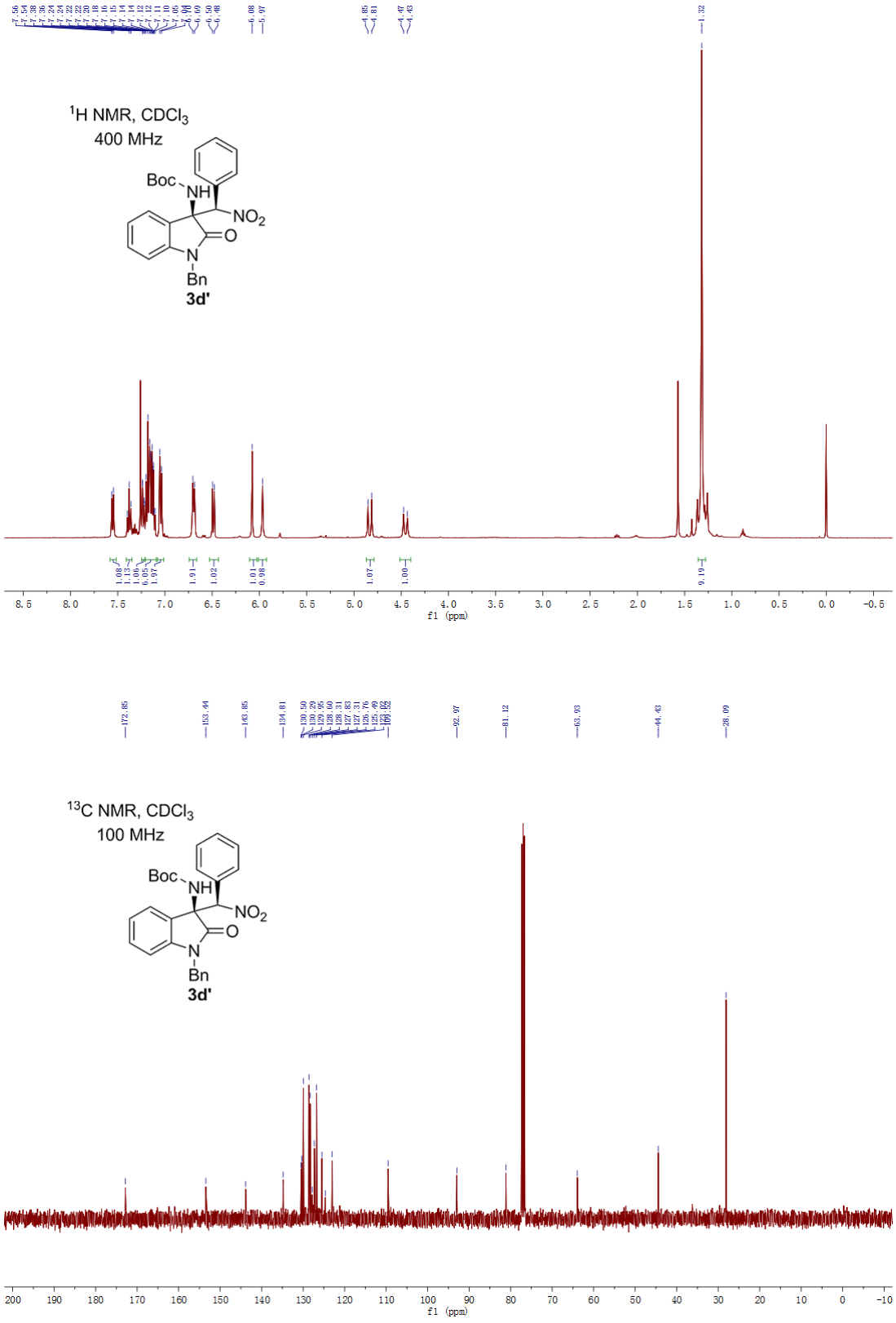


Figure S5. ^{1}H and ^{13}C NMR spectra of **3d'**.

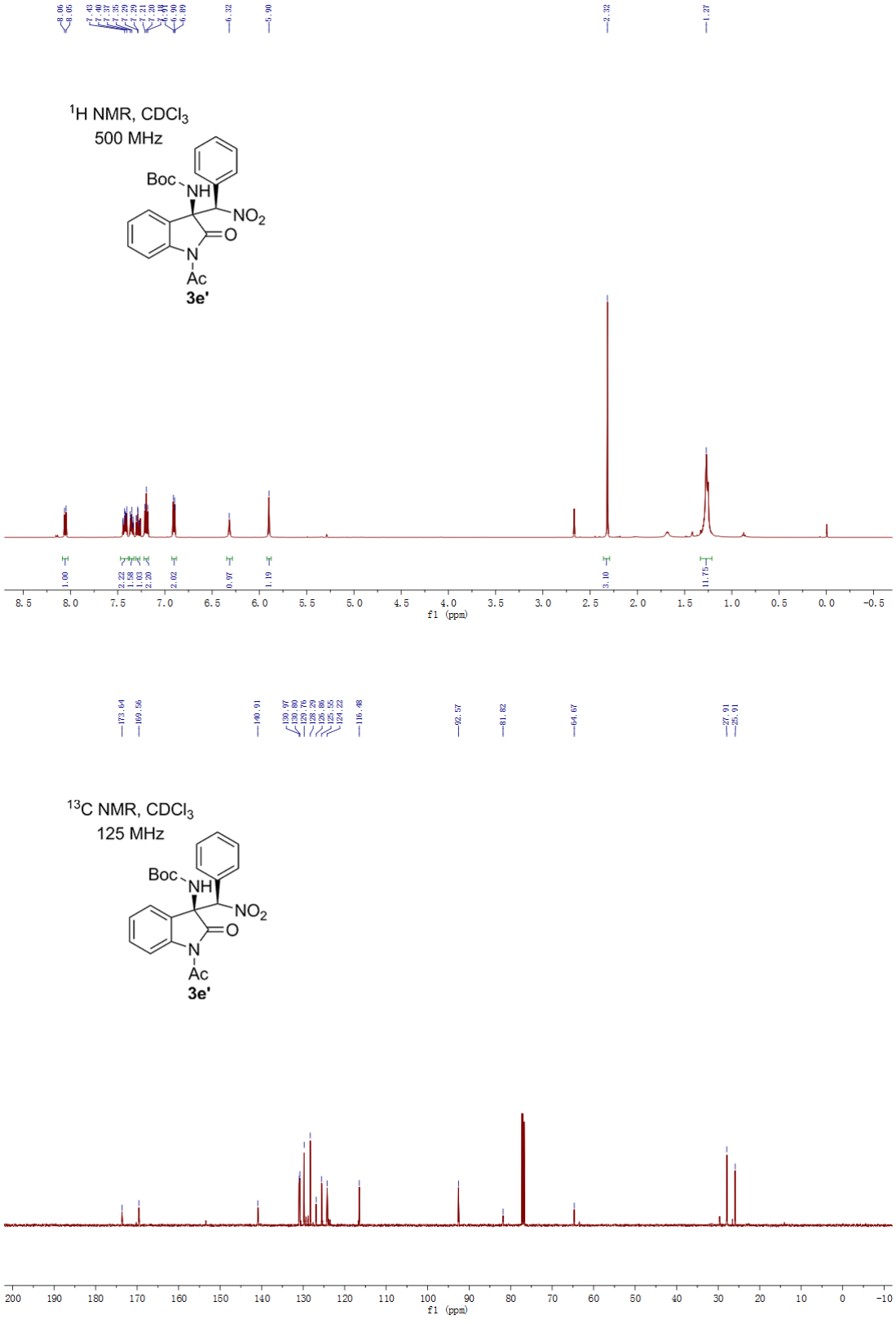


Figure S6. ^{1}H and ^{13}C NMR spectra of **3e'**.

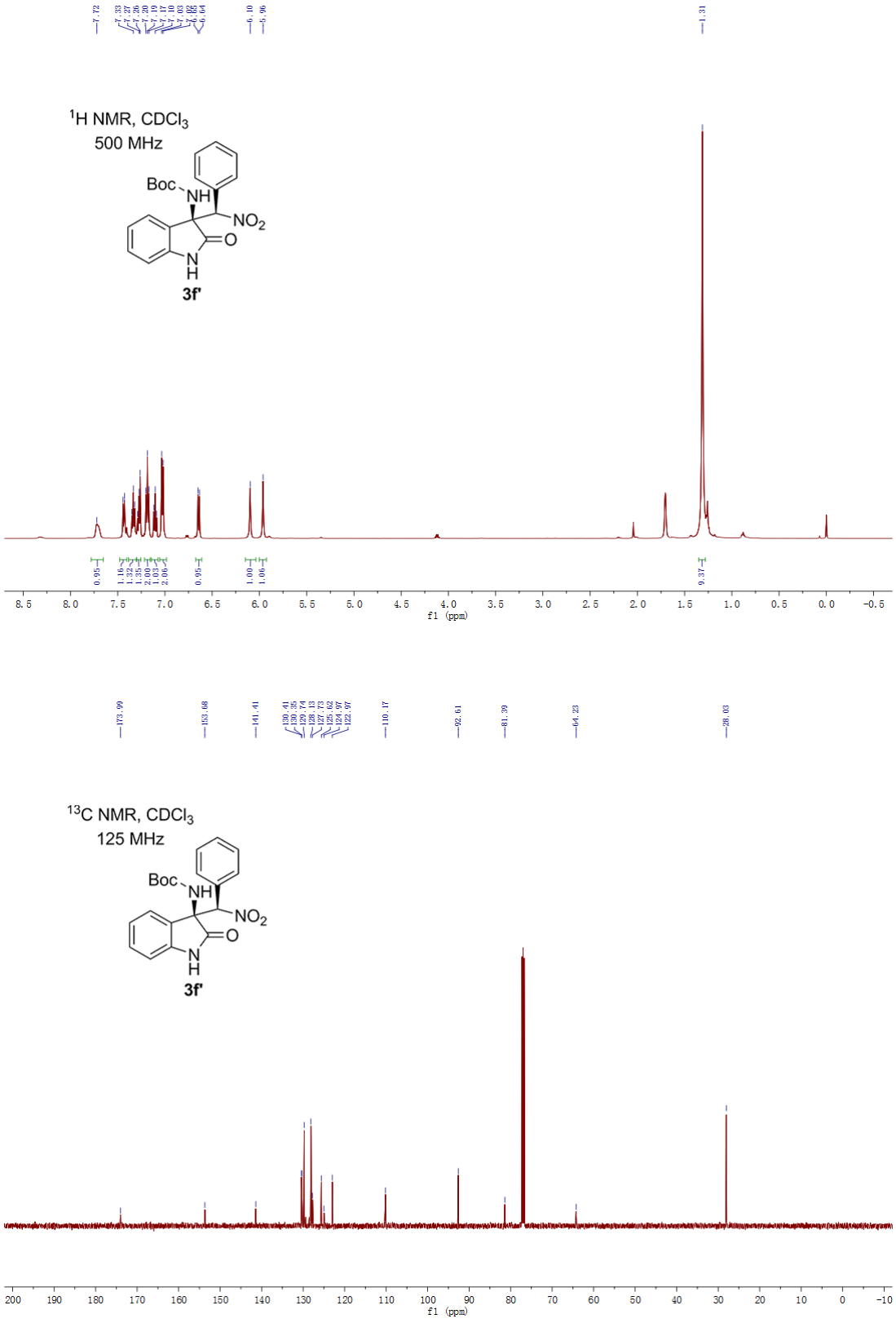


Figure S7. ^{1}H and ^{13}C NMR spectra of **3f'**.

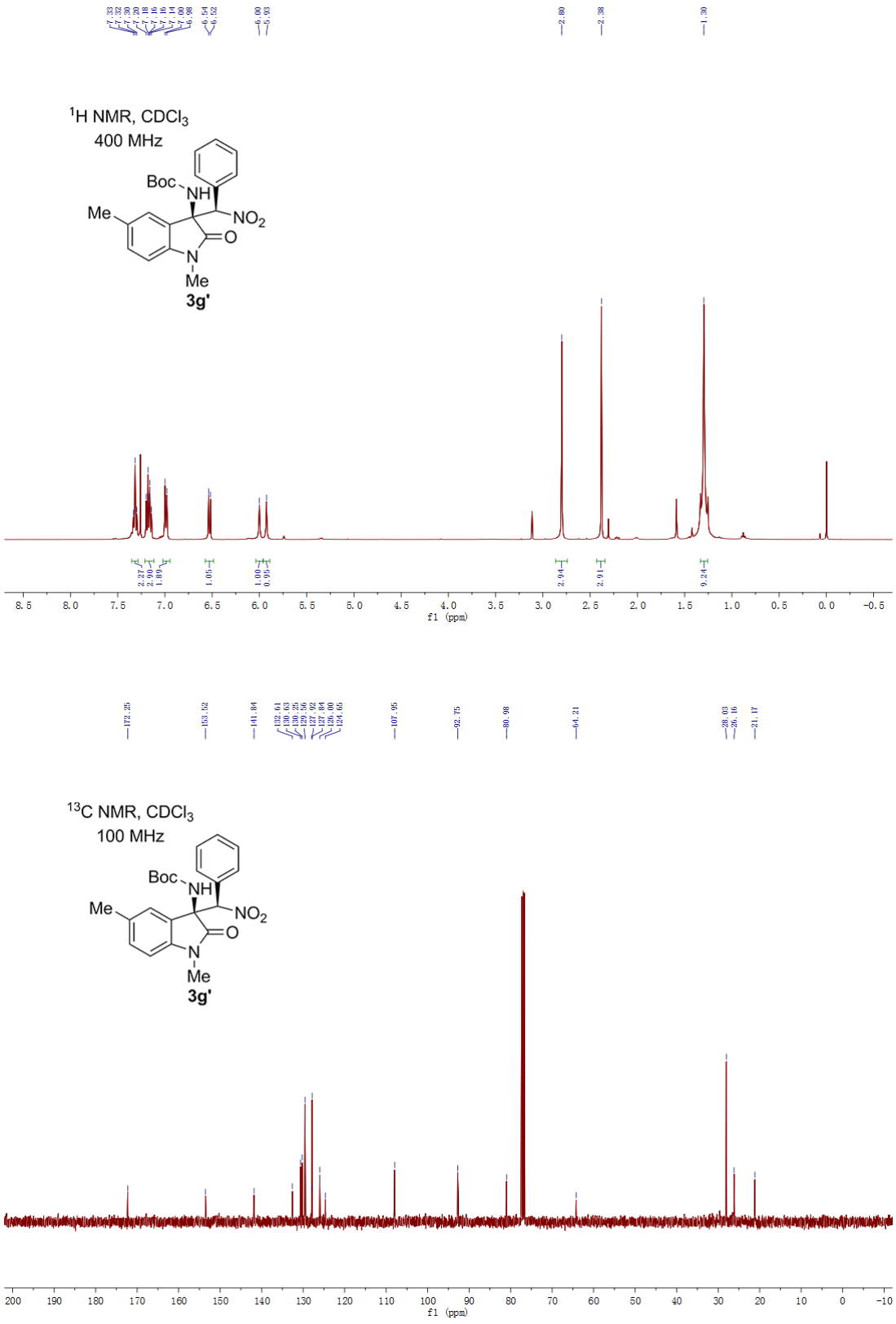


Figure S8. ^{1}H and ^{13}C NMR spectra of **3g'**.

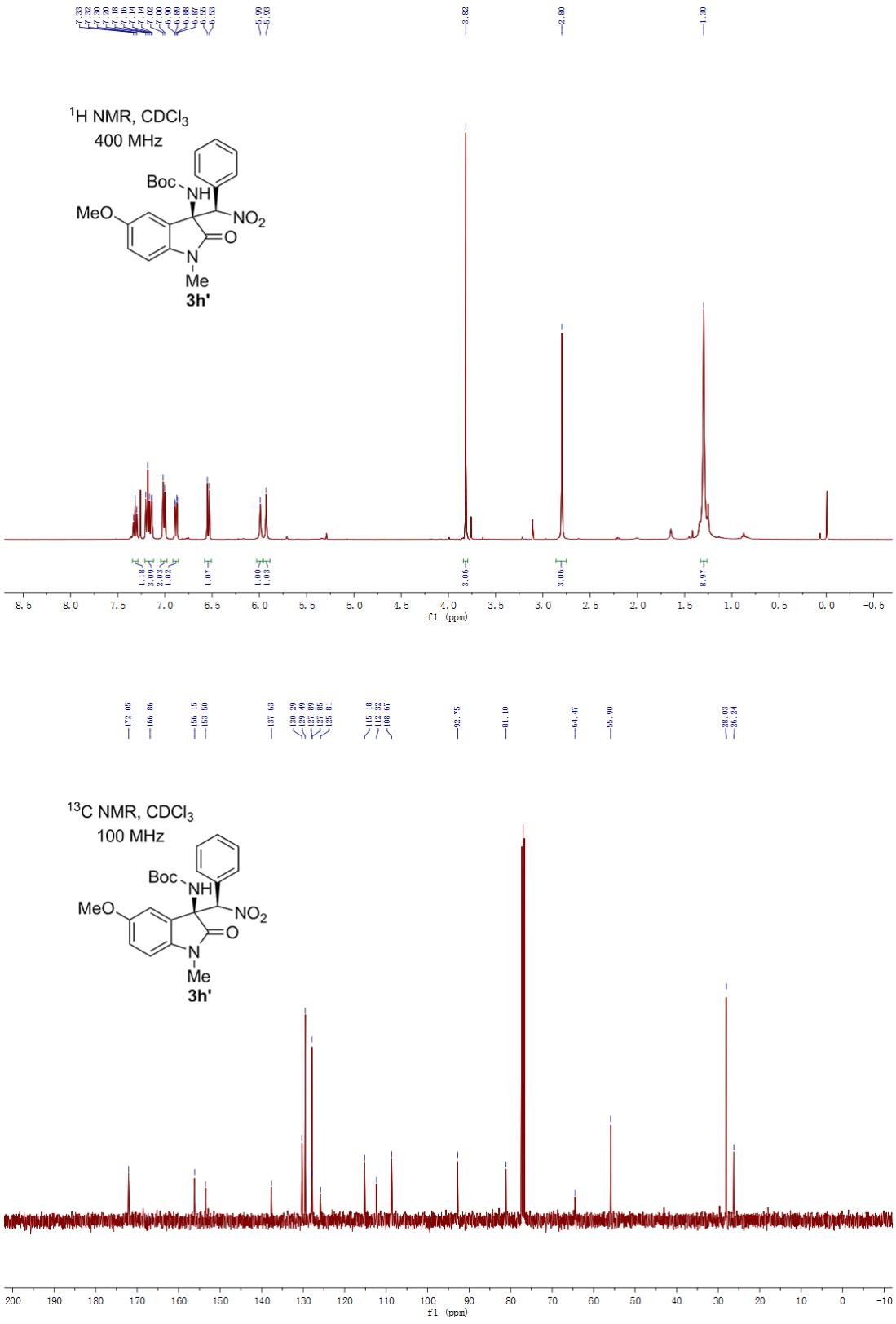


Figure S9. ^{1}H and ^{13}C NMR spectra of **3h'**.

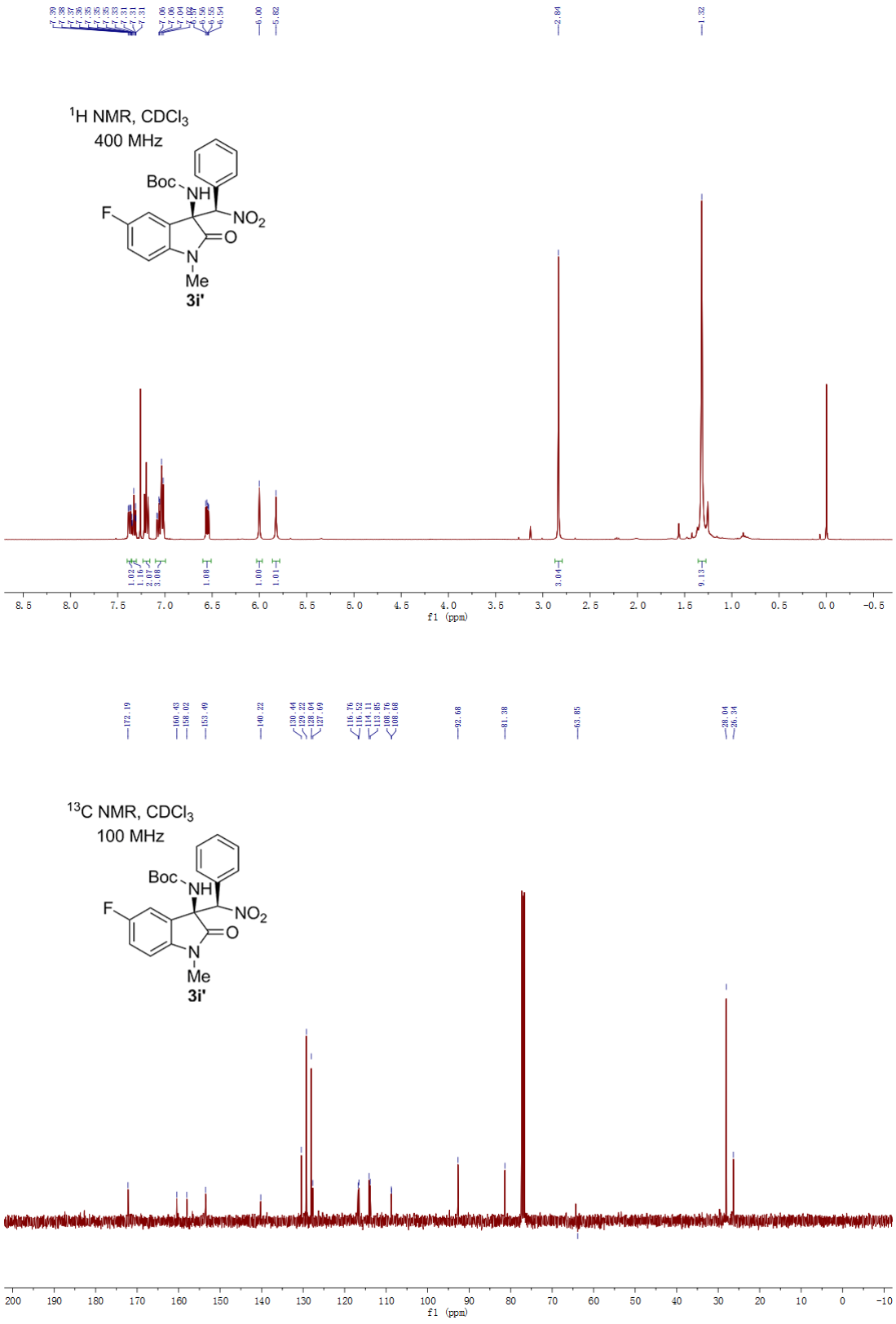


Figure S10. ^{1}H and ^{13}C NMR spectra of **3i'**.

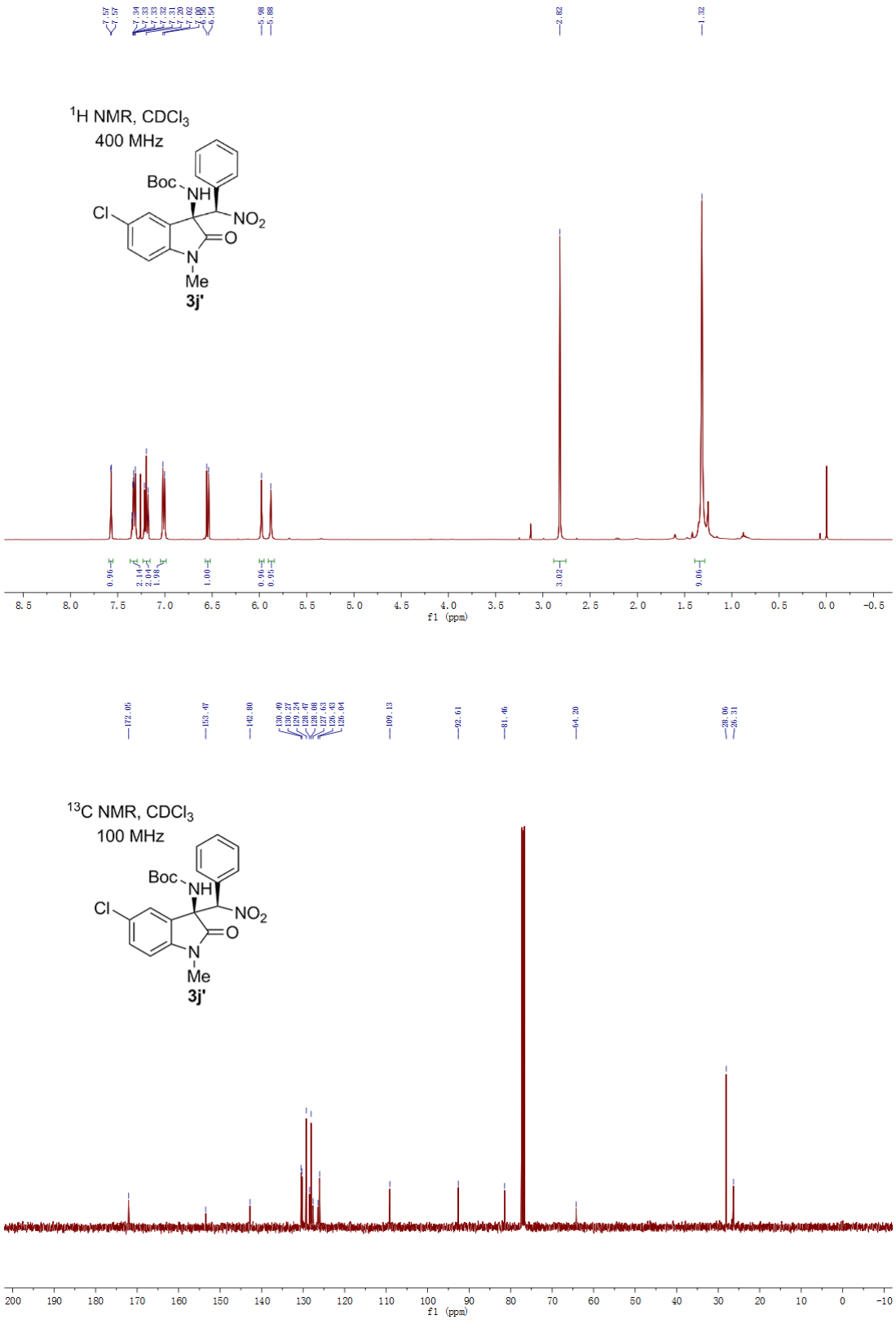


Figure S11. ^{1}H and ^{13}C NMR spectra of **3j'**.

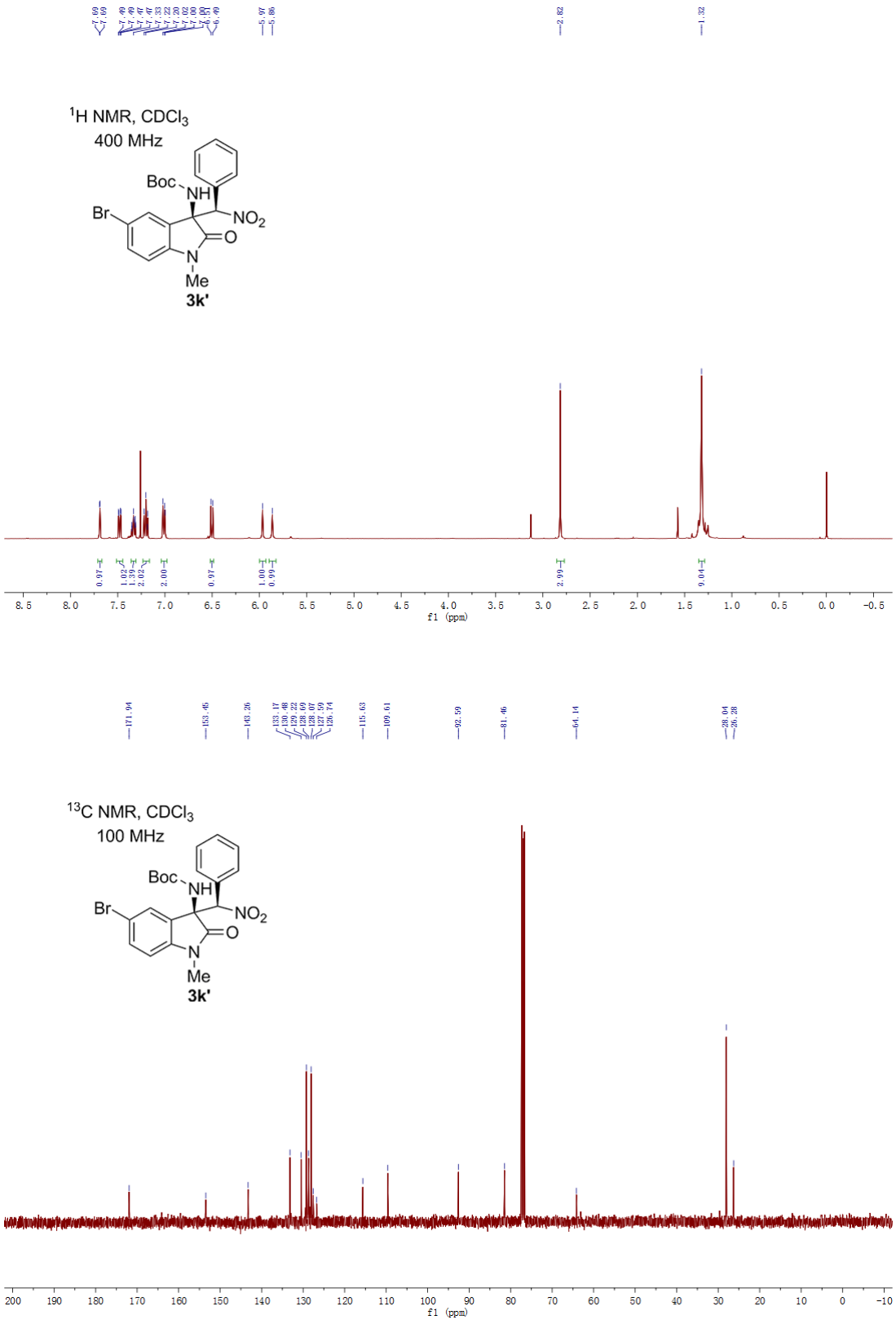


Figure S12. ^{1}H and ^{13}C NMR spectra of **3k'**.

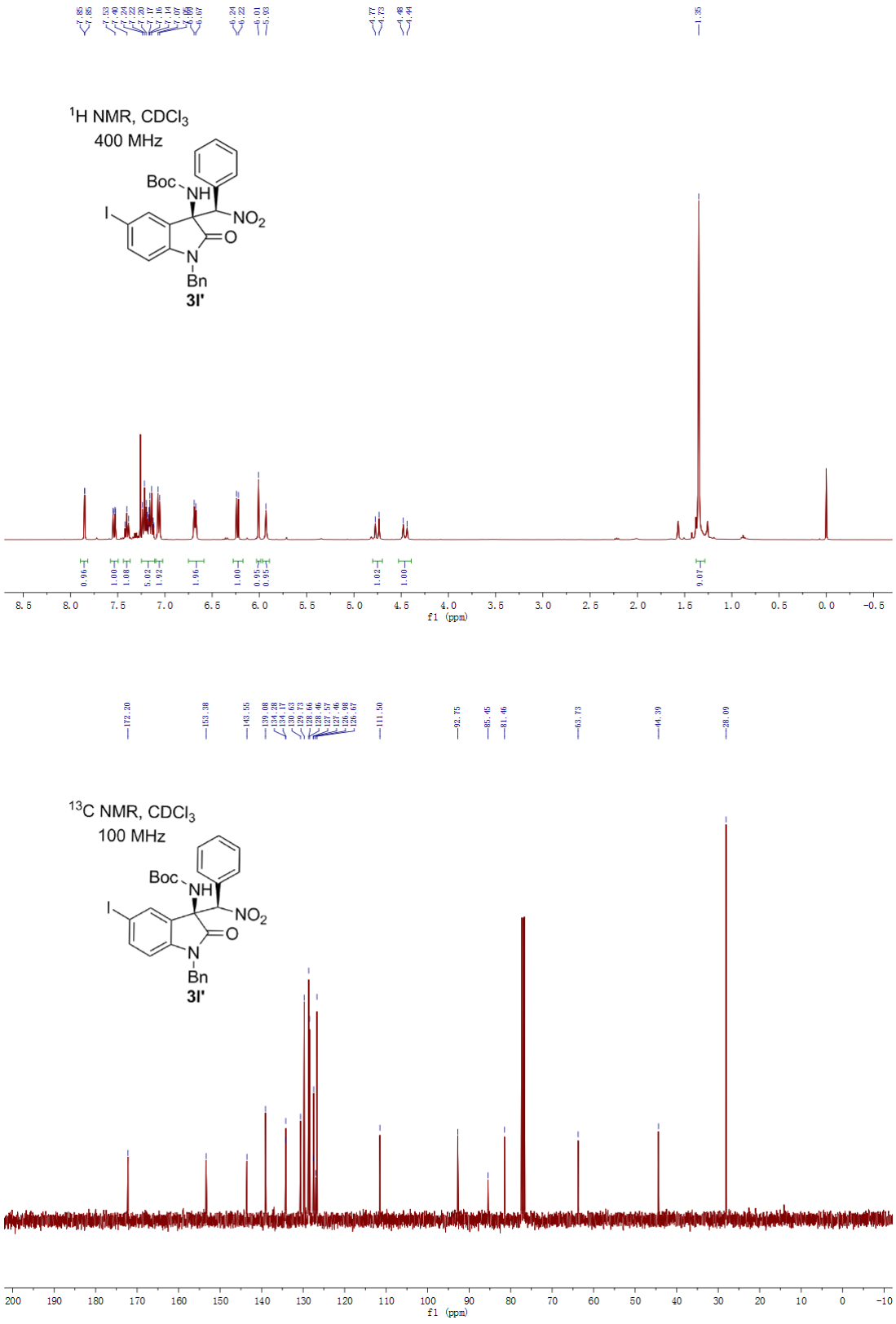


Figure S13. ^{1}H and ^{13}C NMR spectra of **3l'**.

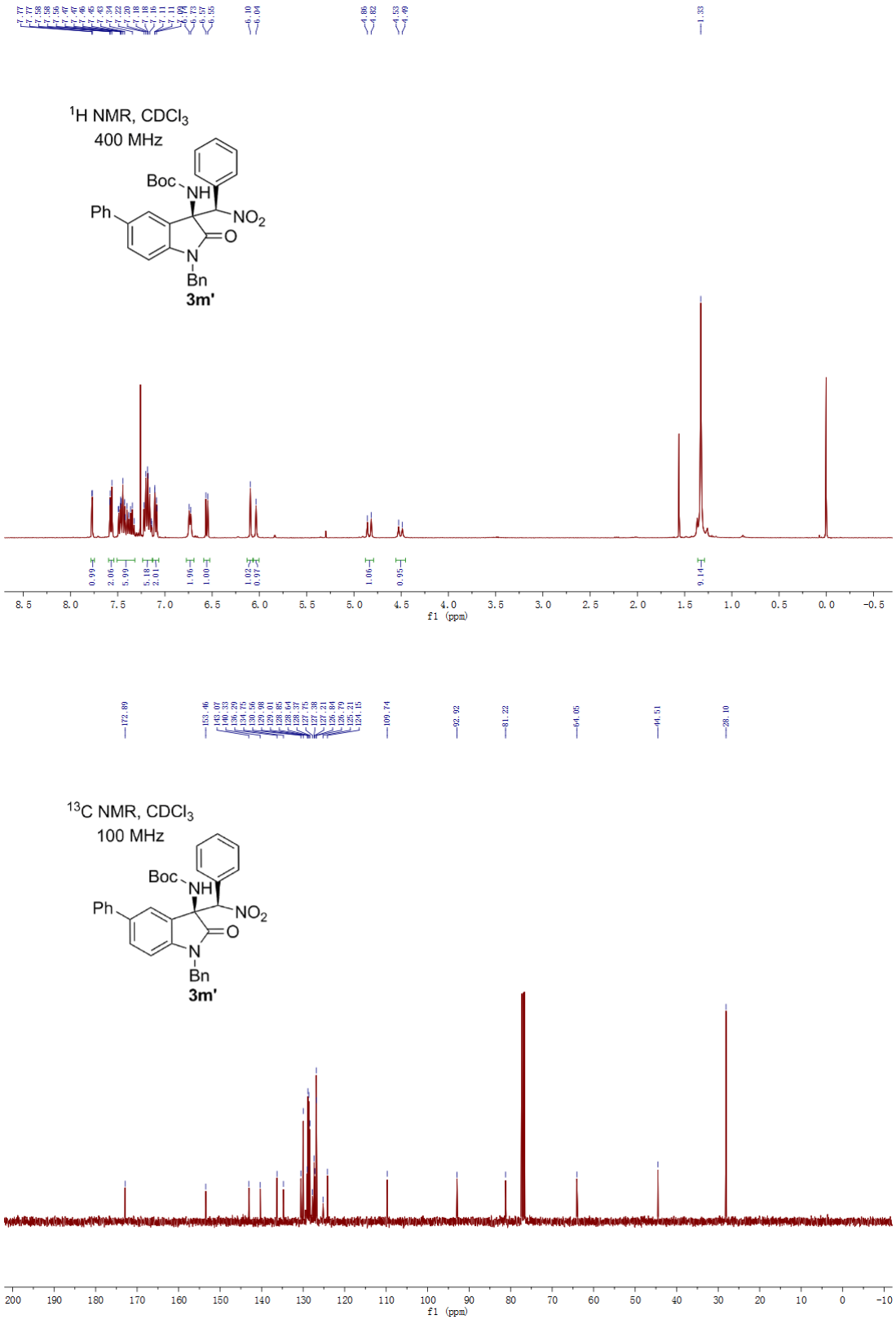


Figure S14. ^{1}H and ^{13}C NMR spectra of **3m'**.

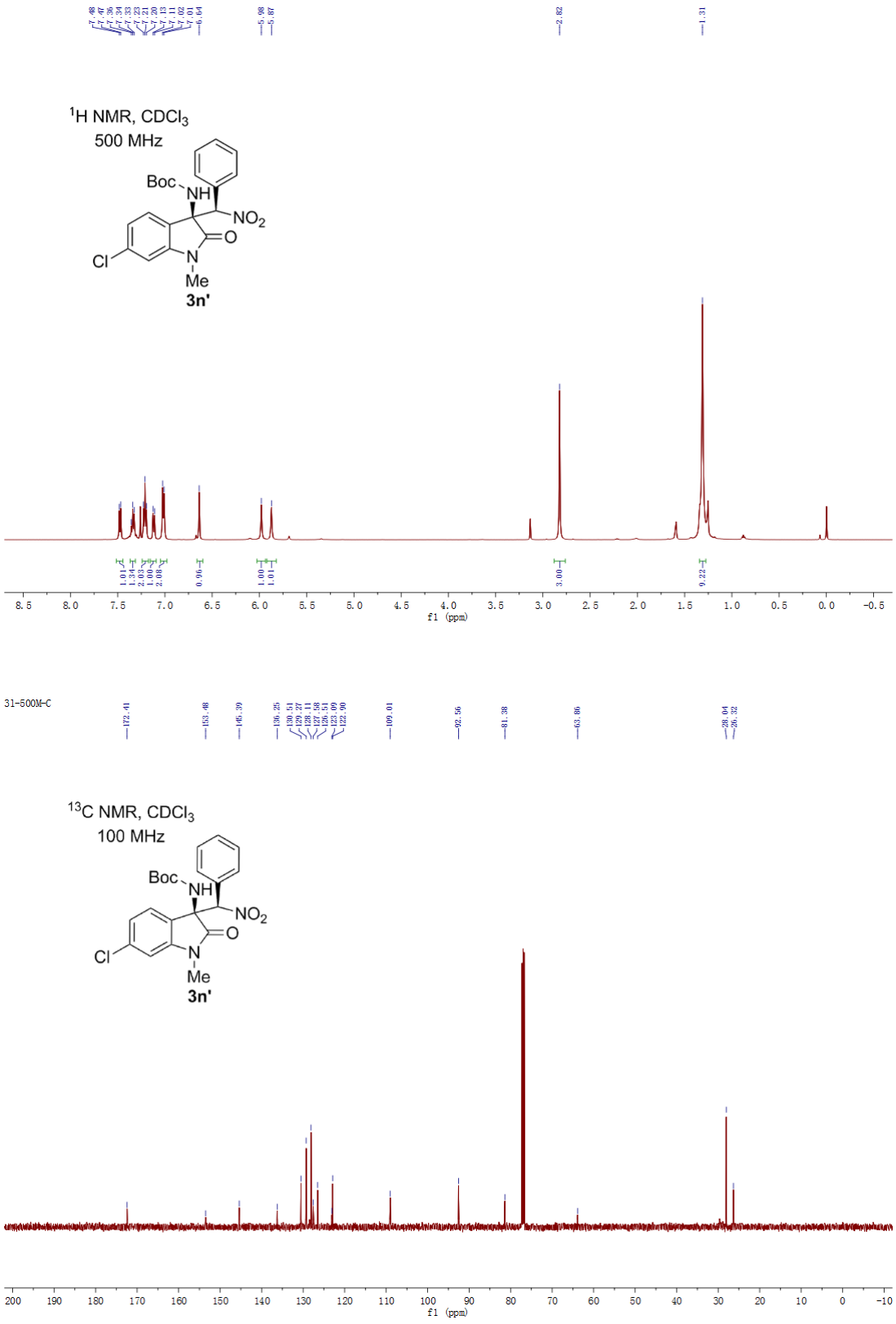


Figure S15. ^{1}H and ^{13}C NMR spectra of **3n'**.

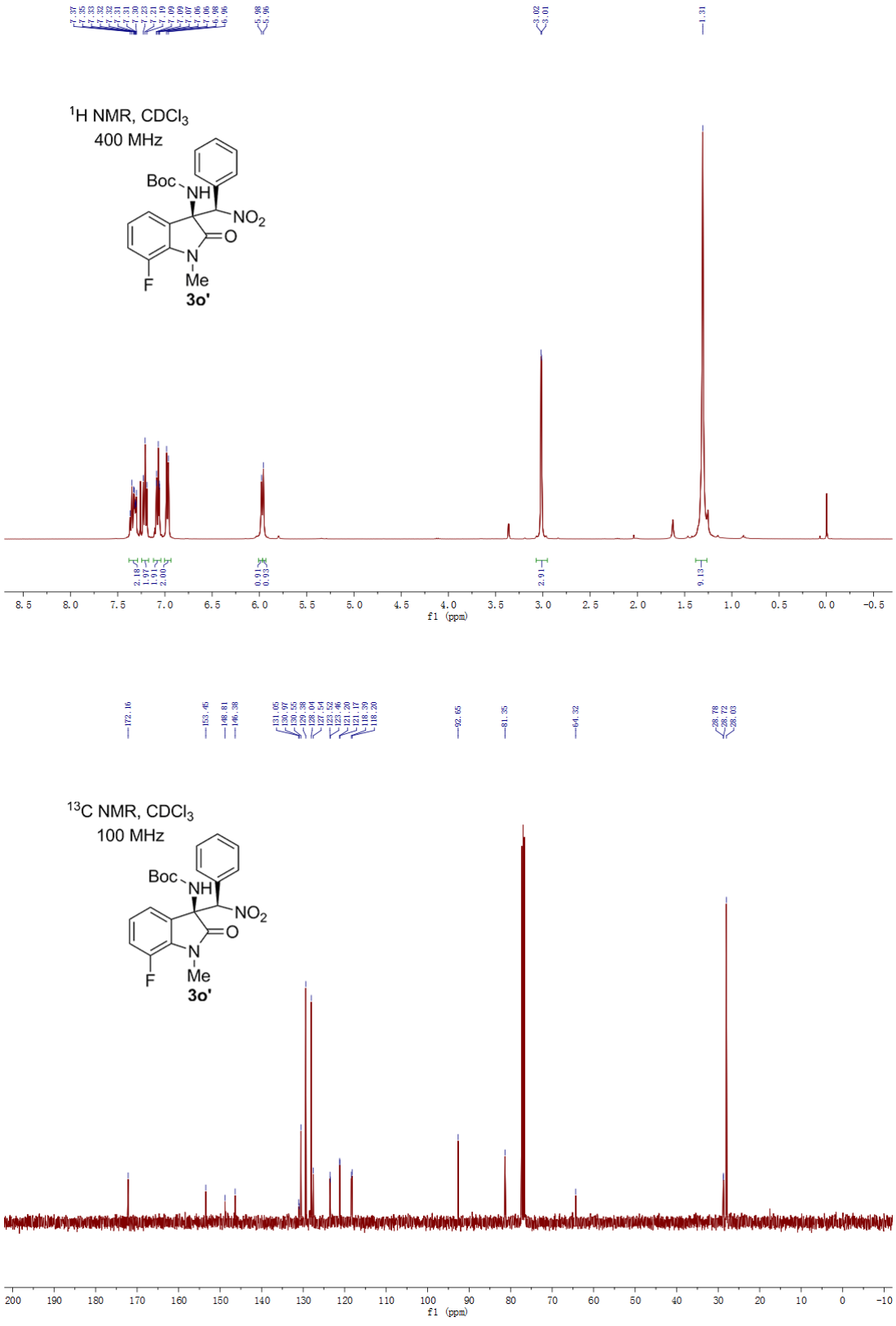


Figure S16. ^{1}H and ^{13}C NMR spectra of **3o'**.

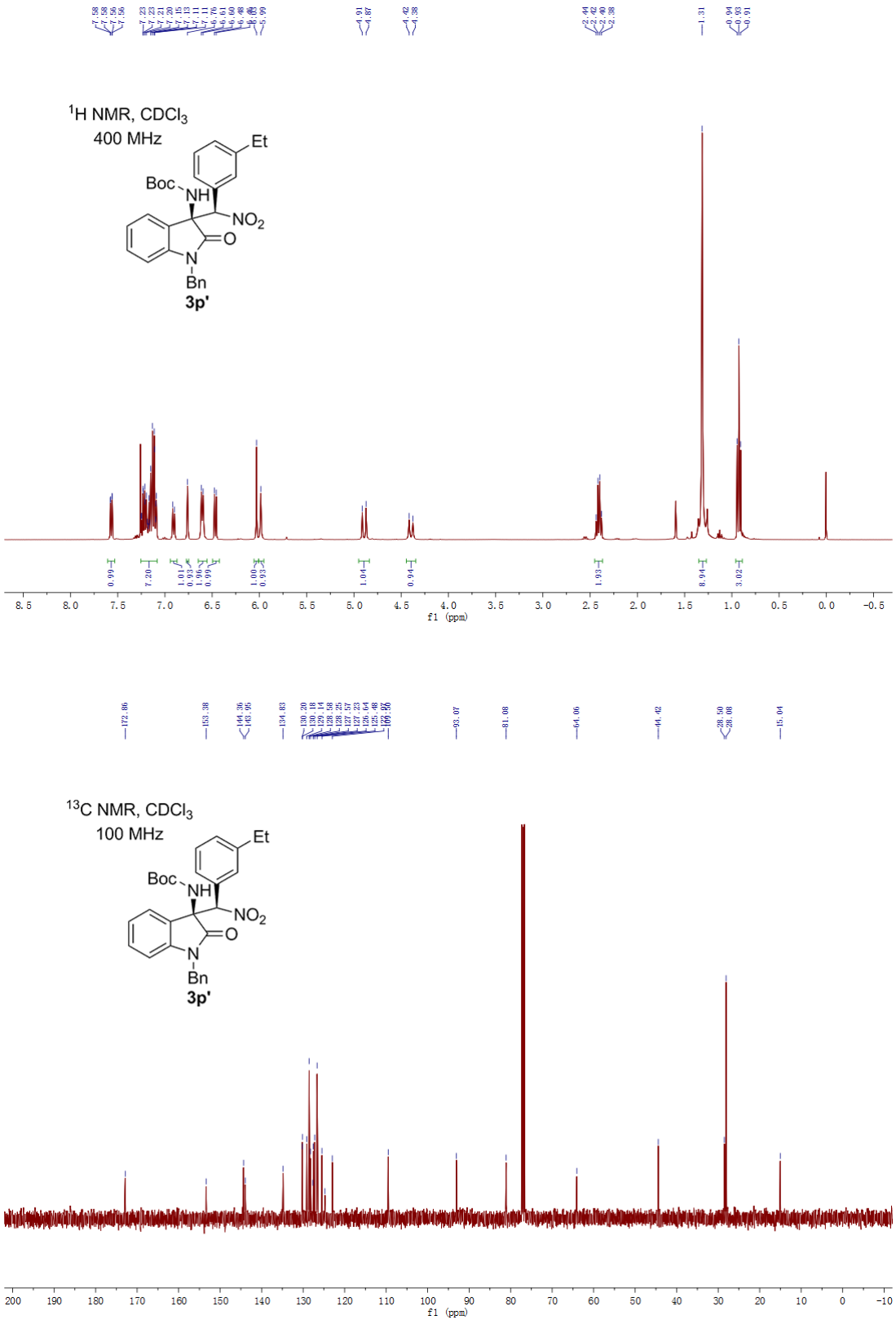


Figure S17. ^{1}H and ^{13}C NMR spectra of **3p'**.

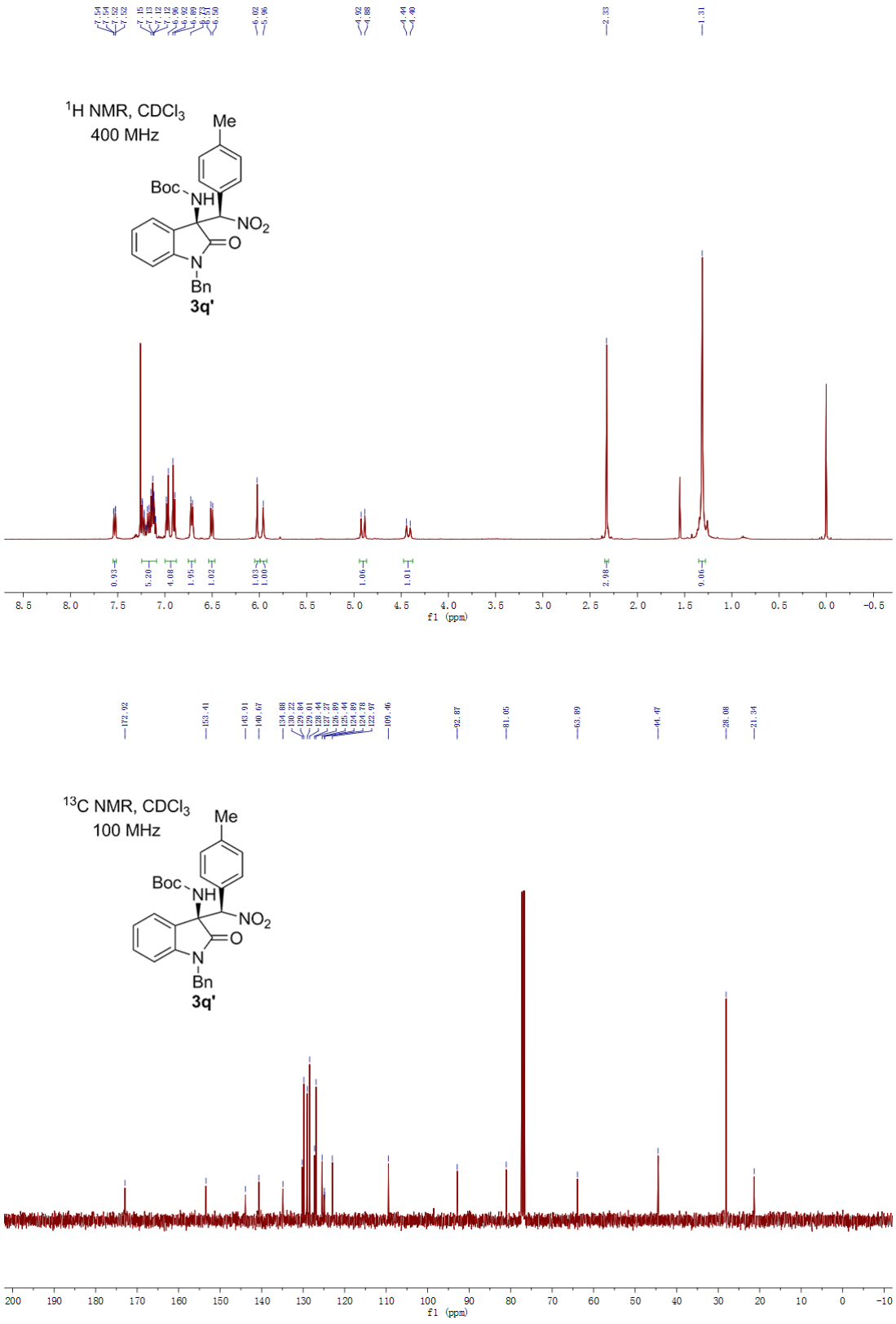


Figure S18. ^{1}H and ^{13}C NMR spectra of **3q'**.

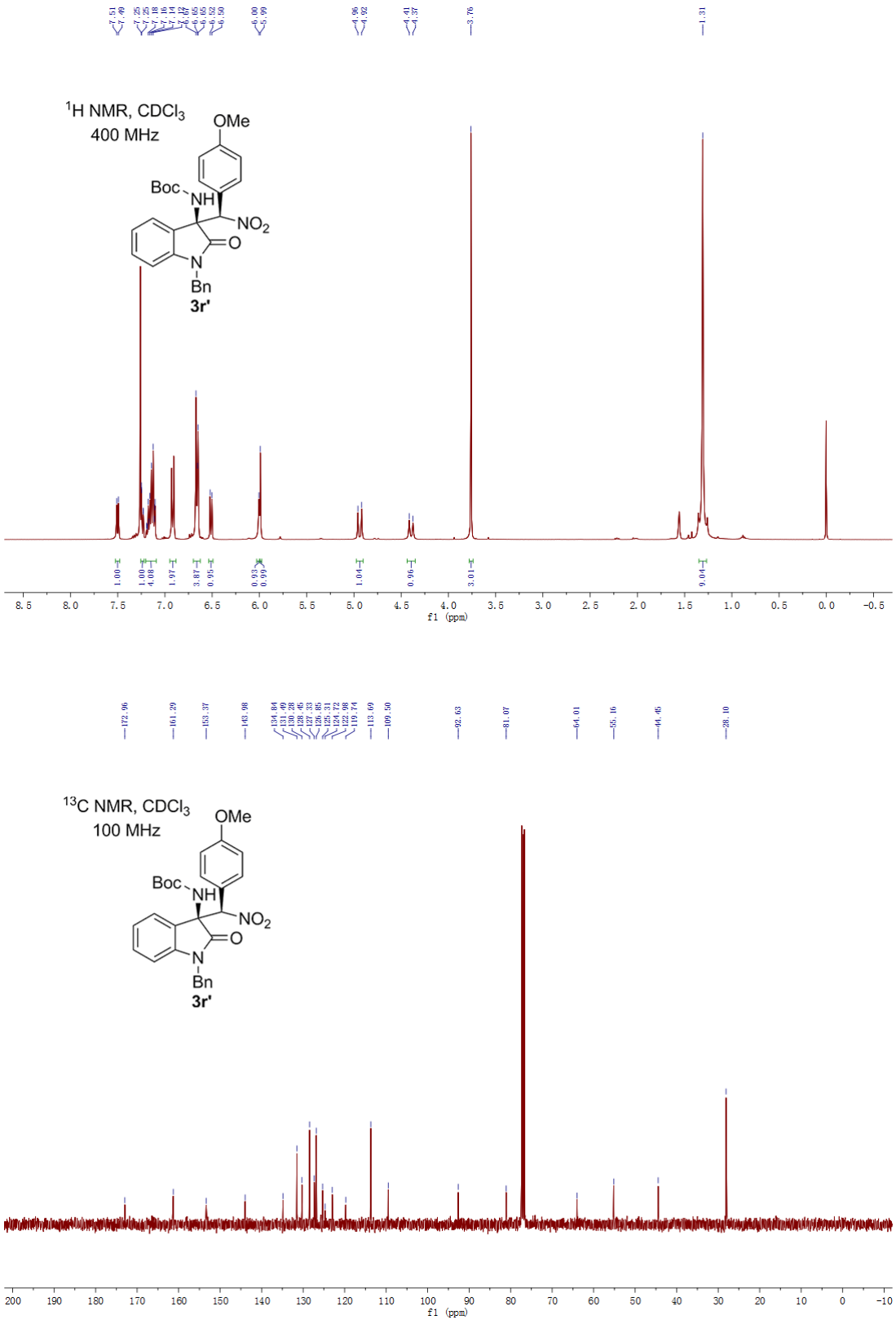


Figure S19. ^{1}H and ^{13}C NMR spectra of **3r'**.

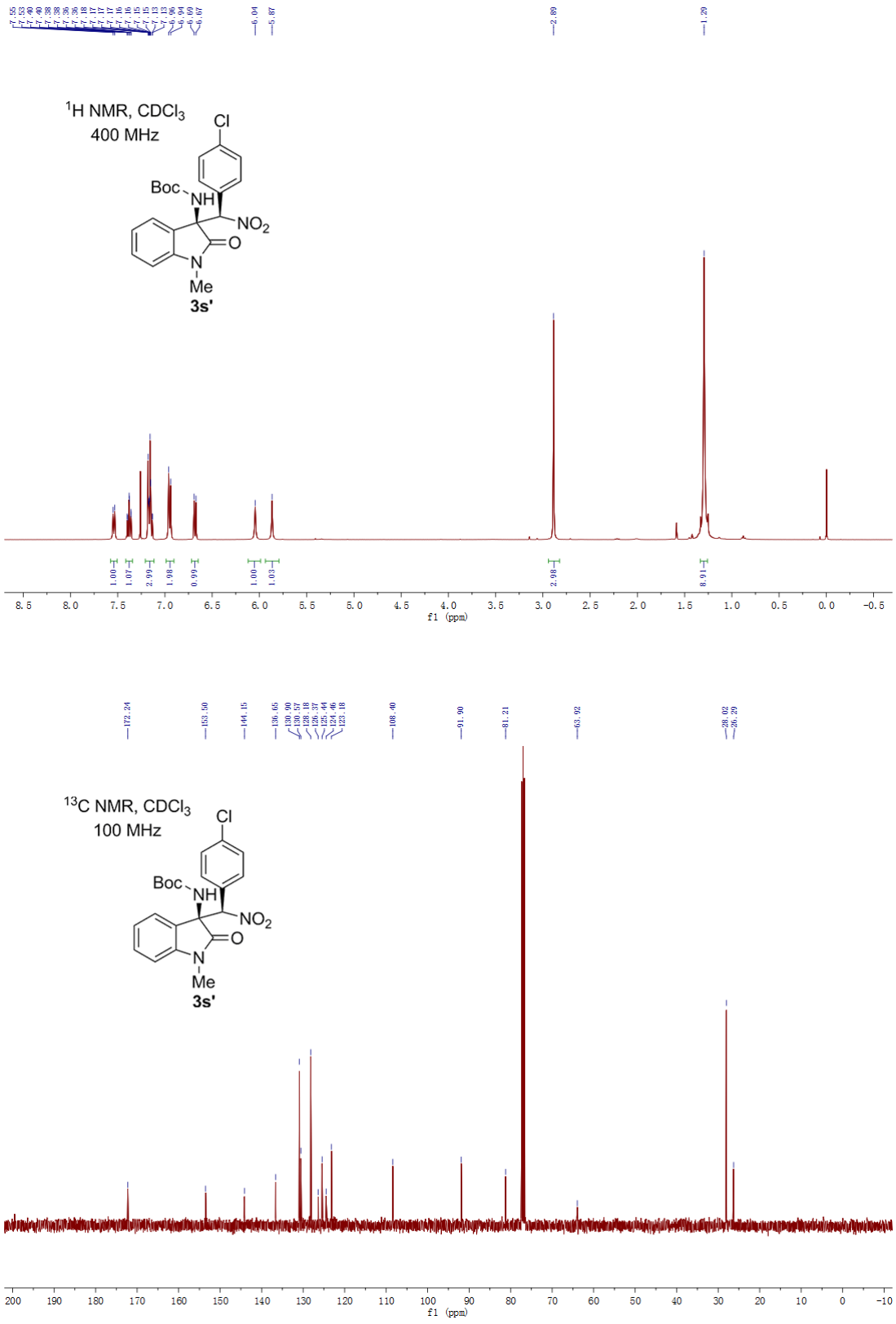


Figure S20. ^{1}H and ^{13}C NMR spectra of **3s'**.

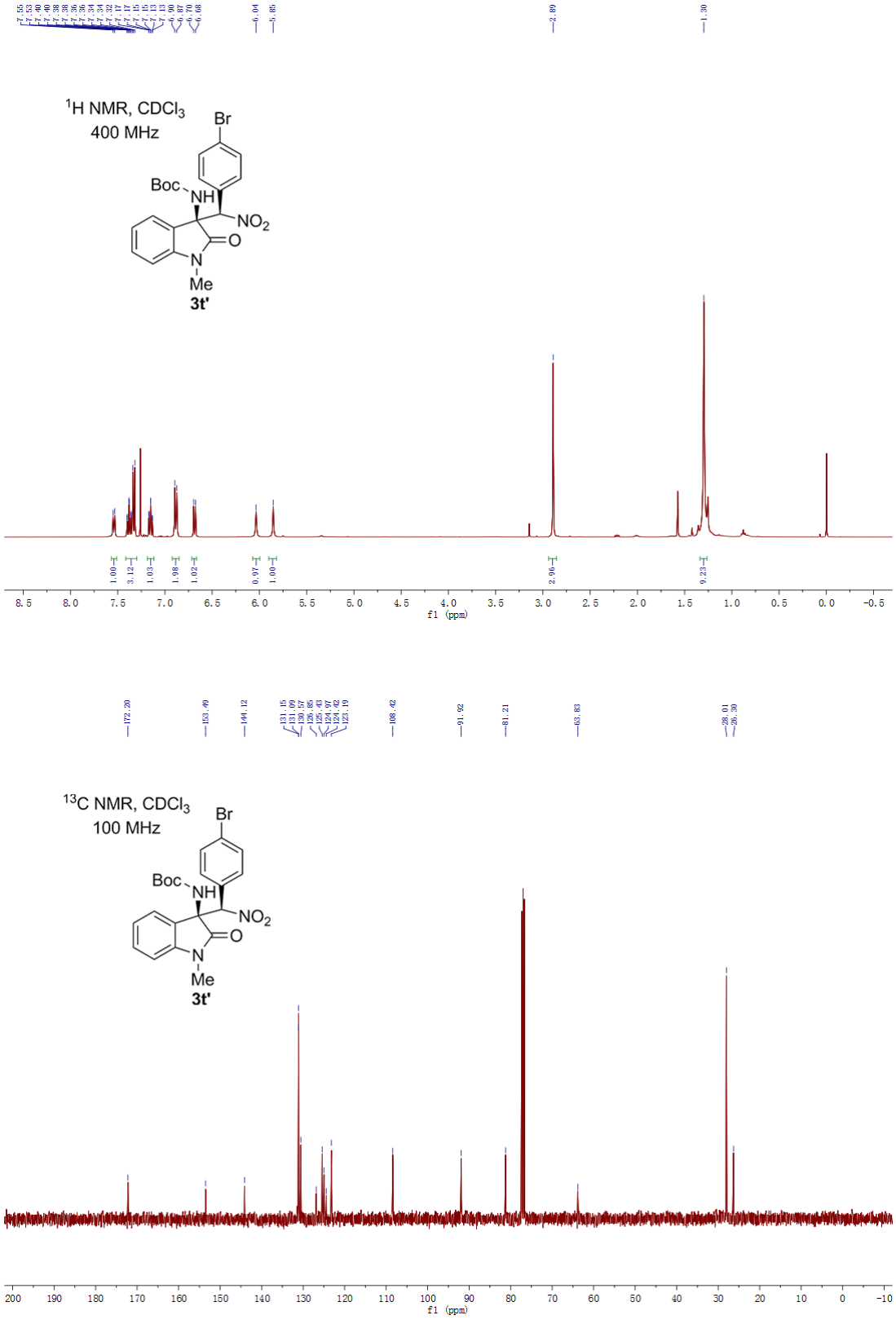


Figure S21. ^{1}H and ^{13}C NMR spectra of **3t'**.

8. Chiral HPLC Traces

Stereoselectives of the asymmetric aza-Henry reactions were determined with a Daicel Chiralpak AD-H, IA or IC HPLC column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*hexane/isopropanol as mobile phase. The column temperature was 25 °C and UV-absorption was measured at 254 nm.

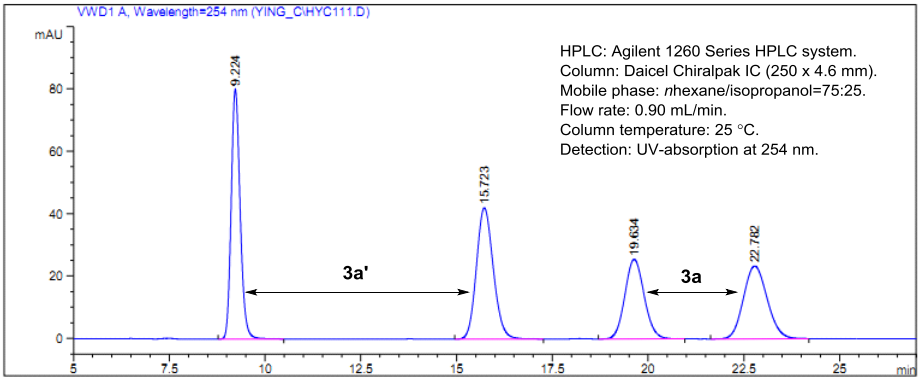
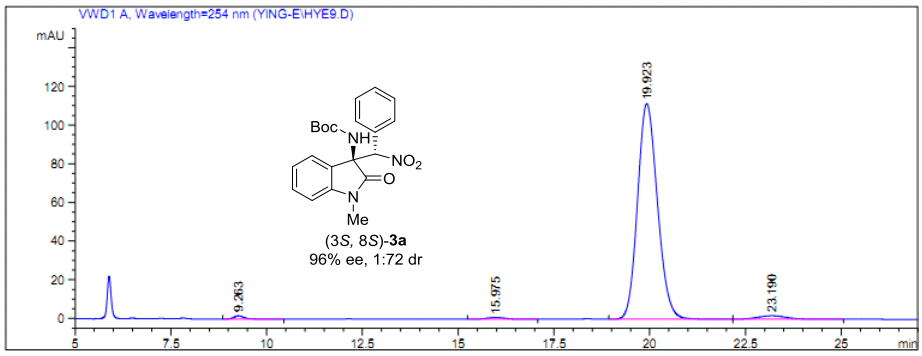
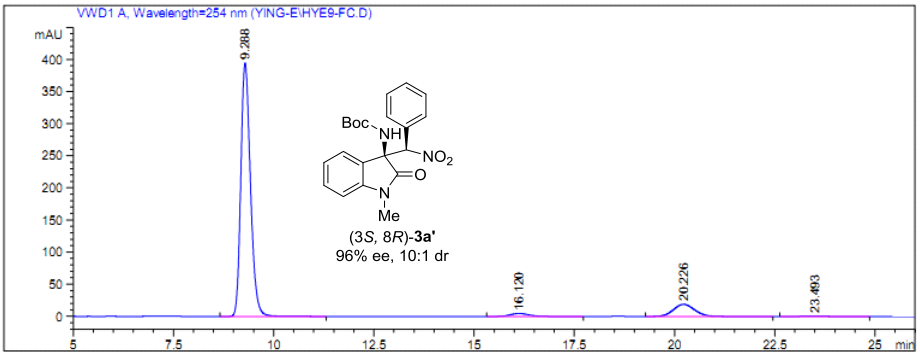


Figure S22. HPLC trace for the racemic reference *rac*-**3a** and **3a'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.263	BB	0.2664	28.23237	1.62748	0.6735
2	15.975	BB	0.4869	29.27027	9.20684e-1	0.6982
3	19.923	BV	0.5628	4040.49561	111.48431	96.3866
4	23.190	VB	0.8136	93.96932	1.79252	2.2417

Figure S23. HPLC trace for (3*S*,8*S*)-**3a**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.288	BB	0.2569	6589.22852	394.48077	88.4869
2	16.120	BB	0.4987	150.10352	4.64922	2.0157
3	20.226	BB	0.5718	694.77826	18.85930	9.3302
4	23.493	BB	0.5593	12.44850	2.74385e-1	0.1672

Figure S24. HPLC trace for (3*S*,8*R*)-**3a'**.

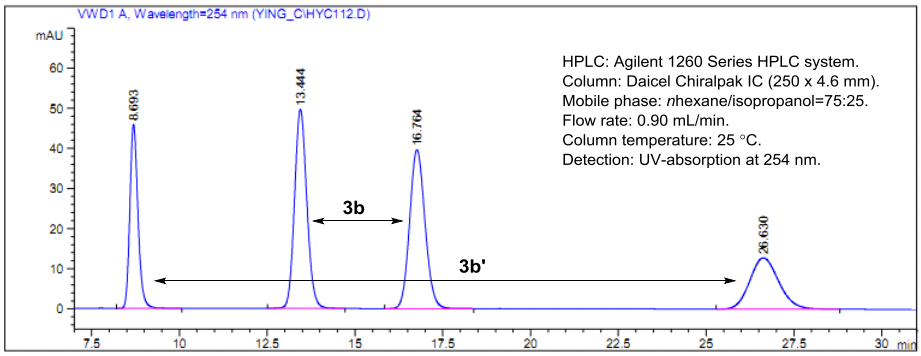
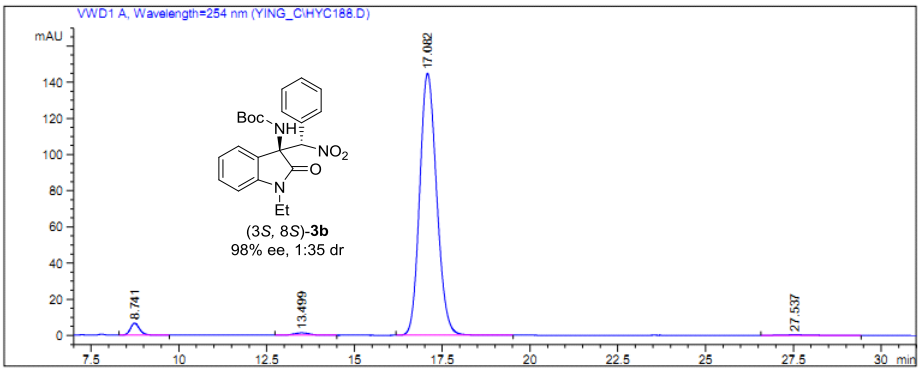
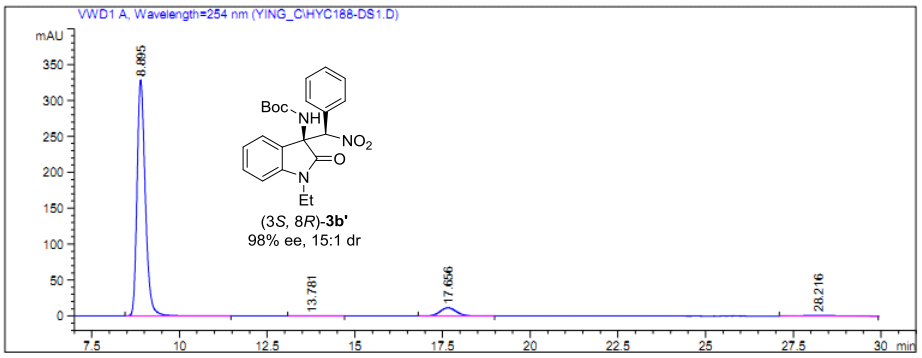


Figure S25. HPLC trace for the racemic reference *rac*-**3b** and **3b'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.741	VV	0.2795	121.21408	6.62484	2.4053
2	13.499	BB	0.4879	40.29931	1.29906	0.7997
3	17.082	BB	0.5216	4858.62158	144.74368	96.4126
4	27.537	BB	0.7235	19.27155	3.19610e-1	0.3824

Figure S26. HPLC trace for (3*S*,8*S*)-**3b**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.895	BB	0.2484	5353.80273	328.06741	92.5143
2	13.781	BB	0.4084	5.05495	1.77408e-1	0.0874
3	17.656	BB	0.4975	368.09915	11.43632	6.3608
4	28.216	BBA	0.8563	60.04295	9.80726e-1	1.0375

Figure S27. HPLC trace for (3*S*,8*R*)-**3b'**.

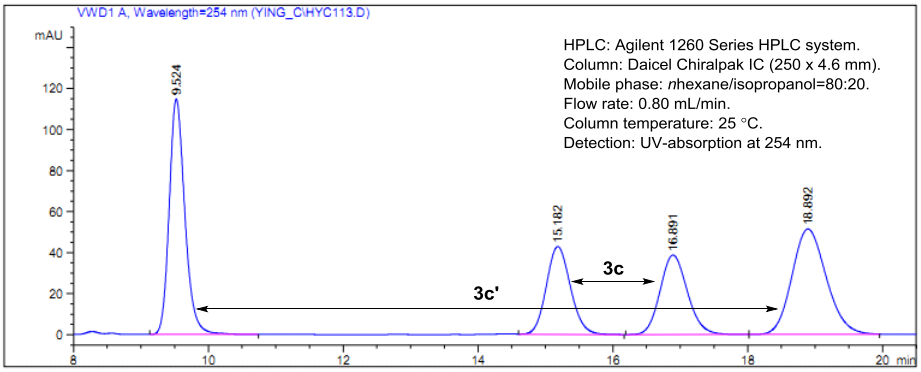
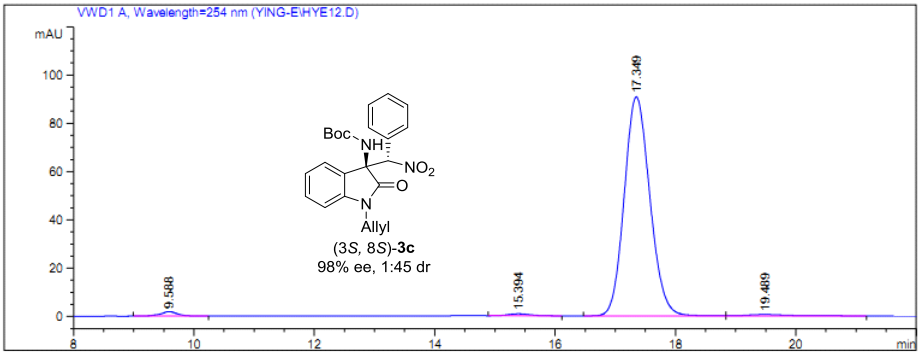
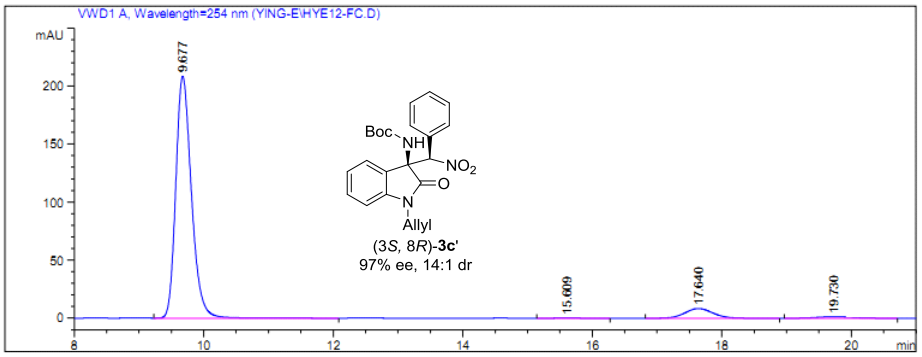


Figure S28. HPLC trace for the racemic reference *rac*-**3c** and **3c'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.588	BB	0.2889	36.47684	1.85952	1.3209
2	15.394	BB	0.3781	20.55685	8.21073e-1	0.7444
3	17.349	BV	0.4587	2680.42236	90.71365	97.0601
4	19.489	VB	0.6274	24.15463	5.32343e-1	0.8747

Figure S29. HPLC trace for (3*S*,8*S*)-**3c**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.677	VV	0.2578	3498.43848	208.48885	91.9035
2	15.609	BB	0.3920	3.91605	1.49305e-1	0.1029
3	17.640	BB	0.4665	251.80075	8.38075	6.6148
4	19.730	MF R	0.6338	52.48641	1.38017	1.3788

Figure S30. HPLC trace for (3*S*,8*R*)-**3c'**.

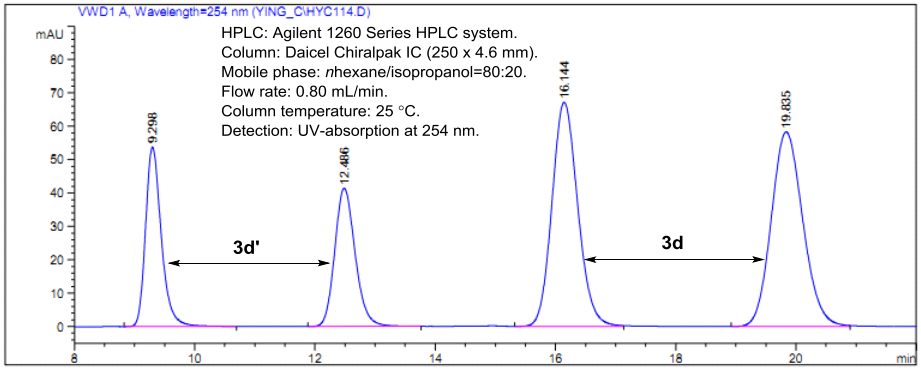
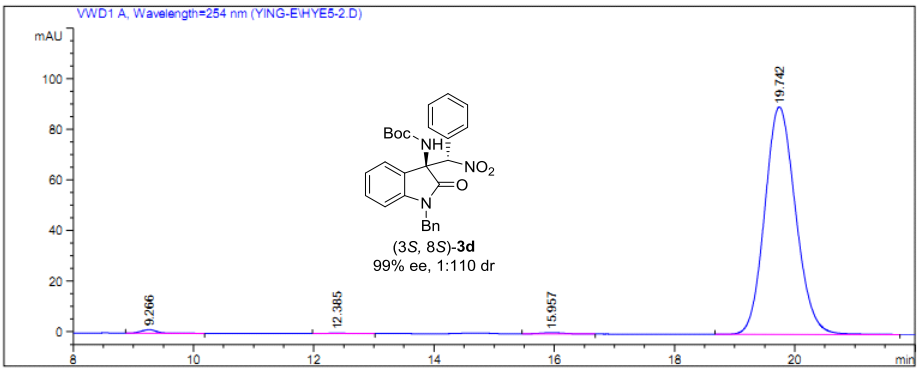
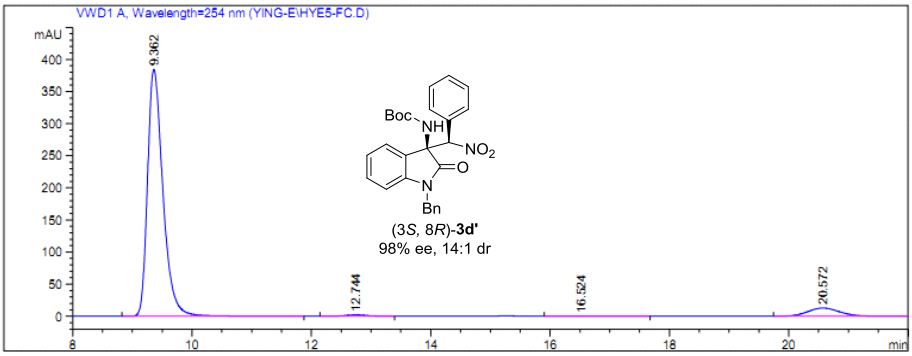


Figure S31. HPLC trace for the racemic reference *rac*-**3d** and **3d'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.266	BB	0.2814	25.50173	1.42093	0.7863
2	12.385	BB	0.3189	3.82097	1.80544e-1	0.1178
3	15.957	BB	0.4005	13.38103	4.90078e-1	0.4126
4	19.742	MF R	0.5937	3200.48633	89.84184	98.6833

Figure S32. HPLC trace for (3*S*,8*S*)-**3d**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.362	BB	0.2728	6879.32031	384.31503	92.7018
2	12.744	BB	0.3670	53.23025	2.25789	0.7173
3	16.524	BB	0.4184	5.06660	1.59585e-1	0.0683
4	20.572	VB	0.5819	483.29840	12.87540	6.5127

Figure S33. HPLC trace for (3*S*,8*R*)-**3d'**.

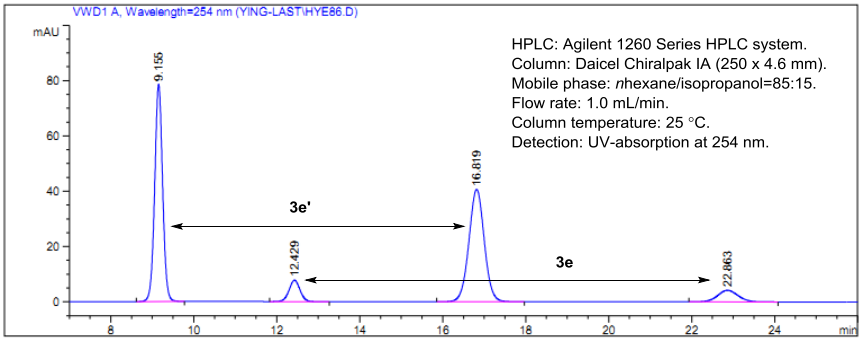
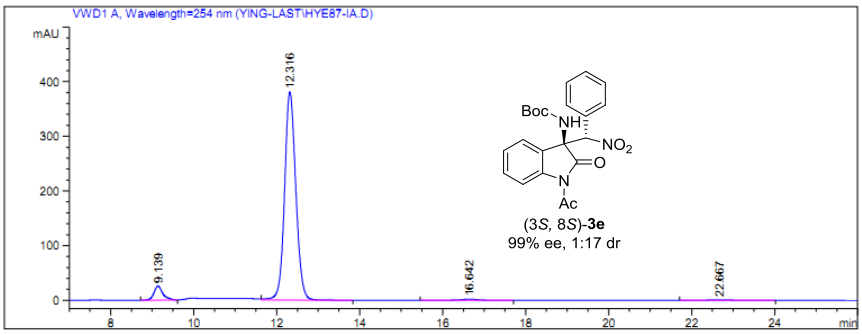
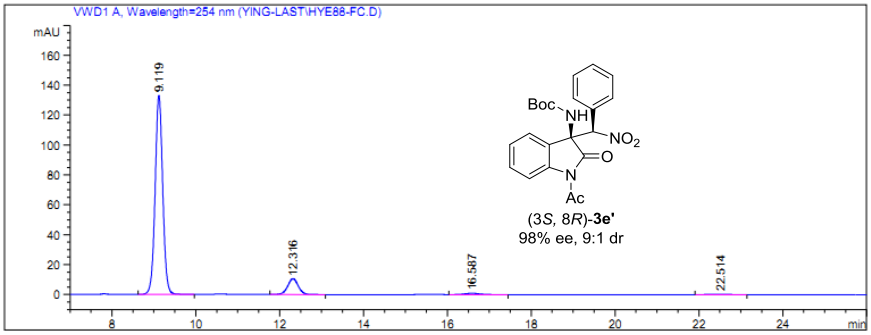


Figure S34. HPLC trace for the racemic reference *rac*-**3e** and **3e'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.155	BB	0.2039	1043.84412	78.60126	43.8883
2	12.429	BB	0.2844	143.02983	7.74828	6.0137
3	16.819	BB	0.3966	1047.72412	40.66008	44.0514
4	22.863	BB	0.5285	143.81267	4.17927	6.0466

Figure S35. HPLC trace for (3*S*,8*S*)-**3e**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.119	BB	0.1950	1676.00464	132.98952	88.8967
2	12.316	VB	0.2700	185.15691	10.58989	9.8209
3	16.587	VB	0.3693	21.79182	9.03669e-1	1.1559
4	22.514	BB	0.3986	2.38618	7.31514e-2	0.1266

Figure S36. HPLC trace for (3*S*,8*R*)-**3e'**.

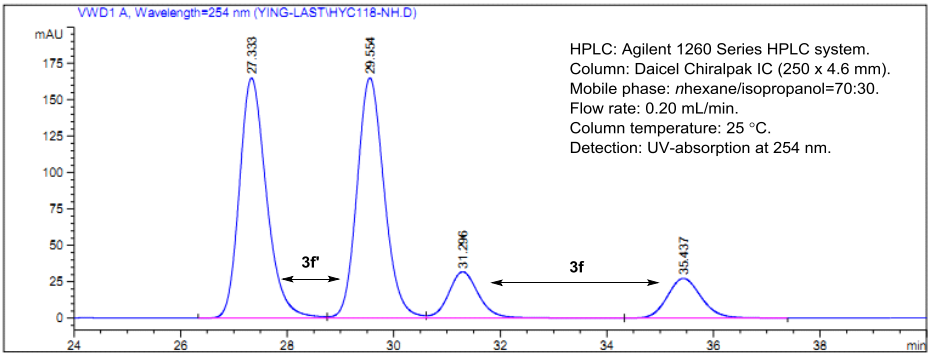
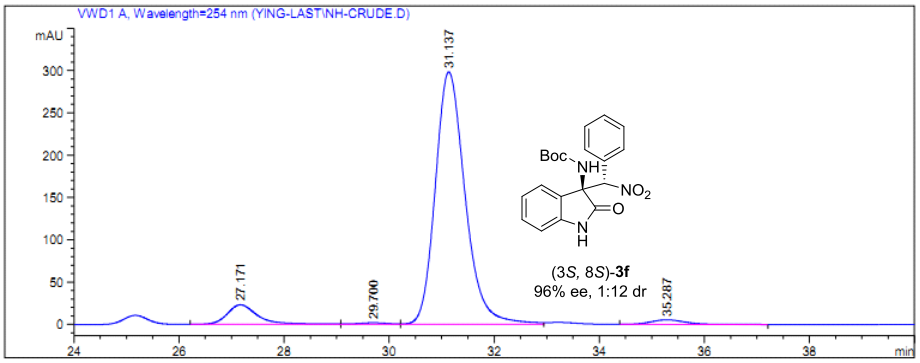
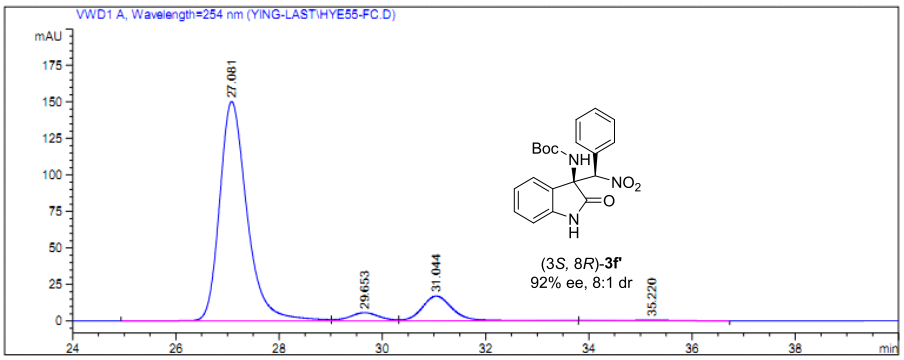


Figure S37. HPLC trace for the racemic reference *rac*-**3f** and **3f'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.171	BV	0.6093	937.73773	23.11249	7.1932
2	29.700	VV	0.5926	72.53629	1.86995	0.5564
3	31.137	VV	0.6052	1.17868e4	298.13199	90.4144
4	35.287	BB	0.6891	239.34392	5.35864	1.8360

Figure S38. HPLC trace for (3*S*,8*S*)-**3f**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.081	BV	0.5620	5531.60791	150.08560	85.7034
2	29.653	VV	0.5918	217.74260	5.57338	3.3736
3	31.044	VB	0.6149	682.39185	16.90484	10.5726
4	35.220	BB	0.7070	22.62178	4.72099e-1	0.3505

Figure S39. HPLC trace for (3*S*,8*R*)-**3f'**.

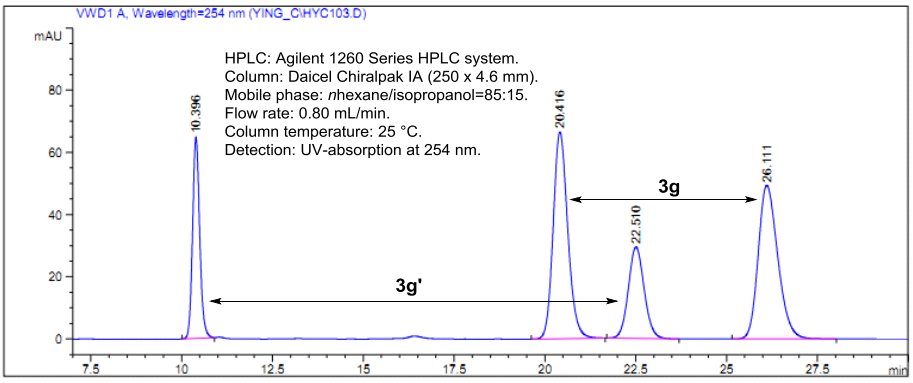
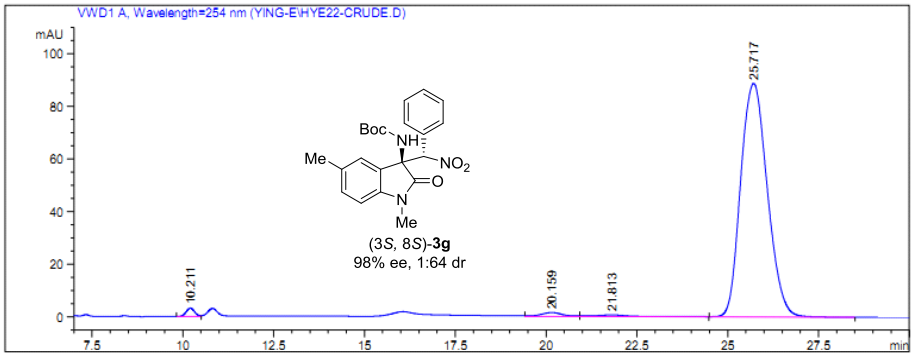
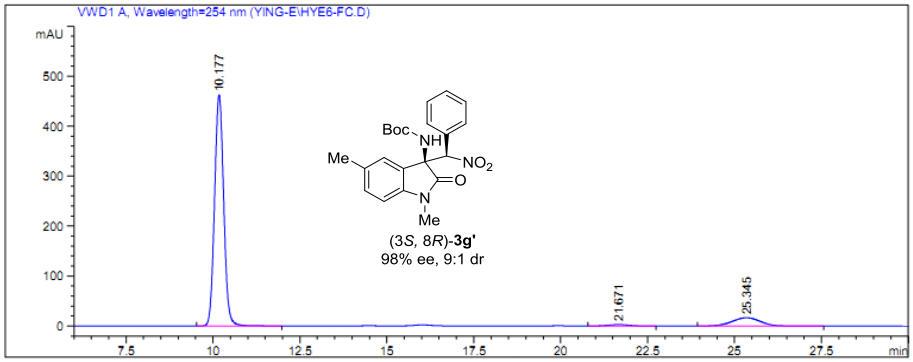


Figure S40. HPLC trace for the racemic reference *rac*-**3g** and **3g'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.211	BV	0.2548	52.35155	3.20154	1.1191
2	20.159	VV	0.6432	65.25138	1.51295	1.3948
3	21.813	VB	0.9905	44.37479	6.29446e-1	0.9486
4	25.717	BB	0.8019	4516.11035	88.71609	96.5375

Figure S41. HPLC trace for (3*S*,8*S*)-**3g**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.177	BB	0.2847	8429.01074	462.27652	89.2078
2	21.671	BB	0.5894	104.78546	2.73271	1.1090
3	25.345	BB	0.8667	914.94031	16.37924	9.6832

Figure S42. HPLC trace for (3*S*,8*R*)-**3g'**.

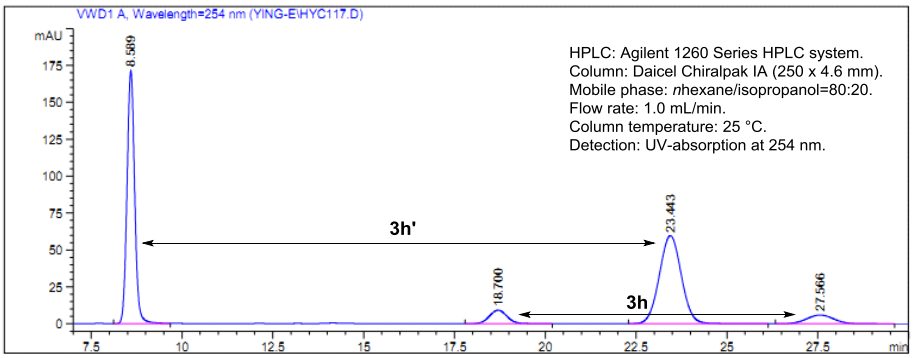
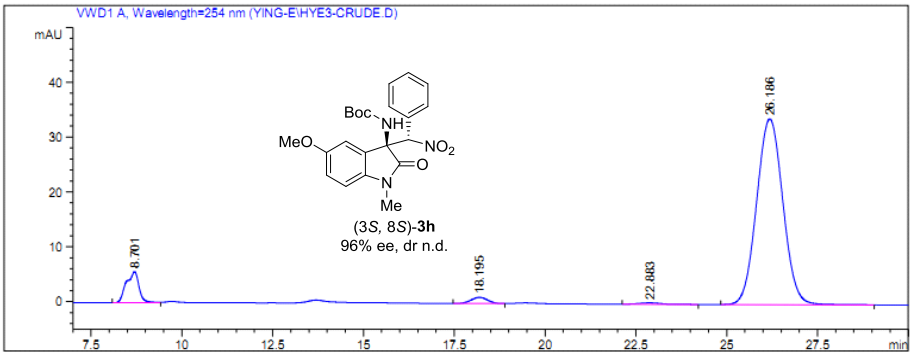
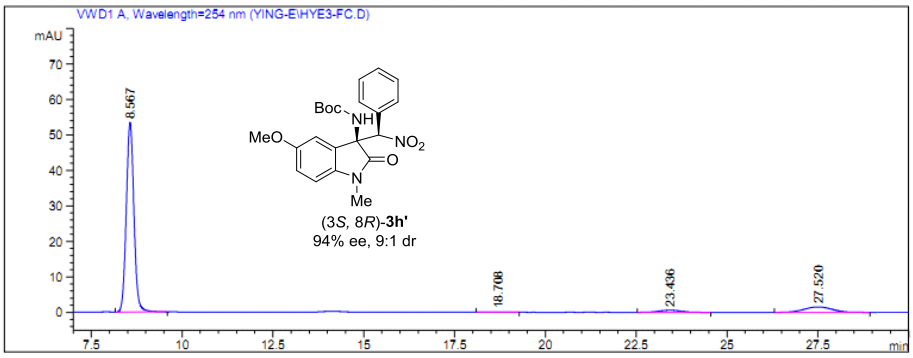


Figure S43. HPLC trace for the racemic reference *rac*-**3h** and **3h'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.701	BV	0.3311	137.46489	5.66400	7.3121
2	18.195	BB	0.5040	35.52972	1.12016	1.8899
3	22.883	BB	0.5034	11.21883	2.69630e-1	0.5968
4	26.186	BB	0.7866	1695.76245	33.84338	90.2013

Figure S44. HPLC trace for (3*S*,8*S*)-**3h**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.567	BB	0.2269	781.69531	53.37572	87.5034
2	18.708	BB	0.3962	2.69608	8.22998e-2	0.3018
3	23.436	BB	0.6403	25.66205	5.91337e-1	2.8726
4	27.520	BB	0.8057	83.27792	1.53797	9.3222

Figure S45. HPLC trace for (3*S*,8*R*)-**3h'**.

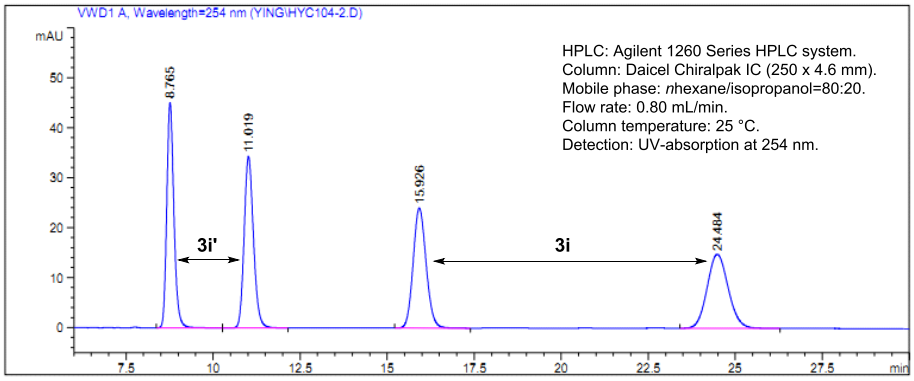
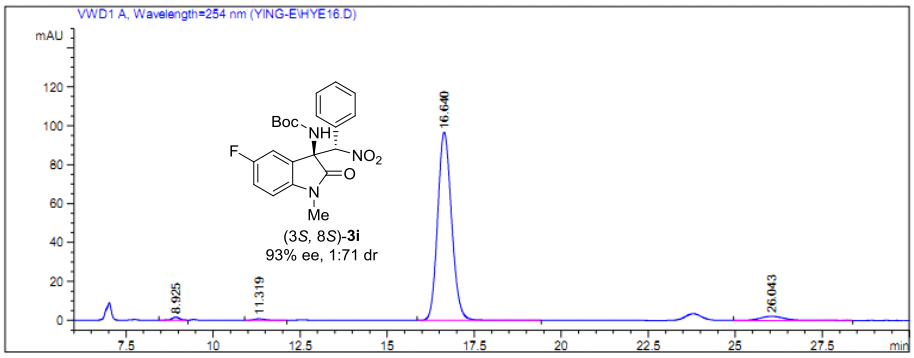
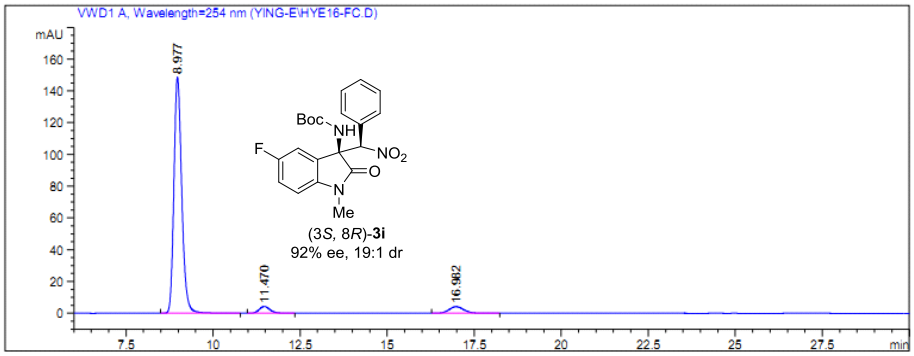


Figure S46. HPLC trace for the racemic reference *rac*-**3i** and **3i'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.925	BV	0.2380	24.70022	1.58304	0.8731
2	11.319	BB	0.3107	14.66149	7.28814e-1	0.5182
3	16.640	VB	0.4286	2688.62134	96.64401	95.0324
4	26.043	VB	0.7247	101.17937	2.15147	3.5763

Figure S47. HPLC trace for (3*S*,8*S*)-**3i**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.977	BB	0.2391	2317.44922	148.49908	91.6115
2	11.470	BB	0.3269	89.94611	4.24992	3.5557
3	16.982	BB	0.4490	122.25400	4.14562	4.8328

Figure S48. HPLC trace for (3*S*,8*R*)-**3i'**.

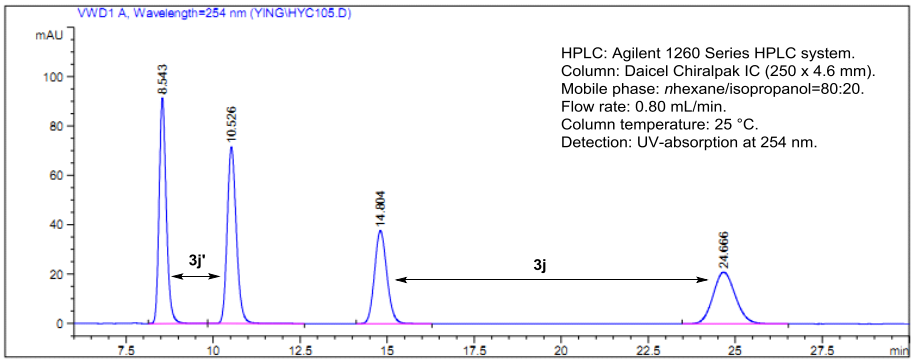
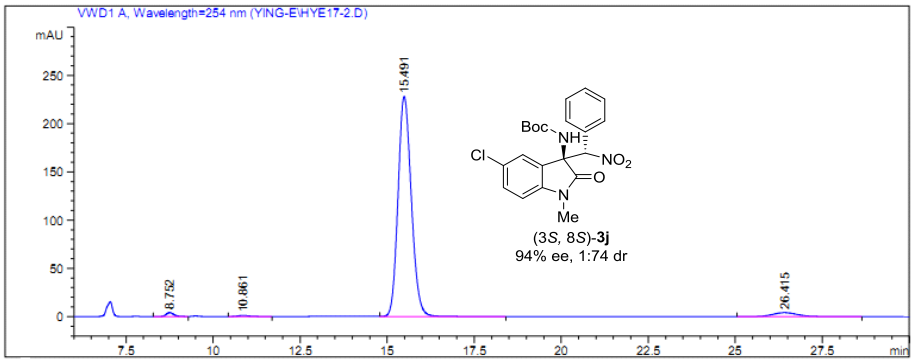
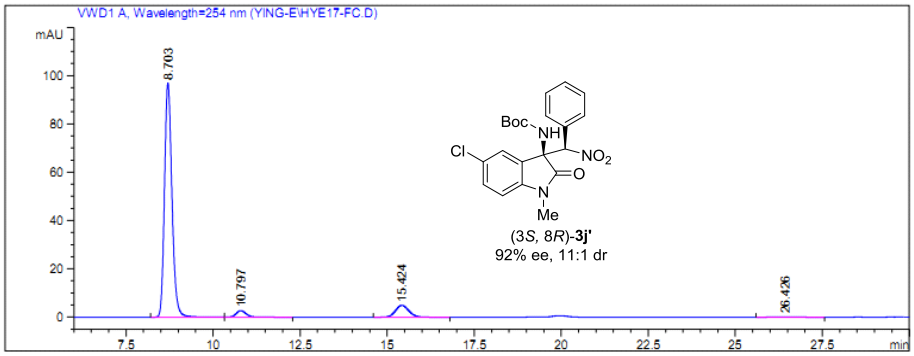


Figure S49. HPLC trace for the racemic reference *rac*-**3j** and **3j'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.752	BV	0.2407	63.06676	4.07160	0.9951
2	10.861	BB	0.3043	21.60856	1.10447	0.3410
3	15.491	VB	0.4138	6053.70605	227.98466	95.5208
4	26.415	BB	0.7586	199.19797	4.07277	3.1431

Figure S50. HPLC trace for (3*S*,8*S*)-**3j**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.703	BV	0.2258	1443.41675	96.91238	88.2772
2	10.797	VB	0.3123	54.92065	2.71138	3.3589
3	15.424	BB	0.4165	132.19112	4.93458	8.0846
4	26.426	BB	0.6342	4.56782	9.47909e-2	0.2794

Figure S51. HPLC trace for (3*S*,8*R*)-**3j'**.

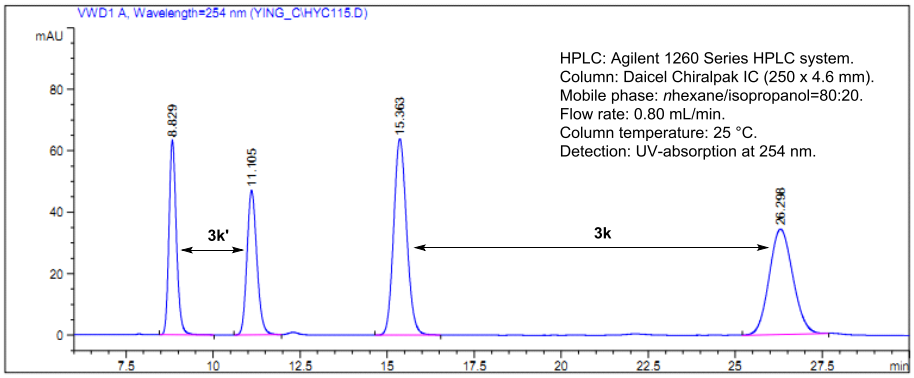
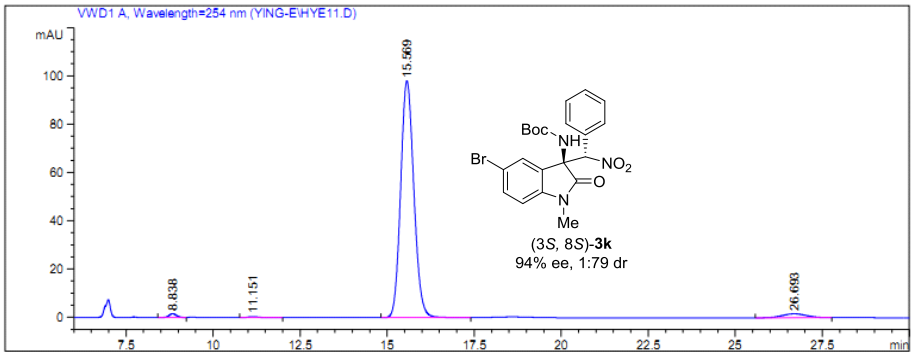
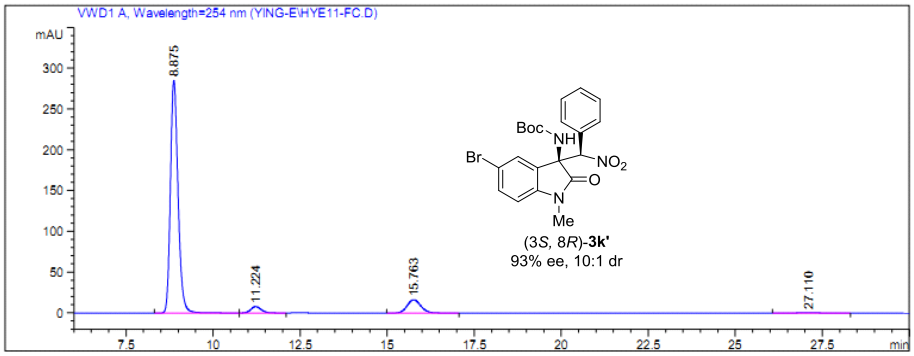


Figure S52. HPLC trace for the racemic reference *rac*-**3k** and **3k'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.838	BV	0.2358	25.14972	1.63159	0.9320
2	11.151	BB	0.3009	8.39401	4.13373e-1	0.3111
3	15.569	BB	0.4096	2586.35010	98.10064	95.8488
4	26.693	BB	0.7342	78.47199	1.64010	2.9081

Figure S53. HPLC trace for (3*S*,8*S*)-**3k**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.875	BV	0.2336	4344.86279	285.40814	87.4825
2	11.224	VV	0.3218	164.94156	7.89223	3.3210
3	15.763	BB	0.4233	440.62915	16.20318	8.8719
4	27.110	BB	0.6339	16.11860	3.26556e-1	0.3245

Figure S54. HPLC trace for (3*S*,8*R*)-**3k'**.

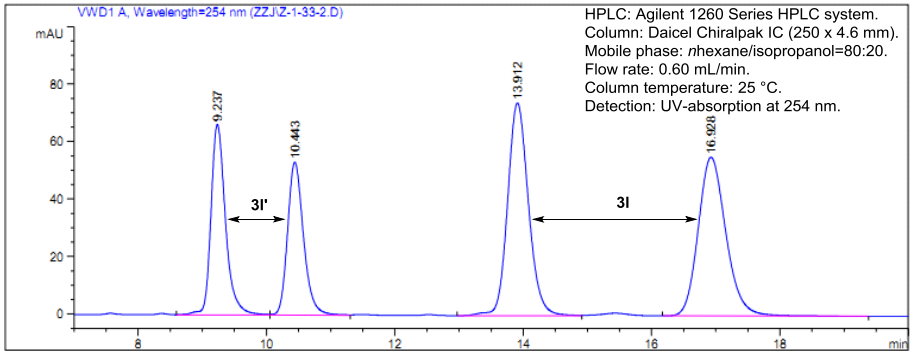
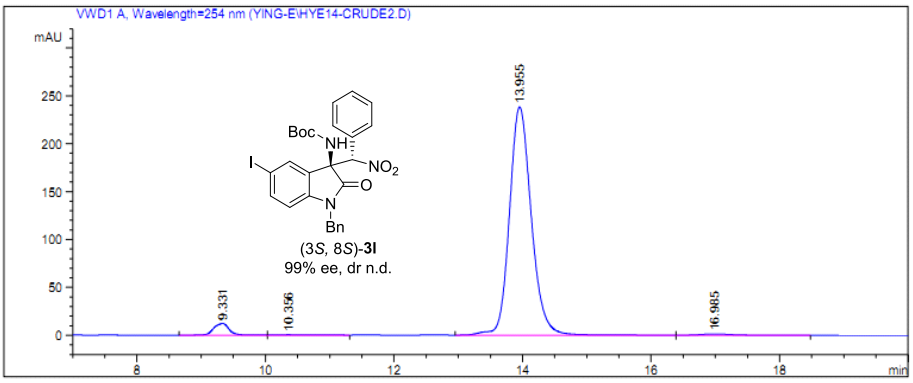
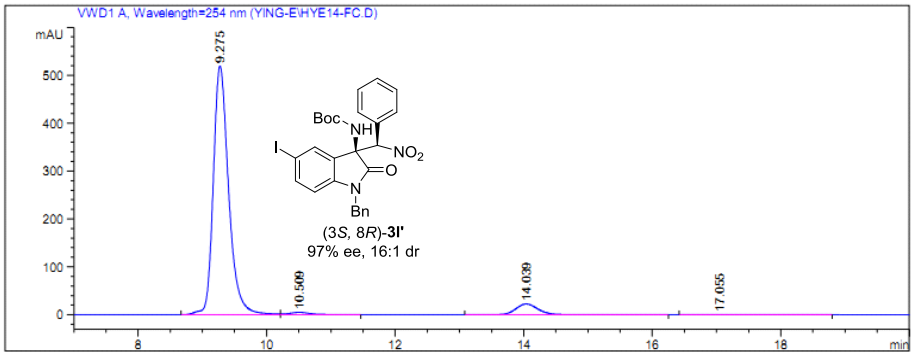


Figure S55. HPLC trace for the racemic reference *rac*-**3l** and **3l'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.331	BV	0.2737	213.74556	12.36103	3.6174
2	10.356	VV	0.4309	17.81842	5.42984e-1	0.3016
3	13.955	VV	0.3600	5634.73682	238.19835	95.3613
4	16.985	VB	0.4844	42.52639	1.36162	0.7197

Figure S56. HPLC trace for (3*S*,8*S*)-**3l**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.275	BV	0.2517	8623.59668	519.42993	92.7778
2	10.509	VV	0.3507	118.80552	4.93870	1.2782
3	14.039	BB	0.3760	546.87946	22.46769	5.8837
4	17.055	BB	0.4636	5.61464	1.65588e-1	0.0604

Figure S57. HPLC trace for (3*S*,8*R*)-**3l'**.

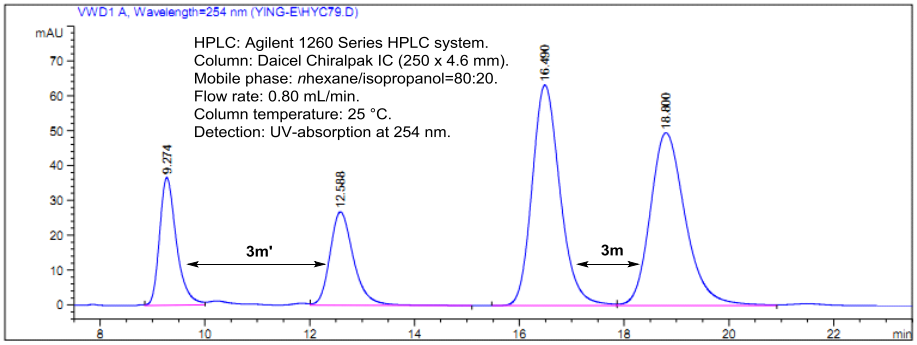
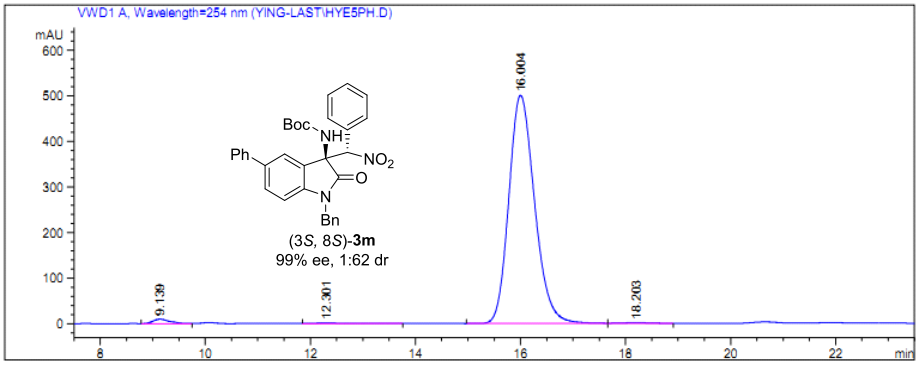
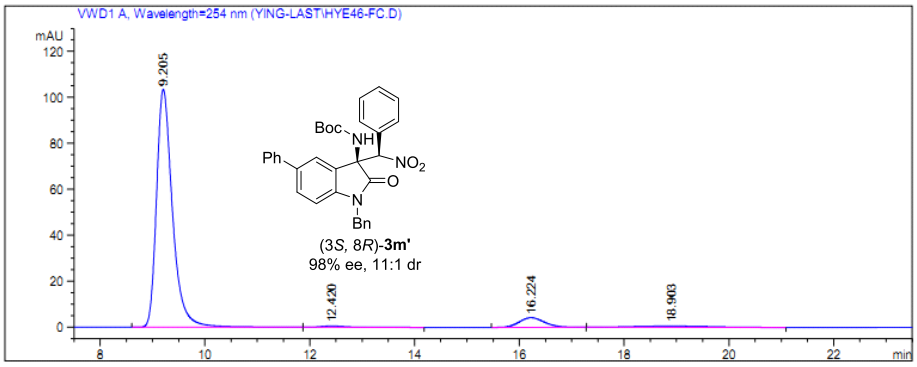


Figure S58. HPLC trace for the racemic reference *rac*-**3m** and **3m'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.139	VV	0.3362	227.39043	10.04233	1.3025
2	12.301	VB	0.6104	49.77075	1.15582	0.2851
3	16.004	BV	0.5303	1.70875e4	500.48105	97.8801
4	18.203	VV	0.6835	92.91899	2.02427	0.5323

Figure S59. HPLC trace for (3*S*,8*S*)-**3m**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.205	BV	0.3209	2192.22461	103.58016	90.9005
2	12.420	VB	0.4852	19.60128	6.03016e-1	0.8128
3	16.224	BB	0.5189	140.86783	4.20436	5.8411
4	18.903	MF R	1.6899	58.98087	5.81692e-1	2.4456

Figure S60. HPLC trace for (3*S*,8*R*)-**3m'**.

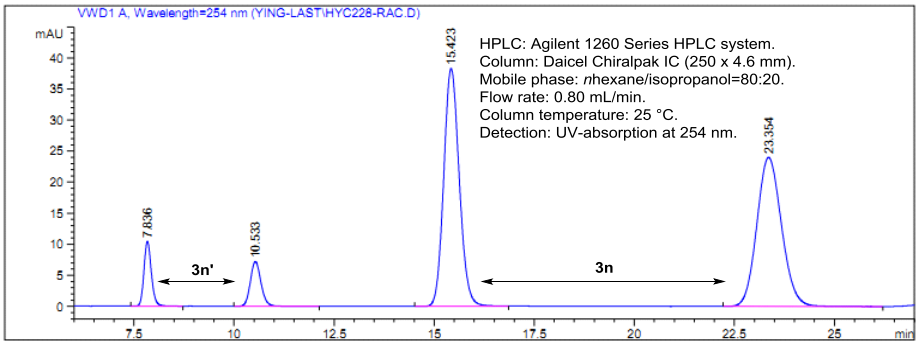
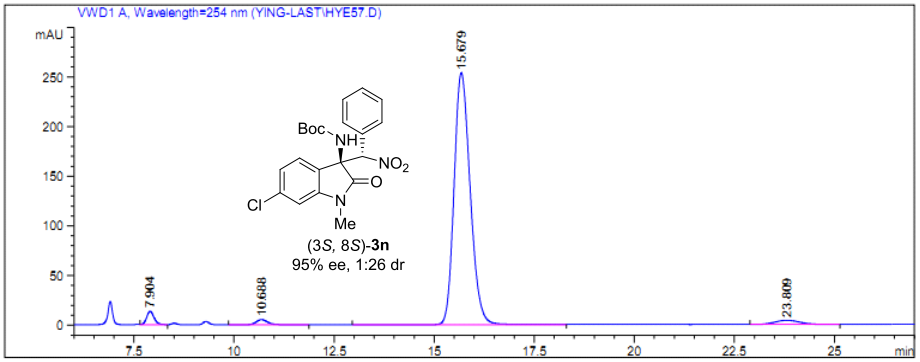
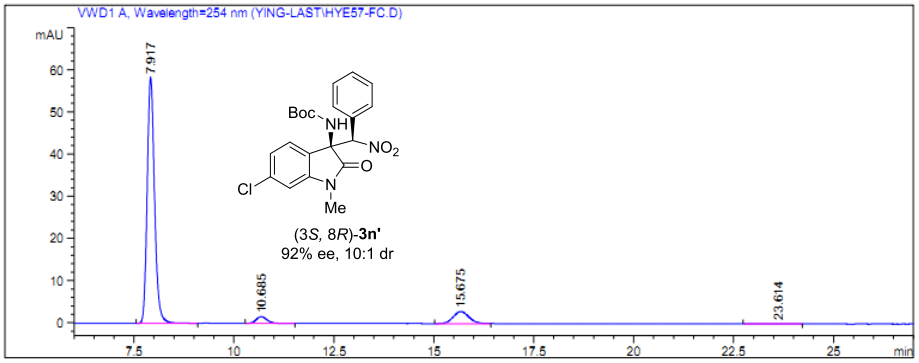


Figure S61. HPLC trace for the racemic reference *rac*-**3n** and **3n'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.904	VV R	0.1994	174.89627	13.47454	2.3143
2	10.688	BV	0.3079	102.73802	5.16769	1.3595
3	15.679	VV	0.4344	7089.93262	253.39262	93.8187
4	23.809	MF R	0.7427	189.49338	4.25231	2.5075

Figure S62. HPLC trace for (3*S*,8*S*)-**3n**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.917	VV	0.1976	747.95593	58.31061	86.8802
2	10.685	VV	0.2930	30.35031	1.60206	3.5254
3	15.675	MF R	0.4578	78.82301	2.86984	9.1558
4	23.614	MF R	0.8013	3.77579	7.85333e-2	0.4386

Figure S63. HPLC trace for (3*S*,8*R*)-**3n'**.

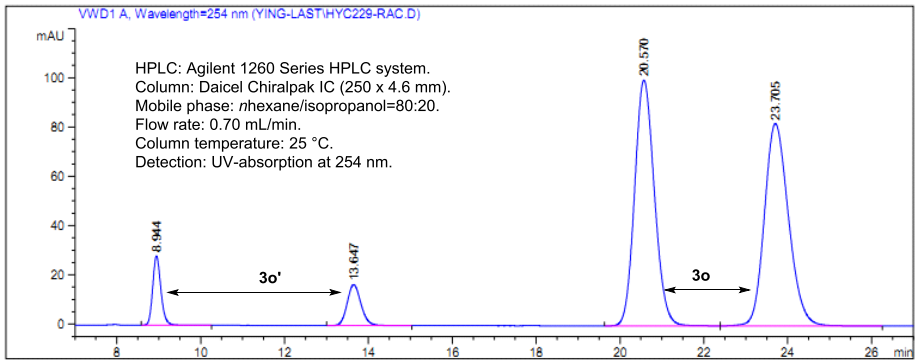
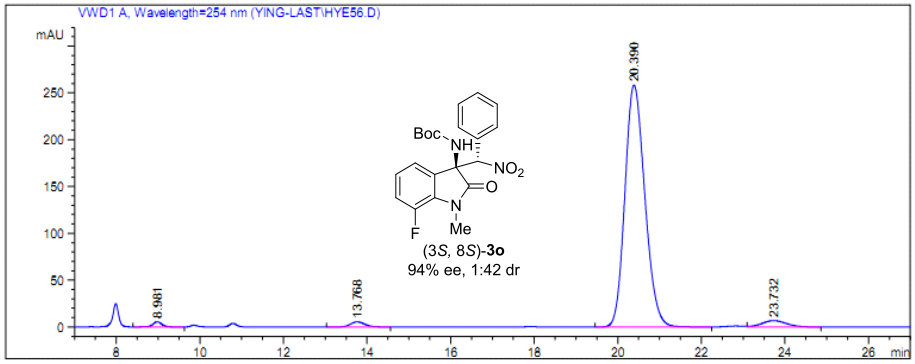
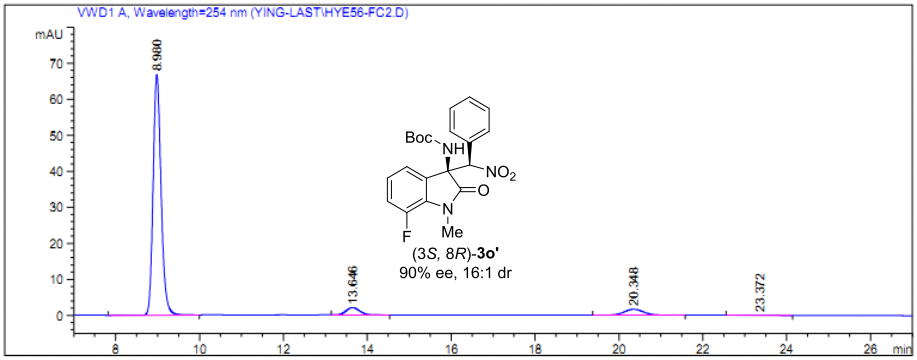


Figure S64. HPLC trace for the racemic reference *rac*-**3o** and **3o'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.981	VV	0.2306	82.58010	5.51933	0.9115
2	13.768	FM R	0.4005	132.00522	5.49306	1.4571
3	20.390	BB	0.5148	8565.62500	258.35818	94.5468
4	23.732	MF R	0.6819	279.45837	6.83052	3.0846

Figure S65. HPLC trace for (3*S*,8*S*)-**3o**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.980	BV	0.2070	886.92645	66.75451	89.6005
2	13.646	VB	0.3488	46.16574	2.06520	4.6638
3	20.348	BB	0.5001	52.98969	1.62636	5.3532
4	23.372	MF R	0.7549	3.78628	8.35906e-2	0.3825

Figure S66. HPLC trace for (3*S*,8*R*)-**3o'**.

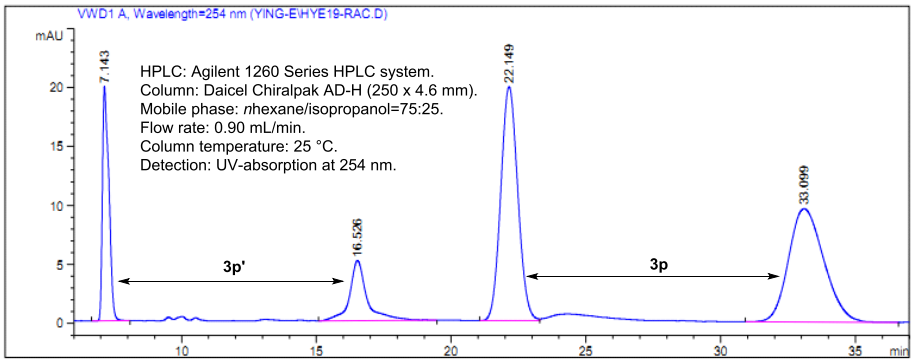
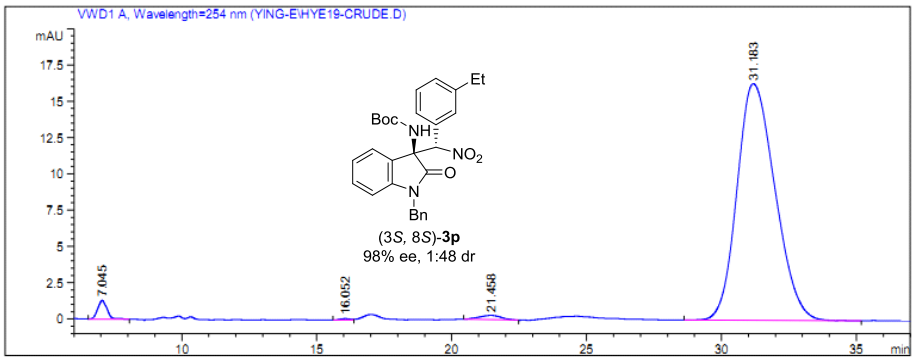
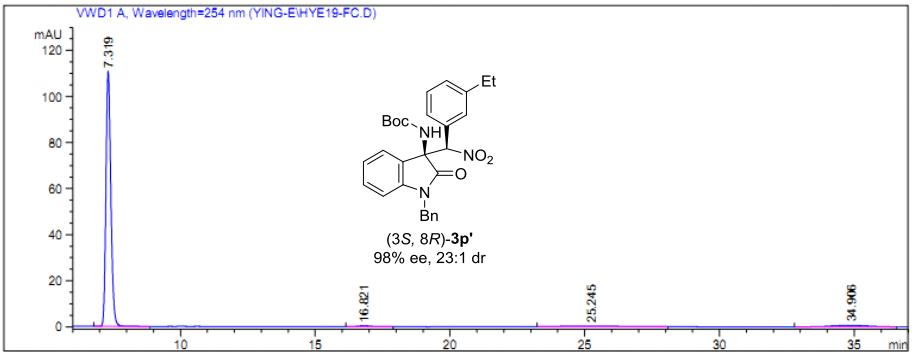


Figure S67. HPLC trace for the racemic reference *rac*-**3p** and **3p'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.045	BB	0.3615	31.49682	1.30543	1.9039
2	16.052	BV	0.4054	2.56577	9.93317e-2	0.1551
3	21.458	BB	0.8536	17.45275	3.00502e-1	1.0550
4	31.183	BB	1.5225	1602.84131	16.31026	96.8861

Figure S68. HPLC trace for (3*S*,8*S*)-**3p**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.319	MF R	0.2110	1403.53503	110.87191	92.6424
2	16.821	BB	0.5167	12.23819	3.75004e-1	0.8078
3	25.245	BB	1.6396	37.51498	2.73618e-1	2.4762
4	34.906	MF R	1.5672	61.71421	6.56296e-1	4.0735

Figure S69. HPLC trace for (3*S*,8*R*)-**3p'**.

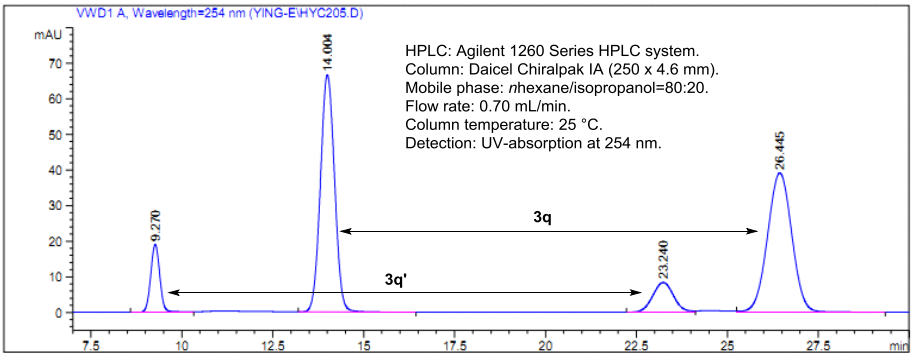
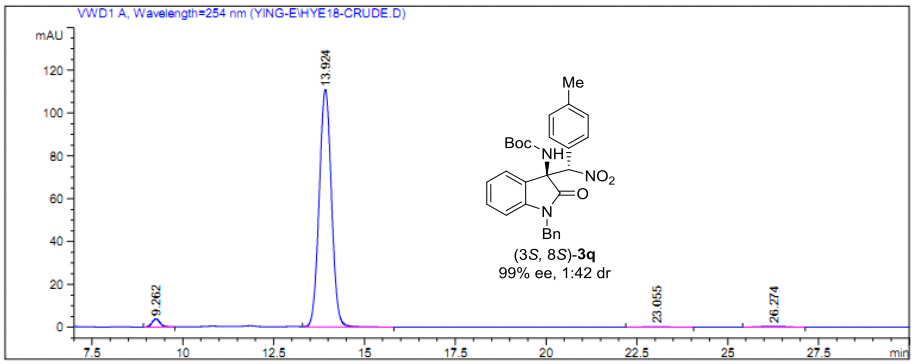
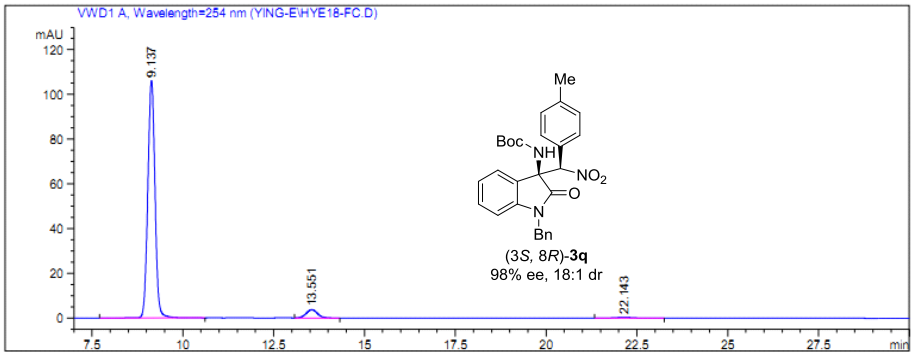


Figure S70. HPLC trace for the racemic reference *rac*-**3q** and **3q'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.262	BB	0.2353	56.00839	3.72685	2.0897
2	13.924	VB	0.3675	2600.13501	110.91512	97.0139
3	23.055	BB	0.5124	6.67760	1.69951e-1	0.2491
4	26.274	BB	0.6105	17.34739	3.99569e-1	0.6473

Figure S71. HPLC trace for (3*S*,8*S*)-**3q**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.137	BB	0.2161	1455.87219	106.06338	93.8773
2	13.551	VB	0.3445	81.40627	3.70341	5.2492
3	22.143	BB	0.5630	13.54640	3.56757e-1	0.8735

Figure S72. HPLC trace for (3*S*,8*R*)-**3q'**.

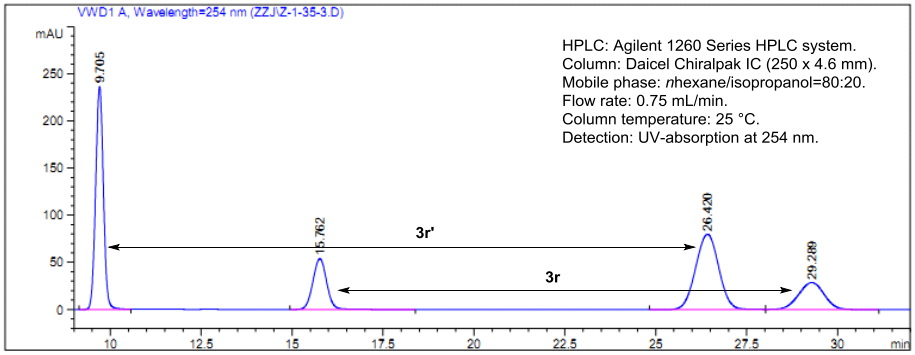
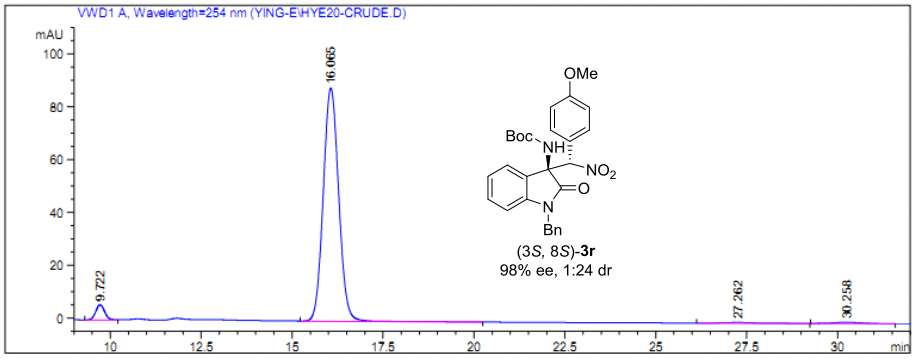
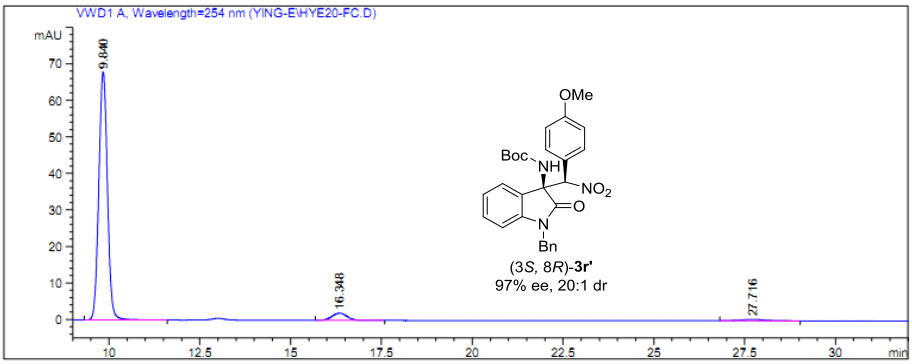


Figure S73. HPLC trace for the racemic reference *rac*-**3r** and **3r'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.722	BV	0.2699	99.65511	5.75902	3.6367
2	16.065	BB	0.4640	2602.17676	88.24977	94.9613
3	27.262	BB	0.7155	14.52029	2.78843e-1	0.5299
4	30.258	BB	0.8272	23.89751	4.50297e-1	0.8721

Figure S74. HPLC trace for (3*S*,8*S*)-**3r**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.840	MF R	0.2742	1116.83252	67.89610	93.7655
2	16.348	BB	0.4509	56.63912	1.96148	4.7552
3	27.716	BB	0.5792	17.61961	3.65006e-1	1.4793

Figure S75. HPLC trace for (3*S*,8*R*)-**3r'**.

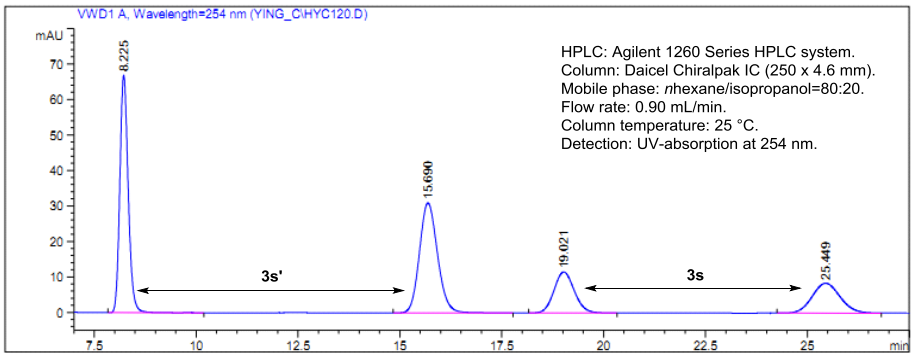
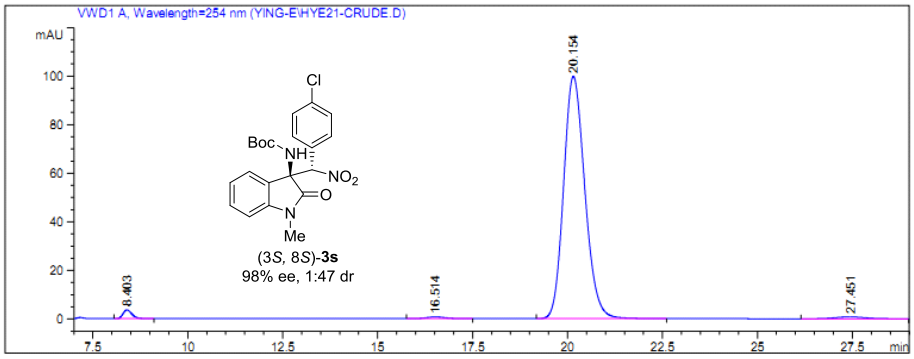
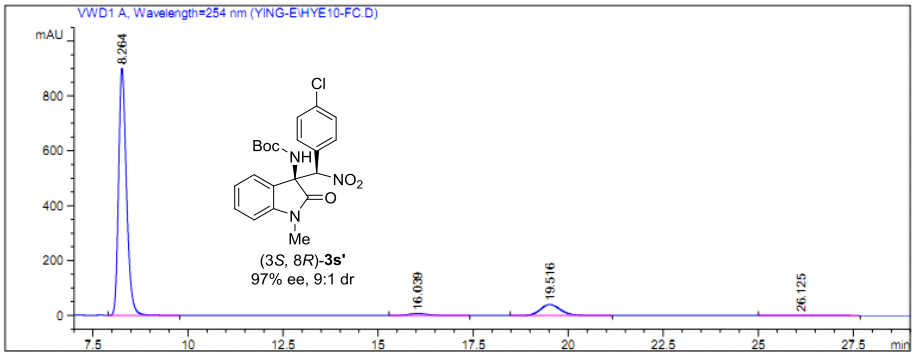


Figure S76. HPLC trace for the racemic reference *rac*-**3s** and **3s'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.403	BB	0.2495	58.31879	3.59137	1.4592
2	16.514	BB	0.5197	24.14027	6.94279e-1	0.6040
3	20.154	MF R	0.6468	3871.26538	99.75557	96.8644
4	27.451	MF R	0.9178	42.85899	7.78277e-1	1.0724

Figure S77. HPLC trace for (3*S*,8*S*)-**3s**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.264	BV	0.2245	1.31578e4	900.33423	88.5604
2	16.039	MF R	0.5381	229.42641	7.10641	1.5442
3	19.516	MF R	0.6061	1444.43335	39.71957	9.7219
4	26.125	MF R	0.8612	25.77541	4.98801e-1	0.1735

Figure S78. HPLC trace for (3*S*,8*R*)-**3s'**.

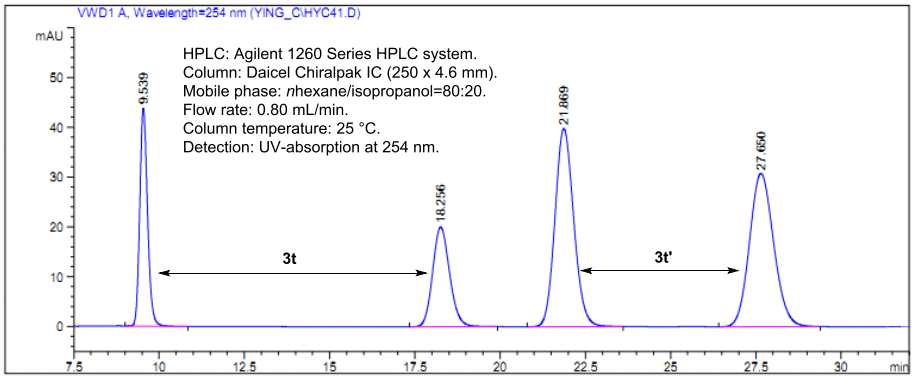
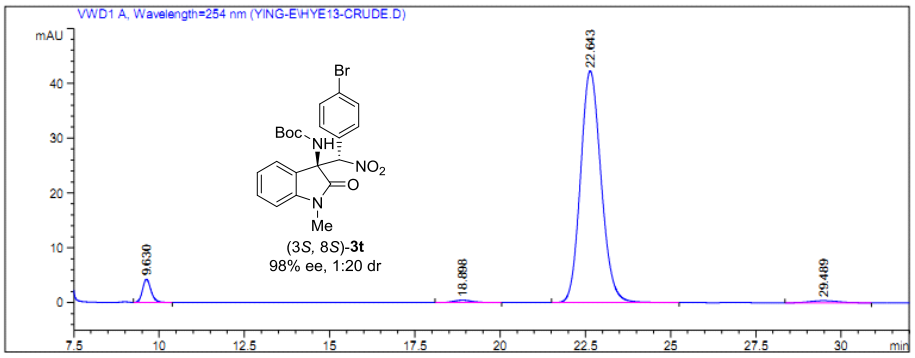
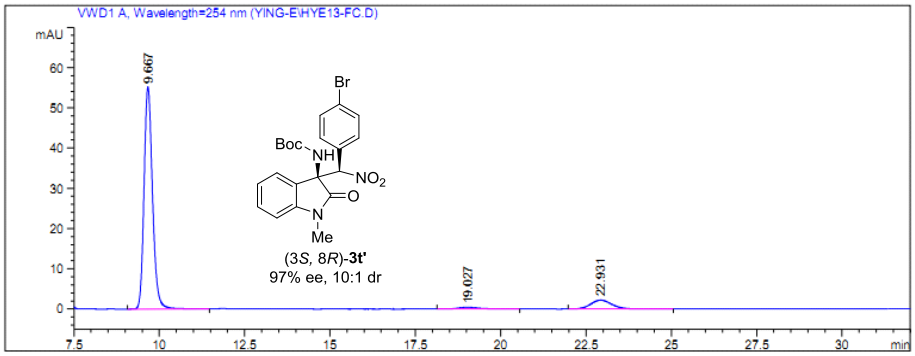


Figure S79. HPLC trace for the racemic reference *rac*-**3t** and **3t'**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.630	VB	0.2667	73.98442	4.25927	3.9281
2	18.898	BB	0.5635	16.36355	4.30502e-1	0.8688
3	22.643	BB	0.6495	1772.29004	42.24362	94.0971
4	29.489	BB	0.6544	20.83076	3.79510e-1	1.1060

Figure S80. HPLC trace for (3*S*,8*S*)-**3t**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.667	BB	0.2648	949.68799	55.19099	89.3372
2	19.027	BB	0.6236	18.49158	4.25007e-1	1.7395
3	22.931	BB	0.6617	94.85851	2.19719	8.9233

Figure S81. HPLC trace for (3*S*,8*R*)-**3t'**.

9. Single Crystal X-Ray Diffraction

9.1 Substrate (*Z*)-1k

Crystals of (*Z*)-**1k** were obtained by slow diffusion from a solution in CH_2Cl_2 layered with *n*hexane. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97[4]. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S82. Crystallographic information is listed in the Table S4.

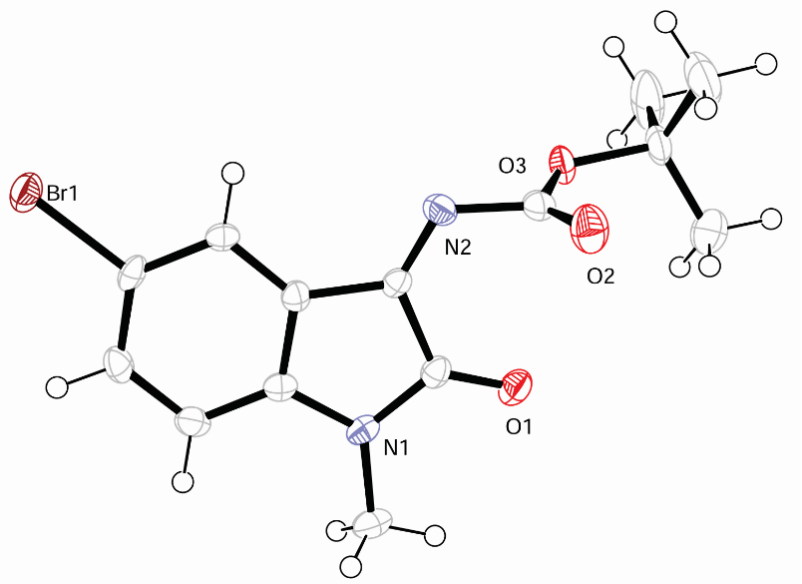


Figure S82. Ortep drawing of ketimine (*Z*)-**1k** with 50% probability thermal ellipsoids. Coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1060112).

Table S4. Crystal data and structure refinement for (*Z*)-**1k**.

Identification code	(*Z*)-**1k**	
Empirical formula	C14 H15 Br N2 O3	
Formula weight	339.19	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 7.1573(4) Å	α = 90°
	b = 21.4898(9) Å	β = 90°
	c = 9.4975(4) Å	γ = 90°
Volume	1460.80(12) $Å^3$	
Z	4	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	2.822 mm^{-1}	
F(000)	688	
Crystal size	0.20 x 0.15 x 0.12 mm^3	
Theta range for data collection	3.42 to 25.98°.	
Index ranges	-8<=h<=7, -26<=k<=24, -8<=l<=11	
Reflections collected	3518	
Independent reflections	2200 [R(int) = 0.0289]	
Completeness to theta = 25.98°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7282 and 0.6022	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2200 / 1 / 181	
Goodness-of-fit on F^2	0.999	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0787	
R indices (all data)	R1 = 0.0376, wR2 = 0.0811	
Absolute structure parameter	0.002(13)	
Largest diff. peak and hole	0.647 and -0.744 $e.Å^{-3}$	

9.2 Compound (*3S*,*8R*)-3k'

Crystals of product **3k'** were obtained by slow diffusion from the solution in CH_2Cl_2 layered with *n*hexane. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F^2 data of one twin domain using SHELXL-97[4]. The absolute configuration was determined. The structure is shown in Figure S83. Crystallographic information is listed in the Table S5.

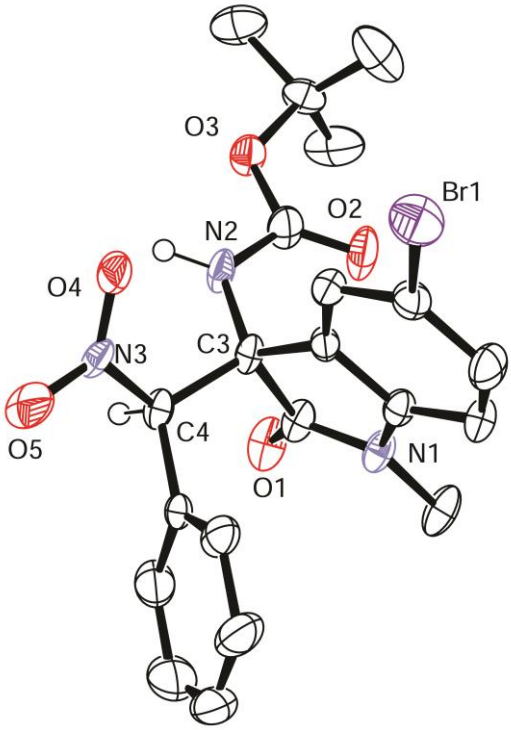


Figure S83. Ortep drawing of. product **3k'** with 50% probability thermal ellipsoids, the absolute configuration was identified as 3*S*, 8*R*. Coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC number 1060102).

Table S5. Crystal data and structure refinement for (3*S*,8*R*)-**3k'**.

Identification code	(3*S*,8*R*)-**3k'**	
Empirical formula	C21 H22 Br N3 O5	
Formula weight	476.33	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.8915(4) Å	α= 90°
	b = 9.4814(4) Å	β= 102.048(4)°
	c = 11.9420(5) Å	γ= 90°
Volume	1095.31(8) $Å^3$	
Z	2	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	1.913 mm^{-1}	
F(000)	488	
Crystal size	0.30 x 0.30 x 0.10 mm^3	
Theta range for data collection	3.49 to 26.00°.	
Index ranges	-12<=h<=5, -11<=k<=11, -13<=l<=14	
Reflections collected	4375	
Independent reflections	3468 [R(int) = 0.0242]	
Completeness to theta = 26.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8317 and 0.5976	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3468 / 1 / 271	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.1030	
R indices (all data)	R1 = 0.0403, wR2 = 0.1077	
Absolute structure parameter	0.002(9)	
Largest diff. peak and hole	0.375 and -0.237 e.$Å^{-3}$	

10. References

[1] R. R. Walvoord, S. Berritt, M. C. Kozlowski, *Org. Lett.* **2012**, *14*, 4086-4089.

[2] J. Ma, X. Ding, Y. Hu, Y. Huang, L. Gong, E. Meggers, *Nat. Commun.* **2014**, *5*, 4531.

[3] W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett.* **2012**, *14*, 2512-2515.

[4] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.