Supporting Information

Enantioselective Synthesis of Chiral 1,2-Oxazinane Spiro-oxindoles via Carbene-Catalyzed [3+3] Annulation of Isatin-Derived Nitrones with Enals

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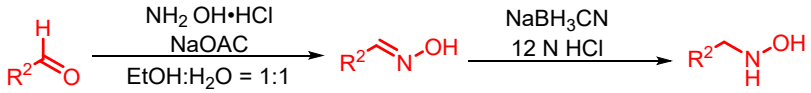
I. General information:

Commercially available materials purchased from regent company were used as received, except aldehydes that were purified via distillation or column chromatography prior to use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (101 MHz) spectrometer. High resolution mass spectrometry (HRMS) analysis was performed using electrospray ionization (ESI) with a quadrupole-time of flight (QTOF) mass analyzer. The determination of er was performed via chiral HPLC analysis using Agilent G7129A HPLC workstation. X-ray crystallography analysis was performed on XtaLAB PRO X-ray diffraction meter. Analytical thin-layer chromatography (TLC) was carried out on GF254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

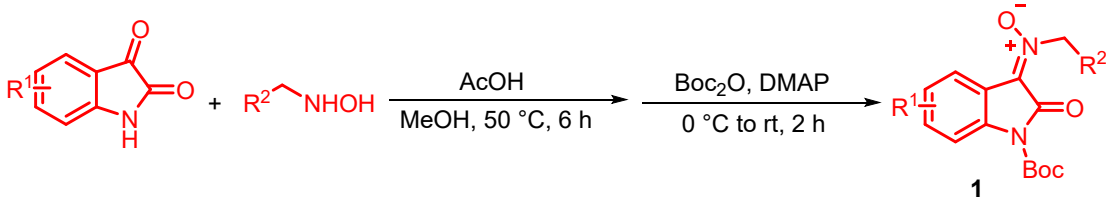
II. Preparation of hydroxylamine derivatives [1-3]:



Dissolve the aldehyde compound (10 mmol) and hydroxylamine hydrochloride (0.83 g, 12 mmol, 1.2 eq) in 20 mL of ethanol-water mixed solvent (1:1), then add sodium acetate (1.64 g, 20 mmol). Stir the reaction solution until the aldehyde compound is completely consumed. After evaporating the solvent, perform liquid-liquid extraction of the residue with ethyl acetate and water. Wash the aqueous layer with ethyl acetate (2×50 mL). Combine the organic layers, dry over anhydrous sodium sulfate, filter, and concentrate to obtain the oxime compound, which can be used in the next reaction without further purification.

Suspend the oxime compound obtained in the above steps in methanol (20 mL), add sodium cyanoborohydride (0.75 g, 12 mmol, 1.2 eq), and then slowly add 12 N hydrochloric acid (8.3 mL, 100 mmol, 10 eq) at 0°C. After stirring at room temperature for 4 h, pour the reaction mixture into water and neutralize to neutral at 0 °C with potassium hydroxide pellets. Then perform an extraction operation, extract the organic phase with ethyl acetate, wash the organic phase sequentially with saturated brine, dry over anhydrous sodium sulfate, and finally concentrate to obtain the crude product. Most of the hydroxylamine product can be used directly without further purification. If necessary (determined by 1H NMR), the crude product can be purified by silica gel column chromatography (hexane/EtOAc = 3:1 to 1:1).

Synthesis of oxime derivatives [4-7]:



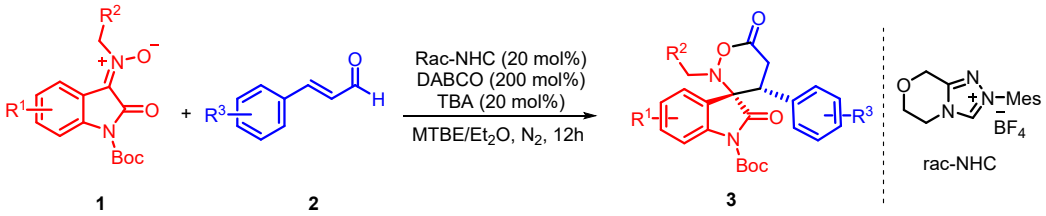
1

Dissolve isatin (1.0 mmol) and hydroxylamine (1.1 mmol) in 4 mL of methanol, then add acetic acid (57.2 μL, 1.0 mmol). Stir the reaction mixture at 50°C for 6 h. After the reaction is complete, cool the mixture to room temperature and filter; wash the collected yellow solid with methanol and petroleum ether to obtain N-(2-oxoindolin-3-ylidene)methylamine oxide.

Dissolve N-(2-oxoindolin-3-ylmethyl)amine oxide (0.8 mmol) and di-tert-butyl dicarbonate (0.18 mL, 0.88 mmol) in 10 mL of dichloromethane and cool the reaction mixture to 0°C. Then add 4-dimethylaminopyridine (9.8 mg, 0.08 mmol), stir at room temperature for 2 h, and monitor the reaction progress by TLC. After the reaction is complete, quench with 1 M hydrochloric acid, then extract with dichloromethane (3×10 mL). Combine the organic layers, wash with saturated brine, dry over anhydrous sodium sulfate, and concentrate under vacuum. Purify by quick silica gel column chromatographyto obtain the yellow solid oxime product **1**.

III. General procedure for the catalytic synthesis of products 3

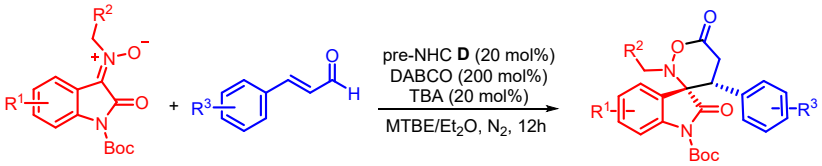
Synthesis of racemic product:



1 2 3

In a 25 mL dried Schlenk tube equipped with a magnetic stirrer, add substrate **1** (0.1 mmol), substrate **2** (0.2 mmol), DABCO (21.2 mg, 0.2 mmol), and Rac-NHC (8.4 mg, 0.02 mmol) sequentially, then perform three N_2 evacuation-refill cycles. At room temperature, add the additive tert-butanol (4.75 uL, 0.05 mmol) and 1 mL of dried MTBE or diethyl ether as the solvent, and continue stirring the reaction at this temperature for 12 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (3:1 ~ 7:1) as eluent to afford the products **3.**

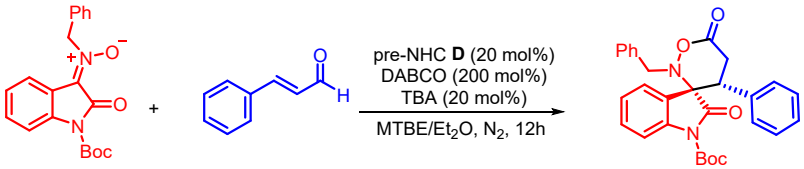
Asymmetric Synthesis of 3:



1 2 3

In a 25 mL dried Schlenk tube equipped with a magnetic stirrer, add substrate **1** (0.1 mmol), substrate **2** (0.2 mmol), DABCO (21.2 mg, 0.2 mmol), and pre-NHC **D** (8.4 mg, 0.02 mmol) sequentially, then perform three N_2 evacuation-refill cycles. At room temperature, add the additive tert-butanol (4.75 uL, 0.05 mmol) and 1 mL of dried MTBE or diethyl ether as the solvent, and continue stirring the reaction at this temperature for 12 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (3:1 ~ 7:1) as eluent to afford the products **3.**

Scale-up reaction of 3a:



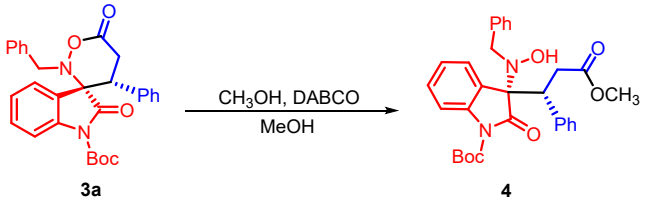
1a 2a 3a

In a 50 mL flask equipped with a magnetic stirrer, add substrate **1a** (528 mg, 1.5 mmol), substrate **2a** (396 mg, 3.0 mmol), DABCO (336 mg, 3.0 mmol) and pre-NHC **D** (125.7 mg, 0.30 mmol) in sequence, and perform three cycles of evacuation and N_2 backfilling. At room temperature, add the additive tert-butanol (28.5 μL, 0.30 mmol) and 15 mL of dry MTBE as the solvent, and continue stirring the reaction at this temperature for 12 h. Once the reaction is complete, Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (7:1) as eluent

to afford the products **3a** (48.6 mg, 67% yield).

IV: Synthetic transformation of the product 3a and 4

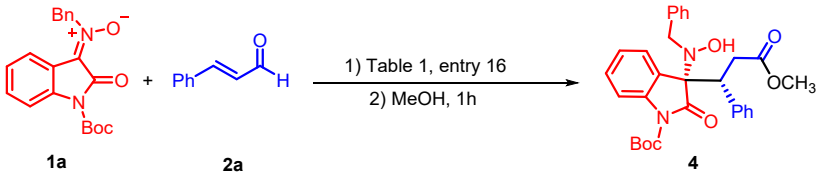
Stepwise reaction:



3a **4**

Put compound **3a** (50 mg, 0.1 mmol) in a reaction vial equipped with a magnetic stir bar, add methanol (4 μL, 0.1 mmol) and DABCO (11.2 mg, 0.1 mmol), and add 1 mL of MTBE as the solvent, stirring at room temperature for 1 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc =10:1 as eluent to afford the products **4** as a Colourless liquid (46 mg, 90% yield).

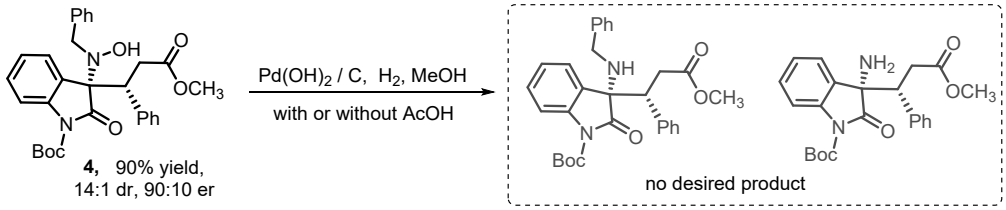
One-pot method:



1a **2a** **4**

In a 25 mL dry Schlenk reaction tube equipped with magnetic stirrer, add substrate **1a** (0.1 mmol), substrate **2a** (0.2 mmol, 2.0 eq), DABCO (21.2 mg, 0.2 mmol, 2.0 eq) and pre-NHC **D** (6.4 mg, 0.02 mmol, 20 mol%) sequentially, and perform three cycles of N_2 evacuation and backfilling. At room temperature, add the additive tert-butanol (0.05 mmol, 20 mol%) and 1 mL dry MTBE as the solvent, and stir the reaction at this temperature for 12 h. After the reaction is complete, add methanol (8 μL, 0.2 mmol) and stir at room temperature for 1 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc =10:1 as eluent to afford the products **4** as a Colourless liquid (37 mg, 74% yield).

N-O bond cleavage of 4 [8]: (*unsuccessful*)

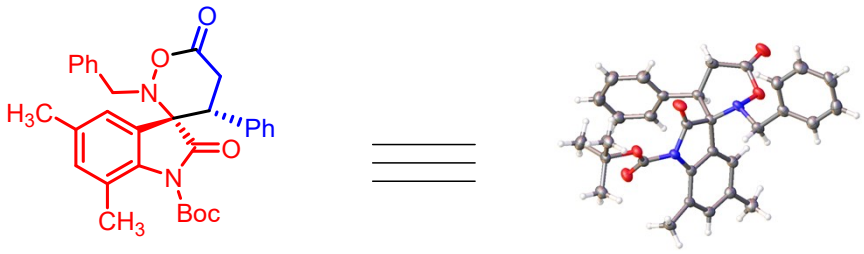


4, 90% yield,
14:1 dr, 90:10 er

To a flame dried 10 mL round bottom flask equipped with magnetic stirring bar was added **4** (51.6 mg, 0.1 mmol). The solid was diluted with MeOH (1 mL, 0.1 M). The flask was purged with nitrogen gas. $Pd(OH)_2/C$ (10 mol %) was then added and the flask was purged with nitrogen for a second time. The flask was purged with hydrogen using a balloon and the reaction was then stirred under the hydrogen atmosphere for 24 hours. *TLC monitoring revealed that in the absence of acetic acid, the reaction scarcely proceeded, with most of the starting material remaining unreacted. Upon the addition of acetic acid (0.06mL, 1 mmol), however, the reaction mixture became highly complex; the starting material was consumed, but the desired product was not observed.*

V: Stereochemistry determination via X-ray crystallographic analysis:

Method for single crystals cultivation: a solid sample (10–20 mg) was dissolved in ethyl acetate (50–100 μL) in a vial at room temperature, and petroleum ether (2–8 mL) was added into the above solution slowly while keeping the sample all dissolved. Then the vial was sealed with a piece of parafilm and stayed quietly for several days to allow the slow evaporation of the solvents until a single crystal was obtained. CCDC 2471507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



3j CCDC 2471507

Table 1 Crystal data and structure refinement for 3j.

Identification code	86_8
Empirical formula	$C_{31}H_{32}N_2O_5$
Formula weight	512.58
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.2948(3)
b/Å	13.5305(5)
c/Å	24.0231(9)
α /°	90
β /°	93.712(2)
γ /°	90
Volume/Å^3	2690.52(17)
Z	4
ρ_{calc}g/cm^3	1.265
μ /mm^{-1}	0.695
F(000)	1088.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.374 to 136.53
Index ranges	-9 ⩽ h ⩽ 9, -16 ⩽ k ⩽ 16, -28 ⩽ l ⩽ 28
Reflections collected	53611
Independent reflections	4890 [R_{int} = 0.0416, R_{sigma} = 0.0208]
Data/restraints/parameters	4890/0/349
Goodness-of-fit on F^2	1.070

Final R indexes [I>=2 σ (I)]	R_1 = 0.0387, wR_2 = 0.0991
Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.1003
Largest diff. peak/hole / e Å^{-3}	0.29/-0.19

References cited in the SI:

[1] Guo C, Saifuddin M, Saravanan T, et al. *ACS catalysis*, **2019**, 9(5): 4369-4373.

[2] Ohmatsu K, Ando Y, Nakashima T, et al. *Chemistry*, **2016**, 1(5): 802-810.

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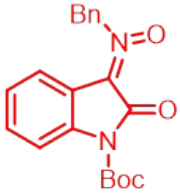
[5] Chen Y R, Zhan G, Du W, et al. *Advanced Synthesis & Catalysis*, **2016**, 358(23): 3759-3764.

[6] Zhan G, Shi M L, Lin W J, et al. *Chemistry–A European Journal*, **2017**, 23(26): 6286-6289.

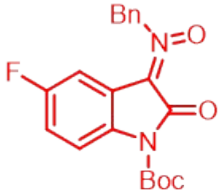
[7] Cheng X, Fei W, Luo Z, et al. *Synthesis*, **2020**, 52(23): 3632-3639.

[8] Phillips E M, Reynolds T E, Scheidt K A, *Journal of the American Chemical Society,* **2008**, 130(8), 2416–2417.

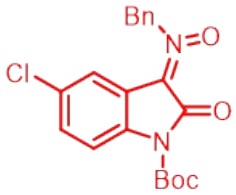
VI. Characterization of Products:



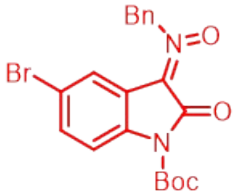
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide (1a): Yield: 1.2 g (84%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 7.8, 1.4 Hz, 1H) , 7.89 (d, *J* = 8.2 Hz, 1H), 7.45 (td, *J* = 7.9, 1.4 Hz, 1H) , 7.23 (td, *J* = 7.6, 1.0 Hz, 3H) , 4.40 (s, 3H) , 1.67 (s, 9H).



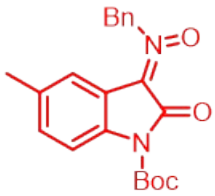
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-fluoro-2-oxoindolin-3-imine oxide (1b): Yield: 820 mg (73%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.81 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.42 – 7.32 (m, 3H), 7.12 (td, *J* = 8.8, 2.9 Hz, 1H), 5.94 (s, 2H), 1.68 (s, 9H). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -116.94 (dt, *J* = 8.3, 4.2 Hz).



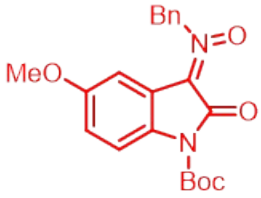
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-chloro-2-oxoindolin-3-imine oxide (1c): Yield: 850 mg (76%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 (d, J = 2.2 Hz, 1H), 7.78 (dd, J = 8.8, 1.9 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.42 – 7.33 (m, 4H), 5.93 (s, 2H), 1.67 (s, 9H).



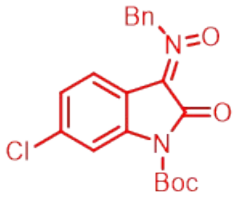
(Z)-N-benzyl-5-bromo-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide (1d): Yield: 954 mg (74%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.65 (d, J = 2.1 Hz, 1H), 7.73 (dd, J = 8.6, 2.1 Hz, 1H), 7.59 (h, J = 3.7, 3.3 Hz, 2H), 7.53 (dt, J = 8.7, 2.0 Hz, 1H), 7.37 (dq, J = 6.2, 3.7, 2.9 Hz, 3H), 5.93 (d, J = 2.3 Hz, 2H), 1.67 (d, J = 2.6 Hz, 9H).



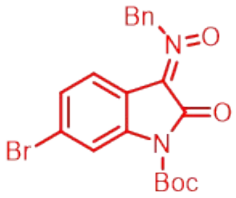
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-methyl-2-oxoindolin-3-imine oxide (1e): Yield: 784 mg (72%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.13 (m, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.41 – 7.31 (m, 3H), 7.23 (ddd, *J* = 8.3, 2.0, 0.9 Hz, 1H), 5.93 (s, 2H), 2.34 (s, 3H), 1.67 (s, 9H).



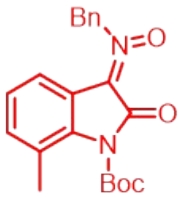
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-methoxy-2-oxoindolin-3-imine oxide (1f): Yield: 840 mg (70%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 2.8 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.42 – 7.31 (m, 3H), 6.97 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.94 (s, 2H), 3.81 (s, 3H), 1.67 (s, 9H).



(Z)-N-benzyl-1-(tert-butoxycarbonyl)-6-chloro-2-oxoindolin-3-imine oxide (1g): Yield: 875 mg (76%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.42 – 7.32 (m, 3H), 7.18 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.91 (s, 2H), 1.68 (s, 9H).

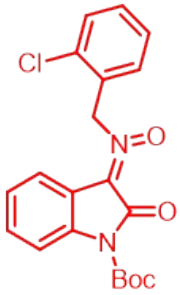


(Z)-N-benzyl-6-bromo-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide (1h): Yield: 961 mg (75%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 1.8 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.42 – 7.31 (m, 4H), 5.90 (s, 2H), 1.68 (s, 9H).

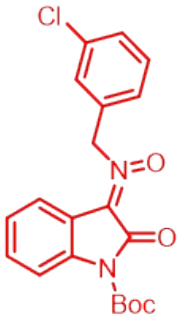


(Z)-N-benzyl-1-(tert-butoxycarbonyl)-7-methyl-2-oxoindolin-3-imine oxide (1i): Yield: 828 mg (76%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.36 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.26 – 7.19 (m, 5H), 5.93 (s, 2H), 2.35 (s, 3H), 1.67 (s, 9H).

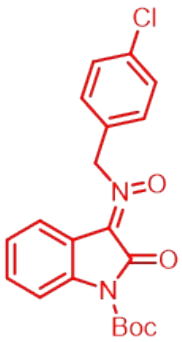
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5,7-dimethyl-2-oxoindolin-3-imineoxide (1j): Yield: 791 mg (70%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.15 (m, 1H), 7.62 – 7.54 (m, 2H), 7.41 7.30 (m, 3H), 7.04 (dt, *J* = 1.7, 0.8 Hz, 1H), 5.91 (s, 2H), 2.30 (s, 3H), 2.21 (s, 3H), 1.66 (s, 9H).



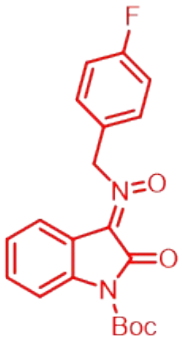
(Z)-1-(tert-butoxycarbonyl)-N-(2-chlorobenzyl)-2-oxoindolin-3-imine oxide (1k): Yield: 840 mg (73%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.18 (m, 7H), 6.12 (s, 2H), 1.68 (s, 9H).



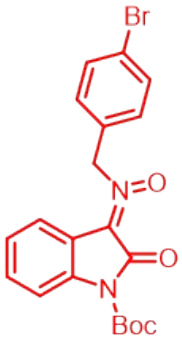
(Z)-N-(4-bromobenzyl)-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide (1l): Yield: 898 mg (78%), yellow powder; 1H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.50 (dt, *J* = 7.1, 1.8 Hz, 1H), 7.44 (td, *J* = 8.0, 1.4 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.91 (s, 2H), 1.68 (s, 9H).



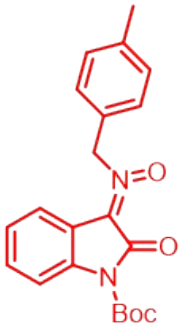
(Z)-1-(tert-butoxycarbonyl)-N-(4-chlorobenzyl)-2-oxoindolin-3-imine oxide(1m): Yield: 991 mg (80%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.42 (td, *J* = 8.0, 1.4 Hz, 1H), 7.19 (td, *J* = 7.7, 1.0 Hz, 1H), 6.92 – 6.84 (m, 2H), 5.87 (s, 2H), 3.79 (s, 3H), 1.68 (s, 9H).



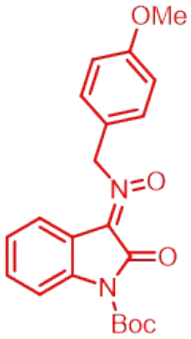
(Z)-1-(tert-butoxycarbonyl)-N-(3-chlorobenzyl)-2-oxoindolin-3-imine oxide (1n): Yield: 890 mg (75%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.43 (td, *J* = 7.9, 1.4 Hz, 1H), 7.20 (td, *J* = 7.7, 1.0 Hz, 1H), 7.09 – 7.00 (m, 2H), 5.89 (s, 2H), 1.68 (s, 9H); ^{19}F NMR (377 MHz, Chloroform-*d*) δ -112.43.



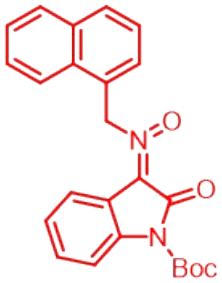
(Z)-1-(tert-butoxycarbonyl)-N-(4-fluorobenzyl)-2-oxoindolin-3-imine oxide (1o): Yield: 1.0 g (79%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 4H), 7.44 (td, *J* = 7.9, 1.5 Hz, 1H), 7.21 (td, *J* = 7.7, 1.0 Hz, 1H), 5.88 (s, 2H), 1.68 (s, 9H).



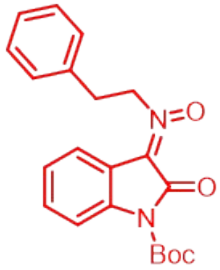
(Z)-1-(tert-butoxycarbonyl)-N-(4-methylbenzyl)-2-oxoindolin-3-imine oxide (1p): Yield: 907 mg (87%) ,yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.53 – 7.46 (m, 2H), 7.42 (td, *J* = 7.9, 1.4 Hz, 1H), 7.23 – 7.14 (m, 3H), 5.90 (s, 2H), 2.33 (s, 3H), 1.68 (s, 9H).



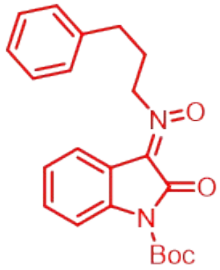
(Z)-1-(tert-butoxycarbonyl)-N-(4-methoxybenzyl)-2-oxoindolin-3-imine oxide (1q): Yield: 956 mg (83%) ,yellow powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.48 (dd, J = 7.8, 1.4 Hz, ^{1}H), 7.82 (d, J = 8.2 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.42 (td, *J* = 8.0, 1.4 Hz, 1H), 7.19 (td, *J* = 7.7, 1.0 Hz, 1H), 6.92 – 6.84 (m, 2H), 5.87 (s, 2H), 3.79 (s, 3H), 1.68 (s, 9H).



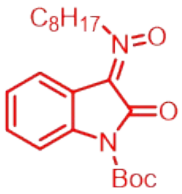
(Z)-1-(tert-butoxycarbonyl)-N-(naphthalen-1-ylmethyl)-2-oxoindolin-3-imine oxide (1r): Yield: 1.0 g (80%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 8.2, 5.0 Hz, 3H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.39 (m, 4H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.47 (s, 2H).



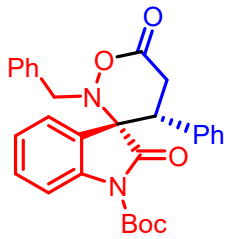
(Z)-1-(tert-butoxycarbonyl)-2-oxo-N-phenethylindolin-3-imine oxide (1s): Yield: 1.0 g (84%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.44 (td, *J* = 7.9, 1.5 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.23 (td, *J* = 7.8, 1.1 Hz, 3H), 5.02 – 4.94 (m, 2H), 3.30 – 3.22 (m, 2H), 1.68 (s, 9H).



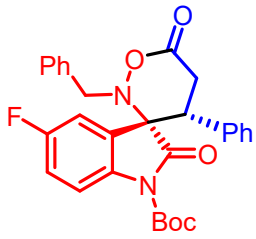
(Z)-1-(tert-butoxycarbonyl)-N-(4-chlorobenzyl)-2-oxoindolin-3-imine oxide (1t): Yield: 1.1 g (83%), yellow powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.44 (td, *J* = 7.9, 1.6 Hz, 1H), 7.32 – 7.12 (m, 7H), 4.82 (t, *J* = 7.3 Hz, 2H), 2.77 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.30 (dq, *J* = 9.7, 7.4 Hz, 2H), 1.68 (s, 9H).



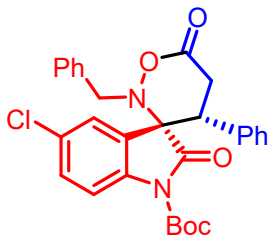
(Z)-1-(tert-butoxycarbonyl)-N-octyl-2-oxoindolin-3-imine oxide (1u): Yield: 1.1 g (86%), yellow liqiud; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.85 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.42 (td, *J* = 7.9, 1.5 Hz, 1H), 7.21 (td, *J* = 7.7, 1.0 Hz, 1H), 4.80 – 4.72 (m, 2H), 1.96 (p, *J* = 7.5 Hz, 2H), 1.68 (s, 9H), 1.46 – 1.39 (m, 2H), 1.37 – 1.23 (m, 8H), 0.91 – 0.83 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.97, 148.83, 136.92, 132.67, 131.64, 124.77, 124.21, 118.71, 114.34, 84.94, 64.02, 31.74, 29.13, 29.07, 28.56, 28.12, 26.56, 22.60, 14.07.



tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-(m-tolyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3a): Yield: 33 mg (70%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 1H), 7.67 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.31 – 7.11 (m, 9H), 6.80 (dt, *J* = 6.7, 1.6 Hz, 2H), 4.04 – 3.90 (m, 2H), 3.71 (dd, *J* = 13.5, 3.4 Hz, 1H), 3.60 (d, *J* = 14.2 Hz, 1H), 2.77 (dd, *J* = 14.9, 3.4 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.10, 170.53, 148.09, 139.69, 134.96, 134.42, 130.48, 129.19, 128.33, 128.26, 128.19, 128.01, 127.93, 125.86, 125.25, 124.21, 115.44, 84.26, 73.17, 57.85, 50.94, 32.53, 27.81; HRMS (ESI, m/z): calcd. for $C_{29}H_{28}N_2O_5$ $[M+Na]^+$ 507.1890, found 507.1894; HPLC analysis: 90:10 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 24.9 min, tR (major) = 30.9 min.

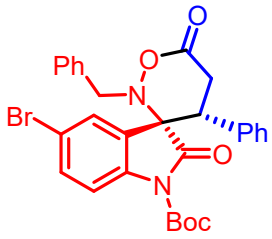


tert-butyl(3R,4'R)-2'-benzyl-5-fluoro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3b): Yield: 25 mg (50%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.40 (dd, *J* = 7.3, 2.8 Hz, 1H), 7.24 (ddt, *J* = 10.4, 7.4, 3.5 Hz, 7H), 7.20 – 7.15 (m, 3H), 7.13 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.82 (dt, *J* = 6.6, 1.6 Hz, 2H), 3.96 (dd, *J* = 14.5, 2.2 Hz, 2H), 3.70 – 3.53 (m, 2H), 2.77 (dd, *J* = 15.0, 3.3 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-d) δ 174.03, 170.48, 162.54 (d, J = 246.3 Hz), 148.03, 139.69, 134.27, 131.04 (d, J = 8.5 Hz), 130.53, 130.50, 128.33, 128.22, 127.99, 125.72, 125.24, 124.18, 115.35 (d, J = 21.4 Hz), 115.03, 84.32, 73.08, 57.14, 50.95, 32.49, 27.78; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -115.58 (q, *J* = 7.3, 5.2 Hz); HRMS (ESI, m/z): calcd. for $C_{29}H_{27}FN_2O_5$ $[M+Na]^+$ 525.1796, found 525.1802; HPLC analysis: 90:10 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 19.3 min, tR (major) =26.5 min.

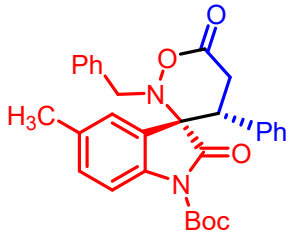


tert-butyl(3R,4'R)-2'-benzyl-5-chloro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3c): Yield: 26.4 mg (51%), white powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.43 (dd, J = 8.7, 2.2 Hz, 1H), 7.32 – 7.09 (m, 10H), 6.83 (dt, J = 6.7, 1.6 Hz, 2H), 4.05 – 3.93 (m, 2H), 3.71 – 3.57 (m, 2H), 2.77 (dd, J = 14.8, 3.2 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-d) δ 173.88, 169.75, 147.89, 138.19, 134.56, 134.02, 130.75,

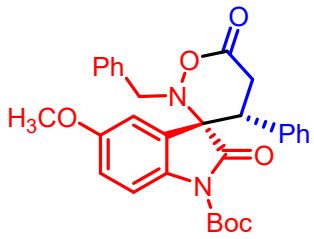
130.55, 129.24, 128.44, 128.38, 128.31, 128.08, 127.99, 127.72, 124.32, 116.78, 84.59, 73.29, 57.93, 51.18, 32.50, 27.77; HRMS (ESI, m/z): calcd. for C29H27ClN2O5 [M+Na]+ 541.1501, found 541.1506; HPLC analysis: 91:9 er (Chiralcel IH N-5, 20:80 iPrOH/Hexane, 0.5 mL/min), tR (minor) = 30.2 min, tR (major) = 39.0 min.



tert-butyl(3R,4'R)-2'-benzyl-5-bromo-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3d): Yield: 31.4 mg (56%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.30 – 7.19 (m, 8H), 7.18 – 7.08 (m, 2H), 6.81 (dt, *J* = 6.7, 1.6 Hz, 2H), 4.03 – 3.93 (m, 2H), 3.70 – 3.56 (m, 2H), 2.76 (dd, *J* = 14.8, 3.2 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.91, 169.63, 147.86, 138.70, 134.53, 134.00, 133.47, 129.24, 128.44, 128.38, 128.30, 128.08, 127.98, 127.14, 118.17, 117.13, 84.61, 73.26, 57.94, 51.21, 32.50, 28.06, 27.76; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}BrN_2O_5$ [M+Na]$^+$ 585.0996, found 585.0992; HPLC analysis: 88.5:11.5 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 32.4 min, tR (major) =41.4 min.

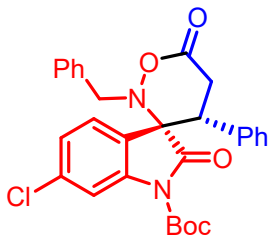


tert-butyl(3R,4'R)-2'-benzyl-5-methyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3e): Yield: 26.4 mg (53%), white powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 (d, J = 8.3 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.32 – 7.23 (m, 8H), 7.22 – 7.15 (m, 3H), 6.86 – 6.79 (m, 2H), 3.96 (d, J = 14.1 Hz, 2H), 3.70 (dd, J = 13.5, 3.2 Hz, 1H), 3.61 (t, J = 14.2 Hz, 1H), 2.77 (dd, J = 14.7, 3.3 Hz, 1H), 2.50 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-d) δ 174.43, 170.60, 148.16, 137.29, 135.13, 134.54, 131.00, 129.14, 128.31, 128.25, 128.15, 127.98, 127.88, 125.87, 124.62, 115.24, 84.05, 73.42, 57.79, 51.06, 32.62, 27.81, 21.25; HRMS (ESI, m/z): calcd. for $C_{29}H_{28}N_2O_5$ [M+Na]$^+$ 521.2047, found 521.2056; HPLC analysis: 92.5:7.5 er (Chiralcel IH N-5, 20:80 iPrOH/Hexane, 0.5 mL/min), tR (minor) = 26.7min, tR (major) =29.0 min.

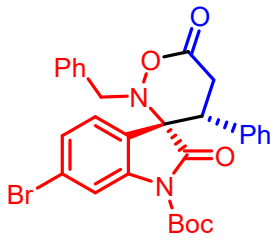


tert-butyl(3R,4'R)-2'-benzyl-5-methoxy-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-

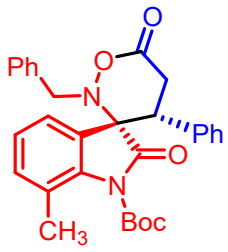
carboxylate(3f): Yield: 33.9 mg (66%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.9 Hz, 1H), 7.34 – 7.19 (m, 9H), 7.17 (d, *J* = 6.3 Hz, 1H), 7.12 (dd, *J* = 5.0, 1.8 Hz, 1H), 6.96 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.87 – 6.81 (m, 2H), 4.02 – 3.90 (m, 5H), 3.75 – 3.57 (m, 3H), 2.78 (dd, *J* = 14.9, 3.3 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.19, 170.52, 157.35, 148.18, 135.02, 134.41, 132.96, 129.16, 128.32, 128.26, 128.19, 128.02, 127.92, 127.02, 116.57, 115.47, 109.75, 84.02, 73.48, 57.83, 55.91, 50.95, 32.55, 29.72, 27.82; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_6$ $[M+Na]^+$ 537.1996, found 537.2000; HPLC analysis: 91:9 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 29.5 min, tR (major) = 34.6 min.



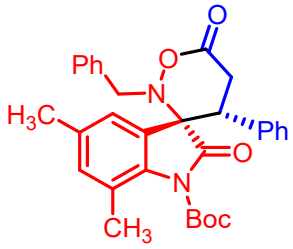
tert-butyl (3R,4'R)-2'-benzyl-6-chloro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3g): Yield: 28.4 mg (55%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.32 – 7.14 (m, 10H), 6.85 – 6.78 (m, 2H), 4.03 – 3.90 (m, 2H), 3.66 (dd, *J* = 13.6, 3.3 Hz, 1H), 3.58 (d, *J* = 14.1 Hz, 1H), 2.76 (dd, *J* = 14.9, 3.3 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.92, 170.00, 147.82, 140.62, 136.38, 134.58, 134.10, 129.20, 128.47, 128.36, 128.31, 128.06, 127.97, 125.37, 125.12, 124.26, 116.21, 84.76, 73.03, 57.89, 51.03, 32.50, 27.75; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}ClN_2O_5$ $[M+Na]^+$ 541.1501, found 541.1513; HPLC analysis: 91:9 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 31.2 min, tR (major) = 45.0 min.



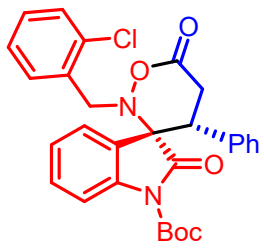
tert-butyl(3R,4'R)-2'-benzyl-6-bromo-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3h): Yield: 36.5 mg (65%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 1.6 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.31 – 7.27 (m, 1H), 7.27 – 7.14 (m, 9H), 6.82 (dt, *J* = 6.4, 1.7 Hz, 2H), 4.03 – 3.90 (m, 2H), 3.65 (dd, *J* = 13.6, 3.3 Hz, 1H), 3.58 (d, *J* = 14.1 Hz, 1H), 2.76 (dd, *J* = 14.9, 3.3 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.92, 169.90, 147.82, 140.69, 134.59, 134.09, 129.19, 128.49, 128.38, 128.32, 128.07, 127.97, 125.42, 124.81, 124.35, 118.96, 84.77, 73.10, 57.89, 50.98, 32.50, 27.75; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}BrN_2O_5$ $[M+Na]^+$ 585.0996, found 585.1005; HPLC analysis: 92:8 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 32.8min, tR (major) =48.8 min.



tert-butyl(3R,4'R)-2'-benzyl-7-methyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3i): Yield: 32.8 mg (66%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.32 – 7.22 (m, 7H), 7.22 – 7.13 (m, 3H), 6.82 (dd, *J* = 7.6, 1.8 Hz, 2H), 4.06 – 3.92 (m, 2H), 3.70 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.60 (d, *J* = 14.3 Hz, 1H), 2.77 (dd, *J* = 14.7, 3.2 Hz, 1H), 2.50 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.37, 170.58, 148.16, 137.31, 135.11, 134.56, 130.99, 129.14, 128.30, 128.24, 128.13, 127.99, 127.87, 125.89, 124.62, 115.23, 84.03, 73.41, 57.80, 51.07, 32.62, 27.81, 21.24; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_5$ $[M+Na]^+$ 521.2047, found 521.2056; HPLC analysis: 87:13 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 25.4 min, tR (major) =27.6 min.

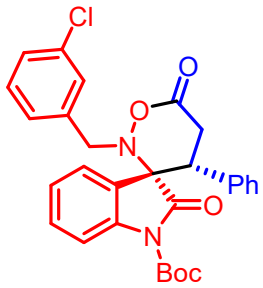


tert-butyl(3R,4'R)-2'-benzyl-5,7-dimethyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3j): Yield: 20 mg (40%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.20 (m, 7H), 7.18 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.04 (d, *J* = 1.7 Hz, 1H), 6.92 – 6.84 (m, 2H), 3.96 (dd, *J* = 14.6, 13.4 Hz, 1H), 3.85 – 3.73 (m, 2H), 3.53 (d, *J* = 14.4 Hz, 1H), 2.77 (dd, *J* = 14.6, 3.3 Hz, 1H), 2.44 (s, 3H), 2.06 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.40, 171.47, 147.69, 135.90, 135.35, 135.05, 134.81, 133.92, 129.00, 128.42, 128.25, 128.05, 127.99, 127.78, 127.13, 124.43, 122.18, 84.39, 73.83, 57.51, 50.49, 32.76, 27.62, 21.10, 19.48; HRMS (ESI, m/z): calcd. for $C_{31}H_{32}N_2O_5$ $[M+Na]^+$ 521.2047, found 521.2056; HPLC analysis: 91:9 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 33.7min, tR (major) =43.9 min.

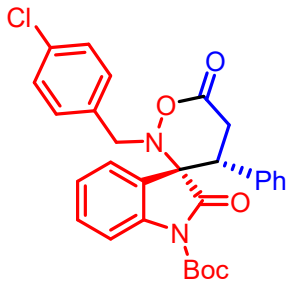


tert-butyl(3R,4'R)-2'-(4-bromobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3k): Yield: 26 mg (50%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 1H), 7.68 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.49 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.29 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.24 – 7.13 (m, 5H), 6.83 (dt, *J* = 6.7, 1.6 Hz,

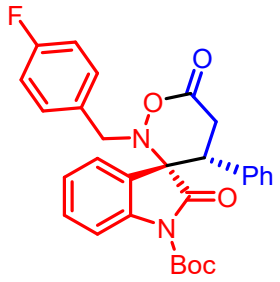
2H), 4.15 (d, *J* = 15.0 Hz, 1H), 3.96 (dd, *J* = 15.2, 13.2 Hz, 1H), 3.75 (dd, *J* = 13.2, 3.6 Hz, 1H), 3.61 (d, *J* = 15.0 Hz, 1H), 2.82 (dd, *J* = 15.1, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.70, 170.29, 148.13, 139.67, 134.47, 133.98, 132.94, 131.15, 130.61, 129.37, 129.23, 129.08, 128.38, 128.23, 128.02, 126.80, 125.60, 125.33, 124.33, 115.46, 84.39, 73.14, 54.77, 50.69, 32.51, 27.84; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}ClN_2NaO_5$ $[M+Na]^+$ 541.1501, found 541.1511; HPLC analysis: 89:11 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) =41.7 min, tR (major) =51.8 min.



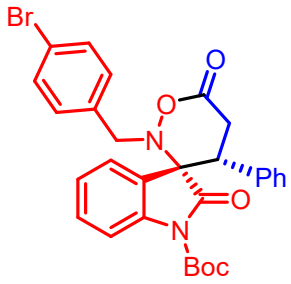
tert-butyl(3R,4'R)-2'-(3-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3l): Yield: 32 mg (62%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 1H), 7.66 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.44 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.25 – 7.05 (m, 7H), 6.81 (dt, *J* = 6.8, 1.6 Hz, 2H), 3.98 (dd, *J* = 15.0, 13.5 Hz, 1H), 3.89 (d, *J* = 14.4 Hz, 1H), 3.71 (dd, *J* = 13.5, 3.4 Hz, 1H), 3.56 (d, *J* = 14.4 Hz, 1H), 2.79 (dd, *J* = 15.0, 3.4 Hz, 1H), 1.43 (s, 8H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.83, 170.52, 148.02, 139.65, 137.09, 134.28, 134.14, 130.62, 129.56, 129.10, 128.38, 128.27, 128.16, 127.98, 127.29, 125.61, 125.34, 124.14, 115.53, 84.42, 73.17, 57.24, 50.86, 32.49, 27.80; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}ClN_2NaO_5$ $[M+Na]^+$ 541.1501, found 541.1511; HPLC analysis: 90:10 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) =39.9 min, tR (major) =44.9 min.



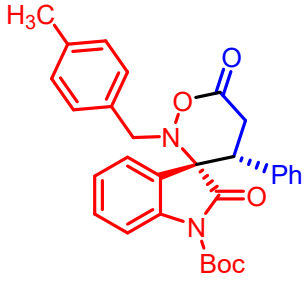
tert-butyl(3R,4'R)-2'-(4-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3m): Yield: 33 mg (65%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 1H), 7.76 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.54 (td, *J* = 7.9, 1.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.1 Hz, 1H), 7.38 – 7.19 (m, 8H), 6.89 (dt, *J* = 6.8, 1.6 Hz, 2H), 4.13 – 3.98 (m, 2H), 3.84 – 3.72 (m, 1H), 3.66 (d, *J* = 14.2 Hz, 1H), 2.88 (dd, *J* = 15.0, 3.3 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.95, 170.49, 148.02, 139.66, 134.24, 133.83, 133.40, 130.62, 130.59, 128.45, 128.36, 128.25, 127.97, 125.65, 125.30, 124.17, 115.48, 84.39, 73.15, 57.16, 50.93, 32.47, 27.80; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}ClN_2O_5$ $[M+Na]^+$ 541.1501, found 541.1510; HPLC analysis: 90:10 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 31.2 min, tR (major) = 39.3 min.



tert-butyl(3R,4'R)-2,6'-dioxo-4'-phenyl-2'-(3-phenylpropyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3n): Yield: 36.6 mg (73%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 1H), 7.69 – 7.62 (m, 1H), 7.44 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.16 (dtd, *J* = 8.5, 6.5, 5.9, 3.6 Hz, 5H), 6.98 – 6.88 (m, 2H), 6.85 – 6.75 (m, 2H), 4.04 – 3.90 (m, 2H), 3.69 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.57 (d, *J* = 14.1 Hz, 1H), 2.77 (dd, *J* = 14.9, 3.3 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, CDCl3) δ 174.03, 170.48, 162.54 (d, *J* = 246.3 Hz), 148.03, 139.69, 134.27, 131.04 (d, *J* = 8.5 Hz), 130.53, 130.50, 128.33, 128.22, 127.99, 125.72, 125.24, 124.18, 115.24, 115.24 (d, *J* = 42.9 Hz), 84.32, 73.08, 57.14, 50.95, 32.49, 27.78; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -114.28; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}FN_2NaO_5$ $[M+Na]^+$ 525.1796, found 525.1798; HPLC analysis: 90:10 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 32.5 min, tR (major) =41.7 min.

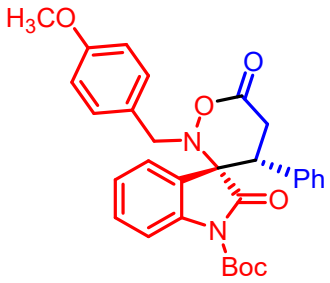


tert-butyl(3R,4'R)-2'-(2-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3o): Yield: 32 mg (58%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.44 (td, *J* = 7.9, 1.5 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.22 – 7.12 (m, 3H), 7.12 – 7.06 (m, 2H), 6.79 (dt, *J* = 6.7, 1.6 Hz, 2H), 3.97 (dd, *J* = 15.0, 13.5 Hz, 1H), 3.89 (d, *J* = 14.3 Hz, 1H), 3.74 – 3.63 (m, 1H), 3.54 (d, *J* = 14.2 Hz, 1H), 2.77 (dd, *J* = 15.0, 3.3 Hz, 1H), 1.42 (s, 8H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.92, 170.48, 148.02, 139.65, 134.24, 133.95, 131.41, 130.93, 130.59, 128.36, 128.26, 127.97, 125.65, 125.30, 124.17, 122.02, 115.48, 84.40, 73.17, 57.21, 50.93, 32.47, 27.81; HRMS (ESI, m/z): calcd. for $C_{29}H_{27}BrN_2NaO_5$ $[M+Na]^+$ 585.0996, found 585.0998; HPLC analysis: 90:10 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) =34.0 min, tR (major) =42.0 min.

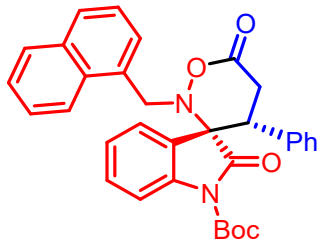


tert-butyl (3R,4'R)-2'-(4-methylbenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-

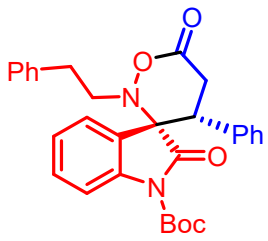
carboxylate(3p): Yield: 21 mg (43%), white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.8, 1.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.23 – 7.10 (m, 3H), 7.10 – 7.01 (m, 4H), 6.79 (dt, *J* = 6.7, 1.6 Hz, 2H), 4.02 – 3.88 (m, 2H), 3.69 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.57 (d, *J* = 14.0 Hz, 1H), 2.76 (dd, *J* = 14.9, 3.4 Hz, 1H), 2.29 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.14, 170.45, 148.10, 139.71, 137.60, 134.46, 131.75, 130.40, 129.27, 128.91, 128.29, 128.14, 128.02, 125.92, 125.17, 124.22, 115.39, 84.13, 73.10, 57.65, 50.99, 32.54, 27.80, 21.16; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_5$ $[M+Na]^+$ 521.2047, found 521.2047; HPLC analysis: 88:12 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 38.1min, tR (major) =45.5 min.



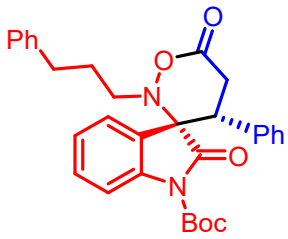
tert-butyl(3R,4'R)-2'-(4-methoxybenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3q): Yield: 36 mg (70%), white powder; ^{1}H NMR (400 MHz, CDCl3) δ 7.74 – 7.68 (m, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.26 (s, 2H), 7.24 – 7.11 (m, 4H), 7.08 – 7.03 (m, 2H), 6.76 (td, *J* = 8.3, 1.7 Hz, 4H), 3.96 (dd, *J* = 14.3, 3.4 Hz, 2H), 3.75 (s, 3H), 3.72 – 3.63 (m, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.76 (dd, *J* = 14.9, 3.3 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.29, 170.40, 159.41, 148.08, 139.74, 134.37, 130.83, 130.39, 128.26, 128.13, 128.05, 126.45, 125.87, 125.12, 124.22, 115.39, 113.58, 84.09, 72.94, 57.41, 55.19, 50.99, 32.51, 27.77; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_6$ $[M+Na]^+$ 537.1996, found 537.2000; HPLC analysis: 93.5:6.5 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 31.5 min, tR (major) = 37.2 min.



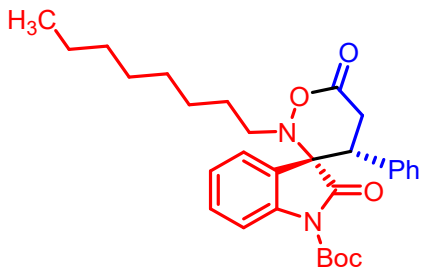
tert-butyl(3R,4'R)-2'-(naphthalen-1-ylmethyl)-2,6'-dioxo-4'-phenylspiro[indoline -3,3'-[1,2]oxazinane]-1-carboxylate (3r): Yield: 38 mg (72%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.75 (dt, *J* = 8.2, 2.0 Hz, 3H), 7.55 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.22 – 7.09 (m, 4H), 6.81 – 6.64 (m, 2H), 4.46 (d, *J* = 13.6 Hz, 1H), 4.12 (d, *J* = 13.6 Hz, 1H), 4.00 (t, *J* = 14.2 Hz, 1H), 3.70 (dd, *J* = 13.6, 3.1 Hz, 1H), 2.73 (dd, *J* = 14.7, 3.1 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.45, 169.94, 148.05, 139.97, 134.31, 133.64, 132.36, 130.54, 129.75, 129.16, 128.80, 128.38, 128.28, 128.15, 128.04, 126.32, 125.80, 125.75, 125.23, 124.94, 124.45, 124.31, 115.49, 84.10, 73.43, 56.19, 51.29, 32.53, 27.76; HRMS (ESI, m/z): calcd. for $C_{33}H_{30}N_2NaO_5$ $[M+Na]^+$ 557.2047, found 557.2047; HPLC analysis: 87.5:12.5 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 18.1 min, tR (major) =19.2 min.



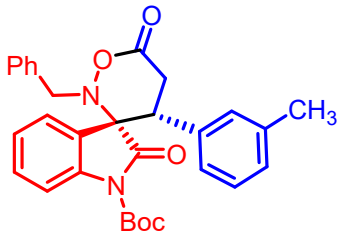
tert-butyl(3R,4'R)-2,6'-dioxo-2'-phenethyl-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3s): Yield: 34 mg (68%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.34 (td, *J* = 7.9, 1.5 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.12 – 7.08 (m, 2H), 7.02 (ddd, *J* = 7.8, 4.3, 2.1 Hz, 1H), 6.79 (ddt, *J* = 6.6, 4.2, 1.9 Hz, 2H), 3.90 (dd, *J* = 15.3, 13.2 Hz, 1H), 3.67 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.05 (tt, *J* = 10.4, 5.0 Hz, 1H), 2.97 – 2.92 (m, 2H), 2.82 (dd, *J* = 15.2, 3.7 Hz, 1H), 2.68 – 2.58 (m, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.00, 170.75, 148.07, 139.46, 138.69, 134.52, 130.30, 128.96, 128.43, 128.35, 128.31, 128.18, 127.96, 126.37, 125.82, 125.21, 124.22, 124.09, 115.35, 84.41, 73.15, 55.52, 50.71, 33.88, 32.50, 27.83; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2NaO_5$ $[M+Na]^+$ 521.2047, found 521.2043; HPLC analysis: 82:18 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 33.2 min, tR (major) =45.6 min.



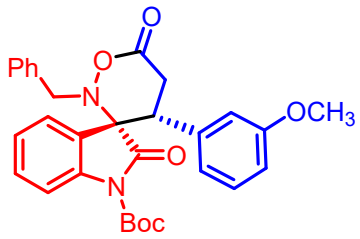
tert-butyl(3R,4'R)-2,6'-dioxo-4'-phenyl-2'-(3-phenylpropyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3t)): Yield: 36 mg (70%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.26 (td, *J* = 7.9, 1.4 Hz, 1H), 7.17 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.15 – 7.07 (m, 3H), 7.07 – 6.91 (m, 6H), 6.72 – 6.64 (m, 2H), 3.80 (dd, *J* = 15.0, 13.4 Hz, 1H), 3.55 (dd, *J* = 13.4, 3.5 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.58 – 2.49 (m, 1H), 2.49 – 2.41 (m, 1H), 2.23 (dt, *J* = 13.7, 7.1 Hz, 1H), 2.02 – 1.84 (m, 1H), 1.78 (dqd, *J* = 9.0, 7.0, 5.2 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.35, 170.67, 148.15, 141.67, 139.52, 134.60, 130.28, 128.50, 128.36, 128.31, 128.17, 127.96, 126.04, 125.81, 125.19, 124.21, 115.34, 84.33, 73.40, 53.28, 50.84, 32.77, 32.52, 28.69, 27.86; HRMS (ESI, m/z): calcd. for $C_{31}H_{32}N_2O_5$ $[M+Na]^+$ 535.2203, found 535.2204; HPLC analysis: 89:11 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 30.1 min, tR (major) = 35.0 min.



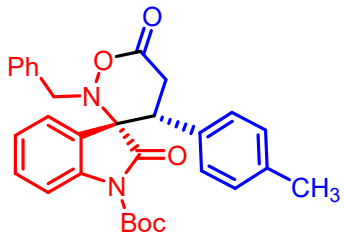
tert-butyl(3R,4'R)-2'-(4-fluorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3u): Yield: 20 mg (50%), white powder; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, J = 8.1 Hz, 1H), 7.54 (dd, J = 7.5, 1.5 Hz, 1H), 7.43 – 6.95 (m, 8H), 6.79 (dt, J = 6.5, 1.6 Hz, 2H), 3.90 (dd, J = 15.0, 13.4 Hz, 1H), 3.66 (dd, J = 13.4, 3.5 Hz, 1H), 2.75 (ddd, J = 21.3, 14.1, 5.1 Hz, 2H), 2.30 (dt, J = 13.3, 7.6 Hz, 1H), 1.63 (q, J = 10.2, 7.8 Hz, 3H), 1.43 (s, 9H), 1.30 – 1.17 (m, 11H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.38, 170.75, 148.21, 139.52, 134.67, 130.20, 128.32, 128.12, 127.95, 126.21, 125.14, 124.18, 115.28, 84.29, 73.37, 54.01, 50.86, 32.55, 31.79, 29.26, 29.13, 27.83, 27.15, 26.71, 22.62, 14.09; HRMS (ESI, m/z): calcd. for $C_{30}H_{38}N_2NaO_5$ $[M+Na]^+$ 431.1577, found 431.1582; HPLC analysis: 82.5:17.5er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) =19.6 min, tR_t(major) =26.9 min.



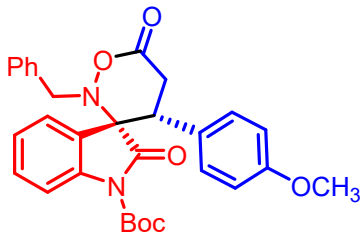
tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-(p-tolyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3v): Yield: 26 mg (52%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.39 (dtd, *J* = 29.0, 7.6, 1.3 Hz, 3H), 7.32 – 7.18 (m, 8H), 7.07 – 6.96 (m, 3H), 6.64 (s, 1H), 6.55 (dd, *J* = 5.4, 3.6 Hz, 1H), 4.01 – 3.89 (m, 2H), 3.71 – 3.57 (m, 2H), 2.76 (dd, *J* = 15.0, 3.4 Hz, 1H), 2.20 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.10, 170.54, 148.16, 139.74, 137.97, 135.01, 134.33, 130.42, 129.20, 128.87, 128.53, 128.26, 128.16, 127.91, 125.97, 125.22, 125.11, 124.19, 115.39, 84.13, 73.17, 57.87, 50.86, 32.49, 27.80, 21.29; HRMS (ESI, m/z): calcd. for $C_{29}H_{28}N_2O_5$ $[M+Na]^+$ 521.2047, found 521.2046; HPLC analysis: 94:6 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 24.1 min, tR (major) = 25.4 min.



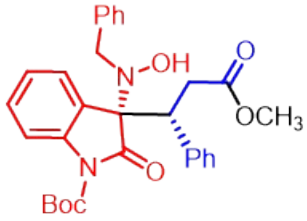
tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3w): Yield: 28 mg (55%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.32 – 7.17 (m, 6H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.68 (dd, *J* = 13.5, 3.4 Hz, 1H), 3.64 – 3.57 (m, 4H), 2.78 (dd, *J* = 15.0, 3.4 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.98, 170.52, 159.36, 148.15, 139.80, 135.87, 134.95, 130.45, 129.31, 129.19, 128.26, 127.93, 125.93, 125.24, 124.19, 120.28, 115.45, 114.42, 112.83, 84.29, 73.09, 57.86, 55.04, 50.94, 32.50, 27.77; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_6$ $[M+Na]^+$ 537.1996, found 537.1989; HPLC analysis: 11:89 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 37.3 min, tR (major) = 44.6 min.



tert-buty(3R,4'R)-2'-benzyl-4'-(3-methoxyphenyl)-2,6'-dioxospiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3x): Yield: 29 mg (60%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 1H), 7.66 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.24 (tq, *J* = 5.0, 2.3 Hz, 6H), 6.75 – 6.65 (m, 4H), 4.00 – 3.88 (m, 2H), 3.71 (s, 3H), 3.66 (dd, *J* = 13.3, 3.2 Hz, 1H), 3.59 (d, *J* = 14.2 Hz, 1H), 2.74 (dd, *J* = 14.9, 3.4 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.19, 170.70, 159.35, 148.14, 139.66, 135.01, 130.40, 129.17, 129.10, 128.25, 127.90, 126.24, 126.00, 125.23, 124.19, 115.47, 113.66, 84.23, 73.30, 57.89, 55.11, 50.36, 32.76, 27.78. HRMS (ESI, m/z): calcd. for $C_{29}H_{28}N_2O_5$ $[M+Na]^+$ 521.2047, found 521.2057; HPLC analysis: 93:7 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 30.4min, tR (major) =37.6 min.



tert-butyl(3R,4'R)-2'-benzyl-4'-(4-methoxyphenyl)-2,6'-dioxospiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3y): Yield: 23 mg (45%), white powder; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.43 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 7.9, 3.5 Hz, 6H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 4.01 – 3.93 (m, 1H), 3.92 (d, *J* = 3.1 Hz, 1H), 3.66 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.58 (d, *J* = 14.2 Hz, 1H), 2.74 (dd, *J* = 14.9, 3.3 Hz, 1H), 2.23 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.24, 170.61, 148.16, 139.68, 137.83, 135.05, 131.34, 130.41, 129.17, 129.02, 128.26, 127.89, 127.86, 125.99, 125.23, 124.20, 115.45, 84.13, 73.30, 57.86, 50.71, 32.64, 27.78, 21.00; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}N_2O_6$ $[M+Na]^+$ 537.1996, found 537.1996; HPLC analysis: 90:10 er (Chiralcel IH N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 35.2 min, tR (major) = 48.8 min.

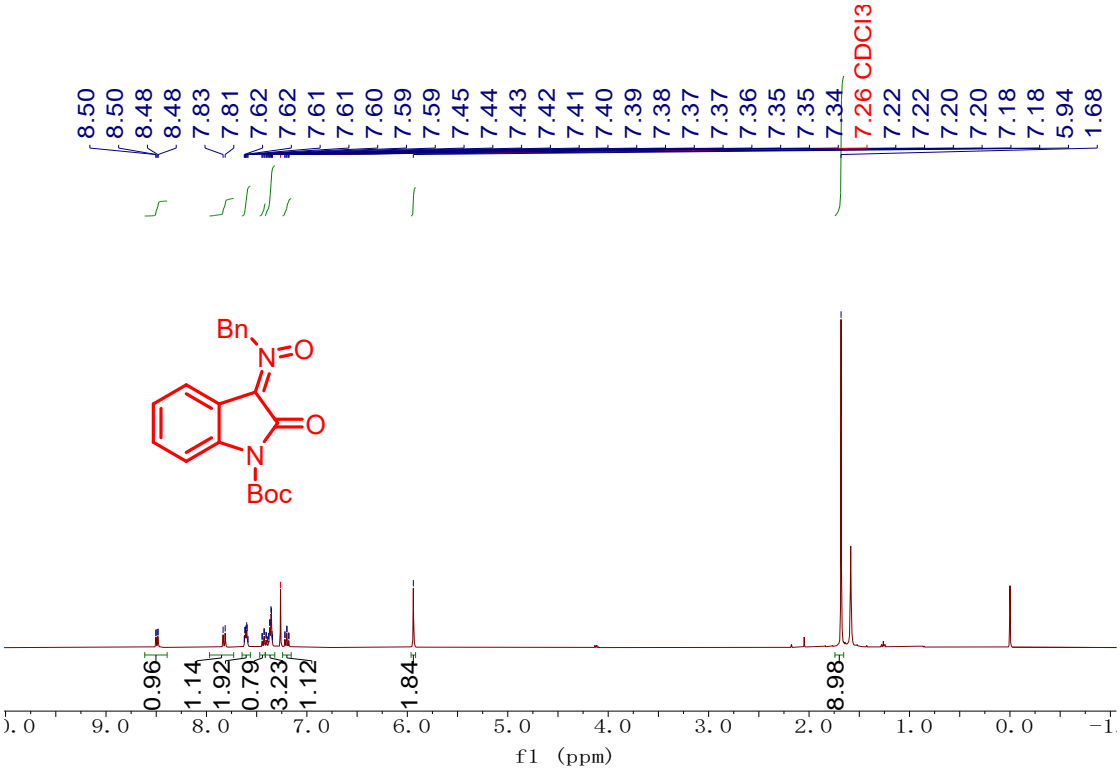


tert-butyl(R)-3-(benzyl(hydroxy)amino)-3-((R)-3-methoxy-3-oxo-1-phenylpropyl)-2-oxoindoline-1-carboxylate (4): Yield: 46 mg (90%), white solid; 1H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 1H), 7.44 – 7.40 (m, 1H), 7.28 (d, *J* = 4.3 Hz, 4H), 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 2H), 7.00 (tdd, *J* = 8.6, 7.0, 4.7 Hz, 3H), 6.92 – 6.88 (m, 2H), 6.18 (s, 1H), 4.27 – 4.13 (m, 2H), 3.62 (s, 4H), 3.33

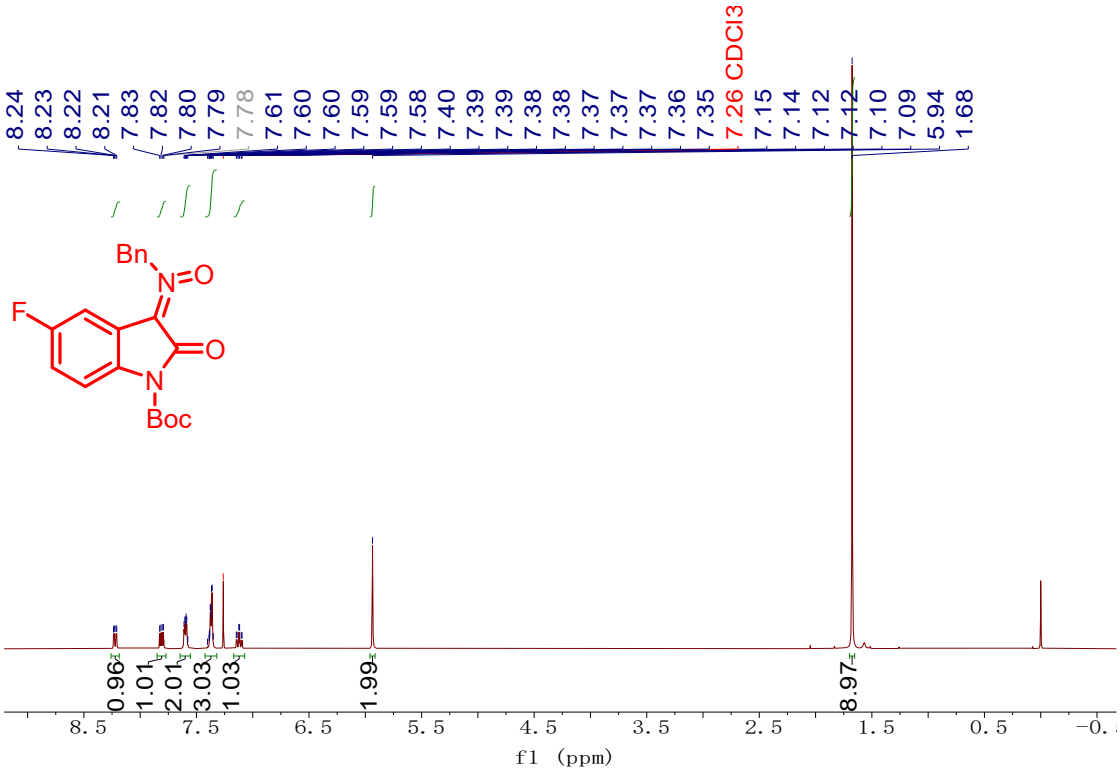
(d, *J* = 12.8 Hz, 1H), 2.67 (dd, *J* = 15.2, 2.2 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.91, 172.81, 148.41, 139.21, 138.05, 137.39, 129.19, 129.11, 129.08, 128.85, 128.05, 127.64, 127.16, 125.80, 124.16, 114.04, 84.31, 75.61, 58.52, 52.24, 47.16, 33.74, 28.10; HRMS (ESI, m/z): calcd. for $C_{30}H_{32}N_2NaO_6$ $[M+Na]^+$ 539.2153, found 539.2155; HPLC analysis: 91:9 er (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), tR (minor) = 9.4 min, tR (major) = 24.3 min.

VII: ^{1}H, ^{13}C, ^{19}F and HPLC spectra:

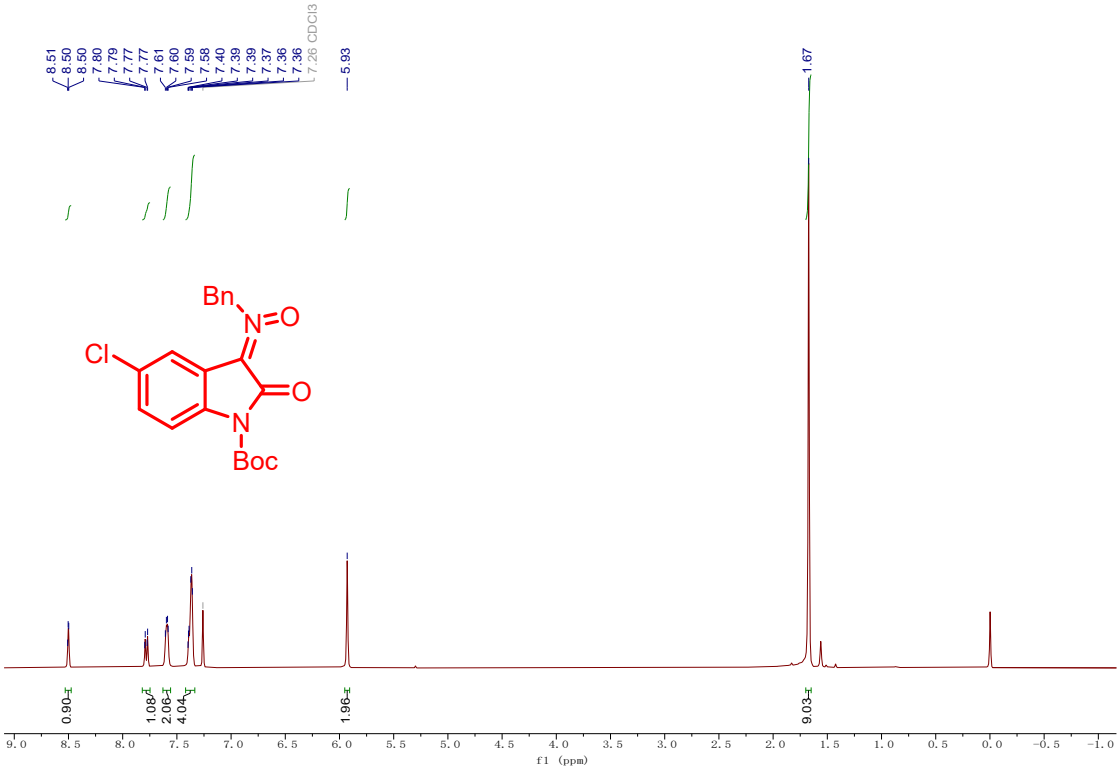
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide (1a)



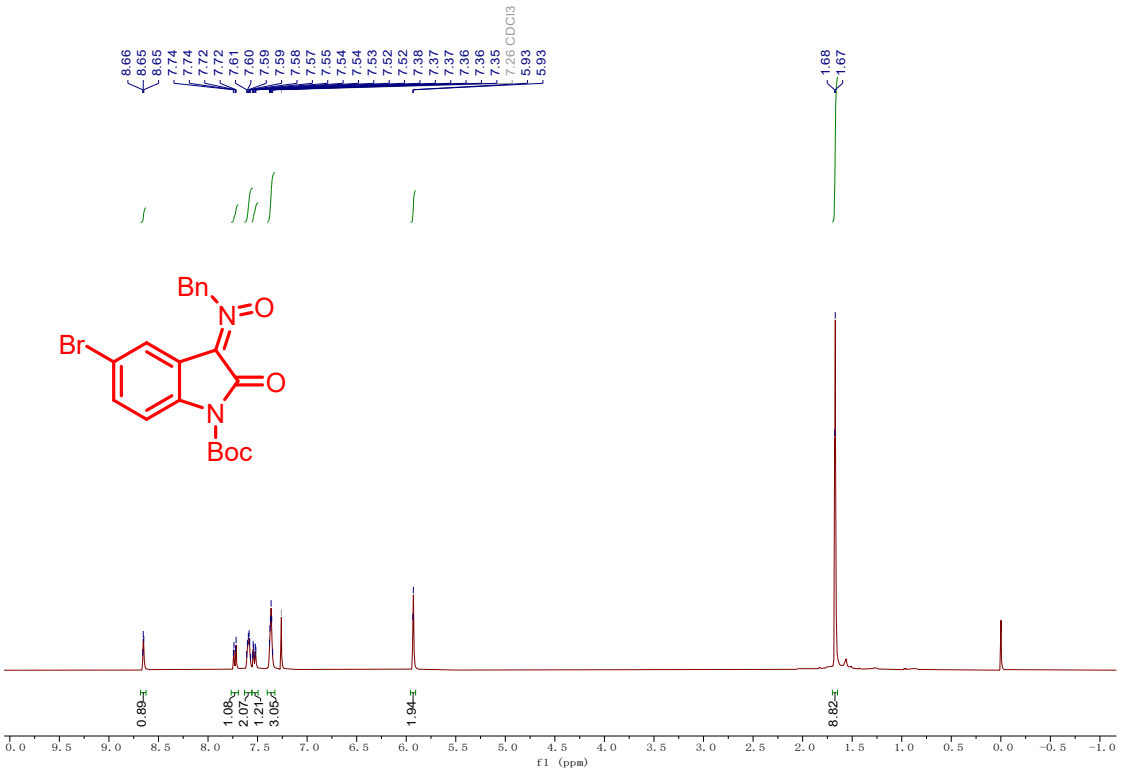
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-fluoro-2-oxoindolin-3-imine oxide(1b)



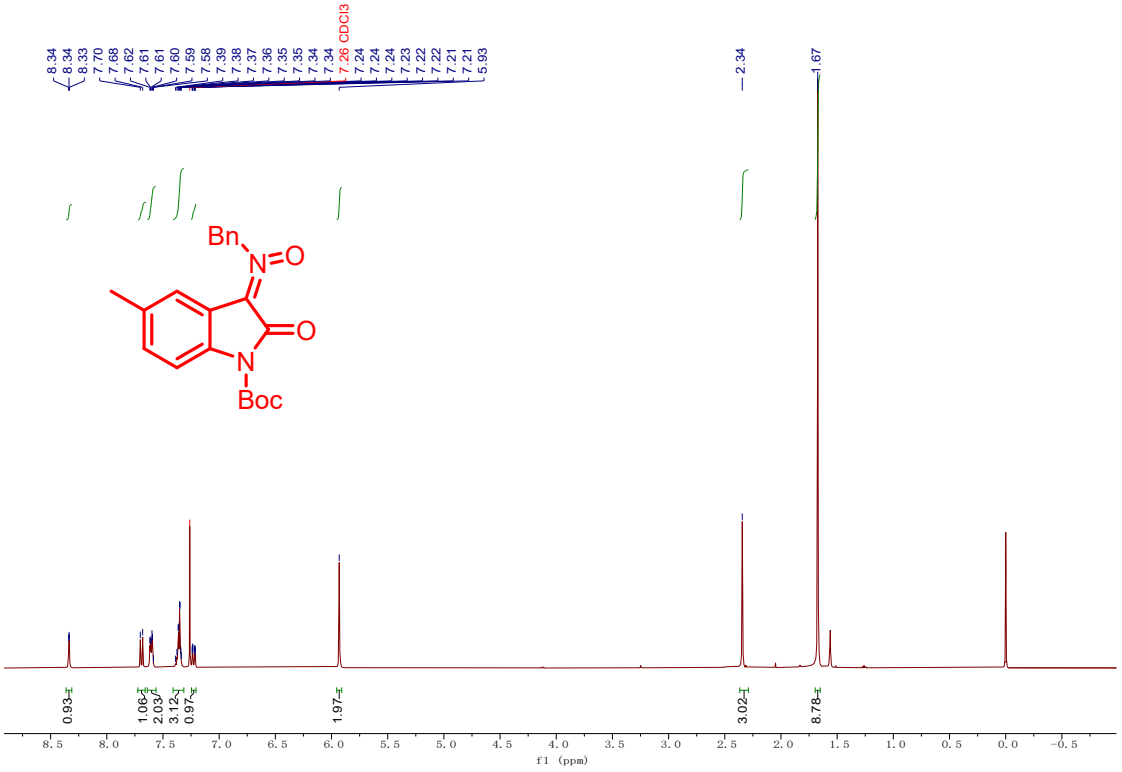
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-chloro-2-oxoindolin-3-imine oxide(1c)



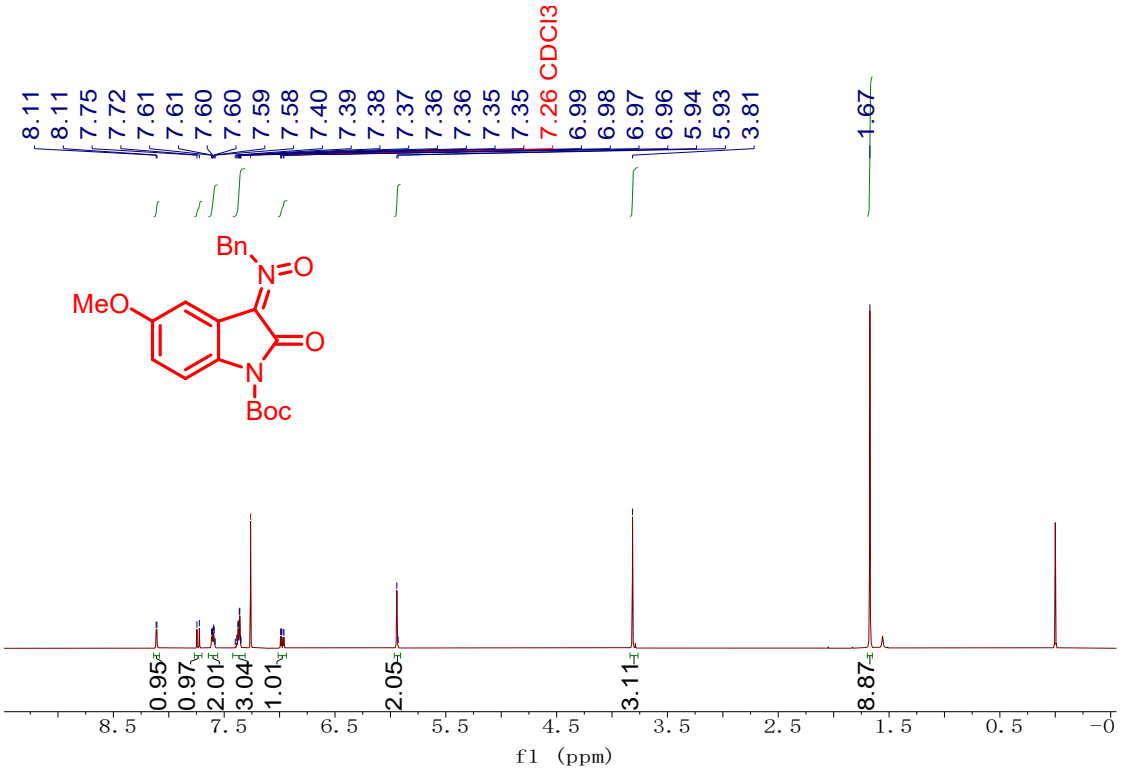
(Z)-N-benzyl-5-bromo-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide(1d)



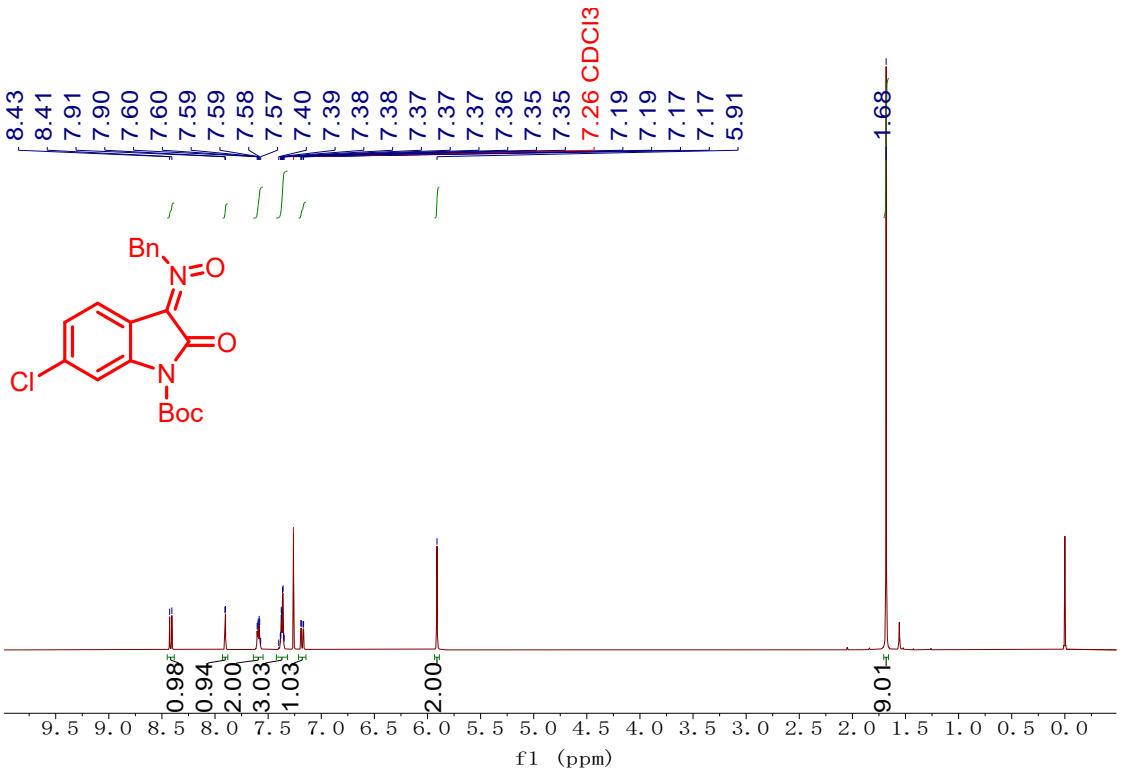
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-methyl-2-oxoindolin-3-imine oxide(1e)



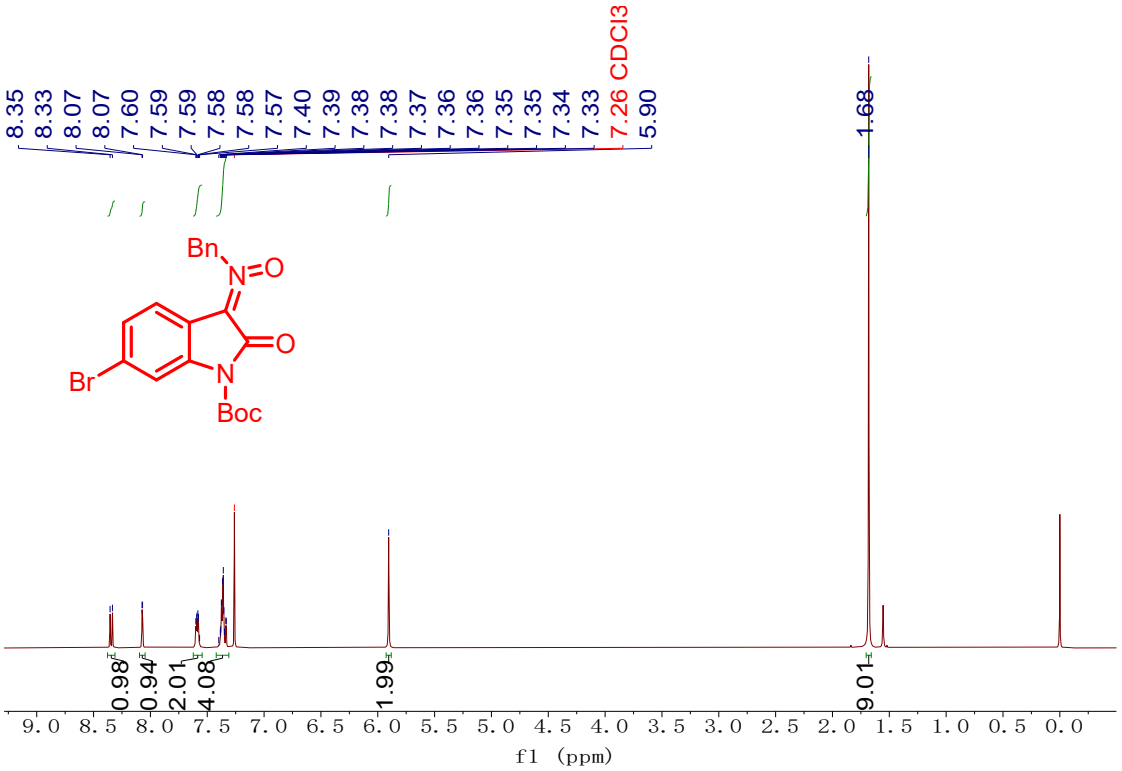
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5-methoxy-2-oxoindolin-3-imine oxide(1f)



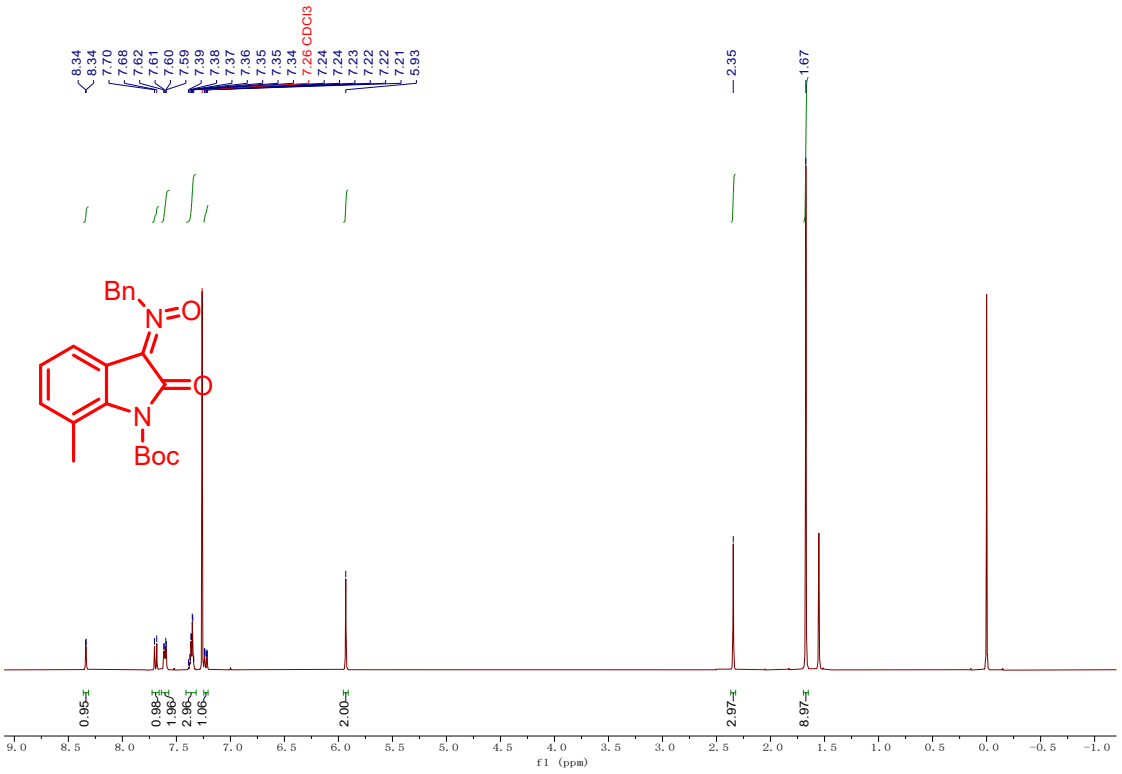
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-6-chloro-2-oxoindolin-3-imine oxide(1g)



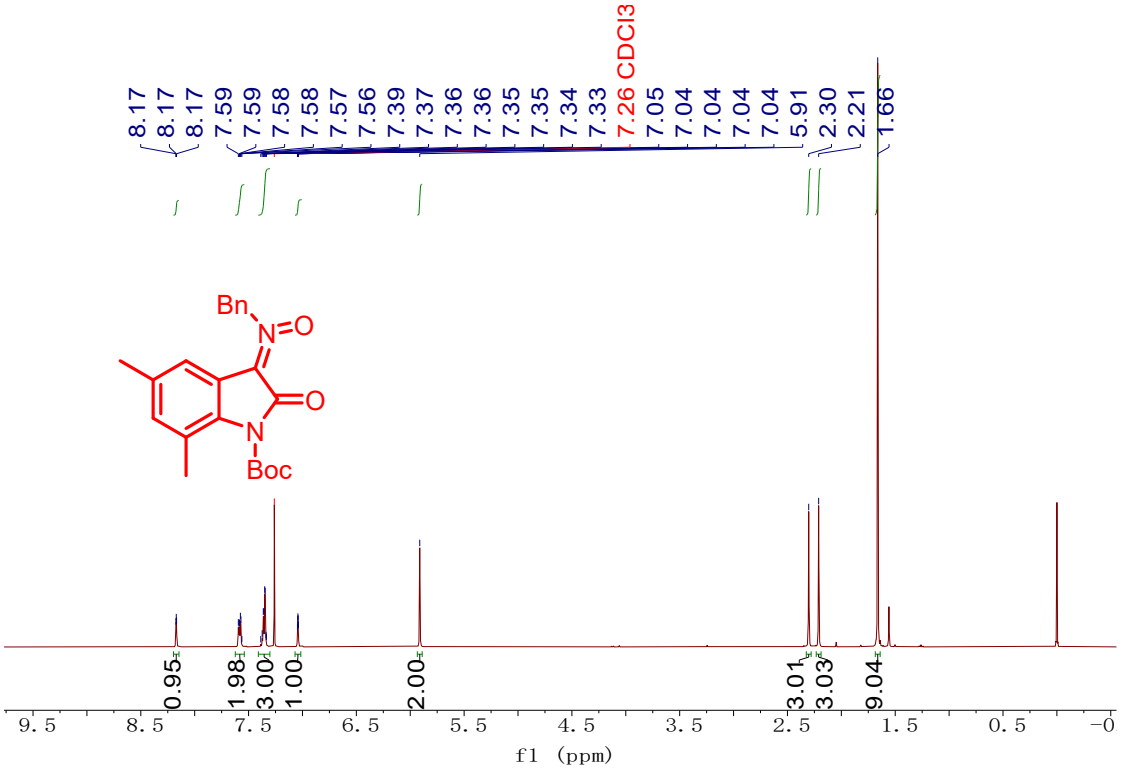
(Z)-N-benzyl-6-bromo-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide(1h)



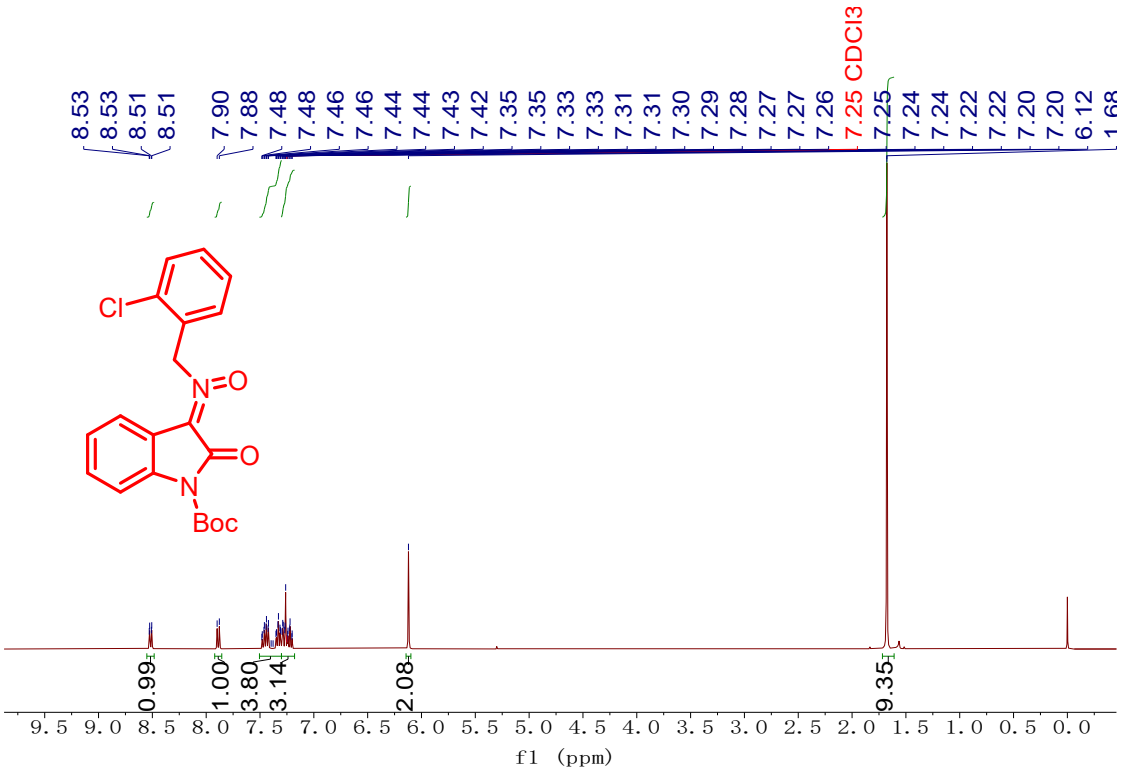
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-7-methyl-2-oxoindolin-3-imine oxide(1i)



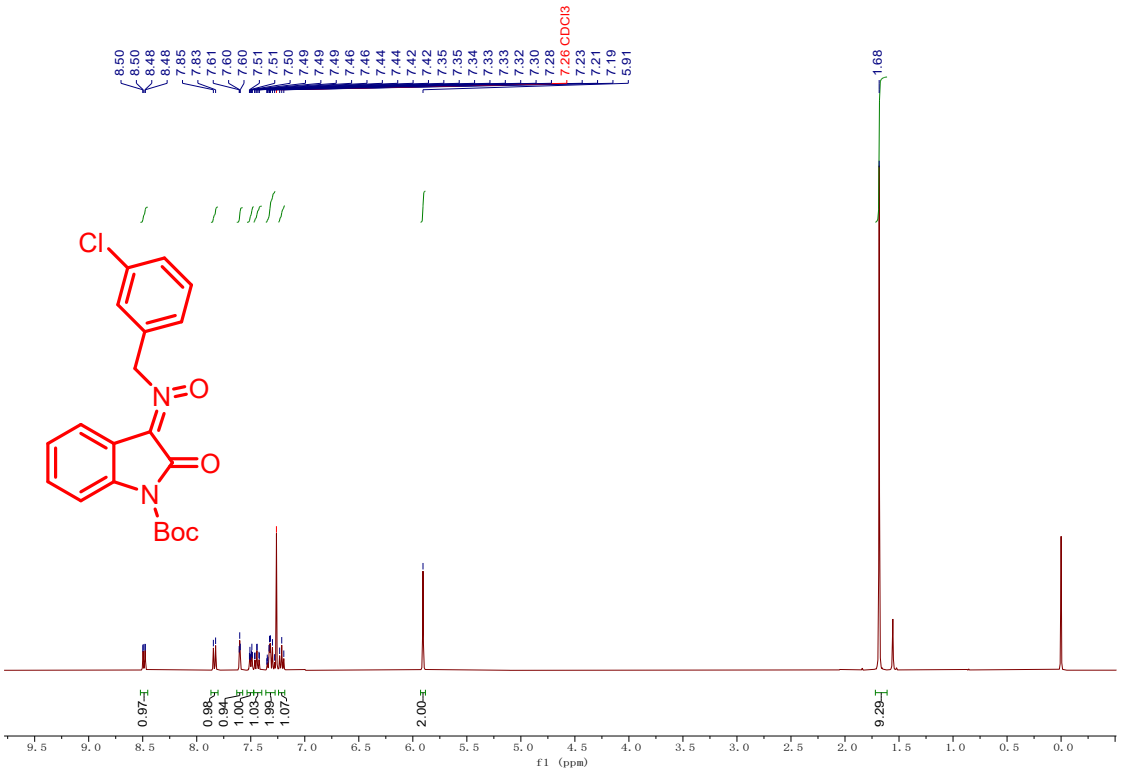
(Z)-N-benzyl-1-(tert-butoxycarbonyl)-5,7-dimethyl-2-oxoindolin-3-imineoxide (1j)



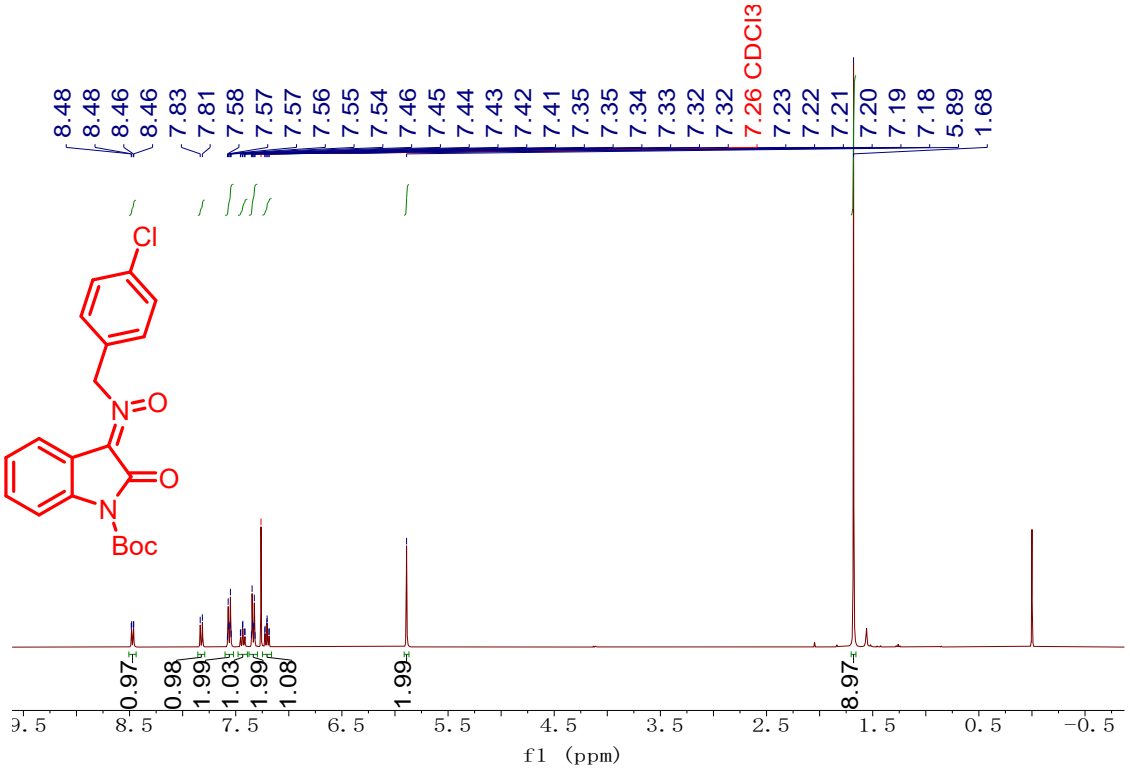
(Z)-1-(tert-butoxycarbonyl)-N-(2-chlorobenzyl)-2-oxoindolin-3-imine oxide(1k)



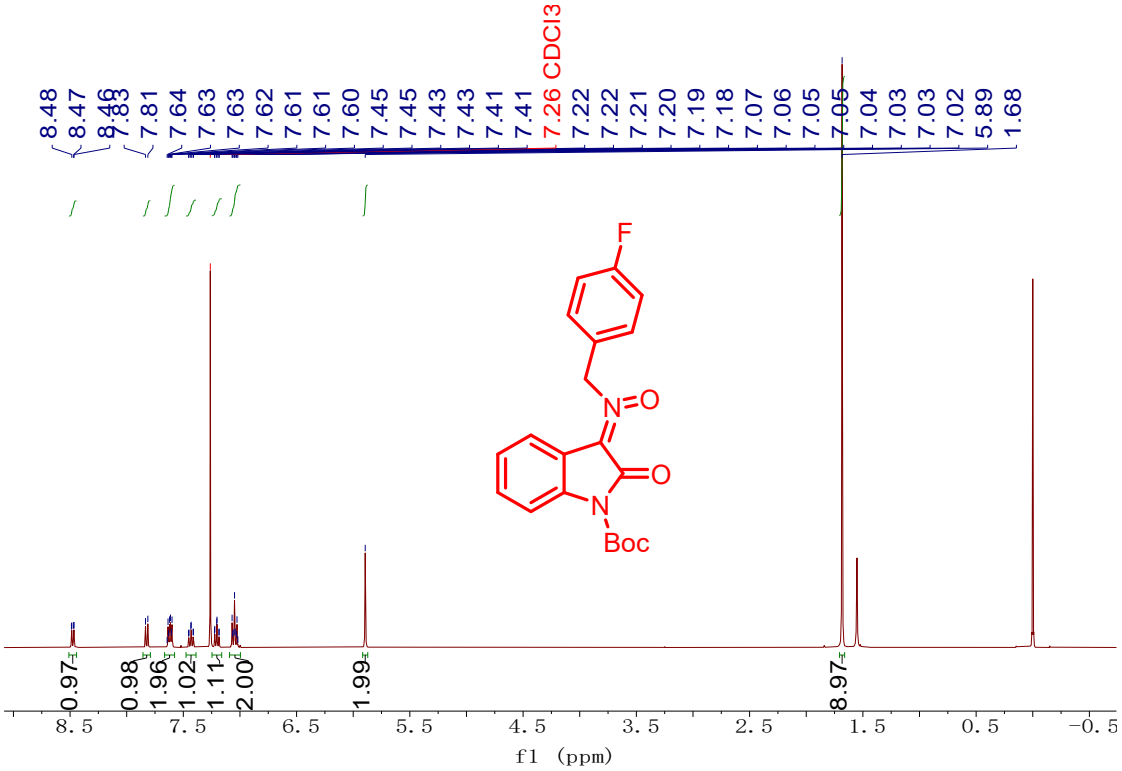
(Z)-N-(4-bromobenzyl)-1-(tert-butoxycarbonyl)-2-oxoindolin-3-imine oxide(1l)



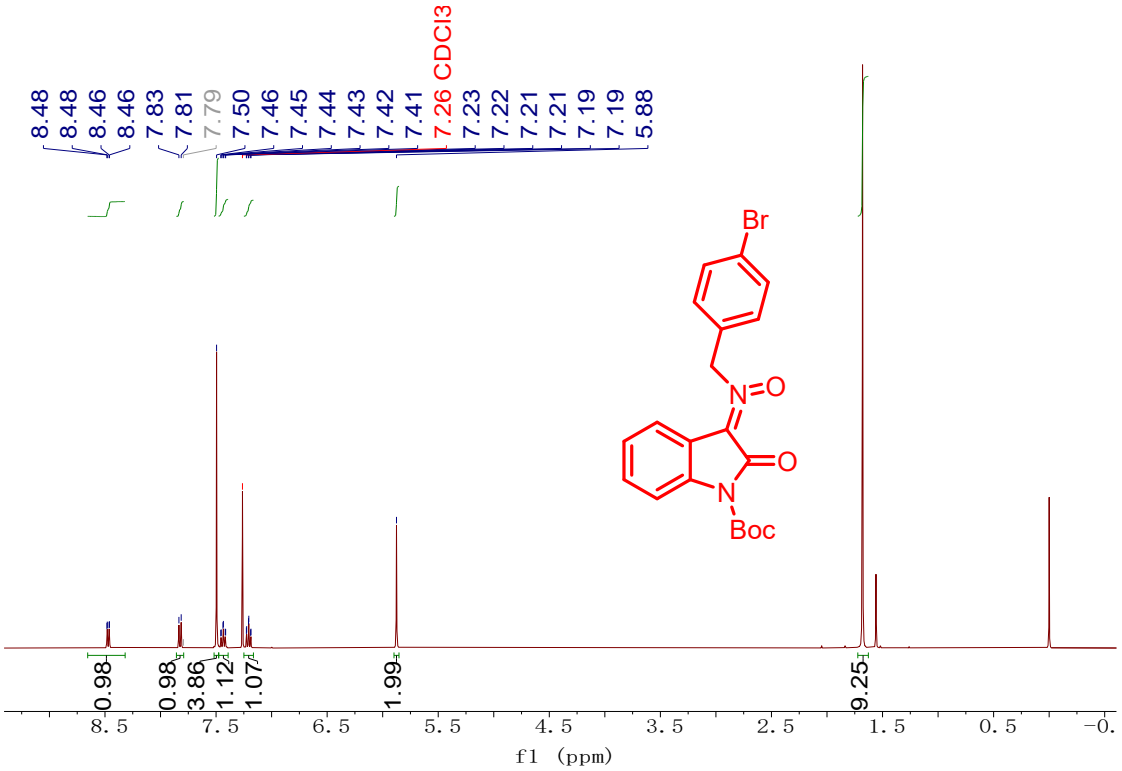
(Z)-1-(tert-butoxycarbonyl)-N-(4-chlorobenzyl)-2-oxoindolin-3-imine oxide(1m)



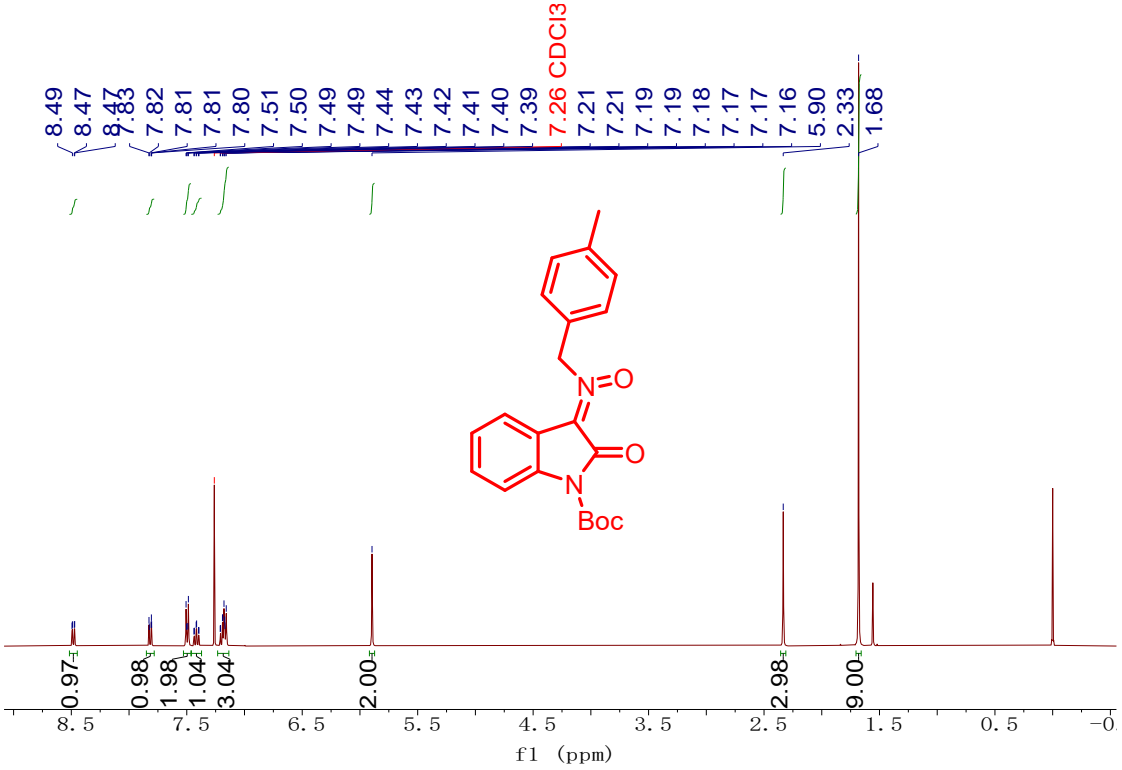
(Z)-1-(tert-butoxycarbonyl)-N-(3-chlorobenzyl)-2-oxoindolin-3-imine oxide(1n)



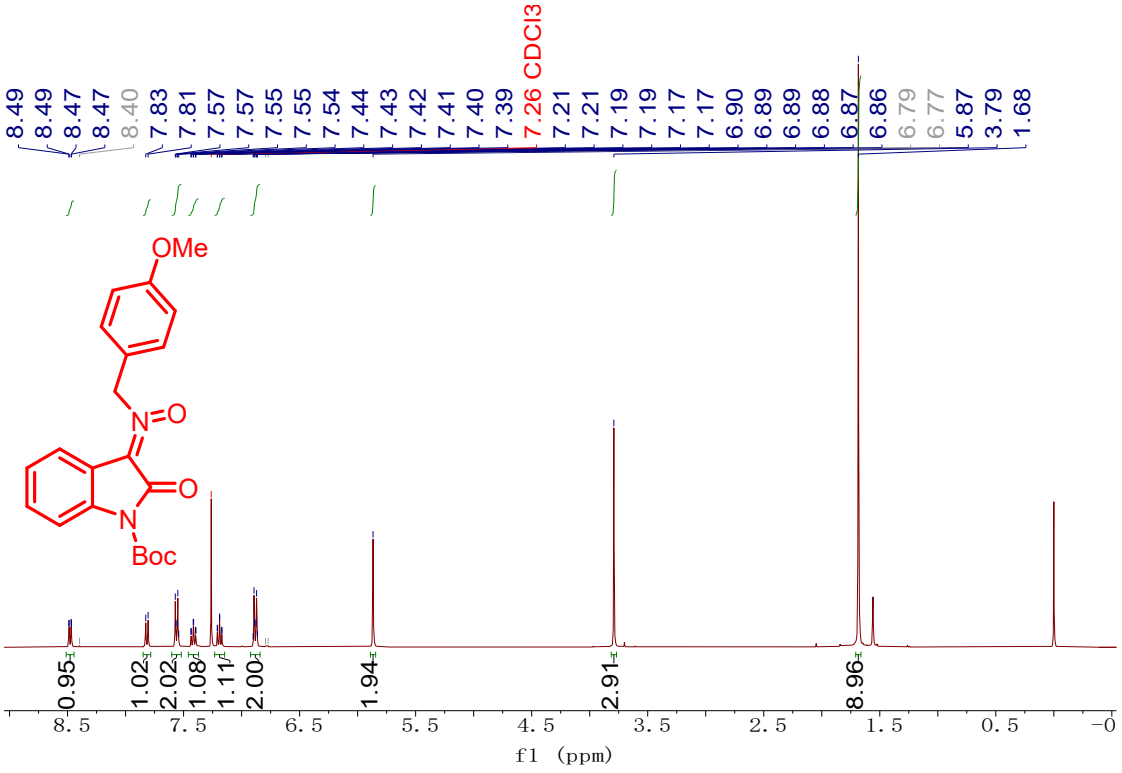
(Z)-1-(tert-butoxycarbonyl)-N-(4-fluorobenzyl)-2-oxoindolin-3-imine oxide(1o)



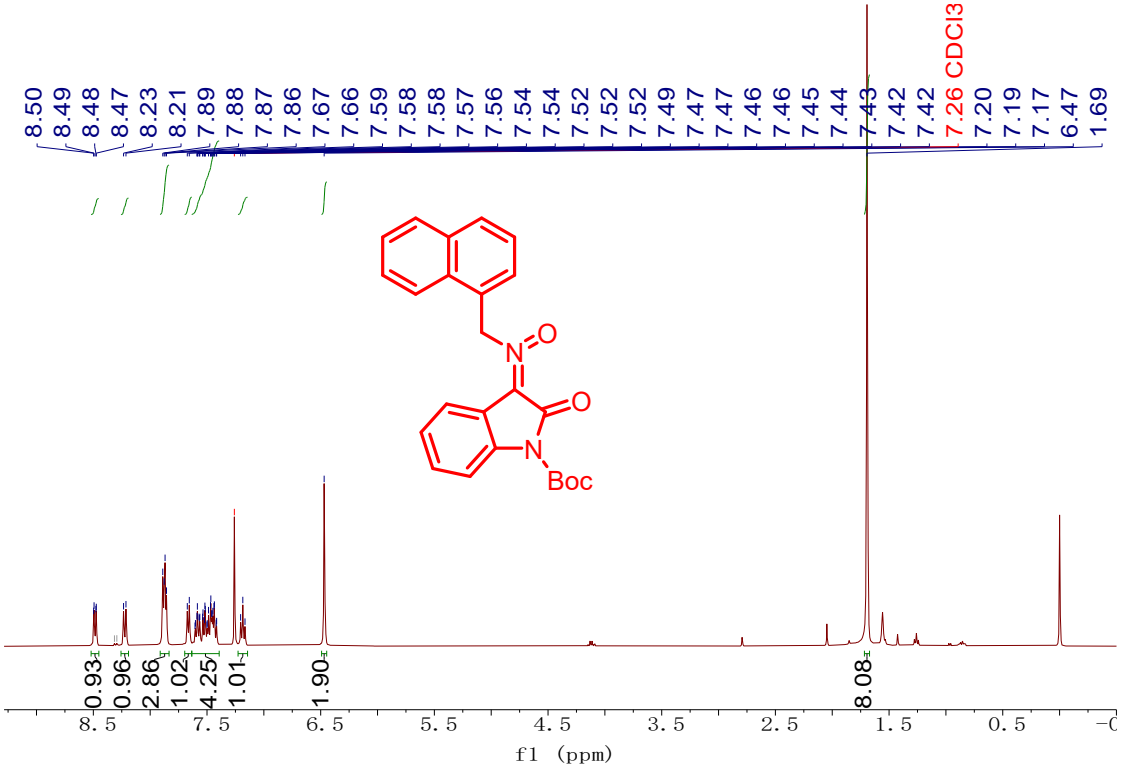
(Z)-1-(tert-butoxycarbonyl)-N-(4-methylbenzyl)-2-oxoindolin-3-imine oxide(1p)



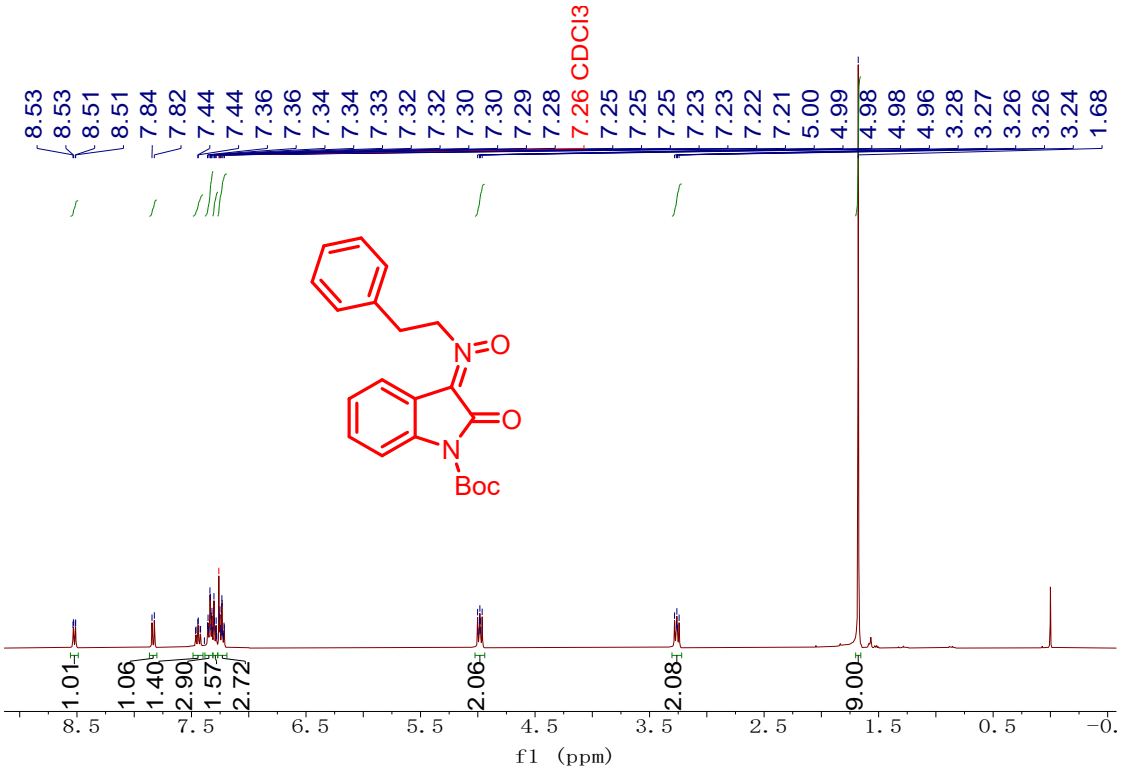
(Z)-1-(tert-butoxycarbonyl)-N-(4-methoxybenzyl)-2-oxoindolin-3-imine oxide(1q)



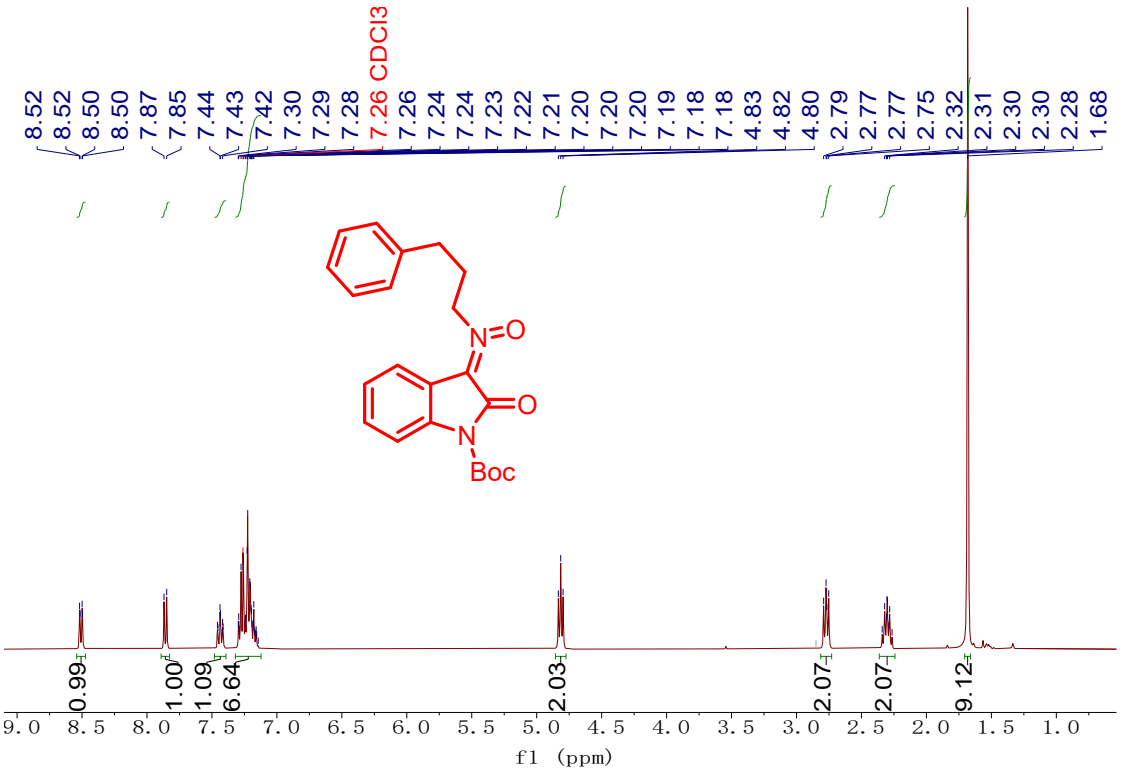
(Z)-1-(tert-butoxycarbonyl)-N-(naphthalen-1-ylmethyl)-2-oxoindolin-3-imine oxide(1r)



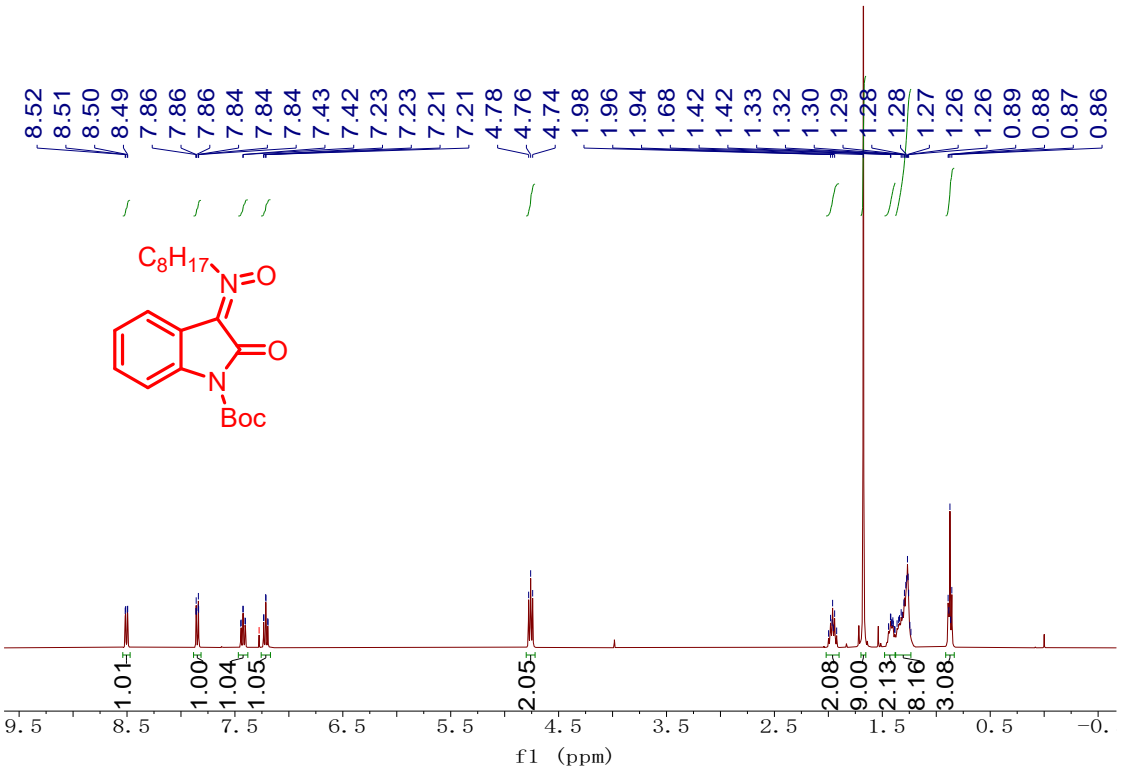
(Z)-1-(tert-butoxycarbonyl)-2-oxo-N-phenethylindolin-3-imine oxide(1s)

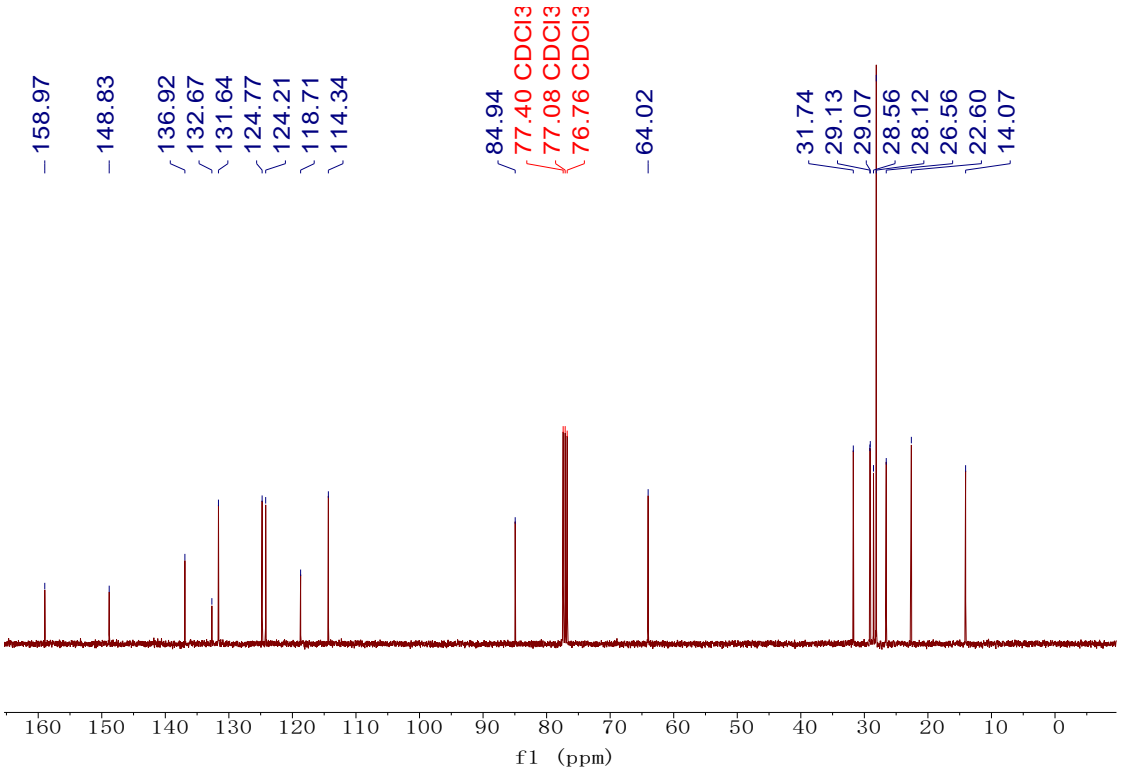


(Z)-1-(tert-butoxycarbonyl)-N-(4-chlorobenzyl)-2-oxoindolin-3-imine oxide(1t)

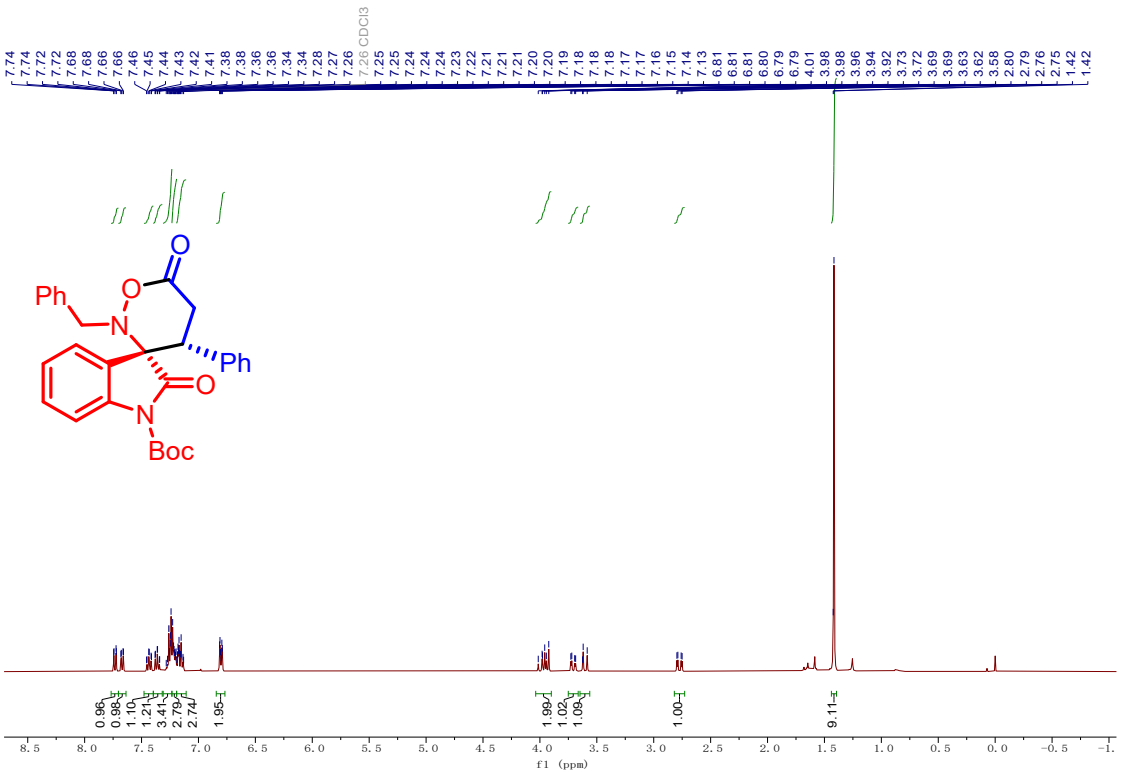


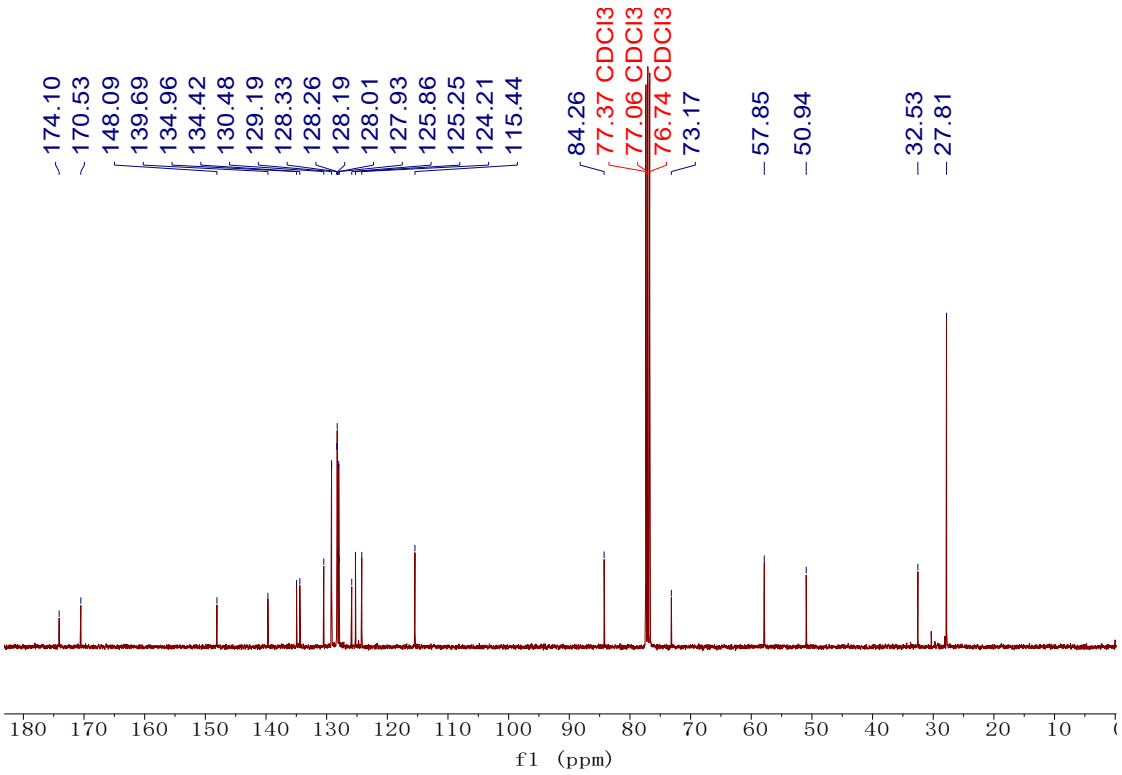
(Z)-1-(tert-butoxycarbonyl)-N-octyl-2-oxoindolin-3-imine oxide(1u)



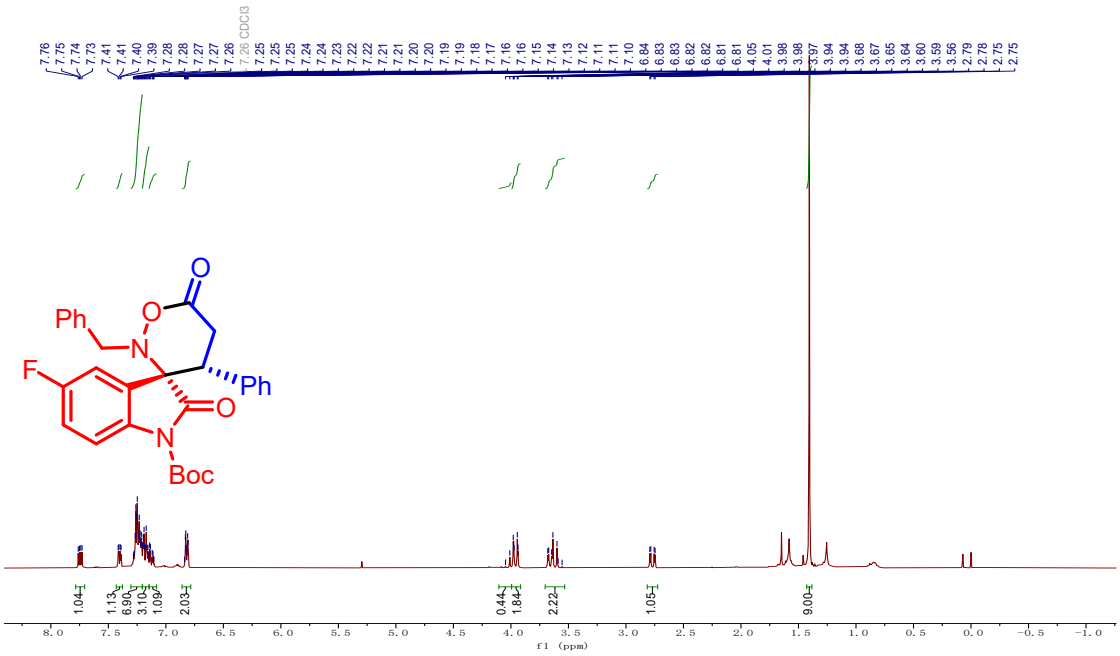


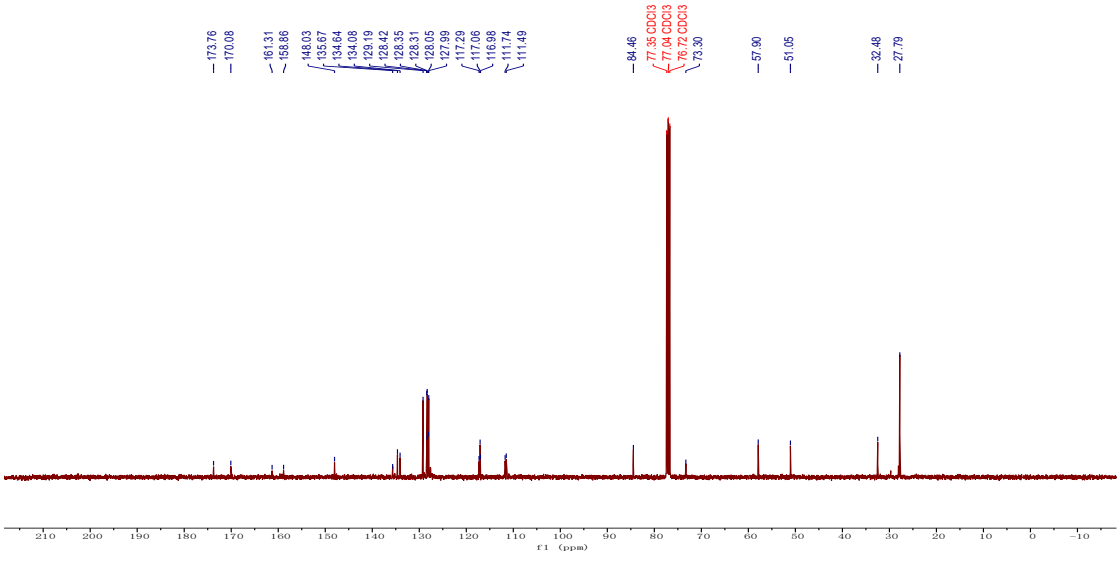
tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-(m-tolyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3a)

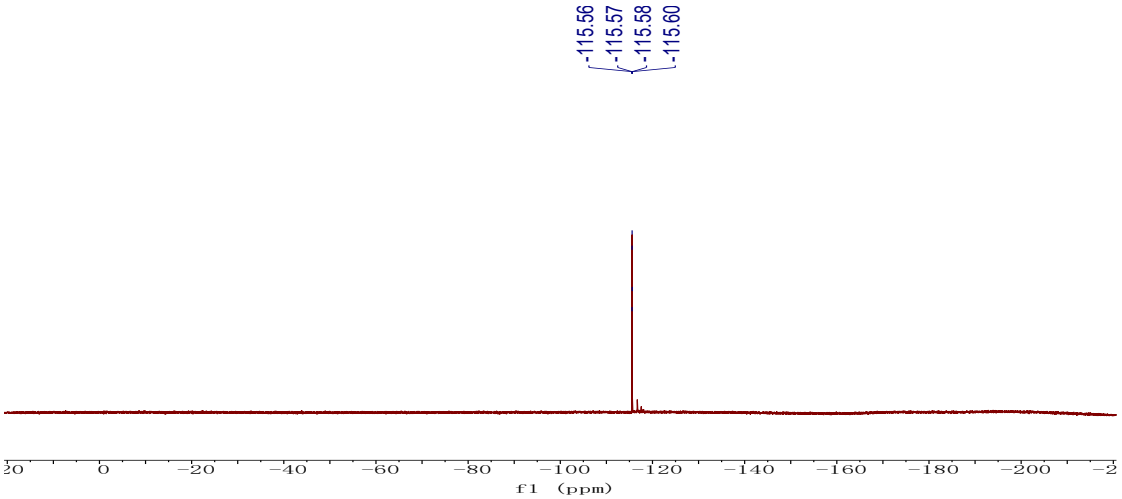




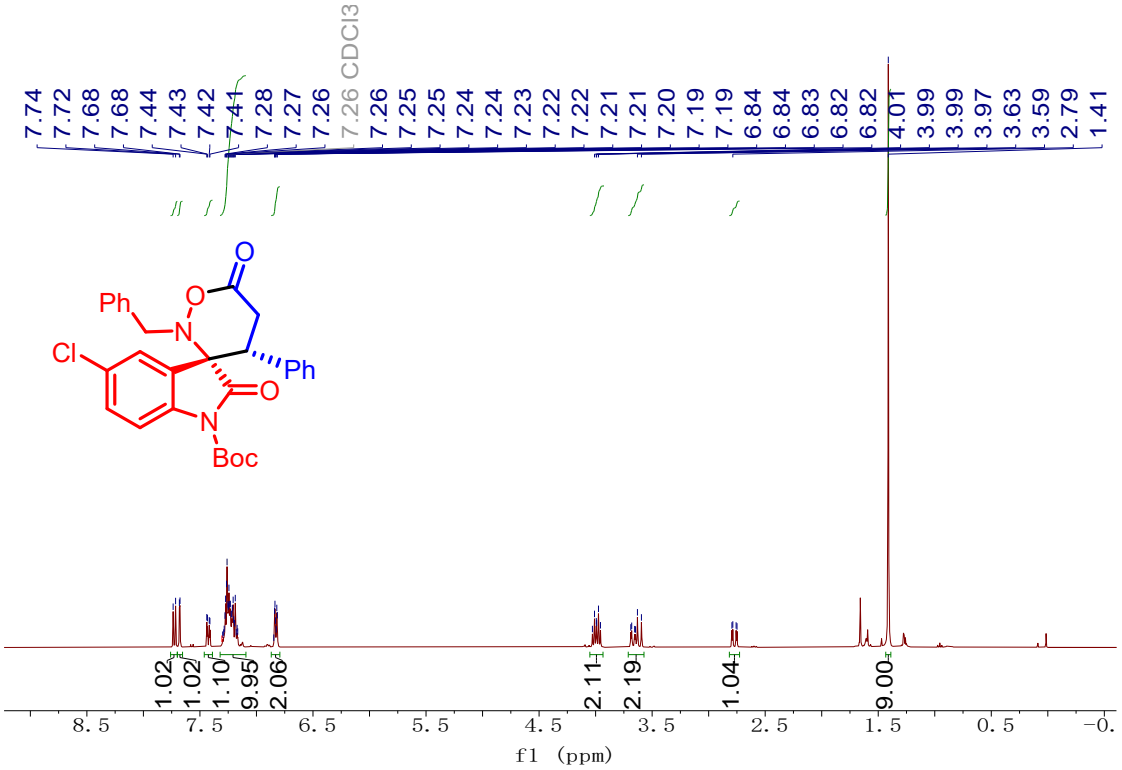
tert-butyl(3R,4'R)-2'-benzyl-5-fluoro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3b)

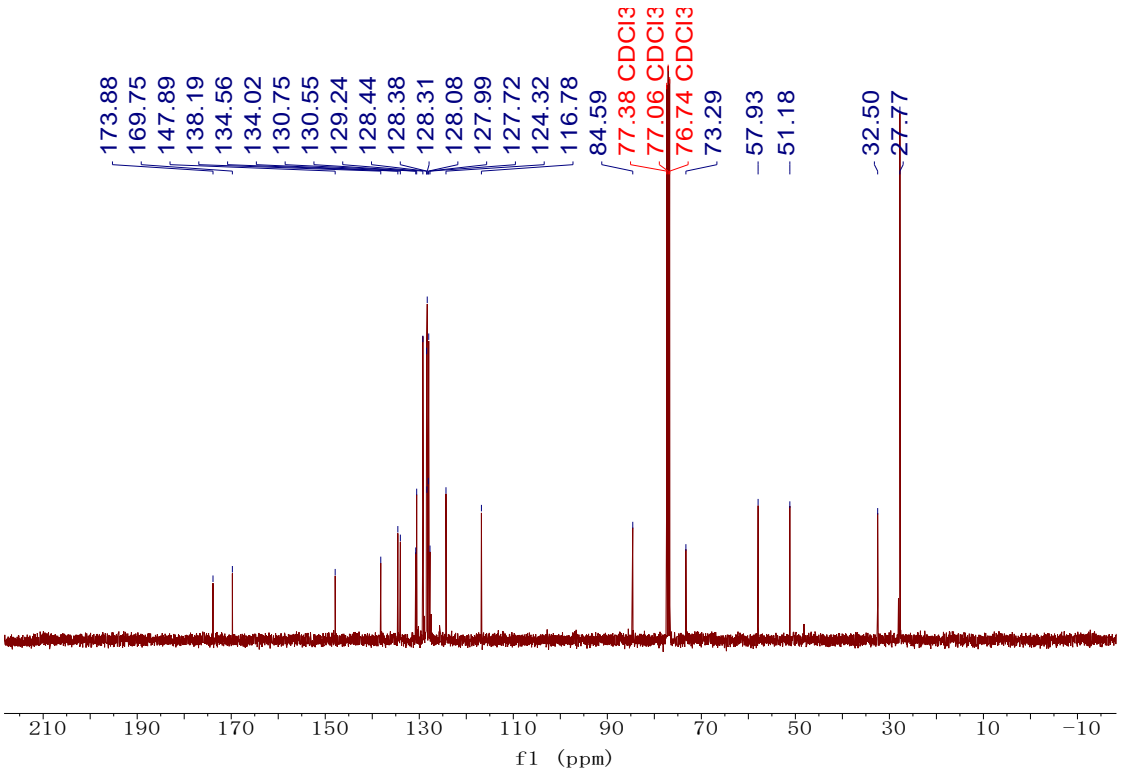




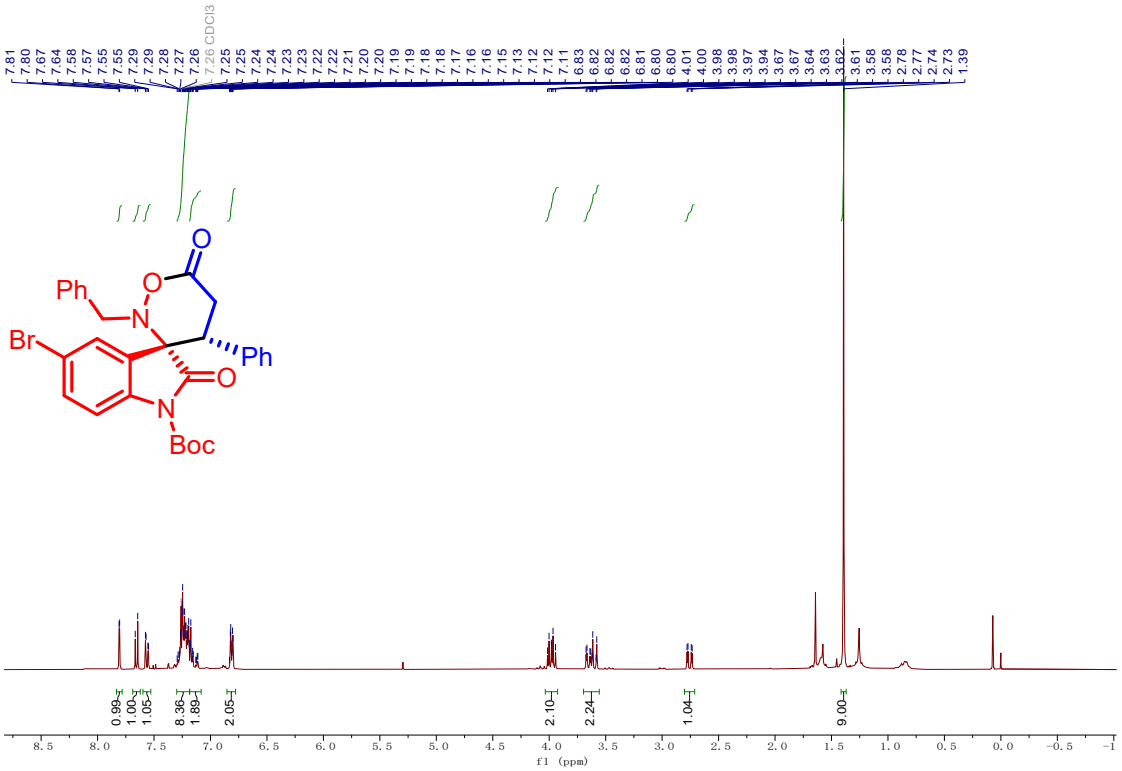


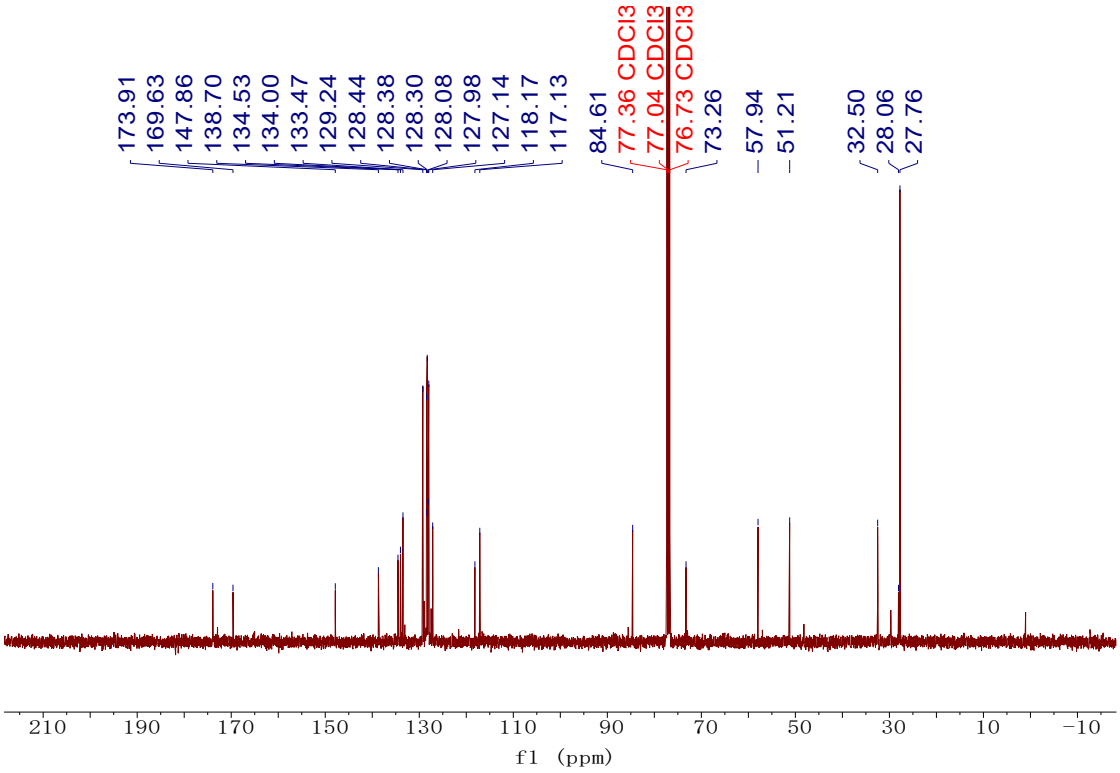
tert-butyl(3R,4'R)-2'-benzyl-5-chloro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3c)



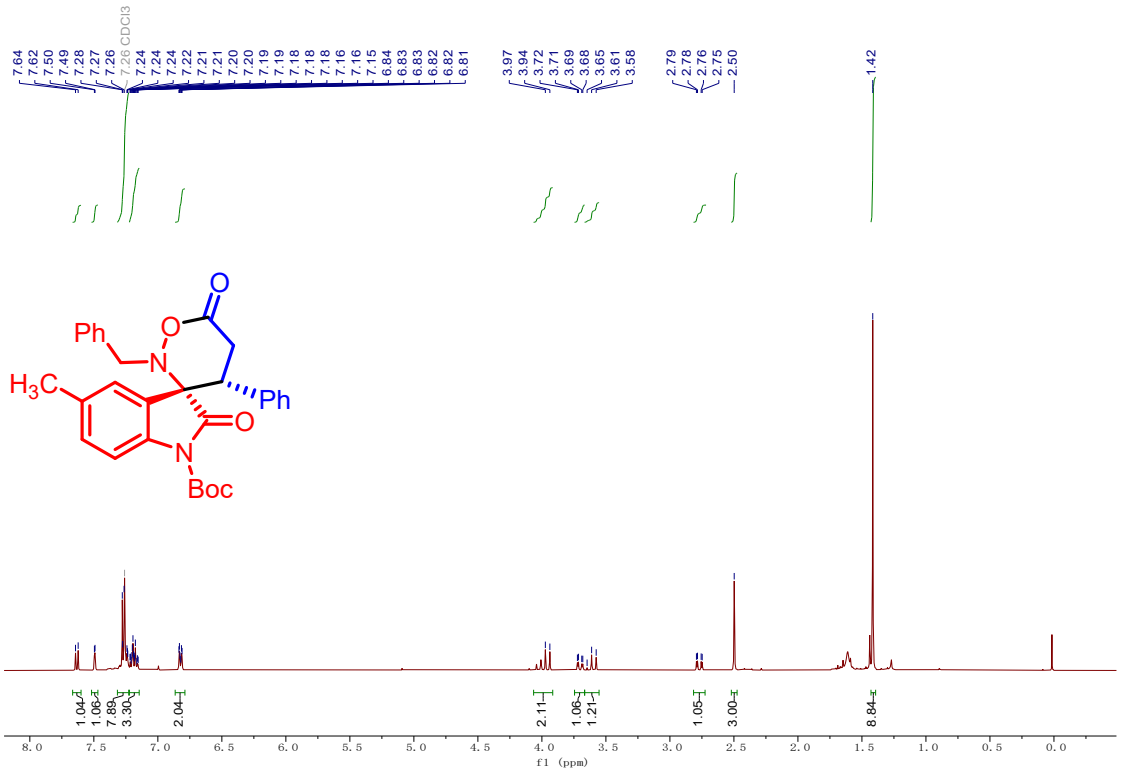


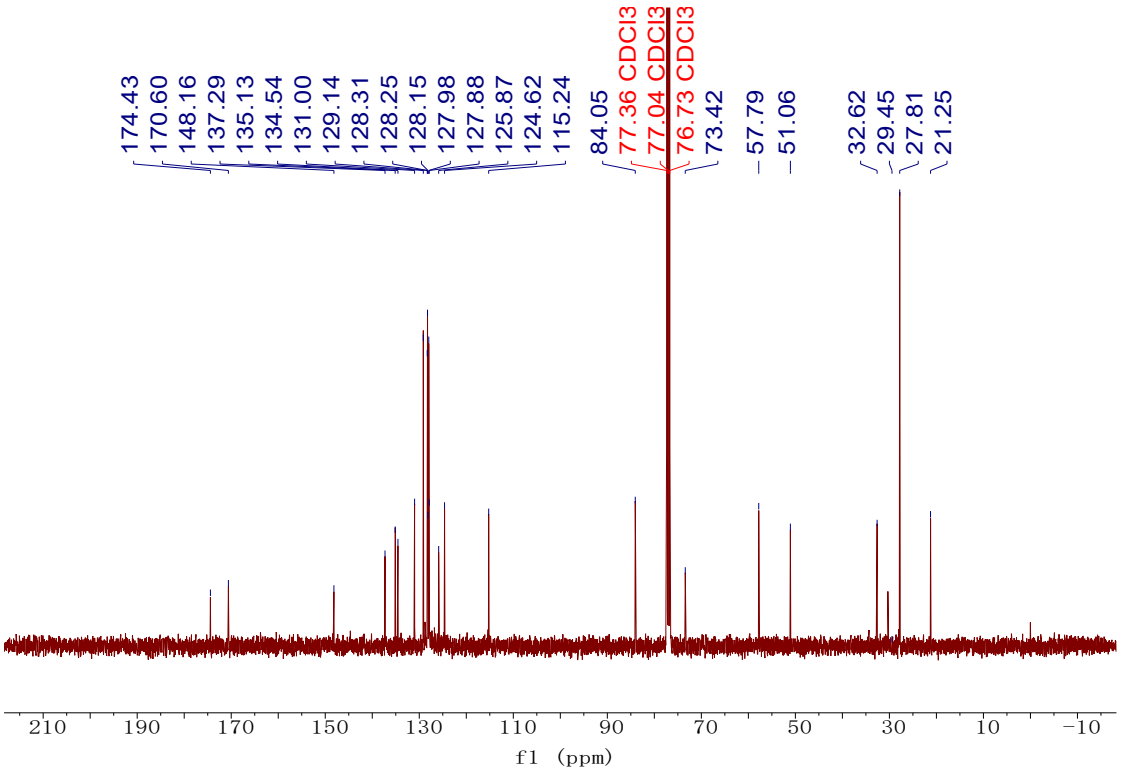
tert-butyl(3R,4'R)-2'-benzyl-5-bromo-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3d)



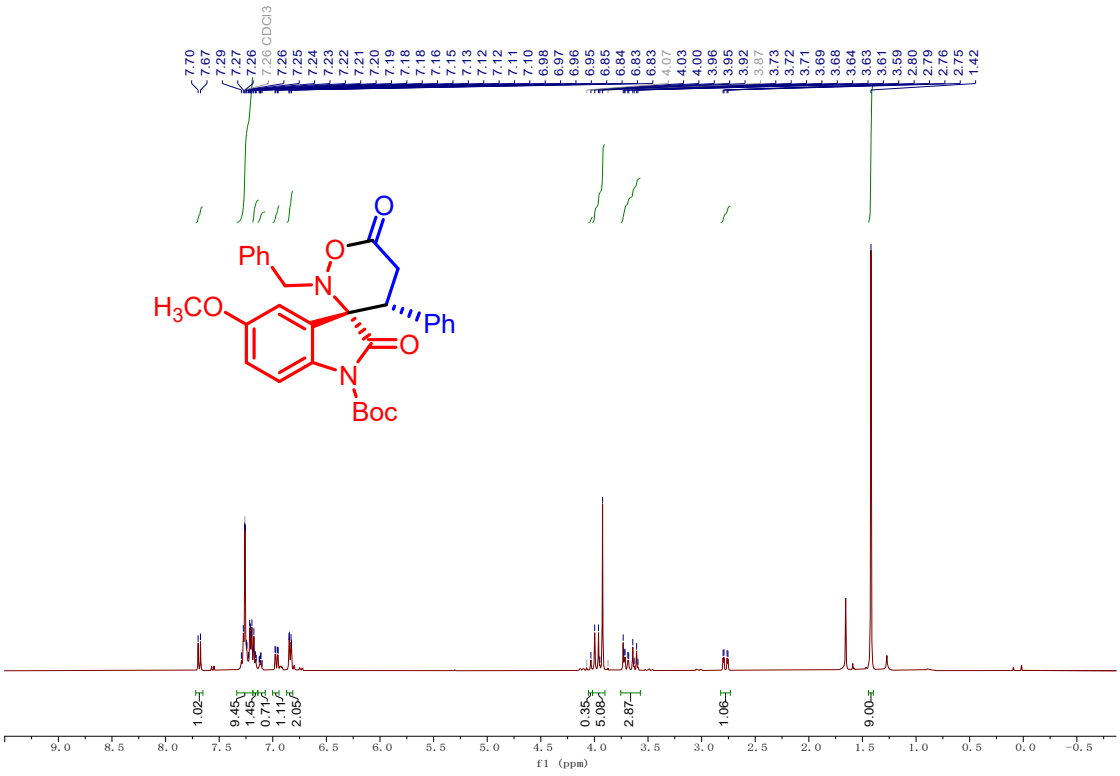


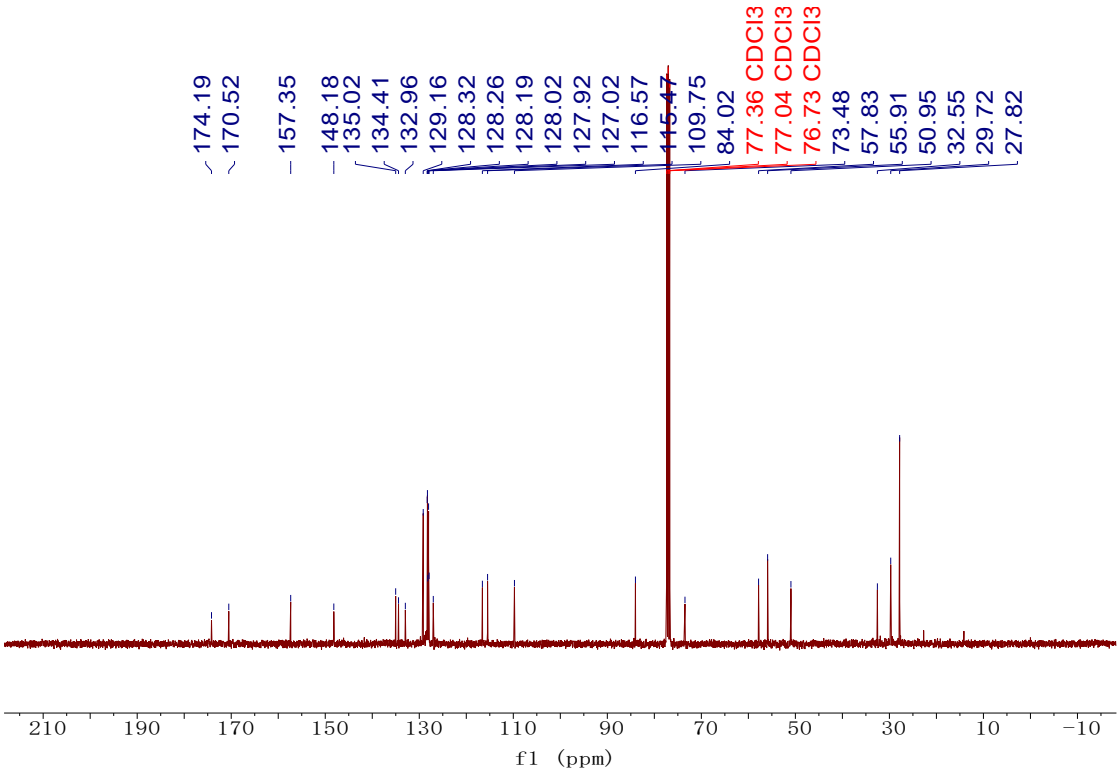
tert-butyl(3R,4'R)-2'-benzyl-5-methyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3e)


7.64
7.62
7.50
7.49
7.28
7.27
7.26
7.26 CDCl3
7.24
7.24
7.24
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.18
7.16
7.16
7.15
6.84
6.83
6.83
6.82
6.82
6.81
3.97
3.94
3.72
3.71
3.69
3.68
3.65
3.61
3.58
2.79
2.78
2.76
2.75
2.50
1.42
Ph
O
N
H3C
Ph
O
N
Boc
1.04
1.06
7.89
3.30
2.04
2.11
1.06
1.21
1.05
3.00
8.84
f1 (ppm)

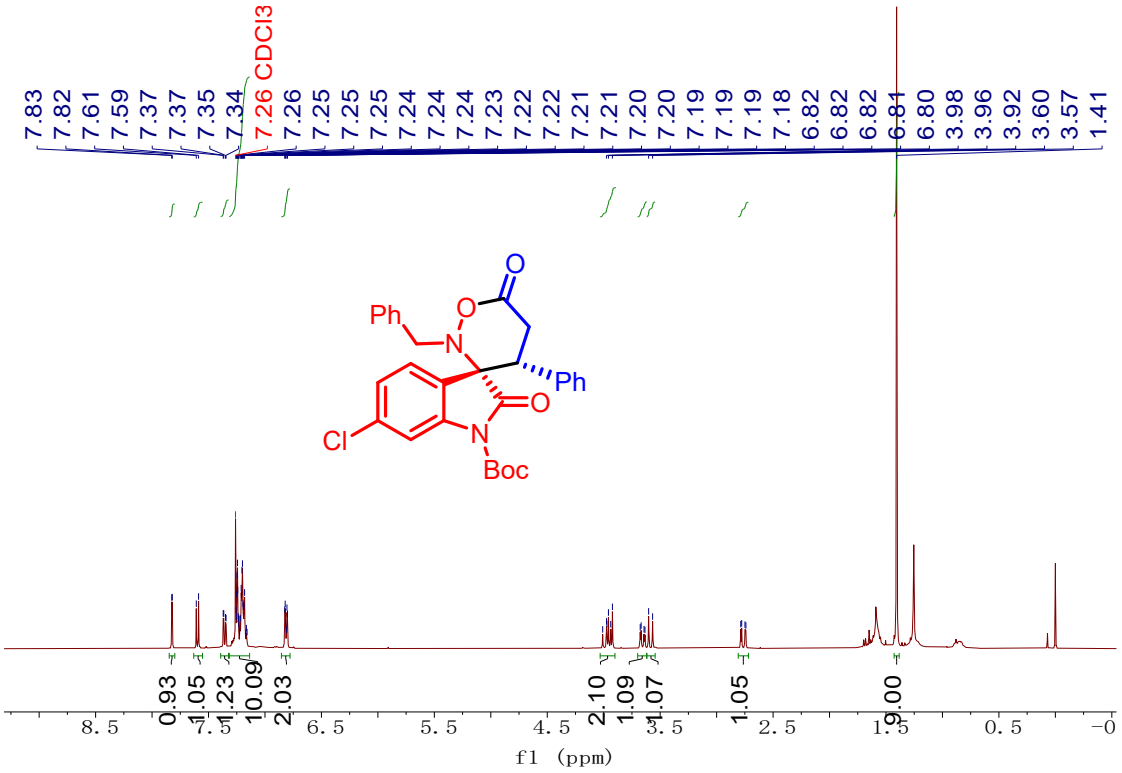

174.43
170.60
148.16
137.29
135.13
134.54
131.00
129.14
128.31
128.25
128.15
127.98
127.88
125.87
124.62
115.24
84.05
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
73.42
57.79
51.06
32.62
29.45
27.81
21.25
f1 (ppm)

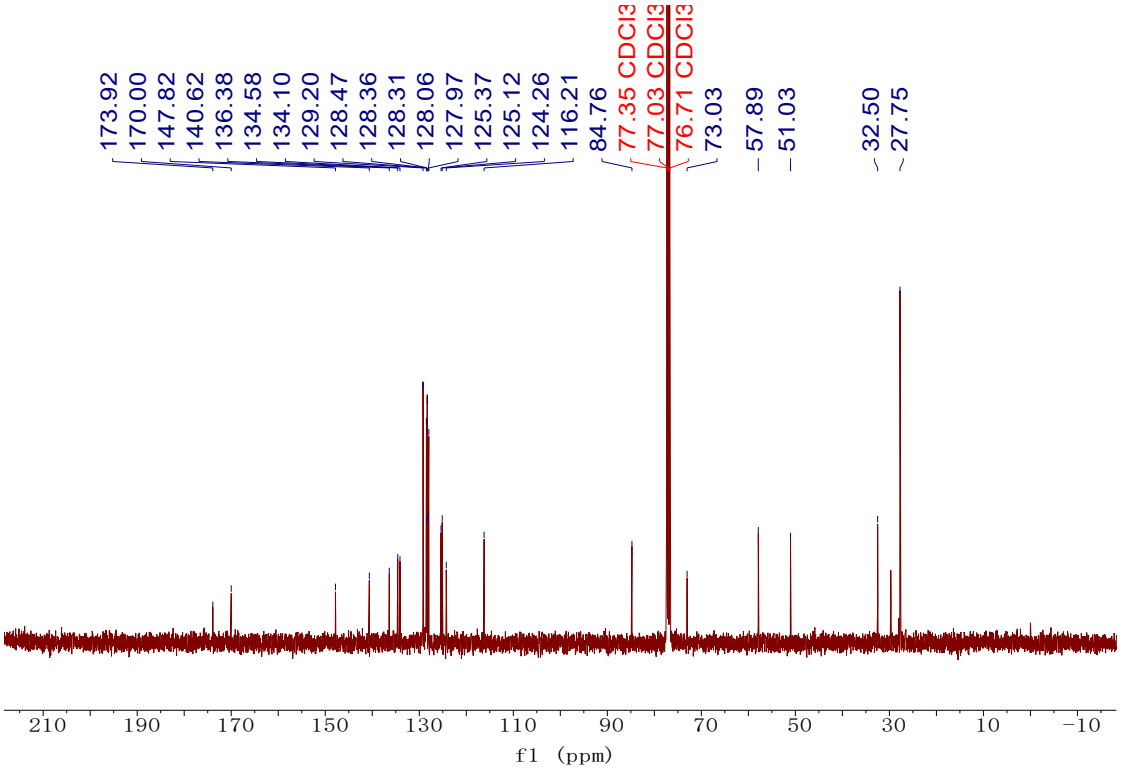
tert-butyl(3R,4'R)-2'-benzyl-5-methoxy-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3f)



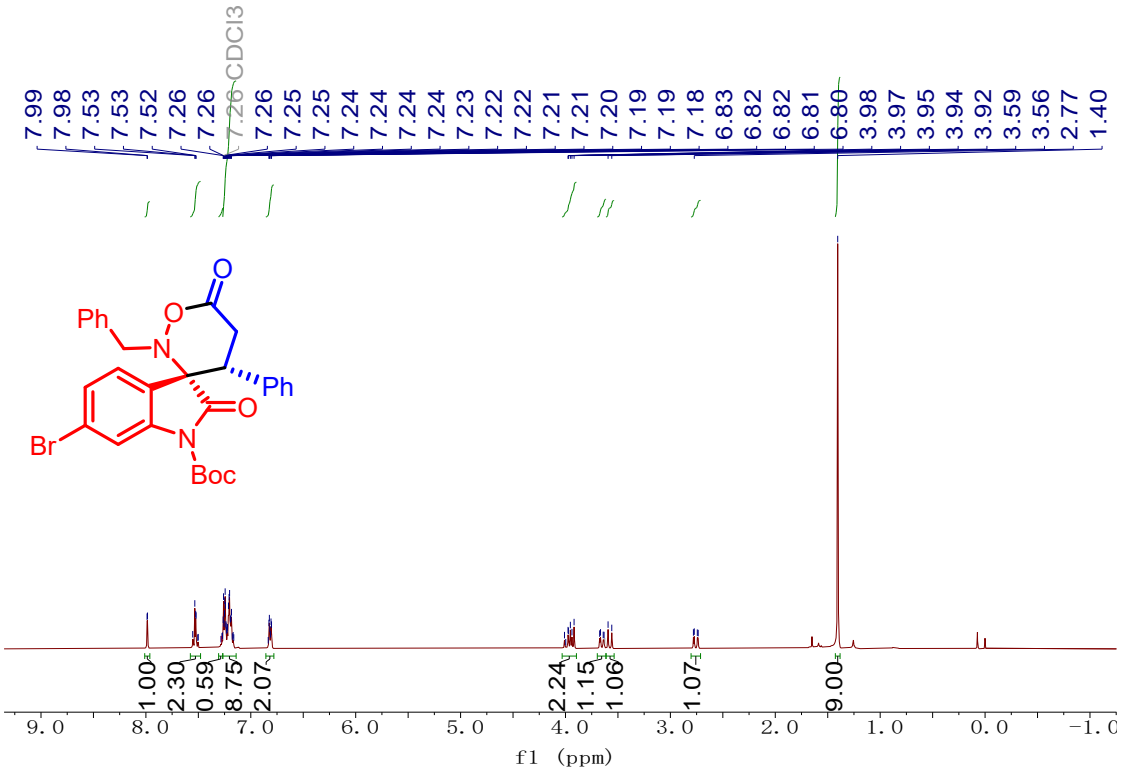


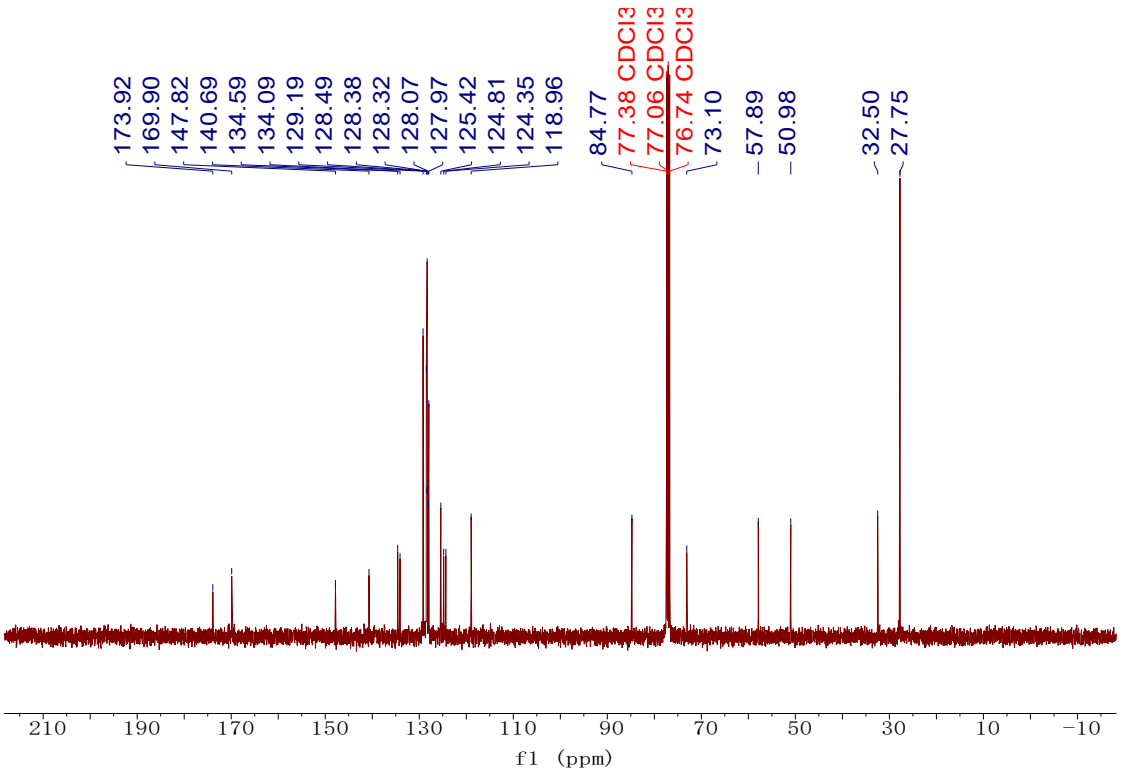
tert-butyl(3R,4'R)-2'-benzyl-6-chloro-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3g)



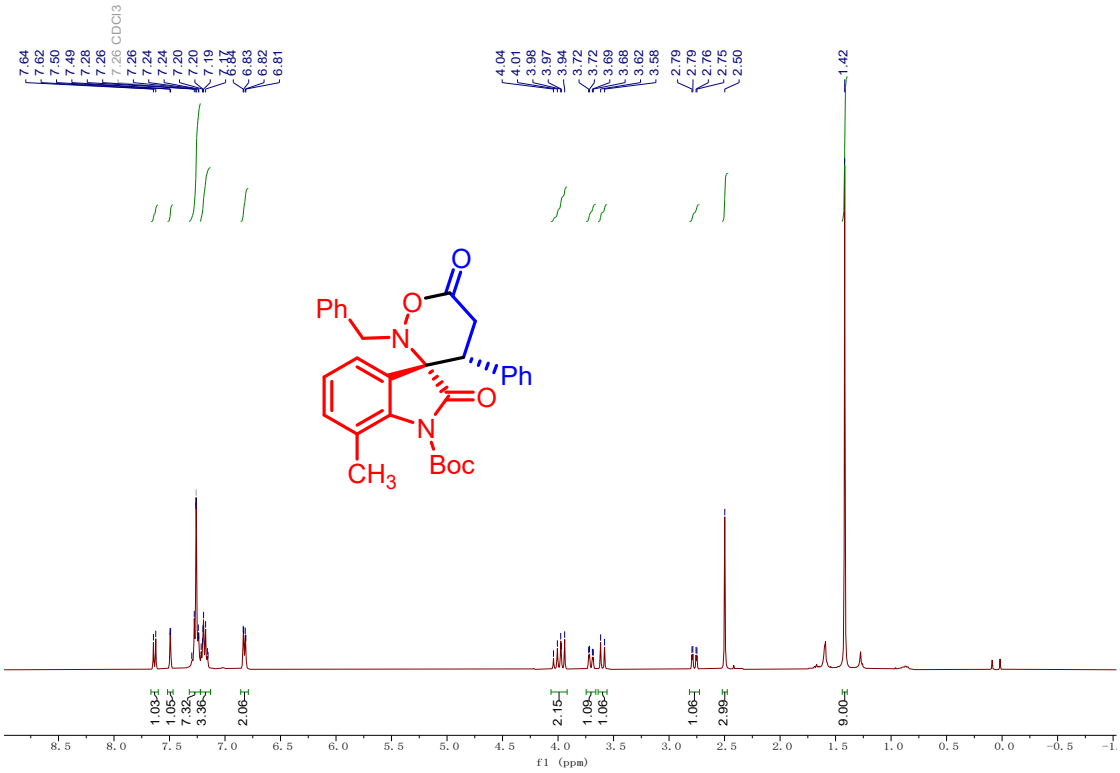


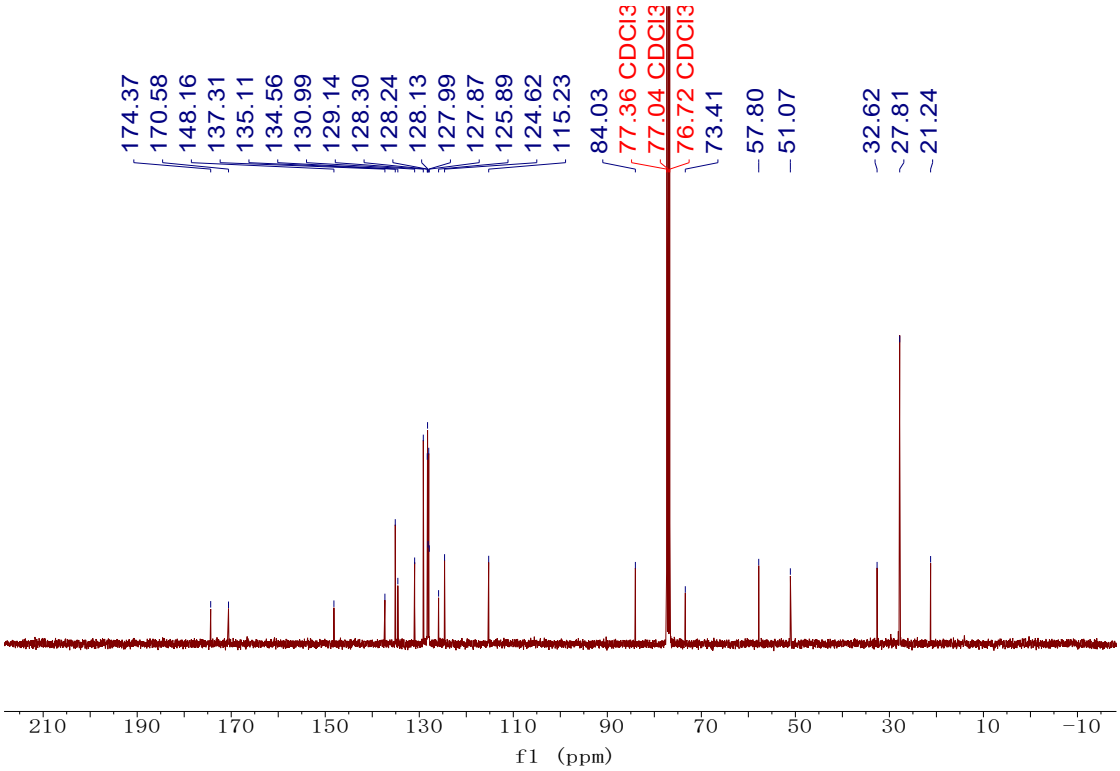
tert-butyl(3R,4'R)-2'-benzyl-6-bromo-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3h)



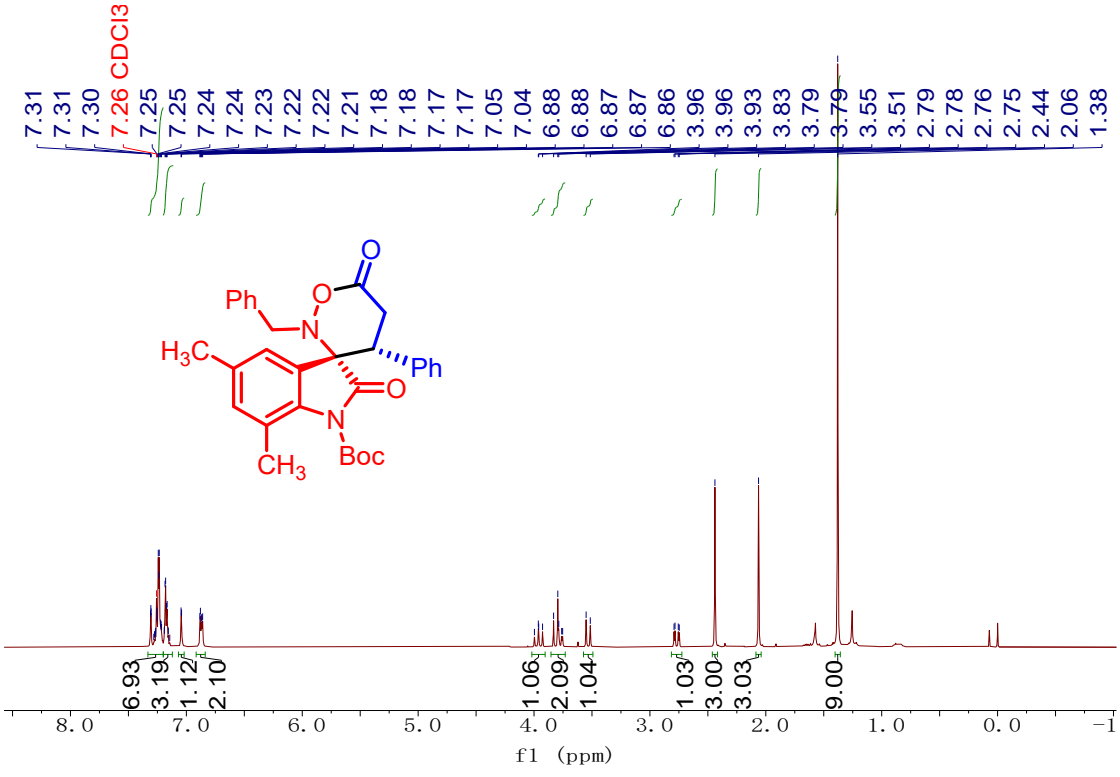


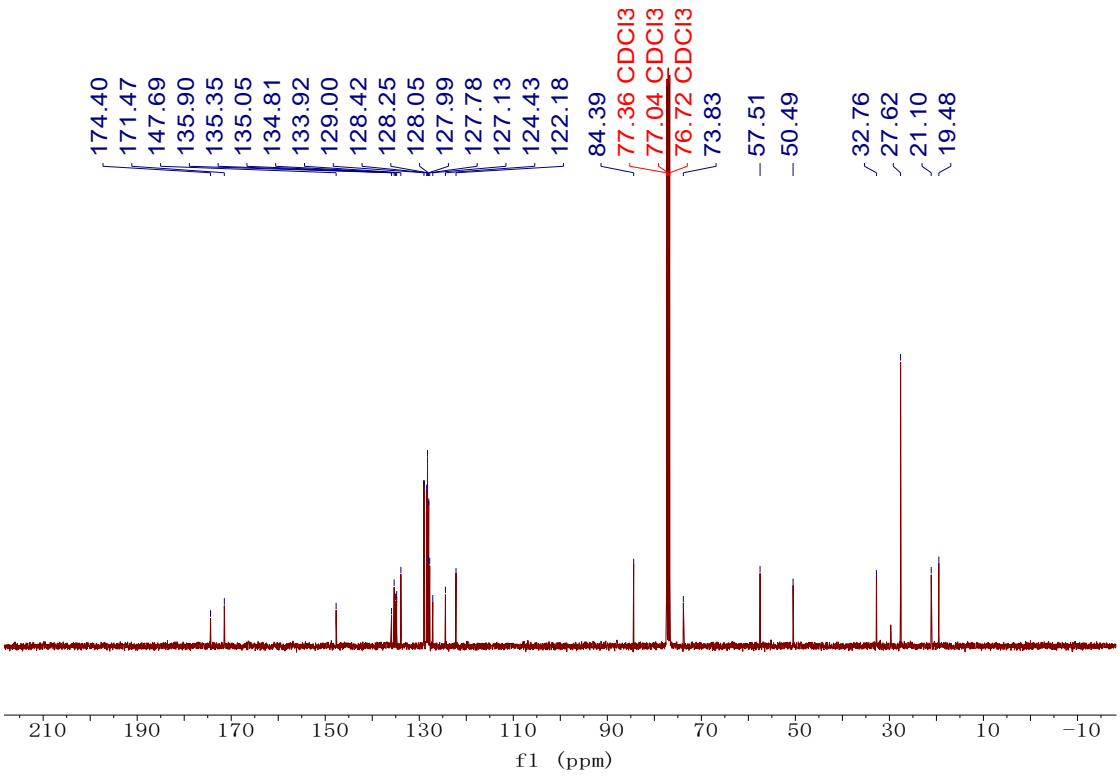
tert-butyl(3R,4'R)-2'-benzyl-7-methyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3i)



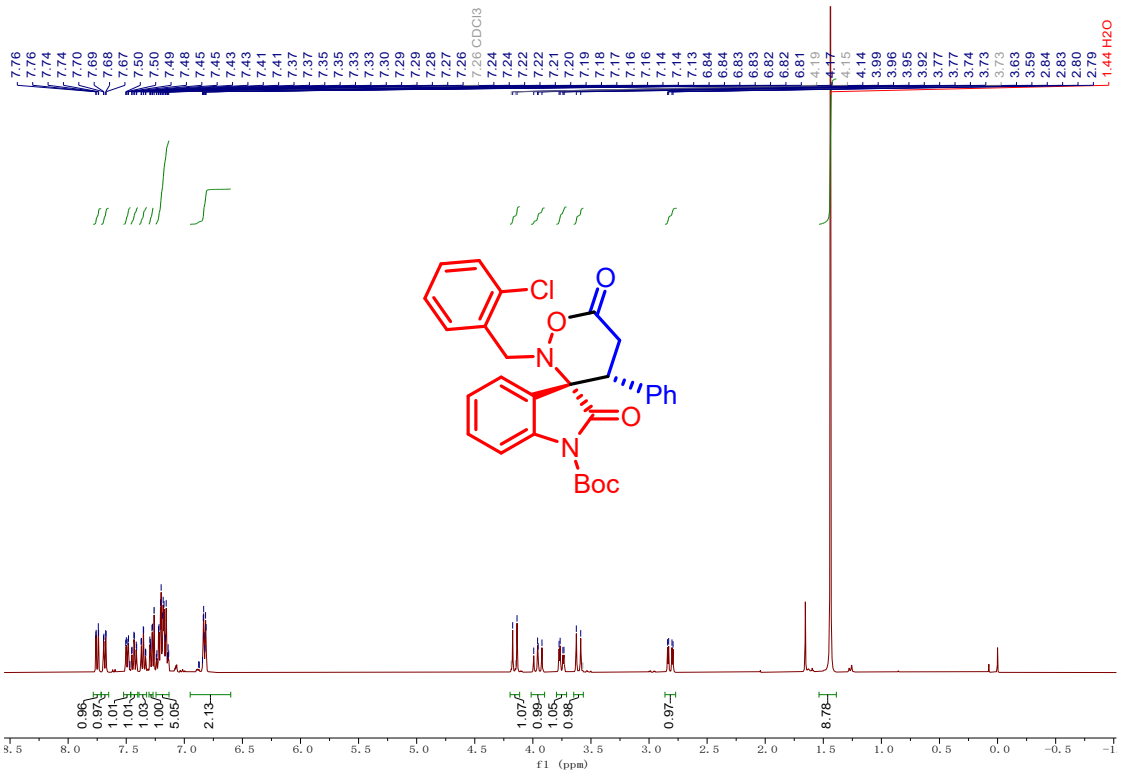


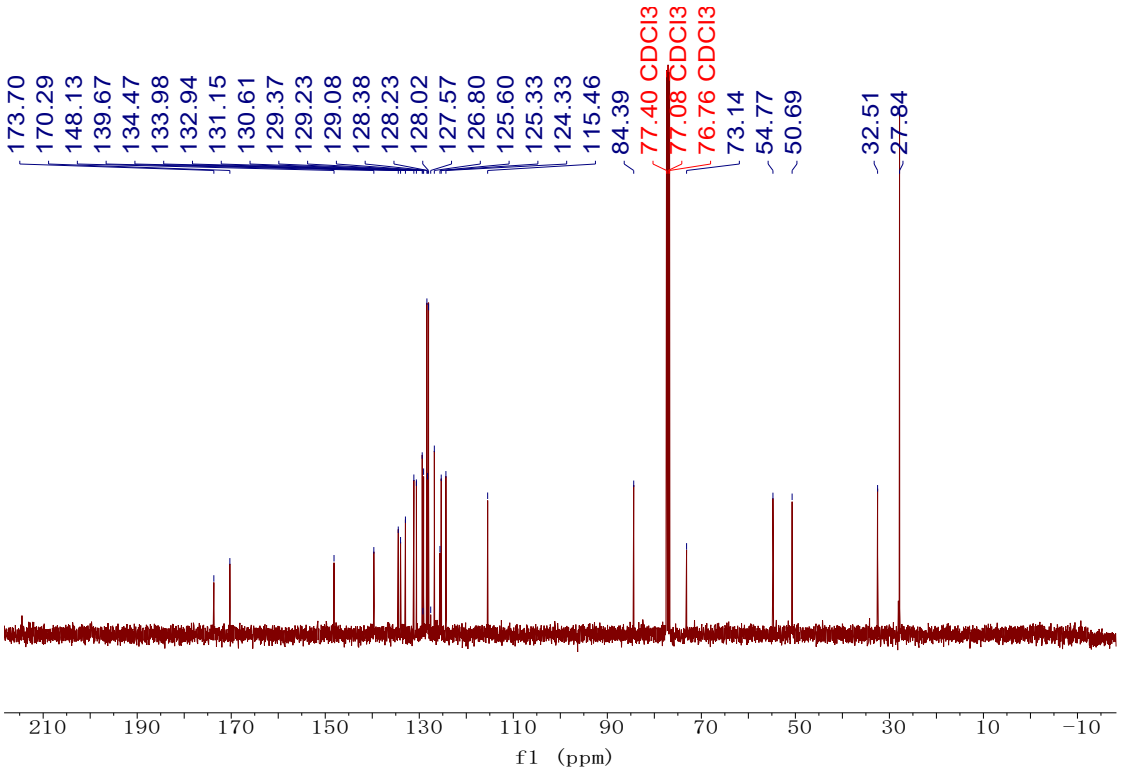
tert-butyl(3R,4'R)-2'-benzyl-5,7-dimethyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3j)



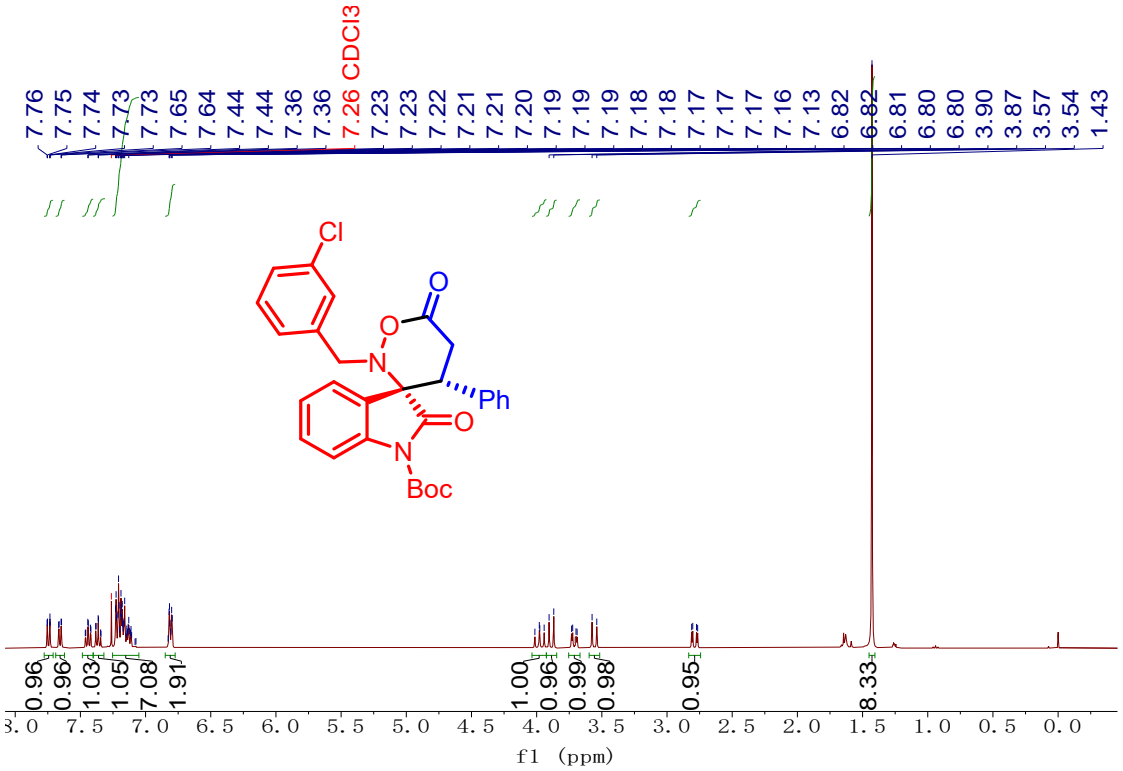


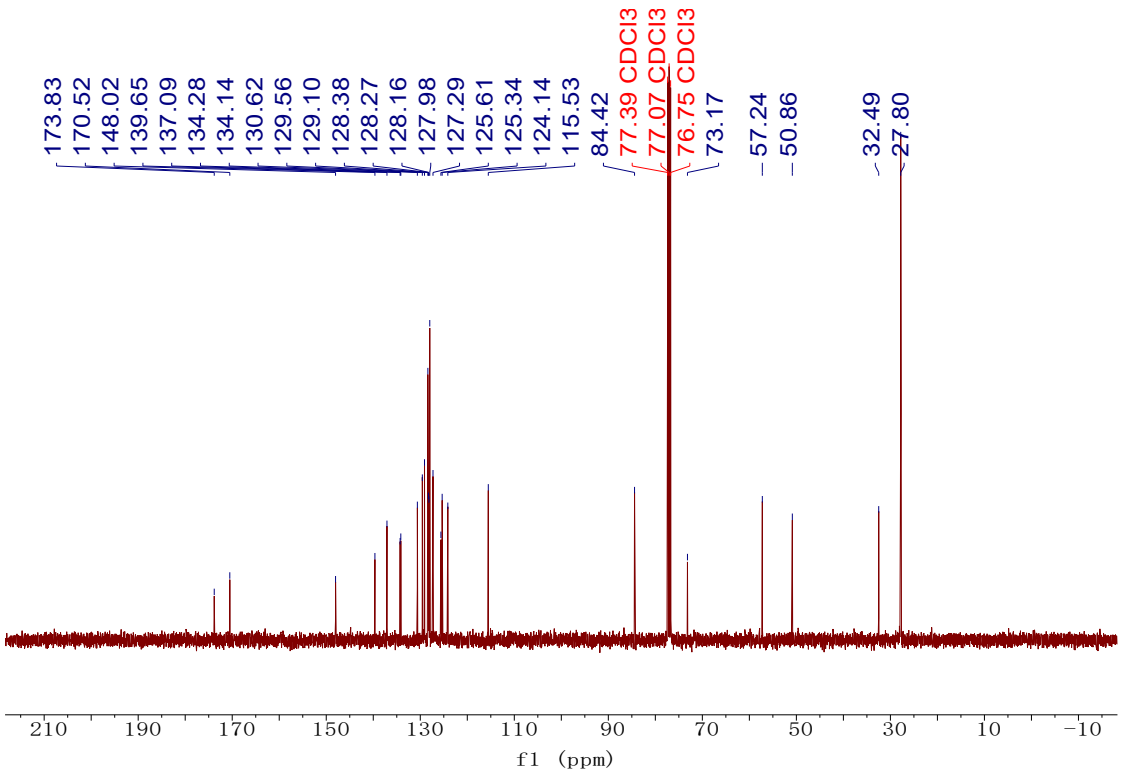
tert-butyl(3R,4'R)-2'-(4-bromobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3k)



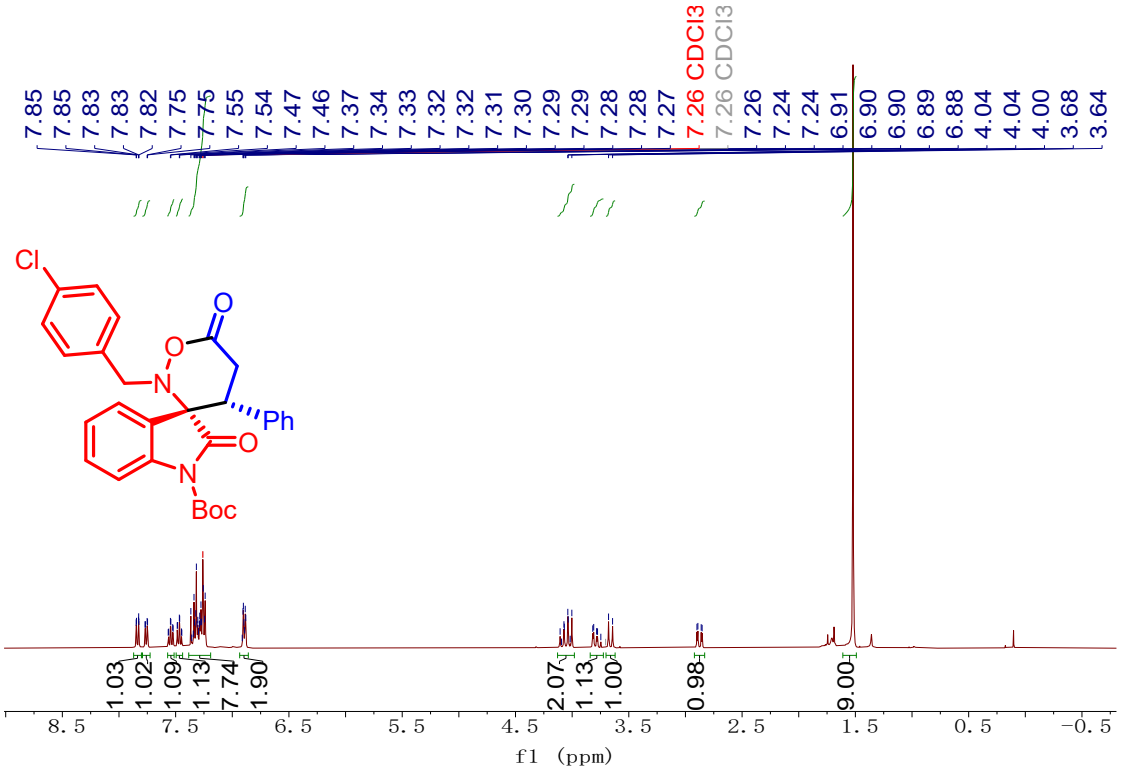


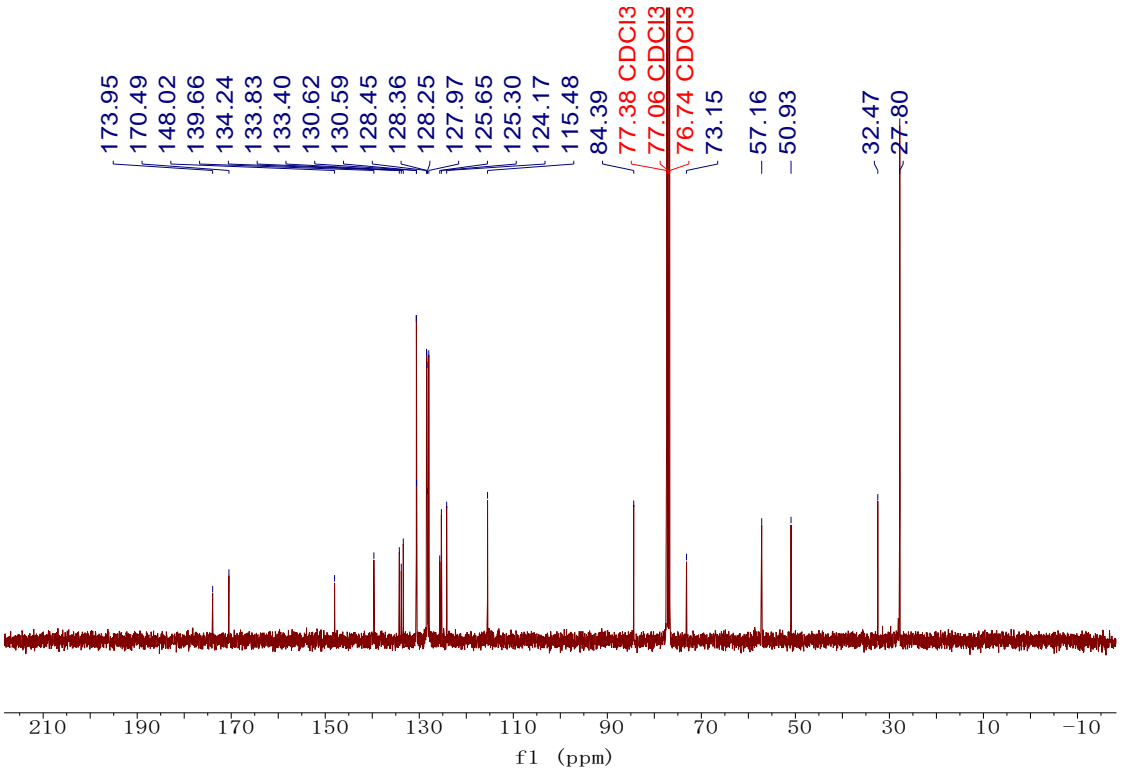
tert-butyl(3R,4'R)-2'-(3-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3l)



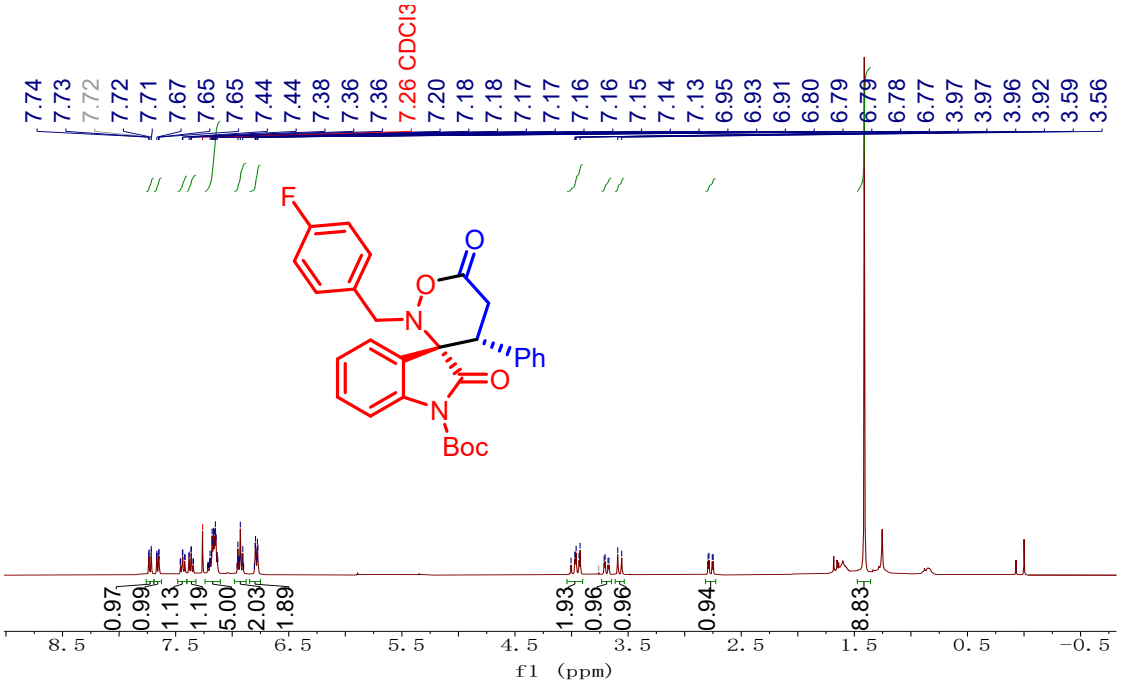


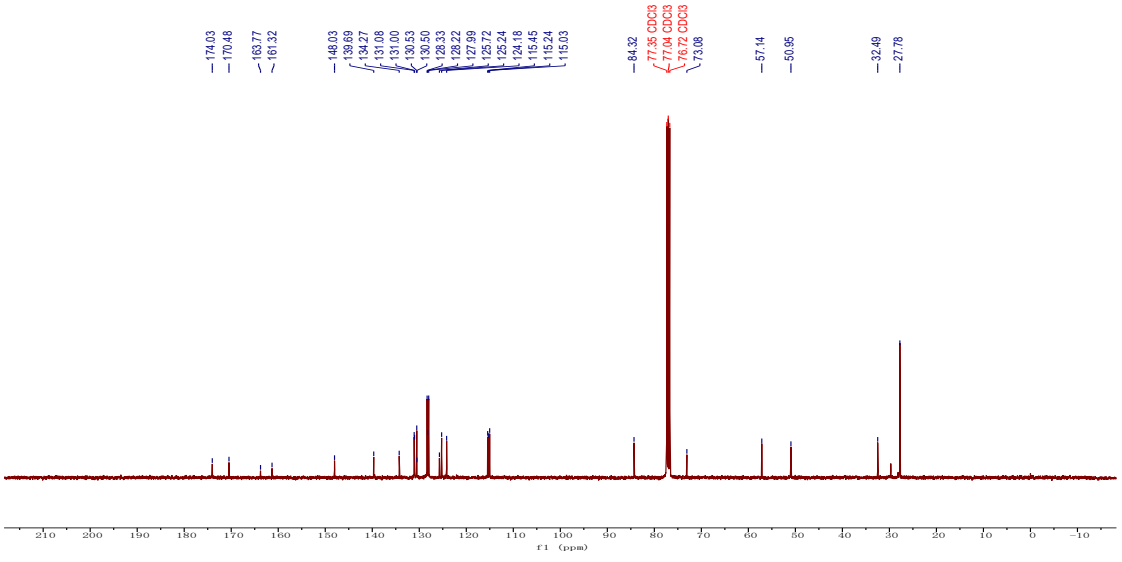
tert-butyl(3R,4'R)-2'-(4-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3m)

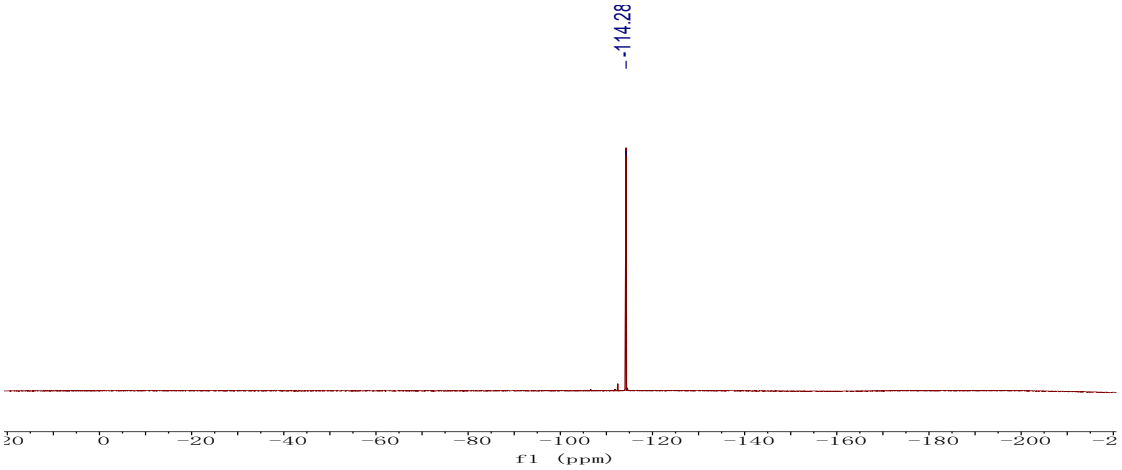

7.85 7.85 7.83 7.83 7.82 7.75 7.75 7.55 7.54 7.47 7.46 7.37 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.26 CDCl3 7.26 CDCl3 7.26 7.24 7.24 6.91 6.90 6.90 6.89 6.88 4.04 4.04 4.00 3.68 3.64
Cl
O
O
N
Ph
O
N
Boc
1.03 1.02 1.09 1.13 7.74 1.90 2.07 1.13 1.00 0.98 9.00
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)


173.95 170.49 148.02 139.66 134.24 133.83 133.40 130.62 130.59 128.45 128.36 128.25 127.97 125.65 125.30 124.17 115.48 84.39 77.38 CDCl3 77.06 CDCl3 76.74 CDCl3 73.15 57.16 50.93 32.47 27.80
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

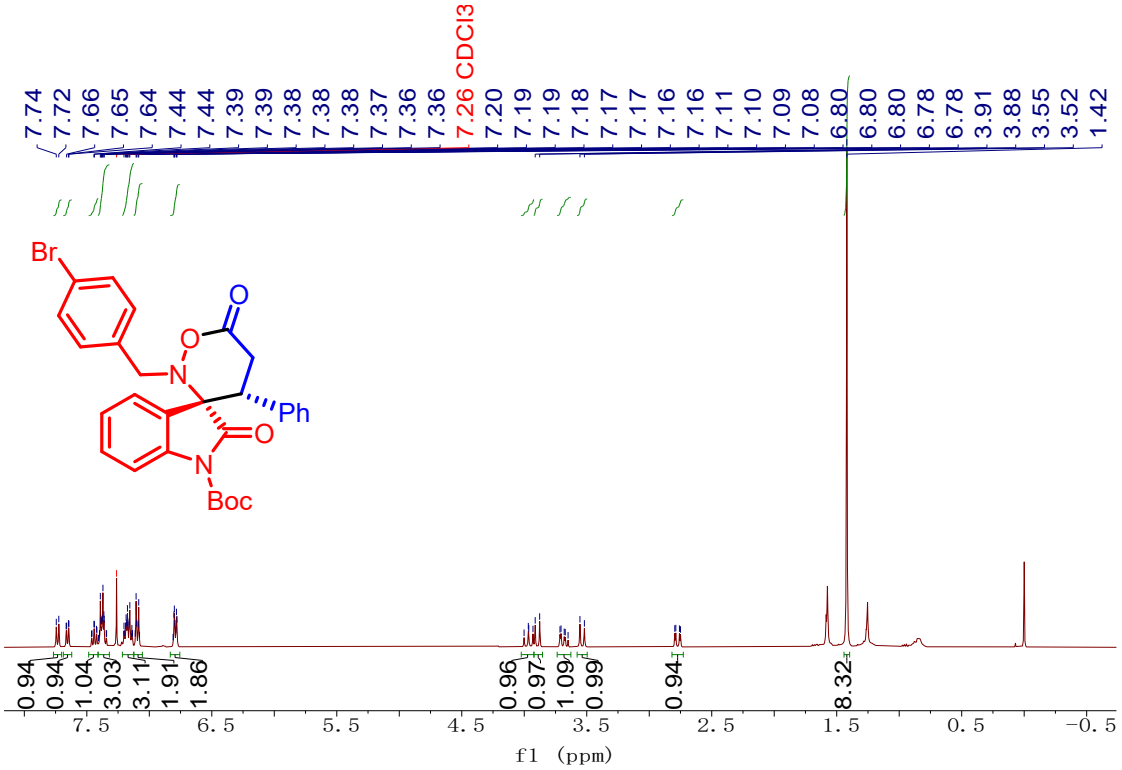
tert-butyl(3R,4'R)-2,6'-dioxo-4'-phenyl-2'-(3-phenylpropyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3n)

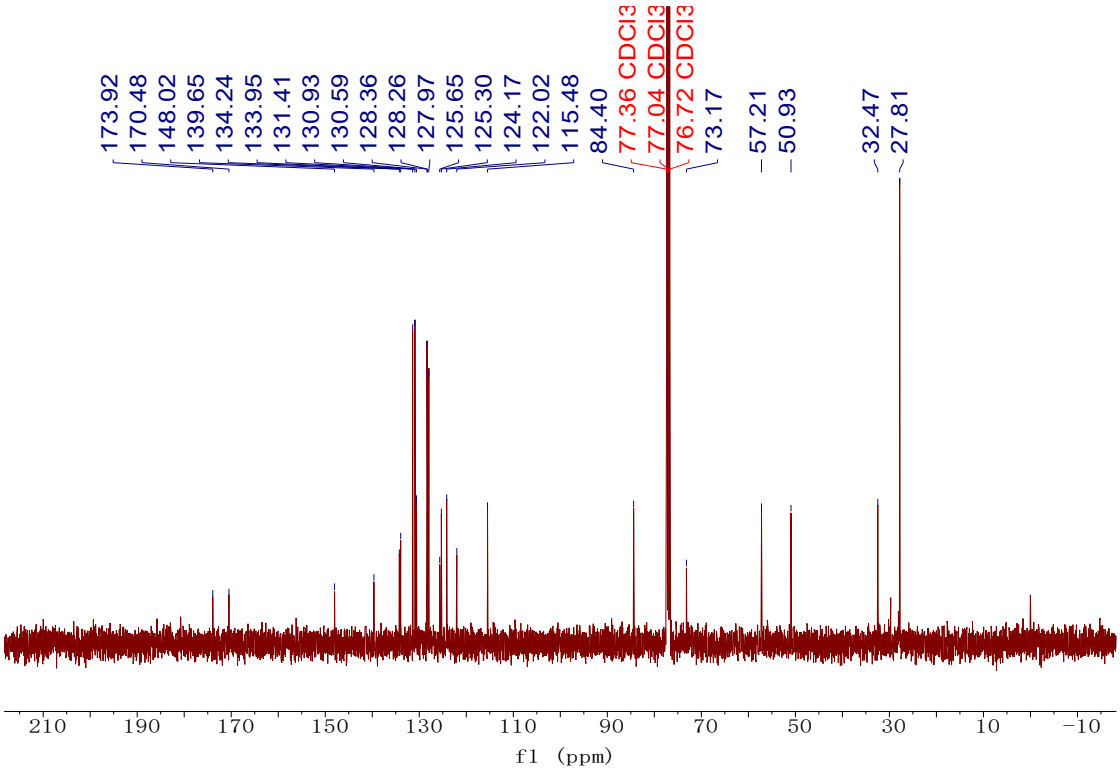




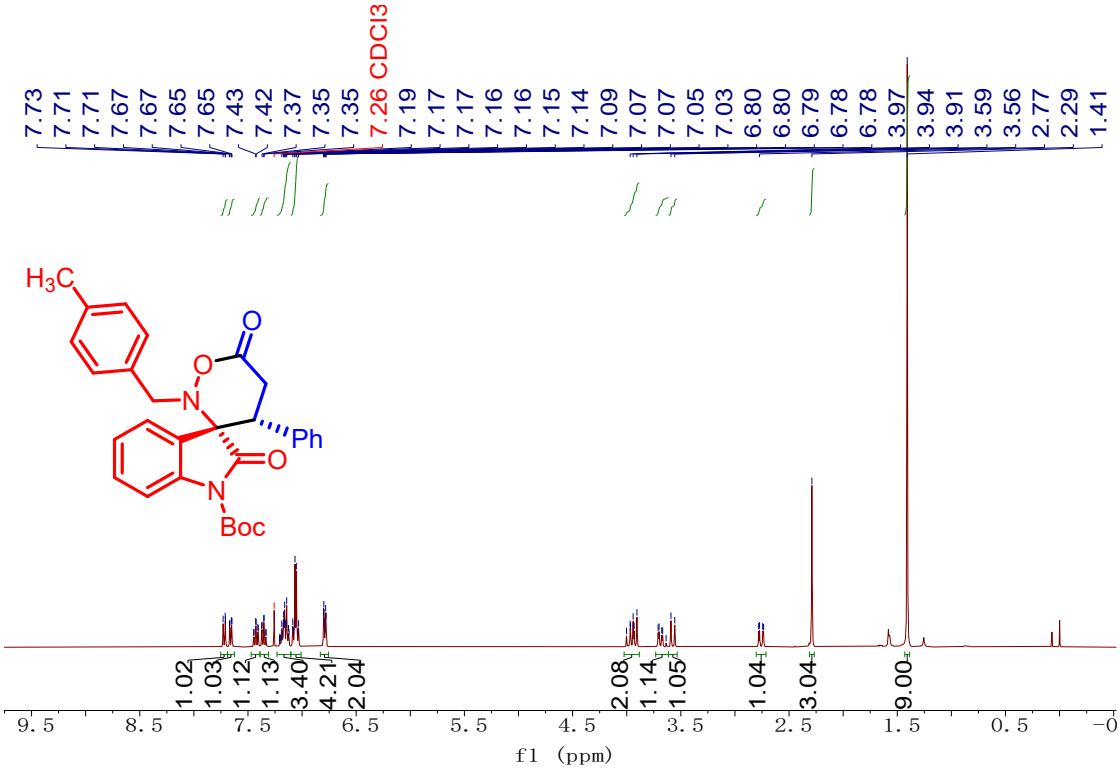


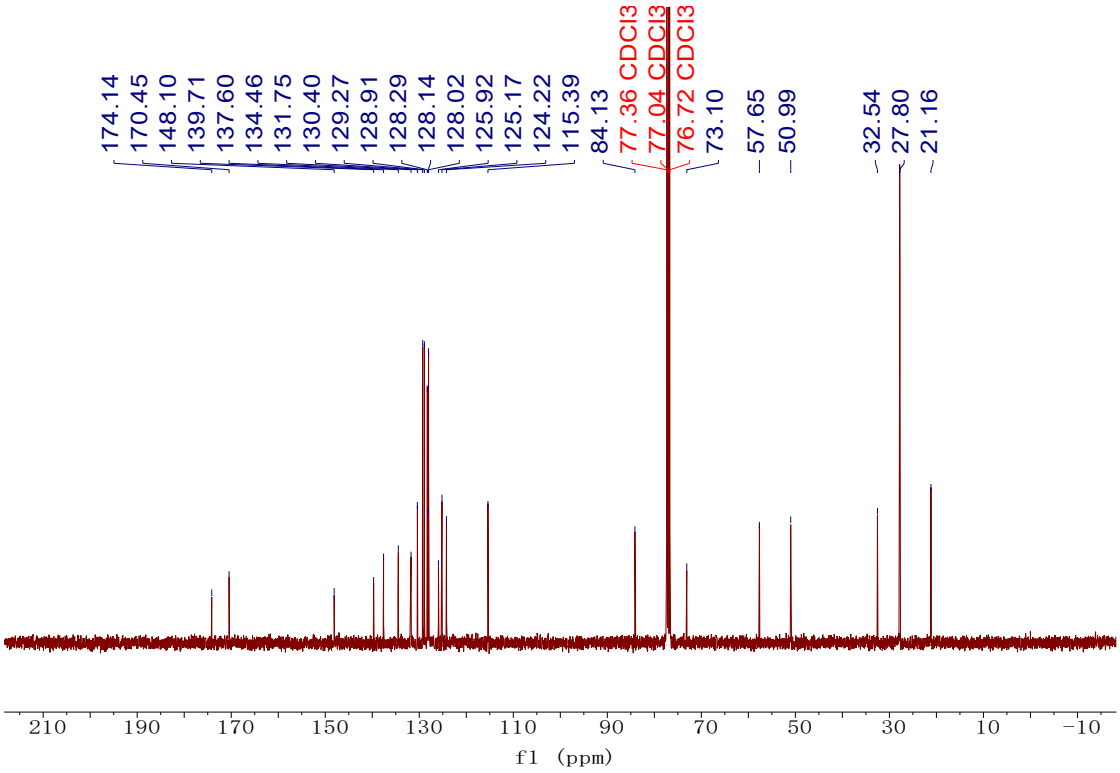
tert-butyl(3R,4'R)-2'-(2-chlorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3o)



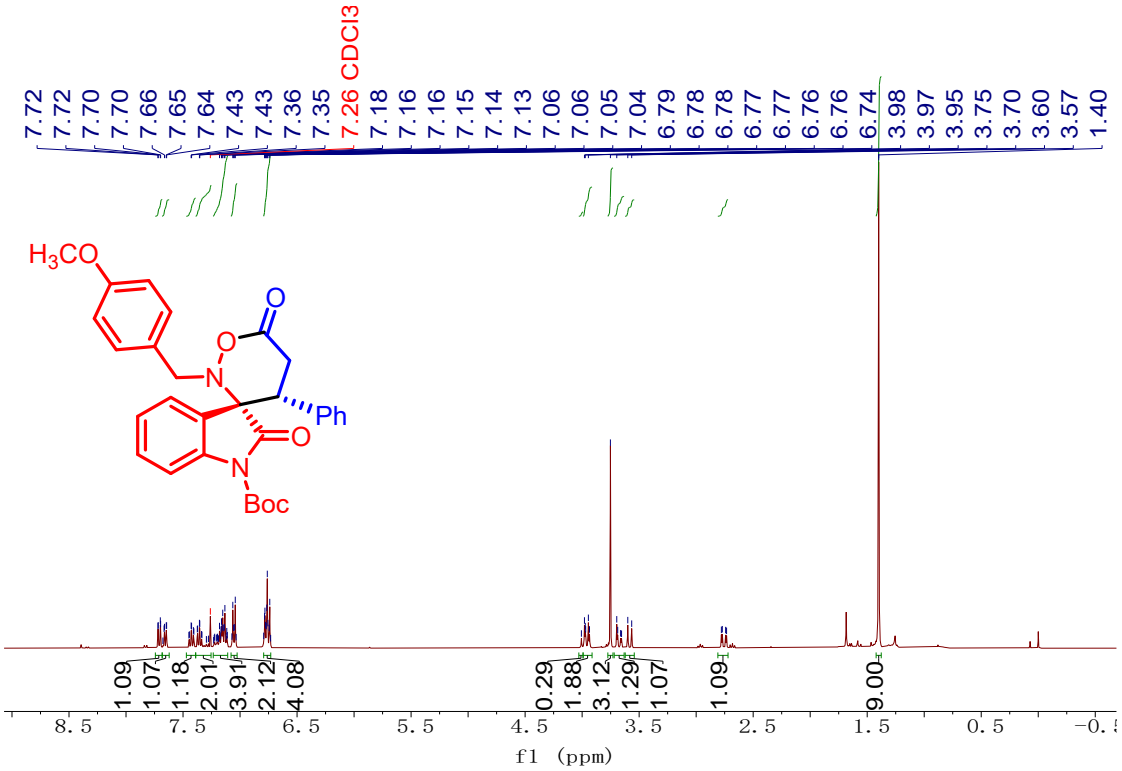


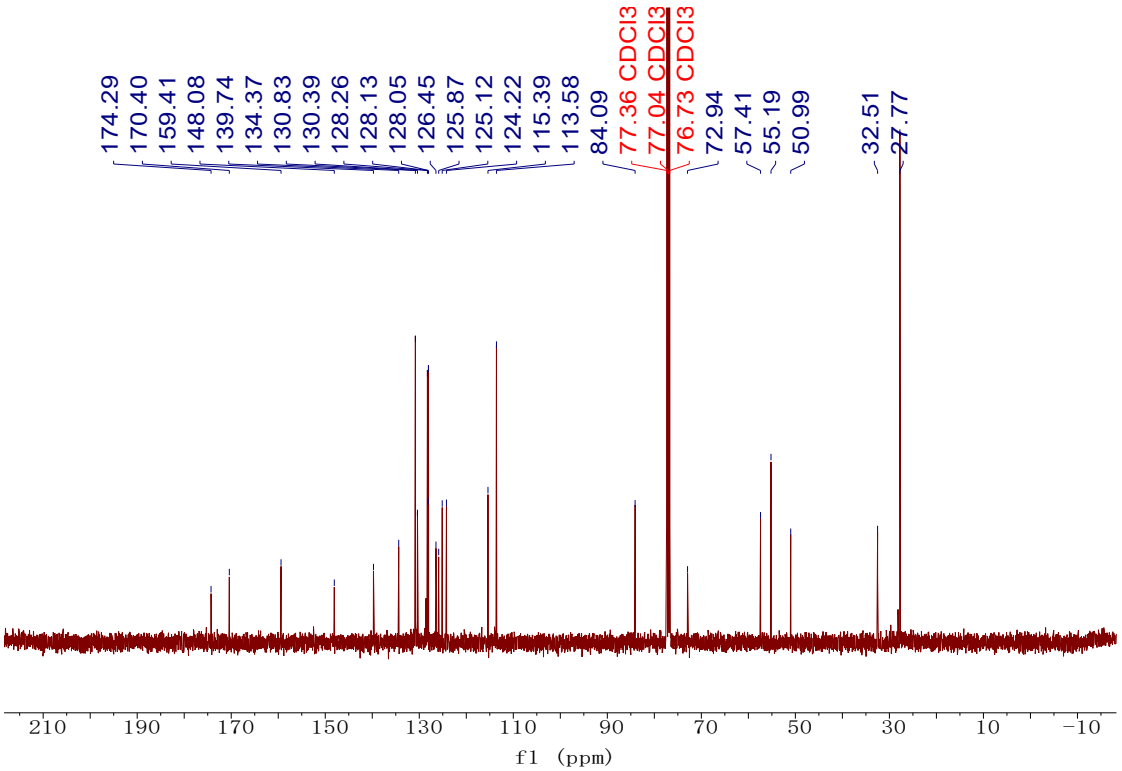
tert-butyl(3R,4'R)-2'-(4-methylbenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3p)



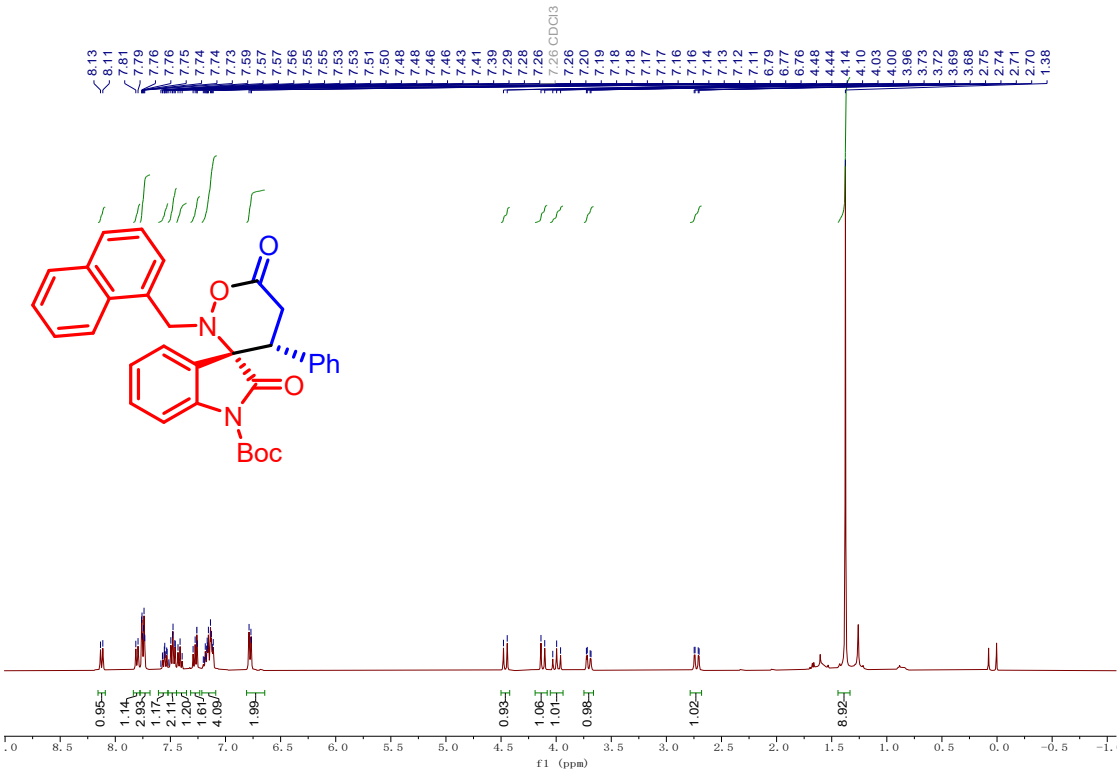


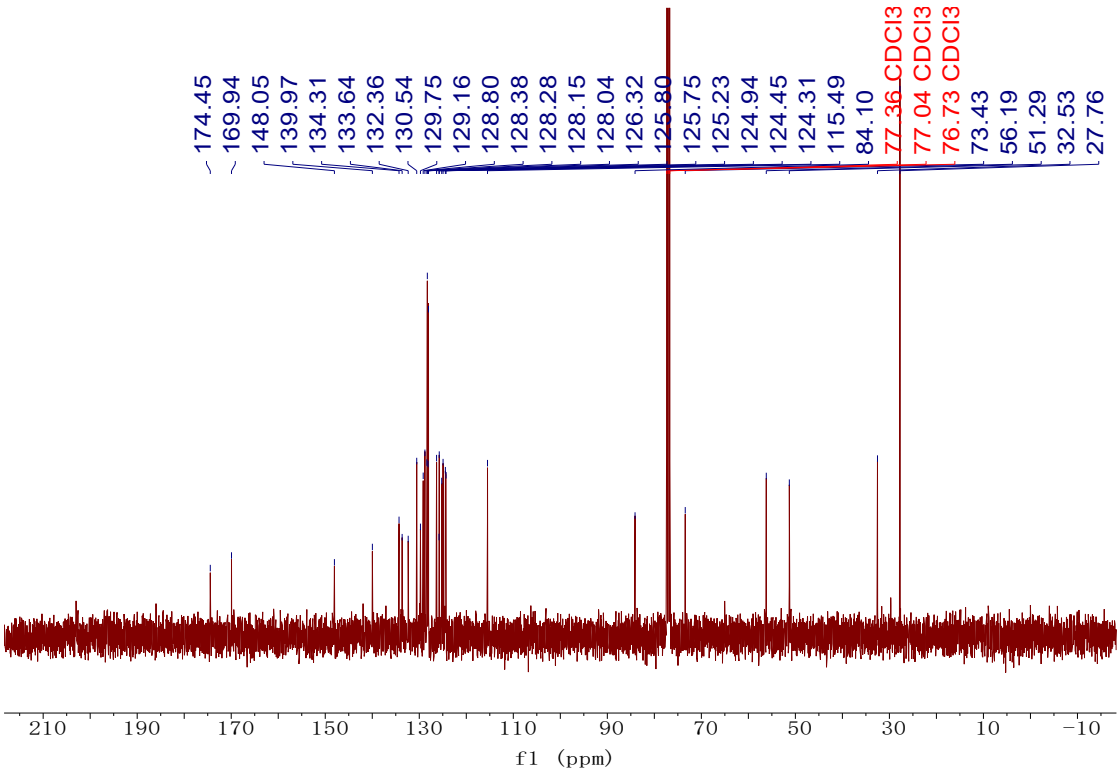
tert-butyl(3R,4'R)-2'-(4-methoxybenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3q)


7.72
7.72
7.70
7.70
7.66
7.65
7.64
7.43
7.43
7.36
7.35
7.26 CDCl3
7.18
7.16
7.16
7.15
7.14
7.13
7.06
7.06
7.05
7.04
6.79
6.78
6.78
6.77
6.77
6.76
6.76
6.74
3.98
3.97
3.95
3.75
3.70
3.60
3.57
1.40
H3CO
O
O
N
Ph
O
N
Boc
1.09
1.07
1.18
2.01
3.91
2.12
4.08
0.29
1.88
3.12
1.29
1.07
1.09
9.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

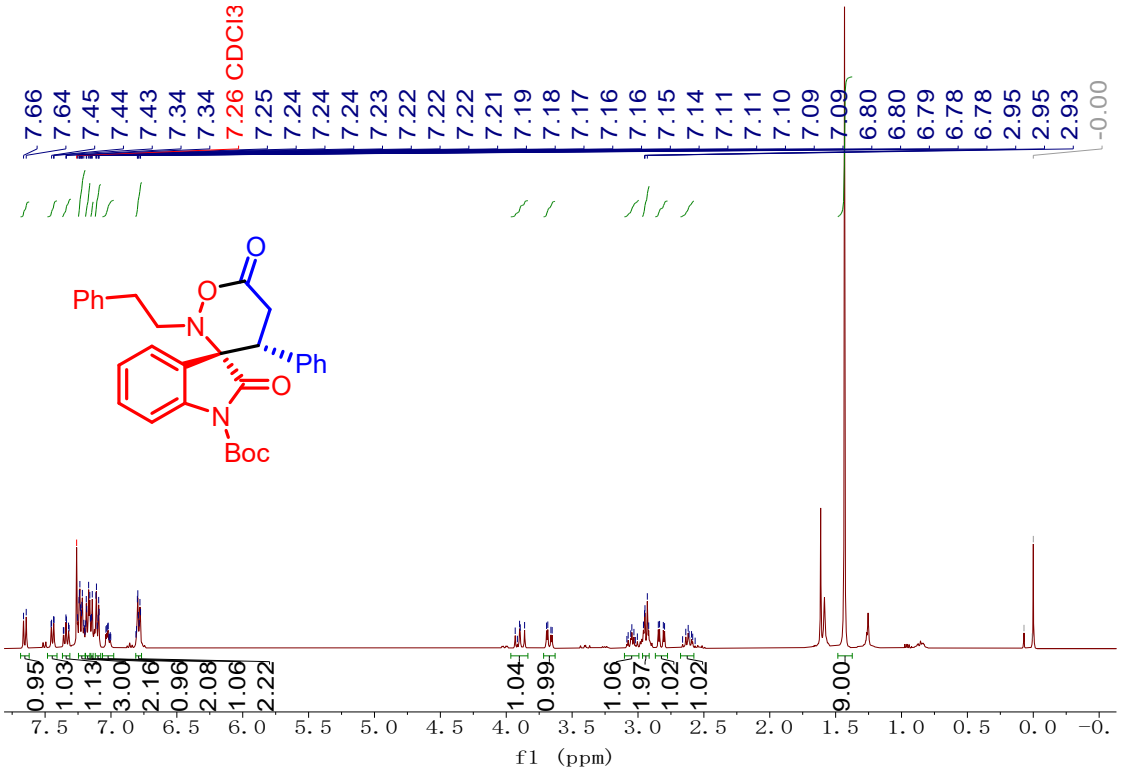

174.29
170.40
159.41
148.08
139.74
134.37
130.83
130.39
128.26
128.13
128.05
126.45
125.87
125.12
124.22
115.39
113.58
84.09
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
72.94
57.41
55.19
50.99
32.51
27.77
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)

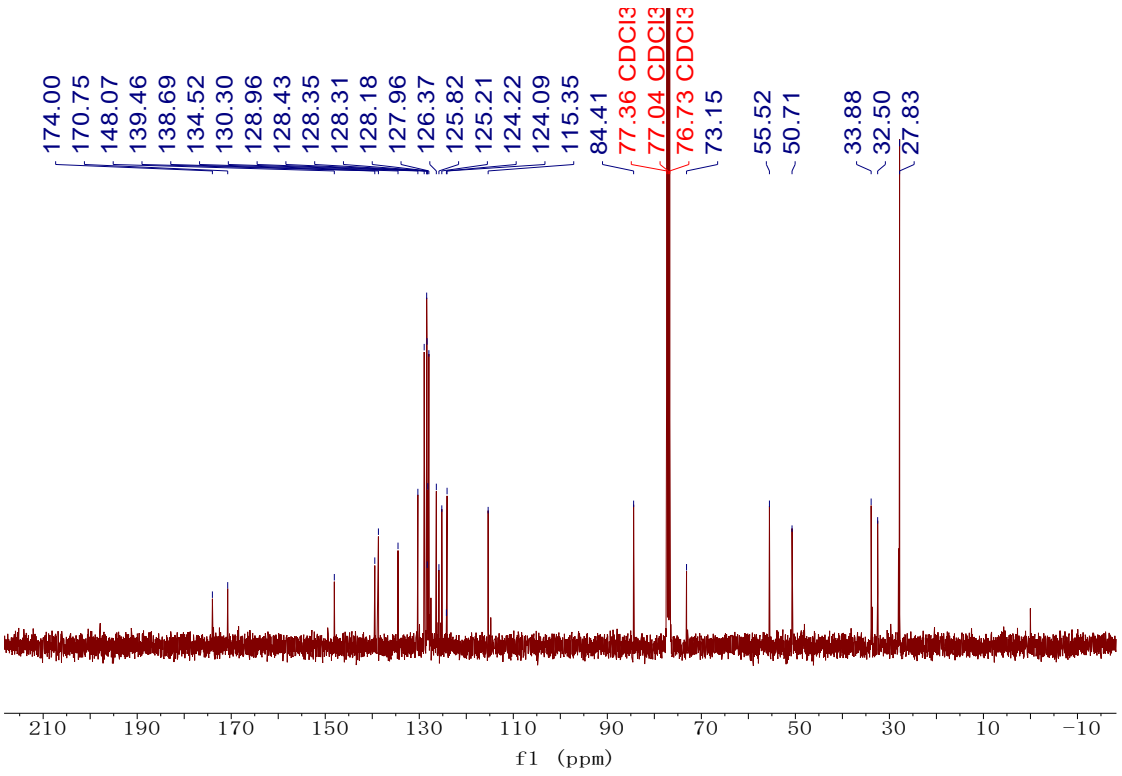
tert-butyl(3R,4'R)-2'-(naphthalen-1-ylmethyl)-2,6'-dioxo-4'-phenylspiro[indoline -3,3'-[1,2]oxazinane]-1-carboxylate (3r)



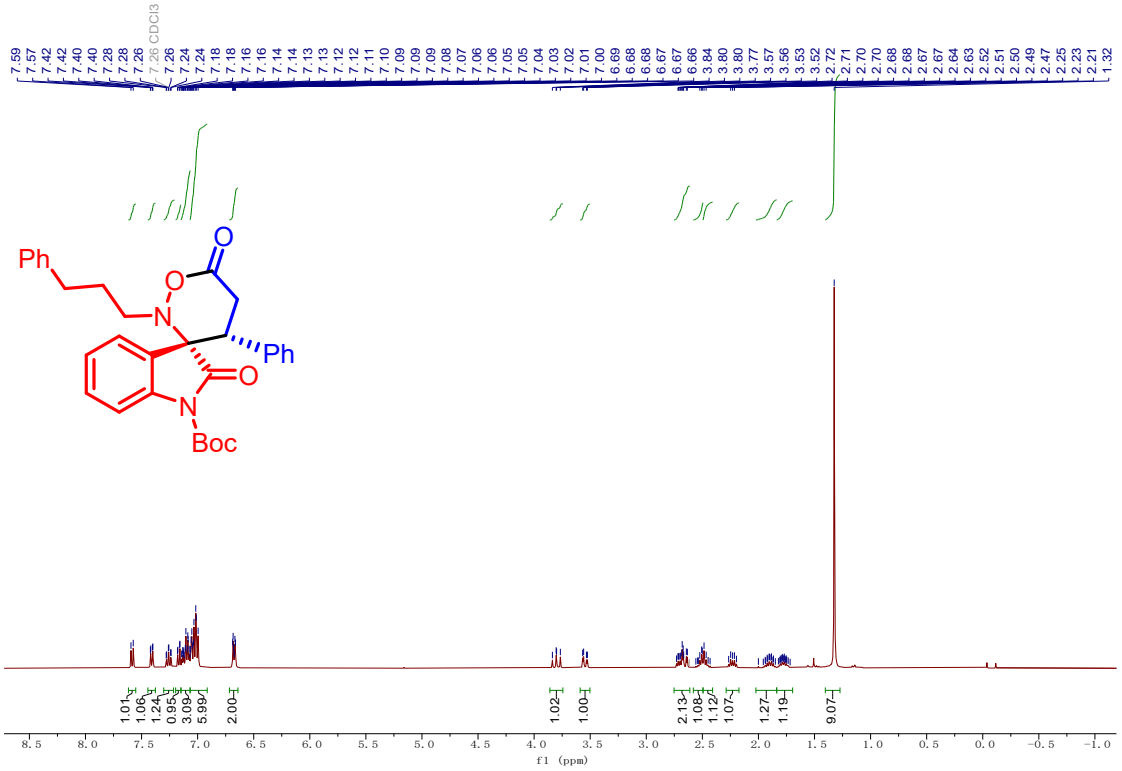


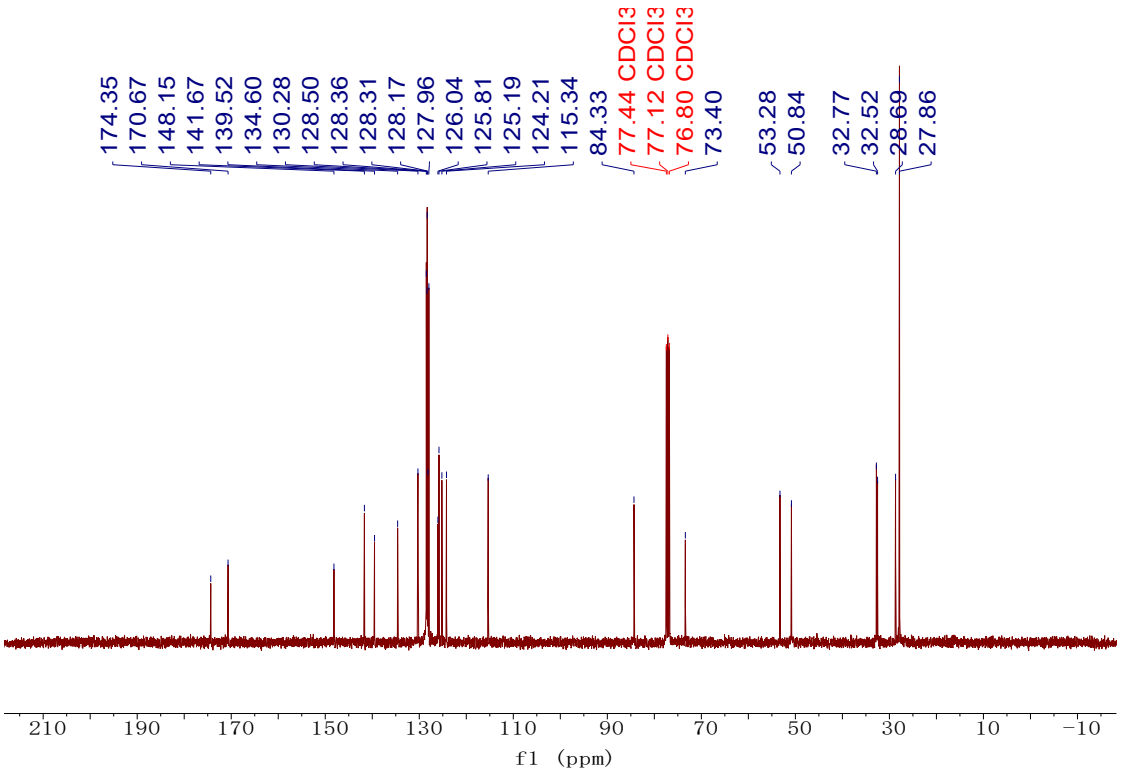
tert-butyl(3R,4'R)-2,6'-dioxo-2'-phenethyl-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3s)



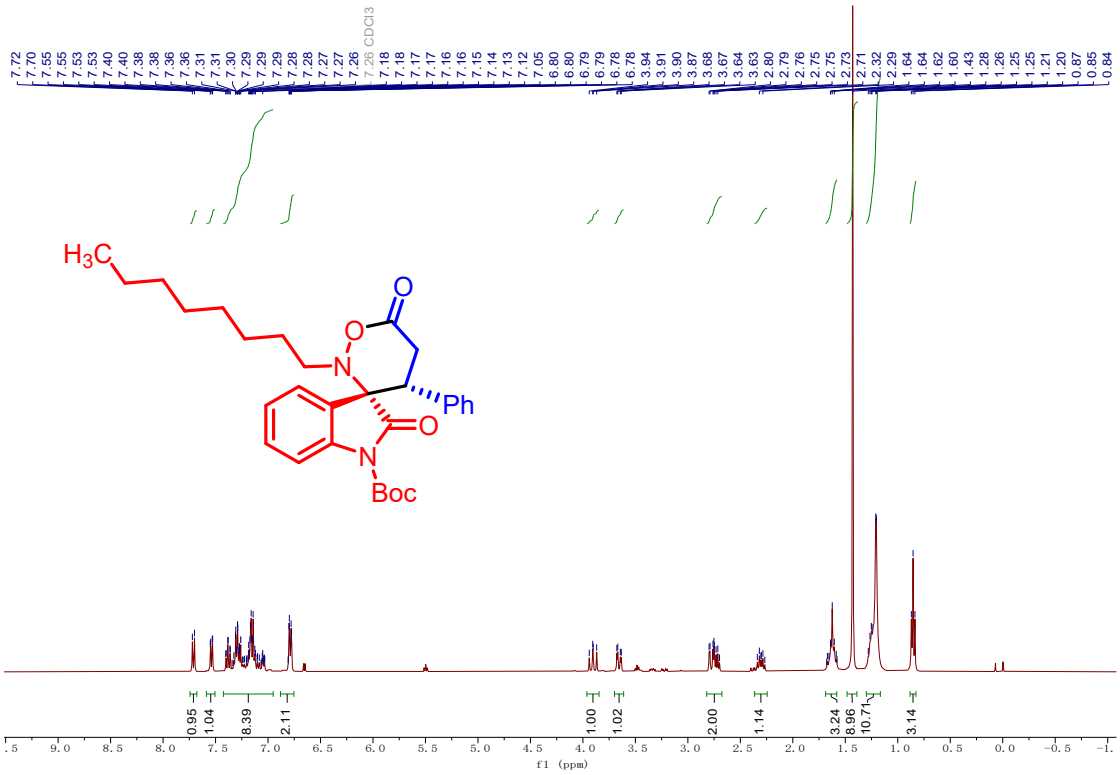


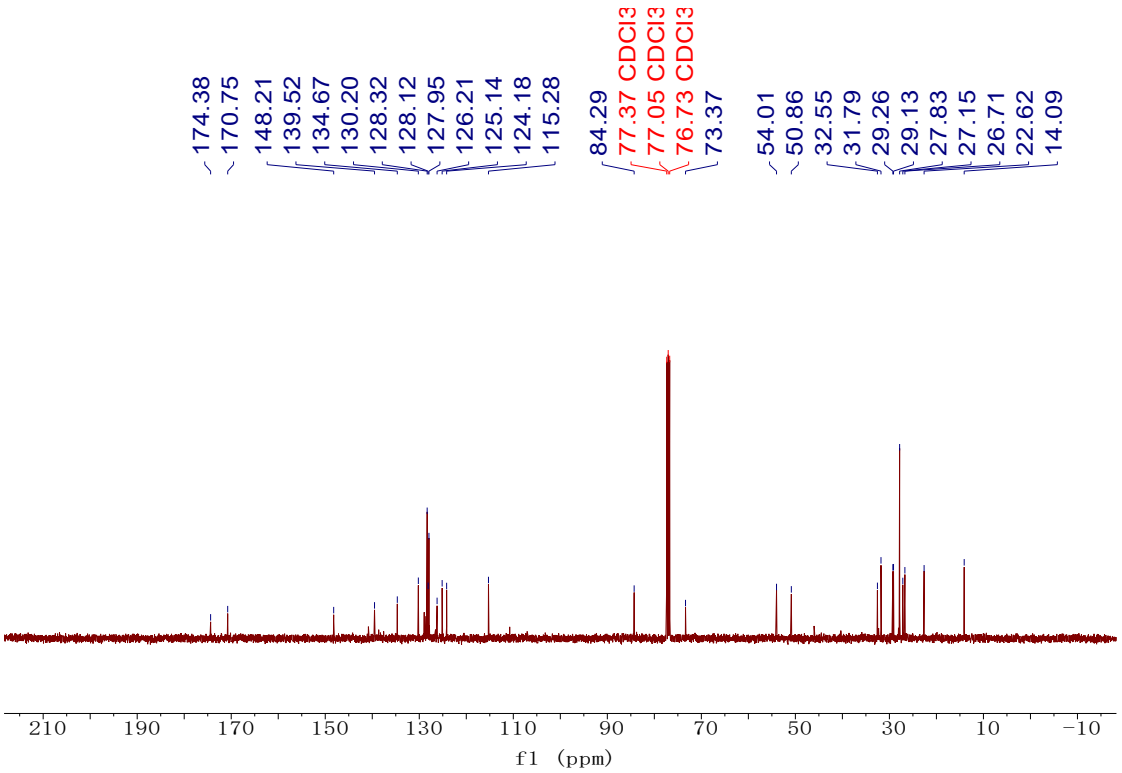
tert-butyl(3R,4'R)-2,6'-dioxo-4'-phenyl-2'-(3-phenylpropyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3t)



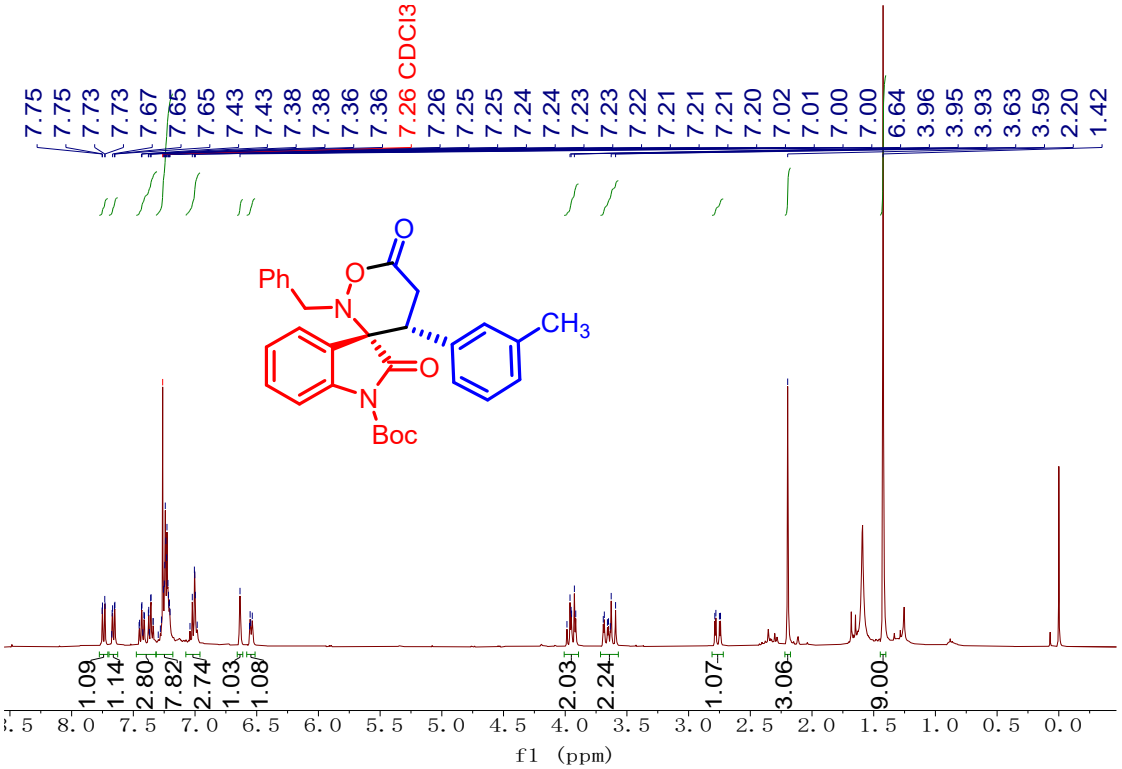


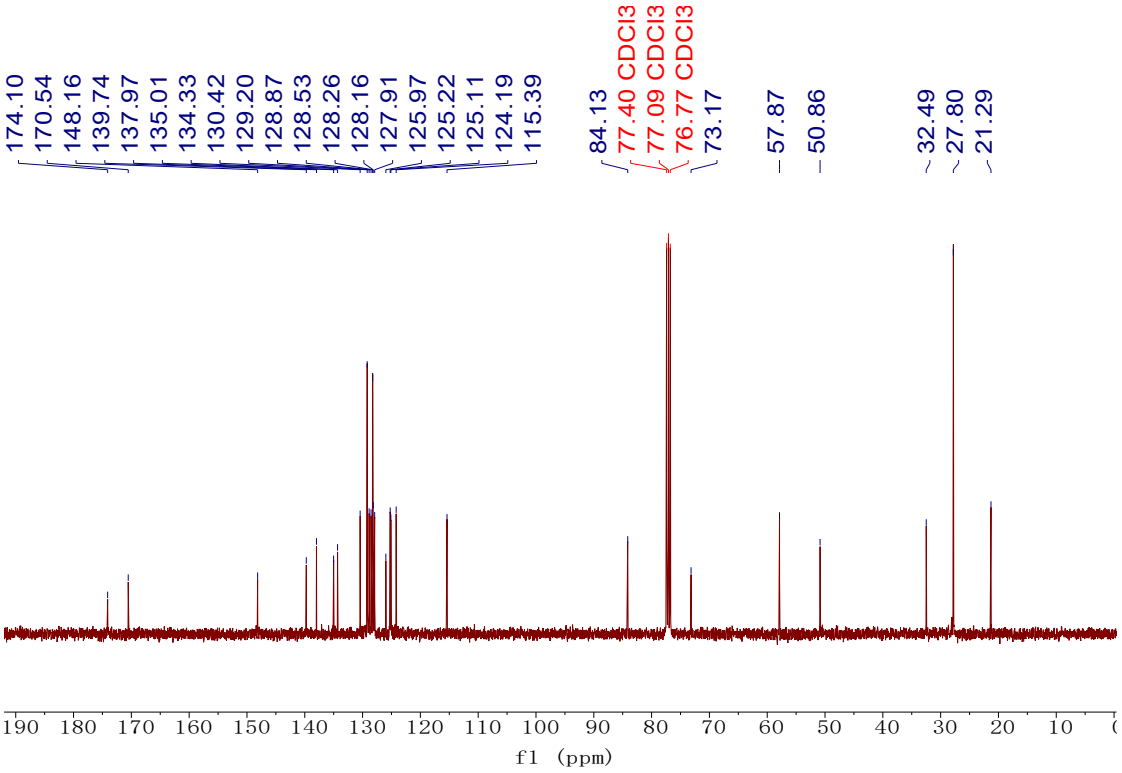
tert-butyl(3R,4'R)-2'-(4-fluorobenzyl)-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3u)



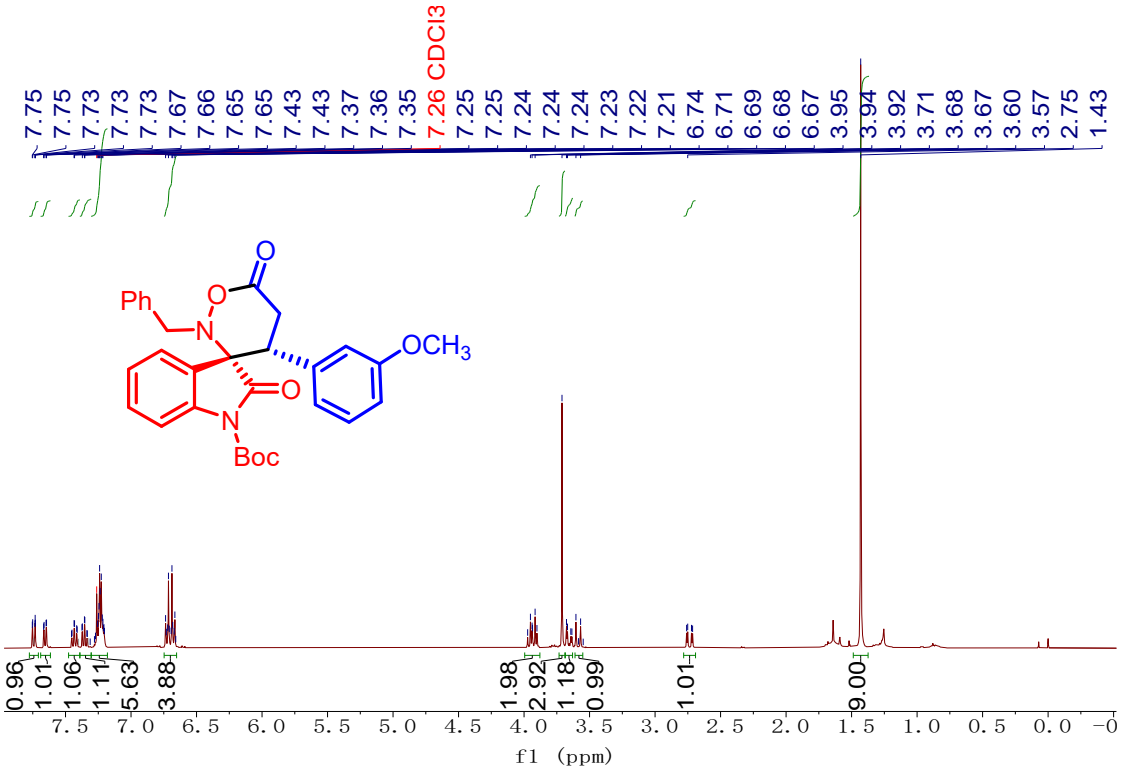


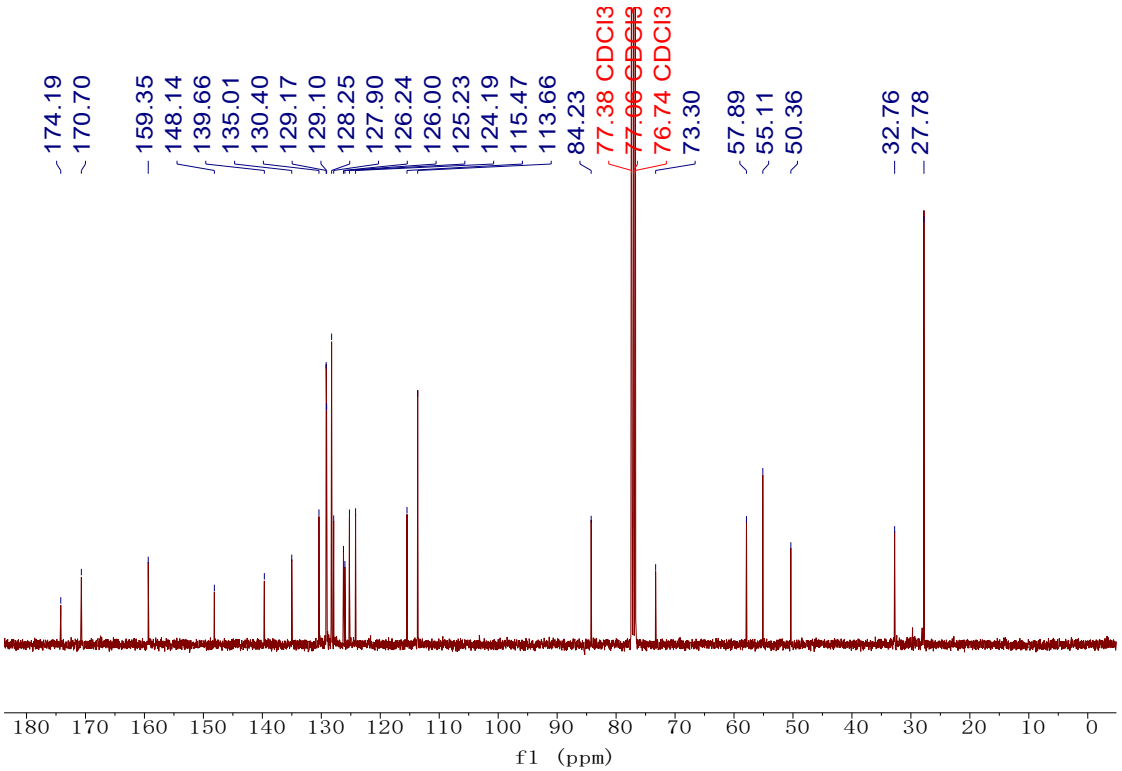
tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-(p-tolyl)spiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3v)



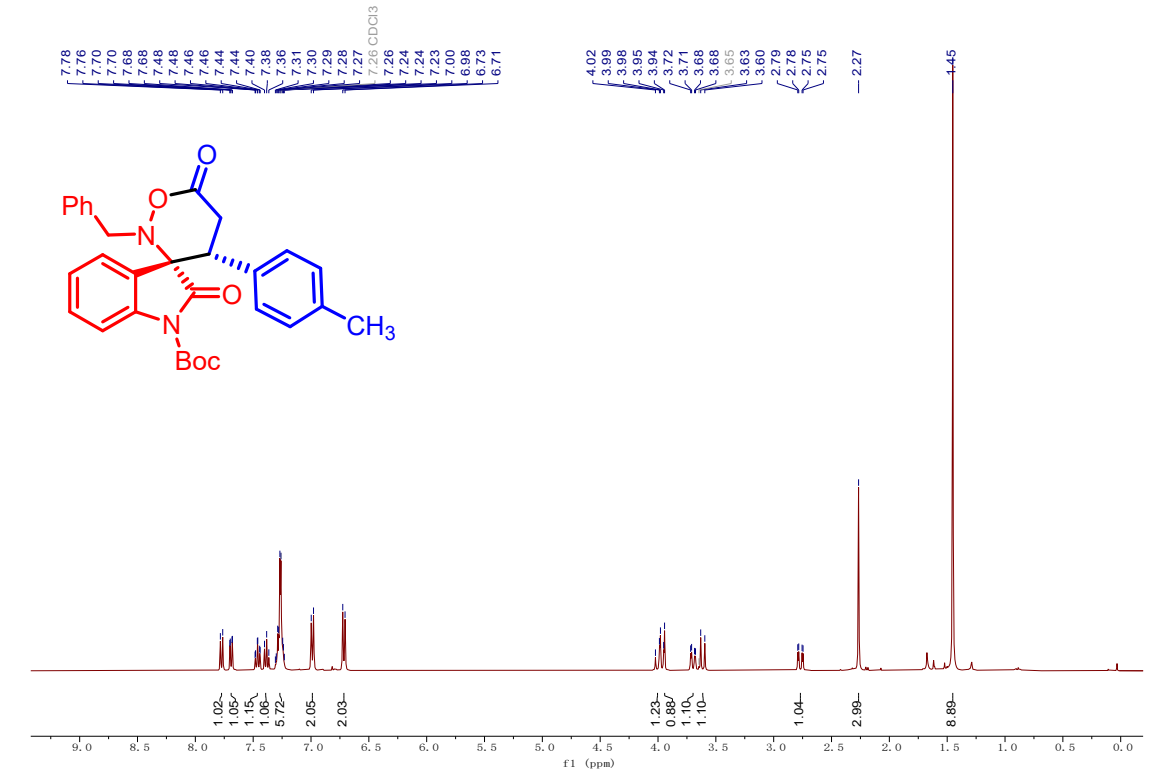


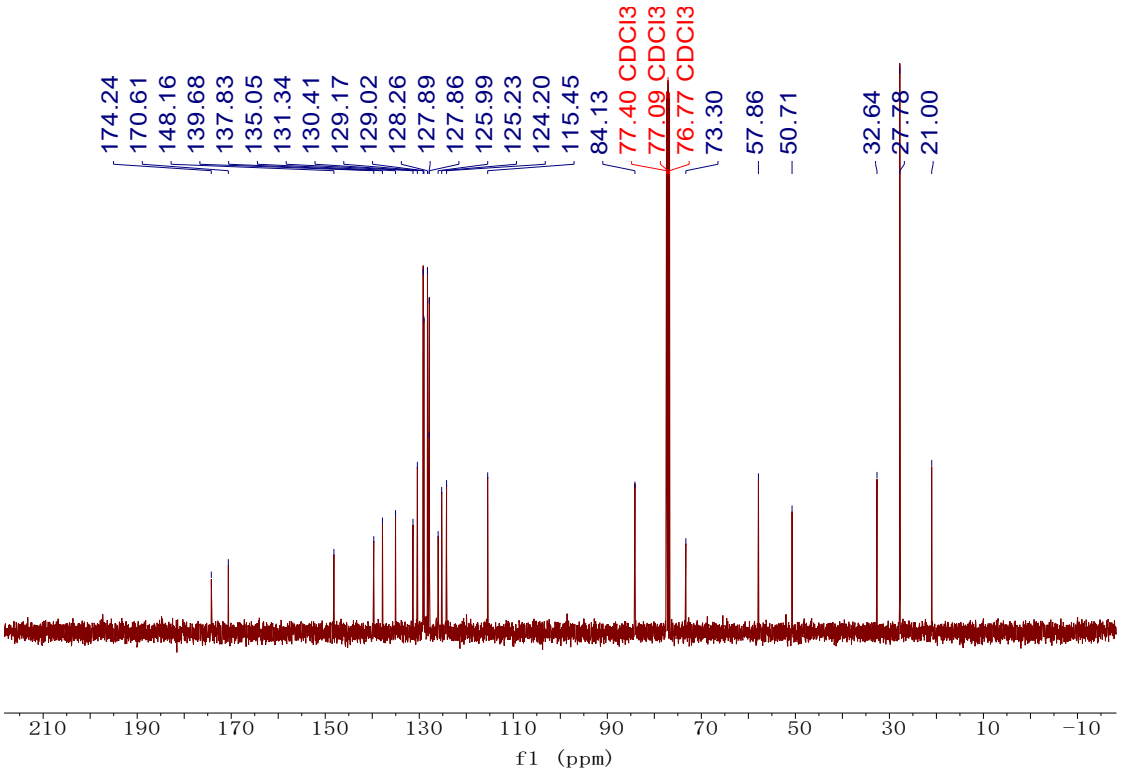
tert-butyl (3R,4'R)-2'-benzyl-4'-(3-methoxyphenyl)-2,6'-dioxospiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3w):


7.75 7.75 7.73 7.73 7.73 7.67 7.66 7.65 7.65 7.43 7.43 7.37 7.36 7.35 7.26 CDCl3 7.25 7.25 7.24 7.24 7.24 7.23 7.22 7.21 6.74 6.71 6.69 6.68 6.67 3.95 3.94 3.92 3.71 3.68 3.67 3.60 3.57 2.75 1.43
Ph
O
N
O
OCH3
O
N
Boc
0.96 1.01 1.06 1.11 5.63 3.88 1.98 2.92 1.18 0.99 1.01 9.00
f1 (ppm)

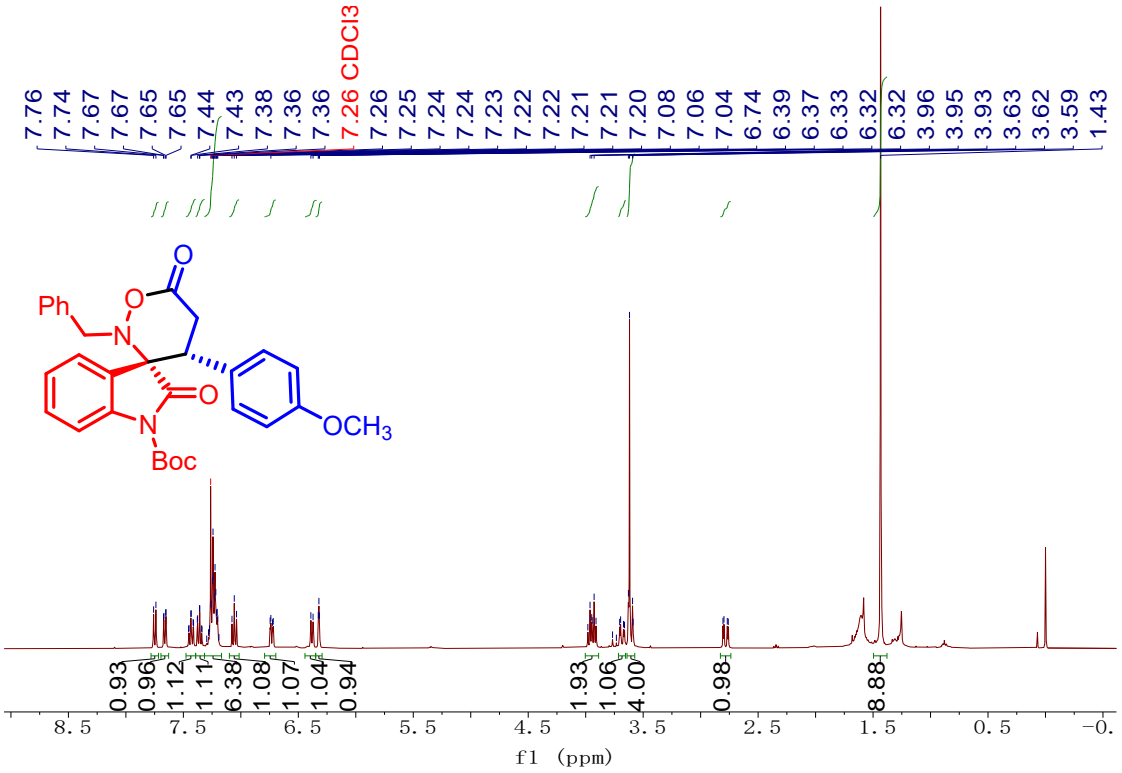

174.19 170.70 159.35 148.14 139.66 135.01 130.40 129.17 129.10 128.25 127.90 126.24 126.00 125.23 124.19 115.47 113.66 84.23 77.38 CDCl3 76.74 CDCl3 73.30 57.89 55.11 50.36 32.76 27.78
f1 (ppm)

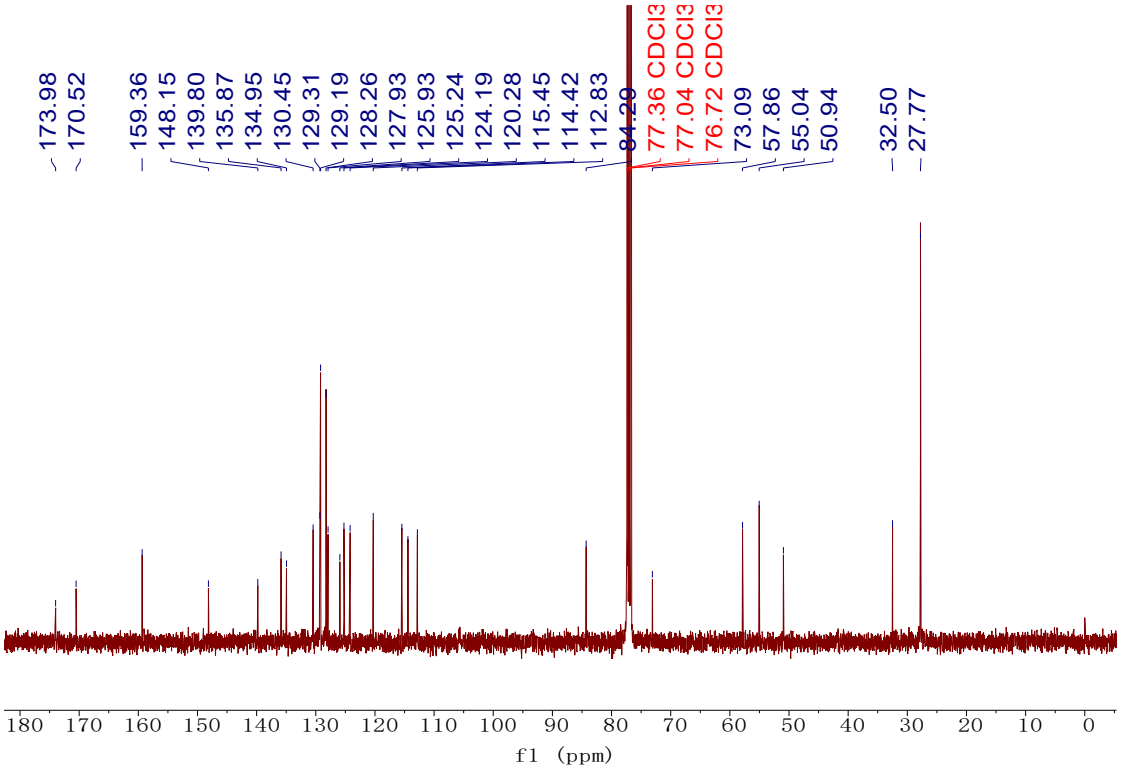
tert-butyl(3R,4'R)-2'-benzyl-2,6'-dioxo-4'-phenylspiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate(3x)



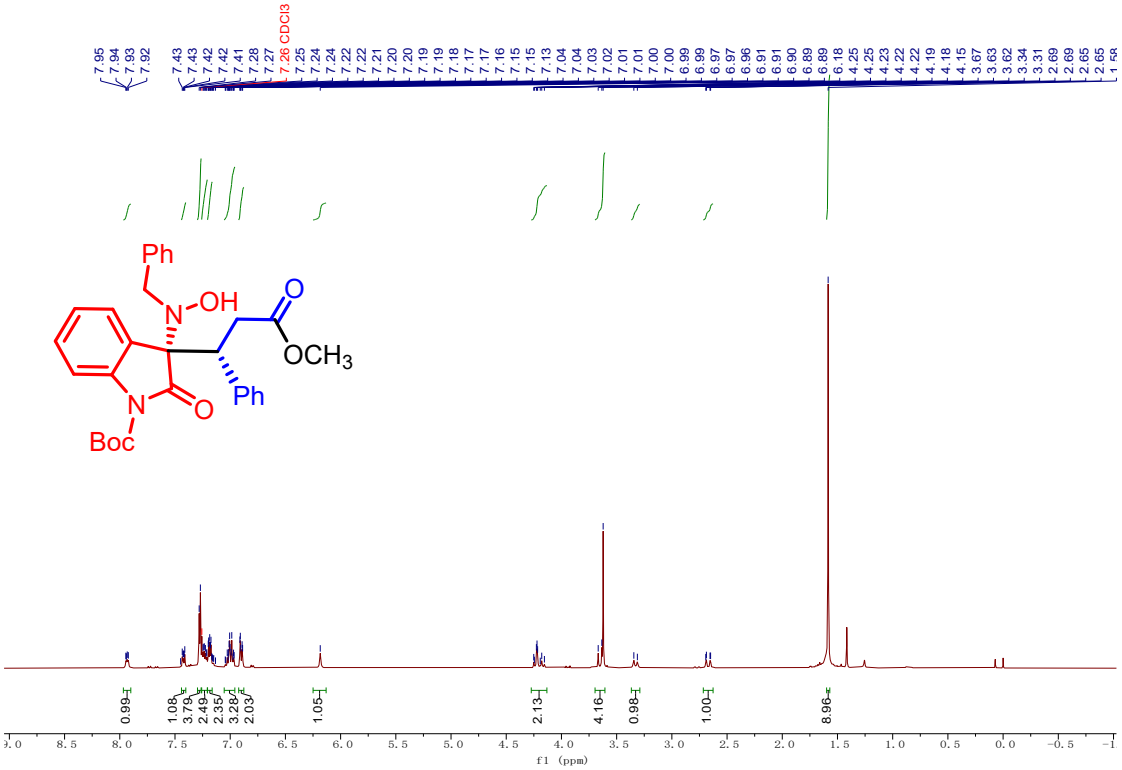


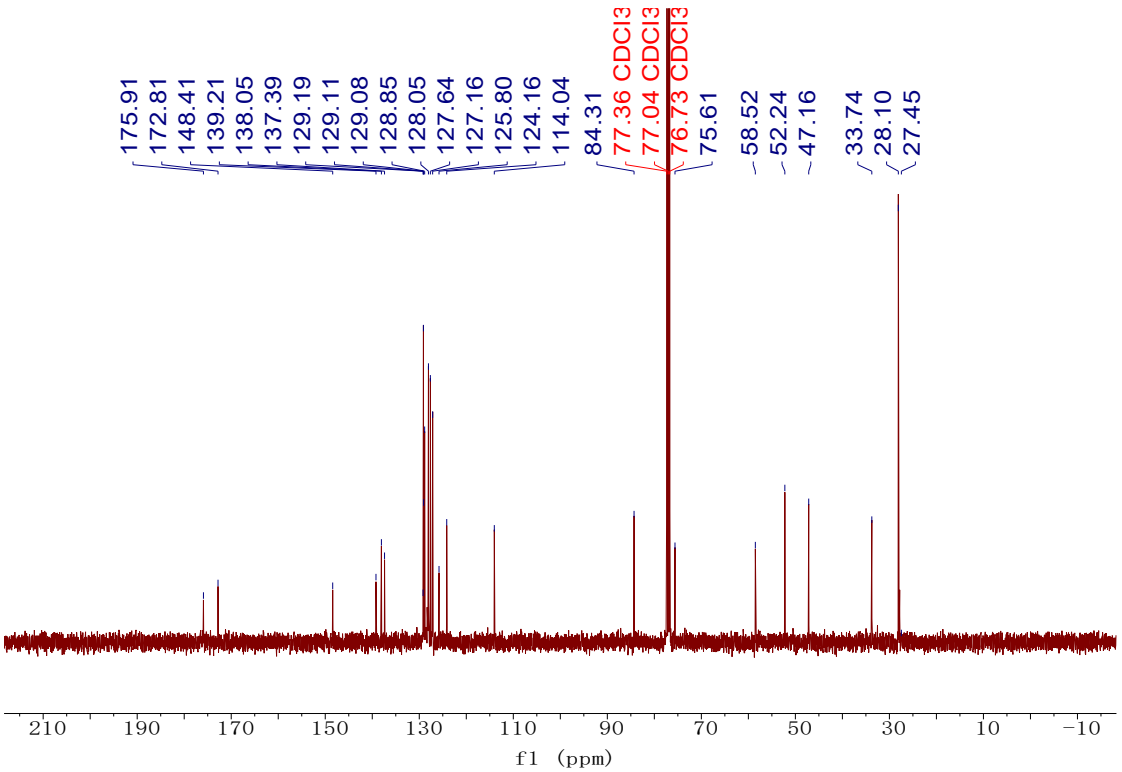
tert-butyl (3R,4'R)-2'-benzyl-4'-(4-methoxyphenyl)-2,6'-dioxospiro[indoline-3,3'-[1,2]oxazinane]-1-carboxylate (3y):



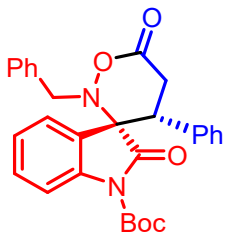


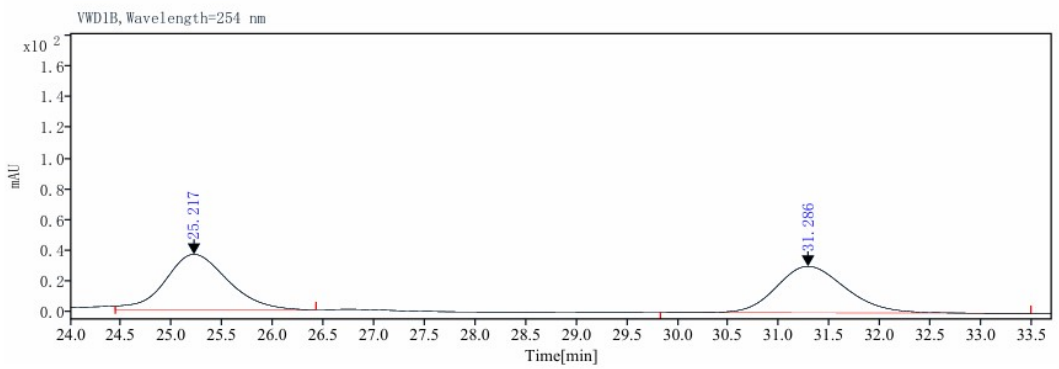
tert-butyl(R)-3-(benzyl(hydroxy)amino)-3-((R)-3-methoxy-3-oxo-1-phenylpropyl)-2-oxoindoline-1-carboxylate (4)





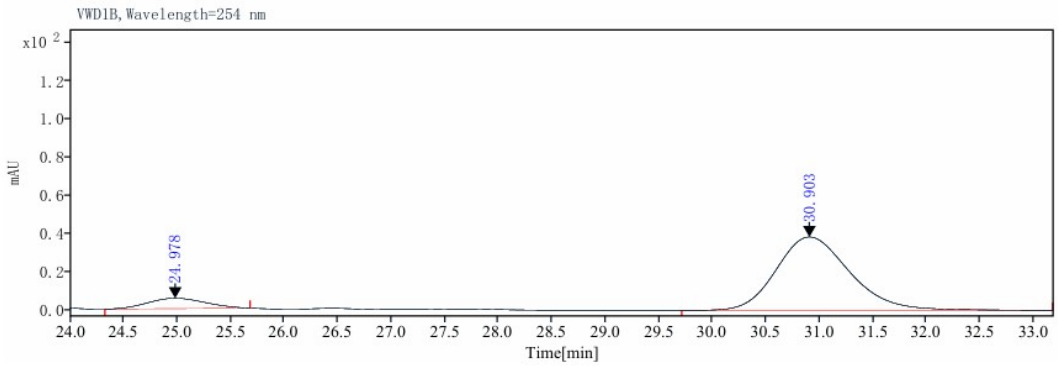
HPLC spectra of product 3a.





VWD1B, Wavelength=254 nm

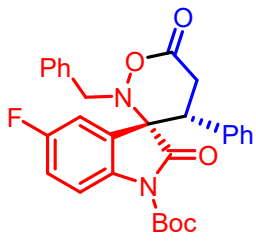
Ret. Time	Area	Height	Area%
25.217	1556.92	36.08	51.98
31.286	1438.47	30.19	48.02
Total	2995.39	66.27	100.00

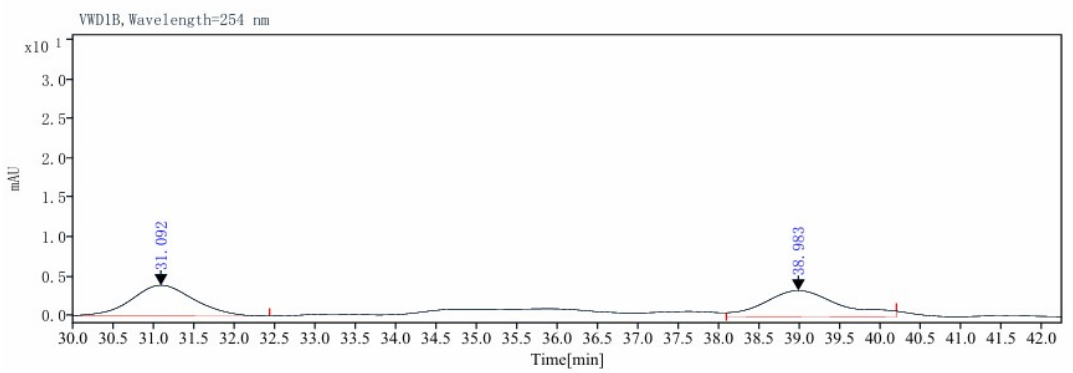


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
24.978	203.62	5.44	10.04
30.903	1824.28	38.35	89.96
Total	2027.89	43.79	100.00

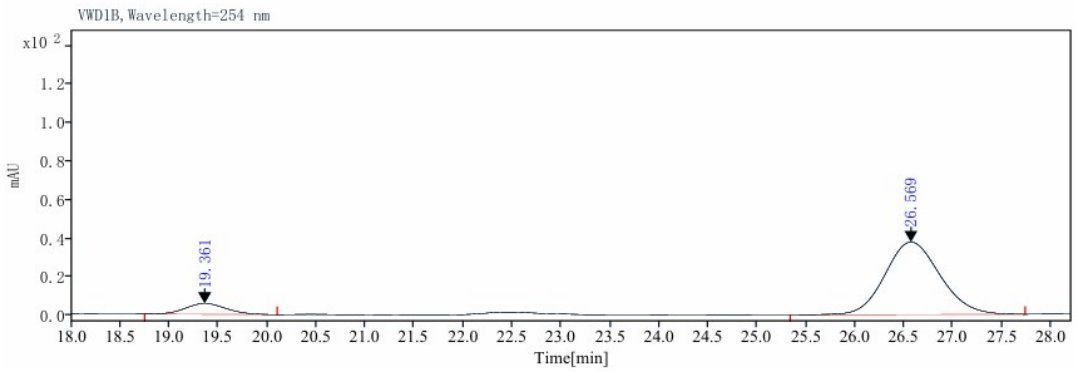
HPLC spectra of product 3b.





VWD1B, Wavelength=254 nm

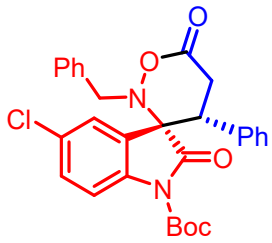
Ret. Time	Area	Height	Area%
31.092	212.06	3.91	49.51
38.983	216.28	3.31	50.49
Total	428.34	7.22	100.00

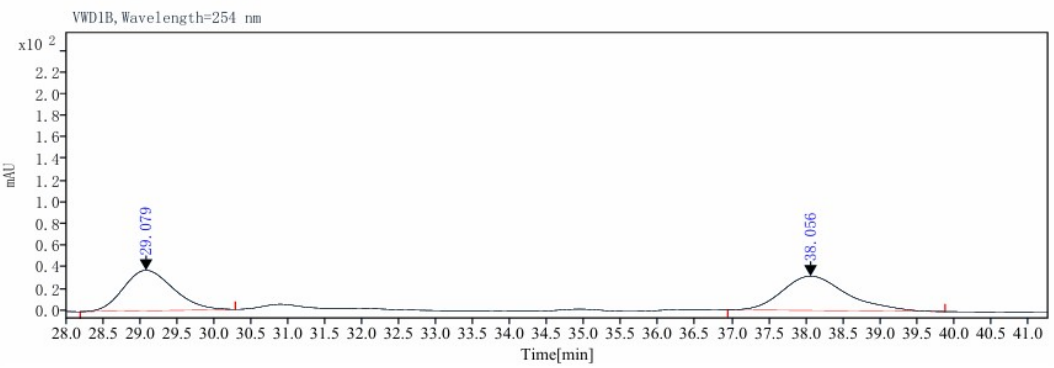


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
19.361	161.01	5.60	9.86
26.569	1471.57	37.65	90.14
Total	1632.58	43.26	100.00

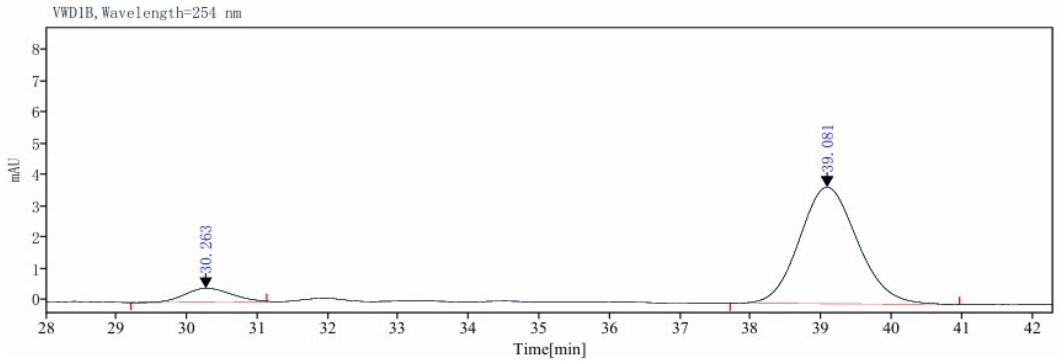
HPLC spectra of product 3c.





VWD1B, Wavelength=254 nm

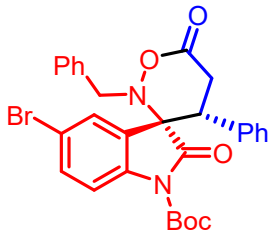
Ret. Time	Area	Height	Area%
29.079	1752.69	37.40	47.73
38.056	1919.17	31.72	52.27
Total	3671.86	69.11	100.00

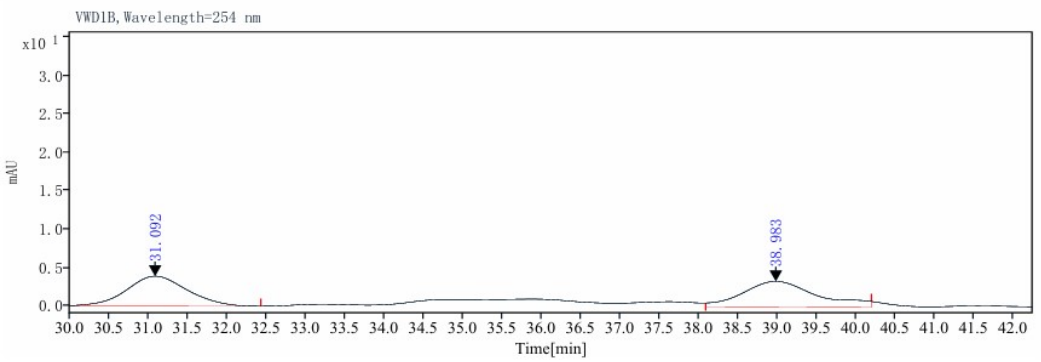


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
30.263	20.86	0.45	8.89
39.081	213.69	3.73	91.11
Total	234.54	4.18	100.00

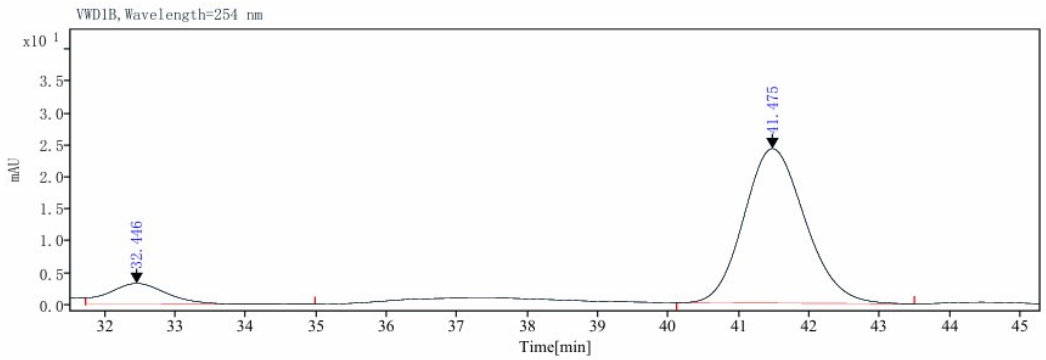
HPLC spectra of product 3d.





VWD1B, Wavelength=254 nm

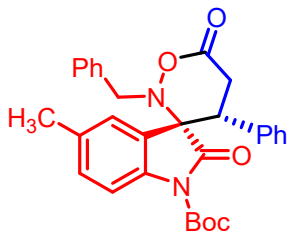
Ret. Time	Area	Height	Area%
31.092	212.06	3.91	49.51
38.983	216.28	3.31	50.49
Total	428.34	7.22	100.00

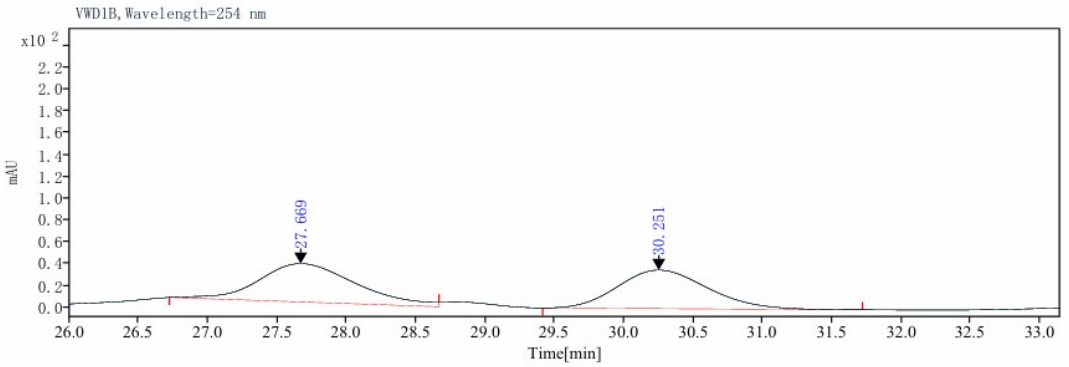


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
32.446	191.53	3.27	11.59
41.475	1460.61	24.14	88.41
Total	1652.14	27.41	100.00

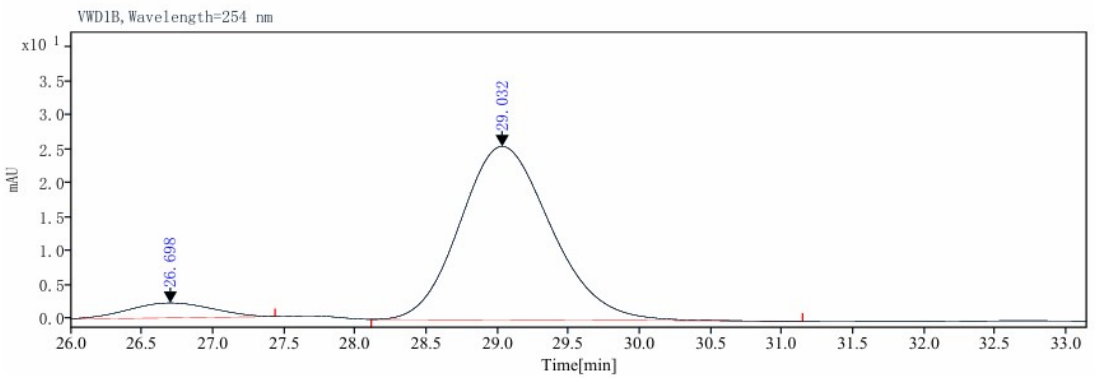
HPLC spectra of product 3e.





VWD1B, Wavelength=254 nm

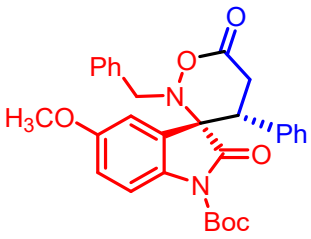
Ret. Time	Area	Height	Area%
27.669	1712.17	35.18	51.75
30.251	1596.18	35.34	48.25
Total	3308.35	70.52	100.00

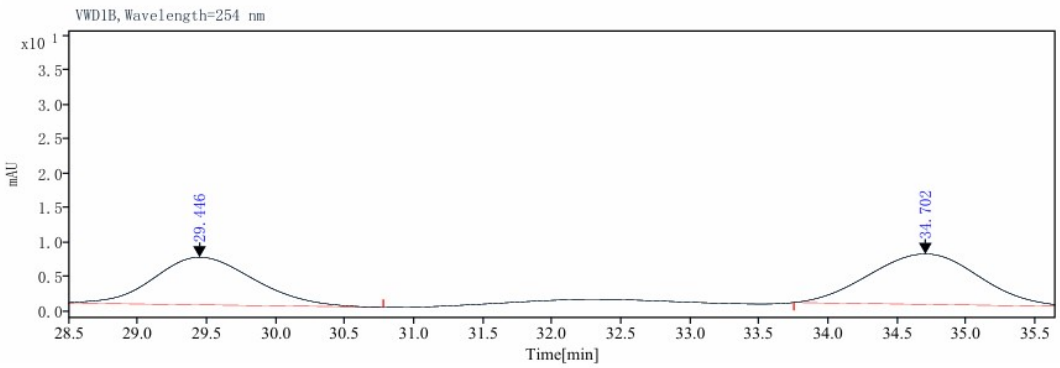


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
26.698	91.57	2.21	7.45
29.032	1137.72	25.55	92.55
Total	1229.28	27.76	100.00

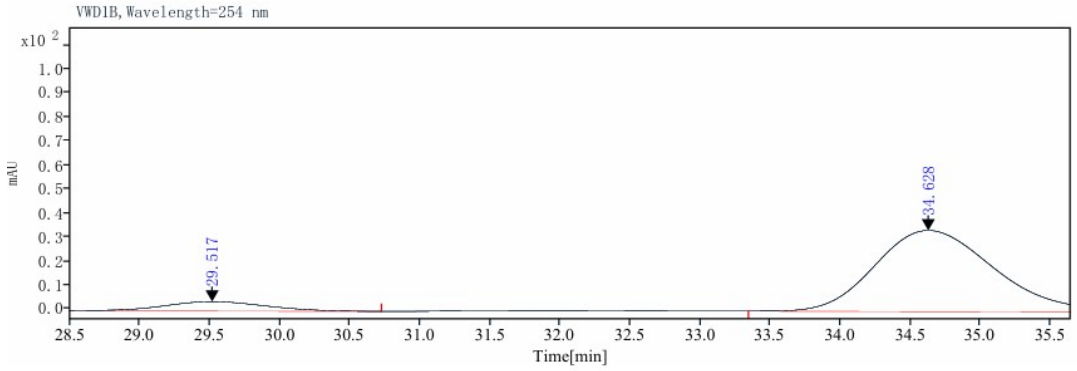
HPLC spectra of product 3f.





VWD1B, Wavelength=254 nm

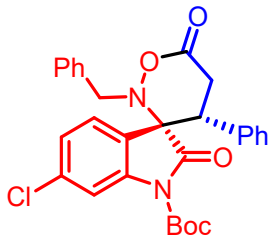
Ret. Time	Area	Height	Area%
29.446	349.16	6.90	46.42
34.702	403.05	7.32	53.58
Total	752.22	14.22	100.00

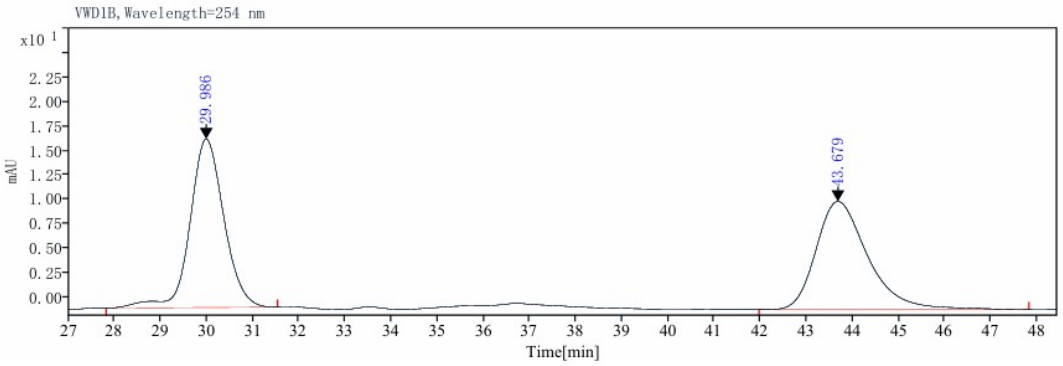


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
29.517	201.46	3.96	9.10
34.628	2011.81	33.82	90.90
Total	2213.27	37.78	100.00

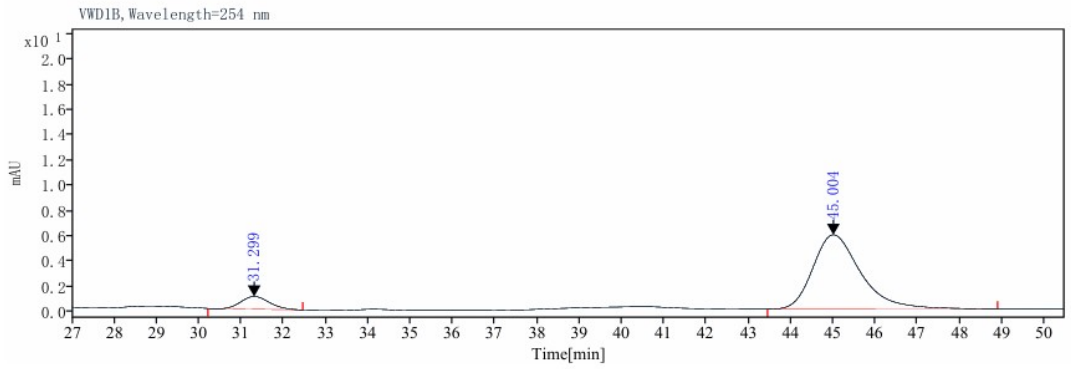
HPLC spectra of product 3g.





VWD1B, Wavelength=254 nm

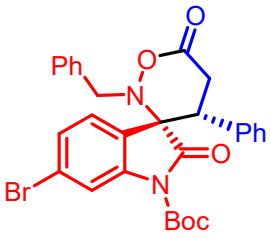
Ret. Time	Area	Height	Area%
29.986	886.72	17.29	50.56
43.679	867.03	11.11	49.44
Total	1753.75	28.40	100.00

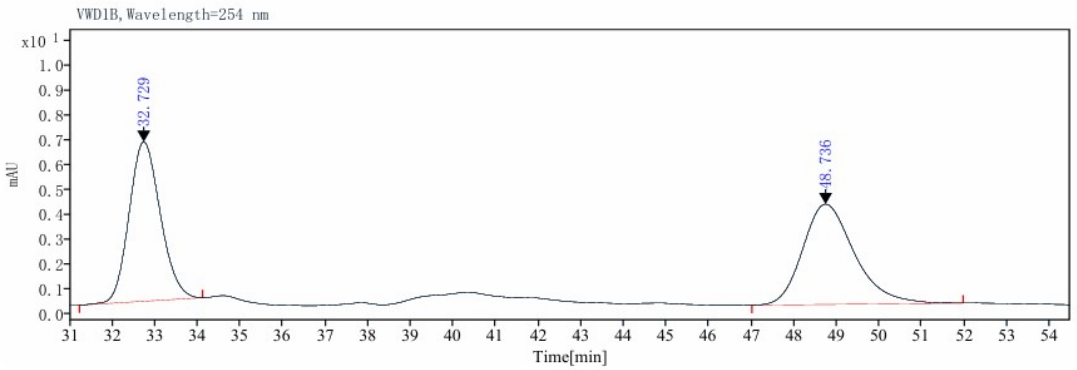


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
31.299	46.94	1.00	9.20
45.004	463.41	5.89	90.80
Total	510.35	6.89	100.00

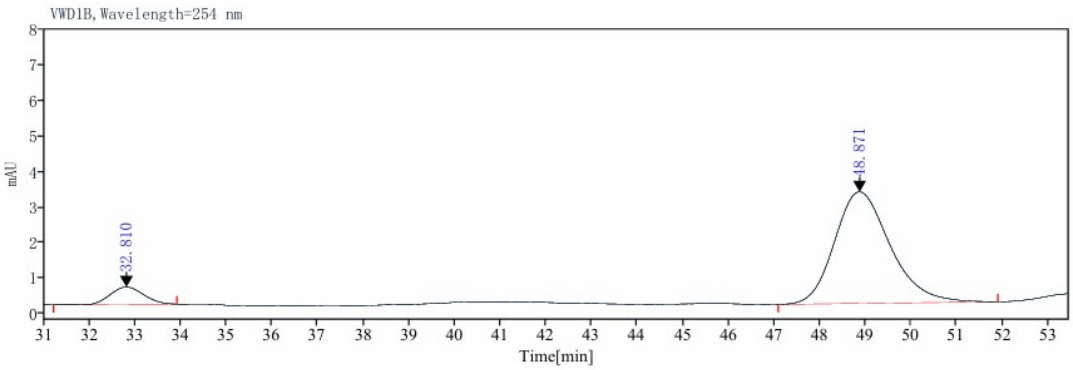
HPLC spectra of product 3h.





VWD1B, Wavelength=254 nm

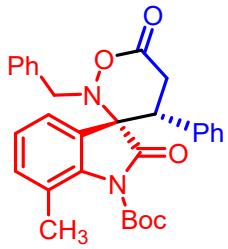
Ret. Time	Area	Height	Area%
32.729	327.40	6.42	48.99
48.736	340.90	4.04	51.01
Total	668.30	10.47	100.00

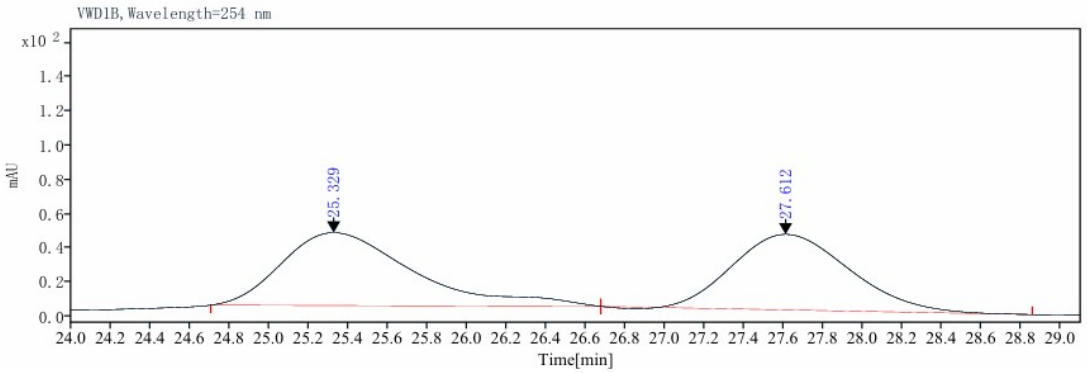


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
32.810	24.18	0.49	8.31
48.871	266.95	3.15	91.69
Total	291.13	3.64	100.00

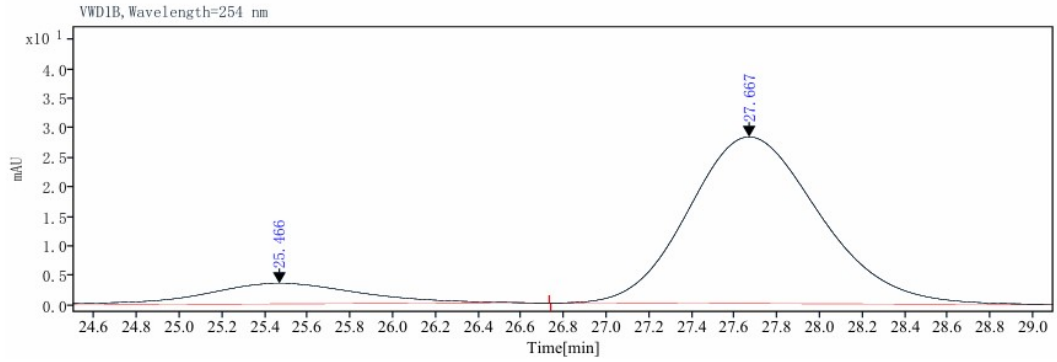
HPLC spectra of product 3i.





VWD1B, Wavelength=254 nm

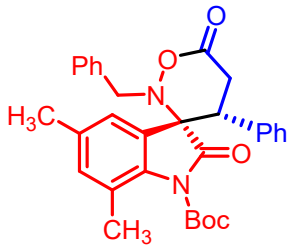
Ret. Time	Area	Height	Area%
25.329	1959.16	42.53	52.10
27.612	1801.50	44.10	47.90
Total	3760.66	86.63	100.00

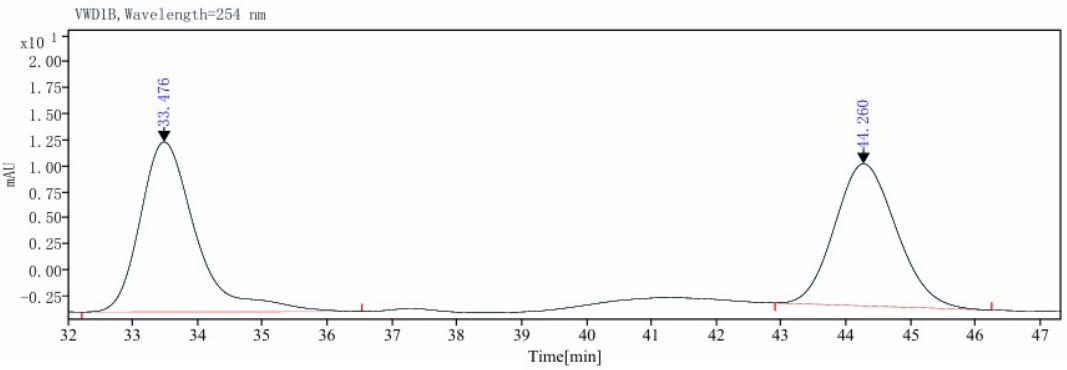


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
25.466	178.93	3.49	12.86
27.667	1211.91	28.29	87.14
Total	1390.84	31.78	100.00

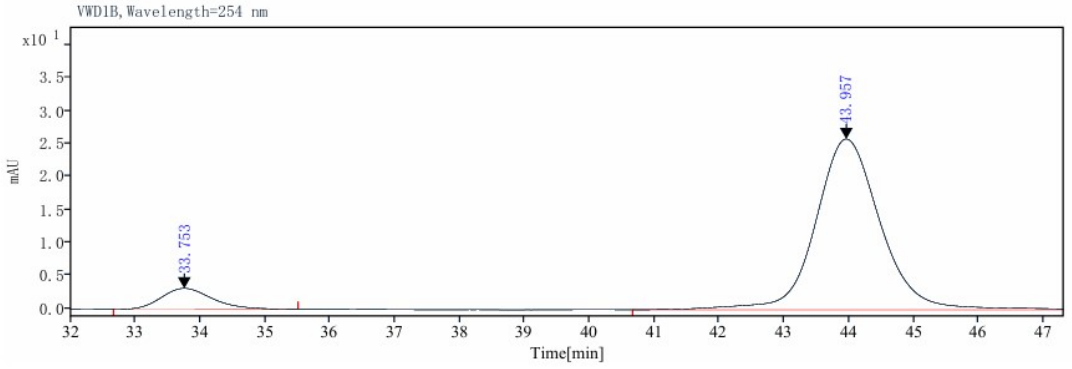
HPLC spectra of product 3j.





VWD1B, Wavelength=254 nm

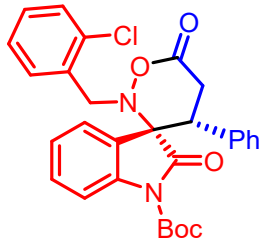
Ret. Time	Area	Height	Area%
33.476	973.73	16.34	51.87
44.260	903.67	13.66	48.13
Total	1877.40	30.00	100.00

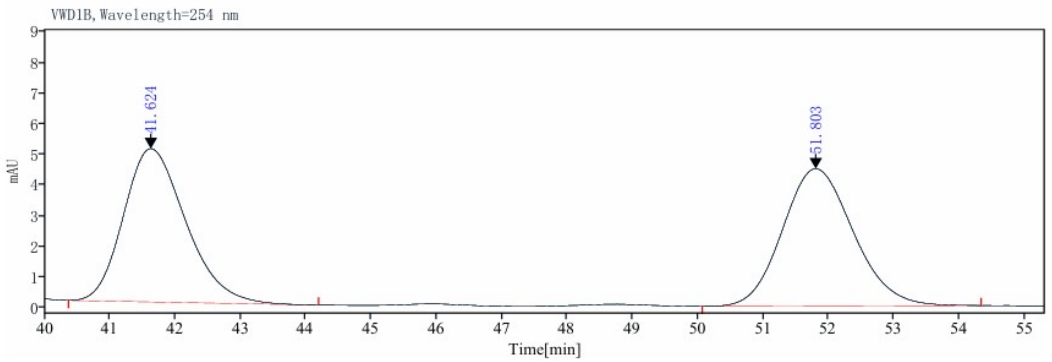


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
33.753	173.77	3.18	8.74
43.957	1814.97	25.96	91.26
Total	1988.74	29.14	100.00

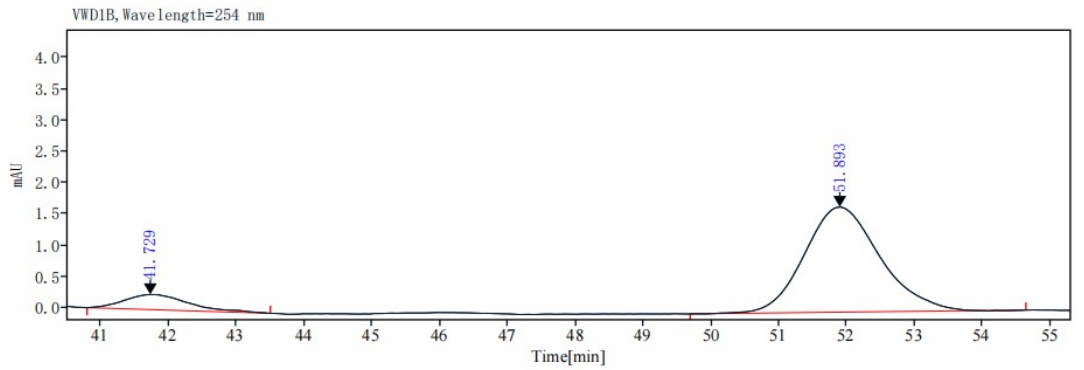
HPLC spectra of product 3k.





VWD1B, Wavelength=254 nm

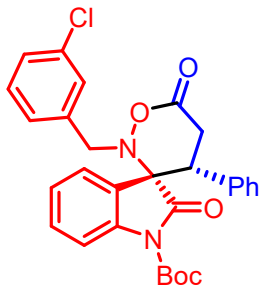
Ret. Time	Area	Height	Area%
41.624	331.88	5.01	49.50
51.803	338.65	4.49	50.50
Total	670.53	9.50	100.00

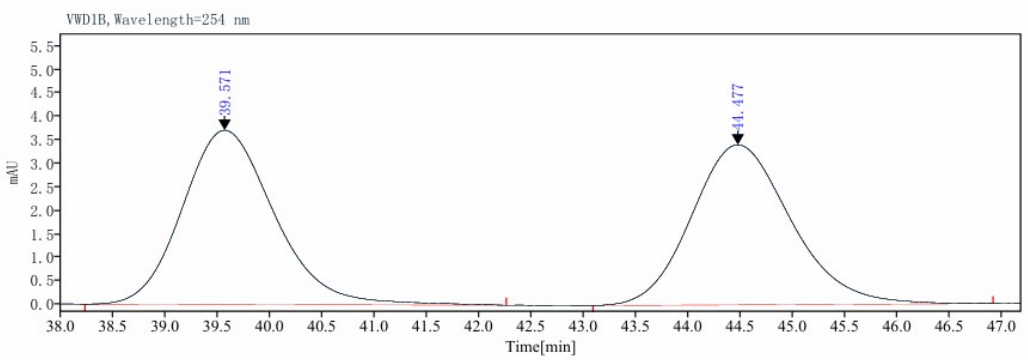


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
41.729	15.92	0.24	10.94
51.893	129.61	1.68	89.06
Total	145.53	1.92	100.00

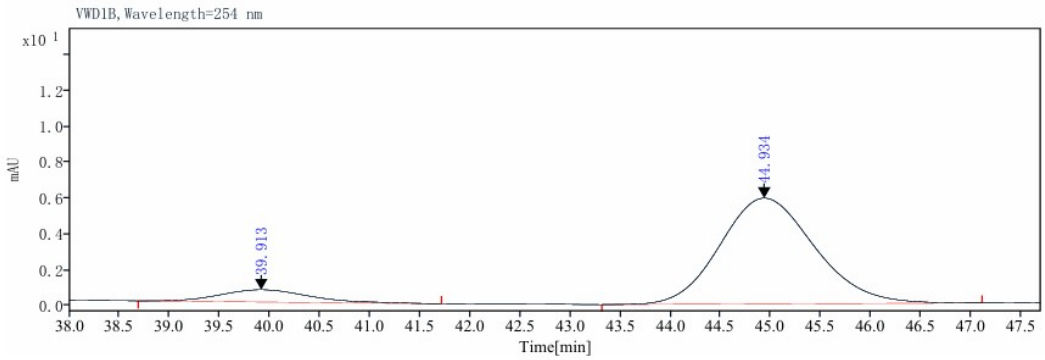
HPLC spectra of product 3l.





VWD1B, Wavelength=254 nm

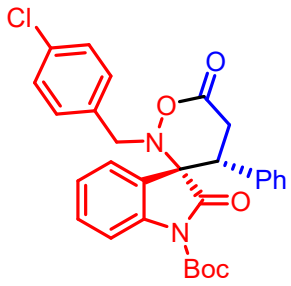
Ret. Time	Area	Height	Area%
39.571	226.74	3.71	50.20
44.477	224.96	3.40	49.80
Total	451.69	7.11	100.00

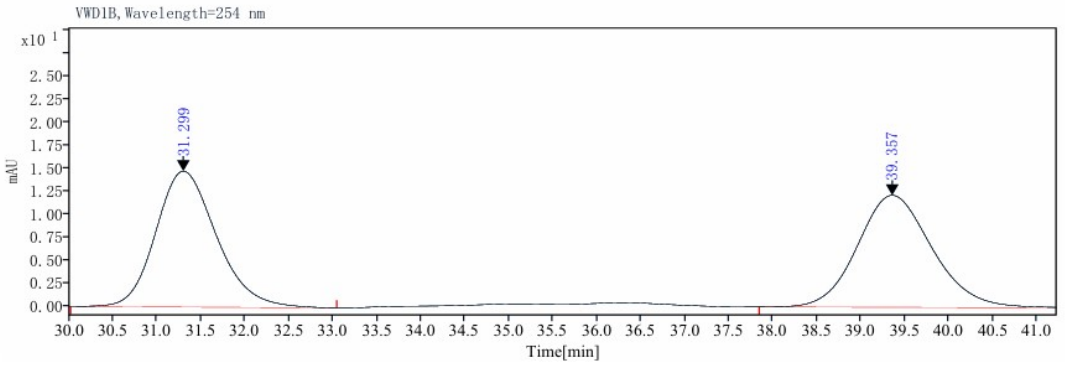


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
39.913	42.59	0.69	9.87
44.934	388.72	5.91	90.13
Total	431.31	6.60	100.00

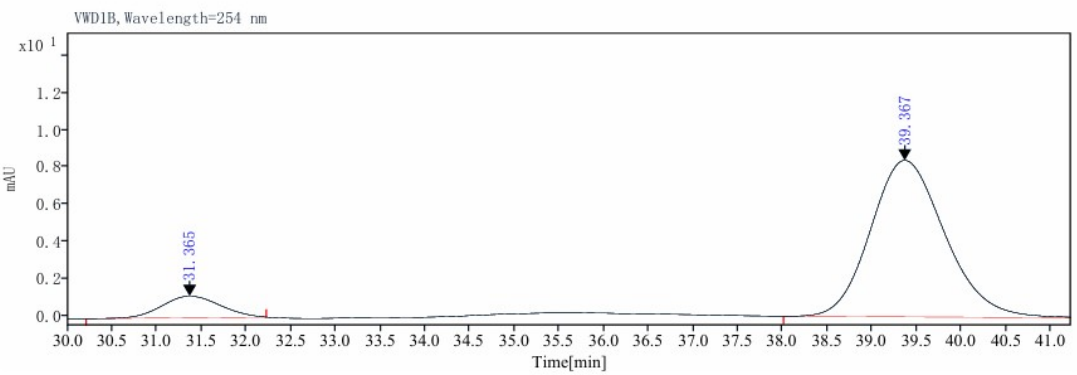
HPLC spectra of product 3m.





VWD1B, Wavelength=254 nm

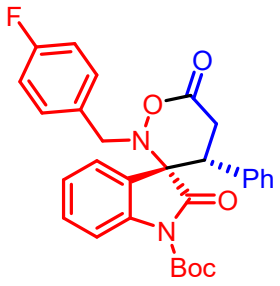
Ret. Time	Area	Height	Area%
31.299	711.36	14.80	49.70
39.357	719.86	12.20	50.30
Total	1431.22	27.00	100.00

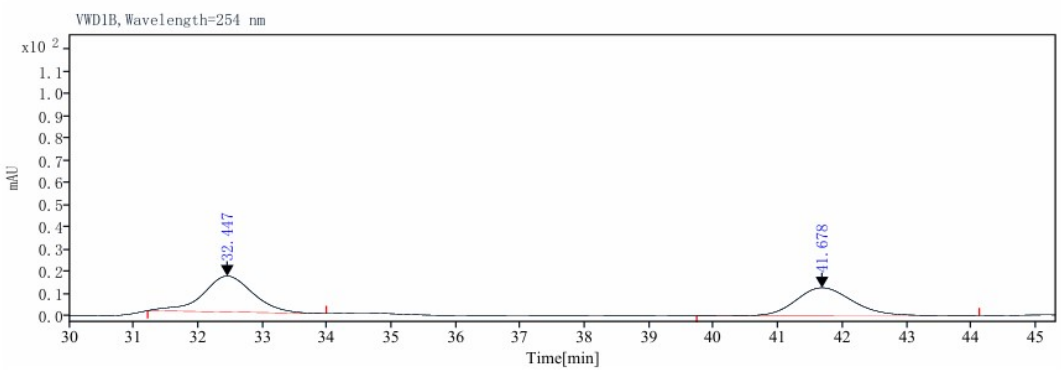


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
31.365	52.47	1.17	9.72
39.367	487.54	8.43	90.28
Total	540.01	9.59	100.00

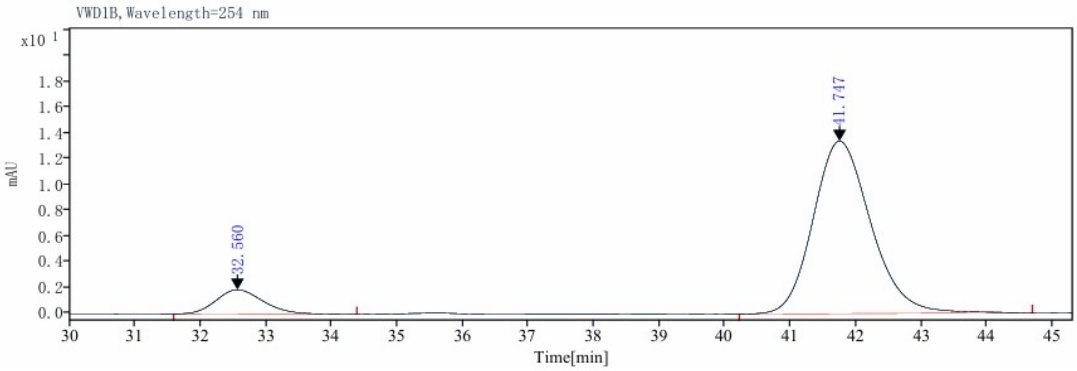
HPLC spectra of product 3n.





VWD1B, Wavelength=254 nm

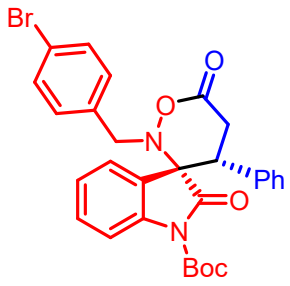
Ret. Time	Area	Height	Area%
32.447	873.18	16.17	52.73
41.678	782.84	12.67	47.27
Total	1656.02	28.84	100.00

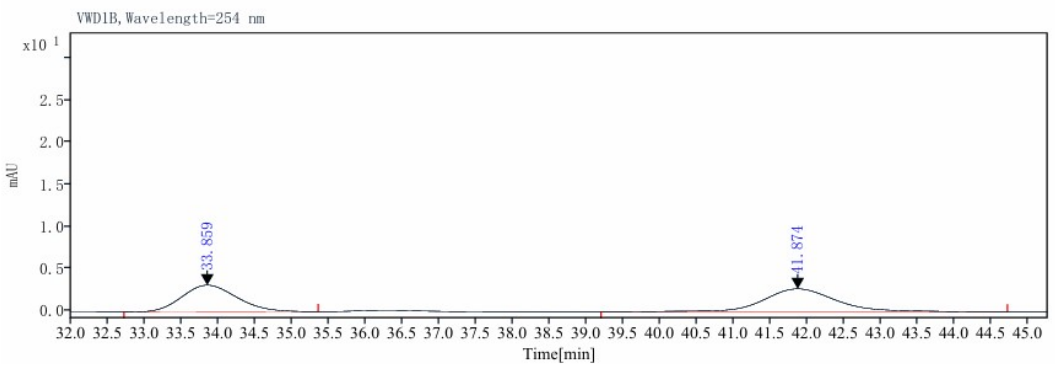


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
32.560	94.00	1.88	10.29
41.747	819.42	13.40	89.71
Total	913.42	15.28	100.00

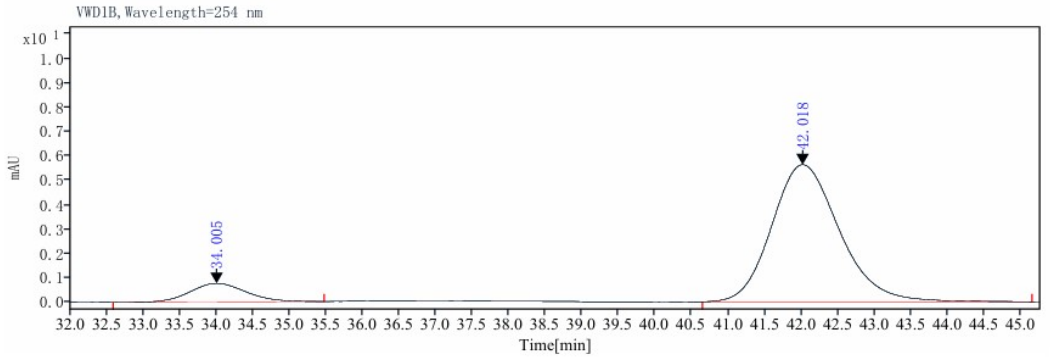
HPLC spectra of product 3o.





VWD1B, Wavelength=254 nm

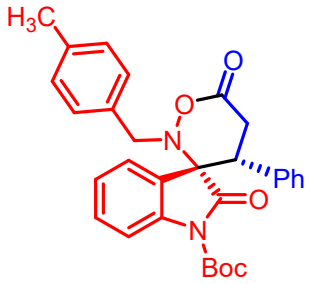
Ret. Time	Area	Height	Area%
33.859	166.06	3.18	46.23
41.874	193.14	2.75	53.77
Total	359.20	5.93	100.00

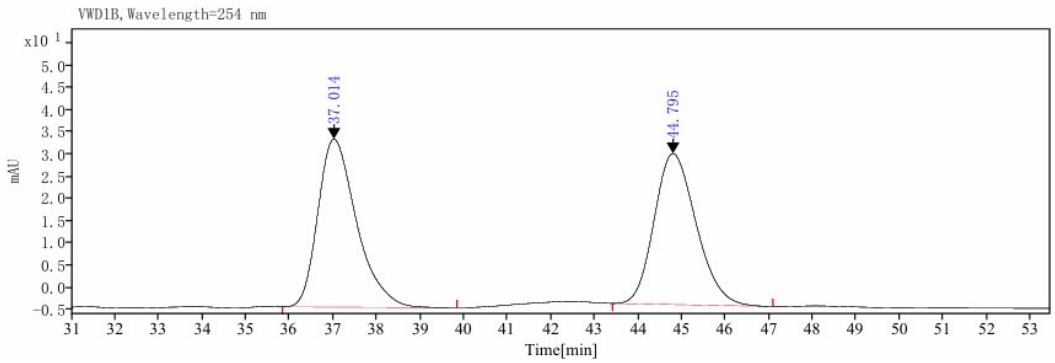


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
34.005	39.99	0.76	9.98
42.018	360.80	5.61	90.02
Total	400.79	6.37	100.00

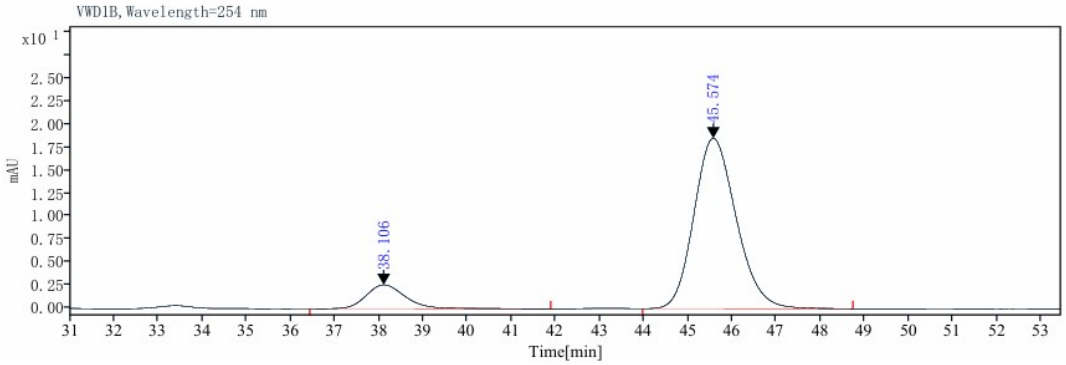
HPLC spectra of product 3p.





VWD1B, Wavelength=254 nm

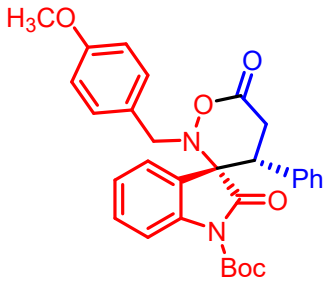
Ret. Time	Area	Height	Area%
37.014	2331.06	37.83	50.61
44.795	2274.59	34.00	49.39
Total	4605.65	71.83	100.00

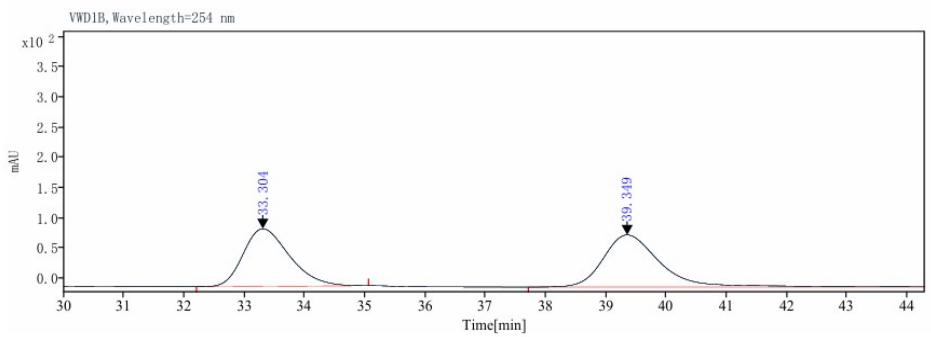


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
38.106	164.33	2.62	11.77
45.574	1231.80	18.54	88.23
Total	1396.13	21.16	100.00

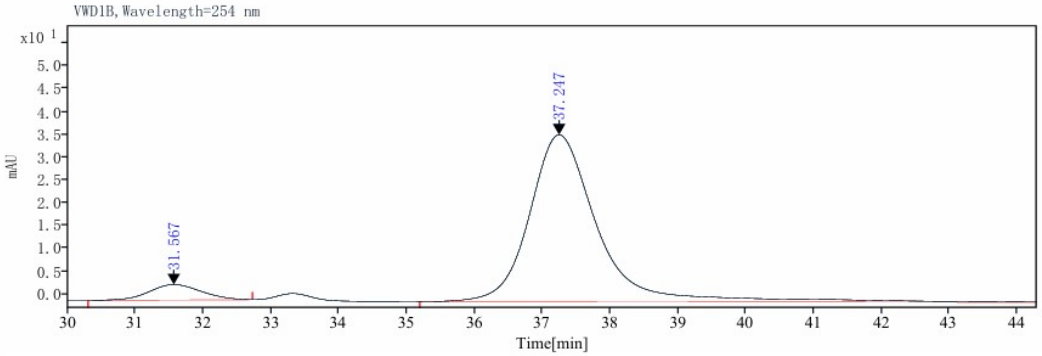
HPLC spectra of product 3q.





VWD1B, Wavelength=254 nm

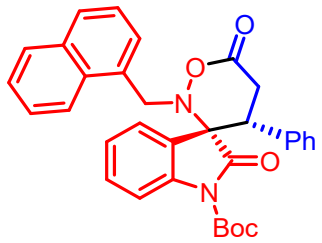
Ret.Time	Area	Height	Area%
33.304	5095.99	95.50	47.12
39.349	5718.47	86.38	52.88
Total	10814.46	181.88	100.00

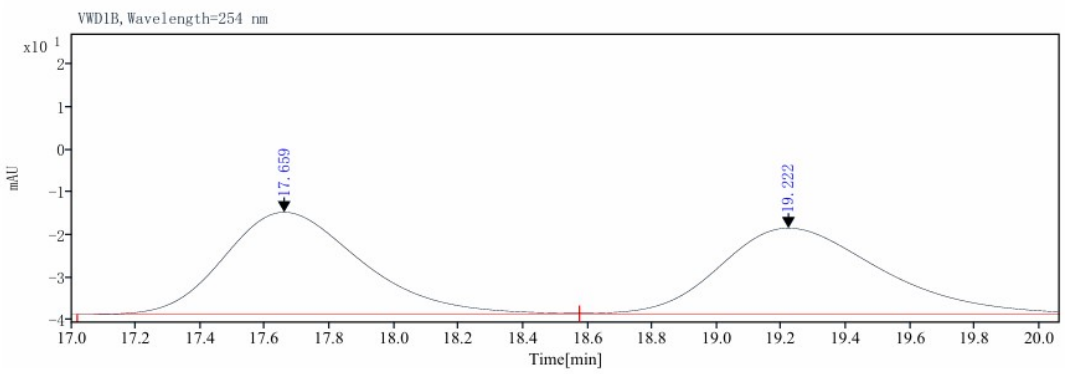


VWD1B, Wavelength=254 nm

Ret.Time	Area	Height	Area%
31.567	180.62	3.39	6.56
37.247	2572.79	36.61	93.44
Total	2753.41	40.00	100.00

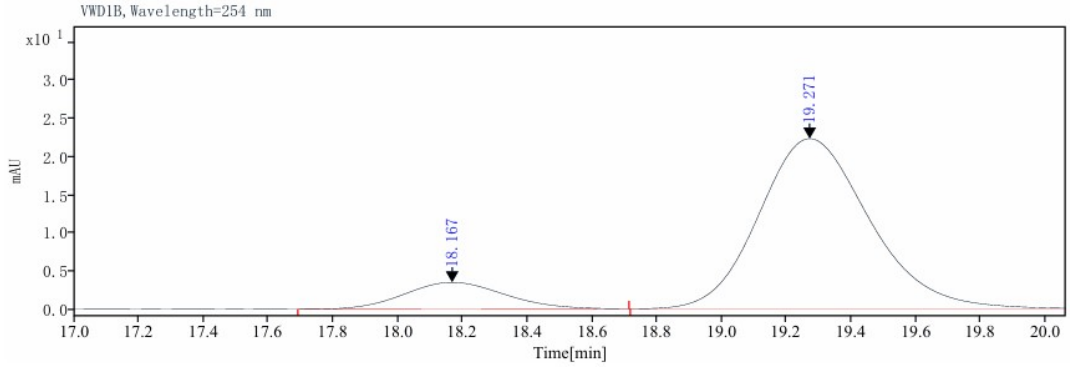
HPLC spectra of product 3r.





VWD1B, Wavelength=254 nm

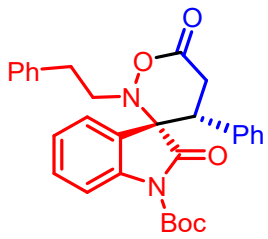
Ret. Time	Area	Height	Area%
17.659	712.36	24.01	50.12
19.222	708.82	20.28	49.88
Total	1421.18	44.29	100.00

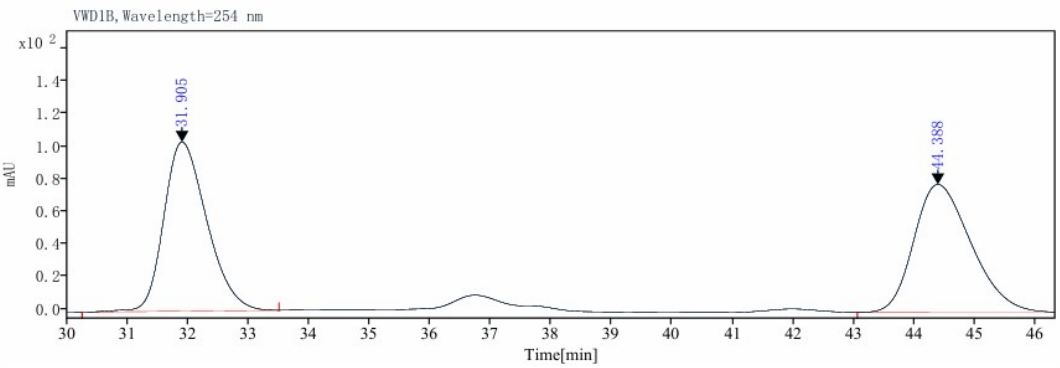


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
18.167	75.74	3.51	12.49
19.271	530.77	22.31	87.51
Total	606.51	25.82	100.00

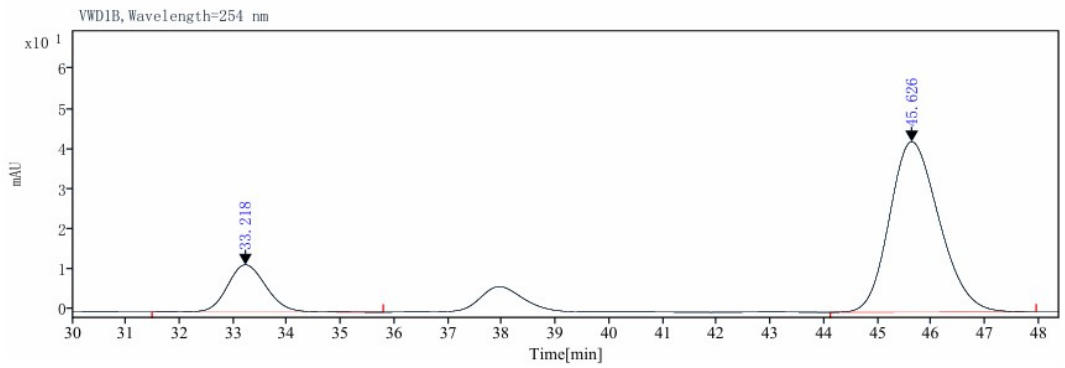
HPLC spectra of product 3s.





VWD1B, Wavelength=254 nm

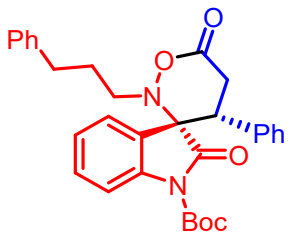
Ret. Time	Area	Height	Area%
31.905	5131.33	103.92	49.86
44.388	5160.97	78.58	50.14
Total	10292.31	182.50	100.00

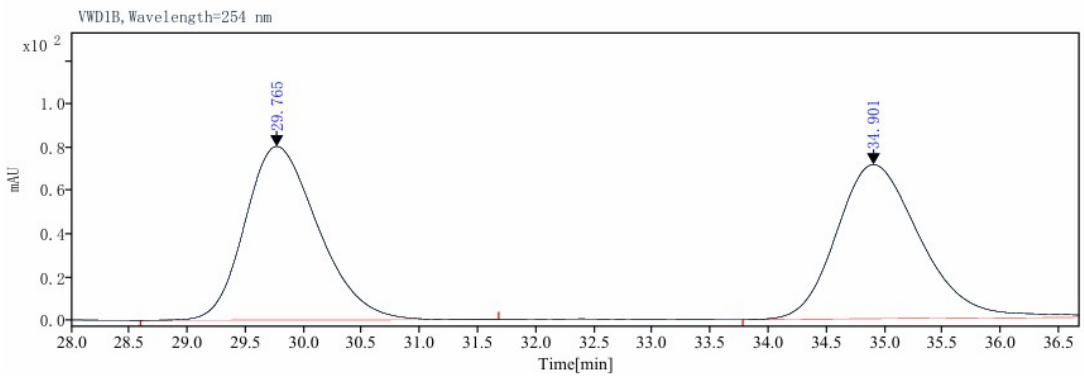


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
33.218	593.30	11.82	17.84
45.626	2731.90	42.55	82.16
Total	3325.20	54.36	100.00

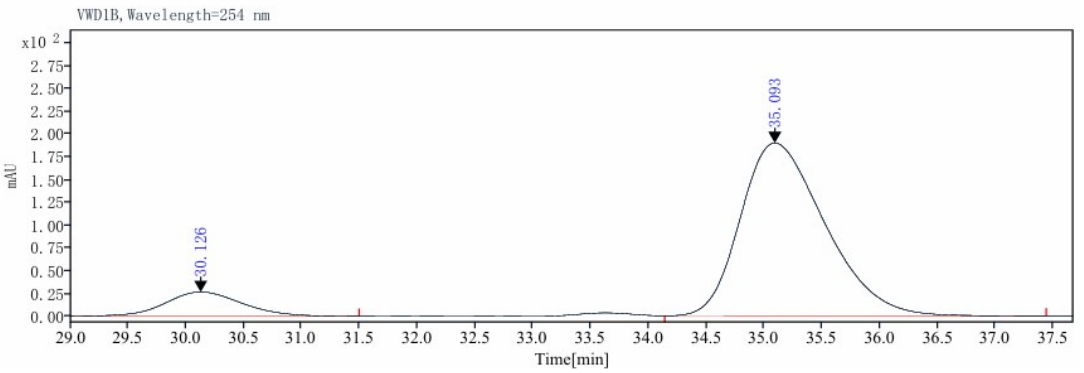
HPLC spectra of product 3t.





VWD1B, Wavelength=254 nm

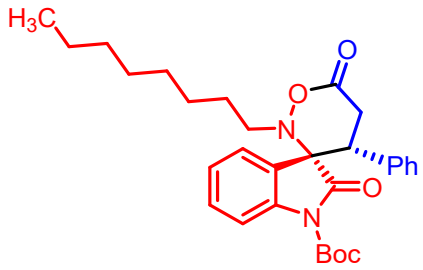
Ret. Time	Area	Height	Area%
29.765	3523.23	80.34	49.42
34.901	3605.77	71.31	50.58
Total	7129.00	151.65	100.00

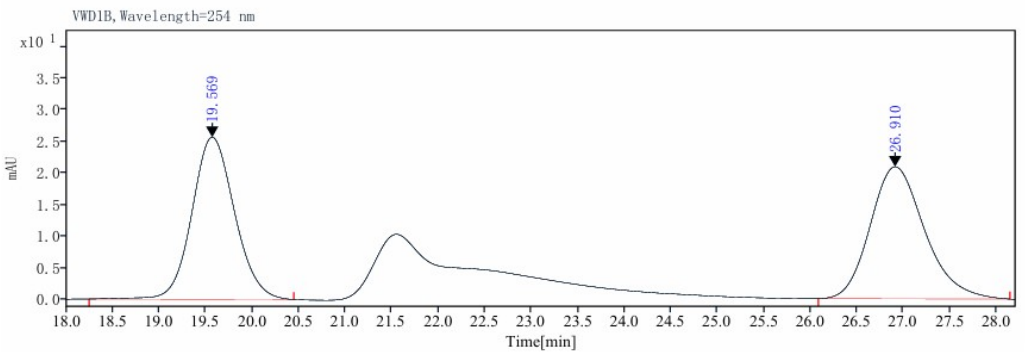


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
30.126	1243.58	26.72	11.38
35.093	9682.29	190.11	88.62
Total	10925.87	216.83	100.00

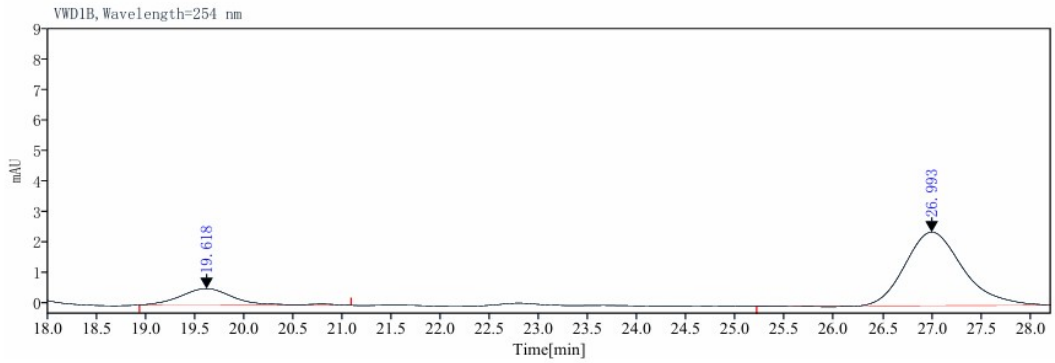
HPLC spectra of product 3u.





VWD1B, Wavelength=254 nm

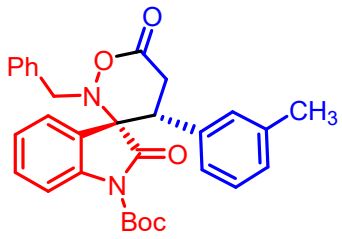
Ret. Time	Area	Height	Area%
19.569	816.67	25.62	49.06
26.910	847.83	20.88	50.94
Total	1664.50	46.50	100.00



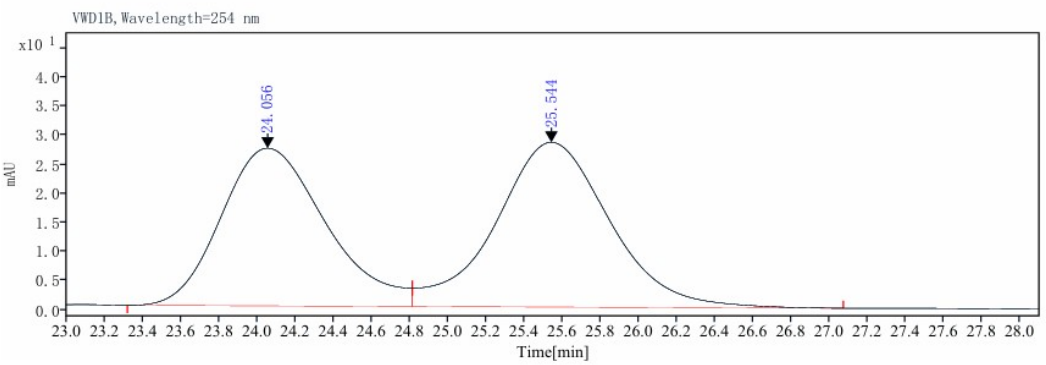
VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
19.618	20.87	0.54	17.44
26.993	98.81	2.43	82.56
Total	119.69	2.97	100.00

HPLC spectra of product 3v.

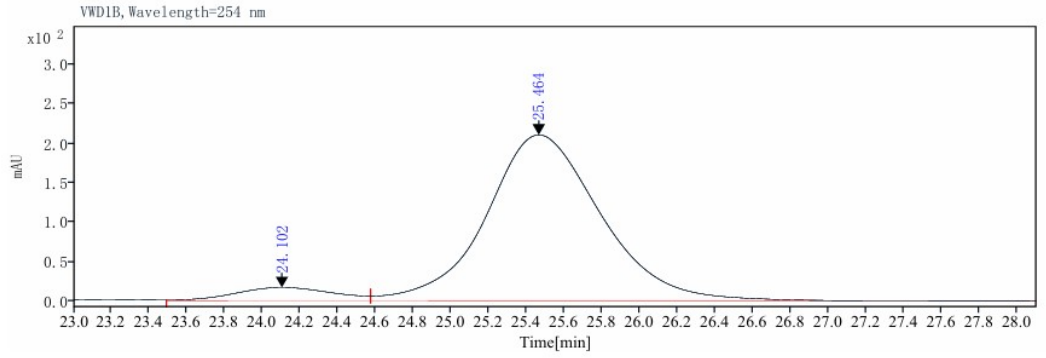


3v



VWD1B, Wavelength=254 nm

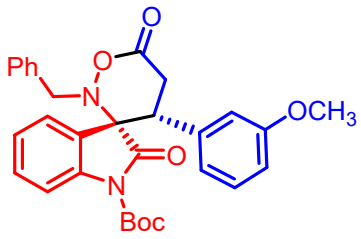
Ret. Time	Area	Height	Area%
24.056	1032.95	27.13	46.74
25.544	1176.97	28.34	53.26
Total	2209.91	55.46	100.00



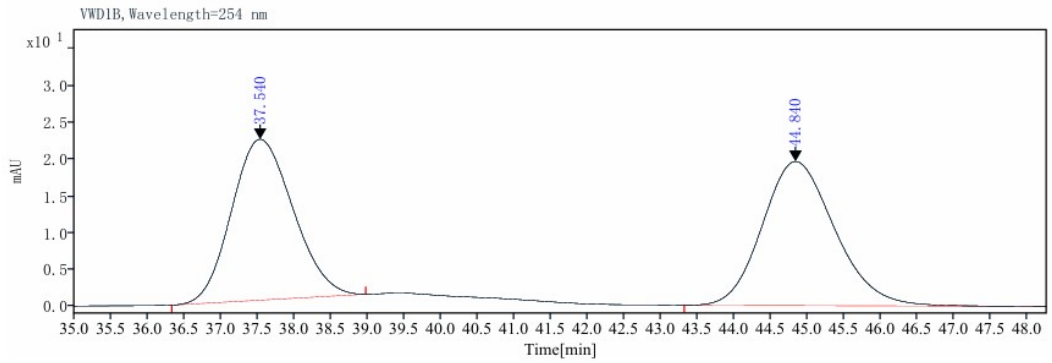
VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
24.102	607.84	16.82	6.35
25.464	8958.63	210.18	93.65
Total	9566.47	227.00	100.00

HPLC spectra of product 3w.

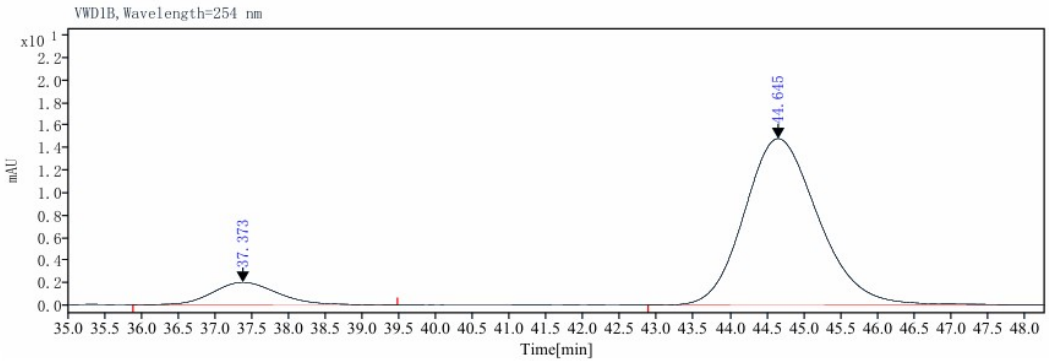


3w



VWD1B, Wavelength=254 nm

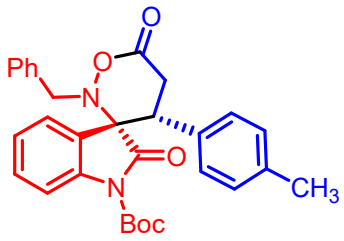
Ret. Time	Area	Height	Area%
37.540	1275.01	21.86	48.65
44.840	1345.54	19.58	51.35
Total	2620.55	41.43	100.00



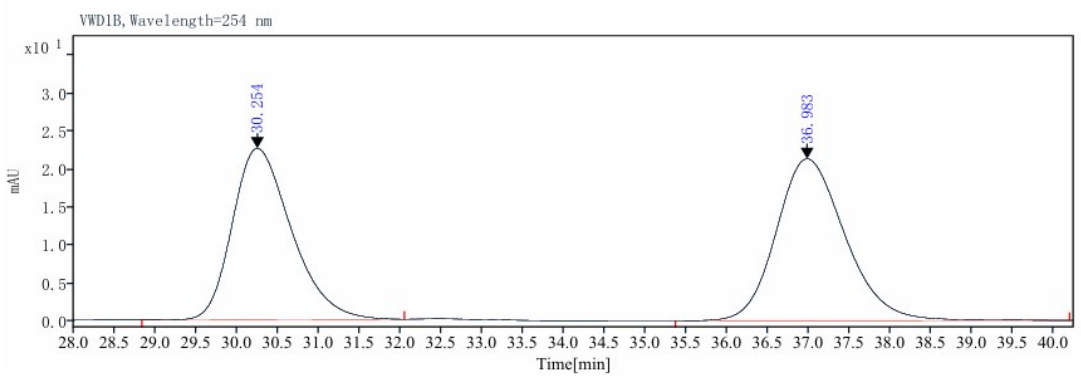
VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
37.373	124.10	2.01	10.72
44.645	1033.30	14.78	89.28
Total	1157.41	16.79	100.00

HPLC spectra of product 3x.

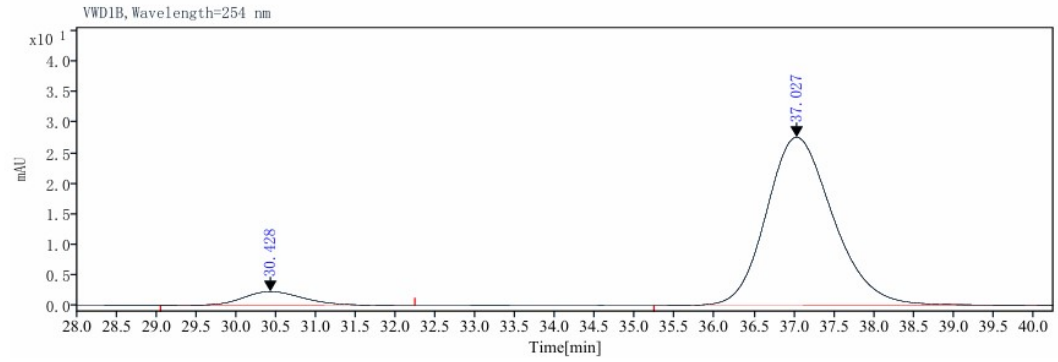


3x



VWD1B, Wavelength=254 nm

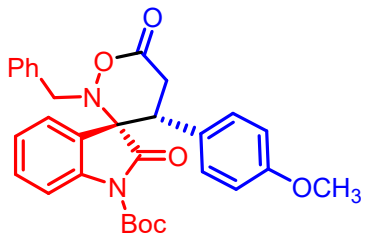
Ret. Time	Area	Height	Area%
30.254	1132.50	22.55	47.59
36.983	1247.24	21.30	52.41
Total	2379.74	43.84	100.00

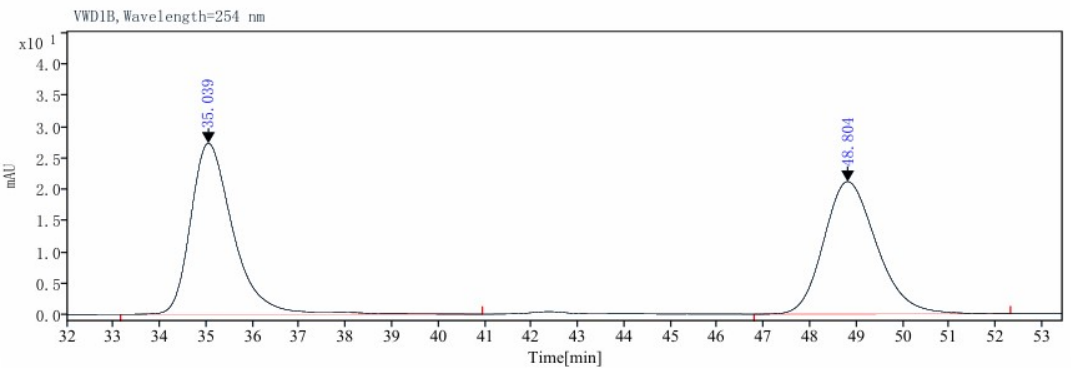


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
30.428	120.27	2.27	6.94
37.027	1611.68	27.61	93.06
Total	1731.95	29.88	100.00

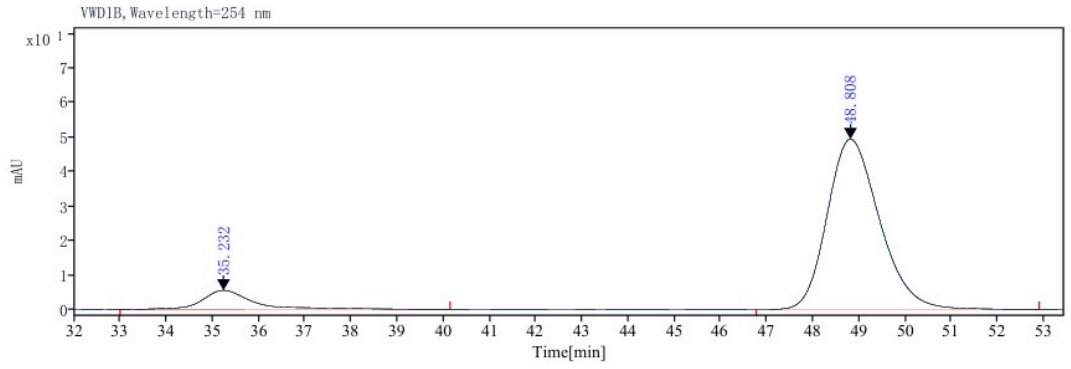
HPLC spectra of product 3y.





VWD1B, Wavelength=254 nm

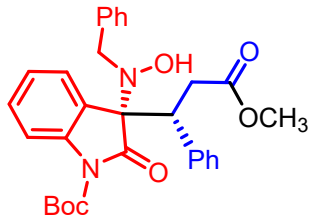
Ret. Time	Area	Height	Area%
35.039	1731.32	27.29	50.88
48.804	1671.21	21.14	49.12
Total	3402.53	48.43	100.00

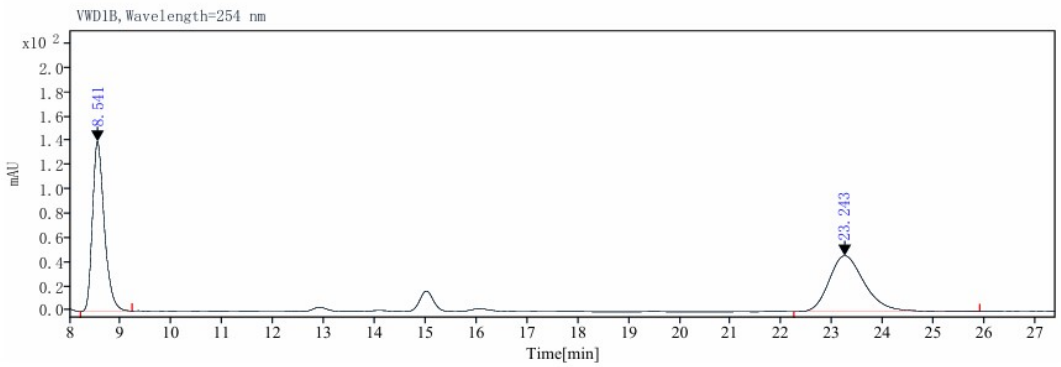


VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
35.232	431.64	5.55	10.02
48.808	3874.48	49.36	89.98
Total	4306.12	54.91	100.00

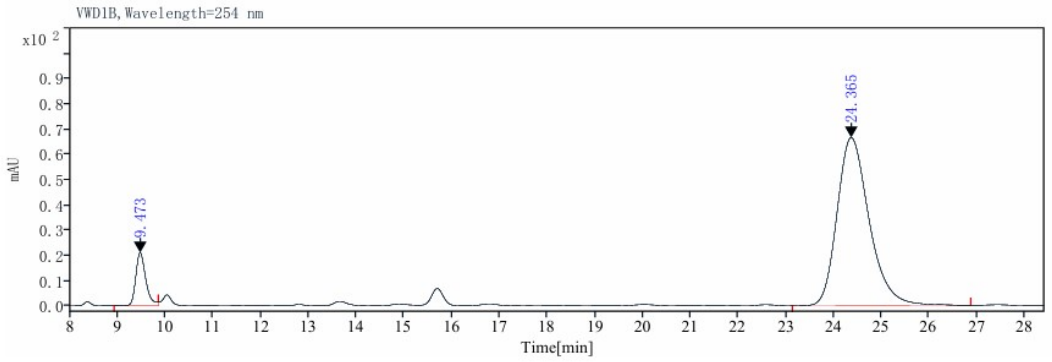
HPLC spectra of product 4.





VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
8.541	2273.91	139.98	50.34
23.243	2243.36	46.15	49.66
Total	4517.26	186.12	100.00



VWD1B, Wavelength=254 nm

Ret. Time	Area	Height	Area%
9.473	311.14	21.14	9.11
24.365	3106.11	66.70	90.89
Total	3417.25	87.84	100.00