

## Supporting Information

# CPA-catalyzed asymmetric domino thia-Michael/aldol reactions for simultaneous chiral centers and axial chirality formation

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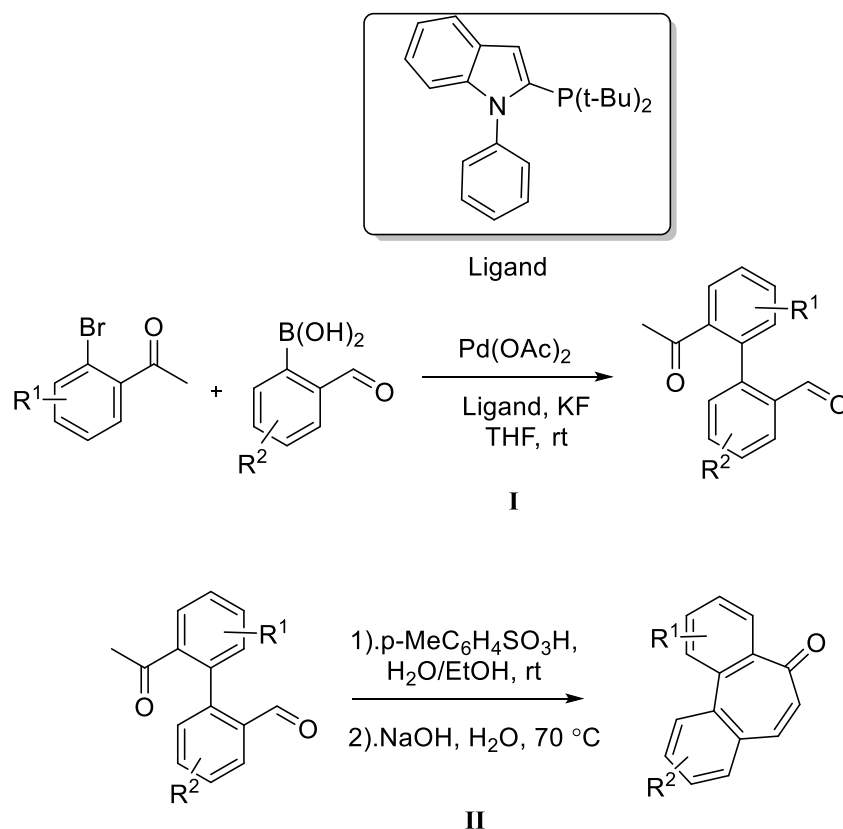
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## 1. General Information

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature on a 500 MHz NMR spectrometer (125 MHz for  $^{13}\text{C}$ ). NMR experiments were reported in  $\delta$  units, parts per million (ppm), and were referenced to  $\text{CDCl}_3$  ( $\delta$  7.26 or 77.0 ppm) as the internal standard. The coupling constants  $J$  were given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

## 2. Synthetic Procedures

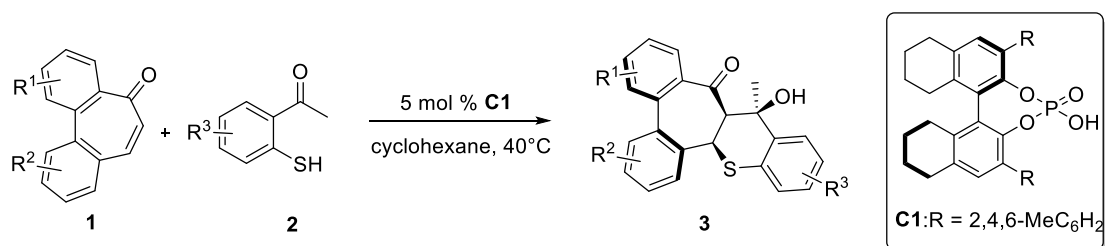


(I) 1-(2-bromophenyl) ethan-1-one (5.0 mmol), (2-formylphenyl) boronic acid (6.0 mmol, 1.2eq.), Pd (OAc)<sub>2</sub>(22.0 mg, 2.0 mol %), KF (870.0 mg, 15.0 mmol), and ligand (60 mg, 4.0 mol %) were sequentially added to an oven-dried microwave vial. The mixture was suspended in THF (15.0 mL) and stirred for 3h at rt. The reaction mixture was directly purified by silica gel column chromatography (hexanes/EtOAc, 16:1) to provide the corresponding 2'-acetyl-[1,1'-biphenyl]-2-carbaldehyde.

(II) Subsequently, to a solution of 2'-acetyl-[1,1'-biphenyl]-2-carbaldehyde (4.0 mmol) in H<sub>2</sub>O/EtOH (3 mL/7 mL) was added *p*-TsOH (172 mg, 8.0 mmol). The mixture was stirred at room temperature for 30 min, and then 20% aq. NaOH solution (32 mg, 0.8 mmol) was added. After being stirred at 70°C for 15 min, the resulting mixture was cooled to rt and diluted with water (20 mL). The aqueous layer was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 16:1) to provide 5H-dibenzo[*a,c*][7]annulen-5-one.<sup>1</sup>

### 3. CPA-Catalyzed Asymmetric Domino Thia-Michael/Aldol

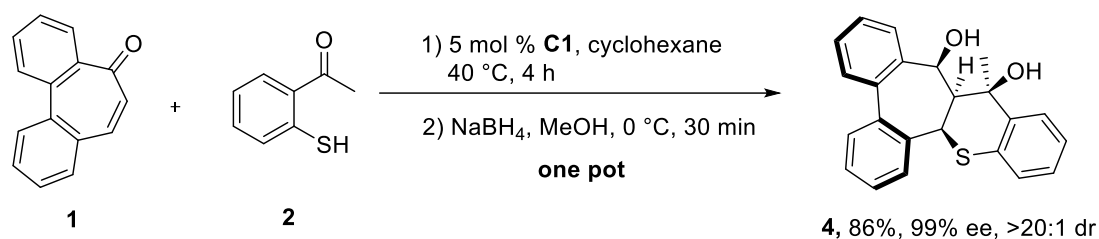
#### Reactions



To a solution of 5H-dibenzo[*a,c*][7]annulen-5-one **1** (0.1 mmol, 1.0 eq.) in cyclohexane (1.5 mL) was added **C1** (5 mol%, 3.0 mg) and 1-(2-mercaptophenyl)ethan-1-one **2** (2.5 equiv). The mixture was vacuumed and refilled with N<sub>2</sub> for 3 times. The reaction mixture was stirred at 40 °C for 3.5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure and the residue was

purified on a silica gel column (hexane/EtOAc, 30:1) to obtain the corresponding 10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-b] thiochromen-9(10H)-one **3**.

#### 4. Derivatization of the Products



To a solution of 5H-dibenzo[a,c][7]annulen-5-one **1** (0.1 mmol, 1.0 eq.) in cyclohexane (1.5 mL) was added **C1** (5 mol%, 3.0 mg) and 1-(2-mercaptophenyl)ethan-1-one **2** (2.5 equiv). The mixture was vacuumed and refilled with N<sub>2</sub> for 3 times. The reaction mixture was stirred at 40 °C for 3.5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. At 0 °C, sodium borohydride (1.5 eq.) was added dropwise to the reaction system by dissolving it in MeOH (1 mL), and the mixture reacted for 30 minutes. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 4:1) to obtain the corresponding (9S,9aS,10R,15aR)-10-methyl-9,9a,10,15a-tetrahydrodibenzo [4,5:6,7] cyclohepta[1,2-b] thiochromene-9,10-diol **4**.

#### 5. Computational Details

DFT calculations were performed using the Gaussian 16 suite of programs.<sup>2</sup> Equilibrium structures and transition states were fully optimized using B3LYP-D3(BJ) density functional method<sup>3</sup> with the 6-31G(d,p) basis sets,<sup>4</sup> while single point energies were computed at B3LYP-D3(BJ)/def2TZVP level.<sup>5</sup> Frequency analyses at 298 K were performed on B3LYP/6-31G\*\* optimized geometries to obtain thermodynamic corrections and to confirm the nature of the stationary points as equilibrium structures

(with all real frequencies) or transition states (with only one imaginary frequency), and relative free energies,  $\Delta G_{298}$ , were reported in these cases. Connections between the key transition-state structures and the corresponding reactants and products were confirmed using intrinsic reaction coordinate calculations.<sup>6</sup> For all calculations mentioned above, the solvent effect was modeled using the SMD model with cyclohexane as the solvent.<sup>7</sup>

**Table S1.** Enthalpy corrections ( $\Delta H$ ), free energy corrections ( $\Delta G$ ) of stationary points computed at the M062X/6-31G(d,p) level, with single point electronic energies ( $E$ ), enthalpies ( $H$ ) and free energies ( $G$ ) computed at the M062X/def2TZVP level. All numbers are in hartrees.

Structure	$\Delta H$	$\Delta G$	$E$	$H$	$G$
<b>3a-GS-1</b>	0.371475	0.303628	-1436.488937	-1436.117462	-1436.185309
<b>3a-GS-2</b>	0.371667	0.302768	-1436.47356	-1436.101893	-1436.170792
<b>3a-TS</b>	0.370845	0.303867	-1436.471757	-1436.100912	-1436.16789

### Cartesian coordinates of DFT-computed structures

<b>3a-GS-1</b>							
C	-1.48441900	-1.28058100	0.22151800	C	3.51924600	0.21331100	0.35790000
C	-2.48113600	-0.20920300	-0.02250500	O	0.58494300	0.26708300	2.68691700
C	-2.10972900	1.08950100	-0.42611000	C	1.77935800	3.15549700	-0.34294700
C	-0.66825100	1.50527700	-0.58688200	O	2.20876100	2.22084800	1.76277100
C	0.11105200	1.51212200	0.72954400	H	-0.66904200	2.53561700	-0.94408200
C	0.09592900	0.22841600	1.55846200	H	1.42603200	-1.96827100	1.85302400
C	-0.31791900	-1.08189700	0.98709600	H	0.97262400	-4.23610400	0.92936800
C	0.54062700	-2.15689200	1.25771700	H	-1.07364100	-4.60286400	-0.44729100
C	0.28393700	-3.41944400	0.73969700	H	-2.62589800	-2.73187200	-0.87298400
C	-0.86239600	-3.62306100	-0.03012900	H	-4.12890600	-1.49581000	0.46429800
C	-1.73904000	-2.56929400	-0.27005700	H	-5.87317300	0.19544000	0.00741000
C	-3.84364000	-0.50466800	0.12726900	H	-5.21107900	2.48319100	-0.73432200
C	-4.82618800	0.45052300	-0.12217000	H	-2.81286900	3.03097000	-1.00733900
C	-4.45687300	1.72942800	-0.53220600	H	1.82389400	-1.63036500	-2.58759900
C	-3.10584500	2.03671900	-0.68162100	H	3.99596200	-2.43743600	-1.71530000
S	0.16548500	0.54530700	-1.95262300	H	5.07894500	-1.26075800	0.19708400
C	1.70518600	0.02905800	-1.22237700	H	3.96020000	0.73214200	1.20104800
C	2.31008600	0.69888500	-0.14380900	H	1.18101700	3.97255200	0.07120400
C	1.62485000	1.89603500	0.51651100	H	2.83063200	3.45019300	-0.31083300
C	2.31635100	-1.10216600	-1.77730900	H	1.50162700	2.98288900	-1.38405500
C	3.53192400	-1.55908900	-1.27720000	H	1.85079100	1.59088500	2.41742600
C	4.13650300	-0.90219900	-0.20466200	H	-0.31891900	2.30021600	1.35805700

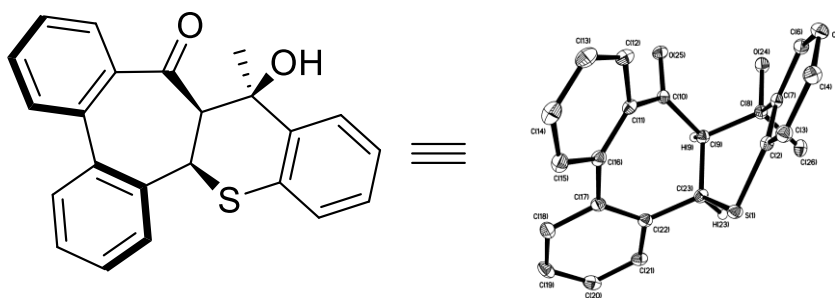
<b>3a-GS-2</b>				H	1.75567200	-2.63828100	0.42667600
C	-2.65573900	-0.59570400	-0.15596700	H	-0.37178600	-0.87327500	1.67411200
C	-2.48607900	0.86578200	0.12672500	<b>3a-TS</b>			
C	-1.31347600	1.52931200	0.55957100	C	-2.59686500	-0.70784200	-0.06008000
C	0.08042000	0.95335300	0.66678400	C	-2.55059300	0.79299400	0.08649300
C	0.27066600	-0.54757400	0.84590600	C	-1.39269000	1.59729100	0.24223300
C	-0.17842300	-1.32301300	-0.38824100	C	0.03489700	1.12810700	0.32369000
C	-1.64581800	-1.49763600	-0.57815200	C	0.33108400	-0.17944600	1.04425400
C	-1.99039800	-2.77506700	-1.05098100	C	-0.05810200	-1.36191500	0.17287700
C	-3.30040400	-3.23089500	-1.04059400	C	-1.49557400	-1.60998600	-0.15941900
C	-4.28678400	-2.40283600	-0.50949500	C	-1.71863900	-2.96276400	-0.48607600
C	-3.96390600	-1.11911900	-0.08537300	C	-2.98361500	-3.49333700	-0.65975300
C	-3.62921500	1.67438700	-0.07976000	C	-4.07394500	-2.64986500	-0.47203300
C	-3.65990200	3.03285200	0.19594300	C	-3.87158600	-1.30752600	-0.18656100
C	-2.51981700	3.65817300	0.69458500	C	-3.77499500	1.50245400	0.01283800
C	-1.36798400	2.90279100	0.85338200	C	-3.87617000	2.88255200	0.09246800
S	0.98645800	1.52565200	-0.84479200	C	-2.72794600	3.65322100	0.24354600
C	2.55734300	0.71419800	-0.61859800	C	-1.51097600	2.99611900	0.31162500
C	2.77806000	-0.34552200	0.27563800	S	0.76561800	1.07817400	-1.37327700
C	1.73032200	-0.90036800	1.24730100	C	2.41830700	0.54634900	-0.95198200
C	3.59795800	1.16845700	-1.44295700	C	2.77535000	-0.03635000	0.27734600
C	4.85346500	0.57584300	-1.39231700	C	1.82441400	-0.24345800	1.46760600
C	5.08523200	-0.47902700	-0.50809500	C	3.37940600	0.70445000	-1.96180800
C	4.05429900	-0.92406900	0.31164700	C	4.68968600	0.28553000	-1.76772100
O	0.62298000	-1.93546800	-1.08307700	C	5.05663900	-0.29491700	-0.55263900
C	2.02733800	-0.40217900	2.66884800	C	4.10434100	-0.44754300	0.44854200
O	1.84584200	-2.32005300	1.33977000	O	0.79216700	-2.18352500	-0.15826400
H	0.56004900	1.44706600	1.51317700	C	2.12338300	0.79168900	2.56236500
H	-1.18127500	-3.41059800	-1.39151900	O	2.08100500	-1.49523600	2.09805400
H	-3.54001700	-4.22629700	-1.39960800	H	0.57911600	1.91382300	0.84483700
H	-5.31143300	-2.75077200	-0.42252800	H	-0.84107100	-3.59073100	-0.57213800
H	-4.75471600	-0.50816200	0.32948600	H	-3.11579600	-4.54180000	-0.90503800
H	-4.51561300	1.22688200	-0.50845400	H	-5.08901900	-3.02689300	-0.55049900
H	-4.56790300	3.59796900	0.01140300	H	-4.76373100	-0.71673800	-0.05624500
H	-2.51883700	4.71717400	0.93079200	H	-4.70205100	0.97372700	-0.13852200
H	-0.45783900	3.38532800	1.19716200	H	-4.85417000	3.34847100	0.02633300
H	3.41155100	1.99122400	-2.12691600	H	-2.77713100	4.73535400	0.30352300
H	5.64646800	0.93822500	-2.03916300	H	-0.59948000	3.57645700	0.41867200
H	6.06088600	-0.95201000	-0.45921900	H	3.08766900	1.16018500	-2.90341400
H	4.21406800	-1.75643700	0.98836700	H	5.41950800	0.41430400	-2.56103500
H	1.28537900	-0.79876000	3.36862800	H	6.07622500	-0.62863400	-0.38784700
H	3.01284200	-0.76334600	2.96925700	H	4.36926000	-0.92053800	1.38789100
H	2.03711300	0.68769600	2.73194800				

H	1.43423100	0.65789600	3.40174200
H	3.14083100	0.63080000	2.92401800
H	2.05693600	1.81943800	2.20083400

H	1.94986100	-2.15345100	1.39485800
H	-0.27492500	-0.22380100	1.95906000

## 6. X-ray Crystal Structure of Enantiopure

The molecular structure and X-ray diffractive data/refinement of 3a were shown below.



## Datablock: fanwx\_98\_200922

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Bond precision: C-C = 0.0040 Å                      Wavelength=1.54184  
Cell:                      a=10.3685(1)      b=10.7520(1)      c=15.8732(1)  
                              alpha=90            beta=99.443(1)      gamma=90  
Temperature:            100 K

	Calculated	Reported
Volume	1745.60(3)	1745.60(3)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C23 H18 O2 S	C23 H18 O2 S
Sum formula	C23 H18 O2 S	C23 H18 O2 S
Mr	358.43	358.43
Dx, g cm <sup>-3</sup>	1.364	1.364
Z	4	4
Mu (mm <sup>-1</sup> )	1.755	1.755
F000	752.0	752.0
F000'	755.32	
h,k,lmax	13,13,20	13,13,20
Nref	7374[ 3891]	7207
Tmin,Tmax	0.620,0.645	0.729,1.000
Tmin'	0.563	

Correction method= # Reported T Limits: Tmin=0.729 Tmax=1.000  
AbsCorr = MULTI-SCAN

Data completeness= 1.85/0.98                      Theta(max)= 77.042

R(reflections)= 0.0373( 7061)                      wR2(reflections)= 0.1008( 7207)

S = 1.126    Npar= 474

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The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level**.  
Click on the hyperlinks for more details of the test.



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● Alert level C		
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds .....	0.00404 Ang.
PLAT790_ALERT_4_C	Centre of Gravity not Within Unit Cell: Resd. # C23 H18 O2 S	1 Note
PLAT934_ALERT_3_C	Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..	1 Check

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● Alert level G		
PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms .....	2 Report
PLAT142_ALERT_4_G	s.u. on b - Axis Small or Missing .....	0.00010 Ang.
PLAT143_ALERT_4_G	s.u. on c - Axis Small or Missing .....	0.00010 Ang.
PLAT153_ALERT_1_G	The s.u.'s on the Cell Axes are Equal ..(Note)	0.0001 Ang.
PLAT791_ALERT_4_G	Model has Chirality at C8 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C9 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C23 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C34 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C35 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C49 (Sohnke SpGr)	R Verify
PLAT912_ALERT_4_G	Missing # of PCF Reflections Above STh/L= 0.600	44 Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	2 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	8 Info

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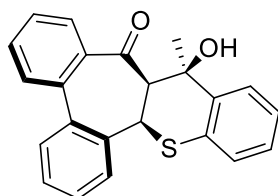
0 ALERT level A - Most likely a serious problem - resolve or explain  
0 ALERT level B - A potentially serious problem, consider carefully  
3 ALERT level C - Check. Ensure it is not caused by an omission or oversight  
13 ALERT level G - General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
2 ALERT type 2 Indicator that the structure model may be wrong or deficient  
2 ALERT type 3 Indicator that the structure quality may be low  
10 ALERT type 4 Improvement, methodology, query or suggestion  
1 ALERT type 5 Informative message, check

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## 7. Characterization Data for the Products

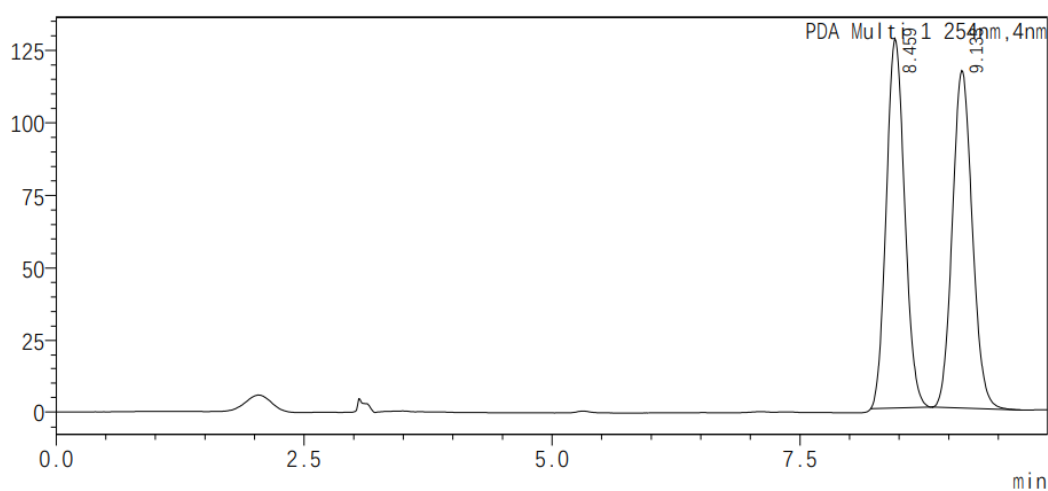
(9*aR*,10*R*,15*aR*)-10-hydroxy-10-methyl-9*a*,15*a*-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (**3a**)



**3a**

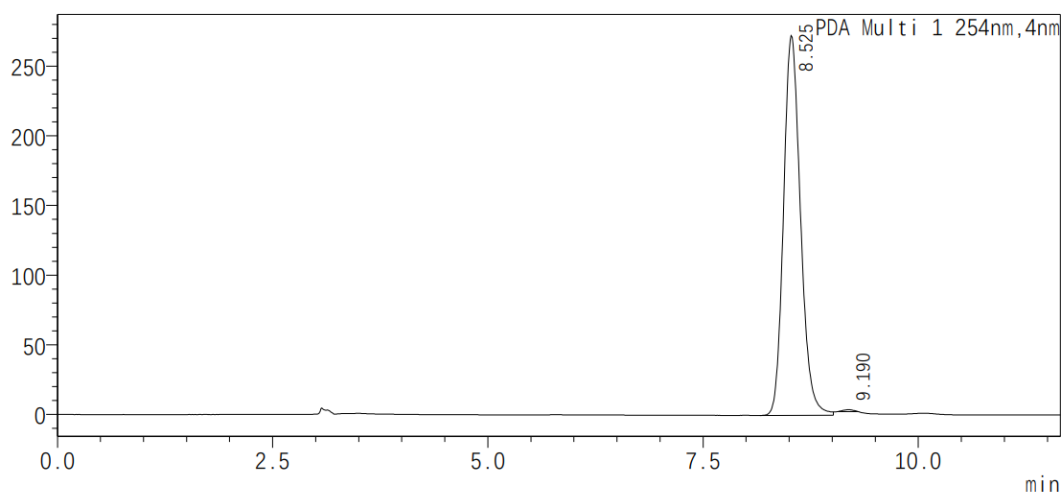
Flash column chromatography on silica gel (hexane/EtOAc, 30:1) gave the product **3a** (31.5 mg, 88% yield) as a white solid.  $[\alpha]_D^{25} = -25$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.45 (dt,  $J = 19.3, 7.2$  Hz, 3H), 7.37 (q,  $J = 7.7$  Hz, 3H), 7.07 (t,  $J = 7.5$  Hz, 1H), 6.97 (t,  $J = 7.5$  Hz, 1H), 6.90 (t,

$J = 7.3$  Hz, 1H), 6.54 (d,  $J = 7.8$  Hz, 1H), 6.43 (d,  $J = 7.7$  Hz, 1H), 5.03 (d,  $J = 5.0$  Hz, 1H), 4.73 (s, 1H), 3.45 (d,  $J = 5.0$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  209.20, 139.92, 139.26, 139.19, 138.85, 136.22, 134.93, 132.53, 131.46, 129.81, 129.73, 128.72, 128.15, 128.11, 127.62, 127.24, 125.25, 124.96, 124.90, 75.12, 64.52, 44.63, 27.09. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{S}^+$  (M+H) $^+$  :359.1100, found 359.1108. The ee of compound **3a** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm),  $n$ -hexane/ $i$ -PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 8.525$  min,  $t(\text{major}) = 9.133$  min.



PDA Ch1 254nm

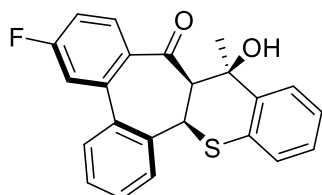
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.459	1653675	127702	50.269	0.355
2	9.133	1635958	116692	49.731	0.379



PDA Ch1 254nm

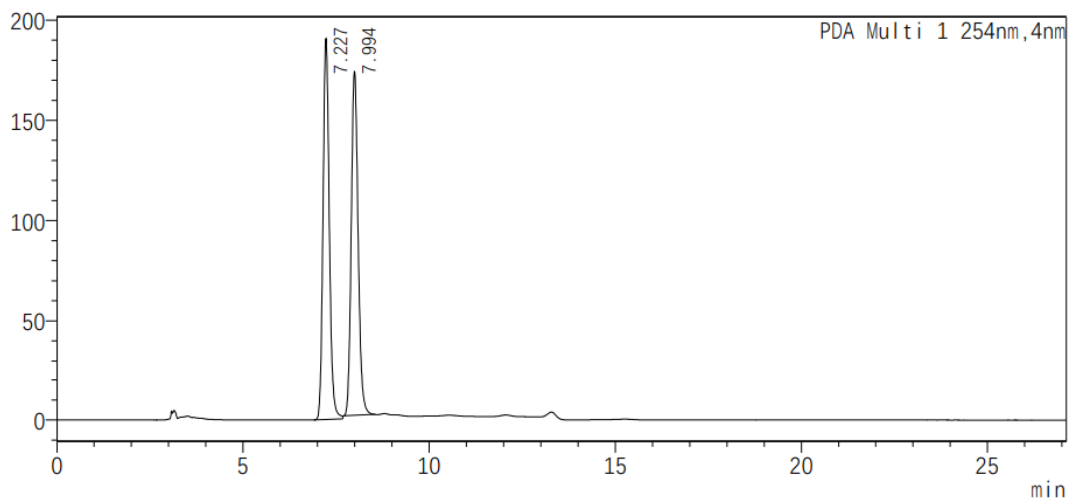
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.525	3738820	272507	99.691	0.366
2	9.190	11599	1371	0.309	0.232

**(9a*R*,10*R*,15a*R*)-6-fluoro-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3b)**



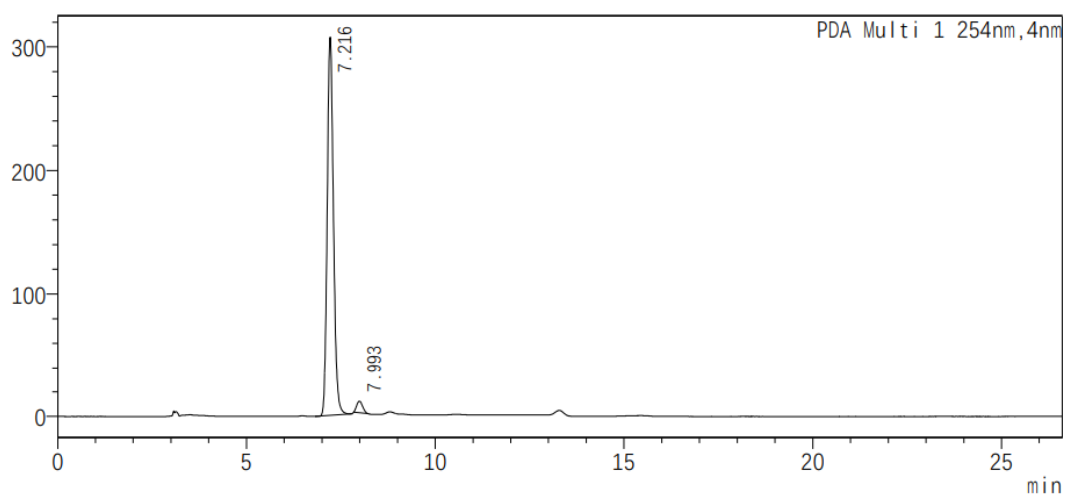
**3b**

Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3b** (33.1 mg, 88% yield) as a white solid.  $[\alpha]_D^{25} = -22$  ( $c = 1.0$  in DCM, 95% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.8$  Hz, 1H), 7.55 – 7.45 (m, 1H), 7.41 (m, 3H), 7.07 (q,  $J = 8.4, 8.0$  Hz, 2H), 6.94 (t,  $J = 7.5$  Hz, 1H), 6.67 (t,  $J = 8.0$  Hz, 1H), 6.62 (d,  $J = 7.8$  Hz, 1H), 6.49 – 6.42 (m, 1H), 5.03 (d,  $J = 4.9$  Hz, 1H), 4.75 (s, 1H), 3.43 (d,  $J = 4.9$  Hz, 1H), 1.71 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.80, 165.31 (d,  $J = 254.52$  Hz), 141.78, 141.71, 139.95, 138.18, 136.44, 135.61, 134.88, 131.36, 130.47 (d,  $J = 8.82$  Hz), 129.93, 129.87, 129.31, 127.36, 125.22, 125.02, 114.87 (d,  $J = 6.30$  Hz), 114.69 (d,  $J = 5.04$  Hz), 75.21, 64.21, 44.55, 27.06.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -93.47. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{FO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  377.1000, found 377.1006. The ee of compound **3b** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 7.216$  min,  $t(\text{major}) = 7.993$  min.



PDA Ch1 254nm

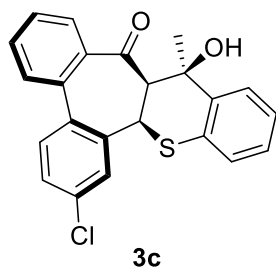
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.227	2240280	190534	50.340	0.316
2	7.994	2209998	172025	49.660	0.345



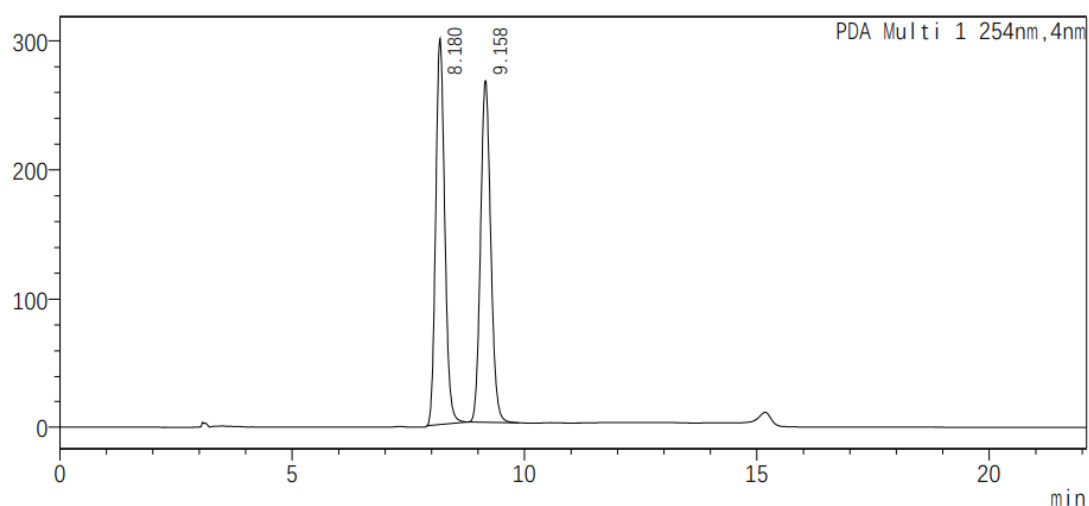
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.216	3533495	306604	97.175	0.312
2	7.993	102716	9401	2.825	0.309

**(9aR,10R,15aR)-2-chloro-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-b] thiochromen-9(10H)-one**

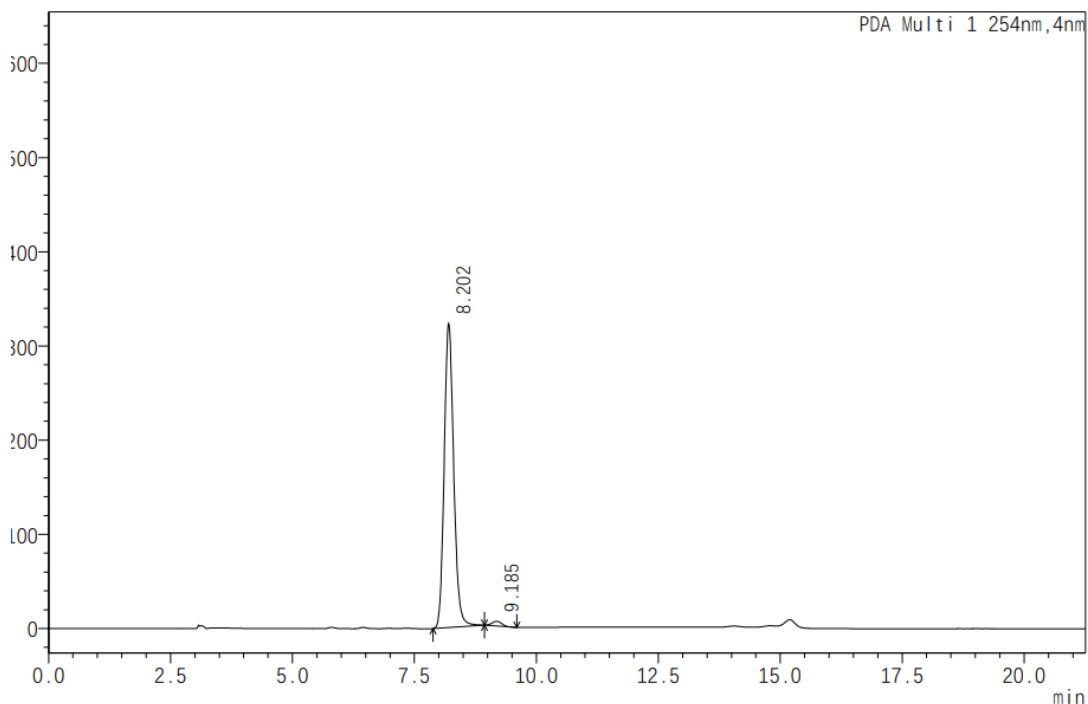


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3b** (32.6 mg, 83% yield) as a white solid.  $[\alpha]_D^{25} = -26$  ( $c = 1.0$  in DCM, 97% ee, >20:1 dr).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.8$  Hz, 1H), 7.56 – 7.39 (m, 3H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.31 (d,  $J = 7.7$  Hz, 1H), 7.08 (t,  $J = 7.4$  Hz, 1H), 6.99 (t,  $J = 7.6$  Hz, 1H), 6.91 (t,  $J = 7.6$  Hz, 1H), 6.53 (d,  $J = 7.8$  Hz, 1H), 6.43 (d,  $J = 7.7$  Hz, 1H), 4.97 (d,  $J = 4.9$  Hz, 1H), 4.67 (s, 1H), 3.45 (d,  $J = 4.9$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.60, 139.87, 139.11, 137.99, 137.77, 137.71, 134.54, 134.35, 132.73, 132.61, 129.70, 128.29, 127.96, 127.33, 125.27, 125.11, 125.01, 75.11, 64.33, 44.27, 26.97. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  393.0711, found 393.0721. The ee of compound **3c** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm),  $n$ -hexane/ $i$ -PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 8.202$  min,  $t(\text{minor}) = 9.185$  min.



PDA Ch1 254nm

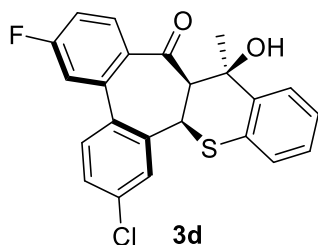
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.180	4054754	299450	50.012	0.364
2	9.158	4052733	265310	49.988	0.409



PDA Ch1 254nm

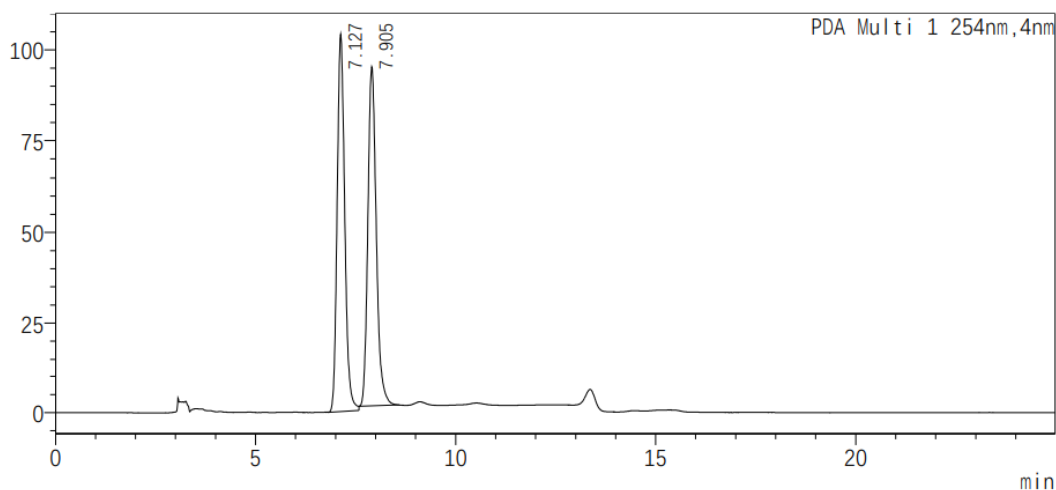
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.202	4368840	322528	98.526	0.362
2	9.185	65347	4886	1.474	0.382

**(9*aR*,10*R*,15*aR*)-2-chloro-6-fluoro-10-hydroxy-10-methyl-9*a*,15*a*-dihydrodibenz -  
o [4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3d)**



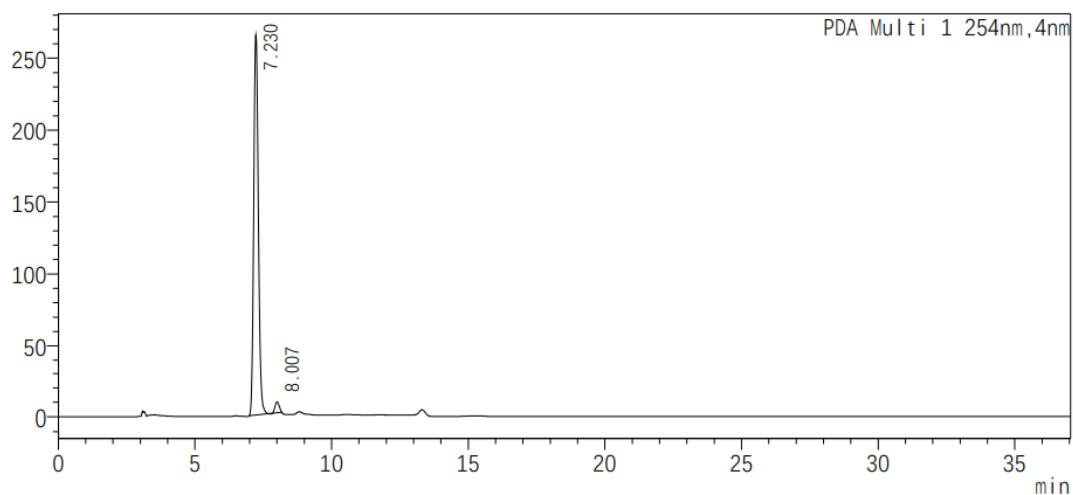
Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3d** (37.4 mg, 85% yield) as a white solid.  $[\alpha]_D^{25} = -22$  ( $c = 1.0$  in DCM, 91% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.55 – 7.39 (m, 2H), 7.34 (d,  $J = 8.2$  Hz, 1H), 7.09 (t,  $J = 7.5$  Hz, 1H), 7.06 – 6.99 (m, 1H), 6.94 (t,  $J = 7.4$  Hz, 1H), 6.68 (t,  $J = 8.2$  Hz, 1H), 6.60 (d,  $J = 7.8$  Hz, 1H), 6.52 – 6.39 (m, 1H), 4.97 (d,  $J = 5.0$  Hz, 1H), 4.69 (s, 1H), 3.43 (d,  $J = 4.9$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.21, 165.29 (d,  $J = 254.52$  Hz), 140.59, 140.52, 139.89, 138.21, 136.65, 135.54, 135.01, 134.48, 132.63, 131.14 (d,  $J = 8.82$  Hz), 129.85, 129.84, 127.45, 125.23,

125.06, 115.10 (d,  $J = 21.42$  Hz), 114.69 (d,  $J = 254.52$  Hz), 75.20, 64.01, 44.18, 26.94.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.12. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{ClFO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  411.0616, found 411.0628. The ee of compound **3d** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm),  $n$ -hexane/ $i$ -PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 7.230$  min,  $t(\text{major}) = 8.007$  min.



PDA Ch1 254nm

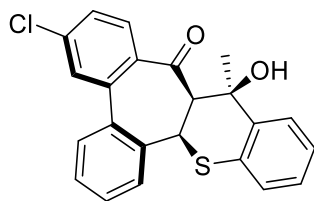
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.127	1373163	103967	50.035	0.353
2	7.905	1371220	93526	49.965	0.386



PDA Ch1 254nm

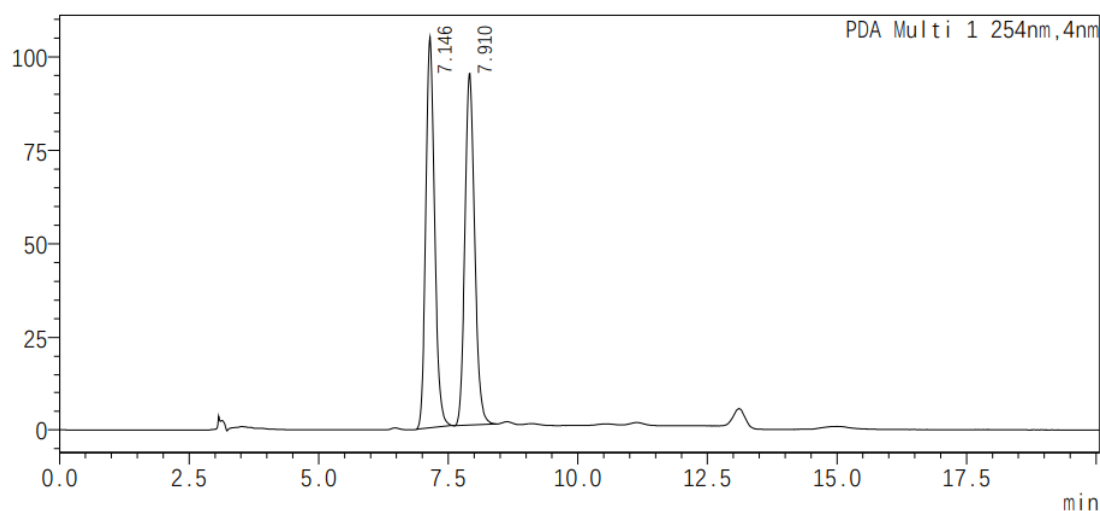
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.230	3065915	264874	97.474	0.314
2	8.007	79445	7617	2.526	0.303

**(9aR,10R,15aR)-6-chloro-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3e)**



**3e**

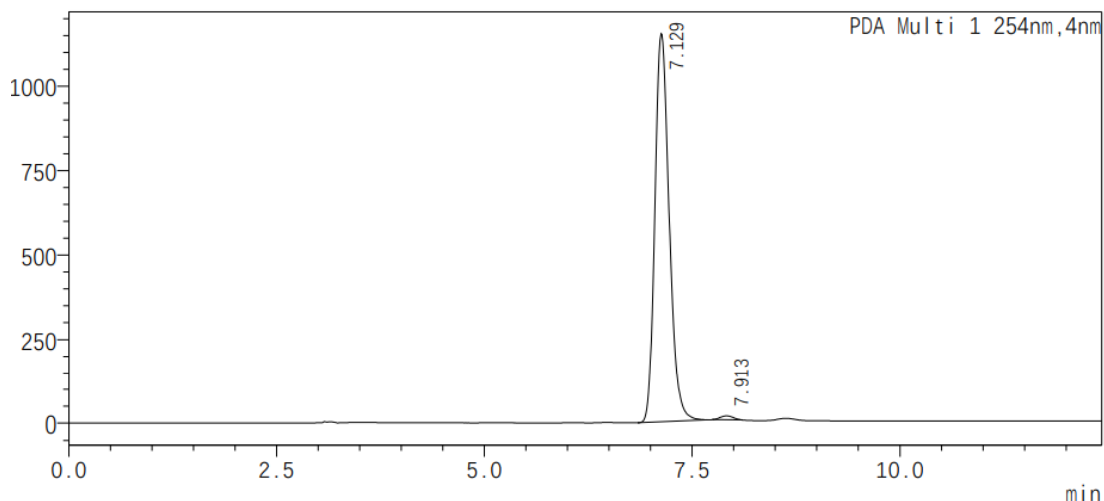
Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3e** (36.1 mg, 92% yield) as a white solid.  $[\alpha]_D^{25} = -28$  ( $c = 1.0$  in DCM, 98% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 7.7$  Hz, 1H), 7.57 – 7.29 (m, 5H), 7.08 (t,  $J = 7.0$  Hz, 1H), 7.02 – 6.80 (m, 1H), 6.62 (d,  $J = 7.7$  Hz, 1H), 6.39 (d,  $J = 7.8$  Hz, 1H), 5.46 – 4.85 (m, 1H), 4.67 (s, 1H), 3.57 – 3.07 (m, 1H), 1.71 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.01, 140.48, 139.96, 138.73, 137.95, 137.57, 136.47, 134.81, 131.35, 129.95, 129.87, 129.67, 129.32, 127.97, 127.67, 127.42, 125.29, 125.04, 125.00, 75.20, 64.36, 44.49, 27.09. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  393.0711, found 393.0724. The ee of compound **3e** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 7.129$  min,  $t(\text{major}) = 7.913$  min.



PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.146	1245112	104630	50.140	0.323
2	7.910	1238158	94272	49.860	0.353

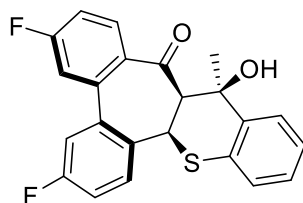




PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	7.129	13811672	1152353	99.098	0.322
2	7.913	125726	11495	0.902	0.311

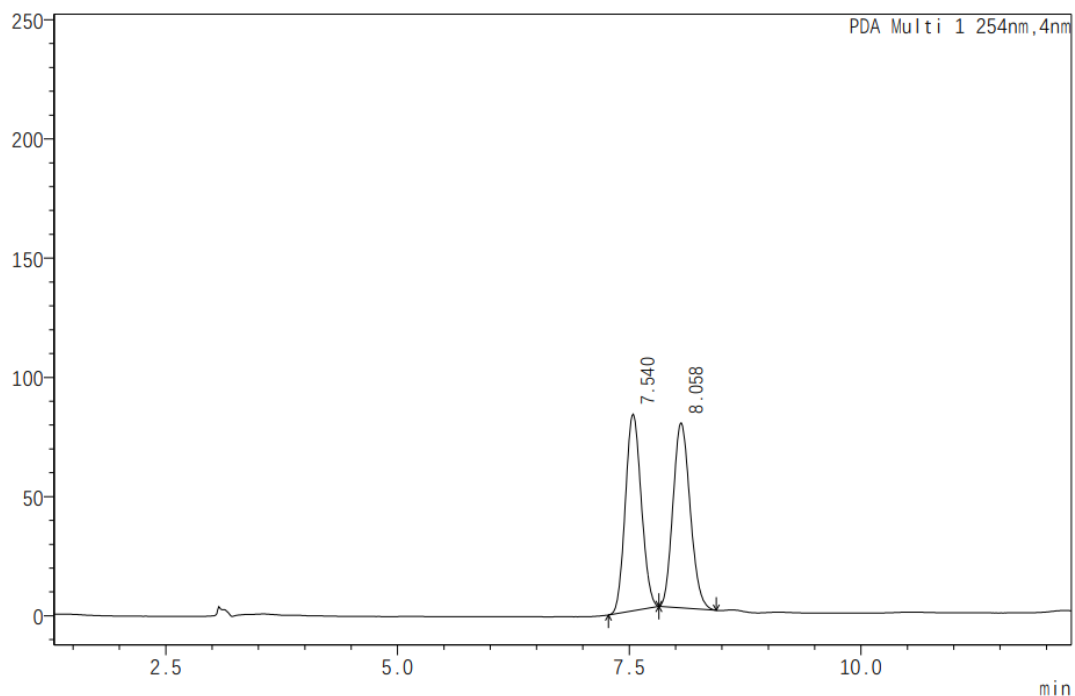
**(9a*R*,10*R*,15a*R*)-3,6-difluoro-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo  
[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3f)**



**3f**

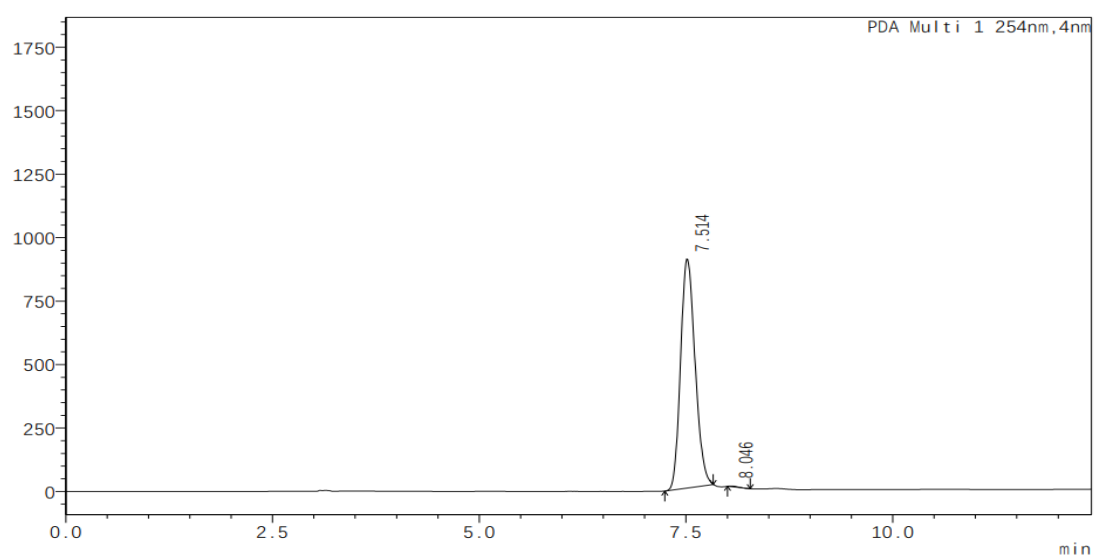
Flash column chromatography on silica gel (hexane/EtOAc, 8:1) gave the product **3f** (34.7 mg, 88% yield) as a white solid.  $[\alpha]_D^{25} = -18$  ( $c = 1.0$  in DCM, 99% ee,  $>20:1$  dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.49 – 7.32 (m, 1H), 7.08 (ddt,  $J = 17.7, 15.0, 9.4$  Hz, 4H), 6.94 (t,  $J = 7.5$  Hz, 1H), 6.69 (t,  $J = 7.4$  Hz, 1H), 6.60 (d,  $J = 7.8$  Hz, 1H), 6.54 – 6.42 (m, 1H), 5.03 (d,  $J = 4.9$  Hz, 1H), 4.68 (s, 1H), 3.41 (d,  $J = 4.9$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.17, 165.13 (d,  $J = 253.3$  Hz), 163.24 (d,  $J = 249.3$  Hz), 140.28 (d,  $J = 10.1$  Hz), 140.15, 139.72, 135.43 (d,  $J = 2.5$  Hz), 134.56, 132.22 (d,  $J = 3.8$  Hz), 131.61 (d,  $J = 7.6$  Hz), 131.00 (d,  $J = 10.1$  Hz), 127.26, 125.03 (d,  $J = 7.6$  Hz), 124.89, 118.13 (d,  $J = 22.7$  Hz), 115.70 (d,  $J = 21.4$  Hz), 115.18 (d,  $J = 21.4$  Hz), 114.60 (d,  $J = 23.9$  Hz), 75.07, 64.10, 43.63, 26.86.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -88.22, -93.96. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{F}_2\text{O}_2\text{S}^+$

$(M+H)^+$  395.0912, found 395.0899. The ee of compound **3f** was determined by HPLC using a MX(2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 7.514$  min,  $t(\text{major}) = 8.046$  min.



PDA Ch1 254nm

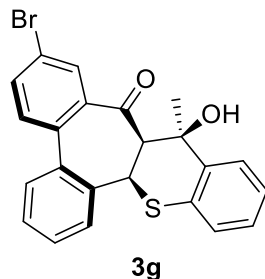
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	7.540	987976	82487	49.720	0.330
2	8.058	999121	77556	50.280	0.351



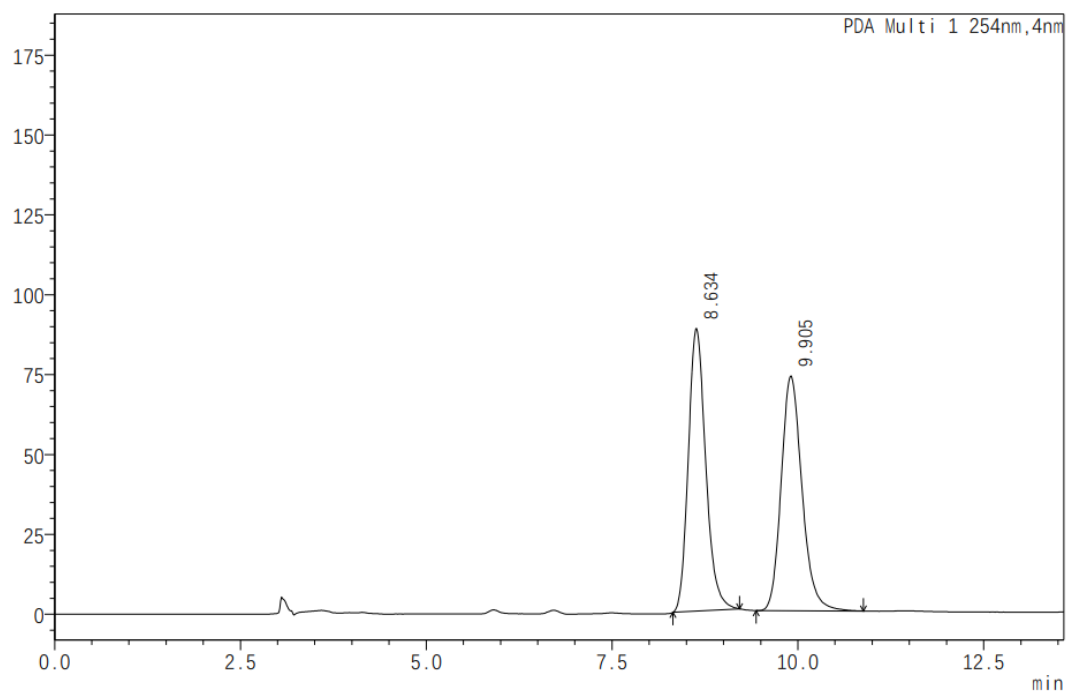
PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	7.514	11006844	902758	99.836	0.333
2	8.046	18049	2775	0.164	0.191

**(9a*R*,10*R*,15a*R*)-7-bromo-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5: 6, 7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3g)**

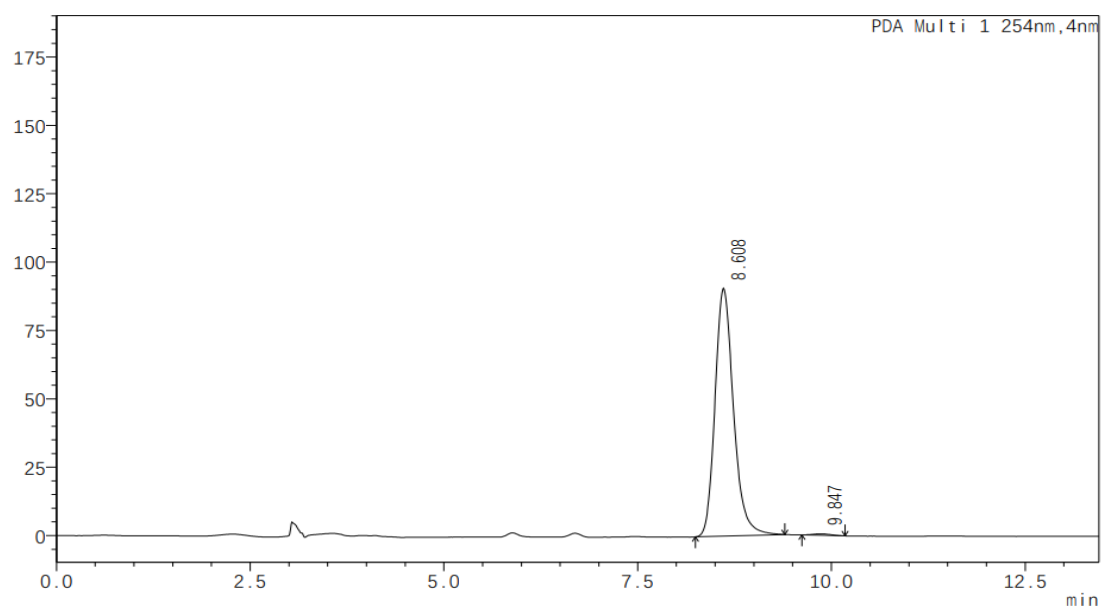


Flash column chromatography on silica gel (hexane/EtOAc, 30:1) gave the product **3g** (39.3 mg, 90% yield) as a white solid.  $[\alpha]_D^{25} = -34$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.64 – 7.55 (m, 2H), 7.48 (t,  $J = 7.5$  Hz, 1H), 7.30 (t,  $J = 7.2$  Hz, 2H), 7.08 (t,  $J = 7.5$  Hz, 1H), 6.99 (t,  $J = 7.5$  Hz, 1H), 6.91 (t,  $J = 7.5$  Hz, 1H), 6.53 (d,  $J = 7.8$  Hz, 1H), 6.43 (d,  $J = 7.6$  Hz, 1H), 4.96 (d,  $J = 5.0$  Hz, 1H), 4.68 (s, 1H), 3.45 (d,  $J = 5.0$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.53, 139.86, 139.05, 138.23, 137.71, 134.52, 132.93, 132.67, 132.61, 132.53, 128.29, 127.98, 127.90, 127.31, 125.25, 125.10, 125.00, 122.38, 75.10, 64.35, 44.16, 26.95. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{BrO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  437.0205, found 437.0210. The ee of compound **3g** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 8.608$  min,  $t(\text{major}) = 9.847$  min.



PDA Ch1 254nm

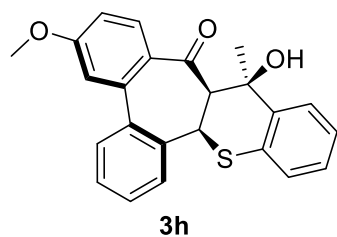
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.634	1443226	88465	50.160	0.431
2	9.905	1434040	73485	49.840	0.510



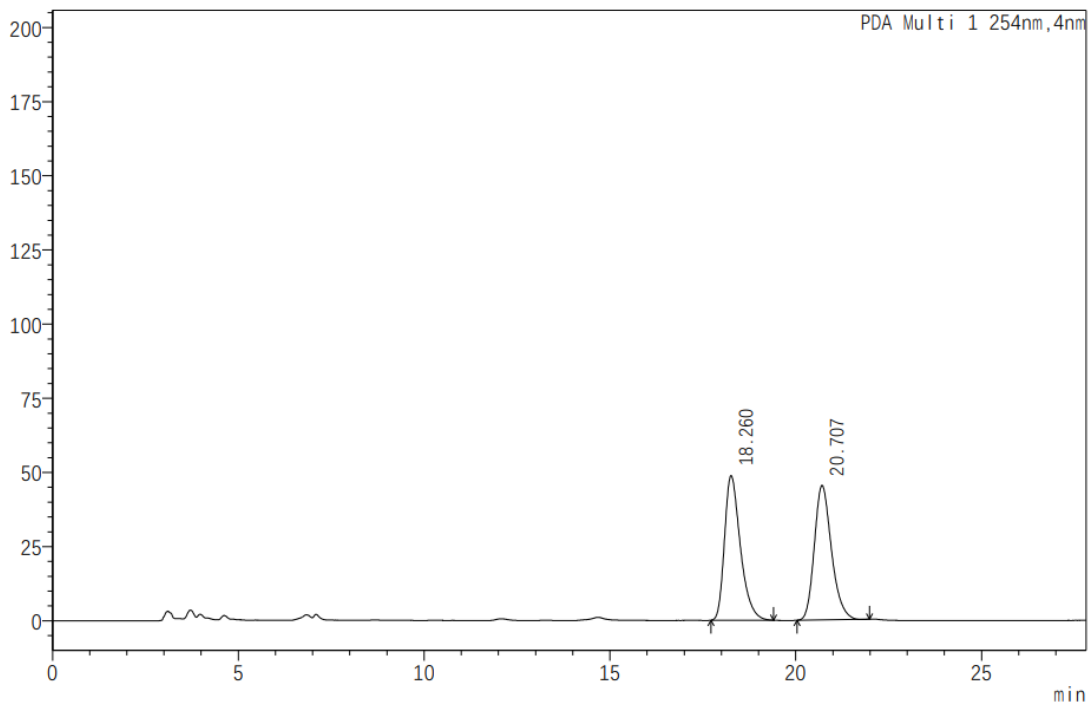
PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.608	1505820	90689	99.403	0.434
2	9.847	9041	553	0.597	0.457

**(9a*R*,10*R*,15a*R*)-10-hydroxy-6-methoxy-10-methyl-9a,15a-dihydrodibenzo  
[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3h)**

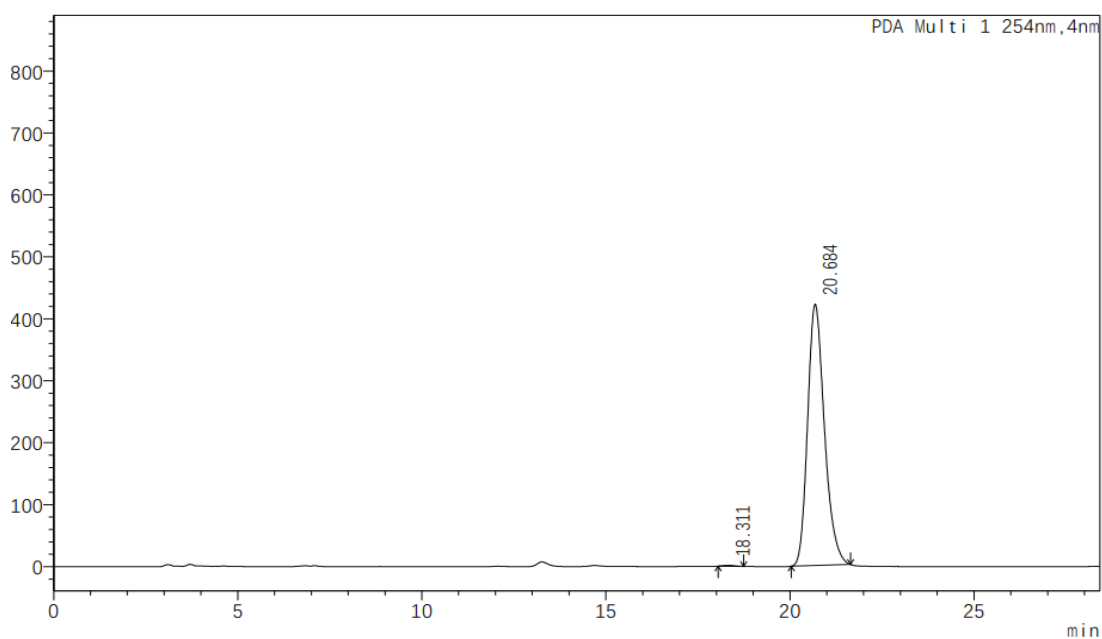


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3h** (31.4 mg, 81% yield) as a white solid.  $[\alpha]_D^{25} = 78$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 7.7$  Hz, 1H), 7.53 – 7.32 (m, 2H), 7.36 (t,  $J = 7.5$  Hz, 2H), 7.07 (t,  $J = 7.5$  Hz, 1H), 6.92 (t,  $J = 7.5$  Hz, 1H), 6.86 (s, 1H), 6.63 (d,  $J = 7.8$  Hz, 1H), 6.52 (s, 2H), 5.11 (s, 1H), 5.05 (d,  $J = 4.8$  Hz, 1H), 3.86 (s, 3H), 3.39 (d,  $J = 4.8$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.72, 163.08, 141.12, 140.07, 139.24, 136.38, 134.85, 132.37, 131.32, 130.71, 129.80, 129.64, 128.84, 127.13, 125.09, 125.02, 124.77, 113.21, 113.18, 75.25, 63.46, 55.59, 44.70, 27.30. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  389.1206, found 389.1205. The ee of compound **3h** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 18.311$  min,  $t(\text{major}) = 20.684$  min.



PDA Ch1 254nm

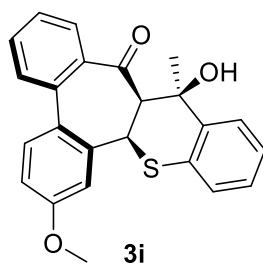
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	18.260	1448077	48794	49.918	0.769
2	20.707	1452817	45351	50.082	0.839



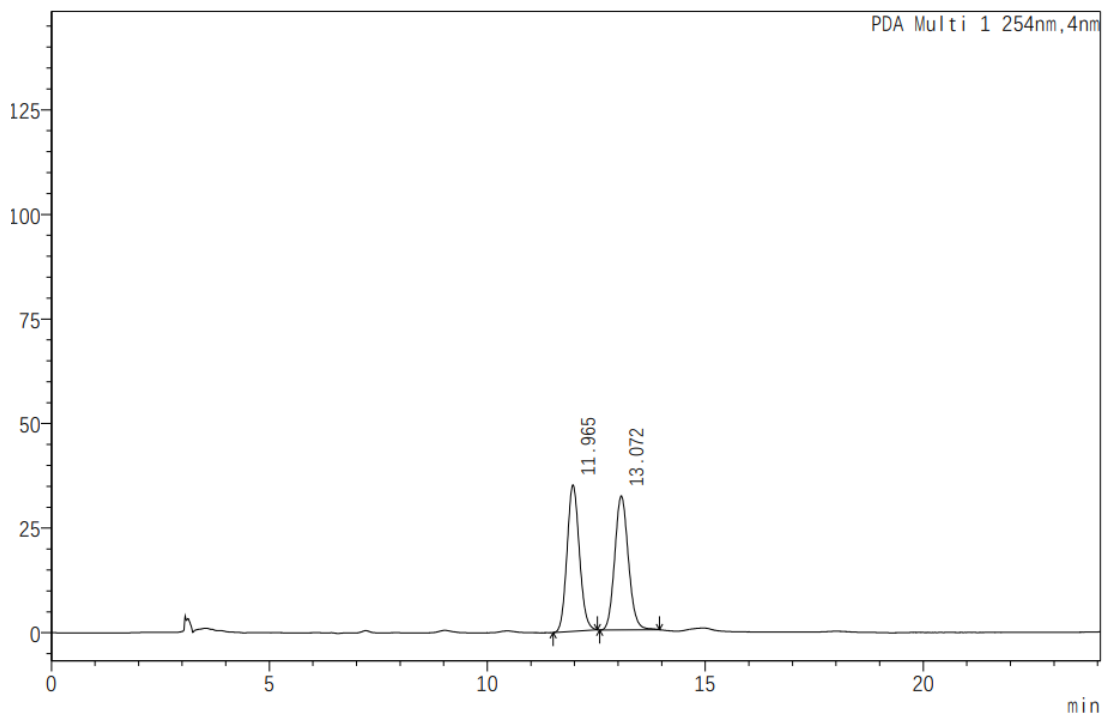
PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	18.311	33520	1526	0.249	0.610
2	20.684	13433371	421779	99.751	0.832

**(9*aR*,10*R*,15*aR*)-10-hydroxy-2-methoxy-10-methyl-9*a*,15*a*-dihydrodibenzo  
[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3i)**

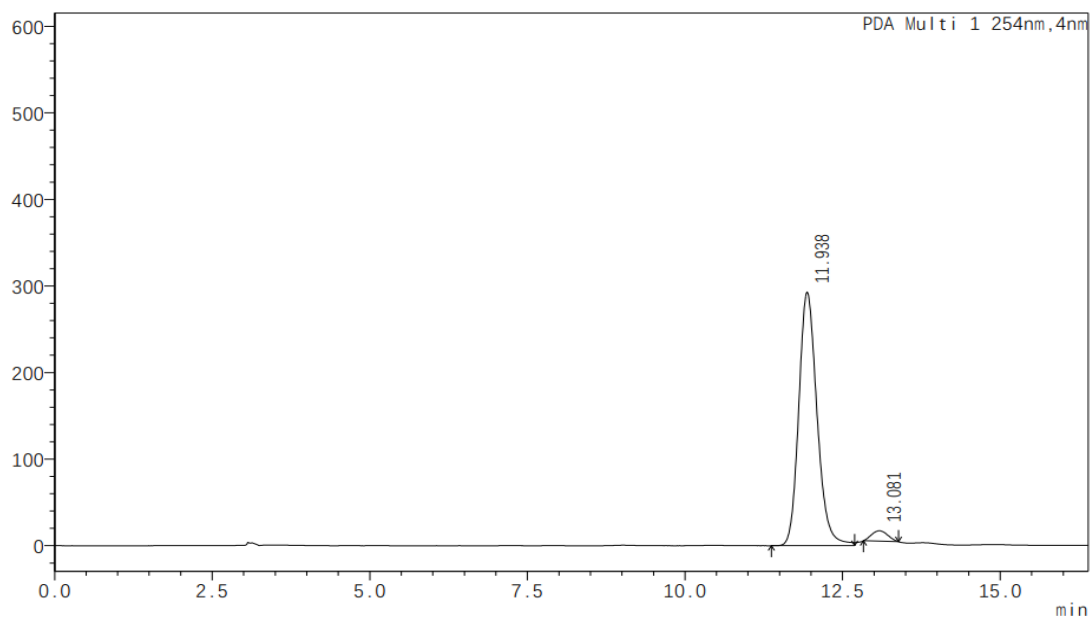


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3i** (30.6 mg, 79% yield) as a white solid.  $[\alpha]_D^{25} = 32$  ( $c = 1.0$  in DCM, 93% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 7.6$  Hz, 1H), 7.45 (t,  $J = 7.3$  Hz, 1H), 7.36 (d,  $J = 8.4$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.07 (t,  $J = 7.2$  Hz, 1H), 6.99 (d,  $J = 8.4$  Hz, 1H), 6.92 (m, 3H), 6.56 (d,  $J = 7.6$  Hz, 1H), 6.43 (d,  $J = 7.4$  Hz, 1H), 5.04 – 4.94 (m, 1H), 4.79 (s, 1H), 3.88 (s, 3H), 3.45 (s, 1H), 1.71 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  209.30, 159.77, 139.90, 139.09, 138.72, 137.47, 134.85, 132.70, 132.47, 131.49, 128.15, 127.86, 127.23, 127.02, 125.21, 124.96, 124.86, 115.52, 114.63, 75.08, 64.14, 55.62, 44.90, 27.16. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  389.1206, found 389.1201. The ee of compound **3i** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 11.938$  min,  $t(\text{major}) = 13.081$  min.



PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.965	691118	35013	49.734	0.526
2	13.072	698517	32026	50.266	0.576

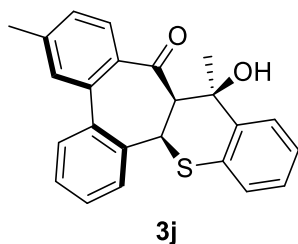


PDA Ch1 254nm

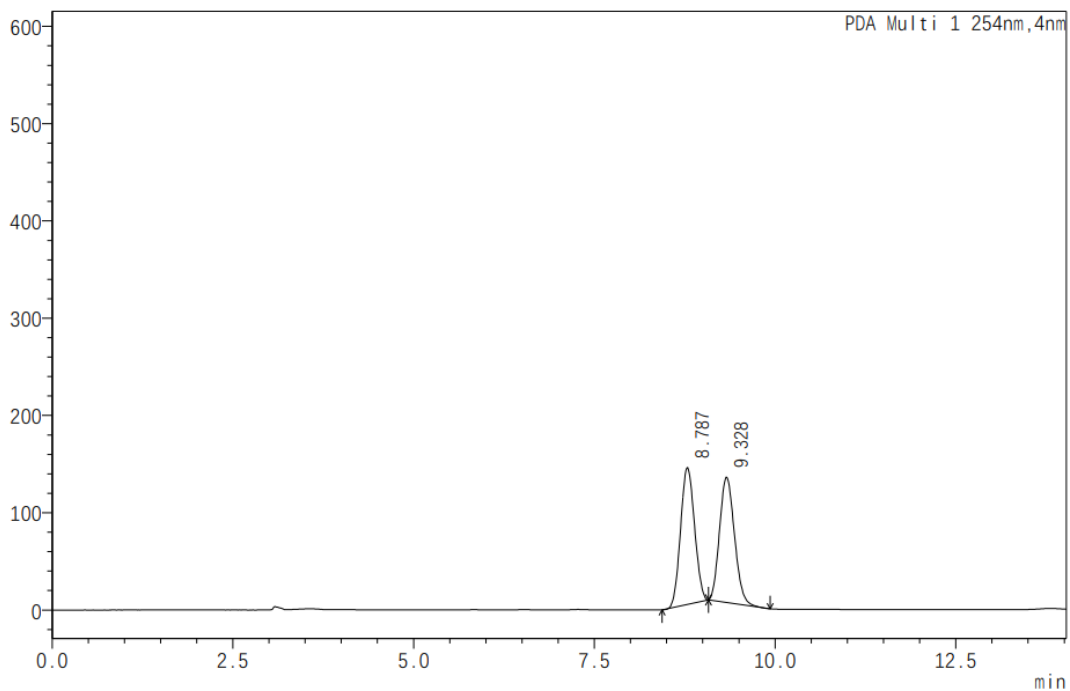
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	11.938	5905203	292890	96.495	0.528
2	13.081	214500	12069	3.505	0.497

**(9a*R*,10*R*,15a*R*)-10-hydroxy-6,10-dimethyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3j)**



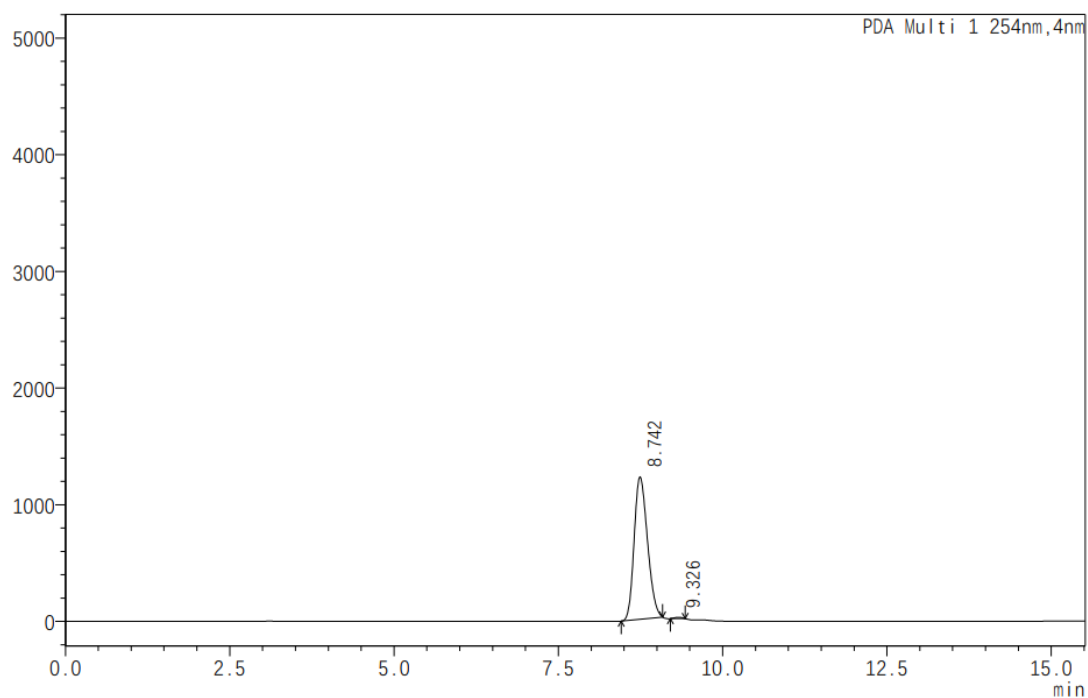


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3j** (31.28 mg, 84% yield) as a white solid.  $[\alpha]_D^{25} = -20$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 7.6$  Hz, 1H), 7.45 (s, 2H), 7.38 (d,  $J = 7.5$  Hz, 2H), 7.18 (s, 1H), 7.07 (t,  $J = 7.1$  Hz, 1H), 6.92 (t,  $J = 7.2$  Hz, 1H), 6.81 (d,  $J = 7.7$  Hz, 1H), 6.58 (d,  $J = 7.5$  Hz, 1H), 6.41 (d,  $J = 7.6$  Hz, 1H), 5.04 (s, 1H), 4.94 (s, 1H), 3.42 (s, 1H), 2.39 (s, 3H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.75, 143.06, 139.90, 139.23, 138.67, 136.60, 136.12, 134.74, 131.25, 129.69, 129.51, 128.63, 128.50, 128.31, 127.04, 125.03, 124.88, 124.67, 75.04, 63.85, 44.59, 27.16, 26.93, 21.66. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  373.1257, found 373.1258. The ee of compound **3j** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 8.742$  min,  $t(\text{major}) = 9.326$  min.



PDA\_Ch1\_254nm

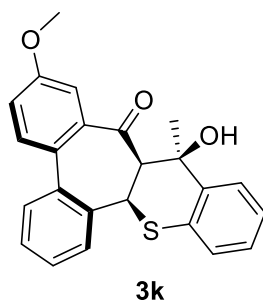
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.787	1892166	140757	50.509	0.371
2	9.328	1854045	128700	49.491	0.391



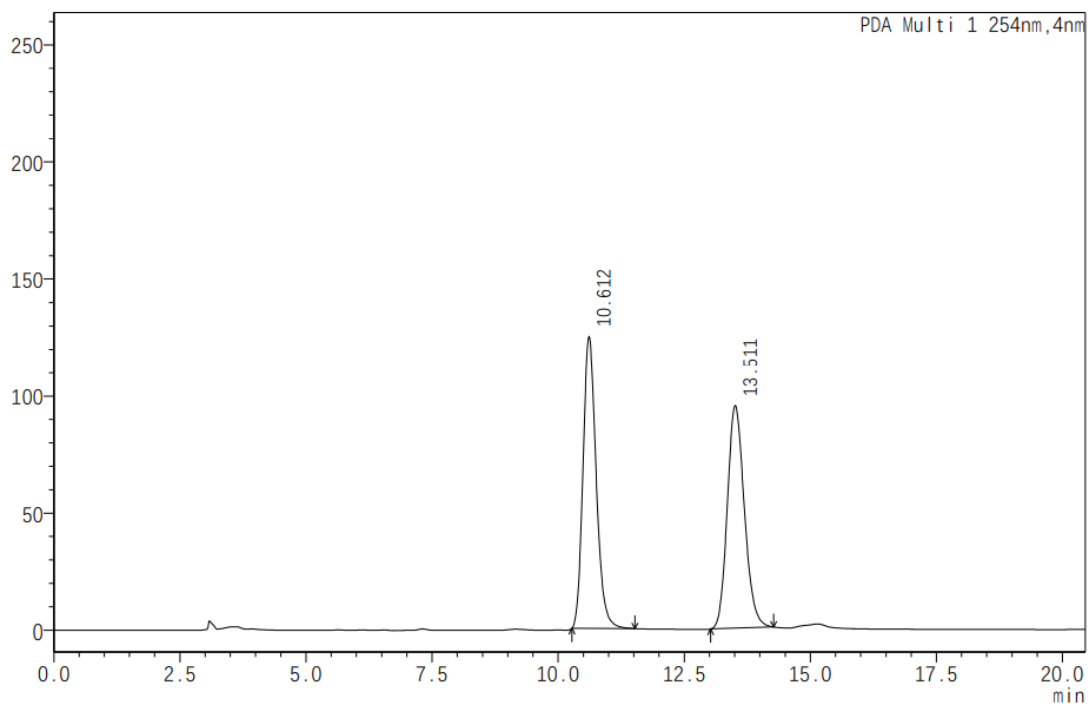
PDA\_Ch1\_254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	8.742	17274955	1220249	99.475	0.386
2	9.326	91200	11277	0.525	0.231

**(9aR,10R,15aR)-10-hydroxy-7-methoxy-10-methyl-9a,15a-dihydrodibenzo  
[4,5:6,7] cyclohepta[1,2-b] thiochromen-9(10H)-one (3k)**

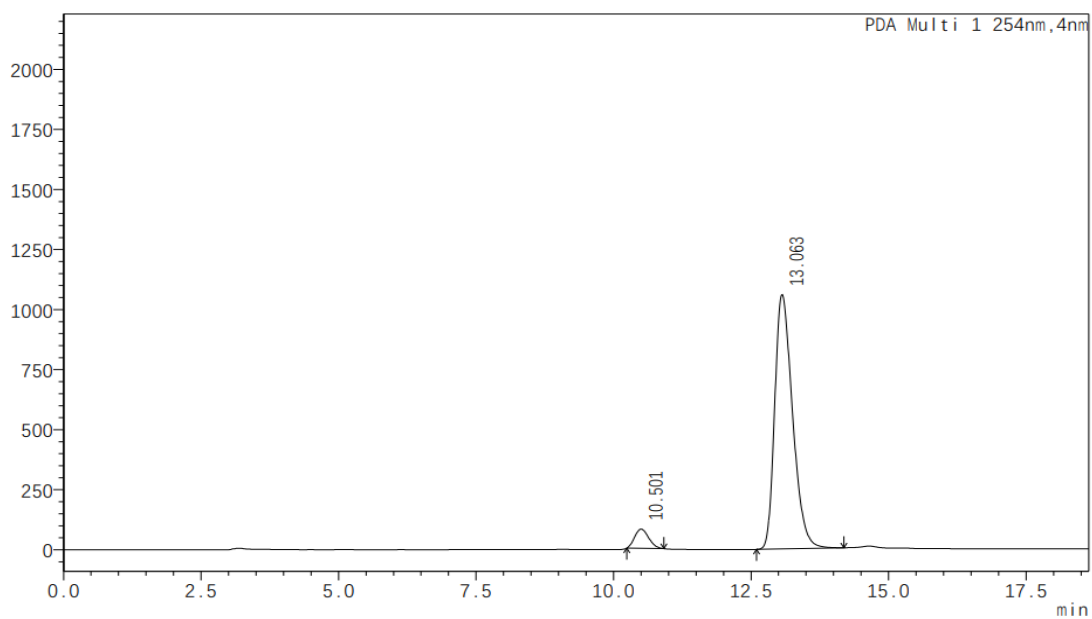


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3k** (29.5mg, 76% yield) as a white solid.  $[\alpha]_D^{25} = 6$  ( $c = 1.0$  in DCM, 89% ee,  $>20:1$  dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 7.7$  Hz, 1H), 7.43 (t,  $J = 7.2$  Hz, 1H), 7.40 – 7.34 (m, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.26 (d,  $J = 8.3$  Hz, 1H), 7.09 (t,  $J = 7.4$  Hz, 1H), 7.03 (d,  $J = 8.5$  Hz, 1H), 6.93 (t,  $J = 7.4$  Hz, 1H), 6.61 (d,  $J = 7.7$  Hz, 1H), 5.86 (s, 1H), 5.02 (d,  $J = 4.9$  Hz, 1H), 4.66 (s, 1H), 3.51 (s, 3H), 3.45 (d,  $J = 4.9$  Hz, 1H), 1.72 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  209.13, 158.83, 140.06, 140.02, 138.97, 135.76, 135.43, 131.60, 131.03, 129.78, 129.66, 129.62, 128.12, 127.11, 125.51, 125.01, 124.71, 120.37, 110.74, 75.13, 64.84, 55.29, 44.71, 26.66. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  389.1206, found 389.1201. The ee of compound **3k** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 10.501$  min,  $t(\text{major}) = 13.063$  min.



PDA Ch1 254nm

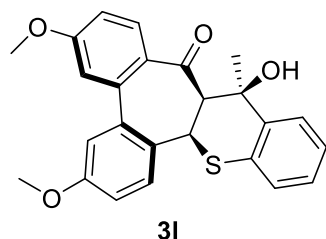
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	10.612	2273903	124843	50.370	0.480
2	13.511	2240535	95143	49.630	0.623



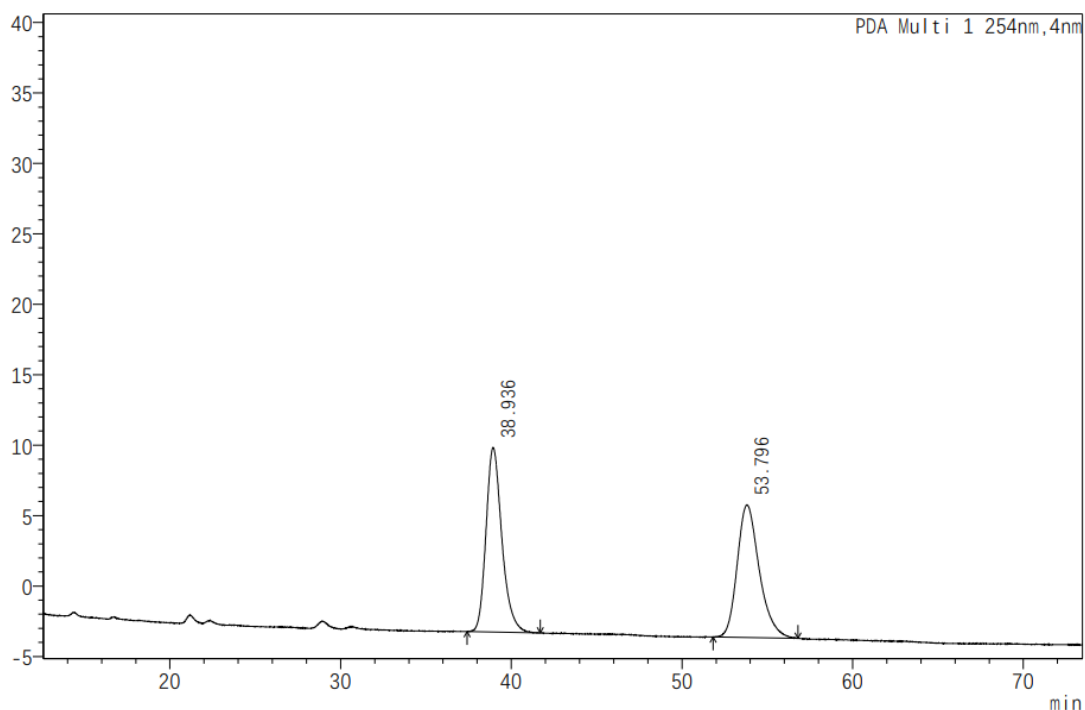
PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	10.501	1413365	80167	5.578	0.482
2	13.063	23926184	1058519	94.422	0.597

**(9a*R*,10*R*,15a*R*)-10-hydroxy-3,6-dimethoxy-10-methyl-9a,15a-dihydrodibenzo  
[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3I)**

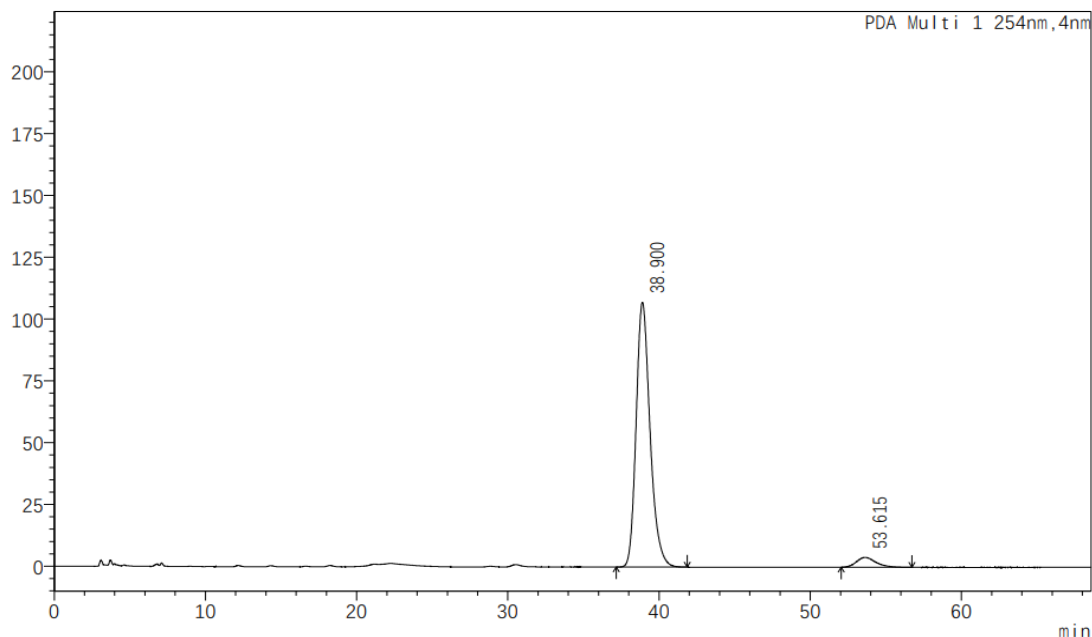


Flash column chromatography on silica gel (hexane/EtOAc, 8:1) gave the product **31** (29.7 mg, 71% yield) as a white solid.  $[\alpha]_D^{25} = -36$  ( $c = 1.0$  in DCM, 90% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 7.7$  Hz, 1H), 7.37 (d,  $J = 8.5$  Hz, 1H), 7.06 (t,  $J = 7.5$  Hz, 1H), 6.98 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.95 – 6.88 (m, 2H), 6.80 (d,  $J = 2.0$  Hz, 1H), 6.63 (d,  $J = 7.7$  Hz, 1H), 6.59 – 6.44 (m, 2H), 5.15 (s, 1H), 4.98 (d,  $J = 4.7$  Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.38 (d,  $J = 4.7$  Hz, 1H), 1.69 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.83, 163.09, 159.89, 141.05, 140.09, 137.68, 134.79, 132.64, 132.34, 131.53, 130.76, 127.17, 125.09, 124.78, 115.50, 114.59, 112.95, 112.67, 75.26, 63.11, 55.65, 55.57, 45.01, 27.42. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{O}_4\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  419.1312, found 419.1298. The ee of compound **31** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 38.900$  min,  $t(\text{minor}) = 53.615$  min.



PDA Ch1 254nm

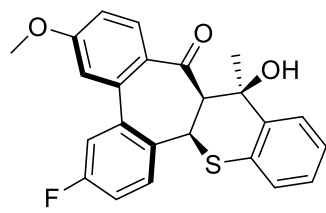
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	38.936	846826	13090	50.018	1.660
2	53.796	846233	9412	49.982	2.332



PDA Ch1 254nm

NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	38.900	6859196	107115	95.105	1.650
2	53.615	353075	3964	4.895	2.300

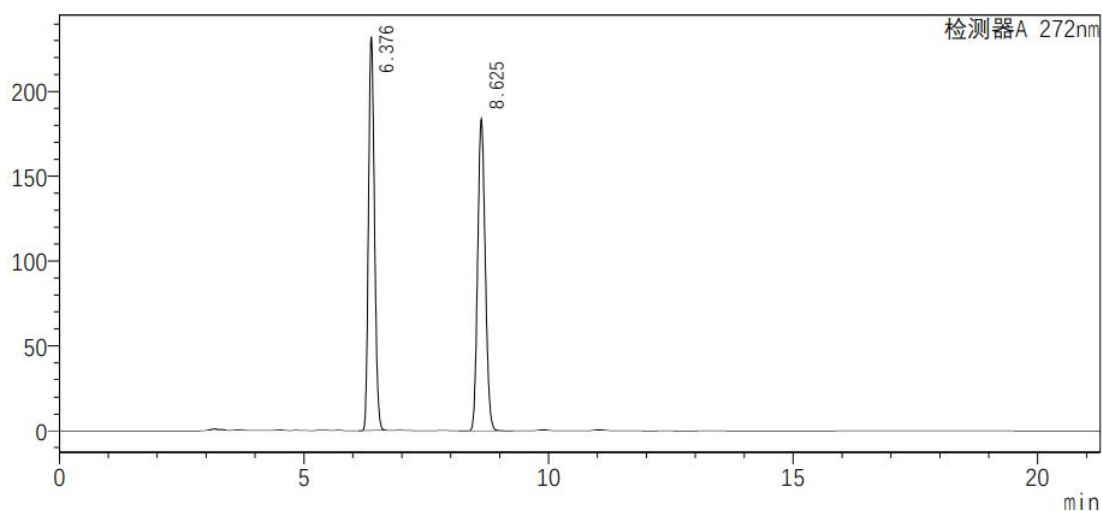
**(9a*R*,10*R*,15a*R*)-3-fluoro-10-hydroxy-6-methoxy-10-methyl-9a,15a-dihydrodi-  
benzo [4,5:6,7] cyclohepta [1,2-*b*] thiochromen-9(10*H*)-one (3m)**



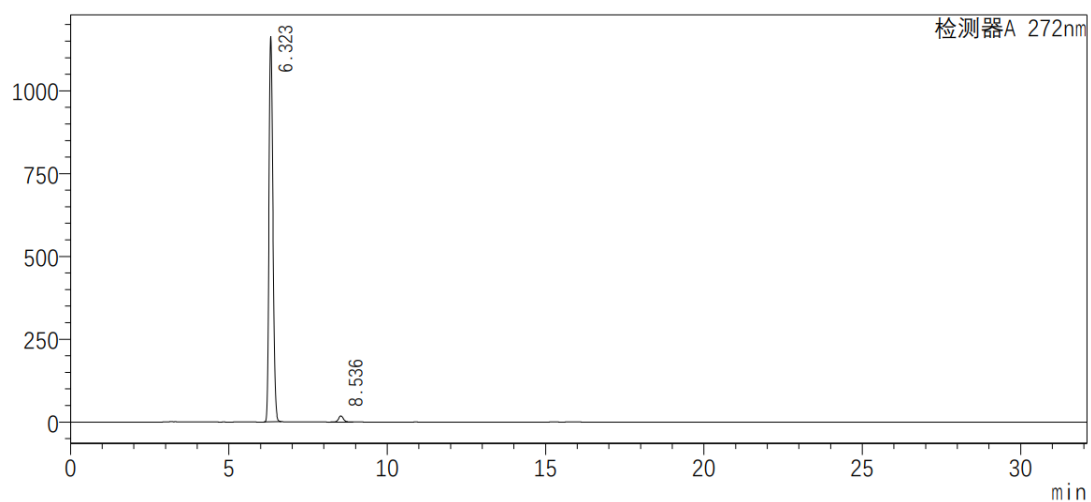
**3m**

Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3m** (38.6 mg, 95% yield) as a white solid.  $[\alpha]_D^{25} = -78$  ( $c = 1.0$  in DCM, 96% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 7.8$  Hz, 1H), 7.39 (t,  $J = 6.7$  Hz, 1H), 7.18 (d,  $J = 9.5$  Hz, 1H), 7.08 (q,  $J = 10.5, 9.0$  Hz, 2H), 6.94 (t,  $J = 7.5$  Hz, 1H), 6.85 (s, 1H), 6.63 (d,  $J = 7.8$  Hz, 1H), 6.56 (d,  $J = 10.9$  Hz, 2H), 5.06 (s, 1H), 3.89 (s, 3H), 3.39 (d,  $J = 4.1$  Hz, 1H), 1.71 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.32, 163.33 (d,  $J = 248.2$  Hz), 163.16, 141.49 (d,  $J = 8.8$  Hz), 140.00, 139.88, 134.70, 132.32,

132.30, 132.27, 131.59 (d,  $J = 7.6$  Hz), 130.88, 127.19, 125.08, 124.90, 118.19 (d,  $J = 22.7$  Hz), 115.34 (d,  $J = 20.2$  Hz), 113.74, 113.11, 75.27, 63.51, 55.66, 43.95, 27.24.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -87.65. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{FO}_3\text{S}^+$  (M+H) $^+$  407.1112, found 407.1134. The ee of compound **3m** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm),  $n$ -hexane/ $i$ -PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 272$  nm,  $t(\text{major}) = 6.376$  min,  $t(\text{minor}) = 8.625$  min.



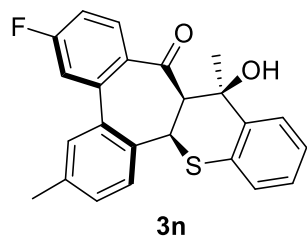
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.376	1965045	231901	49.795	0.234
2	8.625	1981236	183399	50.205	0.293



NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.323	9980740	1163611	98.077	0.237
2	8.536	195658	18242	1.923	0.289

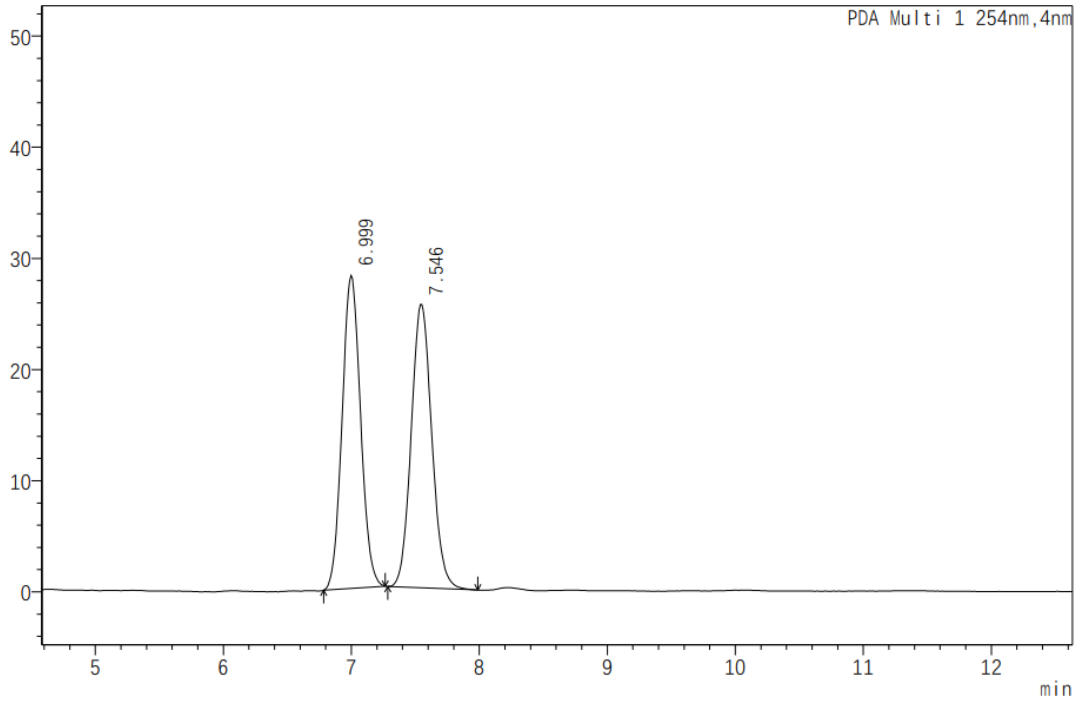
**(9aR,10R,15aR)-6-fluoro-10-hydroxy-3,10-dimethyl-9a,15a-dihydrodibenzo**

**[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3n)**



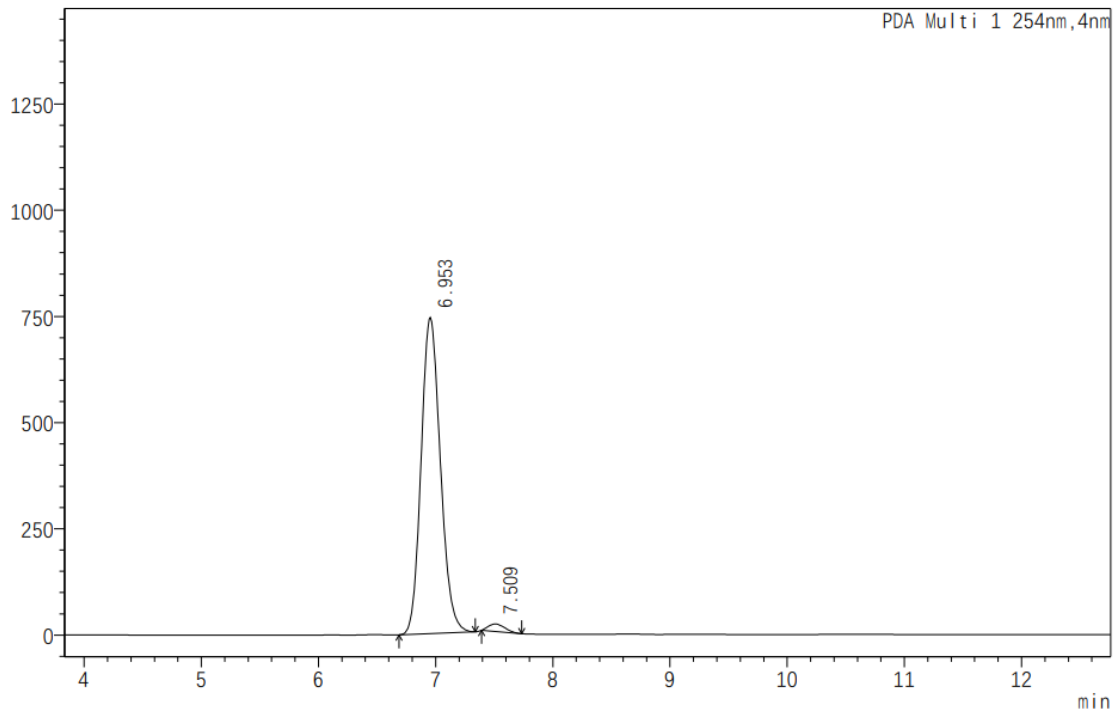
Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3n** (33.9 mg, 87% yield) as a white solid.  $[\alpha]_D^{25} = -44$  ( $c = 1.0$  in DCM, 96% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.6$  Hz, 1H), 7.24 – 7.14 (m, 2H), 7.11 – 7.00 (m, 2H), 6.93 (t,  $J = 7.5$  Hz, 1H), 6.65 (t,  $J = 8.3$  Hz, 1H), 6.61 (d,  $J = 7.8$  Hz, 1H), 6.46 (t,  $J = 7.0$  Hz, 1H), 5.01 (d,  $J = 4.2$  Hz, 1H), 4.74 (s, 1H), 3.40 (d,  $J = 4.2$  Hz, 1H), 2.41 (s, 3H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  207.97, 165.30 (d,  $J = 253.3$  Hz), 141.94, 141.86, 139.94, 139.85, 137.97, 135.72, 135.02, 133.46, 132.06, 130.94 (d,  $J = 10.1$  Hz), 129.90, 129.88, 127.32, 125.11 (d,  $J = 26.5$  Hz), 124.94, 114.78 (d,  $J = 13.9$  Hz), 114.60 (d,  $J = 12.6$  Hz), 75.21, 64.28, 44.20, 27.11, 21.30.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.12. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{FO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  391.1163, found 391.1170. The ee of compound **3n** was determined by HPLC using a MX (2) column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 94/6, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 6.953$  min,  $t(\text{minor}) = 7.509$  min.





PDA Ch1 254nm

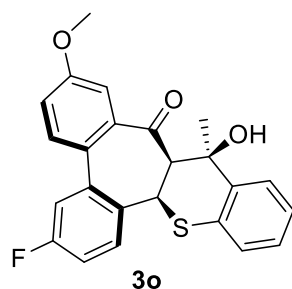
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.999	282209	28149	49.797	0.278
2	7.546	284508	25517	50.203	0.304



PDA Ch1 254nm

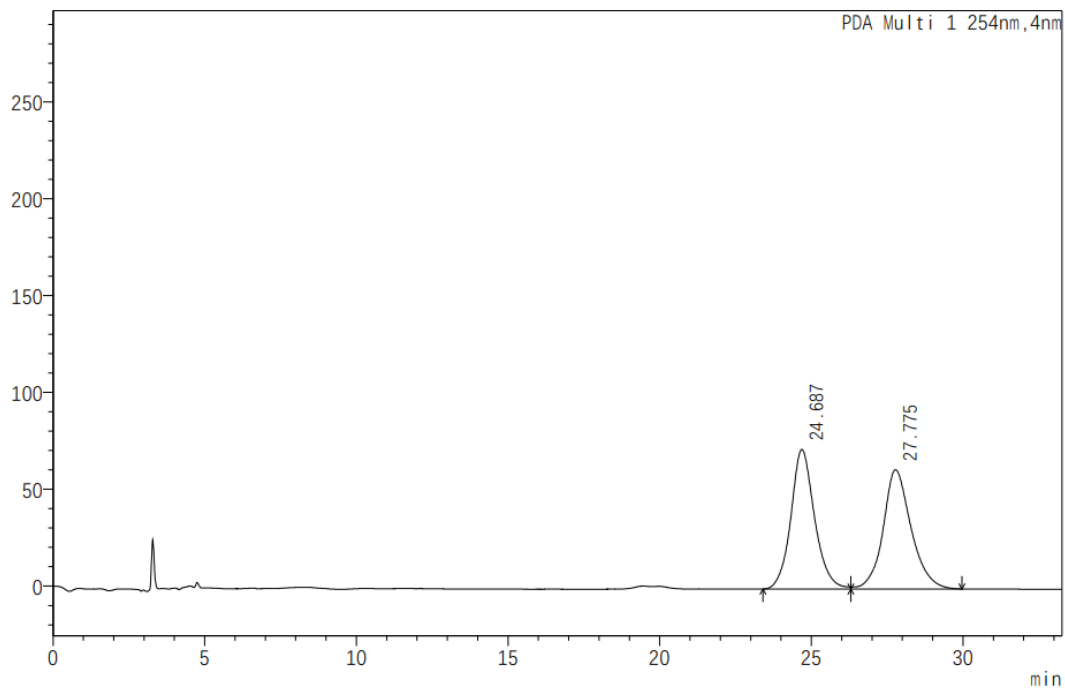
NO.	Ret. Time	Area(uAU*min)	Height(uAU)	Rel. Area %	Resolution(USP)
1	6.953	8509393	744609	98.064	0.312
2	7.509	168034	17381	1.936	0.273

**(9a*R*,10*R*,15a*R*)-3-fluoro-10-hydroxy-7-methoxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7] cyclohepta [1,2-*b*] thiochromen-9(10*H*)-one (3o)**

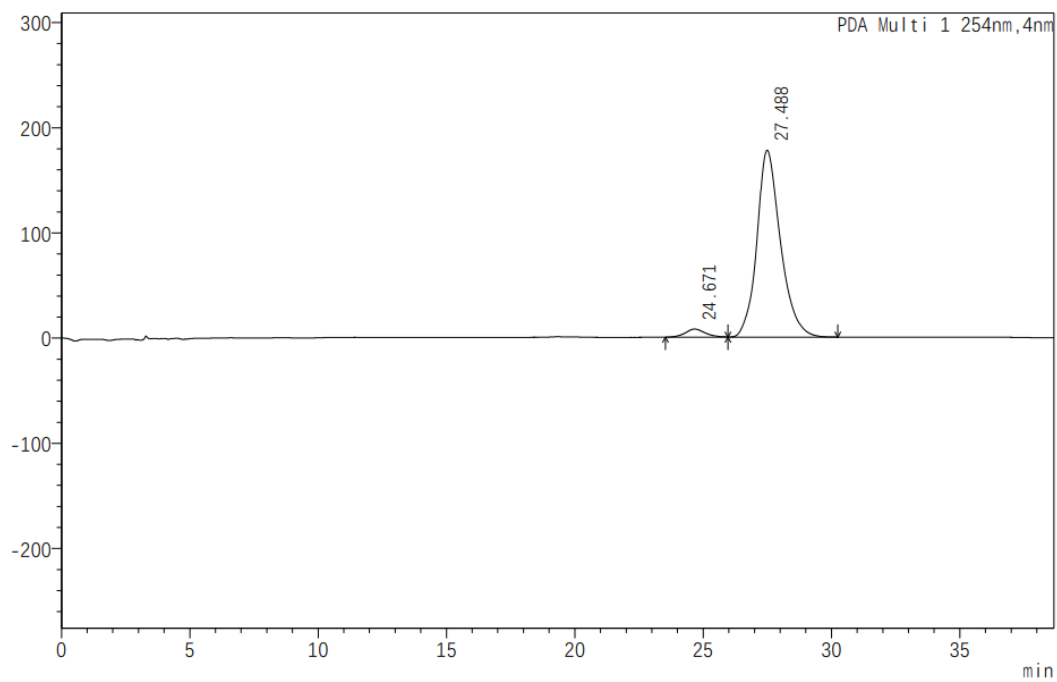


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3o** (35.7 mg, 88% yield) as a white solid.  $[\alpha]_D^{25} = 28$  ( $c = 1.0$  in DCM, 93% ee, > 20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.37 (dd,  $J = 8.4, 5.6$  Hz, 1H), 7.26 (d,  $J = 8.6$  Hz, 1H), 7.15 – 7.09 (m, 2H), 7.08 – 7.00 (m, 2H), 6.96 (td,  $J = 7.7, 1.4$  Hz, 1H), 6.81 – 6.48 (m, 1H), 5.88 (d,  $J = 2.7$  Hz, 1H), 5.04 (d,  $J = 5.1$  Hz, 1H), 4.63 (s, 1H), 3.54 (s, 3H), 3.46 (d,  $J = 5.2$  Hz, 1H), 1.74 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.68, 163.39 (d,  $J = 249$ . Hz), 159.23, 141.25 (d,  $J = 8.1$  Hz), 140.06, 139.96, 135.26, 131.53 (d,  $J = 8.1$  Hz), 131.64 (d,  $J = 3.0$  Hz), 130.36, 129.53, 117.80 (d,  $J = 22.2$  Hz), 127.16, 125.49, 125.03, 124.81, 114.62 (d,  $J = 21.2$  Hz), 120.38, 110.93, 75.14, 64.86, 55.32, 43.95, 26.62.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.44. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{FO}_3\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  407.1112, found 407.1124.

The ee of compound **3o** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{minor}) = 24.687$  min,  $t(\text{major}) = 27.775$  min.



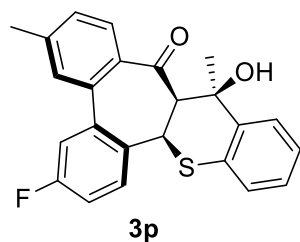
NO.	Ret.Time	Height(uAU)	Area(uAU*min)	Rel.Area %	Resolution(USP)
1	24.687	72104	3923940	49.762	--
2	27.775	61599	3961479	50.238	2.054



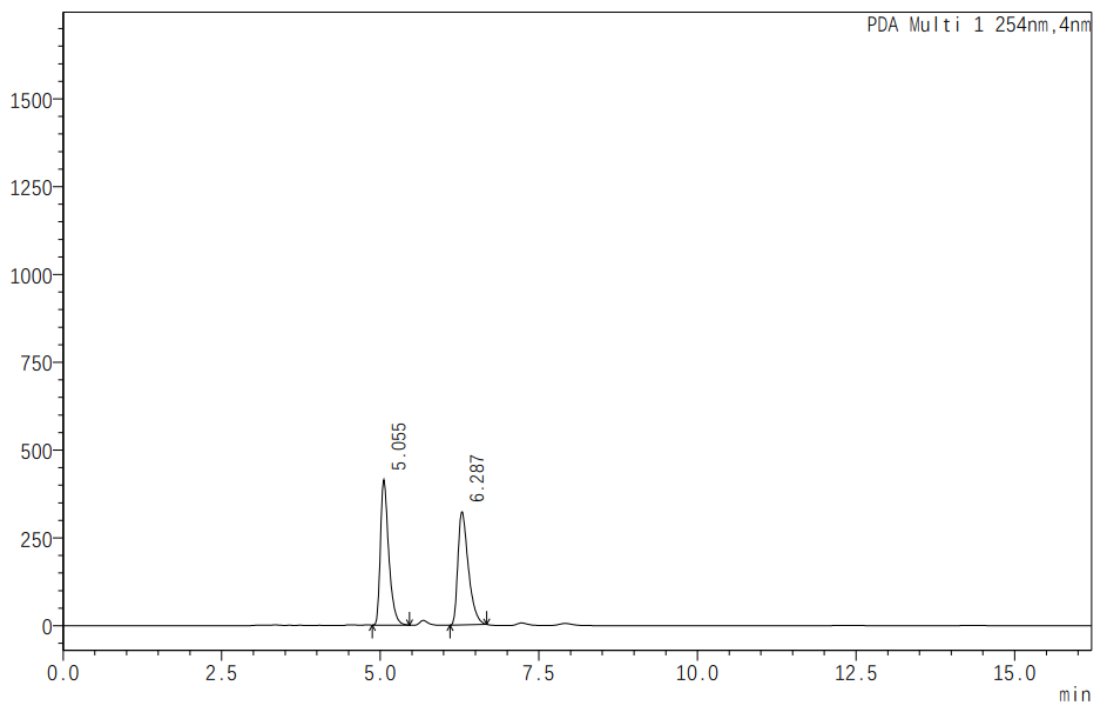
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	24.671	424078	7751	3.593	1.432
2	27.488	11379106	177713	96.407	1.615

**(9aR,10R,15aR)-3-fluoro-10-hydroxy-6,10-dimethyl-9a,15a-dihydrodibenzo**

**[4,5:6,7] cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3p)**

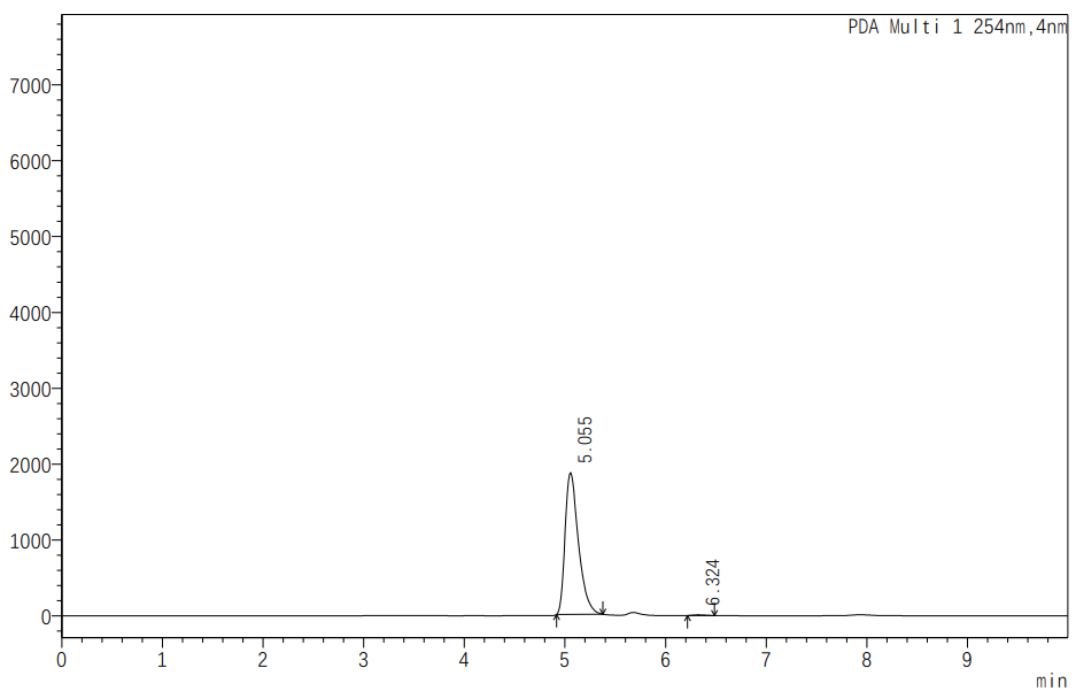


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3p** (32.1 mg, 82% yield) as a white solid.  $[\alpha]_D^{25} = -16$  ( $c = 1.0$  in DCM, 99% ee,  $>20:1$  dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.8$  Hz, 1H), 7.36 (t,  $J = 6.0$  Hz, 1H), 7.16 (d,  $J = 12.7$  Hz, 2H), 7.06 (dt,  $J = 16.4, 7.8$  Hz, 2H), 6.92 (t,  $J = 7.4$  Hz, 1H), 6.83 (d,  $J = 7.7$  Hz, 1H), 6.56 (d,  $J = 7.4$  Hz, 1H), 6.40 (d,  $J = 7.6$  Hz, 1H), 5.03 (s, 1H), 4.86 (s, 1H), 3.39 (s, 1H), 2.40 (s, 3H), 1.69 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.45, 163.38 (d,  $J = 249.5$  Hz), 143.37, 141.64 (d,  $J = 8.8$  Hz), 139.94, 137.62, 136.67, 134.71, 132.14, 131.59 (d,  $J = 8.8$  Hz), 129.00, 128.63, 128.58, 127.23, 125.15, 125.04, 124.93, 118.21 (d,  $J = 23.9$  Hz), 115.14 (d,  $J = 21.4$  Hz), 75.19, 64.02, 43.95, 27.23, 21.77.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -87.56. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{FO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  391.1163, found 391.1170. The ee of compound **3p** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 5.055$  min,  $t(\text{minor}) = 6.324$  min.



PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	5.055	3770823	414057	50.523	0.250
2	6.287	3692814	321712	49.477	0.310

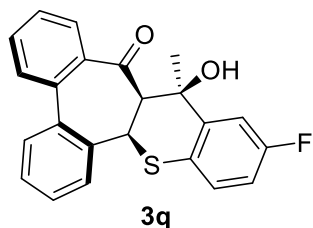


PDA Ch1 254nm

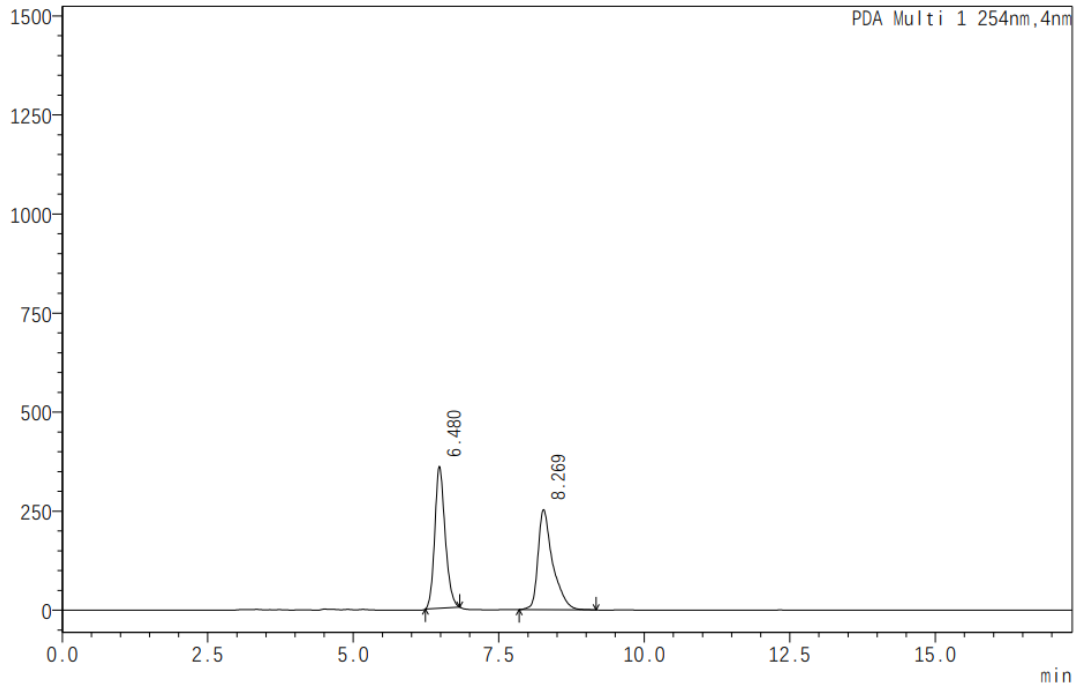
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	5.055	17218544	1867977	99.567	0.253
2	6.324	74807	8743	0.433	0.245

**(9aR,10R,15aR)-12-fluoro-10-hydroxy-10-methyl-9a,15a-dihydrodibenzo [4,5:6,7]**

**cyclohepta[1,2-*b*] thiochromen-9(10*H*)-one (3q)**

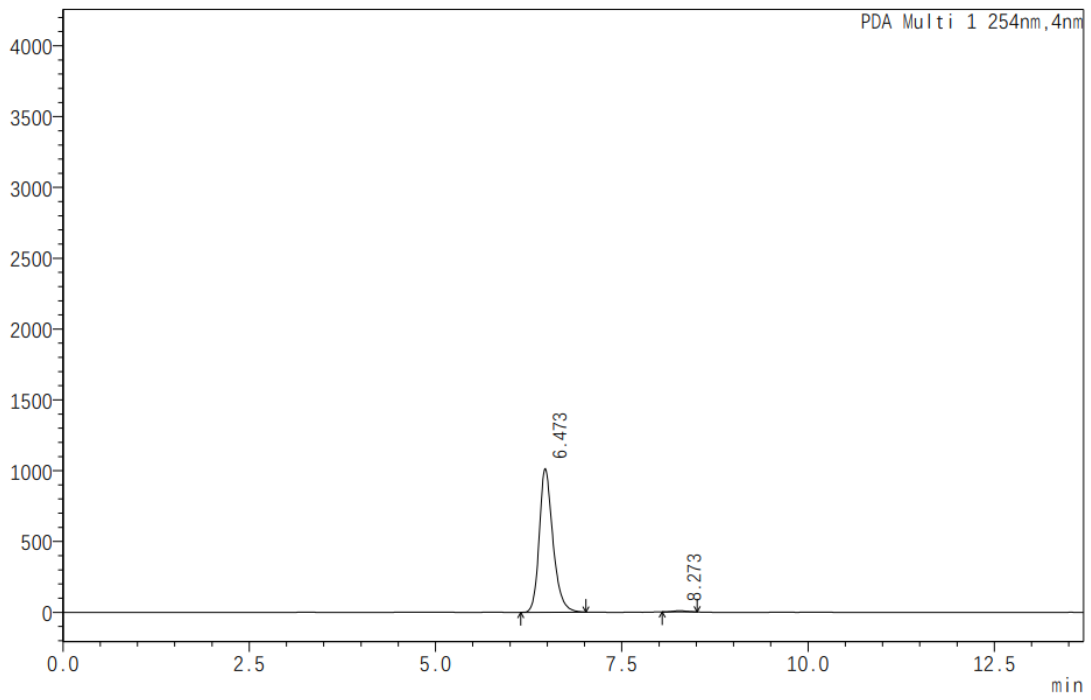


Flash column chromatography on silica gel (hexane/EtOAc, 16:1) gave the product **3q** (33.5 mg, 89% yield) as a white solid.  $[\alpha]_D^{25} = 72$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.41 (m, 4H), 7.37 (m, 3H), 7.02 (t,  $J = 7.1$  Hz, 1H), 6.65 (t,  $J = 8.3$  Hz, 1H), 6.54 (d,  $J = 7.5$  Hz, 1H), 6.53 – 6.47 (m, 1H), 5.02 (d,  $J = 4.3$  Hz, 1H), 4.82 (s, 1H), 3.46 (d,  $J = 4.4$  Hz, 1H), 1.70 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.78, 160.96 (d,  $J = 244.4$  Hz), 142.29, 142.24, 139.22, 139.00, 138.95, 135.99, 132.72, 131.52, 129.83, 129.82, 128.77, 128.19 (d,  $J = 11.3$  Hz), 127.71, 126.63, 126.57, 114.51 (d,  $J = 22.7$  Hz), 112.50 (d,  $J = 23.9$  Hz), 74.97, 64.05, 44.48, 26.76.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -82.90. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{FO}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  377.1006, found 377.1003. The ee of compound **3q** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 6.473$  min,  $t(\text{minor}) = 8.273$  min.



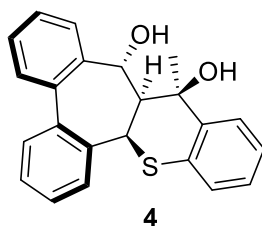
PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	6.480	4438611	357846	49.912	0.334
2	8.269	4454303	253184	50.088	0.428



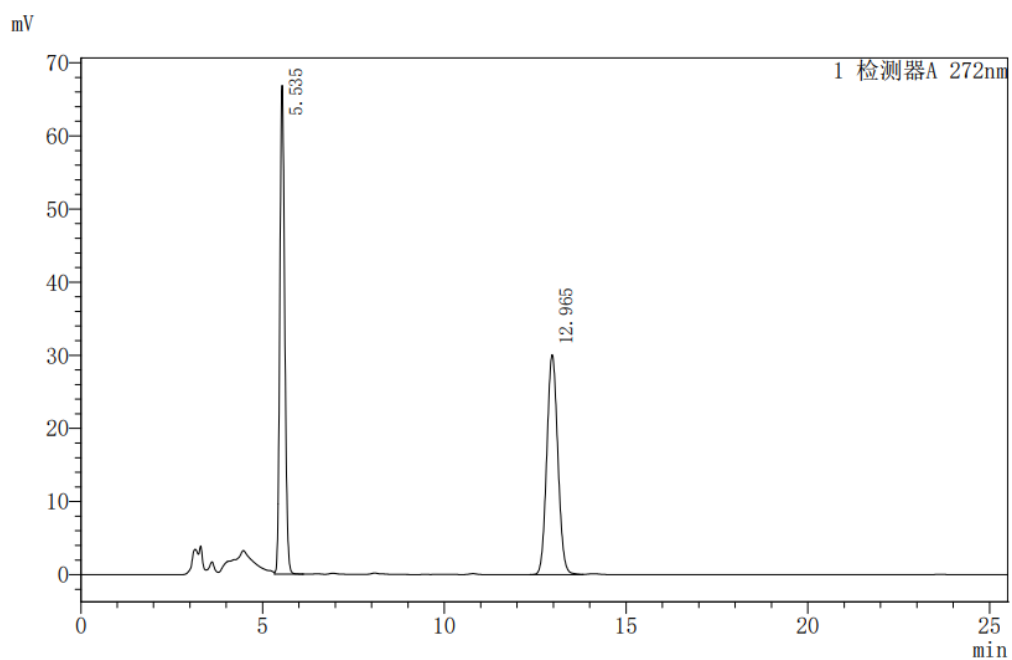
PDA Ch1 254nm

NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	6.473	12911374	1012675	99.264	0.338
2	8.273	95741	8036	0.736	0.333

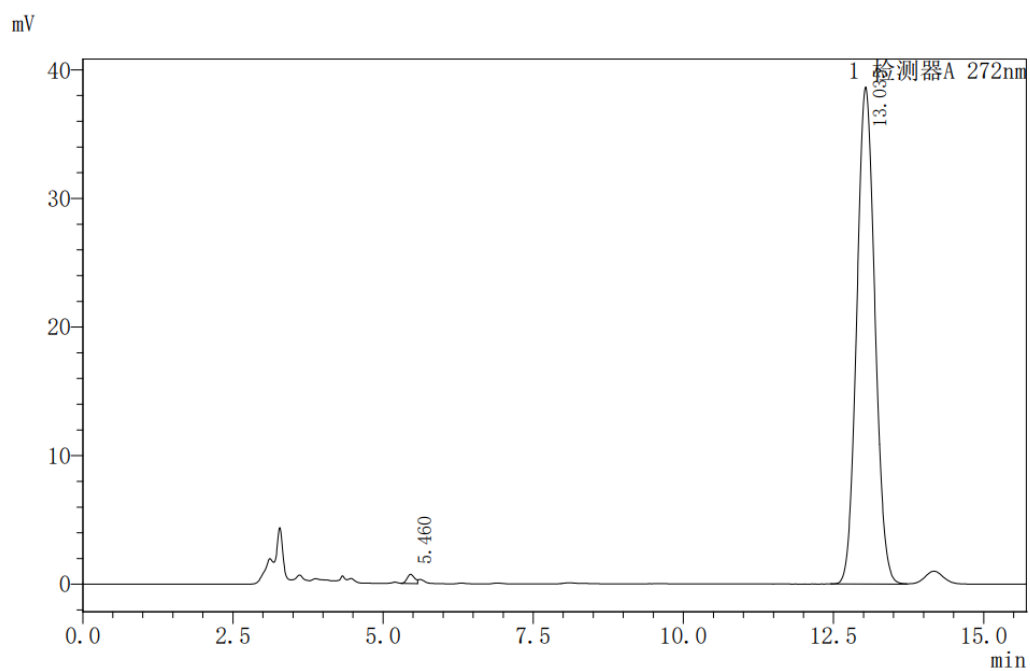


Flash column chromatography on silica gel (hexane/EtOAc, 4:1) gave the product **4** (31.0 mg, 86% yield) as a white solid.  $[\alpha]_D^{25} = 79$  ( $c = 1.0$  in DCM, 99% ee, >20:1 dr).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.7$  Hz, 1H), 7.41 (t,  $J = 7.4$  Hz, 1H), 7.37 – 7.30 (m, 2H), 7.28 (d,  $J = 9.2$  Hz, 2H), 7.16 (t,  $J = 7.4$  Hz, 1H), 7.07 (t,  $J = 7.5$  Hz, 1H), 6.81 (t,  $J = 7.4$  Hz, 1H), 6.74 (t,  $J = 7.4$  Hz, 1H), 6.50 (d,  $J = 7.6$  Hz, 1H), 6.34 (d,  $J = 7.6$  Hz, 1H), 5.74 (s, 1H), 5.05 (d,  $J = 7.1$  Hz, 1H), 4.75 (d,  $J = 7.7$  Hz, 1H), 3.60 (s, 1H), 3.37 (t,  $J = 7.2$  Hz, 1H), 1.64 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.12, 139.92, 138.52, 138.00, 137.78, 135.49, 129.87, 129.05, 128.68, 127.92, 126.93, 126.77, 126.00, 125.17, 124.54, 124.20, 123.74, 75.60, 73.29, 56.06, 46.44, 28.08. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_2\text{S}^+$  ( $\text{M}+\text{H}$ ) $^+$  361.1257, found 361.1264. The ee of compound **4** was determined by HPLC using an AD-H column (0.46 cm x 25 cm), *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t(\text{major}) = 12.965$  min,  $t(\text{minor}) = 5.535$  min.



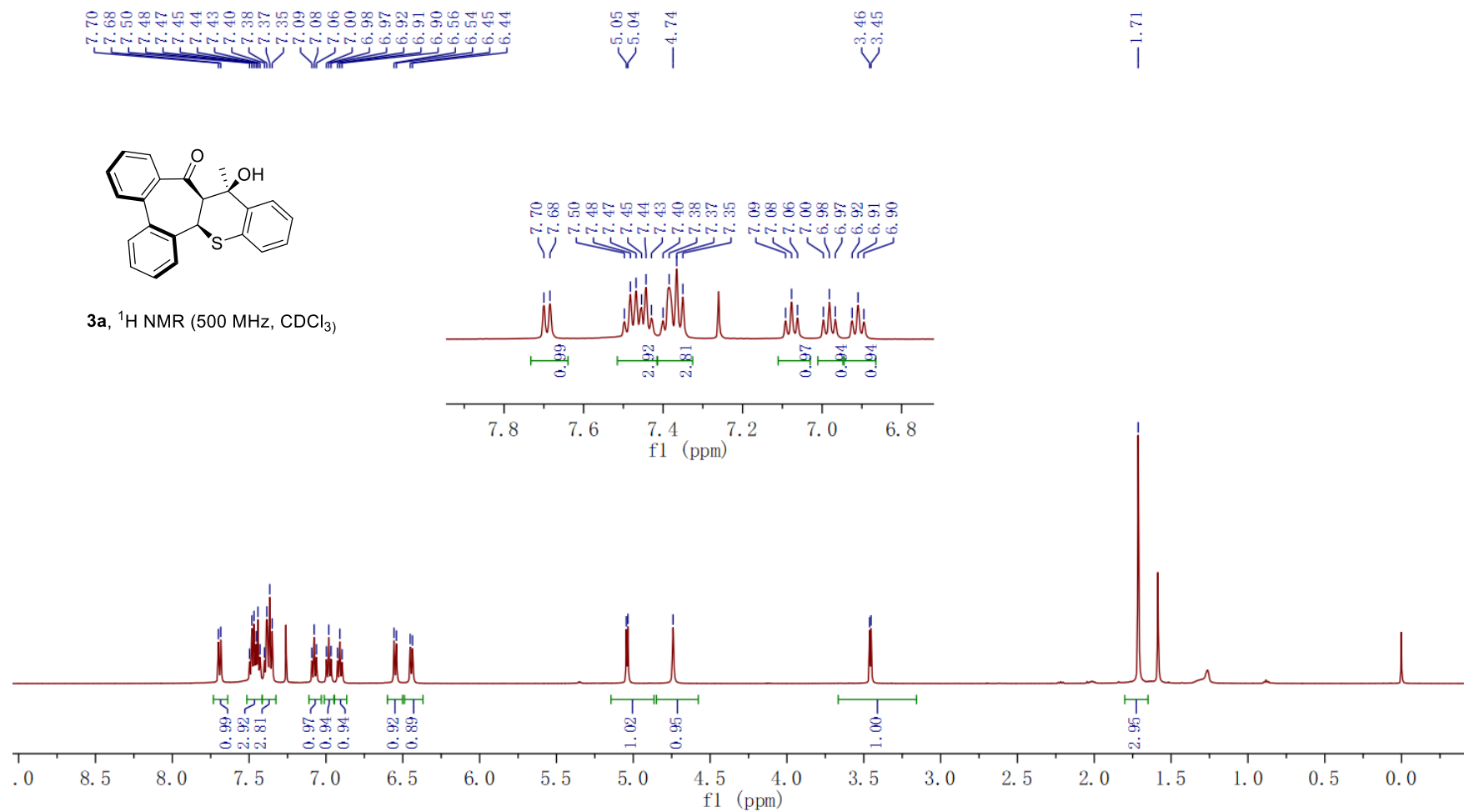


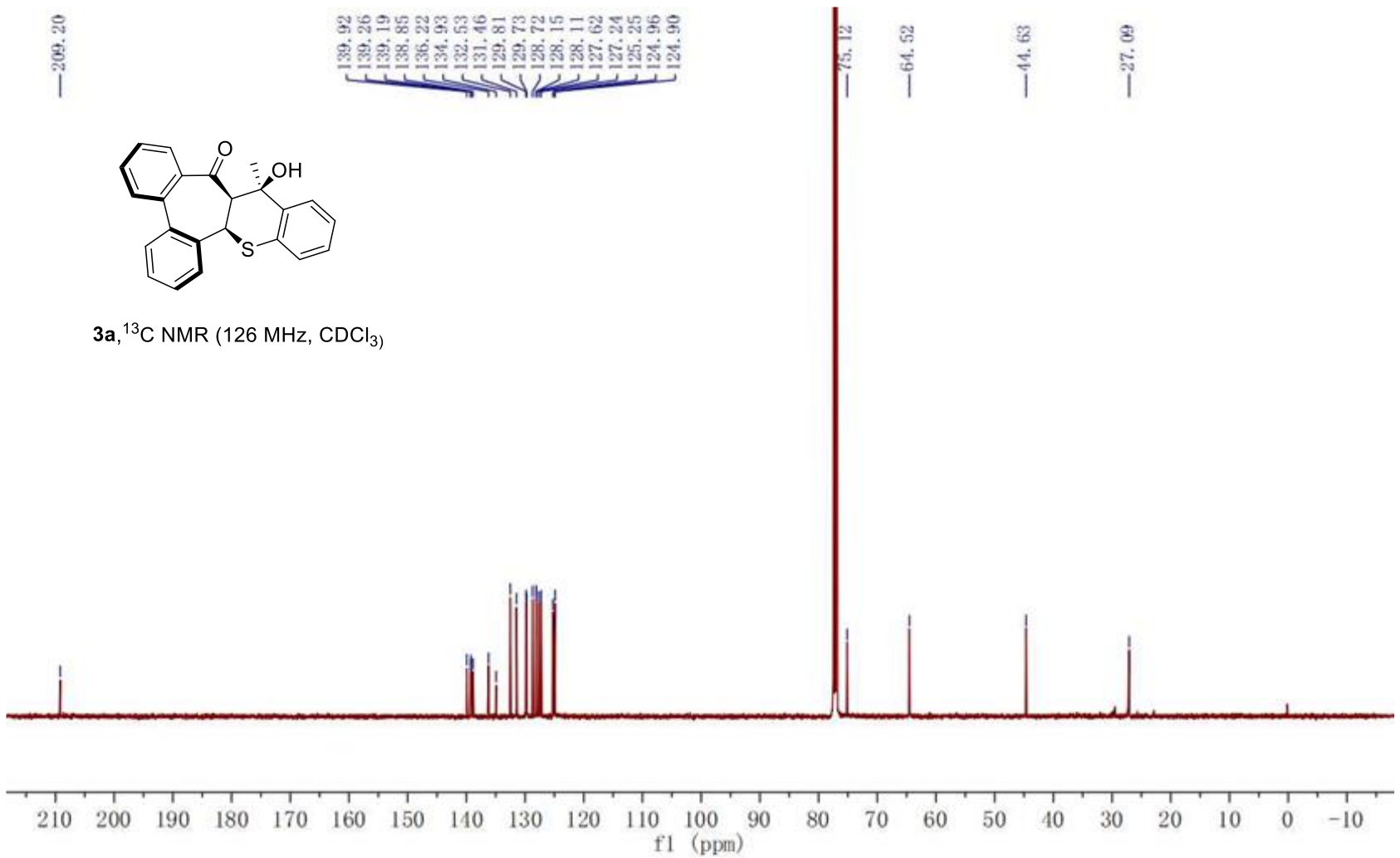
NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.535	66863	631443	49.891	--
2	12.965	30080	634203	50.109	18.179

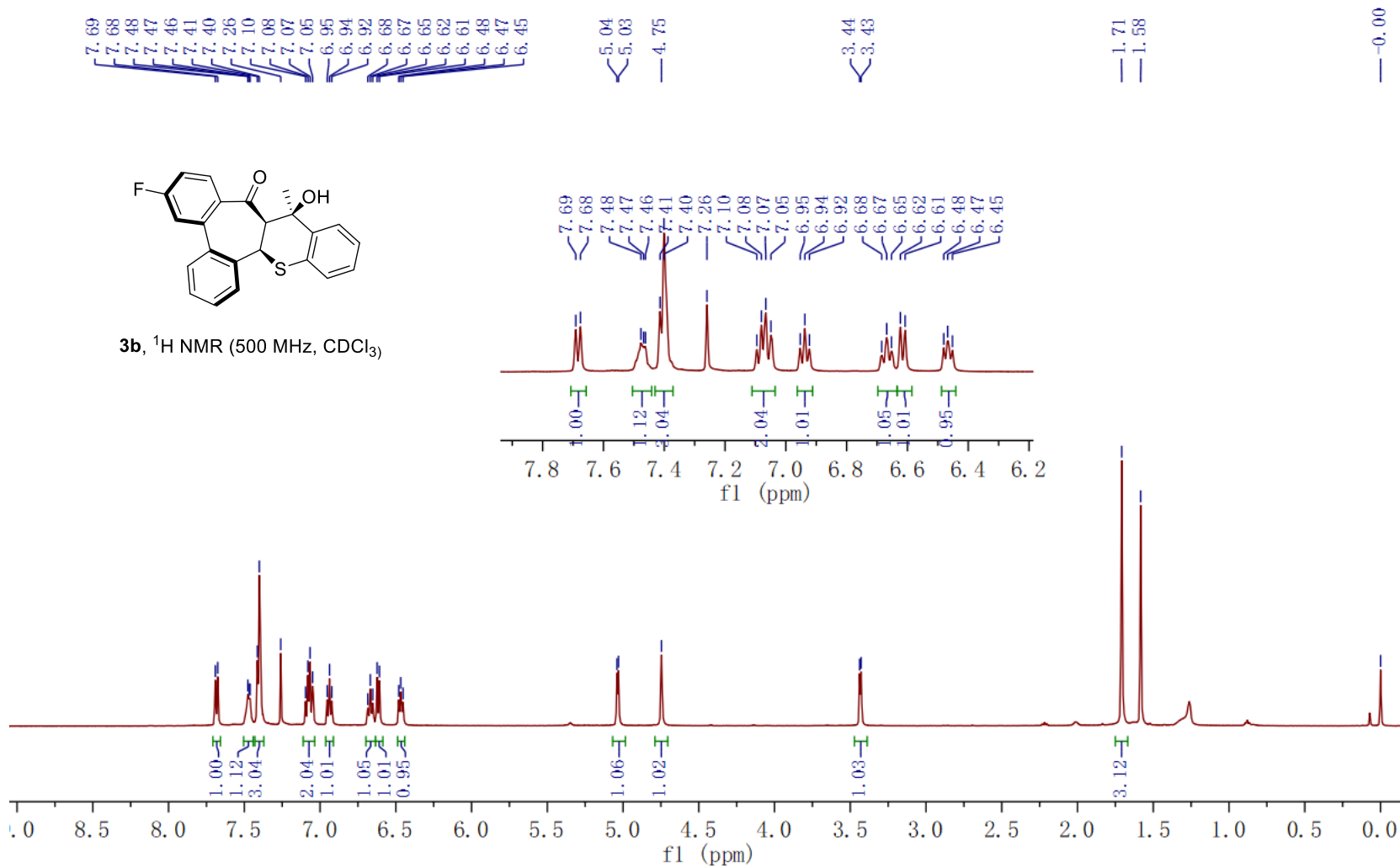


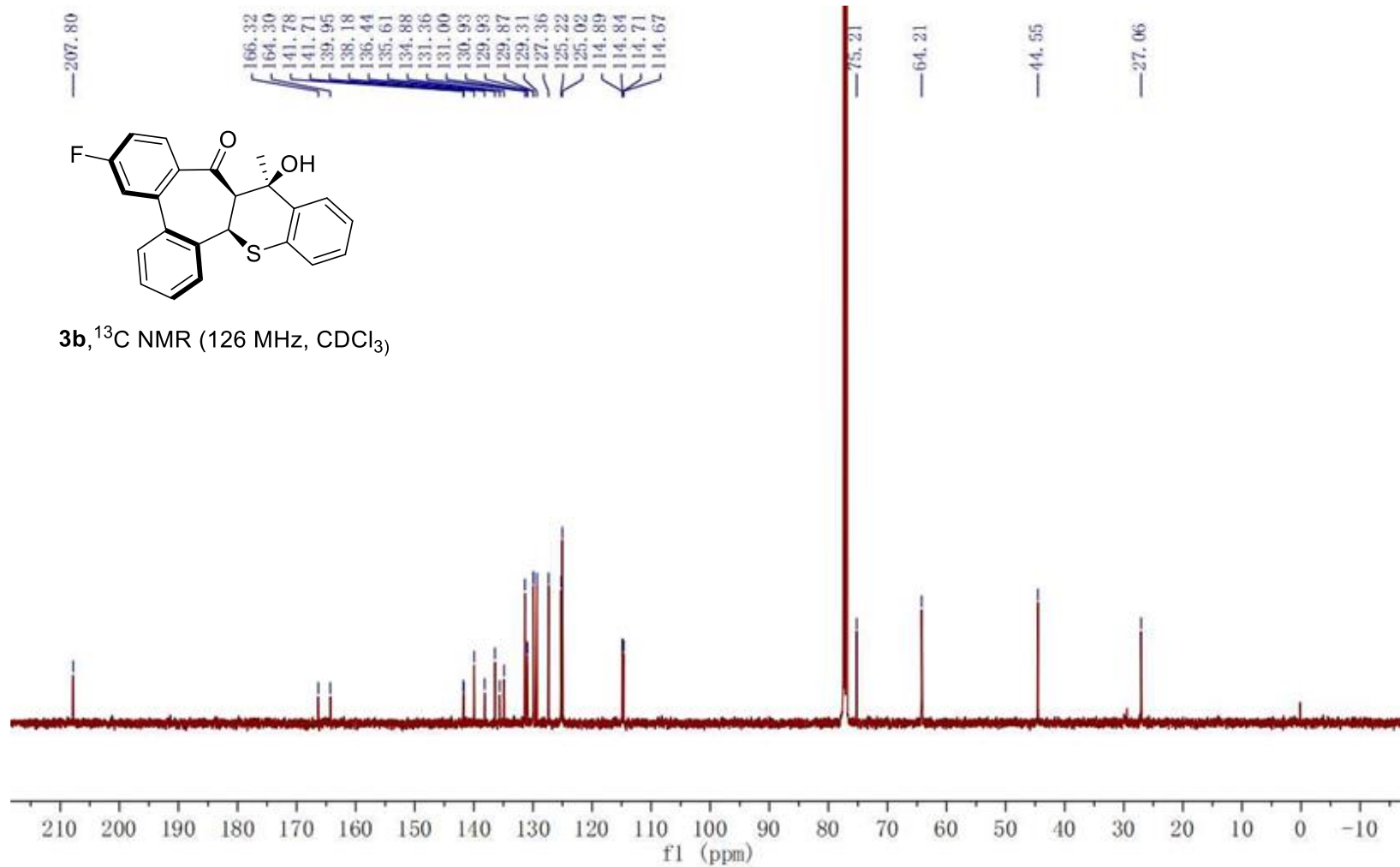
NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.460	716	6301	0.770	--
2	13.035	38660	811675	99.230	18.527

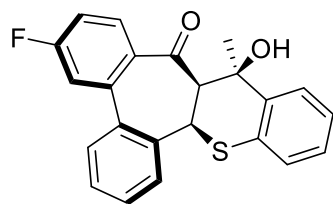
## 8. Copies of NMR Spectra and NOE



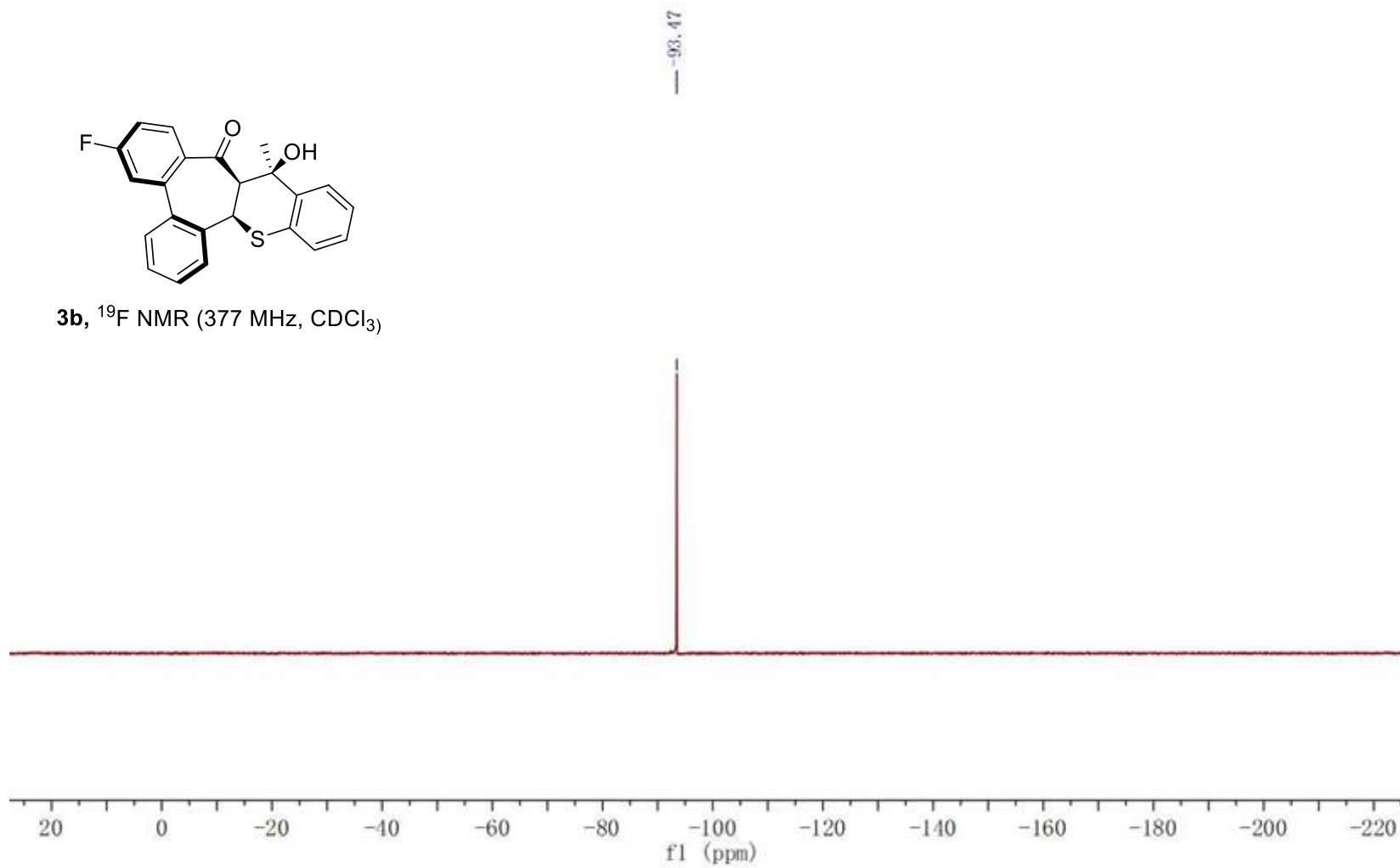


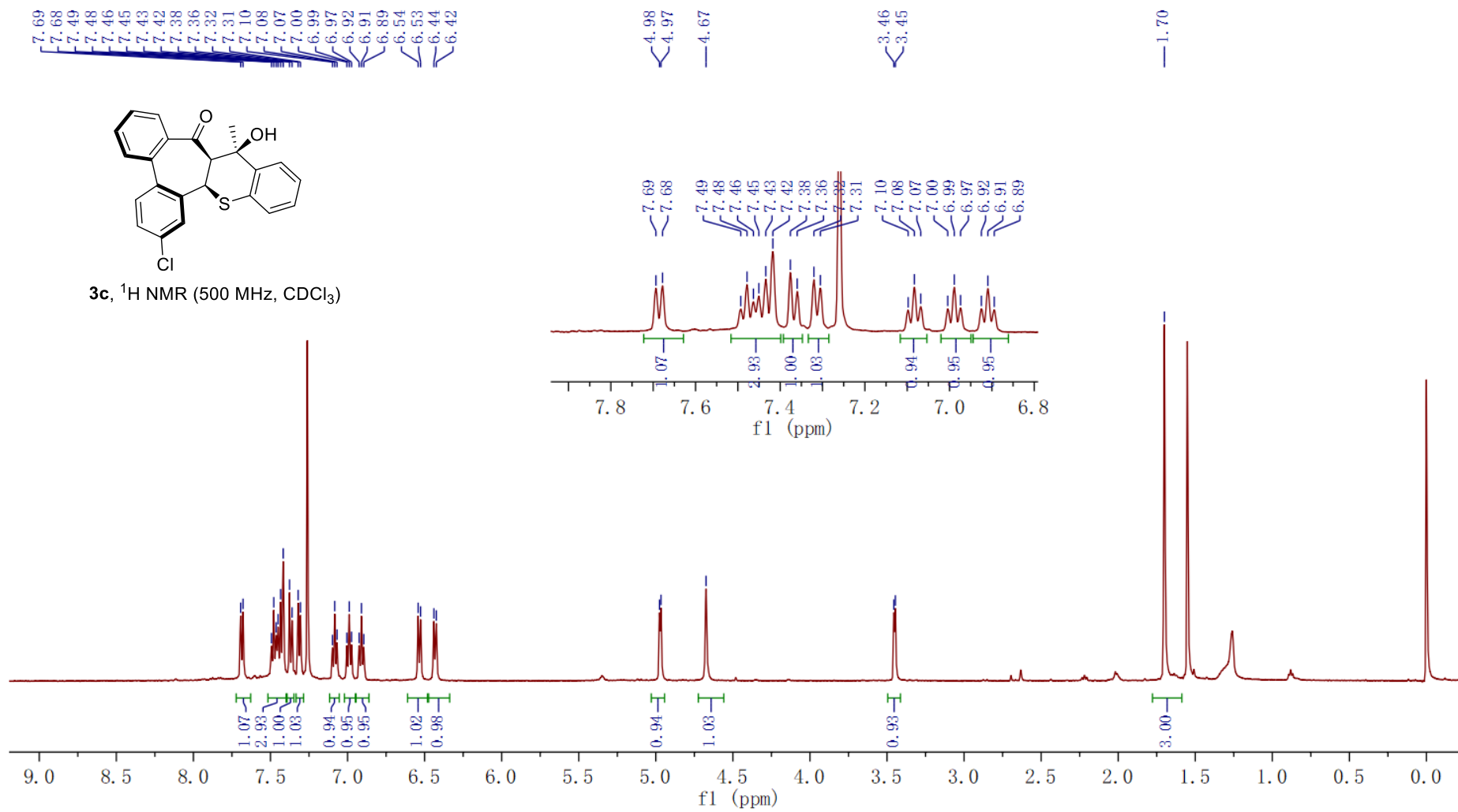


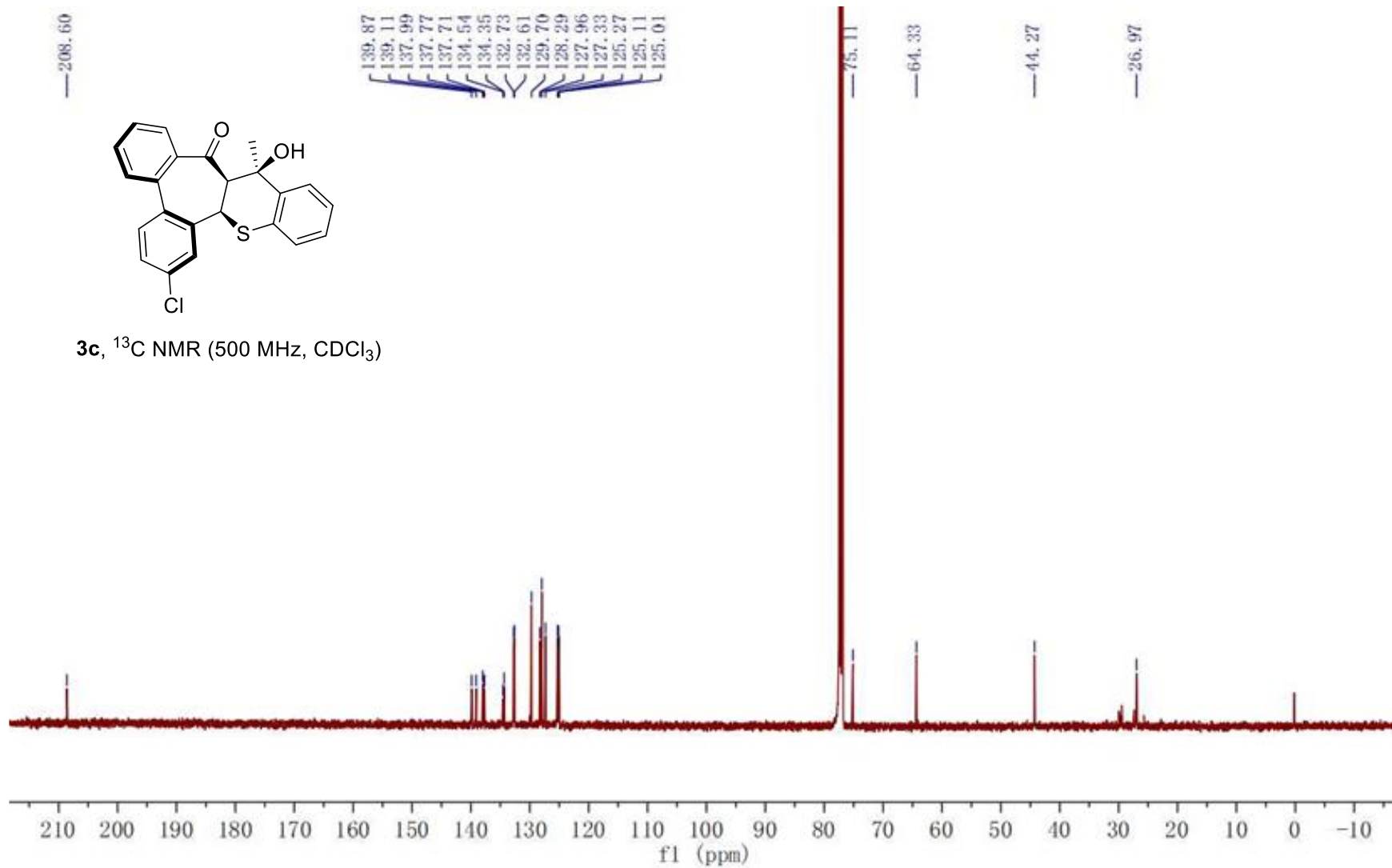




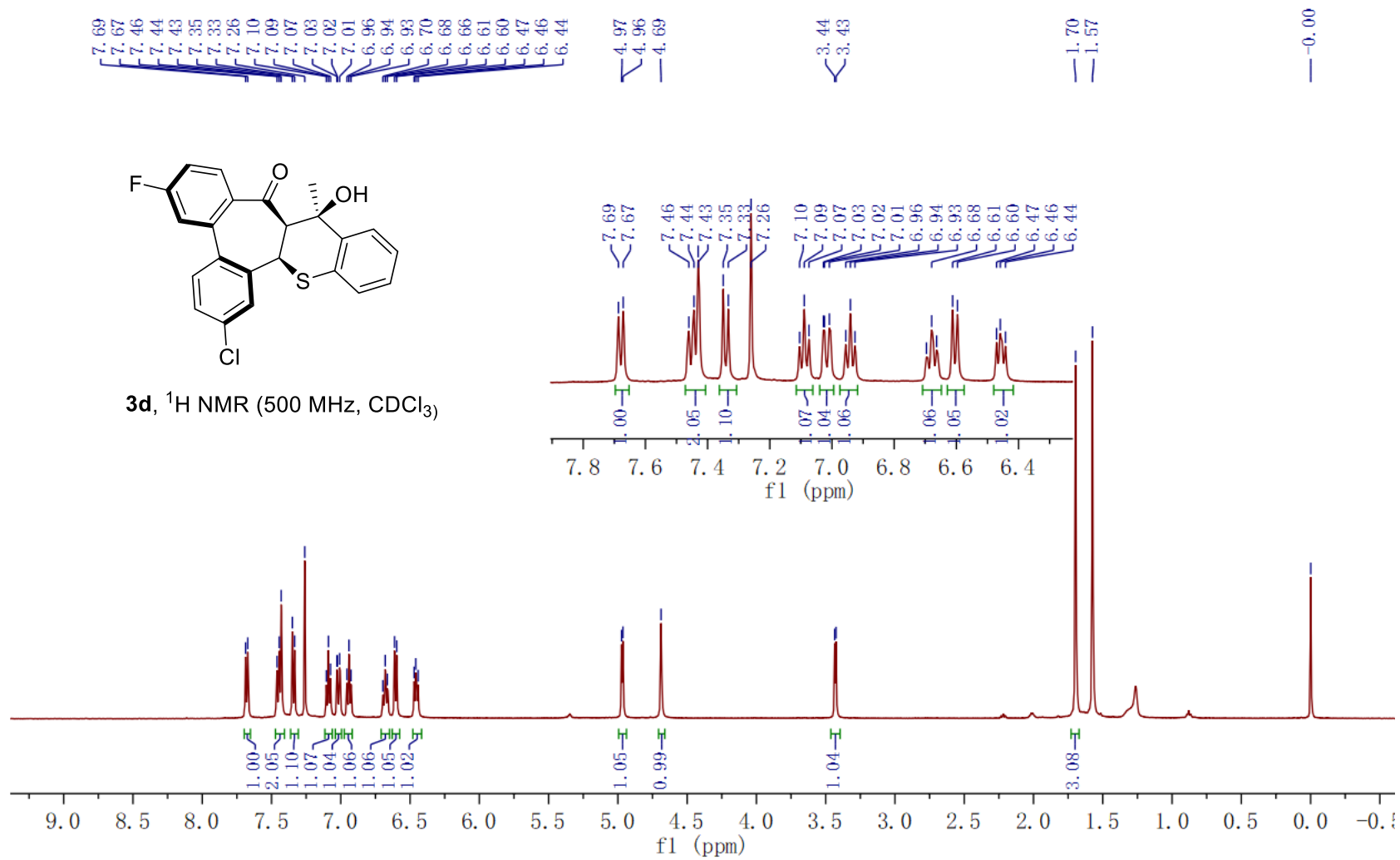
**3b**,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

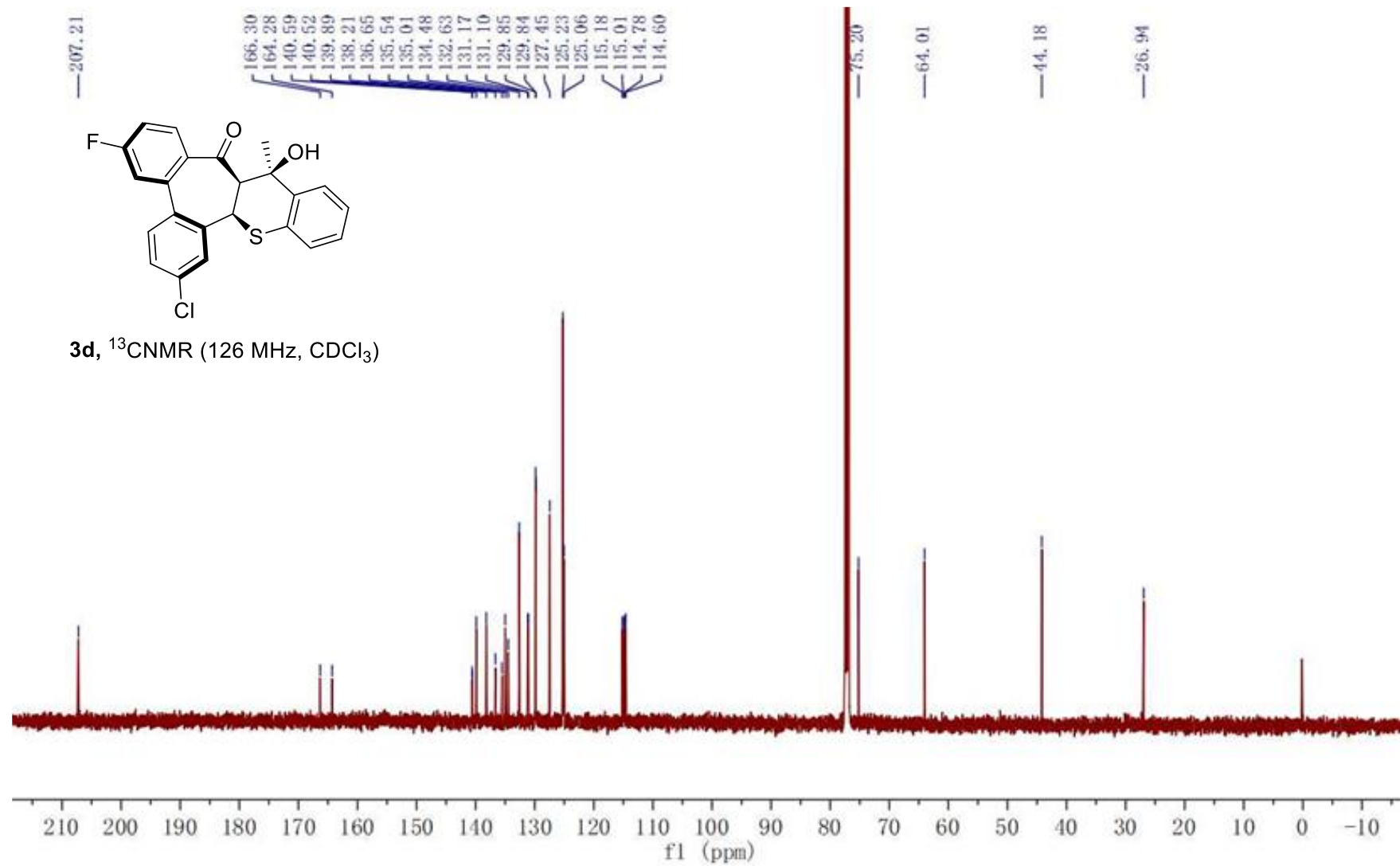


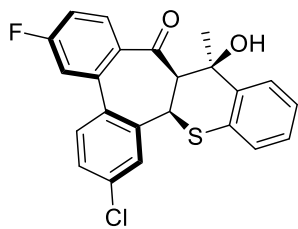




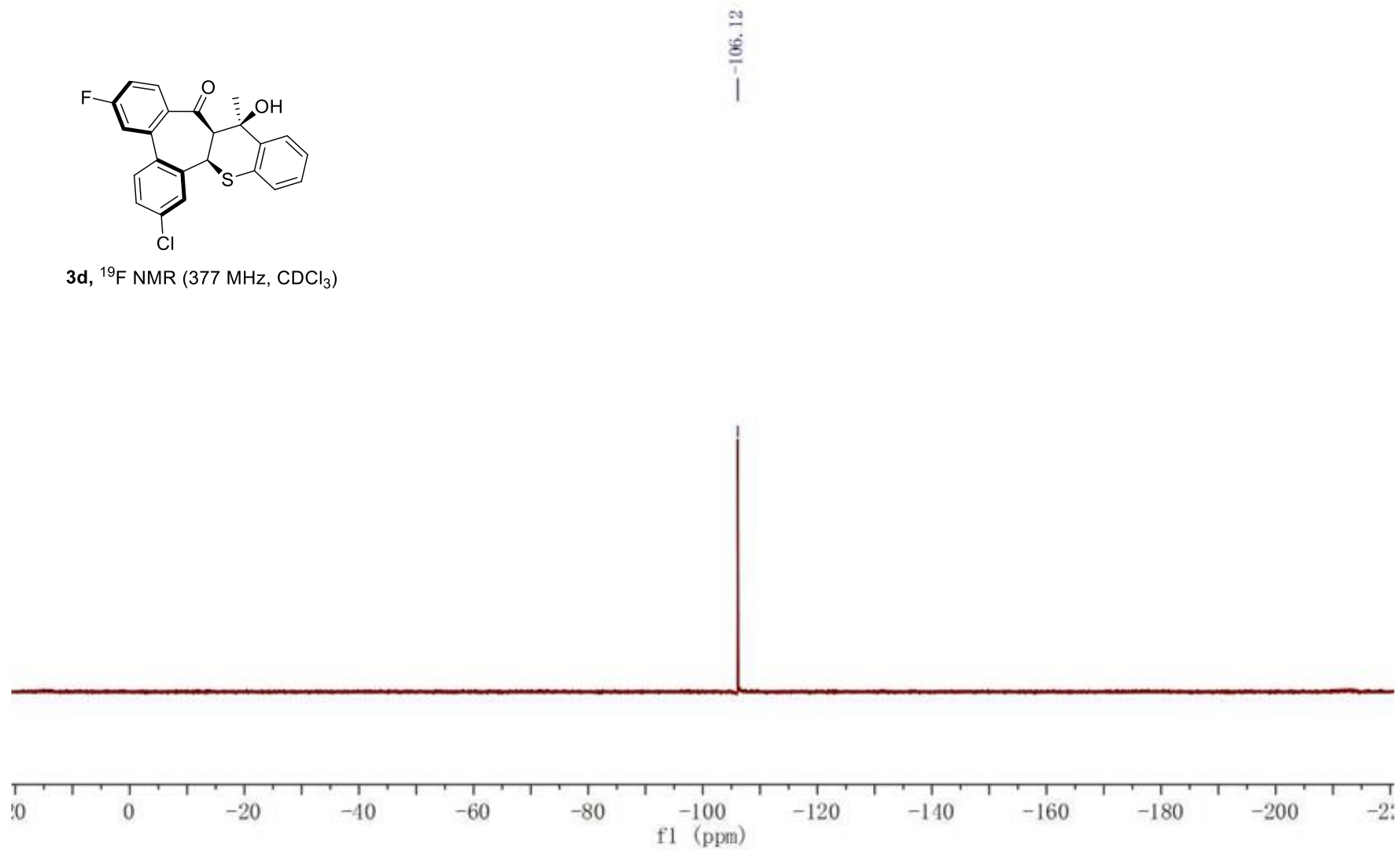








**3d**,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



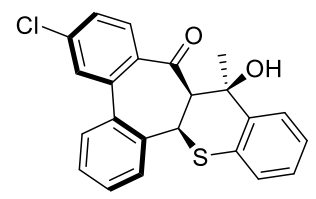
7.69  
7.67  
7.47  
7.47  
7.46  
7.43  
7.41  
7.39  
7.36  
7.10  
7.08  
7.07  
6.96  
6.95  
6.95  
6.83  
6.62  
6.39  
6.38

5.04  
5.03

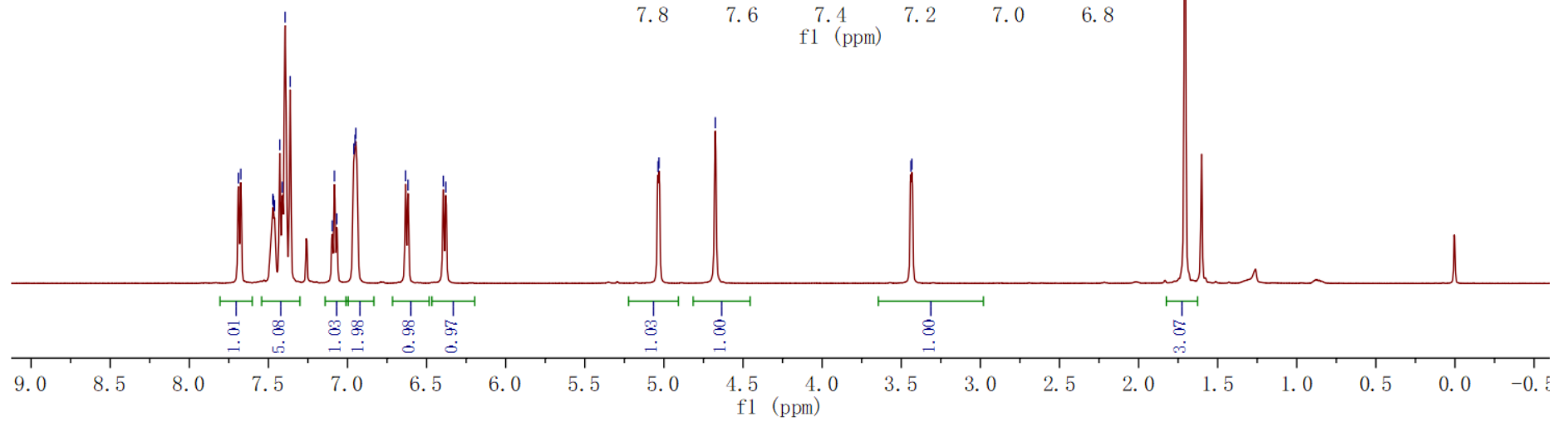
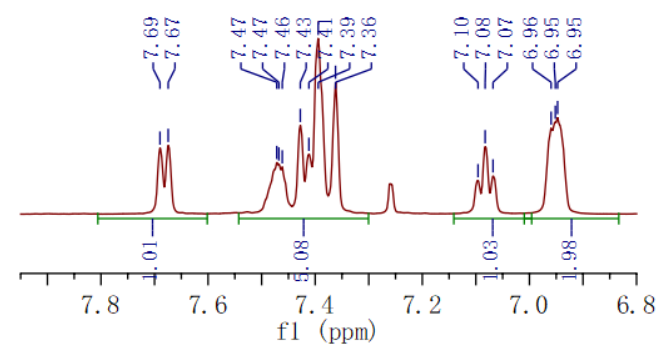
4.67

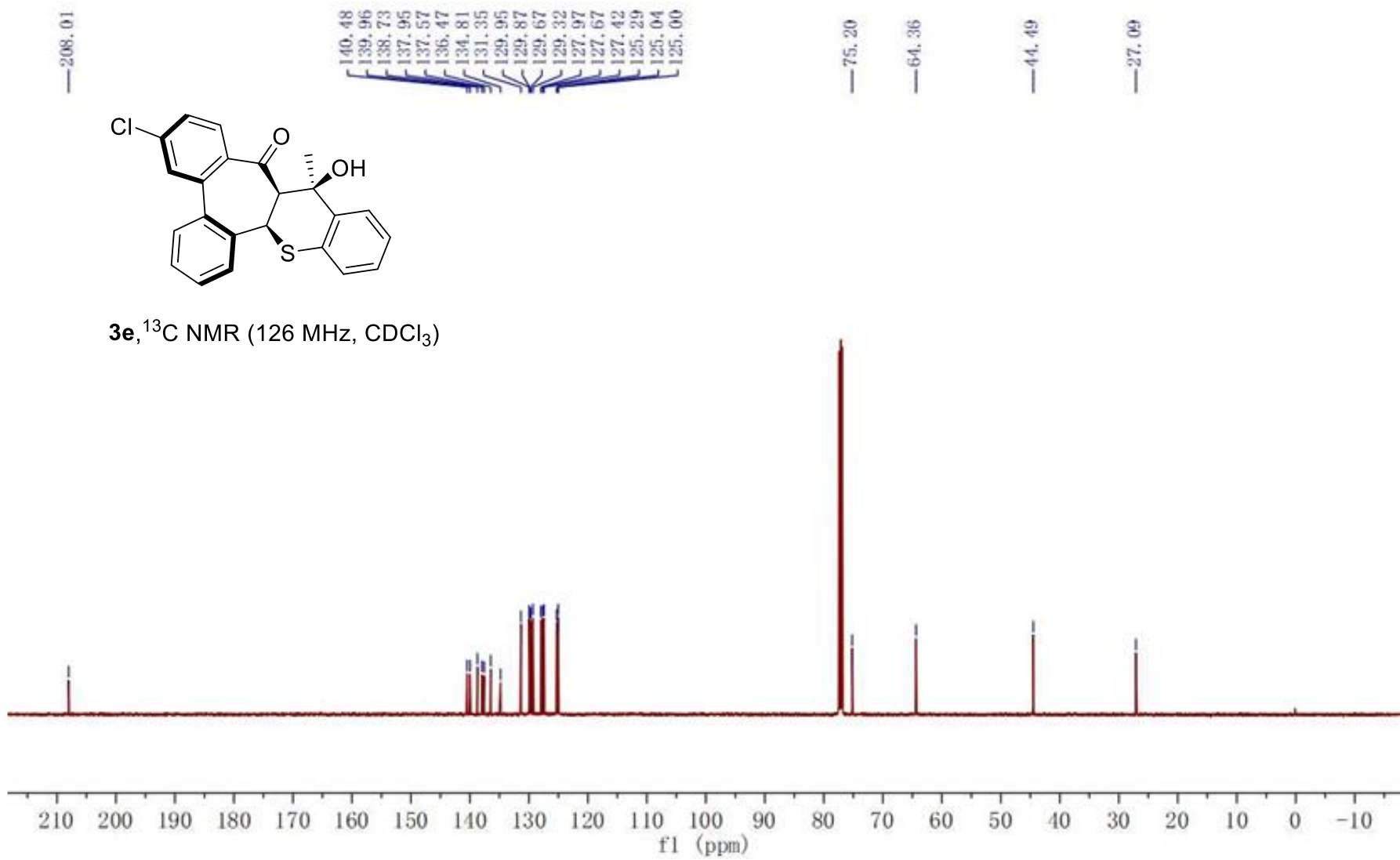
3.44  
3.43

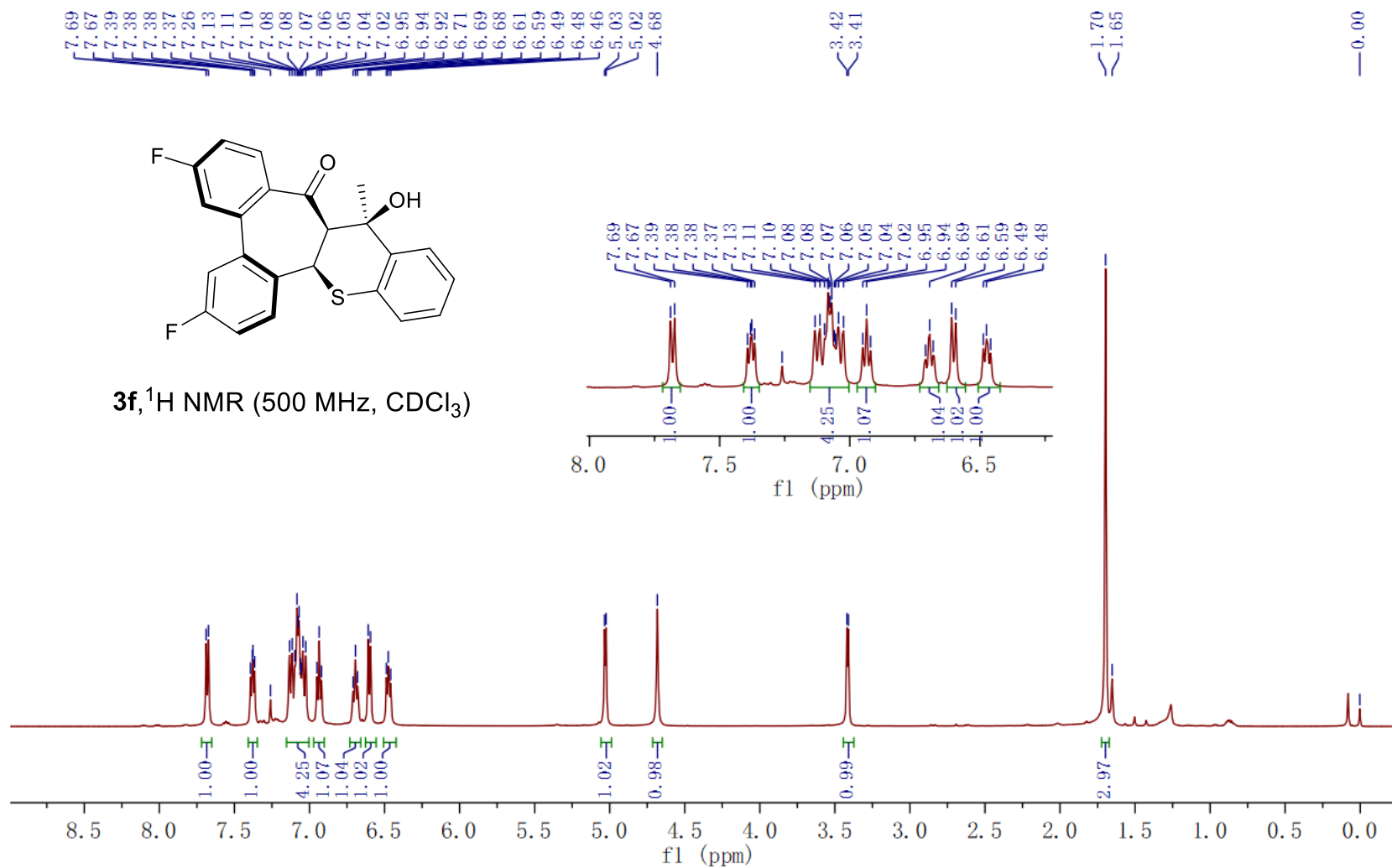
1.71

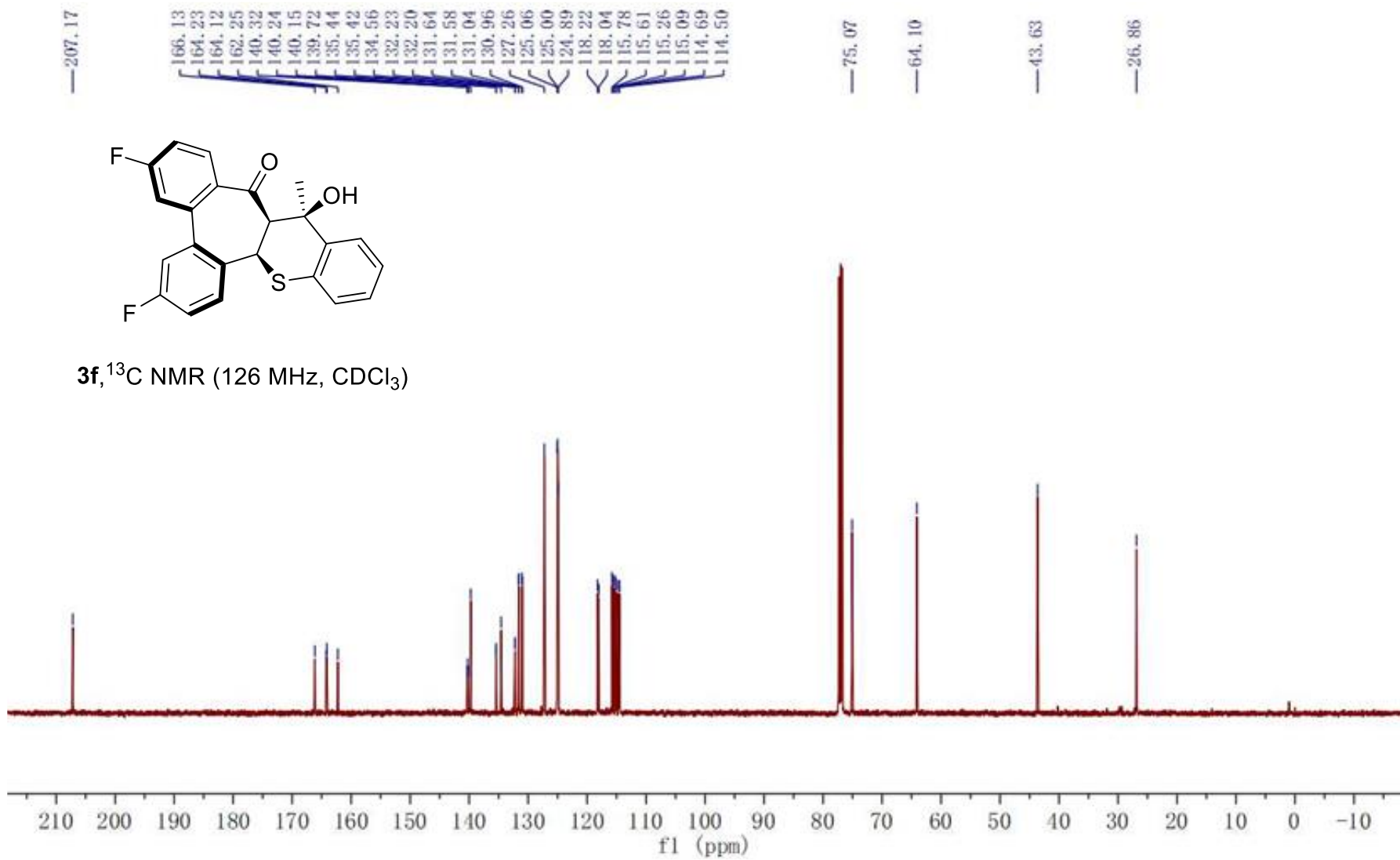


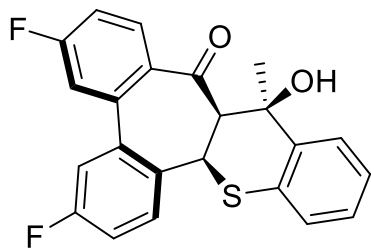
**3e**,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )



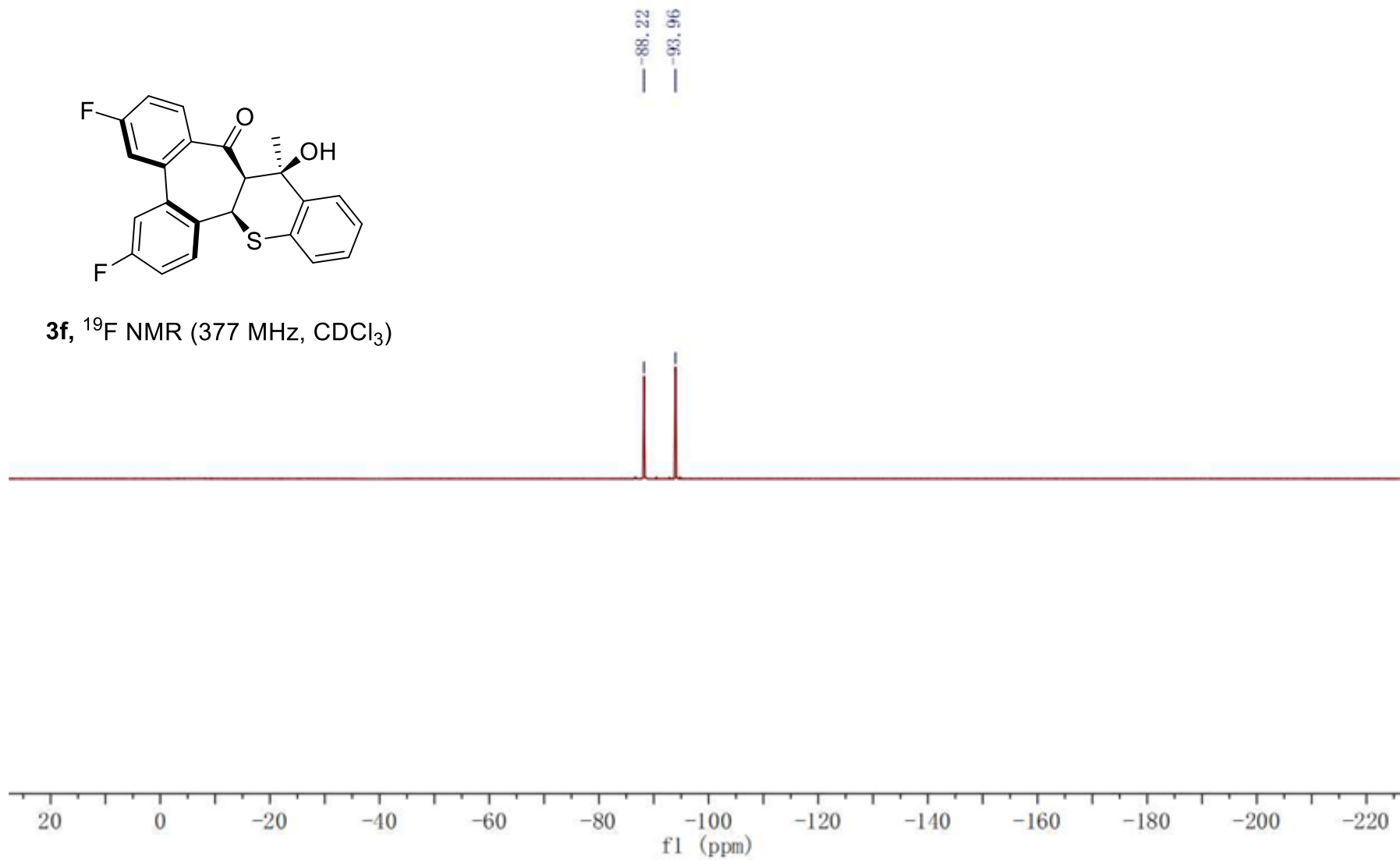




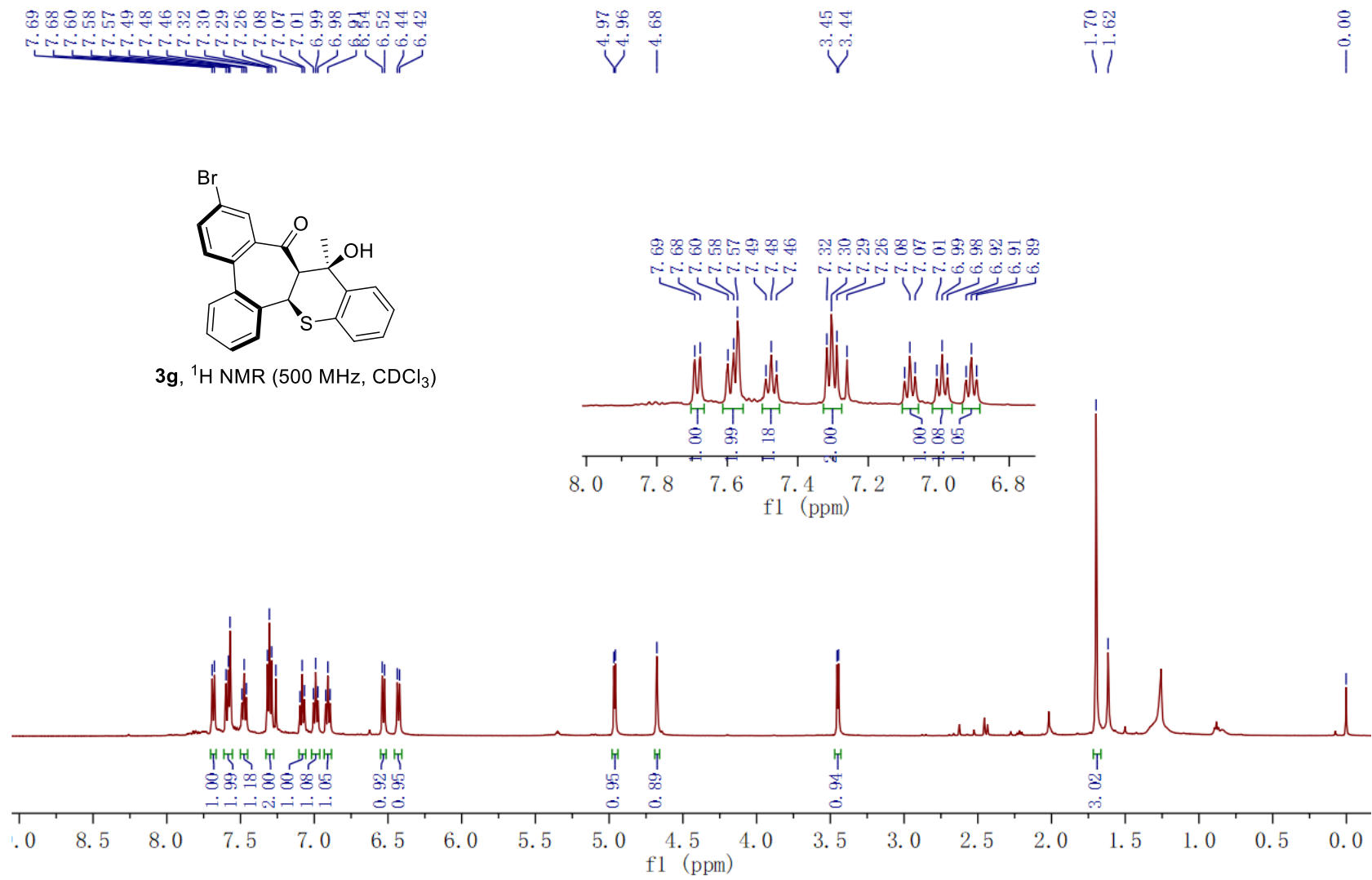


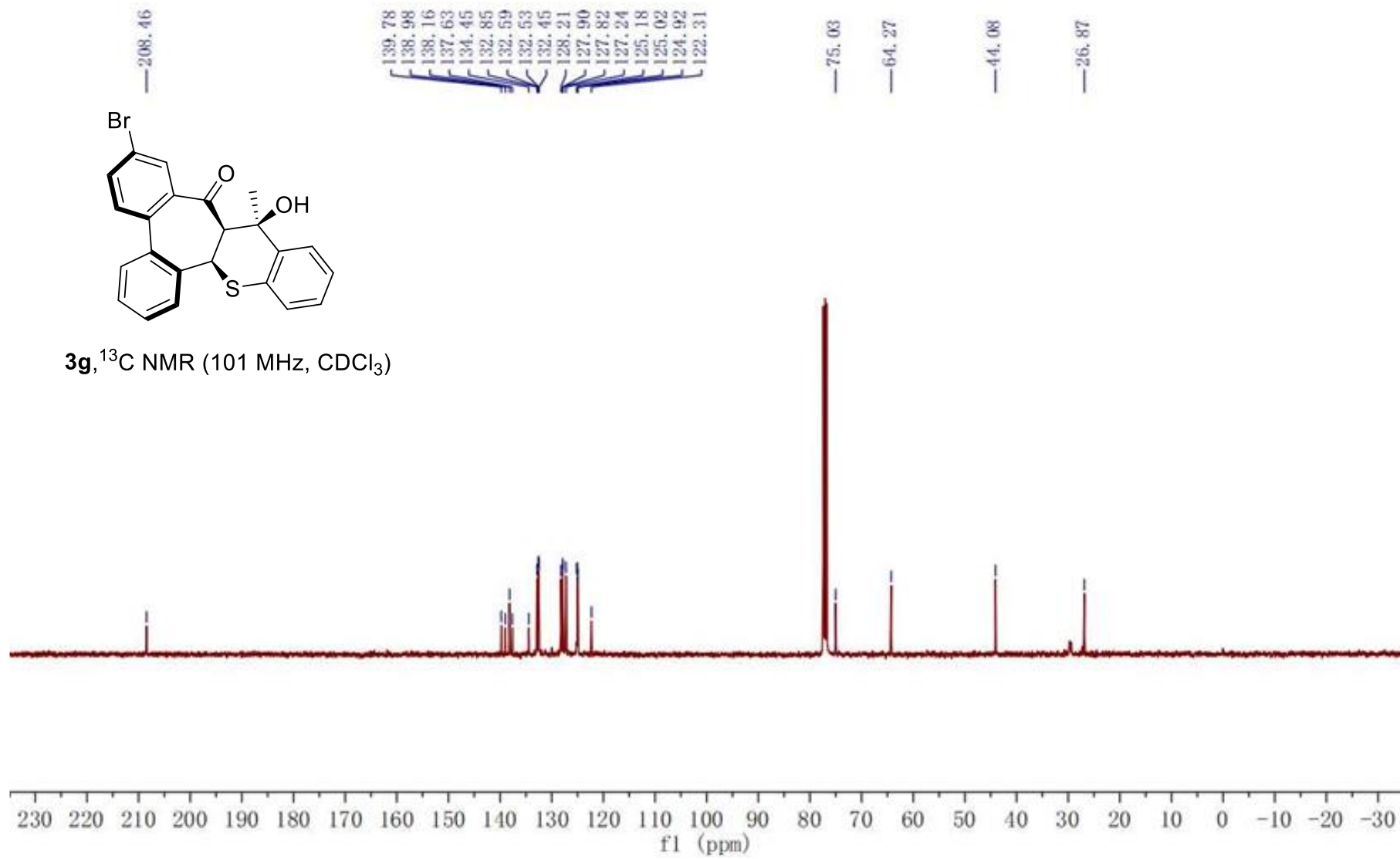


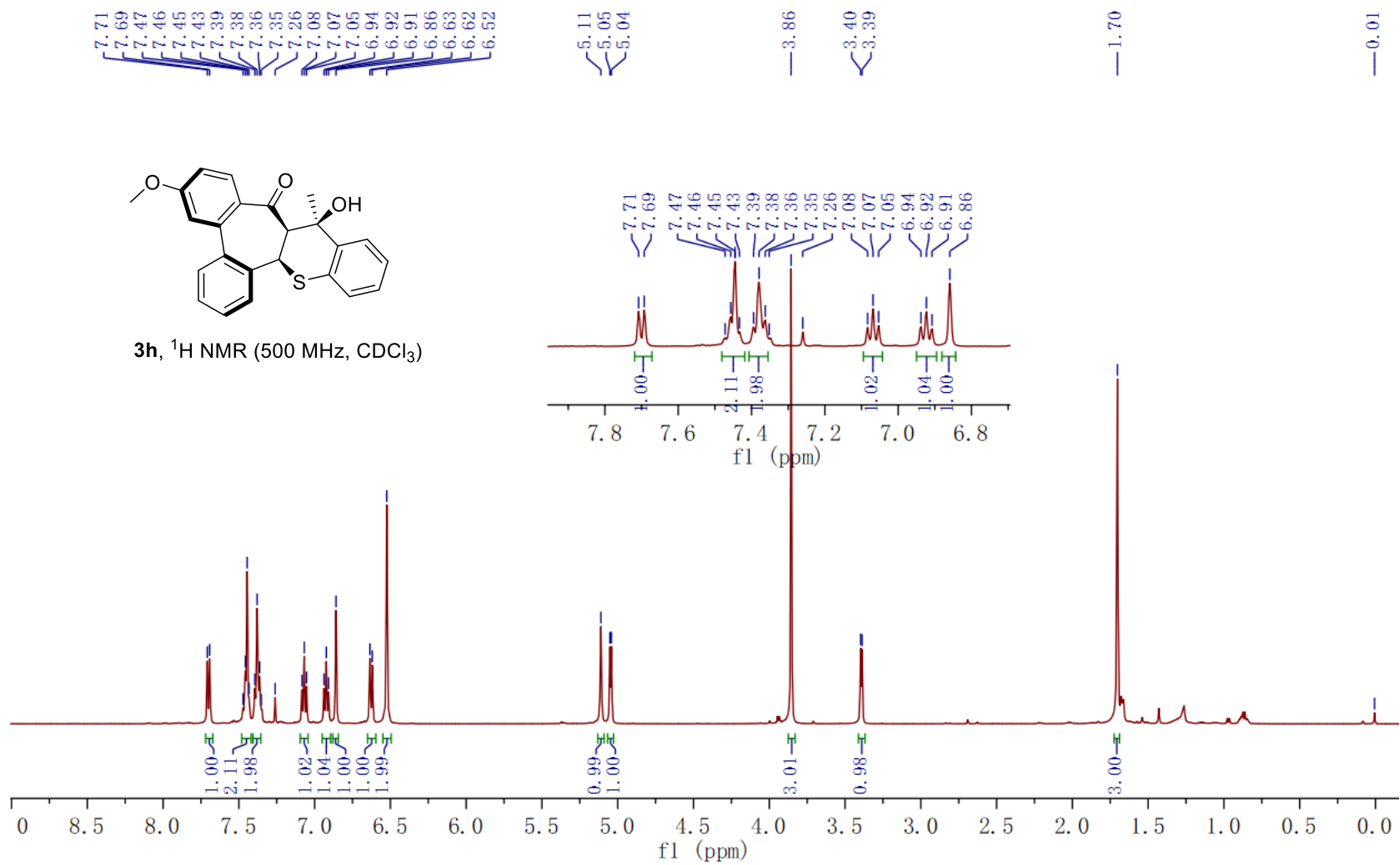
3f,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

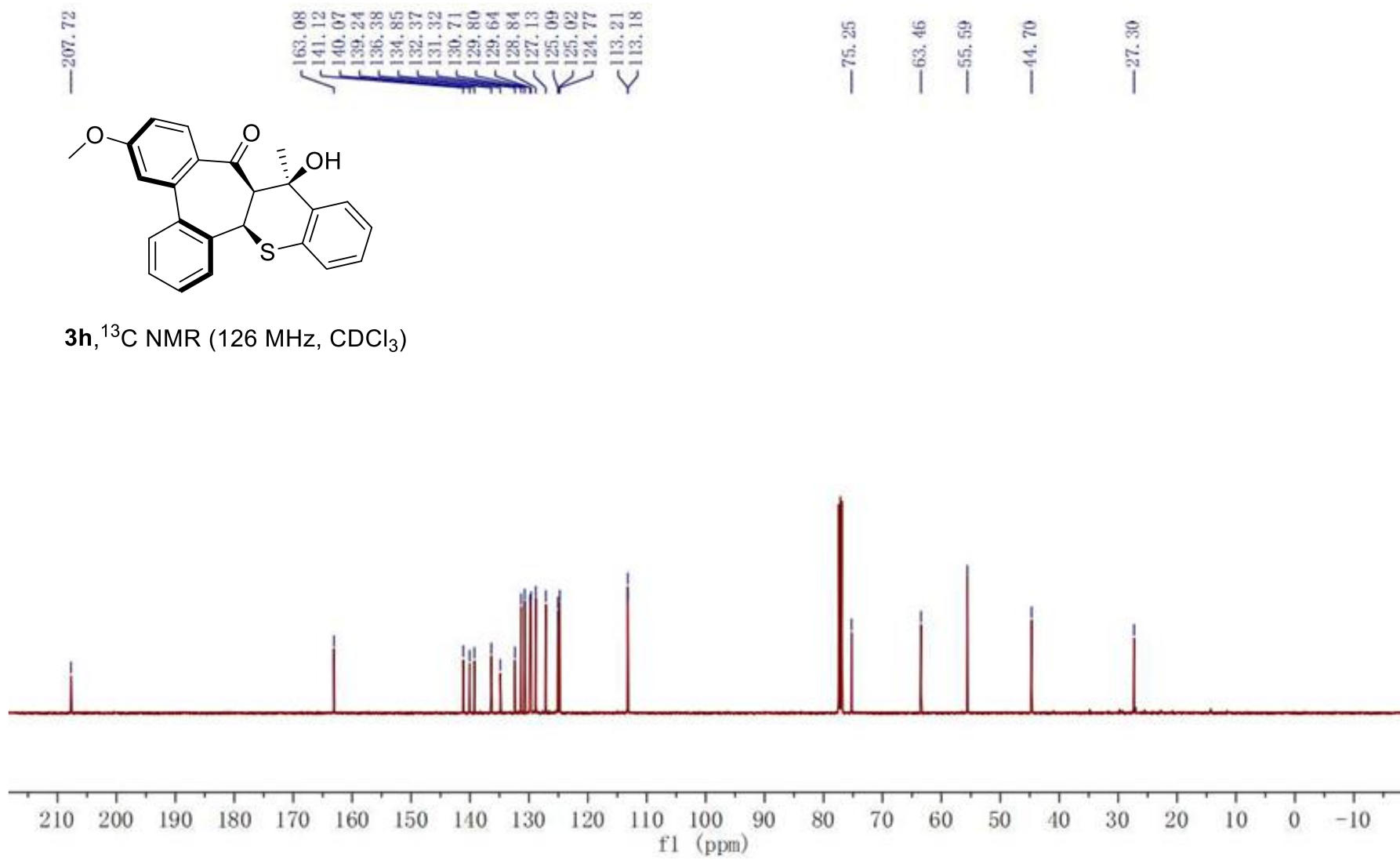


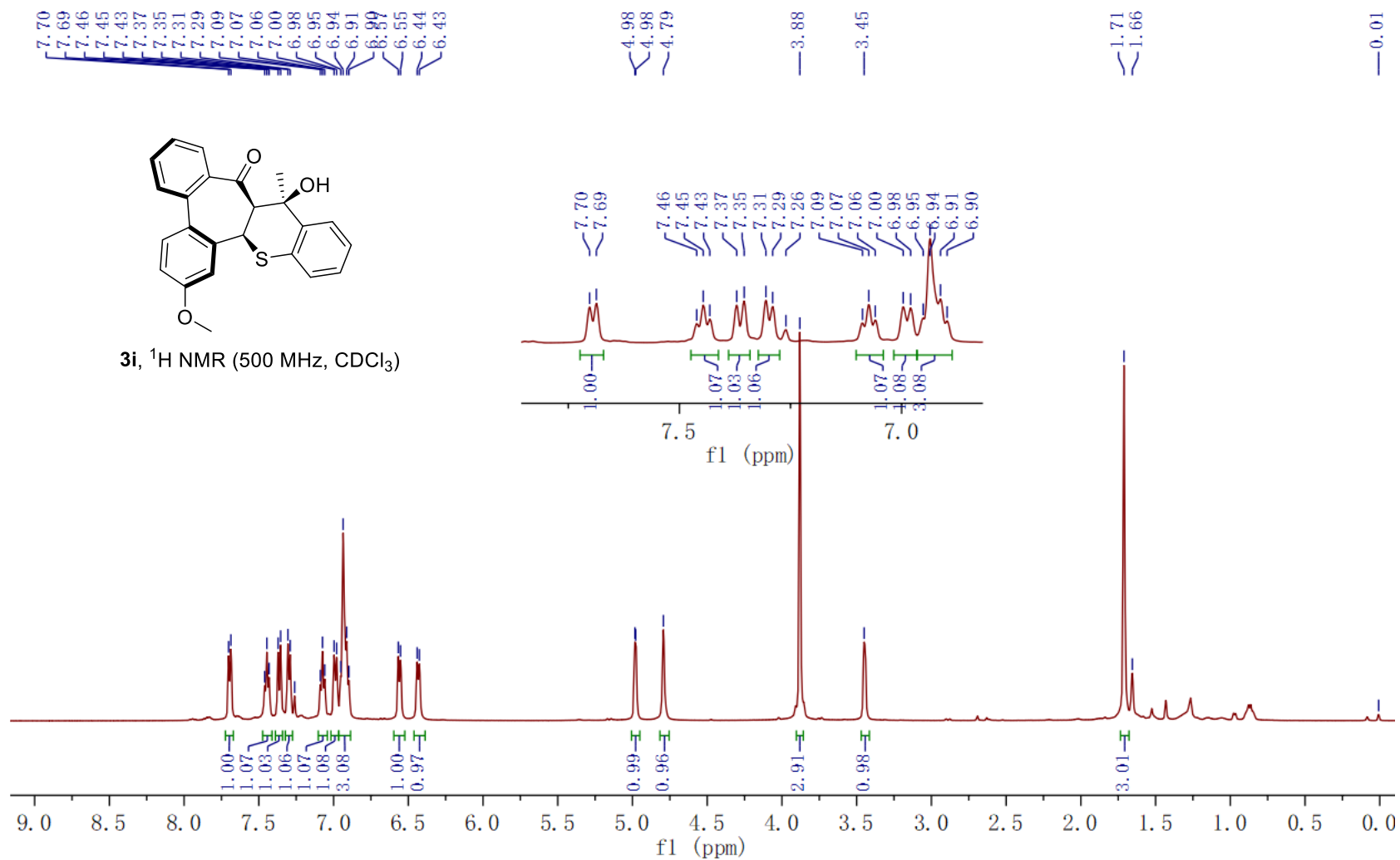


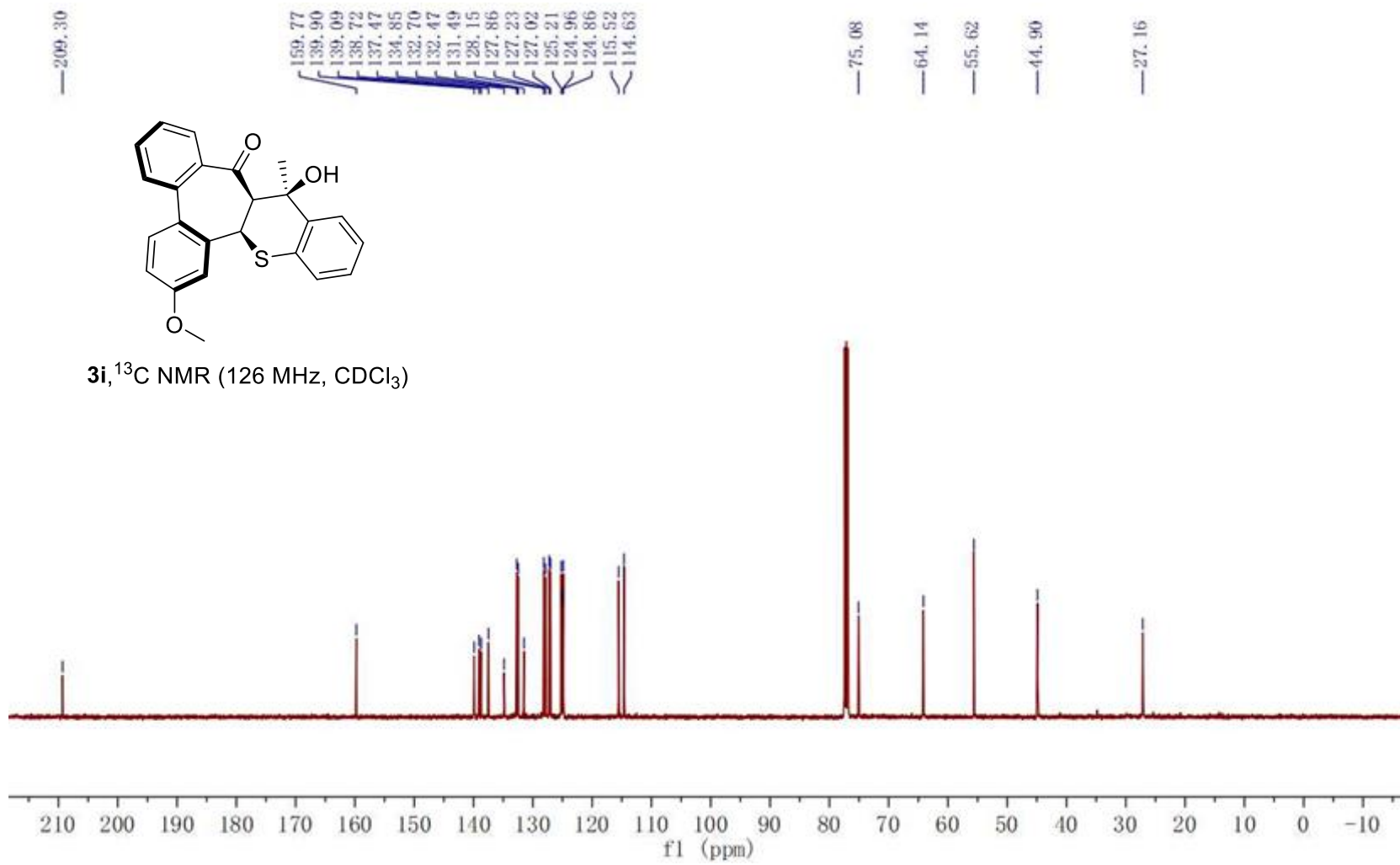


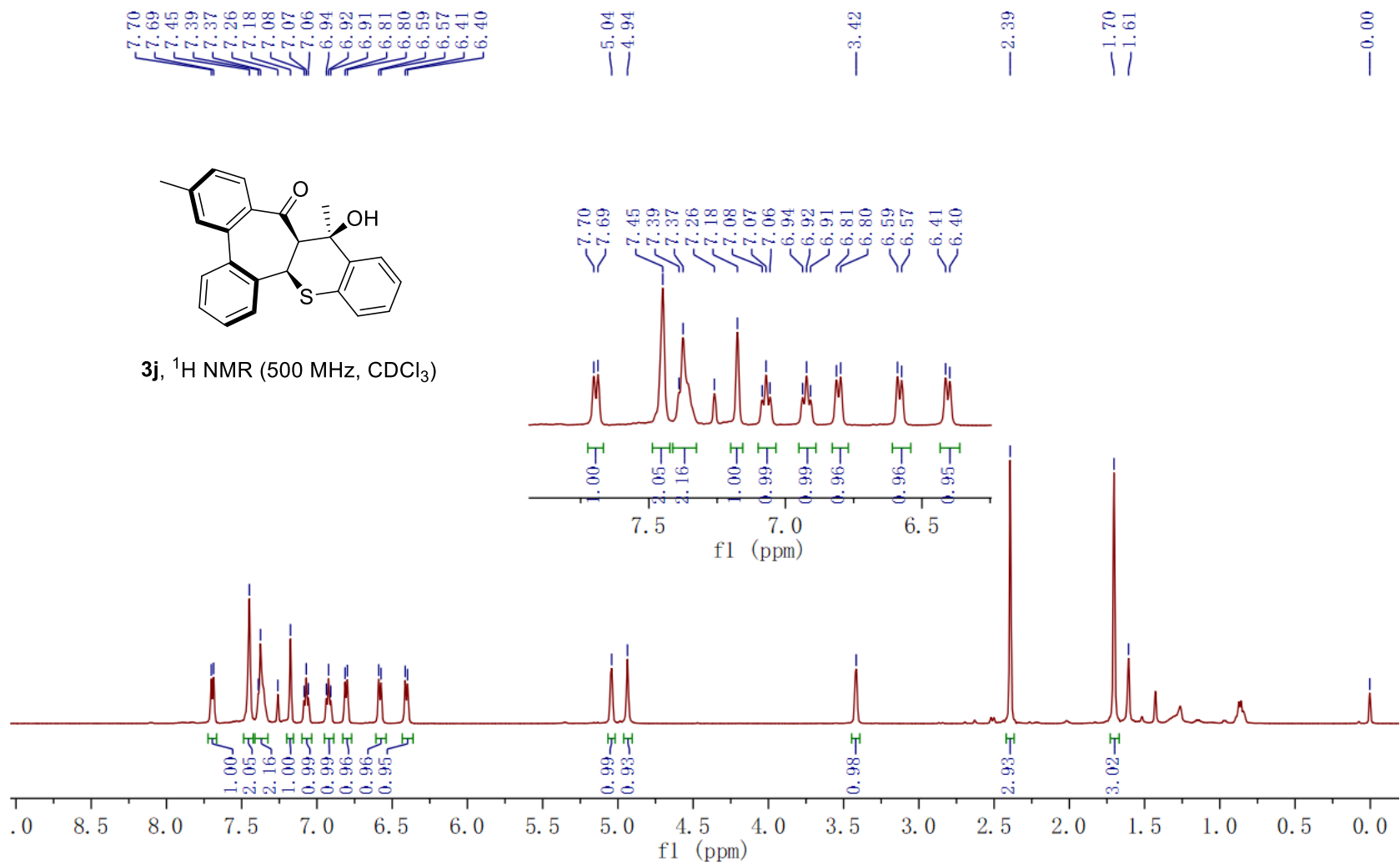


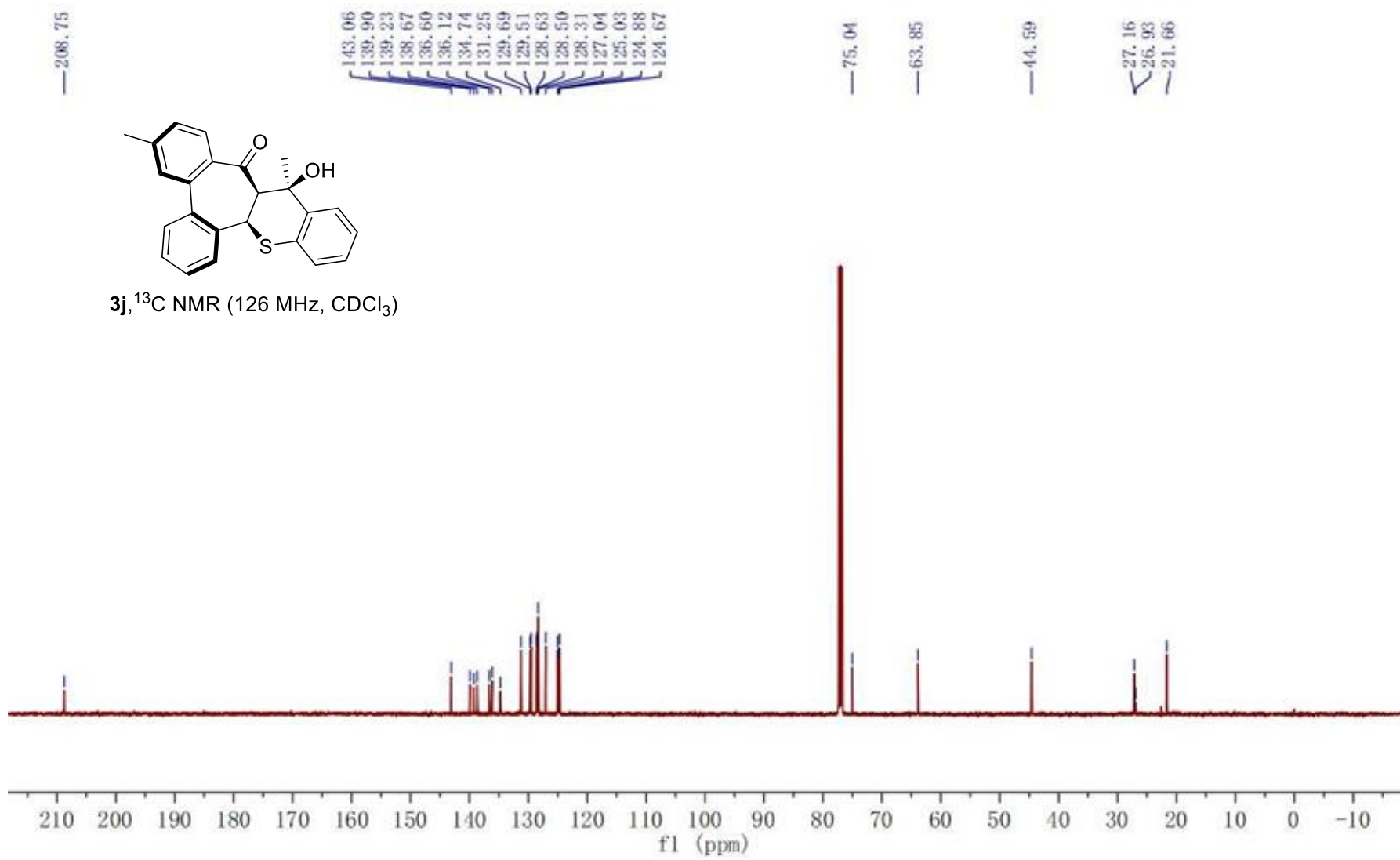




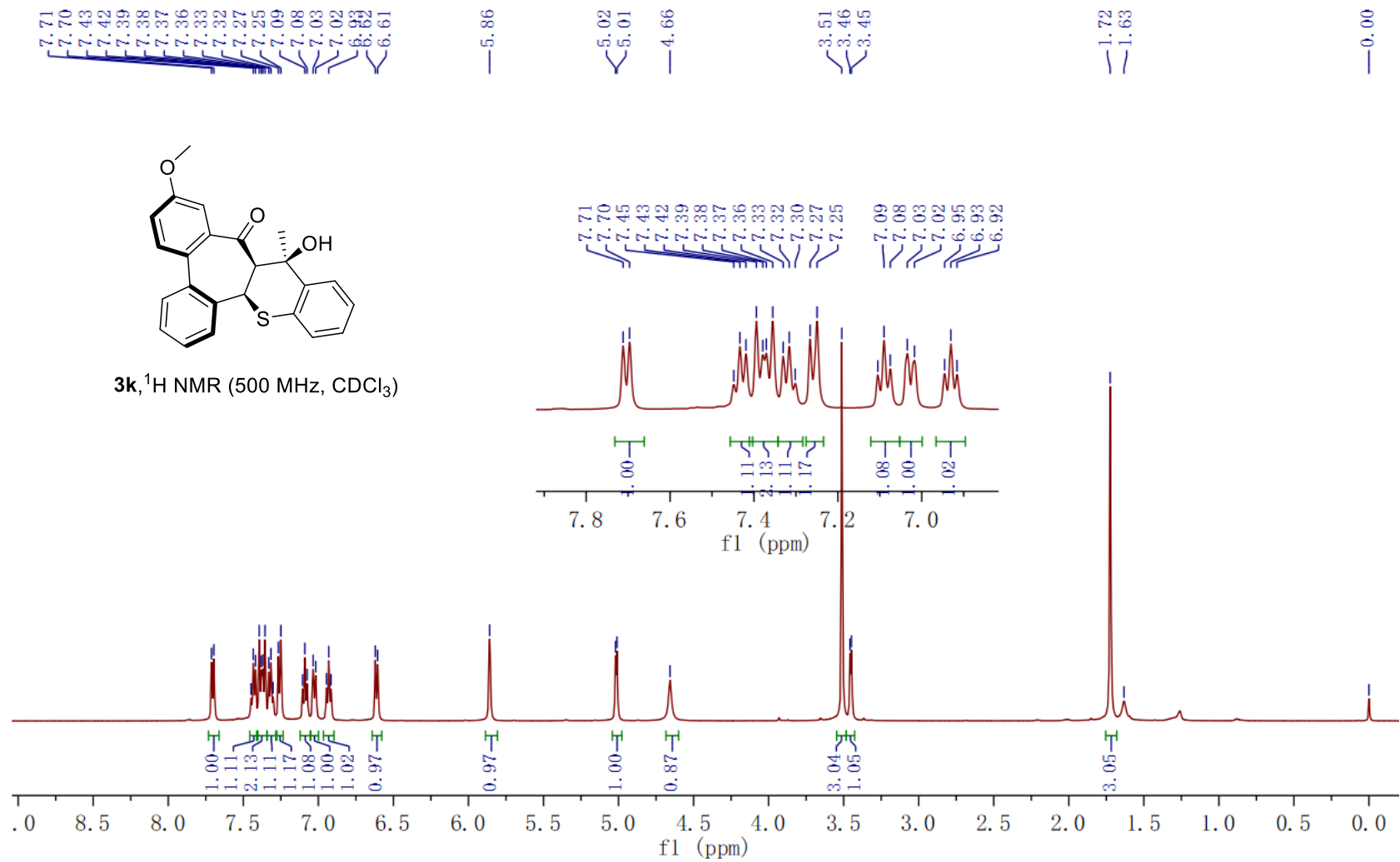












—209.13

158.83  
140.06  
140.02  
138.97  
135.76  
135.43  
131.60  
131.03  
129.78  
129.66  
129.62  
128.12  
127.11  
125.51  
125.01  
124.71  
120.37  
110.74

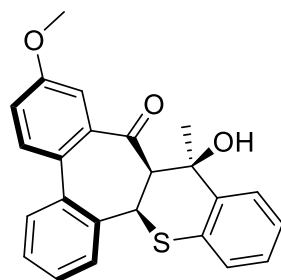
—75.13

—64.84

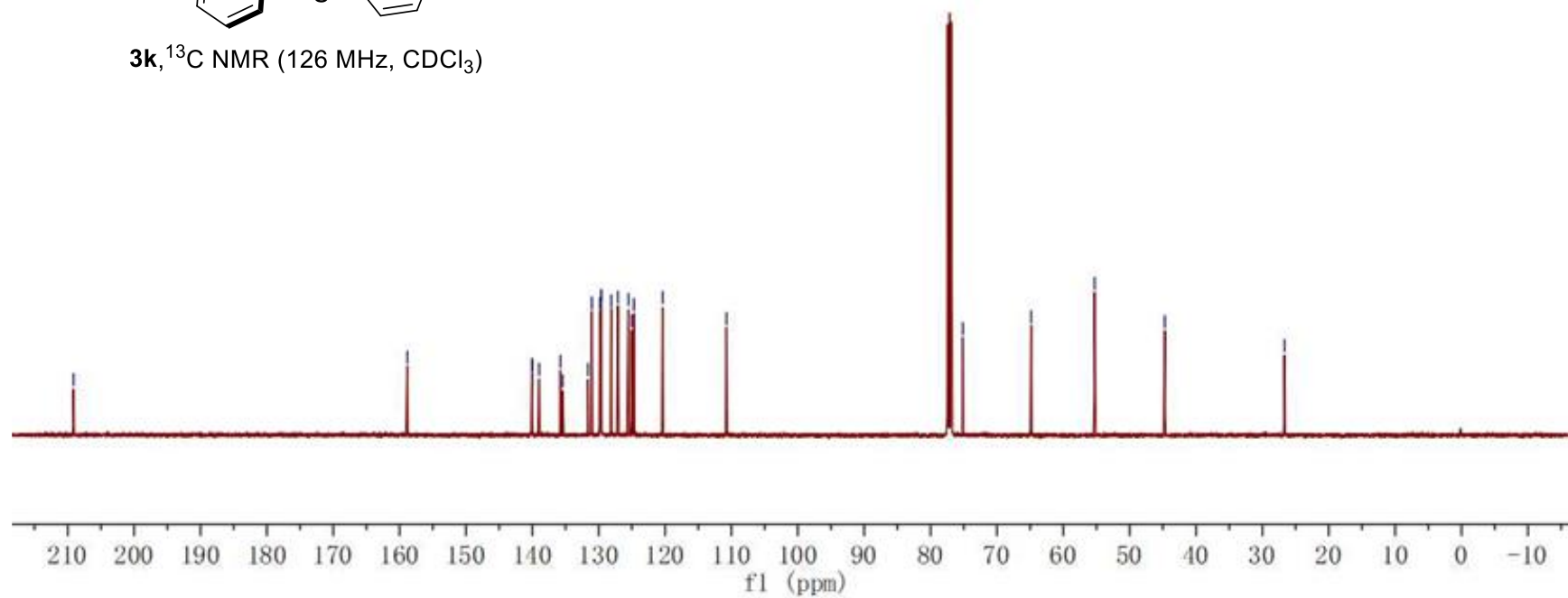
—55.29

—44.71

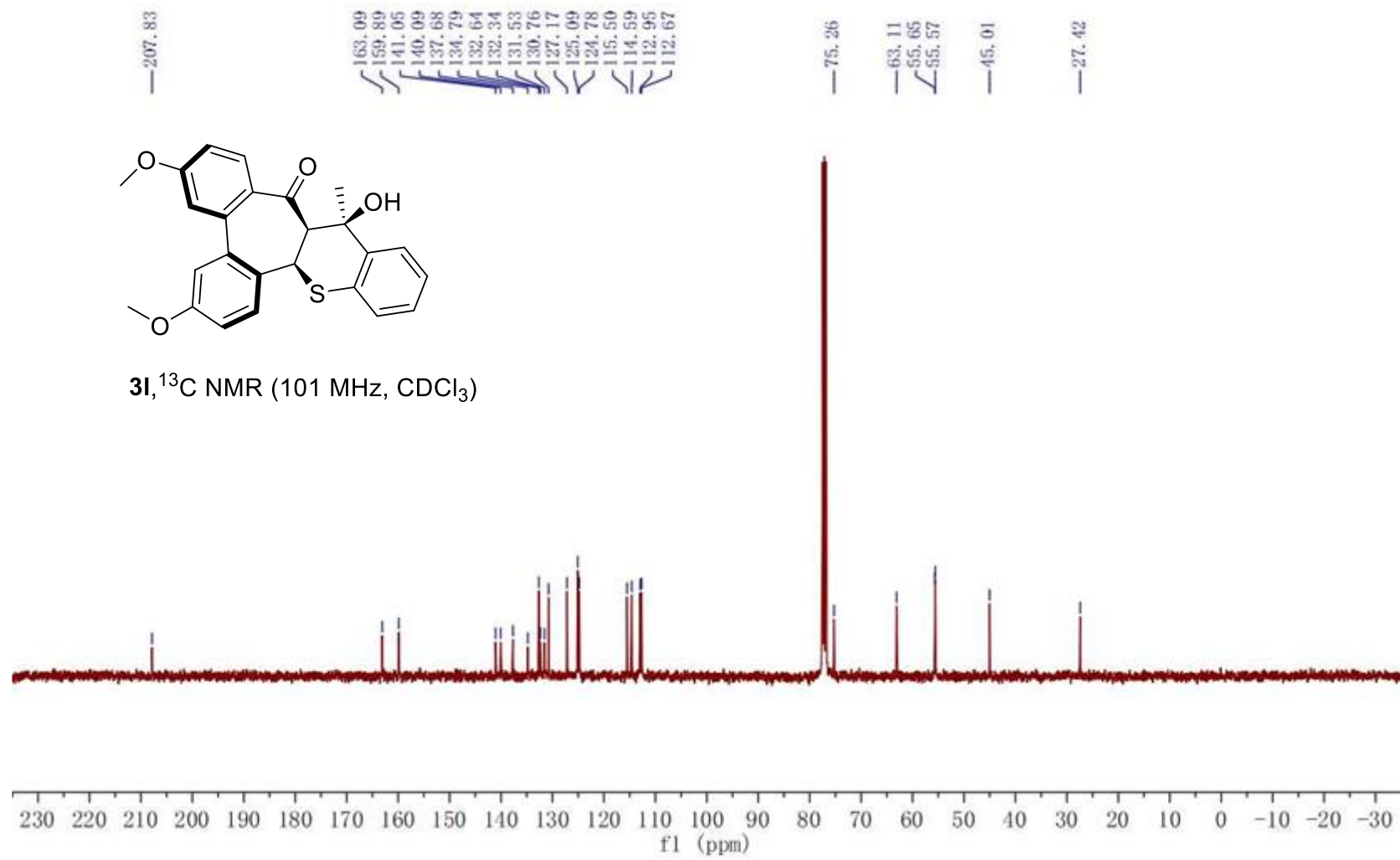
—26.66

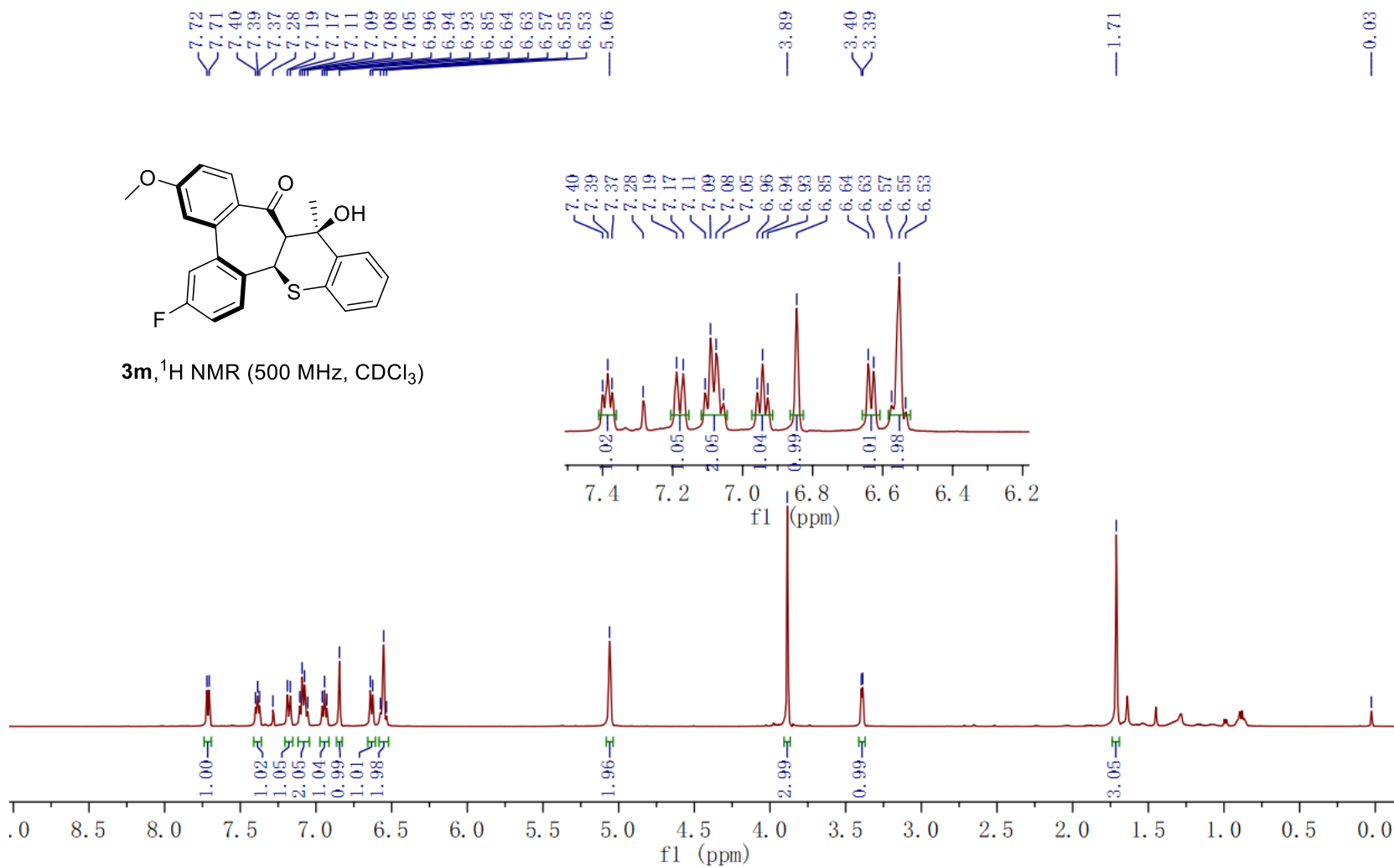


**3k**,  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )









—207.32

164.31  
163.16  
162.34  
141.52  
141.45  
140.00  
139.88  
134.70  
132.32  
132.30  
132.27  
131.62  
131.56  
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124.90  
118.28  
118.10  
115.42  
115.26  
113.74  
113.11

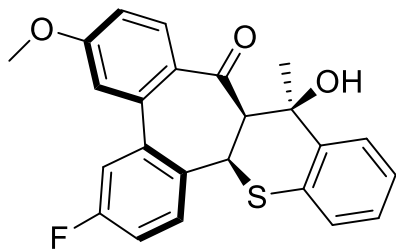
—75.27

—63.51

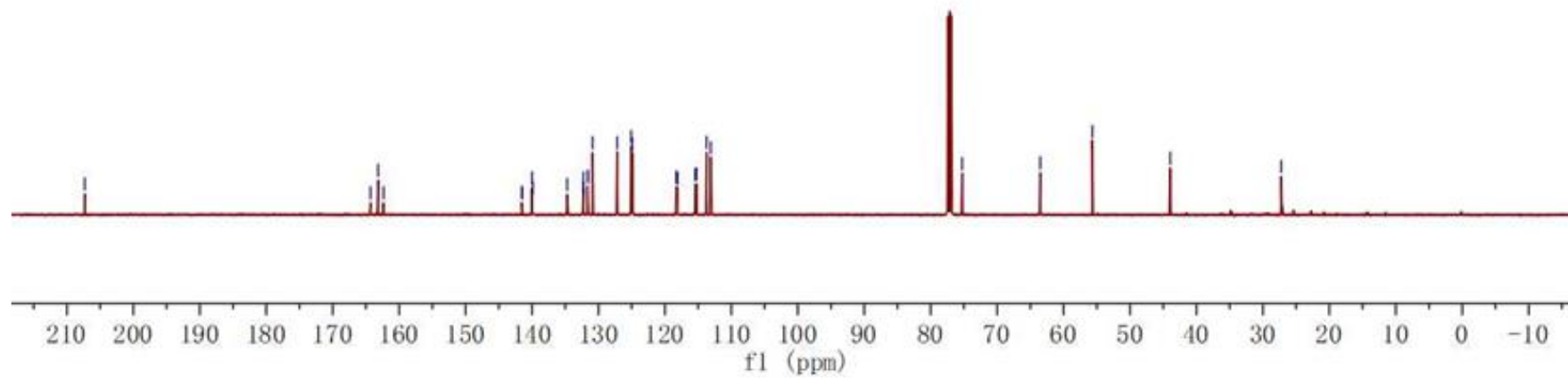
—55.66

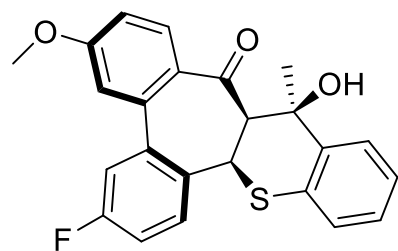
—43.95

—27.24

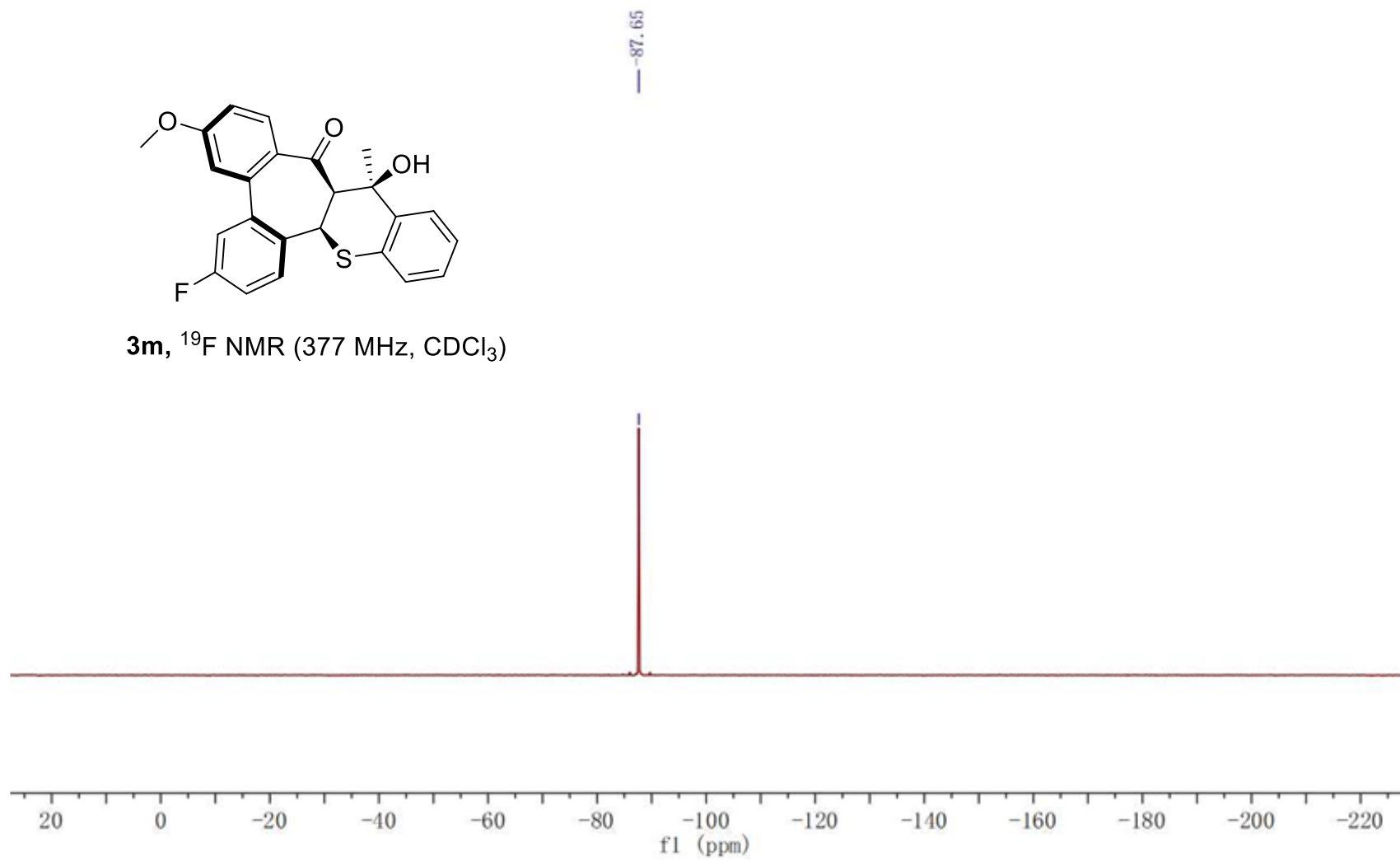


**3m**,  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )





**3m**,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



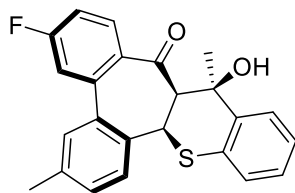
7.71  
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7.31  
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7.28  
7.24  
7.22  
7.21  
7.11  
7.09  
7.07  
7.07  
6.97  
6.95  
6.94  
6.70  
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6.64  
6.63  
6.50  
6.48  
6.47

5.04  
5.03  
4.77

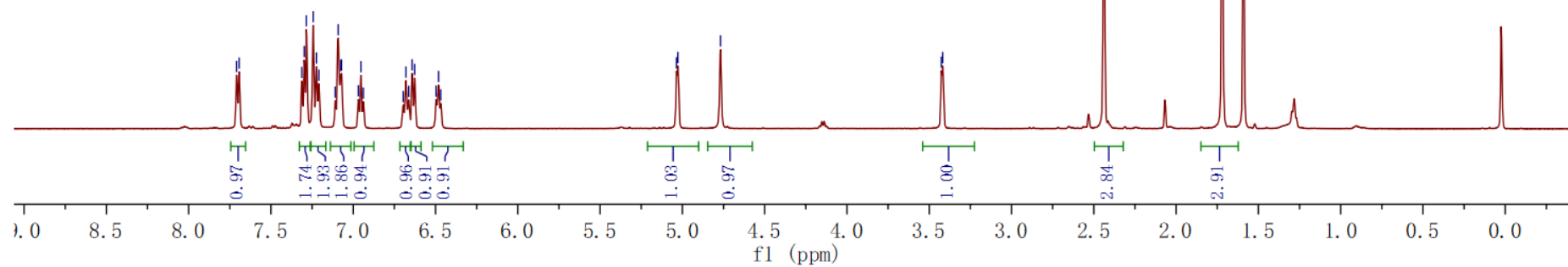
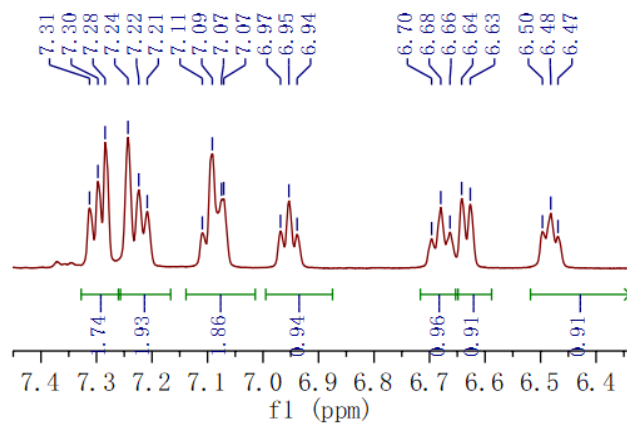
3.43  
3.42

2.44

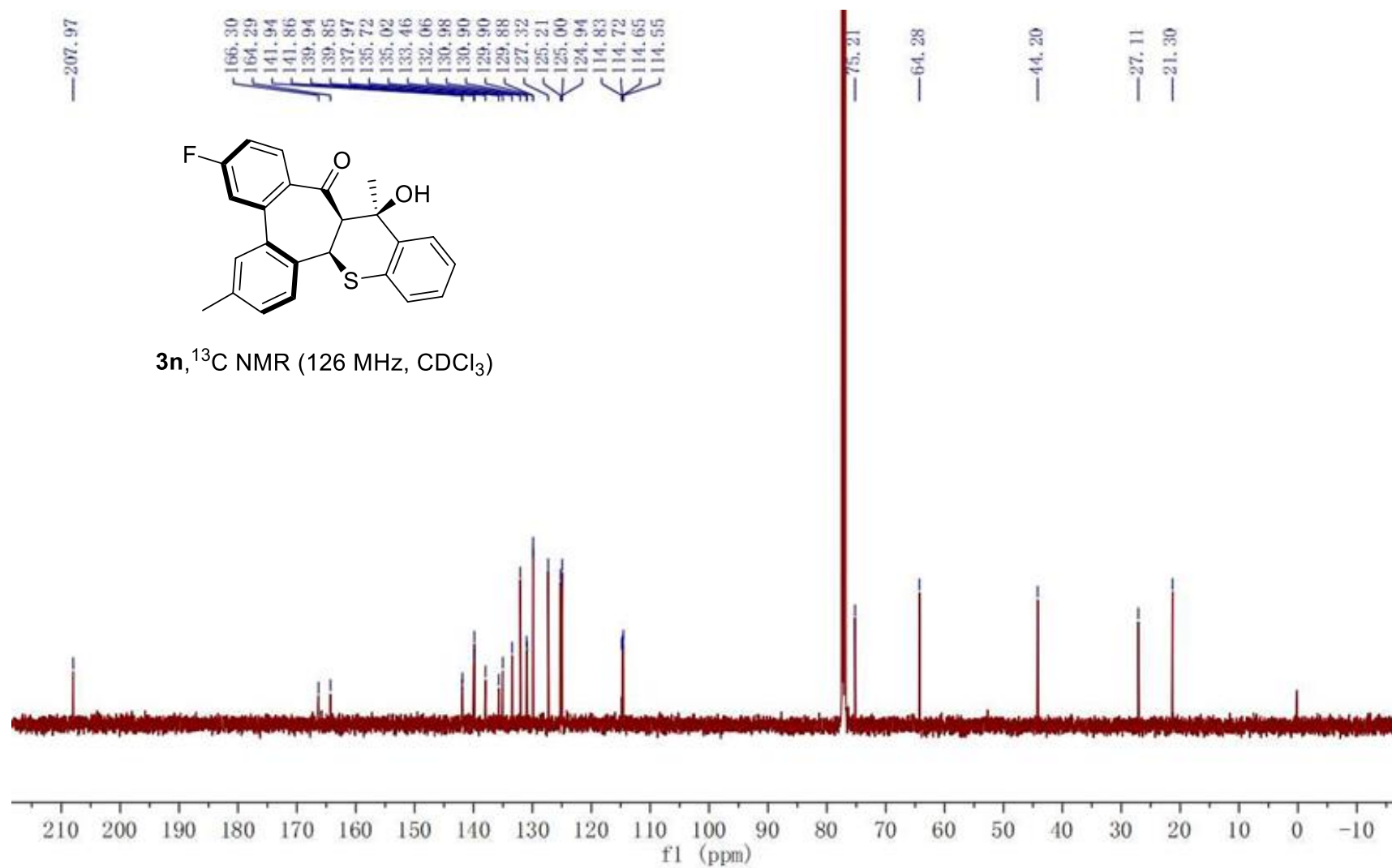
1.72

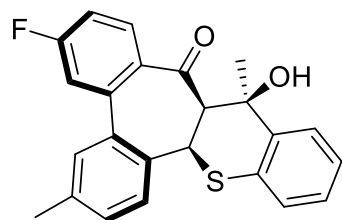


**3n**,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

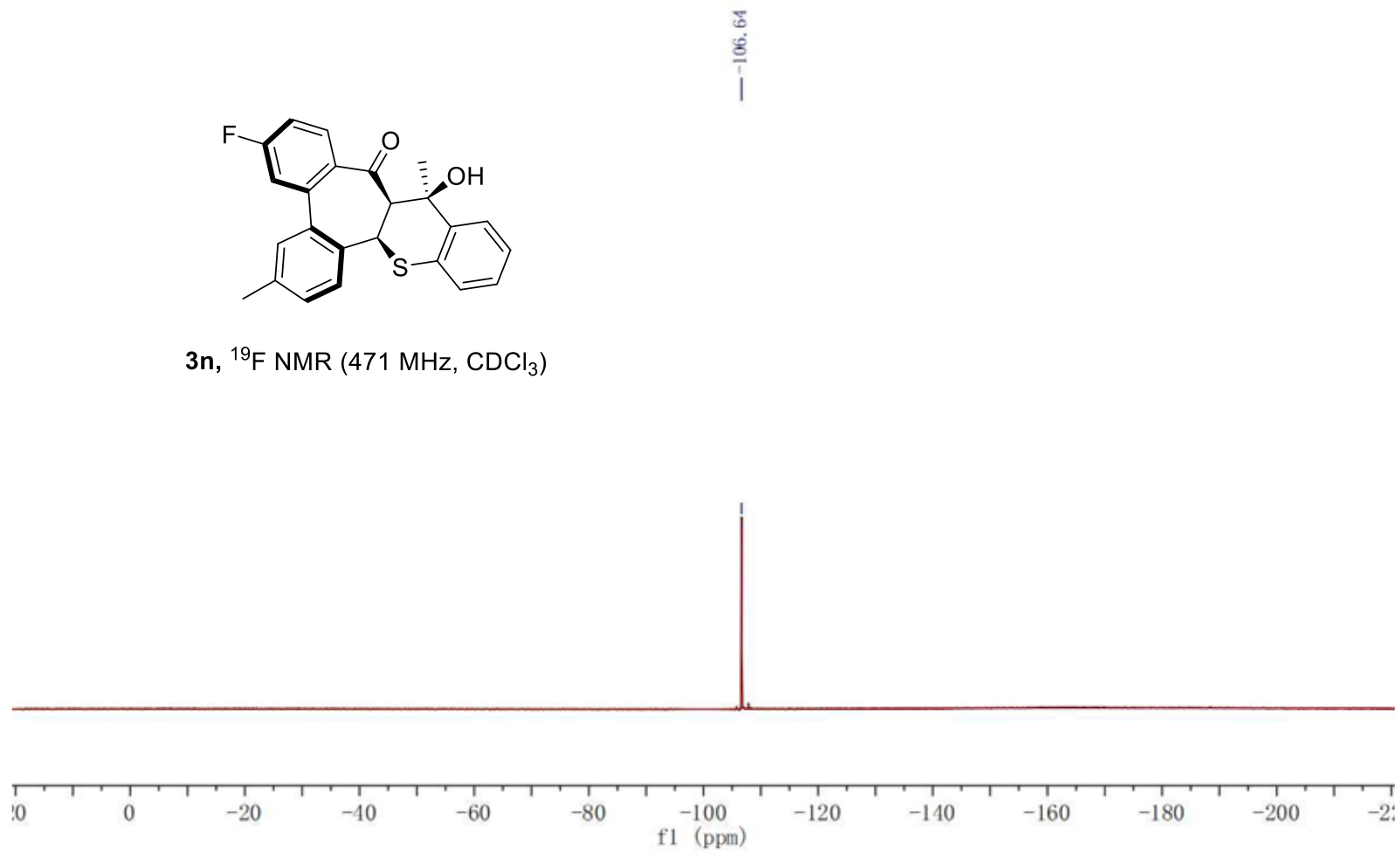


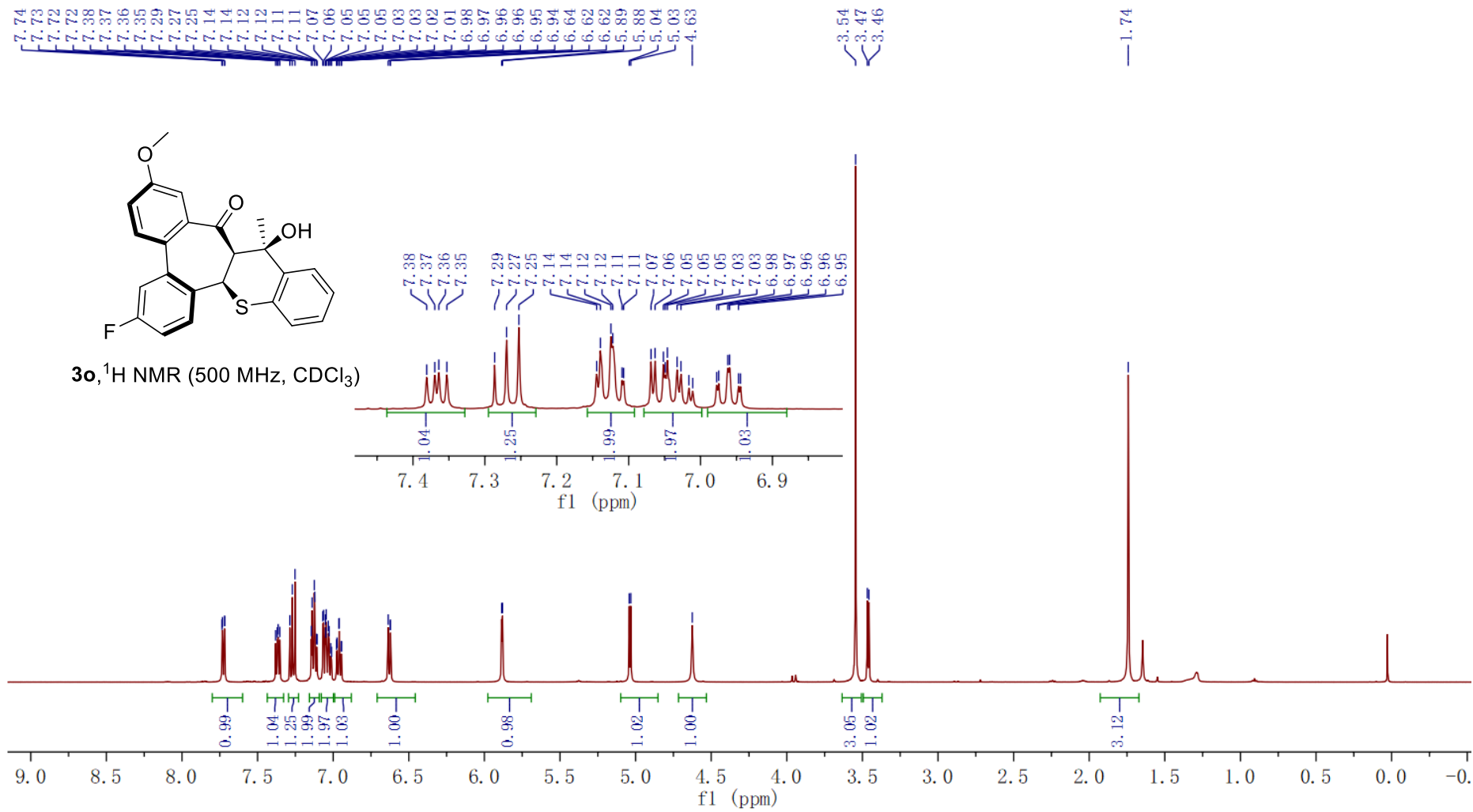


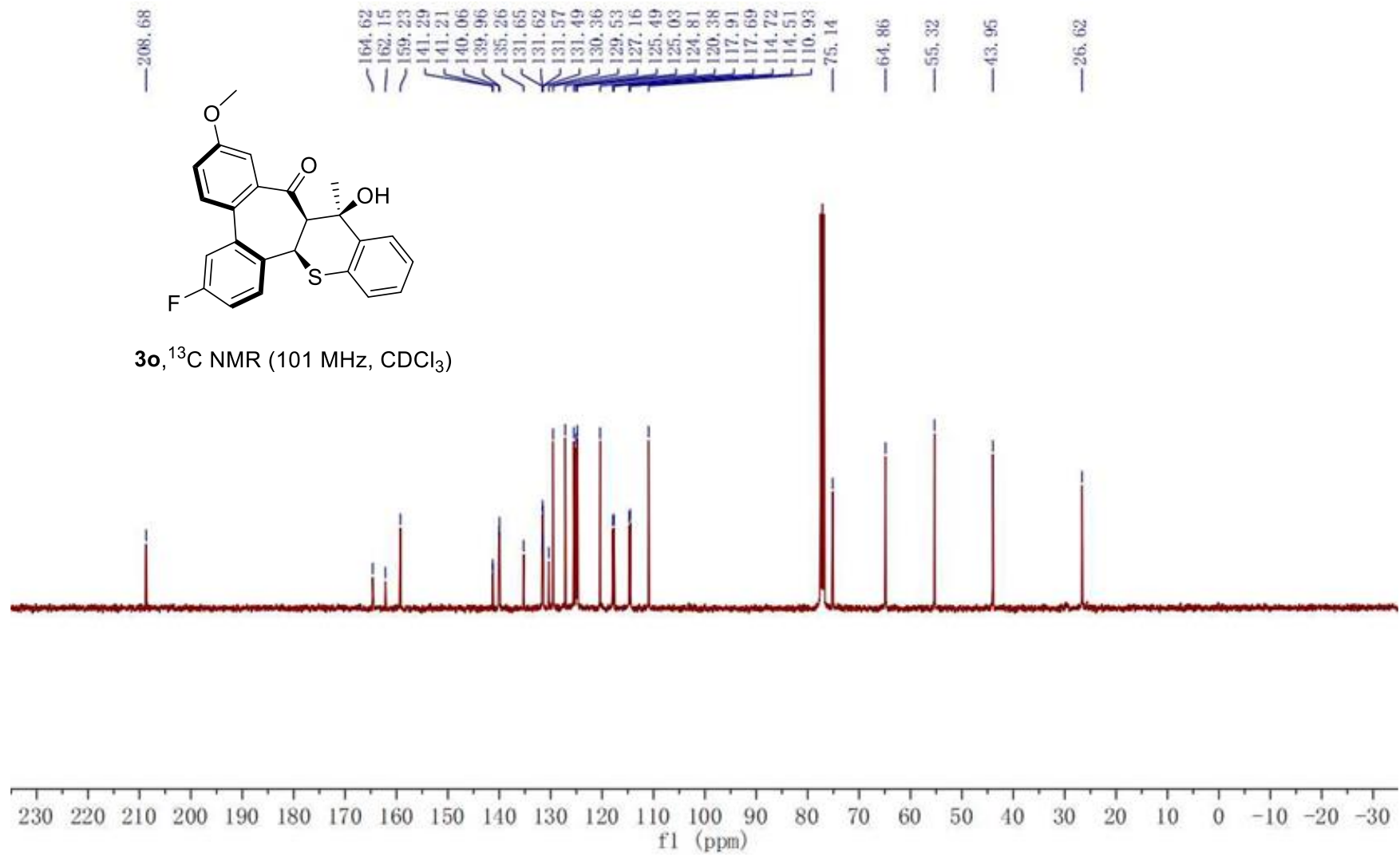


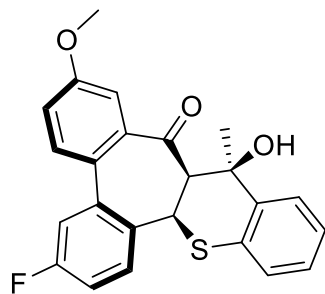


**3n**,  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )

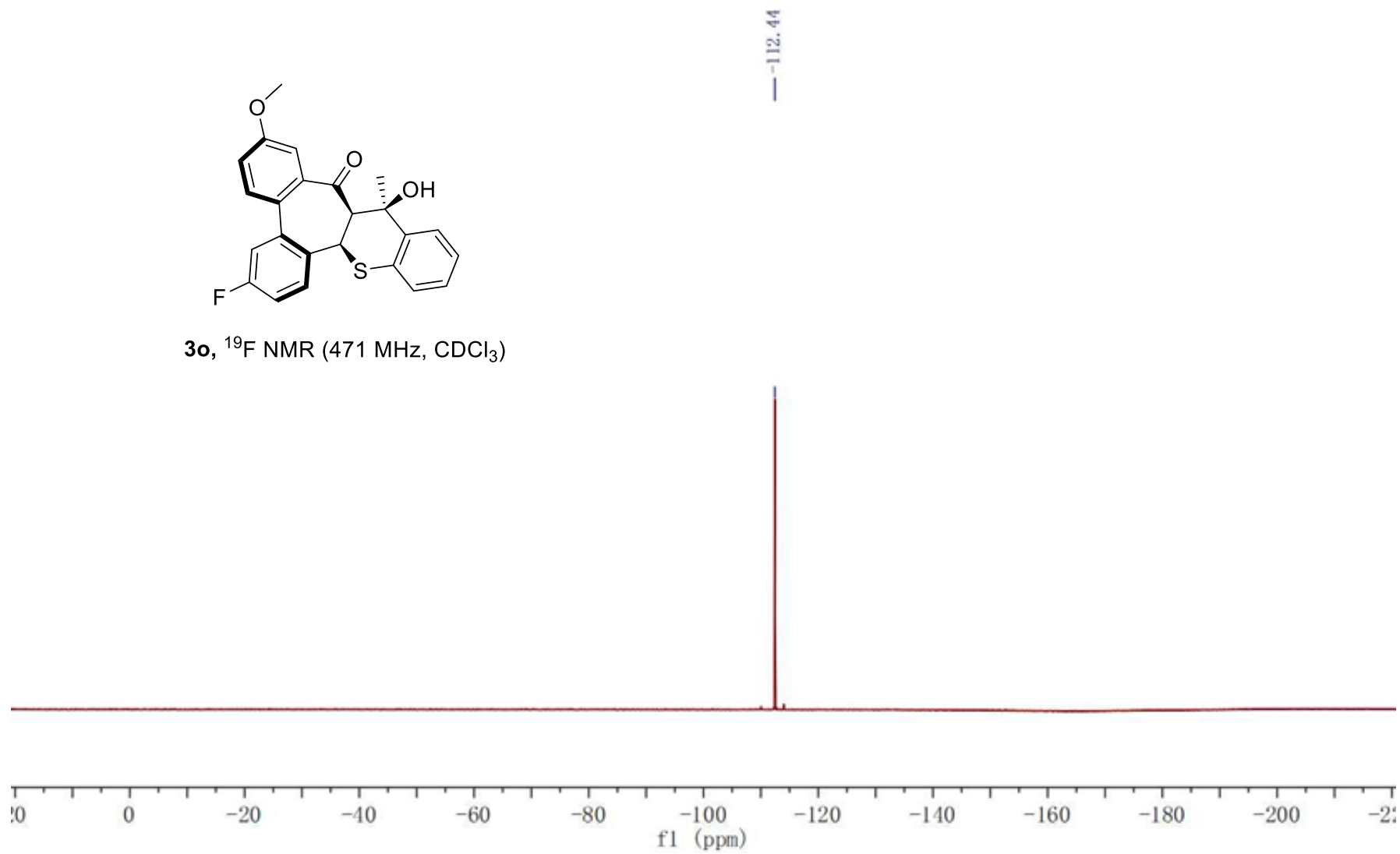








**3o**,  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )



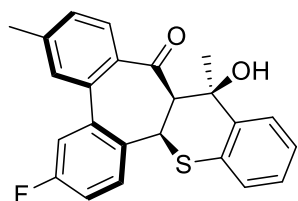
7.69  
7.67  
7.37  
7.36  
7.34  
7.26  
7.17  
7.14  
7.08  
7.07  
7.05  
7.04  
7.02  
6.93  
6.92  
6.90  
6.83  
6.82  
6.57  
6.55  
6.41  
6.39

5.03  
4.86

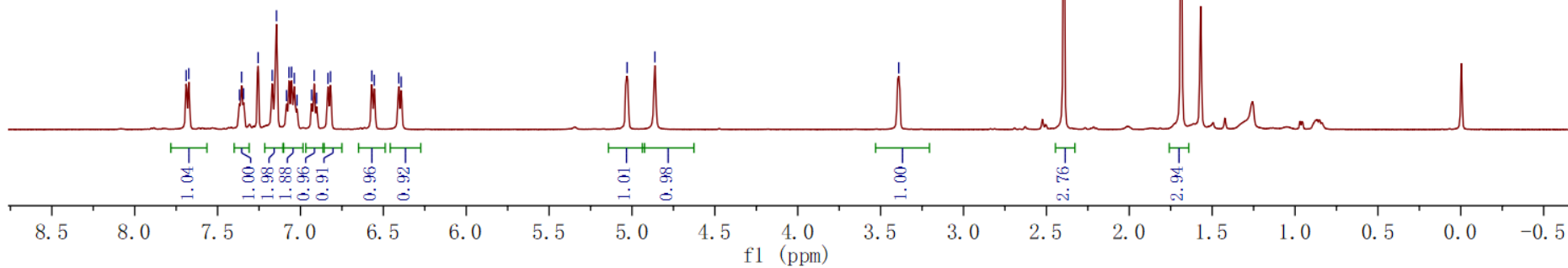
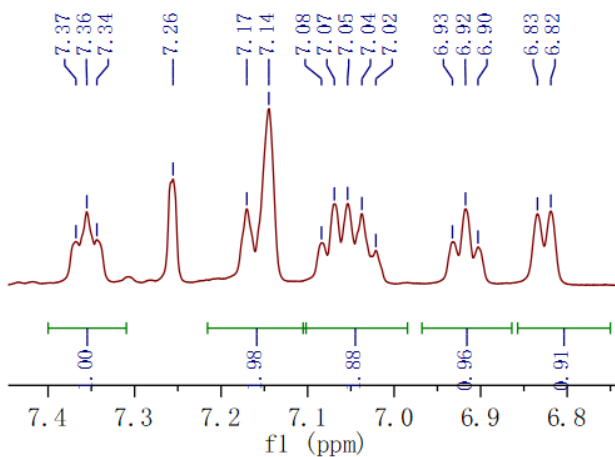
3.39

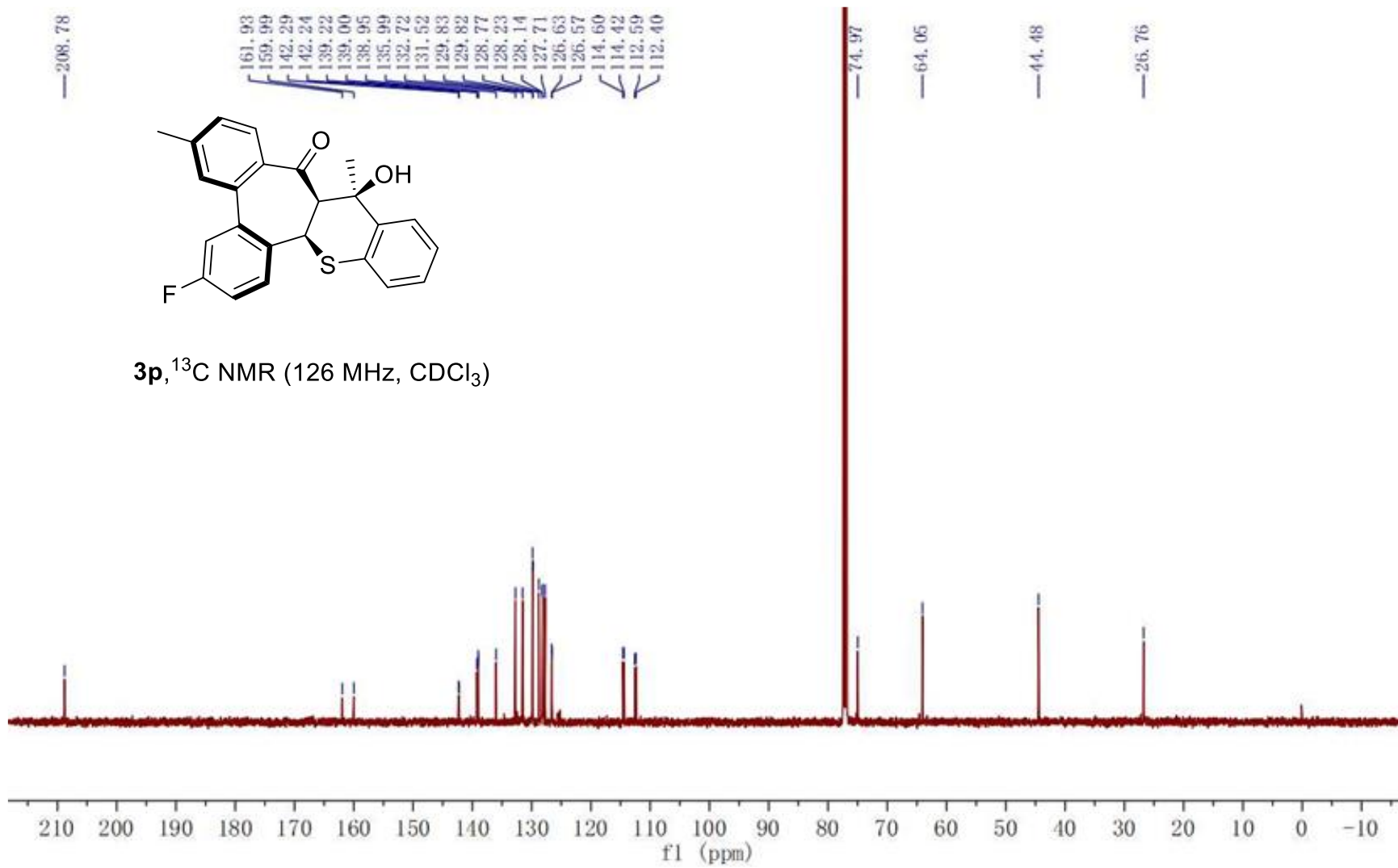
2.39

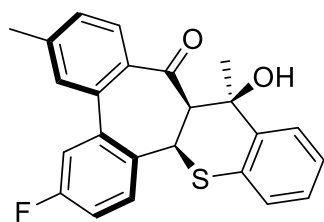
1.69



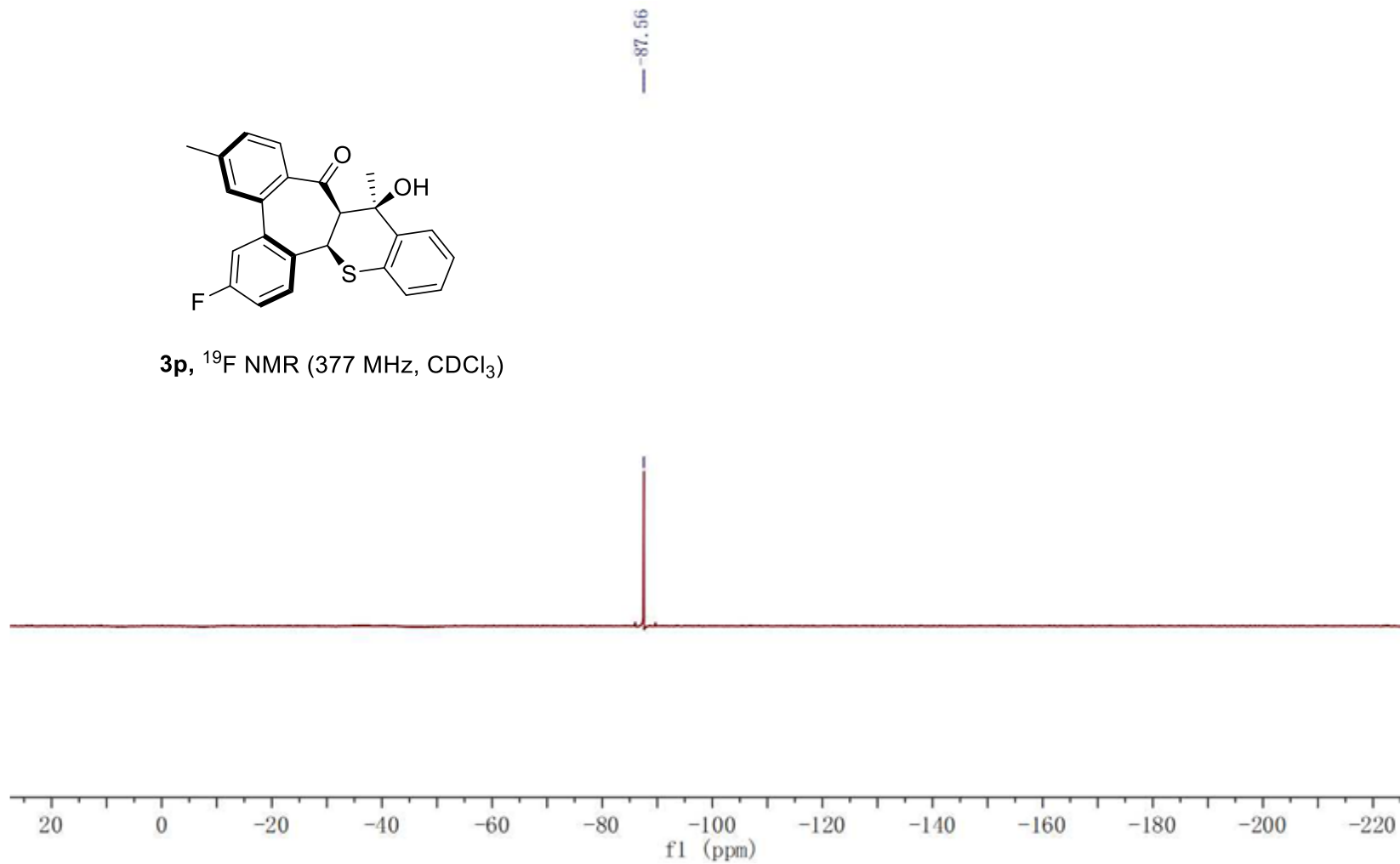
3p,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



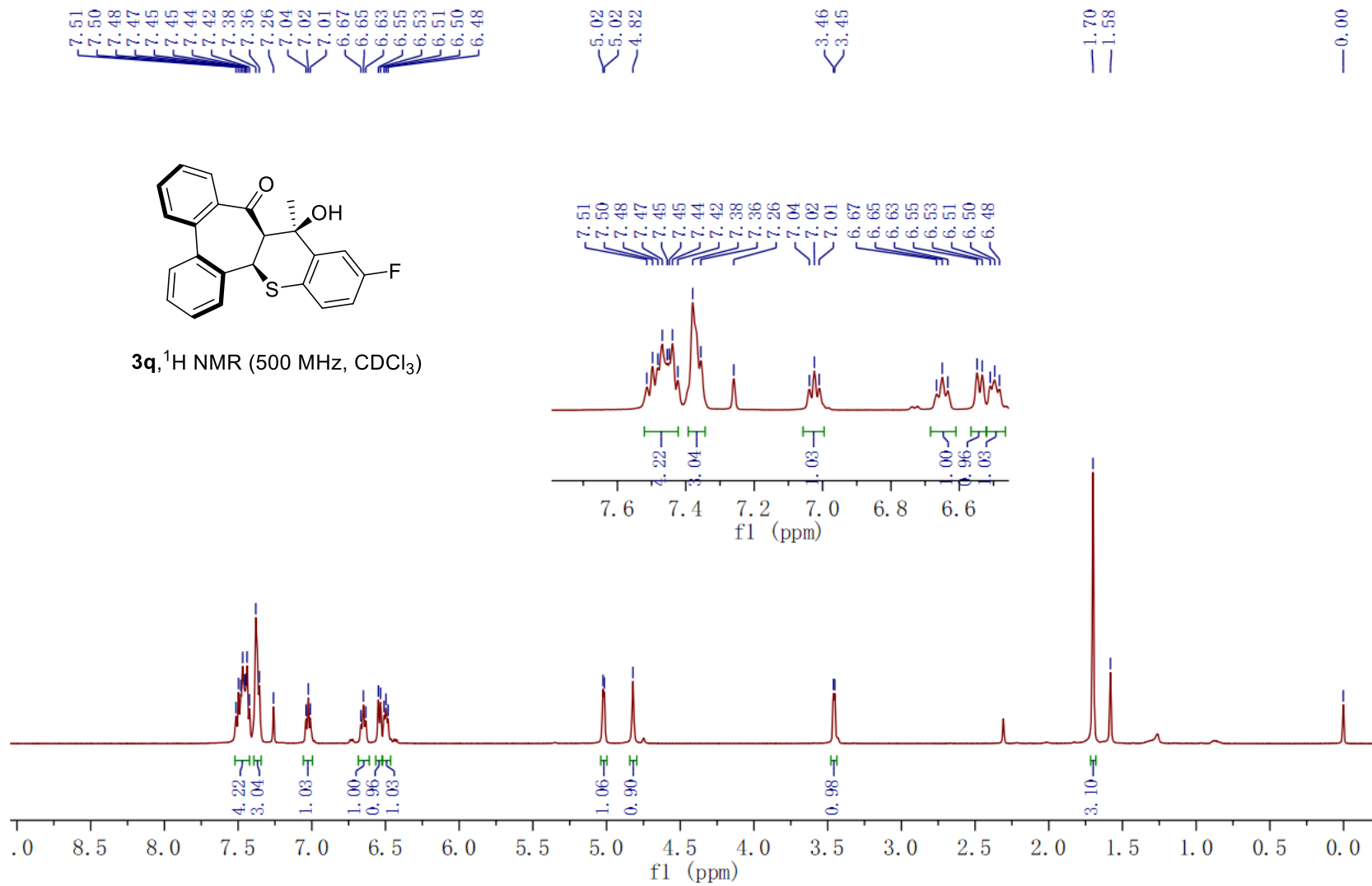


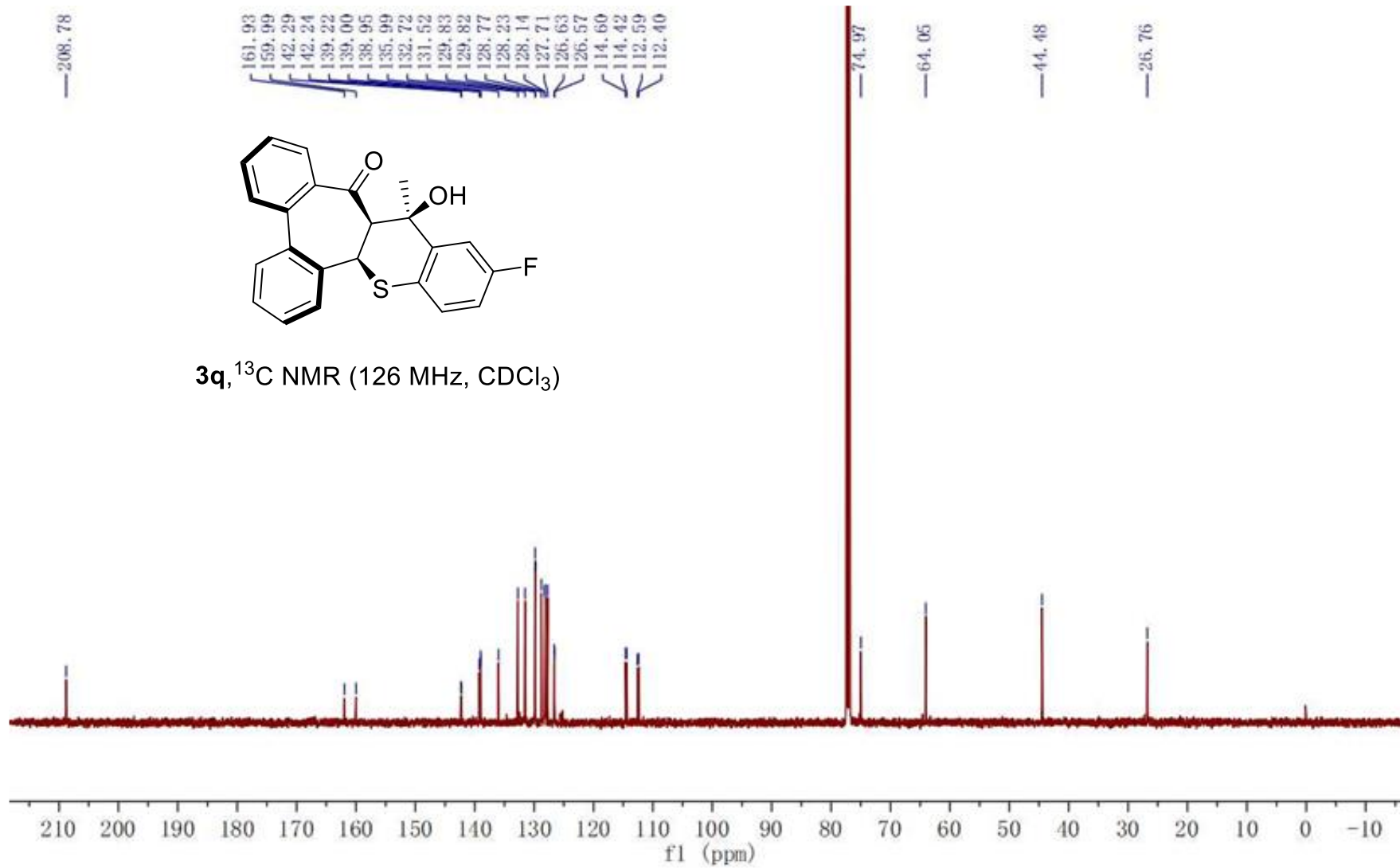


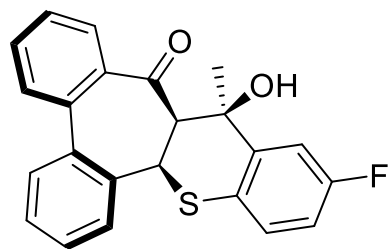
**3p**,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



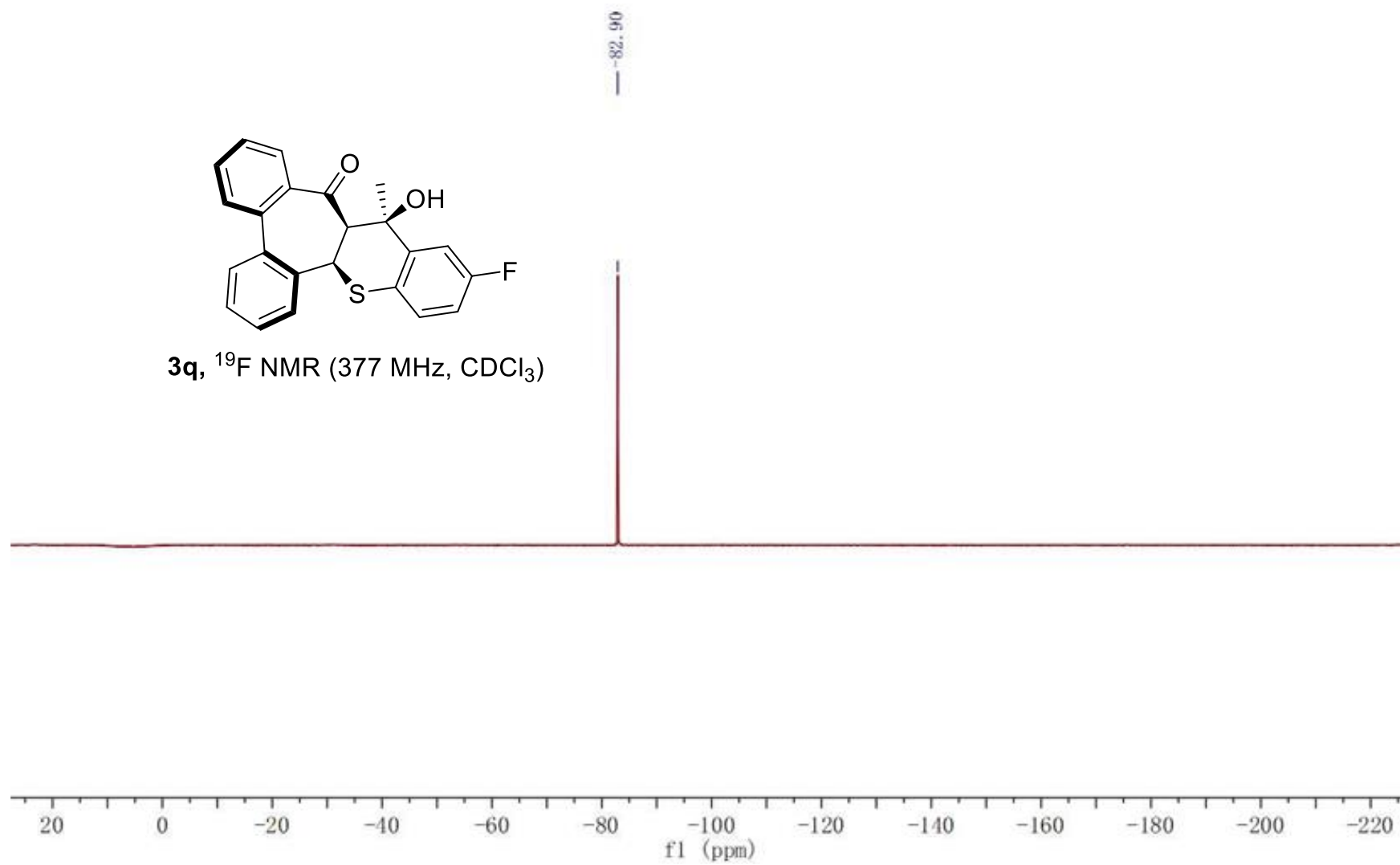








**3q**,  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

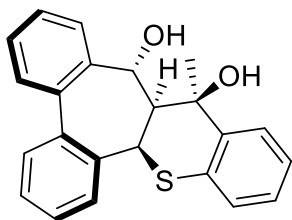


7.70  
7.69  
7.38  
7.37  
7.35  
7.30  
7.30  
7.29  
7.28  
7.25  
7.23  
7.14  
7.12  
7.11  
7.05  
7.03  
7.02  
6.79  
6.77  
6.76  
6.72  
6.70  
6.69  
6.47  
6.45  
6.30  
6.29  
5.70

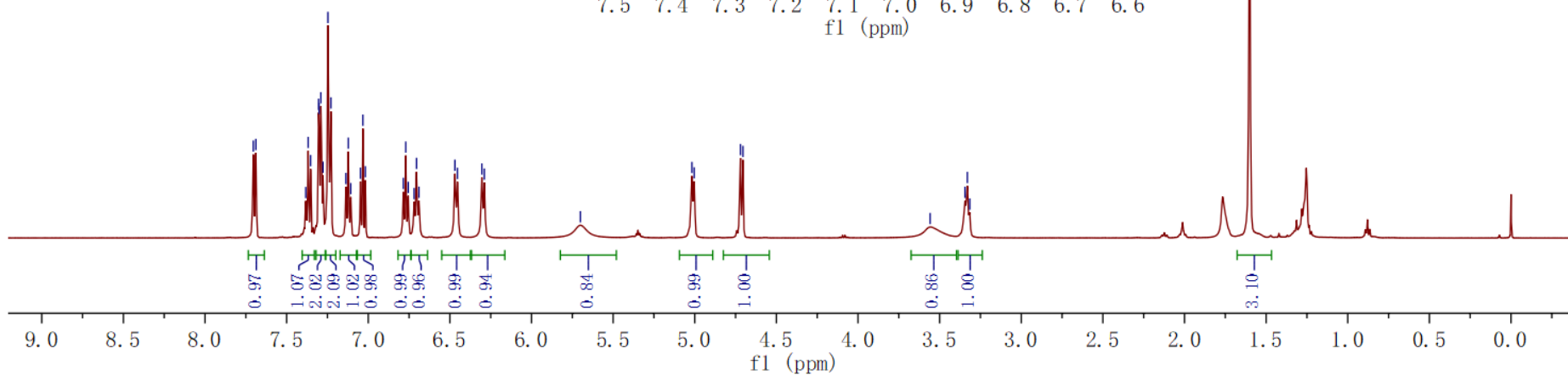
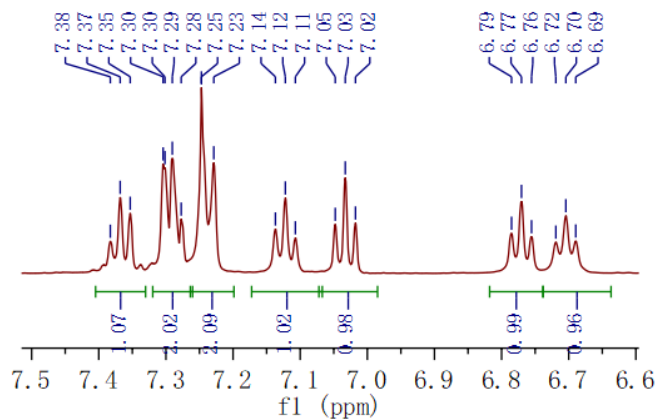
5.02  
5.00  
4.72  
4.70

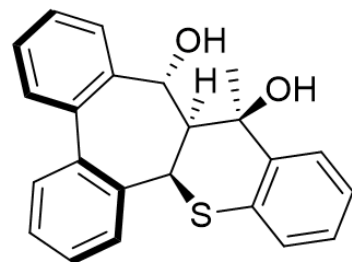
3.56  
3.34  
3.33  
3.32

1.60

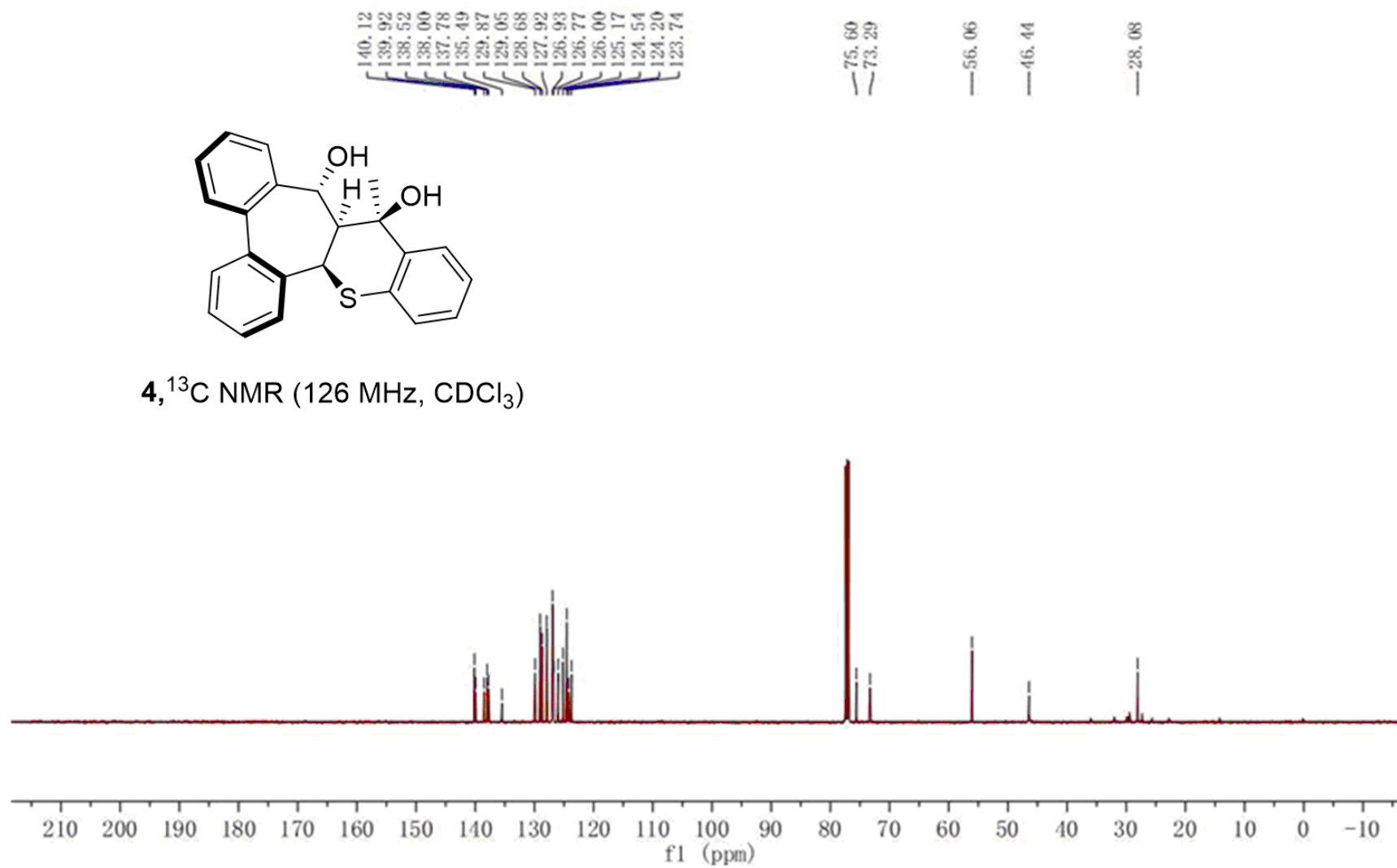


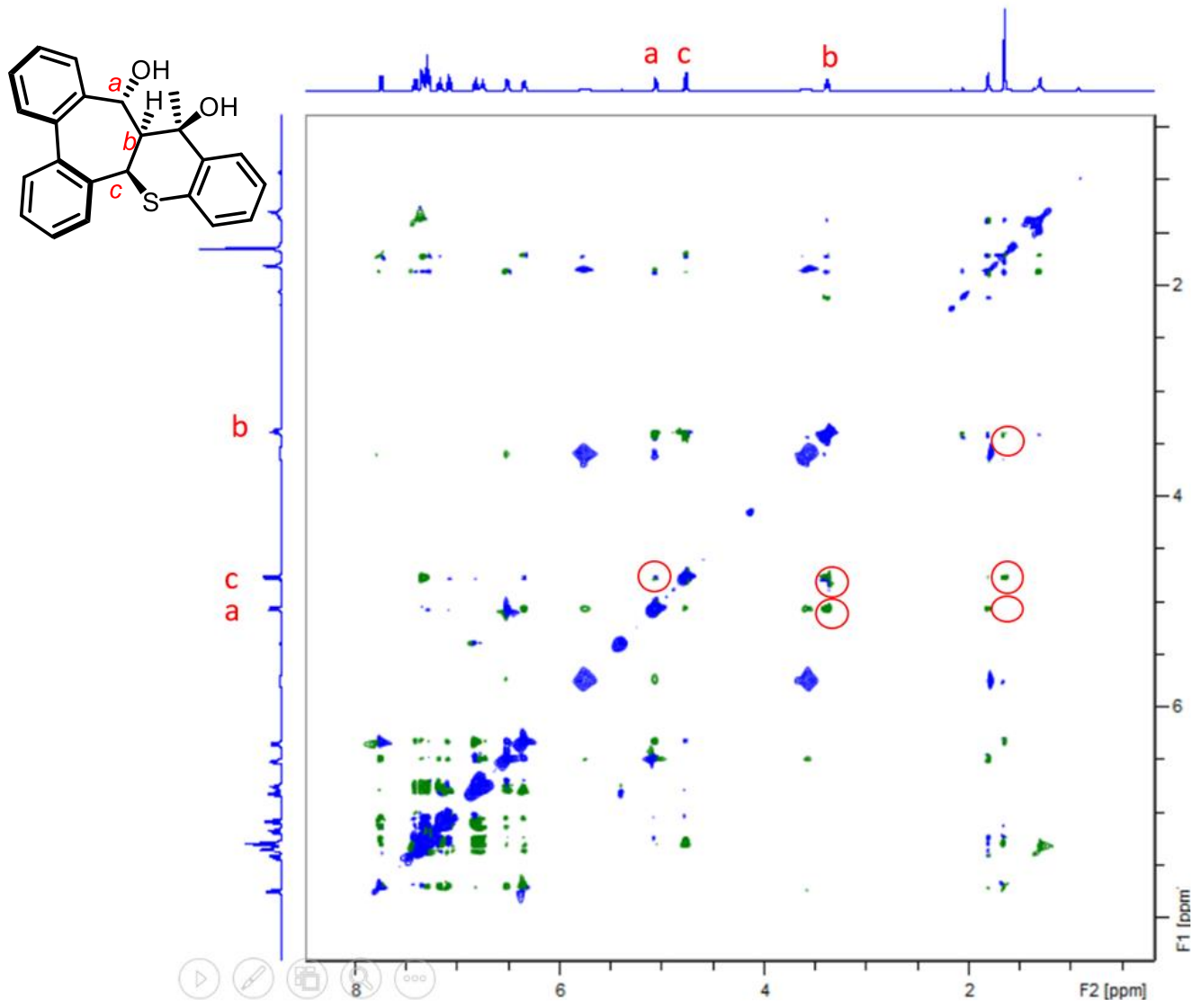
4, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)





**4**,  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )





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