Supporting Information

Asymmetric tandem conjugate addition−protonation to forge chiral secondary C−O bond for quaternary carbon stereocenters at the nonadjacent β-position

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1. General information

General Procedures and Methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reactions mixtures were stirred in 10 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in vacuo under ~30 mmHg and heated with a water bath at 30–35 °C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 °C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $KMnO_4$, ceric molybdate, or anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 200-300 mesh. Columns were packed as slurry of *silica gel* in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2.0 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (^{1}H NMR), carbon NMR (^{13}C NMR) were recorded in $CDCl_3$ otherwise stated. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). HRMS was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in CH_3CN (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]_{\lambda}^{T^{\circ}C}$ (c = g/100 mL, solvent). Melting points were determined on a melting point apparatus.

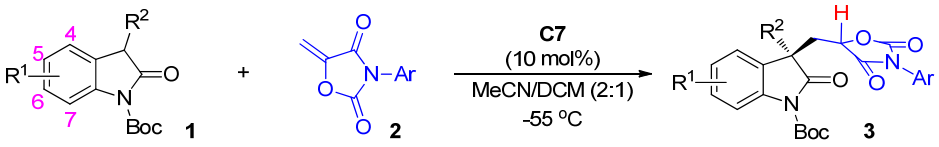
Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm, 230 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Materials

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous dichloromethane (DCM) and CH_3CN were freshly distilled from CaH_2 and stored under N_2 atmosphere. Tetrahydrofuran (THF) and Et_2O were freshly distilled from

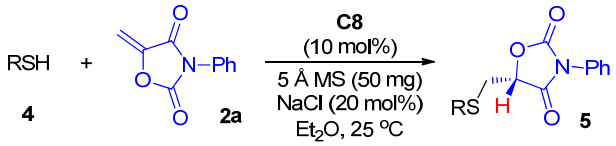
sodium/benzophenone before use. All compounds synthesized were stored in a −20 ^{o}C freezer and light−sensitive compounds were protected with aluminium foil.

2. General experimental procedure for asymmetric conjugate addition-protonation of 3-substituted oxindoles 1 to methylene 1,3-oxazolidine-2,4-diones 2



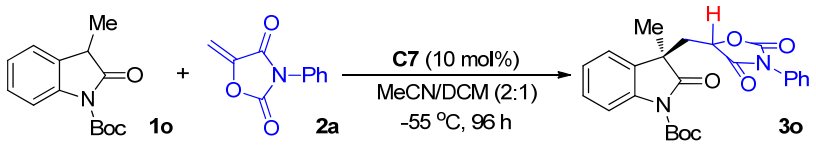
3-Substituted oxindole **1** (0.12 mmol, 1.2 equiv) and catalyst **C7** (4.0 mg, 0.01 mmol, 0.1 equiv) were dissolved in MeCN/DCM = 2:1 (2.0 mL), and stirred at −55 °C for 10 min. Then methylene 1,3-oxazolidine-2,4-dione **2** (0.1 mmol, 1.0 equiv) was added. The reaction mixture was stirred at −55 °C and monitored by TLC. Upon complete consumption of **2**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with PE/EA mixture (20/1−5/1 ratio). Removing the solvent *in vacuo*, afforded adduct **3**.

3. General experimental procedure for asymmetric conjugate addition-protonation of thiols 4 to methylene 1,3-oxazolidine-2,4-diones 2



Thiol **4** (0.15 mmol, 1.5 equiv), NaCl (0.02 mmol, 0.2 equiv), molecular sieves (MS) of 5 Å (50mg) and catalyst **C8** (4.2 mg, 0.01 mmol, 0.1 equiv) were dissolved in Et_2O (2.0 mL) and stirred at 25 ^oC for 10 minutes. Methylene 1,3-oxazolidine-2,4-dione **2a** (0.1 mmol, 1.0 equiv) was added. The reaction mixture was stirred at 25 ^oC and monitored by TLC. Upon complete consumption of methylene **2a**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with PE/EA mixture (20/1−7/1 ratio). Removing the solvent *in vacuo*, afforded adduct **5**.

4. Experimental procedure for gram-scale preparation of 3o

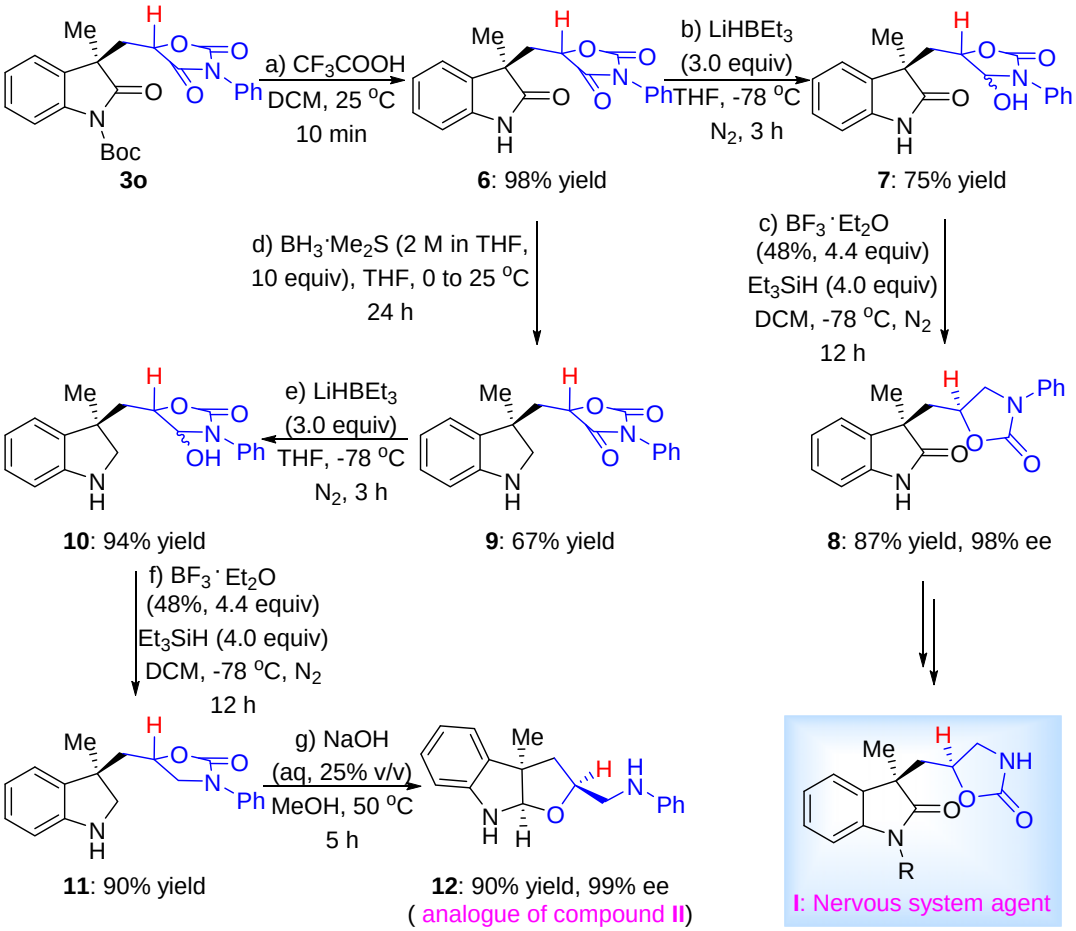


3.0 mmol scale

96% yield (1.25 g)
99% ee, >20:1 dr

3-Substituted oxindole **1o** (3.6 mmol, 1.2 equiv) and catalyst **C7** (120 mg, 0.3 mmol, 0.1 equiv) were dissolved in MeCN/DCM = 2:1 (60 mL), and stirred at −55 °C for 10 minutes. Then methylene 1,3-oxazolidine-2,4-dione **2a** (3.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred at −55 °C and monitored by TLC. Upon complete consumption of **2a**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with PE/EA mixture (20/1−5/1 ratio). Removing the solvent *in vacuo*, afforded adduct **3o** (1.25 g, 96% yield, 99% ee, > 20:1 dr).

5. Experimental procedures for transformations of the corresponding protonation products



a) 3o (350.0 mg, 0.8 mmol) was dissolved in dry CH_2Cl_2 (32 mL), TFA (1.6 mL) was then added dropwise. The resulting mixture was stirred for 10 minutes at 25 °C and evaporated *in vacuo*. The residue was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (3/1 ratio) to give a white solid **6** (263.6 mg) in 98% yield.

b) A 1.0 M solution of lithium triethylborohydride in THF (1.17 mL, 1.17 mmol) was added to a solution of **6** (131.8 mg, 0.39 mmol,) at –78 °C under nitrogen atmosphere. After 3 hours, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1.8 mL) and warmed to 0 °C. 30% H_2O_2 (3 drops) was added and the mixture was stirred at 0 °C. After 20 minutes, the organic solvent was removed *in vacuo*, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (1/1 ratio) to give a colorless oil **7** (99.0 mg) in 75% yield.

c) A solution of **7** (99.0 mg, 0.30 mmol,) and triethylsilane (0.10 mL, 0.6 mmol) in CH_2Cl_2 (6 mL) was cooled at –78 °C and 48% boron trifluoride diethyl etherate (0.17 mL, 0.66 mmol) was added dropwise under nitrogen atmosphere. After 30 minutes, 0.10 mL of triethylsilane and 0.17 mL of boron trifluoride

diethyl etherate were added. The resulting mixture was stirred 12 hours at –78 °C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL), extracted with CH_2Cl_2 (3 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent at reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (3/1 ratio) to give a yellow oil **8** (84.0 mg) in 87% yield.

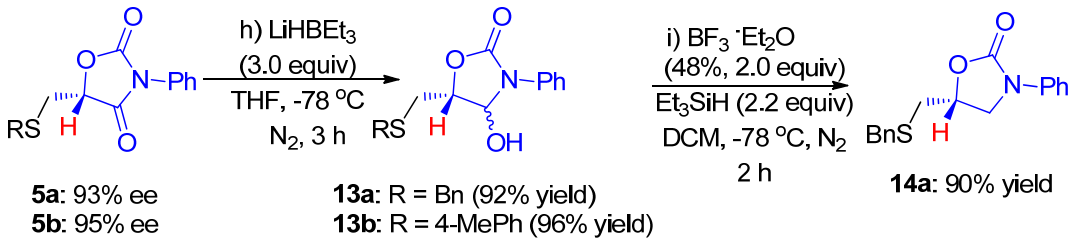
d) The above solid **6** (131.8 mg, 0.39 mmol) was dissolved in dry THF (20 mL), and the solution was cooled at 0 °C by ice bath. BH_3•Me_2S (3.9 mmol, 1.92 mL, 2 M in THF) was then added dropwise over 30 minutes and after removal of the cooling bath the mixture was stirred at room temperature for 24 hours. The excess of BH_3 was eliminated by dropwise addition of MeOH (1.5 mL) at 0 °C. After removal of the solvent under reduced pressure, the residue was dissolved in MeOH (2.0 mL) and then 37% HCl (0.4 mL) was added. The mixture was stirred for 1.0 hours and the solvent was then evaporated at reduced pressure. The reaction mixture was dissolved in 4 *N* NaOH (1.2 mL) and the resulting solution was saturated with NaCl. The solution was extracted with CH_2Cl_2 (3 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent at reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture(5:1) to afford colorless oil **9** (84.2 mg) in 67% yield.

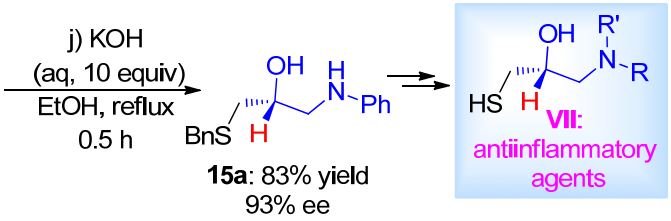
e) A 1.0 M solution of lithium triethylborohydride in THF (0.78 mL, 0.78 mmol) was added to a solution of **9** (84.0 mg, 0.26 mmol,) at –78 °C under nitrogen atmosphere. After 3 hours, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1.2 mL) and warmed to 0 °C. 30% H_2O_2 (2 drops) was added and the mixture was stirred at 0 °C. After 20 minutes, the organic solvent was removed *in vacuo*, and the aqueous layer was extracted with CH_2Cl_2 (3 × 7 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (3/1 ratio) to give a colorless oil **10** (79.3 mg) in 94% yield.

f) A solution of **10** (79.3 mg, 0.24 mmol,) and triethylsilane (80 uL, 0.48 mmol) in CH_2Cl_2 (5 mL) was cooled at –78 °C and 48% boron trifluoride diethyl etherate (0.14 mL, 0.53 mmol) was then added dropwise under nitrogen atmosphere. After 30 minutes, 80 μL of triethylsilane and 0.14 mL of boron trifluoride diethyl etherate were added. The resulting mixture was stirred 12 hours at –78 °C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (0.8 mL), extracted with CH_2Cl_2 (3 × 8 mL) and dried over Na_2SO_4. After evaporation of the solvent at reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (4/1 ratio) gave a yellow oil **11** (66.5 mg) in 90% yield.

g) A 25% NaOH solution (0.66 mL) was added in one portion to a solution of **11** (66.5 mg, 0.22 mmol) in methanol (2.5 mL). The mixture was heated at 50 °C for 5.0 hours. Then, water (3.5 mL) was added, and the methanol was removed under reduced pressure. The aqueous phase was acidified (to pH ~ 7) by the addition of concentrated HCl, and then extracted with EtOAc (3 × 4 mL). The combined organic layers

were washed with brine (4 mL), dried over Na_2SO_4, and concentrated, After evaporation of the solvent at reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (7/1 ratio) to give a slightly yellow oil **12** (55.5mg, 90%) and 99% ee.





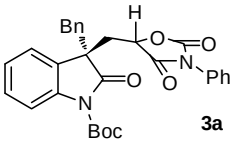
h) A 1.0 M solution of lithium triethylborohydride in THF (1.17 mL, 1.17 mmol) was added to a solution of **5a** (122.2 mg, 0.39 mmol) at –78 °C under nitrogen atmosphere. After 3.0 hours, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1.8 mL) and warmed to 0 °C. 30% H_2O_2 (3 drops) was added and the mixture was stirred at 0 °C. After 20 minutes, the organic solvent was removed *in vacuo*, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (3/1 ratio) to give a colorless oil **13a** (113.2 mg) in 92% yield.

i) A solution of **13a** (113.2 mg, 0.36 mmol,) and triethylsilane (0.12 mL, 0.72 mmol) in CH_2Cl_2 (6 ml) was cooled at –78 °C and 48% boron trifluoride diethyl etherate (0.2 mL, 0.79 mmol) was then added dropwise under nitrogen atmosphere. After 30 minutes, 0.12 mL of triethylsilane and 0.2 mL of boron trifluoride diethyl etherate were added. The resulting mixture was stirred 12 hours at –78 °C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL), extracted with CH_2Cl_2 (3 × 12 mL) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (5/1 ratio) gave a colorless oil **14a** (97.0 mg) in 90% yield.

j) KOH (3.2 mmol) was added to the mixture of crude **14a** (0.32 mmol) in EtOH (3.2 mL). Then the

mixture was refluxed until the complete conversion of **14a**. The solvent was removed *in vacuo*, and the remaining residue was redissolved in water and ethyl acetate. The organic layers were combined, dried over anhydrous Na_2SO_4, After evaporation of the solvent at reduced pressure, the crude product was purified by flash chromatography on *silica gel* eluting with petroleum ether/ethyl acetate mixture (3/1 ratio) to give a white solid **15a** (72.6 mg) in 83% yield and 94% ee.

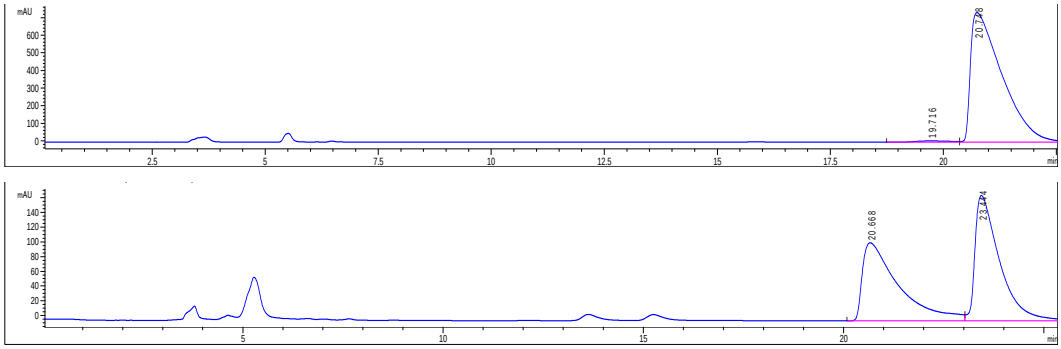
6. Characterization of adducts

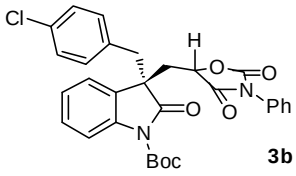


3a

White solid, Mp 70.7−72.5 °C; 50.7 mg (0.1 mmol), 99% yield; > 20:1 dr; 98% ee; $[\alpha]_D^{26}$ −155.4 (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.40–7.29 (m, 3H), 7.23–7.18 (m, 1H), 7.15–7.03 (m, 7H), 6.77–6.74 (m, 2H), 4.92 (dd, *J* = 6.9, 3.7 Hz, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 3.12–3.04 (m, 2H), 2.81 (dd, *J* = 15.0, 3.7 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 171.1, 152.7, 148.6, 140.0, 133.7, 130.4, 130.0, 129.3, 128.8, 128.6, 127.8, 127.1, 126.7, 125.2, 124.8, 124.0, 115.5, 84.2, 76.2, 51.9, 46.1, 35.7, 28.0; HRMS (ESI) m/z 535.1859 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_6Na$ 535.1845.

The ee was determined by HPLC analysis. CHIRALPAK IB-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.7 min (minor) and 20.7 min (major).

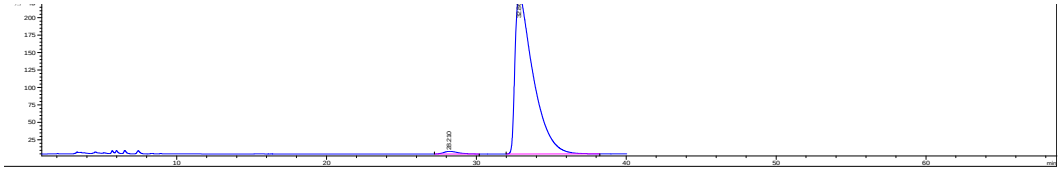


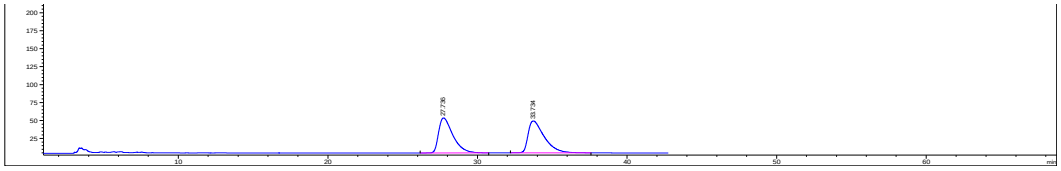


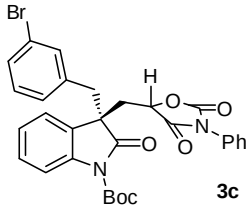
3b

White solid, Mp 74.9−76.6 °C; 49.2 mg (0.1 mmol), 90% yield; > 20:1 dr; 98% ee; $[\alpha]_D^{26}$ −69.7 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.38–7.28 (m, 3H), 7.23–7.17 (m, 1H), 7.15–7.01 (m, 7H), 6.75 (d, *J* = 6.7 Hz, 2H), 4.92 (dd, *J* = 6.9, 3.6 Hz, 1H), 3.18–3.14 (d, 1H), 3.12–3.03 (m, 2H), 2.84–2.78 (m, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 171.1, 152.7, 148.4, 140.0, 133.1, 132.2, 131.2, 130.3, 129.5, 128.9, 128.6, 127.9, 126.4, 125.1, 124.5, 124.2, 115.7, 84.5, 76.1, 51.8, 45.3, 35.8, 28.0; HRMS (ESI) m/z 569.1465 ($M+Na^+$), calc. for $C_{30}H_{27}ClN_2O_6Na$ 569.1455.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 28.0 min (minor) and 32.0 min (major).



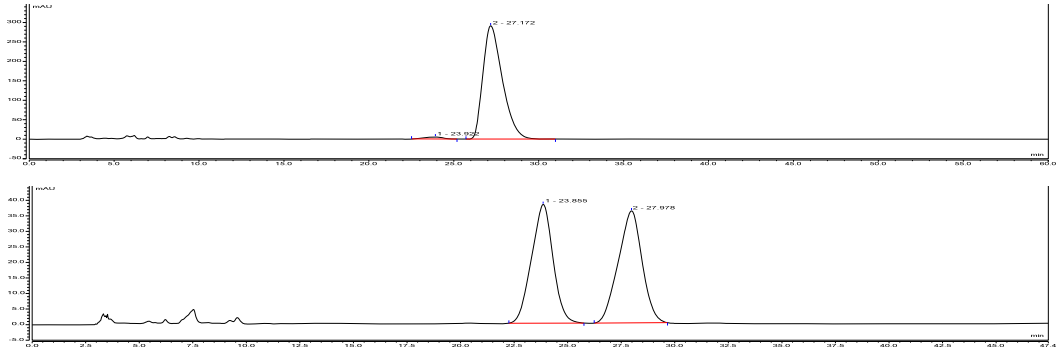


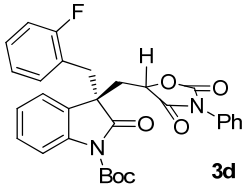


3c

White solid, Mp 71.6−73.4 °C; 47.3 mg (0.1 mmol), 80% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −140.5 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.38–7.28 (m, 3H), 7.23–7.13 (m, 2H), 7.11–7.01 (m, 6H), 6.76 (d, *J* = 6.7 Hz, 2H), 4.92 (dd, *J* = 7.0, 3.6 Hz, 1H), 3.16 (d, *J* = 12.8 Hz, 1H), 3.12–3.03 (m, 2H), 2.81 (dd, *J* = 15.0, 3.6 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 171.1, 152.7, 148.5, 139.9, 133.6, 130.3, 130.0, 129.2, 128.8, 128.6, 127.7, 127.1, 126.6, 125.1, 124.7, 124.0, 115.4, 84.2, 76.2, 51.8, 46.1, 35.6, 28.0; HRMS (ESI) m/z 591.1119 ($M+H^+$), calc. for $C_{30}H_{28}BrN_2O_6$ 591.1131.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 23.9 min (minor) and 27.2 min (major).

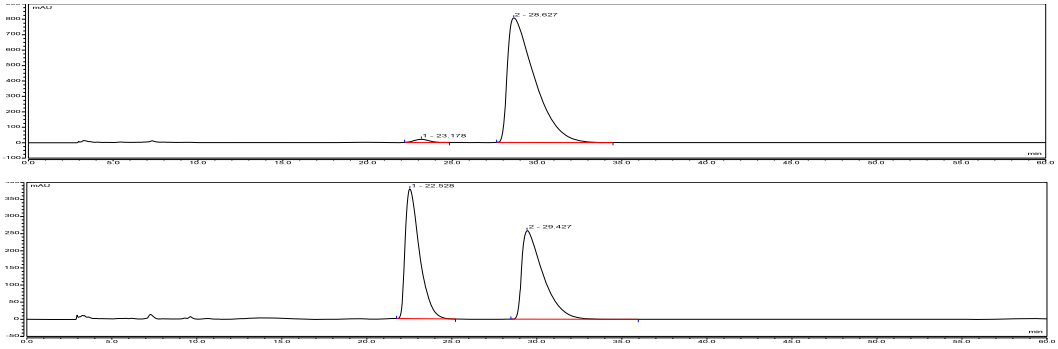


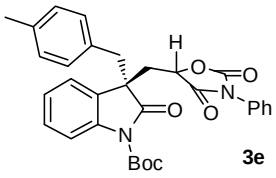


3d

White solid, Mp 73.0−74.8 °C; 52.5 mg (0.1 mmol), 99% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −119.3 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2Hz, 1H), 7.38–7.30 (m, 3H), 7.22–7.17 (m, 1H), 7.15–6.99 (m, 5H), 6.95–6.89 (m, 2H), 6.85–6.79 (m, 1H), 4.90 (dd, *J* = 7.0, 3.5 Hz, 1H), 3.30 (d, *J* = 13.3 Hz, 1H), 3.13–3.03 (m, 2H), 2.84–2.78 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 171.0, 162.5, 159.2, 152.7, 148.7, 139.5, 131.9 (two peaks), 130.3, 129.3, 129.2, 129.1, 128.8, 128.5, 126.2, 125.2(two peaks), 125.1, 124.0, 123.6, 123.5, 121.4, 121.2, 115.3, 115.2, 115.0, 84.4, 76.1, 51.2, 38.0, 35.3, 28.0; HRMS (ESI) m/z 553.1754 ($M+Na^+$), calc. for $C_{30}H_{27}FN_2O_6Na$ 553.1751.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 23.2 min (minor) and 28.6 min (major).

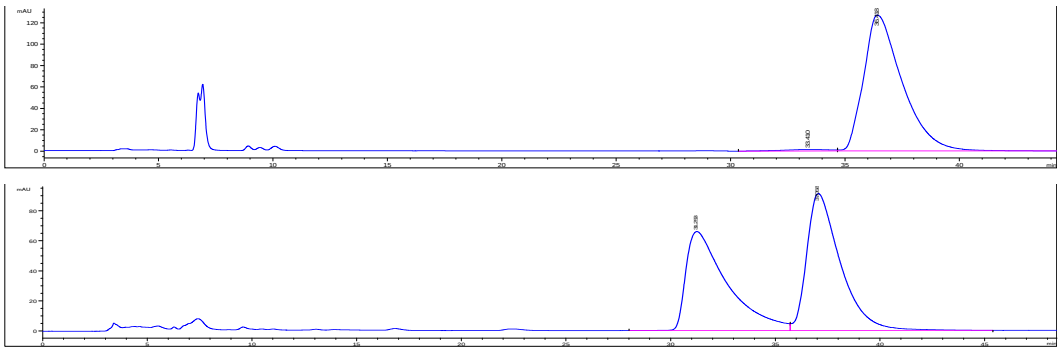


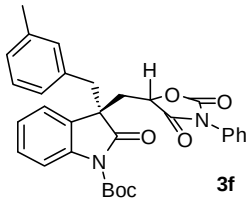


3e

White solid, Mp 137.1−138.0 °C; 52.1 mg (0.1 mmol), 99% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −83.3 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.38–7.28 (m, 3H), 7.24–7.18 (m, 1H), 7.14–7.01 (m, 4H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 2H), 4.91 (dd, *J* = 7.0, 3.6 Hz, 1H), 3.13–3.00 (m, 3H), 2.79 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.21 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 171.1, 152.7, 148.6, 139.9, 136.6, 130.5, 130.3, 129.9, 129.2, 128.8, 128.5, 128.4, 126.8, 125.1, 124.8, 124.0, 115.5, 84.1, 76.2, 51.8, 45.7, 35.5, 28.0, 20.9; HRMS (ESI) m/z 549.2004 ($M+Na^+$), calc. for $C_{31}H_{30}N_2O_6Na$ 549.2002.

The ee was determined by HPLC analysis. CHIRALPAK IB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 33.4 min (minor) and 36.4 min (major).



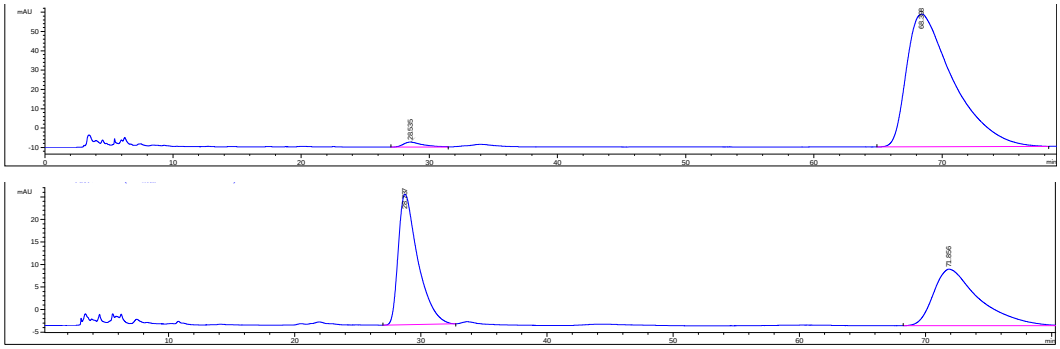


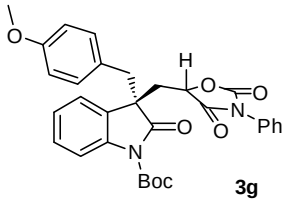
3f

White solid, Mp 87.9−89.6 °C; 45.8 mg (0.1 mmol), 87% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −36.4 (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.38–7.28 (m, 3H), 7.23–7.02 (m, 5H), 6.96–6.92 (m, 2H), 6.58–6.53(m, 2H), 4.92 (dd, *J* = 6.9, 3.6 Hz, 1H), 3.13–3.00 (m, 3H), 2.80 (dd, *J* = 14.9, 3.6 Hz, 1H), 2.15 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 171.2, 152.8, 148.7, 140.0, 137.3, 133.6, 130.8, 130.4, 129.3, 128.9, 128.6, 127.8, 127.6, 127.1, 126.8, 125.2, 124.9, 124.0, 115.5, 84.2, 76.3, 51.9, 46.1, 35.6, 28.0, 21.2; HRMS (ESI) m/z 549.2005 ($M+Na^+$), calc. for $C_{31}H_{30}N_2O_6Na$ 549.2002.

The ee was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol

= 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 28.5 min (minor) and 68.4 min (major).

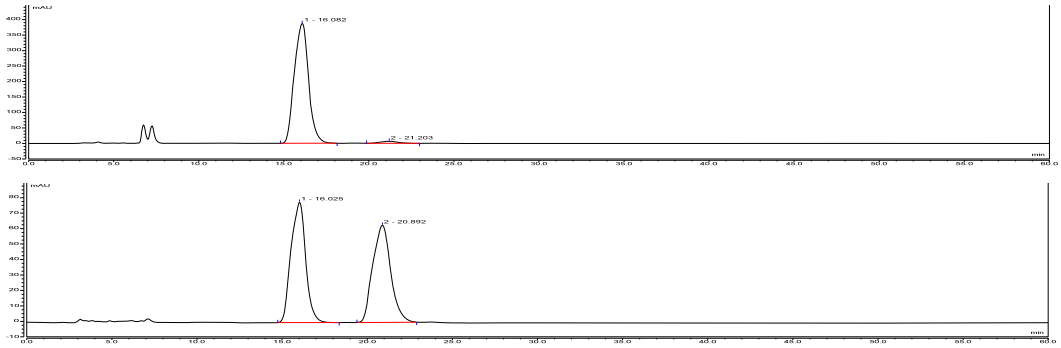


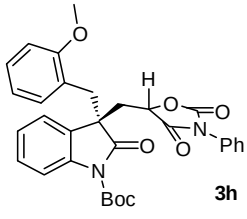


3g

White solid, Mp 132.2−134.1 °C; 43.4 mg (0.1 mmol), 80% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −131.8 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.38–7.28 (m, 3H), 7.23–7.18 (m, 1H), 7.13–7.01 (m, 4H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.91 (dd, *J* = 7.0, 3.5 Hz, 1H), 3.68 (s, 3H), 3.12–2.98 (m, 3H), 2.78 (dd, *J* = 15.0, 3.5 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 171.1, 158.6, 152.7, 148.6, 140.0, 131.0, 130.3, 129.2, 128.8, 128.6, 126.8, 125.6, 125.1, 124.7, 124.0, 115.5, 113.1, 84.2, 76.2, 55.0, 51.9, 45.3, 35.5, 28.0; HRMS (ESI) m/z 565.1953 ($M+Na^+$), calc. for $C_{31}H_{30}N_2O_7Na$ 565.1951.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.2 min (minor) and 16.1 min (major).

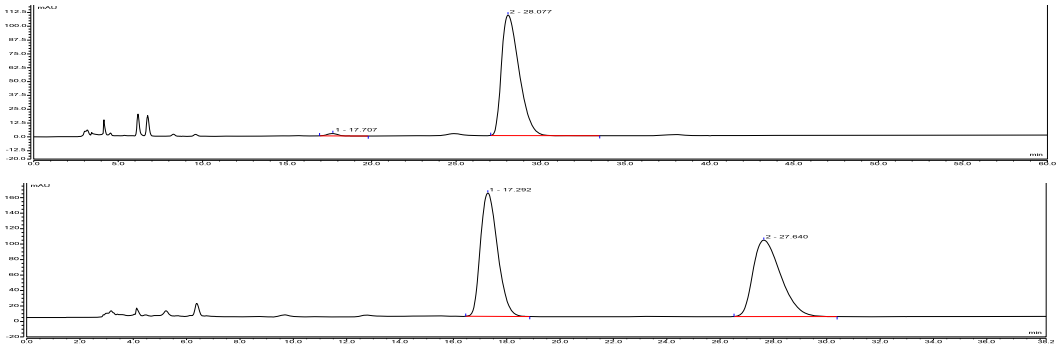


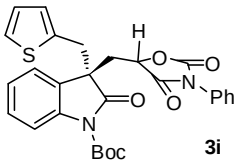


3h

White solid, Mp 134.7−136.5 °C; 43.4 mg (0.1 mmol), 80% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −128.5 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.38–7.30 (m, 3H), 7.19–7.09 (m, 2H), 7.05–7.02 (m, 2H), 6.98–6.89 (m, 3H), 6.7 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 4.87 (dd, *J* = 7.0, 3.7 Hz, 1H), 3.53 (s, 3H), 3.35 (d, *J* = 13.1 Hz, 1H), 3.12–2.99 (m, 2H), 2.79 (dd, *J* = 15.0, 3.7 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 171.2, 157.4, 152.8, 149.0, 139.6, 131.7, 130.4, 128.8 (two peaks), 128.6, 128.5, 127.0, 125.5, 125.1, 123.3, 122.7, 119.8, 115.0, 110.0, 84.1, 76.3, 54.7, 51.3, 38.9, 35.3, 28.1; HRMS (ESI) m/z 565.1954 ($M+Na^+$), calc. for $C_{31}H_{30}N_2O_7Na$ 565.1951.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.7 min (minor) and 28.1 min (major).

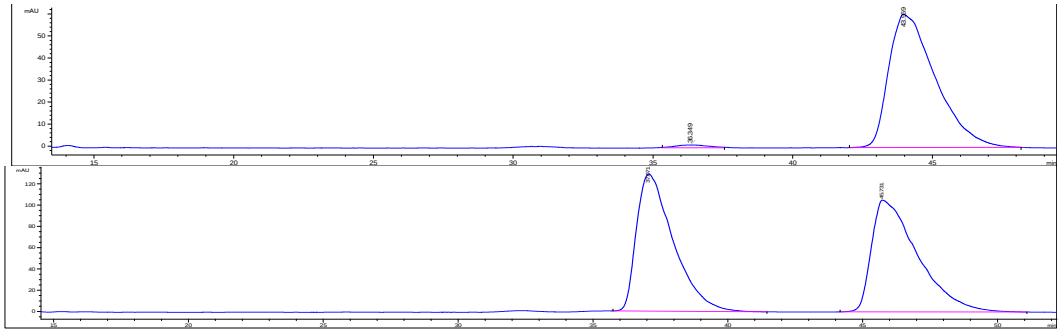


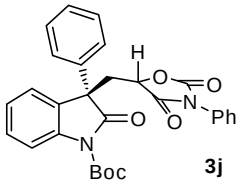


3i

Colorless oil; 49.7 mg (0.1 mmol), 96% yield; > 20:1 d.r.; 97% ee; $[\alpha]_D^{26}$ −247.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.38–7.28 (m, 3H), 7.23–6.97 (m, 6H), 6.76–6.74 (m, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 4.93 (dd, *J* = 6.7, 3.6 Hz, 1H), 3.43 (d, *J* = 14.1 Hz, 1H), 3.28 (d, *J* = 14.1 Hz, 1H), 3.03 (dd, *J* = 14.9, 6.8 Hz, 1H), 2.82 (dd, *J* = 14.9, 3.6 Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 171.0, 152.7, 148.6, 140.3, 135.0, 130.3, 129.6, 128.8, 128.6, 127.7, 126.5, 126.4, 125.1, 125.0, 124.7, 124.3, 115.6, 84.3, 76.1, 51.7, 39.9, 35.8, 28.0.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 36.3 min (minor) and 44.0 min (major).

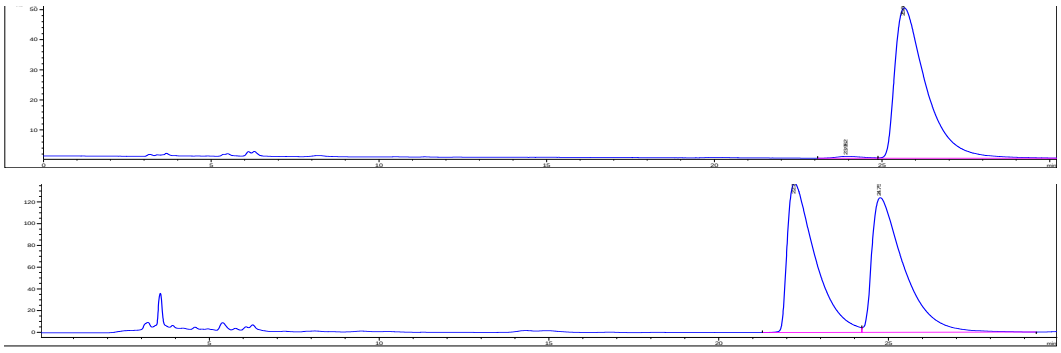


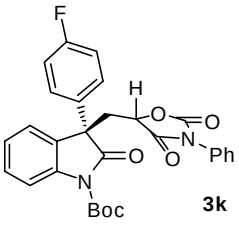


3j

White solid, Mp 141.9−143.6 °C; 48.4 mg (0.1 mmol), 97% yield; > 20:1 dr; 98% ee; $[\alpha]_D^{26}$ −247.2 (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.36–7.28 (m, 4H), 7.24–7.23 (m, 6H), 7.14–7.07 (m, 3H), 4.92 (dd, *J* = 6.8, 3.8 Hz, 1H), 3.50 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.99 (dd, *J* = 14.9, 3.8 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 171.0, 152.8, 149.1, 140.3, 139.1, 130.4, 129.7, 128.9 (two peaks), 128.6, 128.1, 127.6, 126.5, 126.2, 125.1, 124.6, 116.0, 84.7, 76.2, 53.8, 36.9, 28.0; HRMS (ESI) m/z 521.1700 ($M+Na^+$), calc. for $C_{29}H_{26}N_2O_6Na$ 521.1689.

The ee was determined by HPLC analysis. CHIRALPAK IB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.0min (minor) and 25.7 min (major).

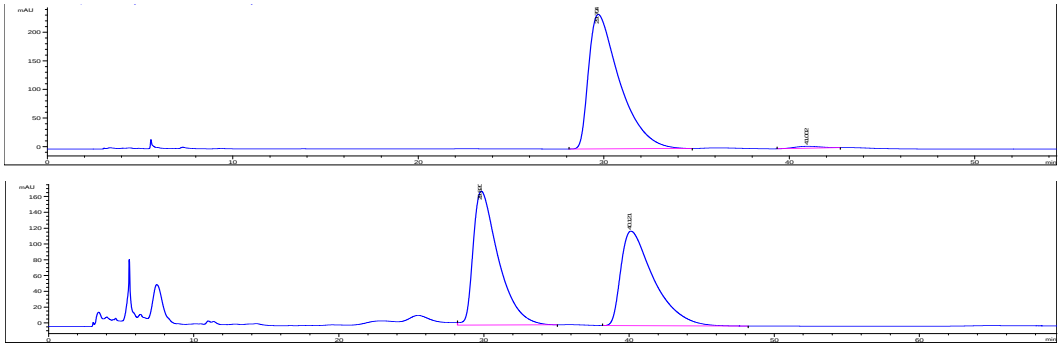


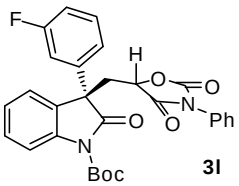


3k

White solid, Mp 82.1−83.9 °C; 49.1 mg (0.1 mmol), 95% yield; > 20:1 dr; 98% ee; $[\alpha]_D^{26}$ −128.2 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.39–7.28 (m, 4H), 7.24–7.21 (m, 3H), 7.18–7.08 (m, 3H), 7.01–6.94 (m, 2H), 4.93 (dd, *J* = 6.8, 3.8 Hz, 1H), 3.48 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.97 (dd, *J* = 14.9, 3.8 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 170.9, 164.0, 160.7, 152.7, 149.0, 140.2, 134.8, 134.7, 130.3, 129.9, 128.9, 128.6, 128.5, 128.4, 127.2, 126.2, 125.0, 124.7, 125.0, 124.7, 84.8, 76.1, 53.2, 37.0, 28.0; HRMS (ESI) m/z 539.1592 ($M+Na^+$), calc. for $C_{29}H_{25}FN_2O_6Na$ 539.1594.

The ee was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 41.0 min (minor) and 29.7 min (major).

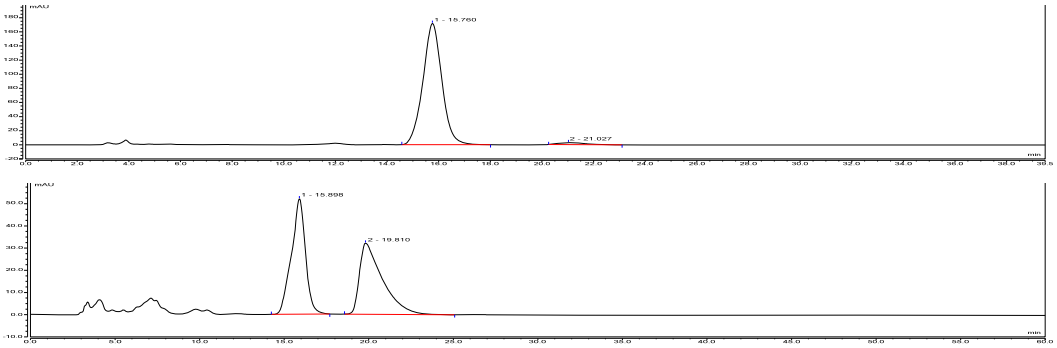


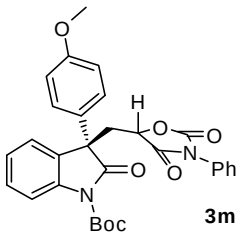


3l

White solid, Mp 139.5−141.2 °C; 46.5 mg (0.1 mmol), 90% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −103.9 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.41–7.27 (m, 5H), 7.25–7.16 (m, 2H), 7.13–7.07 (m, 3H), 7.01–6.96 (m, 2H), 4.96 (dd, *J* = 6.9, 3.7 Hz, 1H), 3.51 (dd, *J* = 14.9, 6.9 Hz, 1H), 3.02 (dd, *J* = 14.9, 3.7 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 170.9, 164.4, 161.2, 152.7, 149.0, 141.5, 141.4, 140.2, 130.4, 130.3 (two peaks), 130.0, 128.9, 128.6, 126.9, 126.2, 125.0, 124.7, 122.3, 122.2, 84.9, 76.0, 53.5 (two peaks), 36.8, 28.0; HRMS (ESI) m/z 539.1595 ($M+Na^+$), calc. for $C_{29}H_{25}FN_2O_6Na$ 539.1594.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.0 min (minor) and 15.8 min (major).

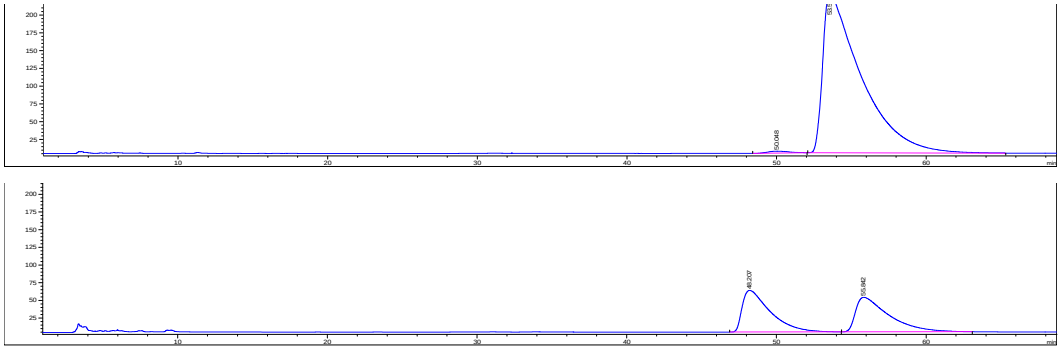


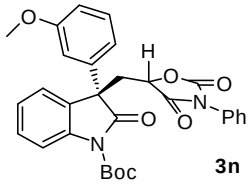


3m

White solid, Mp 82.3−84.0 °C; 51.3 mg (0.1 mmol), 97% yield; > 20:1 dr; 99% ee; $[\alpha]_D^{26}$ −141.7 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.42–7.31 (m, 4H), 7.28–7.27 (m, 1H), 7.23–7.18 (m, 3H), 7.15–7.11 (m, 2H), 6.86–6.81 (m, 2H), 4.96 (dd, *J* = 6.8, 3.8 Hz, 1H), 3.77 (s, 3H), 3.52 (dd, *J* = 14.9, 6.8 Hz, 1H), 3.00 (dd, *J* = 14.9, 3.9 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 171.0, 159.2, 152.8, 149.1, 140.2, 131.1, 130.4, 129.6, 128.8, 128.6, 127.8, 126.1, 125.1, 124.5, 115.9, 114.2, 84.6, 76.2, 55.2, 53.1, 40.0, 28.0; HRMS (ESI) m/z 551.1798 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_7Na$ 551.1794.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 50.0 min (minor) and 53.6 min (major).

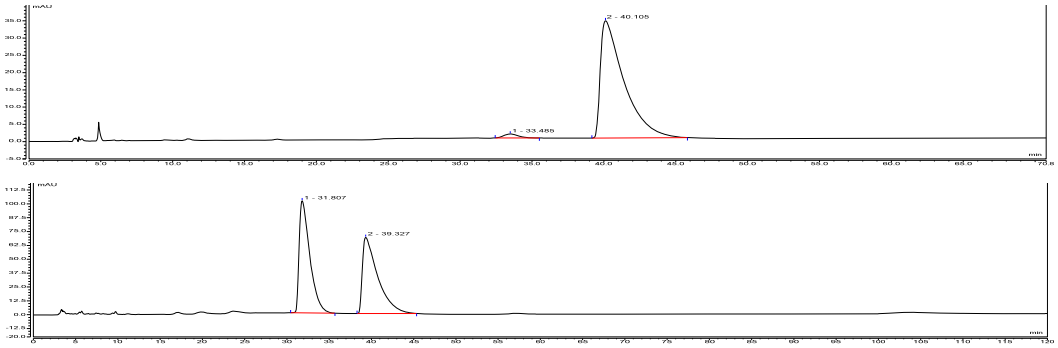


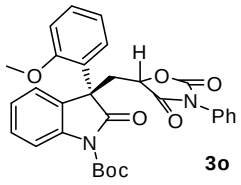


3n

White solid, Mp 72.3−74.0 °C; 49.7 mg (0.1 mmol), 94% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −128.2 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.47–7.36 (m, 4H), 7.33–7.27 (m, 2H), 7.24–7.15 (m, 3H), 6.93–6.86 (m, 3H), 5.02 (dd, *J* = 6.9, 3.7 Hz, 1H), 3.81 (s, 3H), 3.65–3.51 (m, 1H), 3.09 (dd, *J* = 14.9, 3.8 Hz, 1H), 1.70 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 171.0, 159.7, 152.8, 149.0, 140.6, 140.2, 130.3, 129.8, 129.7, 128.8, 128.6, 127.5, 126.2, 125.1, 124.6, 118.8, 115.9, 113.1, 112.8, 84.6, 76.2, 55.2, 53.7, 36.7, 28.0; HRMS (ESI) m/z 551.1795 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_7Na$ 551.1794.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 33.5 min (minor) and 40.1 min (major).

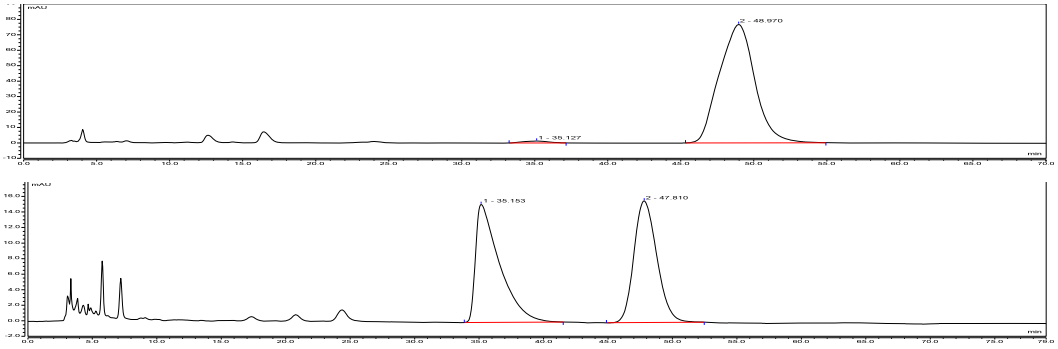


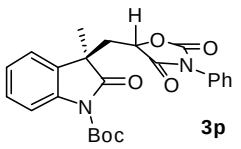


3o

White solid, Mp 81.5−82.0 °C; 42.3 mg (0.1 mmol), 80% yield; > 20:1 dr; 98% ee; $[\alpha]_D^{26}$ −227.13 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.37–7.24 (m, 3H), 7.19–7.14 (m, 4H), 7.01–6.92 (m, 2H), 6.86–6.83 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.07 (dd, *J* = 5.8, 4.2 Hz, 1H), 3.42 (s, 3H), 3.22 (dd, *J* = 15.0, 4.1 Hz, 1H), 2.83 (dd, *J* = 15.1, 5.9 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 171.3, 156.8, 153.1, 149.5, 139.9, 130.6, 130.0, 129.4, 129.0, 128.8, 128.7, 126.7, 125.2, 124.3, 123.8, 121.1, 114.8, 112.7, 84.1, 76.2, 55.7, 51.7, 37.2, 28.1; HRMS (ESI) m/z 551.1803 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_7Na$ 551.1794.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 35.1 min (minor) and 49.0 min (major).

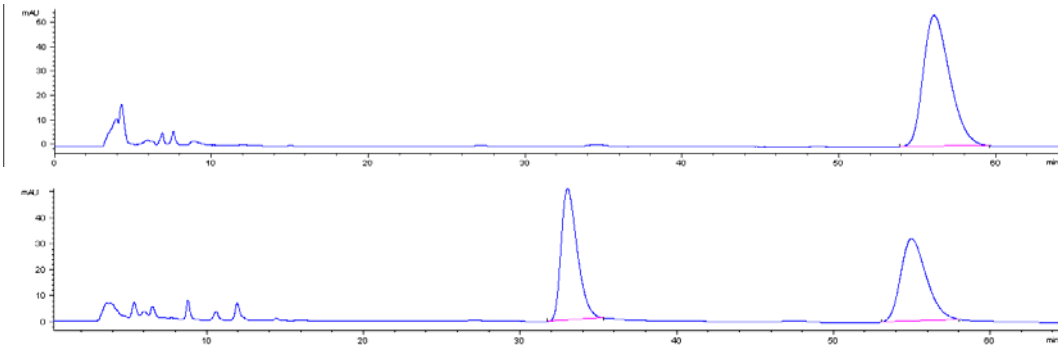


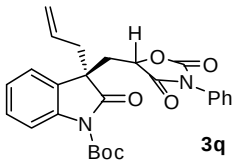


3p

White solid, Mp 65.9−66.3 °C; 41.5 mg (0.1 mmol), 95% yield; > 20:1 dr; 99% ee; $[\alpha]_D^{26}$ −201.9 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.45–7.28 (m, 5H), 7.18–7.09 (m, 3H), 4.94 (dd, *J* = 6.6, 3.8 Hz, 1H), 2.97 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.72 (dd, *J* = 15.1, 3.8 Hz, 1H), 1.72 (s, 9H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 171.0, 152.8, 149.1, 139.1, 130.3, 129.4, 129.2, 128.8, 128.6, 125.1, 124.6, 123.8, 115.8, 84.6, 76.2, 46.1, 37.1, 28.0, 26.3; HRMS (ESI) m/z 459.1537 ($M+Na^+$), calc. for $C_{24}H_{24}N_2O_6Na$ 459.1532.

The ee was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 32.9 min (minor) and 54.3 min (major).

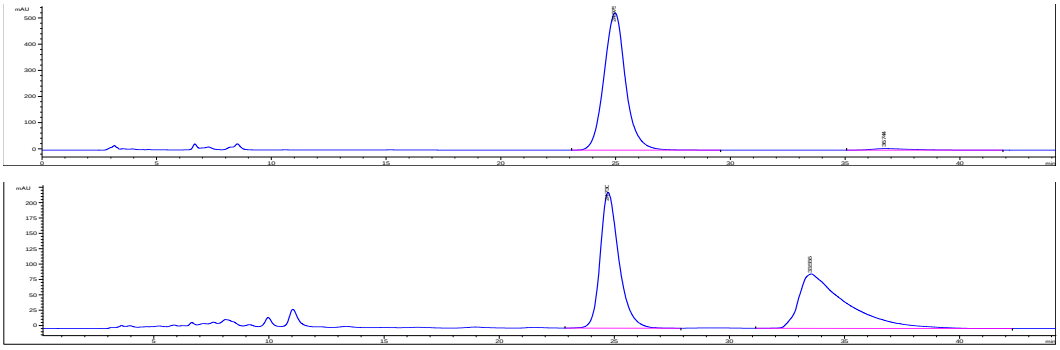


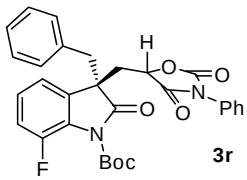


3q

White solid, Mp 143.0−144.5 °C; 41.6 mg (0.1 mmol), 90% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −148.4 (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.38–7.27 (m, 4H), 7.25–7.18 (m, 1H), 7.11–7.00 (m, 3H), 5.47–5.33 (m, 1H), 5.04–4.98 (m, 2H), 4.89 (dd, *J* = 6.8, 3.6 Hz, 1H), 2.91 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.71 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.63–2.50 (m, 2H), 1.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 171.0, 152.7, 148.9, 139.8, 130.3, 130.2, 129.3, 128.8, 128.6, 127.2, 125.1, 124.4 (two peaks), 120.6, 115.7, 84.5, 76.2, 50.1, 43.9, 35.7, 28.0; HRMS (ESI) m/z 485.1698 ($M+Na^+$), calc. for $C_{26}H_{26}N_2O_6Na$ 485.1689.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 36.7 min (minor) and 25.0 min (major).

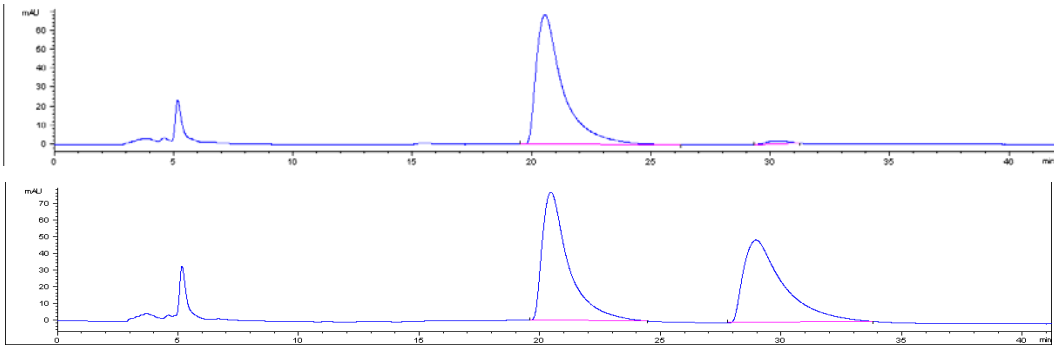


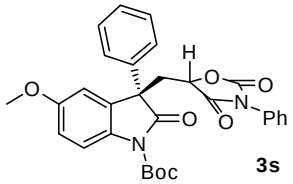


3r

Colorless oil; 49.3 mg (0.1 mmol), 93% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −134.6 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.31 (m, 3H), 7.15–6.92 (m, 8H), 6.75 (d, *J* = 6.8 Hz, 2H), 4.96–4.86 (m, 1H), 3.21 (d, *J* = 12.8 Hz, 1H), 3.05 (dd, *J* = 16.8, 8.9 Hz, 2H), 2.75 (dd, *J* = 15.0, 2.0 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 170.9, 152.7, 150.3, 147.0, 146.4, 133.2, 130.5 (two peaks), 130.4, 129.8, 128.9, 128.6, 128.0, 127.3, 126.9, 126.8, 125.2, 125.0, 120.3 (two peaks), 117.4, 117.2, 84.5, 76.0, 52.8, 46.2, 36.0, 27.4; HRMS (ESI) m/z 553.1755 ($M+Na^+$), calc. for $C_{30}H_{27}FN_2O_6Na$ 553.1751.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 30.3 min (minor) and 20.5 min (major).

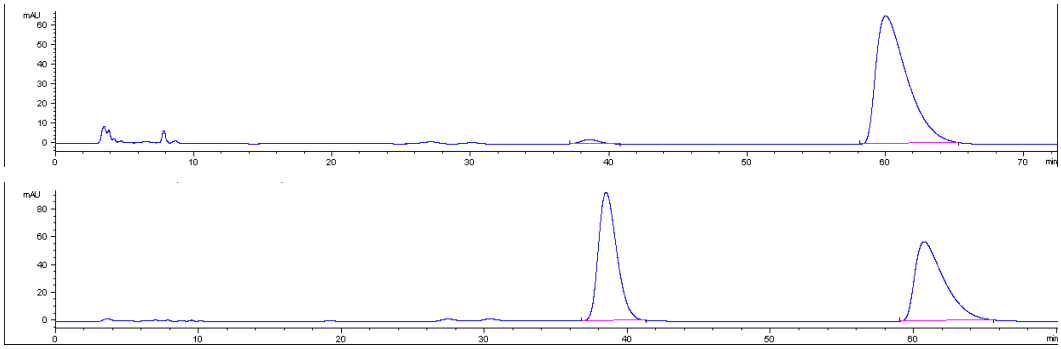


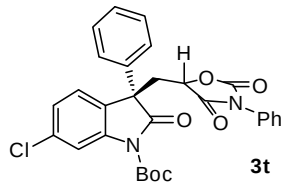


3s

White solid, Mp 184.0−185.6 °C; 47.5 mg (0.1 mmol), 90% yield; > 20:1 dr; 96% ee; $[\alpha]_D^{26}$ −167.8 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.44–7.29 (m, 8H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.85–6.79 (m, 2H), 5.04–4.94 (m, 1H), 3.63 (s, 3H), 3.59–3.54 (m, 1H), 3.04 (d, *J* = 14.8 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 171.2, 156.6, 152.7, 149.2, 139.2, 133.5, 130.5, 128.9, 128.8, 128.7, 128.4, 128.0, 126.5, 124.8, 117.0, 114.9, 112.2, 84.4, 76.1, 55.5, 54.0, 36.4, 28.0; HRMS (ESI) m/z 551.1805 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_7Na$ 551.1794.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol =80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 38.6 min (minor) and 60.0 min (major).



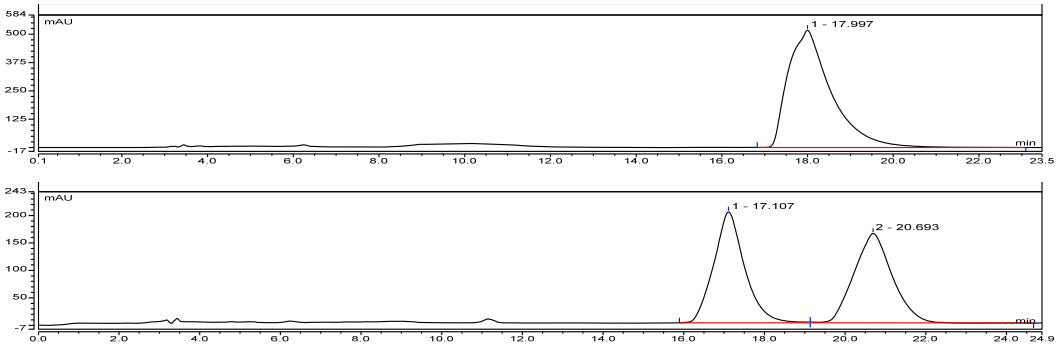


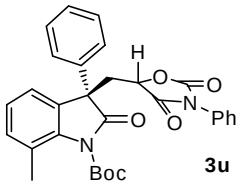
3t

White solid, Mp 108.0−109.3 °C; 48.9 mg (0.1 mmol), 92% yield; > 20:1 dr; > 99% ee; $[\alpha]_D^{26}$ −205.3 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.44–7.30 (m, 9H), 7.19–7.07 (m, 3H), 5.02–4.92 (m, 1H), 3.55 (dd, *J* = 14.9, 6.6 Hz, 1H), 3.04 (d, *J* = 14.7 Hz, 1H), 1.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 171.0, 152.7, 149.1, 140.2, 139.1, 130.4, 129.7, 128.8 (two peaks), 128.5, 128.0, 127.6, 126.5, 126.2, 125.1, 124.6, 115.9, 84.6, 76.2, 53.7, 36.8, 30.0; HRMS (ESI) m/z 555.1298 ($M+Na^+$), calc. for $C_{29}H_{25}ClN_2O_6Na$ 555.1299.

The ee was determined by HPLC analysis. CHIRALPAK IF (4.6 mm i.d. x 250 mm); Hexane/2-propanol

= 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.0 min (major).

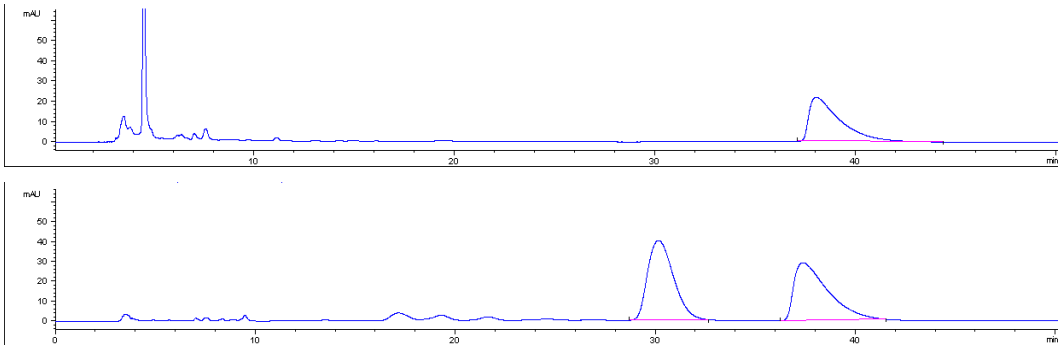


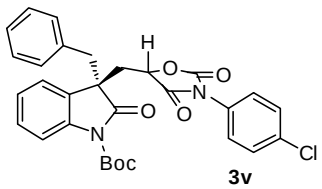


3u

White solid, Mp 178.2−179.6 °C; 48.1 mg (0.1 mmol), 94% yield; > 20:1 dr; > 99% ee; $[\alpha]_D^{26}$ −125.4 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ = 7.45–7.29 (m, 7H), 7.19–7.01 (m, 5H), 5.00–4.90 (m, 1H), 3.48 (dd, *J* = 14.7, 6.1 Hz, 1H), 2.98 (d, *J* = 14.7 Hz, 1H), 2.30 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 171.1, 152.8, 149.0, 139.3, 138.7, 132.4, 130.6, 129.0, 128.9, 128.8, 128.5, 128.0, 126.5, 125.1, 124.5 (two peaks), 123.6, 85.0, 76.2, 54.1, 37.0, 27.7, 19.7; HRMS (ESI) m/z 535.1834 ($M+Na^+$), calc. for $C_{30}H_{28}N_2O_6Na$ 535.1845.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 38.0 min (major).



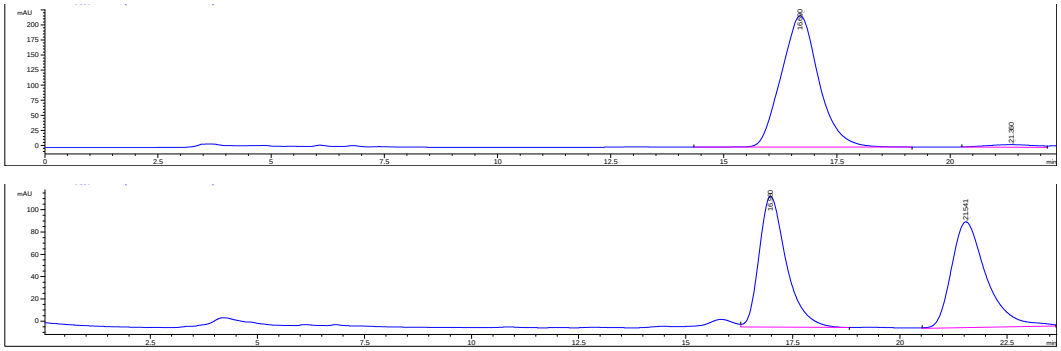


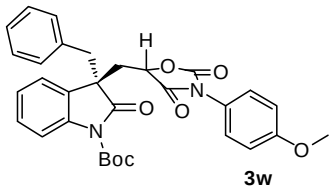
3v

Colorless oil; 49.2 mg (0.1 mmol), 90% yield; > 20:1 dr; 95% ee; $[\alpha]_D^{26}$ −147.0 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.20−6.98 (m, 8H), 6.75 (d, *J* = 6.9 Hz, 2H), 4.96–4.87 (m, 1H), 3.10 (dd, *J* = 34.0, 12.8 Hz, 3H), 2.82 (d, *J* = 14.5 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 170.8, 152.3, 148.5,140.0, 134.3, 133.5, 130.0, 129.3, 128.9, 128.8, 127.8, 127.1, 126.5, 126.2, 124.8, 124.0, 115.5, 84.2, 76.3, 51.7, 46.1, 35.5, 28.0; HRMS (ESI) m/z 569.1458 ($M+Na^+$), calc. for $C_{30}H_{27}ClN_2O_6Na$ 569.1455.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol

= 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.4 min (minor) and 16.7 min (major).

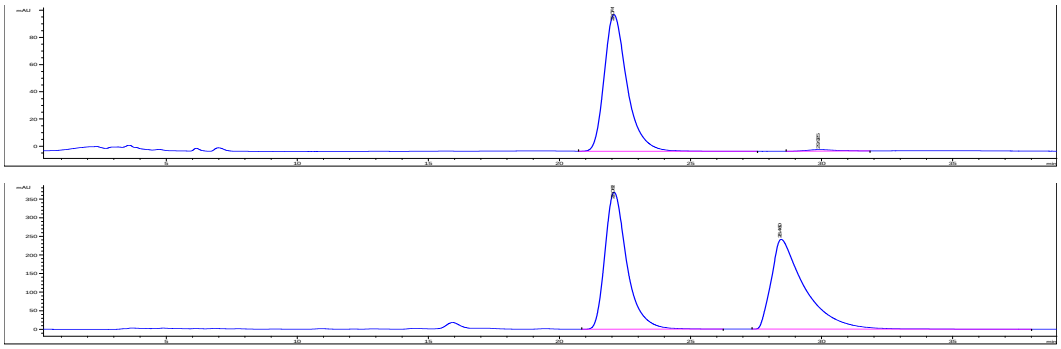


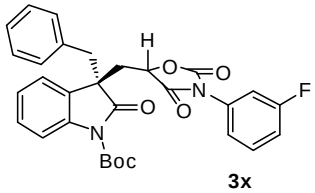


3w

Colorless oil; 51.5 mg (0.1 mmol), 97% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −116.8 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.24–7.02 (m, 6H), 6.94–6.83 (m, 4H), 6.76–6.74 (m, 2H), 4.90 (dd, *J* = 6.9, 3.7 Hz, 1H), 3.78 (s, 3H), 3.18–3.03 (m, 3H), 2.79 (dd, *J* = 15.0, 3.7 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 171.3, 159.4, 153.0, 148.5, 139.9, 133.6, 129.9, 129.1, 127.7, 127.0, 126.7, 126.6, 124.7, 124.0, 122.9, 115.4, 114.0, 84.1, 76.2, 55.4, 51.8, 46.1, 35.6, 27.9; HRMS (ESI) m/z 565.1949 ($M+Na^+$), calc. for $C_{31}H_{30}N_2O_7Na$ 565.1951.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 29.9 min (minor) and 22.1 min (major).

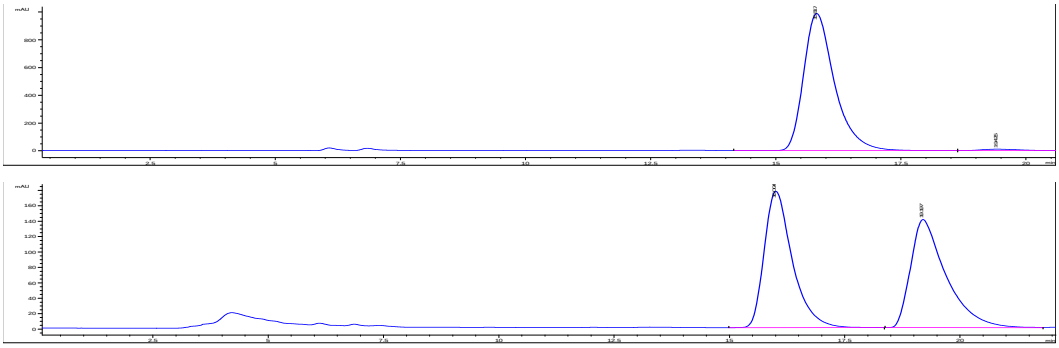


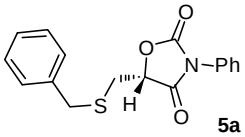


3x

Colorless oil; 53.1 mg (0.1 mmol), 97% yield; > 20:1 dr; 97% ee; $[\alpha]_D^{26}$ −160.2 (*c* 3.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.35–7.27 (m, 1H), 7.22–6.99 (m, 7H), 6.92–6.74 (m, 4H), 4.92 (dd, *J*= 7.1, 3.2 Hz, 1H), 3.18–3.02 (m, 3H), 2.82 (dd, *J* = 15.0, 3.2 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 170.8, 163.8, 160.5, 152.2, 148.5, 140.0, 133.5, 131.6, 131.5, 130.0, 129.9, 129.3, 127.8, 127.1, 126.5, 124.8, 124.0, 120.5 (two peaks), 115.7, 115.5, 115.4, 112.8, 112.5, 84.3, 76.2, 51.7, 46.1, 35.5, 30.0; HRMS (ESI) m/z 553.1764 ($M+Na^+$), calc. for $C_{30}H_{27}FN_2O_6Na$ 553.1751.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.4 min (minor) and 15.8 min (major).

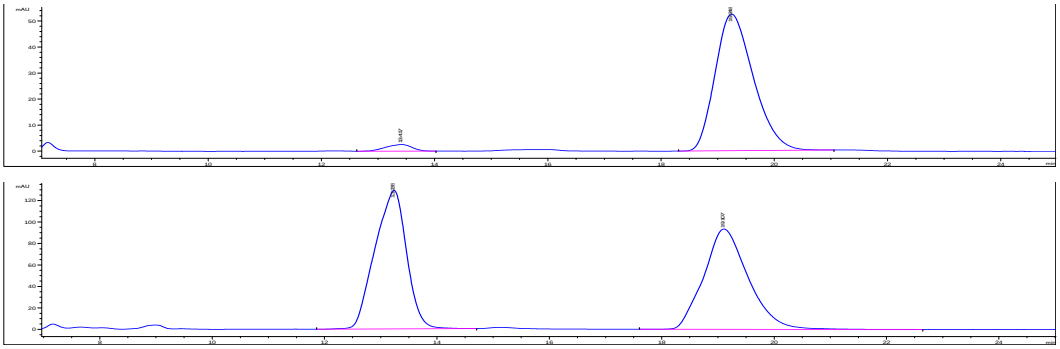


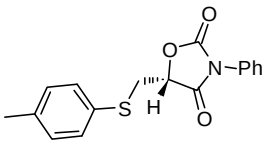


5a

Colorless oil; 28.5 mg (0.1 mmol), 97% yield; 93% ee; $[\alpha]_D^{26}$ −153.6 (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.30 (m, 5H), 7.20–7.08 (m, 5H), 5.05–4.96 (m, 1H), 3.71 (s, 2H), 2.93–2.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 153.9, 136.8, 130.6, 129.3, 129.1, 129.0, 128.6, 127.3, 125.7, 79.2, 37.2, 30.7; HRMS (ESI) m/z 336.0674 ($M+Na^+$), calc. for $C_{17}H_{15}NO_3SNa$ 336.0670.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.1 min (minor) and 11.1 min (major).

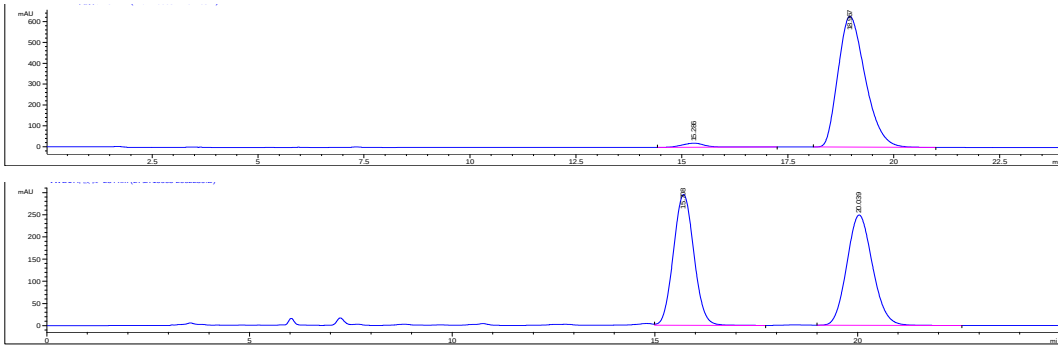


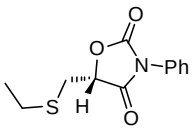


5b

White solid, Mp 104.9−105.9 °C; 32.4 mg (0.1 mmol), 98% yield; 95% ee; $[\alpha]_D^{26}$ −187.5 (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.36 (m, 7H), 7.13 (d, *J* = 6.9 Hz, 2H), 5.18–5.10 (m, 1H), 3.53 (q, *J* = 14.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 153.7, 138.1, 132.0, 130.7, 130.10 (two peaks), 129.3, 129.0, 125.6, 78.1, 36.5, 21.1; HRMS (ESI) m/z 314.0854 ($M+H^+$), calc. for $C_{17}H_{16}NO_3S$ 314.0851.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.3 min (minor) and 19.0 min (major).

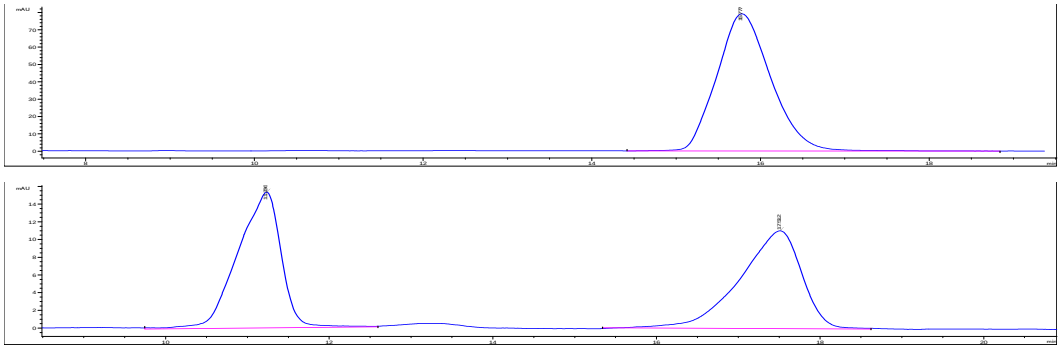


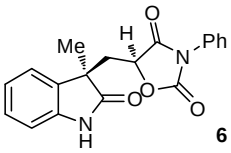


5c

White solid, Mp 80.6−81.8 °C; 21.1 mg (0.1 mmol), 84% yield; > 99% ee; $[\alpha]_D^{26}$ −36.4 (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.44 (m, 5H), 5.23–5.14 (m, 1H), 3.19 (q, *J* = 15.3 Hz, 2H), 2.76–2.45(m, 2H), 1.26 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 154.0, 130.70, 129.3, 129.0, 125.7, 79.2, 32.2, 27.9, 14.7; HRMS (ESI) m/z 274.0516 ($M+Na^+$), calc. for $C_{12}H_{13}NO_3SNa$ 274.0514.

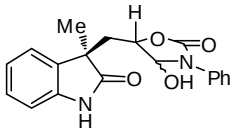
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.8 min (major).





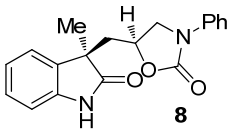
6

White solid, Mp 102.5−103.2 °C; 93% yield; $[\alpha]_D^{26}$ −109.2 (*c* 0.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.41−7.28 (m ,3H), 7.21−7.16 (m, 2H), 7.02−6.97 (m, 4H), 5.01−4.92 (m, 1H), 2.95 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.67 (d, *J* = 15.1 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.9, 171.4, 153.5, 140.7, 131.0, 130.3, 128.9, 128.8, 128.6, 125.3, 124.2, 122.5, 110.7, 76.9, 46.3, 36.2, 25.5.



7

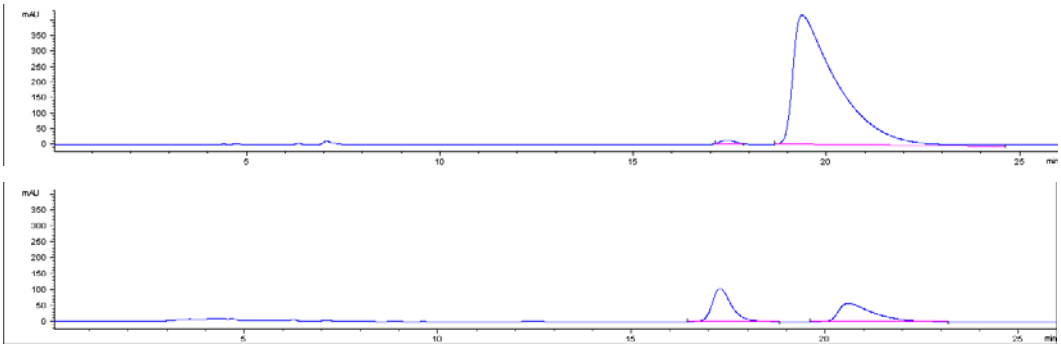
Colorless oil; 75% yield; $[\alpha]_D^{26}$ −89.6 (*c* 0.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.23–7.18 (m, 3H), 7.12 (t, *J* = 7.1 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.50–5.40 (m, 2H), 4.00–3.90 (m, 1H), 2.41–2.34 (m, 1H), 2.26–2.20 (m, 1H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.6, 154.4, 140.1, 135.8, 132.5, 129.0, 128.5, 125.6, 123.1, 123.0, 121.8, 110.7, 85.1, 79.2, 46.8, 40.1, 25.0.

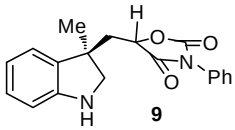


8

Yellow oil; 87% yield; 98% ee; $[\alpha]_D^{26}$ +26.3 (*c* 0.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.47–7.30 (m, 6H), 7.17–7.07 (m, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.41–4.32(m, 1H), 3.97–3.88(m, 1H), 3.77–3.68 (m, 1H), 2.55–2.48 (m, 1H), 2.42–2.35 (m, 1H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 154.3, 139.7, 138.0, 132.6, 129.0, 128.5, 124.1, 123.6, 123.1, 118.3, 110.2, 70.3, 50.9, 46.9, 42.2, 24.9; HRMS (ESI) m/z 323.1401 ($M+H^+$), calc. for $C_{19}H_{19}N_2O_3$ 323.1396.

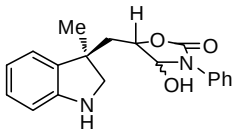
The ee was determined by HPLC analysis. CHIRALPAK INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.4 min (minor) and 19.4 min (major).





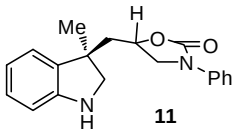
9

White oil; 67% yield; $[\alpha]_D^{26}$ +30.6 (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.48–7.37 (m, 5H), 7.12–7.07 (m, 2H), 6.79 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 5.04 (d, *J* = 10.1 Hz, 1H), 3.61–3.54 (m, 2H), 3.37 (d, *J* = 9.0 Hz, 1H), 2.49 (d, *J* = 14.9 Hz, 1H), 2.12–2.04 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 153.4, 150.1, 133.8, 130.2, 128.7, 128.3, 127.7, 124.9, 122.4, 118.3, 109.5, 76.2, 60.0, 43.4, 40.1, 24.1; HRMS (ESI) m/z 323.1401 ($M+H^+$), calc. for $C_{19}H_{19}N_2O_3$ 323.1396.



10

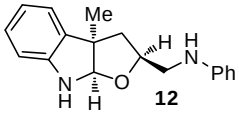
Colorless oil; 94% yield; $[\alpha]_D^{26}$ −30.3 (*c* 1.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.59–7.40 (m, 2H), 7.35–7.30 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11–7.06 (m, 2H), 6.85–6.78 (m, 1H), 6.70–6.65 (m, 1H), 5.39–5.25 (m, 1H), 4.47–4.20 (m, 1H), 4.15 (s, 1H), 3.45–3.20 (m, 2H), 2.20–1.89 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 149.4, 136.3, 135.7, 129.1, 128.2, 125.7, 122.8, 121.8, 120.0, 110.8, 86.2, 80.3, 60.2, 43.8, 43.1, 24.9.



11

Yellow oil; 90% yield; $[\alpha]_D^{26}$ +17.3 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.14−7.05 (m, 3H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.74−4.64 (m, 1H), 4.06−4.00 (m, 1H), 3.59−3.53 (m, 1H), 3.48 (d, *J* = 9.0 Hz, 1H), 3.38 (d, *J* = 9.1 Hz, 1H), 2.12−2.09 (m, 2H), 1.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 150.5, 138.2, 135.3, 129.0, 128.0,124.0, 122.8, 118.9, 118.2, 110.0,

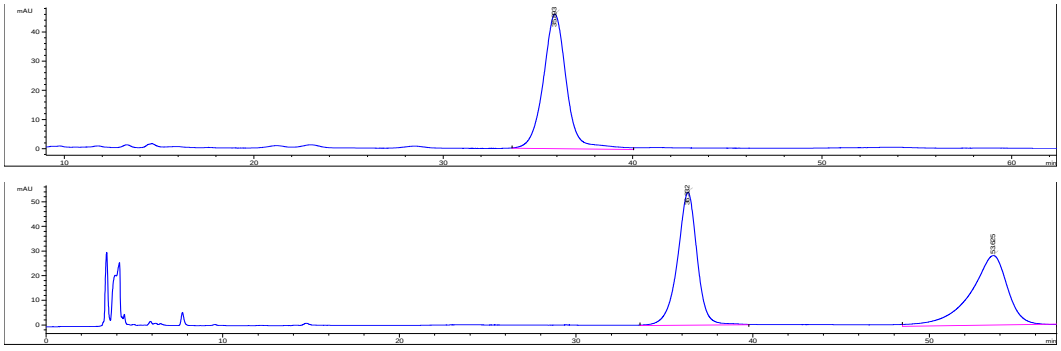
71.1, 61.2, 51.4, 44.6, 43.9, 24.3.

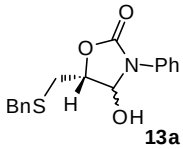


12

Yellow oil; 90% yield; 99% ee; $[\alpha]_D^{26}$ +64.9 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.15–7.07 (m, 4H), 6.80–6.76 (m, 1H), 6.70–6.60 (m, 2H), 6.45 (d, *J* = 7.1 Hz, 2H), 5.24 (s, 1H), 4.37–4.35 (m, 1H), 3.06–2.83 (m, 2H), 2.29–2.22 (m, 1H), 2.14–2.06 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 147.1, 135.6, 129.1, 128.0, 123.0, 119.6, 117.5, 113.1, 109.6, 101.1, 76.9, 53.7, 48.0, 43.3, 24.6; HRMS (ESI) m/z 281.1659 ($M+H^+$), calc. for $C_{18}H_{21}N_2O$ 281.1654.

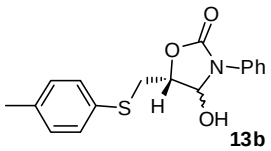
The ee was determined by HPLC analysis. CHIRALPAK INA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/05; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 35.9 min (major).





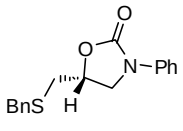
13a

Colorless oil; 94% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.44–7.36 (m, 6H), 7.34–7.28 (m, 2H), 5.40 (d, *J* = 8.9 Hz, 1H), 4.61–4.53 (m 1H), 4.48–4.45 (m, 1H), 3.83 (s, 2H), 2.80–2.65(m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 137.2, 135.9, 129.1, 129.0, 128.7, 127.4, 126.0, 122.2, 84.8, 80.9, 36.6, 32.4.



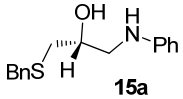
13b

White solid, Mp 104.2−105.3 °C; 96% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.44–7.36 (m, 4H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.57 (d, *J* = 8.5 Hz, 1H), 4.65 (d, *J* = 9.4 Hz, 1H), 4.50–4.41 (m, 1H), 3.33–3.27 (m, 1H), 3.08–3.00 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 137.8, 136.0, 131.8, 130.1, 129.9, 129.1, 125.8, 121.8, 84.4, 80.2, 21.0.



14a

Colorless oil; 90% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.45–7.30 (m, 7H), 7.17 (t, *J* = 7.2 Hz, 1H), 4.73–4.58 (m, 1H), 4.03 (t, *J* = 8.8 Hz, 1H), 3.85 (s, 2H), 3.79–3.74 (m, 1H), 2.92–2.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 138.0, 137.5, 128.9, 128.6, 127.3, 124.0, 118.1, 71.7, 49.4, 36.7, 34.5.

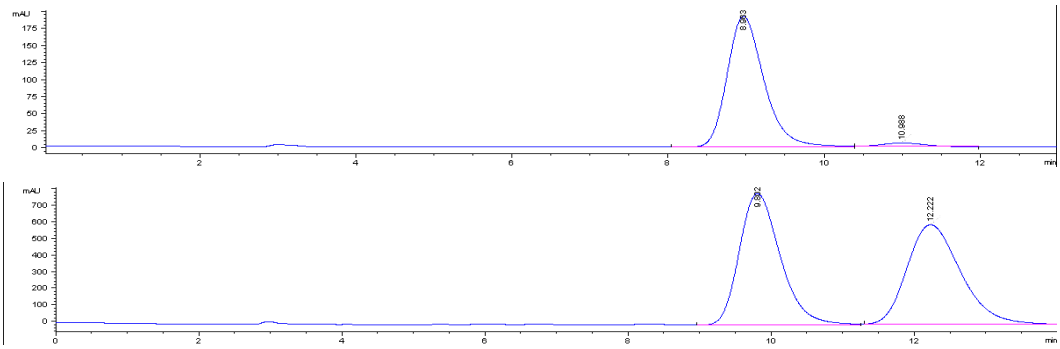


15a

White solid; Mp 53.4−54.5 °C; 83% yield; 94% ee; $[\alpha]_D^{26}$ −59.4 (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 7.19 (t, *J* = 7.3 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 3.96–3.89 (m, 1H), 3.75 (s, 2H), 3.28 (d, *J* = 12.9

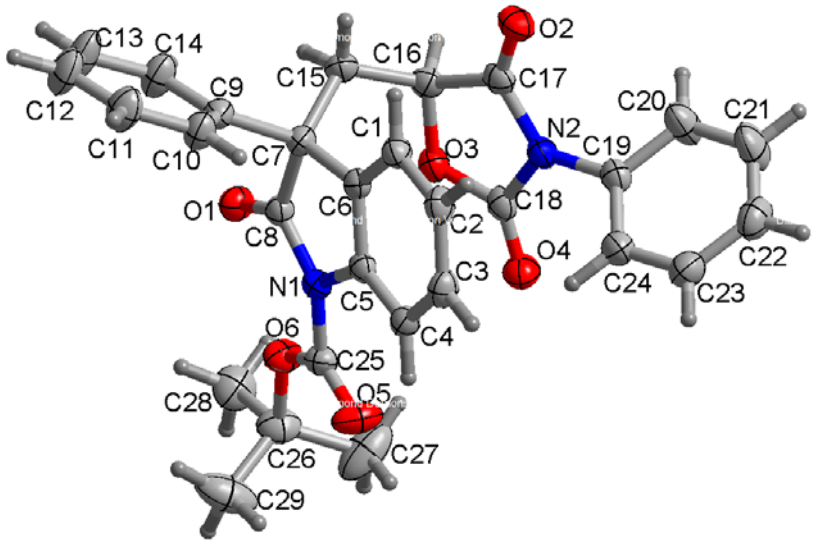
Hz, 1H), 3.12–3.08 (m, 1H), 2.67–2.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 137.7, 129.2 128.9, 128.6, 127.2, 117.9, 113.2, 67.9, 48.6, 36.3, 36.2; HRMS (ESI) m/z 274.1270 ($M+H^+$), calc. for $C_{16}H_{20}NOS$ 274.1266.

The ee was determined by HPLC analysis. CHIRALPAK OF (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.0 min (major) and 11.0 min (minor).



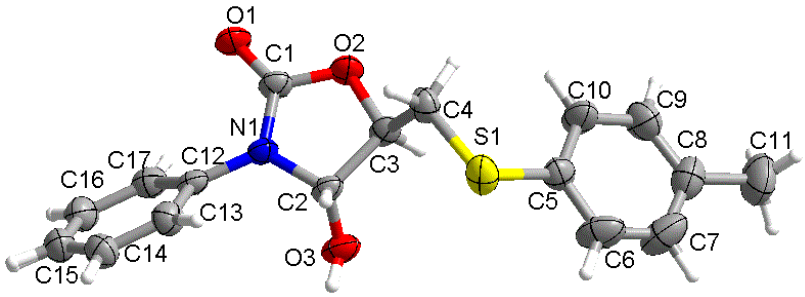
7. Determination of the absolute configuration by X-ray crystallograph

Absolute configurations of **3** and the relevant derivatives (**6**−**12**) are determined by X-ray structure analysis of the product **3i** (CCDC 1531932).



Displacement ellipsoids are drawn at the 30% probability level. (Solvent: ethyl acetate)

Absolute configurations of **5** and the relevant derivatives (**13**−**15**) are determined by X-ray structure analysis of the product **13b** (CCDC 1531893).



Displacement ellipsoids are drawn at the 30% probability level. (Solvent: ethyl acetate)

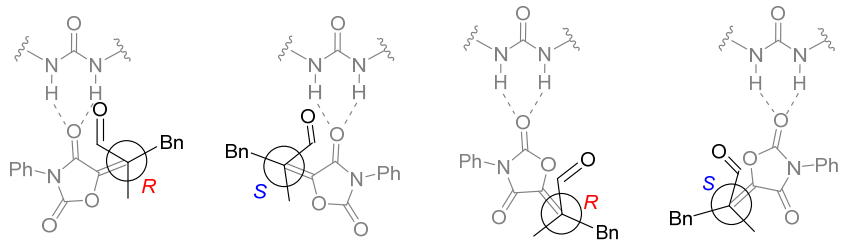
8. Computational method

All theoretical calculations were carried out with Gaussian 09 suit of programs,[1] with all ΔG being reported relative to the individual free starting materials: **catalyst**, **1a** and **2a**. Gas phase optimization of minimum and transition state (TS) electronic structures were first carried out with Becke's three parameter[2] and Lee-Yang-Parr's[3] B3LYP density functional using Pople's[4] 6-31G(d,p) basis set as it has been shown that this level of theory is adequate.[5,6]

B3LYP/6-31G(d,p) thermal and vibrational energy corrections from frequency calculations were added to the electronic energies of the optimized geometries to constitute Gibbs free energy. Second order derivative or Hessian of the completed calculations were verified to ascertain transition state (TS) structures having only one negative eigenvalue and none for minimum. All reported free energy or enthalpy values are in kcal/mol and referenced with respect to free starting materials, i.e. catalyst, **1a** and **2a**.

Theoretical discussion appendix

The first addition process of the organocatalyzed reaction between **1a** and **2a** would generate four possible *R* and *S* stereo-isomers. This is due to the two possible binding modes of the **2a** to the catalyst's urea core as shown in Scheme S1.



Scheme S1 Newman projection of **1a** addition to **2a** and leading to *R* and *S* stereo-isomers.

The optimized TS structures are shown in Fig. S1 corresponding to the hypothesized stereo-configurations from Scheme S1. Activation strain model analysis shows that the stability to **TS1a** is largely due to a relatively less strained TS (small E_{dist}), rather than a large negative E_{int} due to favorable non-covalent interactions. The minimum pre-complex and adduct energies connecting to the four TSs are summarized in Table S1. Optimized TS structures for protonation step are shown in Fig. S2.

Table S1 Free energy and enthalpy of minimum structures connecting the addition process. Values are in kcal/mol and referenced with respect to free starting materials.

	int1 ⟶ **TS1** ⟶ **int2**				
pre-complex	Δ*G*	Δ*H*	adduct	Δ*G*	Δ*H*
int1a	16.8	-9.6	**int2a**	18.8	-10.5
int1b	17.8	-9.2	**int2b**	24.4	-6.2
int1c	14.2	-11.1	**int2c**	28.8	-1.2
int1d	16.7	-10.0	**int2d**	26.3	-2.6

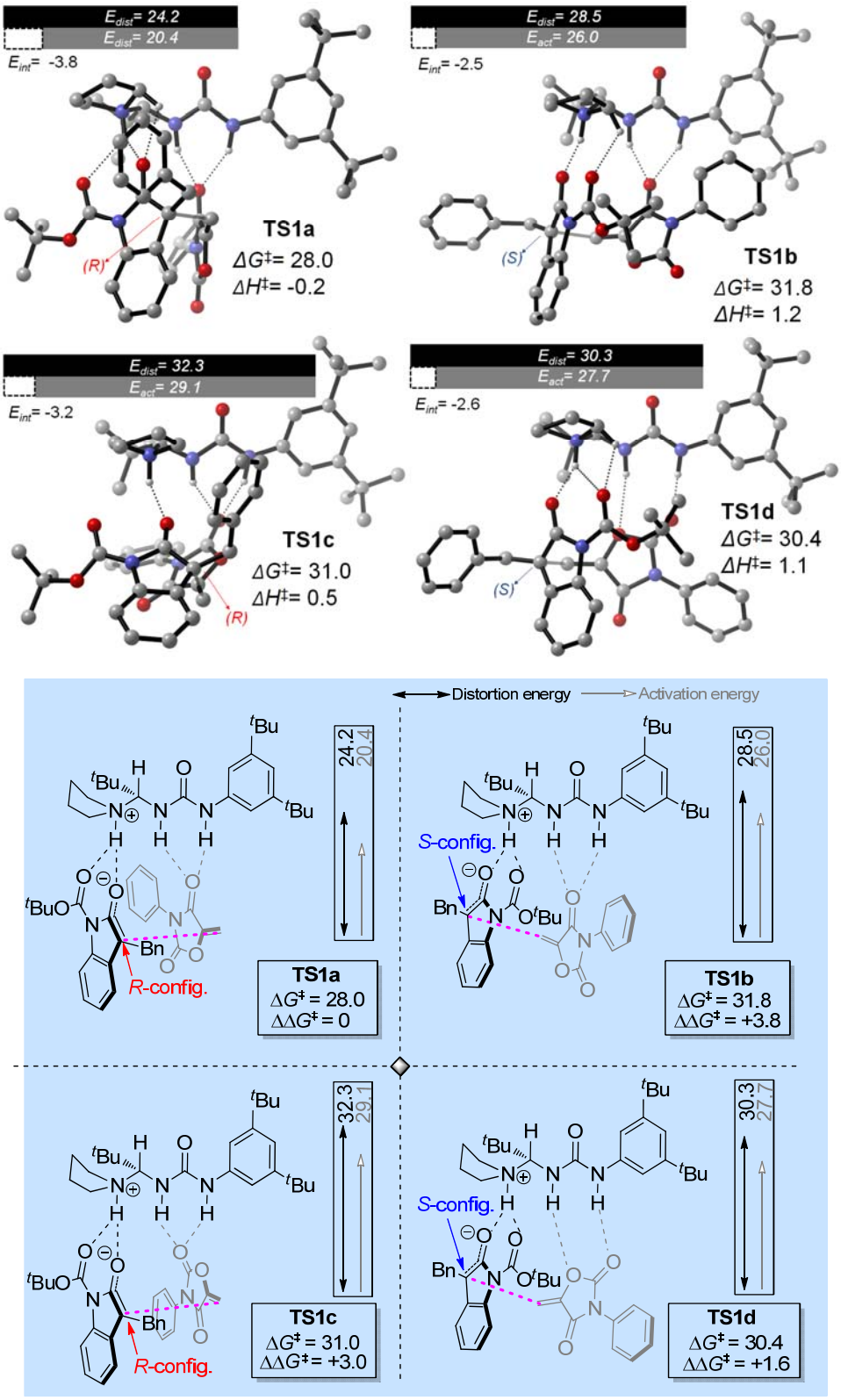


Fig. S1 Optimized TS for the addition process. Activation strain model bar with E_{dist} as distortion energy, E_{int} as interaction energy and E_{act} as activation energy barrier. Values are in kcal/mol.

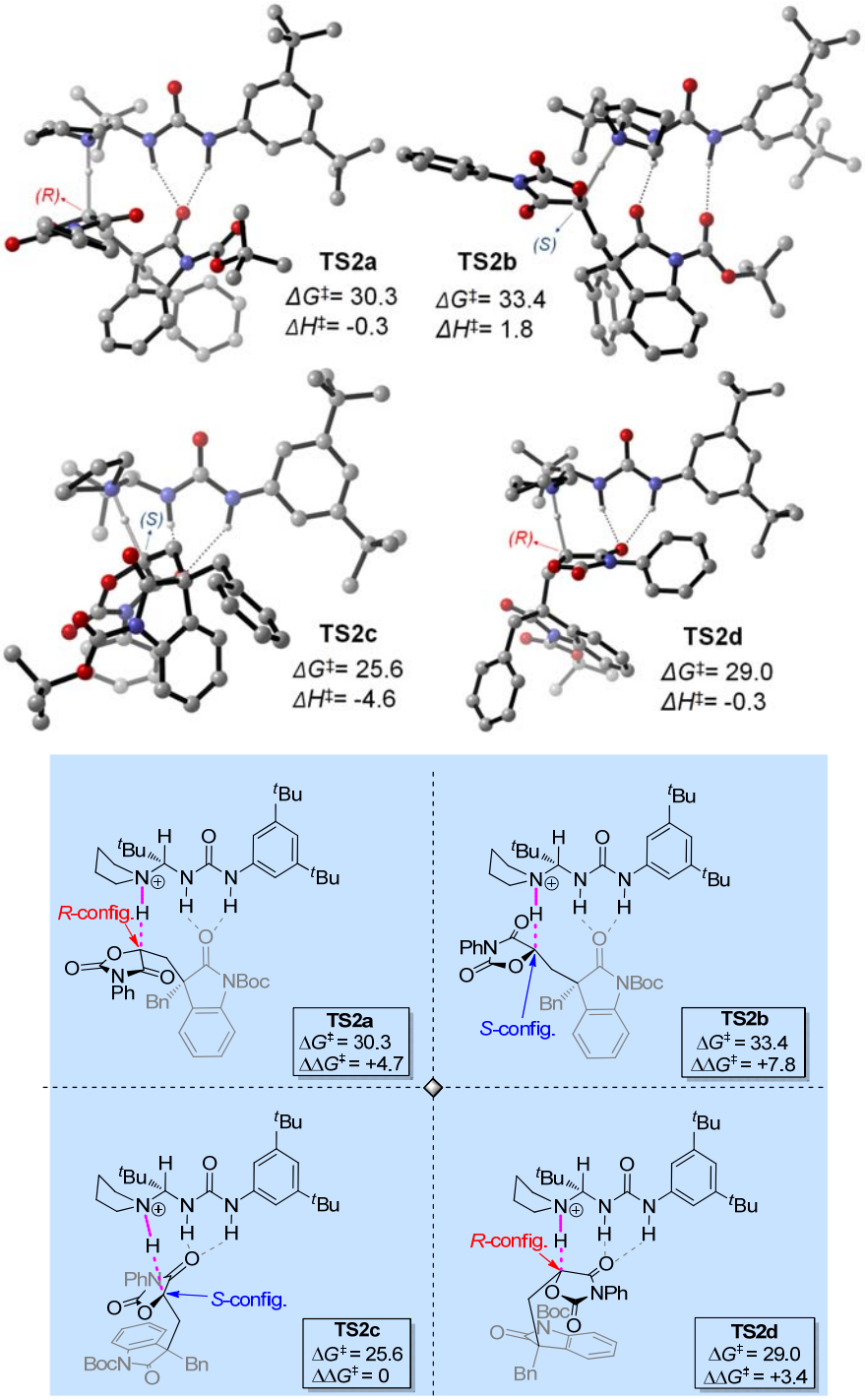


Fig. S2 Optimized TS for the protonation process. Values are in kcal/mol.

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Table S2: Energetics of individual species: E_e is electronic energy, G_{corr}, H_{corr} and ZPE are free energy, enthalpy and zero point energy corrections. G is free energy and H is enthalpy. All values are in hatrees

	E_e	G_{corr}	H_{corr}	ZPE	G	H
catalyst	-1178.8235	0.555702	0.653551	0.620758	-1178.2678	-1178.17
1a	-1055.2783	0.317465	0.39313	0.370532	-1054.9609	-1054.8852
2a	-665.72283	0.116186	0.165453	0.153662	-665.60664	-665.55738
TS1a	-2899.8307	1.040095	1.217883	1.150496	-2898.7906	-2898.6129
TS1b	-2899.8287	1.043928	1.217956	1.150943	-2898.7847	-2898.6107
TS1c	-2899.8298	1.043819	1.218095	1.15095	-2898.786	-2898.6117
TS1d	-2899.8288	1.041937	1.217958	1.150629	-2898.7869	-2898.6109
TS2a	-2899.8281	1.041138	1.215153	1.148509	-2898.787	-2898.613
TS2b	-2899.8244	1.04235	1.214758	1.148308	-2898.782	-2898.6096
TS2c	-2899.8347	1.040091	1.214891	1.14821	-2898.7946	-2898.6198
TS2d	-2899.828	1.038856	1.214927	1.148034	-2898.7891	-2898.6131
int1a	-2899.8448	1.036161	1.216928	1.148353	-2898.8086	-2898.6279
int1b	-2899.8437	1.036799	1.216485	1.14799	-2898.8069	-2898.6272
int1c	-2899.8476	1.03495	1.217356	1.148618	-2898.8127	-2898.6303
int1d	-2899.8454	1.036652	1.216882	1.148353	-2898.8088	-2898.6285
int2a	-2899.8494	1.043964	1.220087	1.152937	-2898.8054	-2898.6293
int2b	-2899.8424	1.045979	1.219907	1.152892	-2898.7964	-2898.6225
int2c	-2899.8346	1.045124	1.220086	1.152857	-2898.7895	-2898.6145
int2d	-2899.8366	1.043234	1.219911	1.152441	-2898.7934	-2898.6167

Gaussian archive files

Catalyst

1\1\GINC-R375\FOpt\RB3LYP\6-31G(d,p)\C24H41N3O1\ROOT\21-Feb-2017\0\\#
B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\Cataly
st\\0,1\C,-0.4481307092,1.0520800938,0.1552843715\O,-0.3500452353,1.39
18473421,-1.0193899064\N,-0.2669869552,-0.2469663003,0.6113556381\H,-0
.4696195948,-0.4168203868,1.5856771393\N,-0.7748274147,1.9333764944,1.
1680897561\H,-0.6283332015,1.6586601667,2.1297243171\C,0.0130555417,-1
.4114211515,-0.1352597152\C,0.570442724,-3.7969086059,-1.4571507476\C,
0.2838805501,-1.399579849,-1.5075811198\C,0.0268927763,-2.6252634216,0
.5647935309\C,0.3044754378,-3.8329351706,-0.0806781908\C,0.5630989651,
-2.5961573171,-2.1799466703\H,0.2636824897,-0.4526254896,-2.0260129119
\H,-0.1843735693,-2.6160558089,1.6318491651\H,0.7862717891,-4.72061887
97,-1.9736725485\C,0.3068583042,-5.1433373464,0.7323297197\C,0.8510192
402,-2.5426916083,-3.694217505\C,-0.3757895232,-1.9518064253,-4.428878
0873\H,-0.6108979407,-0.9427198482,-4.0798062347\H,-1.2624514867,-2.57
49738074,-4.2716551609\H,-0.1850062288,-1.8985260809,-5.5069222814\C,2
.0825990134,-1.6423374779,-3.9517699488\H,1.9223750398,-0.6227334106,-
3.5909806304\H,2.2972125919,-1.5882737912,-5.025256454\H,2.9698235463,
-2.0403037271,-3.4480047071\C,1.1421384072,-3.9327333096,-4.2906121571
\H,2.0223345223,-4.3972946563,-3.8340267498\H,1.3389780021,-3.83831410
45,-5.3634879399\H,0.293959416,-4.6146992644,-4.1704324417\C,0.6294757
491,-6.3739841567,-0.1362398848\H,1.6207745377,-6.300817366,-0.5948168
363\H,-0.1068338191,-6.5140063202,-0.934065615\H,0.6187721052,-7.27557
81811,0.4848537353\C,1.3717388733,-5.0556618706,1.8512030273\H,2.37080
99821,-4.9068464411,1.4289036304\H,1.3852624115,-5.9799830034,2.439977
6679\H,1.1744355643,-4.2273839138,2.5382212282\C,-1.0866618078,-5.3597
853442,1.3685921033\H,-1.3600470623,-4.5410889545,2.0408378293\H,-1.10
10680999,-6.2877089052,1.9516502516\H,-1.8612277016,-5.4302030598,0.59
81069569\C,-0.7956766135,3.3830779139,0.9629049565\H,-0.5300117055,3.5
313320272,-0.096051917\C,-2.2535145792,3.9399828458,1.1547219435\C,-2.
4091864317,5.3545342025,0.5508149397\H,-2.058878151,5.376375323,-0.487
242783\H,-1.8781137373,6.1313882167,1.100645445\H,-3.4682071507,5.6333
410971,0.5435769351\C,-3.2110334483,3.0223522549,0.3583977685\H,-3.267
3608818,2.0219669607,0.7921727046\H,-2.8872107553,2.9160889279,-0.6820
359401\H,-4.2188499157,3.45039403,0.3590900269\C,-2.6735111541,3.93044
23555,2.6357838301\H,-2.620626838,2.9189339195,3.0531413777\H,-3.70987
61353,4.2707361052,2.7372296284\H,-2.0443642639,4.5766209173,3.2531749
494\N,0.2417203136,3.9212328168,1.8594603781\C,1.5954311601,3.45037072
46,1.4979485242\C,2.538027594,4.2687653549,2.3967138962\C,1.7226869781
,5.5404497223,2.7485483947\C,0.4044826633,5.3781068819,1.9711115855\H,
1.808533876,3.6475848601,0.4311215937\H,1.6931861524,2.3736072224,1.65
11796818\H,2.7957683748,3.7111875727,3.3014832297\H,3.4735719478,4.498

7922981,1.8797400062\H,2.2358089836,6.4659639154,2.4731830965\H,1.5240
987546,5.5839811595,3.8231775904\H,0.4858404607,5.8615664979,0.9800636
93\H,-0.4337468076,5.834579095,2.4988169015\\Version=ES64L-G09RevE.01\
State=1-A\HF=-1178.8235318\RMSD=8.508e-09\RMSF=2.367e-06\Dipole=0.1085
879,0.150997,1.2199915\Quadrupole=-4.2070335,4.6396526,-0.4326191,0.77
77879,-1.0846985,2.6327832\PG=C01 [X(C24H41N3O1)]\\@

1a

1\1\GINC-R2425\FOpt\RB3LYP\6-31G(d,p)\C20H21N1O3\ROOT\31-Mar-2017\0\\#
B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\nucle
ophile\\0,1\C,-0.0710062432,-2.8684101374,-0.0664194237\C,-0.228407352
5,-4.303727961,2.2996532069\C,0.5238739827,-2.3695618997,1.1032242809\
C,-0.7456456883,-4.0821011632,-0.0492825604\C,-0.8218180669,-4.8084832
186,1.1429120519\C,0.44830174,-3.0793255322,2.3005192791\H,-1.21338608
02,-4.4600296153,-0.9543792878\H,-1.3440621283,-5.759753493,1.16820641
14\H,0.9011216574,-2.7013391082,3.2037864612\H,-0.2900631696,-4.866492
939,3.2264441827\C,0.9070246489,-0.7518547898,-0.5446373067\N,1.108261
266,-1.0918345136,0.8274105185\O,1.3054591081,0.2391080605,-1.10632896
09\C,0.8223029251,-2.4124214521,-2.4790145423\H,0.1670511853,-3.158493
2106,-2.9415229683\H,0.8805658427,-1.5637921587,-3.1678691686\C,2.2033
046499,-2.9991385947,-2.2686662073\C,4.7714369991,-4.0825291238,-1.874
6224183\C,3.3386981741,-2.1752252171,-2.2818199389\C,2.3782642655,-4.3
737450389,-2.0595333246\C,3.6499407581,-4.9128461805,-1.8633093767\C,4
.6113311279,-2.7120783251,-2.0846996411\H,3.2198377298,-1.1080043479,-
2.4435521852\H,1.5107119714,-5.0279472857,-2.0520642141\H,3.7641022723
,-5.9816044436,-1.7056184957\H,5.4786411194,-2.0582013863,-2.101456425
4\H,5.7627295799,-4.5010694957,-1.7262528548\C,1.8290527816,-0.2394390
097,1.6945035817\O,2.0828619271,0.9114080695,1.4294450409\O,2.18101316
22,-0.8984153019,2.8126729491\C,2.9571843887,-0.2137028125,3.874849526
5\C,3.1200732214,-1.3145088526,4.9250207927\H,2.1473657411,-1.63499386
18,5.3100536307\H,3.713165148,-0.9412767579,5.764841319\H,3.6305912481
,-2.1830635124,4.4998568336\C,2.1523832481,0.9616773604,4.4360732227\H
,1.1653668641,0.6243276241,4.7674872436\H,2.0275111169,1.7479113157,3.
6918417228\H,2.6763591547,1.3770428817,5.3027627656\C,4.3190030605,0.2
154143897,3.3220366194\H,4.9318269708,0.6117398468,4.1378675412\H,4.21
0552869,0.9855558379,2.5585752514\H,4.8420603202,-0.6433644983,2.89045
20457\C,0.118580096,-1.8943384303,-1.1937546323\H,-0.8461692034,-1.469
0541169,-1.5043415059\\Version=ES64L-G09RevE.01\State=1-A\HF=-1055.278
3345\RMSD=7.449e-09\RMSF=2.376e-06\Dipole=-0.1707473,-1.268436,1.00752
6\Quadrupole=3.2789697,-7.6566795,4.3777099,3.3949868,4.9994673,5.1049
607\PG=C01 [X(C20H21N1O3)]\\@

2a

1\1\GINC-R2431\FOpt\RB3LYP\6-31G(d,p)\C10H7N1O3\ROOT\31-Mar-2017\0\\#

B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\electr
ophile\\0,1\C,-0.5801383652,2.5735564016,0.5339878942\O,-1.1050973259,
2.2241072317,-0.5009750805\C,-1.1261141327,2.5075114728,1.9149579983\C
,-2.3098436159,2.0374694111,2.29550679\H,-2.9799214733,1.6524977004,1.
537103116\H,-2.6143562633,2.0305692503,3.3345382512\O,-0.1776449498,3.
0268987443,2.7764644972\C,0.9301689486,3.4199957931,2.0585000748\N,0.6
928702555,3.1420759807,0.7036015802\O,1.9008151986,3.9064727712,2.5664
210339\C,1.6339482966,3.4059177271,-0.3436358911\C,3.45313576,3.906003
2607,-2.3946722578\C,1.1709139718,3.8496750342,-1.5863553011\C,3.00028
63608,3.2085043693,-0.1201732724\C,3.9039225635,3.4673729856,-1.149058
211\C,2.0871293635,4.0921264489,-2.6085789602\H,0.1104704729,3.9862507
9,-1.7531924309\H,3.3493194451,2.8743353224,0.8483106275\H,4.964945561
3,3.3199838067,-0.9729464743\H,1.7268355171,4.4323623071,-3.5744719645
\H,4.1620254109,4.1014591908,-3.1933500195\\Version=ES64L-G09RevE.01\S
tate=1-A\HF=-665.7228304\RMSD=3.414e-09\RMSF=5.866e-05\Dipole=-0.24519
93,-0.1678051,-0.3389164\Quadrupole=5.0065088,-3.0279881,-1.9785207,-0
.600887,-8.0694166,-5.7760675\PG=C01 [X(C10H7N1O3)]\\@

TS1a

1\1\GINC-R2755\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\01-Apr-2017\0\\#
B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine iop(1/8=1)\\TS for Michael addition conf.
2a R-config.\\0,1\C,2.2336062428,-0.3255305172,2.0171942615\O,2.844993
4908,-1.0658337572,2.7888061229\N,2.7537525853,0.2946215382,0.90723963
21\H,2.1149802063,0.9193545406,0.4179525668\N,0.8873839983,-0.02597782
14,2.1872562116\H,0.4409503253,0.5939554419,1.5092800258\C,4.056666972
3,0.1988098265,0.3774408335\C,6.5726592052,0.1132290844,-0.8083715513\
C,5.073511354,-0.5671763372,0.9573898694\C,4.3121050428,0.919985537,-0
.7968474765\C,5.5687053622,0.8895456611,-1.4063738082\C,6.3425025119,-
0.6160439482,0.3660138764\H,4.8539519536,-1.1111106057,1.8644316523\H,
3.5075481591,1.5077127481,-1.2310376844\H,7.5501760939,0.0777019724,-1
.266583344\C,5.8022638972,1.6988492943,-2.6980047186\C,7.438349308,-1.
4713368166,1.0343689659\C,7.6907418821,-0.9527533953,2.4700104404\H,6.
7863648611,-0.9994035052,3.0828286476\H,8.0305819047,0.0881107983,2.45
47660591\H,8.4624859156,-1.5549181214,2.9634212155\C,6.9720950641,-2.9
451599974,1.0990849625\H,6.0459123931,-3.0524758615,1.6703826339\H,7.7
367216849,-3.5669058587,1.5790721386\H,6.7933253294,-3.3424639708,0.09
43643579\C,8.7740709785,-1.4264994182,0.2684913263\H,8.6730744478,-1.8
108383473,-0.7517762903\H,9.5141929897,-2.0481140866,0.7830218578\H,9.
1788115615,-0.4107048148,0.2126396581\C,7.2371168077,1.5458491116,-3.2
370894474\H,7.4710560155,0.5053902377,-3.4847498076\H,7.9828410102,1.9
025262596,-2.5192843792\H,7.3510207556,2.1364471592,-4.1519155569\C,4.
8246947953,1.2146616889,-3.7951884395\H,4.9821943484,0.1542248641,-4.0
18097405\H,4.9765725896,1.7827932853,-4.7199550925\H,3.7801642604,1.34

1226007,-3.4962156368\C,5.553208846,3.1999799718,-2.4183767514\H,4.531
1634181,3.3868083425,-2.0764850634\H,5.7125086349,3.7898831123,-3.3281
573151\H,6.2360352344,3.5723414002,-1.6476949225\C,0.1710687073,-0.429
3966058,3.3490082729\H,0.8889680556,-0.8758764011,4.0409995166\C,-0.52
62237445,0.7749788424,4.0669160582\C,-1.1057107385,0.38345385,5.445132
852\H,-0.3905230484,-0.2013476653,6.0353378108\H,-2.0402935685,-0.1751
046433,5.3828095554\H,-1.3229314884,1.2946016918,6.0106993184\C,0.6013
750389,1.8039256588,4.3326669876\H,1.0140489347,2.2001972866,3.4037097
38\H,1.4210159655,1.3647508401,4.9122395709\H,0.1948999647,2.641848454
1,4.9070144941\C,-1.6105549302,1.4404269328,3.2000502769\H,-1.19095318
02,1.8549215998,2.2785691873\H,-2.0575039369,2.2728759994,3.7536485257
\H,-2.41053221,0.7484238432,2.9269126534\N,-0.725123986,-1.6189026456,
2.8968080349\C,-1.786222045,-2.1846407621,3.7994901839\C,-2.1211670798
,-3.515778866,3.1332022935\C,-0.7467210371,-4.0641421953,2.702117998\C
,0.1387750098,-2.8197898203,2.4923182971\H,-2.626861315,-1.4965379535,
3.8405588948\H,-1.3537806549,-2.3210231653,4.7938351322\H,-2.660004538
7,-4.1842341811,3.8093547769\H,-2.7498190982,-3.3238174268,2.260093167
3\H,-0.8183657388,-4.6571037012,1.7882367729\H,-0.320925905,-4.6997795
632,3.4843736518\H,0.419083819,-2.6626175331,1.4552421825\H,1.03482019
68,-2.8100639694,3.1120206567\C,-2.6374200048,-1.0541350175,-2.9550522
521\C,-4.929158012,0.117564669,-4.0226958833\C,-3.6200581089,-0.489779
6368,-2.1111827811\C,-2.8282045546,-1.0431767366,-4.3392897378\C,-3.98
08829081,-0.4607054424,-4.8681243642\C,-4.7603904865,0.1123953048,-2.6
327216089\H,-2.0826275607,-1.4794964053,-4.9982835069\H,-4.1343455122,
-0.4476789857,-5.9430558381\H,-5.5008852927,0.5659128095,-1.9930444485
\H,-5.815129131,0.5844289883,-4.4417559241\C,-1.5084164787,-1.49241973
71,-2.1476988715\C,-1.9001455256,-1.3347112972,-0.7725651572\N,-3.1811
968615,-0.6658016735,-0.7562482704\O,-1.2618311989,-1.6521349987,0.240
5202285\C,-0.5593151112,-2.6110534201,-2.5334774766\H,-0.3284651378,-2
.5190763606,-3.6029522045\H,0.3917521451,-2.4809089214,-2.006419583\C,
-1.0720100069,-4.0147412118,-2.2450839533\C,-1.9864869979,-6.625547578
7,-1.699383034\C,-0.381025853,-4.8492064181,-1.3572497443\C,-2.2311309
313,-4.5130571763,-2.858196231\C,-2.6843337245,-5.8038906837,-2.587448
4708\C,-0.8301312642,-6.1439081787,-1.0857818143\H,0.525901969,-4.4828
951946,-0.8825761514\H,-2.7844968162,-3.8831532037,-3.5483467334\H,-3.
5833053268,-6.1708173181,-3.0750521508\H,-0.2712742361,-6.7769191423,-
0.4015357509\H,-2.3381042337,-7.6323444178,-1.4930683263\C,-3.91228565
3,-0.4881149944,0.4149753638\O,-3.5058982477,-0.7864299632,1.529566492
3\O,-5.1174950155,0.0381617855,0.1539240553\C,-6.1361326666,0.23564519
95,1.2089150016\C,-7.3185423424,0.8025153539,0.4190484409\H,-7.0483959
005,1.7486174811,-0.0584360347\H,-8.1616040195,0.9850651481,1.09154076
95\H,-7.6396585014,0.1003774088,-0.3552054919\C,-5.6398830829,1.253005
1791,2.2390416766\H,-5.3037889709,2.1669505318,1.7405955465\H,-4.81846
48246,0.8526302029,2.8319541052\H,-6.462092738,1.5164370686,2.91202710

82\C,-6.5020480223,-1.1117816488,1.8371428421\H,-7.3394993499,-0.97404
81337,2.5283057259\H,-5.6610211946,-1.5344965967,2.3867421865\H,-6.813
3166494,-1.8205834819,1.0639636206\H,-1.1996351456,-1.346126686,2.0043
001505\C,-0.2895211566,2.1979432404,-0.84308576\O,0.3400900038,1.91727
79961,0.2052410338\C,-0.5097419935,1.4466784091,-2.0216072139\C,-0.121
3930702,0.1585388944,-2.3399186463\H,0.6051627463,-0.2869039447,-1.668
8242656\H,-0.033215284,-0.0954521578,-3.3903209121\O,-1.2509812004,2.2
330509104,-2.9231129294\C,-1.5036045466,3.4418142644,-2.3606312881\N,-
0.9127704084,3.4446501188,-1.0847568733\O,-2.1275338016,4.3259510936,-
2.8977739546\C,-0.9426838562,4.557576425,-0.1958009217\C,-1.000607448,
6.7408647246,1.5518732633\C,0.1650386199,4.8338497503,0.6161004937\C,-
2.0782116056,5.3755262099,-0.1357221189\C,-2.0966547519,6.4649737234,0
.7333067109\C,0.1258171271,5.9198316742,1.4893814498\H,1.0365301849,4.
1950684963,0.5671325636\H,-2.9207735434,5.1701325916,-0.7828112763\H,-
2.9769628409,7.1001386618,0.7683566624\H,0.9879963396,6.1276474006,2.1
164029839\H,-1.0222119138,7.5902804455,2.2280999936\\Version=ES64L-G09
RevE.01\State=1-A\HF=-2899.8307417\RMSD=4.925e-09\RMSF=2.984e-07\Dipol
e=-1.6756332,-1.6545552,2.8815243\Quadrupole=7.5513868,-9.8784138,2.32
7027,6.1737421,-19.3976151,5.6897767\PG=C01 [X(C54H69N5O7)]\\@

TS1b

1\1\GINC-R3348\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\01-Mar-2017\0\\#
B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine iop(1/8=1)\\PES for Michael addition conf.
1a S-config.\\0,1\C,2.417134048,2.0518849199,0.4147300954\O,2.9938344
79,2.8269879077,1.1804542332\N,3.0052243689,1.0505236223,-0.3122687682
\H,2.3681043812,0.4449797526,-0.8283038483\N,1.0408796836,2.1282087024
,0.2022405248\H,0.6046337381,1.4704864114,-0.4480445594\C,4.3821357547
,0.7671241346,-0.4464684348\C,7.054357759,0.1143546686,-0.8634593561\C
,5.3799242285,1.4141302387,0.2904201809\C,4.7338017469,-0.2114820358,-
1.3857110882\C,6.0703213735,-0.5503986551,-1.6106047964\C,6.7278591291
,1.0919566176,0.0855860565\H,5.085305704,2.1652117776,1.0083579886\H,3
.9421466386,-0.7034509604,-1.9434794423\H,8.0928057645,-0.1345458991,-
1.0263273975\C,6.4122910539,-1.6231339013,-2.6643612171\C,7.7997680441
,1.8296303365,0.9138268488\C,7.7080537567,3.3490000922,0.6367390608\H,
6.7244519484,3.7498714184,0.8965043434\H,7.8870799232,3.5636618556,-0.
422037381\H,8.4580854994,3.890679533,1.2247425696\C,7.5552857183,1.570
4889165,2.4194185484\H,6.5679198134,1.9184846718,2.7353511629\H,8.3048
183639,2.094074694,3.0241473184\H,7.6222734186,0.5013864537,2.64726754
58\C,9.2301312619,1.3680350475,0.5766154261\H,9.3738811501,0.301736499
7,0.7797031711\H,9.9494389399,1.9203610506,1.1902252512\H,9.4818395749
,1.5528736058,-0.4727718347\C,7.9292753691,-1.8574559995,-2.7949899256
\H,8.3702696472,-2.2084809948,-1.8563840535\H,8.458026681,-0.949477874
3,-3.1028217221\H,8.1185413983,-2.6231186168,-3.5544155458\C,5.7521251

863,-2.9648123932,-2.2694314448\H,6.1189804535,-3.3089571515,-1.297183
2777\H,5.9821188134,-3.7363099819,-3.0135065429\H,4.6643830462,-2.8820
610674,-2.1981281918\C,5.8775837597,-1.1776842454,-4.0462180045\H,4.79
24472686,-1.0411690434,-4.0385760827\H,6.1127588836,-1.9305914284,-4.8
07195265\H,6.3311426422,-0.2298177991,-4.3542019156\C,0.2983185349,3.2
273878822,0.7325032318\H,0.9716944901,3.7628423405,1.4067593581\C,-0.1
857786884,4.2364623402,-0.3673353465\C,-0.7619572648,5.5393654068,0.23
09716767\H,-0.1123273697,5.9493299517,1.0128830422\H,-1.7671331482,5.4
238578673,0.6386780816\H,-0.8311395392,6.2932772124,-0.5589206584\C,1.
0913733881,4.6315135081,-1.1508108697\H,1.5083799522,3.7840951122,-1.6
981719075\H,1.870488911,5.0202431008,-0.4875463455\H,0.84091463,5.4112
527844,-1.876299692\C,-1.196707726,3.61401681,-1.343253785\H,-0.781838
9416,2.7288035631,-1.8359898281\H,-1.4461271083,4.3396750722,-2.124362
5114\H,-2.1210818345,3.3114987666,-0.847555339\N,-0.7705786374,2.59839
1774,1.6554029429\C,-1.7374351637,3.5010967997,2.3826999719\C,-2.19122
46539,2.6551213628,3.5673205962\C,-0.8838174837,1.9999787146,4.0341633
513\C,-0.1055884304,1.7294737509,2.7367576499\H,-2.5402324901,3.777599
9947,1.7017774393\H,-1.1968726539,4.3939126935,2.7048837125\H,-2.67442
06262,3.2623884559,4.3370166628\H,-2.8908136853,1.8893040636,3.2233881
073\H,-1.0571854543,1.0735224439,4.5841708209\H,-0.3217621622,2.681302
5557,4.681613264\H,-0.2019375213,0.6968090461,2.4118526187\H,0.9467272
755,2.0061666123,2.7930754792\C,-4.9136734777,-0.9746108534,-1.3197453
106\C,-6.2423994139,-3.3321125582,-0.6798887658\C,-4.6303856036,-1.657
1315,-0.120824585\C,-5.8649219532,-1.4860333821,-2.2021405914\C,-6.528
7458135,-2.6708035392,-1.8749019825\C,-5.2899663468,-2.832387621,0.217
0473741\H,-6.0979615623,-0.9609466353,-3.1233107639\H,-7.2744158269,-3
.0762240279,-2.552321616\H,-5.0788316141,-3.3538205555,1.1378451379\H,
-6.7637674823,-4.2516831528,-0.432267102\C,-4.0460614996,0.1974333037,
-1.4111915268\C,-3.4242051691,0.3366524995,-0.1151424358\N,-3.67132194
72,-0.8764374401,0.6055690045\O,-2.726486659,1.2782714664,0.2996893043
\C,-4.3840461317,1.4121749415,-2.250891913\H,-3.5645162002,2.131952136
8,-2.1506907454\H,-4.4077299111,1.1224538142,-3.309148792\C,-5.6978099
593,2.0974213457,-1.9047746861\C,-8.1203607468,3.3922265858,-1.2773168
843\C,-5.9053087863,2.6571577608,-0.6351706117\C,-6.7233543123,2.20188
78896,-2.8512410117\C,-7.925874187,2.842169107,-2.5433909146\C,-7.1035
024889,3.297604321,-0.323955012\H,-5.1189135898,2.5860508481,0.1108194
208\H,-6.5786361071,1.7796896447,-3.8429572982\H,-8.7090066554,2.90861
62554,-3.2934489841\H,-7.2457111113,3.724697907,0.6651267393\H,-9.0544
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4048\O,-2.2731297897,-0.4794794044,2.4046541547\O,-3.1122092583,-2.555
4053802,1.9862839875\C,-2.4786944229,-3.2444117589,3.1383733155\C,-2.9
564849655,-4.685981515,2.9517786648\H,-4.0455939778,-4.7529481428,3.03
27794004\H,-2.5163220818,-5.3238288637,3.7238812794\H,-2.650478281,-5.
0602847358,1.971373778\C,-3.0049442804,-2.6441577549,4.4437136295\H,-4

.098820872,-2.6707288863,4.4641622177\H,-2.6739596343,-1.612342412,4.5
672809999\H,-2.6360781379,-3.2342383935,5.2884680274\C,-0.9561793225,-
3.1715060674,3.0190155791\H,-0.5056748033,-3.7517158899,3.8306504071\H
,-0.5980674822,-2.144502296,3.0888001\H,-0.6274804816,-3.6067253813,2.
0723179756\H,-1.379554981,1.9584302507,1.093760602\C,-0.2338628447,-1.
2259398391,-1.282991915\O,0.5022306831,-0.2116197022,-1.2519663363\C,-
1.5118294833,-1.4311704102,-1.8473849683\C,-2.3906995613,-0.5503426432
,-2.4708610425\H,-1.9569166272,0.412374321,-2.7226784013\H,-3.07247208
14,-0.9663684717,-3.2060991735\O,-1.8820094427,-2.7813686927,-1.653798
1756\C,-0.903504992,-3.4201428599,-0.9740801295\N,0.131484427,-2.50032
5632,-0.7619685636\O,-0.9579519519,-4.5772607076,-0.6161830893\C,1.341
2480356,-2.834095912,-0.0921144855\C,3.6974354653,-3.5095897251,1.2548
754325\C,1.9019608501,-1.9427898652,0.8296368855\C,1.9582217058,-4.067
4924564,-0.3375353059\C,3.1269638513,-4.4011369564,0.3445192633\C,3.08
36030246,-2.2790996875,1.4892787199\H,1.4196097702,-0.9917680609,1.012
5959779\H,1.5081031846,-4.7618519164,-1.0354820809\H,3.5954300118,-5.3
625674959,0.1562951867\H,3.5225263449,-1.5742484848,2.1885438465\H,4.6
131668526,-3.7711182921,1.7762397199\\Version=ES64L-G09RevE.01\State=1
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861288,1.7056978\Quadrupole=-10.359372,-1.6282099,11.9875819,-14.05232
43,-4.4993072,-0.7226771\PG=C01 [X(C54H69N5O7)]\\@

TS1c

1\1\GINC-R2554\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\24-Feb-2017\0\\#
B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine\\PES for Michael addition conf. 2b R-confi
g.\\0,1\C,2.3979110074,0.3924795581,1.6655888192\O,2.8774945487,-0.150
6485953,2.6629512923\N,3.0511996517,0.6512036429,0.4924655706\H,2.5114
346838,1.1343653878,-0.2262799207\N,1.0603234414,0.7949089216,1.626882
9813\H,0.7597035453,1.3373427864,0.8245423563\C,4.3878439819,0.3532398
307,0.1517889573\C,6.9869757485,-0.160817435,-0.694792935\C,5.28019764
6,-0.302518921,1.0062865797\C,4.8074400387,0.7491588254,-1.1254237247\
C,6.1087953772,0.4994340042,-1.5674313104\C,6.5909878153,-0.5651444956
,0.5871390515\H,4.9351033097,-0.5943330365,1.9872853795\H,4.095516775,
1.2593558008,-1.7683545841\H,7.9970209941,-0.361559017,-1.0211004801\C
,6.5269940801,0.9540300728,-2.980248406\C,7.5472279389,-1.2895333945,1
.556676207\C,7.7044267098,-0.4501999016,2.8468140258\H,6.7456781502,-0
.2952817635,3.3492331568\H,8.1266017561,0.5348903842,2.6222013369\H,8.
3755373245,-0.9548674444,3.5515225091\C,6.960859125,-2.6749560985,1.91
80435721\H,5.9797112965,-2.5881769661,2.3930833555\H,7.62497021,-3.201
5133517,2.6132686571\H,6.845866337,-3.2954226036,1.0229638001\C,8.9482
482847,-1.5068861375,0.9546034386\H,8.9130575385,-2.1229637837,0.05013
11129\H,9.584817441,-2.023266837,1.6806105537\H,9.436104445,-0.5593028
778,0.7039492357\C,7.9904091116,0.5987796989,-3.3044375394\H,8.1651717

802,-0.4814944819,-3.2706132367\H,8.6899468726,1.0801577194,-2.6133834
326\H,8.2366601394,0.9412836291,-4.3147935653\C,5.6232792433,0.2677706
074,-4.0318874545\H,5.7192837692,-0.8216732754,-3.9780818195\H,5.90503
26295,0.5843665991,-5.0426672164\H,4.5681893756,0.5168838002,-3.887262
4304\C,6.369879085,2.4888558496,-3.0954321959\H,5.3377781871,2.8067042
587,-2.9224132904\H,6.6602418895,2.8285590906,-4.0962456769\H,7.003740
0683,3.0021912796,-2.3649492062\C,0.2541695618,0.7938556153,2.80550401
92\H,0.9053924341,0.5209363997,3.6397785344\C,-0.416429536,2.180966205
6,3.0935023343\C,-0.8882187333,2.2936363109,4.5615038082\H,-0.08871868
55,2.0252202709,5.2614074883\H,-1.7634409861,1.6842205292,4.7887823309
\H,-1.1669444004,3.3315022673,4.7672513905\C,0.681992054,3.2556421156,
2.8971367972\H,0.9843306686,3.3555708848,1.853037701\H,1.5742672566,3.
0317918415,3.49201024\H,0.295029005,4.2255413252,3.2232184725\C,-1.586
6313692,2.4727423903,2.1373883929\H,-1.2864318269,2.4042675095,1.08934
58033\H,-1.9447063029,3.49408344,2.2967129406\H,-2.4328367923,1.795175
8779,2.2768348693\N,-0.7265555981,-0.4023150263,2.668953568\C,-1.71283
93691,-0.6699555346,3.7772278411\C,-2.0961666734,-2.1305002726,3.56570
94859\C,-0.7535437033,-2.7963549408,3.2279391196\C,0.0340200669,-1.723
1815793,2.4559864689\H,-2.5514526823,0.016404513,3.688119989\H,-1.1972
81425,-0.5237566385,4.7298324769\H,-2.5800632581,-2.5532486867,4.45001
60194\H,-2.7964394684,-2.1986416628,2.7282850674\H,-0.8678293254,-3.70
40860207,2.6327062736\H,-0.2230066763,-3.0642612728,4.147509161\H,0.05
21804053,-1.8971379408,1.3832016443\H,1.0533920463,-1.5897422598,2.816
0975901\C,-3.3937015596,-2.6521106025,-2.1798386725\C,-6.0282246095,-3
.4925808197,-2.5551336384\C,-4.438357085,-2.1603371122,-1.3657873385\C
,-3.688788269,-3.5660796388,-3.193864975\C,-5.0097019167,-3.9837326906
,-3.3758942253\C,-5.7543337653,-2.5745601487,-1.5340956723\H,-2.897822
8449,-3.9553035159,-3.828600857\H,-5.2452994949,-4.6960093304,-4.16100
86945\H,-6.5457840625,-2.1968490878,-0.901962034\H,-7.0510227561,-3.82
43902279,-2.7054196812\C,-2.1419729803,-1.9927082198,-1.7960215511\C,-
2.4422503371,-1.2617357836,-0.5784731475\N,-3.8614731608,-1.3037567092
,-0.3843266483\O,-1.6598443076,-0.5809492973,0.0964695911\C,-0.7693706
457,-2.6288605735,-1.9478306137\H,-0.6894574243,-3.0269235798,-2.96979
43768\H,-0.015905826,-1.8388534866,-1.8773134537\C,-0.3908550333,-3.73
3602851,-0.968931868\C,0.4309762159,-5.8046782168,0.7654283556\C,0.937
0777979,-3.8221270295,-0.5239246885\C,-1.3018385049,-4.7028813314,-0.5
23674298\C,-0.8949077563,-5.7276458429,0.3334140365\C,1.3474422654,-4.
8447809901,0.3331854758\H,1.6590229276,-3.0796752046,-0.8555370573\H,-
2.3339897899,-4.6627215974,-0.8554726539\H,-1.6168897635,-6.4717618,0.
6589489008\H,2.381975987,-4.8889895995,0.6617900293\H,0.7462762661,-6.
6047756003,1.4290002058\C,-4.5131315612,-0.4591593764,0.5224789088\O,-
3.9818066119,-0.0281251727,1.5319171652\O,-5.7629298808,-0.2103944784,
0.1203924484\C,-6.6024591459,0.8190662039,0.7794151368\C,-7.8604220182
,0.8158390636,-0.0911291529\H,-7.6132536732,1.0708068994,-1.1247682356

\H,-8.5756895311,1.5512671475,0.2882678272\H,-8.3402351393,-0.16722708
97,-0.0800226471\C,-5.8915505504,2.1729874427,0.7009623276\H,-5.537294
464,2.3537318736,-0.3182393076\H,-5.0380099376,2.2139767576,1.37816796
23\H,-6.5935866307,2.9668721699,0.974924396\C,-6.9240032054,0.39281954
59,2.2135259972\H,-7.6279139108,1.1057679924,2.6545930282\H,-6.0234731
528,0.3649715101,2.8271243995\H,-7.3930653748,-0.596011175,2.224147722
2\H,-1.2740058937,-0.2726894164,1.7872999205\C,-2.1476190465,1.9066504
055,-2.1583113168\O,-3.3334012833,2.2355336283,-2.1982040426\C,-1.4734
938002,0.7424073572,-2.5915502474\C,-1.9907499089,-0.4507341559,-3.096
0142137\H,-3.023232529,-0.3610881294,-3.4209856581\H,-1.3637478154,-1.
0288848328,-3.770194515\O,-0.1007009396,0.8483912316,-2.2454988404\C,0
.0947836801,2.00681402,-1.6049549533\N,-1.0696134638,2.7406121461,-1.6
220262983\O,1.1626879771,2.2904753311,-1.0500145342\C,-1.1851680935,4.
0941511829,-1.1924958617\C,-1.4265981138,6.7665510558,-0.3799493933\C,
-2.4198077144,4.582513975,-0.7414045592\C,-0.0744859187,4.949714422,-1
.2438301205\C,-0.2010594693,6.2745501621,-0.8307053282\C,-2.5305129812
,5.9146764414,-0.3439480974\H,-3.2767204275,3.9242115499,-0.7350157546
\H,0.8793893955,4.5746717417,-1.5902413908\H,0.6671687301,6.9259612685
,-0.8713375431\H,-3.4932675639,6.2851662675,-0.0032885542\H,-1.5200476
381,7.8015839304,-0.0649144749\\Version=ES64L-G09RevE.01\State=1-A\HF=
-2899.8298148\RMSD=5.085e-09\RMSF=2.045e-07\Dipole=-1.4008665,-0.77677
92,2.4098624\Quadrupole=0.6971159,-2.3438018,1.6466859,2.2618246,-18.0
577309,4.5031668\PG=C01 [X(C54H69N5O7)]\\@

TS1c

1\1\GINC-R2620\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\25-Feb-2017\0\\#
B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine\\PES for Michael addition conf. 1b S-confi
g.\\0,1\C,-2.2214436785,-2.3244853681,-0.7071203569\O,-2.7084031934,-3
.4377942212,-0.5022000762\N,-2.8747097036,-1.1300047399,-0.6257584713\
H,-2.3198288547,-0.289871589,-0.7934926917\N,-0.8706331543,-2.18595050
27,-1.0564833408\H,-0.4938483354,-1.2687614494,-1.2686177065\C,-4.2378
508763,-0.9028898862,-0.3248138243\C,-6.8879850739,-0.2736937339,0.233
9433514\C,-5.1469225986,-1.9236423776,-0.028655536\C,-4.6641016092,0.4
324497072,-0.3378782857\C,-5.9925434852,0.7655599292,-0.0603003767\C,-
6.4839135654,-1.614964922,0.2539484994\H,-4.7950386735,-2.9445488685,-
0.0259448201\H,-3.9381910638,1.2048826559,-0.5739336665\H,-7.918507126
7,-0.0321308976,0.4496991462\C,-6.4213965668,2.2466011004,-0.082504596
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35321808,-1.1515856364\C,0.5201744472,-3.4324205964,-2.736423948\C,1.1
088817386,-4.8290382908,-3.0420489826\H,0.4298480405,-5.632398556,-2.7
342299679\H,2.0818747332,-5.0018236477,-2.5808552382\H,1.2541238811,-4
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H,-1.1231925504,-2.2450386119,-3.6012230913\H,-1.4793980032,-3.9729471
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\H,-1.0112388702,-0.536697107,2.5833822254\H,-1.2762759233,0.969849356
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\C,2.0496548578,1.5621830113,-1.8298854415\C,3.2455693664,0.914473777,
-2.1257875877\H,3.9925907735,1.5771345687,-2.5533462577\H,3.1863518921
,-0.06740823,-2.5859586603\O,0.8796135146,0.8095037739,-1.5092783801\C
,-0.1313442036,1.6617112993,-1.2325879903\N,0.3224447942,2.9470686991,
-1.3492687112\O,-1.2537230882,1.2550327849,-0.9308326722\C,-0.46025887
23,4.1176597893,-1.134608004\C,-1.9667834677,6.4409606612,-0.721435461
7\C,-0.1866804989,5.2714266925,-1.880629654\C,-1.485872208,4.129128570
5,-0.1798418905\C,-2.2359530632,5.2879544173,0.0165601713\C,-0.9388238
375,6.4250403498,-1.6644269353\H,0.6236307,5.2621254494,-2.5964066941\
H,-1.7025833262,3.2340239595,0.3880274209\H,-3.0331821588,5.2849970697
,0.7540969266\H,-0.717270168,7.3165161902,-2.2438516569\H,-2.551289230
7,7.342172326,-0.5621814135\\Version=ES64L-G09RevE.01\State=1-A\HF=-28
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7877,6.9700455\PG=C01 [X(C54H69N5O7)]\\@

TS2a

1\1\GINC-CN429\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\HNAN_JZY\25-Mar-2017\0
\\# B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200
freq # int=ultrafine cphf=fine\\TS for protonation conf. 2a R,R-confi
g.\\0,1\C,-1.9565755298,-2.2534779314,-0.3466256288\O,-2.5183260832,-3
.2517193909,0.108897434\N,-2.402673561,-0.9635474706,-0.2184860064\H,-
1.806446206,-0.2251349857,-0.5849289144\N,-0.7693440417,-2.3605937727,
-1.0713887695\H,-0.3743078246,-1.525453248,-1.4919467899\C,-3.66685727
82,-0.5479573702,0.263173771\C,-6.1448689722,0.4013479975,1.1018969875
\C,-4.5099762757,-1.3708346711,1.0176066963\C,-4.0685592132,0.75634115
26,-0.0551324884\C,-5.3114490682,1.2472281724,0.3550495936\C,-5.760208
9188,-0.902443609,1.4410763975\H,-4.1789406333,-2.3714776115,1.2514801
121\H,-3.3905819934,1.3797260476,-0.6284994959\H,-7.1100926579,0.76536
87202,1.4228647107\C,-5.7287055824,2.6763614423,-0.0470611643\C,-6.664
0359845,-1.8438657922,2.263114182\C,-6.9753814215,-3.1113852558,1.4322
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.9335001923,-2.253623658,3.563843463\H,-4.9915112342,-2.76787593,3.354

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89461826\C,-4.6948073882,3.6915799162,0.4930427649\H,-4.6520137524,3.6
558358427,1.5869150952\H,-4.970122857,4.7109174541,0.1977171172\H,-3.6
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436184\H,-4.8110088899,2.5610029061,-2.0437082546\H,-6.0778917569,3.78
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,4.0254522654,1.1230852777\H,5.0311670876,4.2651493617,0.8946457712\C,
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,3.0316388628,1.212582761,-4.0757208124\H,1.3382943715,0.7218952728,-4
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41,4.0269890353\H,0.2779789439,3.9555256485,4.7647461579\H,1.345890437
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,2.5158499393\H,-1.4834983077,2.2114881867,4.1981901421\C,-1.191416768
,4.4353665232,2.4450805099\H,-1.7280870875,4.7426362316,3.3482721184\H
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,-0.8978066102,0.386503086\O,1.6876771814,-0.318788254,0.8724989884\C,
2.8256900511,-1.4567600962,-0.9342285738\C,2.4978115415,-0.6605439664,
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1,-0.807751892,-2.8736817079\O,4.2091519843,-1.9262485895,-0.977412741
6\C,4.7748658551,-1.8346570287,0.2425235991\N,3.845748124,-1.233947278
4,1.1053727528\O,5.8809772072,-2.2515887699,0.5120809943\C,4.070777253
3,-1.006242238,2.4945170049\C,4.4828049485,-0.5818102998,5.2311554396\
C,3.5167650792,0.1193221741,3.1190331389\C,4.8353684024,-1.9152654013,
3.2392958059\C,5.0399293136,-1.6944570932,4.6004753237\C,3.7233618696,
0.3186045617,4.483457172\H,2.9245151642,0.8151578817,2.5407444763\H,5.
2903367023,-2.7632721418,2.7445843217\H,5.6403432643,-2.3998090133,5.1
676440192\H,3.2917454746,1.192783588,4.963054929\H,4.6431465064,-0.415
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TS2b

1\1\GINC-CN460\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\HNAN_JZY\24-Mar-2017\0
\\# B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200
freq # int=ultrafine cphf=fine\\TS for protonation conf. 2b R,S-confi
g.\\0,1\C,-1.5355124007,-2.3966428369,-0.17388737\O,-1.6386328561,-3.5
502163448,0.2417216699\N,-2.5851808503,-1.5151180206,-0.3056641062\H,-
2.3655249184,-0.5699942642,-0.5985936872\N,-0.3152887238,-1.8621817453
,-0.5731387424\H,-0.2314798407,-0.8745201045,-0.7930199745\C,-3.959387
6374,-1.8088487047,-0.1451484229\C,-6.6902854393,-2.2611698228,0.10052
58001\C,-4.4214700063,-2.8809096388,0.6189747351\C,-4.8774212822,-0.95
97588383,-0.7879741626\C,-6.2510385837,-1.1734872957,-0.6756924795\C,-
5.7985916837,-3.1210842197,0.7456663522\H,-3.6965888407,-3.5260905386,
1.0921959643\H,-4.4899910755,-0.1482180893,-1.393903723\H,-7.754819873
6,-2.4362017867,0.1909034944\C,-7.2906363901,-0.2792095482,-1.37996300
54\C,-6.2662015714,-4.323824649,1.5890297316\C,-5.6952531511,-5.626473
5423,0.9797919697\H,-4.6025403774,-5.6136773584,0.9439956718\H,-6.0599

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.0270930605,-0.8008556351\C,-6.6384756209,0.8291749541,-2.2269349154\H
,-6.0293796862,1.5030673676,-1.6164132827\H,-7.4155959075,1.4315910081
,-2.7086508795\H,-6.0031856531,0.4168274113,-3.0175888036\C,-8.1642794
098,-1.1424462866,-2.3211022032\H,-8.9090741469,-0.5186824585,-2.82843
62458\H,-8.7009123862,-1.9247134895,-1.7774266969\H,-7.5504912465,-1.6
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424420564,-3.611587481,-0.0864698471\C,1.7034868905,-2.7729982317,-1.7
112821559\C,3.0245637827,-3.5428508355,-1.5156172274\H,2.8679295797,-4
.5359987191,-1.0823764415\H,3.7427527106,-3.0007684184,-0.8966106549\H
,3.4954660488,-3.6889742642,-2.4926903262\C,0.8076478666,-3.6140625106
,-2.6517390439\H,-0.1343213566,-3.1049081785,-2.8690074828\H,0.5705897
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,4.7093057369,-0.2738708643,0.0654390712\O,4.873038378,0.1163073785,-1
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087424,0.7549263552\O,5.7226937871,-1.9955264169,2.9335895729\C,6.8485
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35705\C,6.9295683553,-1.9526763974,-1.1416199612\C,7.9636971356,-1.810
1419833,1.0485836615\C,9.1453607433,-2.3205491157,0.513876587\C,8.1224
875495,-2.4516417429,-1.6623471401\H,6.0757886927,-1.7864747809,-1.783
8929411\H,7.8937165742,-1.5744802547,2.1019047528\H,10.002463306,-2.46
31532907,1.1655849195\H,8.1778397796,-2.6942300018,-2.7196375805\H,10.
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TS2c

1\1\GINC-R2396\FTS\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\10-Apr-2017\0\\#
B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine\\TS for H protonation conf. 3b R,S-config.
\\0,1\C,2.8500372588,2.1547634145,1.1186874296\O,3.3106943382,2.425633
427,2.2259931649\N,3.2800071576,1.1374899451,0.2917079906\H,2.72430850
41,0.9878931441,-0.5447765914\N,1.8025247834,2.8620858788,0.5491484625
\H,1.444468878,2.5300984786,-0.3474696208\C,4.3407399725,0.229485888,0
.4940236735\C,6.3858593309,-1.6344625059,0.7346564202\C,5.2000888819,0
.2817750569,1.5918525564\C,4.5123392959,-0.7630444202,-0.487030353\C,5
.5324126632,-1.7054937615,-0.3819839298\C,6.2365834071,-0.6573166465,1
.721277907\H,5.0448608054,1.0524213284,2.3325366688\H,3.8331721686,-0.
7755307792,-1.3331293151\H,7.1814702926,-2.3628934743,0.825157165\C,5.
7516723589,-2.8058005356,-1.438615559\C,7.1658380491,-0.5685894175,2.9

483903844\C,7.8732621633,0.8073202129,2.9579238749\H,7.1565968379,1.63
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8\H,5.5628569979,0.0570302647,4.3212408274\H,6.9720378101,-0.651289794
8,5.1231480439\H,5.8209327861,-1.6913658403,4.2645098039\C,8.249085286
6,-1.663549795,2.9497368539\H,7.8141335456,-2.6681144865,2.9736031873\
H,8.8792778558,-1.5564584068,3.8385769336\H,8.9015235759,-1.5934368572
,2.0731783656\C,5.6308526999,-4.1954309291,-0.7694333598\H,4.637117402
,-4.3336188507,-0.3309527315\H,6.3673976674,-4.3292906625,0.0277391538
\H,5.7902160756,-4.9897004036,-1.5075714141\C,4.7236308004,-2.73708550
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5618\C,7.163459801,-2.6541988569,-2.0531491304\H,7.3394422304,-3.43387
37872,-2.8030338179\H,7.9477150676,-2.737415958,-1.2954825388\H,7.2742
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,2.9935980746\C,-1.1786090444,1.9498764607,3.7363698537\C,0.1694644199
,2.3881280866,3.1313336475\H,-1.9431892534,4.2048715866,1.3240649409\H
,-1.1879635112,4.6923443842,2.8602741214\H,-2.9596043617,3.2710232385,
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\C,-0.5134400303,-2.021160679,-1.9805111041\C,-1.0459262785,-2.3375533
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,-0.0849772261,-2.3790385233,2.2850401349\C,-0.783077521,-4.0854100189
,1.189714846\C,-1.8380273947,-6.6940051988,1.1051211232\C,-1.712677751
9,-4.5145426358,2.148793447\C,-0.3887215528,-4.9874770305,0.1924592191

\C,-0.9102587849,-6.2805945061,0.1483194139\C,-2.2375980946,-5.8062797
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,-0.0866075937,1.9025431706\O,-2.3389040123,1.092554041,0.0558147933\C
,-2.7340389456,1.5640832186,-1.1474238486\N,-1.5894815914,1.7403833033
,-1.9379624044\O,-3.8841918938,1.8163156522,-1.435617326\C,-1.60542905
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62\C,-0.6997655316,1.7487260201,-4.2158186711\C,-2.5169411035,3.248449
229,-3.6316948712\C,-2.5186111678,3.741540769,-4.9354543654\C,-0.70557
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237\H,-3.2302250112,3.6120952665,-2.9036238959\H,-3.2328564982,4.51200
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TS2d

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B3LYP/6-31g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 fre
q # int=ultrafine cphf=fine\\TS for H protonation conf. 3b2 R,R-config
.\\0,1\C,-3.0943963428,1.3803426802,1.4247269671\O,-3.9866417314,2.157
9833421,1.7597095683\N,-3.2793022741,0.1427778527,0.8495820715\H,-2.43
87701607,-0.3155020943,0.5075422371\N,-1.7486083854,1.6753428313,1.605
799182\H,-1.0610768982,1.00240471,1.2700748233\C,-4.4920998881,-0.5425
201762,0.6162655064\C,-6.776343541,-2.0363775992,0.101977618\C,-5.7407
058279,-0.0535669618,1.0012776359\C,-4.3917592067,-1.7867626987,-0.031
4923486\C,-5.5277566324,-2.5484510722,-0.2973038653\C,-6.9008491945,-0
.8032189498,0.7458674889\H,-5.7908537382,0.9079753959,1.4905799575\H,-

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,-0.0985292758\C,-5.4545353201,-3.9195055824,-0.9978544877\C,-8.262998
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92191125\H,-3.3665854068,-4.3917723391,-0.5020291014\C,-6.0127146118,-
5.0083483279,-0.0508301416\H,-5.972981787,-5.9913832442,-0.5338194712\
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1\C,-0.4965234967,4.3489410291,4.0841276728\H,-1.4292429805,4.91843160
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H,-1.6688894158,1.0966673917,4.0818610764\H,-2.6123255856,2.5636699736
,4.3585430037\H,-1.2376727358,2.182273566,5.4116199662\C,0.7295239683,
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1110597194,2.1609062881,4.4896145289\H,1.4824870704,2.7647865994,2.879
8870416\N,-0.5720683336,3.5962254896,0.8771313535\C,0.1842264581,4.875
215607,1.0700374274\C,0.3990877391,5.3839007621,-0.3538705109\C,-0.939
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int1a

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7)]\\@

int1b

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1282,-1.8825206775,1.0854185127\H,-3.4288179321,-4.0191180379,2.358555
4161\H,-2.0995752526,-6.1102270739,2.5204029242\H,1.3963395616,-3.9890
442874,1.1858600945\H,0.3143688066,-6.0989813761,1.9272291866\\Version
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int1c

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29240355,-2.6948279615,-3.7038980877\H,-0.3799756638,-3.9388976456,-1.
0221445416\H,2.4291225629,-6.8174159659,-2.512447115\C,0.2054610975,-6
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int1d

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X(C54H69N5O7)]\\@

int2a

1\1\GINC-R588\FOpt\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\22-Feb-2017\0\\#

B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\Cataly
st + Michael adduct conf. 2a R-config.\\0,1\C,-2.1036029488,-1.4300985
728,-1.6849747189\O,-2.5127482316,-2.5198606488,-2.0963931175\N,-2.856
9131356,-0.4495155449,-1.0936377612\H,-2.3475334839,0.4107654164,-0.86
95216812\N,-0.7616170484,-1.0650337403,-1.7610567008\H,-0.5216959373,-
0.1038105467,-1.454732916\C,-4.2353016286,-0.4579683723,-0.8098694857\
C,-6.9408325948,-0.3064008551,-0.1684910691\C,-5.0764255571,-1.5455615
663,-1.072226176\C,-4.762930116,0.7028172345,-0.2265305167\C,-6.117335
8425,0.7970874928,0.1016493834\C,-6.4384211373,-1.4771235268,-0.752495
9137\H,-4.6489485725,-2.4265286924,-1.5284893105\H,-4.0916119934,1.535
7198982,-0.0360941217\H,-7.9908308014,-0.2498784204,0.0789973596\C,-6.
6517116407,2.0955174642,0.7394455752\C,-7.3331885467,-2.6956473448,-1.
059294272\C,-7.2979739202,-2.9899197193,-2.5777674662\H,-6.283172249,-
3.2003807438,-2.9262551346\H,-7.6762906843,-2.1357621723,-3.1490472626
\H,-7.9222461072,-3.8598184607,-2.8134459358\C,-6.8051409849,-3.928973
962,-0.2887956497\H,-5.7756995685,-4.1699835338,-0.5679133057\H,-7.425
5763278,-4.8074858875,-0.5014145758\H,-6.8260646992,-3.7520877401,0.79
17987203\C,-8.8012419131,-2.4709807057,-0.6505572259\H,-8.9022520436,-
2.2862348446,0.4239565767\H,-9.3905758904,-3.3626644594,-0.8888418506\
H,-9.2490891388,-1.6273023199,-1.1856712072\C,-8.1610413423,2.02668249
15,1.0396753965\H,-8.4010071978,1.2223833404,1.7427597036\H,-8.7510357
603,1.8730341977,0.1303385244\H,-8.489634351,2.9686932664,1.4908243243
\C,-5.9105949746,2.3596941321,2.0715534084\H,-6.069635705,1.5370088777
,2.7766377703\H,-6.2769541951,3.2821130732,2.5366230018\H,-4.832510341
7,2.4682096362,1.9227447777\C,-6.4085395979,3.2815170667,-0.2237903526
\H,-5.3456634239,3.4178438585,-0.4422324151\H,-6.7805423239,4.21403211
51,0.2159583725\H,-6.9267716611,3.1238738512,-1.1753361526\C,0.1490702
351,-1.8232009428,-2.5314838511\H,-0.4142344066,-2.5701913019,-3.09863
18802\C,0.9974180353,-0.934658218,-3.5041335818\C,1.7719334249,-1.7681
868628,-4.5489486542\H,1.1277815143,-2.5064554545,-5.0404557741\H,2.64
12756156,-2.2844611917,-4.1369810873\H,2.1476440048,-1.0976993243,-5.3
275609552\C,-0.0225176569,-0.0639015543,-4.2798916167\H,-0.5168433905,
0.6567348176,-3.6273938829\H,-0.7880594594,-0.6800368392,-4.7649421164
\H,0.5024680866,0.4952503957,-5.0601814776\C,1.974013921,-0.0093656403
,-2.7532232922\H,1.4515695216,0.6450397152,-2.0513214992\H,2.486291870
7,0.6362417087,-3.473606467\H,2.7411763434,-0.5681861675,-2.2085171974
\N,0.9896157504,-2.6977767829,-1.5256045711\C,1.9259789468,-3.73480416
92,-2.1097812763\C,1.933049224,-4.9253289479,-1.1230061366\C,1.0637640
084,-4.4650584703,0.062194656\C,0.1008188255,-3.4653830894,-0.56369412
01\H,2.9042717256,-3.2749119254,-2.2277226167\H,1.5384594665,-4.019623
9507,-3.0874020771\H,1.4981238634,-5.8066600224,-1.6030837604\H,2.9489
596446,-5.1848432519,-0.8168781028\H,1.6755485316,-3.9596643093,0.8152
965111\H,0.533498602,-5.2890635157,0.5456442335\H,-0.3352344509,-2.758
0056427,0.1346248064\H,-0.6914769018,-3.9319303118,-1.1526468203\C,2.6

215425465,1.3813032487,2.9583744104\C,5.0910862441,2.608151613,3.26232
77619\C,3.7274226793,0.9459027938,2.2195530532\C,2.7544585789,2.433347
2066,3.8561678788\C,3.9993451224,3.0465134153,4.0118813866\C,4.9728999
038,1.5540848914,2.3513821657\H,1.8939411576,2.7884190266,4.4149870596
\H,4.1125566715,3.8754160941,4.7031226464\H,5.8236896016,1.2329602613,
1.7713870616\H,6.0542429622,3.0962115356,3.3755497269\C,1.3944126611,0
.5845913628,2.6002871591\C,1.9145018166,-0.3273948198,1.4926295181\N,3
.3091143424,-0.121151797,1.3437147593\O,1.2452676018,-1.1261636963,0.8
660196946\C,0.8656010688,-0.3001009451,3.7809063305\H,0.5579844052,0.3
899226945,4.5743907602\H,-0.0405307864,-0.8003859771,3.4243461083\C,1.
8246631295,-1.3341272839,4.3328273048\C,3.5950686406,-3.281222478,5.34
19867247\C,1.7456167634,-2.6691663037,3.9094386002\C,2.8031192799,-0.9
948872495,5.2789562457\C,3.6811208865,-1.9576276743,5.7771366153\C,2.6
213596367,-3.6350242745,4.4071713002\H,0.9815371521,-2.9517172107,3.19
0521629\H,2.8769920901,0.0307111015,5.6274387181\H,4.4289572404,-1.673
8038074,6.5120772765\H,2.5354527457,-4.6652205306,4.0727253582\H,4.273
8561454,-4.0318565377,5.7363613059\C,4.0986956042,-0.9635586609,0.5494
119792\O,3.635378099,-1.7829345906,-0.2296767283\O,5.3957163711,-0.755
2842186,0.7776475023\C,6.4530207858,-1.5422270852,0.0901701412\C,7.734
1143737,-0.9525378148,0.682921966\H,7.8256621105,0.1090902305,0.436697
7652\H,8.6042812927,-1.4742667056,0.2747817253\H,7.7435690491,-1.06126
35921,1.7706870613\C,6.3874986779,-1.2957175681,-1.4183621436\H,6.4173
586561,-0.2233643286,-1.6322233241\H,5.4821796866,-1.7174621658,-1.854
4995419\H,7.2550860089,-1.7604811049,-1.8969073295\C,6.3135321997,-3.0
204644212,0.460732761\H,7.1663143419,-3.5751848258,0.0574386066\H,5.39
59705846,-3.4471777775,0.0555624083\H,6.3116524246,-3.1425553689,1.547
7877314\H,1.5409443883,-2.0600944879,-0.9248401003\C,-0.0487810531,2.3
395260111,-0.3564410884\O,-0.7988227148,1.5238558626,-1.0048456692\C,0
.4601091234,2.3337853544,0.9114947287\C,0.1978969155,1.4462156158,2.06
27190285\H,-0.5892918993,0.7495180019,1.7563478632\H,-0.1851581695,2.0
12837736,2.9254488435\O,1.2345809822,3.499538561,1.1208995587\C,1.2534
800205,4.2293745814,-0.0262285974\N,0.4697668979,3.5526215851,-0.95543
84334\O,1.8701706484,5.2702263944,-0.1509330453\C,0.231673144,4.005841
0277,-2.2778253617\C,-0.2416226732,4.8969098063,-4.8974014584\C,-0.991
6361174,3.730279609,-2.9080320285\C,1.2139068243,4.7364531503,-2.96392
59749\C,0.9681437221,5.1806329611,-4.2619660014\C,-1.2154255774,4.1689
023292,-4.2124043568\H,-1.7423433564,3.161962625,-2.3763990523\H,2.144
0125513,4.973471095,-2.4646864153\H,1.7336476521,5.7530808064,-4.77878
80301\H,-2.1660792994,3.946741773,-4.6895173225\H,-0.4257645918,5.2444
905068,-5.9098855685\\Version=ES64L-G09RevE.01\State=1-A\HF=-2899.8493
694\RMSD=5.868e-09\RMSF=3.787e-06\Dipole=3.5566831,-4.4350669,0.454770
4\Quadrupole=18.689822,-22.2092083,3.5193863,-22.7842777,-4.0657527,9.
0503797\PG=C01 [X(C54H69N5O7)]\\@

int2b

1\1\GINC-R2477\FOpt\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\23-Feb-2017\0\\#
B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\Catal
yst + Michael adduct conf. 1a S-config.\\0,1\C,1.9917673583,2.52658884
24,0.6867802776\O,2.2760852826,3.4456298971,1.4603335166\N,2.844886945
4,1.5610541915,0.2245940778\H,2.4087593623,0.8293377212,-0.3424863954\
N,0.7044969615,2.3772690761,0.1707913786\H,0.5177524121,1.5640237907,-
0.4440262695\C,4.2292604194,1.4360175237,0.4612301293\C,6.9687874426,1
.0672815776,0.7862868253\C,4.9587860262,2.3115418585,1.2734455957\C,4.
8826456458,0.3752471192,-0.1808146054\C,6.256996055,0.1759904014,-0.03
09887135\C,6.3378829891,2.1325259739,1.4422622752\H,4.4340179613,3.121
4898964,1.7585609357\H,4.2945136616,-0.2947955411,-0.8009721261\H,8.03
25430841,0.9273354339,0.9121981385\C,6.9344218599,-1.0000012568,-0.763
1419617\C,7.1077289252,3.1190806855,2.3442587746\C,6.9595966165,4.5530
310064,1.7825931821\H,5.9121472984,4.8632671517,1.7353086284\H,7.37357
9412,4.6199588654,0.7709872235\H,7.4944798888,5.2696974751,2.416847020
1\C,6.5239598838,3.0702010636,3.7762084942\H,5.4630506919,3.334829844,
3.7900895715\H,7.0541742616,3.7726564175,4.4299576965\H,6.6240240772,2
.0669951163,4.2039112186\C,8.6107866075,2.793464287,2.4308418811\H,8.7
891138462,1.7981790296,2.8508823898\H,9.1083949424,3.5202448398,3.0815
343163\H,9.0958613768,2.8422409879,1.4504968419\C,8.4511838882,-1.0615
70395,-0.5007955212\H,8.6759992412,-1.2009520731,0.5616417148\H,8.9622
221833,-0.1554073106,-0.8423511272\H,8.8837592652,-1.9088785337,-1.042
9330453\C,6.3106197342,-2.3329421296,-0.2873742779\H,6.4544698328,-2.4
686784808,0.7892869431\H,6.7796286505,-3.1787521489,-0.8037410353\H,5.
2357562499,-2.3761830285,-0.4813271305\C,6.7195607384,-0.8506966072,-2
.2880585628\H,5.6581055871,-0.8494132003,-2.5513560066\H,7.1944100782,
-1.6809005881,-2.8235770259\H,7.1558066645,0.0843895592,-2.6548517559\
C,-0.2604163009,3.4010878506,0.3780744187\H,0.1523913746,4.0868098861,
1.1236045953\C,-0.5902510229,4.2185514078,-0.9197663194\C,-1.437220372
8,5.4798900751,-0.6395052846\H,-1.0365455032,6.0581763947,0.201009206\
H,-2.4893220235,5.2665225921,-0.4434814641\H,-1.4110461975,6.129876362
,-1.5193045757\C,0.7803752821,4.7085019617,-1.4508430002\H,1.404289626
1,3.8760949425,-1.7805895135\H,1.334766519,5.2632664605,-0.6874470035\
H,0.6189183957,5.3721024142,-2.3057479695\C,-1.2608157861,3.3561561444
,-2.0015023258\H,-0.6502774395,2.4807721123,-2.2433620408\H,-1.3803186
047,3.9433294271,-2.9179141826\H,-2.2493654029,3.0009952708,-1.6995042
152\N,-1.4552434579,2.71062591,1.0934605731\C,-2.6487554245,3.54370310
7,1.49812713\C,-3.2783972058,2.7481925843,2.6365127177\C,-2.0554565483
,2.2791835169,3.4364091838\C,-0.9883383317,1.9869206628,2.3704966468\H
,-3.2980631611,3.6762391523,0.6346062423\H,-2.2816411528,4.515682672,1
.8348500435\H,-3.9727559886,3.3588470793,3.2193847214\H,-3.8142560361,
1.8849666006,2.2336857522\H,-2.2653623548,1.3884290248,4.0308284588\H,
-1.7120504769,3.0684031639,4.1133421096\H,-0.9280967775,0.9282997596,2

.12794913\H,0.0015093566,2.3622488743,2.626238865\C,-4.0692670911,-1.8
709062685,-2.3936219666\C,-5.4451906832,-4.212942904,-1.8307454725\C,-
4.2939001421,-2.2646882992,-1.071700922\C,-4.5110095583,-2.6684001052,
-3.4411548756\C,-5.2014213878,-3.8497476043,-3.15496561\C,-4.996550793
8,-3.4243112516,-0.7661831711\H,-4.3201601661,-2.3804339439,-4.4708657
89\H,-5.550149984,-4.4830688144,-3.9646380018\H,-5.1816374061,-3.71979
55763,0.2554249746\H,-5.9883934639,-5.127401323,-1.6130886868\C,-3.318
4680718,-0.5653017663,-2.4257722\C,-3.2921248987,-0.174839596,-0.94588
51566\N,-3.7552445593,-1.2627280309,-0.1879267847\O,-2.9033153471,0.89
74512919,-0.5060721258\C,-3.9532183975,0.5342359792,-3.3198786139\H,-3
.3755414261,1.4508699394,-3.1626592266\H,-3.787804407,0.2375477452,-4.
3616756933\C,-5.4273541354,0.8143822745,-3.1025089681\C,-8.1684094921,
1.3447126185,-2.7098699494\C,-5.859878636,1.6259193767,-2.042876426\C,
-6.3953173114,0.2824449336,-3.9648145445\C,-7.752492493,0.5423806721,-
3.7725434744\C,-7.2158974575,1.8868620715,-1.8457959153\H,-5.125391116
7,2.0561430292,-1.3686374803\H,-6.0822982066,-0.3398315793,-4.79842687
48\H,-8.4838830506,0.1196052544,-4.4553191097\H,-7.528716704,2.5198669
848,-1.0199608589\H,-9.2241571959,1.5501702506,-2.5593952549\C,-3.4164
872839,-1.4171175511,1.1788072138\O,-3.0443645772,-0.492130606,1.87617
58821\O,-3.5472352417,-2.6888949279,1.5343115795\C,-3.1107144925,-3.20
39926156,2.8648498341\C,-3.3825140714,-4.702213454,2.7257385095\H,-4.4
484189562,-4.8968766612,2.572356406\H,-3.0679092153,-5.2188102044,3.63
71240625\H,-2.8196310893,-5.1067994459,1.8807679791\C,-3.972737931,-2.
5682894873,3.9560246242\H,-5.0354878964,-2.7319603349,3.7520192399\H,-
3.7877801368,-1.4960718545,4.0326356878\H,-3.7373218367,-3.0336141784,
4.918180306\C,-1.6150939538,-2.949604125,3.0504014812\H,-1.2937674454,
-3.4062562574,3.9919341339\H,-1.3891916804,-1.8837622145,3.0938519396\
H,-1.0472551842,-3.4113273413,2.2386735672\H,-1.8308540362,1.975607273
6,0.4682065611\C,0.1305968347,-1.101594312,-1.1412937753\O,0.797050440
2,-0.0125092509,-1.0850485645\C,-0.9537420605,-1.4943340373,-1.8813358
04\C,-1.8045577256,-0.7746527493,-2.8534631648\H,-1.3539431241,0.21234
0906,-2.9957703344\H,-1.8366311878,-1.267977093,-3.8366002589\O,-1.279
2482393,-2.8424862967,-1.5816681068\C,-0.4336096329,-3.2979677889,-0.6
274829495\N,0.4611558995,-2.2756800939,-0.3480517982\O,-0.5141380404,-
4.40448439,-0.1184102974\C,1.4671539442,-2.3855728244,0.643395317\C,3.
418313137,-2.6254596926,2.6426817397\C,1.7256407622,-1.315982304,1.509
9927675\C,2.1876633075,-3.5805216274,0.7849341999\C,3.1492604409,-3.69
57203661,1.7870280332\C,2.7063089863,-1.4351429365,2.4943469619\H,1.17
16213216,-0.394971716,1.3900573217\H,1.9695913935,-4.413557745,0.12901
05519\H,3.6958125157,-4.6284726465,1.8931400967\H,2.9117444611,-0.5914
72218,3.1465016891\H,4.1758336351,-2.7178217888,3.4151955095\\Version=
ES64L-G09RevE.01\State=1-A\HF=-2899.8423651\RMSD=2.754e-09\RMSF=6.438e
-07\Dipole=-3.1929765,2.0243271,0.954346\Quadrupole=0.4179926,-7.06625
63,6.6482637,-9.3418959,-3.4908545,-1.2036457\PG=C01 [X(C54H69N5O7)]\\

@

int2c

1\1\GINC-R736\FOpt\RB3LYP\6-31G(d,p)\C54H69N5O7\ROOT\22-Feb-2017\0\\#
B3LYP/6-31G** opt=maxcyc=200 scf=maxcyc=200 int=ultrafine freq\\Cataly
st + Michael adduct conf. 2b R-config.\\0,1\C,-2.2127129135,-1.4414095
182,-1.150220648\O,-2.7505256991,-2.5375253547,-0.9692689399\N,-2.8414
307264,-0.231221335,-1.2178737963\H,-2.2399023327,0.5706520028,-1.4241
887425\N,-0.824244195,-1.322265788,-1.275779722\H,-0.4719888974,-0.409
0191389,-1.5524078117\C,-4.2195194012,0.0459000657,-1.1001987165\C,-6.
8933356889,0.7817147776,-0.8859891824\C,-5.1883442601,-0.9258209634,-0
.8279909728\C,-4.6004795086,1.3845703454,-1.2650885416\C,-5.9383317333
,1.7723229015,-1.1608730189\C,-6.5372239577,-0.5632462512,-0.719080812
2\H,-4.8712380671,-1.9518118566,-0.7114060693\H,-3.8285952576,2.118071
0477,-1.4806246567\H,-7.9324926783,1.064765301,-0.8028563639\C,-6.3117
894056,3.2561997943,-1.3513069191\C,-7.5781390597,-1.6618735106,-0.421
1820775\C,-7.5423587738,-2.72275441,-1.5467321694\H,-6.5560617208,-3.1
863563559,-1.6357454054\H,-7.788018434,-2.2729298175,-2.5143774321\H,-
8.2707424919,-3.5172250261,-1.3465536029\C,-7.2400022769,-2.3389195161
,0.9282817099\H,-6.2454284896,-2.7934245483,0.9151068609\H,-7.96677003
67,-3.1283017379,1.1528319295\H,-7.2650685756,-1.6116767559,1.74673698
11\C,-9.013264807,-1.1095511805,-0.3309804189\H,-9.1173755223,-0.37135
50064,0.4709634196\H,-9.7098191183,-1.9273758281,-0.1187726631\H,-9.33
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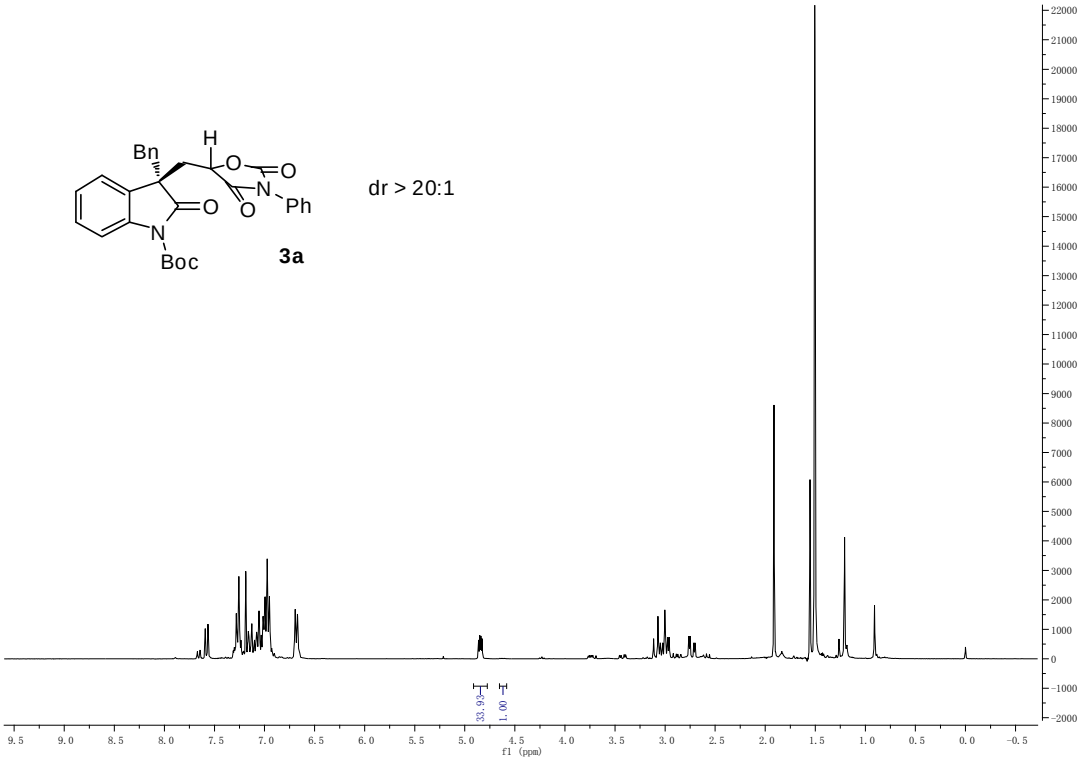

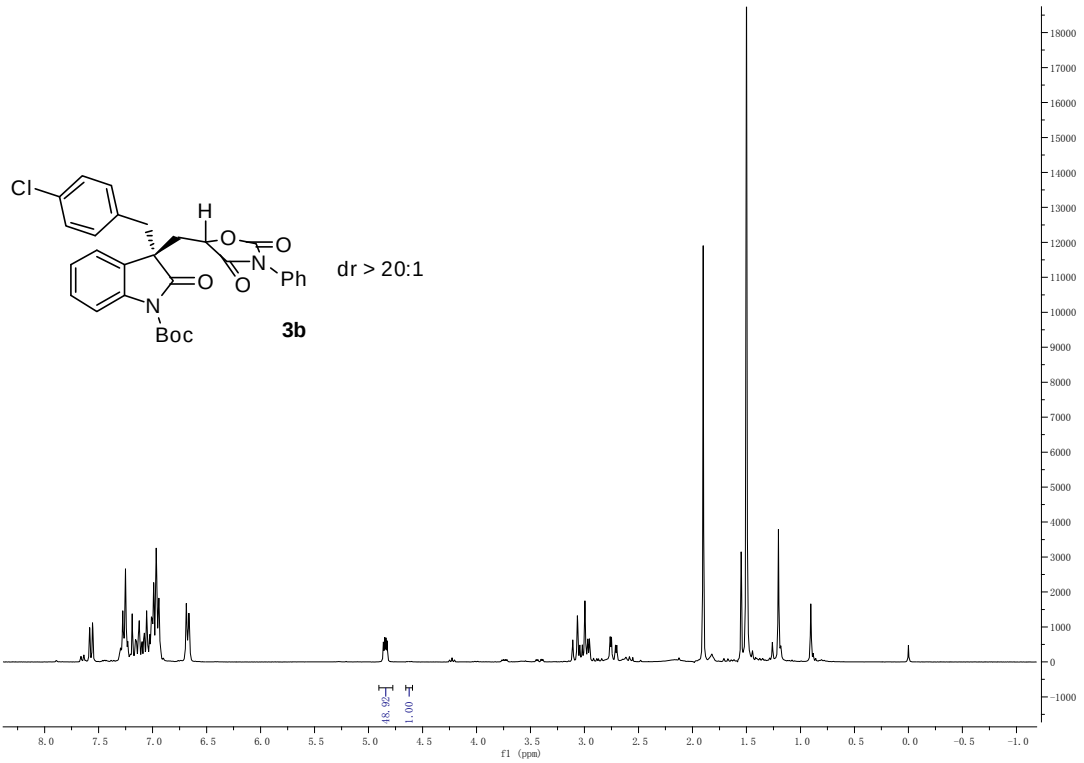

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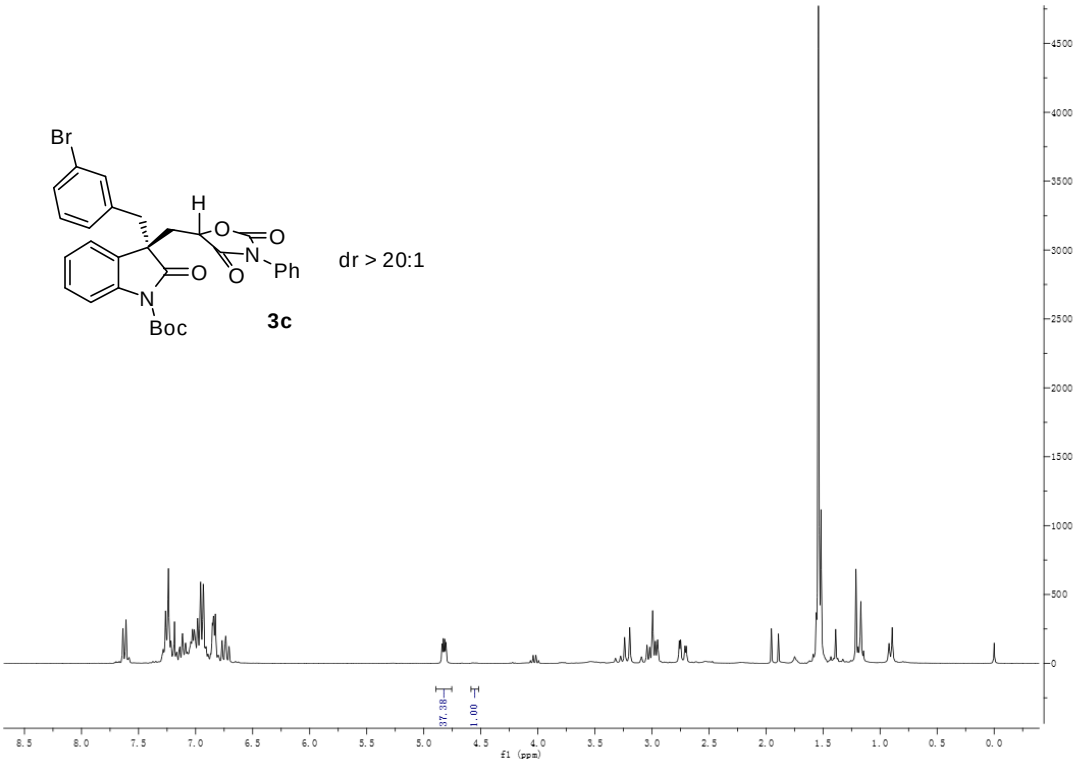

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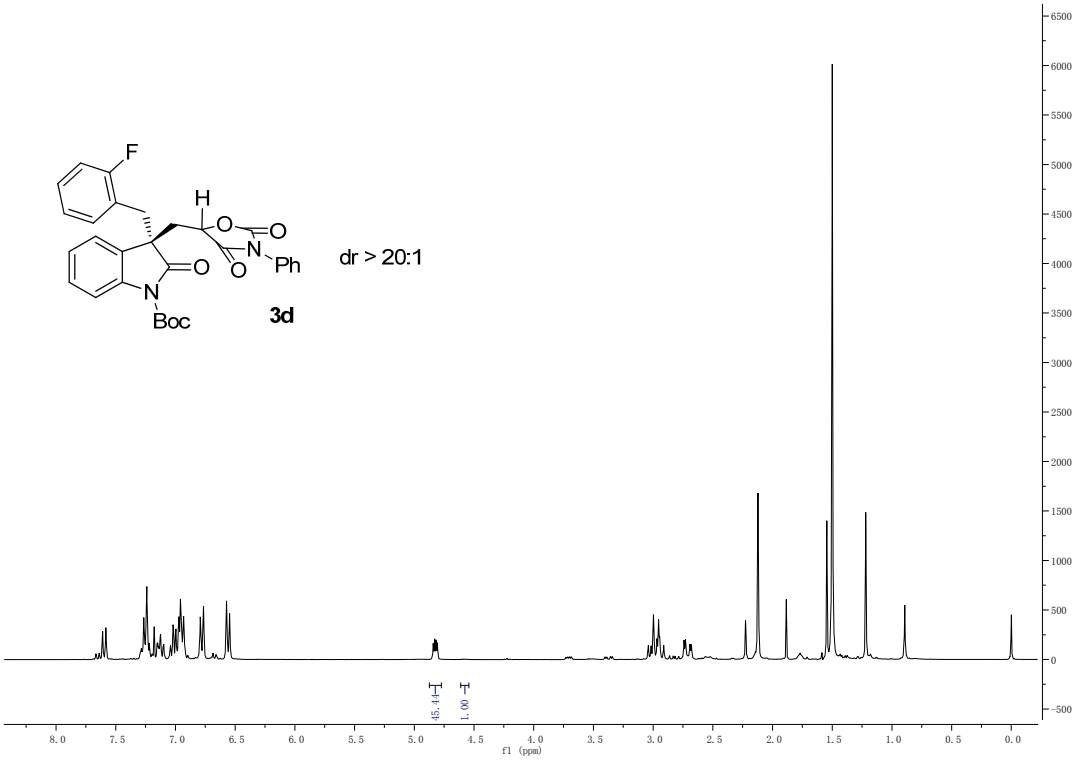

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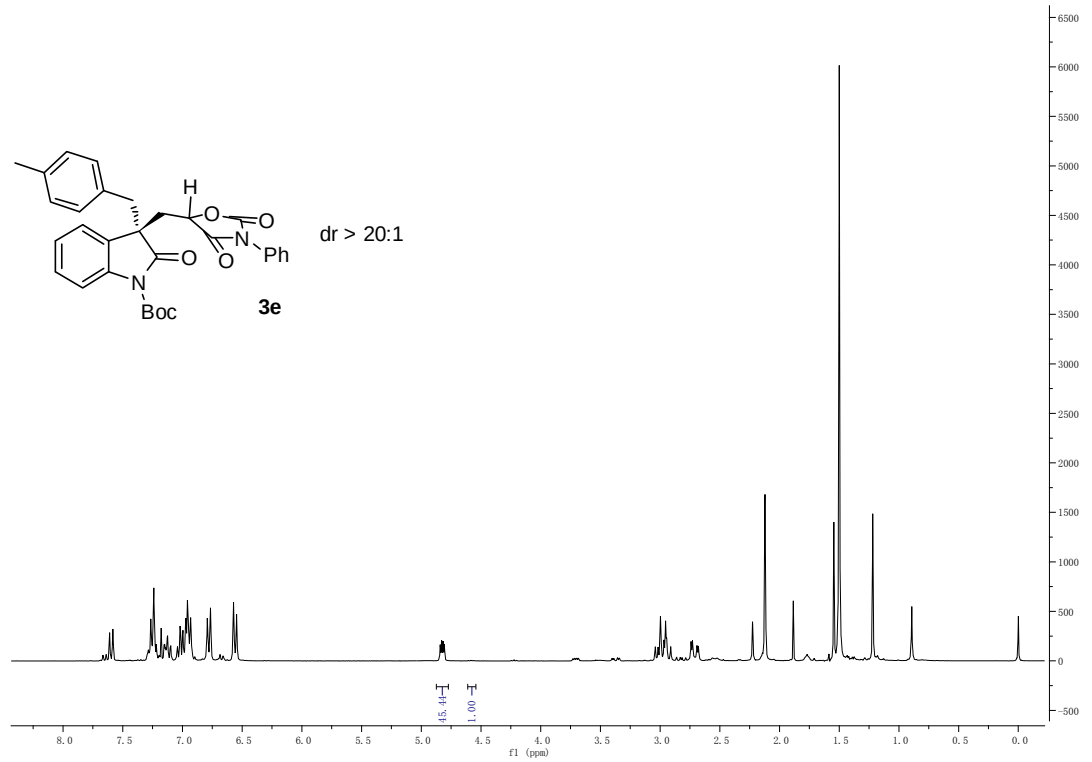

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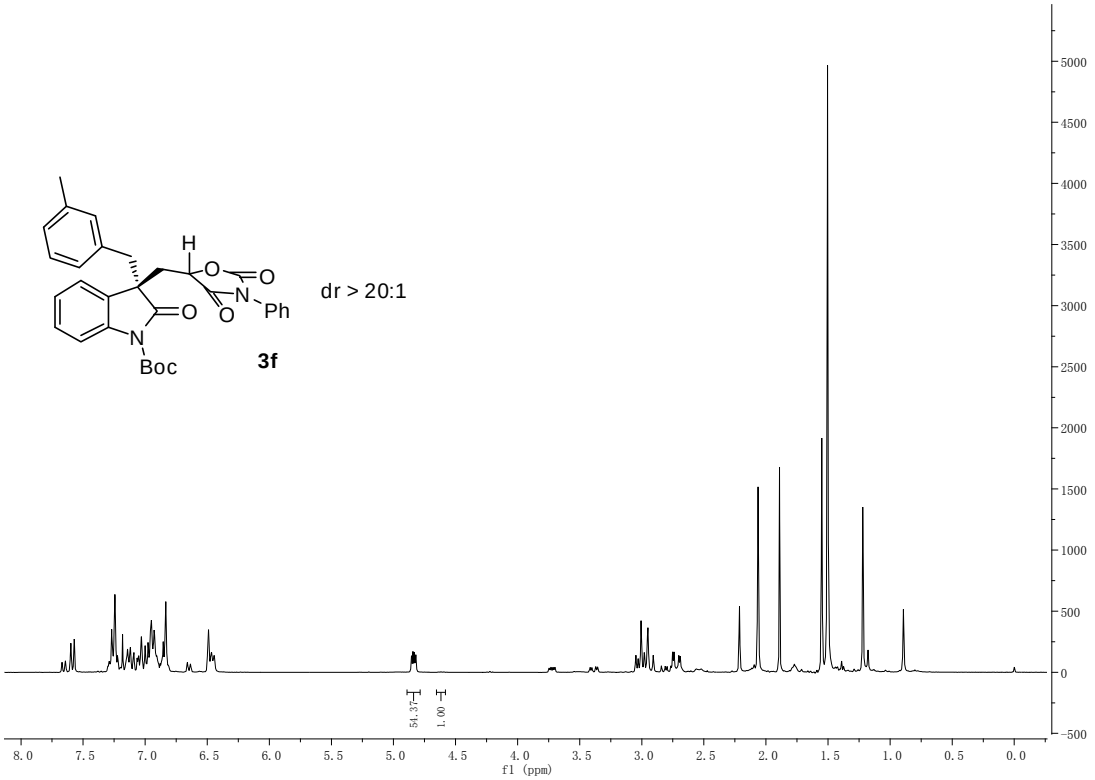

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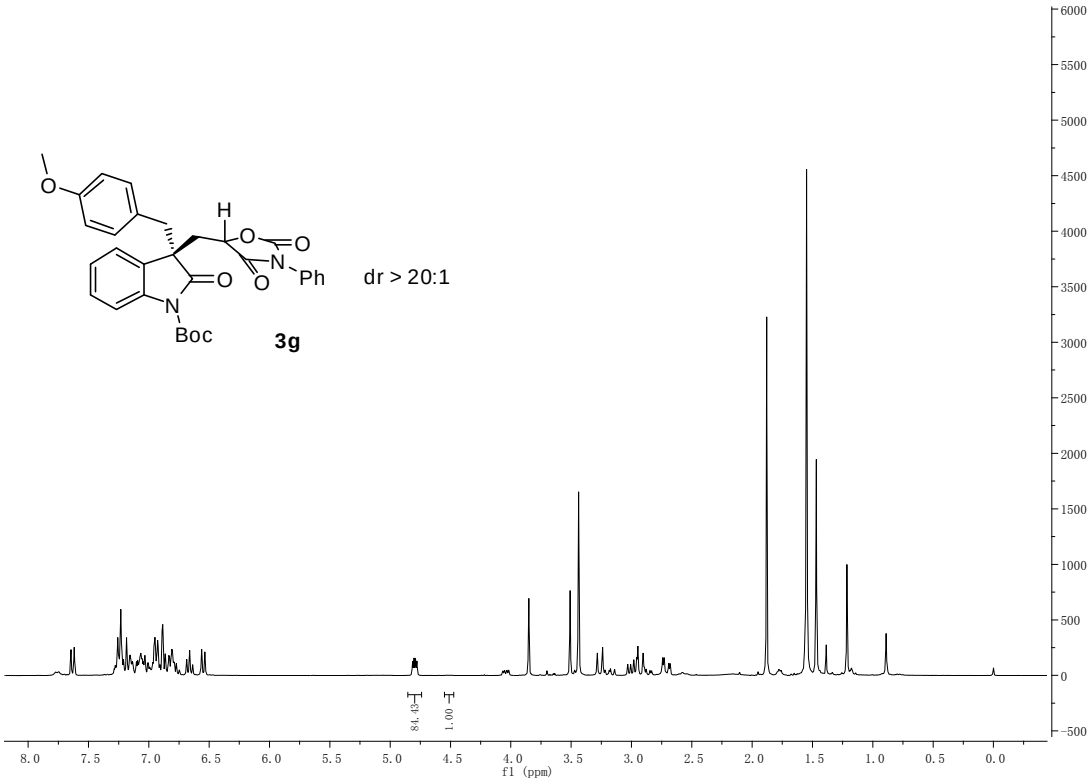

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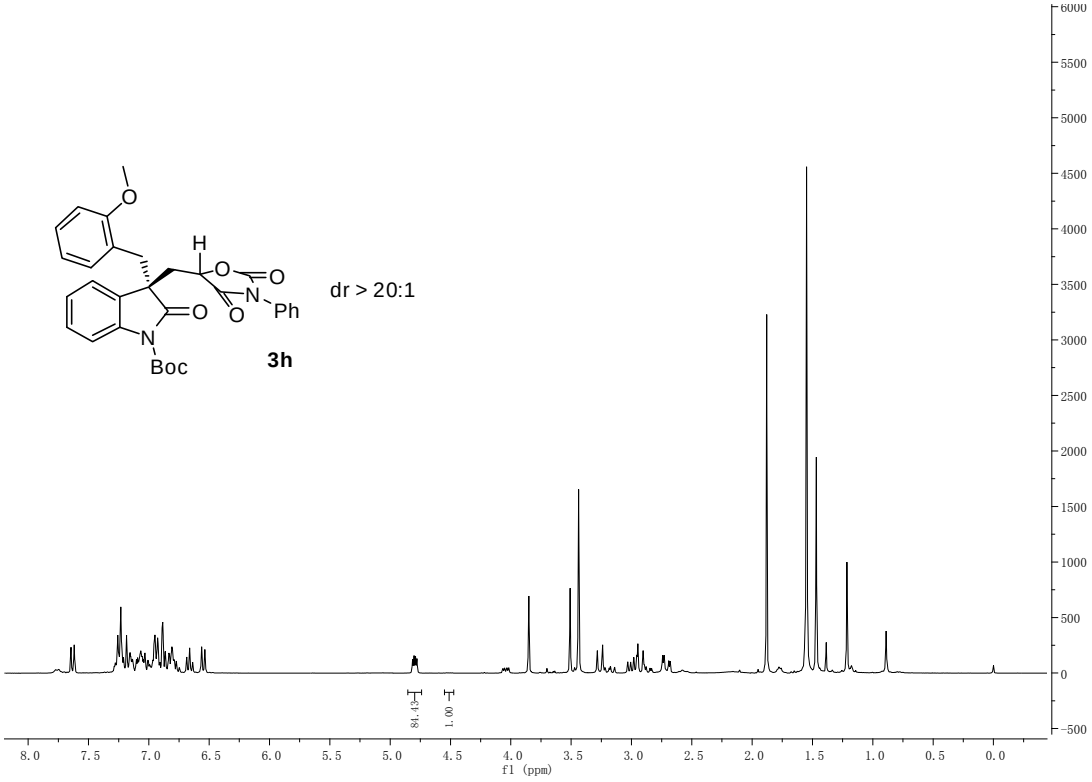

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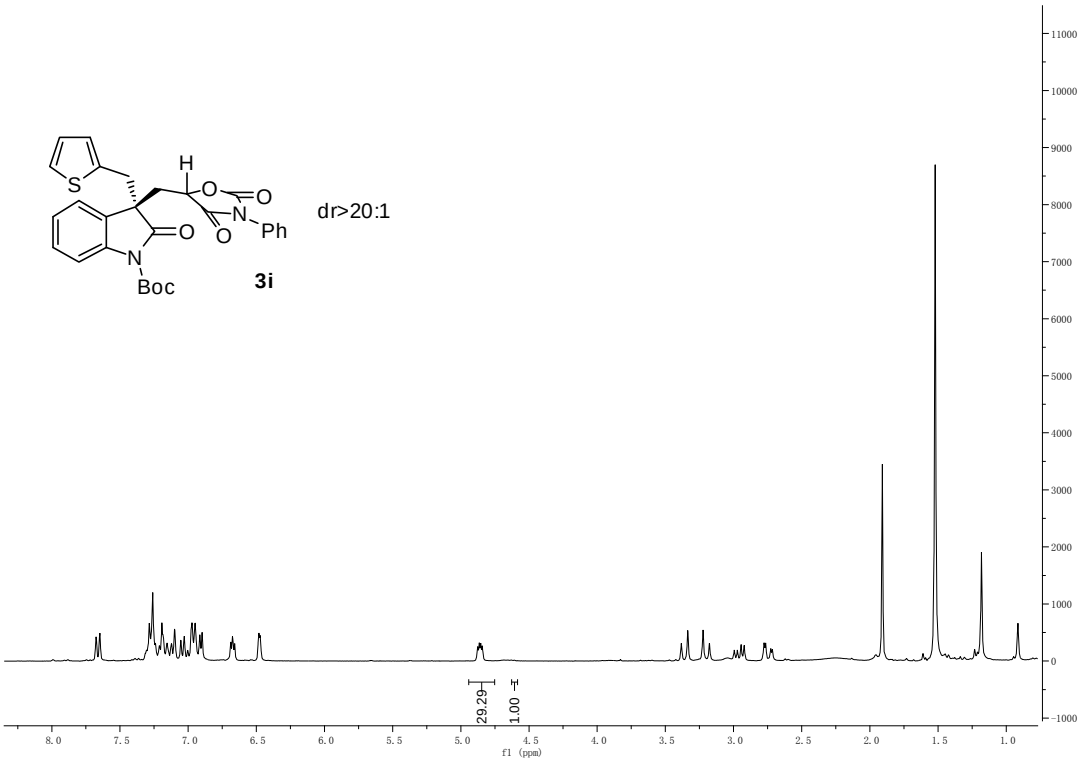

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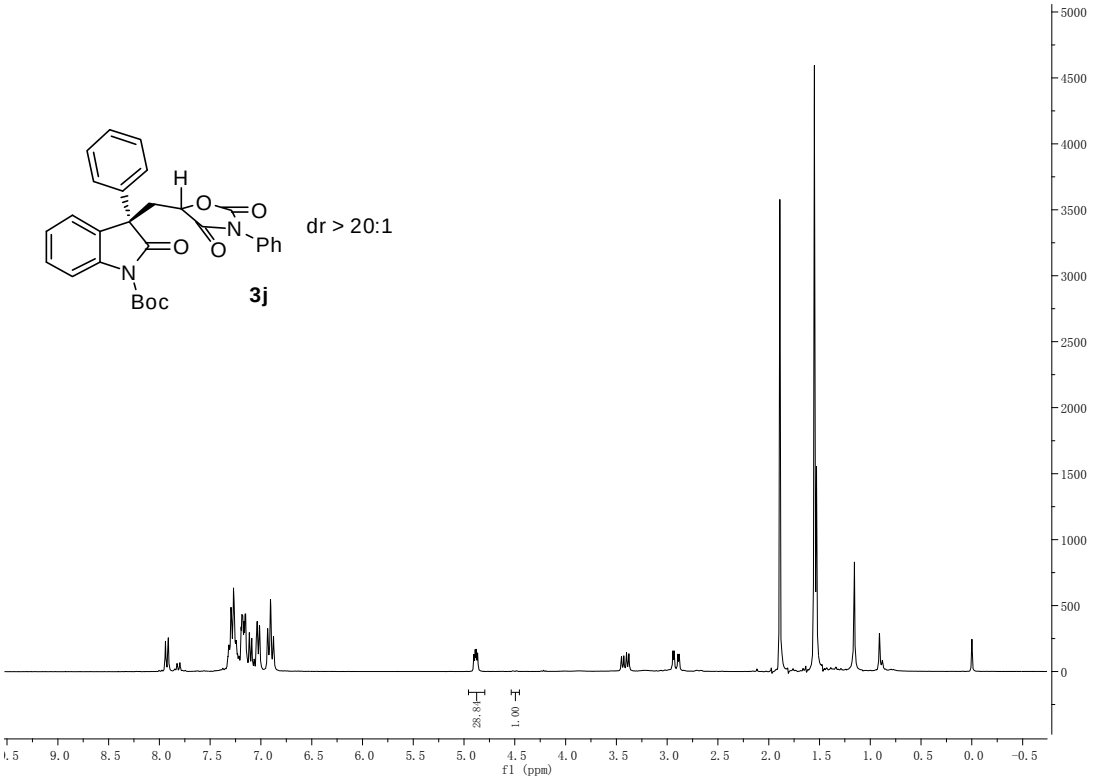

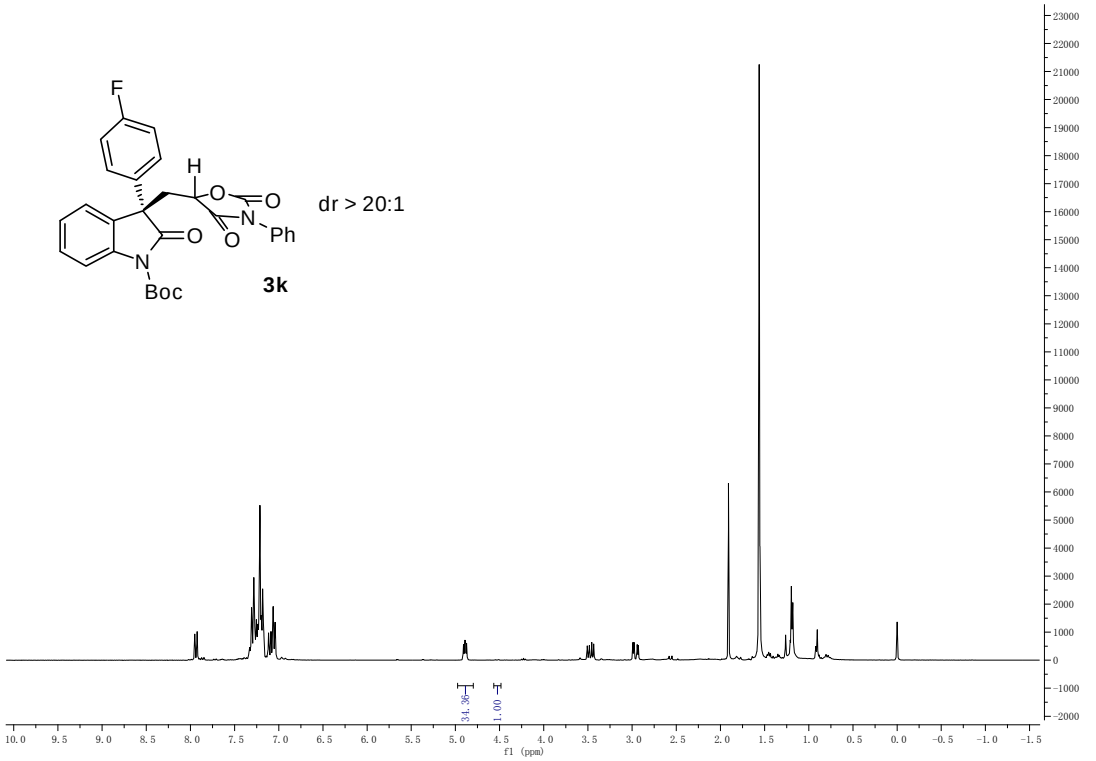
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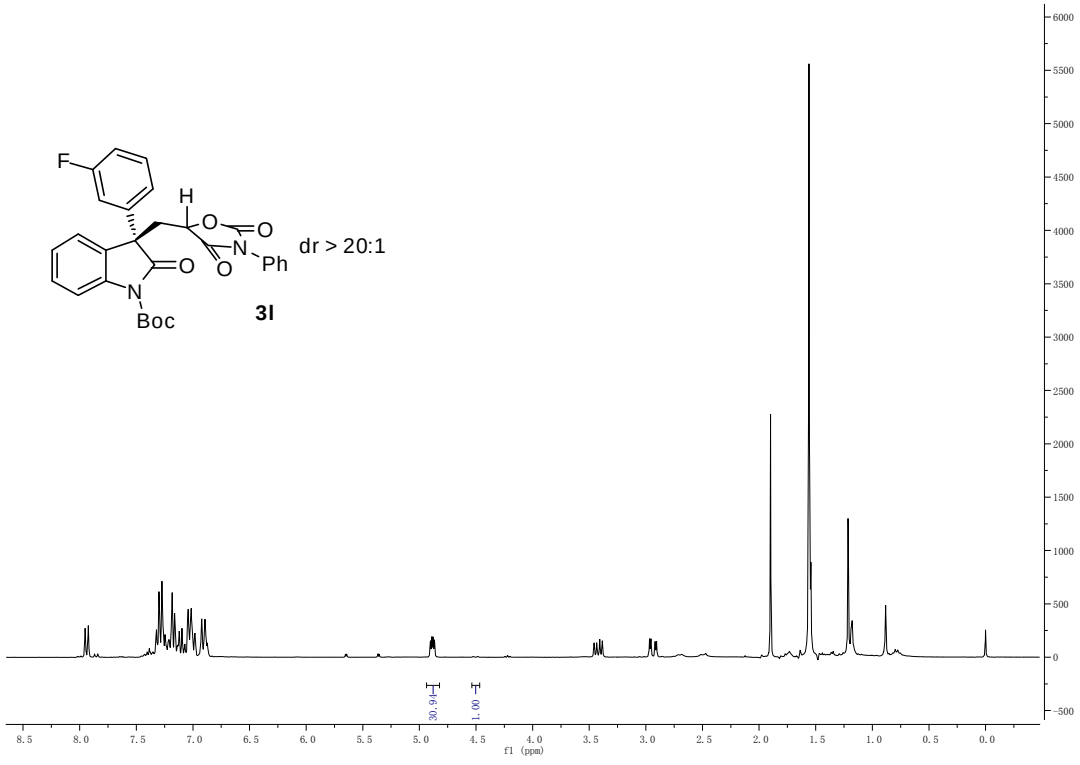
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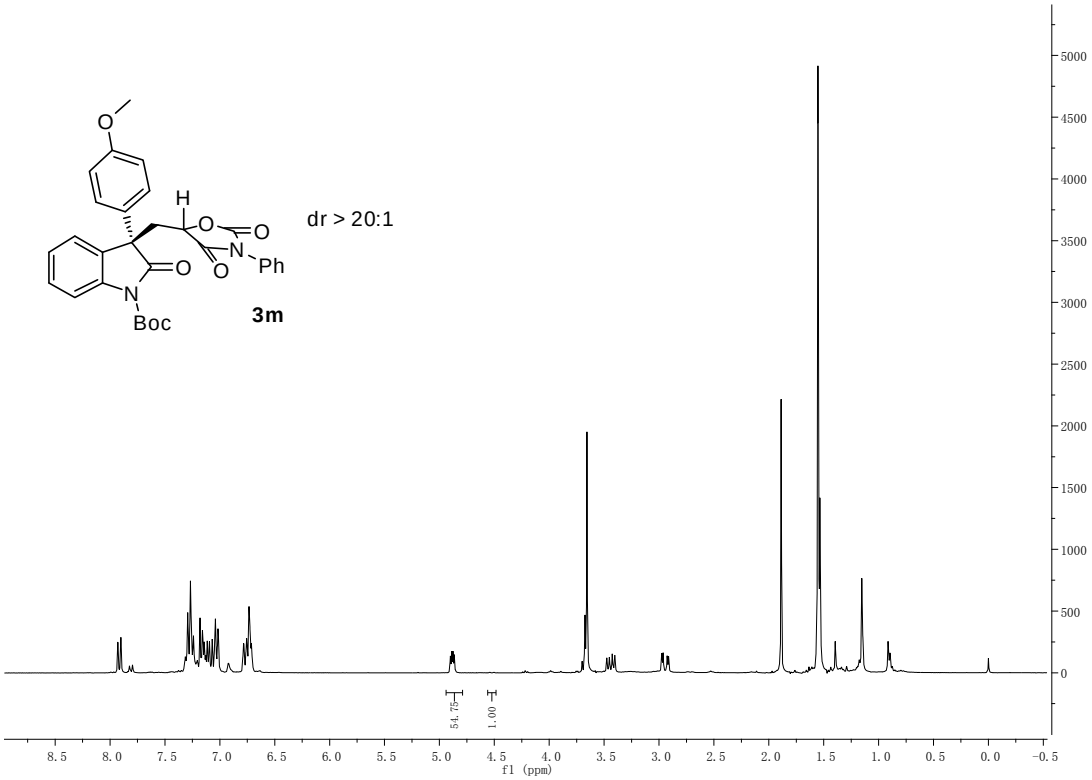
O
N
Ph
O
O
O
N
Boc
3l
dr > 20:1
30.94
1.00
f1 (ppm)

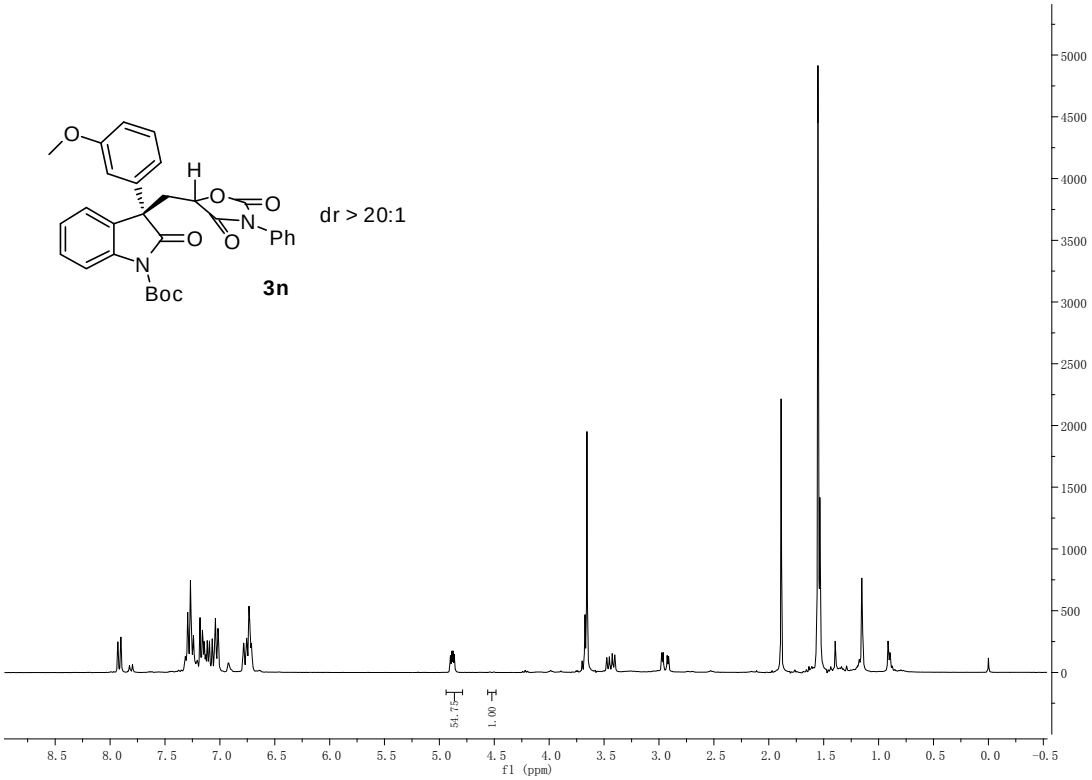
dr > 20:1

3m



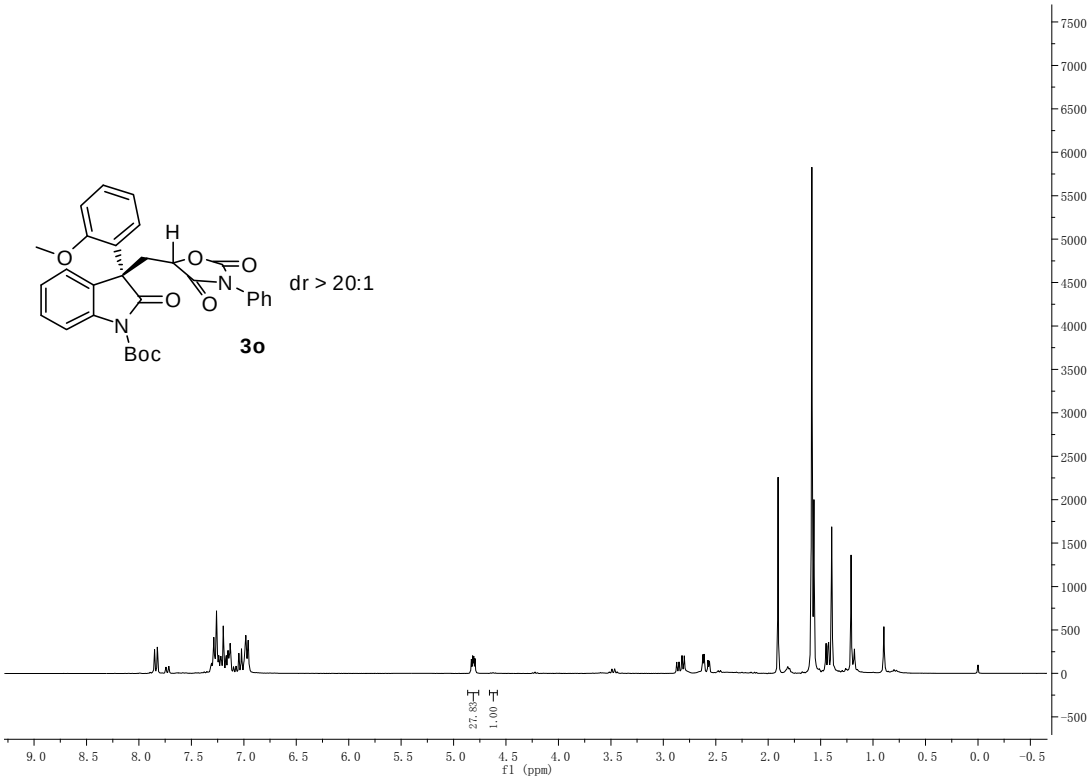
dr > 20:1

3n



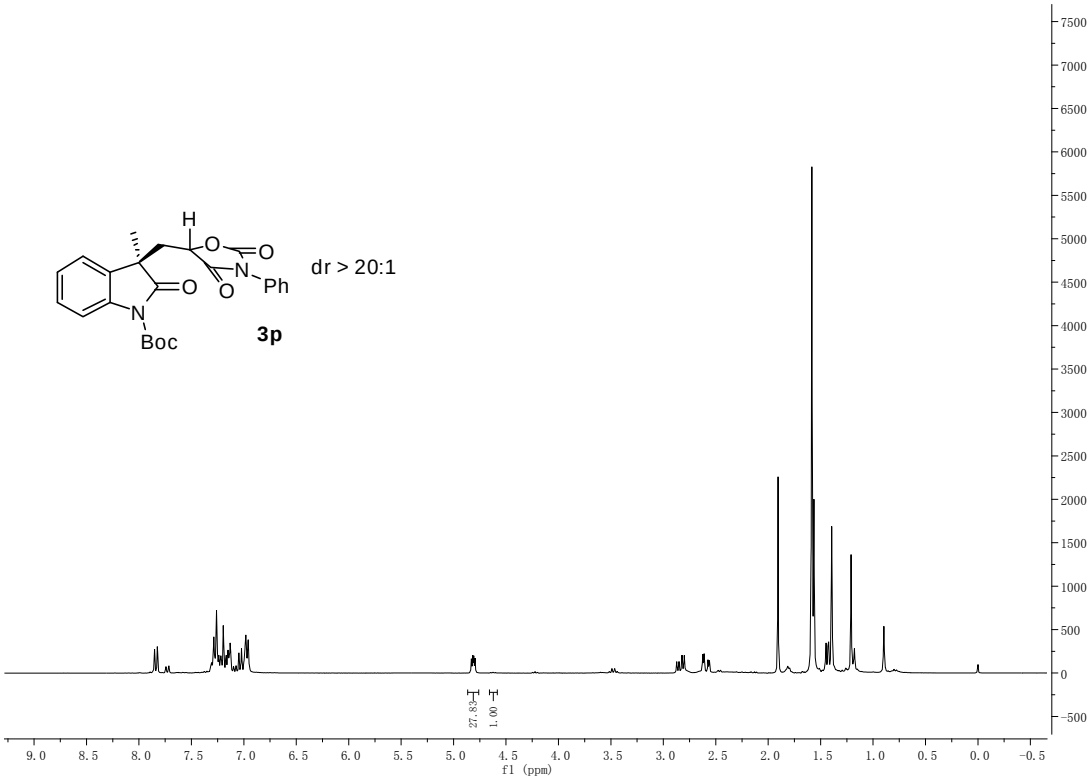
dr > 20:1

3o



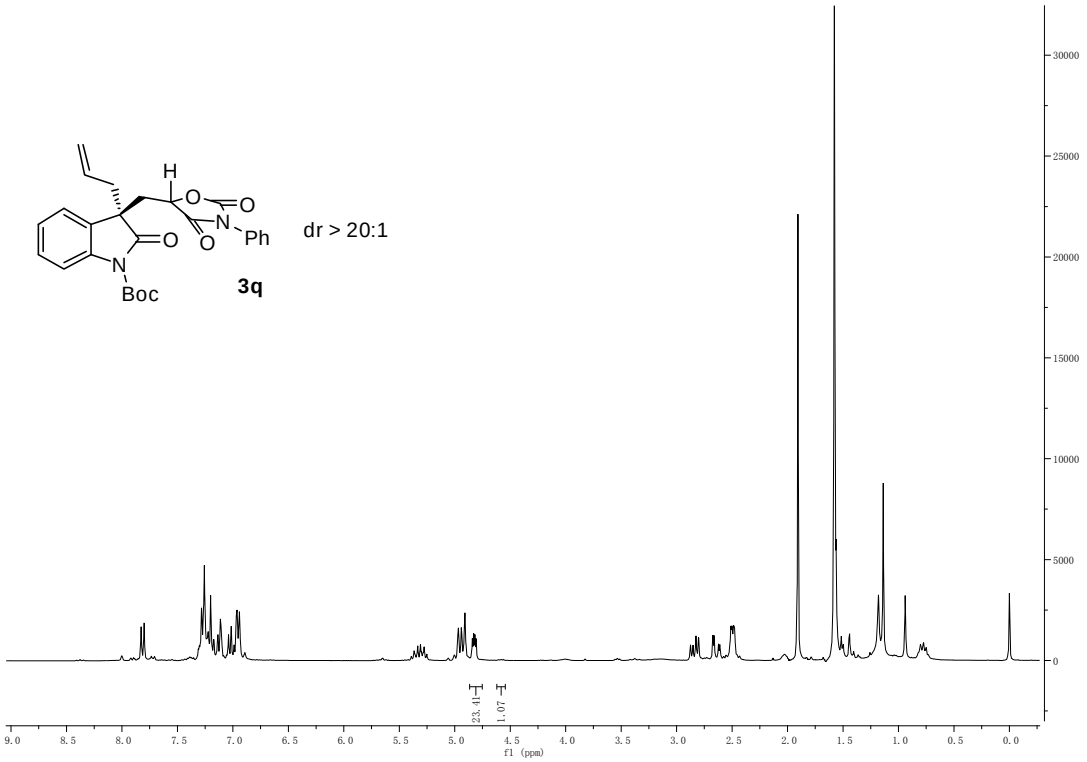
dr > 20:1

3p



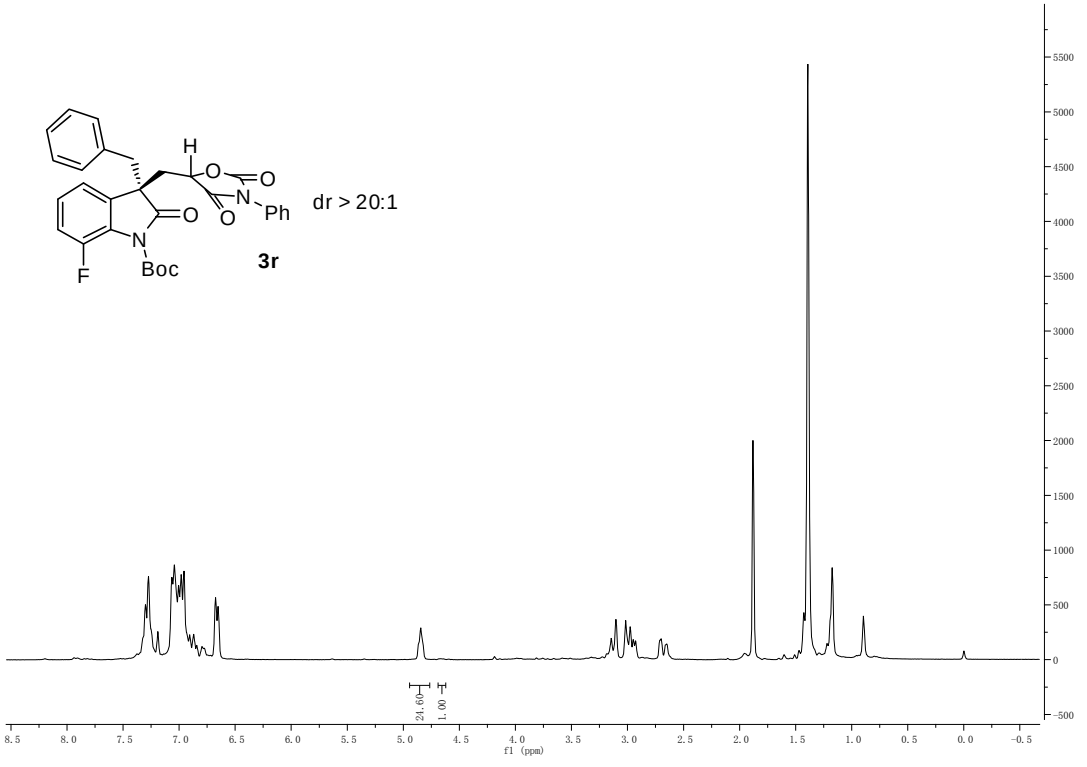
dr > 20:1

3q



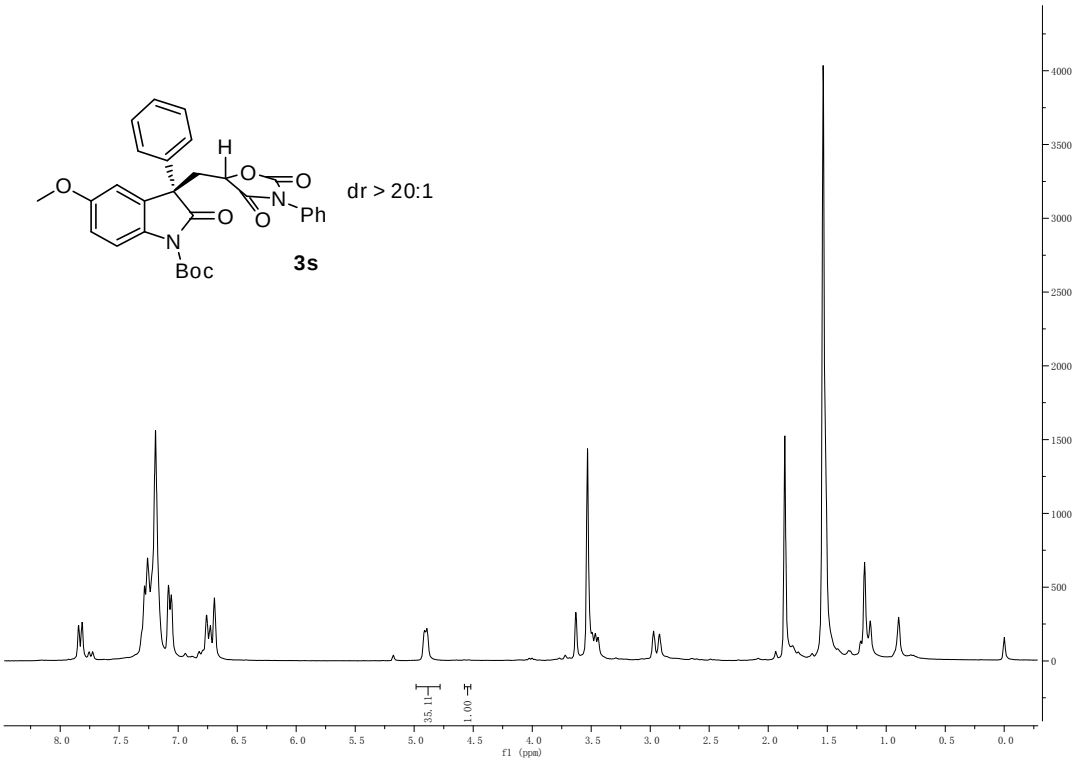
dr > 20:1

3r



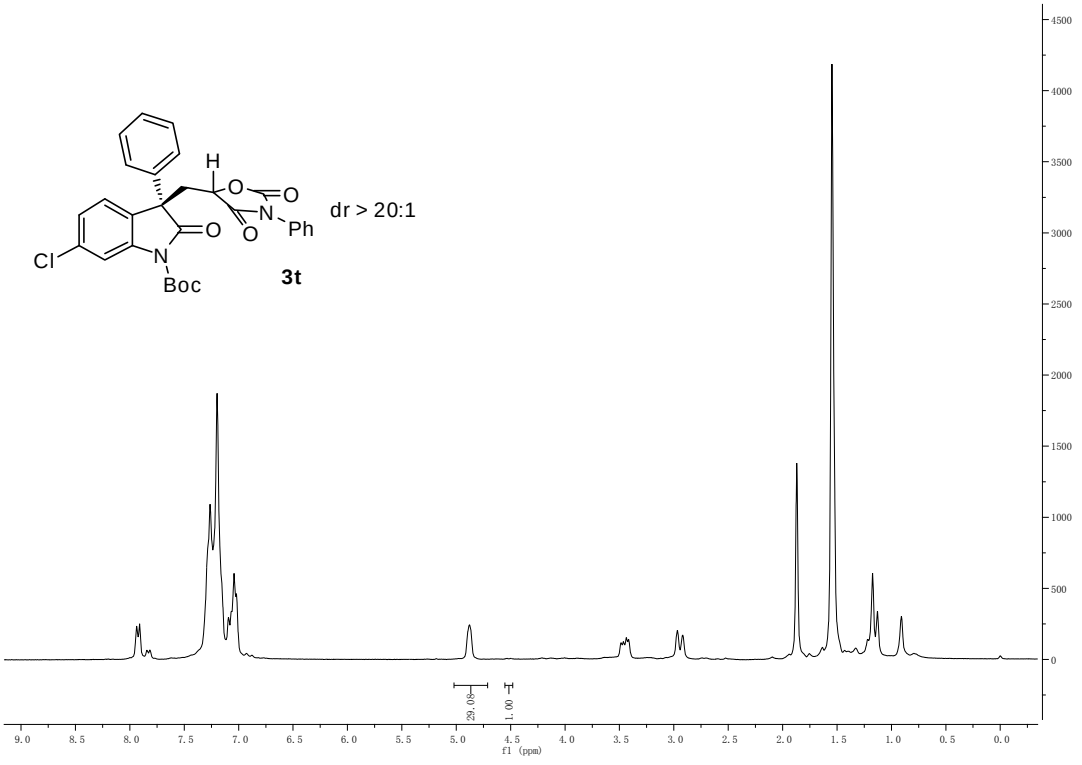
dr > 20:1

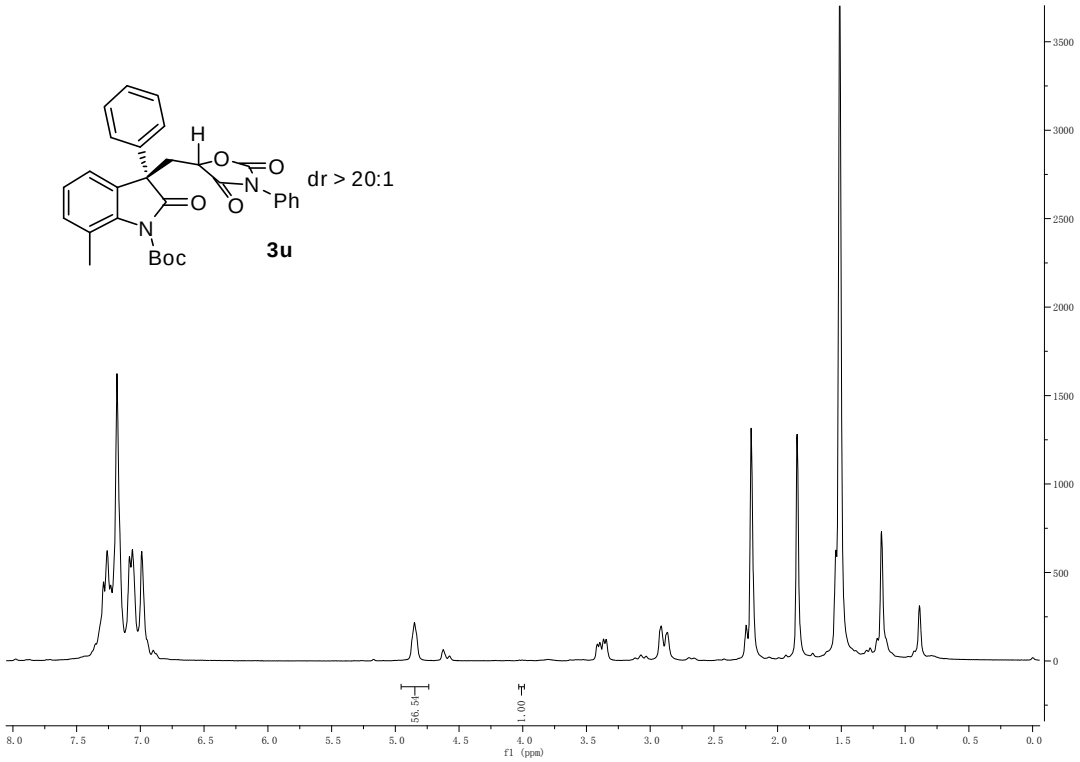
3s

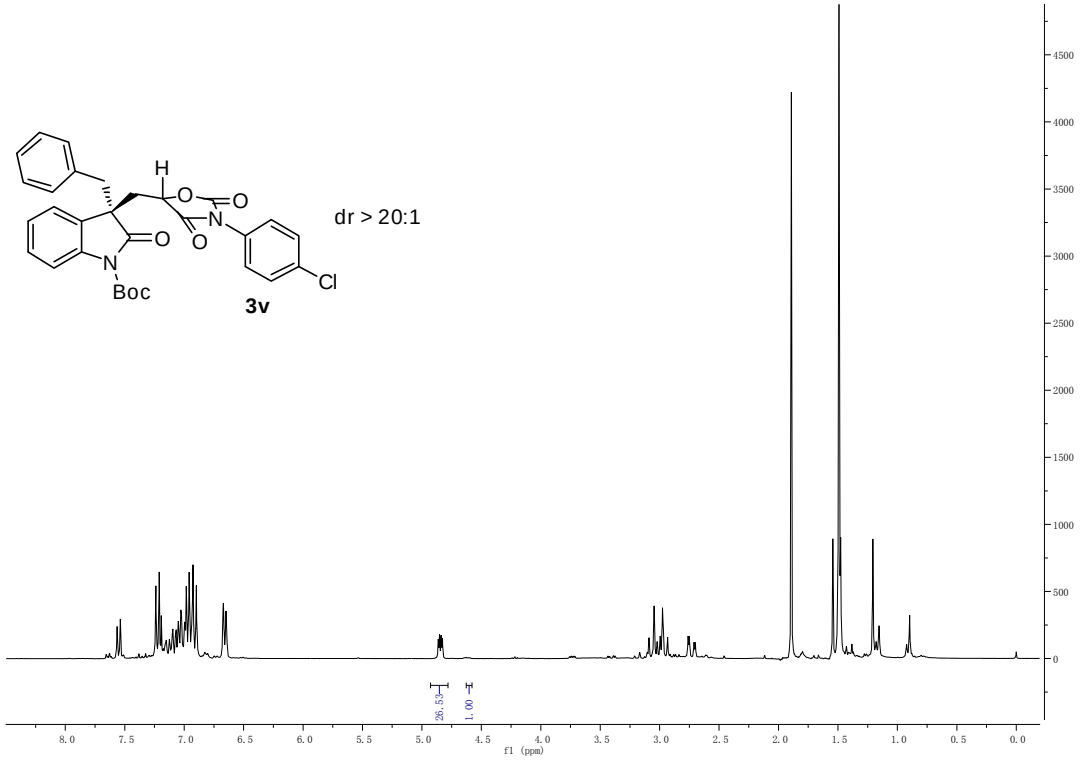


dr > 20:1

3t

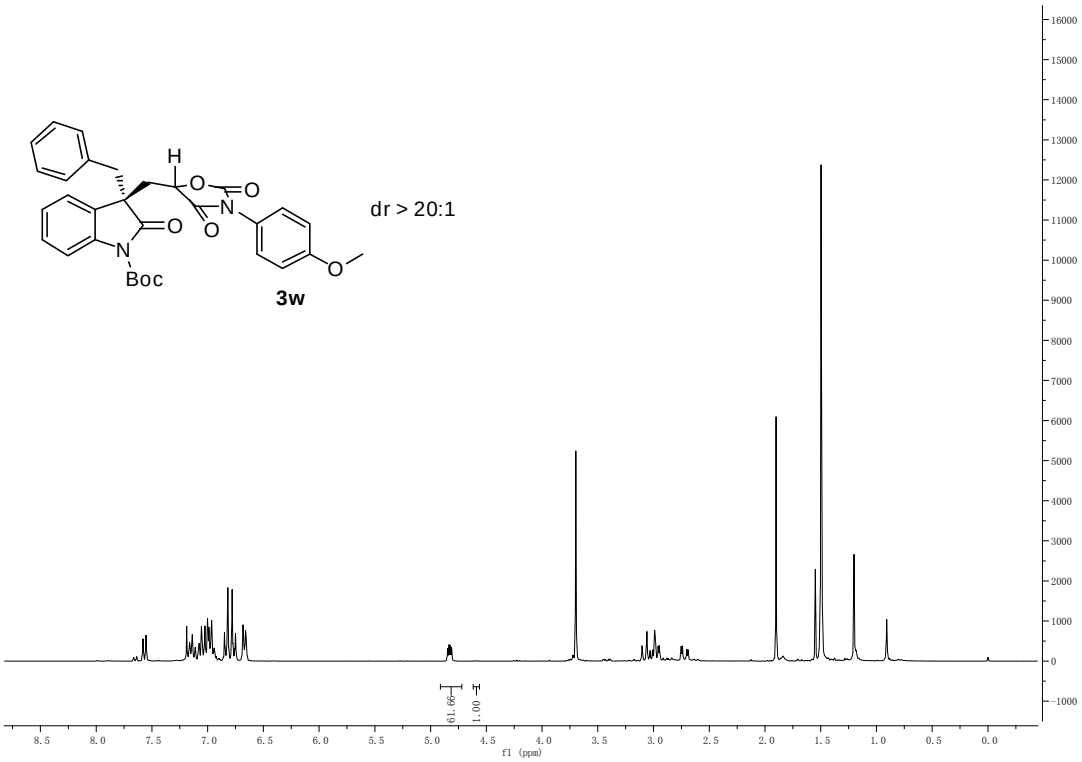



dr > 20:1
3u
56.54
1.00
f1 (ppm)


dr > 20:1
3v
26.53
1.00
f1 (ppm)

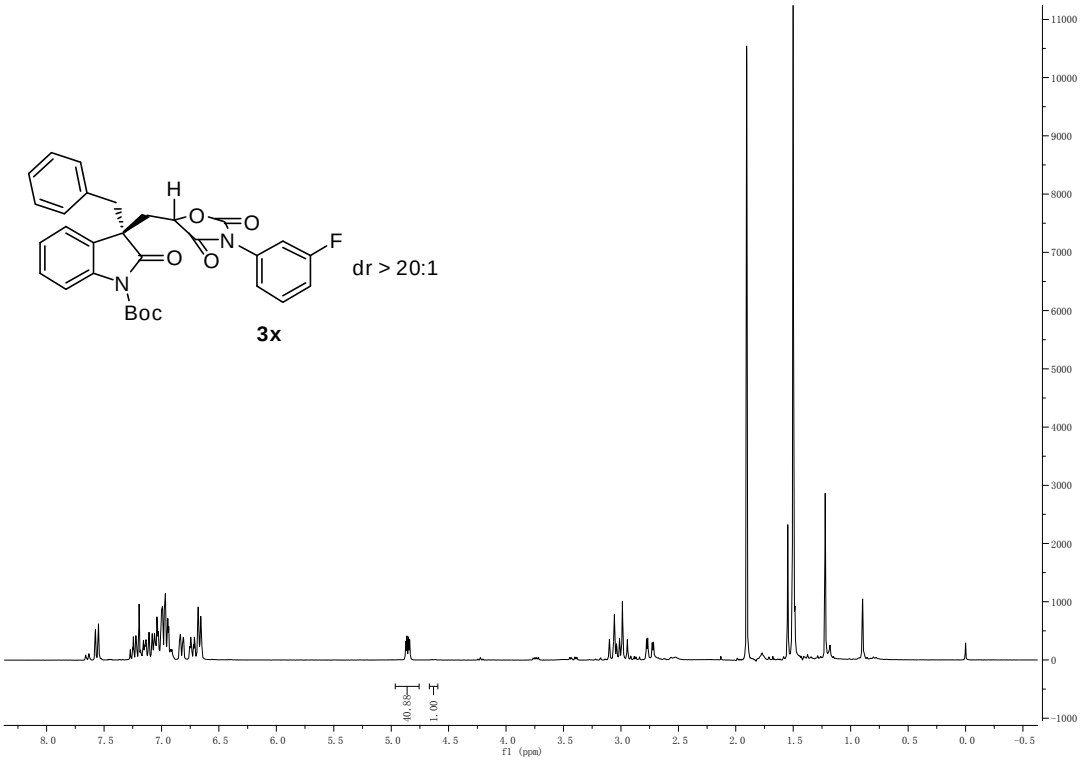
dr > 20:1

3w

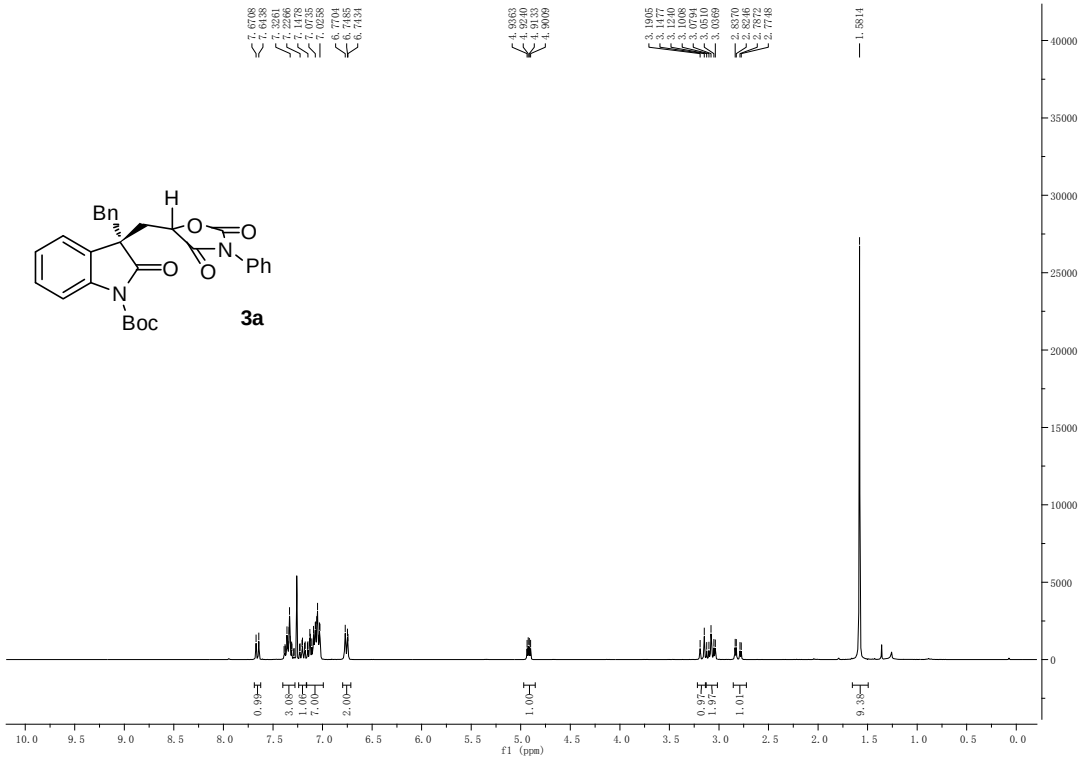


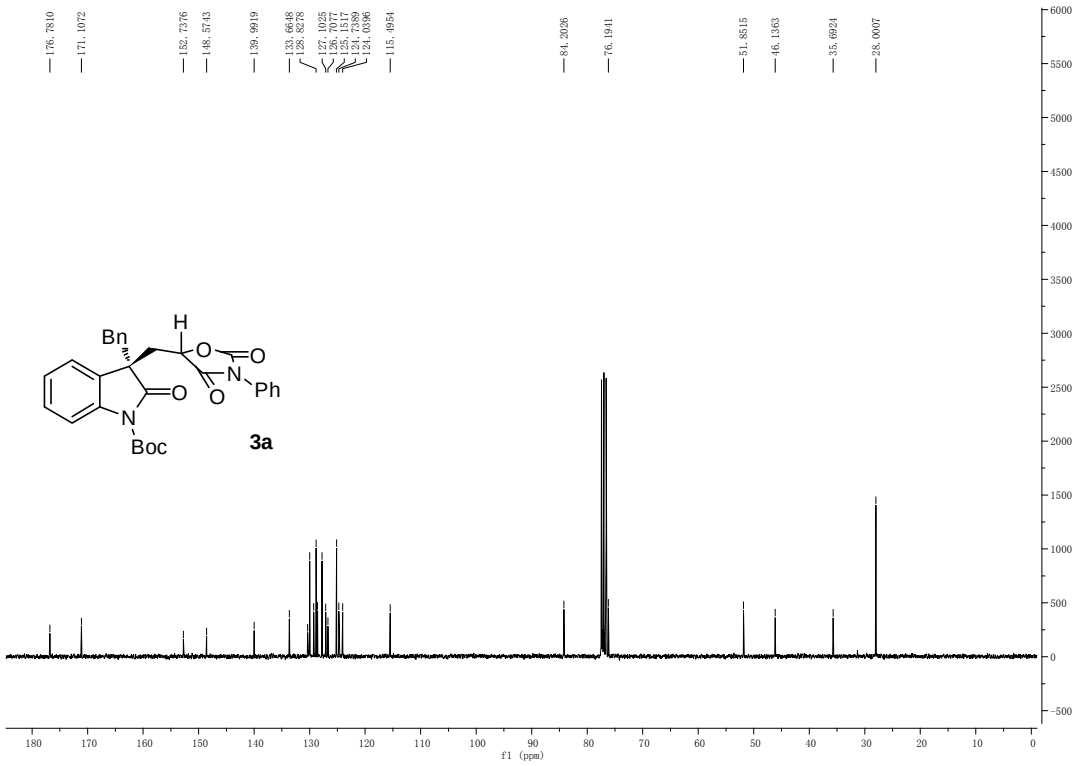
dr > 20:1

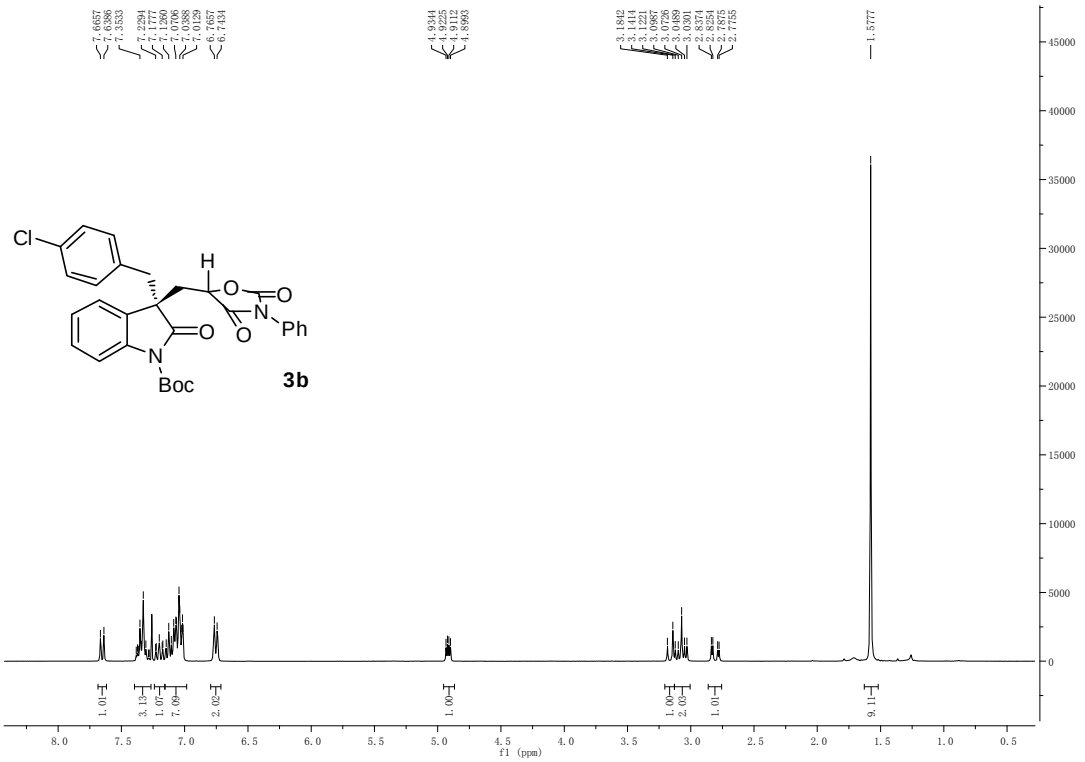
3x



10. Copies of NMR spectra



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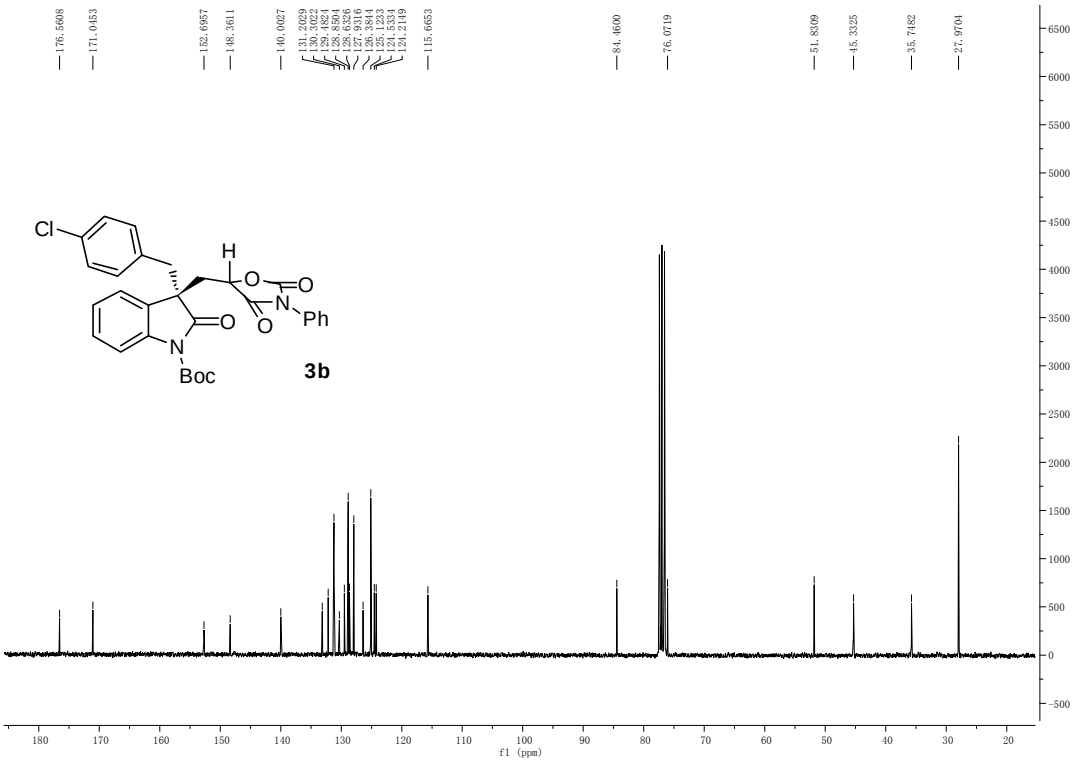
7.6386
7.3533
7.2294
7.1777
7.1260
7.0986
7.0586
7.0129
6.7657
6.7434
4.9344
4.9225
4.8712
4.8993
3.1842
3.1414
3.1221
3.0987
3.0726
3.0508
3.0301
2.8374
2.8254
2.7875
2.7755
1.5777
Cl
H
O
O
N
Ph
O
O
N
Boc
3b
1.01
3.13
1.07
7.69
2.02
1.00
1.00
2.03
1.01
9.11
f1 (ppm)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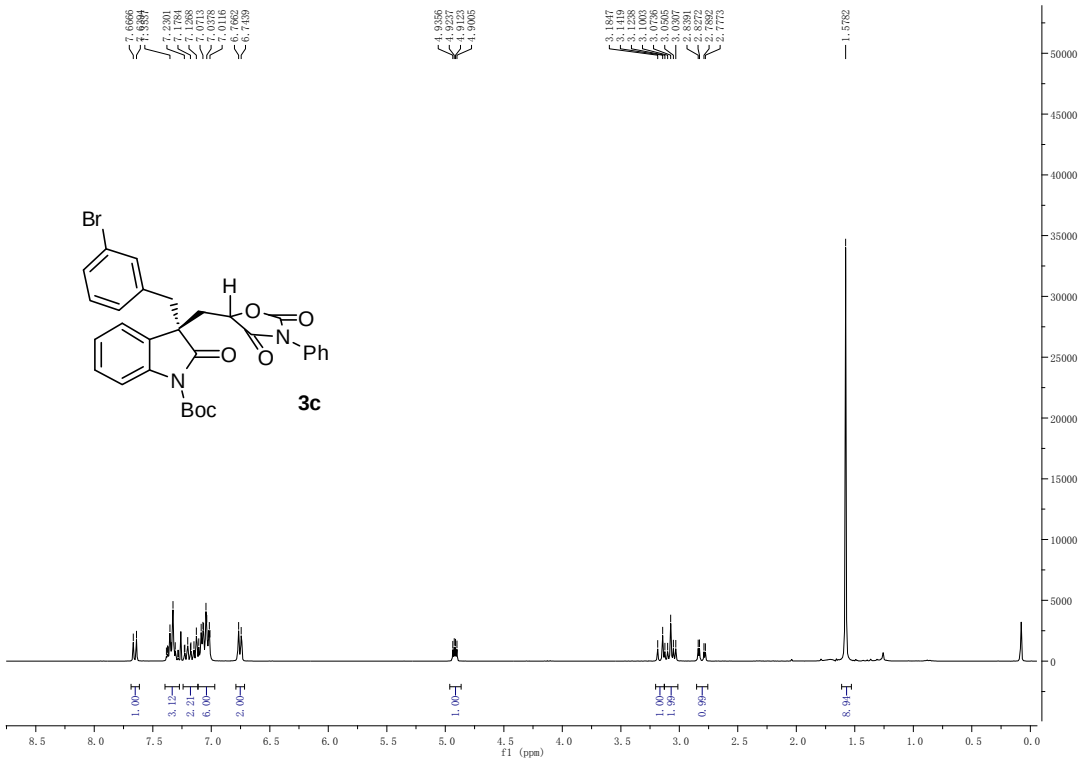
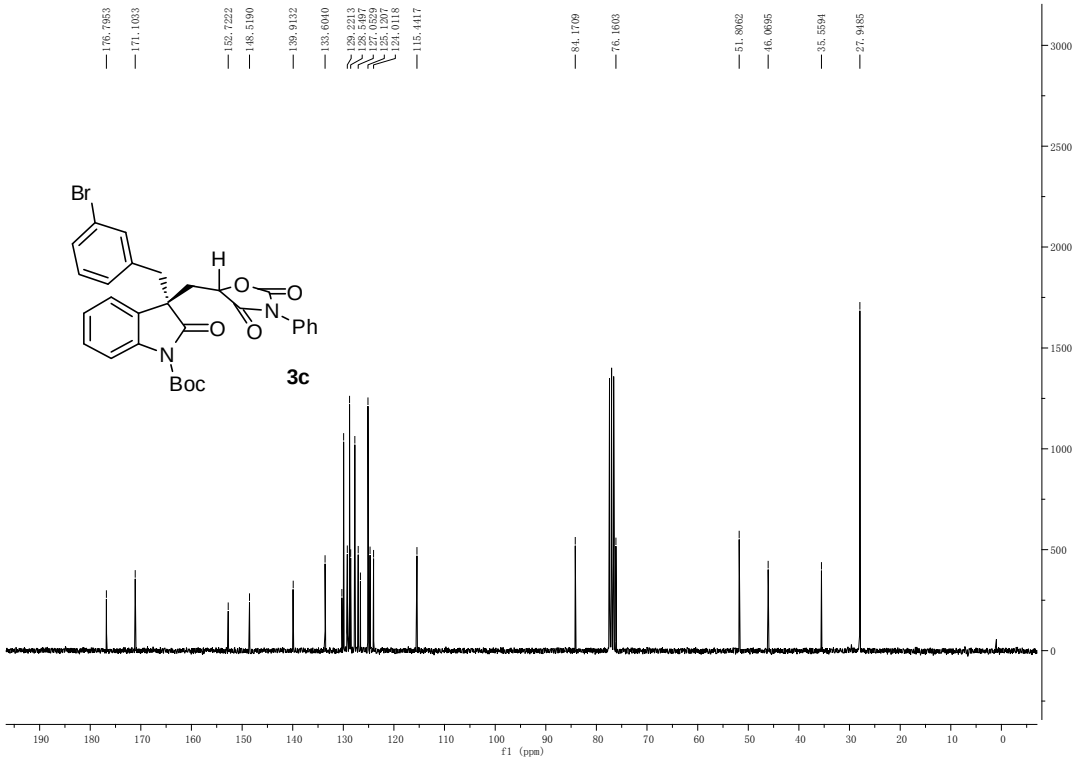
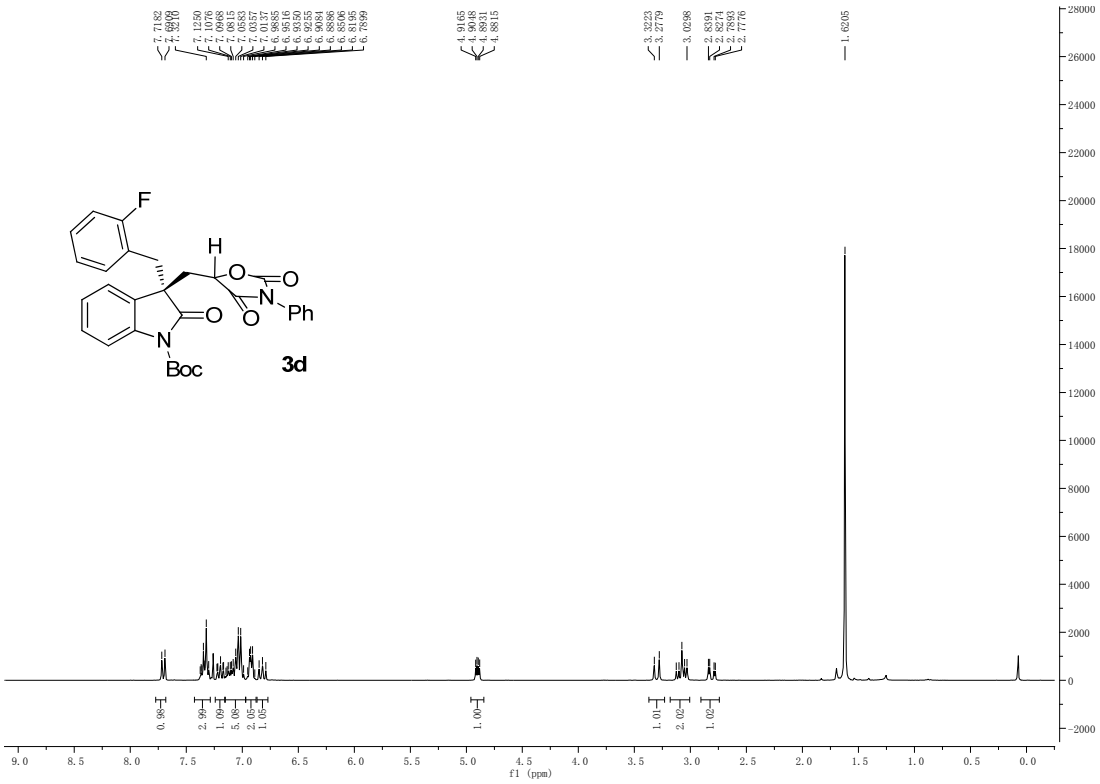
171.0453
152.6957
148.3611
140.0027
131.2029
130.3072
129.4821
128.8504
128.6326
127.9316
126.3841
125.1233
124.5334
124.2149
115.6653
84.4600
76.0719
51.8309
45.3325
35.7482
27.9704
Cl
H
O
O
N
Ph
O
O
N
Boc
3b
f1 (ppm)


Br
H
O
O
N
Ph
O
O
O
N
Boc
3c
f1 (ppm)


Br
H
O
O
N
Ph
O
O
O
N
Boc
3c
f1 (ppm)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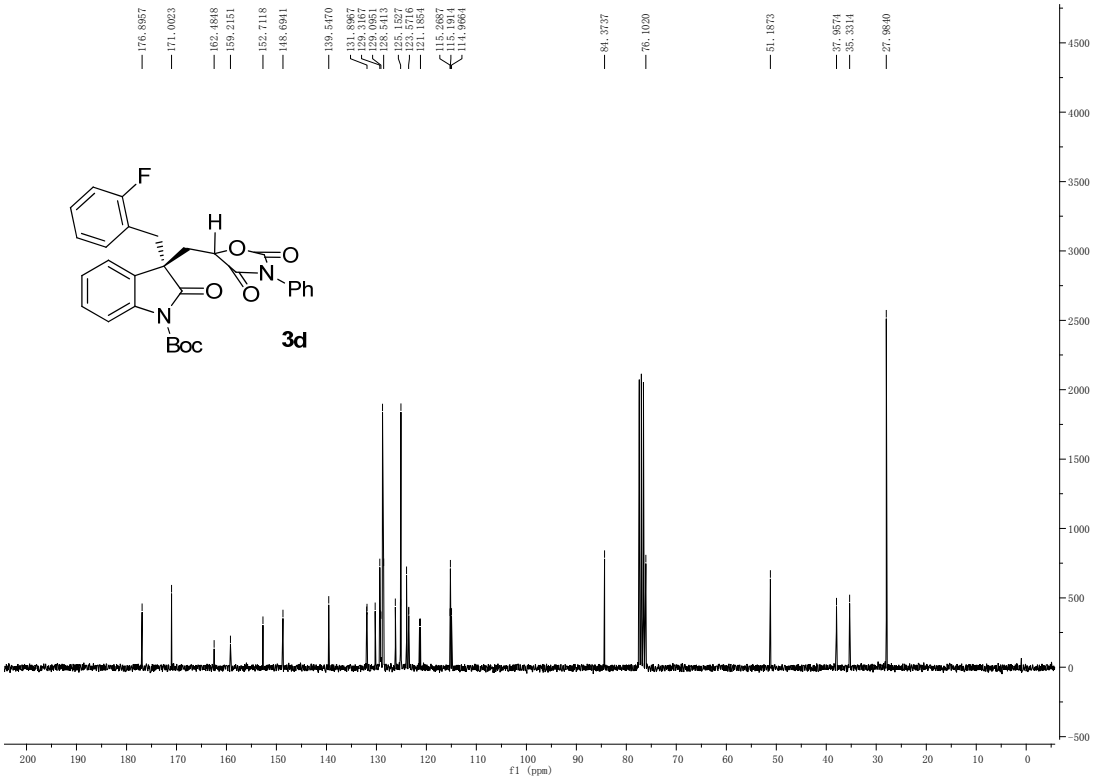
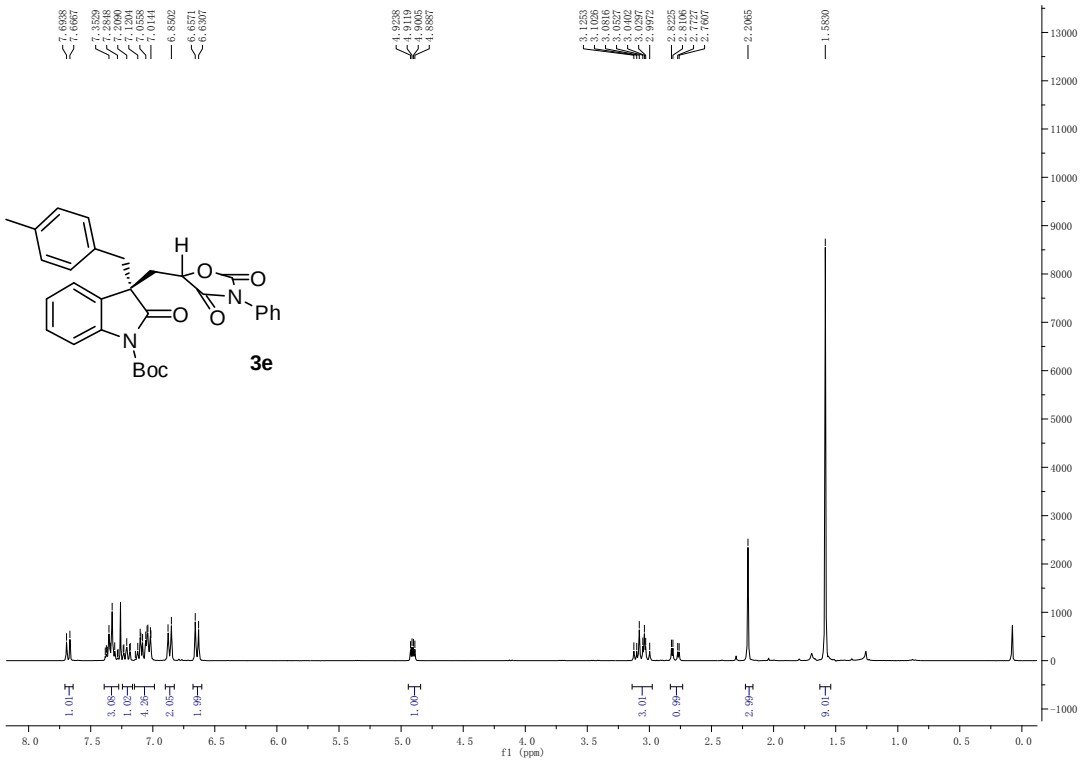
7.7040
7.4240
7.4100
7.1250
7.1076
7.0968
7.0845
7.0683
7.0557
7.0137
6.9885
6.9516
6.9350
6.9255
6.9084
6.8896
6.8596
6.8445
6.7899
4.9165
4.9048
4.8931
4.8815
3.3223
3.2779
3.0298
2.8391
2.8274
2.7793
2.7716
1.6205
F
H
O
O
N
Ph
O
O
N
Boc
3d
0.98
2.99
1.09
5.08
2.05
1.05
1.00
1.01
2.02
1.02
f1 (ppm)


176.8957
171.0023
162.4848
159.2151
152.7118
148.6941
139.5470
131.8967
129.3167
129.0951
128.5413
125.1527
123.5716
121.1854
115.2687
115.0944
114.9664
84.3737
76.1020
51.1873
37.9574
35.3314
27.9840
F
H
O
O
N
Ph
O
O
N
Boc
3d
f1 (ppm)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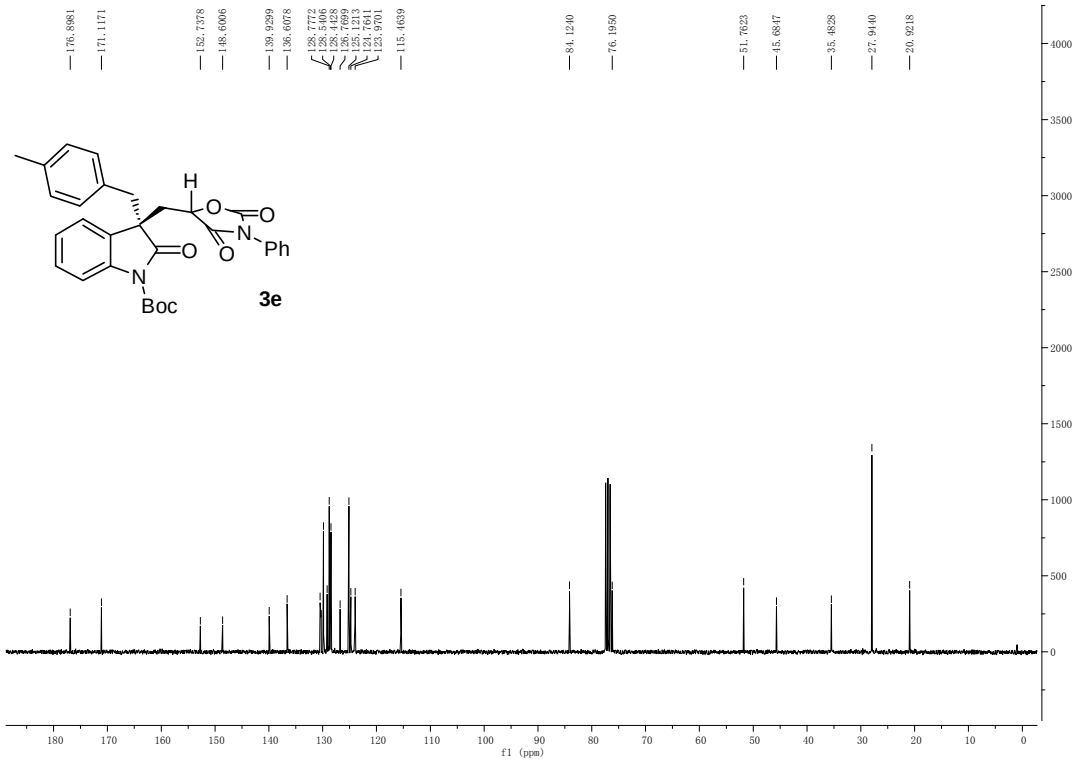
7.3529
7.3048
7.2906
7.1204
7.0558
7.0144
6.8502
6.6571
6.6397
4.9238
4.9119
4.9005
4.8887
3.1253
3.1036
3.0816
3.0527
3.0402
3.0277
2.9972
2.8225
2.8106
2.7727
2.7607
2.2065
1.5830
H
O
O
N
Ph
O
O
N
Boc
3e
1.01
3.08
1.02
4.38
2.05
1.99
1.00
3.01
0.99
2.99
9.01
f1 (ppm)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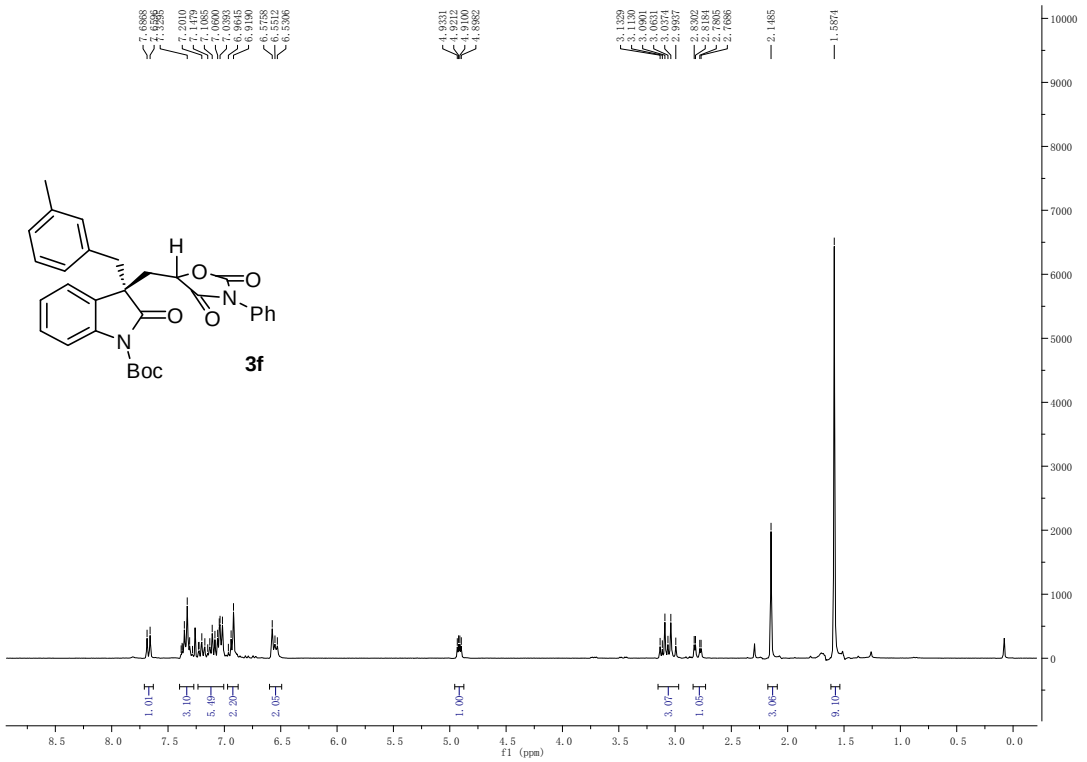
152.7378
148.6006
139.9299
136.6078
128.7772
128.5406
128.4428
126.7899
125.1723
124.7641
123.9701
115.4639
84.1240
76.1950
51.7623
45.6847
35.4828
27.9440
20.9218
H
O
O
N
Ph
O
O
N
Boc
3e
f1 (ppm)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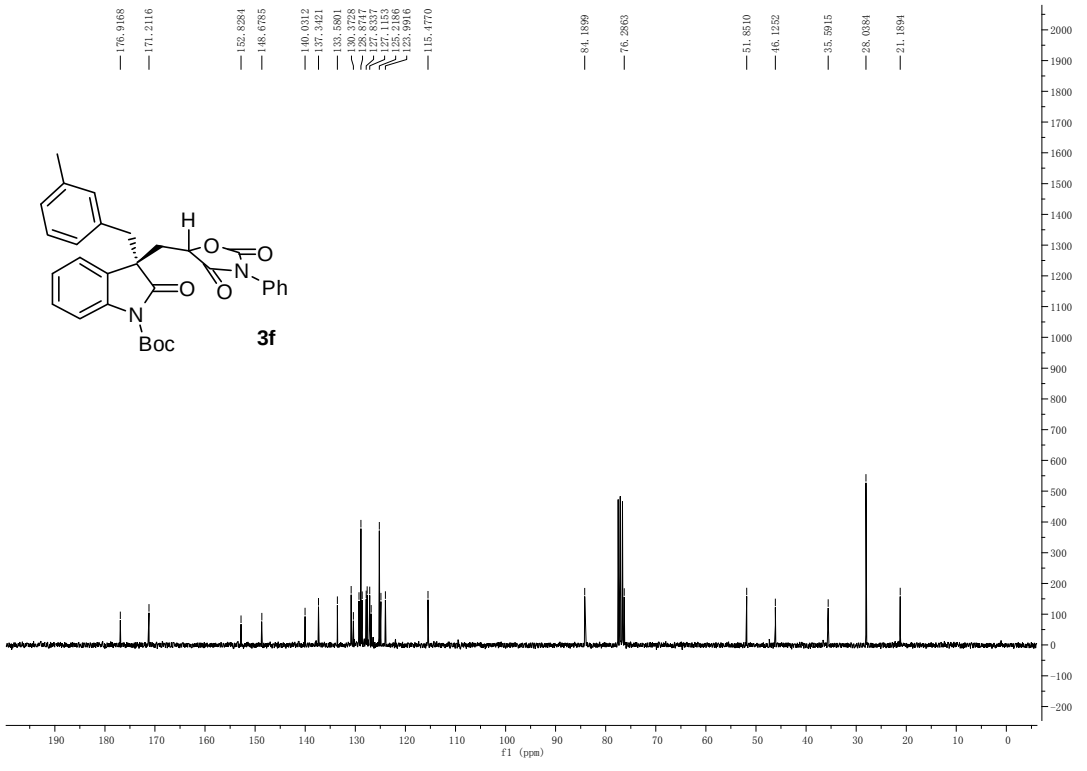
7.6686
7.5295
7.2010
7.1479
7.1065
7.0900
7.0393
6.9645
6.9190
6.5758
6.5702
6.5306
4.9331
4.9212
4.9100
4.8982
3.1329
3.1130
3.0901
3.0631
3.0374
2.9937
2.8302
2.8194
2.7805
2.7686
2.1485
1.5874
1.01
3.10
5.49
2.20
2.05
1.00
3.07
1.05
3.06
9.10
f1 (ppm)
H
O
O
N
Ph
O
O
N
Boc
3f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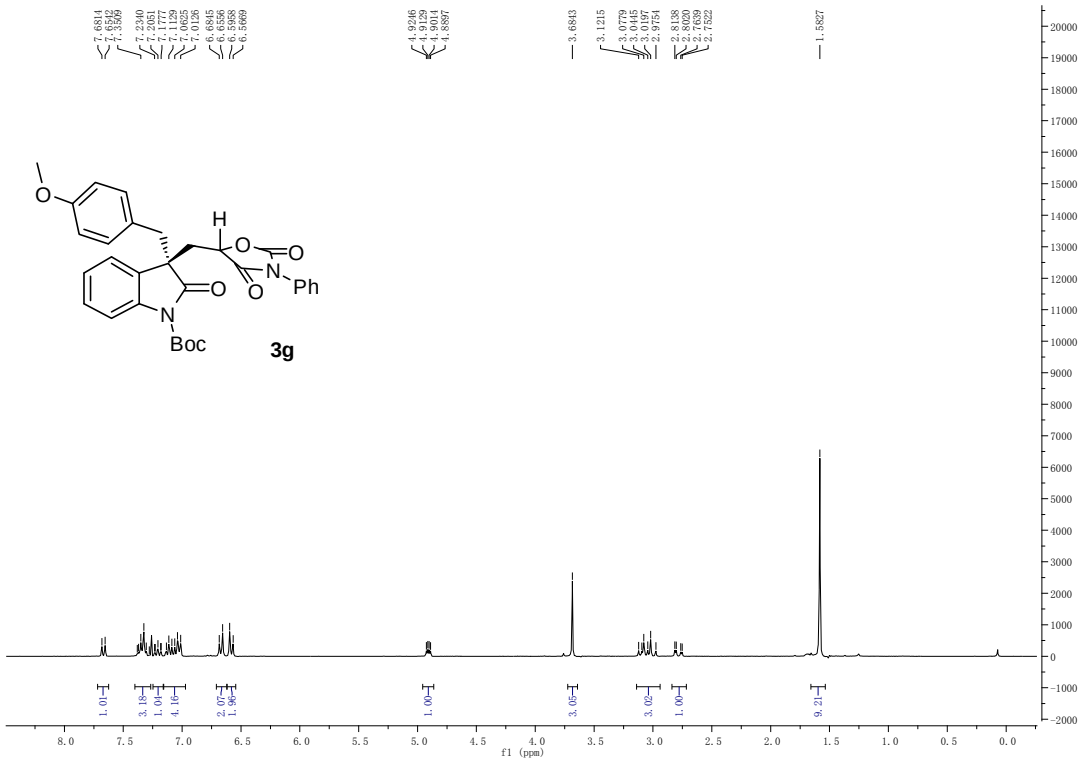
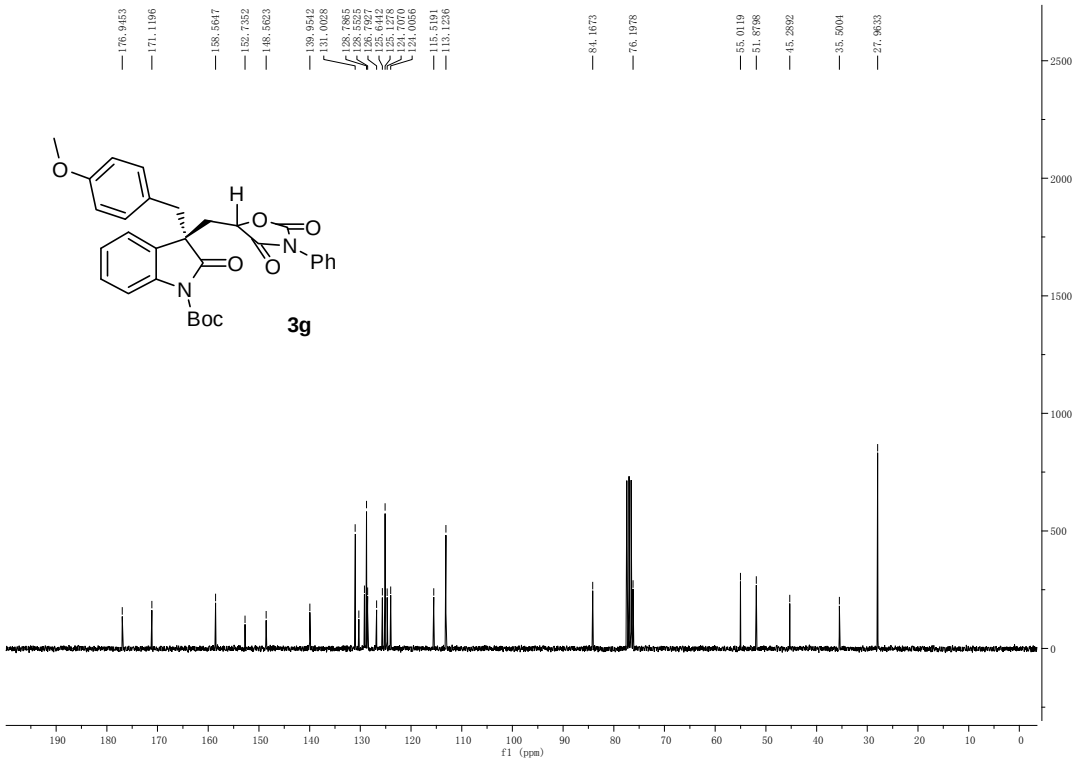
152.8284
148.6785
140.0312
137.3421
133.5801
130.3728
128.8747
127.8337
127.1153
125.2186
123.9916
115.4770
84.1899
76.2863
51.8510
46.1252
35.5915
28.0384
21.1894
f1 (ppm)
H
O
O
N
Ph
O
O
N
Boc
3f


7.6814
7.6542
7.3869
7.2340
7.2051
7.1777
7.1129
7.0625
7.0126
6.6845
6.6536
6.6368
6.5669
4.9246
4.9129
4.9014
4.8897
3.6843
3.1215
3.0779
3.0445
3.0197
2.9754
2.8138
2.8020
2.7639
2.7322
1.5827
1.01
3.18
1.01
4.16
2.07
1.96
1.00
3.05
3.02
1.00
9.21
f1 (ppm)

O
H
O
O
N
Ph
O
O
N
Boc

3g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158.5647
152.7352
148.5623
139.9542
131.0028
128.7865
128.5535
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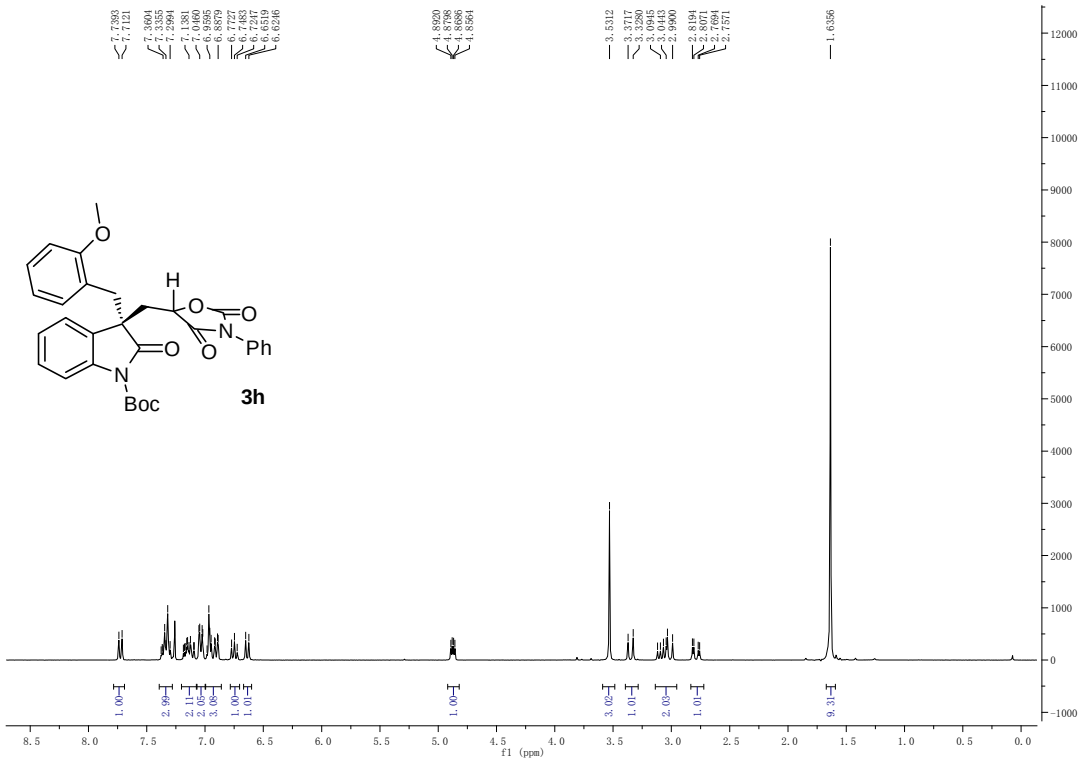
125.6442
125.1278
124.7070
124.0686
115.5191
113.1236
84.1673
76.1978
55.0119
51.8798
45.2892
35.5004
27.9633
f1 (ppm)

O
H
O
O
N
Ph
O
O
N
Boc

3g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7.3604
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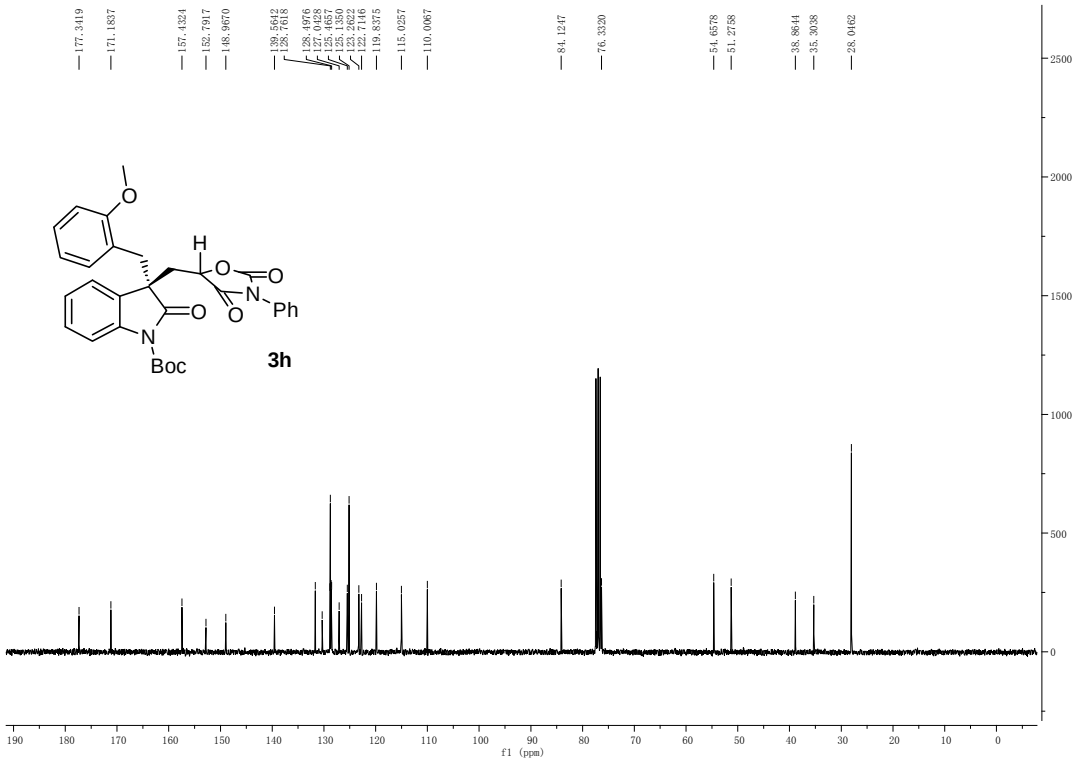
7.2994
7.1381
7.0460
6.9395
6.8879
6.7727
6.7483
6.7247
6.6519
6.6246
4.8920
4.8798
4.8686
4.8564
3.5312
3.3717
3.3280
3.0915
3.0443
2.9900
2.8194
2.8071
2.7694
2.7571
1.6356
1.00
2.99
2.11
2.05
3.08
1.00
1.01
1.00
3.02
1.01
2.03
1.01
9.31
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3h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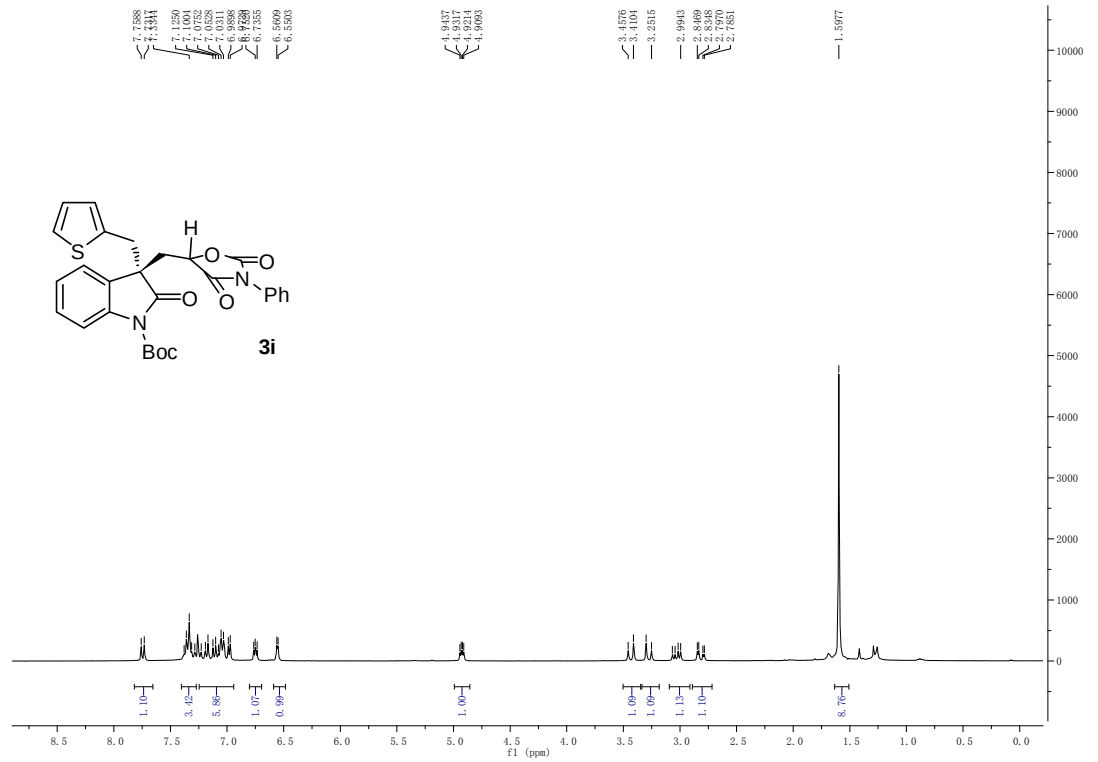
171.1837
157.4324
152.7917
148.9670
130.5642
128.7618
128.4976
127.0428
125.4957
125.1350
123.2622
122.7146
119.8375
115.0257
110.0067
84.1247
76.3320
54.6578
51.2758
38.8644
35.3038
28.0462
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3h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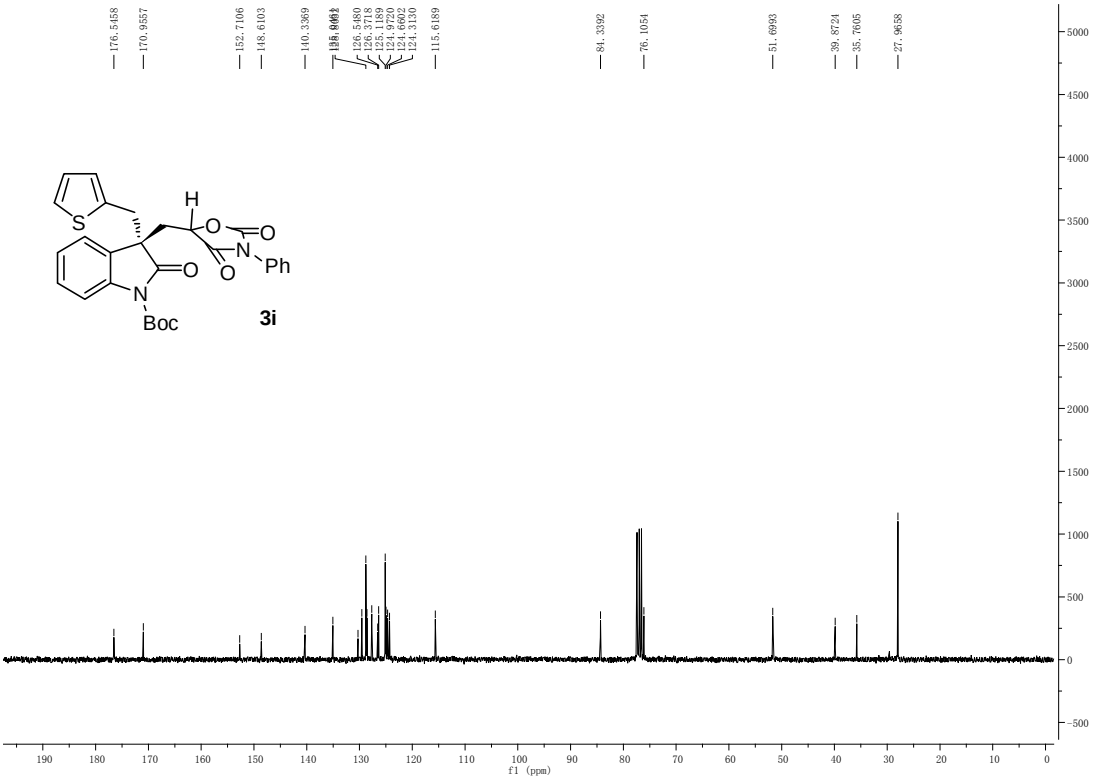
7.4344
7.4317
7.1250
7.1004
7.0752
7.0528
7.0311
6.9898
6.9728
6.9558
6.7355
6.5609
6.5503
4.9437
4.9317
4.9214
4.9093
3.4576
3.4104
3.2515
2.9943
2.8469
2.8348
2.7970
2.7851
1.5977
1.10
3.42
5.88
1.07
0.99
1.00
1.09
1.09
1.13
1.10
8.76
f1 (ppm)
H
O
O
N
Ph
S
O
N
Boc
3i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126.5480
126.3718
125.1184
124.9729
124.6602
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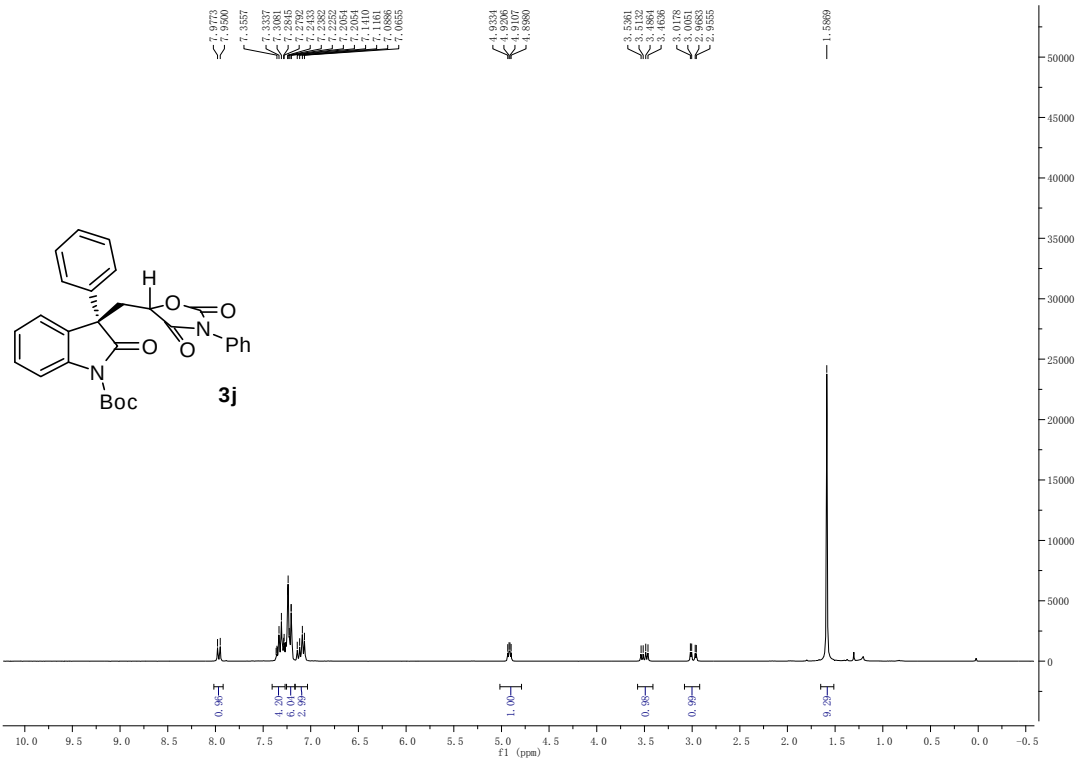
115.6189
84.3392
76.1054
51.6993
39.8724
35.7605
27.9658
f1 (ppm)
H
O
O
N
Ph
S
O
N
Boc
3i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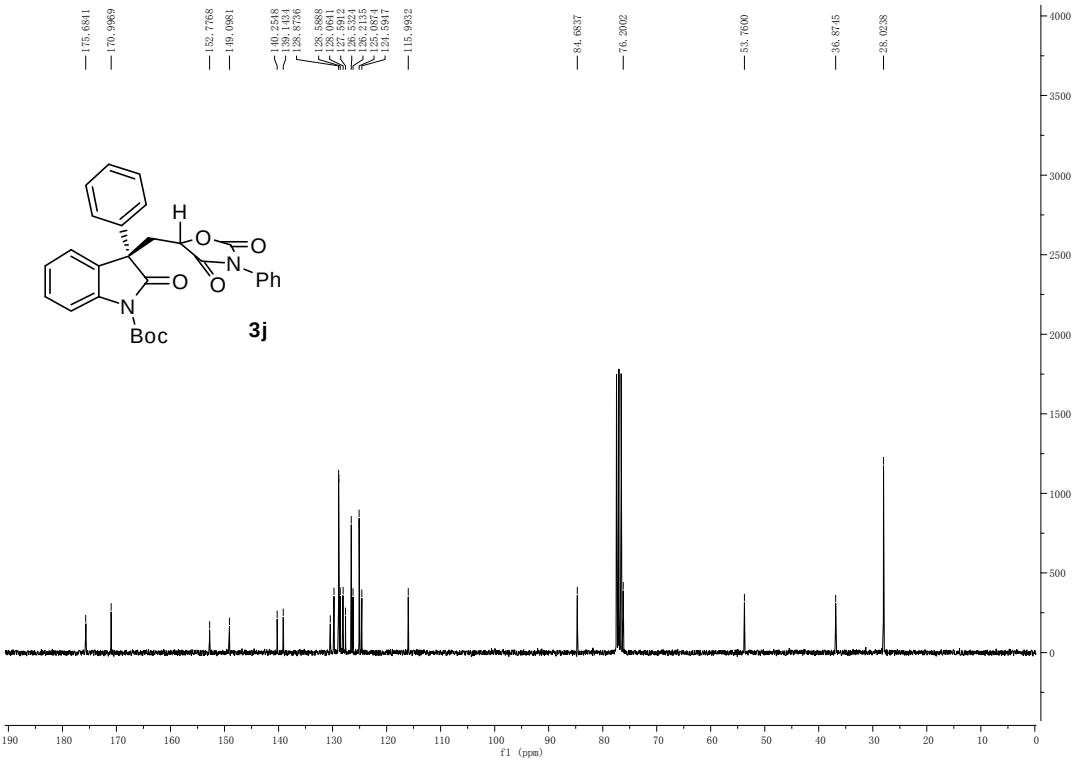
7.2845
7.2732
7.2435
7.2382
7.2252
7.2051
7.2004
7.1410
7.1161
7.0886
7.0655
4.9334
4.9206
4.9107
4.8980
3.5361
3.5132
3.4864
3.4636
3.0178
3.0051
2.9683
2.9555
1.5869
0.96
4.20
6.01
2.99
1.00
0.98
0.99
9.29
f1 (ppm)
3j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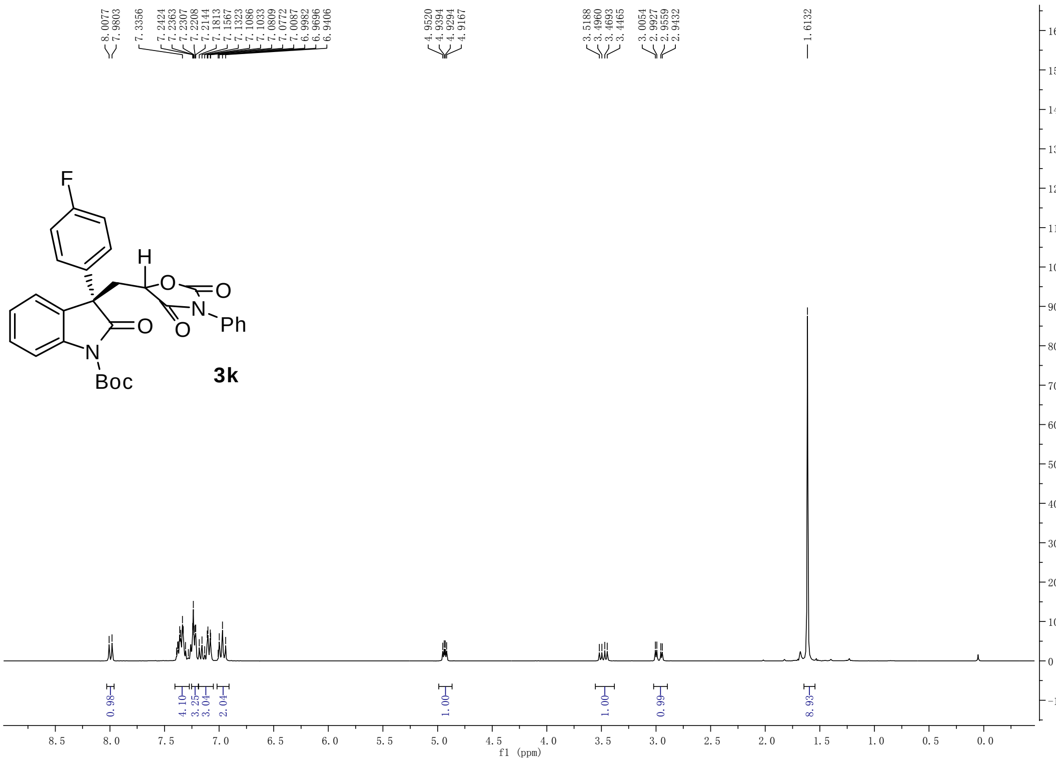
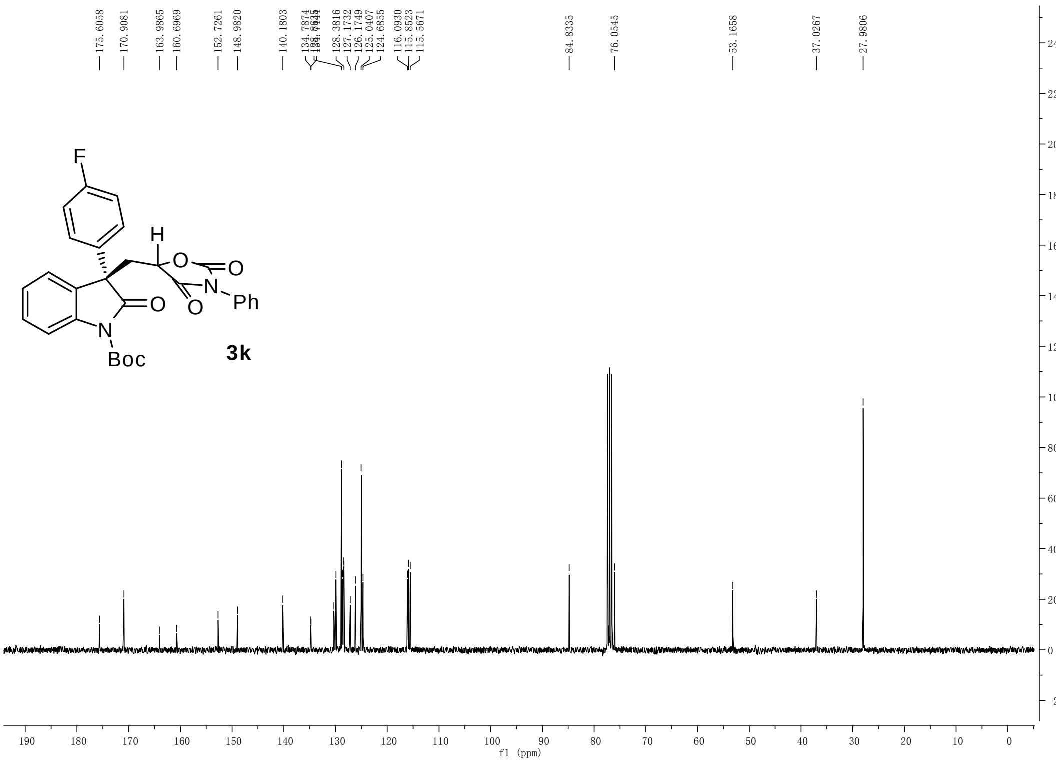
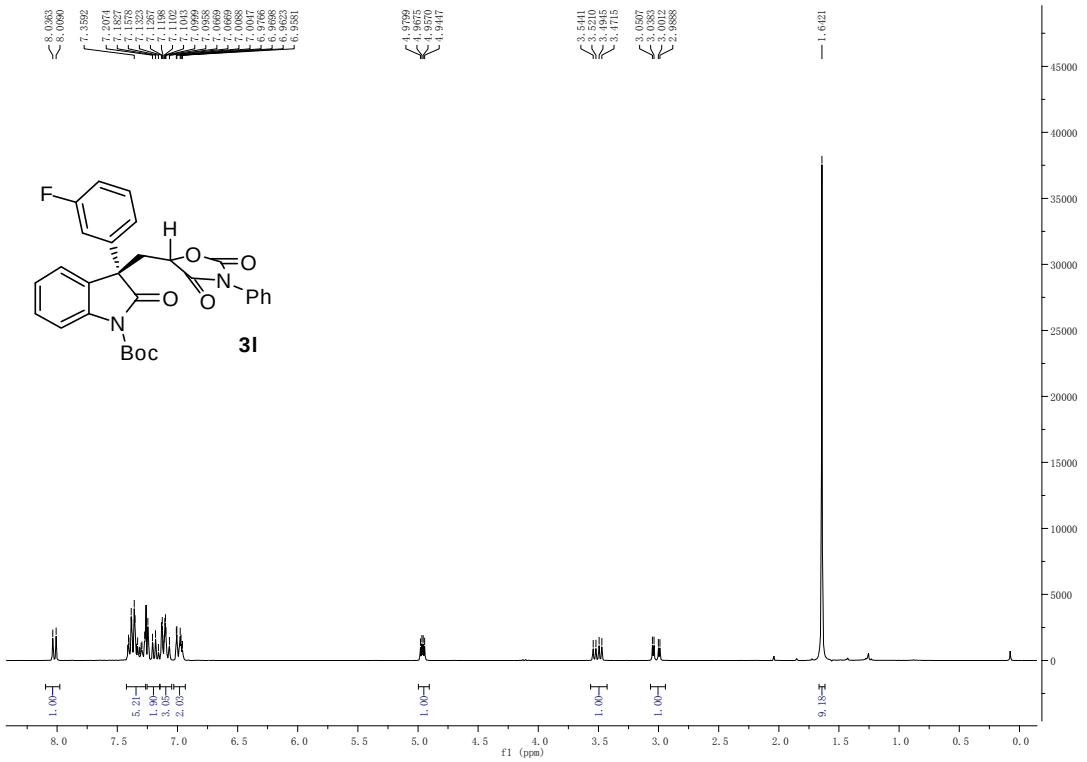
170.9969
152.7768
149.0981
140.2548
130.1434
128.8736
128.5888
128.0641
127.5913
126.5324
126.2135
125.0874
124.5947
115.9932
84.6837
76.2002
53.7600
36.8745
28.0238
f1 (ppm)
3j


F
H
O
O
N
Ph
O
O
N
Boc
3k
f1 (ppm)


F
H
O
O
N
Ph
O
O
N
Boc
3k
f1 (ppm)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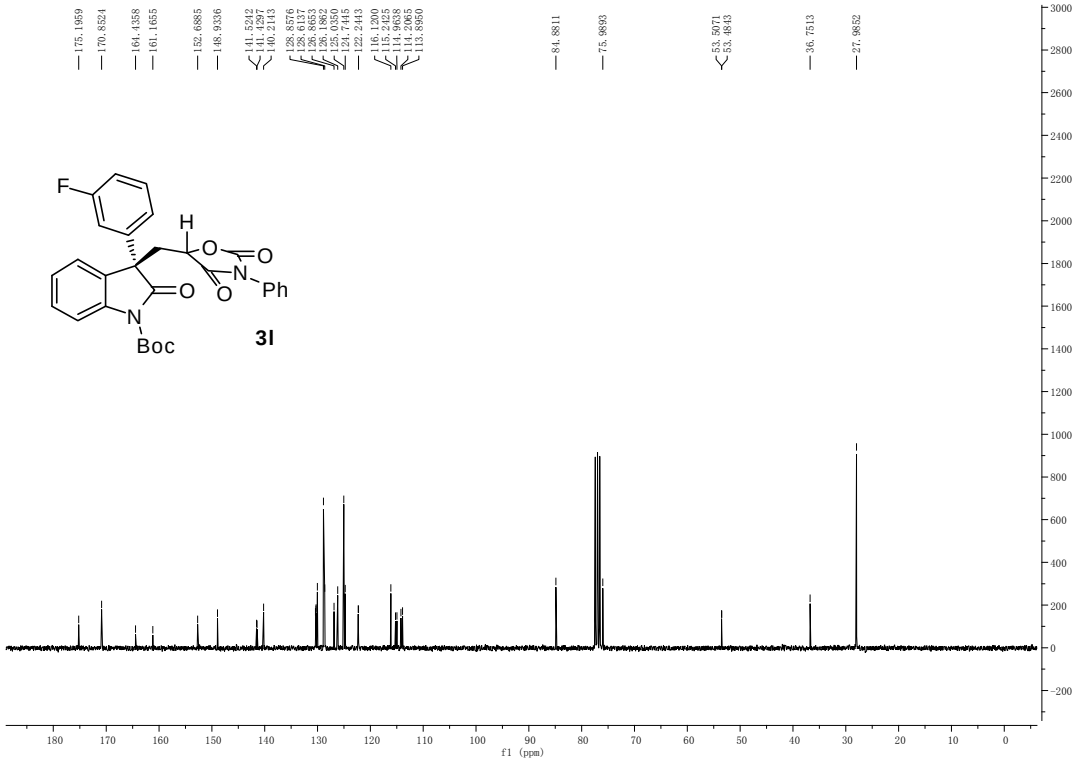
7.3592
7.2074
7.1827
7.1578
7.1323
7.1267
7.1198
7.1102
7.1043
7.0999
7.0988
7.0969
7.0669
7.0088
7.0047
6.9788
6.9698
6.9623
6.9581
4.9799
4.9675
4.9570
4.9447
3.5441
3.5210
3.4945
3.4715
3.0367
3.0253
3.0012
2.9888
1.6421
F
H
O
O
N
Ph
O
O
N
Boc
3l
1.00
5.21
1.90
3.05
2.03
1.00
1.00
1.00
9.18
f1 (ppm)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141.5242
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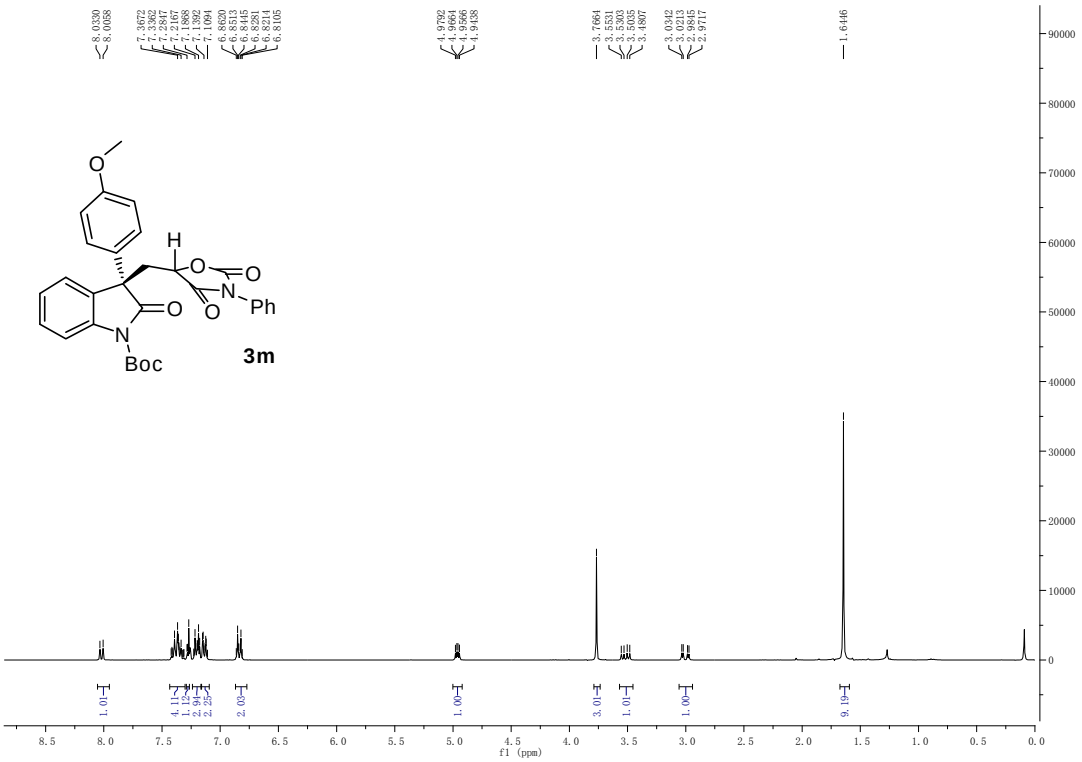
128.8576
128.6517
126.8853
126.1862
125.0350
124.7445
122.2443
116.1200
115.7275
114.9638
114.2065
113.8950
84.8811
75.9893
53.5071
53.4843
36.7513
27.9852
F
H
O
O
N
Ph
O
O
N
Boc
3l
f1 (ppm)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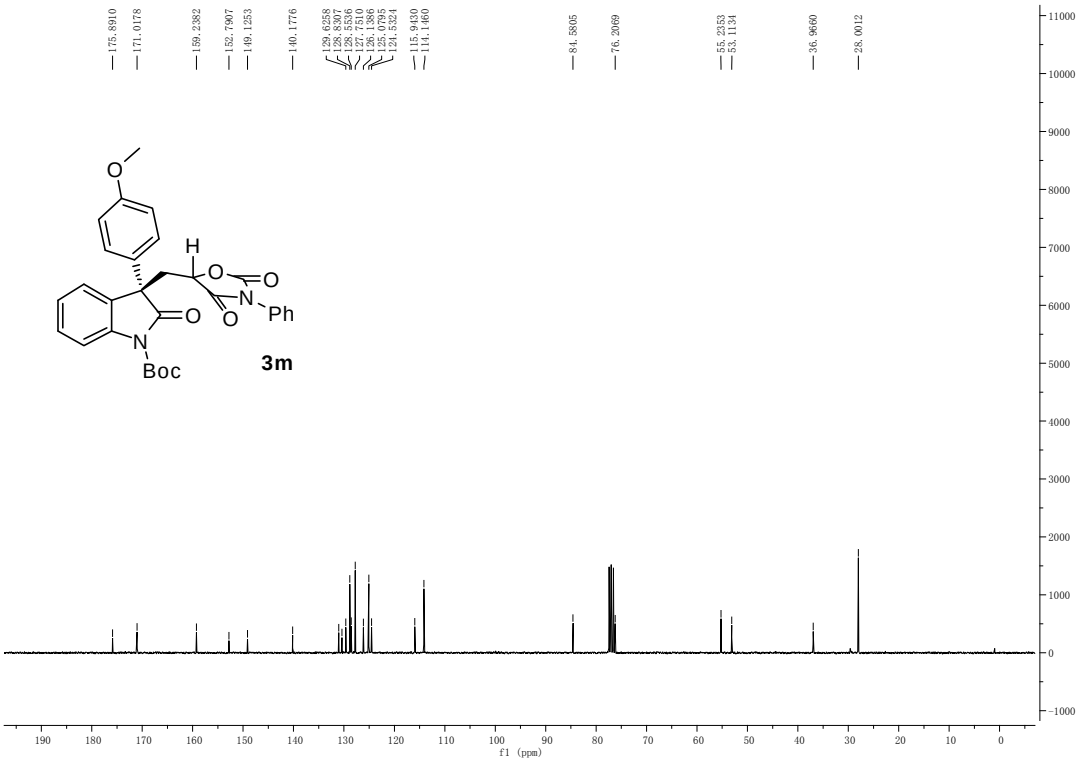
7.3672
7.3362
7.2847
7.2457
7.1988
7.1392
7.1094
6.8620
6.8513
6.8445
6.8281
6.8214
6.8105
4.9782
4.9664
4.9566
4.9438
3.7664
3.5531
3.5283
3.5035
3.4807
3.0342
3.0213
2.9845
2.9717
1.6446
O
H
O
O
N
Ph
O
O
N
Boc
3m
1.01
4.11
1.12
2.14
2.25
2.03
1.00
3.01
1.01
1.00
9.19
f1 (ppm)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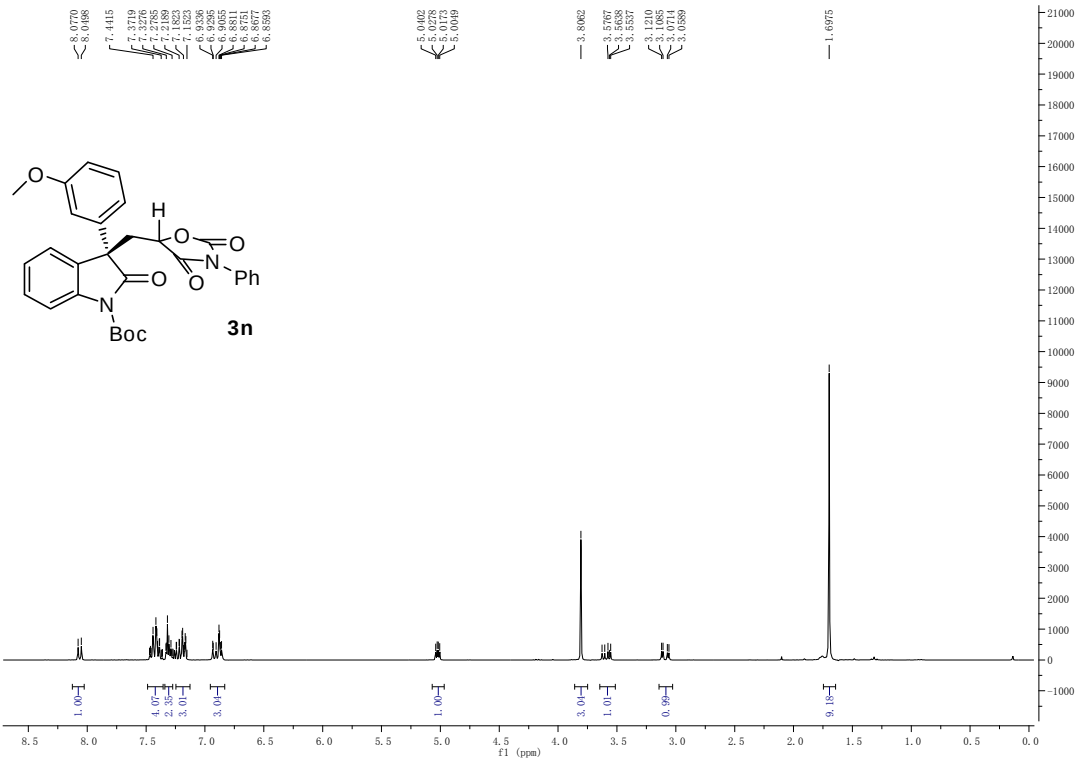
171.0178
159.2382
152.7907
149.1253
140.1776
129.6258
128.8307
128.5536
127.7510
126.1966
125.0795
124.5324
115.9430
114.1460
84.5805
76.2069
55.2253
53.1134
36.9660
28.0012
O
H
O
O
N
Ph
O
O
N
Boc
3m
f1 (ppm)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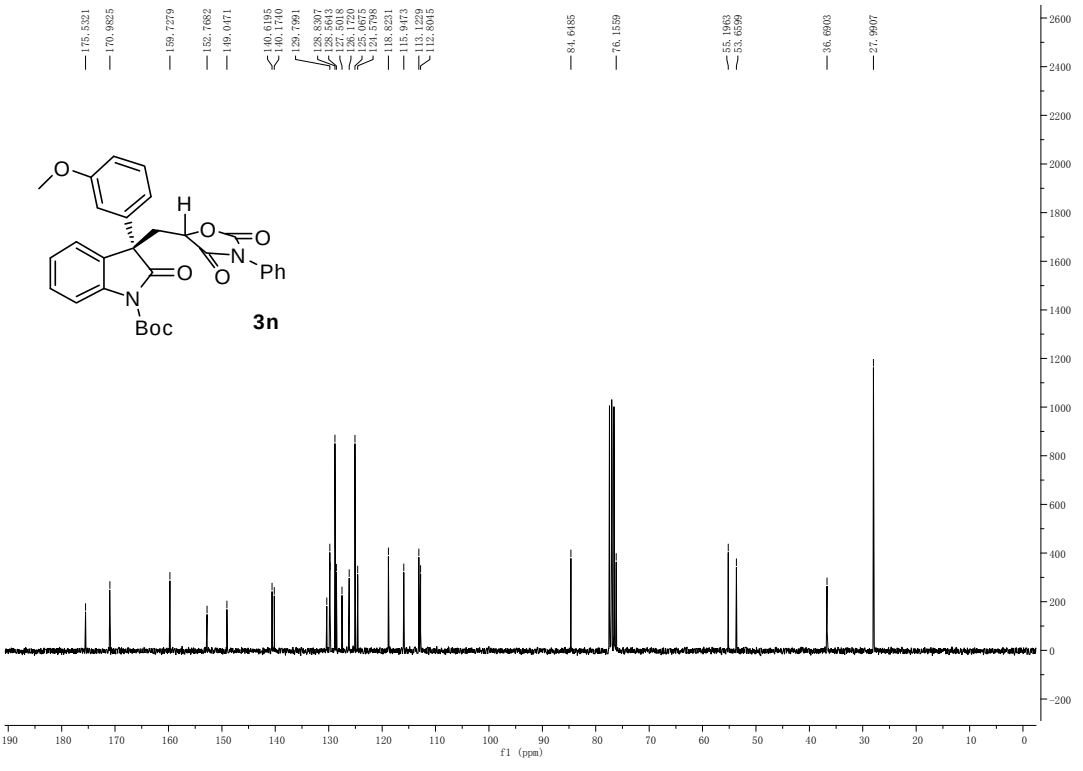
8.0498
7.4415
7.3719
7.3276
7.2785
7.2189
7.1823
7.1523
6.9336
6.9295
6.9055
6.8811
6.8571
6.8477
6.8393
5.0402
5.0278
5.0173
5.0049
3.8062
3.5767
3.5638
3.5537
3.1210
3.1085
3.0714
3.0389
1.6975
1.00
4.07
2.35
3.01
3.04
1.00
3.04
1.01
0.99
9.18
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3n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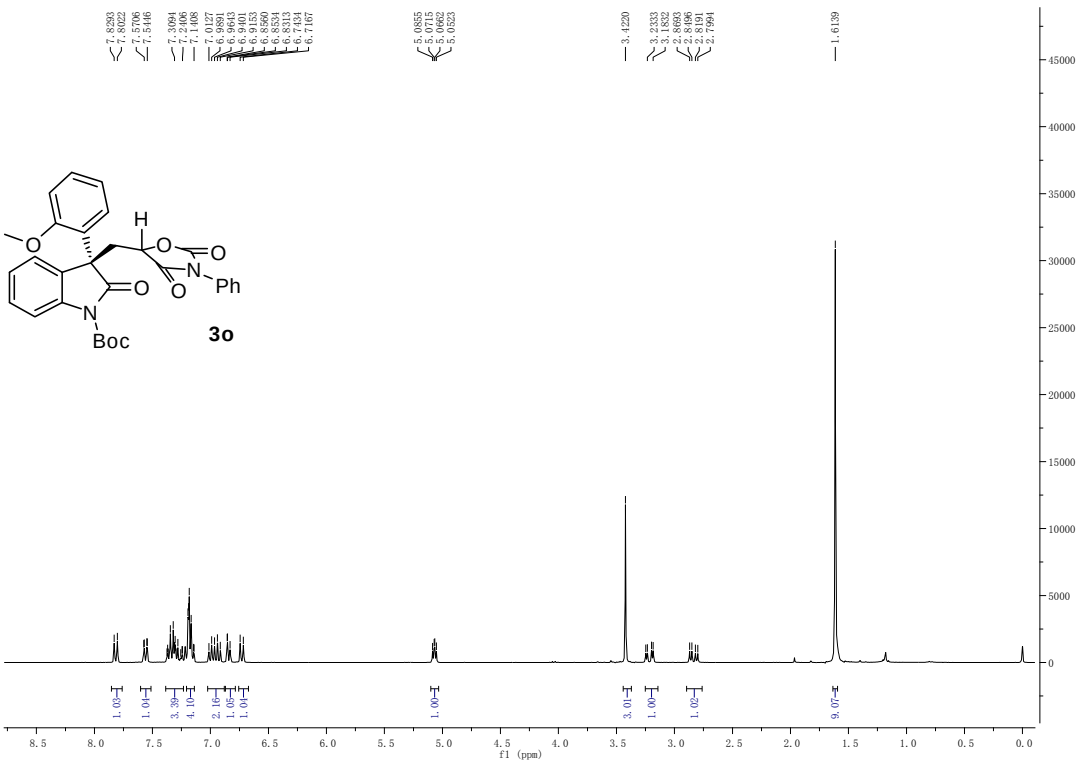
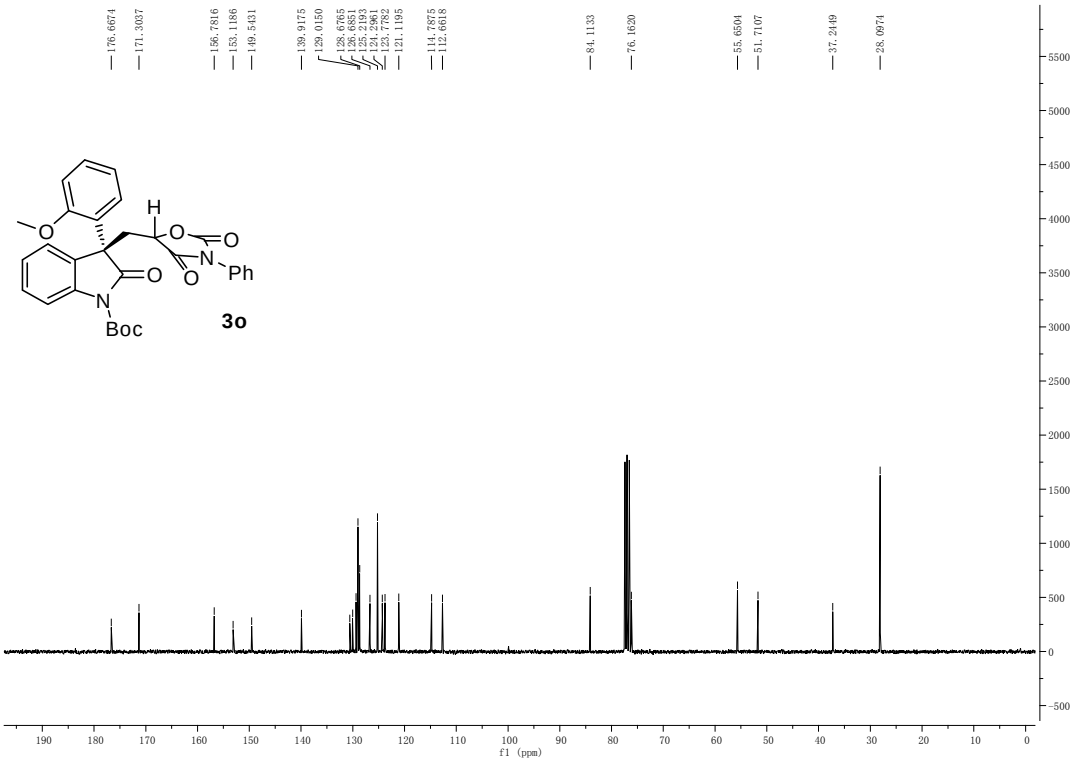
159.7279
152.7682
149.0471
140.6195
140.1740
129.7991
128.8307
128.5643
127.5018
126.1720
125.0675
124.5798
118.8231
115.9473
113.1229
112.8045
84.6485
76.1559
55.1963
53.6599
36.6903
27.9907
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3n


7.8293
7.8022
7.5706
7.5446
7.3094
7.2406
7.1408
7.0127
6.9891
6.9603
6.9401
6.9153
6.8560
6.8534
6.8313
6.7434
6.7167
5.0855
5.0715
5.0662
5.0525
3.4220
3.2333
3.1832
2.8963
2.8496
2.8191
2.7994
1.6139
1.03
1.01
3.39
4.10
2.16
1.05
1.04
1.00
3.01
1.00
1.02
9.07
f1 (ppm)
3o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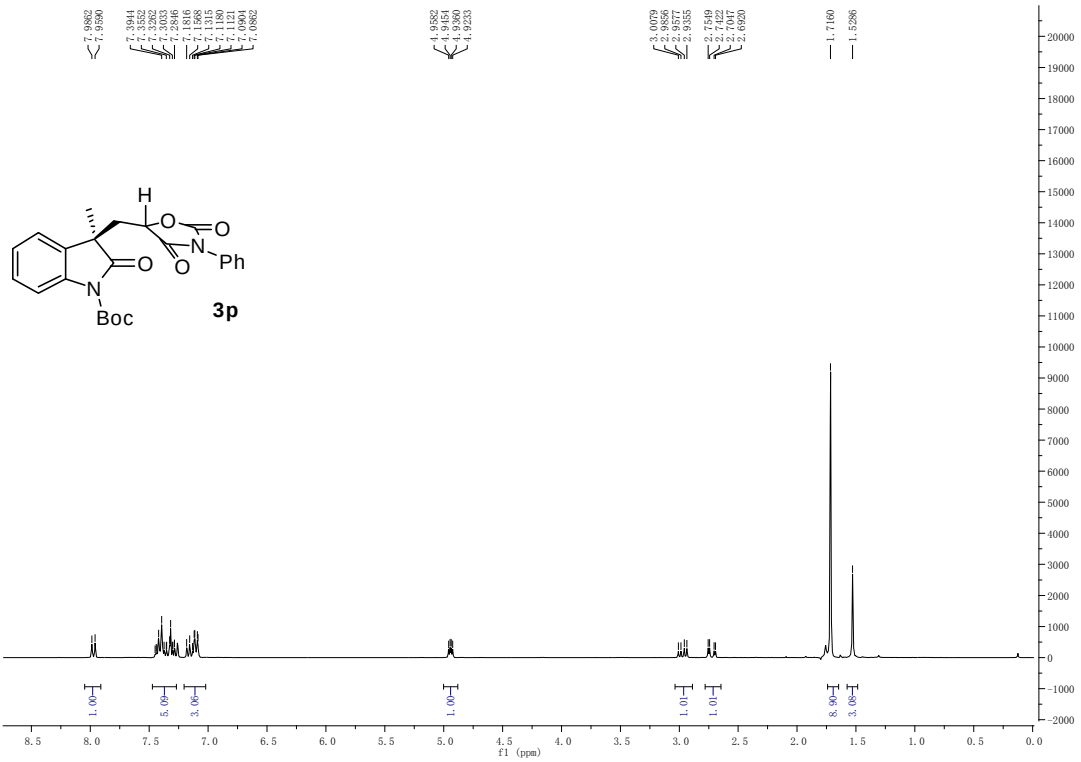
171.3037
156.7816
153.1186
149.5431
139.9175
129.0150
128.6765
126.6851
125.2193
124.2961
123.7782
121.1195
114.7875
112.6618
84.1133
76.1620
55.6504
51.7107
37.2449
28.0974
f1 (ppm)
3o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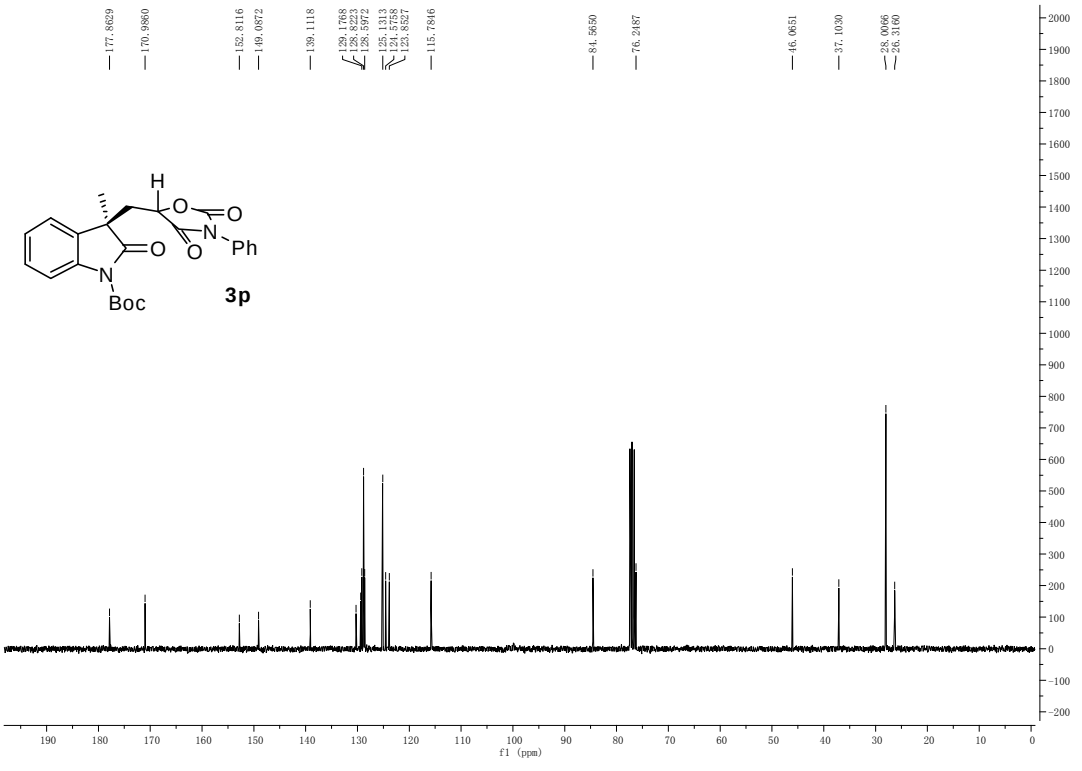
7.9790
7.3944
7.3552
7.3362
7.3033
7.2846
7.2645
7.1968
7.1315
7.1180
7.1021
7.0844
7.0862
4.9582
4.9454
4.9360
4.9253
3.0079
2.9836
2.9577
2.9355
2.7549
2.7472
2.7047
2.6920
1.7160
1.5286
H
O
O
N
Ph
O
O
N
Boc
3p
1.00
5.09
3.06
1.00
1.01
1.01
8.90
3.08
f1 (ppm)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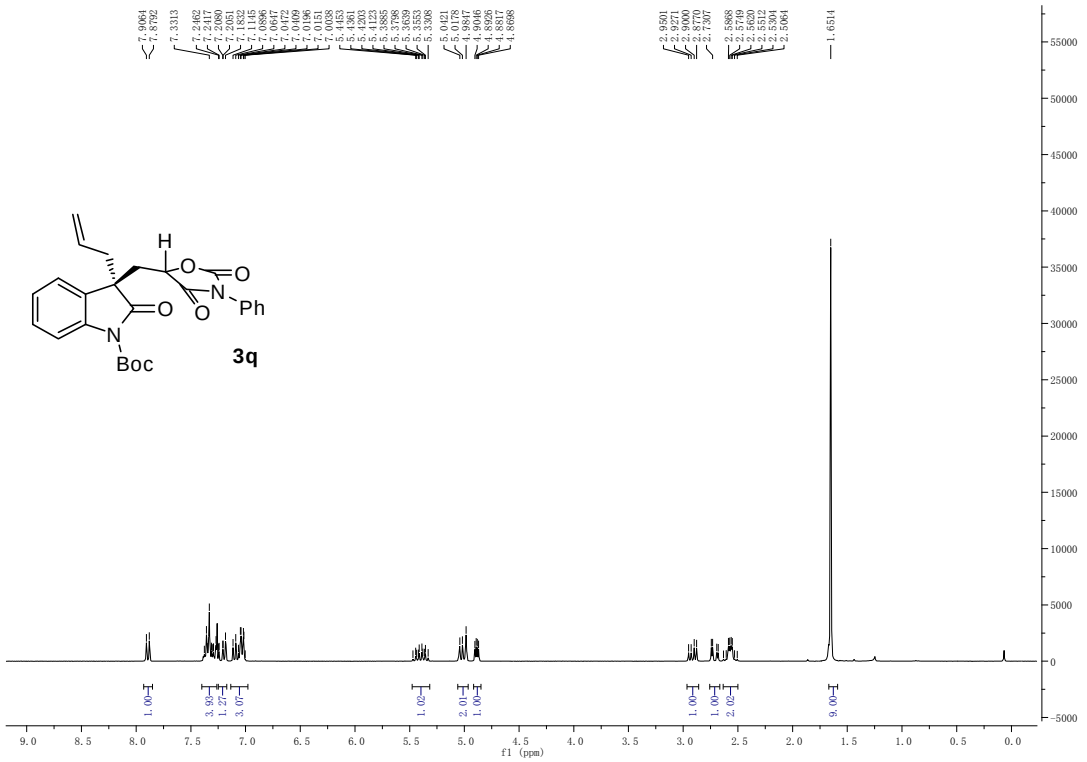
149.0872
139.1118
130.1768
128.8223
128.5972
125.1313
124.5758
123.8527
115.7846
84.5650
76.2487
46.0651
37.1030
28.0066
26.3160
H
O
O
N
Ph
O
O
N
Boc
3p
f1 (ppm)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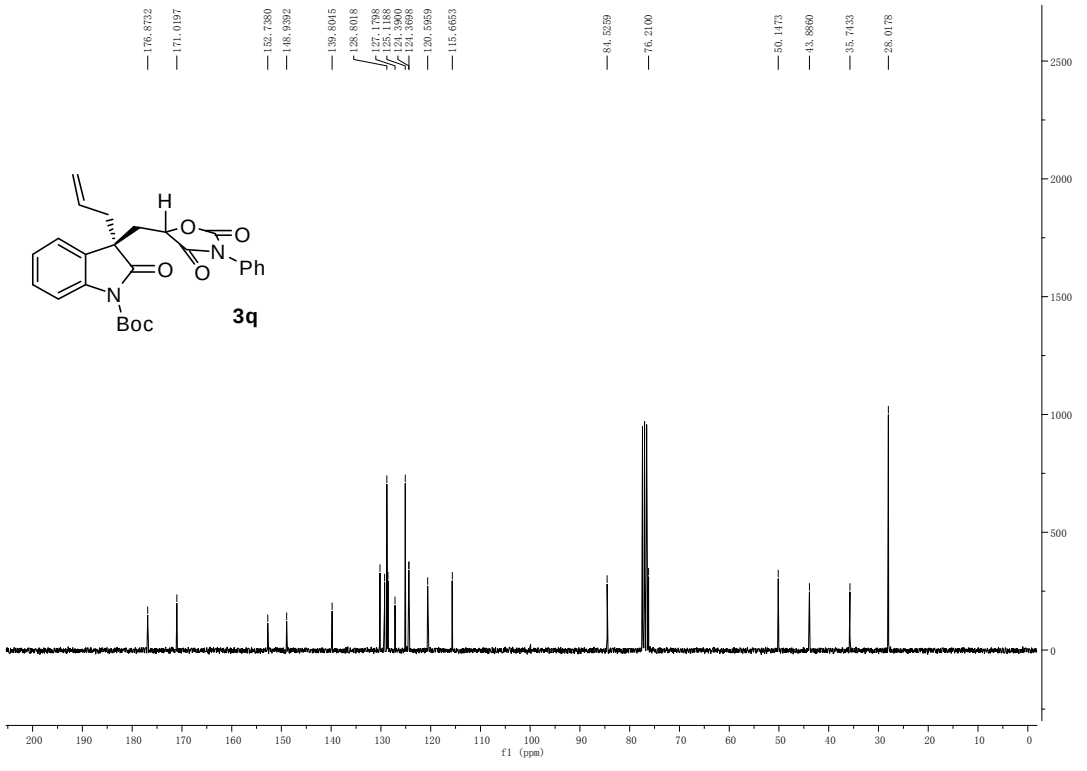
7.2462
7.2417
7.2360
7.2051
7.1832
7.1145
7.0896
7.0647
7.0472
7.0409
7.0196
7.0151
7.0098
5.4453
5.4361
5.4203
5.4123
5.3855
5.3798
5.3639
5.3553
5.3398
5.0121
5.0078
4.9947
4.9046
4.8926
4.8817
4.8698
2.9501
2.9271
2.9000
2.8770
2.7897
2.5888
2.5749
2.5620
2.5512
2.5304
2.5064
1.6514
1.00
3.89
1.27
3.07
1.02
2.01
1.00
1.00
1.00
2.02
9.00
f1 (ppm)
H
O
O
N
Ph
O
O
N
Boc
3q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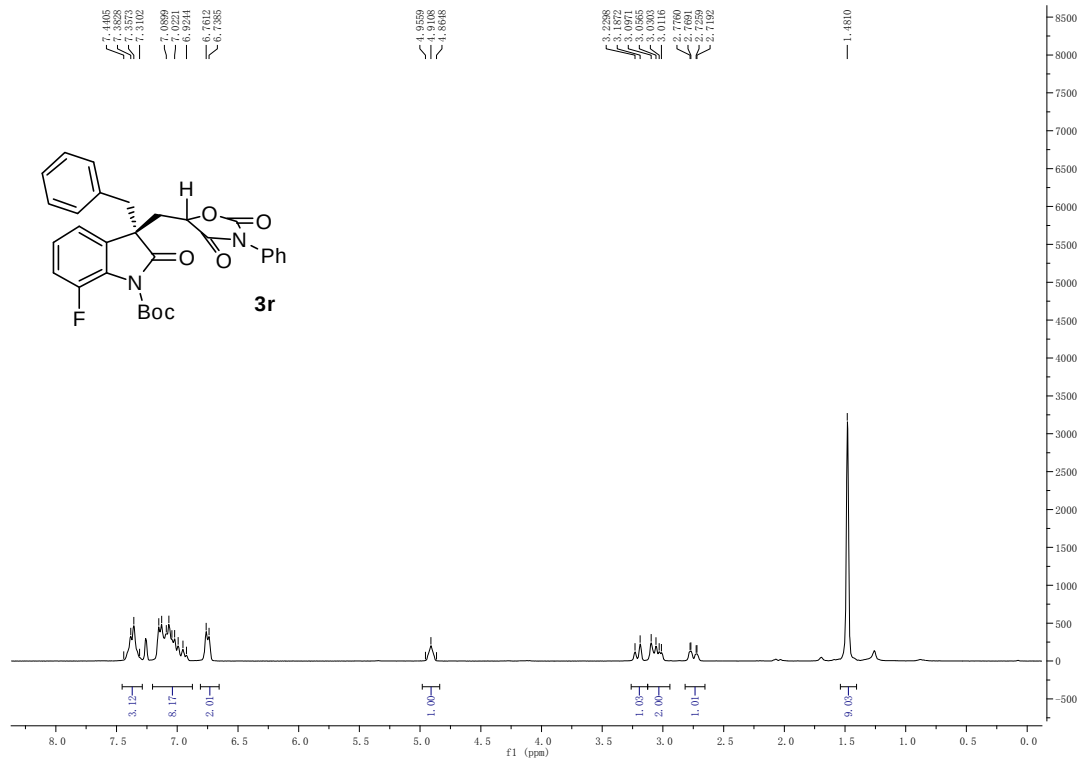
148.9392
139.8045
128.8018
127.1798
125.1498
121.3980
121.3698
120.5959
115.6653
84.5259
76.2100
50.1473
43.8860
35.7433
28.0178
f1 (ppm)
H
O
O
N
Ph
O
O
N
Boc
3q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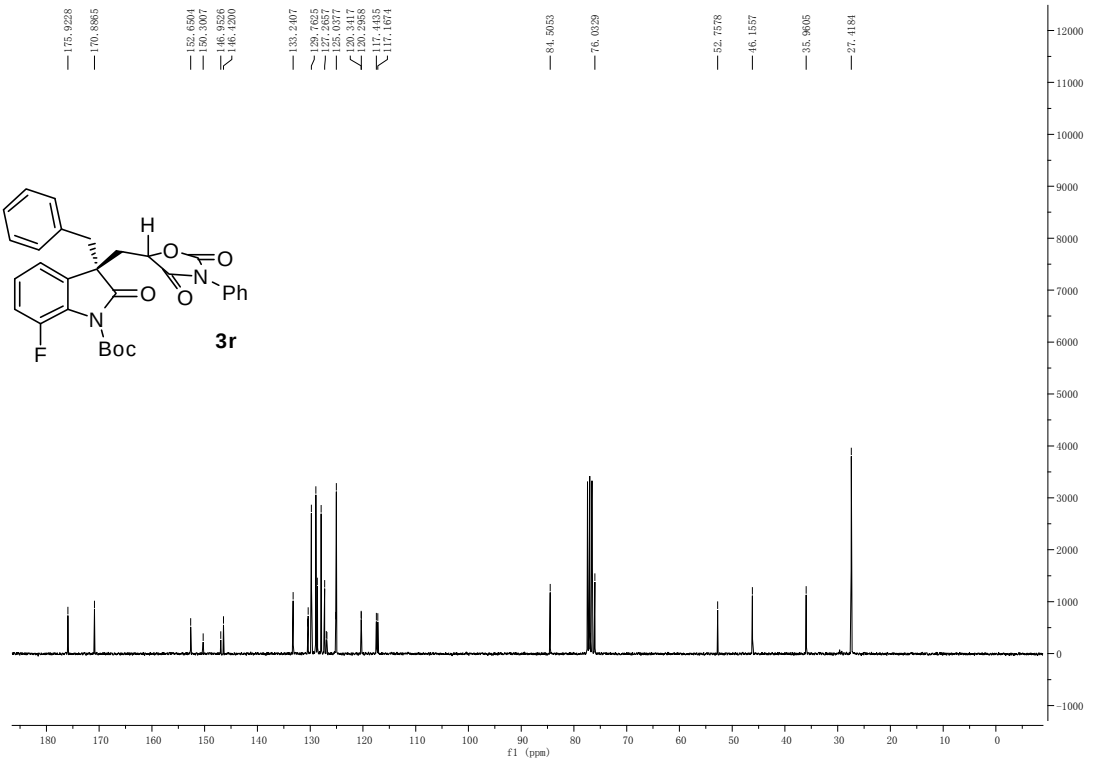
7.3573
7.3102
7.0899
7.0221
6.9244
6.7612
6.7385
4.9559
4.9108
4.8648
3.2298
3.1872
3.0971
3.0965
3.0303
3.0116
2.7760
2.7691
2.7239
2.7192
1.4810
3.12
8.17
2.01
1.00
1.03
2.00
1.01
9.03
f1 (ppm)

H
O
O
N
Ph
O
O
N
Boc
F

3r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133.2407
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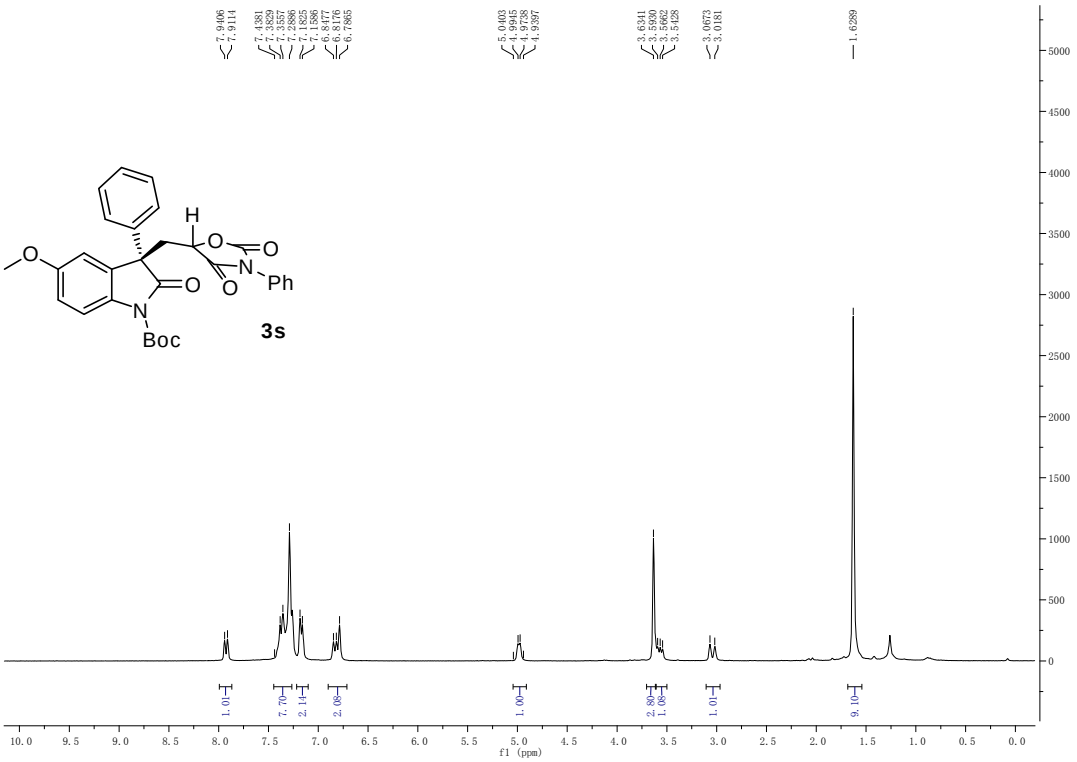
127.2657
125.0377
120.3417
120.2958
117.4435
117.1674
84.5053
76.0329
52.7578
46.1557
35.9605
27.4184
f1 (ppm)

H
O
O
N
Ph
O
O
N
Boc
F

3r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7.1598
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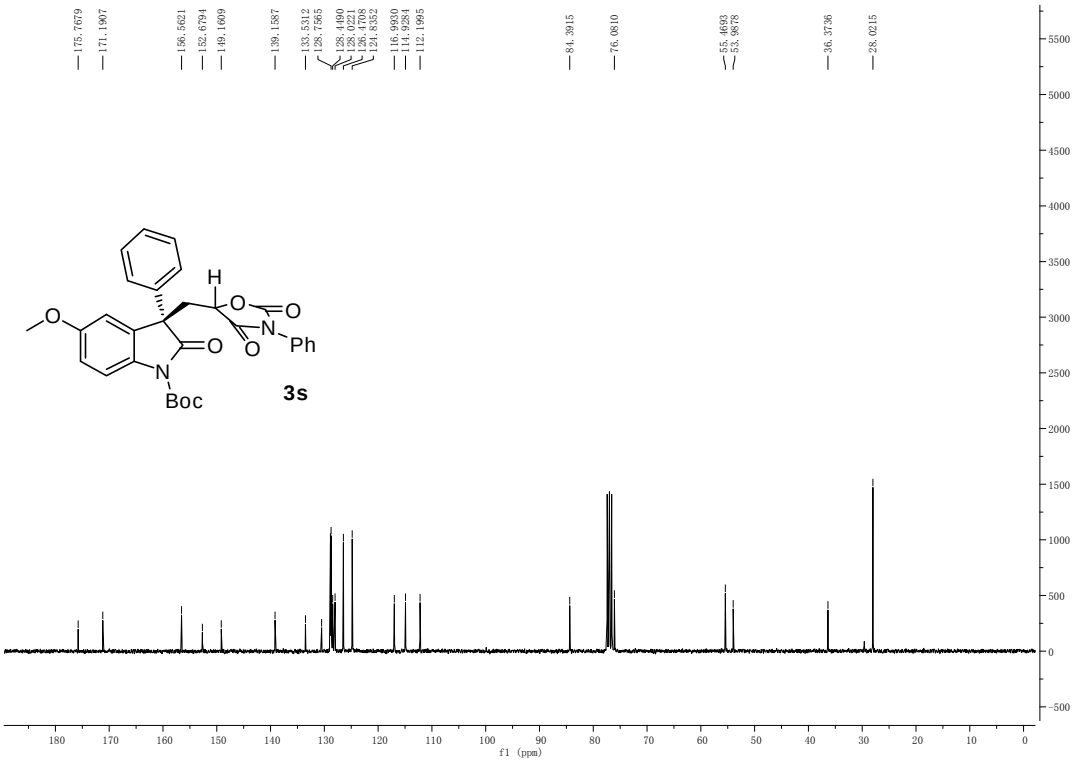
6.8176
6.7865
5.0403
4.9945
4.9738
4.9397
3.6341
3.5950
3.5682
3.5428
3.0673
3.0181
1.6289
1.01
7.70
2.14
2.08
1.00
2.08
1.08
1.01
9.10
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3s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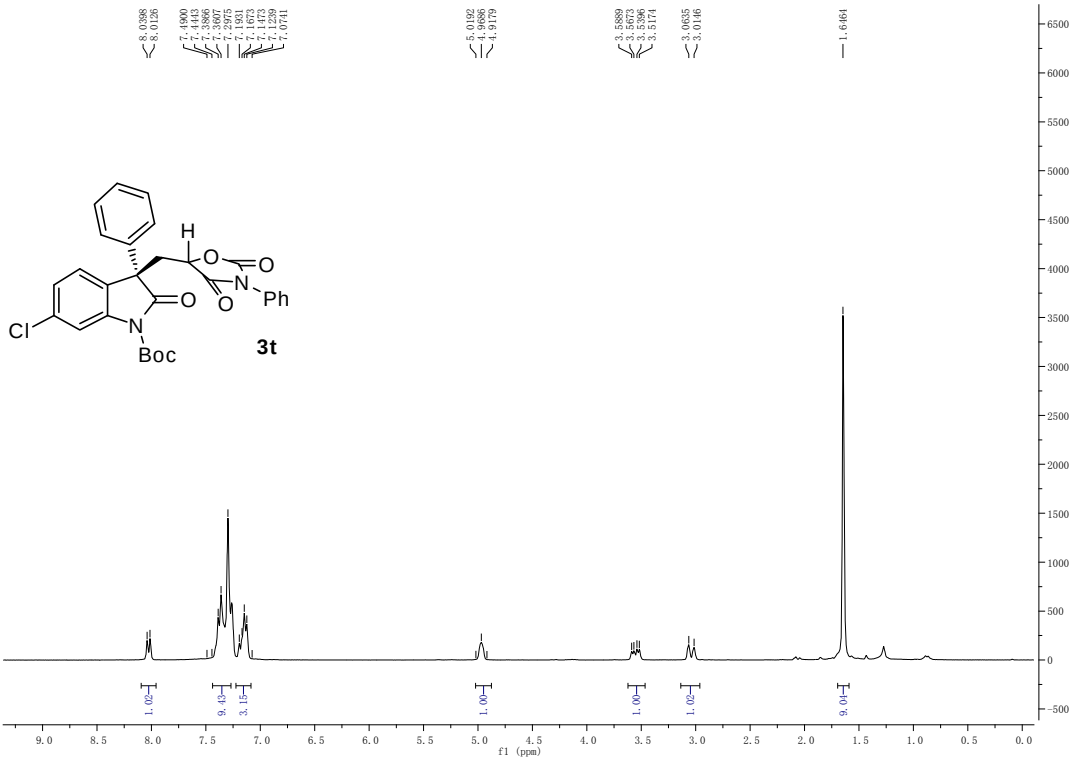
128.4490
128.0221
126.4708
121.8352
116.9930
114.9284
112.1995
84.3915
76.0810
55.4693
53.9878
36.3736
28.0215
f1 (ppm)
O
H
O
O
N
Ph
O
O
N
Boc
3s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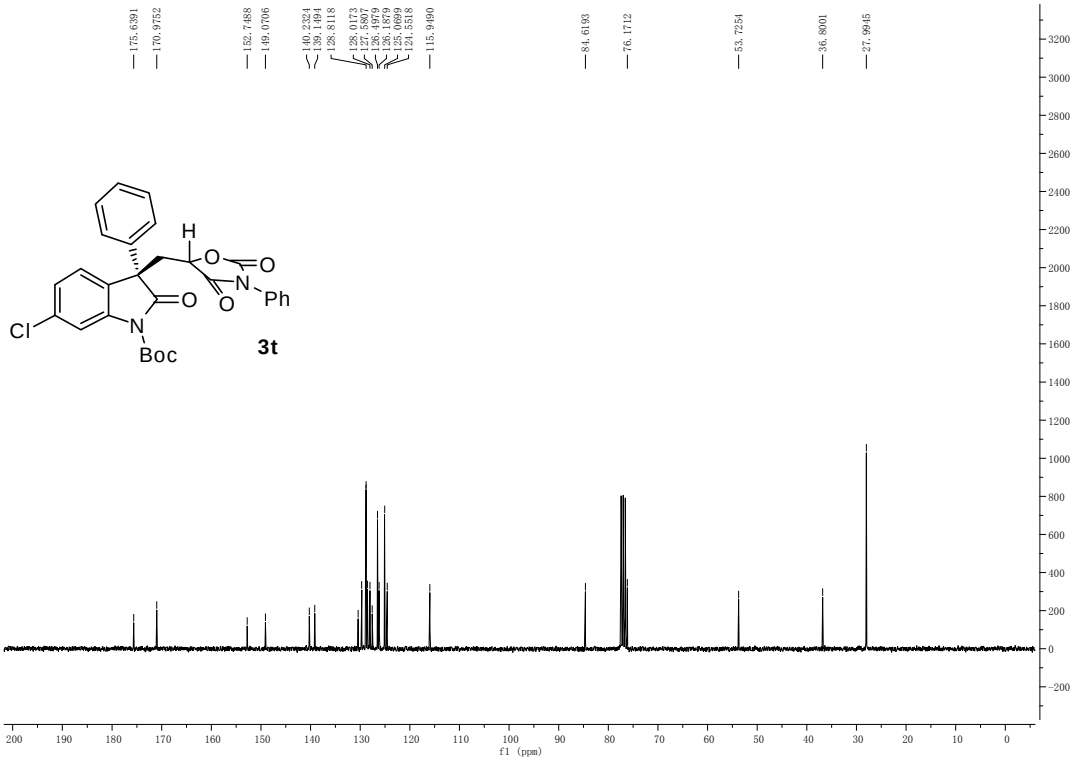
7.2975
7.1931
7.1673
7.1473
7.1239
7.0741
5.0192
4.9956
4.9179
3.5889
3.5673
3.5396
3.5174
3.0635
3.0146
1.6464
1.02
9.43
3.15
1.00
1.00
1.02
9.01
f1 (ppm)
H
O
O
N
Ph
O
O
O
Cl
N
Boc
3t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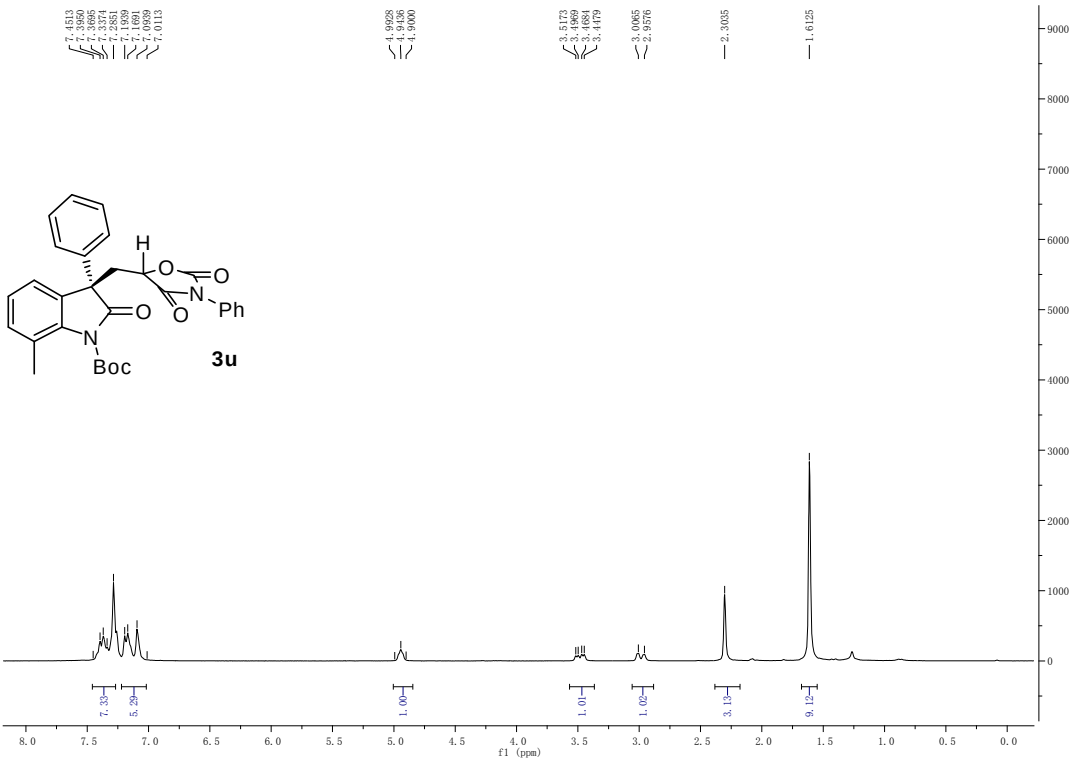
126.1879
125.0680
124.5518
115.9490
84.6193
76.1712
53.7254
36.8001
27.9945
f1 (ppm)
H
O
O
N
Ph
O
O
O
Cl
N
Boc
3t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7.3574
7.2851
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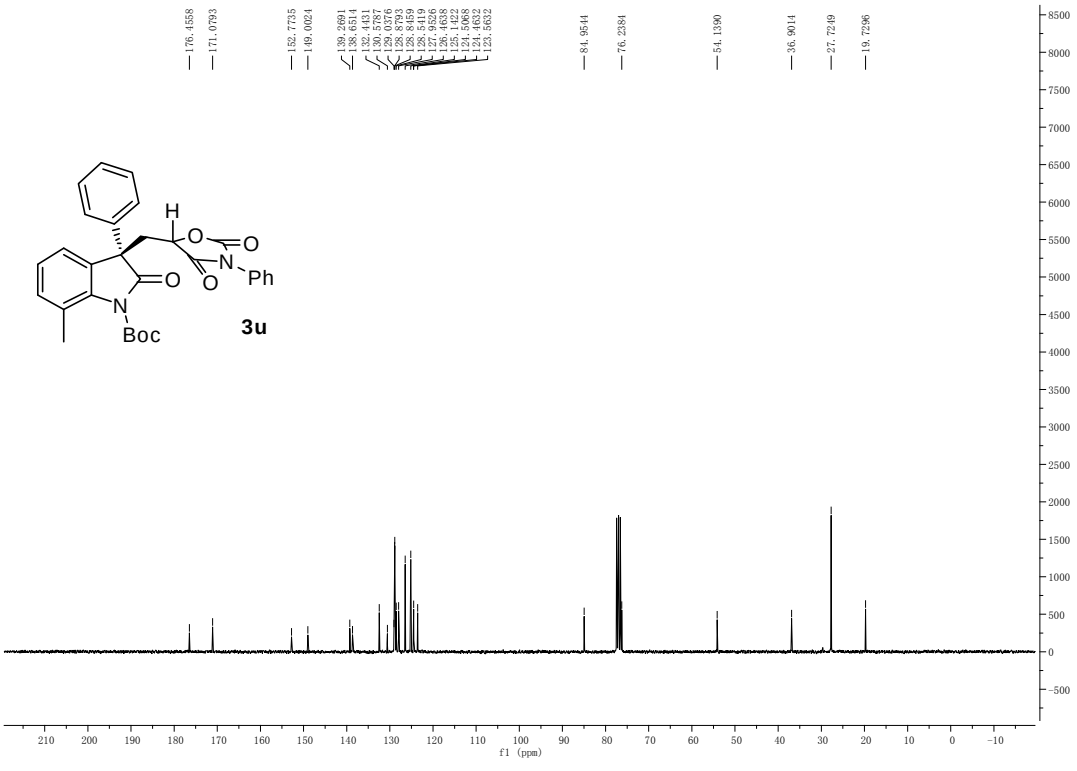
7.1691
7.0939
7.0113
4.9928
4.9436
4.9000
3.5173
3.4969
3.4684
3.4479
3.0065
2.9576
2.3035
1.6125
3u
7.33
5.29
1.00
1.01
1.02
3.13
9.12
f1 (ppm)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128.5419
127.9526
126.4638
125.1472
121.5066
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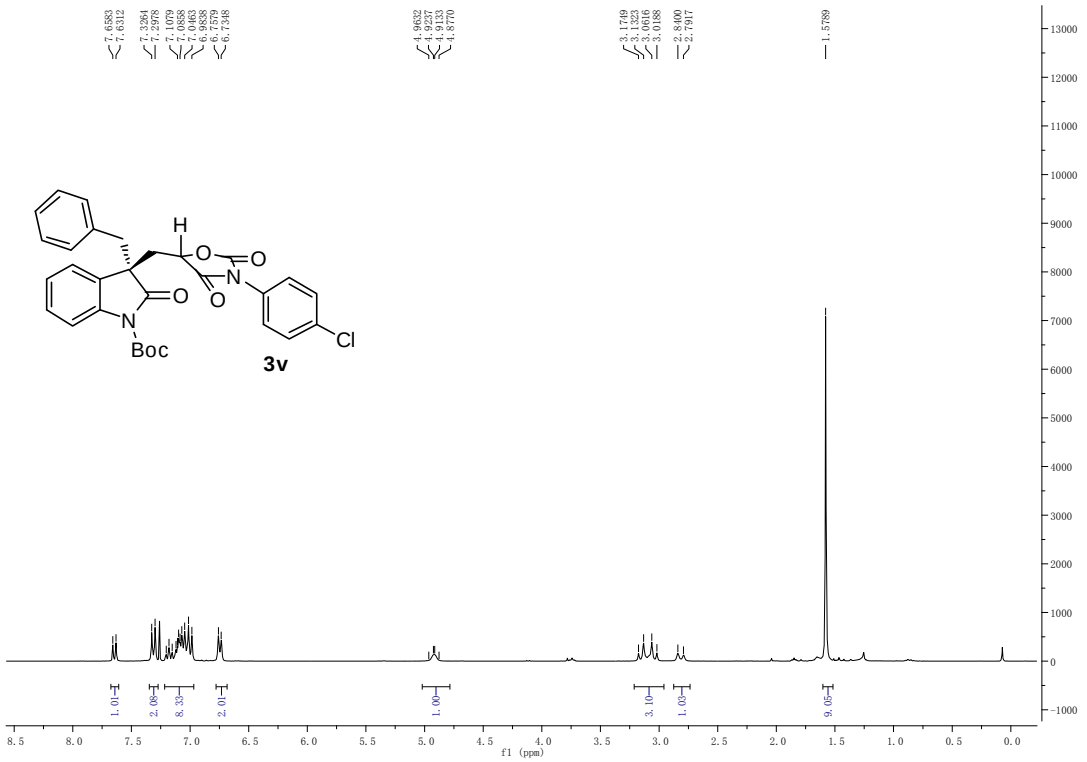
84.9544
76.2384
54.1390
36.9014
27.7249
19.7296
3u
f1 (ppm)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7.1079
7.0888
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6.7579
6.7348
4.9632
4.9327
4.9133
4.8770
3.1749
3.1323
3.0616
3.0188
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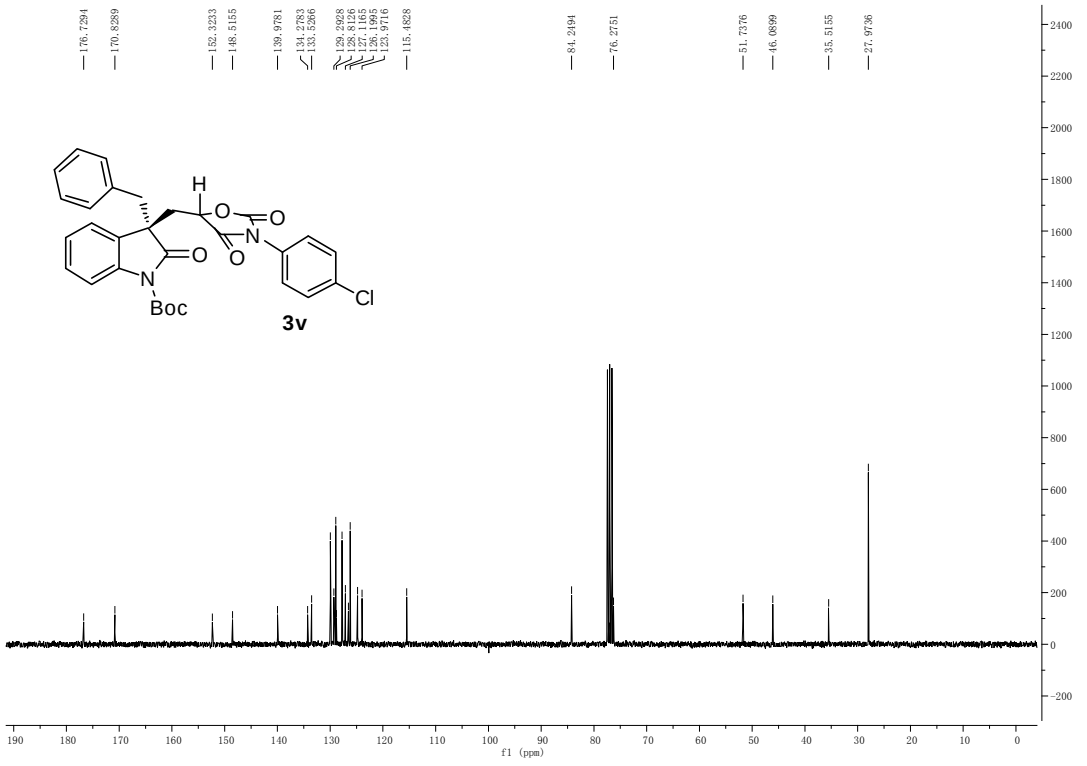
2.7917
1.5789
H
O
O
O
N
O
O
N
Boc
Cl
3v
f1 (ppm)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133.5266
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128.8126
127.1165
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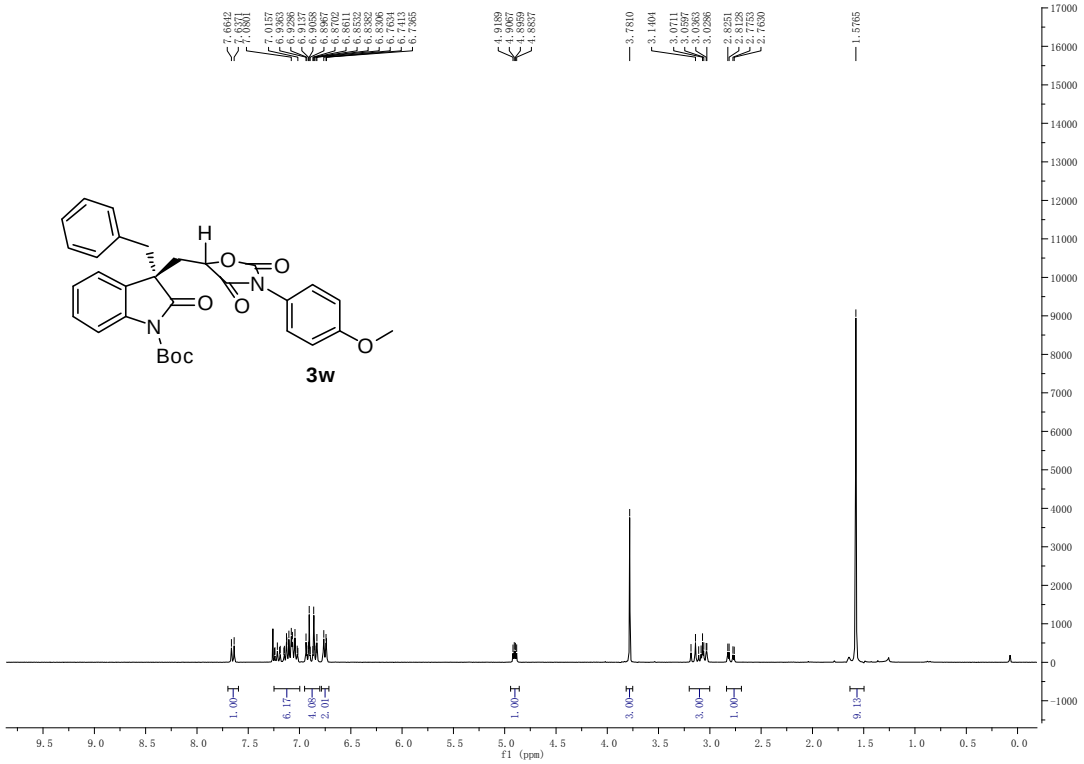
115.4828
84.2494
76.2751
51.7376
46.0899
35.5155
27.9736
H
O
O
O
N
O
O
N
Boc
Cl
3v
f1 (ppm)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6.8611
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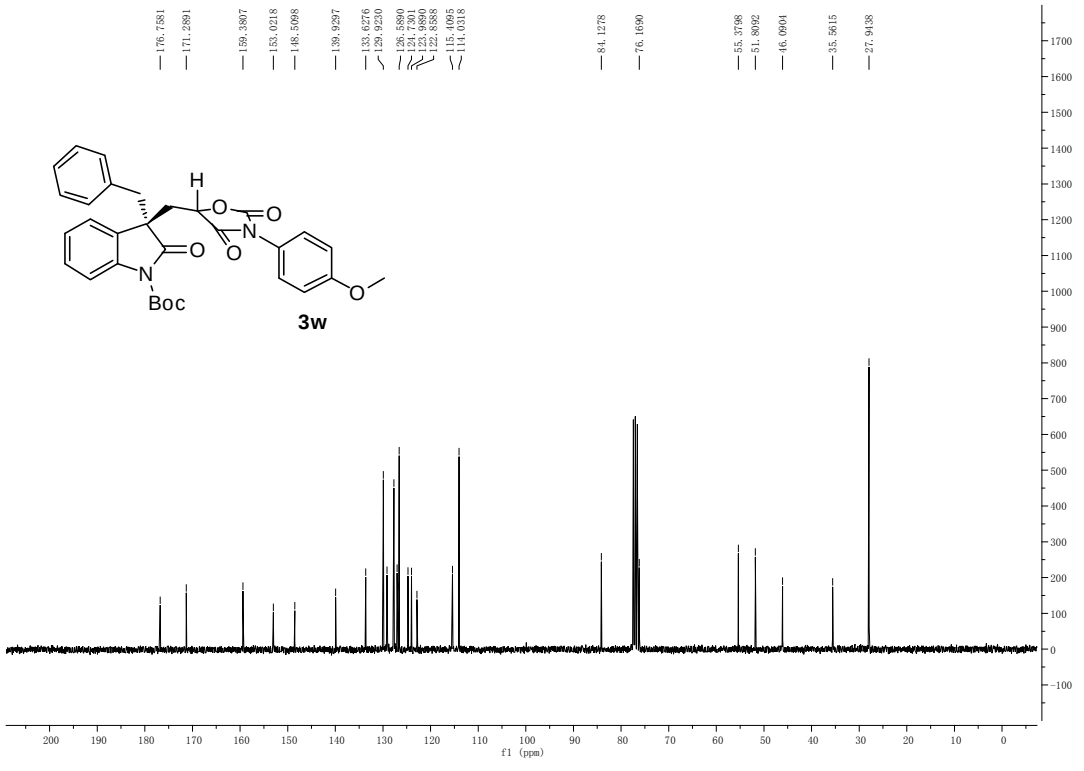
6.8306
6.7634
6.7413
6.7365
4.9189
4.9067
4.8959
4.8837
3.7810
3.1404
3.0711
3.0597
3.0383
3.0286
2.8251
2.8128
2.7753
2.7639
1.5765
1.00
6.17
4.08
2.01
1.00
3.00
3.00
1.00
9.13
f1 (ppm)
H
O
O
N
O
O
O
N
Boc
O
3w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139.9297
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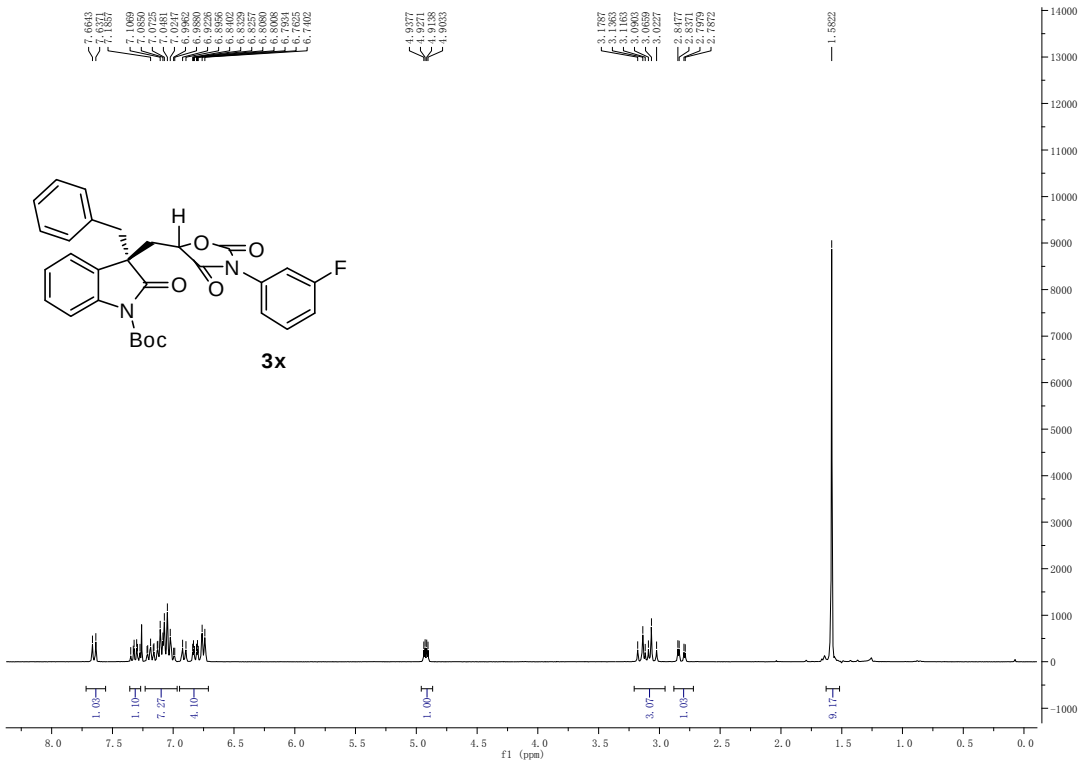
123.9890
122.8588
115.4095
114.0318
84.1278
76.1690
55.3798
51.8092
46.0904
35.5615
27.9438
f1 (ppm)
H
O
O
N
O
O
O
N
Boc
O
3w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7.0481
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6.9226
6.8956
6.8802
6.8329
6.8257
6.8080
6.8008
6.7934
6.7625
6.7402
4.9377
4.9271
4.9138
4.9033
3.1787
3.1363
3.1163
3.0903
3.0659
3.0227
2.8477
2.8371
2.7979
2.7872
1.5822
1.03
1.10
7.27
4.10
1.00
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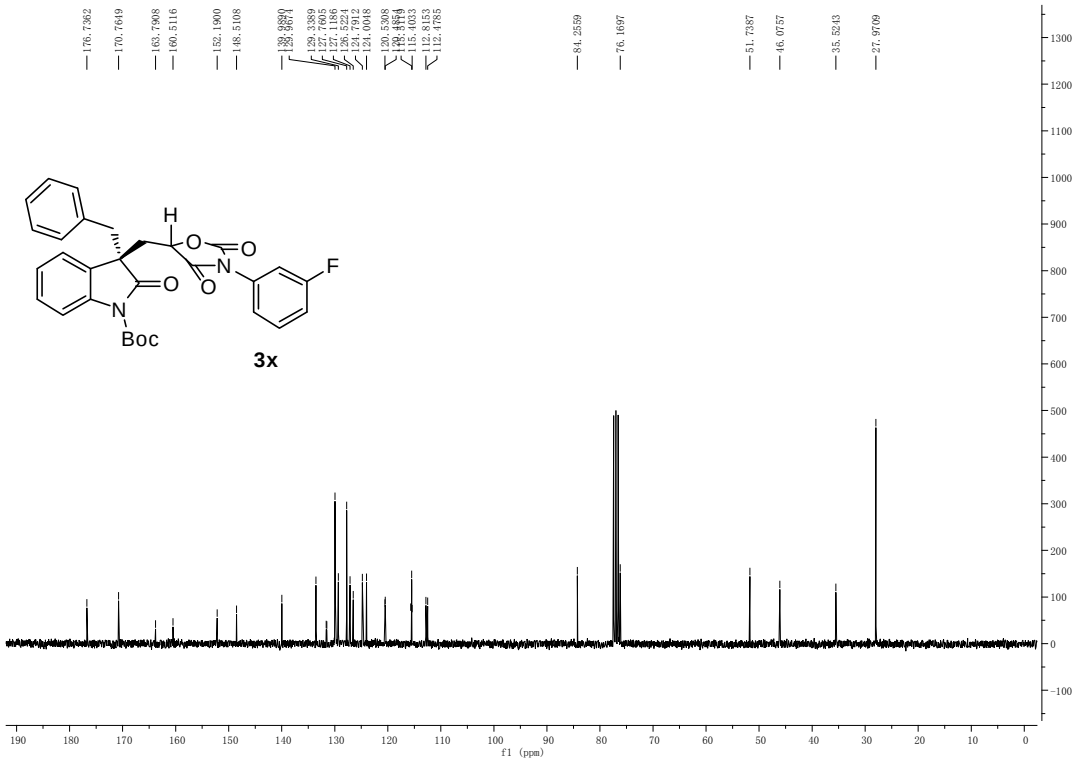
1.03
9.17
f1 (ppm)
H
O
O
N
O
O
F
O
N
Boc

3x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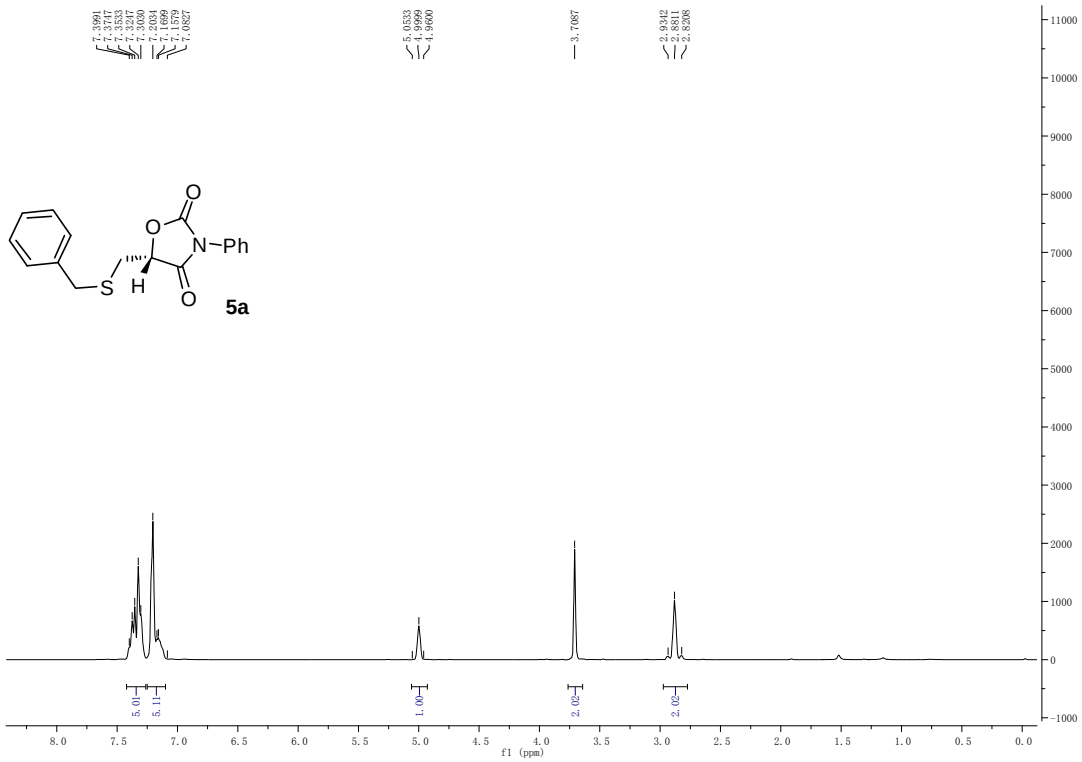
129.3389
127.7605
127.1186
126.5724
124.7943
124.0048
120.5308
120.4864
115.4033
112.8153
112.4785
84.2559
76.1697
51.7387
46.0757
35.5243
27.9709
f1 (ppm)
H
O
O
N
O
O
F
O
N
Boc

3x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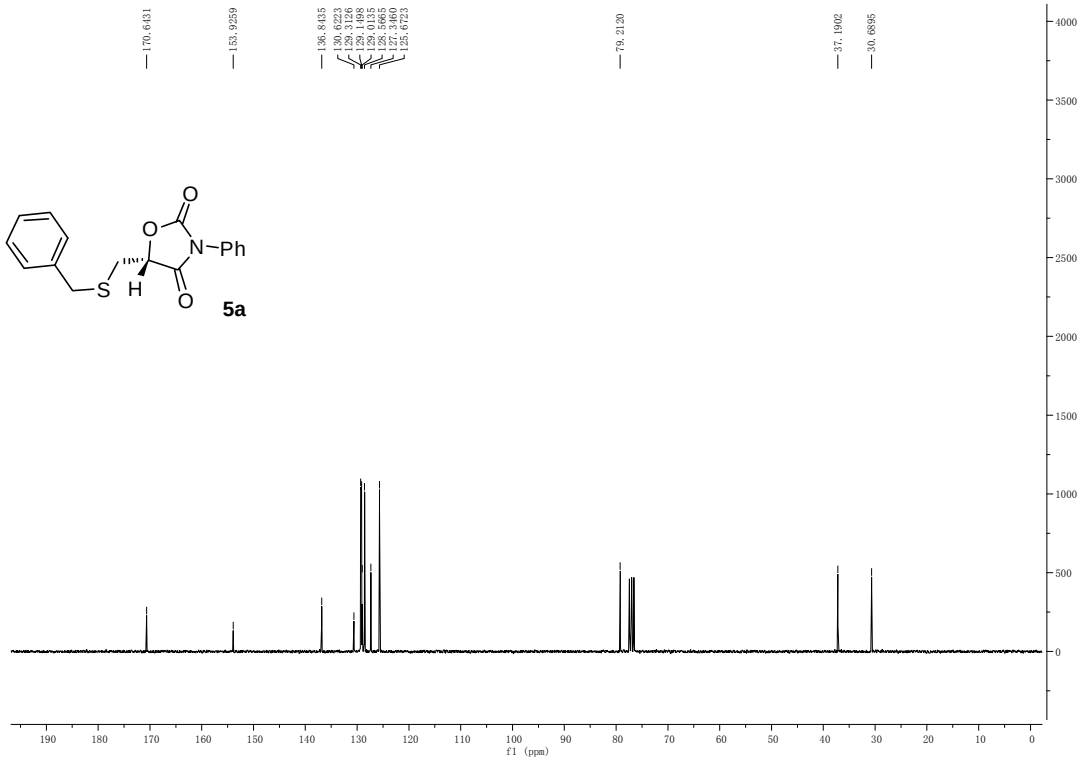
7.3030
7.2034
7.1699
7.1579
7.0827
5.0533
4.9999
4.9600
3.7087
2.9342
2.8811
2.8208
O
O
N–Ph
S
H
O
5a
5.01
5.11
1.00
2.02
2.02
f1 (ppm)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130.6223
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129.0135
128.5665
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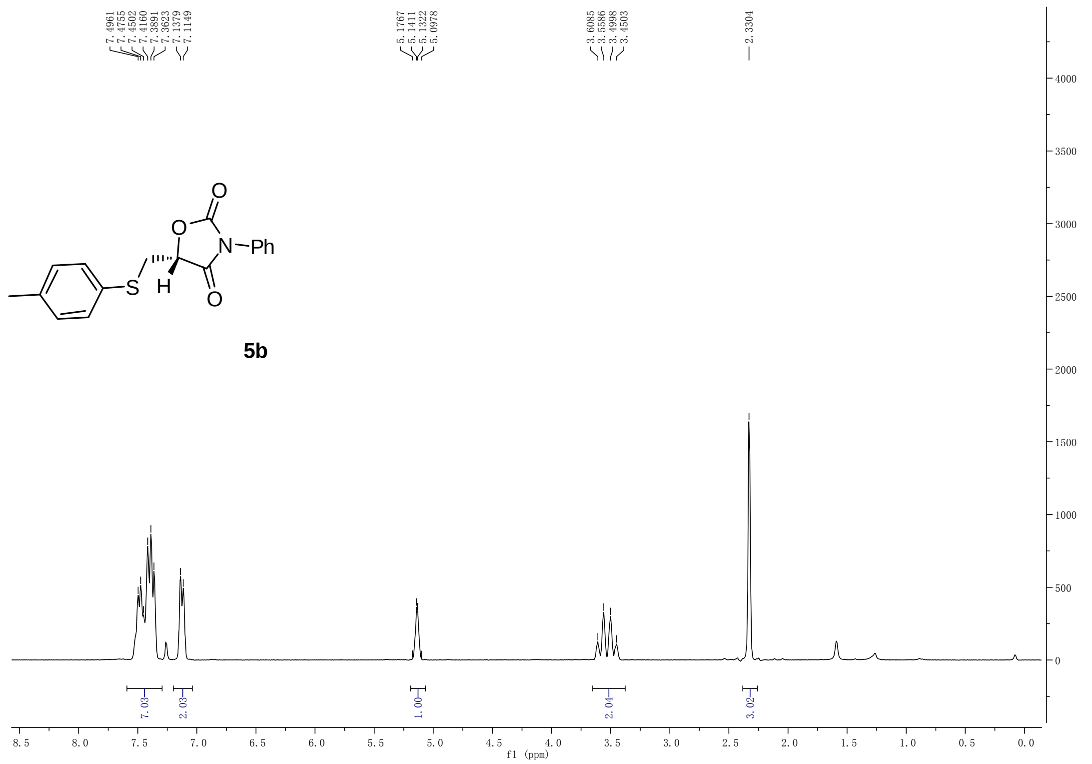
79.2120
37.1902
30.6895
O
O
N–Ph
S
H
O
5a
f1 (ppm)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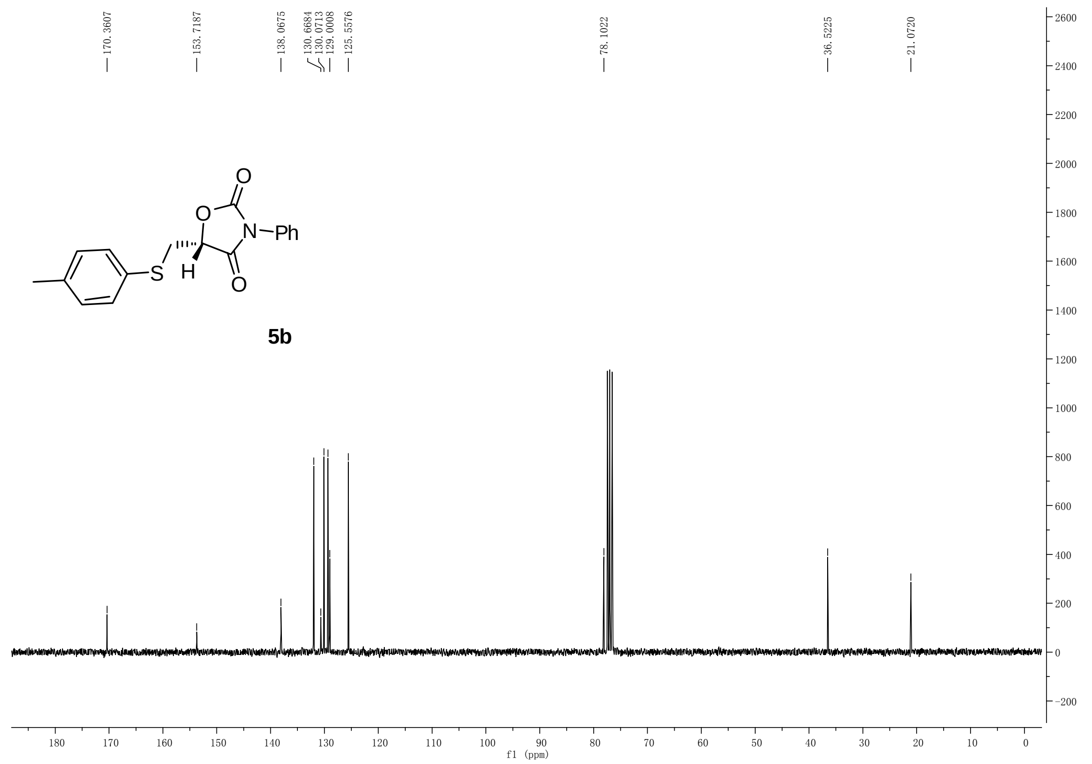
7.4502
7.4160
7.3891
7.3623
7.1379
7.1149
5.1767
5.1411
5.1322
5.0978
3.6085
3.5586
3.4998
3.4503
2.3304
O
O
N
Ph
S
H
O
5b
7.03
2.03
1.00
2.04
3.02
f1 (ppm)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138.0675
130.6684
130.0713
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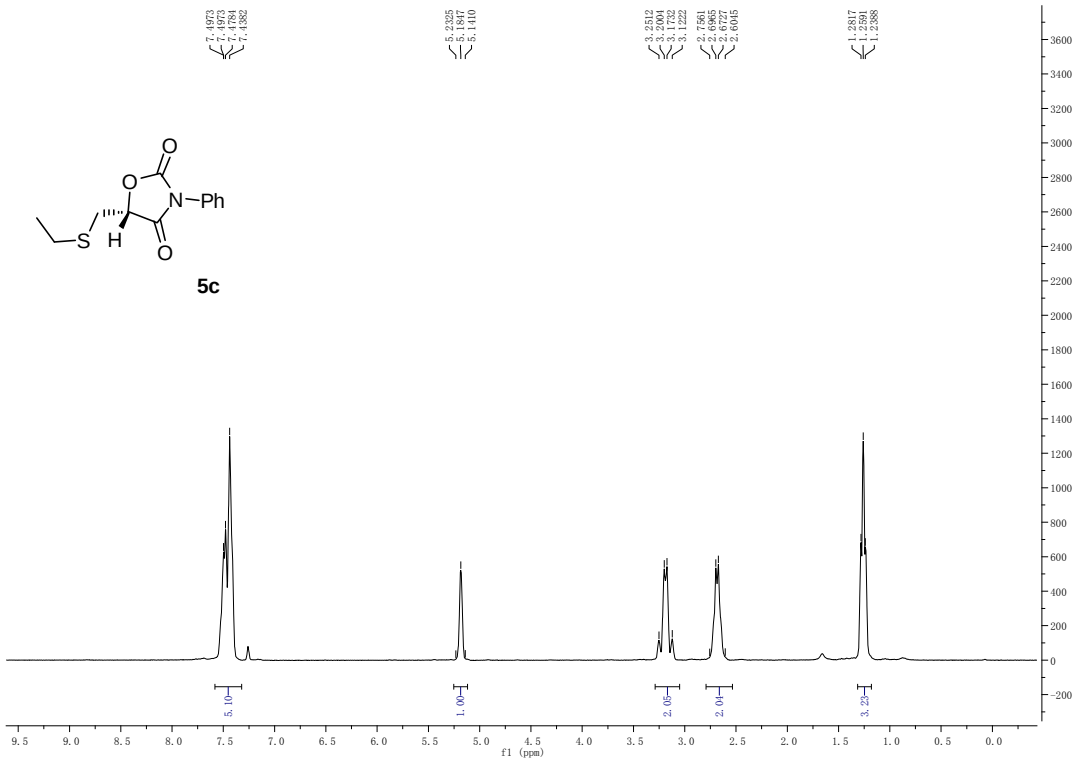
36.5225
21.0720
O
O
N
Ph
S
H
O
5b
f1 (ppm)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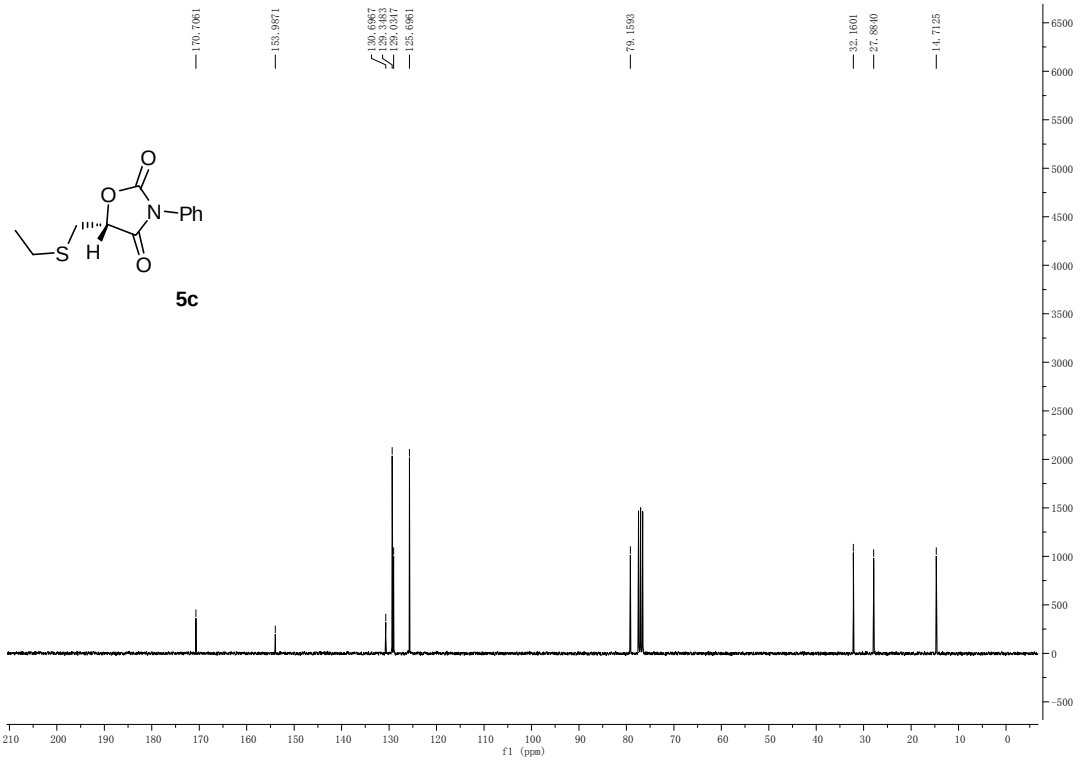
7.4784
7.4784
7.4382
5.2325
5.1847
5.1410
3.2512
3.2004
3.1732
3.1222
2.7561
2.6965
2.6727
2.6415
1.2817
1.2591
1.2391
1.2388
5.10
1.00
2.05
2.01
3.23
f1 (ppm)

5c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153.9871
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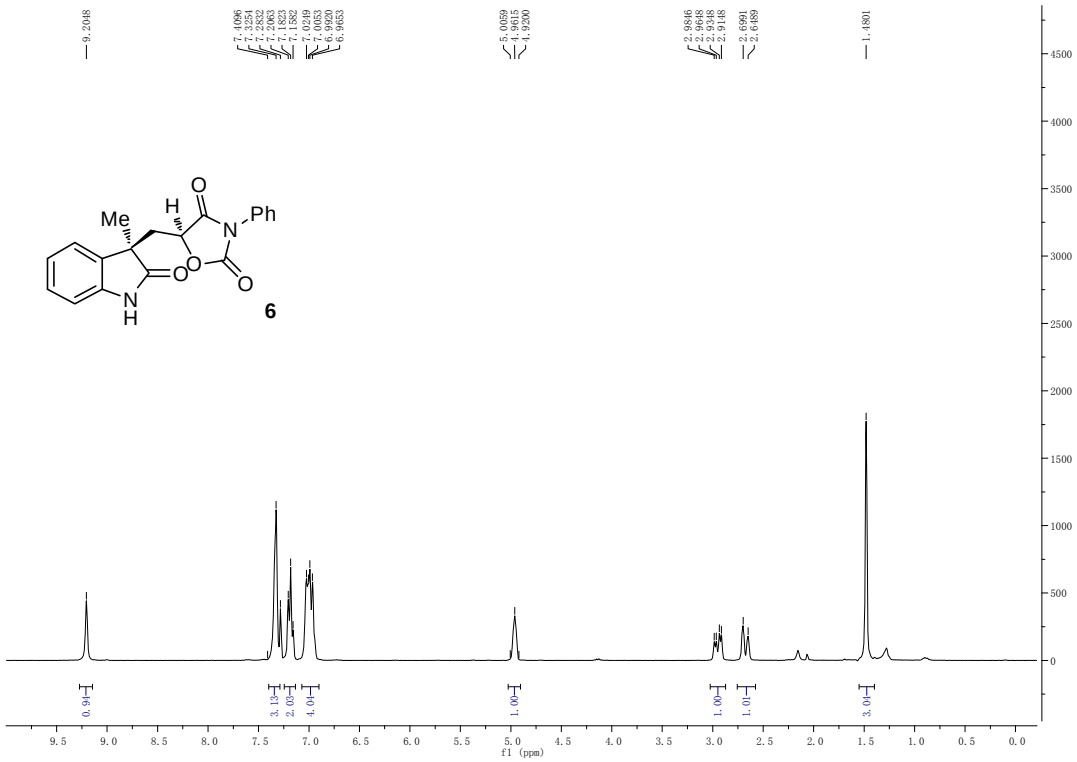
129.3483
129.0347
125.6961
79.1593
32.1601
27.8840
14.7125
f1 (ppm)

5c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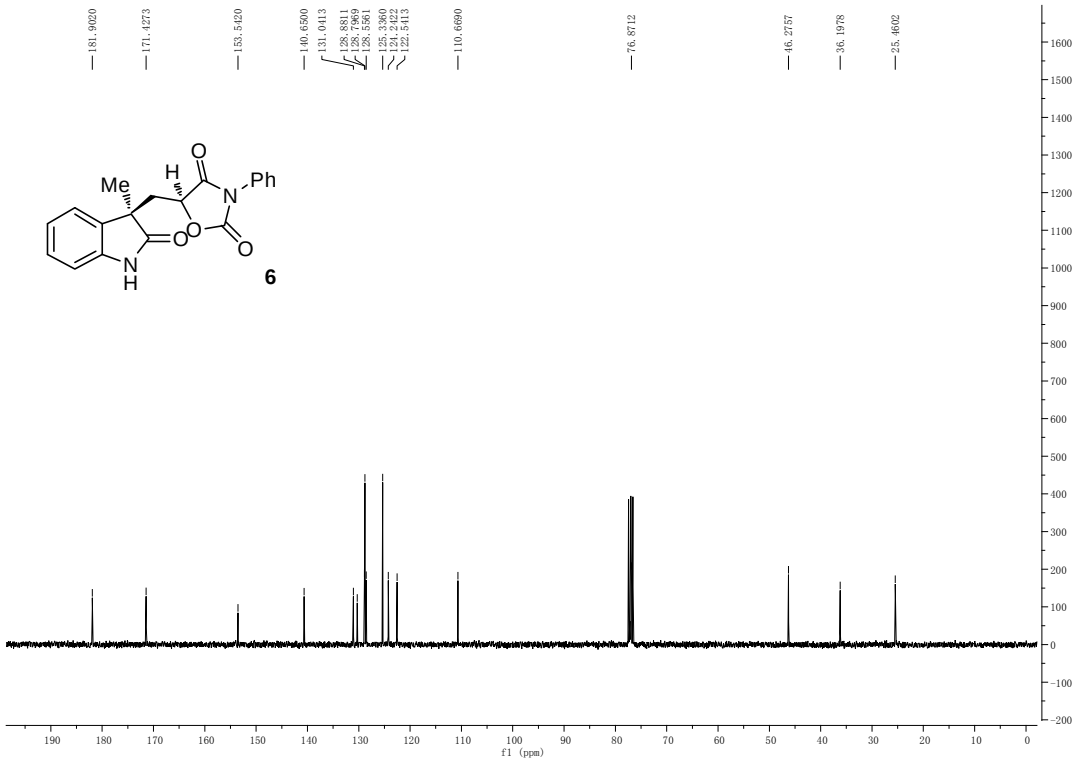
7.4096
7.3251
7.2922
7.2063
7.1823
7.1582
7.0249
7.0053
6.9820
6.9653
5.0059
4.9615
4.9200
2.9846
2.9648
2.9348
2.9148
2.6991
2.6489
1.4801
Me
H
N
Ph
O
O
O
O
N
H
6
0.91
3.13
2.03
4.04
1.00
1.00
1.01
3.04
f1 (ppm)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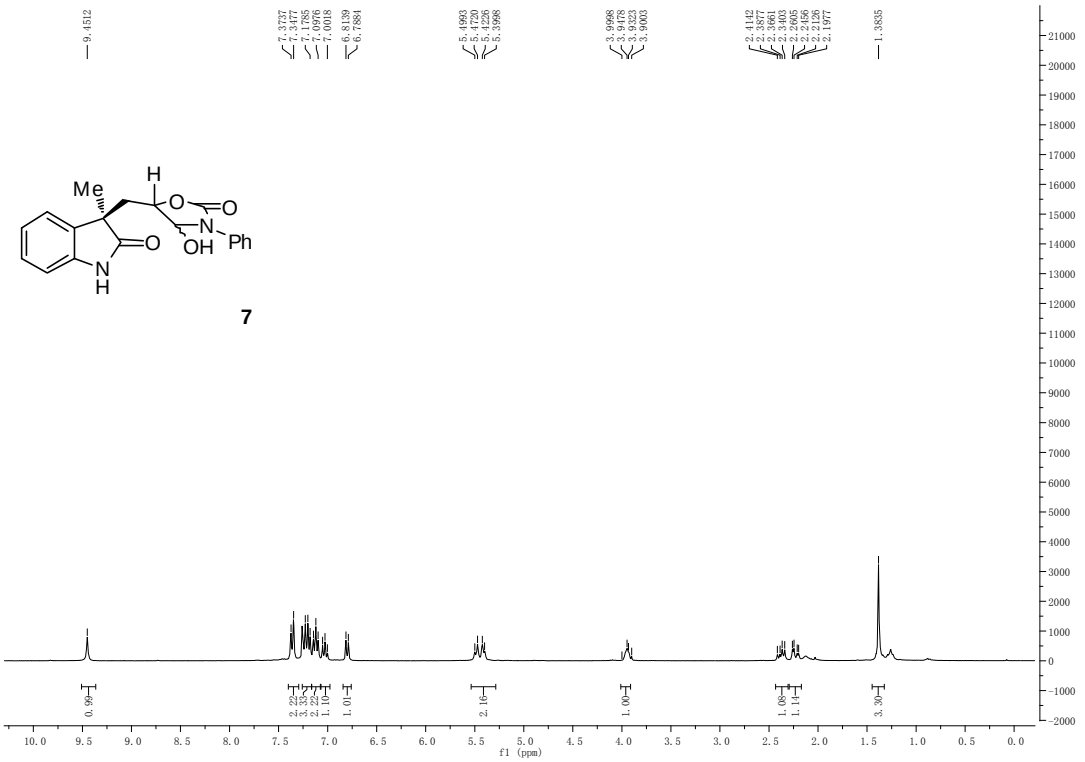
153.5420
140.6500
131.0413
128.8811
128.7969
128.5561
125.3360
124.2422
122.5413
110.6690
76.8712
46.2757
36.1978
25.4602
Me
H
N
Ph
O
O
O
O
N
H
6
f1 (ppm)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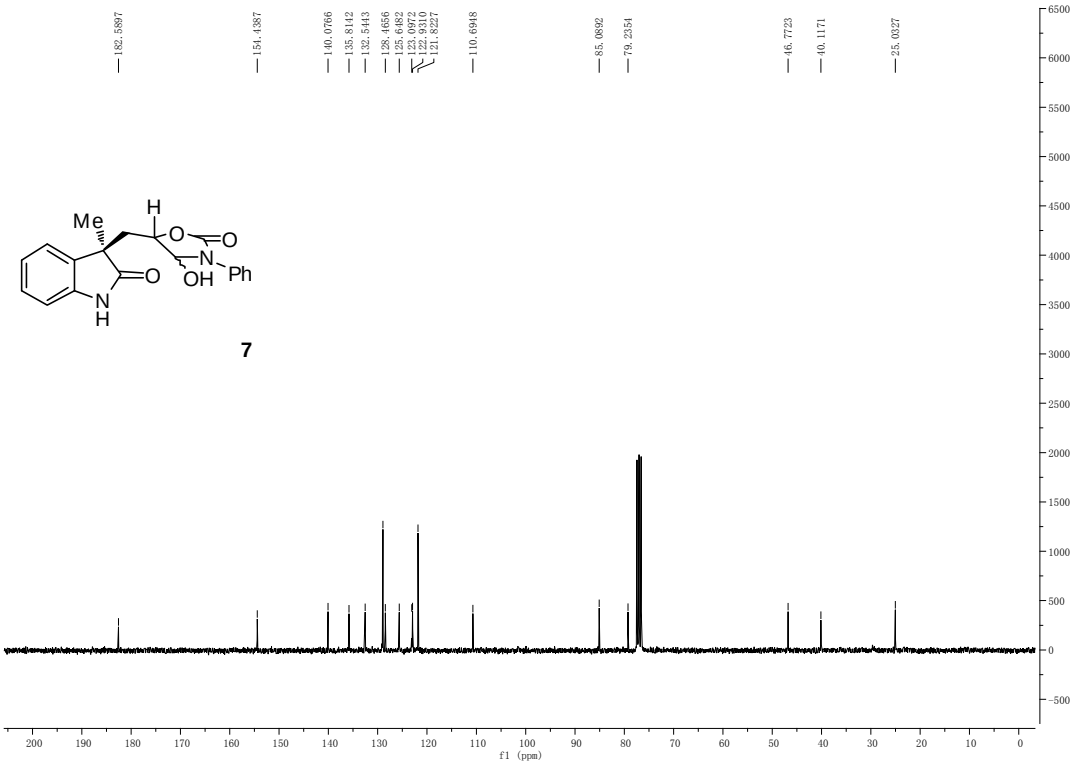
7.3477
7.1785
7.0976
7.0018
6.8139
6.7884
5.4993
5.4720
5.4226
5.3998
3.9998
3.9478
3.9323
3.9003
2.4142
2.3877
2.3661
2.3403
2.2905
2.2456
2.2126
2.1977
1.3835
0.99
2.22
3.25
2.42
1.10
1.01
2.16
1.00
1.08
1.14
3.30
f1 (ppm)

7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135.8142
132.5443
128.4656
125.6482
123.0972
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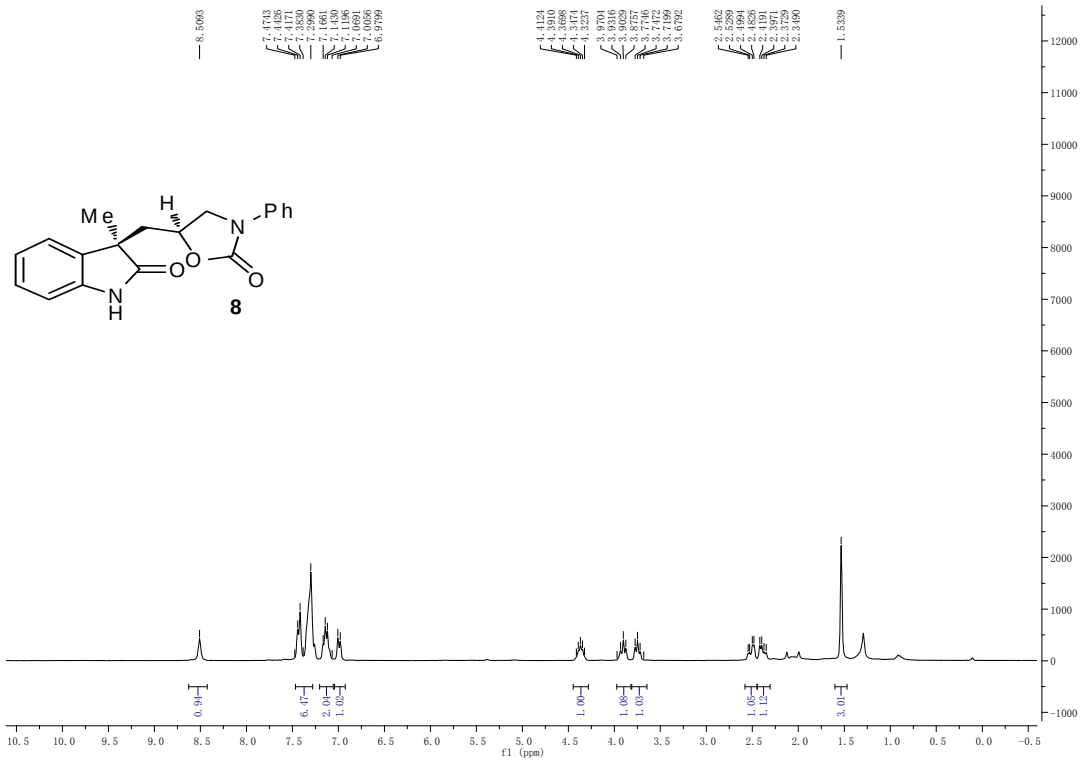
121.8227
110.6948
85.0892
79.2354
46.7723
40.1171
25.0327
f1 (ppm)

7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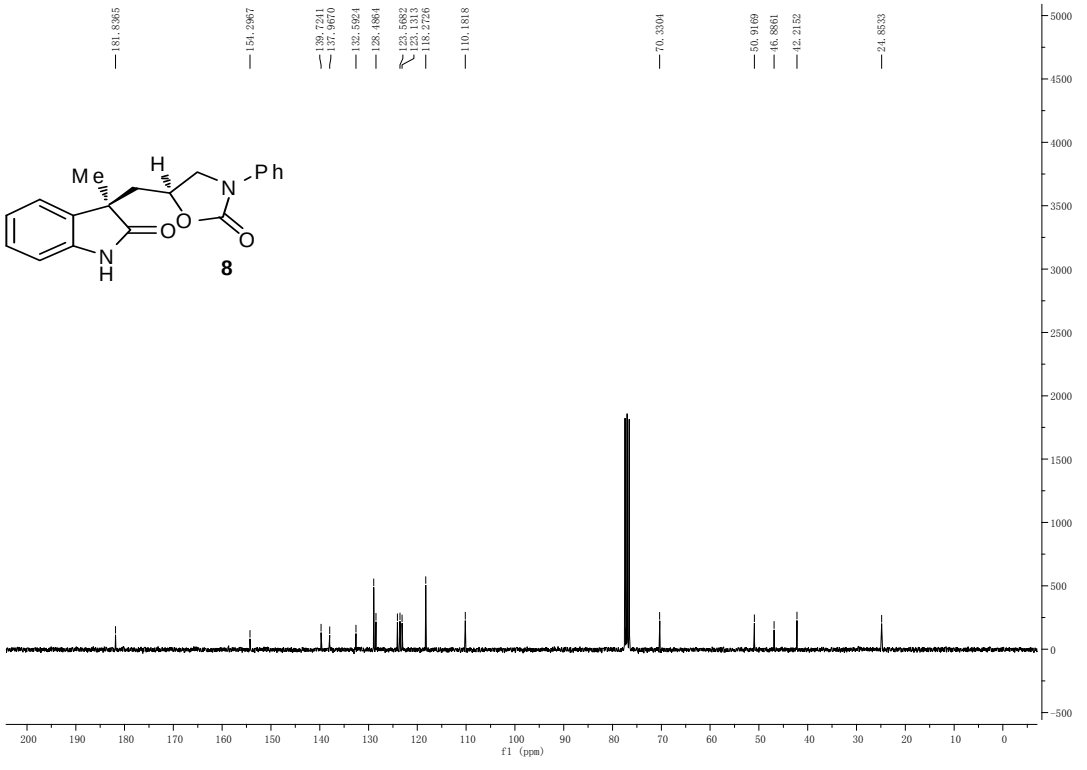
7.4426
7.4171
7.3839
7.2990
7.1661
7.1430
7.1196
7.0691
7.0056
6.9799
4.4124
4.3910
4.3698
4.3474
4.3257
3.9704
3.9516
3.9059
3.8757
3.7746
3.7472
3.7199
3.6792
2.5462
2.5289
2.4994
2.4835
2.4181
2.3971
2.3729
2.3490
1.5339
Me
H
N
Ph
O
O
N
H
8
0.94
6.47
2.01
1.02
1.00
1.08
1.03
1.05
1.12
3.01
f1 (ppm)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137.9670
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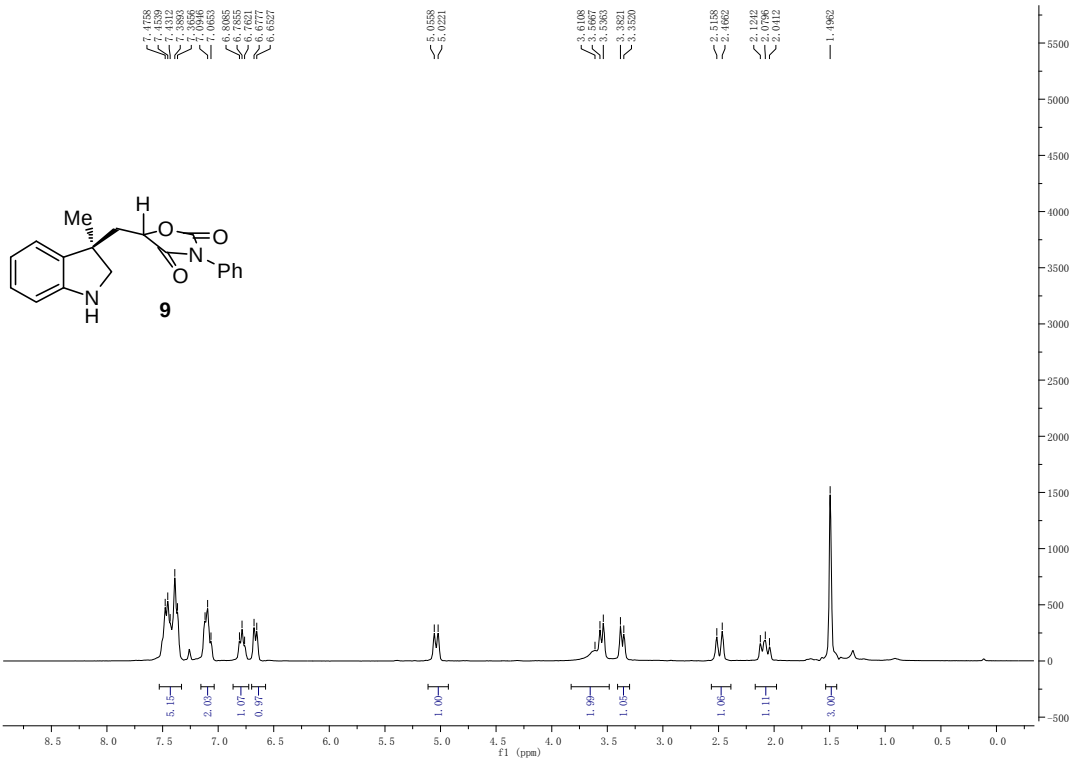
128.4864
123.5682
123.1713
118.2726
110.1818
70.3304
50.9169
46.8861
42.2152
24.8533
Me
H
N
Ph
O
O
N
H
8
f1 (ppm)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7.4312
7.3893
7.3656
7.3046
7.0653
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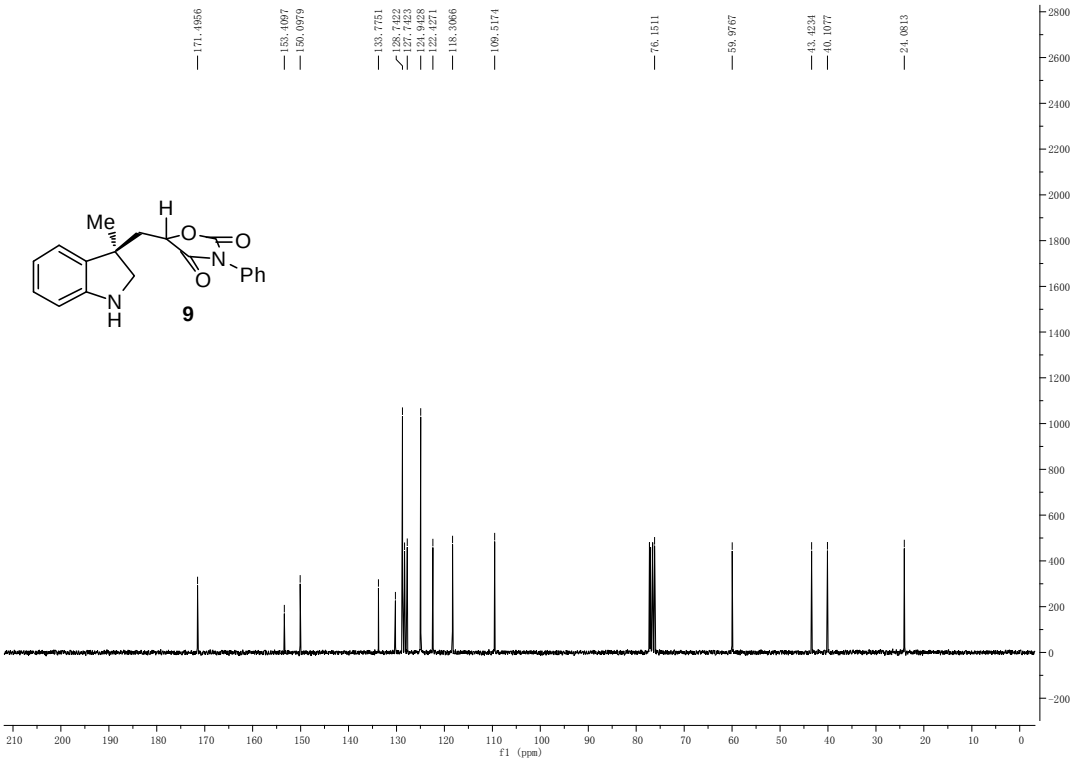
6.7855
6.7621
6.6777
6.6527
5.0558
5.0221
3.6408
3.5957
3.5363
3.3821
3.3520
2.5158
2.4662
2.1242
2.0796
2.0412
1.4962
Me
H
O
O
N
Ph
O
N
H
9
5.15
2.03
1.07
0.97
1.00
1.99
1.05
1.06
1.11
3.00
f1 (ppm)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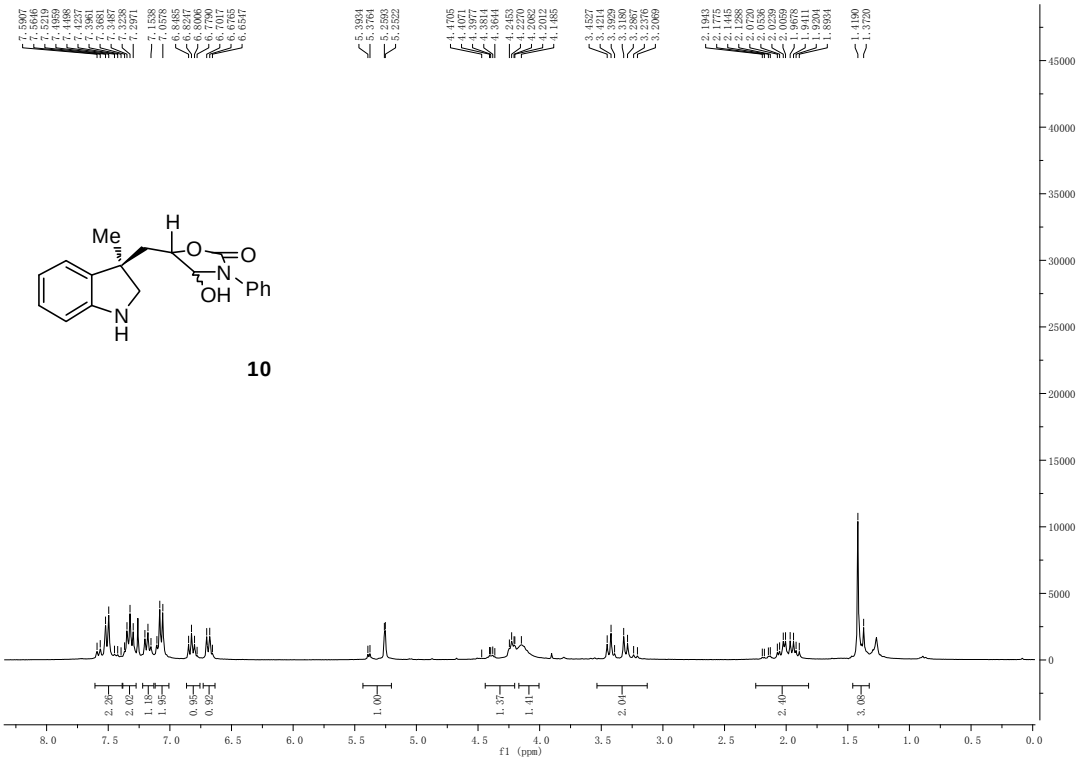
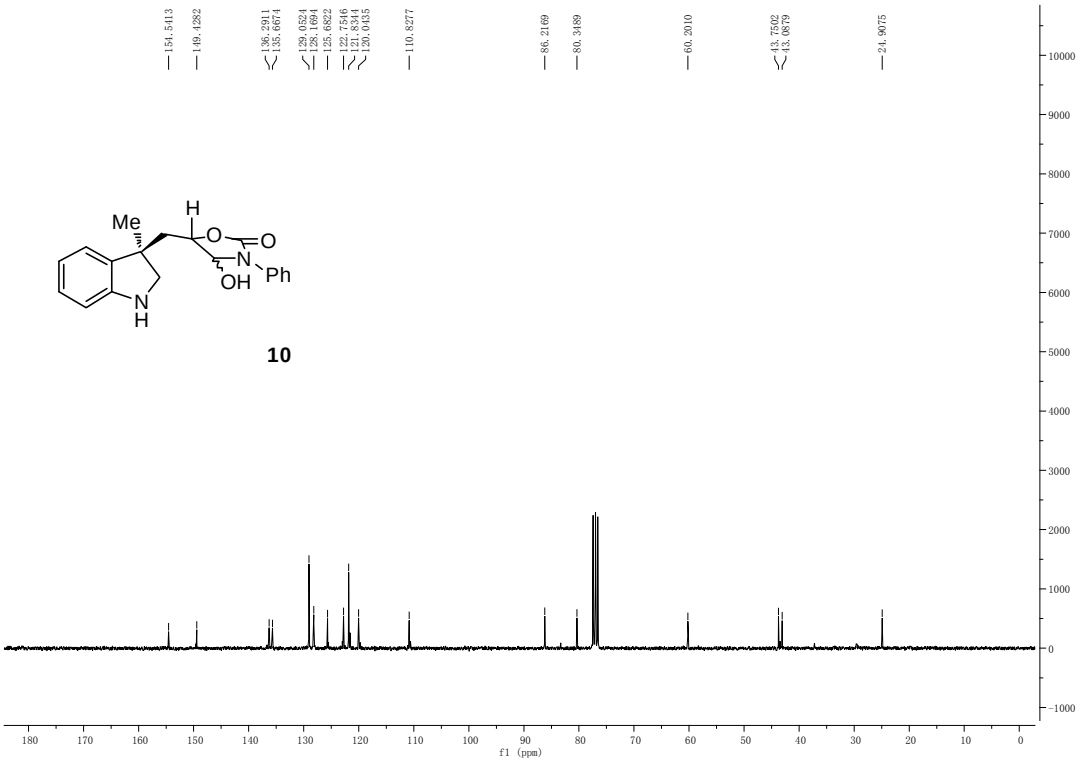
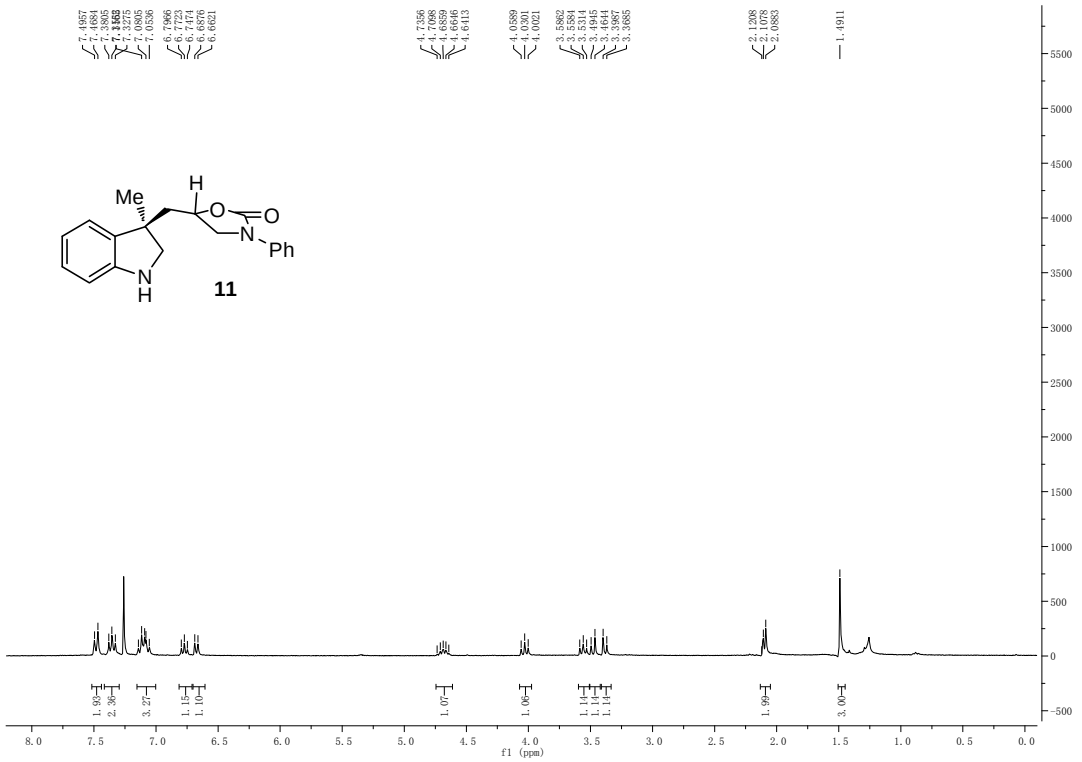
128.7422
127.7423
124.9428
122.4271
118.3066
109.5174
76.1511
59.9767
43.4234
40.1077
24.0813
Me
H
O
O
N
Ph
O
N
H
9
f1 (ppm)



10



10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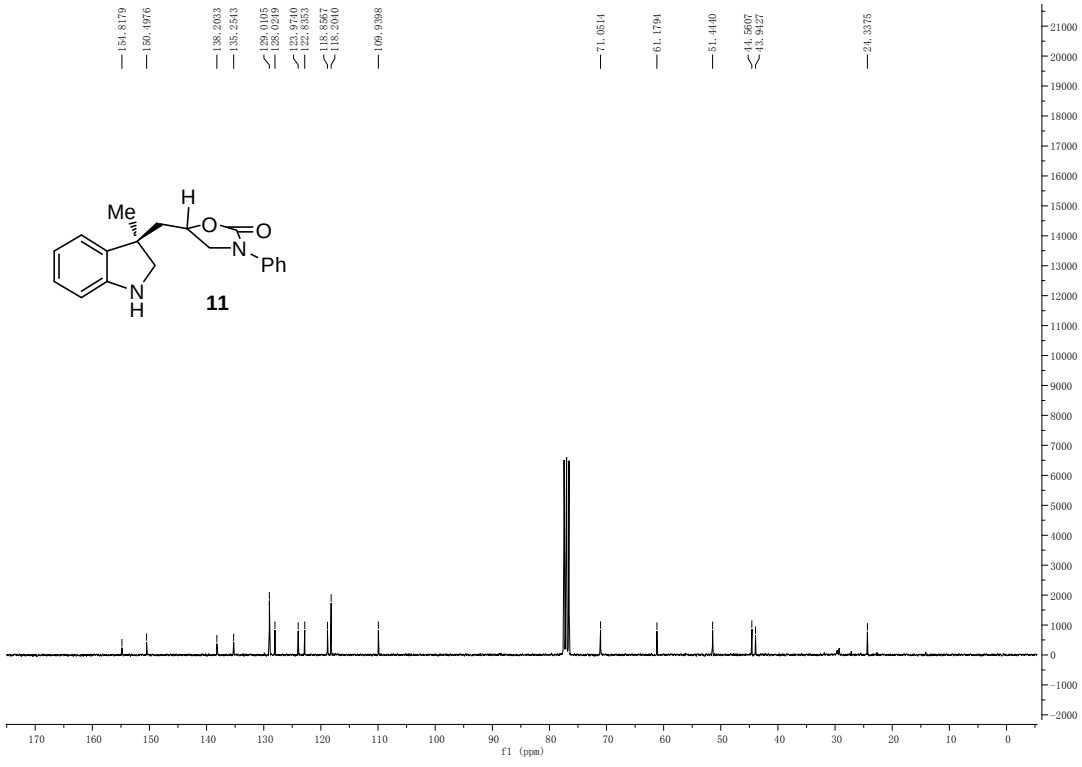
6.7966
6.7723
6.7471
6.6876
6.6621
4.7356
4.7098
4.6839
4.6646
4.6413
4.0389
4.0201
4.0021
3.5862
3.5584
3.5314
3.4945
3.4644
3.3987
3.3685
2.1208
2.1078
2.0883
1.4911
1.93
2.36
3.27
1.15
1.10
1.07
1.06
1.11
1.14
1.14
1.99
3.00
f1 (ppm)

Me
H
O
O
N
Ph
N
H

11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123.9740
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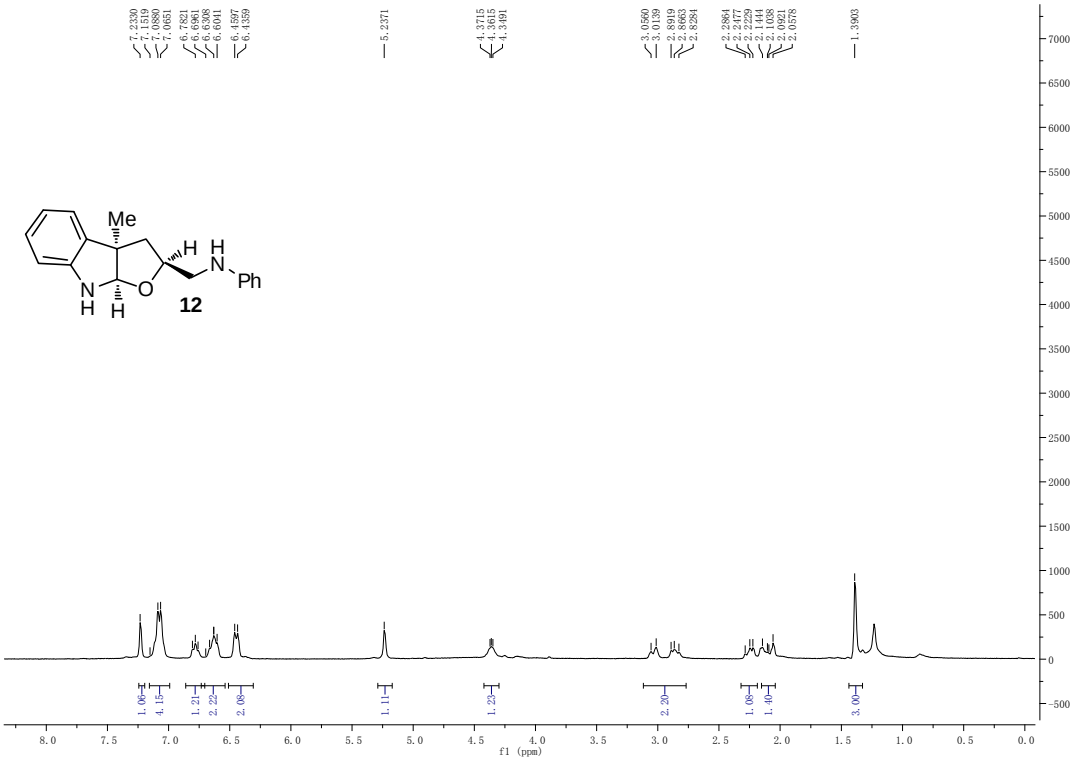
118.8567
118.2040
109.9398
71.0514
61.1794
51.4440
44.5607
43.9427
24.3375
f1 (ppm)

Me
H
O
O
N
Ph
N
H

11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6.6308
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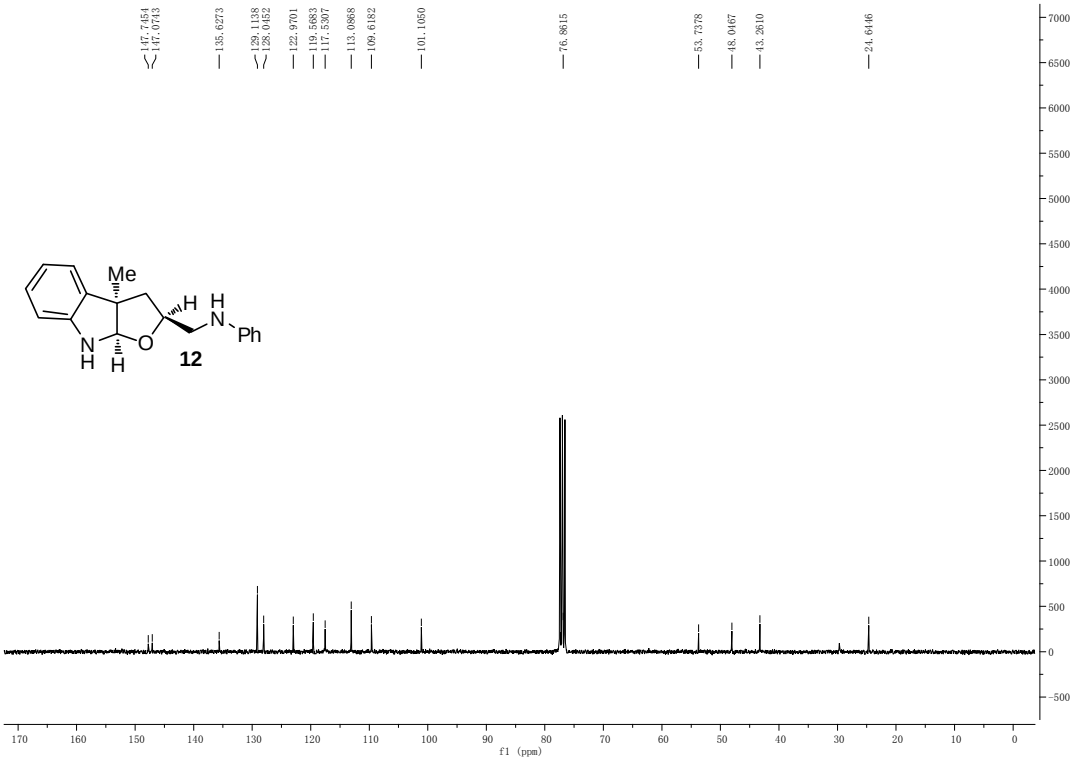
6.4397
6.4339
5.2371
4.3715
4.3615
4.3491
3.0560
3.0139
2.8919
2.8663
2.8284
2.2864
2.2477
2.2239
2.1444
2.1038
2.0921
2.0578
1.3903
1.00
4.15
1.21
2.22
2.08
1.11
1.23
2.20
1.08
1.40
3.00
f1 (ppm)

Me
H
H
N
Ph
N
H
O
H

12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147.0743
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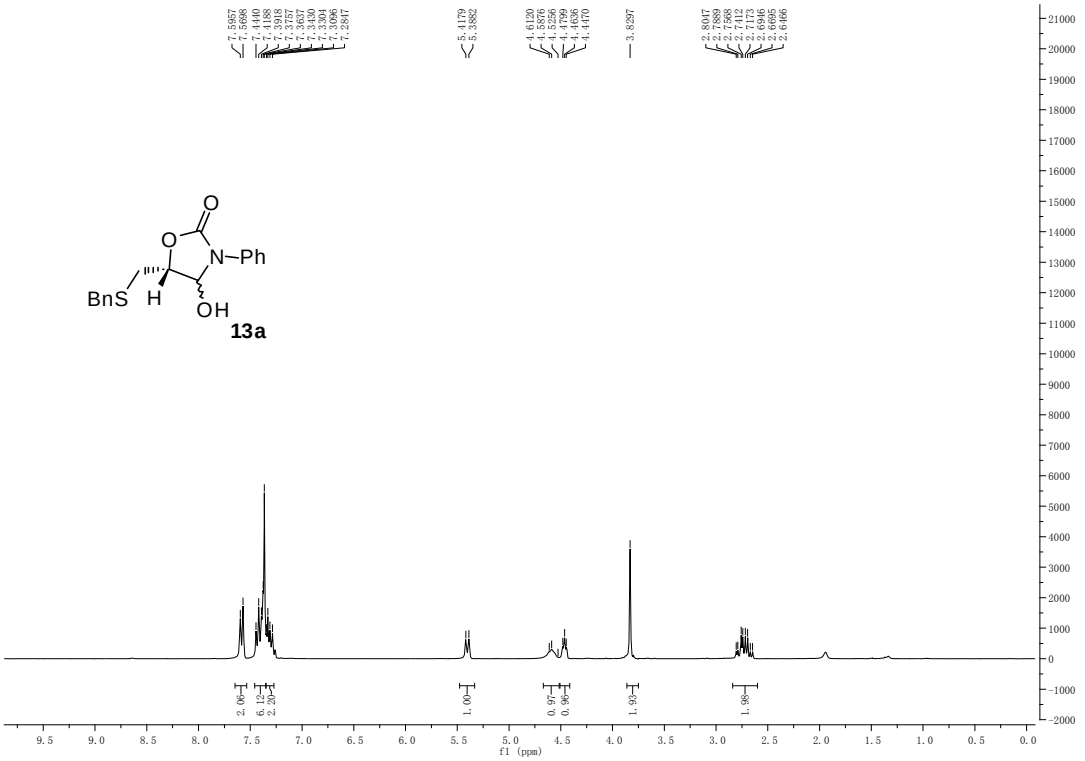
129.1138
128.0452
122.9701
119.5683
117.5307
113.0868
109.6182
101.1050
76.8615
53.7378
48.0467
43.2610
24.6446
f1 (ppm)

Me
H
H
N
Ph
N
H
O
H

12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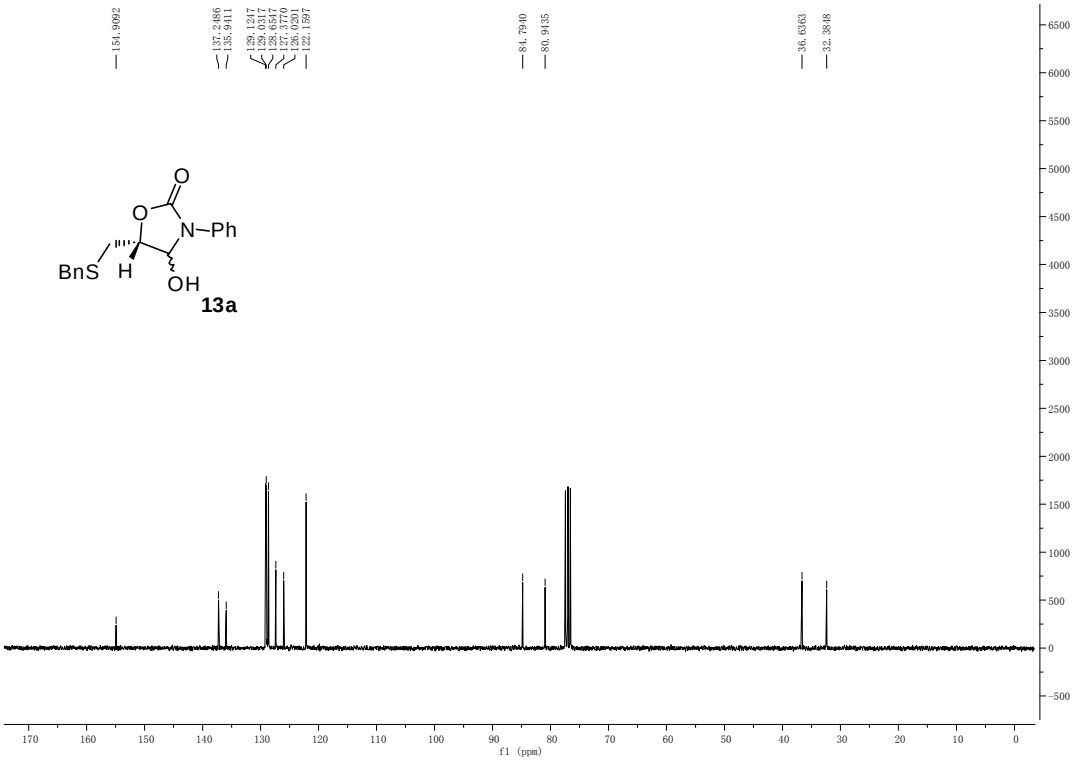
7.4188
7.3918
7.3757
7.3637
7.3430
7.3304
7.3096
7.2847
5.4179
5.3882
4.6120
4.5876
4.5595
4.4759
4.4636
4.4470
3.8297
2.8047
2.7889
2.7568
2.7412
2.7173
2.6946
2.6695
2.6466
O
O
N–Ph
BnS
H
OH
13a
f1 (ppm)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129.0317
128.6547
127.3770
126.0201
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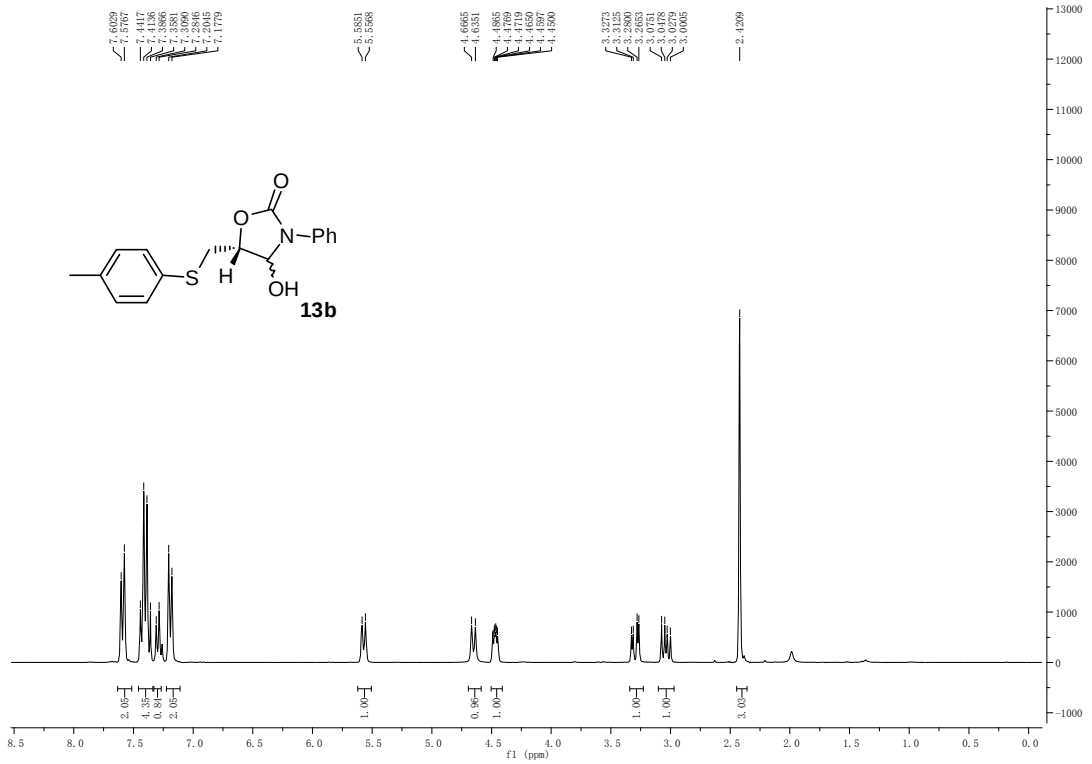
80.9435
36.6363
32.3848
O
O
N–Ph
BnS
H
OH
13a
f1 (ppm)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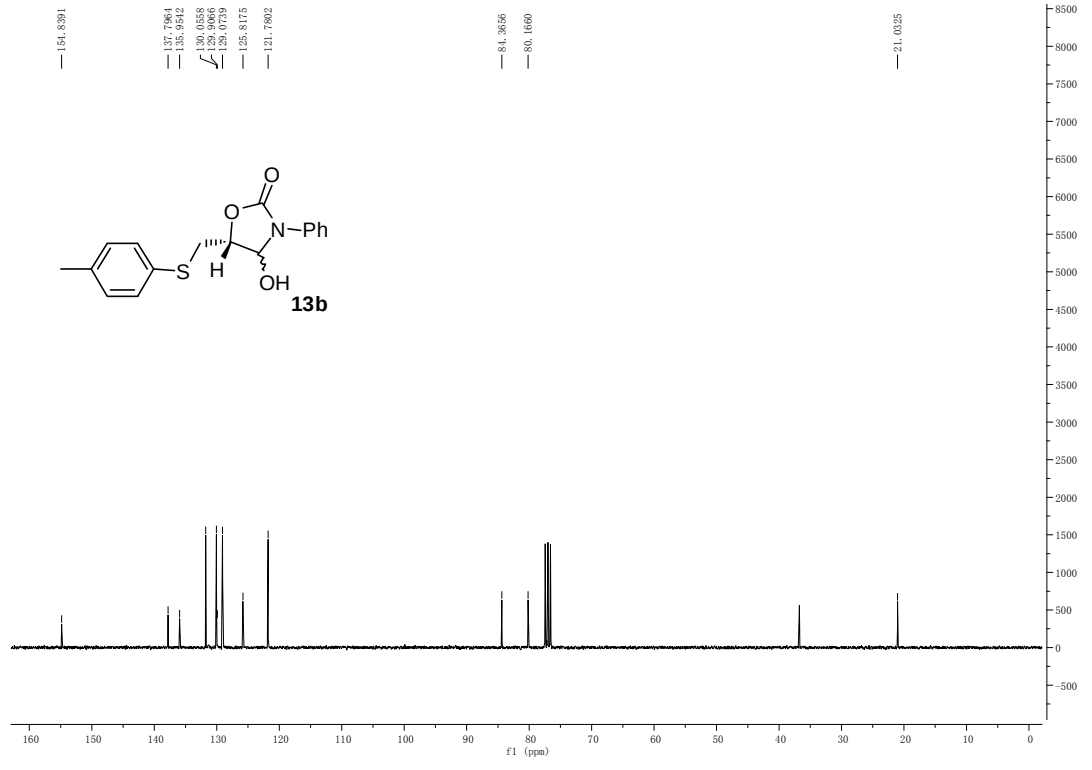
7.4417
7.4138
7.3986
7.3581
7.3090
7.2946
7.2845
7.1779
5.5851
5.5568
4.6665
4.6351
4.4865
4.4769
4.4719
4.4650
4.4597
4.4500
3.3273
3.3125
3.2960
3.2653
3.0751
3.0478
3.0279
3.0085
2.4209
2.05
4.35
0.84
2.05
1.00
0.96
1.00
1.00
1.00
3.03
f1 (ppm)
O
O
N–Ph
S
H
OH
13b


154.8391
137.7964
135.9542
130.0558
129.9066
129.0739
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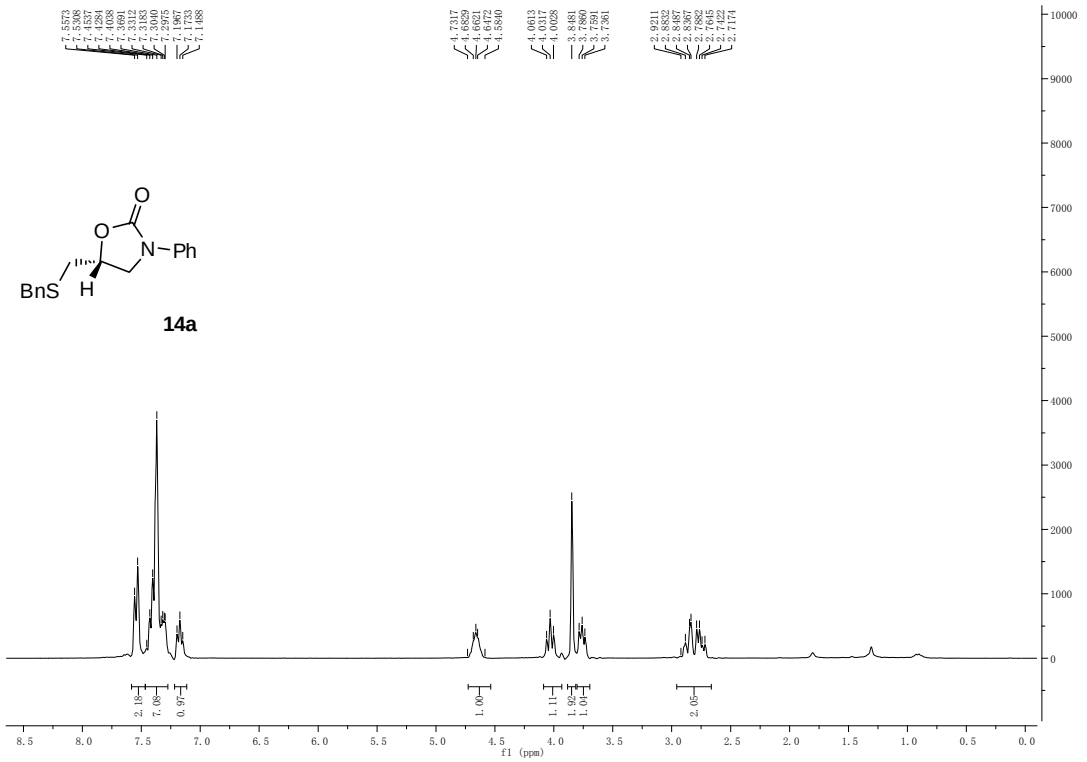
121.7802
84.3656
80.1660
21.0325
f1 (ppm)
O
O
N–Ph
S
H
OH
13b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7.4284
7.4008
7.3891
7.3312
7.3183
7.2975
7.1957
7.1753
7.1488
4.7317
4.6829
4.6621
4.6472
4.5840
4.0613
4.0317
4.0028
3.8481
3.7960
3.7801
3.7361
2.9211
2.8852
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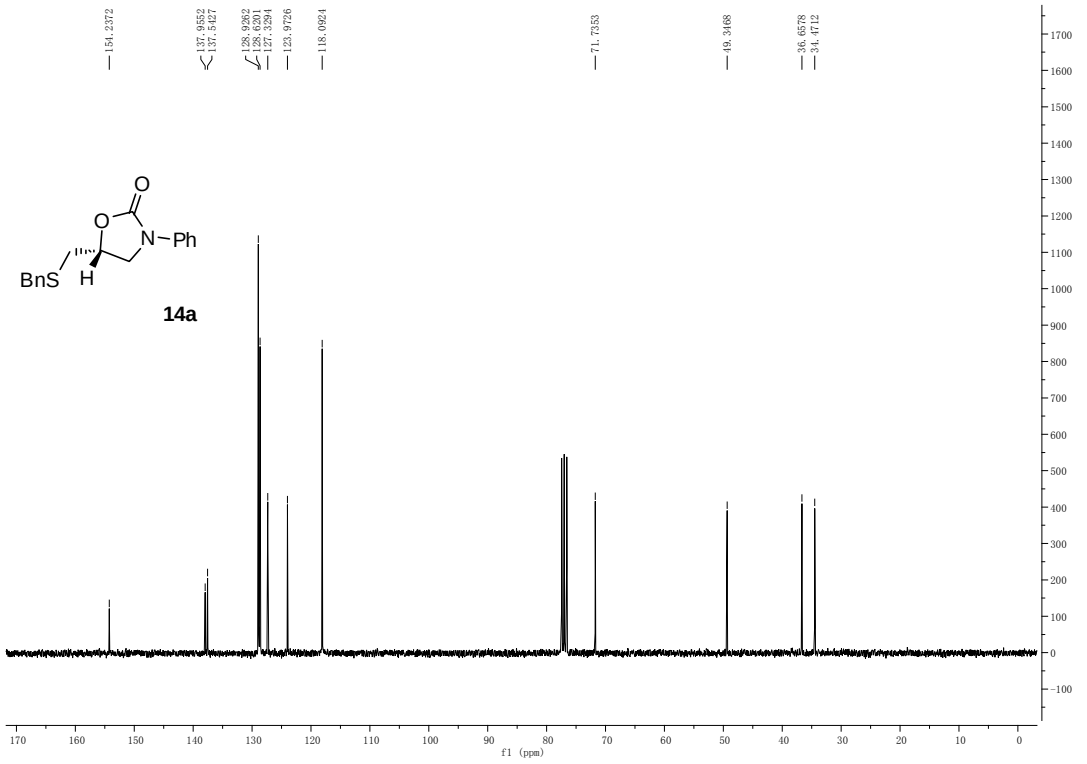
2.7882
2.7645
2.7422
2.7174
O
O
N−Ph
BnS
H
14a
2.18
7.08
0.97
1.00
1.11
1.92
1.04
2.05
f1 (ppm)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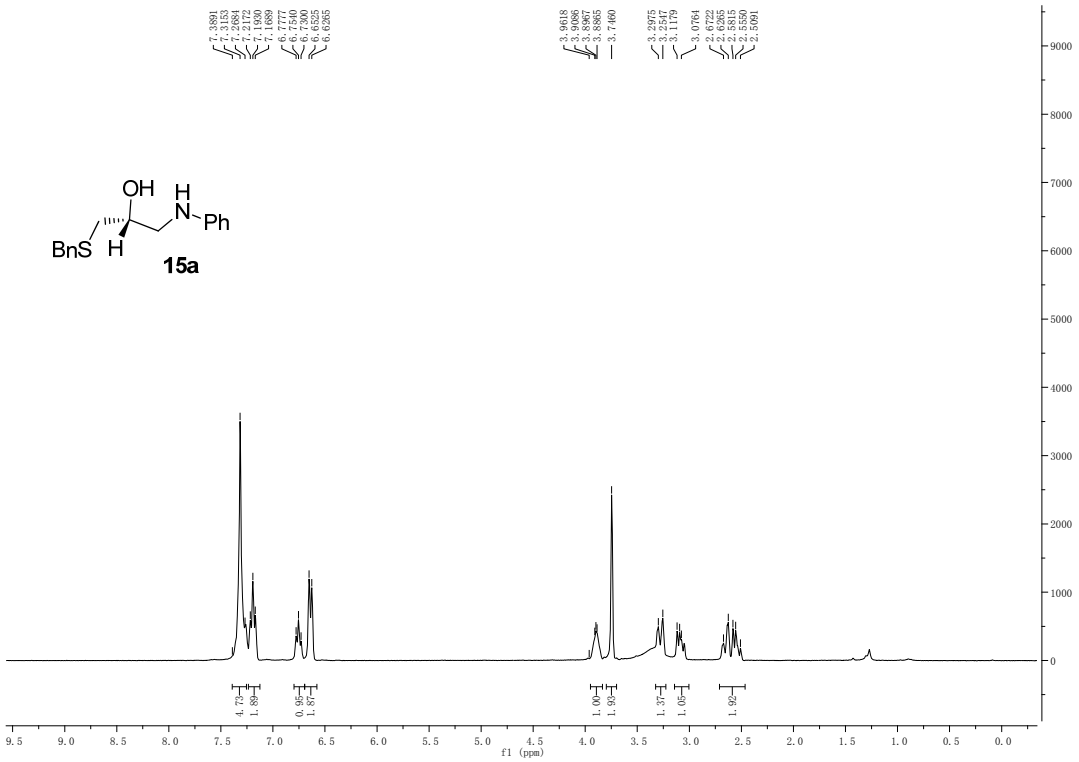
137.5427
128.9262
128.6201
127.3294
123.9726
118.0924
71.7353
49.3468
36.6578
34.4712
O
O
N−Ph
BnS
H
14a
f1 (ppm)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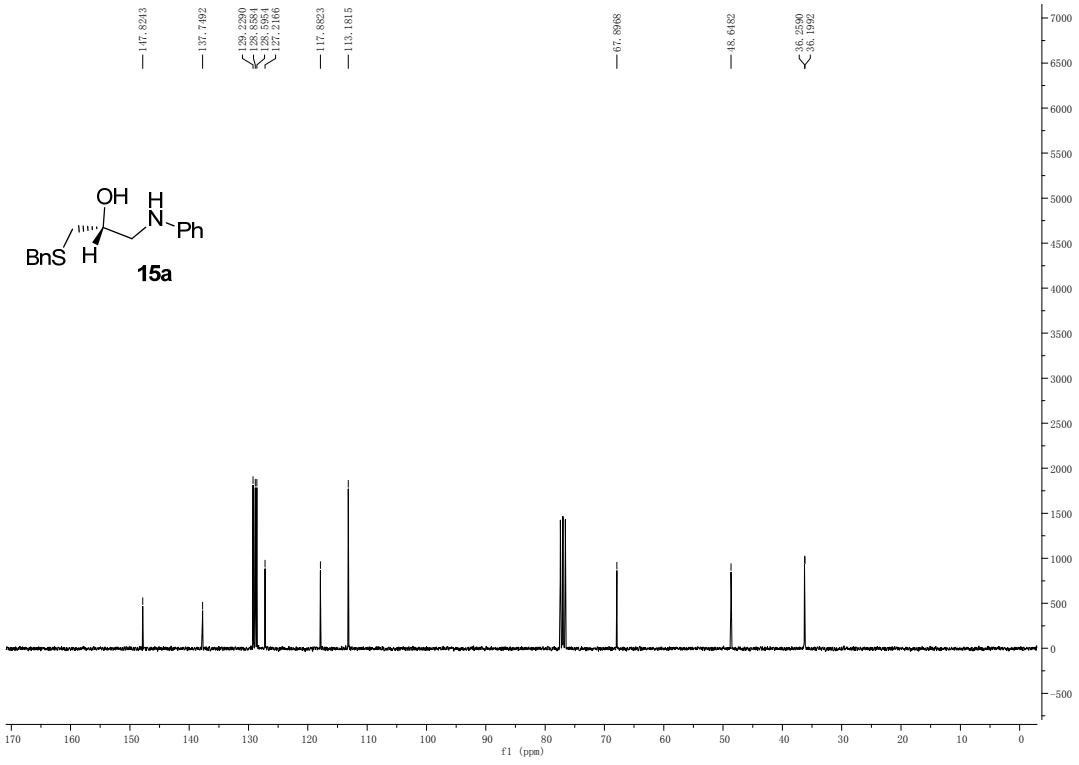
7.3153
7.2684
7.2372
7.1930
7.1689
6.7777
6.7540
6.7300
6.6555
6.6265
3.9618
3.9086
3.8967
3.8865
3.7460
3.2975
3.2547
3.1179
3.0764
2.6722
2.6295
2.5815
2.5550
2.5091
OH
H
N
Ph
BnS
H
15a
4.73
1.89
0.95
1.87
1.00
1.93
1.37
1.05
1.92
f1 (ppm)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137.7492
129.2290
128.8584
128.5954
127.2166
117.8823
113.1815
67.8968
48.6482
36.2590
36.1992
OH
H
N
Ph
BnS
H
15a
f1 (ppm)