Enantioselective Construction of Chiral Thiazolidine: the asymmetric catalytic [3+2] Annulation of 1,4-dithiane-2,5-diol and ketimines

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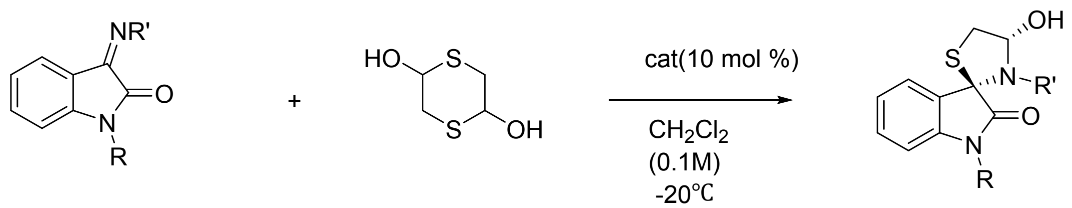
General Information

Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were carried out using silica gel. ^1H and ^{13}C spectra were recorded on a 400 MHz spectrometer (100 MHz for ^{13}C). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartert, m = multiplet, br = broad. 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). Column chromatography was performed on silica gel (300-400 mesh). HPLC analysis was performed on Agilent HPLC 1100 equipped with Daicel chiral AS-H column or OD-H column. High resolution mass spectra for all the new compounds were done by an LTQ-Orbitrap instrument (ESI) (Thermo Fisher Scientific, USA).
Catalysts were purchased from Daicel Chiral Technologies (China) Co., LTD. Substrates 1 were synthesized by following the published procedures. 2,5-Dihydroxy-1,4-dithiane, 2 was purchased from J&K Scientific Company.

Experimental Procedures

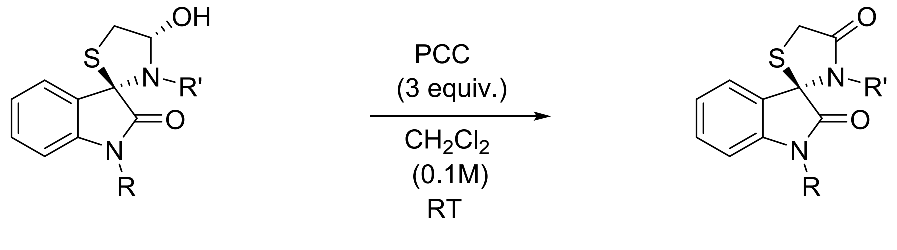
1.Genera experimental procedure for the synthesis, of indoline -3,2'-thiazolidine:



4 (1.0 equiv.) **5** (0.6 equiv.) **6**

To a 10-mL test-tube were sequentially added catalyst **E** (8.6 mg, 0.02 mmol), CH_2Cl_2 (2.0 mL), and the imine **4** (0.2 mmol). The mixture was cooled to -20℃ and stirred for 10 min. Dithiane **5** (18.24 mg, 0.12 mmol) was then added. The reaction mixture was stirred at -20℃ and monitored by TLC. Upon completion (2~10h), the residual was purified by silica gel flash chromatography (petroleum ether:ethyl acetate, 5:1) to afford the desired product **6**. The yield reported here is the major diasteromer. The pure diastereomers were obtained for characterization purpose.
The racemic examples were prepared by the catalysis of the mixture quinine and quindine. The ratio of diastereomer were determined based on the ^1HNMR analysis of the crude with $CDCl_3$ as solvent. Two diasteromers were separated from crude examples to obtain the ^1HNMR,$^{13}CNMR$ and HPLC of major diastereomer.

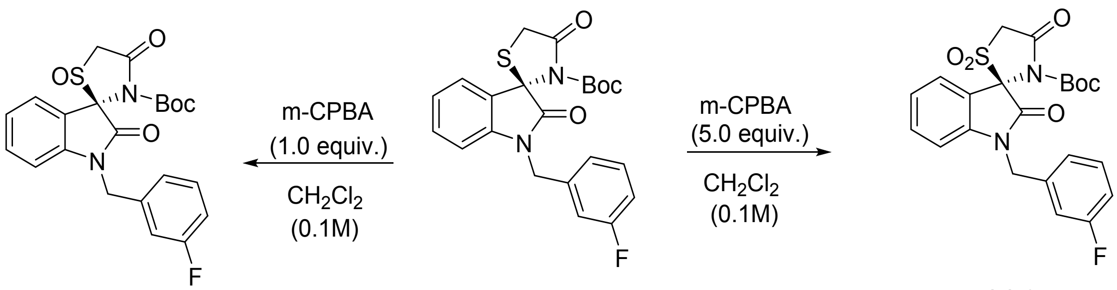
2.Prepare 2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate 7.[1]



6 **7**

To a solution of **6** (86 mg, 0.2 mmol) in CH_2Cl_2 (1.0 mL) was added pyridinium chlorochromate (129 mg, 0.6 mmol) at room temperature . The solution was allowed to stir overnight at room temperature. The reaction mixture was then filtered through celite, washed thoroughly with EtOAc, and concentrated. The crude material was purified by silica gel column chromatography (petroleum ether:ethyl acetate, 5:1) to give product **7** as a white solid (yield:95%).

Oxidation of tert-butyl 1-(3-fluorobenzyl)-2,4'-dioxospiro[indoline-3,2'-thiazo lidine]-3'-carboxylate into sulfoxide 8 and sulfones (+)-3[2]:



8 **7p** **(+)-3**

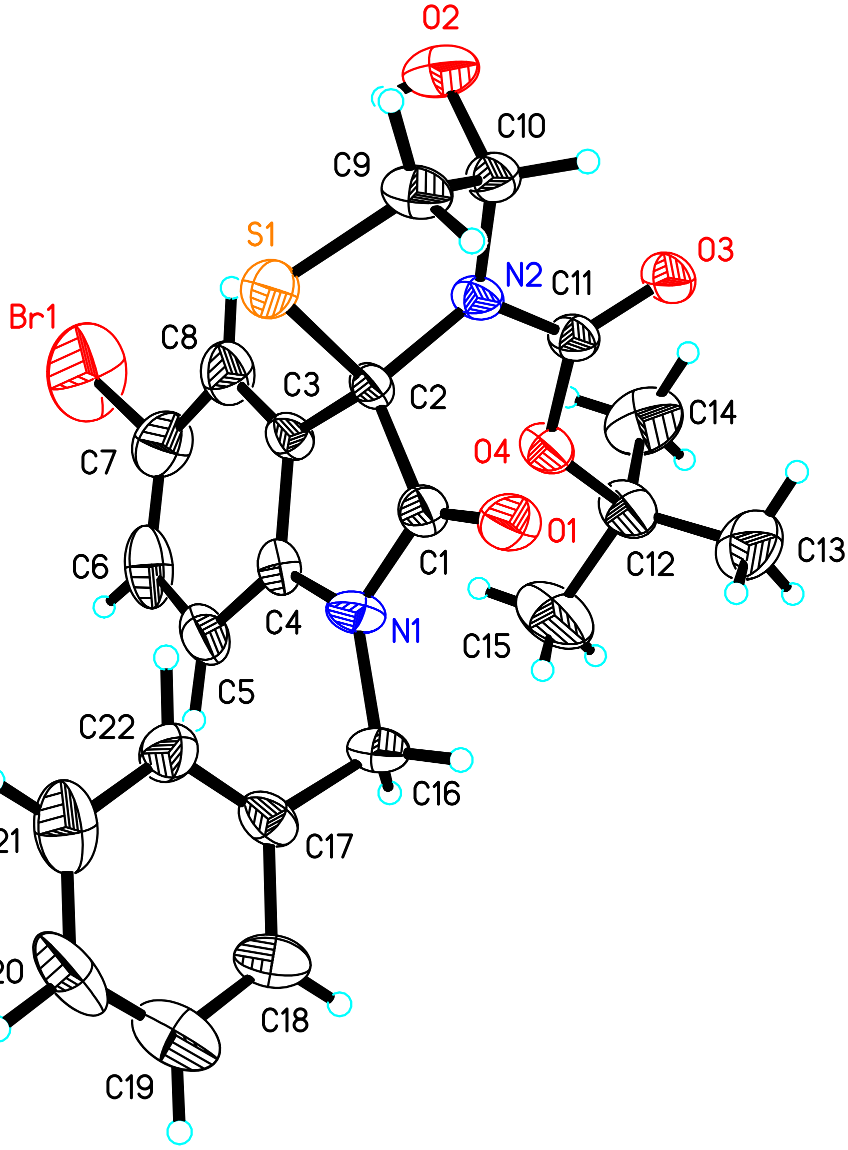
8 (sulfoxide): To a cooled (0 °C) solution of the sulfide **7p** (0.1 mmol,42mg) in 2 mL of CH_2Cl_2 was added m-CPBA (19 mg, 0.11 mmol, 1.1 equiv.). The mixture was stirred for 0.5 h until the reaction was completed at 0°C (minitored by TLC). The reaction mixture was diluted with 15 mL of EtOAc, washed with 15% $NaHSO_3$ solution (2×20 mL), saturated $NaHCO_3$ solution (2×20 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether:ethyl acetate, 3:1) to provide the corresponding sulfoxide **8** as an white solid (yield:90%).

(+)-3 (sulfone):To a cooled (0 °C) solution of the sulfide **7p** (0.1 mmol,42mg) in 2 mL of CH_2Cl_2 was added m-CPBA (86 mg, 0. 5 mmol, 5 equiv.). The resulting solution was allowed to reach room temperature and stirred for 48 h. The reaction mixture was diluted with 15 mL of EtOAc, washed with 15% $NaHSO_3$ solution (2×20 mL), saturated $NaHCO_3$ solution (2×20 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether:ethyl acetate, 3:1) to provide the corresponding sulfone as an white solid (yield:92%).

References

1. M. G. Nilson and R. L. Funk, *Org. Lett.*, 2006, **8** , 3833.
2. V. V. Vintonyak, K. Warburg, B. Over, K. Hübel, D. Rauh and H. Waldmann, *Tetrahedron*, 2011, **67**, 6713.

X-ray Crystal Structure of 6e



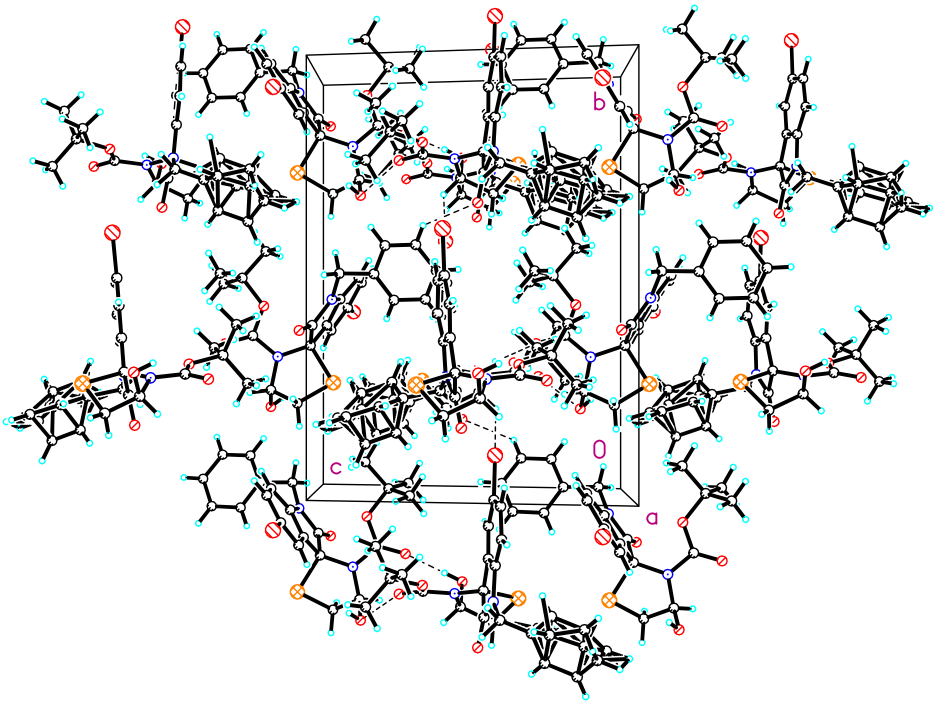


Table 1. Crystal data and structure refinement for cd15013.

Identification code	cd15013	
Empirical formula	C22 H23 Br N2 O4 S	
Formula weight	491.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.3517(8) Å	α= 90°.
	b = 17.5995(15) Å	β= 103.504(2)°.
	c = 13.2555(11) Å	γ = 90°.
Volume	2348.2(3) Å^3	
Z	4	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	1.868 mm^{-1}	
F(000)	1008	
Crystal size	0.180 x 0.160 x 0.110 mm^3	
Theta range for data collection	1.958 to 25.492°.	
Index ranges	-11<=h<=12, -21<=k<=21, -14<=l<=16	
Reflections collected	13809	

Independent reflections	8545 [R(int) = 0.0589]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8545 / 82 / 587
Goodness-of-fit on F^2	0.947
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1187
R indices (all data)	R1 = 0.1506, wR2 = 0.1528
Absolute structure parameter	0.037(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.332 and -0.224 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for cd15013. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	9917(1)	9313(2)	1048(2)	154(1)
Br(2)	7102(1)	10978(1)	4213(1)	101(1)
S(1)	4779(3)	7598(2)	603(2)	60(1)
S(2)	5764(3)	7648(2)	3469(2)	69(1)
N(1)	4030(8)	9560(5)	595(6)	51(2)
N(2)	4568(8)	8215(4)	-1213(6)	44(2)
N(3)	9257(8)	7793(5)	4286(7)	64(3)
N(4)	6550(7)	7774(5)	5471(6)	49(2)
O(1)	2380(7)	8827(4)	-373(6)	65(2)
O(2)	5396(8)	7009(4)	-1498(7)	78(2)
O(3)	4033(7)	8523(4)	-2919(6)	58(2)
O(4)	4565(7)	9417(4)	-1675(5)	58(2)
O(5)	8373(8)	6692(5)	4753(6)	70(2)
O(6)	4213(7)	7906(5)	5240(6)	74(2)
O(7)	6835(7)	7746(5)	7218(5)	67(2)
O(8)	8507(7)	8065(4)	6455(5)	64(2)
C(1)	3538(11)	8952(6)	-20(8)	48(3)
C(2)	4735(9)	8480(6)	-144(7)	43(2)
C(3)	5882(9)	8962(6)	337(8)	45(3)
C(4)	5419(10)	9581(6)	799(8)	49(3)
C(5)	6283(12)	10108(7)	1373(8)	69(3)
C(6)	7648(12)	10007(9)	1412(10)	82(4)
C(7)	8074(11)	9399(10)	933(11)	82(4)
C(8)	7225(11)	8845(8)	412(9)	70(3)
C(9)	3796(10)	7125(6)	-520(8)	59(3)
C(10)	4273(11)	7425(6)	-1417(8)	53(3)
C(11)	4366(10)	8711(6)	-2021(9)	47(3)
C(12)	4451(14)	10086(6)	-2379(9)	73(4)
C(13)	3035(15)	10173(8)	-2990(11)	99(4)
C(14)	5424(14)	9962(8)	-3083(12)	104(5)
C(15)	4878(19)	10722(7)	-1631(11)	126(6)
C(16)	3205(10)	10153(6)	874(8)	58(3)
C(17)	3117(9)	10135(7)	1984(9)	54(3)

C(18)	2543(11)	10772(6)	2351(11)	73(4)
C(19)	2376(16)	10781(10)	3321(14)	100(5)
C(20)	2753(14)	10191(13)	3960(11)	98(5)
C(21)	3296(11)	9544(10)	3610(11)	90(4)
C(22)	3477(10)	9530(8)	2610(9)	68(3)
C(23)	8316(11)	7369(8)	4564(9)	60(3)
C(24)	7099(9)	7892(6)	4575(8)	51(3)
C(25)	7653(10)	8651(6)	4425(8)	50(3)
C(26)	8891(10)	8574(7)	4225(9)	63(3)
C(27)	9609(11)	9188(7)	4036(9)	73(3)
C(28)	9084(12)	9903(7)	4063(10)	70(3)
C(29)	7834(12)	9989(6)	4255(9)	65(3)
C(30)	7091(10)	9368(8)	4418(8)	62(3)
C(31)	5071(11)	7016(6)	4246(8)	65(3)
C(32)	5259(10)	7385(6)	5291(8)	54(3)
C(33)	7289(11)	7854(6)	6458(9)	53(3)
C(34)	9500(11)	8264(9)	7424(10)	74(4)
C(35)	9757(16)	7628(12)	8176(15)	164(9)
C(36)	8997(14)	8949(10)	7894(14)	143(8)
C(37)	10712(12)	8431(12)	7037(12)	143(8)
C(38)	10474(14)	7473(9)	4103(13)	91(5)
C(39)	10660(20)	7220(12)	3163(14)	153(6)
C(40)	11374(19)	7651(10)	2604(16)	157(6)
C(41)	11530(19)	7394(11)	1647(15)	162(6)
C(42)	10970(20)	6707(12)	1251(14)	164(6)
C(43)	10250(20)	6277(10)	1811(19)	160(6)
C(44)	10100(20)	6533(12)	2767(18)	156(6)
C(39')	10270(40)	7300(20)	2972(17)	141(9)
C(40')	11460(30)	7250(30)	2660(30)	143(9)
C(41')	11460(30)	7030(30)	1650(30)	146(9)
C(42')	10270(30)	6850(20)	960(19)	146(9)
C(43')	9080(30)	6903(18)	1273(17)	145(8)
C(44')	9080(30)	7128(18)	2279(19)	143(8)

Table 3. Bond lengths [Å] and angles [°] for cd15013.

Br(1)-C(7)	1.884(11)
Br(2)-C(29)	1.895(11)
S(1)-C(9)	1.798(11)
S(1)-C(2)	1.837(10)
S(2)-C(31)	1.779(11)
S(2)-C(24)	1.816(10)
N(1)-C(1)	1.370(12)
N(1)-C(4)	1.400(12)
N(1)-C(16)	1.450(12)
N(2)-C(11)	1.360(12)
N(2)-C(10)	1.435(13)
N(2)-C(2)	1.463(12)
N(3)-C(23)	1.345(13)
N(3)-C(26)	1.424(14)
N(3)-C(38)	1.451(15)
N(4)-C(33)	1.360(13)
N(4)-C(24)	1.446(11)
N(4)-C(32)	1.470(12)
O(1)-C(1)	1.201(11)
O(2)-C(10)	1.399(11)
O(2)-H(2)	0.8200
O(3)-C(11)	1.206(12)
O(4)-C(11)	1.323(12)
O(4)-C(12)	1.491(12)
O(5)-C(23)	1.216(13)
O(6)-C(32)	1.408(12)
O(6)-H(6)	0.8200
O(7)-C(33)	1.222(11)
O(8)-C(33)	1.316(11)
O(8)-C(34)	1.487(13)
C(1)-C(2)	1.531(13)
C(2)-C(3)	1.476(13)
C(3)-C(8)	1.385(14)
C(3)-C(4)	1.389(13)
C(4)-C(5)	1.386(14)
C(5)-C(6)	1.413(16)

C(5)-H(5)	0.9300
C(6)-C(7)	1.370(18)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.384(18)
C(8)-H(8)	0.9300
C(9)-C(10)	1.488(13)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10)	0.9800
C(12)-C(15)	1.493(17)
C(12)-C(13)	1.508(17)
C(12)-C(14)	1.540(17)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(17)	1.496(14)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(22)	1.349(15)
C(17)-C(18)	1.407(15)
C(18)-C(19)	1.336(17)
C(18)-H(18)	0.9300
C(19)-C(20)	1.34(2)
C(19)-H(19)	0.9300
C(20)-C(21)	1.40(2)
C(20)-H(20)	0.9300
C(21)-C(22)	1.381(16)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-C(24)	1.564(15)
C(24)-C(25)	1.484(14)
C(25)-C(26)	1.375(13)

C(25)-C(30)	1.389(15)
C(26)-C(27)	1.367(14)
C(27)-C(28)	1.376(15)
C(27)-H(27)	0.9300
C(28)-C(29)	1.384(15)
C(28)-H(28)	0.9300
C(29)-C(30)	1.381(15)
C(30)-H(30)	0.9300
C(31)-C(32)	1.501(13)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32)	0.9800
C(34)-C(35)	1.48(2)
C(34)-C(37)	1.491(16)
C(34)-C(36)	1.506(18)
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(37)-H(37A)	0.9600
C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600
C(38)-C(39)	1.38(2)
C(38)-C(39')	1.49(2)
C(38)-H(38B)	0.93(3)
C(38)-H(38A)	0.94(3)
C(39)-C(40)	1.3900
C(39)-C(44)	1.3900
C(40)-C(41)	1.3900
C(40)-H(40)	0.9300
C(41)-C(42)	1.3900
C(41)-H(41)	0.9300
C(42)-C(43)	1.3900
C(42)-H(42)	0.9300
C(43)-C(44)	1.3900
C(43)-H(43)	0.9300

C(44)-H(44)	0.9300
C(39')-C(40')	1.3900
C(39')-C(44')	1.3900
C(40')-C(41')	1.3900
C(40')-H(40')	0.9300
C(41')-C(42')	1.3900
C(41')-H(41')	0.9300
C(42')-C(43')	1.3900
C(42')-H(42')	0.9300
C(43')-C(44')	1.3900
C(43')-H(43')	0.9300
C(44')-H(44')	0.9300
C(9)-S(1)-C(2)	90.4(5)
C(31)-S(2)-C(24)	90.8(5)
C(1)-N(1)-C(4)	110.9(8)
C(1)-N(1)-C(16)	123.7(8)
C(4)-N(1)-C(16)	124.9(9)
C(11)-N(2)-C(10)	119.1(9)
C(11)-N(2)-C(2)	121.3(8)
C(10)-N(2)-C(2)	117.6(8)
C(23)-N(3)-C(26)	110.6(9)
C(23)-N(3)-C(38)	122.9(11)
C(26)-N(3)-C(38)	126.5(10)
C(33)-N(4)-C(24)	122.3(8)
C(33)-N(4)-C(32)	119.4(8)
C(24)-N(4)-C(32)	116.8(8)
C(10)-O(2)-H(2)	109.5
C(11)-O(4)-C(12)	122.8(8)
C(32)-O(6)-H(6)	109.5
C(33)-O(8)-C(34)	122.2(8)
O(1)-C(1)-N(1)	125.0(9)
O(1)-C(1)-C(2)	128.2(9)
N(1)-C(1)-C(2)	106.8(8)
N(2)-C(2)-C(3)	120.1(8)
N(2)-C(2)-C(1)	111.2(8)
C(3)-C(2)-C(1)	103.4(8)
N(2)-C(2)-S(1)	103.5(6)

C(3)-C(2)-S(1)	109.7(7)
C(1)-C(2)-S(1)	108.6(7)
C(8)-C(3)-C(4)	121.9(10)
C(8)-C(3)-C(2)	129.7(10)
C(4)-C(3)-C(2)	108.3(8)
C(5)-C(4)-C(3)	121.5(10)
C(5)-C(4)-N(1)	128.7(10)
C(3)-C(4)-N(1)	109.8(8)
C(4)-C(5)-C(6)	116.6(12)
C(4)-C(5)-H(5)	121.7
C(6)-C(5)-H(5)	121.7
C(7)-C(6)-C(5)	120.5(12)
C(7)-C(6)-H(6A)	119.7
C(5)-C(6)-H(6A)	119.7
C(6)-C(7)-C(8)	123.1(11)
C(6)-C(7)-Br(1)	117.0(11)
C(8)-C(7)-Br(1)	119.8(12)
C(3)-C(8)-C(7)	116.2(12)
C(3)-C(8)-H(8)	121.9
C(7)-C(8)-H(8)	121.9
C(10)-C(9)-S(1)	105.6(7)
C(10)-C(9)-H(9A)	110.6
S(1)-C(9)-H(9A)	110.6
C(10)-C(9)-H(9B)	110.6
S(1)-C(9)-H(9B)	110.6
H(9A)-C(9)-H(9B)	108.8
O(2)-C(10)-N(2)	112.2(9)
O(2)-C(10)-C(9)	108.2(8)
N(2)-C(10)-C(9)	106.8(8)
O(2)-C(10)-H(10)	109.9
N(2)-C(10)-H(10)	109.9
C(9)-C(10)-H(10)	109.9
O(3)-C(11)-O(4)	125.8(10)
O(3)-C(11)-N(2)	123.9(10)
O(4)-C(11)-N(2)	110.3(9)
O(4)-C(12)-C(15)	102.0(9)
O(4)-C(12)-C(13)	109.9(10)
C(15)-C(12)-C(13)	112.4(13)

O(4)-C(12)-C(14)	107.5(10)
C(15)-C(12)-C(14)	112.1(12)
C(13)-C(12)-C(14)	112.3(11)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(1)-C(16)-C(17)	114.3(9)
N(1)-C(16)-H(16A)	108.7
C(17)-C(16)-H(16A)	108.7
N(1)-C(16)-H(16B)	108.7
C(17)-C(16)-H(16B)	108.7
H(16A)-C(16)-H(16B)	107.6
C(22)-C(17)-C(18)	119.6(11)
C(22)-C(17)-C(16)	123.4(10)
C(18)-C(17)-C(16)	116.8(11)
C(19)-C(18)-C(17)	120.1(13)
C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(18)-C(19)-C(20)	121.0(15)
C(18)-C(19)-H(19)	119.5
C(20)-C(19)-H(19)	119.5
C(19)-C(20)-C(21)	120.2(14)
C(19)-C(20)-H(20)	119.9

C(21)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	119.3(15)
C(22)-C(21)-H(21)	120.4
C(20)-C(21)-H(21)	120.4
C(17)-C(22)-C(21)	119.8(13)
C(17)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
O(5)-C(23)-N(3)	126.7(11)
O(5)-C(23)-C(24)	125.1(10)
N(3)-C(23)-C(24)	108.2(10)
N(4)-C(24)-C(25)	118.6(8)
N(4)-C(24)-C(23)	113.2(9)
C(25)-C(24)-C(23)	101.0(8)
N(4)-C(24)-S(2)	105.0(6)
C(25)-C(24)-S(2)	110.4(7)
C(23)-C(24)-S(2)	108.4(7)
C(26)-C(25)-C(30)	119.7(10)
C(26)-C(25)-C(24)	110.2(9)
C(30)-C(25)-C(24)	130.1(9)
C(27)-C(26)-C(25)	121.9(11)
C(27)-C(26)-N(3)	128.7(10)
C(25)-C(26)-N(3)	109.3(9)
C(26)-C(27)-C(28)	118.9(10)
C(26)-C(27)-H(27)	120.5
C(28)-C(27)-H(27)	120.5
C(27)-C(28)-C(29)	119.7(11)
C(27)-C(28)-H(28)	120.1
C(29)-C(28)-H(28)	120.1
C(28)-C(29)-C(30)	121.4(11)
C(28)-C(29)-Br(2)	118.6(9)
C(30)-C(29)-Br(2)	119.9(9)
C(29)-C(30)-C(25)	118.2(9)
C(29)-C(30)-H(30)	120.9
C(25)-C(30)-H(30)	120.9
C(32)-C(31)-S(2)	106.3(7)
C(32)-C(31)-H(31A)	110.5
S(2)-C(31)-H(31A)	110.5
C(32)-C(31)-H(31B)	110.5

S(2)-C(31)-H(31B)	110.5
H(31A)-C(31)-H(31B)	108.7
O(6)-C(32)-N(4)	111.4(9)
O(6)-C(32)-C(31)	107.8(8)
N(4)-C(32)-C(31)	105.6(8)
O(6)-C(32)-H(32)	110.6
N(4)-C(32)-H(32)	110.6
C(31)-C(32)-H(32)	110.6
O(7)-C(33)-O(8)	126.9(10)
O(7)-C(33)-N(4)	122.6(9)
O(8)-C(33)-N(4)	110.5(9)
C(35)-C(34)-C(37)	110.3(14)
C(35)-C(34)-O(8)	112.5(12)
C(37)-C(34)-O(8)	102.5(10)
C(35)-C(34)-C(36)	110.6(14)
C(37)-C(34)-C(36)	112.6(14)
O(8)-C(34)-C(36)	108.1(10)
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(34)-C(37)-H(37A)	109.5
C(34)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(34)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(39)-C(38)-N(3)	125.8(16)
N(3)-C(38)-C(39')	108.9(18)
C(39)-C(38)-H(38B)	114(4)

N(3)-C(38)-H(38B)	106(4)
C(39')-C(38)-H(38B)	123(5)
C(39)-C(38)-H(38A)	110(5)
N(3)-C(38)-H(38A)	109(5)
C(39')-C(38)-H(38A)	123(6)
H(38B)-C(38)-H(38A)	84(7)
C(38)-C(39)-C(40)	120.6(16)
C(38)-C(39)-C(44)	119.4(16)
C(40)-C(39)-C(44)	120.0
C(39)-C(40)-C(41)	120.0
C(39)-C(40)-H(40)	120.0
C(41)-C(40)-H(40)	120.0
C(42)-C(41)-C(40)	120.0
C(42)-C(41)-H(41)	120.0
C(40)-C(41)-H(41)	120.0
C(41)-C(42)-C(43)	120.0
C(41)-C(42)-H(42)	120.0
C(43)-C(42)-H(42)	120.0
C(44)-C(43)-C(42)	120.0
C(44)-C(43)-H(43)	120.0
C(42)-C(43)-H(43)	120.0
C(43)-C(44)-C(39)	120.0
C(43)-C(44)-H(44)	120.0
C(39)-C(44)-H(44)	120.0
C(40')-C(39')-C(44')	120.0
C(40')-C(39')-C(38)	113(2)
C(44')-C(39')-C(38)	127(2)
C(41')-C(40')-C(39')	120.0
C(41')-C(40')-H(40')	120.0
C(39')-C(40')-H(40')	120.0
C(40')-C(41')-C(42')	120.0
C(40')-C(41')-H(41')	120.0
C(42')-C(41')-H(41')	120.0
C(41')-C(42')-C(43')	120.0
C(41')-C(42')-H(42')	120.0
C(43')-C(42')-H(42')	120.0
C(44')-C(43')-C(42')	120.0
C(44')-C(43')-H(43')	120.0

C(42')-C(43')-H(43')	120.0
C(43')-C(44')-C(39')	120.0
C(43')-C(44')-H(44')	120.0
C(39')-C(44')-H(44')	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for cd15013. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	46(1)	239(3)	170(2)	-2(2)	15(1)	-19(1)
Br(2)	104(1)	62(1)	136(1)	-8(1)	25(1)	10(1)
S(1)	82(2)	51(2)	51(2)	11(2)	21(2)	2(2)
S(2)	73(2)	86(2)	46(2)	-19(2)	9(2)	-7(2)
N(1)	52(5)	49(6)	56(6)	-14(5)	24(4)	4(4)
N(2)	60(5)	37(5)	39(5)	-1(4)	20(4)	1(4)
N(3)	56(6)	67(7)	75(7)	12(5)	27(5)	6(5)
N(4)	45(5)	64(6)	40(5)	-7(4)	17(4)	-12(4)
O(1)	39(4)	75(6)	80(6)	-20(4)	10(4)	4(4)
O(2)	94(6)	58(5)	94(7)	0(4)	47(5)	15(5)
O(3)	90(5)	54(5)	35(4)	3(4)	22(4)	7(4)
O(4)	96(5)	36(4)	43(4)	4(4)	16(4)	-6(4)
O(5)	79(5)	66(6)	71(6)	7(5)	29(4)	-3(4)
O(6)	53(4)	111(7)	57(5)	-22(5)	12(4)	3(5)
O(7)	60(5)	95(6)	47(5)	0(4)	15(4)	-12(4)
O(8)	46(4)	102(6)	48(5)	-4(4)	16(4)	-20(4)
C(1)	53(7)	47(7)	44(7)	0(5)	9(5)	0(6)
C(2)	57(6)	40(5)	31(6)	-4(5)	7(5)	0(5)
C(3)	38(6)	54(7)	42(6)	-8(5)	12(5)	-1(5)
C(4)	49(6)	57(8)	37(6)	2(6)	4(5)	-6(6)
C(5)	81(9)	73(8)	47(7)	-8(7)	3(6)	-8(7)
C(6)	59(8)	114(12)	62(9)	15(9)	-9(7)	-39(8)
C(7)	55(8)	97(11)	92(10)	6(9)	14(7)	4(9)
C(8)	51(7)	91(10)	65(8)	-3(7)	7(6)	-3(7)
C(9)	78(8)	48(7)	63(8)	-3(6)	39(7)	-5(6)
C(10)	66(7)	45(7)	48(7)	2(5)	16(6)	6(6)
C(11)	57(7)	40(7)	45(7)	0(6)	16(6)	-1(5)
C(12)	120(11)	40(7)	56(8)	7(6)	15(8)	-15(7)
C(13)	126(12)	89(10)	83(10)	32(9)	25(9)	24(10)
C(14)	125(12)	76(10)	125(13)	33(9)	55(11)	-1(8)
C(15)	250(20)	45(10)	80(10)	1(7)	34(12)	-18(9)
C(16)	69(7)	43(6)	65(8)	-11(6)	22(6)	5(6)
C(17)	44(6)	70(8)	52(7)	-17(7)	18(5)	-9(6)

C(18)	86(9)	50(9)	90(11)	-18(7)	34(8)	-6(6)
C(19)	131(13)	93(14)	91(12)	-27(11)	54(11)	-21(10)
C(20)	93(11)	154(17)	53(9)	-40(11)	28(8)	-30(11)
C(21)	62(8)	137(15)	69(10)	14(10)	9(7)	-21(9)
C(22)	72(7)	79(9)	55(8)	8(7)	21(6)	25(7)
C(23)	67(8)	66(9)	52(7)	6(6)	23(6)	-3(7)
C(24)	47(6)	62(7)	47(6)	-9(5)	19(5)	-9(5)
C(25)	48(6)	60(8)	43(6)	0(6)	15(5)	-2(6)
C(26)	56(7)	65(8)	73(8)	5(7)	26(7)	0(6)
C(27)	64(7)	74(9)	89(10)	20(8)	35(7)	-2(7)
C(28)	66(8)	64(9)	83(10)	7(7)	22(7)	-8(7)
C(29)	65(8)	51(8)	74(9)	-2(6)	9(7)	1(6)
C(30)	58(6)	80(9)	49(7)	-9(7)	10(5)	-10(7)
C(31)	74(8)	59(8)	66(8)	-26(6)	21(6)	-18(6)
C(32)	53(7)	68(8)	42(6)	-16(6)	13(5)	-15(6)
C(33)	59(7)	58(7)	46(7)	-1(6)	22(6)	-6(6)
C(34)	48(7)	114(11)	57(8)	-19(8)	5(6)	-15(7)
C(35)	107(13)	190(20)	157(17)	74(17)	-42(12)	-59(13)
C(36)	87(10)	168(19)	162(17)	-91(15)	5(10)	-18(11)
C(37)	61(9)	280(20)	86(11)	-6(13)	14(8)	-48(12)
C(38)	57(9)	91(11)	137(14)	21(11)	46(10)	6(8)
C(39)	187(13)	129(12)	191(16)	-26(11)	145(12)	-15(10)
C(40)	192(13)	130(12)	195(16)	-26(11)	141(11)	-14(10)
C(41)	197(13)	133(12)	199(16)	-28(11)	137(12)	-13(10)
C(42)	199(13)	136(12)	200(16)	-32(11)	133(12)	-13(10)
C(43)	195(13)	133(12)	198(16)	-30(11)	138(12)	-16(10)
C(44)	191(13)	131(12)	194(16)	-28(11)	141(12)	-17(10)
C(39')	155(19)	210(20)	80(14)	21(16)	69(14)	5(18)
C(40')	157(19)	210(20)	83(14)	20(16)	67(14)	7(18)
C(41')	159(19)	210(20)	86(14)	19(16)	66(14)	7(18)
C(42')	159(19)	210(20)	85(14)	18(16)	66(14)	7(18)
C(43')	158(18)	210(20)	85(14)	20(16)	66(13)	5(18)
C(44')	157(18)	210(20)	82(14)	20(16)	68(13)	4(17)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cd15013.

	x	y	z	U(eq)
H(2)	6064	7216	-1153	117
H(6)	4285	8107	5809	111
H(5)	5980	10508	1714	83
H(6A)	8263	10357	1767	99
H(8)	7537	8419	129	84
H(9A)	3923	6579	-461	71
H(9B)	2860	7236	-597	71
H(10)	3575	7371	-2055	63
H(13A)	2815	9762	-3477	149
H(13B)	2939	10647	-3358	149
H(13C)	2451	10164	-2525	149
H(14A)	6297	9863	-2663	156
H(14B)	5446	10409	-3494	156
H(14C)	5135	9536	-3532	156
H(15A)	4266	10769	-1190	189
H(15B)	4891	11188	-2006	189
H(15C)	5752	10619	-1215	189
H(16A)	2317	10107	435	70
H(16B)	3556	10642	732	70
H(18)	2280	11187	1918	88
H(19)	1993	11203	3555	121
H(20)	2652	10212	4638	118
H(21)	3534	9127	4045	108
H(22)	3846	9104	2370	81
H(27)	10439	9123	3892	87
H(28)	9567	10328	3953	84
H(30)	6238	9429	4520	75
H(31A)	4134	6935	3941	78
H(31B)	5522	6529	4307	78
H(32)	5261	7003	5830	65
H(35A)	9840	7163	7817	246
H(35B)	9033	7586	8512	246

H(35C)	10566	7723	8686	246
H(36A)	8242	8808	8158	214
H(36B)	8741	9335	7375	214
H(36C)	9686	9141	8451	214
H(37A)	11402	8615	7599	214
H(37B)	10508	8810	6503	214
H(37C)	11005	7976	6760	214
H(40)	11749	8110	2869	188
H(41)	12010	7683	1273	194
H(42)	11075	6536	611	197
H(43)	9879	5817	1545	192
H(44)	9619	6245	3141	188
H(40')	12261	7372	3122	172
H(41')	12255	6996	1444	175
H(42')	10266	6703	287	175
H(43')	8282	6786	810	175
H(44')	8287	7162	2489	171
H(38B)	11150(50)	7780(30)	4460(40)	4(19)
H(38A)	10810(80)	7120(40)	4630(50)	30(30)

Table 6. Torsion angles [°] for cd15013.

C(4)-N(1)-C(1)-O(1)	-174.5(10)
C(16)-N(1)-C(1)-O(1)	-2.1(15)
C(4)-N(1)-C(1)-C(2)	6.1(10)
C(16)-N(1)-C(1)-C(2)	178.5(9)
C(11)-N(2)-C(2)-C(3)	-63.5(12)
C(10)-N(2)-C(2)-C(3)	132.6(10)
C(11)-N(2)-C(2)-C(1)	57.3(12)
C(10)-N(2)-C(2)-C(1)	-106.5(10)
C(11)-N(2)-C(2)-S(1)	173.7(7)
C(10)-N(2)-C(2)-S(1)	9.9(9)
O(1)-C(1)-C(2)-N(2)	42.5(14)
N(1)-C(1)-C(2)-N(2)	-138.1(8)
O(1)-C(1)-C(2)-C(3)	172.8(10)
N(1)-C(1)-C(2)-C(3)	-7.9(10)
O(1)-C(1)-C(2)-S(1)	-70.8(12)
N(1)-C(1)-C(2)-S(1)	108.6(8)
C(9)-S(1)-C(2)-N(2)	-26.9(7)
C(9)-S(1)-C(2)-C(3)	-156.3(7)
C(9)-S(1)-C(2)-C(1)	91.3(7)
N(2)-C(2)-C(3)-C(8)	-52.2(15)
C(1)-C(2)-C(3)-C(8)	-176.8(10)
S(1)-C(2)-C(3)-C(8)	67.5(13)
N(2)-C(2)-C(3)-C(4)	131.6(9)
C(1)-C(2)-C(3)-C(4)	7.0(10)
S(1)-C(2)-C(3)-C(4)	-108.8(8)
C(8)-C(3)-C(4)-C(5)	-0.9(16)
C(2)-C(3)-C(4)-C(5)	175.7(9)
C(8)-C(3)-C(4)-N(1)	179.7(9)
C(2)-C(3)-C(4)-N(1)	-3.7(11)
C(1)-N(1)-C(4)-C(5)	178.9(10)
C(16)-N(1)-C(4)-C(5)	6.7(16)
C(1)-N(1)-C(4)-C(3)	-1.7(11)
C(16)-N(1)-C(4)-C(3)	-173.9(9)
C(3)-C(4)-C(5)-C(6)	3.5(15)
N(1)-C(4)-C(5)-C(6)	-177.2(10)
C(4)-C(5)-C(6)-C(7)	-2.3(17)

C(5)-C(6)-C(7)-C(8)	-2(2)
C(5)-C(6)-C(7)-Br(1)	-179.3(9)
C(4)-C(3)-C(8)-C(7)	-2.9(16)
C(2)-C(3)-C(8)-C(7)	-178.7(11)
C(6)-C(7)-C(8)-C(3)	4.2(19)
Br(1)-C(7)-C(8)-C(3)	-178.2(8)
C(2)-S(1)-C(9)-C(10)	37.7(7)
C(11)-N(2)-C(10)-O(2)	95.0(11)
C(2)-N(2)-C(10)-O(2)	-100.8(10)
C(11)-N(2)-C(10)-C(9)	-146.7(9)
C(2)-N(2)-C(10)-C(9)	17.5(11)
S(1)-C(9)-C(10)-O(2)	83.9(9)
S(1)-C(9)-C(10)-N(2)	-37.0(9)
C(12)-O(4)-C(11)-O(3)	-2.6(15)
C(12)-O(4)-C(11)-N(2)	178.4(9)
C(10)-N(2)-C(11)-O(3)	-5.2(15)
C(2)-N(2)-C(11)-O(3)	-168.8(9)
C(10)-N(2)-C(11)-O(4)	173.8(8)
C(2)-N(2)-C(11)-O(4)	10.1(12)
C(11)-O(4)-C(12)-C(15)	-175.2(11)
C(11)-O(4)-C(12)-C(13)	65.4(13)
C(11)-O(4)-C(12)-C(14)	-57.2(13)
C(1)-N(1)-C(16)-C(17)	108.6(11)
C(4)-N(1)-C(16)-C(17)	-80.1(12)
N(1)-C(16)-C(17)-C(22)	-15.8(15)
N(1)-C(16)-C(17)-C(18)	168.4(9)
C(22)-C(17)-C(18)-C(19)	1.0(17)
C(16)-C(17)-C(18)-C(19)	177.0(11)
C(17)-C(18)-C(19)-C(20)	0(2)
C(18)-C(19)-C(20)-C(21)	-2(2)
C(19)-C(20)-C(21)-C(22)	2(2)
C(18)-C(17)-C(22)-C(21)	-0.8(16)
C(16)-C(17)-C(22)-C(21)	-176.5(10)
C(20)-C(21)-C(22)-C(17)	-0.6(17)
C(26)-N(3)-C(23)-O(5)	-174.5(12)
C(38)-N(3)-C(23)-O(5)	4(2)
C(26)-N(3)-C(23)-C(24)	7.0(12)
C(38)-N(3)-C(23)-C(24)	-174.1(11)

C(33)-N(4)-C(24)-C(25)	-60.3(13)
C(32)-N(4)-C(24)-C(25)	134.1(10)
C(33)-N(4)-C(24)-C(23)	57.8(13)
C(32)-N(4)-C(24)-C(23)	-107.8(10)
C(33)-N(4)-C(24)-S(2)	175.9(8)
C(32)-N(4)-C(24)-S(2)	10.3(11)
O(5)-C(23)-C(24)-N(4)	45.3(15)
N(3)-C(23)-C(24)-N(4)	-136.2(9)
O(5)-C(23)-C(24)-C(25)	173.2(11)
N(3)-C(23)-C(24)-C(25)	-8.3(11)
O(5)-C(23)-C(24)-S(2)	-70.8(13)
N(3)-C(23)-C(24)-S(2)	107.7(9)
C(31)-S(2)-C(24)-N(4)	-27.2(7)
C(31)-S(2)-C(24)-C(25)	-156.1(7)
C(31)-S(2)-C(24)-C(23)	94.1(8)
N(4)-C(24)-C(25)-C(26)	131.1(10)
C(23)-C(24)-C(25)-C(26)	6.8(11)
S(2)-C(24)-C(25)-C(26)	-107.8(9)
N(4)-C(24)-C(25)-C(30)	-51.8(15)
C(23)-C(24)-C(25)-C(30)	-176.2(11)
S(2)-C(24)-C(25)-C(30)	69.3(12)
C(30)-C(25)-C(26)-C(27)	1.3(17)
C(24)-C(25)-C(26)-C(27)	178.7(11)
C(30)-C(25)-C(26)-N(3)	179.4(9)
C(24)-C(25)-C(26)-N(3)	-3.2(12)
C(23)-N(3)-C(26)-C(27)	175.3(12)
C(38)-N(3)-C(26)-C(27)	-4(2)
C(23)-N(3)-C(26)-C(25)	-2.7(13)
C(38)-N(3)-C(26)-C(25)	178.5(12)
C(25)-C(26)-C(27)-C(28)	1.0(18)
N(3)-C(26)-C(27)-C(28)	-176.7(12)
C(26)-C(27)-C(28)-C(29)	-1.5(18)
C(27)-C(28)-C(29)-C(30)	-0.3(19)
C(27)-C(28)-C(29)-Br(2)	-176.6(10)
C(28)-C(29)-C(30)-C(25)	2.5(17)
Br(2)-C(29)-C(30)-C(25)	178.8(8)
C(26)-C(25)-C(30)-C(29)	-3.0(15)
C(24)-C(25)-C(30)-C(29)	-179.8(11)

C(24)-S(2)-C(31)-C(32)	37.5(8)
C(33)-N(4)-C(32)-O(6)	93.8(11)
C(24)-N(4)-C(32)-O(6)	-100.2(10)
C(33)-N(4)-C(32)-C(31)	-149.5(9)
C(24)-N(4)-C(32)-C(31)	16.5(12)
S(2)-C(31)-C(32)-O(6)	83.0(9)
S(2)-C(31)-C(32)-N(4)	-36.1(10)
C(34)-O(8)-C(33)-O(7)	-5.0(17)
C(34)-O(8)-C(33)-N(4)	174.3(10)
C(24)-N(4)-C(33)-O(7)	-179.2(10)
C(32)-N(4)-C(33)-O(7)	-14.0(15)
C(24)-N(4)-C(33)-O(8)	1.5(14)
C(32)-N(4)-C(33)-O(8)	166.8(9)
C(33)-O(8)-C(34)-C(35)	59.4(16)
C(33)-O(8)-C(34)-C(37)	177.9(12)
C(33)-O(8)-C(34)-C(36)	-62.9(15)
C(23)-N(3)-C(38)-C(39)	91(2)
C(26)-N(3)-C(38)-C(39)	-90(2)
C(23)-N(3)-C(38)-C(39')	94(2)
C(26)-N(3)-C(38)-C(39')	-88(2)
N(3)-C(38)-C(39)-C(40)	104.3(19)
C(39')-C(38)-C(39)-C(40)	96(7)
N(3)-C(38)-C(39)-C(44)	-75(2)
C(39')-C(38)-C(39)-C(44)	-83(7)
C(38)-C(39)-C(40)-C(41)	-178.8(19)
C(44)-C(39)-C(40)-C(41)	0.0
C(39)-C(40)-C(41)-C(42)	0.0
C(40)-C(41)-C(42)-C(43)	0.0
C(41)-C(42)-C(43)-C(44)	0.0
C(42)-C(43)-C(44)-C(39)	0.0
C(38)-C(39)-C(44)-C(43)	178.8(19)
C(40)-C(39)-C(44)-C(43)	0.0
C(39)-C(38)-C(39')-C(40')	-28(6)
N(3)-C(38)-C(39')-C(40')	158.7(16)
C(39)-C(38)-C(39')-C(44')	145(9)
N(3)-C(38)-C(39')-C(44')	-28(3)
C(44')-C(39')-C(40')-C(41')	0.0
C(38)-C(39')-C(40')-C(41')	174(3)

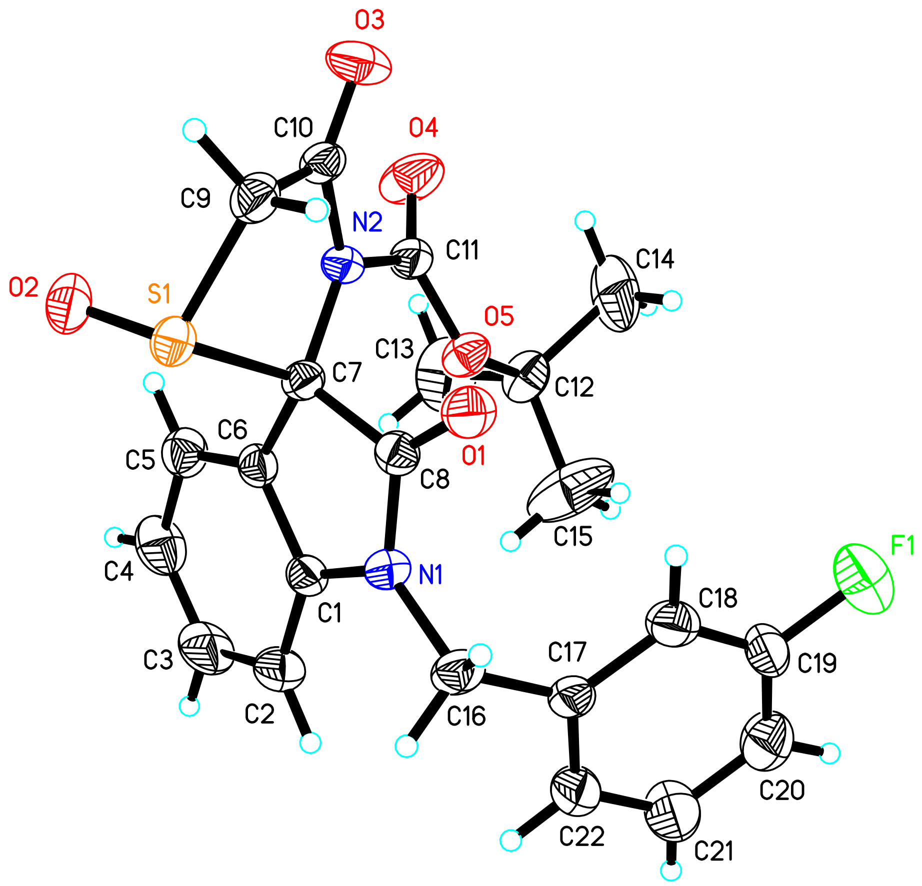
C(39')-C(40')-C(41')-C(42')	0.0
C(40')-C(41')-C(42')-C(43')	0.0
C(41')-C(42')-C(43')-C(44')	0.0
C(42')-C(43')-C(44')-C(39')	0.0
C(40')-C(39')-C(44')-C(43')	0.0
C(38)-C(39')-C(44')-C(43')	-173(4)

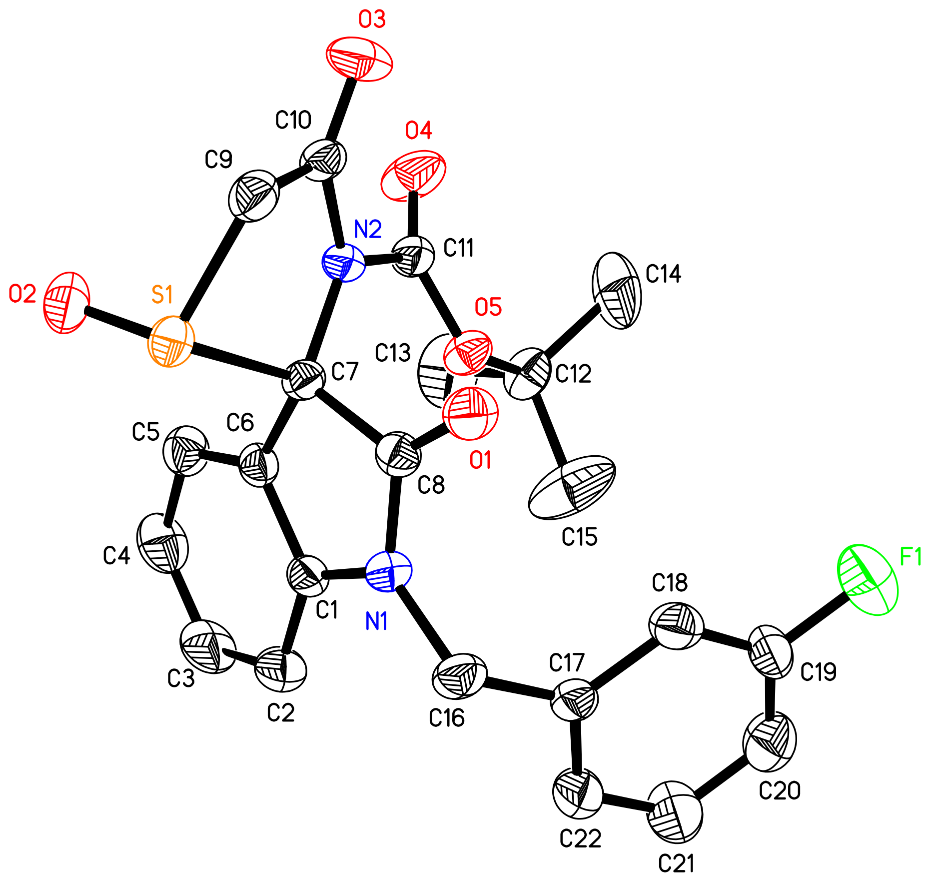
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd15013 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-ray Crystal Structure of 8




O3
C10
O4
C9
N2
C11
C14
O2
S1
O5
C13
C12
C7
C5
C6
O1
C8
C15
C4
F1
C18
C1
N1
C17
C19
C3
C2
C16
C20
C22
C21

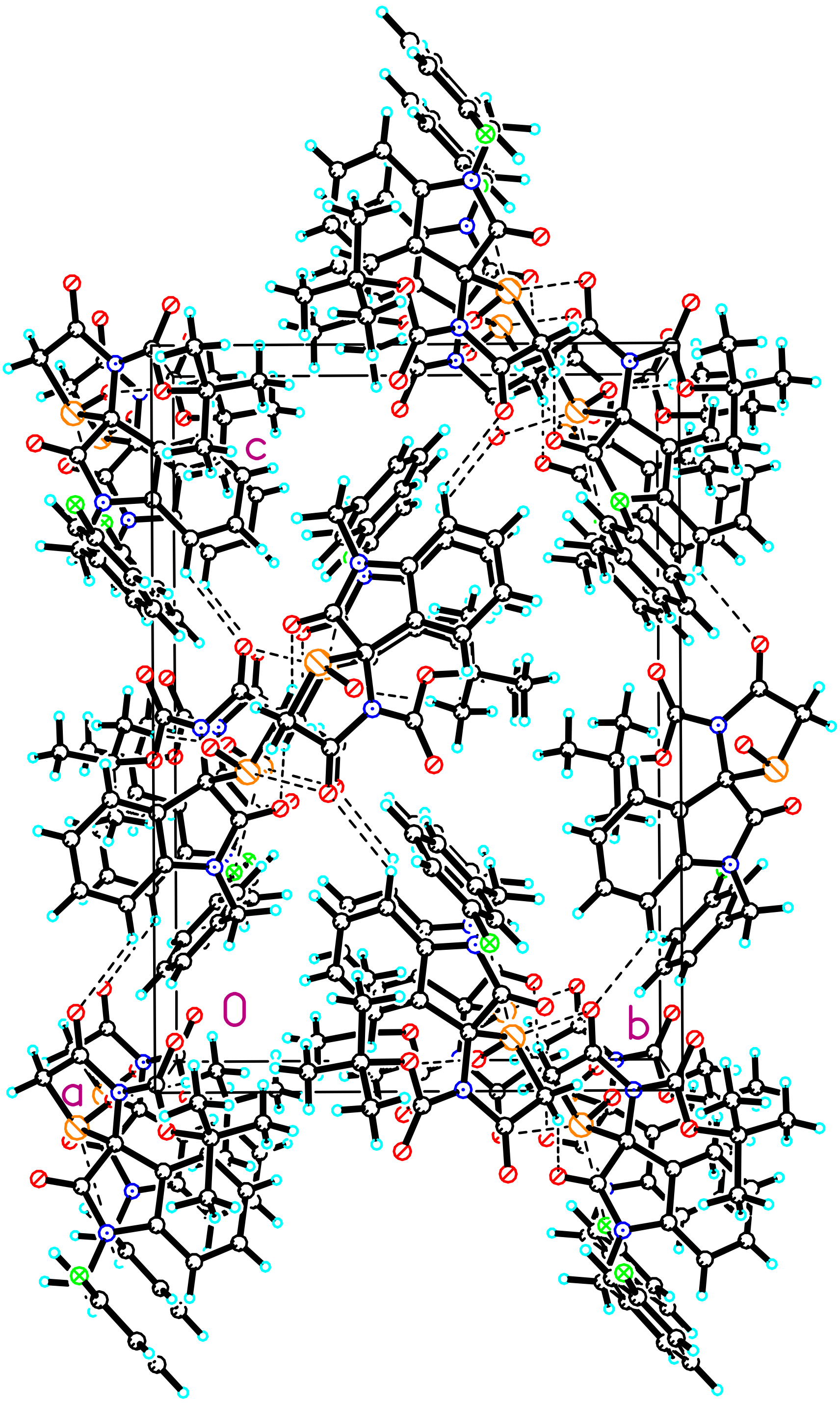

c
0
a
b

Table 1. Crystal data and structure refinement for cd16057.

Identification code	cd16057	
Empirical formula	C22 H21 F N2 O5 S	
Formula weight	444.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.0059(11) Å	α= 90°.
	b = 12.9439(15) Å	β= 90°.
	c = 18.305(2) Å	γ = 90°.
Volume	2133.9(4) Å^3	
Z	4	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.197 mm^{-1}	
F(000)	928	
Crystal size	0.180 x 0.150 x 0.130 mm^3	
Theta range for data collection	1.927 to 25.995°.	
Index ranges	-11<=h<=11, -15<=k<=14, -16<=l<=22	
Reflections collected	12095	
Independent reflections	4187 [R(int) = 0.0348]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6286	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4187 / 0 / 283	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.1033	
R indices (all data)	R1 = 0.0491, wR2 = 0.1081	
Absolute structure parameter	-0.03(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.281 and -0.160 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for cd16057. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4910(1)	1781(1)	712(1)	46(1)
F(1)	13433(3)	1255(2)	2212(2)	104(1)
N(1)	7483(3)	1062(2)	2030(1)	44(1)
N(2)	7200(3)	821(2)	121(1)	40(1)
O(1)	8252(3)	2325(2)	1240(1)	55(1)
O(2)	3770(3)	1126(2)	380(2)	61(1)
O(3)	7337(3)	1648(2)	-982(1)	66(1)
O(4)	8422(4)	-314(3)	-622(1)	82(1)
O(5)	8974(2)	-172(2)	569(1)	47(1)
C(1)	6681(3)	133(2)	1972(2)	43(1)
C(2)	6410(4)	-587(3)	2500(2)	61(1)
C(3)	5605(5)	-1447(3)	2294(3)	74(1)
C(4)	5079(5)	-1575(3)	1598(3)	71(1)
C(5)	5352(4)	-830(3)	1070(2)	55(1)
C(6)	6154(3)	19(2)	1266(2)	41(1)
C(7)	6600(3)	947(2)	848(2)	37(1)
C(8)	7581(3)	1544(2)	1381(2)	40(1)
C(9)	5859(4)	2378(3)	-36(2)	51(1)
C(10)	6858(3)	1596(3)	-376(2)	45(1)
C(11)	8262(3)	54(3)	-32(2)	46(1)
C(12)	10026(4)	-1048(2)	603(2)	55(1)
C(13)	11281(5)	-874(5)	81(3)	100(2)
C(14)	10527(9)	-1009(5)	1378(3)	133(3)
C(15)	9190(7)	-2027(4)	456(4)	103(2)
C(16)	8173(4)	1477(3)	2689(2)	54(1)
C(17)	9681(4)	1061(3)	2842(2)	47(1)
C(18)	10905(4)	1380(3)	2446(2)	56(1)
C(19)	12249(4)	960(3)	2605(2)	62(1)
C(20)	12468(5)	250(4)	3132(3)	76(1)
C(21)	11268(5)	-58(4)	3535(3)	81(1)
C(22)	9885(4)	347(3)	3385(2)	64(1)

Table 3. Bond lengths [Å] and angles [°] for cd16057.

S(1)-O(2)	1.464(3)
S(1)-C(9)	1.789(4)
S(1)-C(7)	1.883(3)
F(1)-C(19)	1.343(4)
N(1)-C(8)	1.345(4)
N(1)-C(1)	1.407(4)
N(1)-C(16)	1.459(4)
N(2)-C(10)	1.389(4)
N(2)-C(11)	1.407(4)
N(2)-C(7)	1.445(4)
O(1)-C(8)	1.205(4)
O(3)-C(10)	1.192(4)
O(4)-C(11)	1.188(4)
O(5)-C(11)	1.306(4)
O(5)-C(12)	1.479(4)
C(1)-C(2)	1.364(5)
C(1)-C(6)	1.385(4)
C(2)-C(3)	1.381(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.368(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.387(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.363(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.480(4)
C(7)-C(8)	1.527(4)
C(9)-C(10)	1.490(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(12)-C(14)	1.489(6)
C(12)-C(13)	1.497(6)
C(12)-C(15)	1.499(6)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600

C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(17)	1.488(5)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(22)	1.369(5)
C(17)-C(18)	1.383(5)
C(18)-C(19)	1.359(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.346(6)
C(20)-C(21)	1.368(6)
C(20)-H(20)	0.9300
C(21)-C(22)	1.379(6)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300

O(2)-S(1)-C(9)	105.52(16)
O(2)-S(1)-C(7)	106.81(14)
C(9)-S(1)-C(7)	87.84(14)
C(8)-N(1)-C(1)	111.3(2)
C(8)-N(1)-C(16)	122.1(3)
C(1)-N(1)-C(16)	126.6(3)
C(10)-N(2)-C(11)	122.0(3)
C(10)-N(2)-C(7)	116.0(2)
C(11)-N(2)-C(7)	121.1(2)
C(11)-O(5)-C(12)	121.5(2)
C(2)-C(1)-C(6)	121.8(3)
C(2)-C(1)-N(1)	128.5(3)
C(6)-C(1)-N(1)	109.7(2)
C(1)-C(2)-C(3)	116.8(4)
C(1)-C(2)-H(2)	121.6
C(3)-C(2)-H(2)	121.6
C(4)-C(3)-C(2)	122.2(3)
C(4)-C(3)-H(3)	118.9

C(2)-C(3)-H(3)	118.9
C(3)-C(4)-C(5)	120.2(4)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	118.1(4)
C(6)-C(5)-H(5)	120.9
C(4)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	120.8(3)
C(5)-C(6)-C(7)	131.5(3)
C(1)-C(6)-C(7)	107.7(3)
N(2)-C(7)-C(6)	119.1(3)
N(2)-C(7)-C(8)	115.4(2)
C(6)-C(7)-C(8)	103.7(2)
N(2)-C(7)-S(1)	104.18(18)
C(6)-C(7)-S(1)	108.3(2)
C(8)-C(7)-S(1)	105.16(19)
O(1)-C(8)-N(1)	127.7(3)
O(1)-C(8)-C(7)	125.3(3)
N(1)-C(8)-C(7)	107.0(3)
C(10)-C(9)-S(1)	108.4(2)
C(10)-C(9)-H(9A)	110.0
S(1)-C(9)-H(9A)	110.0
C(10)-C(9)-H(9B)	110.0
S(1)-C(9)-H(9B)	110.0
H(9A)-C(9)-H(9B)	108.4
O(3)-C(10)-N(2)	124.7(3)
O(3)-C(10)-C(9)	124.7(3)
N(2)-C(10)-C(9)	110.5(3)
O(4)-C(11)-O(5)	128.0(3)
O(4)-C(11)-N(2)	123.1(3)
O(5)-C(11)-N(2)	108.9(3)
O(5)-C(12)-C(14)	102.1(3)
O(5)-C(12)-C(13)	109.9(3)
C(14)-C(12)-C(13)	112.0(5)
O(5)-C(12)-C(15)	108.6(3)
C(14)-C(12)-C(15)	110.6(4)
C(13)-C(12)-C(15)	113.0(4)
C(12)-C(13)-H(13A)	109.5

C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(1)-C(16)-C(17)	114.3(3)
N(1)-C(16)-H(16A)	108.7
C(17)-C(16)-H(16A)	108.7
N(1)-C(16)-H(16B)	108.7
C(17)-C(16)-H(16B)	108.7
H(16A)-C(16)-H(16B)	107.6
C(22)-C(17)-C(18)	118.4(3)
C(22)-C(17)-C(16)	120.2(3)
C(18)-C(17)-C(16)	121.4(3)
C(19)-C(18)-C(17)	118.5(3)
C(19)-C(18)-H(18)	120.8
C(17)-C(18)-H(18)	120.8
F(1)-C(19)-C(20)	117.5(4)
F(1)-C(19)-C(18)	118.6(4)
C(20)-C(19)-C(18)	123.9(4)
C(19)-C(20)-C(21)	118.0(4)
C(19)-C(20)-H(20)	121.0
C(21)-C(20)-H(20)	121.0
C(20)-C(21)-C(22)	119.7(4)
C(20)-C(21)-H(21)	120.2
C(22)-C(21)-H(21)	120.2

C(17)-C(22)-C(21)	121.5(4)
C(17)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for cd16057. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	41(1)	52(1)	44(1)	3(1)	-1(1)	8(1)
F(1)	74(2)	132(3)	105(2)	10(2)	29(2)	-15(2)
N(1)	48(1)	55(2)	29(1)	-1(1)	-2(1)	1(1)
N(2)	41(1)	53(1)	27(1)	1(1)	0(1)	2(1)
O(1)	65(1)	51(1)	49(1)	2(1)	-6(1)	-13(1)
O(2)	42(1)	70(2)	70(2)	6(1)	-8(1)	1(1)
O(3)	94(2)	67(2)	36(1)	3(1)	10(1)	-17(2)
O(4)	88(2)	119(2)	41(2)	-23(2)	-9(1)	44(2)
O(5)	51(1)	52(1)	38(1)	-8(1)	-8(1)	11(1)
C(1)	40(2)	53(2)	37(2)	5(1)	3(1)	4(1)
C(2)	61(2)	76(2)	46(2)	21(2)	6(2)	2(2)
C(3)	77(3)	69(2)	76(3)	33(2)	13(2)	-7(2)
C(4)	70(2)	59(2)	84(3)	13(2)	10(2)	-17(2)
C(5)	53(2)	57(2)	55(2)	0(2)	-4(2)	-7(2)
C(6)	37(1)	46(2)	39(2)	3(1)	2(1)	2(1)
C(7)	39(1)	42(2)	31(2)	1(1)	-1(1)	2(1)
C(8)	40(2)	46(2)	35(2)	-2(1)	1(1)	3(1)
C(9)	54(2)	52(2)	47(2)	11(2)	-8(2)	0(2)
C(10)	51(2)	52(2)	32(2)	1(1)	-5(1)	-12(2)
C(11)	39(1)	63(2)	38(2)	-7(2)	-3(1)	4(2)
C(12)	56(2)	46(2)	64(2)	-7(2)	-7(2)	13(2)
C(13)	51(2)	100(4)	149(5)	9(4)	17(3)	18(3)
C(14)	184(6)	122(4)	93(4)	-21(3)	-64(4)	96(5)
C(15)	105(4)	60(3)	145(5)	-11(3)	-8(4)	0(3)
C(16)	60(2)	68(2)	33(2)	-10(2)	-4(2)	7(2)
C(17)	54(2)	54(2)	34(2)	-7(1)	-2(1)	-6(2)
C(18)	66(2)	60(2)	42(2)	1(2)	3(2)	-8(2)
C(19)	51(2)	74(2)	60(2)	-9(2)	9(2)	-10(2)
C(20)	58(2)	85(3)	84(3)	4(2)	-5(2)	9(2)
C(21)	66(3)	90(3)	86(3)	31(3)	-6(2)	3(2)
C(22)	52(2)	86(3)	55(2)	19(2)	-3(2)	-9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cd16057.

	x	y	z	U(eq)
H(2)	6752	-503	2975	73
H(3)	5413	-1957	2639	89
H(4)	4538	-2163	1479	85
H(5)	4997	-907	597	66
H(9A)	5147	2626	-393	61
H(9B)	6435	2962	137	61
H(13A)	10889	-725	-396	150
H(13B)	11886	-1484	58	150
H(13C)	11871	-302	245	150
H(14A)	10972	-349	1475	199
H(14B)	11241	-1546	1463	199
H(14C)	9689	-1106	1695	199
H(15A)	8349	-2068	777	155
H(15B)	9829	-2608	539	155
H(15C)	8855	-2031	-42	155
H(16A)	7536	1327	3103	65
H(16B)	8239	2222	2643	65
H(18)	10811	1872	2078	67
H(20)	13406	-23	3219	91
H(21)	11384	-538	3909	97
H(22)	9072	130	3658	77

Table 6. Torsion angles [°] for cd16057.

C(8)-N(1)-C(1)-C(2)	176.6(3)
C(16)-N(1)-C(1)-C(2)	-2.0(5)
C(8)-N(1)-C(1)-C(6)	-3.4(4)
C(16)-N(1)-C(1)-C(6)	177.9(3)
C(6)-C(1)-C(2)-C(3)	1.1(5)
N(1)-C(1)-C(2)-C(3)	-179.0(3)
C(1)-C(2)-C(3)-C(4)	-0.8(6)
C(2)-C(3)-C(4)-C(5)	0.2(7)
C(3)-C(4)-C(5)-C(6)	0.3(6)
C(4)-C(5)-C(6)-C(1)	0.0(5)
C(4)-C(5)-C(6)-C(7)	-178.4(3)
C(2)-C(1)-C(6)-C(5)	-0.7(5)
N(1)-C(1)-C(6)-C(5)	179.4(3)
C(2)-C(1)-C(6)-C(7)	178.1(3)
N(1)-C(1)-C(6)-C(7)	-1.9(3)
C(10)-N(2)-C(7)-C(6)	146.1(3)
C(11)-N(2)-C(7)-C(6)	-44.2(4)
C(10)-N(2)-C(7)-C(8)	-89.5(3)
C(11)-N(2)-C(7)-C(8)	80.3(3)
C(10)-N(2)-C(7)-S(1)	25.3(3)
C(11)-N(2)-C(7)-S(1)	-164.9(2)
C(5)-C(6)-C(7)-N(2)	-45.8(5)
C(1)-C(6)-C(7)-N(2)	135.7(3)
C(5)-C(6)-C(7)-C(8)	-175.7(3)
C(1)-C(6)-C(7)-C(8)	5.7(3)
C(5)-C(6)-C(7)-S(1)	72.9(4)
C(1)-C(6)-C(7)-S(1)	-105.6(2)
O(2)-S(1)-C(7)-N(2)	74.0(2)
C(9)-S(1)-C(7)-N(2)	-31.6(2)
O(2)-S(1)-C(7)-C(6)	-53.8(2)
C(9)-S(1)-C(7)-C(6)	-159.3(2)
O(2)-S(1)-C(7)-C(8)	-164.18(19)
C(9)-S(1)-C(7)-C(8)	90.3(2)
C(1)-N(1)-C(8)-O(1)	-176.0(3)
C(16)-N(1)-C(8)-O(1)	2.7(5)
C(1)-N(1)-C(8)-C(7)	7.0(3)

C(16)-N(1)-C(8)-C(7)	-174.3(3)
N(2)-C(7)-C(8)-O(1)	43.1(4)
C(6)-C(7)-C(8)-O(1)	175.2(3)
S(1)-C(7)-C(8)-O(1)	-71.1(3)
N(2)-C(7)-C(8)-N(1)	-139.9(3)
C(6)-C(7)-C(8)-N(1)	-7.7(3)
S(1)-C(7)-C(8)-N(1)	105.9(2)
O(2)-S(1)-C(9)-C(10)	-75.6(2)
C(7)-S(1)-C(9)-C(10)	31.3(2)
C(11)-N(2)-C(10)-O(3)	5.3(5)
C(7)-N(2)-C(10)-O(3)	174.9(3)
C(11)-N(2)-C(10)-C(9)	-172.3(3)
C(7)-N(2)-C(10)-C(9)	-2.6(4)
S(1)-C(9)-C(10)-O(3)	159.3(3)
S(1)-C(9)-C(10)-N(2)	-23.1(3)
C(12)-O(5)-C(11)-O(4)	-6.9(6)
C(12)-O(5)-C(11)-N(2)	172.0(3)
C(10)-N(2)-C(11)-O(4)	-36.9(5)
C(7)-N(2)-C(11)-O(4)	153.9(4)
C(10)-N(2)-C(11)-O(5)	144.2(3)
C(7)-N(2)-C(11)-O(5)	-25.0(4)
C(11)-O(5)-C(12)-C(14)	-179.2(4)
C(11)-O(5)-C(12)-C(13)	61.8(4)
C(11)-O(5)-C(12)-C(15)	-62.3(4)
C(8)-N(1)-C(16)-C(17)	-94.1(4)
C(1)-N(1)-C(16)-C(17)	84.4(4)
N(1)-C(16)-C(17)-C(22)	-104.8(4)
N(1)-C(16)-C(17)-C(18)	75.2(4)
C(22)-C(17)-C(18)-C(19)	1.0(5)
C(16)-C(17)-C(18)-C(19)	-179.0(3)
C(17)-C(18)-C(19)-F(1)	178.8(3)
C(17)-C(18)-C(19)-C(20)	-0.4(6)
F(1)-C(19)-C(20)-C(21)	-179.9(4)
C(18)-C(19)-C(20)-C(21)	-0.7(7)
C(19)-C(20)-C(21)-C(22)	1.1(7)
C(18)-C(17)-C(22)-C(21)	-0.5(6)
C(16)-C(17)-C(22)-C(21)	179.5(4)
C(20)-C(21)-C(22)-C(17)	-0.5(7)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd16057 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0

C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6
C(2)-H(2)...O(3)#4	0.93	2.55	3.299(4)	137.6
C(9)-H(9A)...O(1)#3	0.97	2.31	3.244(4)	162.0
C(9)-H(9B)...O(2)#2	0.97	2.59	3.320(4)	132.1
C(13)-H(13A)...O(4)	0.96	2.32	2.968(6)	124.0
C(13)-H(13C)...O(2)#1	0.96	2.53	3.468(6)	165.6
C(15)-H(15C)...O(4)	0.96	2.49	3.047(7)	116.6

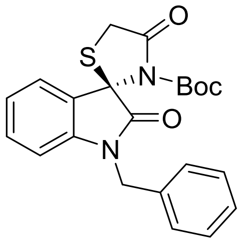
Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x+1/2,-y+1/2,-z #3 x-1/2,-y+1/2,-z

#4 -x+3/2,-y,z+1/2

Compound Characterization Data

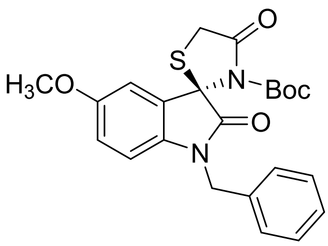
tert-butyl (R)-1-benzyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7a

White solid, yield 51%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.24 (m, 7H), 7.09 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 5.18 (d, J = 15.6 Hz, 1H), 4.60 (d, J = 15.6 Hz, 1H), 4.31 (d, J = 15.7 Hz, 1H), 3.72 (d, J = 15.7 Hz, 1H), 1.09 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.90, 170.67, 147.54, 142.31, 135.25, 130.74, 129.03, 128.06, 127.54, 126.76, 123.93, 123.59, 109.81, 85.08, 66.81, 44.16, 33.18, 27.43.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 20.0 min, t_{minor} = 15.0 min, ***96% ee***, $[\alpha]_D^{20}$ = 26.23 (c = 0.86, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2O_4S$, $[M+Na]^+$: 433.1192, found: 433.1194.

tert-butyl (R)-1-benzyl-5-methoxy-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate

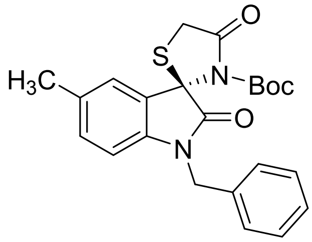


7b

White solid, yield 65%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.25 (m, 5H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.81-6.77 (m, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.15 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 4.30 (d, *J* = 13.5 Hz, 1H), 3.75 (s, 3H), 3.72 (d, *J* = 13.5 Hz, 1H), 1.13 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.73, 170.64, 156.73, 147.60, 135.49, 135.34, 129.00, 128.01, 127.86, 127.50, 115.94, 110.53, 110.24, 85.14, 66.43, 56.01, 44.22, 33.20, 27.50.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 25.8 min, t_{minor} = 23.2 min, ***96% ee***, $[\alpha]_D^{20}$ = 19.60 (c = 0.50, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{23}H_{24}N_2O_5S$, $[M+Na]^+$: 463.1298, found: 463.1304.

tert-butyl(R)-1-benzyl-5-methyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-

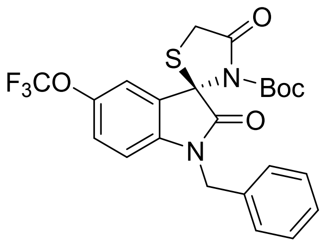
carboxylate



7c

White solid, yield 60%, [1]H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5H), 7.19 (s, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 5.16 (d, J = 15.6 Hz, 1H), 4.57 (d, J = 15.6 Hz, 1H), 4.30 (d, J = 15.6 Hz, 1H), 3.71 (d, J = 15.6 Hz, 1H), 2.30 (s, 3H), 1.10 (s, 9H).; [13]C NMR (100 MHz, $CDCl_3$) δ 174.86, 170.70, 147.60, 139.88, 135.36, 133.43, 130.99, 128.98, 127.98, 127.50, 126.73, 124.54, 109.61, 85.02, 44.15, 33.20, 29.78, 27.43, 21.02.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 mL/min, λ = 254 nm, t_{major} = 26.3 min, t_{minor} = 17.5 min, ***97% ee***, $[\alpha]_D^{20}$ =26.60 (c = 0.50, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{23}H_{24}N_2O_4S$, $[M+Na]^+$: 447.1349, found: 447.1354.

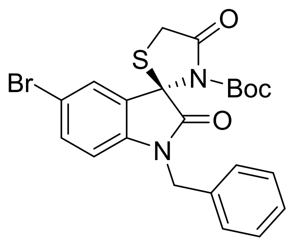
tert-butyl (R)-1-benzyl-2,4'-dioxo-5-(trifluoromethoxy)spiro[indoline-3,2'-thiazo-lidine]-3'-carboxylate



7d

White solid, yield 63%, [1]H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.23 (m, 6H), 7.16-7.11 (m, 1H), 6.74 (d, J = 8.6 Hz, 1H), 5.15 (d, J = 15.7 Hz, 1H), 4.65 (d, J = 15.7 Hz, 1H), 4.30 (d, J = 15.7 Hz, 1H), 3.74 (d, J = 15.7 Hz, 1H), 1.15 (s, 9H).; [13]C NMR (100 MHz, $CDCl_3$) δ 174.77, 170.05, 147.50, 145.25, 140.88, 134.75, 129.14, 128.41, 128.26, 127.52, 123.86, 121.77, 117.81, 110.46, 85.54, 68.96, 44.39, 33.07, 27.45.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 9.9 min, t_{minor} = 8.0 min, ***90% ee***, $[\alpha]_D^{20}$ = 14.89 (c = 0.90, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3N_2O_5S$, $[M+Na]^+$: 517.1015, found: 517.1018.

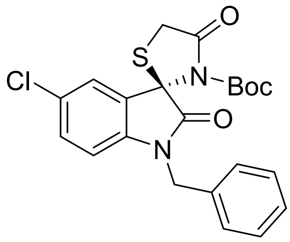
tert-butyl (R)-1-benzyl-5-bromo-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7e

White solid，yield 55%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 1.9 Hz, 1H), 7.40 - 7.25 (m, 6H), 6.62 (d, J = 8.4 Hz, 1H), 5.13 (d, J = 15.7 Hz, 1H), 4.63 (d, J = 15.7 Hz, 1H), 4.29 (d, J = 15.7 Hz, 1H), 3.74 (d, J = 15.7 Hz, 1H), 1.18 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.38, 170.10, 147.57, 141.25, 134.76, 133.49, 129.11, 128.83, 128.21, 127.45, 127.07, 116.06, 111.35, 85.53, 66.48, 44.27, 33.11, 27.57. Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (n-Hexane/i-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 17.0 min, t_{minor} = 14.5 min, ***90% ee***, $[\alpha]_D^{20}$ = 21.86 (c = 0.89, in CH_3COCH_3).; HRMS (ESI) m/z calcd for $C_{22}H_{21}BrN_2O_4S$, $[M+Na]^+$: 511.0298, found: 511.0303.

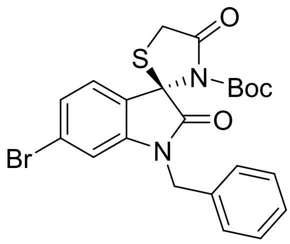
tert-butyl (R)-1-benzyl-5-chloro-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7f

White solid，yield 64%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 7H), 6.66 (d, J = 8.4 Hz, 1H), 5.13 (d, J = 15.7 Hz, 1H), 4.64 (d, J = 15.7 Hz, 1H), 4.29 (d, J = 15.7 Hz, 1H), 3.73 (d, J = 15.7 Hz, 1H), 1.18 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.51, 170.09, 147.60, 140.75, 134.80, 130.58, 129.10, 128.53, 128.19, 127.45, 124.30, 110.88, 110.02, 85.50, 44.30, 33.10, 29.78, 27.57.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 14.7 min, t_{minor} = 13.0 min, ***90% ee***, $[\alpha]_D^{20}$ = 18.97 (c = 0.58, in CH_3COCH_3).; HRMS (ESI) m/z calcd for $C_{22}H_{21}ClN_2O_4S$, $[M+Na]^+$: 467.0803, found: 467.0809.

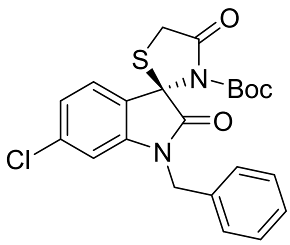
tert-butyl (R)-1-benzyl-6-bromo-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7g

White solid，yield 57%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.21 (m, 7H), 6.90-6.88 (m, 1H), 5.12 (d, J = 15.7 Hz, 1H), 4.61 (d, J = 15.7 Hz, 1H), 4.28 (d, J = 15.7 Hz, 1H), 3.72 (d, J = 15.7 Hz, 1H), 1.18 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.65, 170.16, 147.53, 143.47, 134.61, 129.08, 128.17, 127.36, 126.90, 126.43, 125.05, 124.33, 113.11, 85.40, 66.34, 44.20, 33.05, 27.50.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 22.6 min, t_{minor} = 15.1 min, ***98% ee***, $[\alpha]_D^{20}$ = 21.07 (c = 0.79, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{22}H_{21}BrN_2O_4S$, $[M+Na]^+$: 511.0298, found: 513.0303.

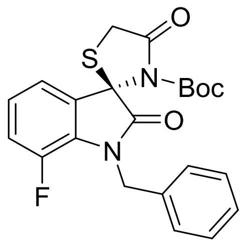
tert-butyl (R)-1-benzyl-6-chloro-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7h

White solid，yield 63%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.23 (m, 6H), 7.13 (dd, J = 8.5, 1.7 Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H), 5.15 (d, J = 15.7 Hz, 1H), 4.65 (d, J = 15.7 Hz, 1H), 4.30 (d, J = 15.7 Hz, 1H), 3.74 (d, J = 15.7 Hz, 1H), 1.15 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.84, 170.22, 147.63, 143.92, 143.48, 136.57, 134.70, 129.15, 128.25, 127.45, 124.84, 123.53, 110.45, 85.44, 66.36, 44.30, 33.13, 27.57.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 20.1 min, t_{minor} = 14.0 min, ***96% ee***, $[\alpha]_D^{20}$ = 25.1 (c = 0.93, in CH_3COCH_3),;HRMS (ESI) m/z calcd for $C_{22}H_{21}ClN_2O_4S$, $[M+Na]^+$: 467.0803, found: 467.0818.

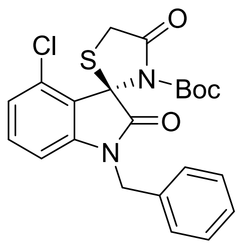
tert-butyl (R)-1-benzyl-7-fluoro-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7i

White solid, yield 58%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 2H), 7.36 - 7.24 (m, 3H), 7.18 -7.14 (m, 1H), 7.08 - 6.99 (m, 2H), 5.18 (d, J = 15.2 Hz, 1H), 4.88 (d, J = 15.2 Hz, 1H), 4.28 (d, J = 15.7 Hz, 1H), 3.71 (d, J = 15.7 Hz, 1H), 1.12 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.72, 151.86, 147.46 (d, $^1J_{C\text{-}F}$ = 243.0 Hz), 136.61, 131.15, 128.75, 127.94(d, $^3J_{C\text{-}F}$ = 9.0 Hz), 124.40, 123.93(d, $^3J_{C\text{-}F}$ = 6.0 Hz), 119.99, 118.80, 117.76(d, $^2J_{C\text{-}F}$ = 19.0 Hz),109.98(d, $^2J_{C\text{-}F}$ = 19.0 Hz), 85.54, 82.62, 45.70, 37.34, 27.60.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 mL/min, λ = 254 nm, t_{major} = 17.1 min, t_{minor} = 12.7 min, ***92% ee***, $[\alpha]_D^{20}$ =28.33 (c = 0.35, in CH_3COCH_3),;HRMS (ESI) m/z calcd for $C_{22}H_{21}FN_2O_4S$, $[M+Na]^+$: 451.1098, found: 451.1099.

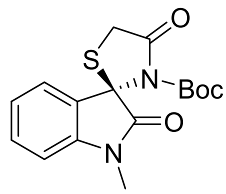
tert-butyl(R)-1-benzyl-4-chloro-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7j

White solid，yield 54%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.25 (m, 5H), 7.22 - 7.15 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 15.6 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 3.86 (d, *J* = 15.6 Hz, 1H), 1.17 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.06, 169.68, 147.54, 143.73, 143.47, 134.87, 131.38, 131.18, 129.08, 128.18, 127.51, 124.35, 108.31, 85.10, 44.43, 33.18, 29.78, 27.50. Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 mL/min, λ = 254 nm, t_{major} = 22.8 min, t_{minor} = 14.6 min, ***88% ee***, $[\alpha]_D^{20}$ =28.33 (c = 0.35, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{22}H_{21}ClN_2O_4S$, $[M+Na]^+$: 467.0803, found: 467.0810.

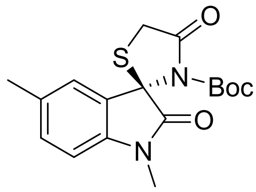
tert-butyl (R)-1-methyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7k

White solid，yield 65%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.34 (m, 2H), 7.15 - 7.08 (m, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.23 (d, J = 15.7 Hz, 1H), 3.69 (d, J = 15.7 Hz, 1H), 3.22 (s, 3H), 1.09 (s, 9H).；^{13}C NMR (100 MHz, $CDCl_3$) 170.56, 167.71, 147.30, 143.20, 130.80, 126.72, 123.87, 123.48, 108.74, 84.79, 33.04, 29.68, 27.33, 26.54.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 21.0 min, t_{minor} = 16.4 min, ***96% ee***, $[\alpha]_D^{20}$ = -3.90 (c = 0.62 in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2O_4S$, $[M+Na]^+$: 357.0879, found: 357.0885.

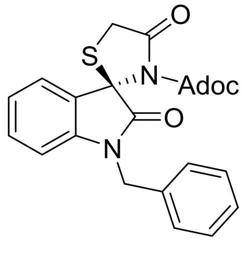
tert-butyl (R)-1,5-dimethyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7l

White solid，yield 55%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 - 7.17 (m, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.24 (d, *J* = 15.7 Hz, 1H), 3.70 (d, *J* = 15.7 Hz, 1H), 3.21 (s, 3H), 2.34 (s, 3H), 1.11 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.57, 170.67, 147.34, 140.79, 133.34, 131.05, 126.65, 124.49, 108.58, 84.74, 66.69, 33.09, 27.33, 26.57, 20.98. Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 22.1 min, t_{minor} = 19.0 min, ***97% ee***, $[\alpha]_D^{20}$ = -7.90 (c = 0.84, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2O_4S$, $[M+Na]^+$: 371.1036, found: 371.1056.

adamantan-1-yl (R)-1-benzyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate

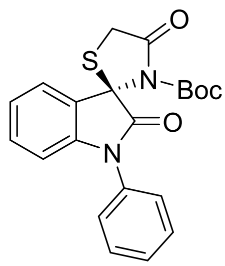


7m

White solid，yield 53%，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.25 (m, 7H), 7.12 –

7.06 (m, 1H), 6.78 (d, J = 7.9 Hz, 1H), 5.12 (d, J = 15.6 Hz, 1H), 4.64 (d, J = 15.6 Hz, 1H), 4.30 (d, J = 15.6 Hz, 1H), 3.71 (d, J = 15.6 Hz, 1H), 1.99 (s, 3H), 1.68-1.56 (m, 6H), 1.54-1.39 (m, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.90, 170.66, 146.93, 142.34, 135.31, 130.65, 129.00, 128.05, 127.75, 126.77, 123.98, 123.57, 109.80, 85.07, 66.81, 44.23, 40.58, 35.78, 33.18, 30.86, 29.78.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} =27.2 min, t_{minor} = 20.6 min, ***97% ee***, $[\alpha]_D^{20}$ = 33.0 (c = 0.7, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{28}H_{28}N_2O_4S$, $[M+Na]^+$: 511.1662, found: 511.1675.

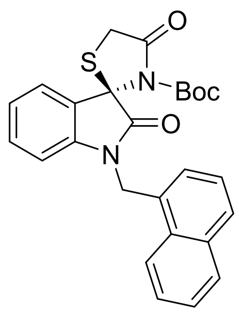
tert-butyl (R)-2,4'-dioxo-1-phenylspiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7n

White solid，yield 55%，^1H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.51 (m, 2H), 7.49 - 7.40 (m, 4H), 7.36 - 7.30 (m, 1H), 7.20 - 7.14 (m, 1H), 6.92 (d, J = 7.9 Hz, 1H), 4.28 (d, J = 15.7 Hz, 1H), 3.72 (d, J = 15.7 Hz, 1H), 1.19 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.86, 170.68, 147.59, 143.01, 133.84, 130.73, 129.81, 128.41, 126.43, 126.02, 124.18, 124.06, 110.22, 85.25, 66.78, 33.15, 27.68.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 26.0 min, t_{minor} = 14.8 min, ***94% ee***, $[\alpha]_D^{20}$ = -1.33 (c = 0.61, in CH_3COCH_3).;HRMS (ESI) mz calcd for $C_{21}H_{20}N_2O_4S$, $[M+Na]^+$: 419.1036, found: 419.1047.

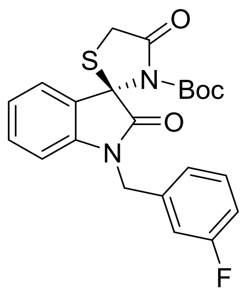
tert-butyl (R)-1-(naphthalen-1-ylmethyl)-2,4'-dioxospiro[indoline-3,2'-thiazolid-ine]-3'-carboxylate



7o

White solid, yield 57%, ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.64 - 7.51 (m, 2H), 7.48 - 7.36 (m, 3H), 7.21 (m, 1H), 7.10 - 7.5(m, 1H), 6.73 (d, J = 7.9 Hz, 1H), 5.72 (d, J = 16.1 Hz, 1H), 5.05 (d, J = 16.1 Hz, 1H), 4.34 (d, J = 15.7 Hz, 1H), 3.75 (d, J = 15.7 Hz, 1H), 1.15 (s, 9H). ;^{13}C NMR (100 MHz, $CDCl_3$) δ 174.94, 170.64, 147.65, 142.67, 133.99, 131.14, 130.76, 130.14, 129.07, 128.82, 126.87, 126.81, 126.22, 125.40, 125.23, 123.85, 123.60, 123.00, 110.29, 85.13, 66.87, 42.55, 33.25, 27.50.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 23.9 min, t_{minor} = 18.4 min, ***96% ee***, $[\alpha]_D^{20}$ = 52.7 (c =0.74, in CH_3COCH_3),;HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_4S$, $[M+Na]^+$: 483.1349, found: 483.1359.

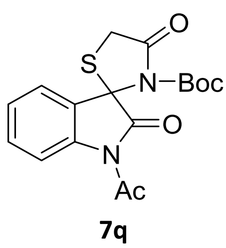
tert-butyl(R)-1-(3-fluorobenzyl)-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-car-boxylate



7p

White solid, yield 58%, ^{1}H NMR (400 MHz, $CDCl_3$) δ7.40 - 7.25 (m, 3H), 7.17 - 7.04 (m, 3H), 7.02 - 6.94 (m, 1H), 6.75-6.70 (m, 1H), 5.12 (d, J = 15.8 Hz, 1H), 4.65 (d, J = 15.8 Hz, 1H), 4.28 (d, J =15.7, 1H), 3.72 (d, J = 15.7 Hz, 1H), 1.12 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.99, 163.20 (d, $^1J_{C-F}$ = 245.0 Hz), 151.92, 141.92, 137.78 (d, $^3J_{C-F}$ = 8.0 Hz), 130.63 (d, $^3J_{C-F}$ = 8.0 Hz), 129.77, 128.05, 124.16, 123.45, 123.09, 115.08 (d, $^2J_{C-F}$ = 21.0 Hz),, 114.49 (d, $^2J_{C-F}$ = 22.0 Hz), 108.87, 85.39, 82.30, 69.41, 43.43, 27.58. Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 20.1 min, t_{minor} = 18.9 min, ***97% ee***, $[\alpha]_D^{20}$ = 15.72 (c = 3.21, in CH_3COCH_3),;HRMS (ESI) m/z calcd for $C_{22}H_{21}FN_2O_4S$, $[M+Na]^+$: 453.1098, found: 453.1109.

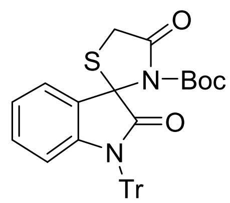
tert-butyl 1-acetyl-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7q

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.19 (m, 1H), 7.47-7.41 (m, 2H), 7.31-7.25 (m, 1H), 4.18 (d, J = 15.8 Hz, 1H), 3.75 (d, J = 15.8 Hz, 1H), 2.70 (s, 3H), 1.11 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) 175.08 (s), 170.52 (s), 170.09 (s), 147.11 (s), 139.66 (s), 131.38 (s), 126.21 (s), 125.85 (s), 123.69 (s), 117.20 (s), 85.88 (s), 67.10 (s), 33.30 (s), 27.34 (s), 26.45 (s).; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1 ml/min, λ = 220 nm, t_{major} = 20.08 min, t_{minor} = 16.98 min, ***86% ee***, $[\alpha]_D^{20}$ = 24.97 (c = 0.15, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{17}H_{18}N_2O_5S$, $[M+Na]^+$: 385.0834, found: 385.0842.

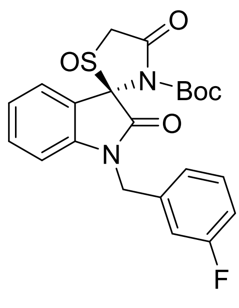
tert-butyl 2,4'-dioxo-1-tritylspiro[indoline-3,2'-thiazolidine]-3'-carboxylate



7r

^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 6H), 7. 30-7.24 (m, 7H), 7.23-7.17 (m, 3H), 7.01-6.96 (m, 2H), 6.40-6.36 (m, 1H), 4.16 (d, J = 15.7 Hz, 1H), 3.65 (d, J = 15.7 Hz, 1H), 0.87 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) 174.81 (s), 170.52 (s), 147.69 (s), 142.34 (s), 141.80 (s), 129.11 (s), 128.81 (s), 127.82 (s), 127.01 (s), 126.76 (s), 122.98 (s), 122.72 (s), 116.25 (s), 84.66 (s), 73.87 (s), 67.42 (s), 32.71 (s), 27.14 (s).; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel OD-H column (*n*-Hexane/*i*-PrOH 95:5 at 0.5 ml/min, λ = 254 nm, t_{major} = 25.3 min, t_{minor} = 21.2 min, ***98% ee***, $[\alpha]_D^{20}$ = 62.56 (c = 0.18, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{34}H_{30}FN_2O_4S$, $[M+Na]^+$: 595.6736, found: 585.6738.

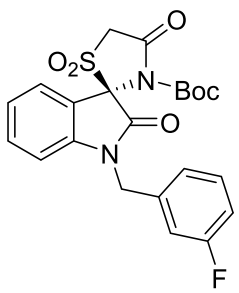
tert-butyl (1'S,3R)-1-(3-fluorobenzyl)-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate 1'-oxide



8

White solid, yield 52%,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.39 (m, 2H), 7.36 -7.29 (m, 1H), 7.21 - 7.10 (m, 2H), 7.07 - 6.97 (m, 2H), 6.90 - 6.86 (m, 1H), 5.06 (d, J = 15.7 Hz, 1H), 4.81 (d, J = 15.7 Hz, 1H) , 4.36 (d, J = 16.6 Hz, 1H), 3.85 (d, J = 16.6 Hz, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.47, 168.21, 163.19(d, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 142.05, 137.14(d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 131.62, 130.79(d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 126.12, 124.12, 123.14, 123.11, 120.54, 115.41(d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 114.62(d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 110.01, 85.77, 82.76, 54.34, 44.10, 27.41.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} = 35.4 min, t_{minor} = 26.7 min, ***91% ee***, $[\alpha]_D^{20}$ = -11.99 (c = 0.33, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{22}H_{21}FN_2O_5S$, $[M+Na]^+$: 467.1047, found: 467.1048

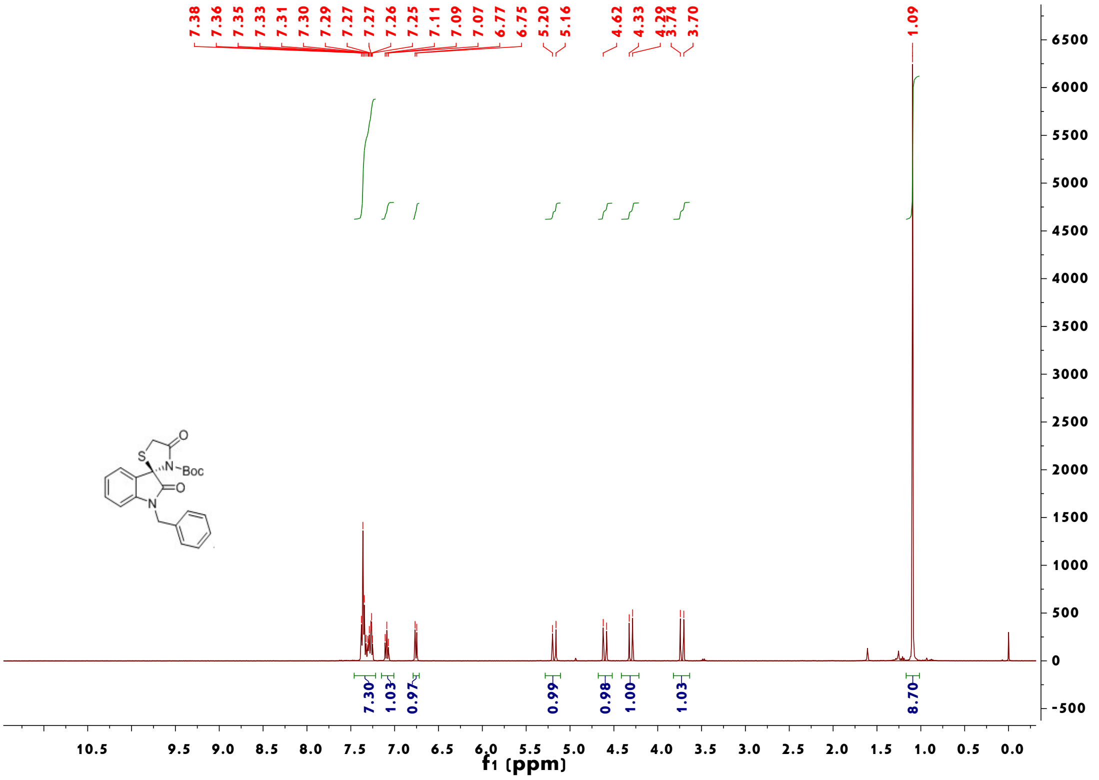
tert-butyl (R)-1-(3-fluorobenzyl)-2,4'-dioxospiro[indoline-3,2'-thiazolidine]-3'-carboxylate 1',1'-dioxide

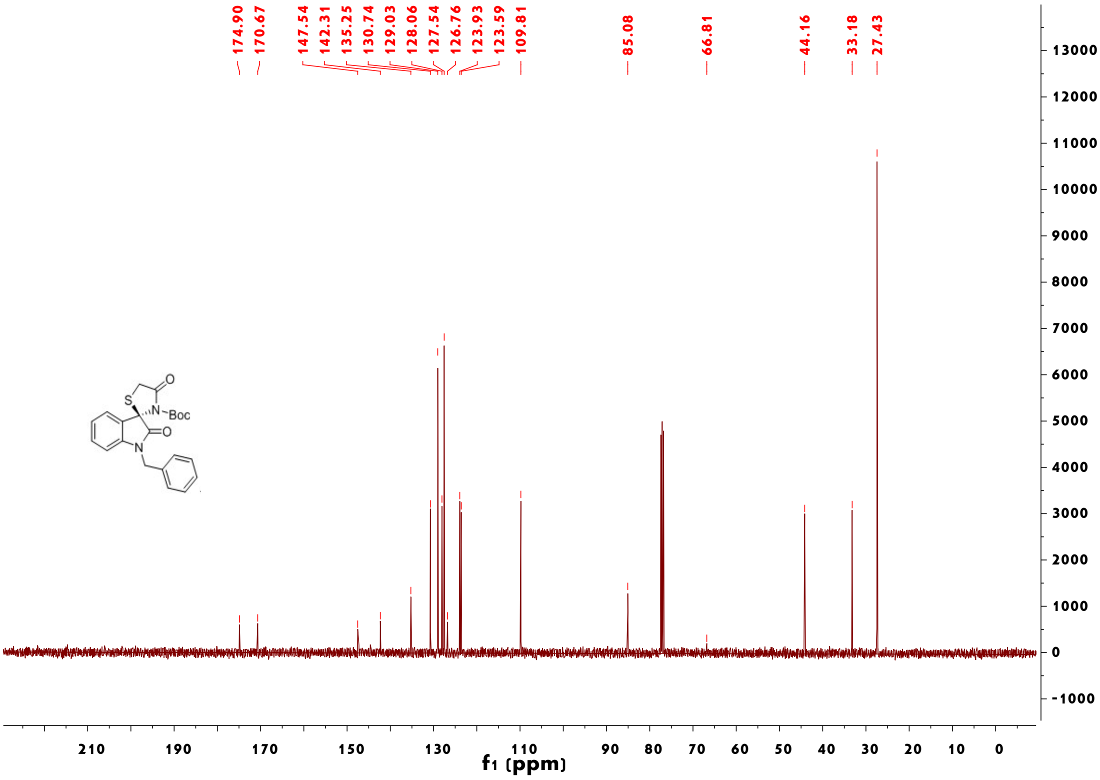


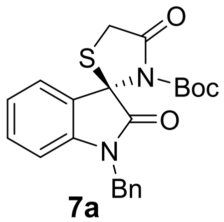
(+)-3

White solid, yield 53%,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.46 (m, 1H), 7.43 - 7.37 (m, 1H), 7.35 - 7.28 (m, 1H), 7.22 - 7.14 (m, 2H), 7.13 - 7.07 (m, 1H), 7.02 - 6.95 (m, 1H), 6.82 - 6.77 (m, 1H), 5.20 (d, J = 16.0 Hz, 1H), 4.69 (d, J = 16.0 Hz, 1H), 4.57 (d, J = 16.1 Hz, 1H), 4.08 (d, J = 16.1 Hz, 1H), 1.14 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ169.19, 163.21(d, $^{1}J_{C\text{-}F}$ = 246.00 Hz), 161.19, 146.19, 143.98, 136.77(d, $^{3}J_{C\text{-}F}$ = 7.00 Hz), 132.47, 130.77(d, $^{3}J_{C\text{-}F}$ = 9.00 Hz), 126.75, 124.10, 122.95, 122.93, 115.29(d, $^{2}J_{C\text{-}F}$ = 21.00 Hz), 114. 44(d, $^{2}J_{C\text{-}F}$ = 22.00 Hz), 110.51, 86.68, 82.47, 51.24, 44.23, 27.36.; Enantiometric excess of the product was determined by chiral stationary phase HPLC analysis using Daicel AS-H column (*n*-Hexane/*i*-PrOH 90:10 at 1.0 ml/min, λ = 254 nm, t_{major} =31.7 min, t_{minor} = 24.0 min, ***97% ee***, $[\alpha]_D^{20}$ = -1.4 (c = 1.40, in CH_3COCH_3).;HRMS (ESI) m/z calcd for $C_{22}H_{21}FN_2O_6S$, $[M+Na]^+$: 483.0997, found: 483.0987

Copy of NMR Spetra and HPLC Chromatograms of substrates

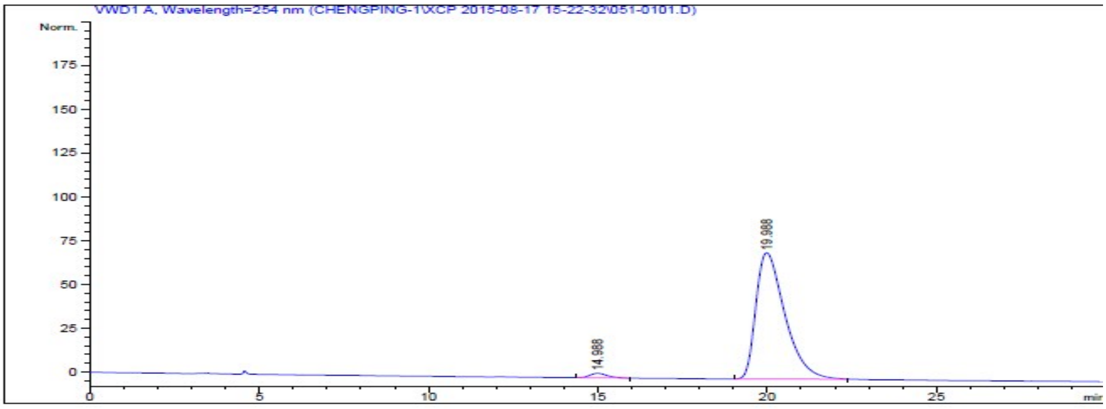






7a

51% yield, 96% ee



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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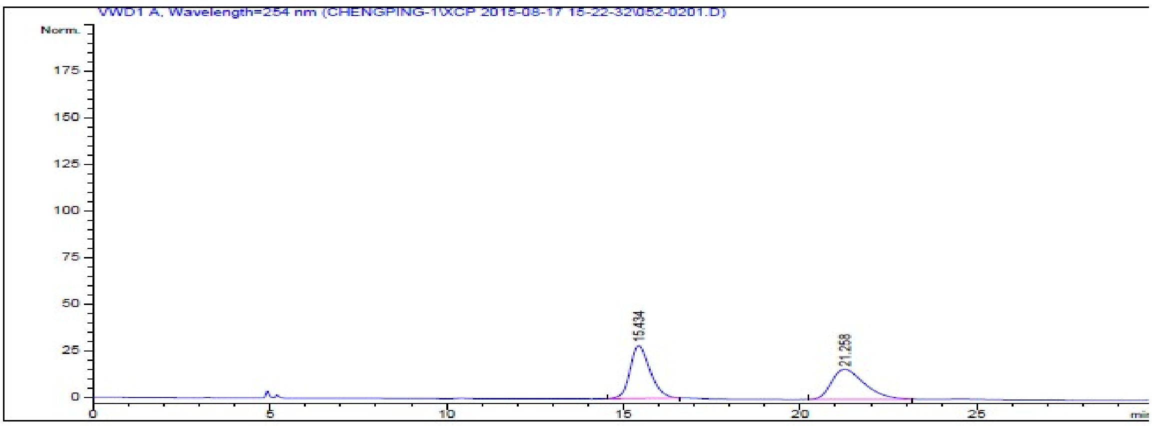
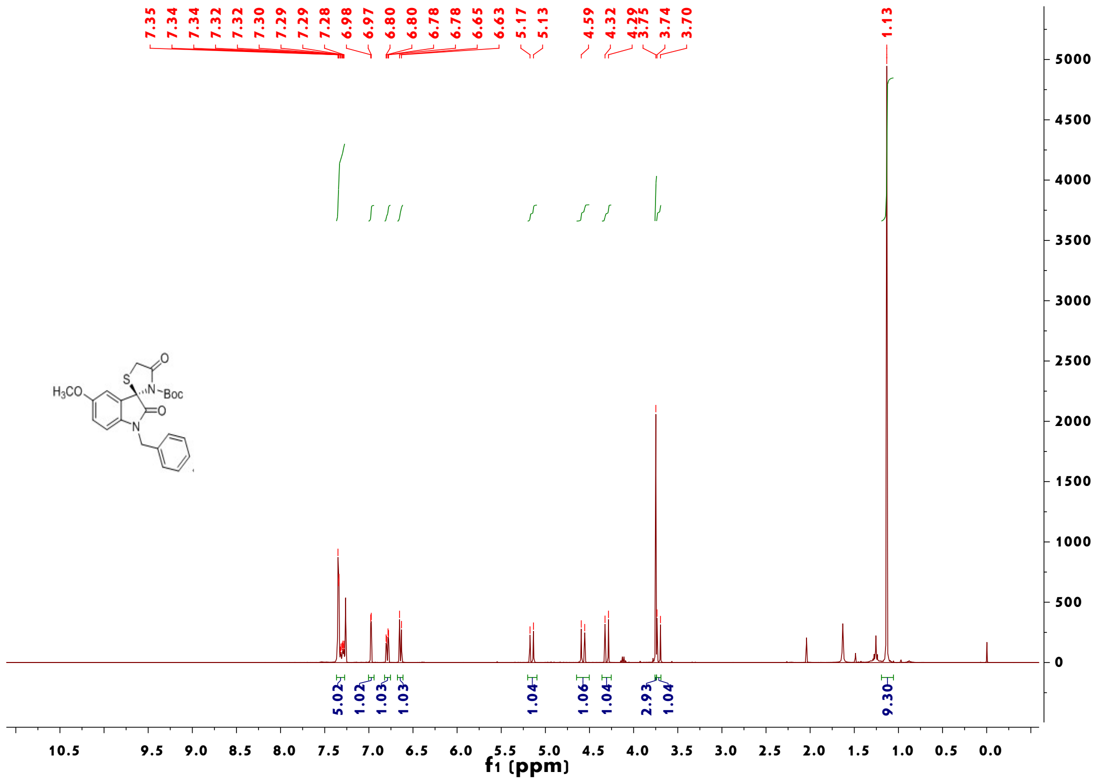


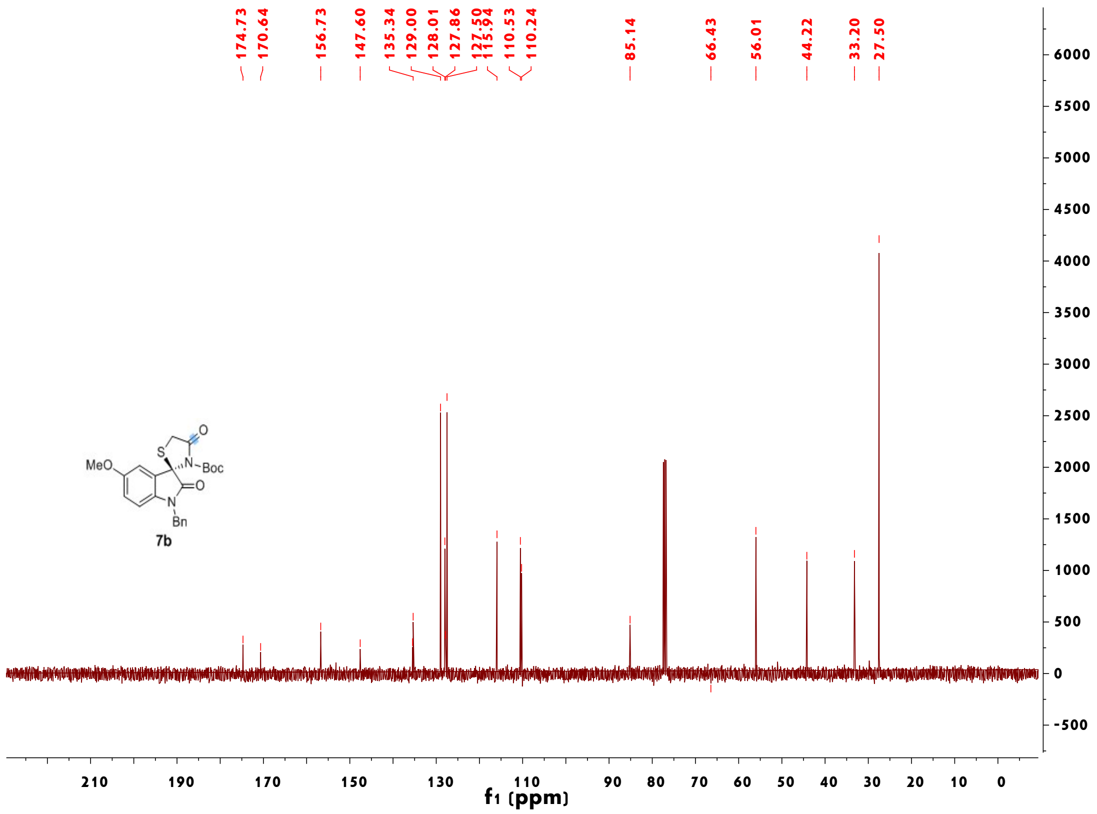
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

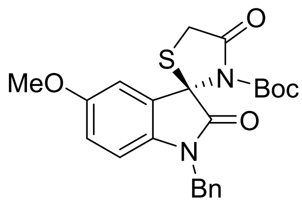
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.434	BB	0.6041	1115.26990	28.30138	51.7843
2	21.258	BB	0.9262	1038.41260	16.06244	48.2157



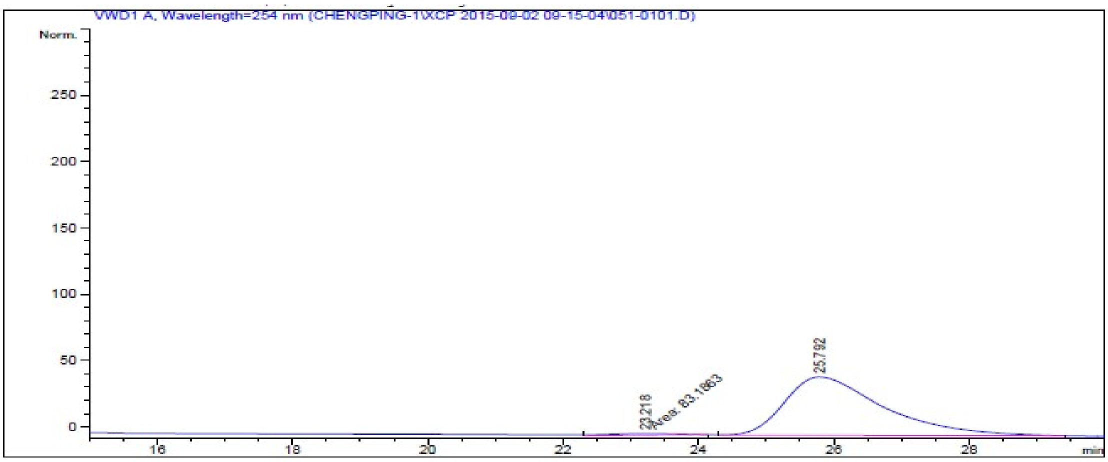


7b



7b

65% yield, 96% ee

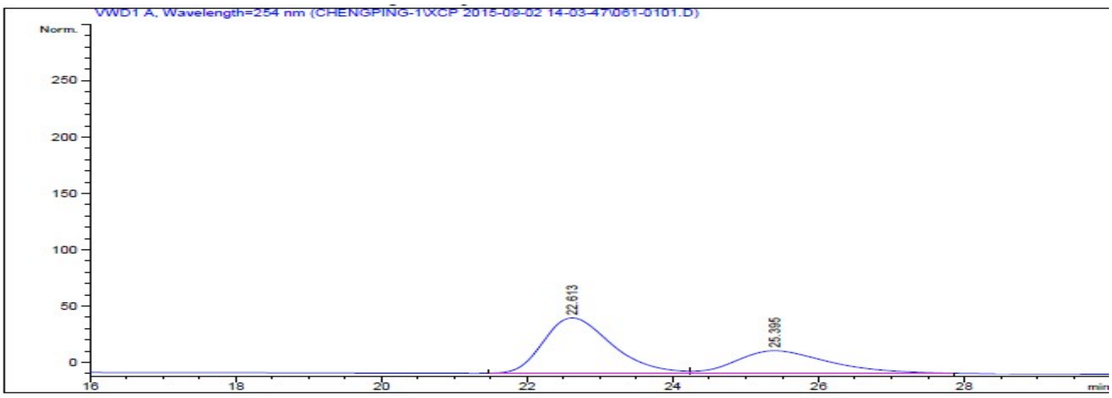


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.218	MM	0.7823	83.18630	1.25649	1.8365
2	25.792	VB	1.4444	4446.50781	44.10642	98.1635

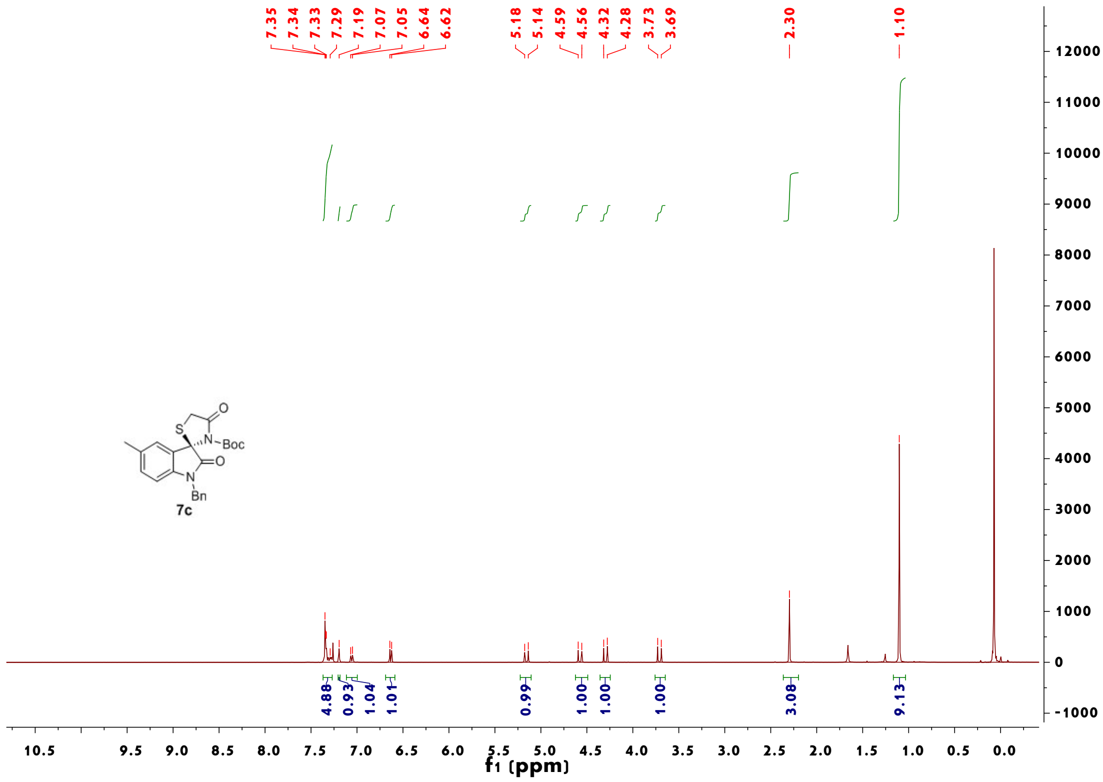


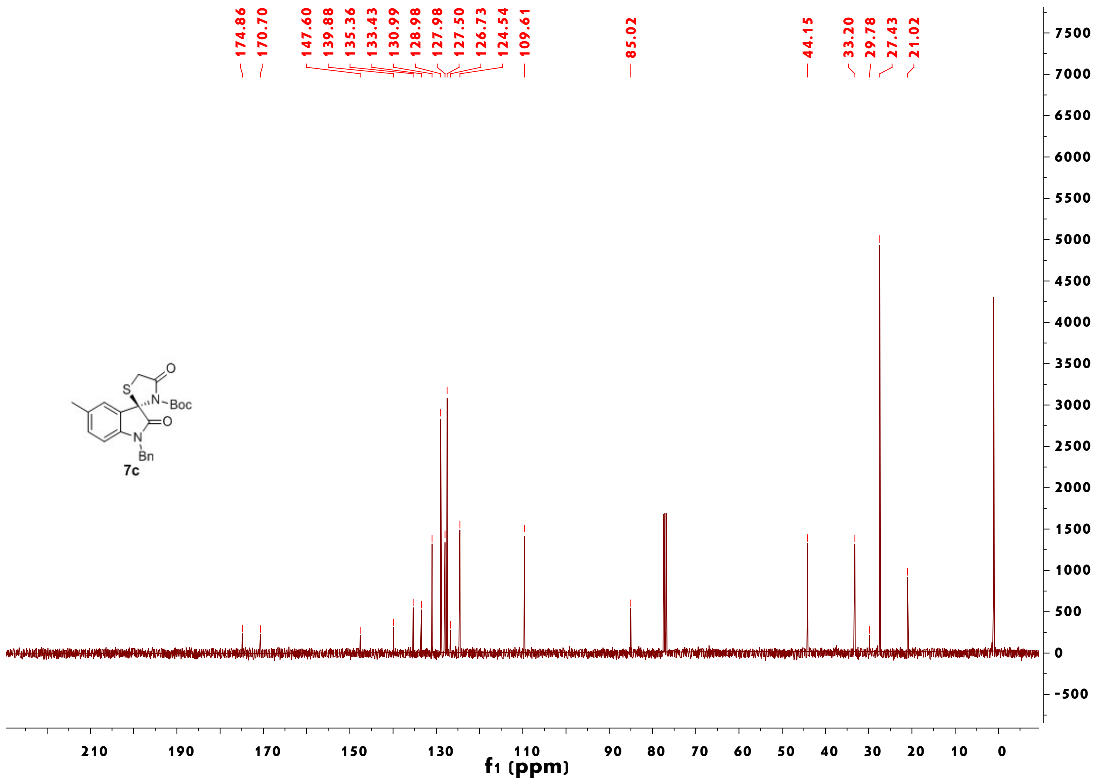
Area Percent Report

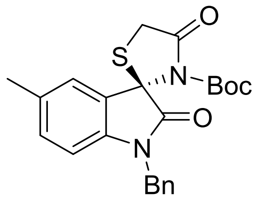
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.613	BV	0.9826	3210.54492	49.12403	64.5305
2	25.395	VB	1.2447	1764.69128	20.09359	35.4695

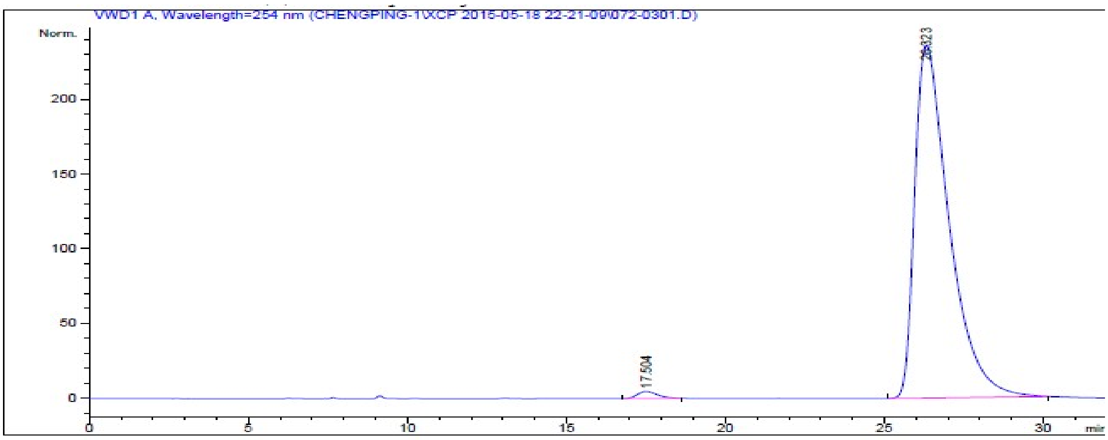

7.35
7.34
7.33
7.29
7.19
7.07
7.05
6.64
6.62
5.18
5.14
4.59
4.56
4.32
4.28
3.73
3.69
2.30
1.10
4.88
0.93
1.04
1.01
0.99
1.00
1.00
1.00
3.08
9.13
S
N
Boc
O
O
N
Bn
7c
f1 (ppm)


174.86
170.70
147.60
139.88
135.36
133.43
130.99
128.98
127.98
127.50
126.73
124.54
109.61
85.02
44.15
33.20
29.78
27.43
21.02
S
N
Boc
O
O
N
Bn
7c
f1 (ppm)



7c

60% yield, 97% ee

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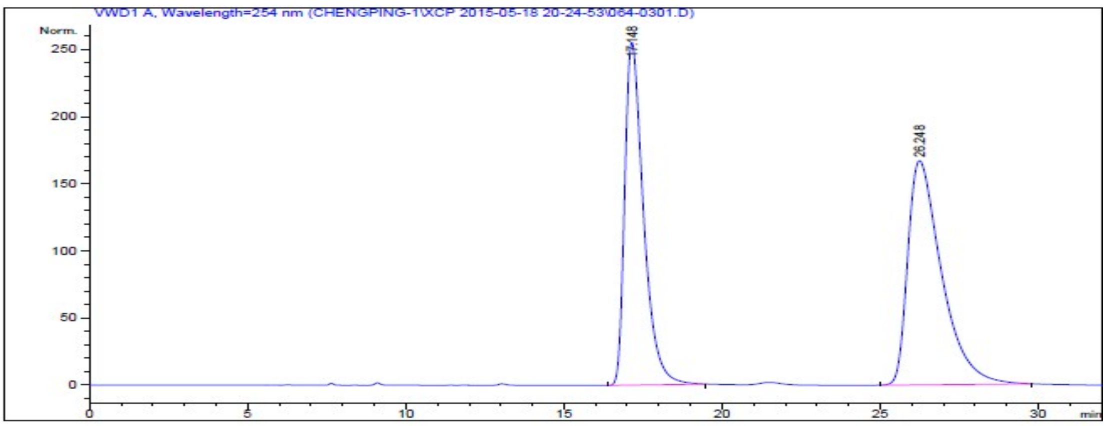
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.504 BB    0.6030  202.66948    4.69248    1.1273
   2  26.323 BB    1.1286 1.77762e4   236.22867   98.8727
```

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.148 BB    0.6284 1.05644e4   255.40074   45.9447
   2  26.248 BB    1.1184 1.24293e4   167.12021   54.0553
```
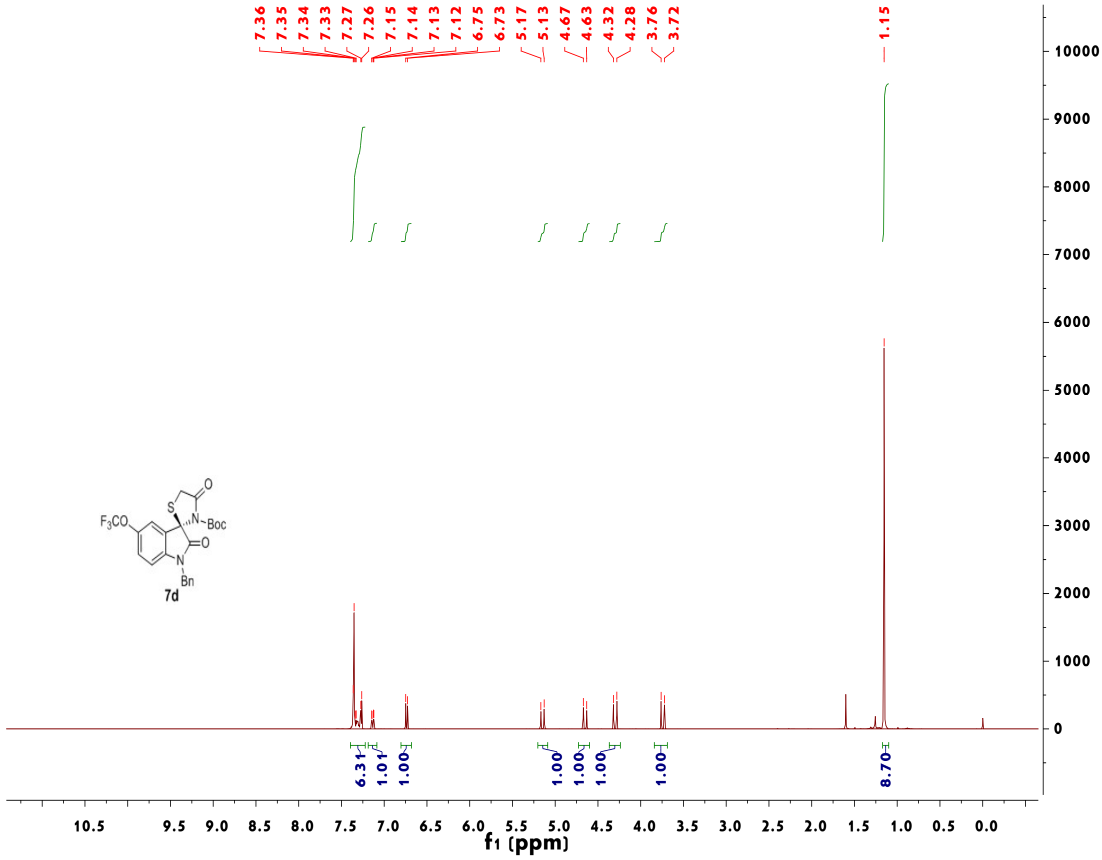
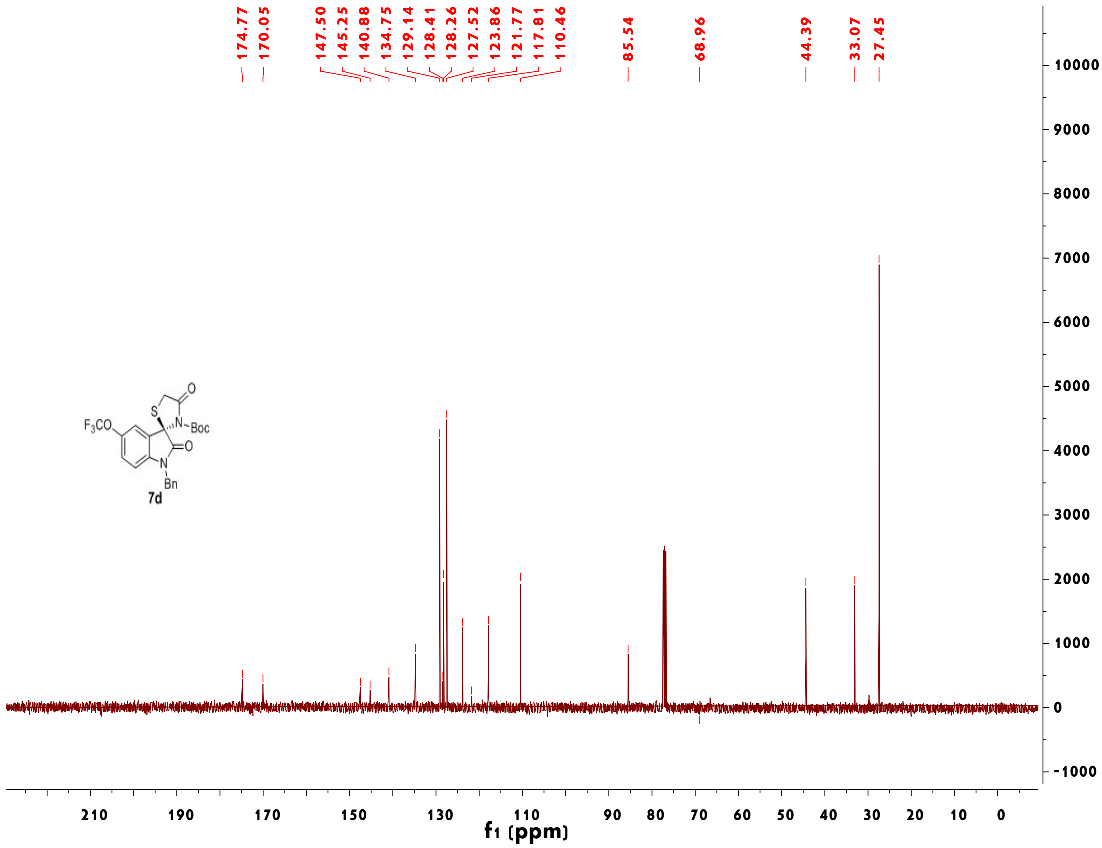
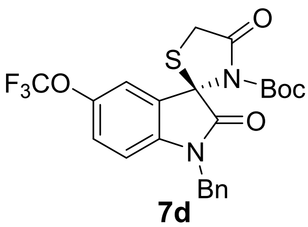
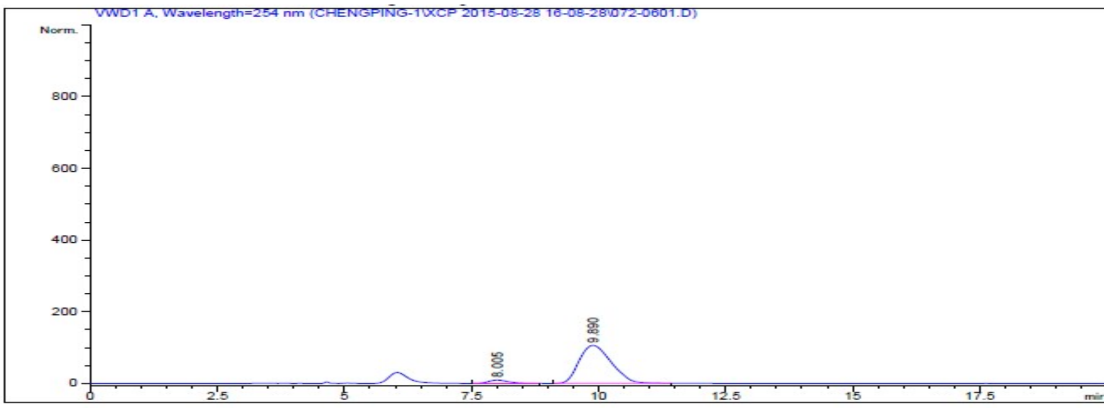


7.36
7.35
7.34
7.33
7.27
7.26
7.15
7.14
7.13
7.12
6.75
6.73
5.17
5.13
4.67
4.63
4.32
4.28
3.76
3.72
1.15
F3CO
S
O
N
Boc
O
N
Bn
7d
6.31
1.01
1.00
1.00
1.00
1.00
1.00
8.70
f1 (ppm)


174.77
170.05
147.50
145.25
140.88
134.75
129.14
128.41
128.26
127.52
123.86
121.77
117.81
110.46
85.54
68.96
44.39
33.07
27.45
F3CO
S
O
N
Boc
O
N
Bn
7d
f1 (ppm)



7d

63% yield, 90% ee

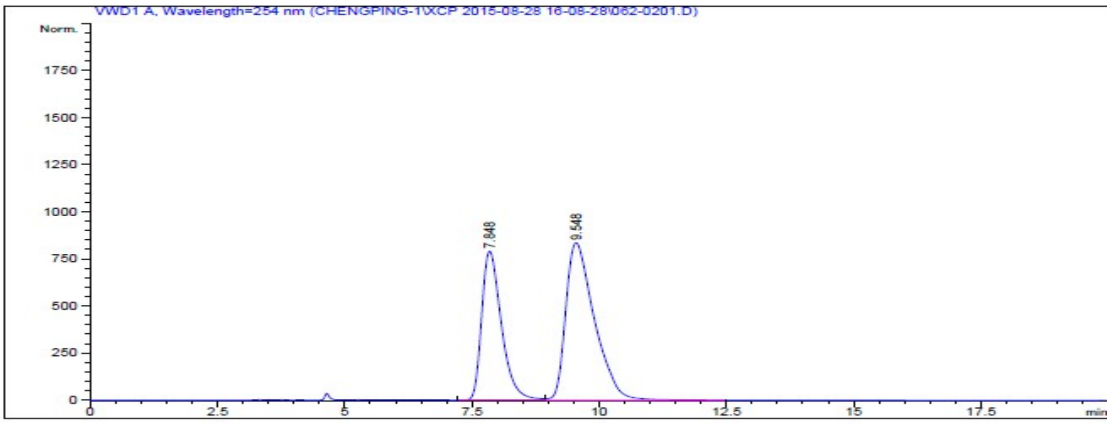


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.005	BB	0.4227	254.91299	9.31616	5.1775
2	9.890	BB	0.7006	4668.55127	105.95785	94.8225

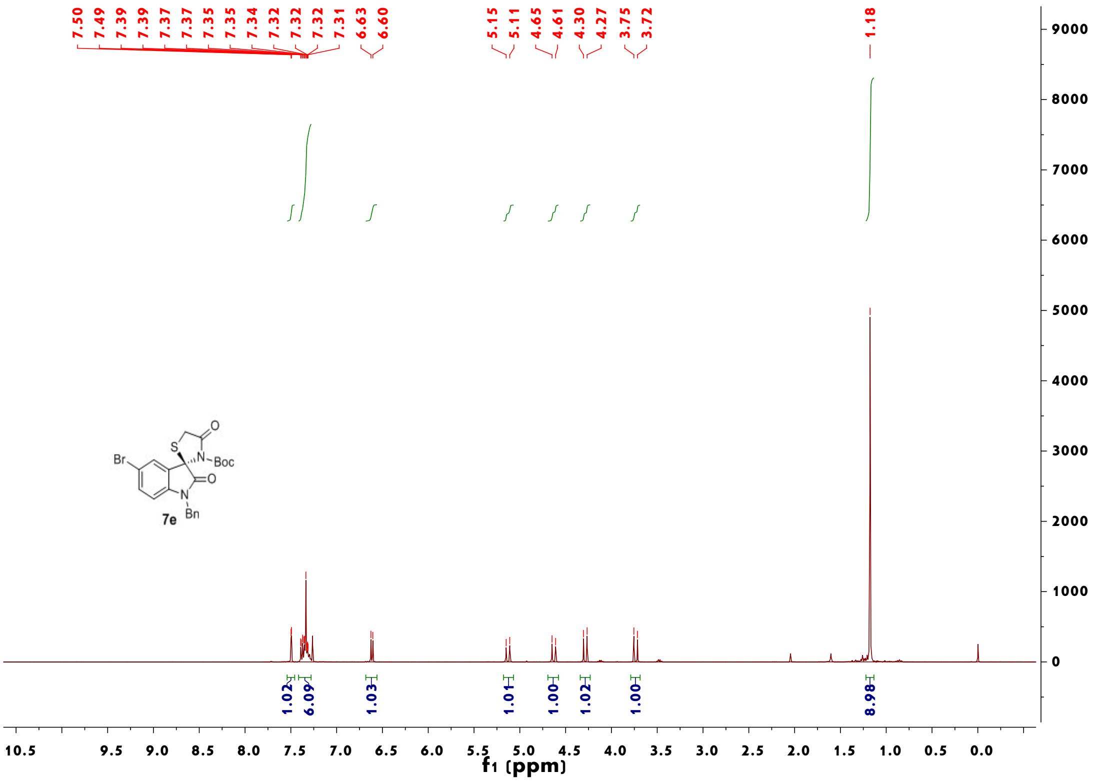


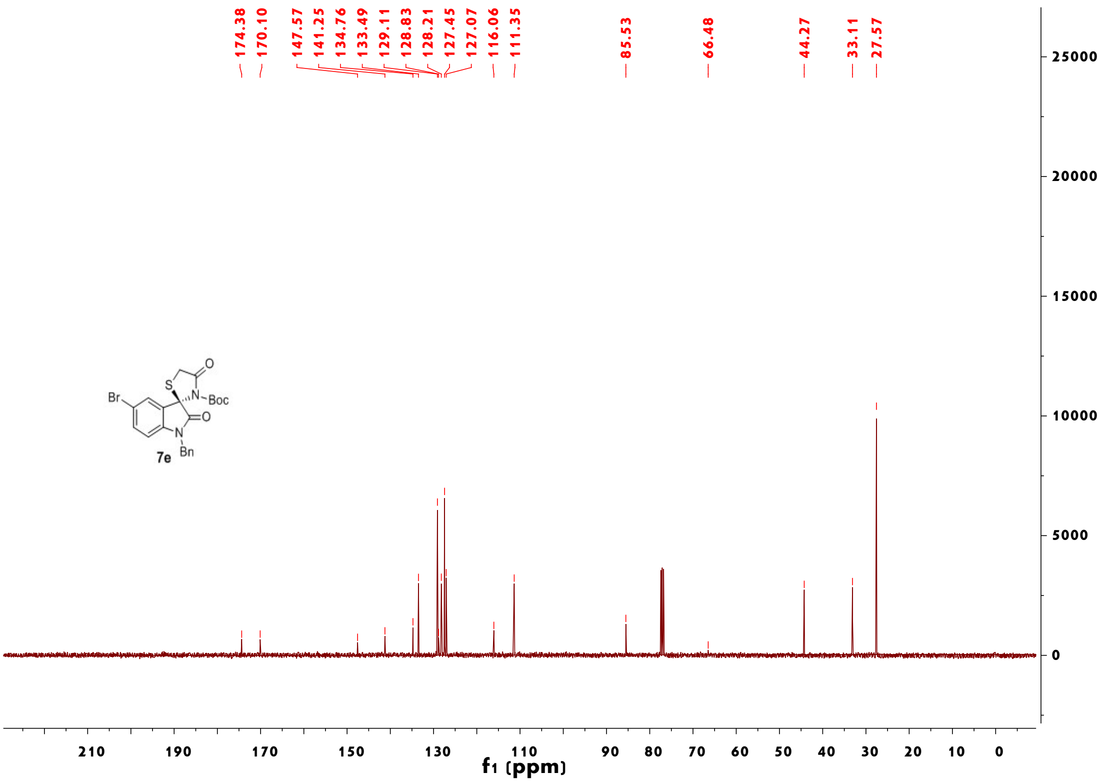
Area Percent Report

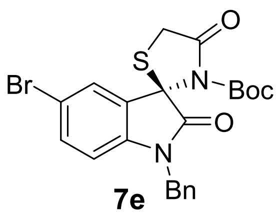
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.848	BV	0.4119	2.12869e4	790.33228	39.4435
2	9.548	VB	0.5847	3.26812e4	835.41962	60.5565

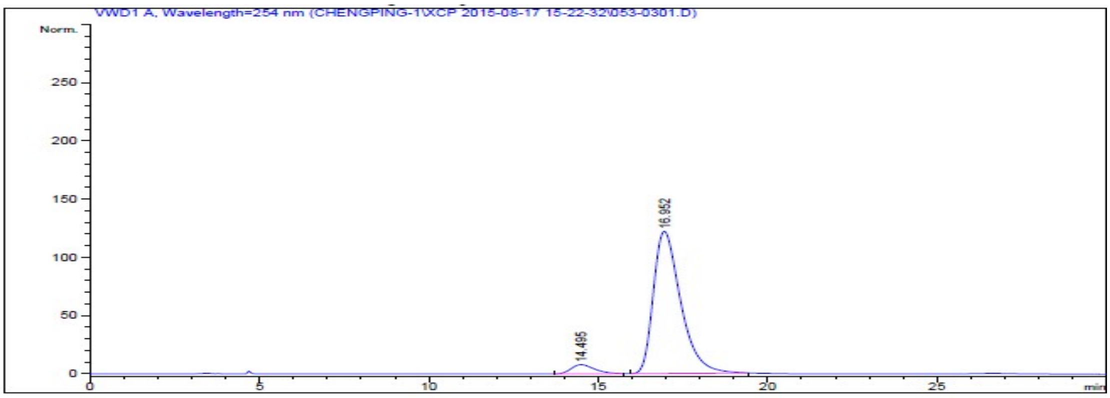

7.50
7.49
7.39
7.39
7.37
7.37
7.35
7.35
7.34
7.32
7.32
7.32
7.31
6.63
6.60
5.15
5.11
4.65
4.61
4.30
4.27
3.75
3.72
1.18
Br
S
O
N
Boc
O
N
Bn
7e
1.02
6.09
1.03
1.01
1.00
1.02
1.00
8.98
f1 (ppm)


174.38
170.10
147.57
141.25
134.76
133.49
129.11
128.83
128.21
127.45
127.07
116.06
111.35
85.53
66.48
44.27
33.11
27.57
Br
S
O
N
Boc
O
N
Bn
7e
f1 (ppm)



7e

55% yield, 90% ee

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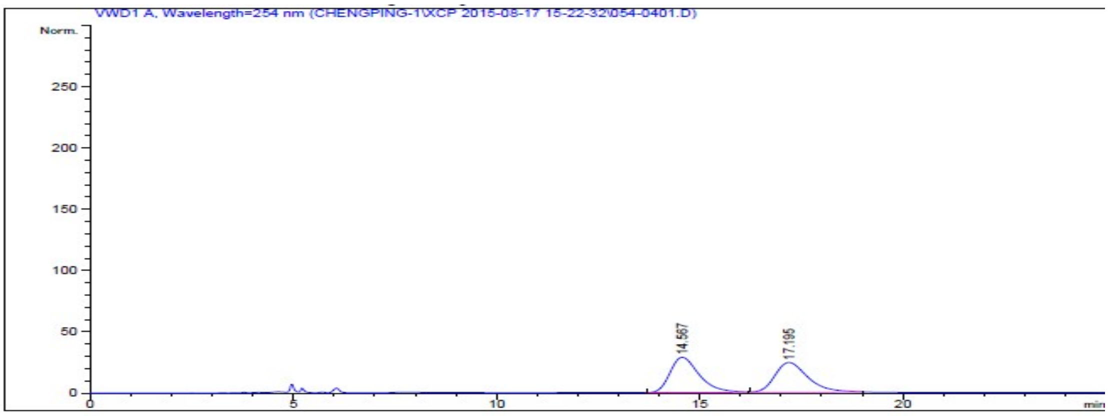
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  14.495 BB    0.6928  378.23825    7.87737   5.2327
   2  16.952 BB    0.8632 6850.11475  122.05778  94.7673
```

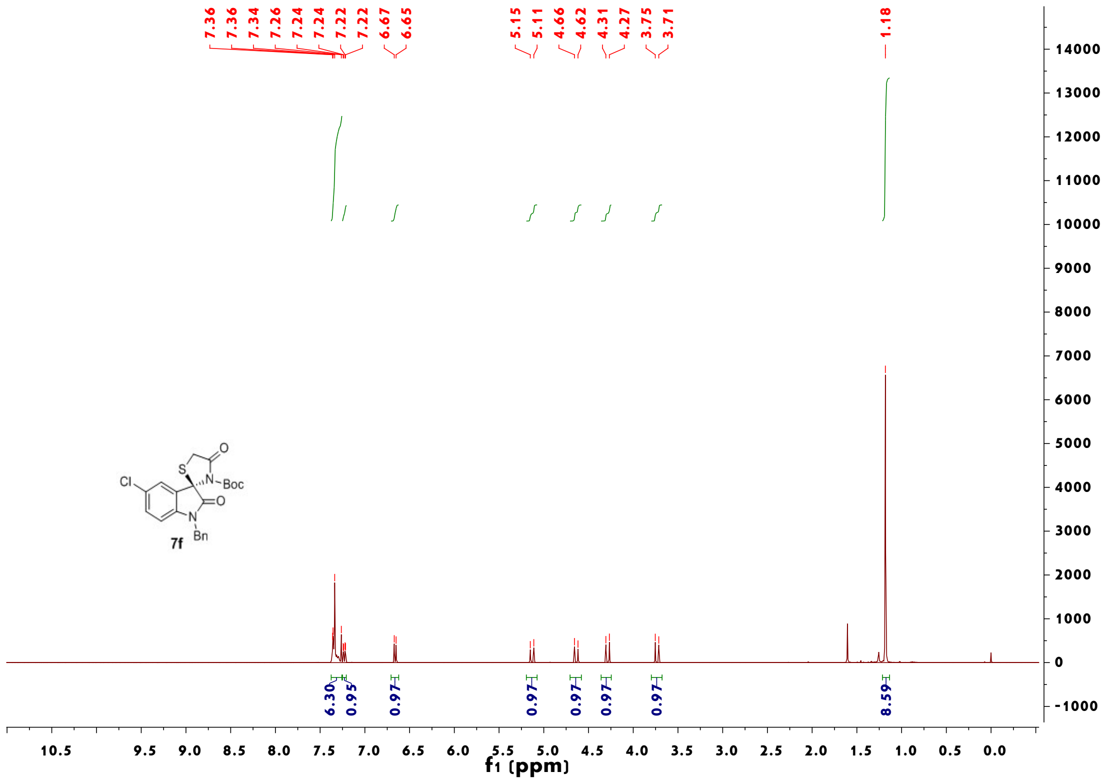


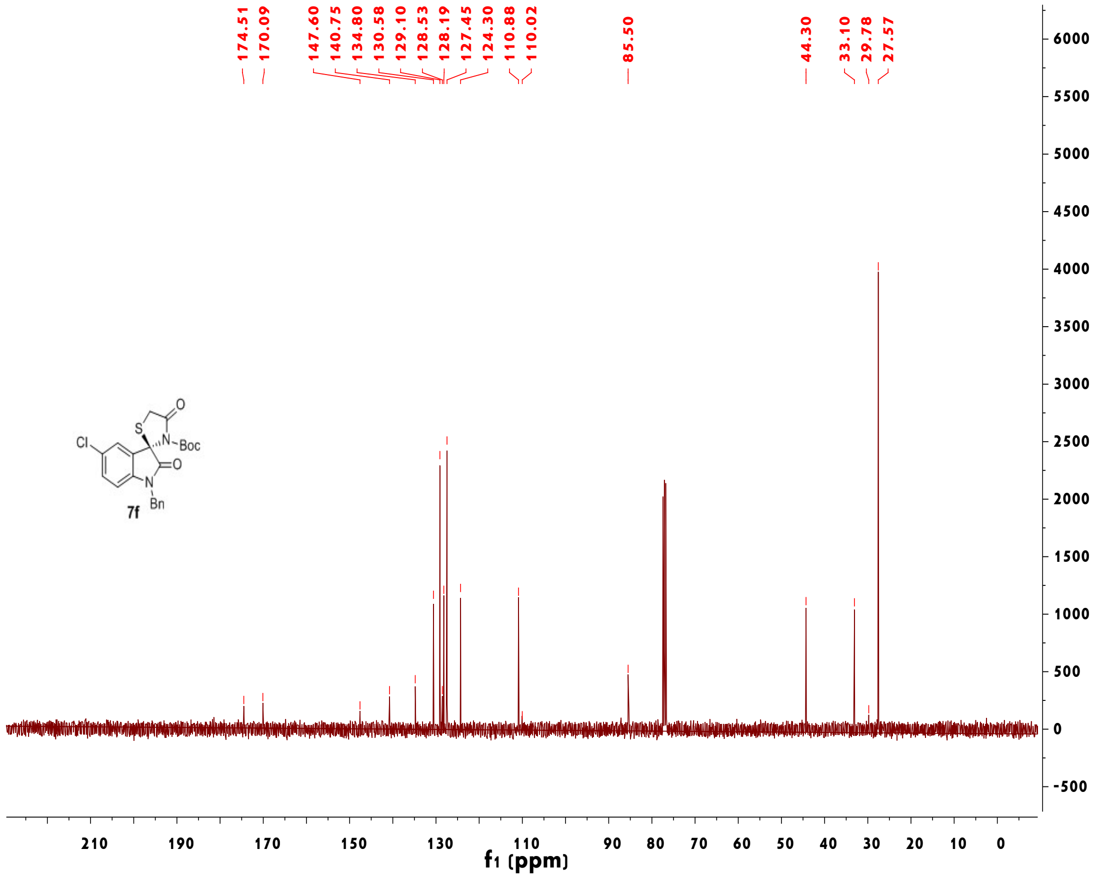

```
=====================================================================
                        Area Percent Report
=====================================================================

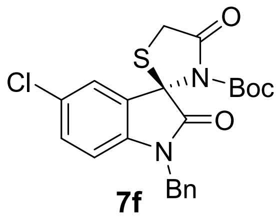
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  14.567 BB    0.7572 1432.75305   28.70770  51.2532
   2  17.195 BB    0.8526 1362.68884   24.18878  48.7468
```

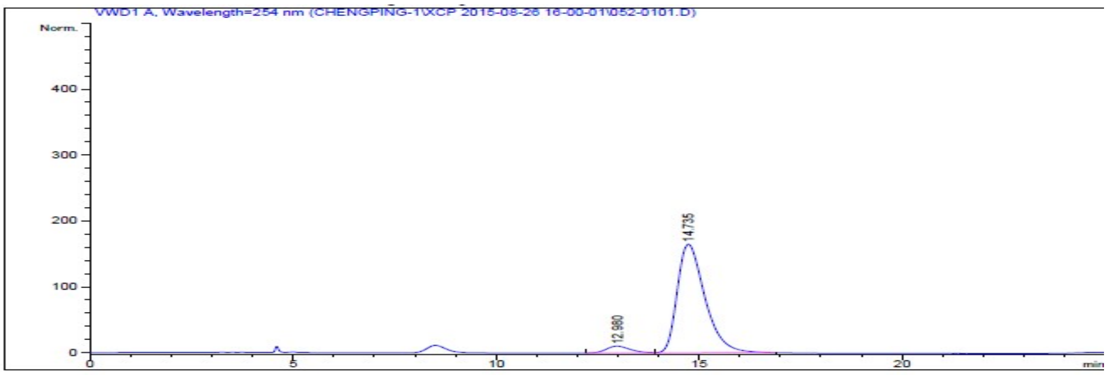

7.36
7.36
7.34
7.26
7.24
7.24
7.22
7.22
6.67
6.65
5.15
5.11
4.66
4.62
4.31
4.27
3.75
3.71
1.18
Cl
S
O
N
Boc
O
N
Bn
7f
6.30
0.95
0.97
0.97
0.97
0.97
0.97
8.59
f1 (ppm)


174.51
170.09
147.60
140.75
134.80
130.58
129.10
128.53
128.19
127.45
124.30
110.88
110.02
85.50
44.30
33.10
29.78
27.57
Cl
S
O
N
Boc
O
N
Bn
7f
f1 (ppm)



7f

64% yield, 90% ee

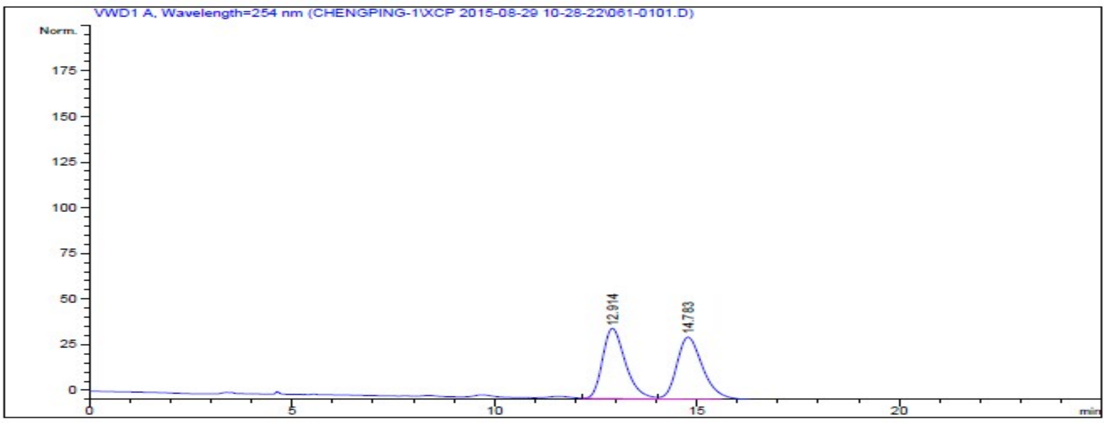


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.980	BV	0.6218	419.55905	10.28321	5.0853
2	14.735	VB	0.7269	7830.91699	165.09505	94.9147

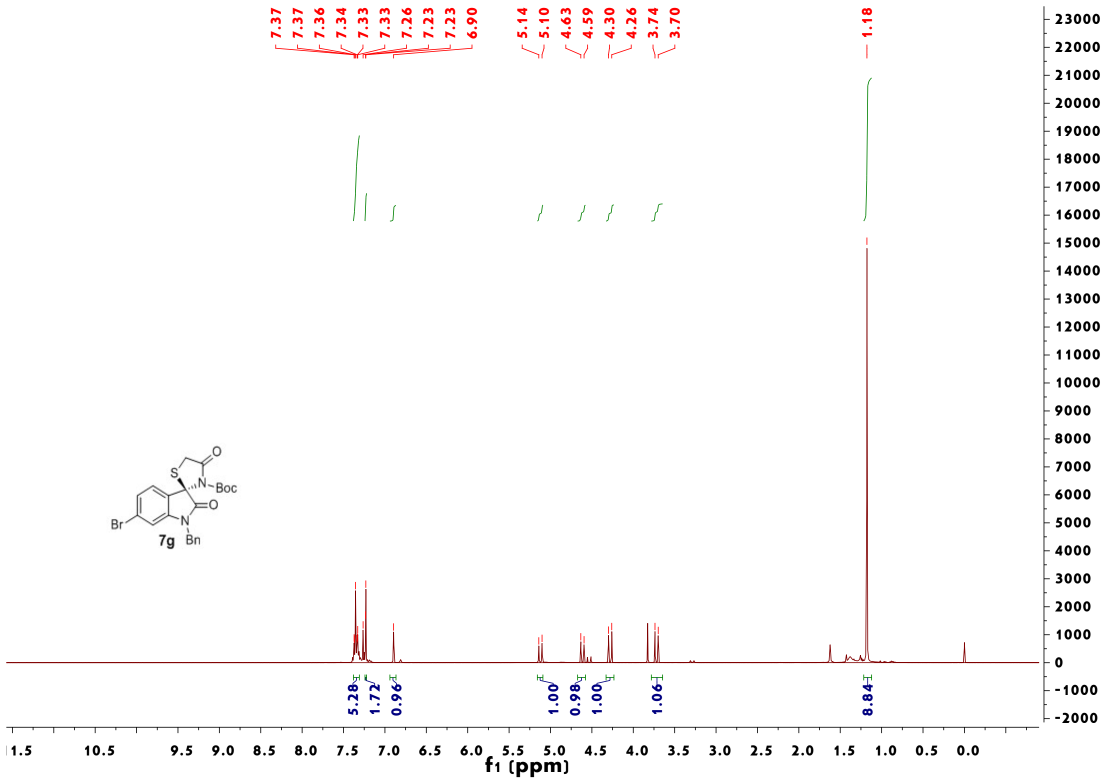


Area Percent Report

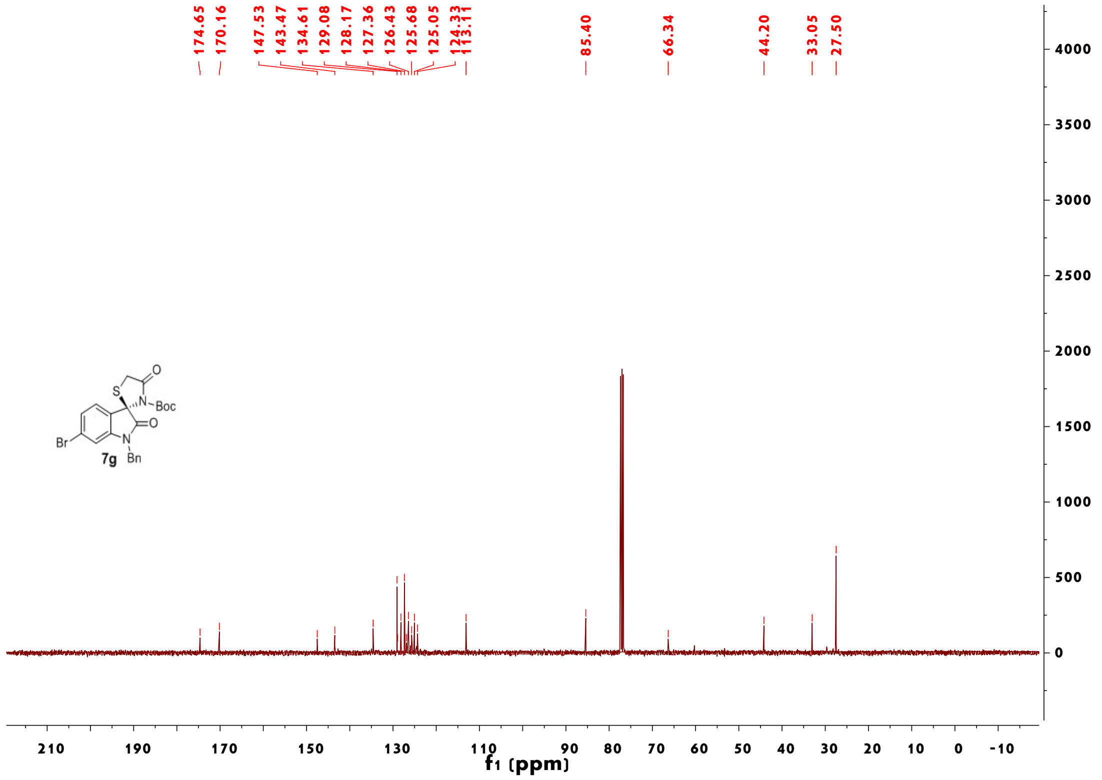
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

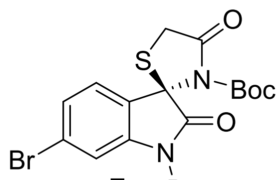
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.914	VB	0.5963	1505.58594	38.36669	49.8677
2	14.783	BB	0.6897	1513.57556	34.01672	50.1323



7.37 7.37 7.36 7.34 7.33 7.33 7.26 7.23 7.23 6.90 5.14 5.10 4.63 4.59 4.30 4.26 3.74 3.70 1.18
5.28 1.72 0.96 1.00 0.98 1.00 1.06 8.84
S
N
Boc
O
O
Br
N
Bn
7g
f1 (ppm)

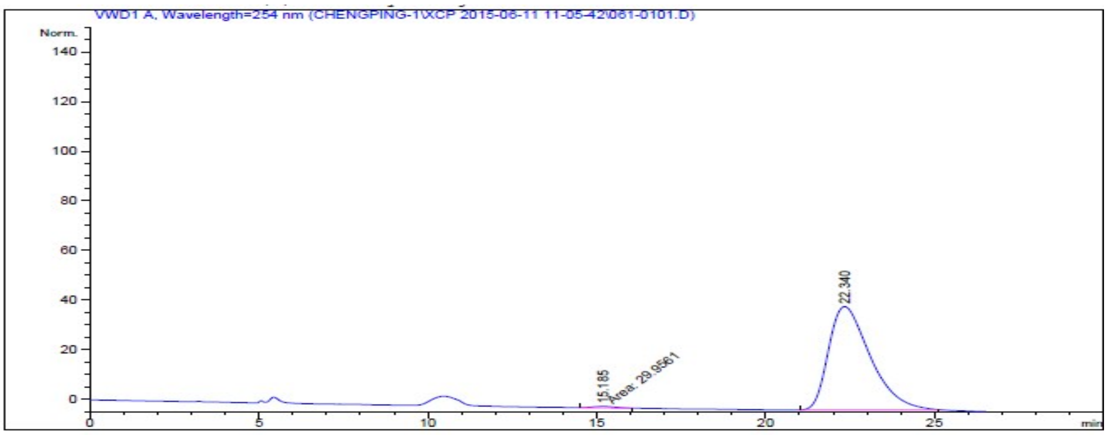


174.65 170.16 147.53 143.47 134.61 129.08 128.17 127.36 126.43 125.68 125.05 124.33 113.11 85.40 66.34 44.20 33.05 27.50
S
N
Boc
O
O
Br
N
Bn
7g
f1 (ppm)



7g

57% yield, 98% ee

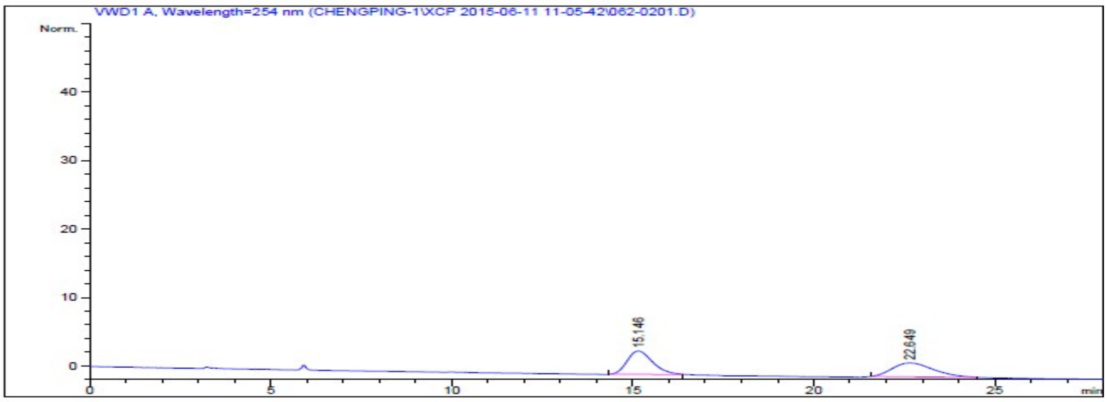


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.185	MM	0.8157	29.95611	6.12088e-1	0.8281
2	22.340	BB	1.2405	3587.53418	41.73580	99.1719

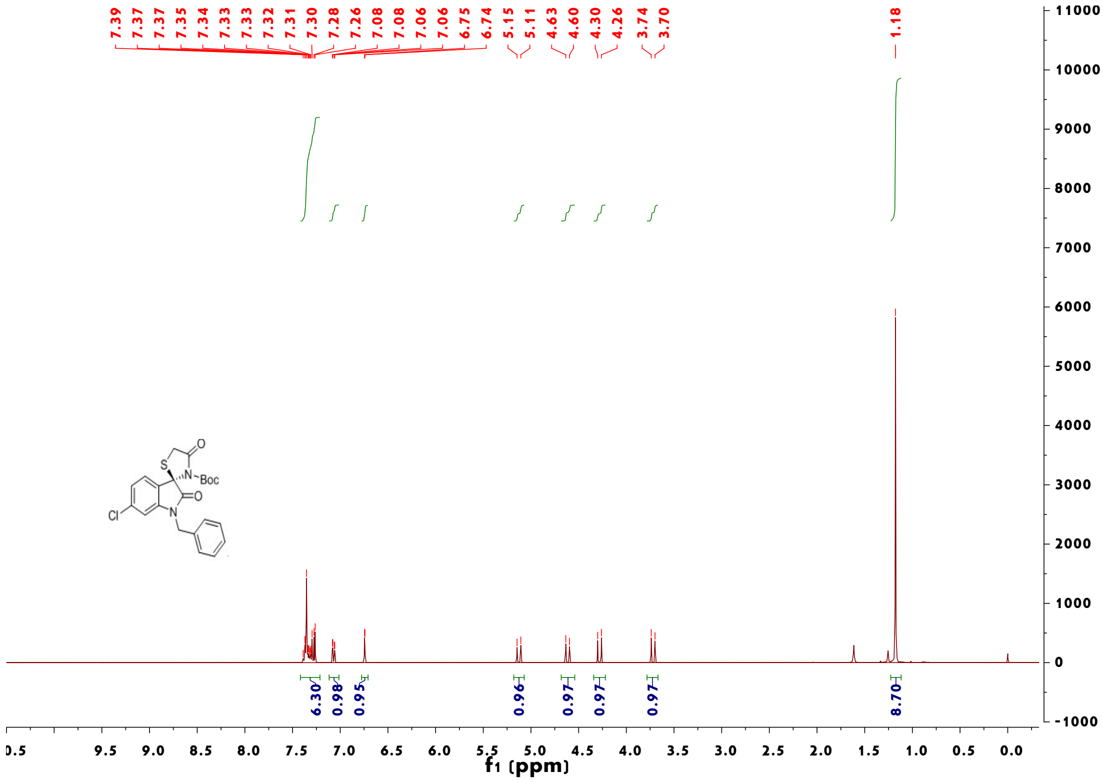


Area Percent Report

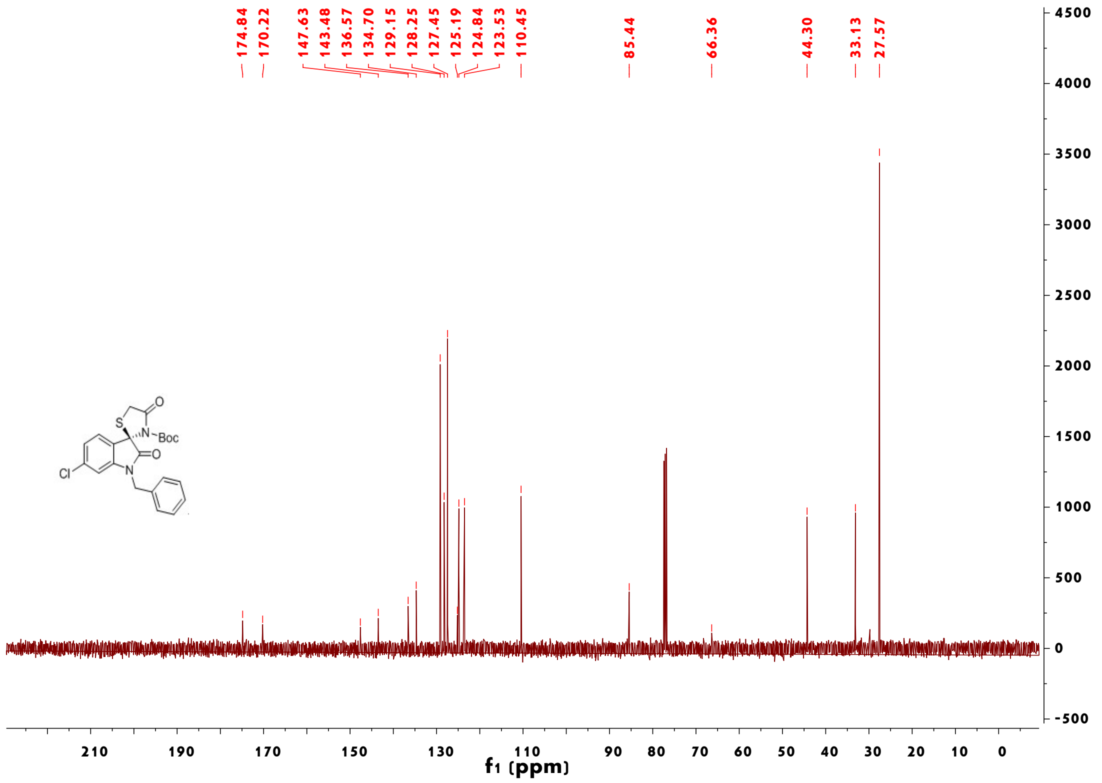
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

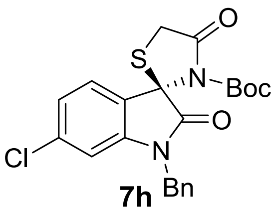
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.146	BB	0.6305	166.68509	3.41632	50.9755
2	22.649	BB	0.9386	160.30540	2.01134	49.0245



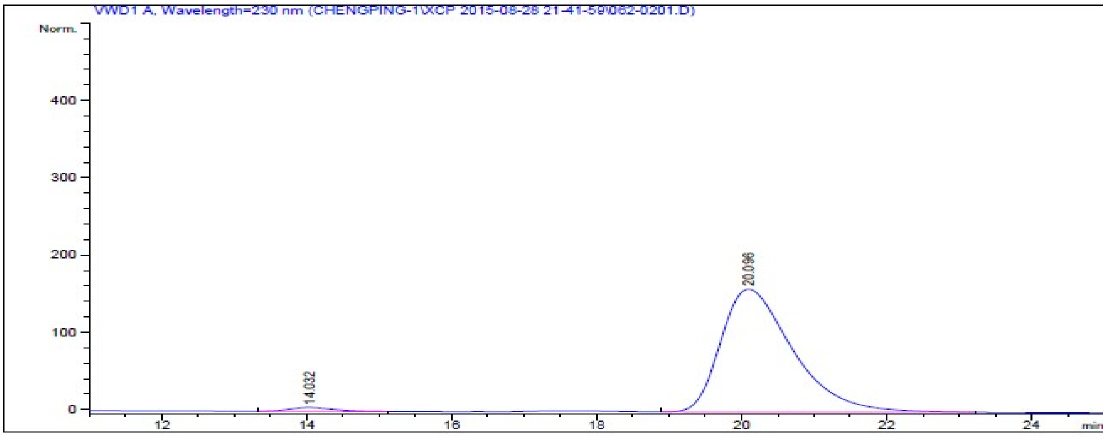
7.39
7.37
7.37
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.28
7.26
7.08
7.08
7.06
7.06
6.75
6.74
5.15
5.11
4.63
4.60
4.30
4.26
3.74
3.70
1.18
6.30
0.98
0.95
0.96
0.97
0.97
0.97
8.70
f1 (ppm)



174.84
170.22
147.63
143.48
136.57
134.70
129.15
128.25
127.45
125.19
124.84
123.53
110.45
85.44
66.36
44.30
33.13
27.57
f1 (ppm)



63% yield, 96% ee

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.032 BB    0.6186  212.73338    5.09250   1.8979
   2  20.096 VB    1.0549 1.09959e4   158.94177  98.1021
```

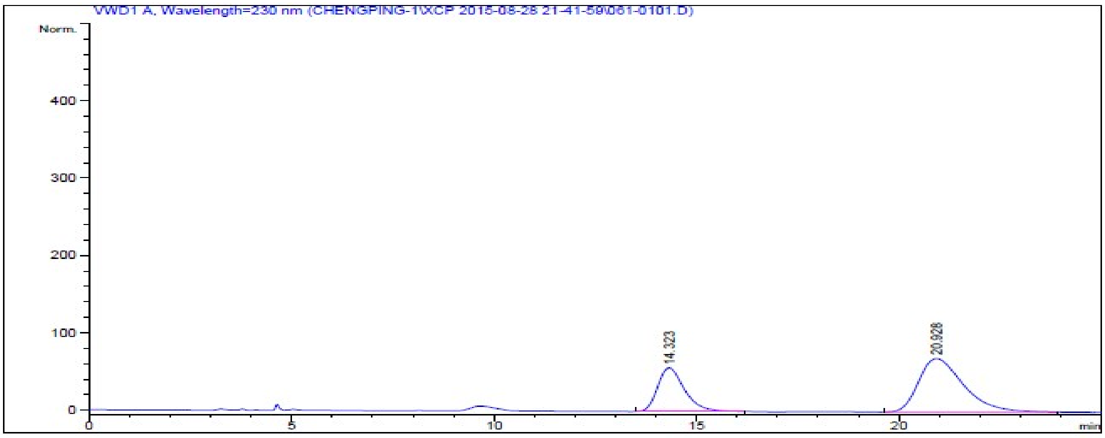


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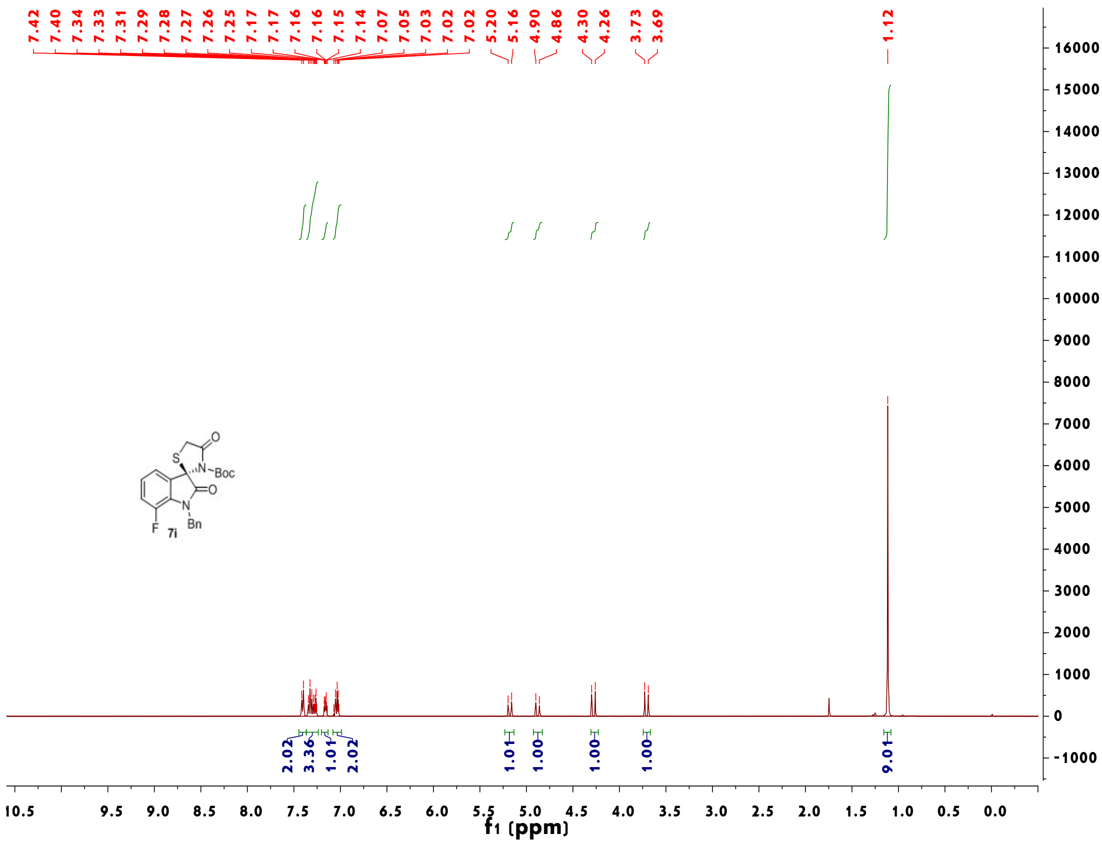
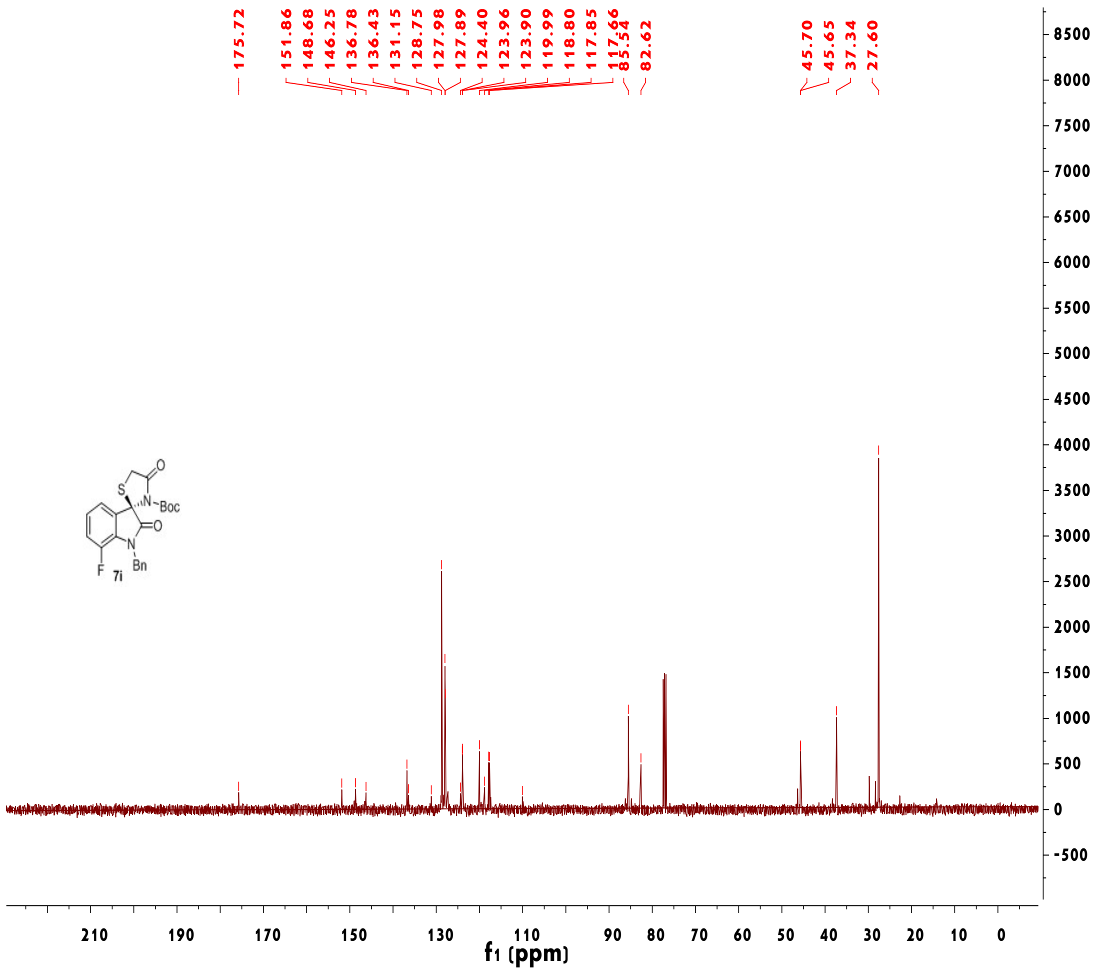
=====================================================================
                        Area Percent Report
=====================================================================

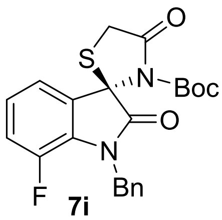
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

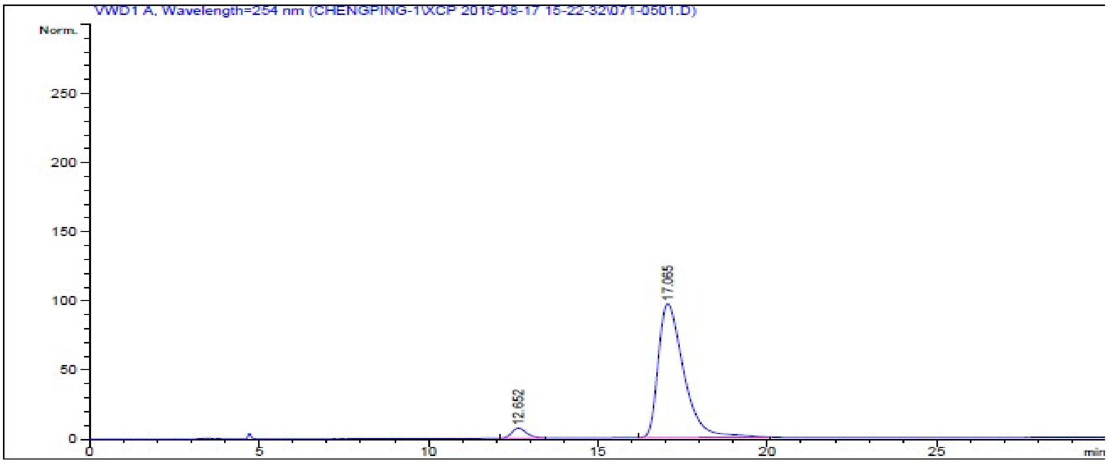
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.323 BB    0.7015 2603.90381   56.44446  32.8287
   2  20.928 BB    1.1848 5327.88770   69.02229  67.1713
```







58% yield, 92% ee

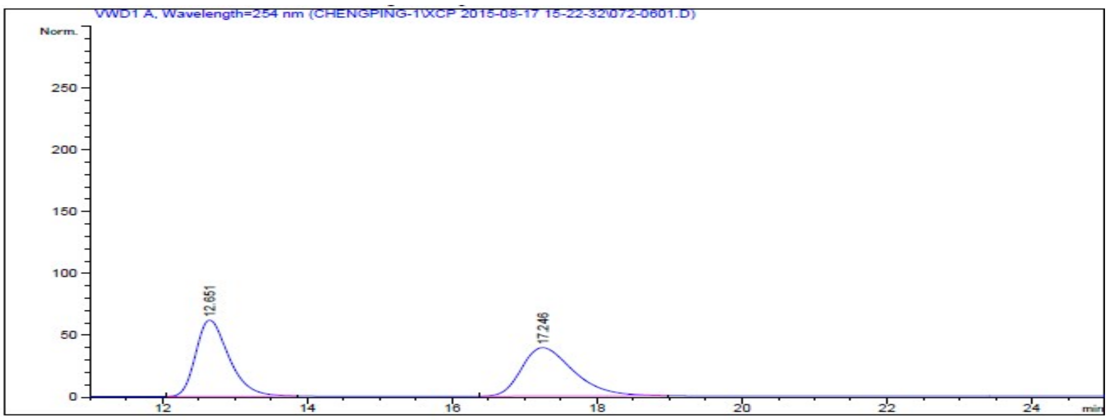


Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.652	BB	0.4652	218.83084	7.17305	4.1559
2	17.065	BB	0.7911	5046.68994	96.70589	95.8441

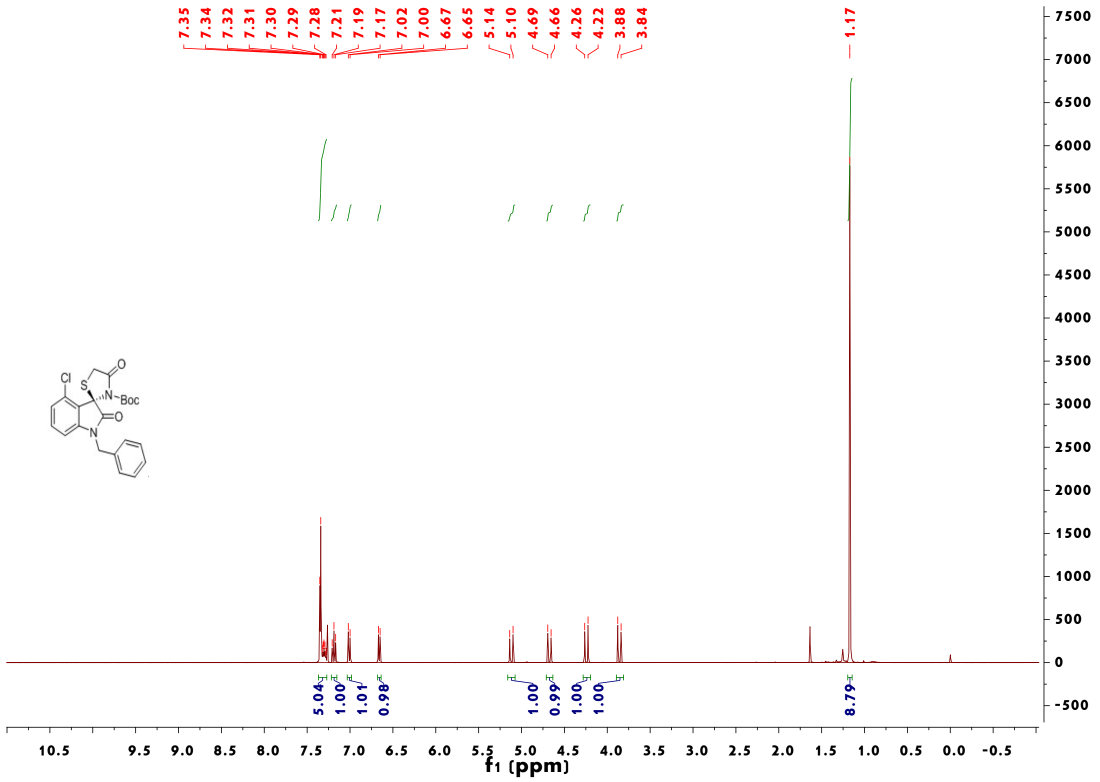


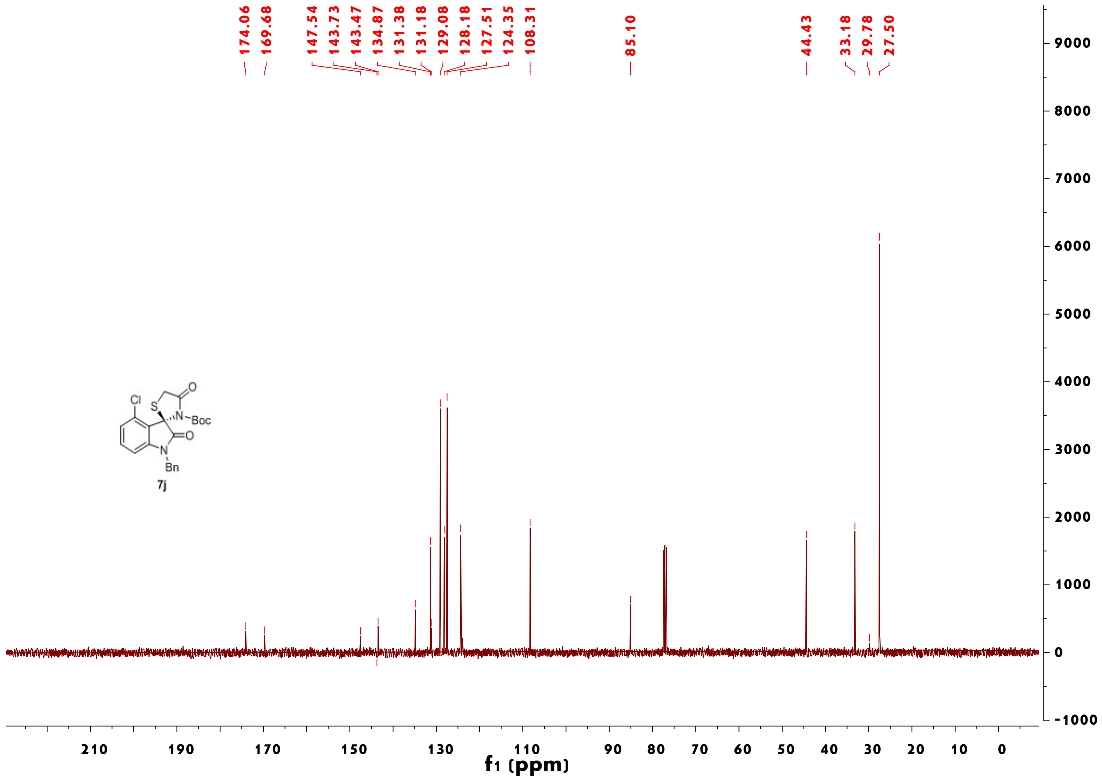
Area Percent Report

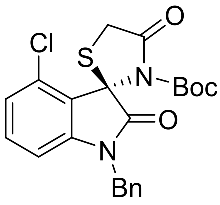
```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.651	BB	0.4888	1958.16650	61.62863	50.1136
2	17.246	BB	0.7594	1949.29175	39.10760	49.8864

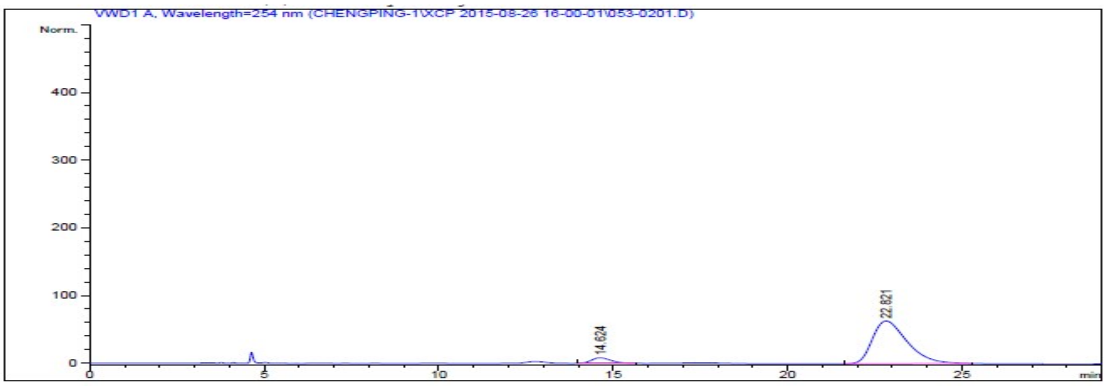

7.35 7.34 7.32 7.31 7.30 7.29 7.28 7.21 7.19 7.17 7.02 7.00 6.67 6.65 5.14 5.10 4.69 4.66 4.26 4.22 3.88 3.84 1.17
Cl
S
O
N
Boc
5.04 1.00 1.01 0.98 1.00 0.99 1.00 1.00 8.79
f1 (ppm)


174.06 169.68 147.54 143.73 143.47 134.87 131.38 131.18 129.08 128.18 127.51 124.35 108.31 85.10 44.43 33.18 29.78 27.50
Cl
S
O
N
Boc
Bn
7j
f1 (ppm)



7j

54% yield, 88% ee

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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.624 BB     0.5824  317.03241    8.14506   6.7881
   2  22.821 BB     1.0384 4353.35010   63.07600  93.2119
```
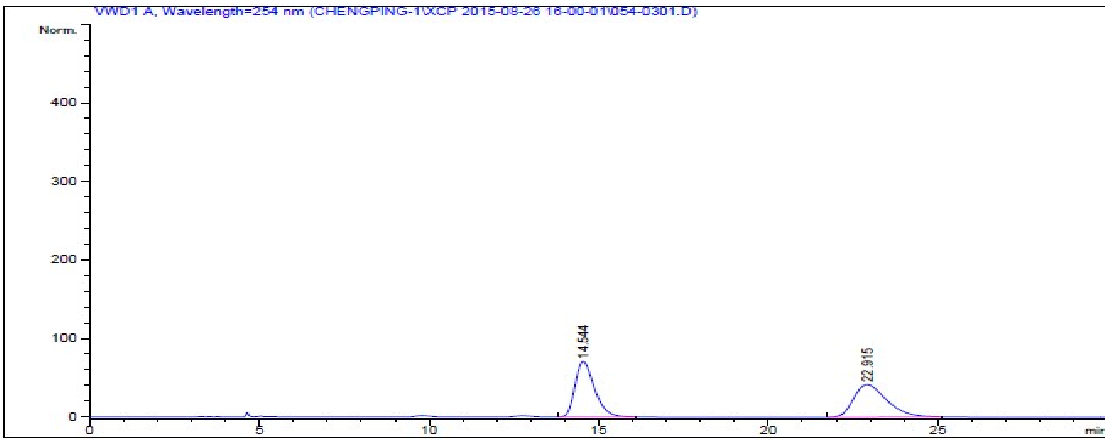
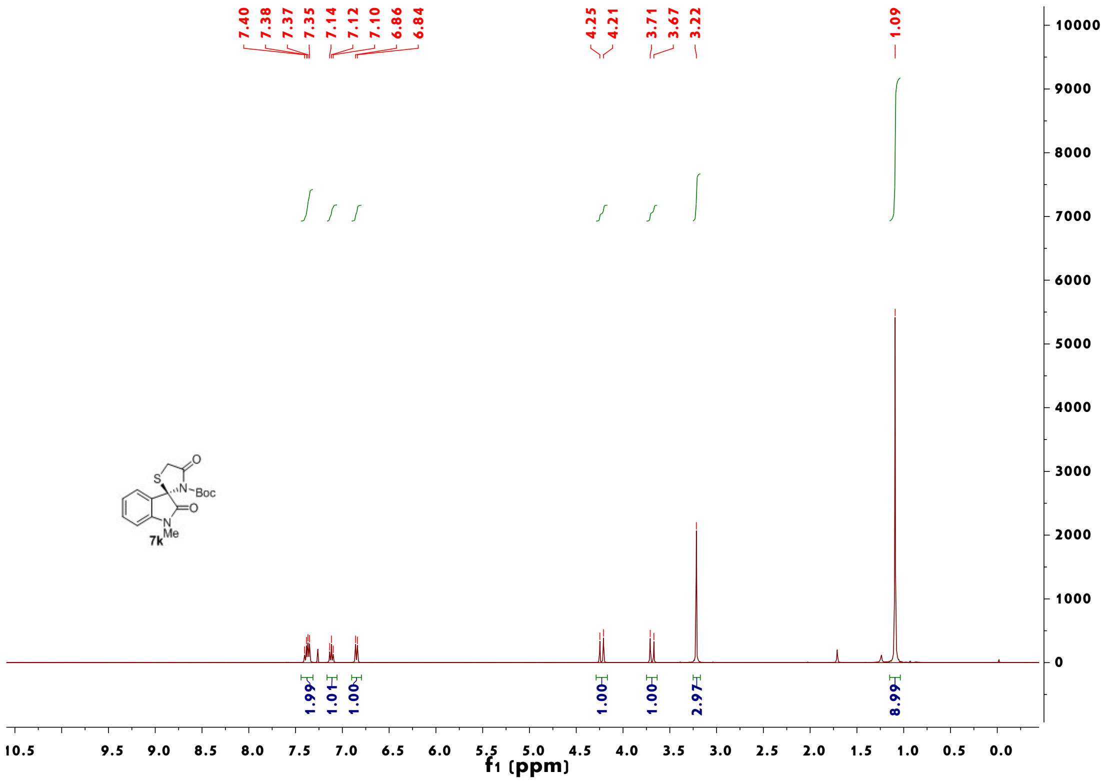
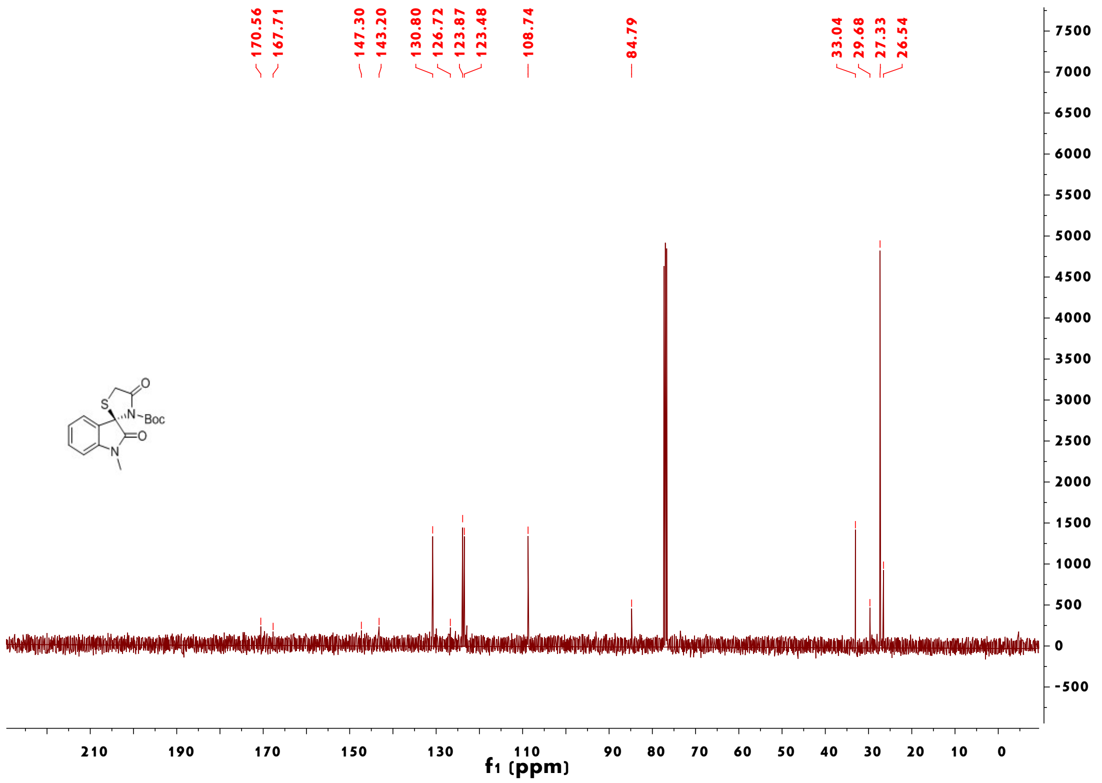
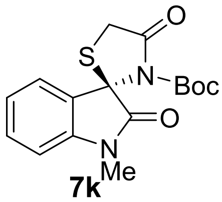




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.544 BB     0.6084 2813.12061   70.71190  50.0548
   2  22.915 BB     1.0421 2806.96582   41.30590  49.9452
```

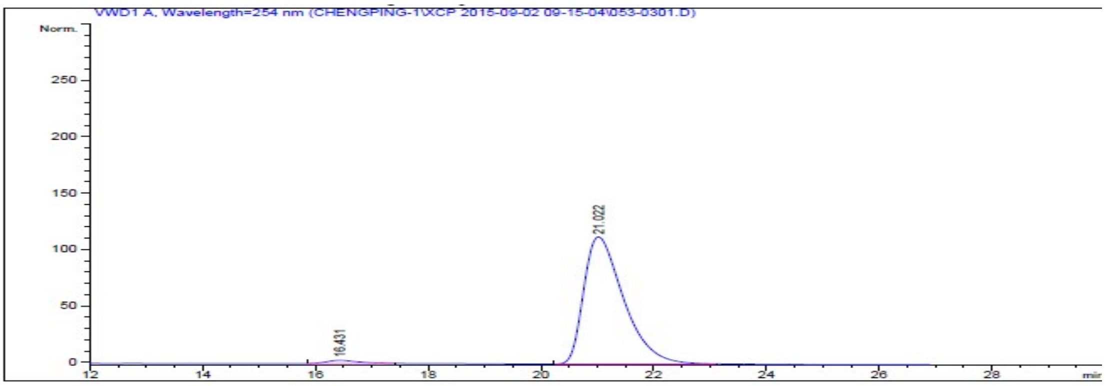

7.40
7.38
7.37
7.35
7.14
7.12
7.10
6.86
6.84
4.25
4.21
3.71
3.67
3.22
1.09
7k
1.99
1.01
1.00
1.00
1.00
2.97
8.99
f1 (ppm)


170.56
167.71
147.30
143.20
130.80
126.72
123.87
123.48
108.74
84.79
33.04
29.68
27.33
26.54
f1 (ppm)



7k

65% yield, 96% e

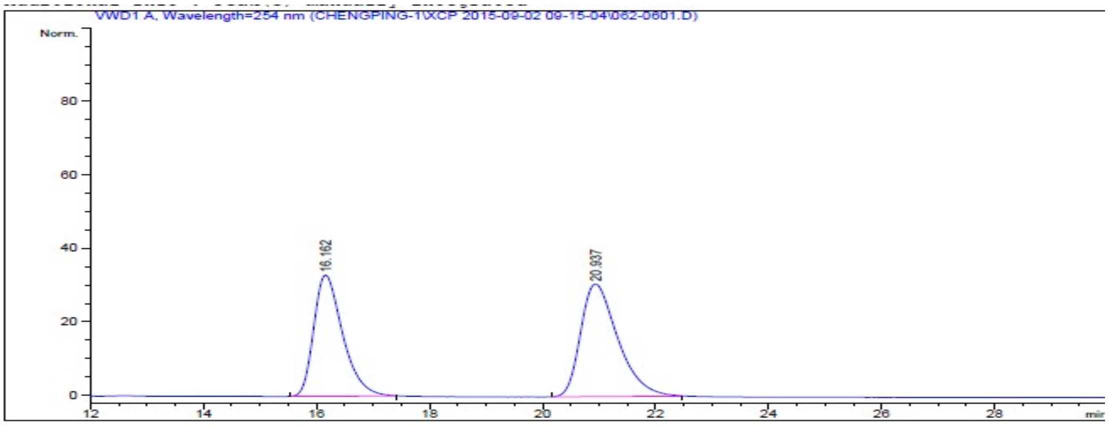


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.431	BB	0.5316	106.05154	2.75879	1.8796
2	21.022	BB	0.7525	5536.19043	112.68056	98.1204

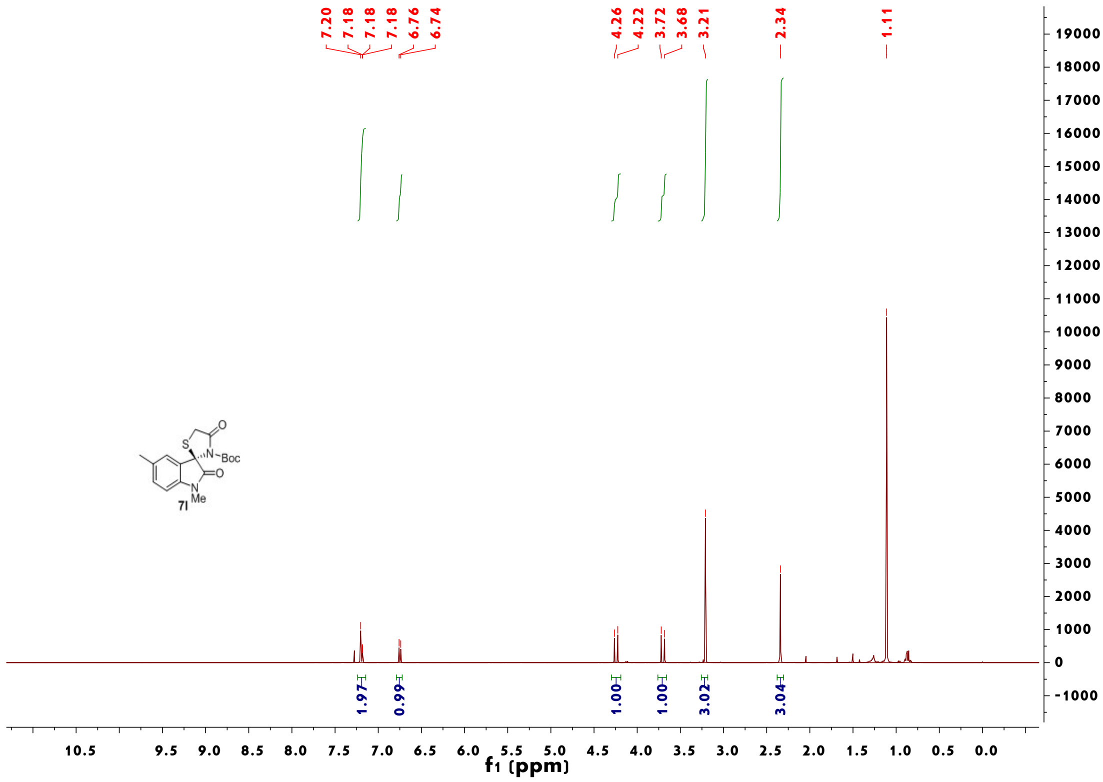


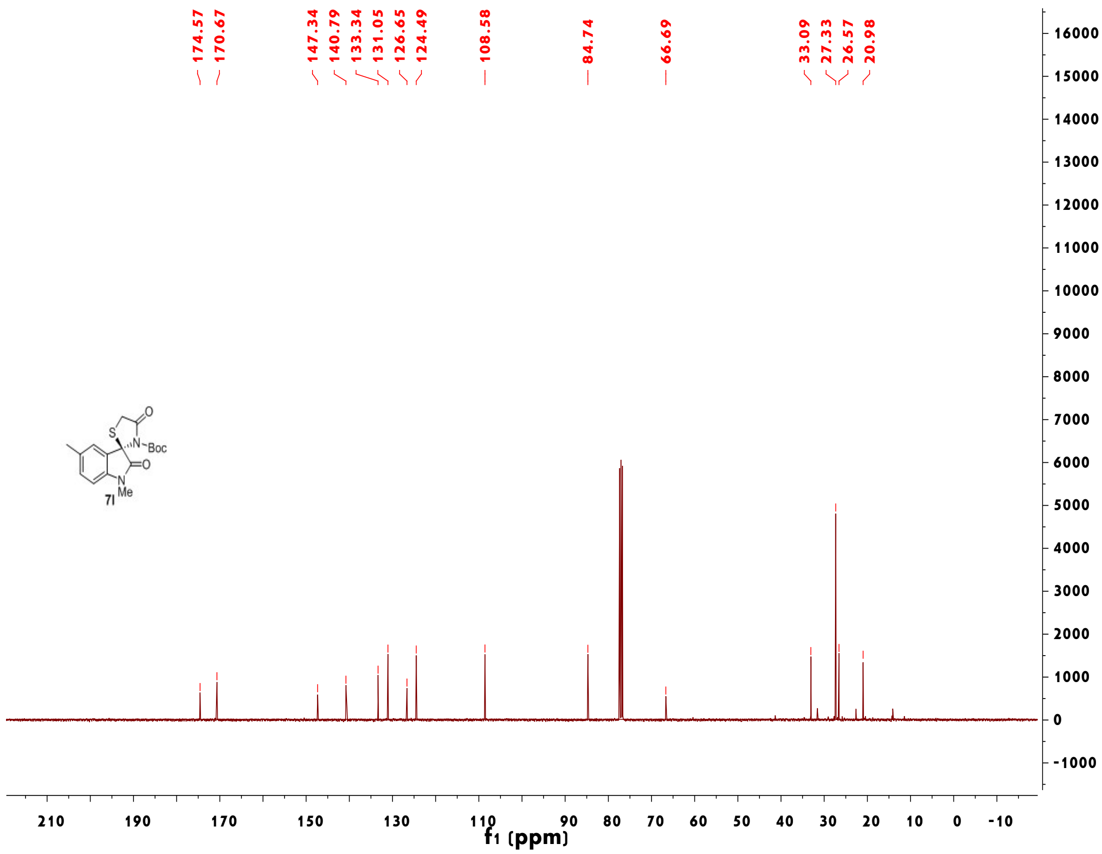
Area Percent Report

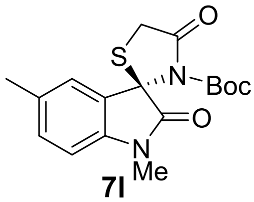
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.162	BB	0.5436	1174.17786	32.98097	45.5332
2	20.937	BB	0.6990	1404.55225	30.66944	54.4668

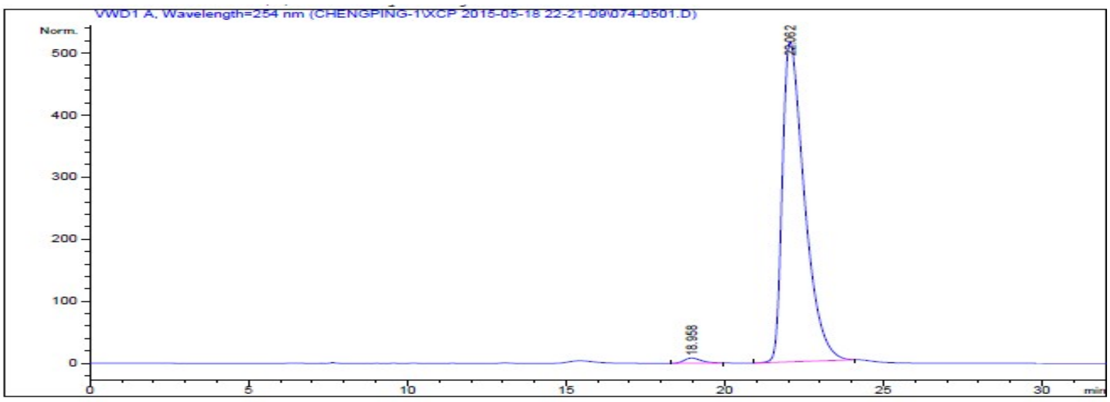

7.20
7.18
7.18
7.18
6.76
6.74
4.26
4.22
3.72
3.68
3.21
2.34
1.11
1.97
0.99
1.00
1.00
3.02
3.04
f1 (ppm)
7l


174.57
170.67
147.34
140.79
133.34
131.05
126.65
124.49
108.58
84.74
66.69
33.09
27.33
26.57
20.98
f1 (ppm)
7l



7l

55% yield, 97% ee

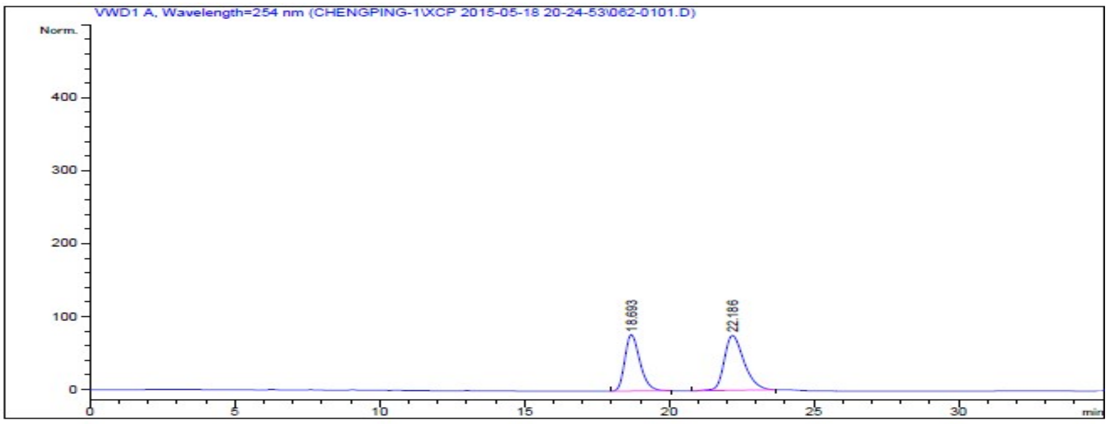


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.958	BB	0.5658	313.16971	8.32238	1.2383
2	22.062	BB	0.7351	2.49767e4	516.16107	98.7617

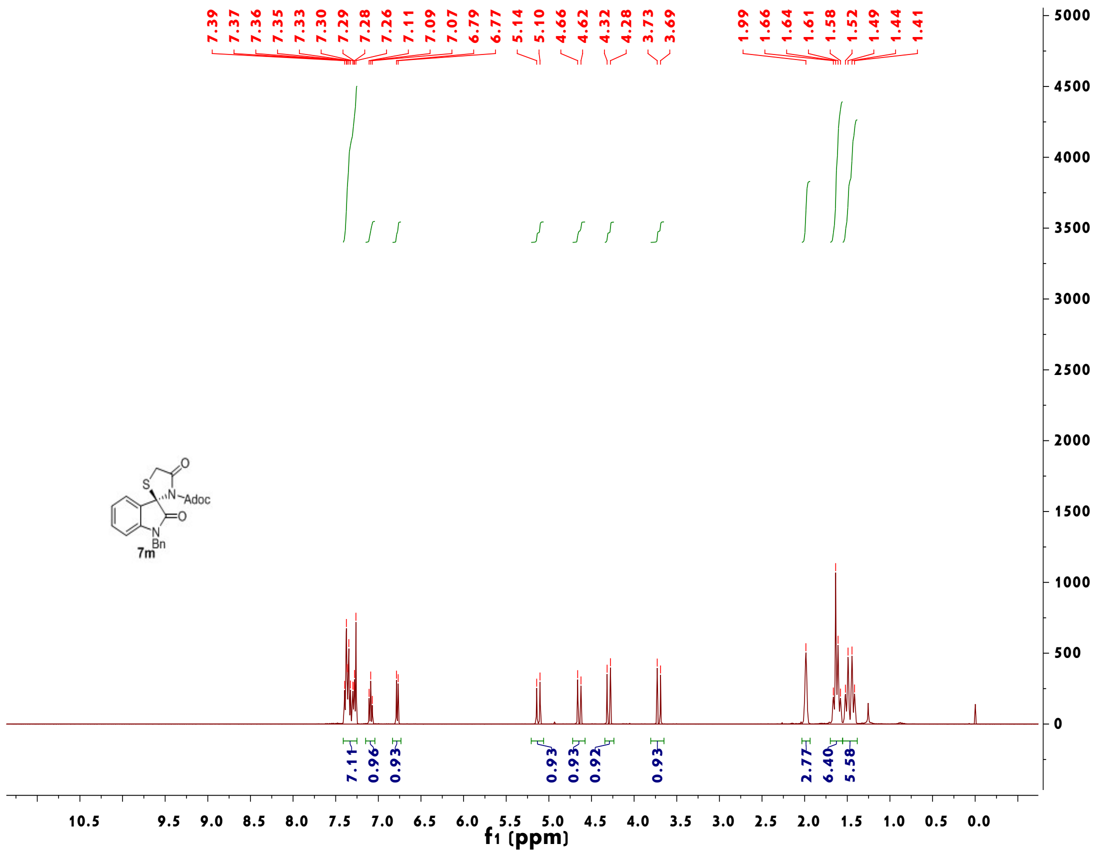


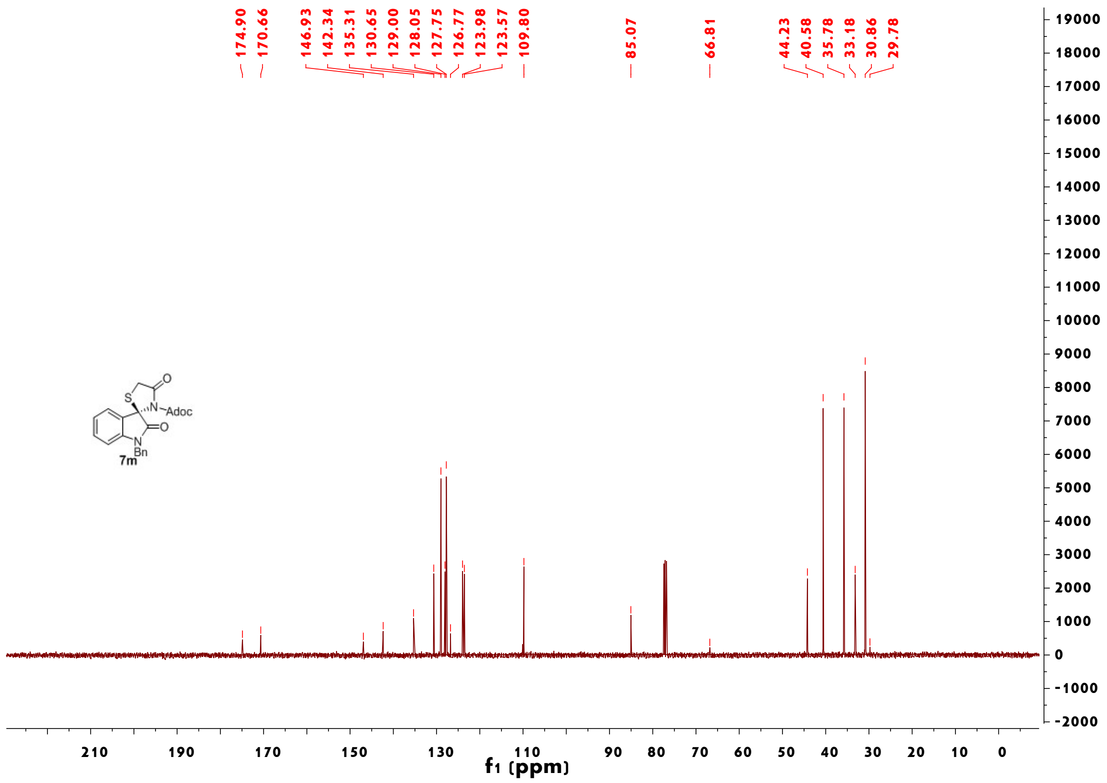
Area Percent Report

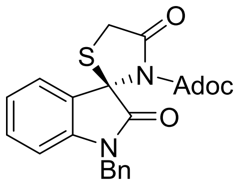
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.693	BB	0.5590	2808.15820	77.38016	43.9496
2	22.186	BB	0.7270	3581.33594	75.28027	56.0504

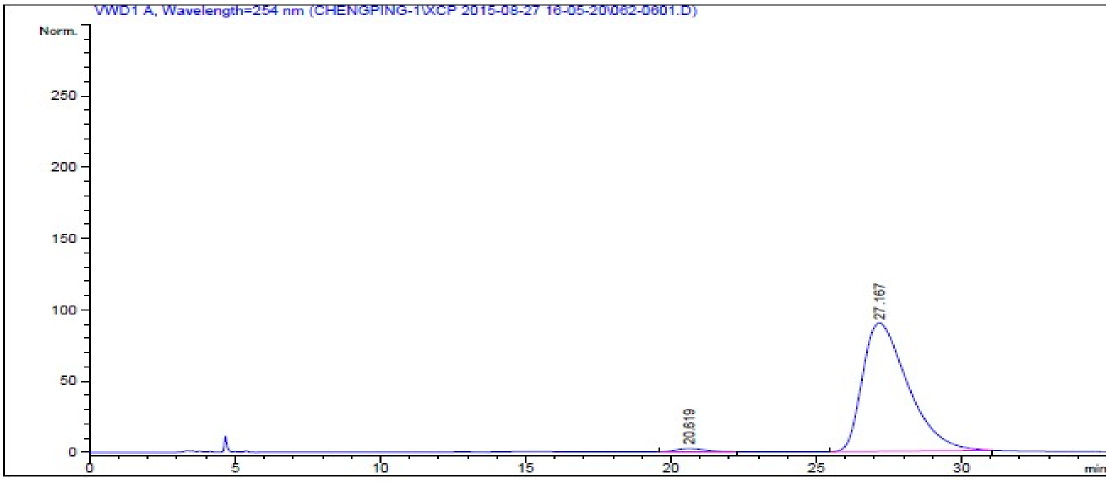

7.39 7.37 7.36 7.35 7.33 7.30 7.29 7.28 7.26 7.11 7.09 7.07 6.79 6.77 5.14 5.10 4.66 4.62 4.32 4.28 3.73 3.69 1.99 1.66 1.64 1.61 1.58 1.52 1.49 1.44 1.41
S
N
Adoc
O
N
Bn
O
7m
7.11 0.96 0.93 0.93 0.93 0.92 0.93 2.77 6.40 5.58
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.90 170.66 146.93 142.34 135.31 130.65 129.00 128.05 127.75 126.77 123.98 123.57 109.80 85.07 66.81 44.23 40.58 35.78 33.18 30.86 29.78
S
N
Adoc
O
N
Bn
O
7m
19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



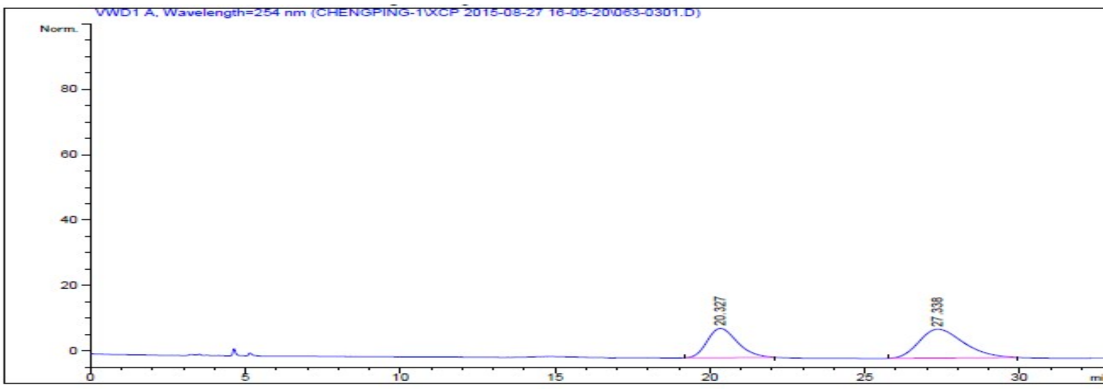
7m

53% yield, 97% ee



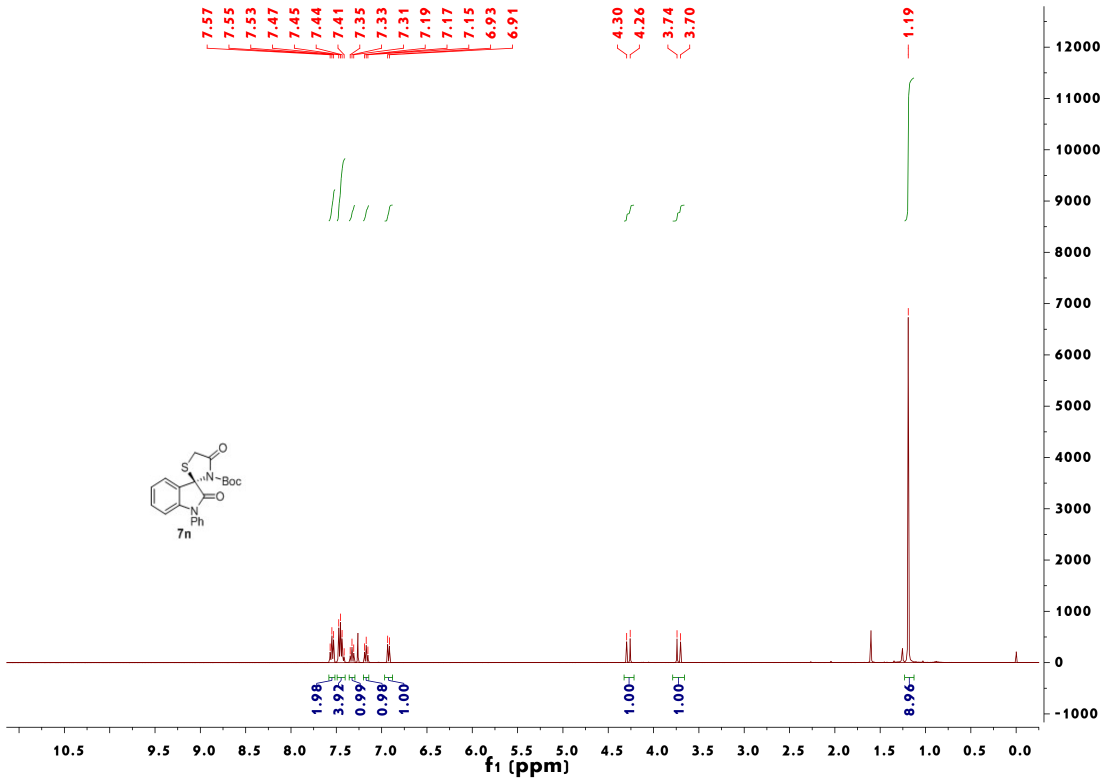

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm
```

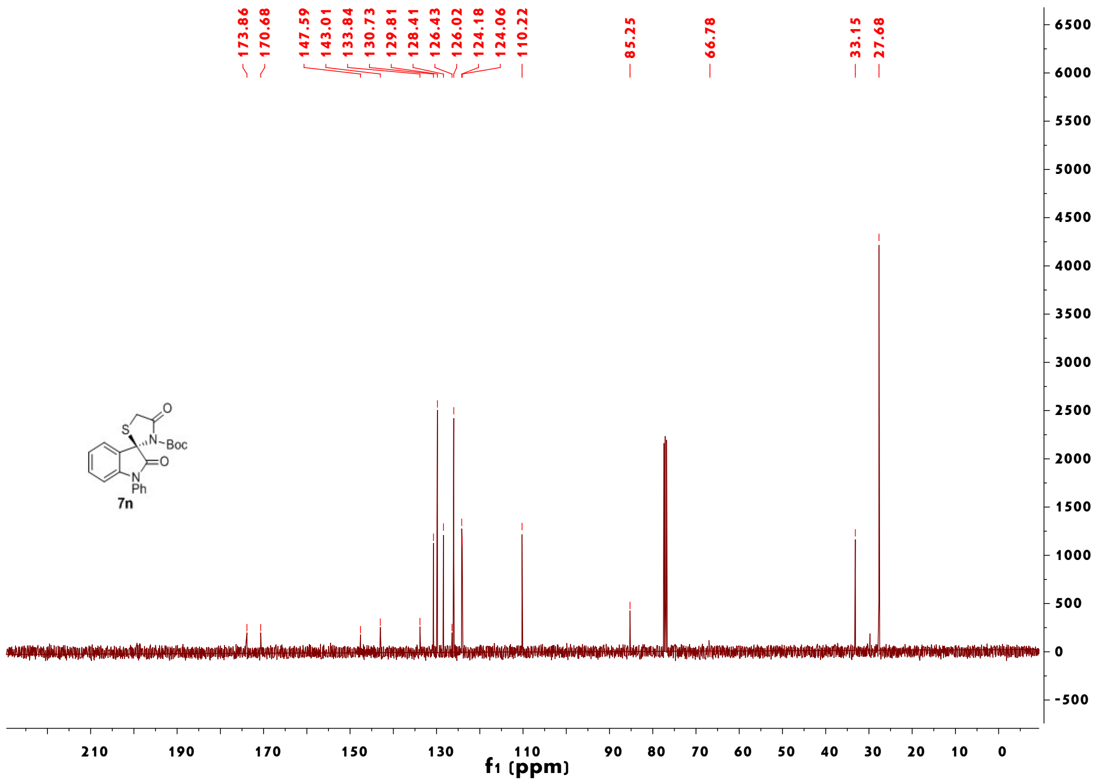
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.619	BB	0.8129	158.63057	2.30558	1.5923
2	27.167	BB	1.6242	9803.77441	90.16543	98.4077

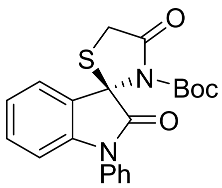



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.327	BB	0.8827	608.43445	8.97533	40.7909
2	27.338	BB	1.1904	883.16064	8.83984	59.2091

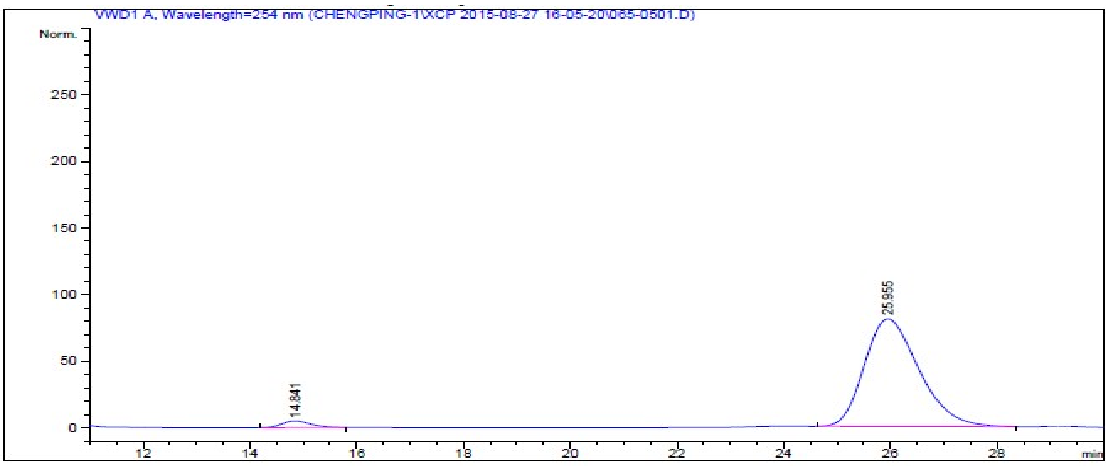

7.57
7.55
7.53
7.47
7.45
7.44
7.41
7.35
7.33
7.31
7.19
7.17
7.15
6.93
6.91
4.30
4.26
3.74
3.70
1.19
1.98
3.92
0.99
0.98
1.00
1.00
1.00
8.96
7n
f1 (ppm)


173.86
170.68
147.59
143.01
133.84
130.73
129.81
128.41
126.43
126.02
124.18
124.06
110.22
85.25
66.78
33.15
27.68
7n
f1 (ppm)

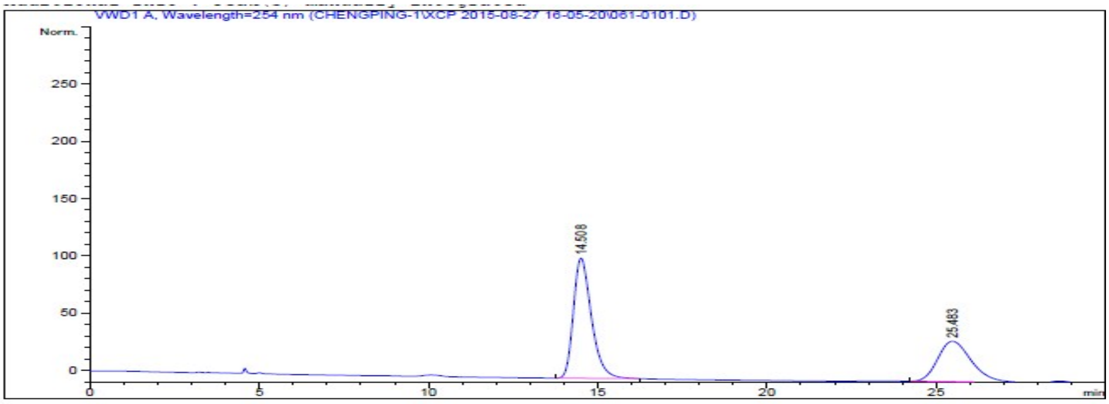


7n

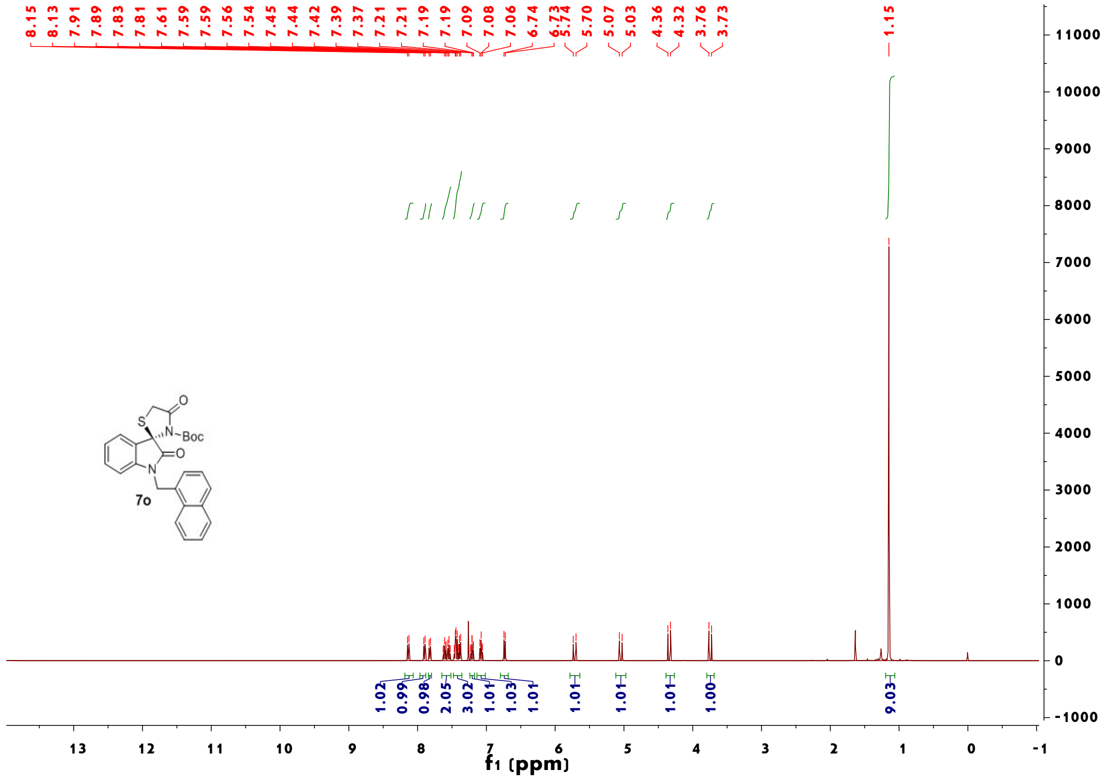
55% yield, 94% ee



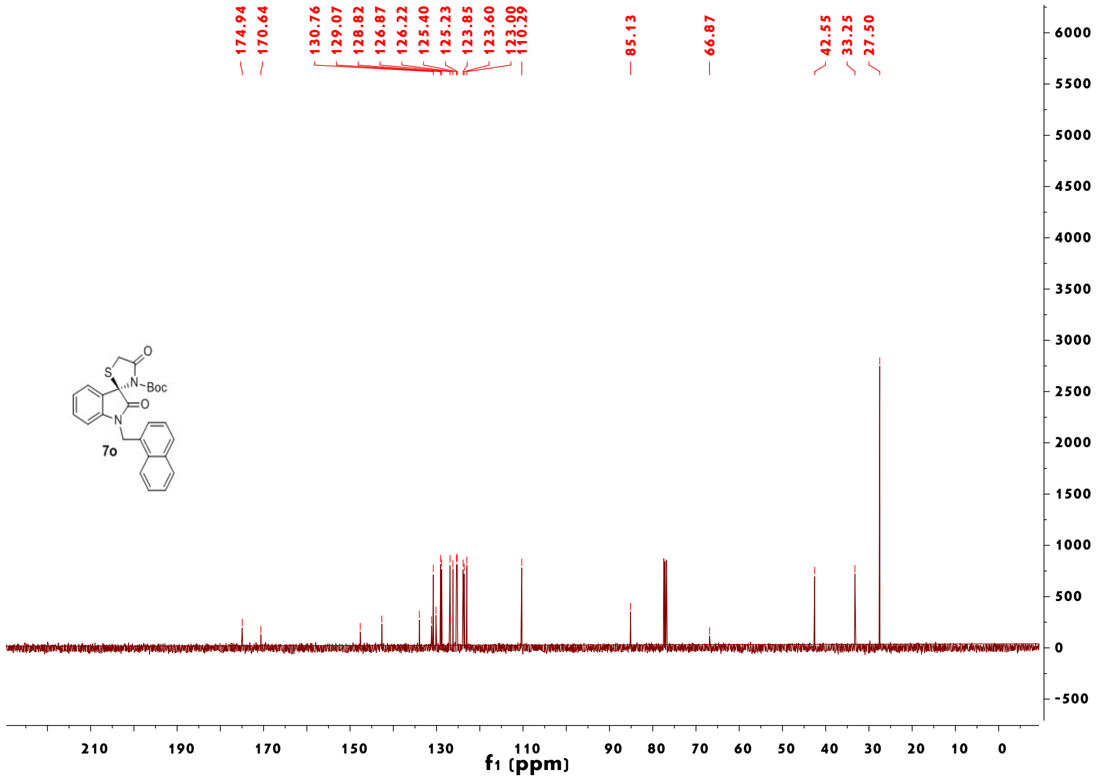

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.841 BB    0.5607  188.10150    5.00784   3.1639
   2  25.955 BB    1.0903 5757.19727   80.70335  96.8361
```



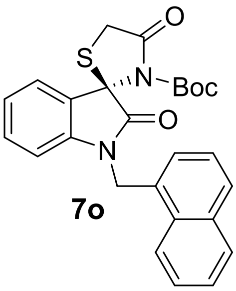

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.508 BB    0.5671 3895.08740  104.94319  61.8110
   2  25.483 BB    1.0411 2406.52271   35.19917  38.1890
```



8.15
8.13
7.91
7.89
7.83
7.81
7.61
7.59
7.59
7.56
7.54
7.45
7.44
7.42
7.39
7.37
7.21
7.21
7.19
7.19
7.09
7.08
7.06
6.74
6.73
5.74
5.70
5.07
5.03
4.36
4.32
3.76
3.73
1.15
1.02
0.99
0.98
2.05
3.02
1.01
1.03
1.01
1.01
1.01
1.01
1.00
9.03
7o
f1 (ppm)

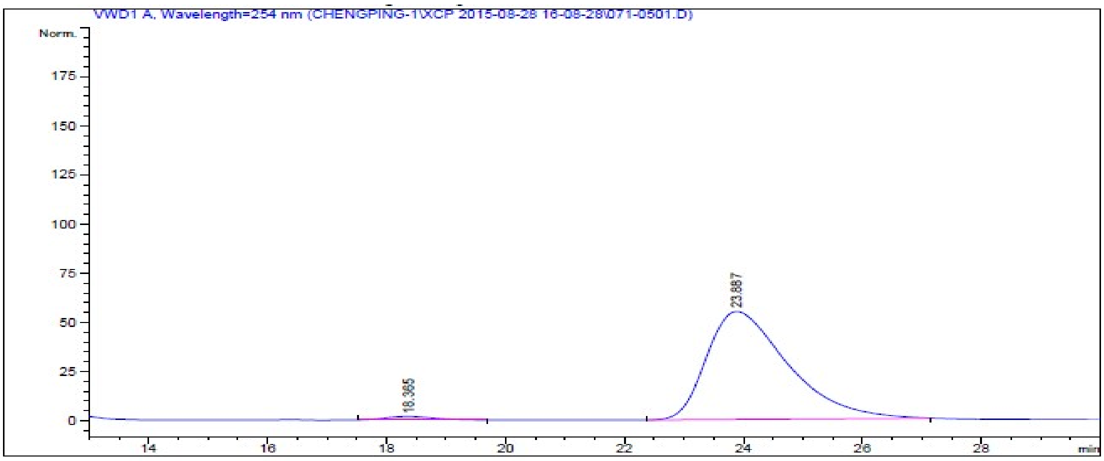


174.94
170.64
130.76
129.07
128.82
126.87
126.22
125.40
125.23
123.85
123.60
123.00
110.29
85.13
66.87
42.55
33.25
27.50
7o
f1 (ppm)

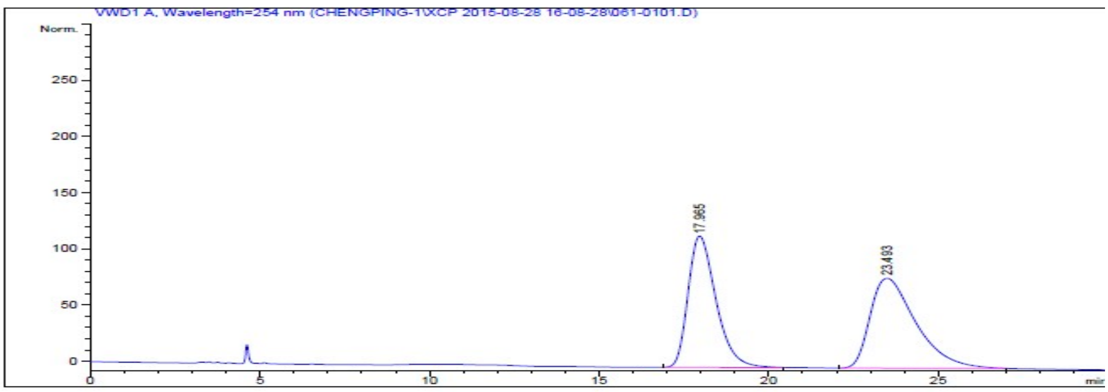


7o

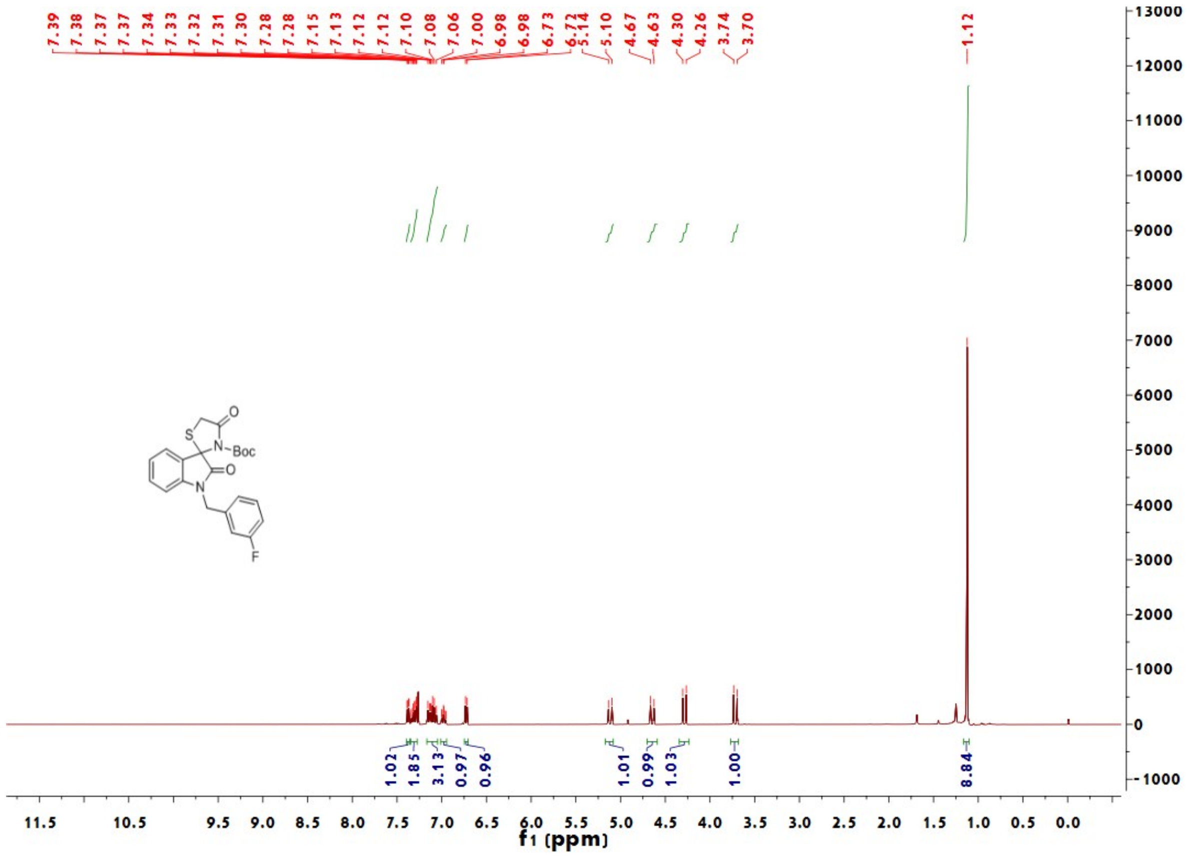
57% yield, 96% ee

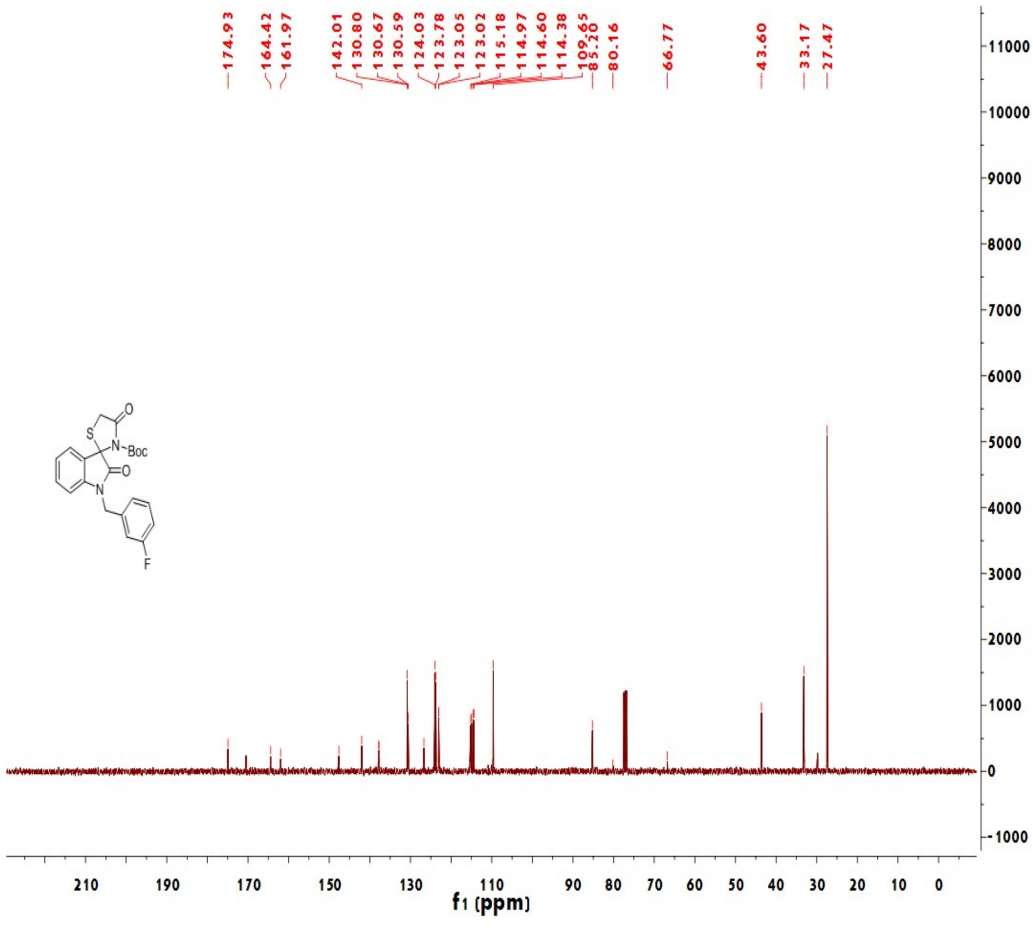


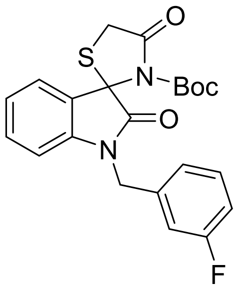

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.365 BB    0.6581   95.67258    1.71894   1.8016
   2  23.887 BB    1.3581 5214.75098   54.93994  98.1984
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.965 BB    0.8818 6685.78857  116.84843  47.0575
   2  23.493 BB    1.3934 7521.91553   79.96079  52.9425
```

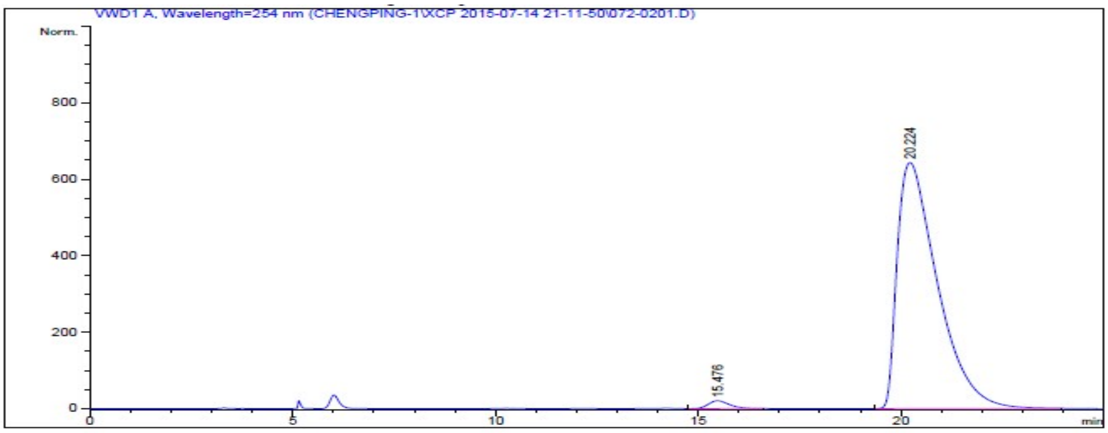

7.39
7.38
7.37
7.37
7.34
7.33
7.32
7.31
7.30
7.28
7.28
7.15
7.13
7.12
7.12
7.10
7.08
7.06
7.00
6.98
6.98
6.73
6.72
5.14
5.10
4.67
4.63
4.30
4.26
3.74
3.70
1.12
1.02
1.85
3.13
0.97
0.96
1.01
0.99
1.03
1.00
8.84
f1 (ppm)


174.93
164.42
161.97
142.01
130.80
130.67
130.59
124.03
123.78
123.05
123.02
115.18
114.97
114.60
114.38
109.65
85.20
80.16
66.77
43.60
33.17
27.47
f1 (ppm)



7p

54% yield, 97% ee

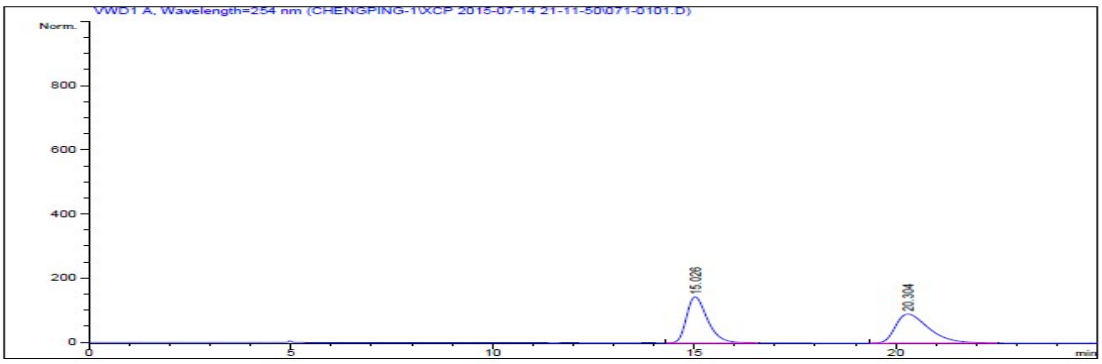


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.476	VB	0.5474	739.29840	20.43605	1.6446
2	20.224	BB	1.0132	4.42141e4	643.30493	98.3554

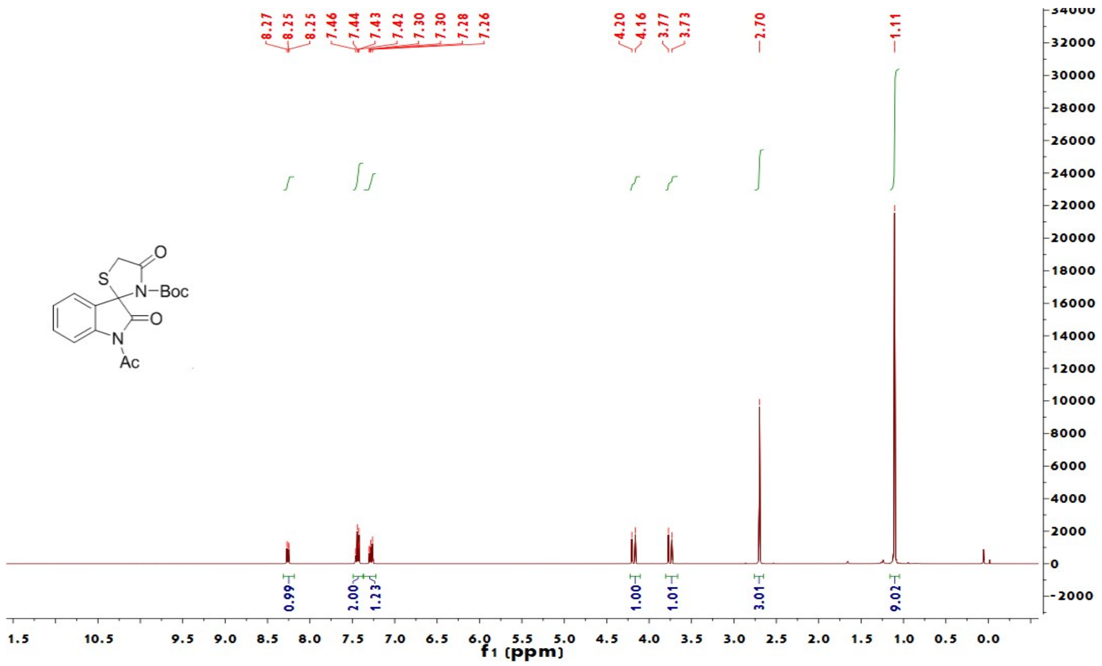


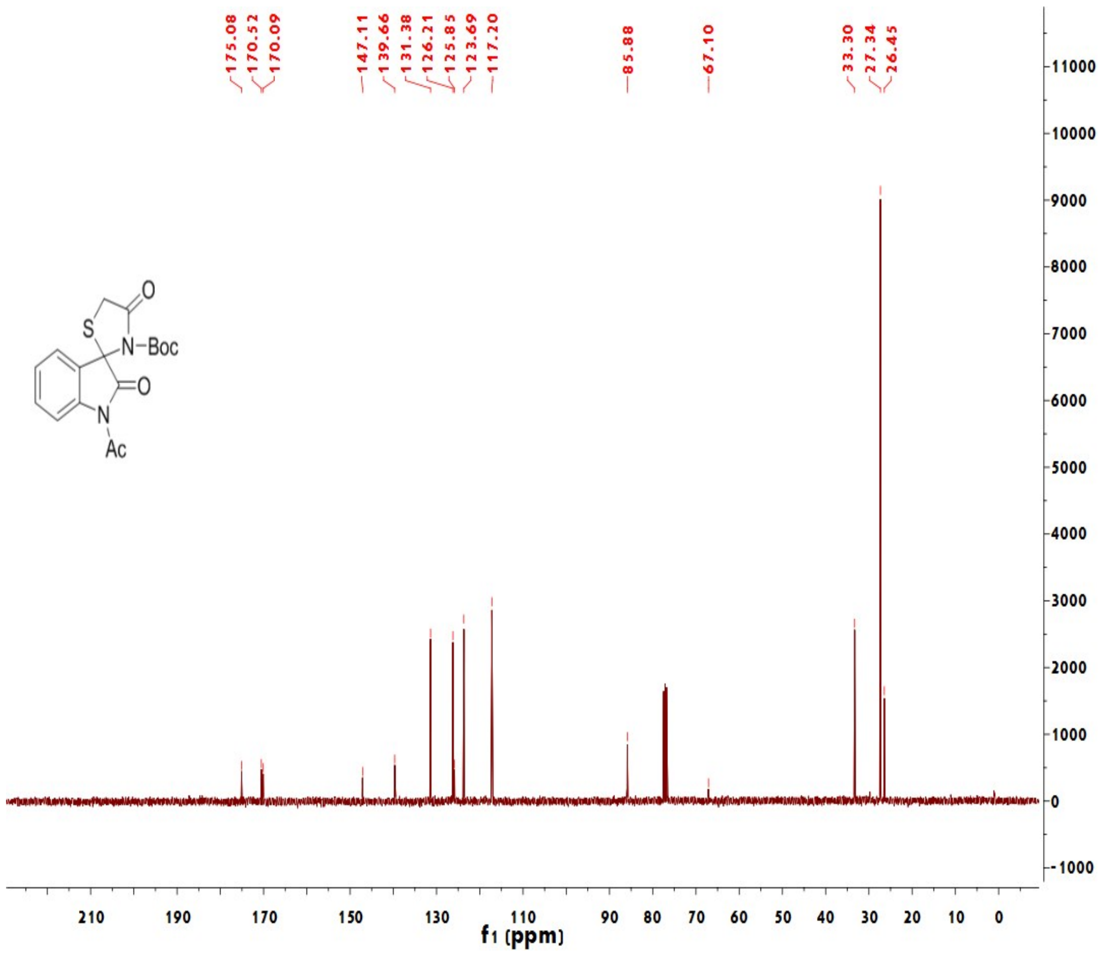
Area Percent Report

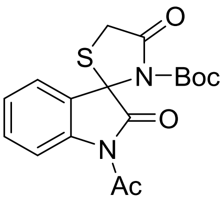
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.026	VB	0.5516	5152.43408	143.48694	50.0191
2	20.304	BB	0.8797	5148.49707	90.26603	49.9809

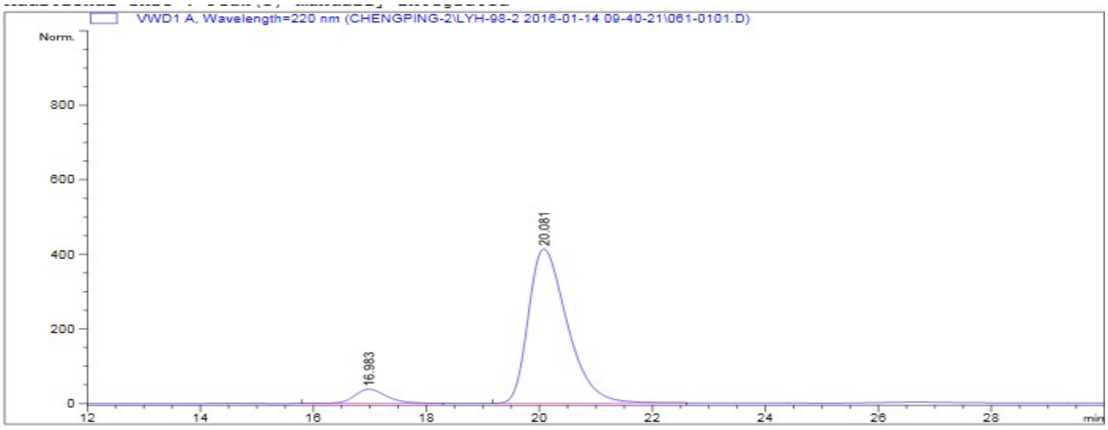

8.27
8.25
8.25
7.46
7.44
7.43
7.42
7.30
7.30
7.28
7.26
4.20
4.16
3.77
3.73
2.70
1.11
0.99
2.00
1.23
1.00
1.01
3.01
9.02
S
N-Boc
O
N
Ac
f1 (ppm)


175.08
170.52
170.09
147.11
139.66
131.38
126.21
125.85
123.69
117.20
85.88
67.10
33.30
27.34
26.45
S
N-Boc
O
N
Ac
f1 (ppm)



7q

58% yield， 86% ee

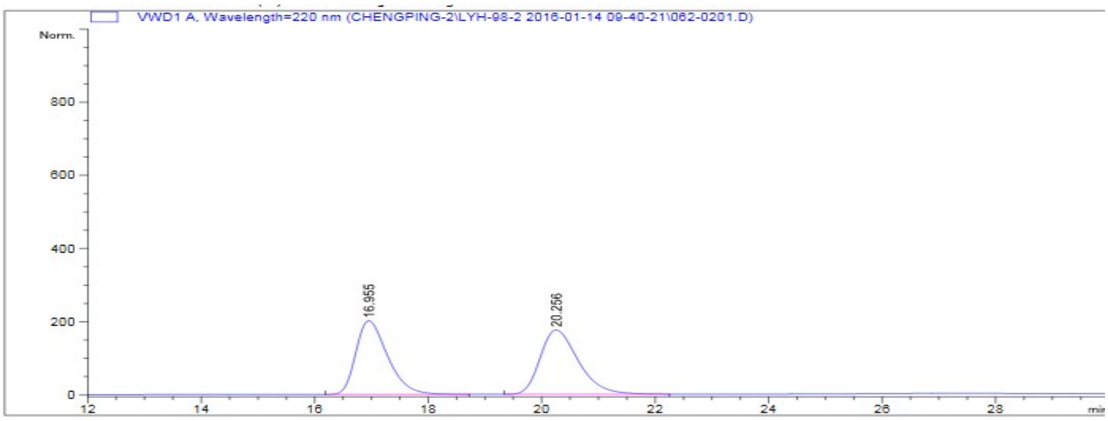


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.983	BB	0.5976	1474.65259	37.69495	6.9522
2	20.081	BB	0.7327	1.97367e4	413.76123	93.0478

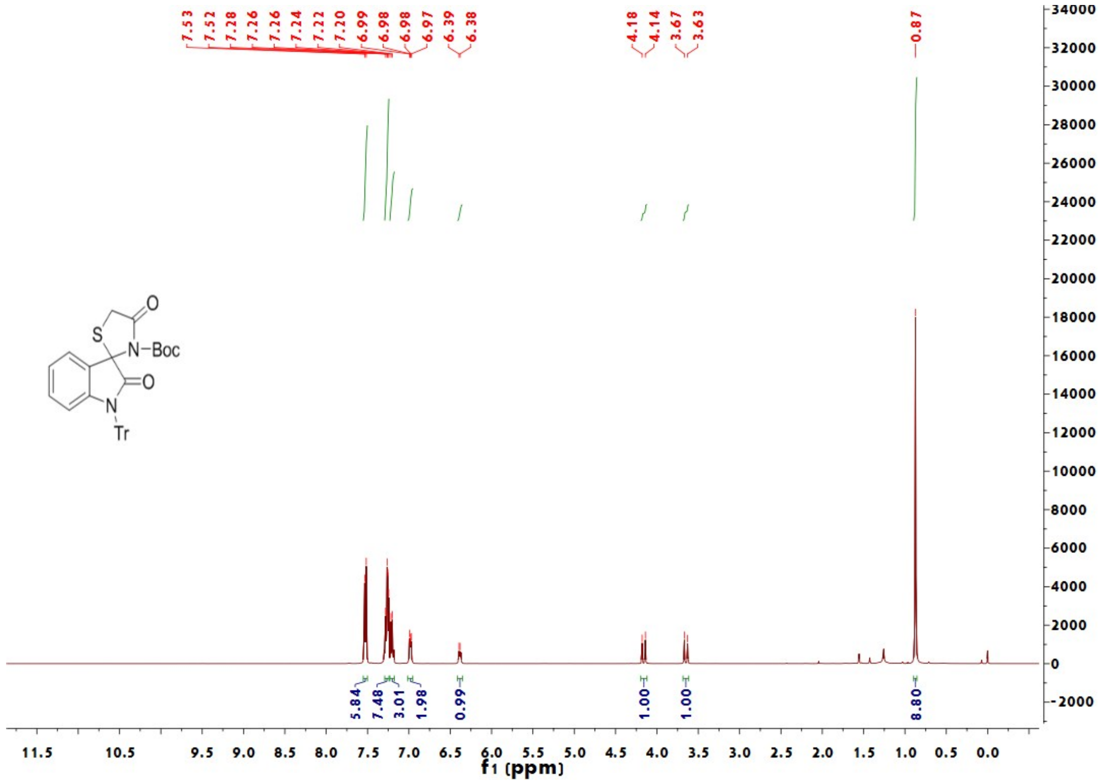


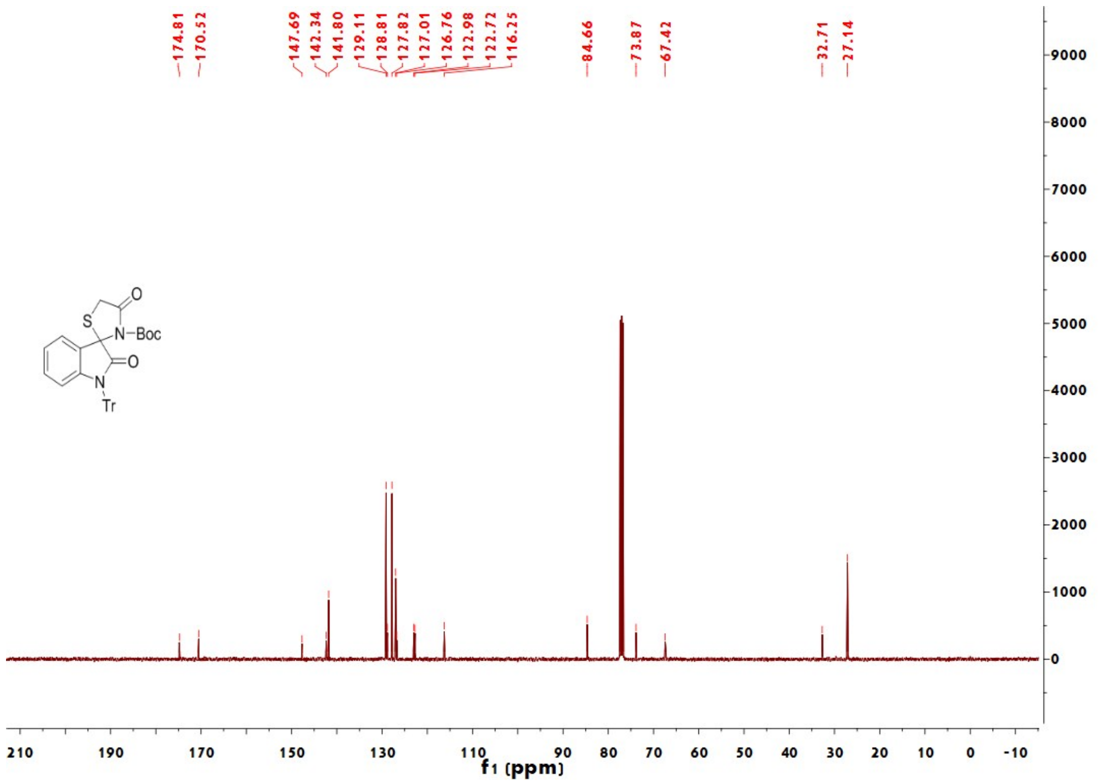
Area Percent Report

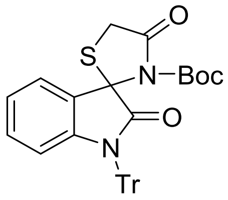
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.955	BB	0.5962	7850.48926	201.31984	48.7463
2	20.256	BB	0.7253	8254.31055	175.82668	51.2537

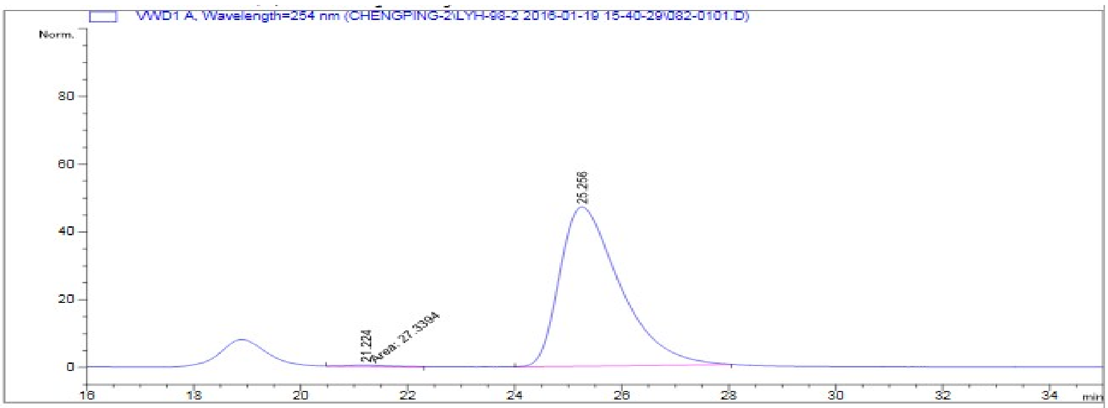

7.53
7.52
7.28
7.26
7.26
7.24
7.22
7.20
6.99
6.98
6.98
6.97
6.39
6.38
4.18
4.14
3.67
3.63
0.87
5.84
7.48
3.01
1.98
0.99
1.00
1.00
8.80
f1 (ppm)


174.81
170.52
147.69
142.34
141.80
129.11
128.81
127.82
127.01
126.76
122.98
122.72
116.25
84.66
73.87
67.42
32.71
27.14
f1 (ppm)

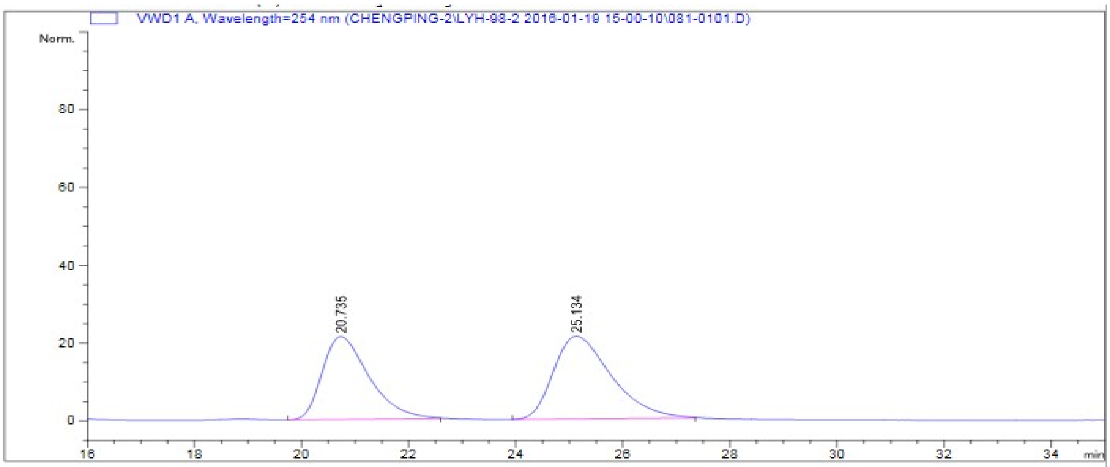


7r

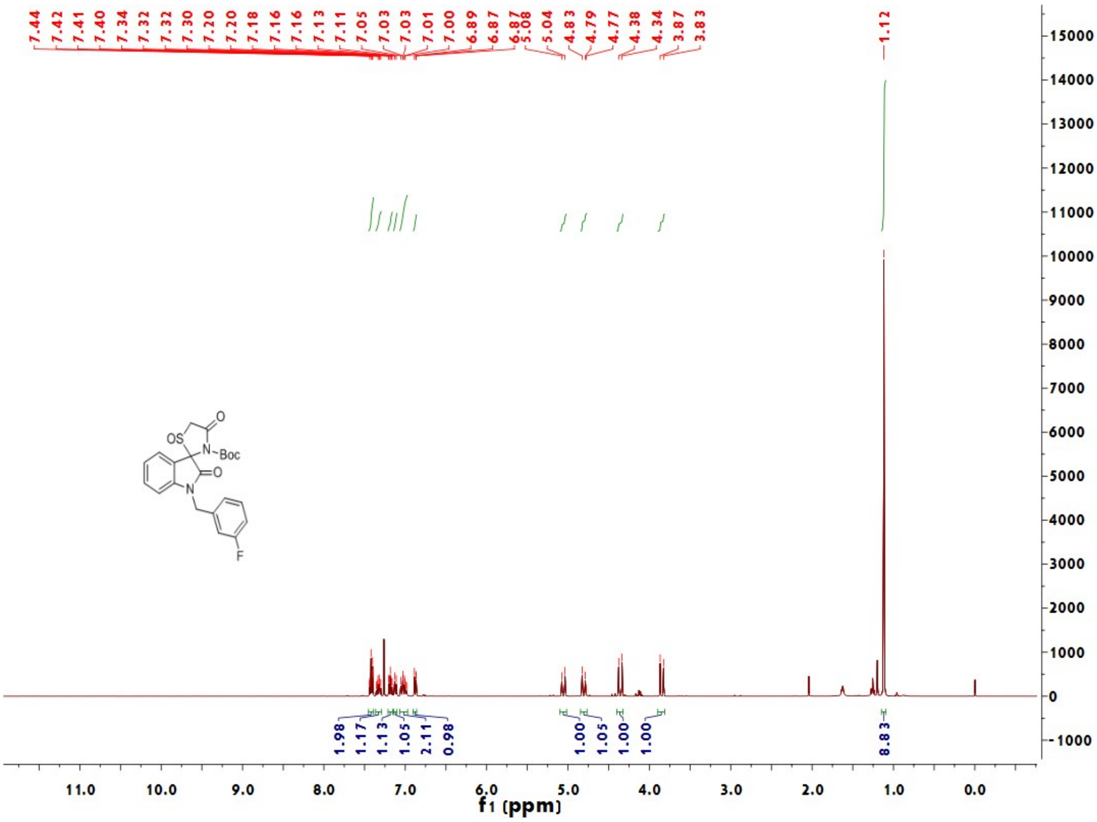
56% yield， 98% ee

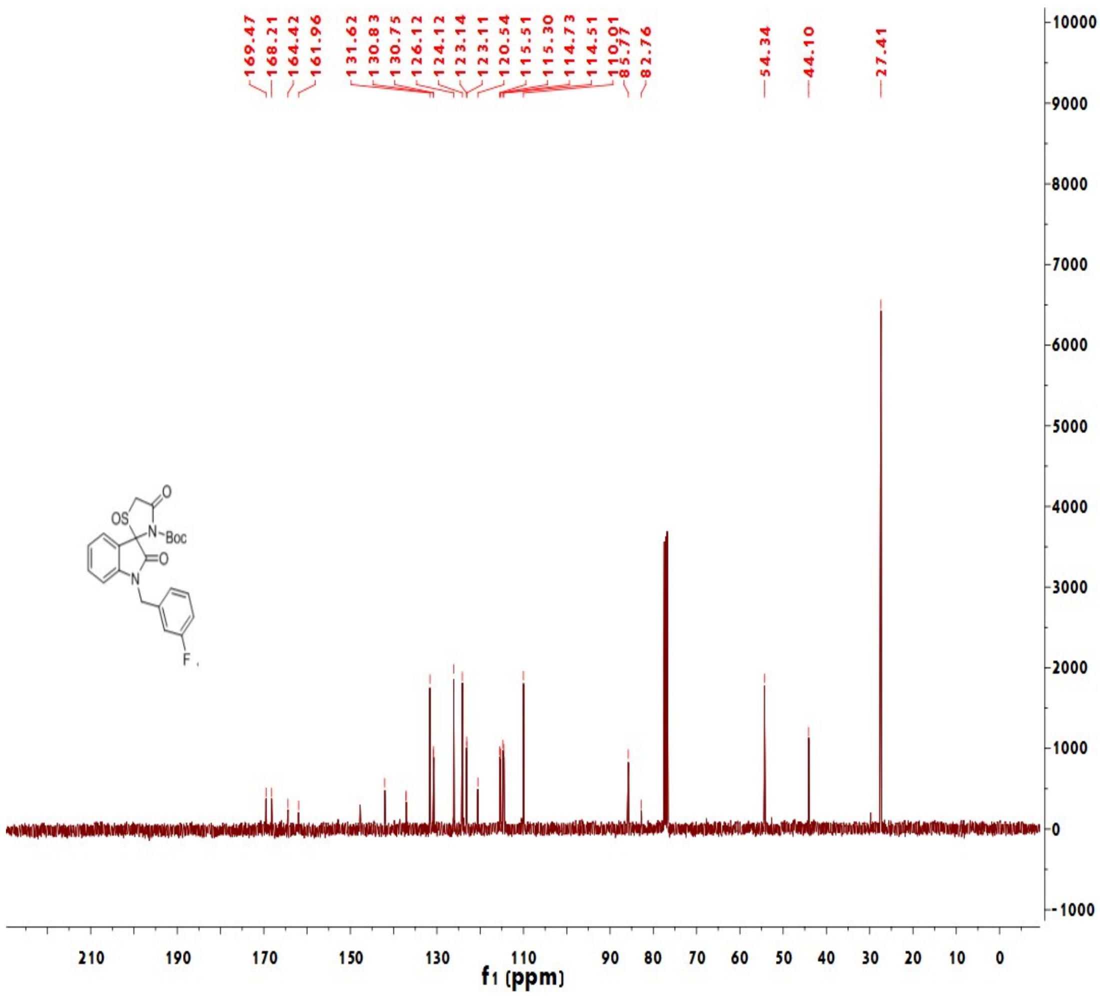


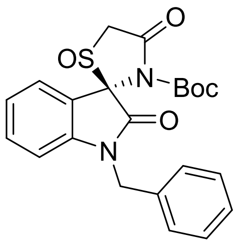

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  21.224 MM    1.0571   27.33936 4.31053e-1   0.7365
   2  25.256 BB    1.1642 3684.72681   46.96967  99.2635
```




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.735 BB    0.9206 1293.76099   21.27338  44.7414
   2  25.134 BB    1.1248 1597.88184   21.25008  55.2586
```

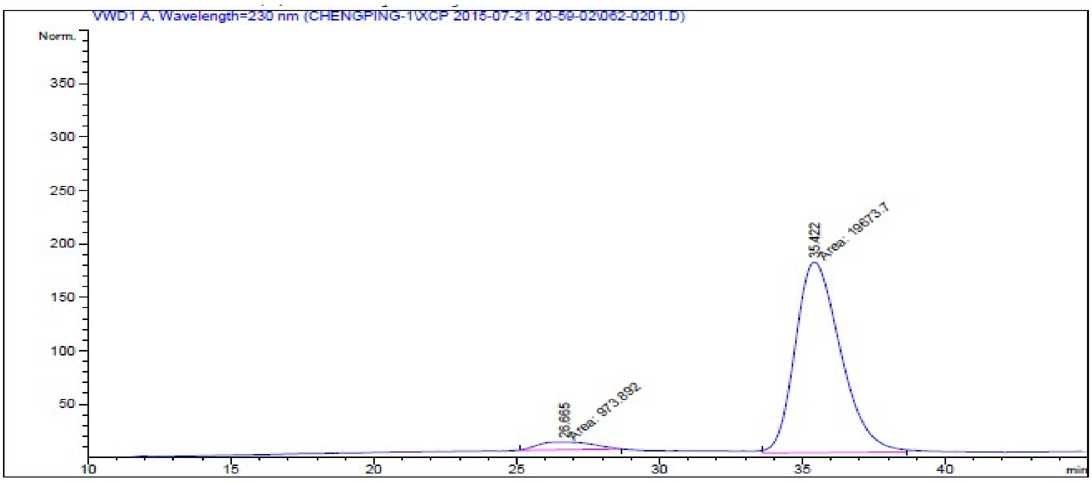

7.44 7.42 7.41 7.40 7.34 7.32 7.30 7.20 7.20 7.18 7.16 7.16 7.13 7.11 7.05 7.03 7.03 7.01 7.00 6.89 6.87 6.87 5.08 5.04 4.83 4.79 4.77 4.38 4.34 3.87 3.83
1.12
OS
N
Boc
O
O
N
F
1.98 1.17 1.13 1.05 2.11 0.98
1.00 1.05 1.00 1.00
8.83
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000


169.47 168.21 164.42 161.96
131.62 130.83 130.75 126.12 124.12 123.14 123.11 120.54 115.51 115.30 114.73 114.51 110.01 85.77 82.76
54.34 44.10 27.41
OS
N
Boc
O
O
N
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000



8

52% yield， 91% ee

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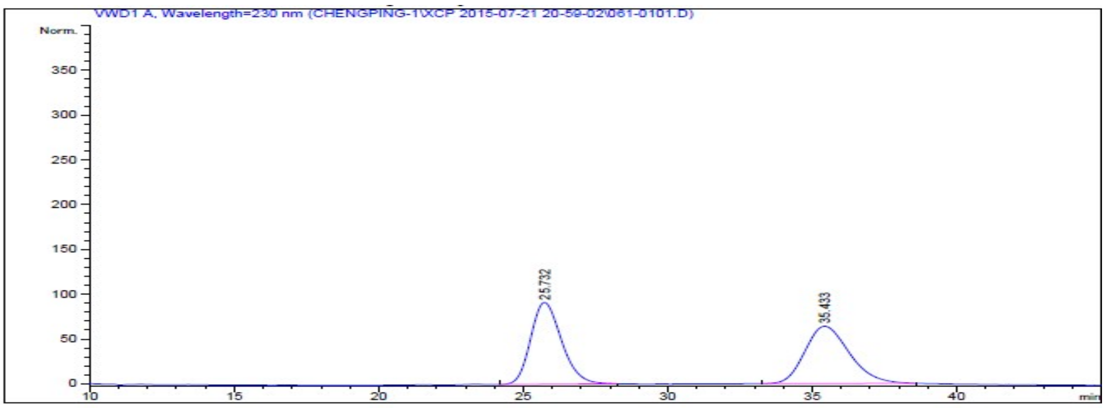
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.665	MM	2.2539	973.89154	7.20140	4.7167
2	35.422	MM	1.8405	1.96737e4	178.15707	95.2833

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm
```
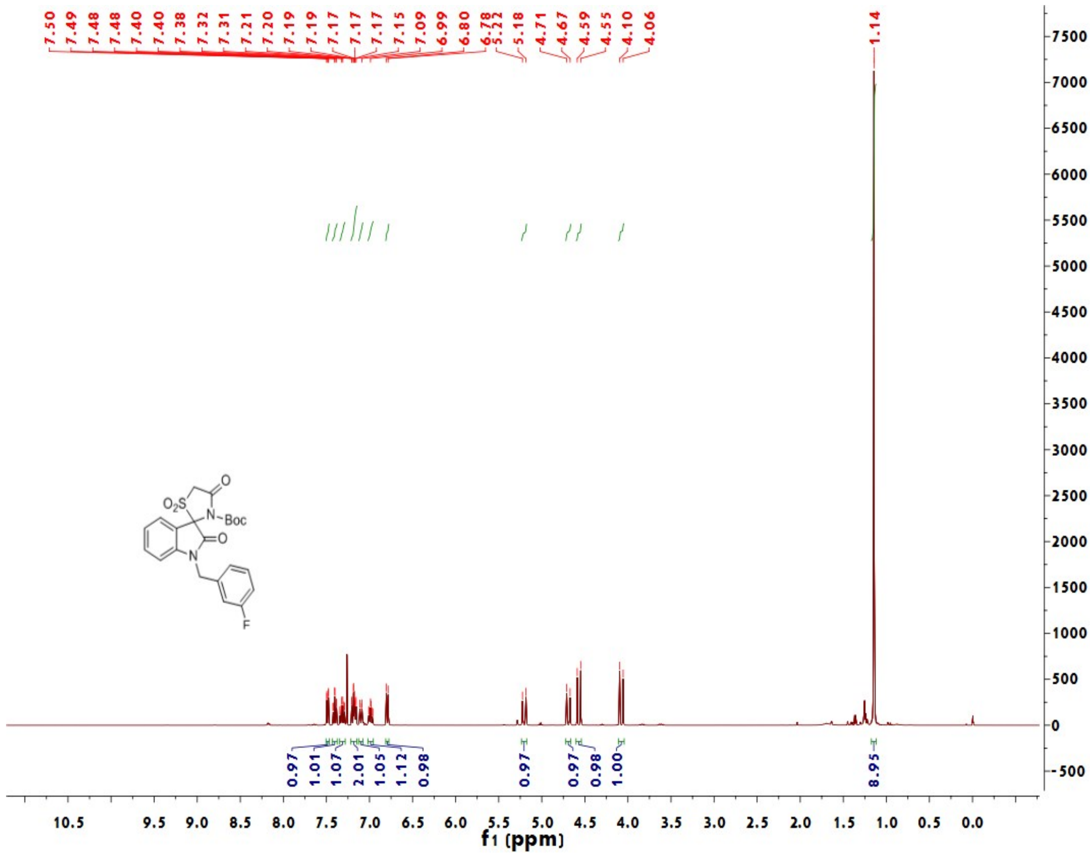
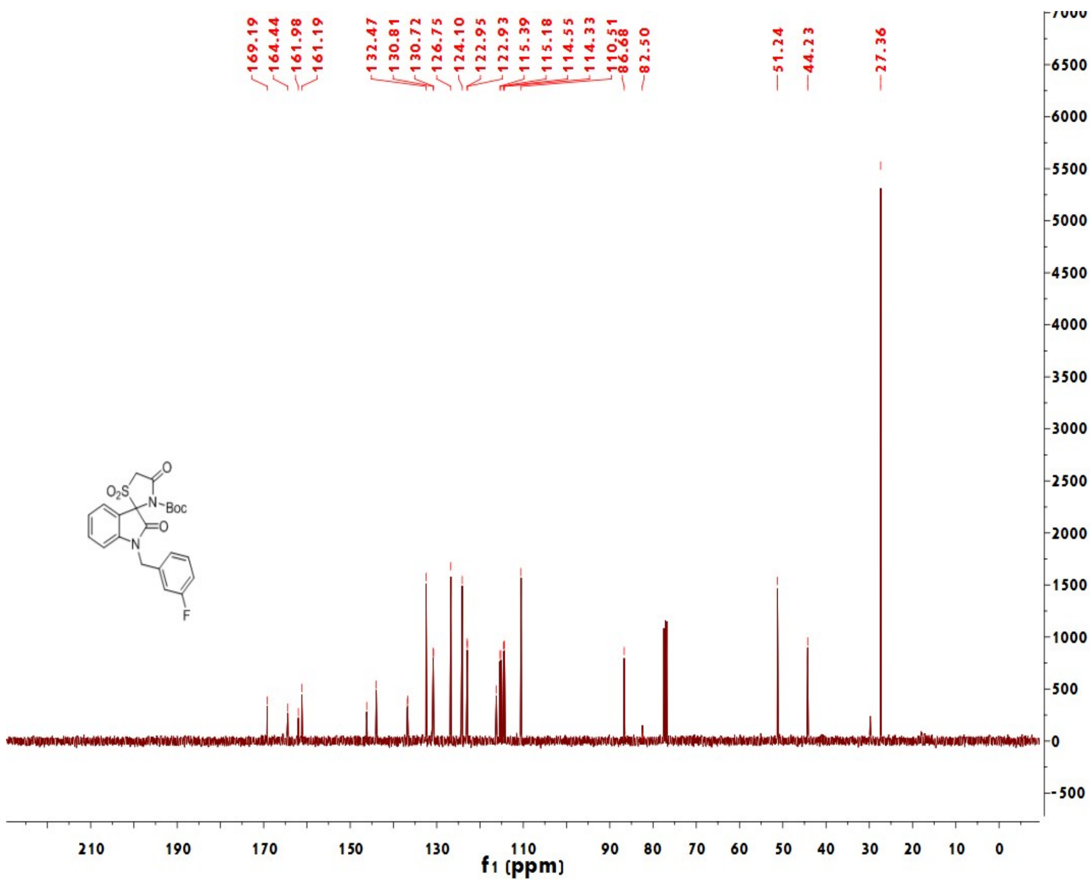
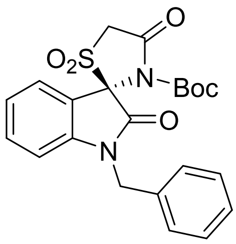

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.732	VB	1.1586	6800.67188	91.35121	49.8015
2	35.433	BB	1.5865	6854.87695	63.99295	50.1985

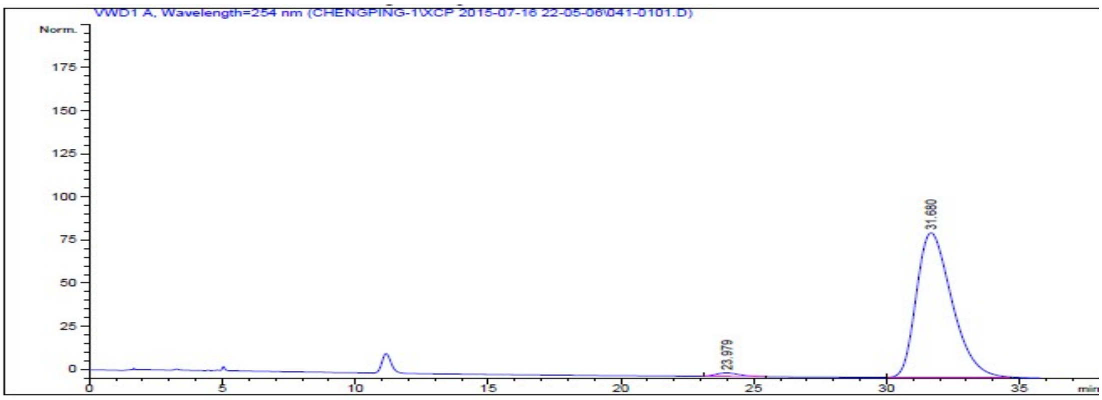




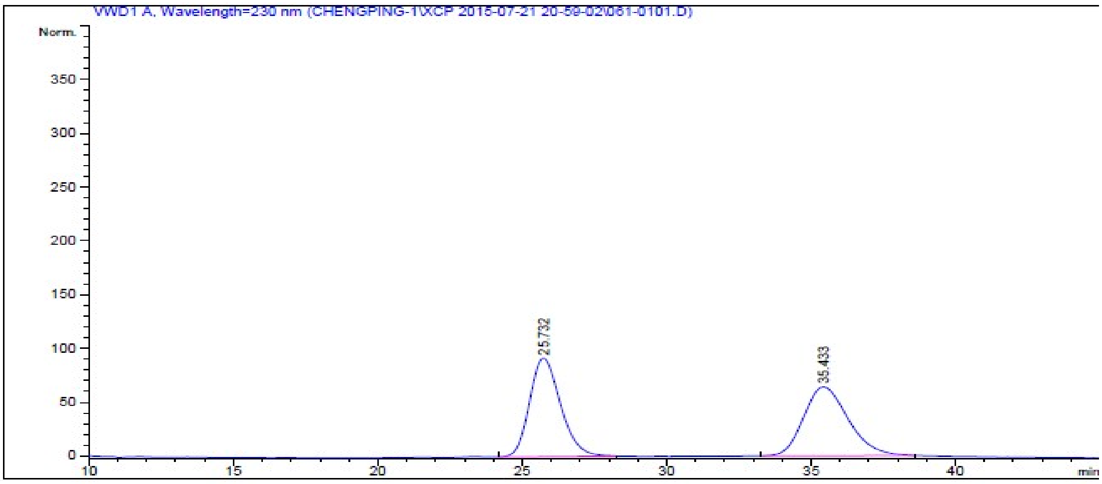


(+)-3

53% yield， 97% ee




```
==================================================================
                     Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.979 BB     0.7325  120.12135    1.98031    1.5222
   2  31.680 BB     1.4022 7771.02979   83.82789   98.4778
```




```
==================================================================
                     Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  25.732 VB     1.1586 6800.67188   91.35121   49.8015
   2  35.433 BB     1.5865 6854.87695   63.99295   50.1985
```