Supporting Information

Organocatalytic Enantioselective Mannich-Type Addition of 5*H*-thiazol-4-ones to Isatin-derived Imines: Access to 3-Substituted 3-amino-2-oxindoles Featured by Vicinal Sulfur-containing Tetrasubstituted Stereocenters

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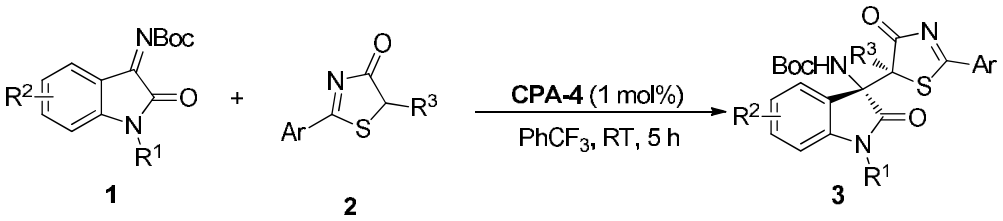
A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (DMSO-*d6*: δ 2.50; $CDCl_3$: δ 7.26; $(CD_3)_2CO$: δ 2.05). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (DMSO-*d6*; δ 39.50; $CDCl_3$: δ 77.0; $(CD_3)_2CO$: δ 29.84, 206.26). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted. *N*-alkoxycarbonyl ketimines and 5*H*-thiazol-4-ones were prepared following the literature procedures.[1, 2]

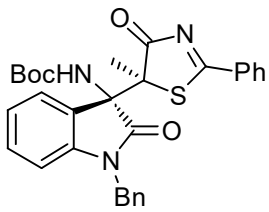
B: General Procedure for Mannich-Type Addition Reaction



To a solution of $PhCF_3$ (0.3 mL) were added *N*-alkoxycarbonyl ketimines **1** (0.05 mmol), 5*H*-thiazol-4-ones **2** (0.06 mmol) and catalyst **CPA-4** (0.0005 mmol). The reaction mixture was stirred at room temperature for 5 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

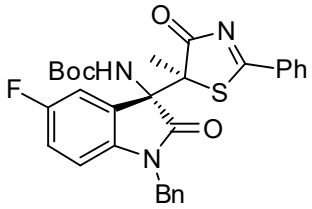
C: Characterization Data

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aa)**



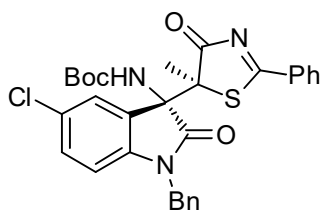
White solid, 22.4 mg, 85% yield. ^{1}H NMR (DMSO-*d6*, 500 MHz): δ (ppm) 7.74-7.69 (m, 3H), 7.53-7.48 (m, 4H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.13-7.12 (m, 1H), 7.00-6.99 (m, 1H), 6.89-6.86 (m, 2H), 4.97 (br, 1H), 4.81 (br, 1H), 2.01 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (DMSO-*d6*, 125 MHz): δ (ppm) 195.9, 192.4, 173.2, 153.8, 144.0, 136.4, 131.2, 130.0, 129.9, 128.8, 128.6, 128.5, 128.0, 127.0, 122.9, 122.7, 109.4, 80.3, 66.3, 63.5, 43.9, 28.2, 20.1. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{30}N_3O_4S$) requires m/z 528.1952, found m/z 528.1946. The enantiomeric excess was determined to be 96% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 20.4 min (major), 26.1 min (minor).

***tert*-butyl ((*S*)-1-benzyl-5-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ba)**



White solid, 25.3 mg, 93% yield. ^{1}H NMR (DMSO-*d6*, 500 MHz): δ (ppm) 7.80-7.72 (m, 3H), 7.56-7.53 (m, 2H), 7.46-7.44 (m, 2H), 7.36-7.23 (m, 4H), 7.04 (s, 1H), 6.87 (br, 1H), 4.93 (br, 1H), 4.79 (br, 1H), 2.01 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (DMSO-*d6*, 125 MHz): δ (ppm) 195.8, 191.6, 173.2, 158.4 (d, *J* = 945.0 Hz), 153.9, 140.3, 136.4, 136.2, 131.3, 129.9, 129.1, 128.8, 128.6, 128.4, 128.0, 116.2 (d, *J* = 95.0 Hz), 111.1 (d, *J* = 100.0 Hz), 110.3 (d, *J* = 30.0 Hz), 80.4, 66.5, 64.0, 44.0, 28.3, 20.3. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}FN_3O_4S$) requires m/z 546.1857, found m/z 546.1857. The enantiomeric excess was determined to be 90% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 95:5, 0.8 mL/min]: 14.9 min (minor), 16.5 min (major).

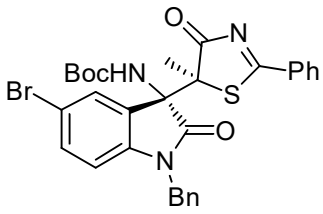
***tert*-butyl((*S*)-1-benzyl-5-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ca)**



White solid, 25.2 mg, 90% yield. ^{1}H NMR (DMSO-*d6*, 500 MHz): δ (ppm) 7.82-7.80 (m, 2H), 7.74-7.71 (m, 1H), 7.55-7.52 (m, 2H), 7.46-7.44 (m, 2H), 7.36-7.28 (m, 3H), 7.24-7.22 (m, 1H), 7.04 (s, 1H), 6.88 (br, 1H), 4.94 (br, 1H), 4.80 (br, 1H), 2.01 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (DMSO-*d6*, 125 MHz): δ (ppm) 195.9, 191.5, 173.0, 153.9, 143.0, 136.4, 136.0, 131.3, 130.0, 129.8, 128.8, 128.7, 128.4, 128.0, 126.7, 123.2, 110.9, 80.5, 66.5, 63.9, 44.0, 28.3, 20.4. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}ClN_3O_4S$) requires m/z 562.1562, found m/z 562.1556. The enantiomeric

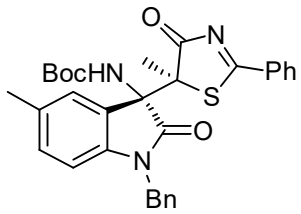
excess was determined to be 93% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 95:5, 0.8 mL/min]: 15.3 min (minor), 17.2 min (major).

tert-butyl ((*S*)-1-benzyl-5-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3da)



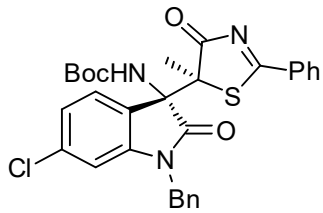
White solid, 25.4 mg, 84% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.82-7.80 (m, 2H), 7.74-7.71 (m, 1H), 7.56-7.53 (m, 2H), 7.45-7.43 (m, 2H), 7.36-7.28 (m, 4H), 7.15 (s, 1H), 6.82 (br, 1H), 4.92 (br, 1H), 4.77 (br, 1H), 2.00 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.9, 191.5, 172.9, 153.9, 143.4, 136.4, 136.0, 132.6, 131.3, 130.0, 128.9, 128.7, 128.4, 128.0, 125.9, 114.3, 111.4, 80.5, 66.5, 63.8, 44.0, 28.3, 20.3. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}BrN_3O_4S$) requires m/z 606.1057, found m/z 606.1050. The enantiomeric excess was determined to be 96% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 70:30, 0.8 mL/min]: 6.8 min (minor), 7.4 min (major).

tert-butyl ((*S*)-1-benzyl-5-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ea)



White solid, 23.8 mg, 88% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.76-7.68 (m, 3H), 7.53-7.46 (m, 4H), 7.36-7.29 (m, 3H), 6.92-6.91 (m, 1H), 6.82 (s, 1H), 6.72 (br, 1H), 4.93 (br, 1H), 4.79 (br, 1H), 2.09 (s, 3H), 2.01 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 196.0, 192.5, 173.1, 153.7, 141.6, 136.5, 136.3, 131.6, 131.3, 130.2, 130.0, 128.8, 128.6, 128.4, 127.9, 127.0, 123.5, 109.1, 80.3, 66.5, 63.6, 43.9, 28.3, 21.0, 20.2. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{32}N_3O_4S$) requires m/z 542.2108, found m/z 542.2100. The enantiomeric excess was determined to be 93% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 0.8 mL/min]: 10.1 min (minor), 10.9 min (major).

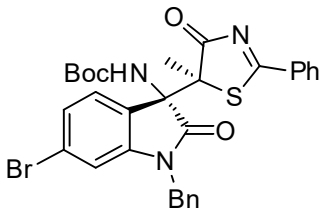
tert-butyl ((*S*)-1-benzyl-6-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3fa)



White solid, 26.4 mg, 94% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.80-7.72 (m, 3H), 7.56-7.53 (m, 2H), 7.47-7.45 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.31 (m, 1H), 7.05-6.96 (m, 3H), 4.94 (br, 1H), 4.82 (br, 1H), 1.99 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.8, 191.8, 173.3, 153.9, 145.5, 136.4, 136.0, 134.3, 131.3, 130.0, 128.9, 128.7, 128.4, 128.0, 126.1, 124.6, 122.4, 109.7, 80.4, 66.4, 63.5, 43.9, 28.3, 20.4. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}Cl\ N_3O_4S$) requires m/z 562.1562, found m/z 562.1560. The enantiomeric excess was determined

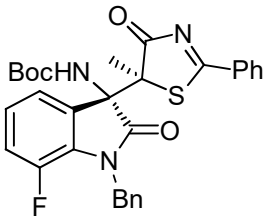
to be 98% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 95:5, 0.8 mL/min]: 11.2 min (minor), 14.9 min (major).

tert-butyl ((*S*)-1-benzyl-6-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ga)



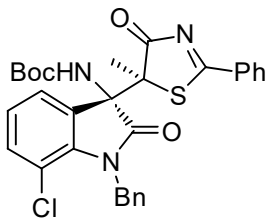
White solid, 28.7 mg, 95% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.81-7.80 (m, 2H), 7.75-7.72 (m, 1H), 7.57-7.54 (m, 2H), 7.46-7.45 (m, 2H), 7.38-7.29 (m, 4H), 7.13-7.11 (m, 1H), 7.00-6.99 (m, 1H), 4.93 (br, 1H), 4.83 (br, 1H), 1.99 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 200.6, 196.5, 178.0, 158.7, 150.4, 141.1, 140.8, 136.0, 134.7, 133.6, 133.5, 133.1, 132.8, 131.3, 130.1, 129.7, 127.5, 117.1, 85.1, 71.1, 68.3, 48.6, 33.0, 25.2. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}BrN_3O_4S$) requires m/z 606.1057, found m/z 606.1050. The enantiomeric excess was determined to be 96% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 12.6 min (minor), 14.1 min (major).

tert-butyl ((*S*)-1-benzyl-7-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ha)



White solid, 25.3 mg, 93% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.80-7.79 (m, 2H), 7.73-7.70 (m, 1H), 7.55-7.52 (m, 2H), 7.42-7.41 (m, 2H), 7.35-7.29 (m, 3H), 7.06-7.05 (m, 1H), 6.92-6.91 (m, 2H), 4.99 (br, 2H), 2.00 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.7, 191.8, 173.2, 153.9, 146.8 (d, *J* = 965.0 Hz), 137.2, 136.4, 131.2, 130.4 (d, *J* = 35.0 Hz), 130.0, 128.8 (d, *J* = 45.0 Hz), 127.8, 123.8, 119.5, 118.2 (d, *J* = 75.0 Hz), 80.5, 66.4, 63.9, 45.8, 28.3, 20.2. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}FN_3O_4S$) requires m/z 546.1857, found m/z 546.1849. The enantiomeric excess was determined to be 96% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 10.9 min (minor), 12.2 min (major).

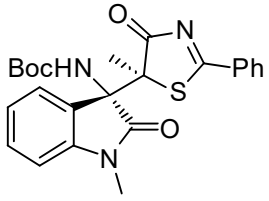
tert-butyl ((S)-1-benzyl-7-chloro-3-((S)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ia)



White solid, 23.3 mg, 83% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.87-7.86 (m, 2H), 7.73-7.70 (m, 1H), 7.56-7.53 (m, 2H), 7.41-7.40 (m, 2H), 7.33-7.18 (m, 4H), 7.09-7.08 (m, 1H), 6.97-6.94 (m, 1H), 5.25-5.16 (m, 2H), 1.99 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.7, 191.7, 174.0, 153.9, 139.9, 137.9, 136.4, 132.3, 131.3, 130.0, 128.7, 128.6, 127.4, 127.2, 124.1, 122.3, 114.4, 80.6, 66.5, 63.5, 45.4, 28.3, 20.5. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}ClN_3O_4S$) requires m/z 562.1562, found m/z 562.1558. The enantiomeric excess was determined to be 94%

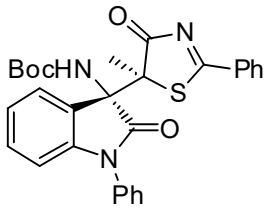
by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 10.6 min (minor), 13.3 min (major).

***tert*-butyl ((*S*)-1-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ja)**



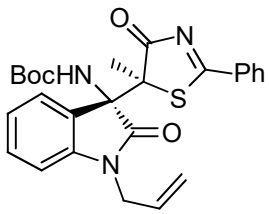
White solid, 20.5 mg, 91% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.87-7.86 (m, 2H), 7.73-7.70 (m, 1H), 7.53-7.50 (m, 2H), 7.24-7.21 (m, 1H), 6.98-6.90 (m, 3H), 3.12 (s, 3H), 1.99 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 196.2, 192.5, 173.0, 153.7, 144.7, 136.4, 131.3, 130.2, 129.9, 129.6, 128.8, 125.2, 122.6, 108.7, 80.2, 66.1, 60.2, 28.2, 26.8, 20.1. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{26}N_3O_4S$) requires m/z 452.1639, found m/z 452.1632. The enantiomeric excess was determined to be 94% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 70:30, 0.8 mL/min]: 5.5 min (minor), 8.2 min (major).

***tert*-butyl ((*S*)-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxo-1-phenylindolin-3-yl)carbamate (3ka)**



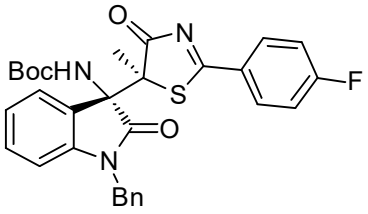
White solid, 23.3 mg, 91% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.95-7.93 (m, 2H), 7.75-7.72 (m, 1H), 7.60-7.53 (m, 4H), 7.48-7.45 (m, 1H), 7.40-7.38 (m, 2H), 7.17-7.12 (m, 2H), 6.96-6.95 (m, 1H), 6.63-6.62 (m, 1H), 2.02 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.9, 192.1, 172.4, 154.0, 144.6, 136.4, 134.5, 131.4, 130.2, 129.9, 128.9, 128.7, 127.0, 123.5, 123.2, 109.1, 80.4, 66.5, 63.7, 28.3, 20.4. HRMS (ESI): exact mass calculated for M^+ ($C_{29}H_{28}N_3O_4S$) requires m/z 514.1795, found m/z 514.1790. The enantiomeric excess was determined to be 94% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 8.6 min (minor), 13.2 min (major).

***tert*-butyl ((*S*)-1-allyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3la)**



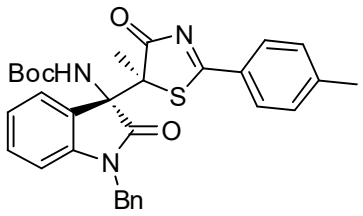
White solid, 21.7 mg, 91% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.87-7.85 (m, 2H), 7.73-7.70 (m, 1H), 7.54-7.51 (m, 2H), 7.20-7.17 (m, 1H), 7.02-7.01 (m, 1H), 6.92-6.86 (m, 2H), 5.86-5.79 (m, 1H), 5.42 (d, *J* = 20.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.39 (br, 1H), 4.20 (br, 1H), 2.00 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 198.2, 196.0, 172.7, 153.7, 143.9, 136.3, 132.1, 131.3, 130.0, 129.9, 128.7, 126.9, 122.8, 122.6, 118.1, 109.3, 80.2, 66.3, 63.6, 42.6, 28.2, 20.2. HRMS (ESI): exact mass calculated for M^+ ($C_{26}H_{28}N_3O_4S$) requires m/z 478.1795, found m/z 478.1787. The enantiomeric excess was determined to be 96% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 8.8 min (minor), 9.4 min (major).

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ab)**



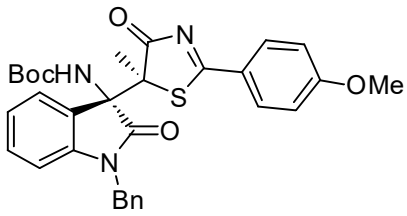
White solid, 24.0 mg, 88% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.83-7.82 (m, 2H), 7.48-7.47 (m, 2H), 7.39-7.35 (m, 4H), 7.31-7.29 (m, 1H), 7.14-7.13 (m, 1H), 7.01-7.00 (m, 1H), 6.90-6.87 (m, 2H), 4.96 (br, 1H), 4.82 (br, 1H), 2.01 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 194.4, 192.1, 173.2, 167.0 (d, *J* = 1015.0 Hz), 153.8, 144.0, 136.4, 131.7 (d, *J* = 45.0 Hz), 130.0, 128.8, 128.4, 128.0, 122.9, 122.7, 117.3 (d, *J* = 40.0 Hz), 109.4, 80.3, 66.8, 63.6, 43.9, 28.2, 20.1. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}FN_3O_4S$) requires m/z 546.1857, found m/z 546.1854. The enantiomeric excess was determined to be 96% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 17.0 min (major), 18.6 min (minor).

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(p-tolyl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ac)**



White solid, 22.2 mg, 82% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.62-7.60 (m, 2H), 7.49-7.48 (m, 2H), 7.38-7.31 (m, 5H), 7.12-7.11 (m, 1H), 6.97-6.96 (m, 1H), 6.87-6.85 (m, 2H), 4.98 (br, 1H), 4.83 (br, 1H), 2.34 (s, 3H), 2.00 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 195.5, 192.6, 173.2, 153.7, 147.7, 144.0, 136.4, 130.5, 130.0, 128.8, 128.7, 128.5, 128.0, 127.0, 122.8, 122.7, 109.3, 80.3, 66.0, 63.5, 43.8, 28.2, 21.9, 20.1. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{32}N_3O_4S$) requires m/z 542.2119, found m/z 542.2101. The enantiomeric excess was determined to be 88% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 0.8 mL/min]: 16.2 min (major), 24.3 min (minor).

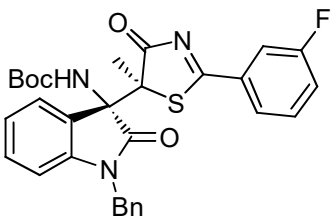
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ad)**



White solid, 24.6 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.71-7.70 (m, 2H), 7.51-7.49 (m, 2H), 7.38-7.31 (m, 3H), 7.10-7.04 (m, 2H), 6.96-6.94 (m, 1H), 6.85-6.78 (m, 3H), 6.65 (br, 1H), 5.15 (br, 1H), 4.84 (br, 1H), 3.83 (s, 3H), 2.14 (s, 3H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 195.2, 194.1, 173.2, 165.8, 153.9, 143.5, 135.9, 131.1, 129.6, 128.6, 128.0, 127.6, 126.6, 124.0, 122.7, 114.4, 108.7, 80.5, 65.8, 63.1, 55.7, 44.4, 28.2, 20.1. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{31}H_{31}N_3NaO_5S$) requires m/z 580.1882, found m/z 580.1868. The enantiomeric excess was determined to be 94% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 11.8 min

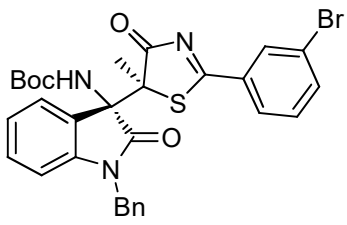
(major), 16.1 min (minor).

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ae)**



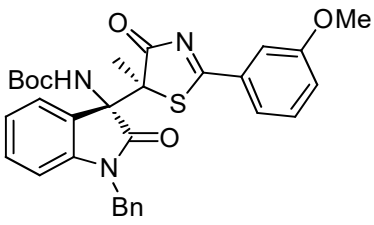
White solid, 24.0 mg, 88% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.57-7.47 (m, 6H), 7.37-7.28 (m, 3H), 7.15-7.14 (m, 1H), 7.03-7.02 (m, 1H), 6.91-6.88 (m, 2H), 4.96 (br, 1H), 4.81 (br, 1H), 2.02 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 194.7, 192.0, 173.2, 162.4 (d, *J* = 980.0 Hz), 153.8, 143.9, 136.4, 133.3 (d, *J* = 30.0 Hz), 132.2 (d, *J* = 30.0 Hz), 130.0, 128.8, 128.5, 127.9, 124.8, 123.1 (d, *J* = 80.0 Hz), 122.7, 114.8 (d, *J* = 90.0 Hz), 109.4, 80.3, 67.0, 63.6, 43.9, 28.2, 20.1. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}FN_3O_4S$) requires m/z 546.1857, found m/z 546.1863. The enantiomeric excess was determined to be 94% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 0.8 mL/min]: 12.7 min (major), 19.3 min (minor).

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-bromophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3af)**



White solid, 28.7 mg, 95% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.91-7.90 (m, 1H), 7.78-7.73 (m, 2H), 7.49-7.47 (m, 3H), 7.38-7.31 (m, 3H), 7.16-7.15 (m, 1H), 7.02-7.01 (m, 1H), 6.91-6.89 (m, 2H), 4.97 (br, 1H), 4.78 (br, 1H), 2.01 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 194.4, 191.8, 173.2, 153.8, 143.9, 138.7, 136.4, 133.2, 132.1, 130.5, 130.0, 128.8, 128.6, 128.0, 127.6, 123.1, 123.0, 122.7, 109.4, 80.3, 67.0, 63.6, 43.9, 28.2, 20.0. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}BrN_3O_4S$) requires m/z 606.1057, found m/z 606.1044. The enantiomeric excess was determined to be 92% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 17.2 min (major), 20.4 min (minor).

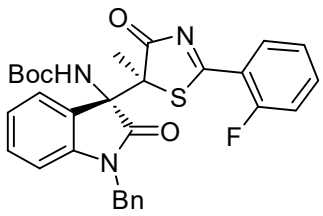
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ag)**



White solid, 24.8 mg, 89% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.51-7.49 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.30 (m, 2H), 7.28-7.23 (m, 2H), 7.12-7.06 (m, 3H), 6.87-6.80 (m, 2H), 6.68 (s, 1H), 5.18 (br, 1H), 4.85 (br, 1H), 3.77 (s, 3H), 2.15 (s, 3H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 197.0, 194.2, 173.1, 159.8, 153.8, 143.5, 135.8, 132.6, 129.9, 129.7, 128.6, 128.1, 127.7, 122.8, 122.6, 122.3, 121.1, 112.4, 108.8, 80.6, 66.0, 63.0, 55.6, 44.4, 28.2, 19.9. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{32}N_3O_5S$) requires m/z 558.2057, found m/z

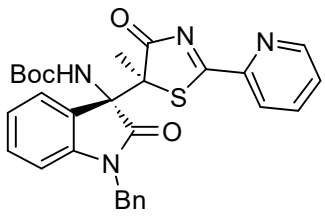
558.2052. The enantiomeric excess was determined to be >99% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 15.2 min (minor), 21.0 min (major).

tert-butyl ((*S*)-1-benzyl-3-((*S*)-2-(2-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ah)



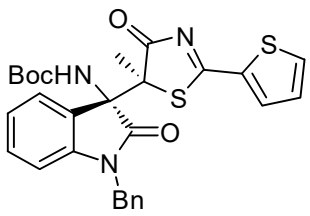
White solid, 25.1 mg, 92% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 7.98-7.95 (m, 1H), 7.74-7.71 (m, 1H), 7.47-7.45 (m, 2H), 7.40-7.25 (m, 6H), 7.14-7.13 (m, 1H), 7.02-7.01 (m, 1H), 6.91-6.83 (m, 2H), 5.00 (br, 1H), 4.77 (br, 1H), 2.01 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 191.8, 191.2, 173.2, 162.1 (d, *J* = 1030.0 Hz), 153.8, 144.1, 138.2 (d, *J* = 35.0 Hz), 136.4, 131.0, 130.1, 128.8, 128.1, 127.9, 126.0, 122.7, 119.2 (d, *J* = 35.0 Hz), 117.5 (d, *J* = 90.0 Hz), 109.3, 80.3, 64.6, 63.5, 44.0, 28.2, 19.9. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{29}FN_3O_4S$) requires m/z 546.1857, found m/z 546.1854. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 16.6 min (minor), 22.2 min (major).

tert-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ai)



White solid, 23.5 mg, 89% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 8.72-8.71 (m, 1H), 8.12-8.11 (m, 1H), 8.02-7.99 (m, 1H), 7.72-7.69 (m, 1H), 7.48-7.46 (m, 2H), 7.34-7.27 (m, 3H), 7.11-7.10 (m, 1H), 7.02-7.01 (m, 1H), 6.89-6.88 (m, 1H), 6.77-6.76 (m, 1H), 4.93 (br, 2H), 2.00 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 198.0, 193.3, 173.4, 153.8, 150.9, 148.1, 144.1, 138.7, 136.4, 130.2, 130.0, 128.8, 128.1, 127.8, 123.6, 122.7, 110.0, 109.4, 80.2, 65.0, 43.9, 28.3, 26.8, 20.2. HRMS (ESI): exact mass calculated for M^+ ($C_{29}H_{29}N_4O_4S$) requires m/z 529.1904, found m/z 529.1897. The enantiomeric excess was determined to be 98% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 60:40, 0.8 mL/min]: 9.3 min (minor), 11.9 min (major).

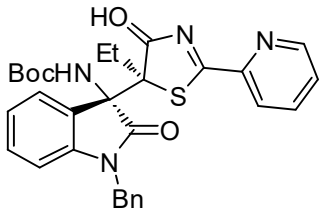
tert-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(thiophen-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aj)



White solid, 21.9 mg, 82% yield. ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ (ppm) 8.10-8.09 (m, 1H), 7.70-7.59 (m, 3H), 7.41-7.33 (m, 3H), 7.24-7.22 (m, 1H), 7.12-7.03 (m, 3H), 6.88-6.80 (m, 2H), 5.03 (br, 2H), 2.14 (s, 3H), 1.32 (s, 9H). ^{13}C NMR ($(CD_3)_2CO$, 125 MHz): δ (ppm) 193.4, 187.6, 173.2, 154.1, 144.6, 138.6, 136.7, 135.7, 135.2, 130.1, 130.0,

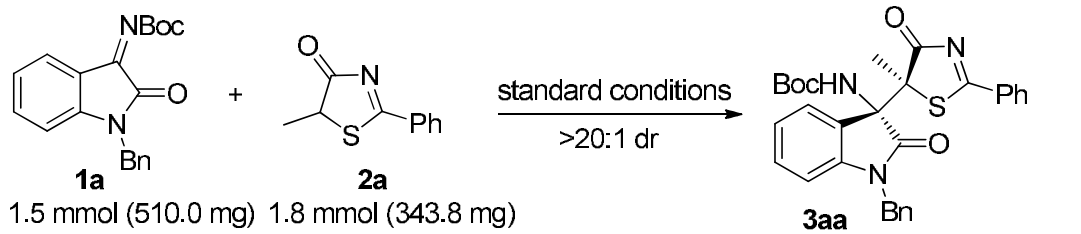
128.9, 128.4, 127.9, 122.7, 109.3, 80.4, 66.7, 63.5, 44.2, 27.9, 19.9. HRMS (ESI): exact mass calculated for M^+ ($C_{28}H_{28}N_3O_4S_2$) requires m/z 534.1516, found m/z 534.1511. The enantiomeric excess was determined to be 94% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 60:40, 0.8 mL/min]: 9.8 min (minor), 10.6 min (major).

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-ethyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ak)**



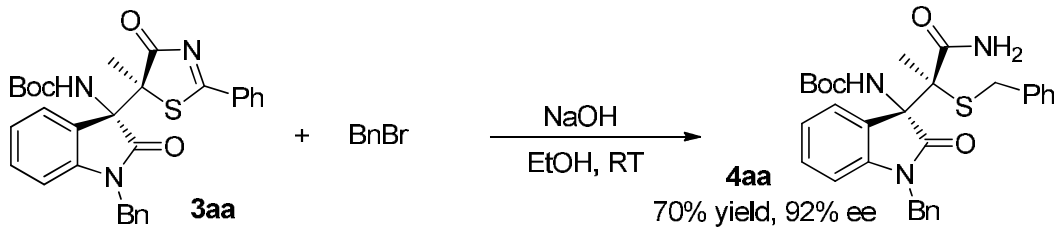
White solid, 23.3 mg, 86% yield. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 8.73-8.72 (m, 1H), 8.11-8.10 (m, 1H), 8.02-7.99 (m, 1H), 7.72-7.69 (m, 1H), 7.46-7.45 (m, 2H), 7.34-7.25 (m, 3H), 7.11-7.01 (m, 2H), 6.89-6.75 (m, 2H), 4.92 (br, 2H), 2.69-2.65 (m, 2H), 1.23 (s, 9H), 0.70 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ (ppm) 199.1, 192.7, 173.3, 153.8, 151.0, 148.0, 144.1, 138.7, 136.4, 130.2, 130.0, 128.8, 128.0, 127.8, 127.2, 123.6, 122.6, 109.4, 80.2, 71.4, 64.3, 43.9, 28.2, 24.3, 8.9. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{31}N_4O_4S$) requires m/z 543.2061, found m/z 543.2057. The enantiomeric excess was determined to be 66% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 60:40, 0.8 mL/min]: 8.4 min (minor), 12.4 min (major).

D: Gram-scale Reaction



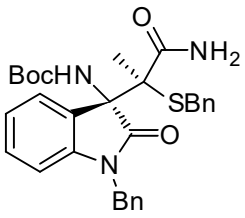
To a solution of $PhCF_3$ (9.0 mL) were added *N*-alkoxycarbonyl ketimines **1a** (510.0 mg, 1.5 mmol), 5*H*-thiazol-4-ones **2a** (343.8 mg, 1.8 mmol) and catalyst **CPA-4** (11.4 mg, 0.015 mmol). The reaction mixture was stirred at room temperature for 5 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography to give the desired product **3aa** as a white solid (656.1 mg, 83% yield, 96% ee).

E:The Synthetic Transformations



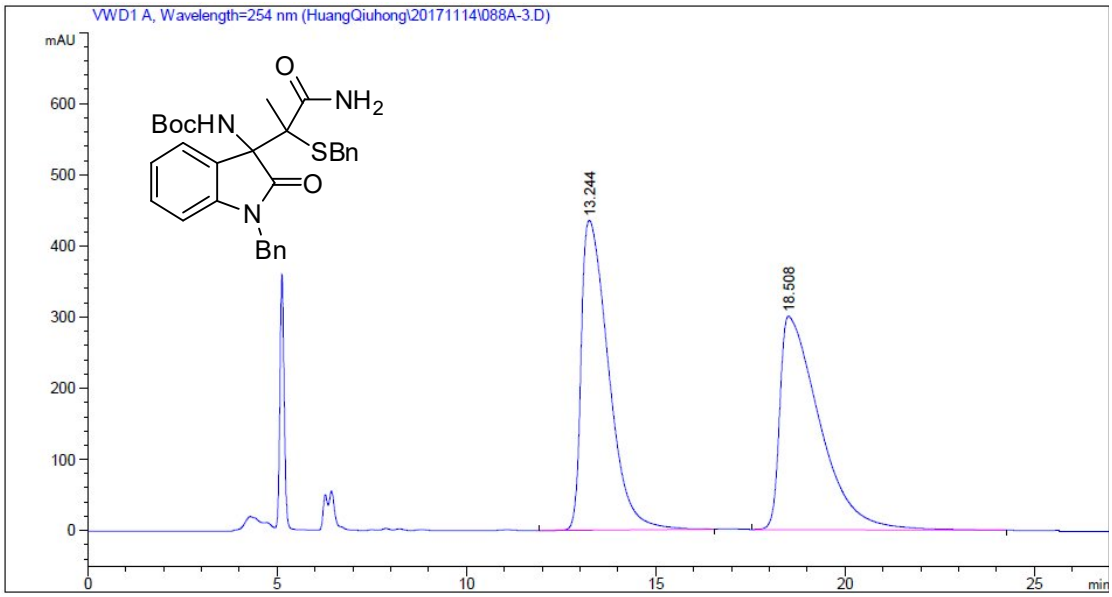
To a solution of **3aa** (0.1 mmol) in EtOH (1 mL) were slowly added benzyl bromide (0.25 mmol) and 2.5 N NaOH (0.05 mL). The reaction mixture was stirred at room temperature for 36 h. After adjusting pH to 2 with 1 N $KHSO_4$, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were then dried over with Na_2SO_4 and were removed under vacuum to give the crude product, which was purified by silica gel chromatography to provide the desired product **4aa** as a white solid (18.2 mg, 70% yield, 92% ee).

***tert*-butyl((*S*)-3-((*S*)-1-amino-2-(benzylthio)-1-oxopropan-2-yl)-1-benzyl-2-oxoindolin-3-yl)carbamate (4aa)**

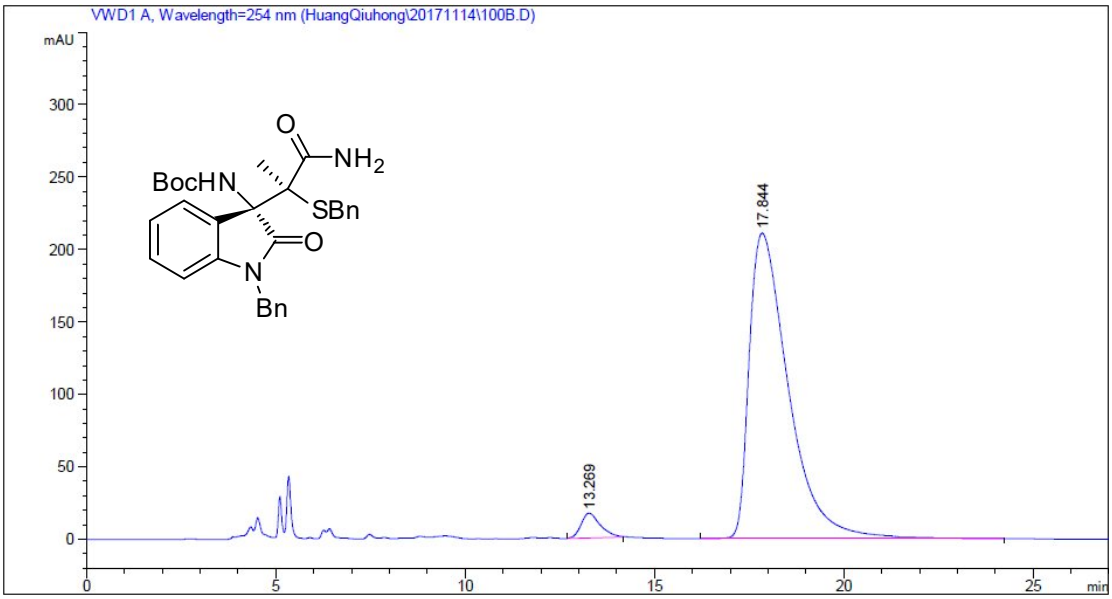


White solid, 18.2 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.49-7.48 (m, 2H), 7.31-7.30 (m, 2H), 7.24-7.23 (m, 5H), 7.18-7.15 (m, 1H), 7.07-7.06 (m, 2H), 6.96-6.93 (m, 1H), 6.66-6.64 (m, 1H), 5.30-5.27 (m, 1H), 4.69 (br, 1H), 3.64 (d, J = 15.0 Hz, 1H), 3.41 (d, J = 15.0 Hz, 1H), 1.98 (s, 3H), 1.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 174.8, 173.9, 153.9, 144.5, 136.0, 135.8, 129.6, 129.0, 128.7, 128.5, 127.8, 127.6, 127.3, 124.2, 122.3, 108.9, 80.0, 64.7, 57.9, 44.8, 34.8, 28.2, 19.5. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{34}N_3O_4S$) requires m/z 532.2265, found m/z 532.2261. The enantiomeric excess was determined to be 92% by HPLC. [ID column, 254 nm, n-hexane:EtOH = 60:40, 0.8 mL/min]:13.2 min (minor), 17.8 min (major).

tert-butyl((_S_)-3-((_S_)-1-amino-2-(benzylthio)-1-oxopropan-2-yl)-1-benzyl-2-oxoindolin-3-yl)carbamate (4aa)

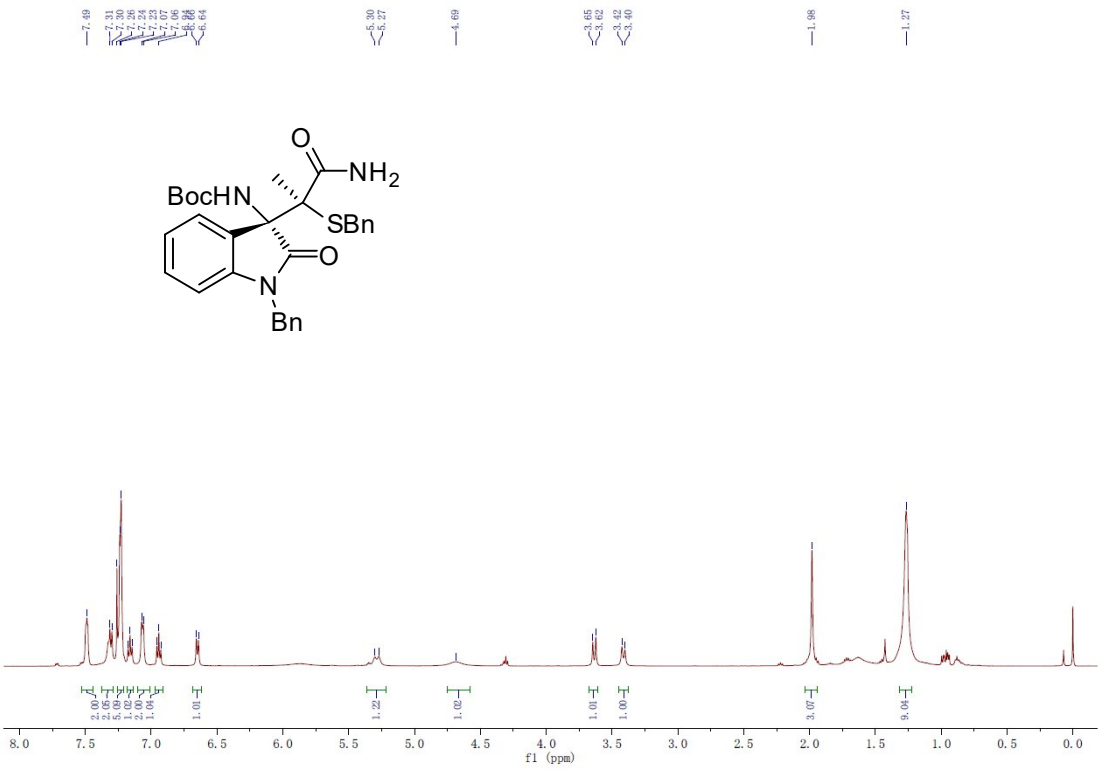


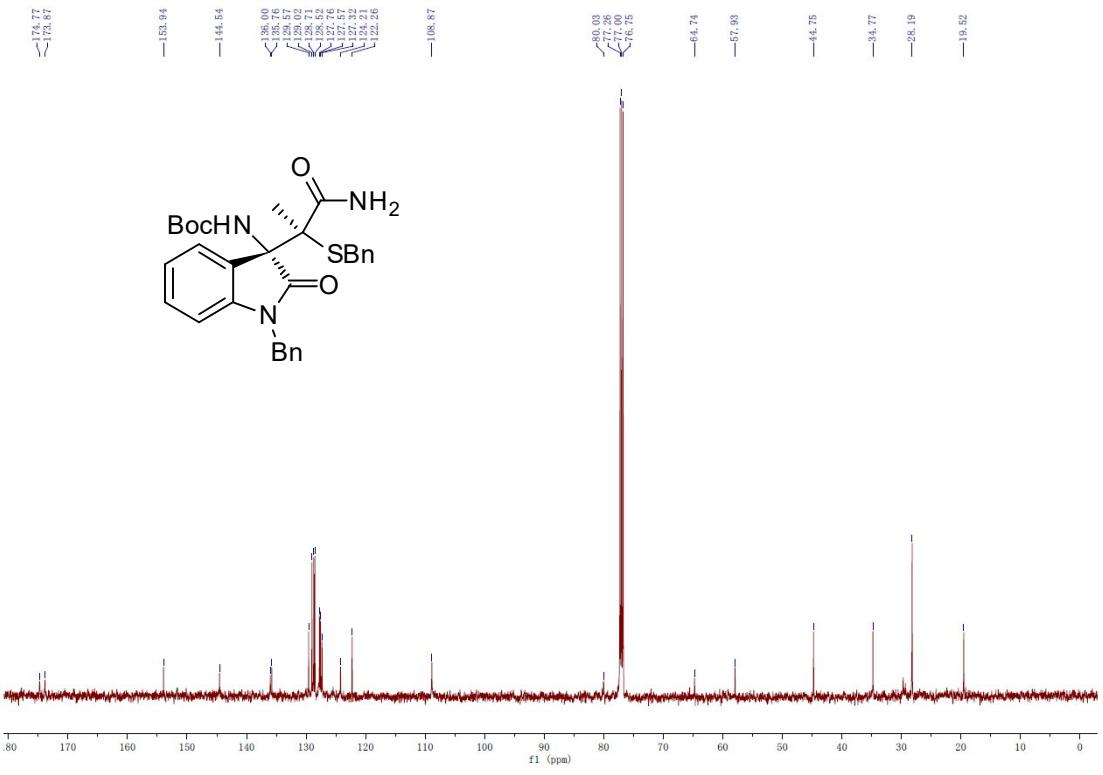
#	Time	Area	Height	Width	Symmetry	Area %
1	13.244	21728.2	435.3	0.7793	0.388	49.914
2	18.508	21803.4	299.7	1.0477	0.265	50.086



#	Time	Area	Height	Width	Symmetry	Area %
1	13.269	598.3	17.1	0.5848	0.683	3.795
2	17.844	15165.4	210.7	1.0917	0.451	96.205

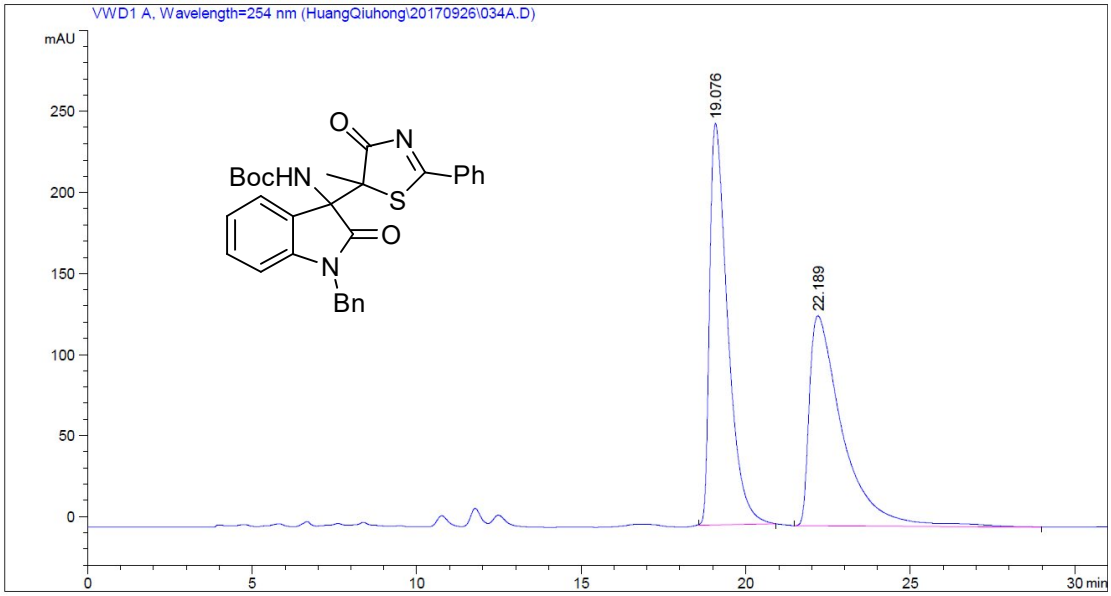
tert-butyl((_S_)-3-((_S_)-1-amino-2-(benzylthio)-1-oxopropan-2-yl)-1-benzyl-2-oxoindolin-3-yl)carbamate (4aa)



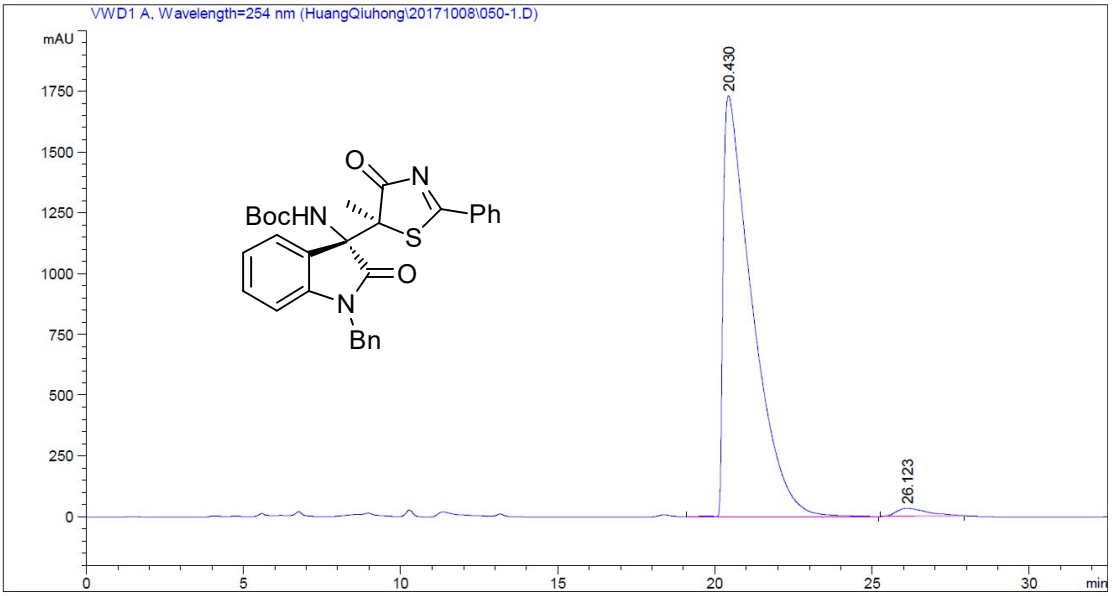


F: HPLC Analysis

tert-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aa)

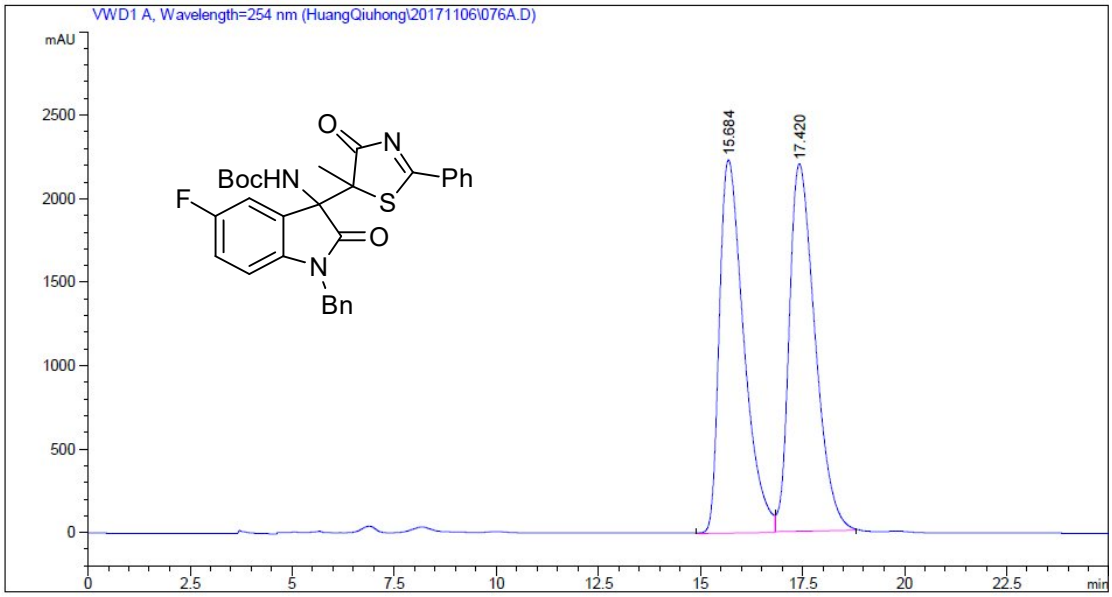


#	Time	Area	Height	Width	Symmetry	Area %
1	19.076	9623.3	248.8	0.5862	0.433	50.738
2	22.189	9343.4	130.5	1.1929	0.326	49.262

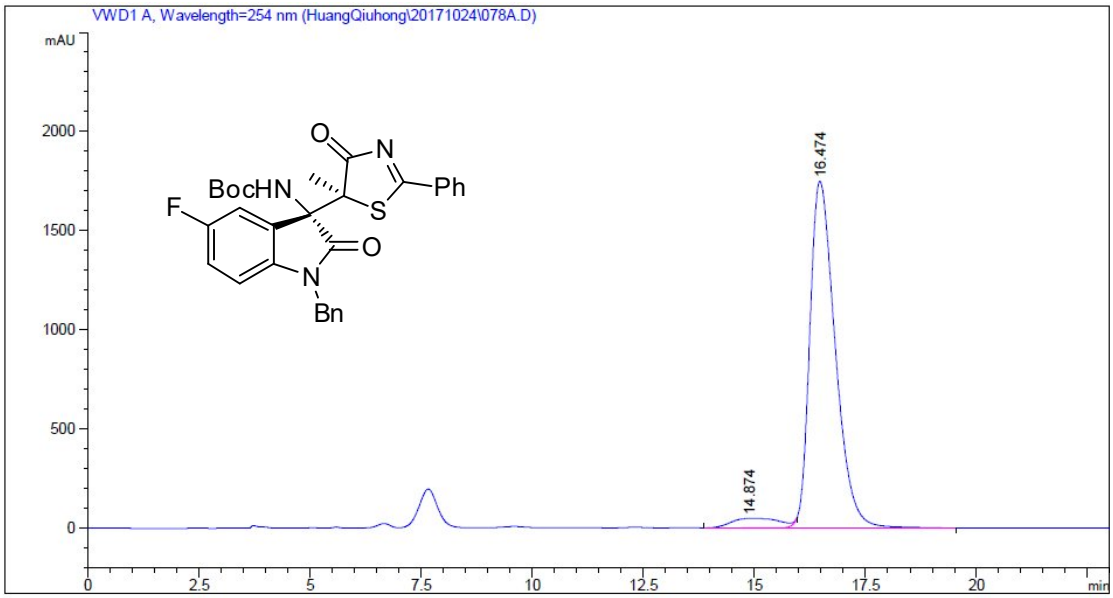


#	Time	Area	Height	Width	Symmetry	Area %
1	20.43	110774.1	1731.7	0.8893	0.199	97.943
2	26.123	2326.5	33.3	1.164	0.563	2.057

***tert*-butyl ((*S*)-1-benzyl-5-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ba)**

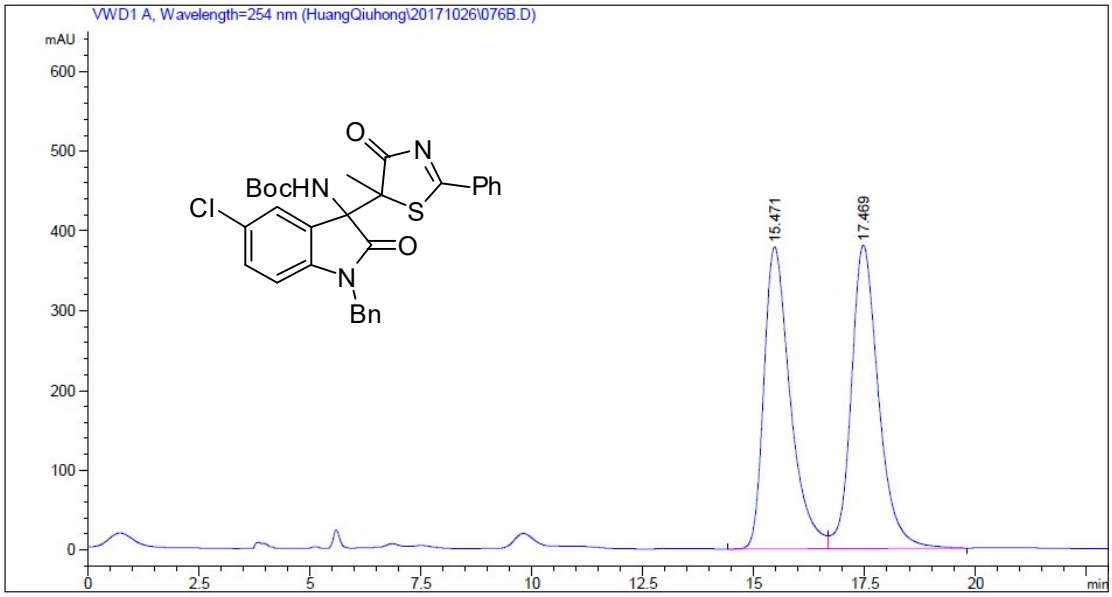


#	Time	Area	Height	Width	Symmetry	Area %
1	15.684	92821.2	2231.6	0.6932	0.561	48.921
2	17.42	96915.3	2201.9	0.7336	0.617	51.079

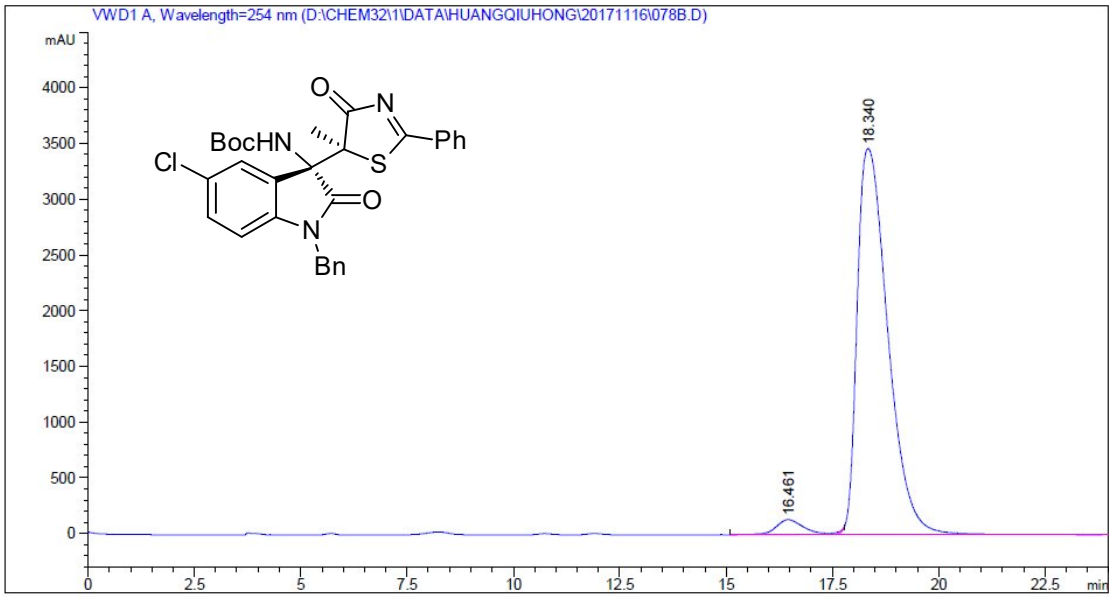


#	Time	Area	Height	Width	Symmetry	Area %
1	14.874	3593.8	47.7	1.0294	0.56	4.909
2	16.474	69609.7	1749.1	0.6133	0.798	95.091

***tert*-butyl ((*S*)-1-benzyl-5-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ca)**

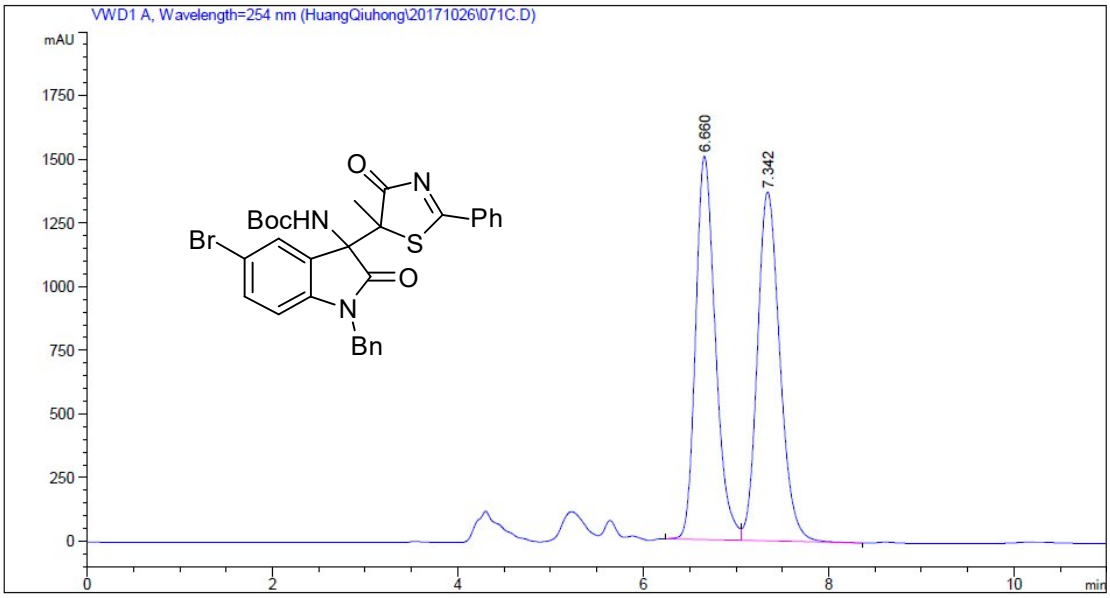


#	Time	Area	Height	Width	Symmetry	Area %
1	15.471	15600	378.2	0.6232	0.628	49.001
2	17.469	16236.2	380.2	0.6462	0.744	50.999

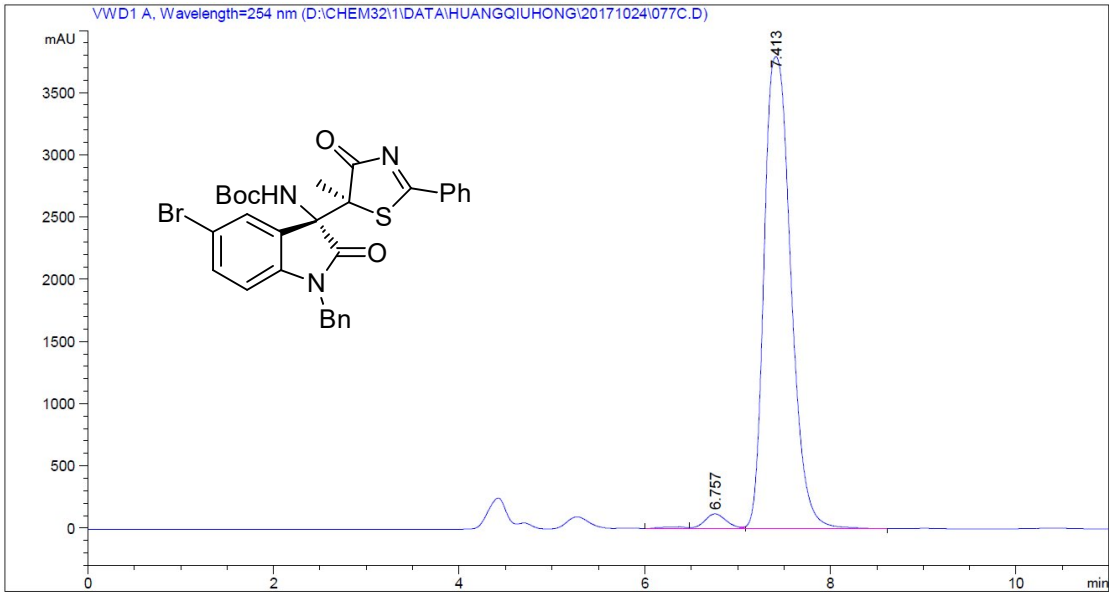


#	Time	Area	Height	Width	Symmetry	Area %
1	16.461	6216.8	134	0.6952	0.709	3.455
2	18.340	173717	3464.9	0.7769	0.616	96.545

***tert*-butyl ((*S*)-1-benzyl-5-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3da)**

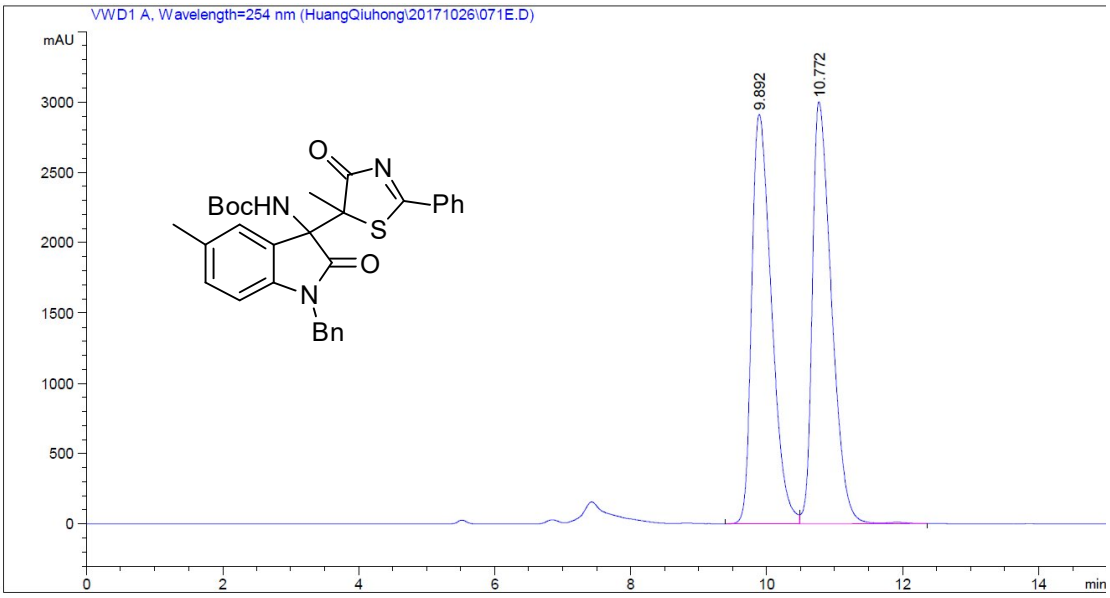


#	Time	Area	Height	Width	Symmetry	Area %
1	6.660	22347.5	1505.2	0.2282	0.757	49.164
2	7.342	23107.5	1369.9	0.2598	0.789	50.836

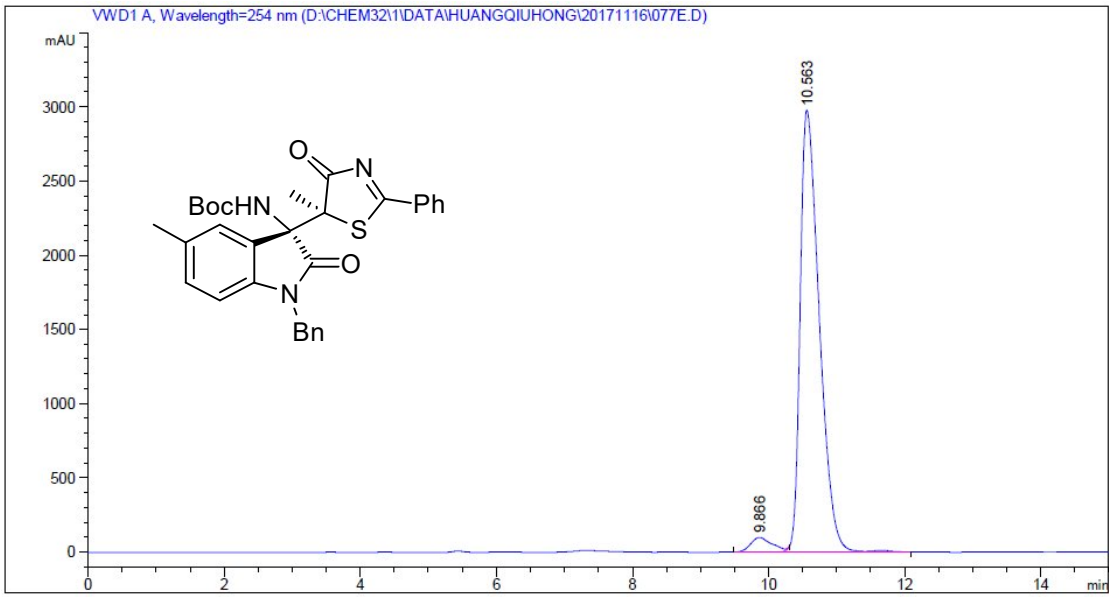


#	Time	Area	Height	Width	Symmetry	Area %
1	6.757	1615.5	110.3	0.244	0.888	2.104
2	7.413	75152.6	3790.5	0.3304	0.744	97.896

***tert*-butyl ((*S*)-1-benzyl-5-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ea)**

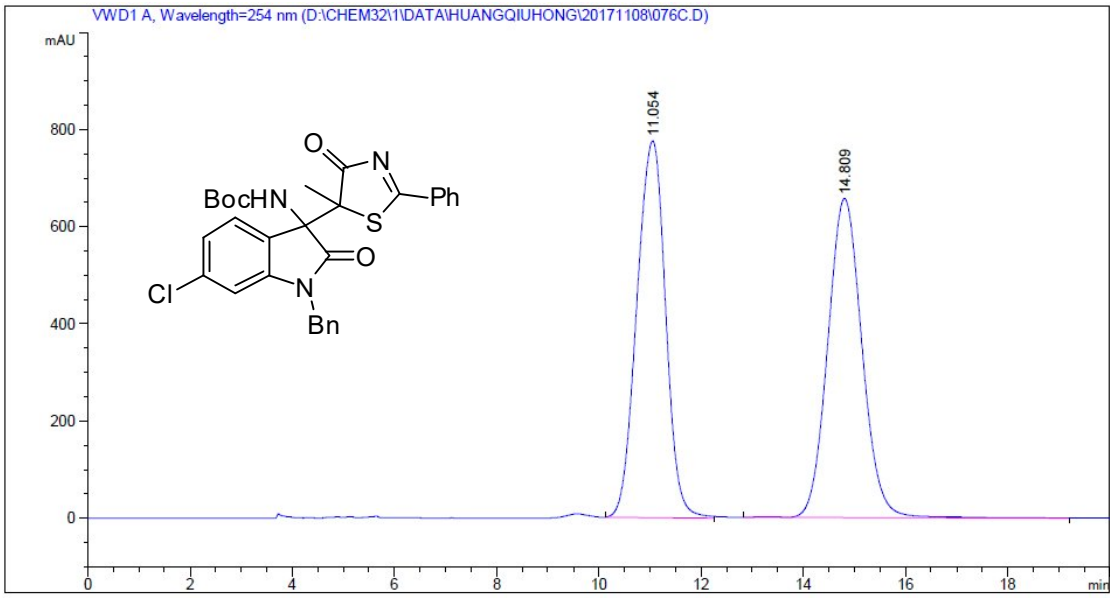


#	Time	Area	Height	Width	Symmetry	Area %
1	9.892	58768.8	2911.4	0.3135	0.574	49.889
2	10.772	59031.3	3001	0.2994	0.511	50.111

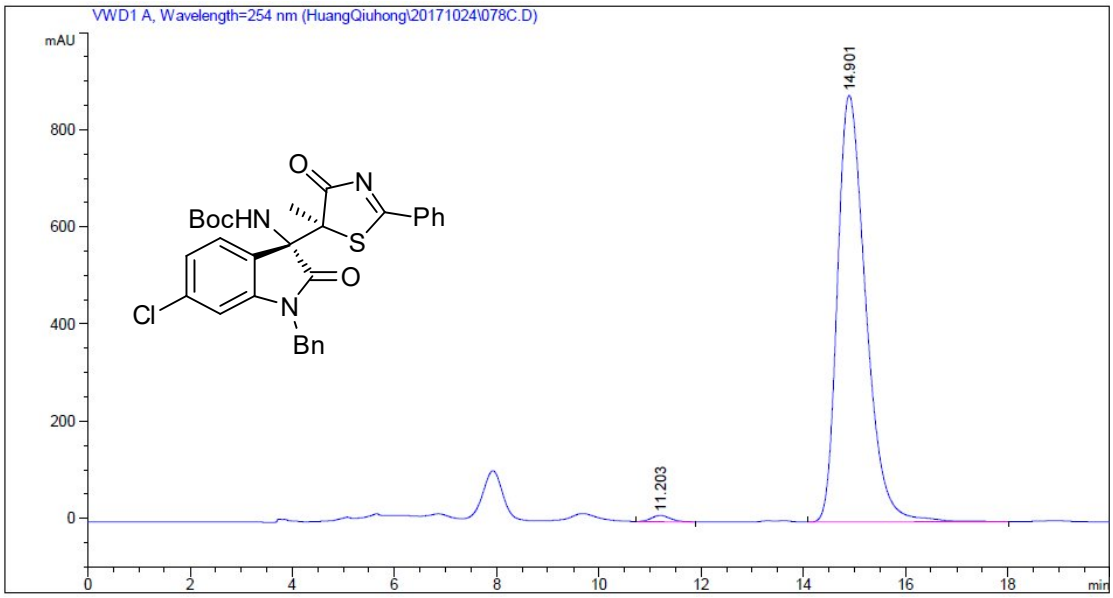


#	Time	Area	Height	Width	Symmetry	Area %
1	9.866	2133.7	97.8	0.3186	0.658	3.551
2	10.563	57955.7	2974.6	0.2984	0.625	96.449

tert-butyl((_S_)-1-benzyl-6-chloro-3-((_S_)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3fa)

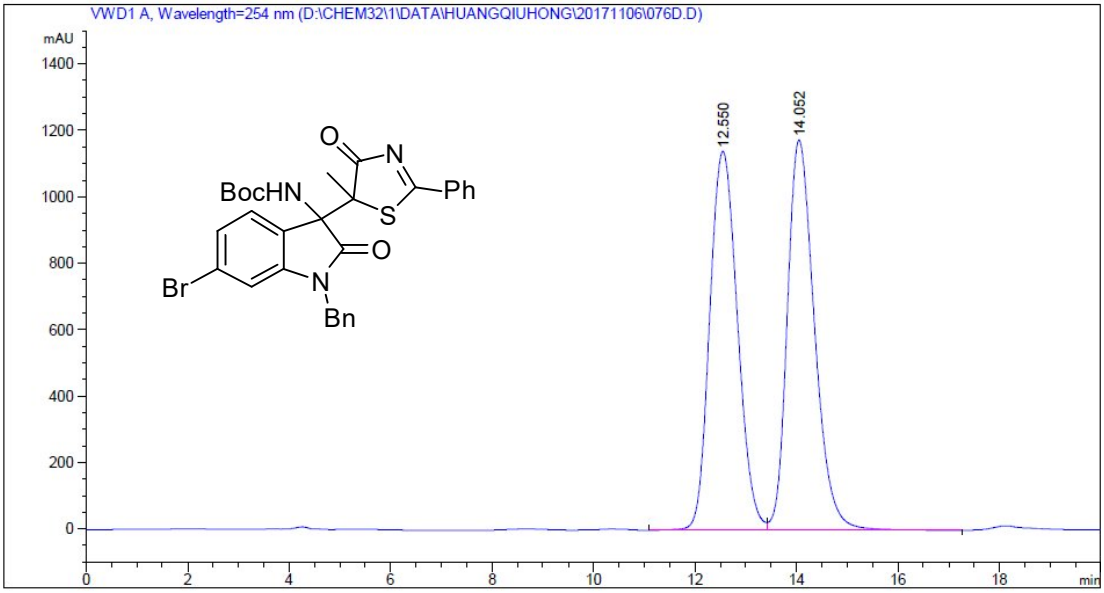


#	Time	Area	Height	Width	Symmetry	Area %
1	11.054	30553.1	775	0.6272	1.211	50.001
2	14.809	30552.4	656.4	0.725	0.905	49.999

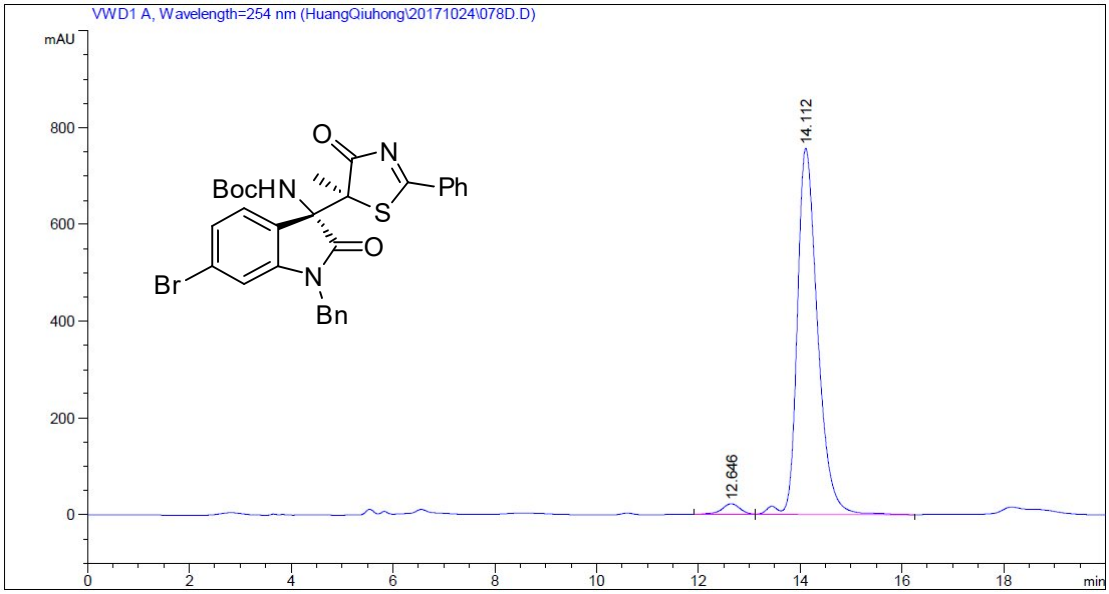


#	Time	Area	Height	Width	Symmetry	Area %
1	11.203	320.6	12.8	0.3906	0.853	0.938
2	14.901	33846.9	878.5	0.5925	0.656	99.062

***tert*-butyl ((*S*)-1-benzyl-6-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ga)**

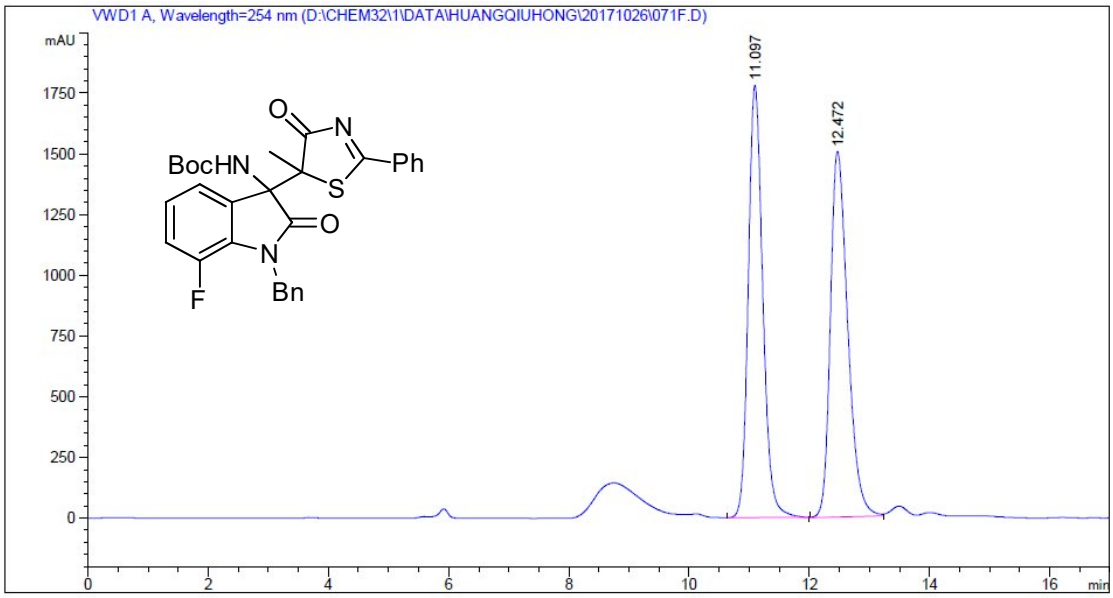


#	Time	Area	Height	Width	Symmetry	Area %
1	12.550	43243.7	1140.2	0.6025	0.856	49.751
2	14.052	43676.4	1174.2	0.576	0.711	50.249

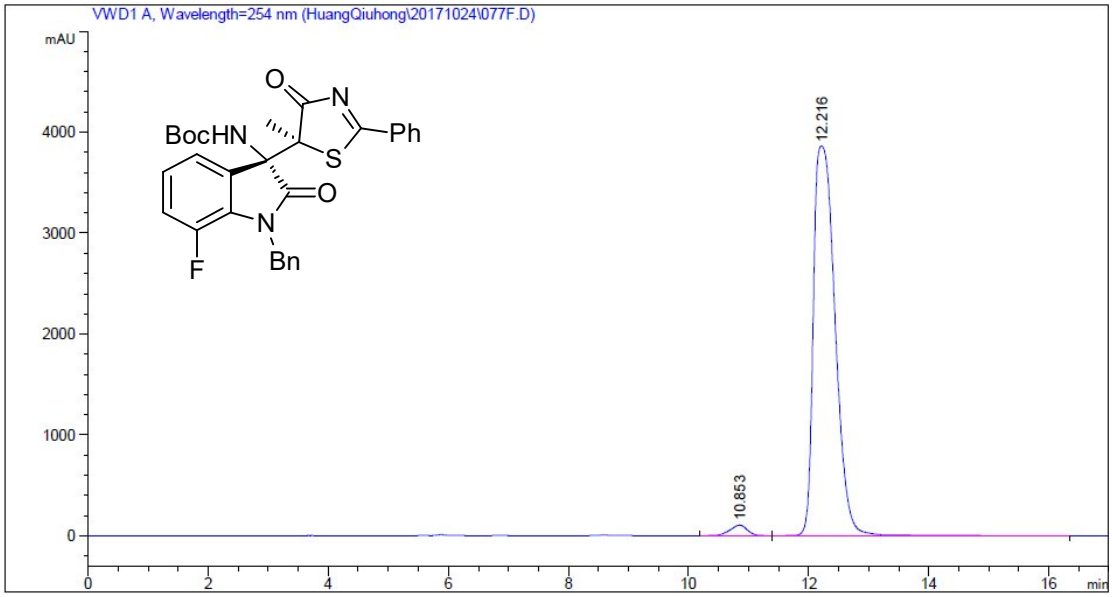


#	Time	Area	Height	Width	Symmetry	Area %
1	12.646	471.5	21.3	0.3689	0.929	2.193
2	14.112	21033.7	756.5	0.4194	0.698	97.807

***tert*-butyl ((*S*)-1-benzyl-7-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ha)**

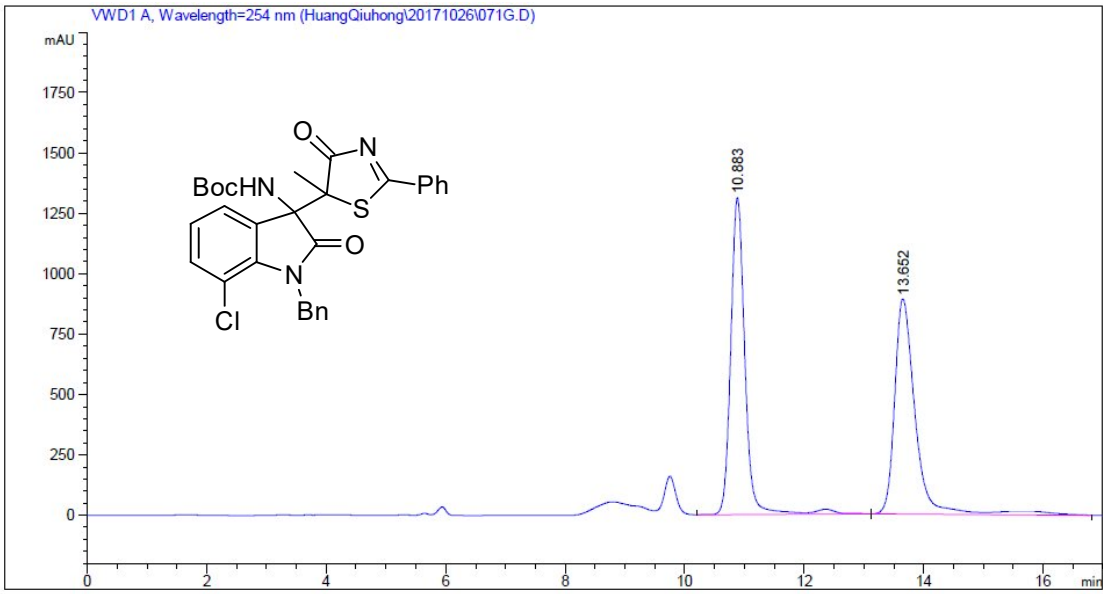


#	Time	Area	Height	Width	Symmetry	Area %
1	11.097	29771.3	1781.3	0.258	0.789	49.626
2	12.472	30219.9	1505.9	0.3345	0.674	50.374

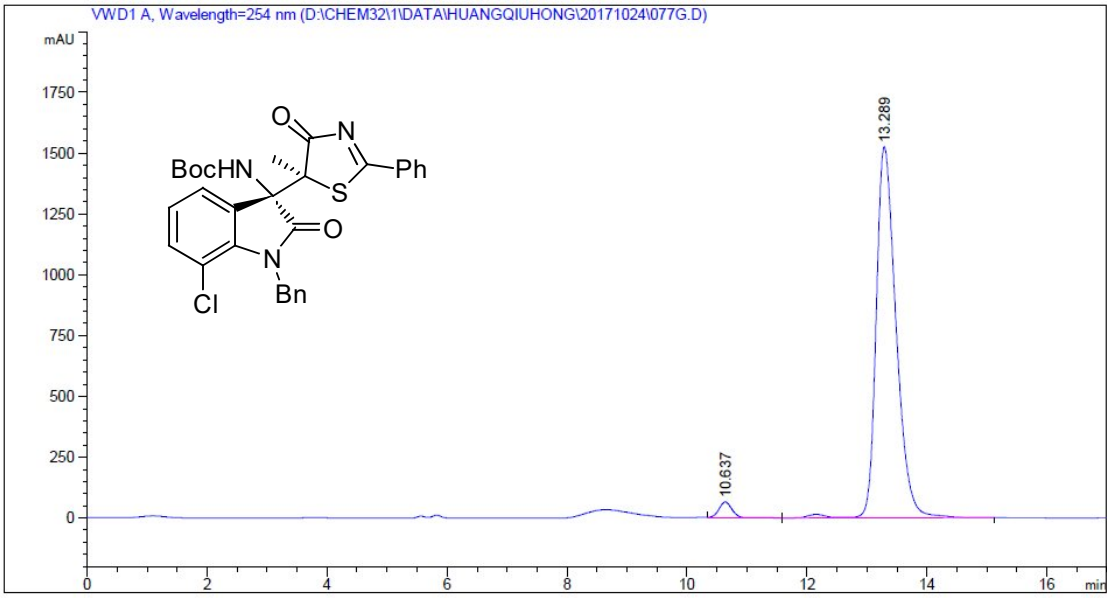


#	Time	Area	Height	Width	Symmetry	Area %
1	10.853	2137.3	106.3	0.2976	1.251	2.164
2	12.216	96634.1	3861.2	0.3908	0.559	97.836

***tert*-butyl ((*S*)-1-benzyl-7-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ia)**

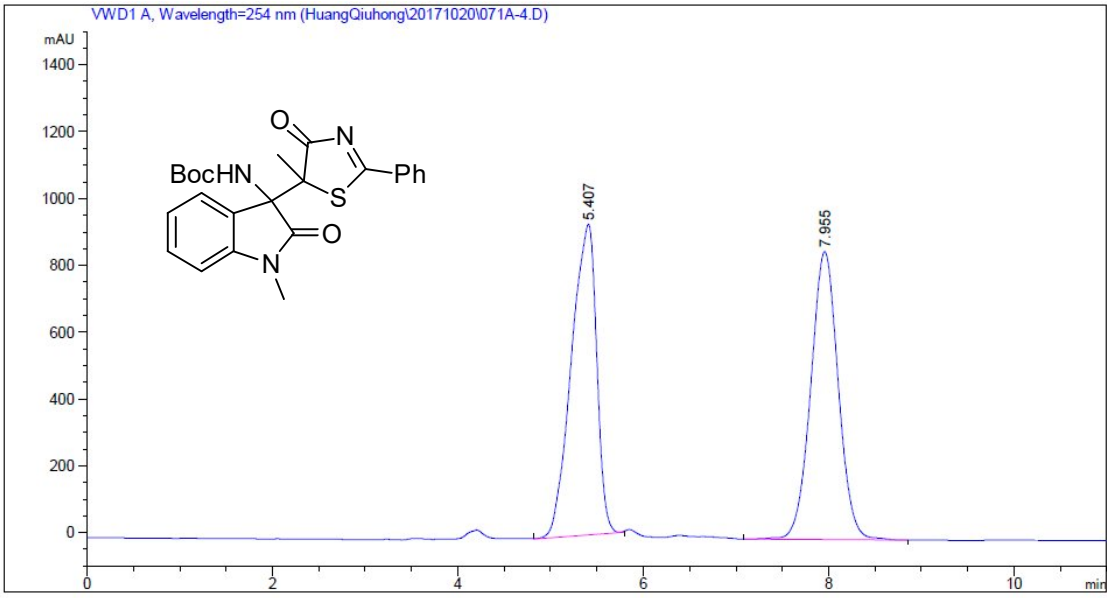


#	Time	Area	Height	Width	Symmetry	Area %
1	10.883	21878.5	1312.3	0.2507	0.824	50.102
2	13.652	21789.1	891.7	0.3546	0.627	49.898

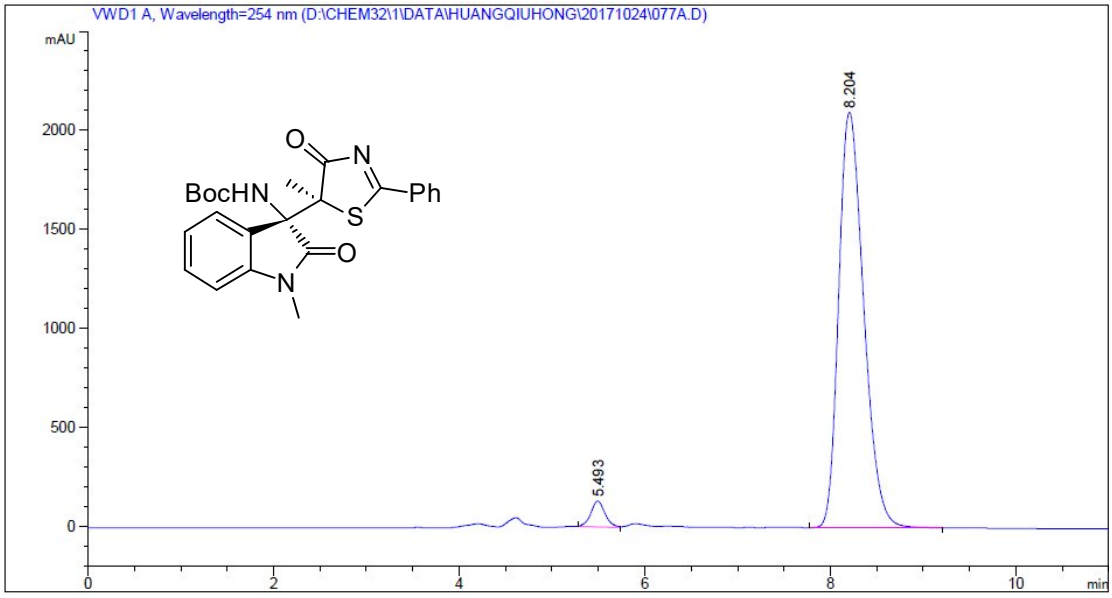


#	Time	Area	Height	Width	Symmetry	Area %
1	10.637	1016.9	65.7	0.2365	0.894	2.805
2	13.289	35232.7	1524.9	0.351	0.674	97.195

***tert*-butyl ((*S*)-1-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ja)**

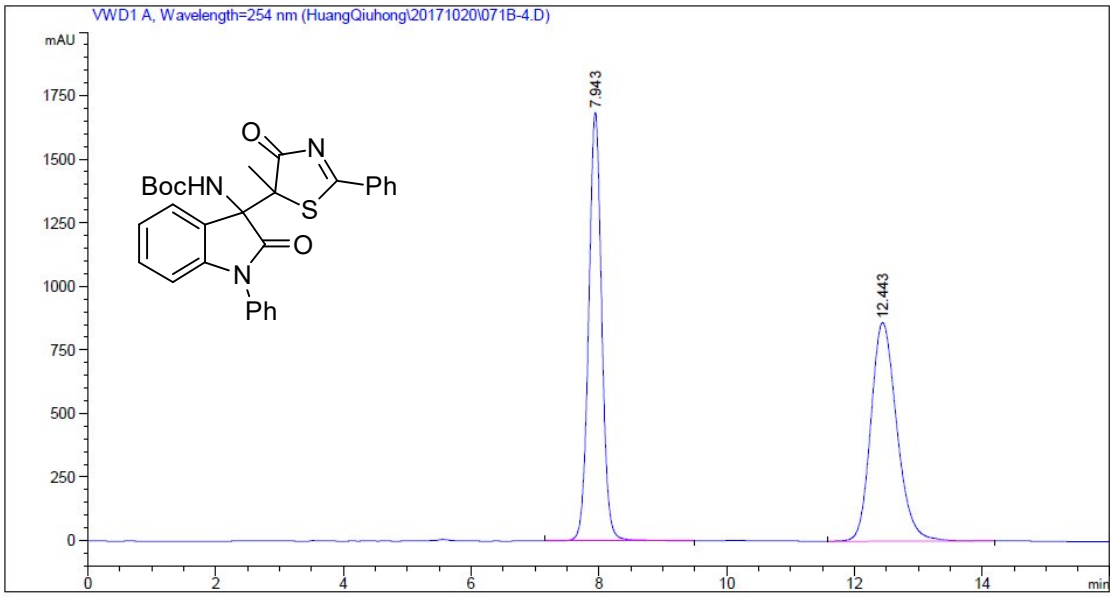


#	Time	Area	Height	Width	Symmetry	Area %
1	5.407	17662	930.4	0.3164	1.919	49.783
2	7.955	17816	862.2	0.3171	0.983	50.217

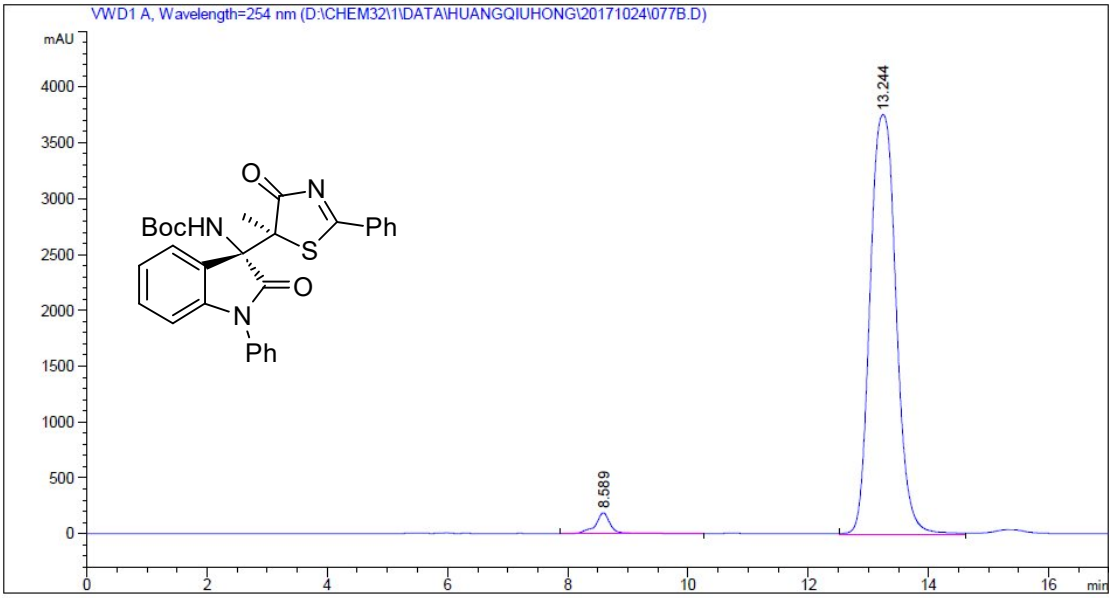


#	Time	Area	Height	Width	Symmetry	Area %
1	5.493	1259	125.7	0.167	0.901	3.109
2	8.204	39234.3	2098.6	0.2911	0.7	96.891

tert-butyl ((_S_)-3-((_S_)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxo-1-phenylindolin-3-yl)carbamate (3ka)

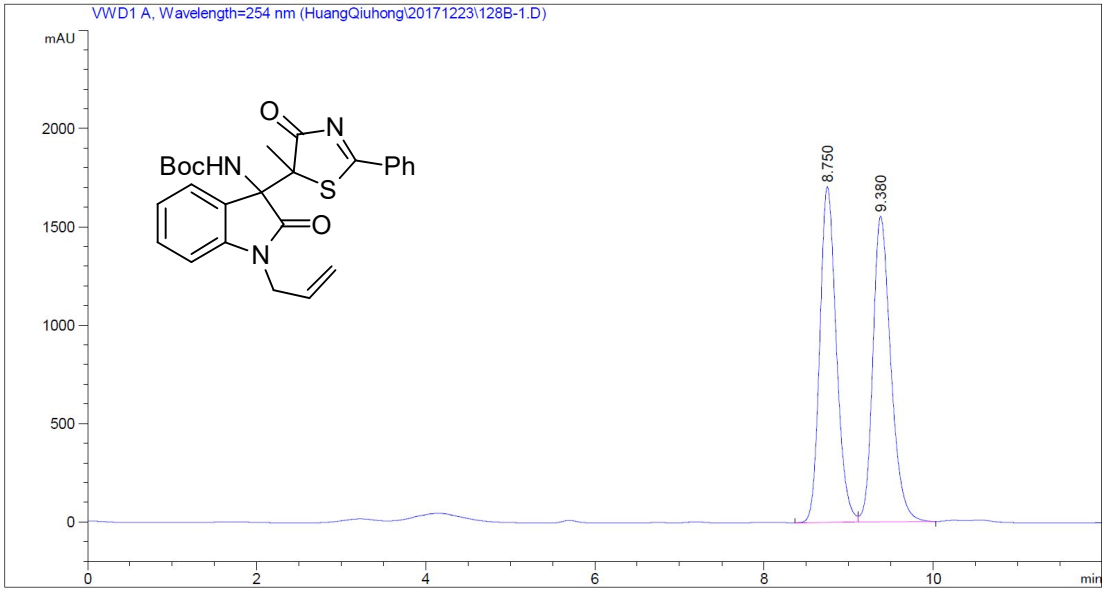


#	Time	Area	Height	Width	Symmetry	Area %
1	7.943	23945.5	1687	0.2176	0.968	49.649
2	12.443	24283.8	860.1	0.4364	0.784	50.351

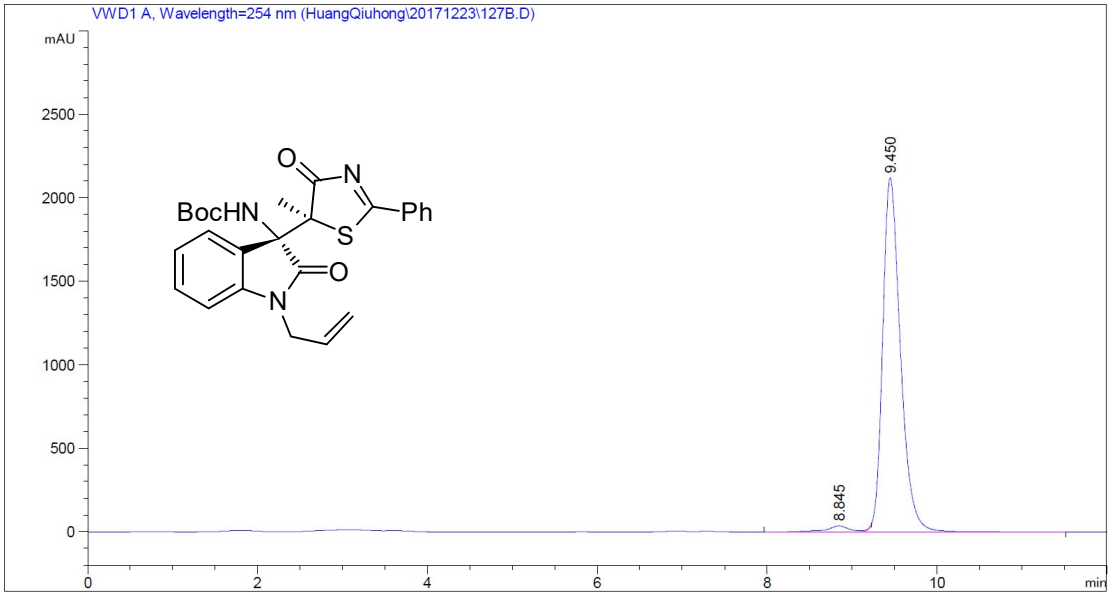


#	Time	Area	Height	Width	Symmetry	Area %
1	8.589	3261.7	186.1	0.2534	1.04	2.792
2	13.244	113544.1	3751.7	0.4742	0.933	97.208

***tert*-butyl ((*S*)-1-allyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3la)**

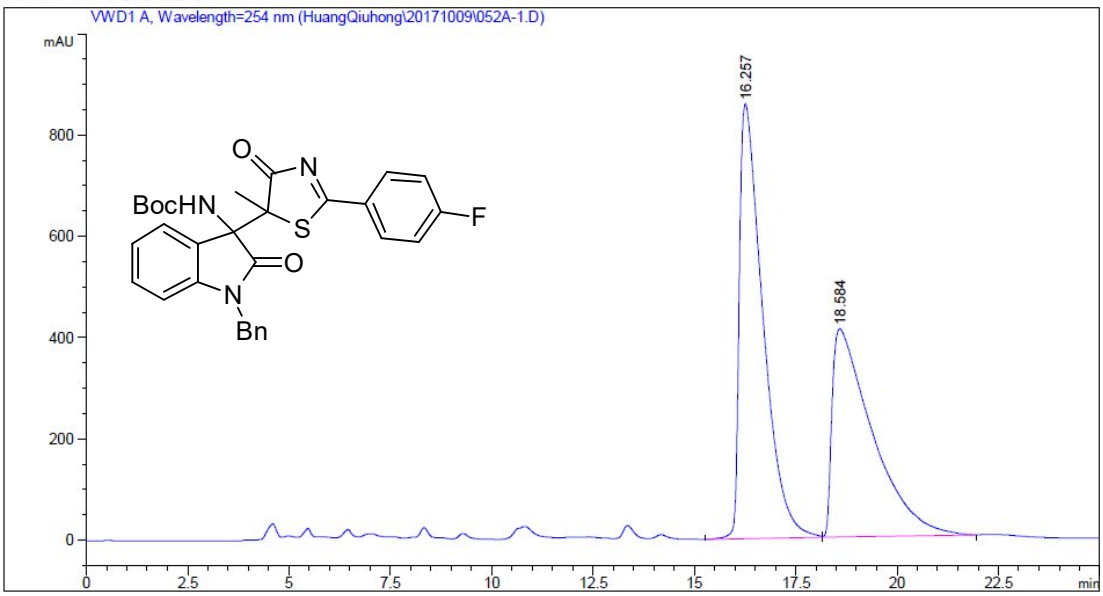


#	Time	Area	Height	Width	Symmetry	Area %
1	8.75	23213.7	1707.8	0.2096	0.798	50.253
2	9.38	22980	1554.4	0.2265	0.718	49.747

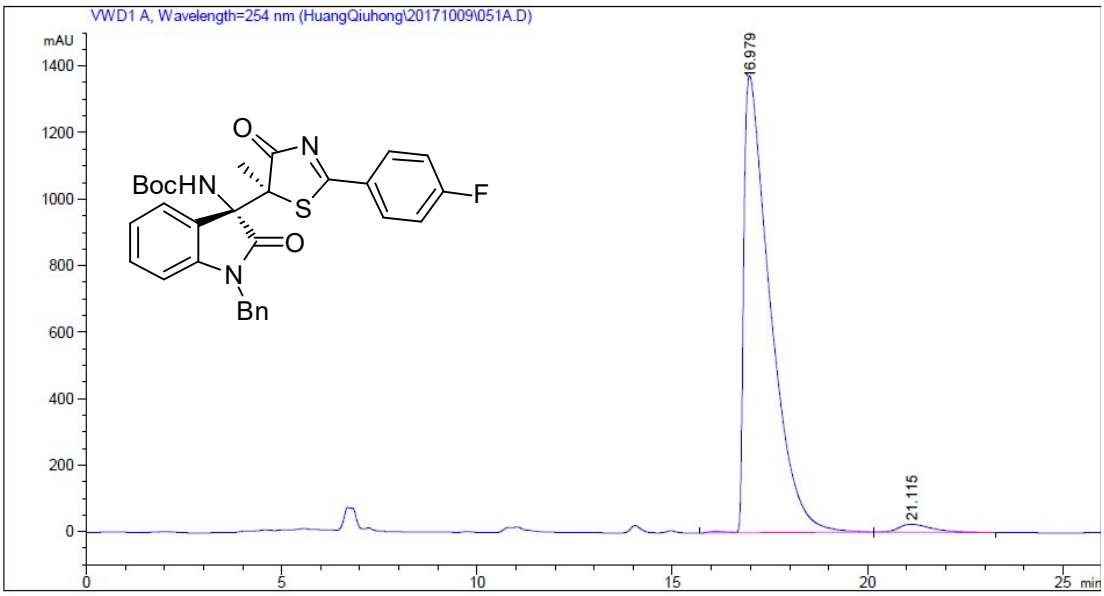


#	Time	Area	Height	Width	Symmetry	Area %
1	8.845	722.9	37	0.2757	1.273	2.284
2	9.45	30927.2	2120.3	0.2222	0.766	97.716

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-fluorophenyl)-5-methyl-4-oxo-4,5-dihydro thiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ab)**

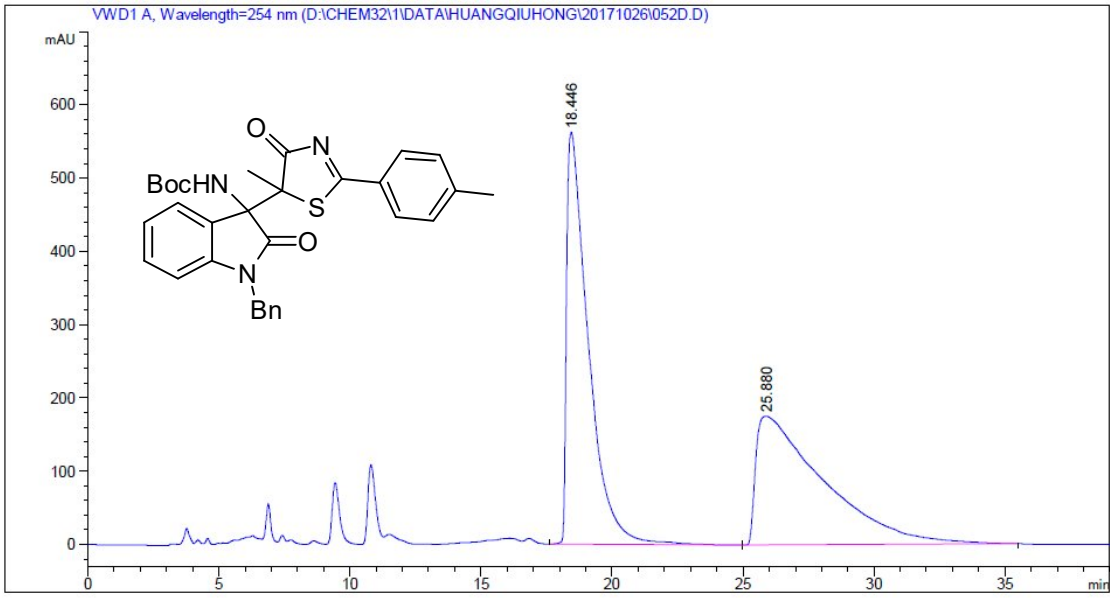


#	Time	Area	Height	Width	Symmetry	Area %
1	16.257	32294.5	834.7	0.6448	0.332	49.733
2	18.584	32641.6	425	1.2799	0.214	50.267

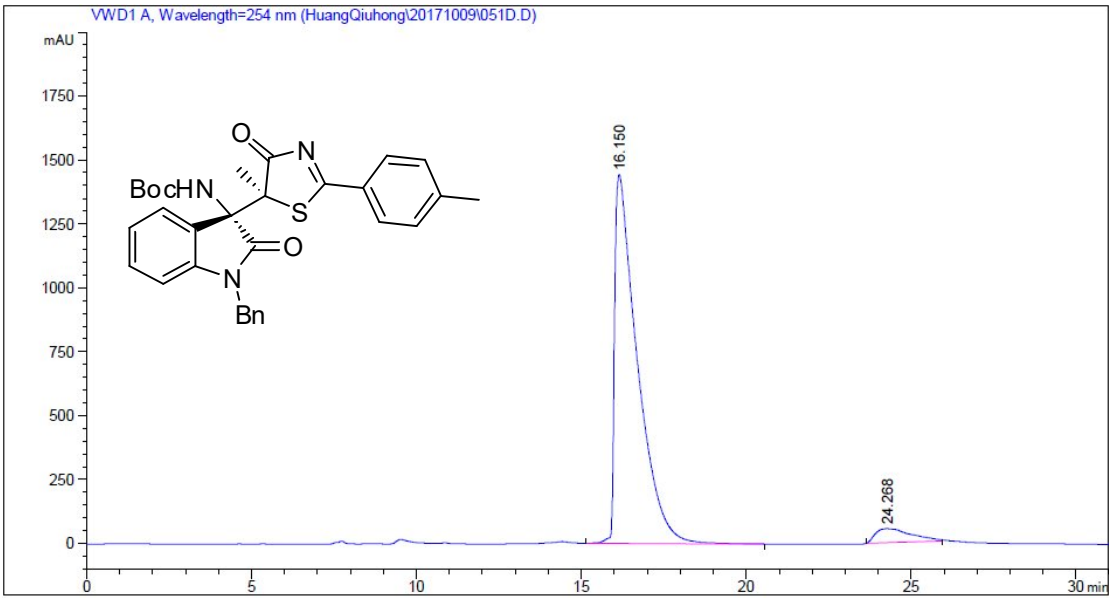


#	Time	Area	Height	Width	Symmetry	Area %
1	16.979	64132.3	1374.2	0.6743	0.253	97.869
2	21.115	1396.4	24	0.8731	0.538	2.131

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(p-tolyl)-4,5-dihydrothiazol-5-yl) -2-oxoindolin-3-yl)carbamate (3ac)**

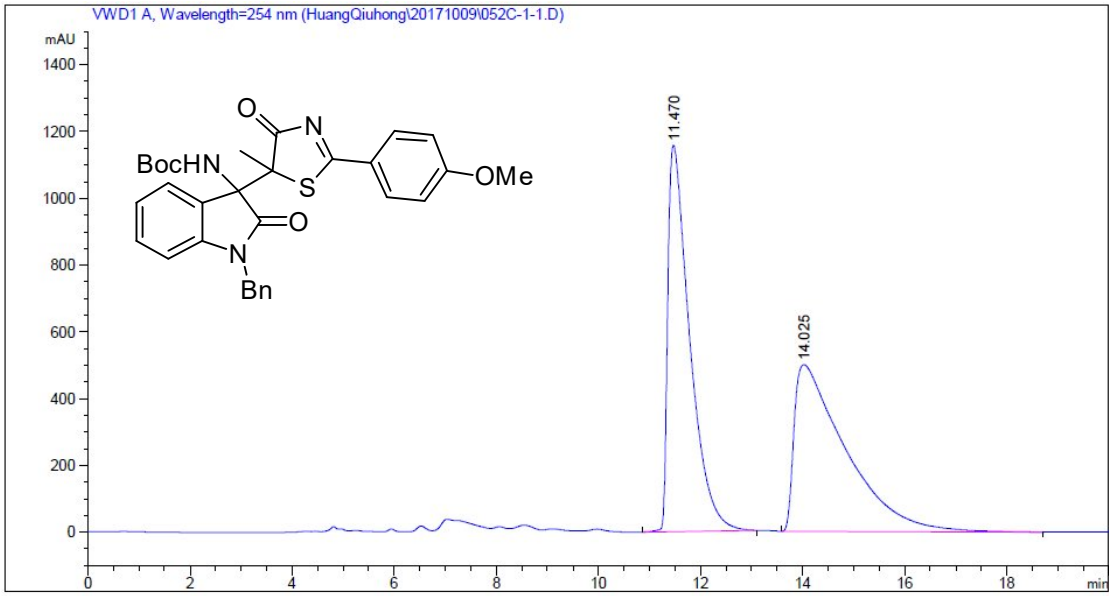


#	Time	Area	Height	Width	Symmetry	Area %
1	18.446	32323.9	562.1	0.8299	0.243	50.495
2	25.880	31690.3	176	2.4002	0.16	49.505

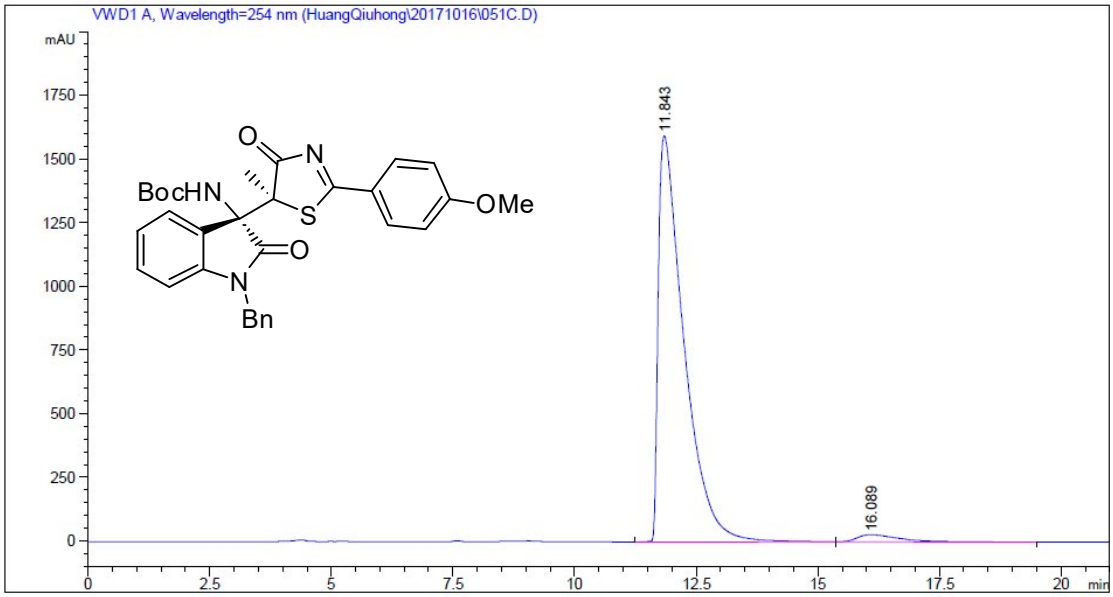


#	Time	Area	Height	Width	Symmetry	Area %
1	16.150	68912.1	1442.7	0.6633	0.234	93.813
2	24.268	4544.5	54.7	1.3844	0.384	6.187

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ad)**

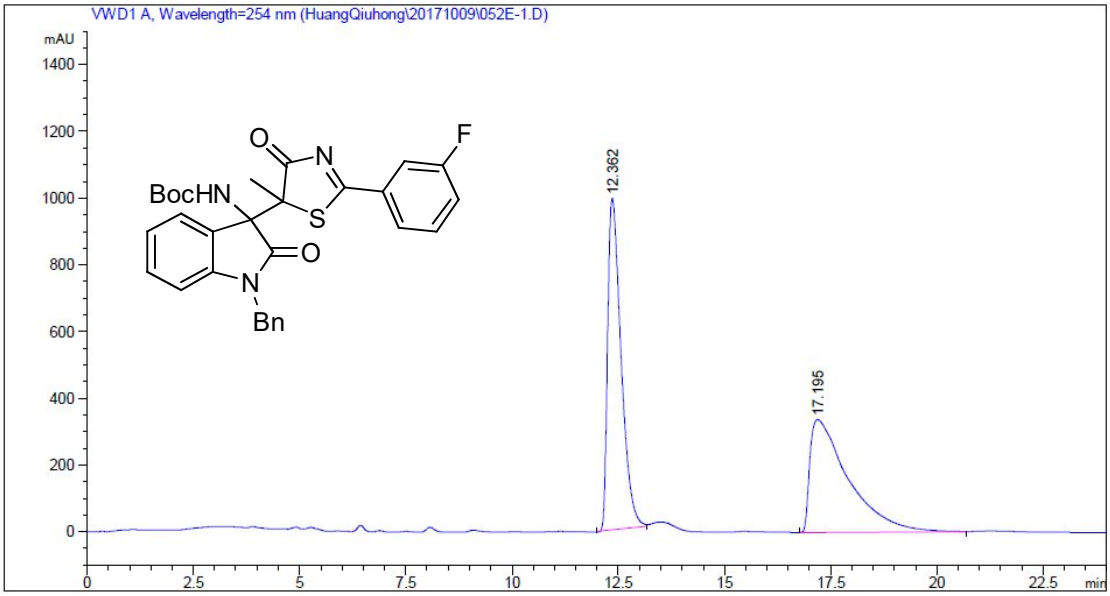


#	Time	Area	Height	Width	Symmetry	Area %
1	11.470	34309	1156.7	0.4371	0.322	49.474
2	14.025	35039.1	499	0.9752	0.211	50.526

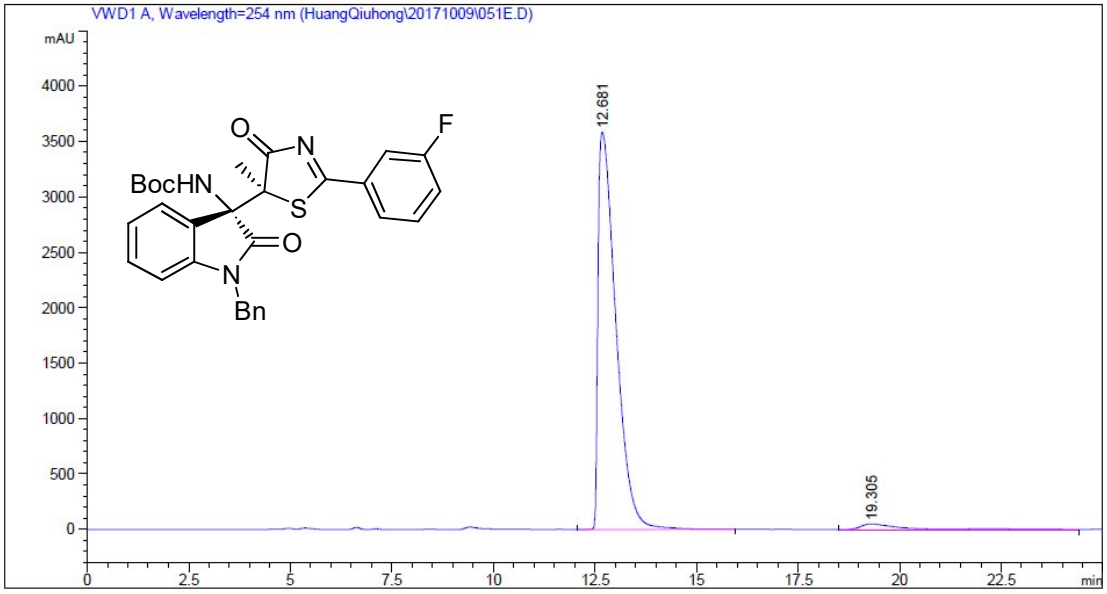


#	Time	Area	Height	Width	Symmetry	Area %
1	11.843	58343.2	1594.5	0.5369	0.274	97.260
2	16.089	1643.5	28.1	0.837	0.434	2.740

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ae)**

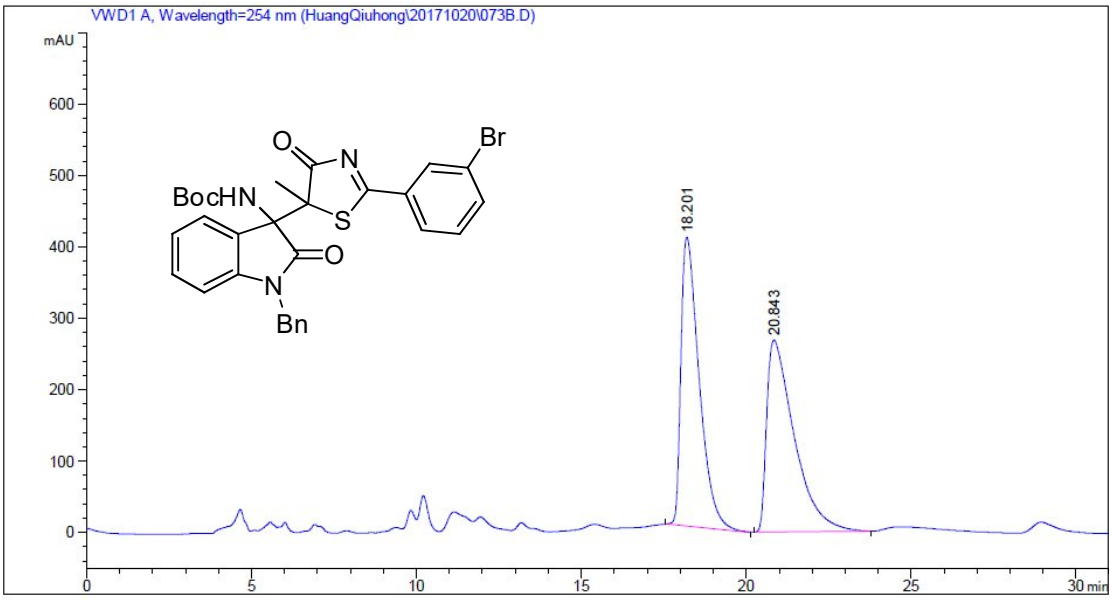


#	Time	Area	Height	Width	Symmetry	Area %
1	12.362	21849.5	994.5	0.3662	0.501	50.758
2	17.195	21197.3	338	0.8537	0.231	49.242

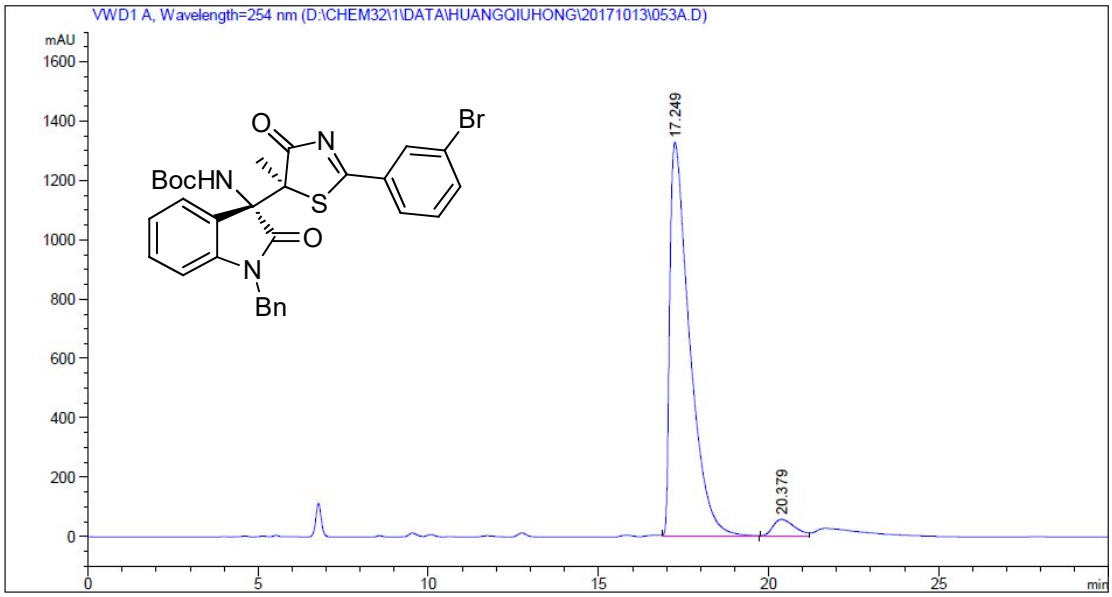


#	Time	Area	Height	Width	Symmetry	Area %
1	12.681	109432.1	3584.5	0.4662	0.283	96.994
2	19.305	3391.4	49.2	0.8614	0.404	3.006

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-bromophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3af)**

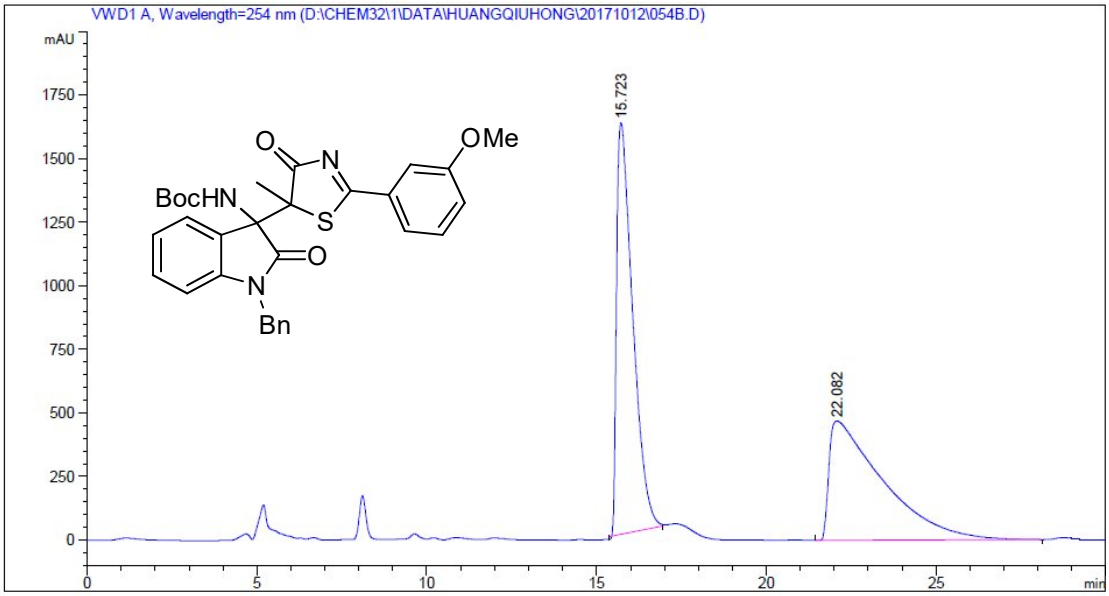


#	Time	Area	Height	Width	Symmetry	Area %
1	18.201	15505.6	404.4	0.639	0.455	49.857
2	20.843	15594.5	268.7	0.872	0.328	50.143

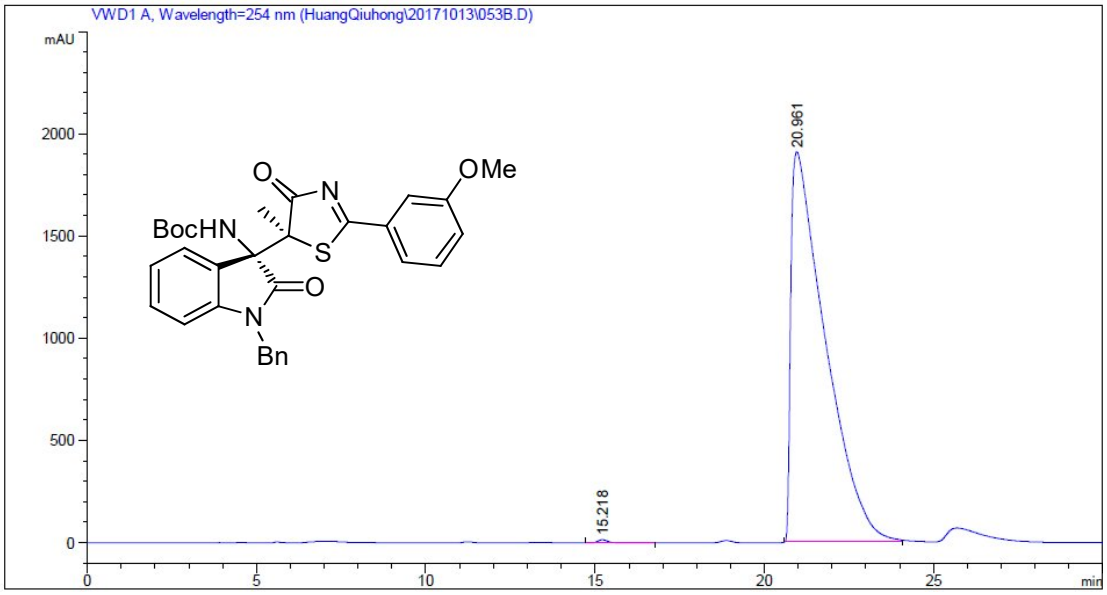


#	Time	Area	Height	Width	Symmetry	Area %
1	17.249	52947	1320.1	0.6685	0.334	96.074
2	20.386	2163.9	51.5	0.6999	0.553	3.926

tert-butyl ((_S_)-1-benzyl-3-((_S_)-2-(3-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ag)

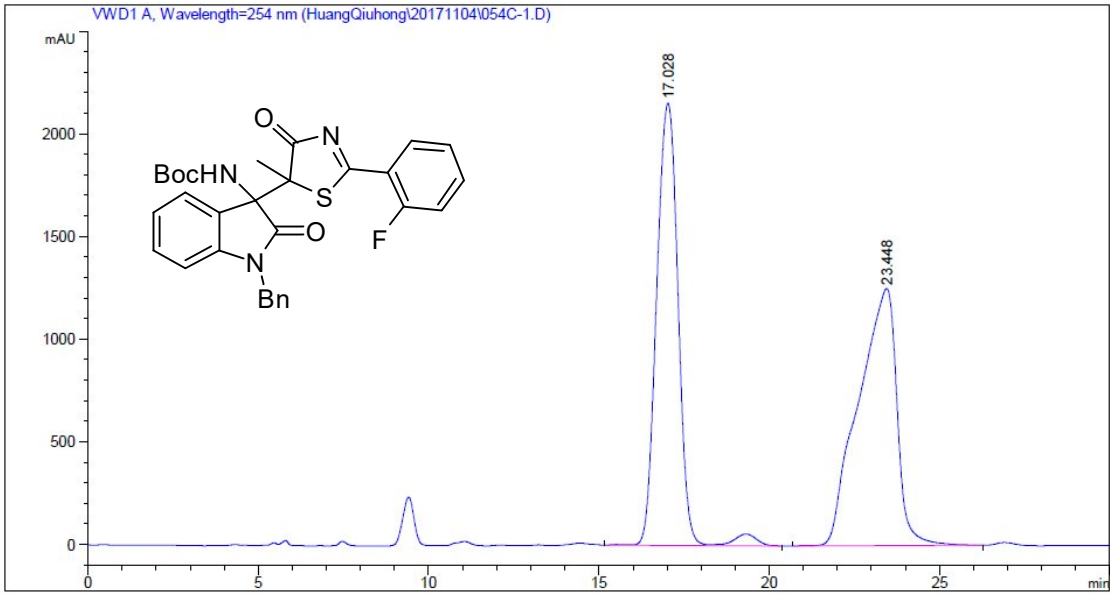


#	Time	Area	Height	Width	Symmetry	Area %
1	15.723	53429.1	1619	0.55	0.355	50.818
2	22.082	51708.8	469	1.4983	0.154	49.182

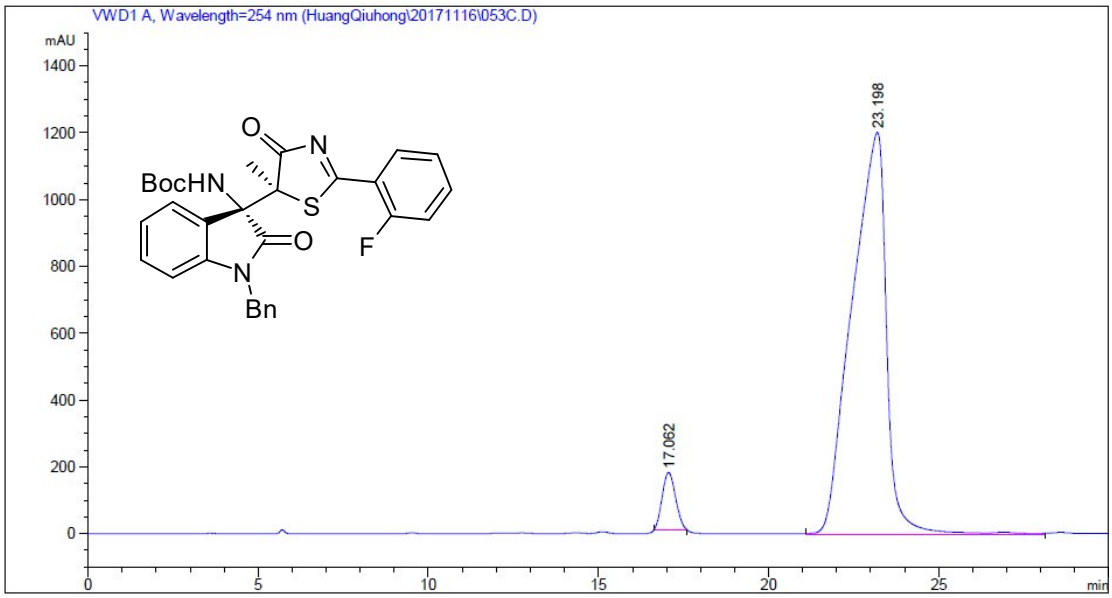


#	Time	Area	Height	Width	Symmetry	Area %
1	15.218	337.9	15.8	0.3189	0.668	0.251
2	20.961	134140.2	1904.9	1.1737	0.197	99.749

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(2-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ah)**

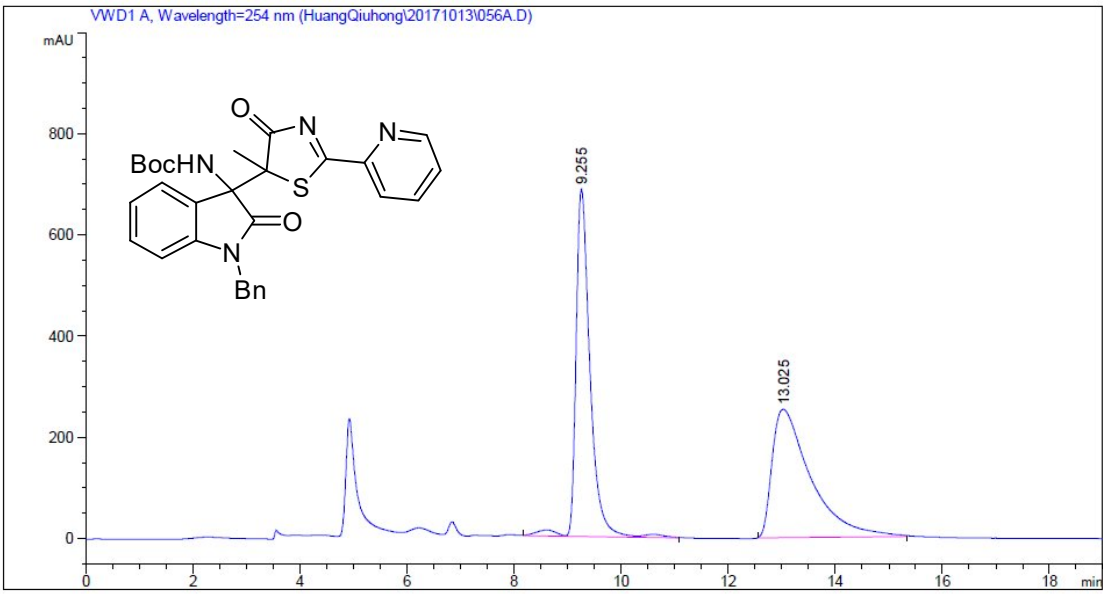


#	Time	Area	Height	Width	Symmetry	Area %
1	17.028	94571.4	2161.8	0.7291	1.063	49.150
2	23.448	97841.7	1250.9	1.1525	2.511	50.850

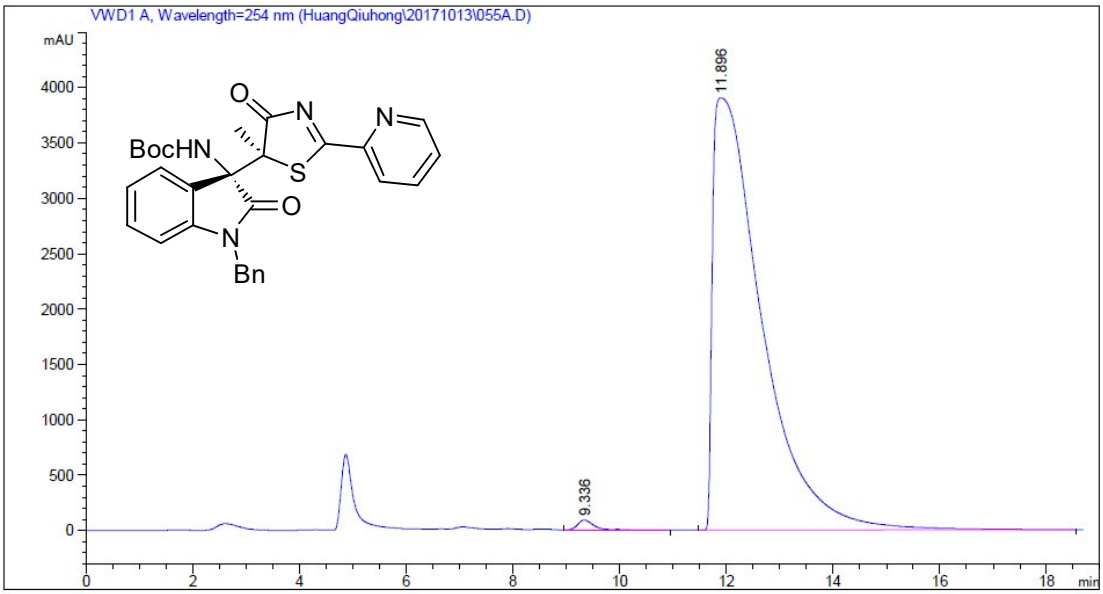


#	Time	Area	Height	Width	Symmetry	Area %
1	17.062	4687.4	171.9	0.4546	0.877	5.266
2	23.198	84330.8	1201.9	1.1694	2.473	94.734

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol -5-yl)-2-oxoindolin-3-yl)carbamate (3ai)**

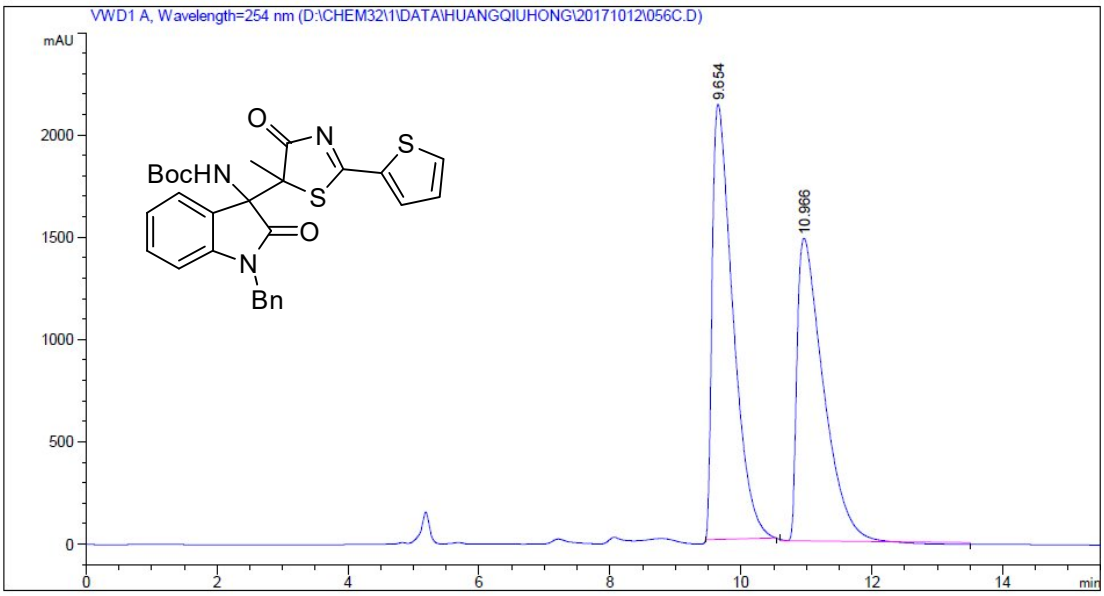


#	Time	Area	Height	Width	Symmetry	Area %
1	9.255	12902.3	687.6	0.2698	0.666	49.169
2	13.025	13338.7	255.8	0.7595	0.348	50.831

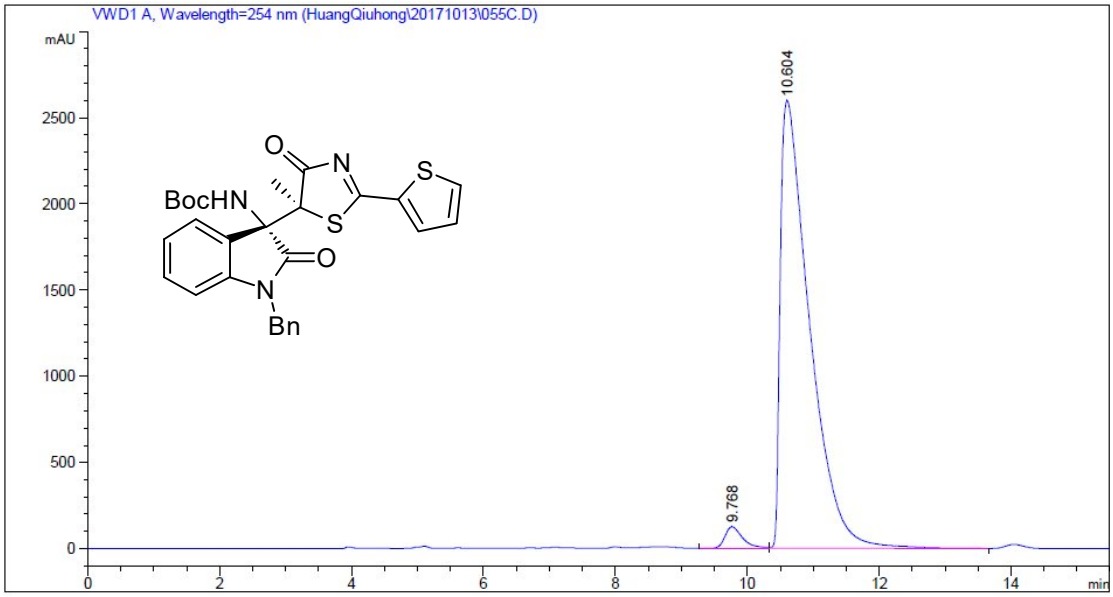


#	Time	Area	Height	Width	Symmetry	Area %
1	9.336	2004.1	90.7	0.3095	0.678	0.793
2	11.896	250738.3	3904.9	0.8121	0.179	99.207

tert-butyl ((_S_)-1-benzyl-3-((_S_)-5-methyl-4-oxo-2-(thiophen-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aj)

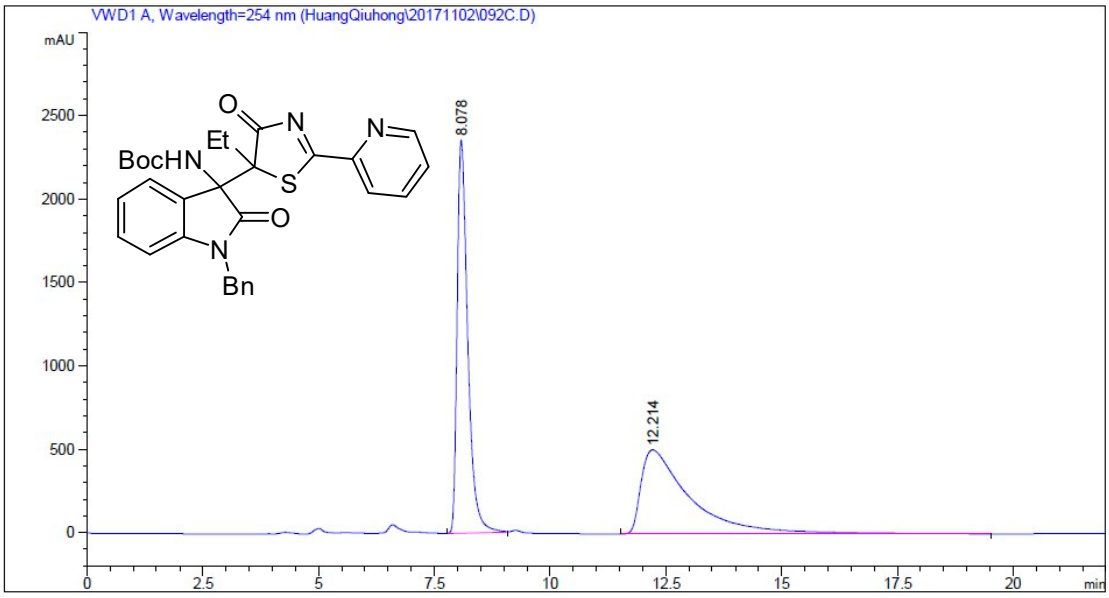


#	Time	Area	Height	Width	Symmetry	Area %
1	9.654	46677.9	2125.9	0.3659	0.666	49.169
2	10.966	41220.4	1478.7	0.4646	0.348	50.831

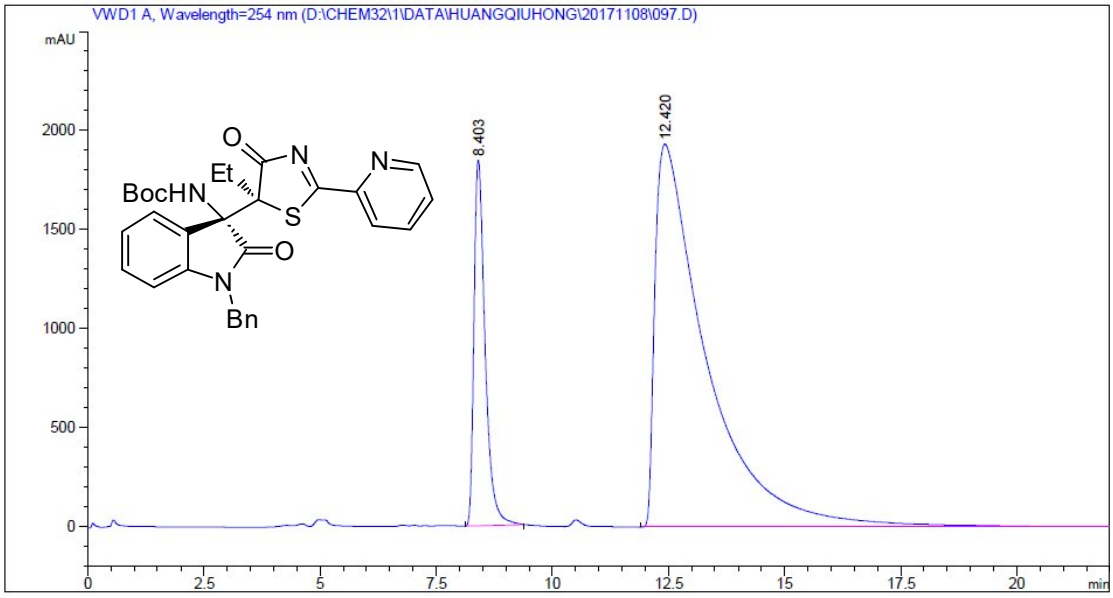


#	Time	Area	Height	Width	Symmetry	Area %
1	9.768	2331.4	125.2	0.2802	0.618	2.831
2	10.604	80011.4	2597.7	0.4523	0.268	97.169

***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-ethyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ak)**



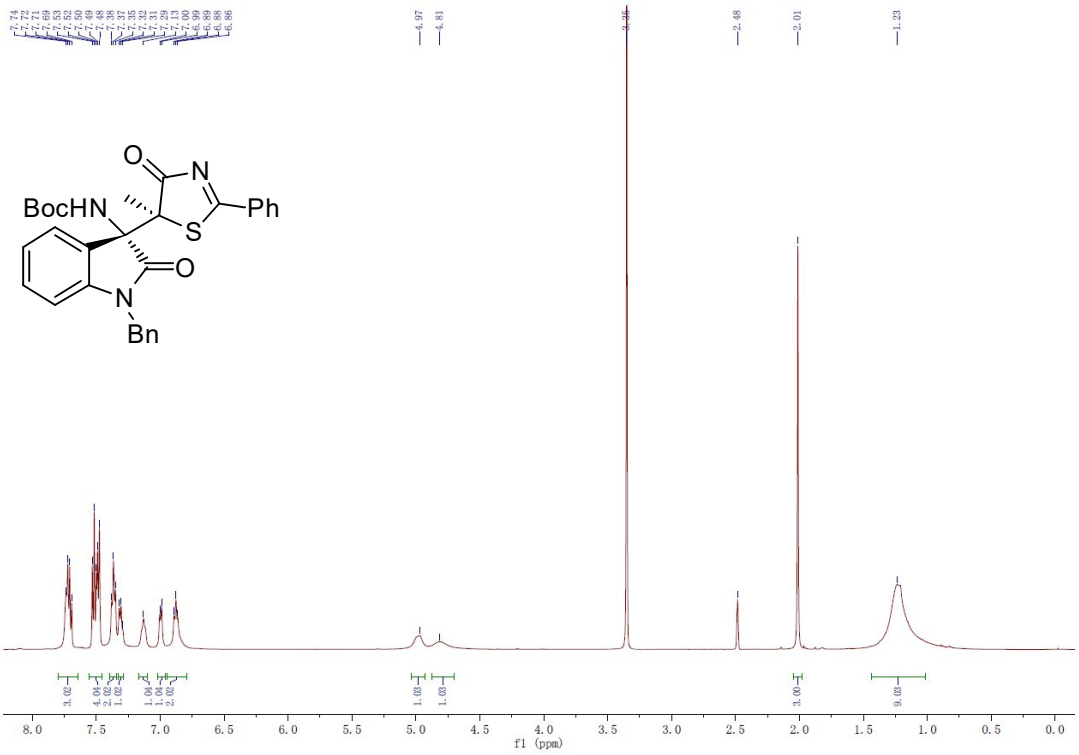
#	Time	Area	Height	Width	Symmetry	Area %
1	8.078	37705.4	2353.5	0.267	0.589	50.253
2	12.214	37325	504.1	1.0558	0.275	49.747

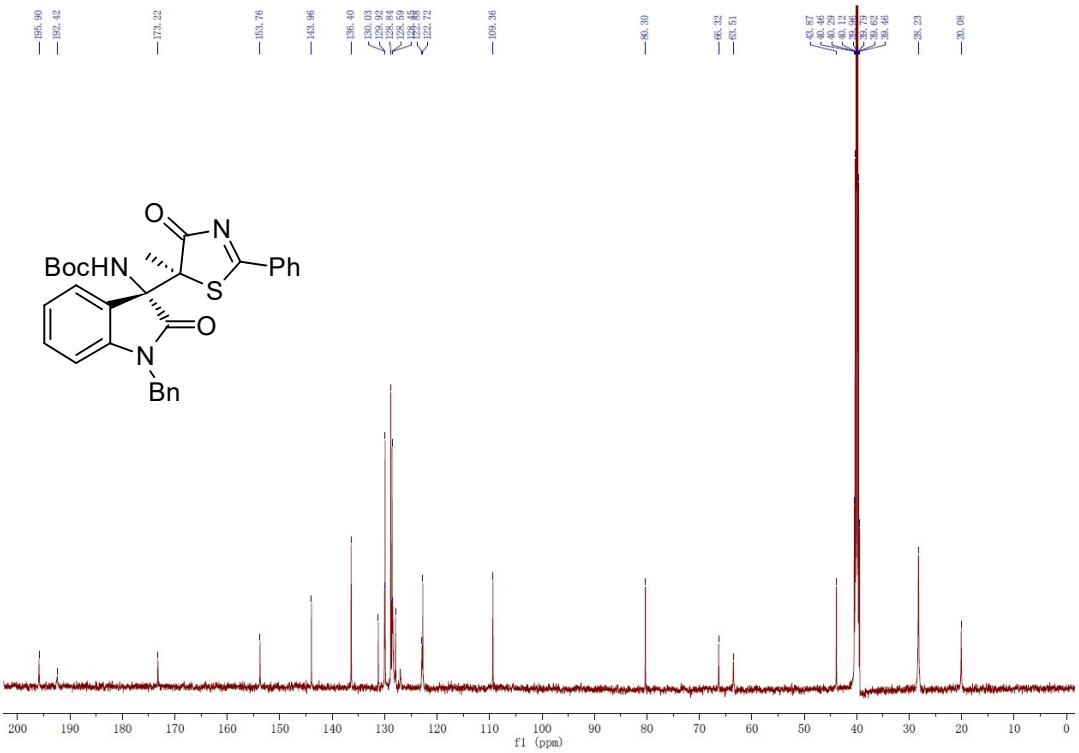


#	Time	Area	Height	Width	Symmetry	Area %
1	8.403	30582.1	1847.4	0.2759	0.589	16.888
2	12.42	150507	1935.4	1.1003	0.206	83.112

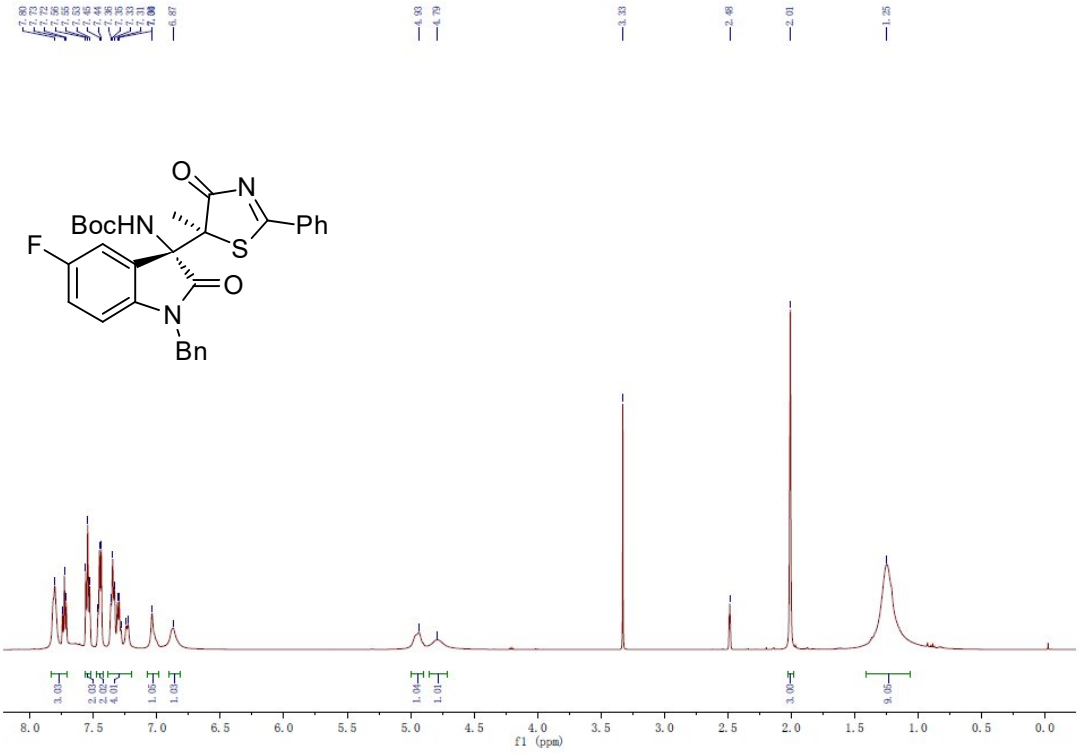
G: NMR Analysis

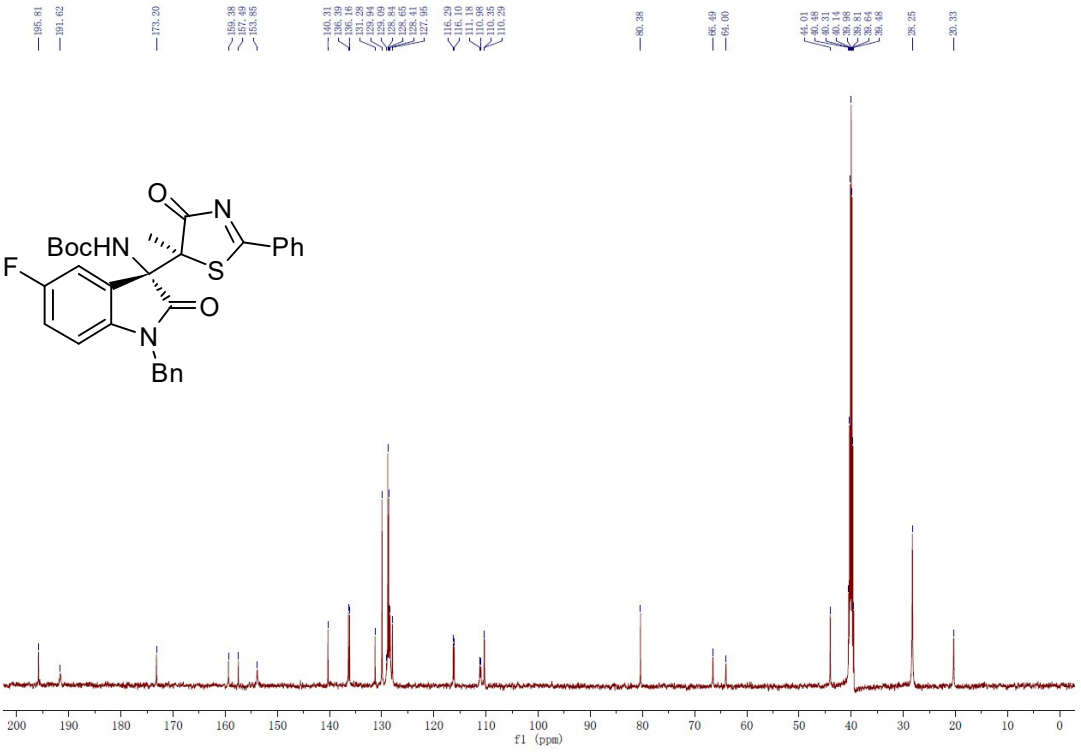
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aa)**



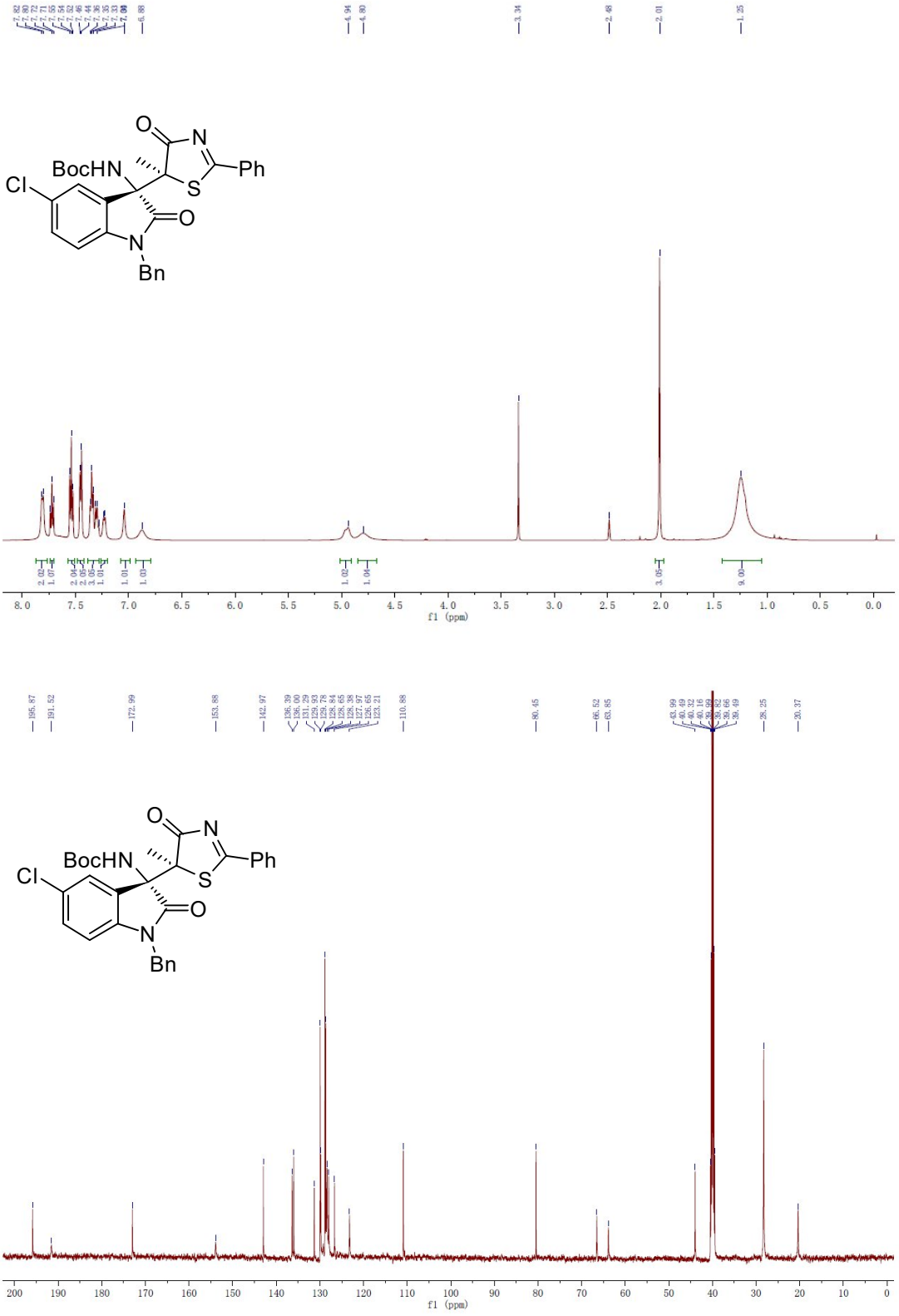


***tert*-butyl ((*S*)-1-benzyl-5-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ba)**

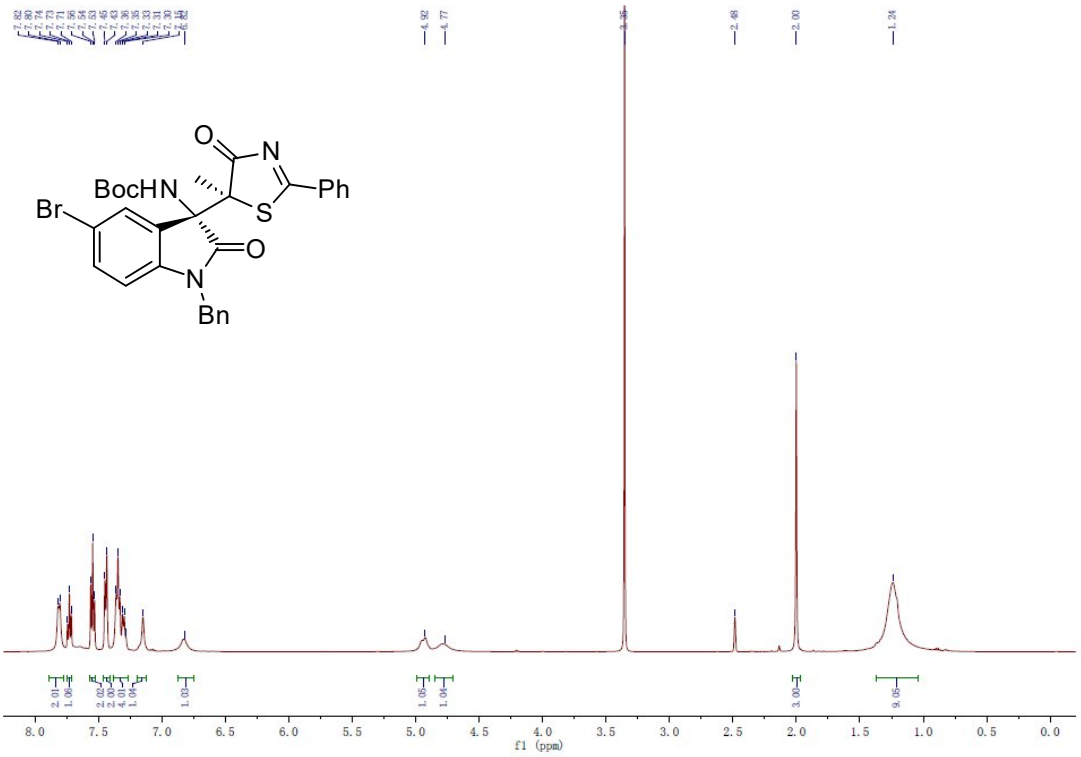


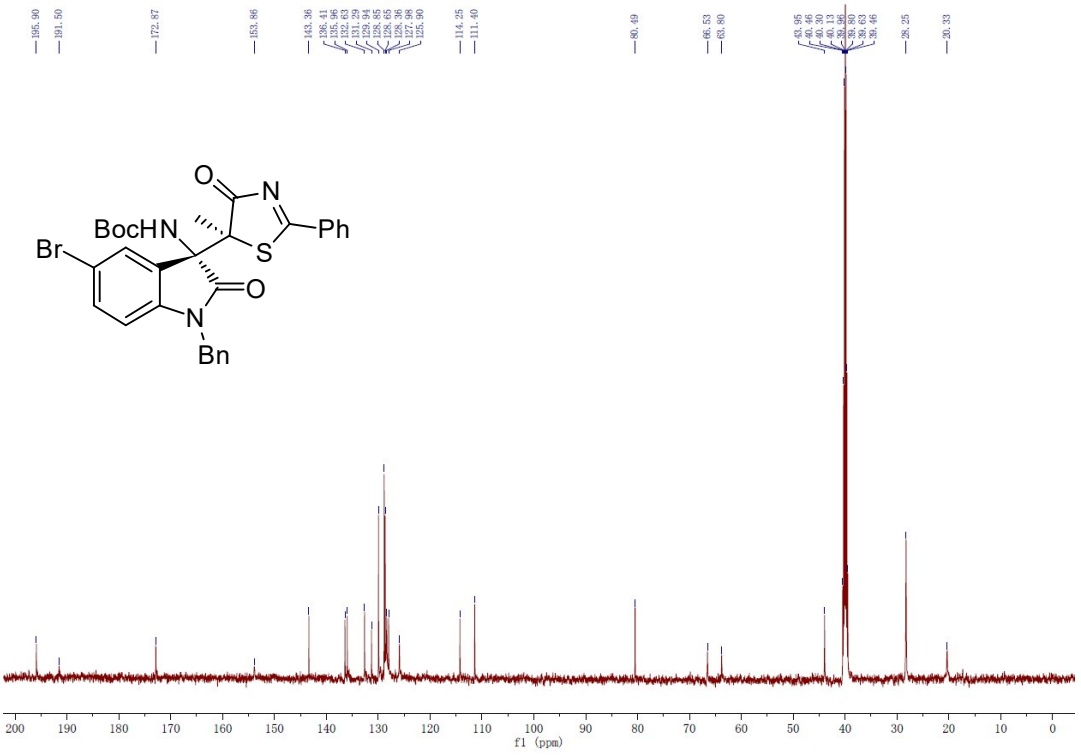


***tert*-butyl ((*S*)-1-benzyl-5-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ca)**

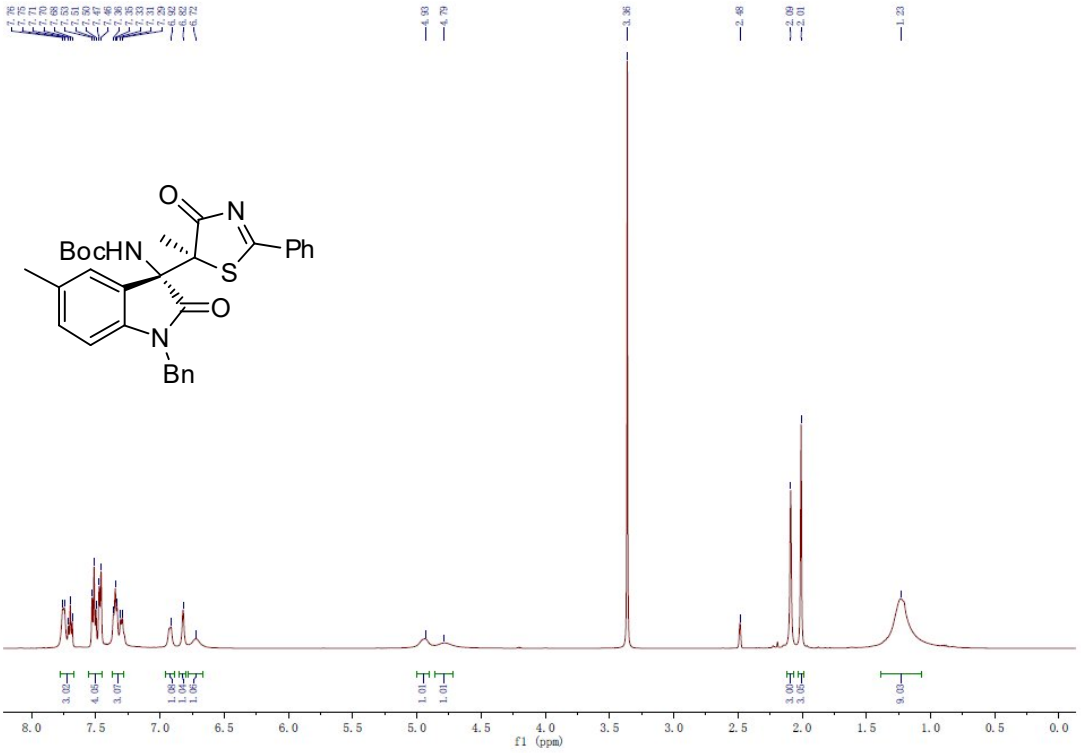


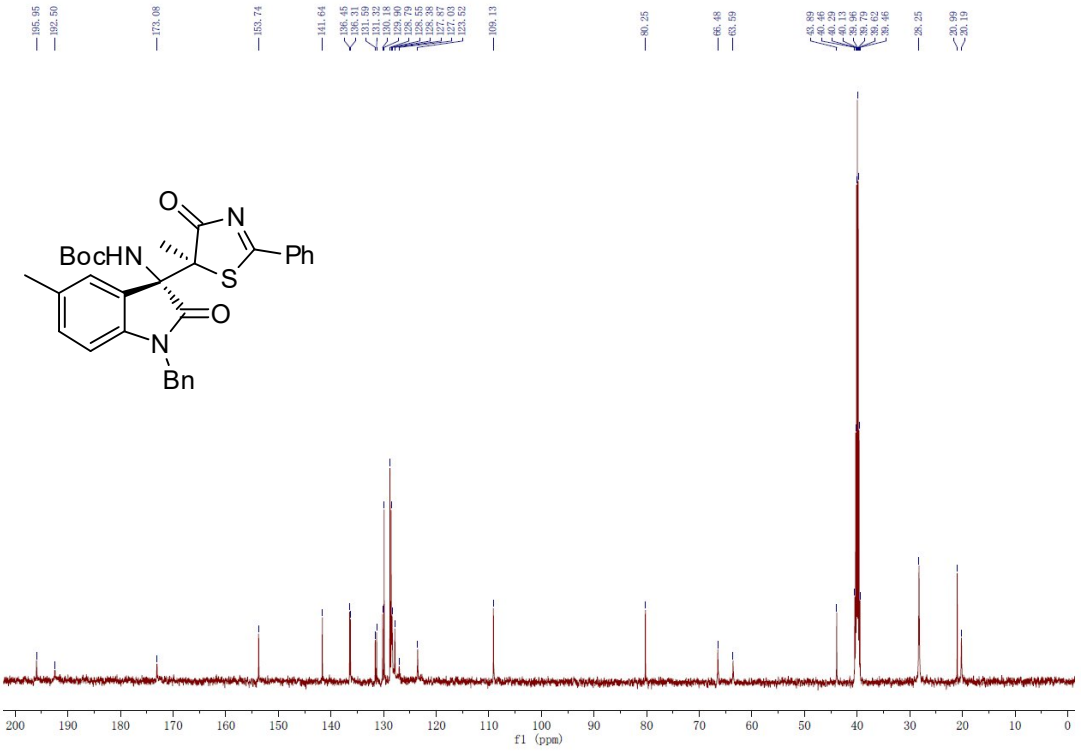
***tert*-butyl ((*S*)-1-benzyl-5-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3da)**



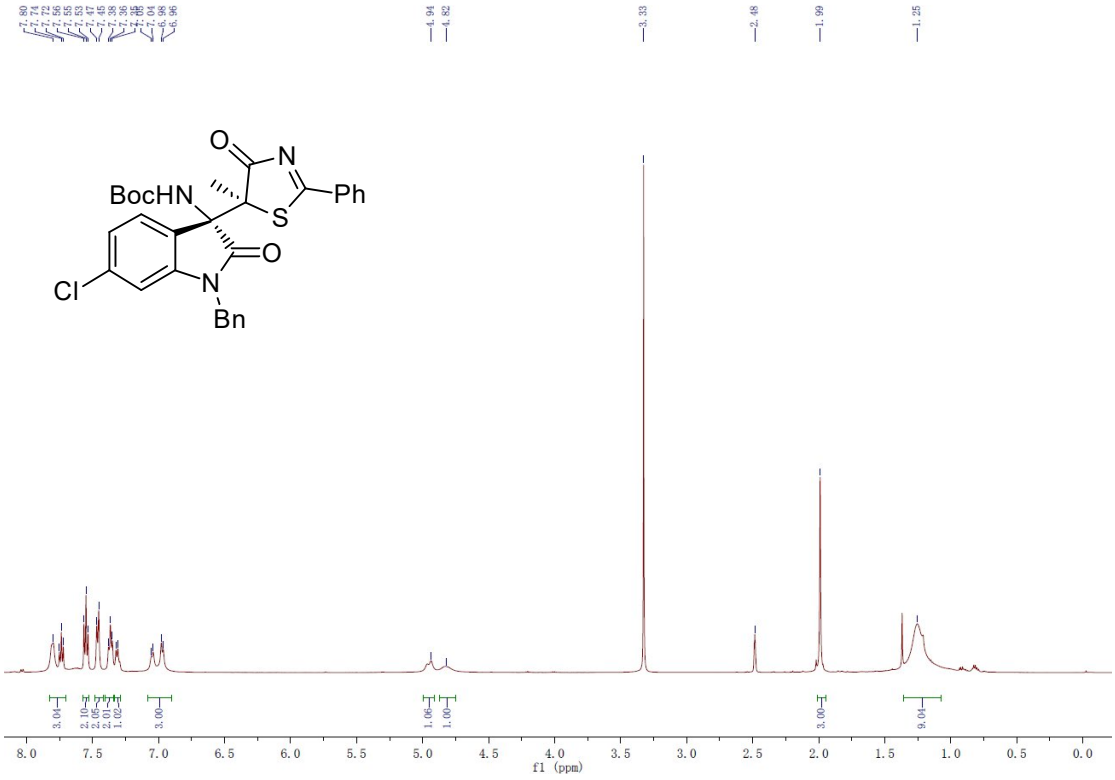


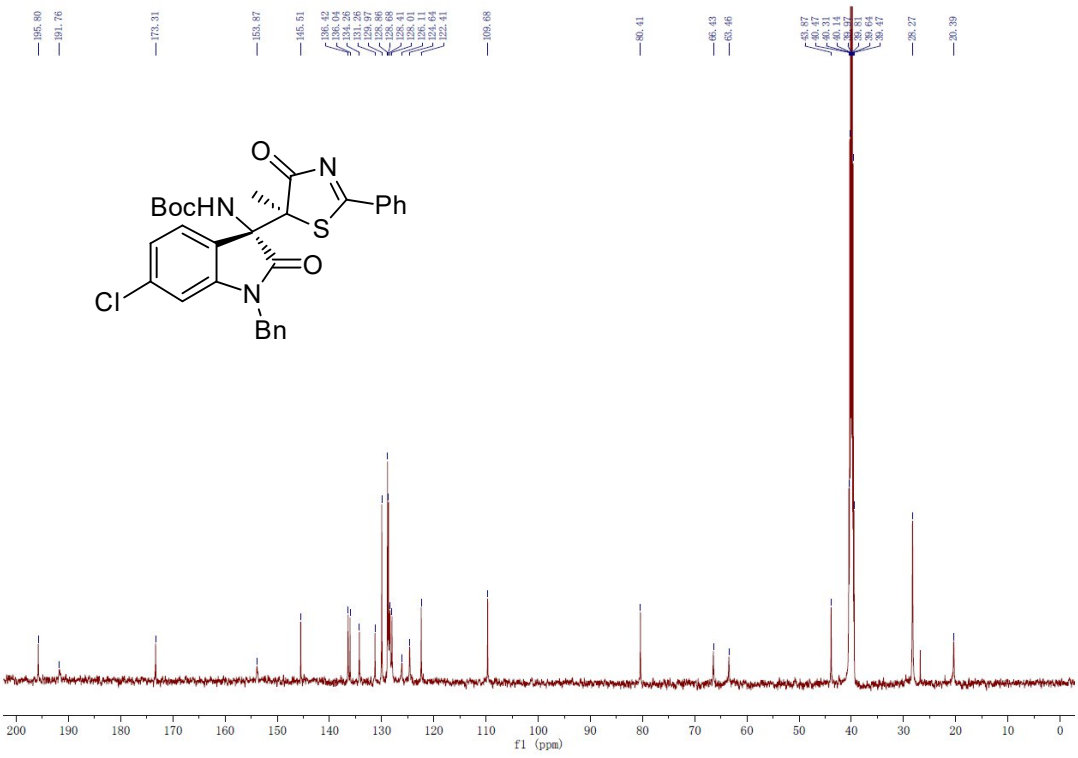
***tert*-butyl ((*S*)-1-benzyl-5-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ea)**



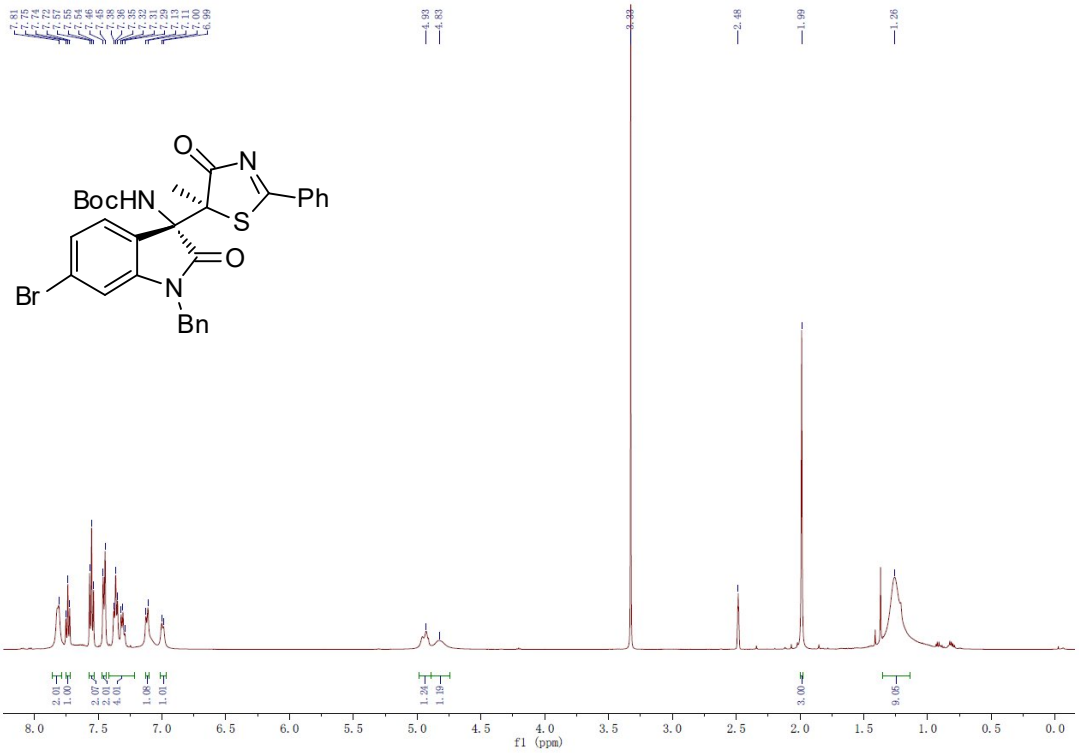


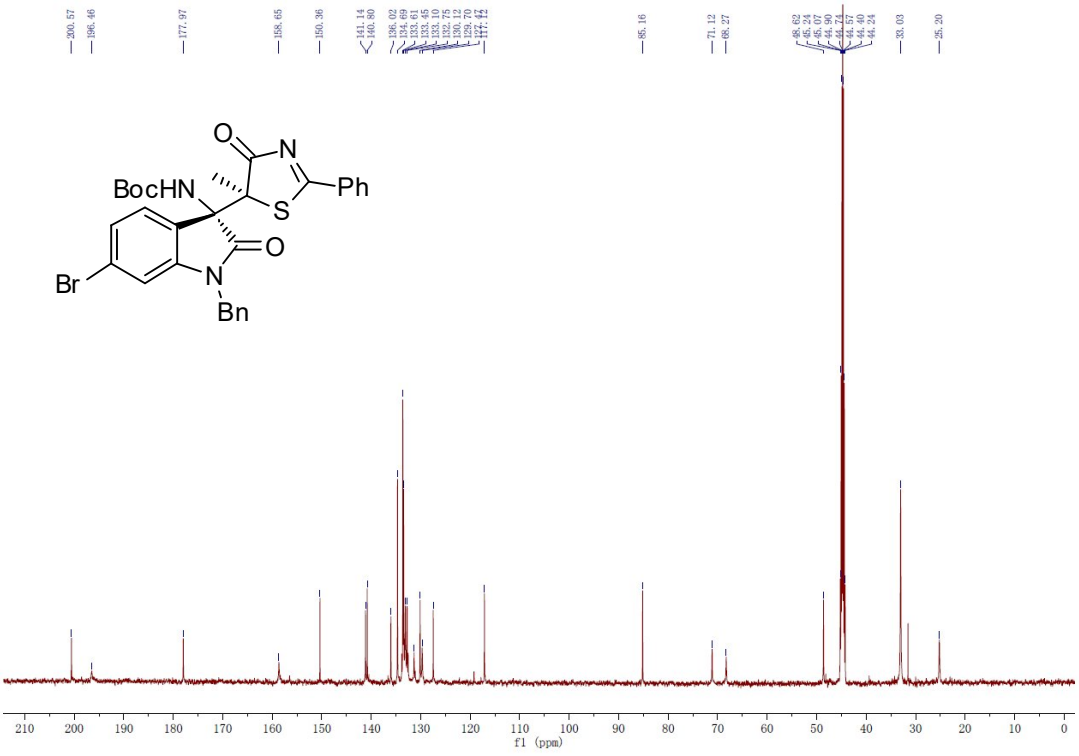
***tert*-butyl ((*S*)-1-benzyl-6-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3fa)**



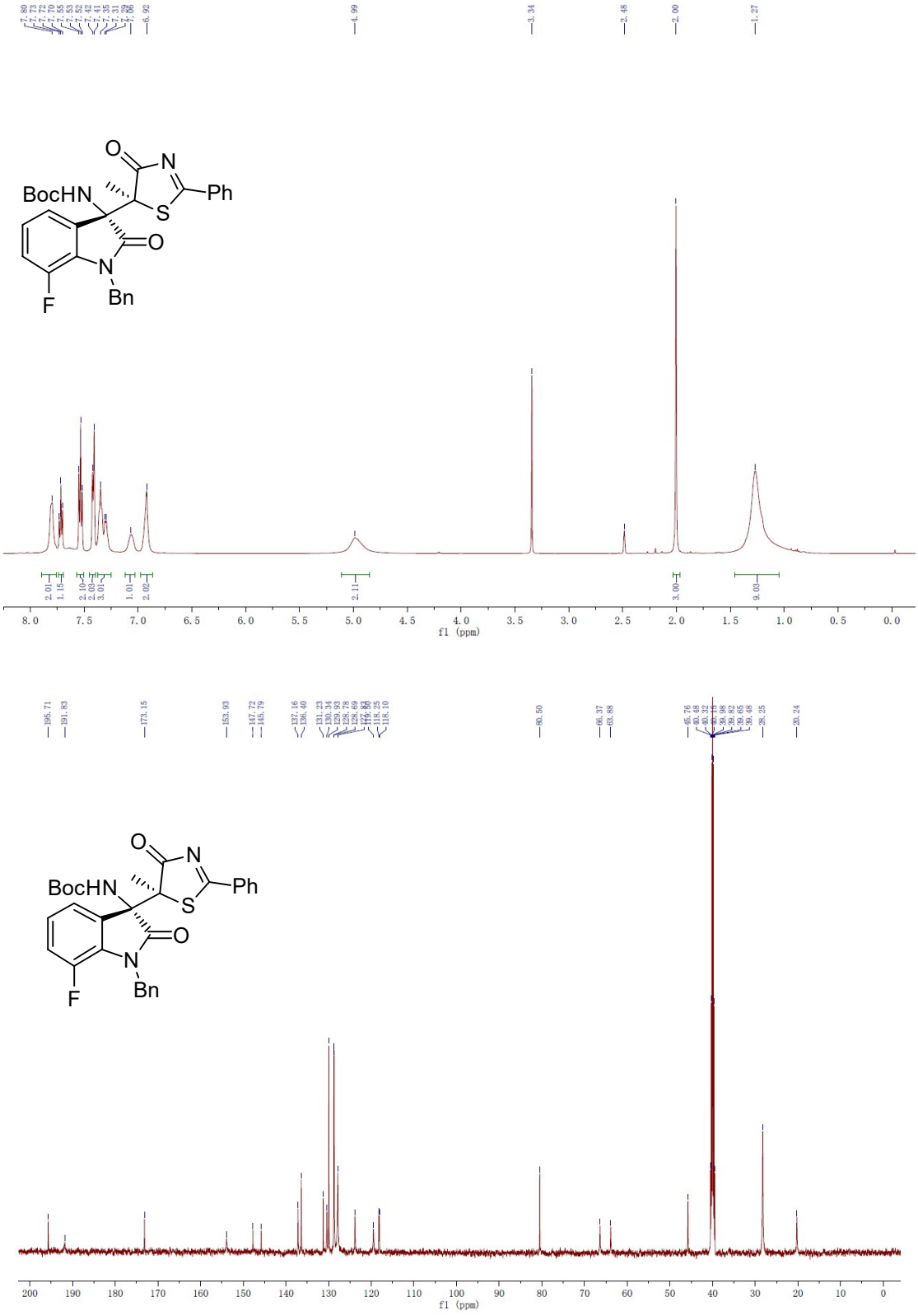


***tert*-butyl ((*S*)-1-benzyl-6-bromo-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ga)**

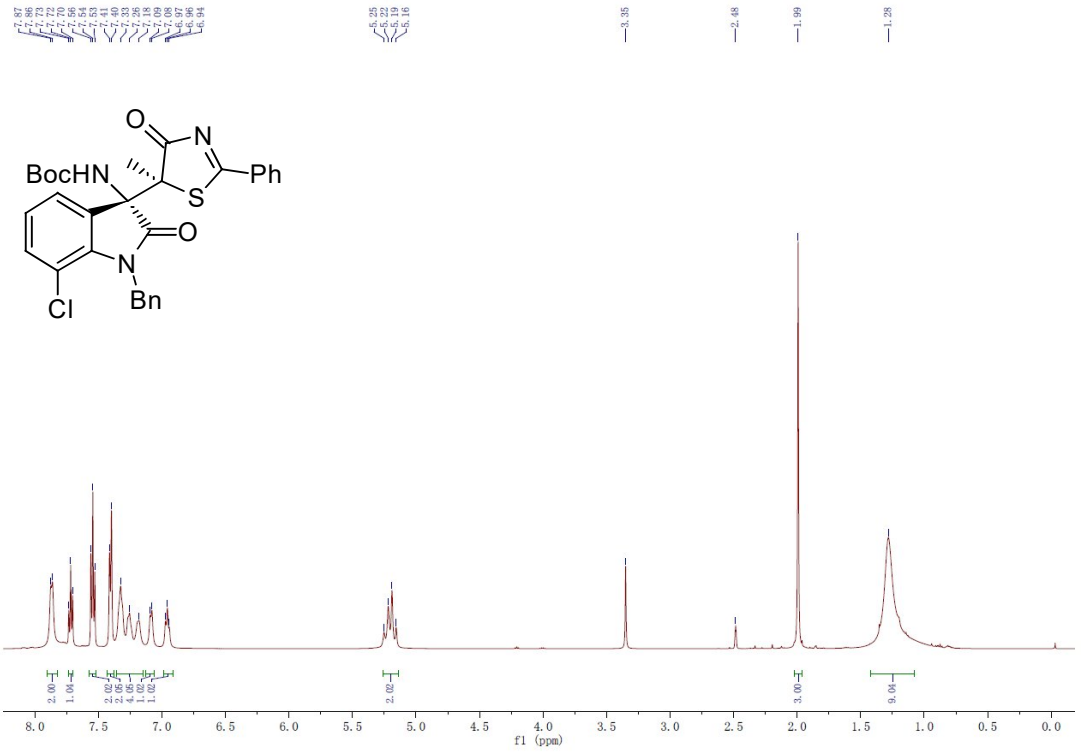


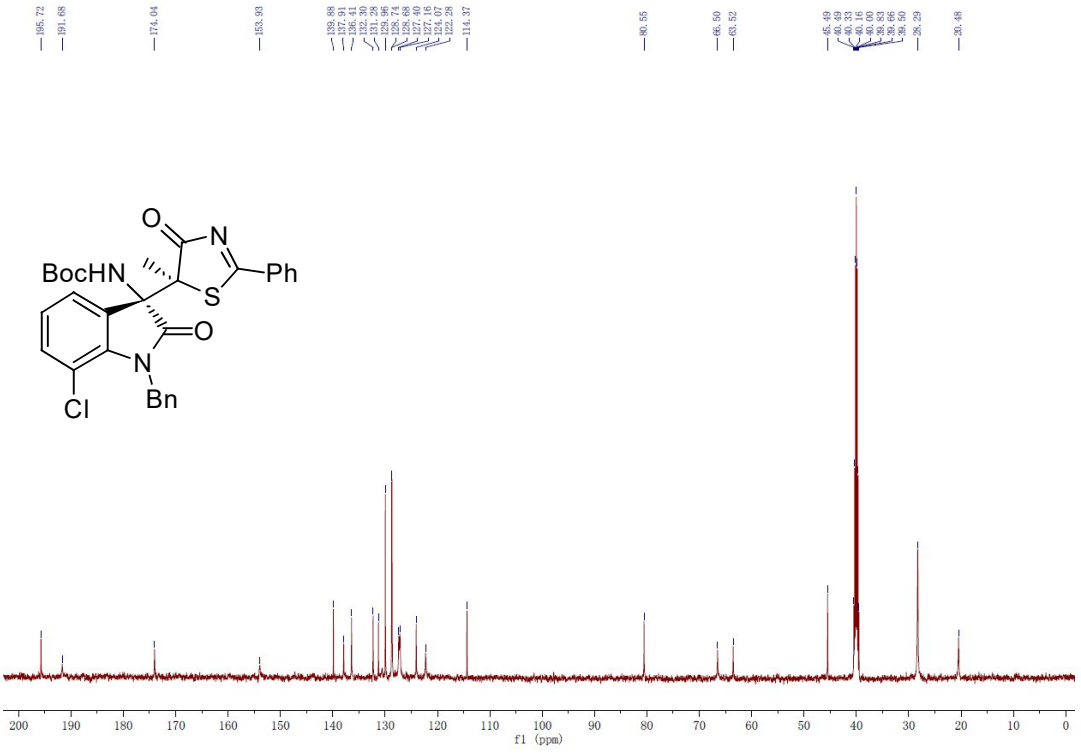


***tert*-butyl ((*S*)-1-benzyl-7-fluoro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ha)**

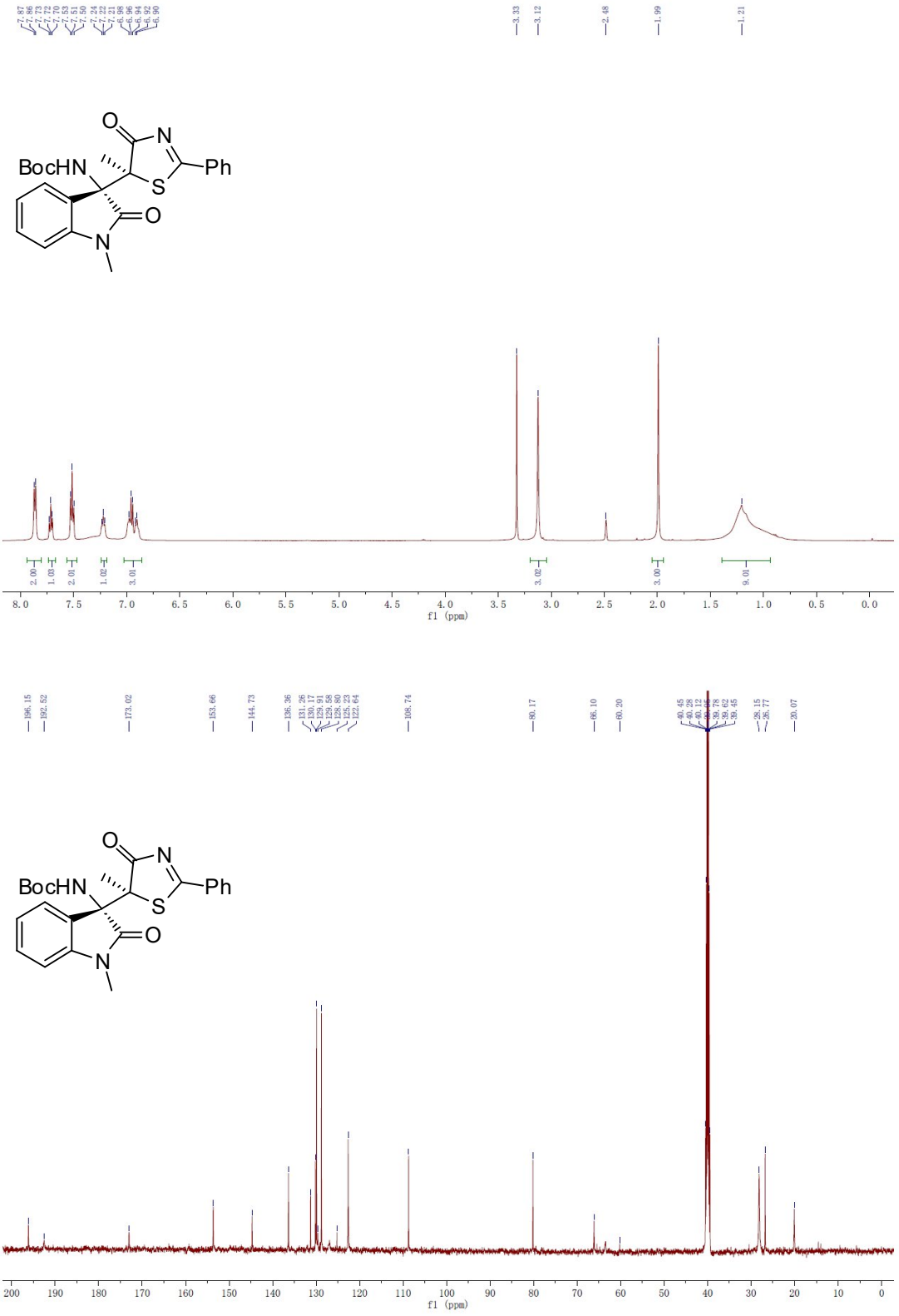


***tert*-butyl ((*S*)-1-benzyl-7-chloro-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ia)**

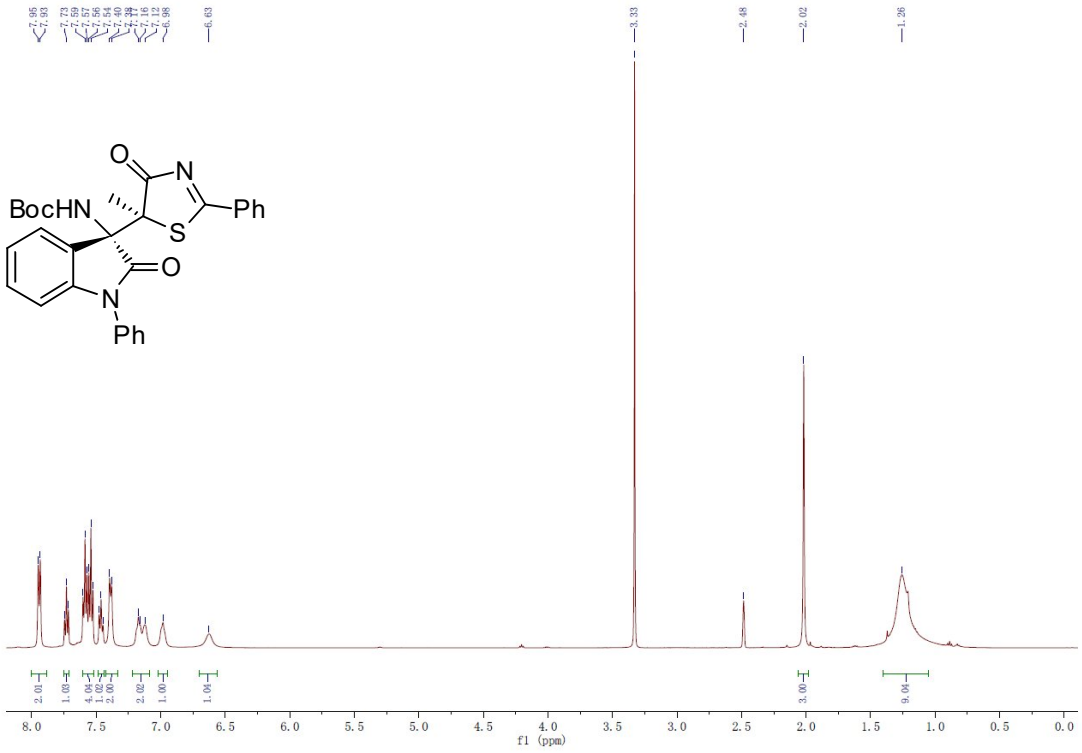


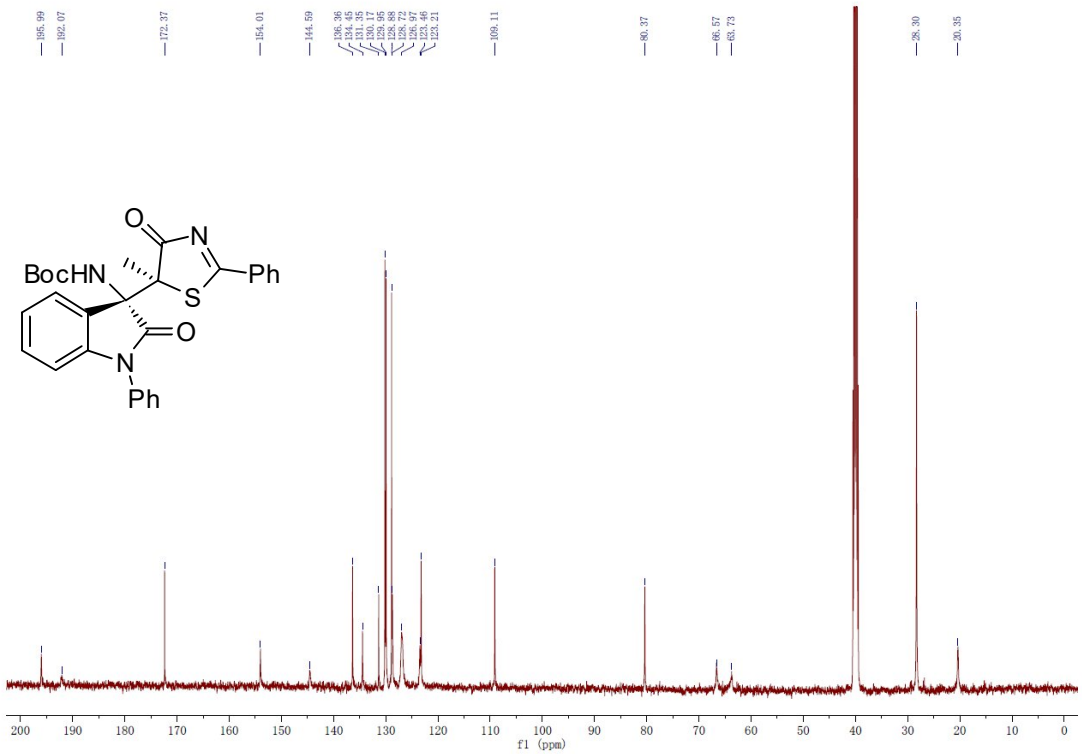


***tert*-butyl ((*S*)-1-methyl-3-((*S*)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ja)**

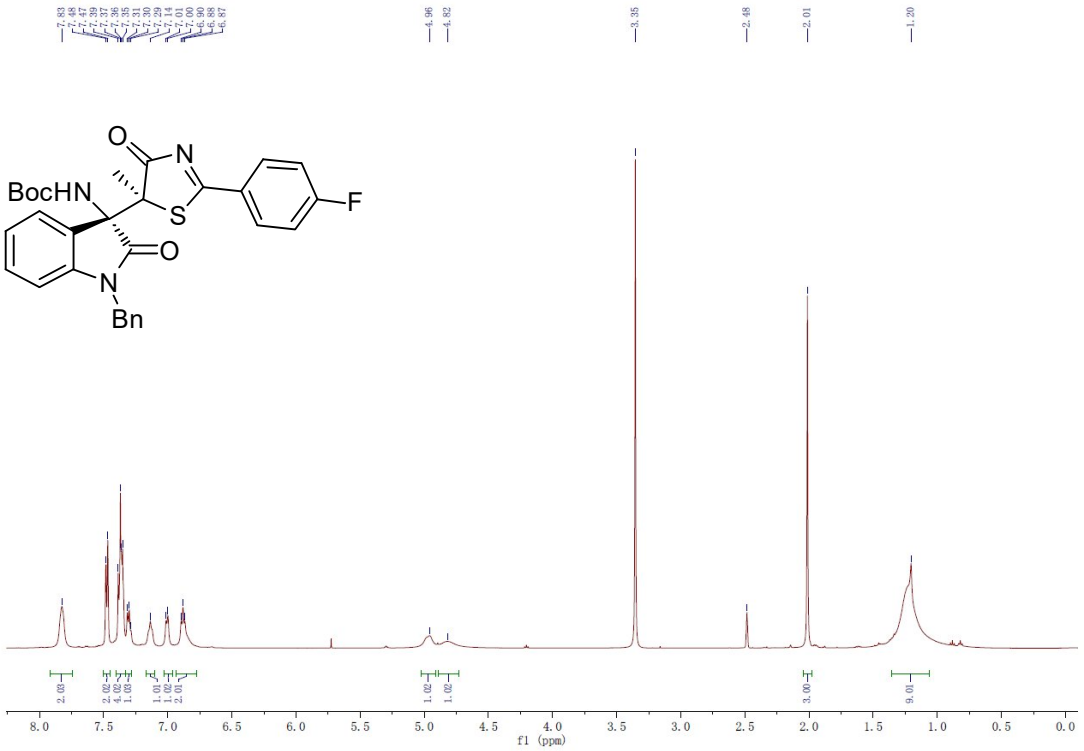


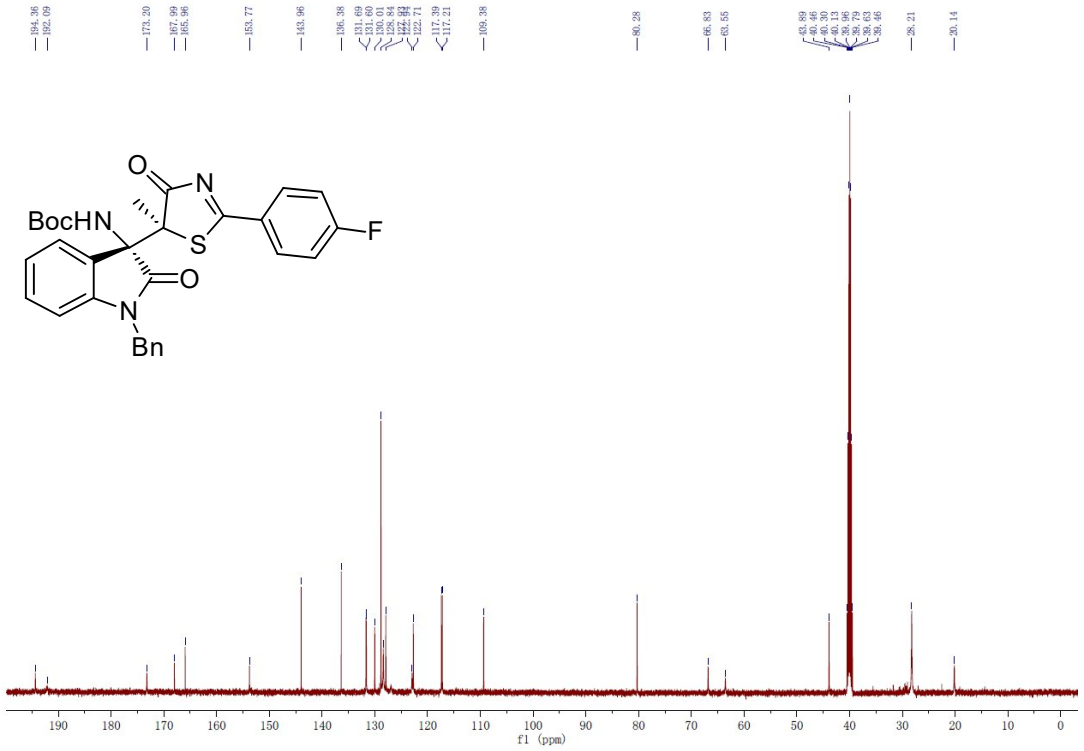
tert-butyl ((_S_)-3-((_S_)-5-methyl-4-oxo-2-phenyl-4,5-dihydrothiazol-5-yl)-2-oxo-1-phenylindolin-3-yl)carbamate (3ka)



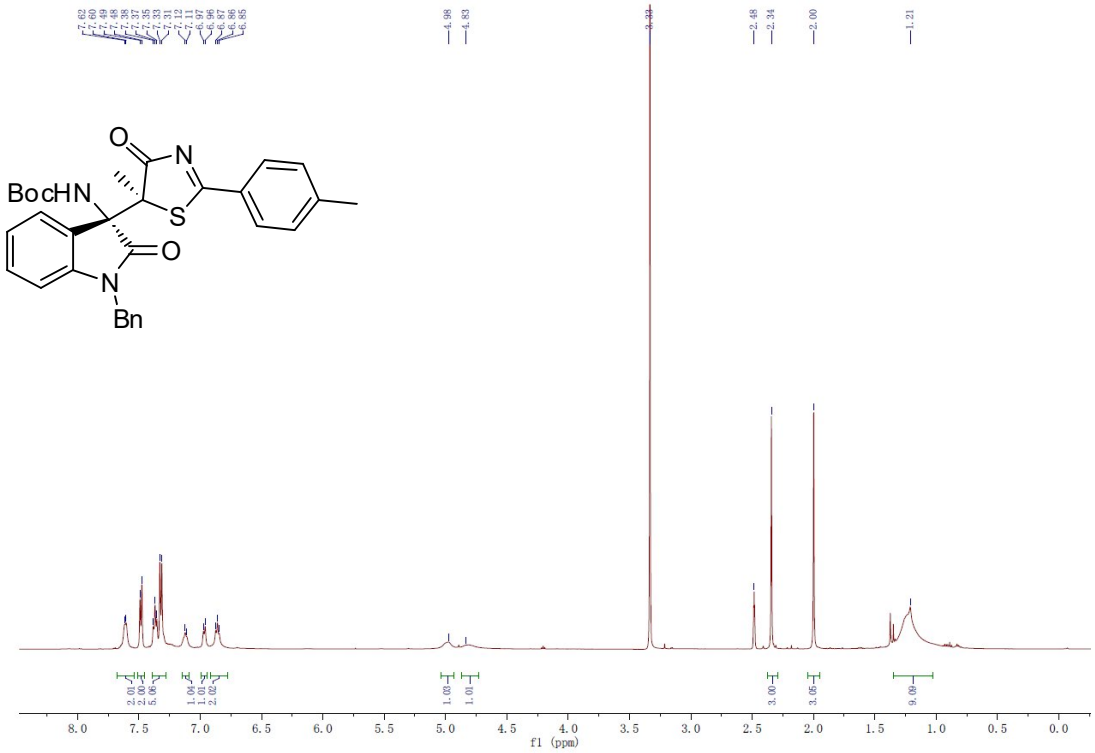


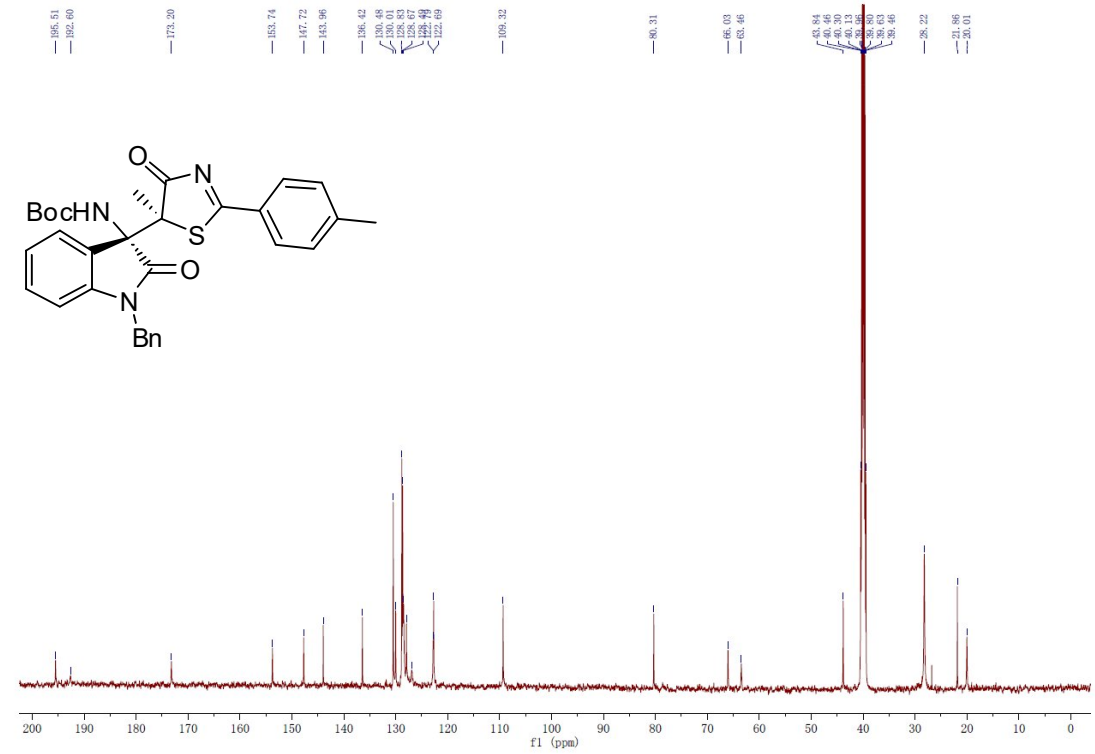
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ab)**



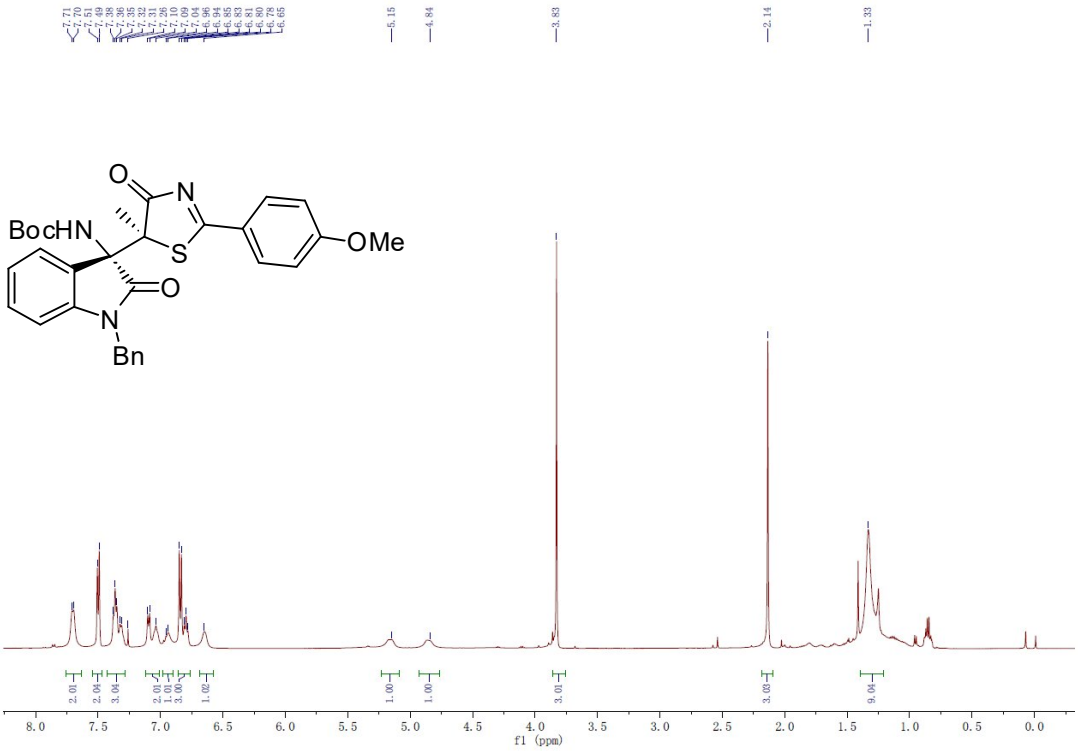


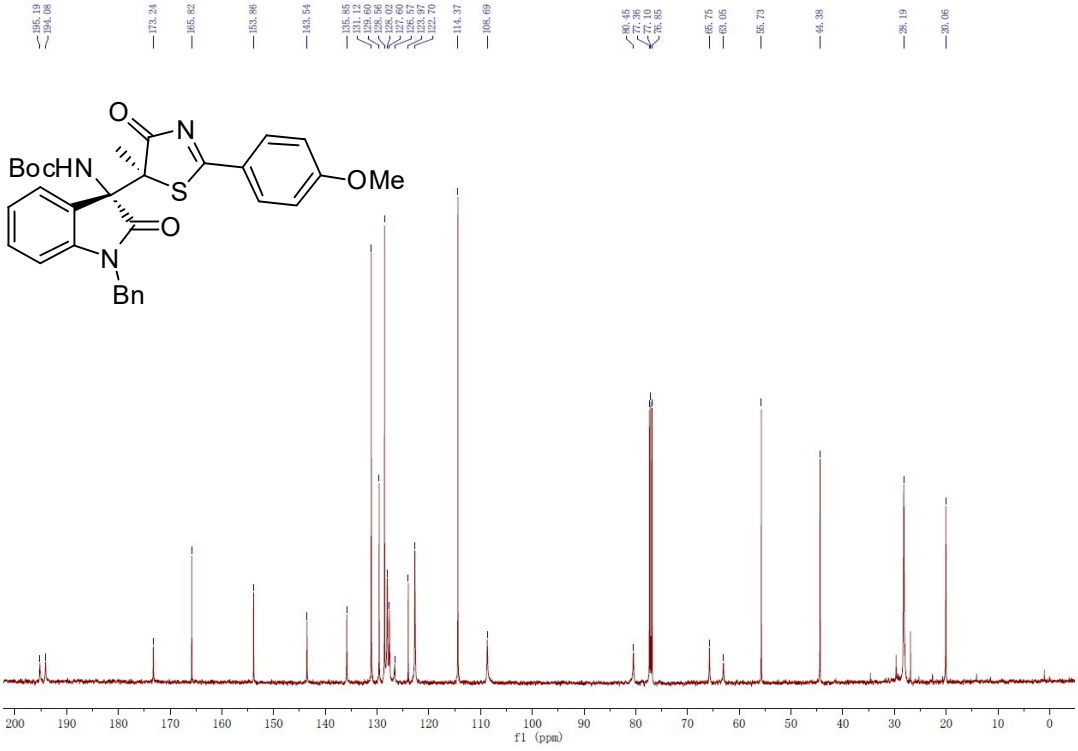
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(p-tolyl)-4,5-dihydrothiazol-5-yl) -2-oxoindolin-3-yl)carbamate (3ac)**



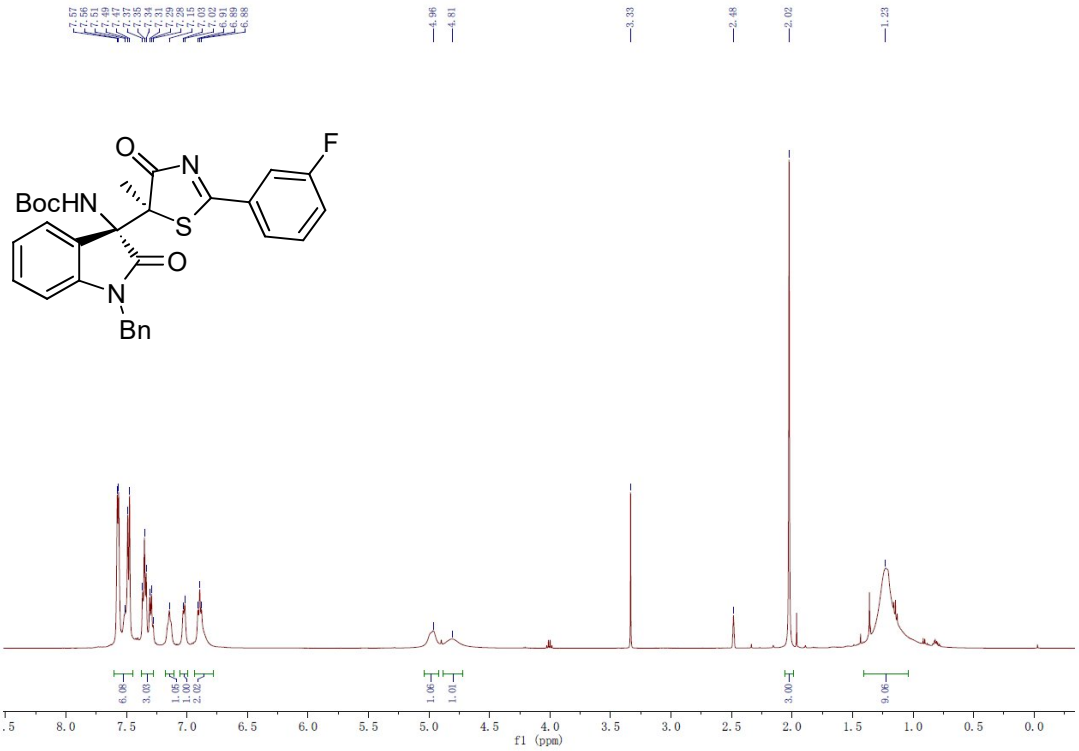


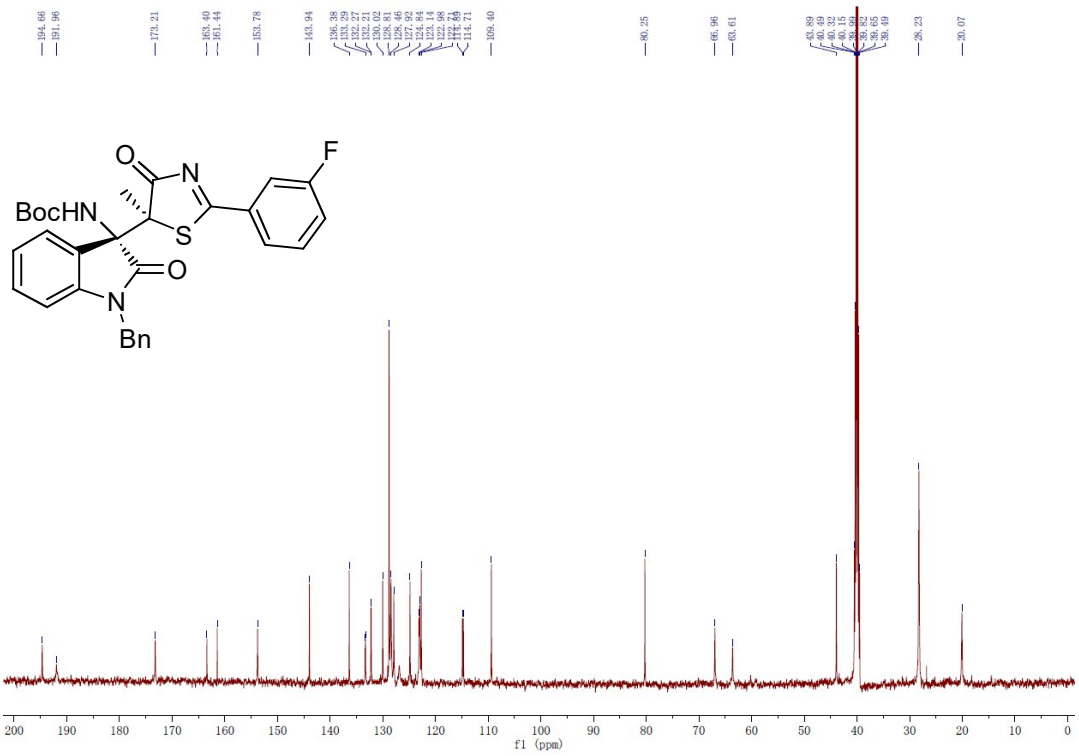
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(4-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ad)**



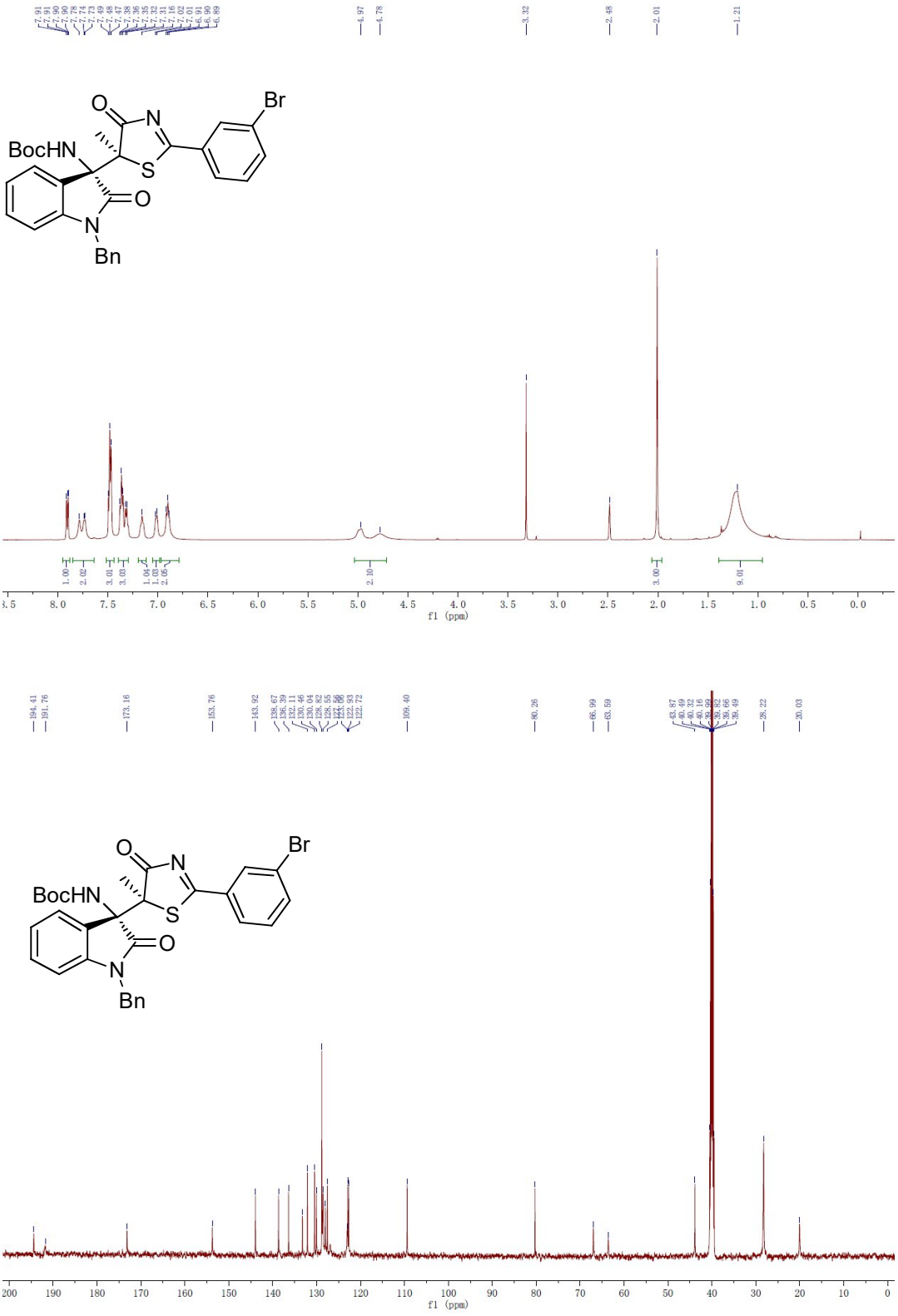


***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ae)**

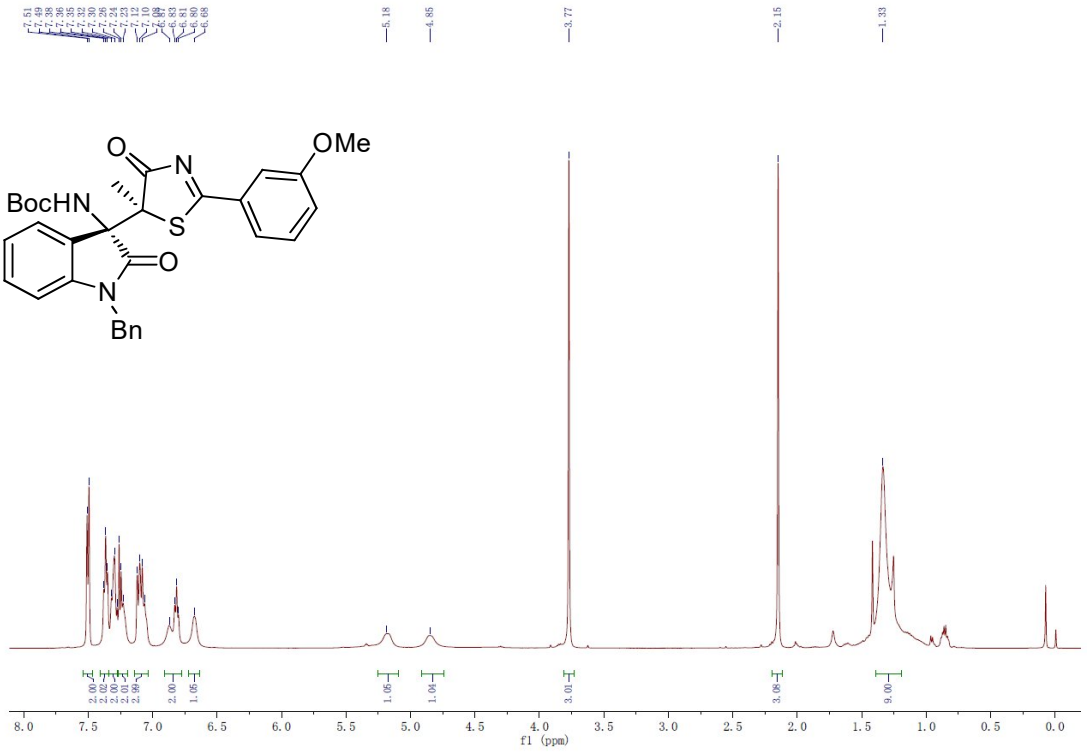


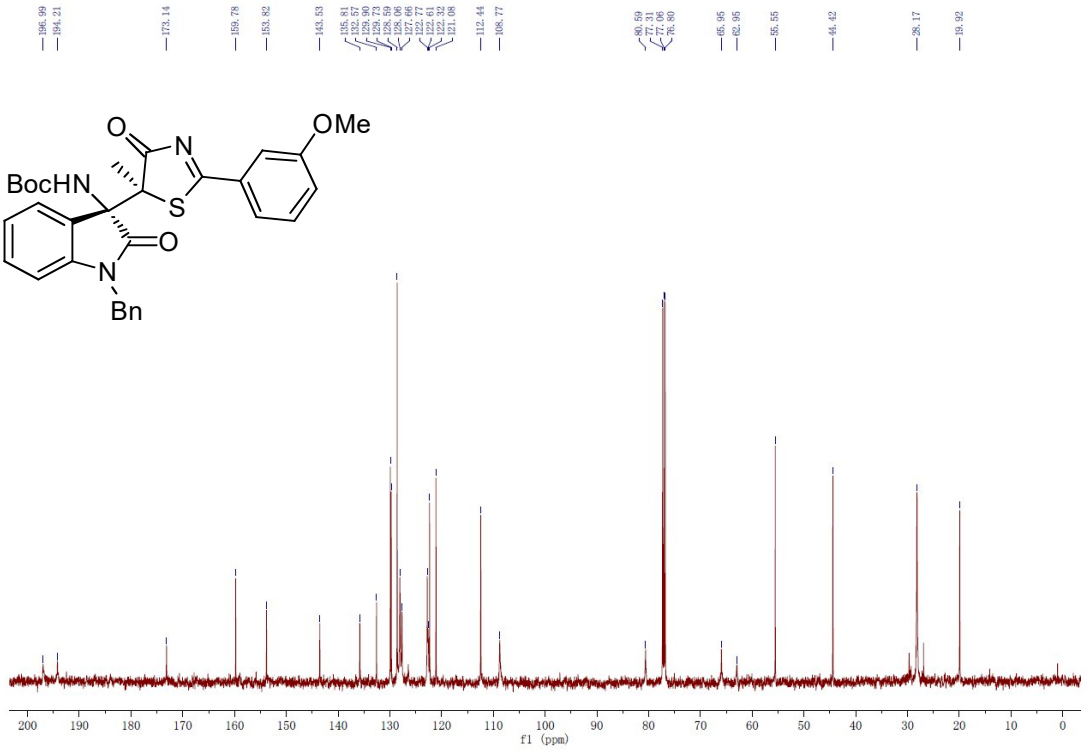


***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-bromophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3af)**

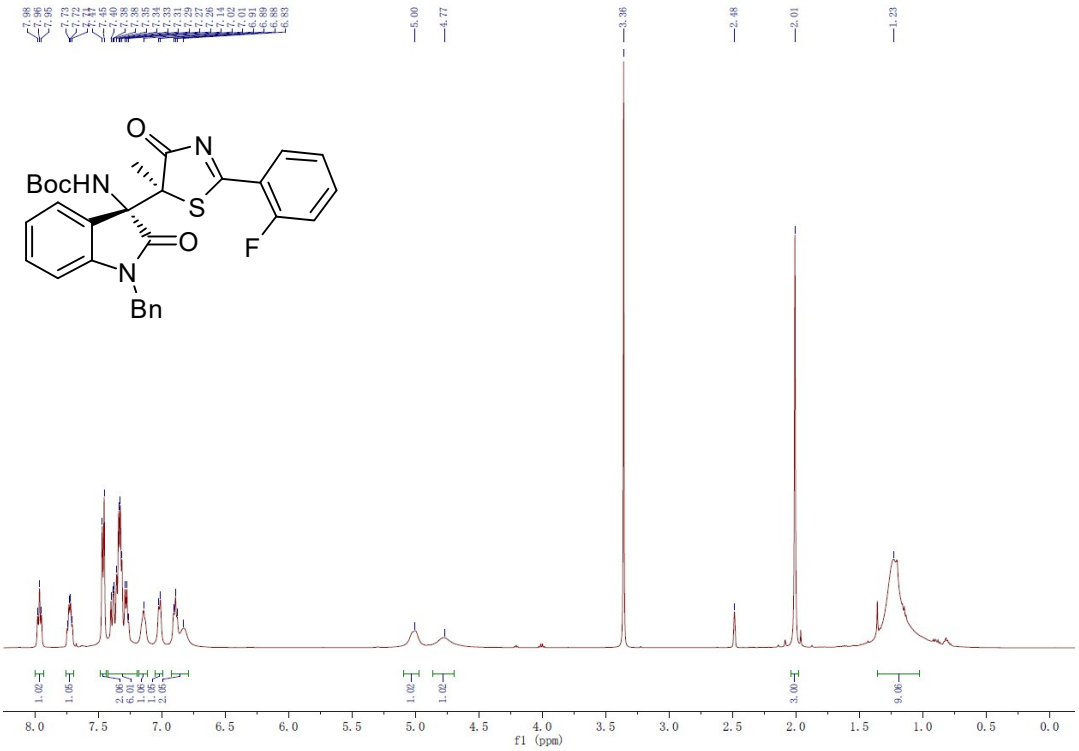


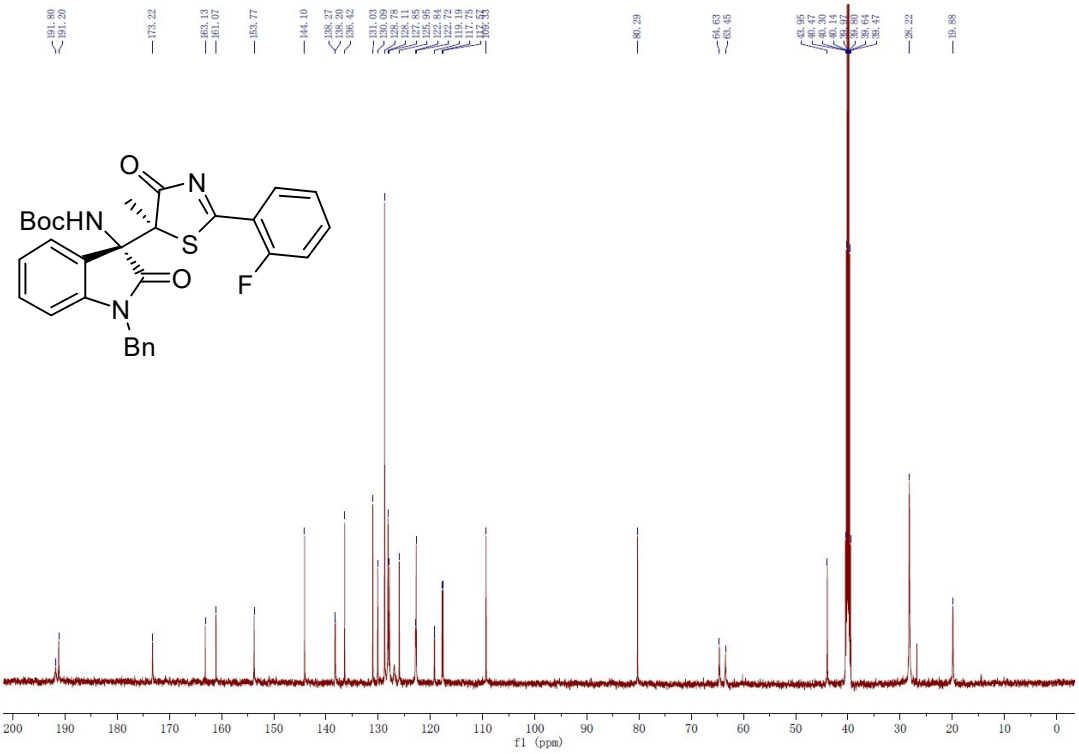
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(3-methoxyphenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ag)**



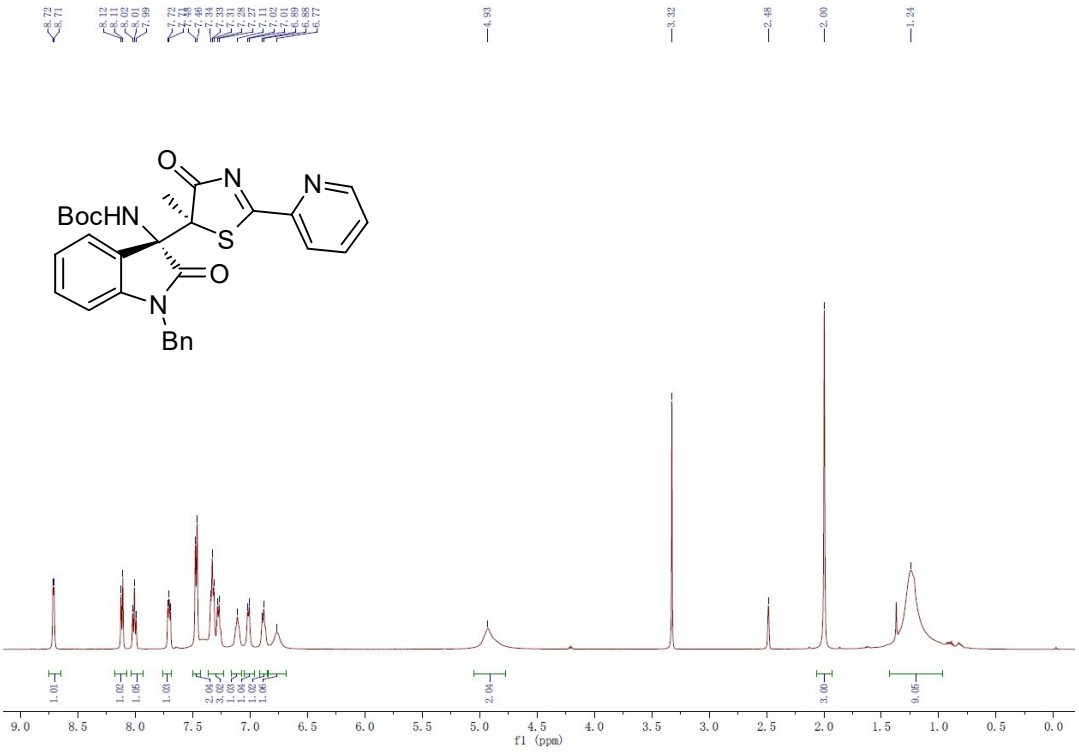


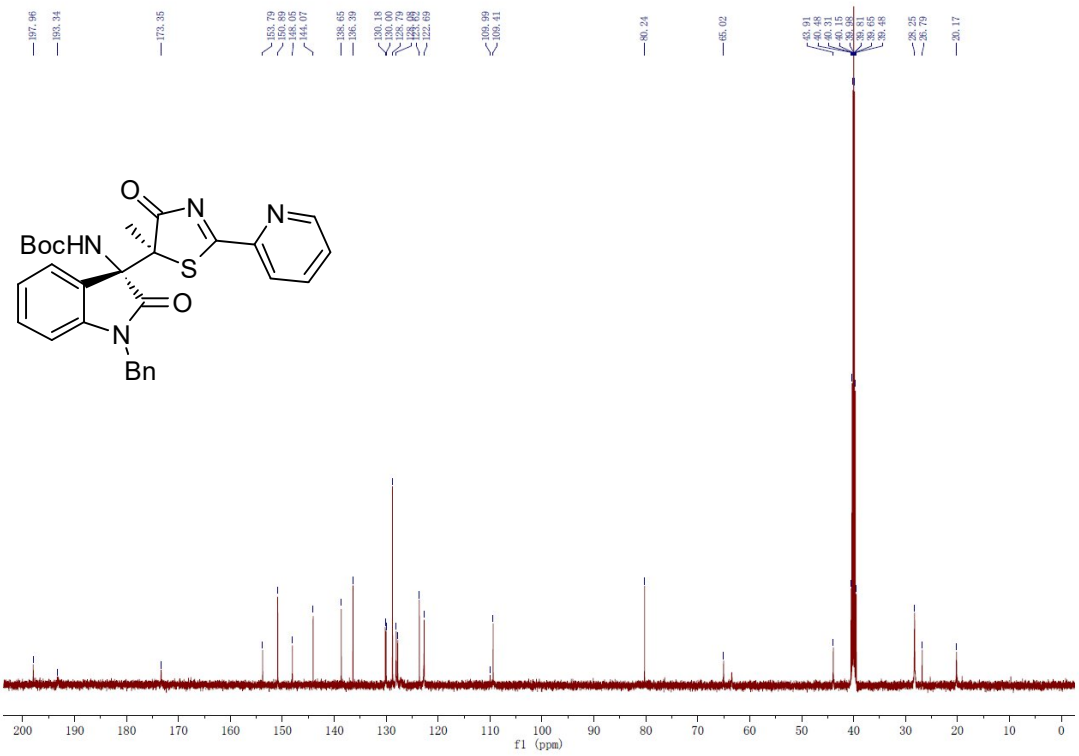
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-2-(2-fluorophenyl)-5-methyl-4-oxo-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ah)**



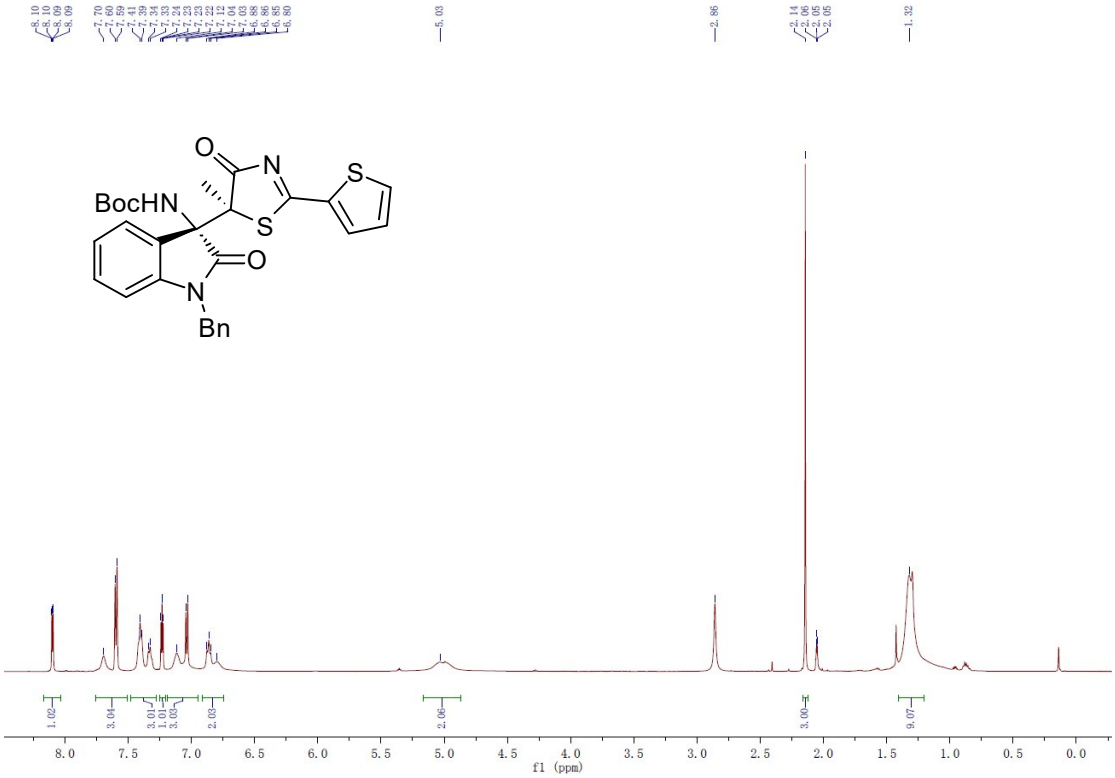


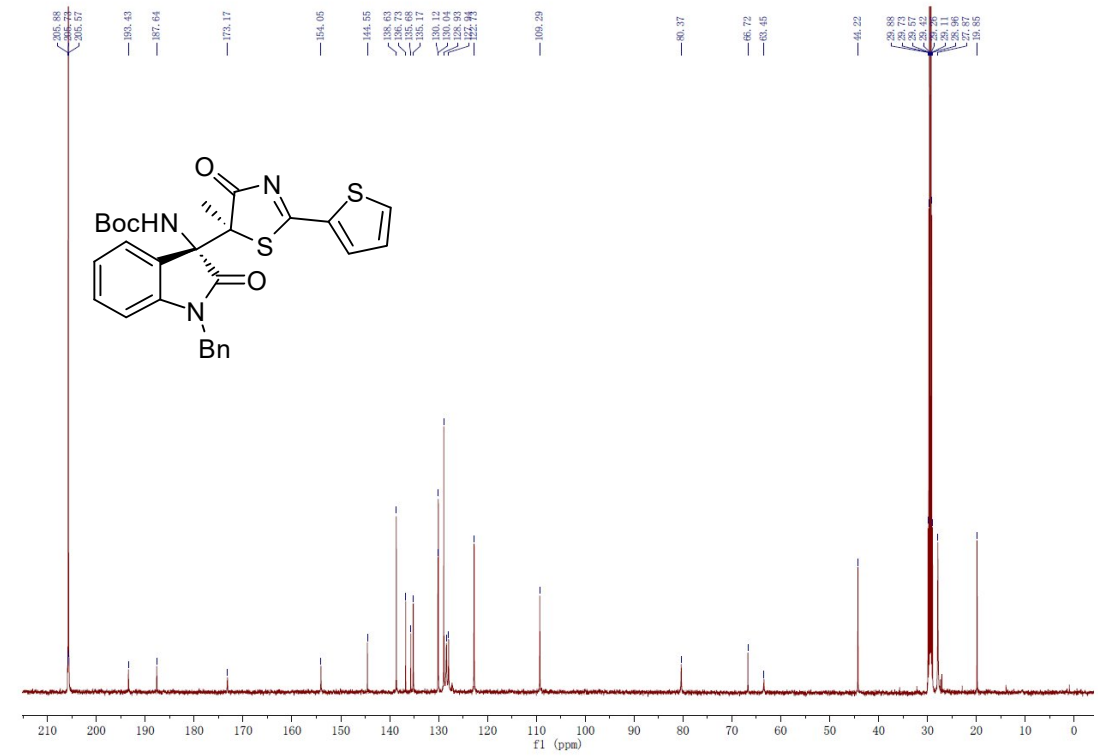
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol -5-yl)-2-oxoindolin-3-yl)carbamate (3ai)**



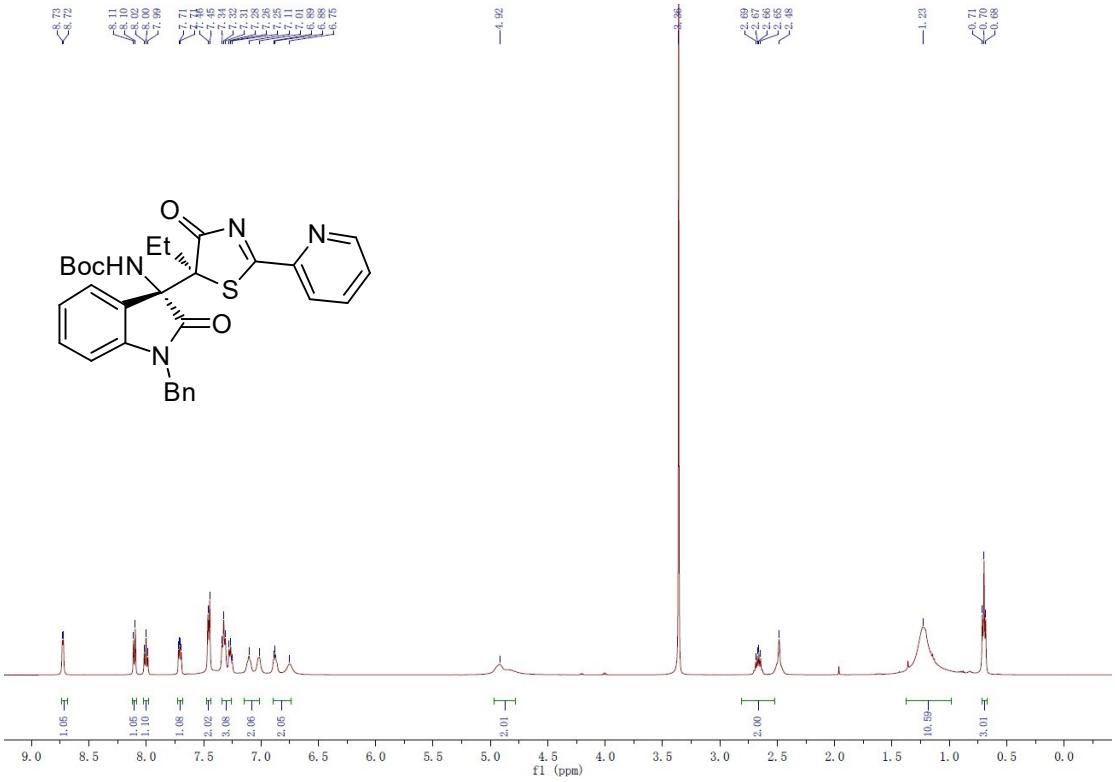


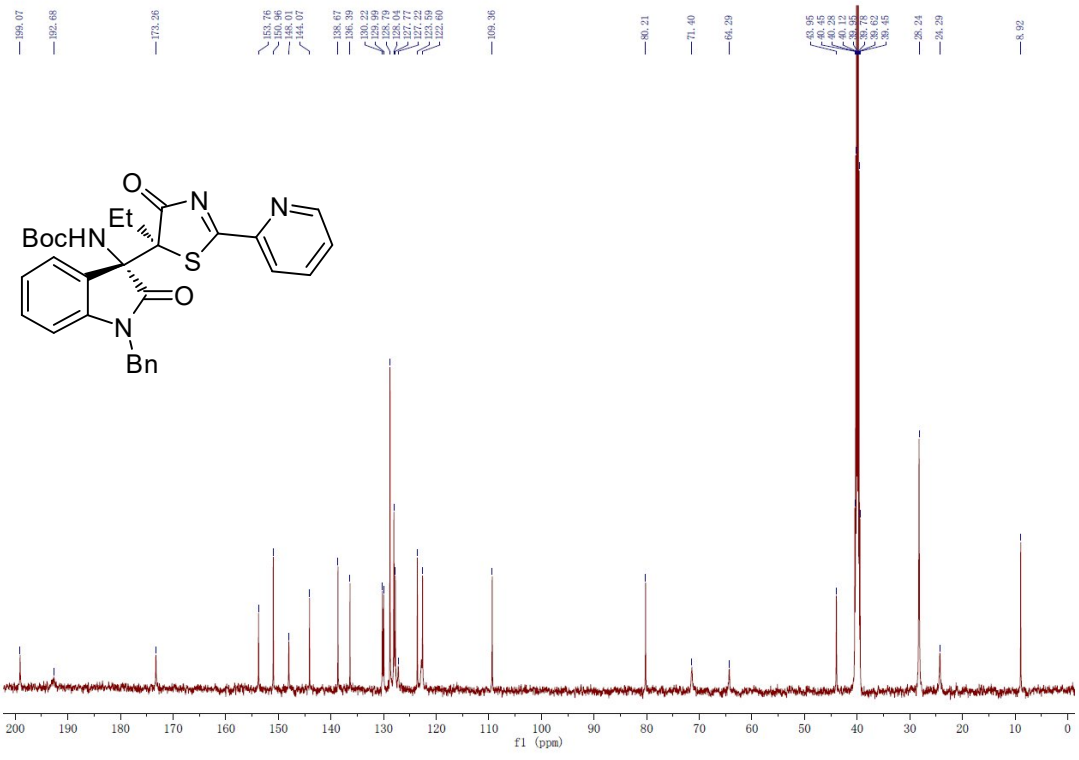
***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-methyl-4-oxo-2-(thiophen-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3aj)**





***tert*-butyl ((*S*)-1-benzyl-3-((*S*)-5-ethyl-4-oxo-2-(pyridin-2-yl)-4,5-dihydrothiazol-5-yl)-2-oxoindolin-3-yl)carbamate (3ak)**





H: X-ray Analysis

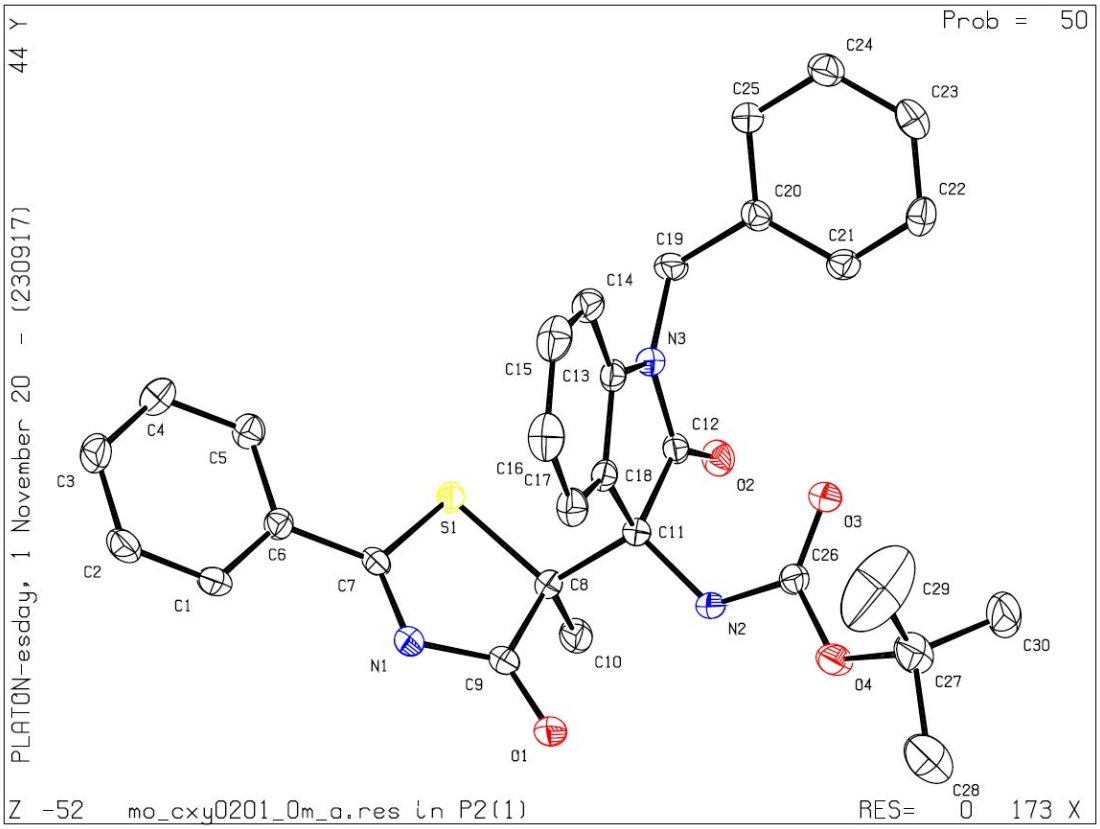


Table Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{30}H_{29}N_3O_4S$
Formula weight	527.62
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.6306(4)
b/Å	10.9636(6)
c/Å	14.5139(7)
α/°	90
β/°	90.644(2)
γ/°	90
Volume/Å^3	1373.25(12)
Z	2
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.158
F(000)	556.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.656 to 55.132
Index ranges	$-9 \le h \le 11$, $-14 \le k \le 14$, $-18 \le l \le 18$
Reflections collected	33514
Independent reflections	6318 [R_{int} = 0.0388, R_{sigma} = 0.0296]
Data/restraints/parameters	6318/1/348
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0767
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.0786
Largest diff. peak/hole / e Å^{-3}	0.34/-0.35
Flack parameter	-0.006(19)

I: Reference

1. Yan, W.; Wang, D.; Feng, J.; Li, P.; Zhao, D.; Wang, R. *Org. Lett.* **2012**, *14*, 2512.
2. (a) Diosdado, S.; Etxabe, J.; Izquierdo, J.; Landa, A.; Mielgo, A.; Olaizola, I.; López, R.; Palomo, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 11846; (b) Chen, W.; Hartwig, J. F. *J. Am. Chem. Soc*. **2014**, *136*, 377.