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Organocatalytic inverse-electron-demand Diels−Alder reaction between 5-alkenyl thiazolones and β,γ-unsaturated carbonyl compounds

Kai-Xuan Yang, Dong-Sheng Ji, Yucheng Gu* and Peng-Fei Xu*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

Supporting Information

1 General Information

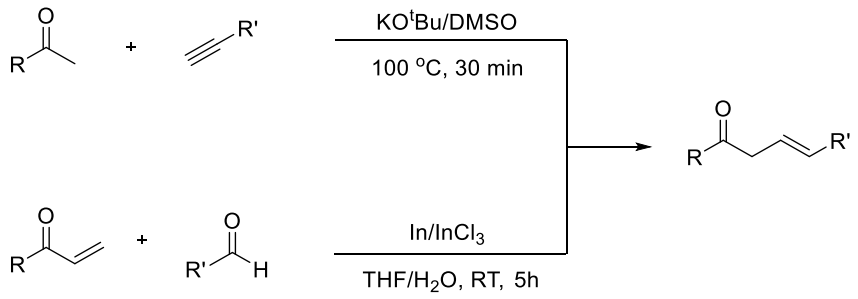
Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C) or a 600 spectrometer (600 MHz ^{1}H, 150 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature, ^{1}H and ^{13}CNMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet , br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on mass instrument (ESI). Enantiomeric excess values were determined by HPLC with Chirapak column on Agilent 1260 series with *i*-PrOH, *n*-hexane, NEt_3 and DCM. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees. Concentration (c) is in 10 g/mL.

2 Procedure of Experiments

2.1 General Procedure for the Synthesis of Substrares.

2.1.1 General procedure for the synthesis of *ß,γ*-Unsaturated Carbonyl Compounds

Method A

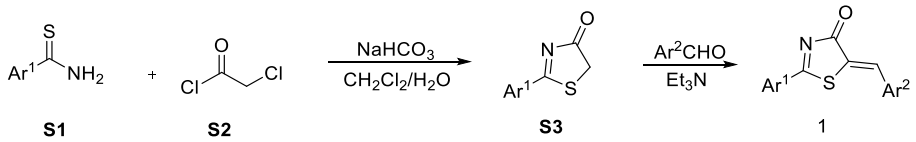


Method A:[1] A mixture of the corresponding methyl ketone (5.0 mmol, 1 equiv.), alkyne (5.0 mmol, 1 equiv.) and KO*t*Bu (561 mg, 5.0 mmol, 1 equiv.) in DMSO (12 mL) was heated to 100 °C and stirred for 30 min. The reaction mixture was cooled to room temperature and was diluted with H_2O (12 mL), neutralized with a saturated aqueous solution of NH_4Cl, and extracted with Et_2O (12 mL × 4). The organic extract was washed with H_2O (6 mL × 3) and dried with $MgSO_4$. After filtration

the solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (eluent hexane/ethyl acetate 97/3).

Method B: [2]A mixture of the corresponding aldehyde (5.0 mmol, 1 equiv.), In powder (1.15 g, 10 mmol, 2 equiv.), $InCl_3$ (553 mg, 2.5 mmol, 0.5 equiv.) and the corresponding vinyl ketone (15 mmol, 3 equiv.) in a mixture of THF and H_2O (1: 1, 30 mL) was stirred at room temperature for 8 h. After the addition of 1 M HCl (15 mL), the reaction mixture was stirred for 30 min and extracted with ethyl acetate (50 mL × 4). The combined organic phases were washed with brine (100 mL) and dried with $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (eluent hexane/ethyl acetate 97/3).

2.1.2 General procedure for the synthesis of 5-alkenyl thiazolone 1



[3]The solution of $NaHCO_3$ (20 mmol in 20 mL water) was added to a CH_2Cl_2 (40 mL) solution of thiobenzamide S1 (10 mmol). After cooling to 0 °C with ice-water bath, chloroacetyl chloride (S2 10 mmol) was added drop-wise to the stirred solution. Then reaction mixture was then stirred overnight at room temperature. The organic phase of the reaction mixture was separated, aqueous phase was extracted with CH_2Cl_2 (50 mL x 2). The combined organic phase was washed with H_2O (40 mL x 2), dried with anhydrous Na_2SO_4, and evaporated to dryness. The solid residue was washed with EtOH and filtered to give S3 (yiled 70%). Compound S3 (1 mmol), benzaldehyde (1.1 mmol), and Et_3N (2 mmol) were dissolved in 20 mL of MeOH, and heated to reflux at 65℃ for 3h, during which some precipitate appear gradually. After cooling to room temperature, the precipitate was filtered, and washed with another 20 mL of cold MeOH. The 5-alkenyl thiazolone 1 was obtained as a solid.

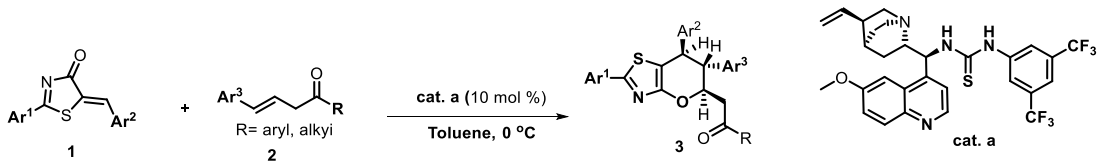
References

[1]B. A. Trofimov, E. Y. Schmidt, N. V. Zorina, E. V. Ivanova, I. A. Ushakov, *J. Org. Chem*. **2012**, *77*, 6880– 6886.

[2] Chen. Y, Wang. Y, Huang. H. *Org. Lett*. **2020**, *22*, 7135−7140. S. Kang, T. S. Jang, G. Keum, S. B. Kang, S. Y. Han, Y. Kim, *Org. Lett*. **2000**, *2*, 3615–3617.

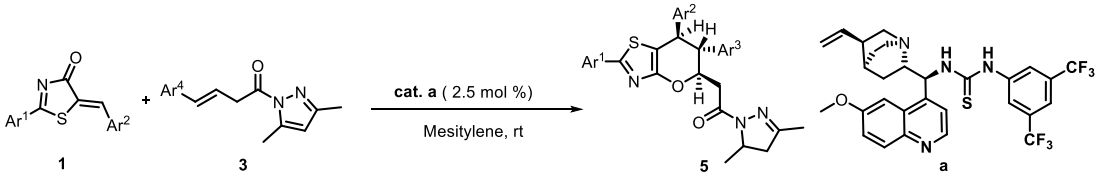
[3] Lin. Li, Yang. Yuhong, Wang. Mei, Lai. Luhao, Guoa. Yarong, Wang. Rui. *Chem. Commun*., **2015**, *51*, 8134--8137

2.2 General Procedure of the oxa-Diels-Alder Reaction.



1 2 3

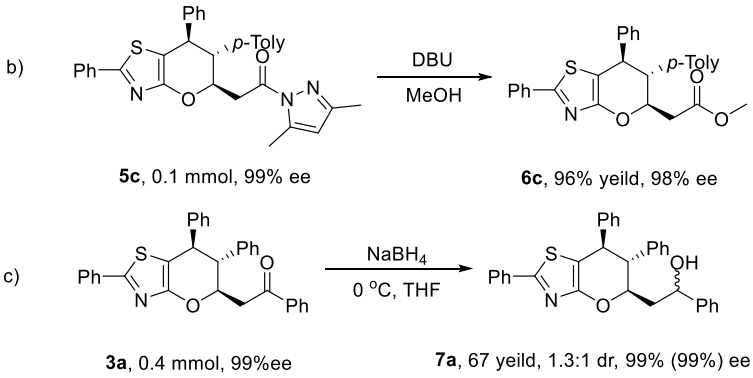
To a test tube (flame dried) with a stirrer were successively added 5-alkenyl thiazolone **1** (0.1 mmol, 26.5 mg), *β,γ*-unsaturated carbonyl compounds **2** (0.15 mmol, 33.3 mg), **catalyst a.**(0.01 mmol, 6.3 mg) and dried toluene (precooled to 0 ℃) (0.5 mL) at 0 ℃. When TLC analysis showed that **1** was completely consumed, the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (Petroleumether/EtOAc/DCM=10:1:2) to give the corresponding compound **3a**. Chiral **3b**-**4l** were synthesized using the same method.



1 3 5 a

To a test tube (flame dried) with a stirrer were successively added 5-alkenyl thiazolone **1** (0.1 mmol, 26.5 mg), *β,γ*-unsaturated carbonyl compounds (0.15 mmol, 36.0 mg), **catalyst a.** (0.0025 mmol, 1.5 mg) and dried mesitylene (0.5 mL) at room temperature. When TLC analysis showed that **1** was completely consumed, the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (Petroleumether/EtOAc=10:1 to 5:1) to give a pair of corresponding enantiomers, **5a** was separated by cyclic preparative HPLC. Chiral **5b-5j** were synthesized using the same method.

2.3 Procedure for the Derivatization.



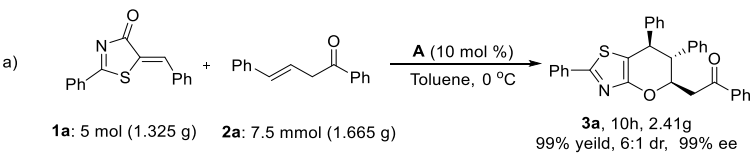
2.3.1 Synthesis of ester 6c

Compound **5c** (52.0 mg, 0.1 mmol) and DBU (3.5 mg, 0.024 mmol) in 1 mL MeOH were stirred for 3 hours at room temperature. After removal of the solvent under reduced press ure, the reaction mixture was purified by silica gel column chromatography (hexane/EtOAc = 8/1) to give product **6c** (96% yield, 43.7 mg, 98% ee).

2.3.2 Synthesis of alcohol 7a

Compound **3a** (195.0 mg, 0.4 mmol, 1.0 equiv.) in THF (3.08 mL) were cooled to 0 °C, then $NaBH_4$ (22.6 mg, 0.6 mmol, 1.5 equiv.) was added. The reaction mixture was warstirred for additional 0.5 hours. After that, the reaction was quenched by 1 N HCl (0.5 mL and extracted with CH_2Cl_2 (15 mL×3). The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to give product **7a** (67% yield, 131.2 mg, 99% ee).

2.4 The Procedure of the Gram-scale Asymmetric Synthesis of 3a



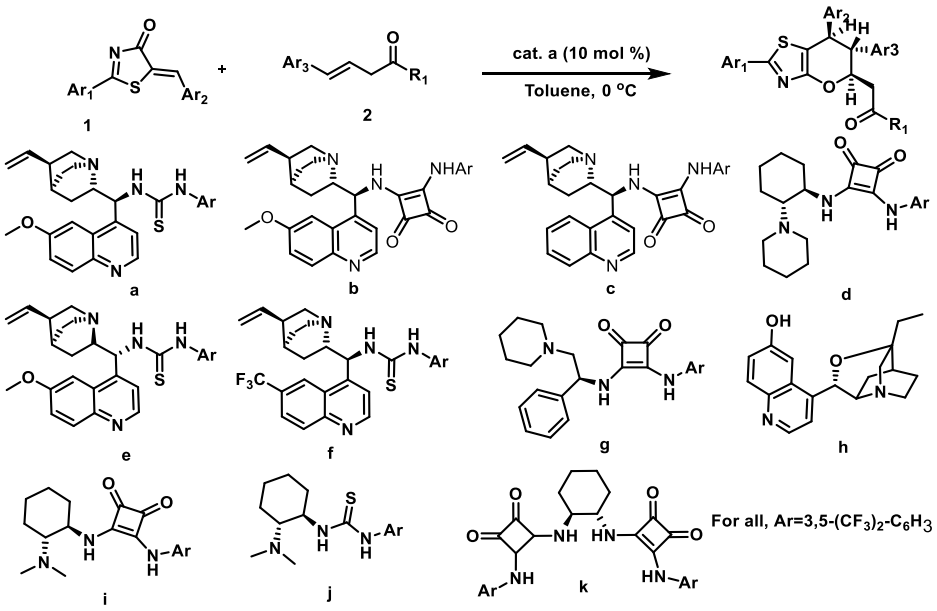
In a 25 mL round-bottomed flame dried flask, **1a** (5 mmol, 1.325g), *β,γ*-unsaturated ketones **2a** (7.5 mmol, 1.665g) and **cat. A** (0.1 mmol, 0.12g) were successively added, 25 mL toluene (precooled to 0 ℃) was added by syringe, and the mixture was stirred for 10 hours at

0 ℃. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (Petroleum ether/EtOAc/DCM=10:1:2) to give the corresponding compound **3a** (2.41g, 99% yield, 6:1 dr, 99% ee).

3 Reaction conditions optimization of *β,γ*-unsaturated amides

3.1 Screening data of *β,γ*-unsaturated ketone

Table S1. Catalyst screening of *β,γ*-unsaturated ketone



Entry[a]	Catalyst	Dr (%)[b]	Yield (%)[c]	ee (%)[d]	Time (h)
1	a	6:1	95	89	6
2	b	4:1	80	96	6
3	c	6:1	77	94	8
4	d	5:1	62	89	12
5	e	5:1	62	-89	12
6	f	5:1	58	90	8
7	g	4:1	53	78	8
8	h	2:1	62	78	12
9	i	3:1	32	64	12
10	j	3:1	93	-90	8
11	k	3:1	73	64	8

Conditions: [a]Reactions performed with 0.1 mmol **1a**, 0.1 mmol **2a**, catalyst (10% mmol) in solvent (1 mL) at rt. [b]Determined by crude ^{1}H NMR analysis. [c]Isolated yield given. [d]Determined by chiral-phase HPLC analysis.

Table S2. Solvent screening of *β,γ*-unsaturated ketone

Entry[a]	Solvent	Dr（%）[b]	Yield (%)[c]	ee (%)[d]	Time (h)
12	DCE	4:1	93	90	5
13	ACN	5:1	96	89	8
14	$CHCl_3$	3:1	87	91	12
15	THF	4:1	93	90	8
16	1,4-dioxane	3:1	85	94	6
17	Xylene	4:1	98	90	8
18	Mesitylene	3:1	83	89	8

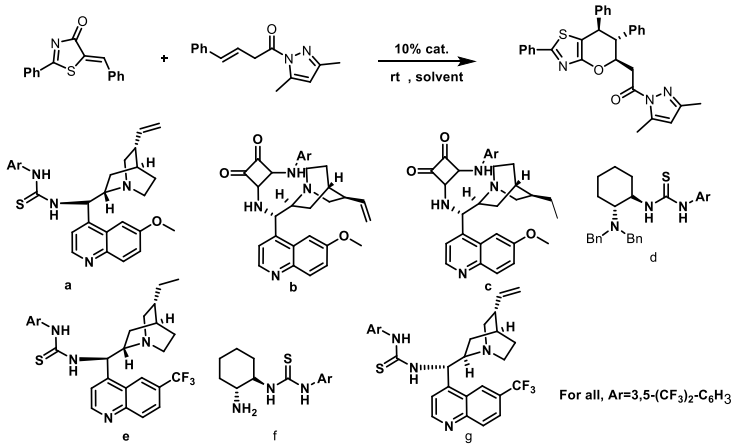
Conditions: [a]Reactions performed with 0.1 mmol **1a**, 0.1 mmol **2a**, catalyst (10% mmol) in solvent (1 mL) at. [b]Determined by crude ^{1}H NMR analysis. [c] Isolated yield given. [d]Determined by chiral-phase HPLC analysis.

Table S3. Optimization of other reaction conditions for β,γ-unsaturated ketone

Entry[a]	1a （mmol）	2a （mmol）	Solvent	Cat (mol%)	Dr(%)[b]	Yield (%)[c]	ee (%)[d]	Time (h)
19	0.1	0.1	1	5	4:1	89	87	10
20	0.1	0.1	1	15	5:1	94	80	4
21	0.1	0.125	1	10	6:1	93	90	6
22	0.1	0.15	1	10	6:1	98	90	6
23	0.125	0.1	1	10	5:1	96	90	6
24	0.15	0.1	1	10	4:1	98	92	6
25	0.1	0.15	0.5	10	6:1	97	92	5
26	0.1	0.15	2	10	5:1	94	87	7
27[e]	0.1	0.15	2	10	5:1	95	83	8
28[f]	**0.1**	**0.15**	**0.5**	**10**	**6:1**	**98**	**99**	**24**
29[h]	0.1	0.15	0.5	10	6:1	94	99	36

Conditions: [a]Reactions performed with catalyst (2.5% mmol) in solvent at rt. [b]Determined by crude ^{1}H NMR analysis. [c]Isolated yield given. [d]Determined by chiral-phase HPLC analysis. [e]4A MS molecular sieve was added. [f]Reactions performed at 0 °C.[h]Reaction performed at -10 ℃

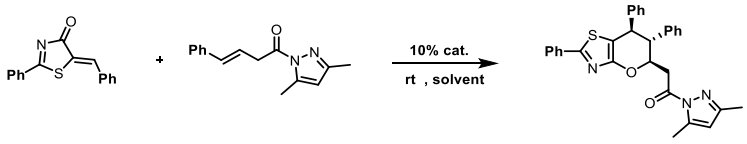
Table S4. Catalyst screening of *β,γ*-unsaturated amides



Entry[a]	Catalyst	Dr(%)[b]	Yield (%)[c]	Ee (%)[d]	Time (h)
1	a	6:1	95	>99	3
2	b	2.5:1	36	87	48
3	c	2.5:1	15	>99	48
4	d	3:1	82	>99	12
5	e	5:1	95	>99	6
6	f	5.2:1	62	83	7
7	g	3:1	73	-35	7

Conditions: [a]Reactions performed with 0.1 mmol **1a**, 0.1 mmol **2a**, catalyst (10% mmol) in solvent (1 mL) at rt. [b]Determined by crude ^{1}H NMR analysis. [c] Isolated yield given. [d]Determined by chiral-phase HPLC analysis.

Table S5. Solvent screening of *β,γ*-unsaturated amides



Entry[a]	Solvent	Dr (%)[b]	Yield (%)[c]	Ee (%)[d]	Time (h)
8	DCM	4:1	94	>99	12
9	DCE	4:1	93	>99	13
10	ACN	4:1	95	>99	8
11	$CHCl_3$	3:1	87	>99	12
12	THF	5:1	85	>99	12
13	1,4-dioxane	7:1	94	>99	4
14	Diethyl ether	2:1	45	>99	24
15	CH_3OH	1:1	35	-	24
16	EA	2:1	89	-	12
17	1,3-Dioxolane	5:1	95	>99	3
18	2-CH_3-THF	4:1	95	>99	10
19	Xylene	6:1	93	>99	3
20	Mesitylene	7:1	96	>99	3
21	PhCl	6:1	87	>99	5
22	PhBr	7:1	83	>99	5
23	$PhCF_3$	5:1	92	>99	5

Conditions: [a]Reactions performed with 0.1 mmol **1a**, 0.1 mmol **2a**, catalyst (10% mmol) in solvent (1 mL) at rt. [b]Determined by crude ^{1}H NMR analysis. [c]Isolated yield given. [d]Determined by chiral-phase HPLC analysis

Table S6. Catalyst dosage screening of β,γ-unsaturated amides

Entry[a]	Cat	Dr (%)[b]	Yield (%)[c]	Ee (%)[d]	Time (h)
24	20 mol%	7:1	99	>99	3
25	15 mol%	8:1	96	>99	3
26	10 mol%	7:1	97	>99	3
27	5 mol%	8:1	98	>99	9
28	2.5 mol%	8:1	92	>99	24
29	1mol%	7:1	76	>99	72

Conditions: *a*Reactions performed with 0.1 mmol **1a**, 0.1 mmol **2a**, catalyst (10% mmol) in solvent (1 mL) at rt. [b]Determined by crude ^{1}H NMR analysis. [c]Isolated yield given. [d]Determined by chiral-phase HPLC analysis.

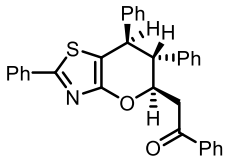
Table S7. Screening of substrate ratio and solvent amount of β,γ-unsaturated amides

Entry[a]	1a (mmol)	2a (mmol)	Dr (%)[b]	Solvent (ml)	Yield (%)[c]	Ee (%)[d]	Time (h)
30	0.1	0.125	8:1	1	99	>99	18
31	0.1	0.15	8:1	1	96	>99	14
32	0.1	0.2	8:1	1	97	>99	9
33	0.125	0.1	7:1	1	98	>99	16
34	0.15	0.1	7:1	1	92	>99	14
35	0.1	0.15	7:1	0.25	91	>99	14
36	**0.1**	**0.15**	**8:1**	**0.5**	**96**	**>99**	**14**
37	0.1	0.15	7:1	2	95	>99	14
38[e]	0.1	0.15	7:1	0.5	94	>99	14
39[f]	0.1	0.15	7:1	0.5	96	>99	10

Conditions: [a]Reactions performed with catalyst (2.5% mmol) in solvent at rt. [b]Determined by crude ^{1}H NMR analysis. [c]Isolated yield given. [d]Determined by chiral-phase HPLC analysis. [e]4A MS molecular sieve was added. [f]Reactions performed at 0 ℃.

4. Characterization Data of Compounds

1-phenyl-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (3a)



White solid (PE/EtOAc/DCM = 10:1:1, 98% isolated yield, 6:1 dr, 47.8 mg);

m. p.: 148-151 ℃;

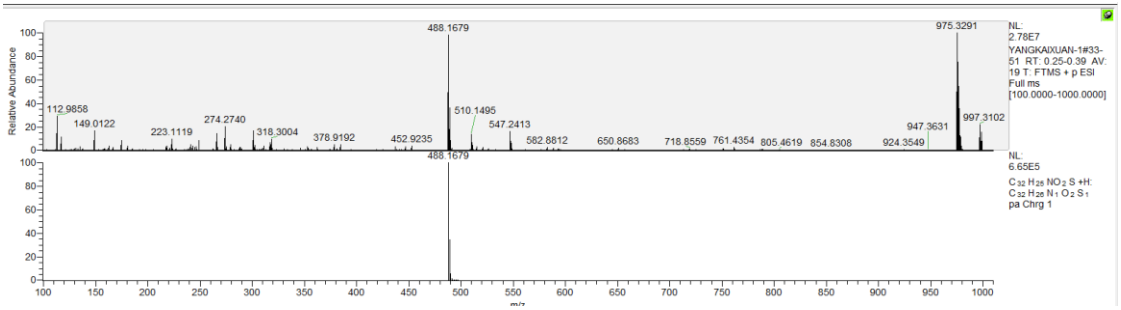
$[\alpha]^{22}_D$ = -14.0 (*c*=1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.36 (ddd, *J* = 11.2, 8.0, 6.0 Hz, 5H), 7.22 – 7.12 (m, 6H), 7.08 – 6.84 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.36 (d, *J* = 10.8 Hz, 1H), 3.45 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.20 (t, *J* = 10.8 Hz, 1H), 2.87 (dd, *J* = 16.8, 2.8 Hz, 1H);

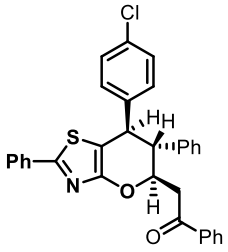
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.9, 159.8, 142.1, 138.7, 137.0, 133.4, 133.0, 129.9, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.4, 127.2, 125.6, 109.4, 77.5, 53.7, 47.7, 41.7.

HPLC (IH, *i*-PrOH/ *n*-hexane = 93/7), flow rate = 1.0 mL/min), t_R = 26.50 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{26}NO_2S]^+$: 488.1679, found: 488.1679.



2-((5R,6R,7R)-7-(4-chlorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3b)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yield, 7:1 dr, 48.6 mg);

m. p.: 66-68 ℃.

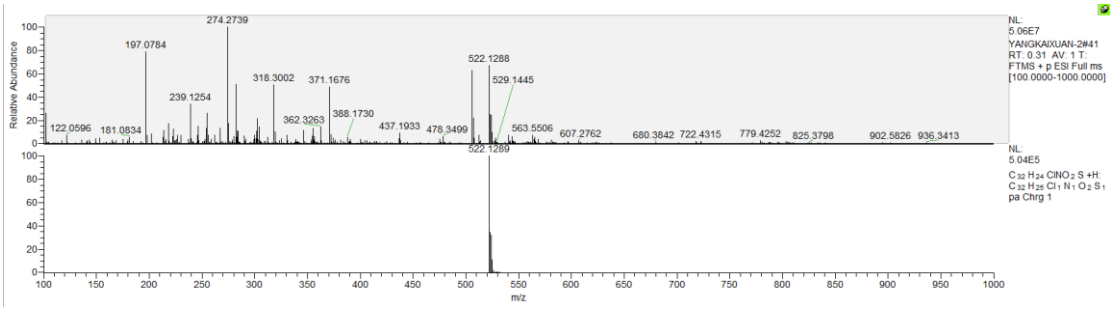
$[\alpha]^{22}_D$ = -8.0 (*c*=1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, *J* = 11.6, 6.8, 1.2 Hz, 4H), 7.55 – 7.47 (m, 1H), 7.38 (m, *J* = 6.4, 5.2 Hz, 5H), 7.28 – 7.08 (m, 5H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.91 – 6.81 (m, 2H), 5.36 (ddd, *J* = 10.8, 8.8, 2.4 Hz, 1H), 4.35 (d, *J* = 10.8 Hz, 1H), 3.44 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.15 (t, *J* = 10.8 Hz, 1H), 2.87 (dd, *J* = 17.2, 2.4 Hz, 1H);

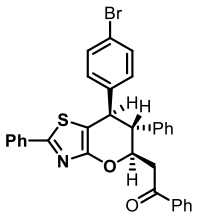
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.2, 157.0, 140.7, 138.4, 137.0, 133.4, 133.1, 133.0, 130.0, 129.3, 129.0, 128.8, 128.5, 128.4, 128.1, 127.6, 125.7, 108.7, 77.5, 53.8, 47.2, 41.7;

HPLC (IF, *i*-PrOH/ *n*-hexane = 85/15), flow rate = 1.0 mL/min), t_R = 46.509 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}ClNO_2S]^+$: 522.1289, found: 522.1288.



2-((5R,6R,7R)-7-(4-bromophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3c)



Brown solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yield, 7:1 dr, 52.6 mg);

m. p.: 68-70 ℃;

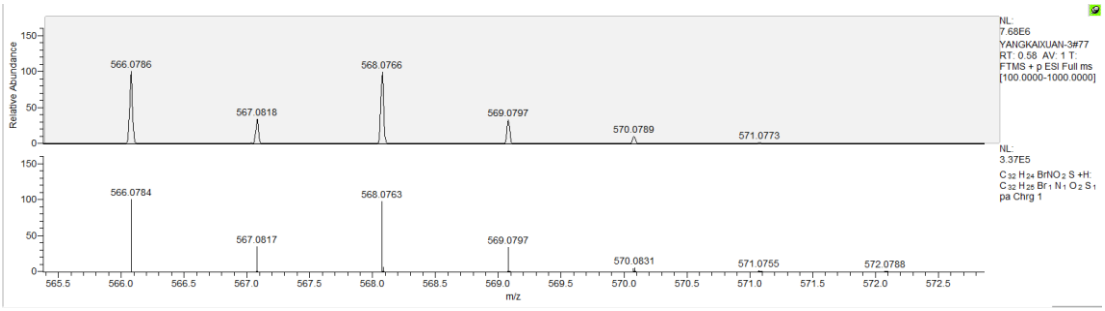
[α]$^{22}_{D}$ = -16.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 4H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.13 (m, 3H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.36 (ddd, *J* = 10.5, 8.4, 2.4 Hz, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 3.44 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.14 (t, *J* = 10.5 Hz, 1H), 2.87 (dd, *J* = 17.2, 2.4 Hz, 1H);

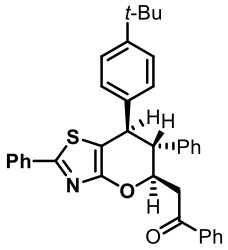
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 164.2, 159.9, 144.4, 138.1, 136.8, 133.3, 133.0, 130. 8, 130.4, 130.0, 129.8, 128.9, 128.7, 128.4, 128.0, 127.6, 126.7, 125.6, 122.3, 108.3, 77.4, 53.5, 47.3, 41.5;

HPLC (IH, *i*-PrOH/ *n*-hexane = 93/7), flow rate = 1.0 mL/min), t_R = 22.8 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}BrNO_2S]^+$: 566.0784, 568.0763, found: 566.0786, 568.0766.



2-((5R,6R,7R)-7-(4-(tert-butyl)phenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one （3d）



White solid (PE/EtOAc/DCM = 10:1:1, 89% isolated yield, 11:1 dr, 48.5 mg);

m. p.: 74-78 ℃;

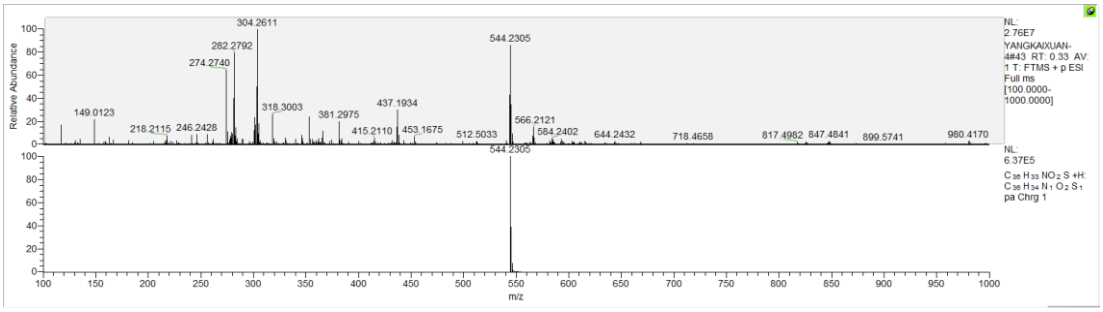
[α]$^{22}_{D}$ = -28.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 4H), 7.55 – 7.45 (m, 1H), 7.46 – 7.31 (m, 5H), 7.24 – 7.10 (m, 5H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.35 (ddd, *J* = 10.4, 8.0, 2.8 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 3.44 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.19 (t, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 17.2, 2.8 Hz, 1H), 1.25 (s, 9H);

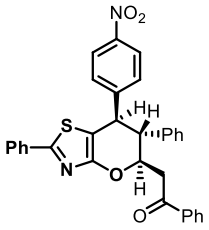
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 163.8, 159.7, 139.0, 139.0, 137.0, 133. 6, 133.0, 129.8, 128.8, 128.7, 128.5, 128.4, 128.1, 127.5, 127.4, 125.7, 125.1, 109.8, 77.6, 53.6, 47.1, 41.8, 34.4, 31.3;

HPLC (IH, *i*-PrOH/ *n*-hexane/ NEt_3/ DCM = 80/10/5/5), flow rate = 1.0 mL/min), t_R = 7.965 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{36}H_{34}NO_2S]^+$: 544.2305, found: 544.2305.



2-((5R,6R,7R)-7-(4-nitrophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d] thiazol-5-yl)-1-phenylethan-1-one (3e)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 97% isolated yield, 6:1 dr, 48.6 mg);

m. p.: 195-198 ℃.

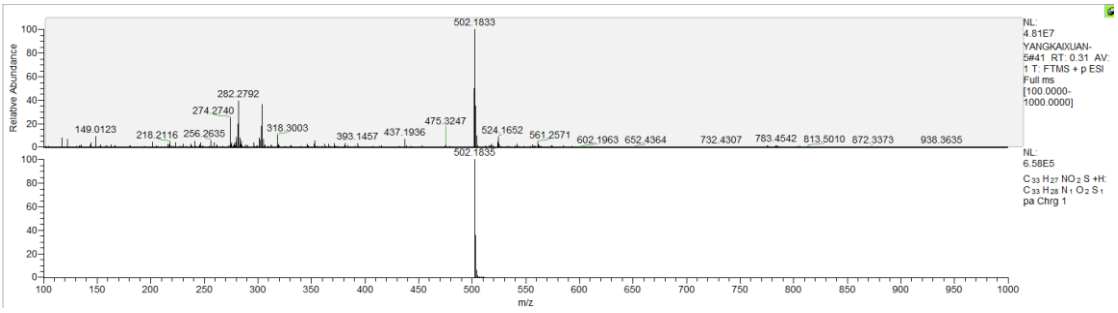
[α]$^{22}_{D}$ = -13.0 (*c* =1.0, CH_2Cl_2, 92% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.89 – 7.75 (m, 4H), 7.52 (t, J = 7.4 Hz, 1H), 7.46 – 7.30 (m, 5H), 7.26 – 7.14 (m, 3H), 7.04 (m, 4H), 5.39 (ddd, J = 10.8, 8.0, 2.8 Hz, 1H), 4.50 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 17.2, 8.4 Hz, 1H), 3.20 (t, J = 10.4 Hz, 1H), 2.90 (dd, J = 17.2, 2.8 Hz, 1H);

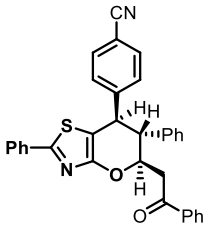
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 164.6, 160.2, 149.7, 147.1, 137.7, 136.8, 133.2, 133.1, 130.3, 129.2, 128.9, 128.8, 128.4, 128.2, 128.0, 127.9, 125.7, 123.6, 107.2, 77.4, 53.6, 47.6, 41.4.

HPLC (IC， *i*-PrOH/ *n*-hexane = 83/17), flow rate = 1.0 mL/min), t_R = 8.444 min (major)t_R = 12.404 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{25}N_2O_4S]^+$: 502.1835, found: 502.1833.



4-((5R,6R,7R)-5-(2-oxo-2-phenylethyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-7-yl)benzonitrile (3f)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 98% isolated yield, 9:1 dr, 50.3 mg);

m. p.: 204-206 ℃.

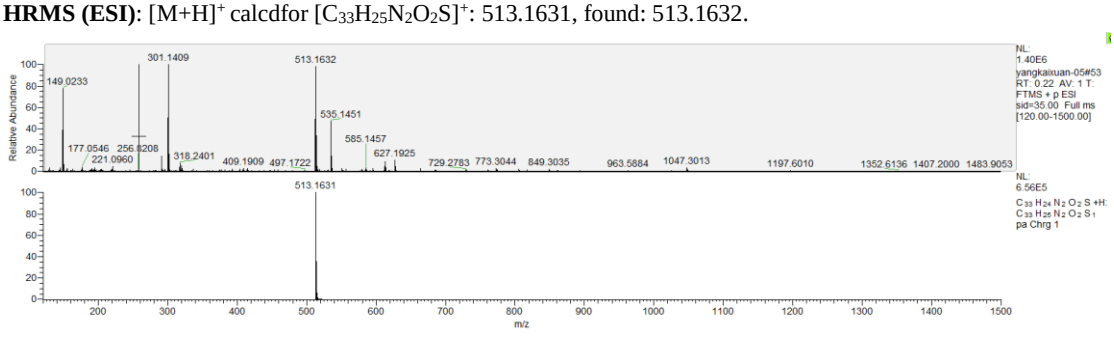
[α]$^{22}_{D}$ = -20.0 (*c* =1.0, CH_2Cl_2, 98% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H), 7.52 (m, 1H), 7.48 – 7.33 (m, 7H), 7.25 – 7.13 (m, 3H), 7.01 (m, 4H), 5.37 (ddd, J = 10.8, 8.0, 2.7 Hz, 1H), 4.48 – 4.41 (m, 1H), 3.43 (dd, J = 17.2, 8.0 Hz, 1H), 3.17 (t, J = 10.8 Hz, 1H), 2.88 (dd, J = 17.2, 2.8 Hz, 1H);

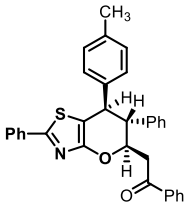
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 164.7, 160.3, 149.7, 147.2, 137.7, 136.8, 133.2, 133.2, 130.3, 129.2, 129.0, 128.9, 128.5, 128.1, 128.0, 125.8, 123.6, 107.2, 77.4, 53.8, 47.7, 41.4, 29.7.

HPLC ((IC， *i*-PrOH/ *n*-hexane = 83/17), flow rate = 1.0 mL/min), t_R = 35,414 min (major)t_R = 100.343 min (major)

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{25}N_2O_2S]^+$: 513.1631, found: 513.1632.



2-((5R,6R,7R)-2,6-diphenyl-7-(p-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3g)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 94% isolated yield, 11:1 dr, 45.6 mg);

m. p.: 148-170 ℃.

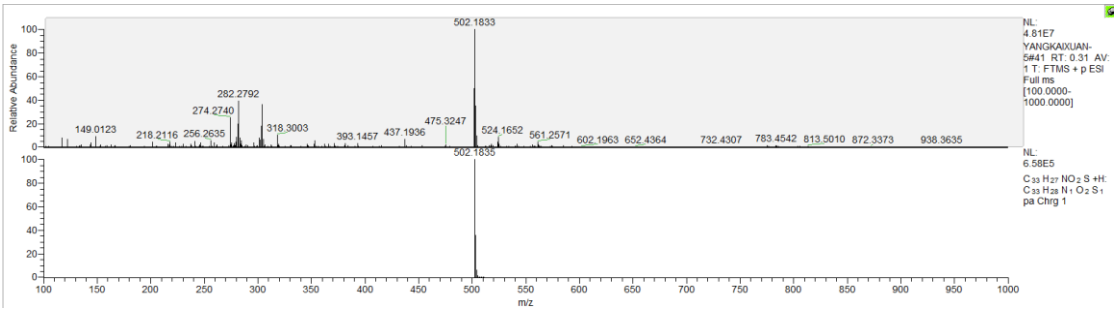
[α]$^{22}_{D}$ = -12.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.71 (m, 4H), 7.63 – 7.28 (m, 7H), 7.18 (m, *J* = 14.4, 6.8 Hz, 3H), 6.99 (dd, *J* = 22.0, 7.6 Hz, 4H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.36 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.34 (d, *J* = 10.4 Hz, 1H), 3.45 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.18 (t, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.26 (s, 3H);

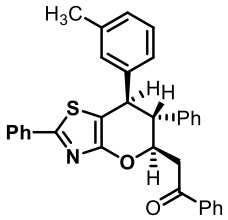
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 163.9, 159.7, 139.1, 138.9, 137.0, 136.8, 133.5, 133.0, 129.9, 129.0, 128.8, 128.7, 128.4, 128.1, 127.9, 127.4, 125.7, 109.8, 77.6, 53.7, 47.2, 41.8, 21.1;

HPLC (OD，*i*-PrOH/ *n*-hexane = 80/20), flow rate = 1.0 mL/min), t_R = 12.786 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1833.



2-((5R,6R,7R)-2,6-diphenyl-7-(m-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3h)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 91% isolated yield, 6:1 dr, 45.8 mg);

m. p.: 104-106 ℃;

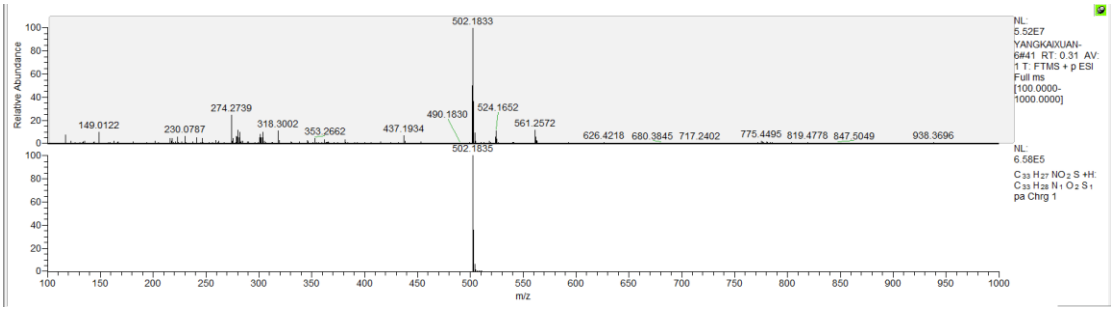
[α]$^{22}_{D}$ = -15.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR (400 MHz, CDCl3) δ 7.90 – 7.79 (m, 4H), 7.49 (m, 1H), 7.41 – 7.30 (m, 5H), 7.23 – 7.11 (m, 3H), 7.08 – 6.93 (m, 4H), 6.77 – 6.67 (m, 2H), 5.36 (ddd, J = 10.8, 8.0, 2.8 Hz, 1H), 4.32 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 17.2, 8.4 Hz, 1H), 3.21 (t, J = 10.4 Hz, 1H), 2.87 (dd, *J* = 16.8, 2.8 Hz 1H), 2.19 (s, 3H).

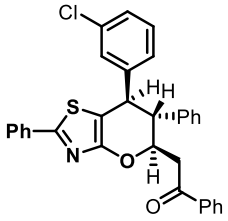
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 163.9, 159.7, 142.1, 138.9, 137.9, 137.0, 133.5, 133.1, 129. 9, 128.8, 128.8, 128.7, 128.4, 128.1, 128.1, 128.0, 127.4, 125. 7, 125.2, 109.7, 77.6, 53.6, 47.6, 41.8, 21.4;

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 65.157 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1833.



2-((5R,6R,7R)-7-(3-chlorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3i)



White solid (PE/EtOAc/DCM = 10:1:1, 94% isolated yeild, 8:1 dr, 47.8 mg);

m. p.: 84-88 ℃.

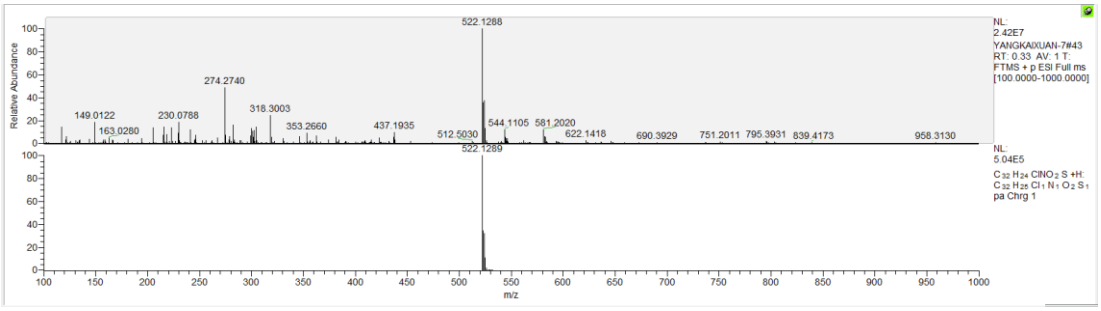
[α]$^{22}_{D}$ = -14.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.75 (m, 4H), 7.55 – 7.46 (m, 1H), 7.46 – 7.31 (m, 5H), 7.26 – 6.88 (m, 8H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.36 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 3.45 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.18 (t, *J* = 10.4 Hz, 1H), 2.87 (dd, *J* = 17.2, 2.8 Hz, 1H);

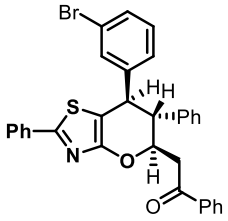
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.3, 159.9, 144.2, 138. 2, 136.9, 134.1, 133.3, 133.1, 130.1, 129.5, 129.0, 128.8, 128.5, 128.1, 128.0, 127.1, 127.5, 126.3, 125.7, 108.4, 77.5, 53.6, 47.4, 41.6;

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 21.7 min (major), t_R = 35.566 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}ClNO_2S]^+$: 522.1289, found: 522.1288.



2-((5R,6R,7R)-7-(3-bromophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3j)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 7:1 dr, 54.4 mg);

m. p.: 94-96 ℃.

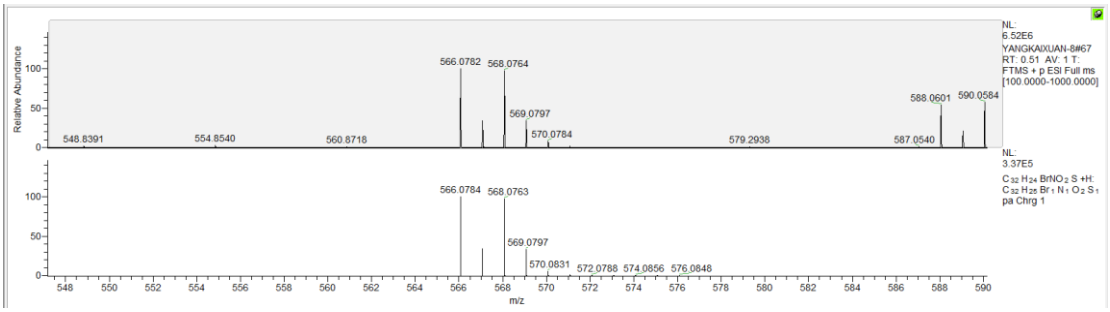
[α]$^{22}_{D}$ = -7.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 4H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (m, 4H), 7.33 – 7.14 (m, 4H), 7.12 – 6.94 (m, 4H), 6.82 (d, J = 7.7 Hz, 1H), 5.36 (ddd, J = 10.8, 8.0, 2.8 Hz, 1H), 4.33 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 17.2, 8.0 Hz, 1H), 3.17 (t, J = 10.4 Hz, 1H), 2.87 (dd, J = 17.2, 2.8 Hz, 1H).

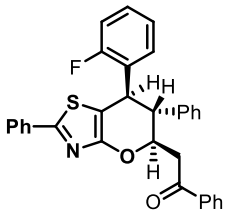
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.3, 159.9, 144.2, 138.2, 136.9, 134.1, 133.3, 133.1, 130.1, 129.5, 129.0, 128.8, 128.4, 128.1, 128.0, 127.7, 127.5, 126.3, 125.7, 108.4, 77.5, 53.6, 47.4, 41.6;

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 45.797 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}BrNO_2S]^+$: 566.0784, 568.0763, found: 566.0782, 568.0764.



2-((5R,6R,7R)-7-(2-fluorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3k)



White solid (PE/EtOAc/DCM = 10:1:1, 89% isolated yeild, 4:1 dr, 45.1 mg);

m. p.: 163-166 ℃.

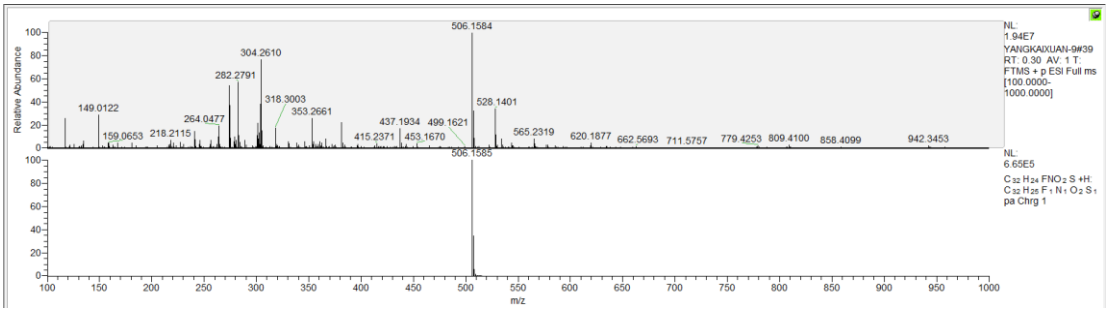
[α]$^{22}_{D}$ = -8.0 (*c* =1.0, CH_2Cl_2, 99% ee);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, *J* = 6.5, 3.5, 2.1 Hz, 4H), 7.55 – 7.48 (m, 1H), 7.45 – 7.31 (m, 5H), 7.24 – 6.97 (m, 8H), 6.86 (dd, *J* = 14.0, 4.8 Hz, 1H), 5.40 (ddd, *J* = 10.8, 8.4, 2.8 Hz, 1H), 4.78 (d, *J* = 10.4 Hz, 1H), 3.46 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.33 (t, *J* = 10.4 Hz, 1H), 2.88 (dd, *J* = 17.2, 2.8 Hz, 1H);

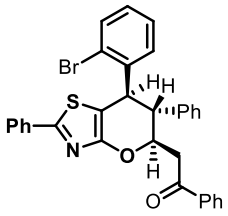
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.8, 161.8, 159.7, 159.3, 138.3, 137.0, 133.05, 133.1, 129.5, 129.0, 128.90, 128.8 (*J* = 230.0 Hz), 128.80, 128.8, 128.4, 128. 3, 128.1, 127.6, 125.7, 124.3(*J* = 4 Hz), 115.5 (*J* = 22 Hz), 108.5, 77.7, 52.1, 41.7;

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 10.956 min (major), t_R = 13.332 min (major);

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{32}H_{25}FNO_2S$]$^+$: 506.1585, found: 506.1584.



2-((5R,6R,7R)-7-(2-bromophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3l)



White solid (PE/EtOAc/DCM = 10:1:1, 95% isolated yeild, 6:1 dr, 53.9 mg).

m. p.: 86-87 ℃.

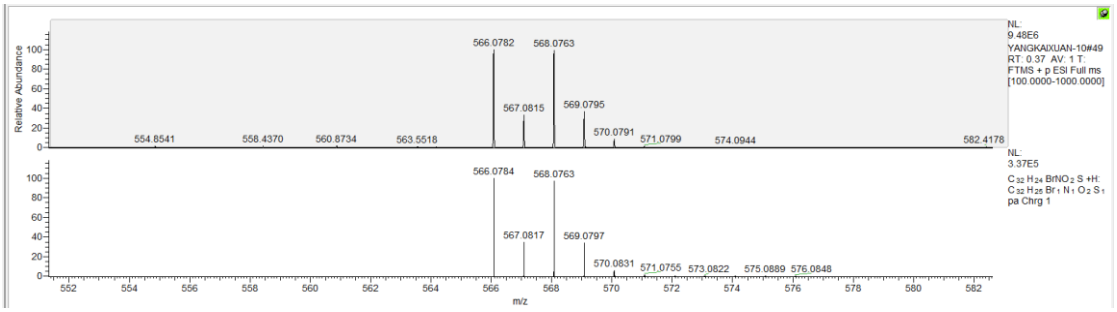
[α]$^{22}_{D}$ = -22.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 5H), 7.50 (t, J = 7.4 Hz, 1H), 7.36 (M, 7H), 7.29 – 7.23 (m, 2H), 7.17 (t, J = 7.6 Hz, 3H), 7.08 (d, J = 6.8 Hz, 2H), 7.04 – 6.98 (m, 1H), 5.44 (ddd, J = 10.4, 8.0, 2.8 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 3.49 – 3.30 (m, 2H), 2.92 (dd, J = 17.2, 2.8 Hz, 1H).

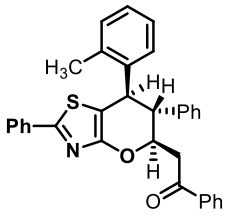
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.1, 159.4, 141.4, 137.6, 137.0, 133.4, 133.1, 132.7, 129.9, 129.2, 128.7, 128.7, 128.4, 128.1, 127.9, 127.6, 125.6, 124.7, 109.1, 77.7, 52.7, 45.0, 41.6.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 27.693 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{32}H_{25}BrNO_2S$]$^+$: 566.0784, 568.0763, found: 566.0782, 568.0763.



2-((5R,6R,7R)-2,6-diphenyl-7-(o-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3m)



White solid (PE/EtOAc/DCM = 10:1:1, 92% isolated yeild, 5:1 dr, 46.1 mg).

m. p.: 146-149 ℃.

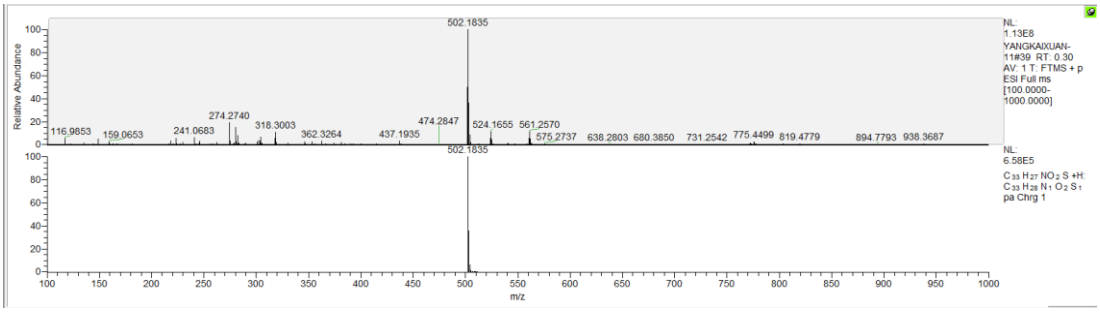
[α]$^{22}_{D}$ = -36.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.79 (m, 4H), 7.50 (dd, *J* = 10.4, 4.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.22 – 7.10 (m, 5H), 7.09 – 6.96 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.56 – 5.41 (m, 1H), 4.67 (d, *J* = 10.4 Hz, 1H), 3.49 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.27 (t, *J* = 10.4 Hz, 1H), 2.89 (dd, *J* = 17.2, 2.4 Hz, 1H), 1.81 (s, 3H).

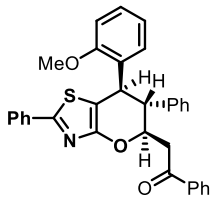
^{13}C NMR (101 MHz, CDCl$_3$) δ 196.5, 163.7, 159.6, 140.7, 138.8, 136.9, 136.0, 133.4, 133.0, 129.9, 129.8, 128.7, 128.7, 128.4, 128.1, 127.6, 127.4, 126.8, 126.4, 125.5, 110.3, 77.3, 53.4, 42.2, 41.7, 19.1.

HPLC (IH, *i*-PrOH/ *n*-hexane = 95/5), flow rate = 1.0 mL/min), t_R = 32.404 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{33}H_{28}NO_2S$]$^+$: 502.1835, found: 502.1835.



2-((5R,6R,7R)-7-(2-methoxyphenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3n)



White solid (PE/EtOAc/DCM = 10:1:1, 97% isolated yeild, 8:1 dr, 50.2 mg).

m. p.: 68-70 ℃.

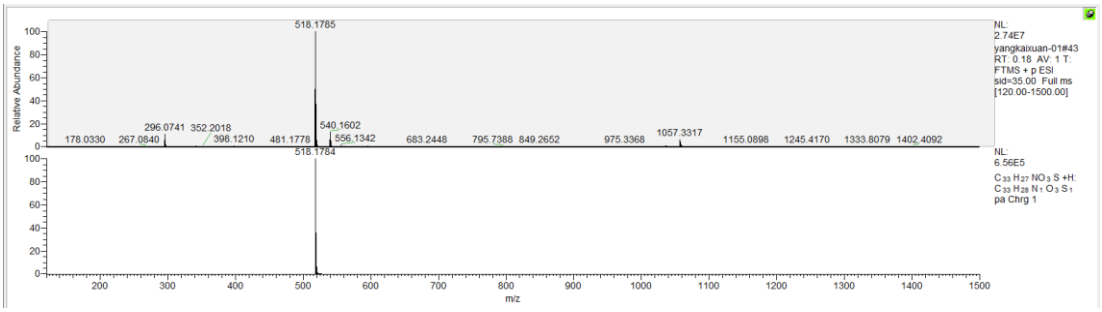
[α]$^{22}_{D}$ = -18.0 (*c* =1.0, CH_2Cl_2, 99% ee).

1H NMR (400 MHz, CDCl3) δ 7.55 – 7.48 (m, 1H), 7.44 – 7.31 (m, 5H), 7.20 – 7.11 (m, 4H), 7.06 (m, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 5.39 (ddd, J = 10.8, 8.4, 2.7 Hz, 1H), 3.52 – 3.38 (m, 4H), 3.32 (s, 1H), 2.87 (dd, J = 17.2, 2.4 Hz, 1H).

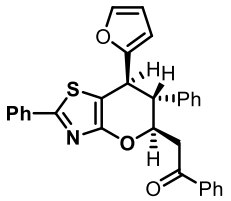
^{13}C NMR (101 MHz, CDCl$_3$) δ 196.6, 157.1, 139.1, 137.1, 133.7, 130.0, 129.7, 128.7, 128.6, 128.4, 128.3, 128.1, 127.2, 125.6, 120.7, 110.8, 109.9, 77.7, 55.2, 42.0.

HPLC (AD, *i*-PrOH/ *n*-hexane = 80/20), flow rate = 1.0 mL/min), t_R = 38.57 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{33}H_{28}NO_3S$]$^+$: 518.1784, found: 518.1785.



2-((5R,6R,7R)-7-(furan-2-yl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3o)



White solid (PE/EtOAc/DCM = 10:1:1, 90% isolated yeild, 15:1 dr, 43.2 mg).

m. p.: 97-101 ℃.

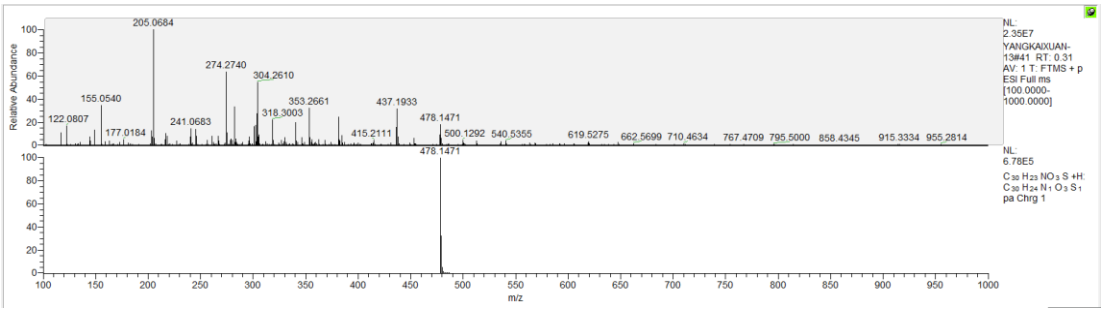
[α]$^{22}_{D}$ = -3.0 (*c* =1.0, CH_2Cl_2, 98% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.78 (m, 4H), 7.52 (m, 1H), 7.44 – 7.33 (m, 5H), 7.28 – 7.09 (m, 6H), 6.19 (dd, J = 3.2, 1.9 Hz, 1H), 5.97 (d, J = 3.2 Hz, 1H), 5.34 (ddd, J = 10.8, 8.0, 2.8 Hz, 1H), 4.56 (d, J = 10.4 Hz, 1H), 3.53 – 3.43 (m, 2H), 2.87 (dd, J = 16.8, 2.8 Hz, 1H).

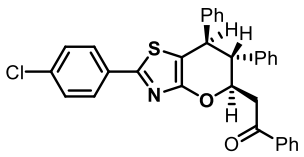
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.0, 159.1, 153.7, 141.9, 138.9, 136.9, 133.5, 133.1, 129.9, 129.0, 128.7, 128.4, 128.2, 128.1, 127.6, 125.7, 110.1, 107.2, 106.5, 77.4, 49.6, 41.7, 41.0.

HPLC (IH, *i*-PrOH/ *n*-hexane = 93/7), flow rate = 1.0 mL/min), t_R = 27.002 min (major), t_R = 32.938 min (major);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{30}H_{24}NO_3S]^+$: 478.1471, found: 478.1471.



2-((5R,6R,7R)-2-(4-chlorophenyl)-6,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3p)



White solid (PE/EtOAc/DCM = 10:1:1, 89% isolated yeild, 6:1 dr, 46.6 mg).

m. p.: 106-108 ℃.

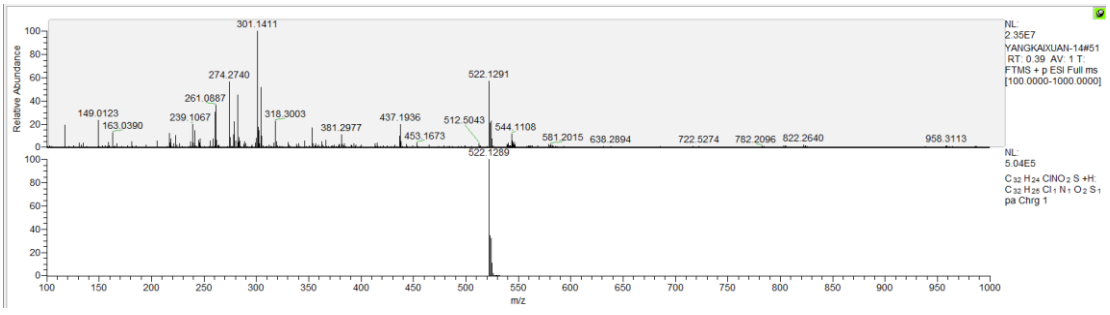
[α]$^{22}_{D}$ = -10.0 (*c* =0.1, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 4H), 7.52 (m, *J* = 10.4, 4.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.23 – 7.13 (m, 6H), 7.08 – 6.88 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.0, 2.4 Hz, 1H), 4.37 (d, *J* = 10.4 Hz, 1H), 3.45 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.86 (dd, *J* = 17.2, 2.8 Hz, 1H).

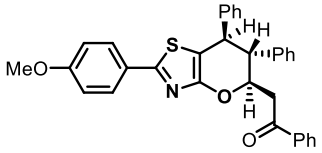
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 162.6, 159.9, 142.0, 138.6, 137.0, 135.8, 133.1, 132.0, 129.0, 128.9, 128.6, 128.4, 128.3, 128.1, 128.0, 127.5, 127.4, 126.9, 110.0, 77.7, 53.7, 47.7, 41.8.

HPLC (IF *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 50.743 min (major)).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}ClNO_2S]^+$: 522.1289, found: 522.1291



2-((5R,6R,7R)-2-(4-methoxyphenyl)-6,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-onex (3q)



White solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 5:1 dr, 48 mg).

m. p.: 98-101 ℃.

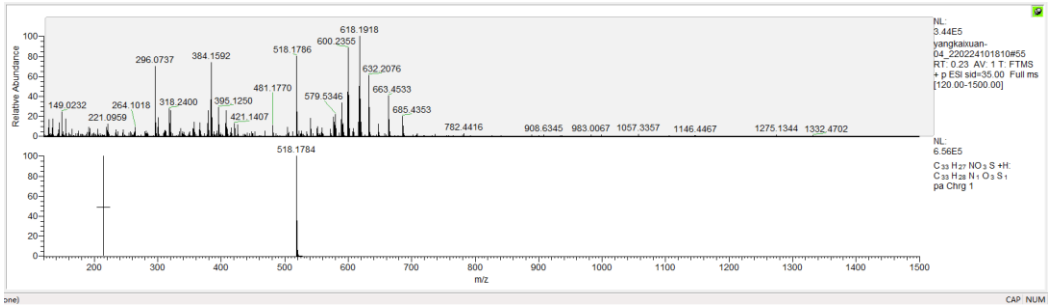
$[\alpha]^{22}_D$ = -14.0 (*c* =1.0, CH_2Cl_2, 97% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.50 (m, 1H), 7.38 (m, 2H), 7.24 – 7.11 (m, 6H), 6.97 (m, 6H), 5.37 (ddd, J = 10.8, 8.4, 2.4 Hz, 1H), 4.35 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 17.2, 8.4 Hz, 1H), 3.20 (t, J = 10.8 Hz, 1H), 2.87 (dd, J = 17.2, 2.8 Hz, 1H).

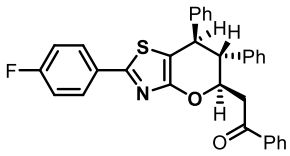
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 165.0, 162.7, 162.5, 159.7, 142.0, 138.6, 136.9, 133.0, 129.8, 129.8, 128.8, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 115.9, 115.7, 109.4, 77.5, 53.6, 47.6, 41.7.

HPLC (Ih *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 40.042 min (minor),.t_R = 47.171 min (major)).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_3S]^+$: 518.1784, found: 518.1786



2-((5R,6R,7R)-2-(4-fluorophenyl)-6,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3r)



White solid (PE/EtOAc/DCM = 10:1:1,96 % isolated yeild, 6:1 dr, 48.6 mg).

m. p.: 96-98 ℃.

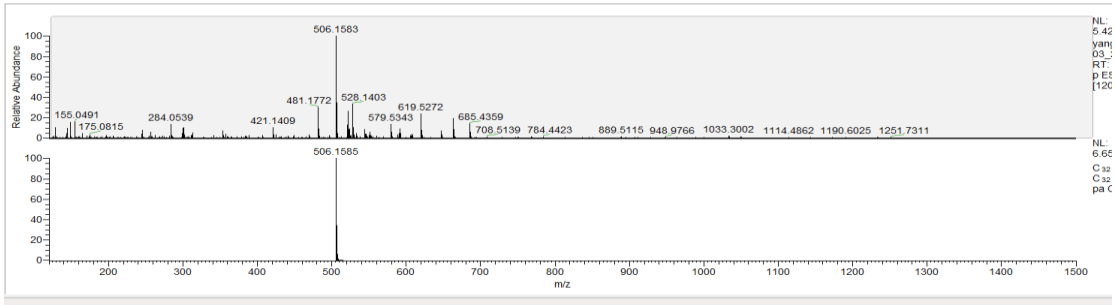
$[\alpha]^{22}_D$ = -14.0 (*c* =1.0, CH_2Cl_2, 97% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.50 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.24 – 7.11 (m, 6H), 6.97 (m, 6H), 5.37 (ddd, J = 10.8, 8.0, 2.8 Hz, 1H), 4.35 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 16.8, 8.0 Hz, 1H), 3.20 (t, J = 10.4 Hz, 1H), 2.87 (dd, J = 17.2, 2.8 Hz, 1H).

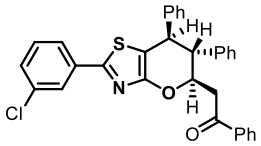
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 165.0, 162.6 (J = 10.3 Hz), 159.7, 142.0, 138.6, 136.9, 133.0, 129.8 (J = 1.2 Hz), 128.8, 128.4, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 127.3, 115.8 (J = 22 Hz), 109.4, 77.5, 53.6, 47.6, 41.7.

HPLC (Ih *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 28.185 min (minor),t_R = 45.243 min (major)).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}FNO_2S]^+$: 506.1585, found: 506.1583



2-((5R,6R,7R)-2-(3-chlorophenyl)-6,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3s)



White solid (PE/EtOAc/DCM = 10:1:1, 94% isolated yeild, 6:1 dr, 48.6 mg).

m. p.: 96-98 ℃.

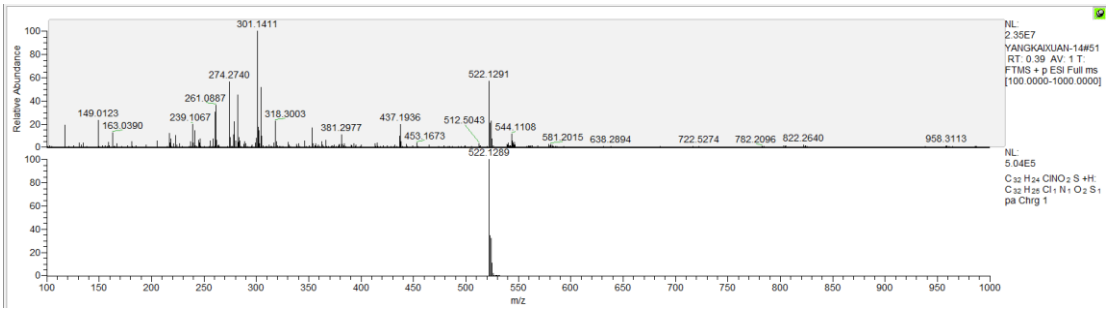
[α]$^{22}_{D}$ = -10.0 (*c* =1.0, CH_2Cl_2, 89% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 3H), 7.70 (m, 1H), 7.52 (m, 1H), 7.40 (m, 2H), 7.35 – 7.24 (m, 3H), 7.22 – 7.11 (m, 6H), 7.01 (d, J = 6.8 Hz, 2H), 6.94 (m, 2H), 5.38 (ddd, J = 10.8, 8.4, 2.8 Hz, 1H), 4.38 (d, J = 8.0 Hz, 1H), 3.50 – 3.41 (dd, J = 17.2 Hz, 8.4 Hz 1H), 3.21 (t, J = 10.4 Hz, 1H), 2.86 (dd, J = 17.2, 2.8 Hz, 1H).

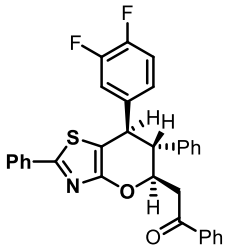
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 162.2, 159.9, 141.9, 138.6, 136.9, 135.1, 134.9, 133.1, 130.0, 129.8, 128.9, 128.4, 128.4, 128.1, 128.0, 127.5, 127.4, 125.7, 123.7, 110.4, 77.6, 77.3, , 53.6, 47.7, 41.7.

HPLC (IF *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 20.39 min (minor),t_R = 30.23 min (major)).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{32}H_{25}ClNO_2S$]$^+$: 522.1289, found: 522.1291



2-((5R,6R,7R)-7-(3,4-difluorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (3t)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 8:1 dr, 50.2 mg).

m. p.: 72-74 ℃.

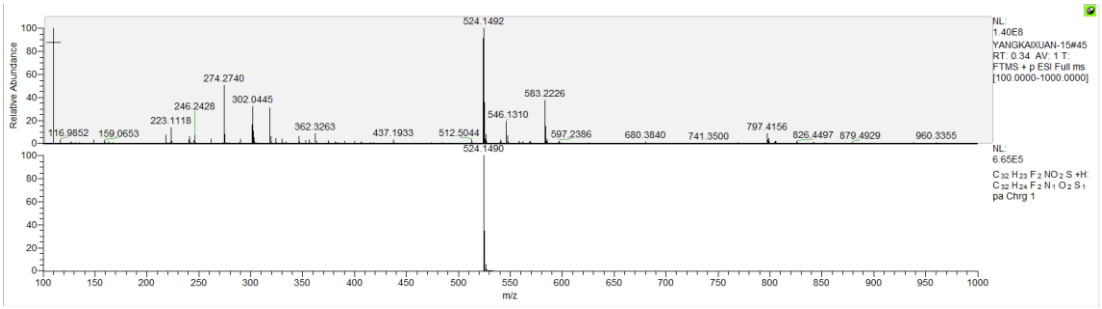
[α]^{22}D = -16.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 1H), 7.43 – 7.30 (m, 5H), 7.25 – 7.14 (m, 3H), 7.06 (m, 3H), 6.75 (m, 1H), 6.64 – 6.54 (m, 1H), 5.39 (ddd, J = 10.4, 8.4, 2.4 Hz, 1H), 4.72 (d, J = 10.4 Hz, 1H), 3.45 (dd, J = 17.2, 8.4 Hz, 1H), 3.28 (t, J = 10.4 Hz, 1H), 2.88 (dd, J = 16.8, 2.4 Hz, 1H).

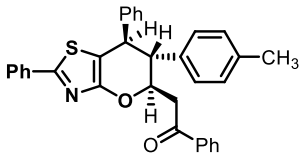
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 164.7, 163.9, 163.1 (J = 48 Hz), 161.7 (J = 48 Hz), 160.6 (J = 48 Hz), 159.8, 159.2 (J = 48 Hz), 153.4, 138.0, 136.9, 133.0, 130.3, 130.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.7, 125.6, 124.9 (J = 12 Hz), 124.7 (J = 12 Hz), 111.7 (J = 16 Hz), 111.5 (J = 16 Hz), 108.0, 103.7 (J = 104 Hz), 77.6, 52.1, 41.6.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 45.533 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{32}H_{24}F_2NO_2S$]$^+$: 524.1490, found: 524.1492



2-((5R,6R,7R)-2,7-diphenyl-6-(p-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (4a)



Brown solid (PE/EtOAc/DCM = 10:1:1, 98% isolated yeild, 7:1 dr, 49.3 mg).

m. p.: 96-98 ℃.

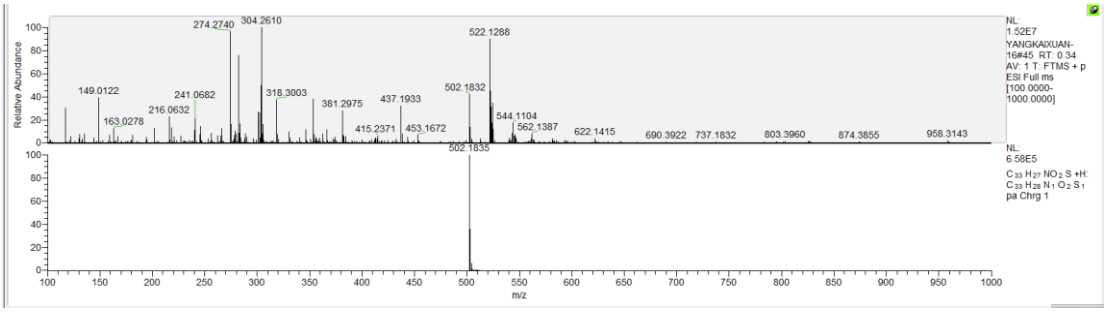
[α]$^{22}_{D}$ = -27.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, *J* = 6.8, 2.8 Hz, 4H), 7.54 – 7.46 (m, 1H), 7.43 – 7.28 (m, 5H), 7.17 (dd, *J* = 6.8, 3.6 Hz, 3H), 7.05 – 6.81 (m, 6H), 5.34 (m, *J* = 10.4, 8.0, 2.4 Hz, 1H), 4.35 (d, *J* = 10.0 Hz, 1H), 3.43 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.16 (t, *J* = 10.4 Hz, 1H), 2.88 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.23 (s, 3H)..

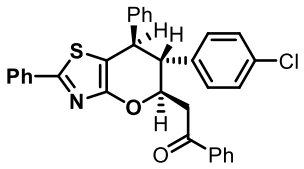
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 164.0, 159.9, 142.3, 137.1, 137.1, 135.6, 133.6, 133.0, 129.9, 129.6, 128.8, 128.4, 128.3, 128.2, 128.1, 127.3, 125.7, 109.6, 77.8, 53.4, 47.7, 41.9, 21.1.

HPLC (If, *i*-PrOH/ *n*-hexane= 83/17), flow rate = 1.0 mL/min), t_R = 33.799 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1832



2-((5R,6R,7R)-6-(4-chlorophenyl)-2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (4b)



Yellow liquid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 10:1 dr, 50.0 mg).

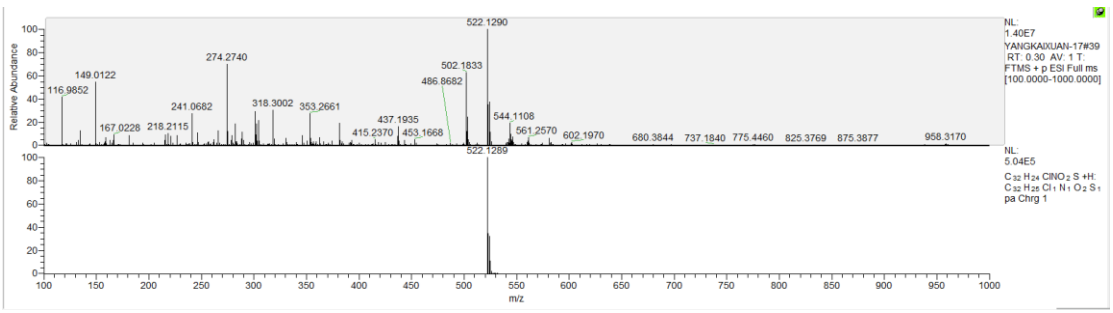
[α]$^{22}_{D}$ = -16.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (td, *J* = 6.9, 2.6 Hz, 4H), 7.54 – 7.46 (m, 1H), 7.43 – 7.28 (m, 5H), 7.17 (dd, *J* = 6.6, 3.6 Hz, 3H), 7.05 – 6.81 (m, 6H), 5.34 (ddd, *J* = 10.7, 8.2, 2.7 Hz, 1H), 4.35 (d, *J* = 10.3 Hz, 1H), 3.43 (dd, *J* = 17.0, 8.2 Hz, 1H), 3.16 (t, *J* = 10.5 Hz, 1H), 2.88 (dd, *J* = 16.9, 2.5 Hz, 1H), 2.23 (s, 3H).

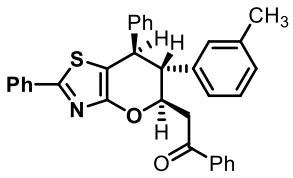
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.1, 159.9, 140.7, 138.3, 136.9, 133.3, 133.0, 133.0, 130.0, 129.3, 129.0, 128.8, 128.5, 128.4, 128.1, 127.6, 125.7, 108.7, 77.5, 53.7, 47.1, 41.6.

HPLC (IH, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 17.337 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 522.1289, found: 522.1290



2-((5R,6R,7R)-2,7-diphenyl-6-(m-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (4c)



White solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 7:1 dr, 46.8 mg).

m. p.: 77-80 ℃.

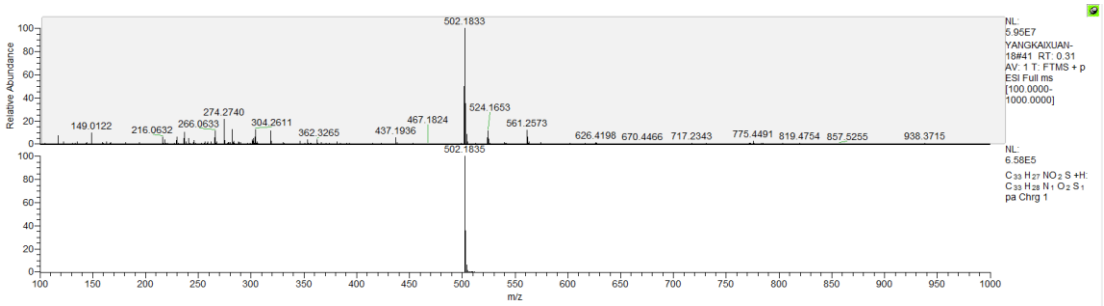
$[\alpha]^{22}_D$ = -26.0 (*c* =1.0, CH_2Cl_2, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 4H), 7.59 – 7.47 (m, 1H), 7.47 – 7.29 (m, 6H), 7.26 – 7.12 (m, 4H), 7.04 – 6.71 (m, 4H), 5.41 – 5.29 (m, 1H), 4.30 (d, *J* = 10.2 Hz, 1H), 3.57 – 3.32 (m, 2H), 2.99 (dd, *J* = 17.0, 1.9 Hz, 1H).

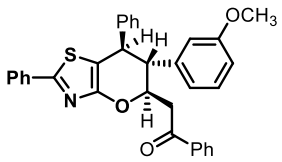
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.9, 159.8, 142.2, 138.6, 138.4, 137.0, 133.5, 133.0, 129.8, 128.9, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 128.0, 127.2, 125.6, 109.5, 77.6, 53.6, 47.5, 41.8, 21.3.

HPLC (If, *i*-PrOH/ *n*-hexane = 83/17), flow rate = 1.0 mL/min), t_R = 31.33 min (major), t_R = 38.60 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1833



2-((5R,6R,7R)-6-(2-methoxyphenyl)-2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one （4d）



Yellow solid (PE/EtOAc/DCM = 10:1:1, 92% isolated yeild, 7:1 dr, 47.8 mg).

m. p.: 90-92 ℃.

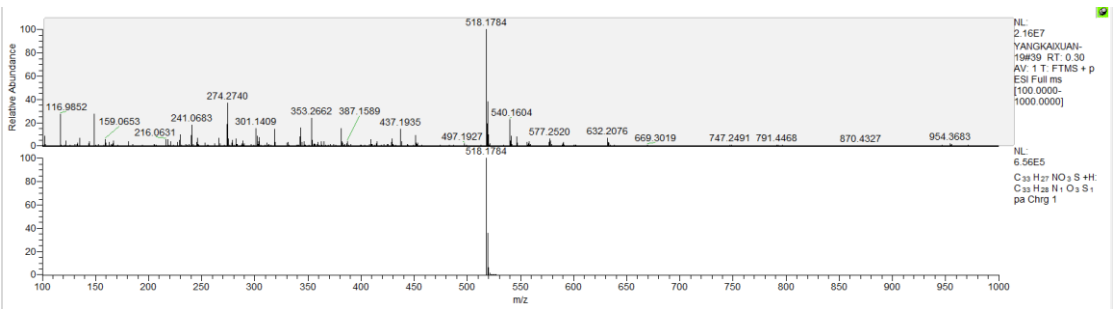
$[\alpha]^{22}_D$ = -34.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.36 (m, *J* = 6.7, 3.6 Hz, 3H), 7.20 – 7.10 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.98 – 6.79 (m, 4H), 5.00 (ddd, *J* = 11.4, 8.3, 3.3 Hz, 1H), 4.35 – 4.25 (m, 1H), 3.62 (s, 3H), 3.07 (t, *J* = 10.5 Hz, 1H), 2.61 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.46 (dd, *J* = 16.2, 3.3 Hz, 1H), 2.27 (s, 3H).

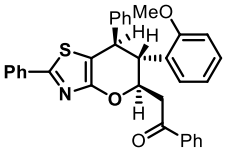
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.9, 159.8, 159.7, 142.1, 140.2, 137.0, 133.5, 133.0, 129.9, 129.9, 128.7, 128.4, 128.3, 128.1, 128.0, 127.3, 125.6, 120.6, 114.3, 112.6, 109.4, 77.5, 55.1, 53.7, 47.6, 41.7.

HPLC (AD, *i*-PrOH/ *n*-hexane = 80/20), flow rate = 1.0 mL/min), t_R = 36.81 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_3S]^+$: 518.1784, found: 518.1784



1-(2-methoxyphenyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4e)



White solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 7:1 dr, 49.7 mg).

m. p.: 73-74 ℃.

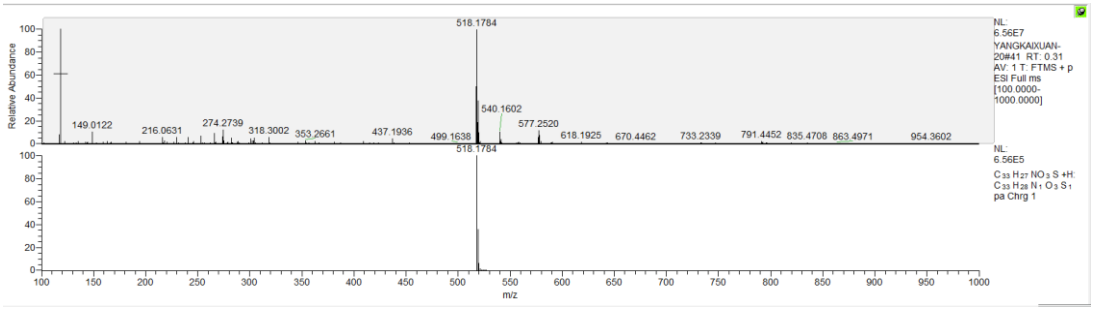
[α]$^{22}_{D}$ = -5.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 4H), 7.50 (m, *J* = 7.2 Hz, 1H), 7.43 – 7.30 (m, 5H), 7.23 – 7.00 (m, 7H), 6.84 (m, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 5.39 (ddd, *J* = 10.8, 8.4, 2.8 Hz, 1H), 4.94 (s, 1H), 3.52 – 3.21 (m, 5H), 2.87 (dd, *J* = 16.8, 2.8 Hz, 1H).

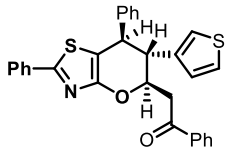
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.7, 157.5, 137.1, 133.6, 132.9, 129.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.0, 125.7, 121.0, 111.2, 109.6, 55.4, 42.0, 29.7.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 28.757 min (major)

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{33}H_{28}NO_3S$]$^+$: 518.1784, found: 518.1784



2-((5R,6R,7R)-2,7-diphenyl-6-(thiophen-3-yl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-phenylethan-1-one (4f)



White solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 4:1 dr, 46.0 mg).

m. p.: 143-146 ℃.

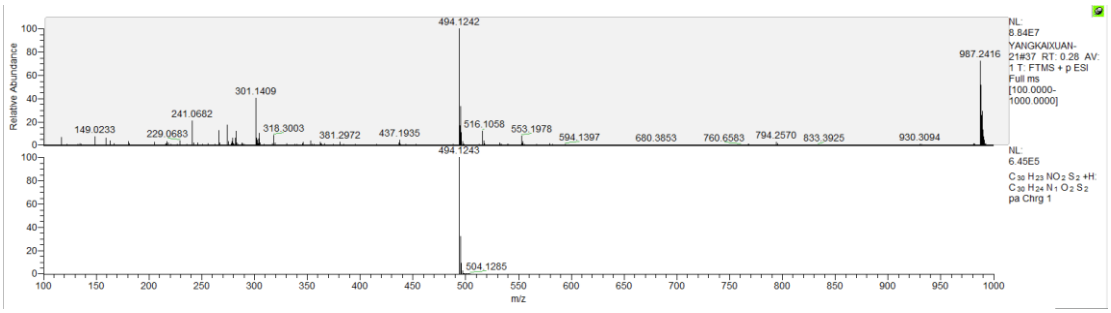
[α]$^{22}_{D}$ = -1.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, *J* = 7.2 Hz, 4H), 7.59 – 7.47 (m, 1H), 7.47 – 7.29 (m, 6H), 7.26 – 7.12 (m, 4H), 7.04 – 6.71 (m, 4H), 5.41 – 5.29 (m, 1H), 4.30 (d, *J* = 10.0 Hz, 1H), 3.57 – 3.32 (m, 2H), 2.99 (dd, *J* = 16.8, 2.8 Hz, 1H).

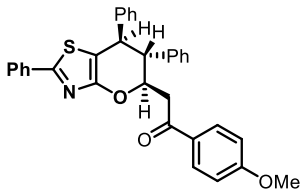
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 164.0, 159.9, 142.2, 138.9, 137.0, 133.4, 133.1, 129.9, 128.7, 128.4, 128.3, 128.1, 127.9, 127.3, 126.7, 126.2, 125.6, 122.9, 109.0, 77.4, 49.3, 47.6, 41.8.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 91/4/5), flow rate = 1.0 mL/min), t_R = 46.791 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{30}H_{24}NO_2S_2$]$^+$: 494.1243, found: 494.1242



1-(4-methoxyphenyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4g)



White solid (PE/EtOAc/DCM = 10:1:1, 89% isolated yeild, 6:1 dr, 46.0 mg).

m. p.: 80-82 ℃.

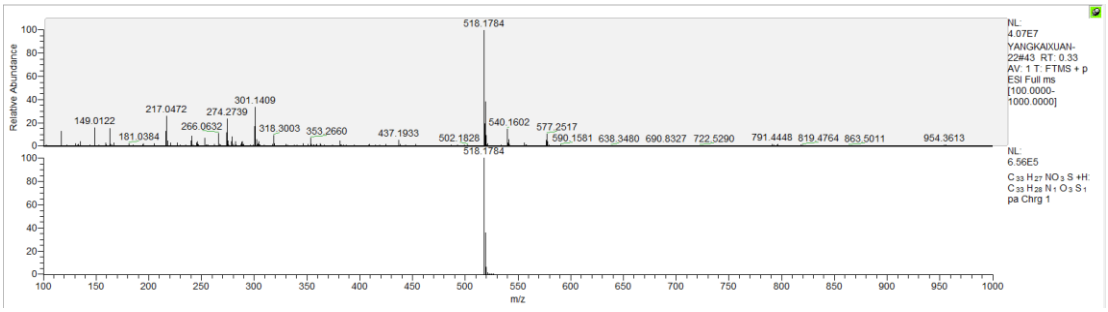
[α]$^{22}_{D}$ = -22.0 (*c* =1.0, CH_2Cl_2, 99% ee).

1H NMR (400 MHz, CDCl3) δ 7.82 (d, J = 7.2 Hz, 1H), 7.33 (s, 1H), 7.14 (dd, J = 7.7, 4.0 Hz, 1H), 6.99 (s, 1H), 6.92 (d, J = 3.6 Hz, 1H), 6.86 (d, J = 6.8 Hz, 4H), 5.43 – 5.28 (m, 1H), 4.35 (d, J = 10.4, 1H), 3.81 (s, 3H), 3.37 (dd, 16.8 Hz, 8.0 Hz,1H), 3.16 (t, 10.8 Hz,1H), 2.80 (dd, J = 16.8 Hz, 2.8 Hz,1H).

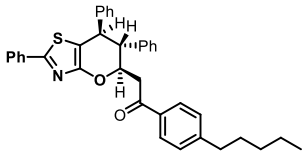
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 163.9, 163.4, 159.8, 142.2, 138.8, 133.5, 130.4, 130.2, 129.8, 128.8, 128.7, 128.4, 128.2, 128.0, 127.4, 127.2, 125.6, 113.5, 109.4, 77.7, 55.4, 53.7, 47.7, 41.3.

HPLC (AD, *i*-PrOH/ *n*-hexane = 80/20), flow rate = 1.0 mL/min), t_R = 47.72 min (major), t_R = 60.828 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_3S]^+$: 518.1784, found: 518.1784



1-(4-pentylphenyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4h)



White solid (PE/EtOAc/DCM = 10:1:1, 90% isolated yeild, 6:1 dr, 50.0 mg).

m. p.: 83-84 ℃.

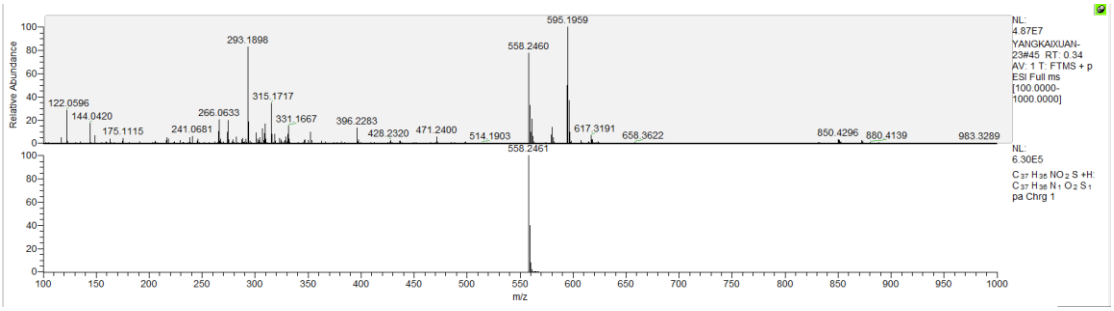
[α]$^{22}_{D}$ = -15.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 4.0, 2.8 Hz, 3H), 7.24 – 7.10 (m, 8H), 7.07 – 6.89 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.4, 2.8 Hz, 1H), 4.36 (d, *J* = 10.4 Hz, 1H), 3.43 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.83 (dd, *J* = 16.8, 2.8 Hz, 1H), 2.68 – 2.54 (m, 2H), 1.59 (dd, *J* = 15.2, 7.4 Hz, 2H), 1.38 – 1.22 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

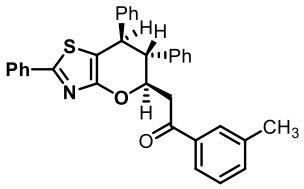
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 163.9, 159.9, 148.8, 142.2, 138.8, 134.7, 133.5, 129.9, 128.8, 128.7, 128.5, 128.3, 128.0, 127.4, 127.3, 125.7, 109.4, 77.6, 53.8, 47.8, 417, 35.9, 31.4, 30.7, 22.5, 14.0.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 94/1/5), flow rate = 1.0 mL/min), t_R = 12.904 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{37}H_{36}NO_2S]^+$: 558.2461, found: 558.2460



1-(m-tolyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4i)



White solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 6:1 dr, 46.6 mg).

m. p.: 83-86 ℃.

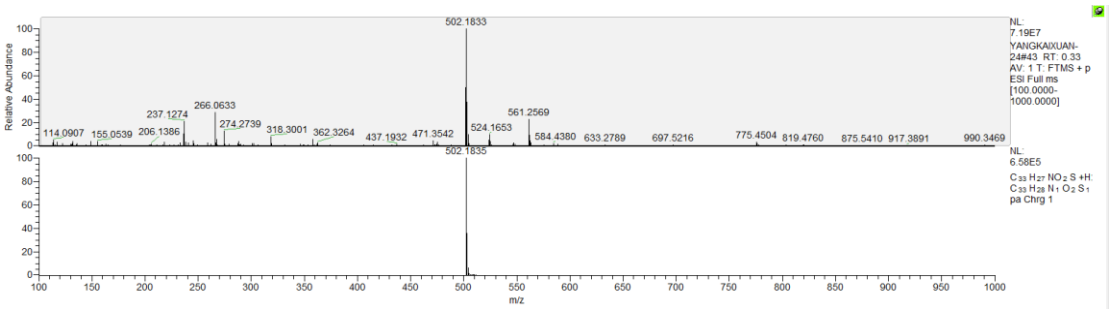
$[\alpha]^{22}_D$ = -5.0 (*c* =1.0, CH_2Cl_2, 97% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.63 (m, 2H), 7.39 – 7.26 (m, 5H), 7.24 – 7.10 (m, 6H), 7.07 – 6.89 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.4, 2.8 Hz, 1H), 4.36 (d, *J* = 10.0 Hz, 1H), 3.44 (dd, *J* = 17.2, 8.4 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.37 (s, 3H).

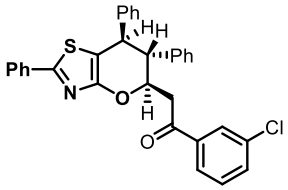
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.9, 159.8, 142.1, 138.8, 138.2, 137.1, 133.8, 133.5, 129.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 127.4, 127.3, 125.7, 125.3, 109.4, 77.6, 53.8, 47.8, 41.9, 21.3.

HPLC (IC, *i*-PrOH/ *n*-hexane = 80/20), flow rate = 1.0 mL/min), t_R = 34.604 min (major), t_R = 39.219 min (minor);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1833



1-(3-chlorophenyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4j)



White solid (PE/EtOAc/DCM = 10:1:1, 97% isolated yeild, 7:1 dr, 50.6 mg).

m. p.: 92-95 ℃.

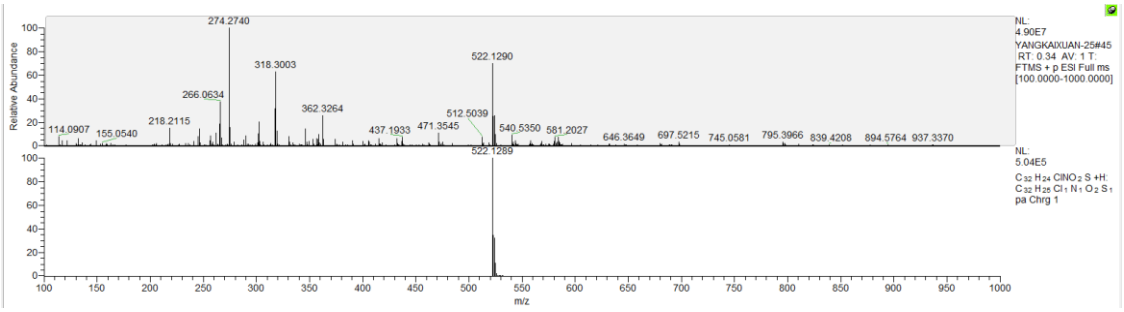
[α]$^{22}_{D}$ = -5.0 (*c* =1.0, CH_2Cl_2, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.63 (m, 2H), 7.39 – 7.26 (m, 5H), 7.24 – 7.10 (m, 6H), 7.07 – 6.89 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.36 (d, *J* = 10.0 Hz, 1H), 3.44 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.20 (t, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.37 (s, 3H).

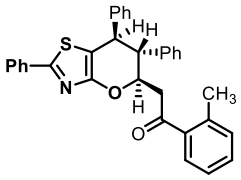
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 164.0, 159.6, 142.0, 138.5, 138.4, 134.7, 133.4, 132.9, 129.9, 129.7, 128.9, 128.7, 128.4, 128.3, 128.2, 128.0, 127.5, 127.3, 126.2, 125.6, 109.5, 77.5, 53.6, 47.6, 41.8.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 94/1/5), flow rate = 1.0 mL/min), t_R = 14.048 min (minor), t_R = 24.264 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{25}ClNO_2S]^+$: 522.1289, found: 522.1290



1-(o-tolyl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (4k)



White solid (PE/EtOAc/DCM = 10:1:1, 88% isolated yeild, 5:1 dr, 44.0 mg).

m. p.: 69-70 ℃.

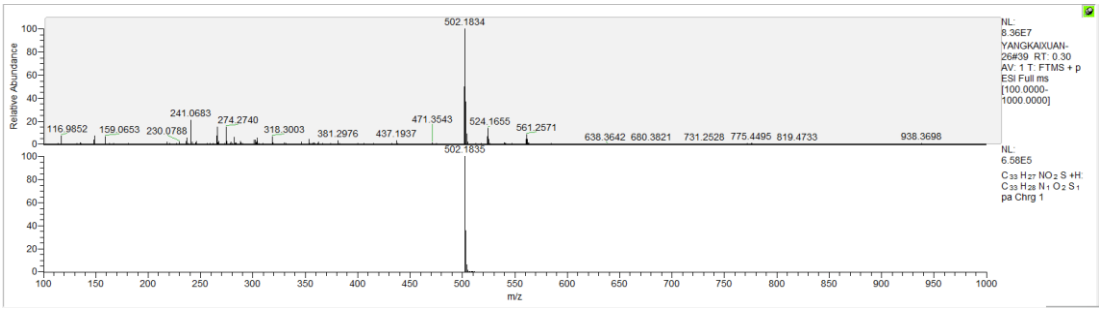
[α]$^{22}_{D}$ = -10.0 (*c* =1.0, CH_2Cl_2, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2H), 7.53 – 7.27 (m, 7H), 7.25 – 7.09 (m, 9H), 7.00 (d, *J* = 6.6 Hz, 2H), 6.92 (m, 2H), 5.29 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.36 (d=, *J* = 10.4, 1H), 3.33 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.17 (t, *J* = 10.4 Hz, 1H), 2.84 (dd, *J* = 16.8, 2.8 Hz, 1H), 2.44 (s, 3H).

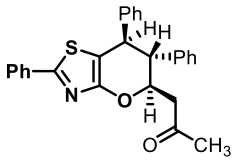
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3 164.0, 159.8, 138.0, 137.0, 133.4, 133.1, 130.1, 128.9, 128.8, 128.5, 128.3, 128.1, 127.7, 125.7, 124.9, 111.8, 111.5, 108.0, 104.0, 103.8, 77.7, 52.2, 41.6, 29.7.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 94/1/5), flow rate = 1.0 mL/min), t_R = 11.274 min (minor), t_R = 12.349 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{33}H_{28}NO_2S]^+$: 502.1835, found: 502.1834



1-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)propan-2-one (4l)



White solid (PE/EtOAc/DCM = 10:1:1, 91% isolated yeild, 9:1 dr, 39.0 mg).

m. p.: 86-88 ℃.

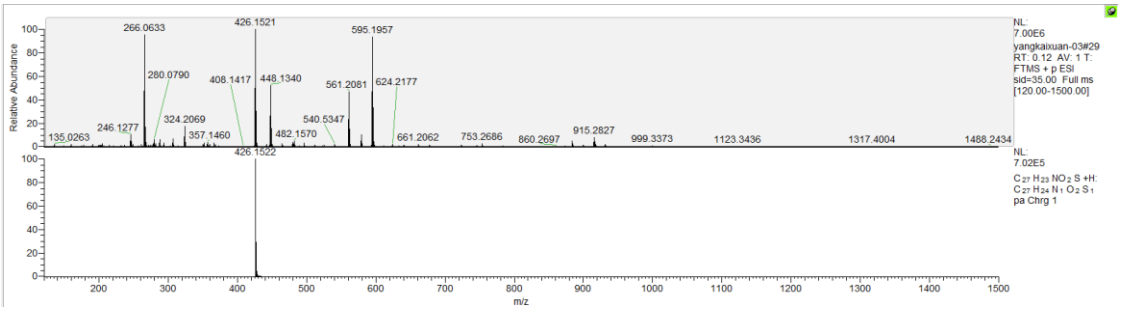
$[\alpha]^{22}_D$ = -7.0 (*c* =1.0, CH_2Cl_2, 98% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, *J* = 5.6, 3.0, 1.5 Hz, 2H), 7.69 – 7.59 (m, 2H), 7.44 – 7.25 (m, 6H), 7.24 – 7.10 (m, 6H), 7.09 – 6.86 (m, 4H), 5.37 (ddd, *J* = 10.8, 8.2, 2.7 Hz, 1H), 4.36 (d, *J* = 10.3 Hz, 1H), 3.44 (dd, *J* = 17.0, 8.2 Hz, 1H), 3.20 (t, *J* = 10.5 Hz, 1H), 2.85 (dd, *J* = 16.9, 2.7 Hz, 1H), 2.36 (s, 3H).

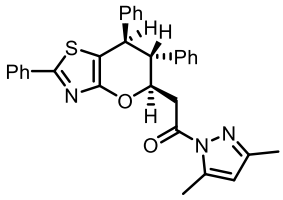
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.9, 159.8, 142.1, 138.8, 138.2, 137.0, 133.8, 133.5, 129.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 127.4, 127.3, 125.7, 125.3, 109.4, 77.6, 53.7, 47.7, 41.8, 21.3.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 94/1/5), flow rate = 1.0 mL/min), t_R = 34.604 min (minor), t_R = 39.219 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor [C27H23NO2S]: 426.1522, found: 426.1521



1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (5a)



White solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 8:1 dr, 48.5 mg).

m. p.: 85-88 ℃.

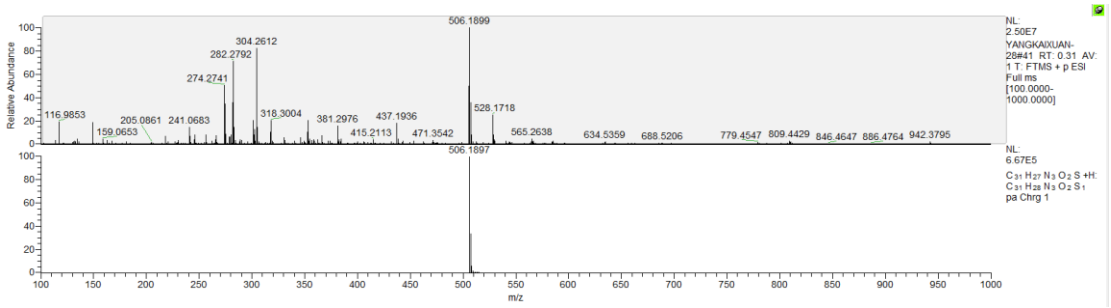
$[\alpha]^{22}_D$ = -14.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (600 MHz, cdcl$_3$) δ 7.96 – 7.75 (m, 2H), 7.36 (d, *J* = 3.0 Hz, 3H), 7.24 – 7.08 (m, 6H), 7.08 – 6.82 (m, 4H), 5.90 (s, 1H), 5.32 (m, 1H), 4.35 (d, *J* = 10.2 Hz, 1H), 3.71 (dd, *J* = 17.0, 9.0 Hz, 1H), 3.20 (t, *J* = 10.8 Hz, 1H), 3.02 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.50 (s, 3H), 2.18 (s, 3H).

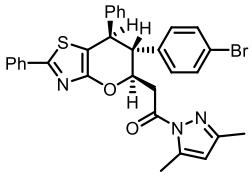
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 159.9, 151.8, 144.2, 142.1, 138.6, 133.5, 129.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.4, 127.3, 125.7, 111.2, 109.5, 77.8, 53.4, 47.8, 39.0, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 93/7), flow rate = 1.0 mL/min), t_R = 49.205 min (minor);

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{31}H_{28}N_3O_2S]^+$: 506.1897, found: 506.1899



2-((5R,6R,7R)-6-(4-bromophenyl)-2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one (5b)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 13:1 dr, 54.2 mg).

m. p.: 94-96 ℃.

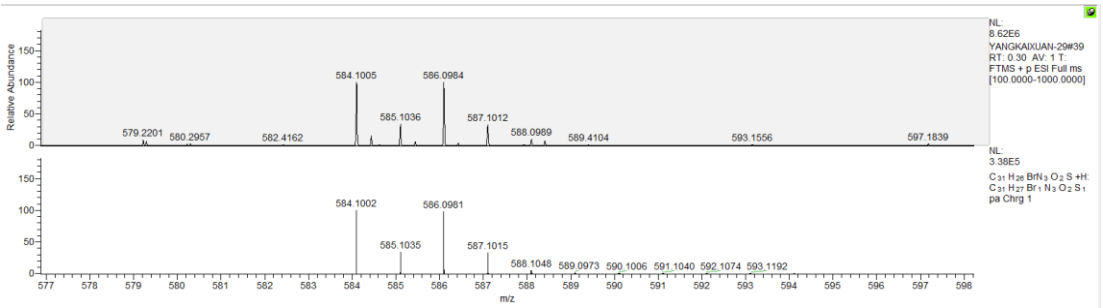
[α]$^{22}_{D}$ = -37.0 (*c* =1.0, CH_2Cl_2, 98% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.77 (m, 2H), 7.48 – 7.13 (m, 8H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.90 (s, 1H), 5.41 – 5.18 (ddd, 10.8 Hz, 8.0 Hz, 2.8 Hz,1H), 4.32 (d, *J* = 10.0 Hz, 1H), 3.70 (dd, *J* = 17.2, 9.2 Hz, 1H), 3.14 (t, *J* = 10.4 Hz, 1H), 3.02 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.18 (s, 3H).

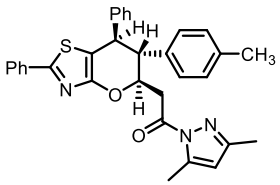
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 164.2, 159.9, 151.9, 144.2, 141.2, 138.2, 133.4, 131.5, 130.1, 129.7, 128.9, 128.8, 128.4, 127.6, 125.7, 121.2, 111.2, 108.6, 77.8, 53.4, 47.3, 38.9, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 33.13 min (major), t_R = 49.953 min (minor).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{31}H_{27}BrN_3O_2S$]$^+$: 584.1002，586.0981, found: 584.1005，586.0984



1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-((5R,6R,7R)-2,7-diphenyl-6-(p-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one（5c）



White solid (PE/EtOAc/DCM = 10:1:1, 99% isolated yeild, 13:1 dr, 51.3 mg).

m. p.: 168-169 ℃.

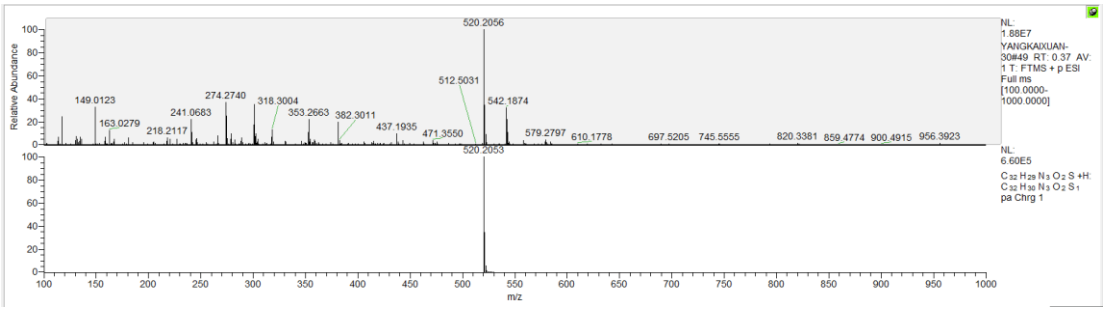
[α]$^{22}_{D}$ = -7.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, *J* = 6.8, 2.8 Hz, 2H), 7.36 (m, *J* = 3.2, 2.8 Hz, 3H), 7.23 – 7.06 (m, 3H), 7.06 – 6.77 (m, 6H), 5.89 (s, 1H), 5.28 (ddd, *J* = 11.2, 8.9, 2.8 Hz, 1H), 4.33 (d, *J* = 10.4 Hz, 1H), 3.68 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.16 (t, *J* = 10.4 Hz, 1H), 3.04 (dd, *J* = 16.8, 2.8 Hz, 1H), 2.49 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H).

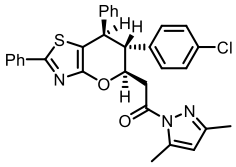
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 163.9, 159.7, 151.8, 144.1, 142.2, 136. 2, 135.4, 133.5, 129.9, 129.4, 128.7, 128.3, 128.3, 128.1, 127.2, 125.7, 111.1, 109.6, 78.0, 53.0, 47.6, 39.1, 2=1.0, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 40.181 min (major), t_R = 56.688 min (minor).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{32}H_{30}N_3O_2S$]$^+$: 520.2053, found: 520.2056



2-((5R,6R,7R)-6-(4-chlorophenyl)-2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one (5d)



White solid (PE/EtOAc/DCM = 10:1:1, 93% isolated yeild, 11:1 dr, 50.3 mg).

m. p.: 176-178 ℃.

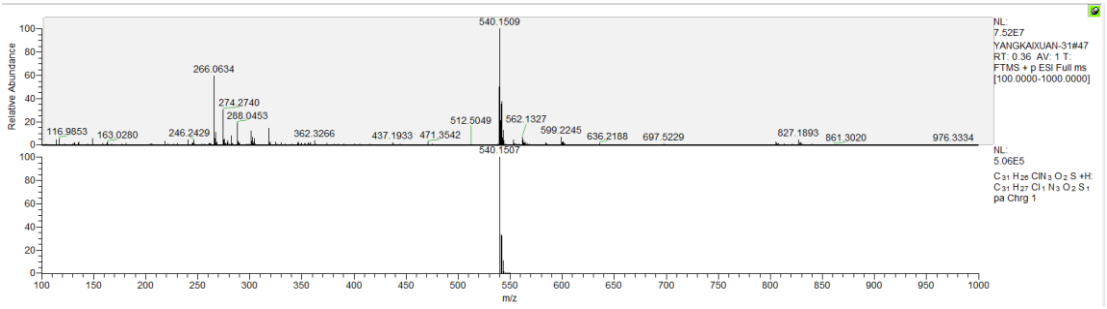
[α]$^{22}_{D}$ = -27.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, CDCl3) δ 7.85 (dt, J = 7.6, 3.2 Hz, 2H), 7.42 – 7.28 (m, 3H), 7.17 (m, 5H), 7.03 – 6.85 (m, 4H), 5.91 (s, 1H), 5.33 – 5.19 (m, 1H), 4.29 (d, J = 10.4 Hz, 1H), 3.64 (dd, J = 16.8, 8.4 Hz, 1H), 3.20 (t, J = 10.4 Hz, 1H), 3.09 (dd, J = 16.8, 3.2 Hz, 1H), 2.49 (s, 3H), 2.18 (s, 3H).

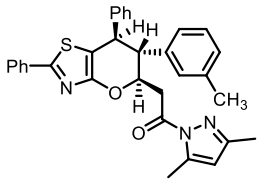
^{13}C NMR (101 MHz, CDCl3) δ 170.1, 164.1, 159.6, 151.9, 144.2, 141.7, 137.0, 133.4, 133.3, 130.0, 129.8, 128.9, 128.76, 128.4, 128.0, 127.5, 125.7, 111.3, 109.2, 77.6, 52.9, 47.7, 39.0, 14.4, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 30.673 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{31}H_{26}ClN_3O_2S$]$^+$: 540.1507, found: 540.1509



1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-((5R,6R,7R)-2,7-diphenyl-6-(m-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (5e)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 95% isolated yeild, 8:1 dr, 51.3 mg).

m. p.: 99-102 ℃.

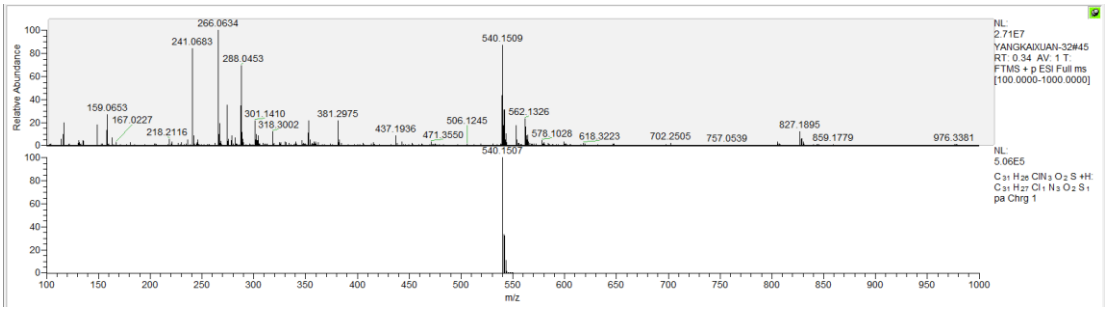
[α]$^{22}_{D}$ = -5.0 (*c* =1.0, CH_2Cl_2, 97% ee).

^{1}H NMR (400 MHz, CDCl3) δ 7.93 – 7.81 (m, 2H), 7.44 – 7.32 (m, 3H), 7.22 – 7.13 (m, 3H), 7.08 (t, J = 7.6 Hz, 1H), 7.01 – 6.88 (m, 3H), 6.80 (d, J = 9.5 Hz, 2H), 5.91 (s, 1H), 5.36 – 5.24 (m, 1H), 4.35 (d, J = 10.0 Hz, 1H), 3.70 (dd, J = 16.8, 9.2 Hz, 1H), 3.15 (t, J = 10.8 Hz, 1H), 3.03 (dd, J = 17.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H).

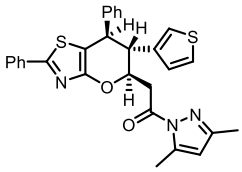
13C NMR (101 MHz, CDCl3) δ 144.2, 142.2, 138.4, 138.3, 133.5, 129.9, 128.8, 128.5, 128.3, 128.2, 128.1, 127.2, 125.7, 111.2, 109.6, 77.9, 53.3, 47.6, 39.0, 21.4, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 29.178 min (major). t_R = 49.0 min (minor)

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{31}H_{27}ClN_3O_2S$]$^+$: 540.1509, found: 540.1507



1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-((5R,6S,7R)-2,7-diphenyl-6-(thiophen-2-yl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (5f)



White solid (PE/EtOAc/DCM = 10:1:1, 98% isolated yeild, 6:1 dr, 50.0 mg).

m. p.: 146-147 ℃.

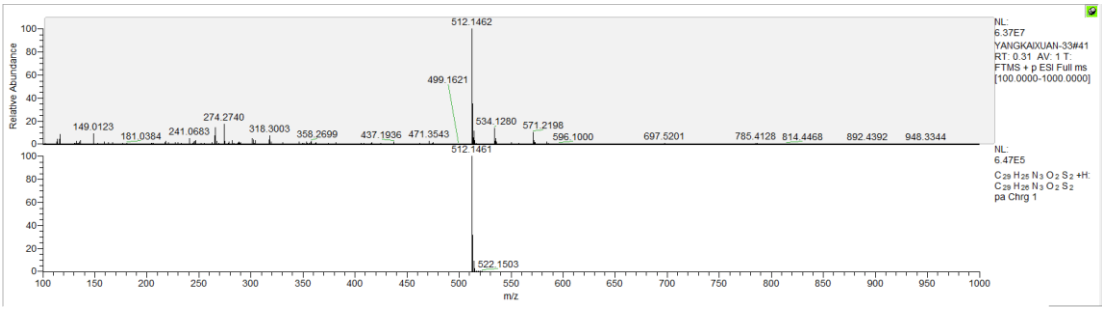
[α]$^{22}_{D}$ = -15.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (m, 2H), 7.39 – 7.32 (m, 3H), 7.25 – 7.18 (m, 3H), 7.16 (m, 1H), 7.07 – 7.00 (m, 2H), 6.82 (dd, *J* = 4.8, 3.0 Hz, 1H), 6.68 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 5.22 (ddd, *J* = 10.8, 9.0, 3.0 Hz, 1H), 4.36 (d, *J* = 10.2 Hz, 1H), 3.75 (dd, *J* = 17.4, 9.0 Hz, 1H), 3.63 (t, *J* = 10.2 Hz, 1H), 3.19 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.53 (d, *J* = 1.1 Hz, 3H), 2.19 (s, 3H).

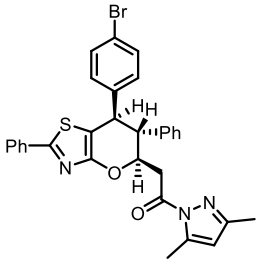
^{13}C NMR (151 MHz, cdcl$_3$) δ 170.2, 165.0, 159.9, 152.0, 144.0, 143.8, 140.6, 133.5, 130.1, 128.8, 128.0, 127.4, 126.6, 126.3, 125.9, 125.0, 111.2, 72.4, 46.5, 45.5, 38.1, 14.4, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 35.996 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{29}H_{26}N_3O_2S_2$]$^+$: 512.1461, found: 512.1462



2-((5R,6R,7R)-7-(4-bromophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one (5g)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 87% isolated yeild, 11:1 dr, 50.8 mg).

m. p.: 78-80 ℃.

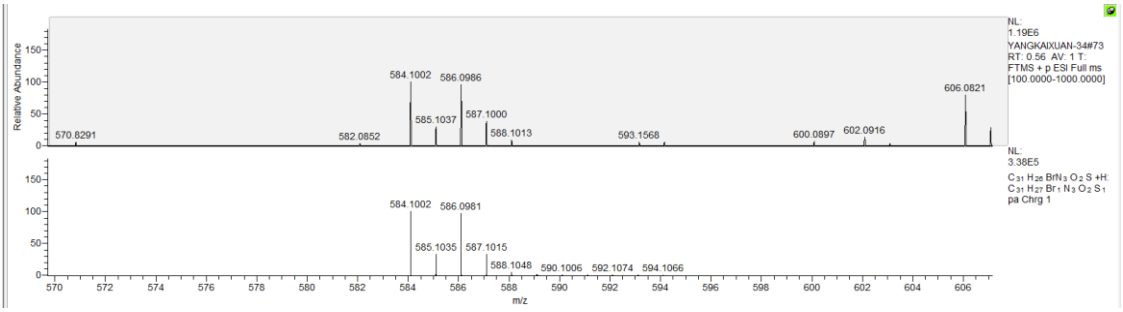
[α]$^{22}_{D}$ = -11.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.77 (m, 2H), 7.47 – 7.13 (m, 8H), 7.12 – 6.93 (m, 2H), 6.91 – 6.70 (m, 2H), 5.90 (d, *J* = 1.2 Hz, 1H), 5.30 (ddd, *J* = 10.8, 8.8, 2.8 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.70 (dd, *J* = 17.2, 9.2 Hz, 1H), 3.14 (t, *J* = 10.4 Hz, 1H), 3.02 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.18 (s, 3H).

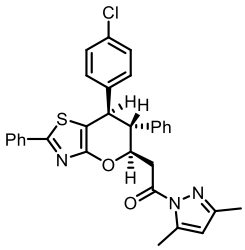
^{13}C NMR (101 MHz, CDCl$_3$) δ 170.3, 164.2, 159.9, 151.9, 144.2, 141.2, 138.2, 133.4, 131.5, 130.1, 129.7, 128.9, 128.8, 128.4, 127.6, 125.7, 121.2, 111.2, 108.6, 77.8, 53.4, 47.3, 38.9, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 42.521 min (major).

HRMS (ESI): [M+H]$^+$ calcdfor [$C_{31}H_{27}BrN_3O_2S$]$^+$: 584.1002, 586.0981, found: 584.1002, 586.0986



2-((5R,6R,7R)-7-(4-chlorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one (5h)



White solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 9:1 dr, 51.8 mg).

m. p.: 124-126 ℃.

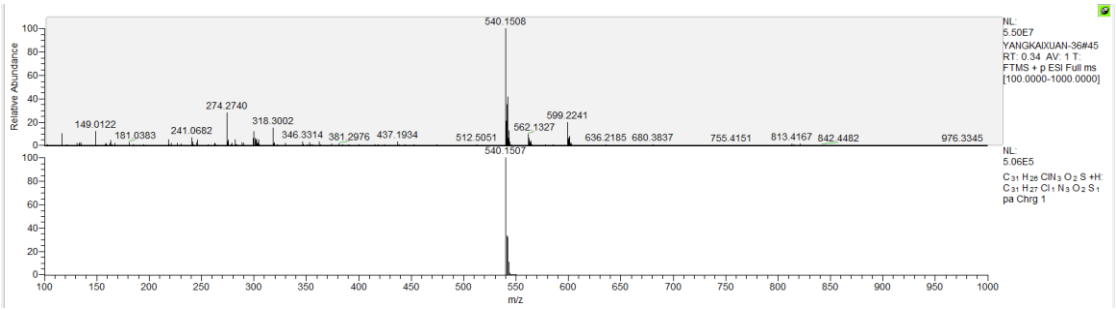
[α]$^{22}_{D}$ = -22.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.74 (m, 2H), 7.53 – 7.31 (m, 3H), 7.25 – 7.09 (m, 5H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.90 (s, 1H), 5.30 (ddd, *J* = 11.2, 8.8, 2.8 Hz, 1H), 4.33 (d, *J* = 10.4 Hz, 1H), 3.70 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.14 (t, *J* = 10.8 Hz, 1H), 3.02 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.17 (s, 3H).

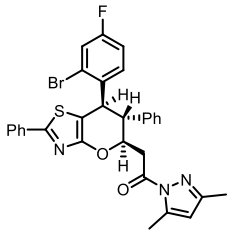
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 164.2, 159.8, 151.9, 144.1, 140.6, 138.2, 133.3, 133.0, 130.0, 129.3, 128.8, 128.8, 128.5, 127.6, 125.7, 111.2, 108.6, 77.7, 53.4, 47.2, 38.9, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 32.774 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{31}H_{27}ClN_3O_2S]^+$: 540.1507, found: 540.1508



2-((5R,6R,7R)-7-(2-bromo-4-fluorophenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one (5i)



Yellow solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yeild, 12:1 dr, 57.5 mg).

m. p.: 74-76 ℃.

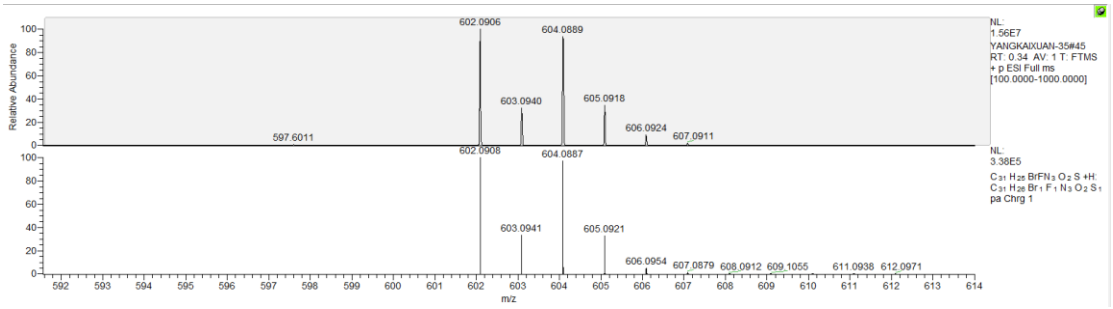
[α]$^{22}_{D}$ = -11.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, 2H), 7.51 – 7.32 (m, 3H), 7.28 – 7.13 (m, 4H), 7.13 – 6.89 (m, 4H), 5.90 (d, *J* = 1.1 Hz, 1H), 5.32 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 3.70 (dd, *J* = 17.2, 9.2 Hz, 1H), 3.27 (t, *J* = 10.4 Hz, 1H), 3.04 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.50 (3, 3H), 2.18 (s, 3H).

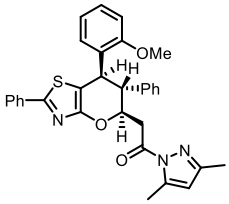
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 164.1, 160.3 (*J* = 250.0 Hz), 159.8, 159.0, 151.9, 144.2, 137.7, 133.3, 130.7, 130.1, 128.9, 128.8, 128.3(*J* =4.3 Hz), 128.1, 127.8, 127.7, 125.7, 121.3(*J* = 4.3 Hz), 119.1, (*J* = 25.7 Hz) 111.2, 107.6, 77.9, 51.8, 38.9, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 72.481 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{31}H_{26}BrFN_3O_2S]^+$: 602.0908, 604.0887 found: 602.0906, 604.0889



1-(3,5-dimethyl-4,5-dihydro-1H-pyrazol-1-yl)-2-((5R,6R,7R)-7-(2-methoxyphenyl)-2,6-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (5j)



White solid (PE/EtOAc/DCM = 10:1:1, 90% isolated yeild, 8:1 dr, 48.2 mg).

m. p.: 118-121 ℃.

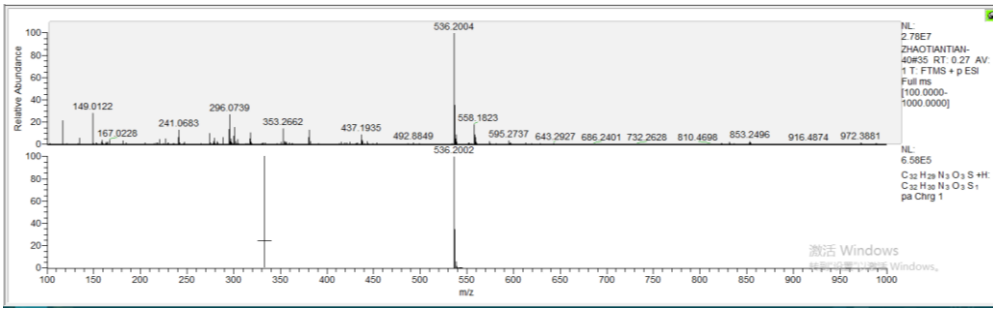
[α]$^{22}_{D}$ = -17.0 (*c* =1.0, CH_2Cl_2, 91% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.75 (m, 2H), 7.35 (m, 3H), 7.23 – 6.95 (m, 7H), 6.94 – 6.56 (m, 2H), 5.90 (d, *J* = 1.1 Hz, 1H), 5.34 (ddd, *J* = 10.4, 9.2, 2.8 Hz, 1H), 4.92 (s, 1H), 3.72 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.41 (s, 4H), 3.01 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.18 (s, 3H).

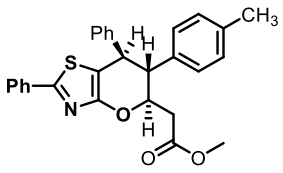
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 163.1, 159.5, 157.1, 151.7, 144.1, 138.9, 133.7, 129.7, 128.7, 128.6, 128.3, 127.1, 125.6, 120.7, 111.1, 110.8, 110.0, 77.9, 55.2, 39.1, 14.5, 13.7.

HPLC (IC, *i*-PrOH/ *n*-hexane = 97/3), flow rate = 1.0 mL/min), t_R = 48.431 min (major), t_R = 56.497 min (minor).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{30}N_3O_3S]^+$: 536.2002, found: 536.2004



methyl 2-((5R,6R,7R)-2,7-diphenyl-6-(p-tolyl)-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)acetate (6c)



White solid (PE/EtOAc/DCM = 10:1:1, 96% isolated yield, 44 mg).

m. p.: 96-99 ℃.

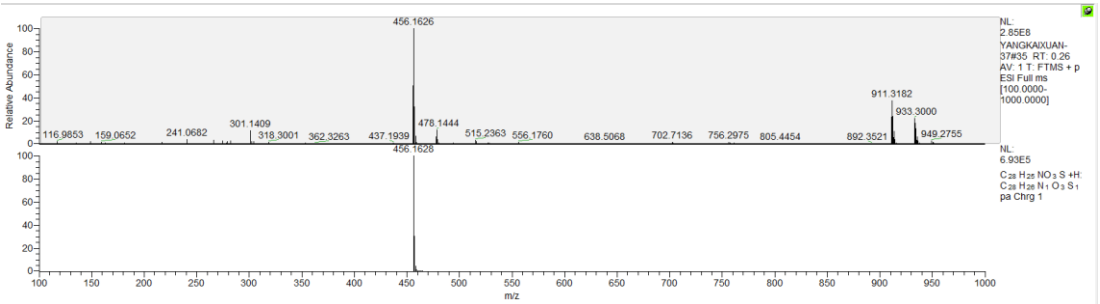
[α]$^{22}_{D}$ = -14.0 (*c* =1.0, CH_2Cl_2, 98% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.53 (s, 1H), 7.43 – 7.37 (m, 5H), 7.07 (q, *J* = 6.0 Hz, 4H), 6.90 (d, *J* = 6.5 Hz, 2H), 5.52 – 5.40 (m, 1H), 4.96 (d, *J* = 6.4 Hz, 1H), 3.59 (m, 2H), 3.16 (dd, *J* = 17.9, 8.0 Hz, 1H).

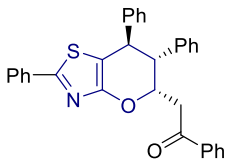
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 164.5, 160.2, 144.8, 139.7, 136.6, 133.4, 133.3, 130.2, 128.9, 128.8, 128.6, 128.5, 128.0, 127.7, 127.4, 127.3, 125.7, 105.5, 72.7, 50.5, 44.4, 40.7.

HPLC (Ic, *i*-PrOH/ *n*-hexane = 90/10), flow rate = 1.0 mL/min), t_R = 38.015min (major), t_R = 48.184min (minor)

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{28}H_{26}NO_3S]^+$: 456.1628, found: 456.1626



1-phenyl-2-((5S,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-one (3a-minor)



White solid (PE/EtOAc/DCM = 10:1:1, 95% isolated yield, 46.3 mg, 99% ee).

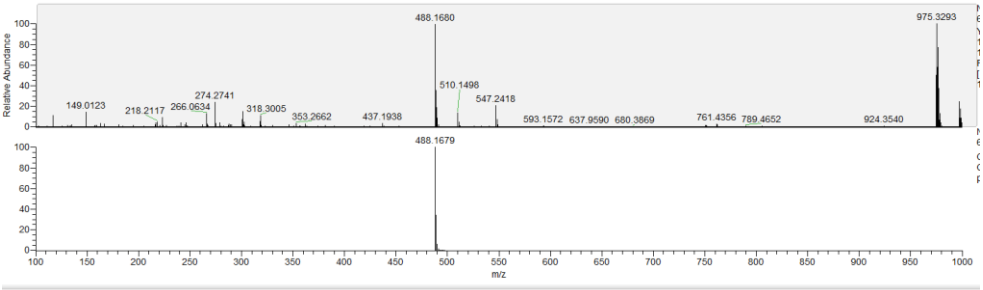
m. p.: 68-69 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.36 (dd, *J* = 6.4, 3.6 Hz, 3H), 7.20 – 7.10 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.98 – 6.79 (m, 4H), 5.00 (ddd, *J* = 11.2, 8.4, 3.6 Hz, 1H), 4.35 – 4.25 (m, 1H), 3.62 (s, 3H), 3.07 (t, *J* = 10.4 Hz, 1H), 2.61 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.46 (dd, *J* = 16.0, 3.6 Hz, 1H), 2.27 (s, 3H).

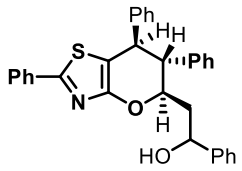
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 164.0, 160.0, 142.0, 137.0, 135.2, 133.5, 129.9, 129.5, 128.7, 128.3, 128.0, 127.2, 125.6, 109.7, 78.2, 52.9, 51.8, 47.3, 38.4, 21.0.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 92/3/5), flow rate = 1.0 mL/min), t_R = 12.779min (major), t_R = 14.048min (minor).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{26}NO_2S]^+$: 488.1679, found: 488.1680



1-phenyl-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-ol-xia (7a-major)



White solid (PE/EtOAc/DCM = 5:1:1, 38% isolated yield, 74.5 mg).

m. p.: 151-152 ℃.

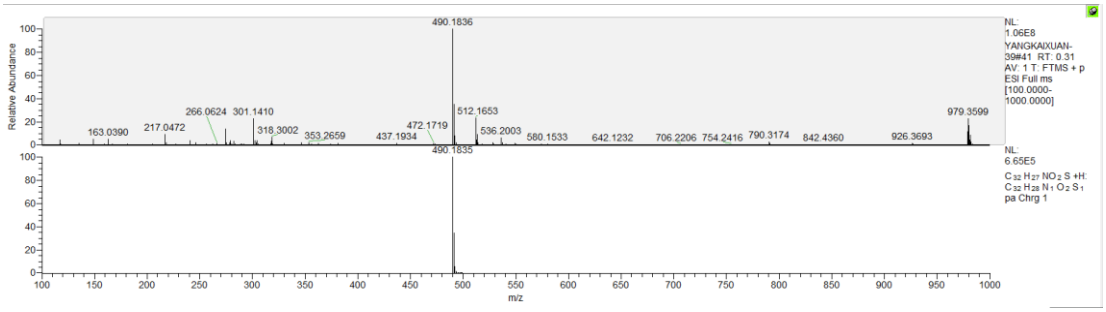
[α]$^{22}_{D}$ = 15.0 (*c* =1.0, CH_2Cl_2, 98% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, *J* = 6.8, 2.8 Hz, 2H), 7.44 – 7.21 (m, 8H), 7.21 – 6.98 (m, 6H), 6.85 (m, *J* = 6.4, 2.8 Hz, 2H), 6.75 (m, *J* = 6.4, 2.8 Hz, 2H), 5.15 (t, *J* = 7.2 Hz, 1H), 4.37 (td, *J* = 10.0, 2.4 Hz, 1H), 4.13 (d, *J* = 10.4 Hz, 1H), 3.17 (s, 1H), 3.01 (t, *J* = 10.3 Hz, 1H), 2.20 (m, 1H), 1.80 (m, 1H).

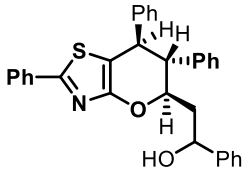
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 159.6, 144.0, 142.0, 138.9, 133.4, 129.9, 128.8, 128.6, 128.4, 128.2, 127.9, 127.6, 127.2, 127.2, 126.5, 125.7, 109.7, 79.9, 71.9, 54.3, 47.6, 42.0.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 92/3/5), flow rate = 1.0 mL/min), t_R = 25.399 min (major).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{28}NO_2S]^+$: 490.1835, found: 490.1836



1-phenyl-2-((5R,6R,7R)-2,6,7-triphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-yl)ethan-1-ol -7a-minor



White solid (PE/EtOAc/DCM = 5:1:1, 29% isolated yield, 56.8mg).

m. p.: 144-146 ℃.

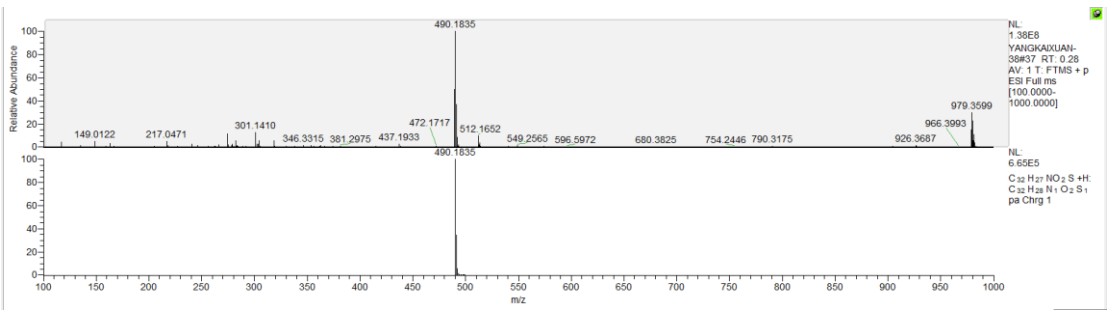
[α]$^{22}_{D}$ = 15.0 (*c* =1.0, CH_2Cl_2, 99% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.81 (m, 2H), 7.45 – 7.34 (m, 3H), 7.26 (m, *J* = 6.4 Hz, 5H), 7.22 – 7.06 (m, 7H), 6.94 – 6.76 (m, 4H), 5.35 (d, *J* = 10.4 Hz, 1H), 5.02 – 4.86 (m, 1H), 4.17 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.03 (dt, *J* = 20.8, 10.4 Hz, 2H), 1.87 (m, 1H), 1.81 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 164.0, 160.0, 142.1, 137.0, 135.2, 133.5, 129.9, 129.5, 128.7, 128.3, 128.0, 127.2, 125.6, 109.7, 78.2, 52.9, 51.8, 47.3, 38.4, 21.0.

HPLC (IH, *i*-PrOH/ *n*-hexane/DCM = 92/3/5), flow rate = 1.0 mL/min), t_R = 12.779 min (major), t_R = 16.048 min (minor).

HRMS (ESI): $[M+H]^+$ calcdfor $[C_{32}H_{28}NO_2S]^+$: 490.1835, found: 490.1835



5 X-ray Crystallographic Data

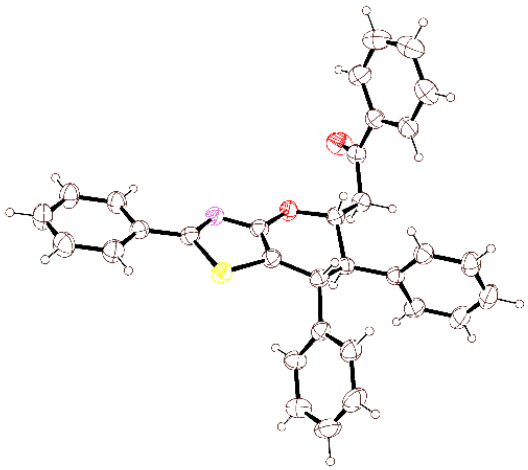
5. 1. Preparation of crystal.

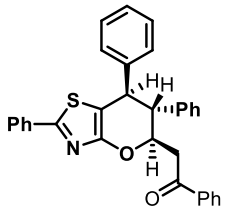
3a-major: The pure compouds (50 mg) of **3a-major** was dissolved in CDCl3 and removed in NMR tube. After the NMR experiments were finished, the tube was placed in the lab for about one week, during which the crystal was formed. The X-ray was detected after the crystal was formed. The X-ray data was detected by Smart APEX II which was purchased from Bruker.

3a-minor: The pure compouds (50 mg) of **3a-minor** was dissolved in DCM in the small bottle,and then the CH_3OH was added slowly until a small amount of precipitation occurs. Continue to add a small amount of DCM to dissolve the precipitate. Place the small bottle in a dry and ventilated place for about one week, during which the crystal was formed. The X-ray data was detected by Smart APEX II which was purchased from Bruker.

3e: The pure compouds (50 mg) of **3e** was dissolved in DCM in the small bottle, and then the CH_3OH was added slowly until a small amount of precipitation occurs. Continue to add a small amount of DCM to dissolve the precipitate. Place the small bottle in a dry and ventilated place for about one week, during which the crystal was formed. The X-ray data was detected by Smart APEX II which was purchased from Bruker.

5. 2 X-ray Crystallographic Data





CCDC 2115385

Bond precision: C-C = 0.0046 A Wavelength=1.54184

Cell: a=11.9830(2) b=13.0537(3) c=16.2653(3)
alpha=90 beta=90 gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	2544.26(9)	2544.27(8)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C32 H25 N O2 S	C32 H25 N O2 S
Sum formula	C32 H25 N O2 S	C32 H25 N O2 S
Mr	487.59	487.59
Dx,g cm-3	1.273	1.273
Z	4	4
Mu (mm-1)	1.359	1.359
F000	1024.0	1024.0
F000'	1028.04	
h,k,lmax	15,16,20	14,16,20
Nref	5428[3057]	5047
Tmin,Tmax	0.907,0.934	0.436,1.000
Tmin'	0.897	

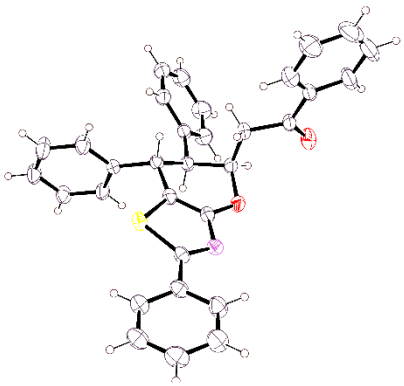
Correction method= # Reported T Limits: Tmin=0.436 Tmax=1.000
AbsCorr = MULTI-SCAN

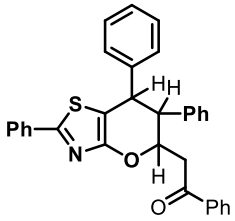
Data completeness= 1.65/0.93 Theta(max)= 77.584

R(reflections)= 0.0374(4304) wR2(reflections)= 0.1010(5047)

S = 1.042 Npar= 325

Displacement ellipsoids are drawn at 30% probability level





CCDC 2115385

Bond precision: C-C = 0.0046 A Wavelength=1.54184

Cell: a=11.9830(2) b=13.0537(3) c=16.2653(3)
alpha=90 beta=90 gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	2544.26(9)	2544.27(8)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C32 H25 N O2 S	C32 H25 N O2 S
Sum formula	C32 H25 N O2 S	C32 H25 N O2 S
Mr	487.59	487.59
Dx,g cm-3	1.273	1.273
Z	4	4
Mu (mm-1)	1.359	1.359
F000	1024.0	1024.0
F000'	1028.04	
h,k,lmax	15,16,20	14,16,20
Nref	5428[3057]	5047
Tmin,Tmax	0.907,0.934	0.436,1.000
Tmin'	0.897	

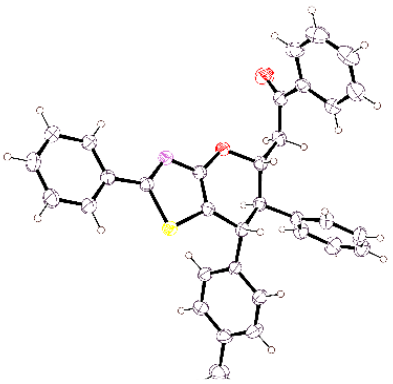
Correction method= # Reported T Limits: Tmin=0.436 Tmax=1.000
AbsCorr = MULTI-SCAN

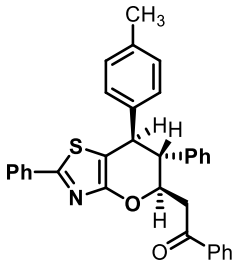
Data completeness= 1.65/0.93 Theta(max)= 77.584

R(reflections)= 0.0374(4304) wR2(reflections)= 0.1010(5047)

S = 1.042 Npar= 325

Displacement ellipsoids are drawn at 30% probability level





CCDC 2118175

Bond precision: C-C = 0.0041 A Wavelength=1.54184

Cell: a=12.0118(2) b=12.7811(2) c=16.9520(3)
alpha=90 beta=90 gamma=90

Temperature: 303 K

	Calculated	Reported
Volume	2602.54(8)	2602.54(8)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C33 H27 N O2 S	C33 H27 N O2 S
Sum formula	C33 H27 N O2 S	C33 H27 N O2 S
Mr	501.62	501.61
Dx,g cm-3	1.280	1.280
Z	4	4
Mu (mm-1)	1.343	1.343
F000	1056.0	1056.0
F000'	1060.11	
h,k,lmax	15,16,21	14,15,21
Nref	5435[3062]	4657
Tmin,Tmax	0.886,0.935	0.099,1.000
Tmin'	0.886	

Correction method= # Reported T Limits: Tmin=0.099 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.52/0.86 Theta(max)= 75.994

R(reflections)= 0.0344(4158) wR2(reflections)= 0.0895(4657)

S = 1.007 Npar= 336

Displacement ellipsoids are drawn at 30% probability level

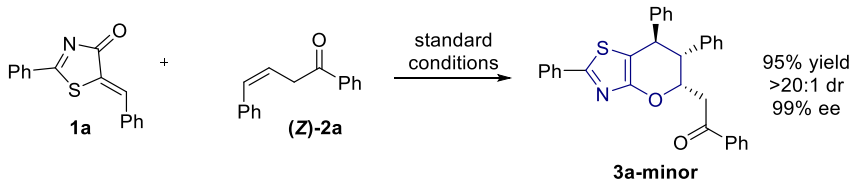
6 The Discussion and Determination of Absolute Configuration of Compound 3a2 and Some Mechanism Vrification Eperiment

6.1 The Discussion and Determination of Absolute Configuration of Compound 3a2

3a[1] and 3a[2] was a pair of enantiomers, The decision configuration of 3a[1] is determined by X-ray crystal, while the relative configuration of 3a[2] is determined by X-ray crystal. Both compounds are attacked by the same ***re*** face, and the same three-dimensional configuration is obtained by one attack. Therefore, the absolute configuration of 3a[2] can be determined. At the same time, it can also be determined that such substrate diastereomers produce in catalysts controling unsaturated carbonyl compounds to produce dienlote.

6.2 some mechanism verification experiment

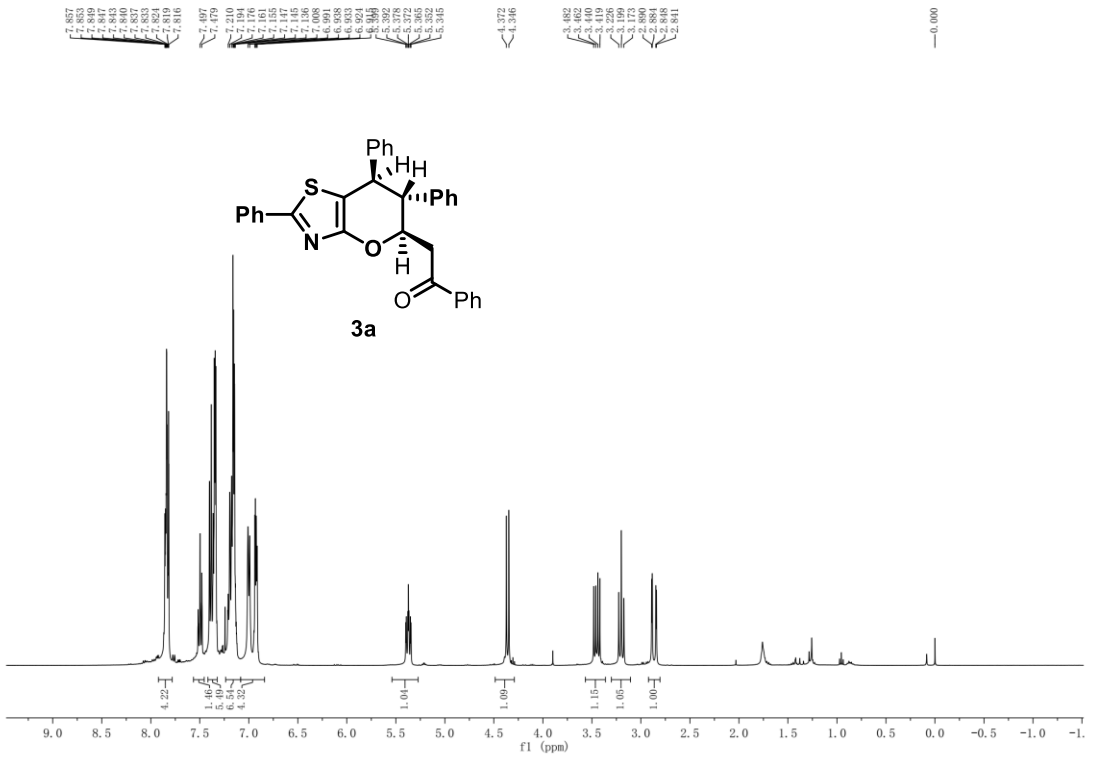
We isolated the 0.5 mmol Z-alkene (in 20 mmol scale reaction) from the mixture of the corresponding acetophenone, phenylacetylene and KO*t*Bu in DMSO. The by-products in the system were identified as Z-alkenes by NMR.



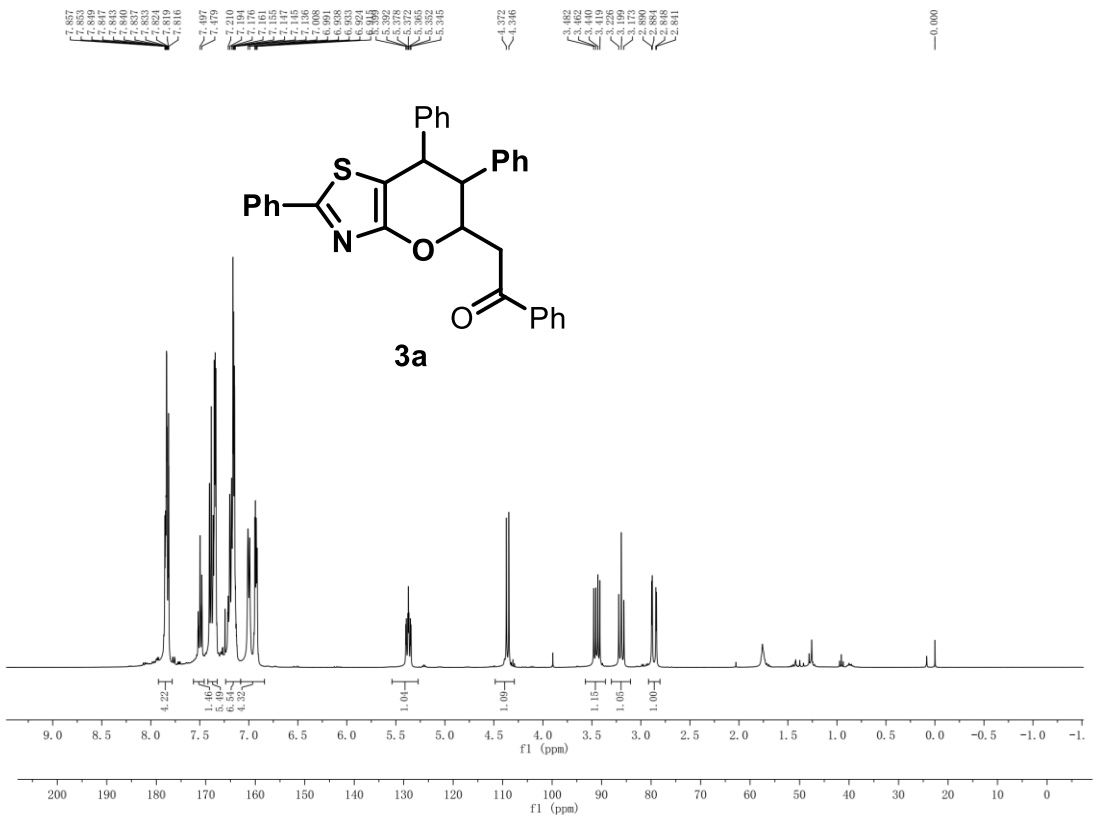
We placed Z-*β*, ***γ***-unsaturated ketone **(*Z*)-2a** (1.25eq) and 5-alkenylthiazolone **1a** under optimal reaction conditions (0.1mmol, 10 mol% cat A, 0 ℃), the minor product of **3a** in the template reaction was obtained with good results (95% yield, >20:1 dr, 99% ee). Therefore, this results are consistent with the postulate mechanism in Figure 1 of manuscript.

7 HPLC and NMR Spectrogram

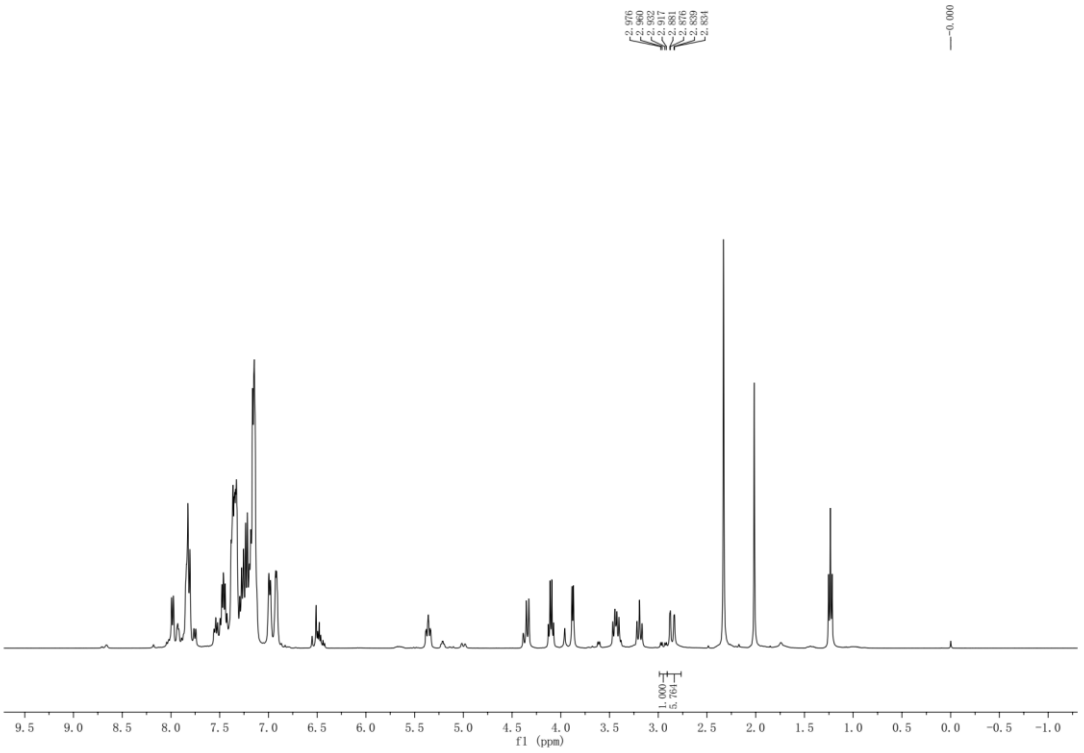
^{1}HNMR of **3a** (400M, $CDCl_3$)



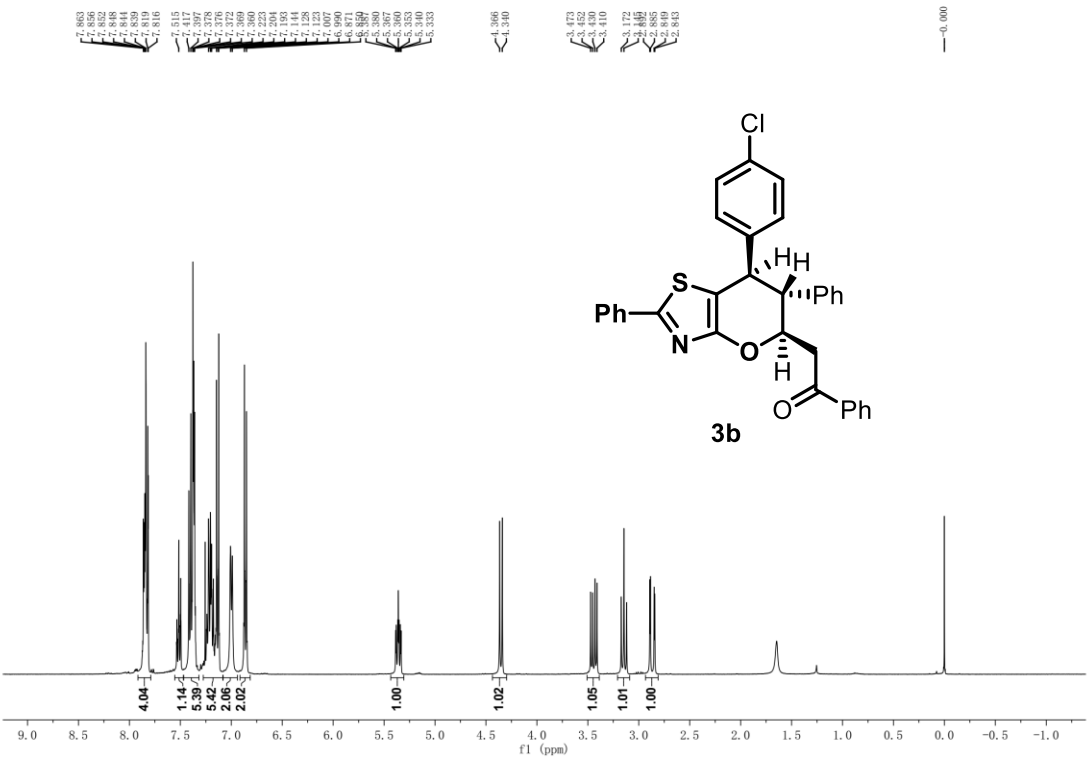
Crude ^{1}HNMR of **3a** (400M, $CDCl_3$)



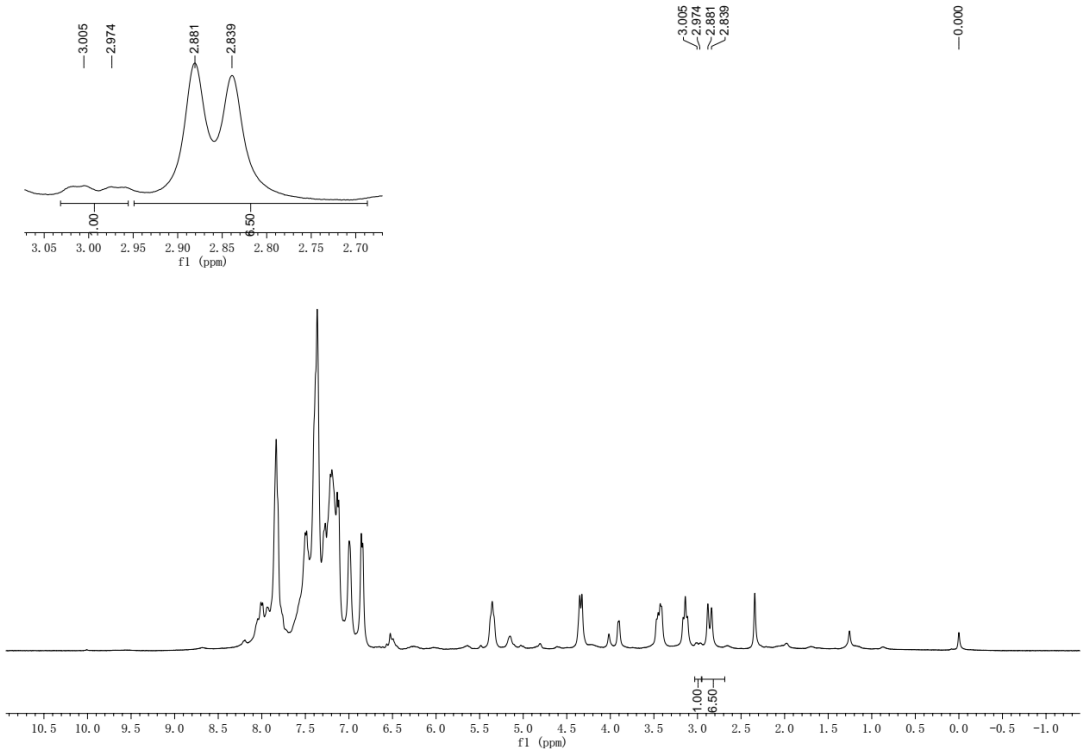
^{13}CNMR of **3a** (101M, $CDCl_3$)



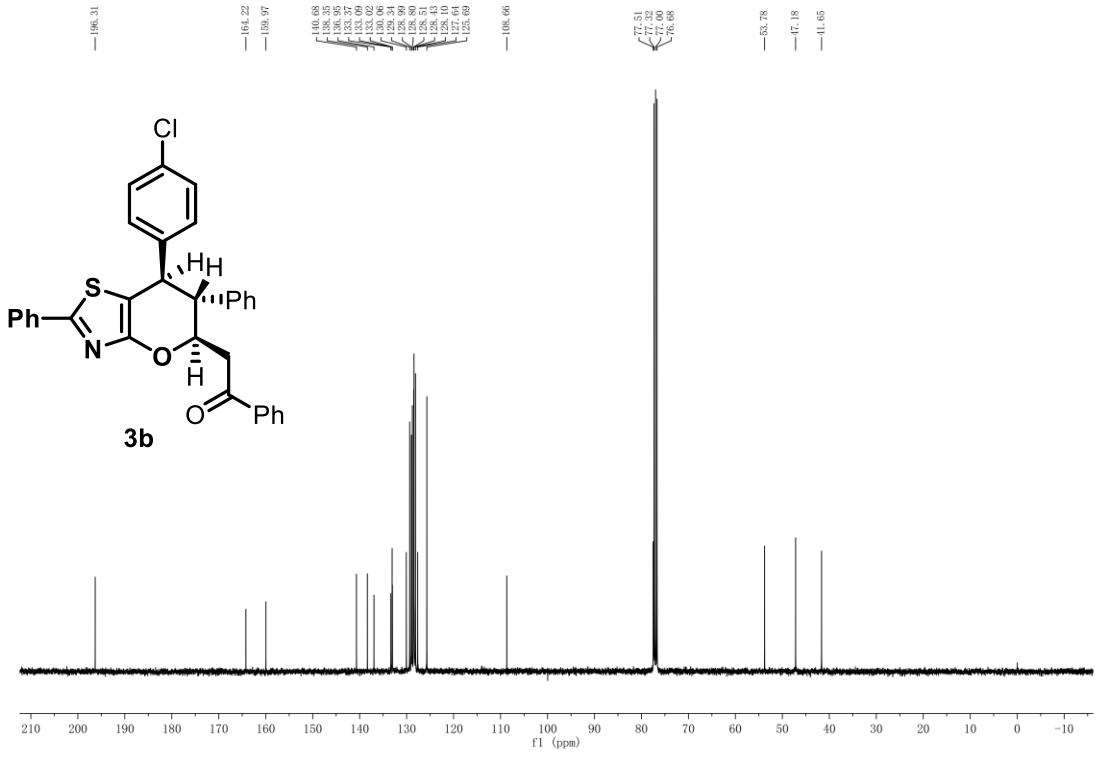
^{1}HNMR of **3b** (400M, $CDCl_3$)



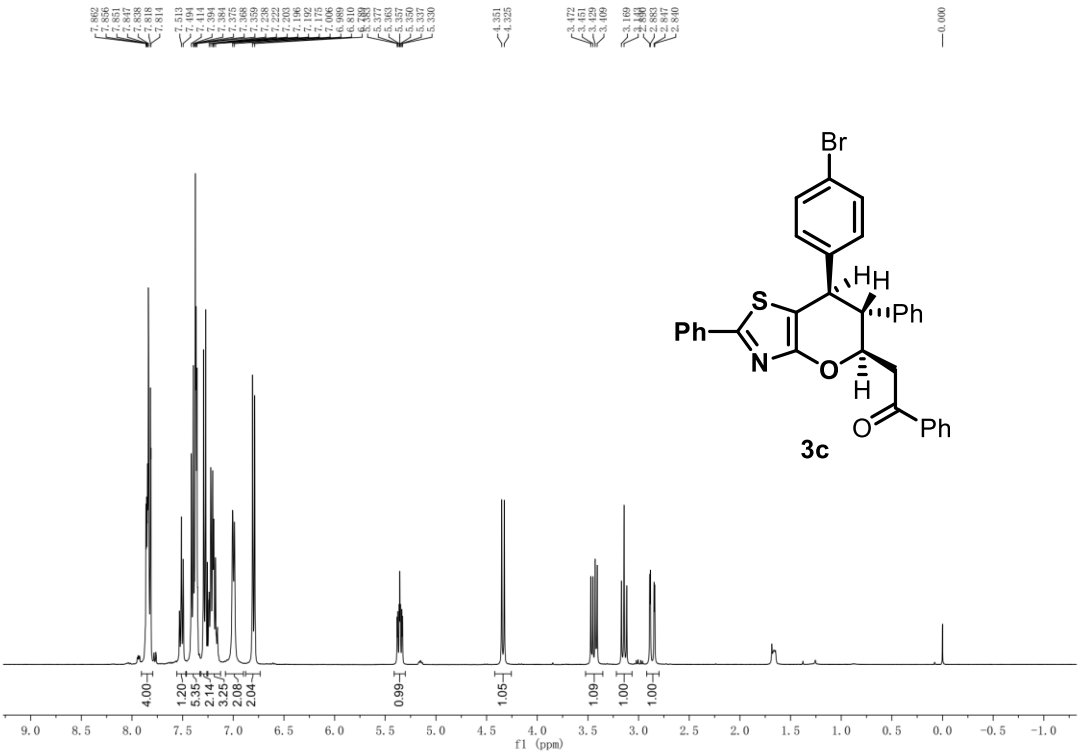
Crude ^{1}HNMR of **3b** (400M, $CDCl_3$)



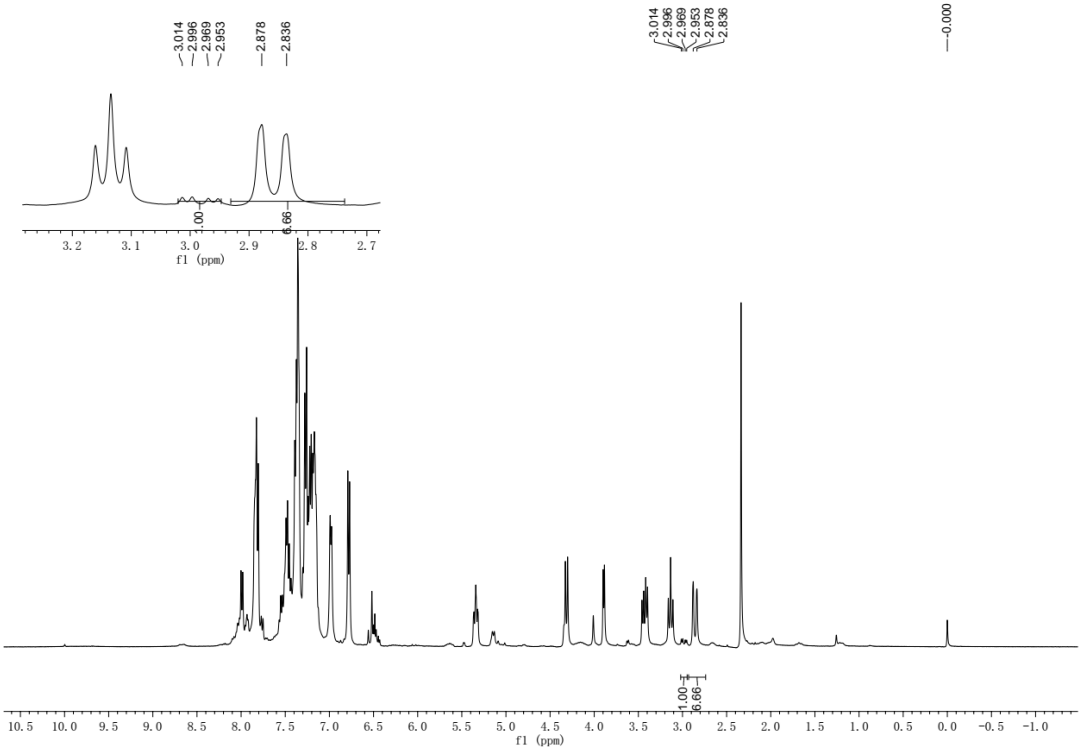
^{13}CNMR of **3b** (101M, $CDCl_3$)



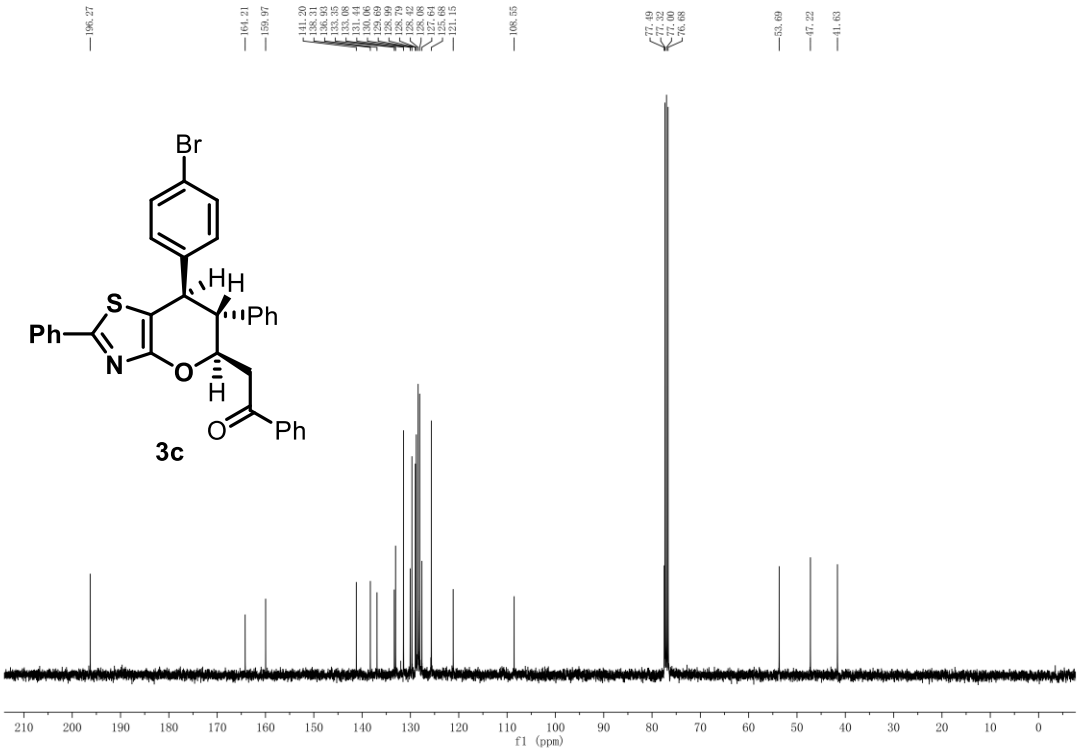
^{1}HNMR of **3c** (400M, $CDCl_3$)



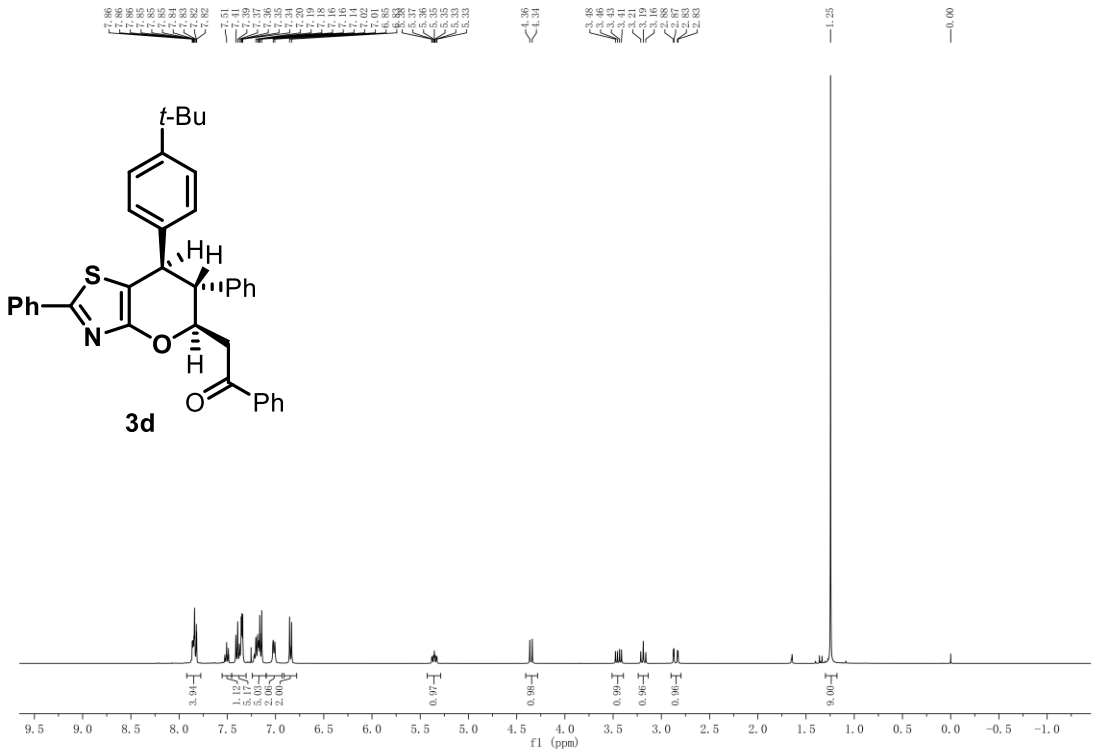
Crude ^{1}HNMR of **3c** (400M, $CDCl_3$)



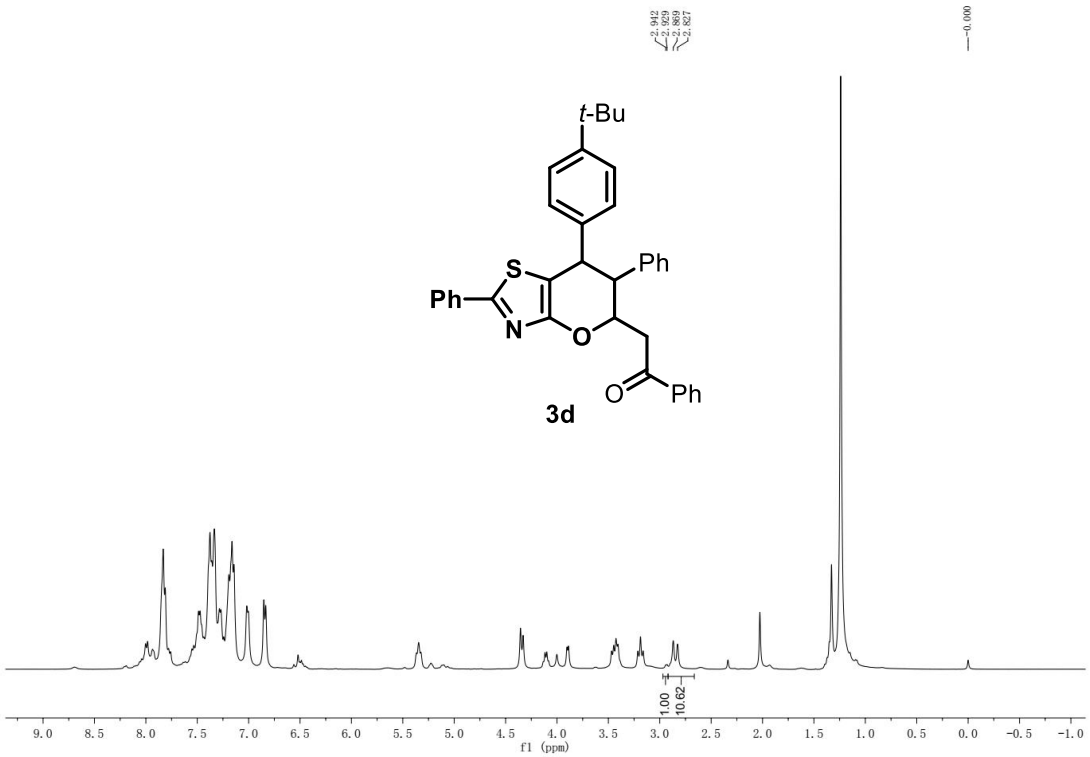
^{13}CNMR of **3c** (101M, $CDCl_3$)



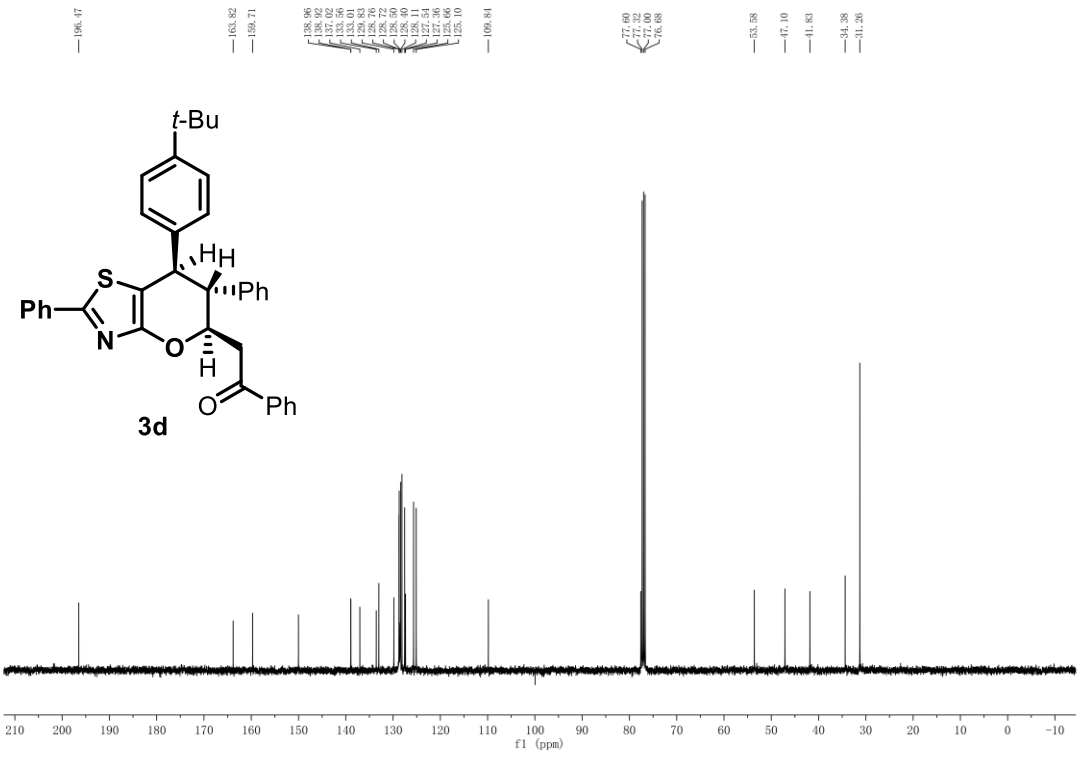
^{1}HNMR of **3d** (400M, $CDCl_3$)



Crude ^{1}HNMR of **3d** (400M, $CDCl_3$)



^{13}CNMR of **3d** (101M, $CDCl_3$)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159.71
138.96
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137.02
133.56
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128.76
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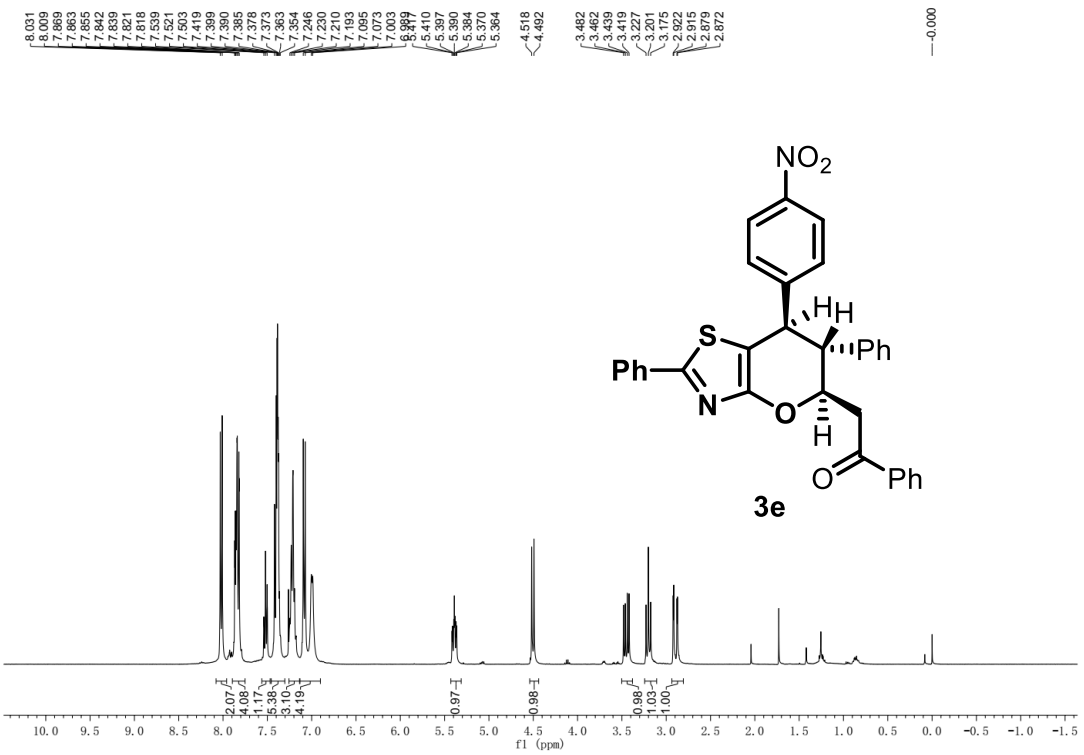
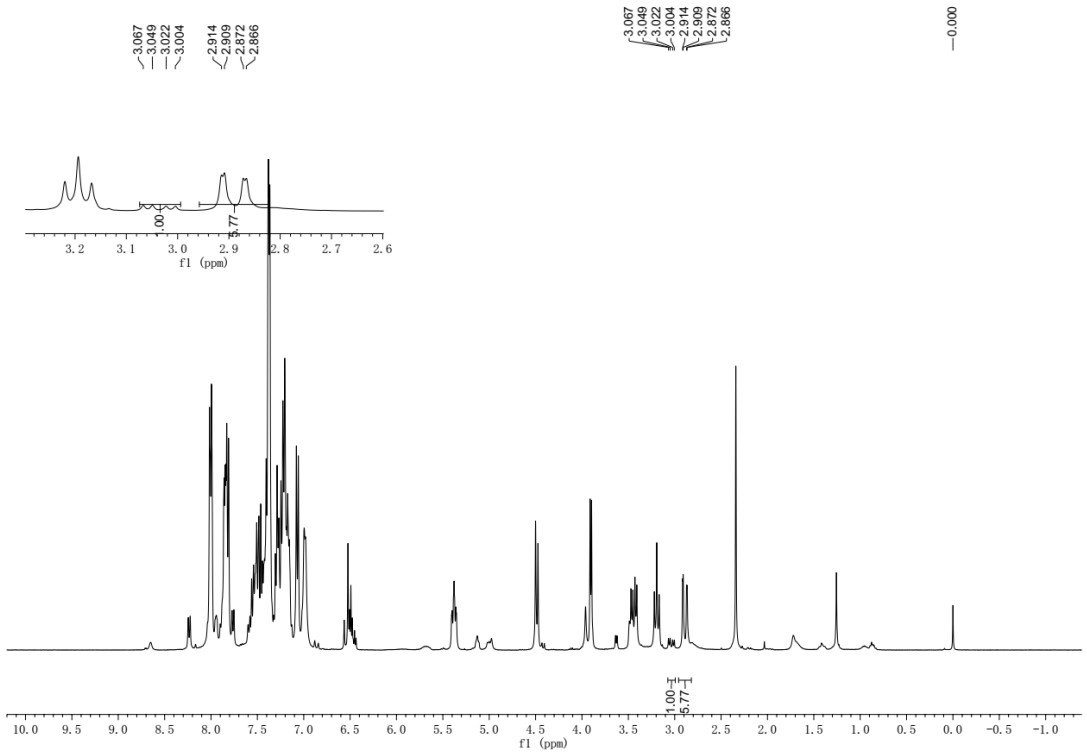
128.50
128.40
128.11
127.54
127.36
125.66
125.10
109.84
77.69
77.32
77.00
76.68
53.58
47.10
41.83
34.38
31.26
t-Bu
Ph
S
N
O
H
H
Ph
H
O
Ph
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

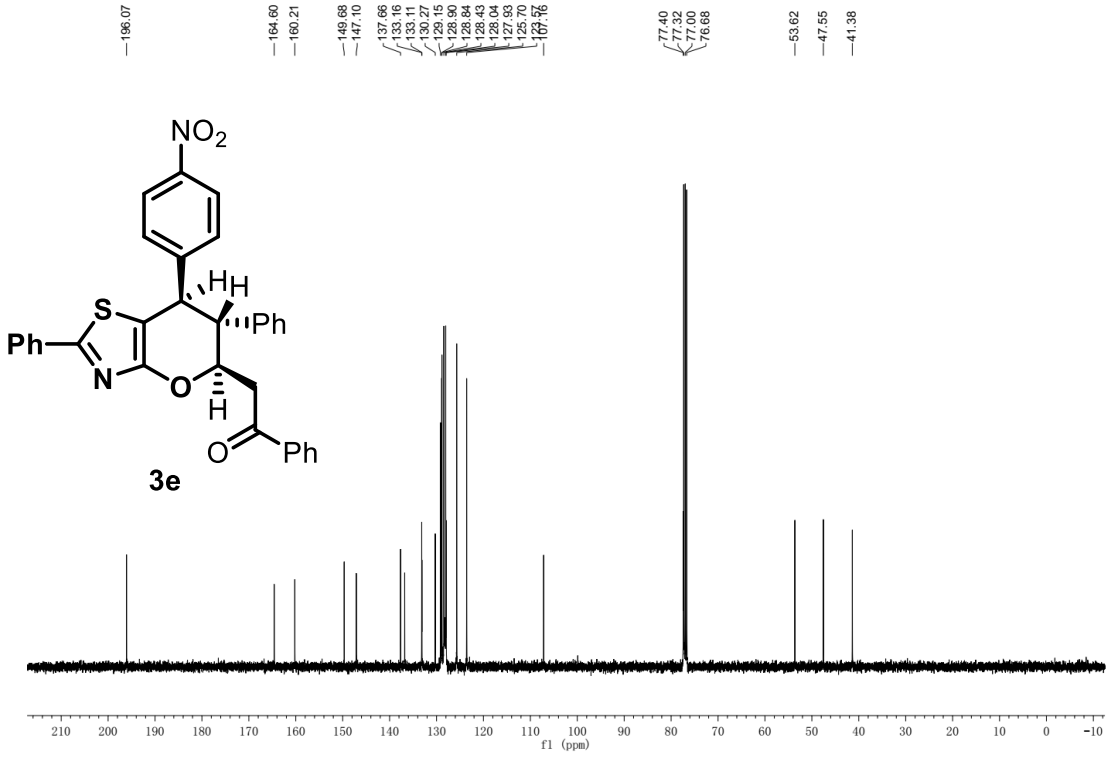
[1]HNMR of **3e** (400M, $CDCl_3$)



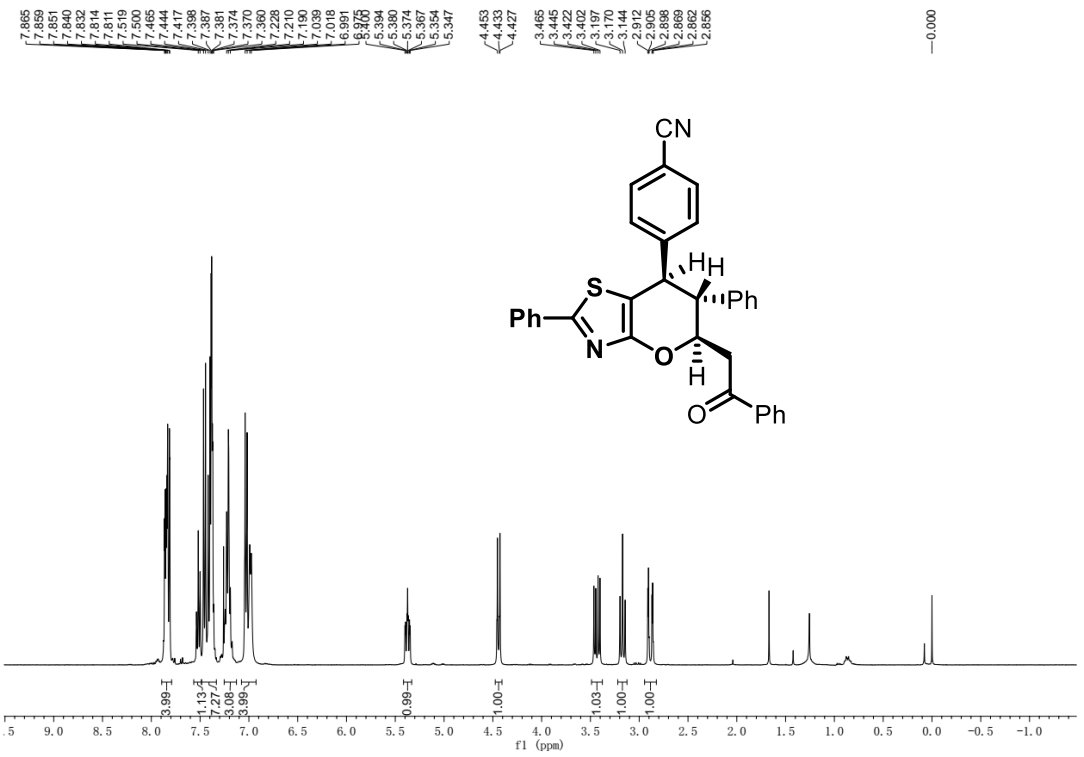
Crude [1]HNMR of **3e** (400M, $CDCl_3$)



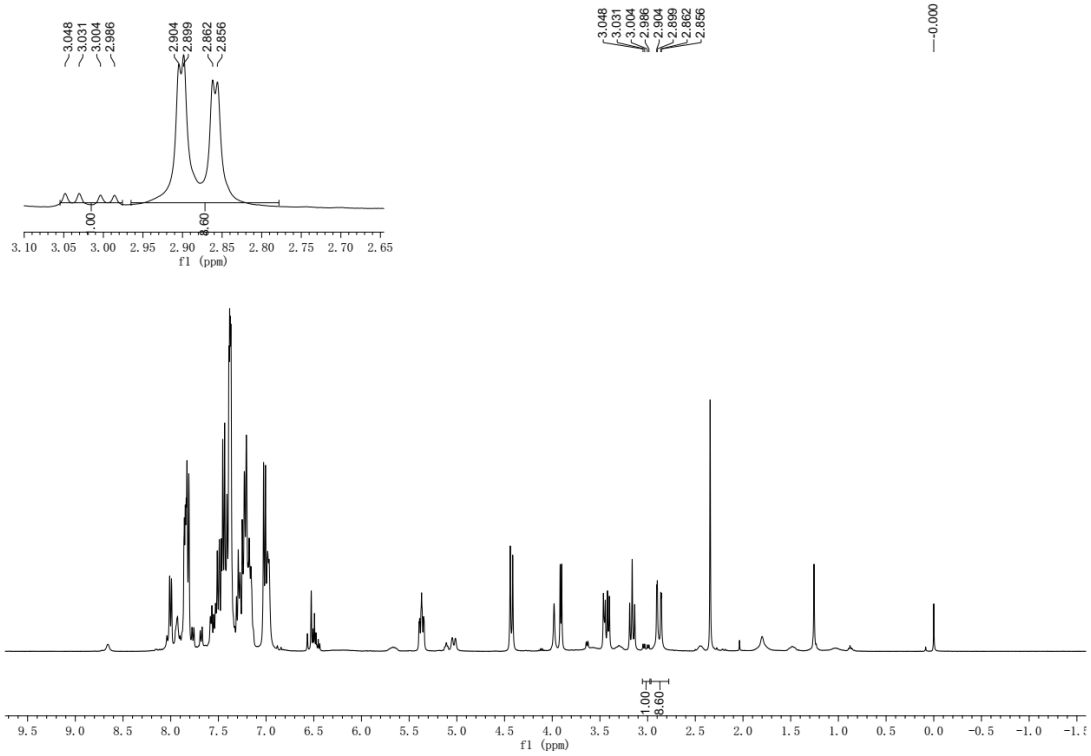
^{13}CNMR of **3e** (101M, $CDCl_3$)



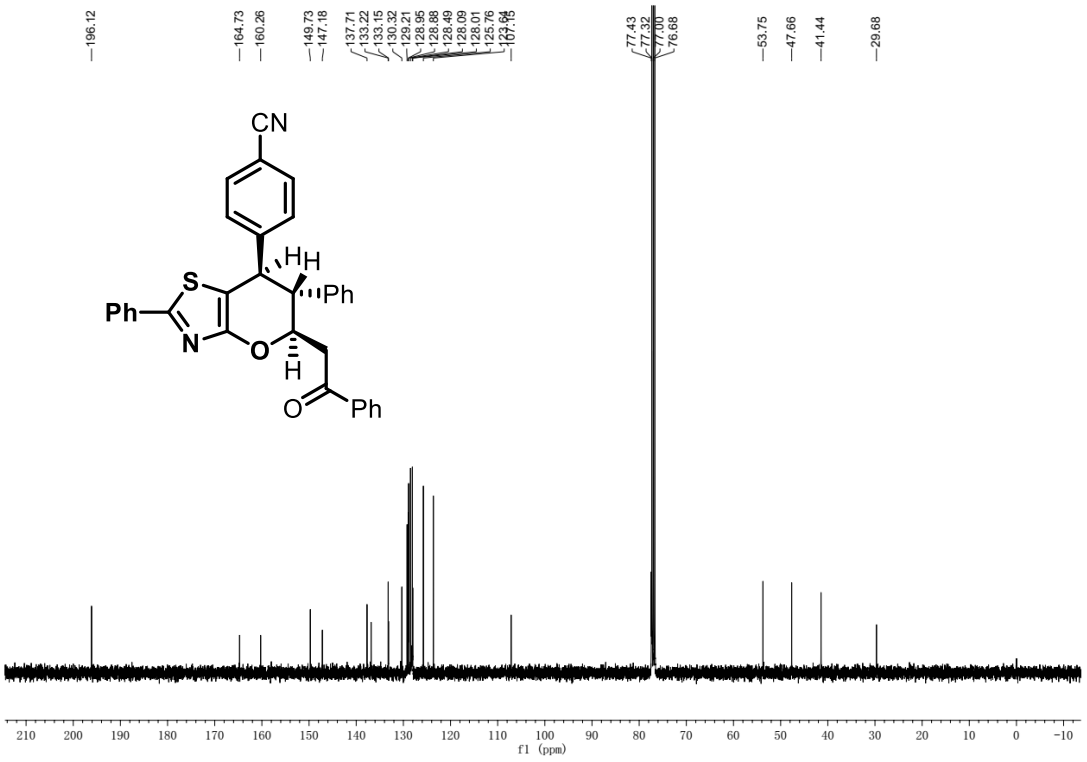
[1]HNMR of **3f** (400M, $CDCl_3$)



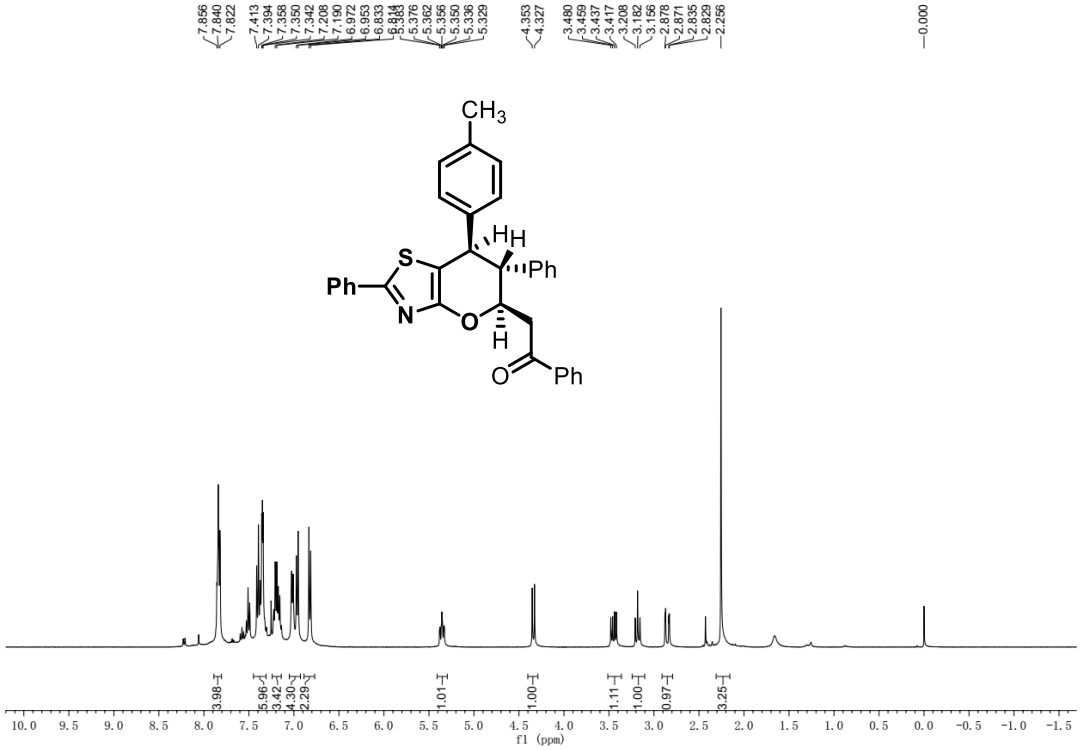
Crude [1]HNMR of **3f** (400M, $CDCl_3$)



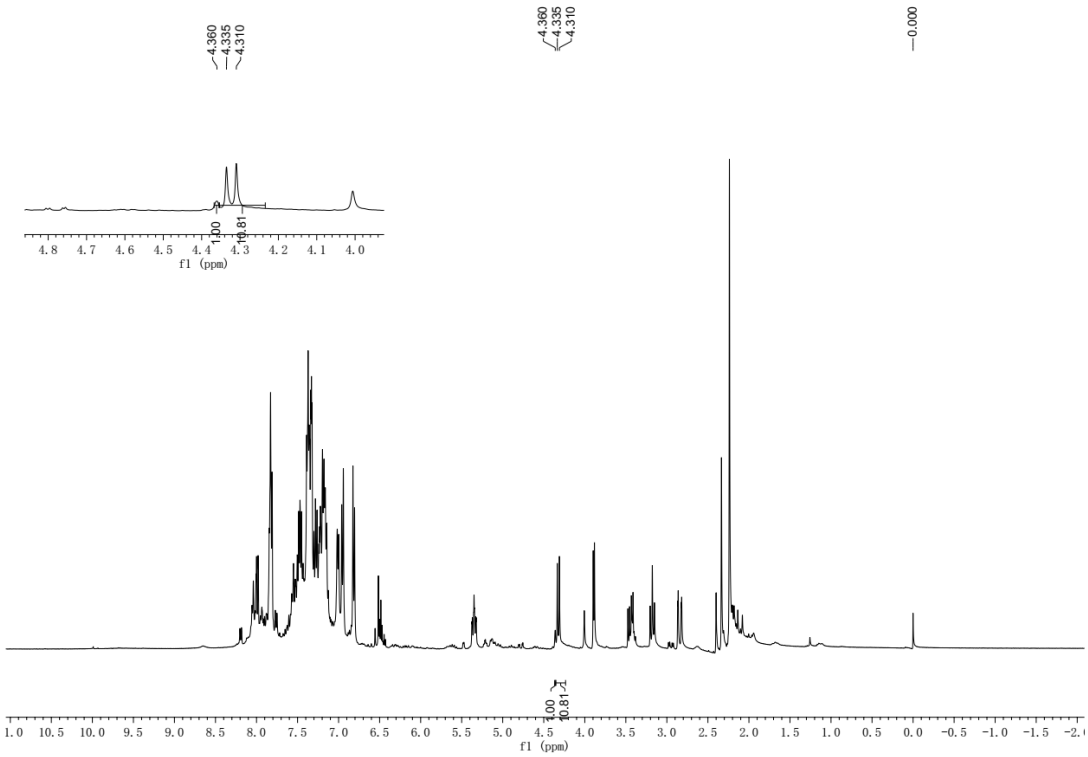
^{13}CNMR of **3f** (101M, $CDCl_3$)



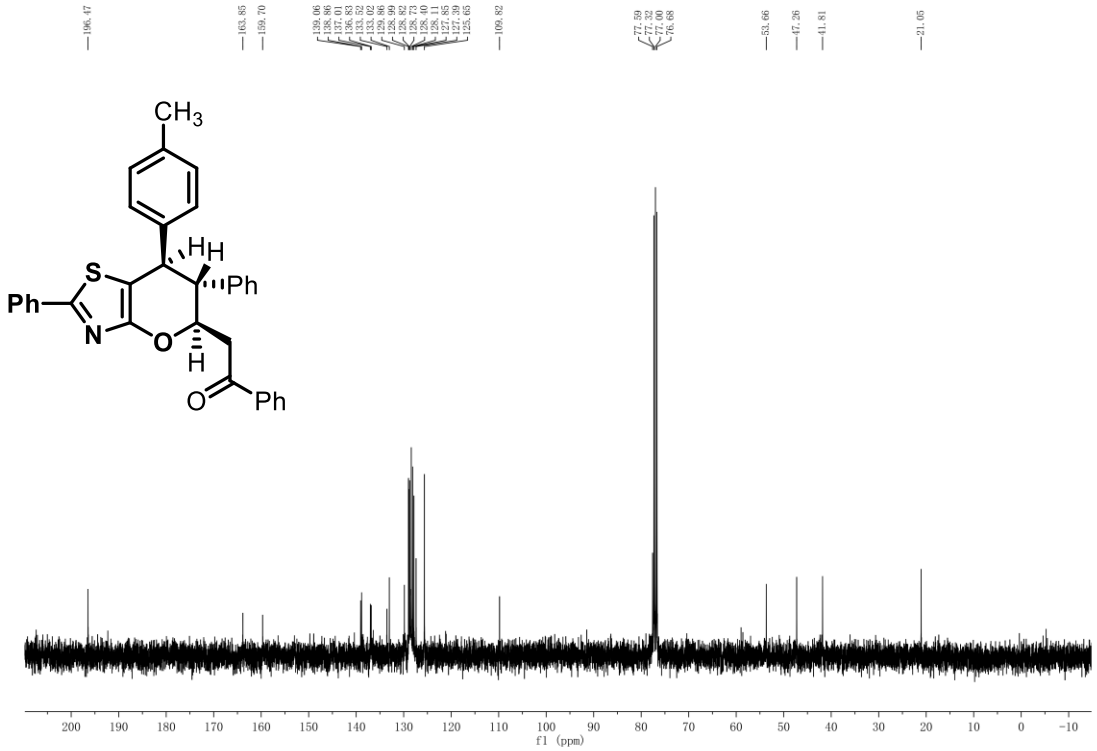
^{1}HNMR of **3g** (400M, $CDCl_3$)



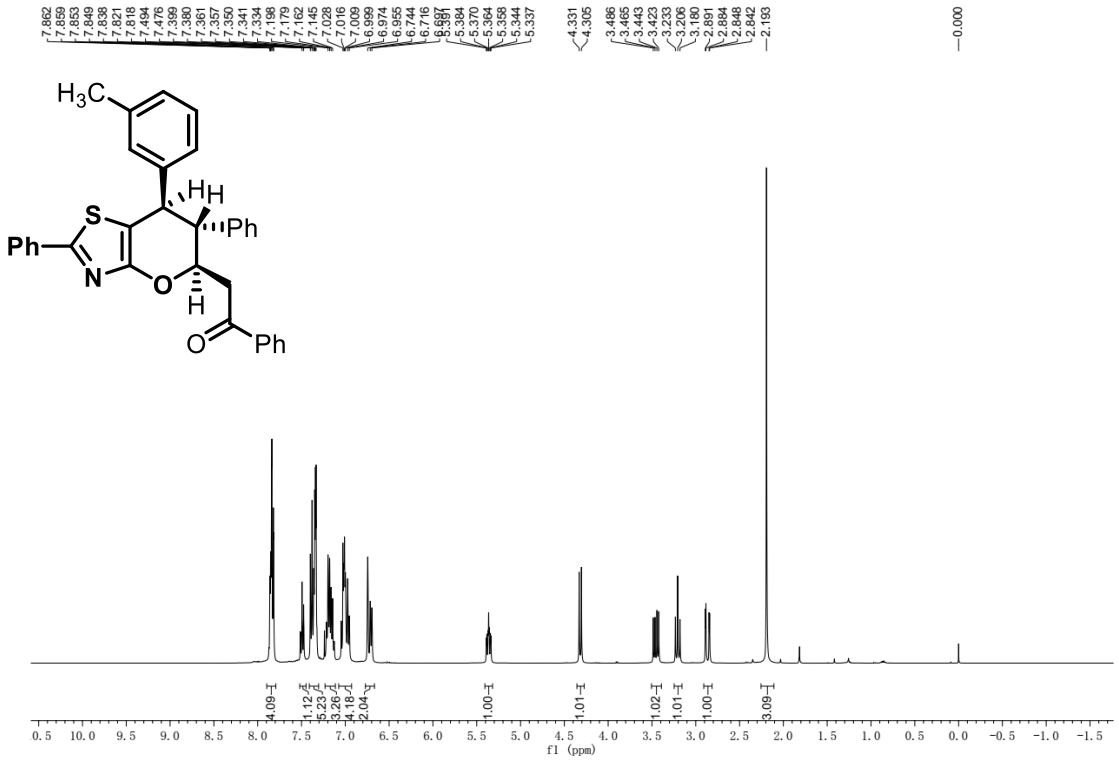
Crude ^{1}HNMR of **3g** (400M, $CDCl_3$)



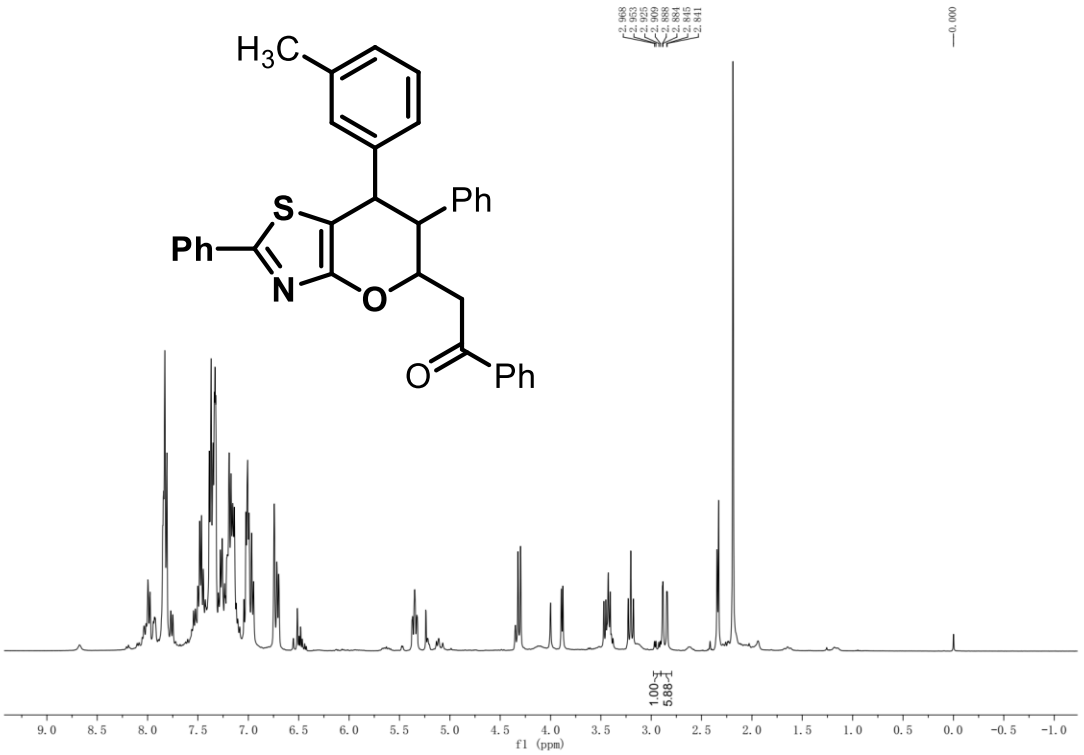
^{13}CNMR of **3g** (101M, $CDCl_3$)



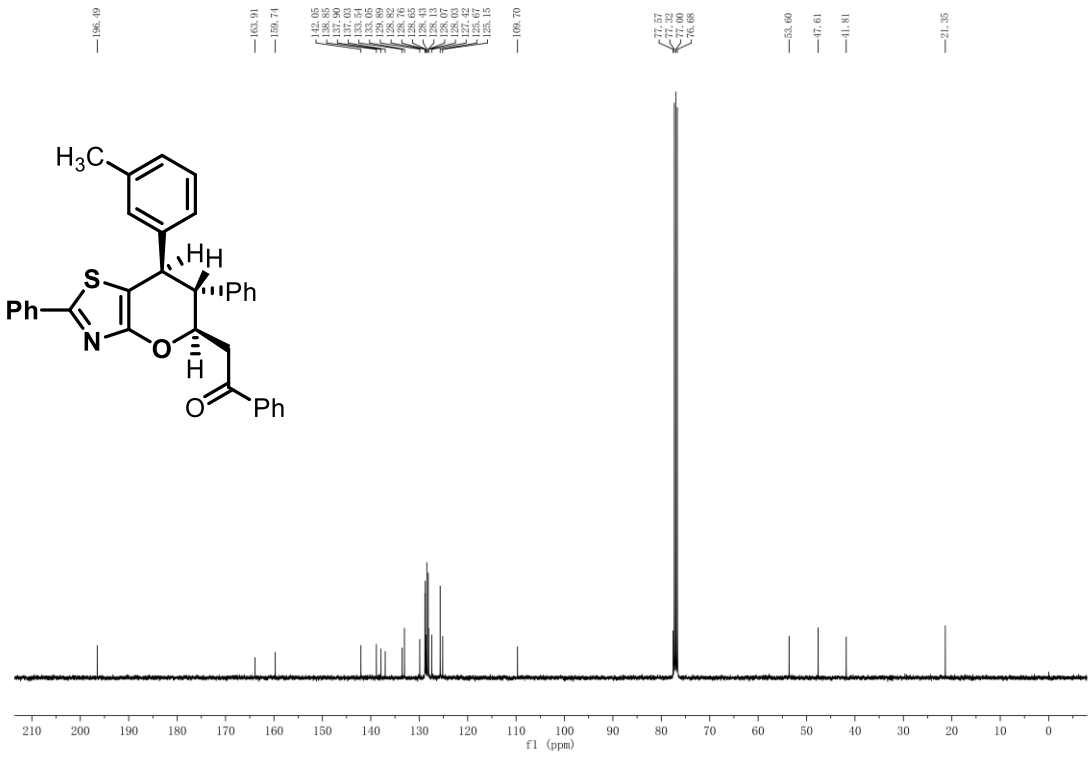
[1]HNMR of **3h** (400M, CDCl3)



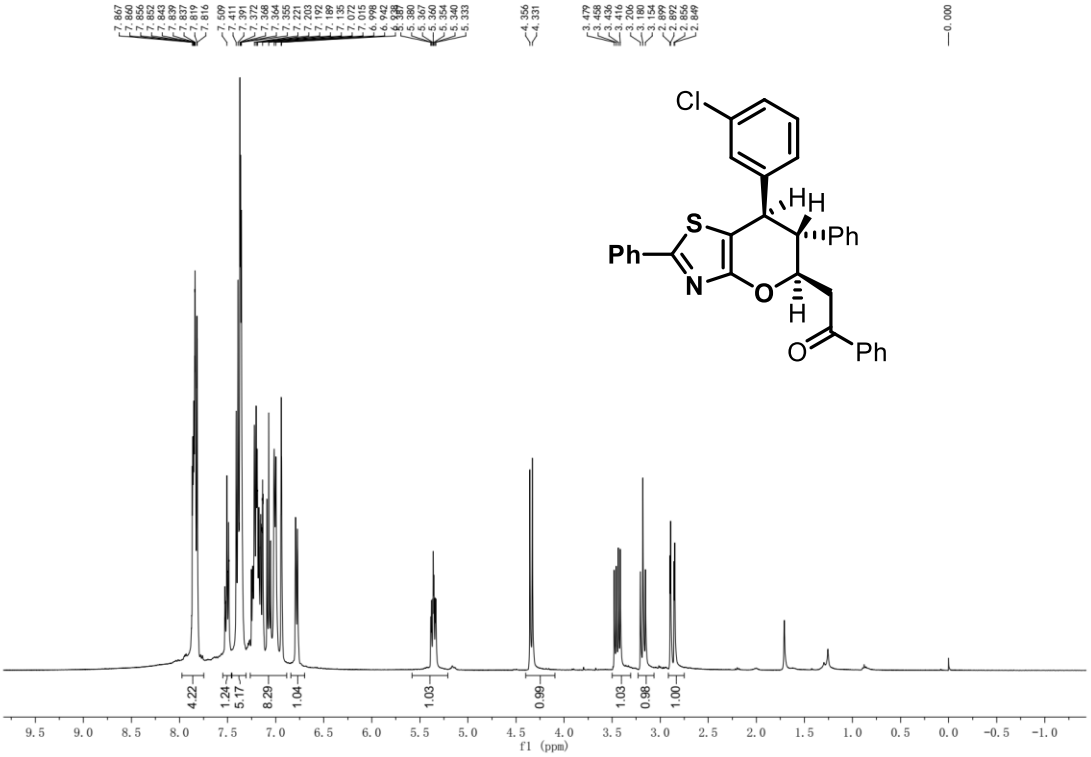
Crude [1]HNMR of **3h** (400M, $CDCl_3$)



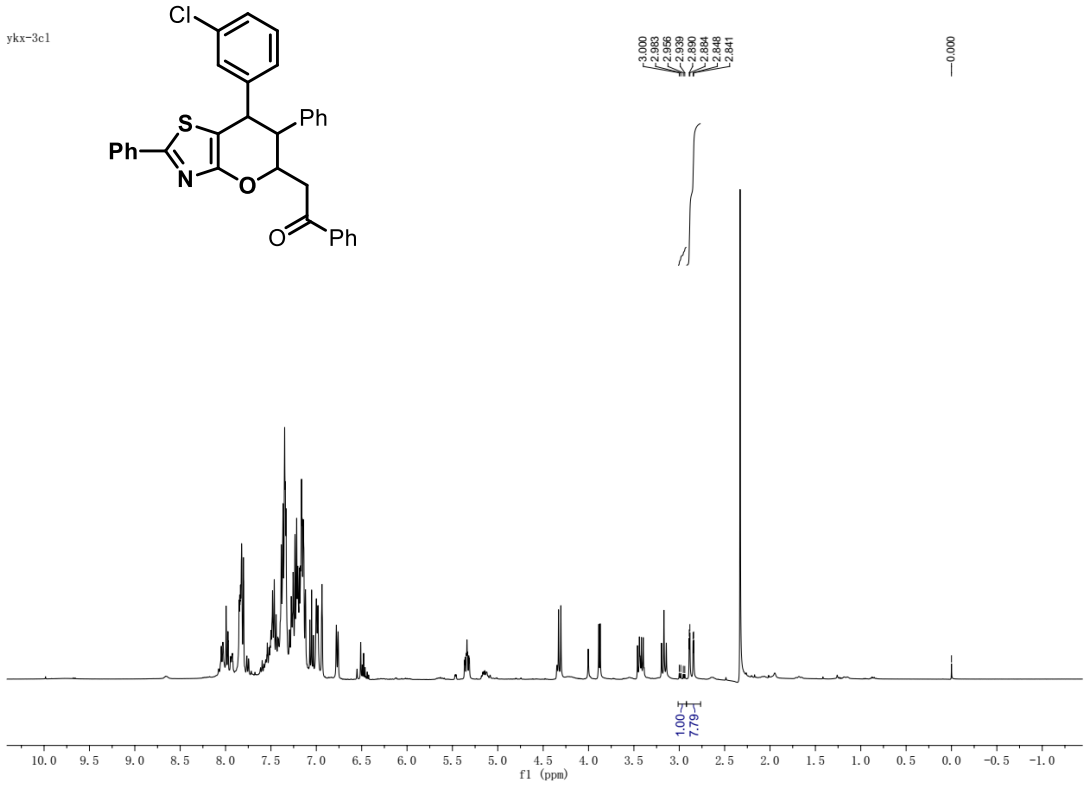
^{13}CNMR of **3h** (101M, CDCl3)



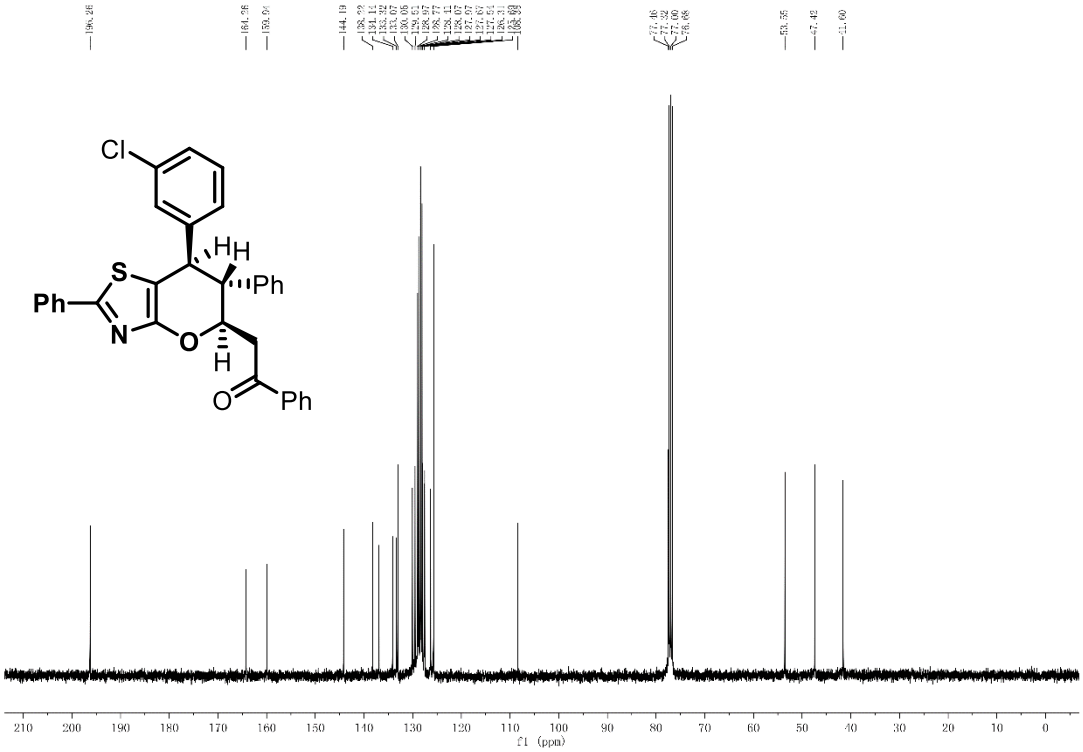
^{1}HNMR of **3i** (400M, $CDCl_3$)



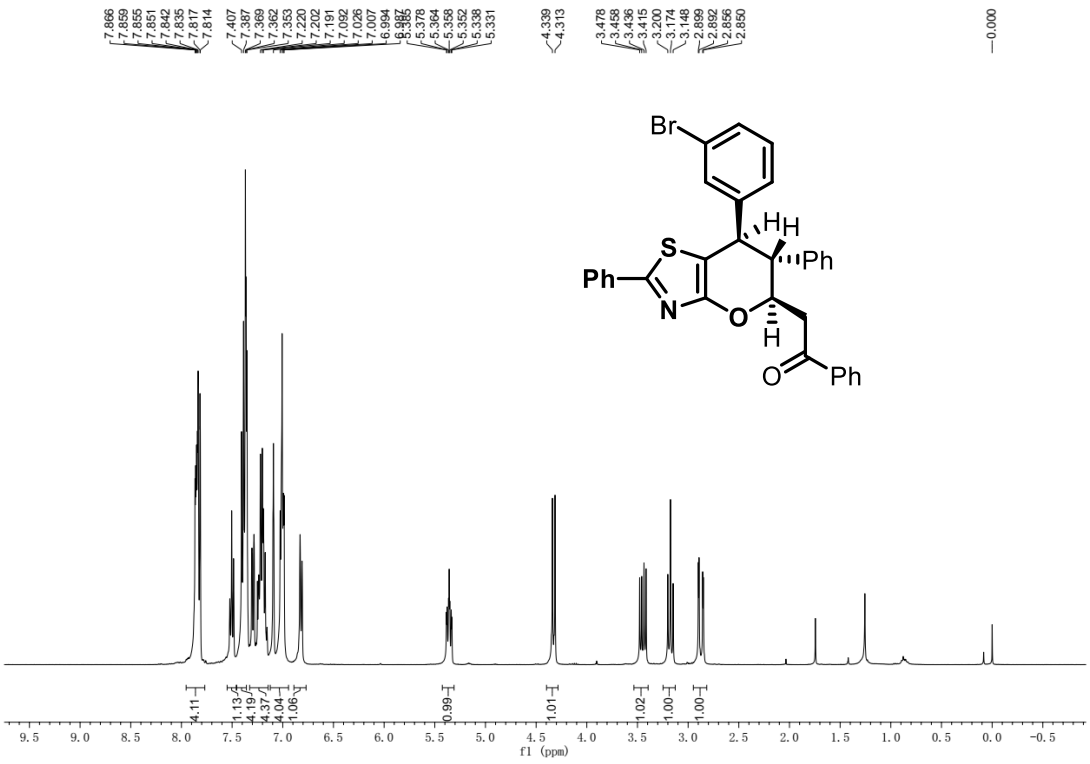
Crude ^{1}HNMR of **3i** (400M, $CDCl_3$)



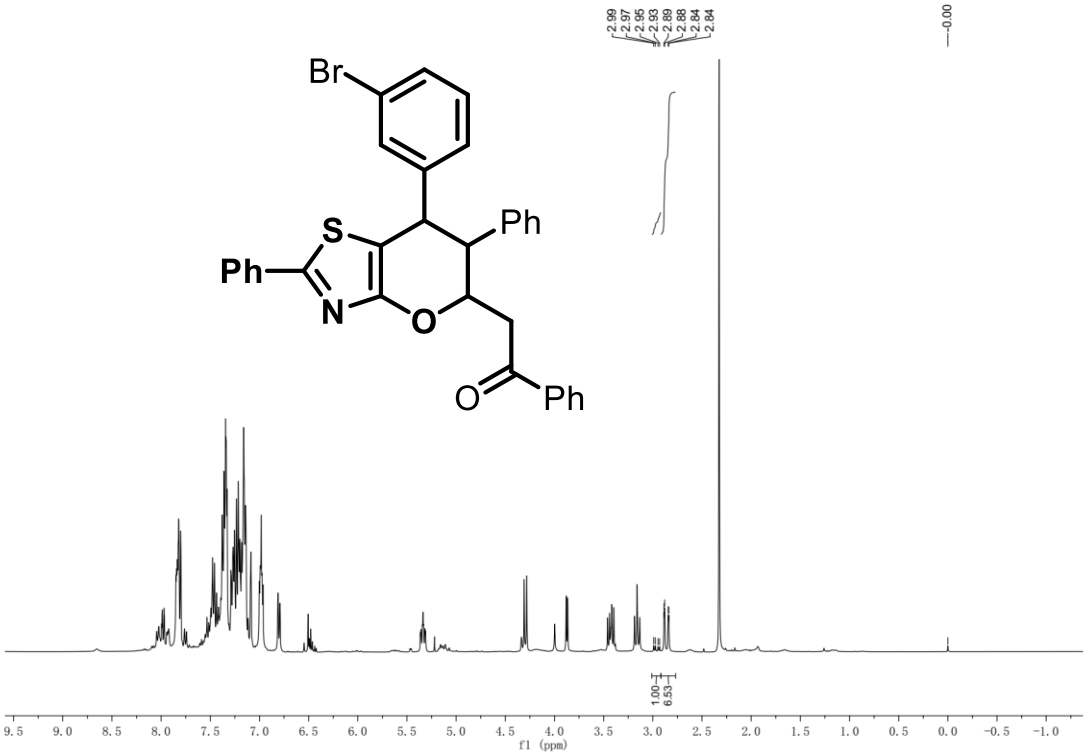
^{13}CNMR of **3i** (101M, $CDCl_3$)



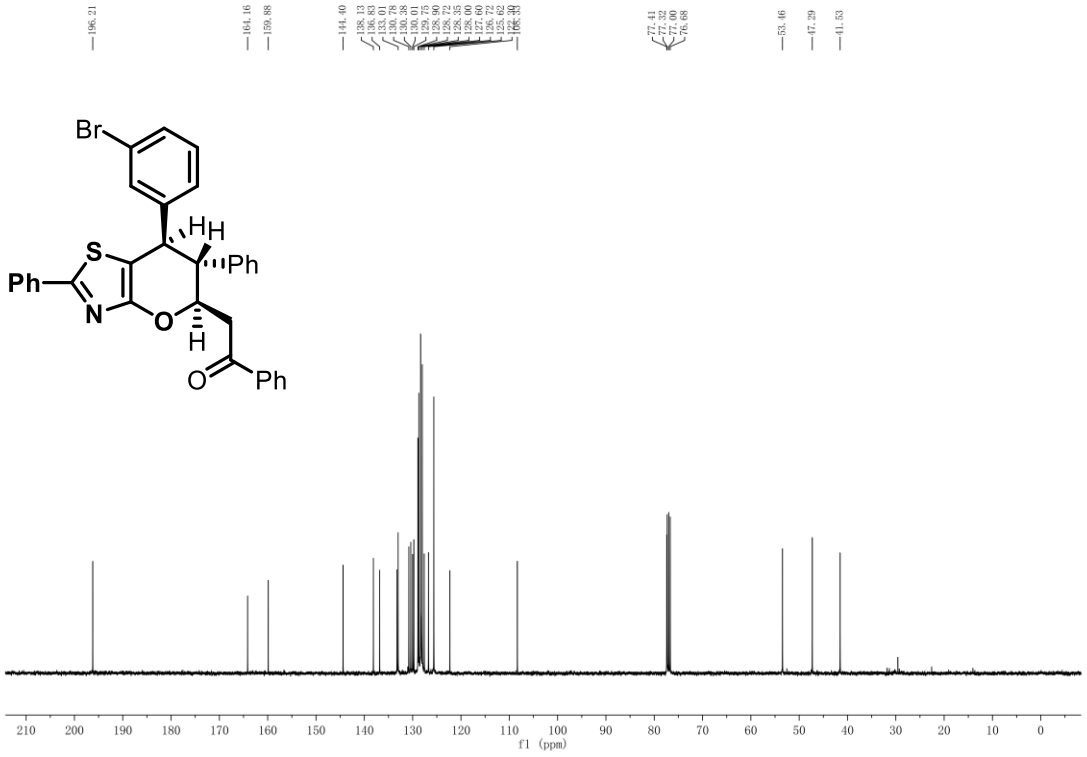
[1]HNMR of **3j** (400M, $CDCl_3$)



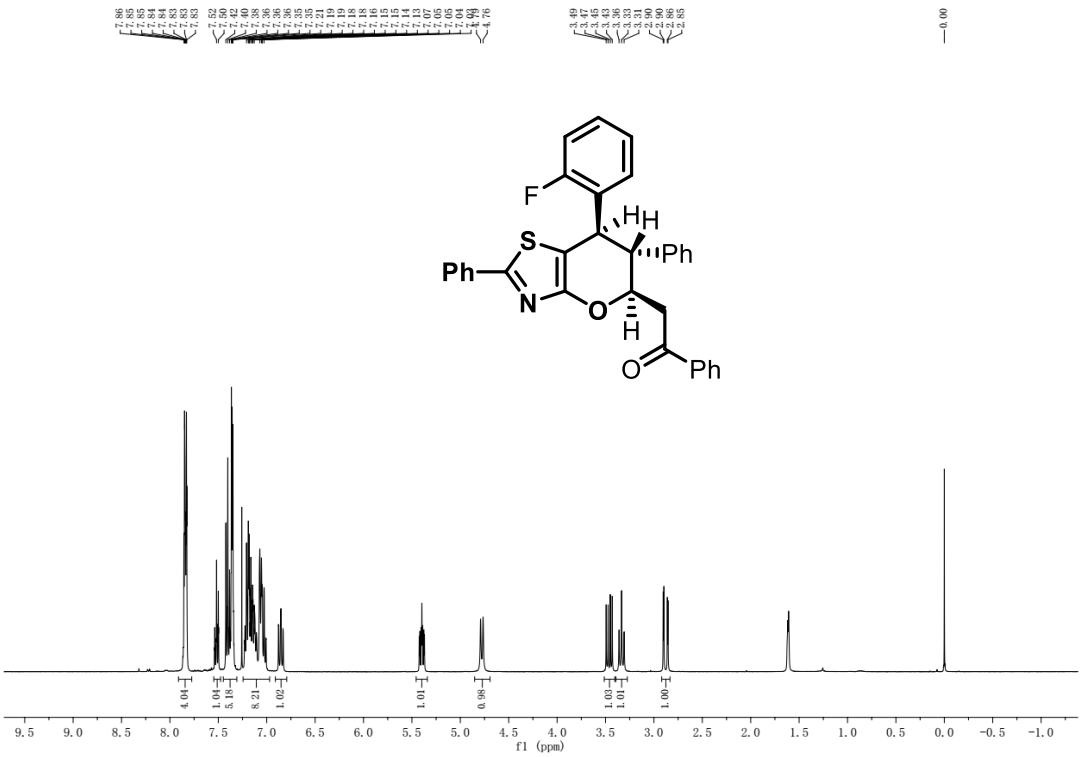
Crude [1]HNMR of **3j** (400M, $CDCl_3$)



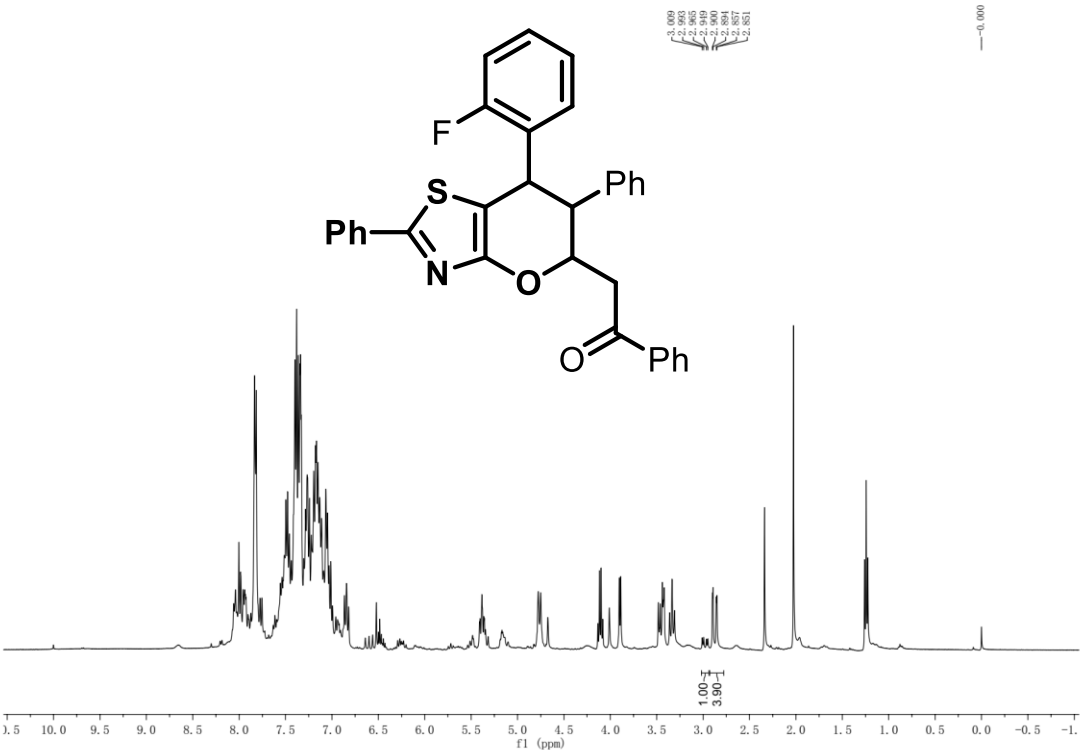
^{13}CNMR of **3j** (101M, $CDCl_3$)



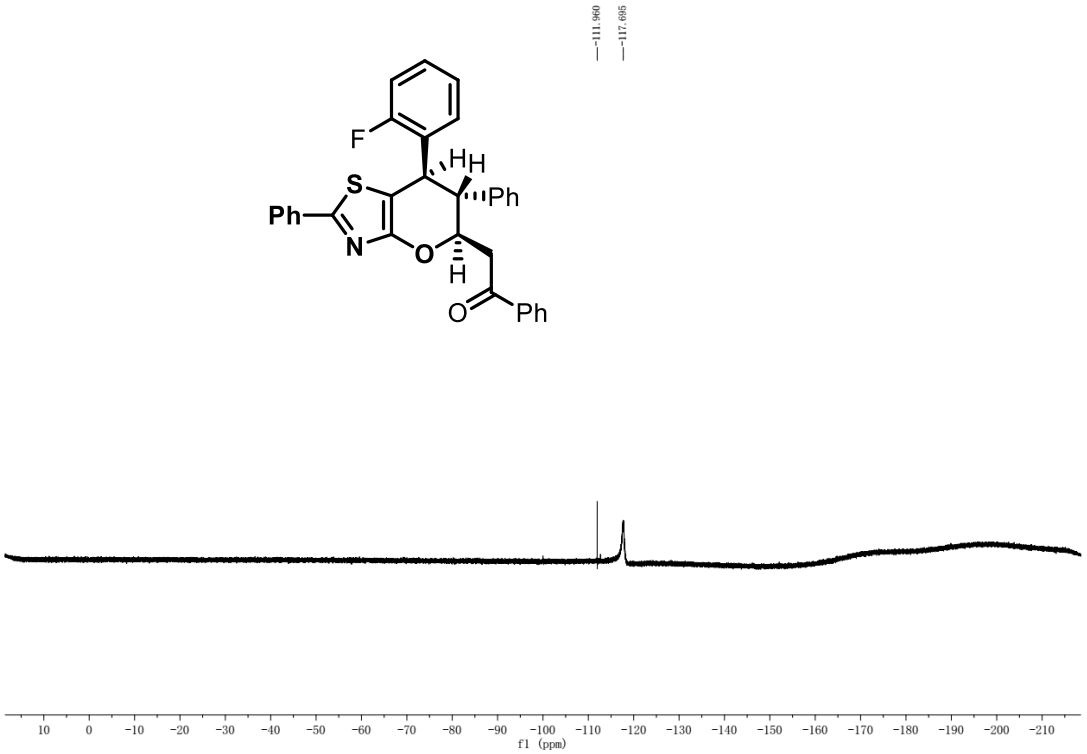
[1]HNMR of **3k** (400M, $CDCl_3$)



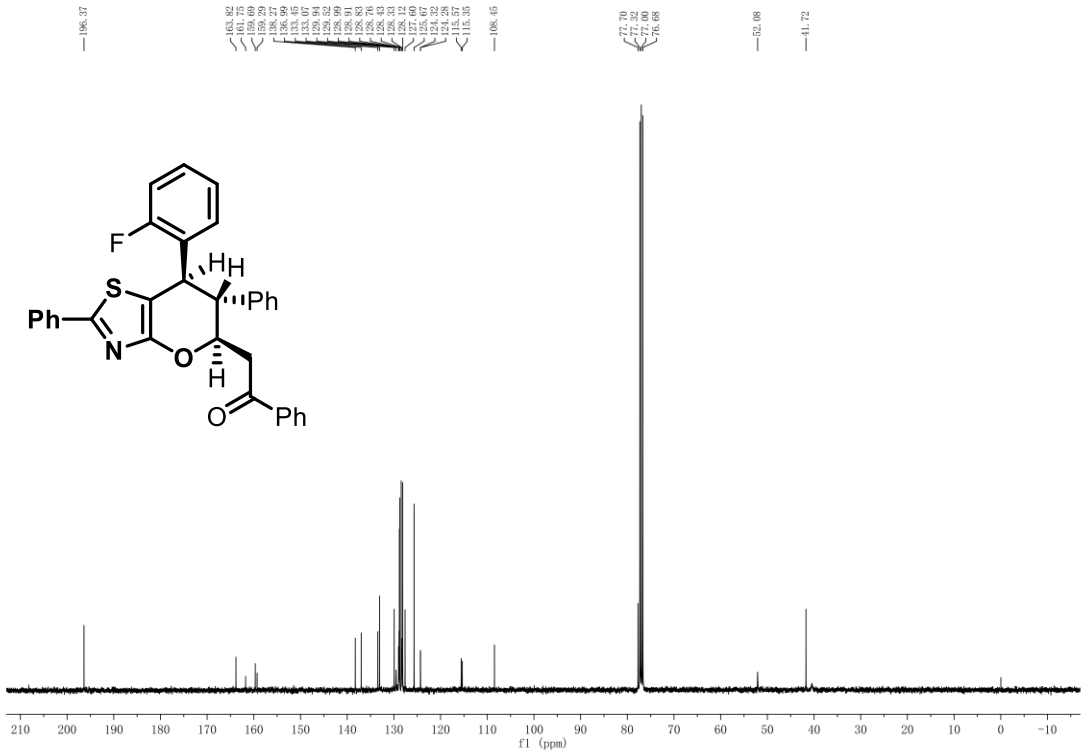
Crude [1]HNMR of **3k** (400M, $CDCl_3$)



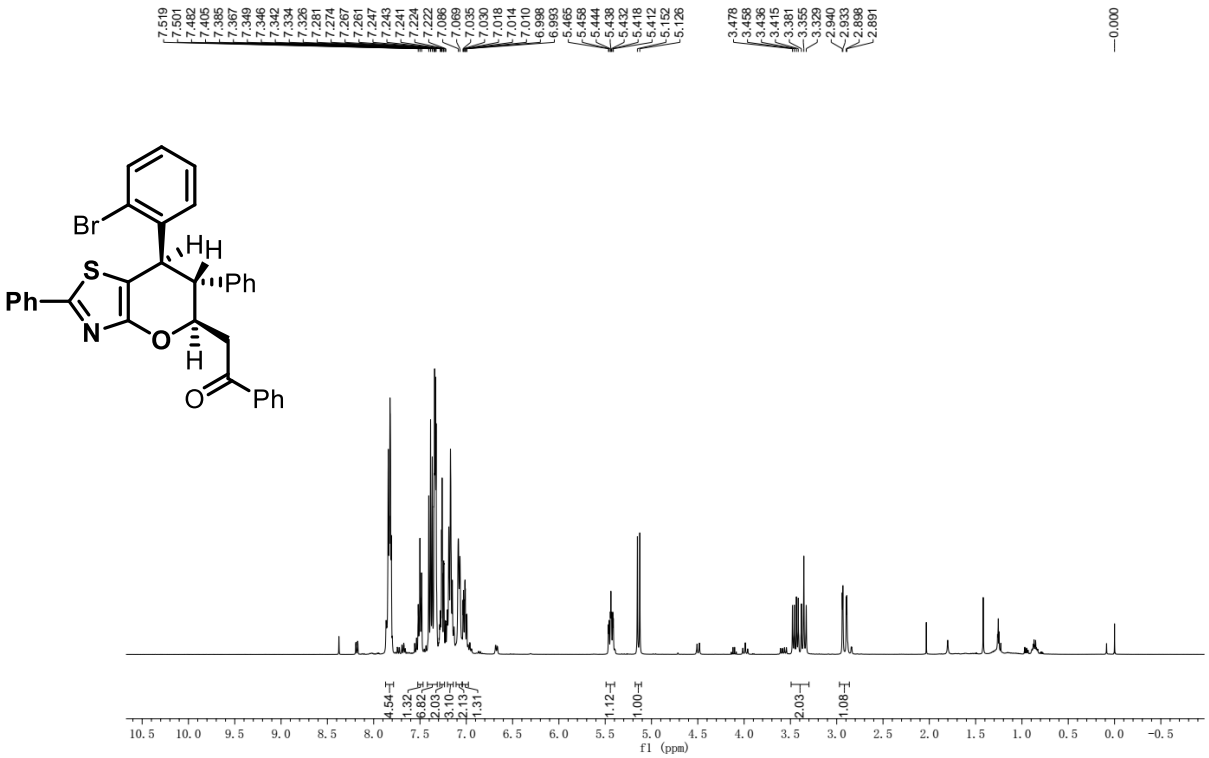
^{19}FNMR of **3k** (400M, $CDCl_3$)



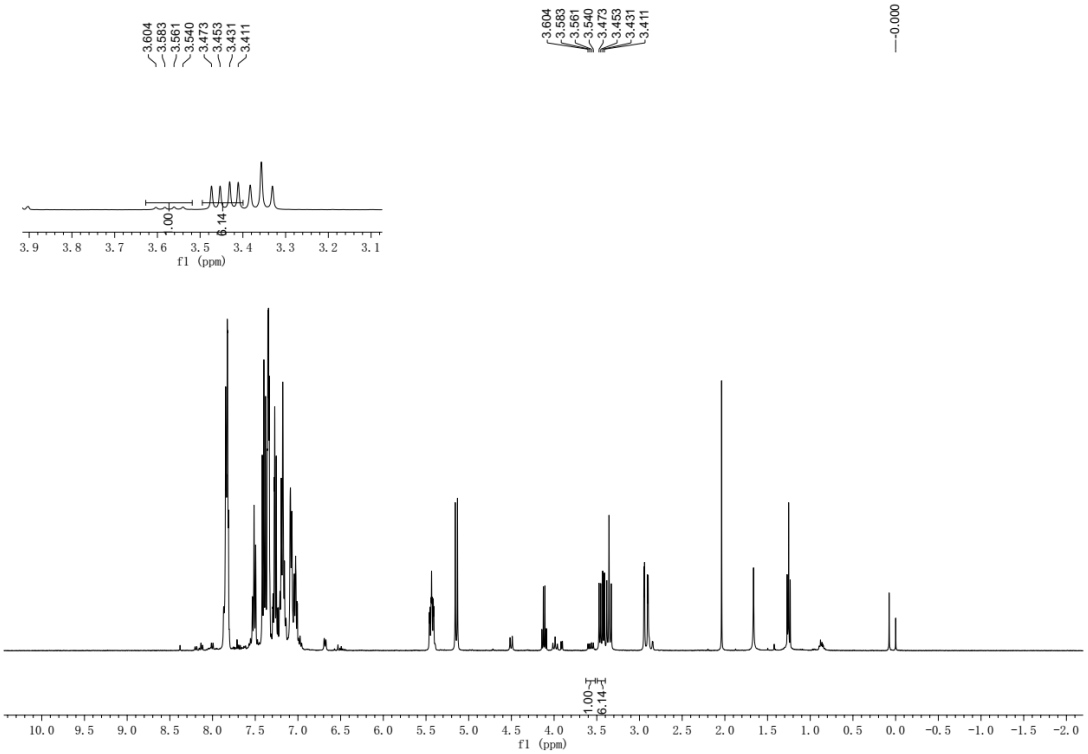
^{13}CNMR of **3k** (101M, $CDCl_3$)



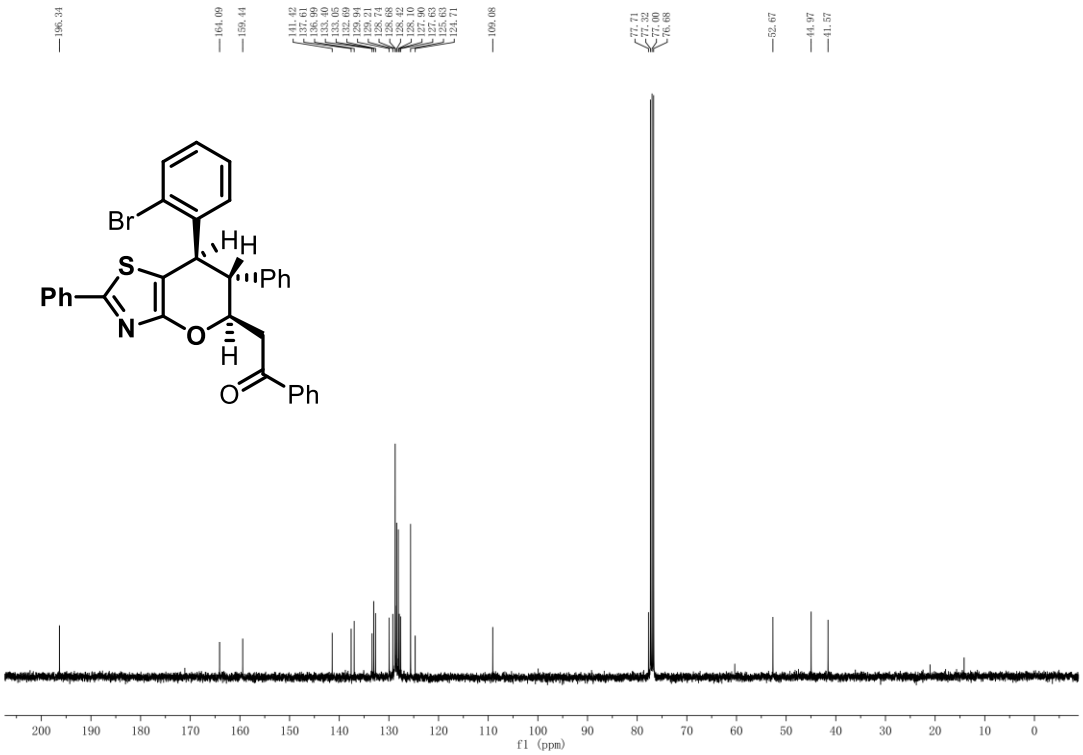
^{1}HNMR of **3l** (400M, $CDCl_3$)



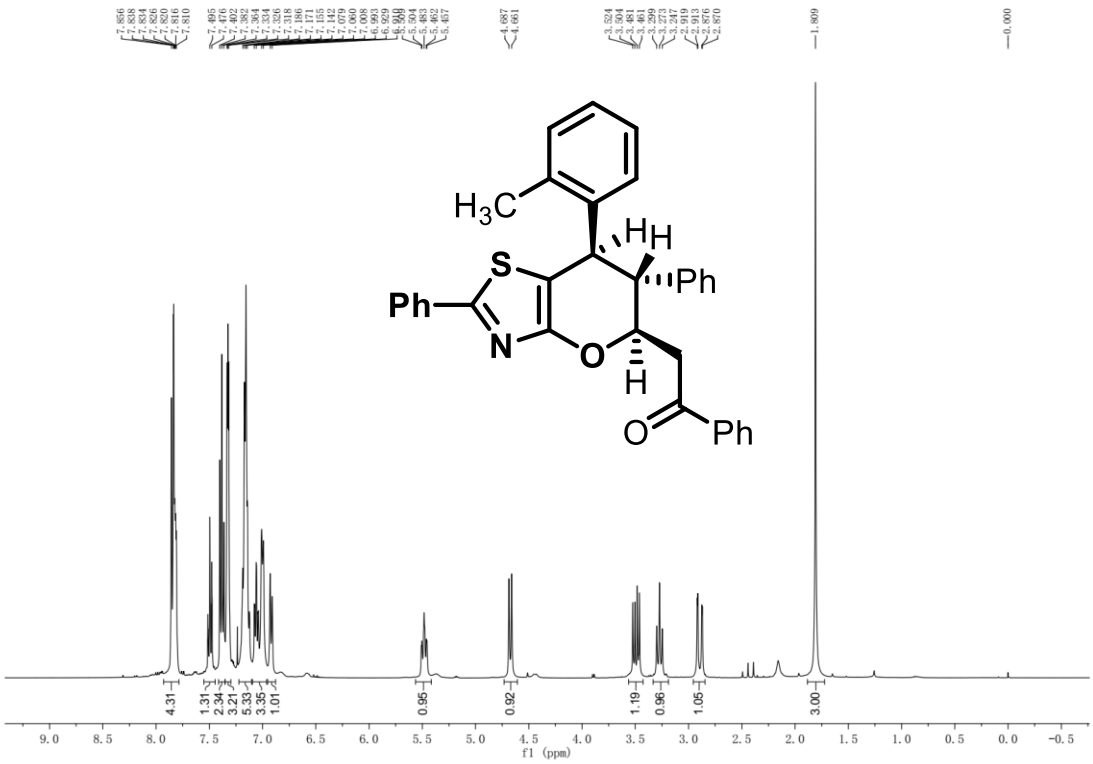
Crude ^{1}HNMR of **3l** (400M, $CDCl_3$)



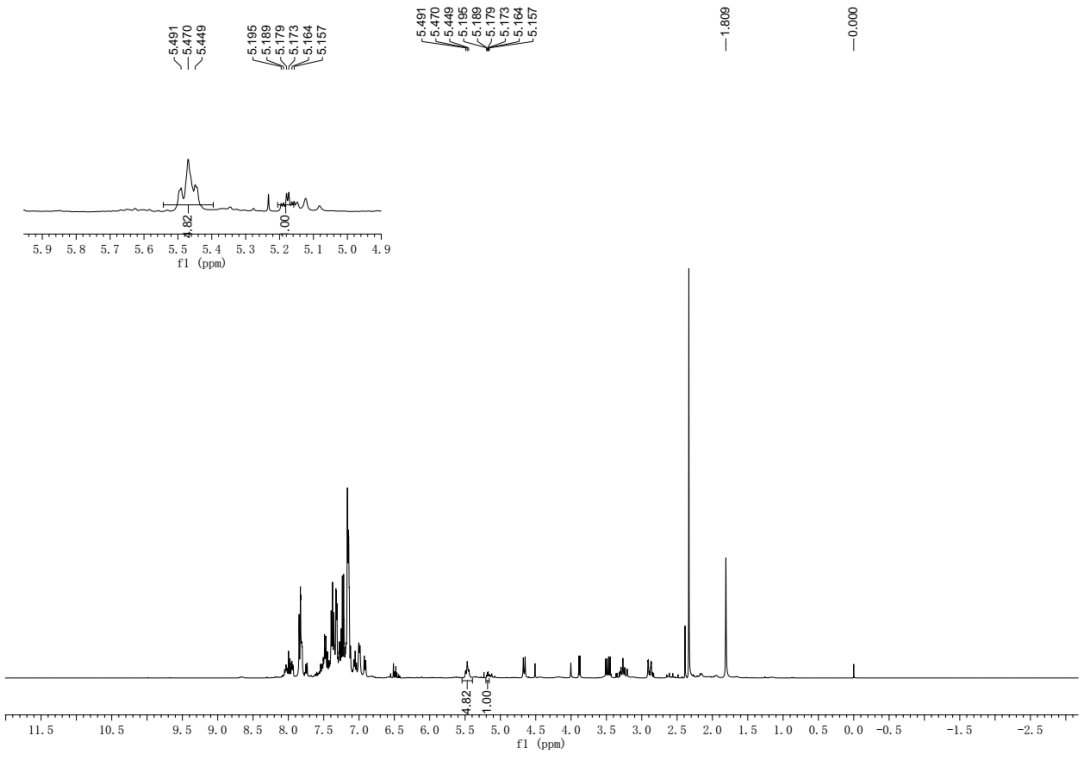
^{13}CNMR of **3l** (101M, $CDCl_3$)



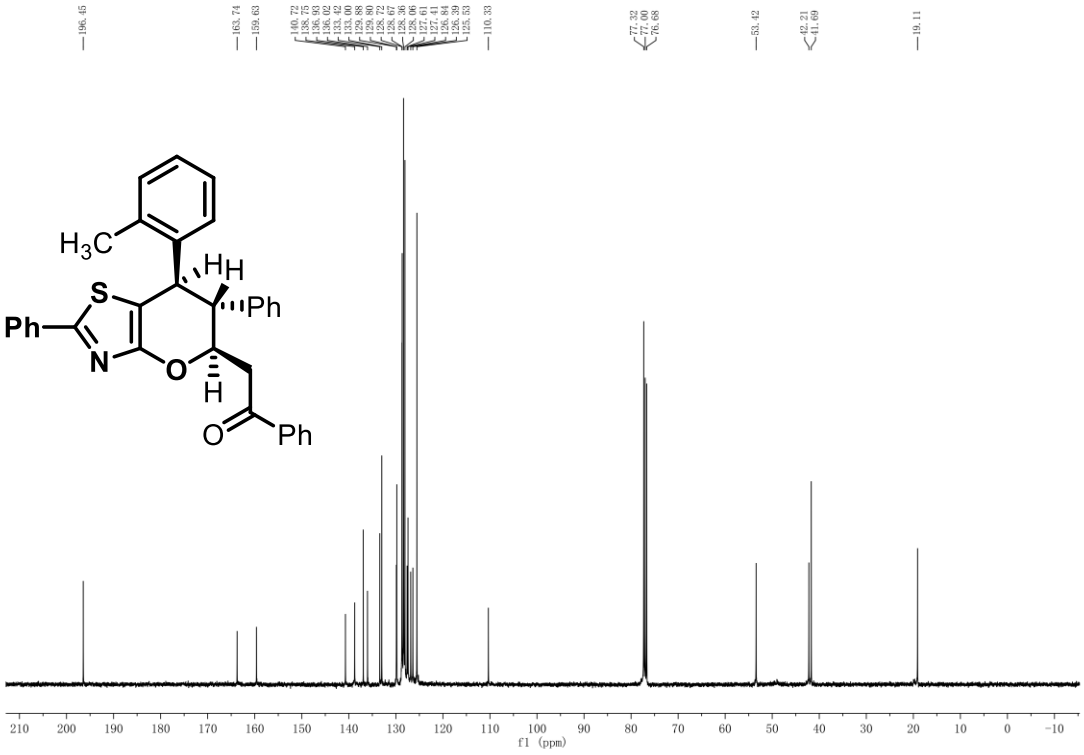
^{1}HNMR of **3m** (400M, $CDCl_3$)



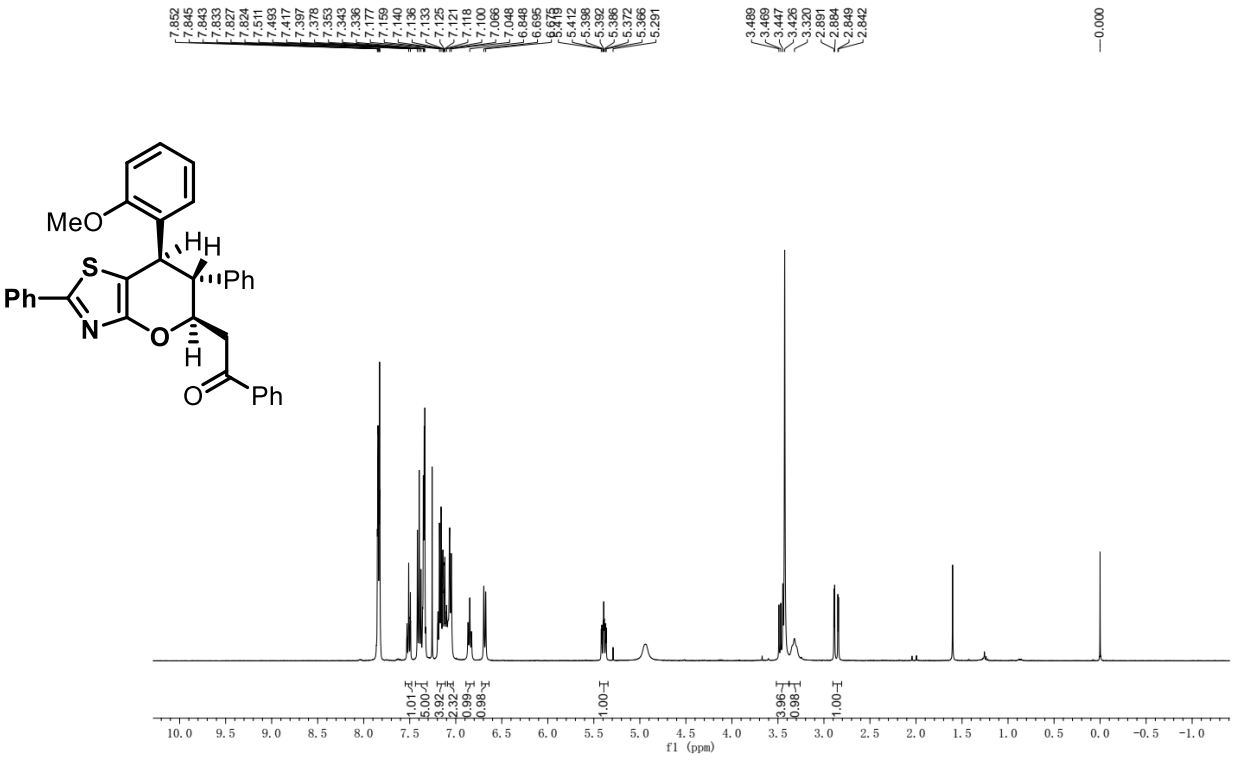
Crude ^{1}HNMR of **3m** (400M, $CDCl_3$)



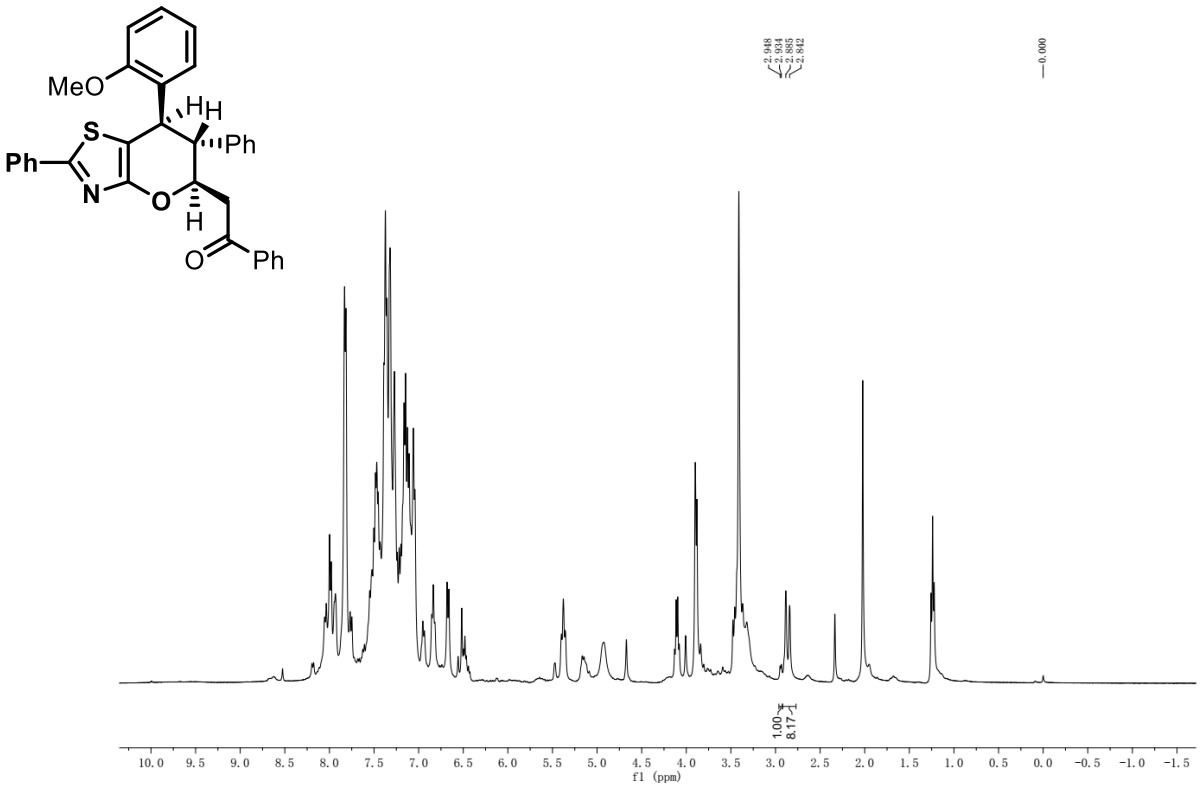
^{13}CNMR of **3m** (101M, $CDCl_3$)



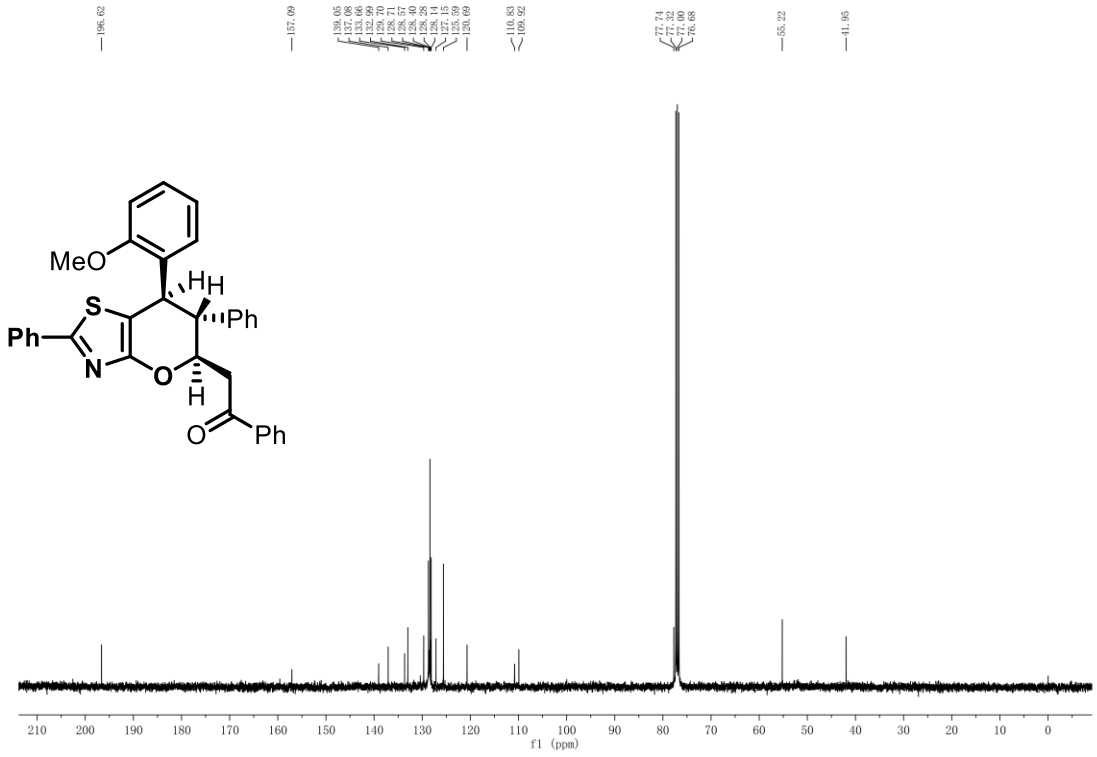
[1]HNMR of **3n** (400M, CDCl)



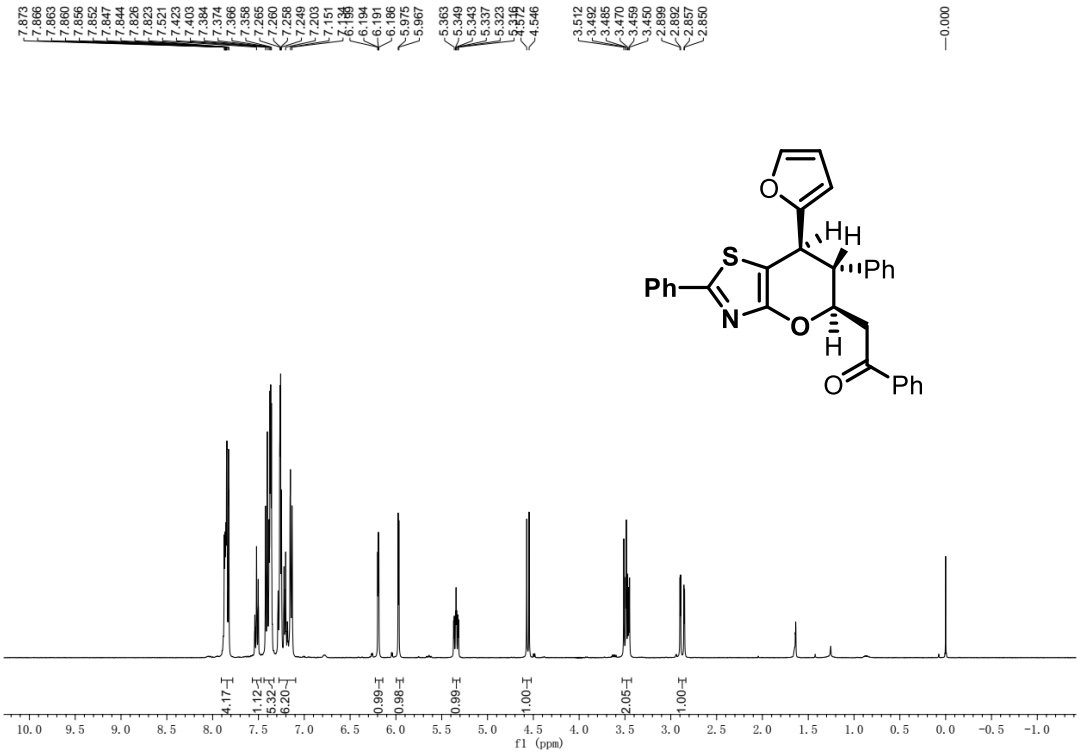
Crude [1]HNMR of **3n** (400M, $CDCl_3$)



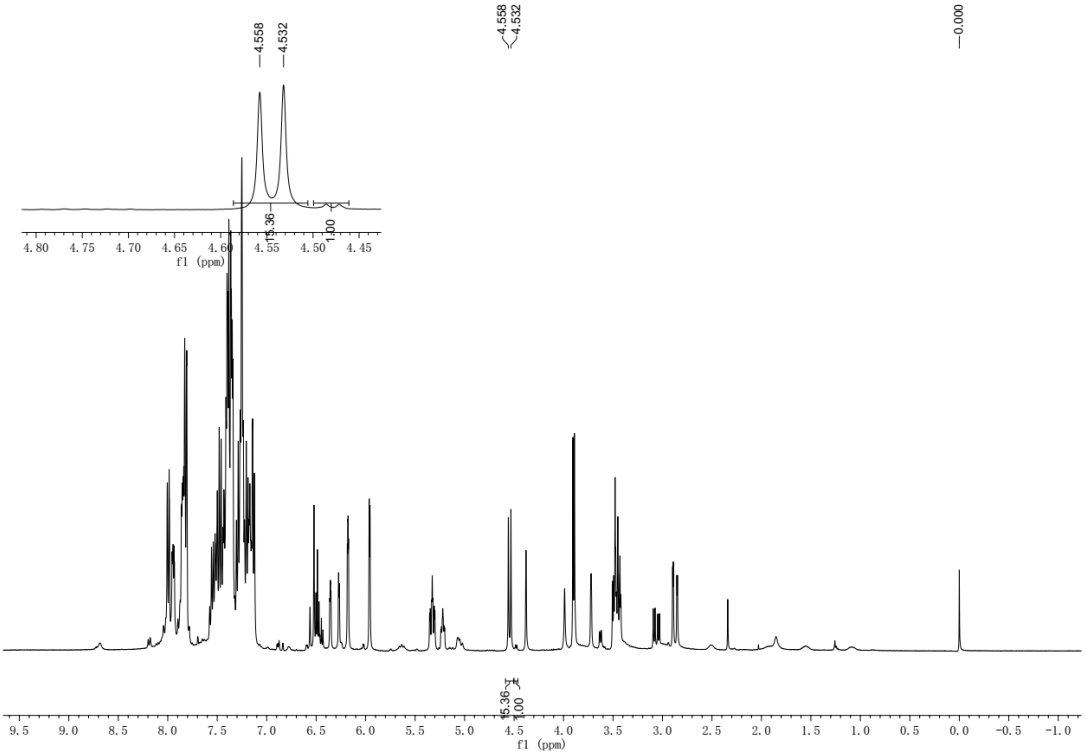
^{13}CNMR of **3n** (101M, $CDCl_3$)



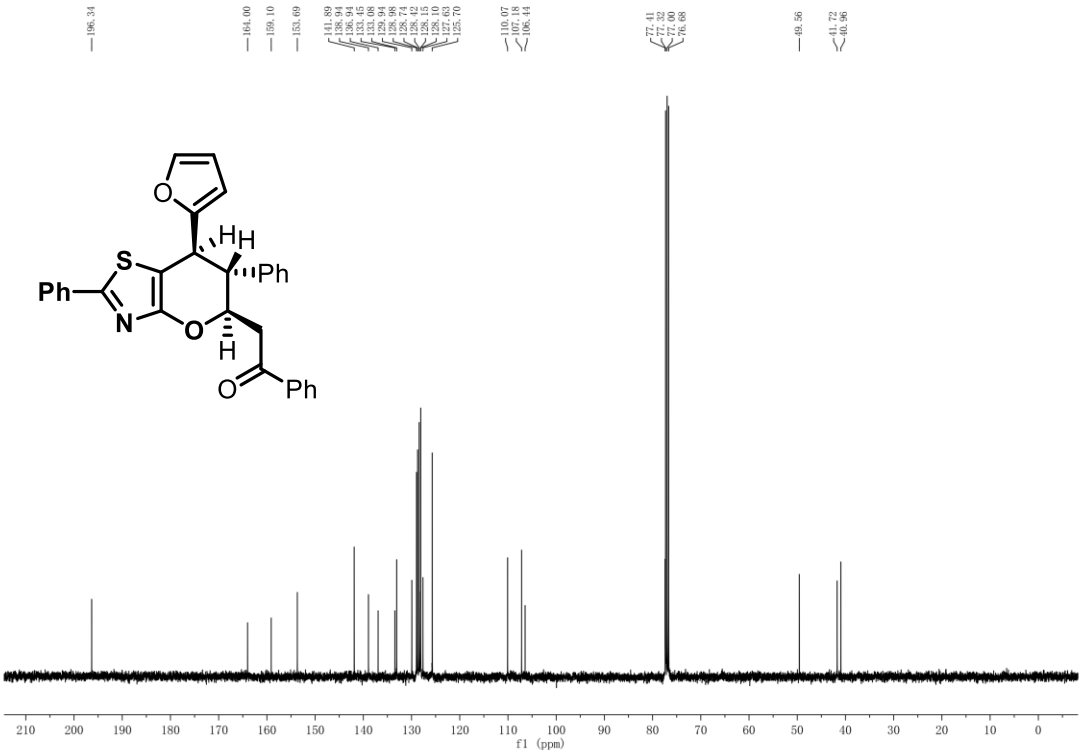
^{1}HNMR of **3o** (400M, $CDCl_3$)



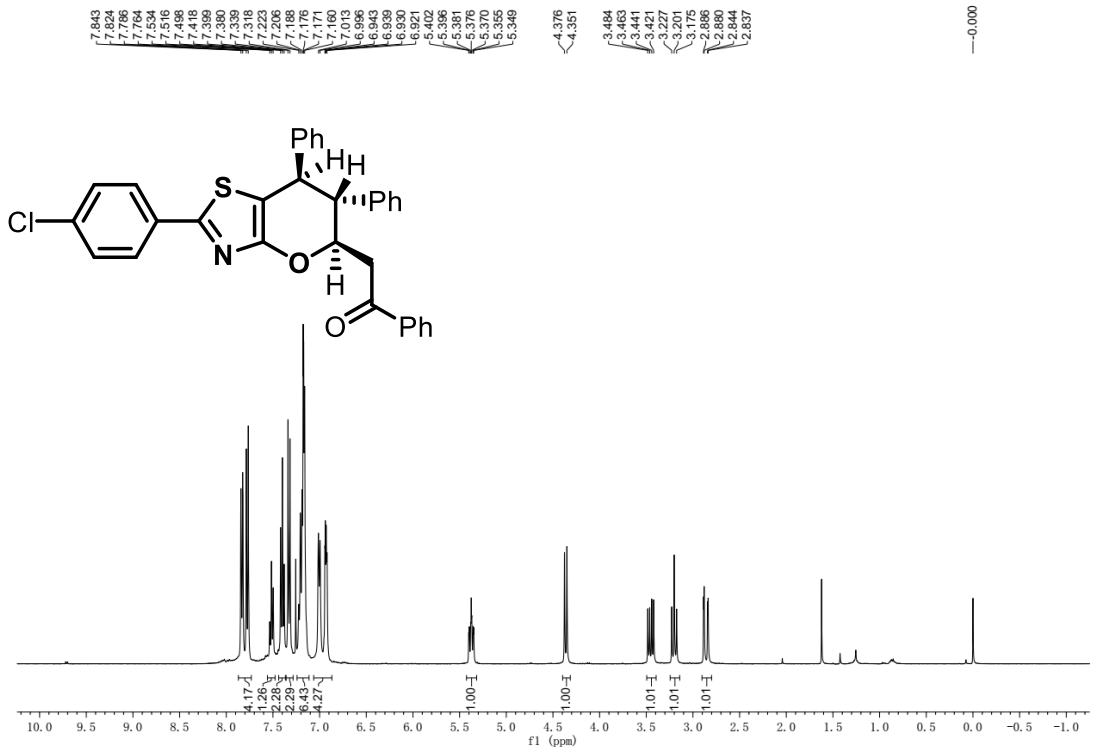
Crude ^{1}HNMR of **3o** (400M, $CDCl_3$)



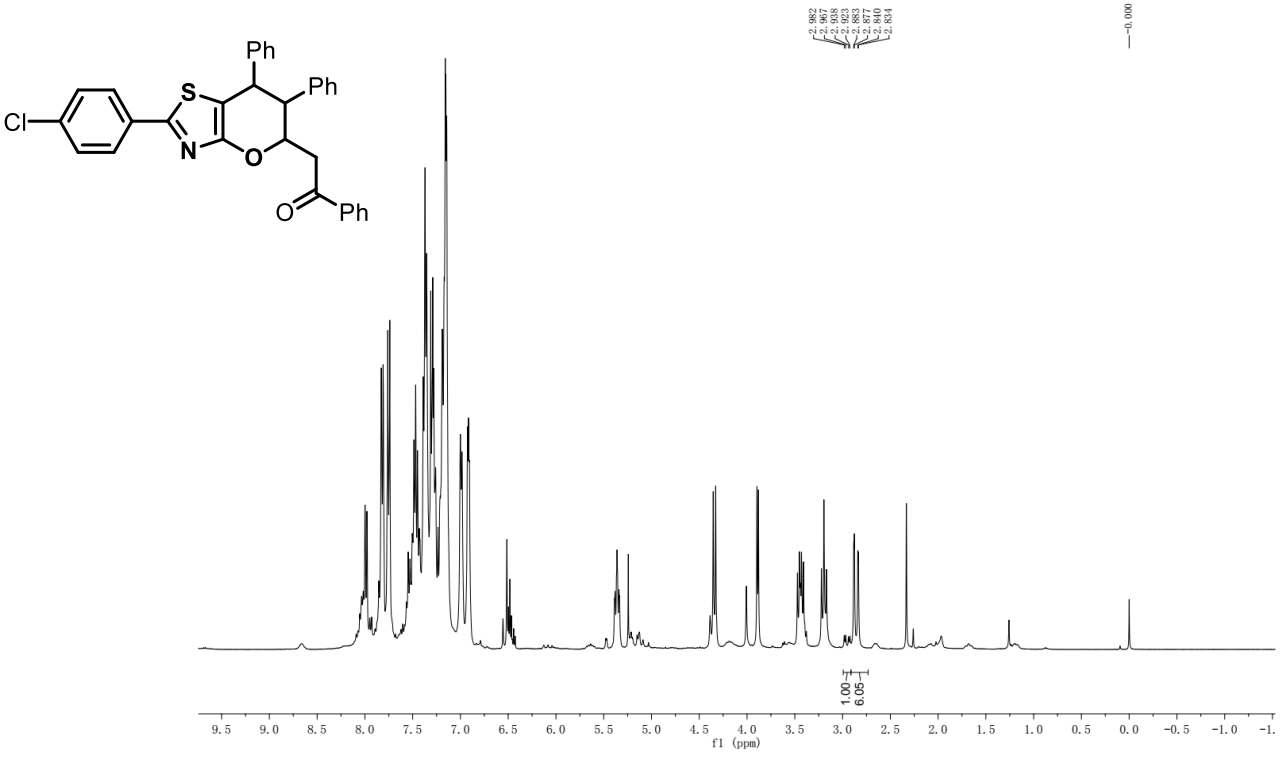
^{13}CNMR of **3o** (101M, $CDCl_3$)



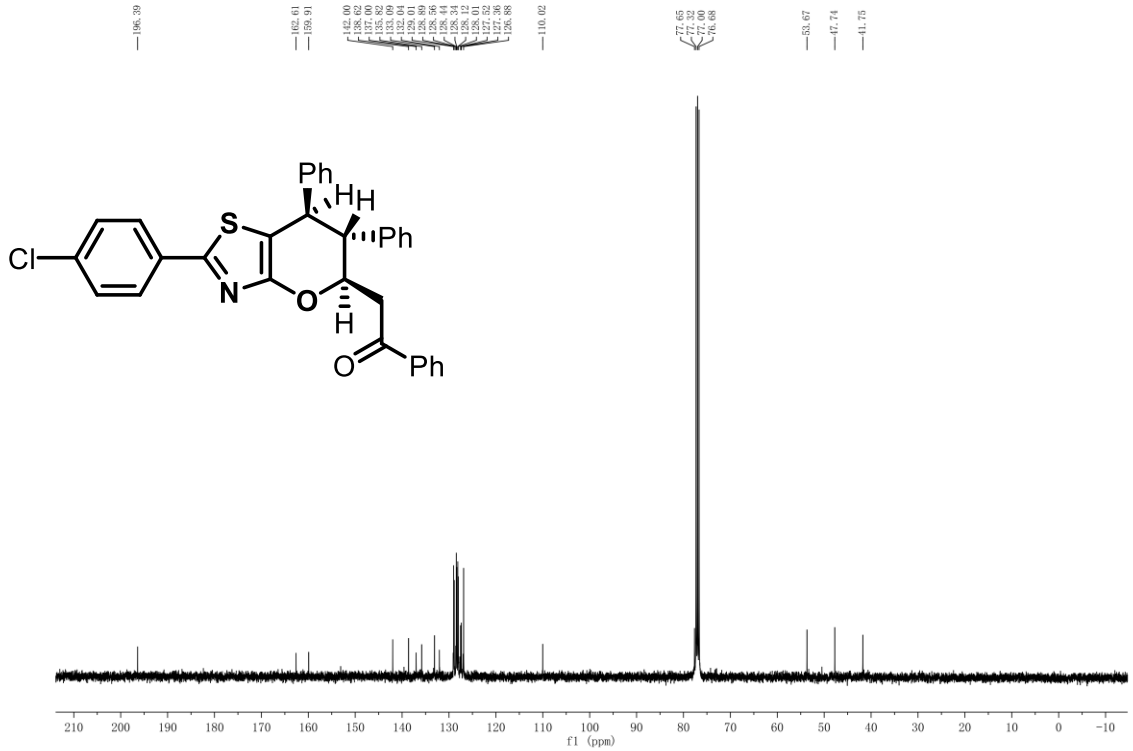
^{1}HNMR of **3p** (400M, $CDCl_3$)



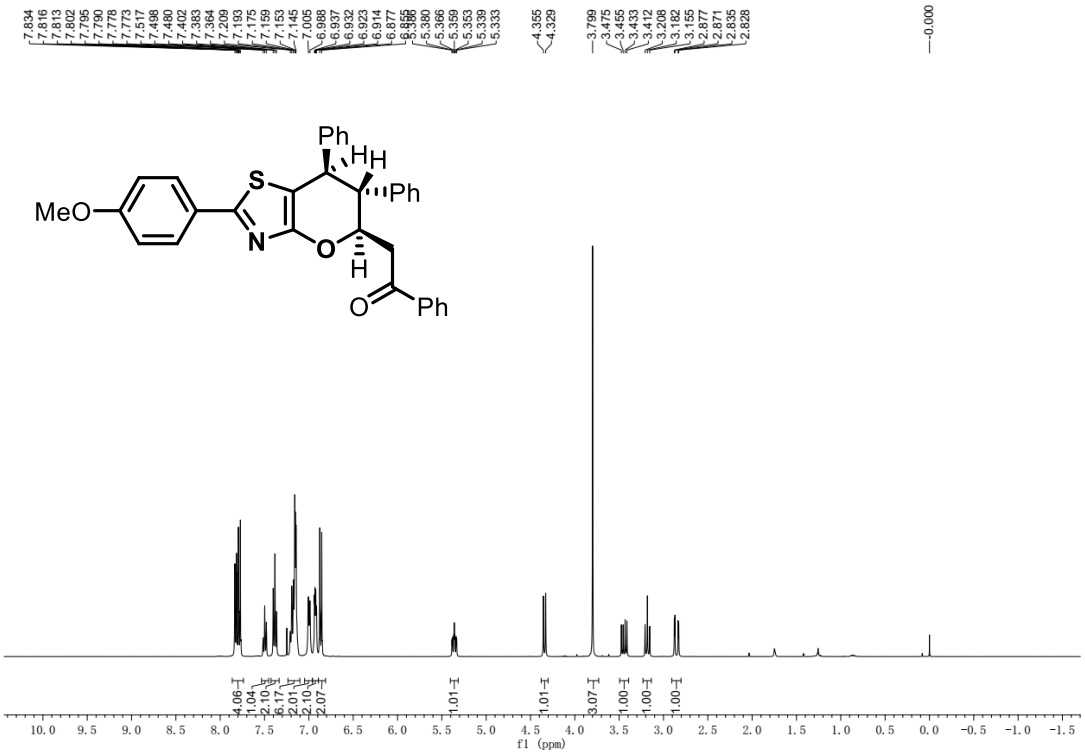
Crude ^{1}HNMR of **3p** (400M, $CDCl_3$)



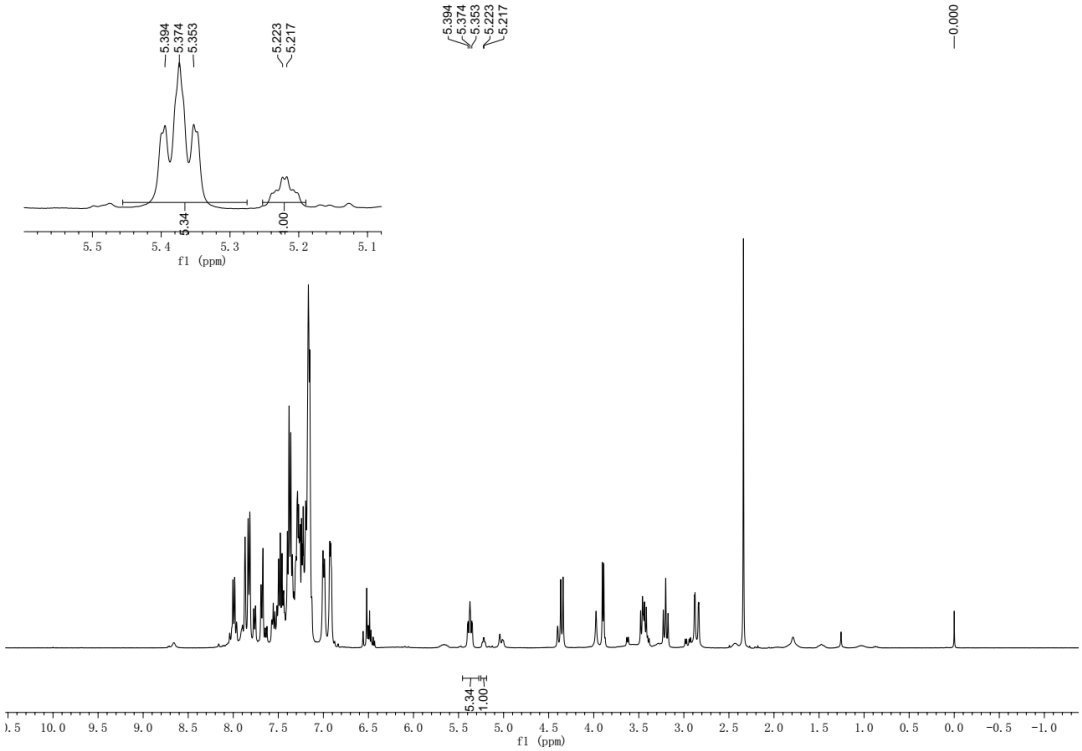
^{13}CNMR of **3p** (101M, $CDCl_3$)



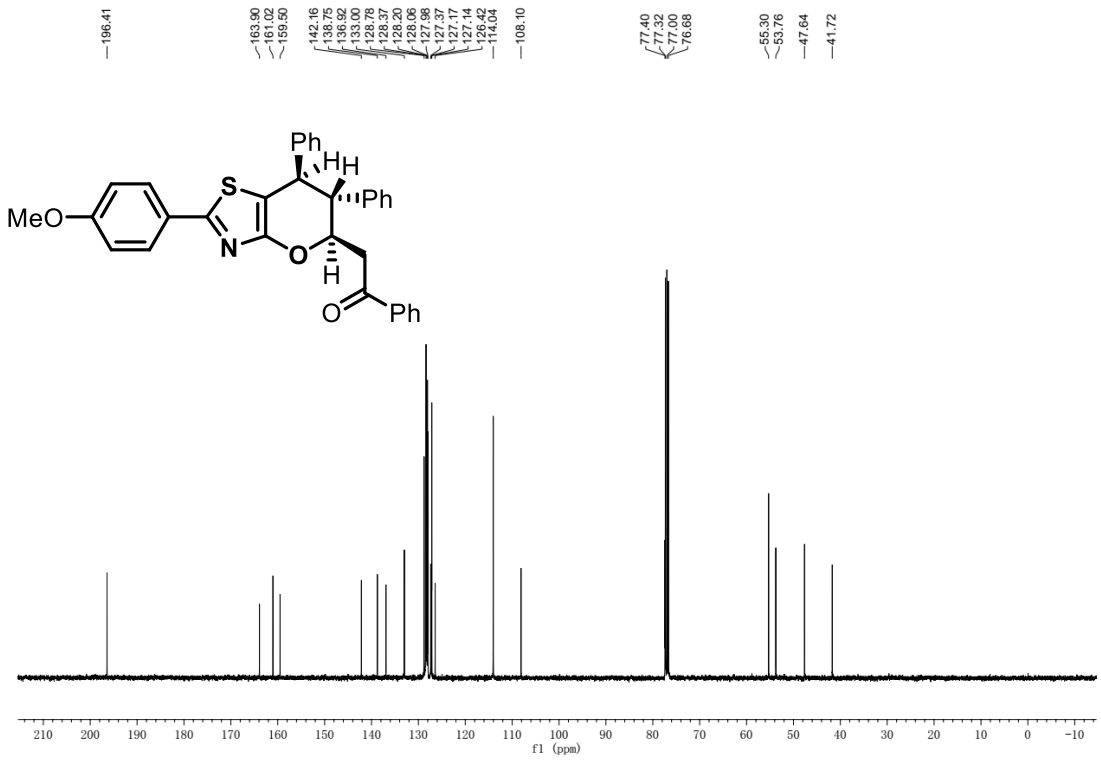
[1]HNMR of **3q** (400M, $CDCl_3$)



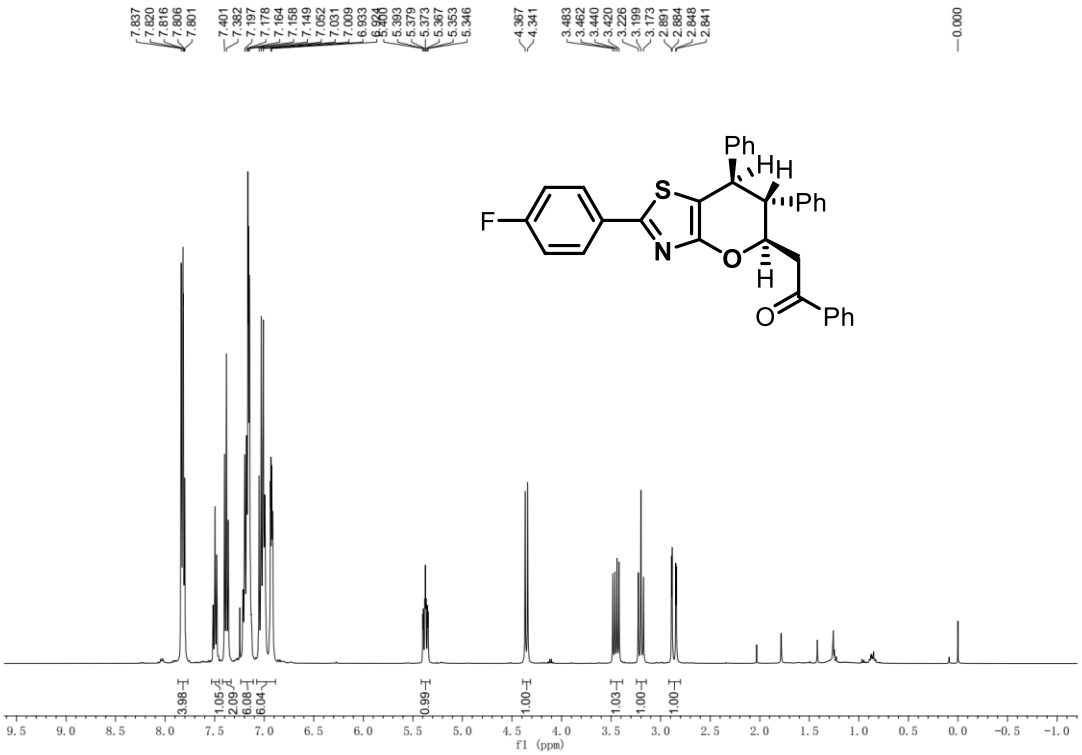
Crude [1]HNMR of **3q** (400M, $CDCl_3$)



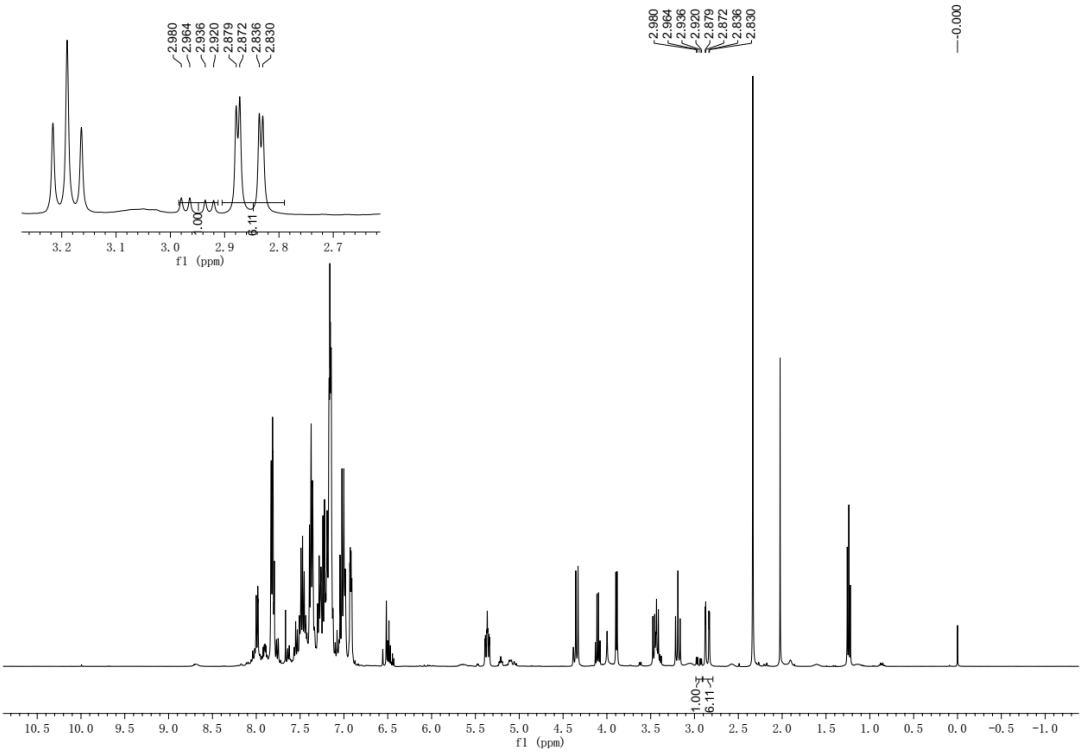
^{13}CNMR of **3q** (101M, $CDCl_3$)



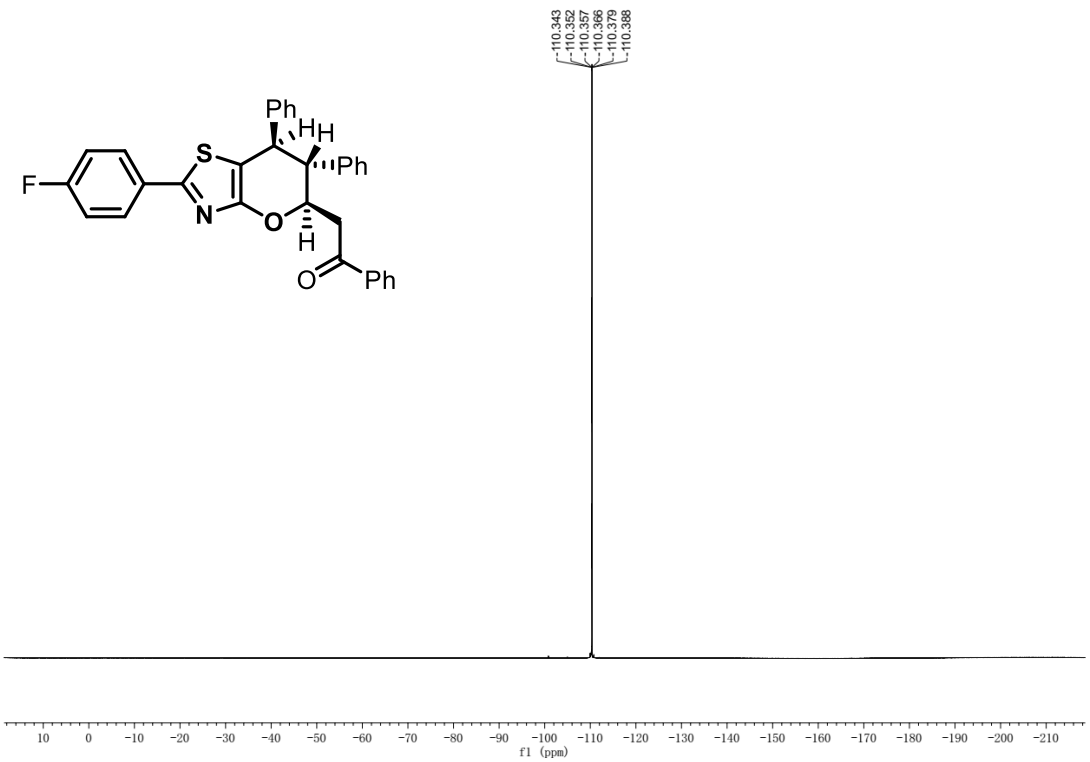
^{1}HNMR of **3r** (400M, $CDCl_3$)



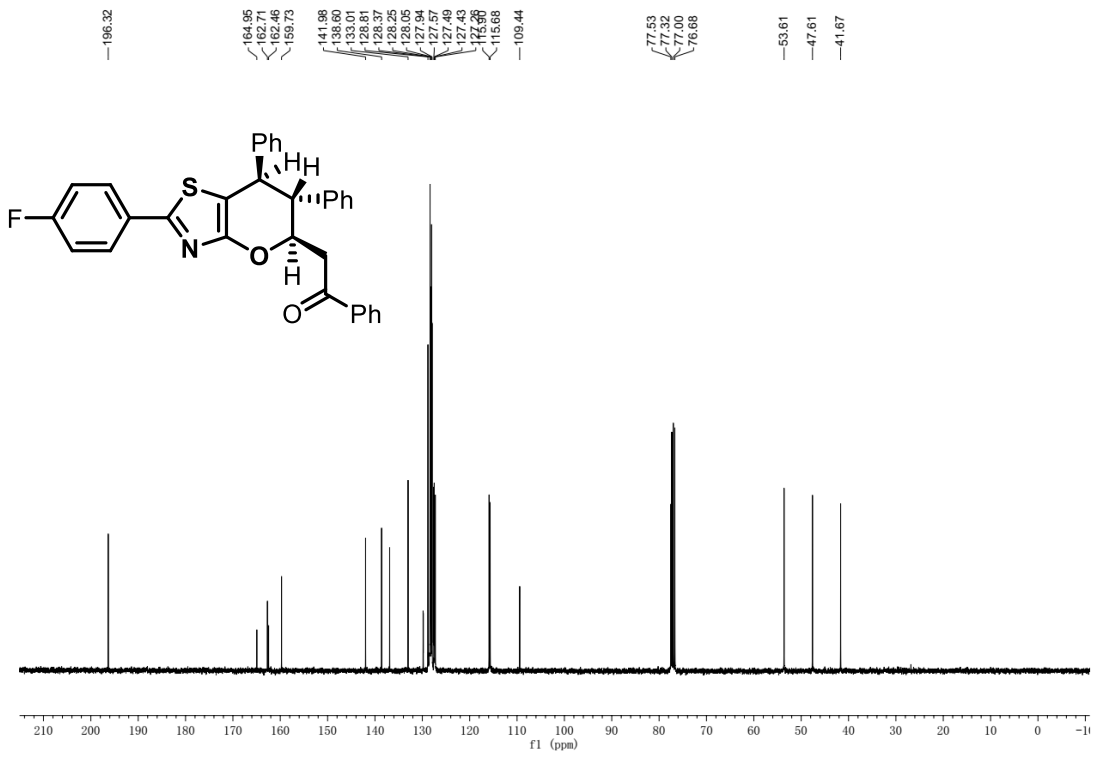
Crude ^{1}HNMR of **3r** (400M, $CDCl_3$)



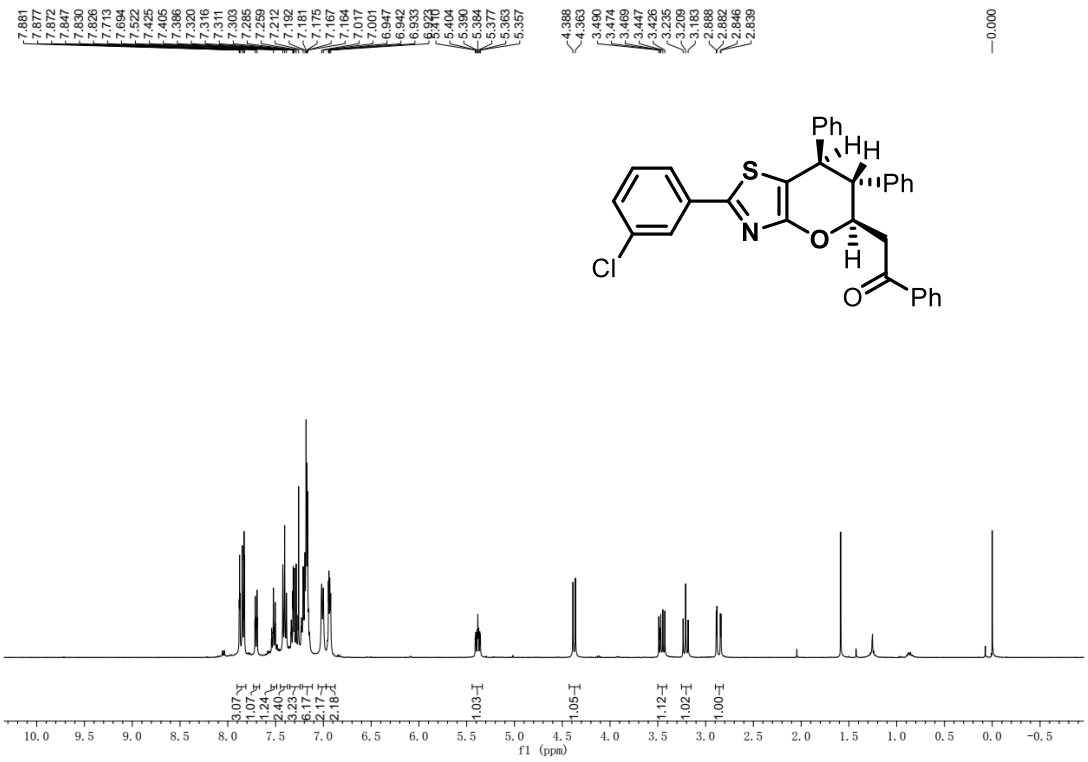
^{19}FNMR of **3k** (400M, $CDCl_3$)



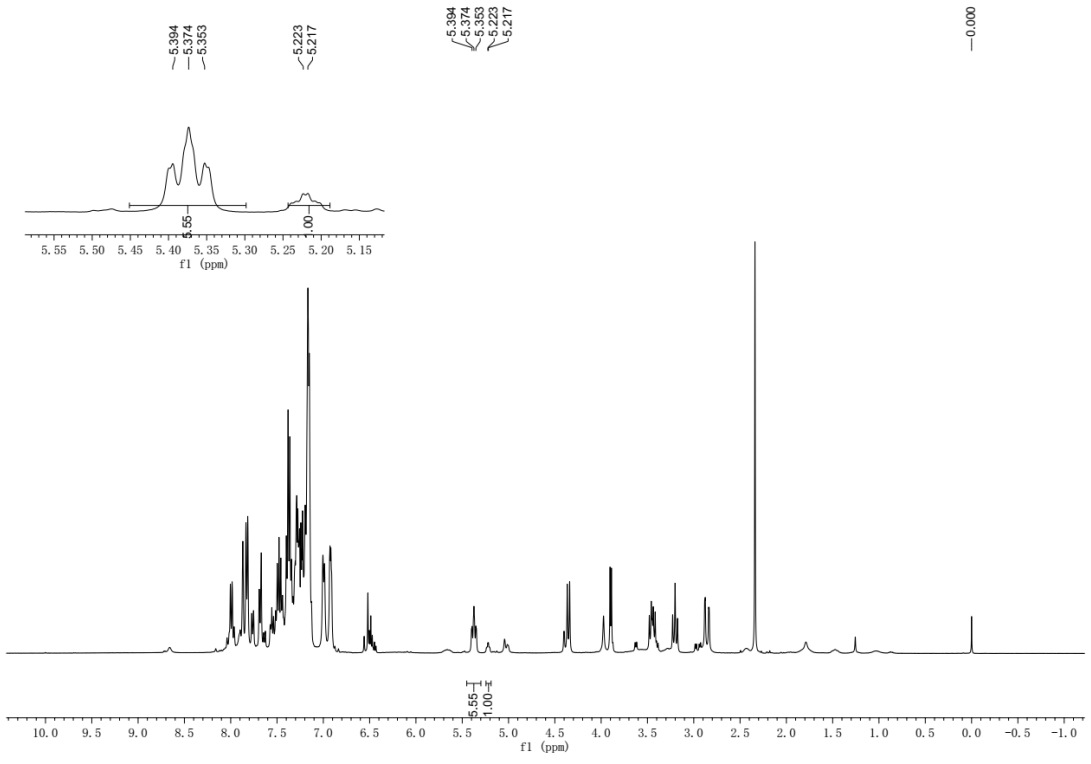
^{13}CNMR of **3r** (101M, $CDCl_3$)



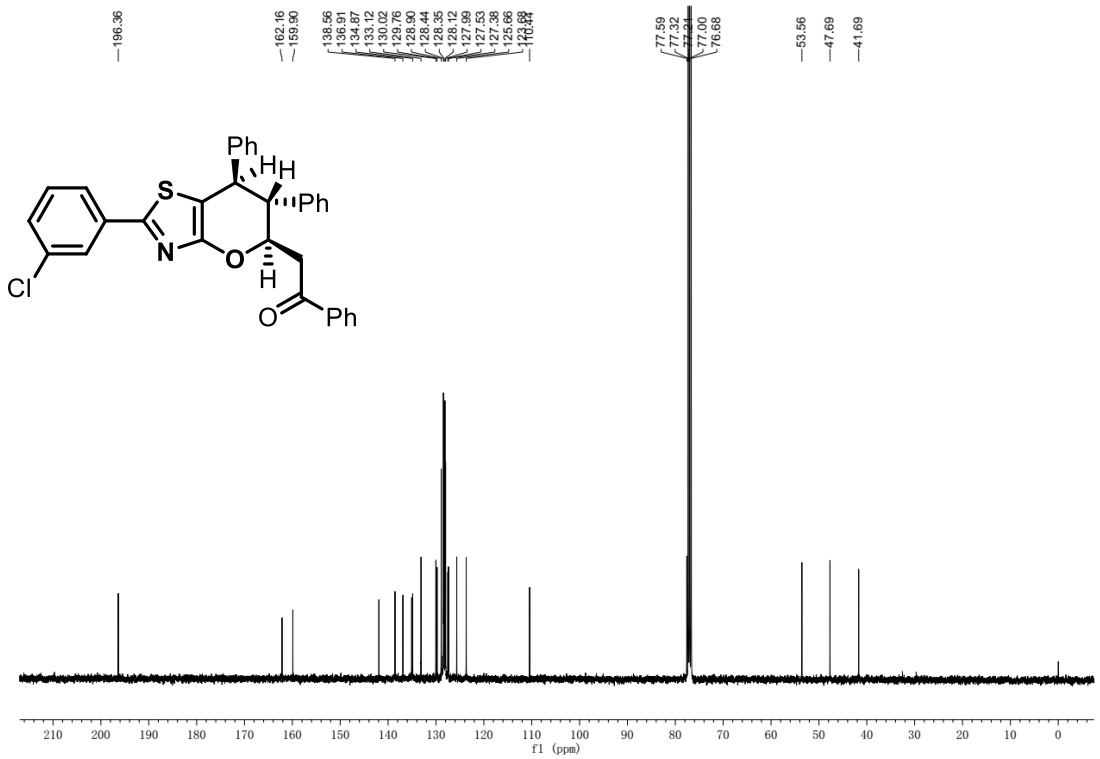
^{1}HNMR of **3s**(400M, $CDCl_3$)



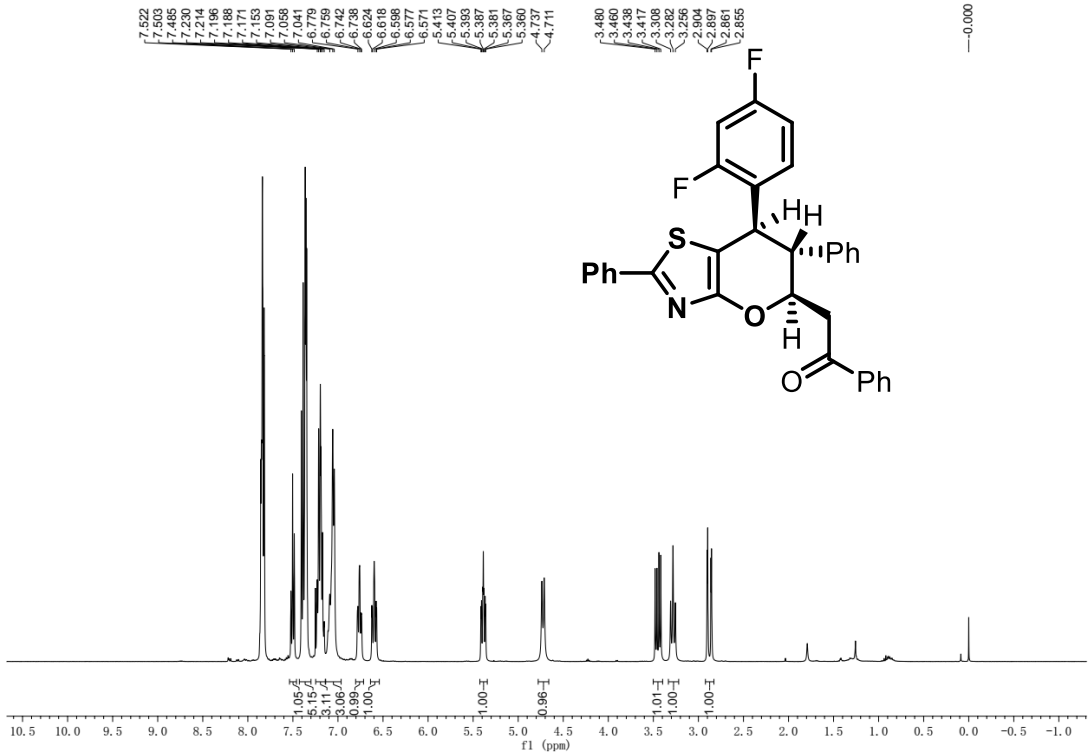
Crude ^{1}HNMR of **3s** (400M, $CDCl_3$)



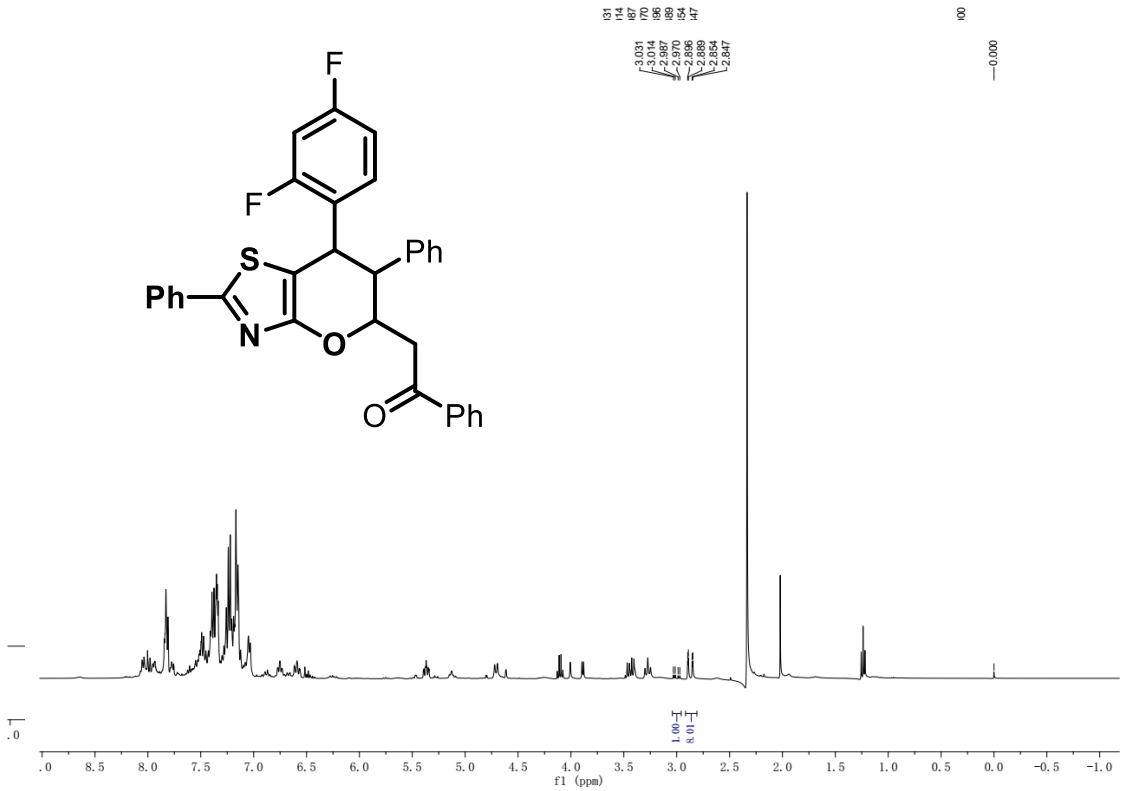
^{13}CNMR of **3s** (101M, $CDCl_3$)



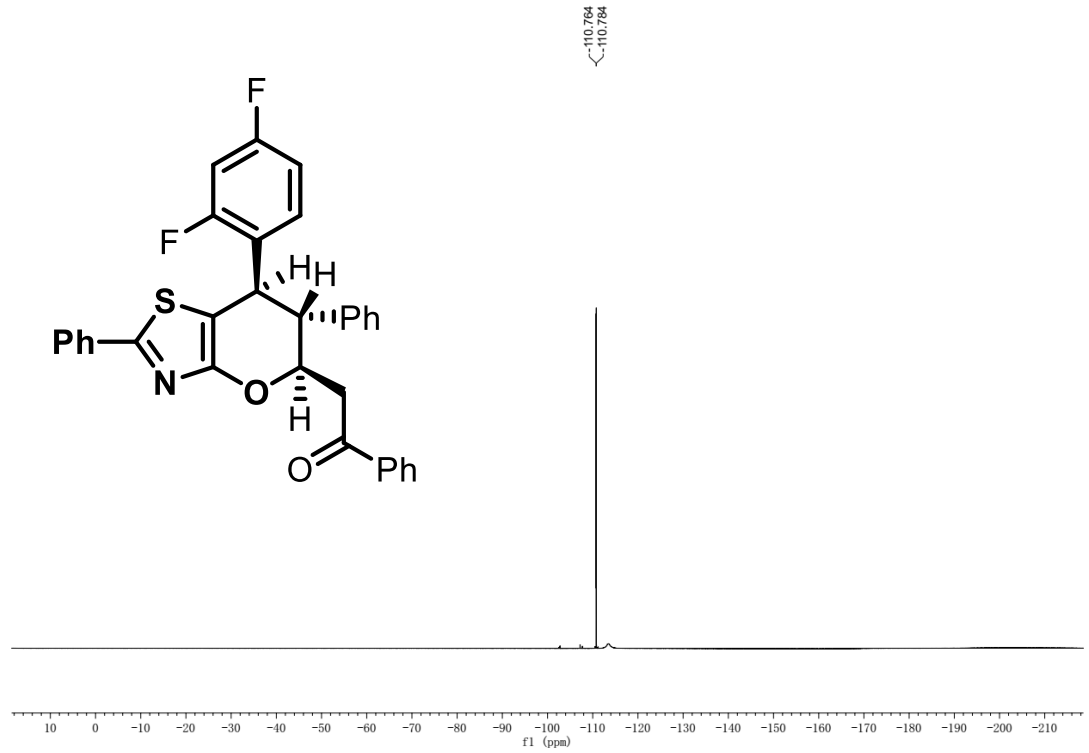
^{1}HNMR of **3t** (400M, $CDCl_3$)



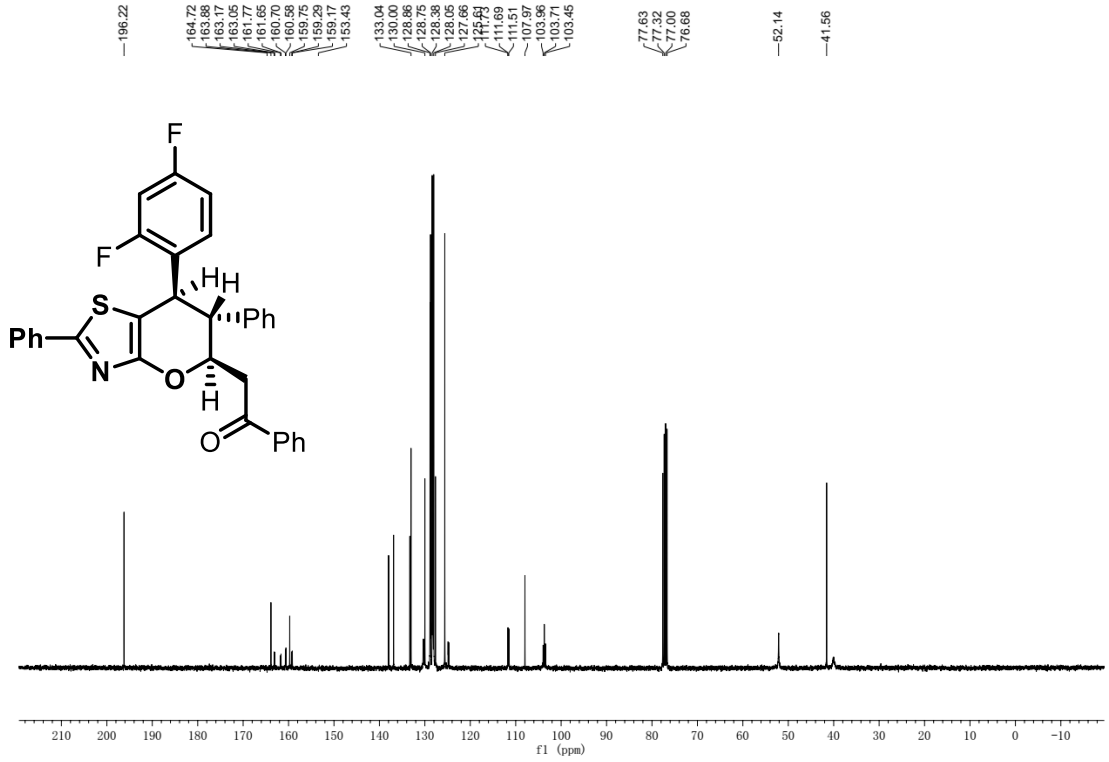
Crude ^{1}H NMR of **3t** (400M, $CDCl_3$)



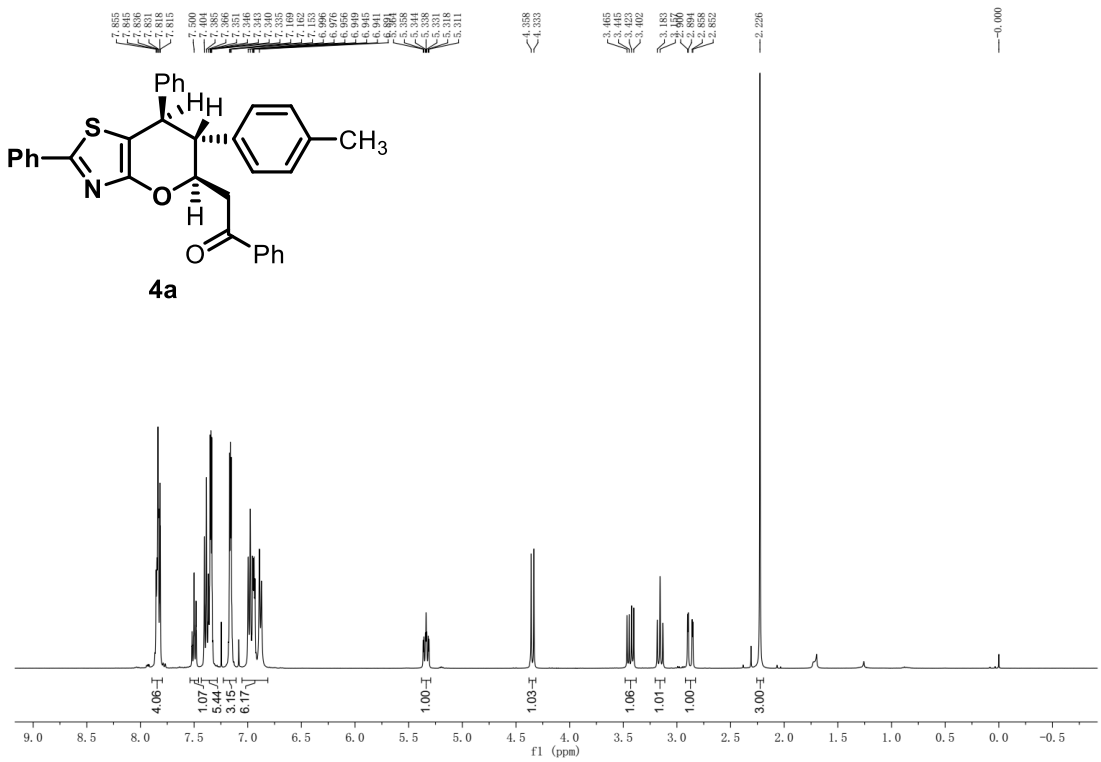
^{19}F NMR of **3t** (400M, $CDCl_3$)



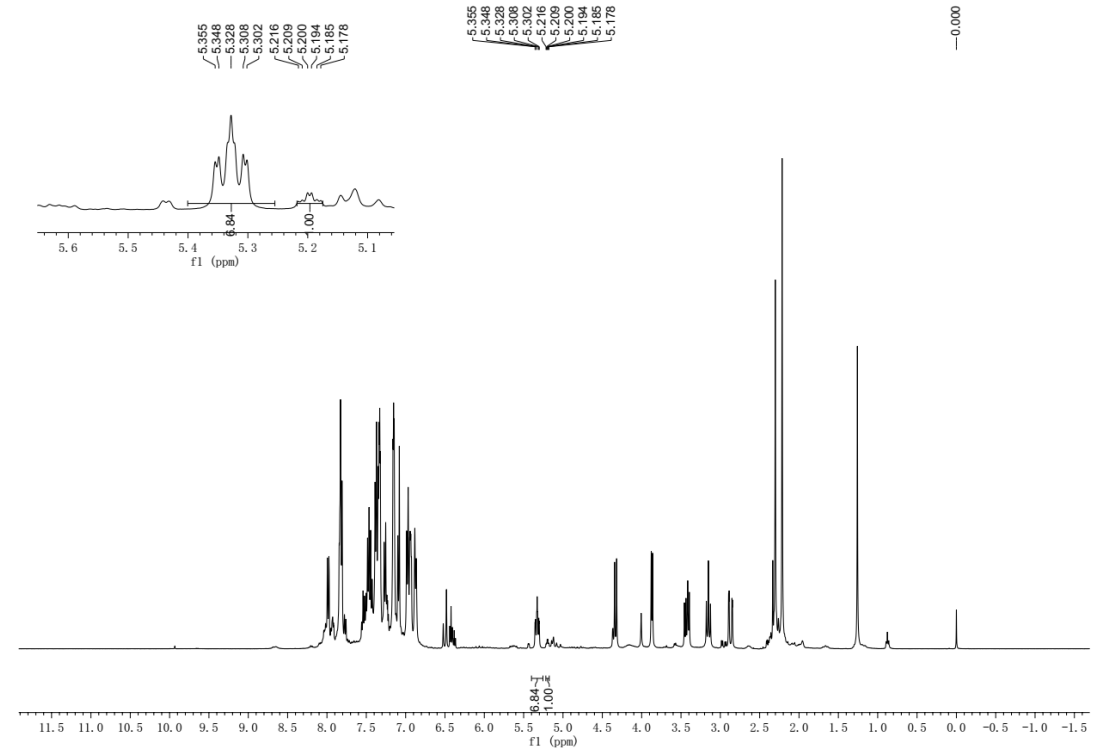
^{13}C NMR of **3t** (101M, $CDCl_3$)



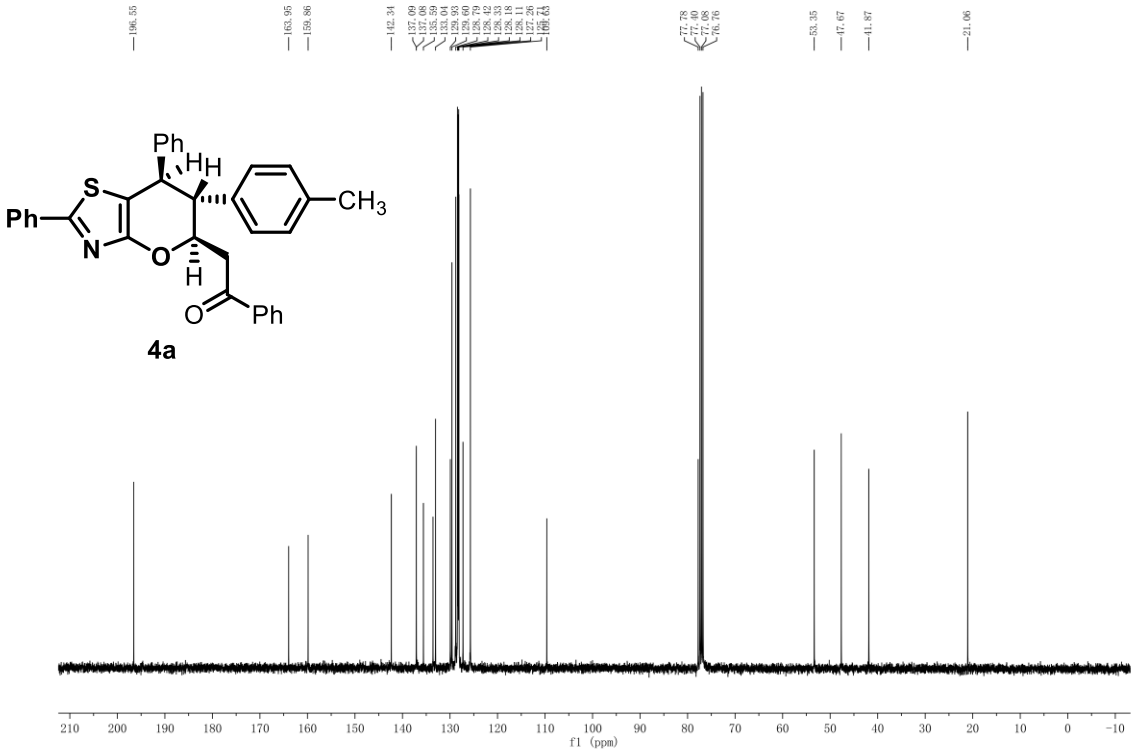
^{1}HNMR of **4a** (400M, $CDCl_3$)



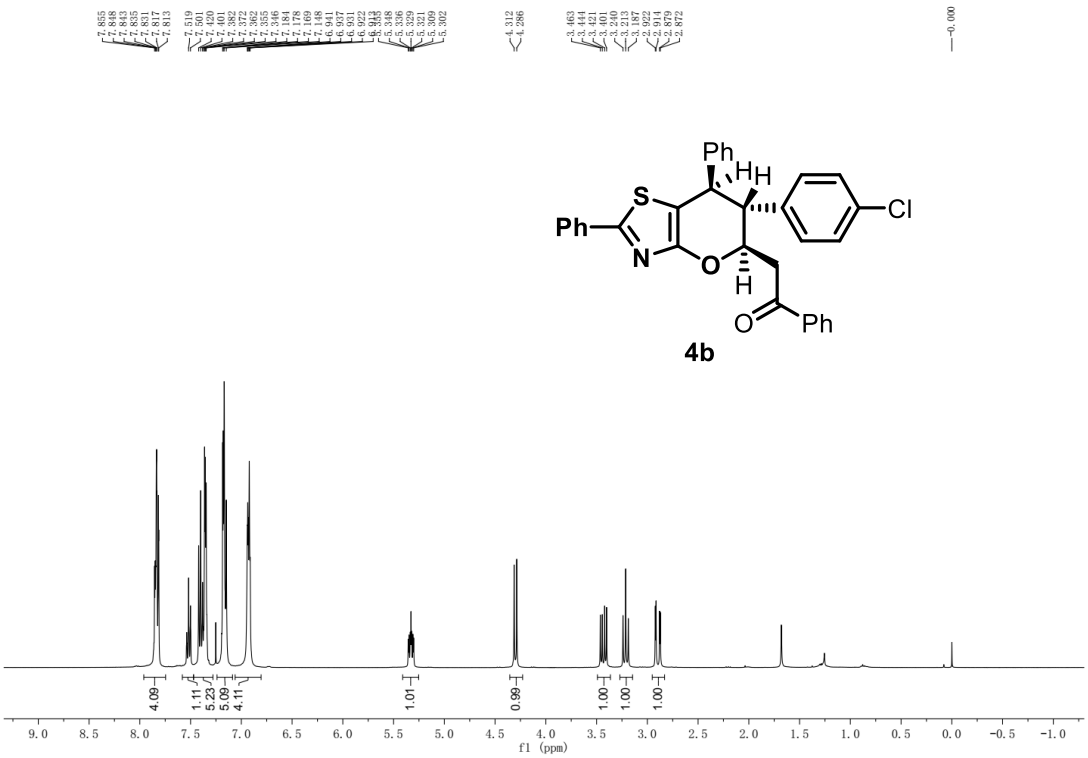
Crude ^{1}H NMR of **4a** (400M, $CDCl_3$)



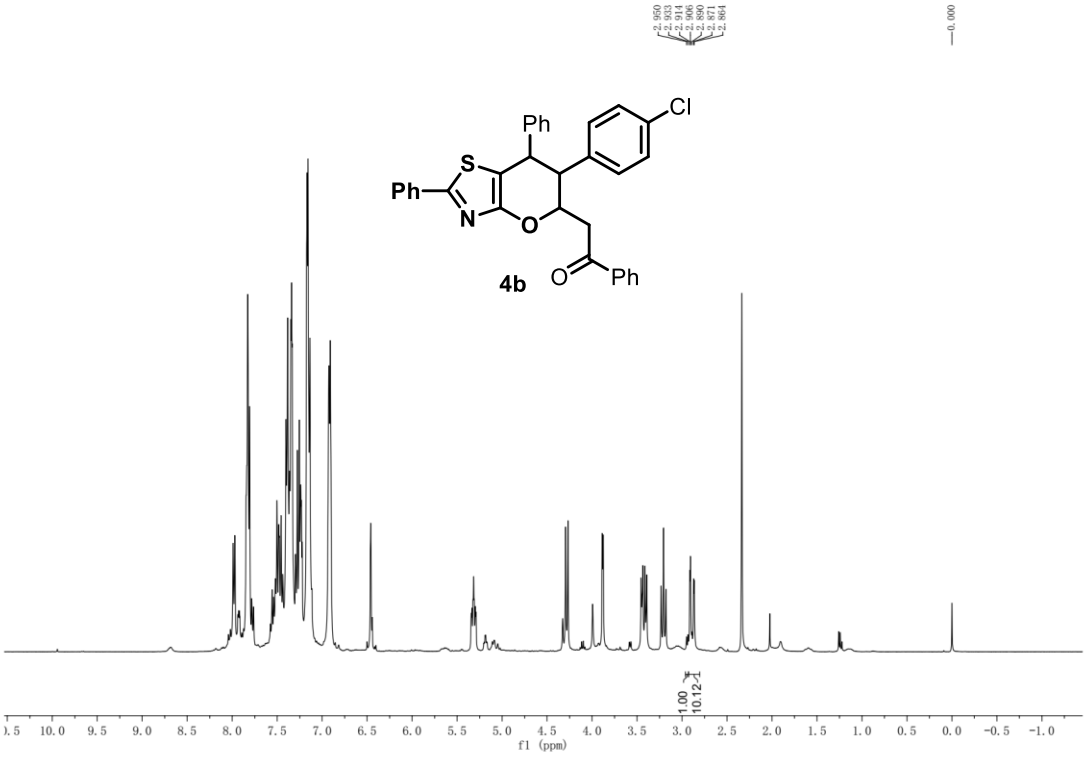
^{13}CNMR of **4a** (101M, $CDCl_3$)



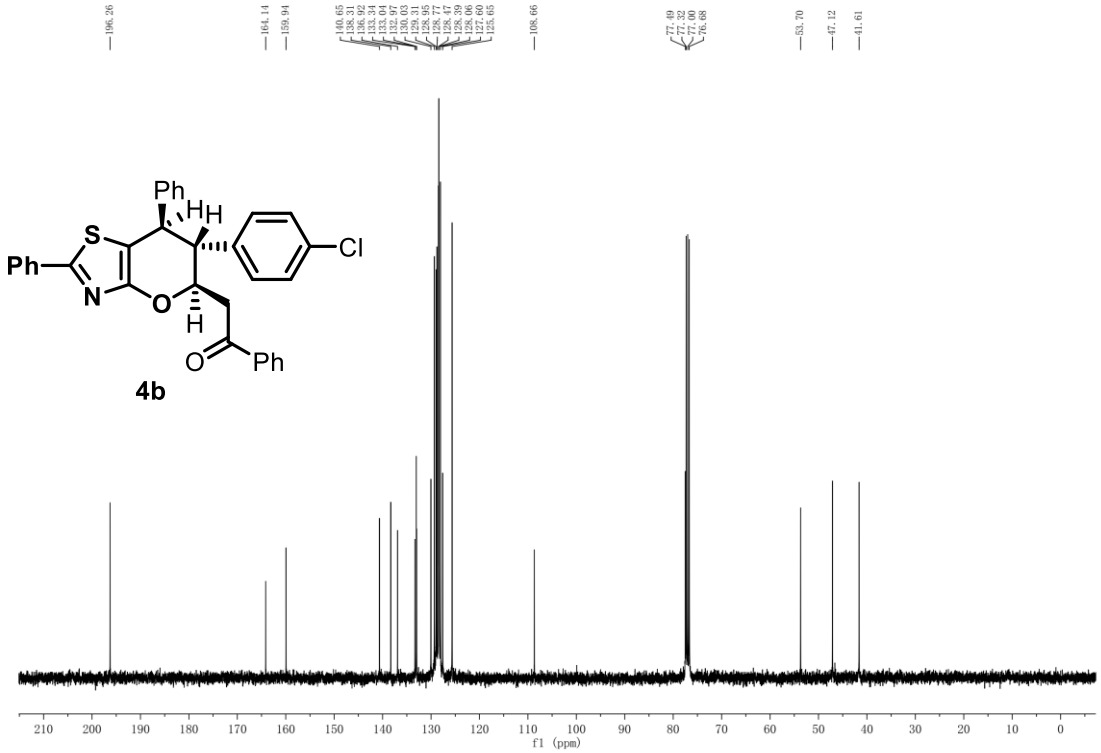
^{1}HNMR of **4b** (400M, $CDCl_3$)



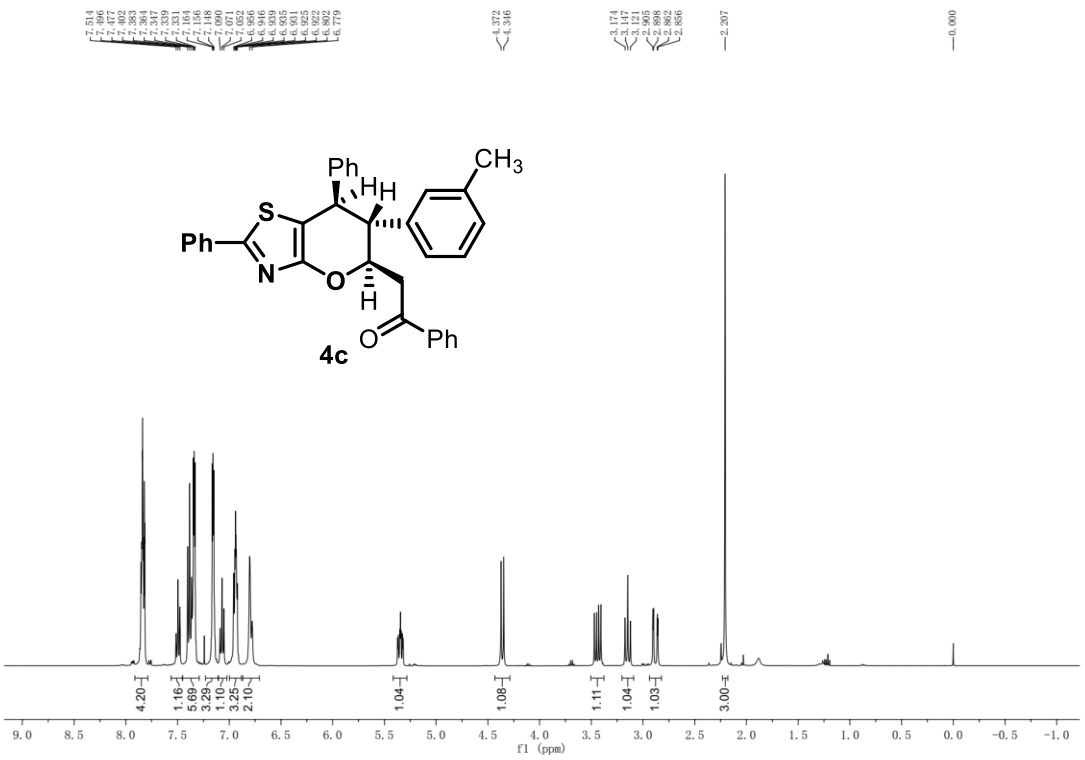
Crude ^{1}H NMR of **4b** (400M, $CDCl_3$)



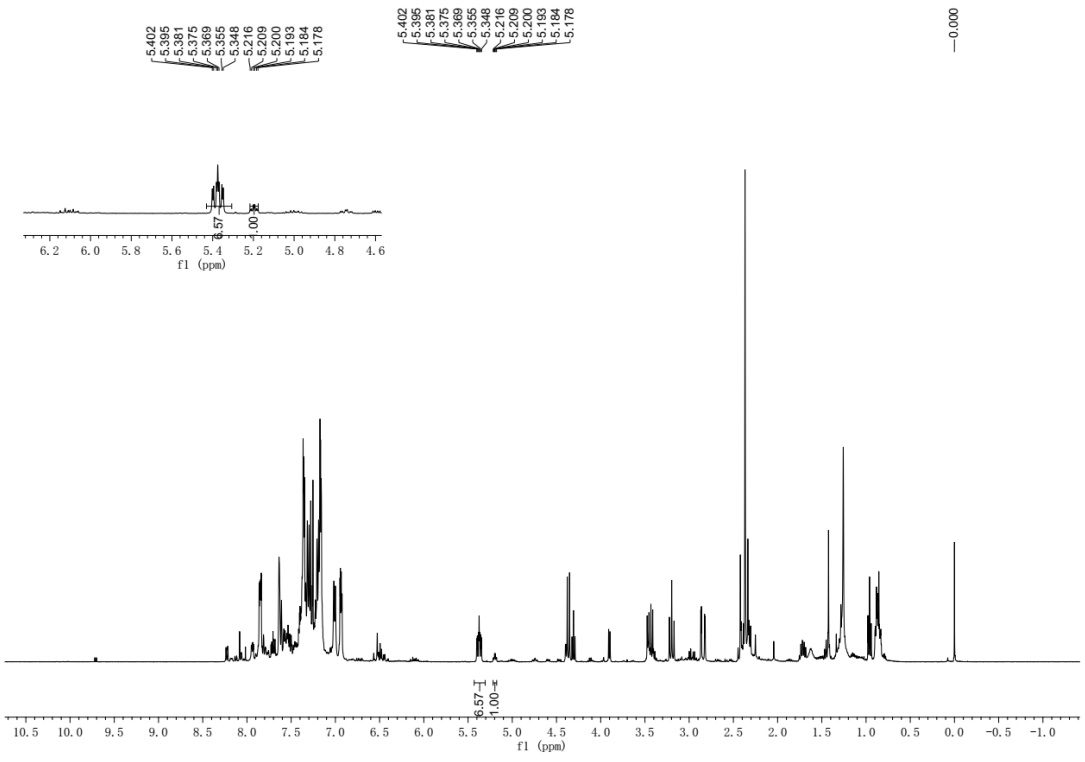
^{13}CNMR of **4b** (101M, $CDCl_3$)



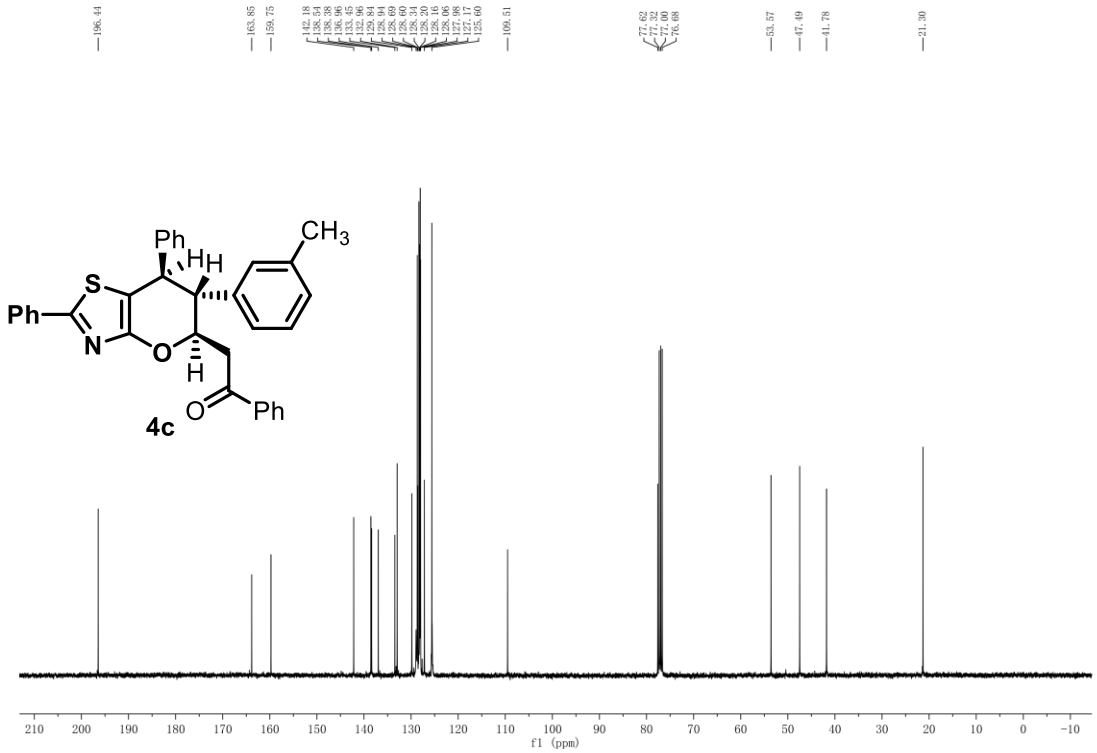
^{1}HNMR of **4c** (400M, $CDCl_3$)



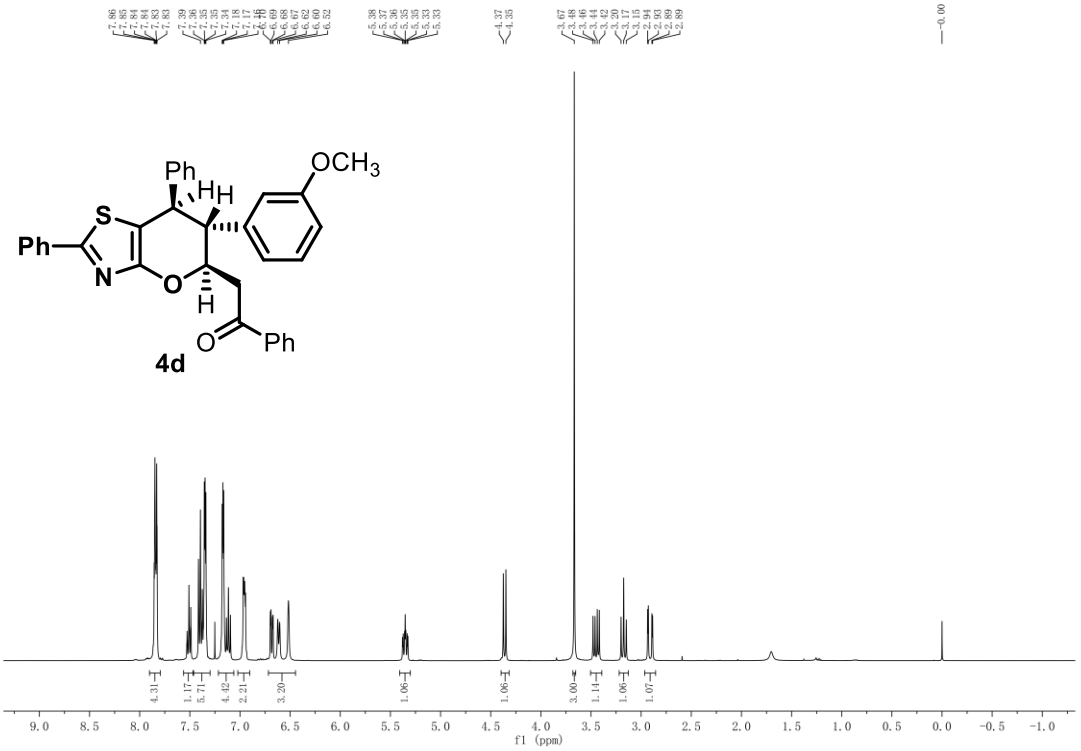
Crude ^{1}H NMR of **4c** (400M, $CDCl_3$)



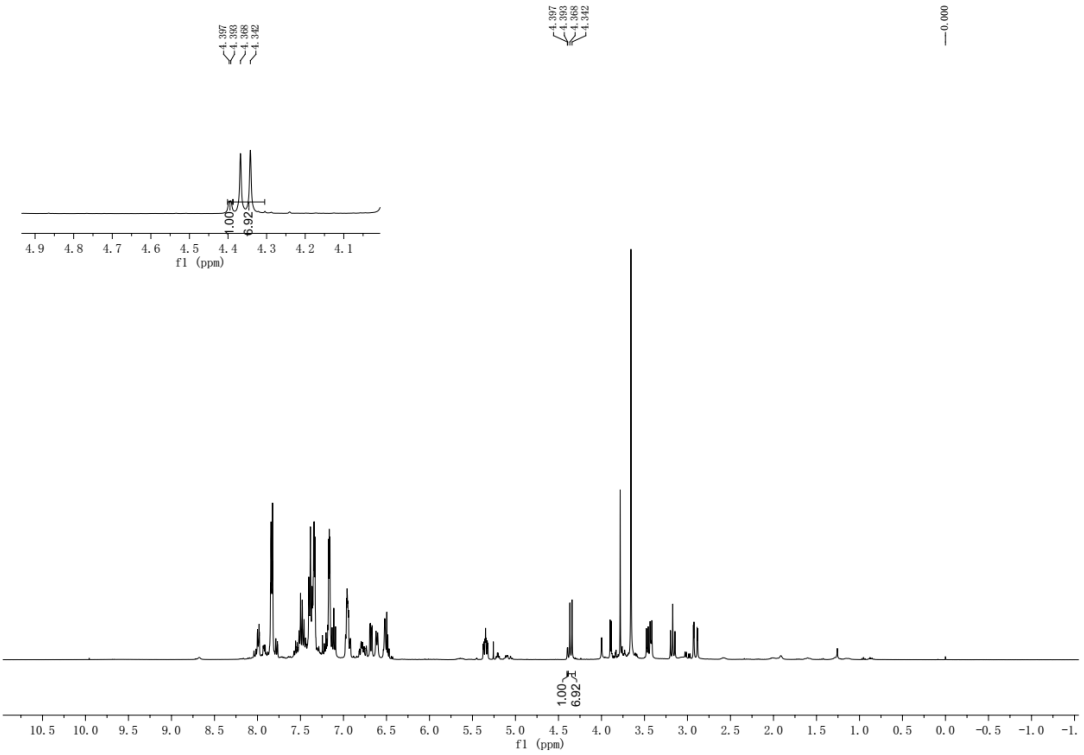
^{13}CNMR of **4c** (101M, $CDCl_3$)



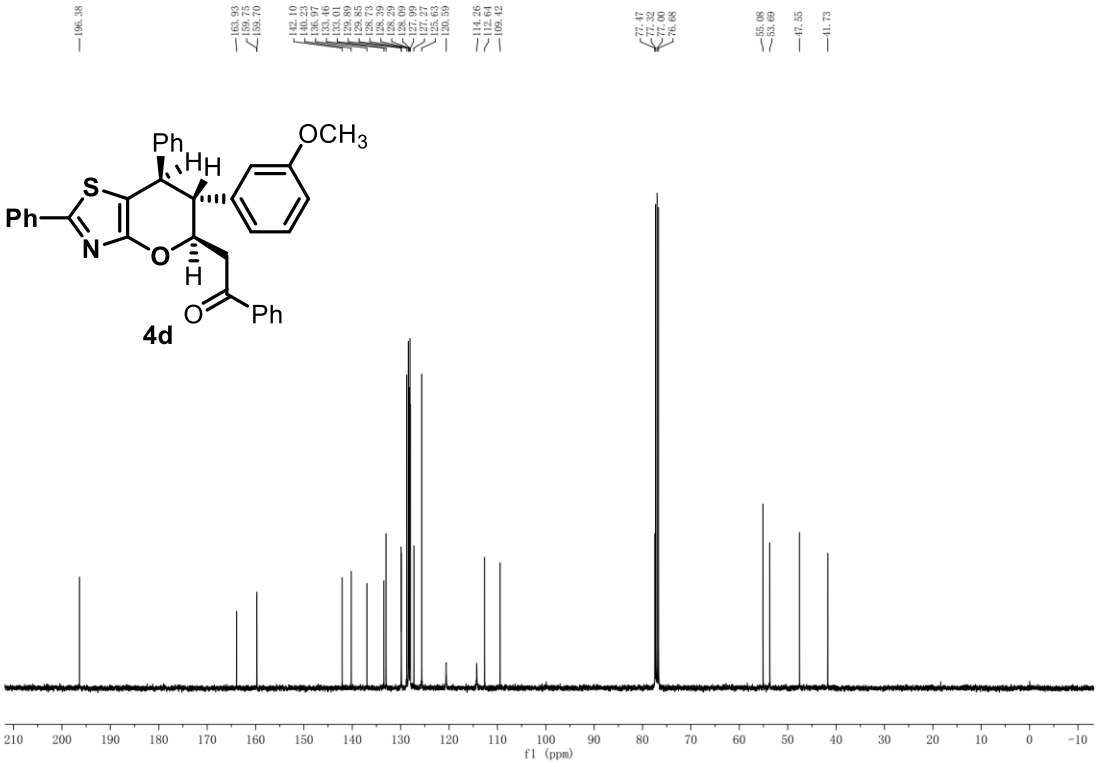
^{1}HNMR of **4d** (400M, $CDCl_3$)



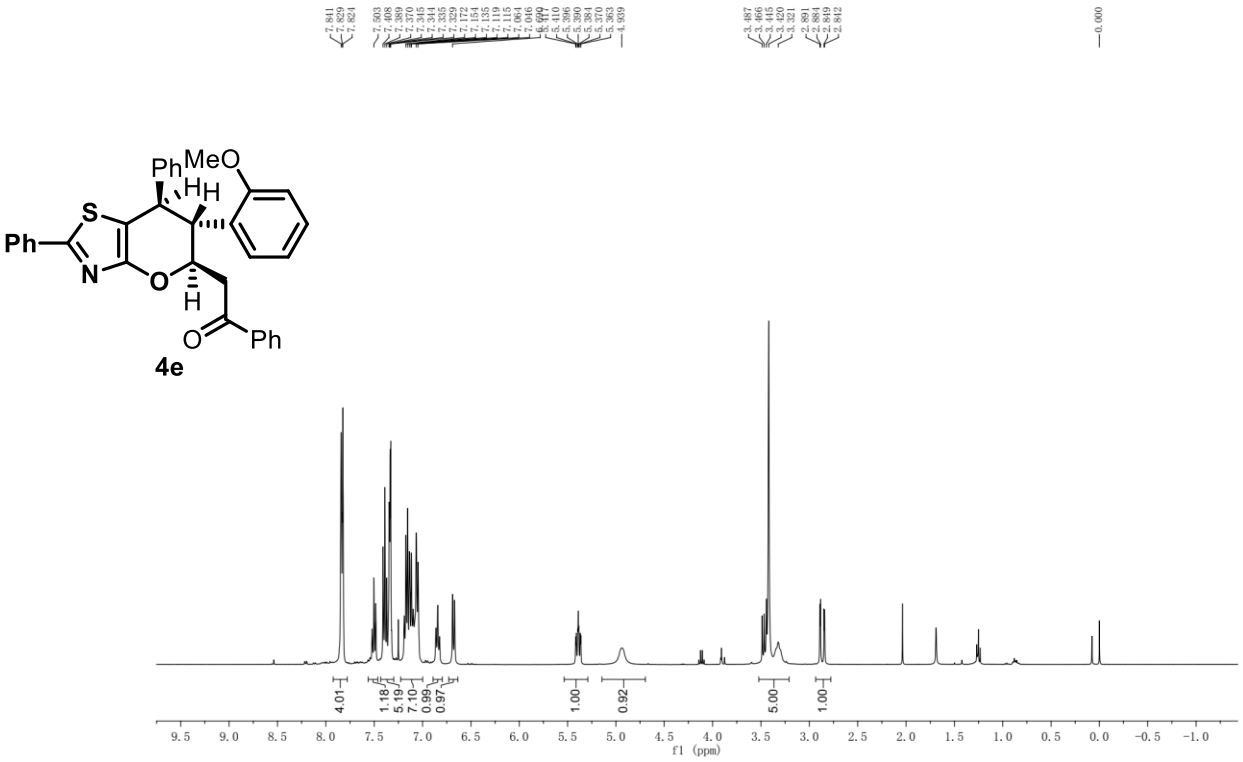
Crude ^{1}H NMR of **4d** (400M, $CDCl_3$)



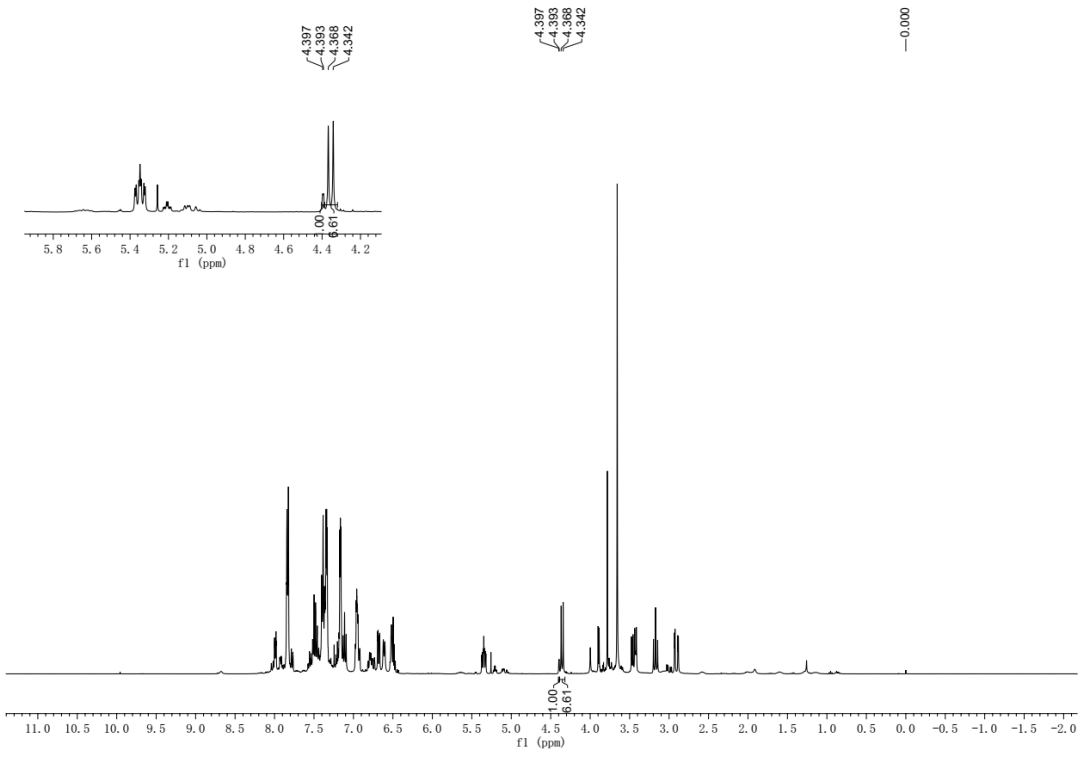
^{13}CNMR of **4d** (101M, $CDCl_3$)



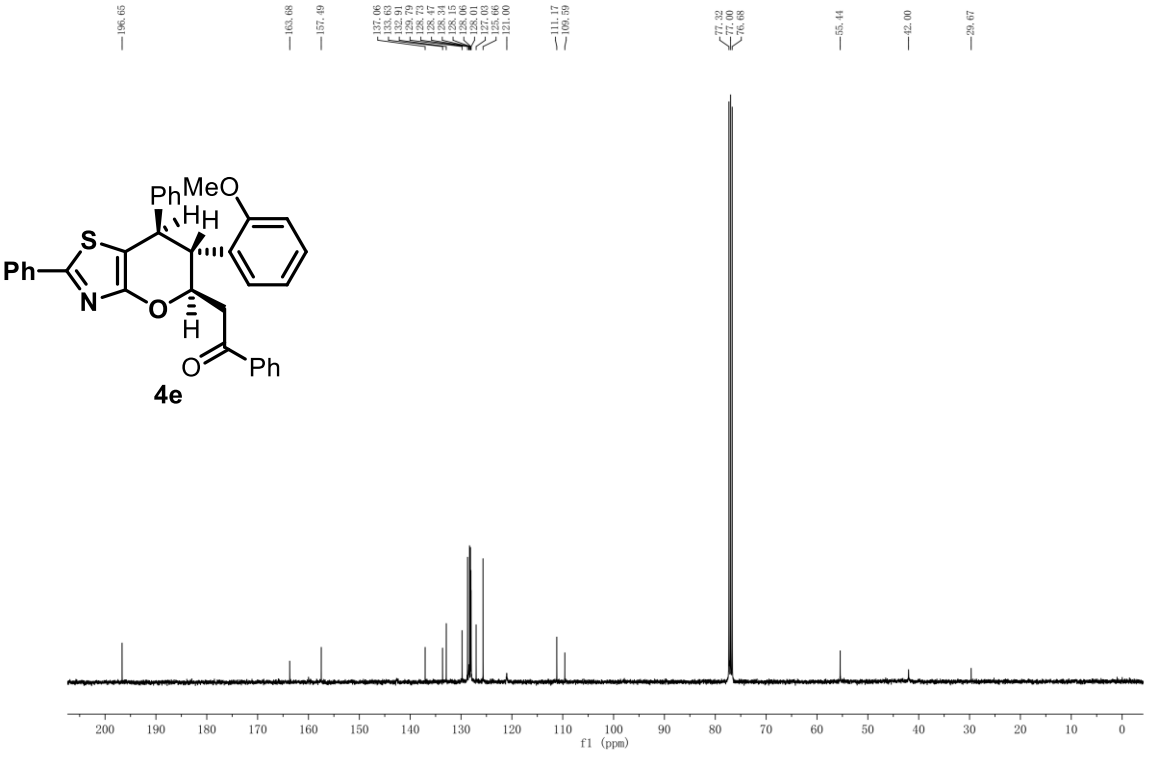
^{1}HNMR of **4e** (400M, $CDCl_3$)



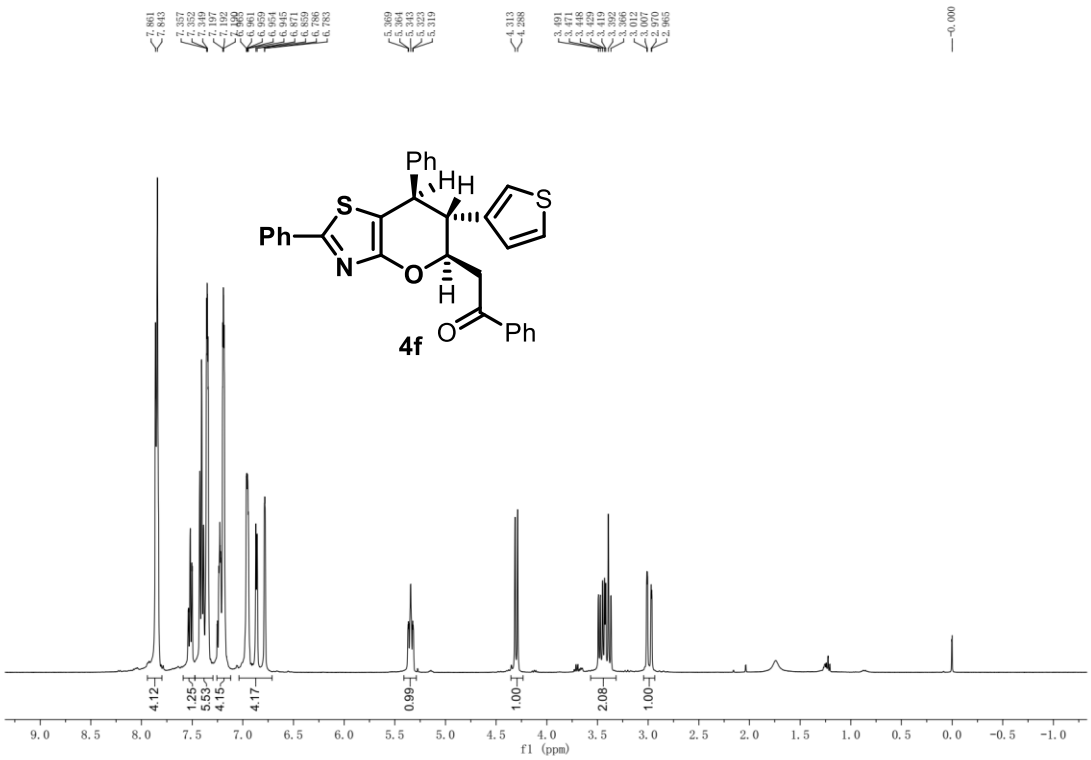
Crude ^{1}H NMR of **4e** (400M, $CDCl_3$)



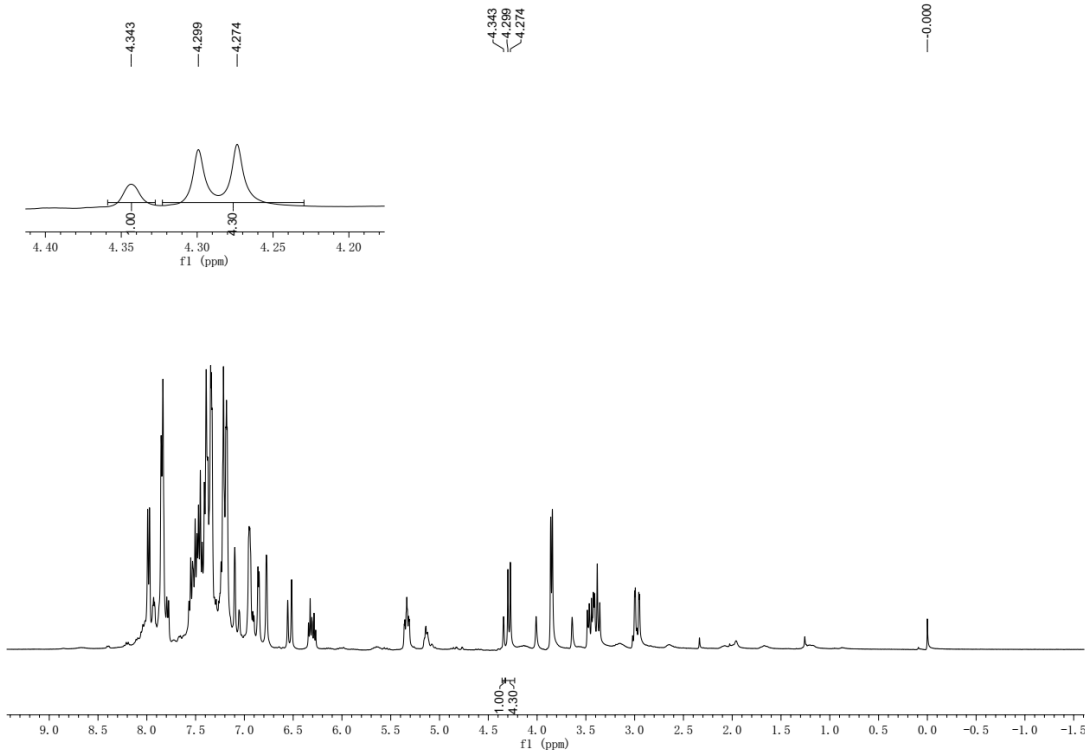
^{13}CNMR of **4e** (101M, $CDCl_3$)



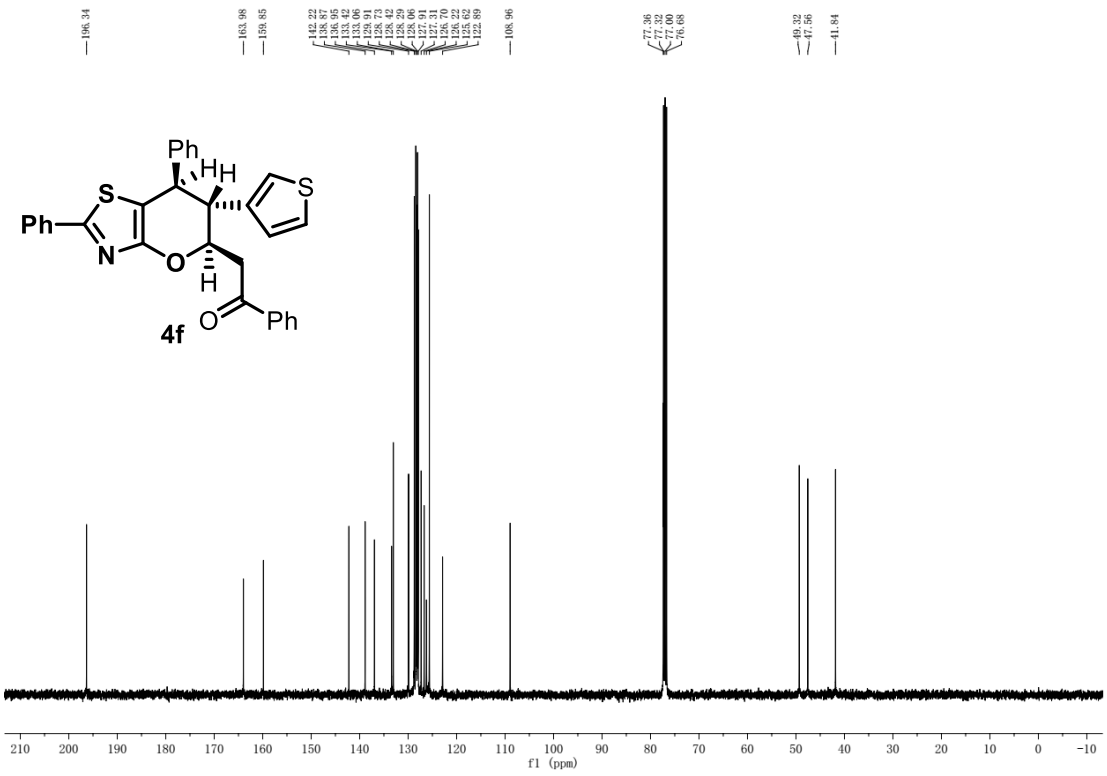
^{1}HNMR of **4f** (400M, $CDCl_3$)



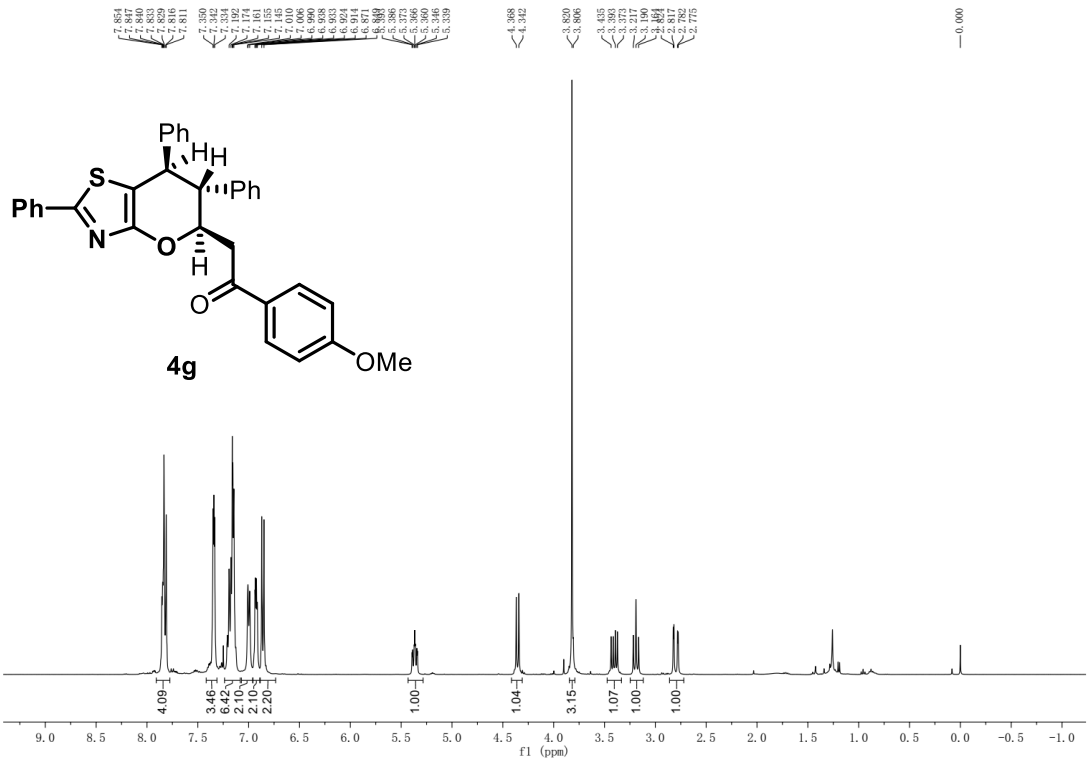
Crude ^{1}H NMR of **4e** (400M, $CDCl_3$)



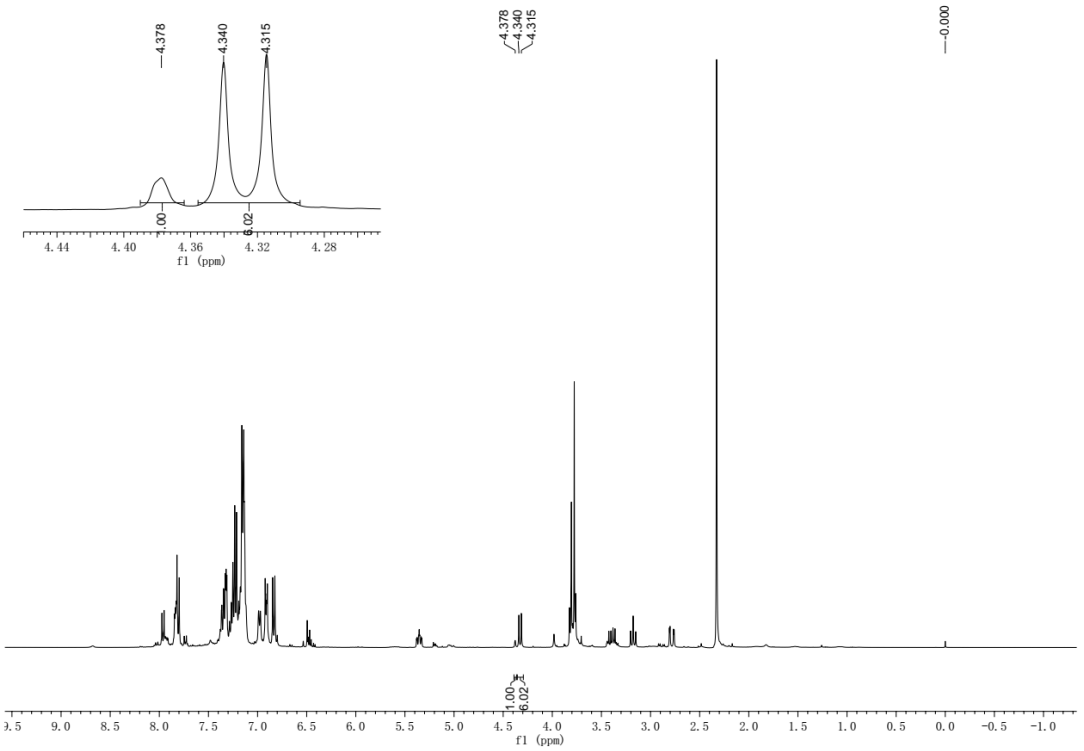
^{13}CNMR of **4f** (101M, $CDCl_3$)



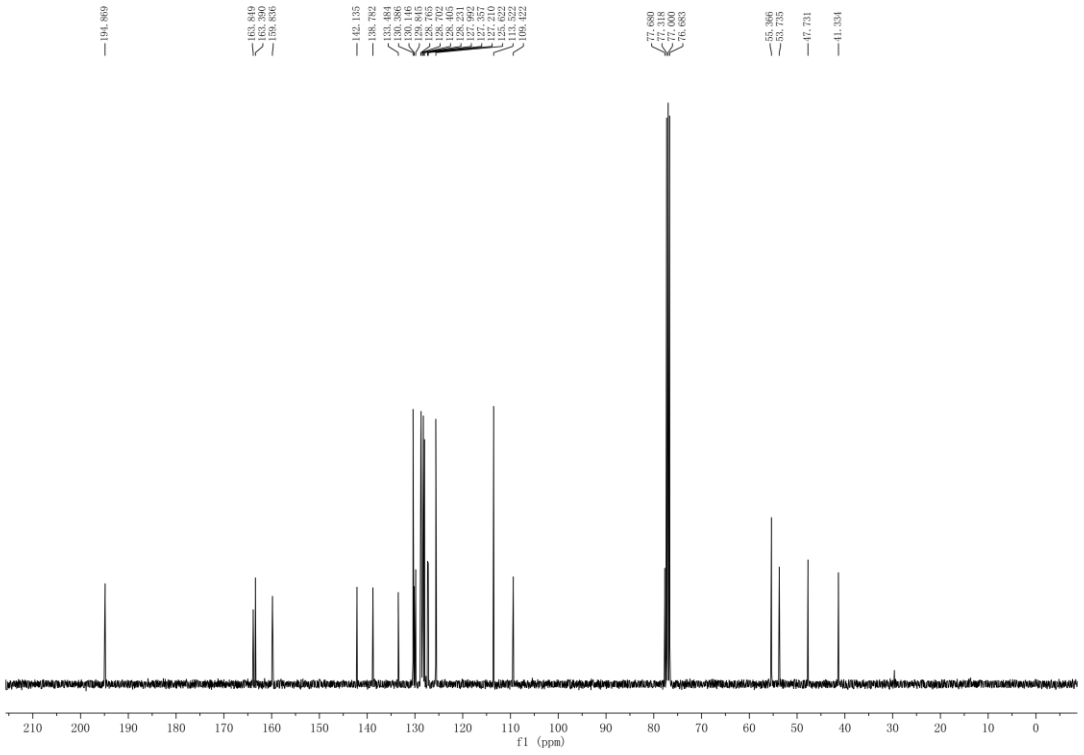
^{1}HNMR of **4g** (400M, $CDCl_3$)



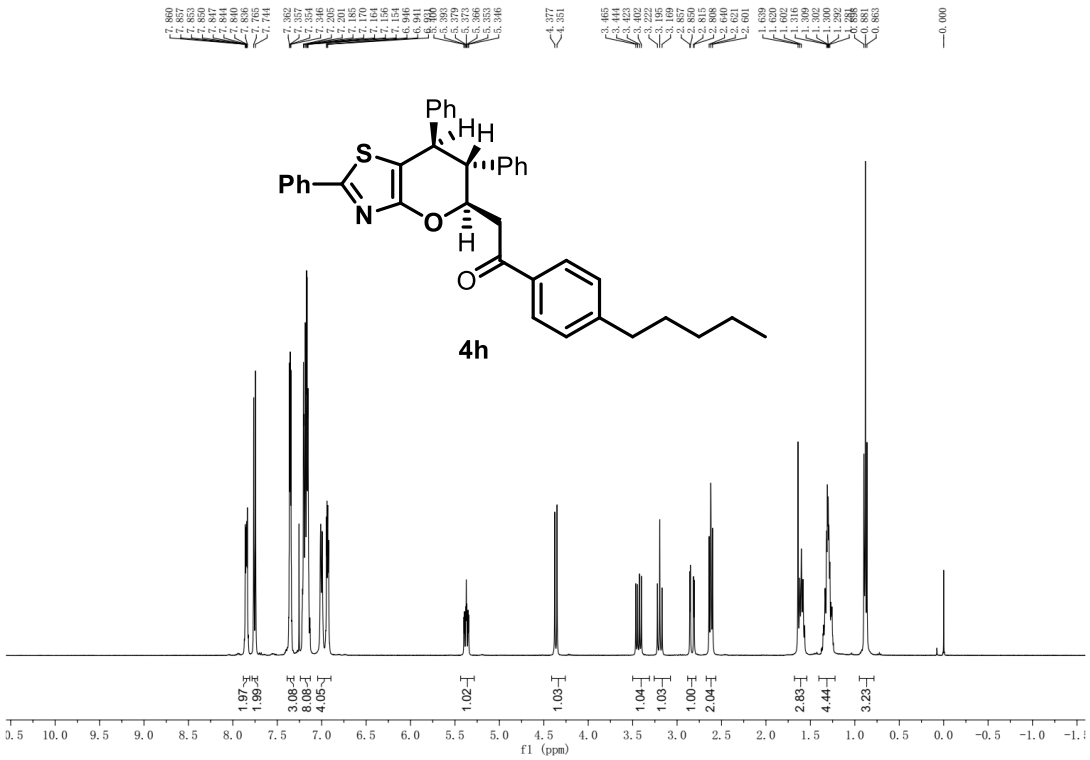
Crude ^{1}H NMR of **4e** (400M, $CDCl_3$)



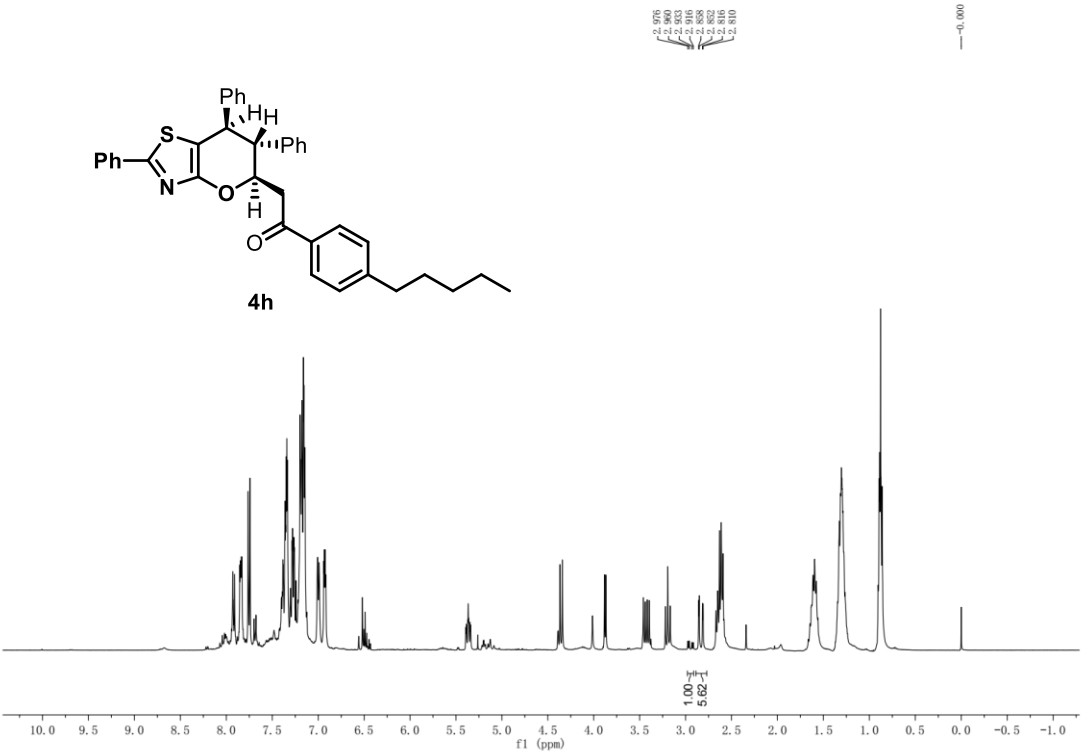
^{13}CNMR of **4g** (101M, $CDCl_3$)



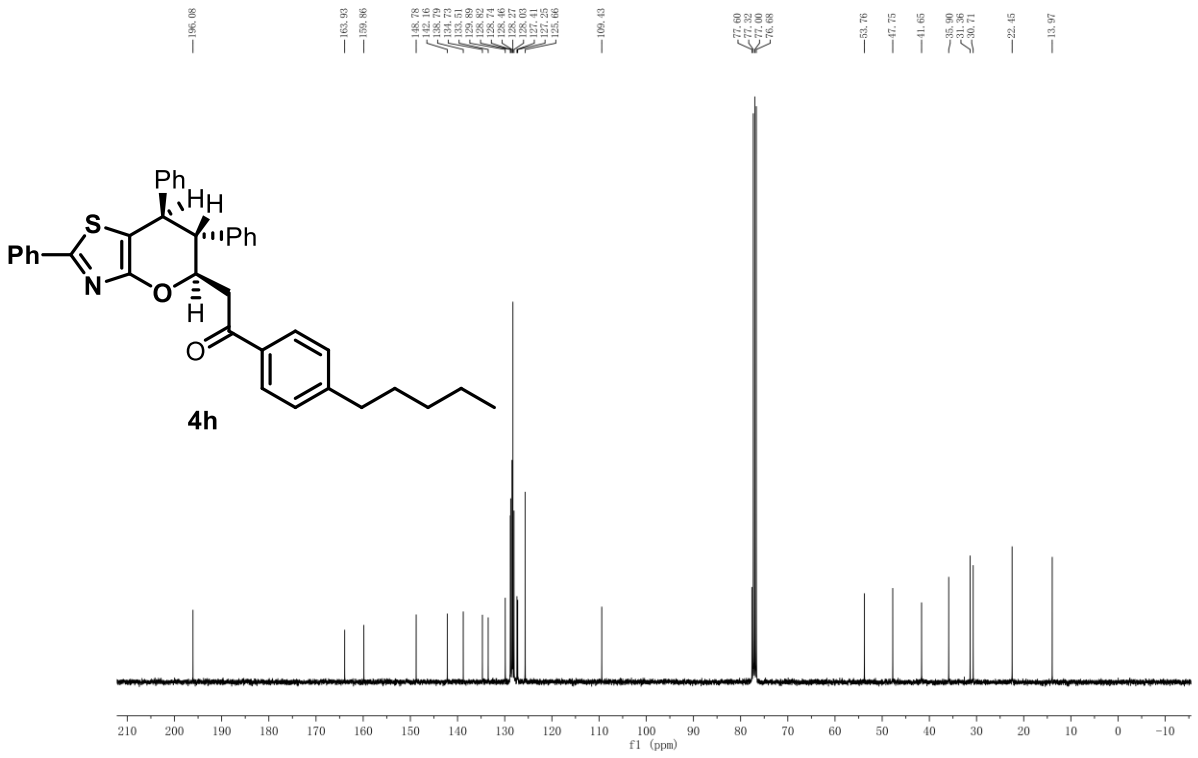
^{1}HNMR of **4h** (400M, $CDCl_3$)



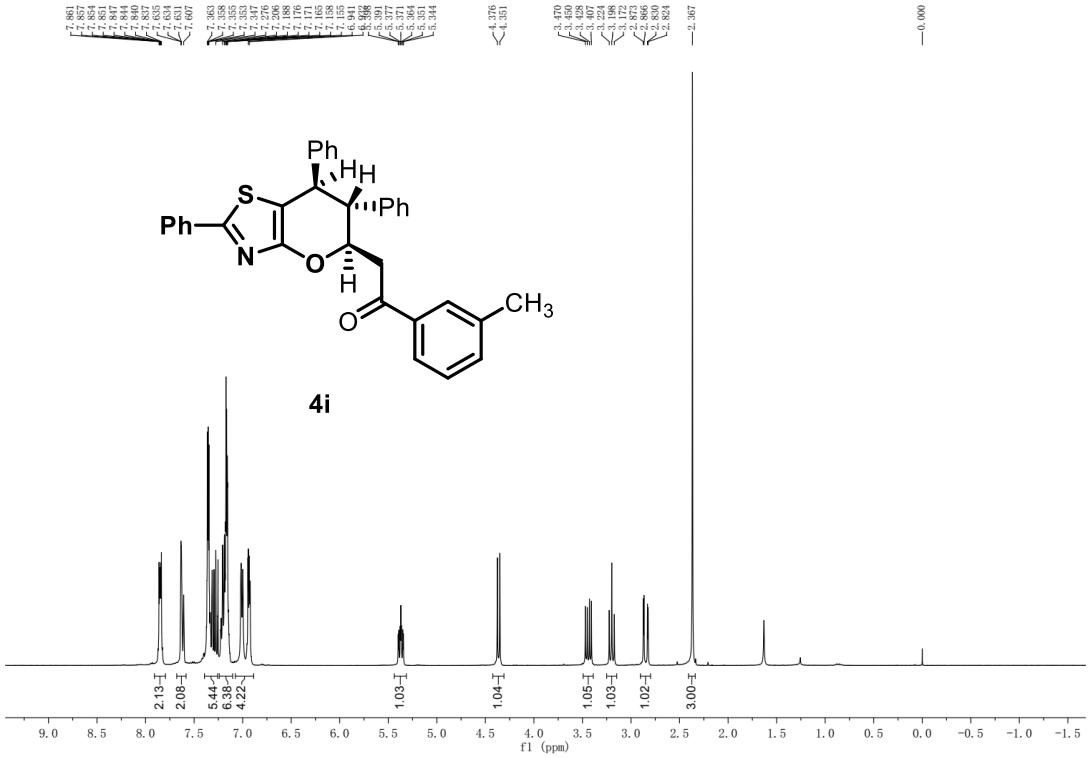
Crude ^{1}H NMR of **4h** (400M, $CDCl_3$)



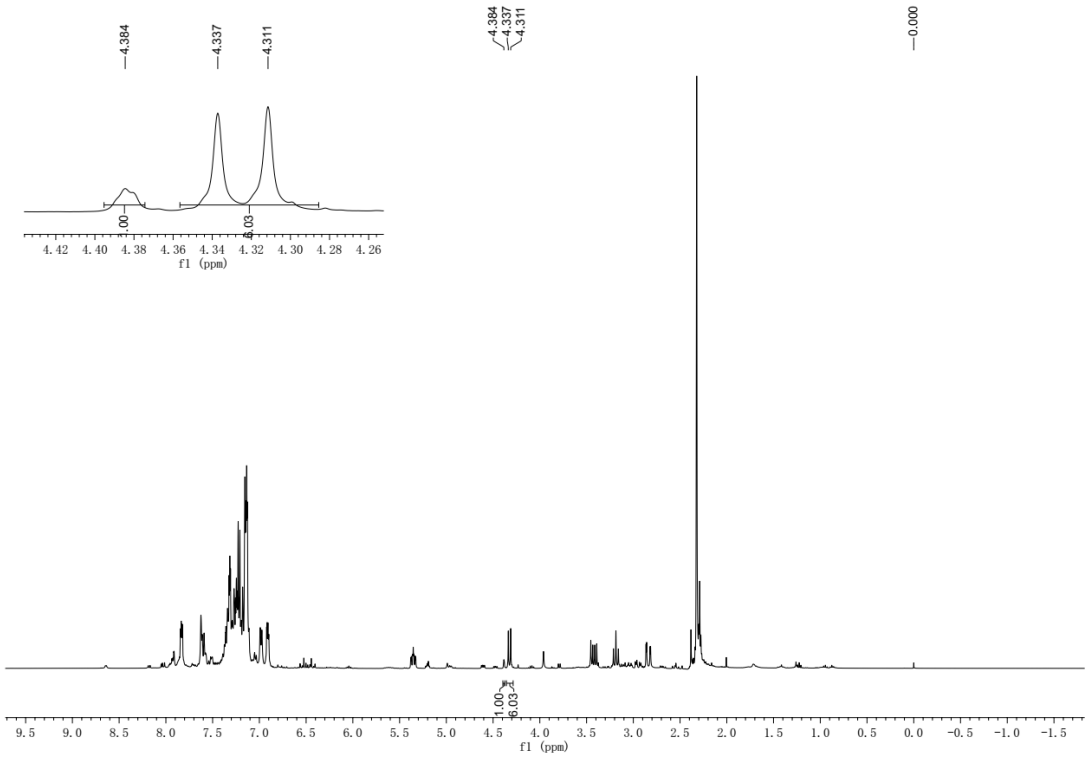
^{13}CNMR of **4h** (101M, $CDCl_3$)



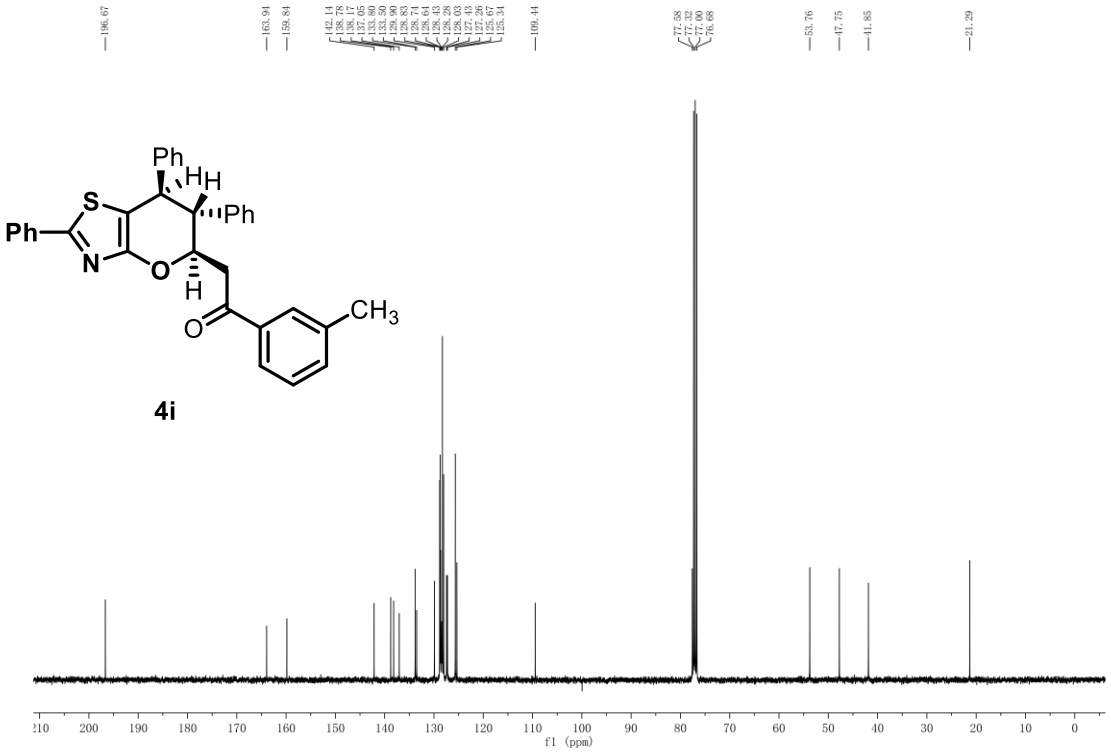
^{1}HNMR of **4i** (400M, $CDCl_3$)



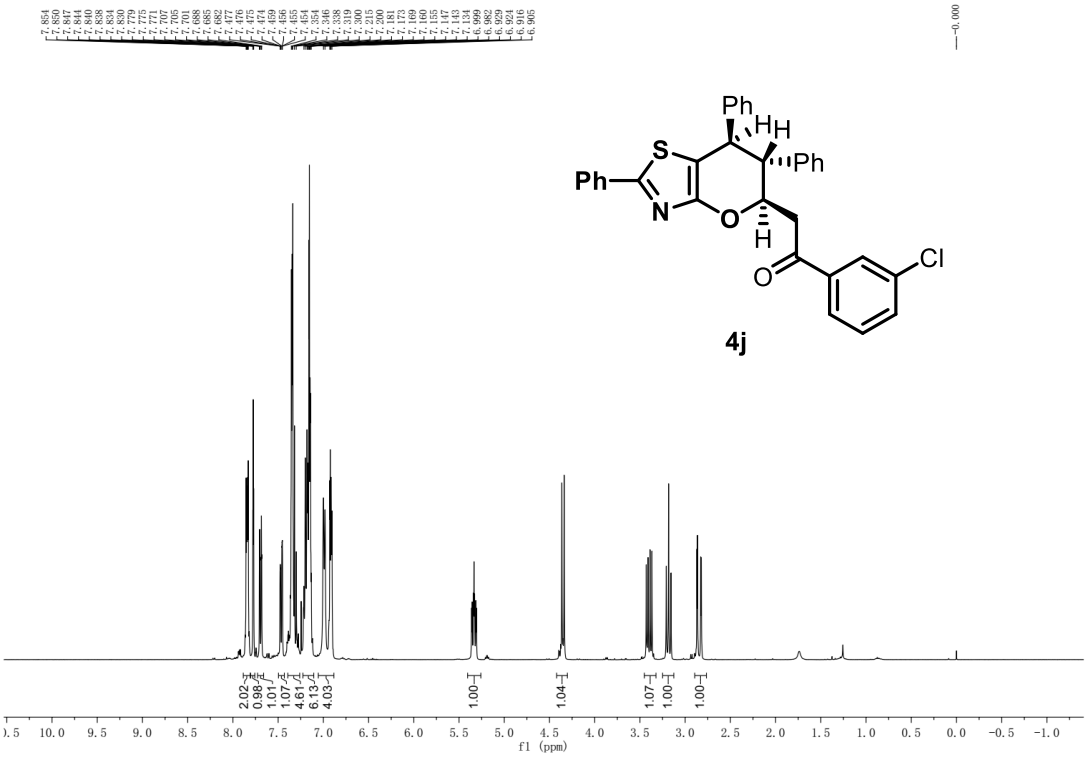
Crude ^{1}H NMR of **4h** (400M, $CDCl_3$)



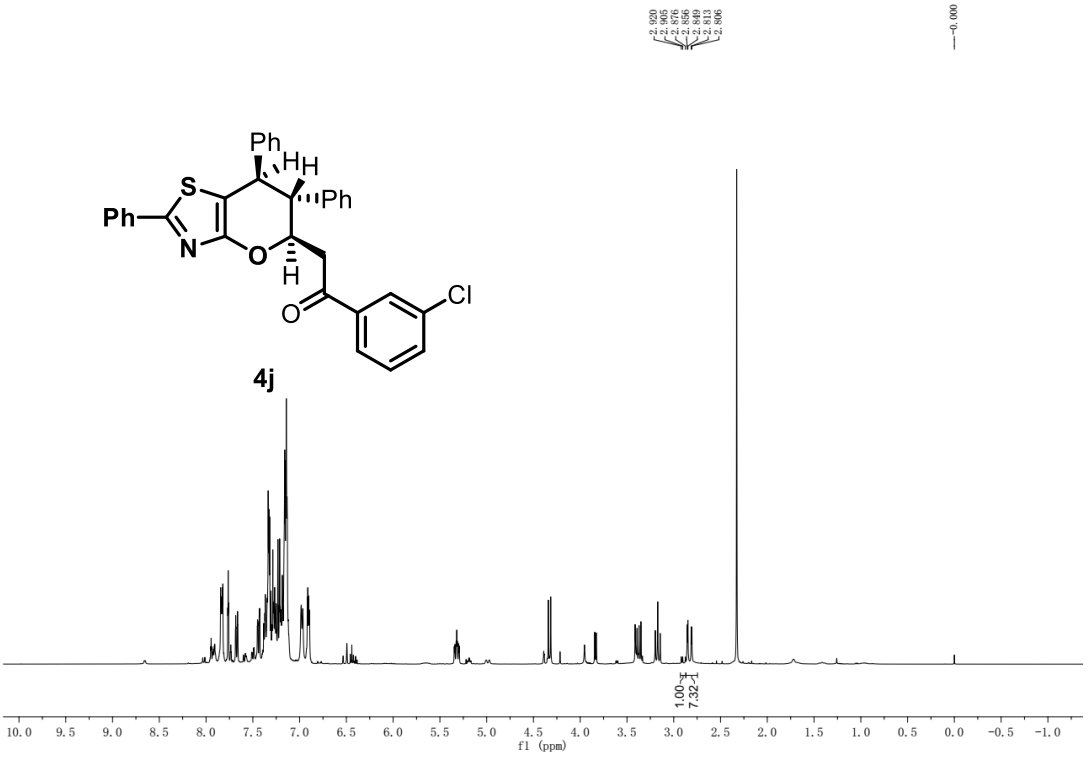
^{13}CNMR of **4i** (101M, $CDCl_3$)



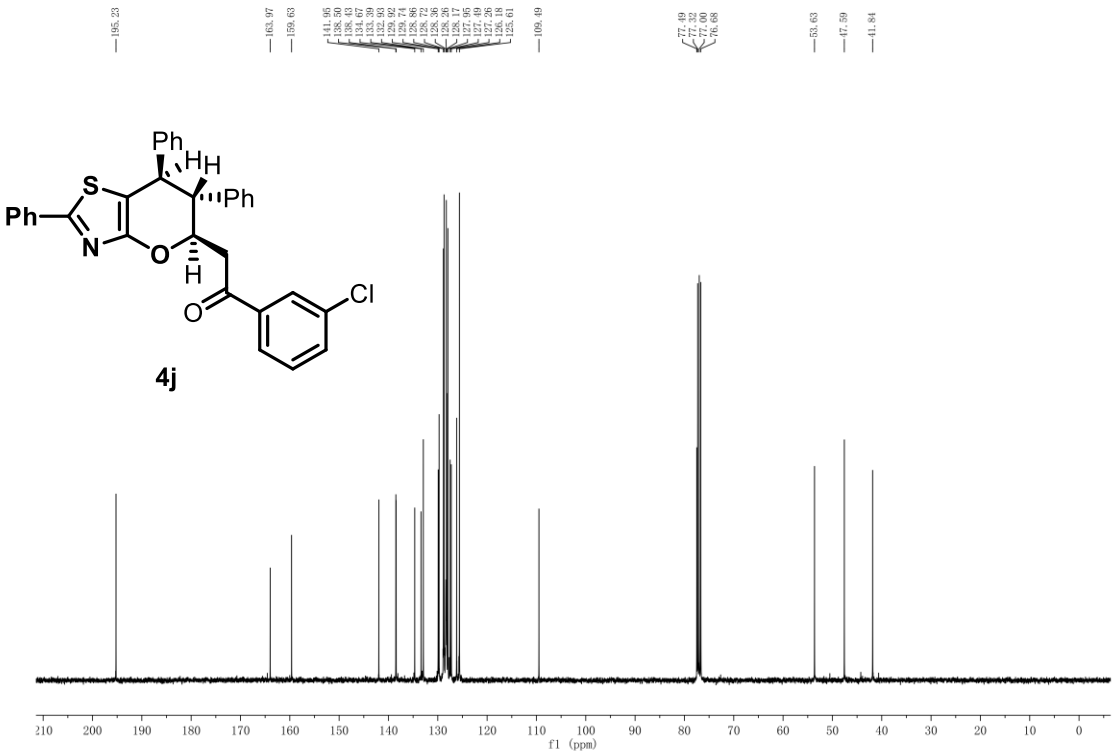
^{1}HNMR of **4j** (400M, $CDCl_3$)



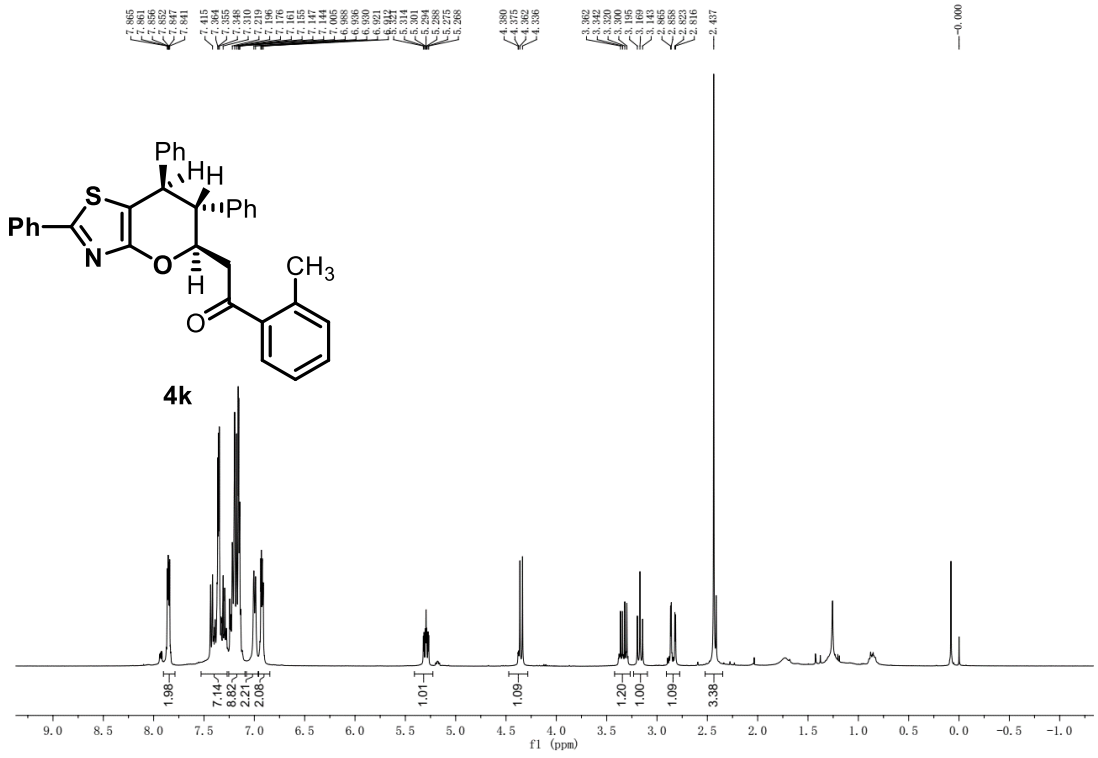
Crude ^{1}H NMR of **4j** (400M, $CDCl_3$)



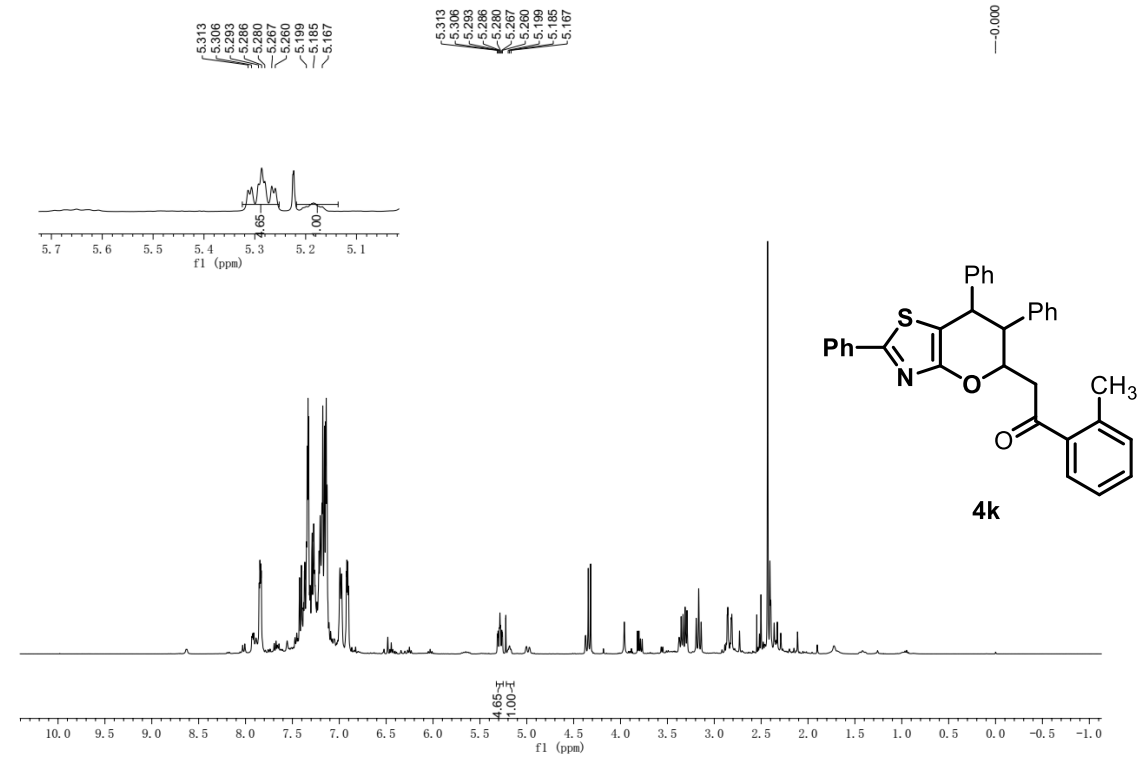
^{13}CNMR of **4j** (101M, $CDCl_3$)



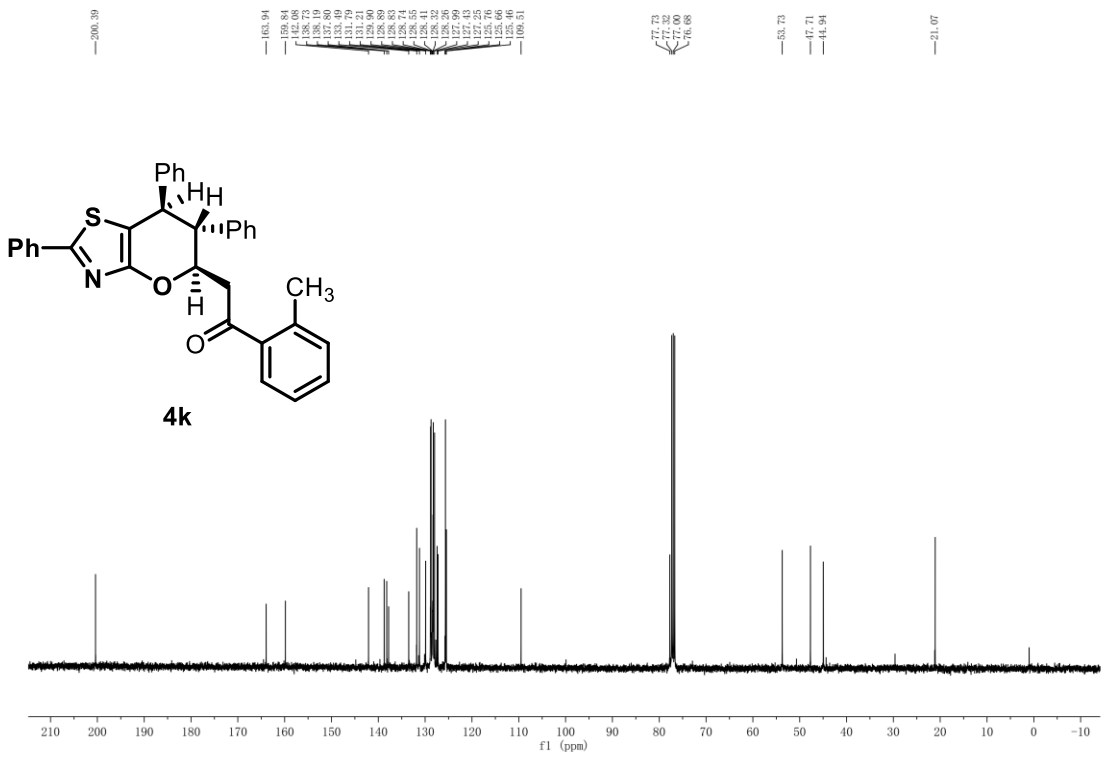
^{1}HNMR of **4k** (400M, $CDCl_3$)



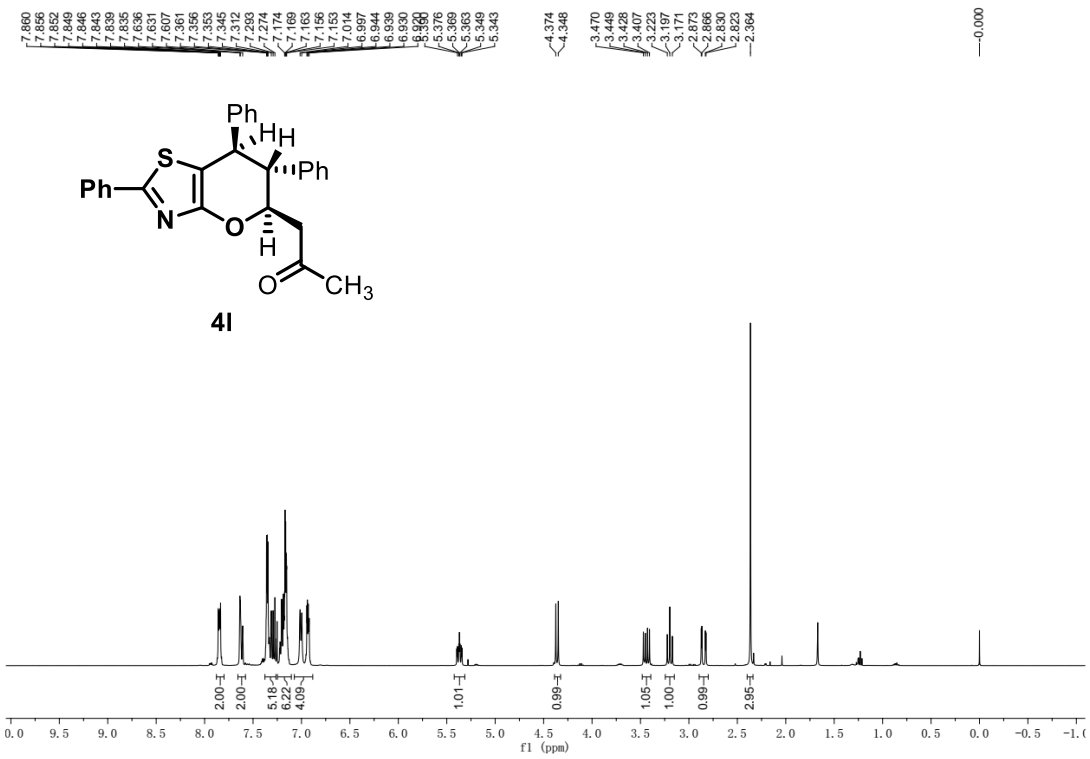
Crude ^{1}HNMR of **4k** (400M, $CDCl_3$)



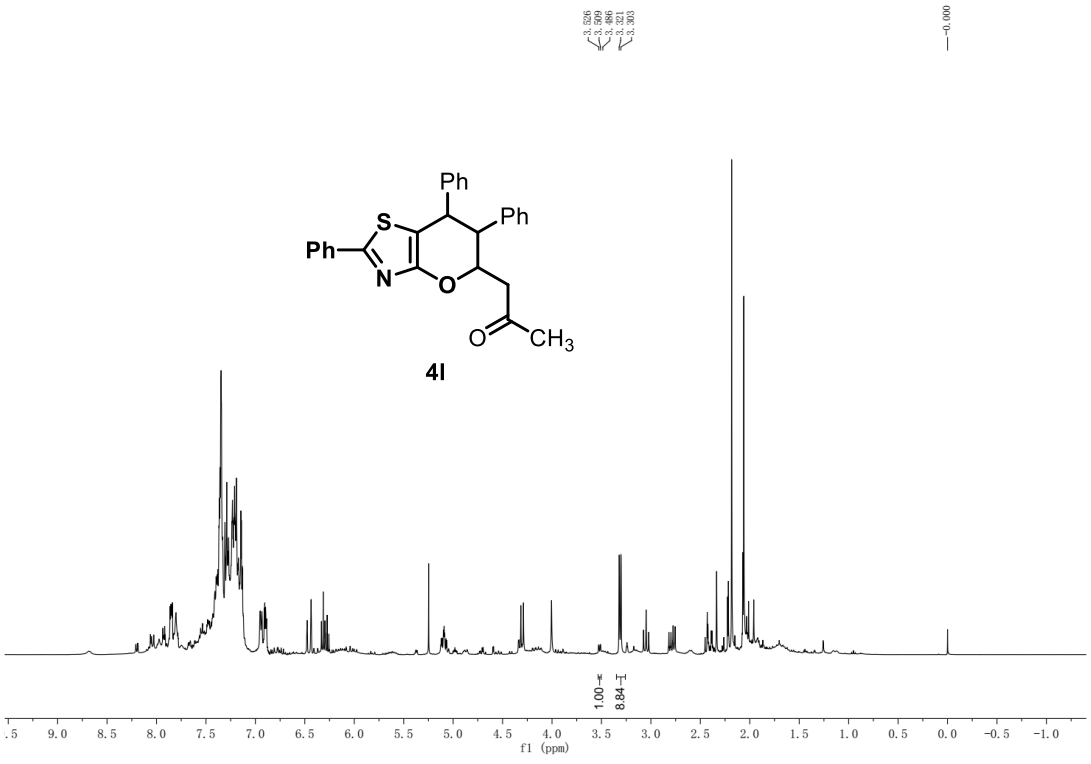
^{13}CNMR of **4k** (101M, $CDCl_3$)



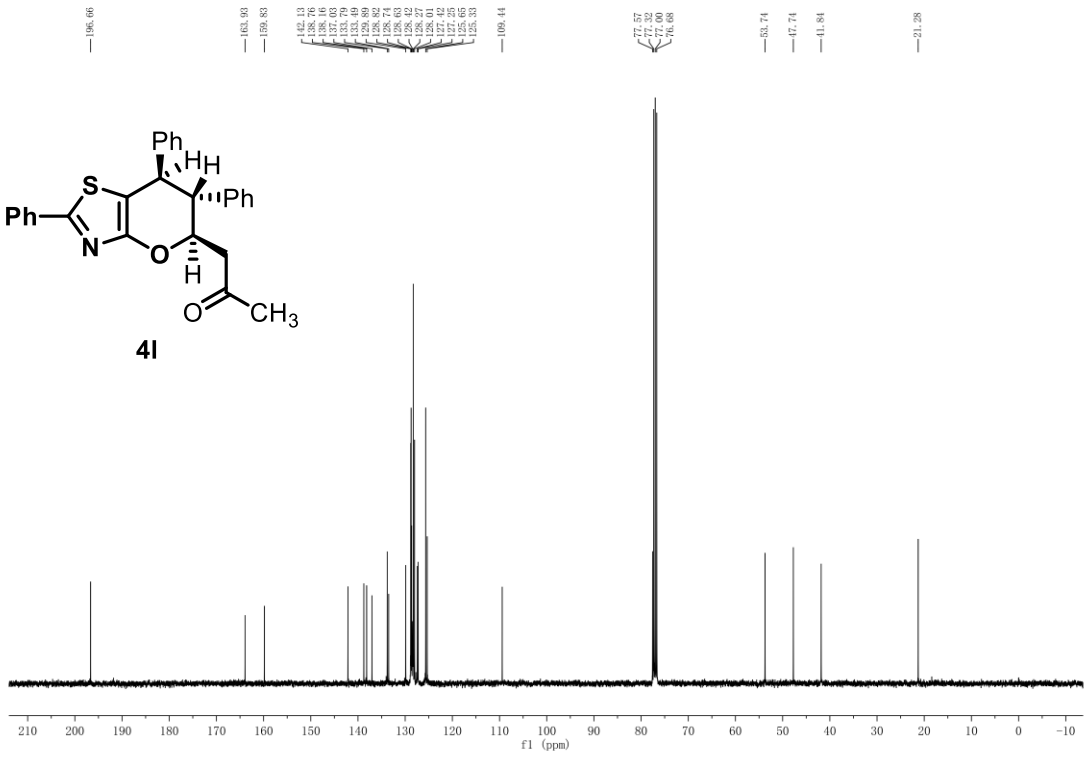
^{1}HNMR of **4l** (400M, $CDCl_3$)



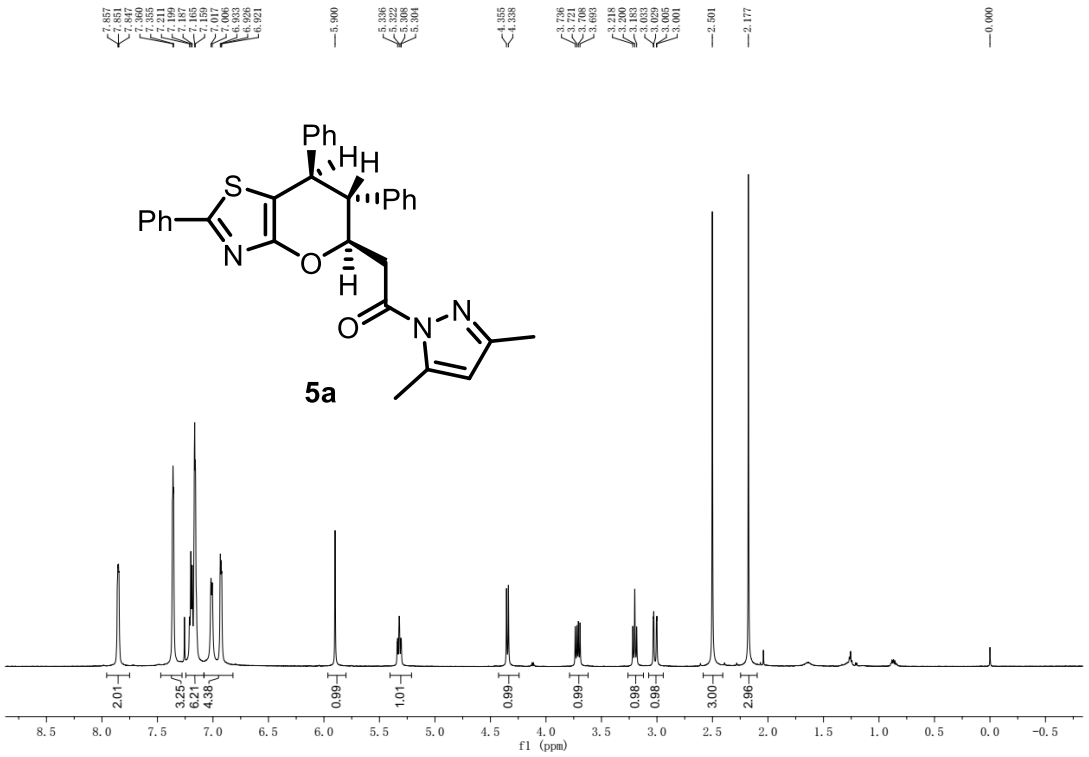
Curde ^{1}HNMR of **4l** (400M, $CDCl_3$)



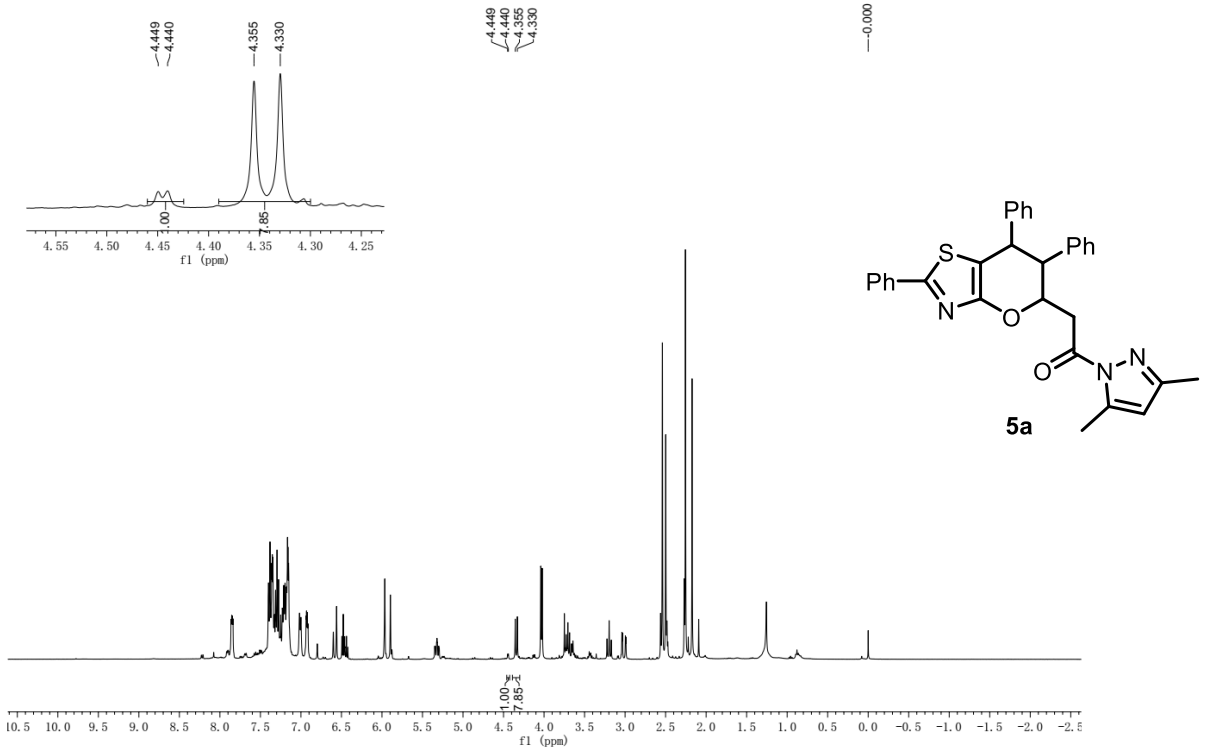
^{13}CNMR of **4k** (101M, $CDCl_3$)



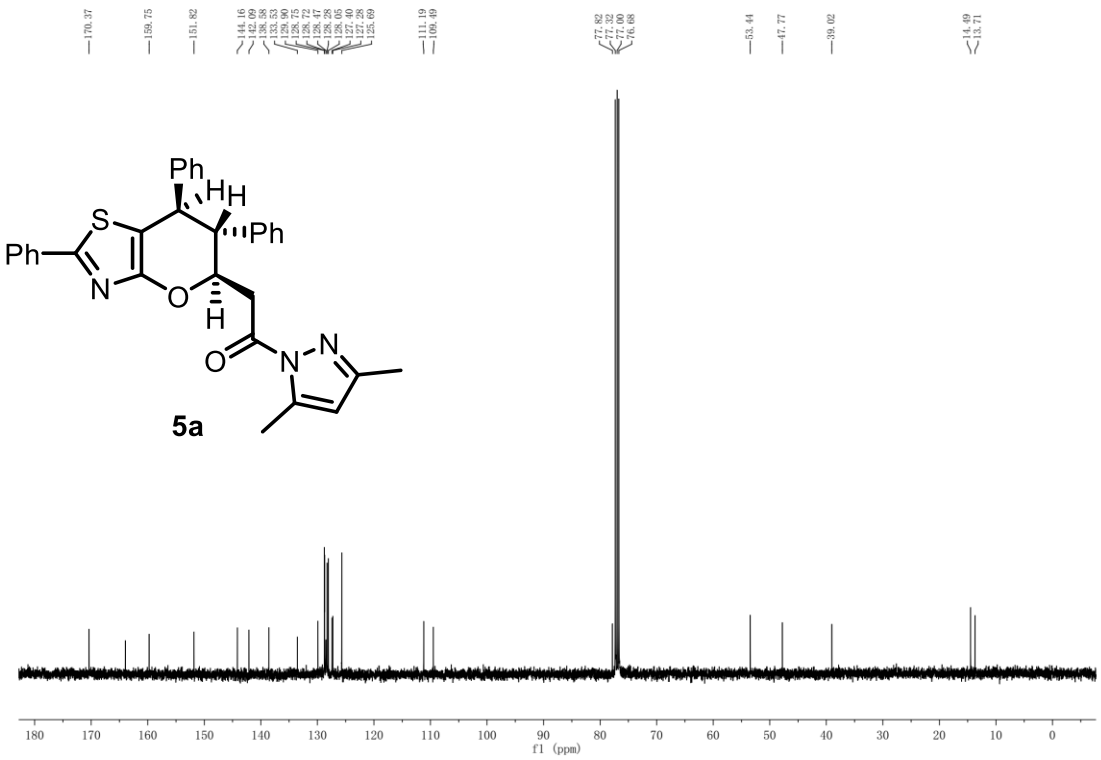
^{1}HNMR of **5a** (600M, $CDCl_3$)



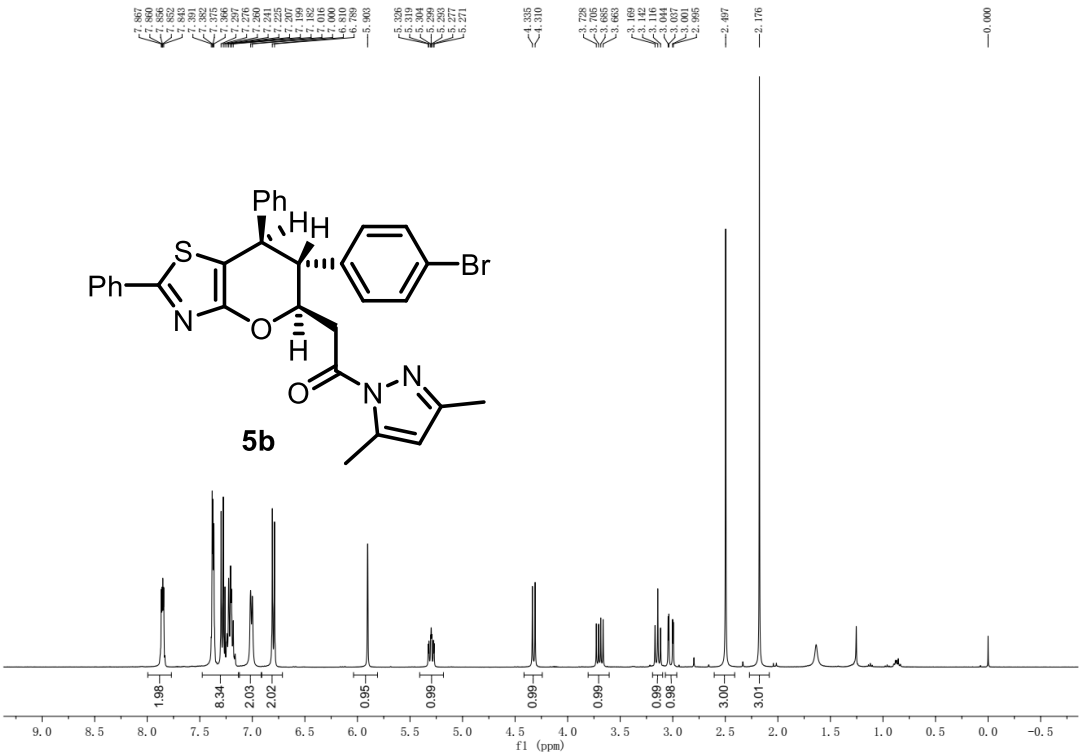
Crude ^{1}HNMR of **5a** (600M, $CDCl_3$)



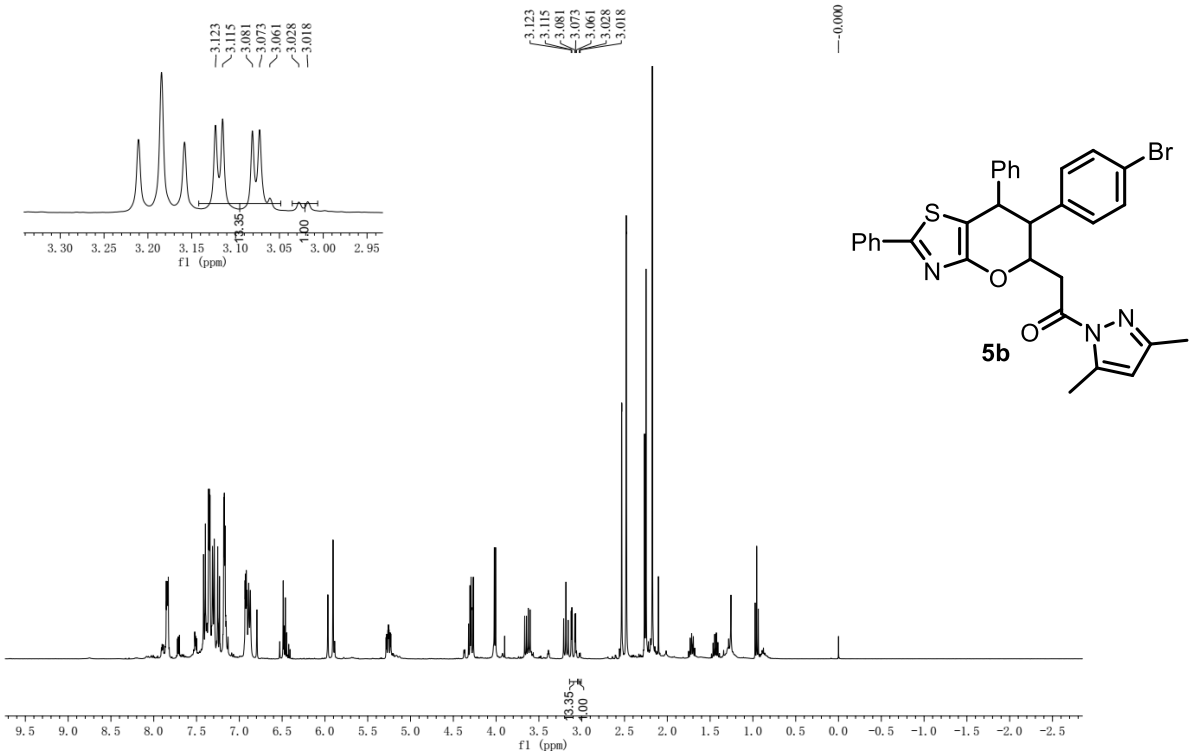
^{13}CNMR of **5a** (101M, $CDCl_3$)



^{1}HNMR of **5b** (400M, $CDCl_3$)

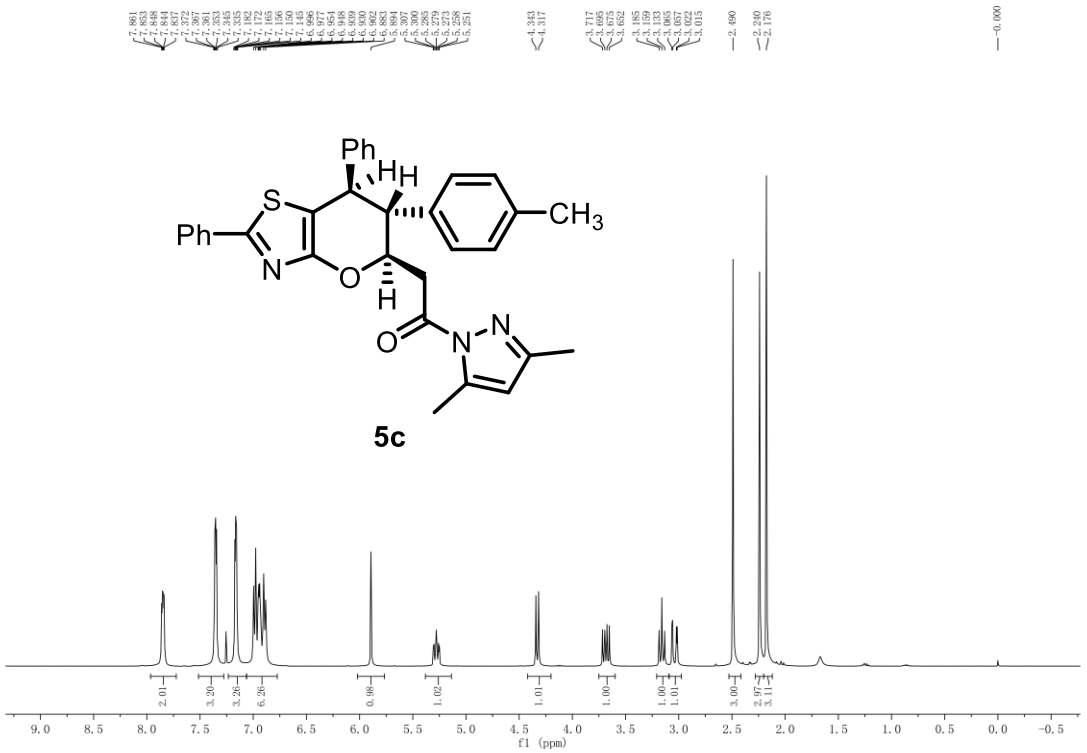


Crude ^{1}HNMR of **5b** (400M, $CDCl_3$) Crude

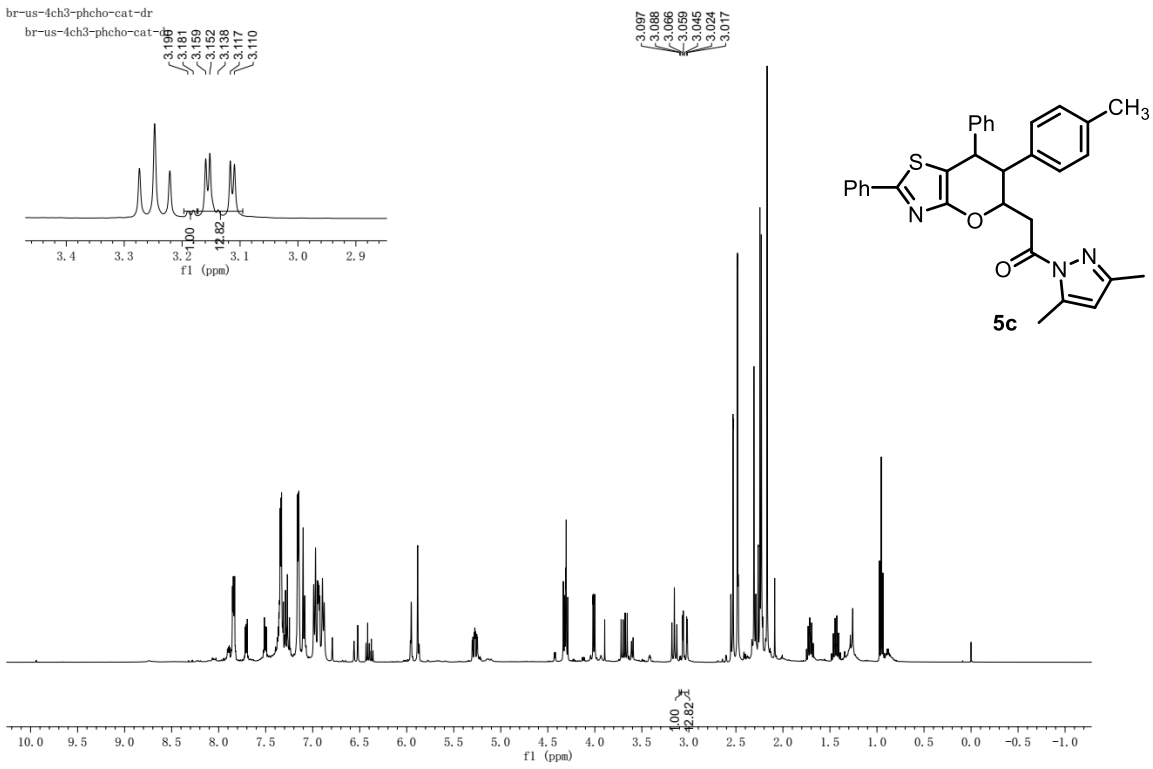


^{13}CNMR of **5b** (101M, $CDCl_3$)

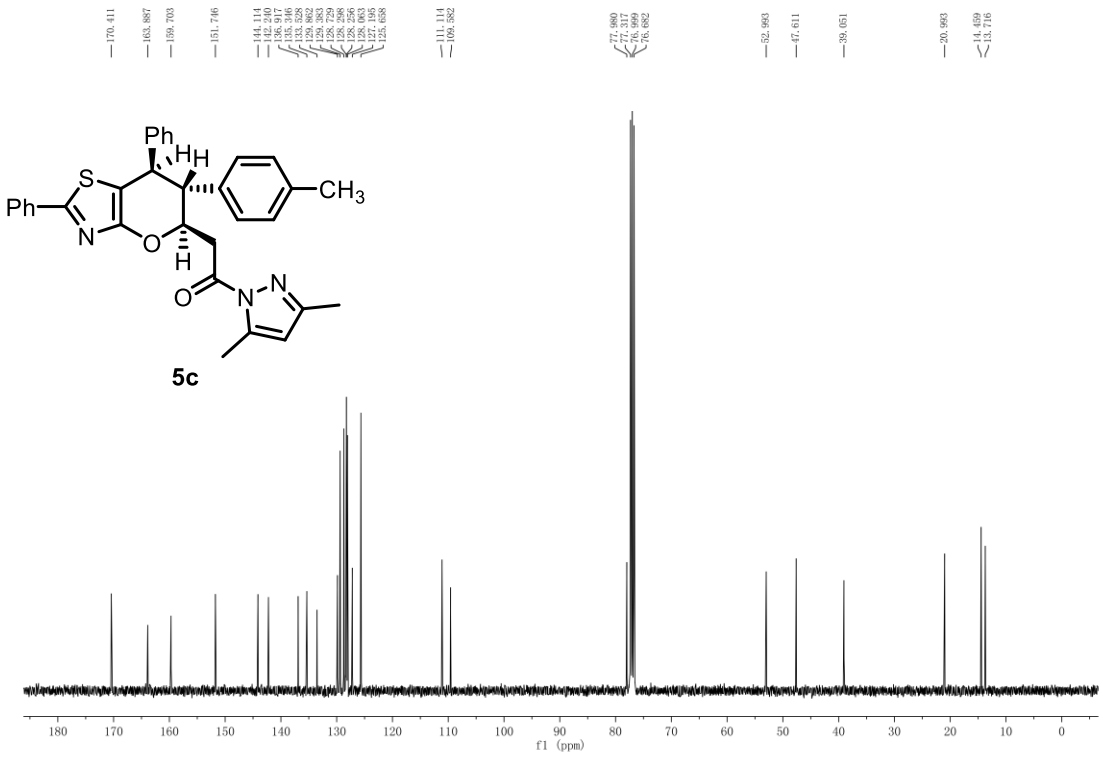
^{1}HNMR of **5c** (400M, $CDCl_3$)



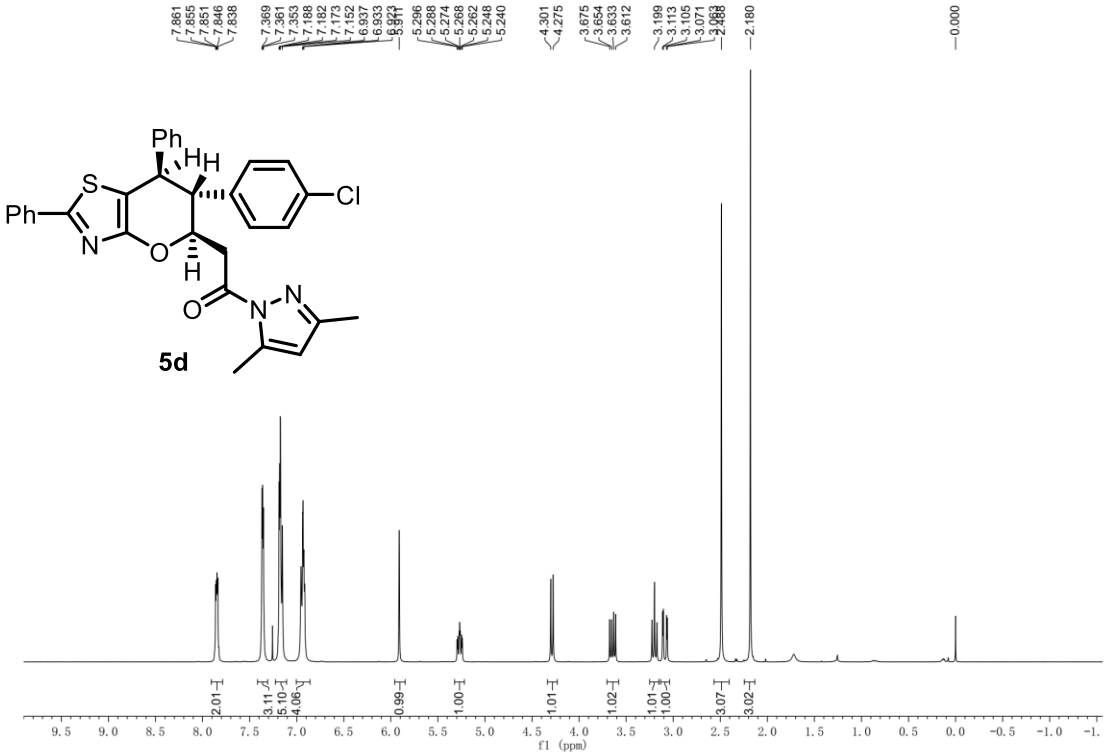
Crude ^{1}HNMR of **5c** (400M, $CDCl_3$)



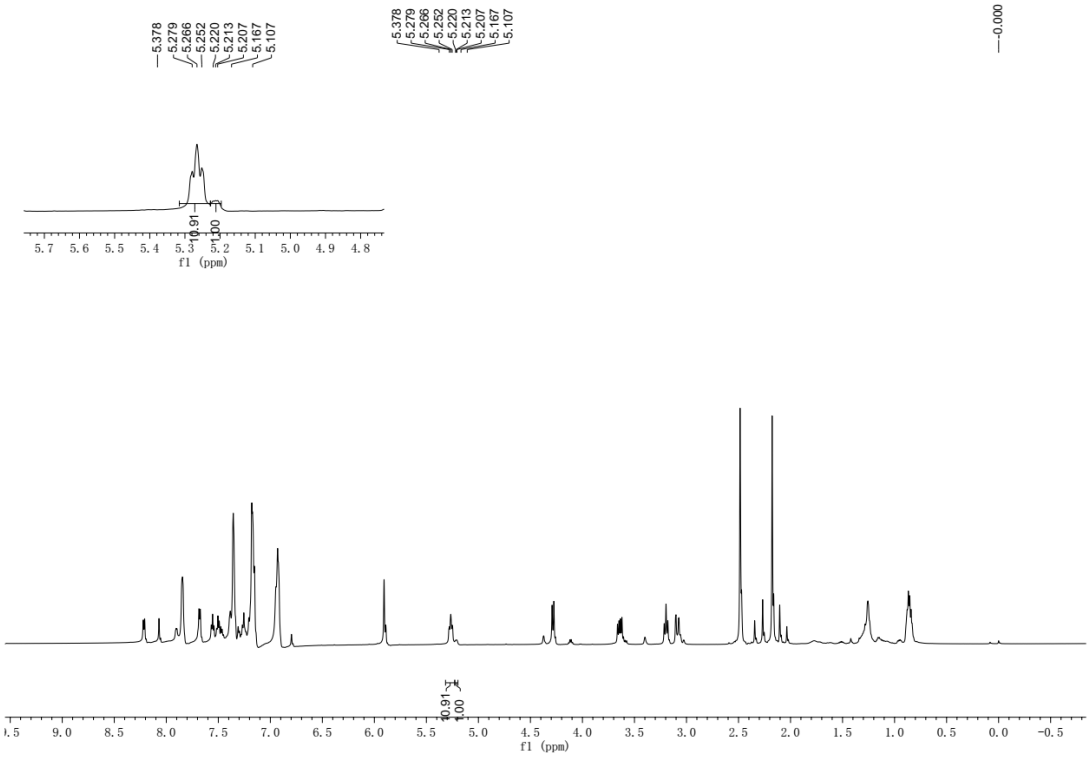
^{13}CNMR of **5c** (101M, $CDCl_3$)



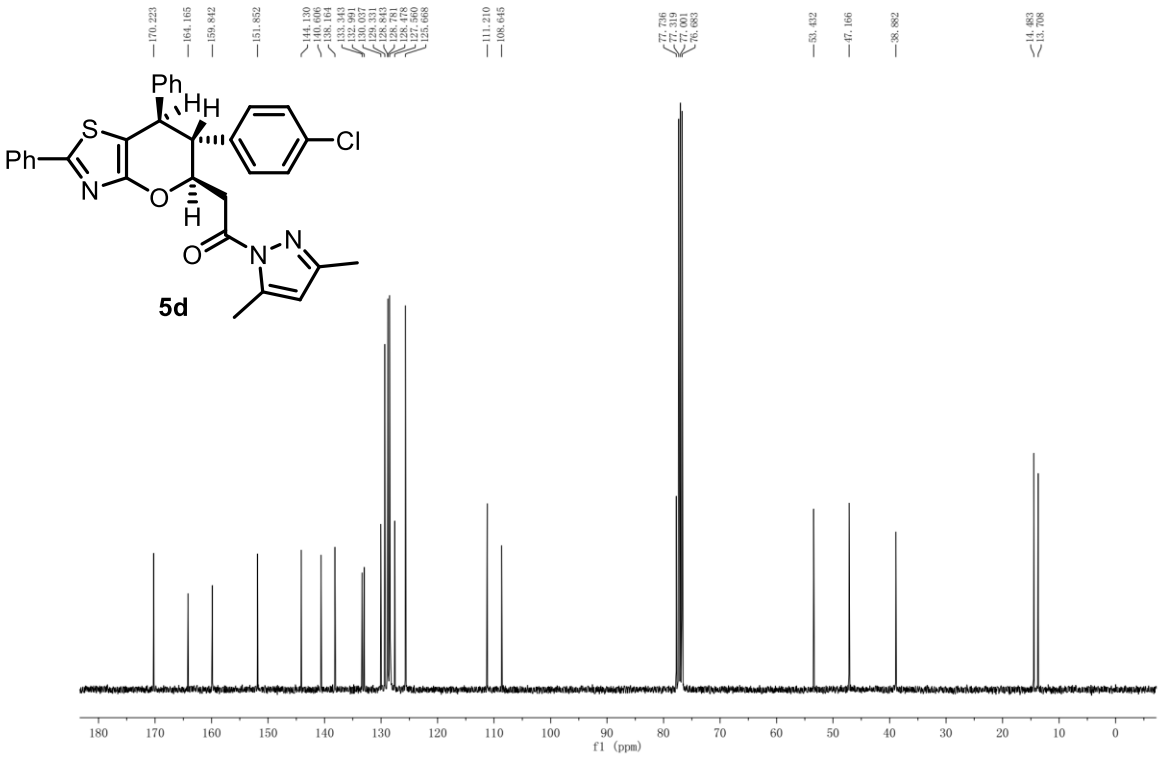
[1]HNMR of **5d** (400M, $CDCl_3$)



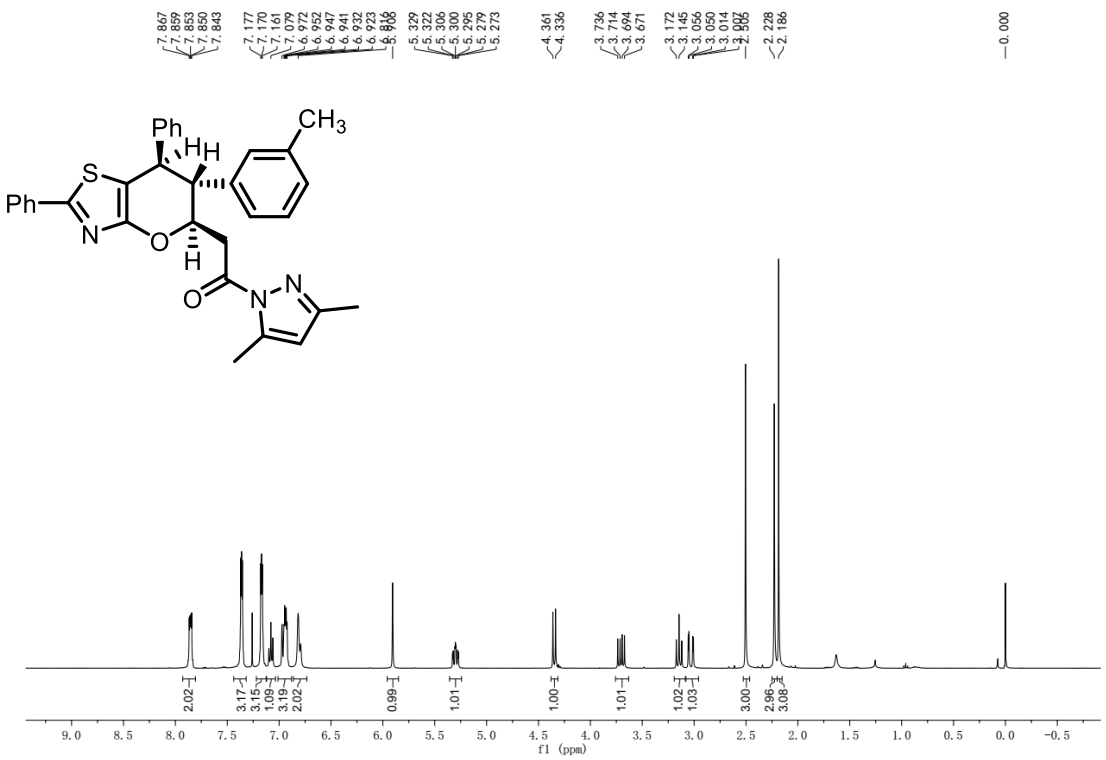
Crude [1]HNMR of **5d** (400M, $CDCl_3$)



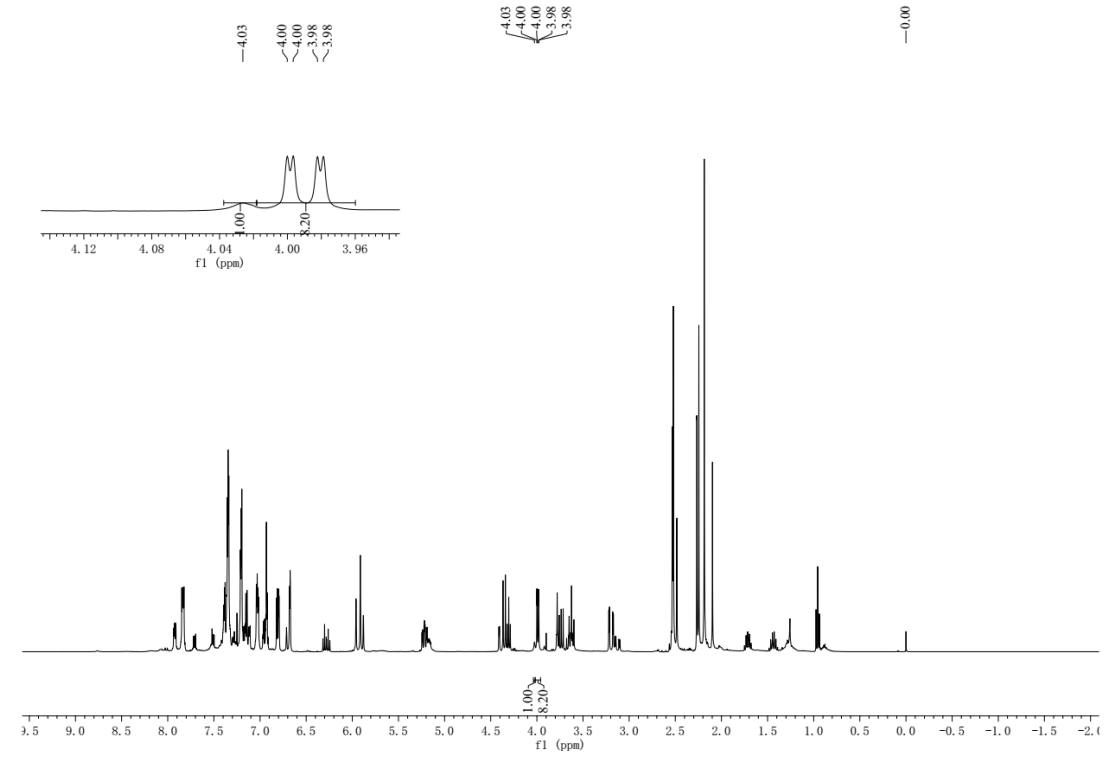
^{13}CNMR of **5d** (101M, $CDCl_3$)



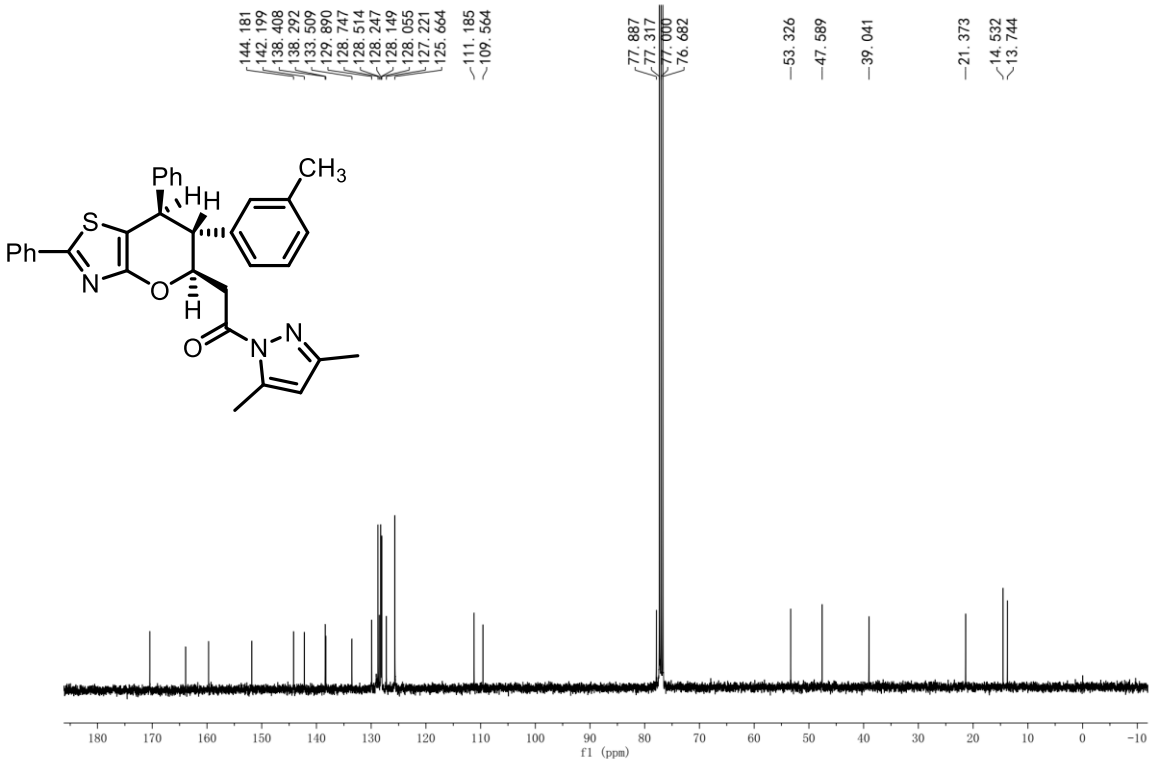
^{1}HNMR of **5e** (400M, $CDCl_3$)



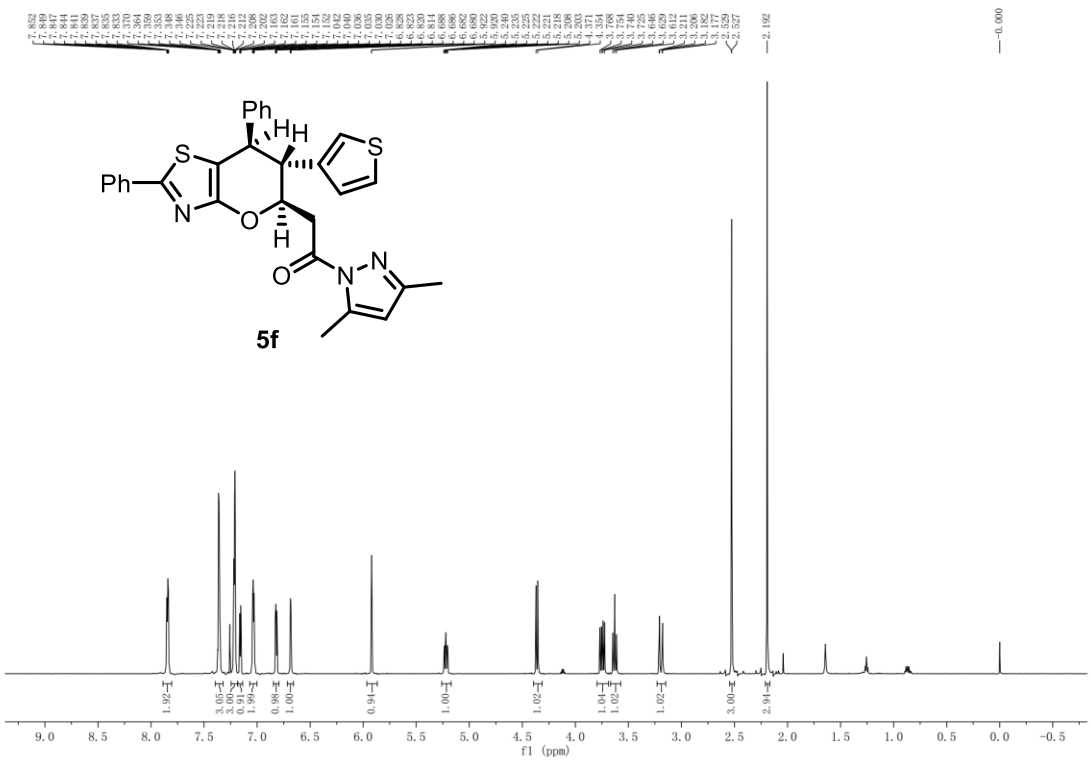
Crude ^{1}HNMR of **5e** (400M, $CDCl_3$)



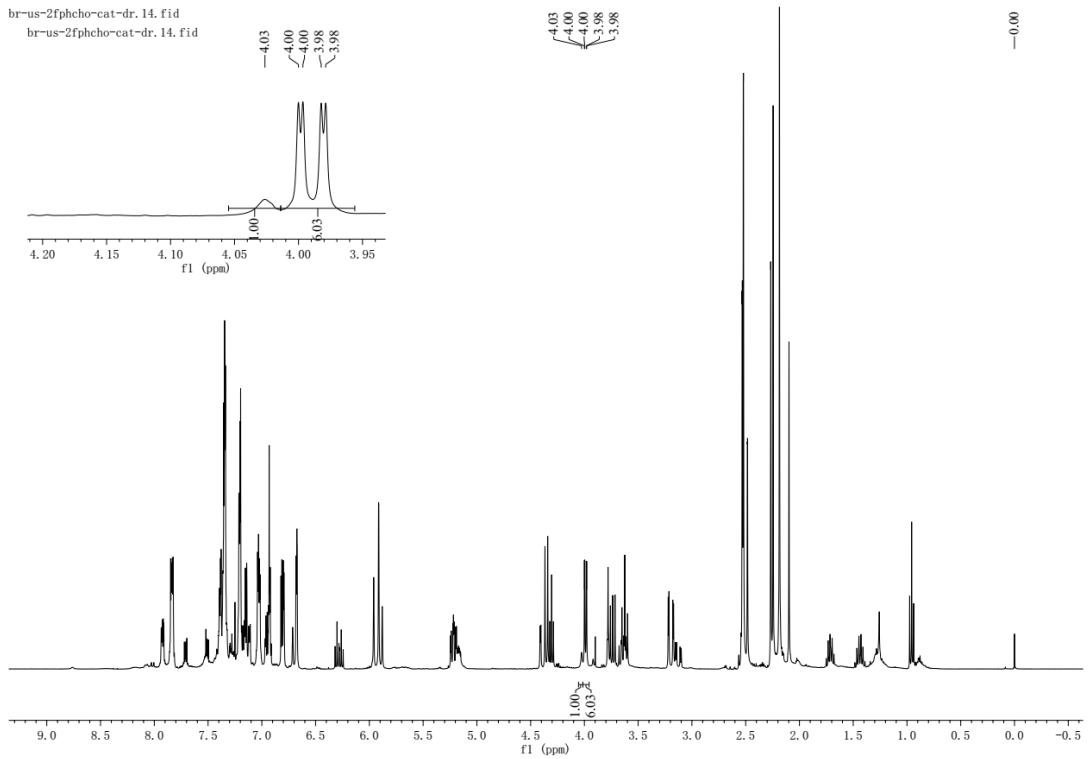
^{13}CNMR of **5e** (101M, $CDCl_3$)



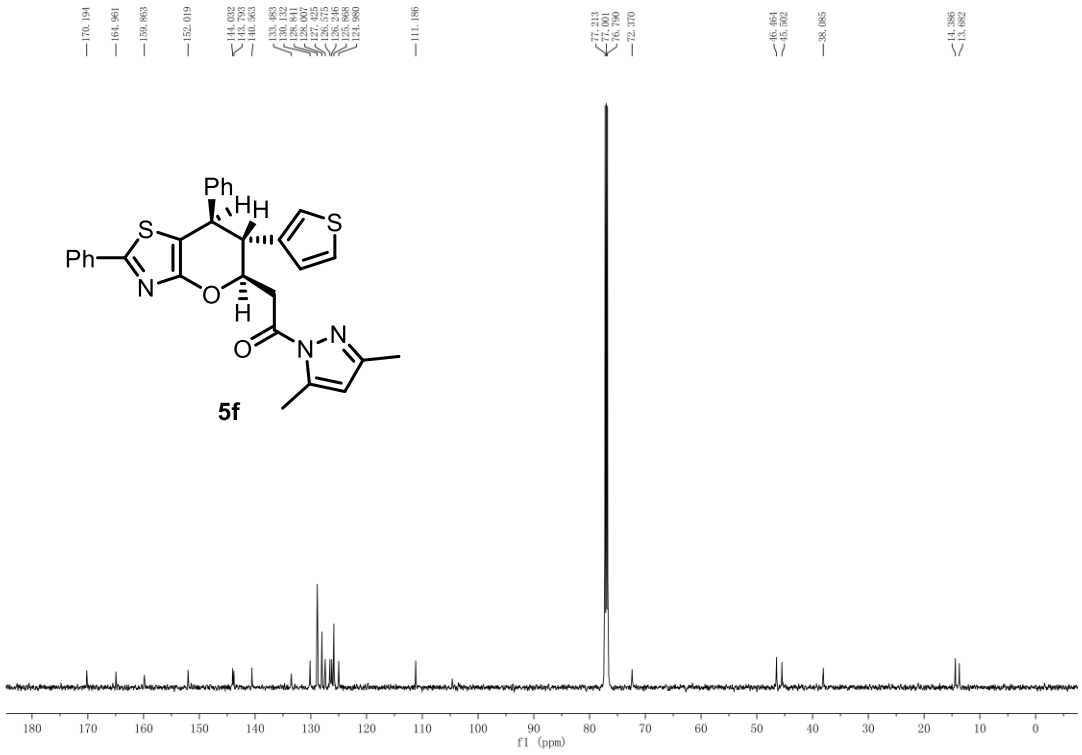
^{1}HNMR of **5f** (400M, $CDCl_3$)



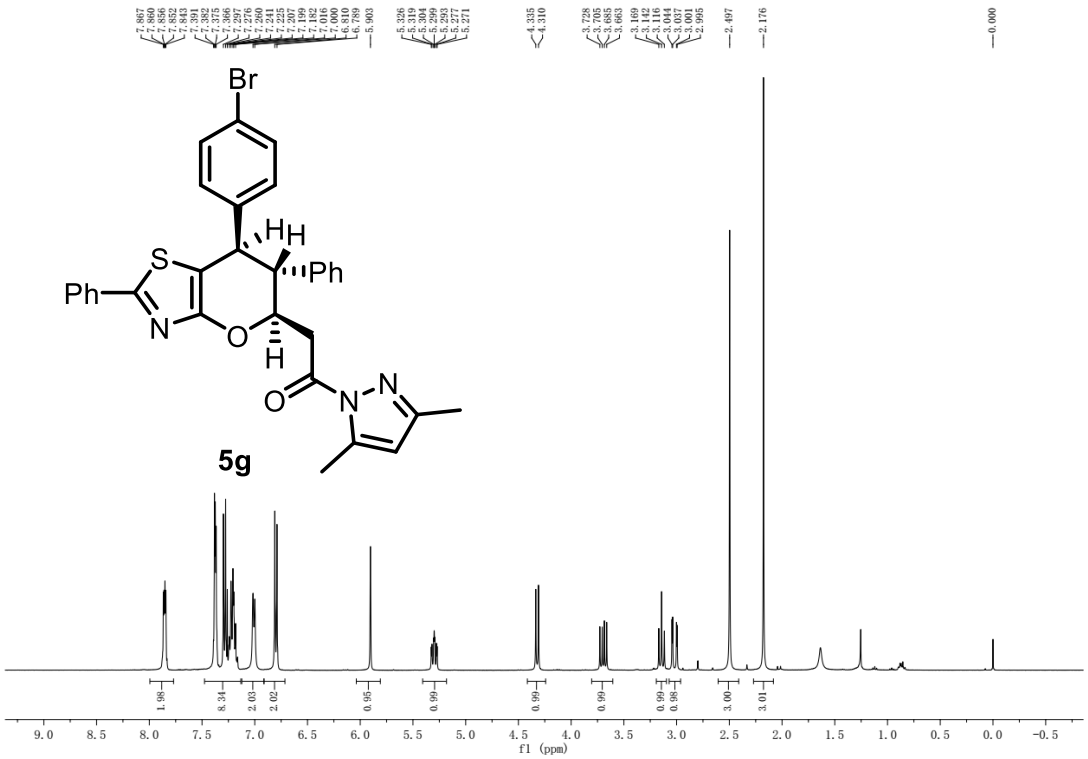
^{1}HNMR of **5f** (400M, $CDCl_3$)



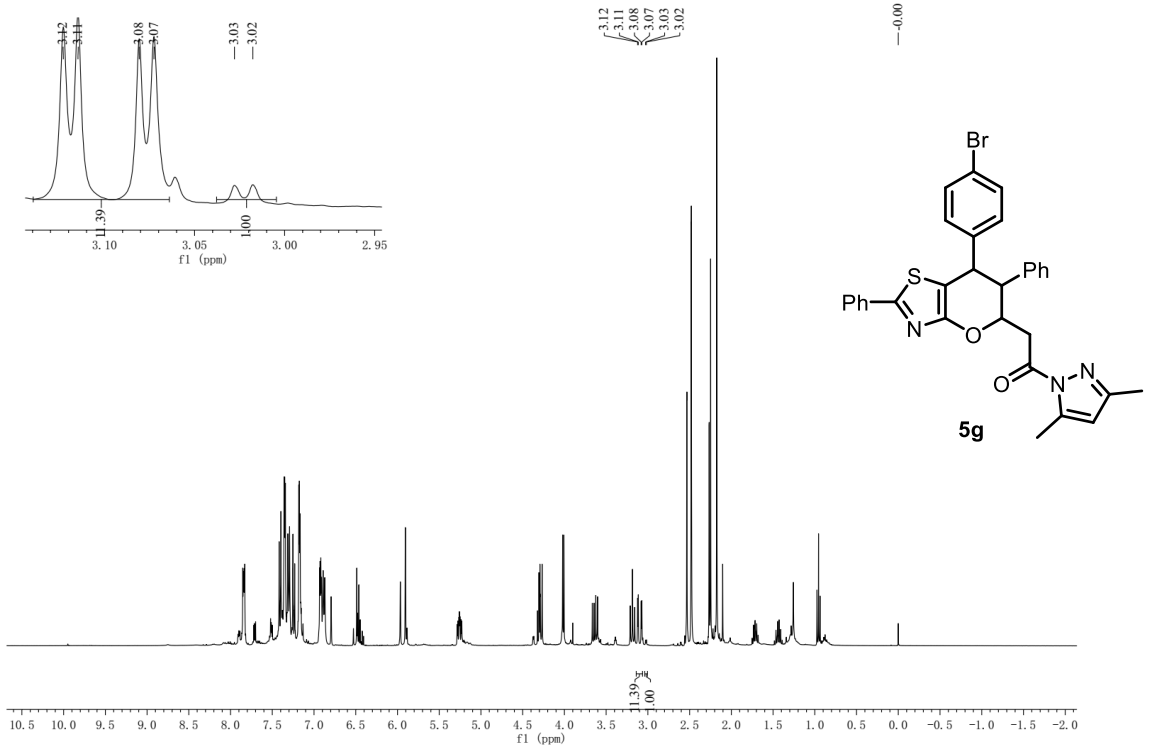
^{13}CNMR of **5f** (101M, $CDCl_3$)


170.194
164.961
159.863
152.019
144.032
143.793
140.563
133.483
130.132
128.841
128.007
127.425
126.575
126.345
125.868
124.980
111.186
77.213
77.001
76.790
72.370
46.464
45.932
38.885
14.386
13.682
Ph
H
S
S
Ph
N
O
H
O
N
N
5f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

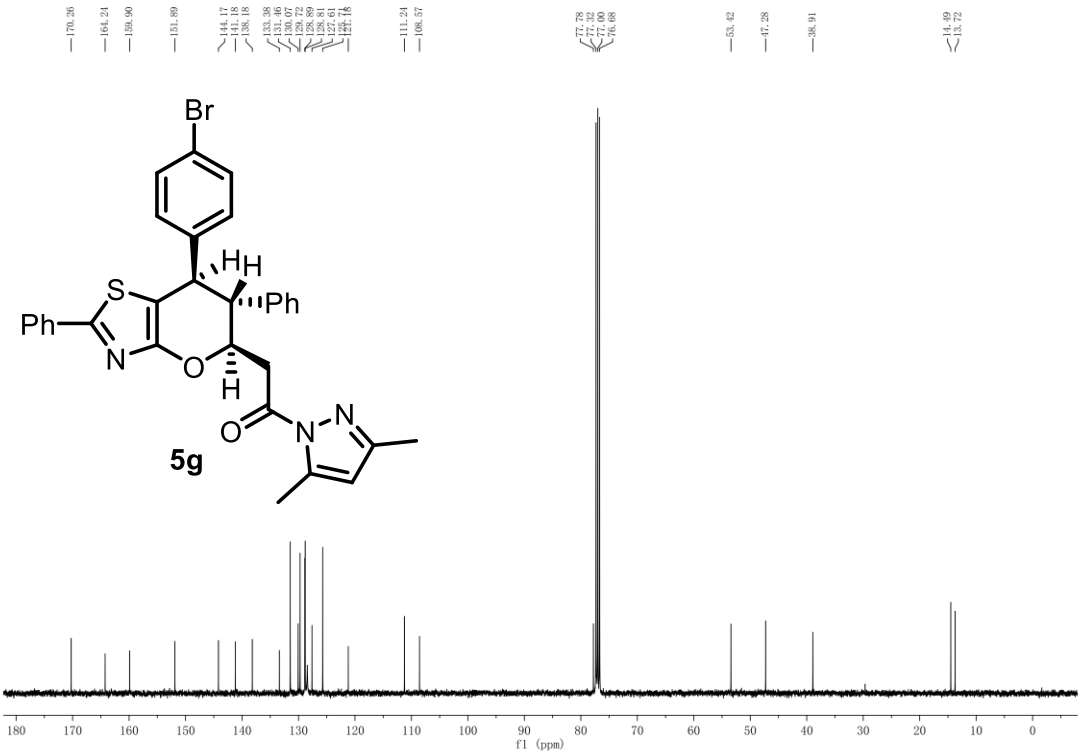
^{1}HNMR of **5g** (400M, $CDCl_3$)



Crude ^{1}HNMR of **5g** (400M, $CDCl_3$)

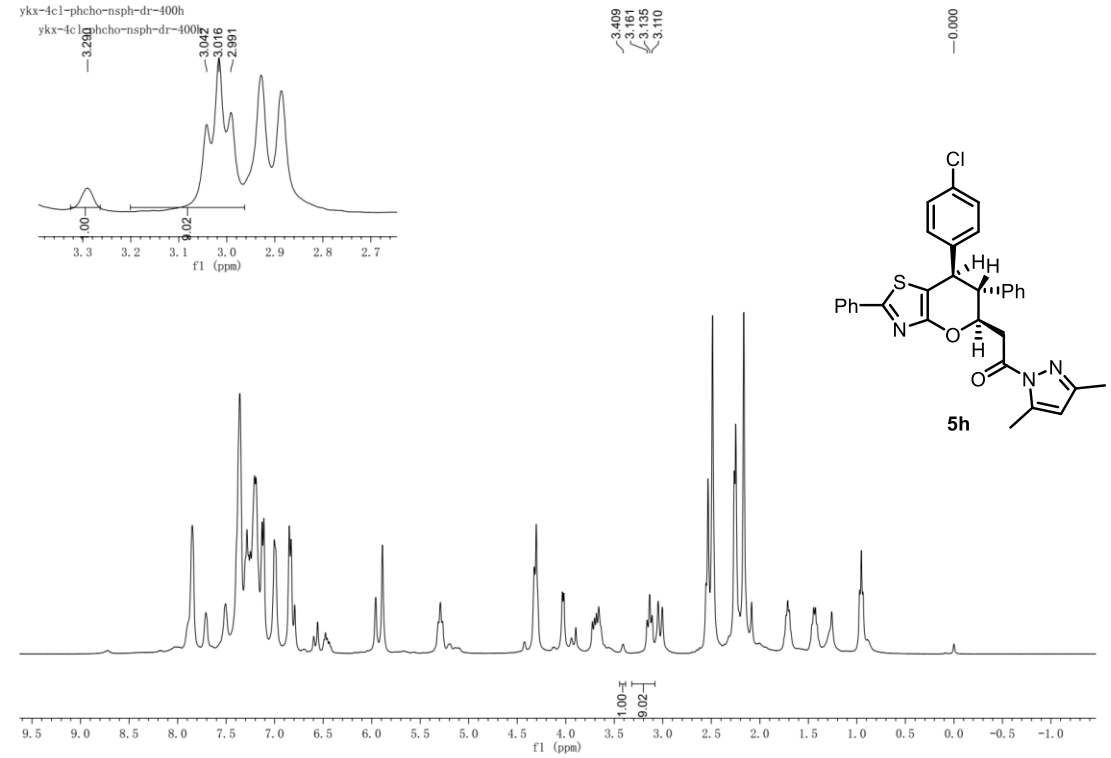


^{13}CNMR of **5g** (101M, $CDCl_3$)


170.26
164.24
159.90
151.89
144.17
141.15
138.18
133.38
131.46
130.07
129.72
128.89
128.81
127.61
127.14
121.18
111.24
106.57
77.78
77.32
77.00
76.68
53.42
47.28
38.91
14.49
13.72
Br
Ph
S
N
O
H
H
Ph
O
N
N
5g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}HNMR of **5h** (400M, $CDCl_3$)

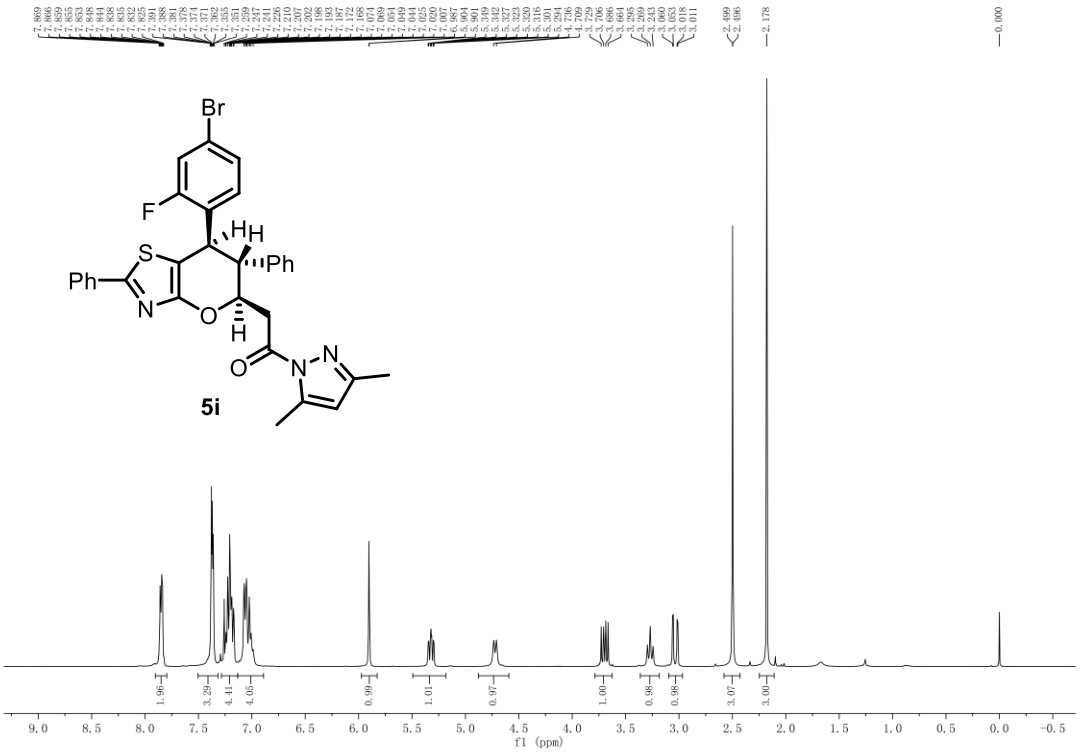
Crude ^{1}HNMR of **5h** (400M, $CDCl_3$)



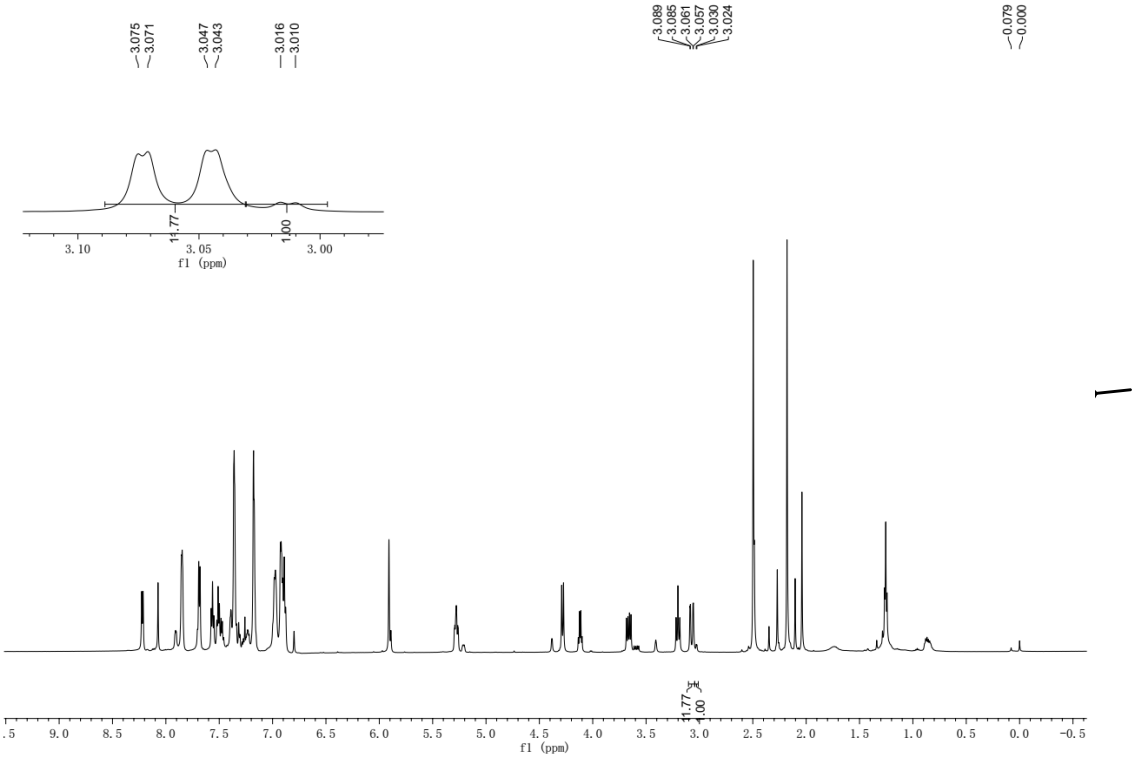
^{13}CNMR of **5h** (101M, $CDCl_3$)


170.223
164.165
159.842
151.852
144.130
140.606
138.164
133.313
132.991
130.037
129.331
128.943
128.781
128.478
127.560
125.668
111.210
108.645
77.736
77.319
77.001
76.683
53.432
47.166
38.882
14.883
13.760
Cl
H
H
S
Ph
Ph
N
O
H
O
N
N
5h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

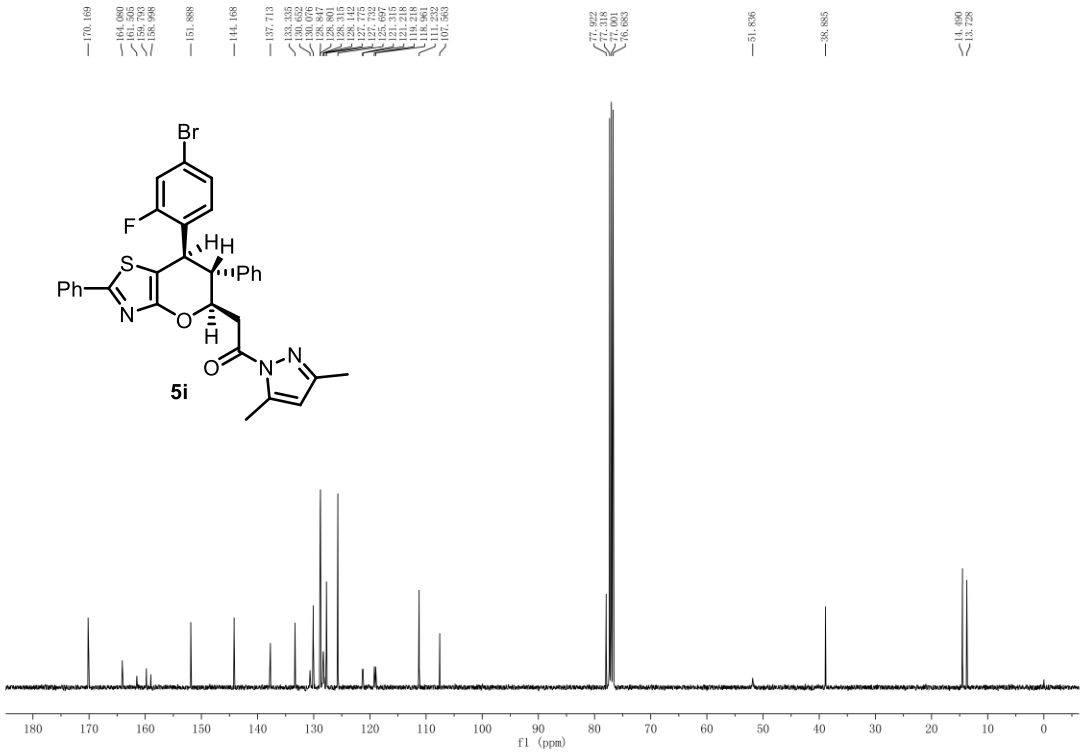
^{1}HNMR of **5i** (400M, $CDCl_3$)



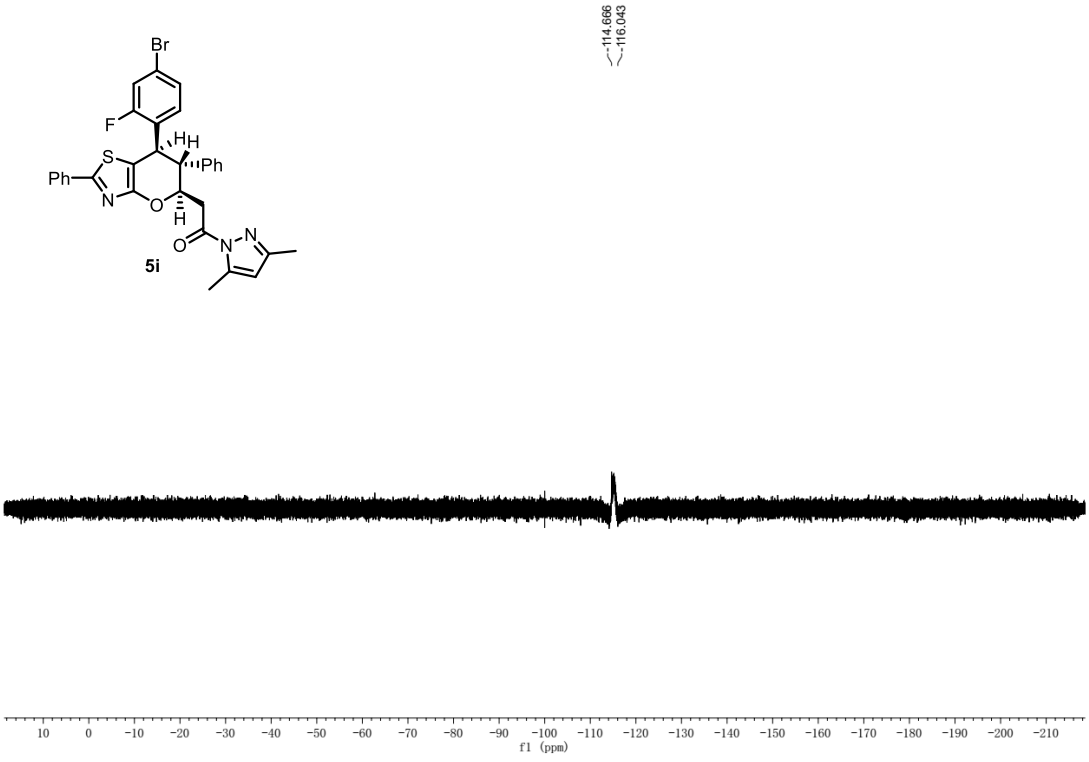
Crude ^{1}HNMR of **5i** (400M, $CDCl_3$)



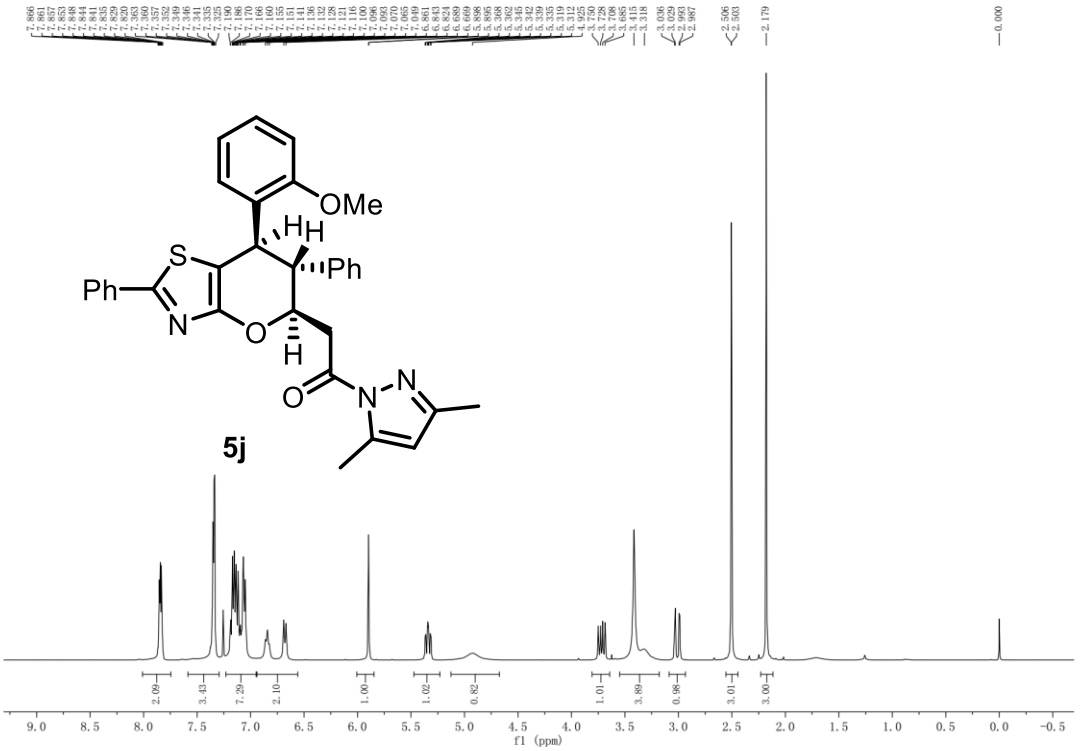
^{13}CNMR of **5i** (101M, $CDCl_3$)

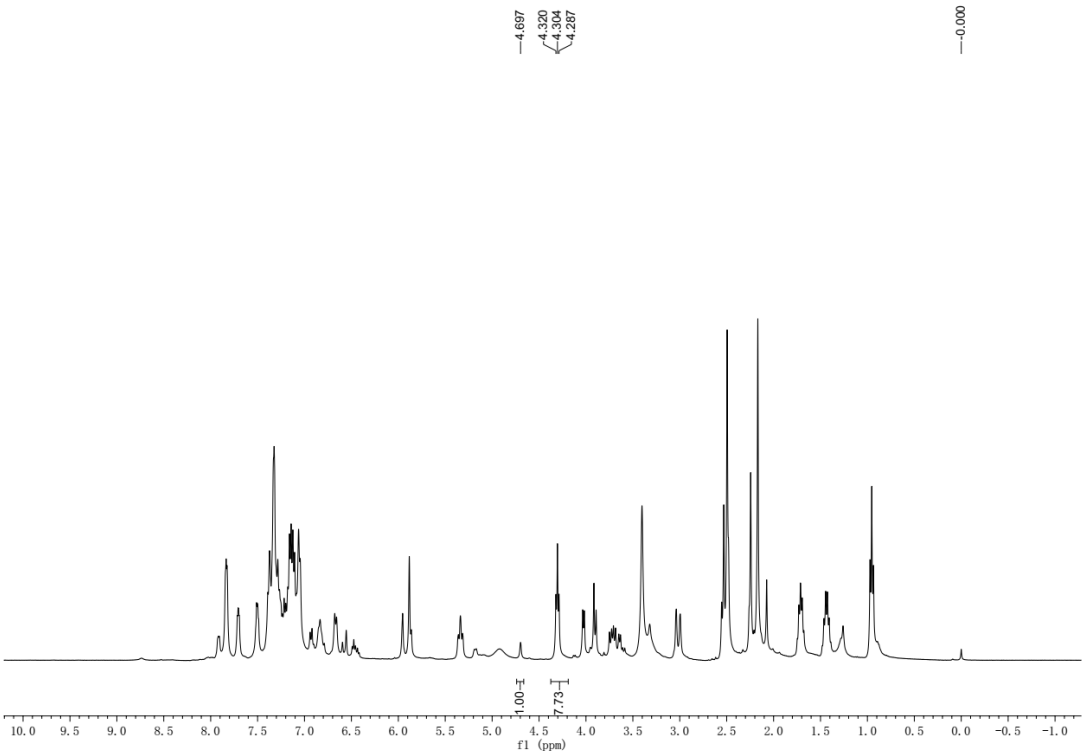


^{19}F NMR of **5i** (101M, $CDCl_3$)



^{1}HNMR of **5j** (400M, $CDCl_3$)

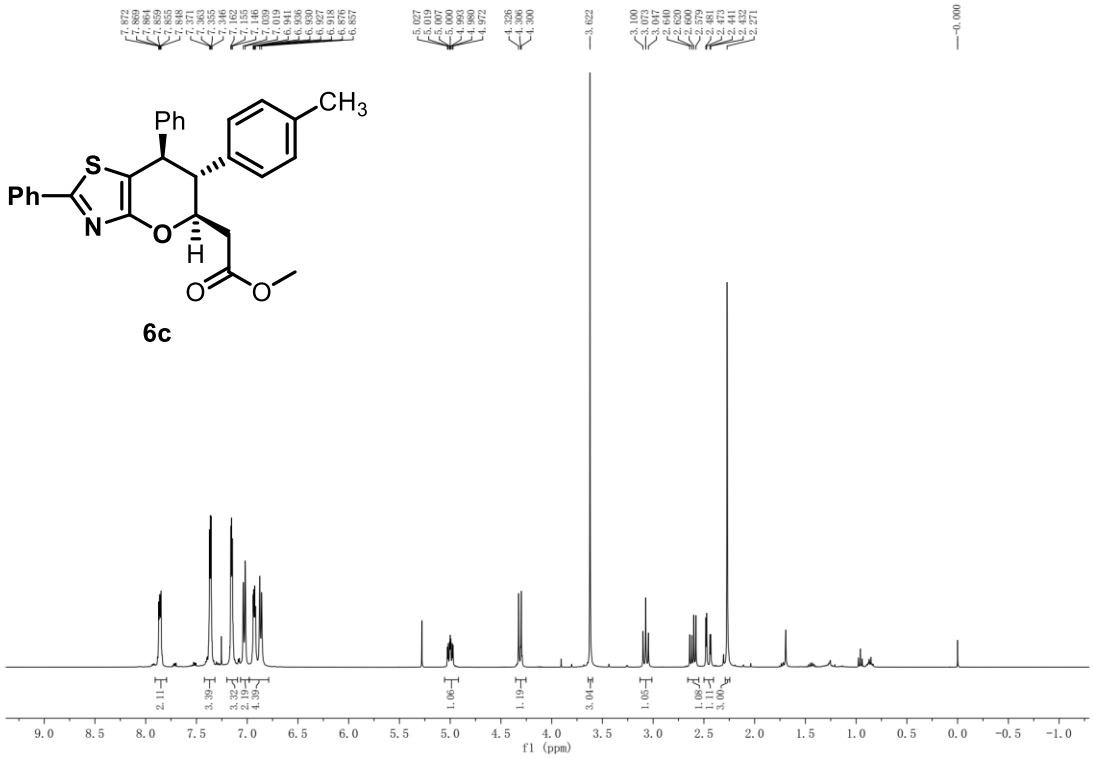




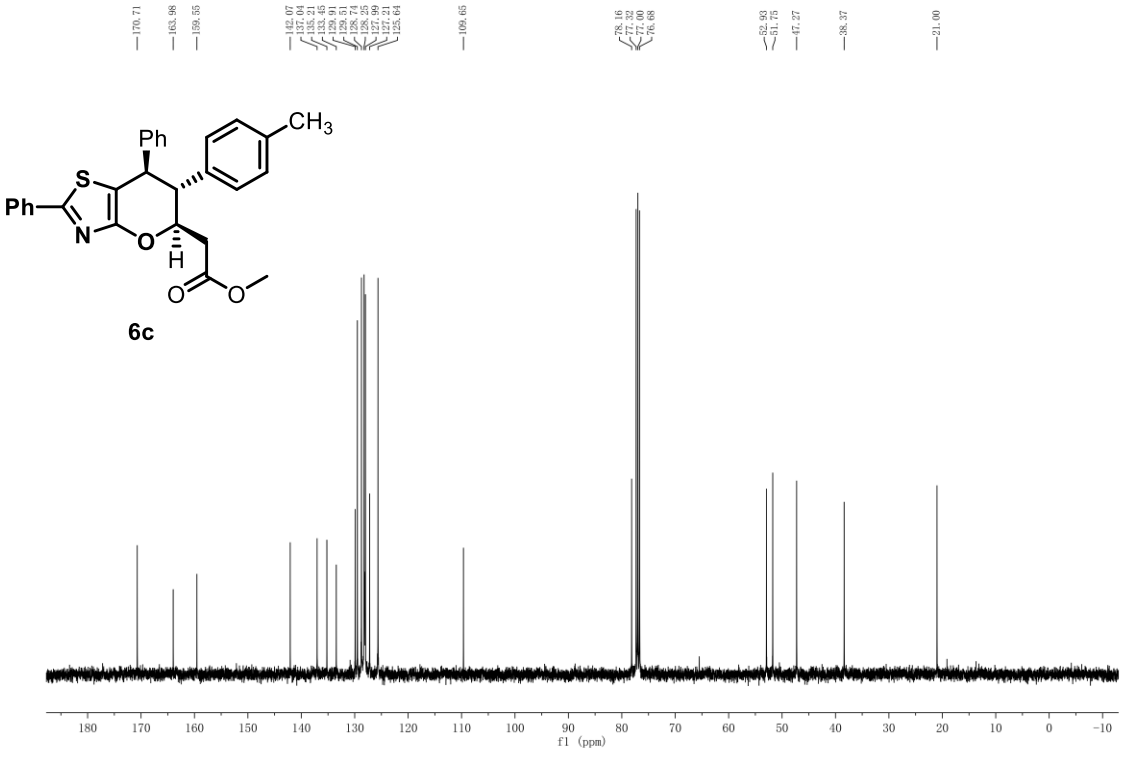
^{13}CNMR of **5j** (101M, $CDCl_3$)


170.486
163.127
159.490
157.067
151.734
144.129
138.860
133.665
129.663
128.695
128.382
128.261
127.607
125.575
120.692
111.127
110.796
109.969
77.344
77.138
77.001
76.683
55.203
39.120
14.506
13.721
OMe
H
H
S
Ph
Ph
N
O
H
O
N
N
5j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

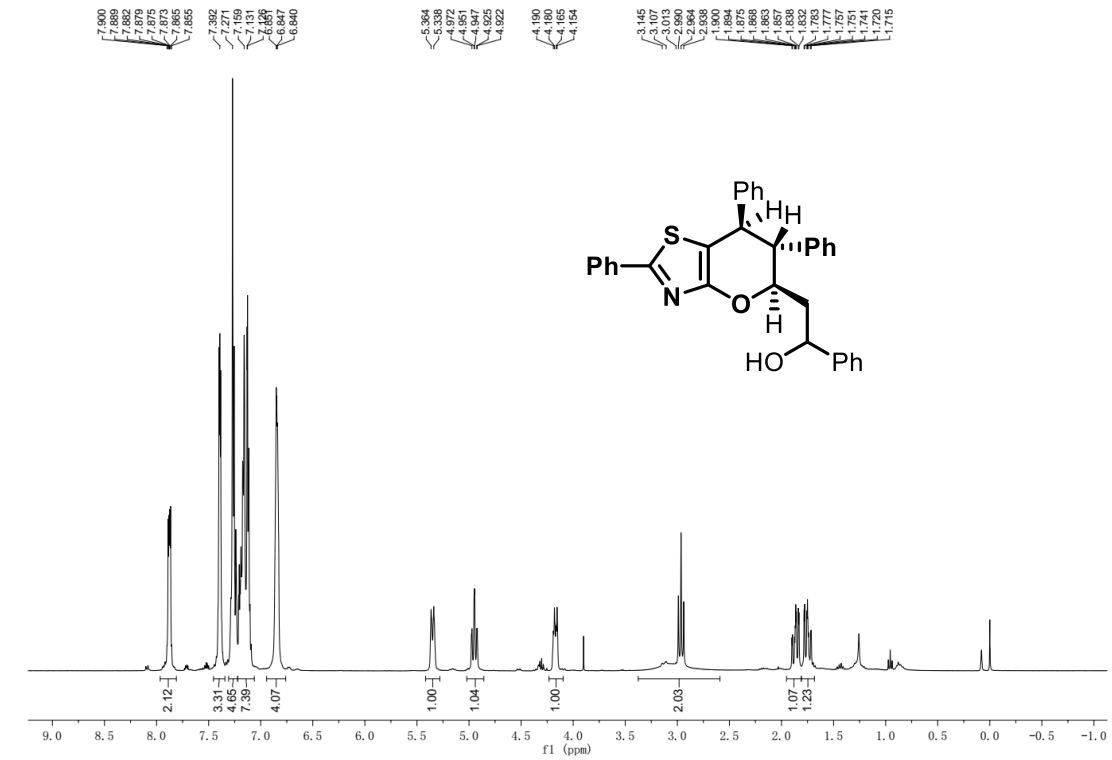
^{1}HNMR of **6c**
(400M, $CDCl_3$)



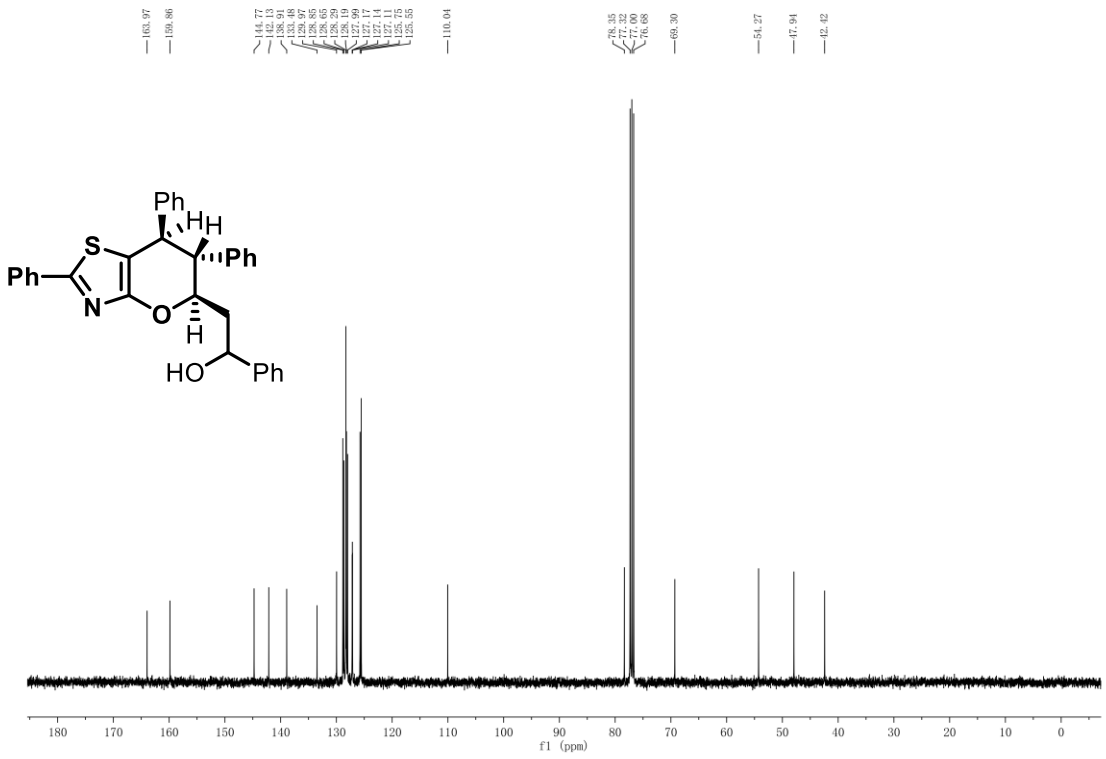
^{13}CNMR of **6c**(101M, $CDCl_3$)



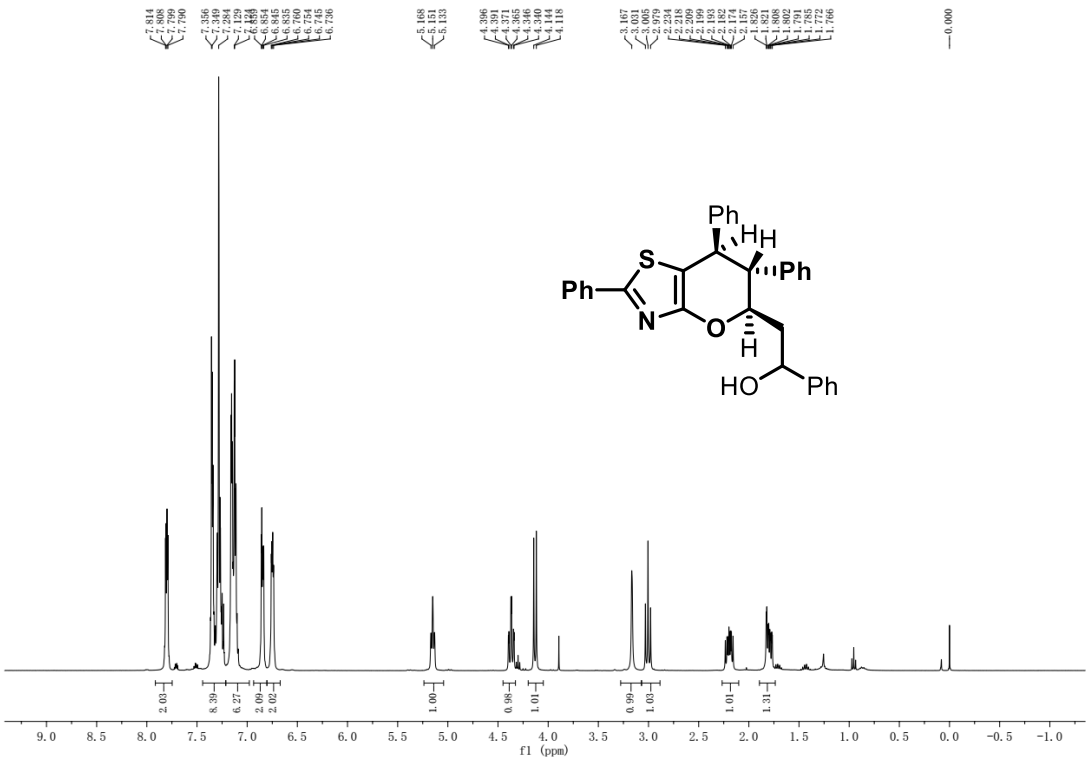
^{1}HNMR of **7a-minor** (400M, $CDCl_3$)



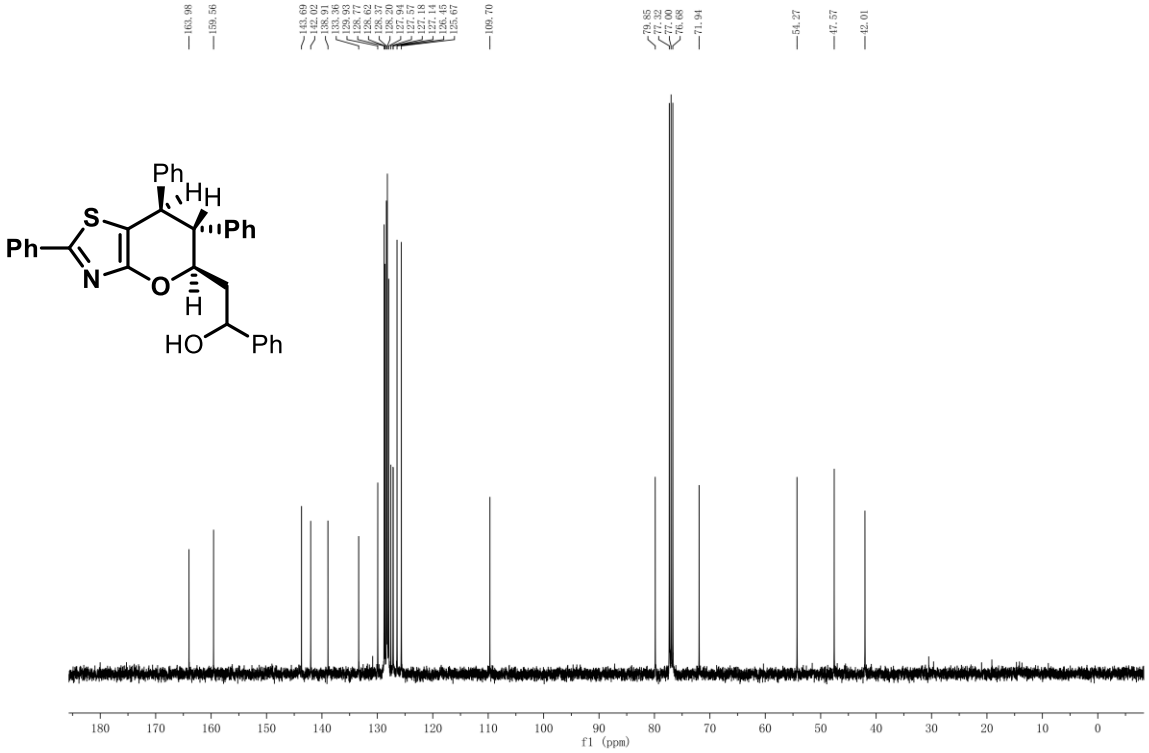
^{13}CNMR of **7a-minor** (101M, $CDCl_3$)



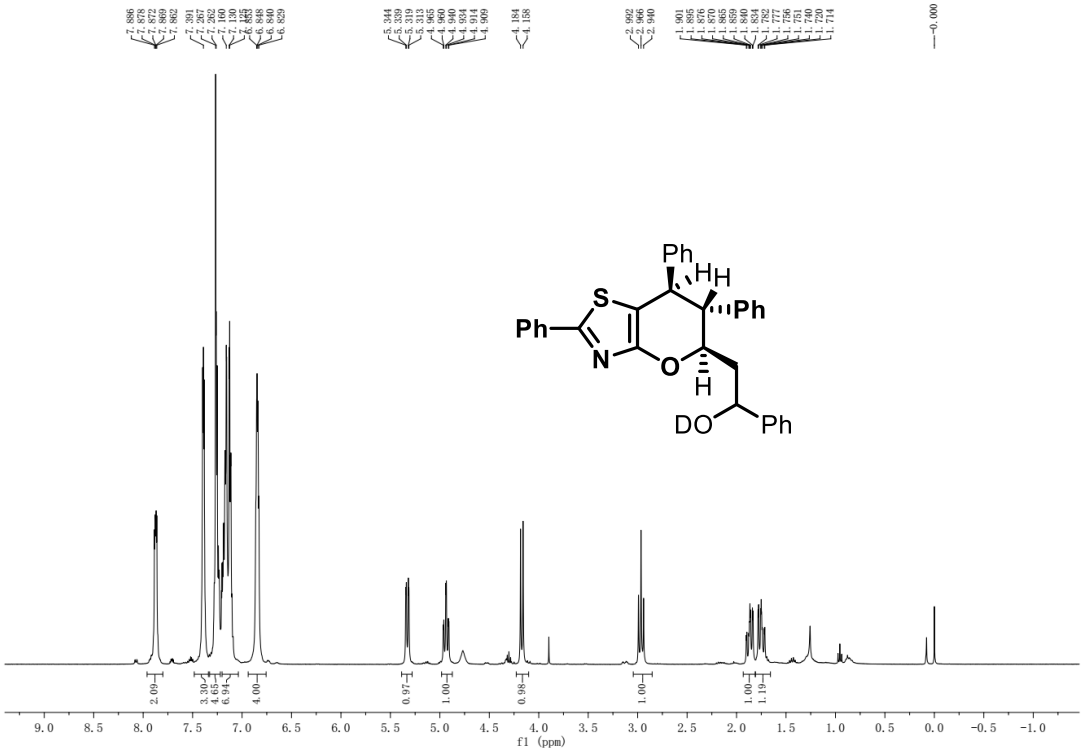
^{1}HNMR of **7a-major** (400M, $CDCl_3$)



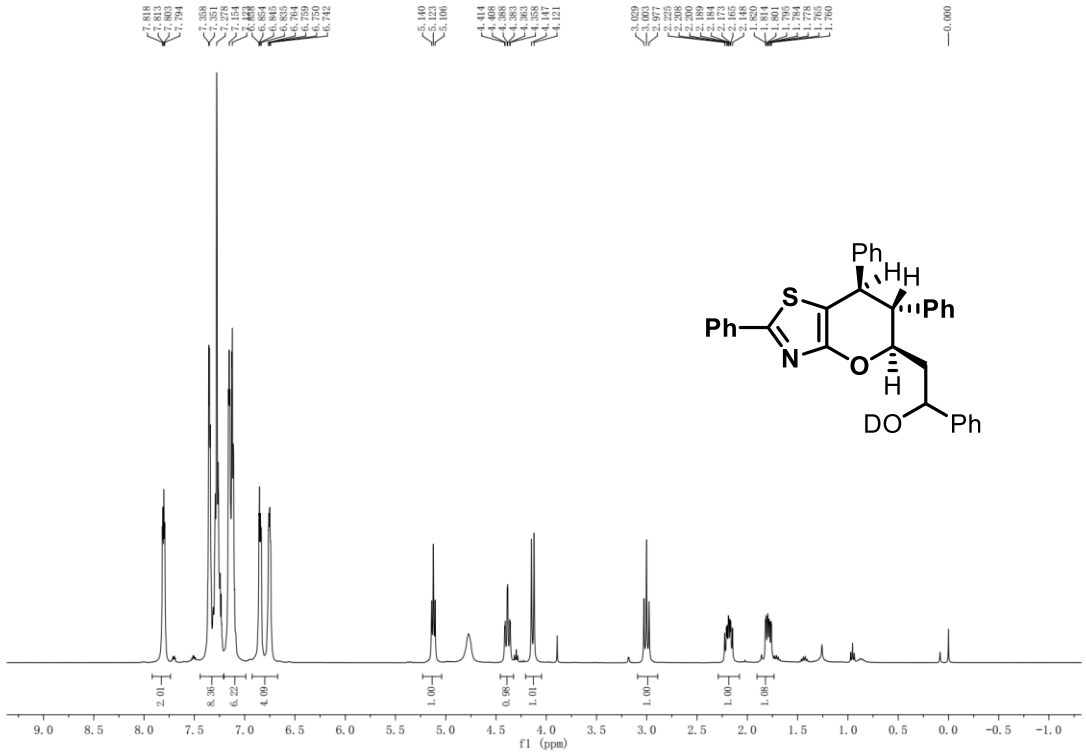
^{13}CNMR of **7a-major** (101M, $CDCl_3$)



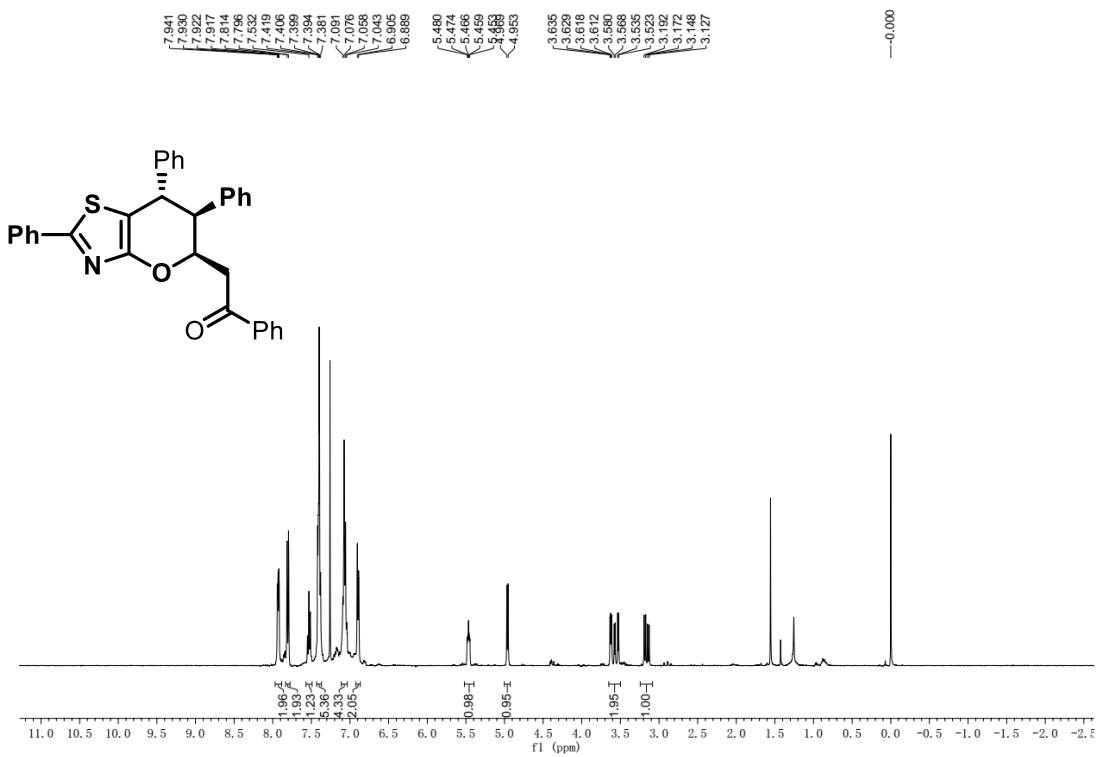
D_20 exchange experiment of **7a-minor**



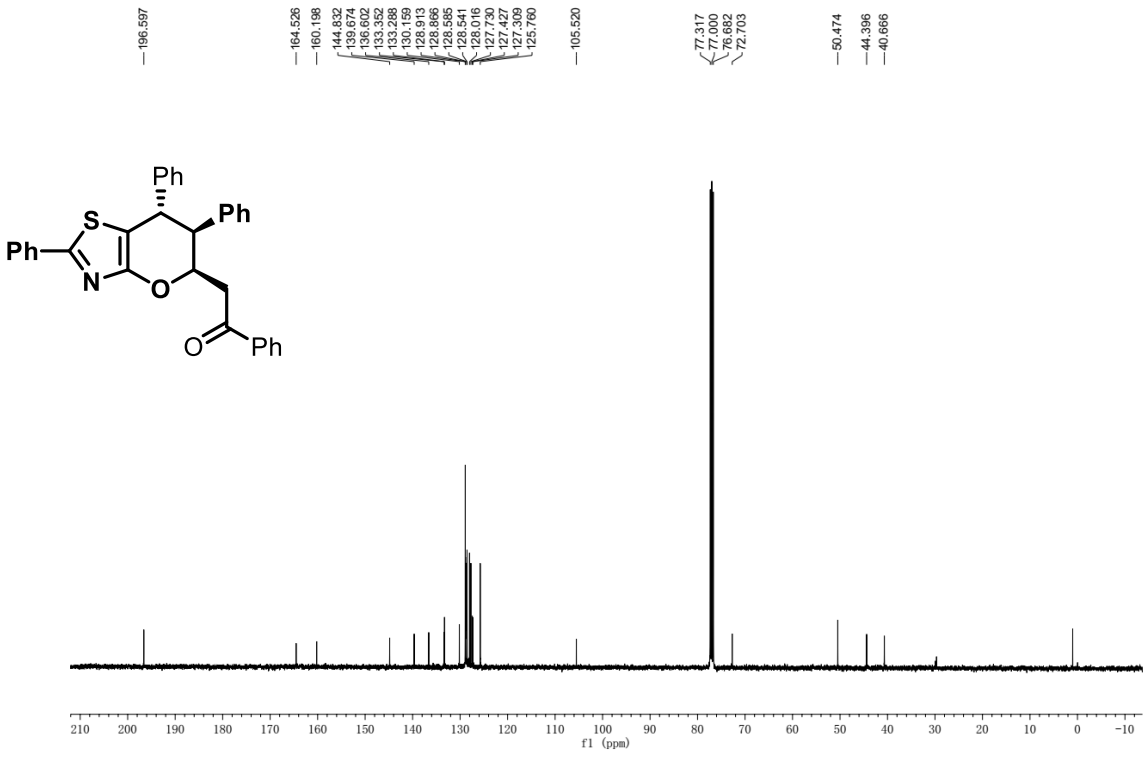
D_20 exchange experiment of **7a-major**



^{1}HNMR of 3**a-minor** (400M, $CDCl_3$)

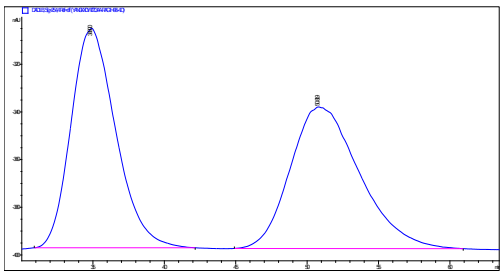


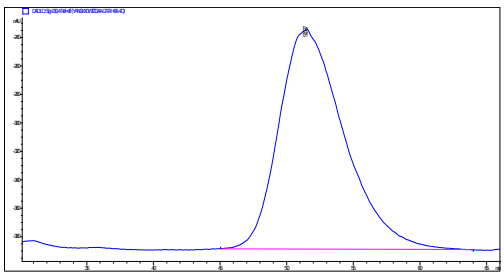
^{13}CNMR of **3a-minor** (101M, $CDCl_3$)



HPLC chromatogram of compound **3a** [Chiralpak IH column, hexane: *i*-PrOH= 93:7, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



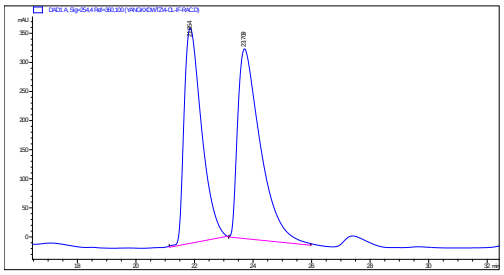


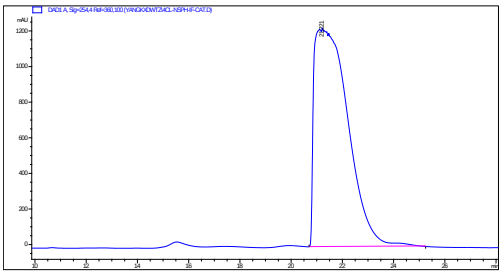
#	Time	Area(%)
1	34.9	49.987
2	50.819	50.013
Total		100.000

#	Time	Area(%)
1	51.507	100.000
Total		100.000

HPLC chromatogram of compound **3b** [Chiralpak IF column, hexane: *i*-PrOH = 85:15, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



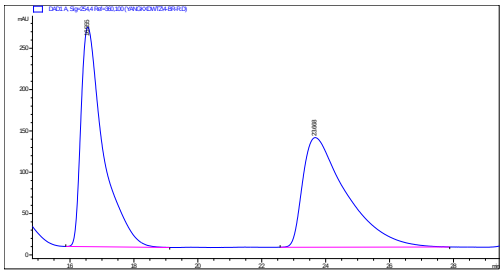


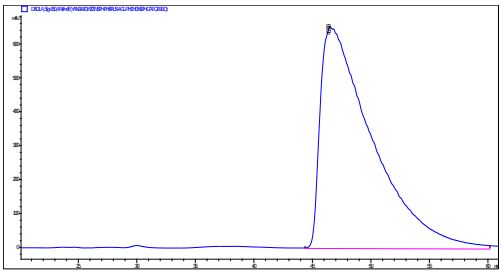
#	Time	Area(%)
1	21.854	49.638
2	23.709	50.362
Total		100.000

#	Time	Area(%)
1	21.221	100.000
Total		100.000

HPLC chromatogram of compound **3c** [Chiralpak IH column, hexane: *i*-PrOH= 93:7, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



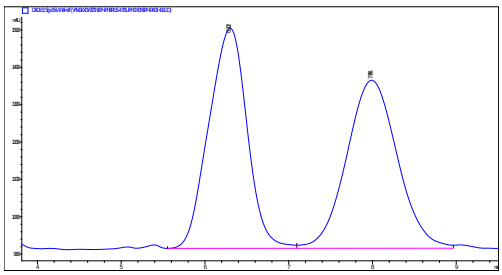


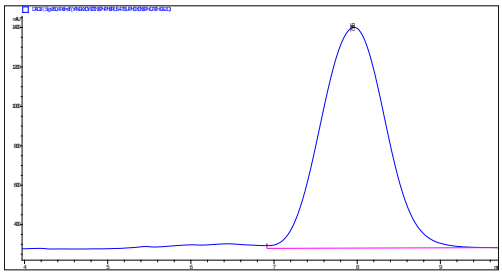
#	Time	Area(%)
1	16.555	50.374
2	23.668	49.626
Total		100.000

#	Time	Area(%)
2	22.852	100.000
Total		100.000

HPLC chromatogram of compound **3d** [Chiralpak IC column, hexane: i-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



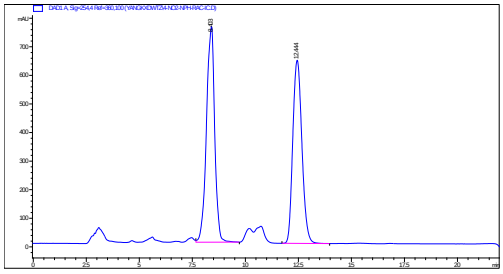


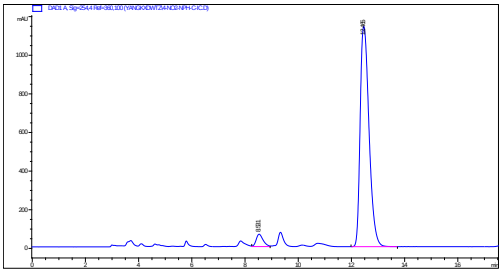
#	Time	Area(%)
1	6.302	49.672
2	7.991	50.328
Total		100.000

#	Time	Area(%)
1	7.965	100.000
Total		100.000

HPLC chromatogram of compound **3e** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



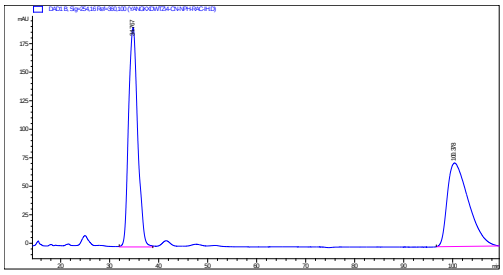


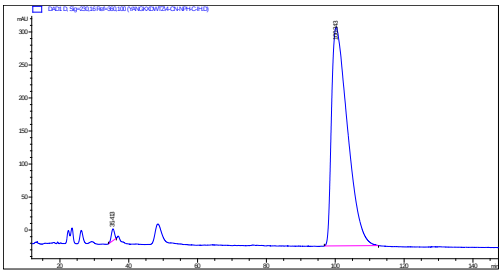
#	Time	Area(%)
1	8.444	51.541
2	12.404	48.459
Total		100.000

#	Time	Area(%)
1	8.531	4.225
2	12.465	95.775
Total		100.000

HPLC chromatogram of compound **3f** [Chiralpak IH column, hexane: i-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



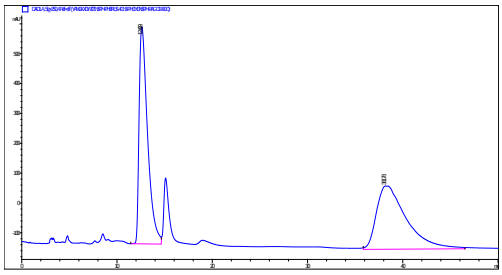


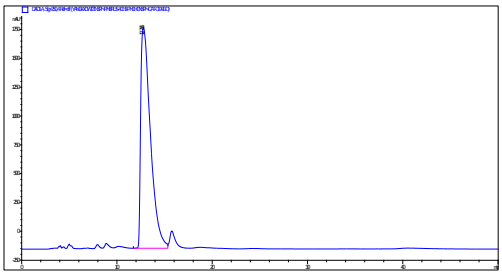
#	Time	Area(%)
1	34.767	53.191
2	100.378	56.809
Total		100.000

#	Time	Area(%)
1	35.414	1.028
2	100.343	98.972
Total		100.000

HPLC chromatogram of compound **3g** [Chiralpak OD column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



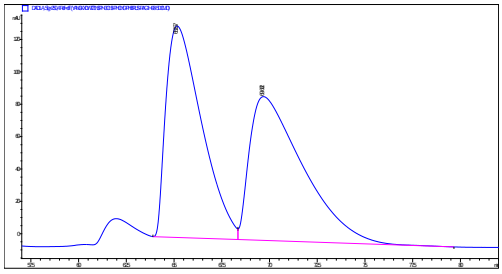


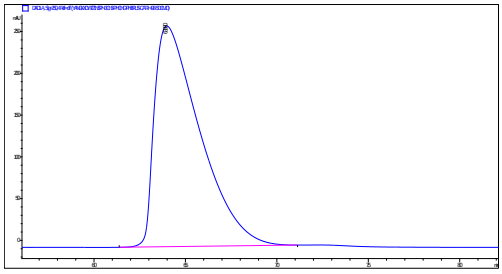
#	Time	Area(%)
1	12.609	49.354
2	38.178	50.646
Total		100.000

#	Time	Area(%)
1	12.786	100.000
Total		100.000

HPLC chromatogram of compound **3h** [Chiralpak IF column, hexane: *i*-PrOH: DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



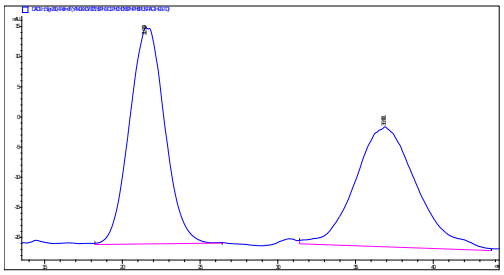


#	Time	Area(%)
1	65.157	49.551
2	69.682	50.449
Total		100.000

#	Time	Area(%)
1	65.157	100.000
Total		100.000

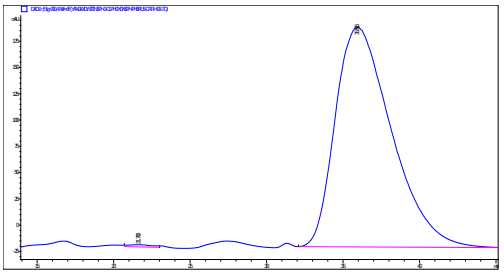
HPLC chromatogram of compound **3i** [Chiralpak IH column, hexane: *i*-PrOH:DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	21.509	50.975
2	36.901	49.025
Total		100.000

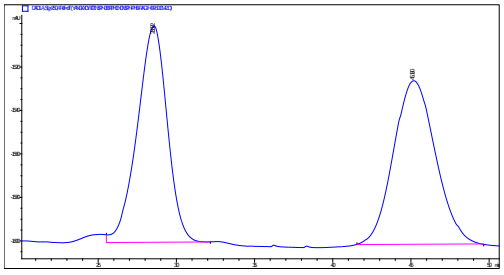
Chiral HPLC chromatogram



#	Time	Area(%)
1	21.7	0.434
2	35.996	99.566
Total		100.000

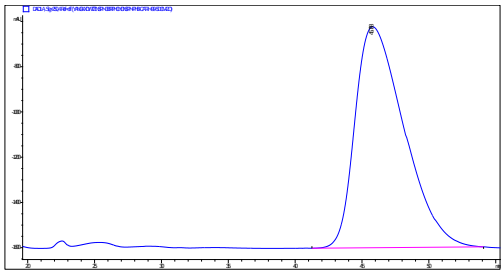
HPLC chromatogram of compound **3j** [Chiralpak IH column, hexane: *i*-PrOH:DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	28.582	48.653
2	45.18	51.347
Total		100.000

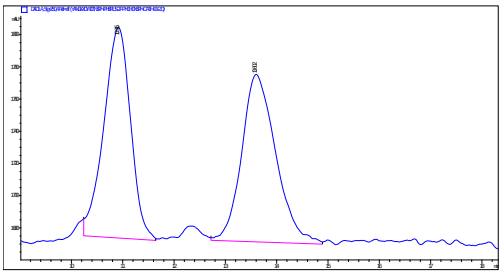
Chiral HPLC chromatogram



#	Time	Area(%)
1	45.797	100.000
Total		100.000

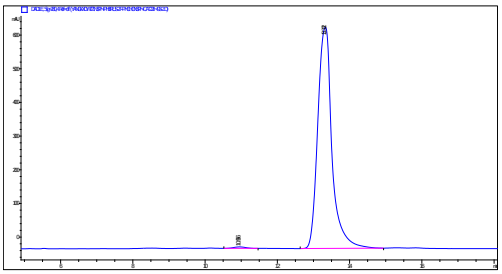
HPLC chromatogram of compound **3k** [Chiralpak IH column, hexane: *i*-PrOH:DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	10.92	48.310
2	13.602	51.690
Total		100.000

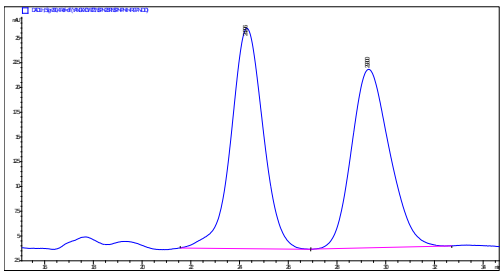
Chiral HPLC chromatogram

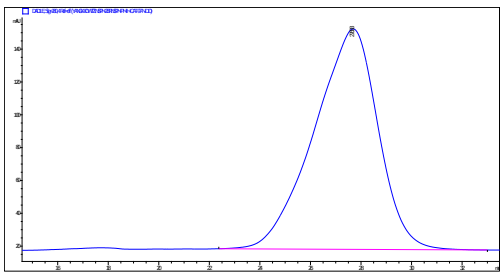


#	Time	Area(%)
1	10.956	0.549
2	13.332	99.451
Total		100.000

HPLC chromatogram of compound **3l** [Chiralpak IH column, hexane: *i*-PrOH = 93:7, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



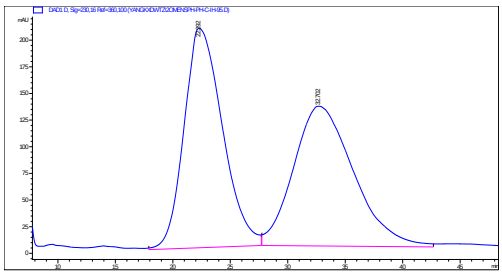


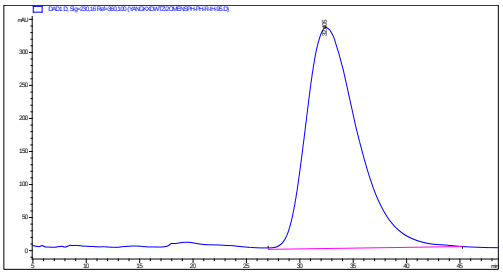
#	Time	Area(%)
1	24.296	50.974
2	29.3	49.026
Total		100.000

#	Time	Area(%)
1	27.693	100.000
Total		100.000

HPLC chromatogram of compound **3m** [Chiralpak IH column, hexane: *i*-PrOH = 93:7, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



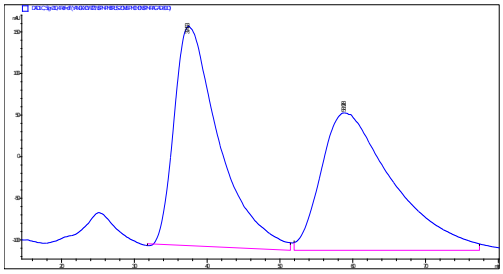


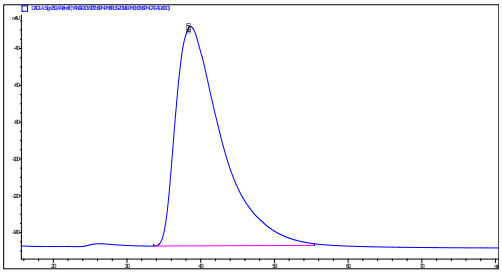
#	Time	Area(%)
1	22.292	49.133
2	32.702	50.867
Total		100.000

#	Time	Area(%)
1	32.405	100.000
Total		100.000

HPLC chromatogram of compound **3n** [Chiralpak AD column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



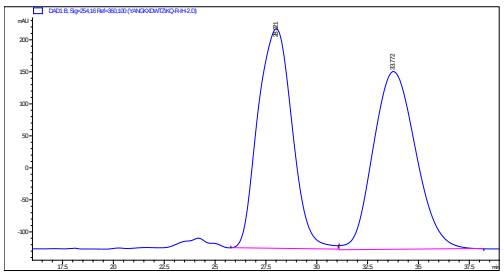


#	Time	Area(%)
1	37.453	50.137
2	58.928	49.863
Total		100.000

#	Time	Area(%)
1	38.57	100.000
Total		100.000

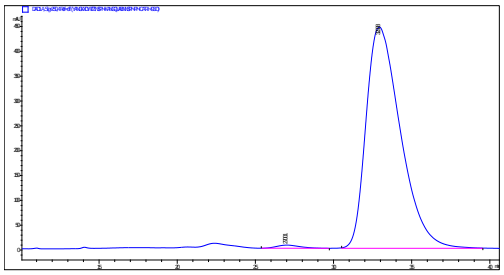
HPLC chromatogram of compound **3o** [Chiralpak IH column, hexane: *i*-PrOH = 93:7, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	28.021	47.989
2	33.7	52.011
Total		100.000

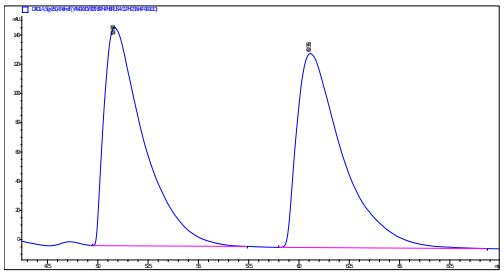
Chiral HPLC chromatogram



#	Time	Area(%)
1	27.002	0.947
2	32.938	99.053
Total		100.000

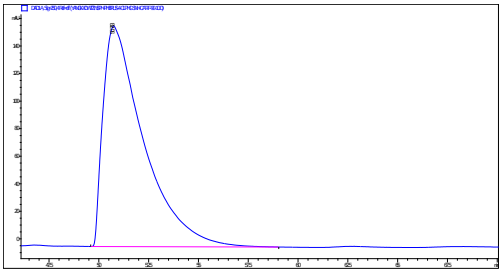
HPLC chromatogram of compound **3p** [Chiralpak IF column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	50.83	49.433
2	60.555	50.567
Total		100.000

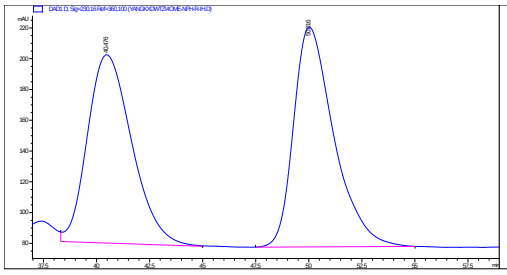
Chiral HPLC chromatogram



#	Time	Area(%)
1	50.743	100.000
Total		100.000

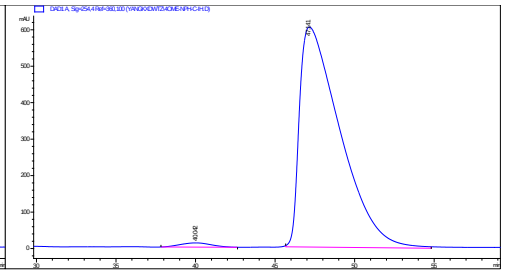
HPLC chromatogram of compound **3q** [Chiralpak IH column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	40.076	48.433
2	50.016	51.567
Total		100.000

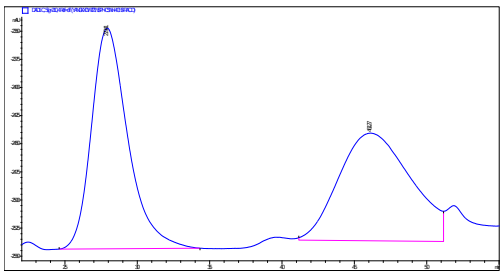
Chiral HPLC chromatogram

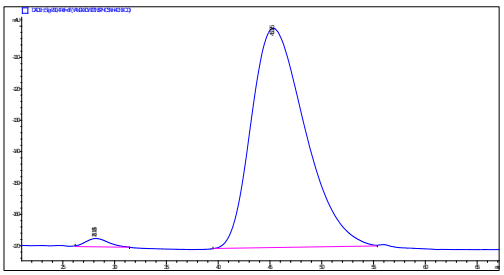


#	Time	Area(%)
1	40.476	1.434
2	47.141	98.566
Total		100.000

HPLC chromatogram of compound **3r** [Chiralpak Ih column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



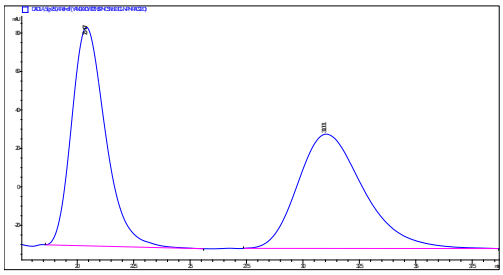


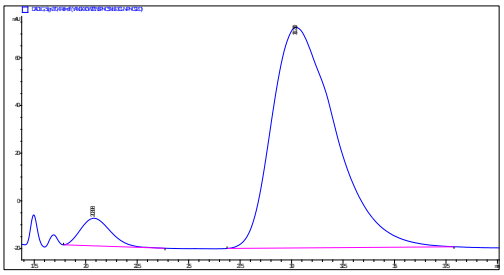
#	Time	Area(%)
1	27.941	50.861
2	46.127	49.139
Total		100.000

#	Time	Area(%)
1	28.185	1.588
2	45.323	98.412
Total		100.000

HPLC chromatogram of compound **3s** [Chiralpak IF column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



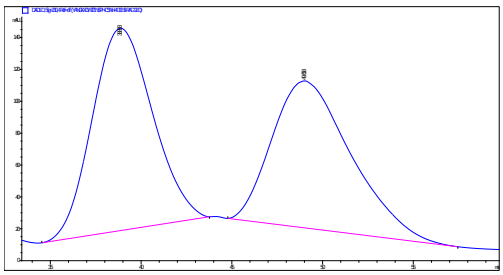


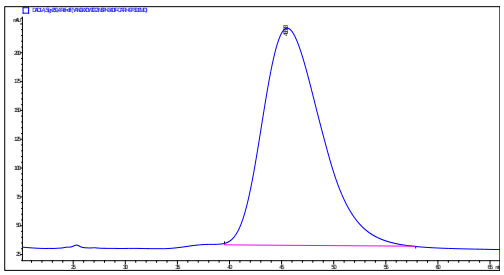
#	Time	Area(%)
1	20.407	49.433
2	31.001	50.567
Total		100.000

#	Time	Area(%)
1	20.398	5.538
2	30.23	94.462
Total		100.000

HPLC chromatogram of compound **3t** [Chiralpak IH column, hexane: *i*-PrOH：DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



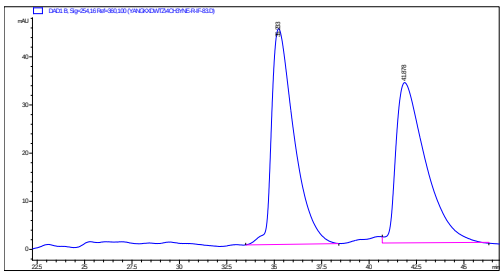


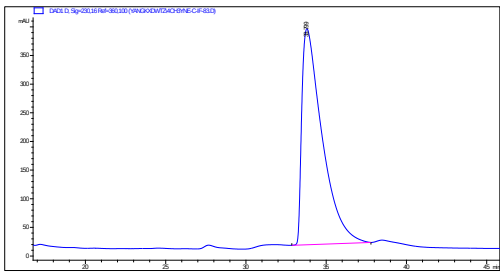
#	Time	Area(%)
1	38.053	51.017
2	49.058	48.983
Total		100.000

#	Time	Area(%)
1	45.533	100.000
Total		100.000

HPLC chromatogram of compound **4a** [Chiralpak IF column, hexane: *i*-PrOH = 83:17, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



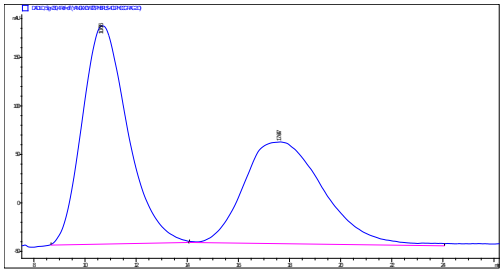


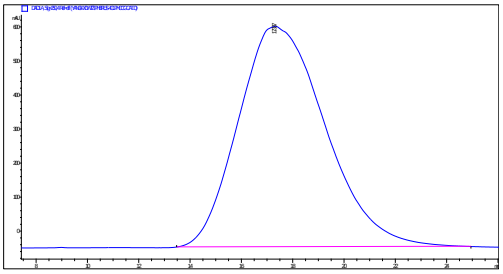
#	Time	Area(%)
1	35.233	50.660
2	41.878	49.340
Total		100.000

#	Time	Area(%)
1	33.799	100.000
Total		100.000

HPLC chromatogram of compound **4b** [Chiralpak IH column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



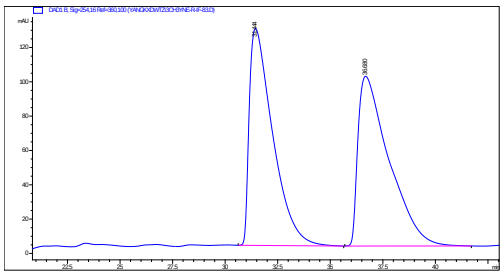


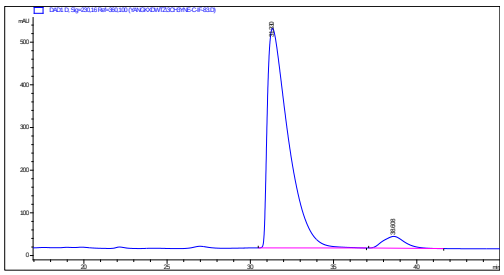
#	Time	Area(%)
1	10.676	55.087
2	17.647	44.913
Total		100.000

#	Time	Area(%)
1	17.337	100.000
Total		100.000

HPLC chromatogram of compound **4c** [Chiralpak IF column, hexane: *i*-PrOH = 83:17, 1.0 mL/min

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



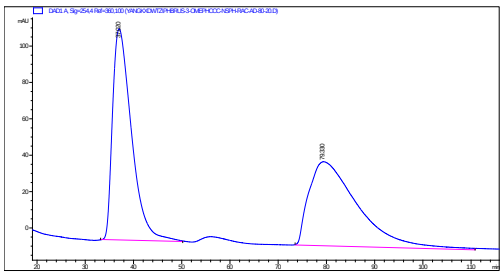


#	Time	Area(%)
1	31.444	49.607
2	36.68	50.393
Total		100.000

#	Time	Area(%)
1	31.33	96.799
2	38.608	3.201
Total		100.000

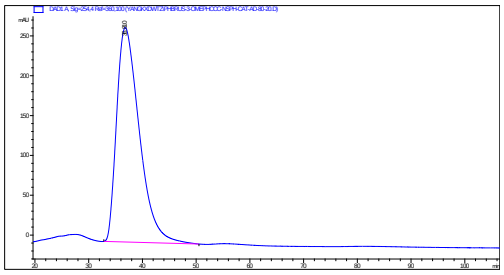
HPLC chromatogram of compound **4d** [Chiralpak AD column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	37.02	49.430
2	79.33	50.570
Total		100.000

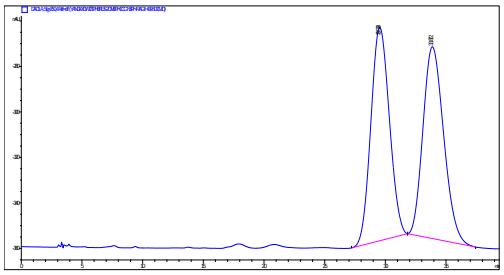
Chiral HPLC chromatogram



#	Time	Area(%)
1	36.81	100.000
Total		100.000

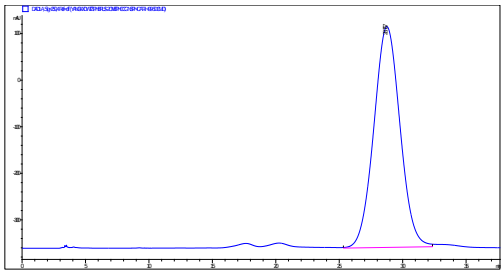
HPLC chromatogram of compound **4e** [Chiralpak IH column, hexane: *i*-PrOH: DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	29.538	49.840
2	33.872	50.160
Total		100.000

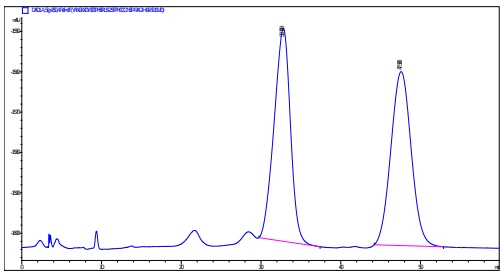
Chiral HPLC chromatogram



#	Time	Area(%)
1	28.757	100.000
Total		100.000

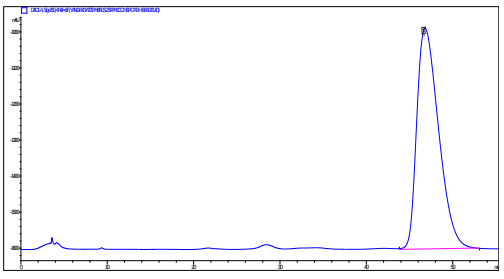
HPLC chromatogram of compound **4f** [Chiralpak IH column, hexane: *i*-PrOH: DCM = 91:4:5, 1.0 mL/min]

Racemic HPLC chromatogram



#	Time	Area(%)
1	32.798	49.637
2	47.58	50.363
Total		100.000

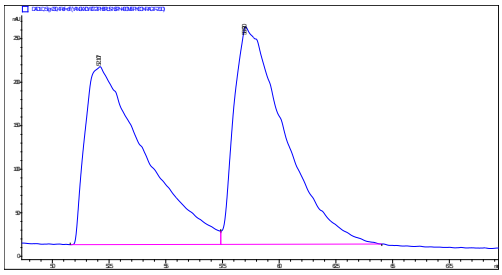
Chiral HPLC chromatogram

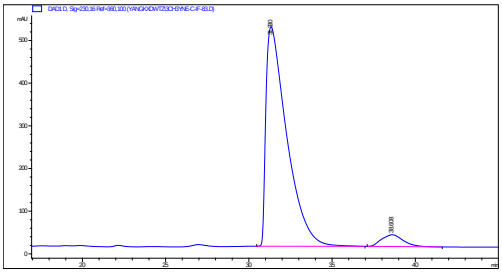


#	Time	Area(%)
1	46.791	100.000
Total		100.000

HPLC chromatogram of compound **4g** [Chiralpak IF column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



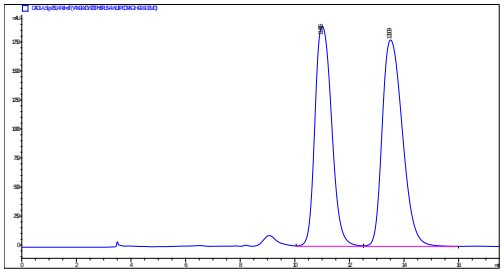


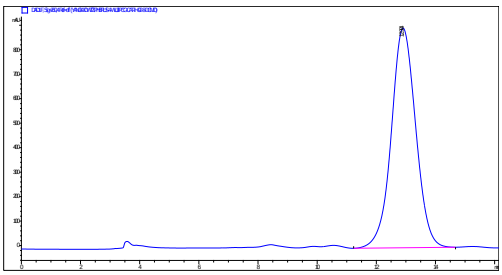
#	Time	Area(%)
1	52.107	48.379
2	58.52	51.621
Total		100.000

#	Time	Area(%)
1	49.399	99.415
2	61.146	0.585
Total		100.000

HPLC chromatogram of compound **4h** [Chiralpak IH column, hexane: *i*-PrOH :DCM = 94:1:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



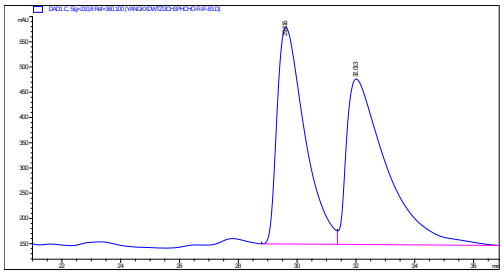


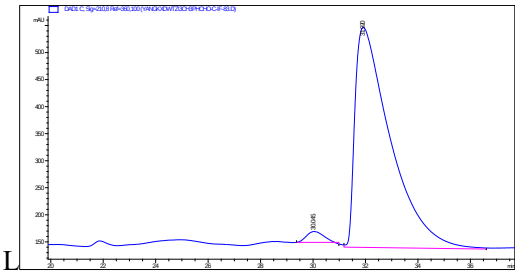
#	Time	Area(%)
1	11.005	46.851
2	13.509	53.149
Total		100.000

#	Time	Area(%)
1	12.904	100.000
Total		100.000

HPLC chromatogram of compound **4i** [Chiralpak IC column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



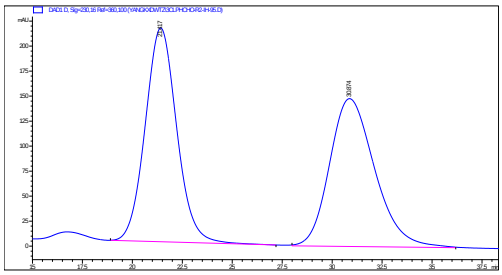


#	Time	Area(%)
1	29.616	48.590
2	32.013	51.410
Total		100.000

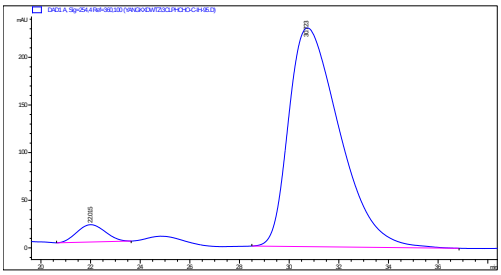
#	Time	Area(%)
1	30.045	1.307
2	31.92	98.693
Total		100.000

HPLC chromatogram of compound **4j** [Chiralpak IH column, hexane: *i*-PrOH = 95:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



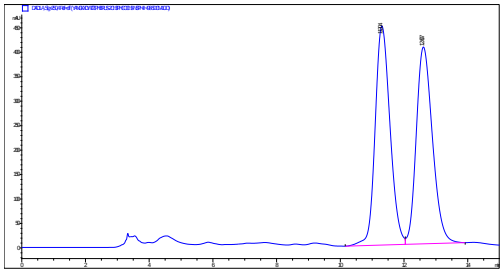
#	Time	Area(%)
1	21.417	50.248
2	30.874	49.752
Total		100.000



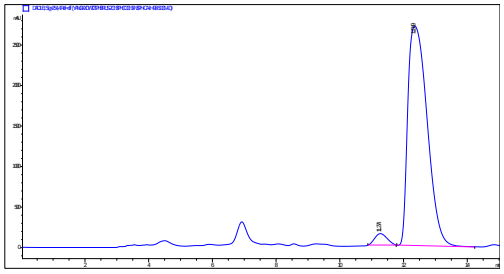
#	Time	Area(%)
1	22.015	3.206
2	30.723	96.794
Total		100.000

HPLC chromatogram of compound **4k** [Chiralpak IH column, hexane: *i*-PrOH :DCM = 94:1:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



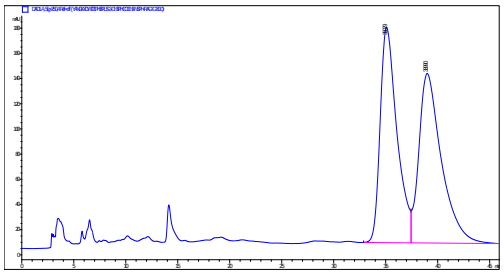
#	Time	Area(%)
1	11.304	46.851
2	12.607	53.149
Total		100.000



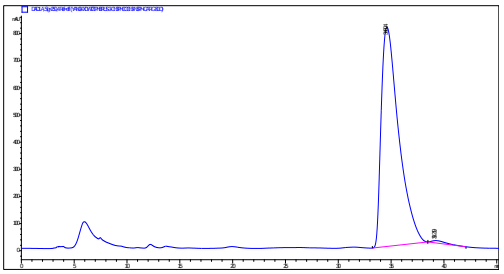
#	Time	Area(%)
1	11.274	3.216
2	12.349	96.784
Total		100.000

HPLC chromatogram of compound **4l** [Chiralpak IC column, hexane: *i*-PrOH = 80:20, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



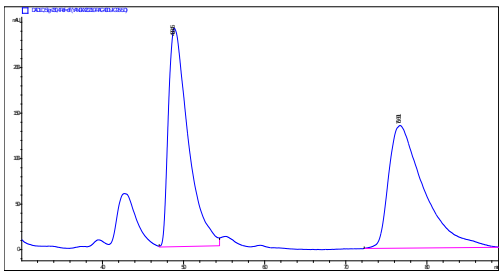
#	Time	Area(%)
1	35.079	48.684
2	38.99	51.316
Total		100.000

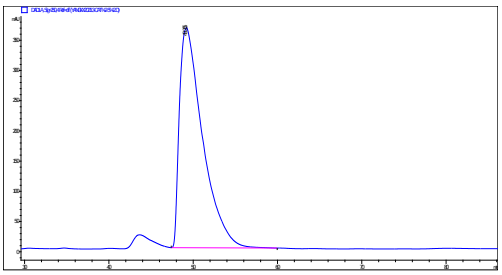


#	Time	Area(%)
1	34.604	99.136
2	39.219	0.864
Total		100.000

HPLC chromatogram of compound **5a** [Chiralpak IC column, hexane: *i*-PrOH = 97:3, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



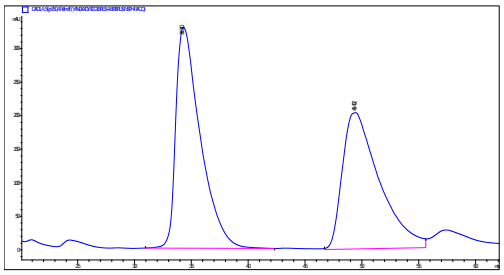


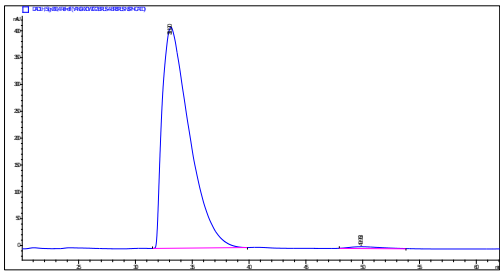
#	Time	Area(%)
1	48.845	50.064
2	76.691	49.936
Total		100.000

#	Time	Area(%)
1	49.205	100.000
Total		100.000

HPLC chromatogram of compound **5b** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



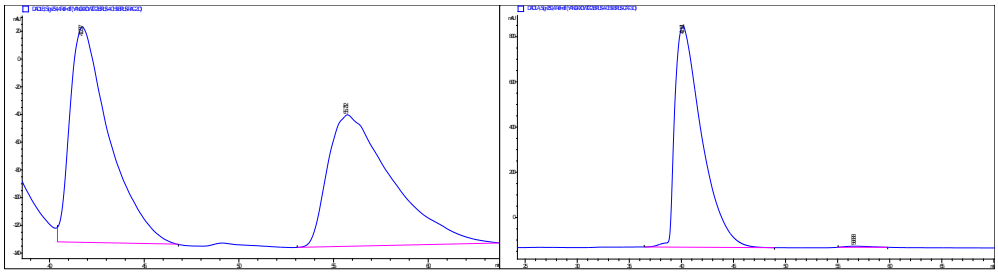


#	Time	Area(%)
1	34.31	51.821
2	49.452	48.179
Total		100.000

#	Time	Area(%)
1	33.13	99.014
2	49.953	0.986
Total		100.000

HPLC chromatogram of compound **5c** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**

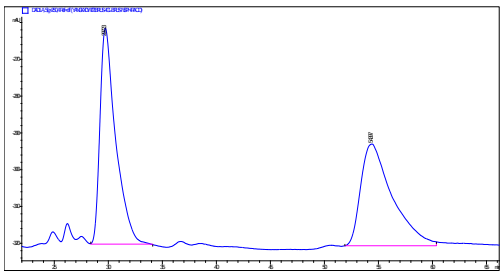


#	Time	Area(%)
1	41.724	50.805
2	55.73	49.195
Total		100.000

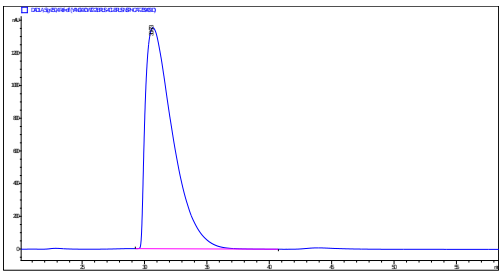
#	Time	Area(%)
1	40.181	99.549
2	56.688	0.451
Total		100.000

HPLC chromatogram of compound **5d** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



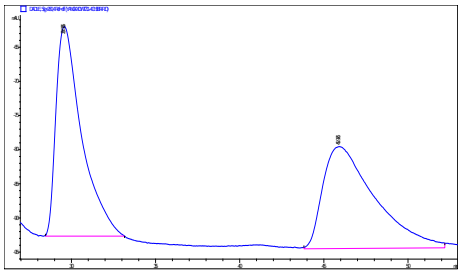
#	Time	Area(%)
1	29.723	51.453
2	54.397	48.547
Total		100.000



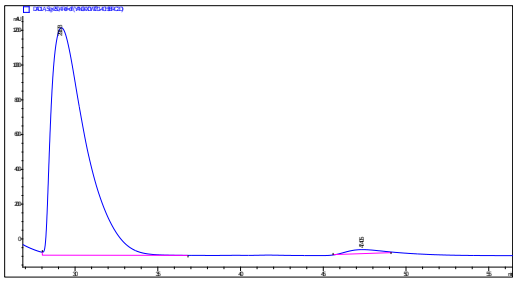
#	Time	Area(%)
1	30.673	100.000
Total		100.000

HPLC chromatogram of compound **5e** [Chiralpak IC column, hexane: *i*-PrOH = 93:7, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



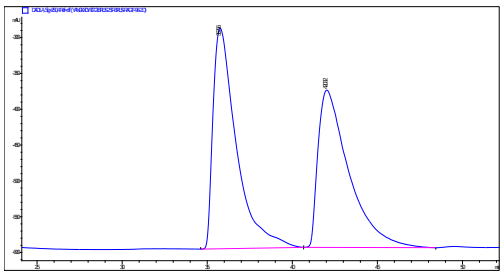
#	Time	Area(%)
1	29.585	50.367
2	45.926	49.633
Total		100.000



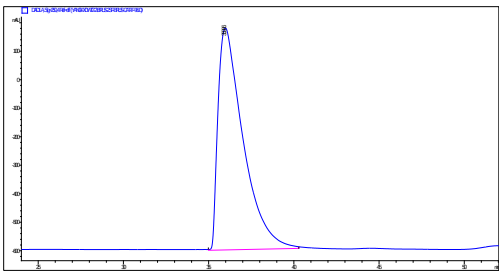
#	Time	Area(%)
1	29.178	98.46
2	47.10	1.540
Total		100.000

HPLC chromatogram of compound **5f** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



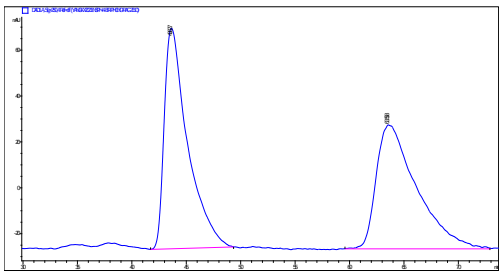
#	Time	Area(%)
1	35.756	51.528
2	42.032	48.472
Total		100.000

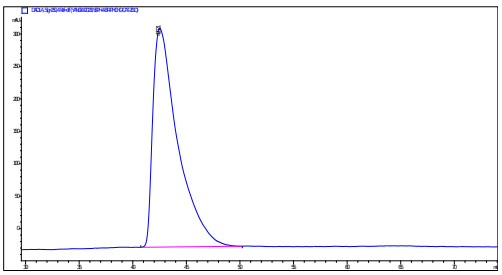


#	Time	Area(%)
1	35.996	100.000
Total		100.000

HPLC chromatogram of compound **5g** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



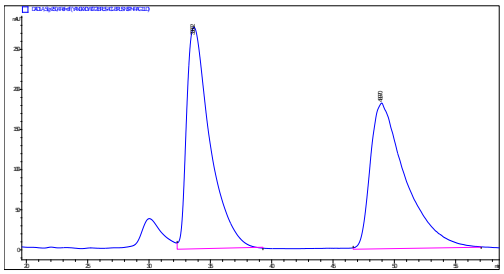


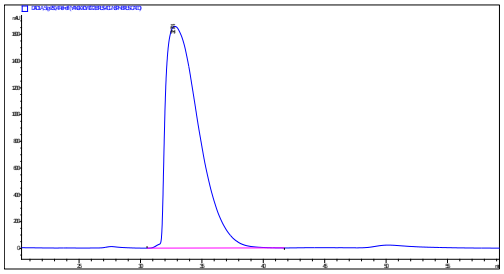
#	Time	Area(%)
1	43.627	50.665
2	63.558	49.335
Total		100.000

#	Time	Area(%)
1	42.521	100.000
Total		100.000

HPLC chromatogram of compound **5h** [Chiralpak IC column, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**





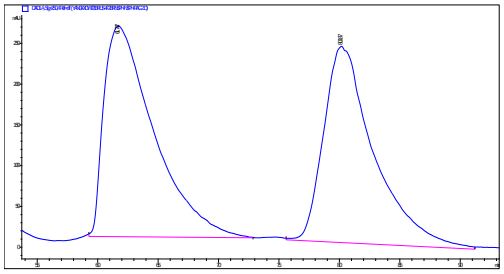
#	Time	Area(%)
1	33.663	50.169
2	48.97	49.831
Total		100.000

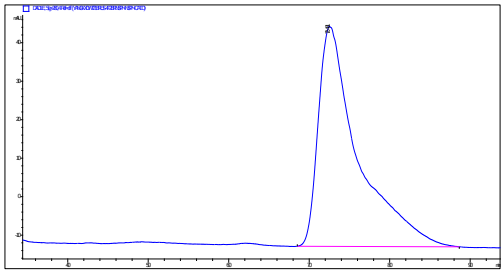
#	Time	Area(%)
1	32.774	100.000
Total		100.000

HPLC chromatogram of compound **5i** [Chiralpak IC column, hexane: *i*-PrOH = 90:10,1.0 mL/min]

Racemic HPLC chromatogram

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



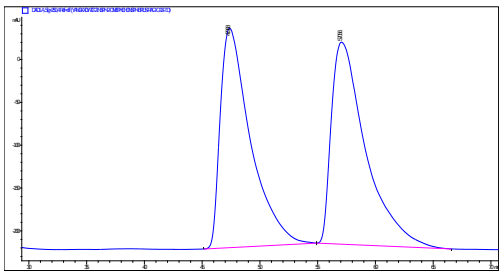


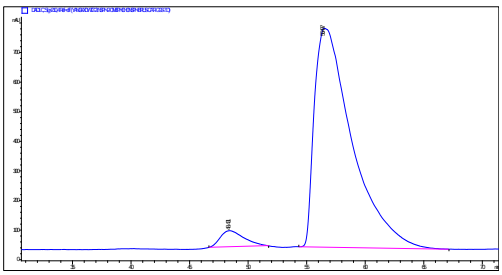
#	Time	Area(%)
1	61.747	51.650
2	80.187	48.350
Total		100.000

#	Time	Area(%)
1	72.481	100.000
Total		100.000

HPLC chromatogram of compound **5j** [Chiralpak IC column, hexane: *i*-PrOH = 97:3, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



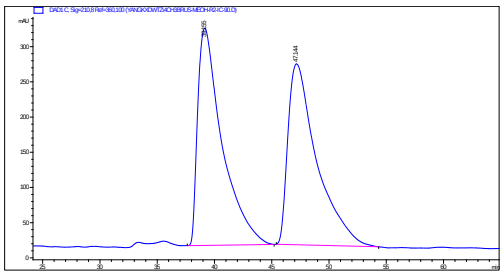


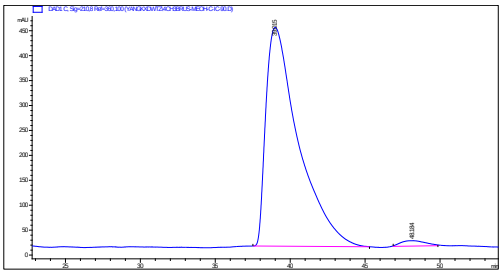
#	Time	Area(%)
1	47.368	48.848
2	57.056	51.152
Total		100.000

#	Time	Area(%)
1	48.431	4.353
2	56.497	95.649
Total		100.000

HPLC chromatogram of compound **6c** [Chiralpak IC colun, hexane: *i*-PrOH = 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



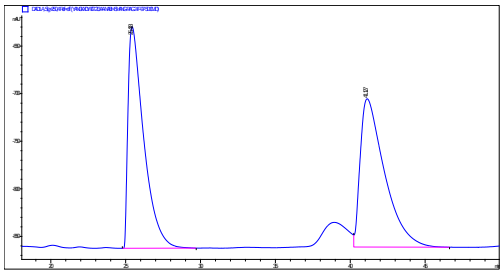


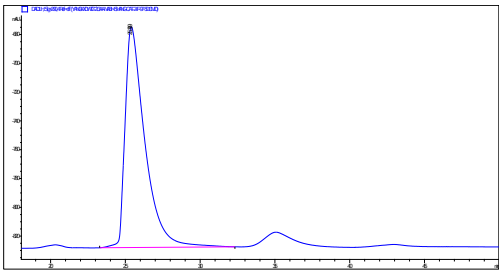
#	Time	Area(%)
1	39.155	50.393
2	47.144	49.607
Total		100.000

#	Time	Area(%)
1	39.015	98.949
2	48.184	1.051
Total		100.000

HPLC chromatogram of compound **7a-minor** [Chiralpak IH column, hexane: *i*-PrOH: DCM = 92:3:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



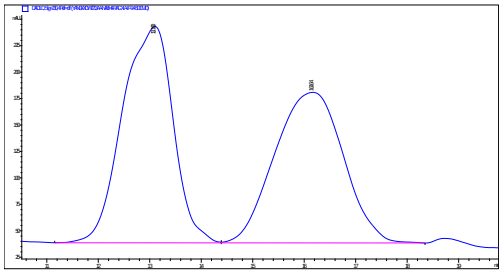


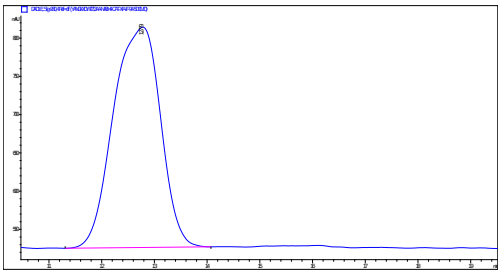
#	Time	Area(%)
1	25.433	49.052
2	41.127	50.948
Total		100.000

#	Time	Area(%)
1	25.399	100.000
Total		100.000

HPLC chromatogram of compound **7a-major** [Chiralpak IH column, hexane: *i*-PrOH: DCM = 92:3:5, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**



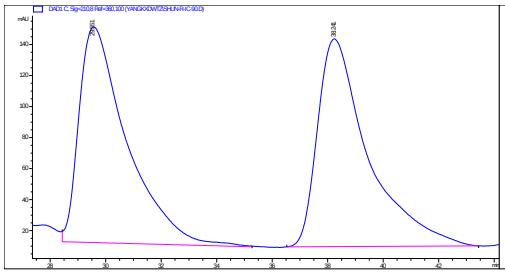


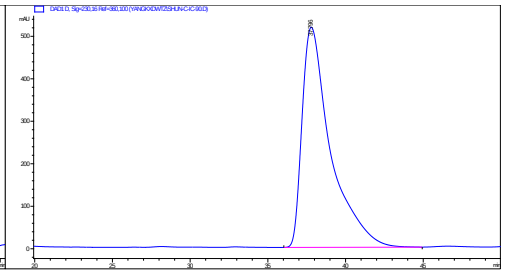
#	Time	Area(%)
1	13.1	50.173
2	16.14	49.827
Total		100.000

#	Time	Area(%)
1	12.779	98.963
2	16.048	1.037
Total		100.000

HPLC chromatogram of compound **3a-minor** [Chiralpak Ic column, hexane: *i*-PrOH= 90:10, 1.0 mL/min]

Racemic HPLC chromatogram **Chiral HPLC chromatogram**





#	Time	Area(%)
1	29.551	49.558
2	38.241	50.402
Total		100.000

#	Time	Area(%)
1	37.796	100.000
Total		100.000