

## Electronic Supplementary Information

### **Organocatalytic asymmetric synthesis of benzothiazolopyrimidines via [4+2] cycloaddition of azlactones with 2-benzothiazolimines**

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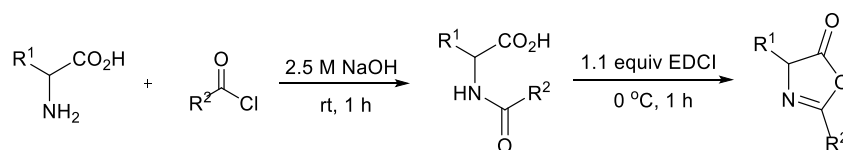
## 1. General Information

NMR characterization data were collected on Bruker ASCEND™ operating at 400 MHz for  $^1\text{H}$  NMR, 101 MHz for  $^{13}\text{C}$  NMR (with complete proton decoupling), and 376 MHz for  $^{19}\text{F}\{^1\text{H}\}$  NMR (with complete proton decoupling).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR: chemical shifts  $\delta$  were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for  $^1\text{H}$  NMR:  $\text{CDCl}_3 = 7.26$  ppm; for  $^{13}\text{C}$  NMR:  $\text{CDCl}_3 = 77.16$  ppm).  $^{19}\text{F}\{^1\text{H}\}$  NMR: chemical shifts are reported in ppm with relative to  $\text{CFCl}_3$  (external reference,  $\delta(^{19}\text{F}(\text{CFCl}_3)) = 0$ ). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration. Enantiomeric excesses (ee) were determined by Ultra Performance Convergence Chromatography (UPCC) on systems on Daicel Chiralcel in the experimental procedures at 35 °C. High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima ( $\nu$ ,  $\text{cm}^{-1}$ ). Circular dichroism spectrum (CD) were recorded on Applied Photophysics Chirascan. Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows:  $[\alpha]_D^{25}$  (c: g/100 mL, in  $\text{CH}_2\text{Cl}_2$ ). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II.

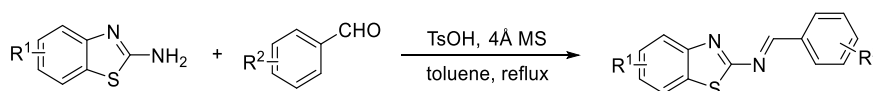
All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether ( $\text{Et}_2\text{O}$ ) were distilled from sodium benzophenone ketyl before use. Ethyl acetate,  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$  before use. The experimental substrates azlactones<sup>1</sup>, 2-benzothiazolimines<sup>2</sup>, and chiral guanidines<sup>3</sup> catalyst were synthesized according to known procedures. The starting materials were purchased from Accela, 3A chemicals, Aladdin, Adamas, Acros, Aldrich or Ark, and used without further purification. Reactions were monitored using thin-layer chromatography (TLC) on GF254 silica gel. Visualization of the developed plates was performed under UV light (254 nm) or using iodine, cobalt thiocyanate or  $\text{KMnO}_4$ . The products were purified by flash column chromatography with Silicycle 300–400 mesh silica gel.

## 2. General procedures for the preparation of substrates

### 2.1 General procedure for the synthesis of azlactones according to the literature procedure.<sup>1</sup>



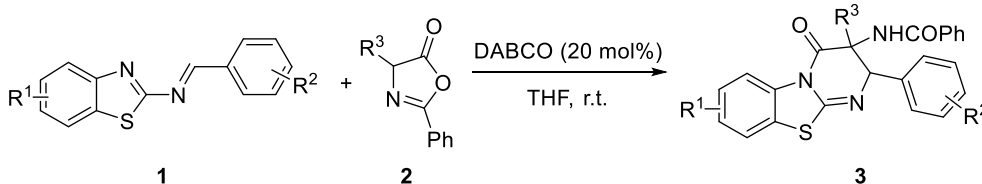
### 2.2 General procedure for the synthesis of 2-benzothiazolimines.<sup>2</sup>



To a 100 mL oven-dried round-bottom flask were added 2-aminobenzothiazole (1.5 g, 10 mmol), 4 Å molecular sieves (1.0 g), and toluene (20 mL). The mixture was refluxed for 0.5 h, then benzaldehyde (1.1 eq, 11 mmol) was added. The mixture was refluxed for 2–4 h (monitored by TLC). After the complete conversion of starting material, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was further recrystallized by n-hexane/ethyl acetate to give the desired 2-benzothiazolimine.

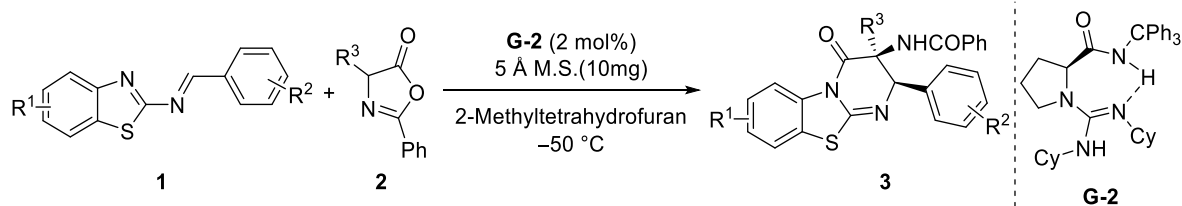
## 3. General procedures for the preparation of products

**General procedure for the synthesis of racemic product:** In a dry tube was charged with the DABCO (20 mol%), **1** (0.10 mmol), and **2** (0.10 mmol) in THF (0.5 mL). The reaction was stirred at r.t. and monitored by TLC. After the complete conversion of starting material, the solvent was removed under reduced pressure, and then the mixture was purified by column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) to afford the product **3**.



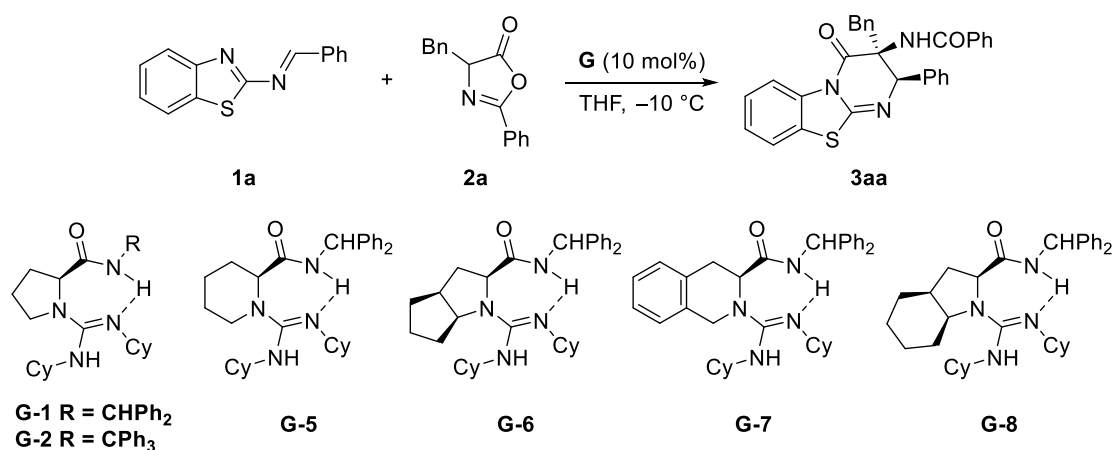
**Typical procedure for the asymmetric reaction:** In a dry tube was charged with the **G-2** (2 mol%), 5 Å MS (10 mg), **1** (0.10 mmol), and **2** (0.10 mmol). Under  $\text{N}_2$  atmosphere, the mixture was stirred at  $-50$  °C for 10 min, and then 2-methyltetrahydrofuran was added.

Next the mixture was stirred at  $-50\text{ }^{\circ}\text{C}$  and monitored by TLC until completion of the reaction. The mixture was purified by column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) to afford the product **3**.



#### 4. Optimization of the reaction conditions

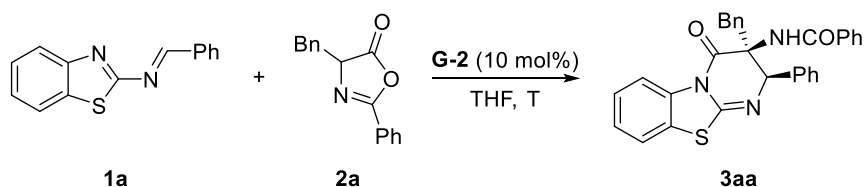
**Table S1.** Screening of the chiral guanidines <sup>[a]</sup>



entry	guanidine	yield (%)	ee (%)	d.r.
1	<b>G-1</b>	92	0	85:15
2	<b>G-2</b>	88	35	82:18
3	<b>G-5</b>	90	32	94:6
4	<b>G-6</b>	51	22	74:26
5	<b>G-7</b>	97	0	>19:1
5	<b>G-8</b>	93	20	82:18

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G** (10 mol%) in THF (0.5 mL) under N<sub>2</sub> at  $-10\text{ }^{\circ}\text{C}$  for 16 h. Isolated yield, ee and d.r. values were determined by UPCC analysis.

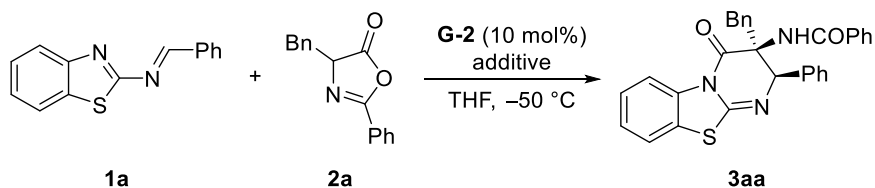
**Table S2.** Screening of the temperature <sup>[a]</sup>



entry	T (°C)	yield (%)	ee (%)	d.r.
1	$-20$	94	68	92:8
2	$-30$	87	82	95:5
3	$-40$	94	89	>19:1
4	$-50$	97	90	>19:1
5	$-60$	75	93	>19:1

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G-2** (10 mol%) in THF (0.5 mL) under N<sub>2</sub> for 16 h. Isolated yield, ee and d.r. values were determined by UPCC analysis.

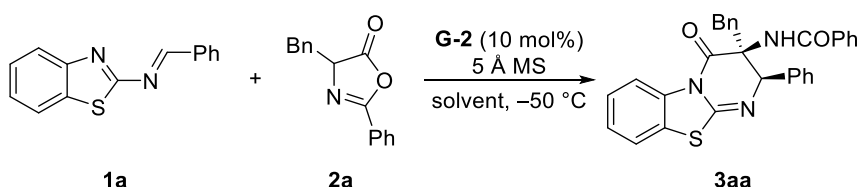
**Table S3.** Screening of the additives<sup>[a]</sup>



entry	additive	yield (%)	ee (%)	d.r.
1	3Å MS (10 mg)	93	92	>19:1
2	4Å MS (10 mg)	97	92	>19:1
3	5Å MS (10 mg)	99	93	>19:1

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), additive and **G-2** (10 mol%) in THF (0.5 mL) under N<sub>2</sub> at -50 °C for 3 h. Isolated yield, ee and d.r. values were determined by UPCC analysis.

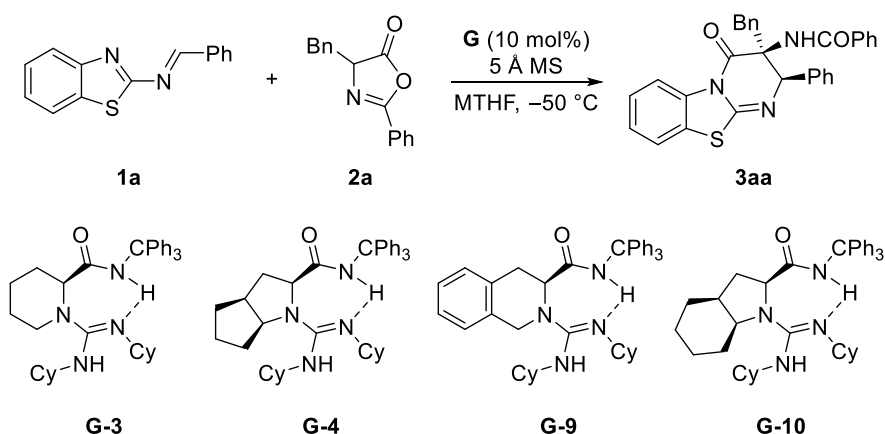
**Table S4.** Screening of the solvents<sup>[a]</sup>



entry	solvent	yield (%)	ee (%)	d.r.
1	THF	99	93	>19:1
2	CH <sub>2</sub> Cl <sub>2</sub>	92	93	>19:1
3	Et <sub>2</sub> O	99	89	>19:1
4	Toluene	97	89	>19:1
5	EA	98	92	>19:1
6	MTHF	95	95	>19:1

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), 5Å MS (10 mg) and **G-2** (10 mol%) in solvent (0.5 mL) under N<sub>2</sub> at -50 °C for 3 h. Isolated yield, ee and d.r. values were determined by UPCC analysis. MTHF = 2-Methyltetrahydrofuran.

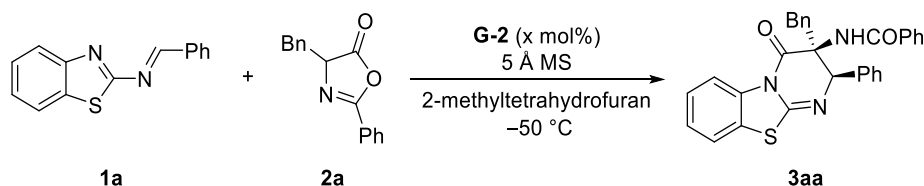
**Table S5.** Screening of the chiral guanidines<sup>[a]</sup>



entry	guanidine	yield (%)	ee (%)	d.r.
1	<b>G-3</b>	99	92	96:4
2	<b>G-4</b>	84	84	93:7
3	<b>G-9</b>	83	26	97:3
4	<b>G-10</b>	89	86	95:5

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G** (10 mol%) in MTHF (0.5 mL) under N<sub>2</sub> at -50 °C for 3 h. Isolated yield, ee and d.r. values were determined by UPCC analysis.

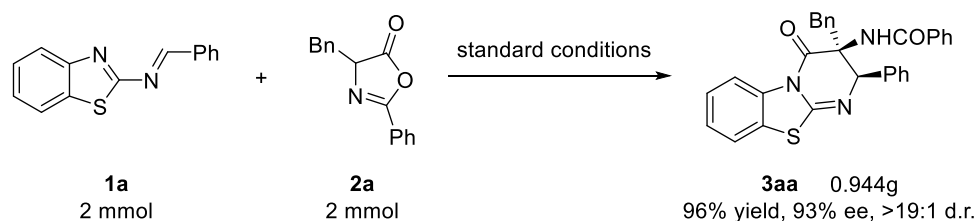
**Table S6.** Screening of the catalyst loading [a]



entry	x	yield (%)	ee (%)	d.r.
1	5	99	96	>19:1
2	2	92	97	>19:1
3 <sup>[b]</sup>	1	91	90	95:5

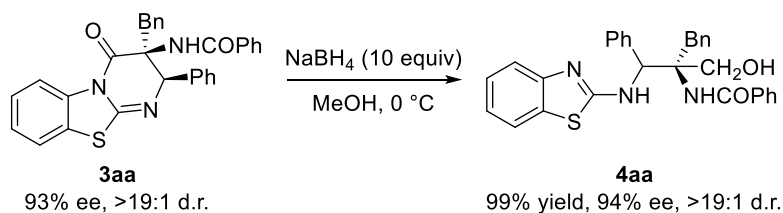
[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), 5 Å MS (10 mg) and **G-2** (10 mol%) in 2-methyltetrahydrofuran (0.5 mL) under N<sub>2</sub> at -50 °C for 3 h. Isolated yield, ee and d.r. values were determined by UPCC analysis. [b] 0.1 mL 2-methyltetrahydrofuran.

## 5. Gram-scale synthesis

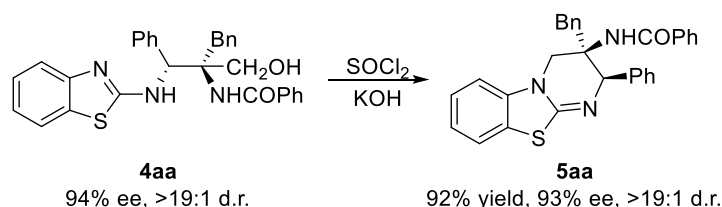


To a 50 mL oven-dried round-bottom flask was charged with the **G-2** (2 mol%), **1a** (2.0 mmol), and **2a** (2.0 mmol). Under N<sub>2</sub> atmosphere, the mixture was stirred at -50 °C for 30 min, and then 2-methyltetrahydrofuran (10 mL) was added. Next the mixture was stirred at -50 °C and monitored by TLC until completion of the reaction. The solvent was removed under reduced pressure, and the mixture was purified by column chromatography to afford the product **3aa**.

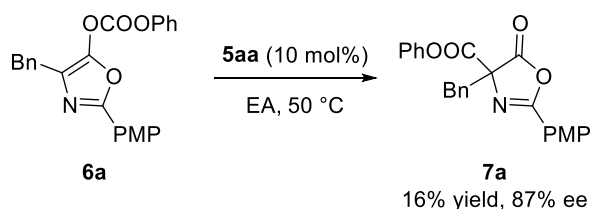
## 6. Further transformations of product



To a solution of **3aa** (0.10 mmol) in MeOH (1.0 mL) was added NaBH<sub>4</sub> (10.0 equiv) at 0 °C. After stirring for 30 minutes at 0 °C, the reaction mixture was quenched with brine and the mixture was diluted with dichloromethane. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated in vacuo, and was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to give product **4aa**.



Thionyl chloride (0.06 mL, 0.81 mmol, 2.2 equiv) was added to a stirred solution of **4aa** (181 mg, 0.367 mmol) in toluene (5 mL) and the reaction mixture was heated to reflux for 4h. Once complete the mixture was allowed to cool to rt and evaporated the solvent. MeOH (5 mL) and KOH was added to the residue and stirred overnight, followed by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated in vacuo, and was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to give product **5aa**.



In a dry tube was charged with the **5aa** (93% ee, 10 mol%), **6a** (0.10 mmol). Under N<sub>2</sub> atmosphere EA (0.5 mL) was added. Next the mixture was stirred at 50 °C for 24h. The solvent was removed under reduced pressure, and the mixture was purified by column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) to afford the product **7a**.

## 7. X-ray diffraction analysis of the compounds 3qa, 4aa and 5aa

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **3qa** in DCM and petroleum ether at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.558 × 0.315 × 0.256 mm<sup>3</sup>, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source ( $K_{\alpha} = 0.71073\text{\AA}$ ).

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **4aa** in MeOH at r.t.. The colourless crystal in rod-shape, with approximate dimensions of 0.276 × 0.107 × 0.072 mm<sup>3</sup>, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 293(2)K equipped with micro-focus Cu radiation source ( $K_{\alpha} = 1.54178\text{\AA}$ ).

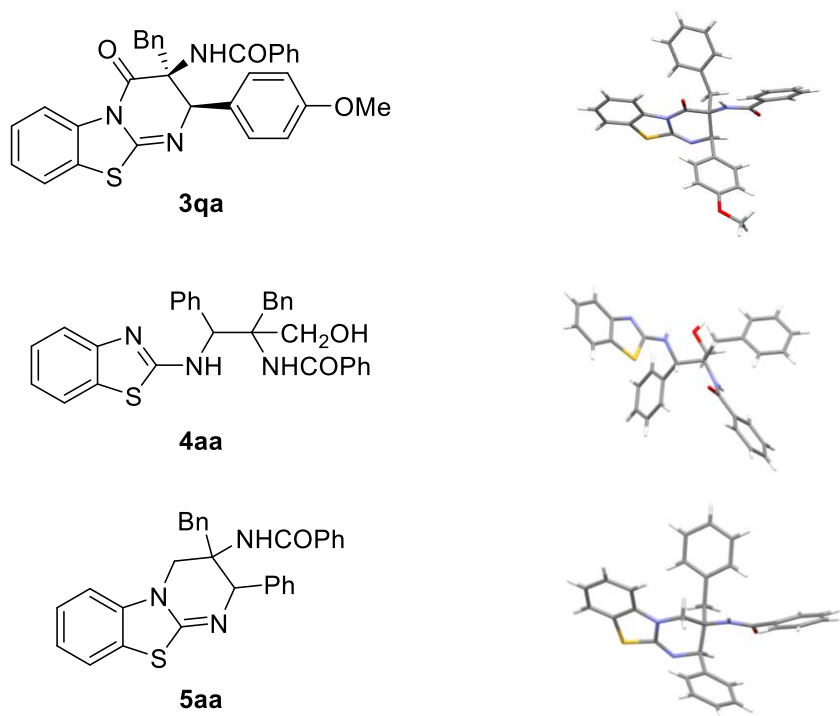
Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **5aa** in CDCl<sub>3</sub> at r.t.. The colourless crystal in block-shape, with approximate dimensions of 0.068 × 0.127 × 0.181 mm<sup>3</sup>, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 172(2)K equipped with micro-focus Cu radiation source ( $K_{\alpha} = 1.54178\text{\AA}$ ).

Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package<sup>a, b, c, d</sup>. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested<sup>e</sup>.

### References:

- <sup>a</sup> Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.  
<sup>b</sup> Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3–8.  
<sup>c</sup> Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3–8.  
<sup>d</sup> Dolomanov, O.V., Bourhis, L. J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339-341.  
<sup>e</sup> Spek, A. L. *J. Appl. Cryst.* **2003**, 36, 7–13.

The crystal data and further details are listed in **Table S7**. CCDC **2050053**, **2070880** and **2081453** which contain the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, <https://www.ccdc.cam.ac.uk/structures/>.



**Table S7.** The crystal data and further details.

compound	<b>3qa</b>	<b>4aa</b>	<b>5aa</b>
Formula	C <sub>31</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> S	C <sub>30</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> S	C <sub>30</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> S
Formula mass (amu)	519.60	493.60	475.59
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	I 41/a	P 21/c
<i>a</i> (Å)	9.6781(3)	22.4794(6)	12.3607(3)
<i>b</i> (Å)	14.9062(5)	22.4794(6)	21.8106(5)
<i>c</i> (Å)	17.7734(6)	20.5397(8)	10.8466(3)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	90	90	113.912(1)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	2564.06(15)	10379.2(7)	2673.20(12)
<i>Z</i>	4	16	4
$\lambda$ (Å)	0.71073	1.54178	1.54178
<i>T</i> (K)	173 K	293 K	172 K
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.346	1.264	1.182
$\mu$ (mm <sup>-1</sup> )	0.165	1.358	1.273
Transmission factors	0.879–0.998	0.764–0.997	0.796–0.952
$2\theta_{\text{max}}$ (deg)	25.349	68.301	68.308
No. of unique data, including $F_o^2 < 0$	4693	4739	4781
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4238	4134	4111
No. of variables	348	337	321
<i>R</i> ( <i>F</i> ) for $F_o^2 > 2\sigma(F_o^2)$ <sup>a</sup>	0.0311	0.0432	0.0557
<i>R</i> <sub>w</sub> ( $F_o^2$ ) <sup>b</sup>	0.0740	0.1096	0.1334
Goodness of fit	1.065	1.030	1.031

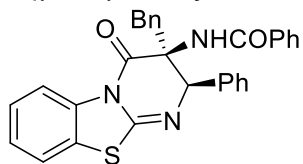
<sup>a</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$ ;  $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$ , where  $p = [\max(F_o^2, 0) + 2F_c^2] / 3$ .



## 8. Characterization of the products

### *N*-((2*R*,3*S*)-3-benzyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3aa)



White solid; m.p. 90–95 °C; 45.2 mg, 92% yield, 97% ee, >19:1 d.r.;  $[\alpha]_D^{22} = +451.36$  ( $c = 5.50$  in  $\text{CH}_2\text{Cl}_2$ ).

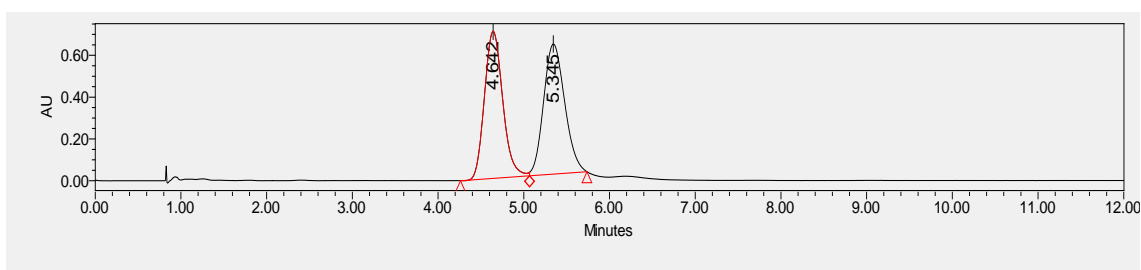
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 215$  nm,  $t_R$  (minor) = 4.59 min,  $t_R$  (major) = 5.22 min.

**IR** (neat): 3401, 1643, 1460, 1368 and 1184  $\text{cm}^{-1}$ .

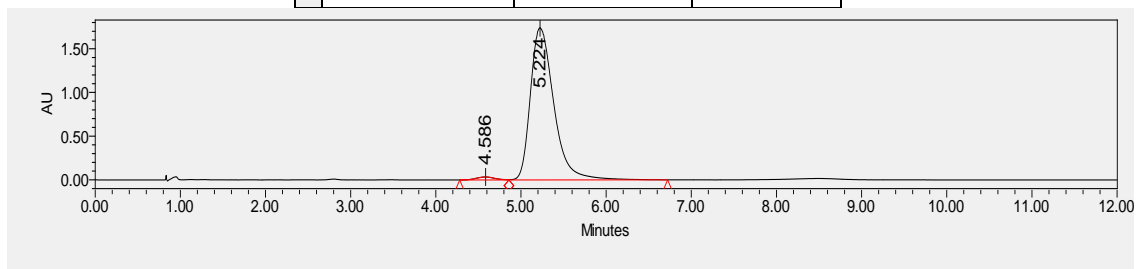
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.07 - 8.00$  (m, 1H), 7.48 – 7.42 (m, 4H), 7.37 – 7.31 (m, 4H), 7.29 – 7.25 (m, 2H), 7.22 – 7.16 (m, 4H), 7.15 – 7.10 (m, 2H), 6.93 – 6.87 (m, 3H), 6.14 (s, 1H), 4.37 (d,  $J = 14.0$  Hz, 1H), 3.50 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.8, 153.8, 135.9, 135.2, 134.9, 134.8, 131.7, 130.1, 128.8, 128.7, 128.6, 128.4, 127.5, 127.3, 127.0, 126.8, 126.4, 123.6, 122.4, 115.9, 67.7, 64.9, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 490.1584, Found 490.1585.

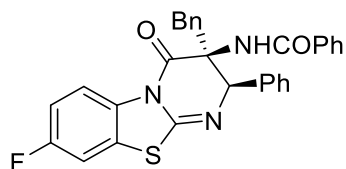


	Retention Time	Area	% Area
1	4.642	10416094	49.48
2	5.345	10633959	50.52



	Retention Time	Area	% Area
1	4.586	510434	1.51
2	5.224	33207114	98.49

***N*-((2*R*,3*S*)-3-benzyl-8-fluoro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ba)**



White solid; m.p. 95–98 °C; 51.5 mg, 99% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{21} = +428.04$  ( $c = 0.94$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral OJH column),  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 218$  nm,  $t_R$  (major) = 5.88 min,  $t_R$  (minor) = 6.45 min.

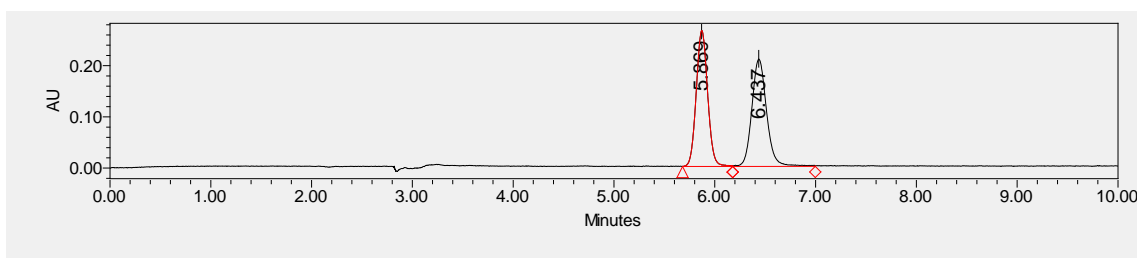
**IR** (neat): 3405, 1651, 1474, 1372 and 1228  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.03 - 7.97$  (m, 1H), 7.48 – 7.43 (m, 3H), 7.37 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.19 (m, 4H), 7.19 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 7.05 – 6.99 (m, 1H), 6.91 – 6.86 (m, 3H), 6.15 (s, 1H), 4.37 (d,  $J = 14.0$  Hz, 1H), 3.48 (d,  $J = 14.0$  Hz, 1H).

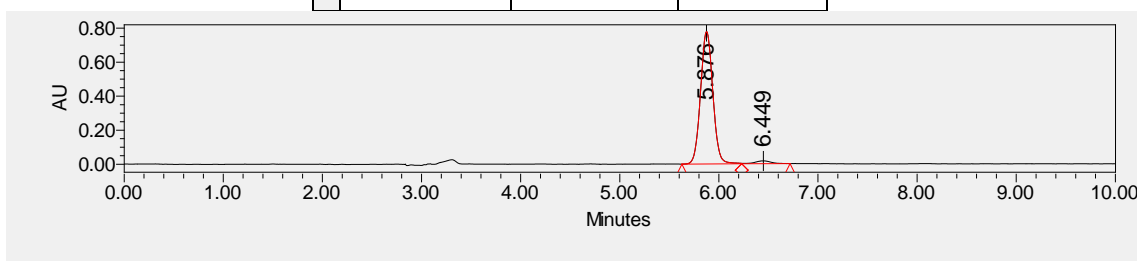
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.6, 160.6$  (d,  $J = 247.5$  Hz), 153.4, 135.7, 135.1, 134.8, 131.7, 131.1 (d,  $J = 2.6$  Hz), 130.1, 128.8, 128.7, 128.6, 128.4, 127.6, 127.2, 126.8, 125.4 (d,  $J = 9.8$  Hz), 117.0 (d,  $J = 8.4$  Hz), 113.8 (d,  $J = 23.1$  Hz), 110.0 (d,  $J = 27.5$  Hz), 67.8, 64.8, 39.7.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -113.8$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1490.

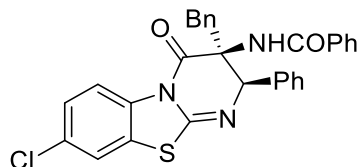


	Retention Time	Area	% Area
1	5.869	2084281	49.39
2	6.437	2135404	50.61



	Retention Time	Area	% Area
1	5.876	6692970	97.24
2	6.449	189836	2.76

***N*-((2*R*,3*S*)-3-benzyl-8-chloro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ca)**



White solid; m.p. 105–110 °C; 50.1 mg, 96% yield, 92% ee, >19:1 d.r.;  $[\alpha]_D^{21} = +320.36$  ( $c = 0.71$  in  $\text{CH}_2\text{Cl}_2$ ).

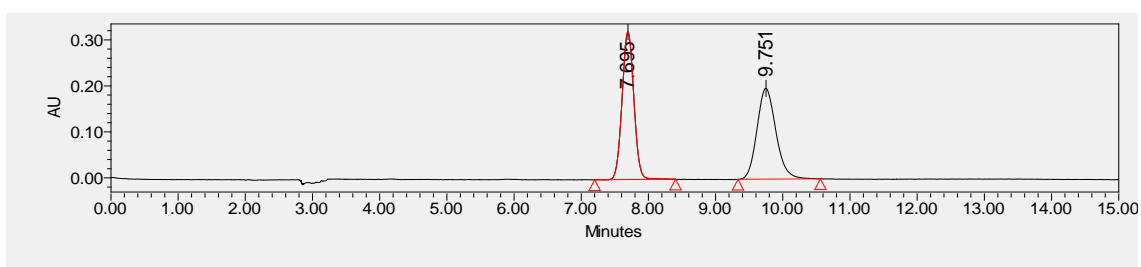
**UPCC** (chiral OJH column),  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 236$  nm,  $t_R$  (major) = 7.68 min,  $t_R$  (minor) = 9.74 min.

**IR** (neat): 3405, 1650, 1462, 1369 and 1186  $\text{cm}^{-1}$ .

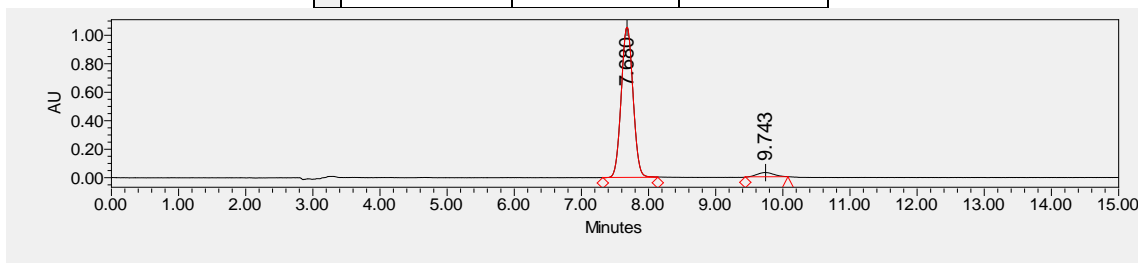
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.96 - 7.92$  (m, 1H), 7.47 – 7.42 (m, 4H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 7.22 – 7.17 (m, 4H), 7.15 – 7.10 (m, 2H), 6.90 – 6.85 (m, 3H), 6.14 (s, 1H), 4.36 (d,  $J = 14.0$  Hz, 1H), 3.46 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.7, 153.0, 135.6, 135.1, 134.8, 133.3, 131.9, 131.8, 130.0, 128.9, 128.7, 128.7, 128.5, 127.6, 127.2, 127.1, 126.8, 125.4, 122.3, 116.7, 67.8, 64.9, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{35}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 524.1194, Found 524.1196,  $\text{C}_{30}\text{H}_{23}^{37}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 526.1165, Found 526.1169.

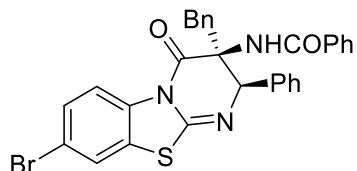


	Retention Time	Area	% Area
1	7.695	3893537	50.22
2	9.751	3859140	49.78



	Retention Time	Area	% Area
1	7.680	12828434	96.19
2	9.743	508285	3.81

***N*-((2*R*,3*S*)-3-benzyl-8-bromo-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3da)**



White solid; m.p. 110–114 °C; 53.5 mg, 94% yield, 87% ee, 93:7 d.r.;  $[\alpha]_D^{21} = +343.28$  ( $c = 0.82$  in  $\text{CH}_2\text{Cl}_2$ ).

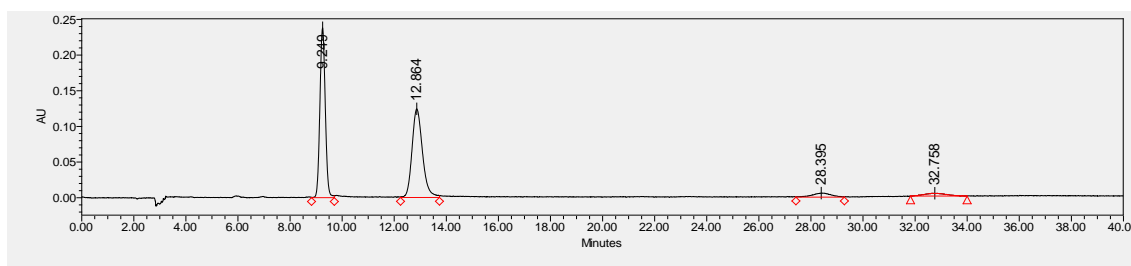
**UPCC** (chiral OJH column),  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 218$  nm,  $t_R$  (major) = 9.24 min,  $t_R$  (minor) = 12.88 min.

**IR** (neat): 3405, 1651, 1460, 1369 and 1186  $\text{cm}^{-1}$ .

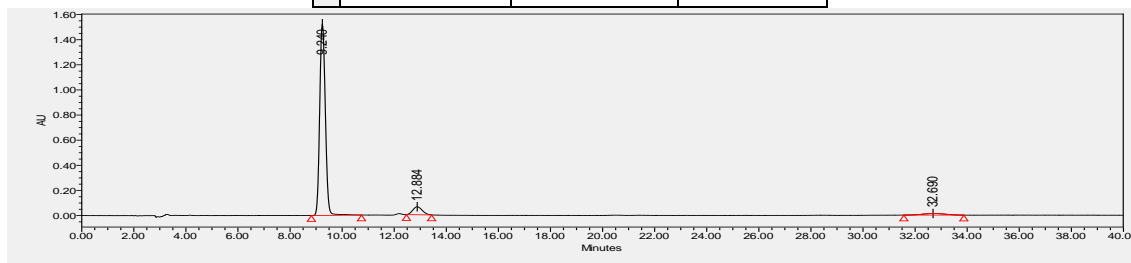
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.92 - 7.81$  (m, 1H), 7.67 – 7.57 (m, 1H), 7.55 – 7.42 (m, 4H), 7.38 – 7.31 (m, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.17 (m, 4H), 7.17 – 7.11 (m, 2H), 6.91 – 6.80 (m, 3H), 6.15 (s, 1H), 4.38 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.7, 153.0, 135.6, 135.0, 134.7, 133.8, 131.8, 130.0, 128.9, 128.7, 128.7, 128.5, 127.6, 127.2, 126.8, 125.6, 125.1, 119.2, 117.0, 67.7, 64.9, 39.6$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{79}\text{BrN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 568.0689, Found 568.0691,  $\text{C}_{30}\text{H}_{23}^{81}\text{Br N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 570.0668, Found 570.0670.

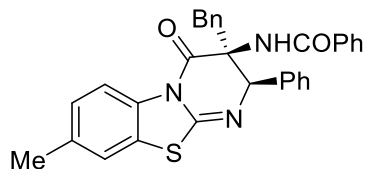


	Retention Time	Area	% Area
1	9.249	3405649	46.10
2	12.864	3462178	46.87
3	28.395	288316	3.90
4	32.758	231174	3.13



	Retention Time	Area	% Area
1	9.240	22878501	90.54
2	12.884	1616134	6.40
3	32.690	774439	3.06

***N*-((2*R*,3*S*)-3-benzyl-8-methyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ea)**



White solid; m.p. 100–103°C; 49.4 mg, 98% yield, 92% ee, >19:1 d.r.;  $[\alpha]_D^{21} = +472.40$  ( $c = 0.87$  in  $\text{CH}_2\text{Cl}_2$ ).

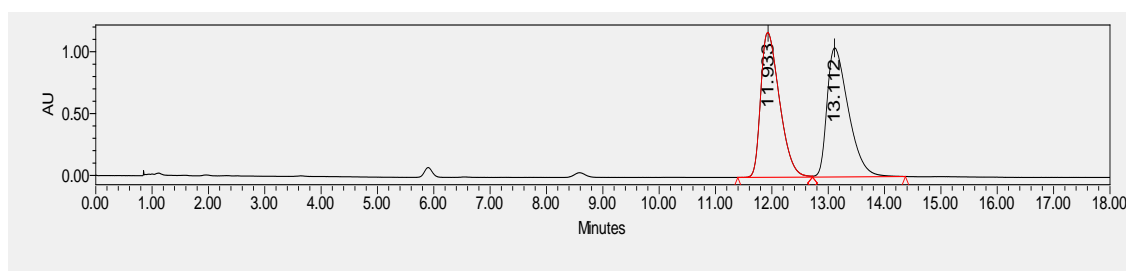
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 216$  nm,  $t_R$  (major) = 11.31 min,  $t_R$  (minor) = 12.73 min.

**IR** (neat): 3405, 1645, 1479, 1370 and 1185  $\text{cm}^{-1}$ .

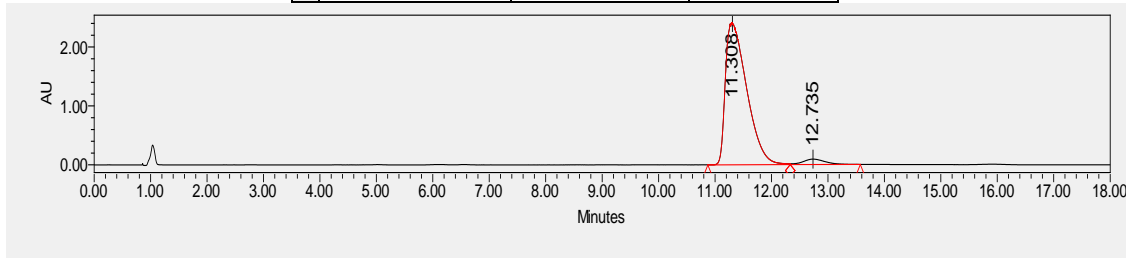
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.94 - 7.90$  (m, 1H), 7.48 – 7.42 (m, 3H), 7.37 – 7.32 (m, 2H), 7.29 – 7.25 (m, 3H), 7.23 – 7.17 (m, 4H), 7.15 – 7.10 (m, 3H), 6.95 – 6.86 (m, 3H), 6.13 (s, 1H), 4.37 (d,  $J = 14.0$  Hz, 1H), 3.49 (d,  $J = 13.9$  Hz, 1H), 2.43 (s, 3H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.5, 154.0, 136.6, 135.9, 135.2, 134.9, 132.5, 131.6, 130.1, 128.8, 128.7, 128.5, 128.4, 127.6, 127.4, 127.3, 126.8, 123.4, 122.7, 115.7, 67.6, 64.8, 39.6, 21.4$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 504.1740, Found 504.1739.

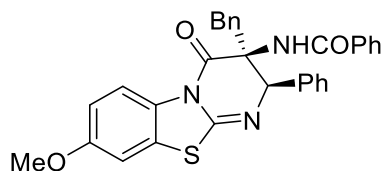


	Retention Time	Area	% Area
1	11.933	27038174	49.67
2	13.112	27395884	50.33



	Retention Time	Area	% Area
1	11.308	62962053	96.02
2	12.735	2610597	3.98

***N*-((2*R*,3*S*)-3-benzyl-8-methoxy-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3fa)**



White solid; m.p. 95–98 °C; 50.1 mg, 99% yield, 96% ee, >19:1 d.r.;  $[\alpha]_D^{21} = +485.24$  ( $c = 0.73$  in  $\text{CH}_2\text{Cl}_2$ ).

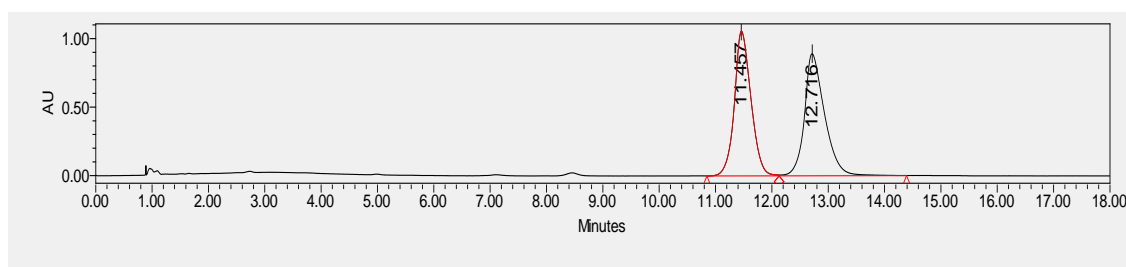
UPCC (chiral IB-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 216$  nm,  $t_R$  (major) = 12.09 min,  $t_R$  (minor) = 13.71 min.

IR (neat): 3403, 1645, 1480, 1373 and 1183  $\text{cm}^{-1}$ .

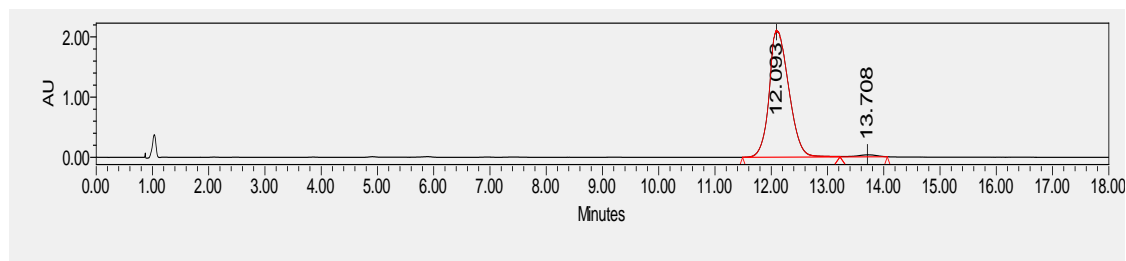
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.99 - 7.93$  (m, 1H), 7.47 – 7.42 (m, 3H), 7.36 – 7.31 (m, 2H), 7.29 – 7.26 (m, 2H), 7.22 – 7.16 (m, 4H), 7.16 – 7.10 (m, 2H), 7.01 – 6.99 (m, 1H), 6.94 – 6.87 (m, 3H), 6.86 – 6.82 (m, 1H), 6.13 (s, 1H), 4.35 (d,  $J = 14.0$  Hz, 1H), 3.87 (s, 3H), 3.48 (d,  $J = 14.0$  Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.2, 158.1, 154.0, 135.9, 135.2, 135.0, 131.7, 130.1, 128.8, 128.7, 128.5, 128.4, 128.4, 127.4, 127.3, 126.8, 124.9, 116.8, 112.3, 108.1, 67.7, 64.8, 56.0, 39.7$ .

HRMS (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_3\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 520.1689, Found 520.1689.

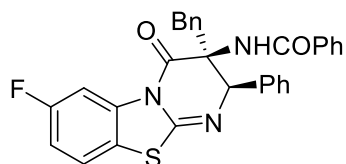


	Retention Time	Area	% Area
1	11.457	21572121	49.49
2	12.716	22016397	50.51



	Retention Time	Area	% Area
1	12.093	50897102	98.37
2	13.708	845023	1.63

***N*-((2*R*,3*S*)-3-benzyl-7-fluoro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ga)**



White solid; m.p. 95–97 °C; 45.4 mg, 89% yield, 89% ee, 93:7 d.r.;  $[\alpha]_D^{21} = +357.60$  ( $c = 0.84$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral QJH column),  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 218$  nm,  $t_{\text{major isomer}} = 5.86$  min (minor), 7.50 min (major);  $t_{\text{minor isomer}} = 14.80$  min (major).

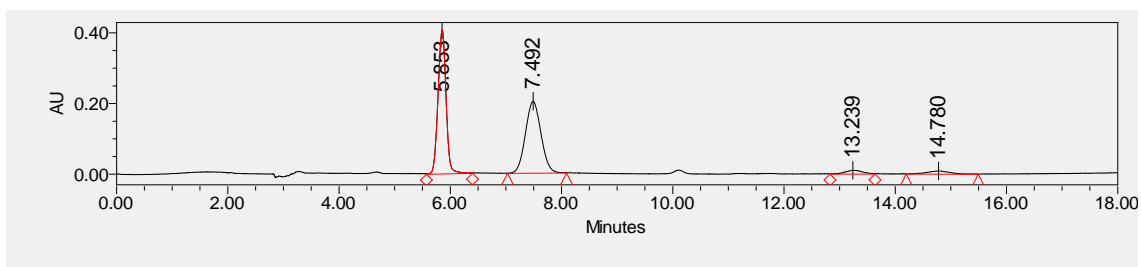
**IR** (neat): 3405, 1651, 1476, 1370 and 1184  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.86 - 7.81$  (m, 1H), 7.49 – 7.42 (m, 3H), 7.41 – 7.32 (m, 3H), 7.29 – 7.24 (m, 2H), 7.24 – 7.19 (m, 4H), 7.18 – 7.11 (m, 2H), 7.11 – 7.04 (m, 1H), 6.92 – 6.80 (m, 3H), 6.16 (s, 1H), 4.38 (d,  $J = 14.0$  Hz, 1H), 3.49 (d,  $J = 14.1$  Hz, 1H).

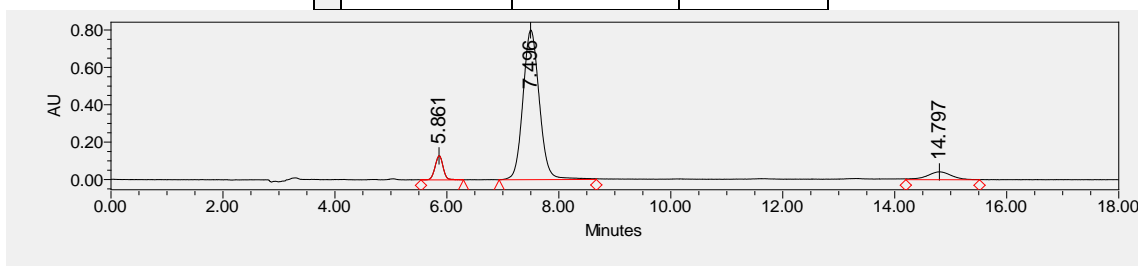
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.8, 161.8$  (d,  $J = 245.1$  Hz), 153.9, 135.6, 135.4 (d,  $J = 11.9$  Hz), 135.0, 134.7, 131.8, 130.0, 128.9, 128.7, 128.7, 128.5, 127.6, 127.2, 126.8, 123.0 (d,  $J = 9.1$  Hz), 118.4 (d,  $J = 3.2$  Hz), 113.6 (d,  $J = 23.6$  Hz), 104.7 (d,  $J = 30.1$  Hz), 67.7, 64.9, 39.7.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -112.5$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1492.

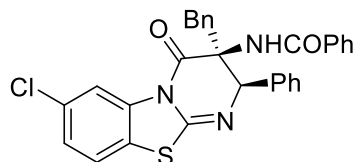


	Retention Time	Area	% Area
1	5.853	4068571	47.61
2	7.492	3965123	46.40
3	13.239	244410	2.86
4	14.780	268145	3.14



	Retention Time	Area	% Area
1	5.861	1292499	6.85
2	7.496	16298185	86.36
3	14.797	1282641	6.80

***N*-((2*R*,3*S*)-3-benzyl-7-chloro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ha)**



White solid; m.p. 103–105 °C; 48.3 mg, 92% yield, 80% ee, 93:7 d.r.;  $[\alpha]_D^{21} = +340.35$  ( $c = 0.81$  in  $\text{CH}_2\text{Cl}_2$ ).

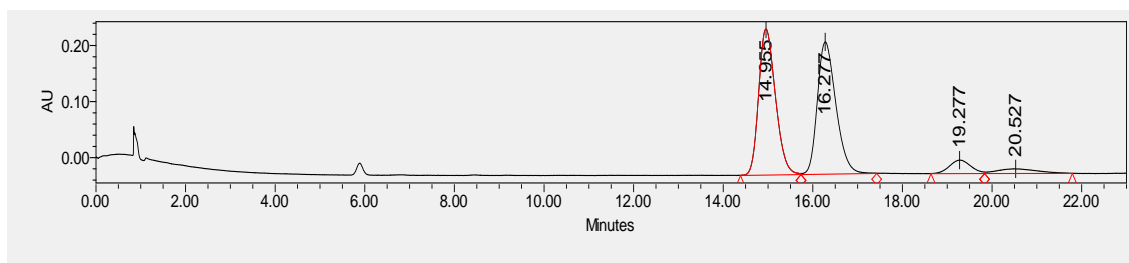
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 223$  nm,  $t_{\text{major isomer}} = 14.21$  min (major), 15.65 min (minor);  $t_{\text{minor isomer}} = 18.89$  min (major).

**IR** (neat): 3405, 1652, 1486, 1367 and 1185  $\text{cm}^{-1}$ .

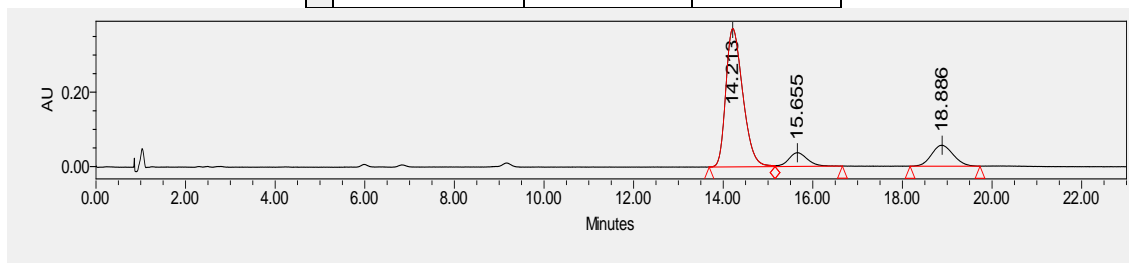
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.08$  (s, 1H), 7.55 – 7.38 (m, 4H), 7.38 – 7.29 (m, 4H), 7.26 – 7.23 (m, 2H), 7.23 – 7.18 (m, 4H), 7.18 – 7.12 (m, 2H), 6.91 – 6.80 (m, 3H), 6.15 (s, 1H), 4.36 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 153.3, 135.6, 135.4, 135.0, 134.7, 133.0, 131.8, 130.0, 128.9, 128.7, 128.7, 128.5, 127.7, 127.2, 126.8, 126.6, 123.0, 121.9, 116.4, 67.7, 64.9, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{35}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 524.1194, Found 524.1195,  $\text{C}_{30}\text{H}_{23}^{37}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 526.1165, Found 526.1168.



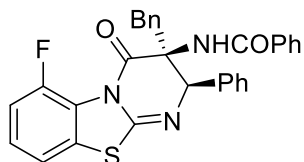
	Retention Time	Area	% Area
1	14.955	6779066	45.52
2	16.277	6791529	45.60
3	19.277	799823	5.37
4	20.527	522150	3.51



	Retention Time	Area	% Area
1	14.213	9763116	76.57
2	15.655	1087292	8.53
3	18.886	1899827	14.90



***N*-((2*R*,3*S*)-3-benzyl-6-fluoro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ia)**



White solid; m.p. 97–100 °C; 47.5 mg, 94% yield, 80% ee, 89:11 d.r.;  $[\alpha]_D^{21} = -55.93$  ( $c = 0.83$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral ID-3 column),  $\text{CO}_2/\text{MeOH} = 95/5$ , flow rate = 1.5 mL/min,  $\lambda = 210$  nm,  $t_{\text{major isomer}} = 44.17$  min (major), 41.06 min (minor);  $t_{\text{minor isomer}} = 37.13$  min (major),  $t_{\text{minor isomer}} = 31.10$  min (minor).

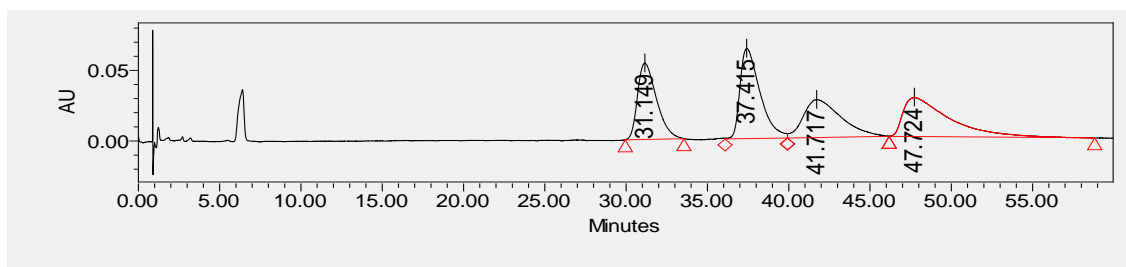
**IR** (neat): 3377, 1816, 1652, 1538 and 978  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.84 - 7.79$  (m, 2H), 7.66 – 7.57 (m, 2H), 7.57 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.10 (m, 4H), 7.05 – 6.96 (m, 2H), 6.50 – 6.39 (m, 1H), 5.19 (d,  $J = 10.0$  Hz, 1H), 3.27 (d,  $J = 13.6$  Hz, 1H), 3.02 (d,  $J = 13.6$  Hz, 1H).

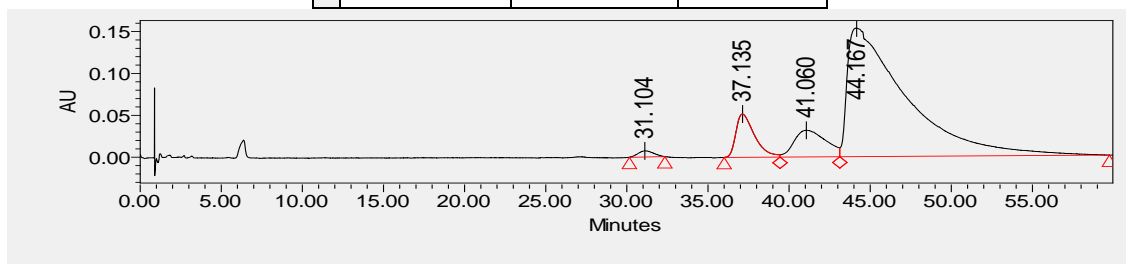
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 178.7, 166.5, 162.2, 153.6$  (d,  $J = 251.1$  Hz), 136.1, 133.4, 133.2, 130.3, 129.0, 128.8, 128.8, 128.5, 128.3, 128.1, 127.5, 125.0, 122.6 (d,  $J = 6.8$  Hz), 116.7 (d,  $J = 3.9$  Hz), 112.2 (d,  $J = 18.2$  Hz), 78.0, 64.2, 41.5.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -125.9$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1490.

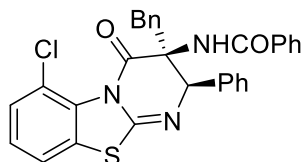


	Retention Time	Area	% Area
1	31.149	4380946	22.30
2	37.415	5473074	27.86
3	41.717	4337053	22.08
4	47.724	5454420	27.76



	Retention Time	Area	% Area
1	31.104	493818	1.03
2	37.135	4134431	8.65
3	41.060	4358556	9.12
4	44.167	38783998	81.19

***N*-((2*R*,3*S*)-3-benzyl-6-chloro-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ja)**



White solid; m.p. 103–107 °C; 52.4 mg, 99% yield, 76% ee, 90:10 d.r.;  $[\alpha]_D^{21} = -42.84$  ( $c = 0.88$  in  $\text{CH}_2\text{Cl}_2$ ).

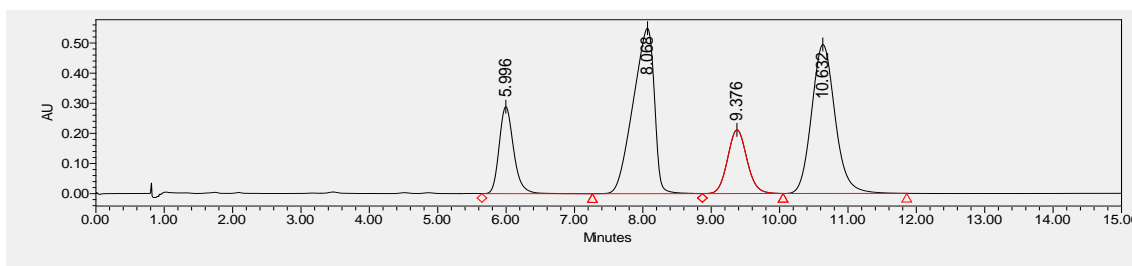
**UPCC** (chiral AD-3 column),  $\text{CO}_2/\text{iPrOH} = 80/20$ , flow rate = 1.5 mL/min,  $\lambda = 229$  nm,  $t_{\text{major isomer}} = 10.90$  min (major),  $t_{\text{minor isomer}} = 8.01$  min (minor);  $t_{\text{minor isomer}} = 6.02$  min (major),  $t_{\text{minor isomer}} = 9.35$  min (minor).

**IR** (neat): 3375, 1815, 1652, 1532 and 978  $\text{cm}^{-1}$ .

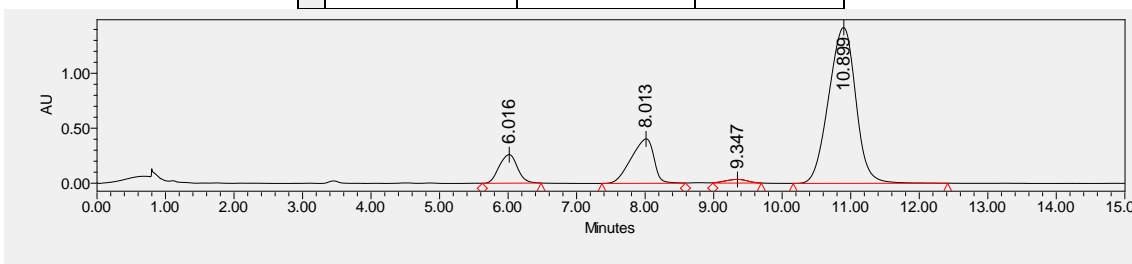
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.86 - 7.80$  (m, 2H), 7.63 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.45 – 7.34 (m, 5H), 7.34 – 7.26 (m, 2H), 7.21 – 7.14 (m, 1H), 7.12 – 7.08 (m, 4H), 7.01 – 6.95 (m, 1H), 6.58 – 6.42 (m, 1H), 5.08 (d,  $J = 7.6$  Hz, 1H), 3.25 (d,  $J = 13.6$  Hz, 1H), 2.99 (d,  $J = 13.6$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 178.6, 167.1, 162.3, 148.8, 136.0, 133.3, 133.2, 132.0, 130.3, 129.1, 128.8, 128.8, 128.6, 128.3, 128.2, 127.5, 126.4, 125.0, 123.9, 122.6, 119.5, 78.0, 64.7, 41.6$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{35}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 524.1194, Found 524.1196,  $\text{C}_{30}\text{H}_{23}^{37}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 526.1165, Found 526.1170.

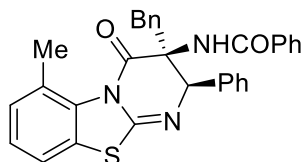


	Retention Time	Area	% Area
1	5.996	4239335	13.27
2	8.068	11793785	36.93
3	9.376	4155093	13.01
4	10.632	11749429	36.79



	Retention Time	Area	% Area
1	6.016	4820428	8.95
2	8.013	9319117	17.31
3	9.347	761815	1.41
4	10.899	38940965	72.32

***N*-((2*R*,3*S*)-3-benzyl-6-methyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ka)**



White solid; m.p. 80–83 °C; 48.4 mg, 96% yield, 91% ee, >19:1 d.r.;  $[\alpha]^{22}_D = -75.38$  ( $c = 0.79$  in  $\text{CH}_2\text{Cl}_2$ ).

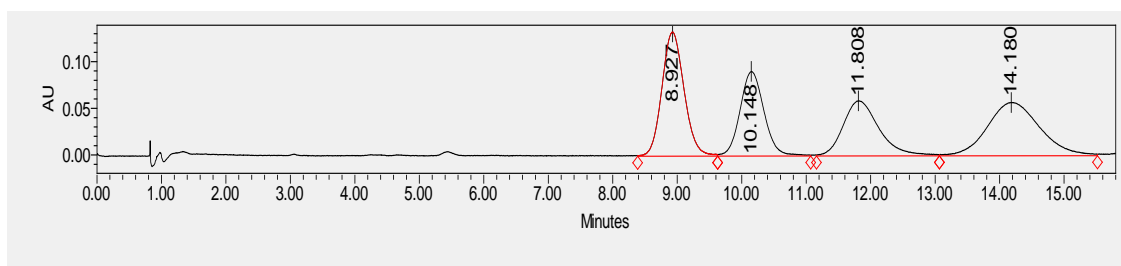
**UPCC** (chiral AD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 227$  nm,  $t_R$  (major) = 11.76 min,  $t_R$  (minor) = 10.18 min.

**IR** (neat): 3375, 1815, 1651, 1536 and 978  $\text{cm}^{-1}$ .

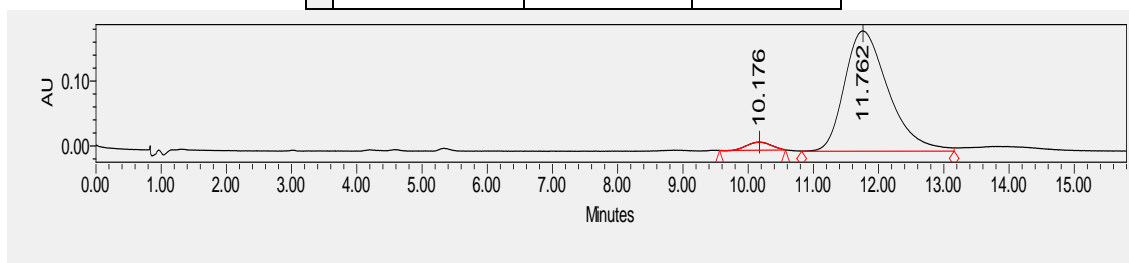
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.82 - 7.78$  (m, 2H), 7.61 – 7.57 (m, 2H), 7.54 – 7.48 (m, 1H), 7.42 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 7.12 – 7.08 (m, 5H), 7.07 – 7.04 (m, 1H), 6.98 – 6.93 (m, 1H), 6.21 (s, 1H), 5.27 (s, 1H), 3.27 (d,  $J = 13.6$  Hz, 1H), 3.02 (d,  $J = 13.6$  Hz, 1H), 2.50 (s, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 178.8, 165.4, 162.0, 136.7, 133.6, 133.1, 130.3, 129.4, 128.8, 128.7, 128.6, 128.3, 128.2, 127.5, 126.9, 125.2, 122.1, 118.4, 78.1, 64.2, 41.7, 18.5$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 504.1740, Found 504.1740.

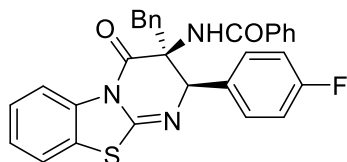


	Retention Time	Area	% Area
1	8.927	3175449	28.73
2	10.148	2342855	21.19
3	11.808	2293356	20.75
4	14.180	3242664	29.33



	Retention Time	Area	% Area
1	10.176	324606	3.61
2	11.762	8660540	96.39

***N*-((2*R*,3*S*)-3-benzyl-2-(4-fluorophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (31a)**



White solid; m.p. 92–95 °C; 52.6 mg, 99% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{25} = +467.09$  ( $c = 0.79$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 95/5$ , flow rate = 1.5 mL/min,  $\lambda = 214$  nm,  $t_R$  (major) = 17.02 min,  $t_R$  (minor) = 16.20 min.

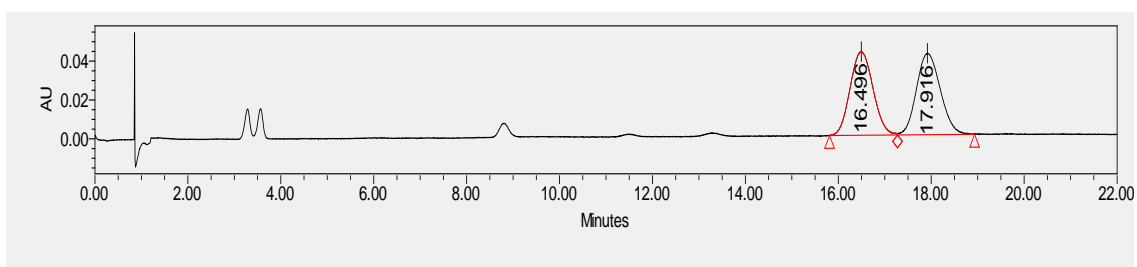
**IR** (neat): 3403, 1646, 1512, 1370 and 1187  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.06 - 8.00$  (m, 1H), 7.51 – 7.44 (m, 4H), 7.40 – 7.32 (m, 4H), 7.28 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 6.96 (s, 1H), 6.92 – 6.86 (m, 4H), 6.15 (s, 1H), 4.33 (d,  $J = 14.0$  Hz, 1H), 3.48 (d,  $J = 14.0$  Hz, 1H).

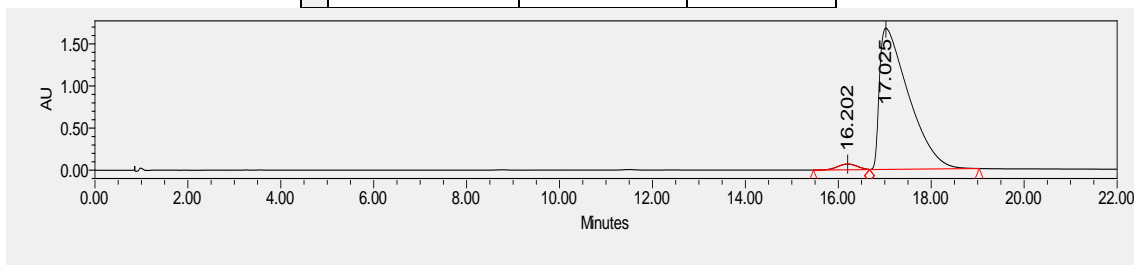
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.6, 162.7$  (d,  $J = 247.3$  Hz), 153.9, 134.9, 134.8 (d,  $J = 2.3$  Hz), 131.9, 131.8 (d,  $J = 3.3$  Hz), 130.1, 129.1 (d,  $J = 8.2$  Hz), 128.8, 128.5, 127.6, 127.1, 126.8, 126.5, 123.5, 122.4, 116.0, 115.8, 115.6, 66.9, 64.9, 39.7.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -113.3$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1489.

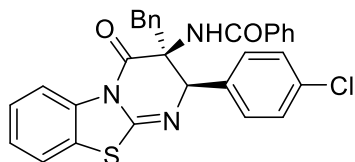


	Retention Time	Area	% Area
1	16.496	1472537	49.62
2	17.916	1494974	50.38



	Retention Time	Area	% Area
1	16.202	1961378	2.61
2	17.025	73054163	97.39

***N*-((2*R*,3*S*)-3-benzyl-2-(4-chlorophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ma)**



White solid; m.p. 93–97 °C; 53.1 mg, 99% yield, 93% ee, >19:1 d.r.;  $[\alpha]_D^{21} = +469.04$  ( $c = 0.69$  in  $\text{CH}_2\text{Cl}_2$ ).

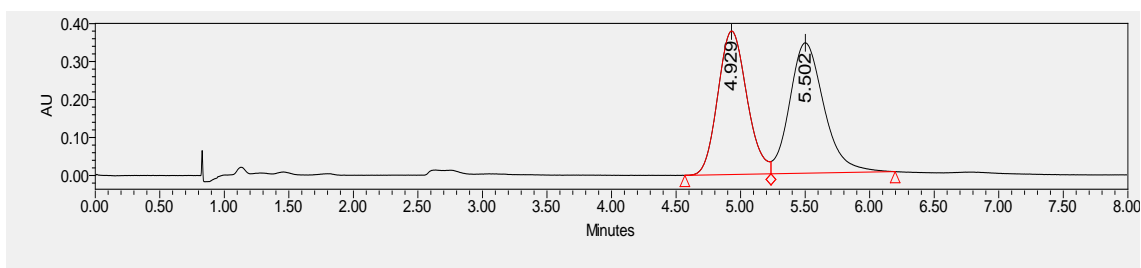
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 93/7$ , flow rate = 1.5 mL/min,  $\lambda = 230$  nm,  $t_R$  (major) = 5.33 min,  $t_R$  (minor) = 4.85 min.

**IR** (neat): 3403, 1645, 1463, 1369 and 1187  $\text{cm}^{-1}$ .

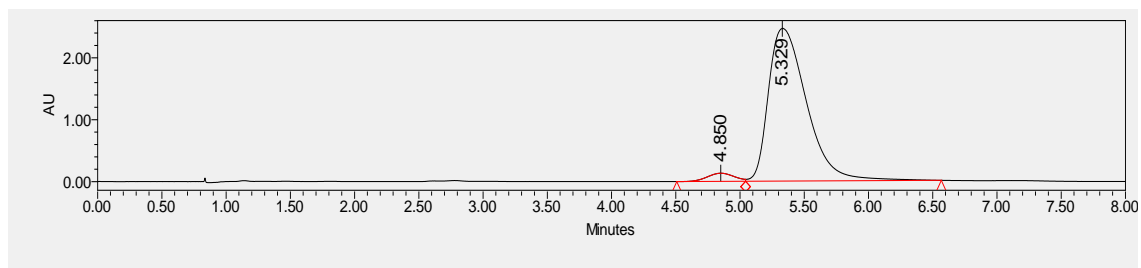
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.06 - 7.99$  (m, 1H), 7.51 – 7.45 (m, 4H), 7.41 – 7.35 (m, 2H), 7.35 – 7.32 (m, 2H), 7.23 – 7.15 (m, 5H), 7.15 – 7.09 (m, 2H), 6.96 (s, 1H), 6.90 – 6.84 (m, 2H), 6.14 (s, 1H), 4.32 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.6, 154.2, 134.9, 134.7, 134.7, 134.5, 134.4, 131.9, 130.1, 129.0, 128.8, 128.7, 128.5, 127.6, 127.1, 126.8, 126.6, 123.5, 122.4, 116.0, 67.0, 64.8, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{35}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 524.1194, Found 524.1194,  $\text{C}_{30}\text{H}_{23}^{37}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 526.1165, Found 526.1168.

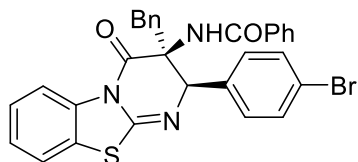


	Retention Time	Area	% Area
1	4.929	5923010	48.31
2	5.502	6338100	51.69



	Retention Time	Area	% Area
1	4.850	1909426	3.62
2	5.329	50839544	96.38

***N*-{(2*R*,3*S*)-3-benzyl-2-(4-bromophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl}benzamide (3na)**



White solid; m.p. 107–110 °C; 57.9 mg, 99% yield, 91% ee, >19:1 d.r.;  $[\alpha]_D^{22} = +422.30$  ( $c = 0.76$  in  $\text{CH}_2\text{Cl}_2$ ).

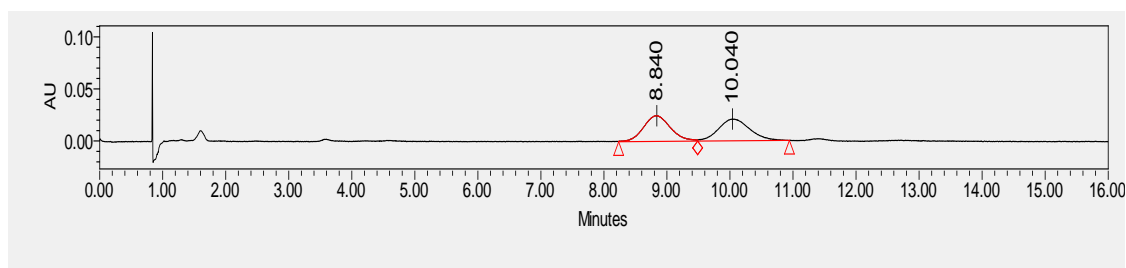
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 93/7$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 9.48 min,  $t_R$  (minor) = 8.60 min.

**IR** (neat): 3403, 1645, 1463, 1369 and 1186  $\text{cm}^{-1}$ .

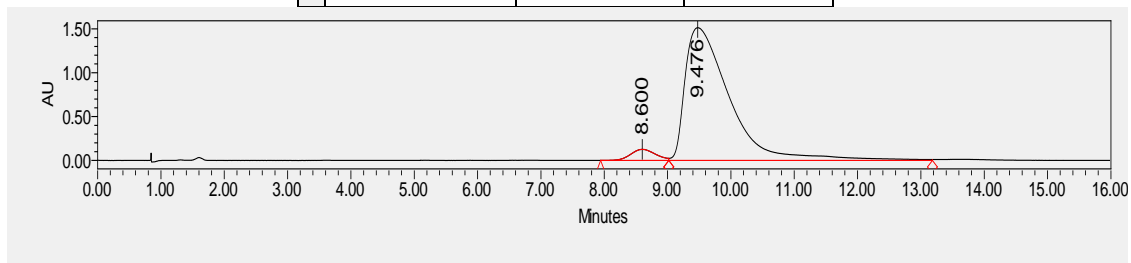
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.05 - 8.00$  (m, 1H), 7.52 – 7.45 (m, 4H), 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 4H), 7.22 – 7.17 (m, 1H), 7.17 – 7.09 (m, 4H), 6.96 (s, 1H), 6.89 – 6.85 (m, 2H), 6.13 (s, 1H), 4.32 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.5, 154.2, 135.0, 134.8, 134.7, 134.7, 131.9, 131.9, 130.1, 129.0, 128.8, 128.5, 127.6, 127.1, 126.8, 126.6, 123.4, 122.6, 122.4, 116.0, 67.0, 64.7, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{79}\text{BrN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 568.0689, Found 568.0689,  $\text{C}_{30}\text{H}_{23}^{81}\text{BrN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 570.0668, Found 570.0668.

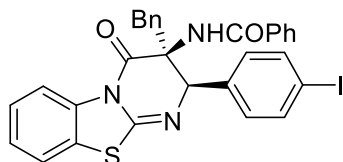


	Retention Time	Area	% Area
1	8.840	736019	50.48
2	10.040	722079	49.52



	Retention Time	Area	% Area
1	8.600	3430058	4.43
2	9.476	73952045	95.57

***N*-((2*R*,3*S*)-3-benzyl-2-(4-iodophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3oa)**



White solid; m.p. 115–117 °C; 60.4 mg, 98% yield, 90% ee, >19:1 d.r.;  $[\alpha]_D^{22} = +421.46$  ( $c = 0.086$  in  $\text{CH}_2\text{Cl}_2$ ).

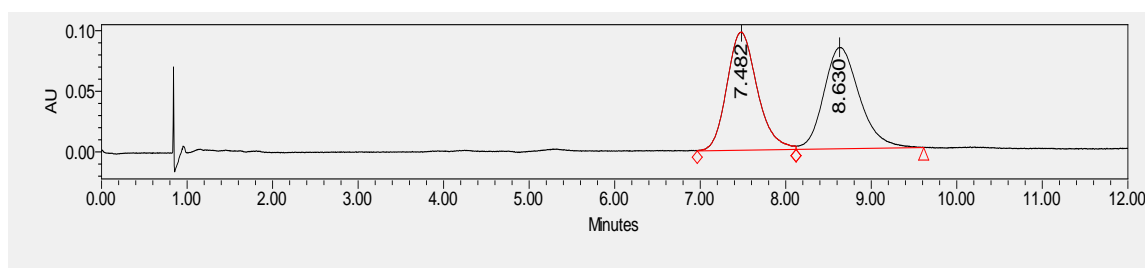
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 8.51 min,  $t_R$  (minor) = 7.41 min.

**IR** (neat): 3401, 1645, 1462, 1369 and 1186  $\text{cm}^{-1}$ .

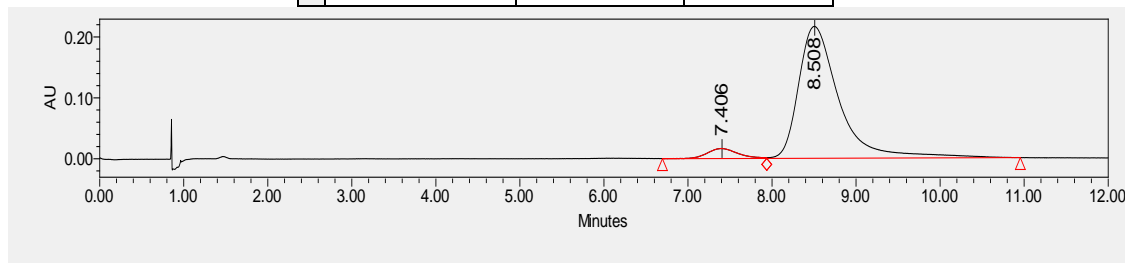
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.05 - 8.00$  (m, 1H), 7.55 – 7.47 (m, 5H), 7.46 – 7.44 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 7.05 – 7.00 (m, 2H), 6.97 (s, 1H), 6.89 – 6.85 (m, 2H), 6.11 (s, 1H), 4.32 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.5, 154.2, 137.8, 135.6, 134.8, 134.7, 134.7, 131.9, 130.1, 129.2, 128.8, 128.4, 127.6, 127.1, 126.8, 126.5, 123.4, 122.4, 116.0, 94.3, 67.1, 64.7, 39.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{IN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 616.0550, Found 616.0549.

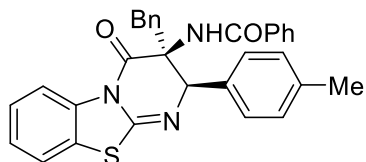


	Retention Time	Area	% Area
1	7.482	2400697	49.71
2	8.630	2428484	50.29



	Retention Time	Area	% Area
1	7.406	411828	5.38
2	8.508	7242248	94.62

***N*-((2*R*,3*S*)-3-benzyl-4-oxo-2-(*p*-tolyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3pa)**



White solid; m.p. 90–93°C; 50.3 mg, 99% yield, 96% ee, >19:1 d.r.;  $[\alpha]_D^{22} = +485.92$  ( $c = 0.71$  in  $\text{CH}_2\text{Cl}_2$ ).

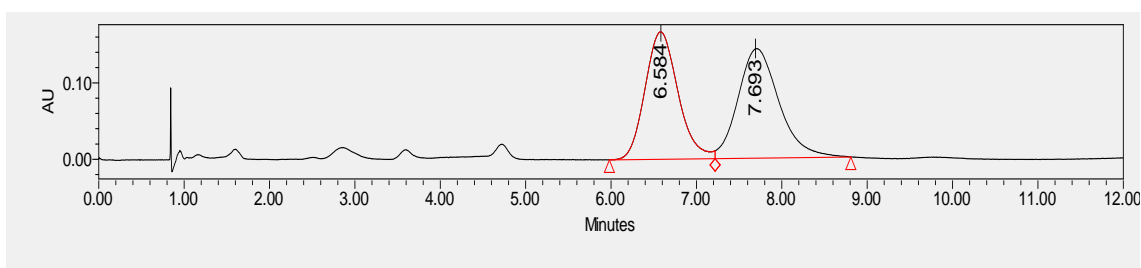
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{EtOH} = 93/7$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 7.36 min,  $t_R$  (minor) = 6.50 min.

**IR** (neat): 3406, 1646, 1463, 1370 and 1186  $\text{cm}^{-1}$ .

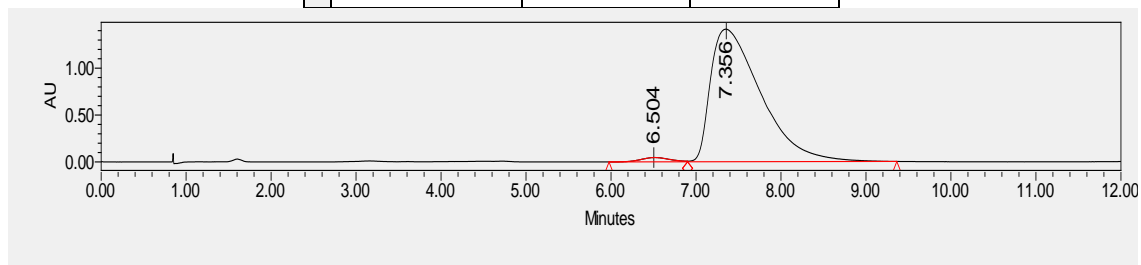
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.06 - 8.00$  (m, 1H), 7.50 – 7.43 (m, 4H), 7.38 – 7.31 (m, 4H), 7.21 – 7.17 (m, 1H), 7.16 – 7.10 (m, 4H), 7.02 – 6.98 (m, 2H), 6.92 (s, 1H), 6.91 – 6.87 (m, 2H), 6.11 (s, 1H), 4.36 (d,  $J = 14.0$  Hz, 1H), 3.49 (d,  $J = 14.0$  Hz, 1H), 2.23 (s, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.8, 153.6, 138.3, 135.3, 135.0, 134.9, 132.7, 131.7, 130.1, 129.5, 128.7, 128.4, 127.5, 127.2, 127.0, 126.9, 126.4, 123.6, 122.4, 115.9, 67.4, 65.0, 39.6, 21.2$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 504.1740, Found 504.1737.



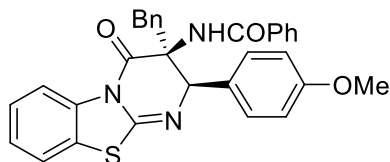
	Retention Time	Area	% Area
1	6.584	4476795	48.39
2	7.693	4773960	51.61



	Retention Time	Area	% Area
1	6.504	1099307	1.86
2	7.356	58027529	98.14



***N*-{((2*R*,3*S*)-3-benzyl-2-(4-methoxyphenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3qa)**



White solid; m.p. 83–88 °C; 44.6 mg, 86% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{22} = +436.46$  ( $c = 0.48$  in  $\text{CH}_2\text{Cl}_2$ ).

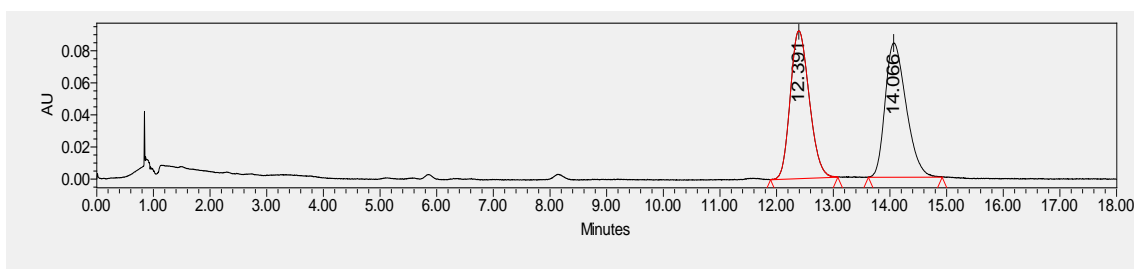
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 5.88 min,  $t_R$  (minor) = 6.45 min.

**IR** (neat): 3405, 1646, 1513, 1463, 1371 and 1183  $\text{cm}^{-1}$ .

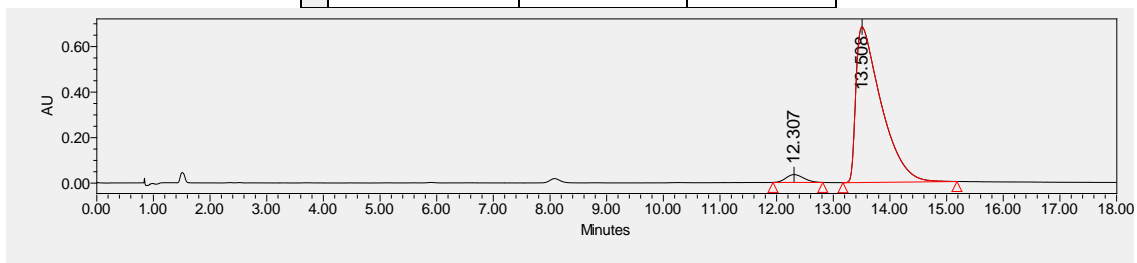
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.06 - 8.00$  (m, 1H), 7.51 – 7.43 (m, 4H), 7.39 – 7.30 (m, 4H), 7.22 – 7.16 (m, 3H), 7.15 – 7.10 (m, 2H), 6.94 (s, 1H), 6.91 – 6.86 (m, 2H), 6.75 – 6.70 (m, 2H), 6.10 (s, 1H), 4.34 (d,  $J = 14.0$  Hz, 1H), 3.69 (s, 3H), 3.47 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.8, 159.6, 153.4, 135.2, 135.0, 134.8, 131.7, 130.1, 128.7, 128.5, 128.4, 127.8, 127.5, 127.0, 126.8, 126.4, 123.6, 122.4, 115.9, 114.2, 67.1, 65.1, 55.3, 39.6$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_3\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 520.1689, Found .520.1689.

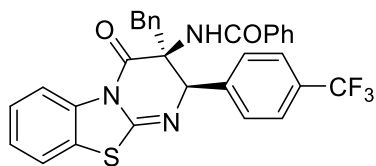


	Retention Time	Area	% Area
1	12.391	2138452	49.82
2	14.066	2153483	50.18



	Retention Time	Area	% Area
1	12.307	746958	3.42
2	13.508	21073901	96.58

***N*-((2*R*,3*S*)-3-benzyl-4-oxo-2-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3*a*)**



White solid; m.p. 97–101°C; 51.2 mg, 92% yield, 82% ee, 94:6 d.r.;  $[\alpha]_D^{23} = +285.62$  ( $c = 0.80$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{EtOH} = 93/7$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm,  $t_{\text{major isomer}} = 7.95$  min (major), 7.09 min (minor);  $t_{\text{minor isomer}} = 12.93$  min (major),  $t_{\text{minor isomer}} = 15.02$  min (minor).

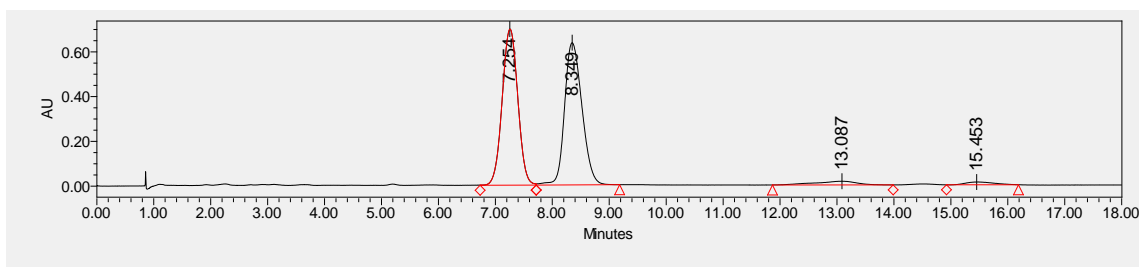
**IR** (neat): 3403, 1645, 1463, 1370, 1325 and 1121  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.07 - 8.02$  (m, 1H), 7.56 – 7.44 (m, 6H), 7.44 – 7.40 (m, 2H), 7.40 – 7.32 (m, 4H), 7.23 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 6.98 (s, 1H), 6.91 – 6.86 (m, 2H), 6.23 (s, 1H), 4.34 (d,  $J = 14.0$  Hz, 1H), 3.50 (d,  $J = 14.0$  Hz, 1H).

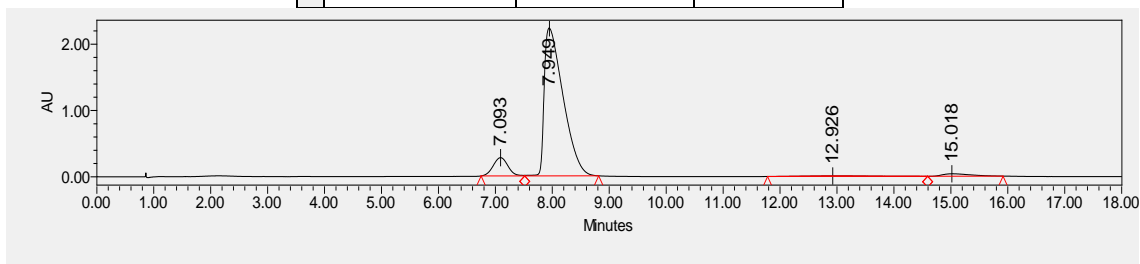
**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9$ , 167.4, 154.6, 140.1, 134.7 (d,  $J = 4.4$  Hz), 134.5, 132.0, 130.1, 128.8, 128.5, 127.8, 127.7, 127.2, 126.8, 126.6, 125.7 (q,  $J = 3.6$  Hz), 123.4, 122.5, 116.0, 67.1, 64.6, 39.8.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -62.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 558.1458, Found 558.1458.

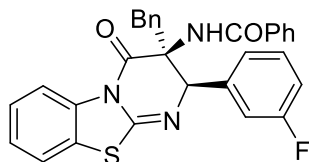


	Retention Time	Area	% Area
1	7.254	13265399	47.35
2	8.349	13486592	48.14
3	13.087	828628	2.96
4	15.453	433151	1.55



	Retention Time	Area	% Area
1	7.093	4961149	8.59
2	7.949	51028902	88.34
3	12.926	542828	0.94
4	15.018	1228296	2.13

***N*-((2*R*,3*S*)-3-benzyl-2-(3-fluorophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3sa)**



White solid; m.p. 86–91 °C; 49.7 mg, 98% yield, 82% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +393.68$  ( $c = 0.74$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral AS-3 column),  $\text{CO}_2/i\text{PrOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 214$  nm,  $t_R$  (major) = 6.18 min,  $t_R$  (minor) = 5.08 min.

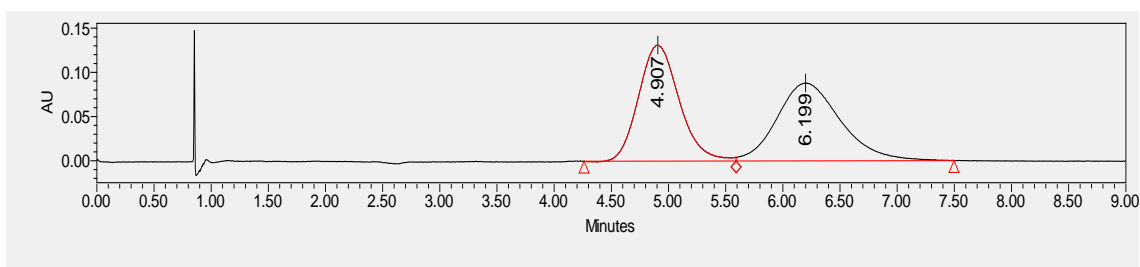
**IR** (neat): 3403, 1647, 1463, 1370 and 1188  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.09 - 7.97$  (m, 1H), 7.53 – 7.41 (m, 4H), 7.40 – 7.31 (m, 4H), 7.23 – 7.05 (m, 5H), 7.03 – 6.97 (m, 1H), 6.96 (s, 1H), 6.93 – 6.82 (m, 3H), 6.15 (s, 1H), 4.34 (d,  $J = 14.0$  Hz, 1H), 3.48 (d,  $J = 14.0$  Hz, 1H)..

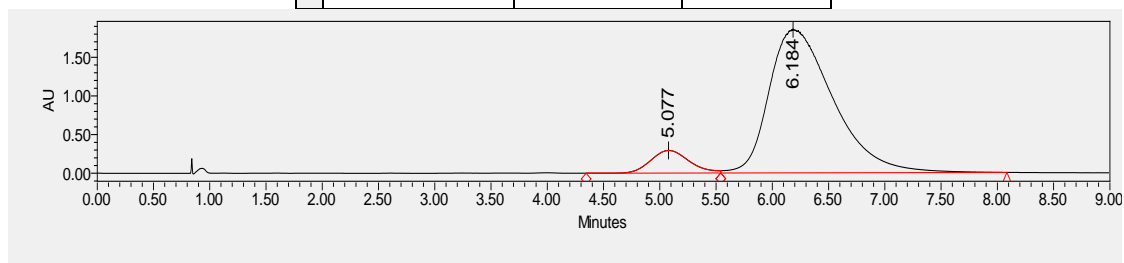
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.5, 162.8$  (d,  $J = 246.8$  Hz), 154.3, 138.4 (d,  $J = 6.9$  Hz), 135.0, 134.7, 134.7, 131.8, 130.3 (d,  $J = 8.3$  Hz), 130.1, 128.8.0, 128.5, 127.6, 127.1, 126.8, 126.6, 123.4, 123.1 (d,  $J = 2.9$  Hz), 122.4, 116.0, 115.6 (d,  $J = 21.1$  Hz), 114.4 (d,  $J = 22.1$  Hz), 67.1, 64.7, 39.7.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -112.2$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1490.

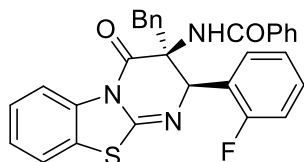


	Retention Time	Area	% Area
1	4.907	3247018	48.84
2	6.199	3400869	51.16



	Retention Time	Area	% Area
1	5.077	6952035	8.65
2	6.184	73416663	91.35

***N*-((2*R*,3*S*)-3-benzyl-2-(2-fluorophenyl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3*ta*)**



White solid; m.p. 97–101 °C; 51.4 mg, 99% yield, 87% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +416.67$  ( $c = 0.77$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{iPrOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 240$  nm,  $t_R$  (major) = 8.48 min,  $t_R$  (minor) = 6.58 min.

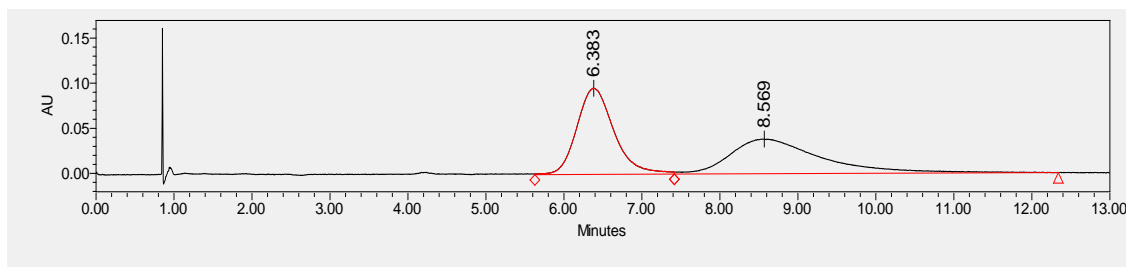
**IR** (neat): 3402, 1651, 1463, 1375 and 1190  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.09 - 8.04$  (m, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.39 (m, 4H), 7.35 – 7.27 (m, 4H), 7.24 – 7.12 (m, 5H), 7.06 – 7.00 (m, 1H), 6.95 – 6.88 (m, 3H), 6.14 (s, 1H), 4.31 (d,  $J = 14.0$  Hz, 1H), 3.44 (d,  $J = 14.0$  Hz, 1H).

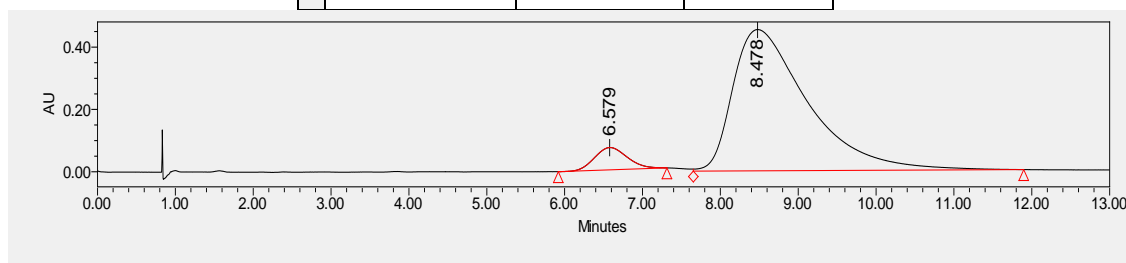
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.4$ , 167.4, 161.4 (d,  $J = 245.9$  Hz), 153.6, 135.1, 134.9, 134.6, 132.3 (d,  $J = 5.0$  Hz), 131.7, 130.3 (d,  $J = 8.5$  Hz), 130.2, 128.7, 128.4, 127.6, 126.9, 126.7, 126.2, 124.4 (d,  $J = 3.2$  Hz), 123.9 (d,  $J = 15.0$  Hz), 123.2, 122.2, 116.0, 115.7 (d,  $J = 22.5$  Hz), 67.4, 63.0, 40.9.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -112.4$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1490.

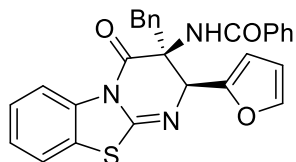


	Retention Time	Area	% Area
1	6.383	3153963	50.13
2	8.569	3137903	49.87



	Retention Time	Area	% Area
1	6.579	2083694	6.43
2	8.478	30312368	93.57

***N*-((2*R*,3*S*)-3-benzyl-2-(furan-2-yl)-4-oxo-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ua)**



White solid; m.p. 88–90 °C; 49.3 mg, 99% yield, 97% ee, >19:1 d.r.;  $[\alpha]_{23}^D = +578.57$  ( $c = 0.78$  in  $\text{CH}_2\text{Cl}_2$ ).

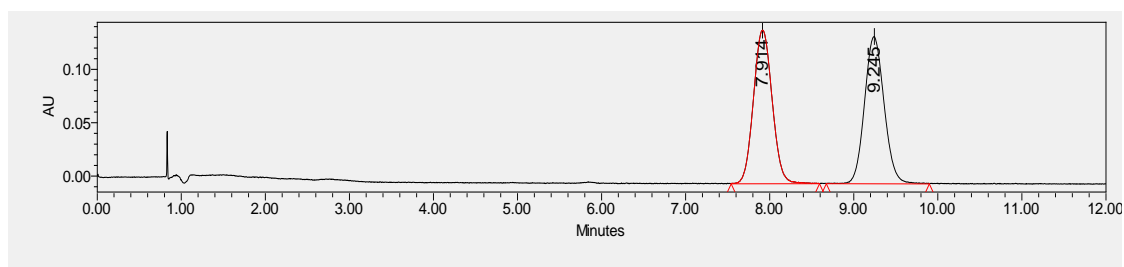
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 8.91 min,  $t_R$  (minor) = 7.58 min.

**IR** (neat): 3406, 1643, 1463, 1366 and 1189  $\text{cm}^{-1}$ .

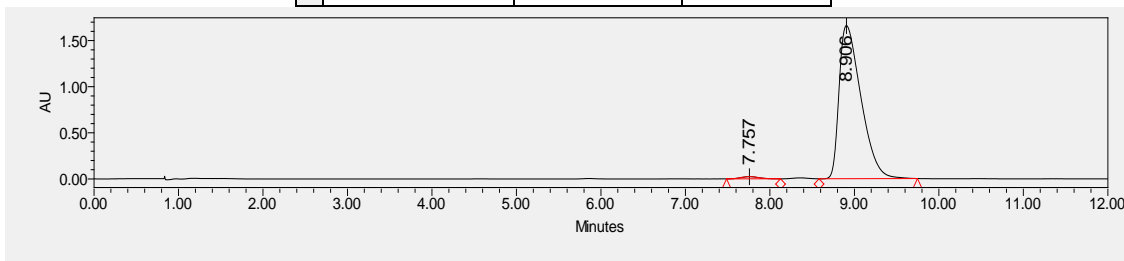
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.12 - 8.06$  (m, 1H), 7.55 – 7.51 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.41 (m, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.27 (m, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.10 (m, 2H), 7.02 (s, 1H), 6.91 – 6.87 (m, 2H), 6.38 – 6.36 (m, 1H), 6.26 (s, 1H), 6.19 – 6.17 (m, 1H), 4.18 (d,  $J = 14.0$  Hz, 1H), 3.44 (d,  $J = 14.0$  Hz, 1H)

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.7, 167.6, 155.4, 149.4, 142.8, 135.2, 134.9, 134.7, 131.8, 130.1, 128.7, 128.4, 127.5, 126.9, 126.9, 126.2, 123.4, 122.2, 116.0, 110.4, 109.7, 63.3, 60.7, 39.1$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{28}\text{H}_{22}\text{N}_3\text{O}_3\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 480.1376, Found 480.1376.

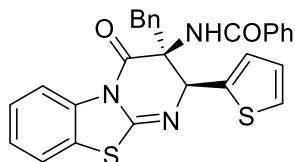


	Retention Time	Area	% Area
1	7.914	2223789	49.82
2	9.245	2240112	50.18



	Retention Time	Area	% Area
1	7.757	348039	1.15
2	8.906	29797618	98.85

***N*-((2*R*,3*S*)-3-benzyl-4-oxo-2-(thiophen-2-yl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3va)**



White solid; m.p. 91–93 °C; 48.2 mg, 97% yield, 88% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +423.36$  ( $c = 0.82$  in  $\text{CH}_2\text{Cl}_2$ ).

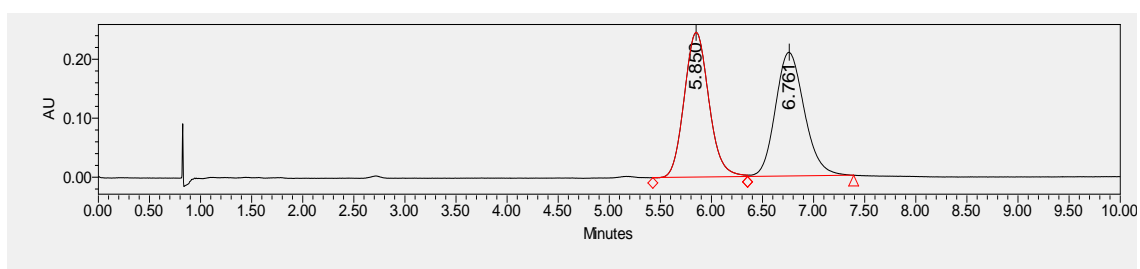
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 5.88 min,  $t_R$  (minor) = 6.45 min.

**IR** (neat): 3405, 1643, 1462, 1364 and 1188  $\text{cm}^{-1}$ .

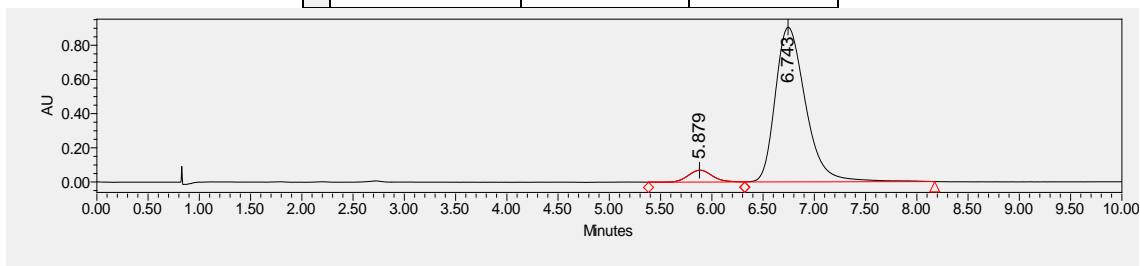
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.10 - 8.04$  (m, 1H), 7.61 – 7.56 (m, 2H), 7.52 – 7.47 (m, 1H), 7.47 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 – 7.09 (m, 3H), 7.07 – 7.01 (m, 2H), 6.91 – 6.86 (m, 2H), 6.85 – 6.82 (m, 1H), 6.53 (s, 1H), 4.26 (d,  $J = 14.0$  Hz, 1H), 3.48 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.8, 167.4, 154.9, 138.0, 135.0, 134.8, 134.8, 131.8, 130.1, 128.8, 128.4, 127.5, 127.0, 127.0, 127.0, 126.9, 126.5, 125.4, 123.5, 122.4, 116.1, 65.2, 62.4, 39.0$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{28}\text{H}_{22}\text{N}_3\text{O}_2\text{S}_2^+$  ( $[\text{M}+\text{H}]^+$ ) = 496.1148, Found 496.1148.

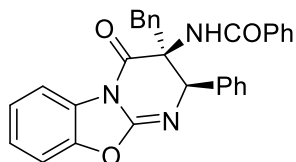


	Retention Time	Area	% Area
1	5.850	4090106	49.91
2	6.761	4105069	50.09



	Retention Time	Area	% Area
1	5.879	1149528	5.82
2	6.743	18591334	94.18

***N*-((2*R*,3*S*)-3-benzyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]oxazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3wa)**



White solid; m.p. 99–102 °C; 43.8 mg, 92% yield, 90% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +402.56$  ( $c = 0.78$  in  $\text{CH}_2\text{Cl}_2$ ).

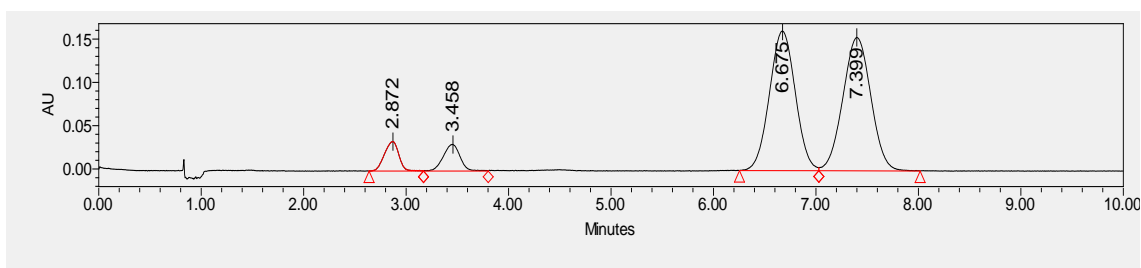
**UPCC** (chiral OJ-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 2.87 min,  $t_R$  (minor) = 3.45 min.

**IR** (neat): 3404, 1730, 1663, 1479 and 1395  $\text{cm}^{-1}$ .

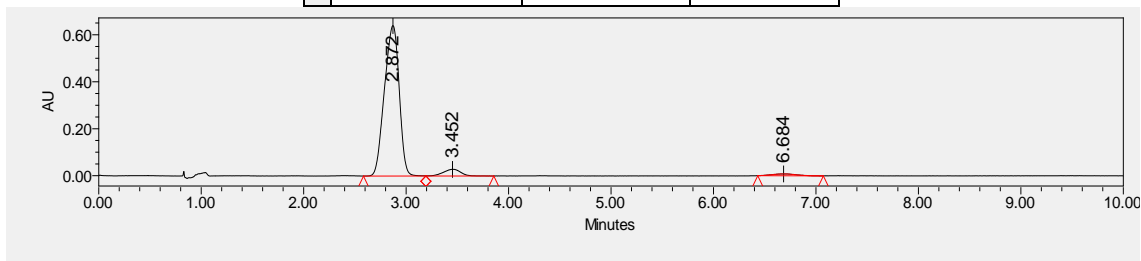
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.76 - 7.72$  (m, 1H), 7.47 – 7.41 (m, 3H), 7.36 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.18 (m, 4H), 7.17 – 7.12 (m, 2H), 6.94 – 6.89 (m, 2H), 6.77 (s, 1H), 6.10 (s, 1H), 4.38 (d,  $J = 14.0$  Hz, 1H), 3.46 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 166.7, 149.5, 145.4, 136.6, 135.1, 134.7, 131.7, 130.1, 128.8, 128.7, 128.5, 128.4, 127.6, 127.2, 126.8, 126.3, 126.2, 124.7, 113.5, 110.8, 65.1, 39.9$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_3\text{O}_3^+$  ( $[\text{M}+\text{H}^+]$ ) = 474.1812, Found 474.1812.

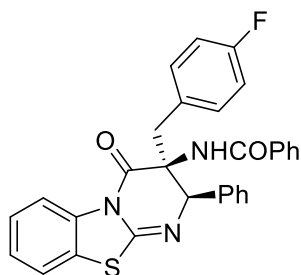


	Retention Time	Area	% Area
1	2.872	333482	5.18
2	3.458	351637	5.47
3	6.675	2825176	43.91
4	7.399	2923402	45.44



	Retention Time	Area	% Area
1	2.872	6404839	93.24
2	3.452	337571	4.91
3	6.684	127002	1.85

***N*-((2*R*,3*S*)-3-(4-fluorobenzyl)-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ab)**



White solid; m.p. 97–101 °C; 50.7 mg, 99% yield, 98% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +478.92$  ( $c = 0.91$  in  $\text{CH}_2\text{Cl}_2$ ).

**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 215$  nm,  $t_R$  (major) = 4.35 min,  $t_R$  (minor) = 3.75 min.

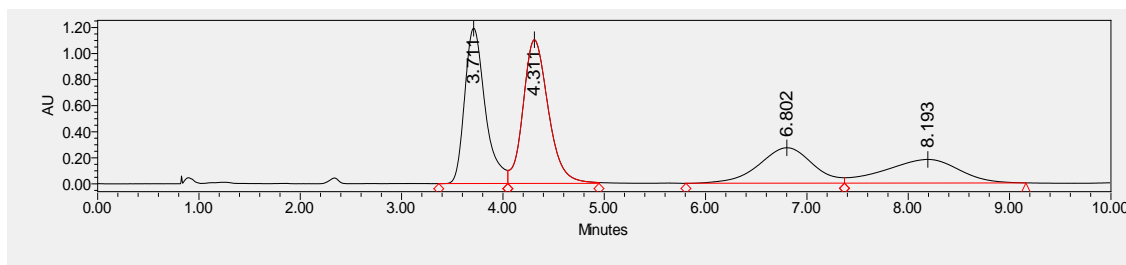
**IR** (neat): 3405, 1647, 1511, 1463, 1371 and 1186  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.07 - 8.01$  (m, 1H), 7.49 – 7.43 (m, 4H), 7.38 – 7.32 (m, 4H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 3H), 6.90 (s, 1H), 6.88 – 6.78 (m, 4H), 6.11 (s, 1H), 4.35 (d,  $J = 14.0$  Hz, 1H), 3.47 (d,  $J = 14.0$  Hz, 1H).

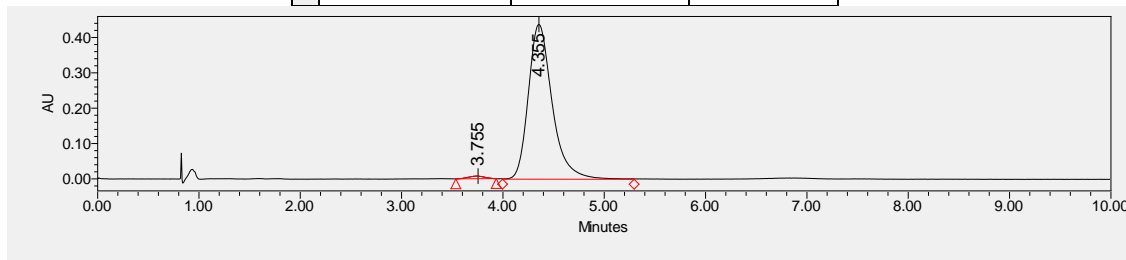
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.7, 162.3$  (d,  $J = 246.0$  Hz), 153.7, 135.8, 135.0, 134.7, 131.8, 131.6 (d,  $J = 8.1$  Hz), 130.7 (d,  $J = 3.3$  Hz), 128.8, 128.8, 128.6, 127.2, 127.1, 126.8, 126.5, 123.6, 122.5, 115.9, 115.4 (d,  $J = 21.3$  Hz), 67.6, 64.8, 38.9.

**$^{19}\text{F}\{^1\text{H}\}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -114.9$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}\text{FN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 508.1490, Found 508.1497.



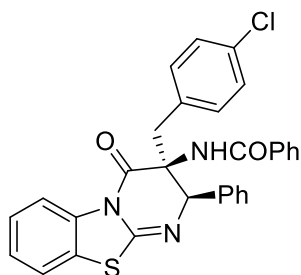
	Retention Time	Area	% Area
1	3.711	16761320	30.50
2	4.311	19018418	34.61
3	6.802	10005573	18.21
4	8.193	9165739	16.68



	Retention Time	Area	% Area
1	3.755	83326	1.15
2	4.355	7147207	98.85



***N*-((2*R*,3*S*)-3-(4-chlorobenzyl)-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ac)**



White solid; m.p. 98–103 °C; 50.7 mg, 97% yield, 96% ee, >19:1 d.r.;  $[\alpha]^{22}_D = +485.42$  ( $c = 0.94$  in  $\text{CH}_2\text{Cl}_2$ ).

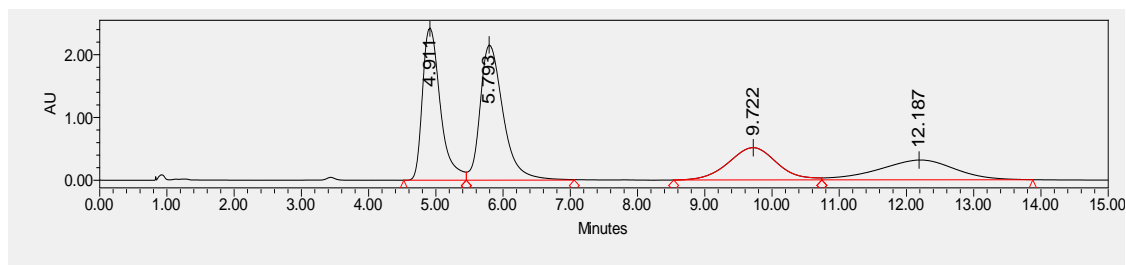
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 5.87 min,  $t_R$  (minor) = 4.98 min.

**IR** (neat): 3403, 1647, 1462, 1370 and 1185  $\text{cm}^{-1}$ .

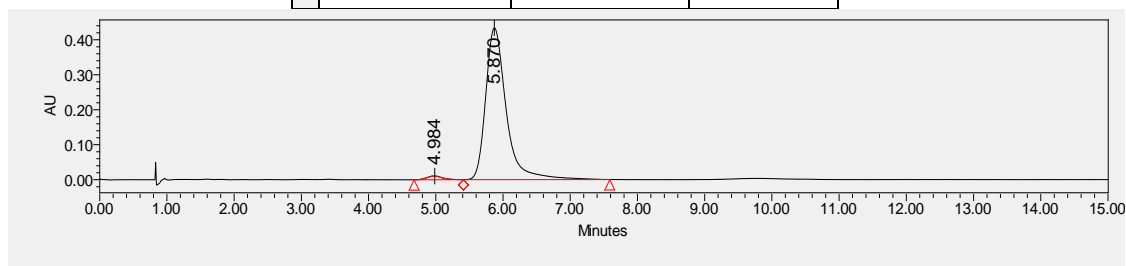
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.09 - 8.00$  (m, 1H), 7.49 – 7.42 (m, 4H), 7.38 – 7.32 (m, 4H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 3H), 7.12 – 7.07 (m, 2H), 6.89 (s, 1H), 6.84 – 6.80 (m, 2H), 6.11 (s, 1H), 4.36 (d,  $J = 14.0$  Hz, 1H), 3.46 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.6, 153.7, 135.7, 134.9, 134.7, 133.5, 133.4, 131.8, 131.4, 128.8, 128.8, 128.6, 128.6, 127.2, 127.1, 126.7, 126.6, 123.5, 122.5, 115.9, 67.6, 64.8, 39.0$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{35}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 524.1194, Found 524.1200,  $\text{C}_{30}\text{H}_{23}^{37}\text{ClN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 526.1165, Found 526.1174.

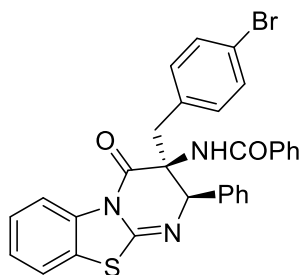


	Retention Time	Area	% Area
1	4.911	44810259	30.58
2	5.793	51200854	34.94
3	9.722	25750479	17.57
4	12.187	24768589	16.90



	Retention Time	Area	% Area
1	4.984	176014	1.87
2	5.870	9219196	98.13

***N*-((2*R*,3*S*)-3-(4-bromobenzyl)-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ad)**



White solid; m.p. 107–112 °C; 55.6 mg, 98% yield, 97% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +439.83$  ( $c = 1.07$  in  $\text{CH}_2\text{Cl}_2$ ).

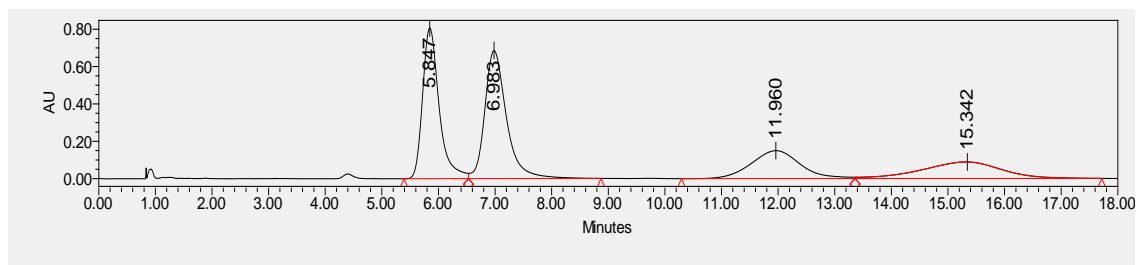
**UPCC** (chiral AS-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 7.02 min,  $t_R$  (minor) = 5.87 min.

**IR** (neat): 3403, 1647, 1462, 1370 and 1185  $\text{cm}^{-1}$ .

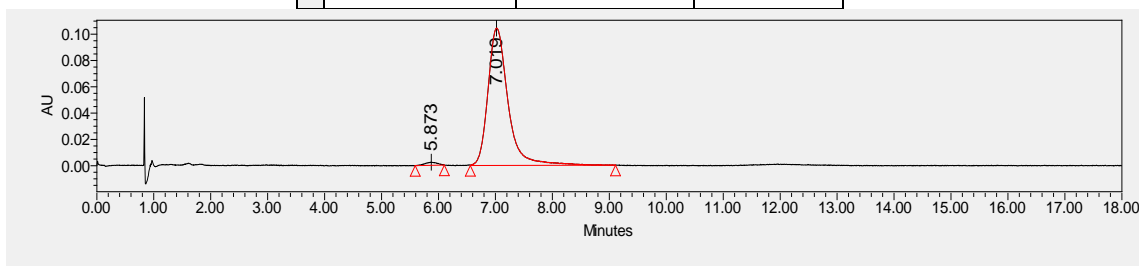
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.07 - 8.00$  (m, 1H), 7.48 – 7.42 (m, 4H), 7.37 – 7.31 (m, 4H), 7.26 – 7.22 (m, 4H), 7.21 – 7.17 (m, 3H), 6.88 (s, 1H), 6.77 – 6.73 (m, 2H), 6.10 (s, 1H), 4.34 (d,  $J = 14.0$  Hz, 1H), 3.43 (d,  $J = 14.0$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 167.9, 167.6, 153.7, 135.6, 134.9, 134.7, 133.9, 131.8, 131.7, 131.6, 128.8, 128.8, 128.6, 127.2, 127.1, 126.7, 126.6, 123.5, 122.5, 121.6, 115.9, 67.6, 64.7, 39.1$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{23}^{79}\text{BrN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 568.0689, Found 568.0697,  $\text{C}_{30}\text{H}_{23}^{81}\text{BrN}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 570.0668, Found 570.0677.

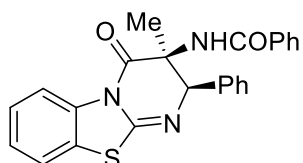


	Retention Time	Area	% Area
1	5.847	16430255	31.35
2	6.983	18200419	34.73
3	11.960	9068321	17.30
4	15.342	8712170	16.62



	Retention Time	Area	% Area
1	5.873	35137	1.36
2	7.019	2552004	98.64

***N*-{(2*R*,3*S*)-3-methyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl}benzamide (3ae)**



White solid; m.p. 87–92 °C; 38.9 mg, 94% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +566.06$  ( $c = 0.71$  in  $\text{CH}_2\text{Cl}_2$ ).

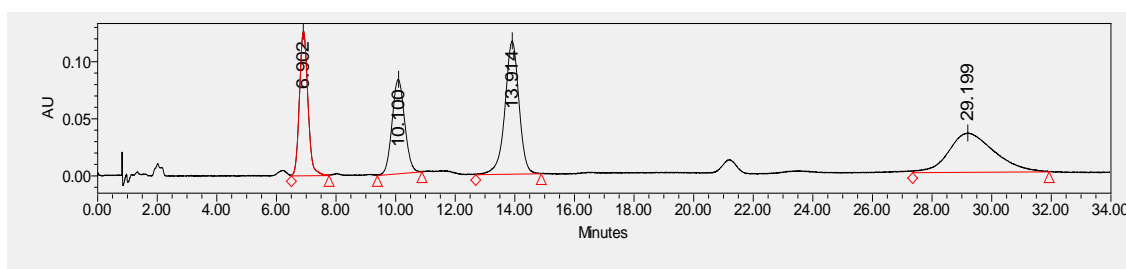
**UPCC** (chiral AD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 220$  nm,  $t_R$  (major) = 14.46 min,  $t_R$  (minor) = 27.70 min.

**IR** (neat): 3406, 1648, 1462, 1349 and 1181  $\text{cm}^{-1}$ .

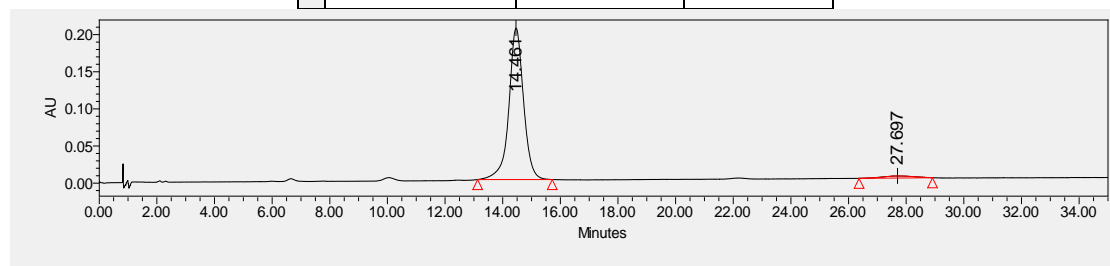
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.29 - 8.26$  (m, 1H), 7.54 – 7.52 (m, 1H), 7.52 – 7.50 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.39 (m, 1H), 7.38 – 7.33 (m, 3H), 7.33 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.20 (m, 3H), 7.08 (s, 1H), 5.86 (s, 1H), 2.05 (s, 3H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 169.6, 167.3, 154.2, 136.0, 135.2, 134.8, 131.7, 128.8, 128.6, 128.5, 127.3, 126.9, 126.8, 126.4, 123.7, 122.2, 116.4, 67.3, 59.3, 22.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 414.1271, Found 414.1263.

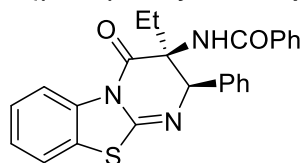


	Retention Time	Area	% Area
1	6.902	2481859	20.02
2	10.100	2437804	19.66
3	13.914	3811147	30.74
4	29.199	3668666	29.59



	Retention Time	Area	% Area
1	14.461	7195395	97.10
2	27.697	214612	2.90

***N*-((2*R*,3*S*)-3-ethyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3af)**



White solid; m.p. 86–90 °C; 38.6 mg, 90% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +610.34$  ( $c = 0.75$  in  $\text{CH}_2\text{Cl}_2$ ).

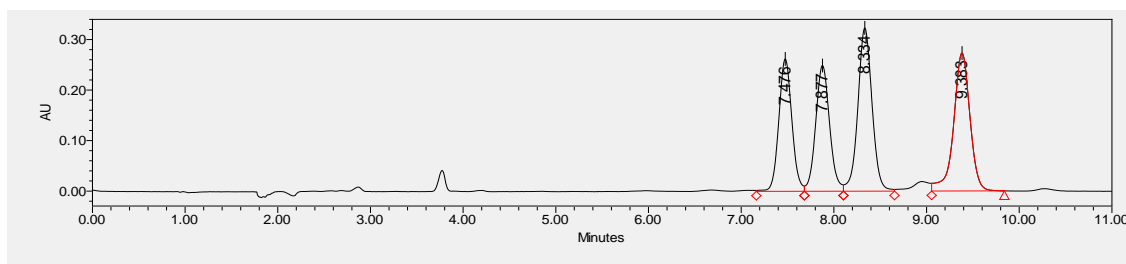
**UPCC** (chiral ODH column),  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 221$  nm,  $t_R$  (major) = 8.28 min,  $t_R$  (minor) = 9.34 min.

**IR** (neat): 3409, 1650, 1462, 1371 and 1178  $\text{cm}^{-1}$ .

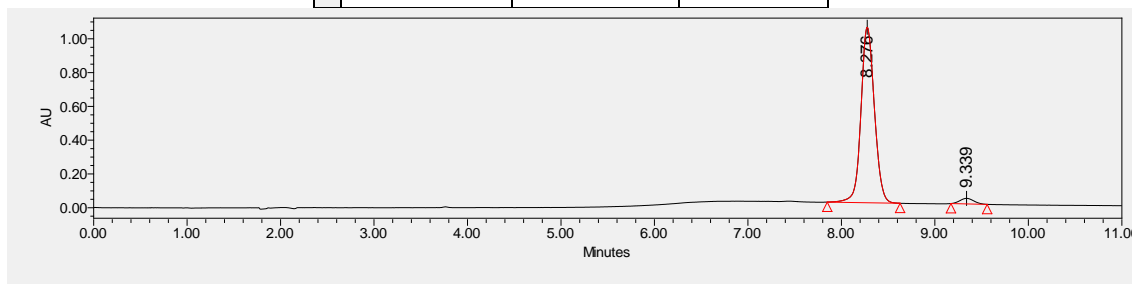
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.26 - 8.22$  (m, 1H), 7.54 – 7.50 (m, 2H), 7.48 – 7.44 (m, 1H), 7.42 – 7.39 (m, 1H), 7.39 – 7.33 (m, 3H), 7.32 – 7.30 (m, 1H), 7.29 – 7.25 (m, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.18 (m, 3H), 7.06 (s, 1H), 5.94 (s, 1H), 3.17 – 3.06 (m, 1H), 2.27 – 2.16 (m, 1H), 0.89 (t,  $J = 7.6$  Hz, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 168.8, 167.2, 153.6, 136.2, 135.0, 134.9, 131.7, 128.8, 128.7, 128.4, 127.2, 126.9, 126.8, 126.3, 123.7, 122.3, 116.0, 67.6, 64.0, 27.2, 8.5$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{25}\text{H}_{22}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 428.1427, Found 428.1432.

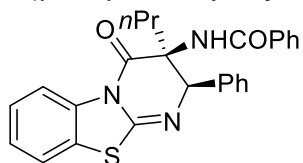


	Retention Time	Area	% Area
1	7.476	2562788	21.44
2	7.877	2600982	21.76
3	8.334	3436049	28.74
4	9.383	3354795	28.06



	Retention Time	Area	% Area
1	8.276	10395363	96.86
2	9.339	336731	3.14

***N*-{(2*R*,3*S*)-4-oxo-2-phenyl-3-propyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl}benzamide (3*g*)**



White solid; m.p. 87–92 °C; 37.5 mg, 85% yield, 93% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +611.96$  ( $c = 0.46$  in  $\text{CH}_2\text{Cl}_2$ ).

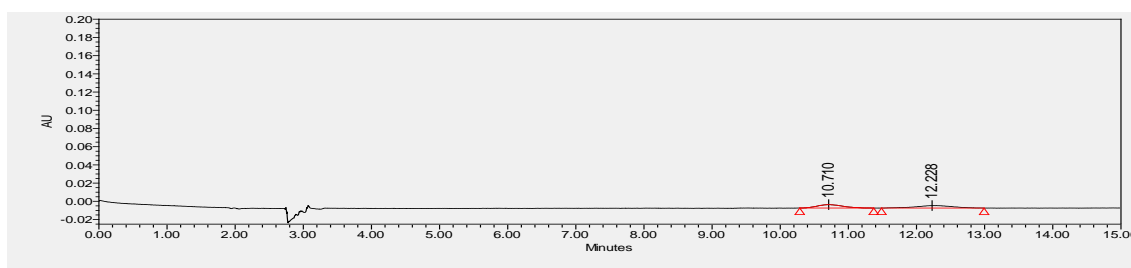
**UPCC** (chiral AYH column),  $\text{CO}_2/\text{EtOH} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 221$  nm,  $t_R$  (major) = 12.11 min,  $t_R$  (minor) = 12.78 min.

**IR** (neat): 3409, 1650, 1462, 1376 and 1177  $\text{cm}^{-1}$ .

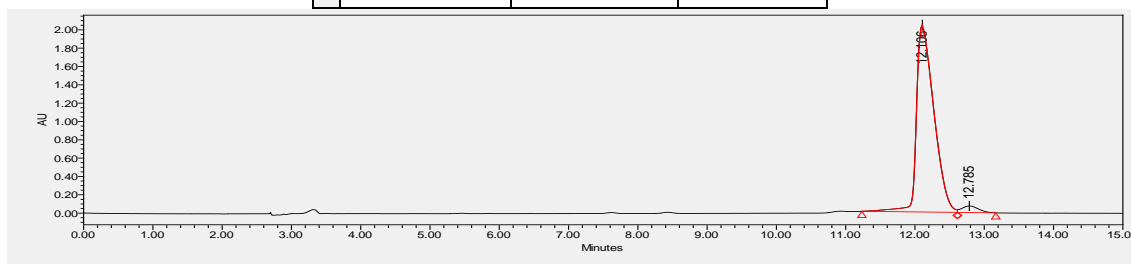
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.27 - 8.21$  (m, 1H), 7.55 – 7.49 (m, 2H), 7.49 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 7.39 – 7.31 (m, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.17 (m, 5H), 7.07 (s, 1H), 5.93 (s, 1H), 3.12 – 2.98 (m, 1H), 2.19 – 2.07 (m, 1H), 1.52 – 1.37 (m, 1H), 1.20 – 1.07 (m, 1H), 0.89 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 169.0, 167.2, 153.6, 136.2, 135.0, 135.0, 131.7, 128.8, 128.7, 128.5, 127.3, 126.9, 126.8, 126.4, 123.8, 122.3, 116.1, 67.8, 36.0, 17.5, 14.0$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{26}\text{H}_{24}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 442.1584, Found 442.1583.

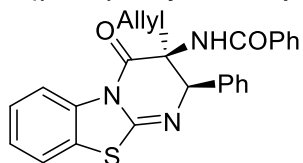


	Retention Time	Area	% Area
1	10.710	95929	48.33
2	12.228	102568	51.67



	Retention Time	Area	% Area
1	12.106	35511070	96.74
2	12.785	1196643	3.26

***N*-((2*R*,3*S*)-3-allyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ah)**



White solid; m.p. 79–83 °C; 40.1 mg, 91% yield, 95% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +585.73$  ( $c = 0.722$  in  $\text{CH}_2\text{Cl}_2$ ).

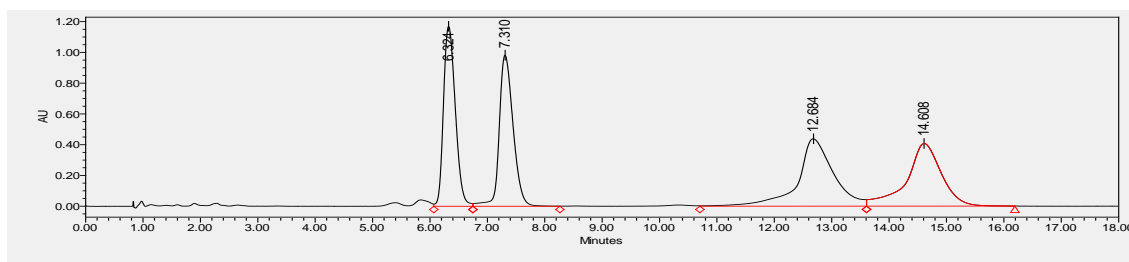
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 221$  nm,  $t_R$  (major) = 5.88 min,  $t_R$  (minor) = 6.88 min.

**IR** (neat): 3405, 1647, 1463, 1368 and 1177  $\text{cm}^{-1}$ .

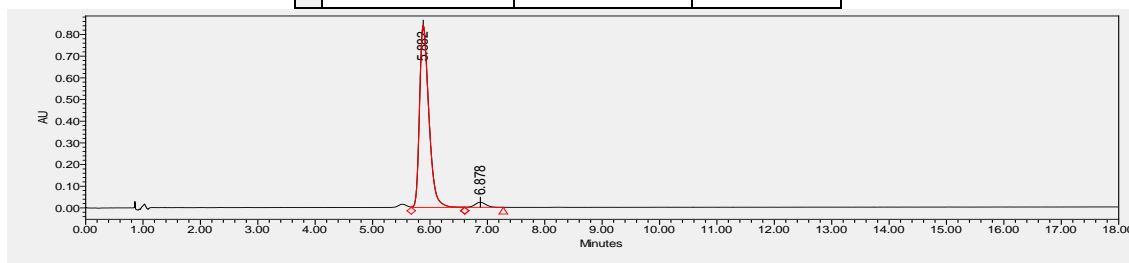
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.23 - 8.19$  (m, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.18 (m, 6H), 7.05 (s, 1H), 5.97 (s, 1H), 5.74 – 5.60 (m, 1H), 5.08 (d,  $J = 4.4$  Hz, 1H), 5.04 (d,  $J = 11.6$  Hz, 1H), 3.83 (dd,  $J = 14.4, 7.6$  Hz, 1H), 2.90 (dd,  $J = 14.4, 7.2$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 168.2, 167.4, 153.8, 135.9, 135.0, 135.0, 131.7, 131.1, 128.8, 128.7, 128.5, 127.3, 126.9, 126.8, 126.4, 123.6, 122.3, 120.4, 116.1, 67.3, 63.6, 38.3$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 440.1427, Found 440.1426.

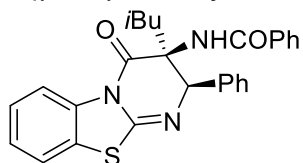


	Retention Time	Area	% Area
1	6.324	16737325	24.18
2	7.310	16482553	23.82
3	12.684	18827335	27.20
4	14.608	17158845	24.79



	Retention Time	Area	% Area
1	5.882	9461512	96.76
2	6.878	317029	3.24

***N*-((2*R*,3*S*)-3-isobutyl-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ai)**



White solid; m.p. 90–93 °C; 42.3 mg, 93% yield, 97% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +571.43$  ( $c = 0.53$  in  $\text{CH}_2\text{Cl}_2$ ).

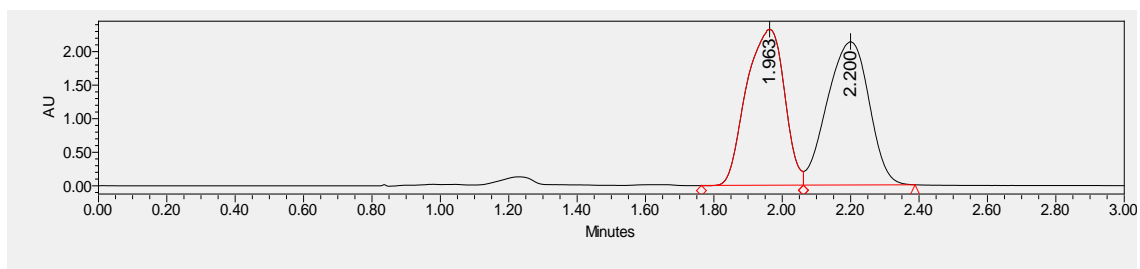
**UPCC** (chiral OJ-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 221$  nm,  $t_R$  (major) = 2.21 min,  $t_R$  (minor) = 1.97 min.

**IR** (neat): 3410, 1649, 1463, 1373 and 1177  $\text{cm}^{-1}$ .

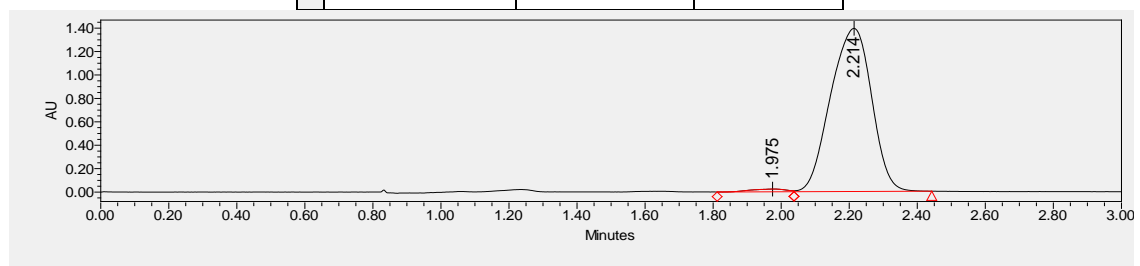
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.23 - 8.19$  (m, 1H), 7.52 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 7.39 – 7.32 (m, 3H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 5H), 7.13 (s, 1H), 5.91 (s, 1H), 3.11 (dd,  $J = 14.9, 5.8$  Hz, 1H), 2.10 (dd,  $J = 14.8, 6.5$  Hz, 1H), 1.76 – 1.62 (m, 1H), 0.94 (d,  $J = 6.8$  Hz, 3H), 0.77 (d,  $J = 6.8$  Hz, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 169.6, 167.2, 153.7, 135.9, 135.2, 134.9, 131.6, 128.8, 128.7, 128.5, 127.3, 127.0, 126.8, 126.3, 123.7, 122.4, 115.9, 68.3, 63.3, 42.1, 24.7, 24.0, 23.8$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{27}\text{H}_{26}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) = 456.1740, Found 456.1739.

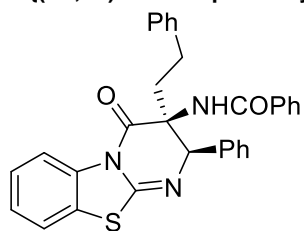


	Retention Time	Area	% Area
1	1.963	17936736	49.69
2	2.200	18157906	50.31



	Retention Time	Area	% Area
1	1.975	171064	1.45
2	2.214	11651856	98.55

***N*-((2*R*,3*S*)-4-oxo-3-phenethyl-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3aj)**



White solid; m.p. 82–86 °C; 45.7 mg, 91% yield, 95% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +496.88$  ( $c = 0.86$  in  $\text{CH}_2\text{Cl}_2$ ).

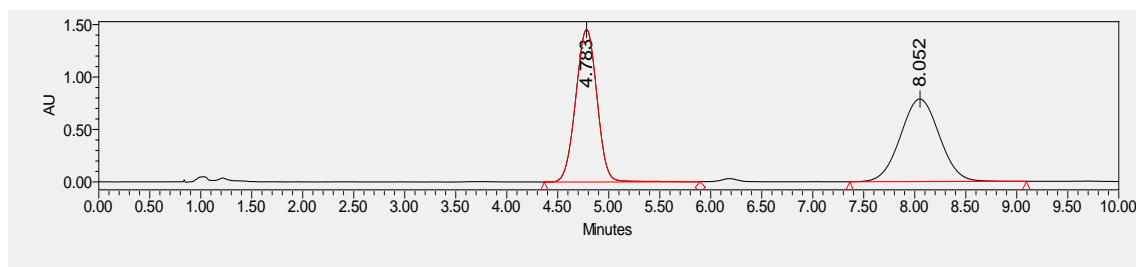
**UPCC** (chiral OJ-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 240$  nm,  $t_R$  (major) = 8.13 min,  $t_R$  (minor) = 4.85 min.

**IR** (neat): 3405, 1648, 1462, 1376 and 1184  $\text{cm}^{-1}$ .

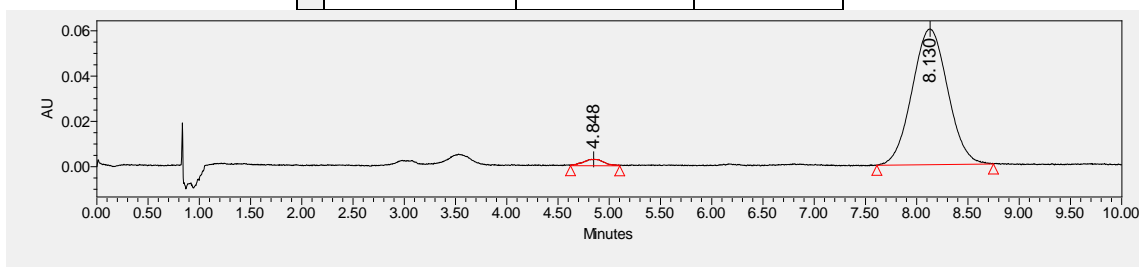
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.18 - 8.14$  (m, 1H), 7.54 – 7.50 (m, 2H), 7.50 – 7.45 (m, 1H), 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.23 – 7.19 (m, 3H), 7.17 – 7.08 (m, 5H), 7.08 – 7.02 (m, 1H), 5.99 (s, 1H), 3.56 – 3.45 (m, 1H), 2.83 – 2.74 (m, 1H), 2.59 – 2.44 (m, 2H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 168.7, 167.3, 153.7, 140.1, 135.9, 134.8, 131.7, 128.8, 128.7, 128.5, 128.5, 128.3, 127.2, 126.8, 126.4, 126.2, 123.6, 122.2, 116.2, 67.7, 63.3, 34.7, 30.3$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{31}\text{H}_{26}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 504.1740, Found 504.1743.



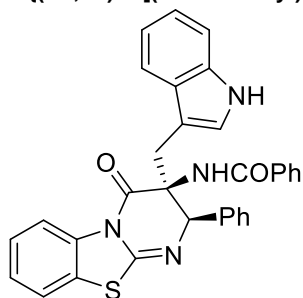
	Retention Time	Area	% Area
1	4.783	21055131	50.15
2	8.052	20926273	49.85



	Retention Time	Area	% Area
1	4.848	40462	2.72
2	8.130	1445419	97.28



***N*-((2*R*,3*S*)-3-[(1*H*-indol-3-yl)methyl]-4-oxo-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3ak)**



White solid; m.p. 140–145 °C; 56.9 mg, 99% yield, 92% ee, >19:1 d.r.;  $[\alpha]_D^{23} = +317.70$  ( $c = 0.97$  in  $\text{CH}_2\text{Cl}_2$ ).

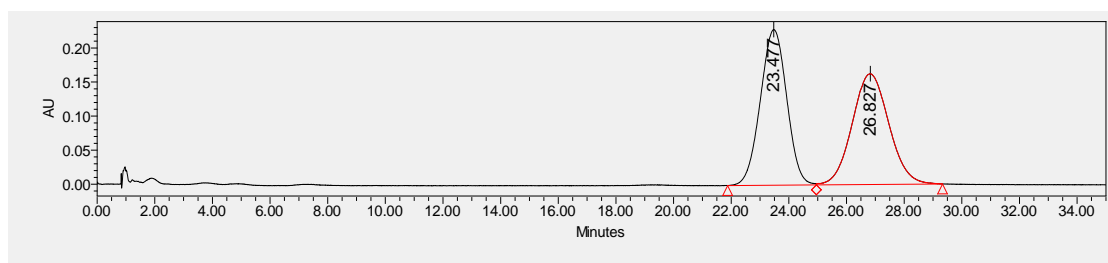
**UPCC** (chiral OJ-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 215$  nm,  $t_R$  (major) = 23.49 min,  $t_R$  (minor) = 26.95 min.

**IR** (neat): 3401, 1644, 1461, 1373 and 1188  $\text{cm}^{-1}$ .

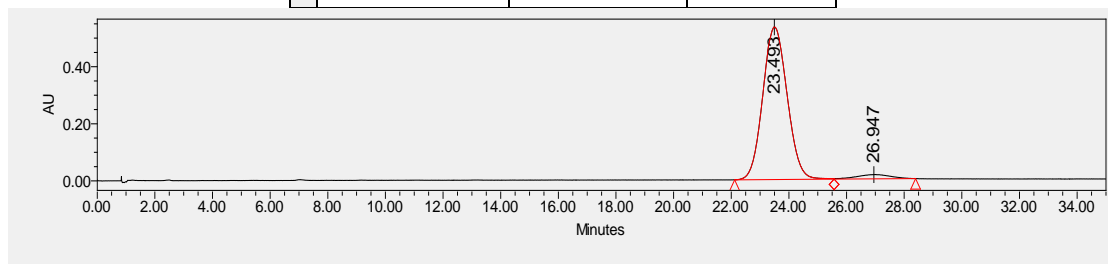
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.17$  (s, 1H), 7.84 – 7.78 (m, 1H), 7.48 – 7.41 (m, 4H), 7.35 – 7.27 (m, 5H), 7.24 – 7.17 (m, 5H), 7.09 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.80 (d,  $J = 2.4$  Hz, 1H), 6.62 (t,  $J = 7.2$  Hz, 1H), 6.21 (s, 1H), 4.53 (d,  $J = 14.8$  Hz, 1H), 3.79 (d,  $J = 14.8$  Hz, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 168.0, 167.8, 154.2, 136.2, 135.7, 135.2, 135.1, 131.6, 128.8, 128.7, 128.5, 127.5, 127.3, 126.8, 126.8, 126.3, 124.1, 123.3, 122.2, 122.0, 119.5, 118.3, 116.3, 111.2, 109.0, 67.4, 64.7, 29.7$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{32}\text{H}_{25}\text{N}_4\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 529.1693, Found 529.1701.

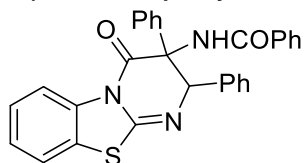


	Retention Time	Area	% Area
1	23.477	14533043	50.27
2	26.827	14378396	49.73



	Retention Time	Area	% Area
1	23.493	31375380	96.17
2	26.947	1250811	3.83

***N*-(4-oxo-2,3-diphenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (3a1)**



White solid; m.p. 187–188 °C; 10.1 mg, 21% yield, race, >19:1 d.r..

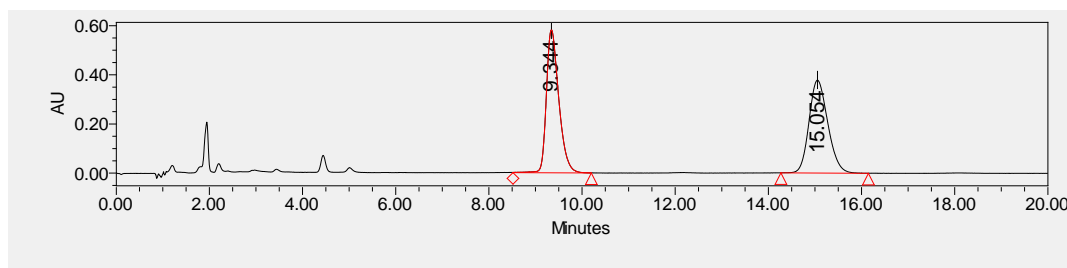
**UPCC** (chiral IC-3 column), CO<sub>2</sub>/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 240 nm, *t<sub>R</sub>* (major) = 9.32 min, *t<sub>R</sub>* (minor) = 15.02 min.

**IR** (neat): 3407, 3062, 1708, 1648, 1459, 1353 and 1180 cm<sup>-1</sup>.

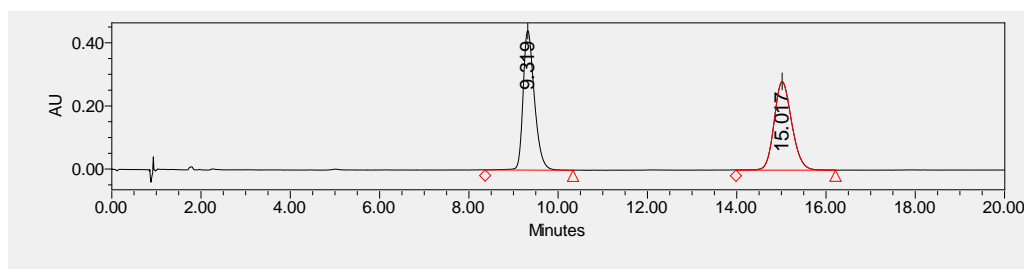
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 8.21 – 8.14 (m, 1H), 7.74 – 7.66 (m, 3H), 7.49 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.31 (m, 4H), 7.31 – 7.26 (m, 4H), 7.25 – 7.17 (m, 5H), 6.58 (s, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ = 166.3, 137.3, 135.7, 131.7, 129.1, 129.0, 128.9, 128.6, 127.6, 126.9, 126.8, 126.3, 122.1, 116.1, 64.2.

**HRMS** (ESI-FT) calcd for C<sub>32</sub>H<sub>25</sub>N<sub>4</sub>O<sub>2</sub>S<sup>+</sup> ([M+Na<sup>+</sup>]) = 498.1247, Found 498.1239.

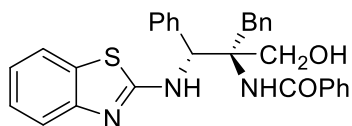


	Retention Time	Area	% Area
1	9.344	10718268	50.30
2	15.054	10590477	49.70



	Retention Time	Area	% Area
1	9.319	7785535	50.28
2	15.017	7698083	49.72

***N*-((1*R*)-1-(benzo[*d*]thiazol-2-ylamino)-2-benzyl-3-hydroxy-1-phenylpropan-2-yl)benzamide (4aa)**



White solid; m.p. 130–135 °C; 49.1 mg, 99% yield, 94% ee, >19:1 d.r.;  $[\alpha]_D^{23} = -67.15$  ( $c = 0.83$  in  $\text{CH}_2\text{Cl}_2$ ).

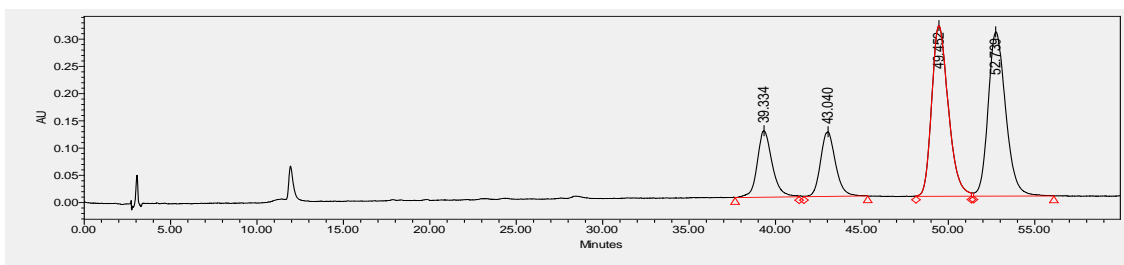
**UPCC** (chiral OXH column),  $\text{CO}_2/\text{MeOH} = 85/15$ , flow rate = 1.0 mL/min,  $\lambda = 221$  nm,  $t_R$  (major) = 48.88 min,  $t_R$  (minor) = 52.75 min.

**IR** (neat): 3309, 1646, 1546 and 704  $\text{cm}^{-1}$ .

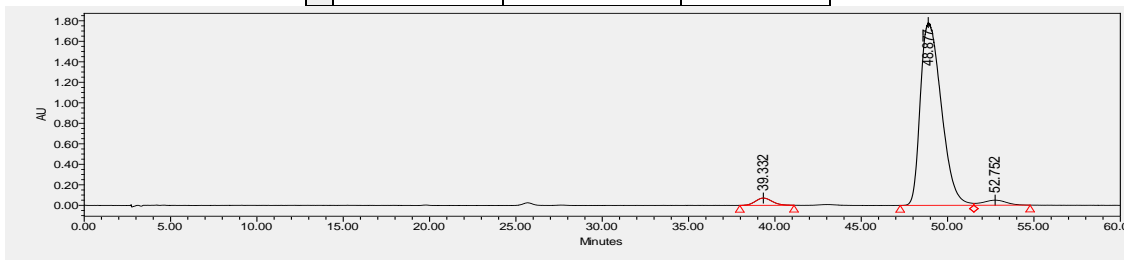
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.97$  (s, 1H), 7.60 – 7.56 (m, 2H), 7.55 – 7.52 (m, 1H), 7.49 – 7.44 (m, 3H), 7.40 – 7.34 (m, 3H), 7.34 – 7.27 (m, 5H), 7.25 – 7.17 (m, 4H), 7.09 – 7.04 (m, 1H), 5.78 (s, 1H), 5.54 (s, 1H), 4.06 (d,  $J = 10.8$  Hz, 1H), 3.74 (d,  $J = 13.6$  Hz, 1H), 3.64 (d,  $J = 10.8$  Hz, 1H), 3.39 (d,  $J = 13.6$  Hz, 1H), 1.95 (s, 1H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 169.2, 169.1, 137.9, 136.1, 135.2, 131.9, 130.9, 128.9, 128.8, 128.8, 128.6, 128.2, 127.2, 126.9, 126.2, 121.9, 121.2, 118.3, 63.6, 63.0, 61.1, 37.3$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}^+]$ ) = 494.1897, Found 494.1902.

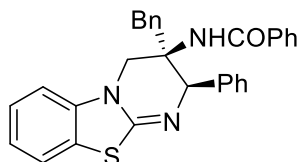


	Retention Time	Area	% Area
1	39.334	7345421	12.95
2	43.040	7138445	12.58
3	49.452	20935534	36.90
4	52.739	21322991	37.58



	Retention Time	Area	% Area
1	39.332	4783850	2.99
2	48.877	150367116	94.09
3	52.752	4663090	2.92

***N*-((2*R*,3*R*)-3-benzyl-2-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidin-3-yl)benzamide (5a)**



White solid; m.p. 126–129 °C; 161.1 mg, 92% yield, 93% ee, >19:1 d.r.;  $[\alpha]_D^{20} = +320.83$  ( $c = 0.10$  in  $\text{CH}_2\text{Cl}_2$ ).

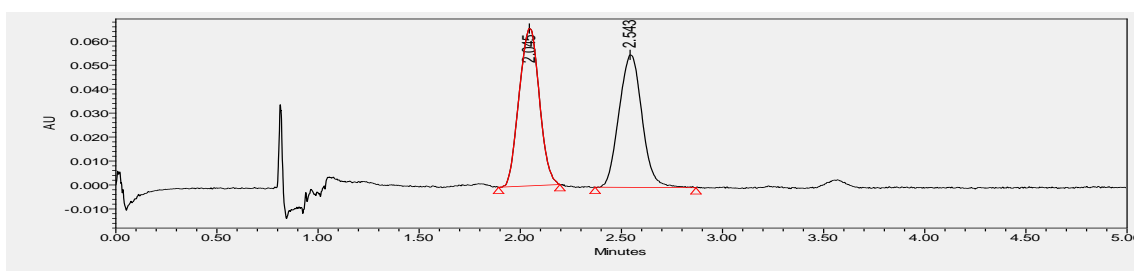
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{EtOH} = 70/30$ , flow rate = 1.5 mL/min,  $\lambda = 267$  nm,  $t_R$  (major) = 2.02 min,  $t_R$  (minor) = 2.52 min.

**IR** (neat): 3028, 1622, 1588, 1476, 1300, 742 and 702  $\text{cm}^{-1}$ .

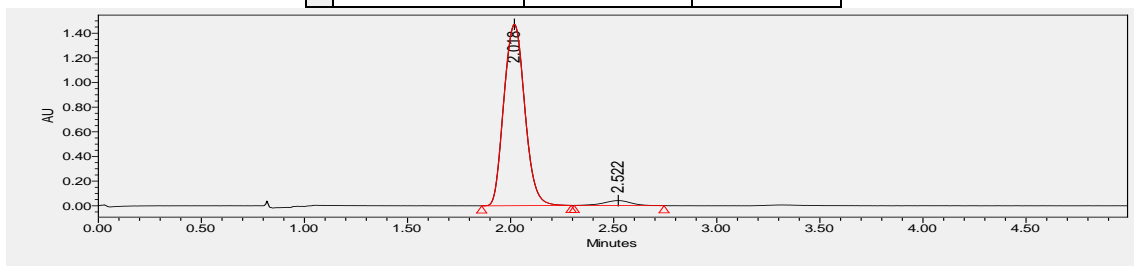
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.45 - 7.35$  (m, 4H), 7.34 – 7.25 (m, 5H), 7.25 – 7.17 (m, 7H), 7.14 (m, 2H), 7.07 (m, 1H), 6.77 (m, 1H), 5.77 (s, 1H), 4.96 (s, 1H), 4.42 (d,  $J = 12.0$  Hz, 1H), 3.63 (d,  $J = 12.0$  Hz, 1H), 3.58 – 3.44 (m, 2H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta = 168.1, 157.5, 139.9, 139.8, 136.2, 131.7, 130.9, 128.9, 128.7, 128.4, 128.2, 128.1, 127.0, 126.7, 126.2, 123.2, 122.5, 122.2, 108.1, 63.9, 54.4, 45.0, 38.1$ .

**HRMS** (ESI-FT) calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_3\text{OS}^+$  ( $[\text{M}+\text{H}^+]$ ) = 476.1791, Found 476.1793.

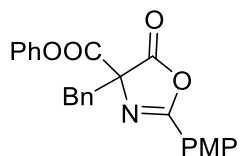


	Retention Time	Area	% Area
1	2.045	456330	51.05
2	2.543	437620	48.95



	Retention Time	Area	% Area
1	2.018	10332230	96.55
2	2.522	369197	3.45

**Phenyl 4-benzyl-2-(4-methoxyphenyl)-5-oxo-4,5-dihydrooxazole-4-carboxylate (7a)**



Colorless oil; 6.6 mg, 16% yield, 87% ee;  $[\alpha]_D^{25} = +156.10$  ( $c = 0.33$  in  $\text{CH}_2\text{Cl}_2$ ).

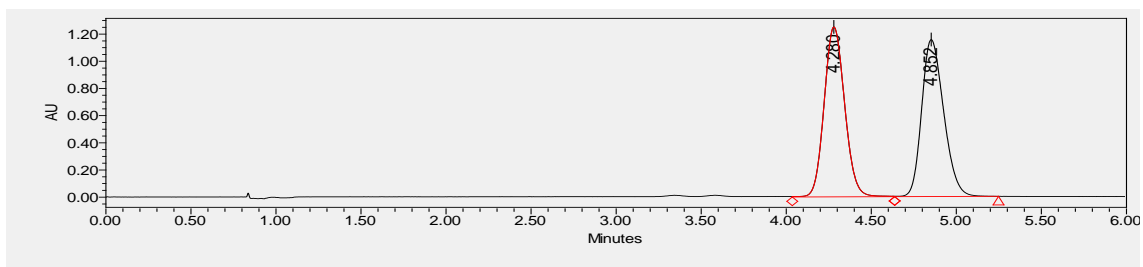
**UPCC** (chiral OD-3 column),  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 271$  nm,  $t_R$  (major) = 4.41 min,  $t_R$  (minor) = 4.98 min.

**IR** (neat): 2934, 1740, 1606, 1492, 1260, 1191, 1026, 844 and 701  $\text{cm}^{-1}$ .

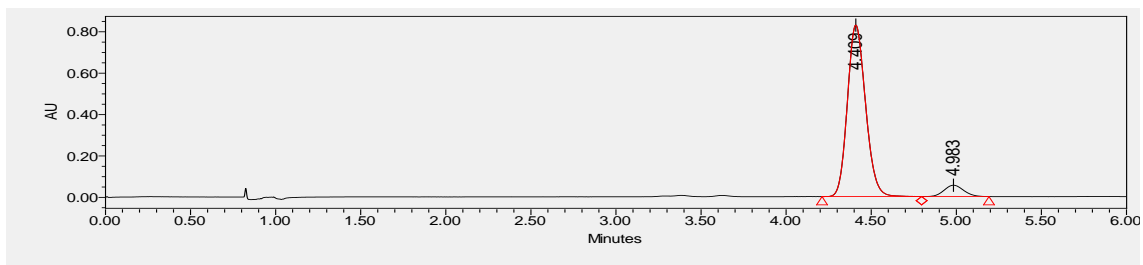
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.90 - 7.85$  (m, 2H), 7.41 - 7.34 (m, 2H), 7.27 (m, 1H), 7.26 - 7.23 (m, 2H), 7.23 - 7.16 (m, 3H), 7.14 - 7.08 (m, 2H), 6.97 - 6.91 (m, 2H), 3.86 (s, 3H), 3.72 (d,  $J = 13.6$  Hz, 1H), 3.60 (d,  $J = 13.6$  Hz, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 163.8, 150.4, 132.9, 130.6, 130.4, 129.7, 128.4, 127.8, 126.7, 121.27$  3, 117.3, 114.4, 77.6, 55.7, 40.4.

**HRMS** (ESI-FT) calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_5^+$  ( $[\text{M}+\text{H}^+]$ ) = 402.1336, Found 402.1332.



	Retention Time	Area	% Area
1	4.280	10474461	50.24
2	4.852	10376184	49.76



	Retention Time	Area	% Area
1	4.409	6147335	93.32
2	4.983	439962	6.68

## 9. Copies of NMR spectra for products

Figure S1. <sup>1</sup>H NMR of 3aa

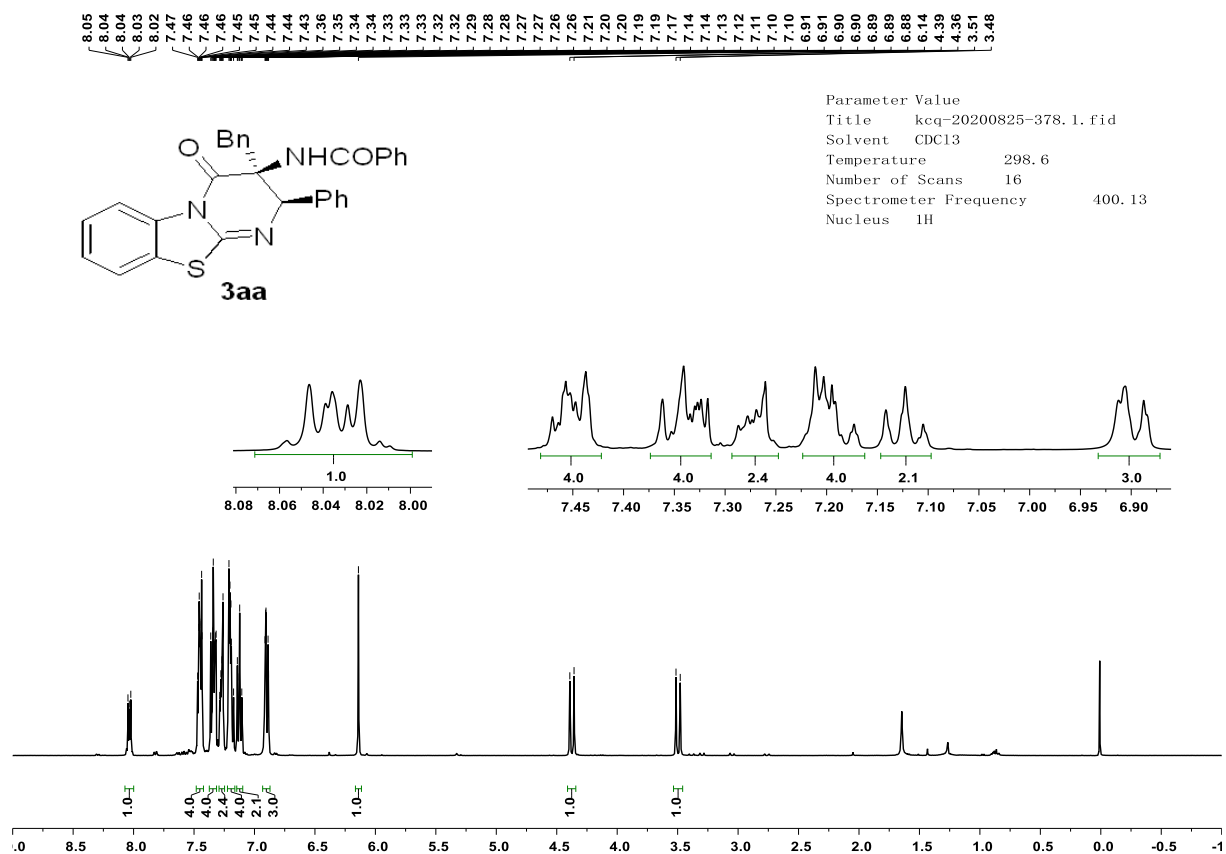


Figure S2. <sup>13</sup>C NMR of 3aa

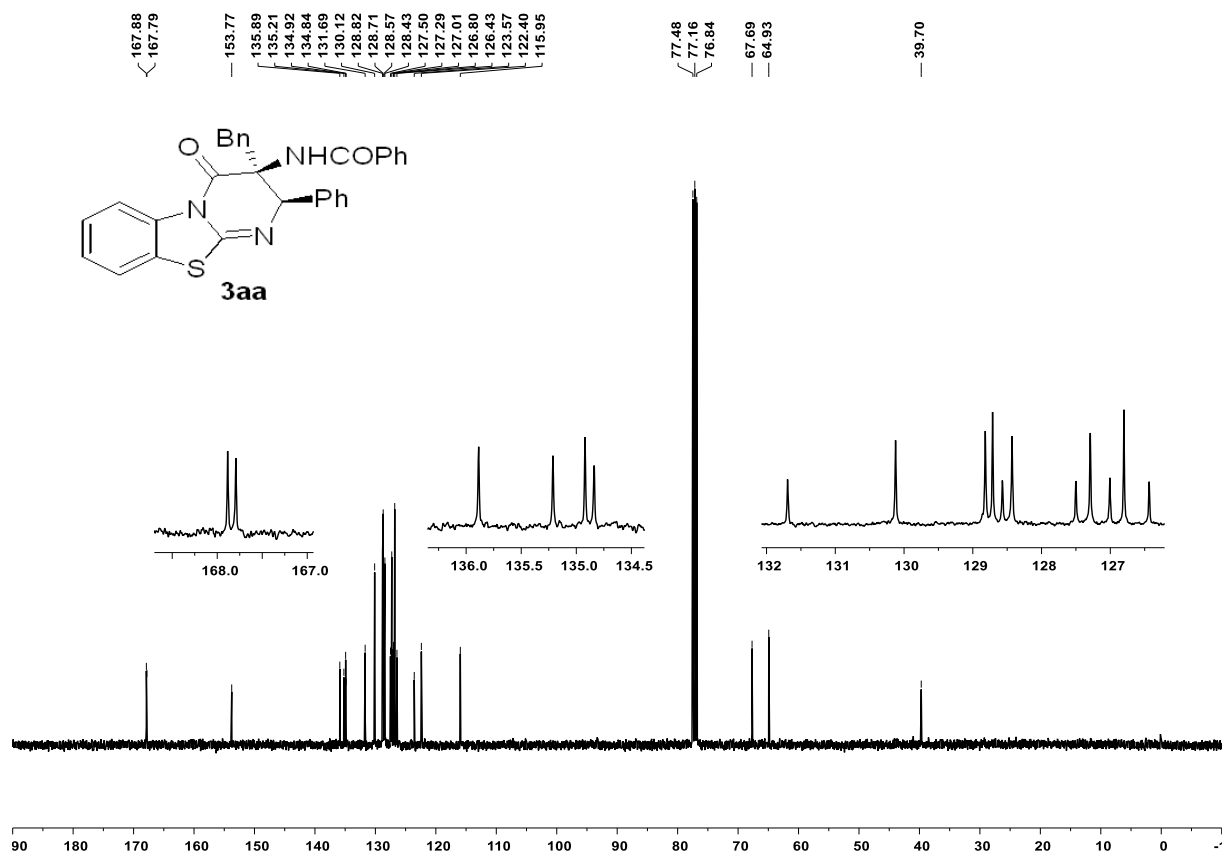


Figure S3. <sup>1</sup>H NMR of 3ba

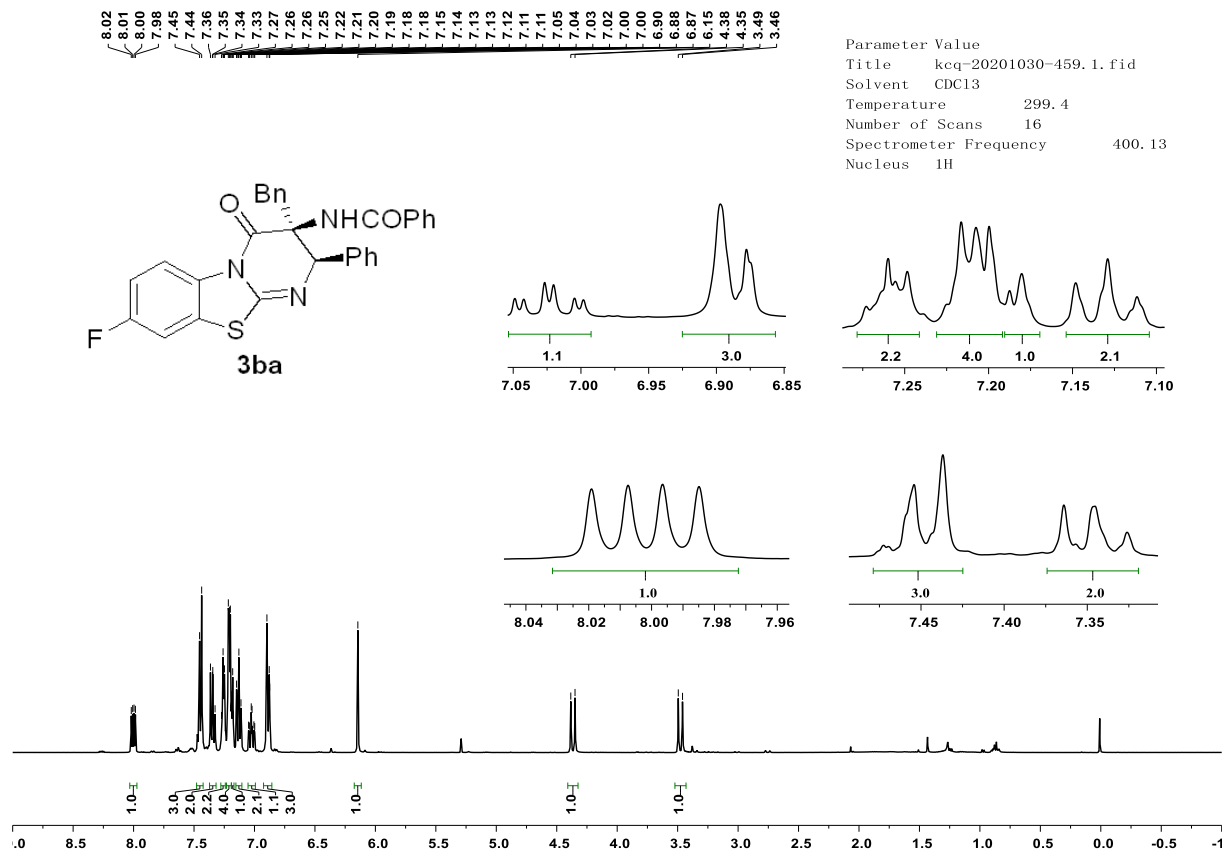


Figure S4. <sup>13</sup>C NMR of 3ba

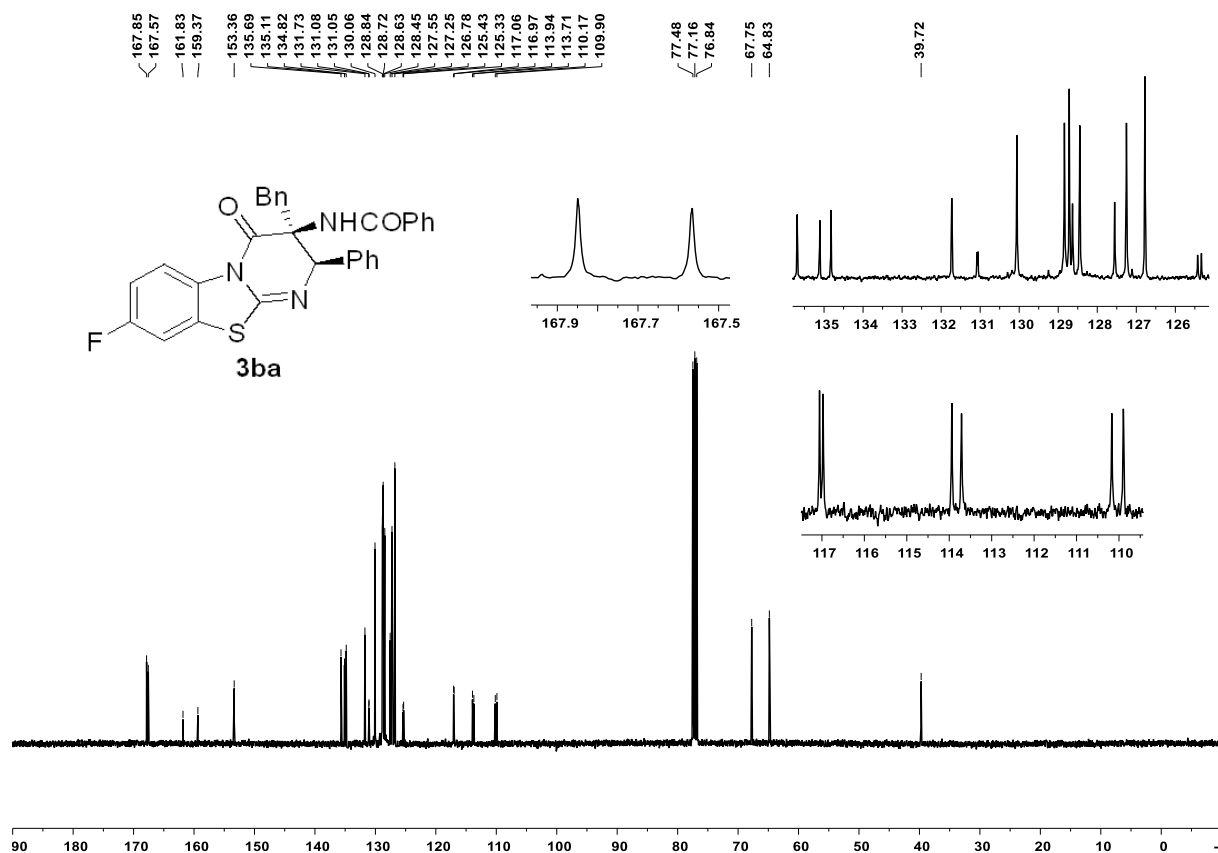


Figure S5.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3ba

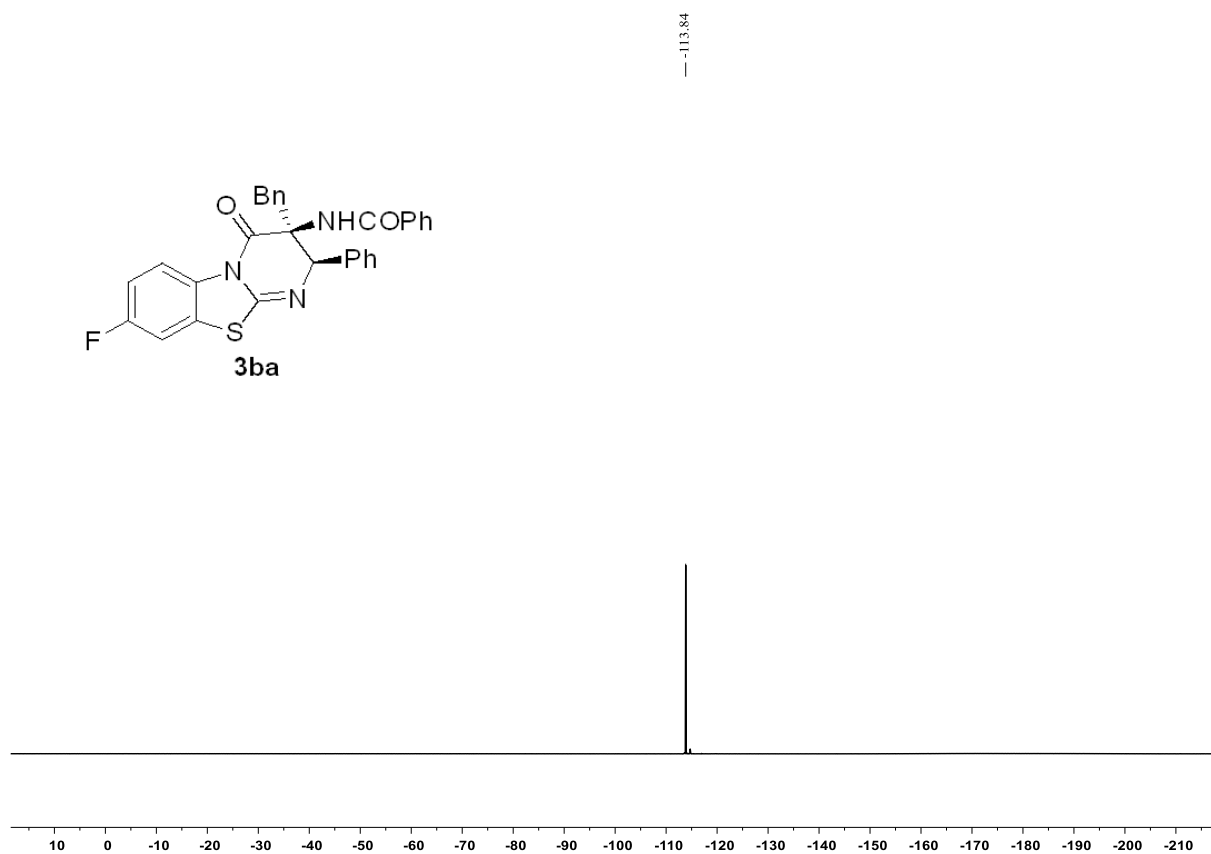


Figure S6.  $^1\text{H}$  NMR of 3ca

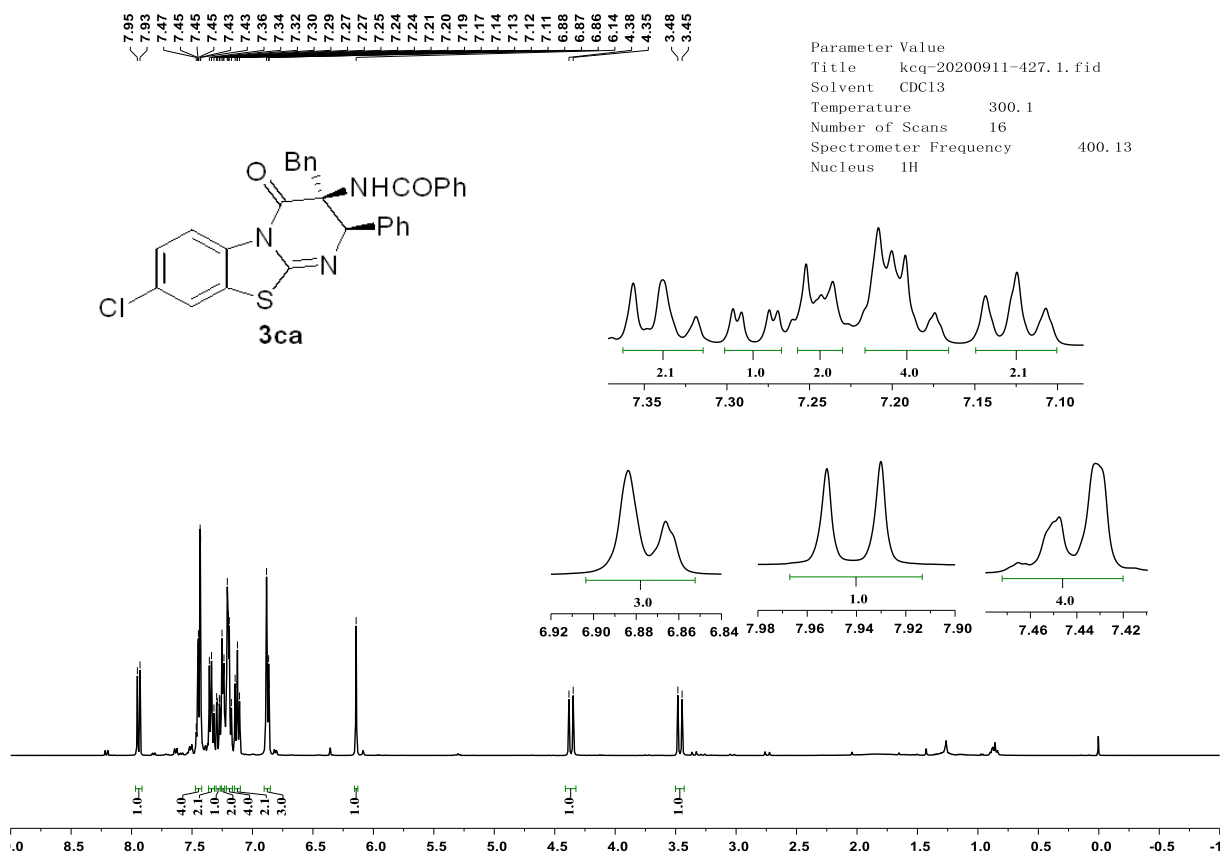




Figure S7. <sup>13</sup>C NMR of 3ca

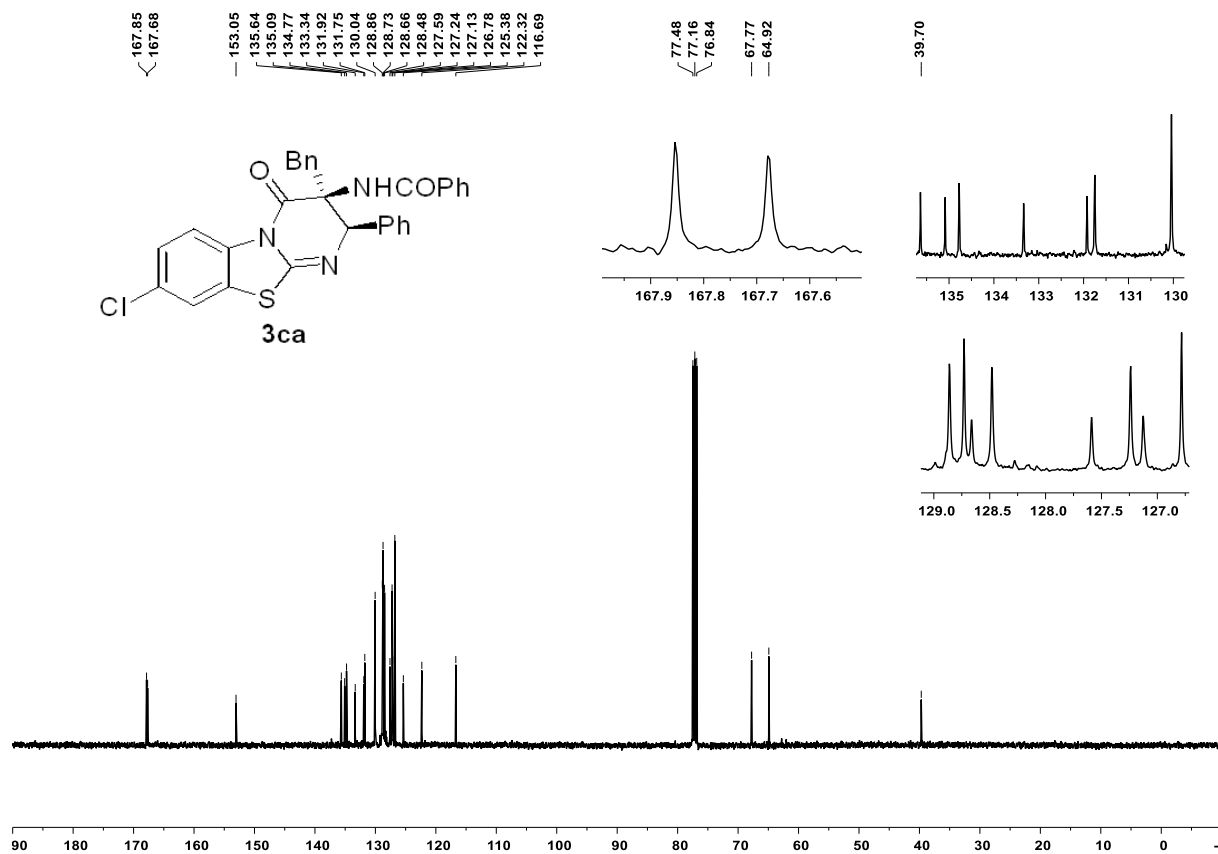


Figure S8. <sup>1</sup>H NMR of 3da

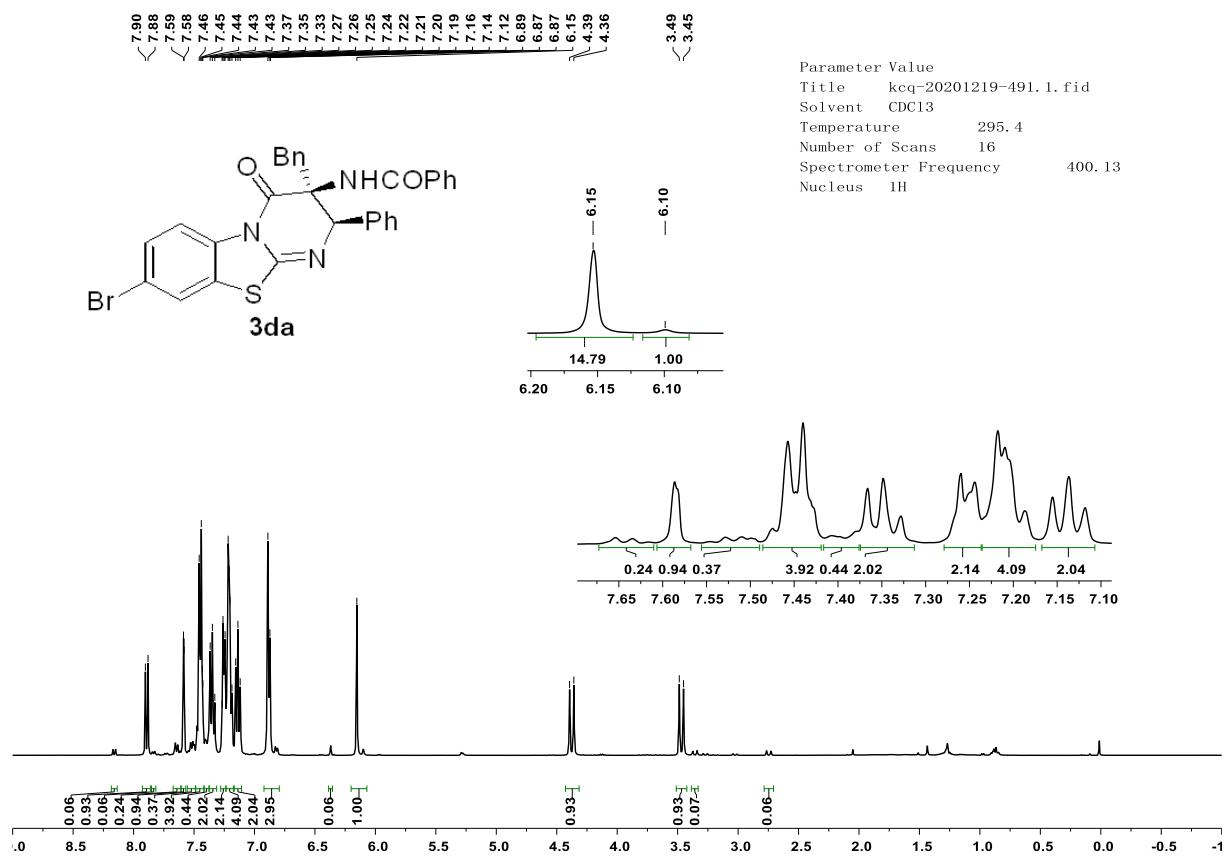


Figure S9.  $^{13}\text{C}$  NMR of 3da

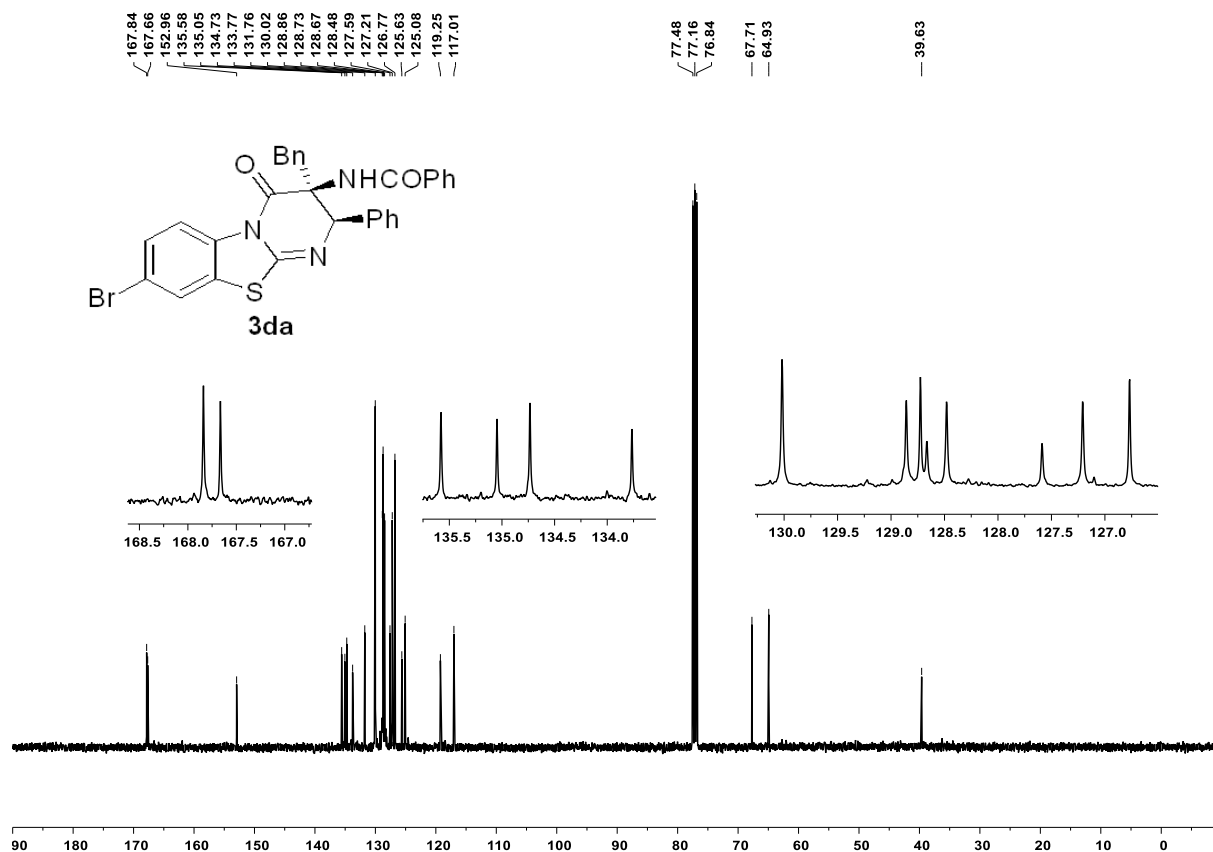


Figure S10.  $^1\text{H}$  NMR of 3ea

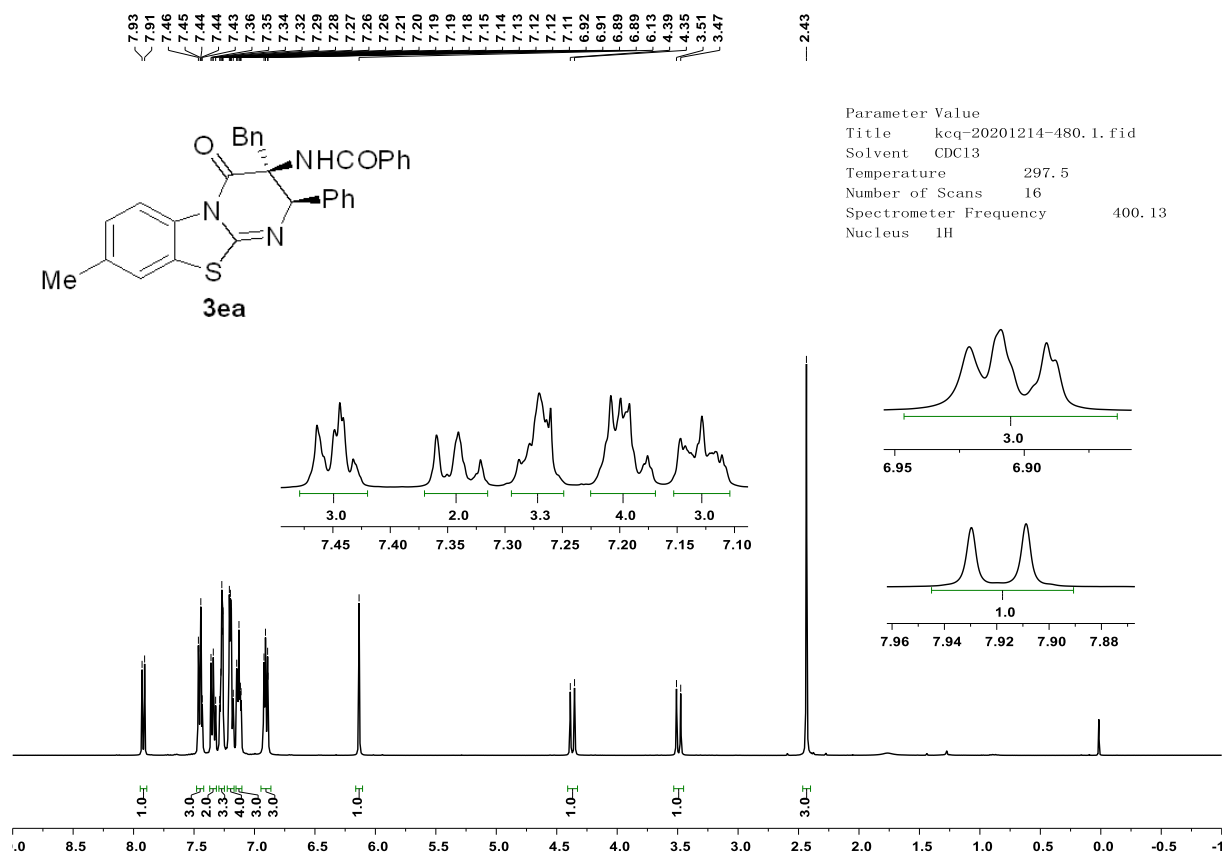


Figure S11. <sup>13</sup>C NMR of 3ea

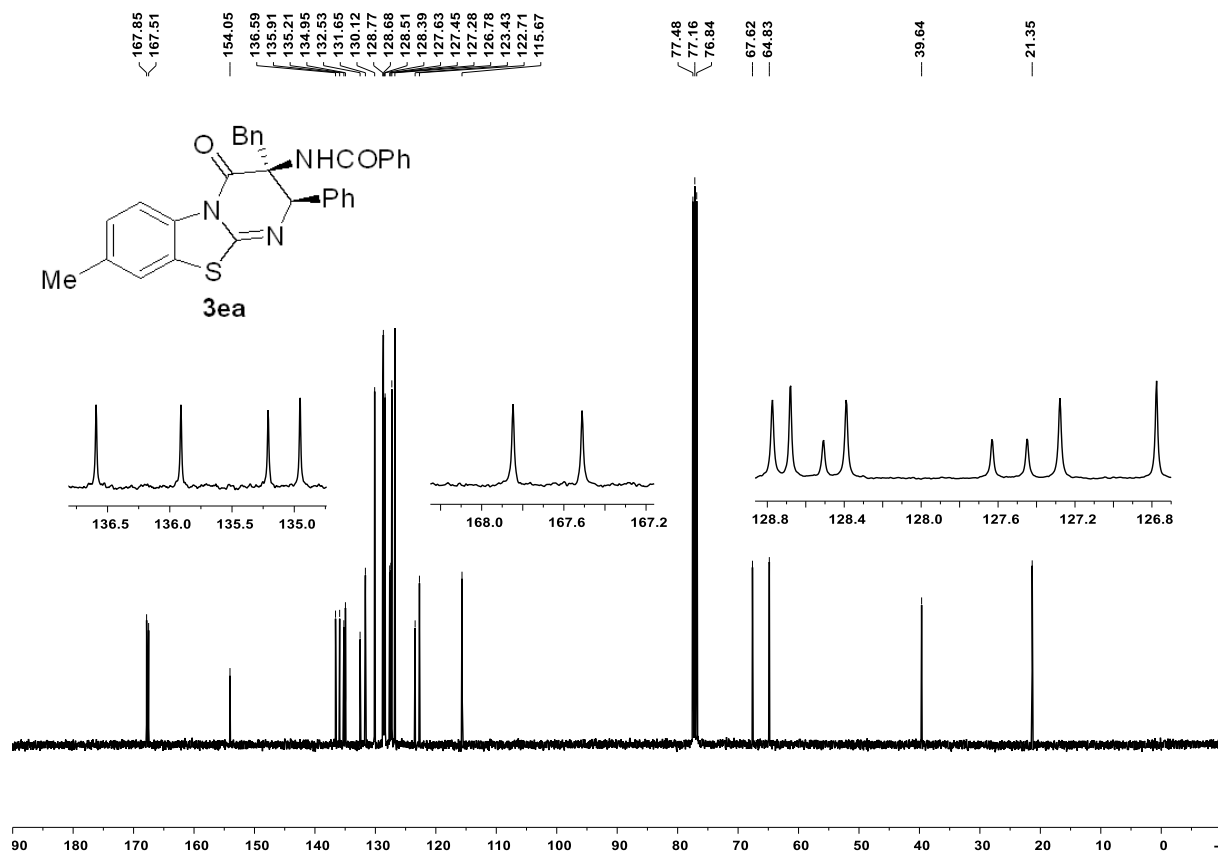


Figure S12. <sup>1</sup>H NMR of 3fa

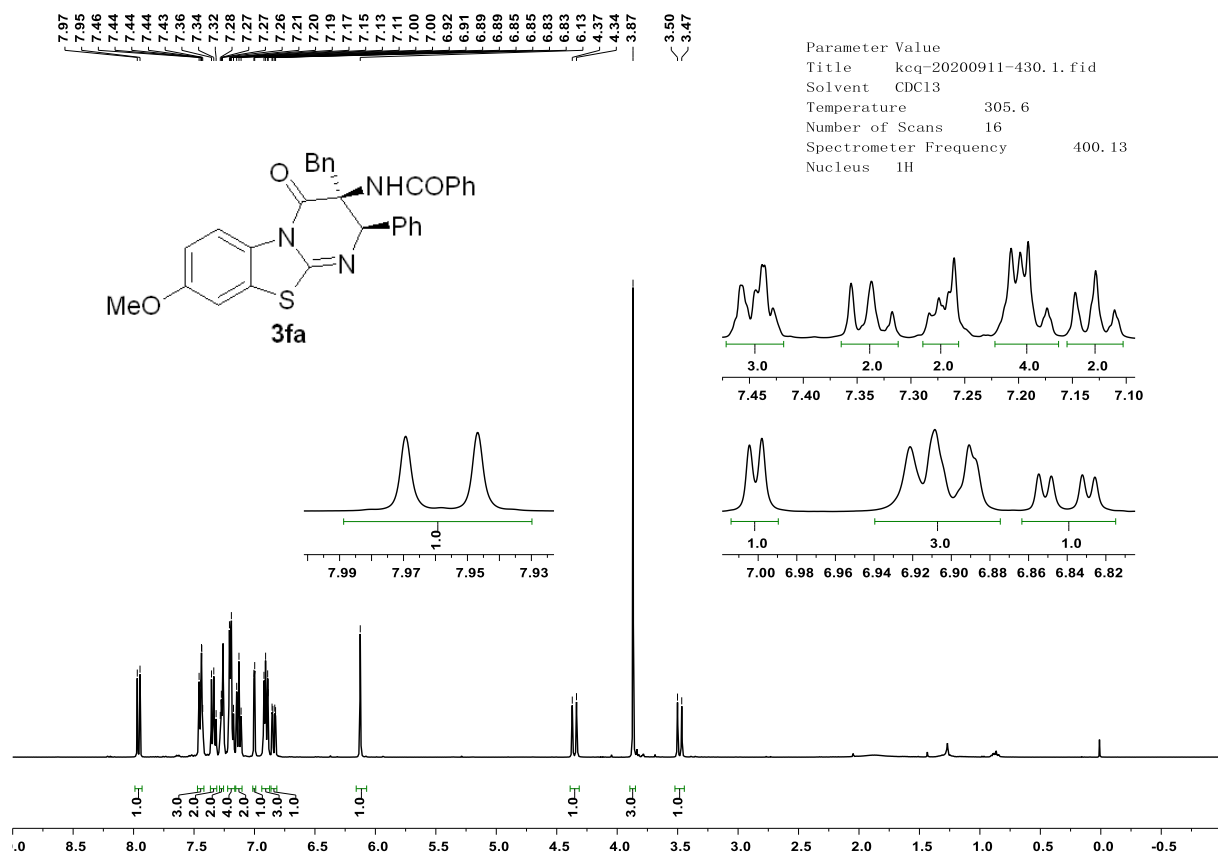


Figure S13. <sup>13</sup>C NMR of 3fa

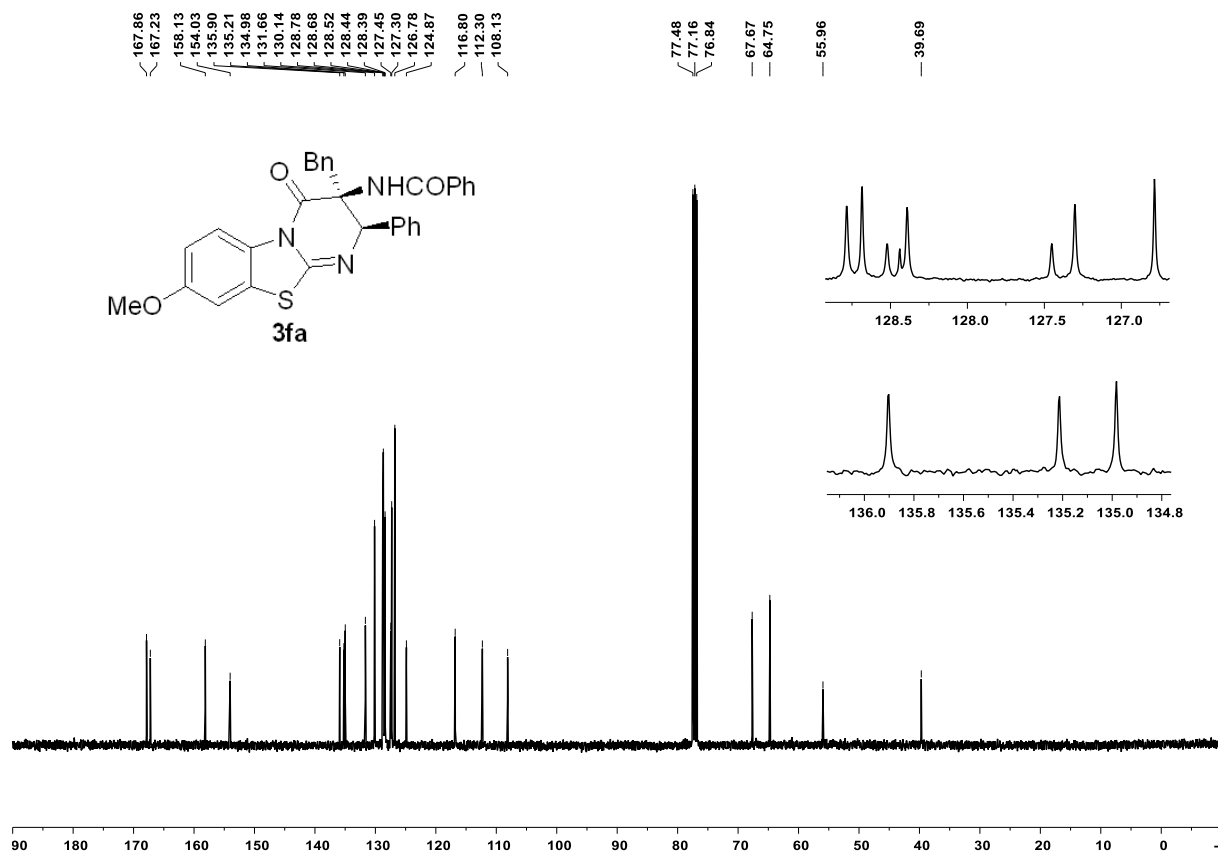


Figure S14. <sup>1</sup>H NMR of 3ga

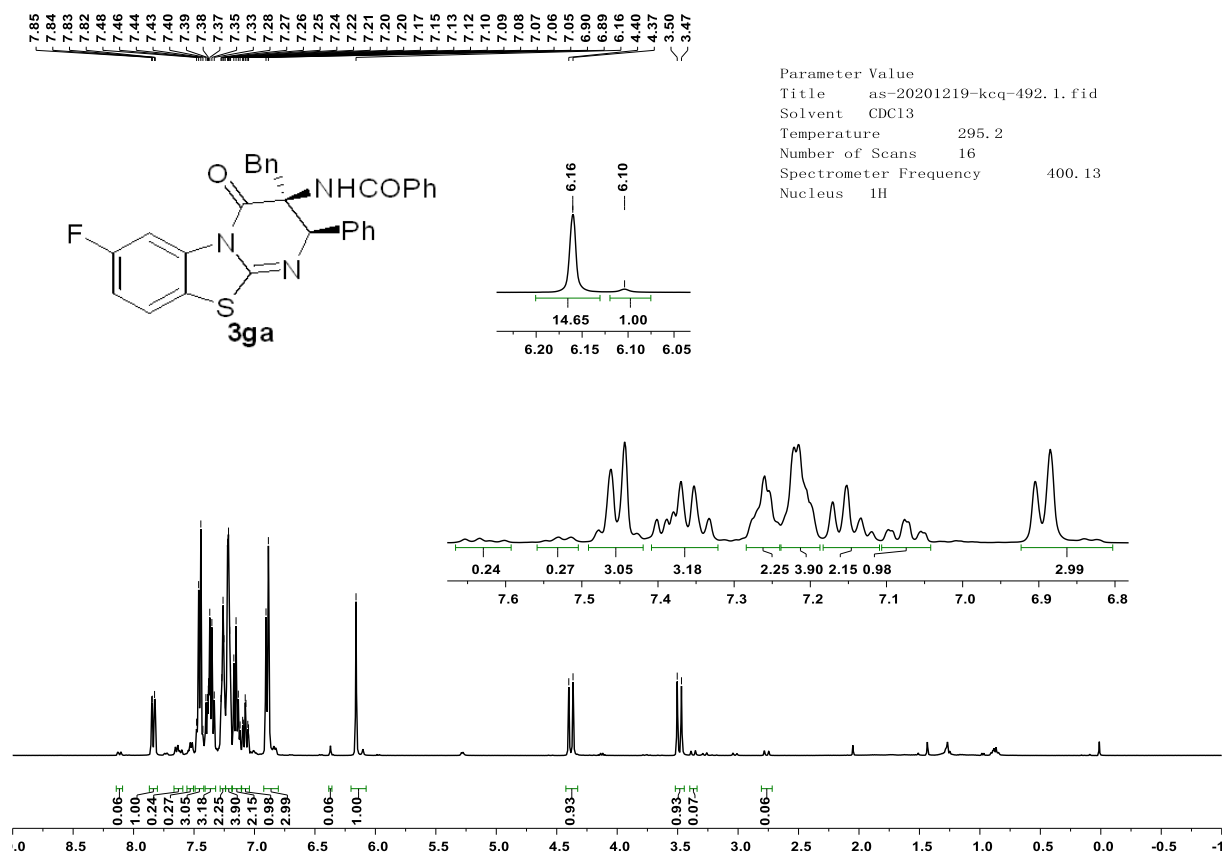


Figure S15.  $^{13}\text{C}$  NMR of 3ga

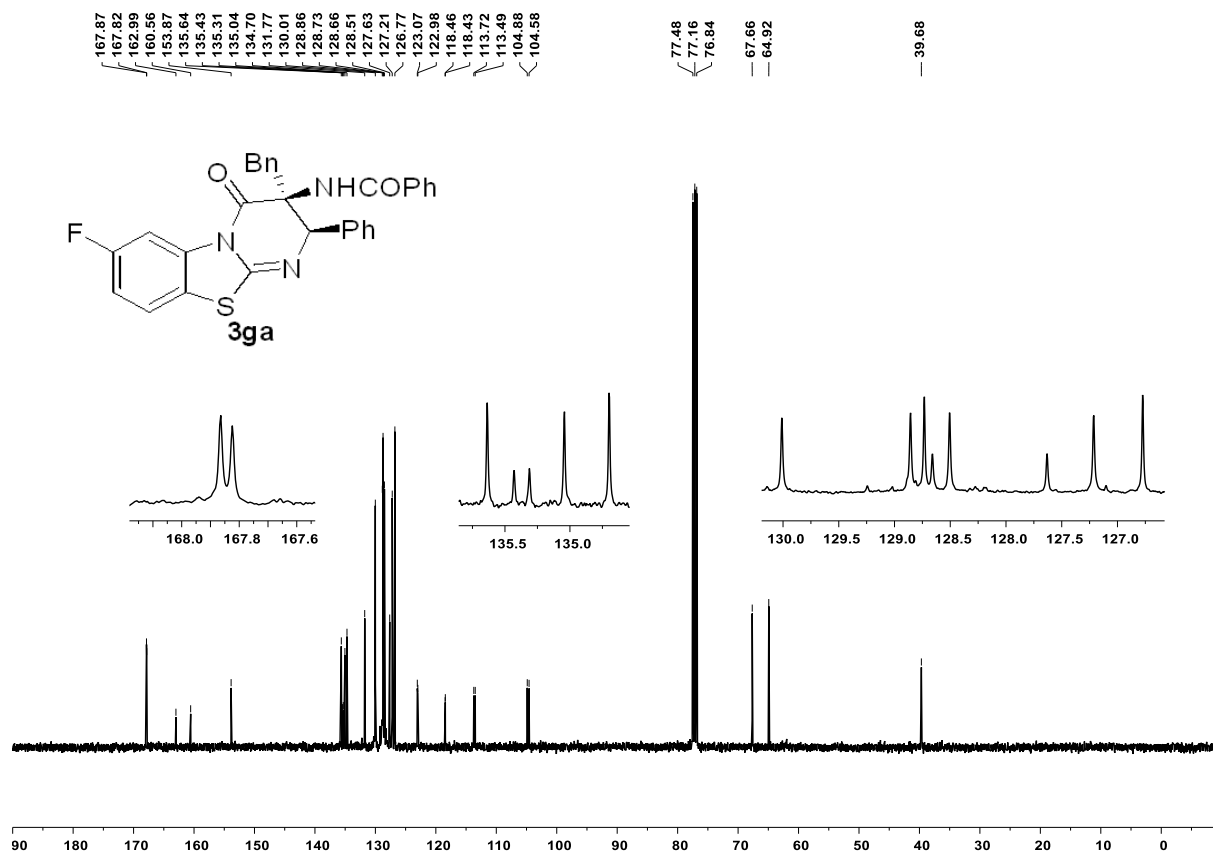


Figure S16.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3ga

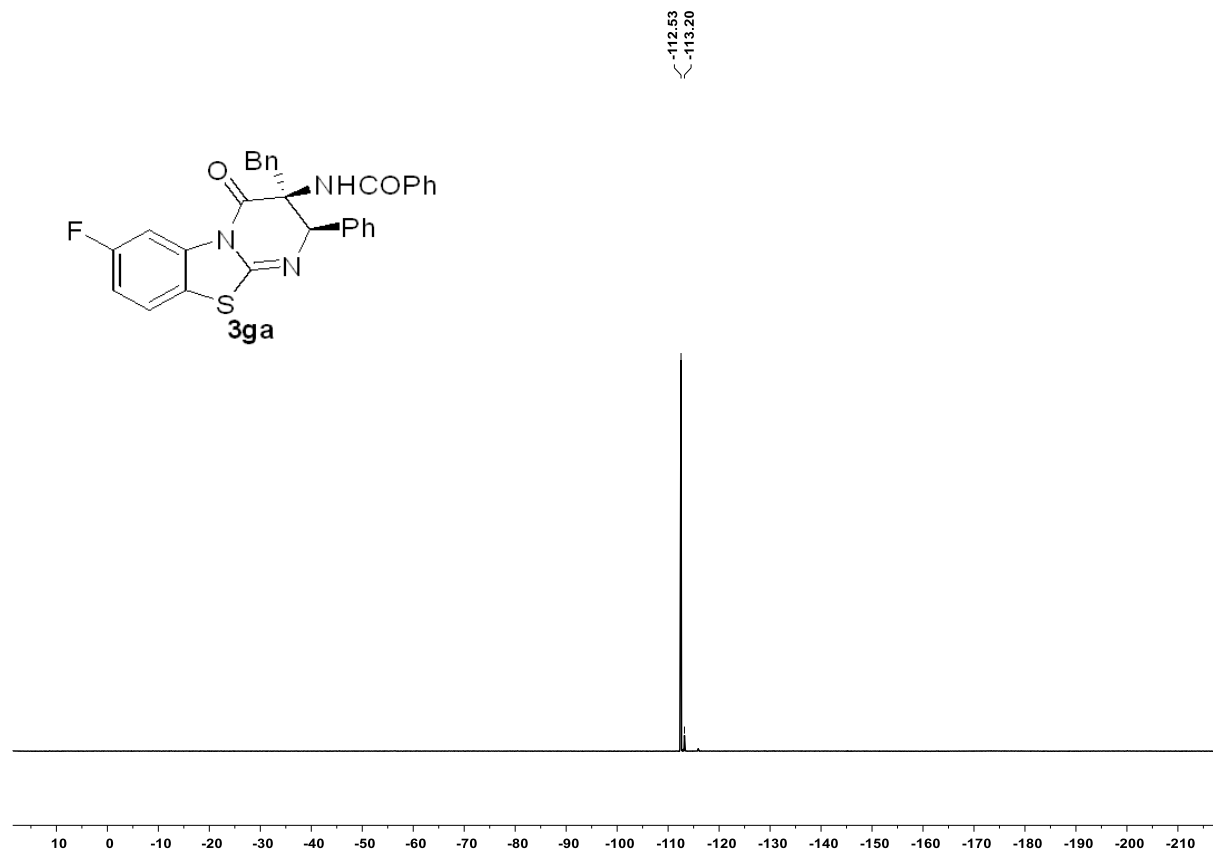


Figure S17. <sup>1</sup>H NMR of 3ha

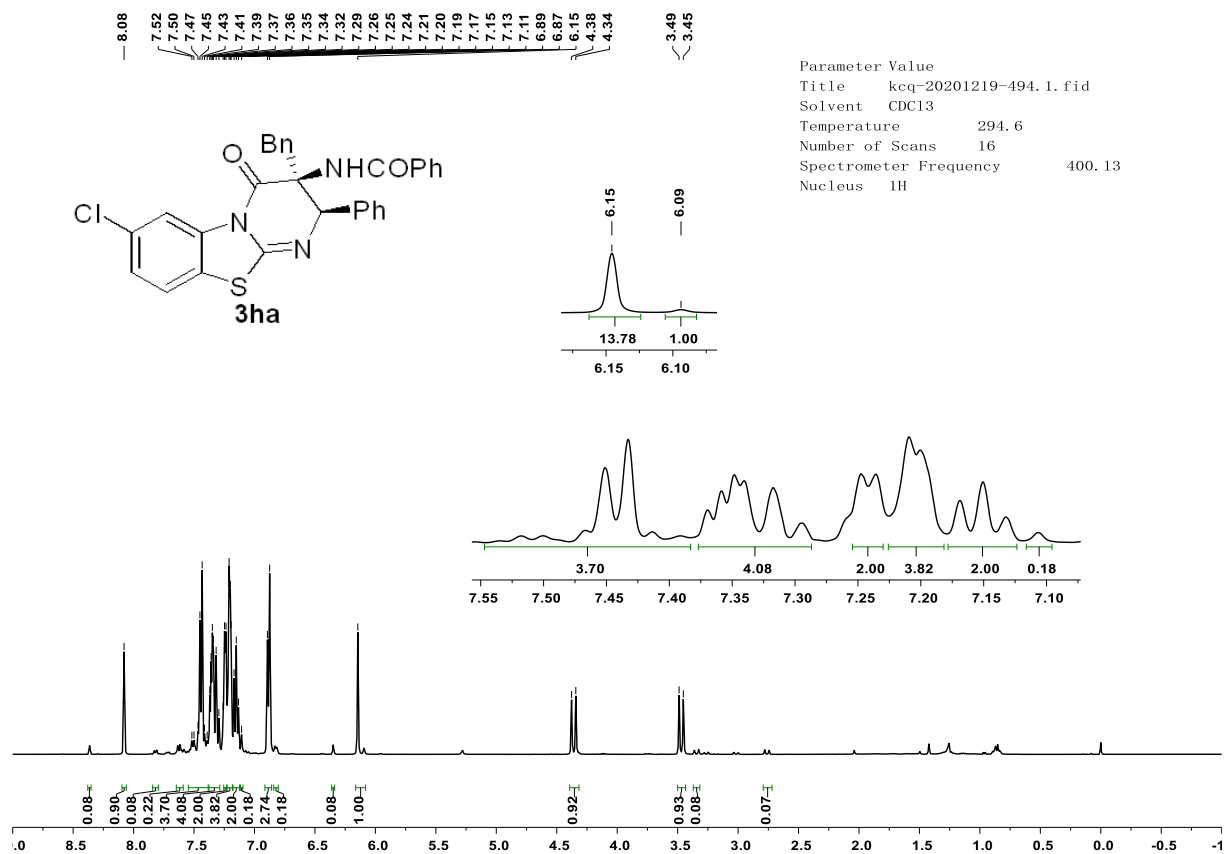


Figure S18. <sup>13</sup>C NMR of 3ha

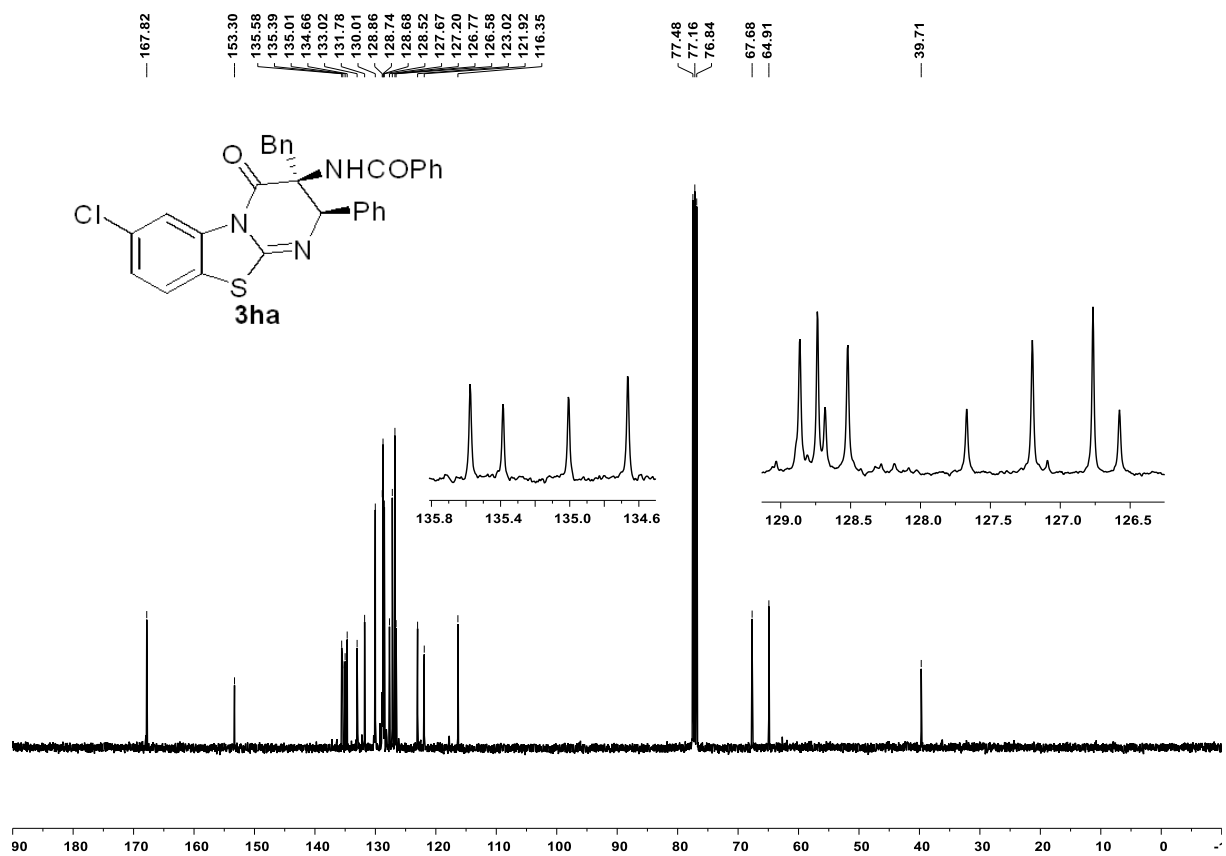


Figure S19. <sup>1</sup>H NMR of 3ia

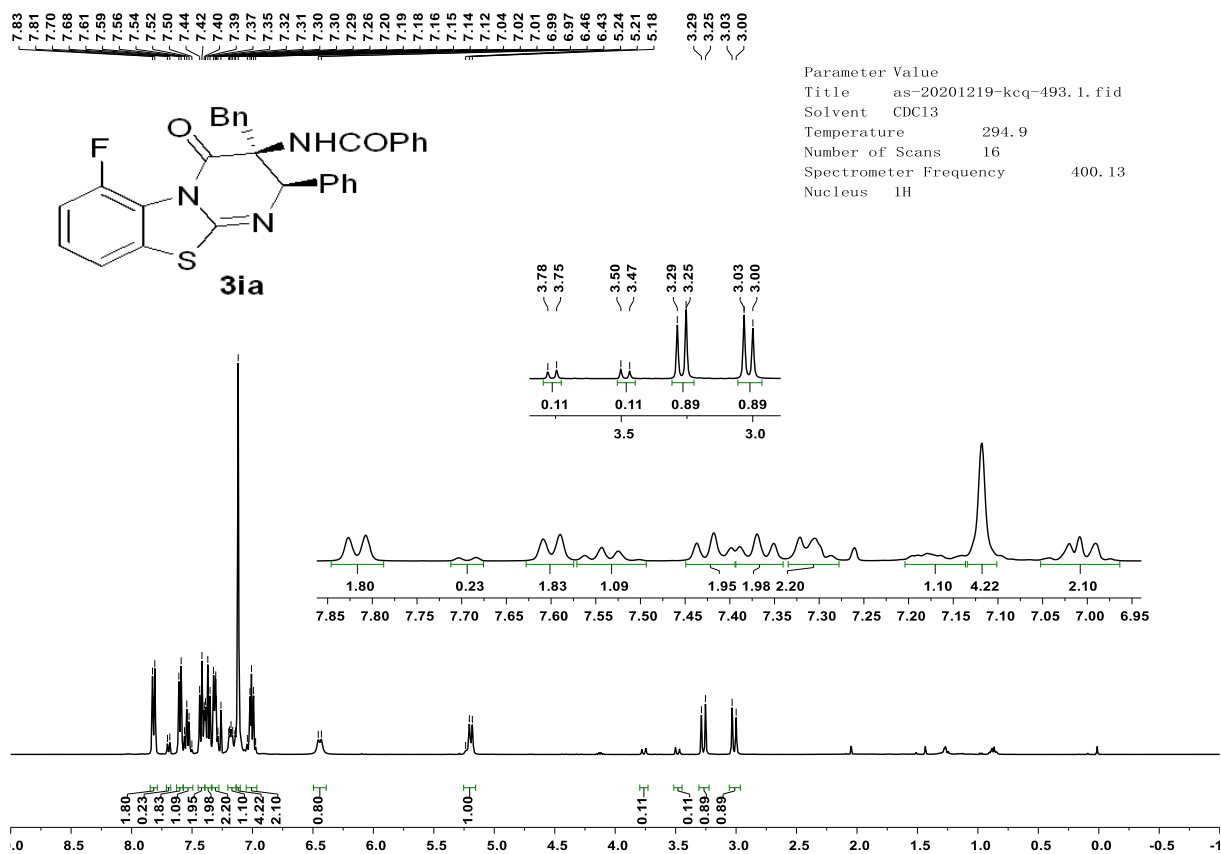


Figure S20. <sup>13</sup>C NMR of 3ia

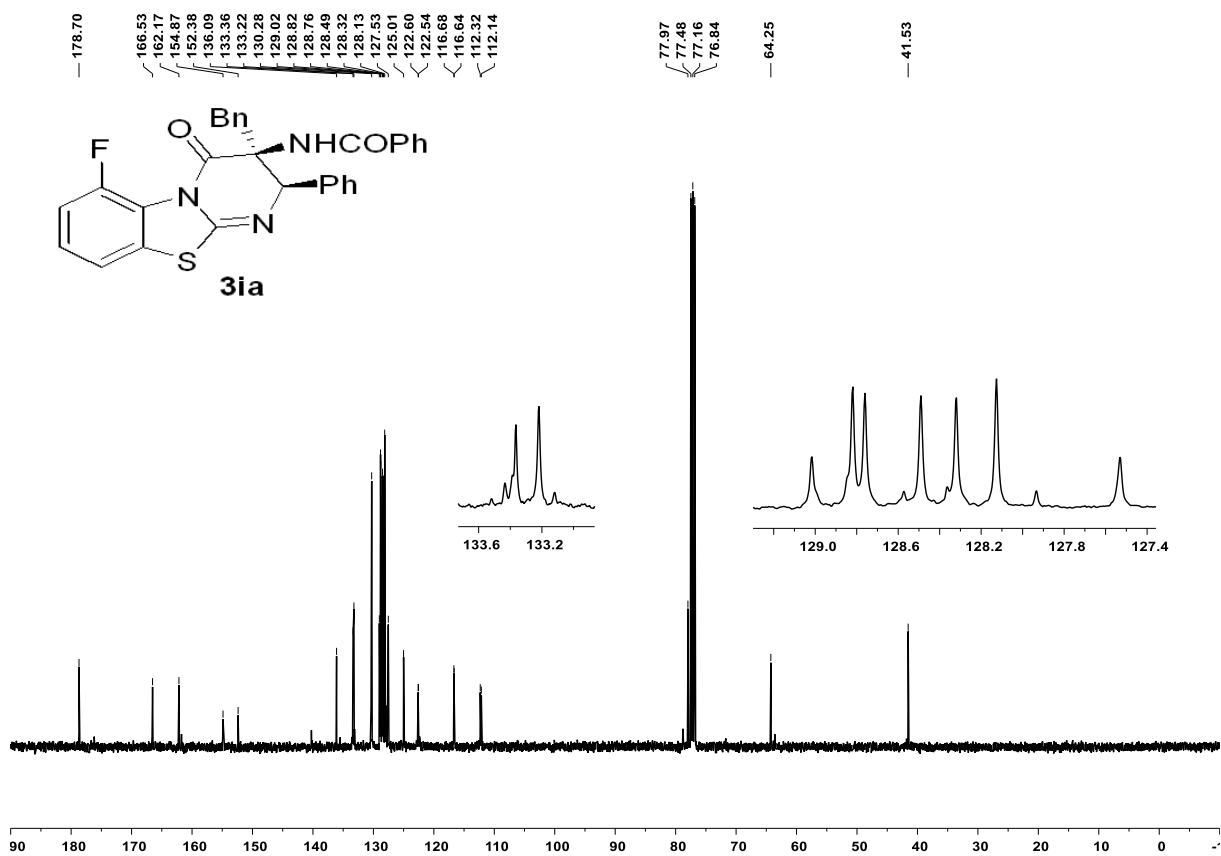


Figure S21.  $^{19}\text{F}\{^1\text{H}\}$  NMR of **3ia**

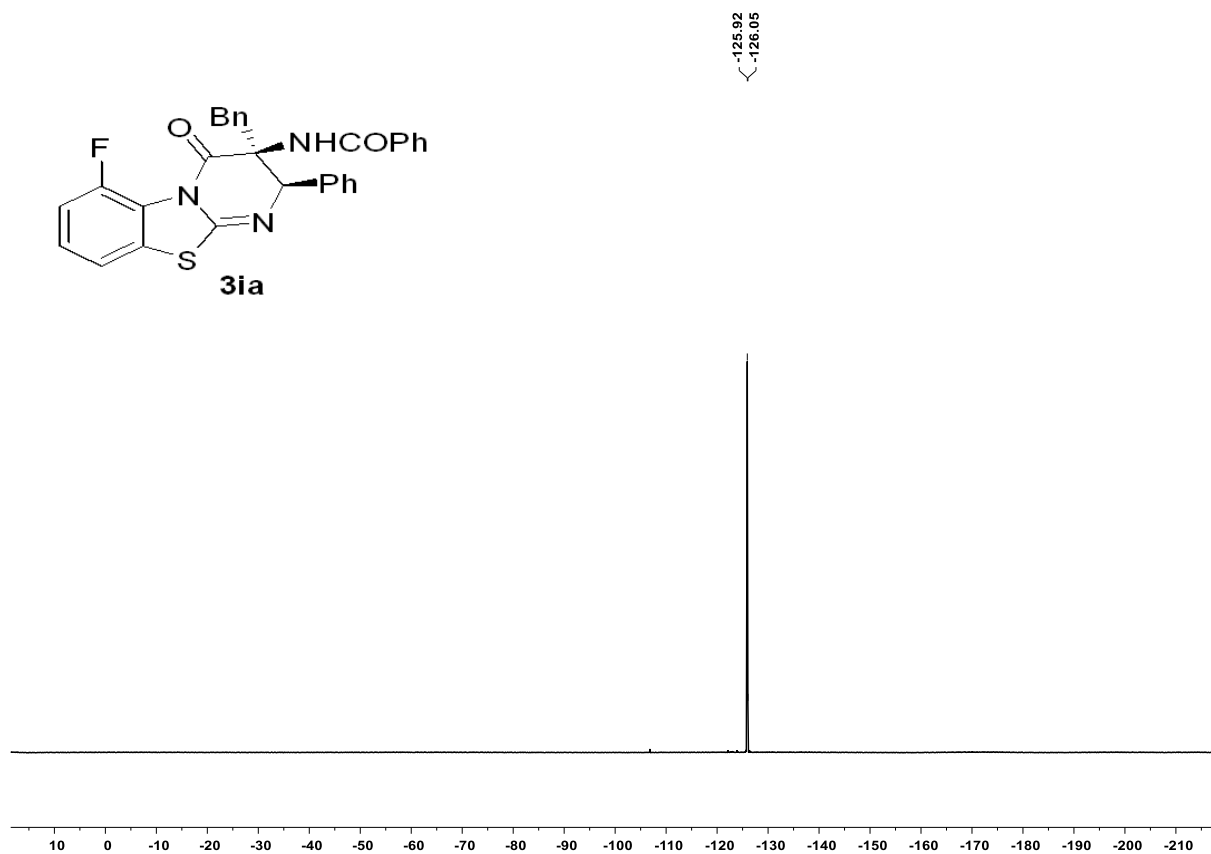


Figure S22.  $^1\text{H}$  NMR of **3ja**

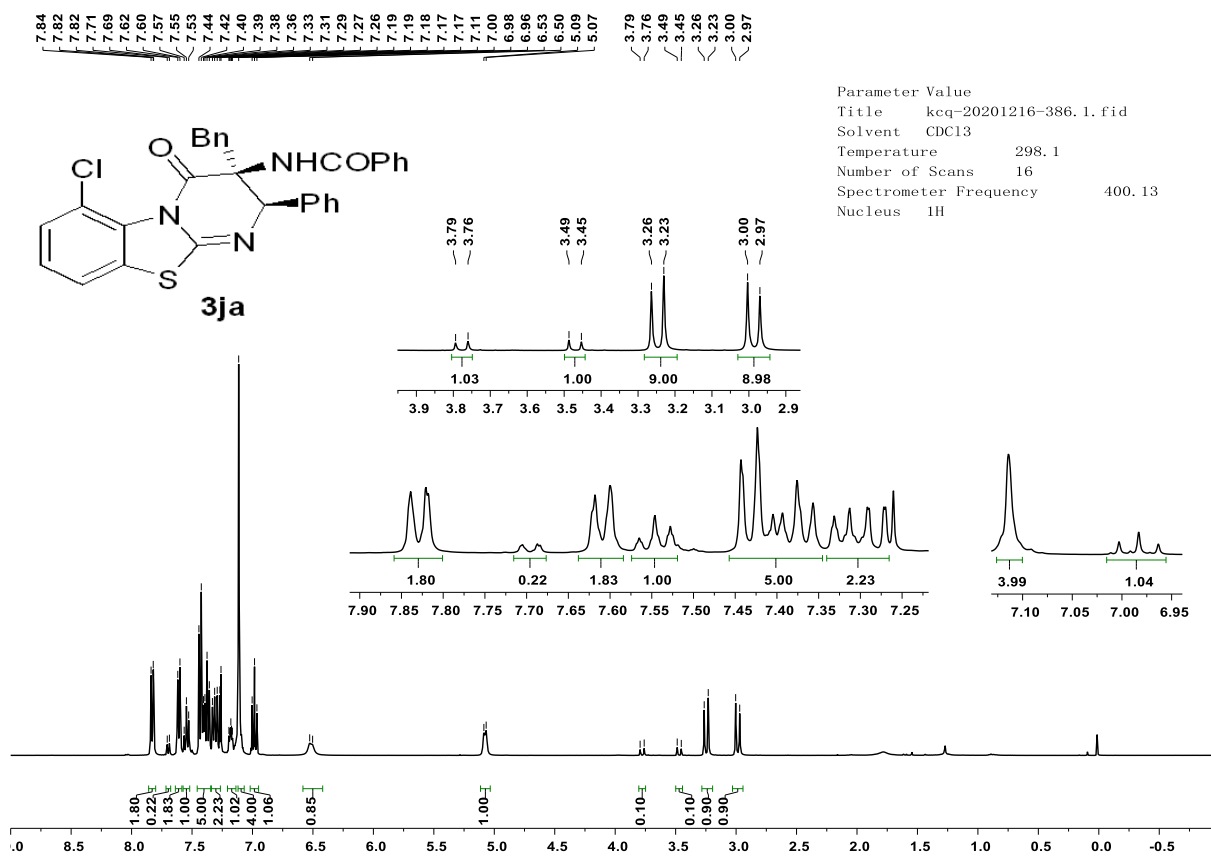




Figure S23. <sup>13</sup>C NMR of 3ja

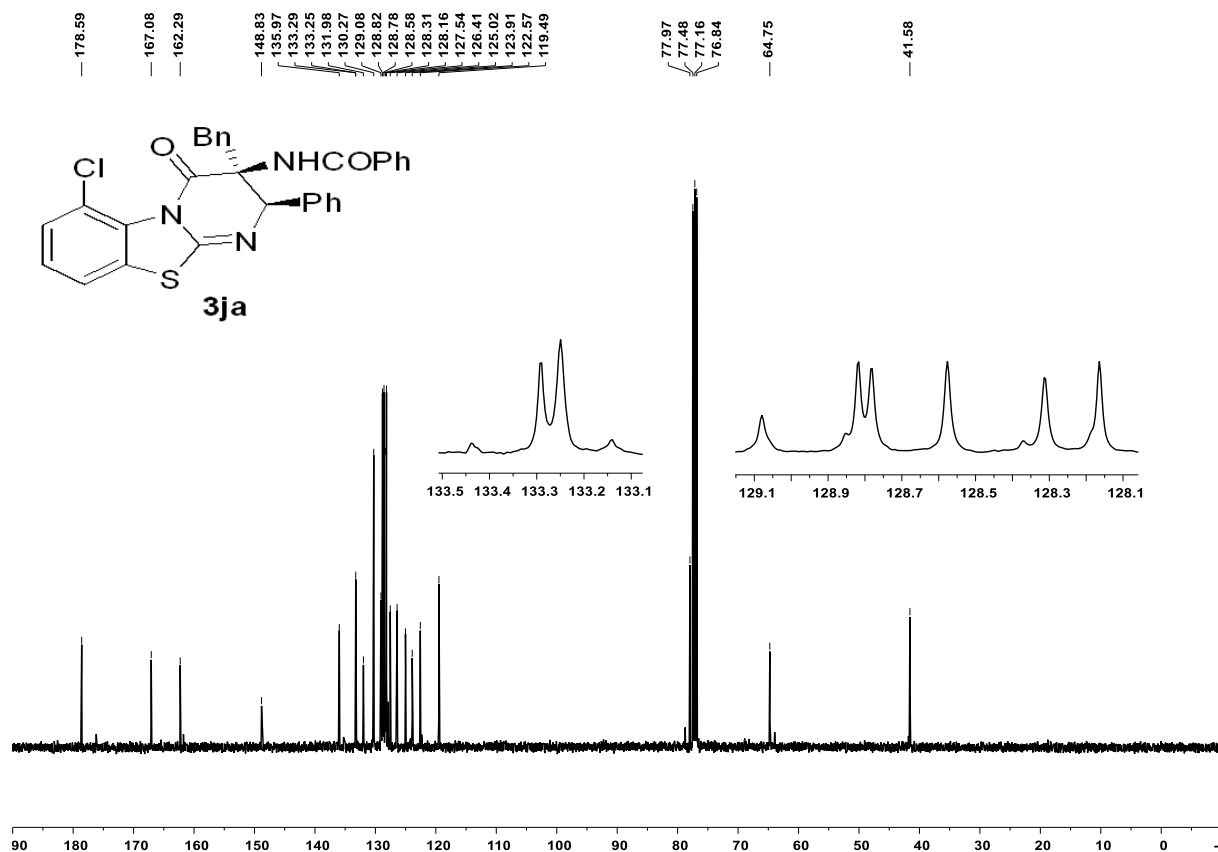


Figure S24. <sup>1</sup>H NMR of 3ka

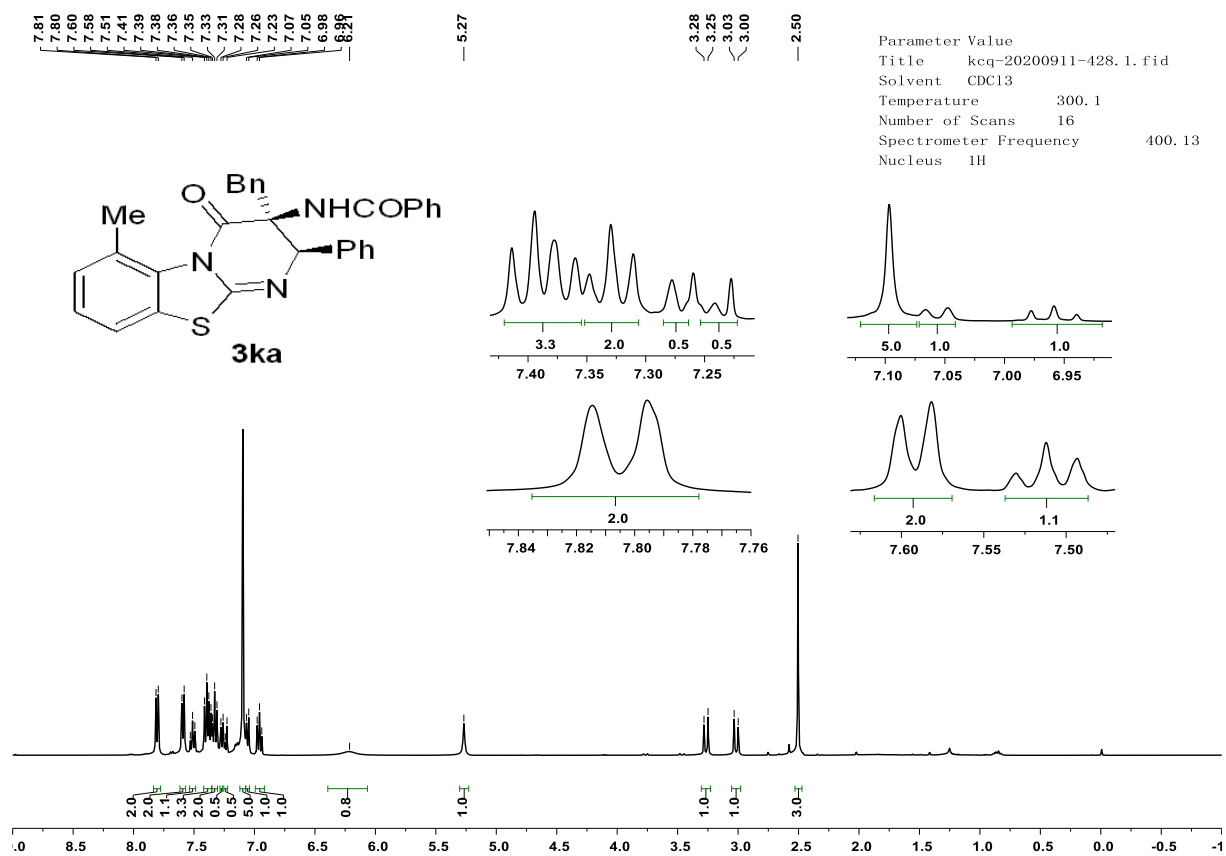


Figure S25. <sup>13</sup>C NMR of 3ka

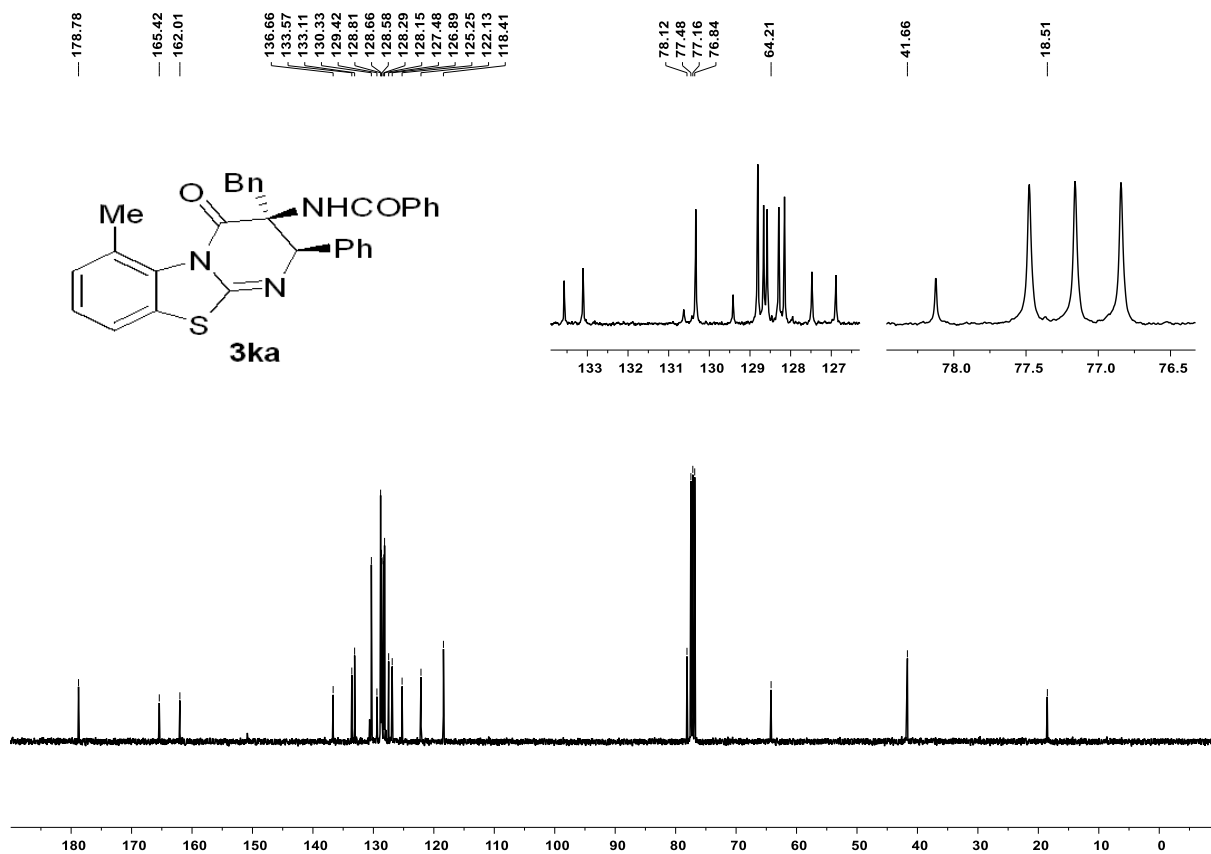


Figure S26. <sup>1</sup>H NMR of 3la

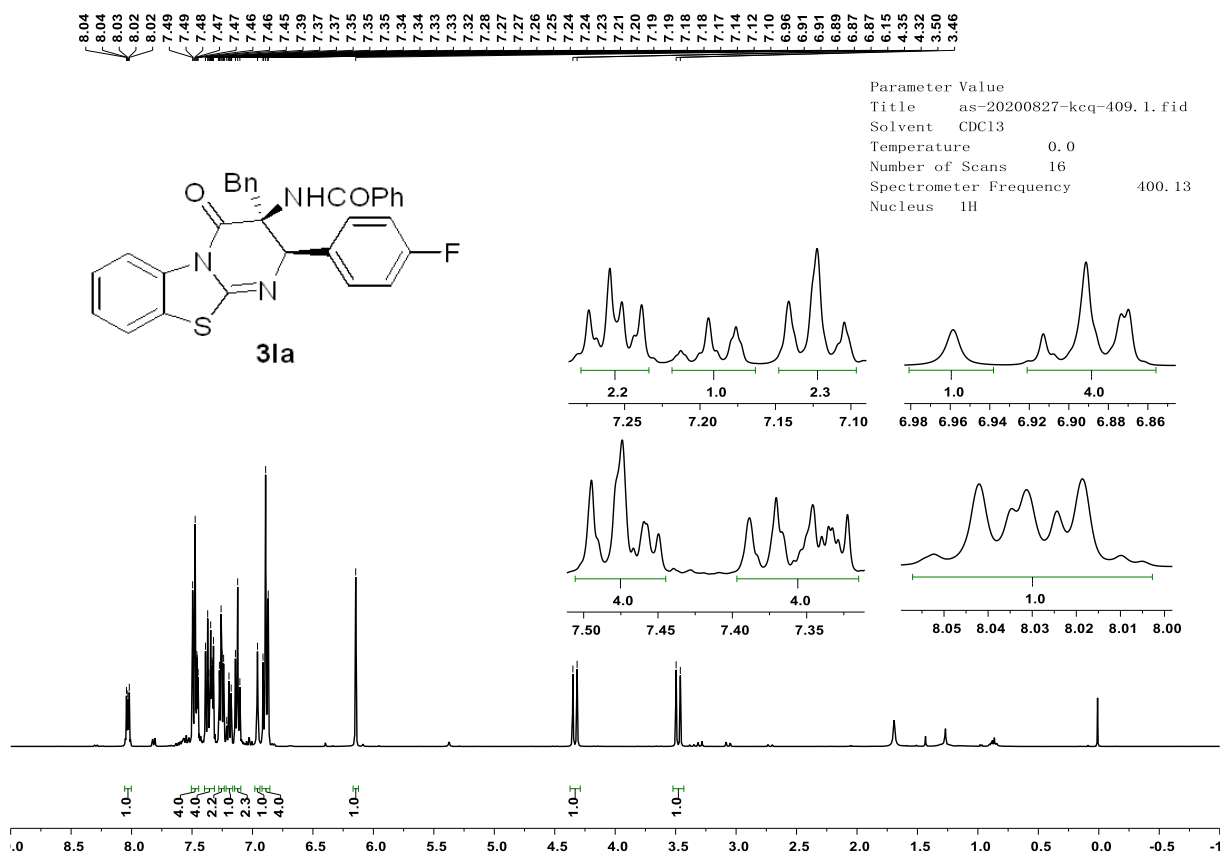


Figure S27.  $^{13}\text{C}$  NMR of 3la

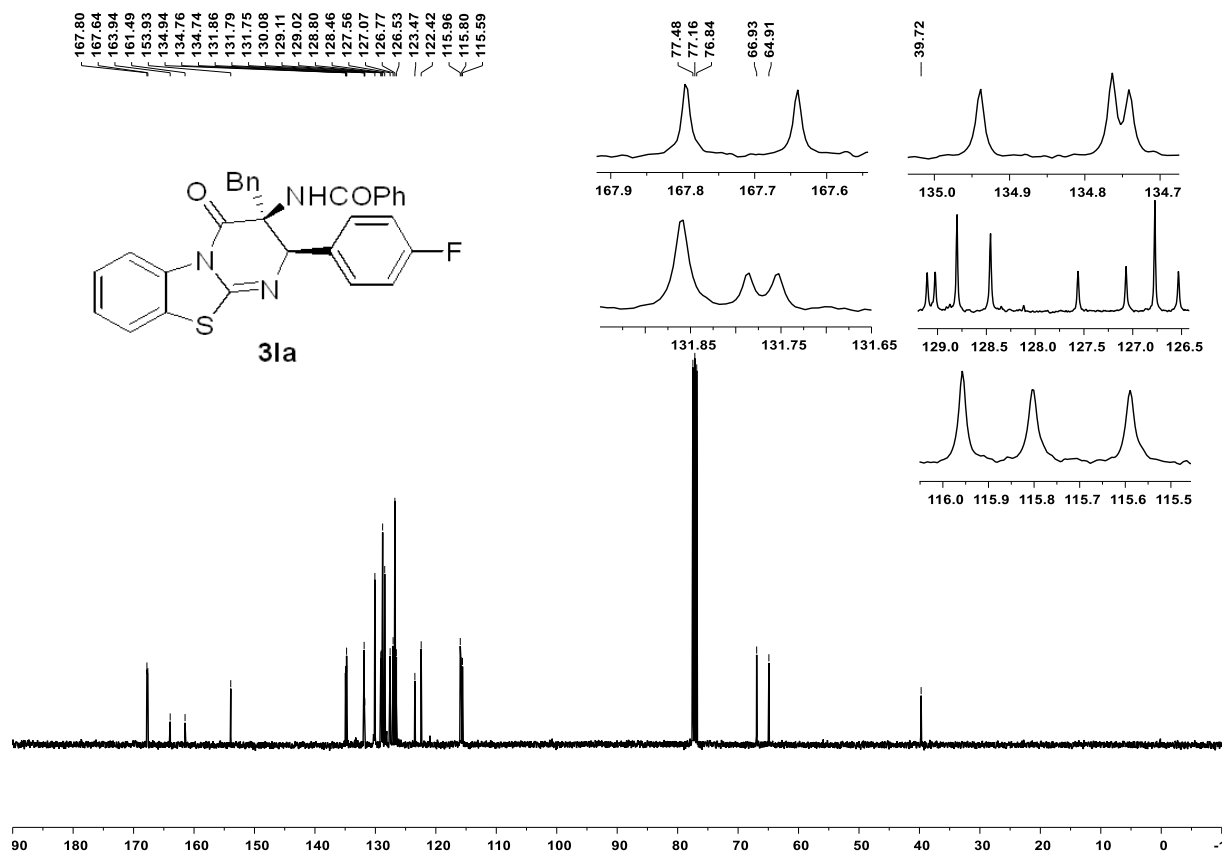


Figure S28.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3la

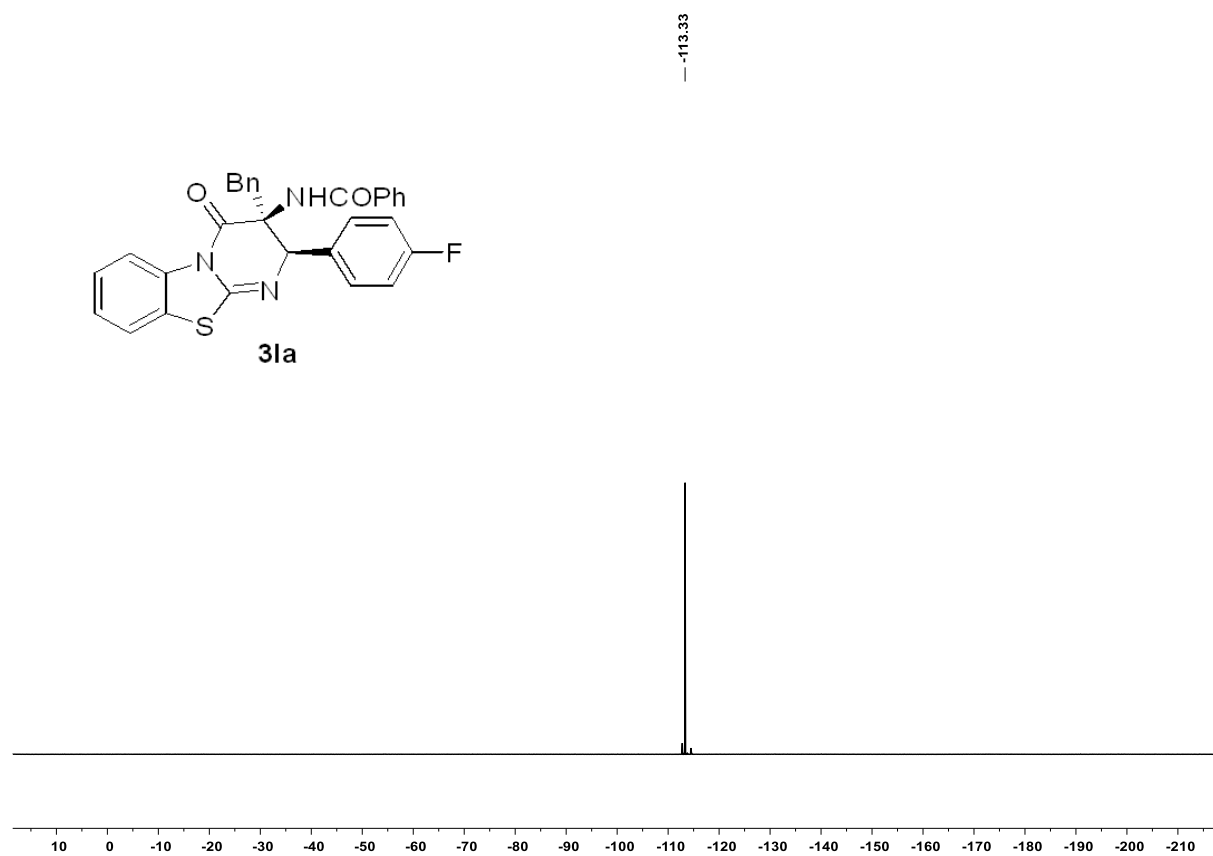


Figure S29. <sup>1</sup>H NMR of 3ma

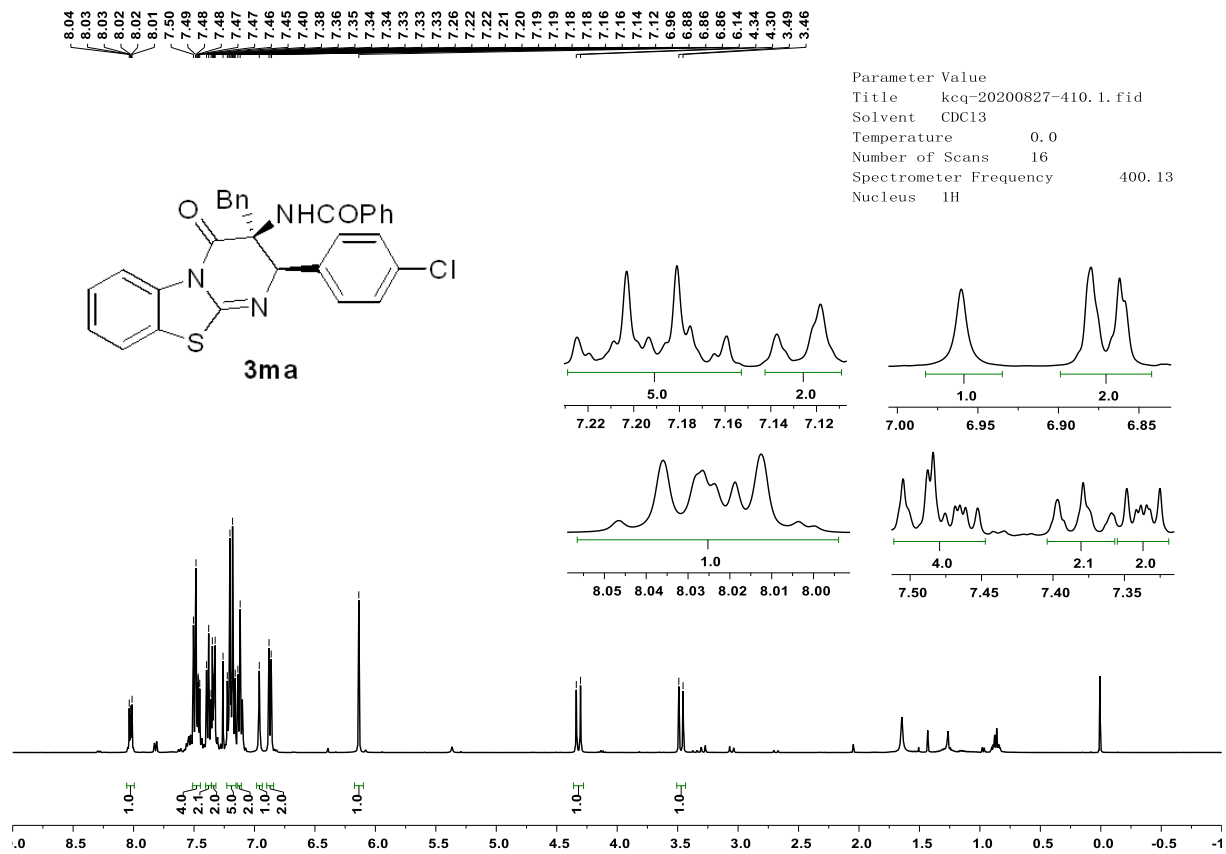


Figure S30. <sup>13</sup>C NMR of 3ma

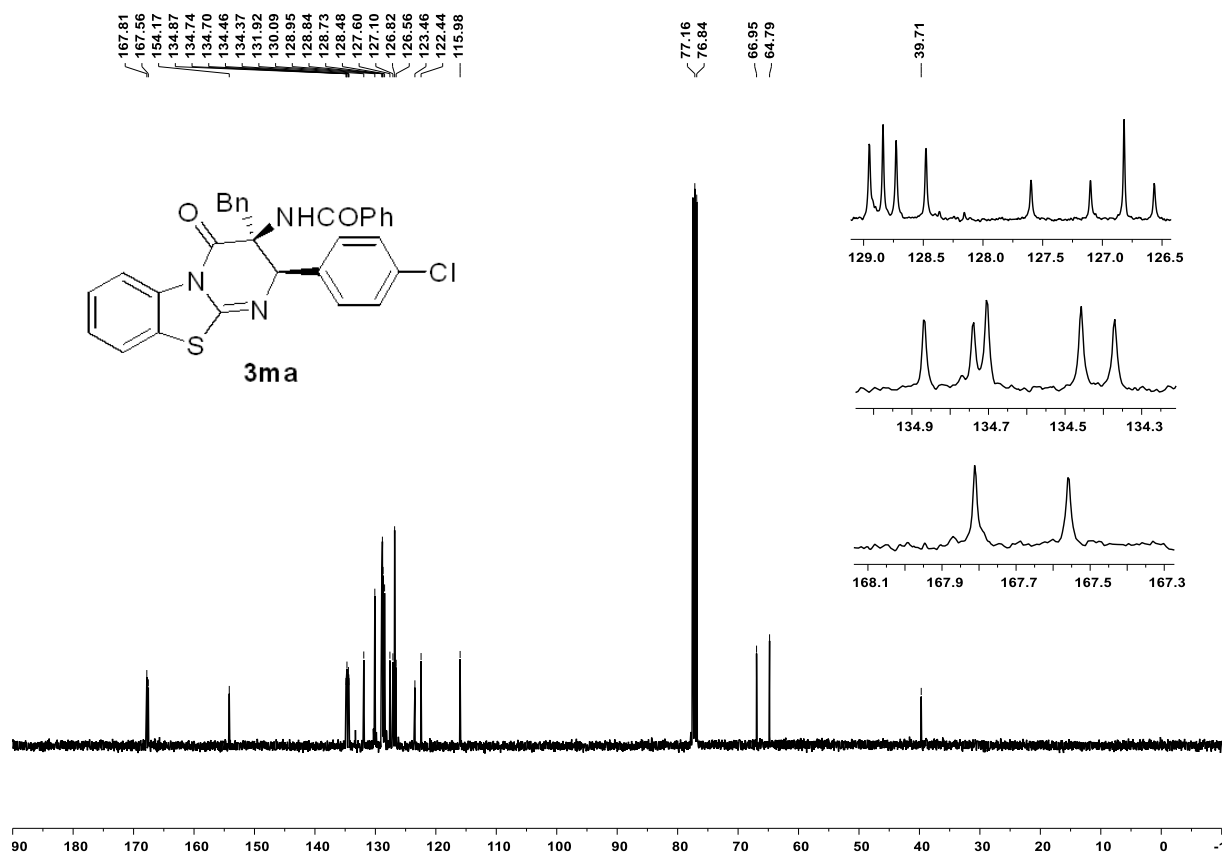


Figure S31. <sup>1</sup>H NMR of 3na

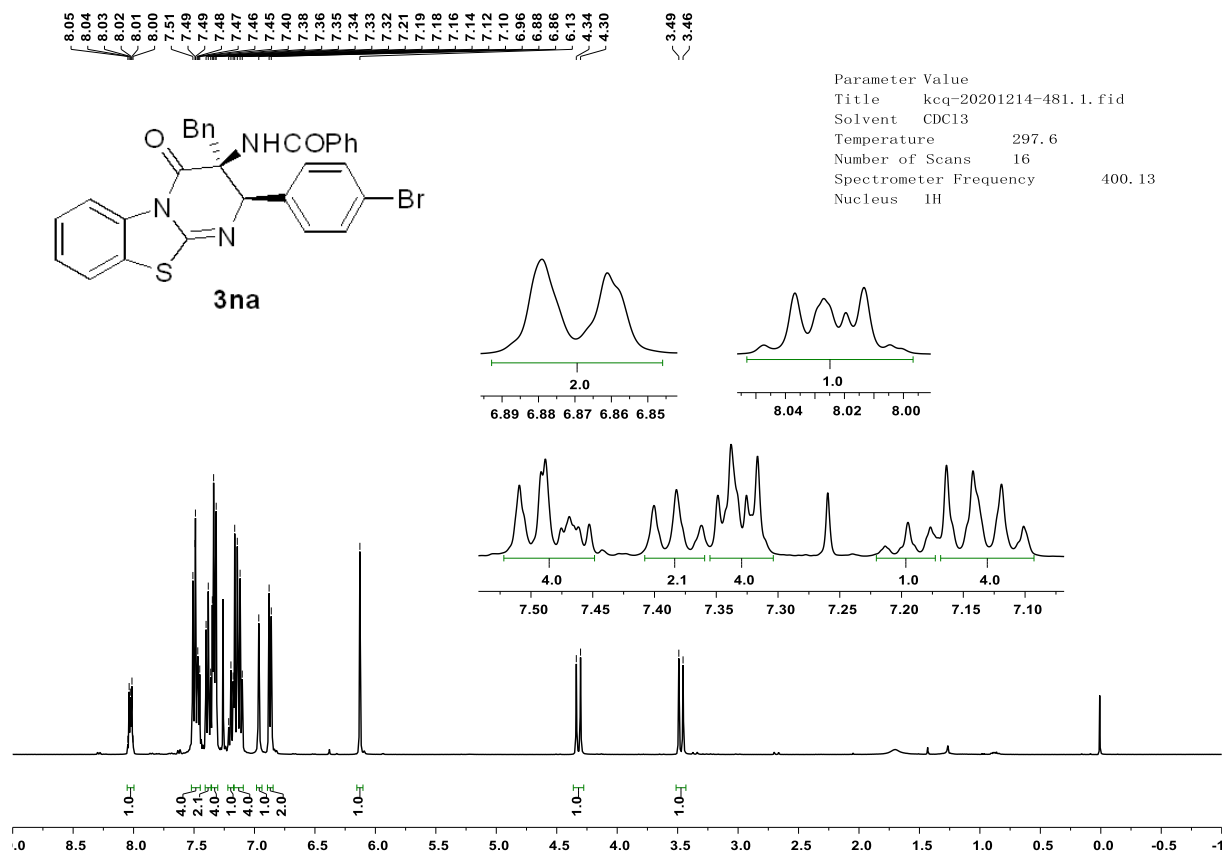


Figure S32. <sup>13</sup>C NMR of 3na

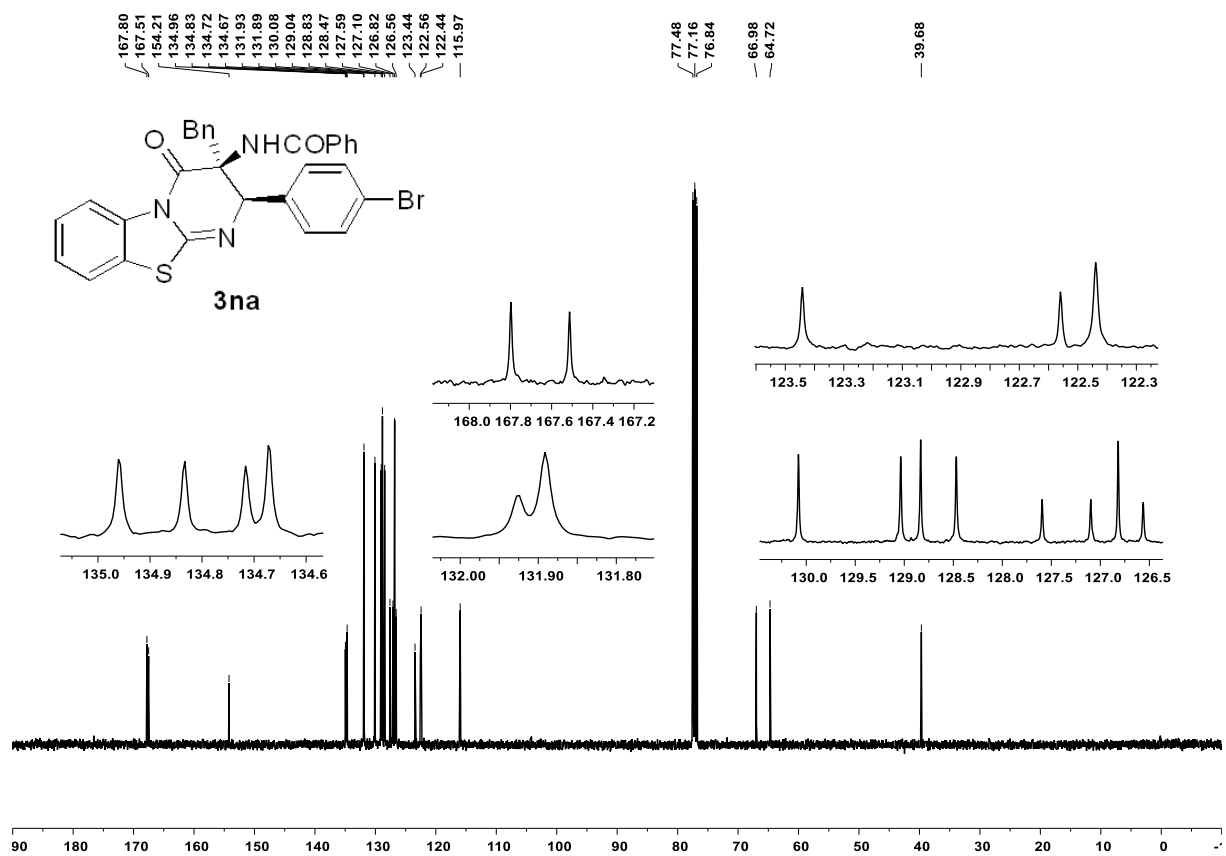


Figure S33. <sup>1</sup>H NMR of 30a

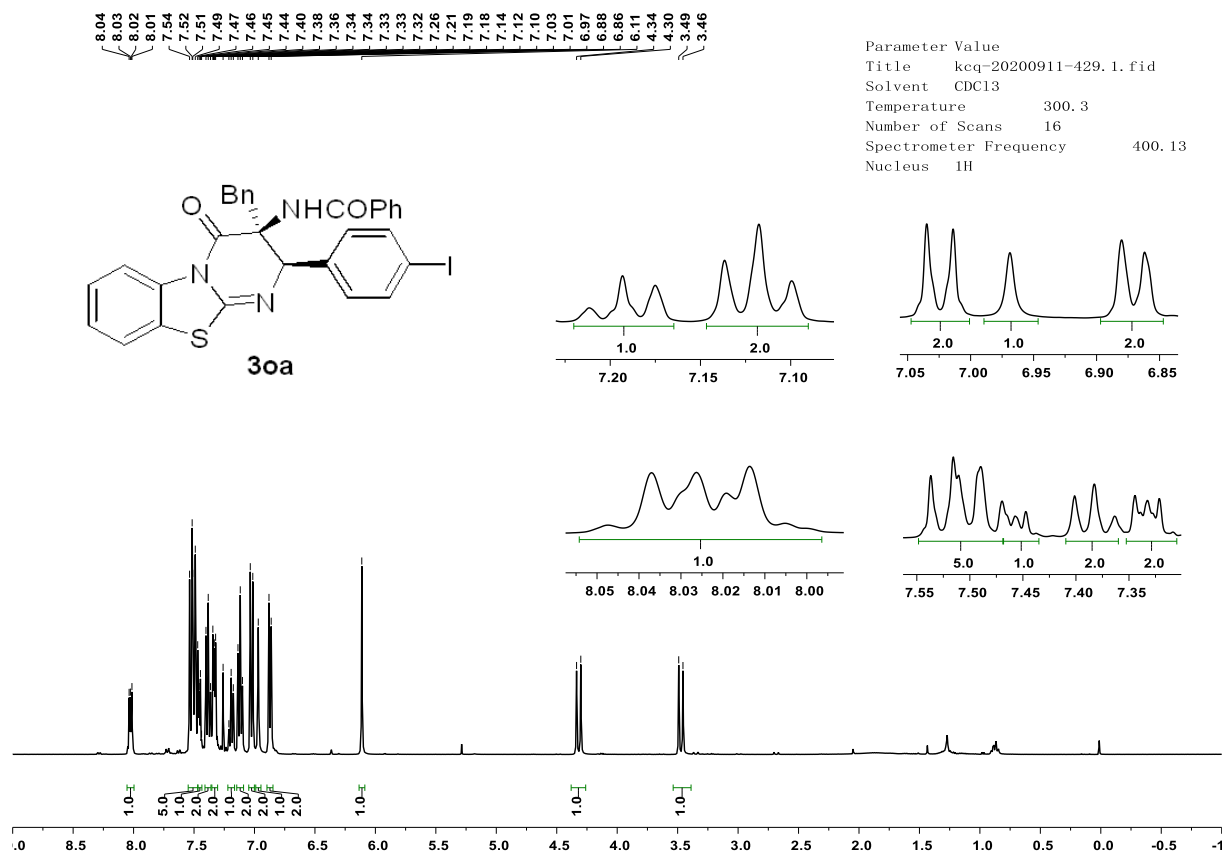


Figure S34. <sup>13</sup>C NMR of 30a

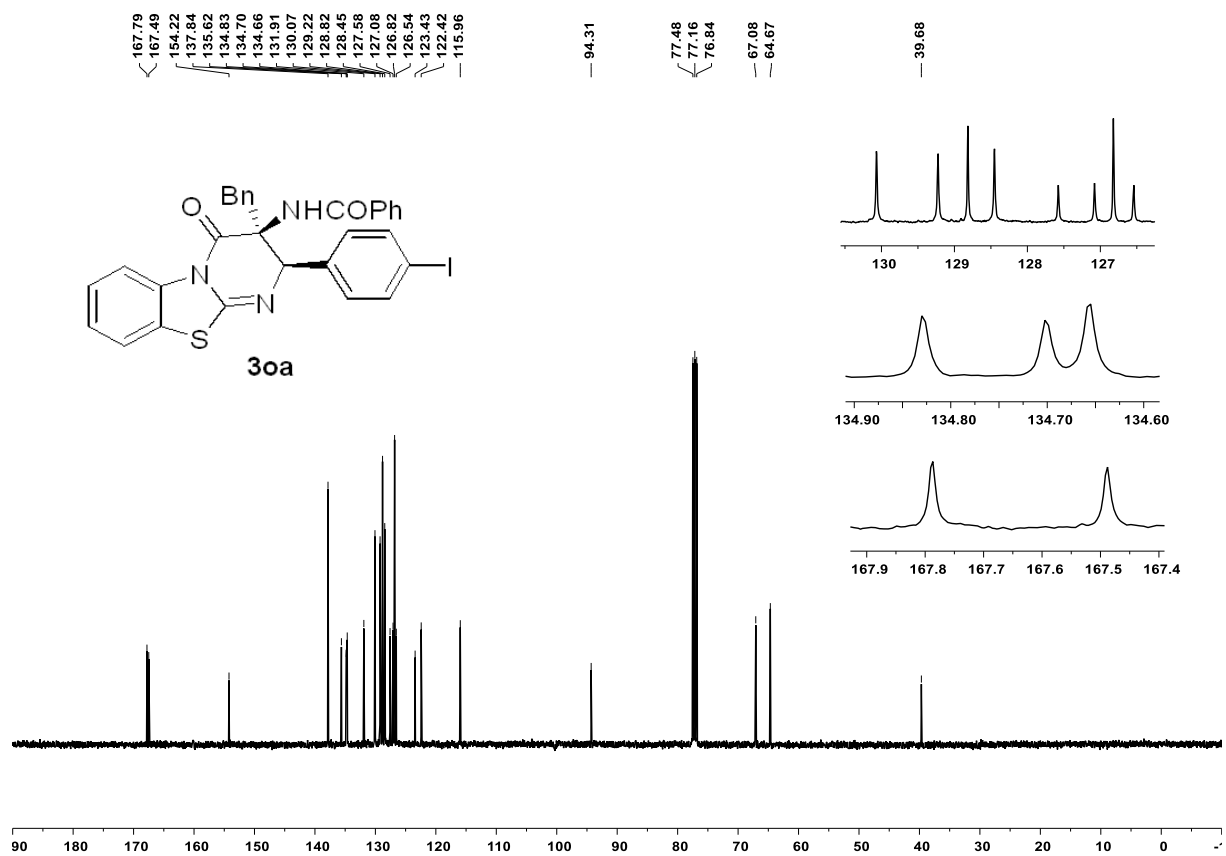


Figure S35. <sup>1</sup>H NMR of 3pa

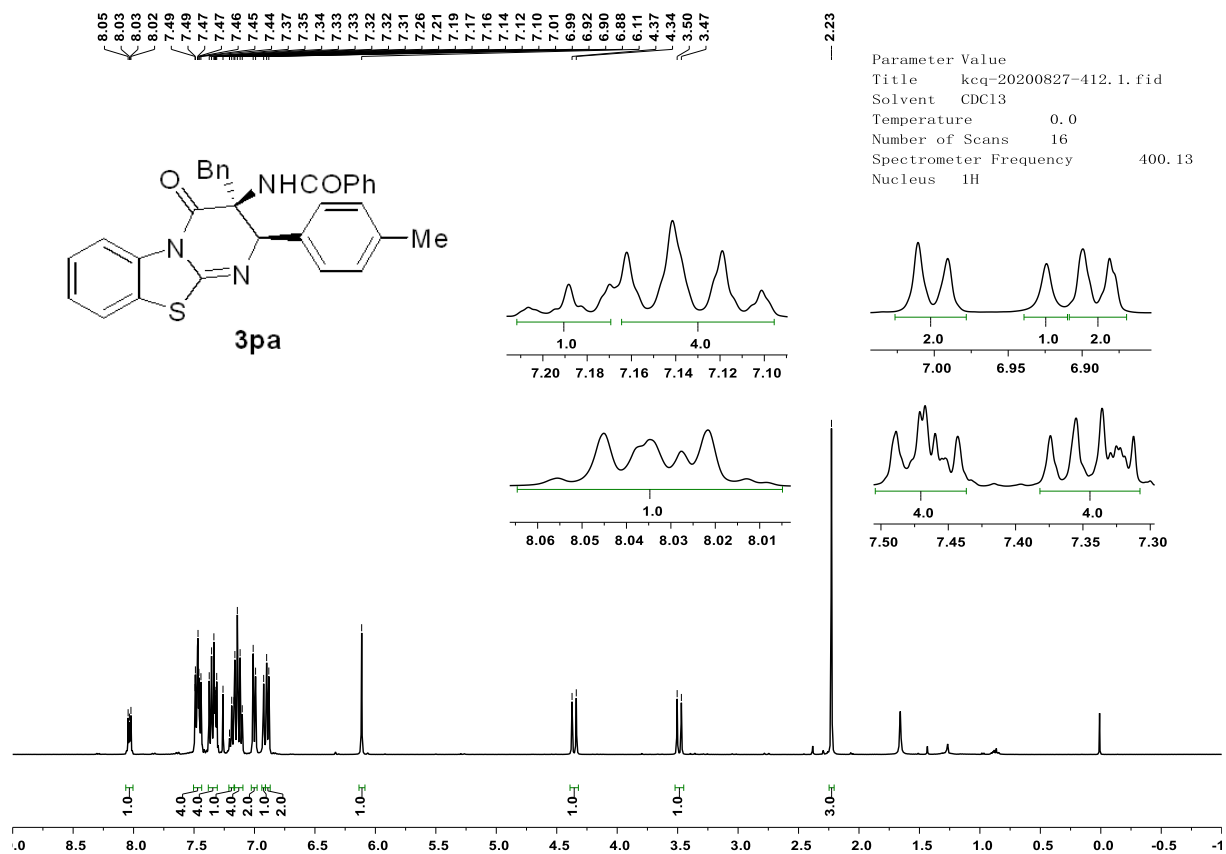


Figure S36. <sup>13</sup>C NMR of 3pa

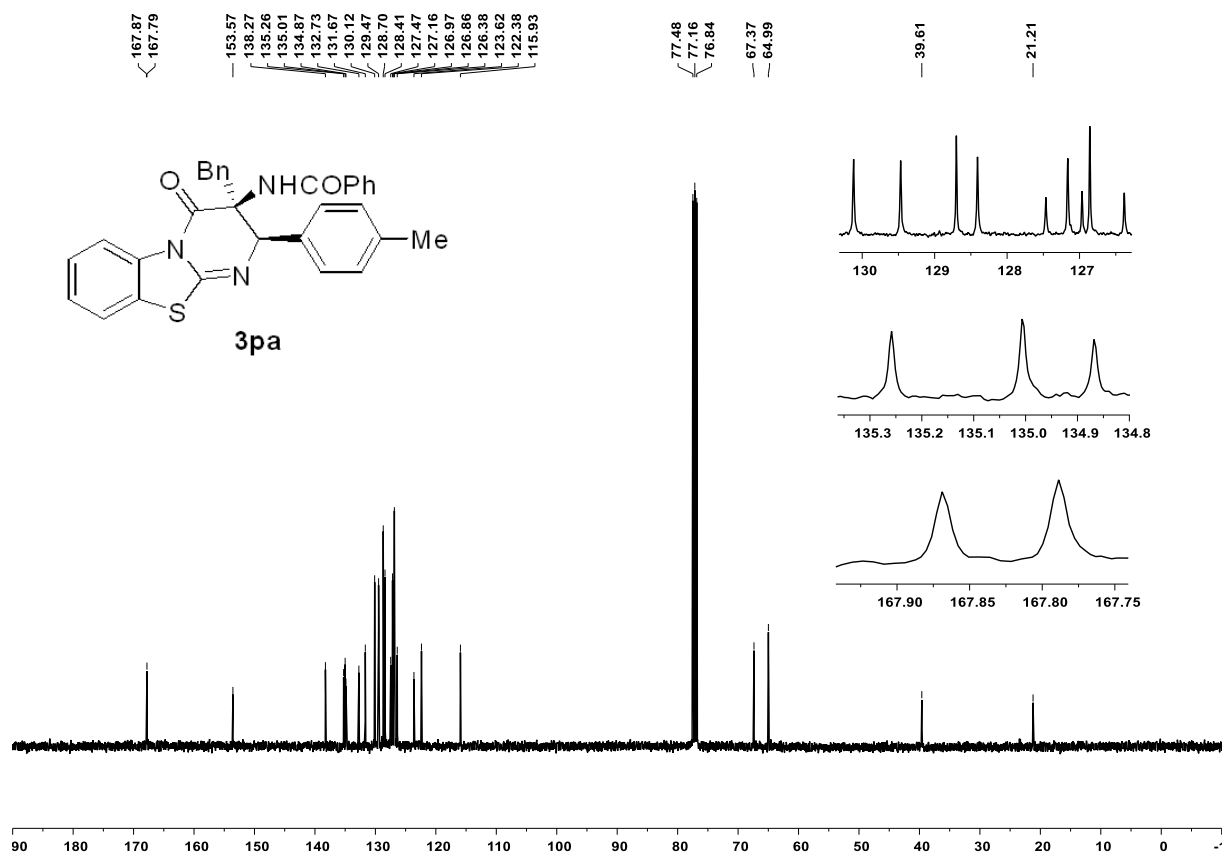


Figure S37. <sup>1</sup>H NMR of 3qa

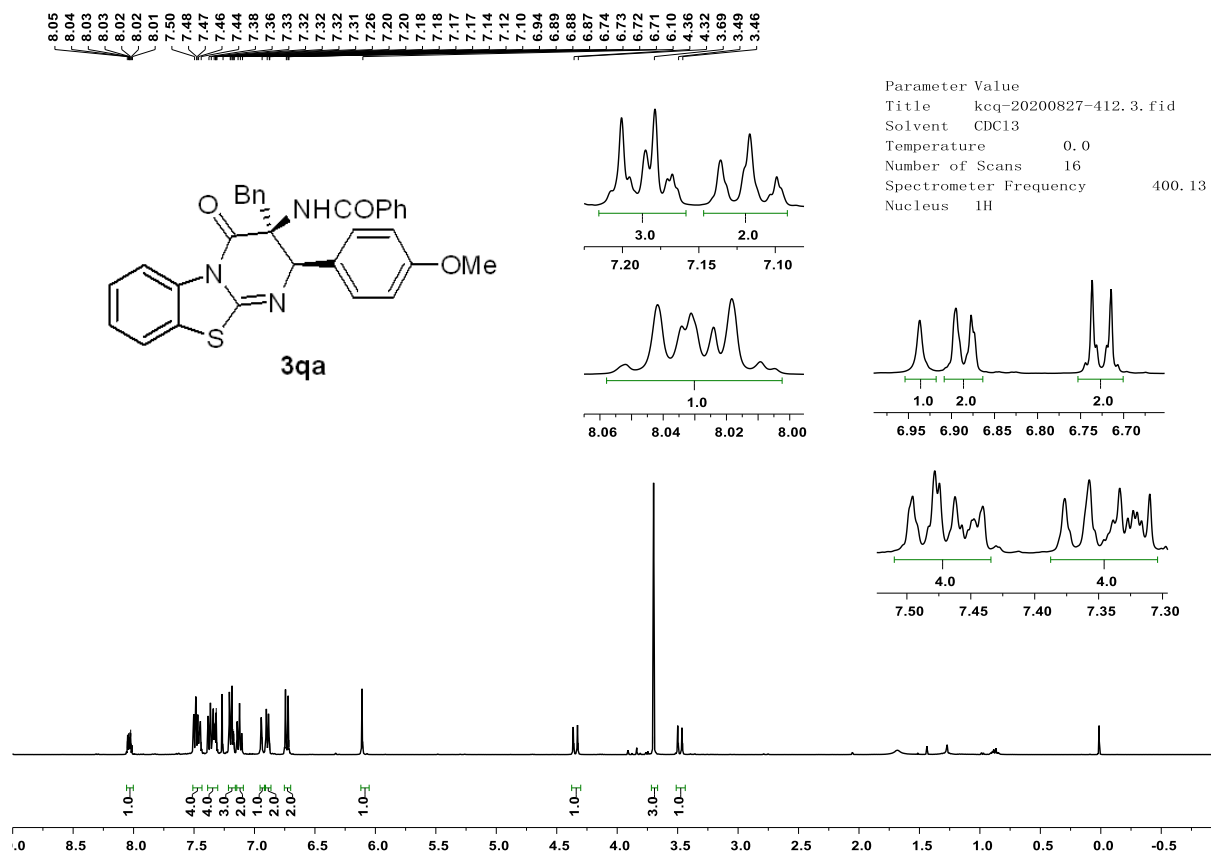


Figure S38. <sup>13</sup>C NMR of 3qa

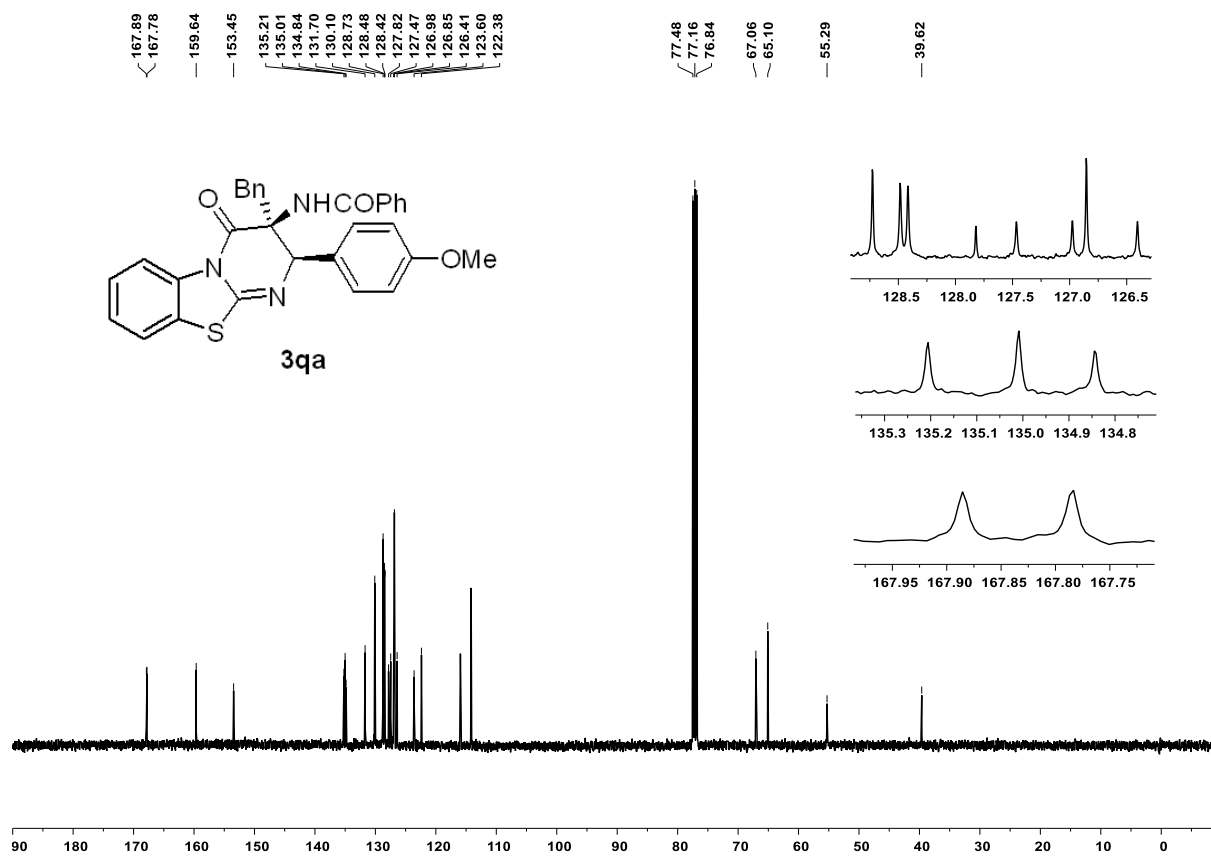




Figure S39. <sup>1</sup>H NMR of 3ra

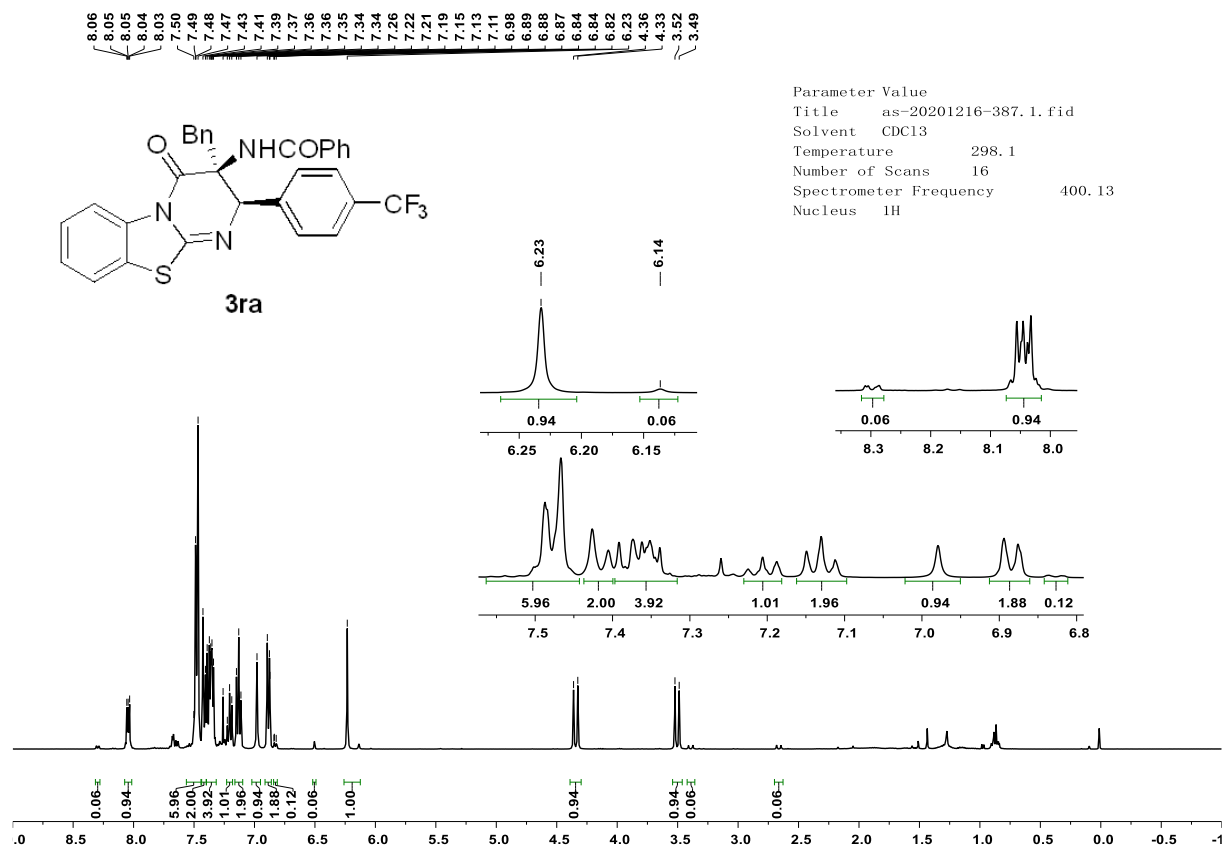


Figure S40. <sup>13</sup>C NMR of 3ra

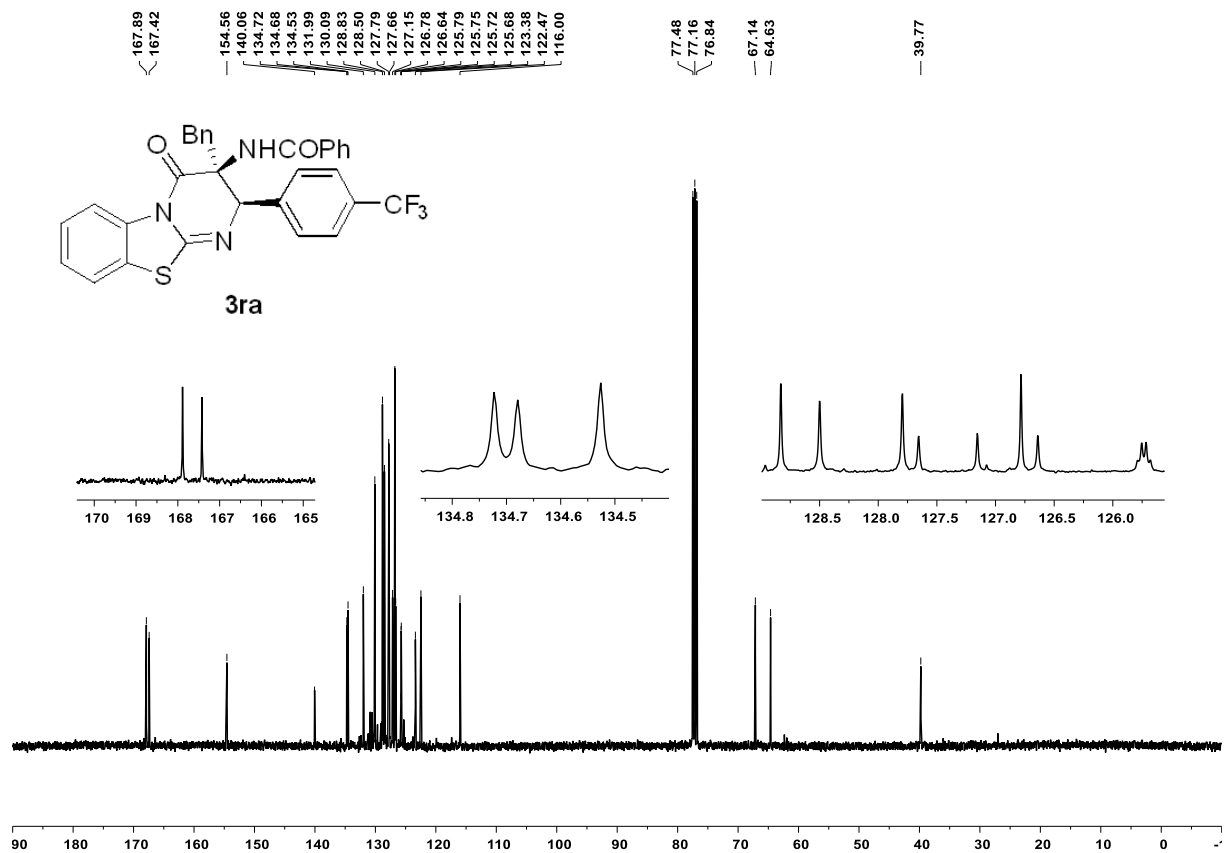


Figure S41.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3ra

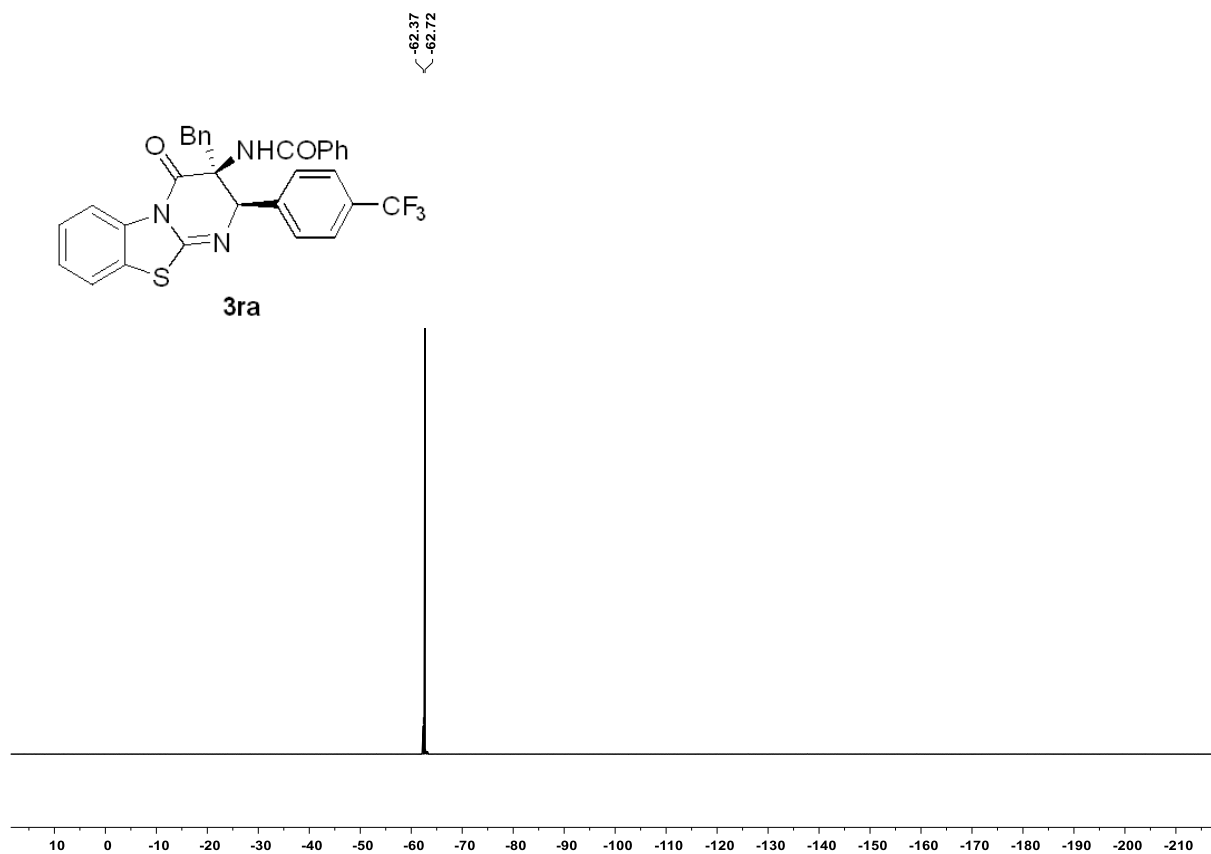


Figure S42.  $^1\text{H}$  NMR of 3sa

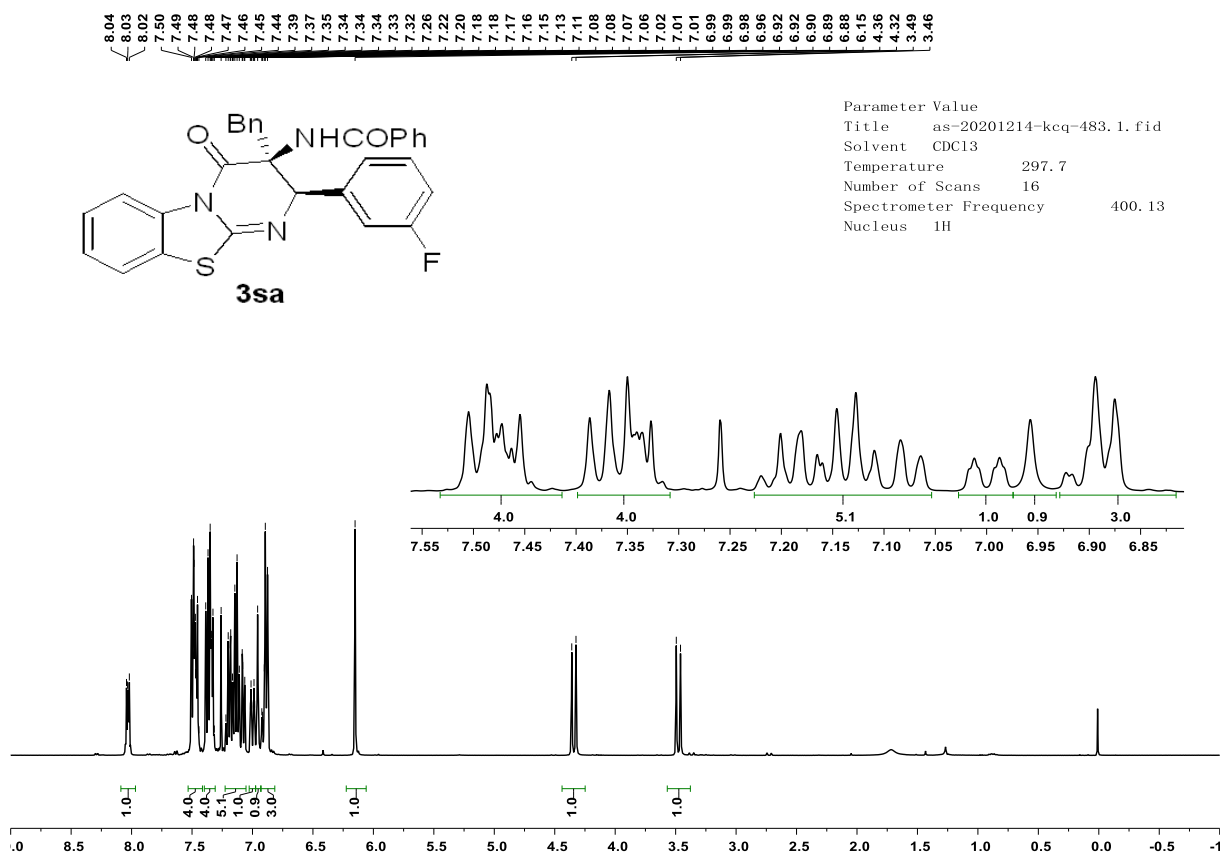


Figure S43.  $^{13}\text{C}$  NMR of 3sa

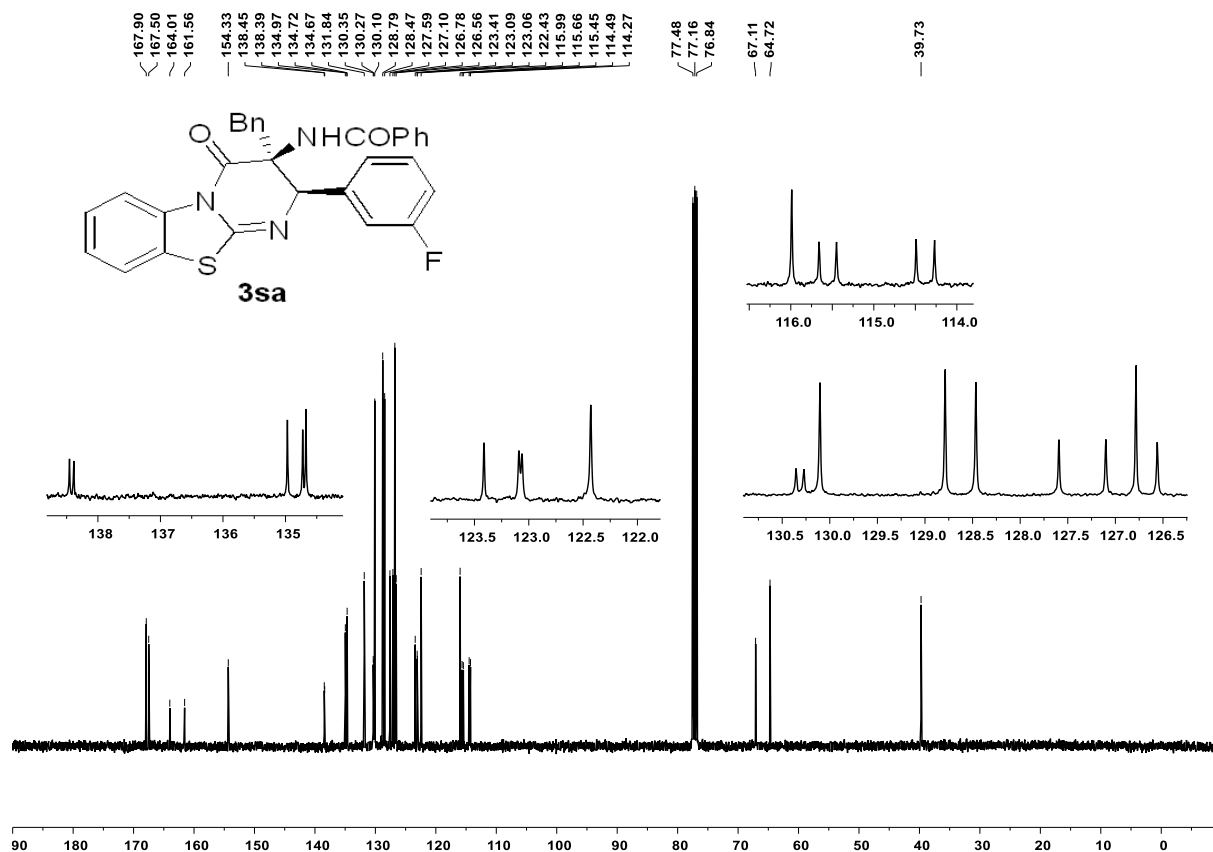


Figure S44.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3sa

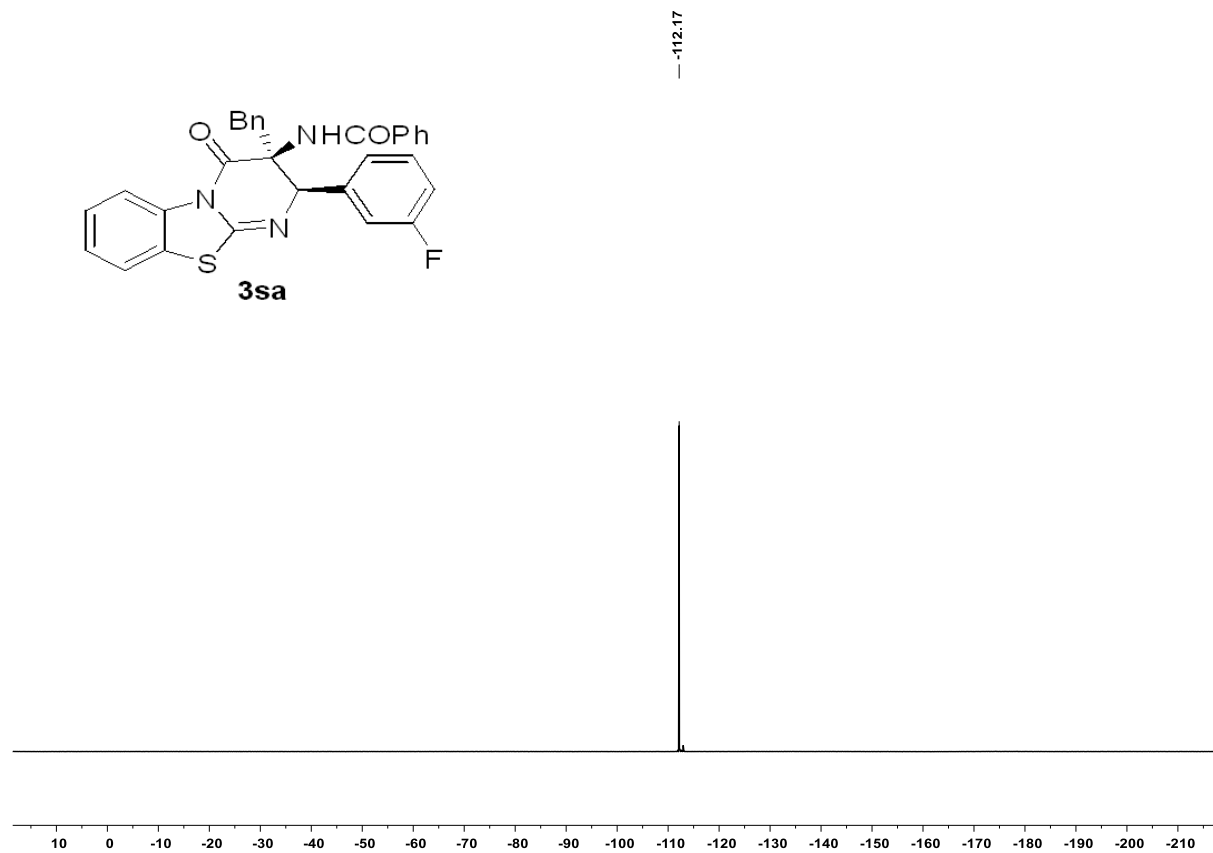


Figure S45. <sup>1</sup>H NMR of 3ta

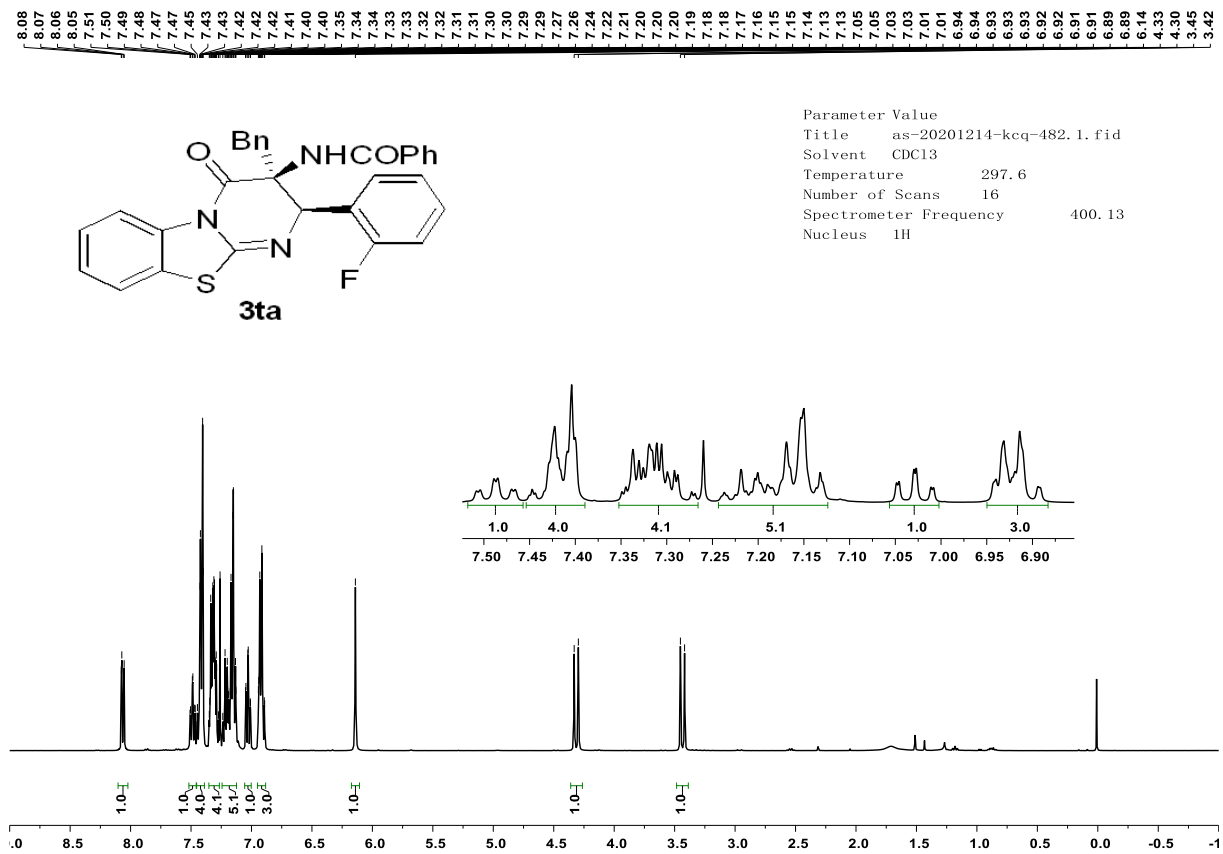


Figure S46. <sup>13</sup>C NMR of 3ta

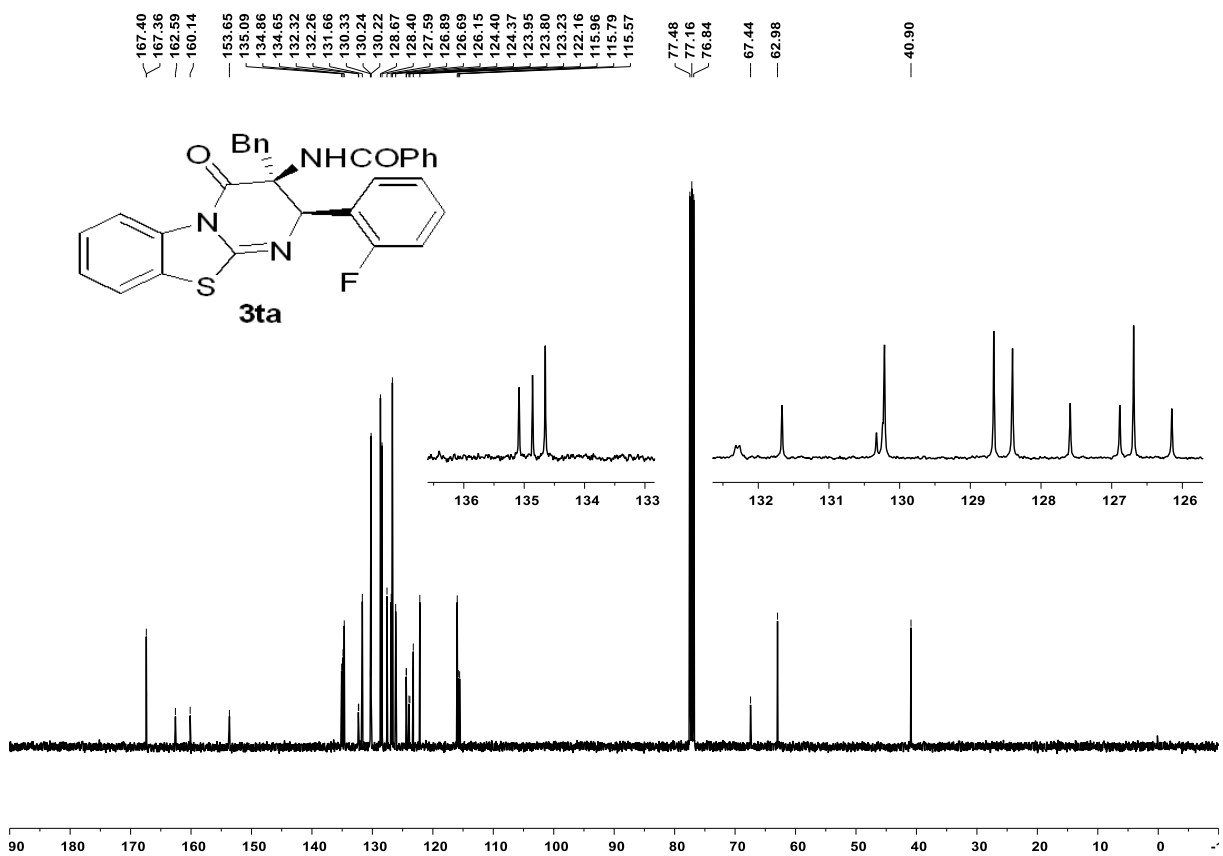




Figure S49. <sup>13</sup>C NMR of 3ua

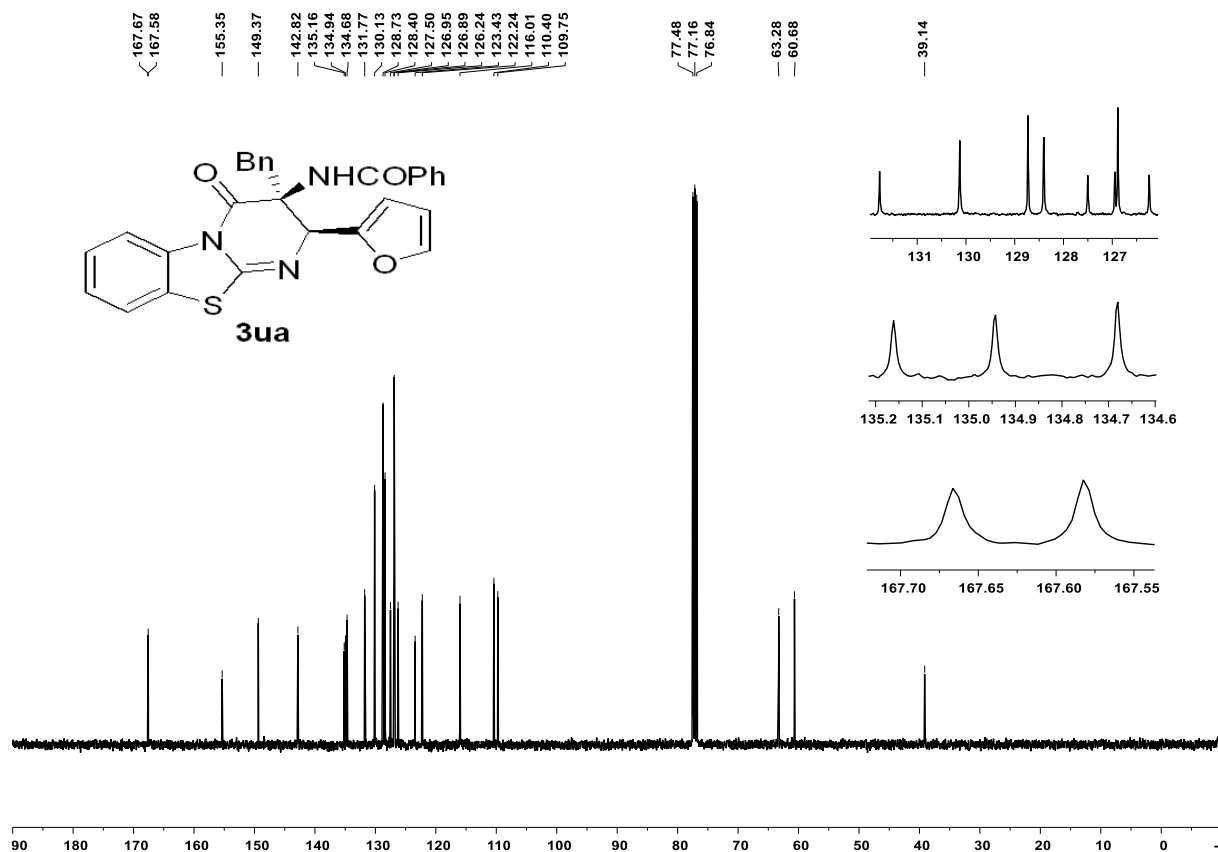


Figure S50. <sup>1</sup>H NMR of 3va

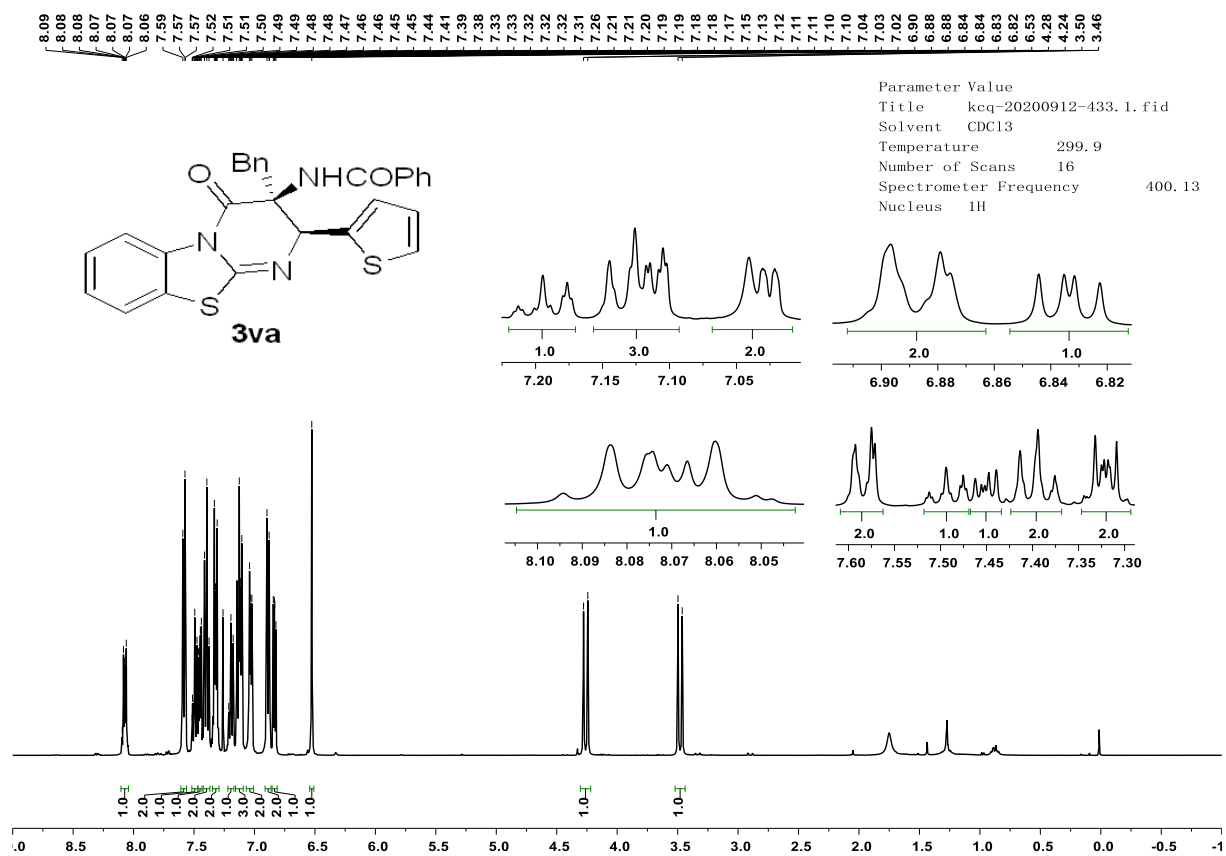


Figure S51.  $^{13}\text{C}$  NMR of 3va

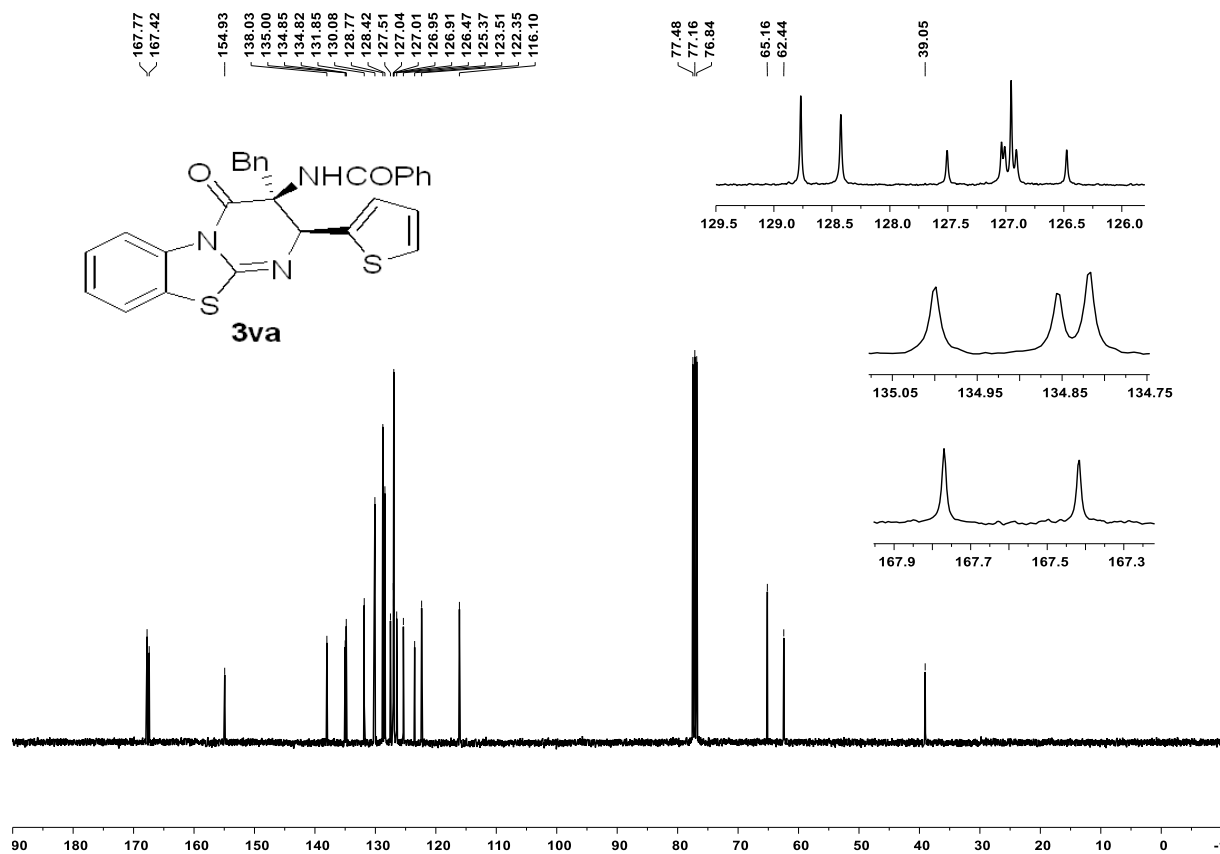


Figure S52.  $^1\text{H}$  NMR of 3wa

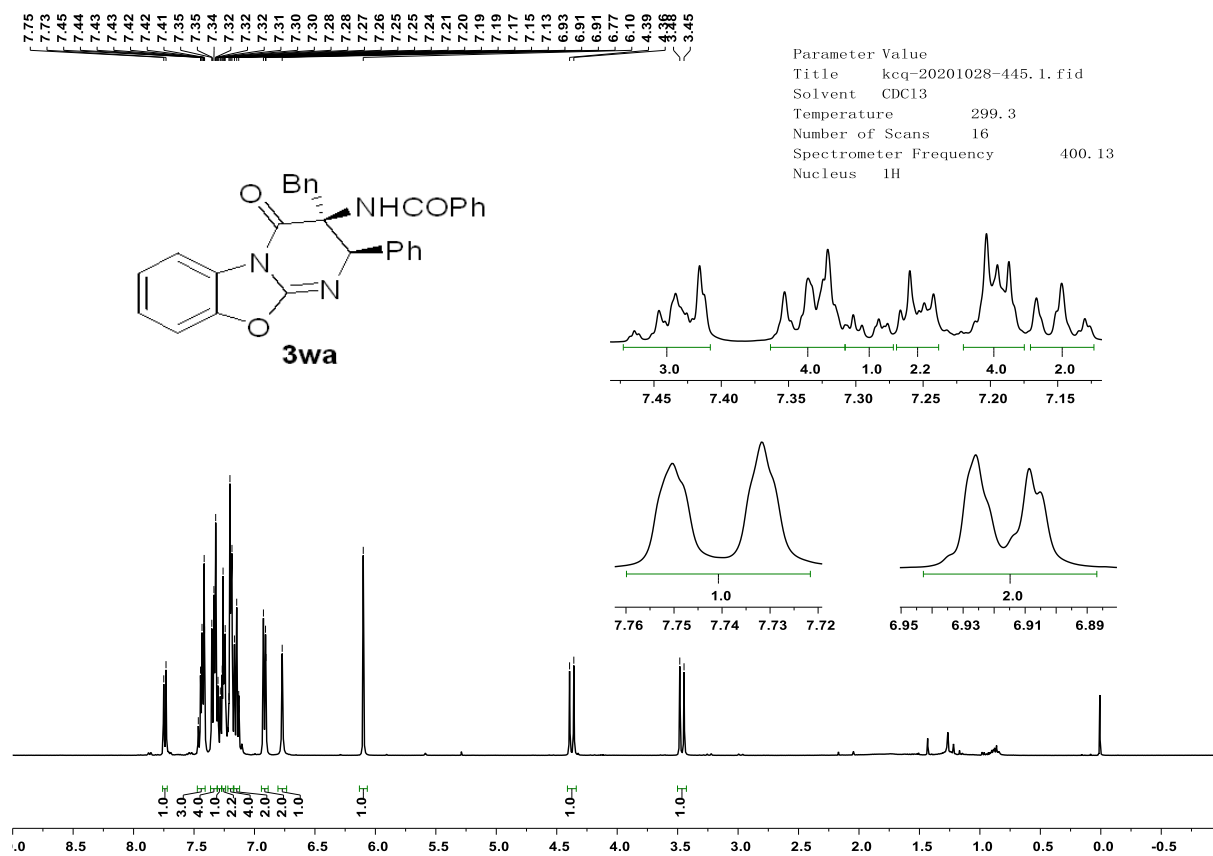


Figure S53. <sup>13</sup>C NMR of 3wa

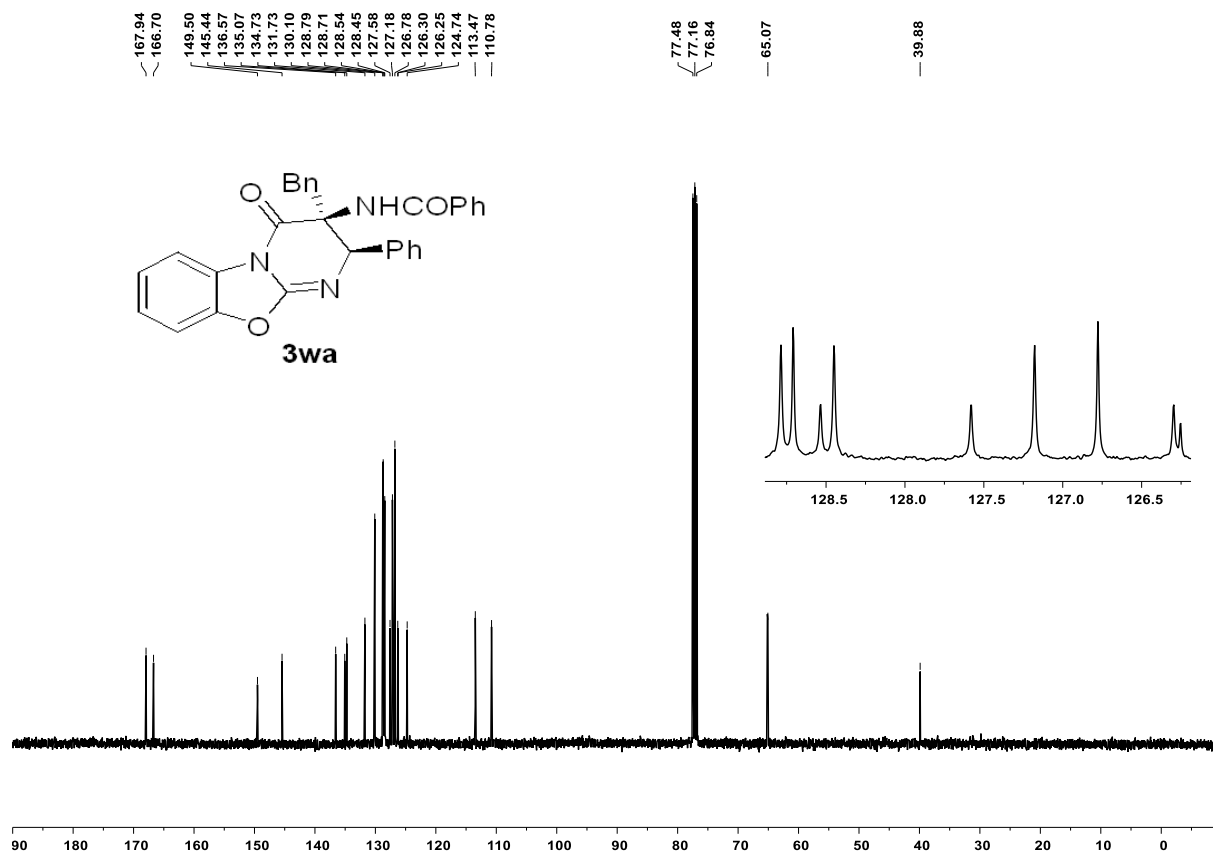


Figure S54. <sup>1</sup>H NMR of 3ab

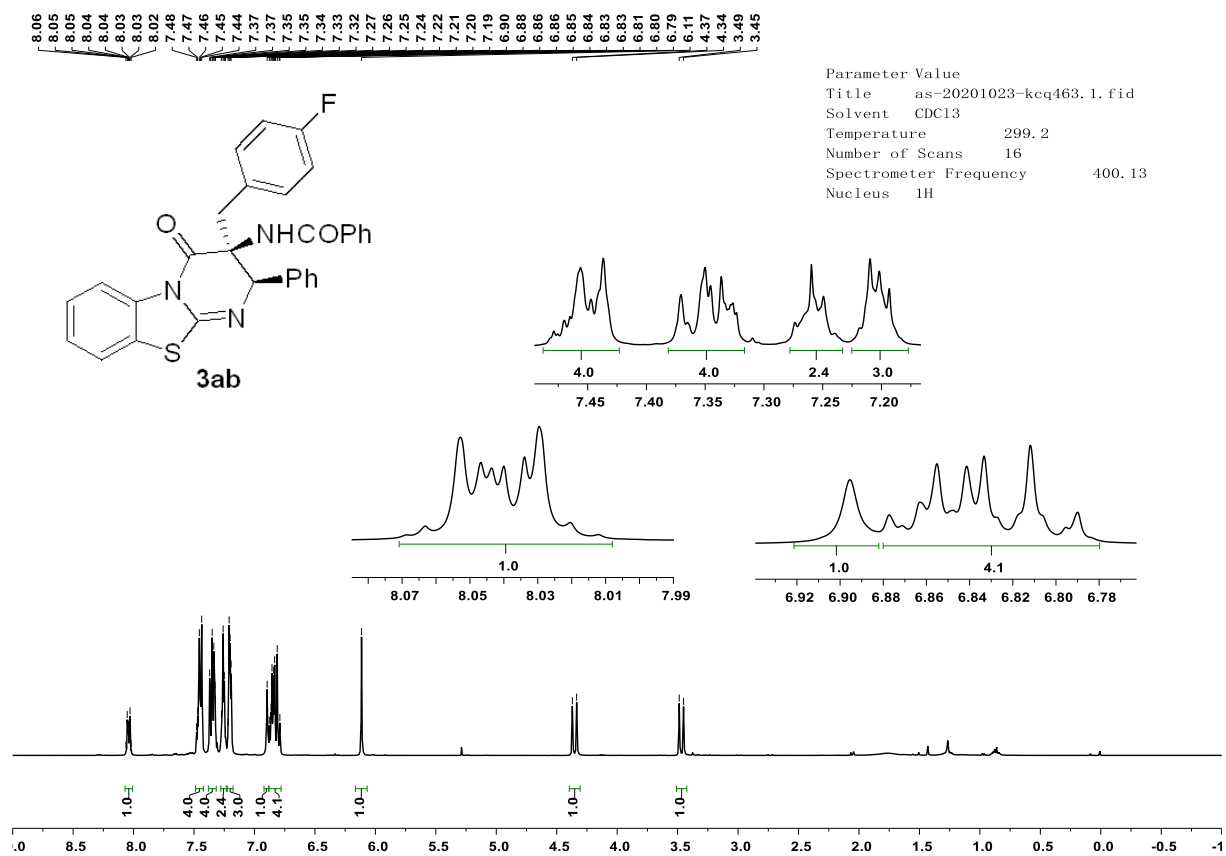




Figure S55.  $^{13}\text{C}$  NMR of 3ab

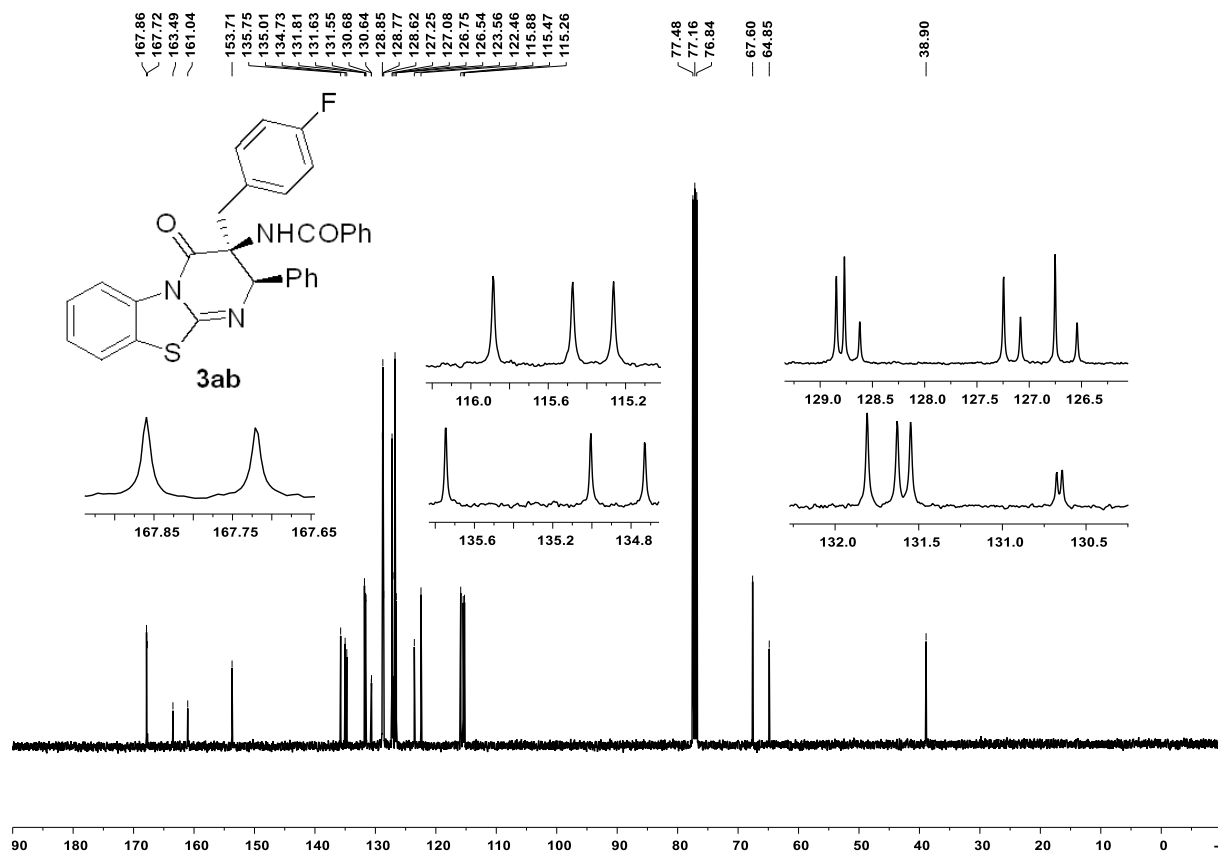
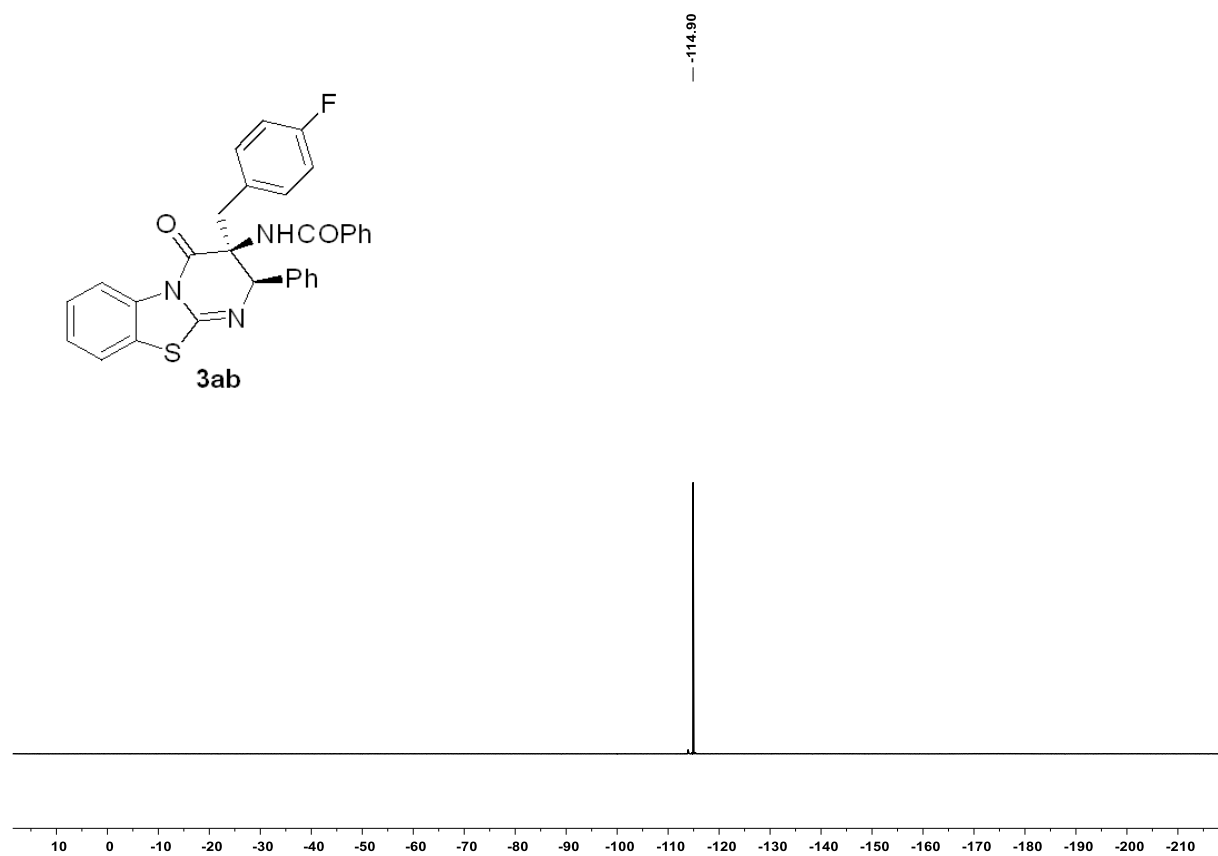
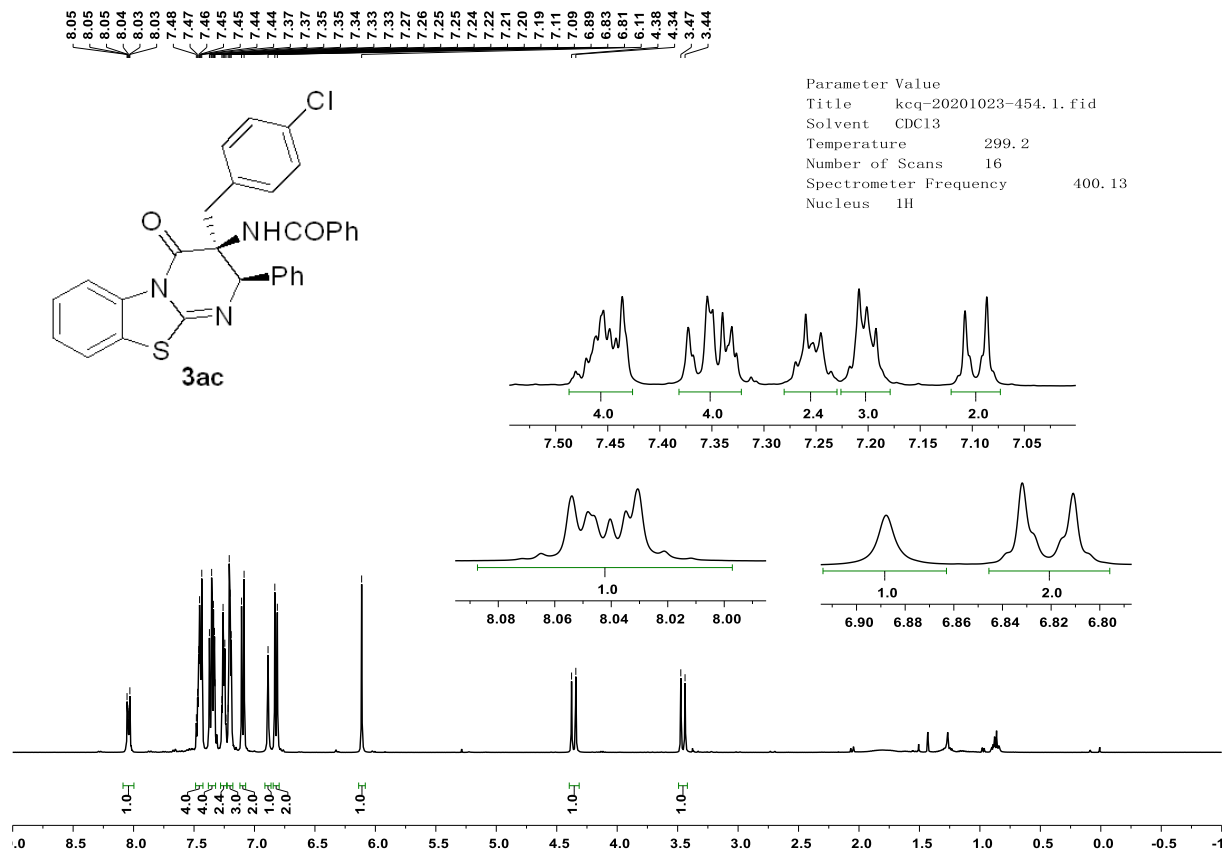


Figure S56.  $^{19}\text{F}\{^1\text{H}\}$  NMR of 3ab



**Figure S57. <sup>1</sup>H NMR of 3ac**



**Figure S58. <sup>13</sup>C NMR of 3ac**

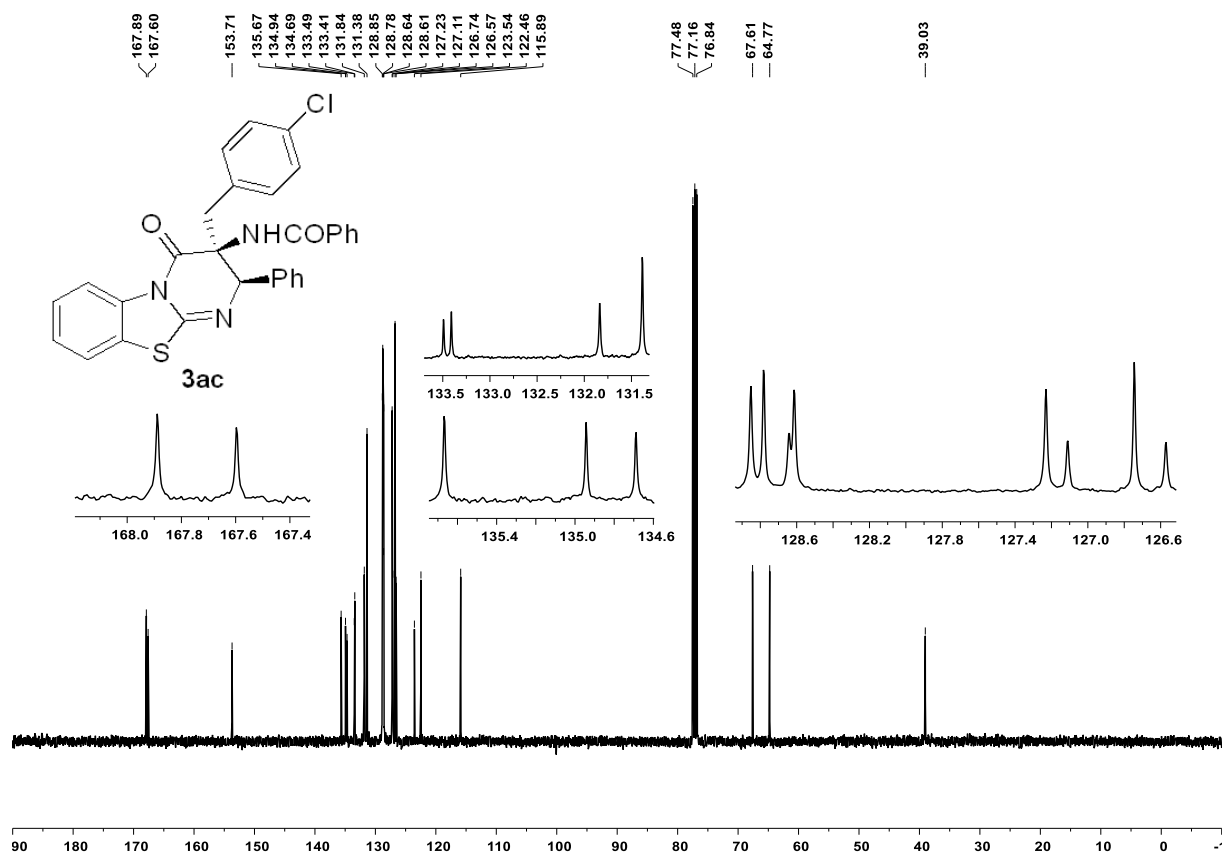


Figure S59. <sup>1</sup>H NMR of 3ad

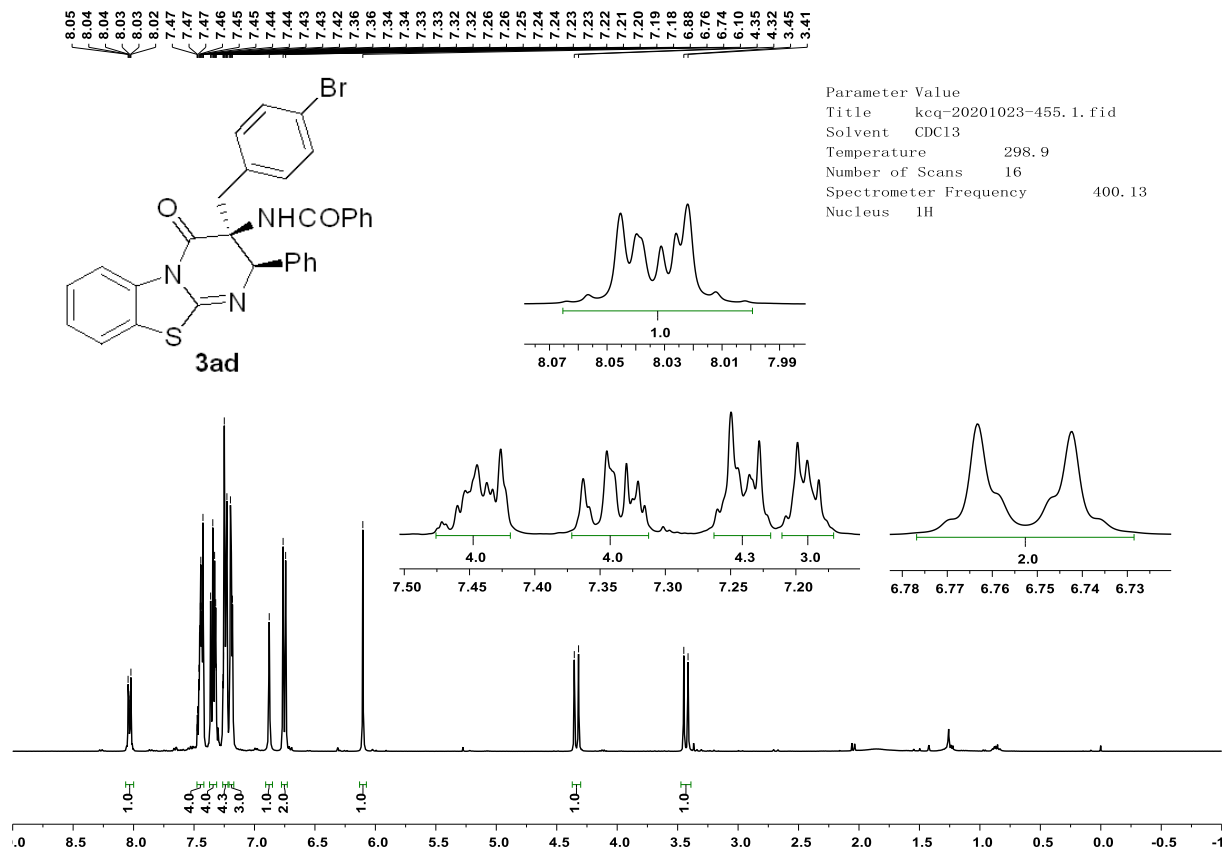


Figure S60. <sup>13</sup>C NMR of 3ad

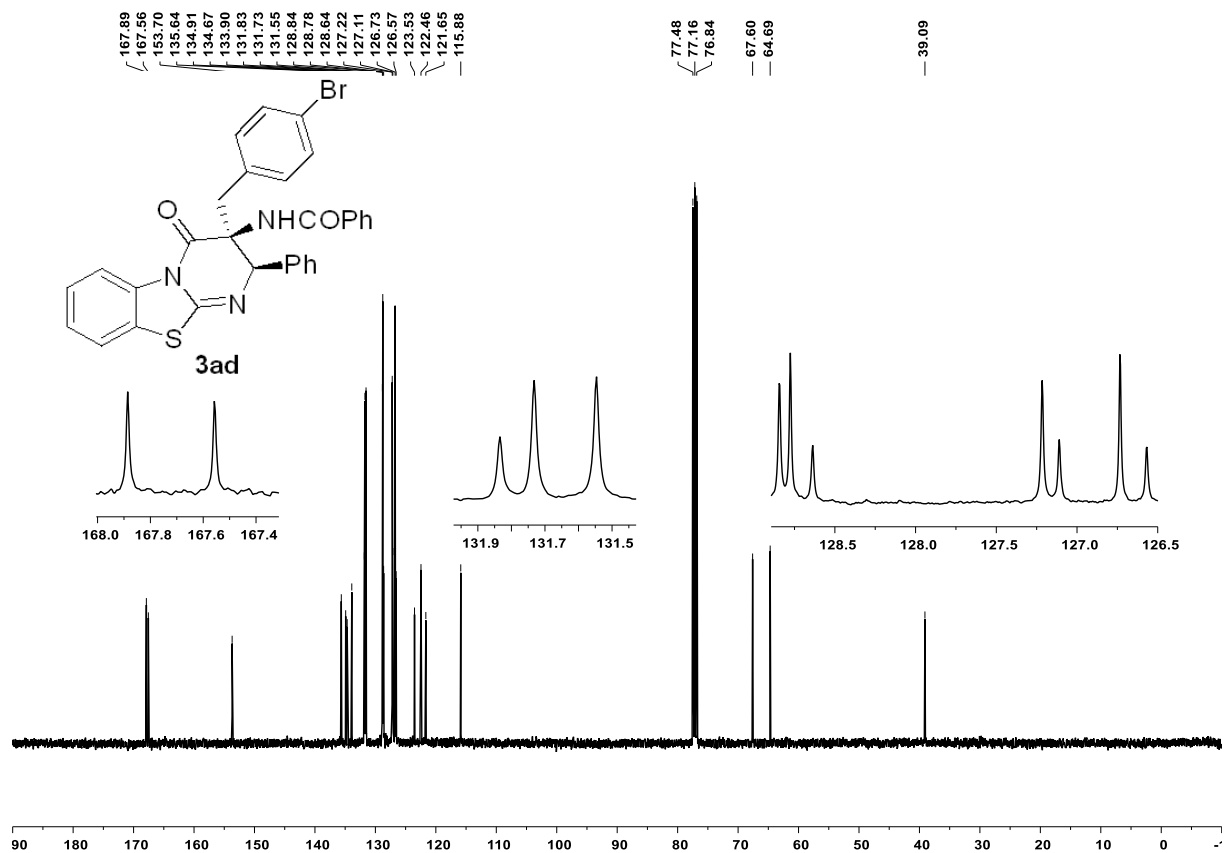


Figure S61. <sup>1</sup>H NMR of 3ae

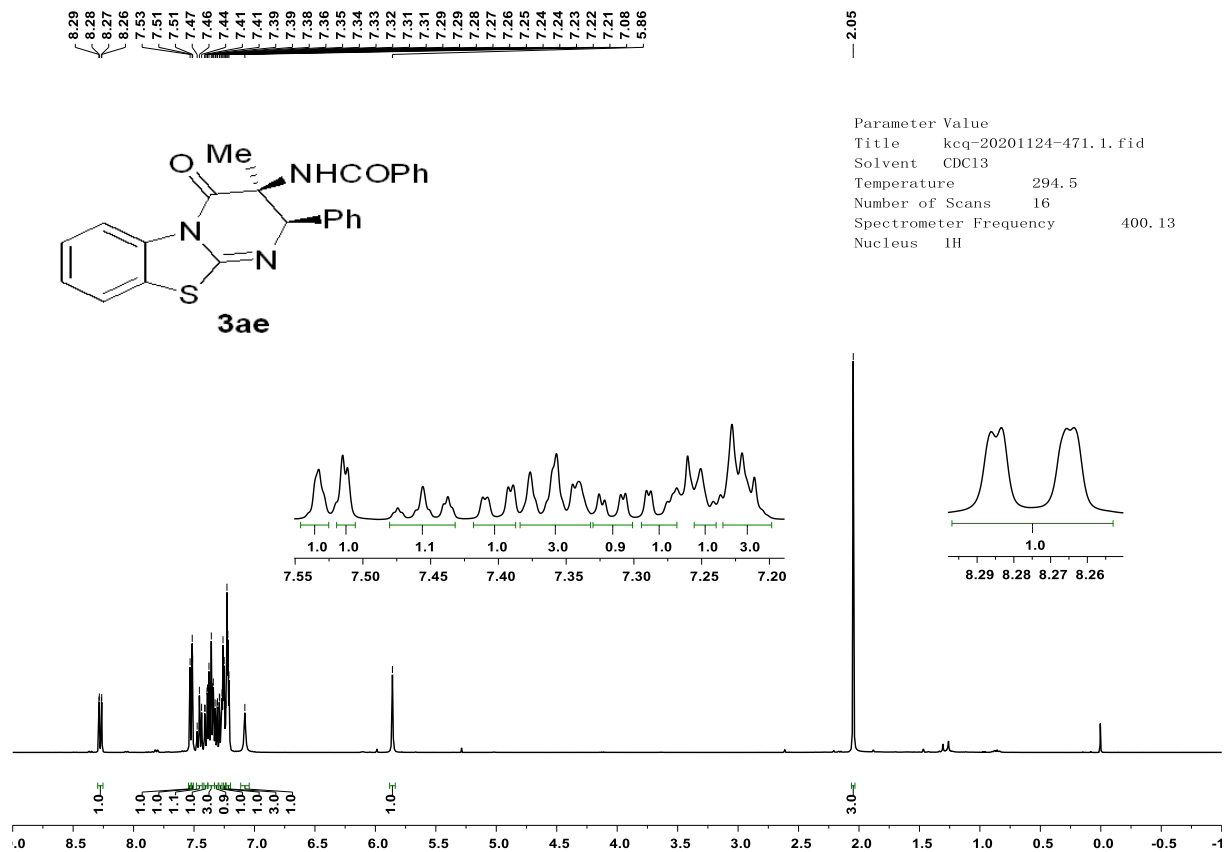


Figure S62. <sup>13</sup>C NMR of 3ae

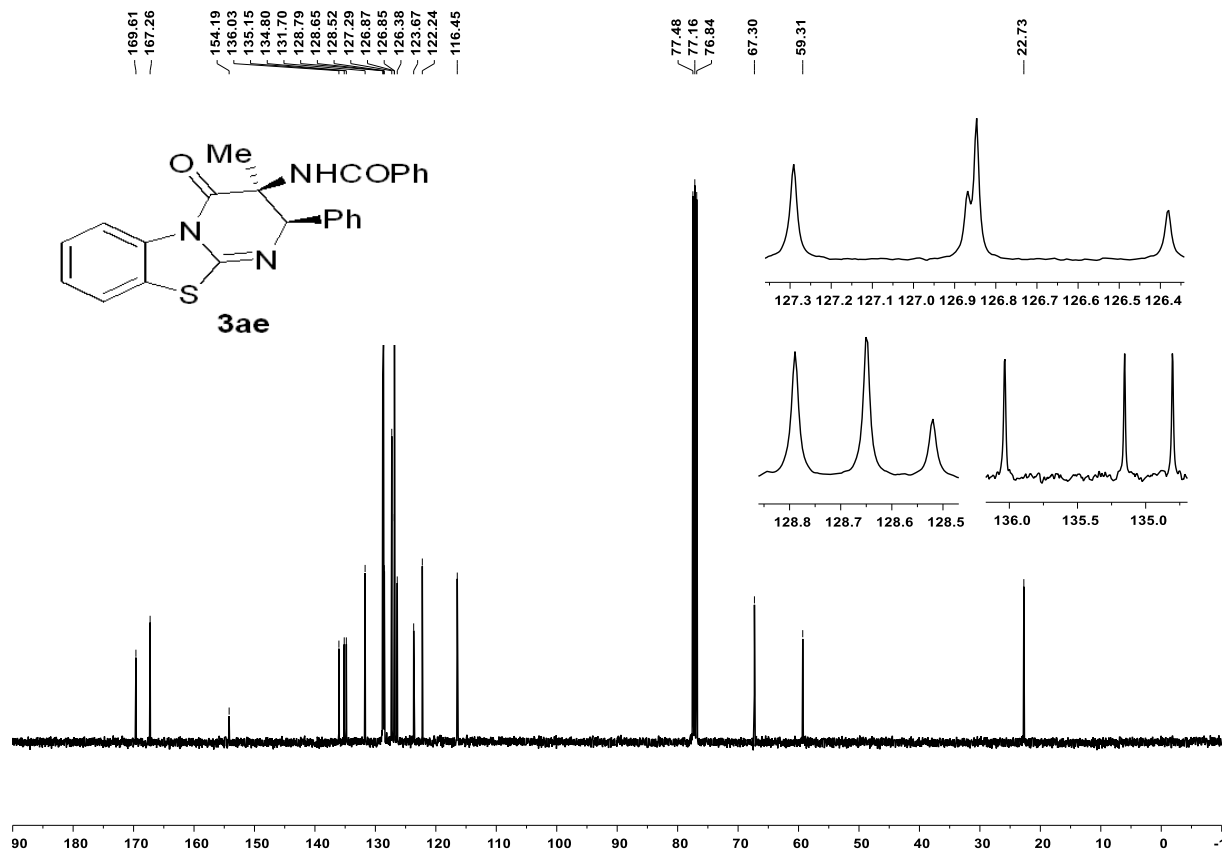


Figure S63. <sup>1</sup>H NMR of 3af

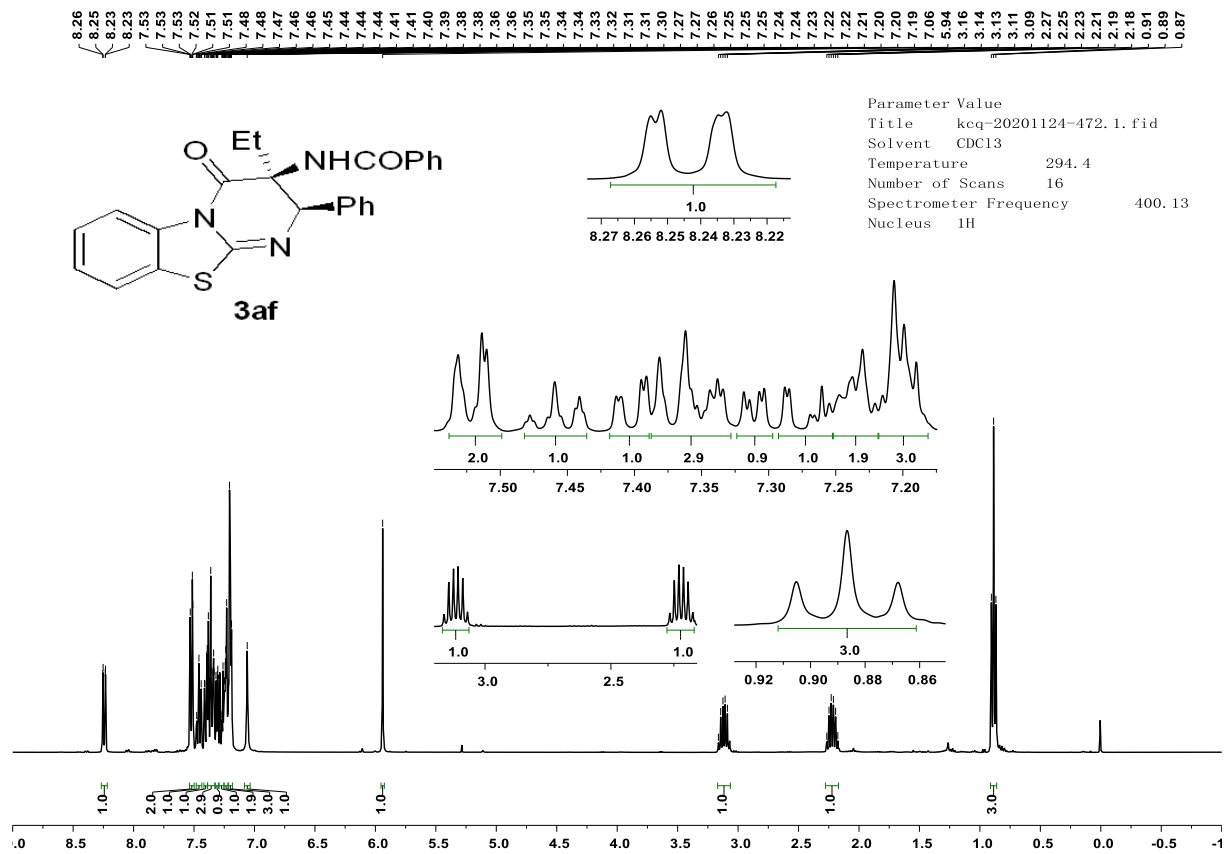


Figure S64. <sup>13</sup>C NMR of 3af

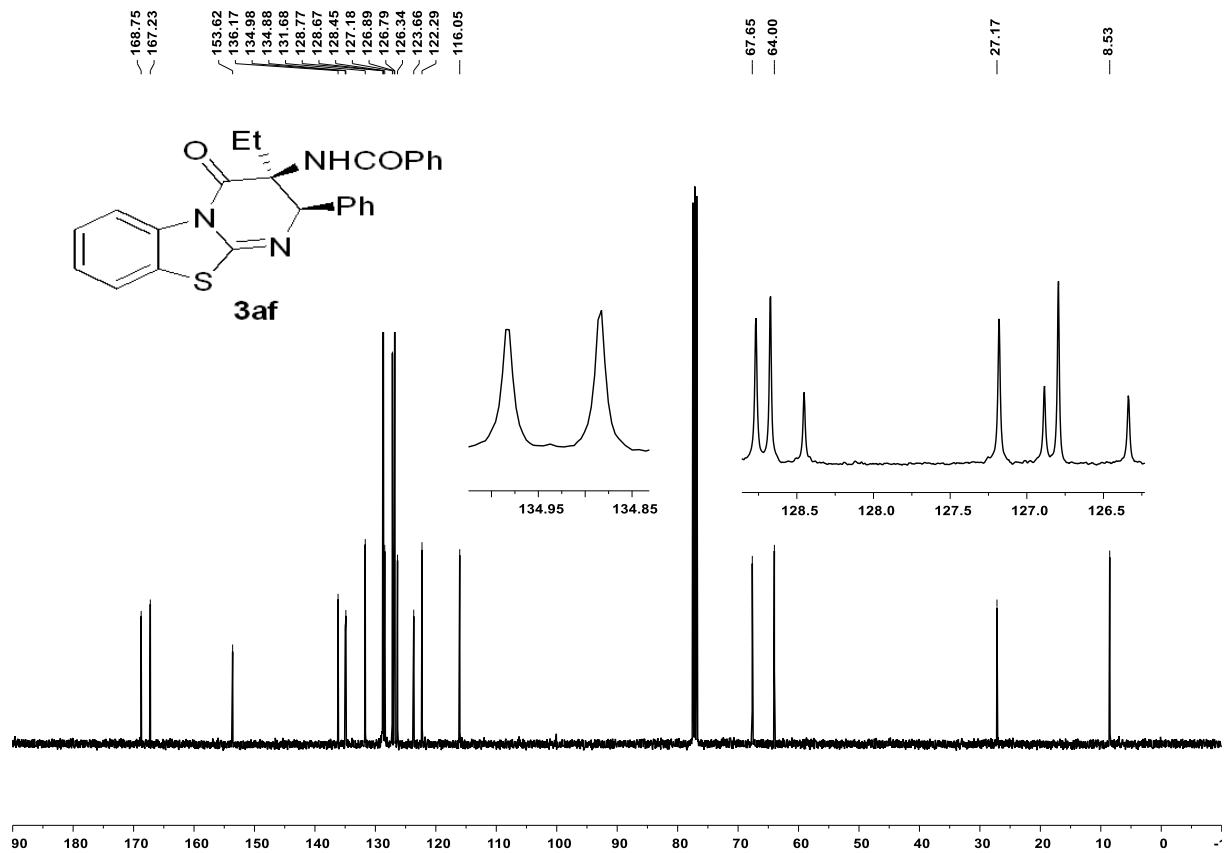


Figure S65. <sup>1</sup>H NMR of 3ag

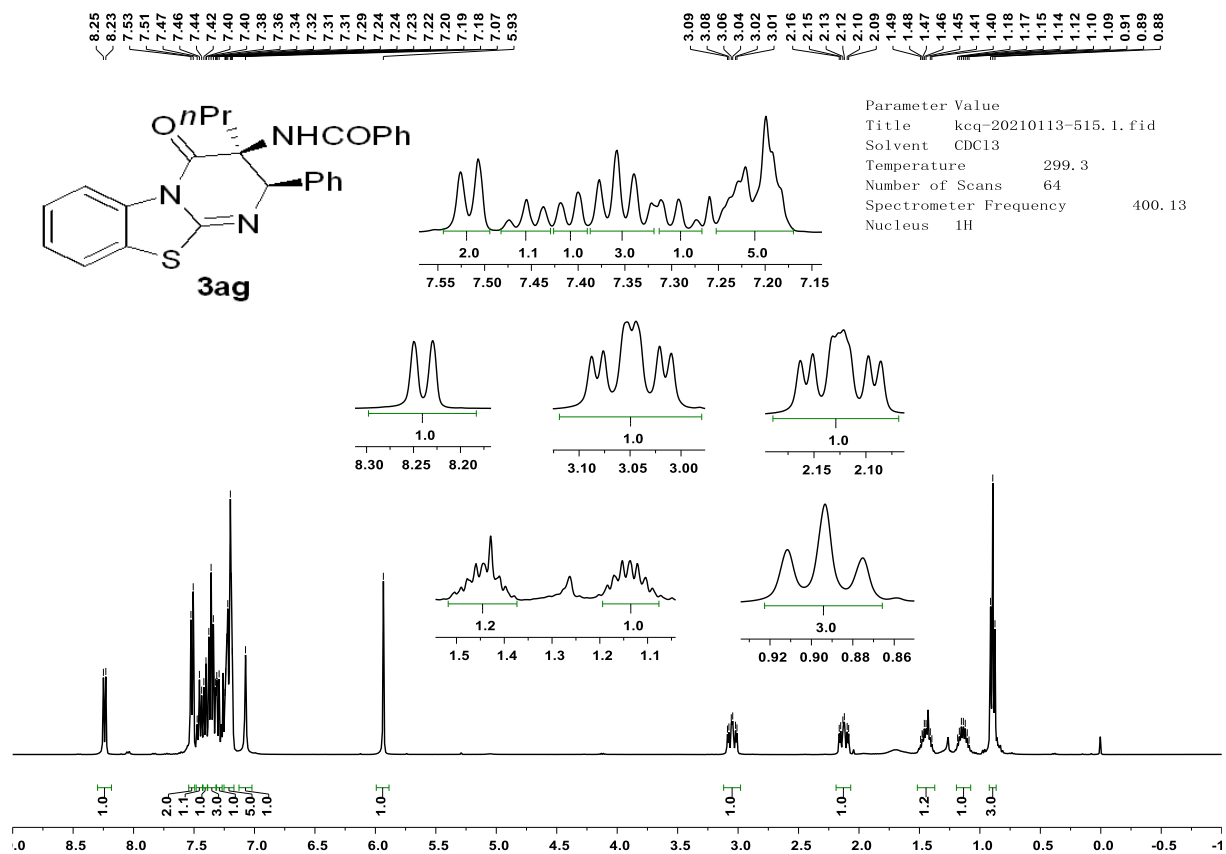


Figure S66. <sup>13</sup>C NMR of 3ag

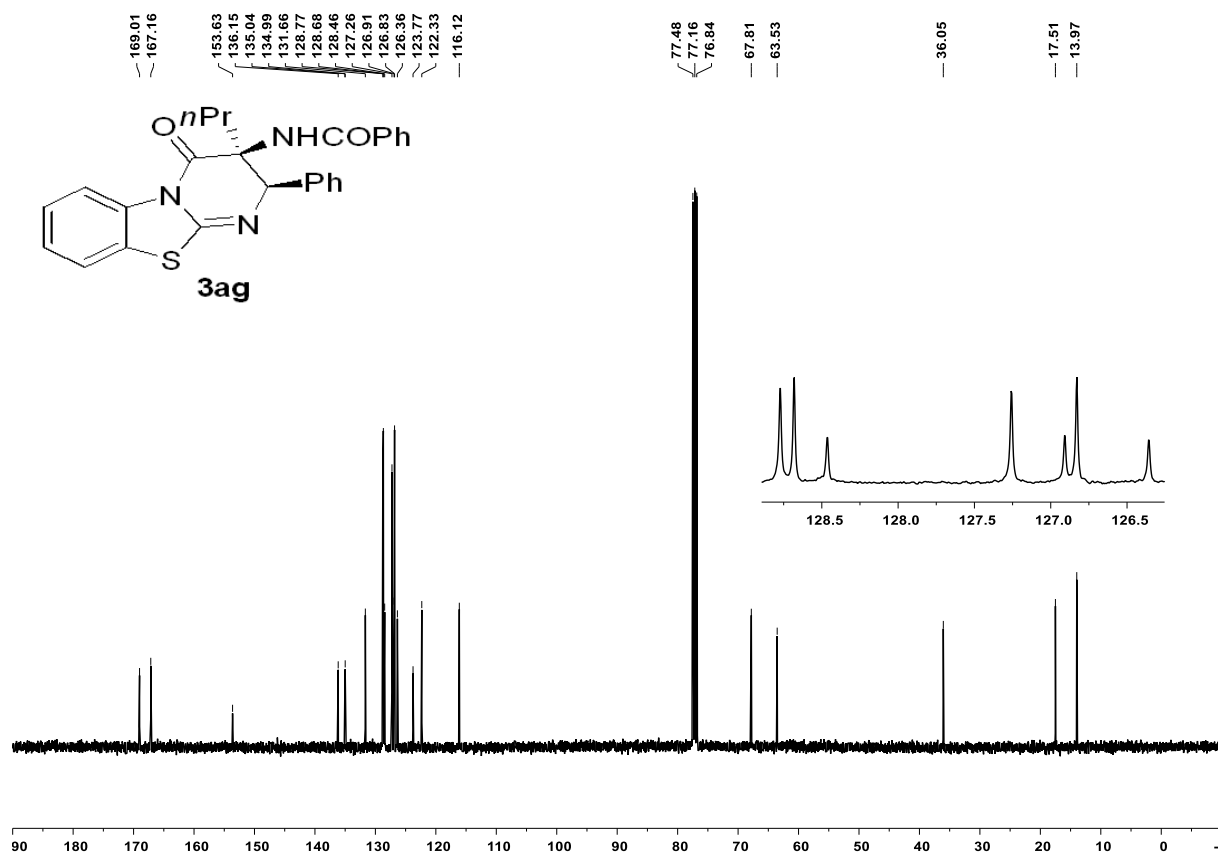


Figure S67. <sup>1</sup>H NMR of 3ah

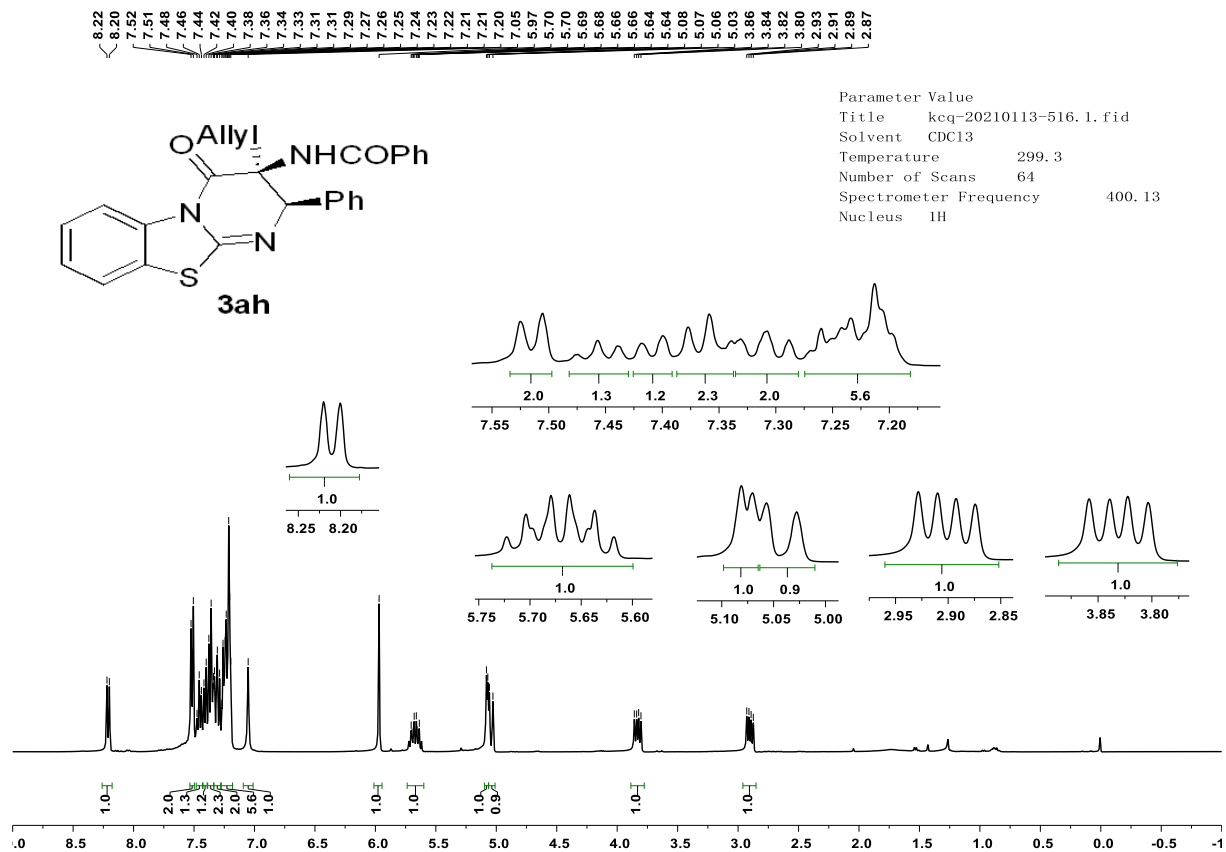


Figure S68. <sup>13</sup>C NMR of 3ah

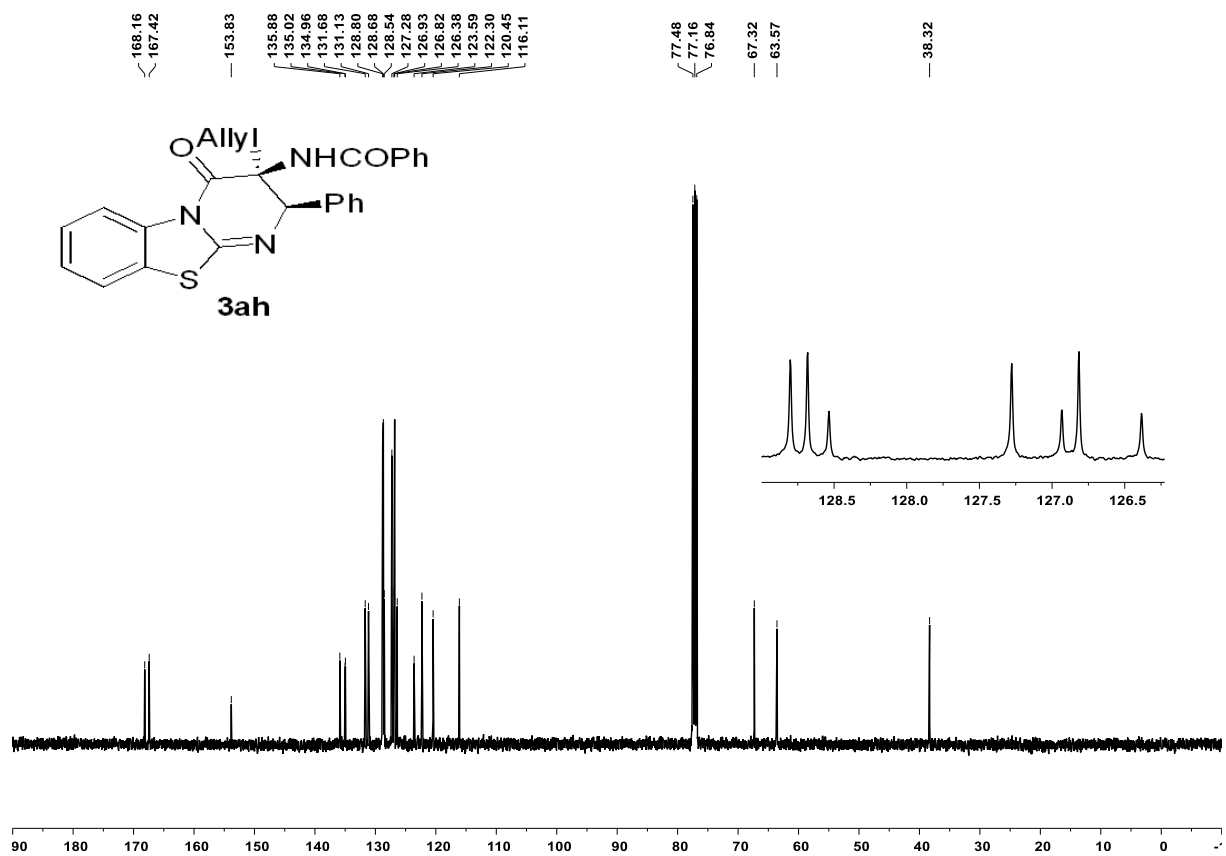


Figure S69. <sup>1</sup>H NMR of 3ai

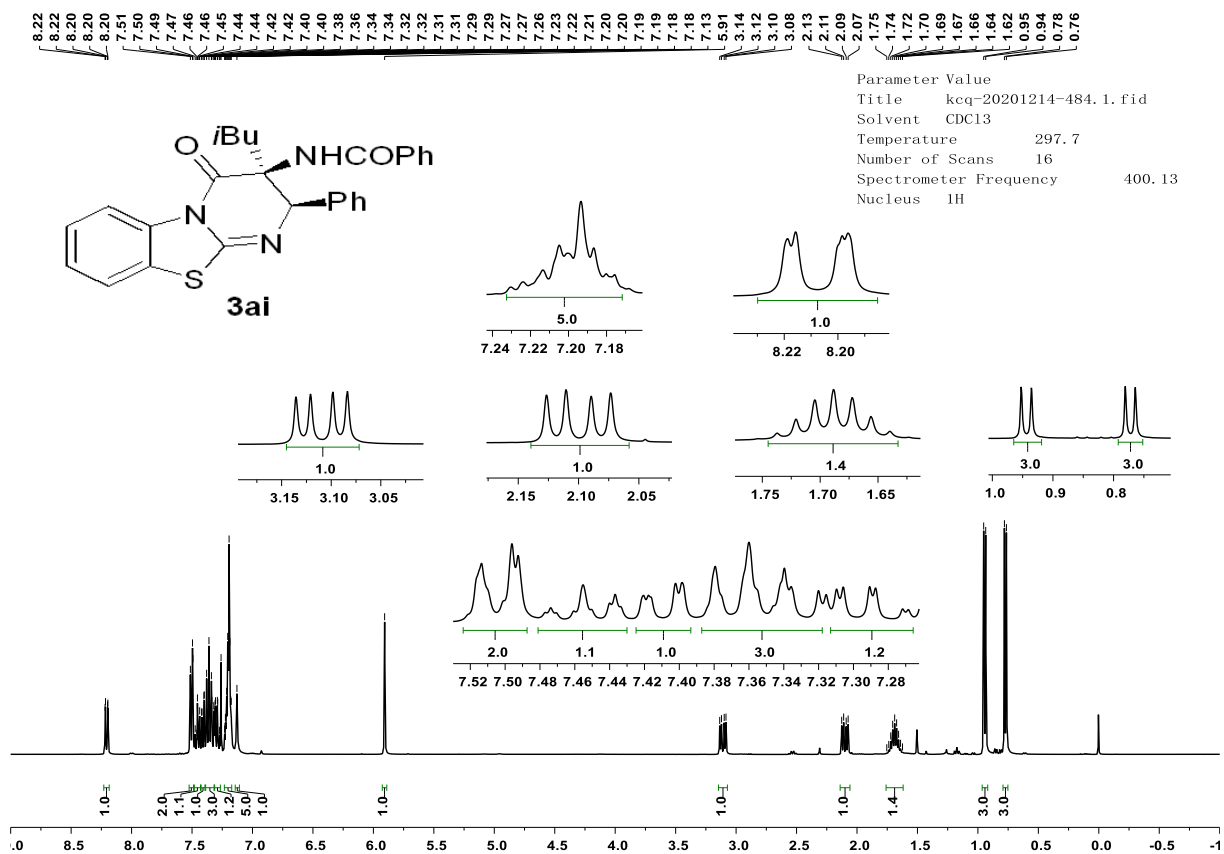


Figure S70. <sup>13</sup>C NMR of 3ai

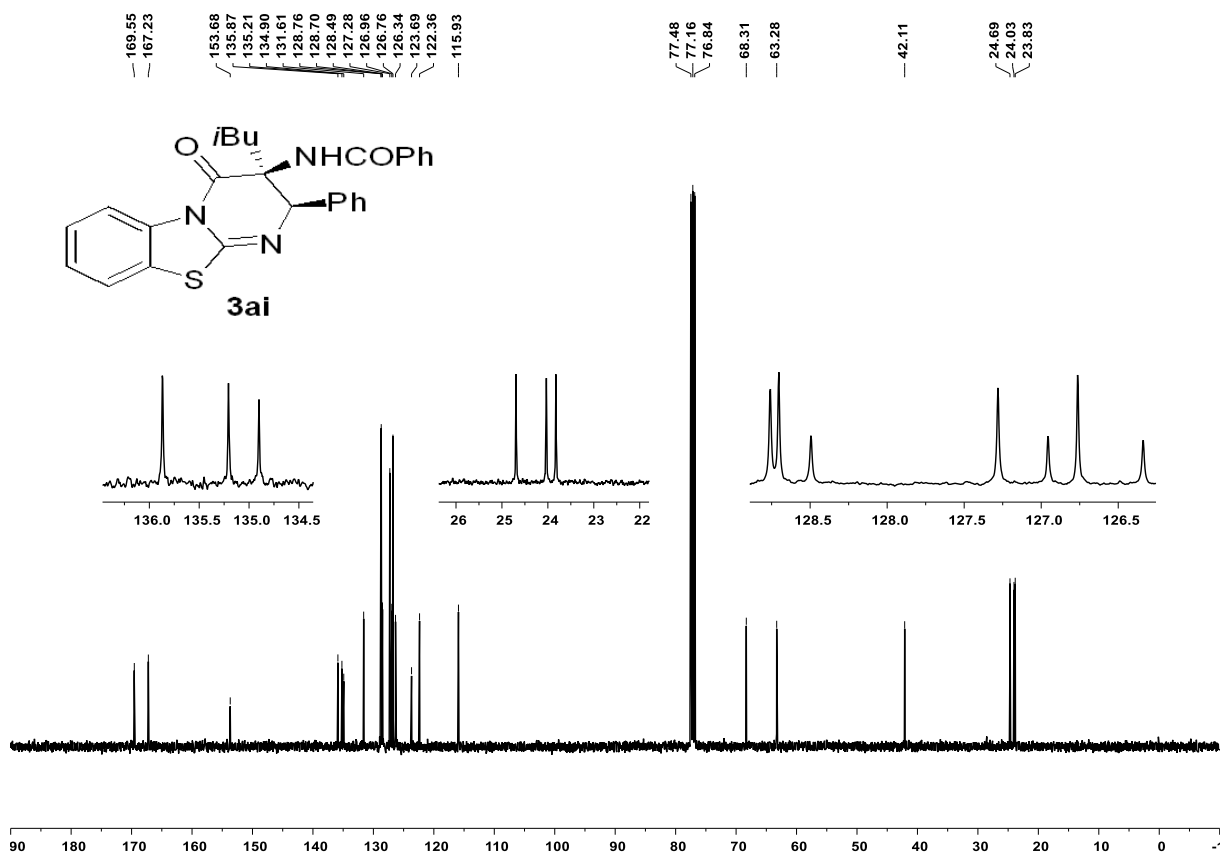




Figure S71. <sup>1</sup>H NMR of 3aj

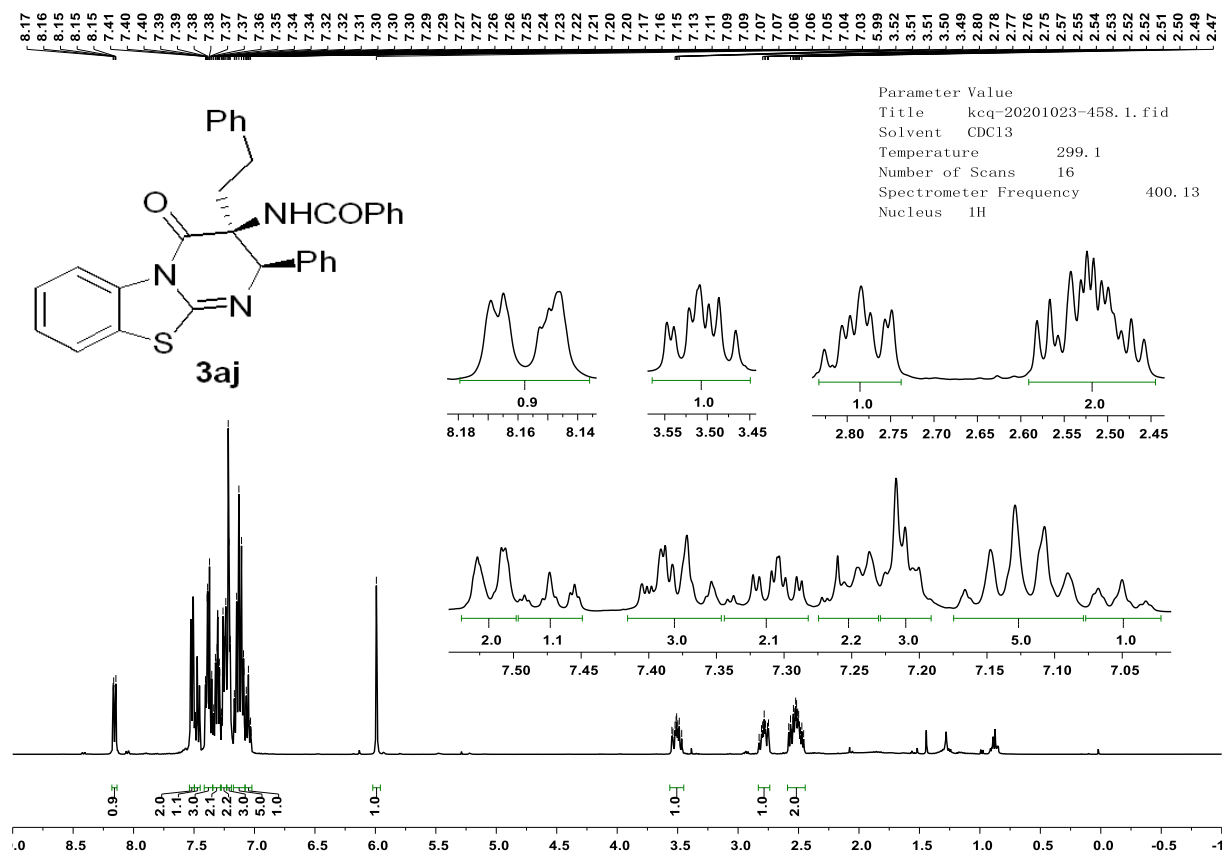


Figure S72. <sup>13</sup>C NMR of 3aj

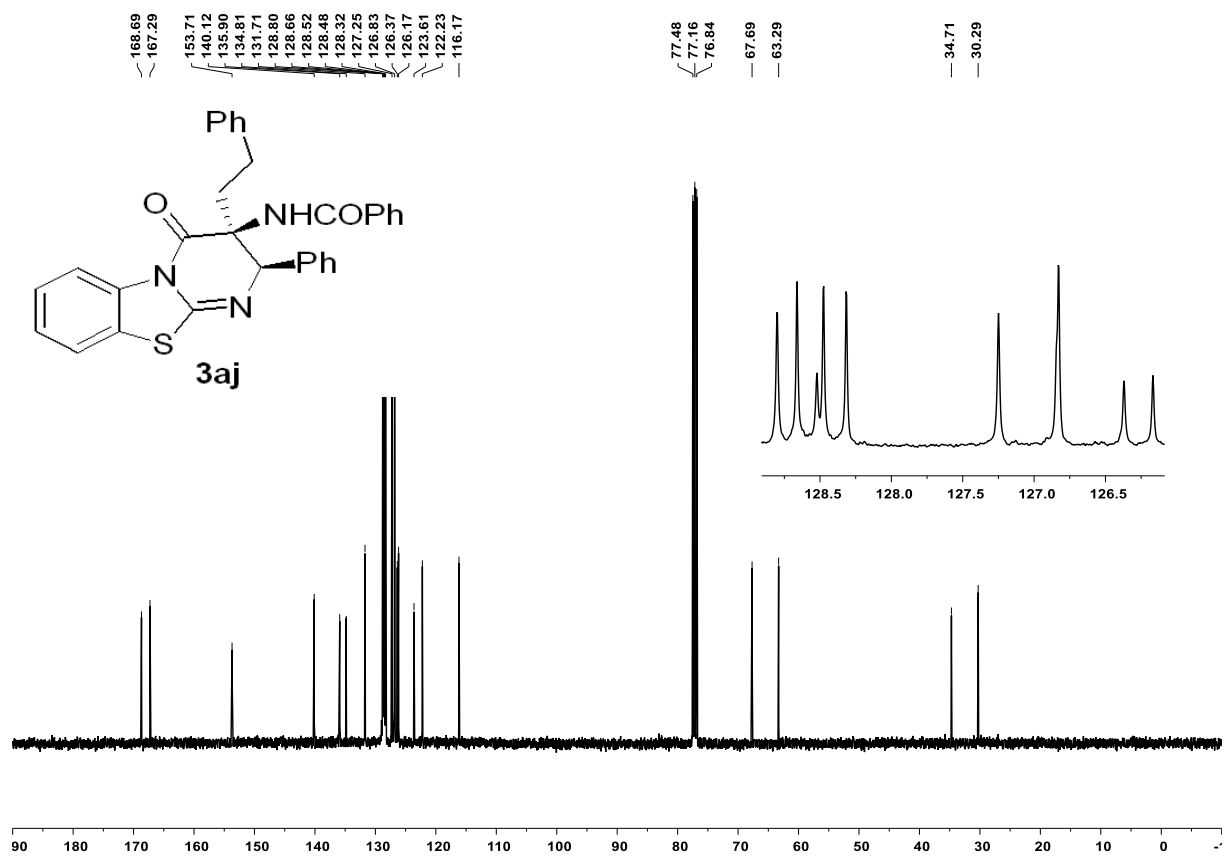


Figure S73. <sup>1</sup>H NMR of 3ak

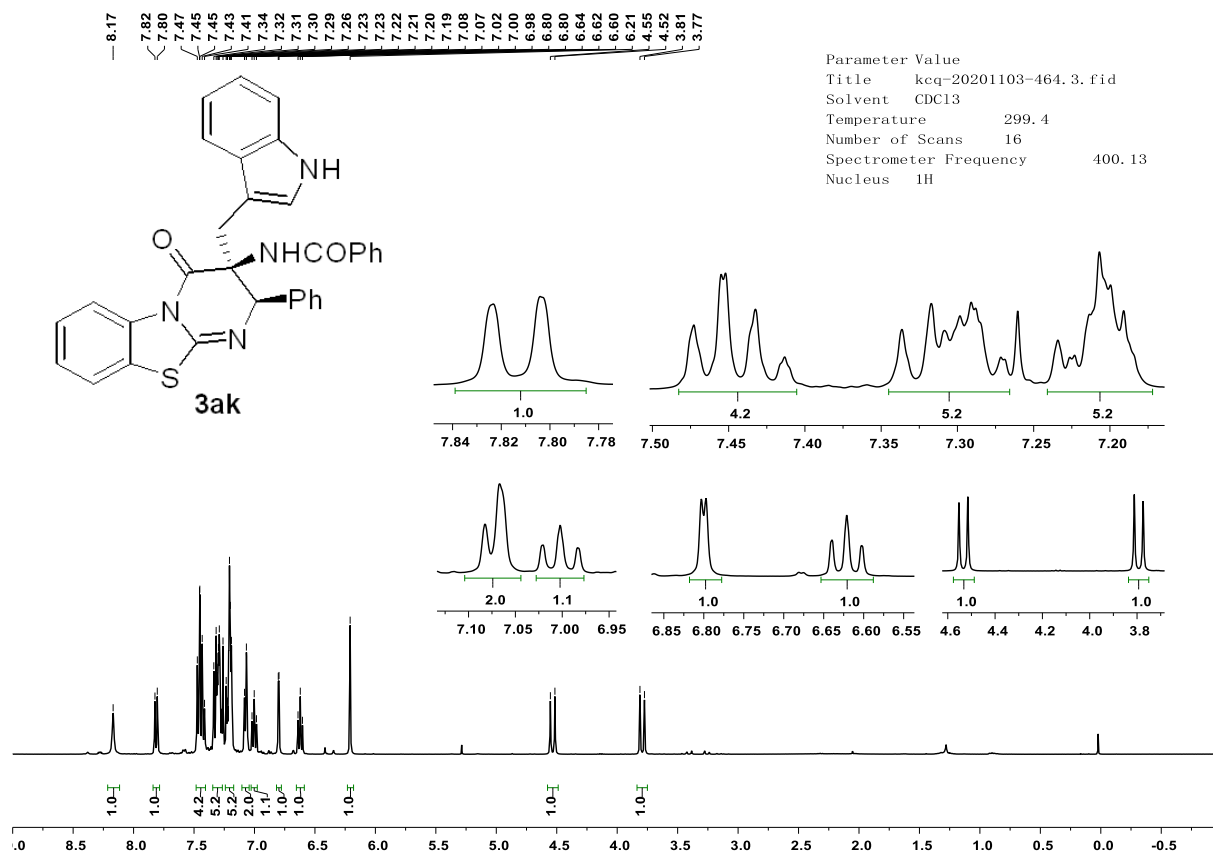


Figure S74. <sup>13</sup>C NMR of 3ak

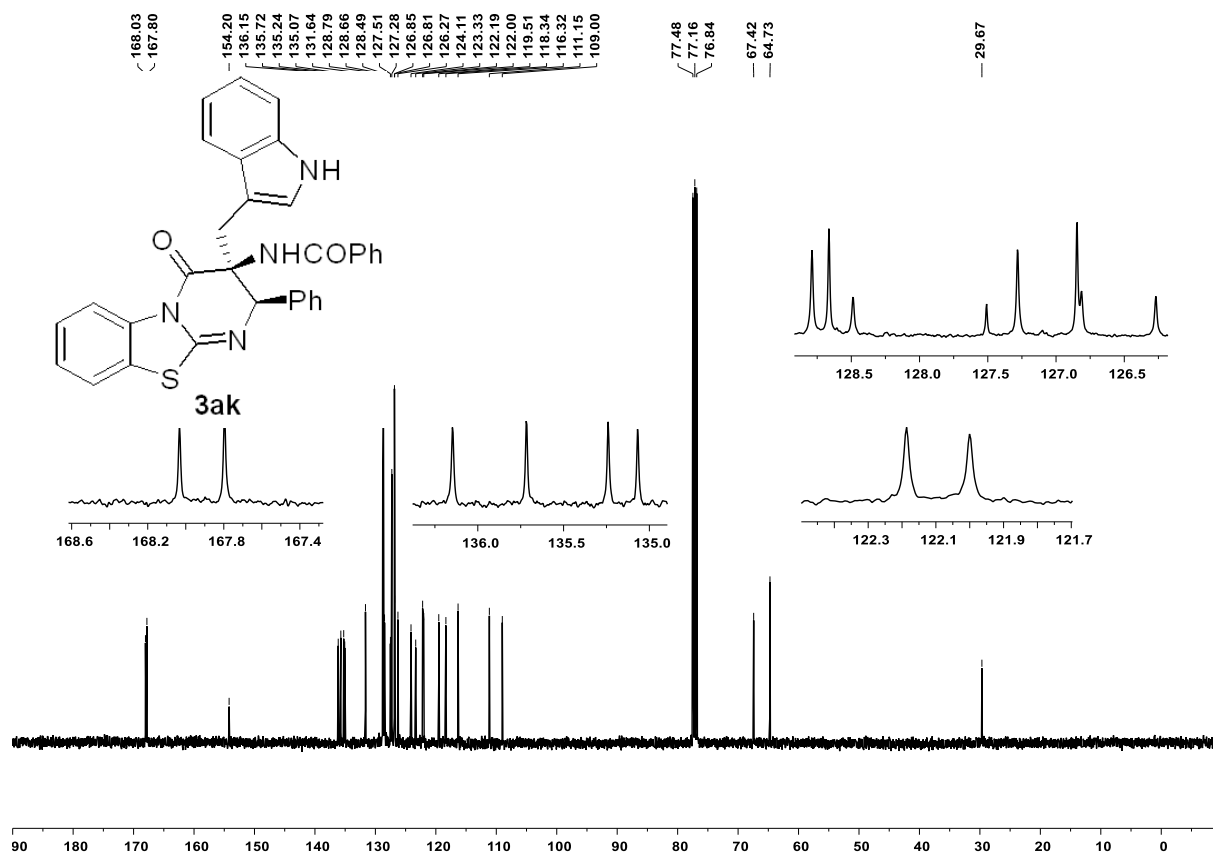


Figure S75. <sup>1</sup>H NMR of 3al

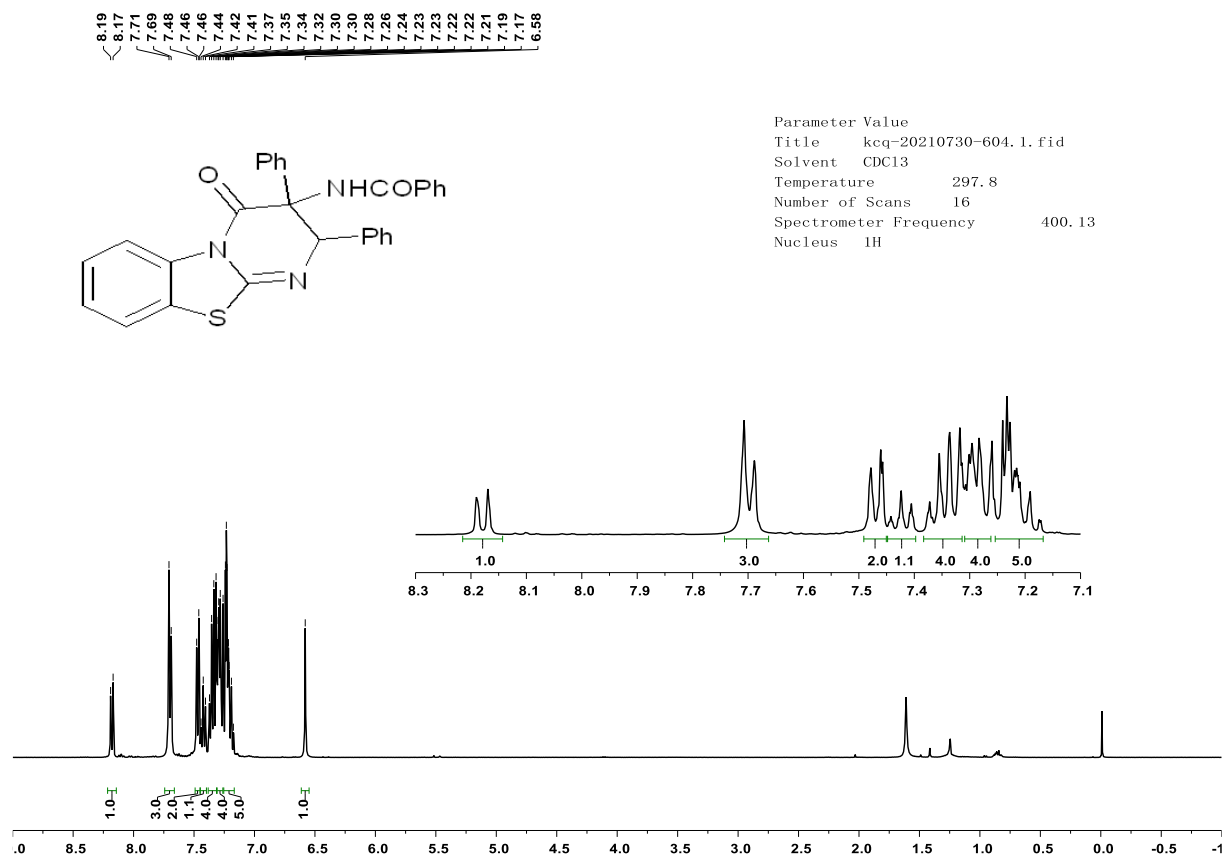


Figure S76. <sup>13</sup>C NMR of 3al

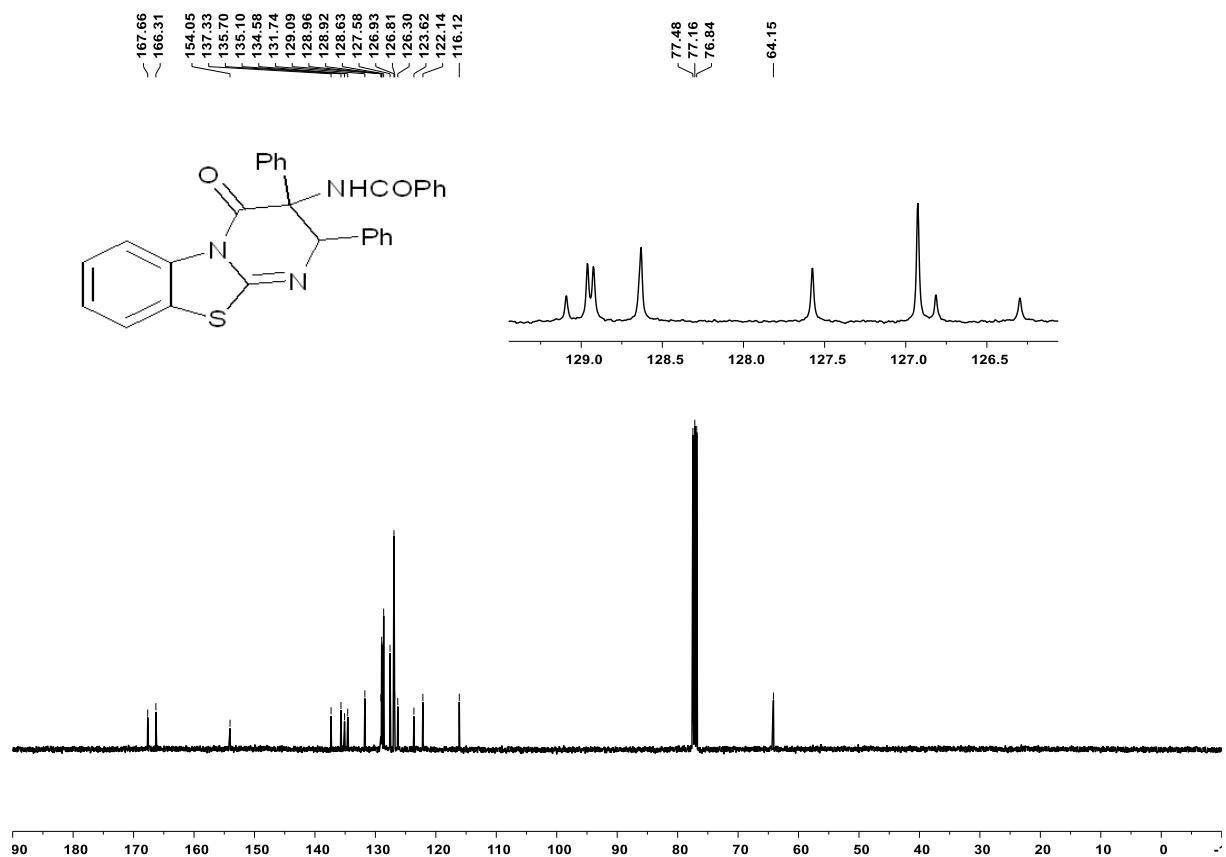


Figure S77. <sup>1</sup>H NMR of 4aa

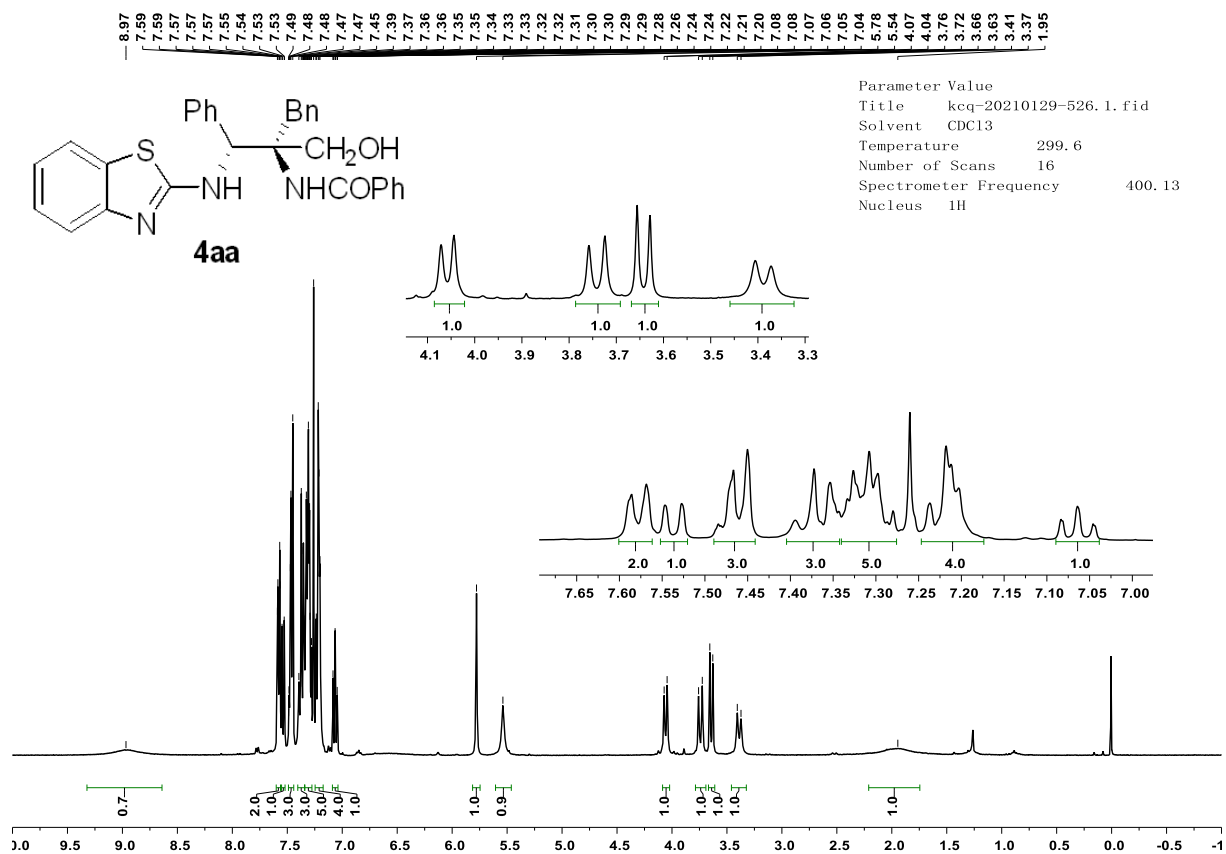


Figure S78. <sup>13</sup>C NMR of 4aa

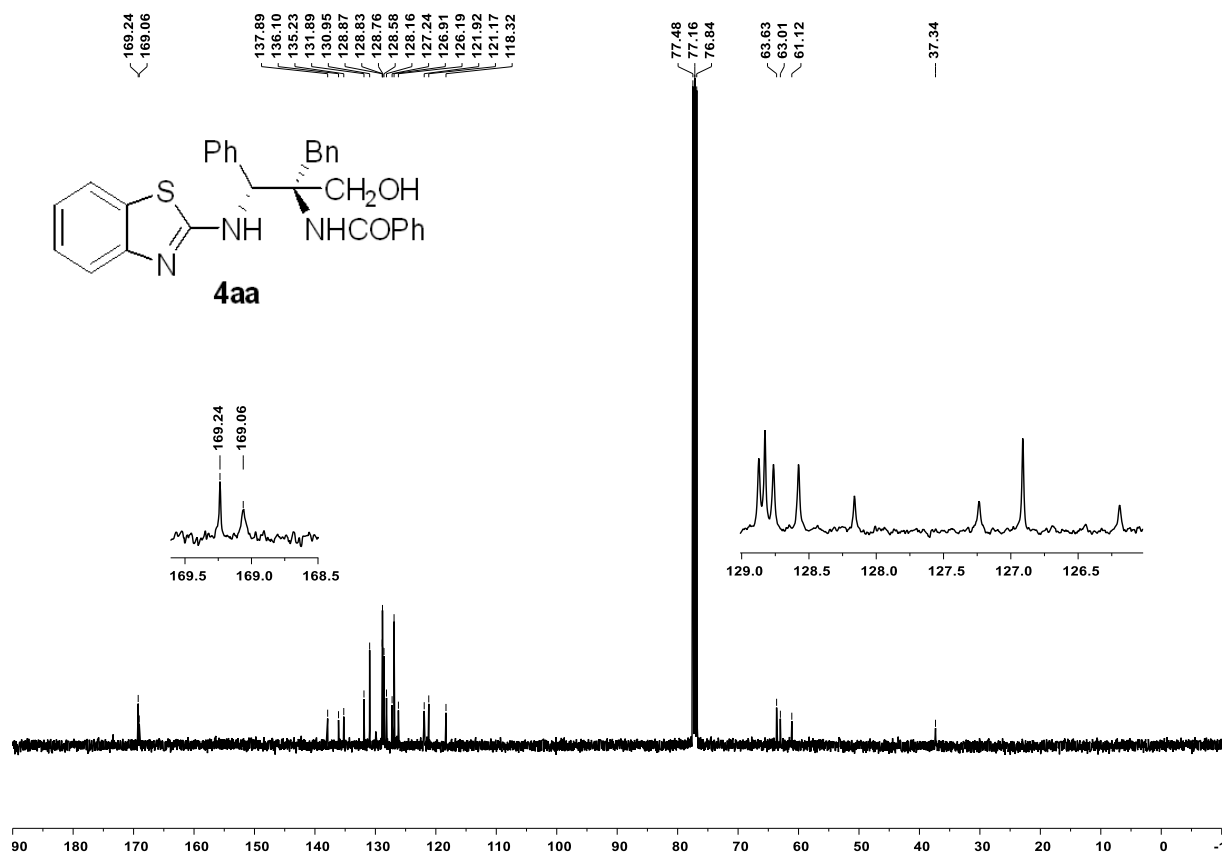


Figure S79. <sup>1</sup>H NMR of 5aa

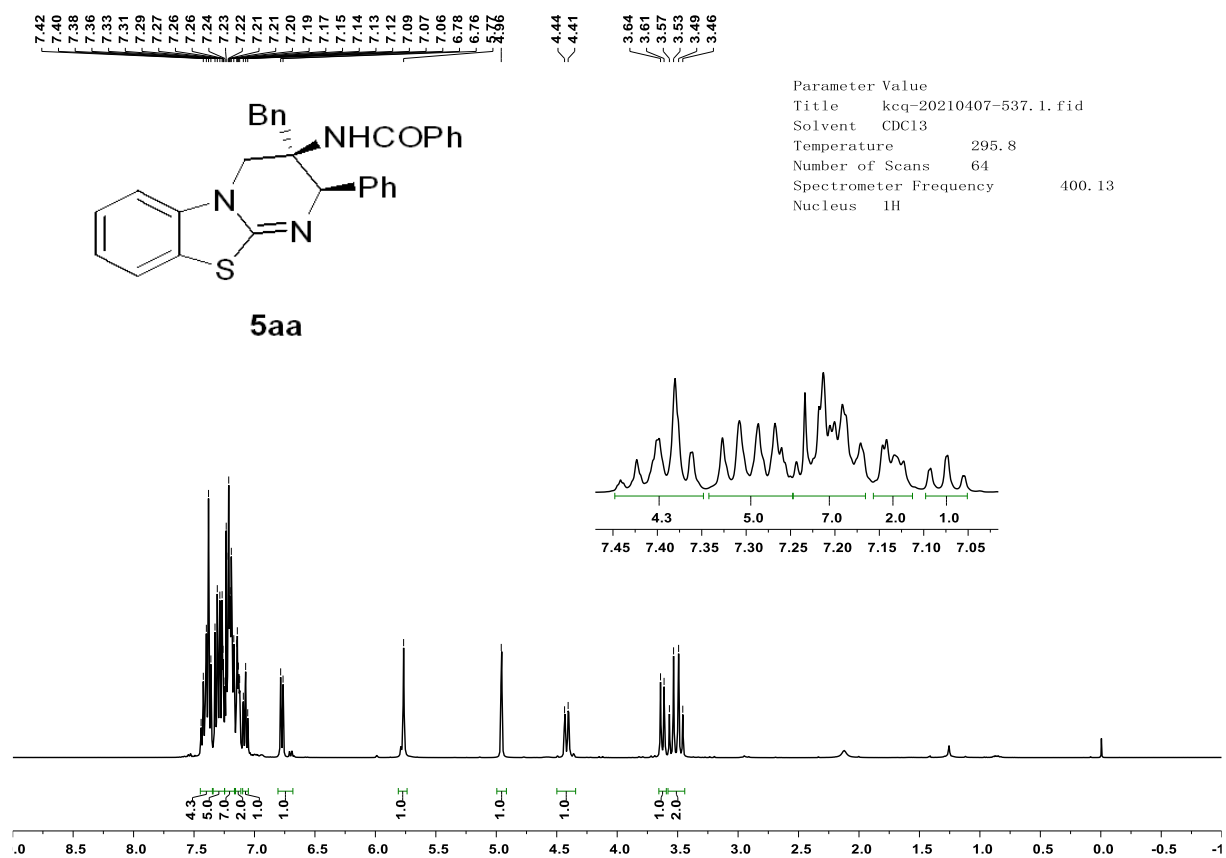


Figure S80. <sup>13</sup>C NMR of 5aa

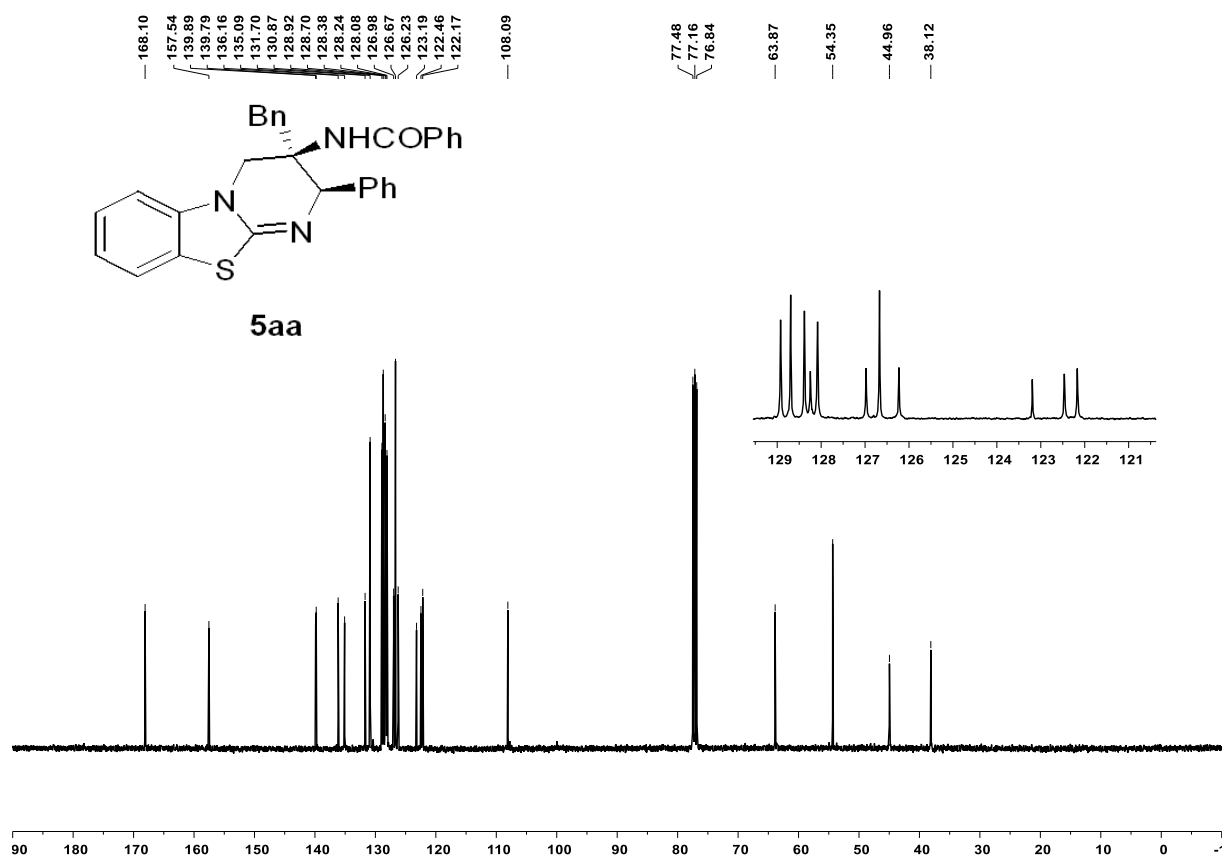


Figure S81. <sup>1</sup>H NMR of 7a

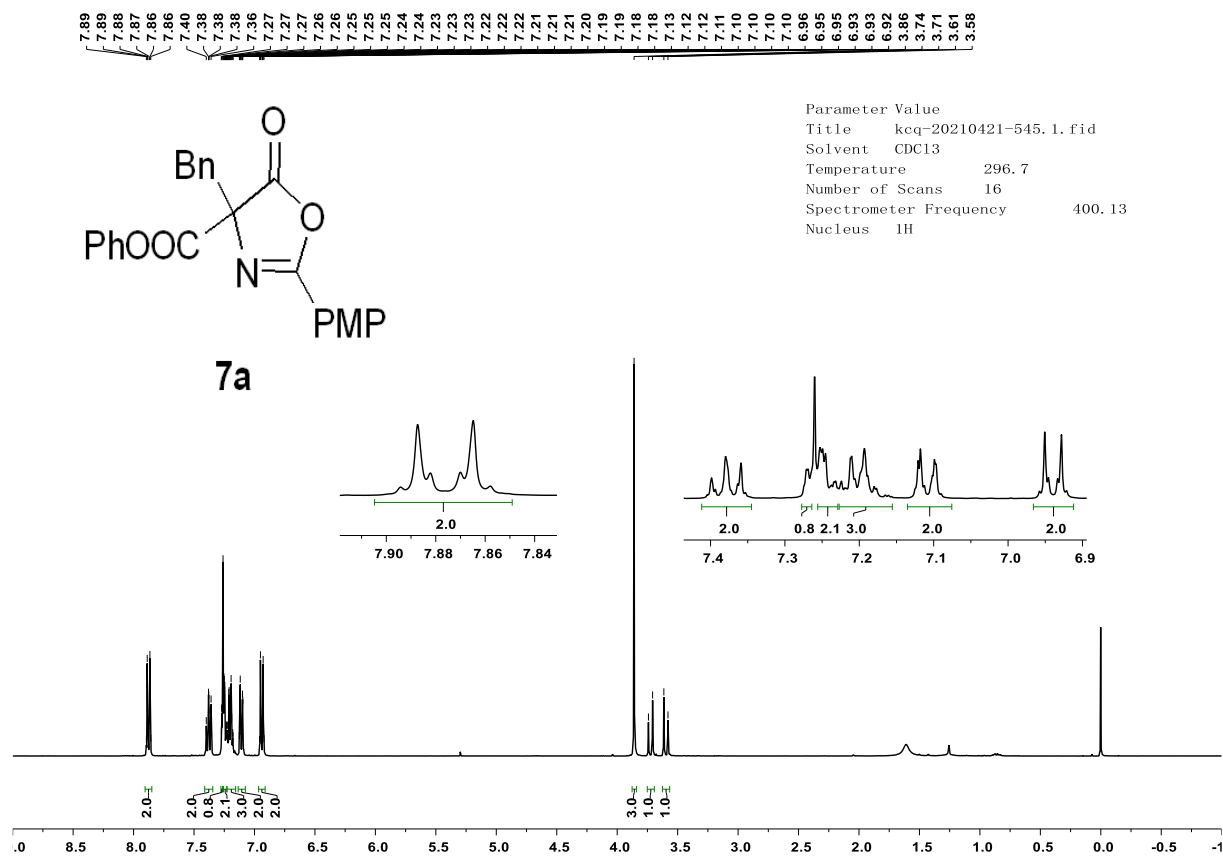
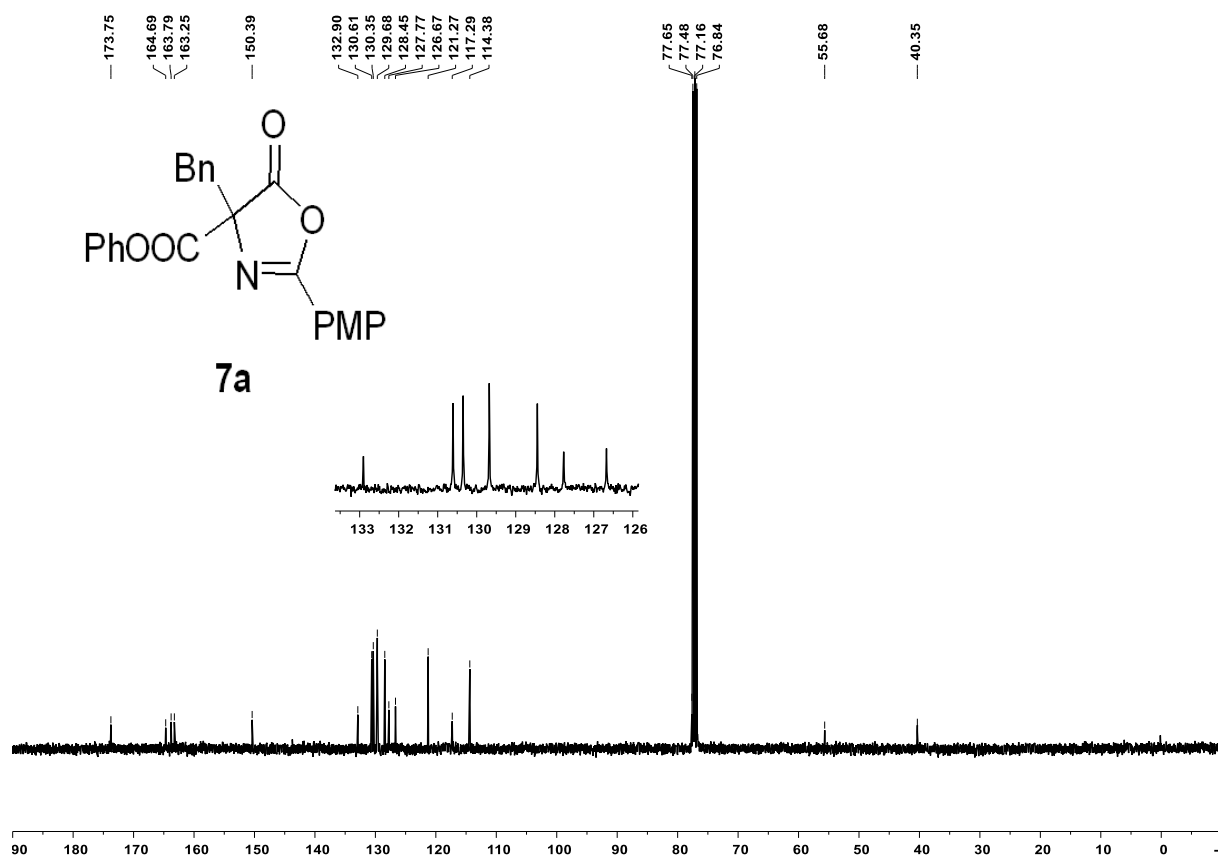


Figure S82. <sup>13</sup>C NMR of 7a



## 10. Copies of CD spectra for products

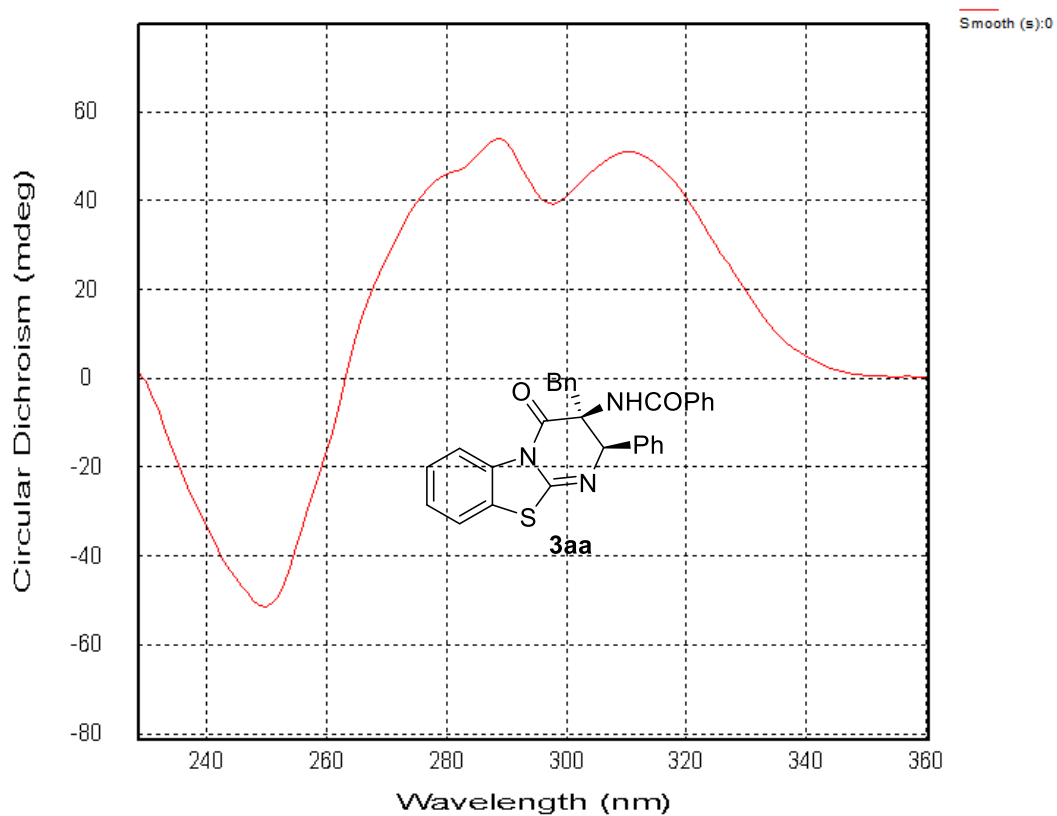


Figure S83.

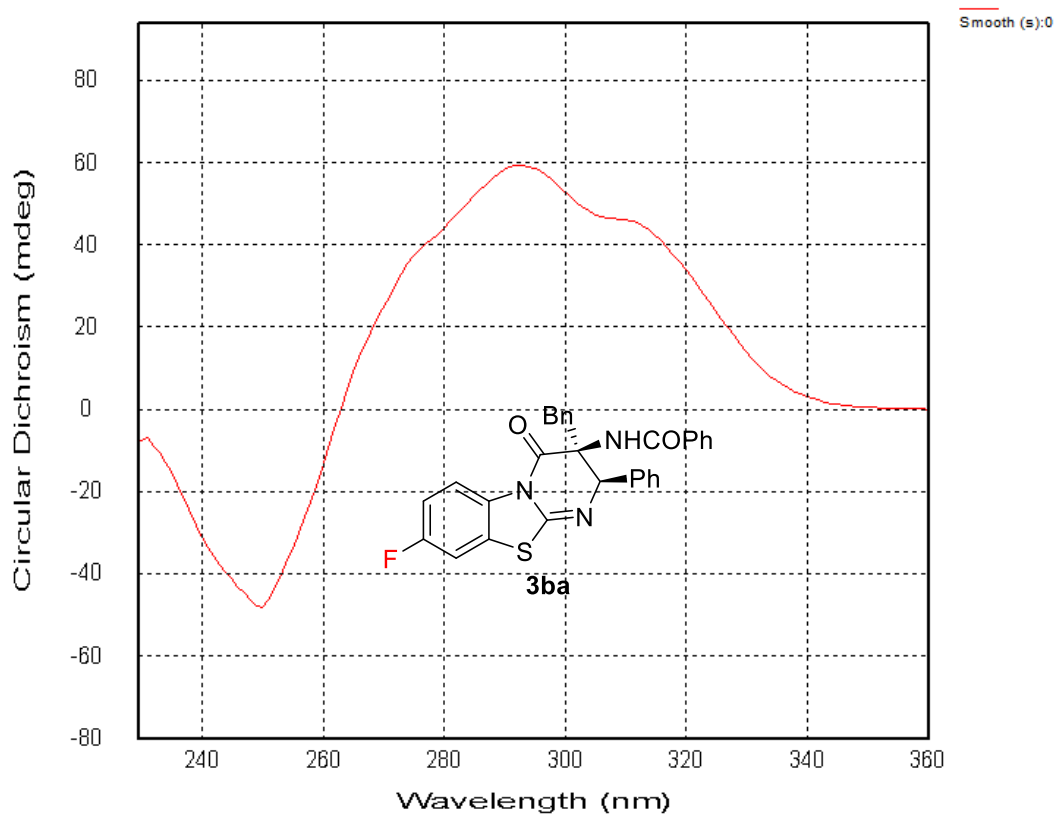


Figure S84.

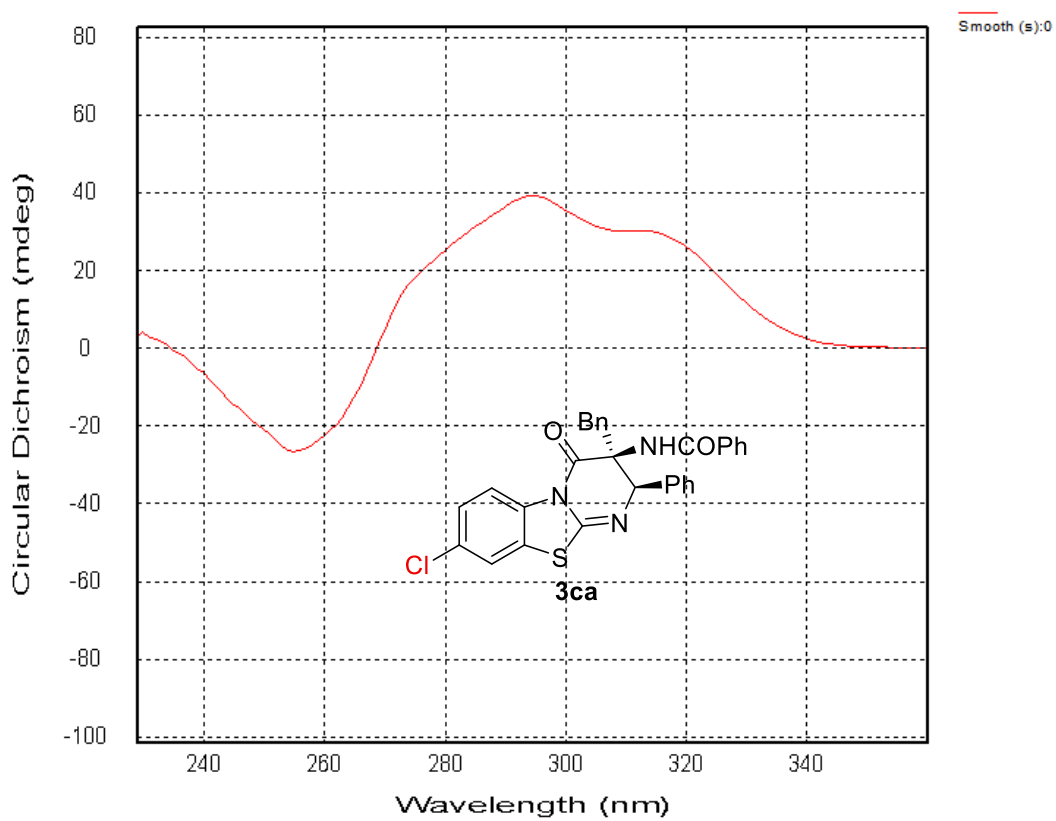


Figure S85.

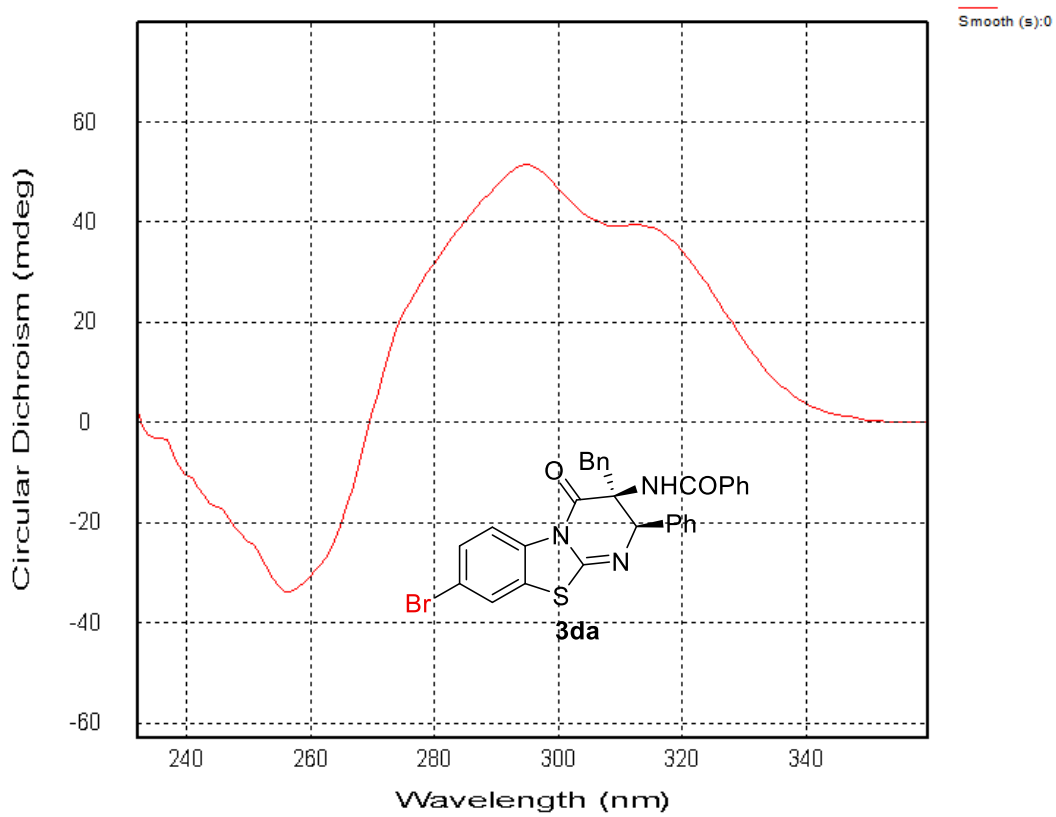


Figure S86.



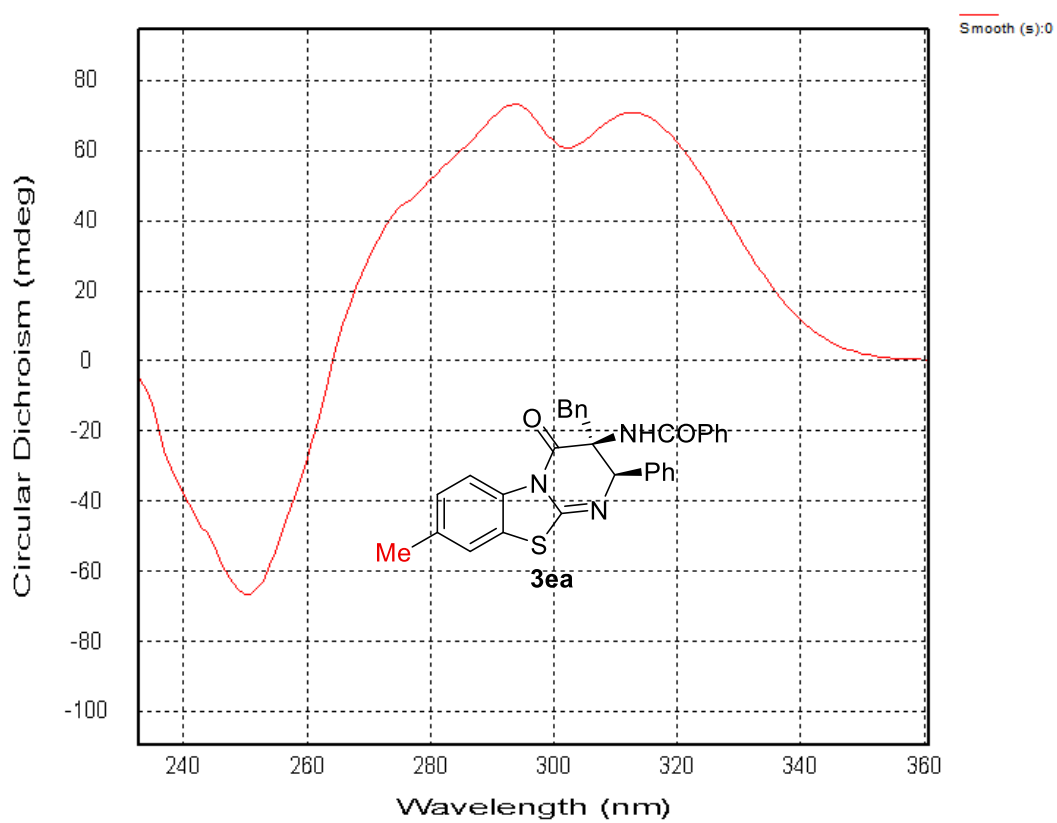


Figure S87.

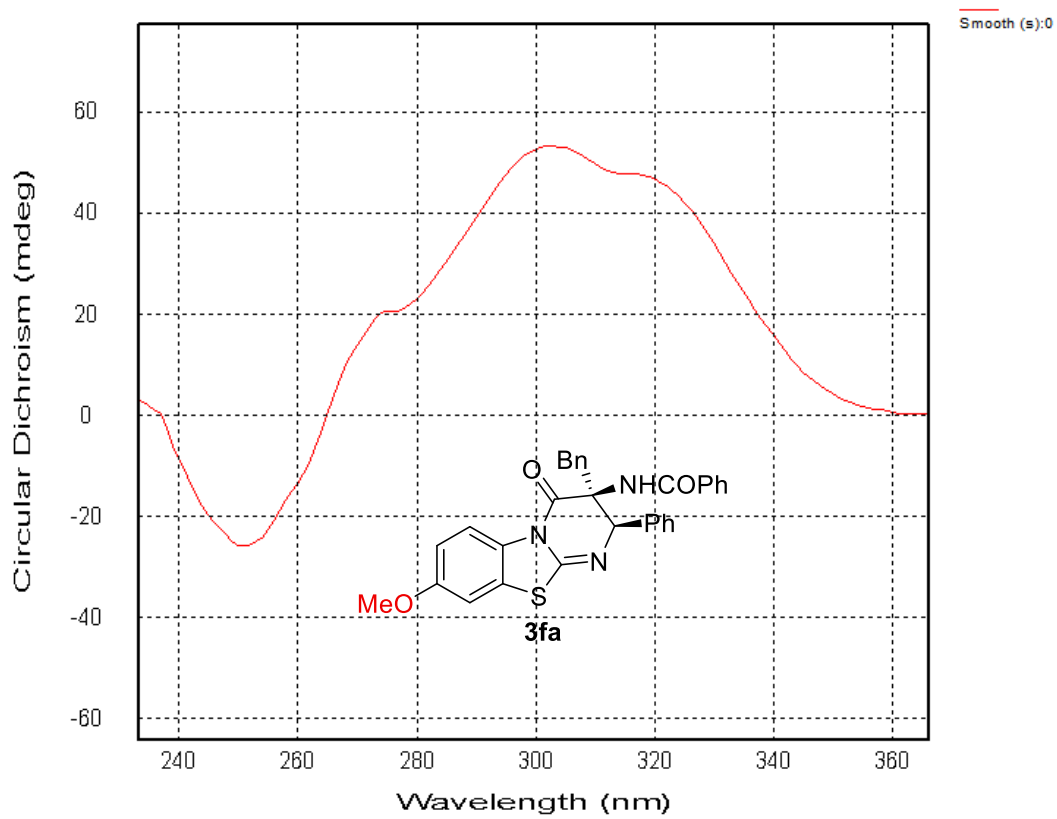


Figure S88.

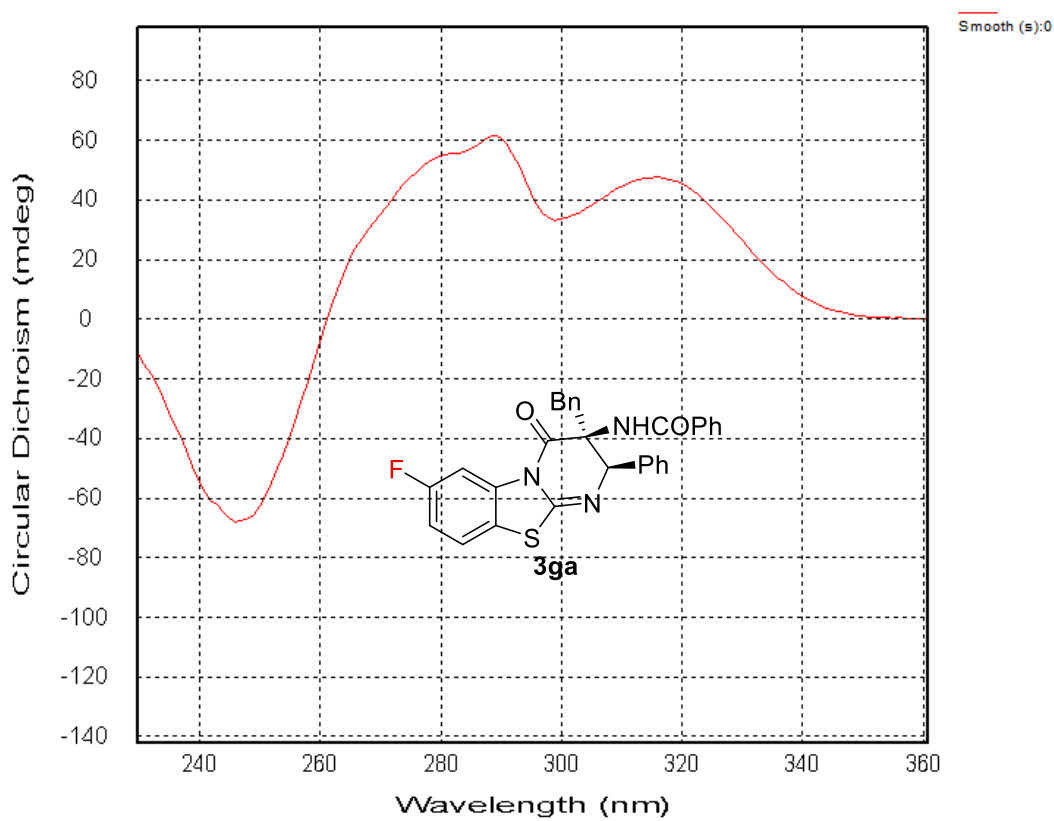


Figure S89.

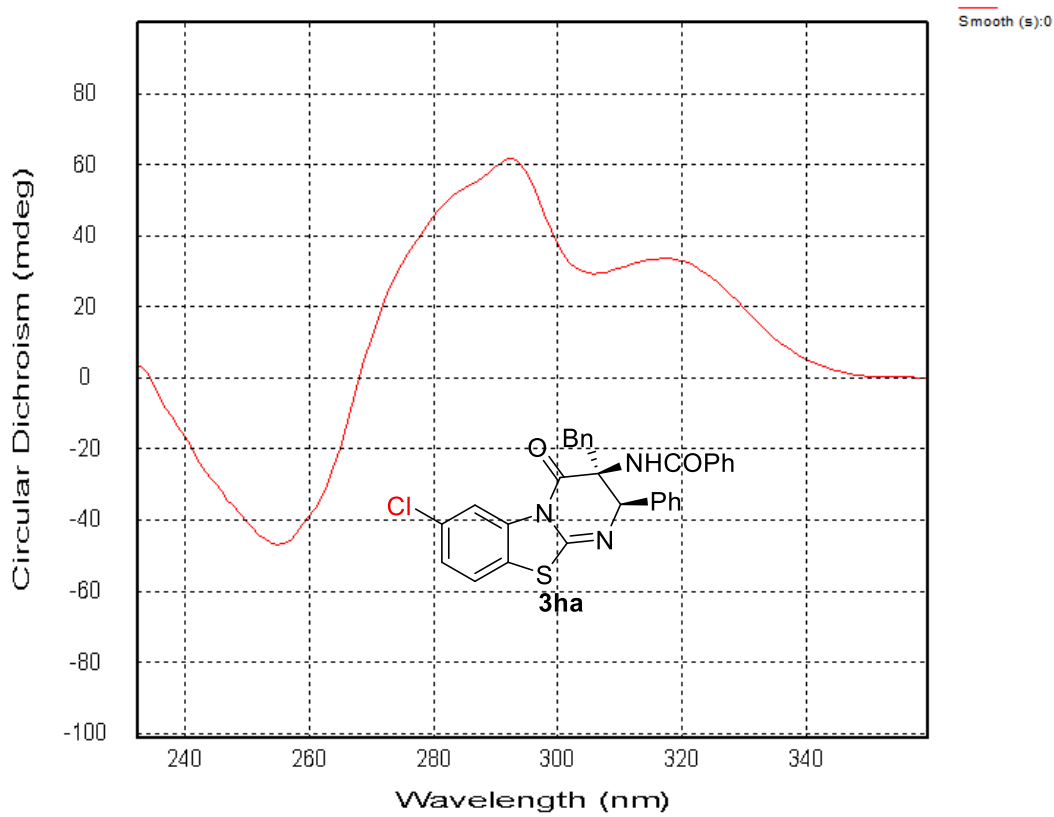


Figure S90.

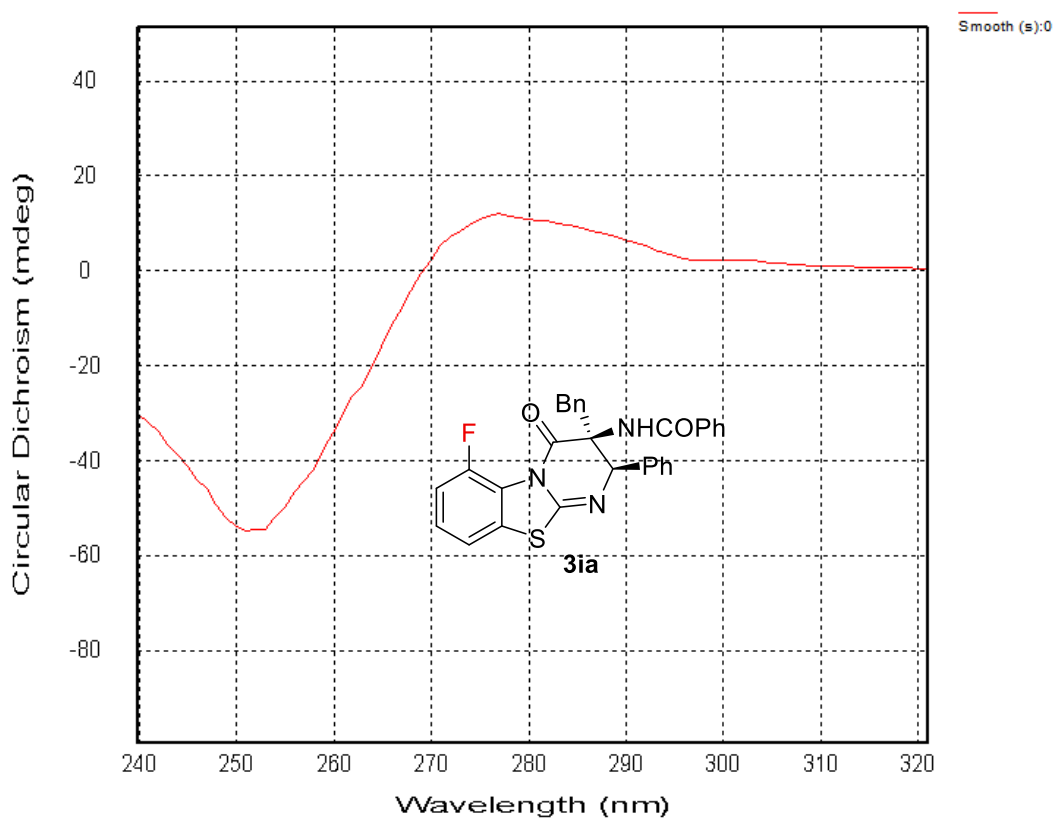


Figure S91.

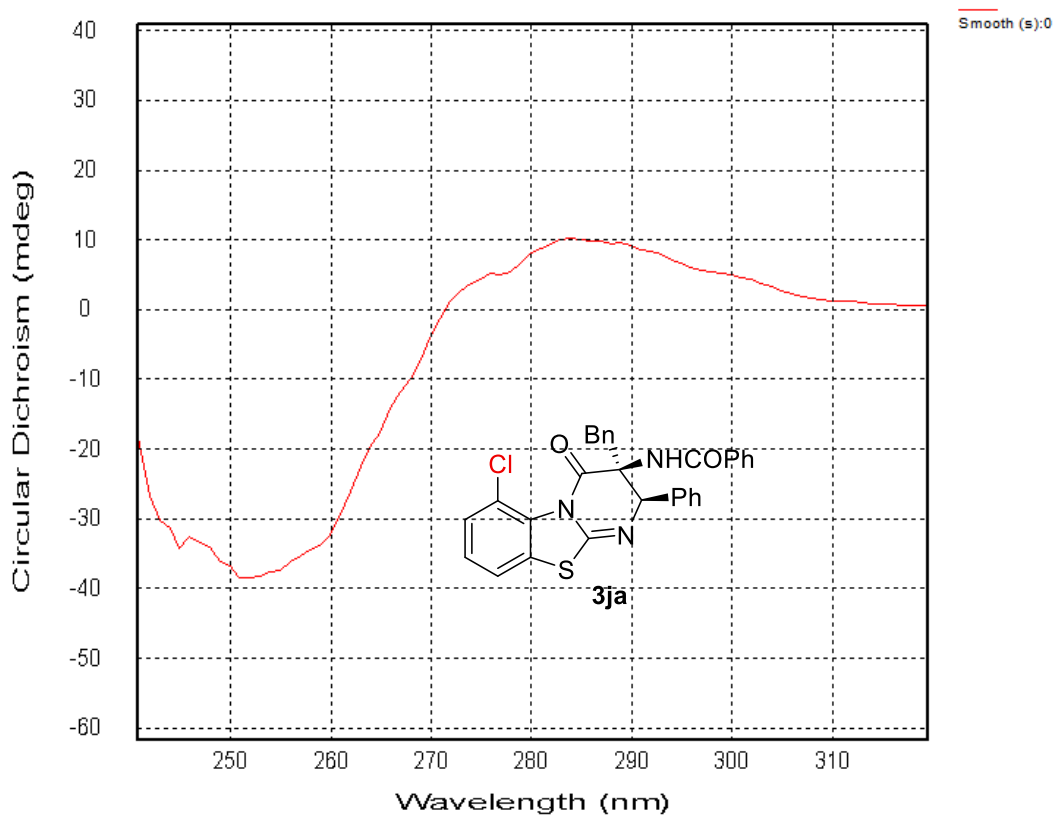


Figure S92.

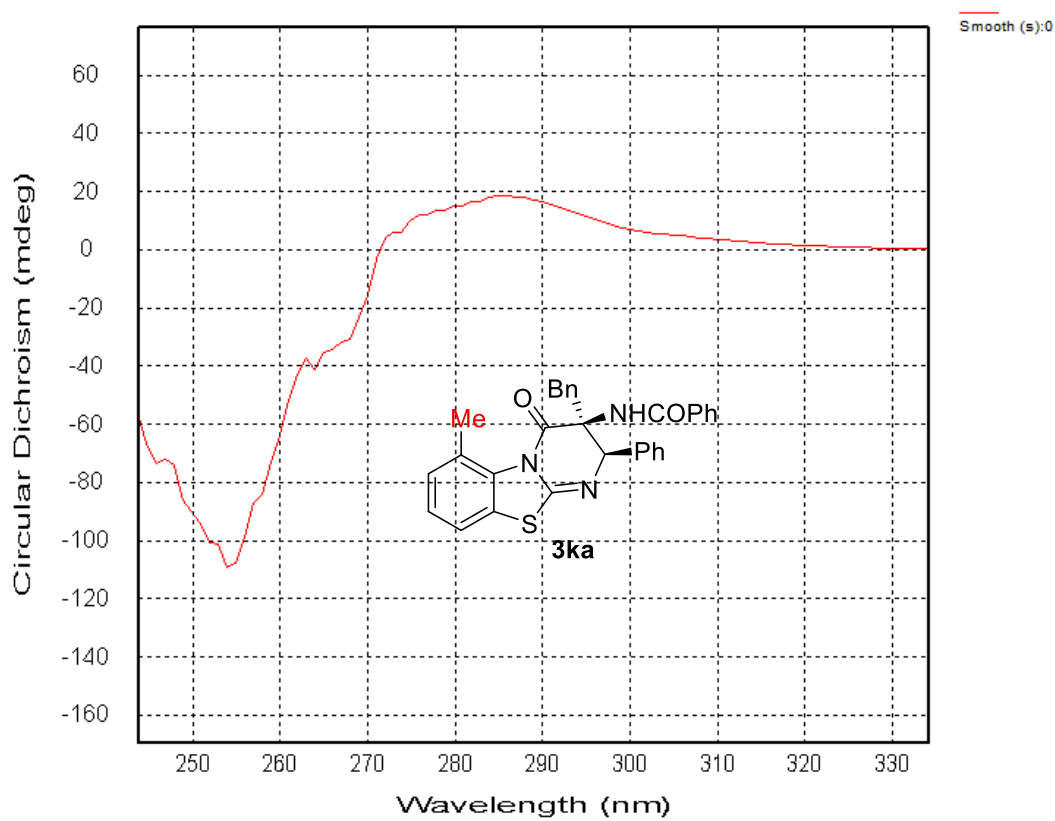


Figure S93.

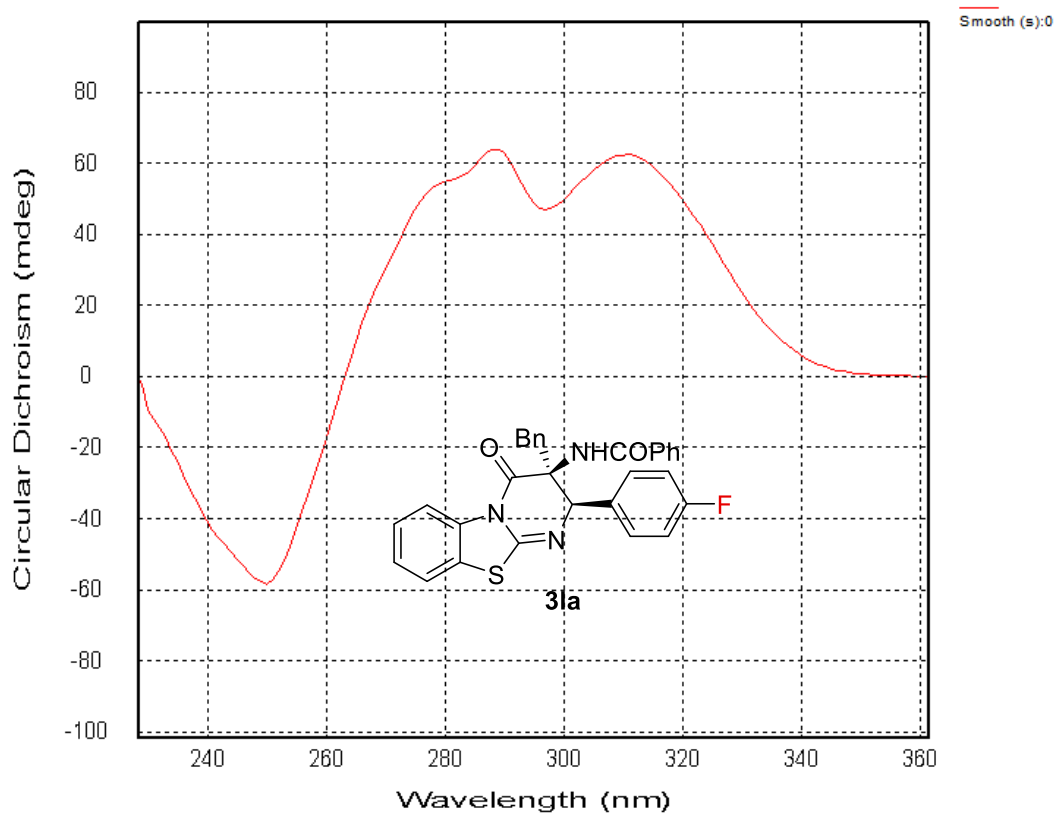


Figure S94.

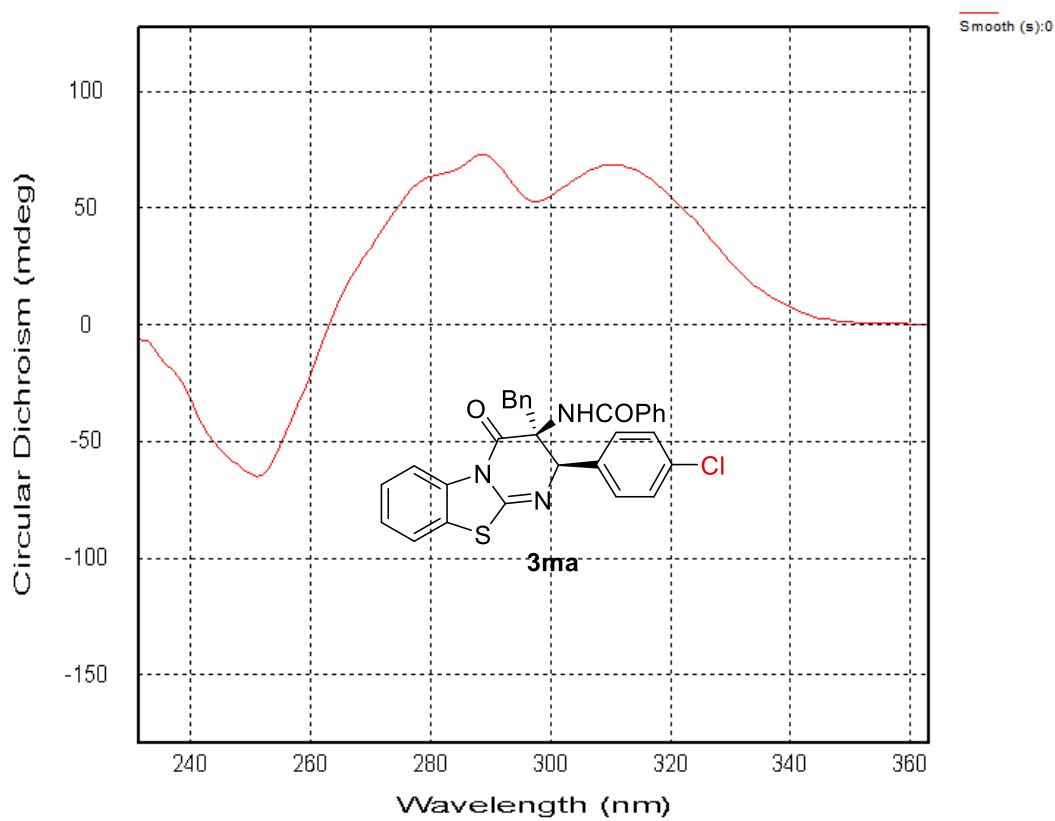


Figure S95.

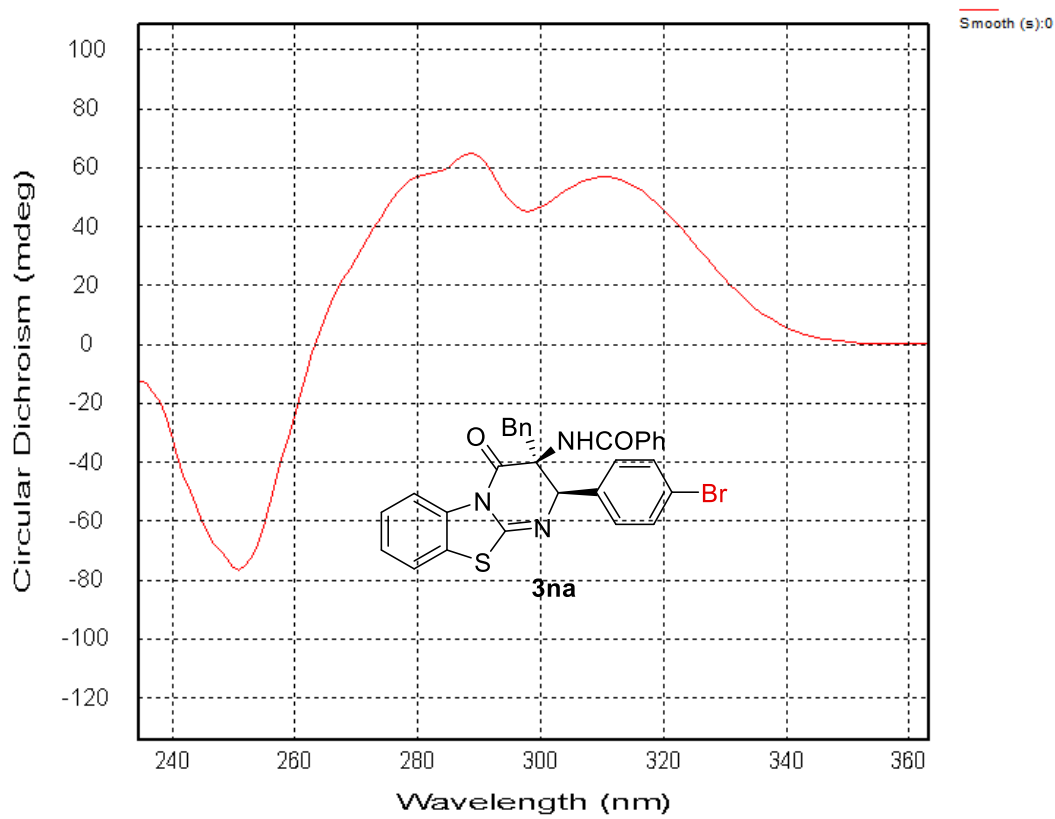


Figure S96.

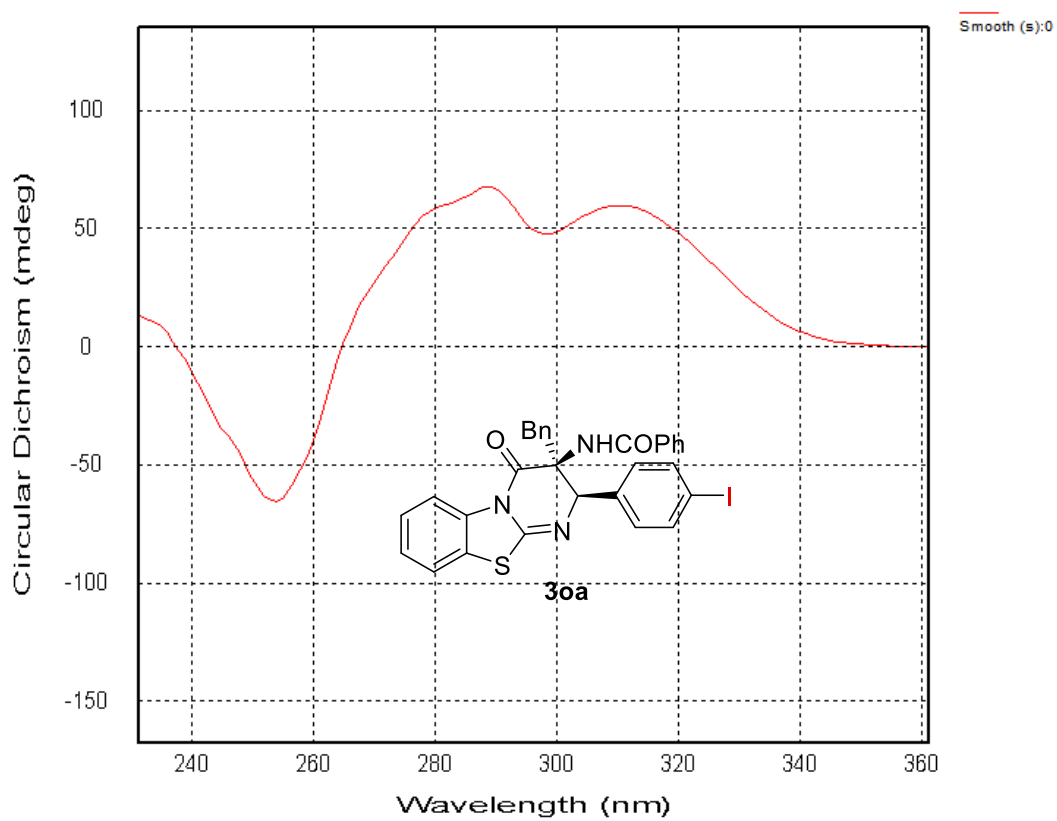


Figure S97.

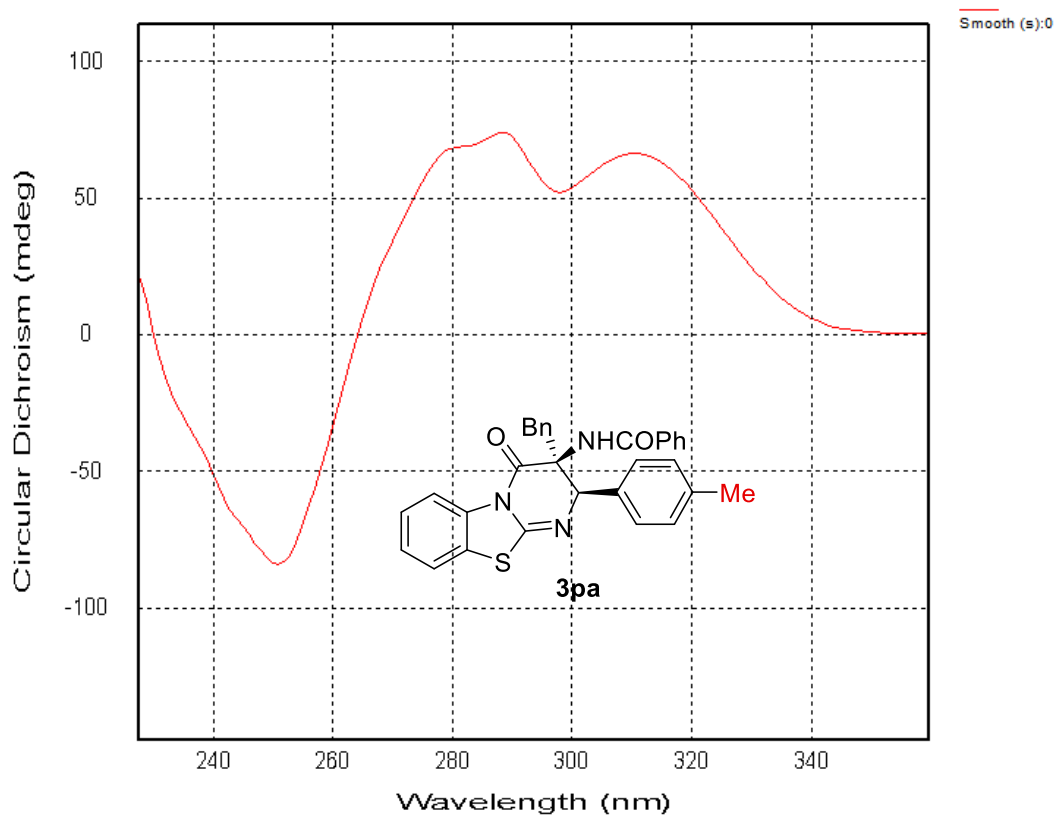


Figure S98.

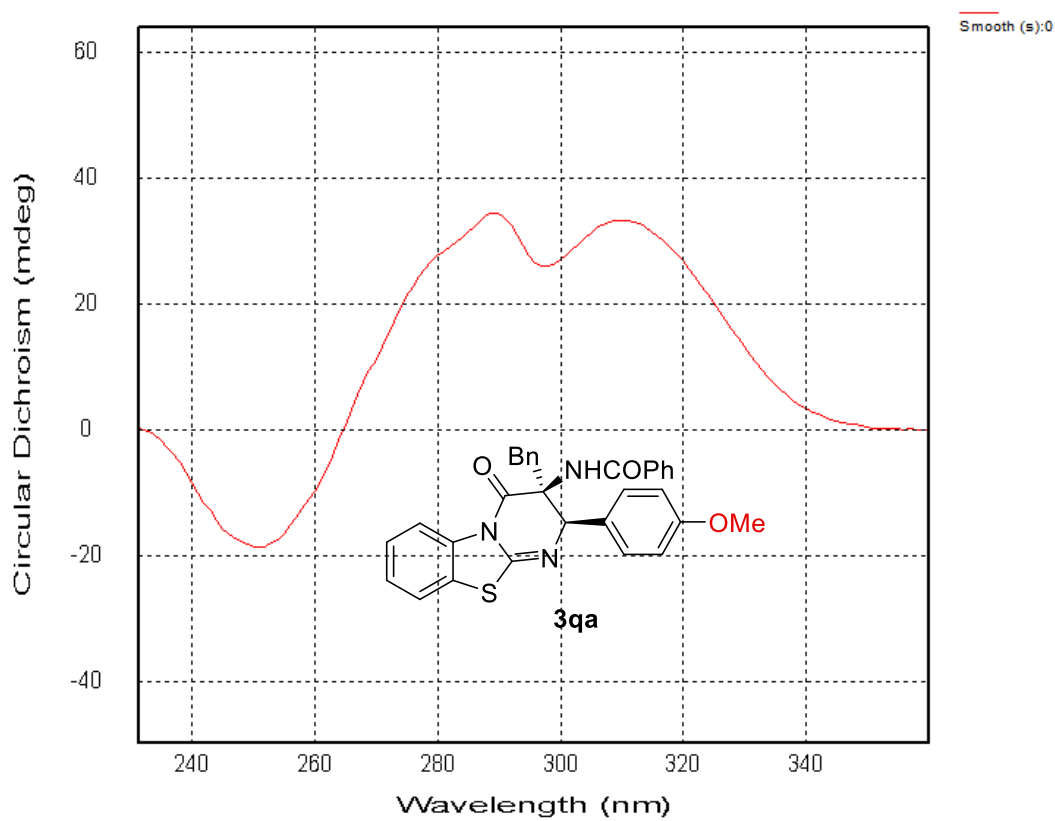


Figure S99.

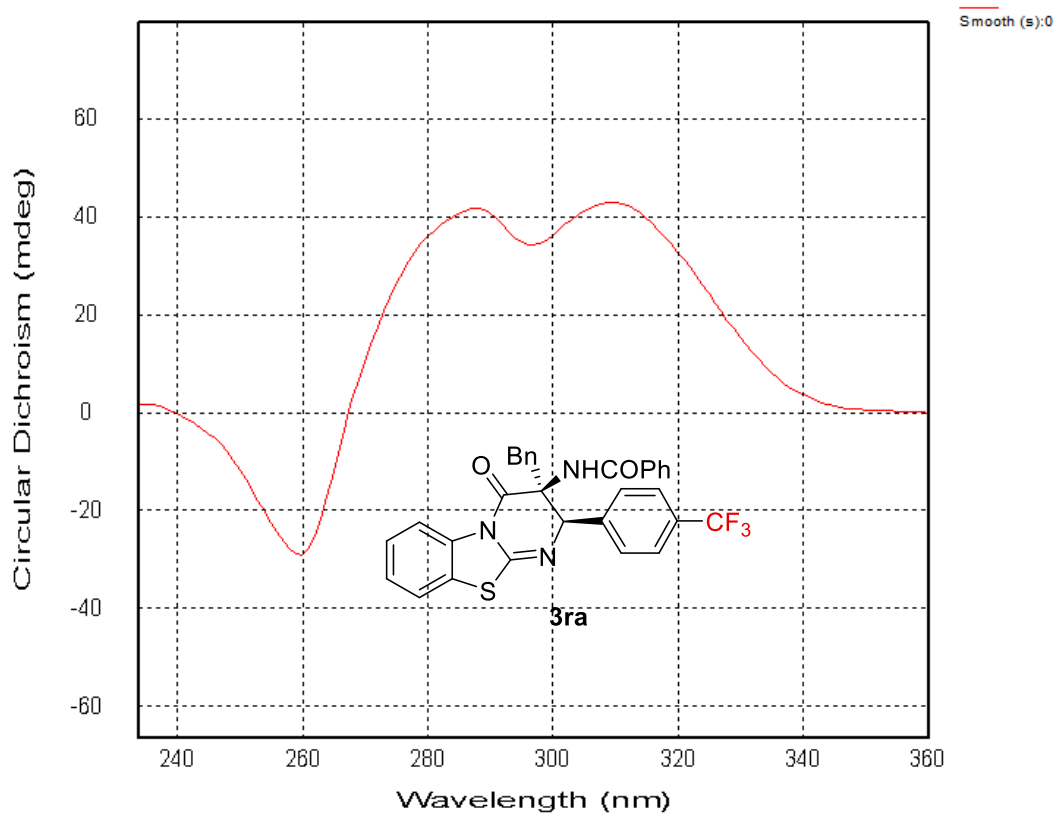


Figure S100.

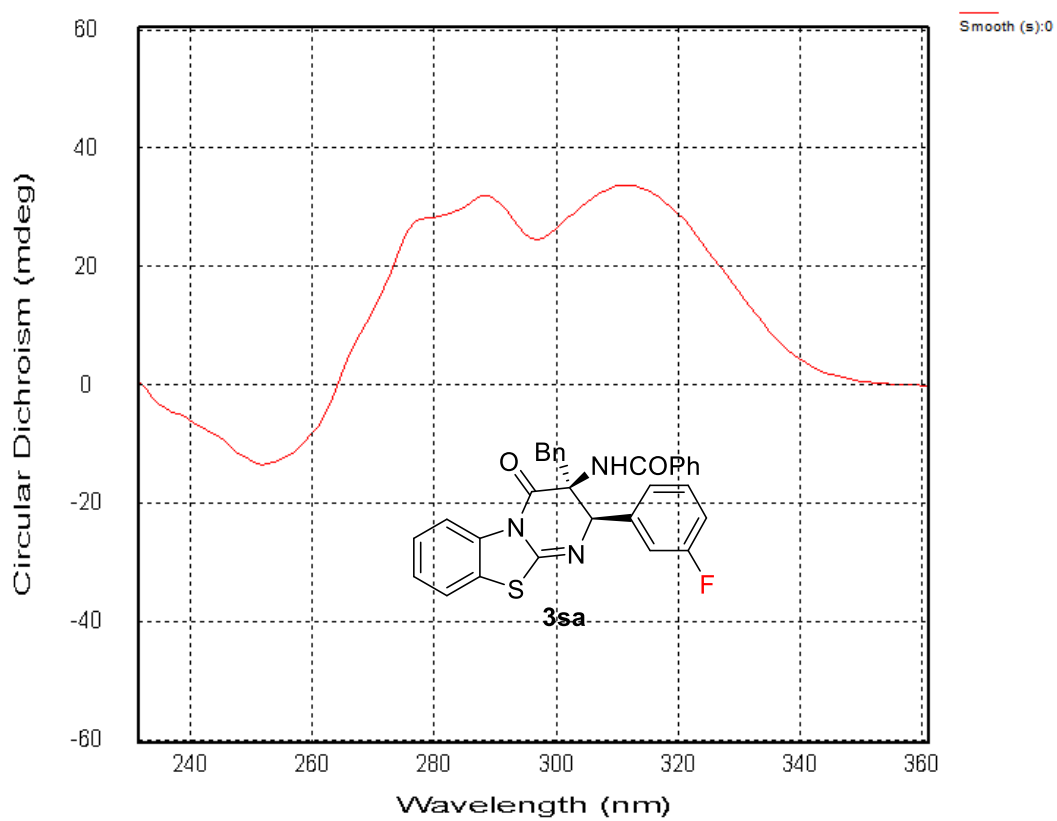


Figure S101.

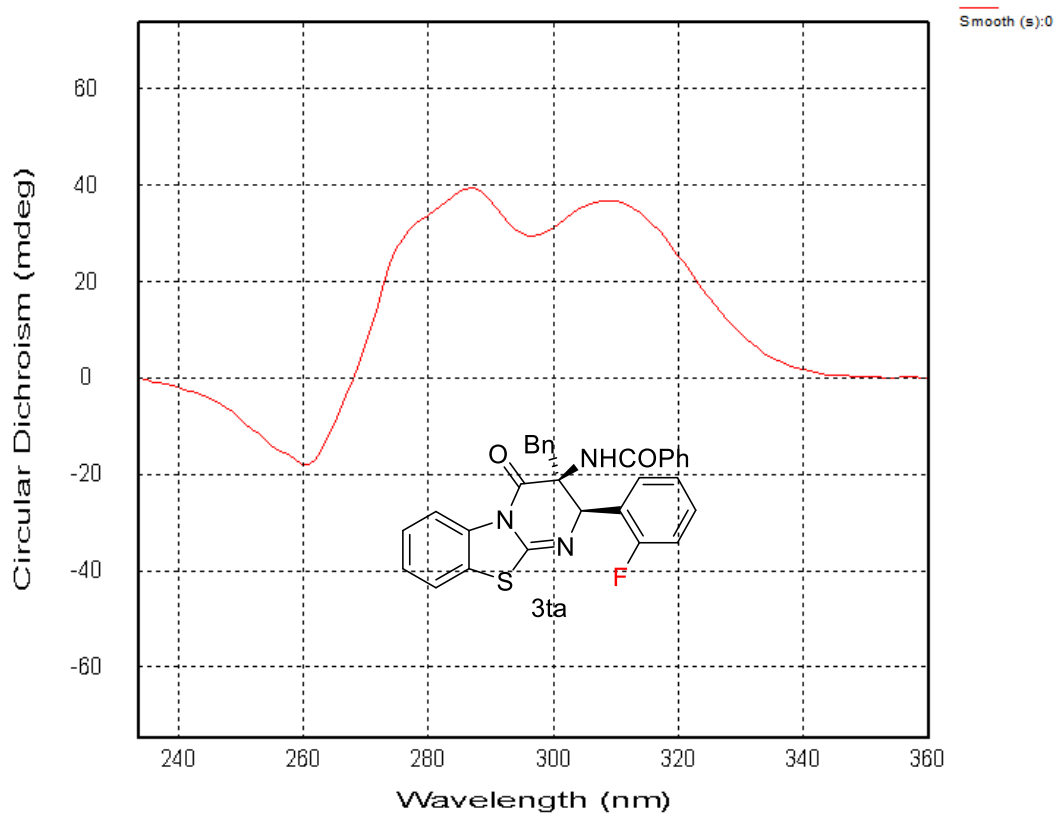


Figure S102.



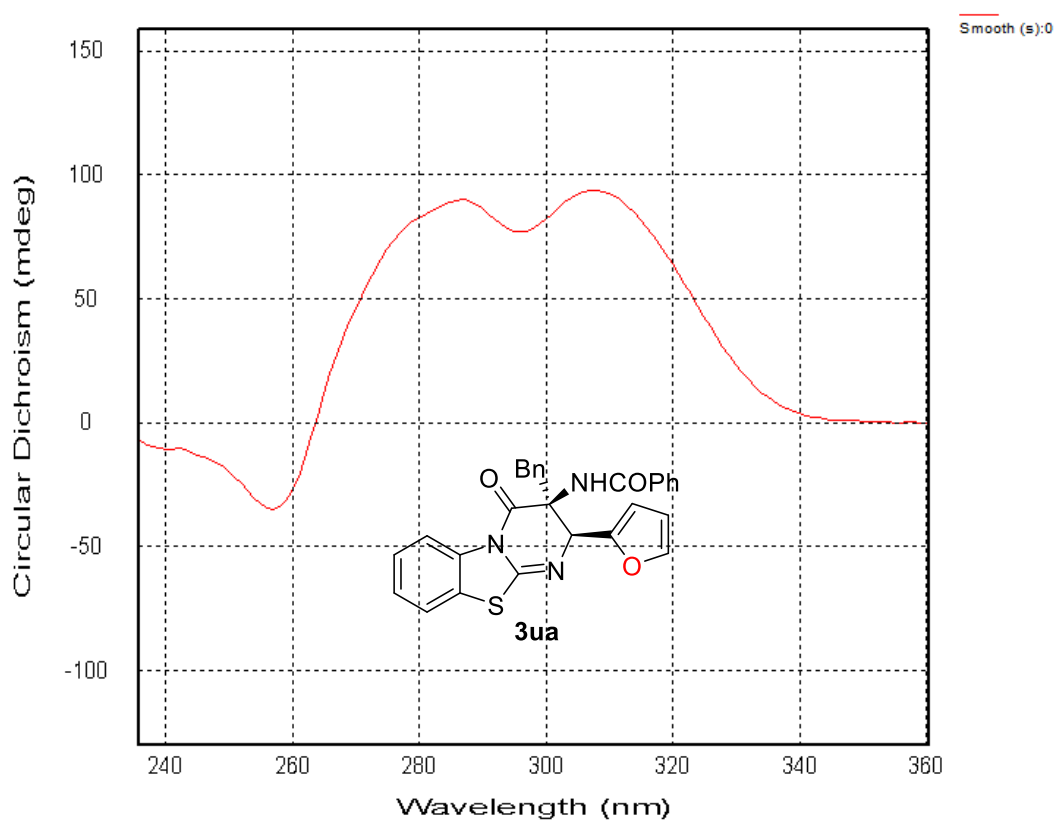


Figure S103.

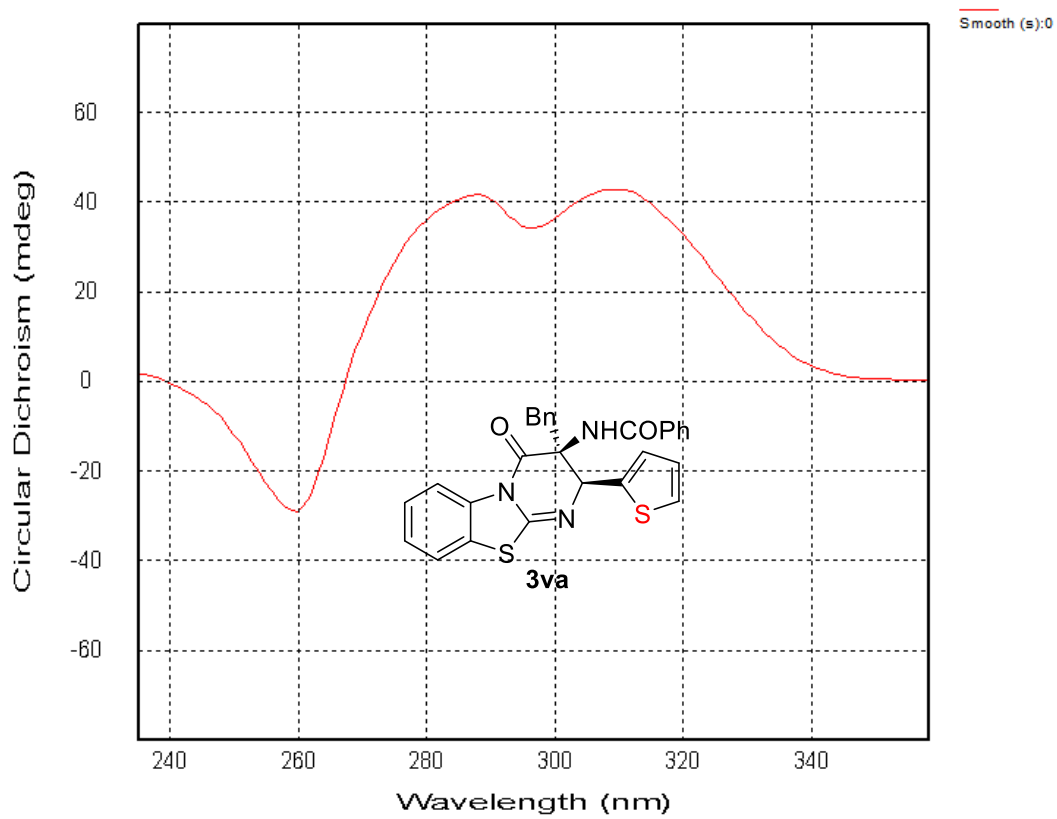


Figure S104.

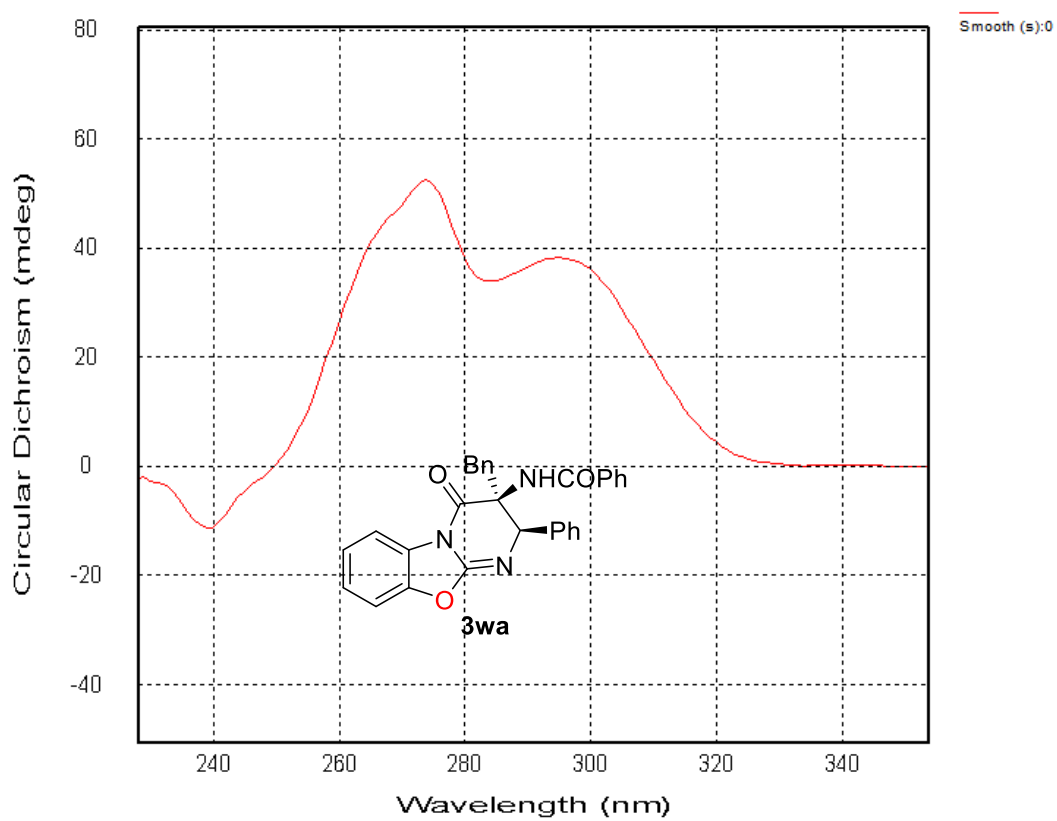


Figure S105.

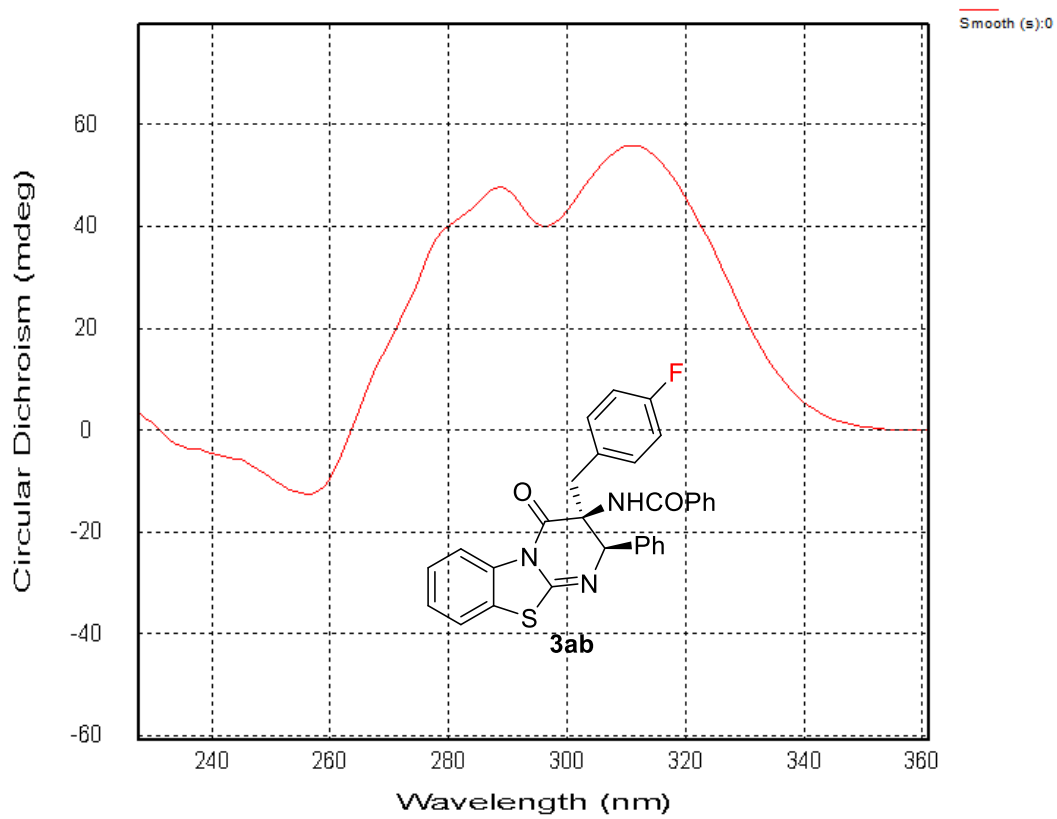


Figure S106.

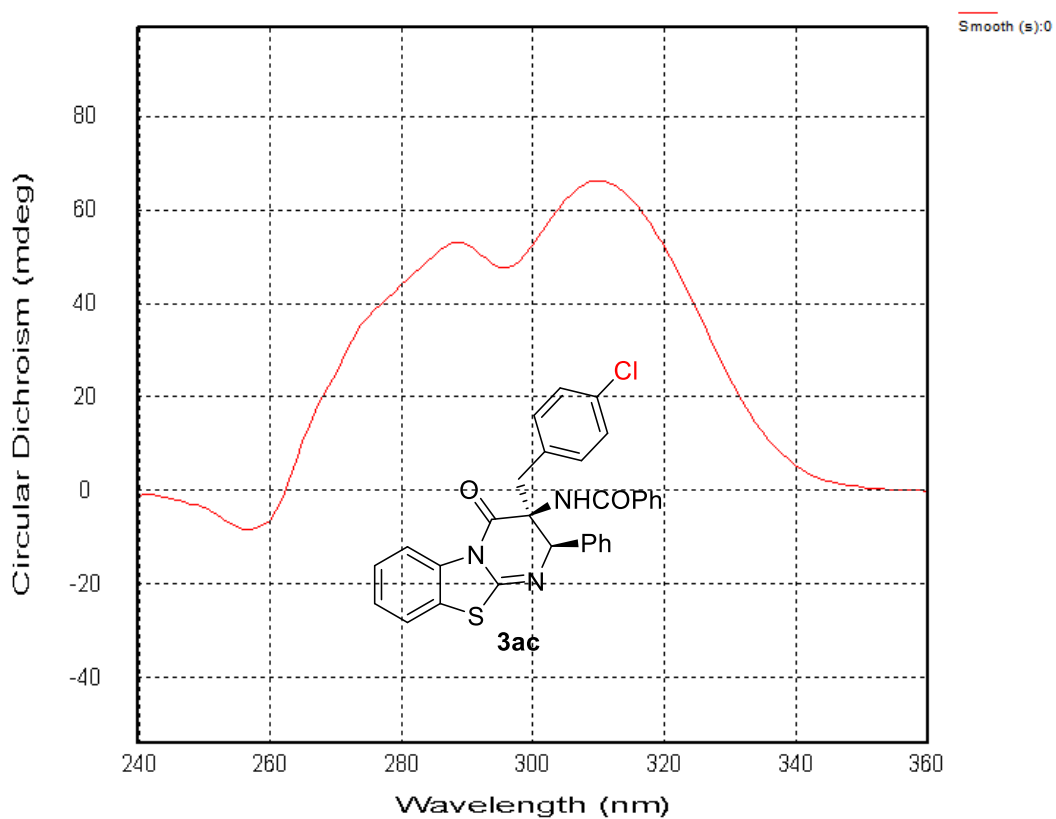


Figure S107.

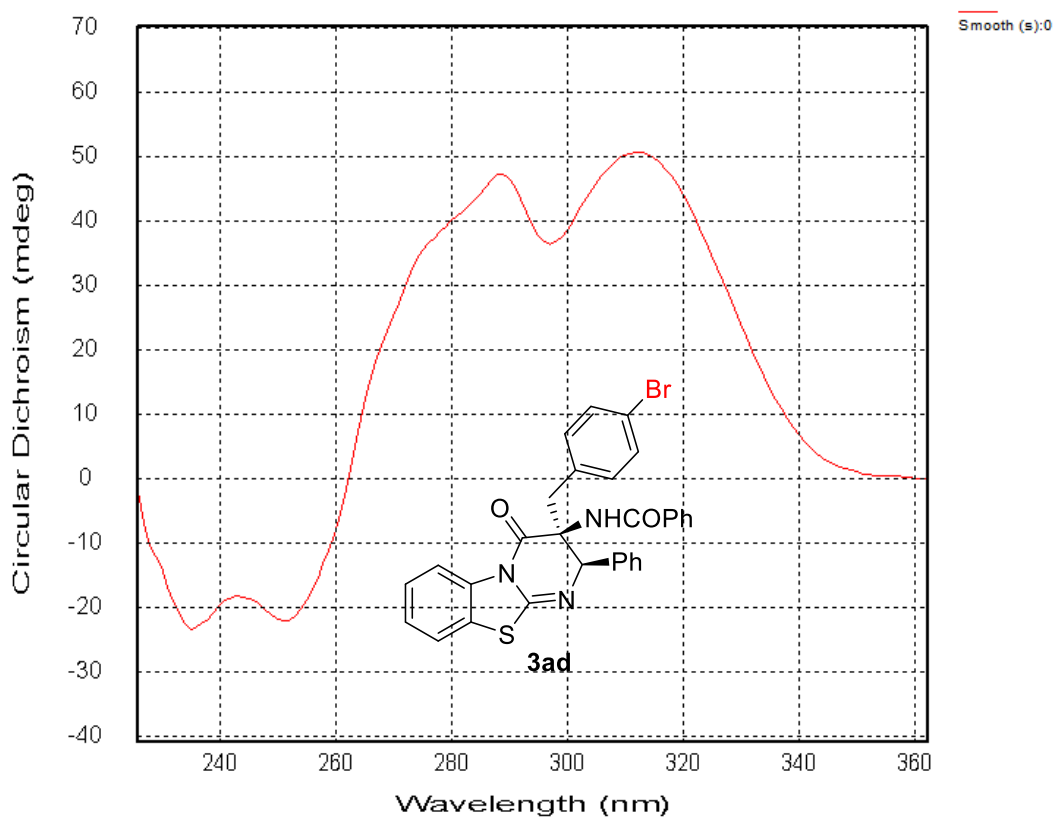


Figure S108.

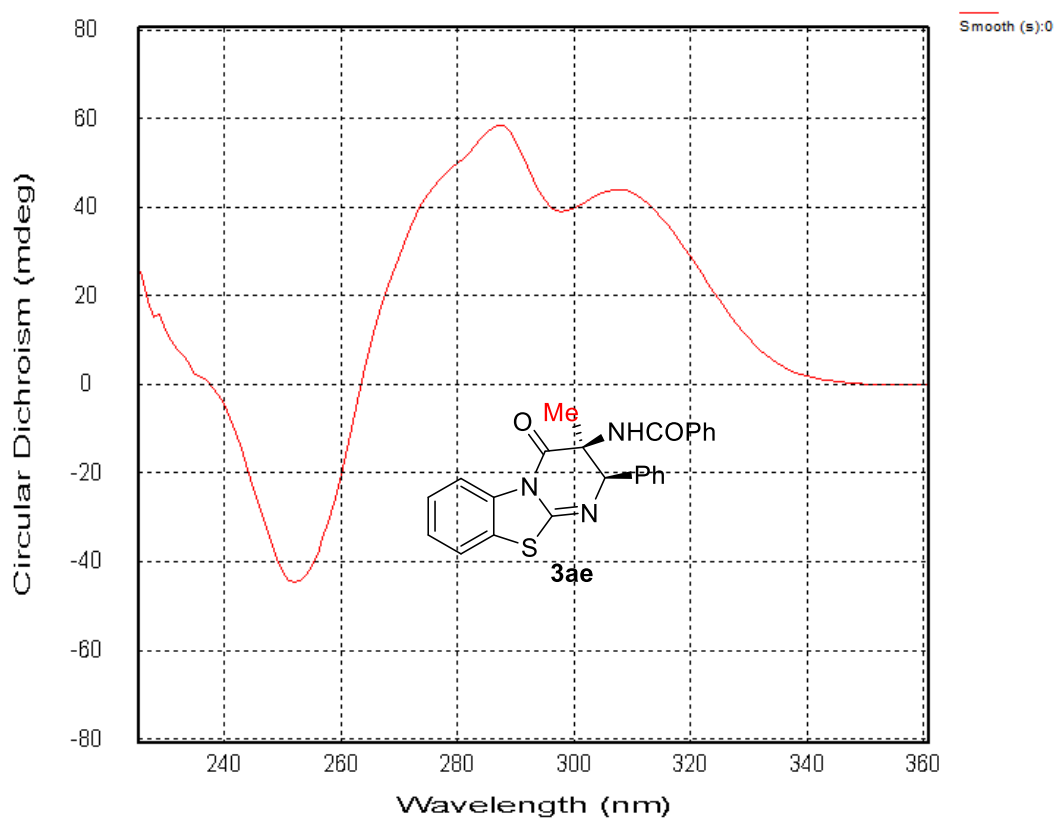


Figure S109.

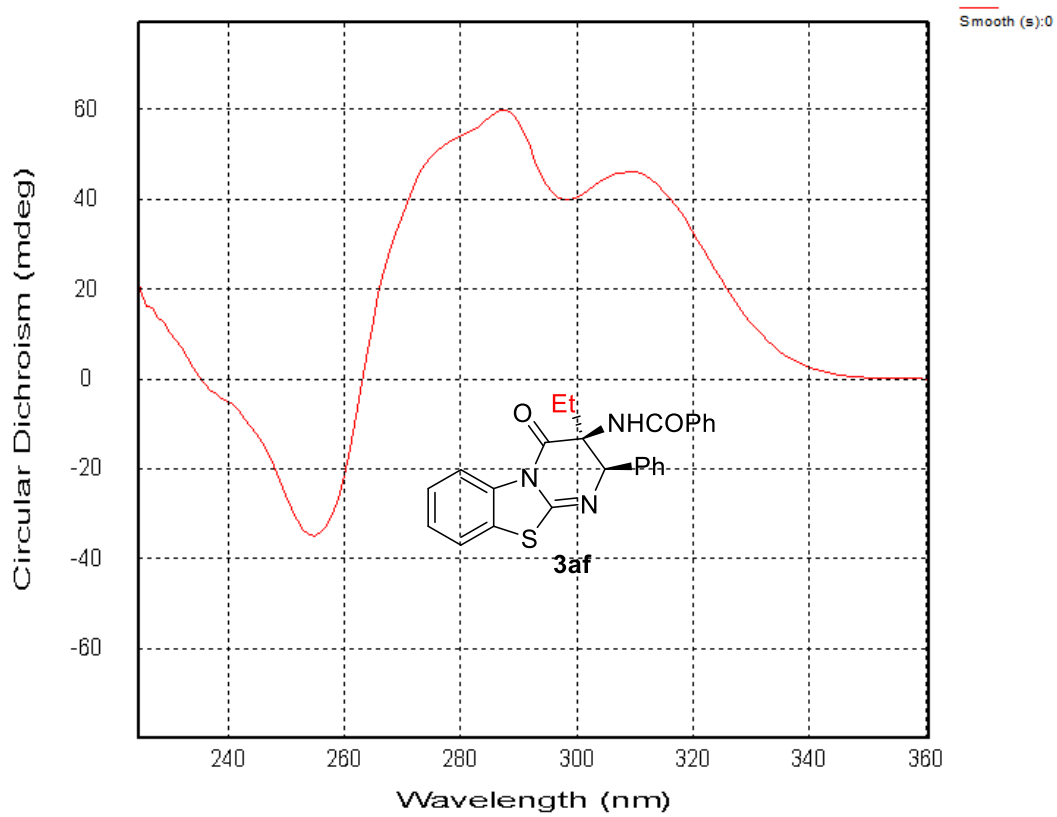


Figure S110.

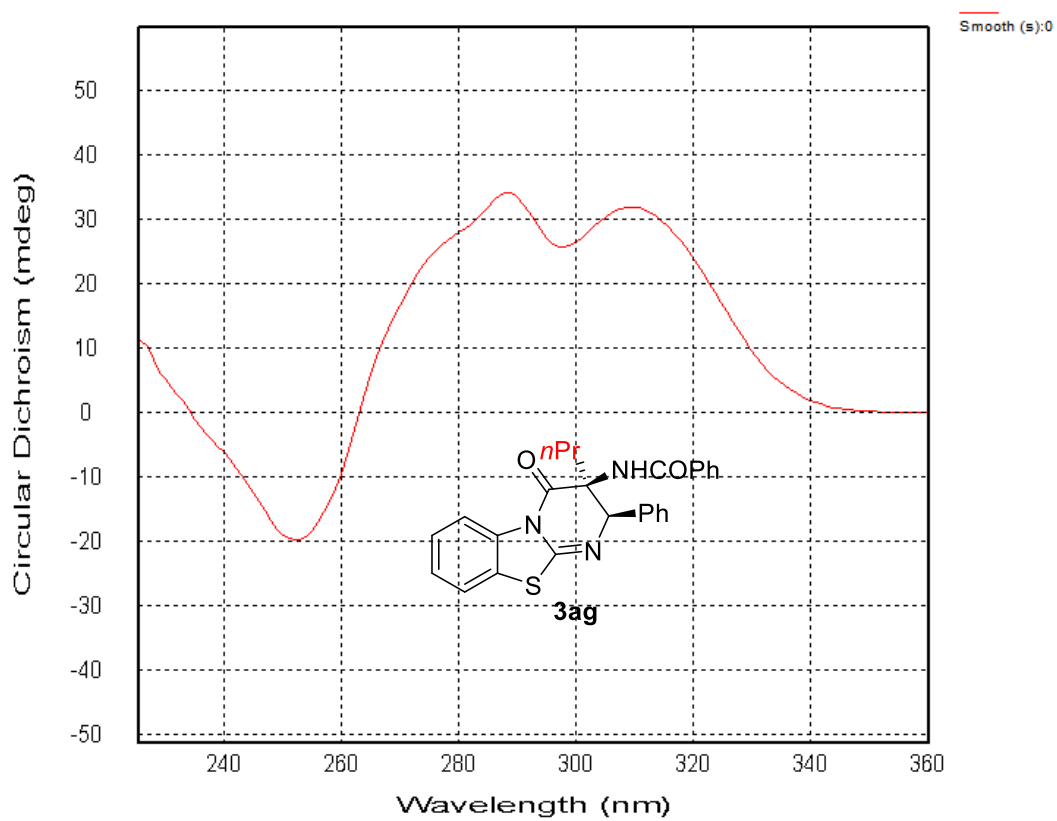


Figure S111.

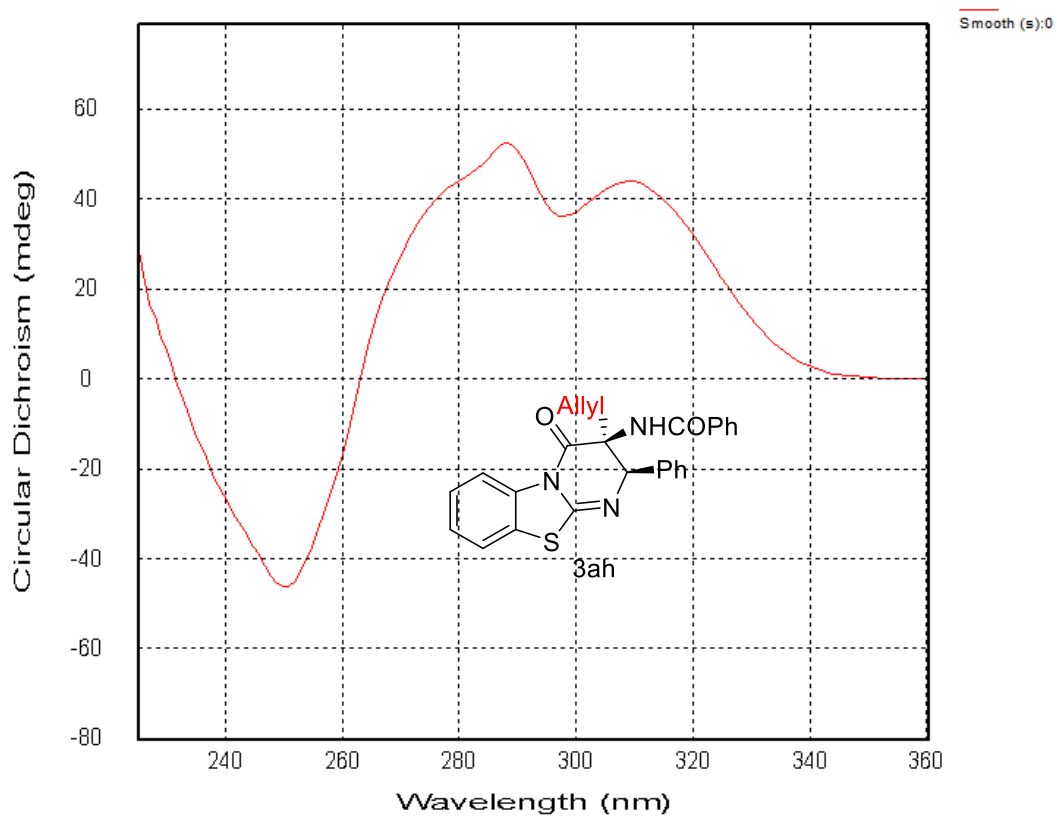


Figure S112.

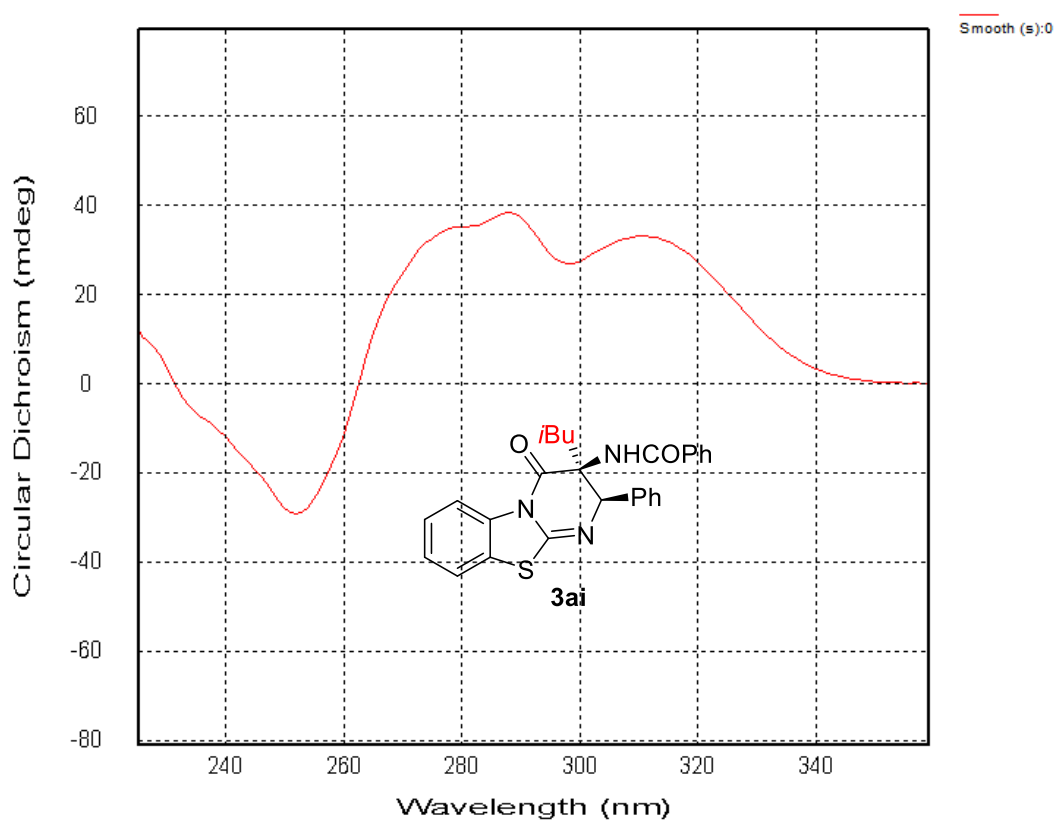


Figure S113.

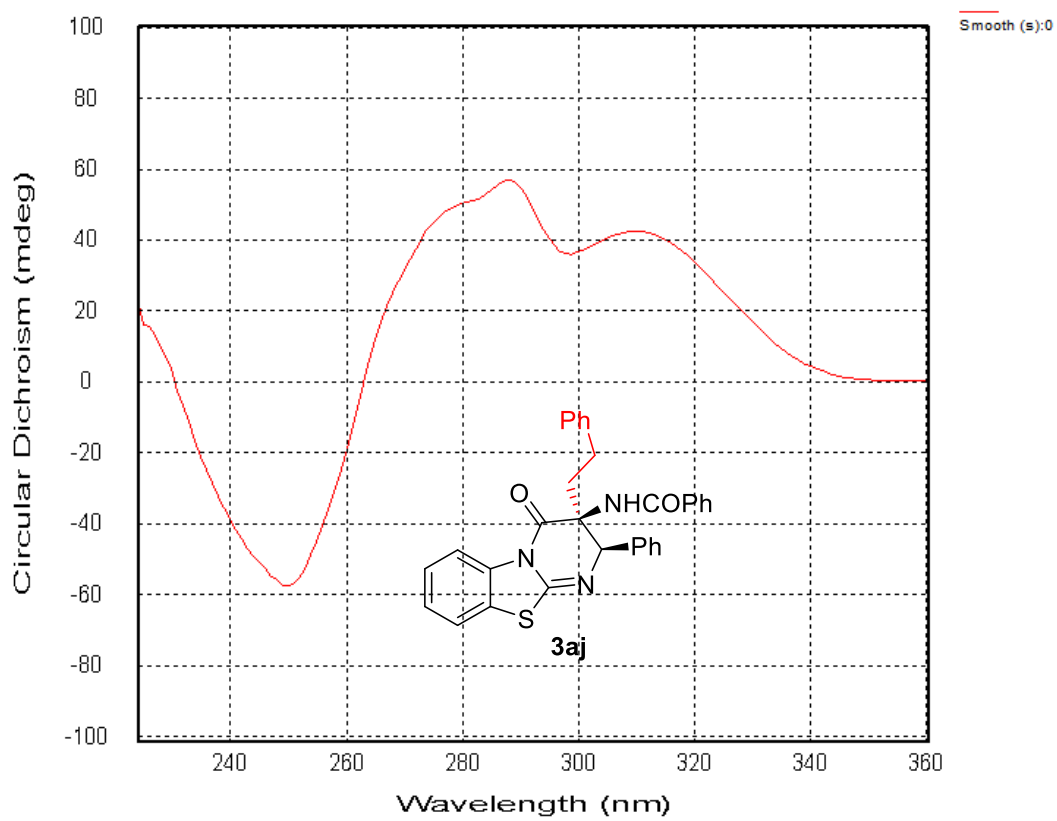


Figure S114.

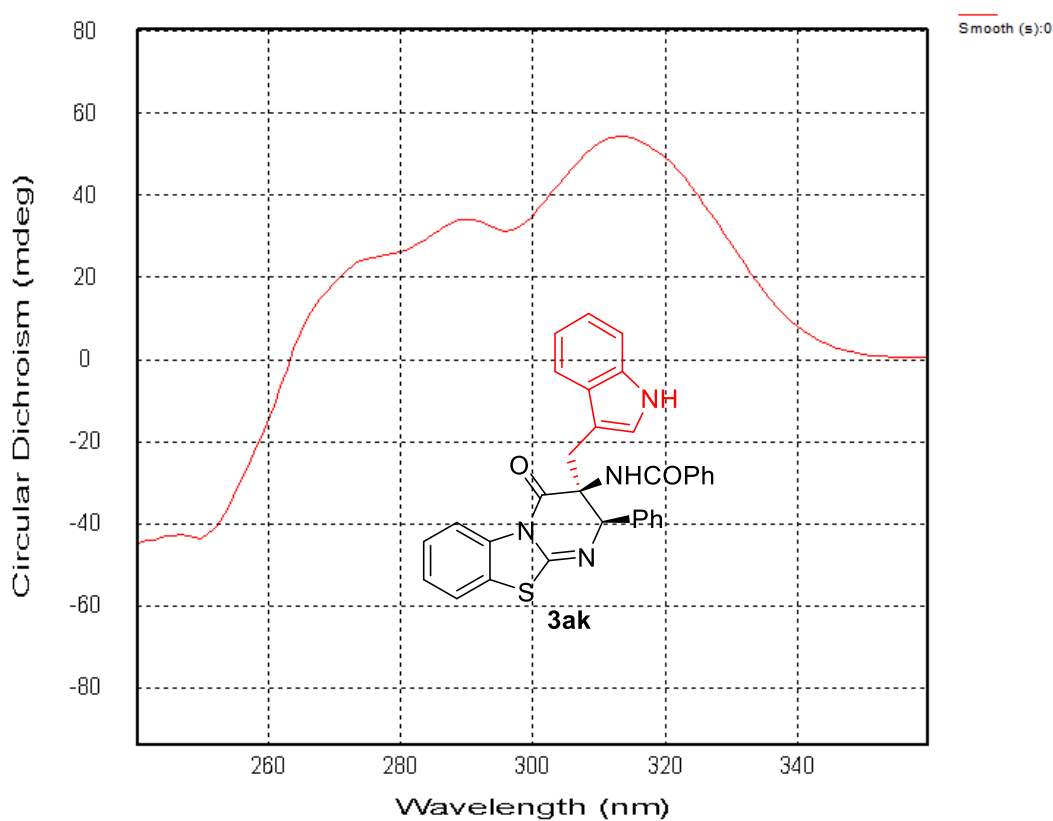
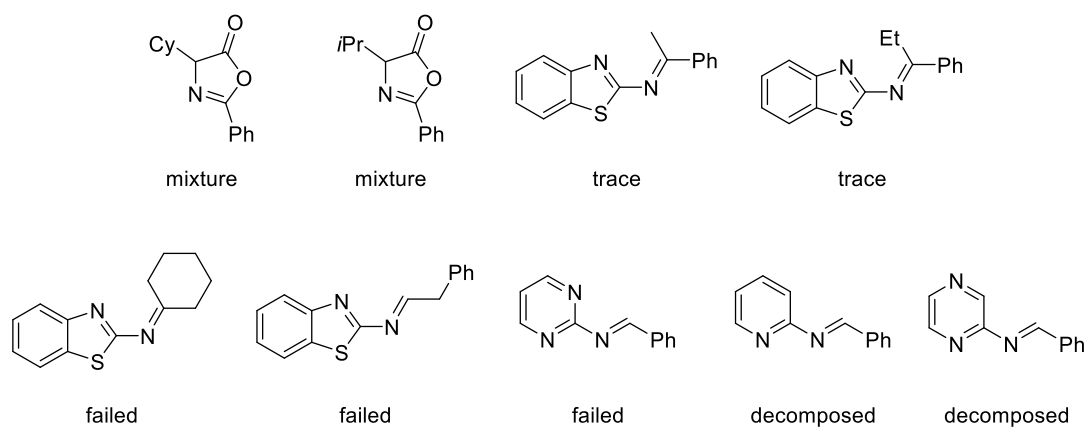


Figure S115.

## 11. Unsuccessful substrate scope



## 12. Reference

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