Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

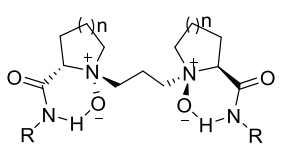
Supporting Information

1. General remarks

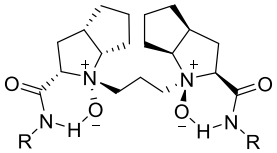
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC and SFC analysis on Daicel Chiralcel IA, IB, IC, ID, and OD-3 at 23 ℃ with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. CD spectra were determined by Chirascan CD (DCM as the solvent) which was purchased from Applied photophysics Ltd. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Melting points were recorded on a melting point apparatus.

2. General procedure for the catalyst preparation

The following *N*,*N*'-dioxide ligands were synthesized by the same procedure in the literature.[1]



L-Pic*P*: R = cyclopentyl, n = 2
L-Pic*H*: R = cyclohexyl, n = 2
L-PiPh: R = C_6H_5, n = 2
L-Pi*m*Bu$_2$: R = 3,5-^{t}Bu$_2$C$_6$H$_3$, n = 2
L-Pi*m*Me$_2$: R = 3,5-Me$_2$C$_6$H$_3$, n = 2
L-Prc*P*: R = cyclopentyl, n = 1

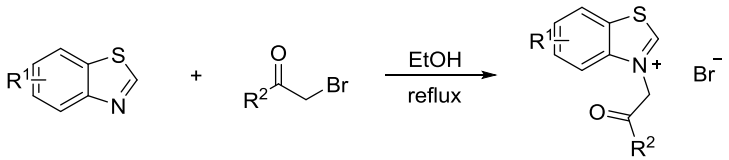


L-Rac*P*: R = cyclopentyl, n = 2

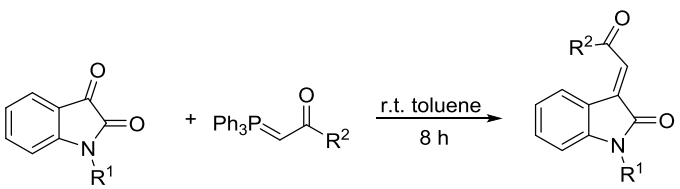
In a test tube with a magnetic stirring bar, *N*,*N*'-dioxide ligand (0.20 mmol), and metal salt (1.0 equiv), in THF (10.0 mL) were stirred at 35 ℃ for 1 h. Then the mixture was concentrated in vacuo to afford the corresponding catalysts as a white solid.

3. General procedure for the synthesis of the substrates

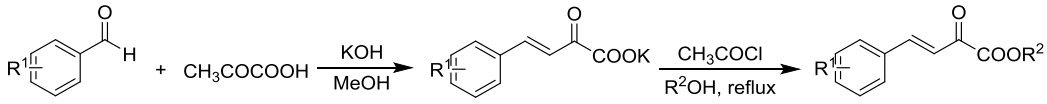
(a) Method A: Thiazolium salts were prepared according to the literature procedure.[2]



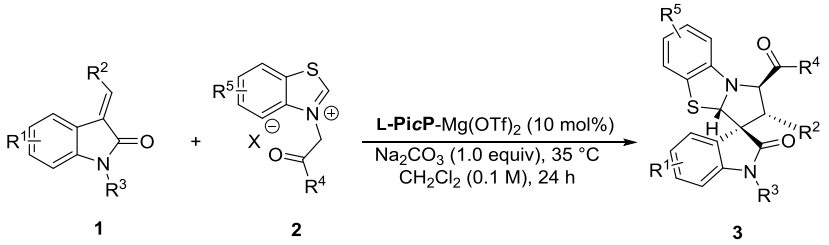
(b) Method B: Methyleneindolinone derivatives were prepared according to the literature procedure.[3]



(c) Method C: β,γ-Unsaturated α-ketoesters were prepared according to the literature procedure.[4]

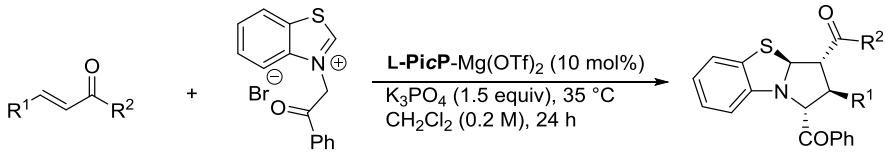


4. General procedure for the catalytic asymmetric reaction



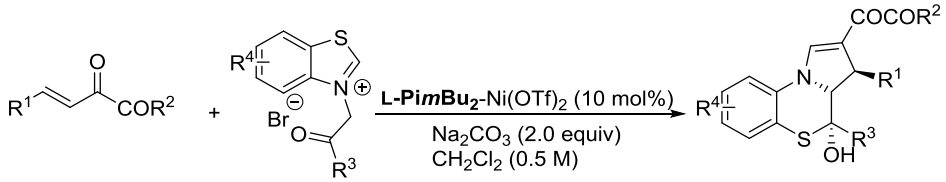
1 2 3

In a test tube with a magnetic stirring bar, catalyst **L-PicP**-$Mg(OTf)_2$ (10 mol%), substrate **1** (0.10 mmol), thiazolium salt **2** (1.1 equiv), and Na_2CO_3 (0.10 mmol) in CH_2Cl_2 (1.0 mL) were stirred at 35 ℃ for 24 h. The reaction mixture was detected by TLC. After completion, flash column chromatography (eluent: EtOAc/pet = 1/6) was carried out to provide the desired product **3**. The enantiomeric excess was determined by chiral HPLC and the product was determined by NMR analysis.



4 2a 5

In a test test with a magnetic stirring bar, catalyst **L-PicP**-$Mg(OTf)_2$ (10 mol%), chalcones **4** (0.10 mmol), thiazolium salt **2a** (0.15 mmol), and K_3PO_4 (0.15 mmol) in CH_2Cl_2 (0.5 mL) were stirred at 35 ℃ for 24 h. The reaction mixture was detected by TLC. After completion, flash column chromatography (eluent: EtOAc/pet = 1/6) was carried out to provide the desired product **5**. The enantiomeric excess was determined by chiral HPLC and product was determined by NMR analysis.

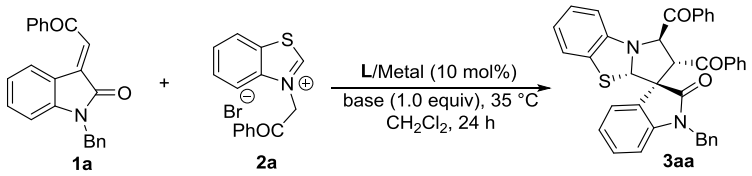


6 2 7

In a test tube with a magnetic stirring bar, catalyst **L-PimBu$_2$**-$Ni(OTf)_2$ (10 mol%), β,γ-unsaturated α-ketoester **6** (0.10 mmol), thiazolium salt **2** (0.10 mmol), and Na_2CO_3 (0.20 mmol) in CH_2Cl_2 (0.2 mL) were stirred at 0 ℃ for 24 h. Then the reaction mixture warmed to 35 ℃ for 36 h. After completion, flash column chromatography (eluent: EtOAc/pet = 1/2) was carried out to provide the desired product **7**. The enantiomeric excess was determined by chiral SFC and the product was determined by NMR analysis.

5. Optimization of the reaction conditions

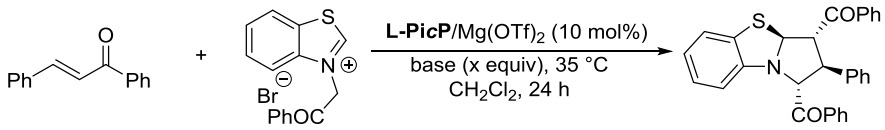
(a) Screen of reaction condition using methyleneindolinone 1a.



Entry[a]	Metal salt	L	Base	Yield [%][b]	ee [%][c]
1	$Mg(OTf)_2$	**L-Pic*P***	-	15	95
2	$Mg(OTf)_2$	**L-Pic*P***	Et_3N	99	86
3	$Mg(OTf)_2$	**L-PiPr$_2$**	Et_3N	90	4
4	$Sc(OTf)_3$	**L-Pic*P***	Et_3N	84	8
5	$Ni(OTf)_2$	**L-Pic*P***	Et_3N	87	10
6	$Mg(OTf)_2$	**L-Pic*H***	Et_3N	93	75
7	$Mg(OTf)_2$	**L-PiPh**	Et_3N	80	10
8	$Mg(OTf)_2$	**L-Prc*P***	Et_3N	93	14
9	$Mg(OTf)_2$	**L-Rac*P***	Et_3N	90	33
10	$Mg(OTf)_2$	**L-Pic*P***	K_2CO_3	99	90
11	$Mg(OTf)_2$	**L-Pic*P***	Na_2CO_3	99	98
12	$Mg(OTf)_2$	**L-Pim*B*u$_2$**	K_2CO_3	98	0
13	$Ni(OTf)_2$	**L-Pim*B*u$_2$**	Na_2CO_3	98	0

[a] Unless otherwise noted, the reaction was performed with Metal/Ligand (10 mol%), **1a** (0.10 mmol), **2a** (1.1 equiv) in 1.0 mL CH_2Cl_2. [b] Yield of isolated product. The dr value was >19:1, as determined by ^{1}H NMR analysis. [c] The ee value was determined by chiralphase HPLC analysis.

(b) Screen of reaction condition using chalcone 4a.



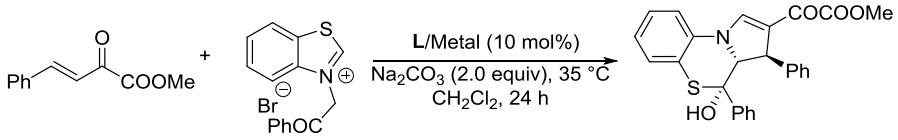
4a **2a** **5aa**

Entry[a]	Base	Yield [%][b]	ee [%][c]
1	Et_3N	51	62
2	ProtonSponge	51	77
3	K_2CO_3	35	99
4	Na_2CO_3	42	99
5	Cs_2CO_3	57	99
6	KH_2PO_4	32	99
7	K_3PO_4	70	99
8	$K_3PO_4 \cdot 7H_2O$	28	91
9	Na_3PO_4	50	99
10[d]	K_3PO_4	79	99
11[d,e]	K_3PO_4	94	99

[a] Unless otherwise noted, the reaction was performed with $Mg(OTf)_2$/**L-Pic*P*** (10 mol%), **4a** (0.10 mmol), **2a** (1.0 equiv) and base (1.0 equiv) in 1.0 mL CH_2Cl_2. [b] Yield of isolated product. The dr value was >19:1, as

determined by ^{1}H NMR analysis. [c] The ee value was determined by chiralphase HPLC analysis. [d] In CH_2Cl_2 (0.5 mL). [e] K_3PO_4 (1.5 equiv), **2a** (1.5 equiv).

(c) Screen of reaction condition using β,γ-unsaturated α-ketoester 6a.



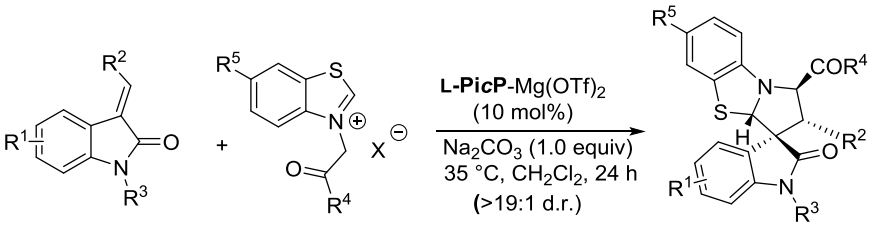
6a **2a** **7aa**

Entry[a]	metal	ligand	Yield (%)[b]	ee (%)[c]
1[d]	$Mg(OTf)_2$	**L-PicP**	78	-53
2[d]	$Ni(OTf)_2$	**L-PicP**	61	-60
3	$Ni(OTf)_2$	**L-PicP**	65	-62
4	$Ni(OTf)_2$	**L-PicH**	70	-68
5	$Ni(OTf)_2$	**L-PiPh**	58	-33
6	$Ni(OTf)_2$	**L-PiPr$_2$**	86	-48
7	$Ni(OTf)_2$	**L-PimBu$_2$**	57	85
8[e]	$Ni(OTf)_2$	**L-PimBu$_2$**	79	86
9[f]	$Ni(OTf)_2$	**L-PimBu$_2$**	86	93

[a] Unless otherwise noted, the reaction was performed with metal/ligand (10 mol%), **6a** (0.10 mmol), **2a** (1.0 equiv) and Na_2CO_3 (2.0 equiv) in CH_2Cl_2 (1.0 mL), 4 days. [b] Yield of isolated product. The dr value was >19:1, as determined by ^{1}H NMR analysis. [c] The ee value was determined by SFC analysis. [d] Na_2CO_3 (1.0 equiv). [e] Run with CH_2Cl_2 (0.5 mL), 3days. [f] The reaction was performed at 0 ℃ 24 h, then at 35 ℃ 36 h in CH_2Cl_2 (0.2 mL).

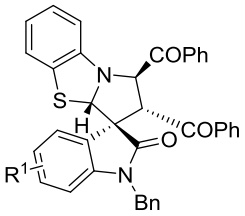
6. Full list of the substrate scope

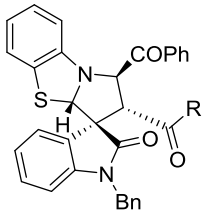
(a) Substrate scope for methyleneindolinone derivatives and thiazolium salts in [3+2] cycloaddition.[a]



1 **2a** X = Br **2a'** X = Cl **3**

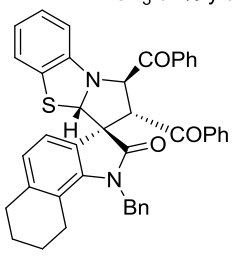
a) Variation of oxindole-derived enones:



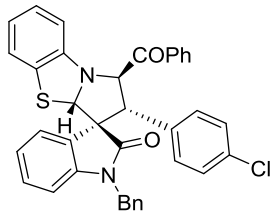


3aa R^1 = H 99% yield, 98% *ee*
R^1 = H 80% yield, 93% *ee*[b]
3ba R^1 = 5-Cl 99% yield, 95% *ee*
3ca R^1 = 5-Me 99% yield, 98% *ee*
3cas R^1 = 5-OMe 99% yield, 98% *ee*
3da R^1 = 6-Cl 99% yield, 97% *ee*
3ea R^1 = 7-CF_3 94% yield, 93% *ee*

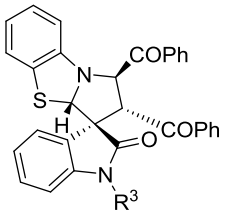
3fa R = *o*-FC_6H_4 94% yield, 98% *ee*
3ga R = *m*-MeC_6H_4 99% yield, 96% *ee*
3gas R = *m*-$MeOC_6H_4$ 96% yield, 98% *ee*
3ha R = *p*-ClC_6H_4 99% yield, 96% *ee*
3ia R = *p*-$MeOC_6H_4$ 95% yield, 97% *ee*
3ias R = 2-naphthyl 99% yield, 97% *ee*
3ja R = O*i*Pr 99% yield, 99% *ee*



3eas 99% yield, 99% *ee*

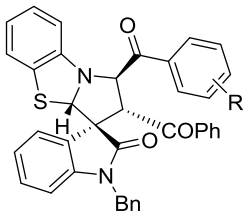


3ka 74% yield, 99% *ee*

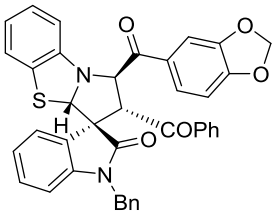


3la R^3 = Me 99% yield, 96% *ee*
3ma R^3 = Boc 99% yield, 72% *ee*

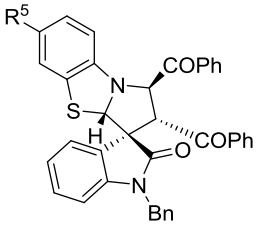
b) Variation of thiazolium salts:



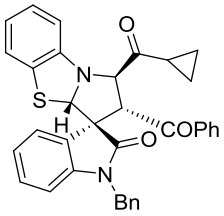
3ab R = *o*-F 99% yield, 94% *ee*
3acs R = *o*-OMe 89% yield, 96% *ee*
3ac R = *m*-OMe 99% yield, 98% *ee*
3ad R = *p*-Cl 99% yield, 98% *ee*
3ads R = *p*-NO_2 99% yield, 90% *ee*
3ae R = *p*-Me 99% yield, 99% *ee*
3af R = *p*-CF_3 99% yield, 96% *ee*
3ag R = *p*-*t*Bu 99% yield, 97% *ee*
3ah R = *p*-OEt 99% yield, 97% *ee*



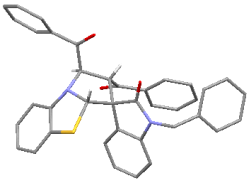
3ahs 98% yield, 98% *ee*



3aj R^5 = OH 99% yield, 97% *ee*
3ak R^5 = OMe 98% yield, 98% *ee*



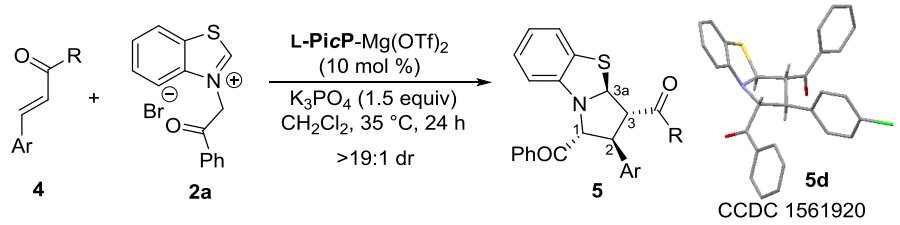
3ai 95% yield, 87% *ee*



3aa CCDC 1508734

[a] The reactions were carried out $Mg(OTf)_2$-**L-PicP** (1:1, 10 mol%), **1** (0.10 mmol), **2** (1.1 equiv X = Br) and Na_2CO_3 (1.0 equiv) in CH_2Cl_2 (0.1 M) at 35 °C for 24 h. Isolated yield. The dr determined by ^1H NMR analysis. The ee determined by chiralphase HPLC analysis. [b] **2a'** (X = Cl).

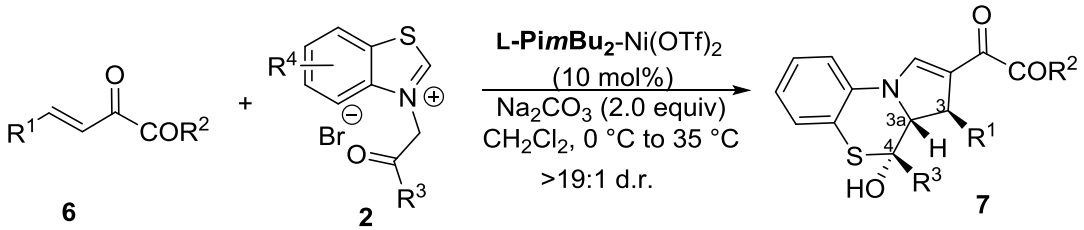
(b) **Substrate scope for chalcones in [3 + 2] cycloaddition**

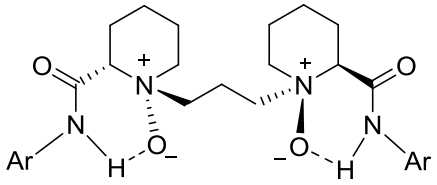


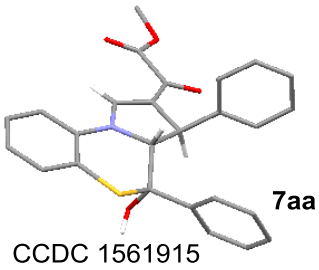
Entry[a]	**5**: Ar; R	Yield [%][b]	ee [%][c]
1	**5aa**: Ph; Ph	94	99
2	**5ba**: 3-ClC_6H_4; Ph	92	96
3	**5ca**: 4-MeC_6H_4; Ph	99	99
4	**5da**: 4-ClC_6H_4; Ph	99	98
5	**5ea**: Ph; 2-naphthyl	99	99
6	**5fa**: Ph; 3-MeC_6H_4	92	99
7	**5ga**: Ph; 4-ClC_6H_4	99	99
8	**5ha**: Ph; CH=CHPh	81	99

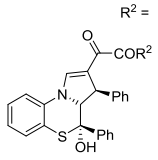
[a] The reactions were performed with $Mg(OTf)_2$-**L-PicP** (1:1, 10 mol%), **4** (0.10 mmol), **2a** (1.5 equiv) and K_3PO_4 (1.5 equiv) in CH_2Cl_2 (0.2 M). [b] Isolated yield. [c]The ee value was determined by chiralphase HPLC analysis. The dr value was determined by ^1H NMR analysis.

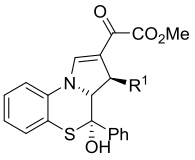
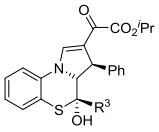
(c) **Substrate scope for β,γ-unsaturated α-ketoesters and thiazolium salts in [3 + 2] cycloaddition/rearrangement.**







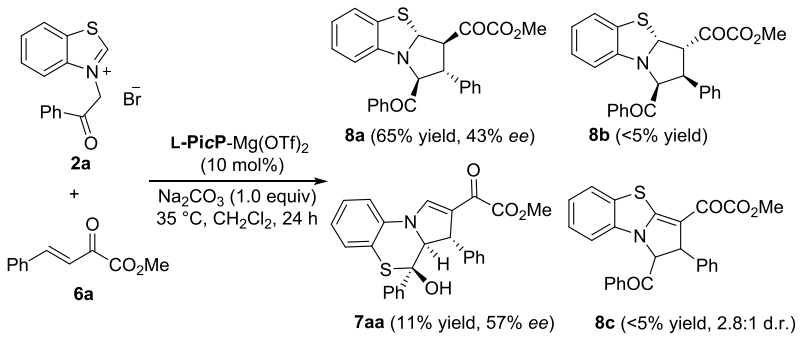
Entry[a]	Product **7**		Yield [%][b]	ee [%][c]
1	 **6a-6e/2a**	OMe (**7aa**)	86	93
2		OEt (**7ba**)	99	90
3		O^{i}Pr (**7ca**)	94	95
4		OBn (**7da**)	87	96
5		NH^{t}Bu (**7ea**)	94	87
6		4-$MeOC_6H_4$ (**7fa**)	68	95
7		4-PhC_6H_4 (**7ga**)	74	92

8	R^1 =  **6f-6m/2a**	4-FC_6H_4 (**7ha**)	84	92
9		4-BrC_6H_4 (**7has**)	83	90
10		3-$MeOC_6H_4$ (**7ia**)	88	90
11		3-Thienyl (**7ja**)	78	92
12		Cyclohexyl (**7ka**)	61	54
13		 (**7la**)	76	84
14	R^3 =  **6c/2b-2f, 2i**	2-FC_6H_4 (**7cb**)	78	96
15		3-$MeOC_6H_4$ (**7cc**)	76	95
16		4-ClC_6H_4 (**7cd**)	99	93
17		4-MeC_6H_4 (**7ce**)	76	94
18		4-$F_3CC_6H_4$ (**7cf**)	92	92
19		 (**7ci**)	46	95

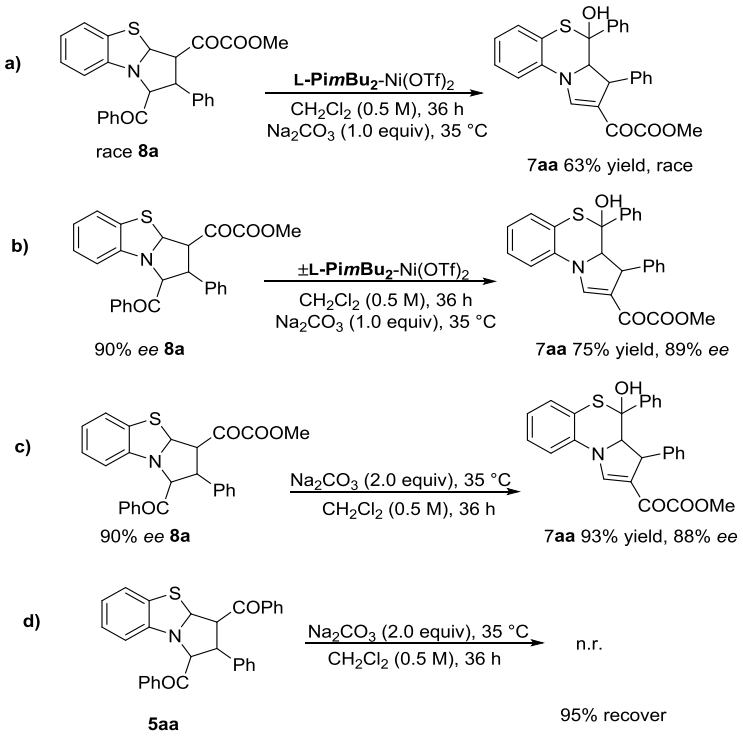
[a] The reactions were performed with $Ni(OTf)_2$-**L-Pi*m*Bu$_2$** (1:1, 10 mol%), **6** (0.10 mmol), **2** (1.0 equiv) and Na_2CO_3 (2.0 equiv) in CH_2Cl_2 (0.5 M) at 0 ^oC for 24 h, then at 35 ^oC for 36 h. [b] Isolated product. [c] The ee and dr values were determined by chiralphase SFC analysis and ^1H NMR analysis, respectively.

7. Proposed reaction mechanism

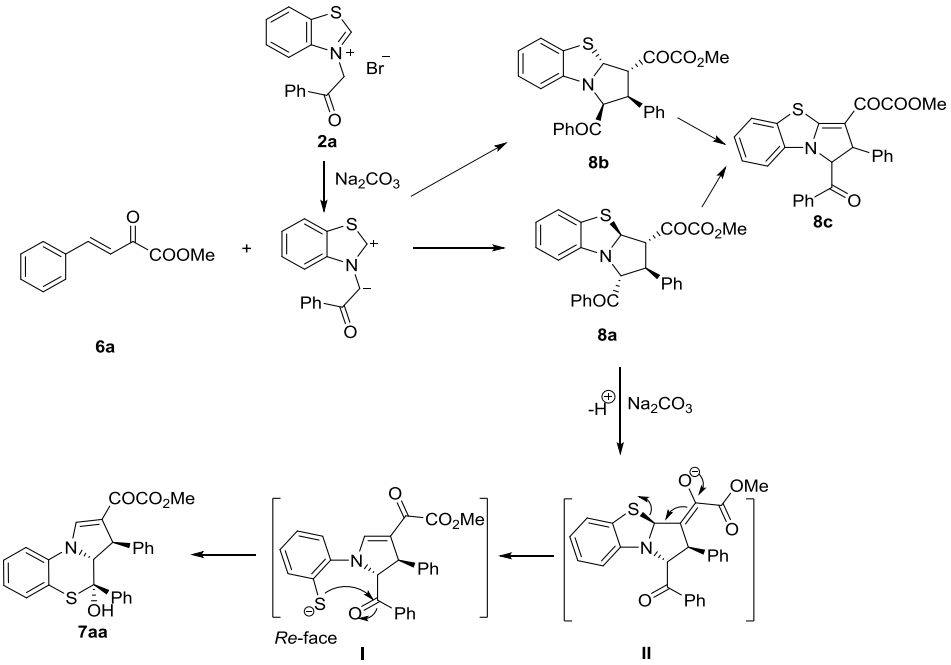
(a) Detected the main product



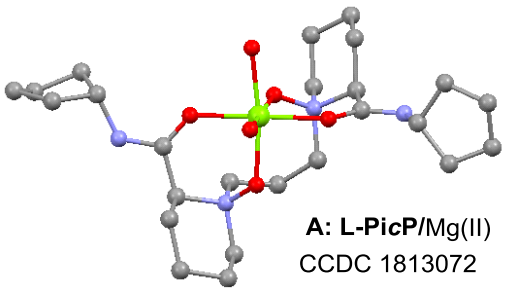
(b) Control experiments

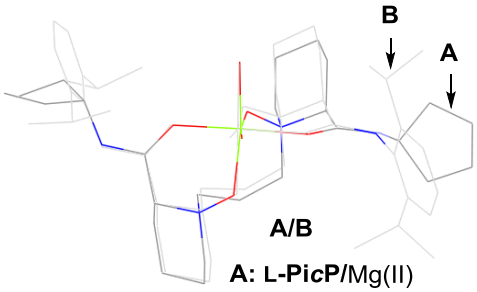


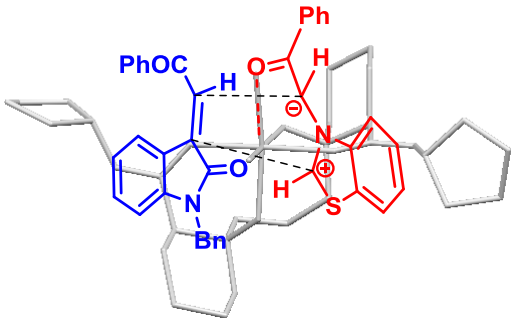
(c) Reaction mechanism

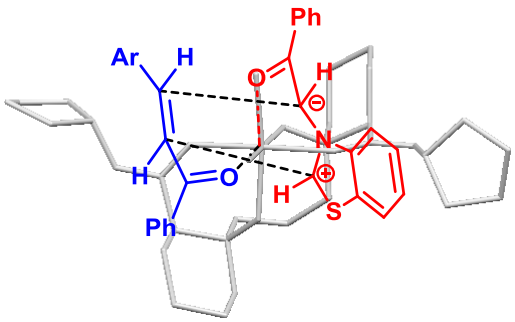


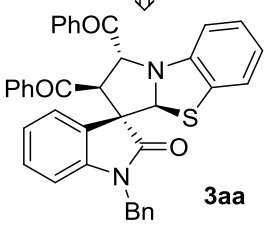
(d) Propose transition state based on X-ray crystal structures of the catalystIII.



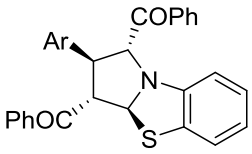








3aa

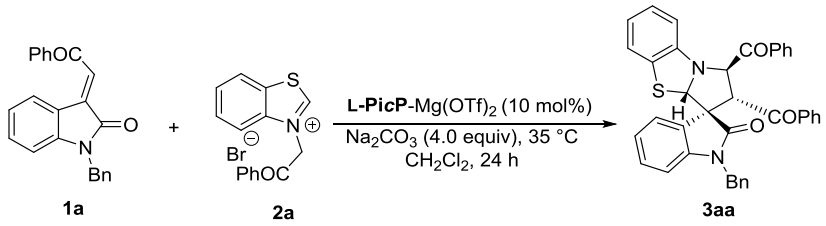


5da Ar = 4-ClC$_6$H$_4$

The structure of chiral **L-PicP**-Mg(OTf)$_2$ complex catalyst was determined by X-ray crystal analysis. The chiral ligand **L-PicP** coordinates to Mg(OTf)$_2$ to form an octahedral complex with two amine oxide oxygens and two amide oxygens, which is in consist with several other metal complexes of *N*,*N*'-dioxides. However, the superimposed crystal structures of **L-PiPr$_2$**-Ni(II) complex **A** and **L-PicP**-Mg(II) complex **B** indicates an open chiral pocket when cyclopenamine derived ligand **L-PicP** is used. We propose that the extremely low enantioselectivity from **L-PicP**-Ni(II) catalyst is due to that less active chiral Ni(II) catalyst bows to the base-initiated strong background reaction. While the poor result from **L-PiPr$_2$**-Mg(II) complex is owing to the narrow space created by the steric hindered 2,6-diisopropylaniline of the ligand, which is unable to load the two bulky reactants intothe chiral pocket, thus a non-asymmetric catalytic process dominated. Based on these information as well as the absolute configuration of products, we proposed models for the enantiocontrol observed in chiral *N*,*N*'-dioxide-Mg(II) complex promoted [3 + 2] cycloaddition reactions. Chiral **L-PicP**-Mg(OTf)$_2$ complex actives the two reactants by substitution of the auxiliary ligands. The α,β-unsaturated compound **1** or **4** is activated through bonding its carbonyl group to the metal center at the equatorial position, while the thiazolium *N*-ylide **2** bonds to the metal center with the benzoyl group at the upper axial position. The two-reactant monodentate bonding mode enable perfect enantioselective plane and position, then a [3 + 2] cycloaddition reaction occurs to yield the targeted product **3** and **5**.

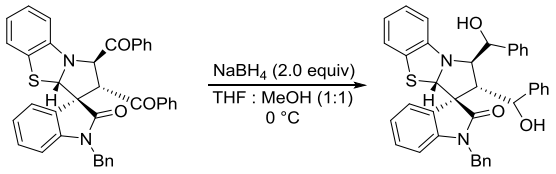
8. Experimental procedure for the scale-up reaction and transformations of the product

(a) Scale-up reaction

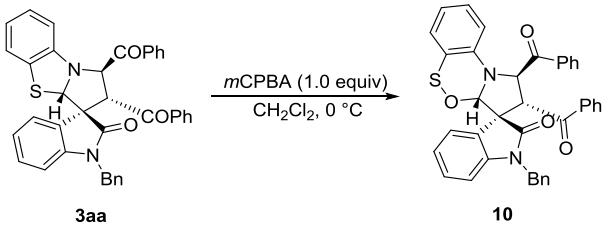


A dry round-bottom flask was charged with the catalyst **L-Pic*P*-**Mg(OTf)$_2$ (10 mol%, 78.8 mg), substrate **1a** (2.0 mmol, 0.679 g), thiazolium salt **2a** (1.1 equiv, 0.702 g), and Na_2CO_3 (4.0 equiv, 0.848 g) in CH_2Cl_2 (20.0 mL) were stirred at 35 ℃ for 48 h. The reaction mixture was detected by TLC. And then directly purified by flash chromatography (Eluent: petroleum ether/ethyl acetate = 10:1) on silica gel to afford the product **3aa** (1.176 g, 99% yield, 98% ee).

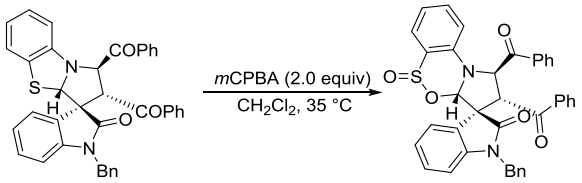
(b) Transformations of the product



(a) A dry test tube was charged with **3aa** (0.10 mmol, 98% ee), then, methanol (0.5 mL) and THF (0.5 mL) was added and the mixture was cooled to 0 ℃, $NaBH_4$ (2 equiv) was added in portion-wise to the solution of **3aa** at 0 ℃. The mixture was stirred for 60 minutes at 0 ℃. The reaction was quenched with aqueous NH_4Cl and the mixture was diluted with dichloromethane. The layers were separated and the aqueous layer was extracted with dichloromethane and dried over Na_2SO_4. Evaporation of the solvent afforded the residue. The residue was purified by silica gel column chromatography (Eluent: petroleum ether/ethyl acetate = 3/1) to obtain the product **9** (89% yield, >19:1 dr, 98% ee).



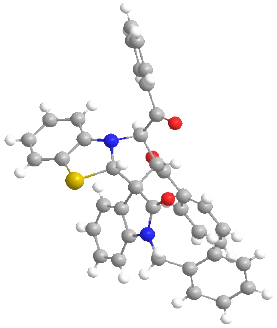
(b) To a solution of **3aa** (0.10 mmol) in CH_2Cl_2 (1.0 mL) was added *m*CPBA (1.0 equiv) at 0 ℃. After stirring for 60 minutes at 0 ℃, the reaction mixture was quenched with aqueous $NaHCO_3$ and the mixture was diluted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, evaporated in vacuo, and was purified by column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate = 2/1) to give product **10** (96% yield, >19:1 dr, 99% ee).

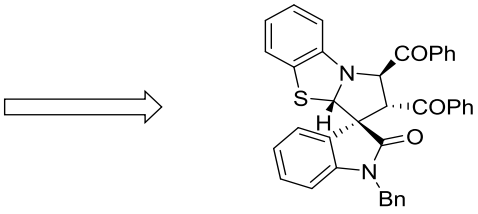


3aa **11**

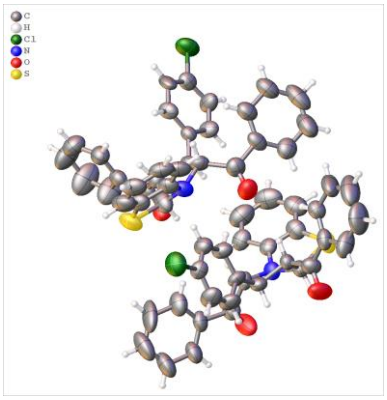
(c) To a solution of **3aa** (0.10 mmol) in CH_2Cl_2 (1.0 mL) was added *m*CPBA (2.0 equiv). After stirring for 24 h at 35 ℃, the reaction mixture was quenched with aqueous $NaHCO_3$ and the mixture was diluted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, evaporated in vacuo, and was purified by column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate = 3/1) to give product **11** (88% yield, 9:1 dr).

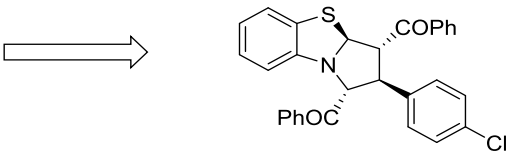
9. Determination of the absolute configuration of 3aa, 5da, 7aa, 10 and catalyst A by X-ray Crystallography.



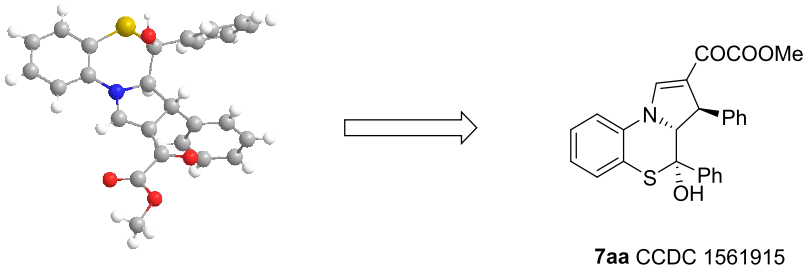


3aa CCDC 1508734

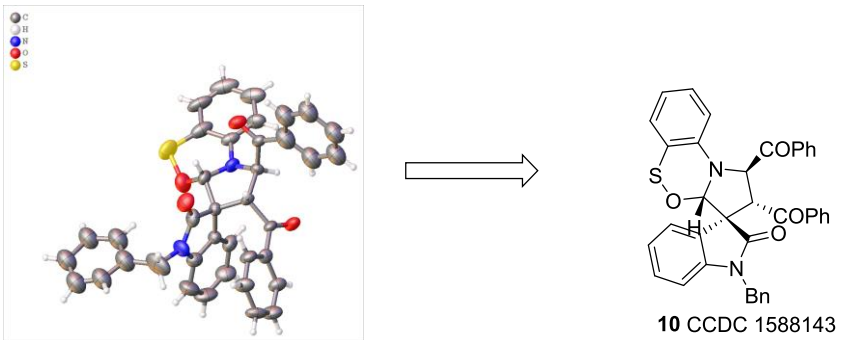




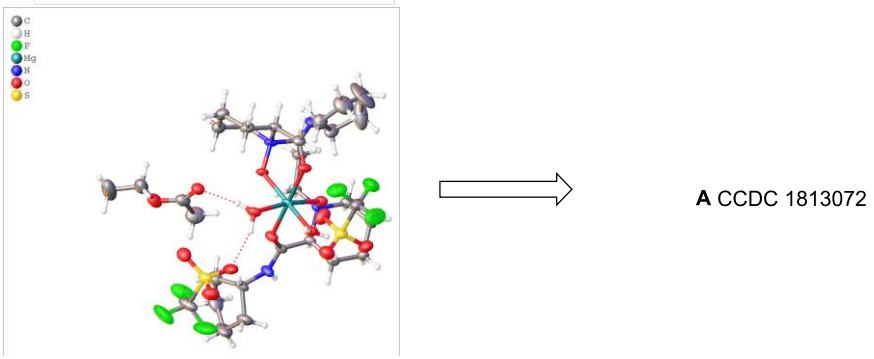
5da CCDC 1561920



7aa CCDC 1561915



10 CCDC 1588143



A CCDC 1813072

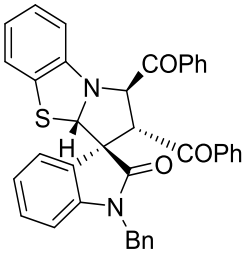
These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.

10. References

1. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett*, 2005, 2445; (b) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 1308; (c) K. Zheng, B. Qin, X. H. Liu, X. M. Feng, *J. Org. Chem.*, 2007, **72**, 8478; (d) X. Zhang, D. H. Chen, X. H. Liu, X. M. Feng, *J. Org. Chem.*, 2007, **72**, 5227; (*e*) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.*, 2009, **11**, 1401.
2. A. N. Matralis, A. P. Kourounakis, *J. Med. Chem.*, 2014, **57**, 2568.
3. X. Zhang, S. Cao, Y. Wei and M. Shi, *Chem. Commun.*, 2011, **47**, 1548.
4. Y. Hua, M. Liu, P. Huang, X. Song, M. Wang, and J. Chang, *Chem. Eur. J.*, 2015, **21**, 11994.

11. Spectral characterization data for the products

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3aa)



Light yellow solid; 99% yield, 98% ee; $[\alpha]^{33.4}_{D} = -255$ (*c* = 1.02, CH_2Cl_2);

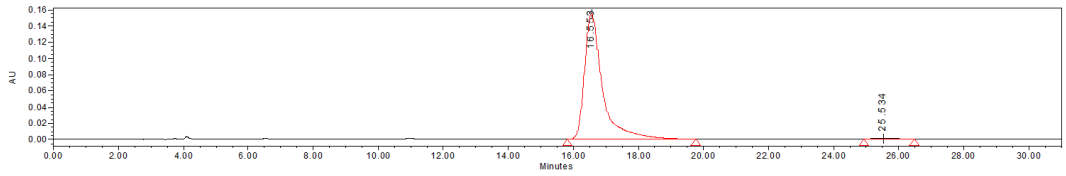
80% yield, 93% ee; $[\alpha]^{26.8}_{D} = -243$ (*c* = 0.81, CH_2Cl_2).

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.65 min, 25.53 min; m.p. 190-192 ℃.

^{1}H NMR: (400 MHz, $CDCl_3$) δ = 8.37 – 8.21 (m, 2H), 7.66 – 7.59 (m, 1H), 7.57 – 7.48 (m, 2H), 7.45 – 7.35 (m, 3H), 7.25 – 7.14 (m, 5H), 7.08 – 7.01 (m, 1H), 6.98 – 6.87 (m, 3H), 6.80 – 6.68 (m, 3H), 6.65 – 6.57 (m, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 6.32 – 6.20 (m, 2H), 6.13 (s, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$) δ = 198.6, 195.2, 174.1, 147.5, 142.8, 136.1, 135.7, 134.8, 133.8, 133.2, 129.1, 128.9, 128.7, 128.6, 128.2, 128.1, 127.5, 126.6, 126.5, 126.1, 125.9, 124.6, 121.97, 121.8, 121.0, 108.8, 108.7, 81.1, 67.3, 64.6, 57.5, 43.8.

HRMS (ESI-TOF) calcd for $C_{38}H_{28}N_2NaO_3S^+$ ([M]+Na^+) = 615.1713, Found 615.1721.



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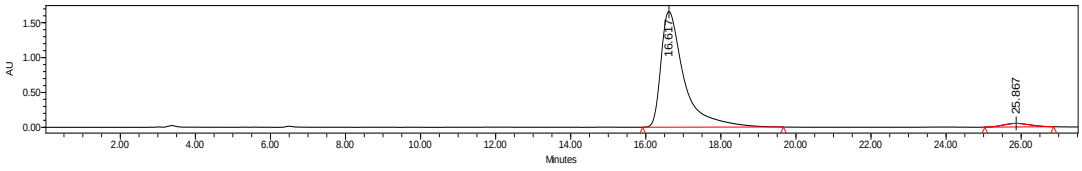
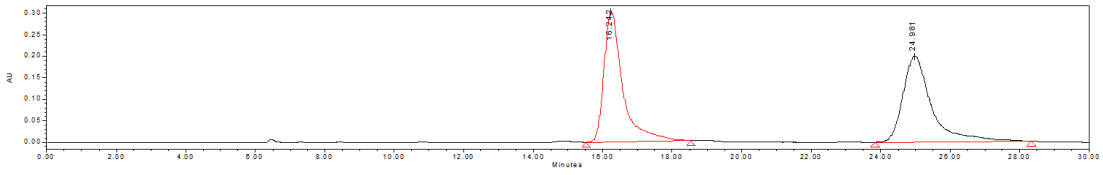
2	25.534	60544	1.00	1349

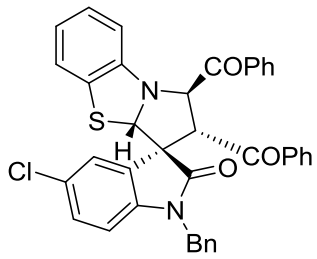


	Retention Time	Area	% Area	Height
1	16.617	70945109	96.59	1660885
2	25.867	2501010	3.41	50867



	Migration Time	Area	% Area	Height
1	16.242	11328361	49.92	300476
2	24.981	11363834	50.08	198430

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-5'-chloro-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3ba)



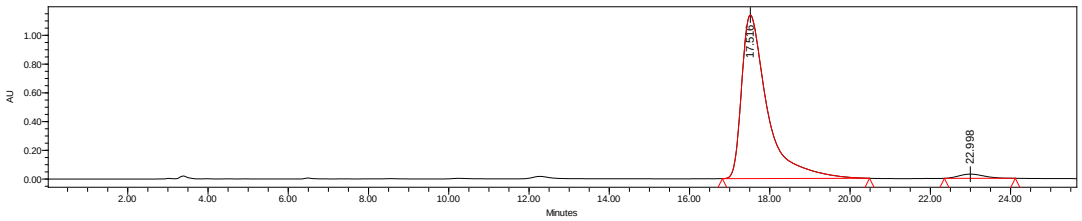
Light yellow solid; 99% yield, 95% ee; $[\alpha]^{25.6}_{D}$ = –248 (*c* = 1.08, CH_2Cl_2); m.p. 193-195 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.52 min, 23.00 min.

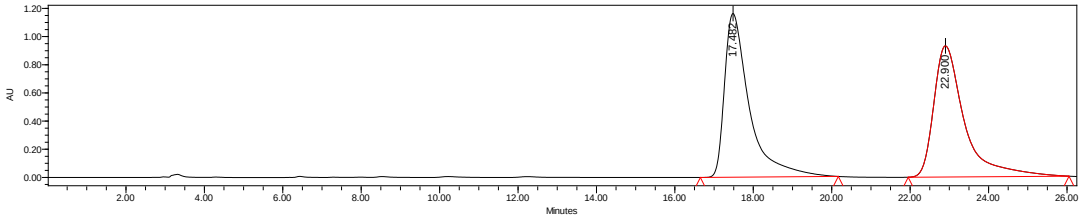
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 3H), 7.25 – 7.15 (m, 5H), 7.14 – 7.06 (m, 1H), 6.98 – 6.70 (m, 6H), 6.44 (d, *J* = 6.8 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 6.14 – 5.90 (m, 2H), 5.19 (d, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.2, 194.9, 173.8, 147.2, 141.3, 135.9, 135.5, 134.3, 133.9, 133.4, 129.1, 129.0, 128.8, 128.6, 128.3, 128.2, 127.1, 127.5, 126.8, 126.5, 126.4, 126.2, 126.1, 122.0, 121.5, 109.5, 109.0, 81.2, 67.3, 65.0, 56.9, 43.9.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}{}^{35}ClN_2NaO_3S^+$ ([M]+Na^+) = 649.1323, Found 649.1320. $C_{38}H_{27}{}^{37}ClN_2NaO_3S^+$ ([M]+Na^+) = 651.1294, Found 651.1311.

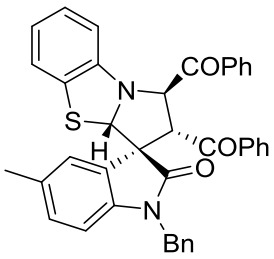


	Retention Time	Area	% Area	Height
1	17.516	50558086	97.52	1138170
2	22.998	1285364	2.48	29396



	Retention Time	Area	% Area	Height
1	17.482	51049947	50.29	1162404
2	22.900	50467888	49.71	931163

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-5'-methyl-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3ca)



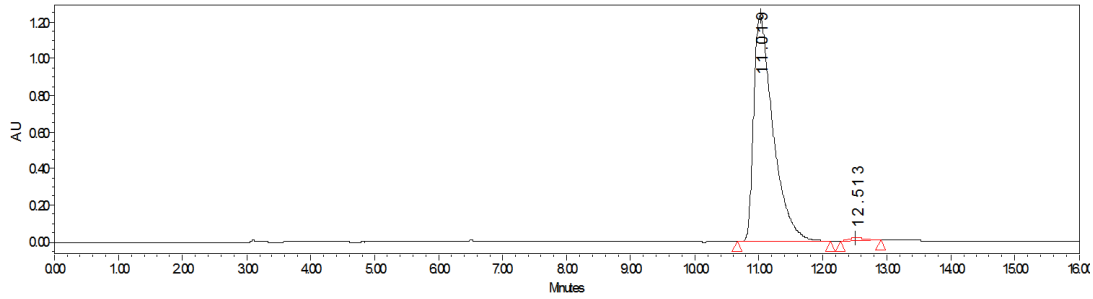
Light yellow solid; 99% yield, 98% ee; $[\alpha]^{33.4}_{D} = -249$ (*c* = 0.87, CH_2Cl_2); m.p. 187-189 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.02 min, 12.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 – 8.24 (m, 2H), 7.65 – 7.59 (m, 1H), 7.57 – 7.50 (m, 2H), 7.45 – 7.38 (m, 3H), 7.24 – 7.15 (m, 5H), 7.11 – 7.04 (m, 1H), 6.94 – 6.86 (m, 2H), 6.82 – 6.69 (m, 4H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 5.97 (s, 1H), 5.15 (d, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 15.6 Hz, 1H), 1.90 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.6, 195.3, 174.0, 147.8, 140.4, 136.2, 135.7, 134.9, 133.8, 133.1, 131.4, 129.1, 128.9, 128.8, 128.7, 128.2, 128.1, 127.4, 127.3, 126.6, 126.6, 125.8, 124.6, 121.7, 120.9, 108.9, 108.3, 81.1, 67.4, 64.7, 57.2, 43.8, 20.8.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_3S^+$ ([M]+Na^+) = 629.1869, Found 629.1871.



	Migration Time	Area	% Area	Height
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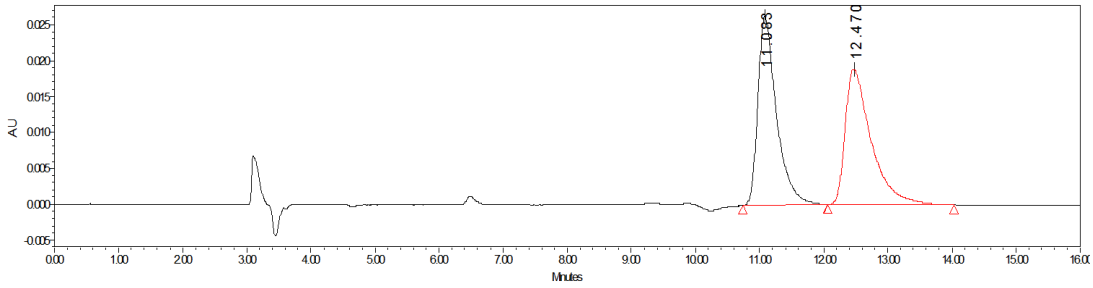
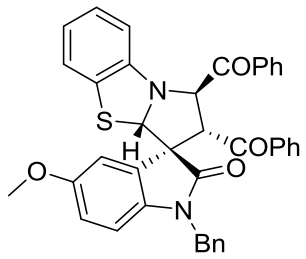
2	12.513	319117	1.21	16378



	Migration Time	Area	% Area	Height
1	11.083	530774	50.18	26367
2	12.470	526887	49.82	18859

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-5'-methoxy-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3cas)



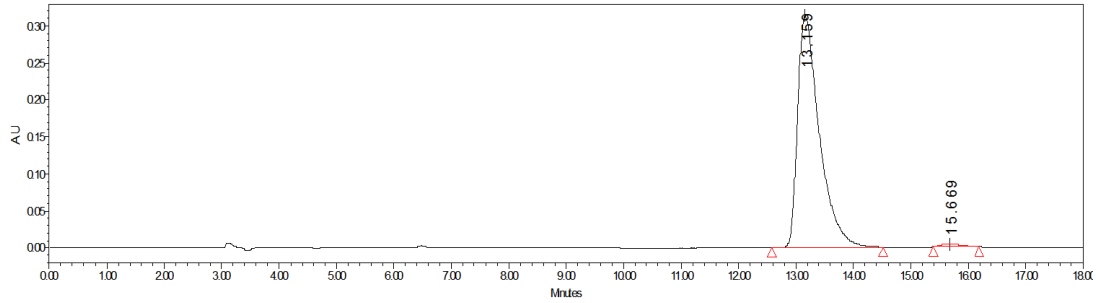
Light yellow solid; 99% yield, 98% ee; $[\alpha]^{33.3}_{D}$ = –249 (*c* = 0.61, CH_2Cl_2); m.p. 197-200 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.16 min, 15.67 min.

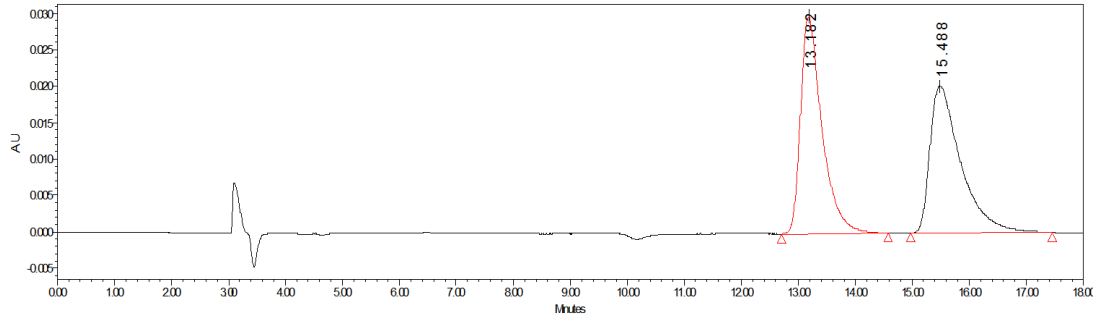
^{1}H NMR: (400 MHz, $CDCl_3$) δ = 8.38 – 8.17 (m, 2H), 7.65 – 7.59 (m, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.35 (m, 3H), 7.26 – 7.12 (m, 5H), 7.10 – 7.01 (m, 1H), 6.97 – 6.87 (m, 2H), 6.85 – 6.65 (m, 3H), 6.48 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.27 – 6.02 (m, 2H), 5.88 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 3.25 (s, 3H).

^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$) δ = 198.5, 195.1, 173.8, 155.1, 147.6, 136.2, 136.1, 135.6, 134.9, 133.9, 133.2, 129.1, 129.0, 128.7, 128.2, 128.2, 127.5, 126.9, 126.6, 125.9, 125.5, 122.0, 120.9, 115.8, 111.2, 109.4, 108.6, 80.9, 67.2, 65.3, 57.4, 55.2, 43.9.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1815.

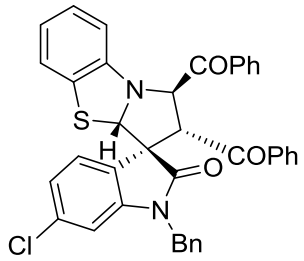


	Migration Time	Area	% Area	Height
1	13.159	8260458	98.83	313209
2	15.669	98056	1.17	3755



	Migration Time	Area	% Area	Height
1	13.182	778727	50.54	29788
2	15.488	762103	49.46	20243

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-6'-chloro-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3da)



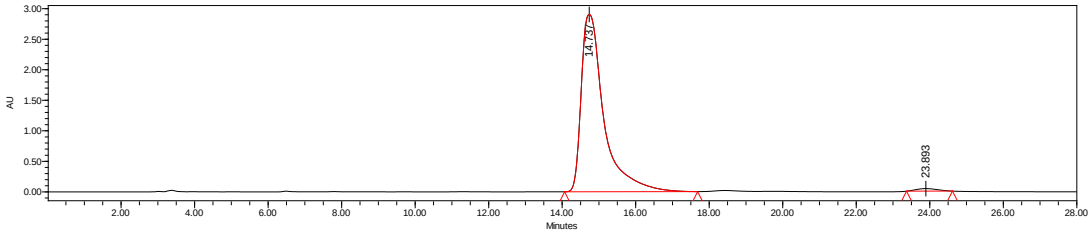
Light yellow solid; 99% yield, 97% ee; $[\alpha]^{25.7}_{D}$ = –309 (*c* = 0.76, CH_2Cl_2); m.p. 180-184 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.74 min, 23.89 min.

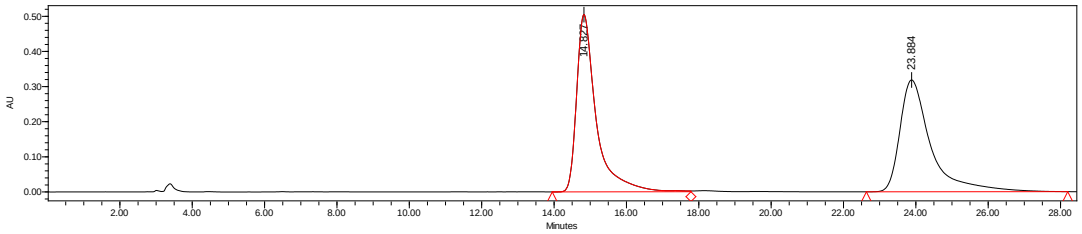
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.26 – 7.15 (m, 5H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 – 6.84 (m, 2H), 6.83 – 6.69 (m, 3H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 6.8 Hz, 1H), 6.27 (s, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.3, 195.0, 174.3, 147.3, 144.0, 135.9, 135.6, 134.4, 134.2, 133.9, 133.5, 129.1, 129.0, 128.9, 128.3, 128.2, 127.7, 127.0, 126.5, 126.3, 126.1, 123.1, 122.0, 121.9, 121.2, 109.3, 108.9, 81.1, 67.3, 64.5, 57.2, 44.0.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}{}^{35}ClN_2NaO_3S^+$ ([M+Na$^+$]) = 649.1323, Found 649.1326.
$C_{38}H_{27}{}^{37}ClN_2NaO_3S^+$ ([M+Na$^+$]) = 651.1294, Found 651.1363.

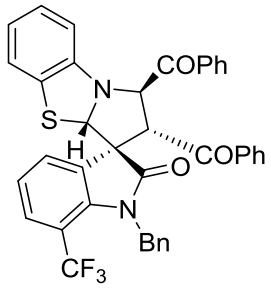


	Retention Time	Area	% Area	Height
1	14.737	123564678	98.67	2903386
2	23.893	1667028	1.33	41501



	Retention Time	Area	% Area	Height
1	14.827	19002386	50.20	504811
2	23.884	18853482	49.80	318315

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-2'-oxo-7'-(trifluoromethyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3ea)



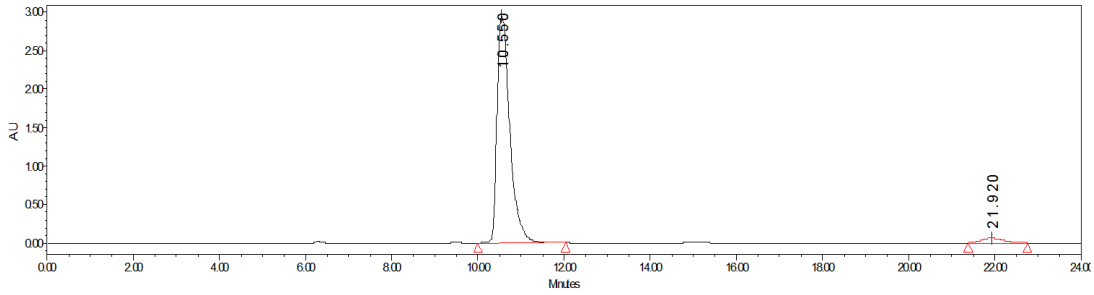
Light yellow solid; 94% yield, 93% ee; $[\alpha]^{33.3}_{D}$ = –193 (*c* = 0.96, CH_2Cl_2); m.p. 148-150 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.55 min, 21.92 min.

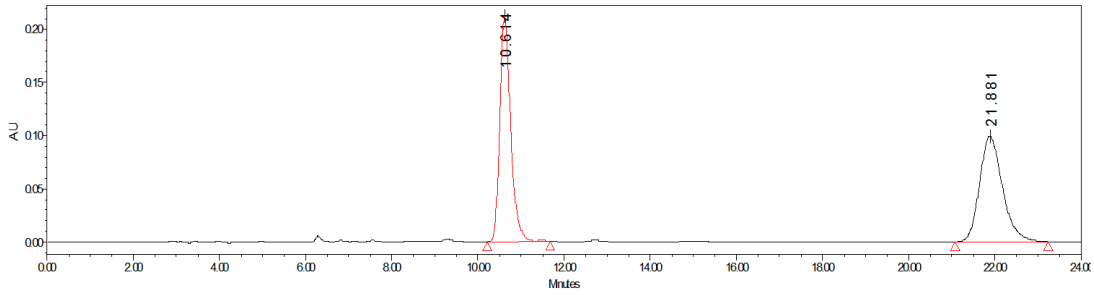
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.15 (m, 7H), 7.12 – 7.04 (m, 1H), 6.94 (d, *J* = 6.8 Hz, 2H), 6.87 – 6.63 (m, 4H), 6.45 (dd, *J* = 14.8, 7.6 Hz, 2H), 6.09 (s, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.57 (d, *J* = 17.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.2, 195.5, 175.7, 147.2, 141.1, 136.1, 135.6, 135.6, 134.0, 133.5, 129.4, 129.1, 129.0, 128.4, 128.2, 127.8, 127.8, 127.0, 126.9, 126.3, 126.2, 125.4, 122.9 (d, *J* = 273.0 Hz) 122.0, 121.5, 121.2, 112.5 (d, *J* = 33.1 Hz), 108.8, 81.4, 66.9, 63.2, 58.6, 45.6 (q, *J* = 5.4 Hz).

HRMS (ESI-TOF) calcd for $C_{39}H_{27}F_3N_2NaO_3S^+$ ([M]+Na^+) = 683.1587, Found 683.1588.

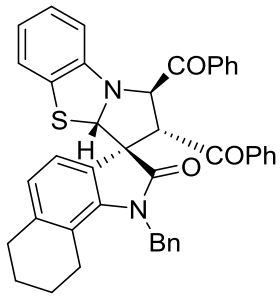


	Migration Time	Area	% Area	Height
1	10.550	60650459	96.58	2941412
2	21.920	2150060	3.42	61063



	Migration Time	Area	% Area	Height
1	10.614	3709827	50.20	211763
2	21.881	3679692	49.80	99348

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-2'-oxo-1,1',2,2',6',7',8',9'-octahydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-benzo[g]indole]-1,2-diyl}bis(phenylmethanone) (3eas)



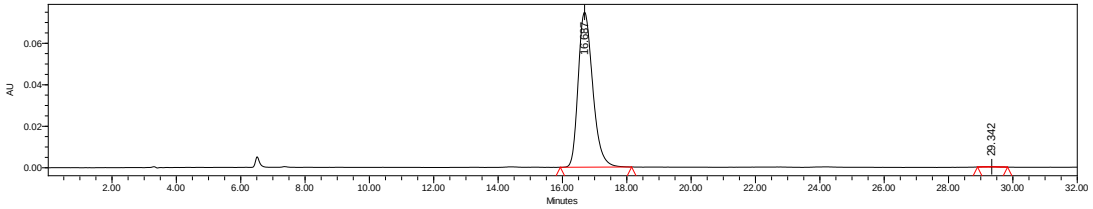
Light yellow solid; 99% yield, 99% ee; $[\alpha]^{33.3}_{D} = -225$ (*c* = 1.40, CH_2Cl_2); m.p. 182-183 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.69 min, 29.34 min.

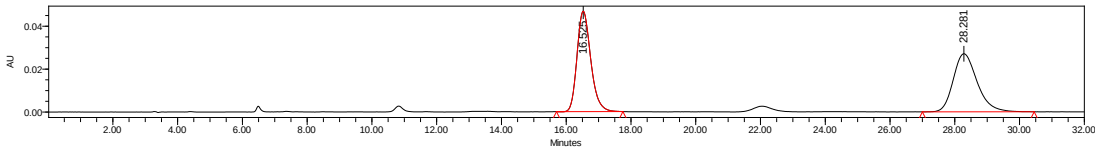
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 7.2 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 6.49 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.14 (m, 5H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 6.05 (d, *J* = 7.6 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.45 (d, *J* = 16.8 Hz, 1H), 2.70 – 2.51 (m, 2H), 2.45 – 2.33 (m, 1H), 2.28 – 2.16 (m, 1H), 1.62 – 1.53 (m, 1H), 1.49 – 1.35 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.9, 195.7, 175.7, 147.6, 140.8, 139.2, 137.0, 136.6, 135.7, 133.8, 132.8, 129.1, 128.9, 128.8, 128.0, 127.8, 127.0, 126.7, 125.8, 125.2, 123.6, 123.0, 122.3, 121.7, 120.8, 120.2, 108.7, 80.8, 67.2, 63.6, 58.8, 45.7, 30.2, 24.4, 22.6, 21.9.

HRMS (ESI-TOF) calcd for $C_{42}H_{34}N_2NaO_3S^+$ ([M]+Na^+) = 669.2182, Found 669.2183.

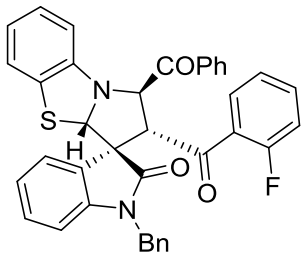


	Retention Time	Area	% Area	Height
1	16.687	2341210	99.82	74740
2	29.342	4148	0.18	139



	Retention Time	Area	% Area	Height
1	16.525	1378844	49.83	46852
2	28.281	1388034	50.17	27100

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(2-fluorobenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3fa)



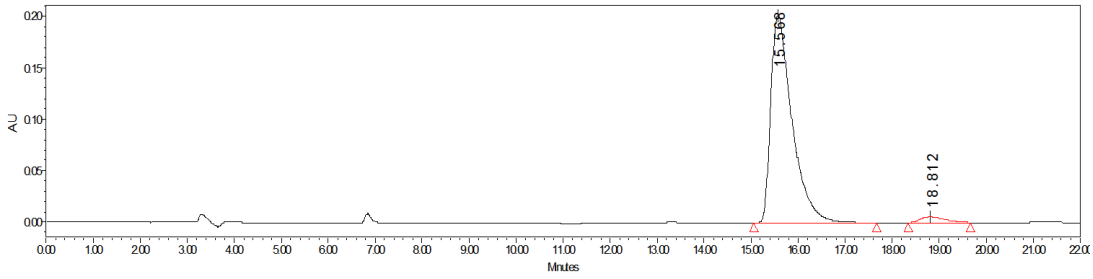
Light yellow solid; 94% yield, 98% ee; $[\alpha]^{33.3}_{D}$ = –211 (*c* = 0.61, CH_2Cl_2); m.p. 177-178 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.67 min, 18.81 min.

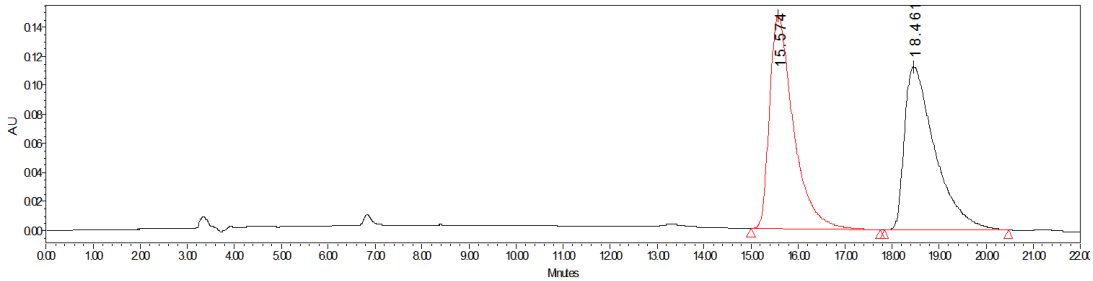
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 – 8.26 (m, 2H), 7.68 – 7.61 (m, 1H), 7.60 – 7.49 (m, 2H), 7.37 – 7.26 (m, 2H), 7.26 – 7.16 (m, 2H), 7.09 – 6.96 (m, 4H), 6.94 – 6.83 (m, 2H), 6.82 – 6.68 (m, 4H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.40 – 6.30 (m, 2H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 5.14 (d, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.96 (d, *J* = 15.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.5, 193.9, 173.7, 160.1 (d, *J* = 258.6 Hz), 147.5, 143.1, 135.8, 134.9, 133.9 (d, *J* = 8.6 Hz), 133.9, 129.6 (d, *J* = 1.8 Hz),129.2, 129.0, 128.9, 128.8, 127.6, 126.8, 126.5, 126.0, 125.9, 125.6 (d, *J* = 12.1 Hz), 124.8, 123.6 (d, *J* = 3.6 Hz), 122.2, 121.8, 121.1, 116.0 (d, *J* = 22.0 Hz), 108.8, 108.8, 80.8, 66.6, 64.1, 60.6, 43.8.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}FN_2NaO_3S^+$ ([M]+Na^+) = 633.1619, Found 633.1623.

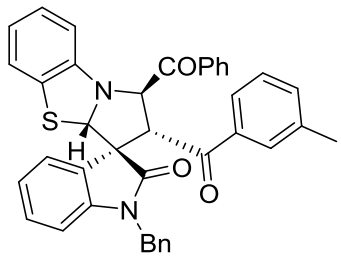


	Migration Time	Area	% Area	Height
1	15.568	6380174	96.76	201962
2	18.812	213304	3.24	5829



	Migration Time	Area	% Area	Height
1	15.574	5156191	50.51	146459
2	18.461	5051428	49.49	112167

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(3-methylbenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ga)



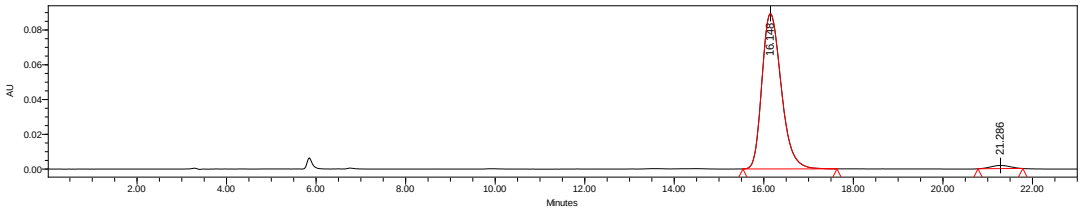
Light yellow solid; 99% yield, 96% ee; $[\alpha]^{33.3}_{D}$ = –263 (*c* = 1.23, CH_2Cl_2); m.p. 175-177 ℃

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.15 min, 21.29 min.

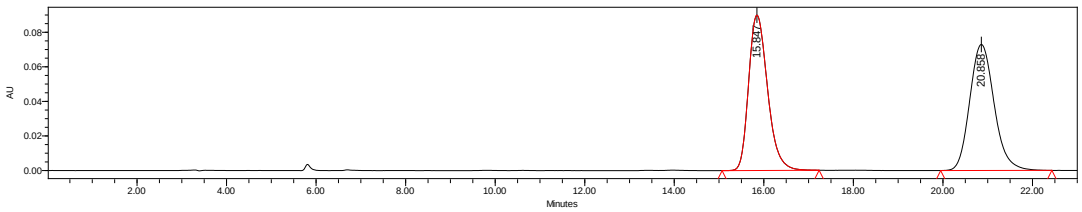
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.59 (d, 1H), 7.57 – 7.46 (m, 2H), 7.25 – 7.14 (m, 6H), 7.13 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 6.97 – 6.86 (m, 3H), 6.80 – 6.67 (m, 3H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.26 (t, *J* = 8.4 Hz, 2H), 6.13 (s, 1H), 5.14 (d, *J* = 7.2 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.7, 195.4, 174.2, 147.5, 142.9, 138.1, 136.2, 135.7, 134.9, 133.9, 133.8, 129.1, 128.9, 128.7, 128.7, 128.5, 128.1, 127.4, 126.5, 126.1, 125.9, 125.3, 124.7, 122.0, 121.8, 120.9, 108.8, 108.7, 81.1, 67.3, 64.7, 57.6, 43.8, 21.0.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_3S^+$ ([M]+Na^+) = 629.1869, Found 629.1870.

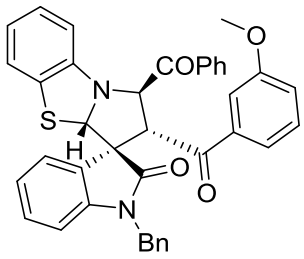


	Retention Time	Area	% Area	Height
1	16.148	2672136	97.95	89347
2	21.286	55849	2.05	1843



	Retention Time	Area	% Area	Height
1	15.847	2637603	48.87	89912
2	20.858	2759213	51.13	72930

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(3-methoxybenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3gas)



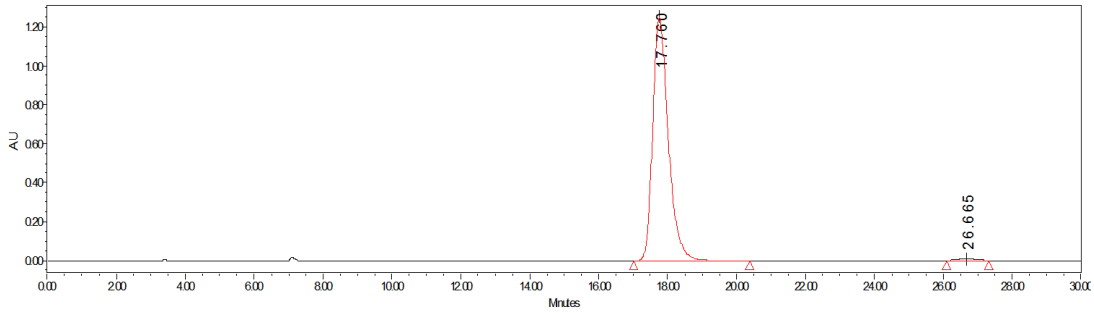
Light yellow solid; 96% yield, 98% ee; $[\alpha]^{33.3}_{D}$ = –243 (*c* = 1.01, CH_2Cl_2); m.p. 189-190 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.76 min, 26.67 min.

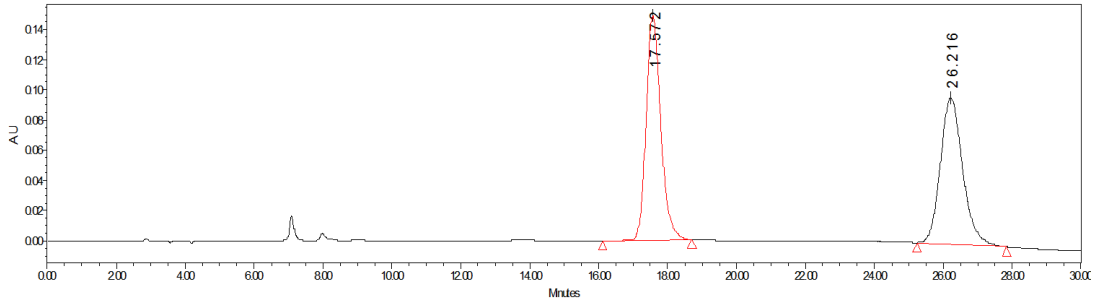
^{1}H NMR: (400 MHz, $CDCl_3$) δ = 8.43 – 8.12 (m, 2H), 7.66 – 7.60 (m, 1H), 7.59 – 7.45 (m, 2H), 7.25 – 7.15 (m, 3H), 7.14 – 7.08 (m, 2H), 7.08 – 7.01 (m, 2H), 7.01 – 6.85 (m, 4H), 6.84 – 6.78 (m, 1H), 6.78 – 6.66 (m, 3H), 6.64 – 6.56 (m, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 6.26 – 6.18 (m, 1H), 6.13 (s, 1H), 5.14 (d, *J* = 7.2 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.66 (s, 3H).

^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$) δ = 198.7, 195.1, 174.2, 159.3, 147.5 142.9, 137.4, 135.7, 134.8, 133.9, 129.1, 129.1, 128.9, 128.7, 128.6, 127.5, 126.6, 126.5, 126.1, 125.9, 124.7, 122.0, 121.8, 121.0, 120.7, 111.3, 108.8, 108.8, 81.0, 67.3, 64.6, 57.7, 55.2, 43.8.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1819.

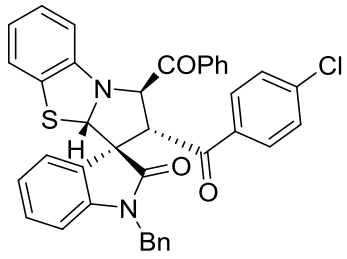


	Migration Time	Area	% Area	Height
1	17.760	39286997	99.04	1252210
2	26.665	378929	0.96	9930



	Migration Time	Area	% Area	Height
1	17.572	4387714	50.18	148608
2	26.216	4355896	49.82	97150

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(4-chlorobenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ha)



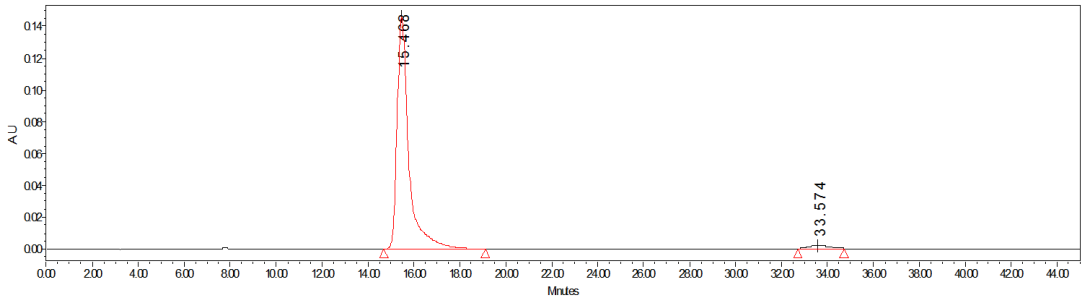
Light yellow solid; 99% yield, 96% ee; $[\alpha]^{25.4}_{D}$ = –289 (*c* = 1.29, CH_2Cl_2); m.p. 170-173 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.47 min, 35.57 min.

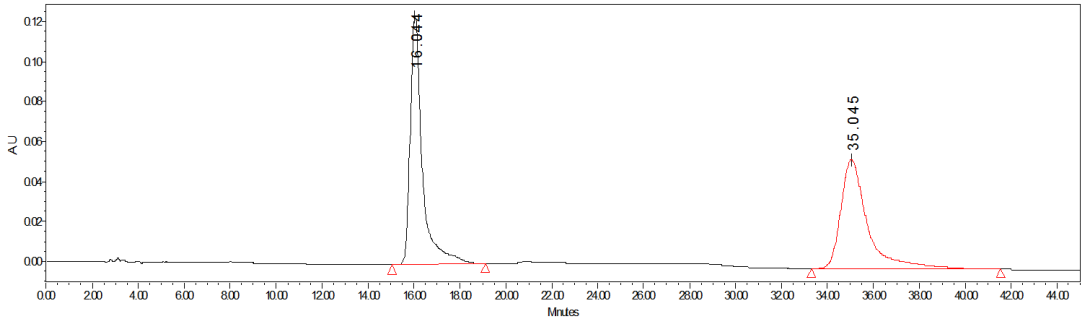
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.59 (m, 1H), 7.58 – 7.45 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.02 (m, 1H), 7.01 – 6.84 (m, 3H), 6.84 – 6.65 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.39 (t, *J* = 7.6 Hz, 2H), 6.23 (d, *J* = 7.6 Hz, 1H), 6.09 (s, 1H), 5.14 (d, *J* = 7.2 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.43 (d, *J* = 15.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)δ = 198.5, 193.9, 174.1, 147.4, 142.8, 139.8, 135.7, 134.7, 134.3, 133.9, 129.6, 129.1, 128.9, 128.7, 128.5, 127.6, 126.7, 126.5, 126.3, 125.9, 124.5, 122.0, 121.8, 121.1, 108.9, 108.8, 81.3, 67.6, 64.6, 57.1, 44.0.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}{}^{35}ClN_2NaO_3S^+$ ([M+Na$^+$) = 649.1323, Found 649.1328. $C_{38}H_{27}{}^{37}ClN_2NaO_3S^+$ ([M+Na$^+$) = 651.1294, Found 651.1313.

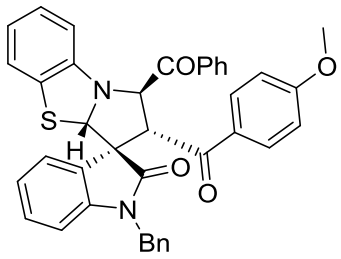


	Migration Time	Area	% Area	Height
1	15.468	5131537	97.73	145924
2	33.574	119072	2.27	2026



	Migration Time	Area	% Area	Height
1	16.044	4569747	50.81	124030
2	35.045	4423460	49.19	54489

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(4-methoxybenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ia)



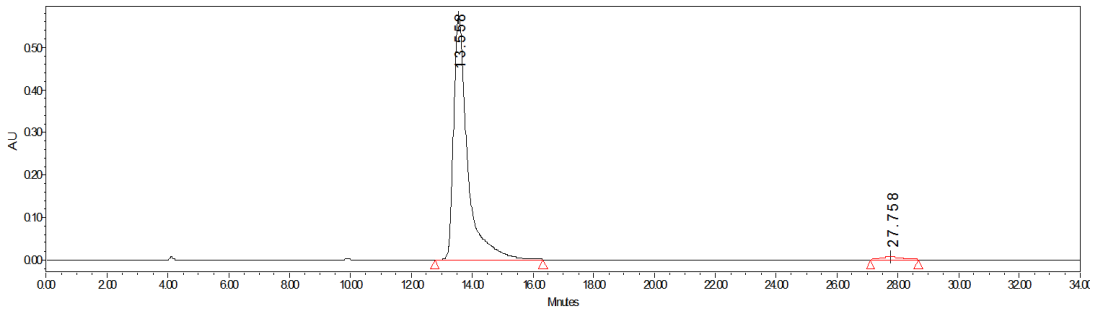
Light yellow solid; 95% yield, 97% ee; $[\alpha]^{33.3}_{D}$ = –165 (*c* = 0.94, CH_2Cl_2); m.p. 173-175 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.56 min, 27.76 min.

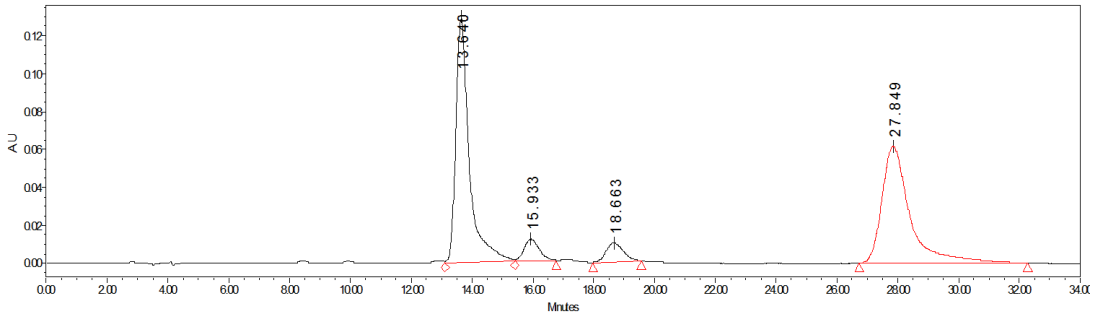
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 – 8.20 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 4H), 7.20 – 7.11 (m, 3H), 7.05 – 7.00 (m, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 6.8 Hz, 2H), 6.78 – 6.71 (m, 2H), 6.70 – 6.65 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.33 (dd, *J* = 11.6, 8.0 Hz, 2H), 6.14 (s, 1H), 5.12 (d, *J* = 7.6 Hz, 1H), 4.78 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.9, 192.8, 174.1, 163.8, 147.6, 142.7, 135.6, 134.8, 133.8, 130.8, 129.1, 128.9, 128.8, 128.6, 128.5, 127.4, 126.5, 126.4, 125.9, 124.6, 121.9, 121.7, 120.9, 113.5, 108.8, 81.4, 67.7, 64.9, 56.6, 55.4, 43.9.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1816.

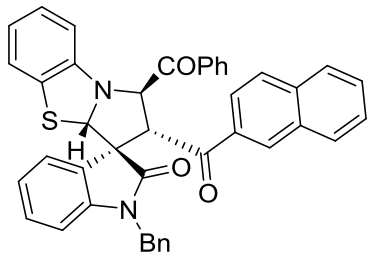


	Migration Time	Area	% Area	Height
1	13.558	18158016	98.42	567862
2	27.758	290792	1.58	6222



	Migration Time	Area	% Area	Height
1	13.640	3944830	45.59	129075
2	15.933	389236	4.50	11334
3	18.663	384514	4.44	9807
4	27.849	3934923	45.47	61516

(1*R*,2*R*,3*R*,3a*S*)-2-(2-Naphthoyl)-1-benzoyl-1'-benzyl-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ias)



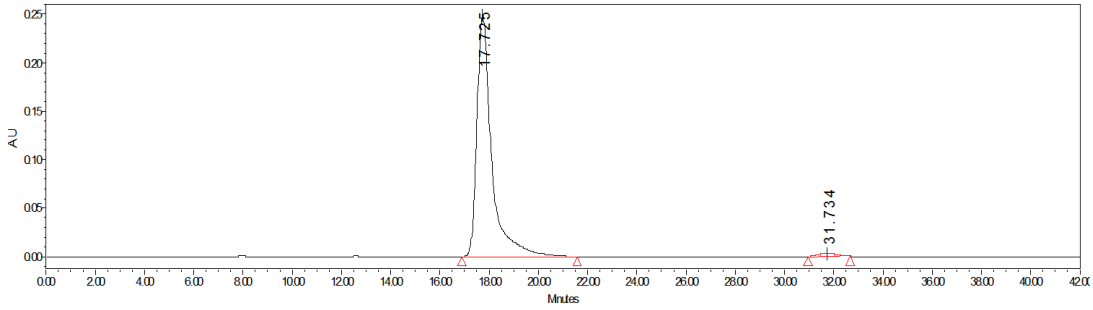
Light yellow solid; 99% yield, 97% ee; $[\alpha]^{33.3}_{D}$ = –394 (*c* = 1.34, CH_2Cl_2); m.p. 141-142 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.73 min, 31.74 min.

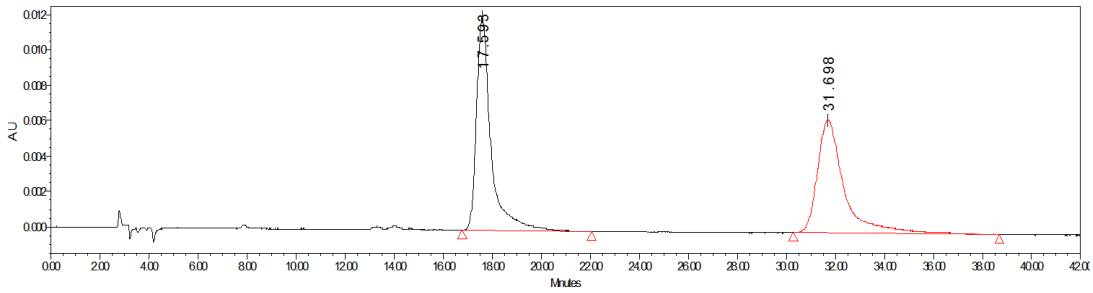
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 8.0 Hz, 2H), 8.13 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.47 (m, 6H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.94 – 6.84 (m, 3H), 6.80 – 6.67 (m, 5H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 7.6 Hz, 1H), 6.19 (s, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.36 (d, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 16.0 Hz, 1H), 3.95 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.7, 194.8, 174.3, 147.6, 142.7, 135.7, 135.4, 134.6, 133.8, 133.3, 132.0, 130.4, 129.7, 129.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.5, 127.3, 126.9, 126.5, 126.3, 126.2, 125.9, 124.6, 123.6, 122.0, 121.8, 121.0, 108.8, 108.8, 81.2, 67.5, 64.8, 57.4, 43.7.

HRMS (ESI-TOF) calcd for $C_{42}H_{30}N_2NaO_3S^+$ ([M]+Na^+) = 665.1869, Found 665.1872.

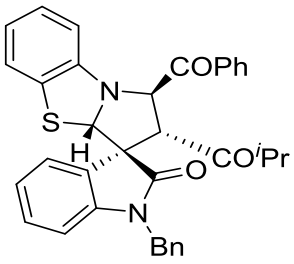


	Migration Time	Area	% Area	Height
1	17.725	10395945	98.45	248125
2	31.734	163254	1.55	3065



	Migration Time	Area	% Area	Height
1	17.593	494749	50.44	12017
2	31.698	486084	49.56	6359

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-isobutyryl-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ja)

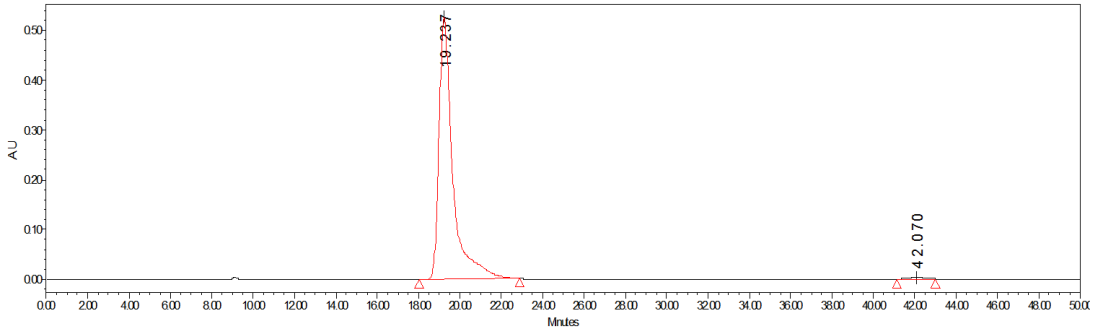


Light yellow solid; 99% yield, 99% ee; $[\alpha]^{33.2}_{D} = -307$ (*c* = 1.25, CH_2Cl_2); m.p. 173-175 ℃.

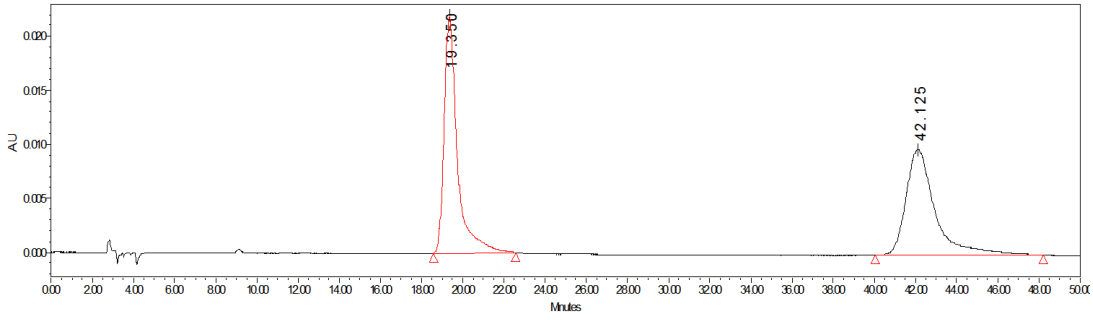
HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.24 min, 42.07 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 – 8.20 (m, 2H), 7.70 – 7.64 (m, 1H), 7.61 – 7.53 (m, 2H), 7.41 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 7.13 – 7.06 (m, 1H), 7.00 – 6.93 (m, 1H), 6.79 – 6.72 (m, 2H), 6.72 – 6.67 (m, 1H), 6.66 – 6.60 (m, 1H), 6.55 (d, *J* = 7.6 Hz 1H), 6.34 (d, *J* = 7.2 Hz, 1H), 6.03 (s, 1H), 5.94 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.62 – 4.51 (m, 1H), 4.39 (d, *J* = 8.0, 1H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.26 (d, *J* = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.5, 174.0, 168.0, 147.6, 143.7, 135.9, 135.4, 133.8, 129.1, 128.9, 128.8, 127.7, 127.4, 126.6, 125.9, 125.8, 124.6, 121.9, 121.7, 121.0, 108.9, 108.7, 80.0, 69.3, 67.4, 63.4, 54.6, 44.3, 21.3, 20.1.

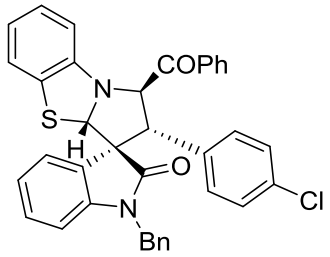


	Migration Time	Area	% Area	Height
1	19.237	24512263	99.26	525928
2	42.070	181790	0.74	2897



	Migration Time	Area	% Area	Height
1	19.350	980058	50.57	21908
2	42.125	957819	49.43	9780

(1*R*,2*R*,3*R*,3a*S*)-1-Benzoyl-1'-benzyl-2-(4-chlorophenyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ka)



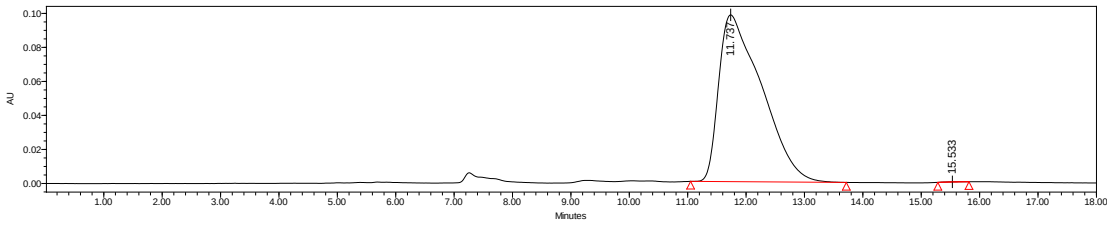
Light yellow solid; 74% yield, 99% ee; $[\alpha]^{25.9}_{D}$ = –260 (*c* = 0.61, CH_2Cl_2); m.p. 172-173 ℃..

HPLC DAICEL CHIRALCEL **IC**, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.74 min, 15.53 min.

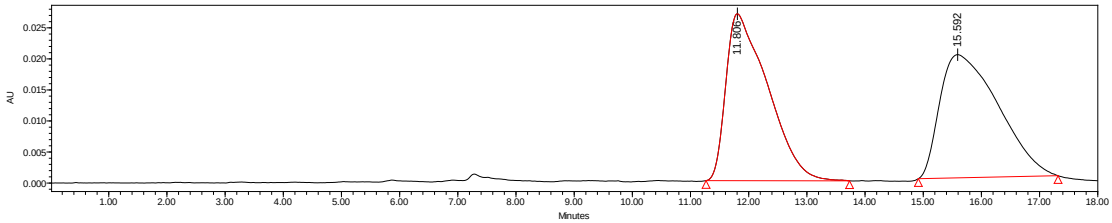
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.08 (m, 4H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.74 (m, 7H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 1H), 5.29 (d, *J* = 11.6 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.52 (d, *J* = 16.0 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 199.1, 173.5, 147.5, 142.9, 135.4, 134.5, 134.2, 133.7, 130.6, 130.2, 129.2, 128.8, 128.7, 128.6, 128.4, 128.3, 127.5, 126.4, 125.8, 125.2, 125.1, 122.2, 121.5, 121.4, 109.8, 109.7, 77.9, 74.0, 66.3, 58.3, 43.7.

HRMS (ESI-TOF) calcd for $C_{37}H_{27}{}^{35}ClN_2NaO_2S^+$ ([M]+Na^+) = 621.1374, Found 621.1376. $C_{37}H_{27}{}^{37}ClN_2NaO_2S^+$ ([M]+Na^+) = 623.1344, Found 623.1342.

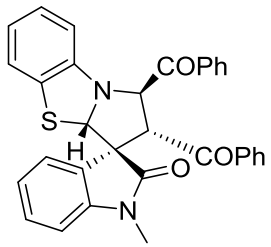


	Retention Time	Area	% Area	Height
1	11.737	5005295	99.93	98081
2	15.533	3281	0.07	158



	Retention Time	Area	% Area	Height
1	11.806	1342519	49.24	26889
2	15.592	1384109	50.76	19855

((1*R*,2*R*,3*R*,3a*S*)-1'-Methyl-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl)bis(phenylmethanone) (3la)



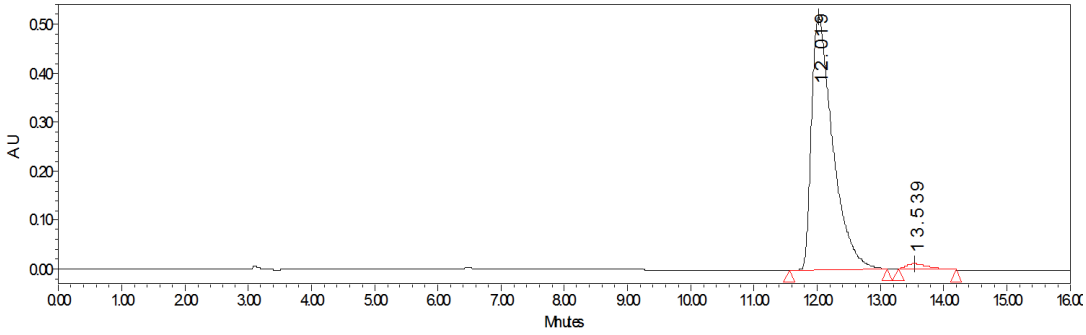
Light yellow solid; 99% yield, 96% ee; $[\alpha]^{33.3}_{D}$ = –253 (*c* = 0.80, CH_2Cl_2); m.p. 190-191 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.02 min, 13.54 min.

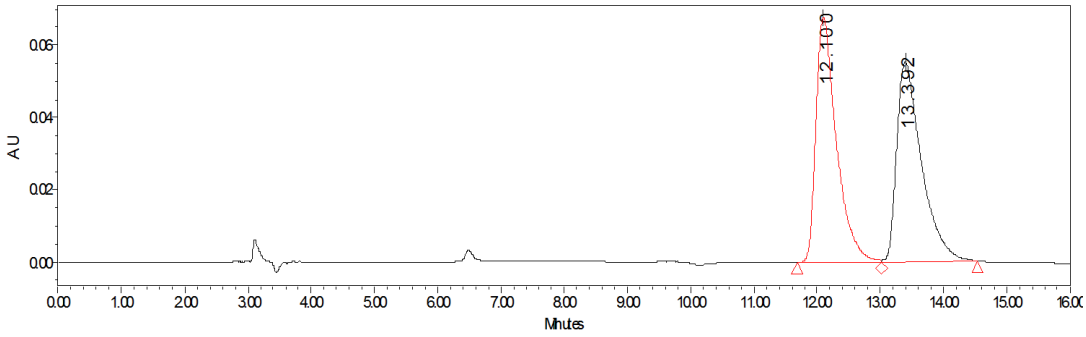
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 – 8.18 (m, 2H), 7.65 – 7.58 (m, 1H), 7.58 – 7.48 (m, 2H), 7.38 – 7.32 (m, 1H), 7.24 – 7.10 (m, 4H), 7.10 – 6.98 (m, 2H), 6.86 – 6.68 (m, 3H), 6.67 – 5.58 (m, 1H), 6.37 (dd, *J* = 14.0, 7.2 Hz, 2H), 6.22 – 6.11 (m, 1H), 6.06 (s, 1H), 5.01 (d, *J* = 6.8 Hz, 1H), 2.77 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.6, 195.6, 174.2, 147.4, 143.5, 136.3, 135.7, 133.9, 132.8, 129.1, 128.9, 128.8, 127.9, 127.8, 126.6, 125.9, 125.8, 124.8, 122.1, 121.7, 121.0, 108.9, 107.5, 80.0, 66.6, 64.4, 58.6, 26.2.

HRMS (ESI-TOF) calcd for $C_{32}H_{24}N_2NaO_3S^+$ ([M]+Na^+) = 539.1400, Found 539.1402.

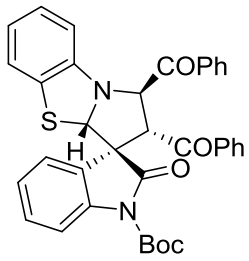


	Migration Time	Area	% Area	Height
1	12.019	12053887	98.02	516392
2	13.539	243763	1.98	10461



	Migration Time	Area	% Area	Height
1	12.100	1523702	50.28	67594
2	13.392	1506607	49.72	55219

***tert*-Butyl (1*R*,2*R*,3*R*,3a*S*)-1,2-dibenzoyl-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo [2,1-b]thiazole-3,3'-indoline]-1'-carboxylate (3ma)**



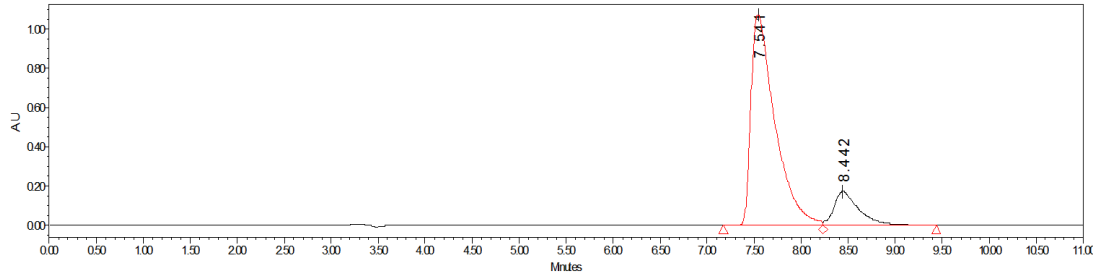
Light yellow solid; 99% yield, 72% ee; $[\alpha]^{33.2}_{D}$ = –115 (*c* = 0.66, CH_2Cl_2); m.p. 155-156 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.54 min, 8.44 min.

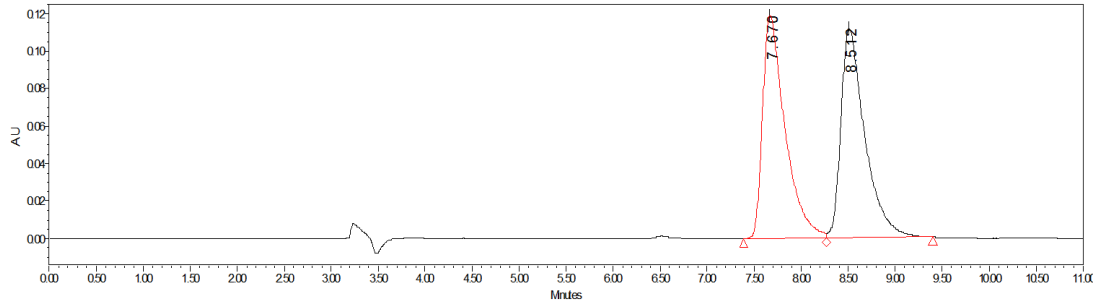
^{1}H NMR: (400 MHz, $CDCl_3$) δ = 8.33 – 8.21 (m, 2H), 7.66 – 7.60 (m, 1H), 7.57 – 7.50 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.23 – 7.13 (m, 4H), 7.11 – 7.00 (m, 2H), 6.80 – 6.65 (m, 4H), 6.37 (d, *J* = 7.2 Hz, 1H), 6.25 – 6.18 (m, 1H), 6.11 (s, 1H), 5.07 (d, *J* = 7.2 Hz, 1H), 1.56 (s, 9H).

^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$) δ = 198.5, 195.6, 173.6, 148.0, 147.2, 139.8, 136.3, 135.7, 134.0, 133.1, 129.2, 129.0, 128.2, 127.7, 126.6, 126.0, 125.5, 123.8, 121.8, 121.1, 114.3, 108.7, 84.6, 81.4, 66.5, 64.9, 59.9, 28.0.

HRMS (ESI-TOF) calcd for $C_{36}H_{30}N_2NaO_5S^+$ ([M]+Na^+) = 625.1768, Found 625.1771.

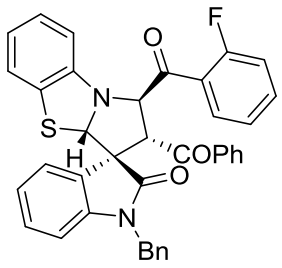


	Migration Time	Area	% Area	Height
1	7.541	19027597	85.80	1075622
2	8.442	3148841	14.20	171063



	Migration Time	Area	% Area	Height
1	7.670	1971580	49.95	118624
2	8.512	1975911	50.05	111564

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(2-fluorobenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ab)



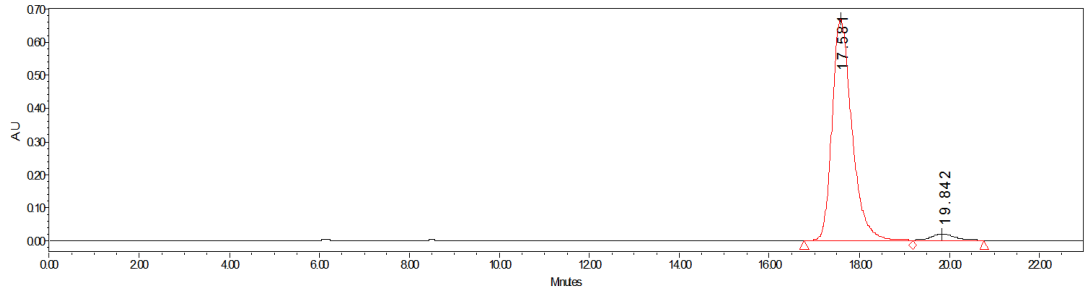
Light yellow solid; 99% yield, 94% ee; $[\alpha]^{25.4}_{D} = -191$ (*c* = 1.31, CH_2Cl_2); m.p. 190-191 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.58 min, 19.84 min.

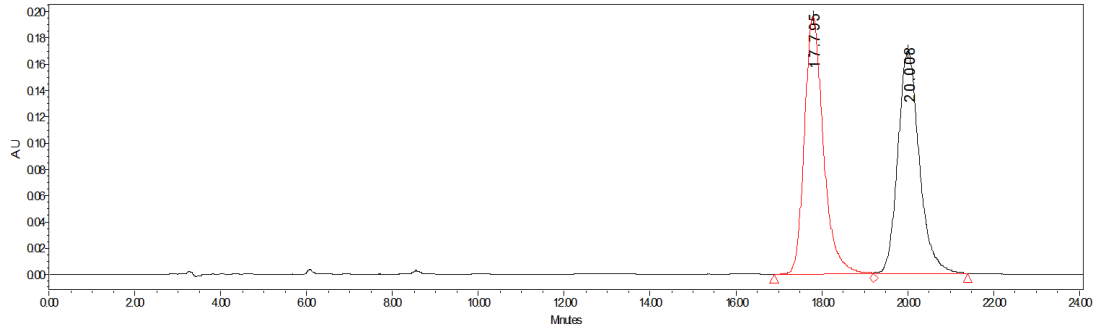
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (t, *J* = 7.3 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.43 – 7.34 (m, 3H), 7.26 – 7.11 (m, 7H), 7.09 – 7.02 (m, 1H), 6.96 – 6.85 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.76 – 6.64 (m, 2H), 6.55 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 6.8 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 5.24 (d, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.5 (d, *J* = 2.8 Hz), 194.8, 174.4, 160.5 (d, *J* = 254.5 Hz), 147.4, 142.8, 136.2, 134.9, 134.3, 134.2 (d, *J* = 8.7 Hz), 133.1, 130.4 (d, *J* = 2.8 Hz), 128.8, 128.6, 128.2, 128.1, 127.6, 126.7, 126.4, 126.2 (d, *J* = 20.0 Hz), 126.1 (d, *J* = 14.7 Hz), 124.8 (d, *J* = 3.3 Hz), 124.62, 122.0, 121.8, 121.2, 116.5 (d, *J* = 22.2 Hz), 109.1 (d, *J* = 2.7 Hz), 108.7, 80.7, 70.7 (d, *J* = 3.6 Hz), 64.6, 56.0, 43.9.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}FN_2NaO_3S^+$ ([M]+Na^+) = 633.1619, Found 633.1624.

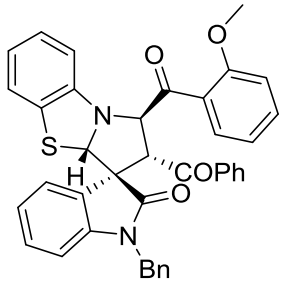


	Migration Time	Area	% Area	Height
1	17.581	20407426	96.76	669308
2	19.842	683914	3.24	19689



	Migration Time	Area	% Area	Height
1	17.795	6015343	50.51	196086
2	20.008	5893583	49.49	170001

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(2-methoxybenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3acs)



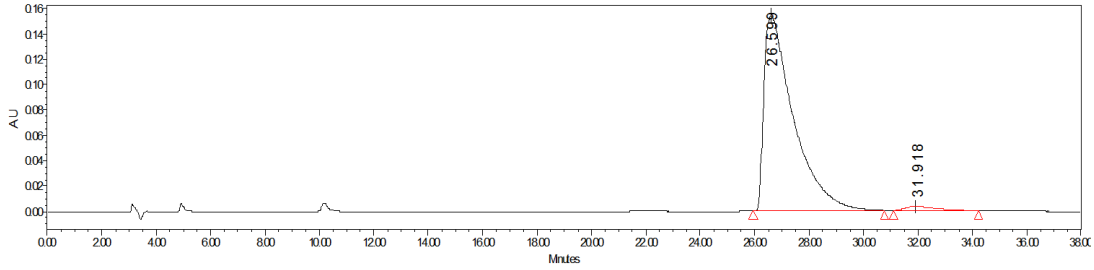
Light yellow solid; 89% yield, 96% ee; $[\alpha]^{25.5}_{D} = -203$ (*c* = 1.03, CH_2Cl_2); m.p. 184-186 ℃

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 26.60 min, 31.91 min.

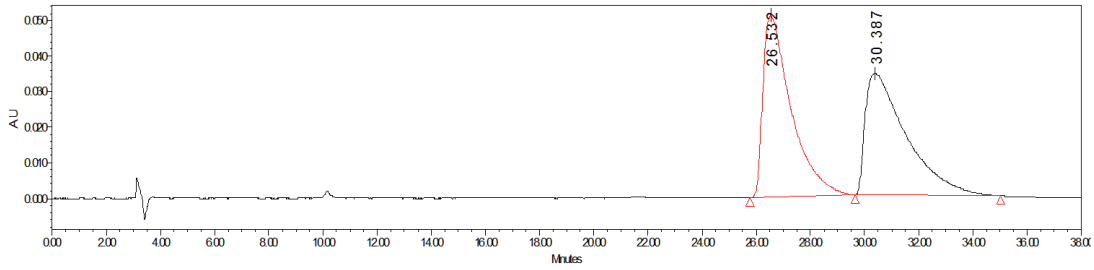
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.53 (m, 1H), 7.48 – 7.34 (m, 4H), 7.25 – 7.10 (m, 5H), 7.08 – 7.01 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.85 (m, 4H), 6.81 – 6.63 (m, 3H), 6.58 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.21 (d, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 5.21 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.32 (d, *J* = 15.6 Hz, 1H), 3.97 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 202.3, 194.5, 174.3, 157.2, 147.7, 142.7, 136.3, 134.8, 133.0, 132.9, 129.4, 128.7, 128.5, 128.2, 128.1, 127.4, 126.6, 126.4, 126.3, 125.8, 124.8, 121.9, 121.5, 121.0, 120.7, 111.1, 108.8, 108.7, 80.7, 71.3, 64.7, 55.6, 55.5, 43.8.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1821.

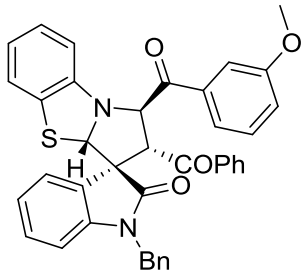


	Migration Time	Area	% Area	Height
1	26.599	11624211	97.81	154465
2	31.918	259770	2.19	3165



	Migration Time	Area	% Area	Height
1	26.532	3697964	50.68	51181
2	30.387	3599108	49.32	34031

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(3-methoxybenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ac)



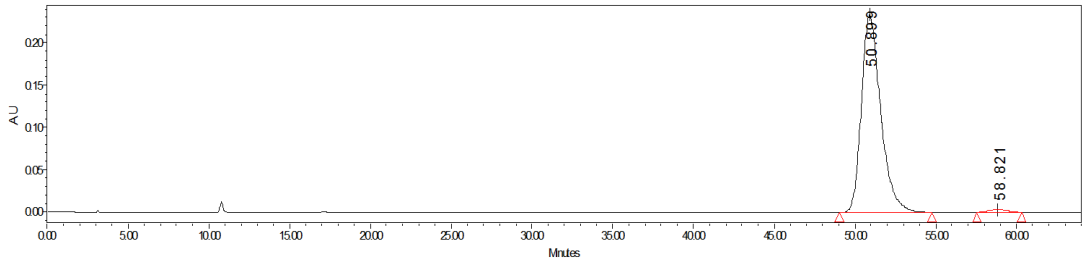
Light yellow solid; 99% yield, 98% ee; $[\alpha]^{26.5}_{D}$ = –235 (*c* = 0.87, CH_2Cl_2); m.p. 141-144 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 50.90 min, 58.82 min.

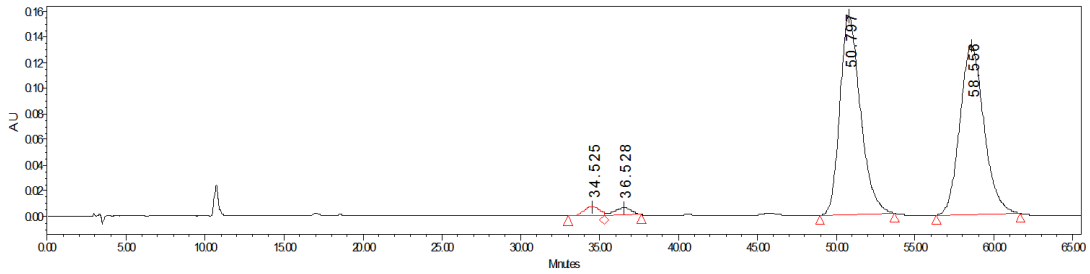
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.6 Hz, 1H), 7.73 (s, 1H), 7.43 (q, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 6H), 7.09 – 7.02 (m, 1H), 6.97 – 6.86 (m, 3H), 6.82 – 6.70 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 6.8 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 6.24 (d, *J* = 7.6 Hz, 1H), 6.13 (s, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.4, 195.3, 174.2, 160.0, 147.5, 142.8, 136.9, 136.2, 134.9, 133.3, 130.0, 128.8, 128.7, 128.2, 128.2, 127.5, 126.7, 126.5, 126.2, 126.0, 124.7, 122.1, 121.9, 121.7, 121.0, 121.0, 113.0, 108.9, 108.8, 81.1, 67.4, 64.7, 57.6, 55.5, 43.9.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1821.

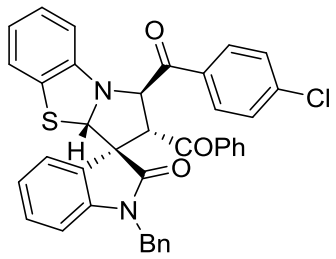


	Migration Time	Area	% Area	Height
1	50.899	19537268	98.63	233840
2	58.821	271181	1.37	3302



	Migration Time	Area	% Area	Height
1	34.525	458812	1.58	6996
2	36.528	416238	1.44	5431
3	50.797	14065145	48.57	154652
4	58.556	14019278	48.41	131488

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-chlorobenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ad)



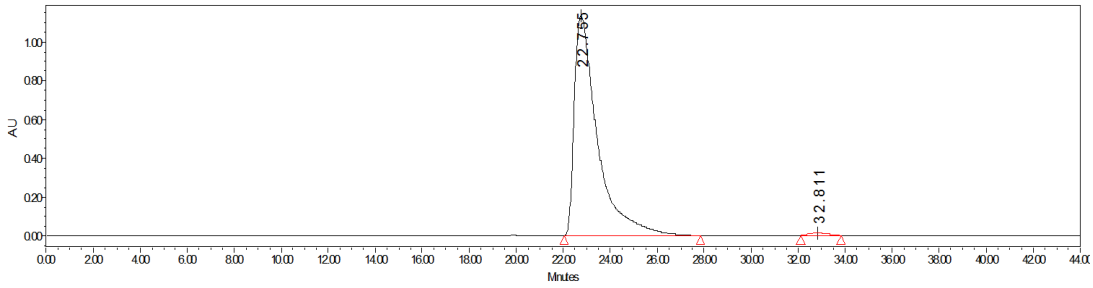
Light yellow solid; 99% yield, 98% ee; $[\alpha]^{26.5}_{D}$ = –190 (*c* = 1.28, CH_2Cl_2); m.p. 186-187 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.76 min, 32.81 min.

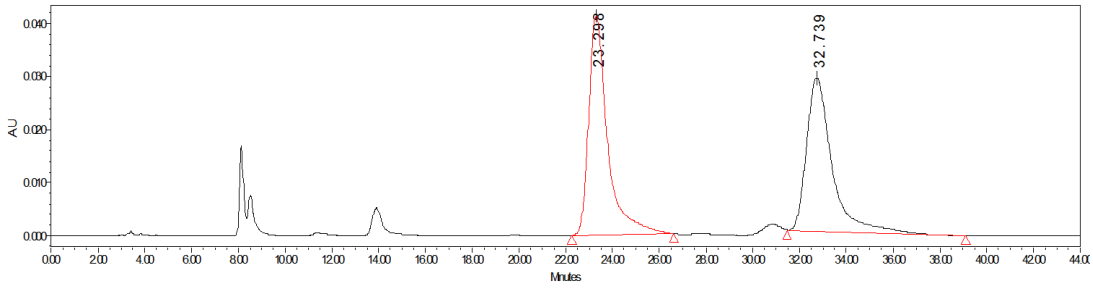
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.26 – 7.13 (m, 5H), 7.10 – 7.03 (m, 1H), 6.99 – 6.84 (m, 3H), 6.83 – 6.66 (m, 3H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 7.6 Hz, 1H), 6.10 (s, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.6, 195.2, 174.1, 147.3, 142.8, 140.5, 136.0, 134.7, 133.9, 133.3, 130.6, 129.3, 128.7, 128.7, 128.2, 128.1, 127.5, 126.6, 126.5, 126.0, 125.9, 124.5, 122.0, 121.9, 121.2, 108.8, 81.0, 67.5, 64.5, 57.5, 43.9.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}{}^{35}ClN_2NaO_3S^+$ ([M+Na$^+$]) = 649.1323, Found 649.1324.
$C_{38}H_{27}{}^{37}ClN_2NaO_3S^+$ ([M+Na$^+$]) = 651.1294, Found 651.1320.

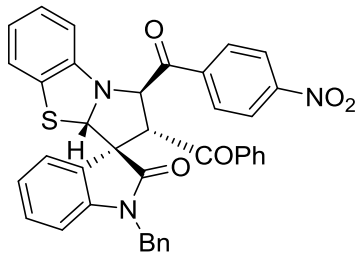


	Migration Time	Area	% Area	Height
1	22.755	77680512	99.10	1129161
2	32.811	702277	0.90	12957



	Migration Time	Area	% Area	Height
1	23.298	2326990	51.53	41330
2	32.739	2189042	48.47	28910

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-nitrobenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ads)



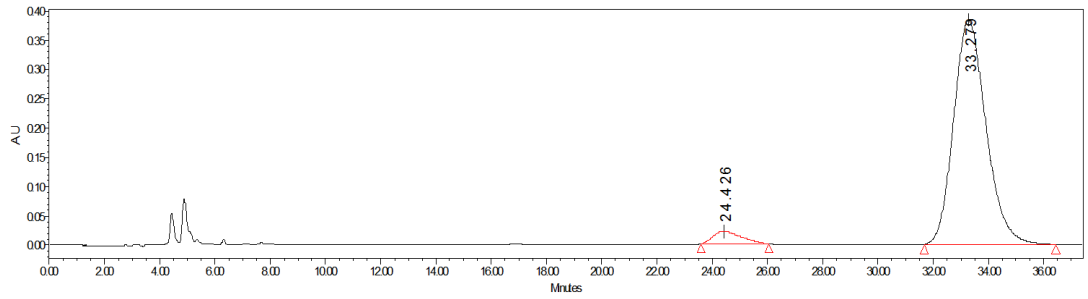
Light yellow solid; 99% yield, 90% ee; $[\alpha]^{26.4}_{D}$ = –165 (*c* = 0.81, CH_2Cl_2); m.p. 192-198 ℃.

HPLC DAICEL CHIRALCEL **IC**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 24.43 min, 33.28 min.

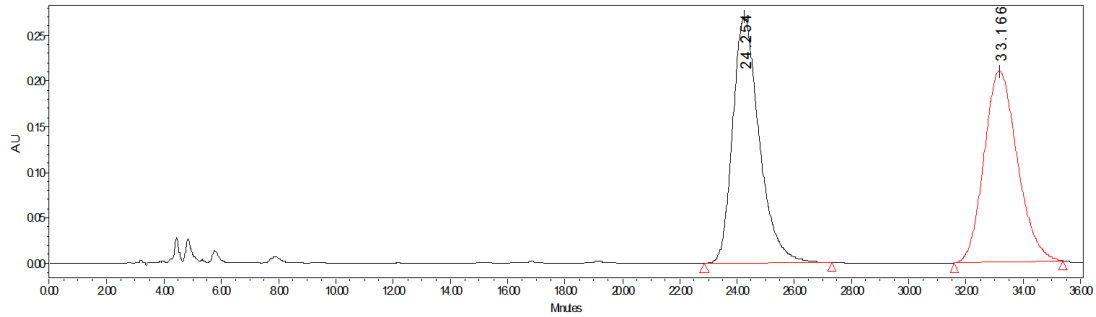
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 – 8.22 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 5H), 7.11 – 7.04 (m, 1H), 6.99 – 6.86 (m, 3H), 6.84 – 6.75 (m, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.4 Hz, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 6.01 (s, 1H), 5.19 (d, *J* = 7.4 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.8, 195.1, 174.1, 150.5, 147.0, 142.8, 140.6, 135.9, 134.7, 133.4, 130.2, 128.8, 128.7, 128.2, 128.1, 127.5, 126.6, 126.6, 126.0, 126.0, 124.3, 124.0, 122.1, 122.1, 121.6, 108.8, 80.9, 68.4, 64.5, 57.2, 43.9.

HRMS (ESI-TOF) calcd for $C_{38}H_{27}N_3NaO_5S^+$ ([M]+Na$^+$) = 660.1564, Found 660.1564.

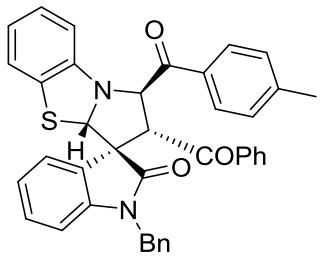


	Migration Time	Area	% Area	Height
1	24.426	1520275	4.64	21479
2	33.279	31261802	95.36	382547



	Migration Time	Area	% Area	Height
1	24.254	17417204	50.68	269726
2	33.166	16947005	49.32	210277

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-methylbenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ae)



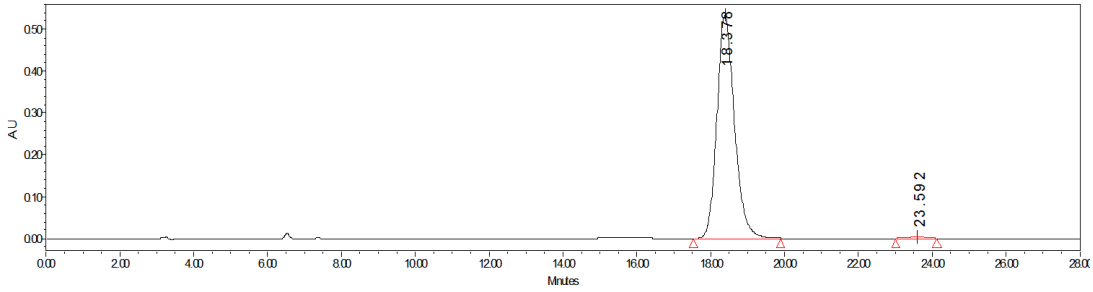
Light yellow solid; 99% yield, 99% ee; $[\alpha]^{26.3}_{D}$ = –268 (*c* = 0.59, CH_2Cl_2); m.p. 190-191 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.38 min, 23.59 min.

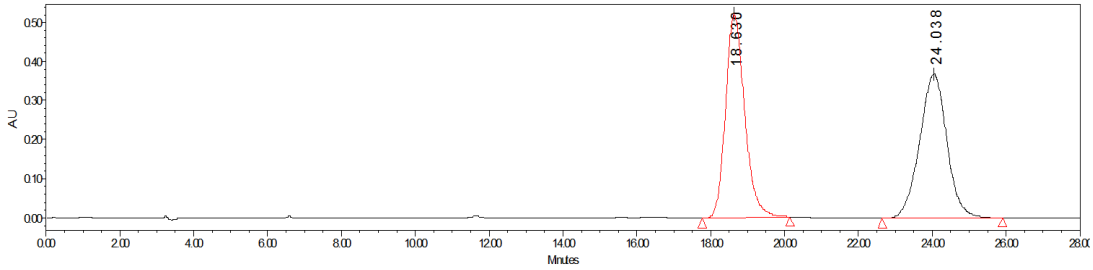
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 5H), 7.08 – 7.01 (m, 1H), 6.99 – 6.85 (m, 3H), 6.80 – 6.67 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.32 – 6.21 (m, 2H), 6.15 (s, 1H), 5.13 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.2, 195.3, 174.1, 147.6, 145.0, 142.8, 136.1, 134.8, 133.2, 133.0, 129.7, 129.3, 128.7, 128.6, 128.2, 128.2, 127.5, 126.6, 126.5, 126.1, 125.9, 124.7, 122.0, 121.7, 120.9, 108.8, 108.7, 81.1, 67.1, 64.6, 57.7, 43.8, 21.7.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_3S^+$ ([M]+Na^+) = 629.1869, Found 629.1871.

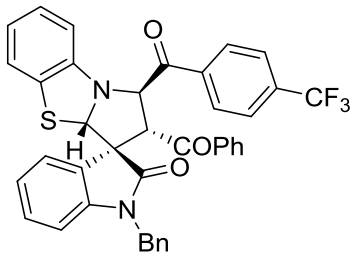


	Migration Time	Area	% Area	Height
1	18.378	17698605	99.29	532928
2	23.592	125696	0.71	3458



	Migration Time	Area	% Area	Height
1	18.630	18681937	49.61	520344
2	24.038	18974514	50.39	368934

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-(trifluoromethyl)benzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3af)



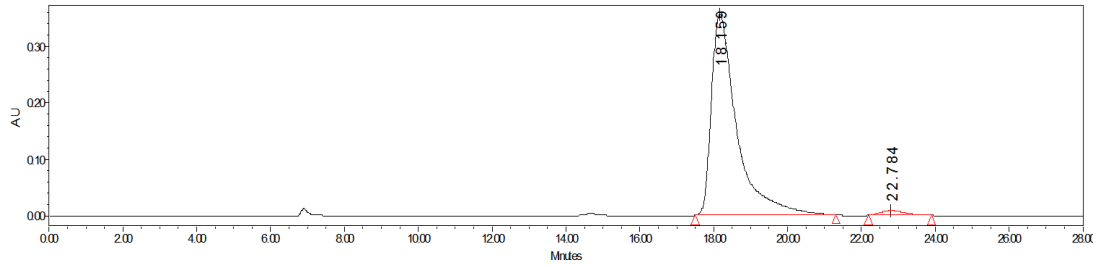
Light yellow solid; 99% yield, 96% ee; $[\alpha]^{26.4}_{D}$ = –163 (*c* = 0.27, CH_2Cl_2); m.p. 188-190 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.16 min, 22.78 min.

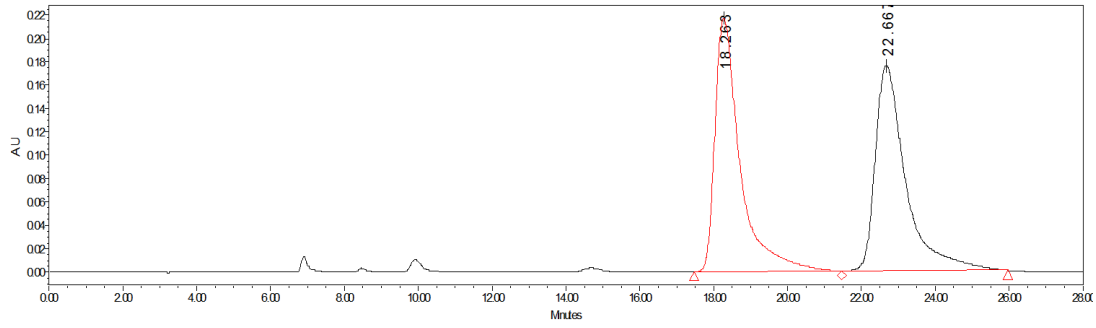
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 5H), 7.12 – 7.06 (m, 1H), 7.00 – 6.88 (m, 3H), 6.83 – 6.68 (m, 3H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 7.2 Hz, 1H), 6.07 (s, 1H), 5.18 (d, *J* = 7.2 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.1, 195.2, 174.2, 147.3, 142.9, 138.6, 134.9 (q, *J* = 32.7 Hz), 134.8, 133.4, 129.5, 128.8, 128.3, 128.2, 127.6, 126.7, 126.6, 126.1, 126.1, 126.0 (q, *J* = 3.6 Hz), 124.5, 123.5 (d, *J* = 274.0 Hz), 122.1, 122.1, 121.4, 108.9, 108.9, 81.0, 68.0, 64.6, 57.4, 43.4

HRMS (ESI-TOF) calcd for $C_{39}H_{27}F_3N_2NaO_3S^+$ ([M]+Na^+) = 683.1587, Found 683.1592.

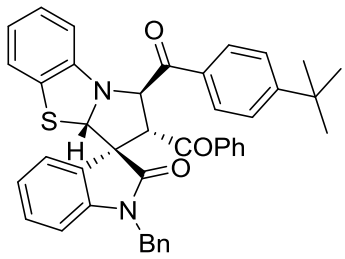


	Migration Time	Area	% Area	Height
1	18.159	17034968	98.00	354380
2	22.784	347064	2.00	7930



	Migration Time	Area	% Area	Height
1	18.263	10237349	50.43	217063
2	22.667	10062066	49.57	175452

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-(tert-butyl)benzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ag)



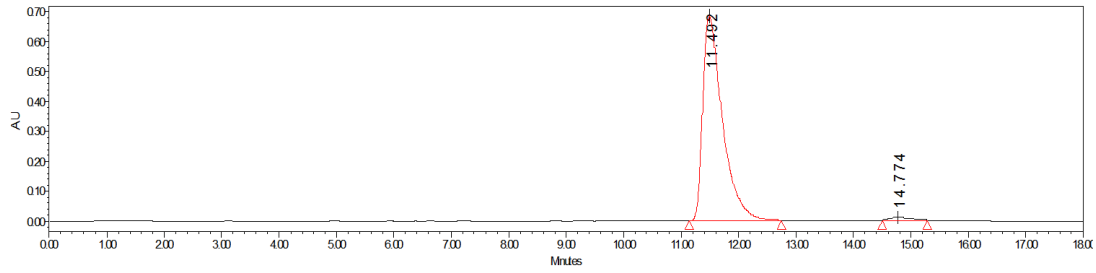
Light yellow solid; 99% yield, 97% ee; $[\alpha]^{26.6}_{D}$ = –193 (*c* = 1.24, CH_2Cl_2); m.p. 182-183 ℃.

HPLC DAICEL CHIRALCEL **IB**, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.49 min, 14.77 min.

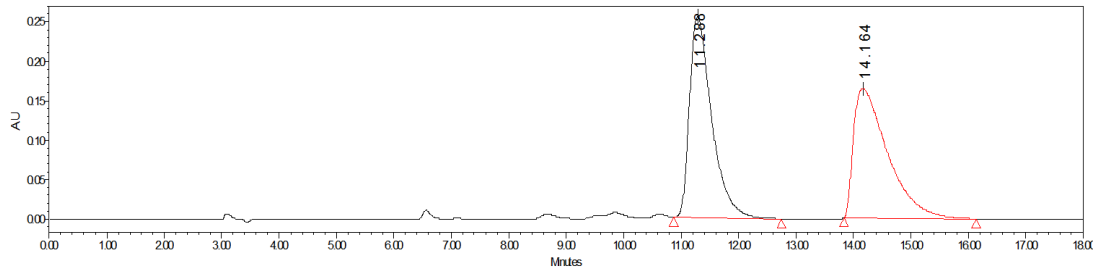
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.26 – 7.15 (m, 5H), 7.09 – 7.02 (m, 1H), 6.99 – 6.86 (m, 3H), 6.84 – 6.68 (m, 3H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.27 (t, *J* = 7.2 Hz, 2H), 6.15 (s, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 4.85 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 1.35 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.2, 195.2, 174.2, 157.8, 147.5, 142.8, 136.1, 134.8, 133.1, 132.8, 129.2, 128.7, 128.6, 128.2, 128.1, 127.4, 126.6, 126.5, 126.1, 125.9, 125.9, 124.7, 121.9, 121.7, 120.9, 108.8, 108.7, 81.2, 67.0, 64.6, 57.7, 43.8, 35.2, 31.0.

HRMS (ESI-TOF) calcd for $C_{42}H_{36}N_2NaO_3S^+$ ([M]+Na^+) = 671.2339, Found 671.2347.

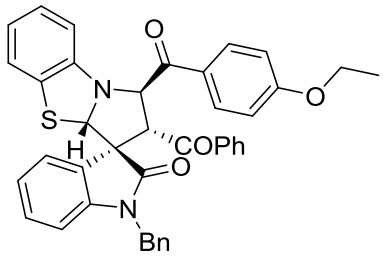


	Migration Time	Area	% Area	Height
1	11.492	16283304	98.59	683115
2	14.774	232825	1.41	9097



	Migration Time	Area	% Area	Height
1	11.288	6825367	50.38	255196
2	14.164	6721845	49.62	163806

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(4-ethoxybenzoyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ah)



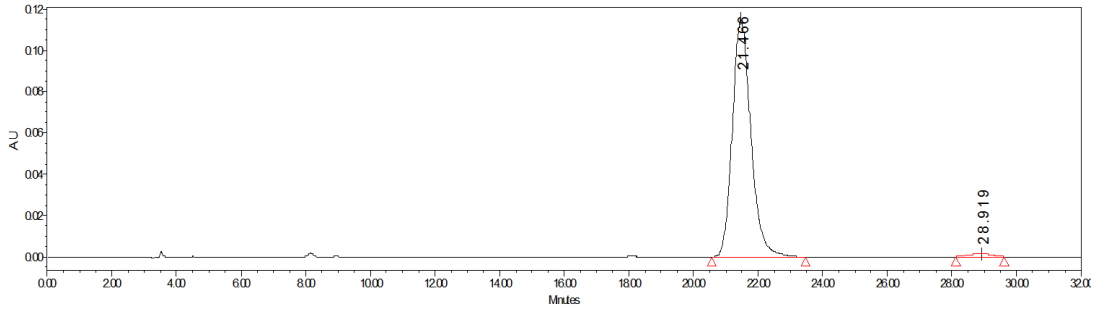
Light yellow solid; 99% yield, 97% ee; $[\alpha]^{25.3}_{D}$ = –209 (*c* = 1.12, CH_2Cl_2); m.p. 193-195 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 21.47 min, 28.92 min.

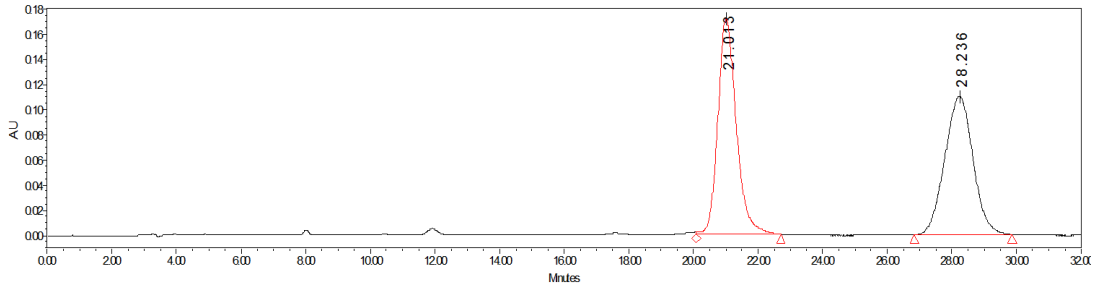
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.25 – 7.11 (m, 5H), 7.08 – 7.02 (m, 1H), 7.02 – 6.96 (m, 2H), 6.96 – 6.85 (m, 3H), 6.81 – 6.67 (m, 3H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 2H), 6.18 (s, 1H), 5.12 (d, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H), 4.11 (q, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.0, 195.3, 174.1, 163.6, 147.6, 142.7, 136.1, 134.8, 133.2, 131.7, 128.7, 128.6, 128.1, 127.4, 126.5, 126.5, 126.1, 125.8, 124.7, 121.9, 121.7, 120.8, 114.6, 108.8, 108.7, 81.2, 66.8, 64.6, 63.8, 57.8, 43.8, 14.6.

HRMS (ESI-TOF) calcd for $C_{40}H_{32}N_2NaO_4S^+$ ([M]+Na^+) = 659.1975, Found 659.1978.

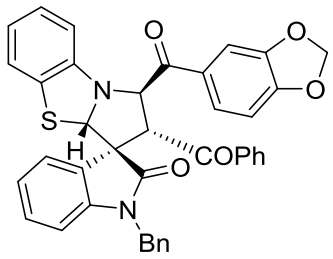


	Migration Time	Area	% Area	Height
1	21.466	4589374	98.54	115213
2	28.919	67824	1.46	1380



	Migration Time	Area	% Area	Height
1	21.013	6770220	50.42	170874
2	28.236	6656874	49.58	109845

(1*R*,2*R*,3*R*,3a*S*)-1-(Benzo[d][1,3]dioxole-5-carbonyl)-2-benzoyl-1'-benzyl-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ahs)



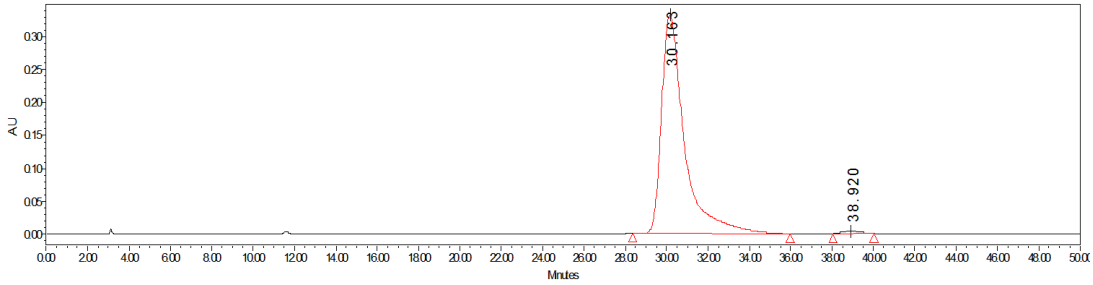
Light yellow solid; 98% yield, 98% ee; $[\alpha]^{26.5}_{D}$ = –253 (*c* = 0.74, CH_2Cl_2); m.p. 189-190 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 30.16 min, 38.92 min.

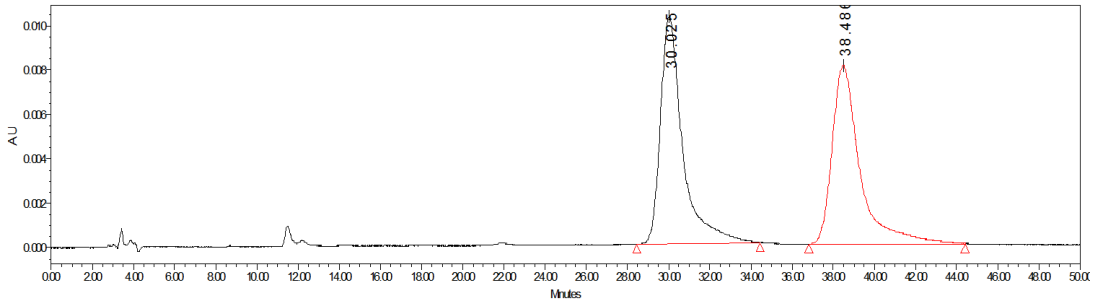
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.95 (m, 1H), 7.71 (s, 1H), 7.47 – 7.35 (m, 3H), 7.25 – 7.11 (m, 5H), 7.08 – 7.01 (m, 1H), 7.00 – 6.85 (m, 4H), 6.82 – 6.67 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 6.26 (t, *J* = 6.8 Hz, 2H), 6.17 (s, 1H), 6.06 (s, 2H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 196.7, 195.3, 174.1, 152.7, 148.6, 147.6, 142.7, 136.1, 134.8, 133.2, 130.2, 128.7, 128.6, 128.2, 128.2, 127.4, 126.6, 126.5, 126.1, 125.9, 125.9, 124.6, 122.0, 121.7, 120.9, 108.8, 108.8, 108.2, 102.0, 81.2, 66.9, 64.6, 57.9, 43.8.

HRMS (ESI-TOF) calcd for $C_{39}H_{28}N_2NaO_5S^+$ ([M]+Na^+) = 659.1611, Found 659.1617.

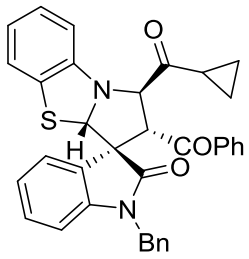


	Migration Time	Area	% Area	Height
1	30.163	25302426	99.07	330606
2	38.920	238172	0.93	3721



	Migration Time	Area	% Area	Height
1	30.025	769080	50.56	10214
2	38.486	751962	49.44	8045

(1*R*,2*R*,3*R*,3a*S*)-2-Benzoyl-1'-benzyl-1-(cyclopropanecarbonyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (3ai)



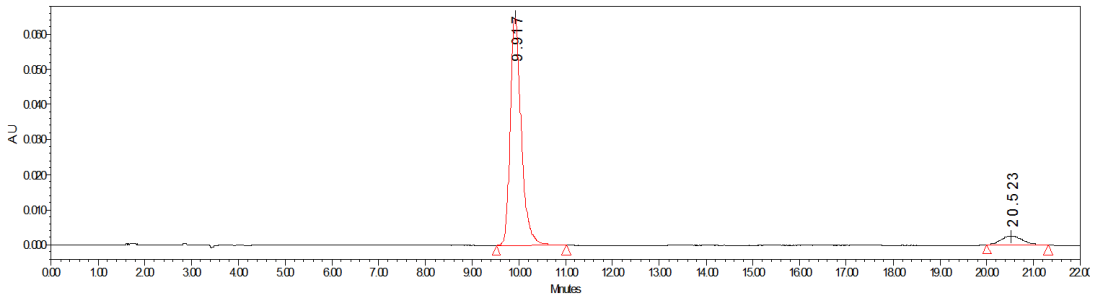
Light yellow solid; 95% yield, 87% ee; $[\alpha]^{25.4}_{D}$ = –129 (*c* = 1.06, CH_2Cl_2); m.p. 175-177 ℃

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.92 min, 20.52 min.

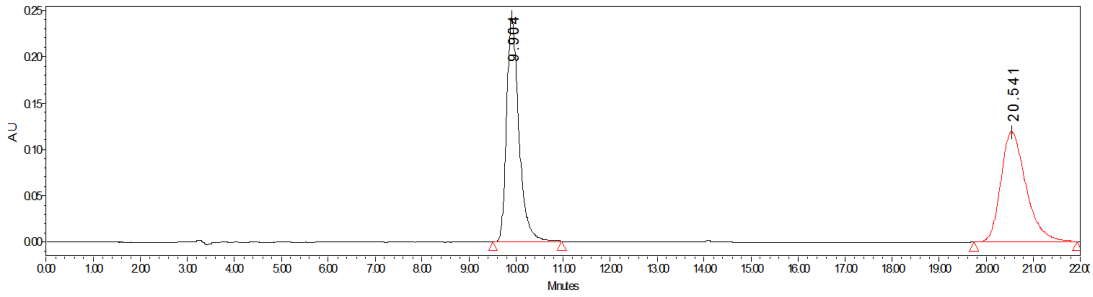
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 – 7.41 (m, 3H), 7.29 – 7.24 (m, 2H), 7.21 – 7.09 (m, 4H), 6.97 – 6.84 (m, 4H), 6.83 – 6.71 (m, 2H), 6.62 – 6.52 (m, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 7.2 Hz, 1H), 5.94 (s, 1H), 5.59 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 16.0 Hz, 1H), 2.67 – 2.49 (m, 1H), 1.33 – 1.27 (m, 1H), 1.23 – 1.16 (m, 1H), 1.13 – 1.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.3, 194.7, 174.1, 148.3, 142.6, 136.1, 134.7, 133.1, 128.7, 128.6, 128.3, 128.2, 127.4, 126.6, 126.5, 126.2, 126.1, 124.4, 122.1, 121.8, 121.2, 108.8, 108.8, 80.6, 72.7, 64.4, 55.1, 43.8, 17.8, 13.1, 12.1.

HRMS (ESI-TOF) calcd for $C_{35}H_{28}N_2NaO_3S^+$ ([M]+Na^+) = 579.1713, Found 579.1714.

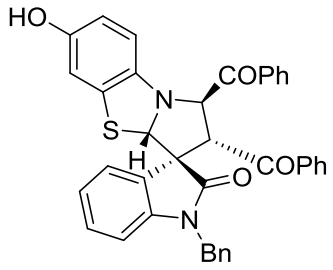


	Migration Time	Area	% Area	Height
1	9.917	1064566	92.72	64921
2	20.523	83646	7.28	2574



	Migration Time	Area	% Area	Height
1	9.904	4393694	50.08	241781
2	20.541	4379361	49.92	118626

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-6-hydroxy-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3aj)



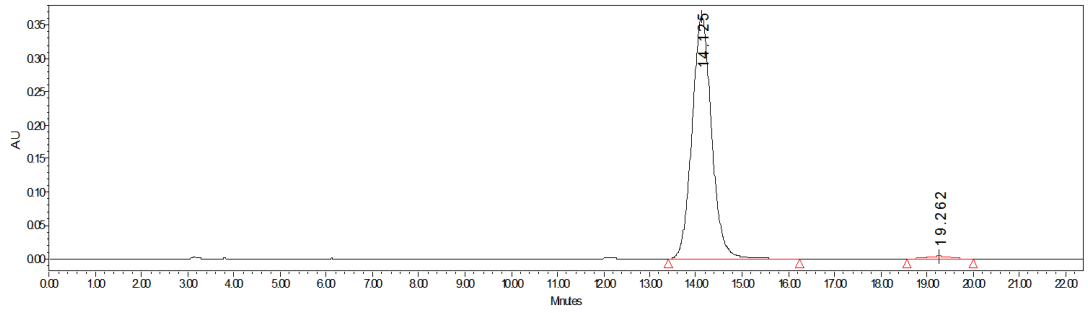
Light yellow solid; 99% yield, 97% ee; $[\alpha]^{26.7}_{D}$ = –222 (*c* = 0.74, CH_2Cl_2); m.p. 140-141 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.13 min, 19.36 min.

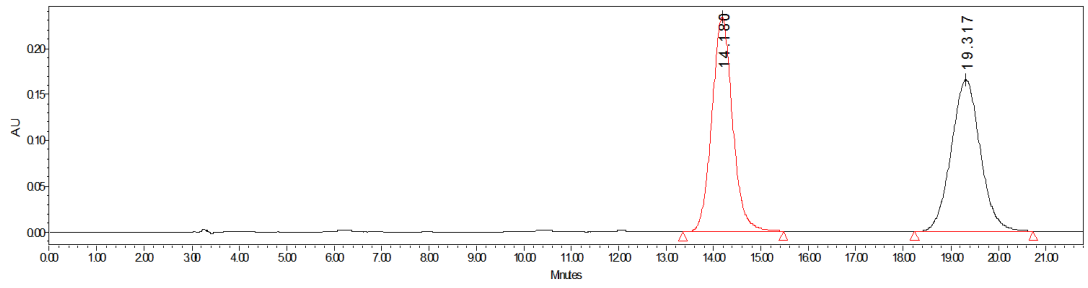
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.25 – 7.09 (m, 5H), 6.98 – 6,82 (m, 3H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.55 (s, 2H), 6.42 – 6.18 (m, 4H), 6.08 (s, 1H), 5.38 (s, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 199.0, 195.5, 174.4, 150.7, 142.7, 141.8, 136.1, 135.7, 134.7, 133.9, 133.3, 129.2, 128.9, 128.7, 128.6, 128.2, 128.1, 127.8, 127.5, 126.6, 126.2, 124.7, 122.2, 112.3, 109.9, 109.4, 108.8, 81.7, 68.2, 64.8, 57.6, 43.9.

HRMS (ESI-TOF) calcd for $C_{38}H_{28}N_2NaO_4S^+$ ([M]+Na^+) = 631.1662, Found 631.1669.

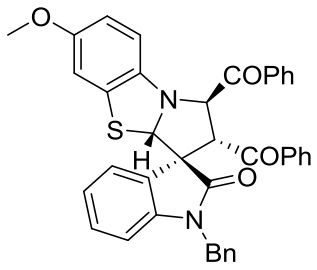


	Migration Time	Area	% Area	Height
1	14.125	10658703	98.51	361785
2	19.262	161058	1.49	4190



	Migration Time	Area	% Area	Height
1	14.180	7061276	50.10	233605
2	19.317	7032587	49.90	165004

{(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-6-methoxy-2'-oxo-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (3ak)



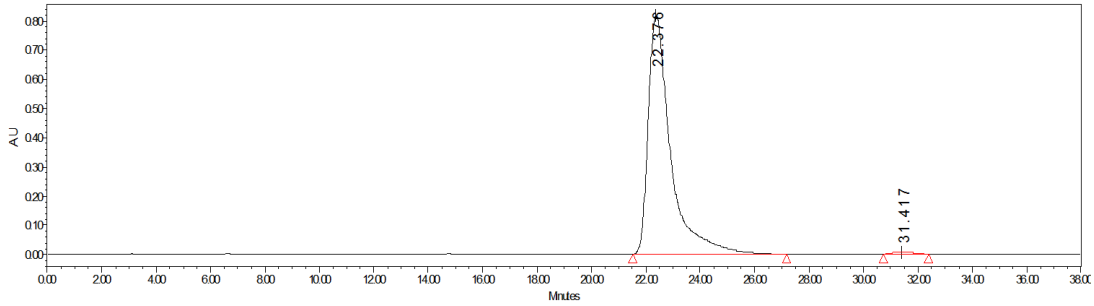
Light yellow solid; 98% yield, 98% ee; $[\alpha]^{26.4}_{D}$ = –236 (*c* = 1.04, CH_2Cl_2); m.p. 175-177 ℃.

HPLC DAICEL CHIRALCEL **IA**, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.38 min, 31.42 min.

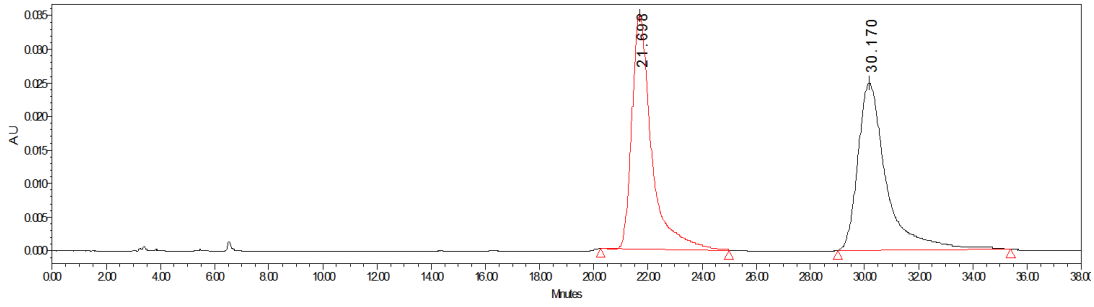
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.25 – 7.09 (m, 5H), 6.99 – 6.83 (m, 3H), 6.71 – 6.51 (m, 3H), 6.39 (d, *J* = 2.0 Hz, 1H), 6.34 (d, *J* = 7.2 Hz, 1H), 6.32 – 6.23 (m, 2H), 6.10 (s, 1H), 5.19 (d, *J* = 7.6 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.8, 195.3, 174.3, 154.8, 142.7, 141.9, 136.1, 135.8, 134.8, 133.8, 133.2, 129.1, 128.9, 128.7, 128.6, 128.1, 128.1, 127.8, 127.5, 126.6, 126.2, 124.7, 122.1, 110.6, 109.2, 108.7, 81.7, 68.1, 64.7, 57.6, 55.8, 43.8.

HRMS (ESI-TOF) calcd for $C_{39}H_{30}N_2NaO_4S^+$ ([M]+Na^+) = 645.1818, Found 645.1824.

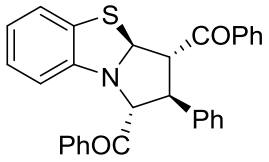


	Migration Time	Area	% Area	Height
1	22.376	46891487	99.16	815477
2	31.417	399334	0.84	7623



	Migration Time	Area	% Area	Height
1	21.698	1755137	49.18	34657
2	30.170	1813761	50.82	24904

{(1*R*,2*S*,3*S*,3a*S*)-2-Phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazole-1,3-diyl}bis(phenylmethanone) (5aa)



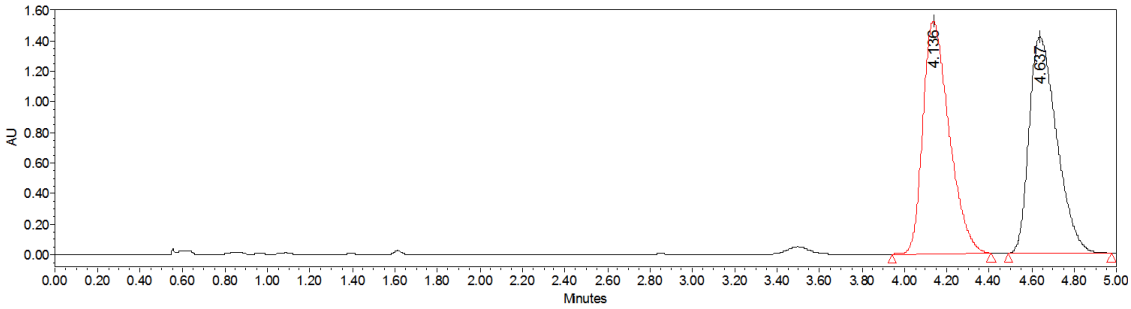
94% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 71-74 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.08 min, t_r (minor) = 4.74 min. ee = 99%. $[\alpha]^{25.9}_D$ = –186.9 (*c* = 0.66, in CH_2Cl_2).

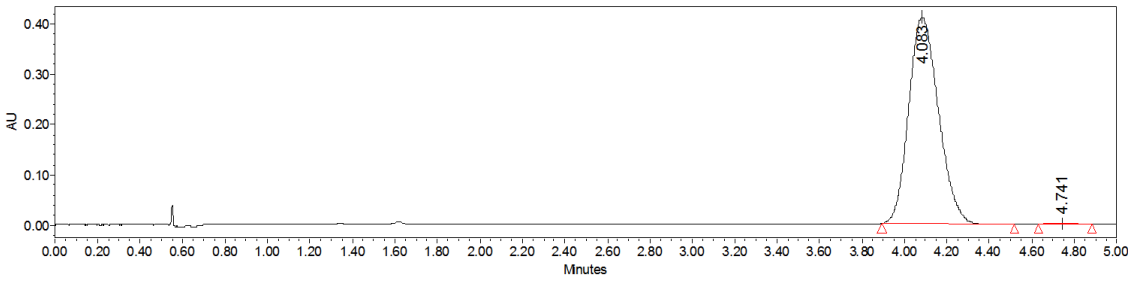
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.68 (m, 4H), 7.53 – 7.45 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.23 – 7.13 (m, 4H), 7.13 – 7.07 (m, 2H), 7.03 – 6.96 (m, 1H), 6.89 – 6.81 (m, 1H), 6.53 (d, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 8.4 Hz, 1H), 5.24 (d, *J* = 8.4 Hz, 1H), 4.56 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.11 (dd, *J* = 10.4, 8.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.8, 197.3, 147.6, 138.4, 136.8, 135.3, 133.6, 133.4, 129.0, 128.8, 128.7, 128.5, 128.4, 127.7, 127.6, 127.1, 125.9, 122.3, 121.7, 110.9, 76.2, 75.7, 62.6, 54.6.

HRMS (ESI-TOF) calcd for $C_{30}H_{23}NNaO_2S^+$ ([M]+Na^+) = 484.1342, Found 484.1336.

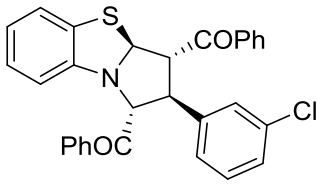


	Retention Time	Area	% Area	Height
1	4.136	13087623	50.56	1518589
2	4.637	12799530	49.44	1415809



	Retention Time	Area	% Area	Height
1	4.083	4013482	99.56	409675
2	4.741	17921	0.44	2005

{(1*R*,2*S*,3*S*,3a*S*)-2-(3-Chlorophenyl)-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazole-1,3-diyl}bis(phenylmethanone) (5ba)



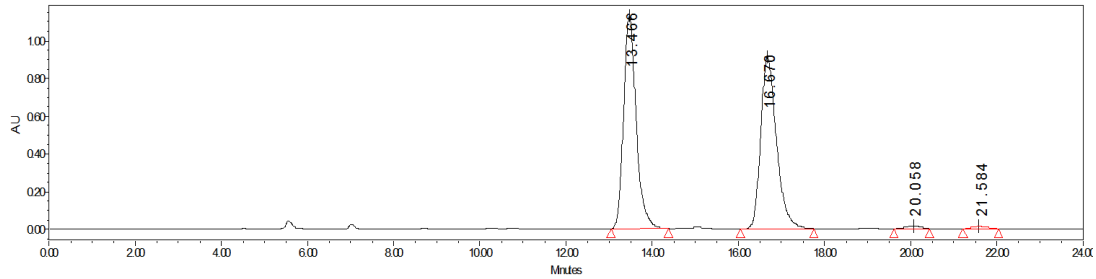
99% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 128-129 ℃.

Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =13.49 min, t (major) = 16.52 min. ee = 96%. $[\alpha]^{20.5}_{D}$ = –194.6 (*c* = 0.09, in CH_2Cl_2).

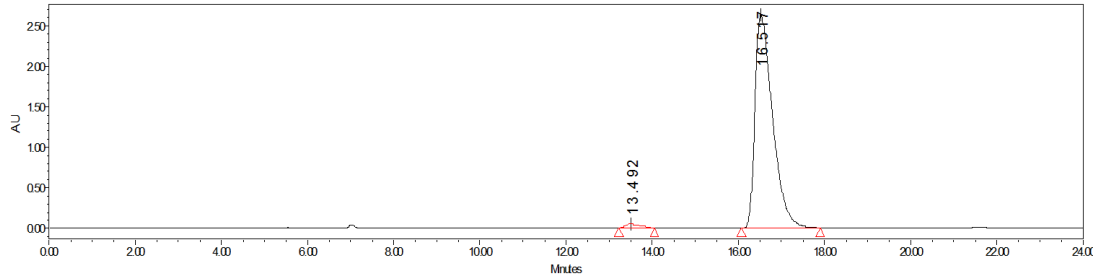
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.73 (m, 4H), 7.57 – 7.51 (m, 2H), 7.43 – 7.32 (m, 4H), 7.18 – 7.14 (m, 1H), 7.15 – 7.05 (m, 3H), 7.05 – 7.00 (m, 1H), 7.00 – 6.94 (m, 1H), 6.85 – 6.92 (m, 1H), 6.53 (d, *J* = 7.2 Hz, 1H), 5.84 (d, *J* = 8.4 Hz, 1H), 5.15 (d, *J* = 8.4 Hz, 1H), 4.50 (dd, *J* = 10.0, 8.4 Hz, 1H), 4.14 (dd, *J* = 10.0, 8.0 Hz, 1H)..

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.6, 196.9, 147.5, 140.6, 136.6, 135.3, 134.8, 133.9, 133.6, 130.3, 128.8, 128.8, 128.7, 128.6, 128.0, 127.9, 127.2, 126.0, 125.9, 122.5, 122.0, 111.2, 76.2, 75.7, 62.4, 53.7.

HRMS (ESI-FT) calcd for $C_{30}H_{23}{}^{35}ClNO_2S^+$([M]+H$^+$) = 496.1133, Found 496.1123.
$C_{30}H_{23}{}^{35}ClNO_2S^+$([M]+H$^+$) = 498.1103, Found 498.1093.

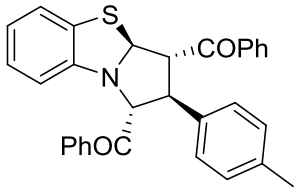


	Migration Time	Area	% Area	Height
1	13.466	22944967	49.03	1128197
2	16.670	23146248	49.46	909599
3	20.058	351867	0.75	14282
4	21.584	356962	0.76	13302



	Migration Time	Area	% Area	Height
1	13.492	1333119	1.75	51441
2	16.517	74656941	98.25	2631229

{(1*R*,2*S*,3*S*,3a*S*)-2-(*p*-Tolyl)-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazole-1,3-diyl}bis(phenylmethanone) (5ca)



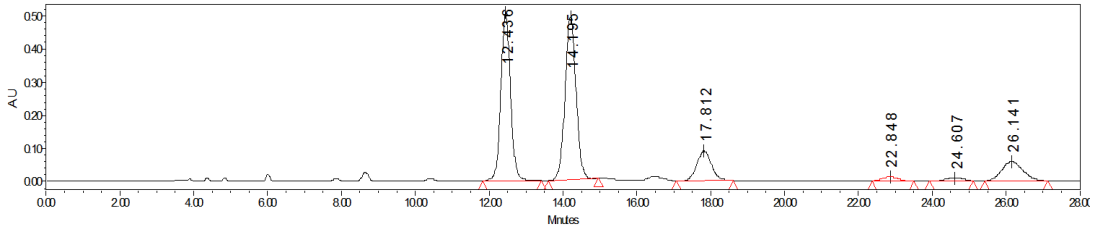
99% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 134-135 ℃.

Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =12.38 min, t (major) = 14.10 min. ee = 99%. $[\alpha]^{23.0}_{D}$ = –196.8 (*c* = 0.41, in CH_2Cl_2).

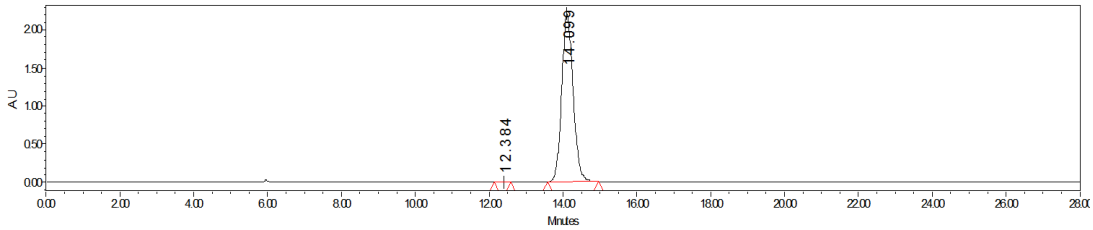
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 – 7.71 (m, 4H), 7.55 – 7.47 (m, 2H), 7.43 – 7.28 (m, 4H), 7.16 – 7.11 (m, 1H), 7.11 – 6.92 (m, 5H), 6.90 – 6.81 (m, 1H), 6.60 – 6.42 (m, 1H), 5.88 (d, *J* = 8.8 Hz, 1H), 5.16 (d, *J* = 8.4 Hz, 1H), 4.54 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.08 (dd, *J* = 10.4, 8.4 Hz, 1H), 2.23 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.1, 197.4, 147.7, 137.5, 136.9, 135.4, 135.2, 133.6, 133.4, 129.7, 128.9, 128.8, 128.5, 128.5, 127.5, 127.2, 125.8, 122.3, 121.7, 111.0, 76.5, 75.8, 62.7, 54.3, 21.0.

HRMS (ESI-TOF) calcd for $C_{31}H_{25}NNaO_2S^+$ ([M]+Na^+) = 498.1498, Found 498.1501.

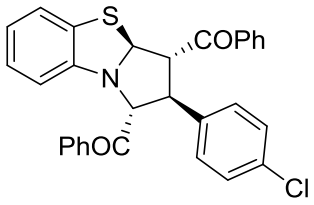


	Migration Time	Area	% Area	Height
1	12.436	9216921	36.90	508795
2	14.195	10127126	40.54	490228
3	17.812	2517908	10.08	90906
4	22.848	398483	1.60	12841
5	24.607	349687	1.40	10521
6	26.141	2370156	9.49	58841



	Migration Time	Area	% Area	Height
1	12.384	66656	0.14	4815
2	14.099	47477255	99.86	2202981

{(1*R*,2*S*,3*S*,3a*S*)-2-(4-Chlorophenyl)-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazole-1,3-diyl}bis(phenylmethanone) (5da)



99% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 112-113 ℃.

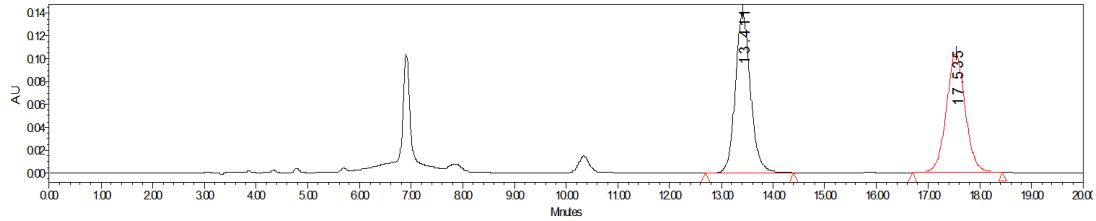
Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =13.42 min, t (major) = 17.44 min. ee = 98%. $[\alpha]^{23.0}_{D}$ = –161.6 (*c* = 0.35, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.74 (m, 4H), 7.58 – 7.50 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 4H), 7.21 – 7.10 (m, 3H), 7.09 – 6.94 (m, 3H), 6.93 – 6.83 (m, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 5.85 (d, *J* = 8.8 Hz, 1H), 5.13 (d, *J* = 8.0 Hz, 1H), 4.49 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.12 (dd, *J* = 10.4, 8.4 Hz, 1H).

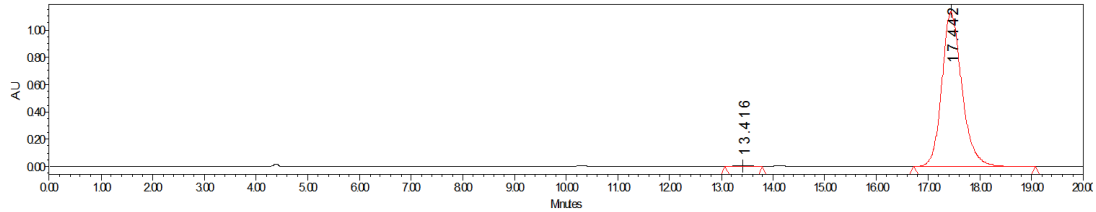
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.7, 197.0, 147.5, 137.0, 136.7, 135.3, 133.9, 133.6, 133.6, 129.2, 129.0, 128.8, 128.7, 128.7, 128.6, 127.2, 126.0, 122.4, 121.9, 111.1, 76.3, 75.7, 62.5, 53.7.

HRMS (ESI-TOF) calcd for $C_{30}H_{22}{}^{35}ClNNaO_2S^+$ ([M]+Na$^+$) = 518.0952, Found 518.0952.

$C_{30}H_{22}{}^{37}ClNNaO_2S^+$ ([M]+Na$^+$) = 520.0922, Found 520.0934.

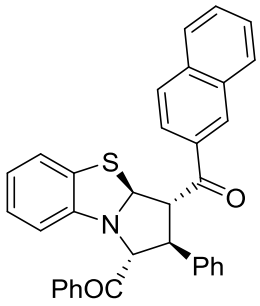


	Migration Time	Area	% Area	Height
1	13.411	2864669	51.79	140853
2	17.535	2666134	48.21	104080



	Migration Time	Area	% Area	Height
1	13.416	229643	0.75	10997
2	17.442	30589650	99.25	1129296

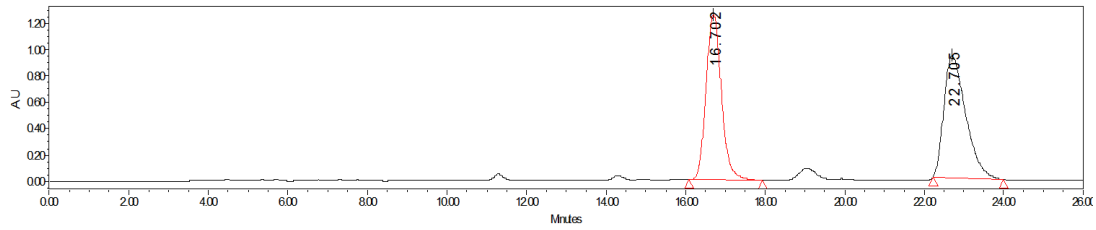
{(1*R*,2*S*,3*S*,3a*S*)-3-(2-Naphthoyl)-2-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazol-1-yl}(phenyl)methanone (5ea)



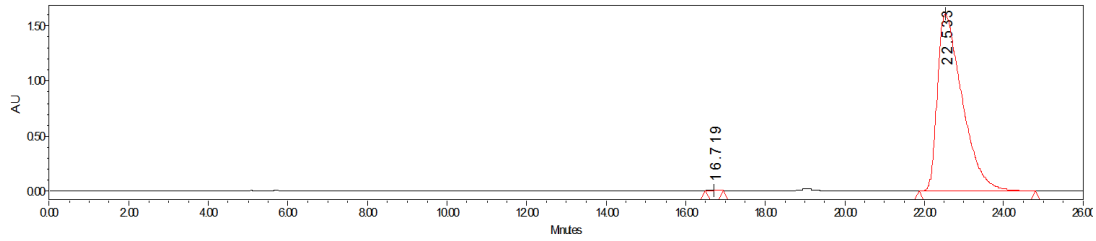
99% yield; yellow oil; R_f = 0.5 (petroleum/ethyl acetate = 6/1). Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =16.72 min, t (major) = 22.53 min. ee = 99%. $[\alpha]^{22.6}_{D}$ = –272 (*c* = 0.86, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 7.90 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.87 – 7.68 (m, 5H), 7.59 – 7.46 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.12 (m, 5H), 7.05 – 6.98 (m, 1H), 6.93 – 6.80 (m, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 5.30 (d, *J* = 8.0 Hz, 1H), 4.68 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.14 (dd, *J* = 10.4, 8.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.8, 197.0, 147.7, 138.7, 135.7, 135.3, 134.1, 133.5, 132.1, 131.4, 129.7, 129.1, 128.8, 128.8, 128.5, 128.4, 127.8, 127.8, 127.6, 127.1, 126.7, 125.9, 123.8, 122.4, 121.7, 111.0, 76.3, 75.7, 63.0, 54.6.

HRMS (ESI-TOF) calcd for $C_{34}H_{25}NNaO_2S^+$ ([M]+Na^+) = 534.1498, Found 534.1498.

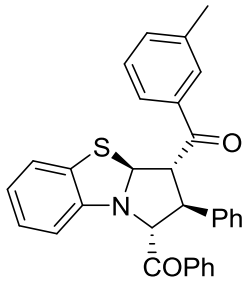


	Migration Time	Area	% Area	Height
1	16.702	33844351	48.91	1261629
2	22.705	35345845	51.09	930338



	Migration Time	Area	% Area	Height
1	16.719	89023	0.13	5495
2	22.533	69594832	99.87	1608825

{(1*R*,2*S*,3*S*,3a*S*)-1-Benzoyl-2-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazol-3-yl}(m-tolyl)methanone (5fa)

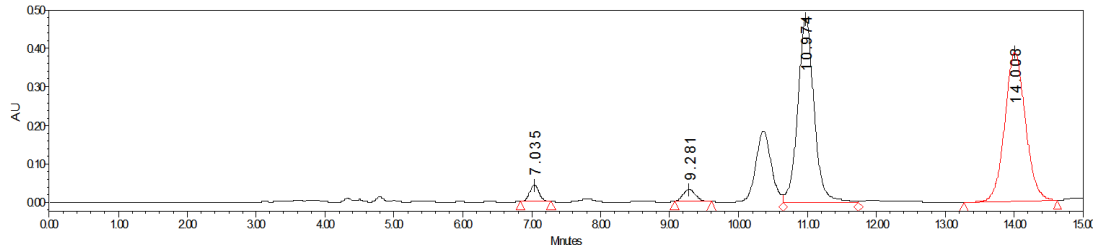


92% yield; yellow oil; R_f = 0.5 (petroleum/ethyl acetate = 6/1). Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =11.02 min, t (major) = 13.96 min. ee = 99%. $[\alpha]^{22.9}_{D}$ = –171.9 (*c* = 0.29, in CH_2Cl_2).

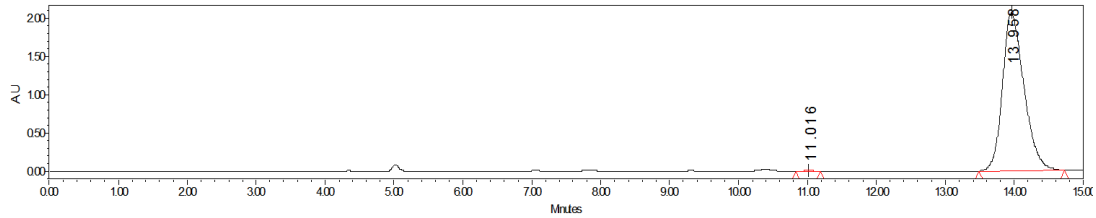
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 – 7.74 (m, 2H), 7.57 – 7.47 (m, 3H), 7.36 – 7.28 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.13 (m, 4H), 7.12 – 7.05 (m, 2H), 7.04 – 6.97 (m, 1H), 6.94 – 6.80 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.90 (d, *J* = 8.4 Hz, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 4.51 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.06 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.27 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.9, 197.5, 147.7, 138.6, 138.3, 136.8, 135.4, 134.4, 133.4, 129.3, 129.0, 128.8, 128.5, 128.3, 127.7, 127.3, 126.0, 125.9, 122.4, 121.7, 111.0, 76.3, 75.7, 62.9, 54.6, 21.2.

HRMS (ESI-TOF) calcd for $C_{31}H_{25}NNaO_2S^+$ ([M]+Na^+) = 498.1498, Found 498.1494.

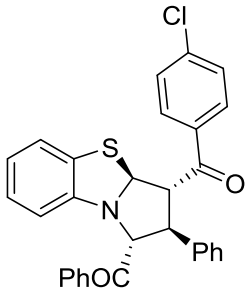


	Migration Time	Area	% Area	Height
1	7.035	411984	2.48	43097
2	9.281	397984	2.39	31584
3	10.974	7811346	46.96	475917
4	14.008	8014314	48.18	386194



	Migration Time	Area	% Area	Height
1	11.016	83147	0.19	6967
2	13.958	44673882	99.81	2058019

{(1*R*,2*S*,3*S*,3a*S*)-1-Benzoyl-2-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazol-3-yl}(4-chlorophenyl)methanone (5ga)



99% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 128-129 ℃.

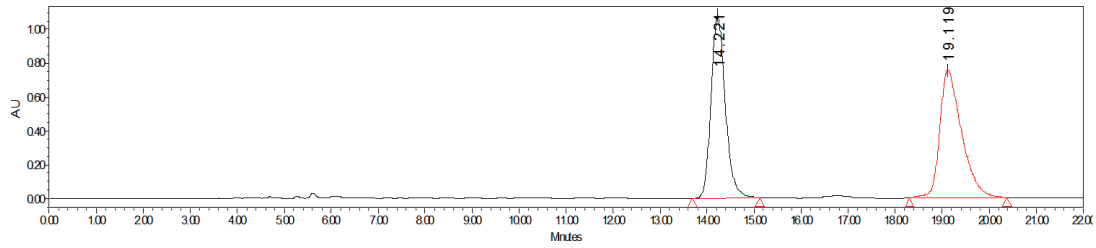
Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) =14.28 min, t (major) = 18.93 min. ee = 99%. $[\alpha]^{20.5}_{D}$ = –154.8 (*c* = 0.52, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.74 (m, 2H), 7.70 – 7.62 (m, 2H), 7.54 – 7.49 (m, 1H), 7.38 – 7.28 (m, 4H), 7.22 – 7.12 (m, 4H), 7.12 – 7.05 (m, 2H), 7.04 – 6.98 (m, 1H), 6.93 – 6.83 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.86 (d, *J* = 8.8 Hz, 1H), 5.23 (d, *J* = 8.0 Hz, 1H), 4.45 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.06 (dd, *J* = 10.4, 8.0 Hz, 1H).

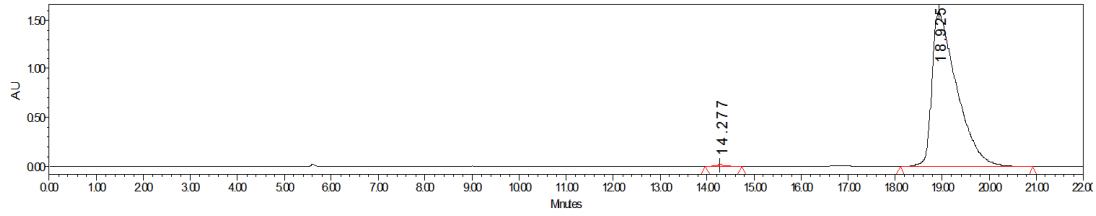
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.7, 196.2, 147.6, 140.3, 138.4, 135.3, 135.1, 133.5, 130.1, 129.1, 128.8, 128.8, 128.6, 127.9, 127.6, 126.8, 126.0, 122.5, 121.8, 110.9, 76.1, 75.6, 62.9, 54.5.

HRMS (ESI-TOF) calcd for $C_{30}H_{22}{}^{35}ClNNaO_2S^+$ ([M]+Na^+) = 518.0952, Found 518.0949.

$C_{30}H_{22}{}^{37}ClNNaO_2S^+$ ([M]+Na^+) = 520.0922, Found 520.0933.

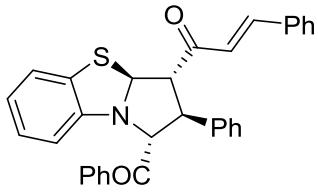


	Migration Time	Area	% Area	Height
1	14.221	22821865	48.41	1081074
2	19.119	24324520	51.59	755880



	Migration Time	Area	% Area	Height
1	14.277	316514	0.55	16477
2	18.925	57731776	99.45	1582241

(*E*)-1-{(1*R*,2*S*,3*S*,3a*S*)-1-Benzoyl-2-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b]thiazol-3-yl}-3-phenylprop-2-en-1-one (5ha)



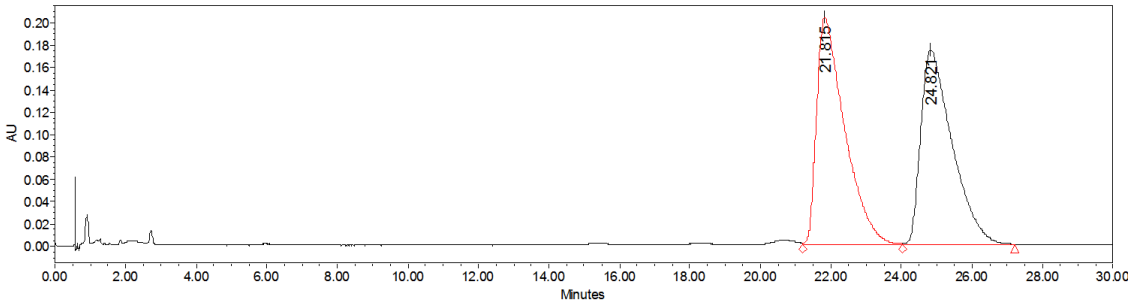
81% yield; yellow solid; R_f = 0.5 (petroleum/ethyl acetate = 6/1); m.p. 127-130 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 90/10, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 21.68 min, t_r (minor) = 24.79 min. ee = 99%. $[\alpha]^{20.6}_D$ = –115.1 (*c* = 0.36, in CH_2Cl_2).

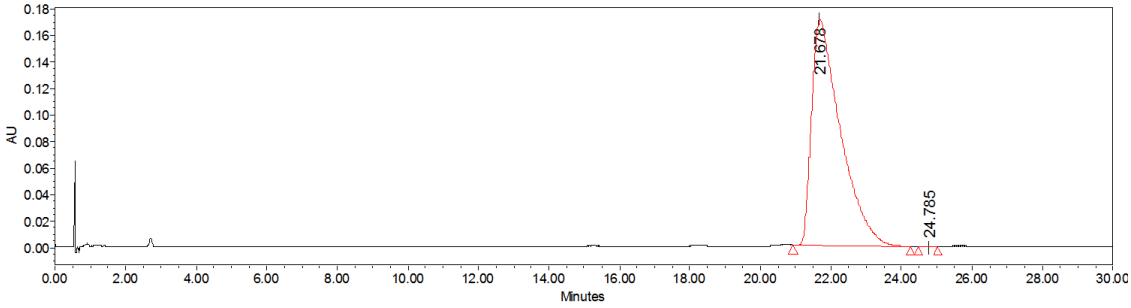
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.74 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 – 7.31 (m, 8H), 7.25 – 7.20 (m, 3H), 7.18 – 7.12 (m, 3H), 7.03 – 6.97 (m, 1H), 6.89 – 6.84 (m, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 5.84 (d, *J* = 8.4 Hz, 1H), 5.20 (d, *J* = 7.6 Hz, 1H), 4.06 – 3.92 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.9, 196.0, 147.6, 144.8, 138.8, 135.3, 134.0, 133.5, 130.9, 129.1, 128.9, 128.8, 128.5, 128.5, 127.8, 127.0, 125.9, 125.8, 122.4, 121.7, 110.9, 76.2, 74.6, 65.8, 53.4.

HRMS (ESI-TOF) calcd for $C_{32}H_{25}NNaO_2S^+$ ([M]+Na^+) = 510.1498, Found 510.1495.

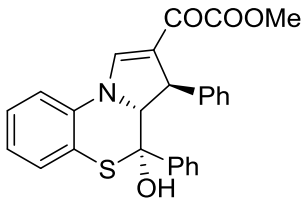


	Retention Time	Area	% Area	Height
1	21.815	11265143	51.06	203318
2	24.821	10799072	48.94	173859



	Retention Time	Area	% Area	Height
1	21.678	9679217	99.98	170126
2	24.785	2277	0.02	-161

Methyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7aa)



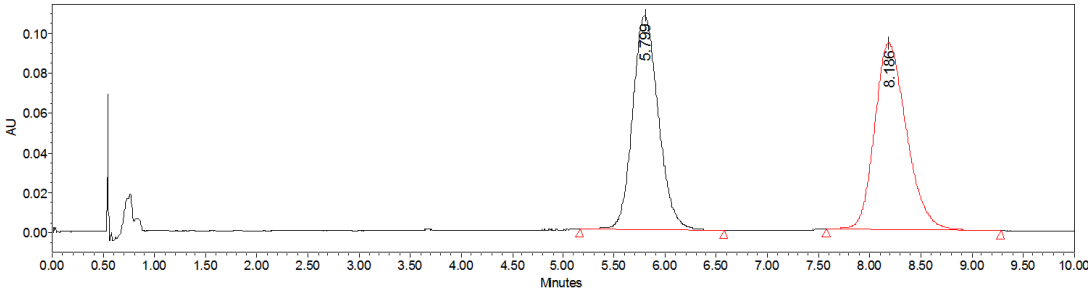
86% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 201-202 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 5.73 min, t_r (minor) = 7.92 min. ee = 93%. $[\alpha]^{26.3}_D$ = –76.3 (*c* = 0.67, in CH_2Cl_2).

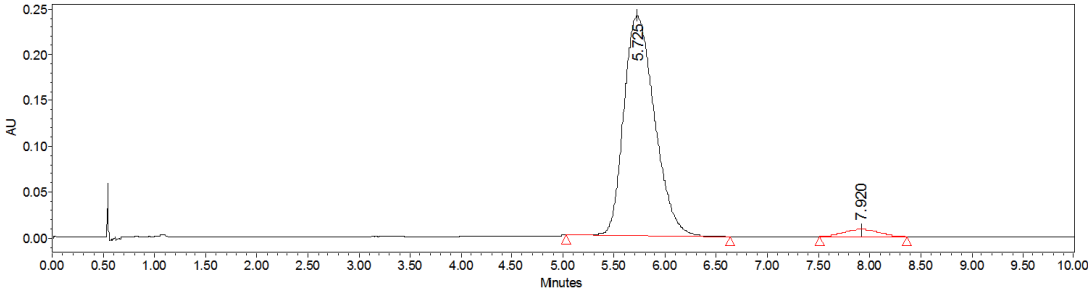
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 7.61 – 7.51 (m, 2H), 7.46 – 7.32 (m, 4H), 7.23 – 7.16 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.05 – 6.92 (m, 3H), 6.58 – 6.33 (m, 2H), 4.37 (d, *J* = 5.6 Hz, 1H), 4.32 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.30 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.4, 150.1, 142.3, 137.5, 133.4, 129.1, 128.7, 128.3, 127.2, 126.8, 126.5, 126.0, 124.5, 122.8, 118.4, 117.6, 82.1, 52.4, 48.2.

HRMS (ESI-TOF) calcd for $C_{26}H_{21}NNaO_4S^+$ ([M]+Na^+) = 466.1083, Found 466.1085.

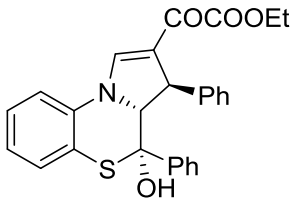


	Retention Time	Area	% Area	Height
1	5.799	1879175	48.03	107308
2	8.186	2032992	51.97	93586



	Retention Time	Area	% Area	Height
1	5.725	5045440	96.40	240129
2	7.920	188582	3.60	8150

Ethyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ba)



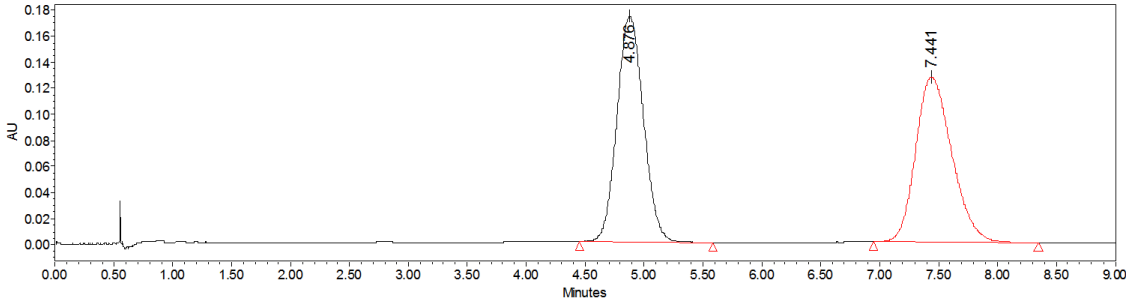
99% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 158-159 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 5.00 min, t_r (minor) = 7.19 min. ee = 90%. $[\alpha]^{26.7}_D$ = –72.3 (*c* = 0.84, in CH_2Cl_2).

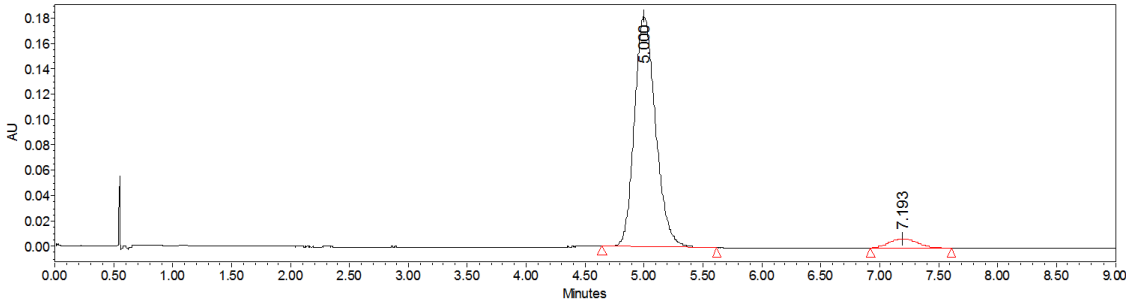
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (s, 1H), 7.62 – 7.50 (m, 2H), 7.46 – 7.32 (m, 4H), 7.21 – 7.15 (m, 1H), 7.14 – 7.09 (m, 1H), 7.08 – 7.04 (m, 1H), 7.04 – 6.94 (m, 3H), 6.68 – 6.33 (m, 2H), 4.38 (d, *J* = 5.2 Hz, 1H), 4.38 (d, *J* = 5.6 Hz, 1H), 4.28 – 4.12 (m, 2H), 3.47 (s, 1H), 1.29 (t, *J* = 6.8 Hz, 3H).

. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.0, 149.9, 142.4, 137.6, 133.4, 129.0, 128.6, 128.2, 127.1, 126.9, 126.5, 125.9, 124.3, 122.8, 118.4, 117.5, 82.1, 61.7, 48.2, 13.9.

HRMS (ESI-TOF) calcd for $C_{27}H_{23}NNaO_4S^+$ ([M]+Na^+) = 480.1240, Found 480.1248.

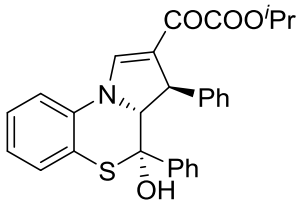


	Retention Time	Area	% Area	Height
1	4.876	2723150	50.01	173167
2	7.441	2721604	49.99	127110



	Retention Time	Area	% Area	Height
1	5.000	2284372	94.82	182066
2	7.193	124898	5.18	7432

Isopropyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ca)



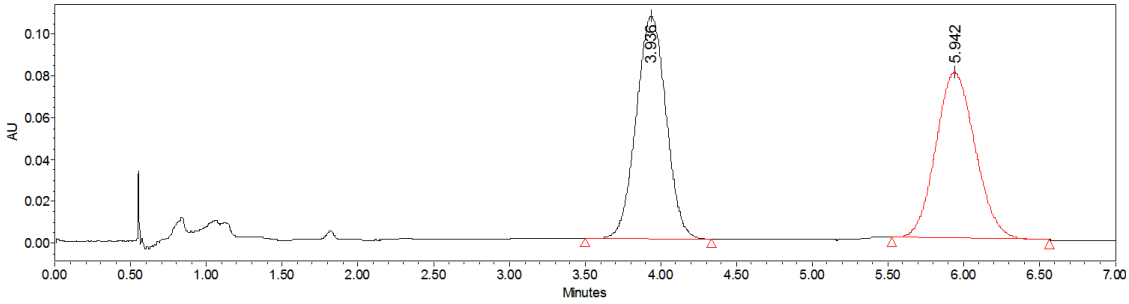
94% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 123-125 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.01 min, t_r (minor) = 5.77 min. ee = 95%. $[\alpha]^{26.7}_D$ = –77.0 (*c* = 0.86, in CH_2Cl_2).

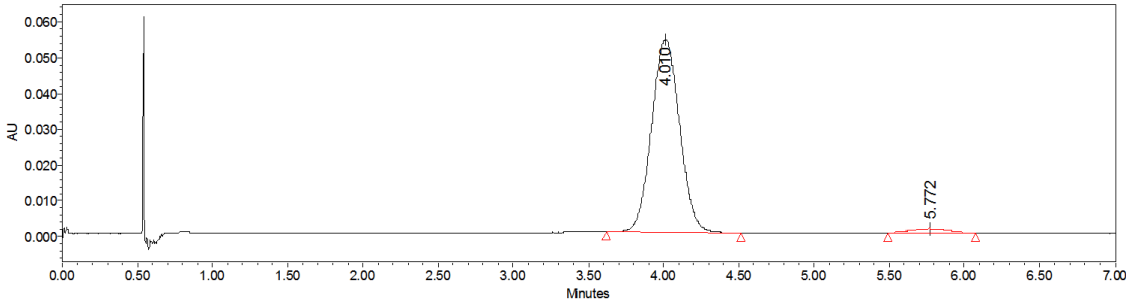
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69 (s, 1H), 7.60 – 7.50 (m, 2H), 7.43 - 7.32 (m, 4H), 7.21 – 7.16 (m, 1H), 7.12 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.04 – 6.95 (m, 3H), 6.56 – 6.37 (m, 2H), 5.07 (s, 1H), 4.38 (d, *J* = 5.2 Hz, 1H), 4.31 (d, *J* = 5.6 Hz, 1H), 3.46 (s, 1H), 1.34 – 1.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.5, 149.6, 142.6, 137.6, 133.5, 129.0, 128.6, 128.2, 127.2, 127.1, 126.9, 126.4, 125.9, 124.3, 122.8, 118.5, 117.5, 82.1, 69.7, 48.3, 21.5.

HRMS (ESI-TOF) calcd for $C_{28}H_{25}NNaO_4S^+$ ([M]+Na^+) = 494.1397, Found 494.1400.

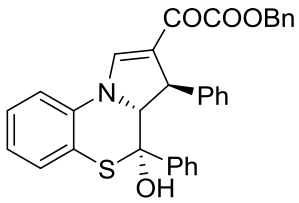


	Retention Time	Area	% Area	Height
1	3.936	1467527	50.46	106455
2	5.942	1440491	49.54	79696



	Retention Time	Area	% Area	Height
1	4.010	695321	97.42	53741
2	5.772	18426	2.58	1185

Benzyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7da)



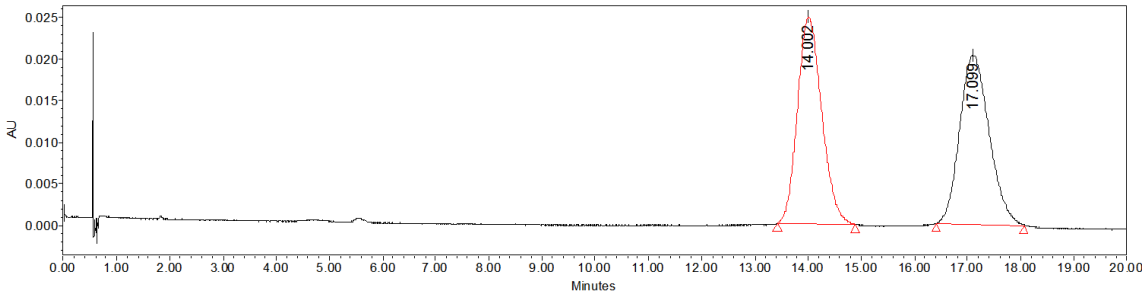
87% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 101-102 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 14.33 min, t_r (minor) = 16.85 min. ee = 96%. $[\alpha]^{26.7}_D$ = –49.3 (*c* = 0.90, in CH_2Cl_2).

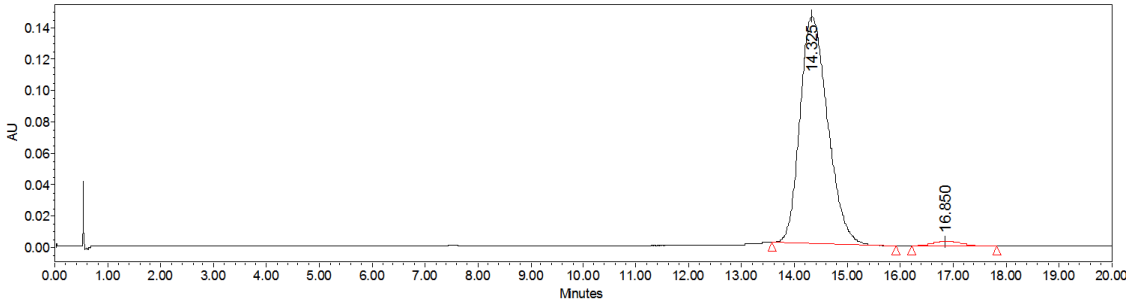
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.42 – 7.31 (m, 8H), 7.25 – 7.21 (m, 1H), 7.18 – 7.13 (m, 1H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.08 – 6.94 (m, 4H), 6.58 – 6.36 (m, 2H), 5.22 (s, 2H), 4.37 (d, *J* = 5.6 Hz, 1H), 4.31 (d, *J* = 5.6 Hz, 1H), 3.42 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.7, 149.9, 142.4, 137.5, 135.1, 133.4, 129.0, 128.6, 128.6, 128.4, 128.4, 128.3, 127.2, 127.1, 126.8, 126.5, 125.9, 124.4, 122.8, 118.5, 117.5, 82.1, 67.2, 48.2.

HRMS (ESI-TOF) calcd for $C_{32}H_{25}NNaO_4S^+$ ([M]+Na^+) = 542.1397, Found 542.1396.

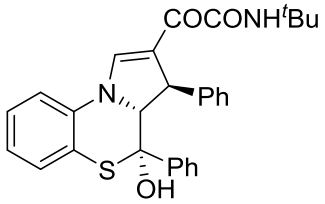


	Retention Time	Area	% Area	Height
1	14.002	788062	50.21	24873
2	17.099	781513	49.79	20318



	Retention Time	Area	% Area	Height
1	14.325	5270418	97.87	144453
2	16.850	114716	2.13	2995

***N*-(*tert*-butyl)-2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetamide (7ea)**



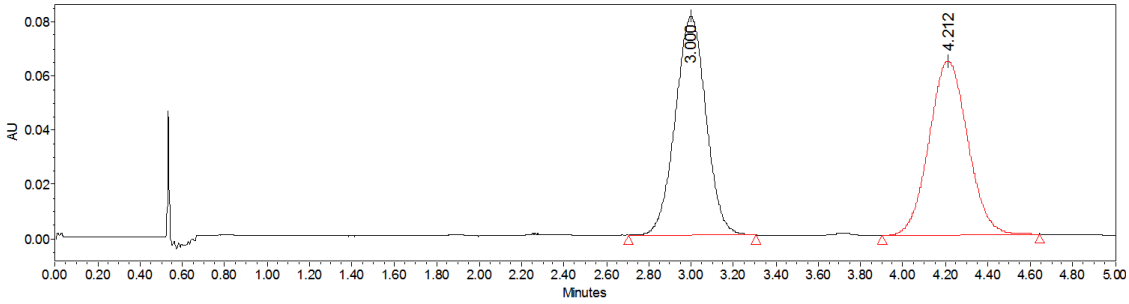
94% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 146-148 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 2.96 min, t_r (minor) = 4.27 min. ee = 87%. $[\alpha]^{26.4}_D$ = –24.2 (*c* = 0.70, in CH_2Cl_2).

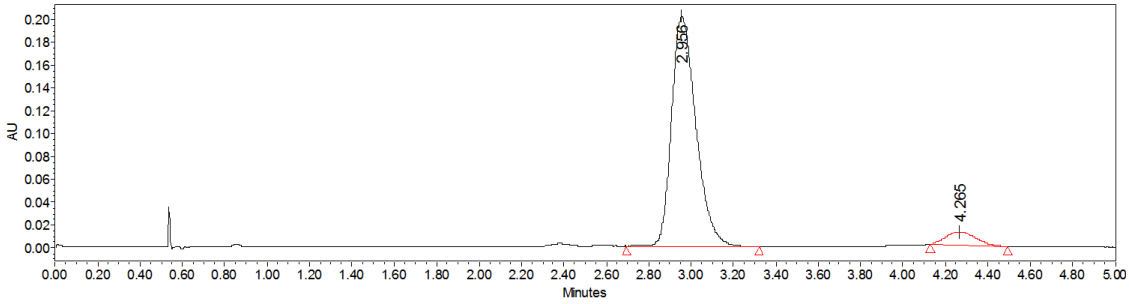
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.42 (s, 1H), 7.56 – 7.50 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 – 7.09 (m, 1H), 7.07 – 6.99 (m, 4H), 6.55 – 6.39 (m, 2H), 4.34 (d, *J* = 5.6 Hz, 1H), 4.26 (d, *J* = 5.6 Hz, 1H), 3.24 (s, 1H), 1.33 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 178.5, 161.8, 151.2, 143.0, 137.7, 133.5, 129.0, 128.6, 128.2, 127.1, 127.1, 126.9, 126.5, 126.0, 124.3, 122.5, 117.9, 117.2, 81.9, 75.8, 50.8, 48.9, 28.3.

HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2NaO_3S^+$ ([M+Na$^+$]) = 507.1713, Found 507.1711.

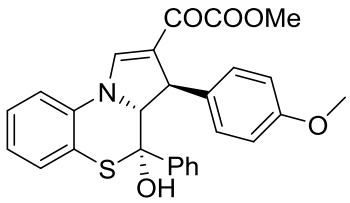


	Retention Time	Area	% Area	Height
1	3.000	814527	50.00	80653
2	4.212	814499	50.00	64236



	Retention Time	Area	% Area	Height
1	2.956	1613750	93.44	201355
2	4.265	113241	6.56	11597

Methyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3-(4-methoxyphenyl)-4-phenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7fa)



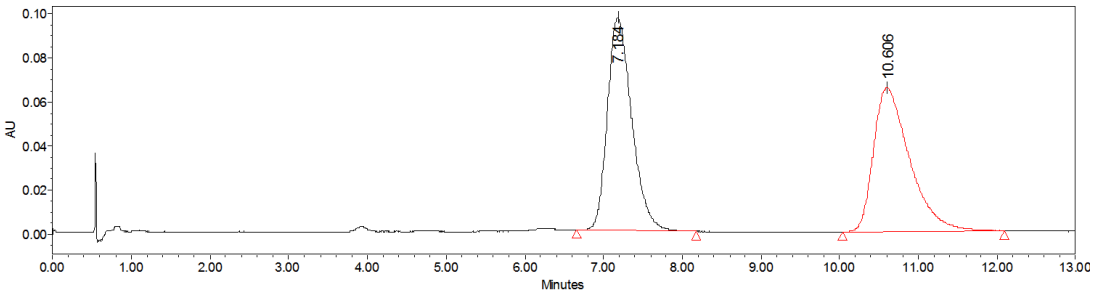
68% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 127-128 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 7.19 min, t_r (minor) = 10.89 min. ee = 95%. $[\alpha]^{26.6}_D$ = –107.1 (*c* = 0.58, in CH_2Cl_2).

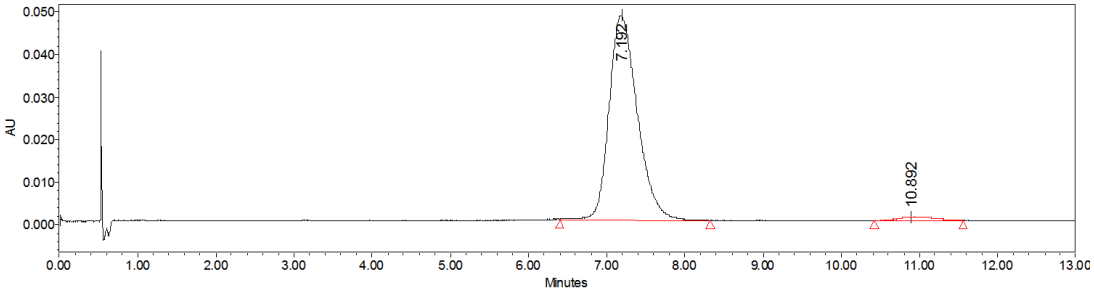
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 1H), 7.64 – 7.52 (m, 2H), 7.48 – 7.38 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.15 – 7.10 (m, 1H), 7.09 – 6.97 (m, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.36 (d, *J* = 8.8 Hz, 2H), 4.34 (d, *J* = 5.6 Hz, 1H), 4.28 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.26 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.4, 158.1, 149.8, 137.5, 134.7, 133.4, 129.0, 128.7, 127.8, 127.2, 127.1, 126.0, 124.4, 122.8, 118.6, 117.6, 113.7, 82.1, 55.1, 52.4, 47.4.

HRMS (ESI-TOF) calcd for $C_{27}H_{23}NNaO_5S^+$ ([M]+Na^+) = 496.1189, Found 496.1192.

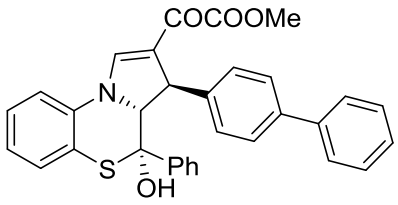


	Retention Time	Area	% Area	Height
1	7.184	2091640	50.04	96550
2	10.606	2088433	49.96	65343



	Retention Time	Area	% Area	Height
1	7.192	1200768	97.59	47898
2	10.892	29602	2.41	918

Methyl 2-{(3*R*,3a*R*,4*R*)-3-([1,1'-biphenyl]-4-yl)-4-hydroxy-4-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ga)



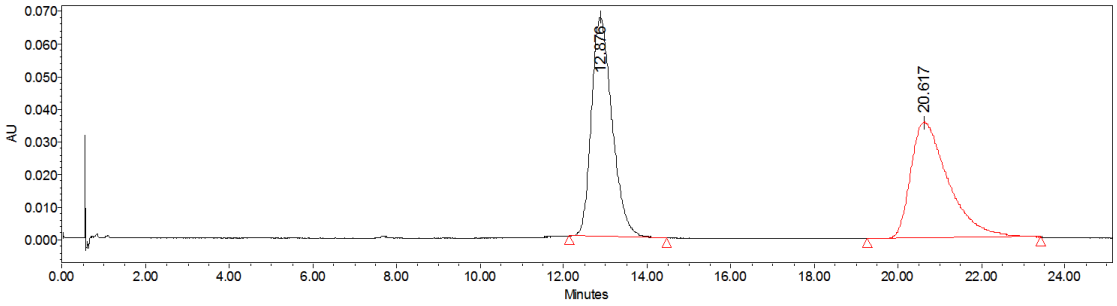
74% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 132-133 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 6.48 min, t_r (minor) = 10.64 min. ee = 92%. $[\alpha]^{26.6}_D$ = –214 (*c* = 0.77, in CH_2Cl_2).

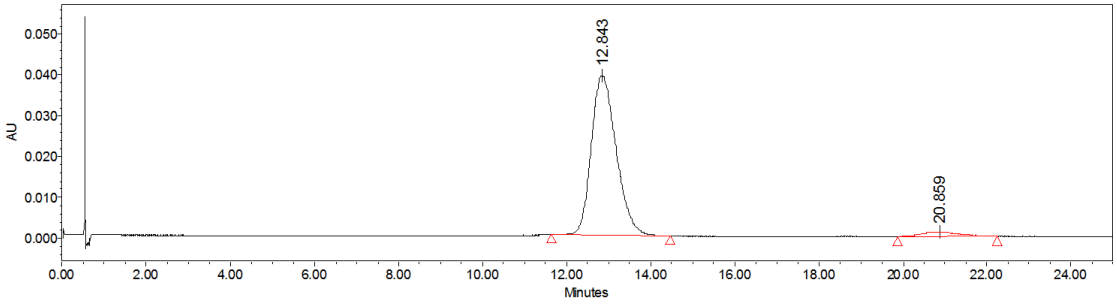
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 (s, 1H), 7.64 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 7.45 – 7.34 (m, 6H), 7.33 – 7.28 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.11 (m, 1H), 7.11 – 7.03 (m, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 4.41 (d, *J* = 5.2 Hz, 1H), 4.38 (d, *J* = 5.2 Hz, 1H), 3.80 (s, 3H), 3.22 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.4, 150.1, 141.4, 140.9, 139.4, 137.5, 133.4, 129.1, 128.8, 128.6, 127.2, 127.2, 127.1, 127.0, 126.9, 126.0, 124.5, 122.8, 118.3, 117.6, 82.1, 52.5, 47.9.

HRMS (ESI-TOF) calcd for $C_{32}H_{25}NNaO_4S^+$ ([M]+Na^+) = 542.1397, Found 542.1395.

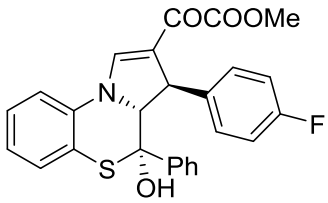


	Retention Time	Area	% Area	Height
1	12.876	2297139	50.77	67024
2	20.617	2227651	49.23	35569



	Retention Time	Area	% Area	Height
1	12.843	1606957	96.02	39170
2	20.859	66610	3.98	1100

Methyl 2-{(3*R*,3a*R*,4*R*)-3-(4-fluorophenyl)-4-hydroxy-4-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ha)



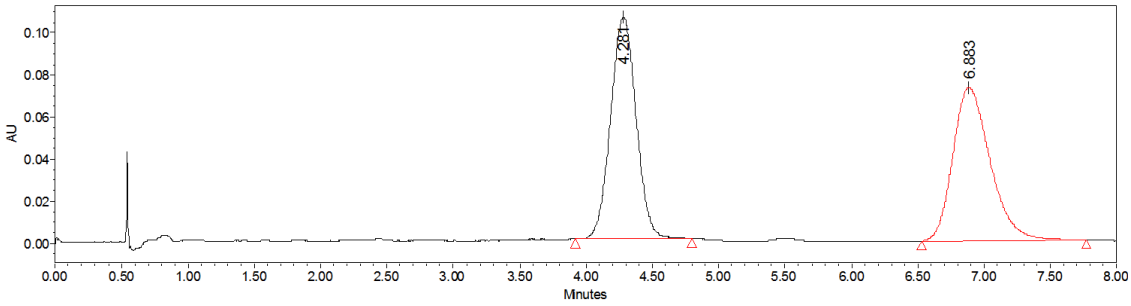
84% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 180-181 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.24 min, t_r (minor) = 6.91 min. ee = 92%. $[\alpha]^{26.6}_D$ = –61.2 (*c* = 0.77, in CH_2Cl_2).

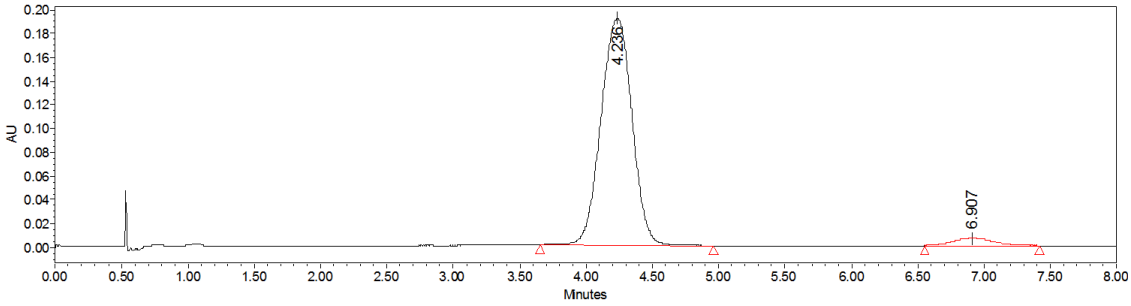
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 7.59 – 7.49 (m, 2H), 7.45 – 7.34 (m, 4H), 7.23 – 7.17 (m, 1H), 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.76 – 6.63 (m, 2H), 6.47 – 6.33 (m, 2H), 4.38 – 4.22 (m, 2H), 3.78 (s, 3H), 3.32 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.4, 161.5 (d, *J* = 245.4 Hz), 150.1, 138.2 (d, *J* = 3.1 Hz), 137.5, 133.3, 129.2, 128.8, 128.4 (d, *J* = 8.1 Hz), 127.3, 127.2, 125.3 (d, *J* = 152.8 Hz), 122.8, 118.3, 117.6, 115.2, 115.0, 82.0, 52.5, 47.6.

HRMS (ESI-TOF) calcd for $C_{26}H_{20}FNNaO_4S^+$ ([M]+Na^+) = 484.0989, Found 484.0990.

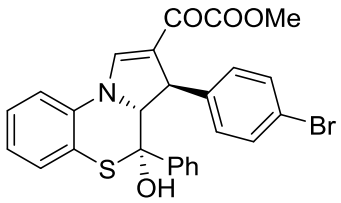


	Retention Time	Area	% Area	Height
1	4.281	1414620	49.88	105307
2	6.883	1421457	50.12	72748



	Retention Time	Area	% Area	Height
1	4.236	3091712	95.79	190792
2	6.907	135722	4.21	6370

Methyl 2-{(3*R*,3a*R*,4*R*)-3-(4-bromophenyl)-4-hydroxy-4-phenyl-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7has)

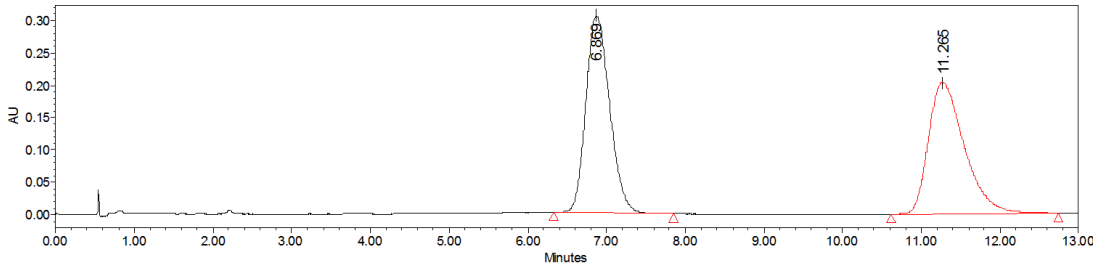


83% yield; yellow oil; R_f = 0.4 (petroleum/ethyl acetate = 2/1). Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 6.94 min, t_r (minor) = 11.49 min. ee = 90%. $[\alpha]^{26.4}_D$ = –130.8 (*c* = 0.82, in CH_2Cl_2).

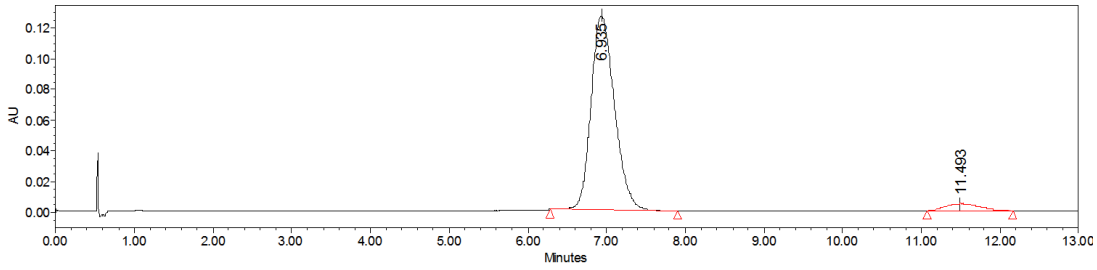
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.38 (m, 3H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.17 – 7.10 (m, 3H), 7.10 – 7.01 (m, 1H), 6.30 (d, *J* = 8.4 Hz, 2H), 4.31 (d, *J* = 5.6 Hz, 1H), 4.28 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.33 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.2, 150.2, 141.5, 137.4, 133.2, 131.3, 129.2, 128.8, 128.6, 127.3, 127.1, 126.1, 124.6, 122.7, 120.4, 117.9, 117.6, 81.9, 52.5, 47.8.

HRMS (ESI-TOF) calcd for $C_{26}H_{20}{}^{79}BrNNaO_4S^+$ ([M]+Na^+) = 544.0189, Found 544.0189, calcd for $C_{26}H_{20}{}^{81}BrNNaO_4S^+$ ([M]+Na^+) = 546.0168, Found 546.0195.

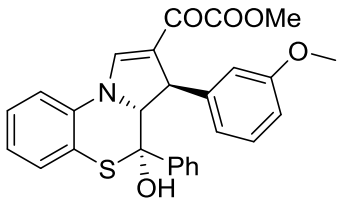


	Retention Time	Area	% Area	Height
1	6.869	6397414	49.90	304368
2	11.265	6424124	50.10	202688



	Retention Time	Area	% Area	Height
1	6.935	2621754	94.96	126534
2	11.493	139202	5.04	4691

Methyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3-(3-methoxyphenyl)-4-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ia)



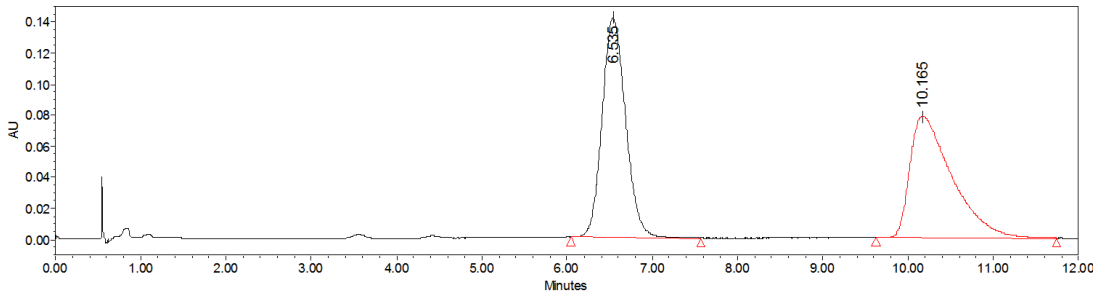
88% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 119-120 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 6.48 min, t_r (minor) = 10.64 min. ee = 90%. $[\alpha]^{26.6}_D$ = –74.9 (*c* = 0.73, in CH_2Cl_2).

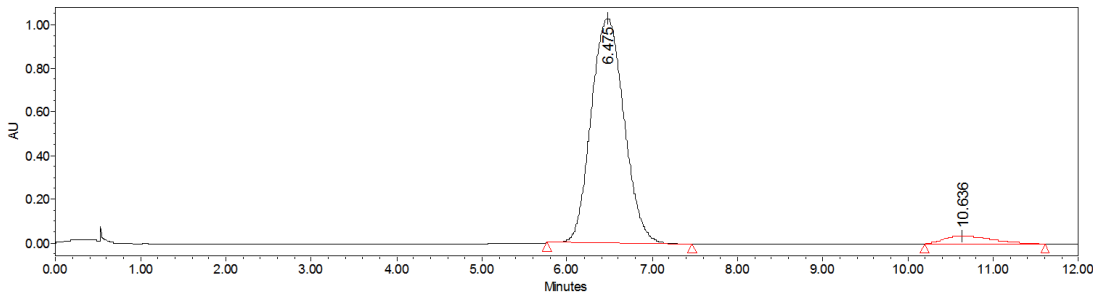
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (s, 1H), 7.63 – 7.52 (m, 2H), 7.50 – 7.38 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 1H), 7.09 – 7.01 (m, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.11 (d, *J* = 7.6 Hz, 1H), 6.01 – 5.88 (m, 1H), 4.35 (d, *J* = 5.2 Hz, 1H), 4.29 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.57 (s, 3H), 3.32 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.3, 159.4, 150.2, 144.0, 137.6, 133.4, 129.3, 129.1, 128.7, 127.2, 127.1, 126.0, 124.5, 122.8, 119.0, 118.3, 117.7, 112.4, 112.2, 82.2, 55.0, 52.4, 48.2.

HRMS (ESI-TOF) calcd for $C_{27}H_{23}NNaO_5S^+$ ([M]+Na^+) = 496.1189, Found 496.1188.

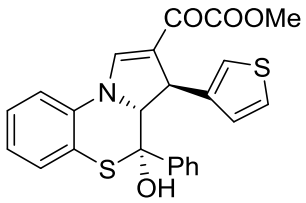


	Retention Time	Area	% Area	Height
1	6.535	2709244	50.19	141478
2	10.165	2688241	49.81	78228



	Retention Time	Area	% Area	Height
1	6.475	27737565	95.06	1027464
2	10.636	1442166	4.94	36387

Methyl 2-{(3*S*,3a*R*,4*R*)-4-hydroxy-4-phenyl-3-(thiophen-3-yl)-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ja)



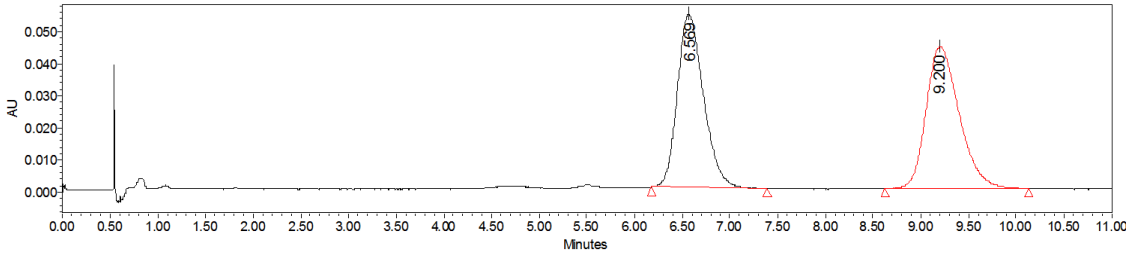
78% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 146-147 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 6.55 min, t_r (minor) = 9.56 min. ee = 92%. $[\alpha]^{26.4}_D$ = –8.9 (*c* = 0.60, in CH_2Cl_2).

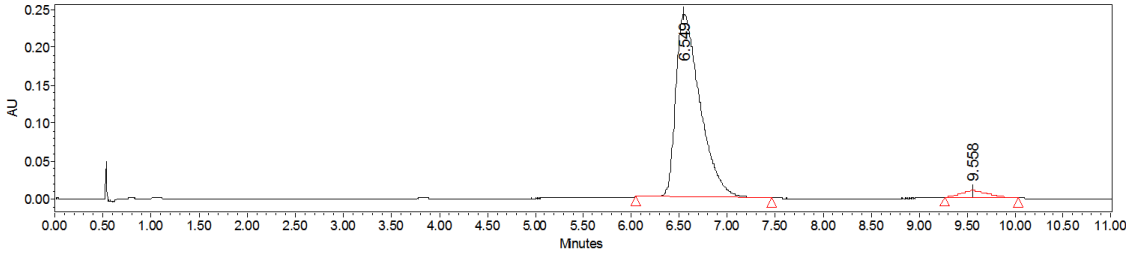
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (s, 1H), 7.66 – 7.53 (m, 2H), 7.50 – 7.37 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.14 – 7.09 (m, 1H), 7.08 – 7.02 (m, 1H), 6.99 (dd, *J* = 4.8, 2.8 Hz, 1H), 6.38 – 6.22 (m, 1H), 6.17 (dd, *J* = 4.8, 0.8 Hz, 1H), 4.47 (d, *J* = 5.2 Hz, 1H), 4.32 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.44 – 3.26 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.4, 150.1, 142.6, 137.6, 133.3, 129.2, 128.7, 127.2, 127.1, 126.1, 126.0, 125.5, 124.5, 122.8, 120.8, 117.8, 117.6, 82.2, 52.4, 43.2.

HRMS (ESI-TOF) calcd for $C_{24}H_{19}NNaO_4S_2^+$ ([M]+Na$^+$) = 472.0648, Found 472.0645.

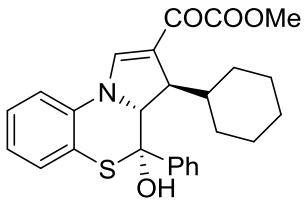


	Retention Time	Area	% Area	Height
1	6.569	1020230	49.07	53766
2	9.200	1058751	50.93	44050



	Retention Time	Area	% Area	Height
1	6.549	4286847	95.82	241488
2	9.558	186912	4.18	8934

Methyl 2-{(3*R*,3a*R*,4*R*)-3-cyclohexyl-4-hydroxy-4-phenyl-3a,4-dihydro-3H-benzo[b] pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ka)



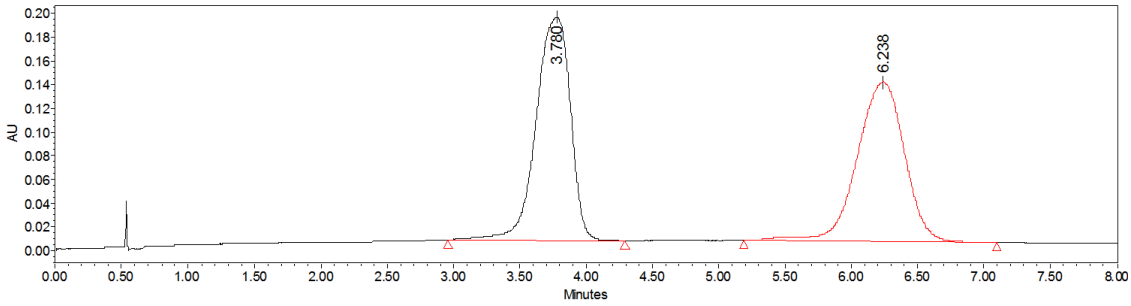
61% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 170-171 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 2.78 min, t_r (minor) = 6.26 min. ee = 54%. $[\alpha]^{26.7}_D$ = –161.7 (*c* = 0.53, in CH_2Cl_2).

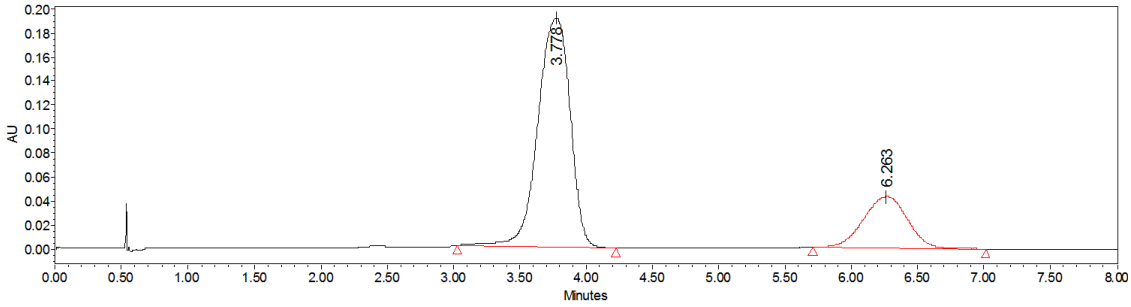
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 7.74 – 7.60 (m, 2H), 7.47 – 7.36 (m, 3H), 7.26 – 7.21 (m, 1H), 7.21 – 7.13 (m, 2H), 7.13 – 7.05 (m, 1H), 4.10 (d, *J* = 3.6 Hz, 1H), 3.83 (s, 3H), 3.25 (t, *J* = 3.4 Hz, 1H), 3.07 – 2.83 (m, 1H), 1.80 – 1.39 (m, 5H), 1.05 – 0.86 (m, 3H), 0.73 – 0.57 (m, 1H), 0.43 – 0.25 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 174.8, 163.7, 151.5, 137.9, 133.6, 129.1, 128.5, 127.7, 126.9, 125.7, 124.8, 123.5, 118.5, 117.4, 84.2, 68.6, 52.4, 47.4, 37.8, 29.2, 26.8, 26.3, 26.2, 26.1.

HRMS (ESI-TOF) calcd for $C_{26}H_{27}NNaO_4S^+$ ([M]+Na^+) = 472.1553, Found 472.1557.

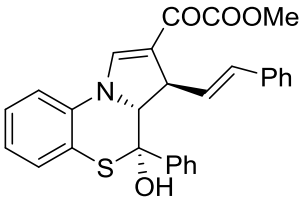


	Retention Time	Area	% Area	Height
1	3.780	3375331	50.28	187711
2	6.238	3337674	49.72	134353



	Retention Time	Area	% Area	Height
1	3.778	3227181	76.73	190237
2	6.263	978593	23.27	42762

Methyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-4-phenyl-3-((E)-styryl)-3a,4-dihydro-3H-benzo[b] pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7la)



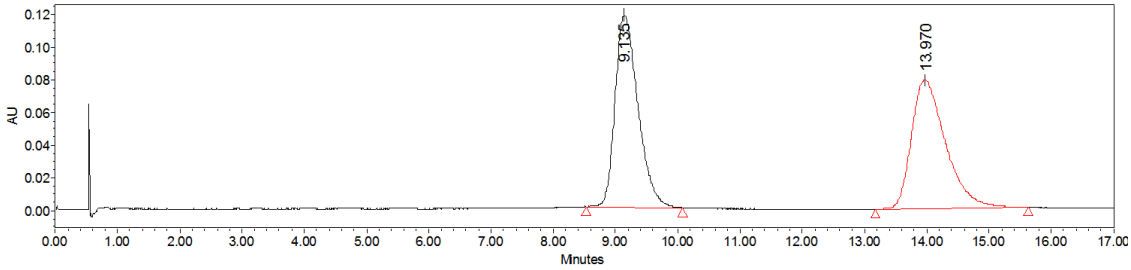
76% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 164-166 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 9.16 min, t_r (minor) = 14.31 min. ee = 84%. $[\alpha]^{26.7}_D$ = –19.1 (*c* = 0.63, in CH_2Cl_2).

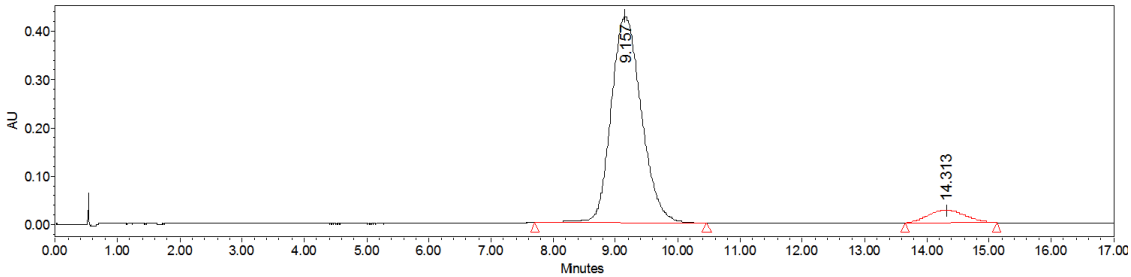
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 7.66 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.52 – 7.38 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 – 7.10 (m, 5H), 7.10 – 6.96 (m, 3H), 5.96 – 5.73 (m, 1H), 5.60 (d, *J* = 15.6 Hz, 1H), 4.38 (d, *J* = 6.0 Hz, 1H), 4.09 – 3.96 (m, 1H), 3.81 (s, 3H), 3.29 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 174.9, 163.5, 149.8, 137.5, 136.8, 133.3, 131.1, 129.2, 129.1, 128.7, 128.2, 127.2, 127.1, 127.1, 126.2, 126.0, 124.5, 122.6, 117.3, 117.1, 81.8, 73.9, 52.5, 45.5.

HRMS (ESI-TOF) calcd for $C_{28}H_{23}NNaO_4S^+$ ([M]+Na^+) = 492.1235, Found 492.1242.

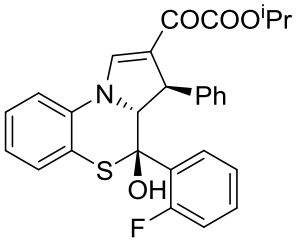


	Retention Time	Area	% Area	Height
1	9.135	2994504	50.03	117440
2	13.970	2990963	49.97	78646



	Retention Time	Area	% Area	Height
1	9.157	14456546	92.84	426597
2	14.313	1115292	7.16	26436

Isopropyl 2-{(3*R*,3a*R*,4*S*)-4-(2-fluorophenyl)-4-hydroxy-3-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7cb)



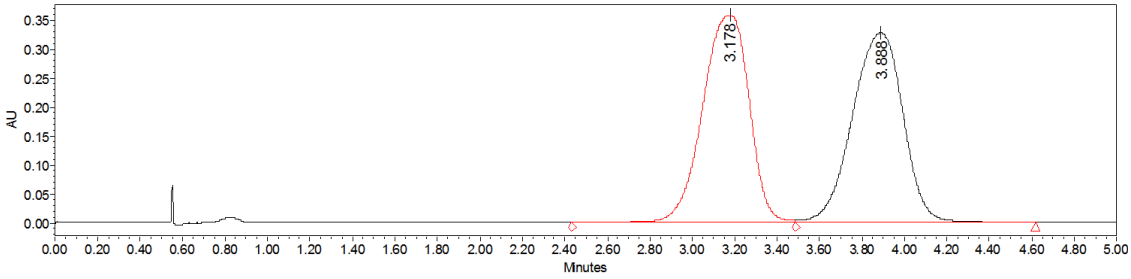
78% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 113-115 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 3.19 min, t_r (minor) = 3.91 min. ee = 96%. $[\alpha]^{26.2}_D$ = +25.12 (*c* = 0.77, in CH_2Cl_2).

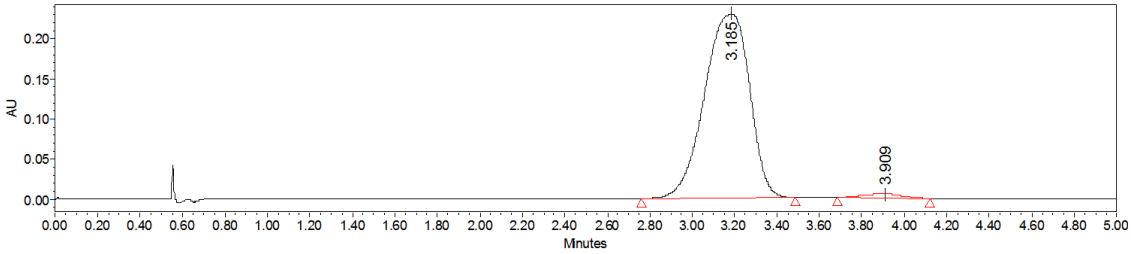
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69 (s, 1H), 7.86 (s, 1H), 7.45 – 7.39 (m, 1H), 7.38 – 7.33 (m, 1H), 7.30 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.02 (m, 5H), 6.94 – 6.84 (m, 1H), 6.76 – 6.53 (m, 2H), 5.17 – 4.98 (m, 1H), 4.86 (d, *J* = 5.6 Hz, 1H), 4.24 (d, *J* = 5.2 Hz, 1H), 3.65 (s, 1H), 1.33 – 1.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.5, 149.5, 142.3, 133.6, 131.5 (d, *J* = 8.8 Hz), 129.3, 128.4, 127.1, 127.04, 126.7, 126.0, 124.8 (d, *J* = 10.8 Hz), 124.5, 124.4 (d, *J* = 3.4 Hz), 118.9, 117.6, 116.5 (d, *J* = 23.5 Hz), 76.6 (d, *J* = 727.1 Hz), 69.8, 49.1, 21.6.

HRMS (ESI-TOF) calcd for $C_{28}H_{24}FNNaO_4S^+$ ([M]+Na$^+$) = 512.1302, Found 512.1306.

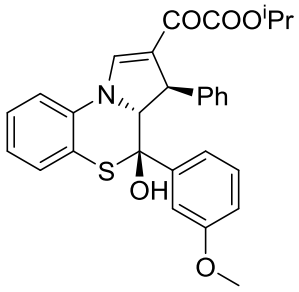


	Retention Time	Area	% Area	Height
1	3.178	5436108	50.09	356871
2	3.888	5416857	49.91	326671



	Retention Time	Area	% Area	Height
1	3.185	3384201	98.16	228963
2	3.909	63560	1.84	4671

Isopropyl 2-{(3*R*,3a*R*,4*S*)-4-hydroxy-4-(3-methoxyphenyl)-3-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7cc)



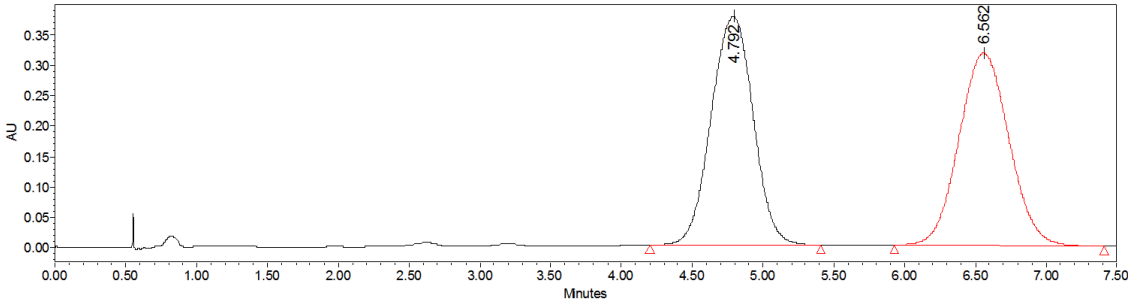
76% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 121-122 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.78 min, t_r (minor) = 6.52 min. ee = 95%. $[\alpha]^{26.2}_D$ = –81.7 (*c* = 0.78, in CH_2Cl_2).

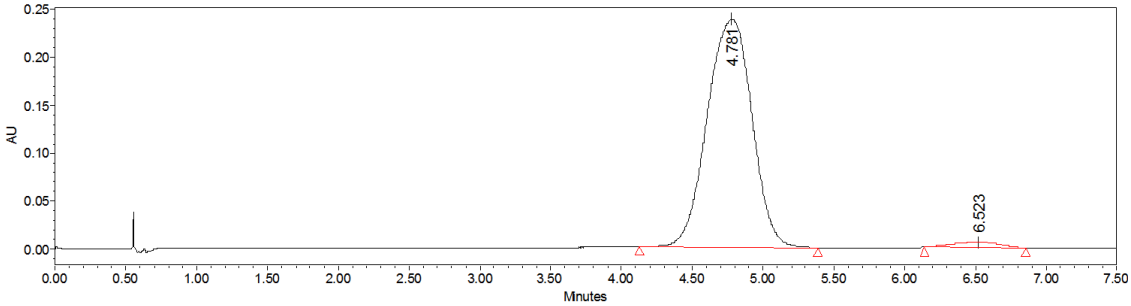
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (s, 1H), 7.38 – 7.33 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.08 (m, 2H), 7.08 – 6.98 (m, 5H), 6.96 – 6.90 (m, 1H), 6.60 – 6.45 (m, 2H), 5.07 (s, 1H), 4.40 (d, *J* = 5.2 Hz, 1H), 4.31 (d, *J* = 5.6 Hz, 1H), 3.69 (s, 3H), 3.39 (s, 1H), 1.32 – 1.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.5, 159.9, 149.5, 142.6, 139.1, 133.5, 129.7, 128.2, 127.2, 126.9, 126.5, 126.0, 124.2, 122.6, 119.4, 118.5, 117.4, 115.1, 112.3, 81.9, 69.7, 55.3, 48.4, 21.6.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}NNaO_5S^+$ ([M]+Na^+) = 524.1502, Found 524.1501.

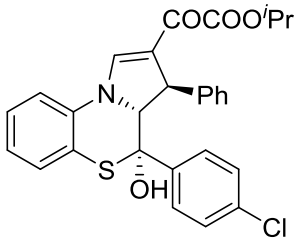


	Retention Time	Area	% Area	Height
1	4.792	7748200	49.88	375171
2	6.562	7785686	50.12	316218



	Retention Time	Area	% Area	Height
1	4.781	5211753	97.55	236861
2	6.523	130893	2.45	5780

Isopropyl 2-{(3*R*,3a*R*,4*R*)-4-(4-chlorophenyl)-4-hydroxy-3-phenyl-3a,4-dihydro-3H-benzo [b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7cd)



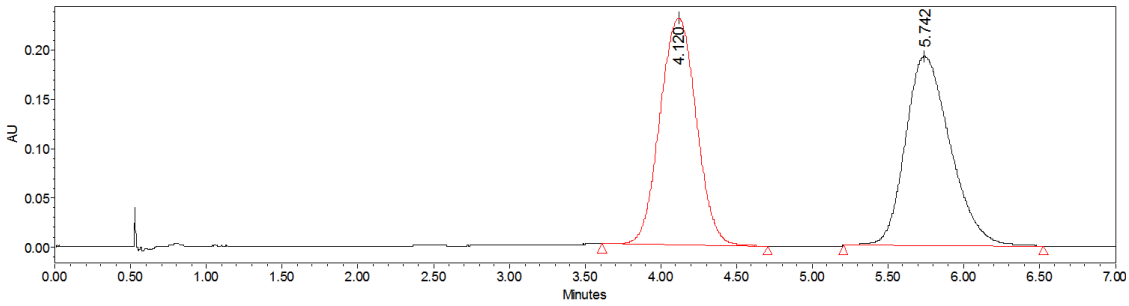
99% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 118-120 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.08 min, t_r (minor) = 5.84 min. ee = 93%. $[\alpha]^{26.1}_D$ = –75.9 (*c* = 0.92, in CH_2Cl_2).

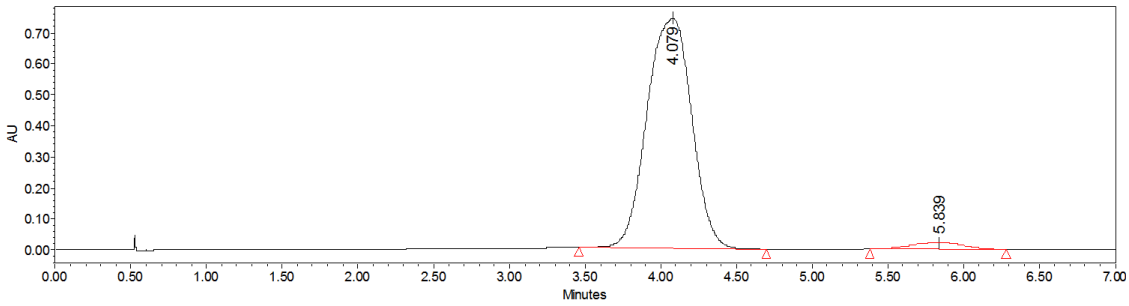
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.13 – 7.01 (m, 5H), 6.54 (dd, *J* = 5.6, 2.0 Hz, 2H), 5.22 – 4.86 (m, 1H), 4.38 (d, *J* = 5.6 Hz, 1H), 4.24 (d, *J* = 5.2 Hz, 1H), 3.99 (s, 1H), 1.28 – 1.20 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.4, 149.8, 142.4, 136.4, 135.0, 133.4, 128.7, 128.4, 127.2, 126.9, 126.6, 126.0, 124.4, 122.7, 118.5, 117.5, 81.7, 69.8, 48.4, 21.5.

HRMS (ESI-TOF) calcd for $C_{28}H_{24}{}^{35}ClNNaO_4S^+$ ([M]+Na^+) = 528.1007, Found 528.1027.calcd for $C_{28}H_{24}{}^{37}ClNNaO_4S^+$ ([M]+Na^+) = 530.0977, Found 530.1004.

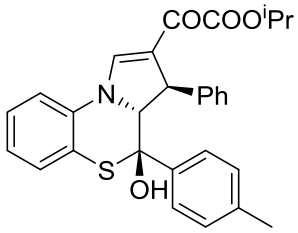


	Retention Time	Area	% Area	Height
1	4.120	3856170	49.30	230344
2	5.742	3965841	50.70	192546



	Retention Time	Area	% Area	Height
1	4.079	15210119	96.66	740265
2	5.839	526058	3.34	21453

Isopropyl 2-{(3*R*,3a*R*,4*S*)-4-hydroxy-3-phenyl-4-(p-tolyl)-3a,4-dihydro-3H-benzo[b] pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ce)



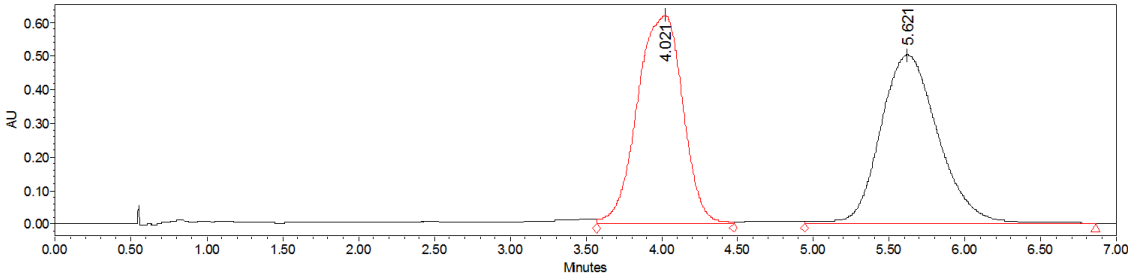
76% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 121-122 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 4.05 min, t_r (minor) = 5.79 min. ee = 94%. $[\alpha]^{26.2}_D$ = –61.7 (*c* = 0.71, in CH_2Cl_2).

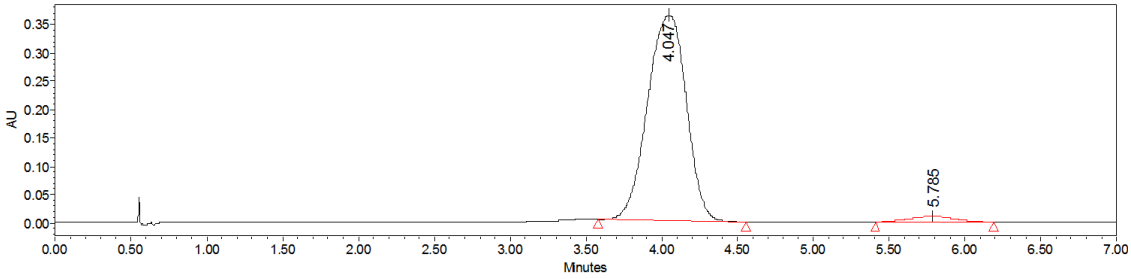
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.11 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.08 – 6.94 (m, 4H), 6.50 (dd, *J* = 5.2, 1.6 Hz, 2H), 5.07 (s, 1H), 4.36 (d, *J* = 5.2 Hz, 1H), 4.30 (d, *J* = 5.6 Hz, 1H), 3.27 (s, 1H), 2.40 (s, 3H), 1.34 – 1.24 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.5, 149.6, 142.6, 138.9, 134.6, 133.5, 129.3, 128.2, 127.2, 127.0, 126.9, 126.4, 125.9, 124.2, 122.9, 118.5, 117.5, 82.1, 69.7, 48.3, 21.6, 21.1.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}NNaO_4S^+$ ([M]+Na^+) = 508.1553, Found 508.1559.

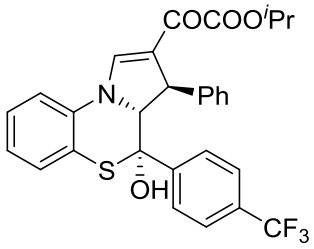


	Retention Time	Area	% Area	Height
1	4.021	12991686	49.51	621753
2	5.621	13249813	50.49	503231



	Retention Time	Area	% Area	Height
1	4.047	6471586	96.77	362367
2	5.785	216131	3.23	9930

Isopropyl 2-{(3*R*,3a*R*,4*R*)-4-hydroxy-3-phenyl-4-(4-(trifluoromethyl)phenyl)-3a,4-dihydro-3H-benzo[b]pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7cf)



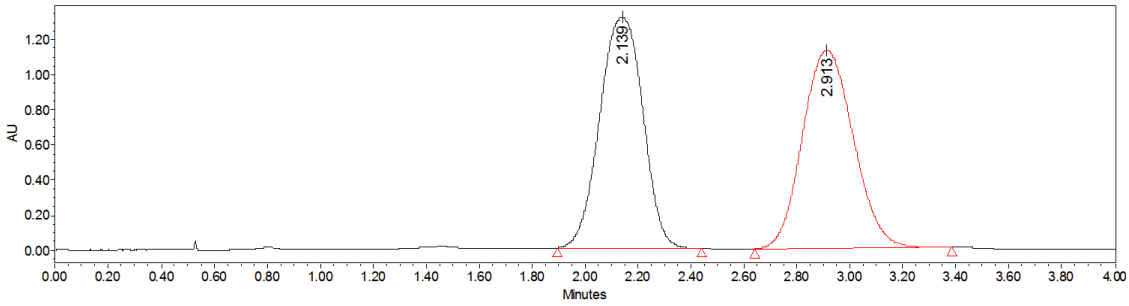
92% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 121-123 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 2.13 min, t_r (minor) = 2.96 min. ee = 92%. $[\alpha]^{26.0}_D$ = –87.8 (*c* = 1.00, in CH_2Cl_2).

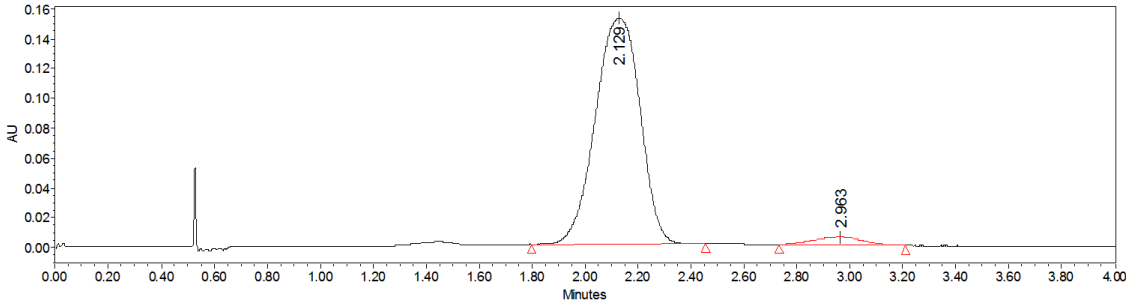
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (s, 1H), 7.58 (dd, *J* = 21.2, 8.0 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.13 – 6.97 (m, 5H), 6.48 – 6.36 (m, 2H), 5.11 – 4.91 (m, 1H), 4.42 (d, *J* = 5.6 Hz, 1H), 4.26 (s, 1H), 4.22 (d, *J* = 5.6 Hz, 1H), 1.28 – 1.20 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 175.4, 162.3, 149.7, 142.4, 141.9, 133.4, 131.1 (d, *J* = 32.8 Hz),, 128.4, 127.8, 127.3, 126.9, 126.8, 126.2, 125.5 (q, *J* = 3.6 Hz), 123.9 (d, *J* = 290.6 Hz), 124.5, 122.4, 118.5, 117.4, 81.5, 69.9, 48.6, 21.5.

HRMS (ESI-TOF) calcd for $C_{29}H_{24}F_3NNaO_4S^+$ ([M]+Na^+) = 562.1270, Found 562.1278.

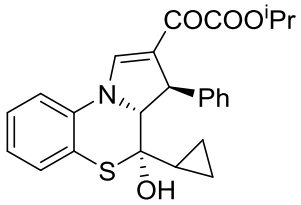


	Retention Time	Area	% Area	Height
1	2.139	14980386	49.82	1315395
2	2.913	15089320	50.18	1128569



	Retention Time	Area	% Area	Height
1	2.129	1784786	96.19	151339
2	2.963	70607	3.81	5430

Isopropyl 2-{(3*R*,3a*R*,4*R*)-4-cyclopropyl-4-hydroxy-3-phenyl-3a,4-dihydro-3H-benzo[b] pyrrolo[1,2-d][1,4]thiazin-2-yl}-2-oxoacetate (7ci)



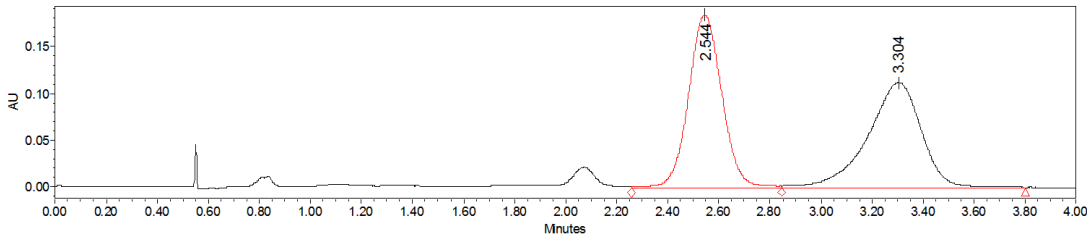
46% yield; yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 123-125 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 80/20, flow rate 2.0 mL/min, λ = 254 nm) t_r (major) = 2.57 min, t_r (minor) = 3.36 min. ee = 95%. $[\alpha]^{26.2}_D$ = –95.6 (*c* = 0.39, in CH_2Cl_2).

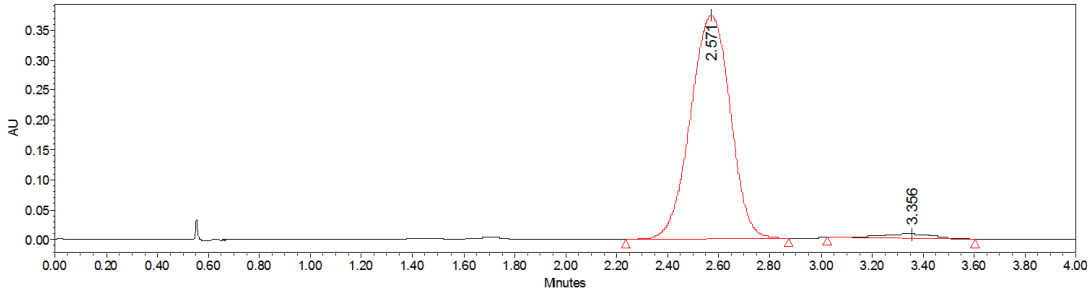
^{1}H NMR (400 MHz, $CDCl_3$) δ =8.64 (s, 1H), 7.36 – 7.27 (m, 5H), 7.21 – 7.13 (m, 2H), 7.09 – 7.00 (m, 2H), 5.12 – 5.03 (m, 1H), 4.81 (d, *J* = 5.6 Hz, 1H), 4.35 (d, *J* = 5.6 Hz, 1H), 2.58 (s, 1H), 1.32 – 1.26 (m, 6H), 1.22 – 1.05 (m, 3H), 0.68 – 0.56 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.5, 149.0, 143.4, 133.4, 128.6, 127.6, 127.1, 126.8, 125.8, 124.5, 122.8, 119.0, 117.1, 81.2, 69.7, 48.0, 21.6, 17.1, 3.5, -0.2.

HRMS (ESI-TOF) calcd for $C_{25}H_{25}NNaO_4S^+$ ([M]+Na^+) = 458.1397, Found 458.1398.

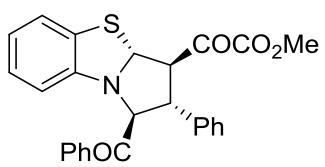


	Retention Time	Area	% Area	Height
1	2.544	1685905	50.92	184303
2	3.304	1625237	49.08	111972



	Retention Time	Area	% Area	Height
1	2.571	4008452	97.48	371204
2	3.356	103747	2.52	6898

Methyl 2-(1-benzoyl-2-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b] thiazol-3-yl)-2-oxoacetate (8a)

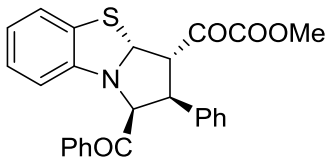


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.70 (m, 2H), 7.53 – 7.49 (m, 1H), 7.35 – 7.30 (m, 2H), 7.24 – 7.19 (m, 3H), 7.16 (dd, *J* = 7.6, 1.2, 1H), 7.14 – 7.08 (m, 2H), 6.99 – 6.94 (m, 1H), 6.91 – 6.84 (m, 1H), 6.56 – 6.41 (m, 1H), 5.85 (d, *J* = 8.4, 1H), 5.17 (d, *J* = 8.0, 1H), 4.44 (dd, *J* = 10.4, 8.4, 1H), 3.95 (dd, *J* = 10.4, 8.0, 1H), 3.69 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.6, 191.5, 160.8, 147.2, 137.6, 135.3, 133.6, 129.1, 128.7, 128.6, 128.1, 127.7, 127.7, 125.9, 122.4, 122.3, 111.6, 75.8, 74.2, 63.2, 53.2.

HRMS (ESI-FT) calcd for $C_{26}H_{22}NO_4S^+$([M]+H^+) = 444.1264, Found 444.1266.

Methyl 2-(1-benzoyl-3-phenyl-1,2,3,3a-tetrahydrobenzo[d]pyrrolo[2,1-b] thiazol-2-yl)-2-oxoacetate (8b)

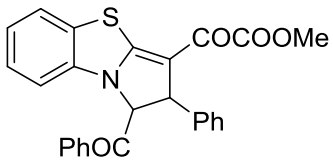


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.38 (m, 1H), 7.33 – 7.19 (m, 2H), 7.14 – 6.88 (m, 7H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.53 (d, *J* = 8.0 Hz, 1H), 5.01 – 4.71 (m, 1H), 4.37 – 4.17 (m, 1H), 3.90 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.5, 190.2, 160.4, 148.2, 136.4, 135.6, 133.3, 128.9, 128.5, 128.5, 128.4, 128.1, 127.6, 125.8, 122.8, 121.8, 112.9, 73.7, 72.5, 57.7, 53.5, 48.4.

HRMS (ESI-FT) calcd for $C_{26}H_{22}NO_4S^+$([M]+H^+) = 444.1264, Found 444.1258.

Methyl 2-(1-benzoyl-2-phenyl-1,2-dihydrobenzo[d]pyrrolo[2,1-b]thiazol-3-yl)-2-oxoacetate (8c)

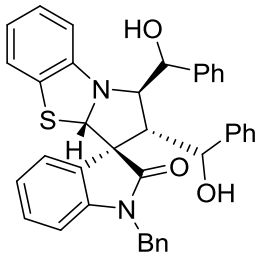


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.75 – 7.68 (m, 2H), 7.57 – 7.52 (m, 2H), 7.42 – 7.26 (m, 5H), 7.26 – 7.20 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 0.71H), 6.78 (d, *J* = 8.0 Hz, 0.25H), 5.93 (d, *J* = 3.2 Hz, 0.74H), 5.77 (d, *J* = 2.8 Hz, 0.26H), 5.15 (d, *J* = 3.6 Hz, 1H), 4.85 (d, *J* = 3.2 Hz, 0.26H), 3.85 (s, 0.79H), 3.55 (s, 2.23H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 190.7, 171.2, 163.3, 143.0, 136.7, 134.8, 132.8, 131.1, 129.4, 129.2, 129.0, 127.9, 127.6, 127.5, 127.3, 124.1, 123.5, 110.7, 106.4, 73.5, 54.7, 52.0.

HRMS (ESI-FT) calcd for $C_{26}H_{20}NO_4S^+$([M]+H^+) = 442.1108, Found 442.1104.

(1*R*,2*R*,3*R*,3a*S*)-1'-Benzyl-1,2-bis(hydroxy(phenyl)methyl)-1,2-dihydro-3aH-spiro[benzo[d]pyrrolo[2,1-b]thiazole-3,3'-indolin]-2'-one (9)



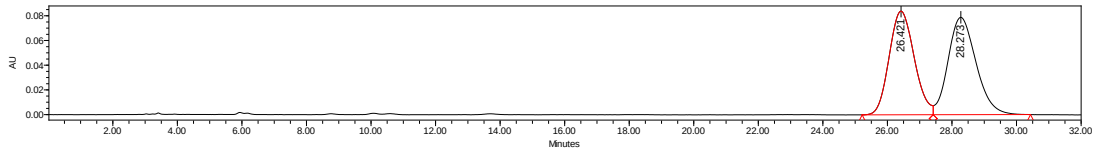
89% yield; light yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 246-248 ℃.

Dissolved in *i*PrOH for HPLC; **HPLC** (Daicel chiralpak **IA**, n-hexane/*i*PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 26.30 min, t (major) = 28.11 min. ee = 98%. $[\alpha]^{22.9}_{D}$ = –204.9 (*c* = 1.03, in CH_2Cl_2).

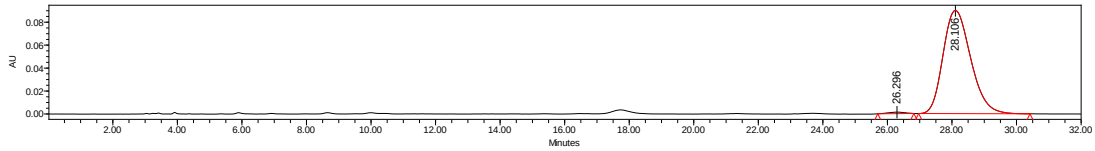
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.36 (m, 6H), 7.35 – 7.26 (m, 4H), 7.25 – 7.19 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.91 (m, 2H), 6.78 – 6.43 (m, 5H), 6.22 (d, *J* = 7.6 Hz, 1H), 5.89 (s, 1H), 4.95 – 4.89 (m, 2H), 4.45 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.96 – 3.84 (m, 1H), 3.74 (dd, *J* = 22.0, 8.4 Hz, 2H), 3.14 (d, *J* = 8.4 Hz, 1H), 2.11 (d, *J* = 4.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 175.9, 148.7, 144.2, 142.8, 142.0, 135.7, 129.2, 129.1, 128.7, 128.2, 127.6, 127.4, 127.3, 127.2, 126.6, 126.6, 125.8, 125.3, 125.1, 121.13, 121.09, 120.3, 109.3, 108.3, 79.5, 75.6, 73.4, 73.1, 64.8, 55.1, 44.0.

HRMS (ESI-TOF) calcd for $C_{38}H_{32}N_2NaO_3S^+$ ([M]+Na$^+$) = 619.2026, Found 619.2025.

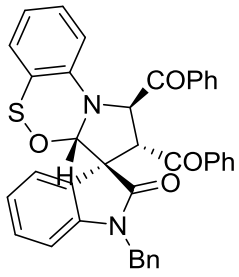


	Retention Time	Area	% Area	Height
1	26.421	4519640	48.82	83877
2	28.273	4737570	51.18	78830



	Retention Time	Area	% Area	Height
1	26.296	47477	0.88	1305
2	28.106	5345983	99.12	89945

{(1*R*,2*R*,3*S*,3a*S*)-1'-Benzyl-2'-oxo-1,2-dihydro-3aH-spiro[benzo[c]pyrrolo[1,2-e][1,2,5]oxathiazine-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (10)



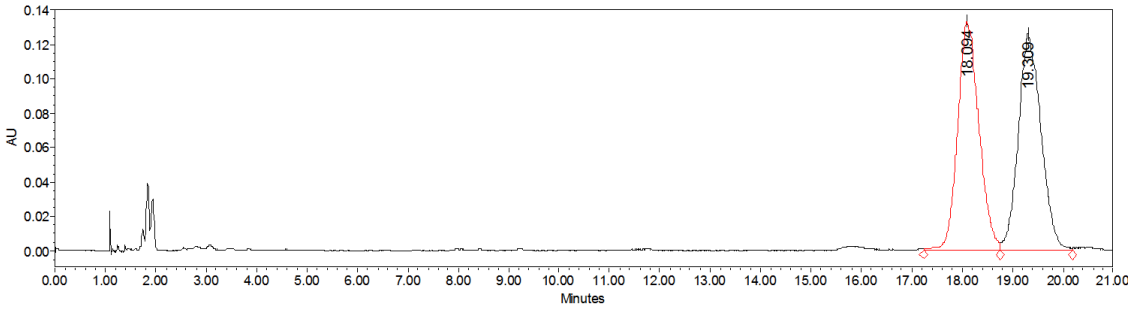
96% yield; light yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 2/1); m.p. 177-179 ℃.

Dissolved in *i*PrOH for SFC; **SFC** (Daicel chiralcel **OD-3**, CO_2/*i*PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 17.99 min, t_r (major) = 19.28 min. ee = 99%. $[\alpha]^{20.9}_D$ = –112.1 (*c* = 0.78, in CH_2Cl_2).

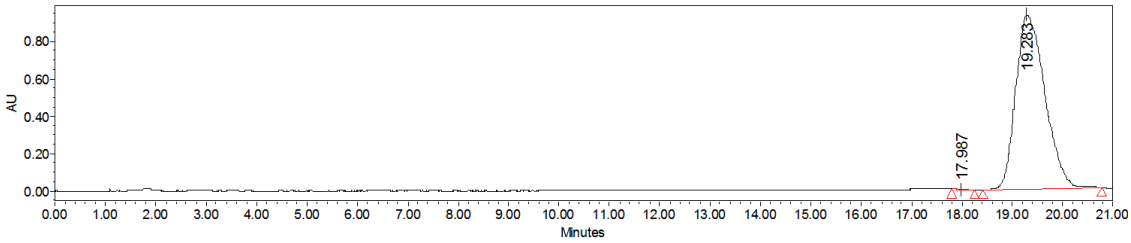
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.47 – 7.40 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.13 (m, 5H), 7.08 – 6.84 (m, 5H), 6.55 (t, *J* = 7.6 Hz, 1H), 6.28 (dd, *J* = 22.0, 7.6 Hz, 2H), 5.92 (d, *J* = 7.6 Hz, 1H), 5.71 (s, 1H), 5.40 (d, *J* = 7.6 Hz, 1H), 4.93 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 15.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.4, 194.5, 173.1, 152.6, 142.3, 135.6, 135.5, 134.9, 134.4, 134.0, 133.6, 131.3, 129.3, 129.1, 129.0, 128.9, 128.3, 128.2, 128.1, 127.7, 126.7, 126.1, 123.0, 122.1, 121.5, 111.4, 109.5, 96.7, 65.7, 59.8, 57.8, 44.2.

HRMS (ESI-TOF) calcd for $C_{38}H_{28}N_2NaO_4S^+$ ([M]+Na$^+$) = 631.1662, Found 631.1661.

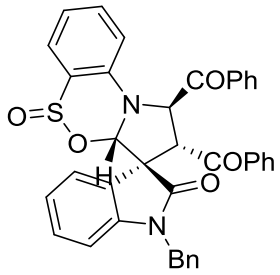


	Retention Time	Area	% Area	Height
1	18.094	3920277	49.89	133105
2	19.309	3937807	50.11	125805



	Retention Time	Area	% Area	Height
1	17.987	14185	0.04	-1017
2	19.283	37417651	99.96	932148

{(1*R*,2*R*,3*S*,3a*S*)-1'-Benzyl-5-oxido-2'-oxo-1,2-dihydro-3aH-spiro[benzo[c]pyrrolo[1,2-e][1,2,5]oxathiazine-3,3'-indoline]-1,2-diyl}bis(phenylmethanone) (11)



95% yield; light yellow solid; R_f = 0.4 (petroleum/ethyl acetate = 3/1); m.p. 220-222 ℃.

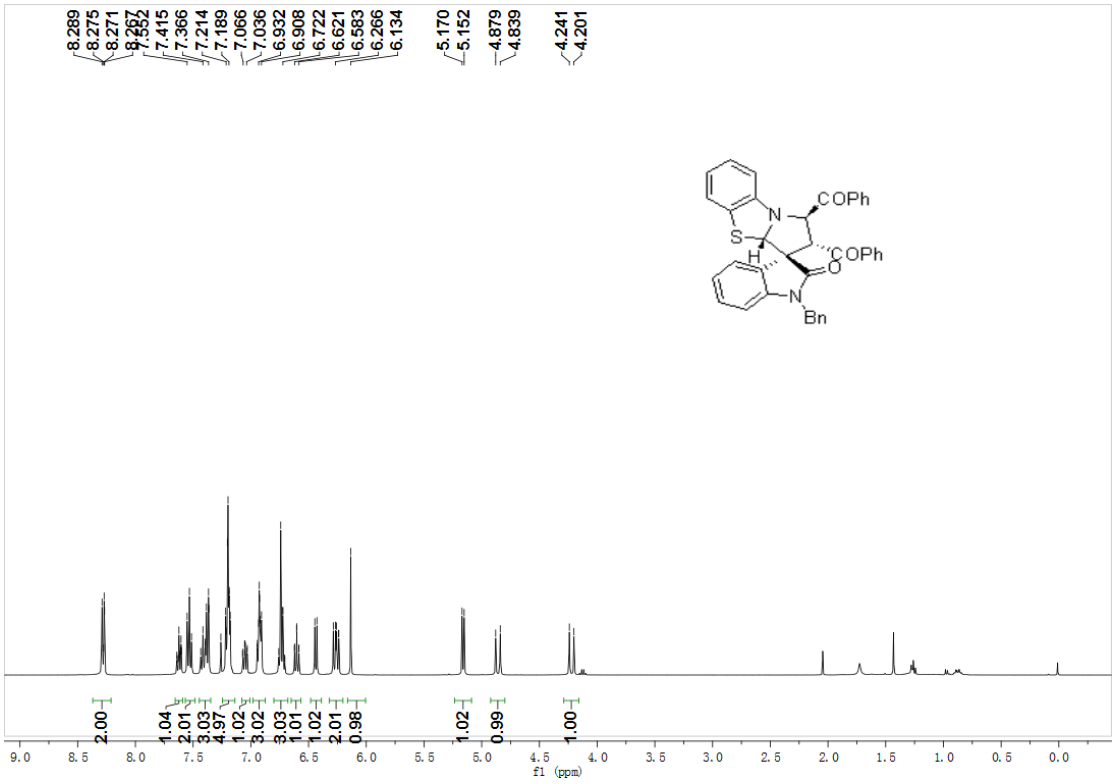
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 - 8.10 (m, 2H), 7.71 - 7.62 (m, 1H), 7.59 – 7.43 (m, 4H), 7.38 – 7.28 (m, 3H), 7.26 – 7.14 (m, 5H), 7.07 – 6.83 (m, 5H), 6.66 – 6.55 (m, 1H), 6.46 – 6.36 (m, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 6.09 (d, *J* = 7.6 Hz, 1H), 5.79 – 5.46 (m, 1H), 5.31 – 5.08 (m, 1H), 5.00 – 4.80 (m, 1H), 4.15 – 3.90 (m, 1H).

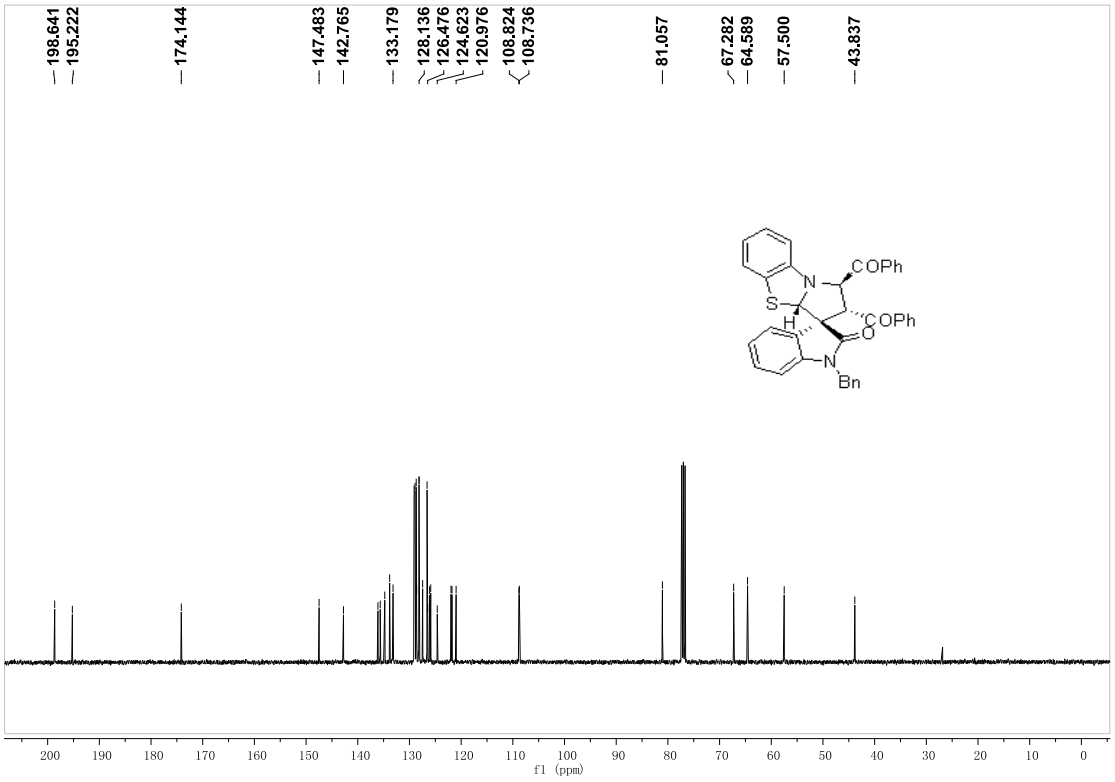
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.4, 194.4, 172.8, 147.8, 143.1, 135.8, 135.5, 135.4, 134.4, 134.28, 133.7, 129.2, 129.1, 128.8, 128.4, 128.2, 127.5, 126.6, 125.9, 125.4, 122.4, 122.2, 121.5, 111.9, 109.6, 84.9, 65.2, 60.7, 58.9, 44.2.

HRMS (ESI-TOF) calcd for $C_{38}H_{28}N_2NaO_{24}S^+$ ([M]+Na^+) = 647.1611, Found 647.1614.

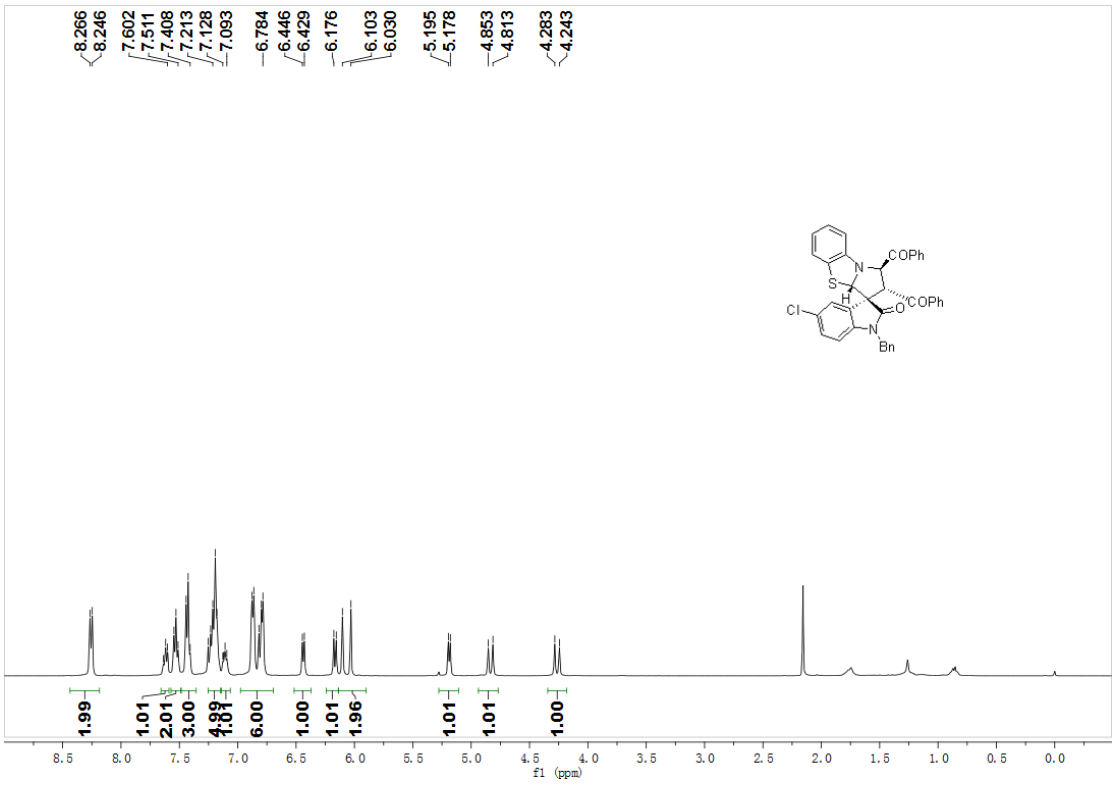
12. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra

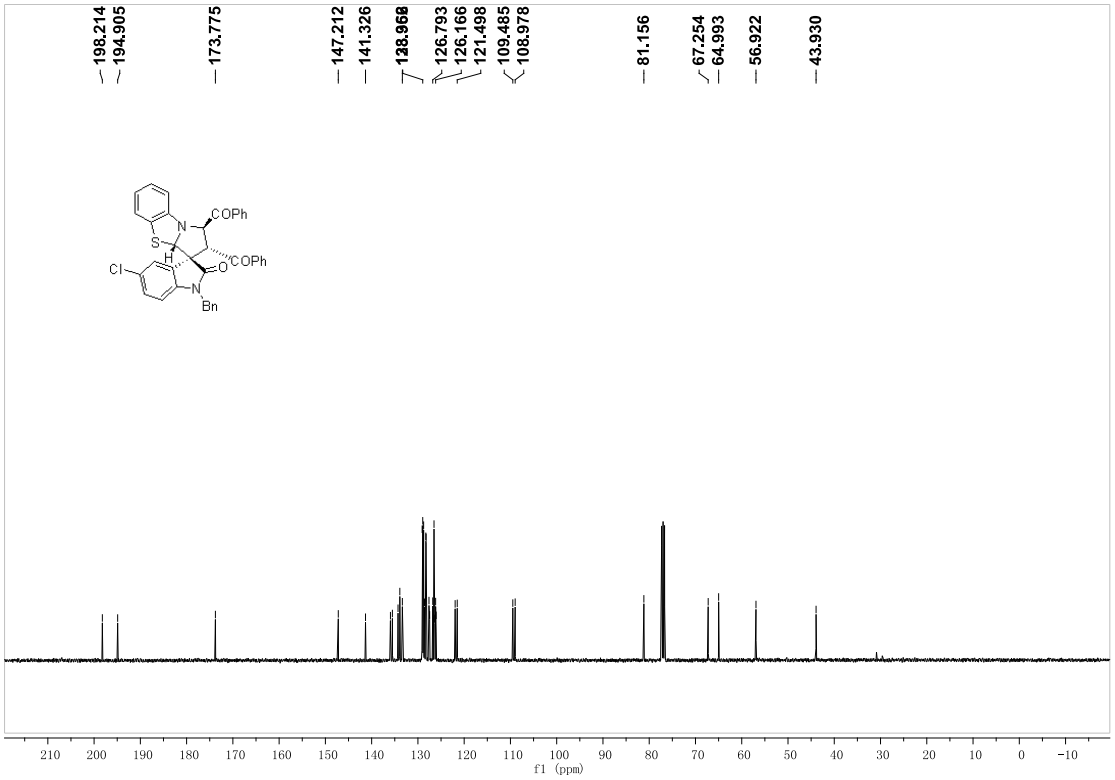
Compound 3aa



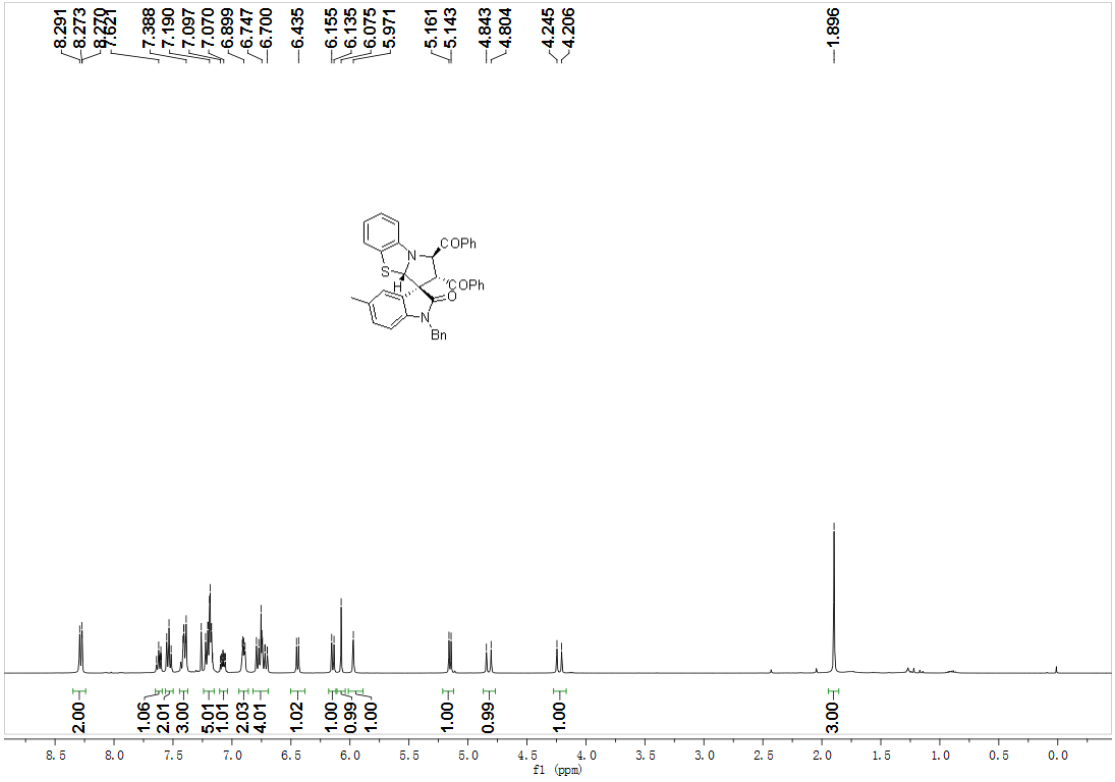


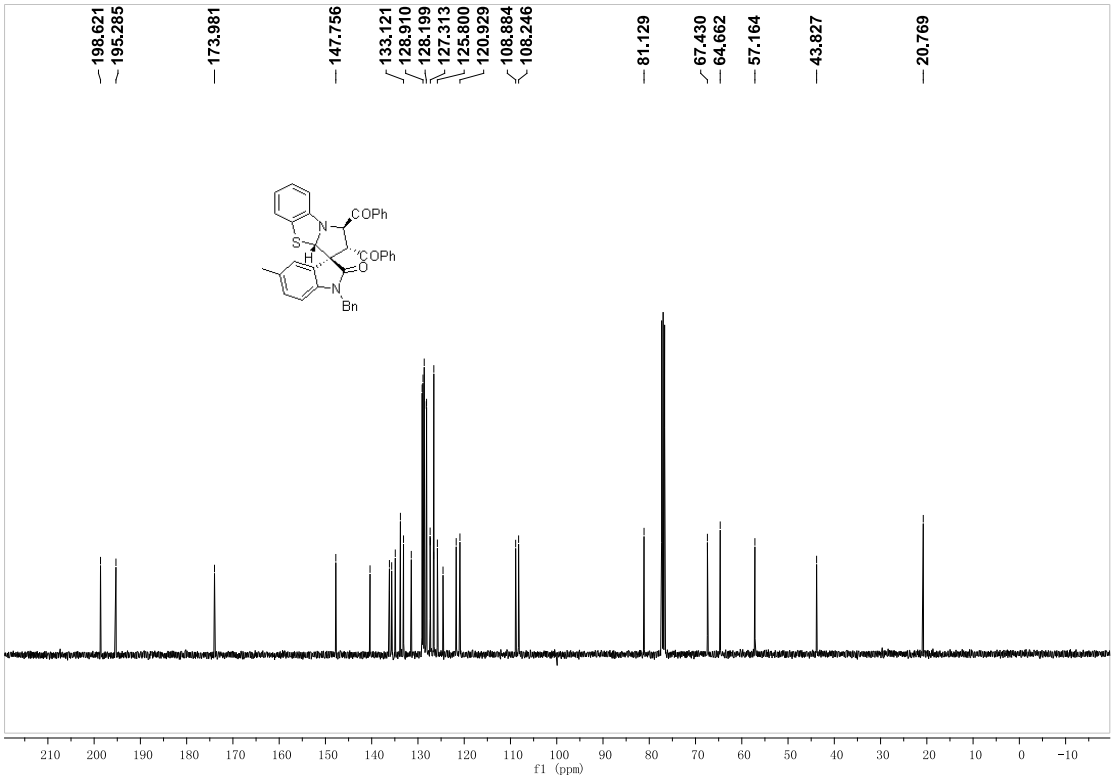
Compound 3ba



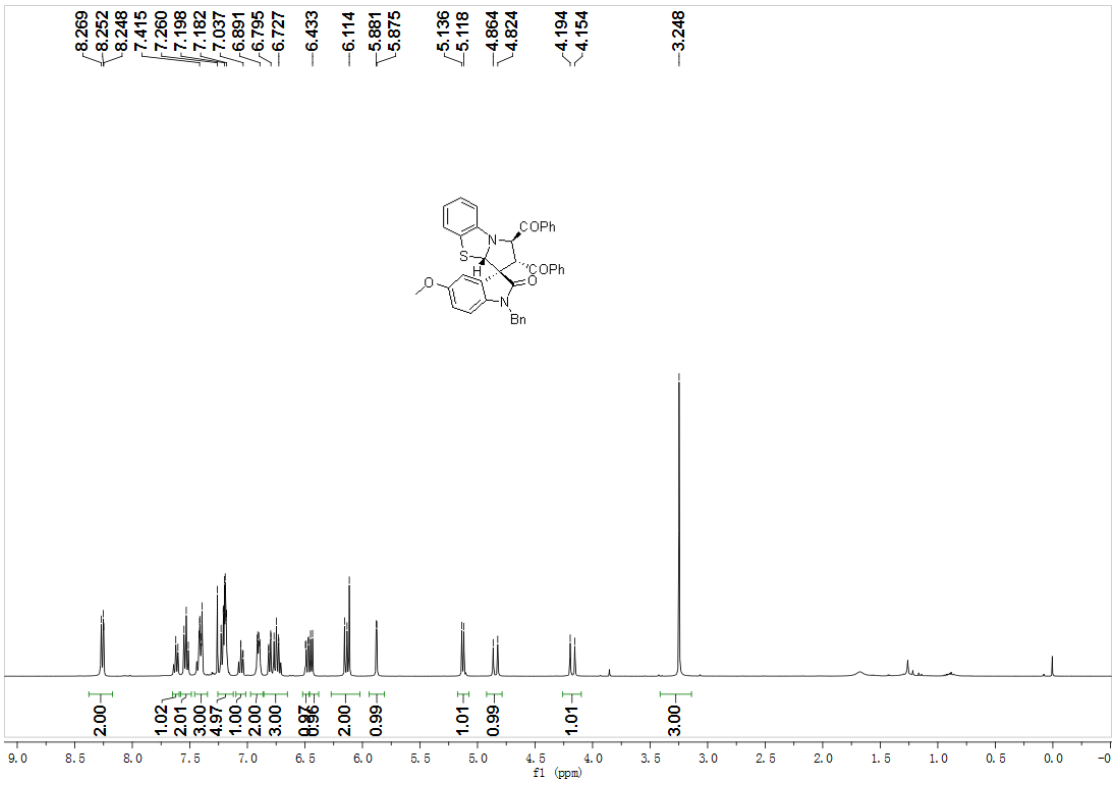


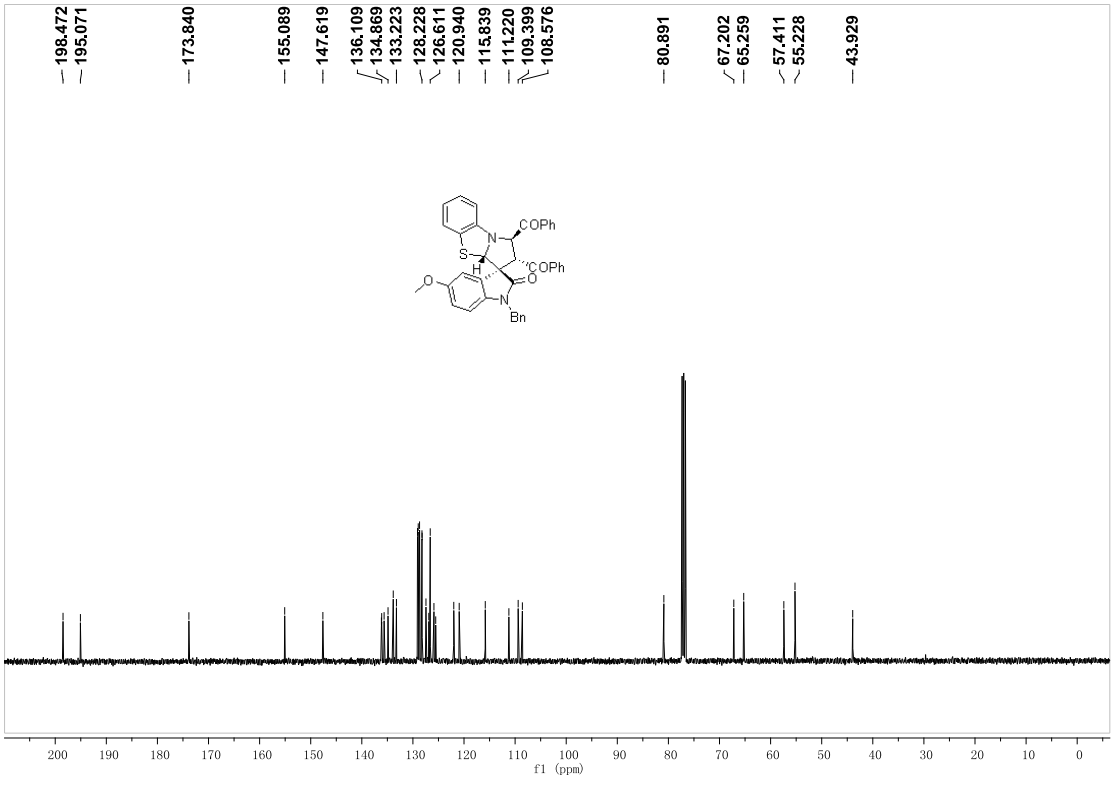
Compound 3ca



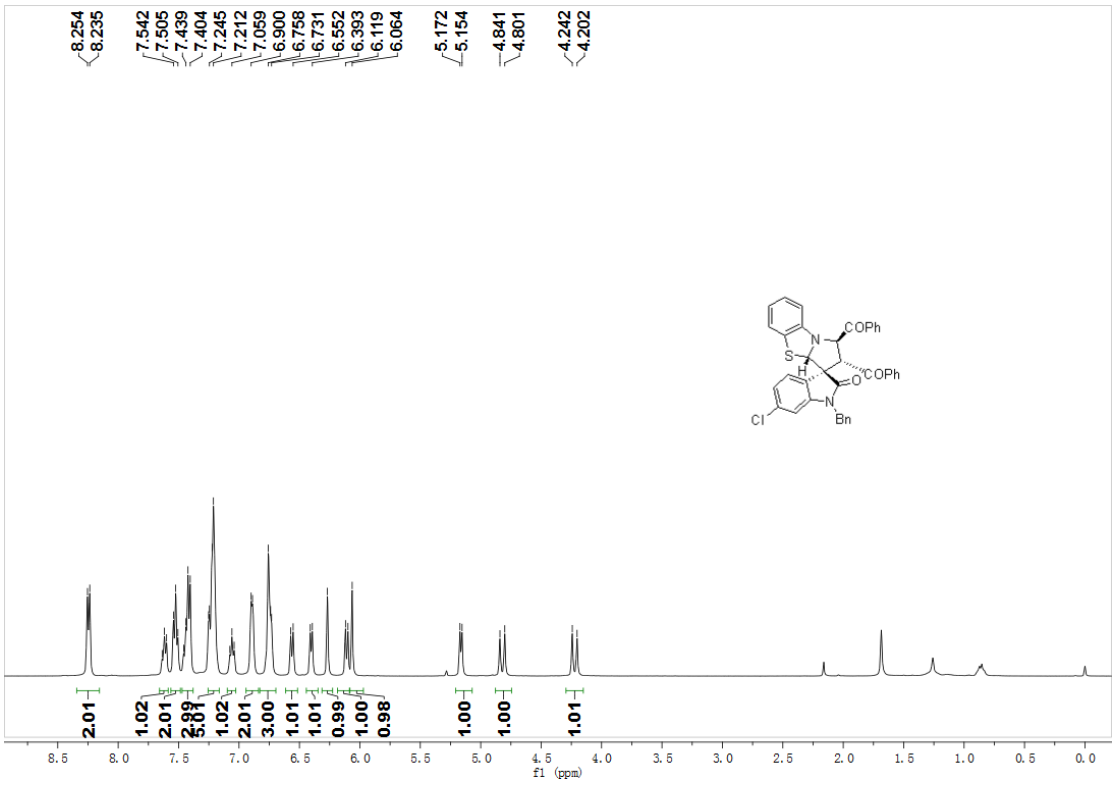


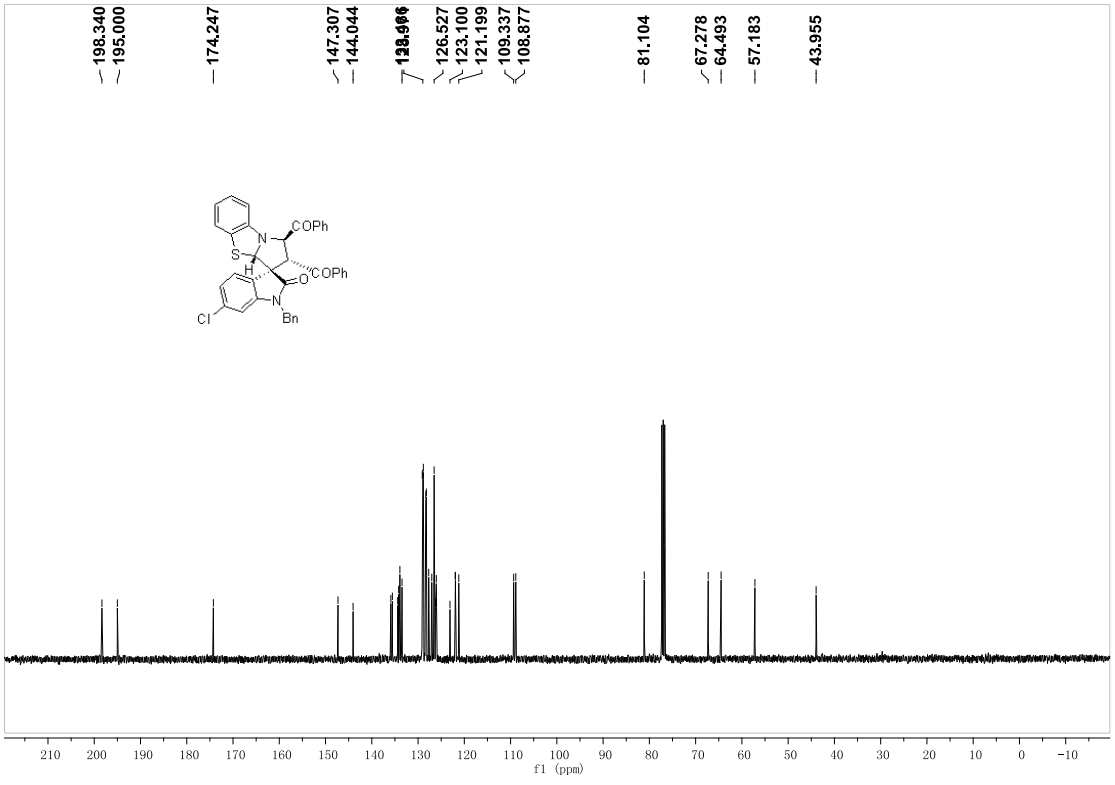
Compound 3cas



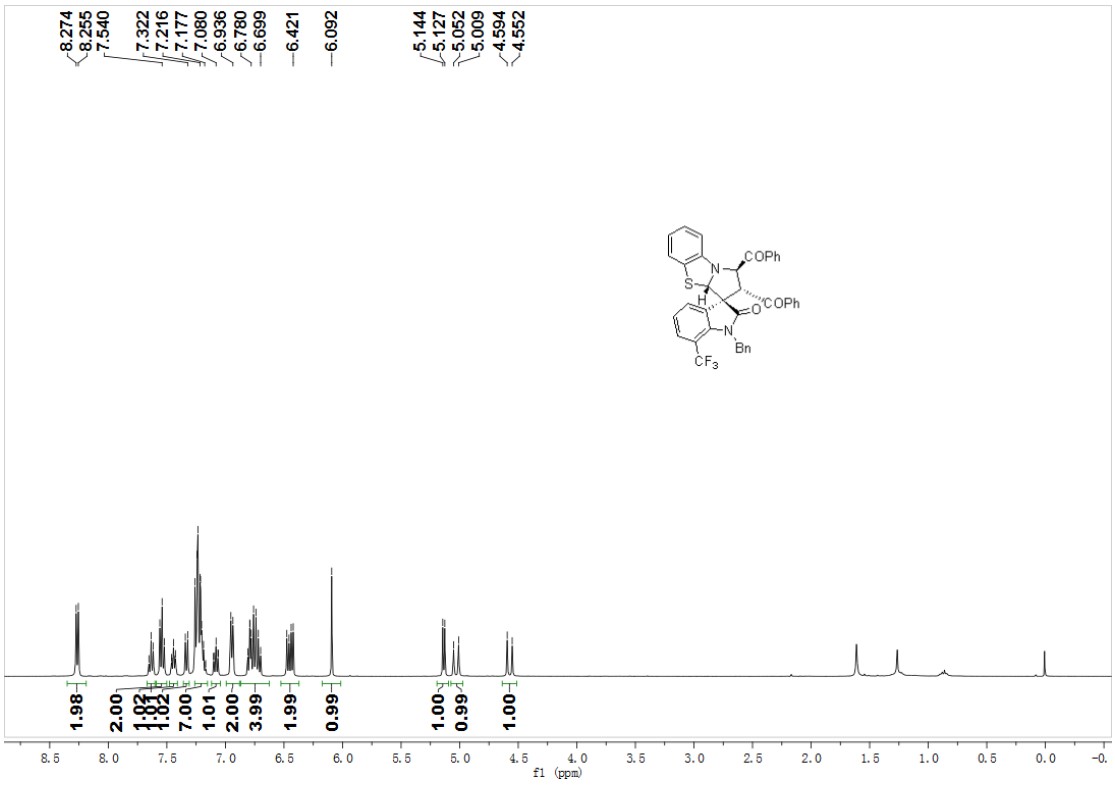


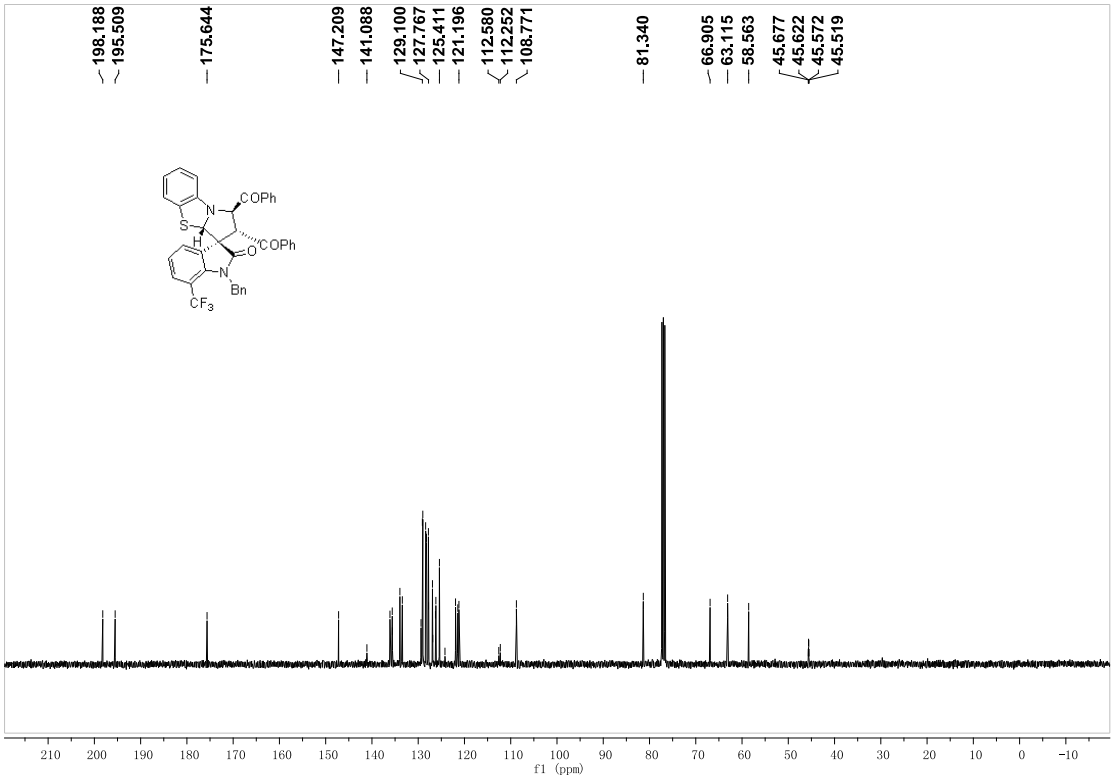
Compound 3da



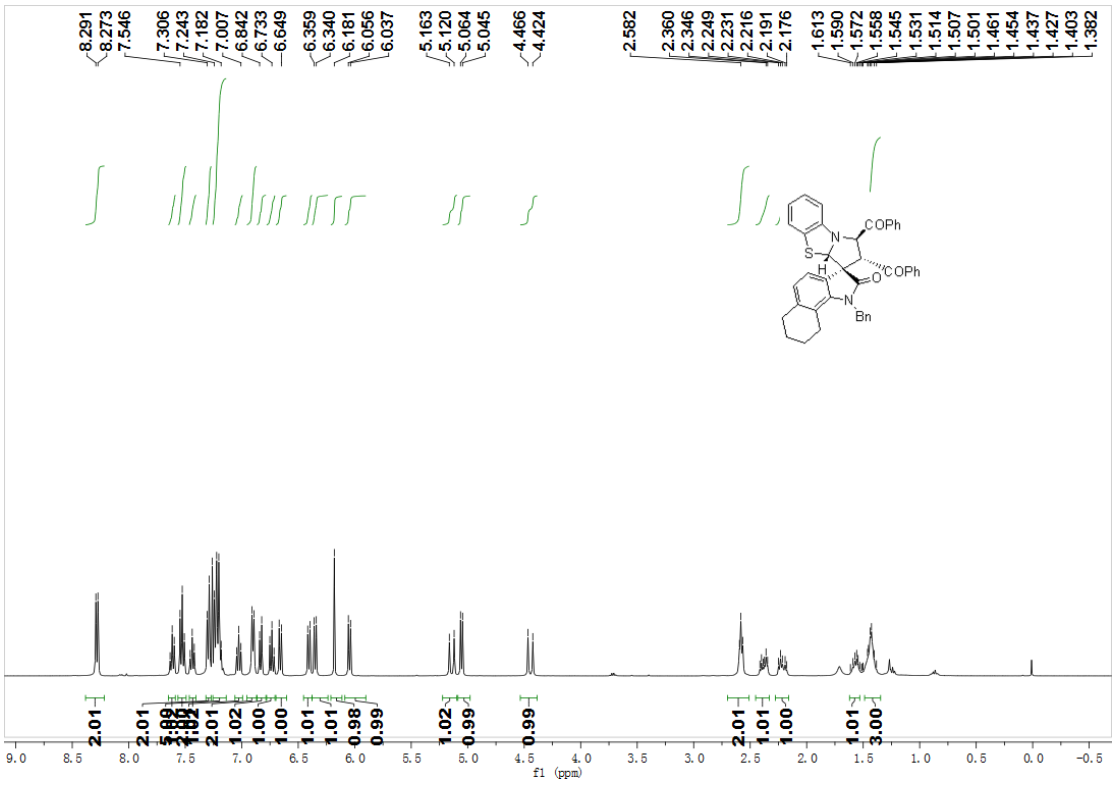


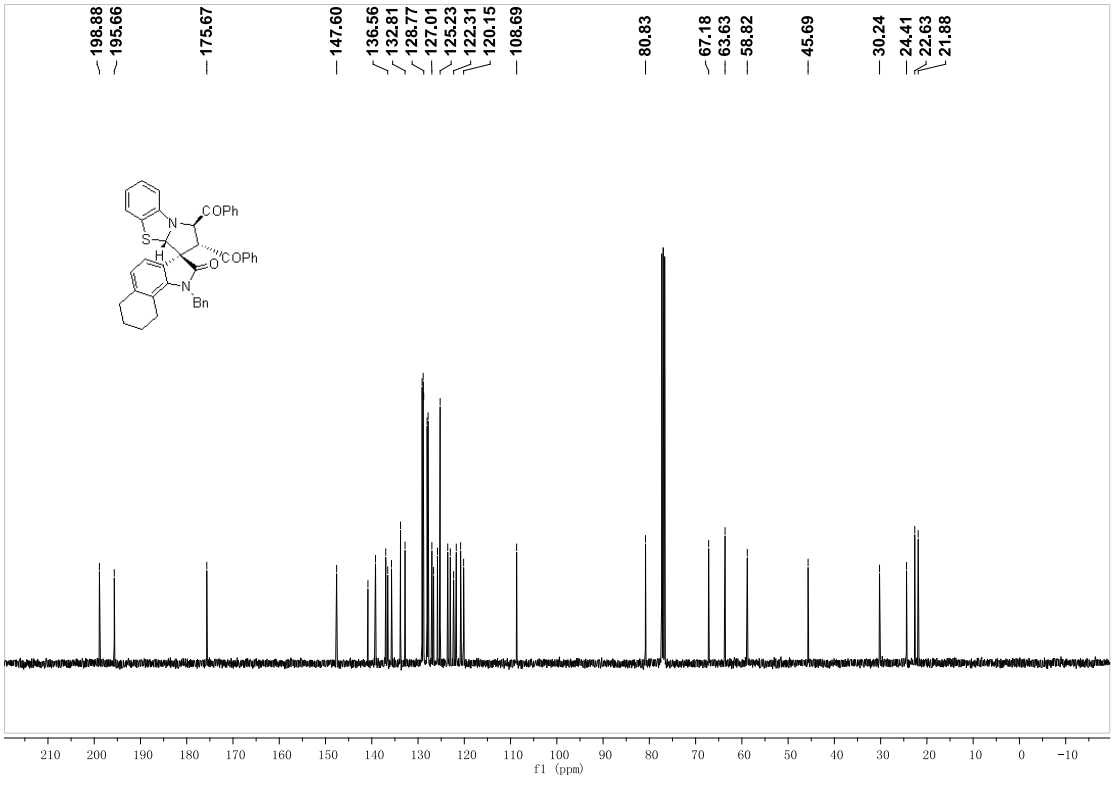
Compound 3ea



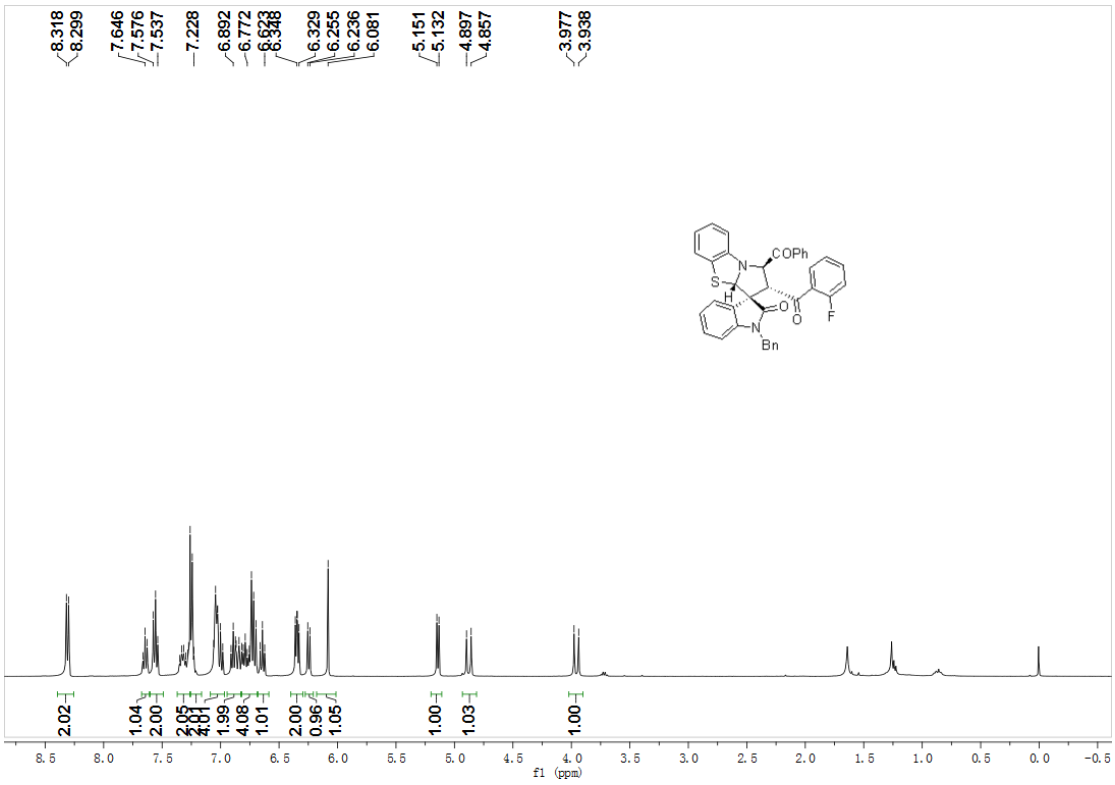


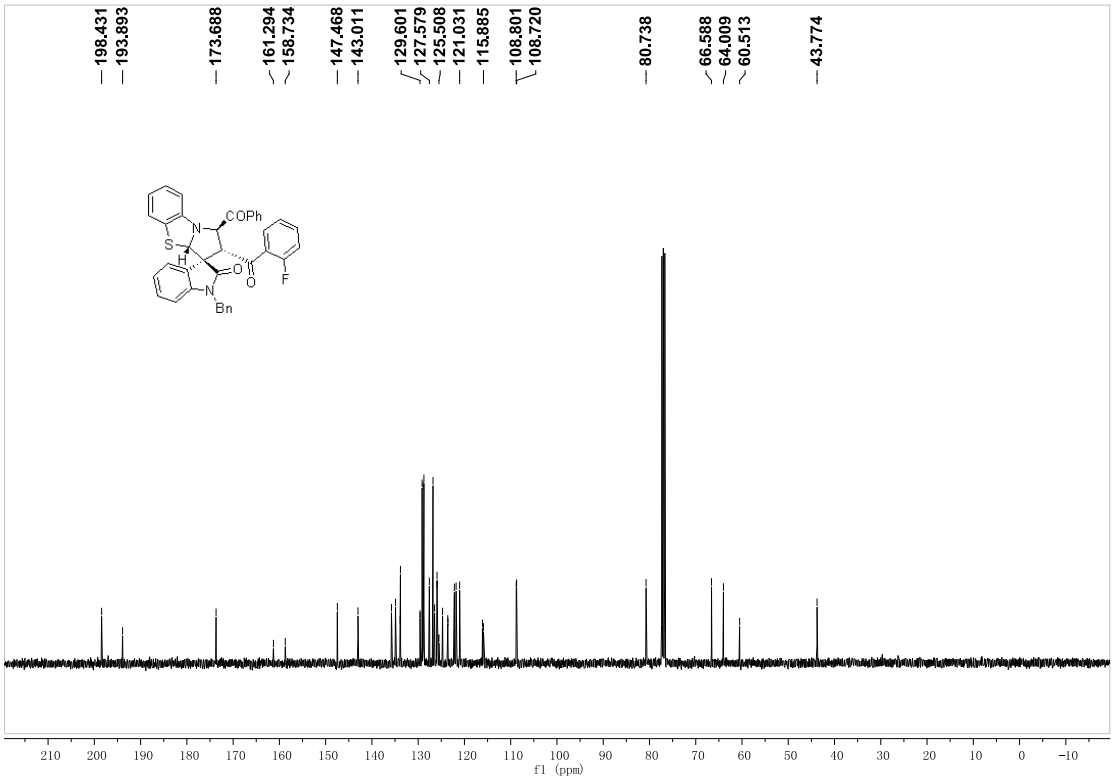
Compound 3eas



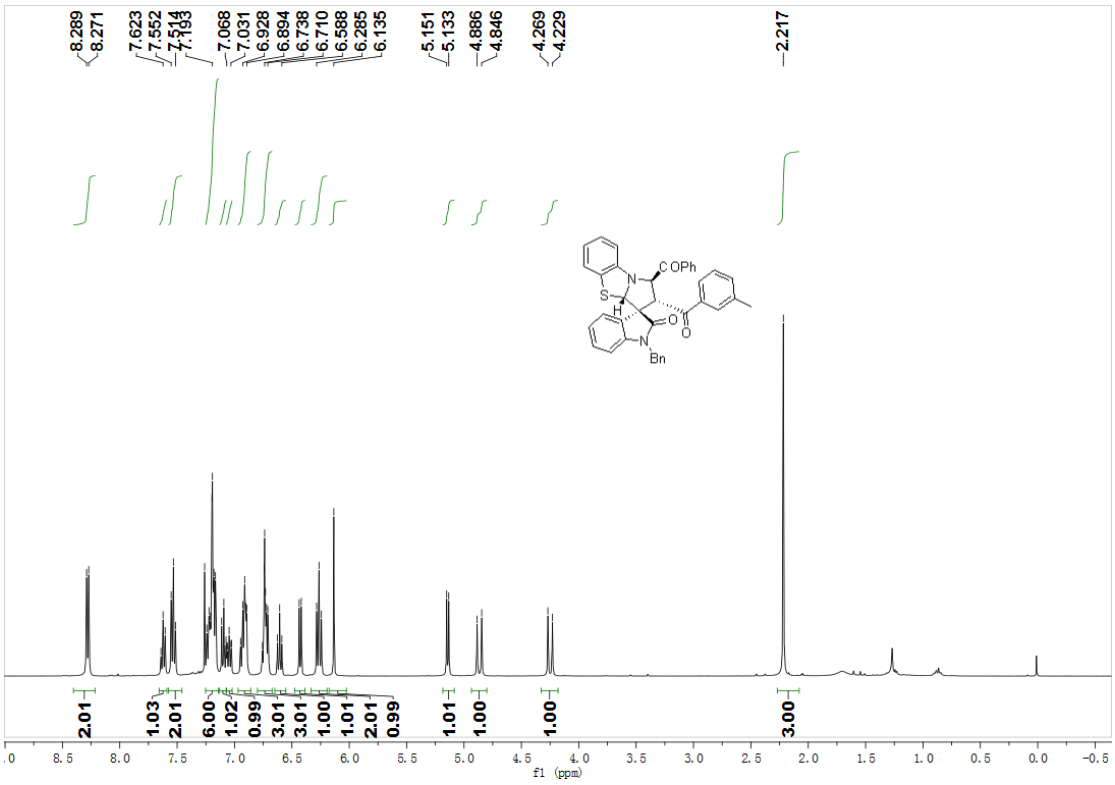


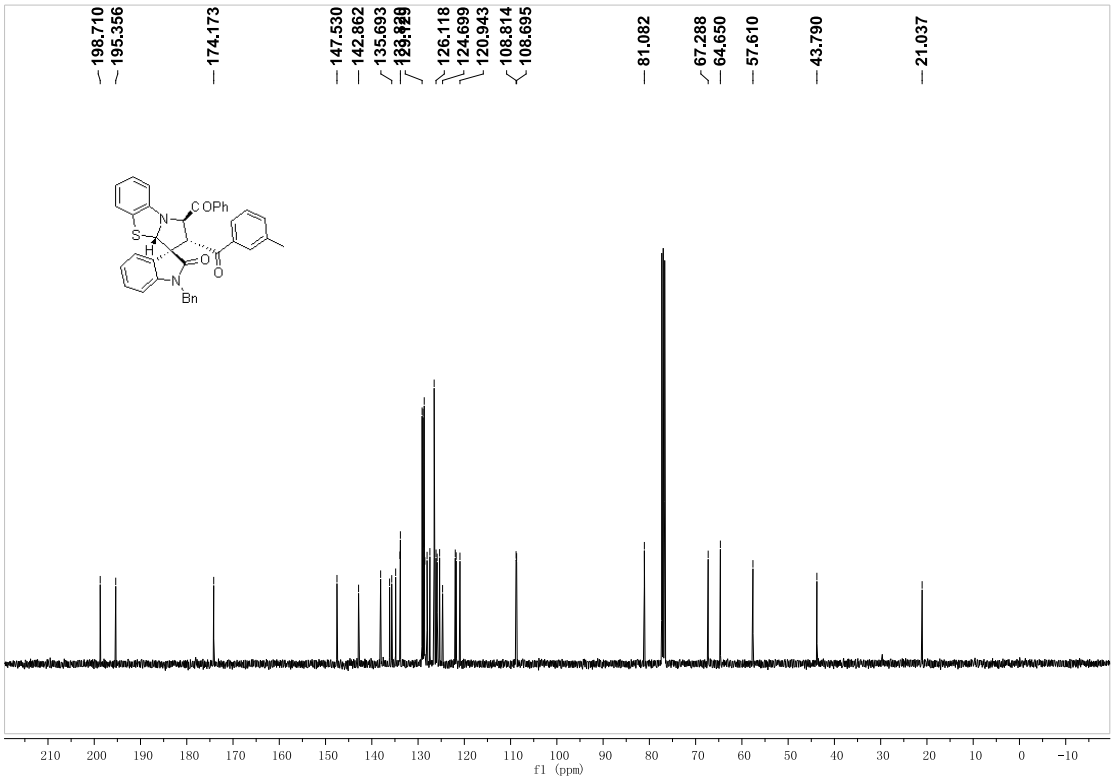
Compound 3fa



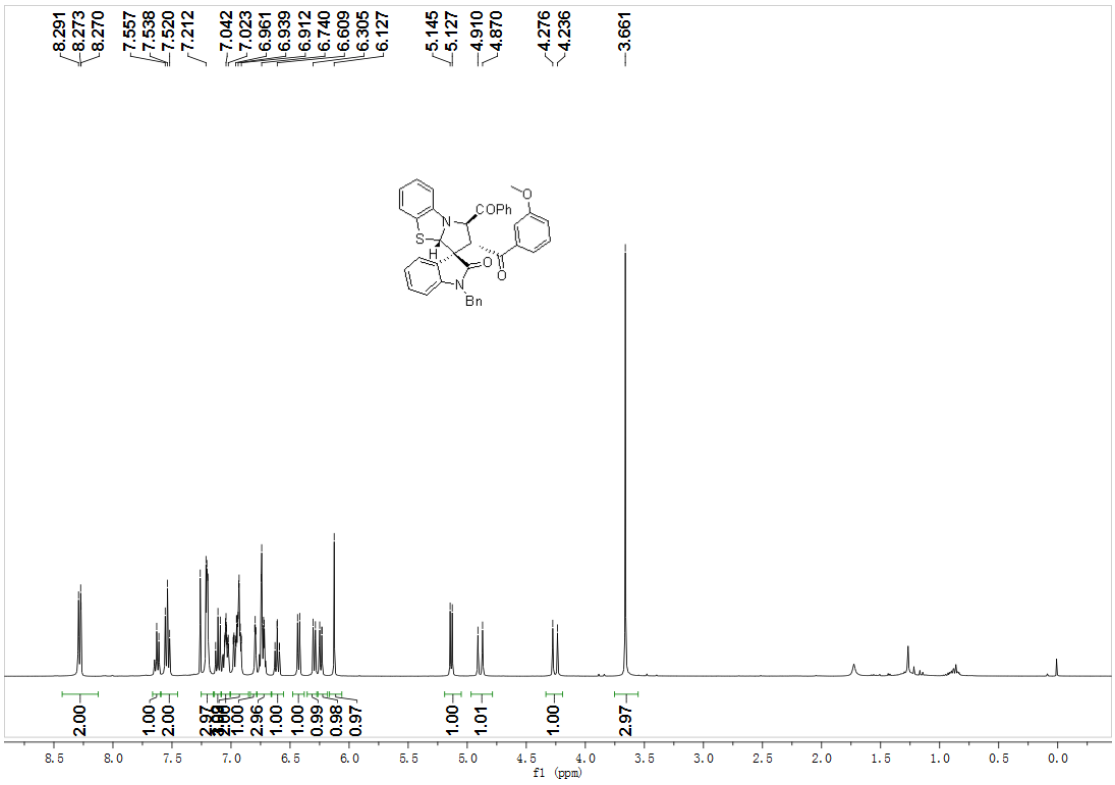


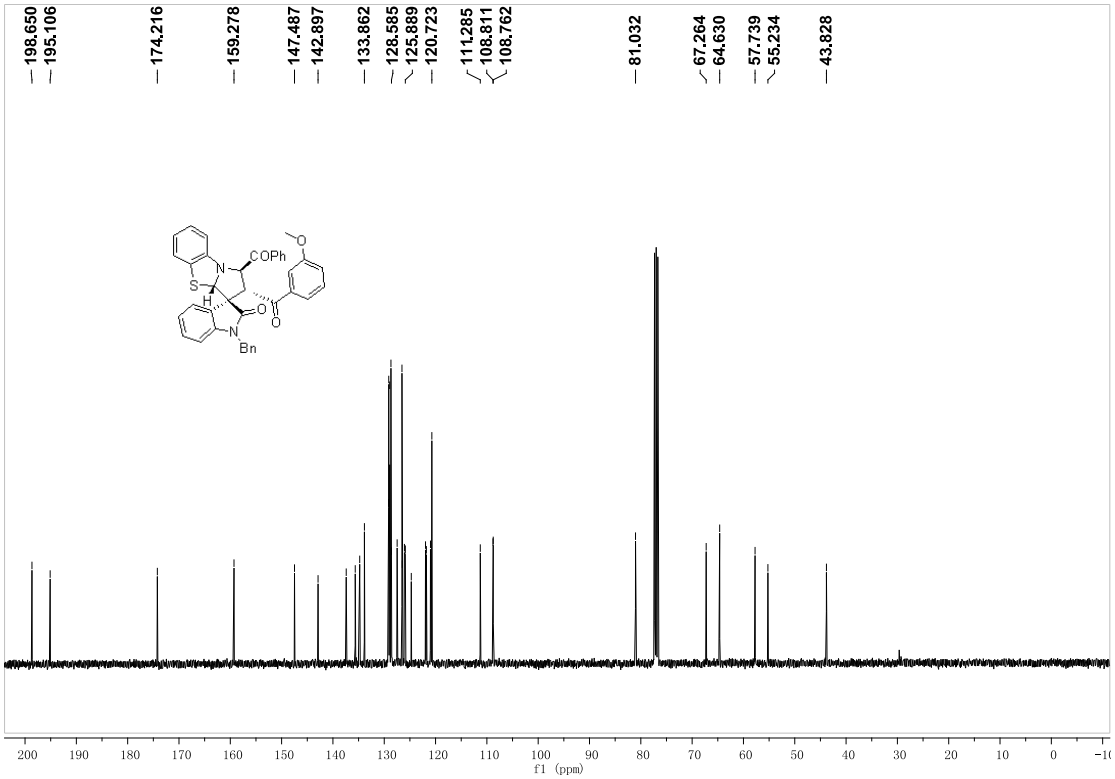
Compound 3ga



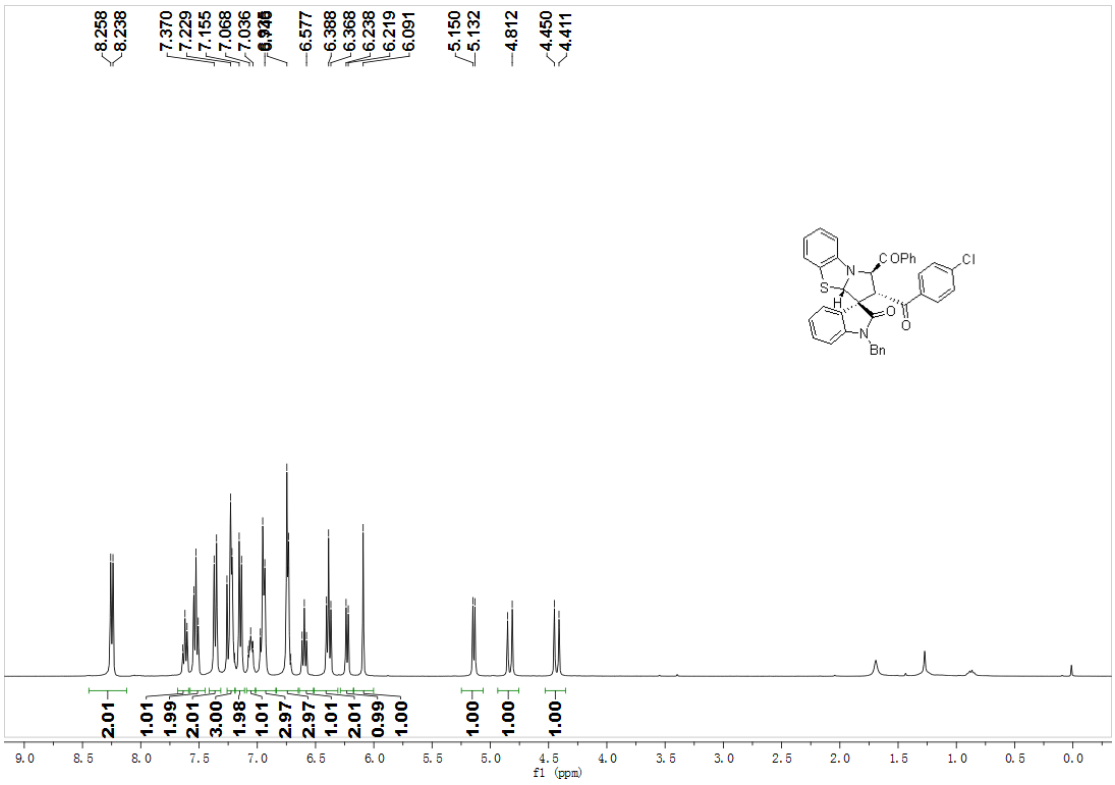


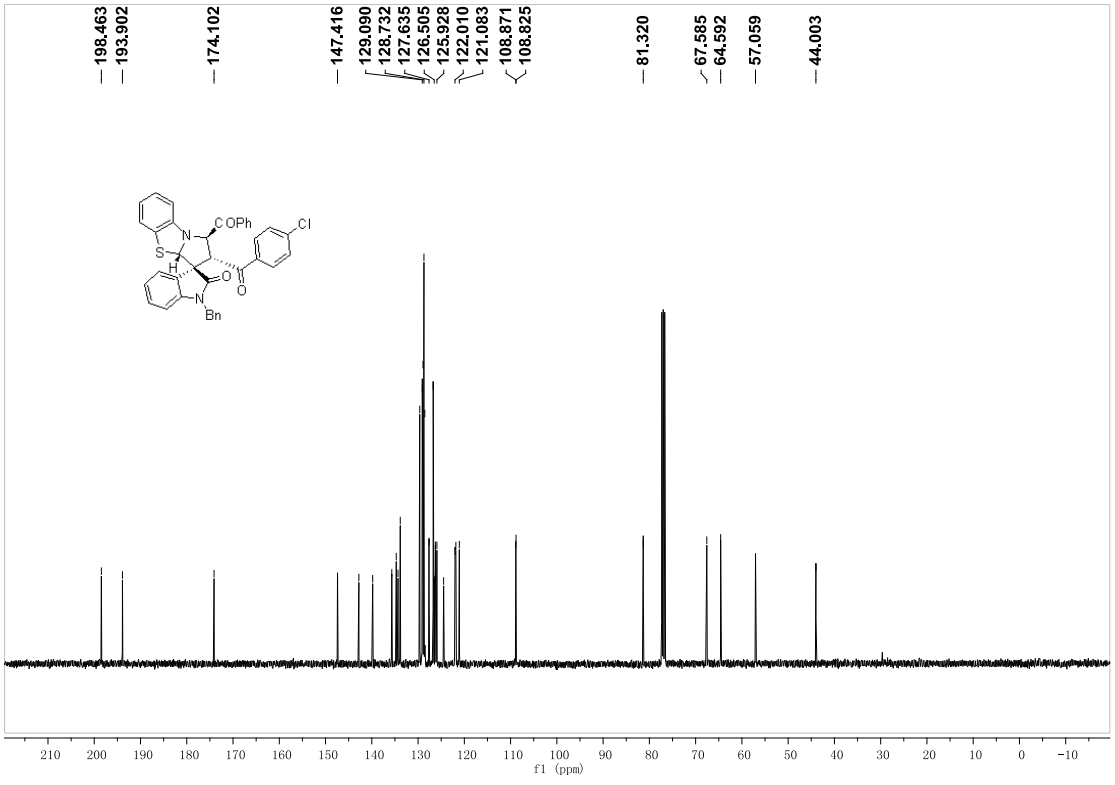
Compound 3gas



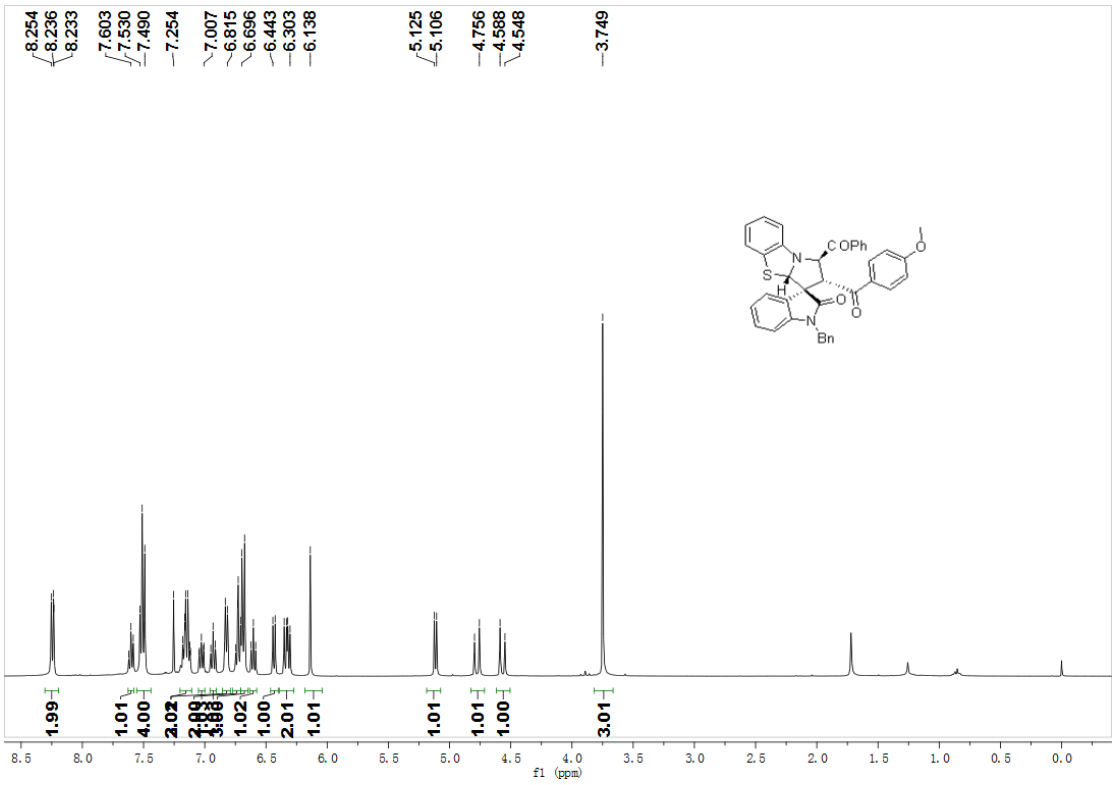


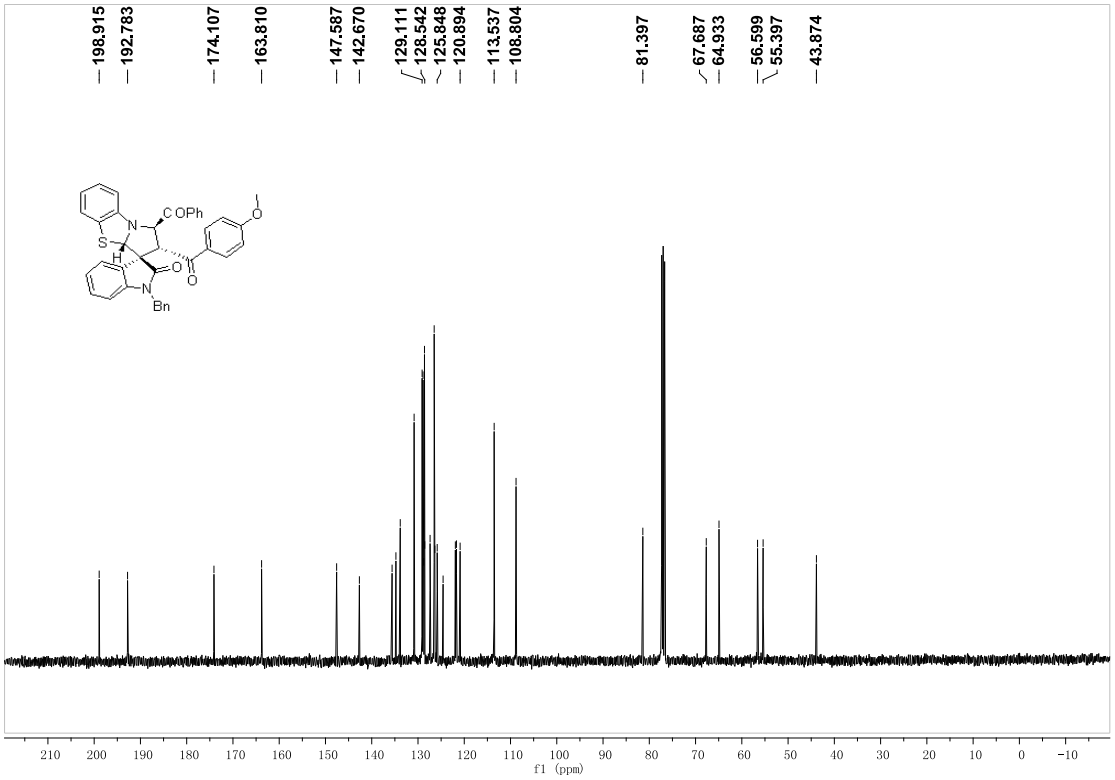
Compound 3ha





Compound 3ia





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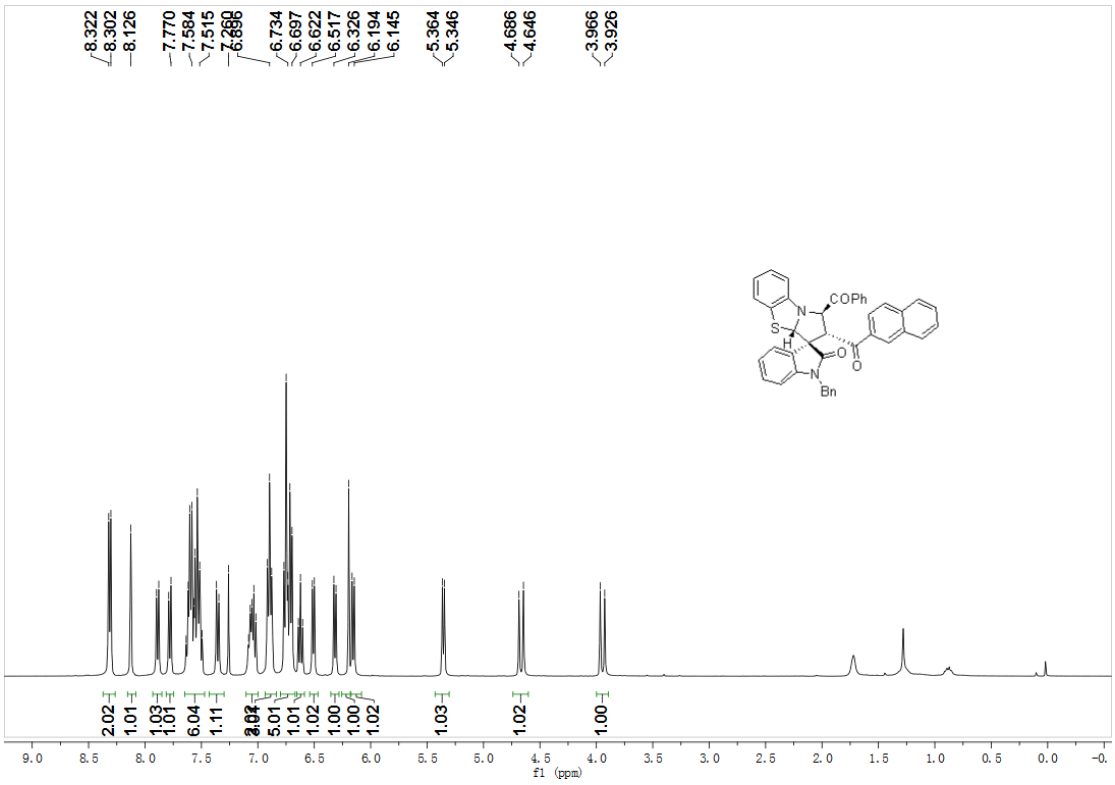

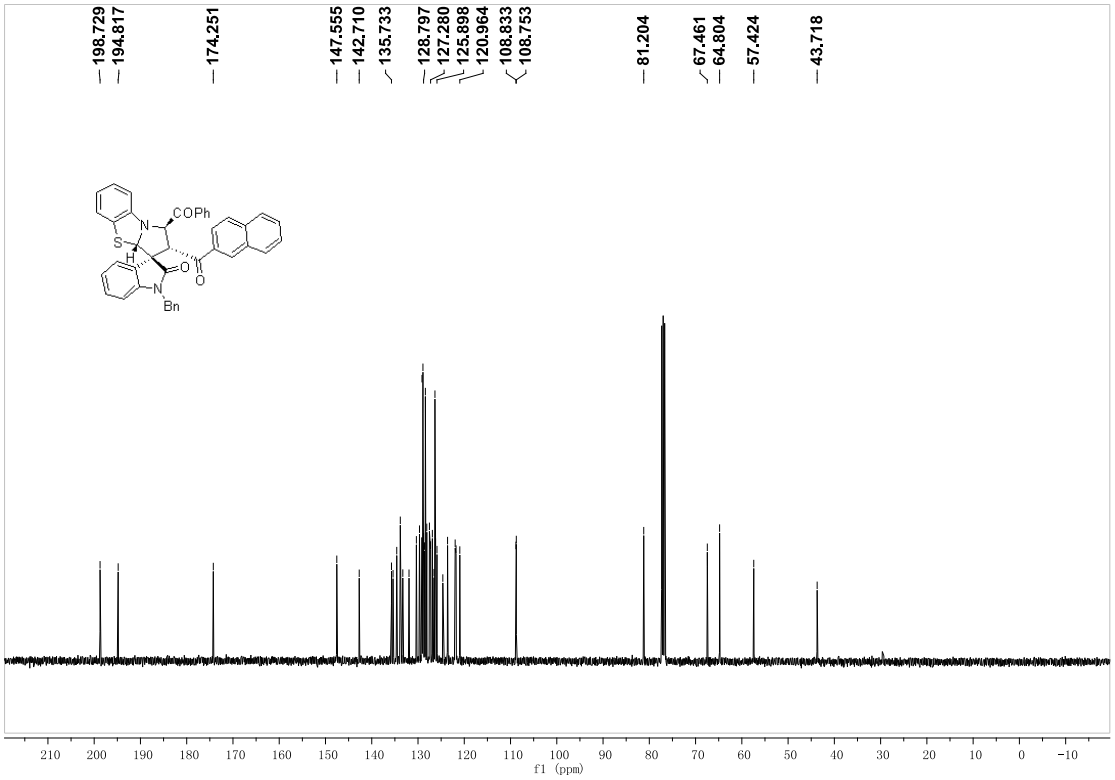

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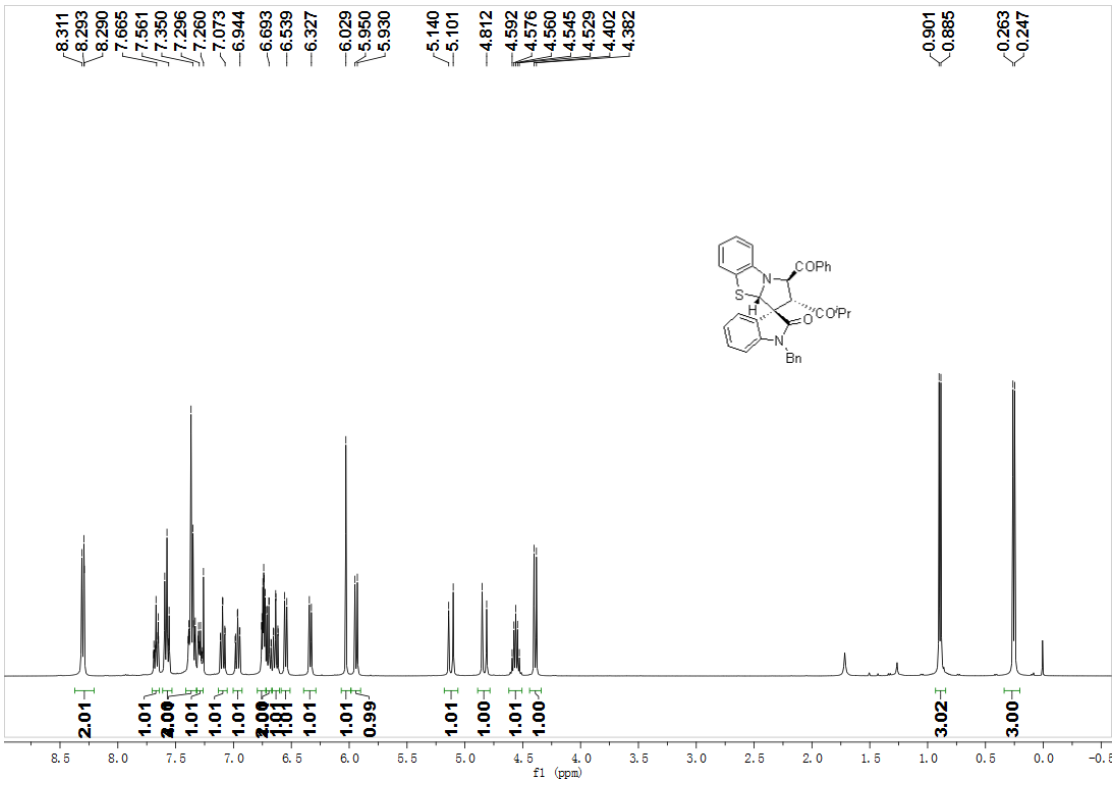

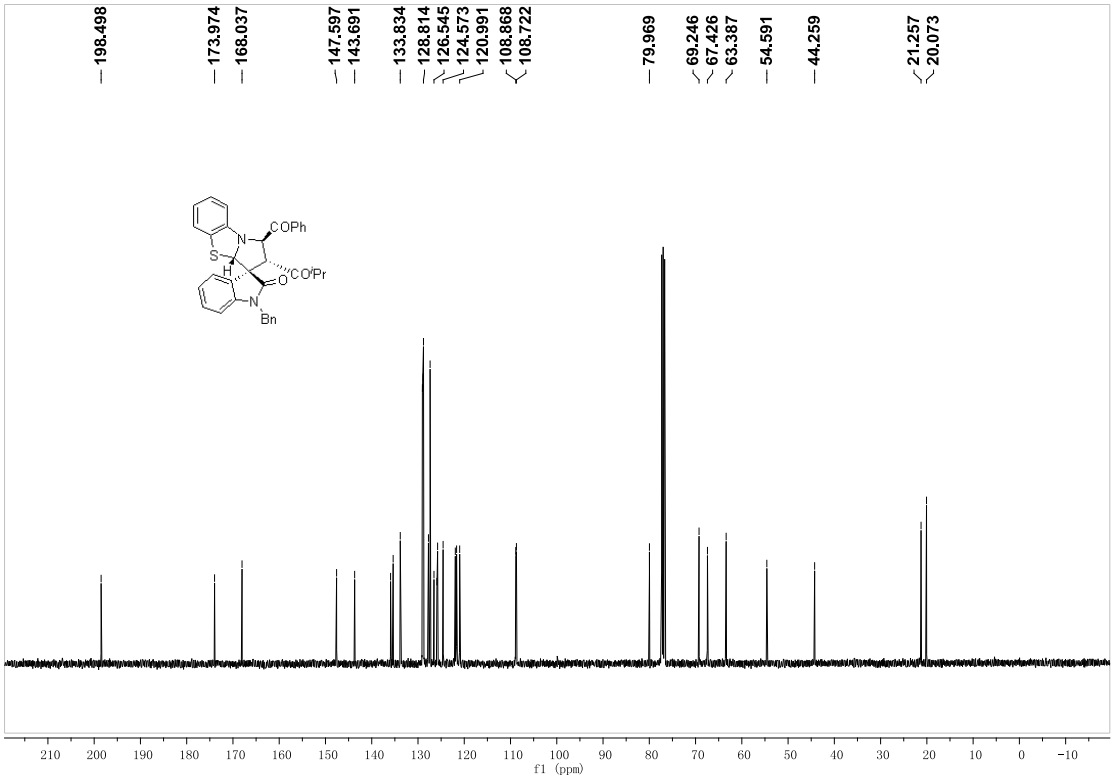

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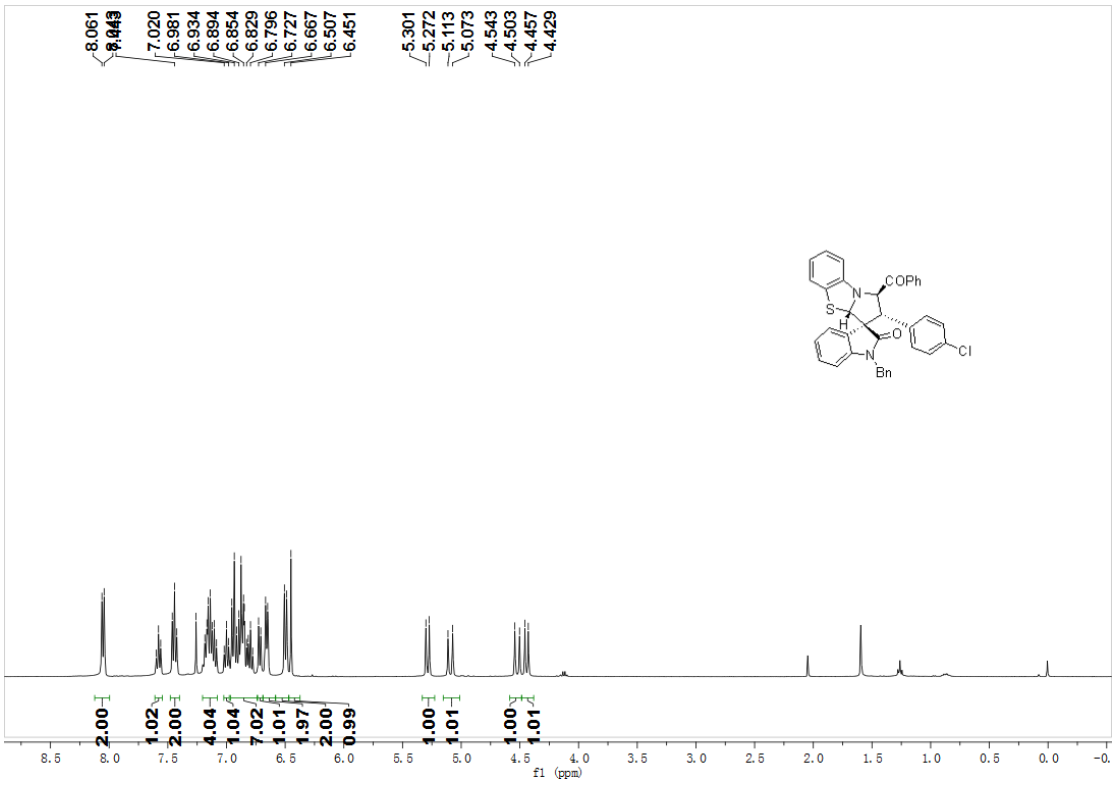

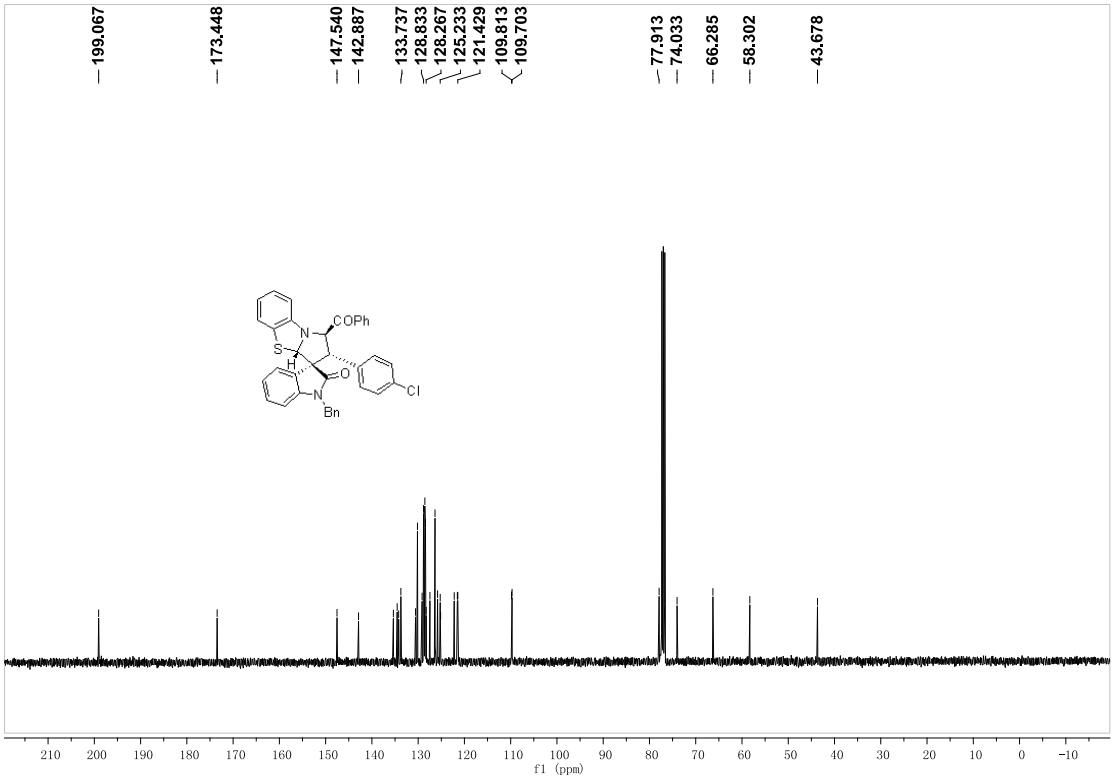

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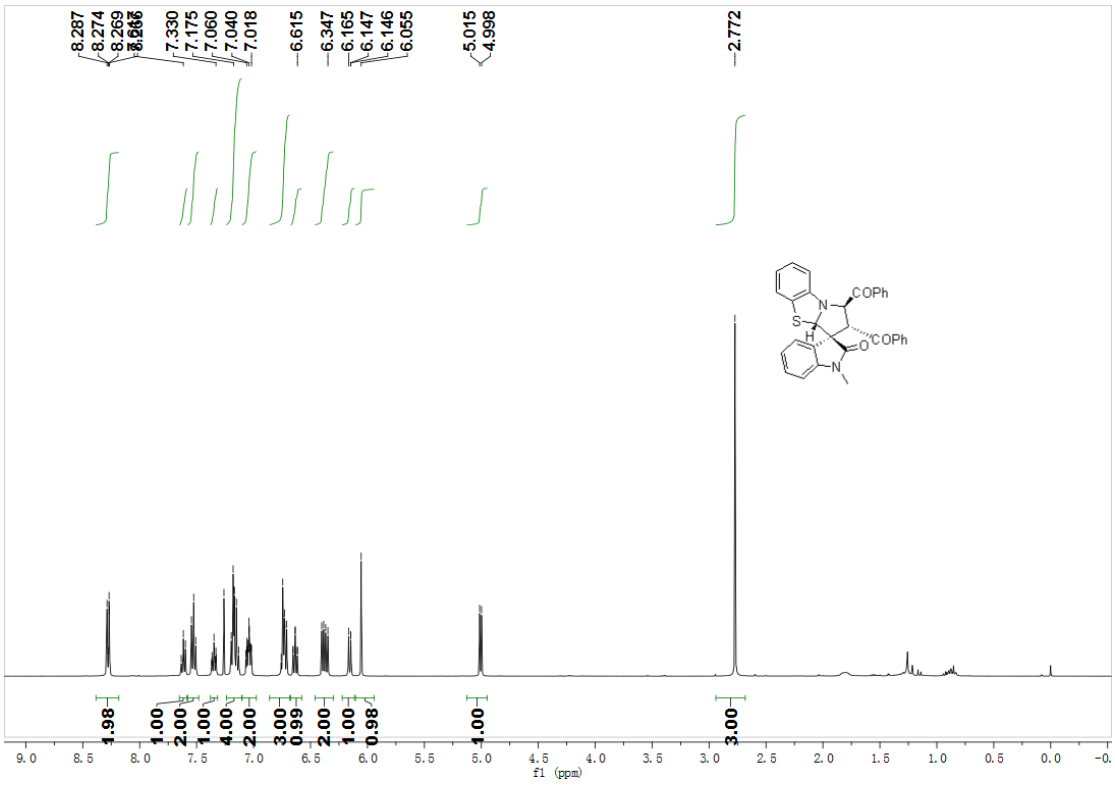

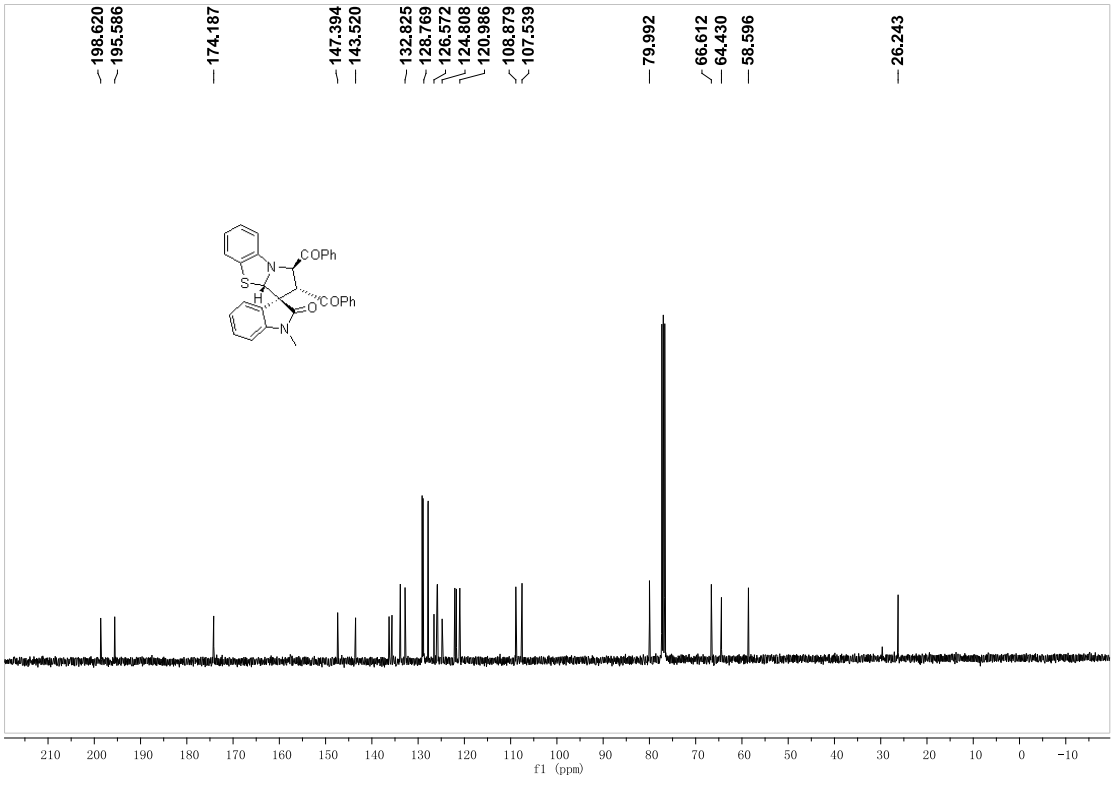

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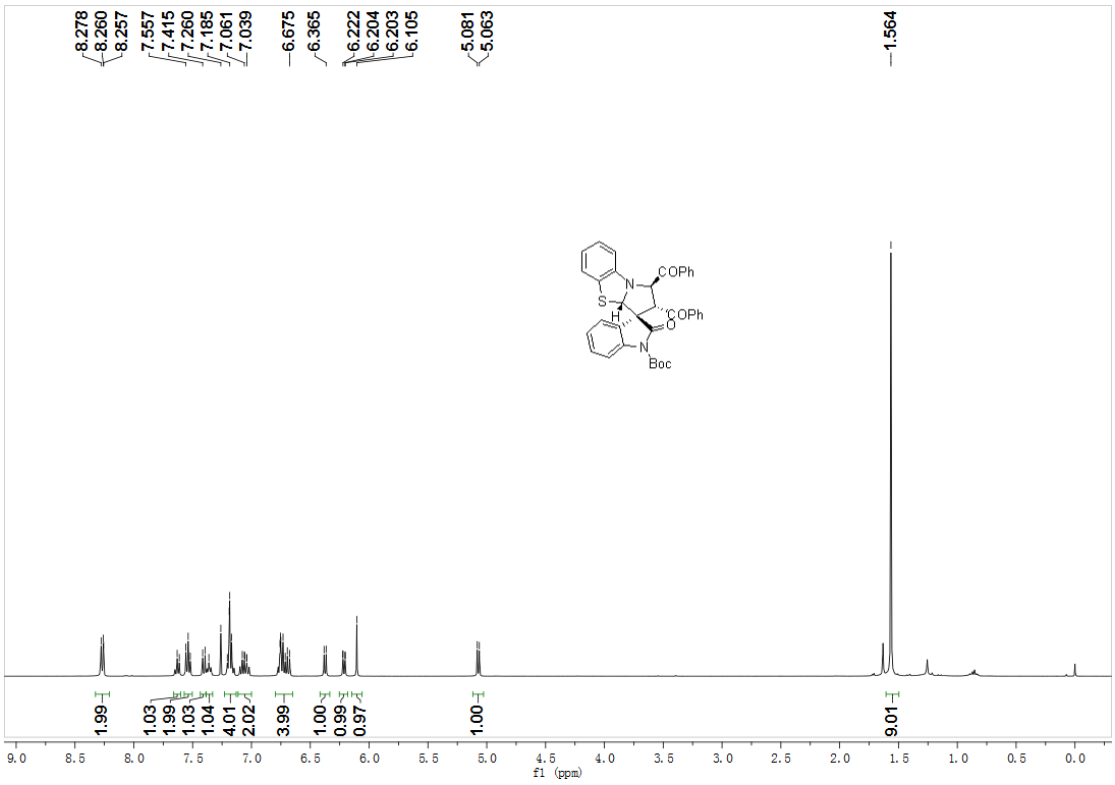

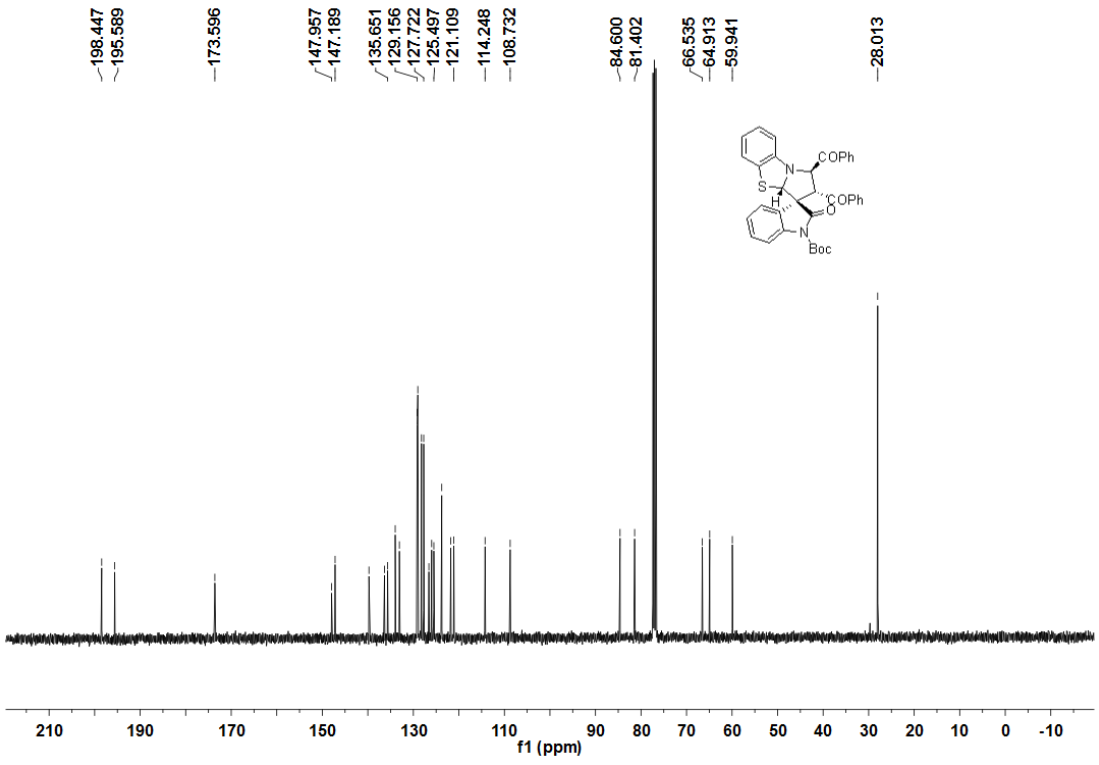

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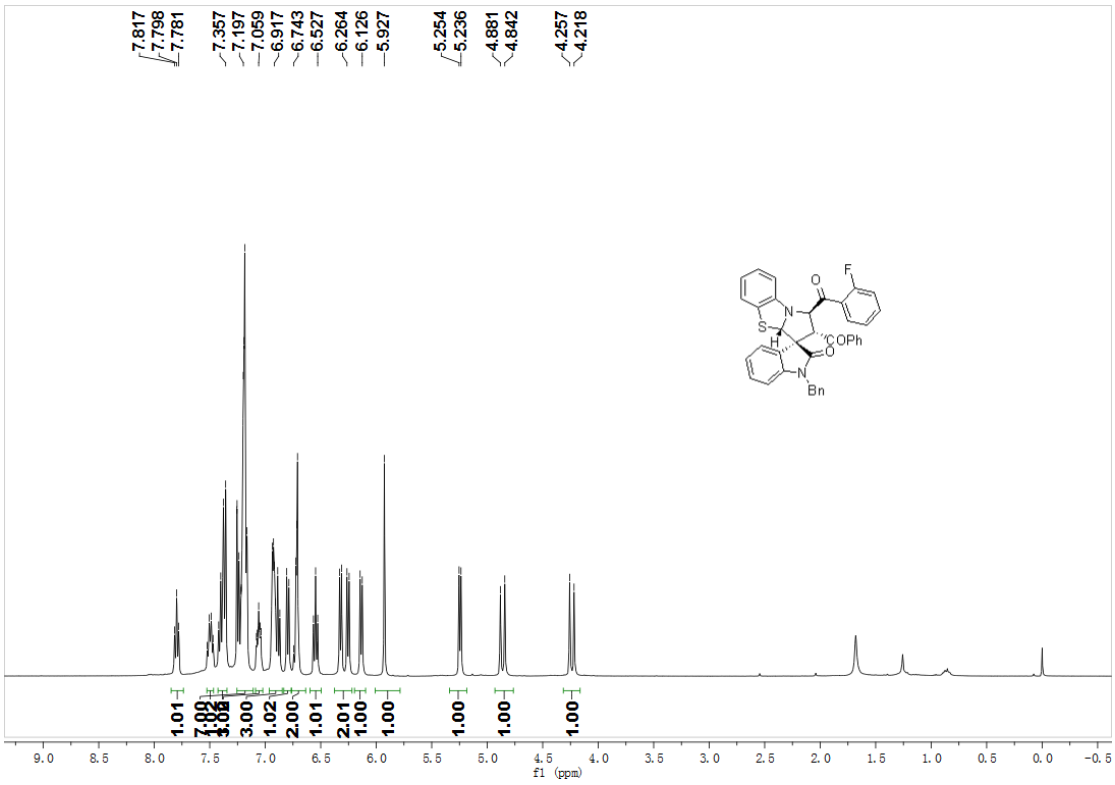

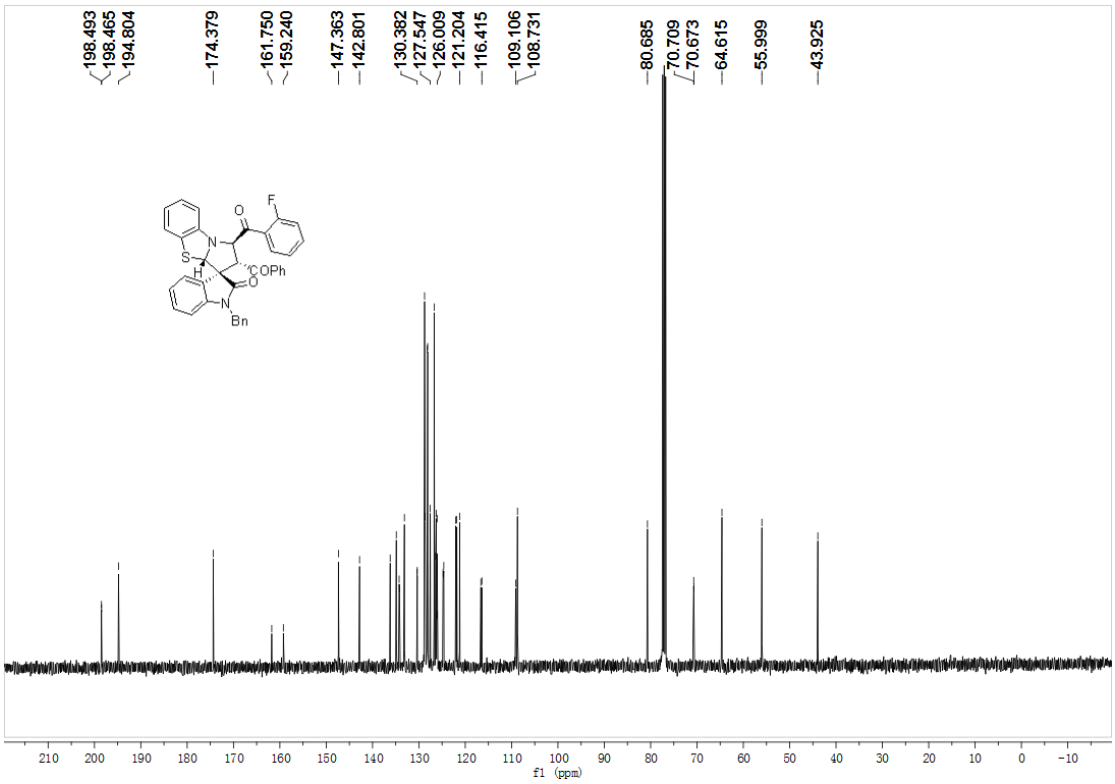

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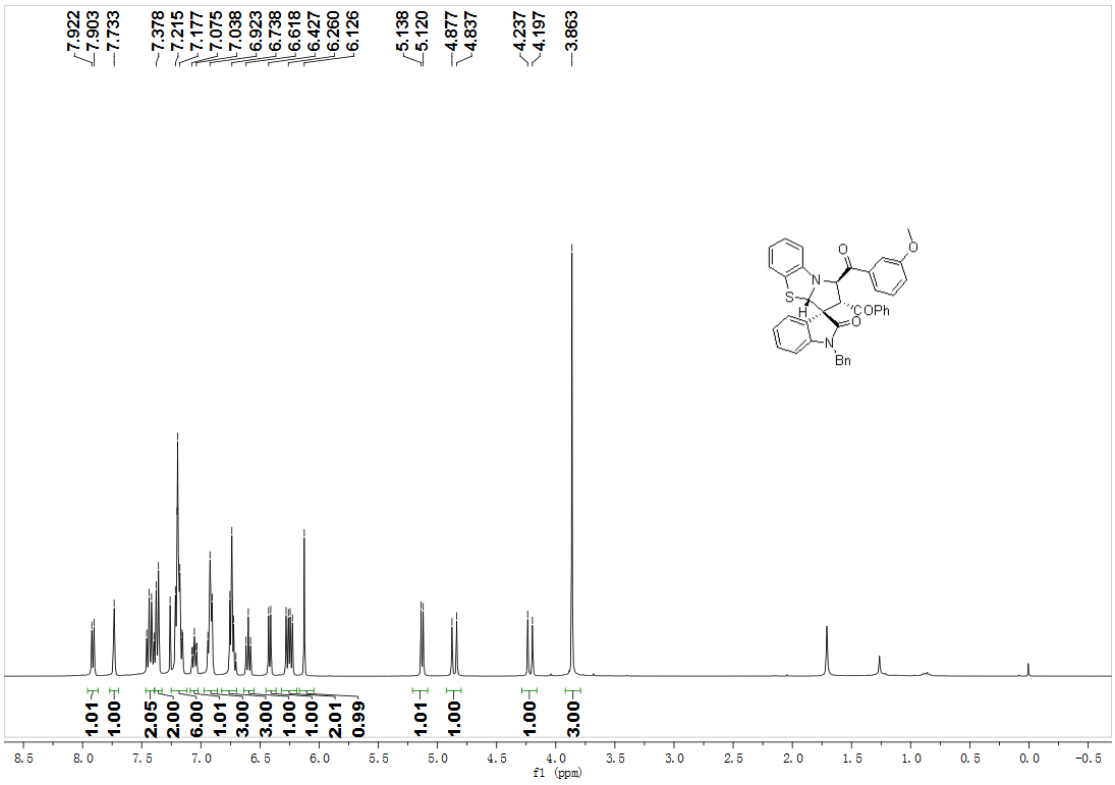

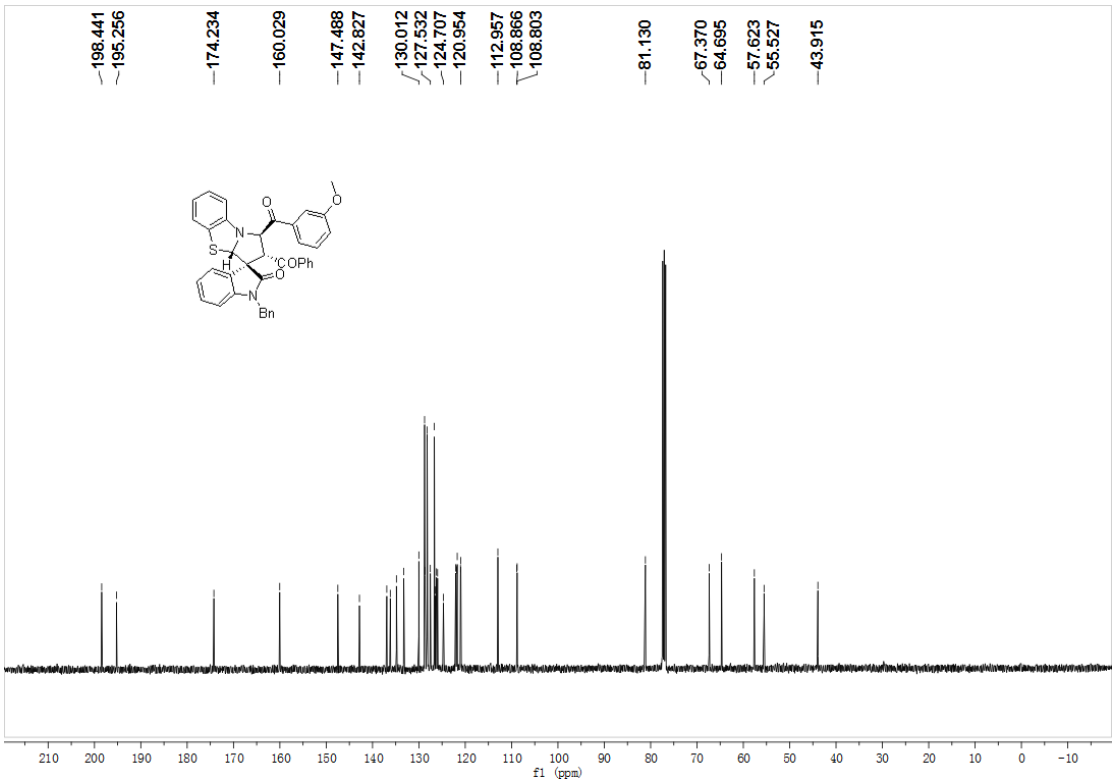

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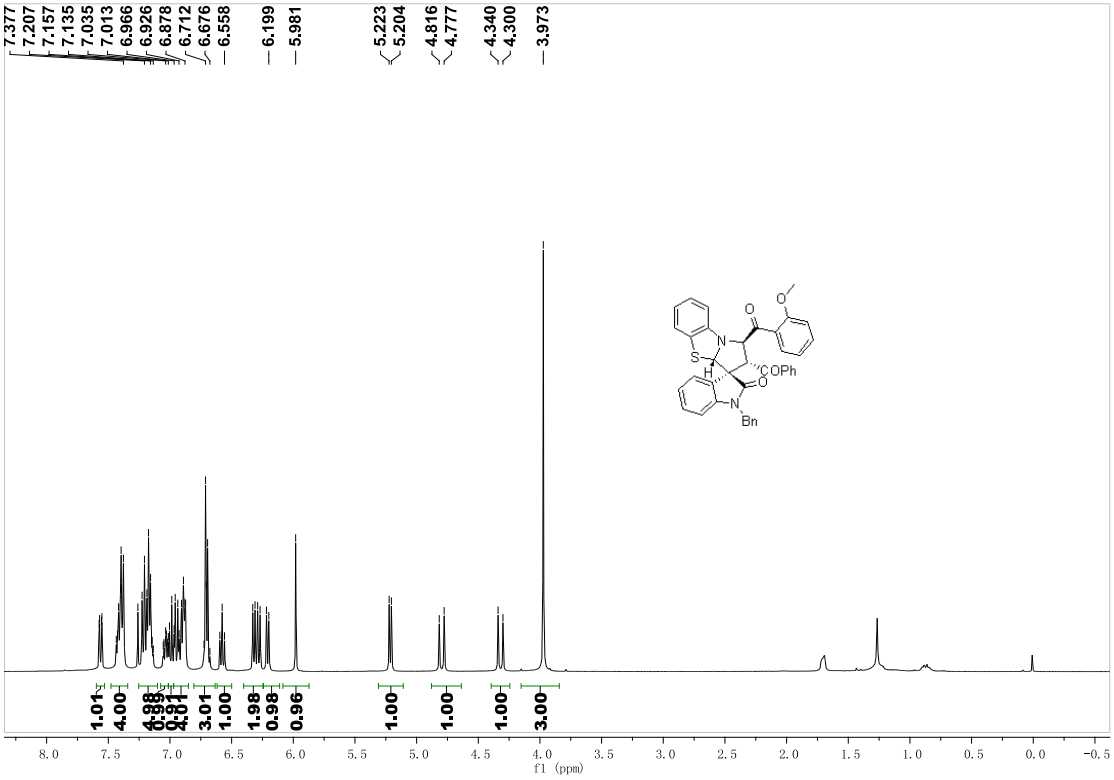

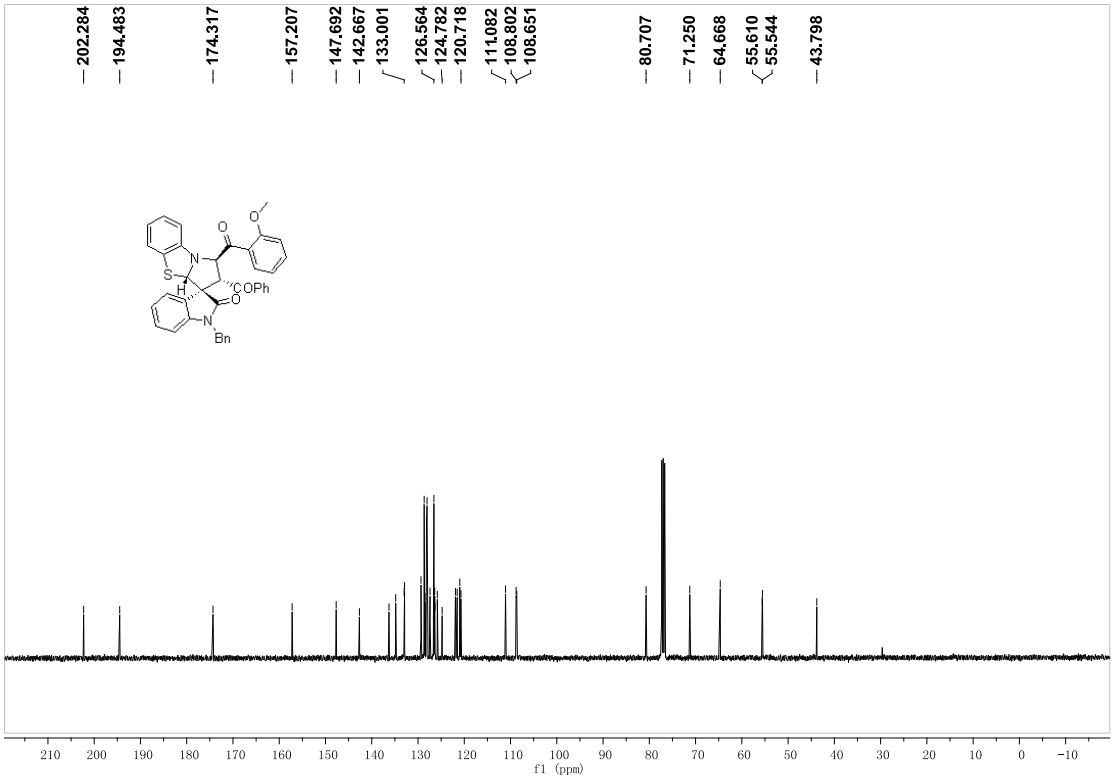

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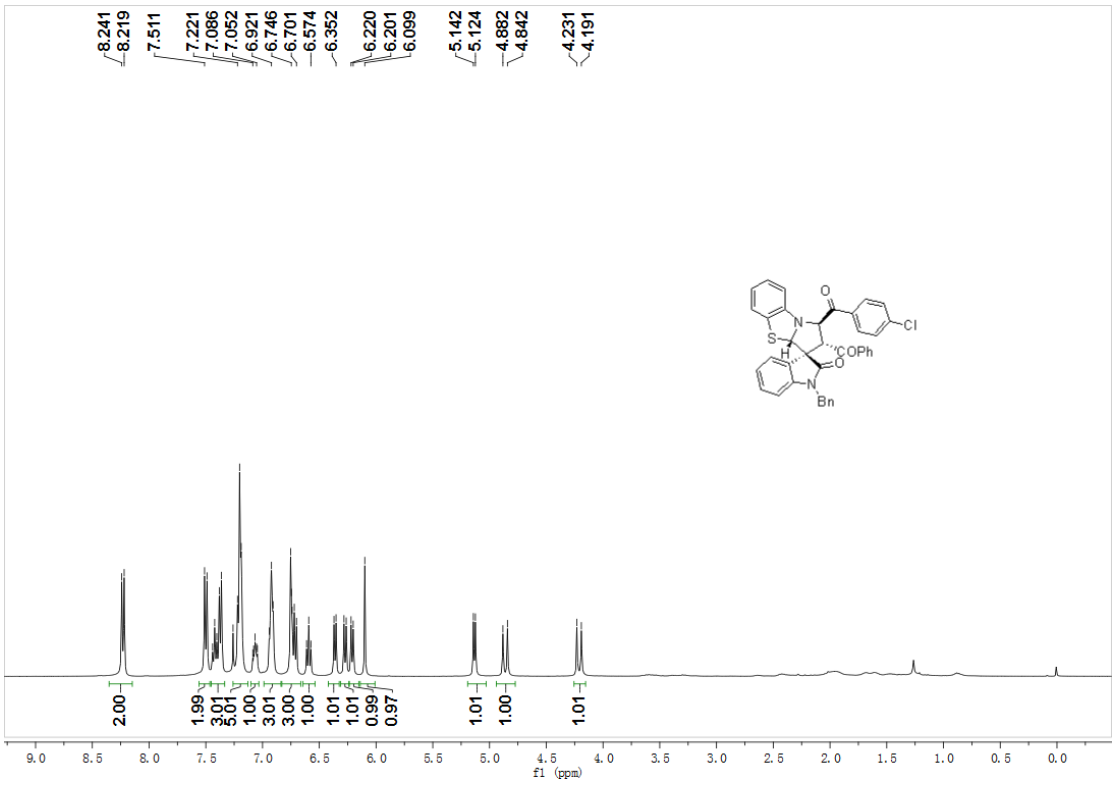

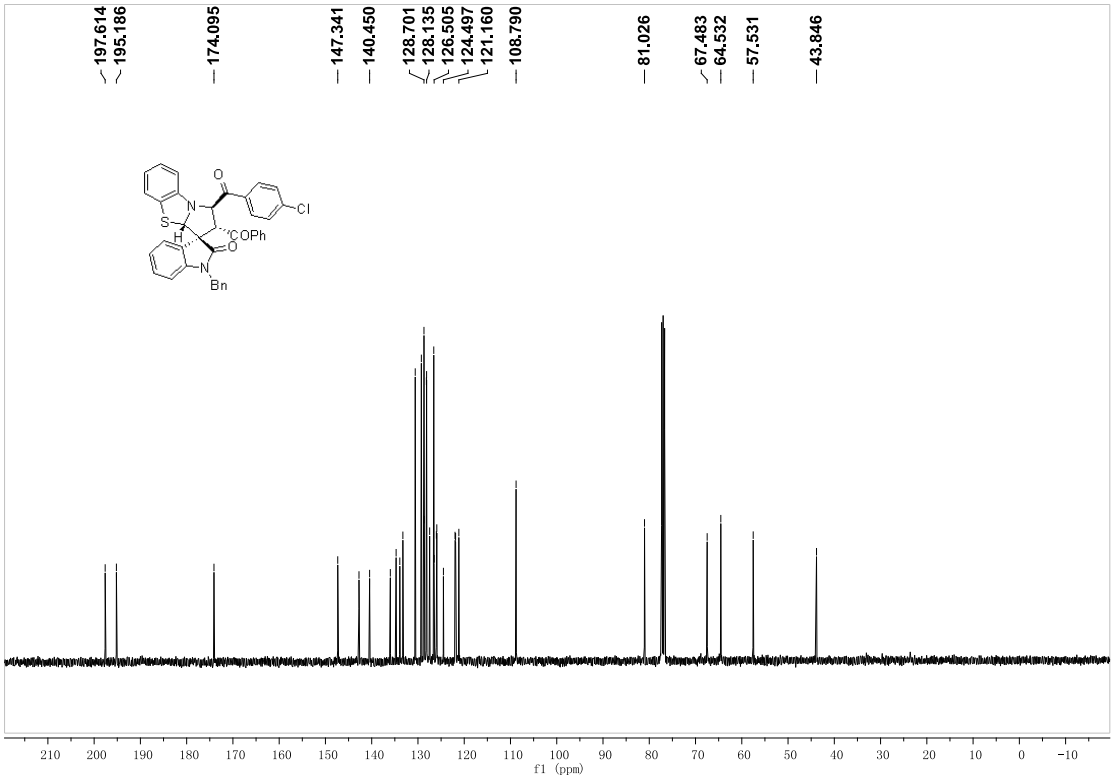

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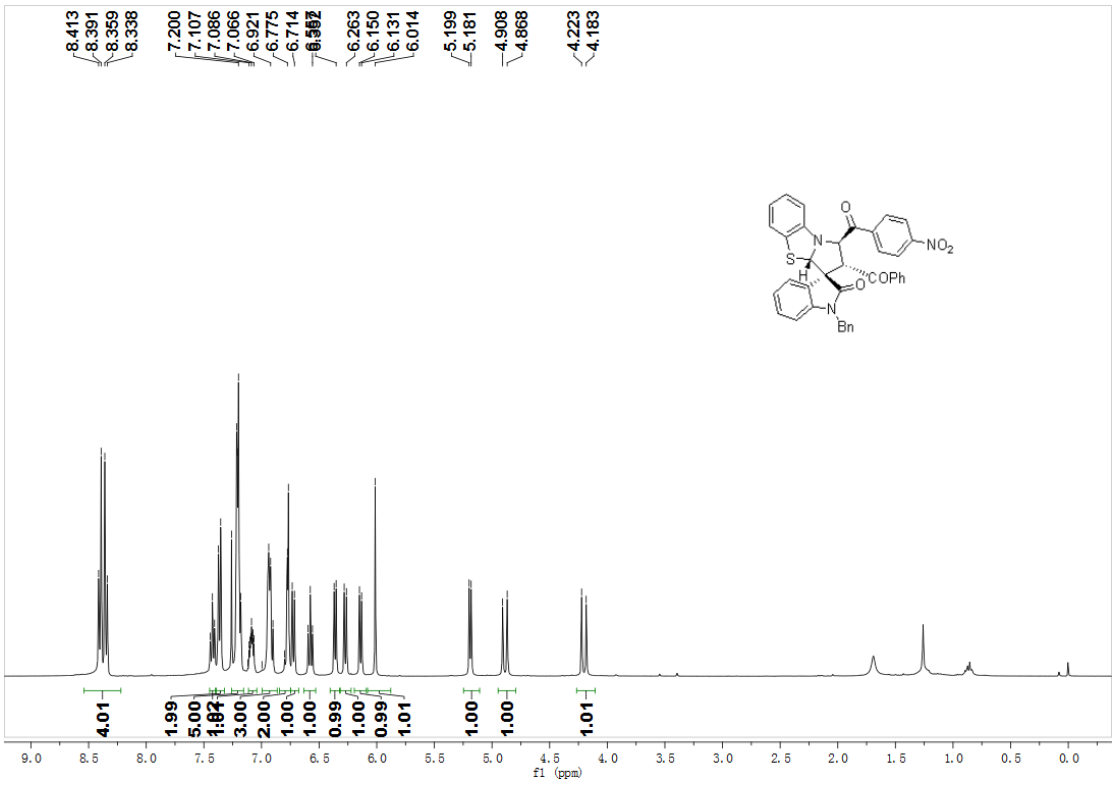

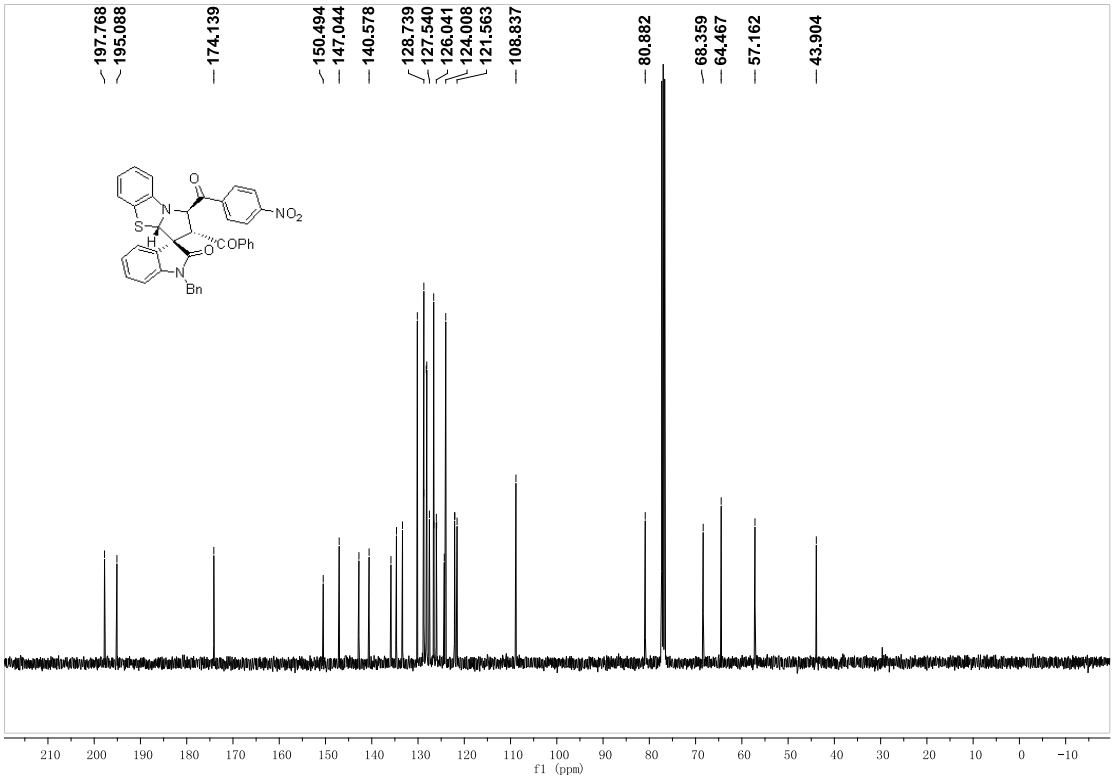

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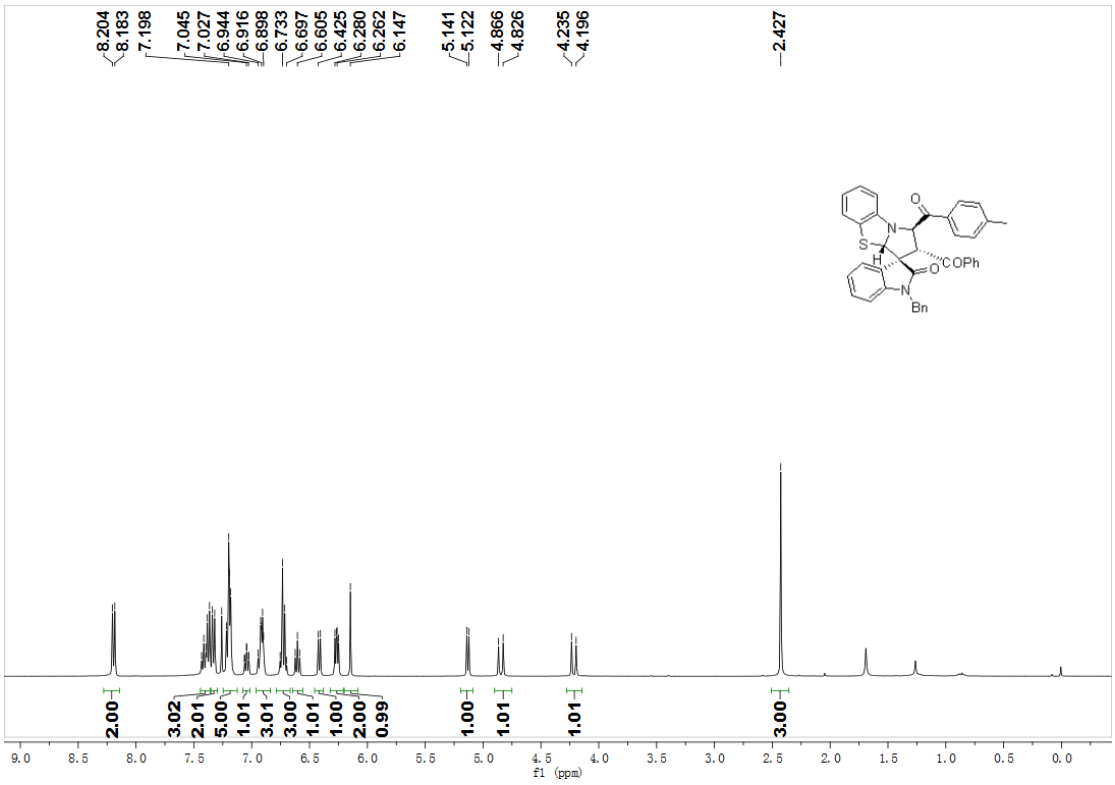

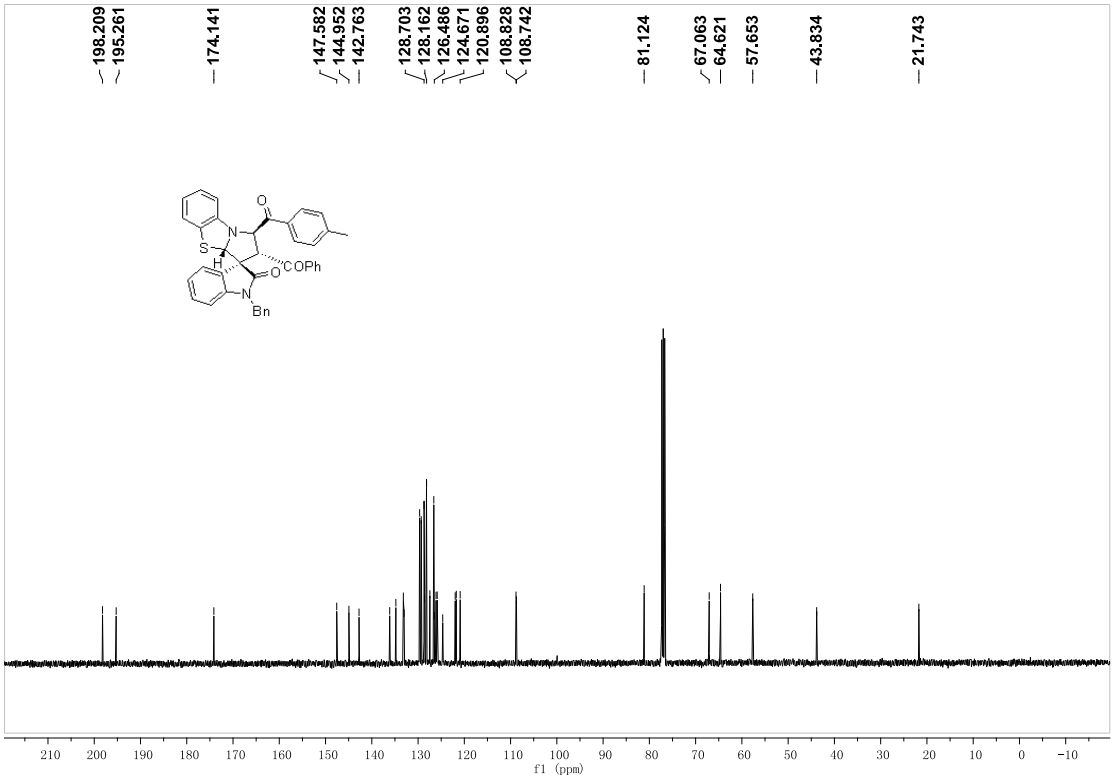

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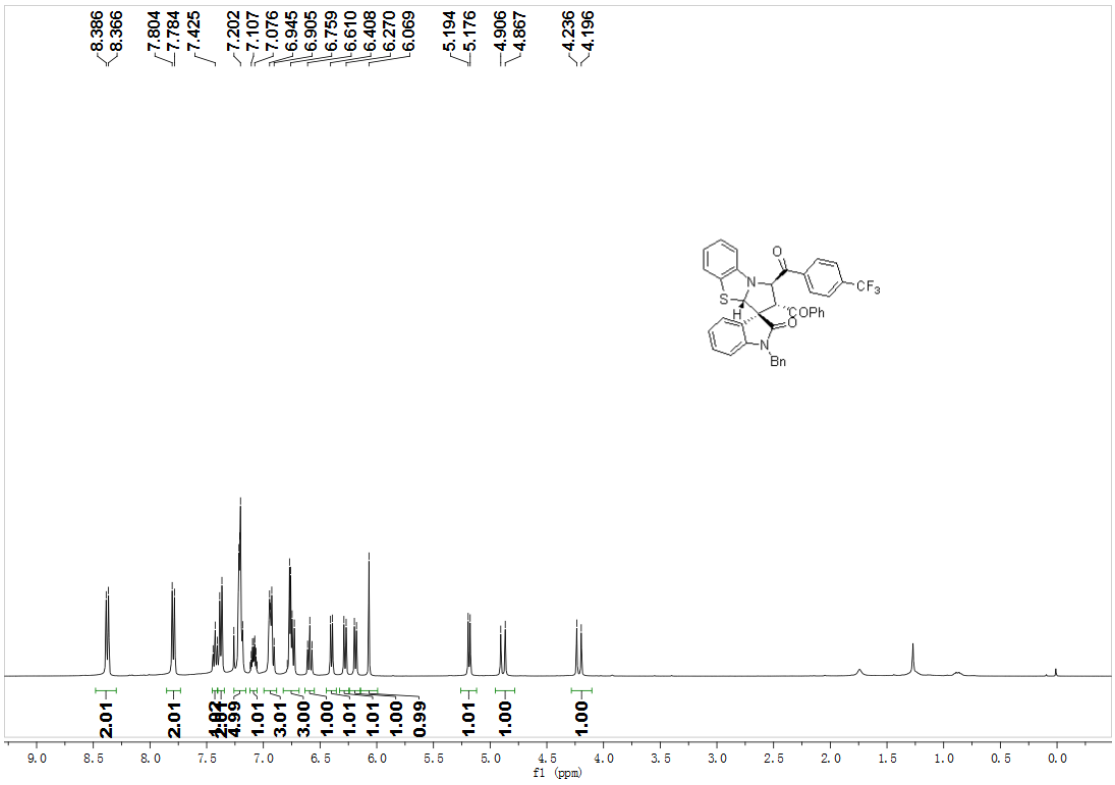

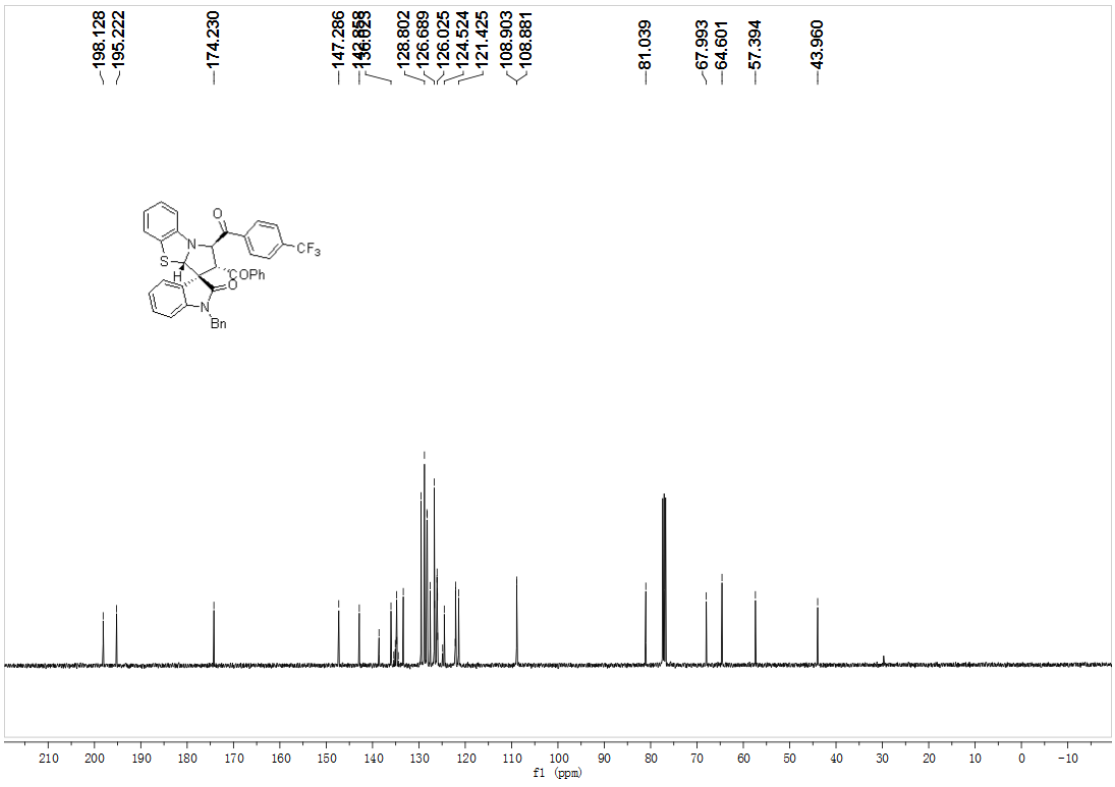

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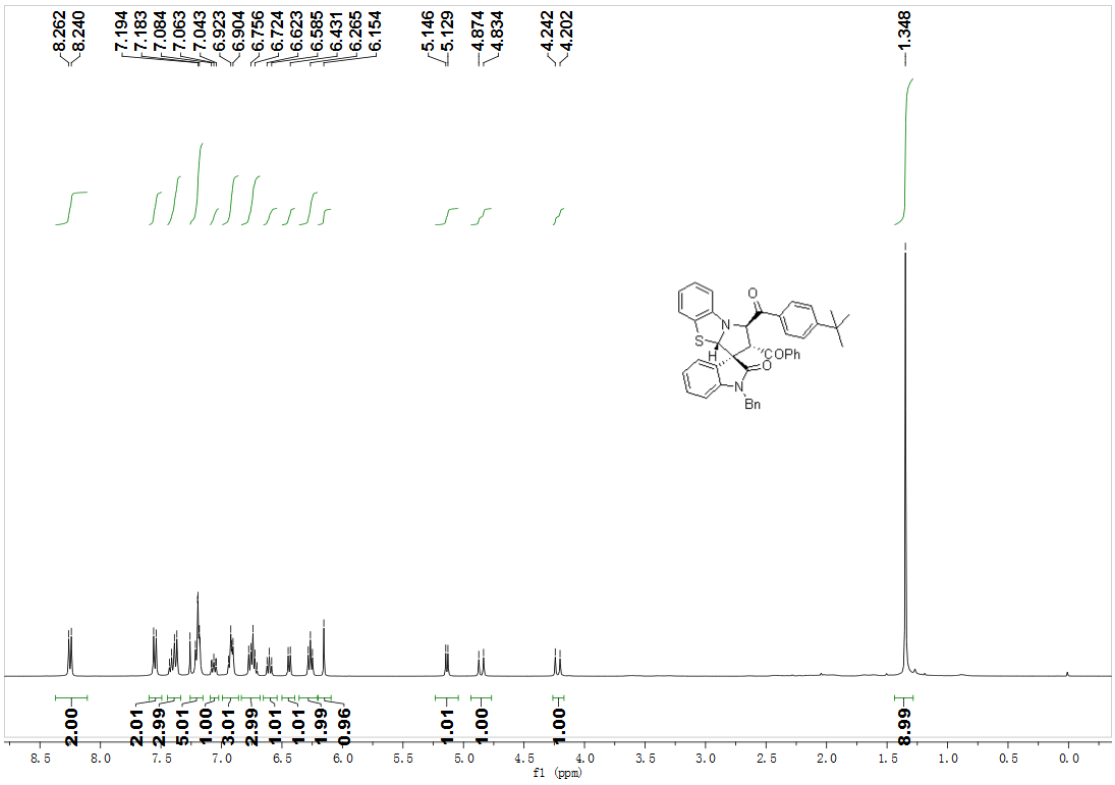
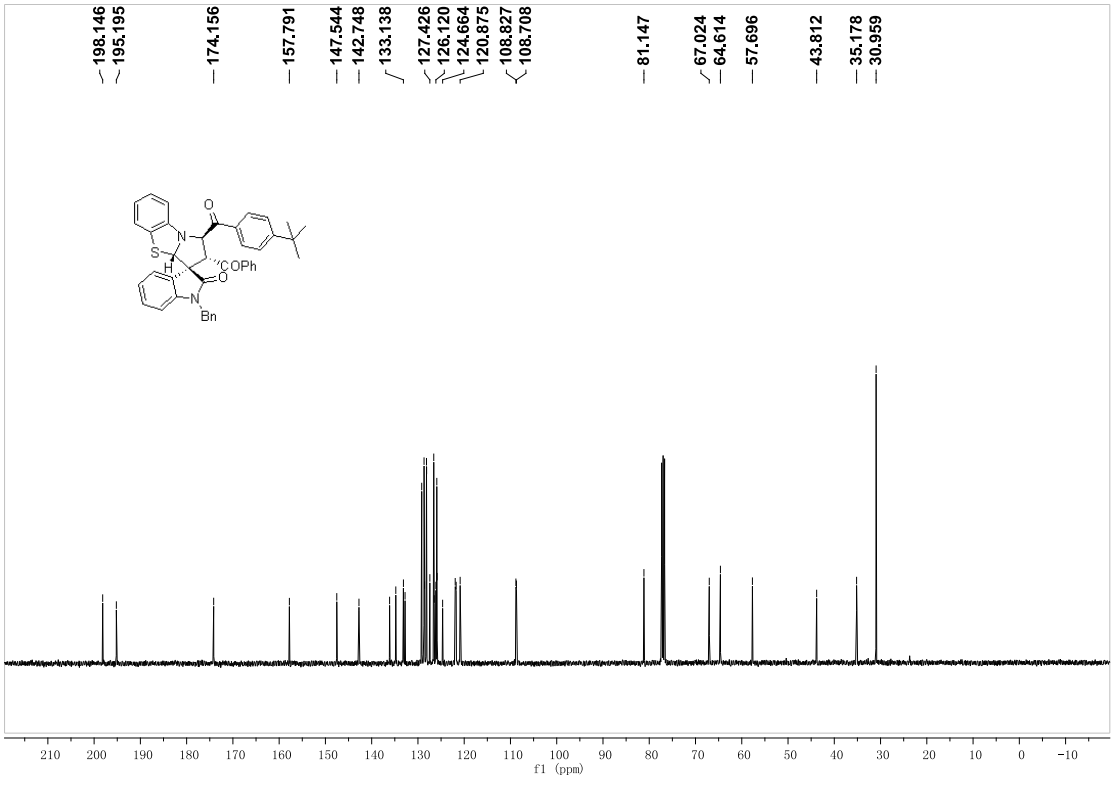
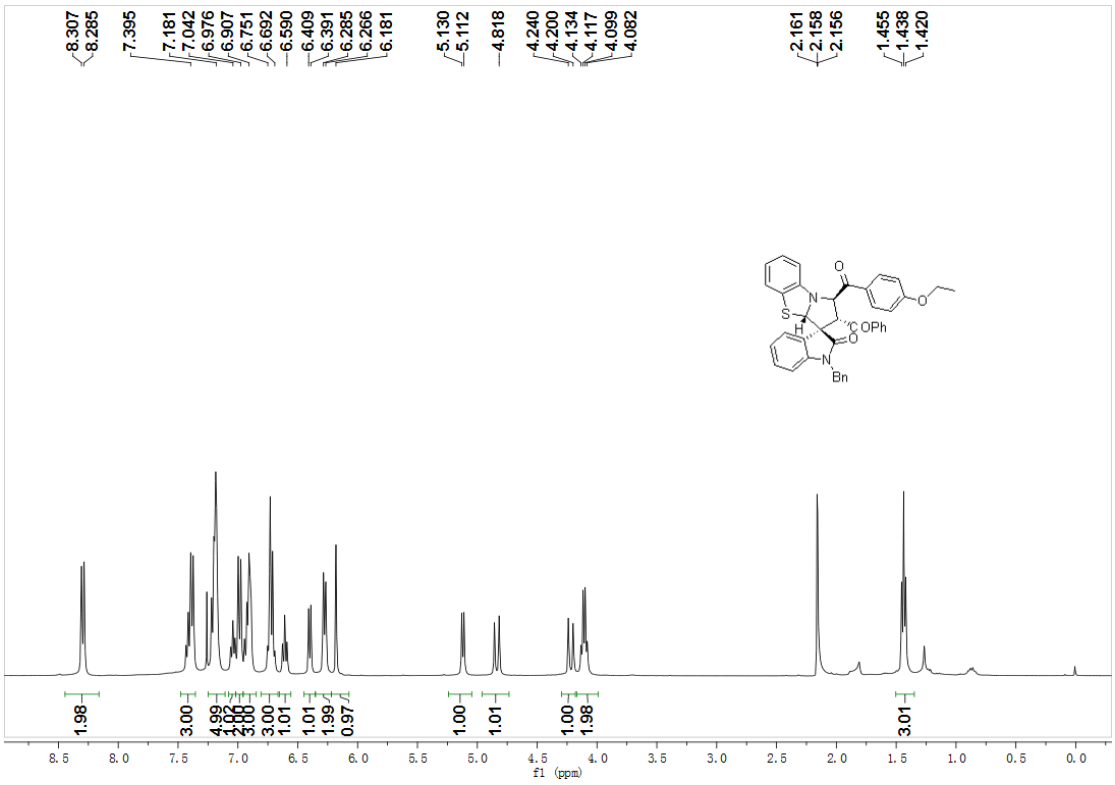
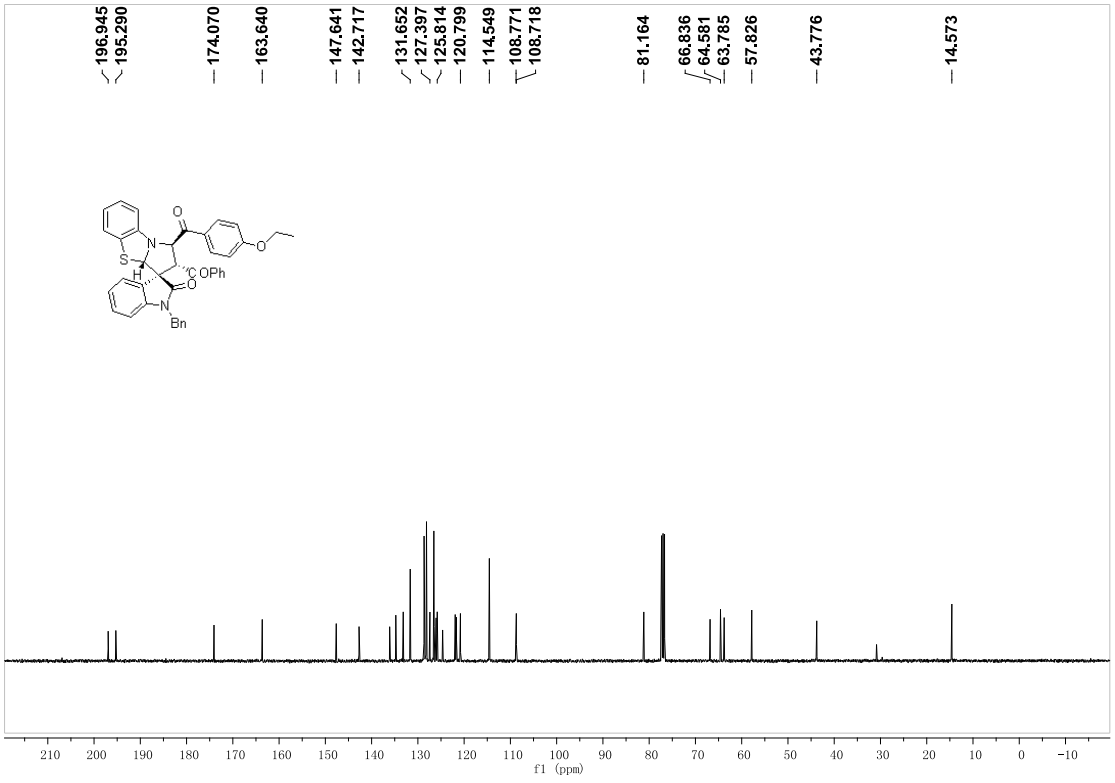


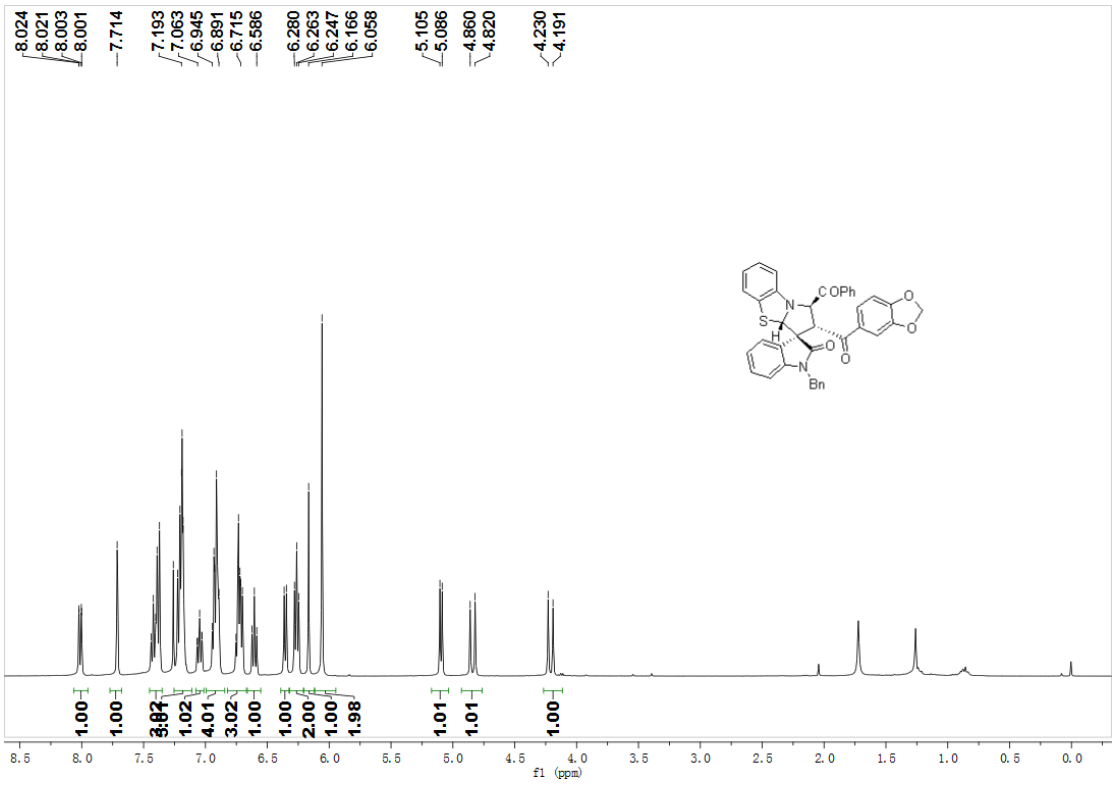


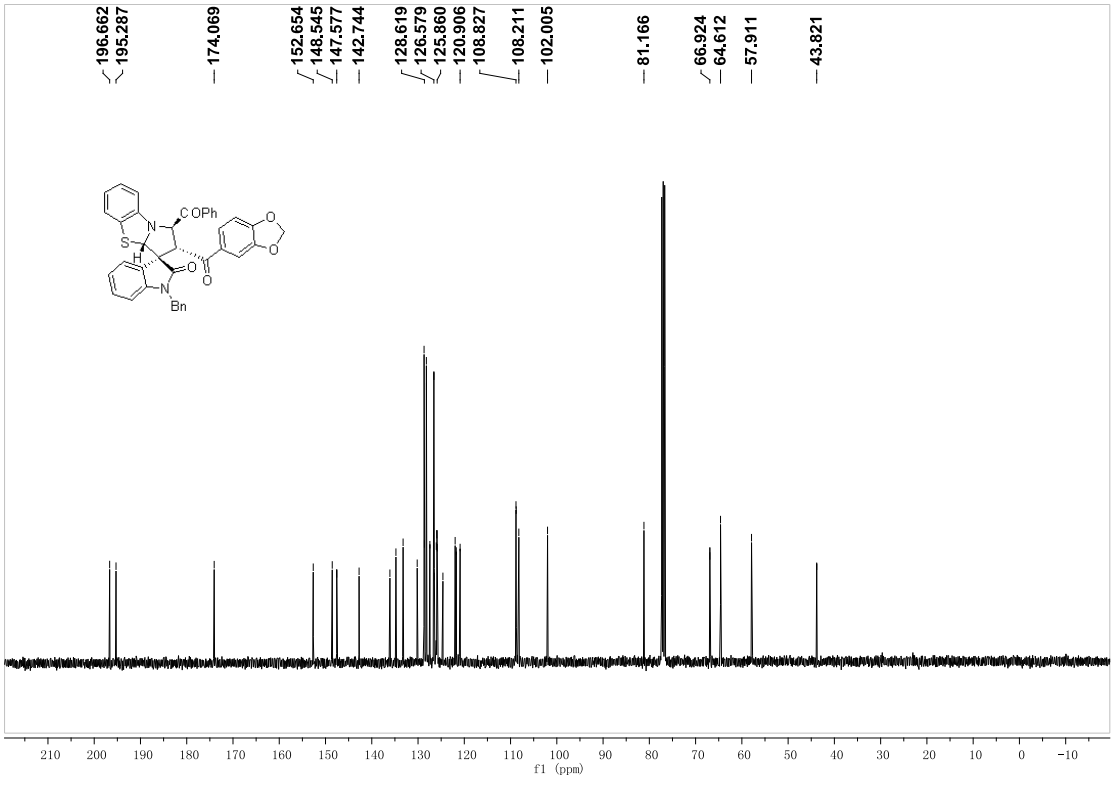
Compound 3ah



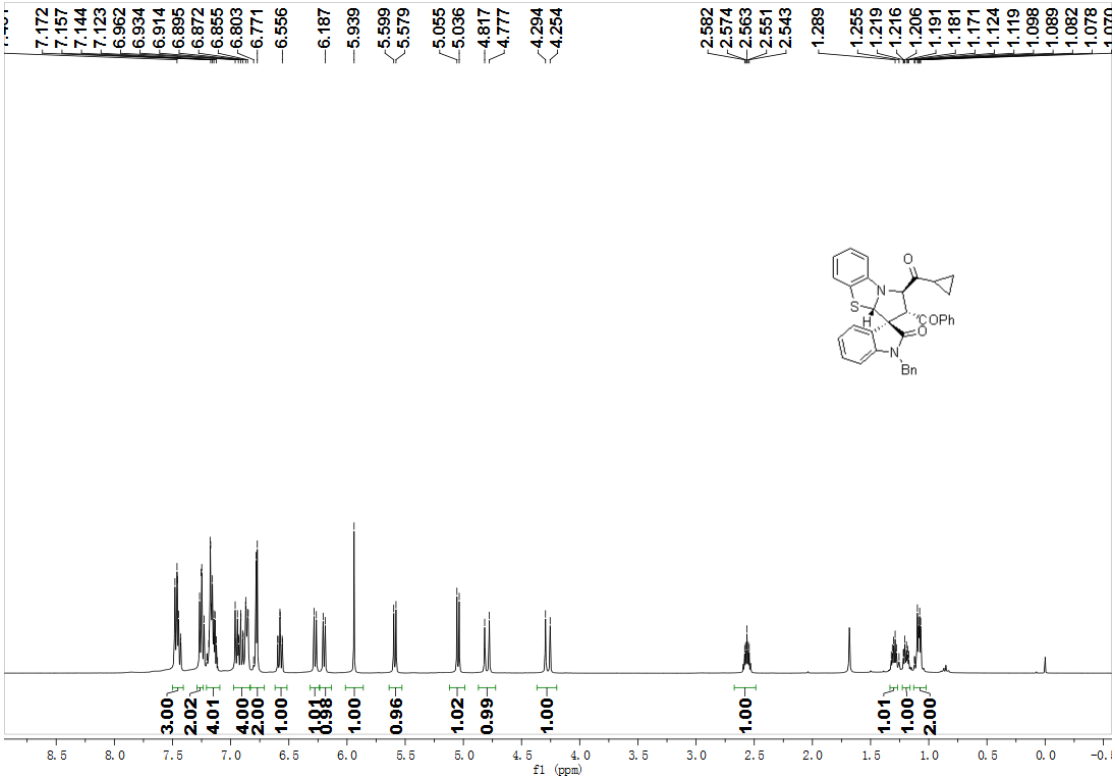


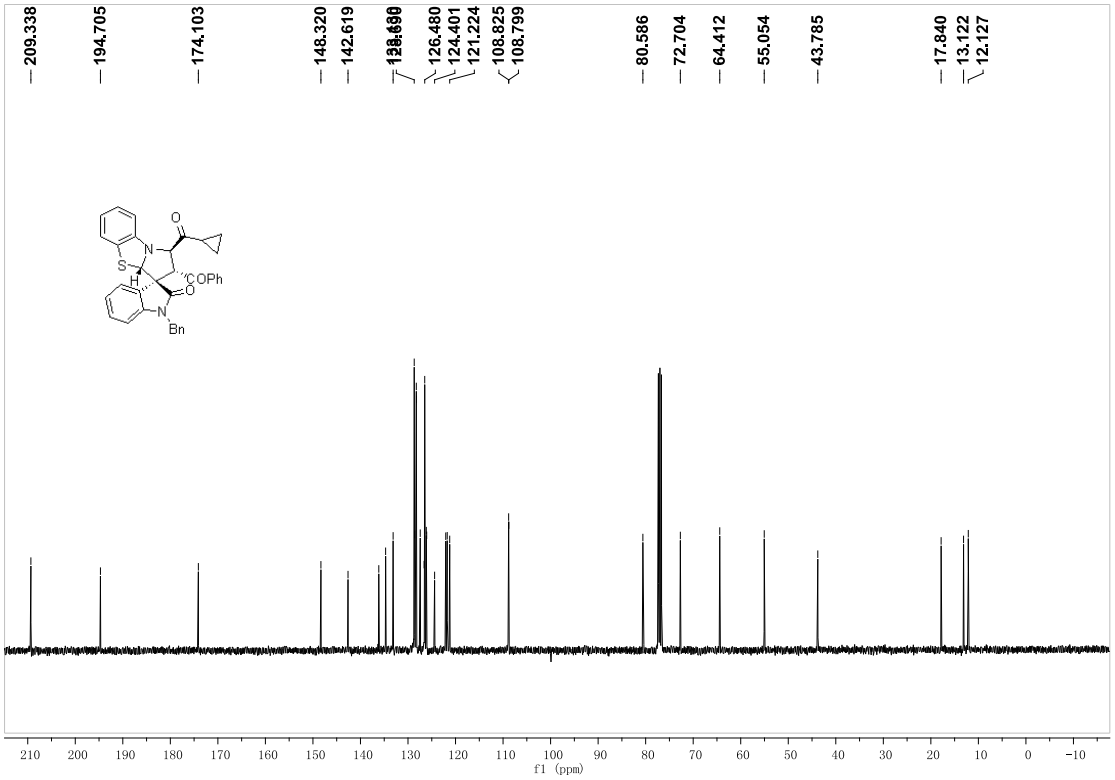
Compound 3ahs



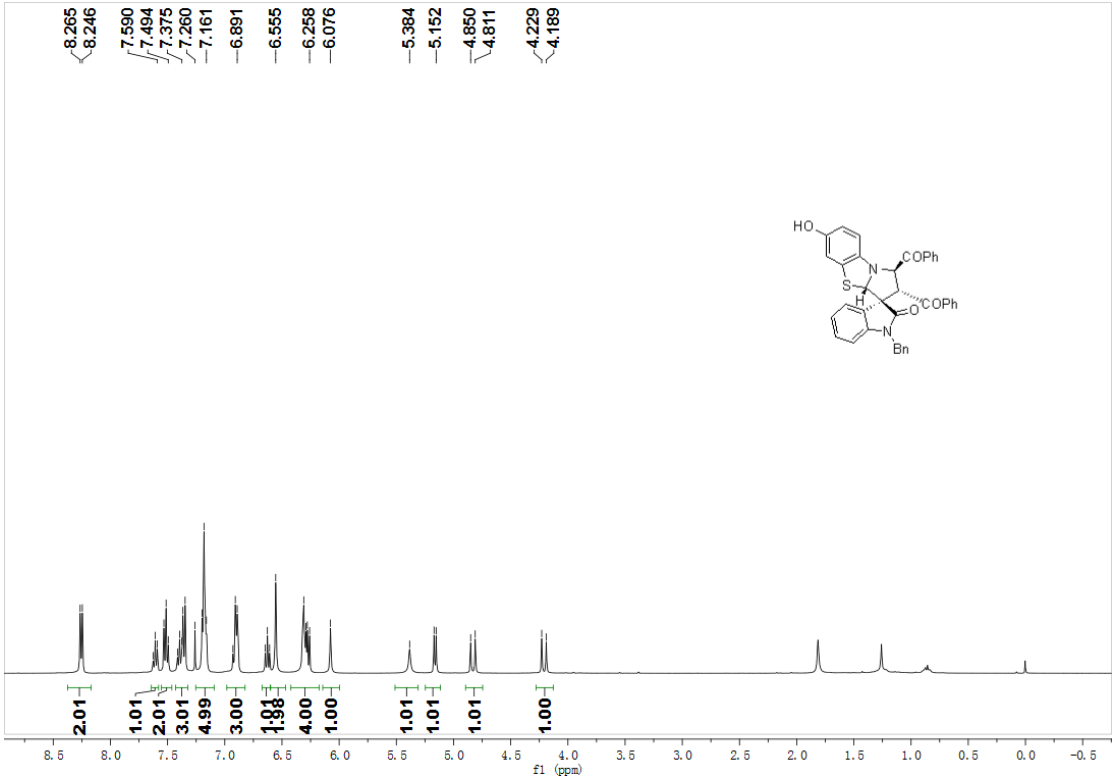


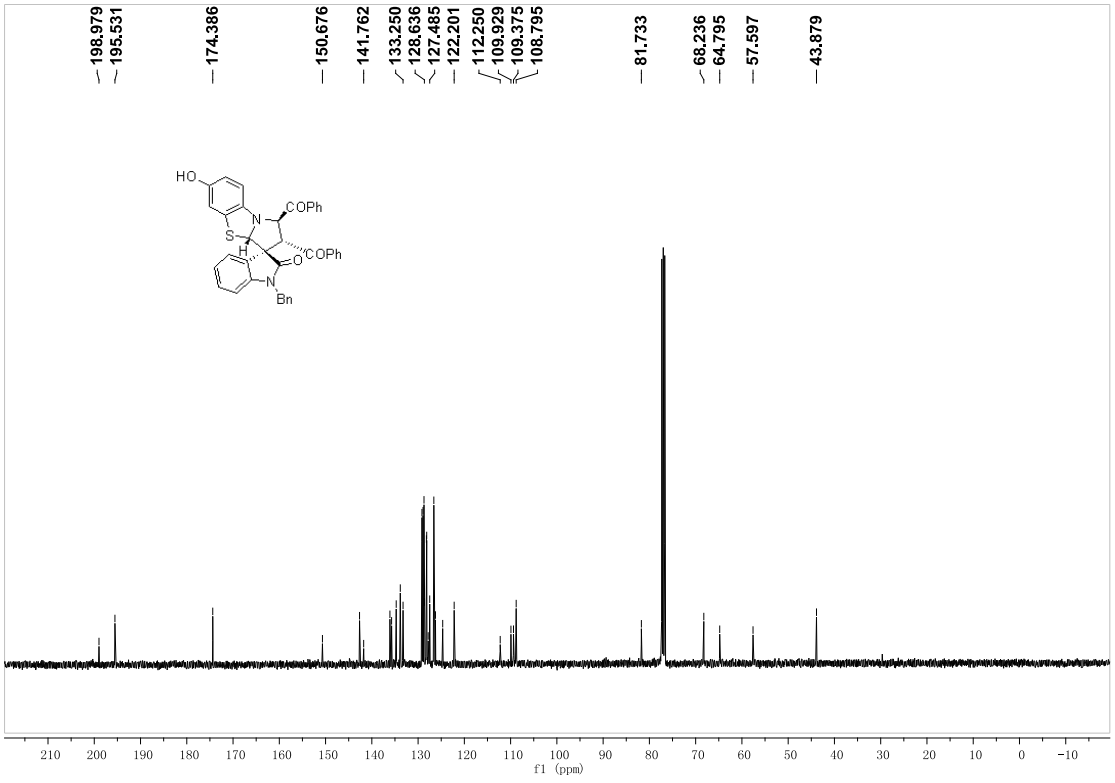
Compound 3ai



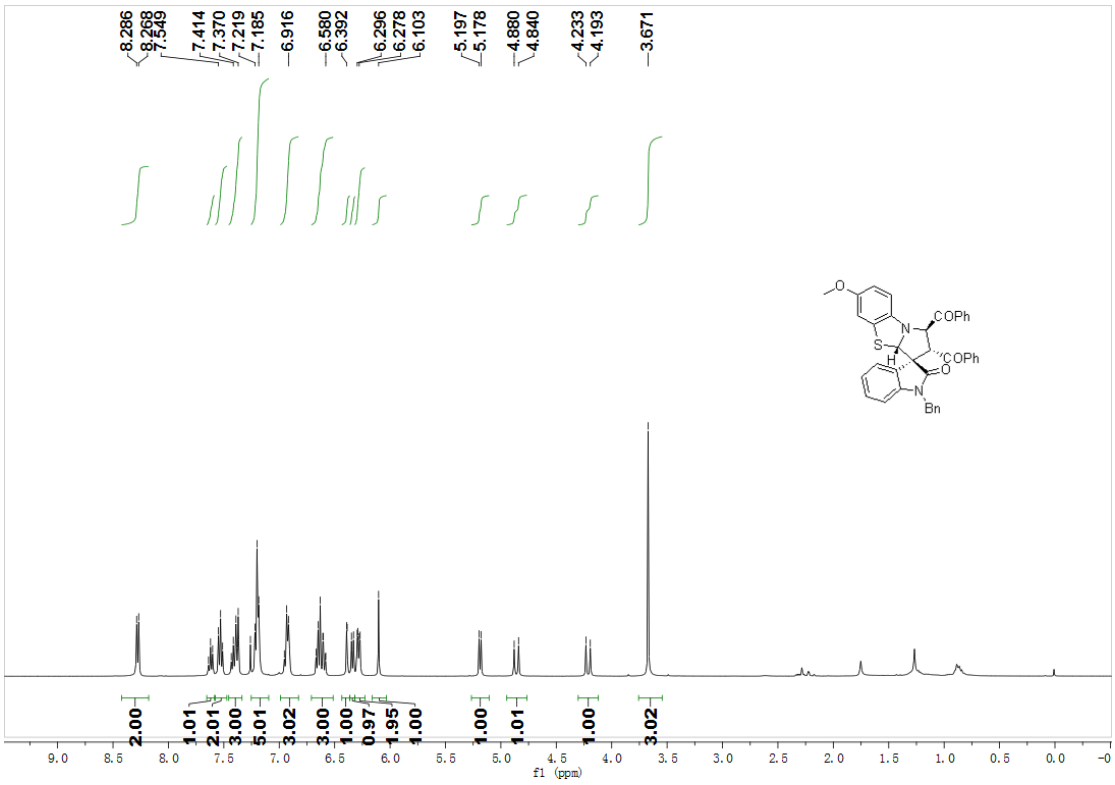


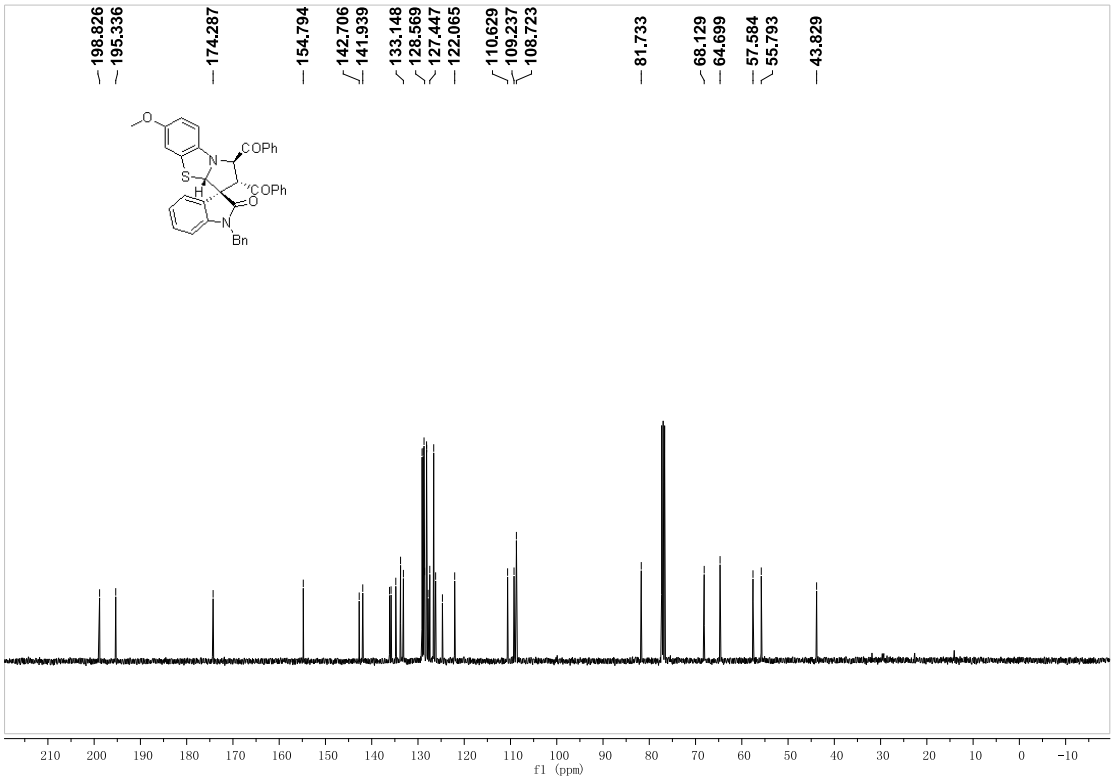
Compound 3aj



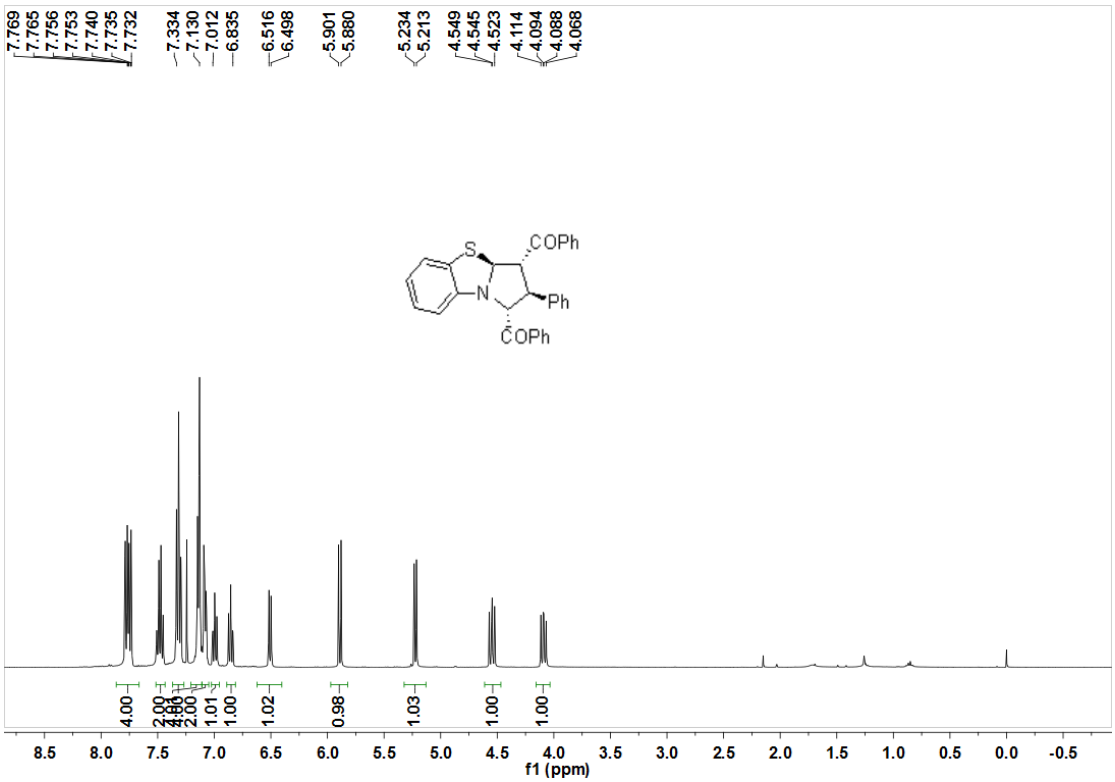


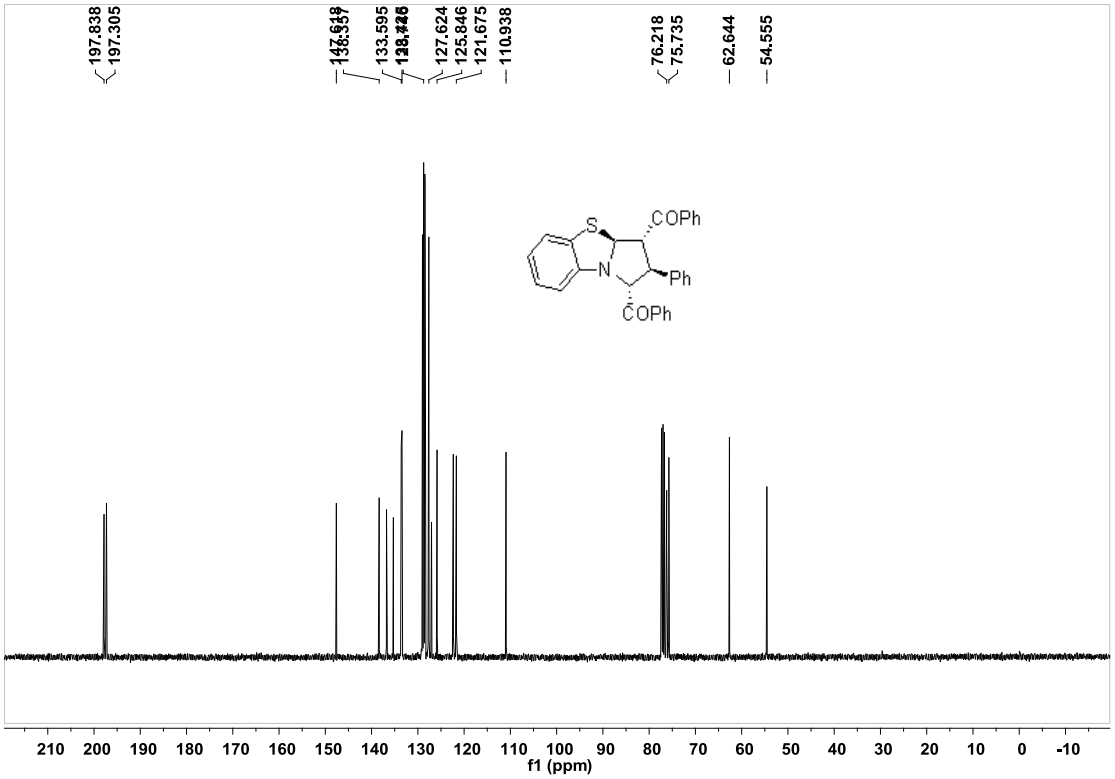
Compound 3ak



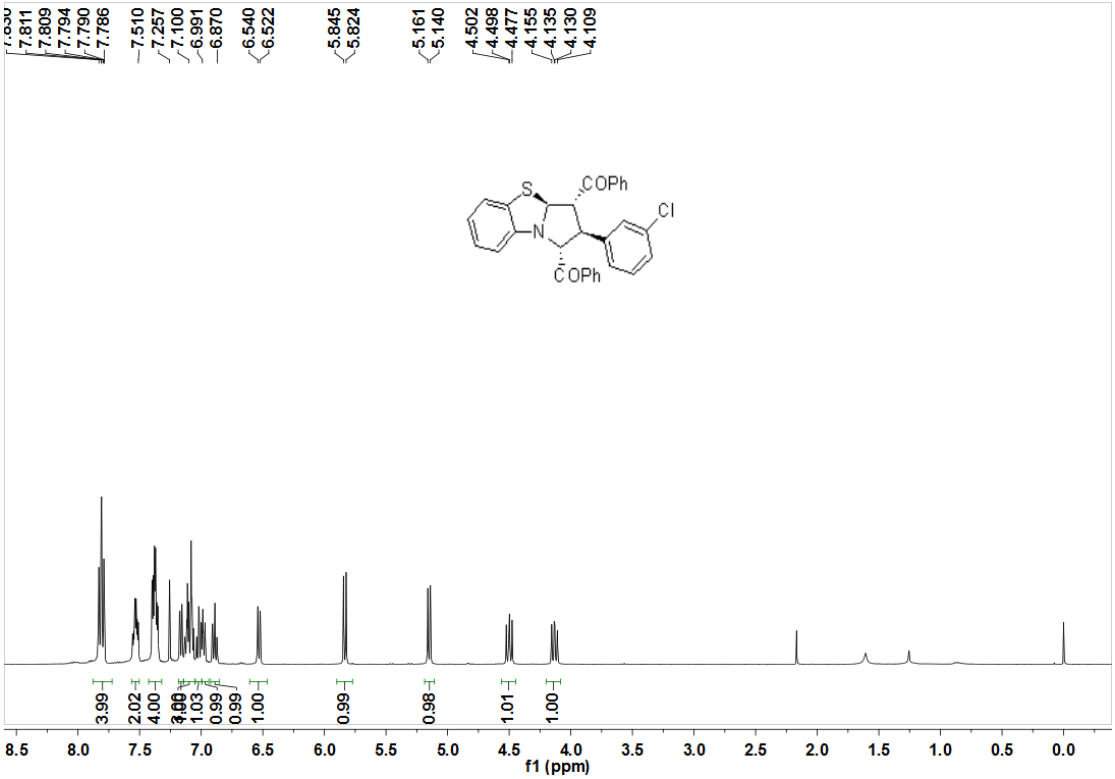


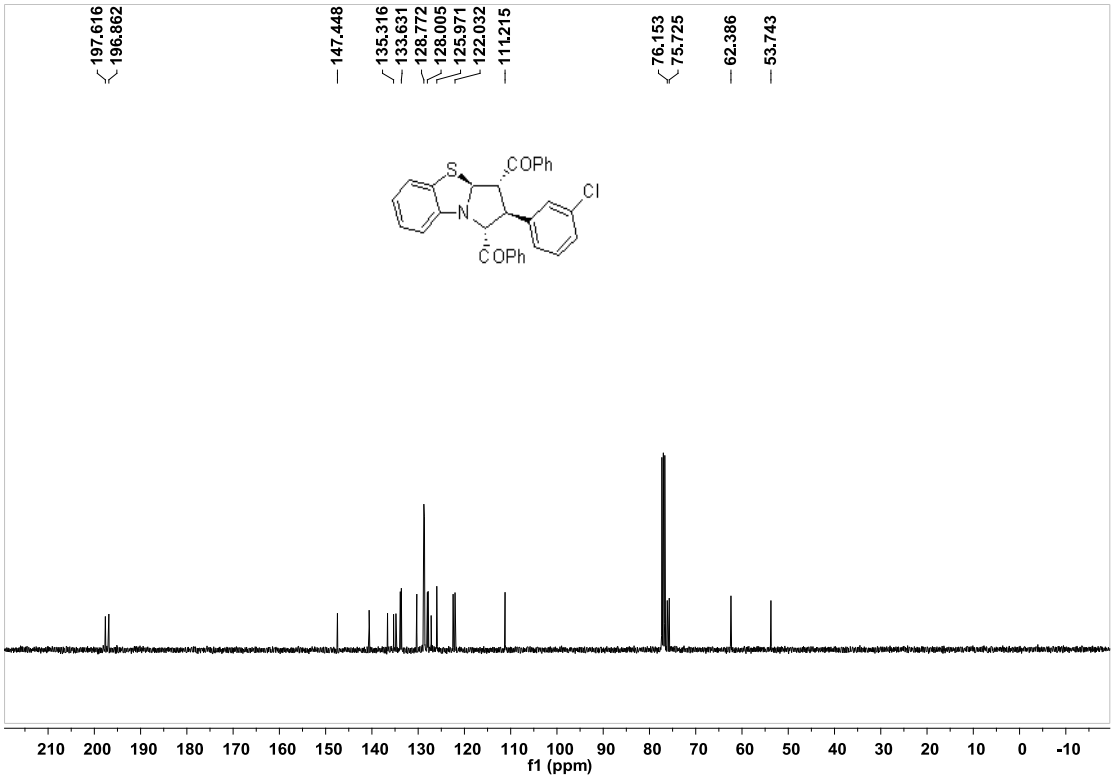
Compound 5aa





Compound 5ba





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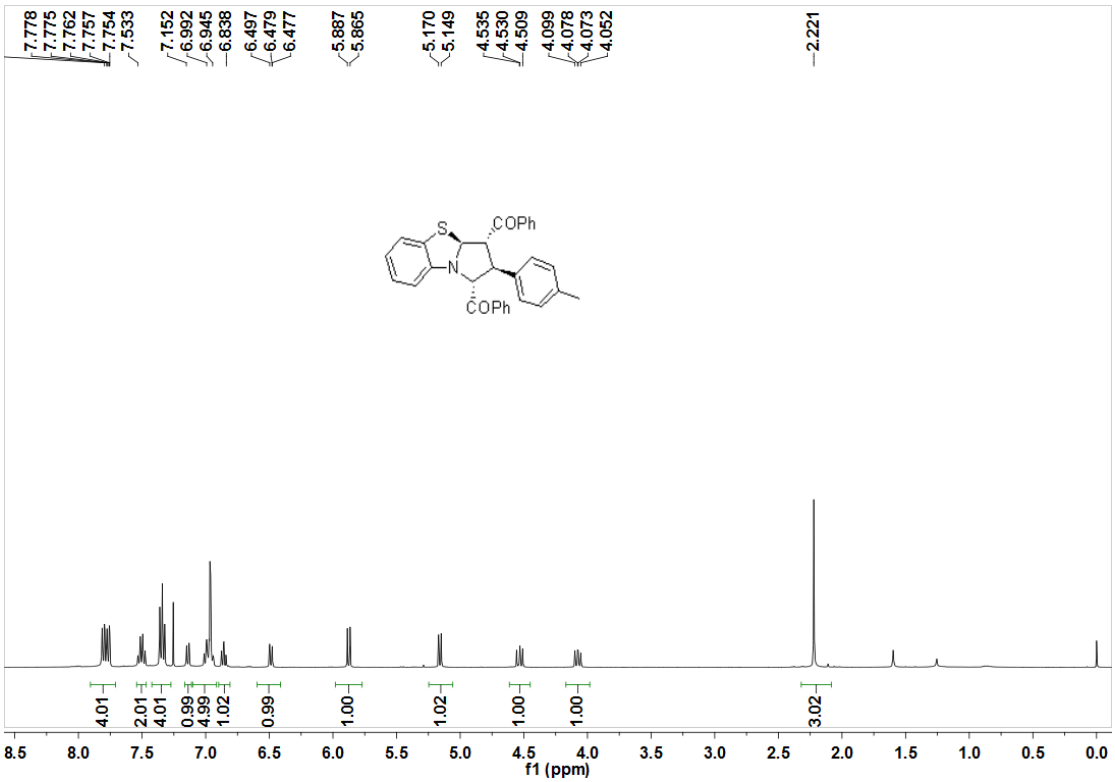

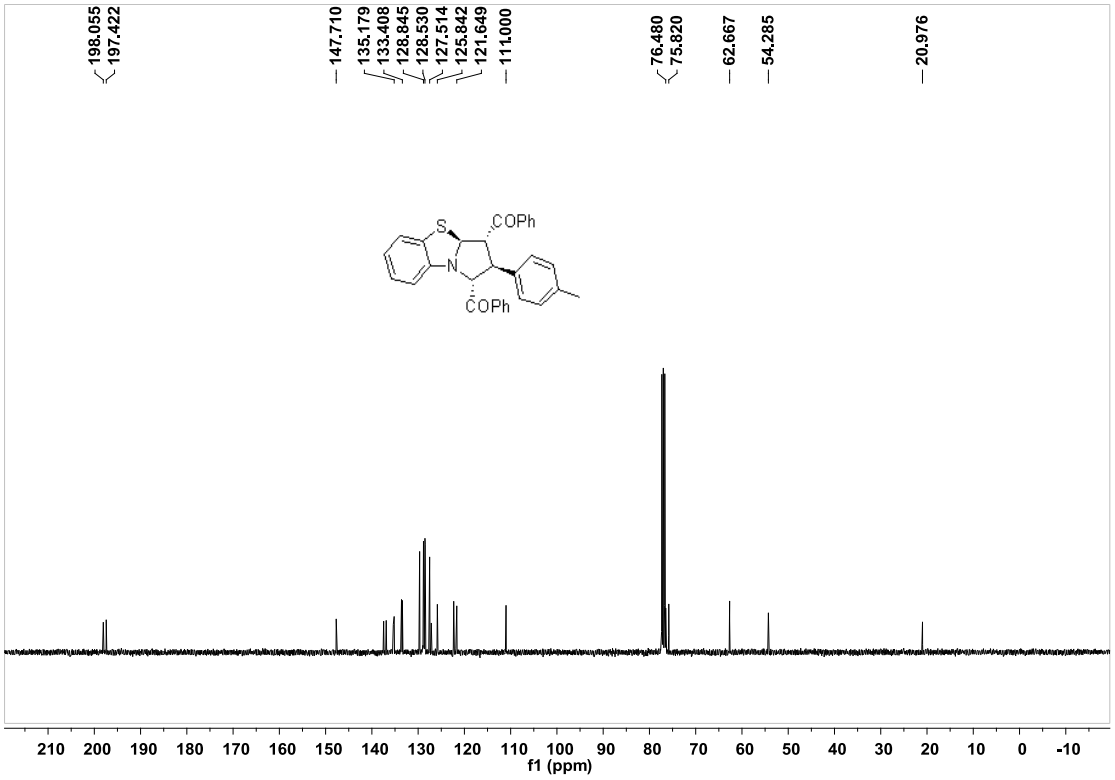

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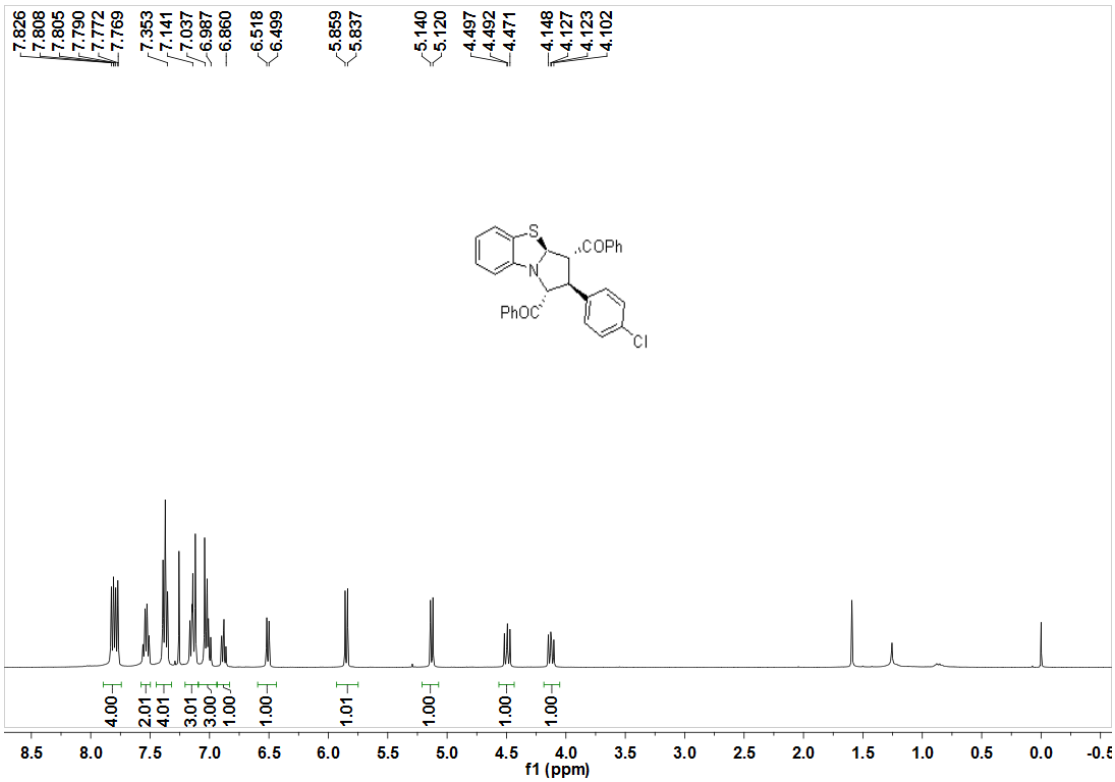
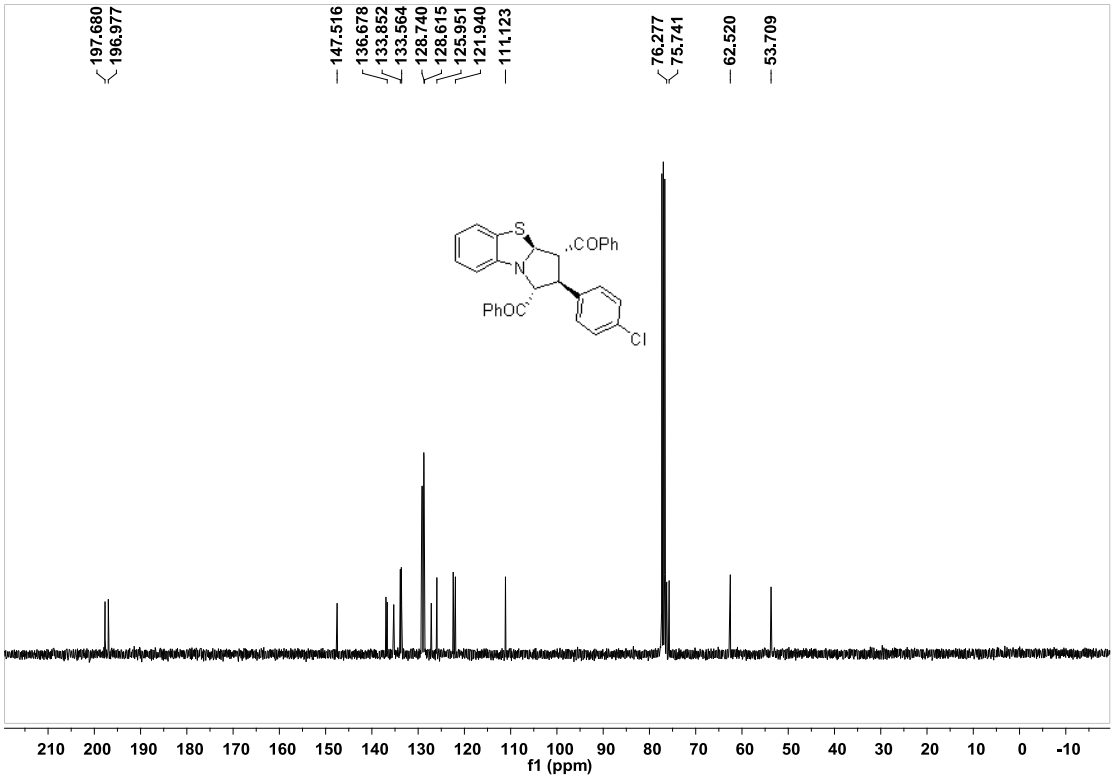
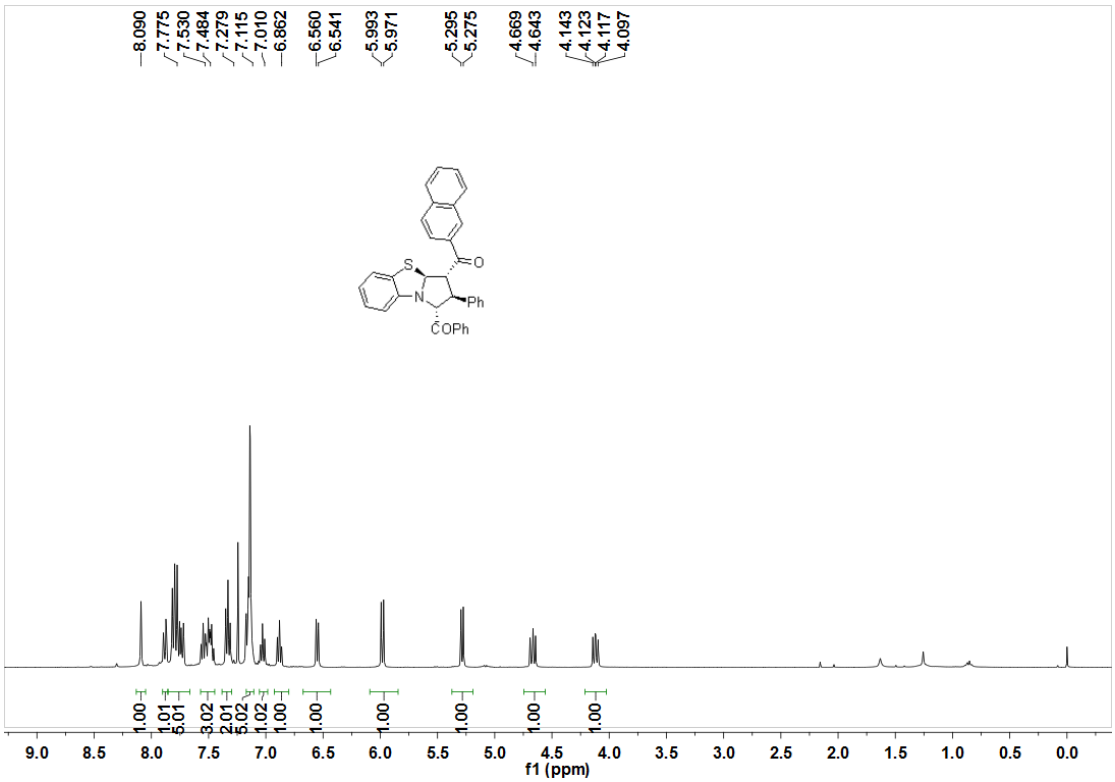
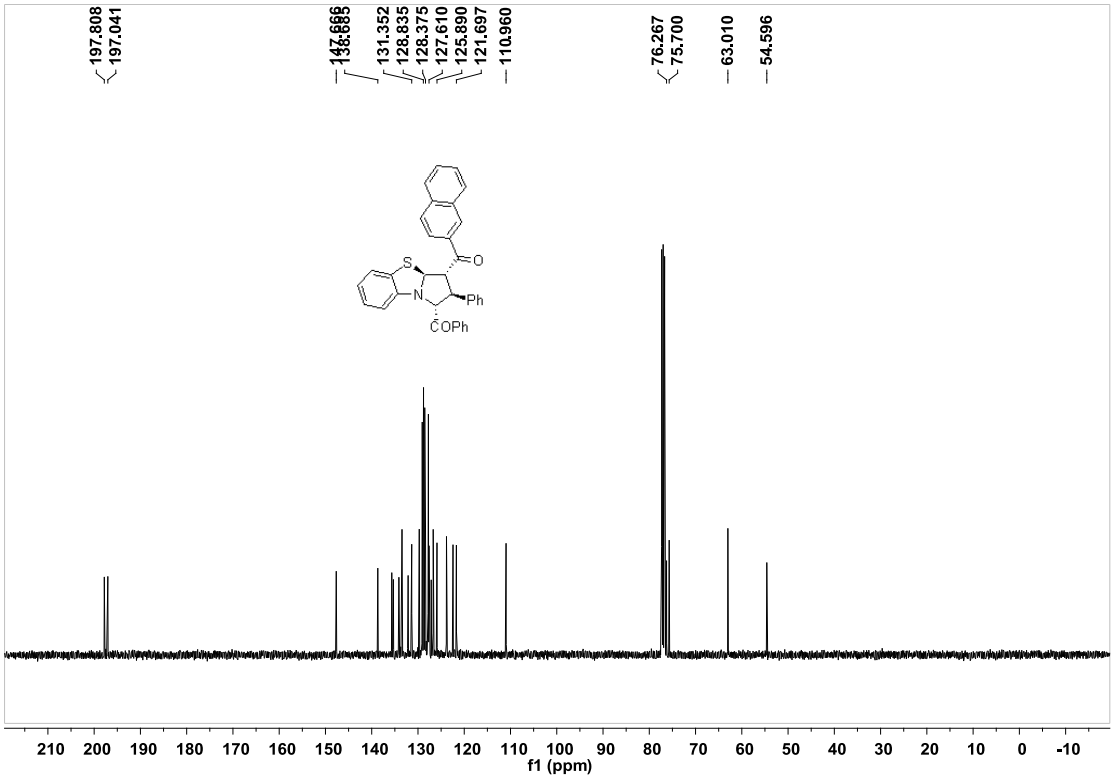




Compound 5ea





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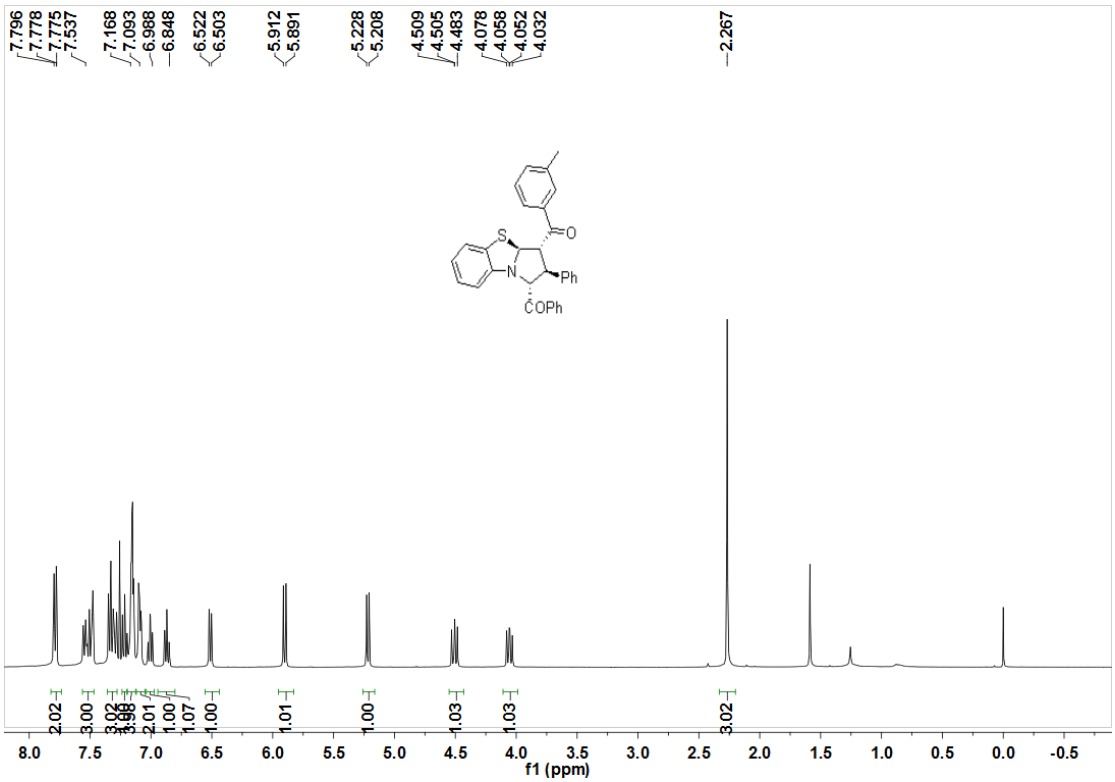
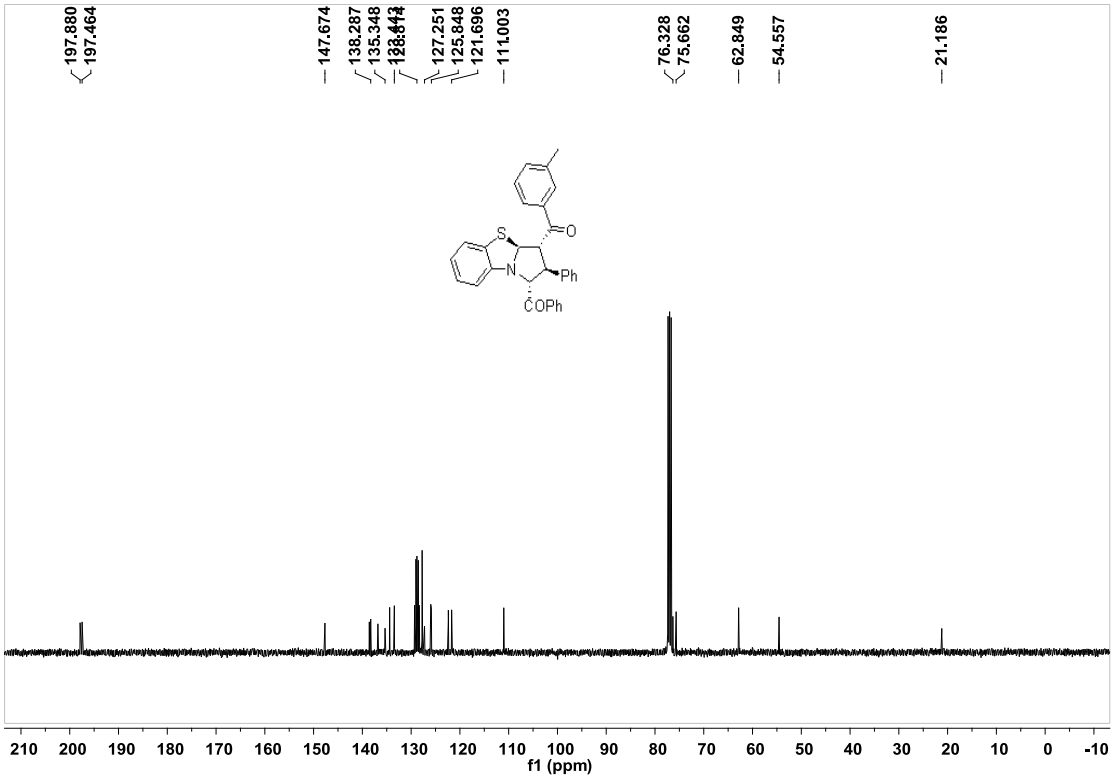
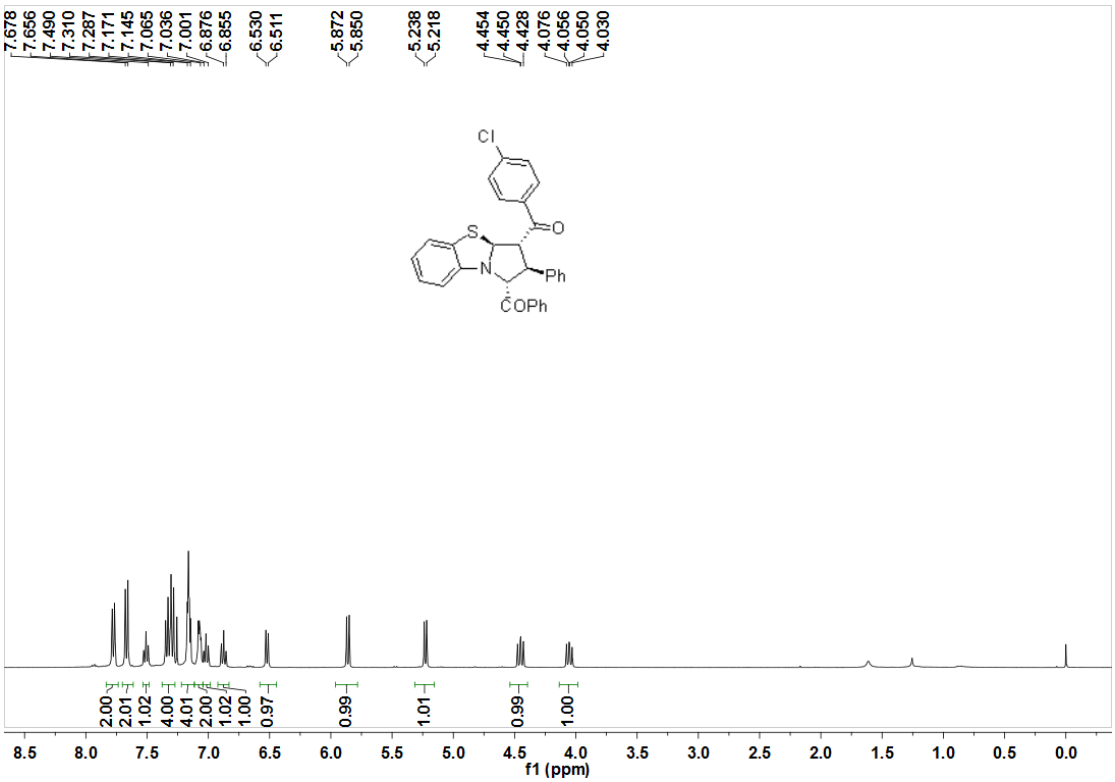
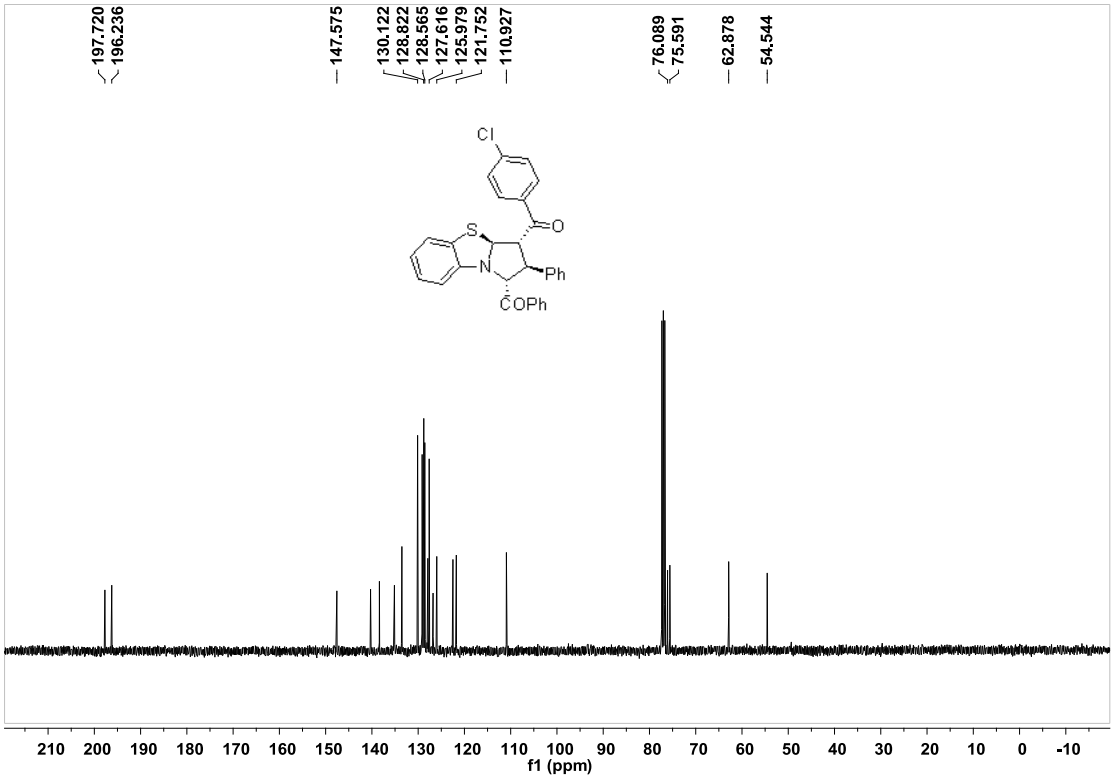


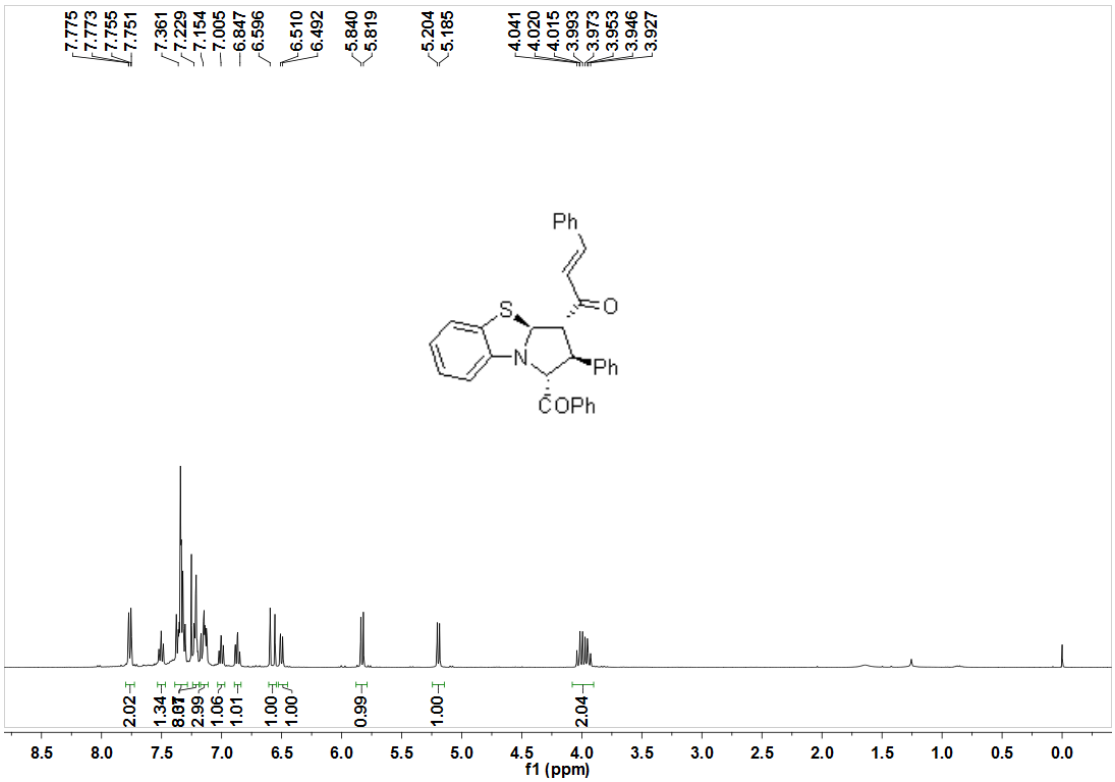


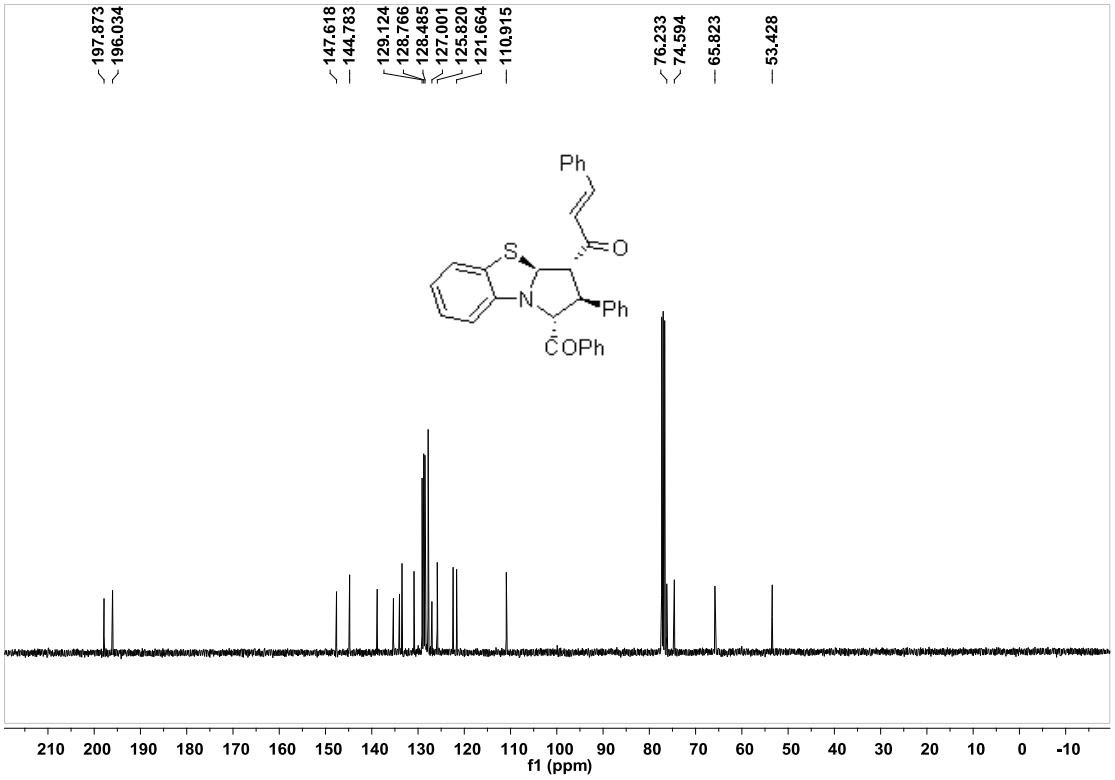
Compound 5ga



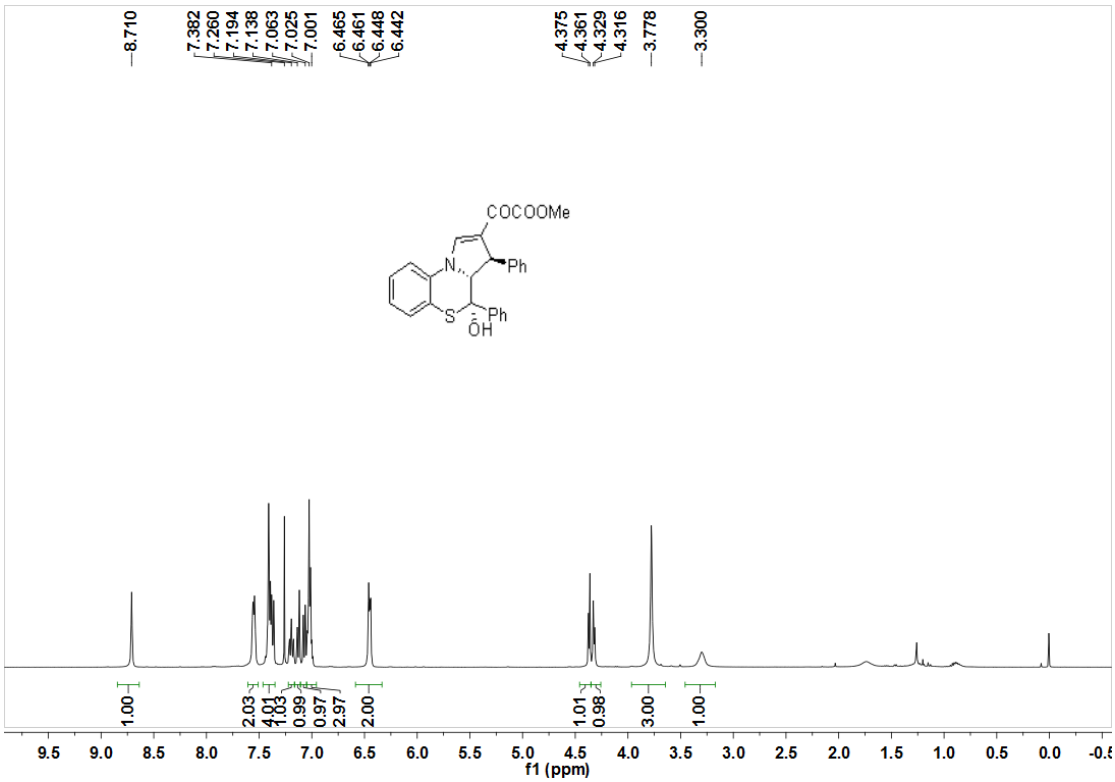


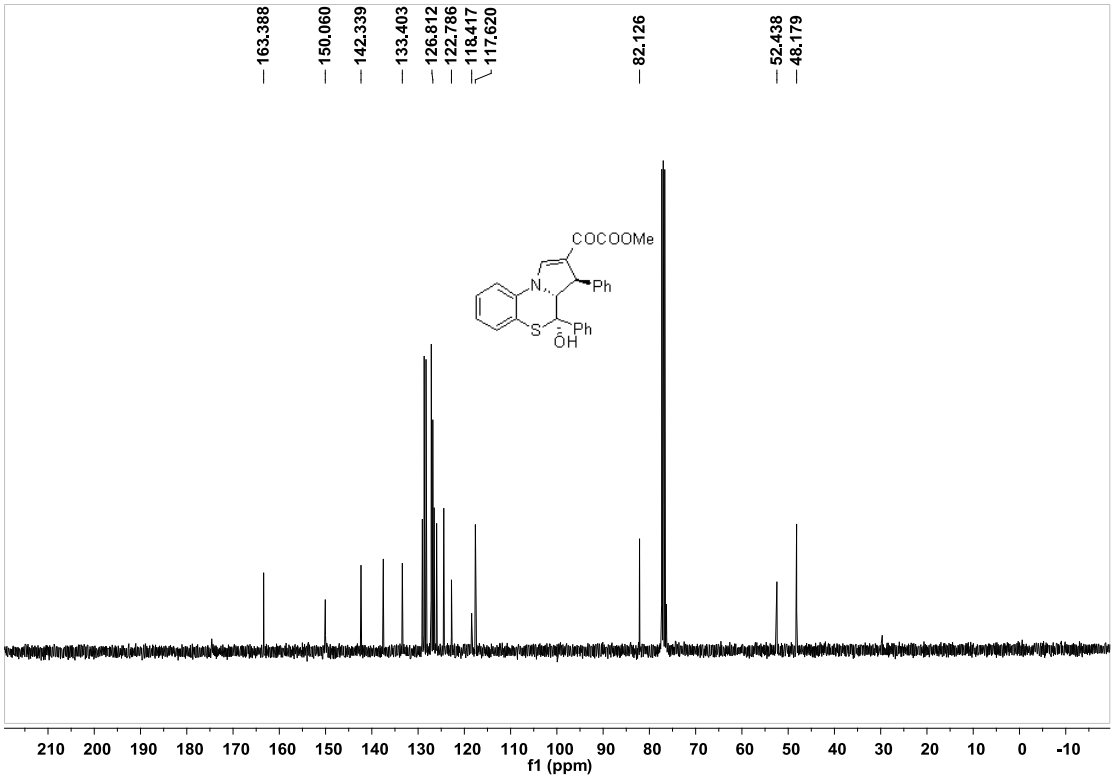
Compound 5ha



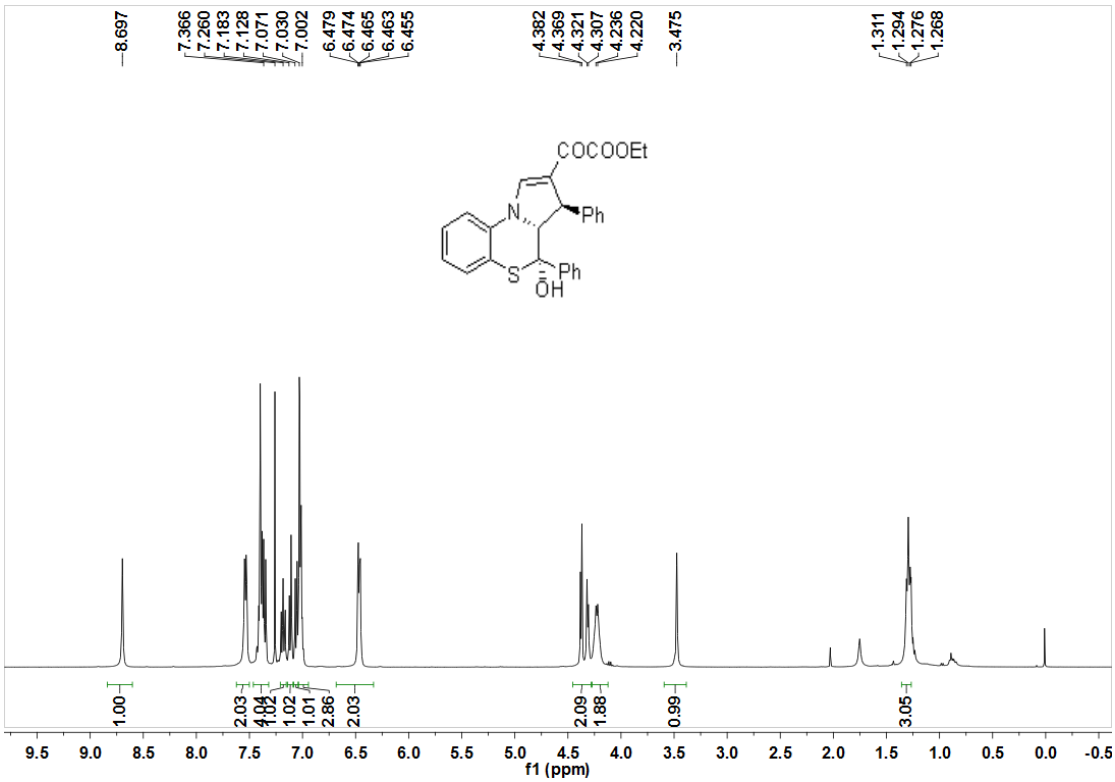


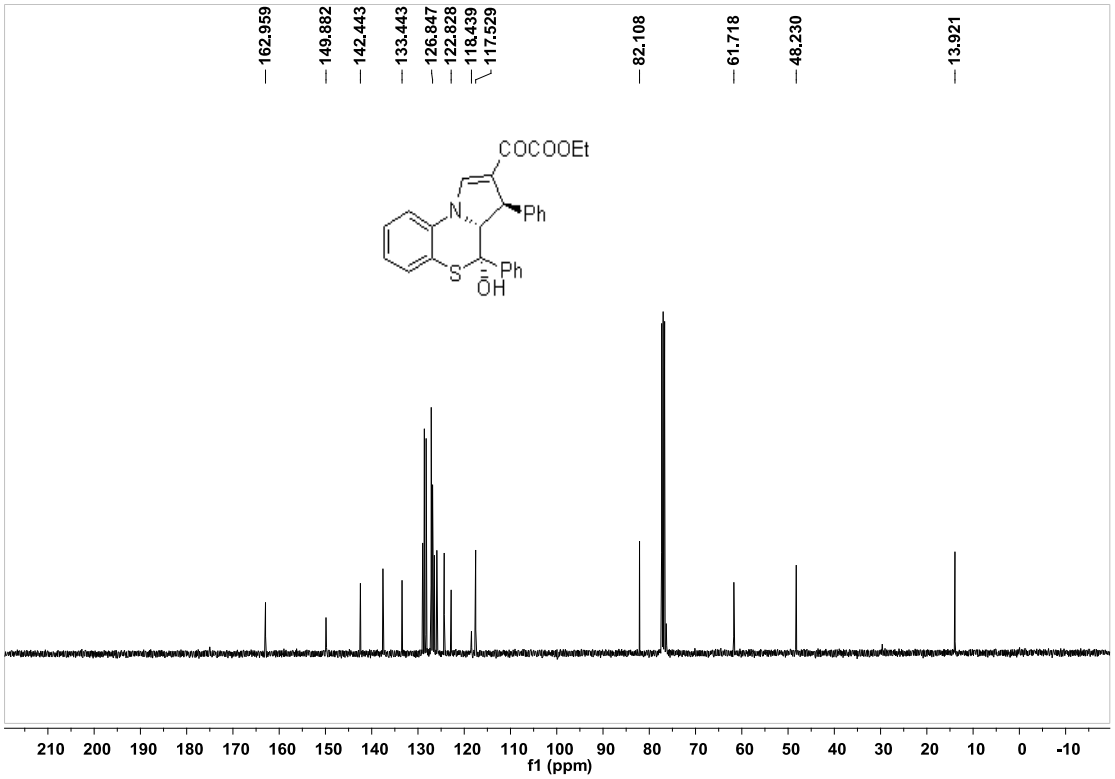
Compound 7aa





Compound 7ba





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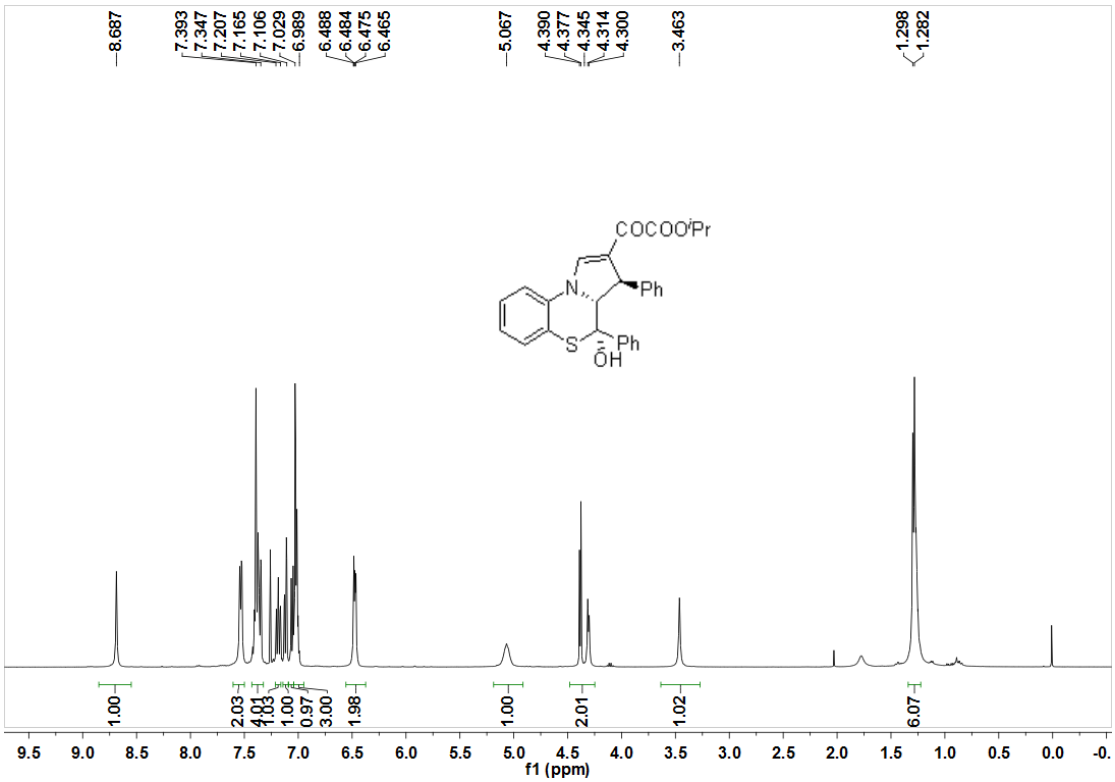

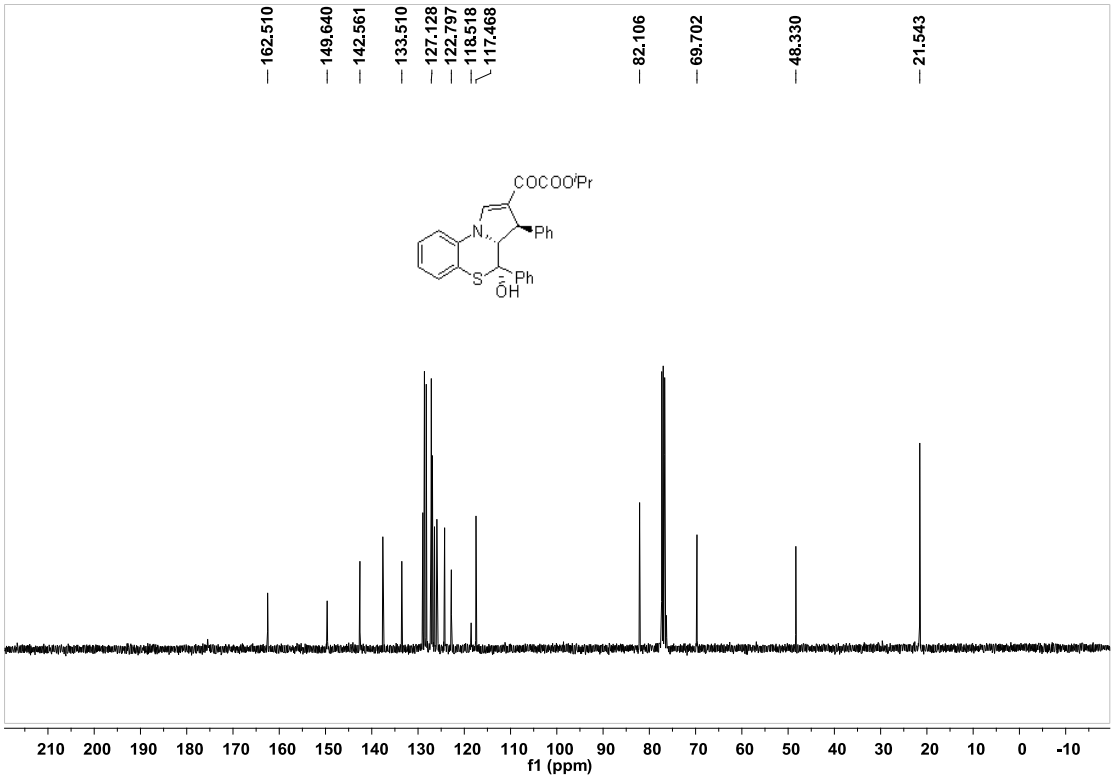

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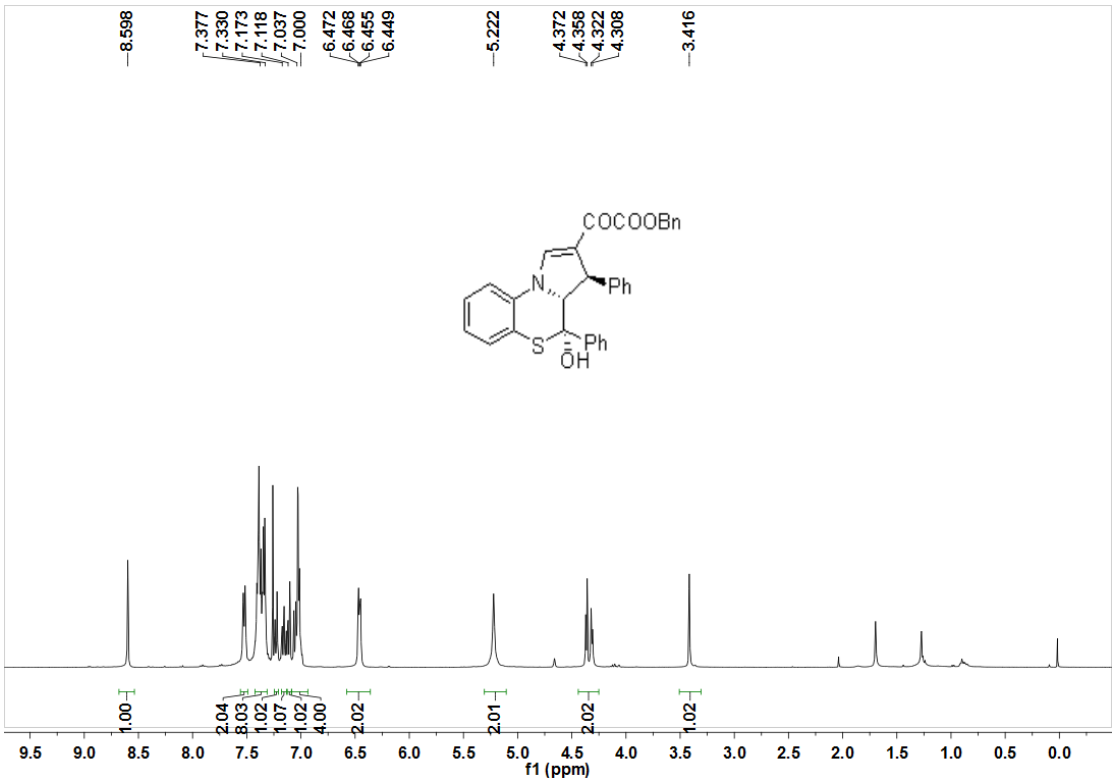

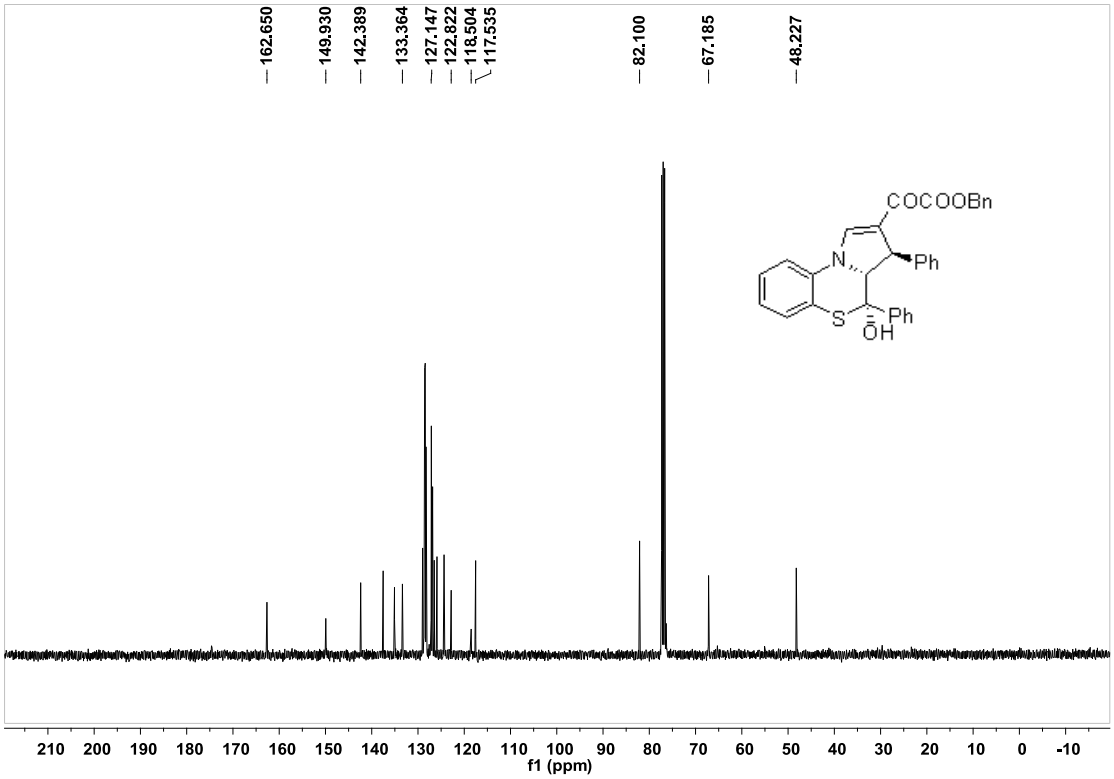

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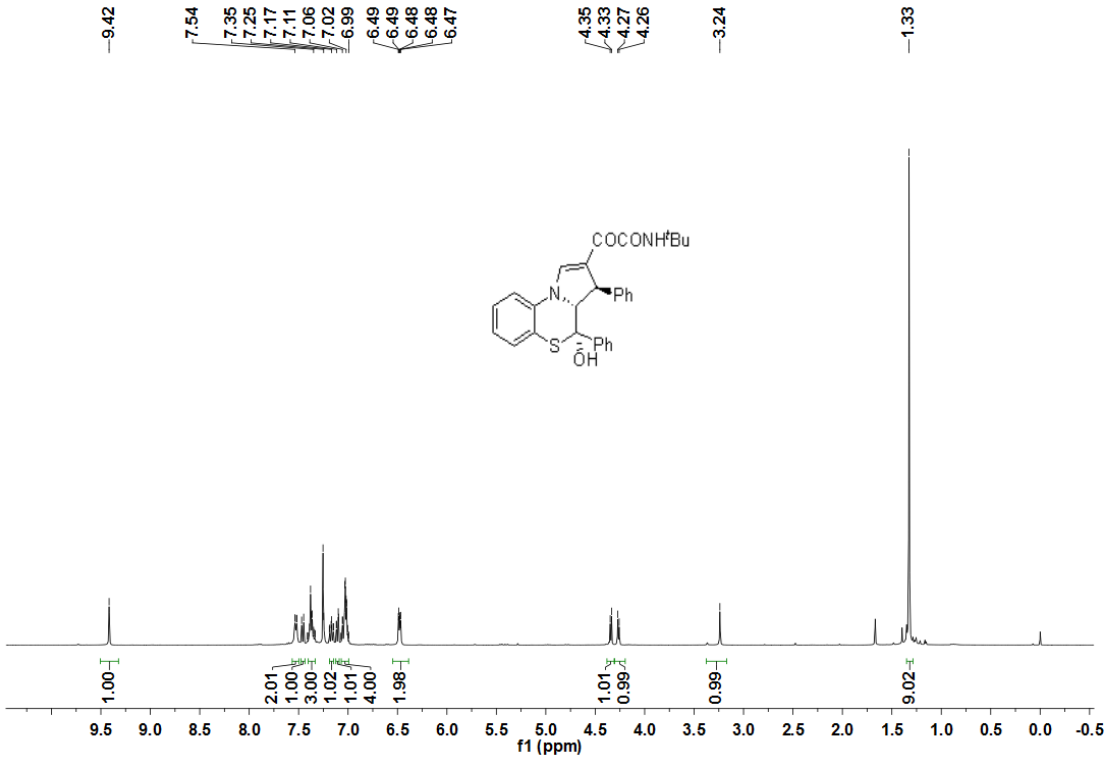
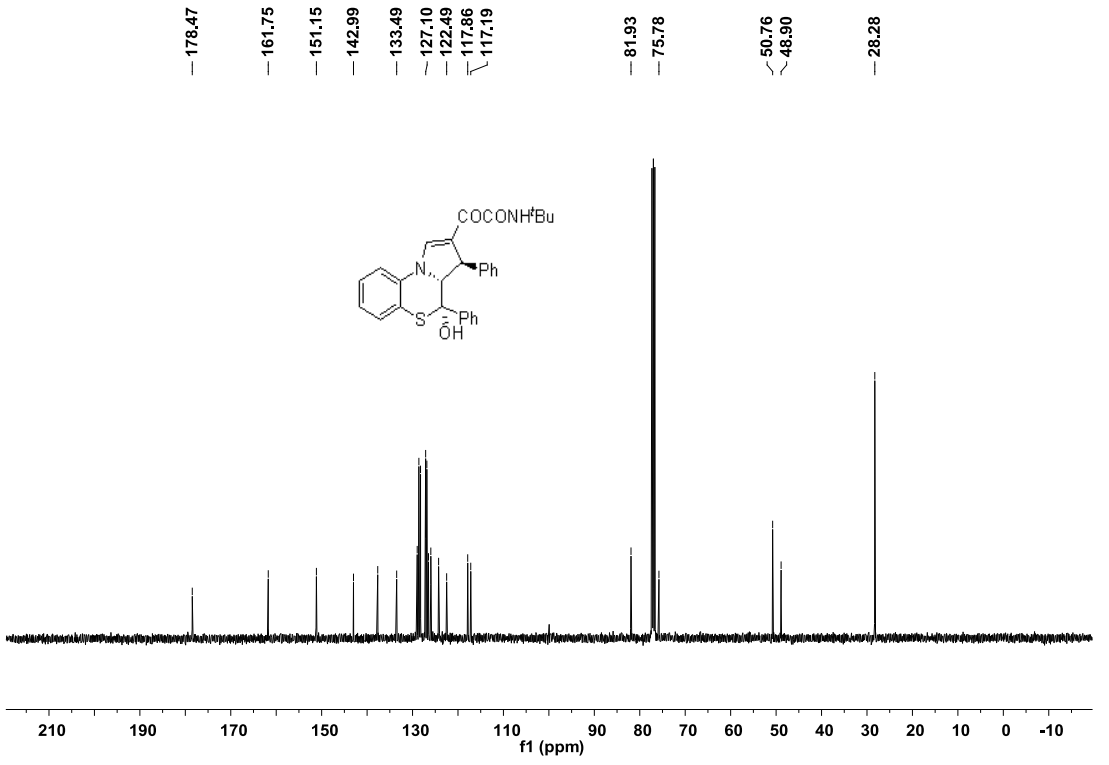
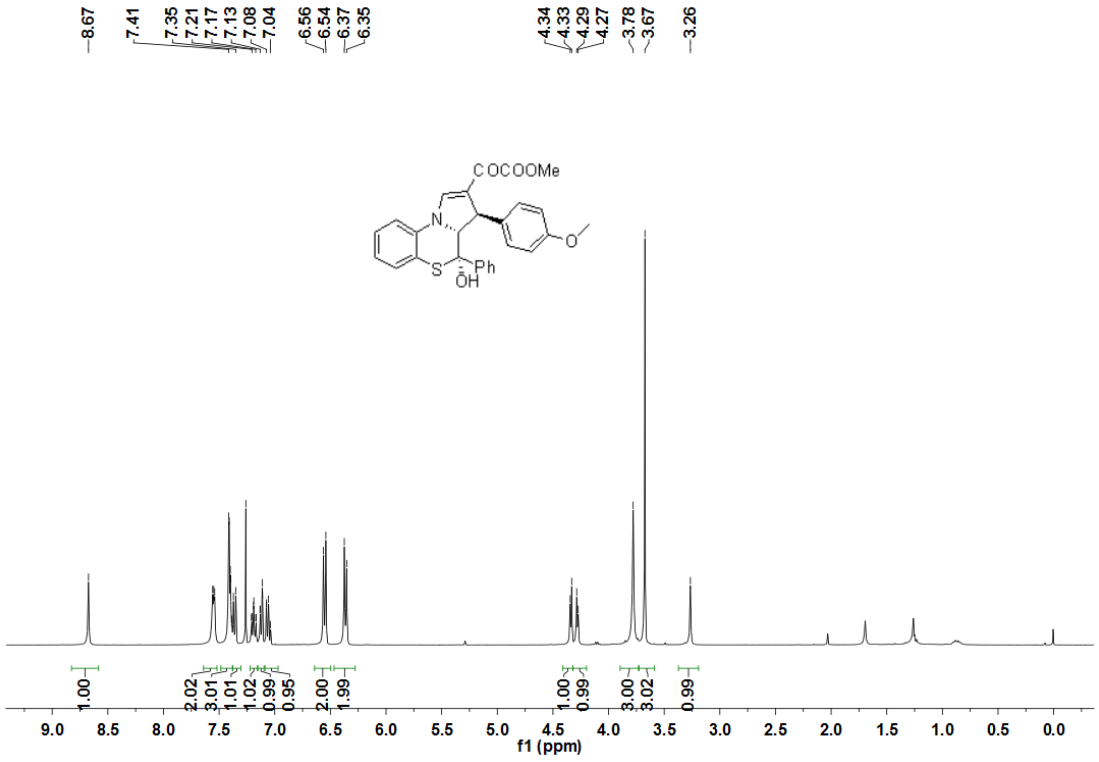
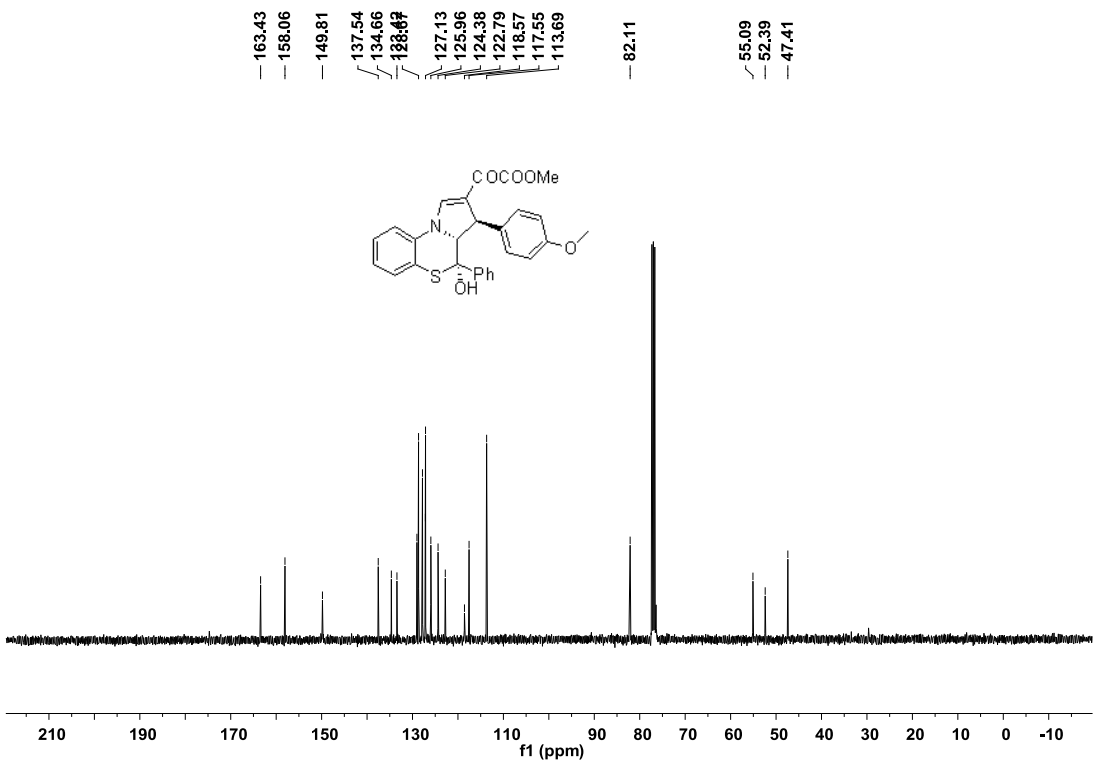


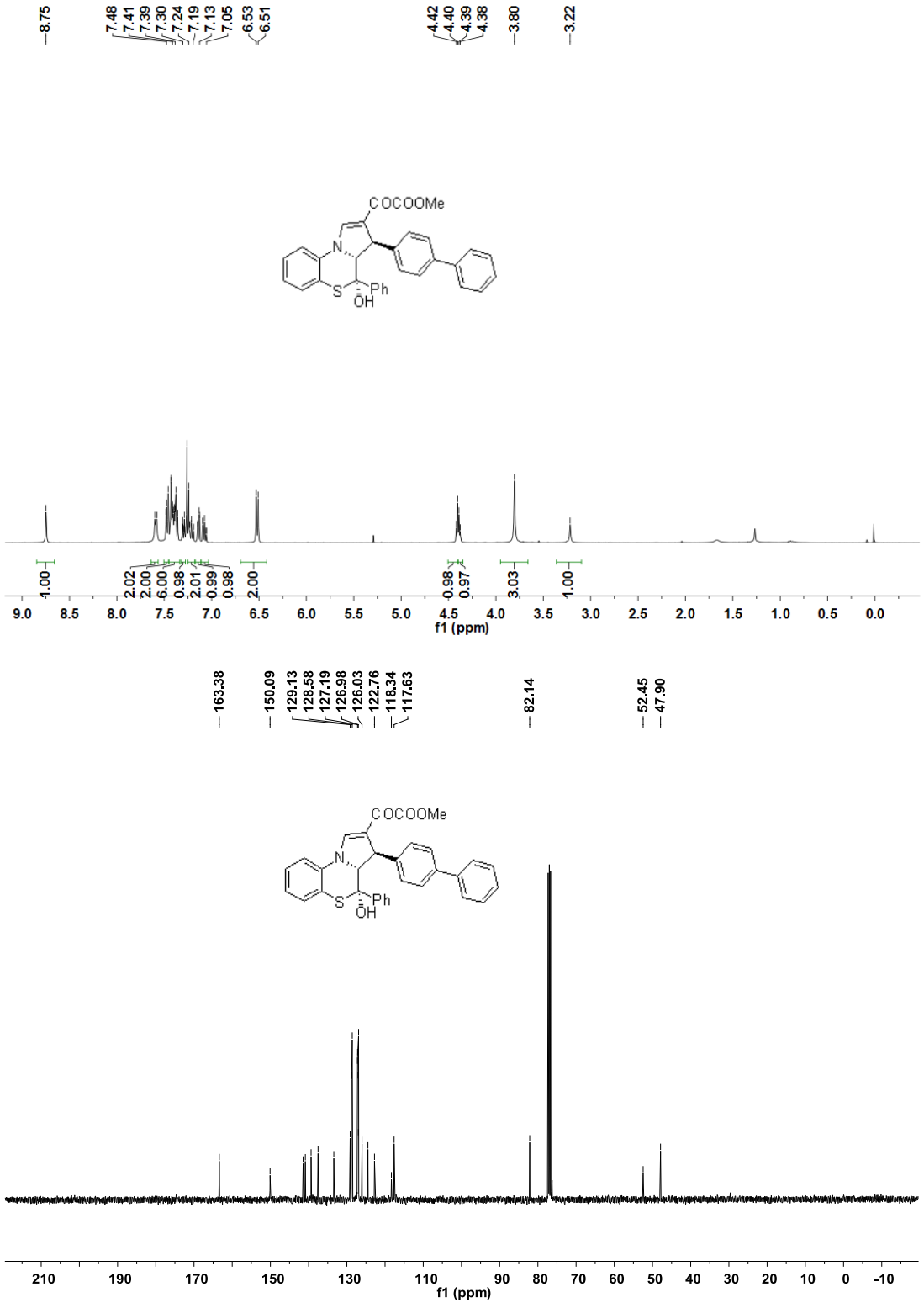


Compound 7fa





Compound 7ga



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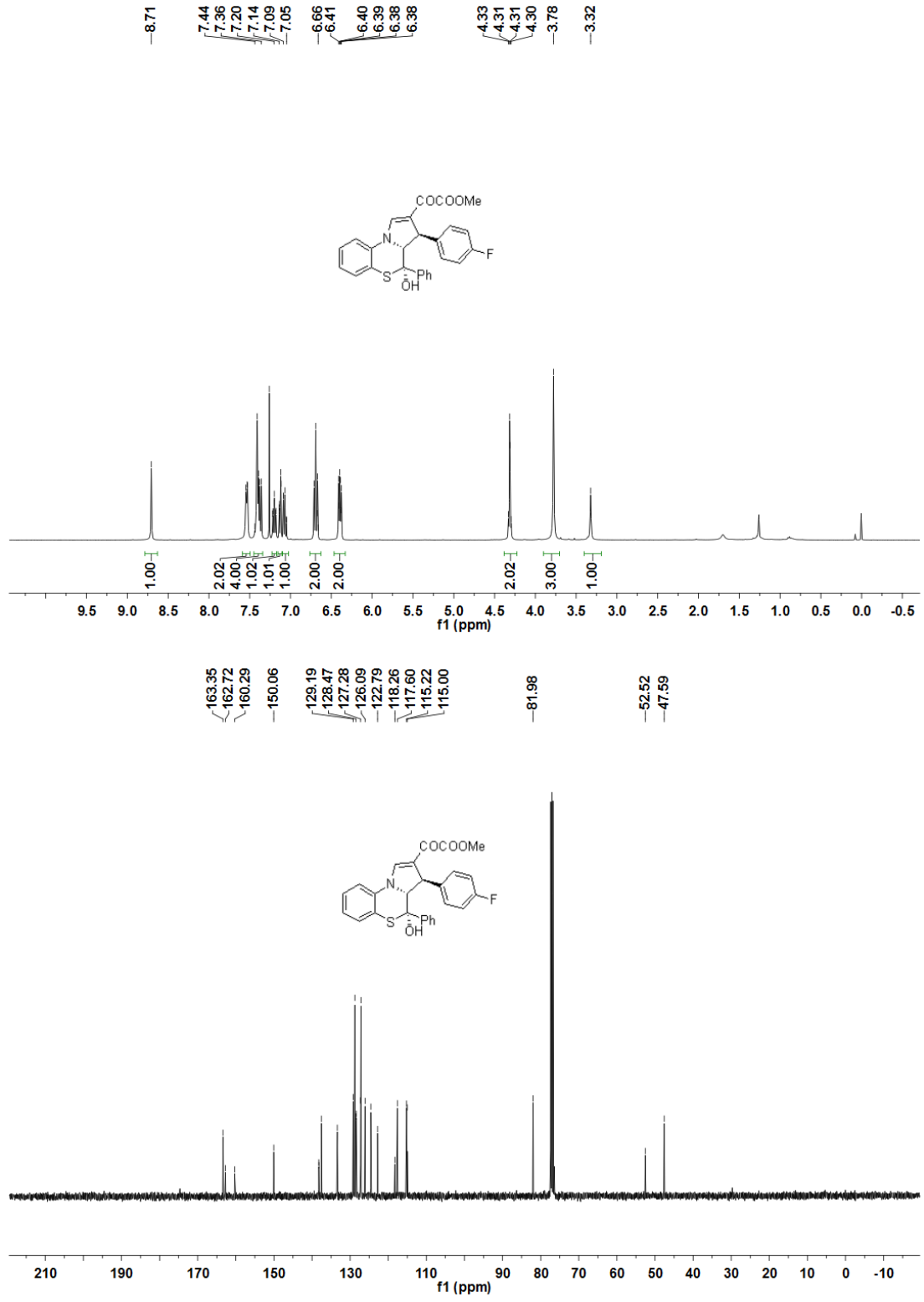

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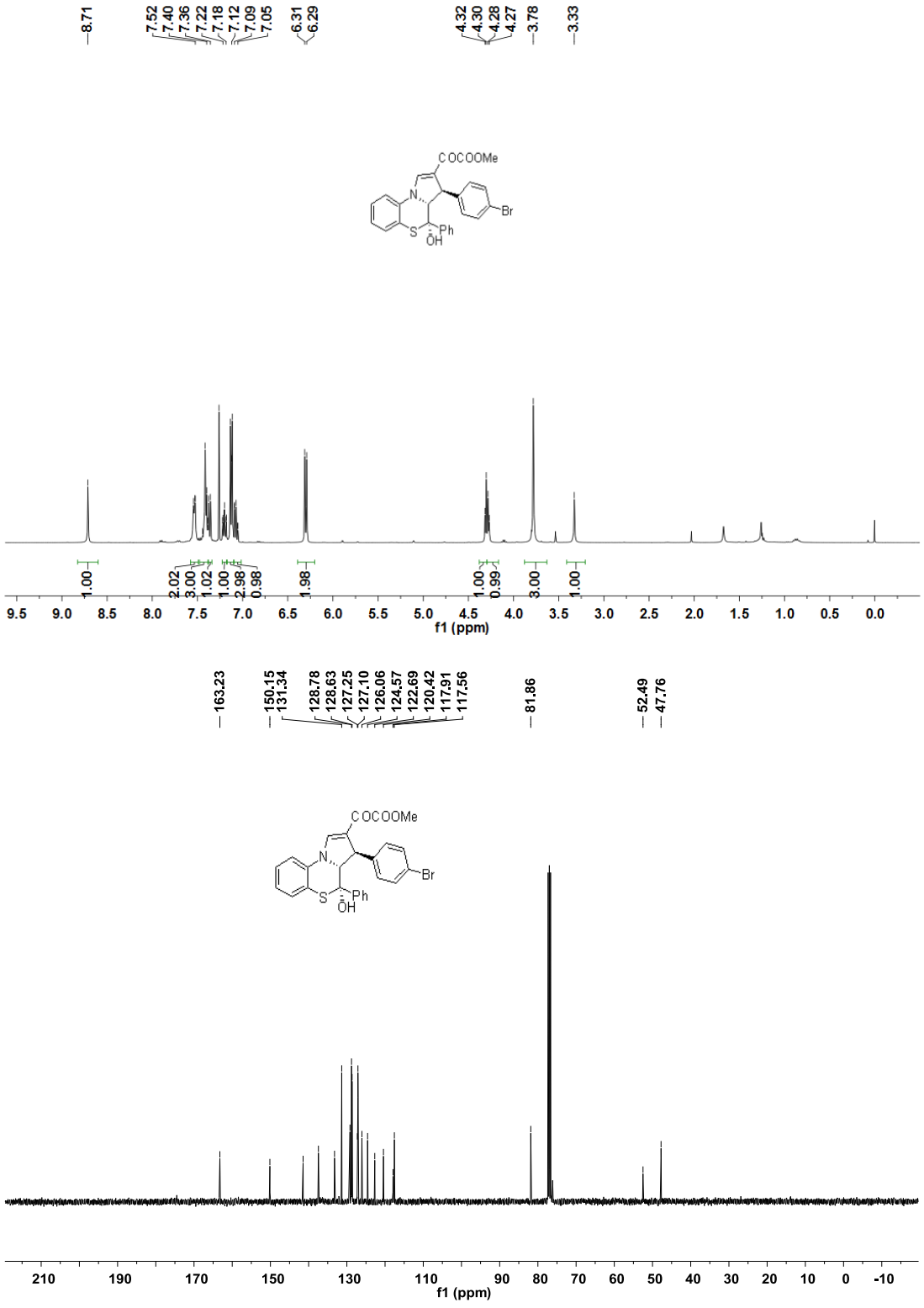

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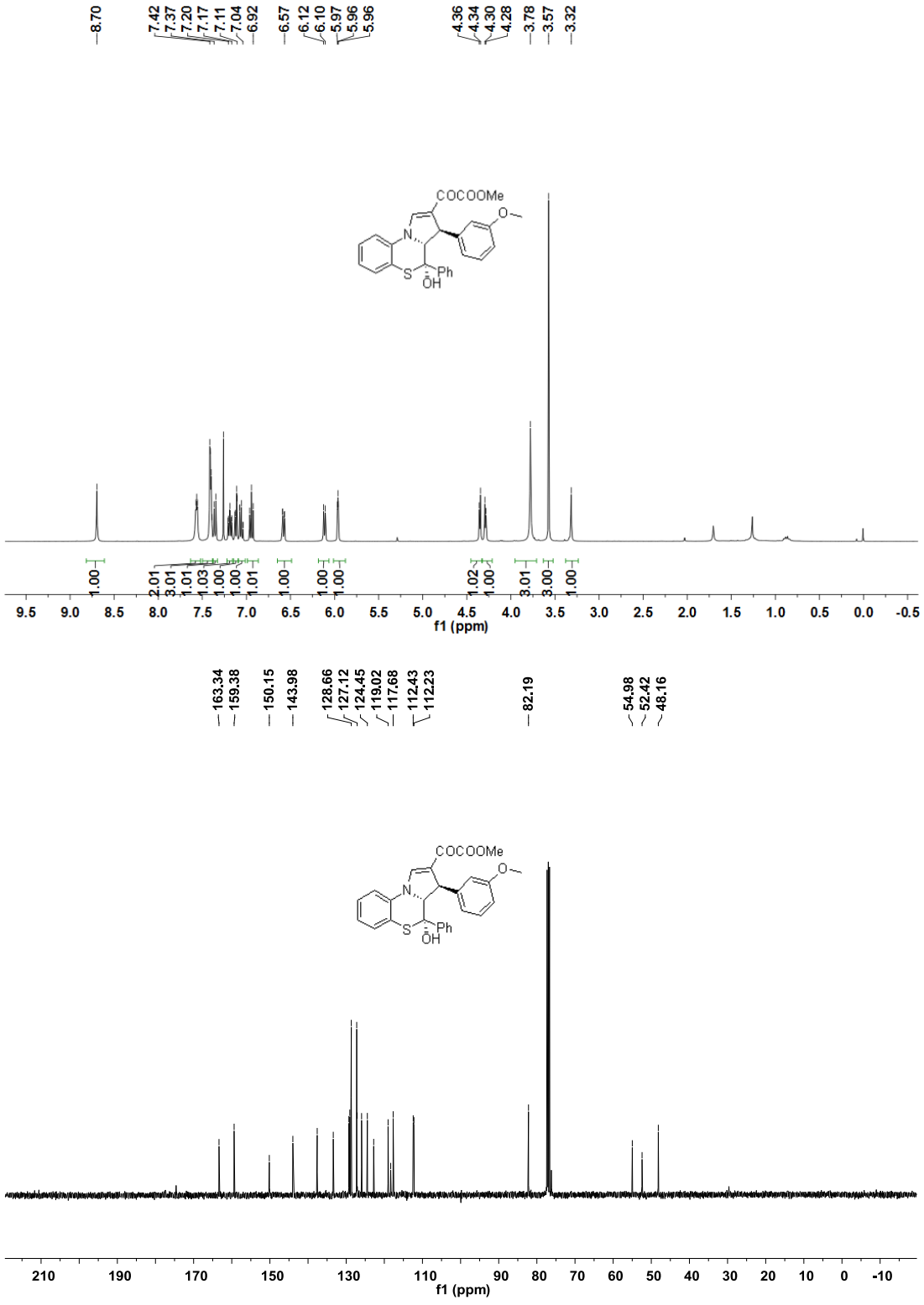

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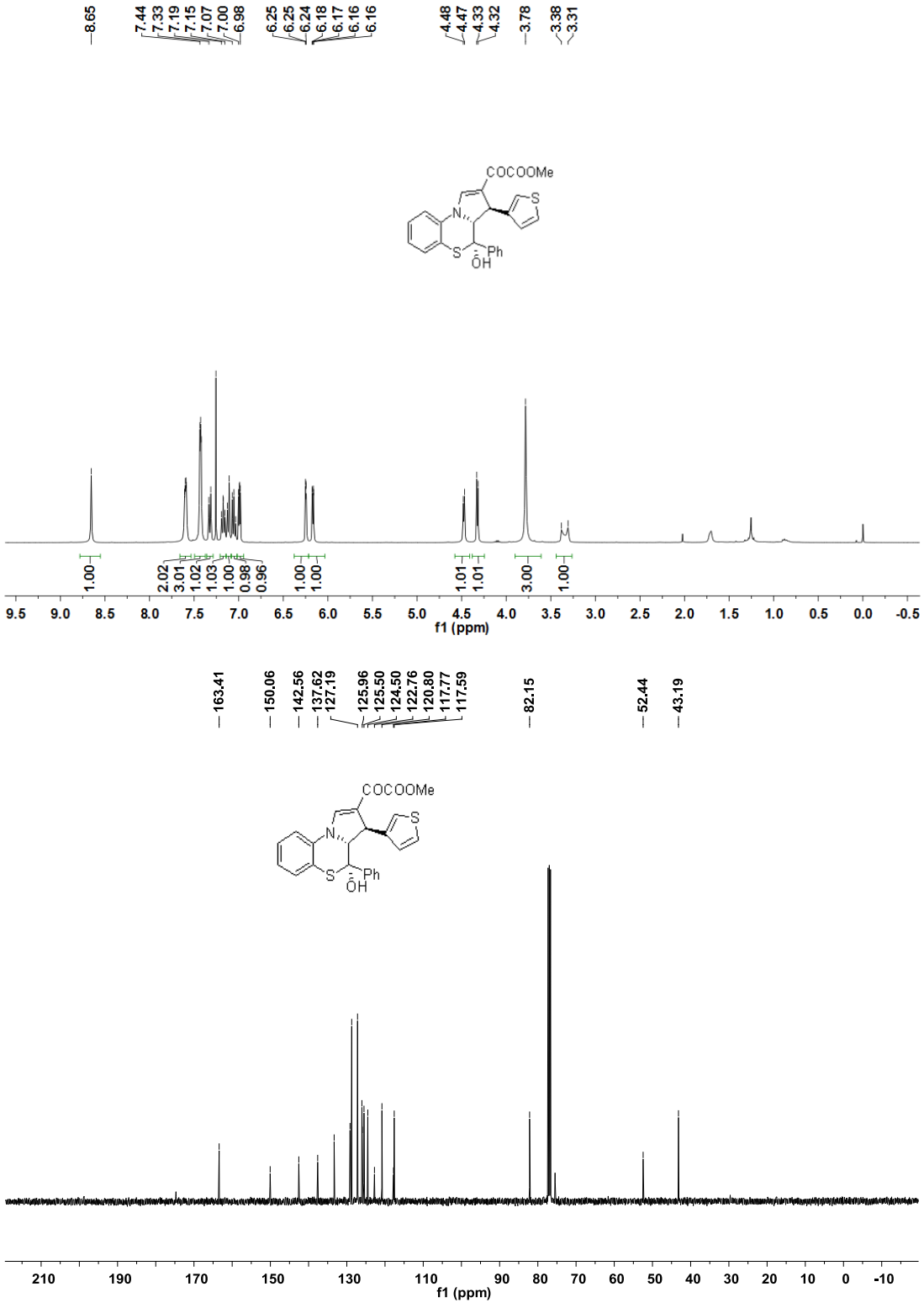

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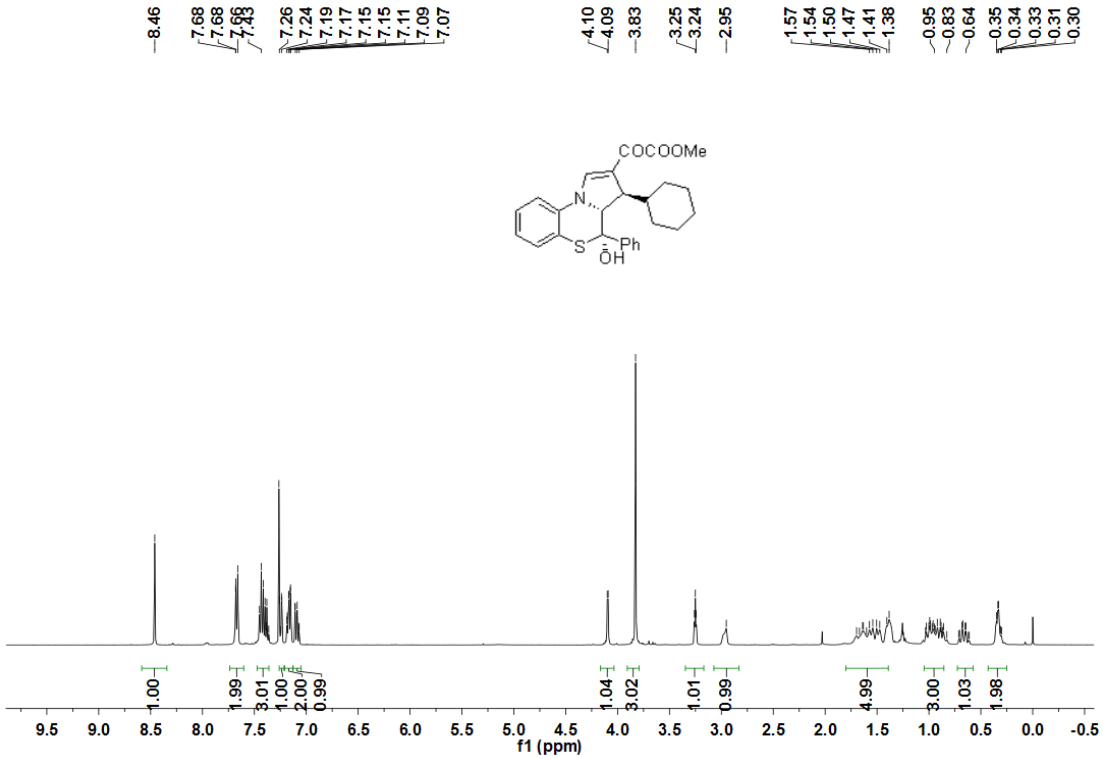

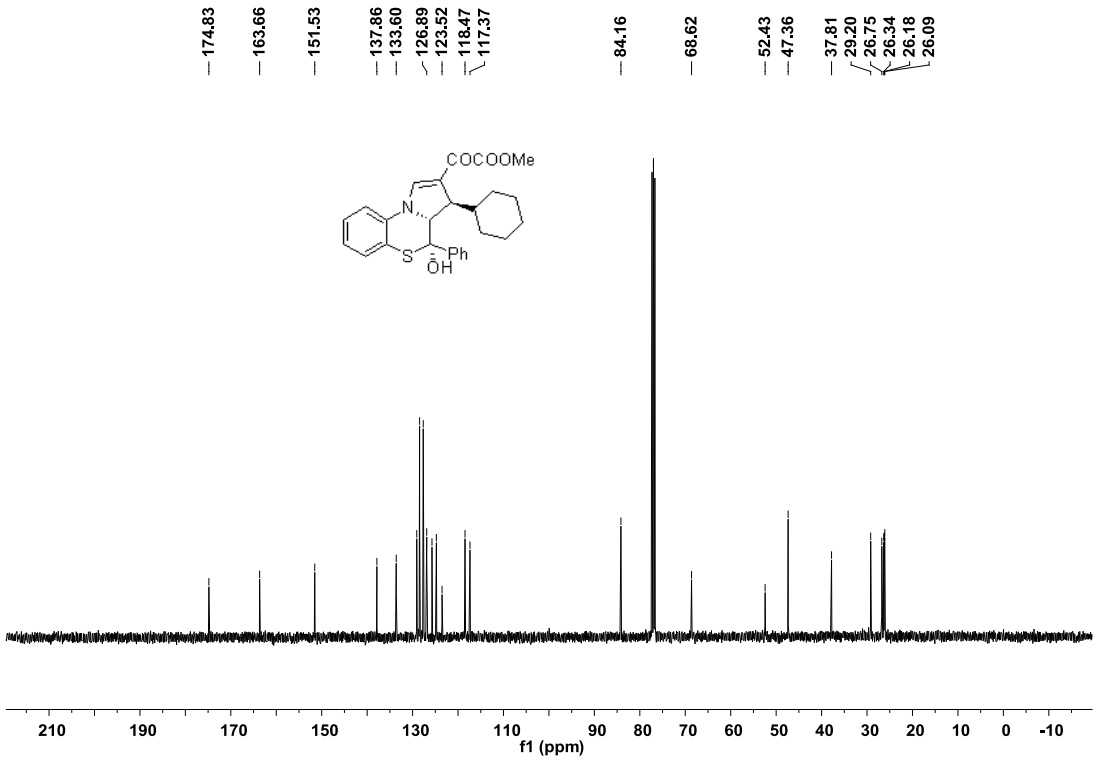

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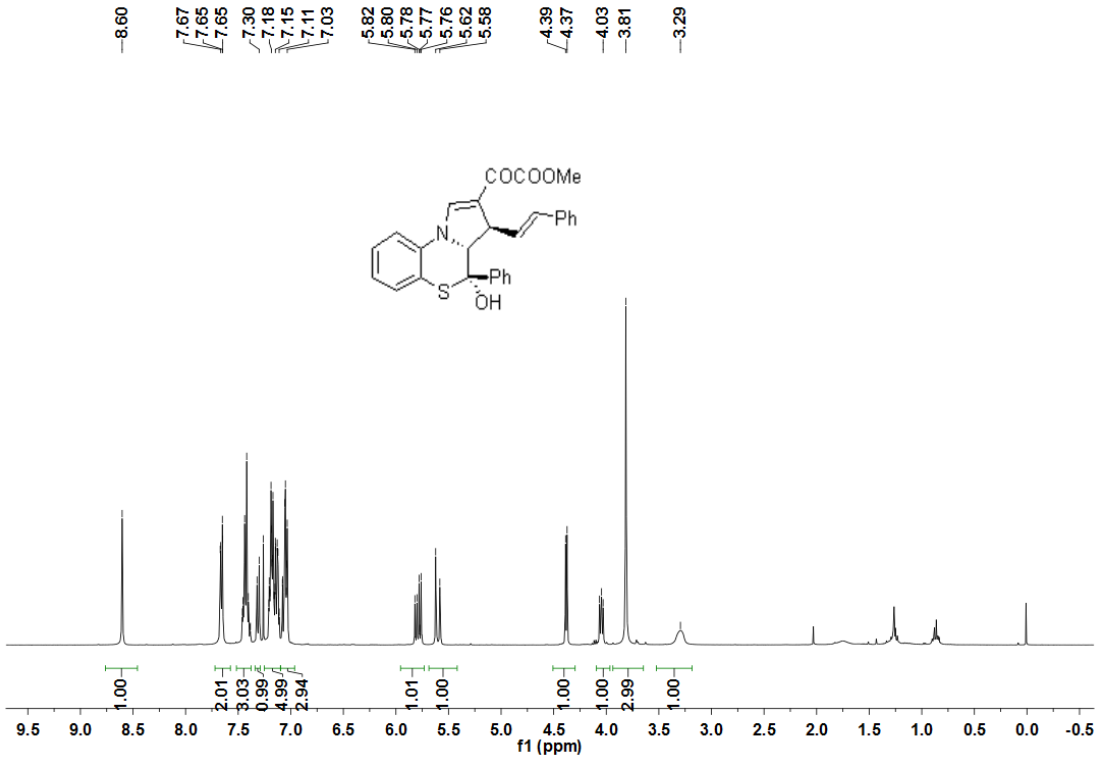

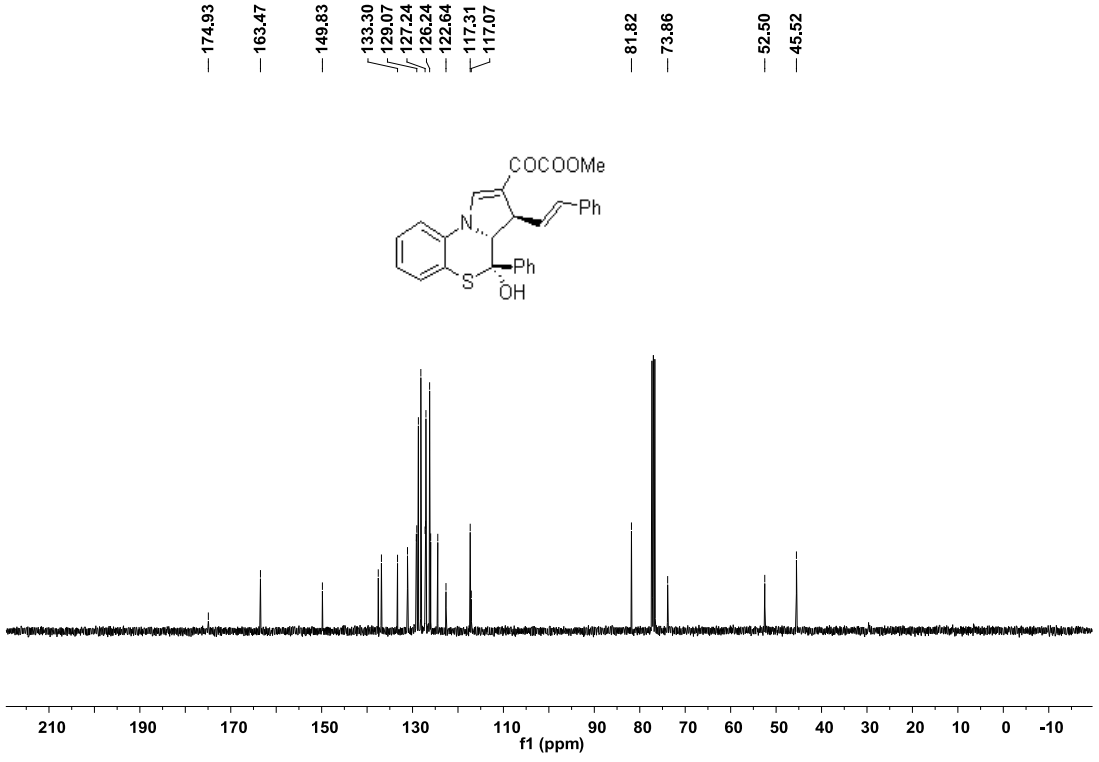

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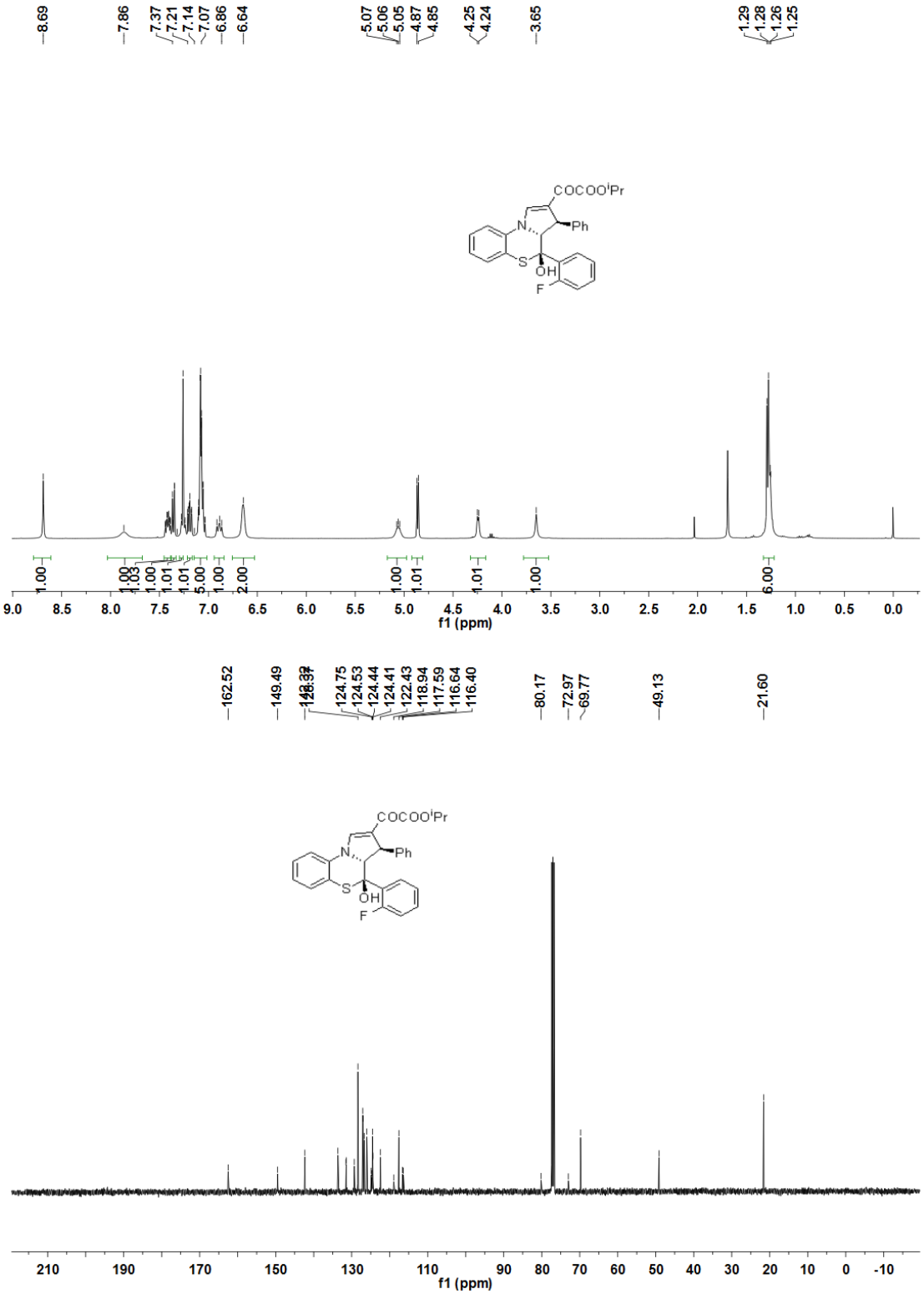

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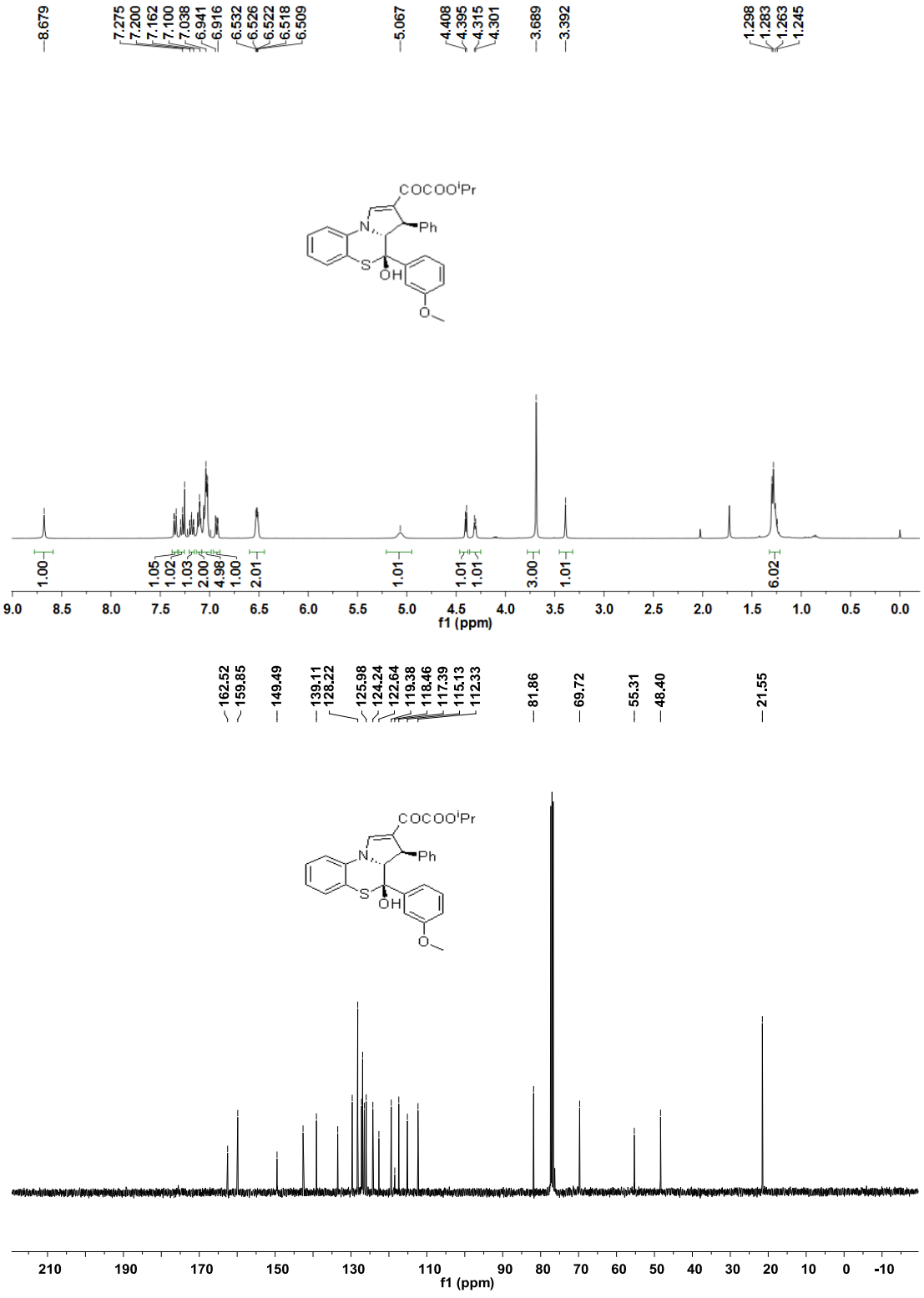
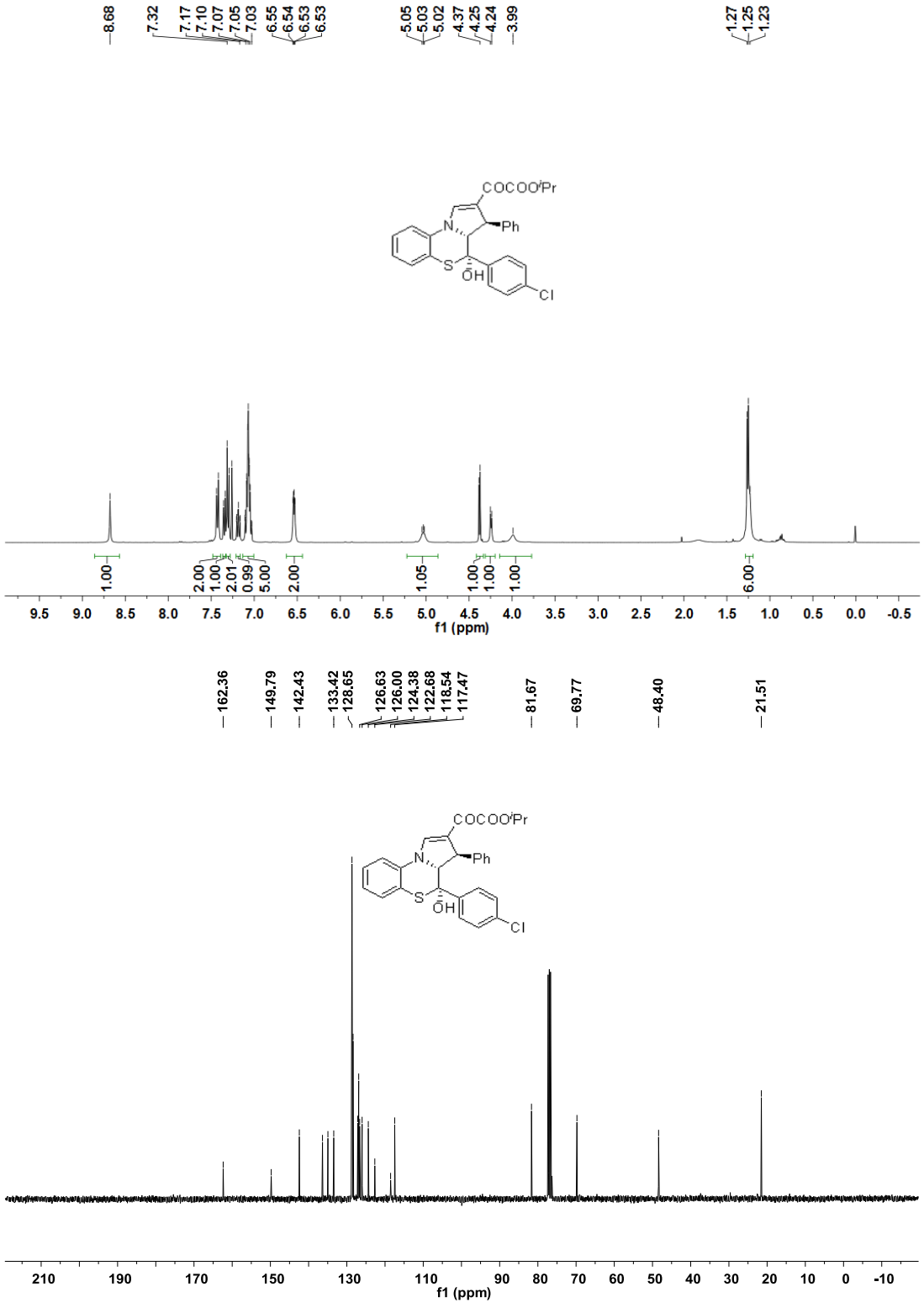
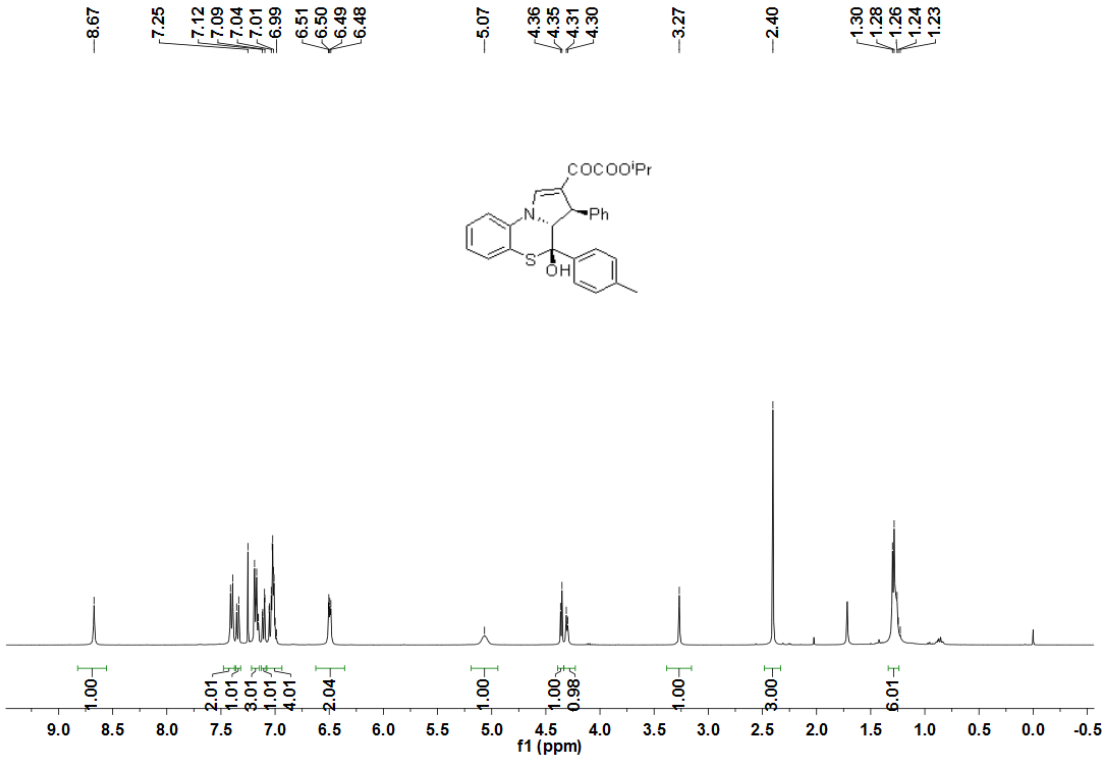
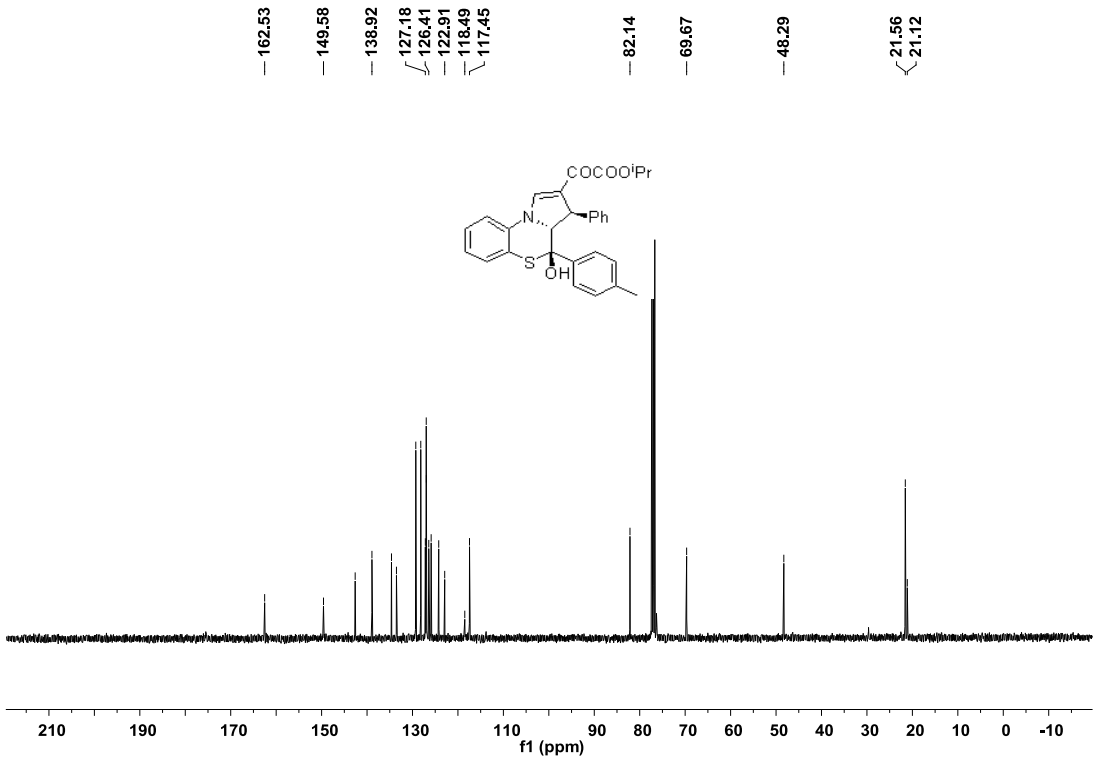


Compound 7cd



Compound 7ce





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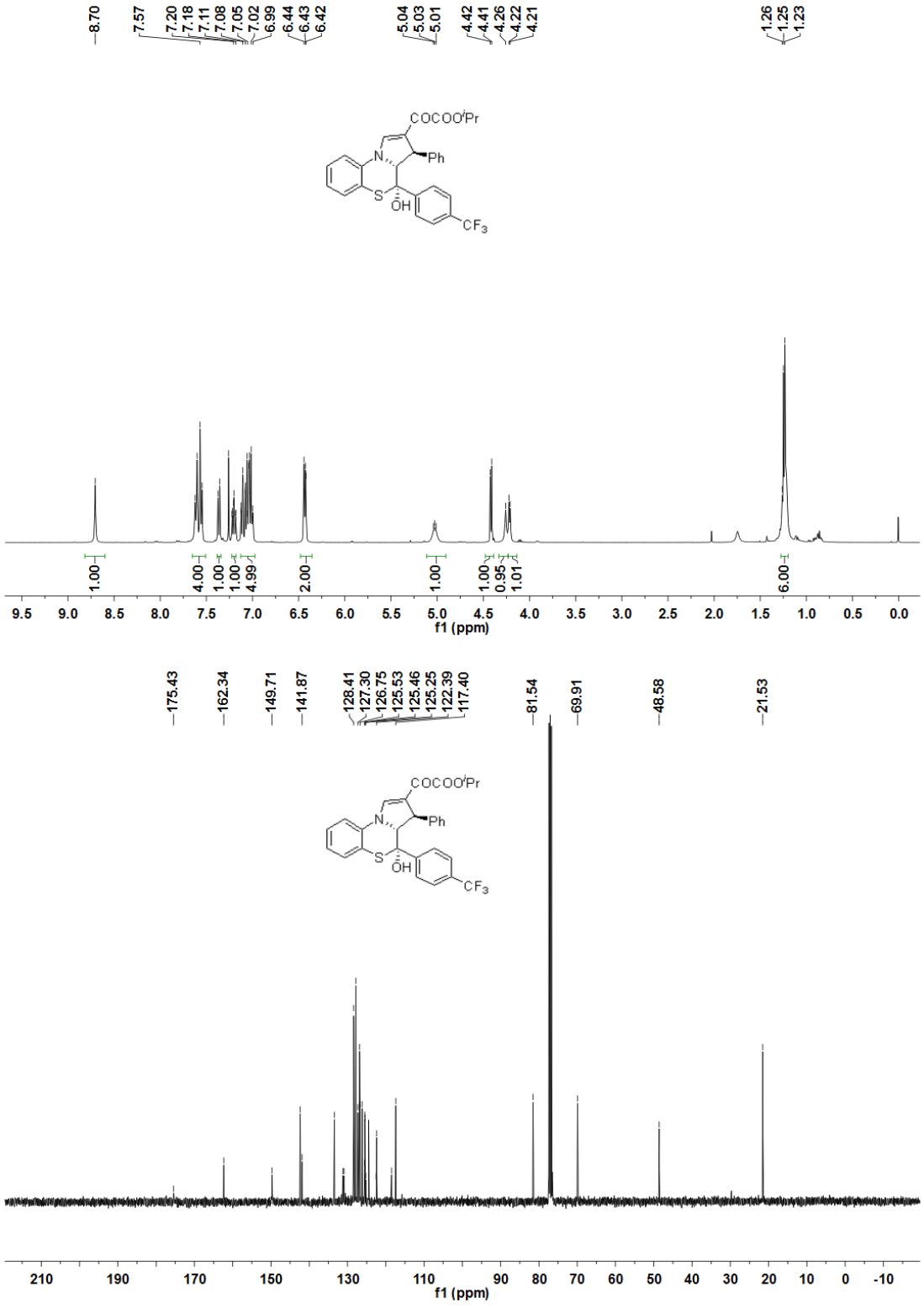

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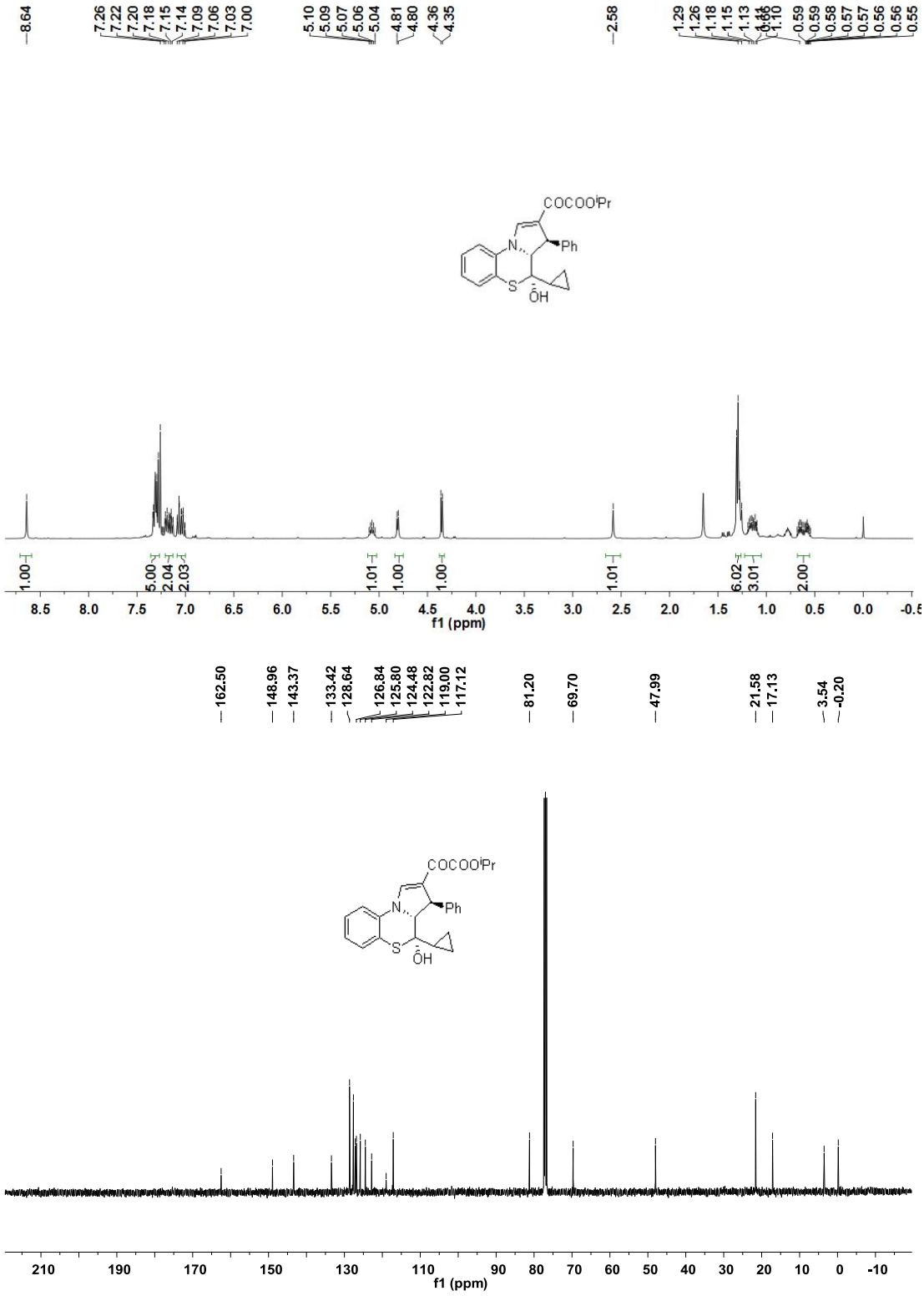
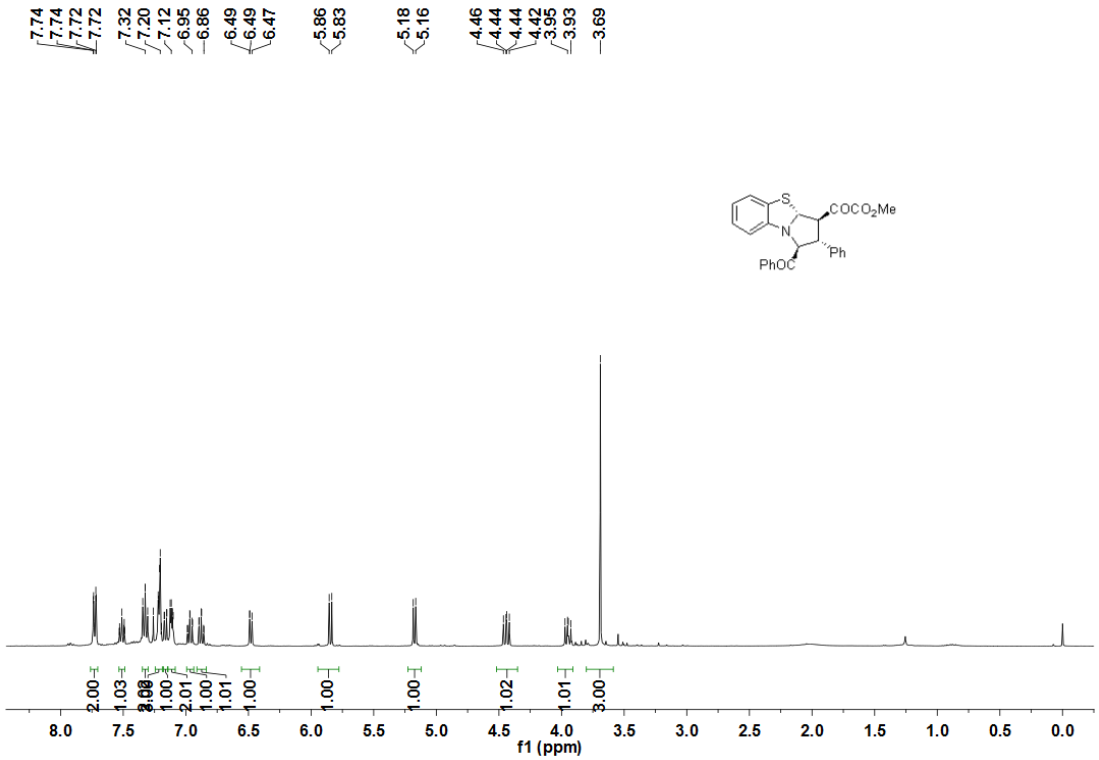


Compound 8a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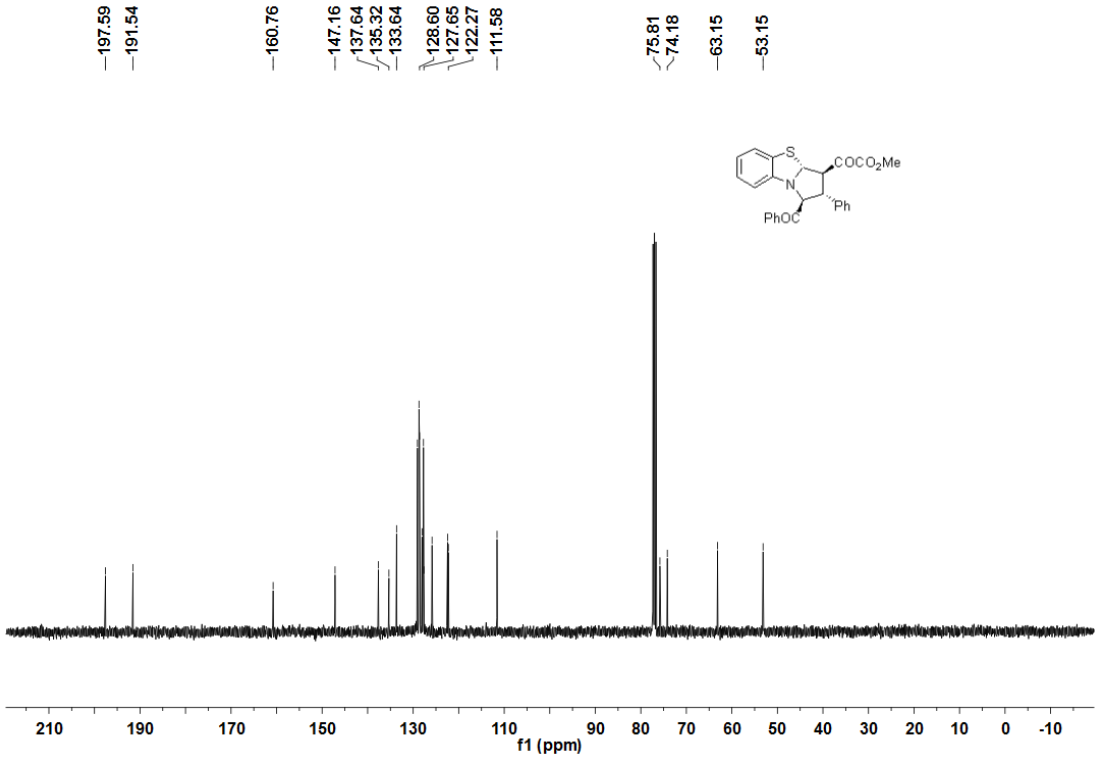
7.74
7.72
7.72
7.32
7.20
7.12
6.95
6.86
6.49
6.49
6.47
5.86
5.83
5.18
5.16
4.46
4.44
4.44
4.42
3.95
3.93
3.69
COCO2Me
Ph
PhOC
2.00
1.03
1.00
2.01
1.00
1.01
1.00
1.00
1.00
1.02
1.01
3.00
f1 (ppm)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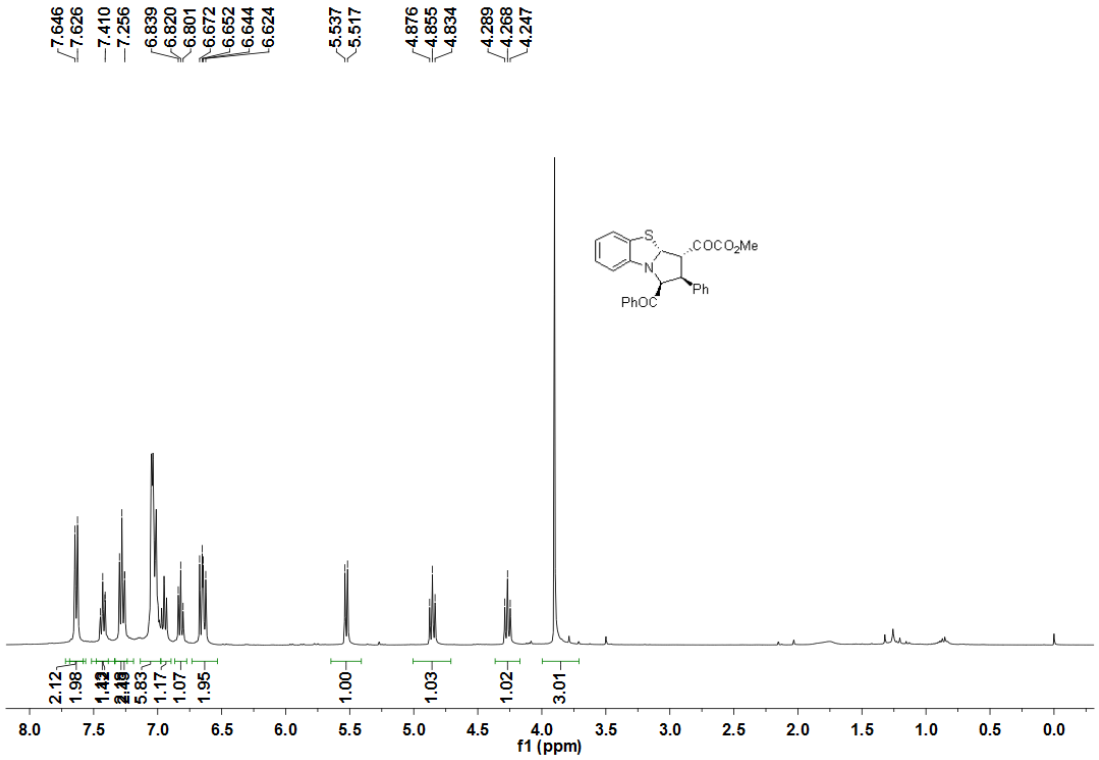
191.54
160.76
147.16
137.64
135.32
133.64
128.60
127.65
122.27
111.58
75.81
74.18
63.15
53.15
COCO2Me
Ph
PhOC
f1 (ppm)

Compound 8b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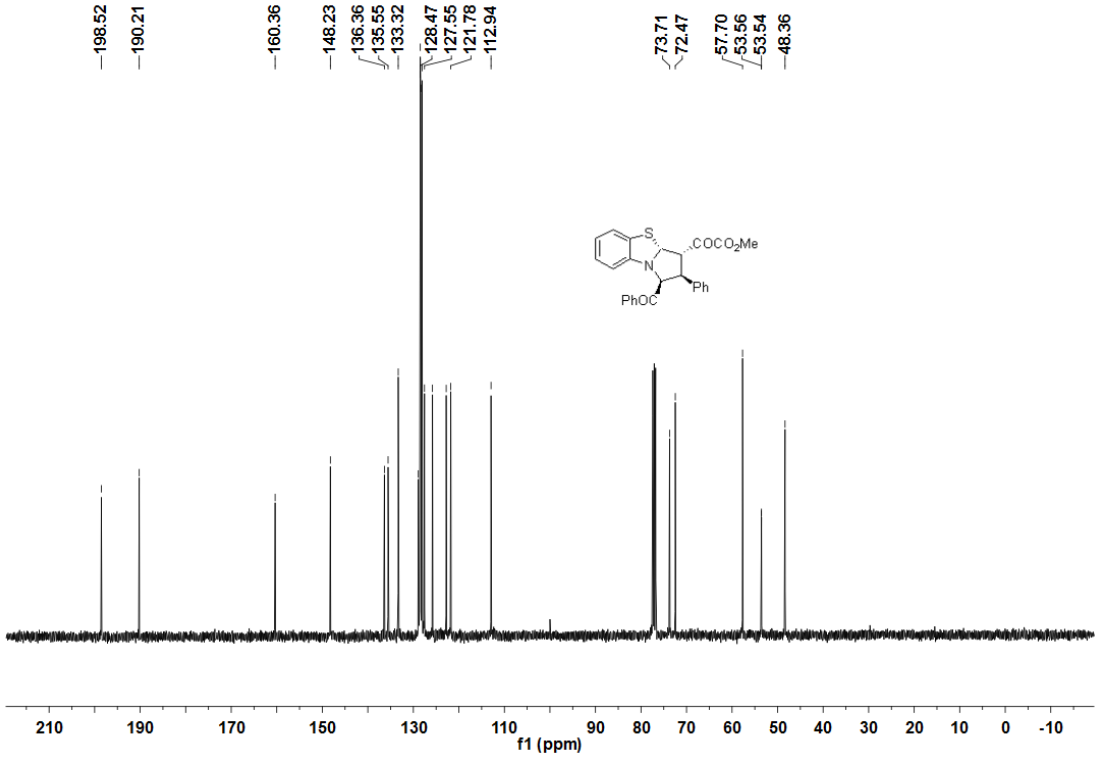
6.820
6.801
6.672
6.652
6.644
6.624
5.537
5.517
4.876
4.855
4.834
4.289
4.268
4.247
COCO2Me
Ph
PhOC
2.12
1.98
5.83
1.17
1.07
1.95
1.00
1.03
1.02
3.01
f1 (ppm)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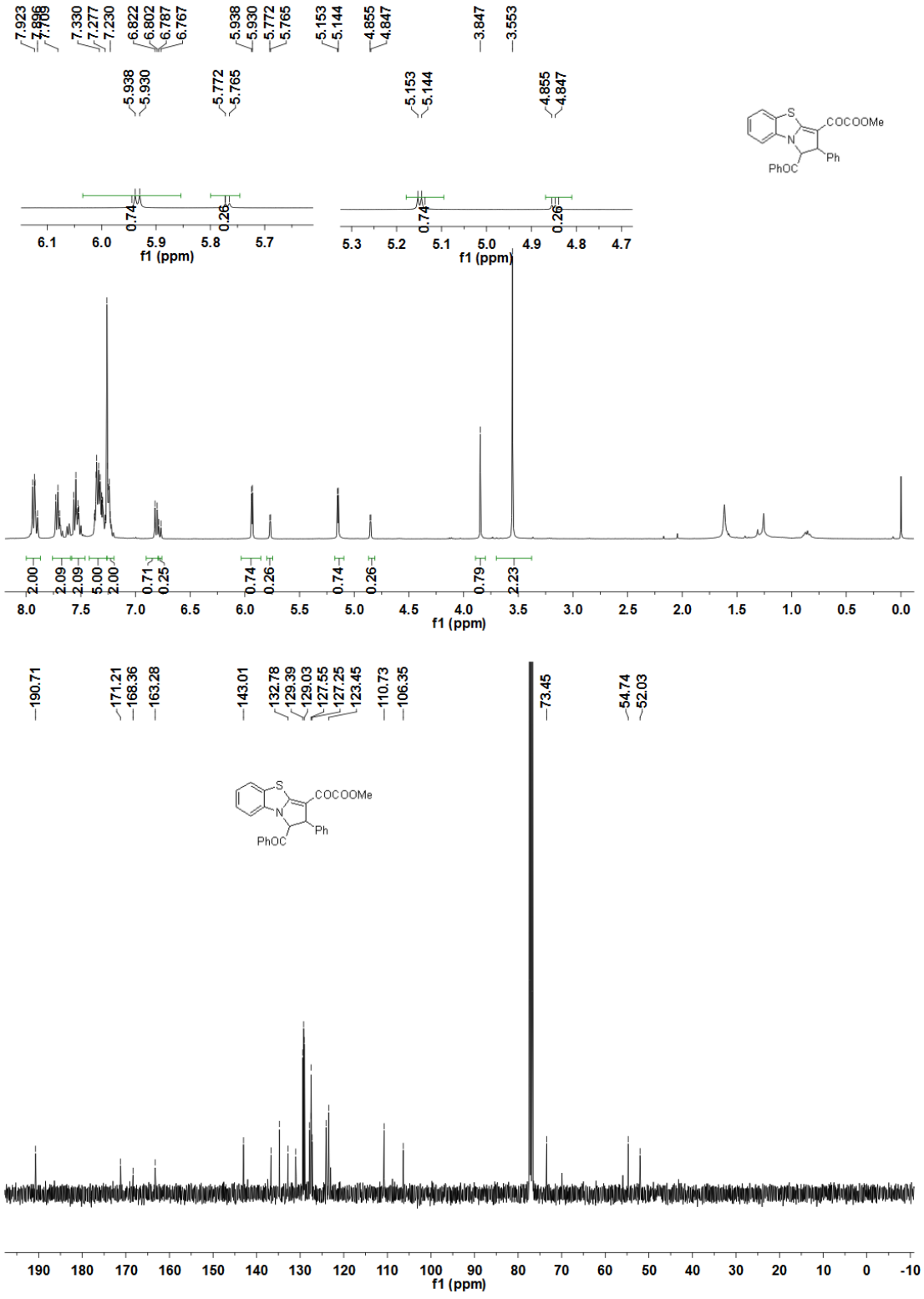
136.36
135.55
133.32
128.47
127.55
121.78
112.94
73.71
72.47
57.70
53.56
53.54
48.36
COCO2Me
Ph
PhOC
f1 (ppm)

Compound 8c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5.772
5.765
5.153
5.144
4.855
4.847
3.847
3.553
COCOOMe
Ph
PhOC
f1 (ppm)
2.00
2.09
2.09
5.00
2.00
0.71
0.25
0.74
0.26
0.74
0.26
0.79
2.23
190.71
171.21
168.36
163.28
143.01
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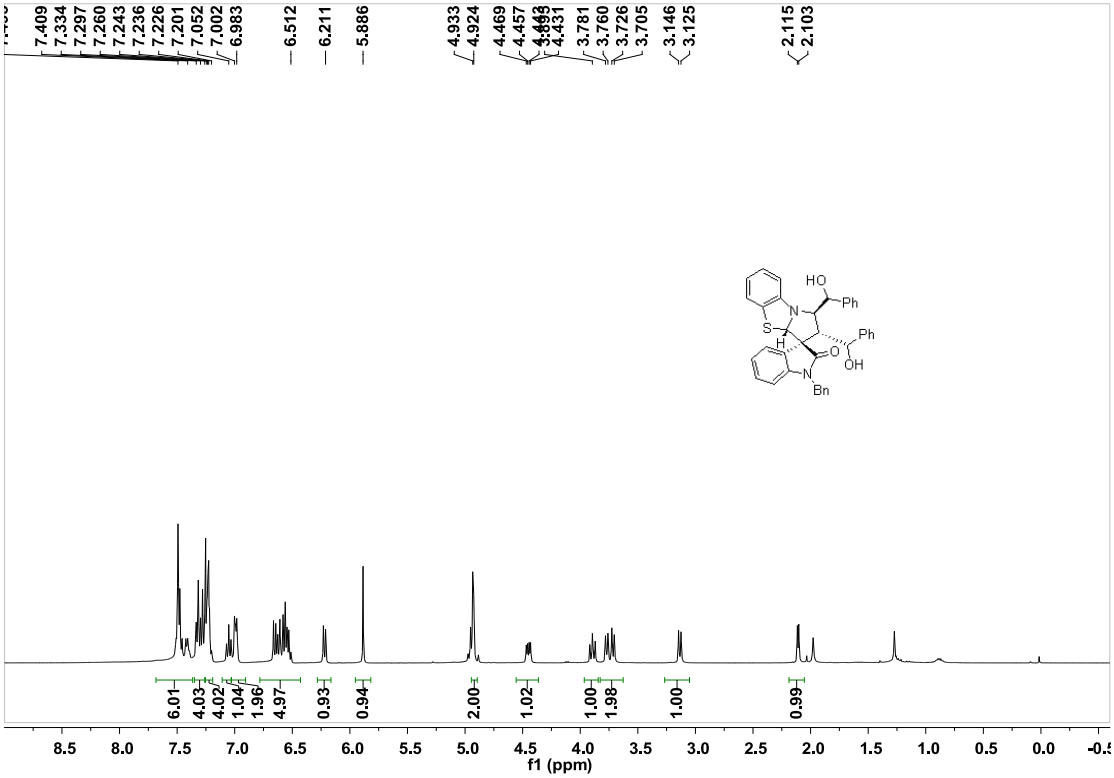
123.45
110.73
106.35
73.45
54.74
52.03

Compound 9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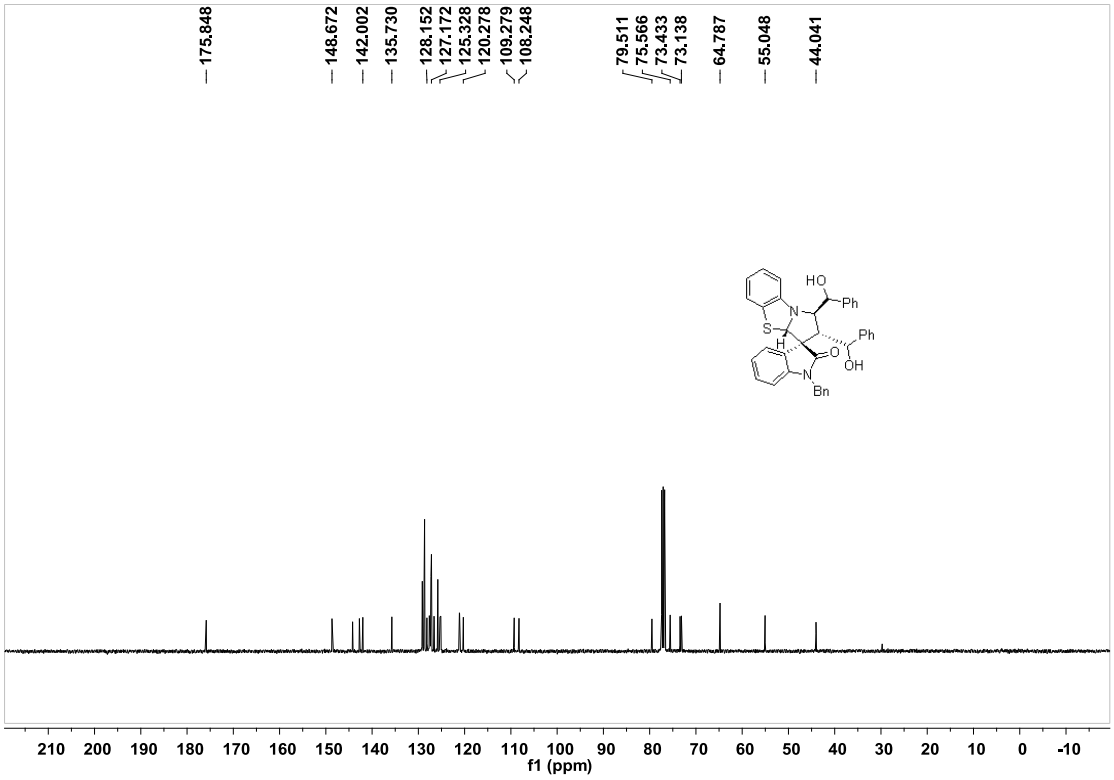
6.211
5.886
4.933
4.924
4.469
4.457
4.431
3.781
3.760
3.726
3.705
3.146
3.125
2.115
2.103
HO
Ph
Ph
OH
Bn
6.01
4.03
4.02
1.04
1.96
4.97
0.93
0.94
2.00
1.02
1.00
1.98
1.00
0.99
f1 (ppm)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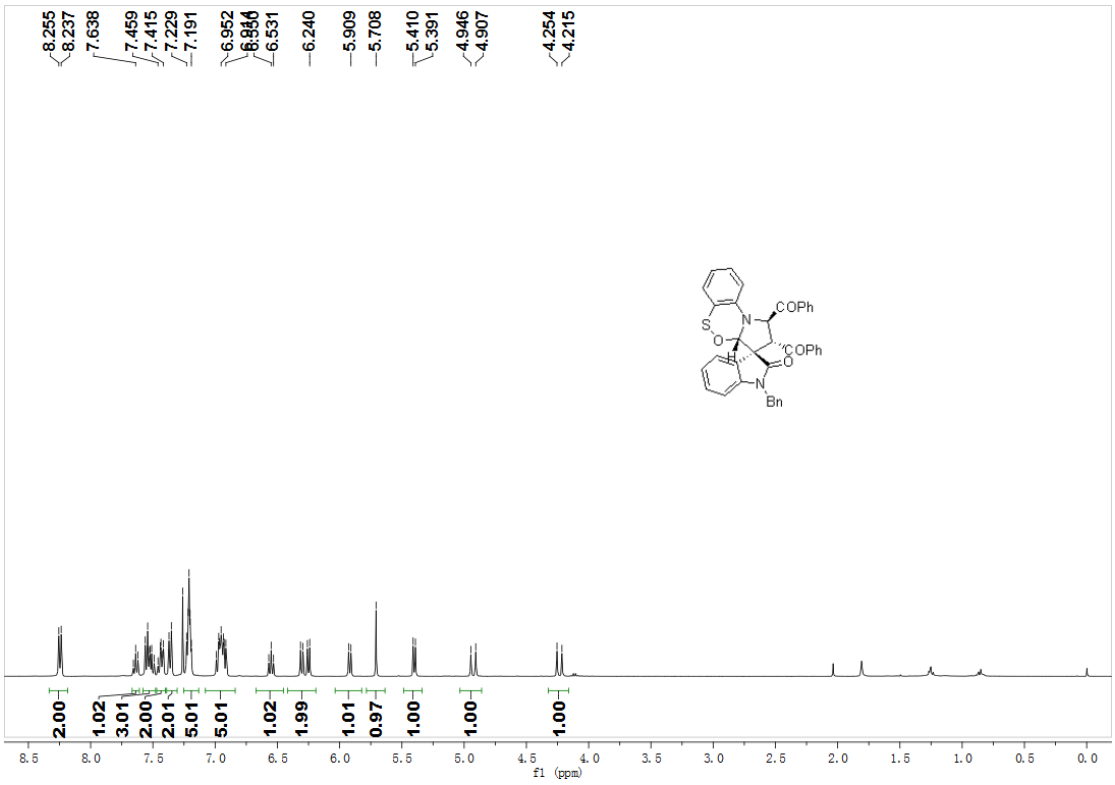
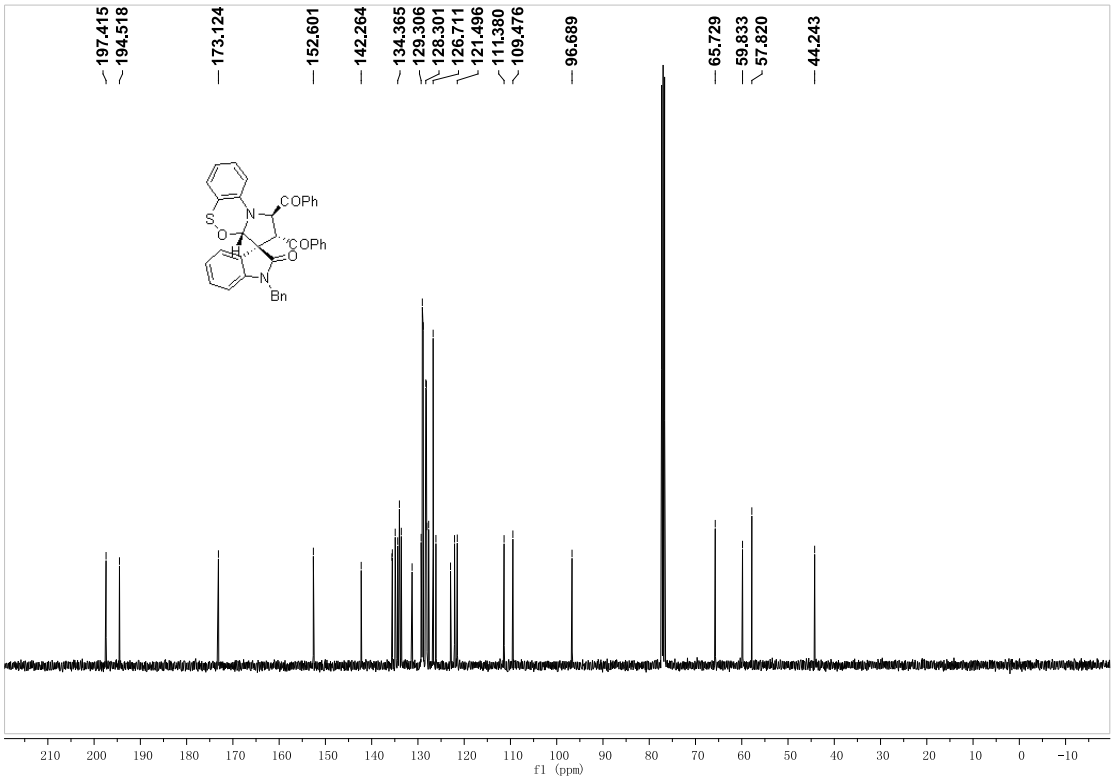
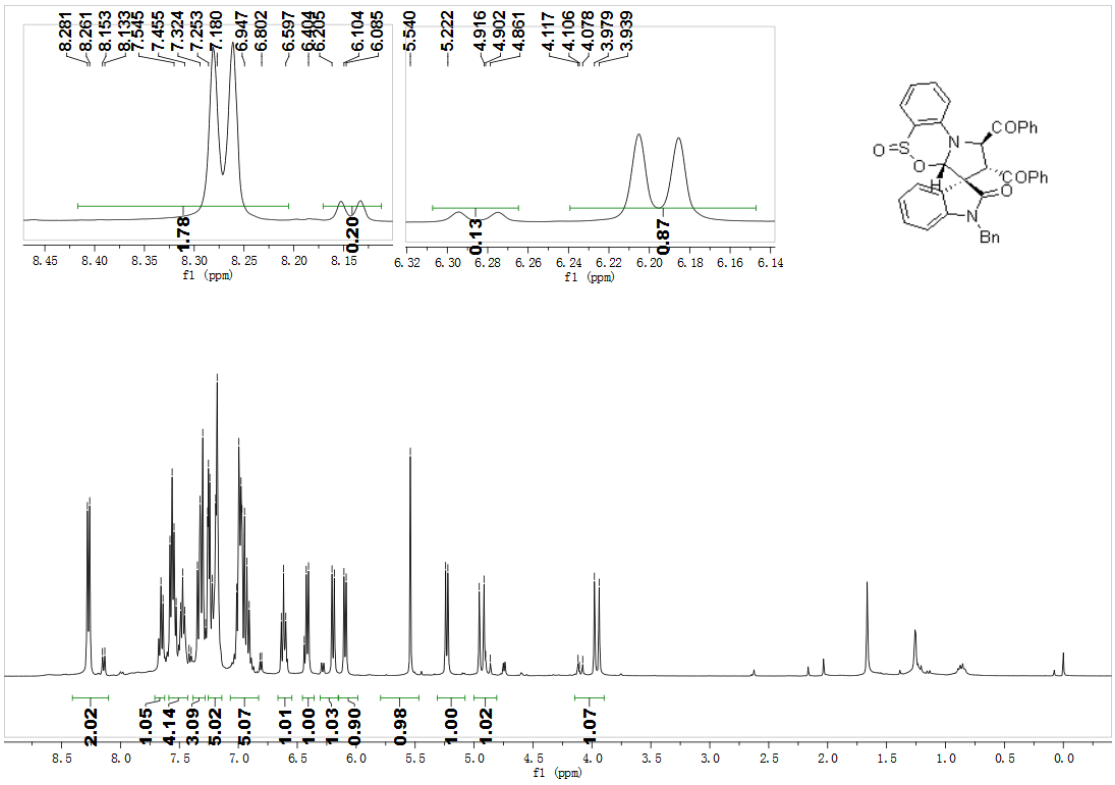
109.279
108.248
79.511
75.566
73.433
73.138
64.787
55.048
44.041
HO
Ph
Ph
OH
Bn
f1 (ppm)

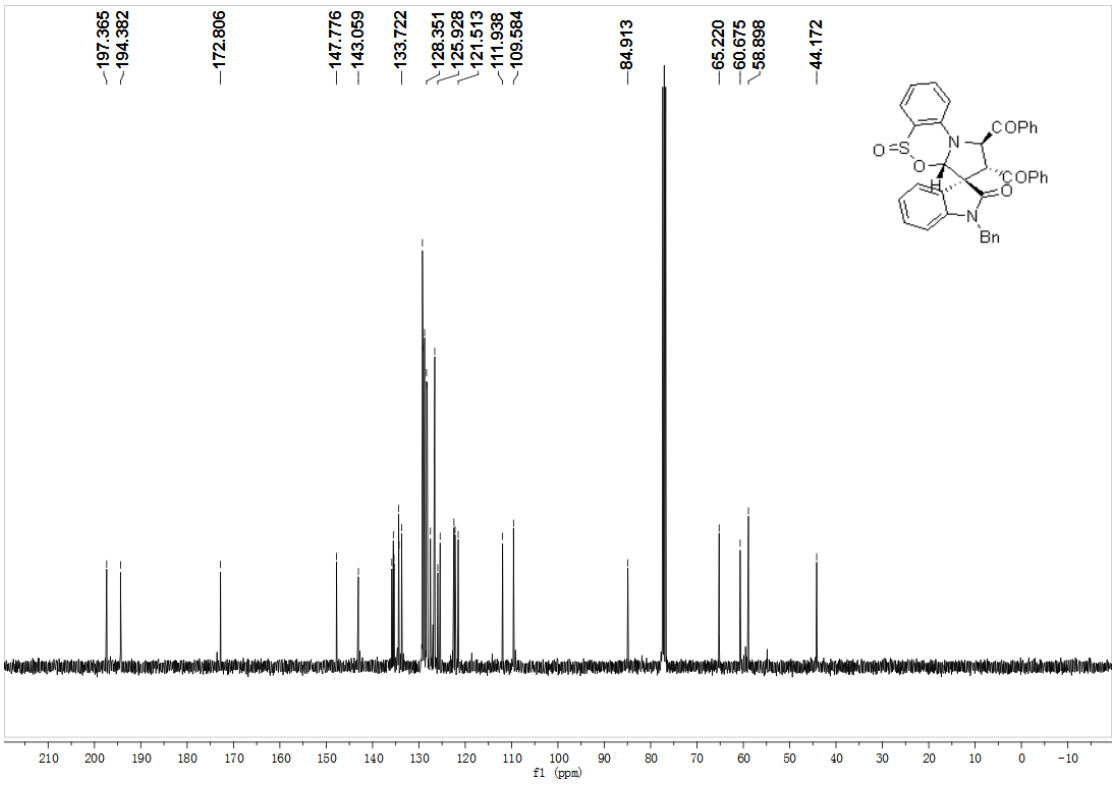
Compound 10


8.255
8.237
7.638
7.459
7.415
7.229
7.191
6.952
6.531
6.240
5.909
5.708
5.410
5.391
4.946
4.907
4.254
4.215
COPh
COPh
Bn
2.00
1.02
3.01
2.00
2.01
5.01
5.01
1.02
1.99
1.01
0.97
1.00
1.00
1.00
f1 (ppm)


197.415
194.518
173.124
152.601
142.264
134.365
129.306
128.301
126.711
121.496
111.380
109.476
96.689
65.729
59.833
57.820
44.243
COPh
COPh
Bn
f1 (ppm)

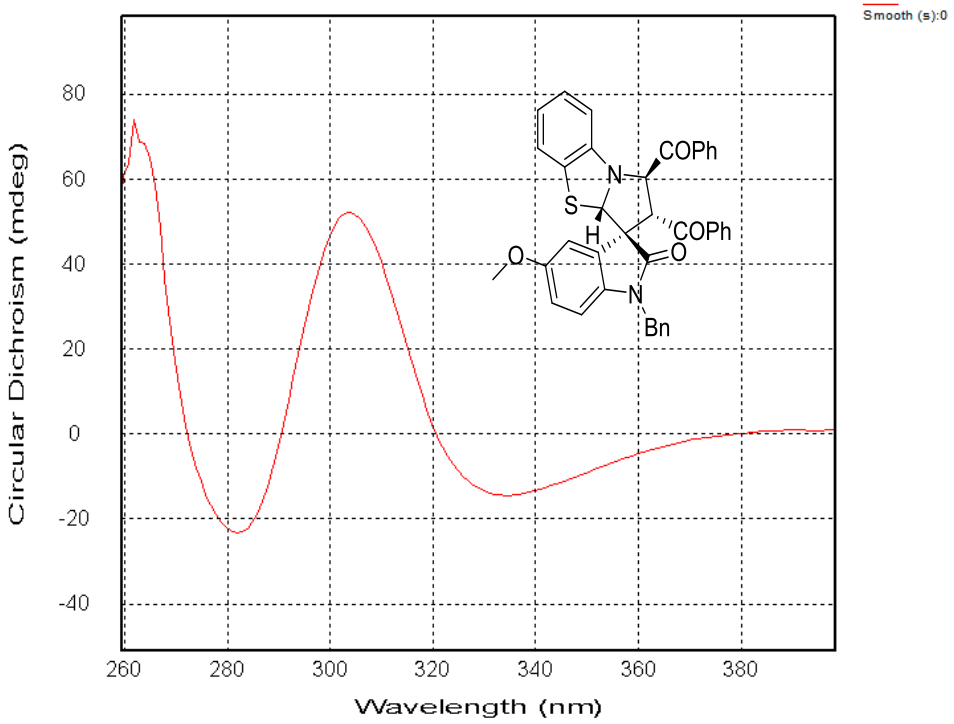
Compound 11


8.281
8.261
8.153
8.133
7.545
7.455
7.324
7.253
7.180
6.947
6.802
6.597
6.404
6.205
6.104
6.085
5.540
5.222
4.916
4.902
4.861
4.117
4.106
4.078
3.979
3.939
1.78
0.20
0.13
0.87
f1 (ppm)
COPh
COPh
Bn
2.02
1.05
4.14
3.09
5.02
5.07
1.01
1.00
1.03
0.90
0.98
1.00
1.02
1.07

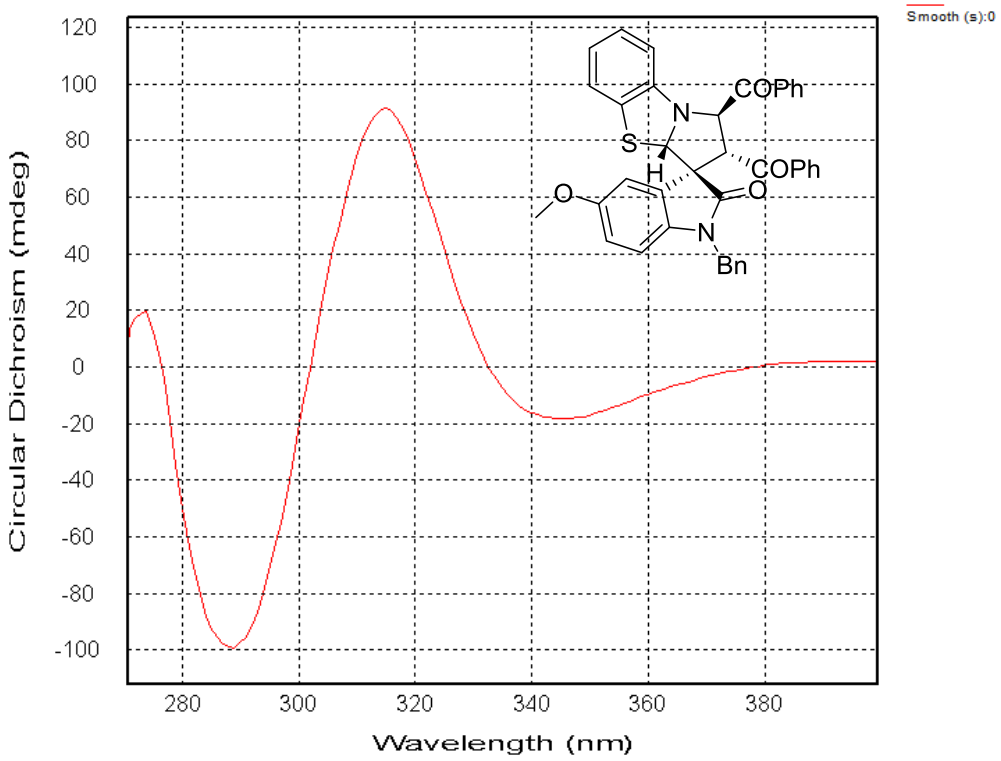

197.365
194.382
172.806
147.776
143.059
133.722
128.351
125.928
121.513
111.938
109.584
84.913
65.220
60.675
58.898
44.172
COPh
COPh
Bn
f1 (ppm)

13. CD spectra in CH_2Cl_2.

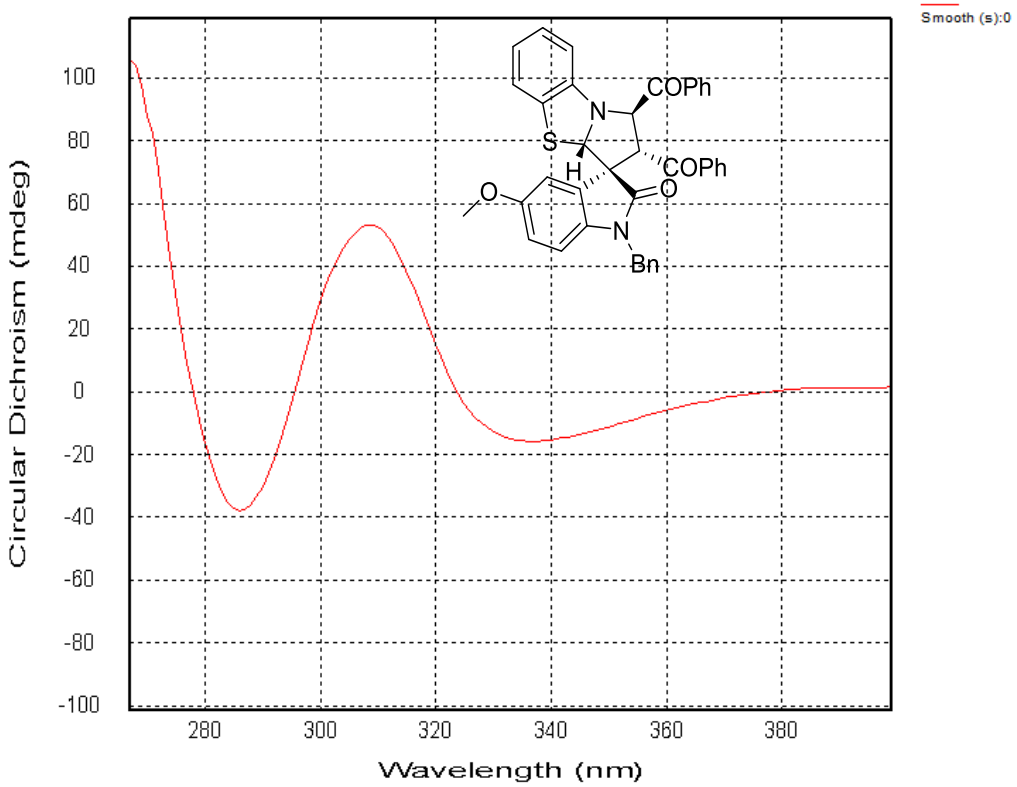
Compound 3aa



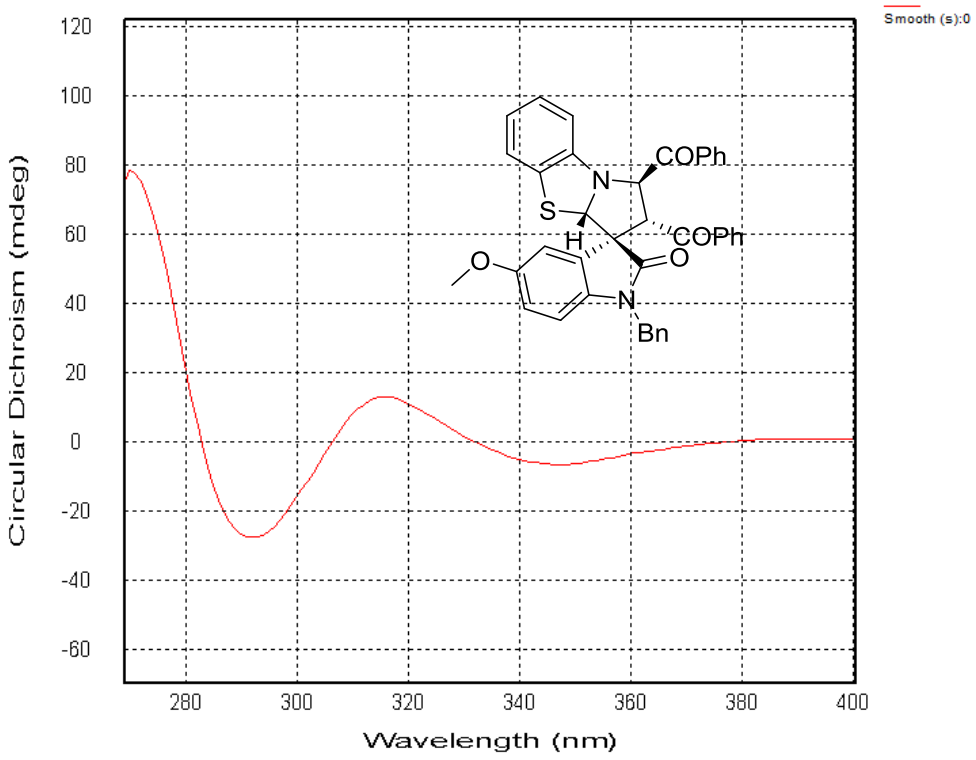
Compound 3ba



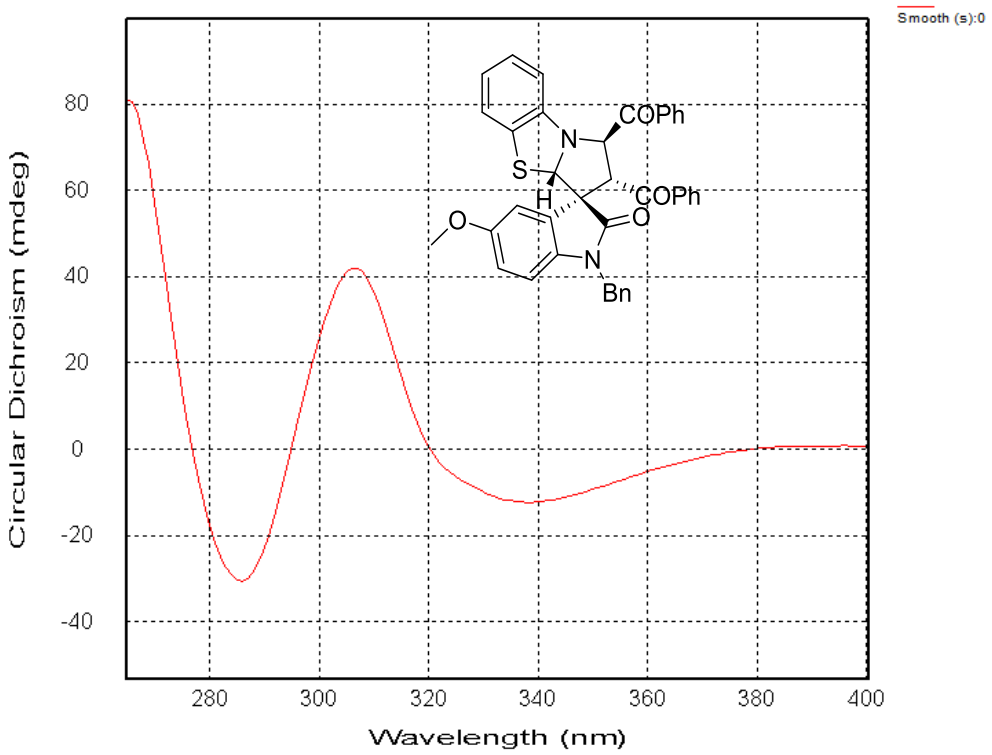
Compound 3ca



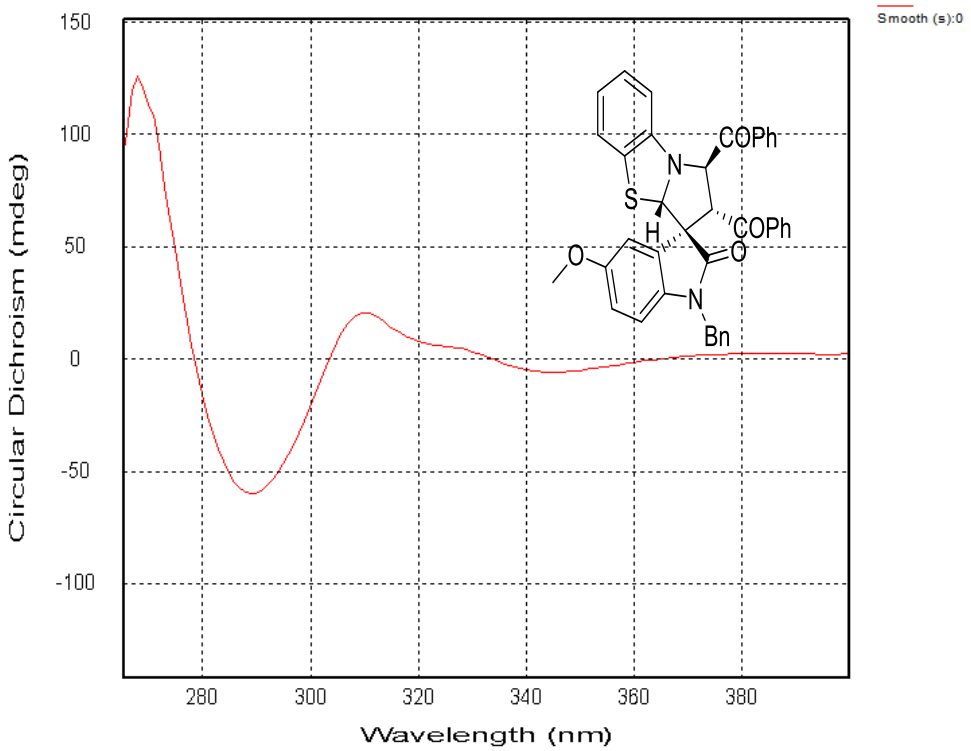
Compound 3das



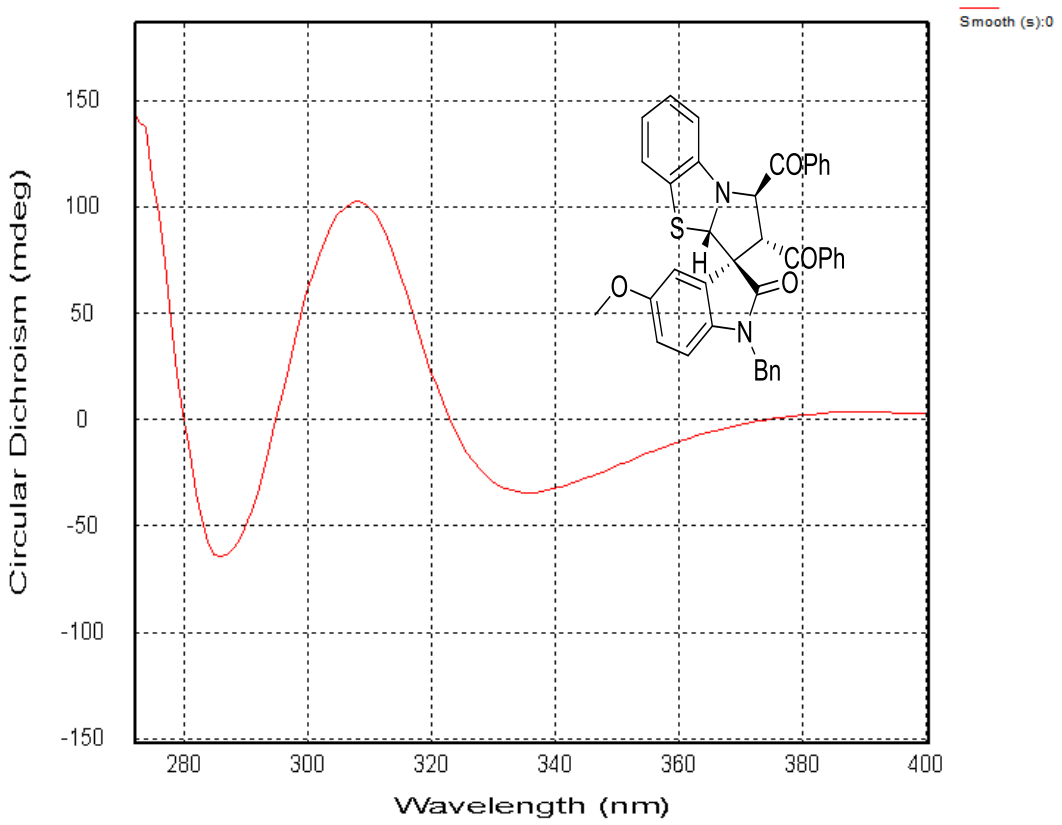
Compound 3da



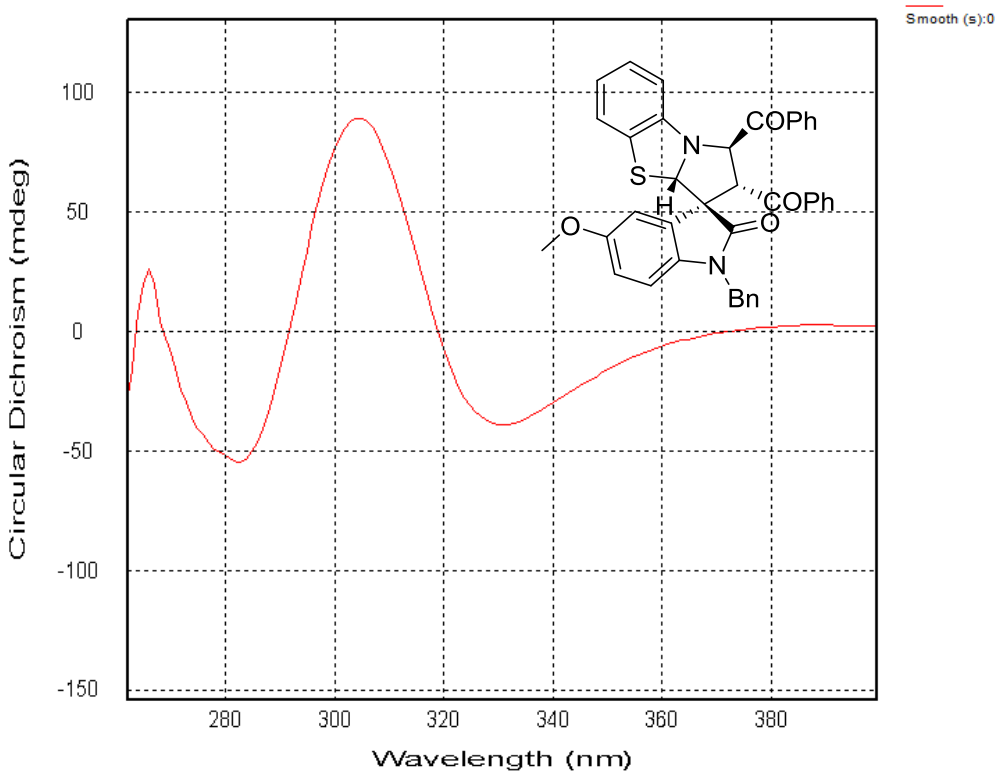
Compound 3ea



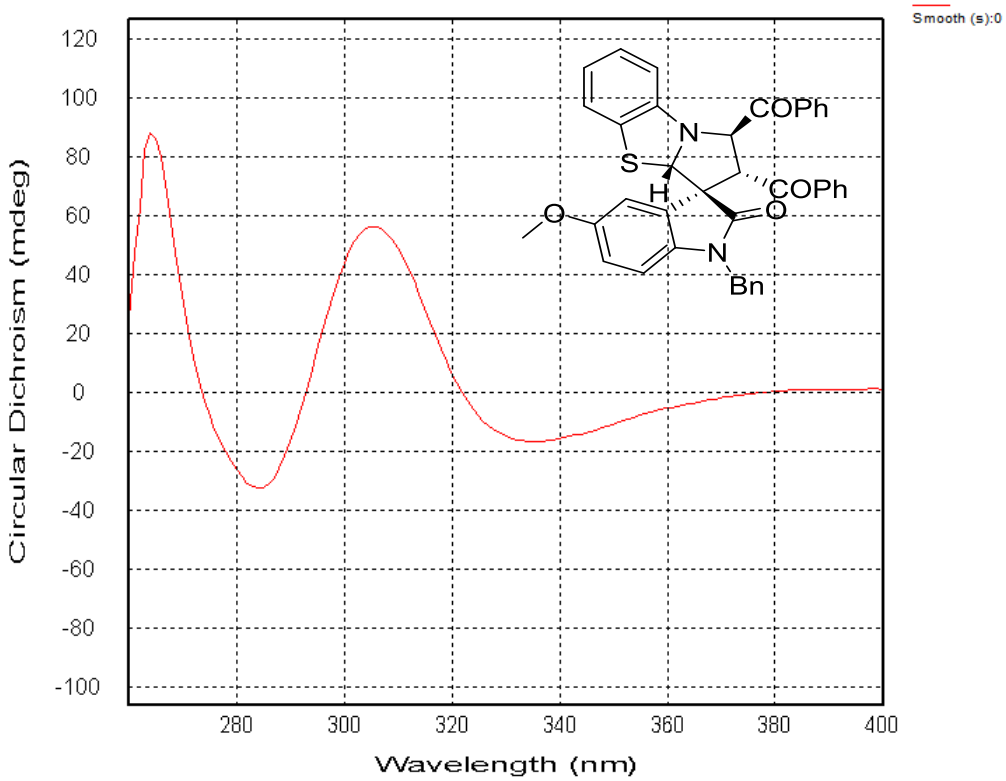
Compound 3eas



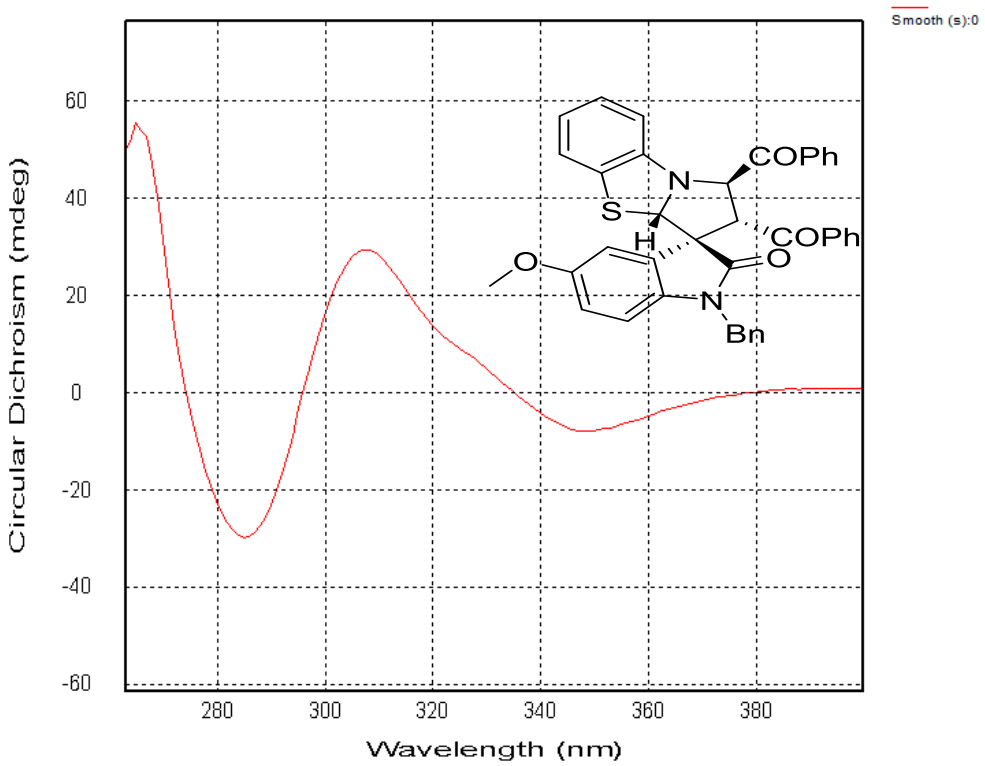
Compound 3fa



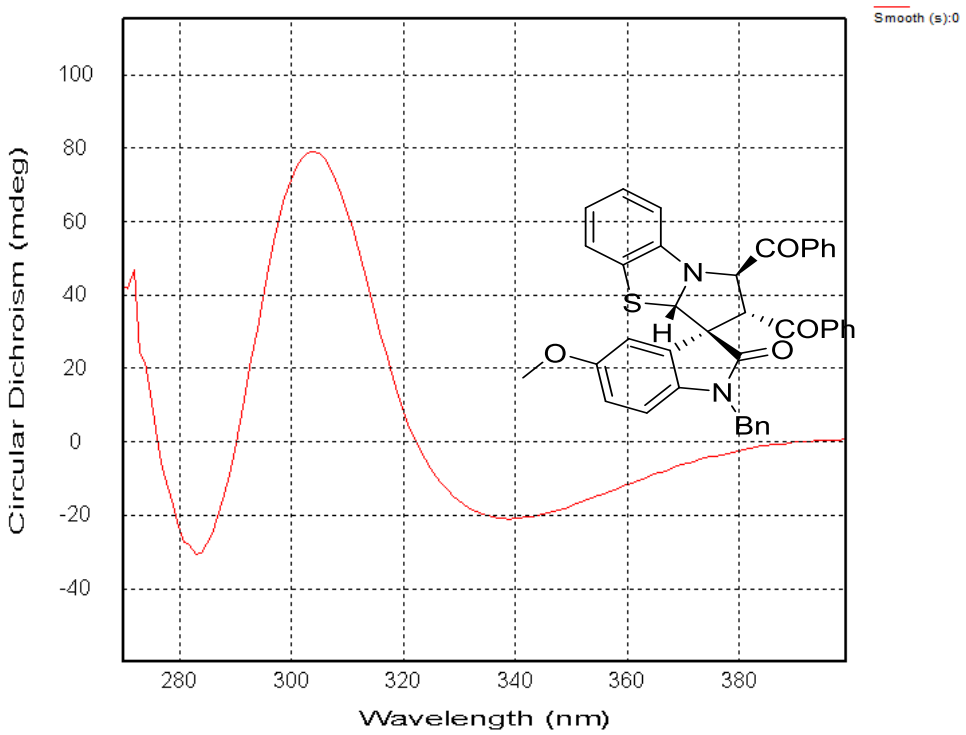
Compound 3ga



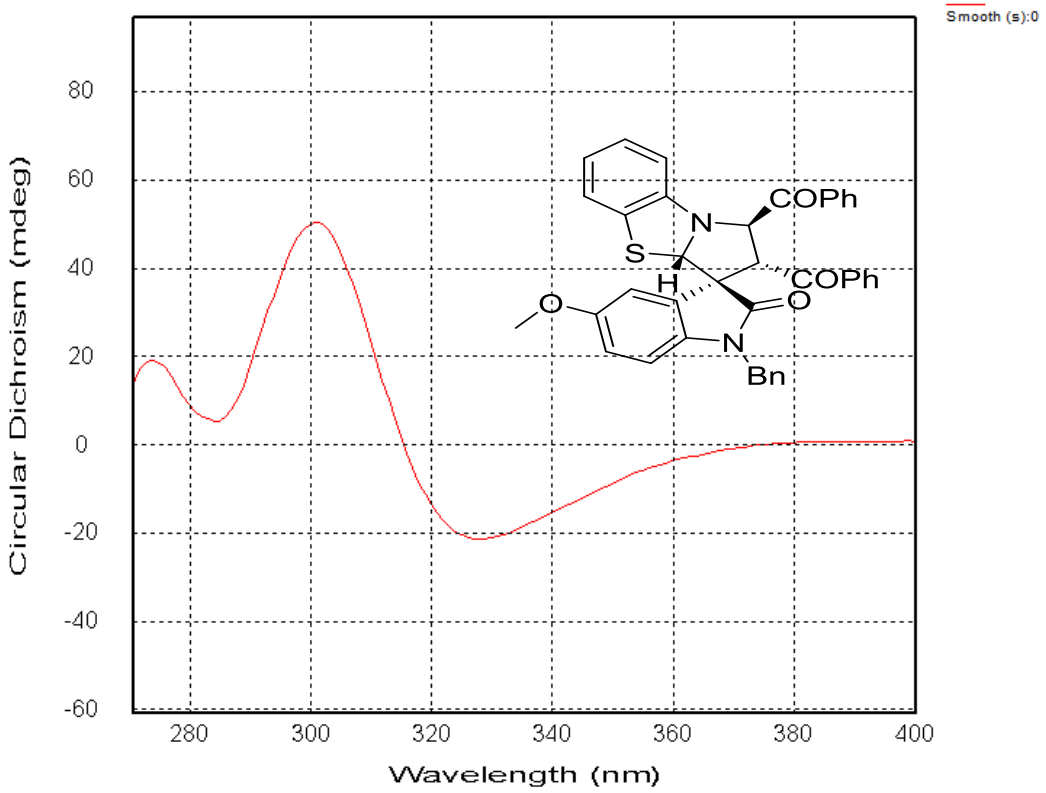
Compound 3gas



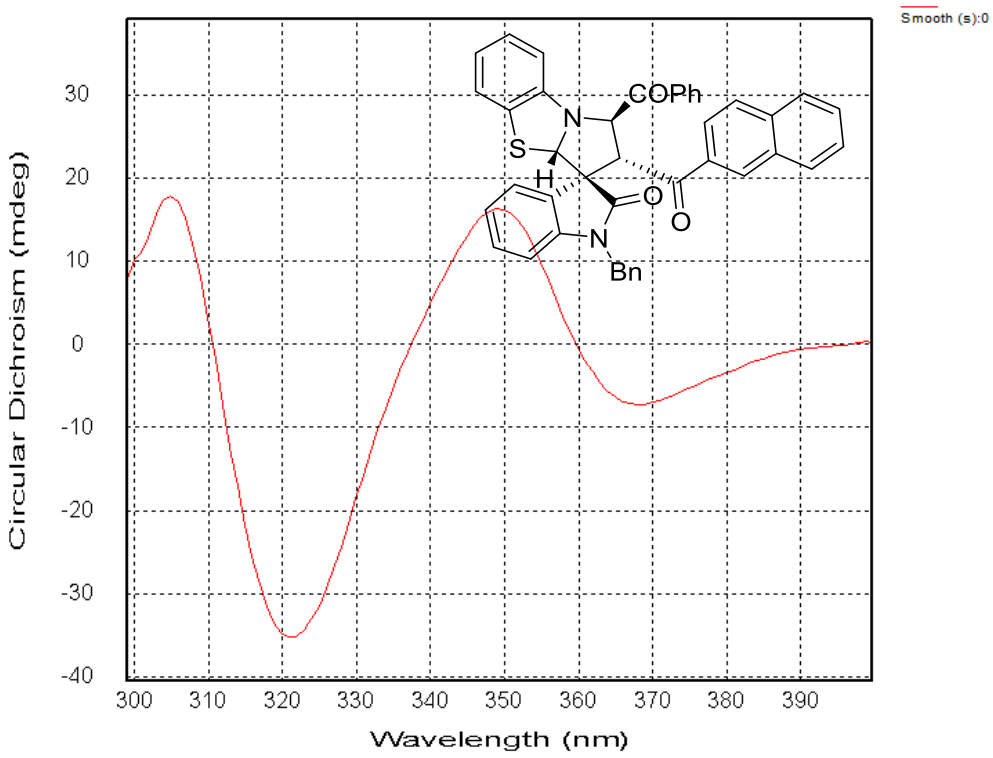
Compound 3ha



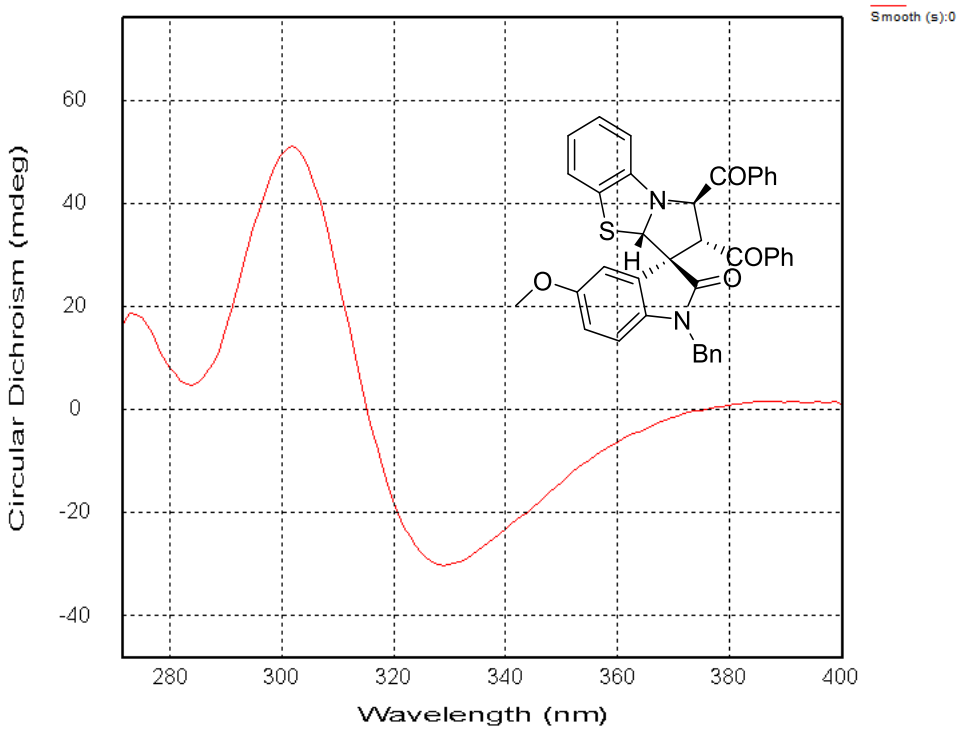
Compound 3ia



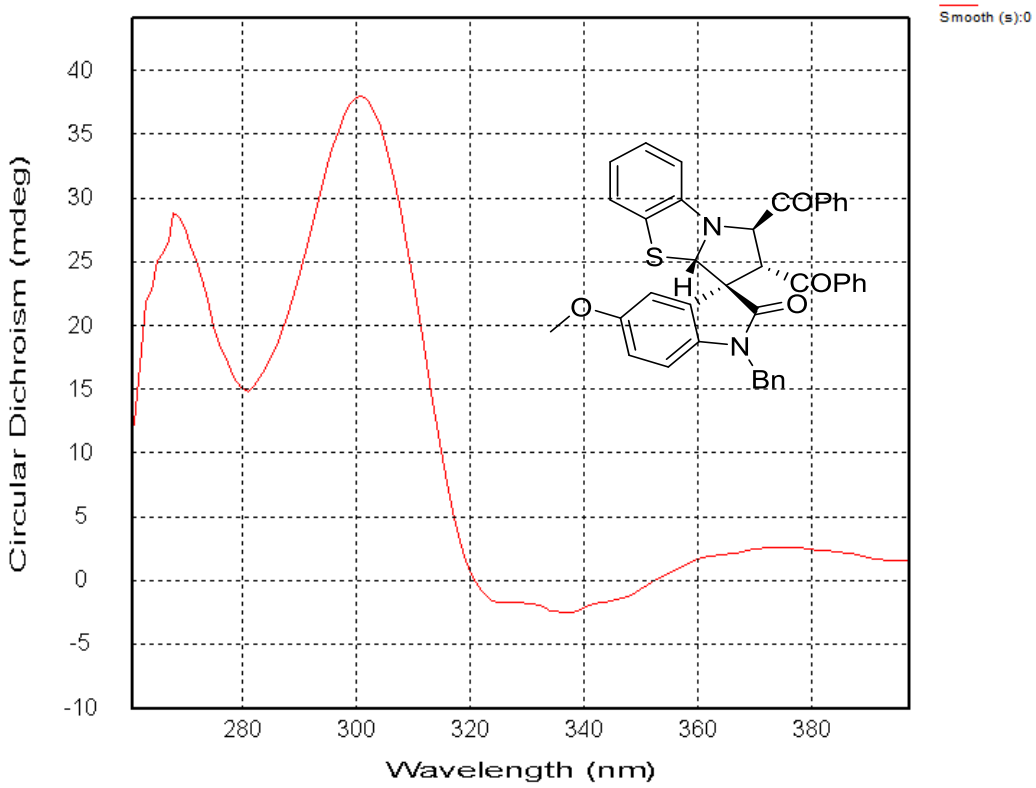
Compound 3ias



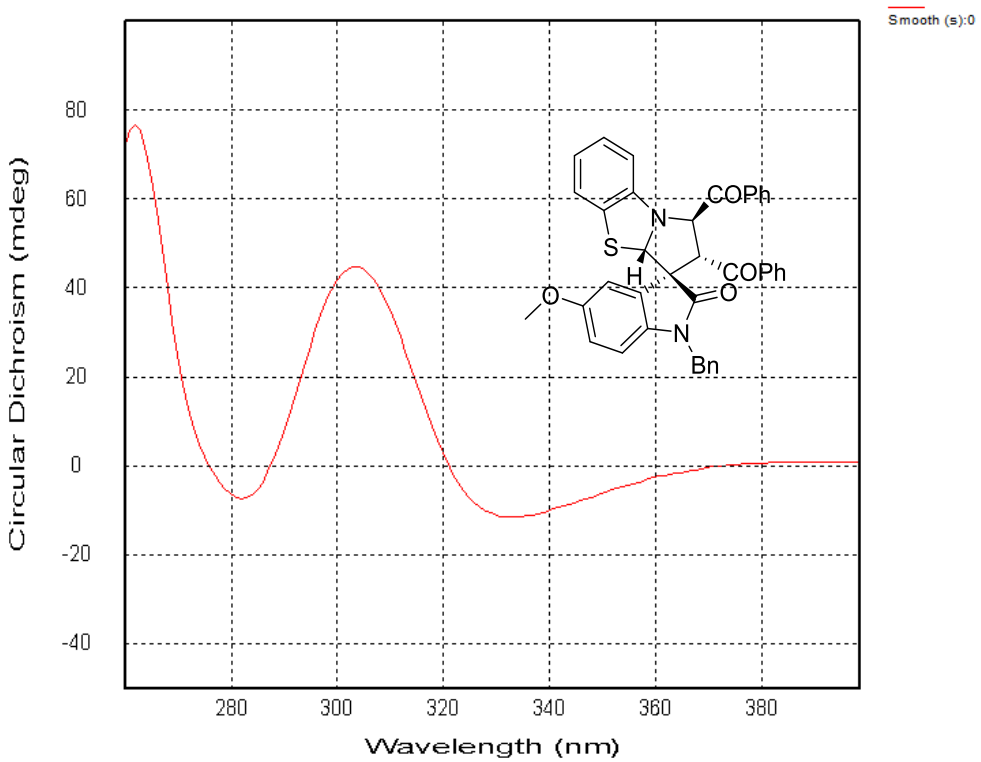
Compound 3ja



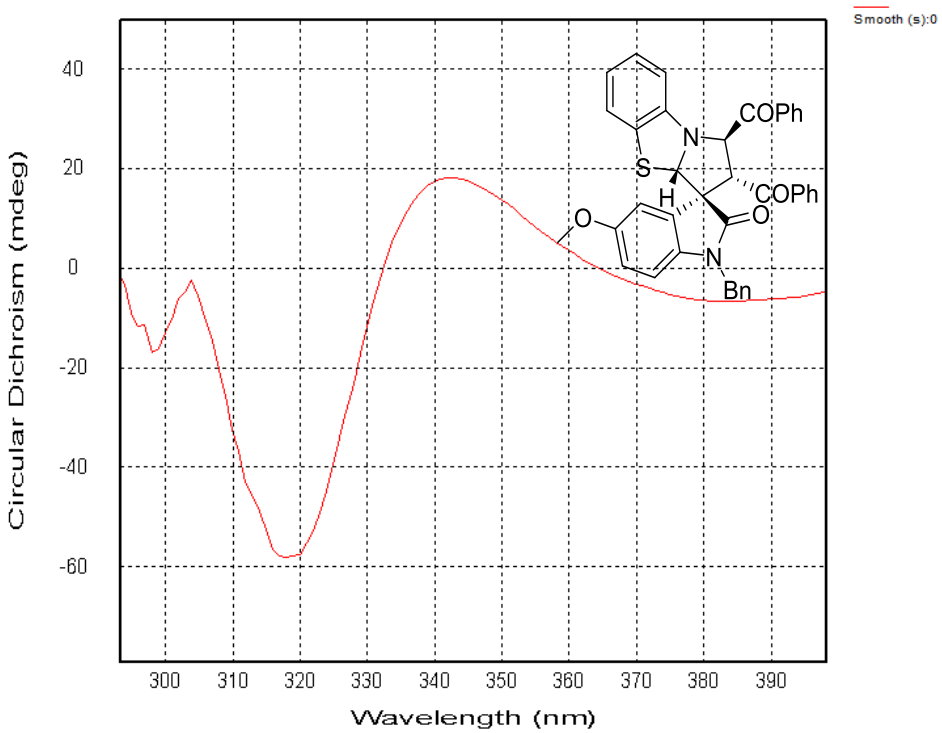
Compound 3ka



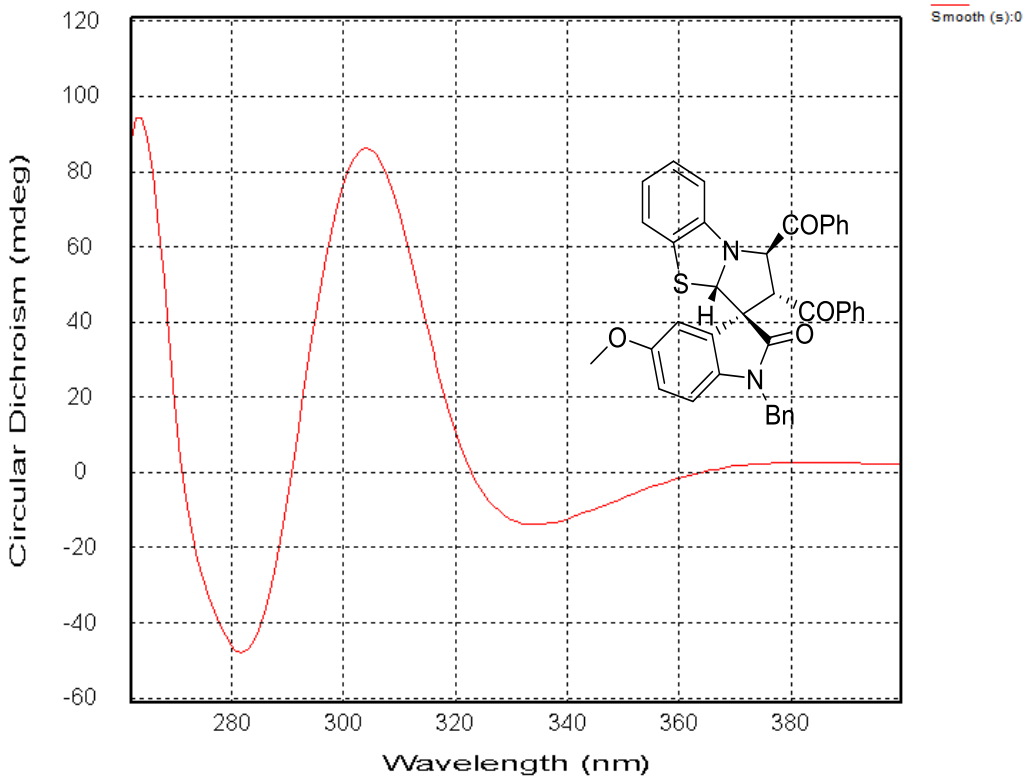
Compound 3la



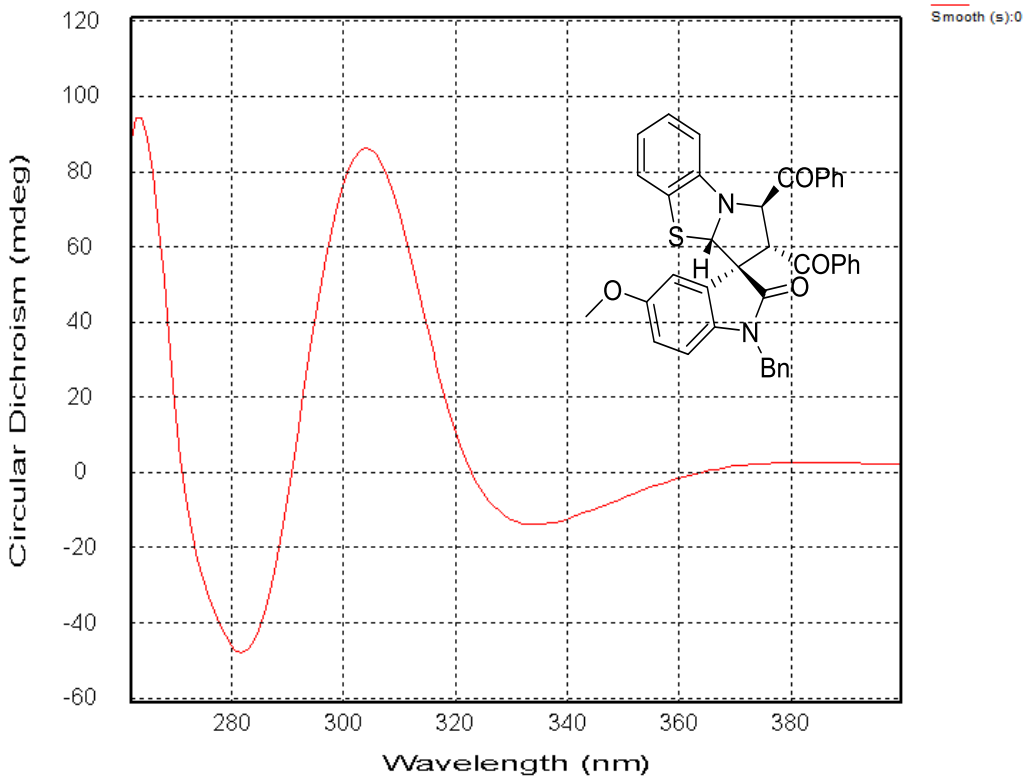
Compound 3ma



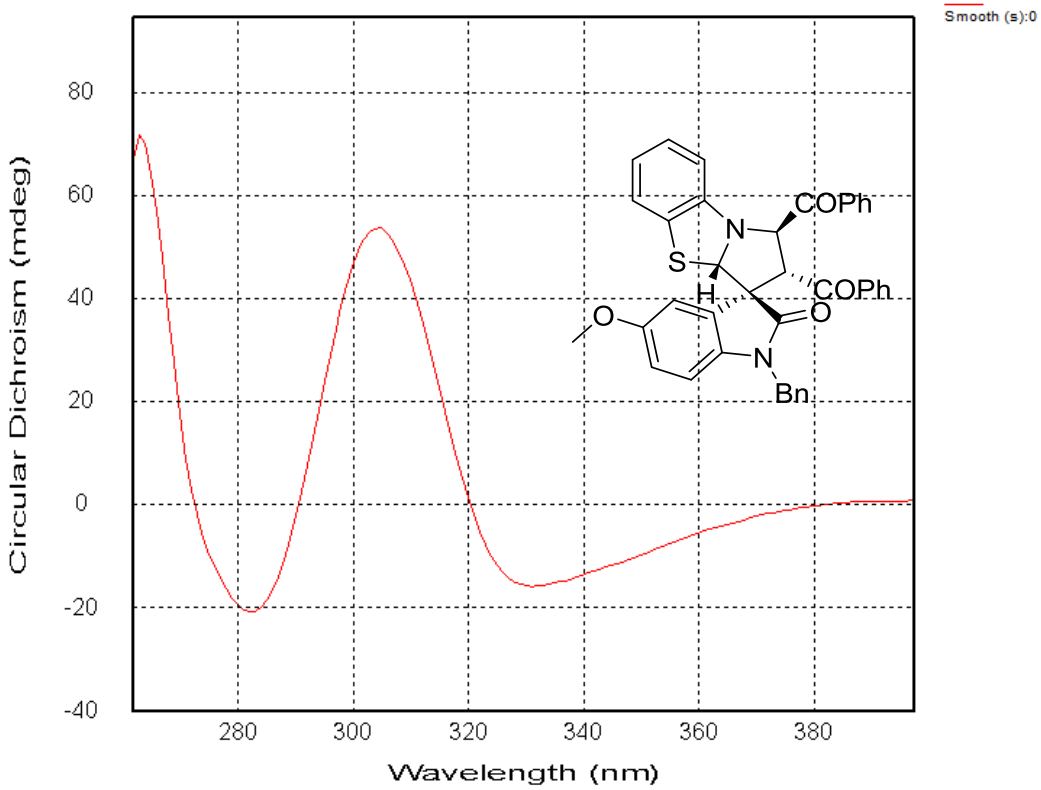
Compound 3ab



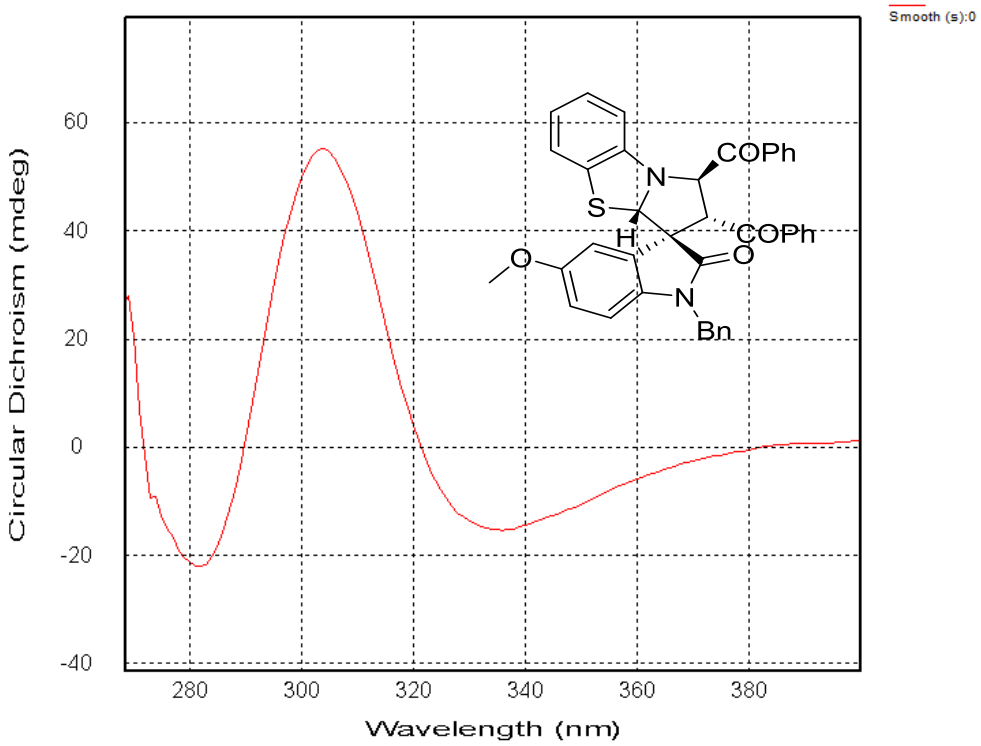
Compound 3acs



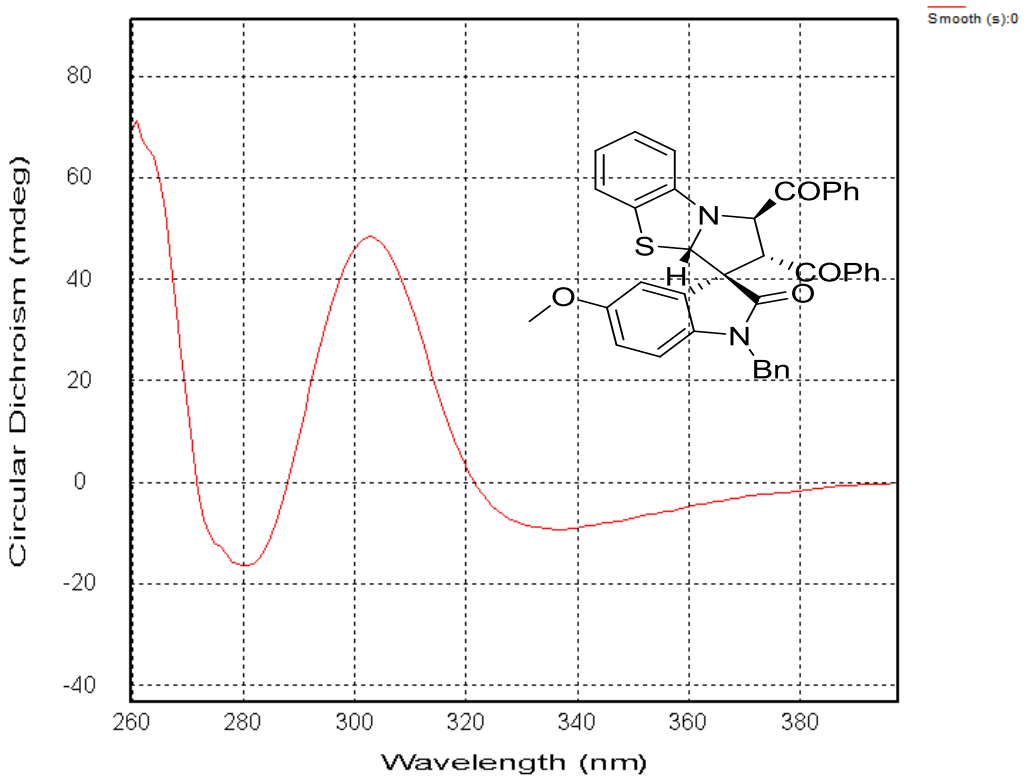
Compound 3ac



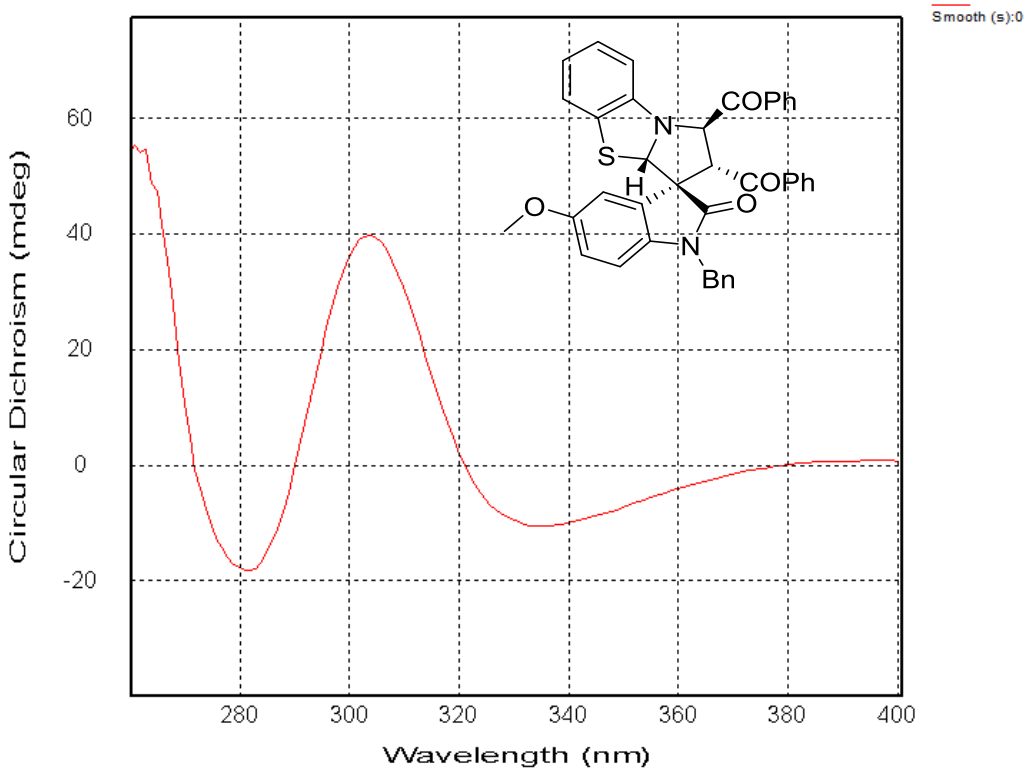
Compound 3ad



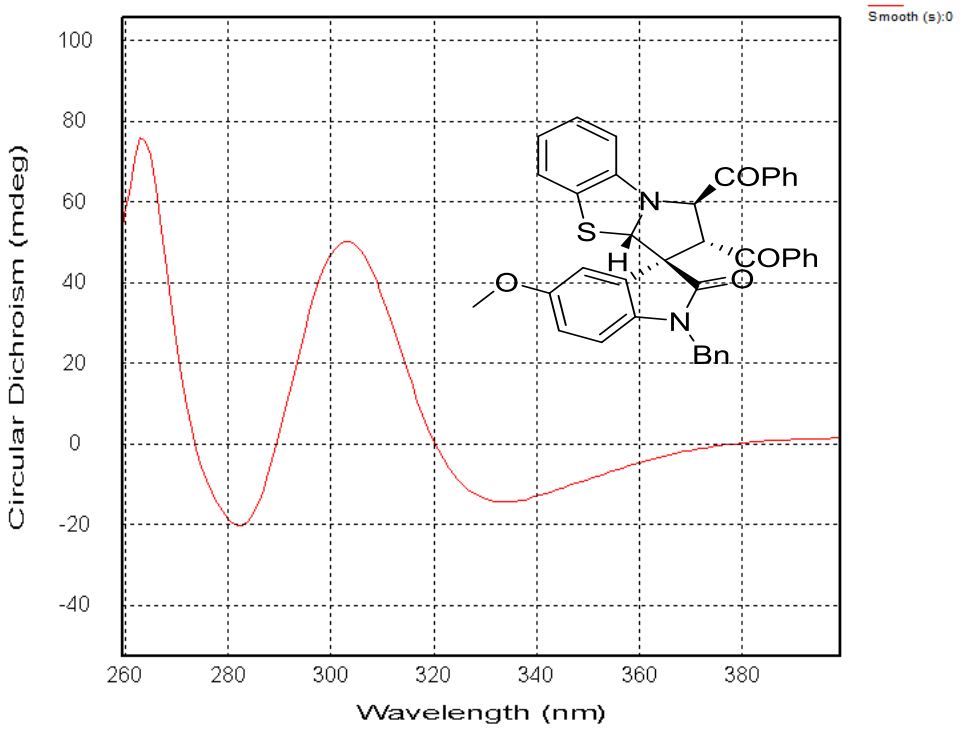
Compound 3ads



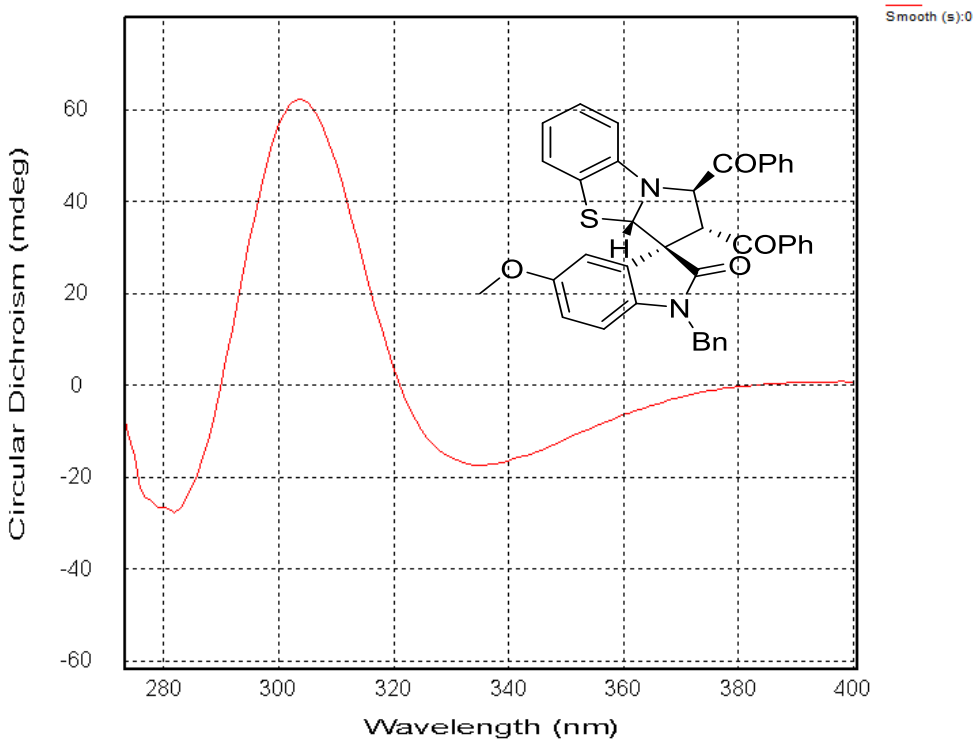
Compound 3ae



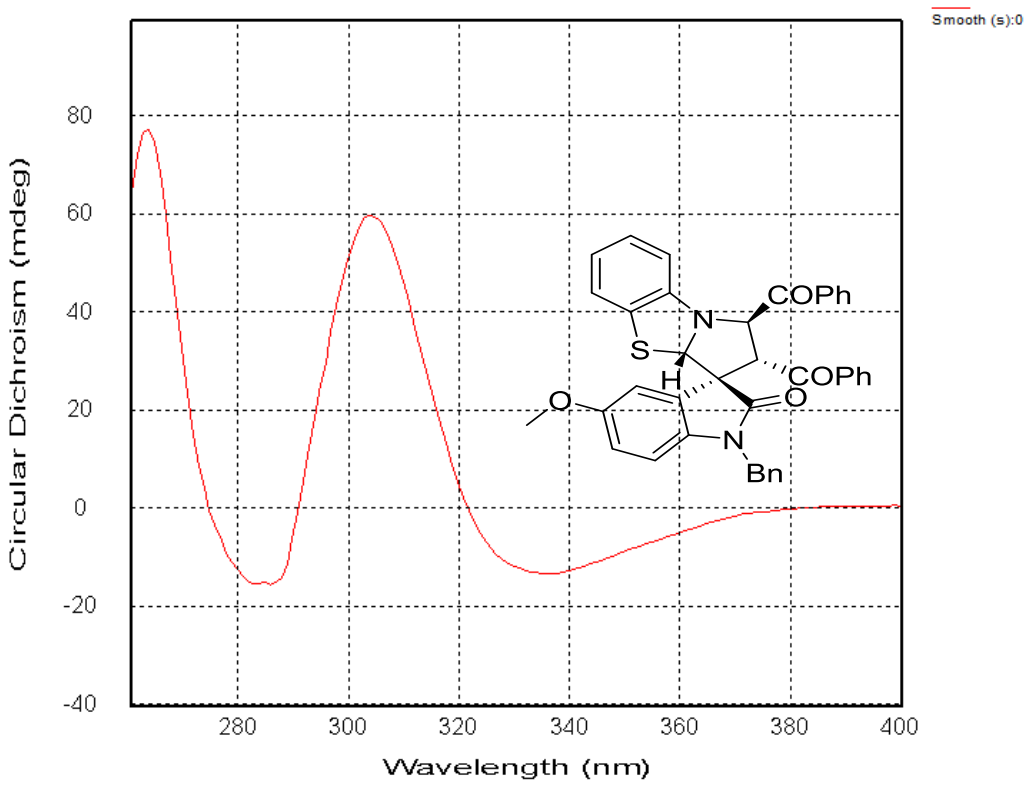
Compound 3af



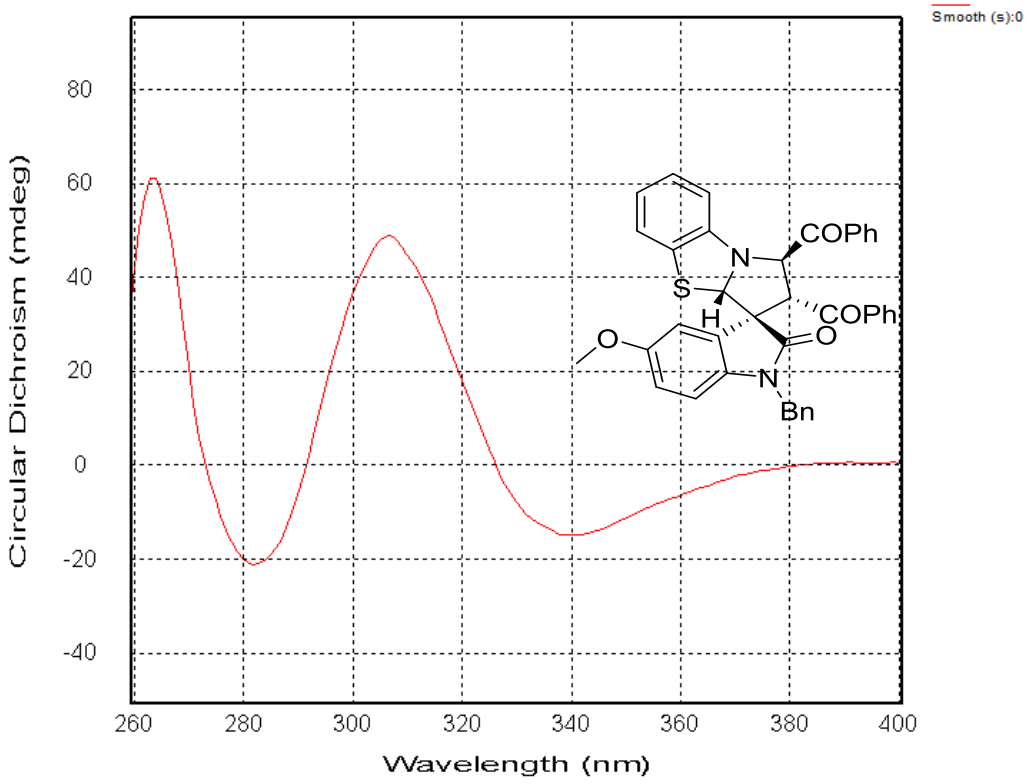
Compound 3ag



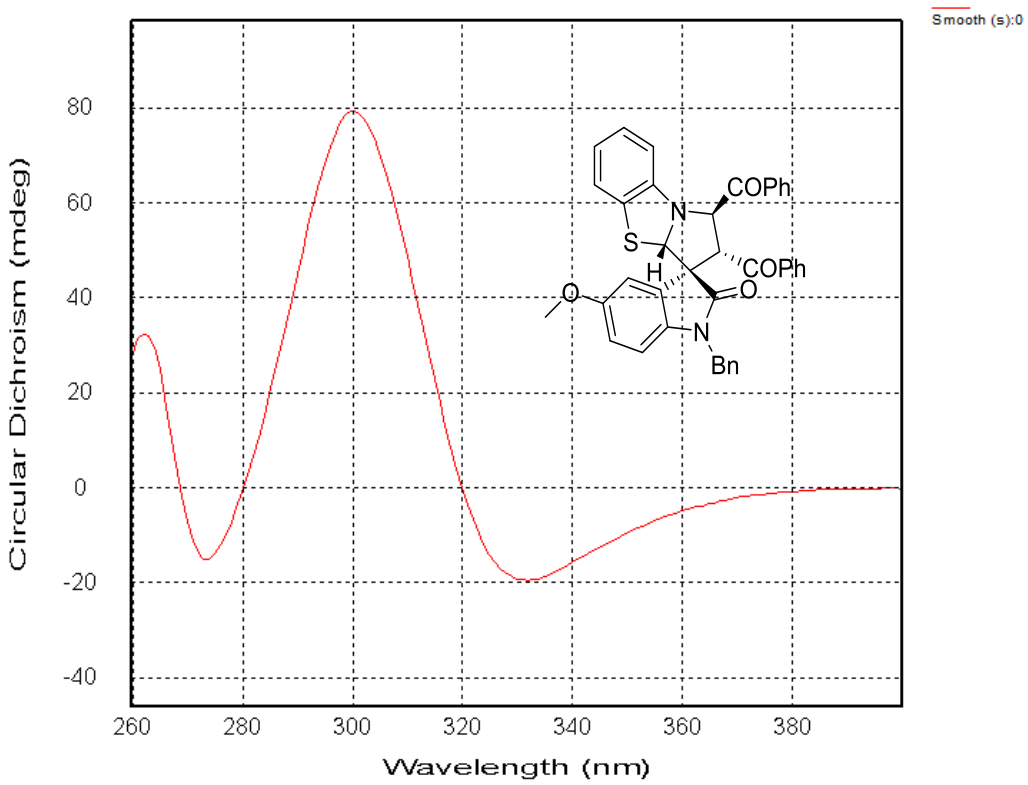
Compound 3ah



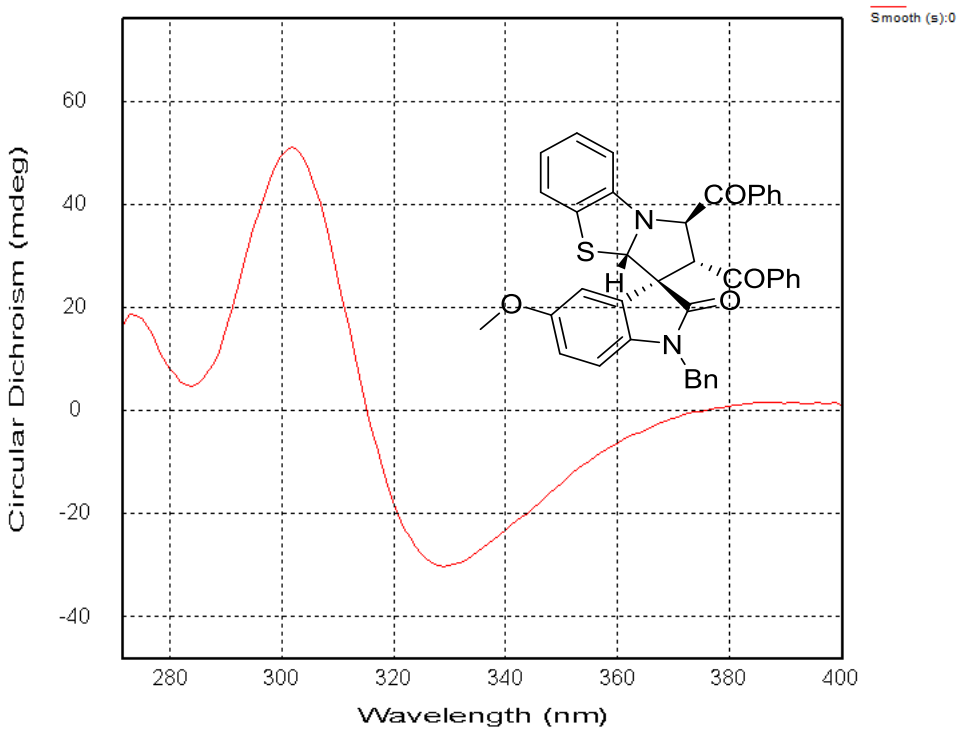
Compound 3ahs



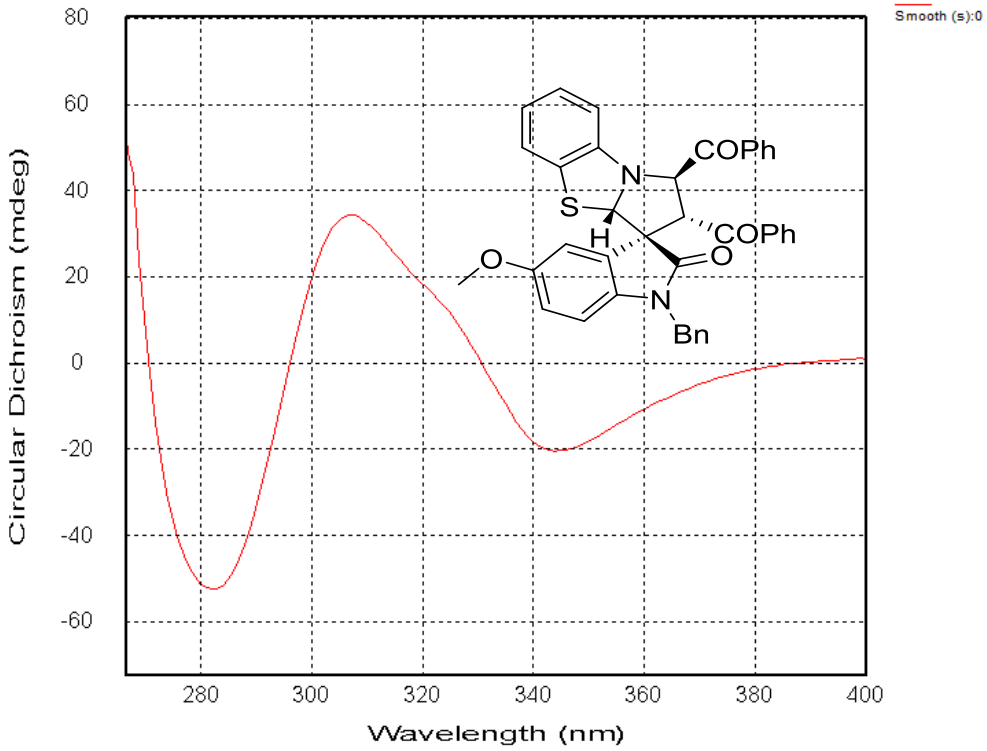
Compound 3ai



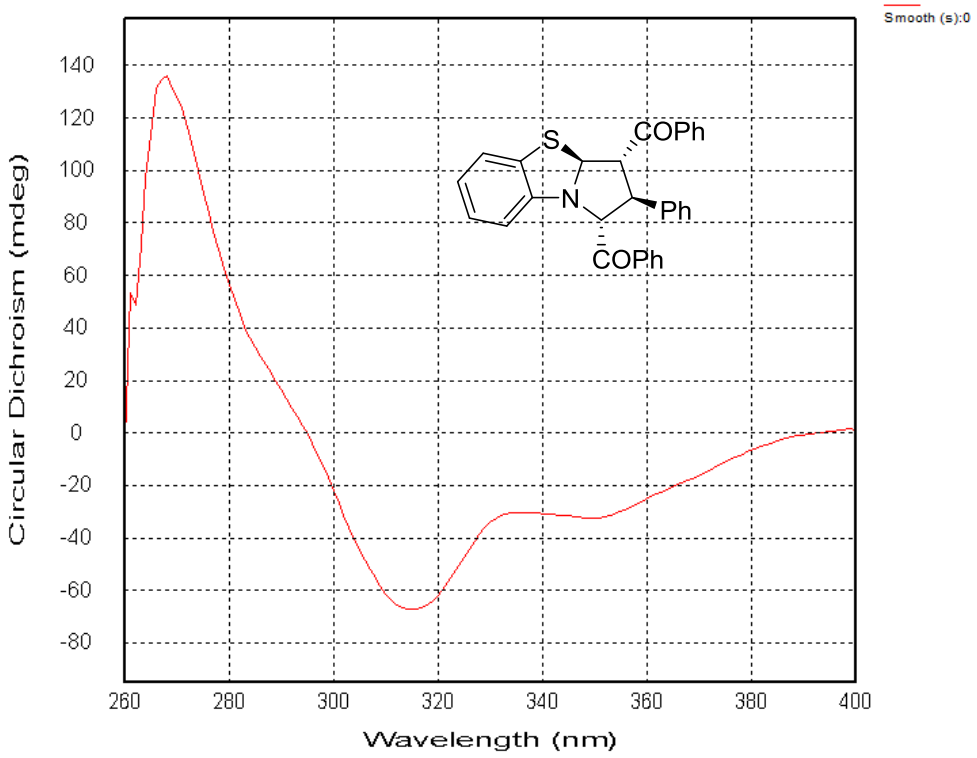
Compound 3aj



Compound 3ak



Compound 5aa



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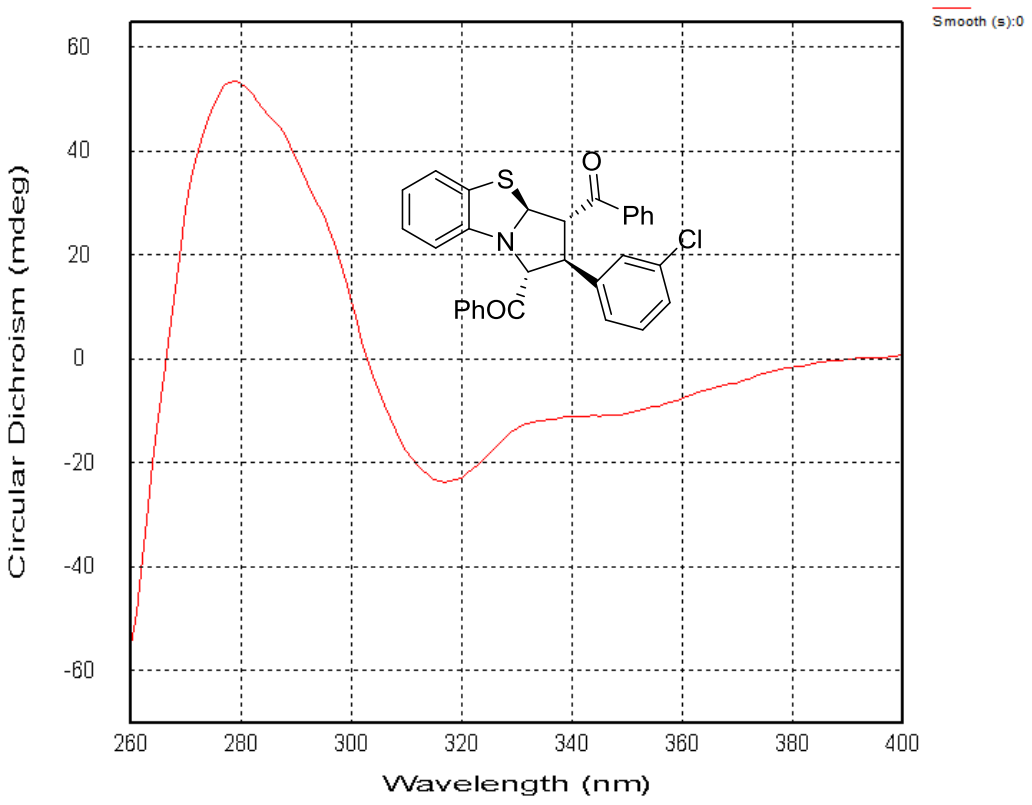
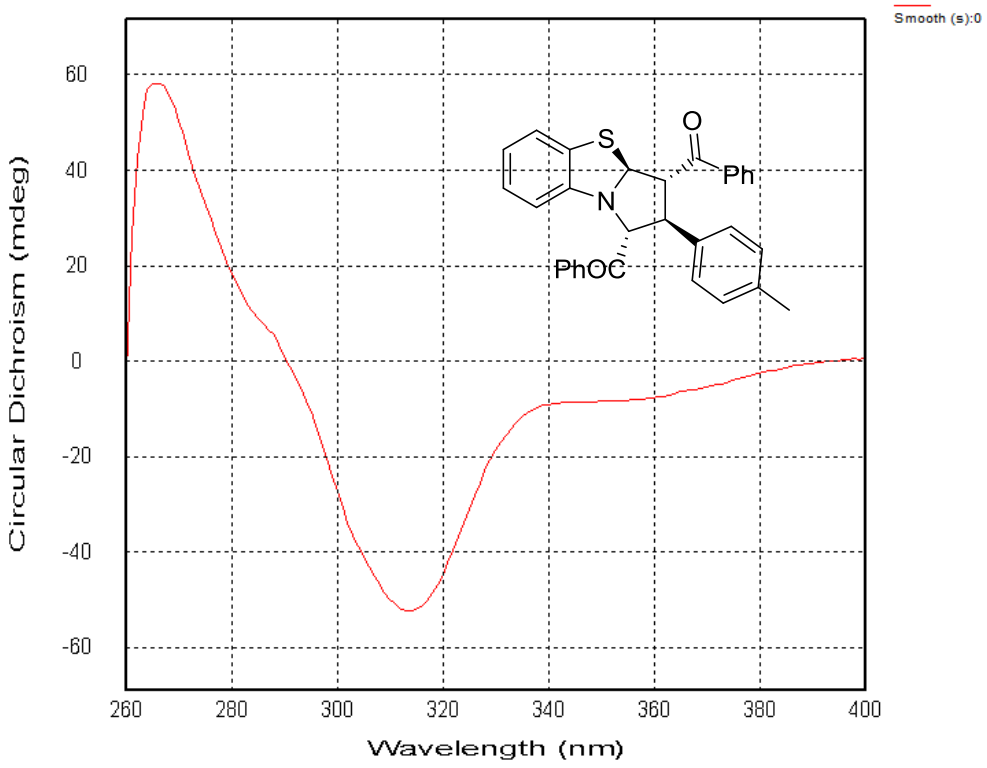
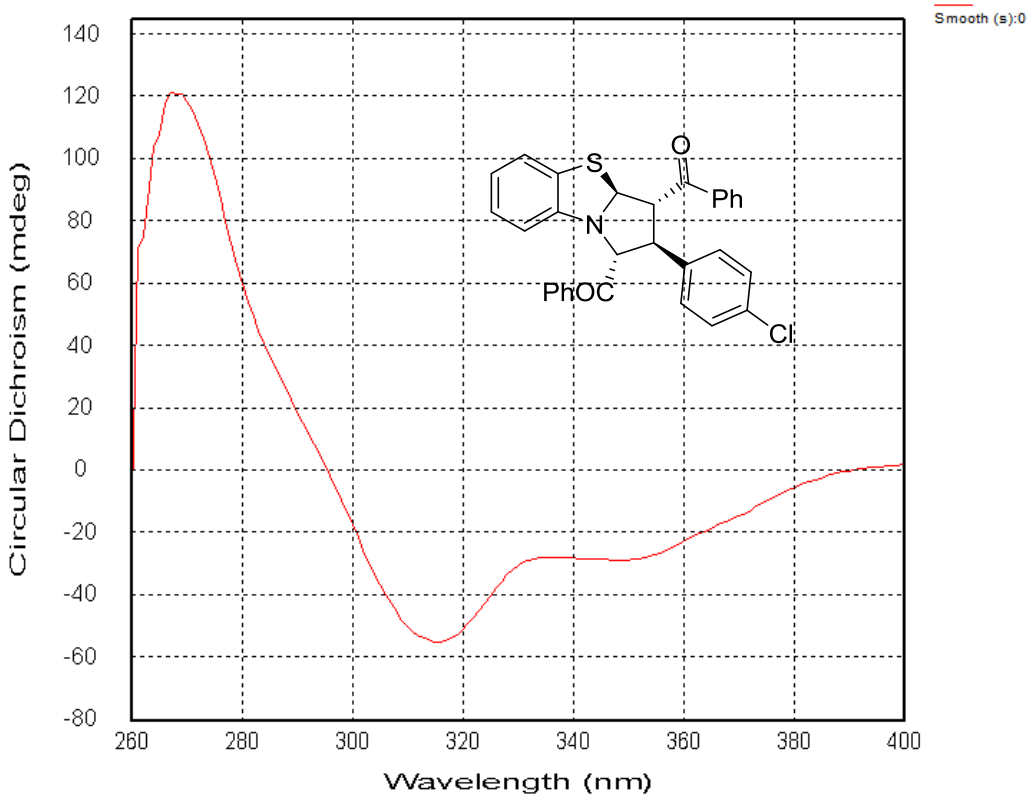


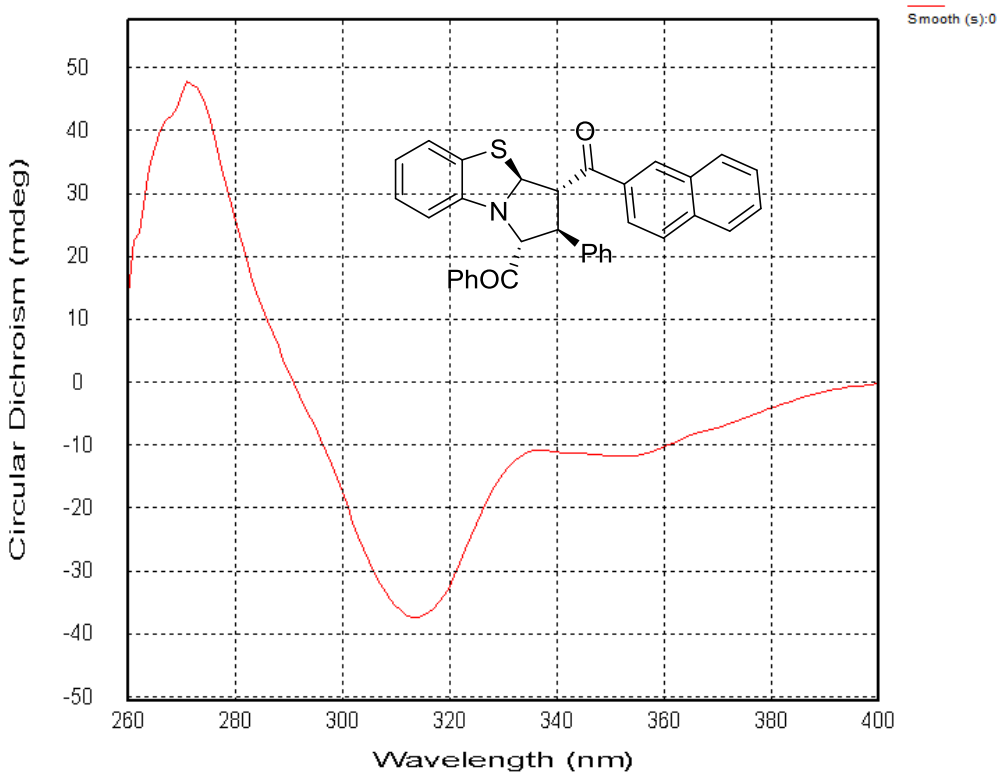
Compound 5ca



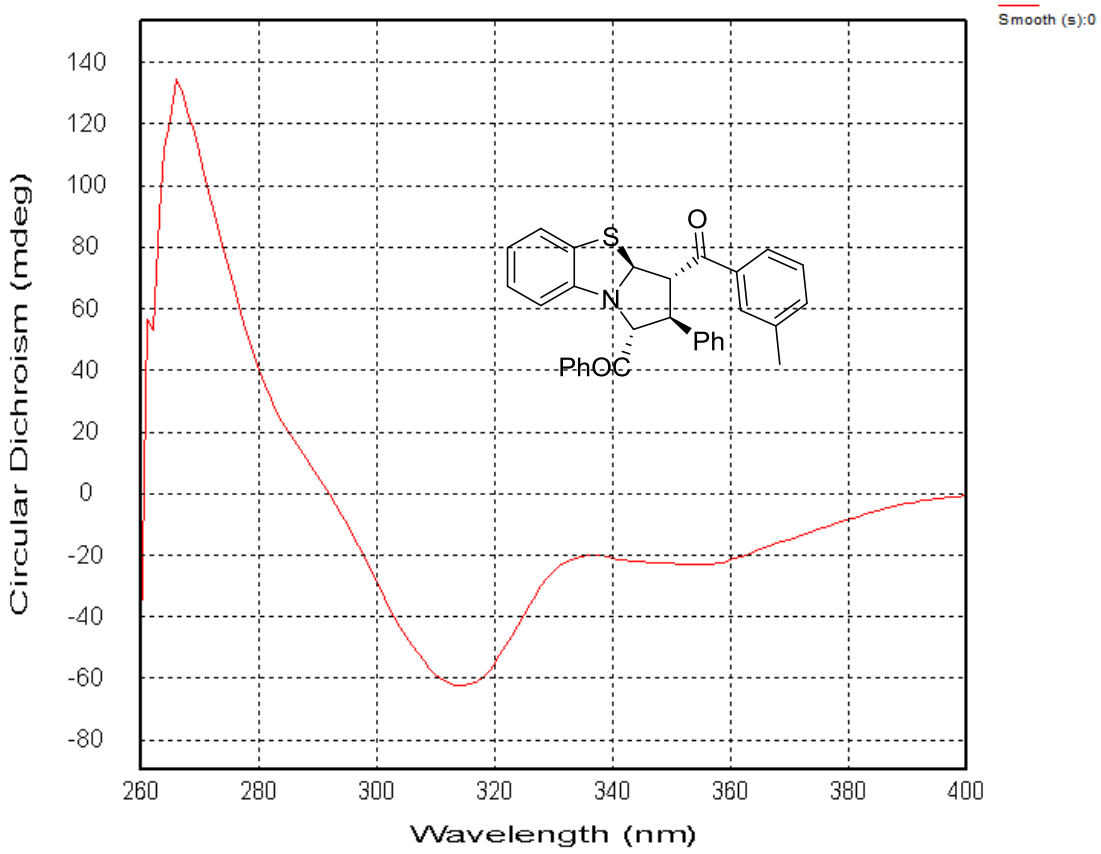
Compound 5da



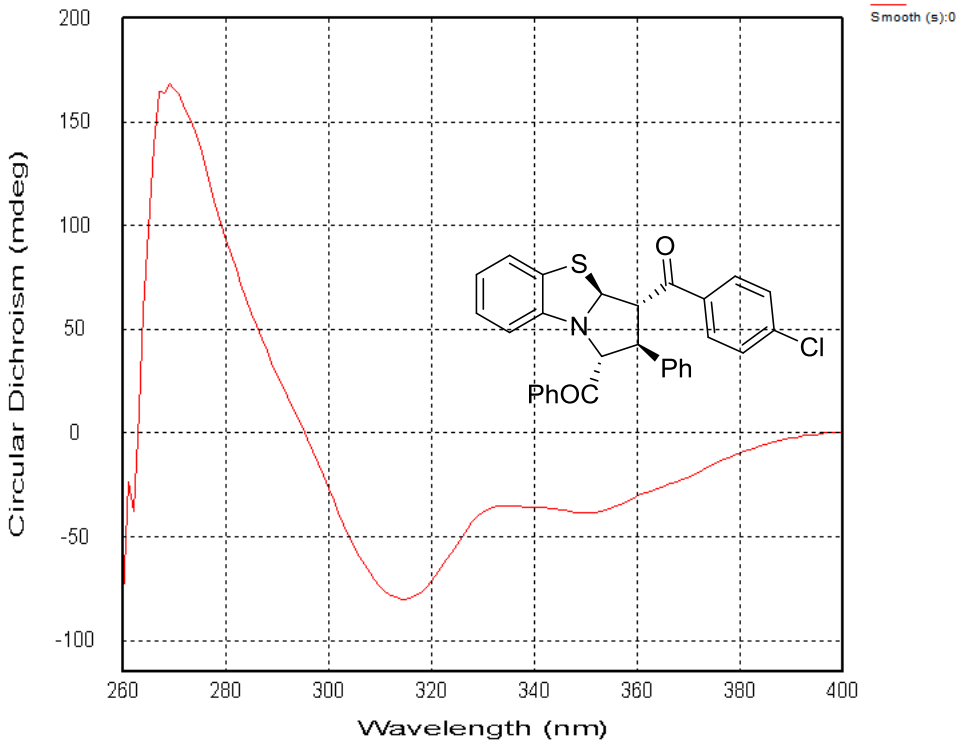
Compound 5ea



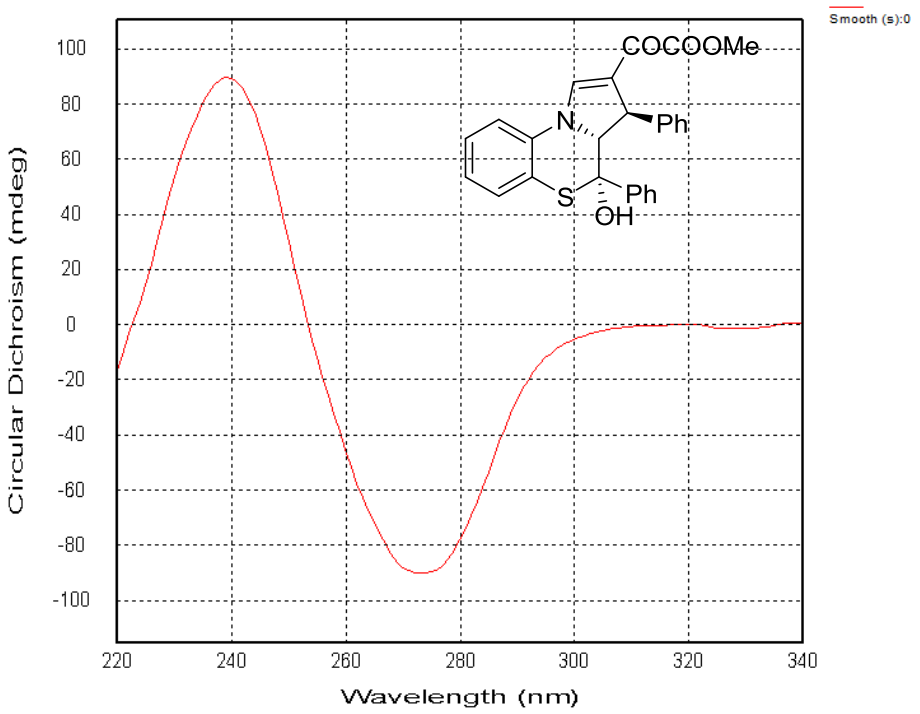
Compound 5fa



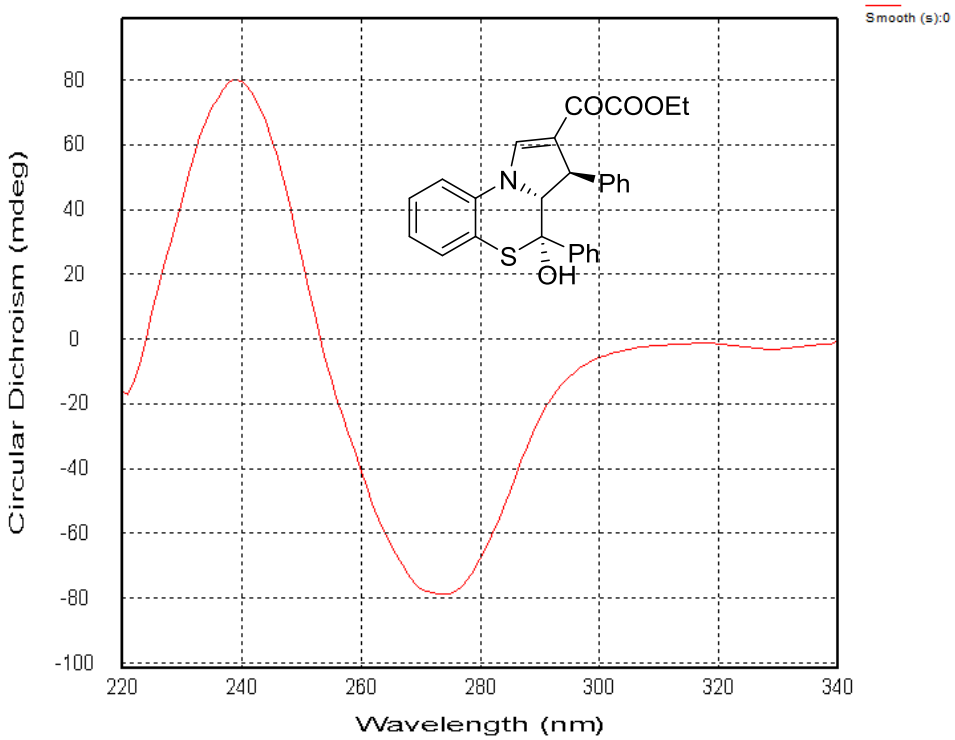
Compound 5ga



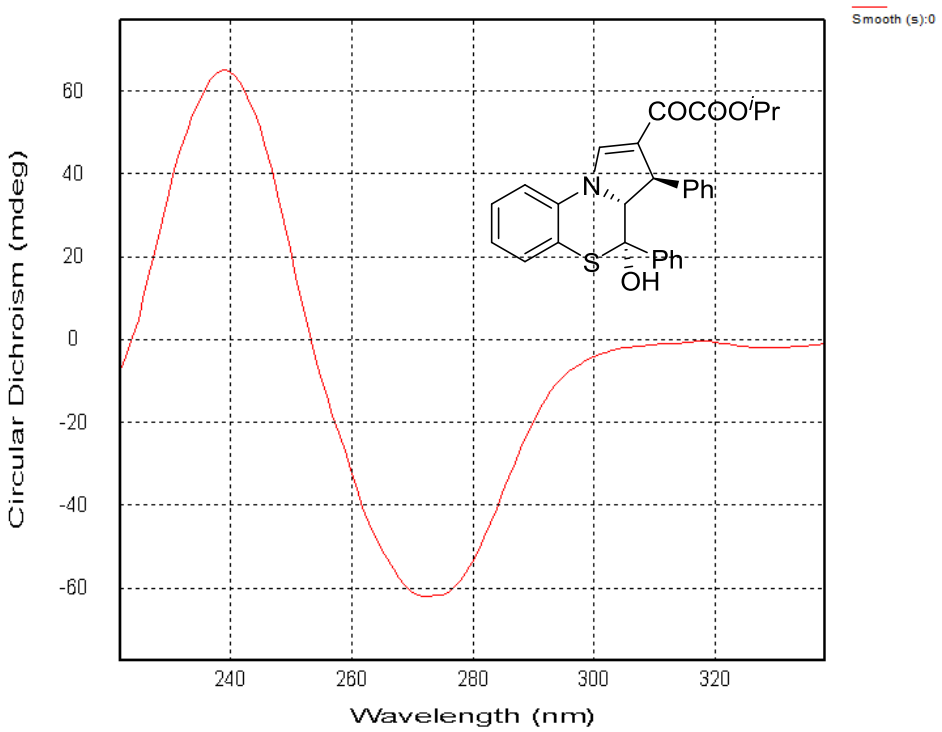
Compound 7aa



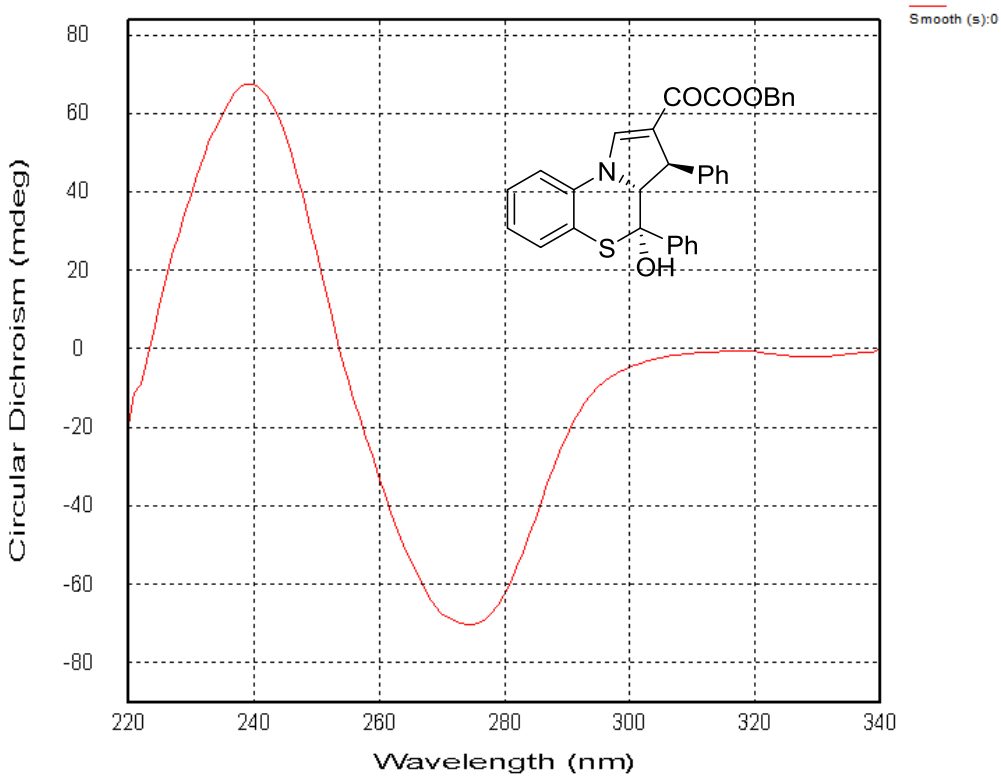
Compound 7ba



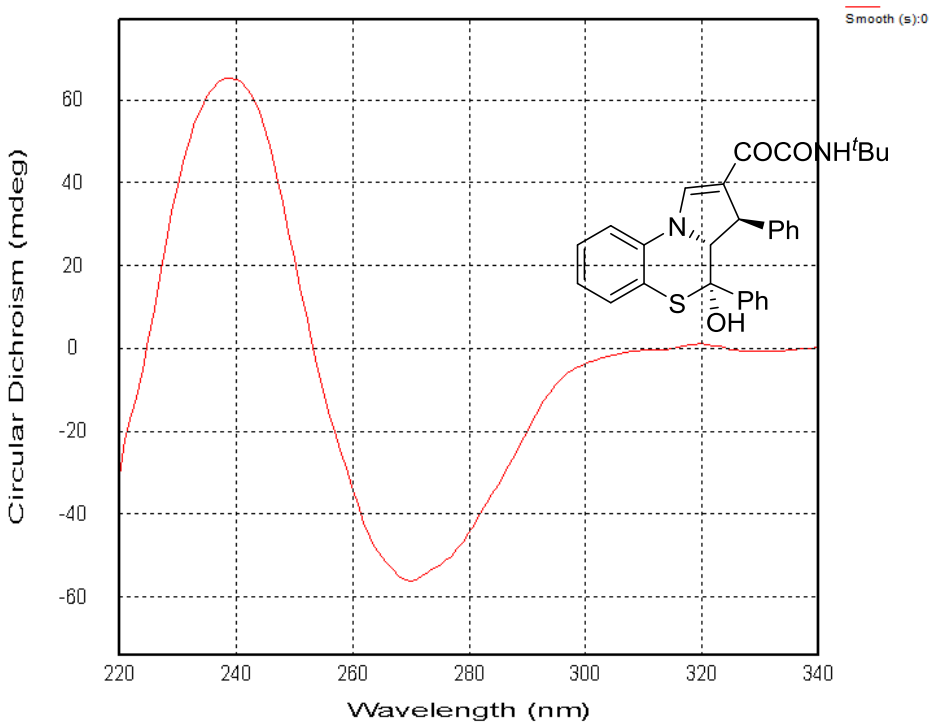
Compound 7ca



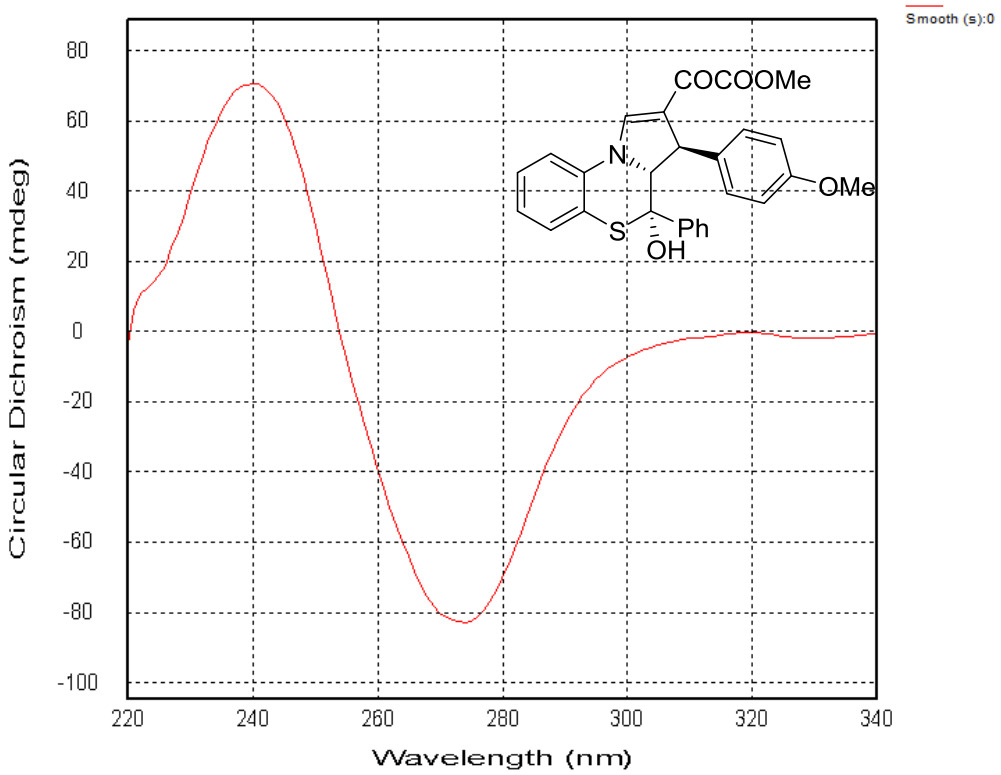
Compound 7da



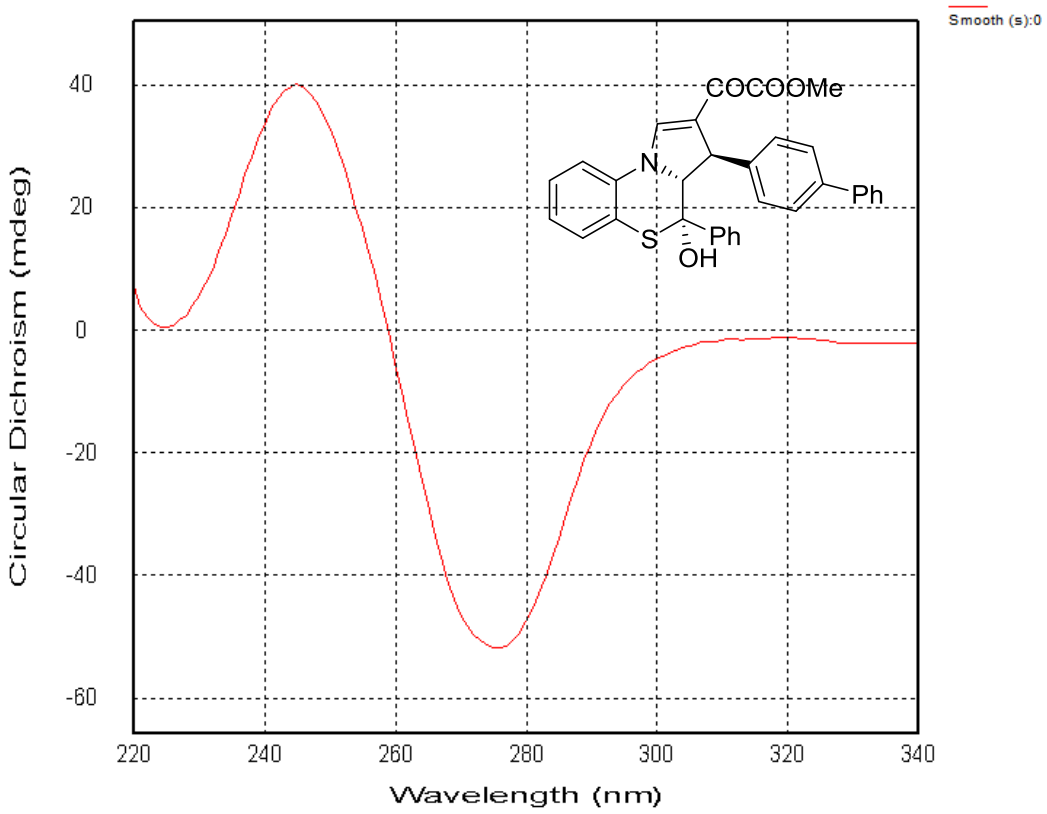
Compound 7ea



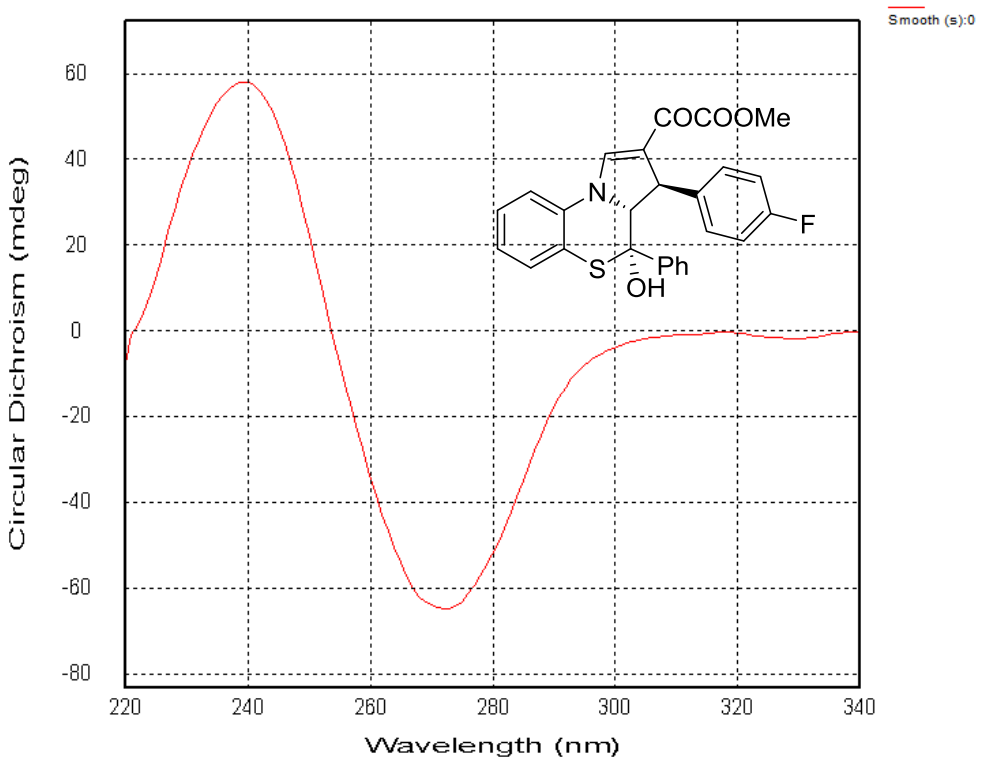
Compound 7fa



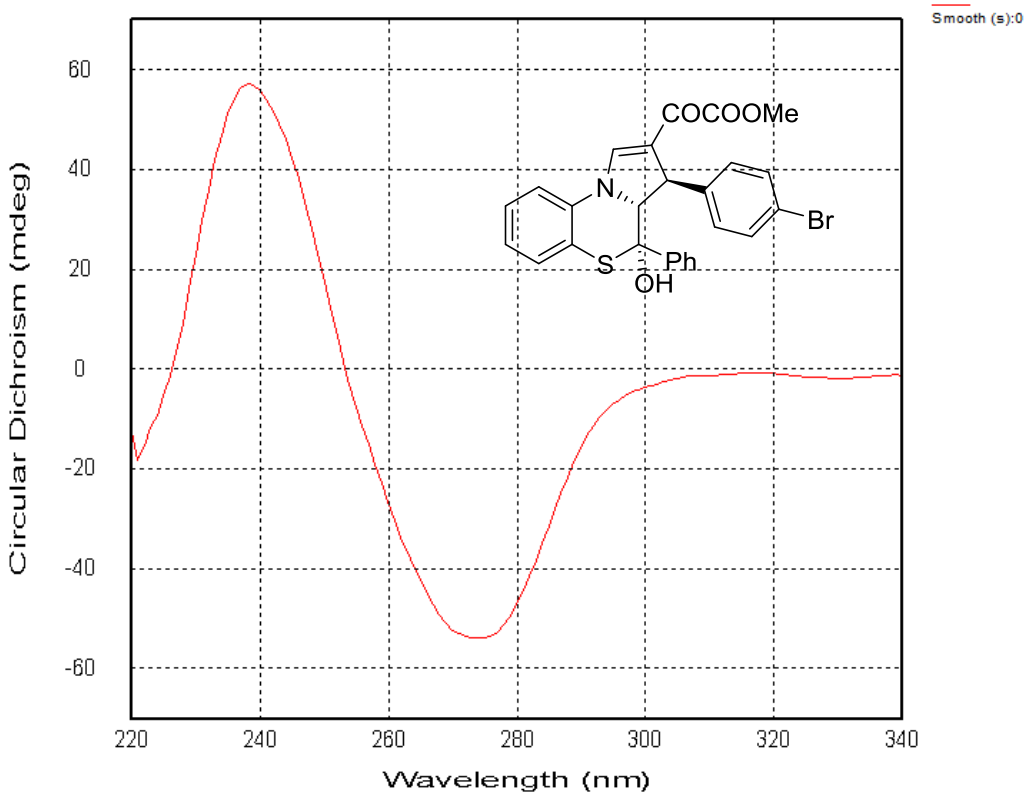
Compound 7ga



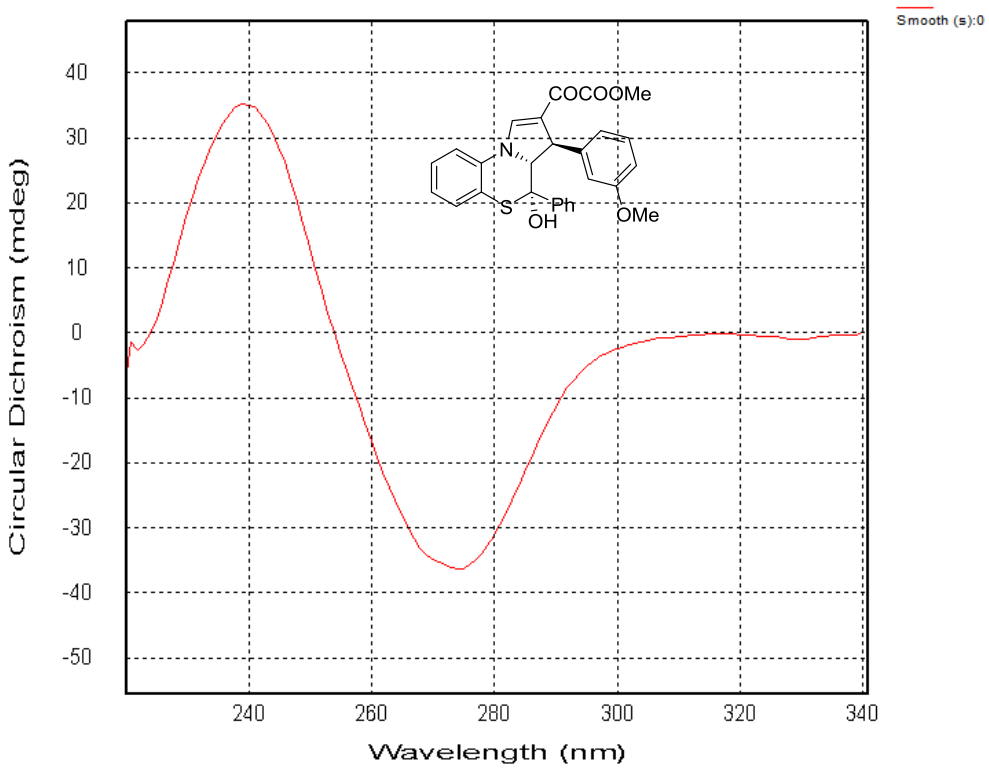
Compound 7ha



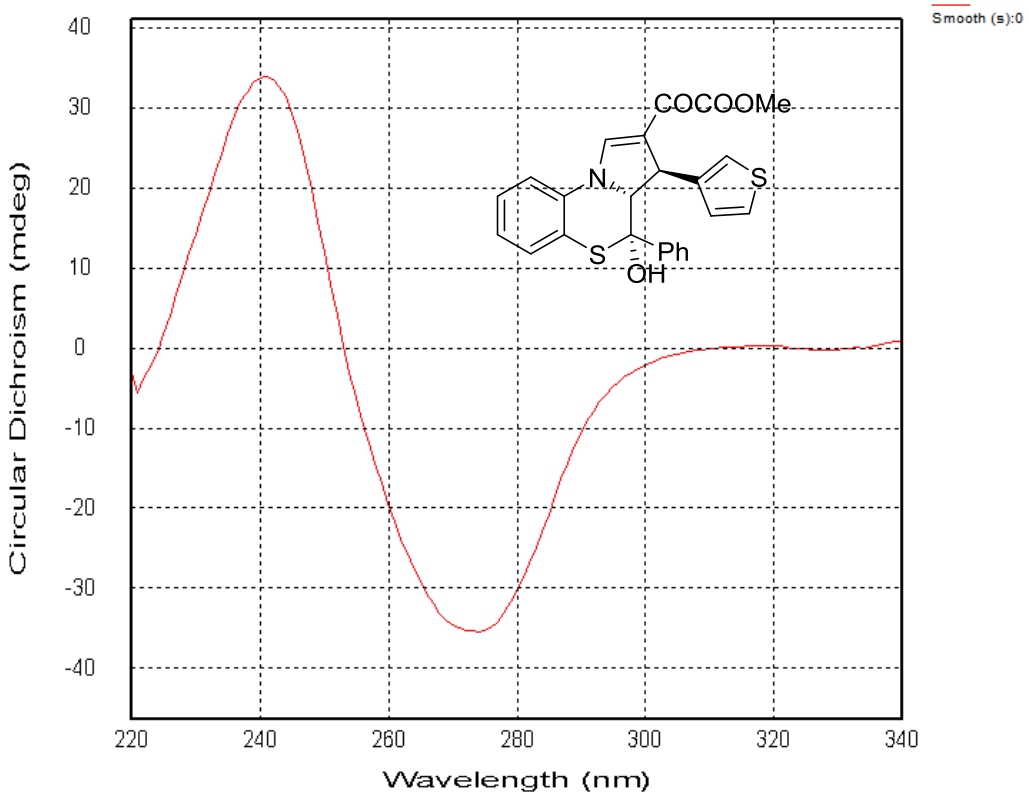
Compound 7has



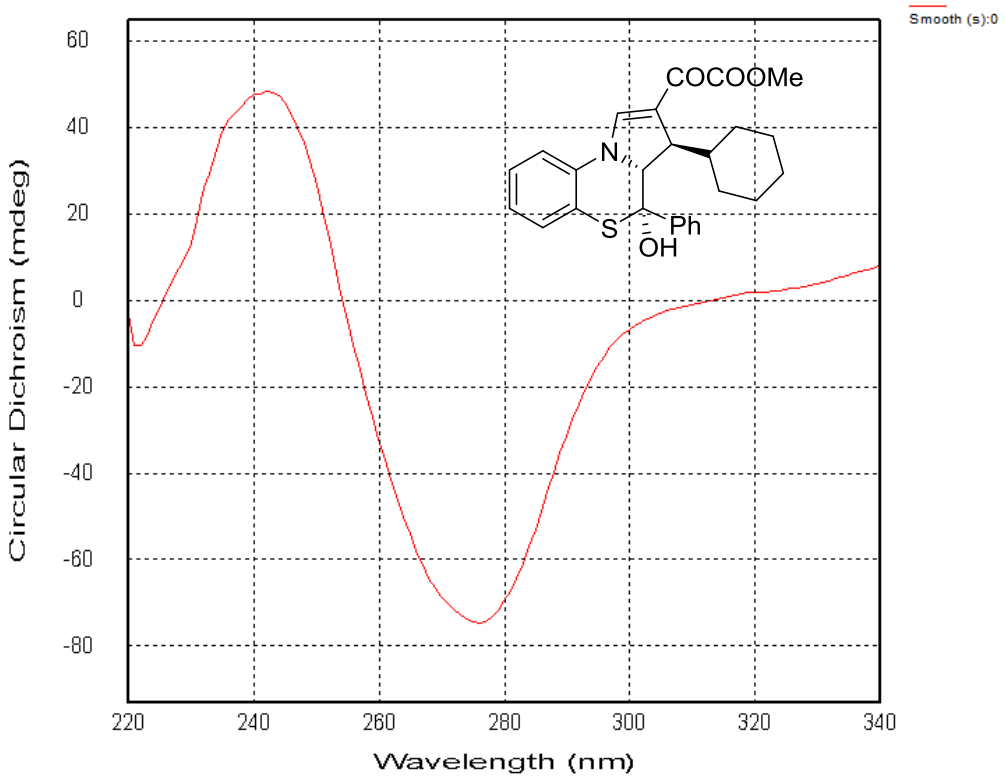
Compound 7ia



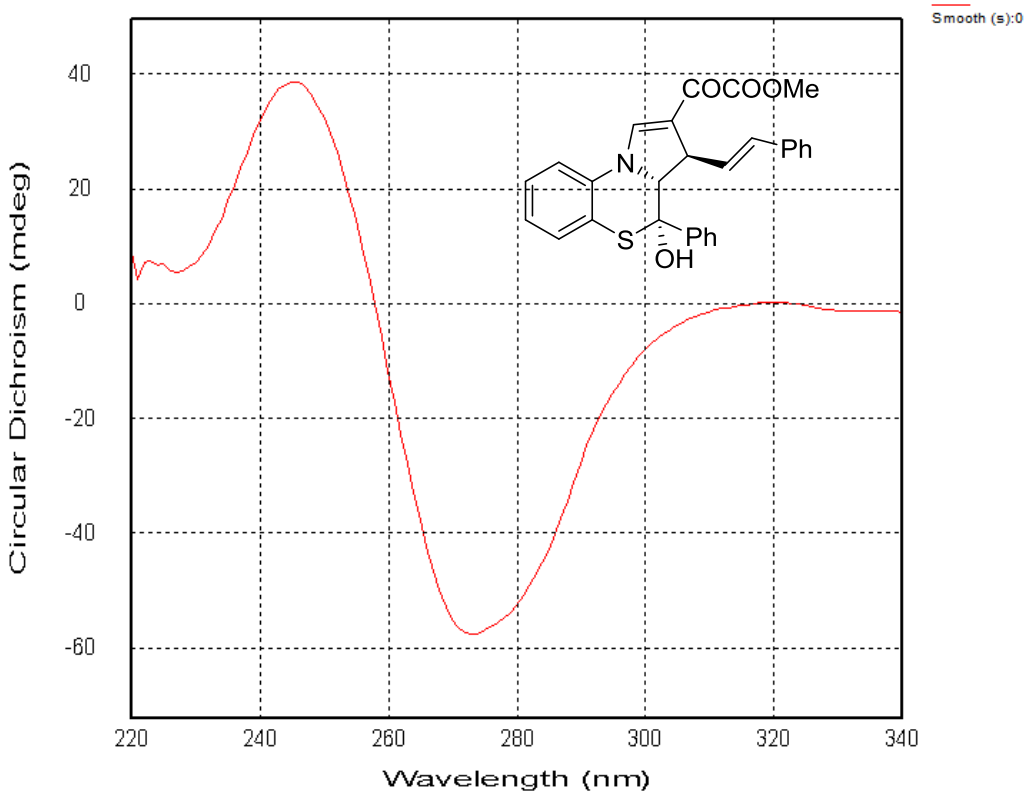
Compound 7ja



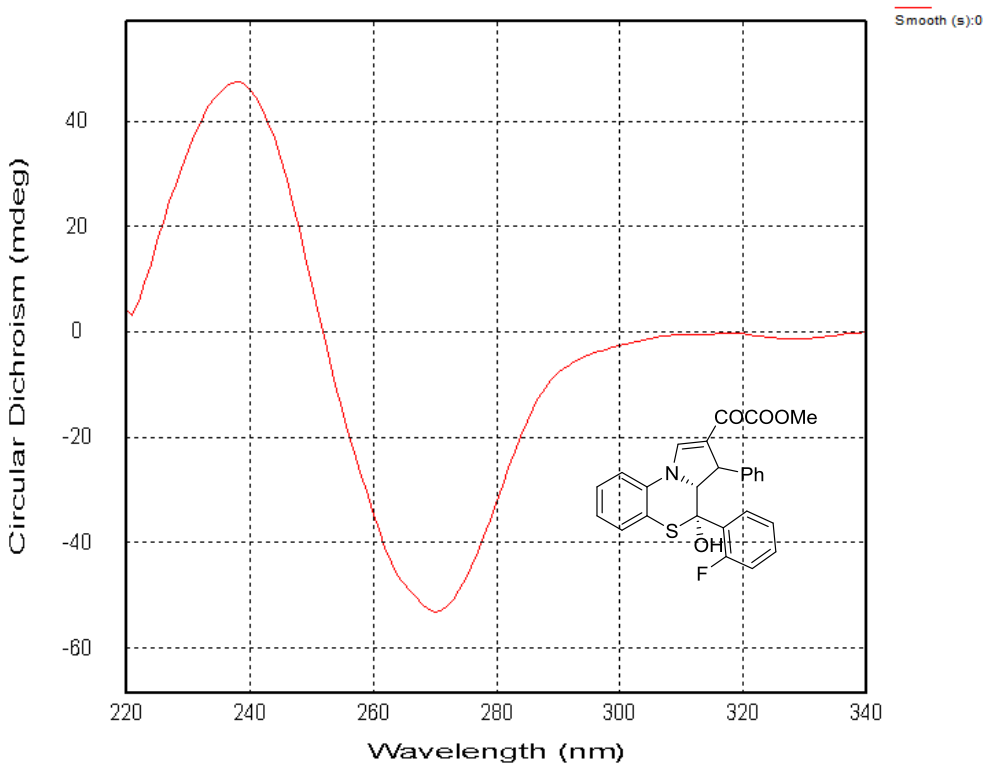
Compound 7ka



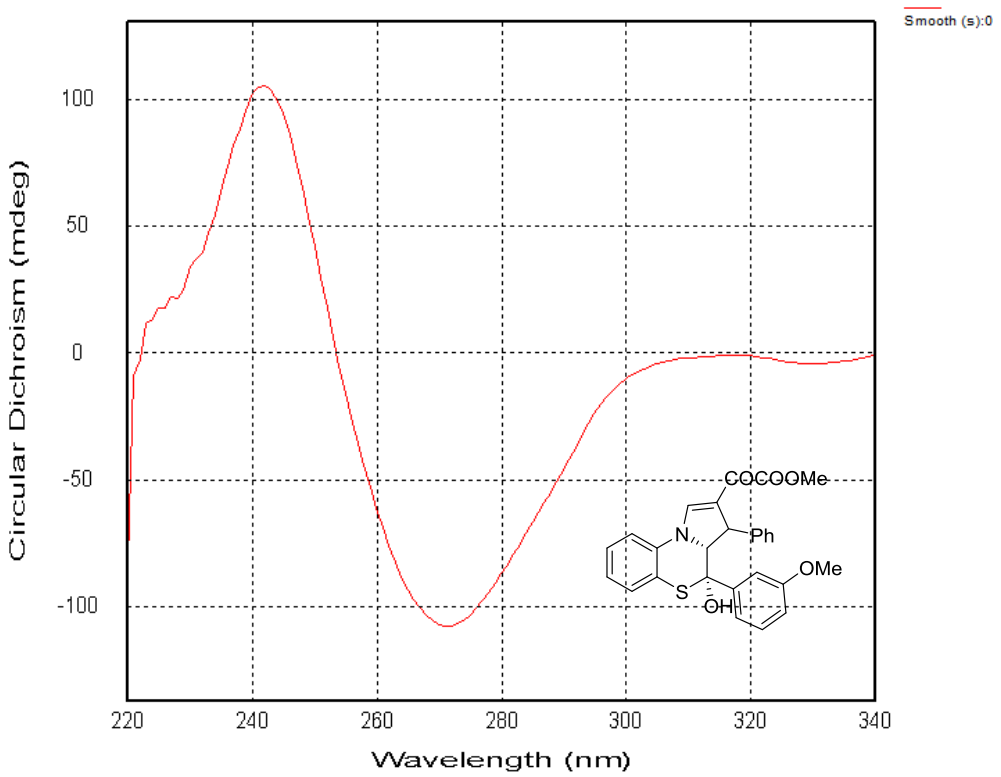
Compound 7la



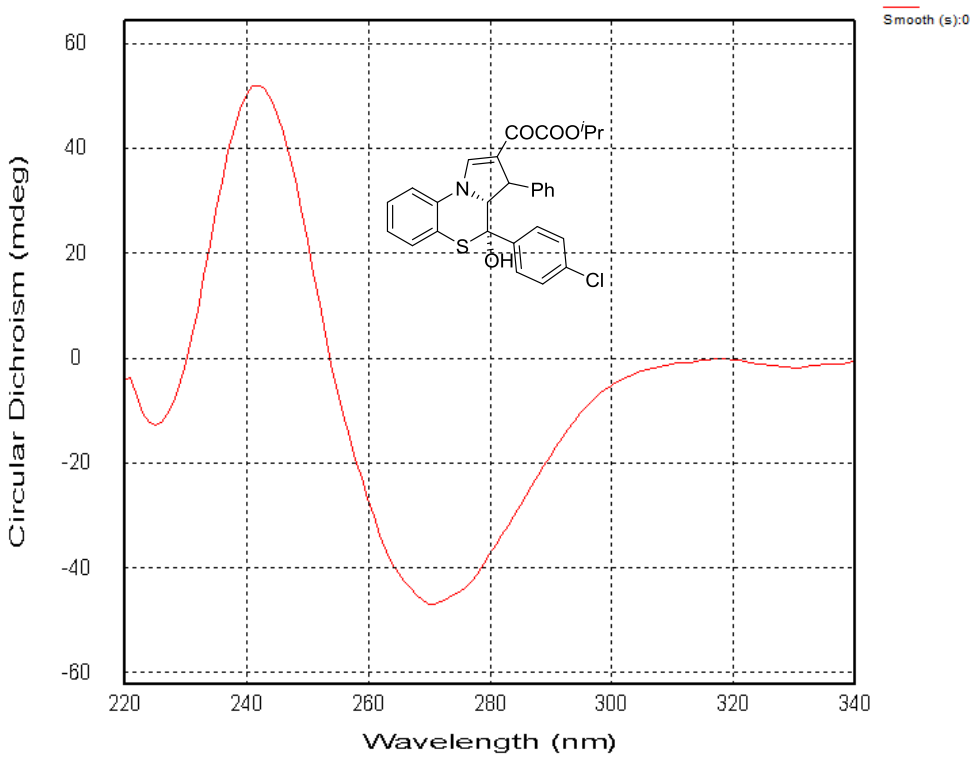
Compound 7cb



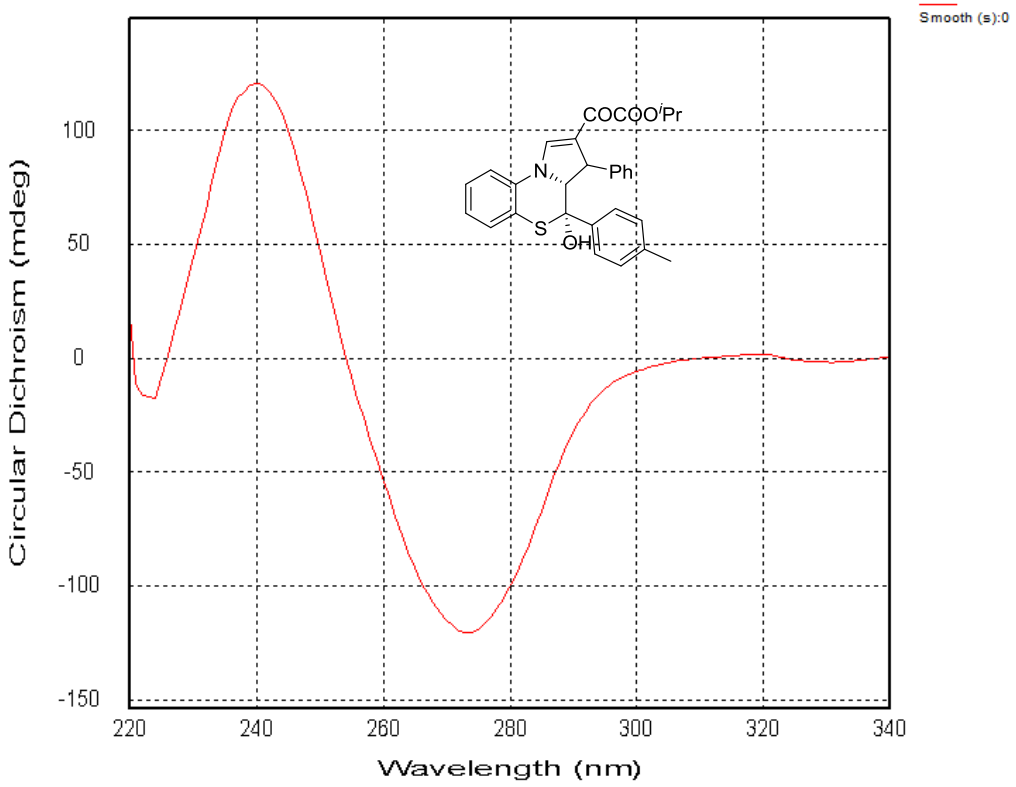
Compound 7cc



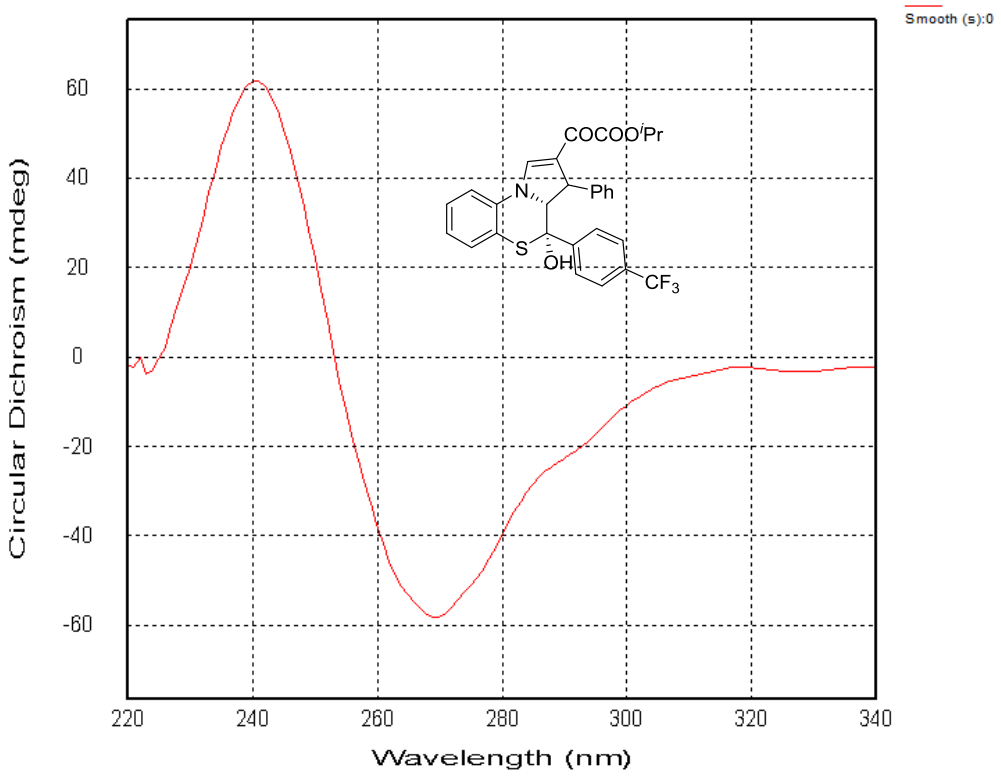
Compound 7cd



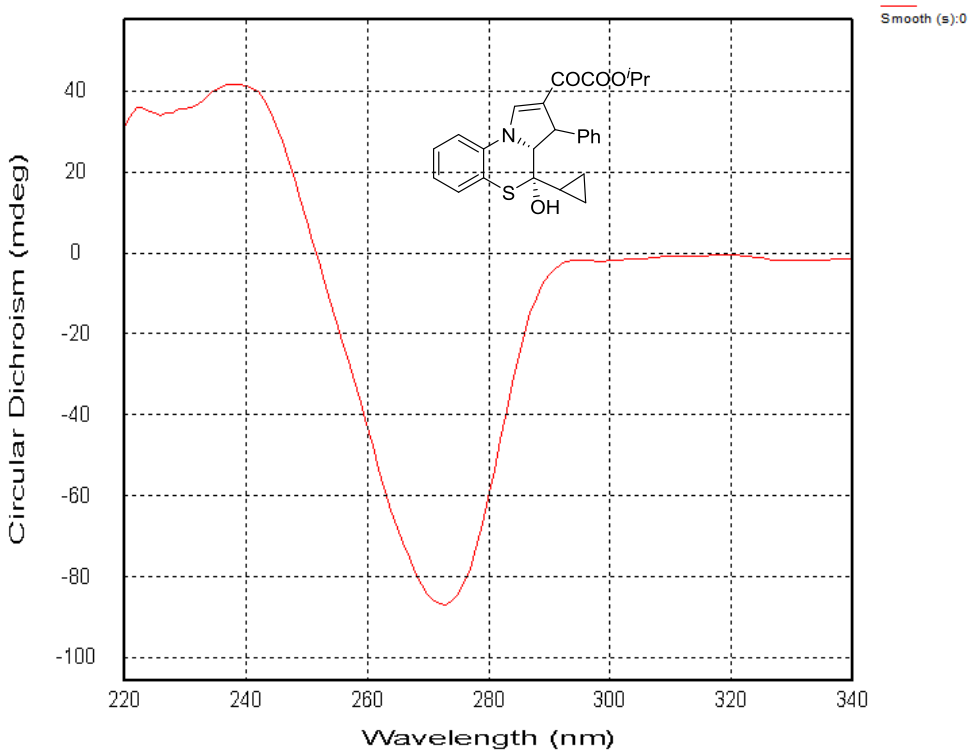
Compound 7ce



Compound 7cf

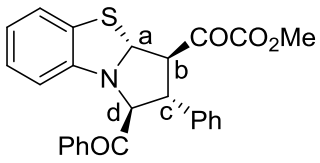


Compound 7ci

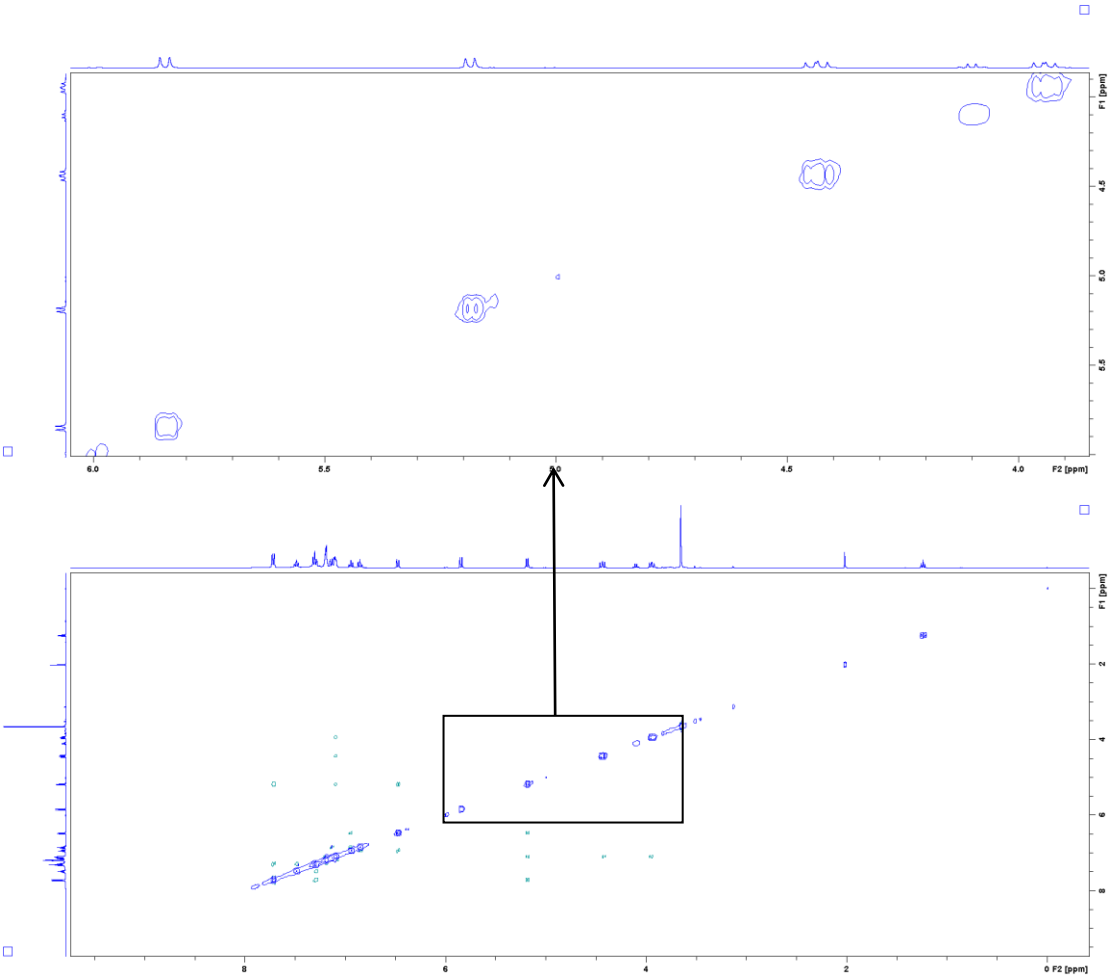


14. NOESY spectra of 8a and 8b.

Compound 8a

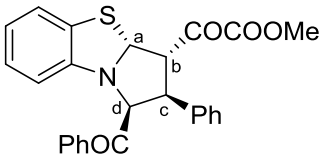


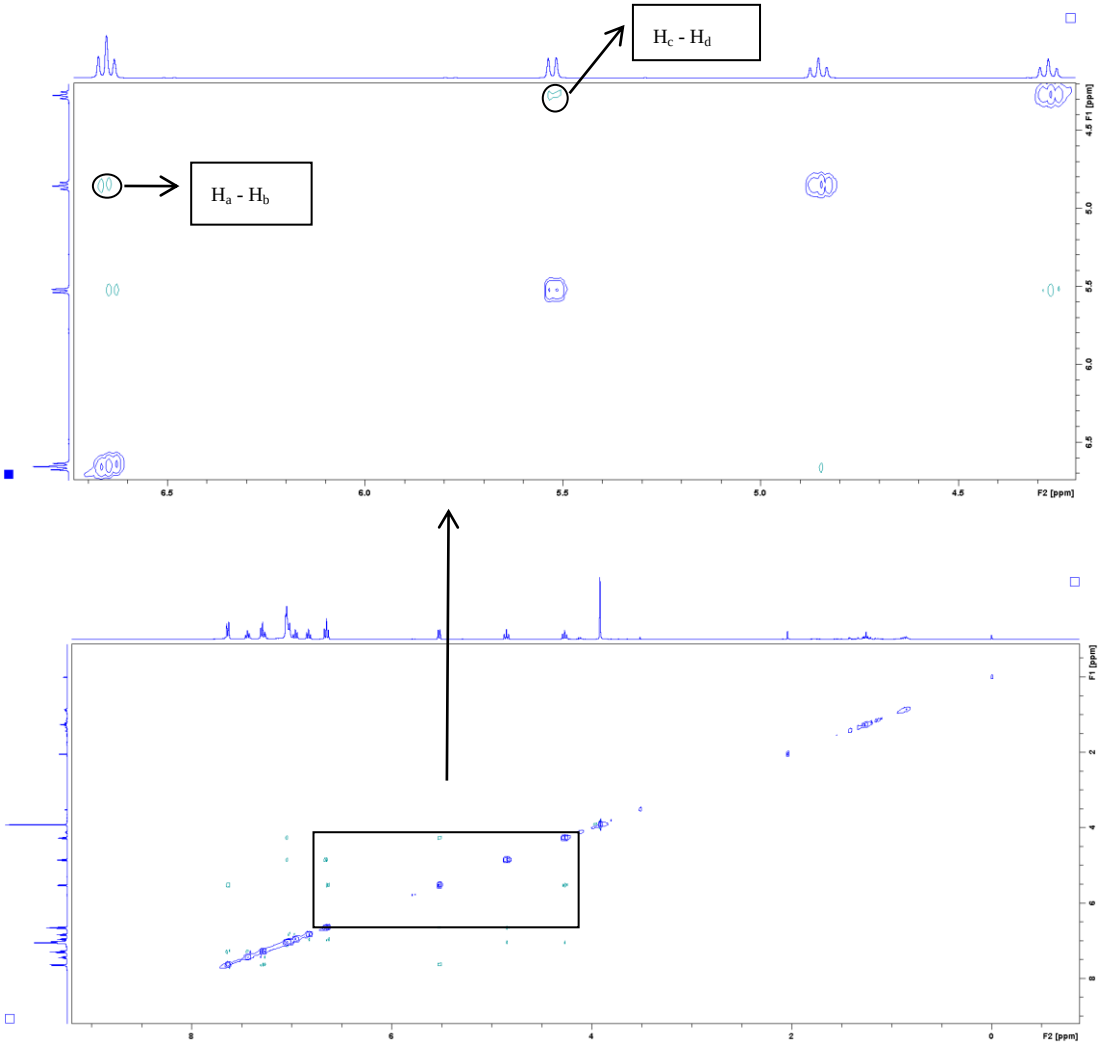
8a



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.85 (d, *J* = 8.4, $1H_a$), 5.17 (d, *J* = 8.0, $1H_d$), 4.44 (dd, *J* = 10.4, 8.4, $1H_b$), 3.95 (dd, *J* = 10.4, 8.0, $1H_c$),

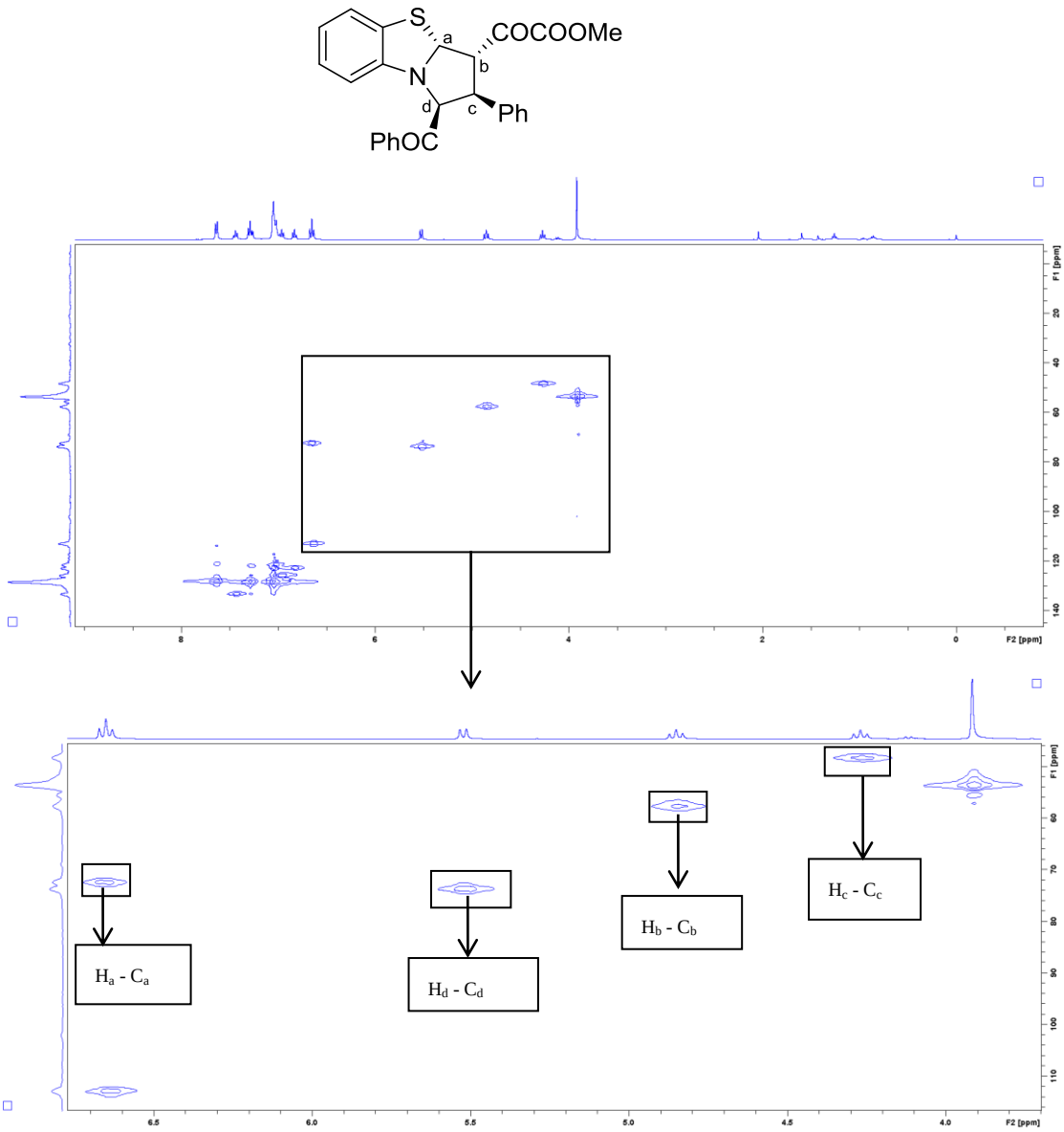
Compound 8b





^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 8.0 Hz, $1H_a$), 5.52 (d, *J* = 8.0 Hz, $1H_d$), 5.01 - 4.71 (m, $1H_b$), 4.37 - 4.17 (m, $1H_c$)

15. HMQC spectra of 8b.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 8.0 Hz, $1H_a$), 5.52 (d, *J* = 8.0 Hz, $1H_d$), 5.01 – 4.71 (m, $1H_b$), 4.37 – 4.17 (m, $1H_c$)

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 73.7 ($1C_d$), 72.5 ($1C_a$), 57.7 ($1C_b$), 48.4 ($1C_c$).

16. HMBC spectra of 8b.

Fig. 1

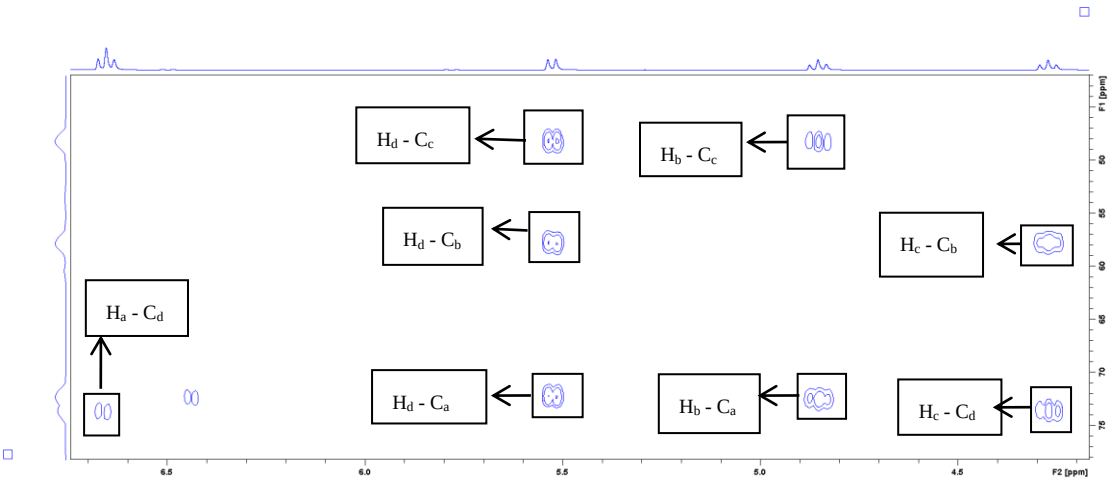


Fig. 2

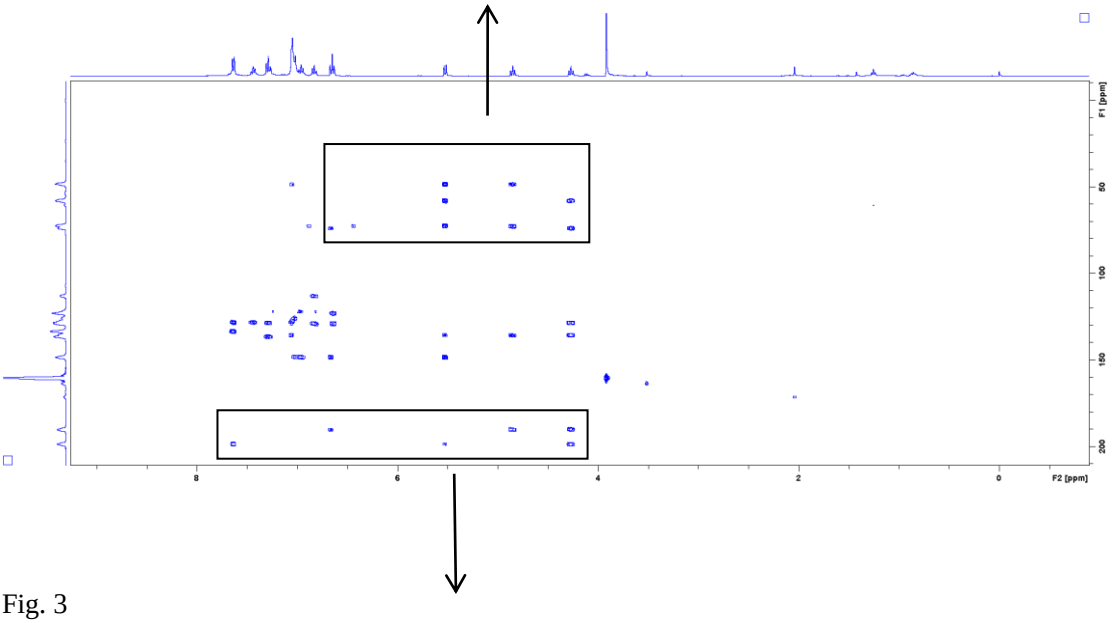
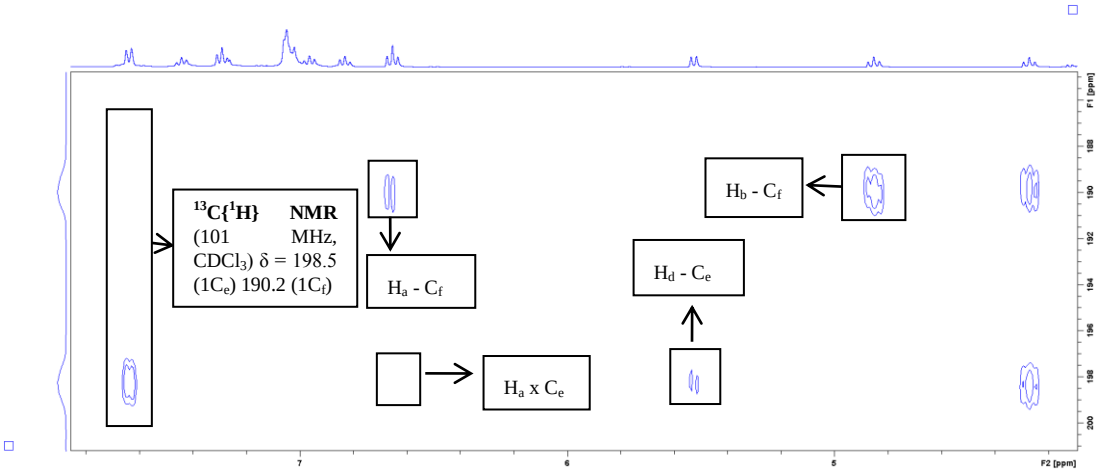
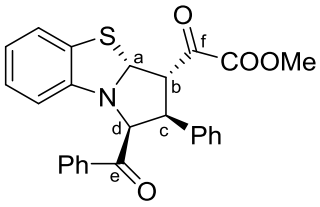


Fig. 3


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 198.5 ($1C_e$) 190.2 ($1C_f$)
H_a - C_f
H_a x C_e
H_d - C_e
H_b - C_f
F2 [ppm]
F1 [ppm]


S
a
O
f
COOMe
b
N
d
c
Ph
Ph
e
O