Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Lewis acid catalysed asymmetric cascade reaction of cyclopropyl ketones: concise synthesis of pyrrolobenzothiazoles

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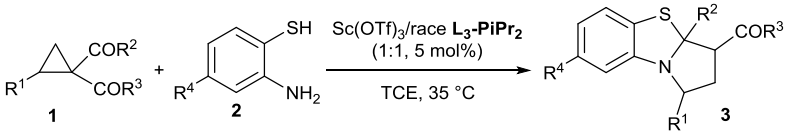
(A) General Information

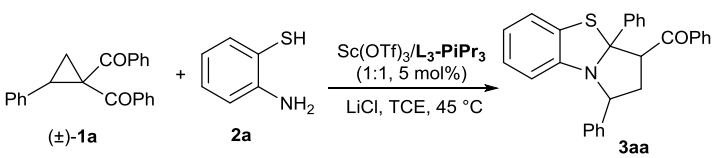
^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane at 0.00 ppm (δ ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm). ^{19}F{^{1}H} NMR spectra were collected at 376 MHz with complete proton decoupling. Optical rotations were reported as follows: $[\alpha]_\lambda^T$ = (*c*: g/100 mL, in solvent, λ: 589 nm). All *ee* values were determined by chiral HPLC analysis on Daicel chiralpak IA, ID, IE, IG, AD-H and UPC[2] analysis on chiral Daicel chiralcel OJ-3, in comparison with the authentic racemates. IR spectra were recorded on commercial instrument and the wave numbers of the absorption peaks are given in cm^{-1}. HRMS were recorded on a commercial apparatus (ESI source) and methanol was used to dissolve the sample. Reactions were monitored by thin layer chromatography (TLC). All reactions were performed in sealed oven-dried glass tubes unless otherwise noted. 1,1,2,2-tetrachloroethane (TCE) was distilled over powered CaH_2. The *N,N'*-Dioxide were prepared according to the methods reported in the literature.[1] Donor-Acceptor cyclopropanes were prepared according to previous work.[2] Unless noted, other commercial reagents were used without further purification.

(B) Typical Procedure for Preparation of the Racemic Products



Racemic ligand (±)-**L_3-PiPr$_2$** (5 mol%), $Sc(OTf)_3$ (5 mol%), and D-A cyclopropane **1** (0.10 mmol) were stirred in 0.5 mL of 1,1,2,2-tetrachloroethane at 35 °C under nitrogen atmosphere for 0.5 h. Then, 2-aminothiophenol **2** (0.10 mmol) was added and the mixture was stirred at 35 °C for 48 h. Then, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2/1) to afford the desired racemic product.

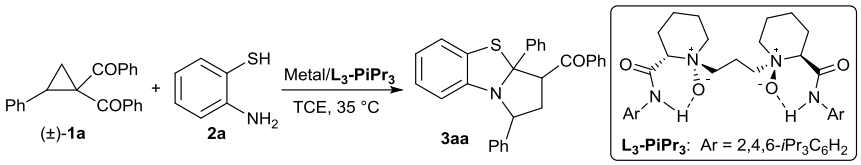
(C) Typical Procedure for Catalytic Asymmetric Reaction of D-A Cyclopropane with 2-Aminothiophenol



N,N'-Dioxide ligand **L_3-PiPr$_3$** (5 mol%), Sc(OTf)$_3$ (5 mol%), LiCl (30 mol%) and D-A cyclopropane **1a** (0.22 mmol) were stirred in 0.5 mL of 1,1,2,2-tetrachloroethane at 35 °C under nitrogen atmosphere for 0.5 h. Then, 2-aminothiophenol **2a** (0.10 mmol) was added and the mixture was stirred at 45 °C for 48 h. Then, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2/1) to afford the desired product as a yellow foam in 85% yield with 83:17 d.r. and 95% ee.

(D) Optimization of the Reaction Conditions

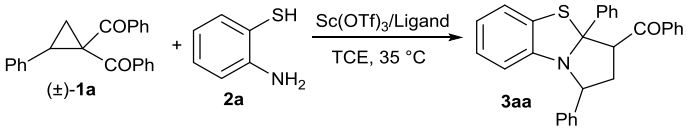
Table S1. Screening of Metals.



Entry[a]	Metal	Yield (%)[b]	d.r.[c]	*ee* (%)[c]
1	Y(OTf)$_3$	39	76:24	58/60
2	Yb(OTf)$_3$	40	70:30	46/56
3	Mg(OTf)$_2$	n.r.	--	--
4	Zn(OTf)$_2$	n.r.	--	--
5	Al(OTf)$_3$	n.r.	--	--
6	Sc(OTf)$_3$	60	65:35	93/93
7	ScCl$_3$·6H$_2$O	12	60:40	96/96
8	Hf(OTf)$_4$	8	59:41	2/0
9	Tb(OTf)$_3$	18	78:22	56/54
10	In(OTf)$_3$	9	83:17	0/0
11	Ga(OTf)$_3$	12	80:20	4/4
12	Sm(OTf)$_3$	16	79:21	63/64

[a] All reaction were performed with metal/**L_3-PiPr$_3$** (10 mol%, 1:1), D-A cyclopropane **1a** (0.22 mmol), 2-aminothiophenol **2a** (0.1 mmol) in 1,1,2,2-tetrachloroethane (0.5 mL) at 35 °C for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID.

Table S2. Screening of Ligands.



Entry[a]	Ligand	Yield (%)[b]	d.r.[c]	ee (%)[c]
1	**L_3-RaPr$_2$**	28	53:47	90/89
2	**L_3-PrPr$_2$**	34	64:36	80/80
3	**L_3-PiPr$_2$**	62	73:27	91/92
4	**L_3-TQ*t*Bu**	26	69:31	-16/-26
5	**L_3-PePr$_2$**	34	75:25	88/87
6	**L_3-PiPh**	18	77:23	24/32
7	**L_3-PiBn**	30	82:18	5/5
8	**L_3-PiMe$_2$**	34	81:19	35/29
8	**L_3-PiEt$_2$**	44	82:18	60/59
9	**L_3-PiPr$_3$**	60	65:35	93/93

10	**L_2-PiPr$_3$**	74	82:18	34/31
11	**L_4-PiPr$_3$**	10	45:55	64/70
12	**PyBox**	42	78:22	-15/-11
13	**Box**	<5	-	-

[a] All reaction were performed with Sc(OTf)$_3$/ligand (1:1, 10 mol%), D-A cyclopropane **1a** (0.22 mmol), 2-aminothiophenol **2a** (0.1 mmol) in 1,1,2,2-tetrachloroethane (0.5 mL) at 35 °C for 26 h. [b] Isolated yield. *c* Determined by HPLC analysis on Daicel chiralpak ID.

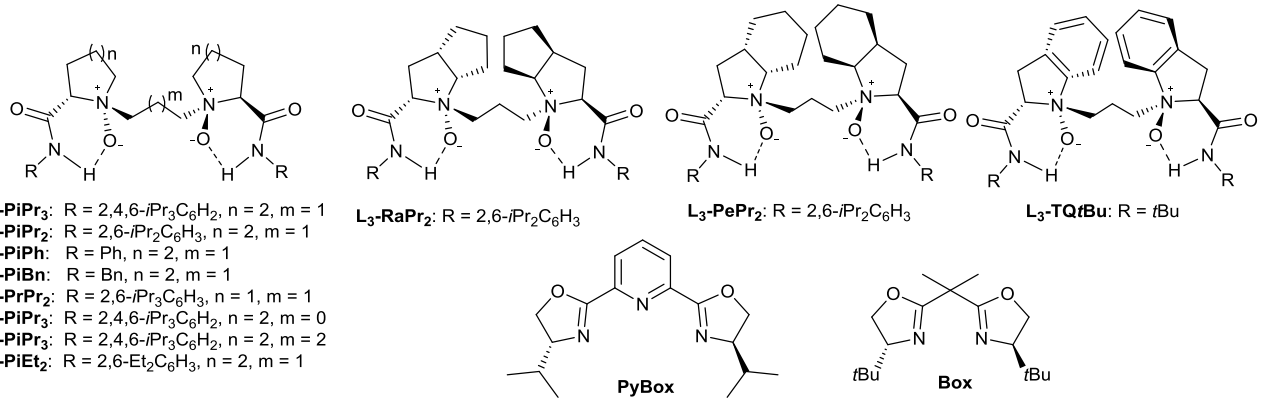
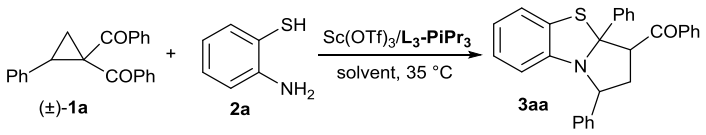


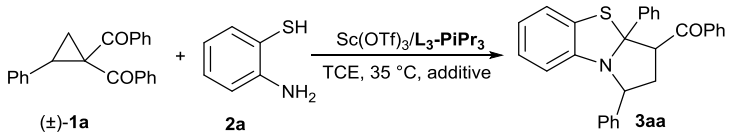
Table S3. Screening of Solvents.



Entry[a]	Solvent	Yield (%)[b]	d.r.[c]	*ee* (%)[c]
1	Tetrahydrofuran	<5	66:34	73/84
2	Toluene	12	66:34	50/55
3	Dichloromethane	22	54:46	92/93
4	Dichloroethane	35	64:36	89/91
5	Trichloromethane	51	67:33	93/94
6	1,1,2,2-tetrachloroethane	60	65:35	93/93

[a] All reaction were performed with Sc(OTf)$_3$/**L$_3$-PiPr$_3$** (10 mol%, 1:1), D-A cyclopropane **1a** (0.22 mmol), 2-aminothiophenol **2a** (0.1 mmol) in solvent (0.5 mL) at 35 °C for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID.

Table S4. Screening of Additives.

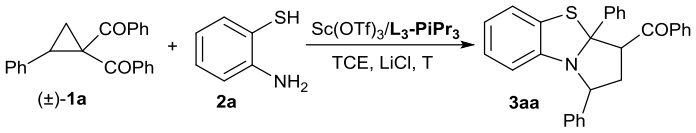


Entry[a]	Additive	Yield (%)[b]	d.r.[c]	ee (%)[c]
1	3 Å M.S.	6	80:20	55/60
2	4 Å M.S.	12	79:21	53/55
3	5 Å M.S.	23	77:23	53/56

4	H_2O	67	61:39	93/94
5	LiCl	75	80:20	95/95
6	LiBr	63	76:24	91/91
7	$LiNTf_2$	42	56:44	64/64
8	$CaCl_2$	73	80:20	96/95
9	NaCl	76	72:28	95/95
10	$MgBr_2$	52	66:34	96/96

[a] All reaction were performed with $Sc(OTf)_3$/**L_3-PiPr$_3$** (10 mol%, 1:1), D-A cyclopropane **1a** (0.22 mmol), 2-aminothiophenol **2a** (0.1 mmol), additive (1 equiv) in 1,1,2,2-tetrachloroethane (0.5 mL) at 35 °C for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID.

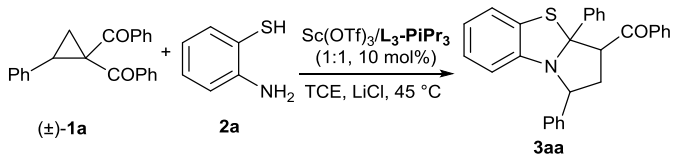
Table S5. Screening of Temperature.



Entry[a]	Temperature (°C)	Yield (%)[b]	d.r.[c]	*ee* (%)[c]
1	30	65	76:24	96/96
2	35	75	81:19	96/96
3	40	65	84:16	96/96
4	45	72	83:17	96/96
5	50	71	85:15	96/96

[a] All reaction were performed with $Sc(OTf)_3$/**L_3-PiPr$_3$** (10 mol%, 1:1), D-A cyclopropane **1a** (0.22 mmol), 2-aminothiophenol **2a** (0.1 mmol), LiCl (50 mol%) in 1,1,2,2-tetrachloroethane (0.5 mL) for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID.

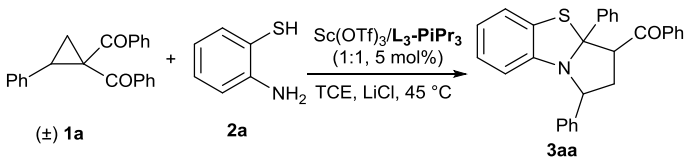
Table S6. Screening the Ratio of Substrates.



Entry[a]	**1a**:**2a**	Yield (%)[b]	d.r.[c]	*ee* (%)[c]
1	2.1:1	62	82:18	93/93
2	2.2:1	72	83:17	96/96
3	2.5:1	62	82:18	95/96
4	2:1	65	85:15	95/96
5	1:1.2	58	82:18	51/41
6[d]	2.2:1	78	83:17	95/95

[a] All reaction were performed with $Sc(OTf)_3$/**L_3-PiPr$_3$** (10 mol%, 1:1), LiCl (1 equiv) in 1,1,2,2-tetrachloroethane (0.2 M) for 26 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID. [d] $Sc(OTf)_3$/**L_3-PiPr$_3$** (5 mol%, 1:1), LiCl (50 mol%) in 1,1,2,2-tetrachloroethane (0.2 M) for 48 h.

Table S7. Screening the Amount of LiCl.

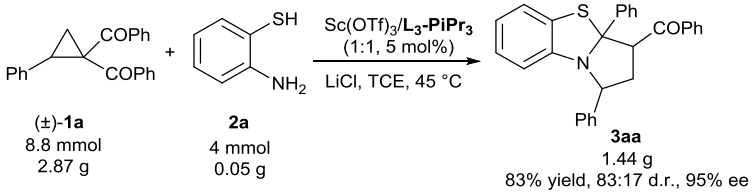


(±) **1a** **2a** **3aa**

Entry[a]	Amount of LiCl (mol%)	Yield (%)[b]	d.r.[c]	*ee* (%)[c]
1	50	79	82:18	95/95
2	45	68	83:17	96/95
3	40	80	83:17	96/95
4	35	72	83:17	94/94
5	30	85	83:17	95/96
6	25	84	80:20	95/95
7	10	77	85:15	95/95

[a] All reaction were performed with Sc(OTf)$_3$/**L$_3$-PiPr$_3$** (5 mol%, 1:1) in 1,1,2,2-tetrachloroethane (0.2 M) at 45 °C for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiralpak ID.

(E) Gram-Scale Synthesis of 3aa.



(±)-**1a**
8.8 mmol
2.87 g

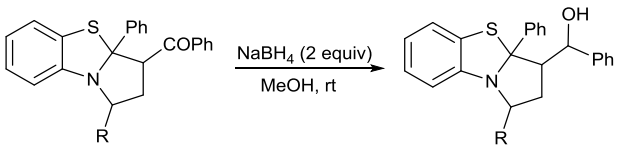
2a
4 mmol
0.05 g

3aa
1.44 g
83% yield, 83:17 d.r., 95% ee

A 100 mL of dry round-bottom flask was charged with *N,N'*-dioxide ligand **L$_3$-PiPr$_3$** (0.2 mmol), Sc(OTf)$_3$ (0.2 mmol), LiCl (1.0 mmol) and **1a** (8.8 mmol) under nitrogen atmosphere. The 1,1,2,2-tetrachloroethane (20 mL) was added and the mixture were stirred at 35 °C for 2 h. Then, **2a** (4.0 mmol) was added. The mixture was stirred at 45 °C for 2 days. The reaction mixture was purified by flash chromatography (petroleum ether/dichloromethane = 2/1) on silica gel to afford the desired product in 83% yield (1.44 g) with 83:17 d.r. and 95% ee as a yellow foam.

(F) Transformation of the Product 3ga.

1) Transformation of **3ga** to **4**



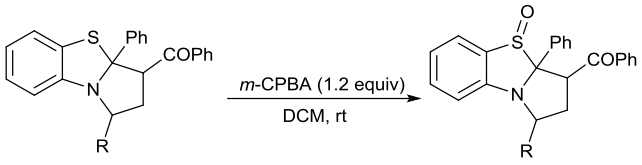
3ga: R = 3-MeOC$_6$H$_4$
>19:1 d.r., 95% ee

4
99% yield, >19:1 d.r., 95% ee

The **3ga** with high diastereoselectivity (>19:1 d.r.) was separated from the mixture of diastereoisomers by flash chromatography (petroleum ether/dichloromethane = 2/1).

A solution of product **3ga** (0.1 mmol), $NaBH_4$ (0.2 mmol) in MeOH (0.5 mL) was stirred at r.t. for 10 min. The reaction mixture was quenched at 0 °C with water and was then extracted with DCM (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel to furnished alcohol **4** in 99% yield with >19:1 d.r. and 95% ee.

2) Transformation of **3ga** to **5**



3ga: R = 3-MeOC$_6$H$_4$

>19:1 d.r., 95% ee

5

63% yield, >19:1 d.r., 96% ee

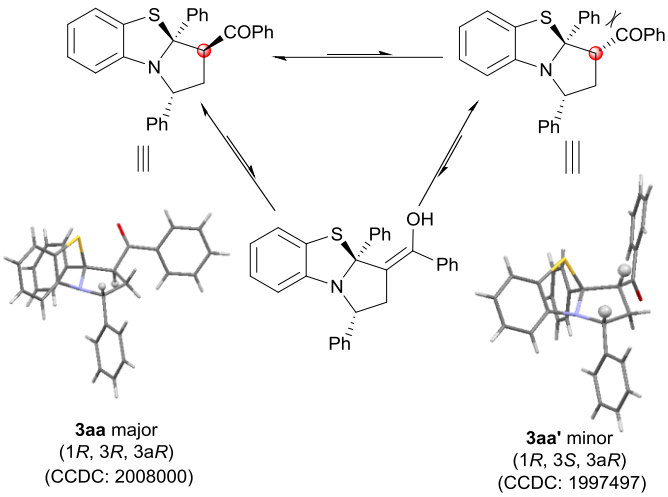
The **3ga** with high diastereoselectivity (>19:1 d.r.) was separated from the mixture of diastereoisomer by flash chromatography (petroleum ether/ dichloromethane = 2/1).

A solution of product **3ga** (0.1 mmol), *m*-CPBA (1.2 equiv) in DCM (2.0 mL) was stirred at r.t. and monitored by TLC. After the **3ga** was consumed, the reaction mixture was purified by flash column chromatography on silica gel to furnished sulfoxide **5** in 63% yield with >19:1 d.r. and 96% ee.

(G) Control Experiments:

3aa	**3aa'**	d.r.		d.r.	**3aa**	**3aa'**
(96% ee)	(99% ee)	3/97	a	82/18	(99% ee)	(99% ee)
(92% ee)	(79% ee)	92/8	a	83/17	(91% ee)	(88% ee)
(90% ee)	(99% ee)	74/26	b	81/19	(91% ee)	(91% ee)
(92% ee)	(79% ee)	92/8	b	81/19	(92% ee)	(91% ee)

[a] standard contions; [b] at 70 °C without catalyst

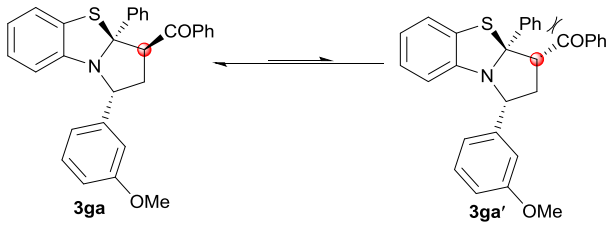


3aa major
(1*R*, 3*R*, 3a*R*)
(CCDC: 2008000)

3aa' minor
(1*R*, 3*S*, 3a*R*)
(CCDC: 1997497)

Condition a: *N,N'*-Dioxide ligand **L$_3$-PiPr$_3$** (5 mol%), Sc(OTf)$_3$ (5 mol%), LiCl (30 mol%) and **3aa** (0.1 mmol) with different diastereoselectivity were stirred in 0.5 mL of 1,1,2,2-tetrachloroethane at 45 °C under nitrogen atmosphere for 24 h. Then, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2/1) to afford the product, which was further analyzed by HPLC.

Condition b: **3aa** (0.1 mmol) were stirred in 0.5 mL of 1,1,2,2-tetrachloroethane at 70 °C under nitrogen atmosphere for 24 h. Then, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2/1) to afford the product, which was further analyzed by HPLC.



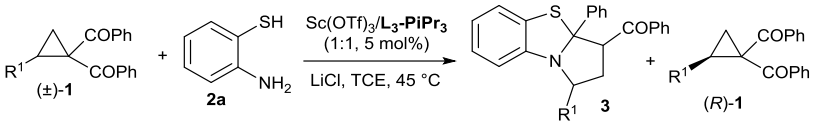
3ga **3ga′**

3ga:3ga′ = 19:1 $\xrightarrow[\text{TCE, 35 °C}]{\text{Sc(OTf)}_3\text{/L}_3\text{-PiPr}_3\text{, with LiCl}}$ **3ga:3ga′** = 87:13 (about 20 minutes)

3ga:3ga′ = 19:1 $\xrightarrow[\text{TCE, 35 °C}]{\text{Sc(OTf)}_3\text{/L}_3\text{-PiPr}_3\text{, without LiCl}}$ **3ga:3ga′** = 87:13 (about 30 minutes)

The d.r. values were determined by HPLC analysis on Daicel chiralpak IE.

(H) The Kinetic Resolution Experiments.



Entry	R^1	**3**			**1**	
		Yield (%)[b]	d.r.	ee (%)[c]	Yield (%)[b]	ee (%)[c]
1	Ph	37	85:15	95	54	88
2	1-naphthyl	37	91:9	94	51	90
3	3-BrC_6H_4	41	77:23	70/85	52	84
4	4-BrC_6H_4	41	83:17	95	49	86

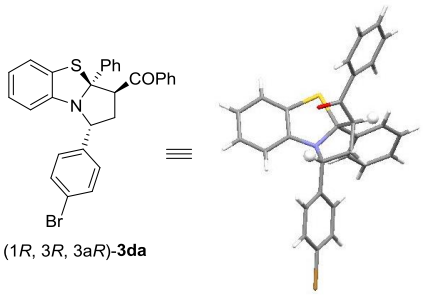
[a] All reaction were performed with $Sc(OTf)_3$/**L_3-PiPr$_3$** (5 mol%, 1:1), D-A cyclopropane **1** (0.2 mmol), 2-aminothiophenol **2a** (0.1 mmol), LiCl (30 mol%) in 1,1,2,2-tetrachloroethane (0.5 mL) for 48 h. [b] Isolated yield based on the amount of cyclopropanes. [c] Determined by HPLC on Daicel chiralpak ID, IE.

The kinetic resolution experiments were operated according to the typical procedure for catalytic asymmetric reaction of D-A cyclopropane with 2-aminothiophenol. When 0.2 mmol D-A cyclopropane reacted with 0.1 mmol 2-aminothiophenol, the products **3** were obtained in 37–41% yield with 77:23–91:9 d.r. and 70–95% ee. Meanwhile, the D-A cyclopropane **1** were recovered in 49–54% yield with 84–90% ee. The absolute configuration of the recovered D-A cyclopropane **1** was determined to be (*R*) by comparing their circular dichroism spectra with previous report.[2a]

(I) Crystal Data of Products

(1) The following single crystal **3da** [$C_{29}H_{22}BrNOS$] was recrystallized from ethyl acetate/ethanol. The absolute configuration of **3da** was determined by X-ray diffraction. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC1997496).

The colourless crystals in block-shape were selected and mounted for the single-crystal X-ray diffraction. The data set was collected at 300(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package.[3] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[4]



(1*R*, 3*R*, 3a*R*)-**3da**

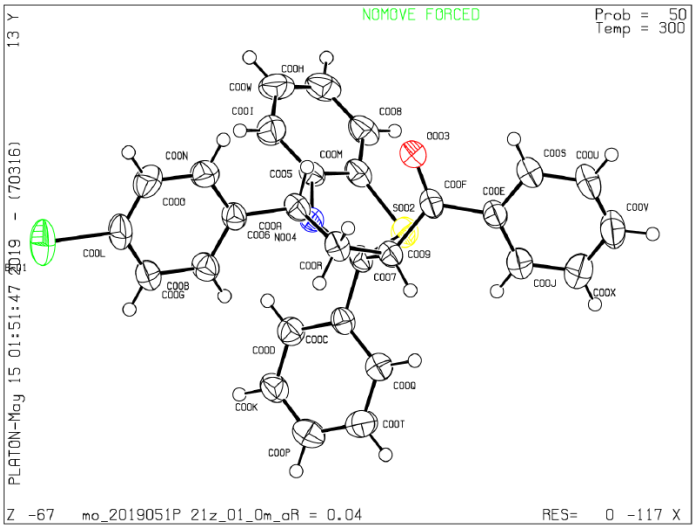


Figure S1. the thermal ellipsoid figure of **3da** with 50% probabilities

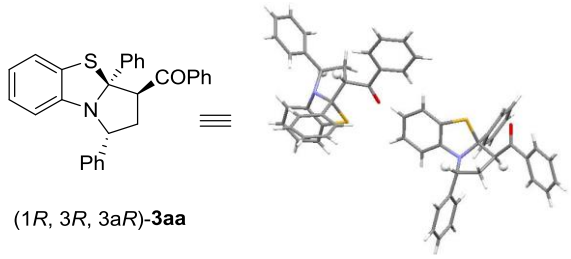
Table S9 Crystal data and structure refinement for (1*R*, 3*R*, 3a*R*)-**3da**.

Empirical formula	$C_{29}H_{22}BrNOS$
Formula weight	512.44
Temperature/K	300(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.6630(14)
b/Å	9.0225(9)
c/Å	12.3447(16)
α/°	90
β/°	90.216(5)
γ/°	90
Volume/Å	1187.6(2)
Z	2
ρ_{calc}g/cm^3	1.433
μ/mm^{-1}	1.841
F(000)	524.0
Crystal size/mm^3	
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.592 to 52.796
Index ranges	-12 ≤ h ≤ 13, -10 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	8989
Independent reflections	4595 [R_{int} = 0.0228, R_{sigma} = 0.0601]
Data/restraints/parameters	4595/1/298
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0864
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.0908

Largest diff. peak/hole / e Å-3	0.33/-0.44
Flack parameter	0.042(6)

2) The following single crystal of major diastereomer **3aa** [$C_{29}H_{23}NOS$] was recrystallized from ether/petroleum ether. The absolute configuration of **3aa** was determined by X-ray diffraction. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2008000).

The colourless crystals in block-shape were selected and mounted for the single-crystal X-ray diffraction. The data set was collected at 170(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package.[3] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[4]



(1*R*, 3*R*, 3a*R*)-**3aa**

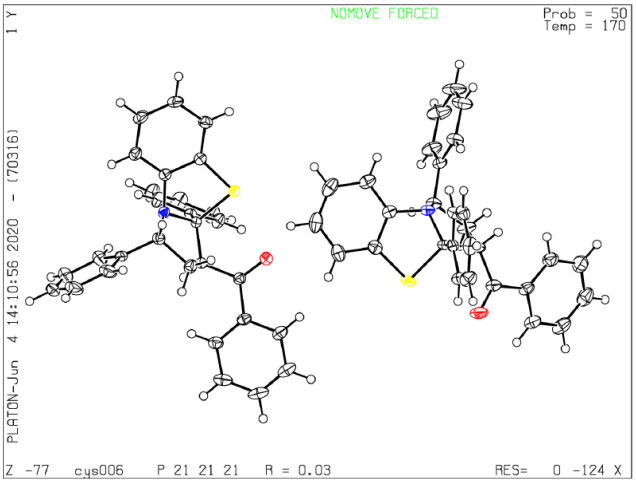


Figure S2. the thermal ellipsoid figure of **3aa** with 50% probabilities

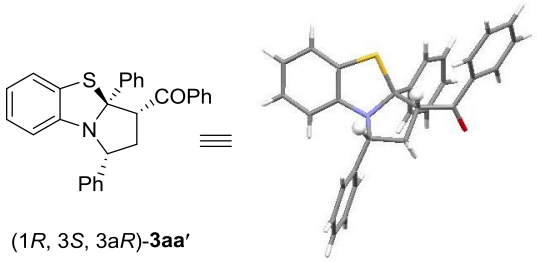
Table S10 Crystal data and structure refinement for (1*R*, 3*R*, 3a*R*)-**3aa**.

Empirical formula	$C_{58}H_{46}N_2O_2S_2$
Formula weight	867.09
Temperature/K	170(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.0966(5)
b/Å	16.0127(8)
c/Å	27.6462(14)
α/°	90
β/°	90
γ/°	90
Volume/Å	4469.7(4)

Z	4
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	1.444
F(000)	1824.0
Crystal size/mm^3	0.318 × 0.212 × 0.125
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.378 to 161.376
Index ranges	-11 ≤ h ≤ 12, -20 ≤ k ≤ 20, -35 ≤ l ≤ 35
Reflections collected	81260
Independent reflections	9717 [R_{int} = 0.0625, R_{sigma} = 0.0451]
Data/restraints/parameters	9717/0/578
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0672
Final R indexes [all data]	R_1 = 0. 0.0336, wR_2 = 0. 0.0691
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21
Flack parameter	0.010(3)

3) The following single crystal of minor diastereomer **3aa'** [$C_{29}H_{23}NOS$] was recrystallized from ethyl acetate/ethanol. The absolute configuration of **3aa'** was determined by X-ray diffraction. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC1997497).

The colourless crystals in block-shape were selected and mounted for the single-crystal X-ray diffraction. The data set was collected at 303(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package.[3] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[4]



(1*R*, 3*S*, 3a*R*)-**3aa′**

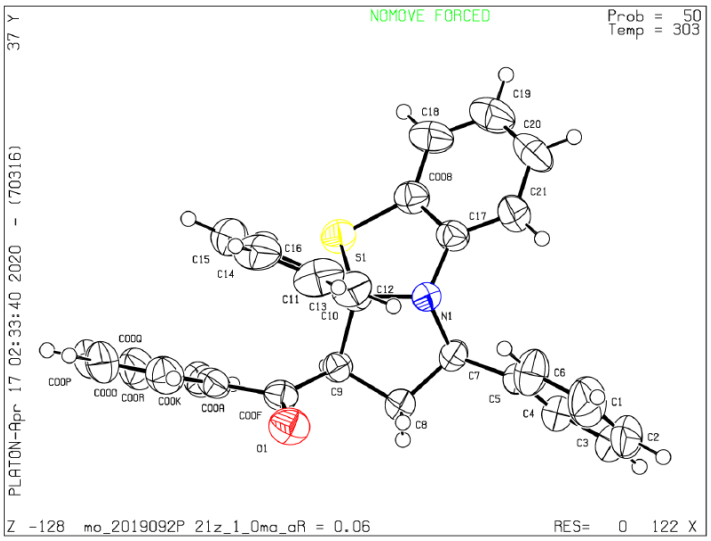


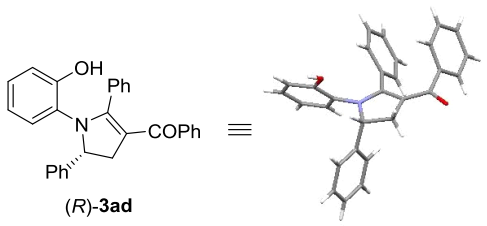
Figure S3. the thermal ellipsoid figure of **3aa′** with 50% probabilities

Table S11 Crystal data and structure refinement for (1*R*, 3*S*, 3a*R*)-**3aa'**.

Empirical formula	$C_{29}H_{23}NOS$
Formula weight	433.54
Temperature/K	303(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.7976(15)
b/Å	8.7230(9)
c/Å	14.089(2)
α/°	90
β/°	110.142(5)
γ/°	90
Volume/Å	1130.5(3)
Z	2
ρ_{calc}g/cm^3	1.274
μ/mm^{-1}	0.165
F(000)	456.0
Crystal size/mm^3	
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.594 to 56.532
Index ranges	-13 ≤ h ≤ 11, -11 ≤ k ≤ 10, -18 ≤ l ≤ 18
Reflections collected	10157
Independent reflections	5121 [R_{int} = 0.0632, R_{sigma} = 0.1074]
Data/restraints/parameters	5121/1/289
Goodness-of-fit on F^2	0.975
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1226
Final R indexes [all data]	R_1 = 0.1420, wR_2 = 0.1772
Largest diff. peak/hole / e Å^{-3}	0.19/-0.23
Flack parameter	0.11(8)

4) The following single crystal of **3ad** [$C_{29}H_{23}NO_2$] was recrystallized from DMSO. The absolute configuration of **3ad** was determined by X-ray diffraction. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2032629).

The colourless crystal in flake-shape, with approximate dimensions of 0.076 × 0.11 × 0.366 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 143(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package.[3] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggestedd.[4]



(*R*)-**3ad**

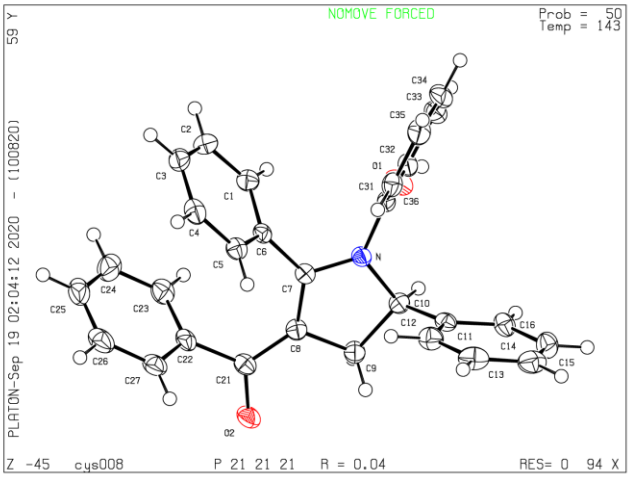


Figure S4. the thermal ellipsoid figure of **3ad** with 50% probabilities

Table S12 Crystal data and structure refinement for (*R*)-**3ad**.

Empirical formula	$C_{29}H_{23}NO_2$
Formula weight	417.48
Temperature/K	143(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.1433(2)
b/Å	16.4271(5)
c/Å	18.9190(6)
α/°	90
β/°	90
γ/°	90
Volume/Å	2220.03(12)
Z	2
ρ_{calc}g/cm^3	1.249
μ/mm^{-1}	0.613
F(000)	880.0
Crystal size/mm^3	0.076 × 0.11 × 0.366
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.126 to 144.762
Index ranges	-8 ≤ h ≤ 7, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23

Reflections collected	19698
Independent reflections	4355 [R_{int} = 0.0662, R_{sigma} = 0.0594]
Data/restraints/parameters	4355/1/293
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.0994
Final R indexes [all data]	R_1 = 0.0455, wR_2 = 0.1013
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.30
Flack parameter	0.02(9)

(J) References

1 (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, and X. M. Feng, *Synlett*. 2005, **16**, 2445; (b) X. H. Liu, L. L. Lin, and X. M. Feng, *Acc. Chem. Res.* 2011, **44**, 574; (c) X. H. Liu, L. L. Lin, and X. M. Feng, *Org. Chem. Front*. 2014, **1**, 298–302.

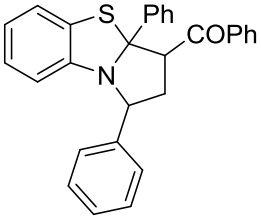
2 (a) Y. Xia, X. H. Liu, H. F. Zheng, L. L. Lin, and X. M. Feng, *Angew. Chem. Int. Ed.* 2015, **54**, 227. (b) Y. Xia, L. L. Lin, F. Z. Chang, Y. T. Liao, X. H. Liu, and X. M. Feng, *Angew. Chem. Int. Ed.* 2016, **55**, 12228. (c) F. Z. Chang, L. L. Lin, Y. Xia, H. Zhang, S. X. Dong, X. H. Liu, and X. M. Feng, *Adv. Synth. Catal.* 2018, **360,** 2608. (d) Y. Xia, X. H. Liu, H. Z. Zheng, L. L. Lin, and X. M. Feng, *Angew. Chem. Int. Ed*. 2015, **54**, 227.

3 (a) Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112; (b) Sheldrick, G. M. *Acta Cryst.* 2015, **A71**, 3; (c) Sheldrick, G. M. *Acta Cryst*. 2015, **C71**, 3.

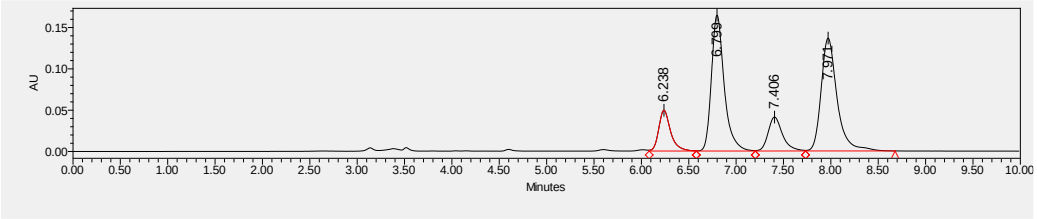
4 Spek, A. L. *J. Appl. Cryst*. 2003, **36**, 7.

(K) Spectral Characterization Data for the Products

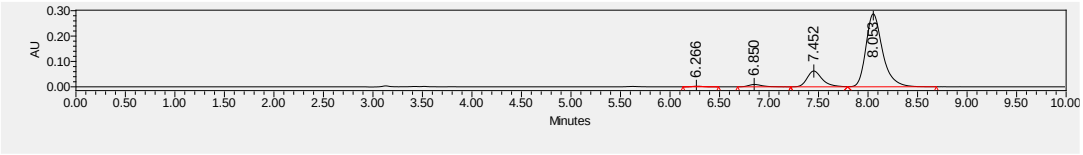
(1,3a-Diphenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl)(phenyl)methanone (3aa).



(**$C_{29}H_{23}NOS$**) Prepared according to the general procedure for 48 h. 36.7 mg, 85% yield; yellow foam. Melting point: 60 – 64 °C. $[\alpha]^{20}_D$ = +506.5 (*c* 0.69, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 95% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 8.05 min (major), 6.85 min (minor); $t_{minor\ isomer}$ = 7.45 min (major), 6.27 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 4H), 7.63 – 7,58 (m, 2H), 7.57 – 7.42 (m, 1H), 7.47 – 7.41 (m, 4H), 7.38 – 7.34 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.03 (m, 1H), 6.87 – 6.79 (m, 2H), 6.68 – 6.62 (m, 1H), 4.78 (dd, *J* = 6.0, 8.0 Hz, 1H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.01 – 2.90 (m, 1H), 2.42 – 2.31 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ198.3, 148.6, 147.4, 144.3, 137.1, 133.6, 133.2, 128.9, 128.9, 128.8, 128.4, 127.7, 127.6, 127.2, 125.9, 124.9, 124.4, 121.7, 116.2, 91.1, 70.8, 56.0, 40.3. **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NO_2S^+$ ([M]+H$^+$) = 434.1573, Found 434.1576; **IR (neat)**: 3059, 1681, 1579, 1491, 1451, 1262, 1220, 1024, 736, 699 cm^{-1}

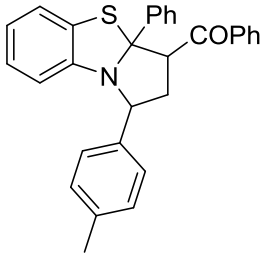


	Retention Time	Area	% Area
1	6.238	430218	10.74
2	6.799	1545187	38.56
3	7.406	433557	10.82
4	7.971	1597767	39.88

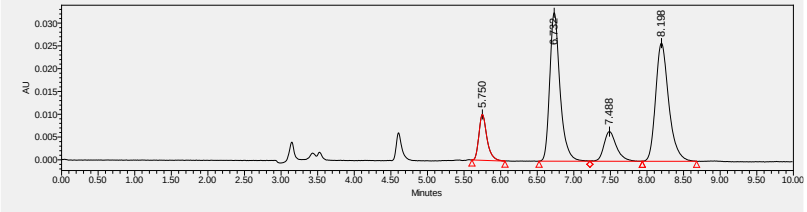


	Retention Time	Area	% Area
1	6.266	16398	0.40
2	6.850	88036	2.14
3	7.452	660590	16.06
4	8.053	3348253	81.40

Phenyl{3a-phenyl-1-(*p*-tolyl)-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}methanone (3ba)

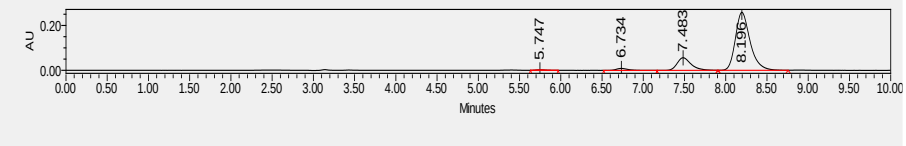


(**$C_{30}H_{25}NOS$**) Prepared according to the general procedure for 48 h. 31.9 mg, 71% yield; yellow foam. Melting point: 78 – 82 °C. $[\alpha]^{20}_D$ = +472.0 (*c* 0.60, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 95% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 8.20 min (major), 6.73 min (minor); $t_{minor\ isomer}$ = 7.48 min (major), 5.75 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7,80 (m, 4H), 7.52 – 7.39 (m, 5H), 7.32 – 7.23 (m, 5H), 7.08 – 7.03 (m, 1H), 6.86 – 6.81 (m, 2H), 6.69 – 6.63 (m, 1H), 4.75 (dd, *J* = 4.0, 8.0 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.41 (s, 3H), 2.39 – 2.32 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.4, 148.6, 147.5, 141.3, 137.2, 137.1, 133.6, 133.2, 129.6, 128.9, 128.8, 128.4, 127.7, 127.1, 125.9, 124.9, 124.3, 121.7, 116.2, 91.1, 70.6, 56.1, 40.3, 21.3. **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NOS^+$ ([M]+H$^+$) = 448.1730, Found 448.1736; **IR (neat)**: 3056, 1681, 1596, 1579, 1446, 1260, 1219, 749, 697 cm^{-1}



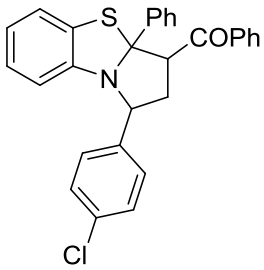
	Retention Time	Area	% Area
1	5.750	77331	9.70
2	6.732	318438	39.96

3	7.488	77953	9.78
4	8.198	323099	40.55

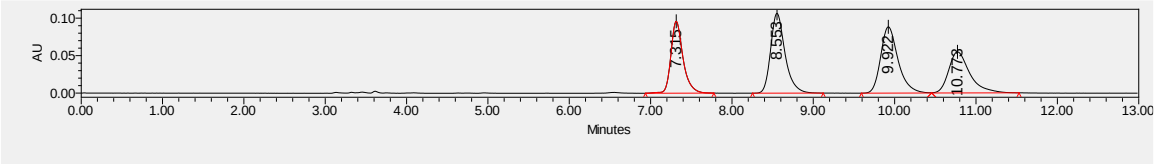


	Retention Time	Area	% Area
1	5.747	16695	0.42
2	6.734	84691	2.13
3	7.483	664753	16.72
4	8.196	3209735	80.73

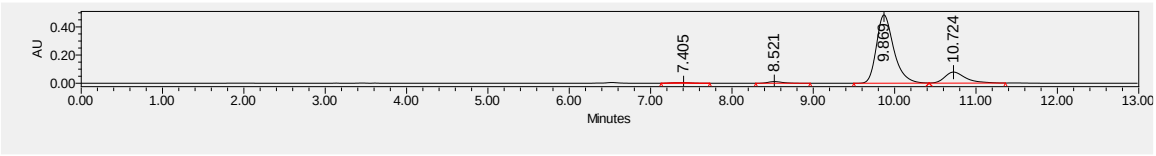
{1-(4-Chlorophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3ca)



(**$C_{29}H_{22}ClNOS$**) Prepared according to the general procedure for 48 h. 36.8 mg, 79% yield; yellow foam. Melting point: 70 – 74 °C. $[\alpha]^{20}_{D}$ = +445.9 (*c* 0.73, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 92% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 9.87 min (major), 8.52 min (minor); $t_{minor\ isomer}$ = 10.72 min (major), 7.41 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7,83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.58 – 7.51 (m, 3H), 7.47 – 7.39 (m, 4H), 7.34 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.08 – 7.02 (m, 1H), 6.90 – 6.80 (m, 2H), 6.64 – 6.59 (m, 1H), 4.76 (t, *J* = 6.8 Hz, 1H), 4.65 (t, *J* = 7.2 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.37 – 2.21 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.2, 148.3, 147.2, 142.8, 137.0, 133.7, 133.3, 133.1, 129.1, 128.9, 128.8, 128.5, 128.5, 127.8, 125.8, 125.0, 124.5, 121.8, 116.1, 91.0, 70.2, 55.8, 40.1. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{35}ClNOS^+$ ([M]+H$^+$) = 468.1183, Found 468.1184; calcd for $C_{29}H_{23}{}^{37}ClNOS^+$ ([M]+H$^+$) = 470.1154, Found 470.1161; **IR (neat)**: 3056, 1681, 1596, 1579, 1461, 1264, 1219, 735, 697 cm^{-1}

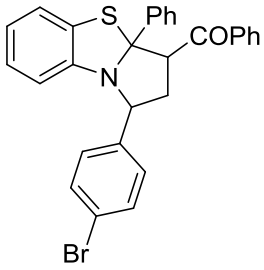


	Retention Time	Area	% Area
1	7.315	991102	21.51
2	8.553	1310884	28.45
3	9.922	1316686	28.58
4	10.773	988624	21.46

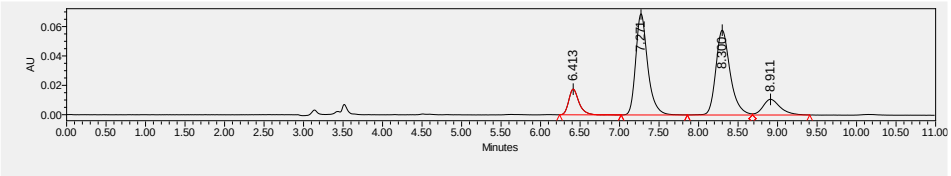


	Retention Time	Area	% Area
1	7.405	58871	0.67
2	8.521	145510	1.66
3	9.869	7154047	81.77
4	10.724	1390897	15.90

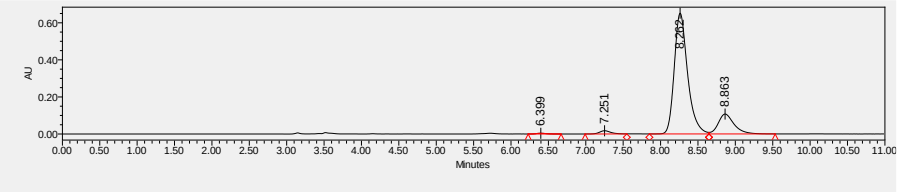
{1-(4-Bromophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3da)



(**$C_{29}H_{22}BrNOS$**) Prepared according to the general procedure for 72 h. 43.0 mg, 84% yield; yellow foam. Melting point: 64 – 68 °C. $[\alpha]^{20}_{D}$ = +394.8 (*c* 0.74, CH_2Cl_2). 82:18 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 96% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 8.26 min (major), 7.25 min (minor); $t_{minor\ isomer}$ = 8.86 min (major), 6.40 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7,83 (m, 2H), 7.80 – 7.75 (m, 2H), 7.58 – 7.54 (m, 3H), 7.50 – 7.42 (m, 4H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.08 – 7.02 (m, 1H), 6.88 – 6.81 (m, 2H), 6.64 – 6.59 (m, 1H), 4.74 (dd, *J* = 6.4, 8.4 Hz, 1H), 4.65 (t, *J* = 7.2 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.35 – 2.25 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.2, 148.3, 147.1, 143.3, 137.0, 133.7, 133.1, 132.1, 128.9, 128.9, 128.8, 128.5, 127.8, 125.8, 125.0, 124.5, 121.8, 121.4, 116.1, 91.0, 70.2, 55.8, 40.1. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{79}BrNO_2S^+$ ([M]+H$^+$) = 512.0678, Found 512.0676; calcd for $C_{29}H_{23}{}^{81}BrNO_2S^+$ ([M]+H$^+$) = 514.0658, Found 514.0650; **IR (neat)**: 3059, 1681, 1588, 1487, 1465, 1355, 1261, 1219, 1010, 823, 749, 696 cm^{-1}

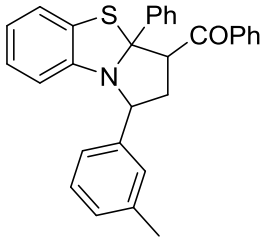


	Retention Time	Area	% Area
4	8.911	162192	9.14
1	6.413	158368	8.93
2	7.271	726921	40.98
3	8.300	726559	40.96

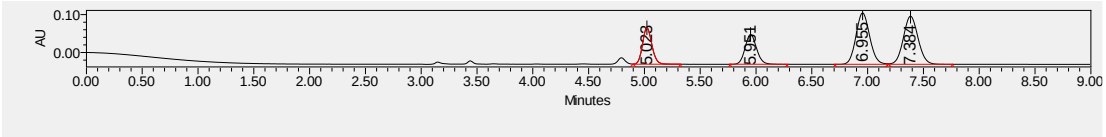


	Retention Time	Area	% Area
1	6.399	33860	0.34
2	7.251	183340	1.86
3	8.262	8062309	81.84
4	8.863	1572321	15.96

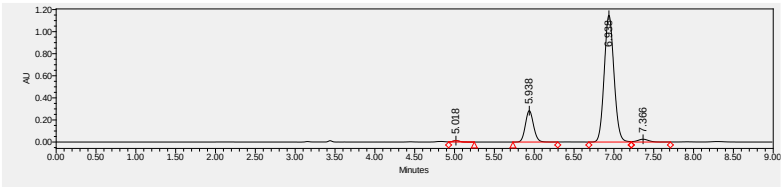
Phenyl[3a-phenyl-1-(*m*-tolyl)-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl]methanone (3ea)



(**$C_{30}H_{25}NOS$**) Prepared according to the general procedure for 48h. 38.5 mg, 86% yield; yellow foam. Melting point: 92 – 96 °C. $[\alpha]^{20}_D$ = +449.0 (*c* 0.21, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 93% *ee* for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 6.94 min (major), 7.37 min (minor); $t_{minor\ isomer}$ = 5.94 min (major), 5.02 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 4H), 7.58 – 7,52 (m, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.41 (m, 3H), 7.37 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.13 (m, 1H), 7.06 – 7.02 (m, 1H), 6.86 – 6.81 (m, 2H), 6.69 – 6.65 (m, 1H), 4.75 (dd, *J* = 6.0, 8.0 Hz, 1H), 4.67 (t, *J* = 7.2 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.41 (s, 3H), 2.39 – 2.31 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.4, 148.6, 147.4, 144.3, 138.5, 137.1, 133.6, 133.1, 128.9, 128.8, 128.8, 128.4, 128.3, 127.9, 127.7, 126.0, 124.9, 124.3, 124.2, 121.7, 116.2, 91.1, 70.8, 56.0, 40.3, 21.8. **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NOS^+$ ([M]+H$^+$) = 448.1730, Found; 448.1733; **IR (neat)**: 3057, 1681, 1587, 1450, 1353, 1263, 1218, 1023, 734, 698 cm^{-1}

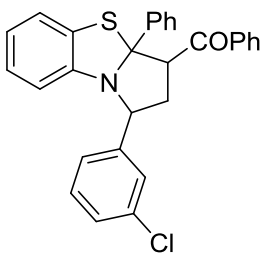


	Retention Time	Area	% Area
1	5.023	561703	16.31
2	5.951	560190	16.27
3	6.955	1160817	33.71
4	7.384	1160639	33.71



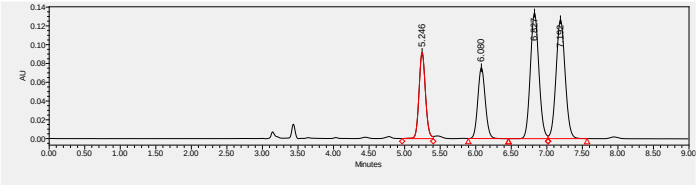
	Retention Time	Area	% Area
1	5.018	77255	0.64
2	5.938	2016529	16.65
3	6.938	9773090	80.69
4	7.366	245319	2.03

{1-(3-Chlorophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3fa)

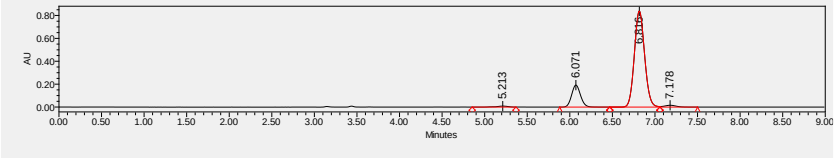


(**$C_{29}H_{22}ClNOS$**) Prepared according to the general procedure for 72 h. 33.8 mg, 72% yield; yellow foam. Melting point: 70 – 73 °C. $[\alpha]^{20}_D$ = +441.3 (*c* 1.04, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 88% *ee* for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane =

20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 6.82 min (major), 7.18 min (minor); $t_{minor\ isomer}$ = 6.07 min (major), 5.21 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7,83 (m, 2H), 7.81 – 7.76 (m, 2H), 7.62 – 7.54 (m, 2H), 7.49 – 7.42 (m, 3H), 7.39 – 7.35 (m, 1H), 7.35 – 7.28 (m, 3H), 7.25 – 7.19 (m, 1H), 7.08 – 7.03 (m, 1H), 6.89 – 6.81 (m, 2H), 6.68 – 6.61 (m, 1H), 4.75 (dd, *J* = 6.4, 8.4 Hz, 1H), 4.66 (t, *J* = 7.6 Hz, 1H), 3.00 – 2.84 (m, 1H), 2.36 – 2.26 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.2, 148.3, 147.0, 146.5, 137.0, 134.8, 133.7, 133.1, 130.3, 128.9, 128.8, 128.5, 127.9, 127.8, 127.3, 125.8, 125.3, 125.0, 124.6, 121.8, 116.1, 91.0, 70.3, 55.8, 40.1. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{35}ClNO_2S^+$ ([M]+H$^+$) = 468.1183, Found 468.1185; calcd for $C_{29}H_{23}{}^{37}ClNO_2S^+$ ([M]+H$^+$) = 470.1154, Found 470.1156; **IR (neat)**: 3060, 1680, 1592, 1576, 1466, 1451, 1352, 1262, 1218, 1023, 752, 695 cm^{-1}

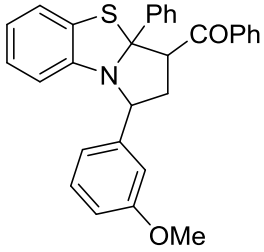


	Retention Time	Area	% Area
1	5.246	577917	17.08
2	6.080	552347	16.32
3	6.827	1124629	33.23
4	7.192	1129254	33.37

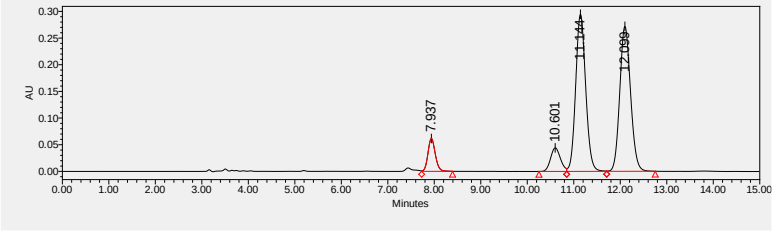


	Retention Time	Area	% Area
1	5.213	88722	1.03
2	6.071	1402081	16.22
3	6.816	7004487	81.01
4	7.178	151138	1.75

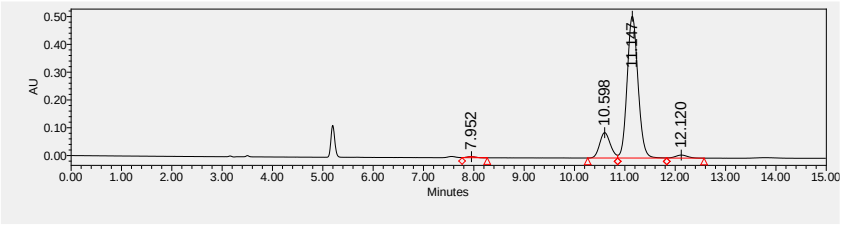
{1-(3-Methoxyphenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3ga)



(**$C_{30}H_{25}NO_2S$**) Prepared according to the general procedure for 36 h. 35.6 mg, 77% yield; yellow foam. Melting point: 65 – 70 °C. $[\alpha]^{20}_D$ = +495.0 (*c* 0.62, CH_2Cl_2). 90:10 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 93% *ee* for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 11.15 min (major), 12.12 min (minor); $t_{minor\ isomer}$ = 10.60 min (major), 7.95 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7,84 (m, 2H), 7.84 – 7.78 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 7.38 – 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.15 (m, 2H), 7.06 – 7.02 (m, 1H), 6.91 – 6.87 (m, 1H), 6.87 – 6.83 (m, 2H), 6.72 – 6.68 (m, 1H), 4.77 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.68 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.01 – 2.91 (m, 1H), 2.41 – 2.31 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.4, 160.1, 148.6, 147.4, 146.1, 137.1, 133.6, 133.0, 130.0, 128.9, 128.8, 128.5, 127.7, 125.9, 125.0, 124.3, 121.6, 119.4, 116.0, 113.0, 112.6, 90.8, 70.8, 55.9, 55.4, 40.3, **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NO_2S^+$ ([M]+H$^+$) = 464.1679, Found 464.1682; **IR (neat)**: 3058, 1680, 1590, 1463, 1261, 1219, 1044, 754, 697 cm^{-1}

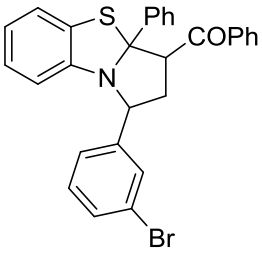


	Retention Time	Area	% Area
1	7.937	673683	6.67
2	10.601	649230	6.43
3	11.144	4399681	43.55
4	12.099	4380807	43.36

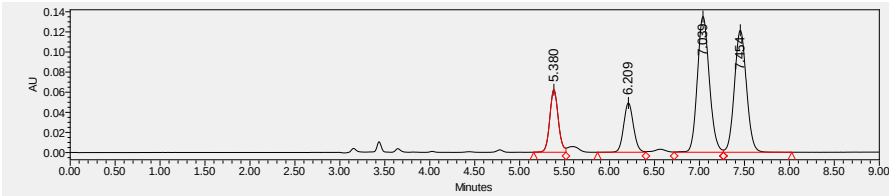


	Retention Time	Area	% Area
1	7.952	47778	0.52
2	10.598	1346033	14.59
3	11.147	7647241	82.91
4	12.120	182846	1.98

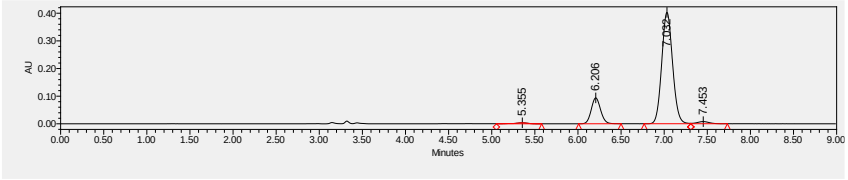
{1-(3-Bromophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3ha)



(**$C_{29}H_{22}BrNOS$**) Prepared according to the general procedure for 48 h. 41.5 mg, 81% yield; yellow foam. Melting point: 72 – 76 °C. $[\alpha]^{20}_D$ = +394.1 (*c* 0.66, CH_2Cl_2). 82:18 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 90% ee for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 7.03 min (major), 7.45 min (minor); $t_{minor\ isomer}$ = 6.21 min (major), 5.36 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7,83 (m, 2H), 7.81 – 7.74 (m, 3H), 7.57 – 7.50 (m, 2H), 7.48 – 7.42 (m, 3H), 7.34 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 7.08 – 7.02 (m, 1H), 6.88 – 6.82 (m, 2H), 6.68 – 6.61 (m, 1H), 4.75 (dd, *J* = 6.0, 8.0 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.00 – 2.83 (m, 1H), 2.36 – 2.26 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.2, 148.3, 147.0, 146.7, 137.0, 133.7, 133.0, 130.7, 130.6, 130.2, 128.9, 128.8, 128.5, 127.9, 125.8, 125.8, 125.1, 124.5, 123.1, 121.8, 116.1, 91.0, 70.2, 55.8, 40.1, **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{79}BrNO_2S^+$ ([M]+H$^+$) = 512.0680, Found 512.0682; calcd for $C_{29}H_{23}{}^{81}BrNO_2S^+$ ([M]+H$^+$) = 514.0662, Found 514.0660; **IR (neat)**: 3058, 1680, 1590, 1573, 1466, 1450, 1351, 1262, 1218, 734, 696 cm^{-1}

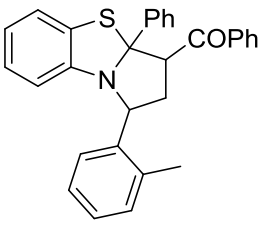


	Retention Time	Area	% Area
1	5.380	409214	12.96
2	6.209	371389	11.76
3	7.039	1247748	39.51
4	7.454	1129612	35.77



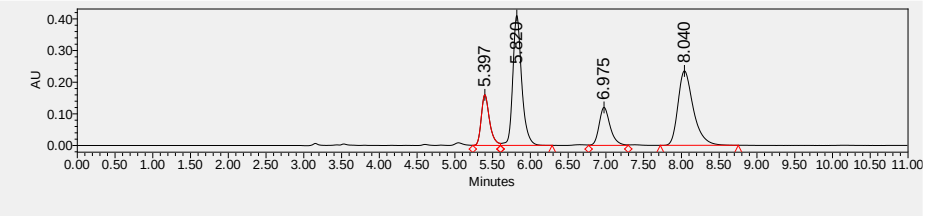
	Retention Time	Area	% Area
1	5.355	35534	0.82
2	6.206	702822	16.22
3	7.032	3520070	81.21
4	7.453	75840	1.75

Phenyl{3a-phenyl-1-(*o*-tolyl)-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}methanone (3ia)

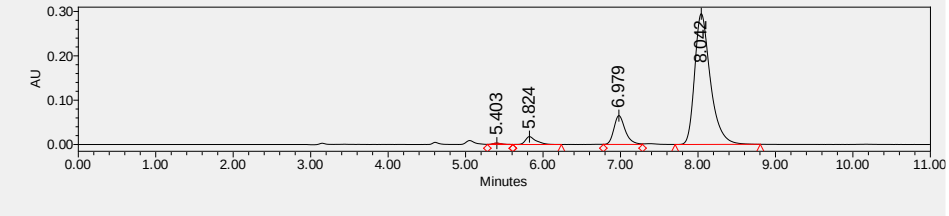


(**$C_{30}H_{25}NOS$**) Prepared according to the general procedure for 48 h. 36.7 mg, 82% yield; yellow foam. Melting point: 60 – 64 °C. $[\alpha]^{20}_D$ = +419.7 (*c* 0.79, CH_2Cl_2). 87:13 d.r. (determined by ^{1}H NMR), 92% *ee* for the major isomer and 92% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 8.04 min (major), 5.82 min (minor); $t_{minor\ isomer}$ = 6.98 min (major), 5.40 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.89 – 7,79 (m, 4H), 7.57 – 7.52 (m, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 7.14 – 7.09 (m, 1H), 6.92 – 6.85 (m, 1H), 6.84 – 6.78 (m, 1H), 6.72 – 6.66 (m, 1H), 4.87 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.66 (dd, *J* = 7.6, 9.2 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.26 (s, 3H), 2.25 - 2.20 (m, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.3, 148.9, 147.0, 142.4, 136.8, 135.1, 134.2, 133.7, 130.8, 128.9, 128.8, 128.4, 127.7, 127.2, 127.2, 126.6, 126.5, 126.0, 125.0, 124.9, 122.0, 117.0, 91.6, 67.8, 55.6, 39.7, 19.7. **HRMS (FTMS+c ESI)**

calcd for $C_{30}H_{26}NO_2S^+$ ([M]+H^+) = 448.1730, Found 448.1734; **IR (neat)**: 3059, 1681, 1596, 1452, 1356, 1263, 1221, 1023, 754, 696 cm^{-1}

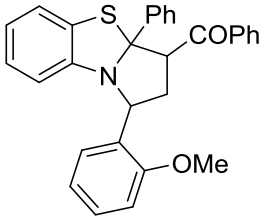


	Retention Time	Area	% Area
1	5.397	1216497	13.35
2	5.820	3362718	36.90
3	6.975	1218011	13.37
4	8.040	3314678	36.38

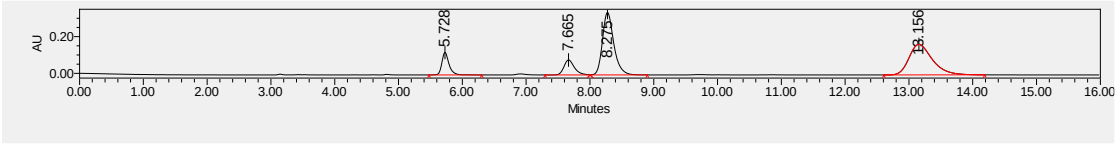


	Retention Time	Area	% Area
1	5.403	23865	0.48
2	5.824	171088	3.42
3	6.979	661569	13.21
4	8.042	4152477	82.90

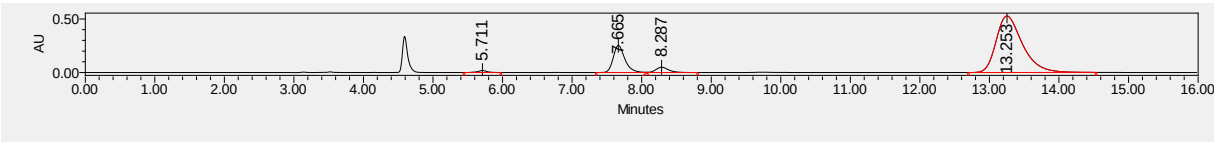
{1-(2-Methoxyphenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (3ja)



(**$C_{30}H_{25}NO_2S$**) Prepared according to the general procedure for 72 h. 32.4 mg, 70% yield; yellow foam. Melting point: 58 – 64 °C. $[\alpha]^{20}_D$ = +423.0 (c 0.59, CH_2Cl_2). 84:16 d.r. (determined by ^{1}H NMR), 91% *ee* for the major isomer and 89% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 13.25 min (major), 8.29 min (minor); $t_{minor\ isomer}$ = 7.67 min (major), 5.71 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.87 – 7,78 (m, 4H), 7.54 – 7.47 (m, 1H), 7.41 – 7.30 (m, 3H), 7.29 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 – 7.06 (m, 1H), 6.93 – 6.78 (m, 4H), 4.89 (dd, *J* = 3.6, 9.6 Hz, 1H), 4.63 (dd, *J* = 7.6, 10.8 Hz, 1H), 3.77 (s, 3H), 3.10 – 2.97 (m, 1H), 2.35 – 2.25 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.4, 156.6, 149.4, 147.0, 136.8, 134.3, 133.5, 132.8, 128.8, 128.7, 128.4, 128.3, 127.6, 127.6, 126.0, 124.8, 124.8, 121.9, 120.6, 116.9, 110.5, 91.6, 66.4, 56.0, 55.3, 39.8, **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NO_2S^+$ ([M]+H^+) = 464.1679, Found 464.1678; **IR (neat)**: 3059, 1681, 1594, 1487, 1455, 1357, 1237, 1026, 754, 696 cm^{-1}

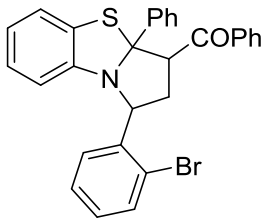


	Retention Time	Area	% Area
1	5.728	962681	9.32
2	7.665	933555	9.04
3	8.275	4208913	40.76
4	13.156	4221971	40.88

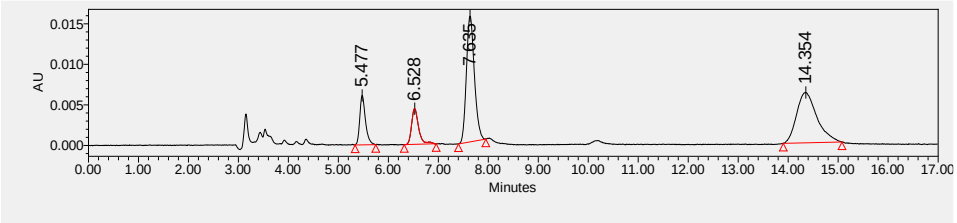


	Retention Time	Area	% Area
1	5.711	175957	1.00
2	7.665	2950777	16.78
3	8.287	631064	3.59
4	13.253	13832051	78.64

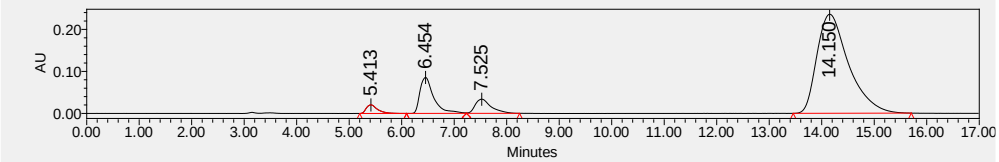
[1-(2-Bromophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl](phenyl)methanone (3ka)



(**$C_{29}H_{22}BrNO_2S$**) Prepared according to the general procedure for 96 h. 45.6 mg, 89% yield; yellow foam. Melting point: 75 – 80 °C. $[\alpha]^{20}_D$ = +387.9 (*c* 0.73, CH_2Cl_2). 87:13 d.r. (determined by ^{1}H NMR), 87% *ee* for the major isomer and 68% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 14.15 min (major), 7.53 min (minor); $t_{minor\ isomer}$ = 6.45 min (major), 5.41 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 7.85 – 7.78 (m, 4H), 7.63 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.36 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 7.17 – 7.12 (m, 1H), 6.95 – 6.83 (m, 2H), 6.77 – 6.72 (m, 1H), 4.95 (dd, *J* = 3.6, 9.2 Hz, 1H), 4.62 (dd, *J* = 7.6, 10.4 Hz, 1H), 3.22 – 3.09 (m, 1H), 2.36 – 2.25 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ198.0, 148.7, 146.6, 143.5, 136.7, 134.2, 133.7, 133.4, 129.0, 128.9 (2C), 128.7 (2C), 128.6, 128.4 (2C), 127.9, 127.8, 125.8 (2C), 125.2, 125.1, 122.9, 122.1, 116.9, 91.5, 70.6, 55.2, 39.9. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{79}BrNO_2S^+$ ([M]+H$^+$) = 512.0678, Found; 512.0680; calcd for $C_{29}H_{23}{}^{81}BrNO_2S^+$ ([M]+H$^+$) = 514.0658, Found 514.0660; **IR (neat)**: 3059, 1681, 1588, 1451, 1353, 1260, 1220, 1022, 753, 695 cm^{-1}

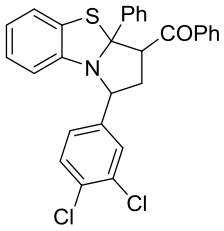


	Retention Time	Area	% Area
1	5.477	48202	10.98
2	6.528	42833	9.76
3	7.635	172579	39.32
4	14.354	175279	39.94

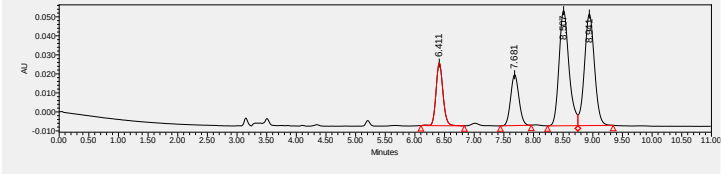


	Retention Time	Area	% Area
1	5.413	304335	2.44
2	6.454	1569187	12.58
3	7.525	715087	5.73
4	14.150	9885164	79.25

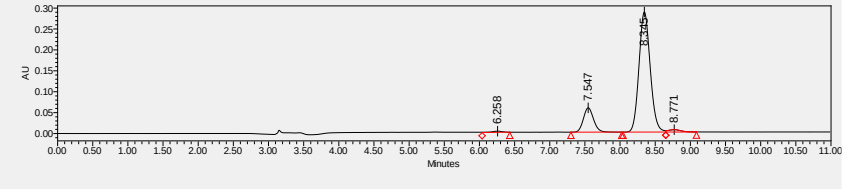
[1-(3,4-Dichlorophenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl](phenyl)methanone (3la)



(**$C_{29}H_{21}Cl_2NOS$**) Prepared according to the general procedure for 72 h. 38.5 mg, 77% yield; yellow foam. Melting point: 70 – 74 °C. $[\alpha]^{20}_D$ = +487.9 (*c* 0.24, CH_2Cl_2). 83:17 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 90% *ee* for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ =8.35 min (major), 8.77 min (minor); $t_{minor\ isomer}$ =7.55 min (major), 6.26 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.80 – 7.75 (m, 2H), 7.71 – 7.67 (m, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.48 (m, 1H), 7.48 – 7.46 (m, 1H), 7.46 – 7.41 (m, 2H), 7.36 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 7.07 – 7.01 (m, 1H), 6.89 – 6.82 (m, 2H), 6.66 – 6.59 (m, 1H), 4.74 (dd, *J* = 6.0, 8.0 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.32 – 2.23 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ198.1, 148.1, 146.9, 144. 7, 137.0, 133.7, 133.1, 133.0, 131.6, 131.0, 129.1, 129.0, 128.8, 128.6, 128.6, 128.0, 126.5, 125.8, 125.1, 124.7, 121.9, 116.0, 90.9, 69.8, 55.6, 40.0. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{22}{}^{35}Cl^{35}ClNOS^+$ ([M]+H$^+$) = 502.0794, Found 502.0790; calcd for $C_{29}H_{22}{}^{35}Cl^{37}ClNOS^+$ ([M]+H$^+$) = 504.0764, Found 504.0760; calcd for $C_{29}H_{22}{}^{37}Cl^{37}ClNOS^+$ ([M]+H$^+$) = 506.0735, Found 506.0742; **IR (neat)**: 3060, 1682, 1588, 1467, 1351, 1263, 1220, 1027, 737, 698 cm^{-1}

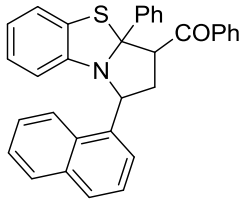


	Retention Time	Area	% Area
1	6.411	269767	14.02
2	7.681	259545	13.49
3	8.507	706829	36.73
4	8.941	688392	35.77

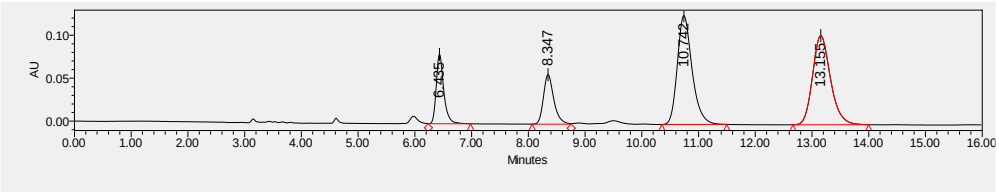


	Retention Time	Area	% Area
1	6.258	30665	0.79
2	7.547	583645	15.09
3	8.345	3186074	82.35
4	8.771	68476	1.77

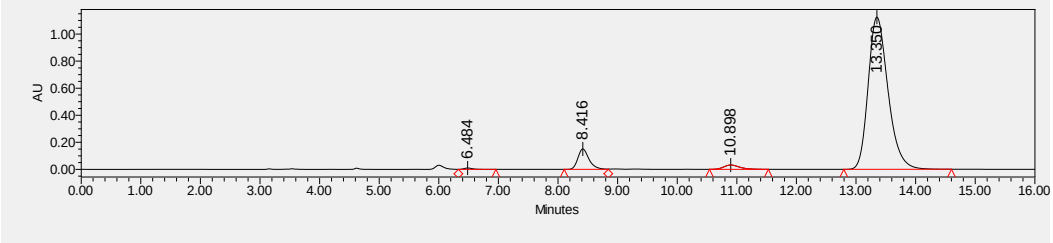
[1-(Naphthalen-1-yl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl](phenyl)methanone (3ma)



(**$C_{33}H_{25}NOS$**) Prepared according to the general procedure for 48 h. 40.6 mg, 84% yield; yellow foam. Melting point: 91 – 93 °C. $[\alpha]^{20}_D$ = +511.3 (*c* 0.68, CH_2Cl_2). 94:6 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 90% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 13.35 min (major), 10.90 min (minor); $t_{minor\ isomer}$ = 8.42 min (major), 6.48 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 1H), 7.95 – 7.89 (m, 4H), 7.89 – 7.85 (m, 1H), 7.80 – 7.74 (m, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.43 (m, 3H), 7.38 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 7.19 – 7.15 (m, 1H), 6.94 – 6.86 (m, 1H), 6.84 – 6.77 (m, 2H), 5.38 (dd, *J* = 4.0, 9.6 Hz, 1H), 4.68 (dd, *J* = 7.2, 10.4 Hz, 1H), 3.37 – 3.18 (m, 1H), 2.47 – 2.35 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.2, 149.1, 146.8, 140.0, 136.6, 134.4, 134.2, 133.7, 130.6, 129.1, 128.9, 128.7, 128.4, 128.1, 127.8, 126.4, 126.0, 125.9, 125.8, 125.1, 125.0, 123.9, 123.4, 122.1, 117.1, 91.6, 68.2, 55.8, 40.6. **HRMS (FTMS+c ESI)** calcd for $C_{33}H_{26}NOS^+$ ([M]+H$^+$) = 484.1730, Found 448.1734; **IR (neat)**: 3058, 1680, 1593, 1451, 1260, 1221, 734, 696 cm^{-1}

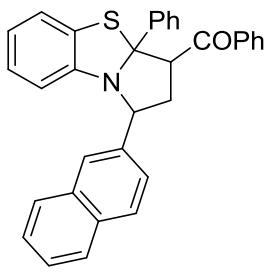


	Retention Time	Area	% Area
1	6.435	744183	12.34
2	8.347	731975	12.14
3	10.742	2282596	37.85
4	13.155	2271765	37.67



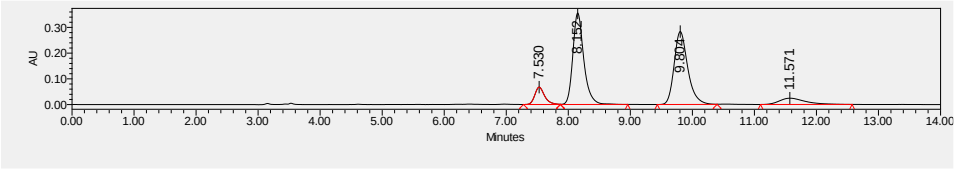
	Retention Time	Area	% Area
3	10.898	587313	2.05
1	6.484	104522	0.37
2	8.416	1958224	6.84
4	13.350	25985981	90.75

[1-(Naphthalen-2-yl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl](phenyl)methanone (3na)

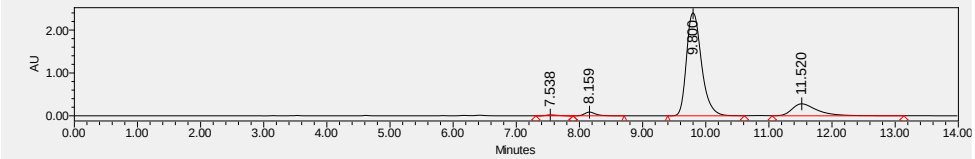


(**$C_{33}H_{25}NOS$**) Prepared according to the general procedure for 48 h. 33.8 mg, 70% yield; yellow foam. Melting point: 76 – 79 °C. $[\alpha]^{20}_D$ = +402.2 (*c* 1.19, CH_2Cl_2). 84:16 d.r. (determined by ^{1}H NMR), 95% *ee* for the major isomer and 94% *ee* for the minor isomer. **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 9.80 min (major), 8.16 min (minor); $t_{minor\ isomer}$ =11.52 min (major), 7.54 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.93 – 7.83 (m, 7H), 7.73 – 7.68 (m, 1H), 7.54 – 7.48 (m, 3H), 7.44 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.26 – 7.20 (m,1H), 7.08 – 7.03 (m, 1H), 6.87 – 6.75 (m, 2H), 6.68 – 6.63 (m, 1H), 4.93 (dd, *J* = 6.4, 8.4 Hz, 1H), 4.72 (t, *J* = 7.6 Hz, 1H), 3.07 – 2.96 (m, 1H), 2.49 – 2.38 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.3, 148.5, 147.4, 141.6, 137.0, 133.6, 133.5, 133.2, 133.1, 128.9, 128.9, 128.8, 128.5, 128.2, 127.9, 127.8, 126.5, 126.1, 126.0, 125.9, 125.1, 125.0, 124.4, 121.7, 116.3, 91.1, 70.9, 56.0, 40.1. **HRMS**

(FTMS+c ESI) calcd for $C_{33}H_{26}NOS^+$ ([M]+H^+) = 484.1730, Found 484.1728; **IR (neat)**: 3057, 1680, 1464, 1450, 1264, 1219, 749, 695 cm^{-1}

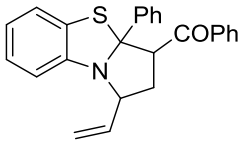


	Retention Time	Area	% Area
1	7.530	743715	7.32
2	8.152	4372547	43.05
3	9.804	4329819	42.63
4	11.571	709724	6.99

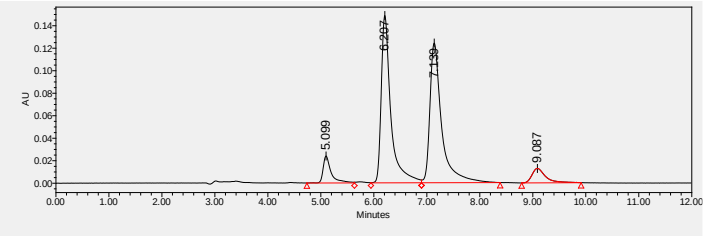


	Retention Time	Area	% Area
1	7.538	236917	0.49
2	8.159	1067791	2.20
3	9.800	39500358	81.23
4	11.520	7824128	16.09

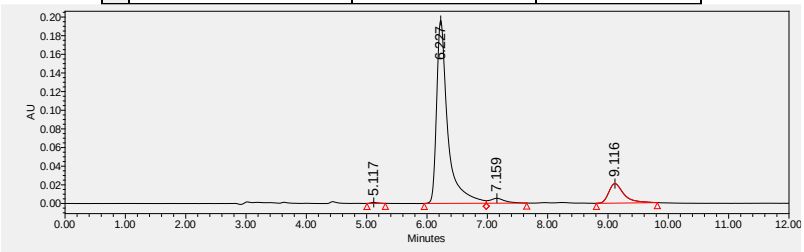
Phenyl(3a-phenyl-1-vinyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl)methanone (3oa)



($C_{25}H_{21}NOS$) Prepared according to the general procedure for 96 h. 13.9 mg, 36% yield; yellow oil. $[\alpha]^{20}_D$ = +443.2 (*c* 0.22, CH_2Cl_2). 85:15 d.r. (determined by ^1H NMR), 93% *ee* for the major isomer and 95% *ee* for the minor isomer. **HPLC** (Chiral **ADH** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 6.23 min (major), 7.16 min (minor); $t_{minor\ isomer}$ =9.12 min (major), 5.12 min (minor). Major isomer：**^1H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.74 – 7.68 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.44 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m,1H), 7.02 – 6.92 (m, 3H), 6.84 – 6.79 (m, 1H), 6.23 – 6.08 (m, 1H), 5.60 – 5.52 (m, 1H), 5.33 – 5.28 (m, 1H), 4.55 (t, *J* = 6.8 Hz, 1H), 4.30 (dd, *J* = 6.8, 14.0 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.15 – 2.05 (m, 1H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 198.5, 148.7, 147.8, 141.1, 137.3, 133.5, 132.0, 128.9, 128.7, 128.4, 127.6, 125.7, 125.0, 123.3, 121.3, 116.4, 114.7, 90.3, 69.5, 56.1, 36.9. **HRMS (FTMS+c ESI)** calcd for $C_{25}H_{22}NOS^+$ ([M]+H^+) = 384.1417, Found 384.1418; **IR (neat)**: 3060, 1681, 1579, 1467, 1264, 1219, 1022, 994, 931, 753, 697 cm^{-1}



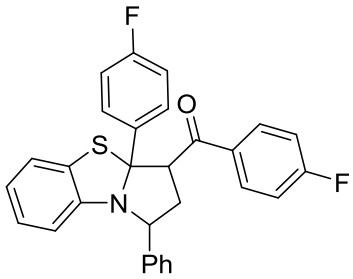
	Retention Time	Area	% Area
1	5.099	252937	5.92
2	6.207	1874459	43.88
3	7.139	1916659	44.86
4	9.087	228144	5.34



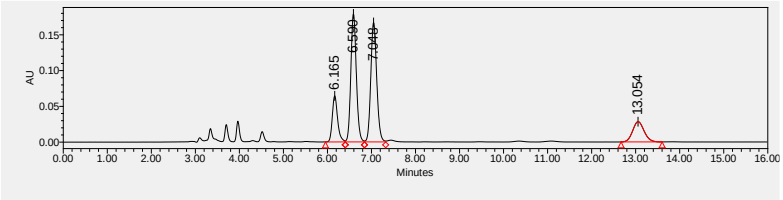
	Retention Time	Area	% Area
1	5.117	9001	0.30

2	6.227	2519020	84.36
3	7.159	91123	3.05
4	9.116	366736	12.28

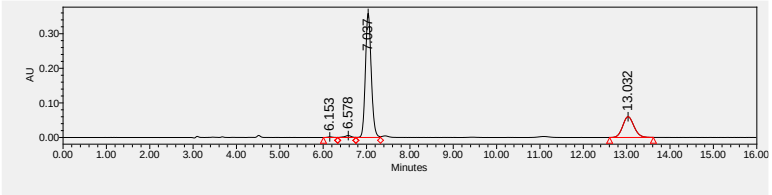
(4-Fluorophenyl){3a-(4-fluorophenyl)-1-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}methanone (3pa)



($C_{29}H_{21}F_2NOS$) Prepared according to the general procedure for 48 h. 40.4 mg, 86% yield; yellow foam. Melting point: 58 – 62 °C. $[\alpha]^{20}_D$ = +404.6 (*c* 0.68, CH_2Cl_2). 77:23 d.r. (determined by ^{1}H NMR), 96% *ee* for the major isomer and 97% *ee* for the minor isomer. **HPLC** (Chiral **IA** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 7.04 min (major), 6.58 min (minor); $t_{minor\ isomer}$ =13.03 min (major), 6.15 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.61 – 7.55 (m, 2H), 7.48 – 7.42 (m, 3H), 7.13 – 7.05 (m, 3H), 7.00 – 6.93 (m, 2H), 6.91 – 6.80 (m, 2H), 6.69 – 6.65 (m, 1H), 4.69 (dd, *J* = 5.2, 8.4 Hz, 1H), 4.55 (t, *J* = 8.0 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.43 – 2.34 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ196.4, 166.1 (d, *J* = 254.7 Hz), 162.2 (d, *J* = 245.3 Hz), 148.4, 144.1, 142.6 (d, *J* = 2.9 Hz), 133.4, 133.2 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 9.3 Hz), 129.0, 129.0, 128.2, 127.8 (d, *J* = 8.0 Hz), 127.7, 127.1, 125.1, 124.9, 121.9, 116.9, 116.0 (d, *J* = 21.8 Hz), 115.0 (d, *J* = 21.4 Hz), 91.0, 70.6, 56.3, 40.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -103.9, -114.9. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{22}F_2NOS^+$ ([M]+H$^+$) = 470.1385, Found 470.1376; **IR (neat)**: 3064, 1682, 1596, 1502, 1462, 1225, 1156, 835, 743, 701 cm^{-1}

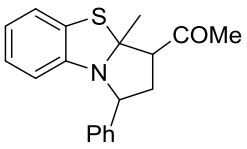


	Retention Time	Area	% Area
1	6.165	540557	12.96
2	6.590	1557441	37.33
3	7.048	1562679	37.46
4	13.054	511249	12.25

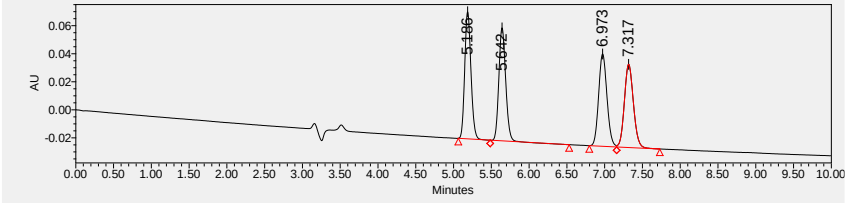


	Retention Time	Area	% Area
1	6.153	14738	0.33
2	6.578	59045	1.31
3	7.037	3355368	74.29
4	13.032	1087190	24.07

1-(3a-Methyl-1-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl)ethan-1-one (3qa)

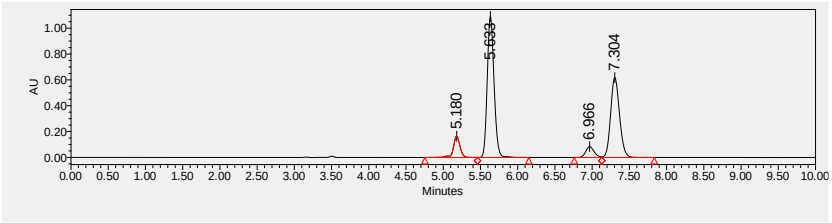


($C_{25}H_{21}NOS$) Prepared according to the general procedure for 96 h. 20.0 mg, 65% yield; yellow oil. $[\alpha]^{20}_D$ = +138.9 (*c* 0.31, CH_2Cl_2). 53:47 d.r. (determined by ^{1}H NMR), 74% *ee* for the major isomer and 77% *ee* for the minor isomer. **HPLC** (Chiral **IE** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 5.63 min (major), 5.18 min (minor); $t_{minor\ isomer}$ =7.30 min (major), 6.97 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 3H), 7.34 – 7.28 (m, 2H), 7.06 – 7.01 (m, 1H), 6.84 – 6.76 (m, 2H), 6.26 – 6.15 (m, 1H), 4.47 (dd, *J* = 6.8, 10.4 Hz, 1H), 3.75 (dd, *J* = 6.8, 12.8 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.41 – 2.33 (m, 1H), 2.31 (s, 3H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.2, 148.7, 144.3, 132.2, 129.0, 127.6, 126.2, 125.4, 123.5, 121.7, 115.4, 82.8, 68.5, 60.5, 38.0, 33.6, 29.8. **HRMS (FTMS+c ESI)** calcd for $C_{25}H_{22}NOS^+$ ([M]+H$^+$) = 310.1260, Found 310.1256; **IR (neat)**: 2969, 1710, 1579, 1466, 1360, 1272, 1264, 1219, 1169, 1133, 1029, 749, 702 cm^{-1}



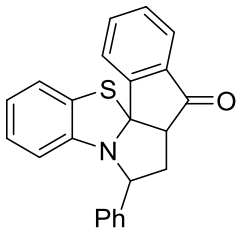
	Retention Time	Area	% Area
1	5.186	519417	25.62
2	5.642	509869	25.15

3	6.973	504657	24.89
4	7.317	493617	24.35

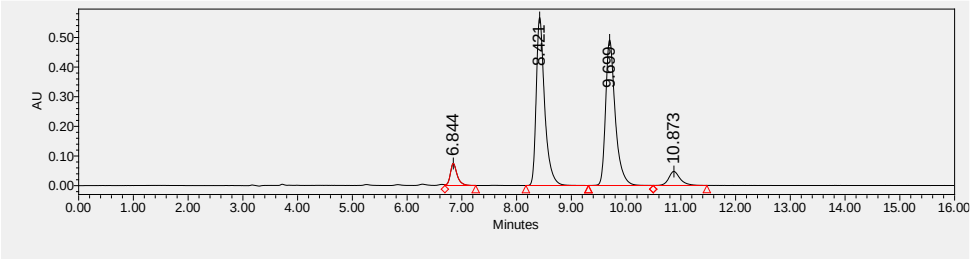


	Retention Time	Area	% Area
1	5.180	1012704	7.37
2	5.633	6934463	50.49
3	6.966	659977	4.81
4	7.304	5126702	37.33

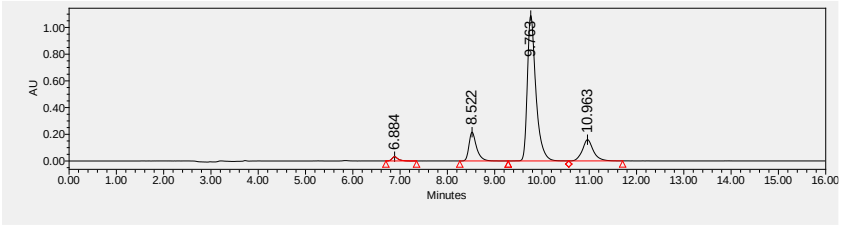
6-phenyl-7,7a-dihydrobenzo[*d*]indeno[1',2':2,3]pyrrolo[2,1-*b*]thiazol-8(6*H*)-one (3ra)



($C_{23}H_{17}NOS$) Prepared according to the general procedure. 30.7 mg, 86% yield; yellow foam. Melting point: 50 – 56 °C. $[\alpha]^{20}_D$ = +154.5 (*c* 0.61, CH_2Cl_2). 86:14 d.r. (determined by ^{1}H NMR), 70% *ee* for the major isomer and 80% *ee* for the minor isomer. **HPLC** (Chiral **IB** column), *i*PrOH/*n*Hexane = 5/95, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ =9.76 min (major), 8.52 min (minor); $t_{minor\ isomer}$ =10.96 min (major), 6.88 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.64 – 7.60 (m, 1H), 7.49 – 7.42 (m, 1H), 7.25 – 7.19 (m, 6H), 6.99 – 6.91 (m, 1H), 6.89 – 6.80 (m, 1H), 6.33 – 6.25 (m, 1H), 4.76 (dd, *J* = 6.8, 8.8 Hz, 1H), 3.73 (dd, *J* = 7.6, 10.0 Hz, 1H), 2.93 – 2.83 (m, 1H), 2.27 – 2.17 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.5, 156.5, 147.6, 141.5, 136.7, 132.7, 132.1, 129.8, 128.7, 127.8, 127.2, 125.4, 125.4, 124.0, 123.2, 121.3, 116.1, 88.6, 74.0, 59.3, 38.3. **HRMS (FTMS+c ESI)** calcd for $C_{23}H_{18}NOS^+$ ([M]+H$^+$) = 356.1104, Found 356.1096; **IR (neat)**: 3059, 1718, 1599, 1463, 1264, 733, 701 cm^{-1}

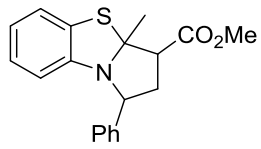


	Retention Time	Area	% Area
1	6.844	646158	4.83
2	8.421	6055085	45.23
3	9.699	5996084	44.79
4	10.873	691078	5.16



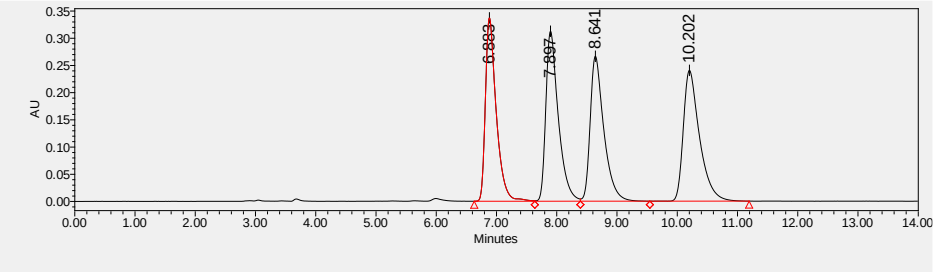
	Retention Time	Area	% Area
1	6.884	288471	1.53
2	8.522	2389299	12.69
3	9.763	13592745	72.18
4	10.963	2560749	13.60

Methyl 3a-methyl-1-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazole-3-carboxylate (3sa)

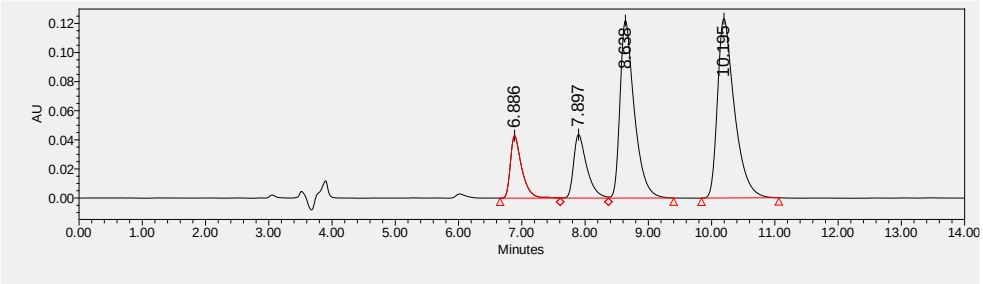


($C_{19}H_{19}NO_2S$) Prepared according to the general procedure for 48 h. 26.9 mg, 83% yield; yellow oil. $[\alpha]^{20}_D$ = +115.6 (*c* 0.55, CH_2Cl_2). 51:49 d.r. (determined by ^{1}H NMR), 57% *ee* for the major isomer and 56% *ee* for the minor isomer. **HPLC** (Chiral **AD-H** column), *i*PrOH/*n*Hexane = 2/98, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 10.20 min (major), 7.90 min (minor); $t_{minor\ isomer}$ = 8.64 min (major), 6.89 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.35 (m, 4H), 7.34 – 7.31 (m, 1H), 7.13 – 7.07 (m, 1H), 6.81 – 6.74 (m, 2H), 6.21 – 6.14 (m, 1H), 4.47 (dd, *J* = 6.4, 10.4 Hz, 1H), 3.77 (s, 3H), 3.26 (t, *J* = 7.2 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.29 – 2.21 (m, 1H), 1.71 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 172.2, 147.7, 144.0,

129.6, 129.0, 127.7, 126.4, 125.1, 121.9, 121.2, 112.5, 83.3, 70.6, 54.2, 52.1, 37.4, 29.8. **HRMS (FTMS+c ESI)** calcd for $C_{20}H_{19}NO_2S^+$ ([M]+H$^+$) = 326.1209, Found 326.1214; **IR (neat)**: 2978, 1736, 1493, 1265, 1202, 1027, 734, 701 cm^{-1}

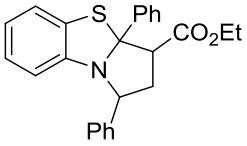


	Retention Time	Area	% Area
1	6.883	4203113	24.20
2	7.897	4483622	25.81
3	8.641	4191738	24.13
4	10.202	4490682	25.85

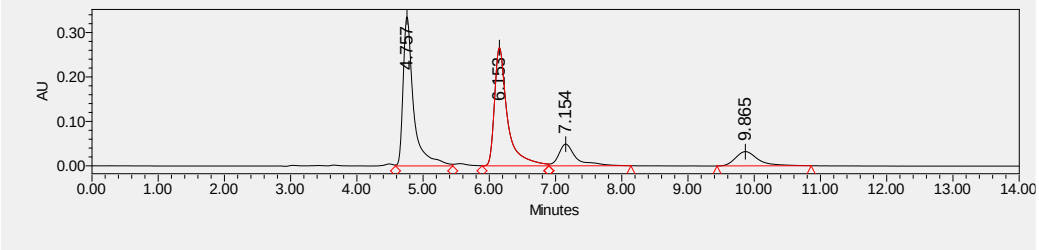


	Retention Time	Area	% Area
1	6.886	537875	9.99
2	7.897	629990	11.70
3	8.638	1915871	35.59
4	10.195	2299287	42.71

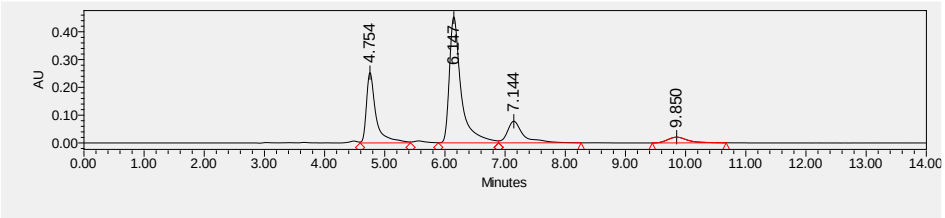
Ethyl 1,3a-diphenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazole-3-carboxylate (3ta)



($C_{25}H_{23}NO_2S$) Prepared according to the general procedure for 48 h. 27.3 mg, 68% yield; yellow oil. $[\alpha]^{20}_D$ = +253.6 (*c* 0.55, CH_2Cl_2). 82:18 d.r. (determined by ^{1}H NMR), 38% *ee* for the major isomer and 50% *ee* for the minor isomer. **HPLC** (Chiral **AD-H** column), *i*PrOH/*n*Hexane = 10/90, Flow rate: 1.0 mL/min, 227 nm, $t_{major\ isomer}$ = 6.15 min (major), 4.75 min (minor); $t_{minor\ isomer}$ = 7.14 min (major), 9.85 min (minor). Major isomer：**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.56 – 7.50 (m, 2H), 7.44 – 7.31 (m, 5H), 7.27 – 7.21 (m, 1H), 7.02 – 6.97 (m, 1H), 6.85 – 6.74 (m, 2H), 6.47 – 6.41 (m, 1H), 4.78 (dd, *J* = 6.8, 8.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.75 (dd, *J* = 3.6, 7.6 Hz, 1H), 2.88 – 2.76 (m, 1H), 2.24 – 2.10 (m, 1H),1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ172.0, 148.5, 148.2, 143.3, 132.1, 128.9, 128.5, 128.1, 127.8, 127.5, 127.4, 125.5, 124.9, 124.0, 121.4, 115.8, 90.7, 70.7, 61.4, 56.0, 38.6, 14.3. **HRMS (FTMS+c ESI)** calcd for $C_{25}H_{23}NNaO_2S^+$ ([M]+Na$^+$) = 424.1342, Found 424.1349; **IR (neat)**: 2927, 1733, 1462, 1255, 1180, 1027, 742, 698 cm^{-1}

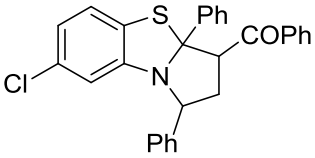


	Retention Time	Area	% Area
1	4.757	3695380	41.18
2	6.153	3620707	40.35
3	7.154	891947	9.94
4	9.865	765376	8.53

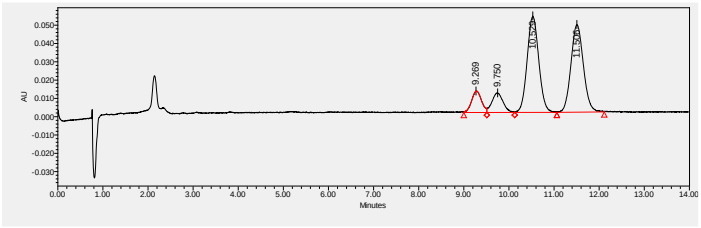


	Retention Time	Area	% Area
1	4.754	2807752	25.76
2	6.147	6177256	56.68
3	7.144	1436587	13.18
4	9.850	477009	4.38

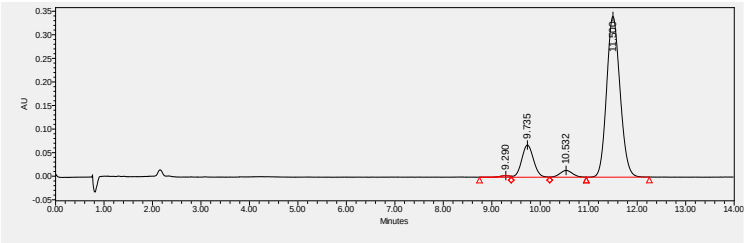
(7-Chloro-1,3a-diphenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl)(phenyl)methanone (3ab)



(**$C_{29}H_{22}ClNOS$**) Prepared according to the general procedure for 48 h. 40.0 mg, 85% yield; yellow foam. Melting point: 74 – 78 °C. $[\alpha]^{20}_D$ = +446.1 (*c* 0.77, CH_2Cl_2). 85:15 d.r. (determined by ^1H NMR), 92% *ee* for the major isomer and 91% *ee* for the minor isomer. **UPCC** (Chiral **OJ-3** column), EtOH/CO_2 = 10/90, Flow rate: 1.5 mL/min, 227 nm, $t_{major\ isomer}$ =11.50 min (major), 10.53 min (minor); $t_{minor\ isomer}$ =9.74 min (major), 9.29 min (minor). Major isomer：**^1H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.79 – 7.73 (m, 2H), 7.60 – 7.54 (m, 3H), 7.48 – 7.42 (m, 4H), 7.39 – 7.29 (m, 3H), 7.27 – 7.21 (m, 1H), 6.94 – 6.90 (m, 1H), 6.84 – 6.78 (m, 1H), 6.66 – 6.61 (m, 1H), 4.84 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.70 (t, *J* = 7.2 Hz, 1H), 2.99 – 2.89 (m, 1H), 2.42 – 2.27 (m, 1H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ198.3, 149.9, 146.9, 143.7, 137.0, 133.7, 131.4, 130.3, 129.1, 129.0, 128.7, 128.6, 127.9, 127.8, 126.9, 125.7, 123.9, 122.1, 115.8, 91.5, 70.7, 55.6, 40.1. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{23}{}^{35}ClNOS^+$ ([M]+H$^+$) = 468.1183, Found 468.1188; calcd for $C_{29}H_{23}{}^{37}ClNOS^+$ ([M]+H$^+$) = 470.1154, Found 470.1165; **IR (neat)**: 3059, 1680, 1575, 1449, 1357, 1264, 1219, 1079, 739, 697 cm^{-1}

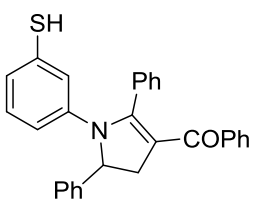


	Retention Time	Area	% Area
1	9.269	177304	7.99
2	9.750	182691	8.23
3	10.529	940894	42.41
4	11.506	917612	41.36

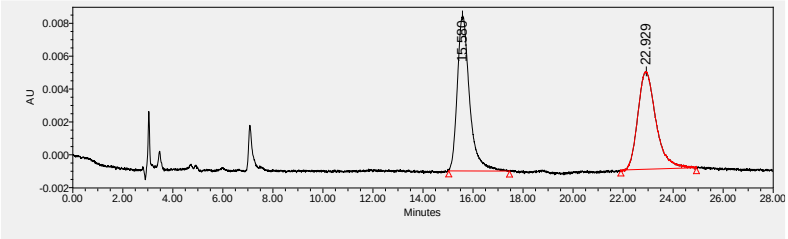


	Retention Time	Area	% Area
1	9.290	52294	0.65
2	9.735	1156337	14.39
3	10.532	261797	3.26
4	11.500	6564697	81.70

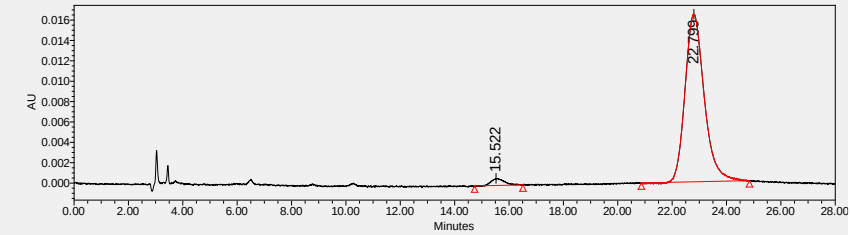
[1-(3-Mercaptophenyl)-2,5-diphenyl-4,5-dihydro-1*H*-pyrrol-3-yl](phenyl)methanone (3ac)



(**$C_{29}H_{23}NOS$**) Prepared according to the general procedure for 24 h. 17.5 mg, 40% yield; yellow oil. $[\alpha]^{20}_D$ = +185.8 (c 0.10, CH_2Cl_2). 94% *ee*. **HPLC** (Chiral **IG** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 230 nm, t_{major} = 22.80 min, t_{minor} = 15.52 min. **^1H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 7.27 – 7.22 (m, 2H), 7.11 – 7.02 (m, 4H), 7.00 – 6.92 (m, 4H), 6.84 – 6.77 (m, 1H), 6.77 – 6.71 (m, 1H), 6.50 – 6.44 (m, 1H), 6.40 – 6.28 (m, 1H), 5.19 (dd, *J* = 4.8, 11.2 Hz, 1H), 3.95 (dd, *J* = 11.2, 15.2 Hz, 1H), 3.13 (s, 1H), 3.08 (dd, *J* = 4.8, 15.2 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 193.5, 157.6, 143.3, 143.1, 140.5, 131.2, 131.2, 130.2, 129.9, 129.3, 129.3, 129.0, 128.6, 128.0, 128.0, 127.3, 126.1, 124.7, 123.8, 120.6, 114.2, 68.9, 41.9. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{24}NOS^+$ ([M]+H$^+$) = 434.1573, Found 434.1578; **IR (neat)**: 3056, 2925, 2852, 1581, 1555, 1477, 1373, 1264, 736, 699 cm^{-1}

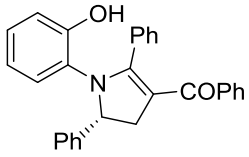


	Retention Time	Area	% Area
1	15.580	320385	51.72
2	22.929	299047	48.28

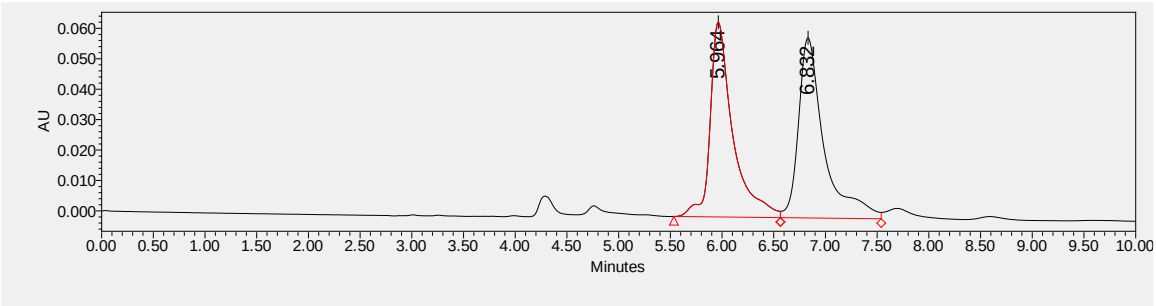


	Retention Time	Area	% Area
1	15.522	23598	2.83
2	22.799	809265	97.17

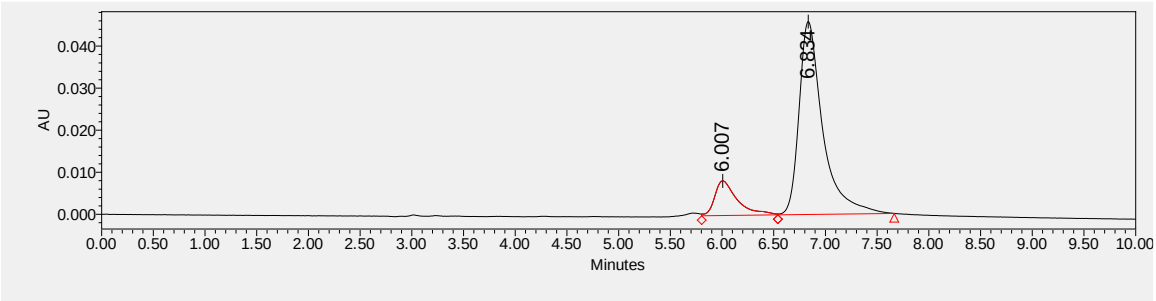
(*R*)-[1-(2-hydroxyphenyl)-2,5-diphenyl-4,5-dihydro-1H-pyrrol-3-yl](phenyl)methanone (3ad)



($C_{29}H_{23}NO_2$) Prepared according to the general procedure for 96 h. 9.9 mg, 24% yield; yellow oil. $[\alpha]^{20}_D$ = -156.6 (*c* 0.20, MeOH). 71% *ee*. **HPLC** (Chiral **IA** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 227 nm, t = 6.83 min (major), 6.01 min (minor); **^{1}H NMR** (400 MHz, d_6-DMSO) δ 9.71 (s, 1H), 7.50 – 7.45 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 1H), 7.12 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 6.97 – 6.89 (m, 5H), 6.86 – 6.75 (m, 3H), 6.65 – 6.50 (m, 2H), 6.42 – 6.30 (m, 1H), 3.35 (dd, *J* = 9.2, 11.6 Hz, 1H), 3.86 (dd, *J* = 12.0, 15.2 Hz, 1H), 3.00 (dd, *J* = 9.2, 15.2 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, d_6-DMSO) δ190.27, 153.63, 141.31, 131.18, 129.59, 128.56, 128.46, 128.19, 127.95, 127.55, 127.51, 127.45, 127.15, 126.85, 126.73, 118.29, 115.84, 79.14, 67.15, 40.65. **HRMS (FTMS+c ESI)** calcd for $C_{29}H_{24}NO_2^+$ ([M]+H$^+$) = 418.1802, Found 418.1810; **IR (neat)**: 3394, 1659, 1265, 1024, 1005, 1029, 822, 759, 729 cm^{-1}



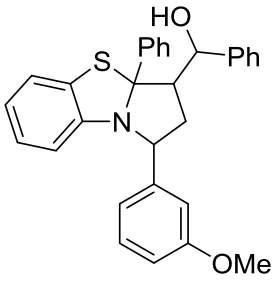
	Retention Time	Area	% Area
1	5.964	975666	49.02
2	6.832	1014731	50.98



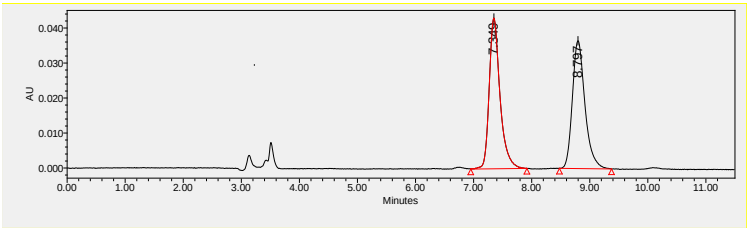
	Retention Time	Area	% Area

1	6.007	125008	14.64
2	6.834	728667	85.36

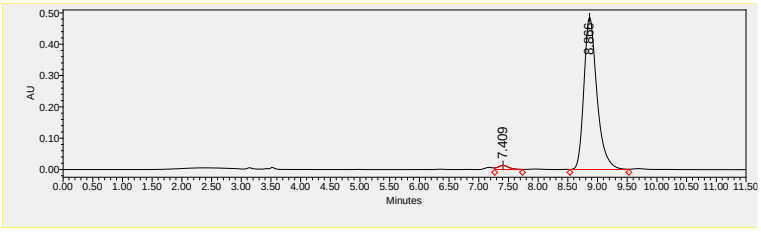
{1-(3-Methoxyphenyl)-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanol (4)



($C_{30}H_{27}NO_2S$) 99% yield; yellow oil. $[\alpha]^{20}_D$ = +455.0 (*c* 0.40, CH_2Cl_2). **HPLC** (Chiral **ID** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 230 nm, tr (minor) = 7.41 min, tr (major) = 8.87 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.42 – 7.31 (m, 6H), 7.31 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 7.12 – 7.07 (m, 1H), 7.03 – 6.96 (m, 2H), 6.90 – 6.78 (m, 3H), 6.50 – 6.42 (m, 1H), 5.04 (dd, *J* = 3.6, 9.2 Hz, 1H), 4.44 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.24 – 3.11 (m, 1H), 2.71 (d, *J* = 3.2 Hz, 1H), 1.92 – 1.82 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ160.0, 149.7, 147.9, 145.0, 142.7, 131.8, 129.8, 128.8, 128.4, 128.4, 127.2, 127.2, 126.1, 125.0, 123.8, 121.6, 119.7, 115.7, 113.1, 112.9, 93.5, 69.4, 77.2, 56.8, 55.3, 39.7. **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{28}NO_2S^+$ ([M]+H$^+$) = 466.1835, Found 466.1825; **IR (neat)**: 3551, 3466, 3058, 2936, 1601, 1488, 1462, 1262, 1158, 1129, 1037, 893, 748, 700 cm^{-1} .

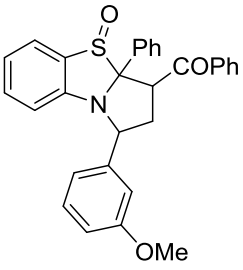


	Retention Time	Area	% Area
1	7.349	557022	50.36
2	8.797	548981	49.64

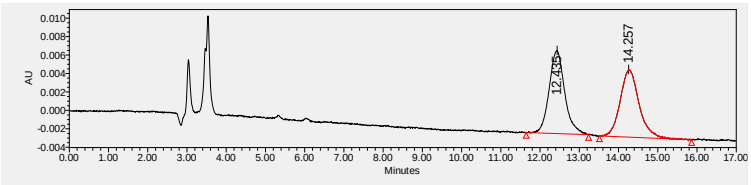


	Retention Time	Area	% Area
1	7.409	171807	2.27
2	8.866	7409782	97.73

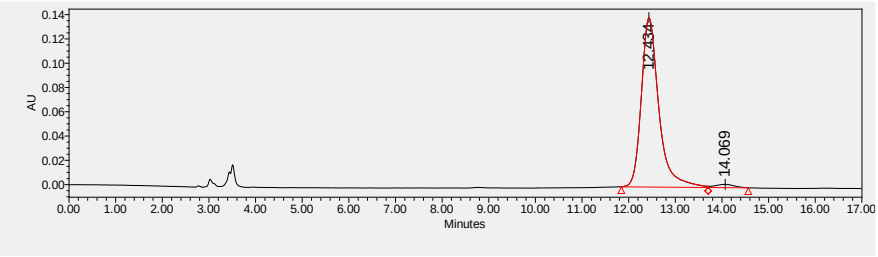
{1-(3-Methoxyphenyl)-4-oxido-3a-phenyl-1,2,3,3a-tetrahydrobenzo[*d*]pyrrolo[2,1-*b*]thiazol-3-yl}(phenyl)methanone (5)



($C_{30}H_{25}NO_2S$) 63% yield; yellow oil. $[\alpha]^{20}_D$ = +883.7 (c 0.10, CH_2Cl_2). **HPLC** (Chiral **IA** column), *i*PrOH/*n*Hexane = 20/80, Flow rate: 1.0 mL/min, 220 nm, tr (minor) = 14.07 min, tr (major) = 12.43 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 7.74 – 7.69 (m, 1H), 7.68 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 7.46 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 7.15 – 7.10 (m, 2H), 7.05 – 7.00 (m, 1H), 7.00 – 6.95 (m, 1H), 6.62 – 6.56 (m, 1H), 5.24 (dd, *J* = 6.4, 12.0 Hz, 1H), 4.67 (dd, *J* = 5.2, 11.6 Hz, 1H), 3.89 (s, 3H), 3.26 – 3.12 (m, 1H), 2.71 – 2.61 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ196.7, 160.1, 143.2, 137.9, 135.3, 134.8, 133.9, 133.7, 133.6, 130.1, 129.2, 129.0, 128.9, 128.6, 128.3, 128.0, 124.1, 120.1, 118.2, 113.6, 113.5, 10 1.0, 69.5, 55.3, 46.1, 41.9. **HRMS (FTMS+c ESI)** calcd for $C_{30}H_{26}NO_2S^+$ ([M]+H$^+$) = 480.1628, Found 480.1624; **IR (neat)**: 3061, 3466, 3058, 2936, 1601, 1590, 1463, 1262, 1158, 1129, 1040, 755, 700 cm^{-1} .



	Retention Time	Area	% Area
1	12.435	247055	50.28
2	14.257	244316	49.72

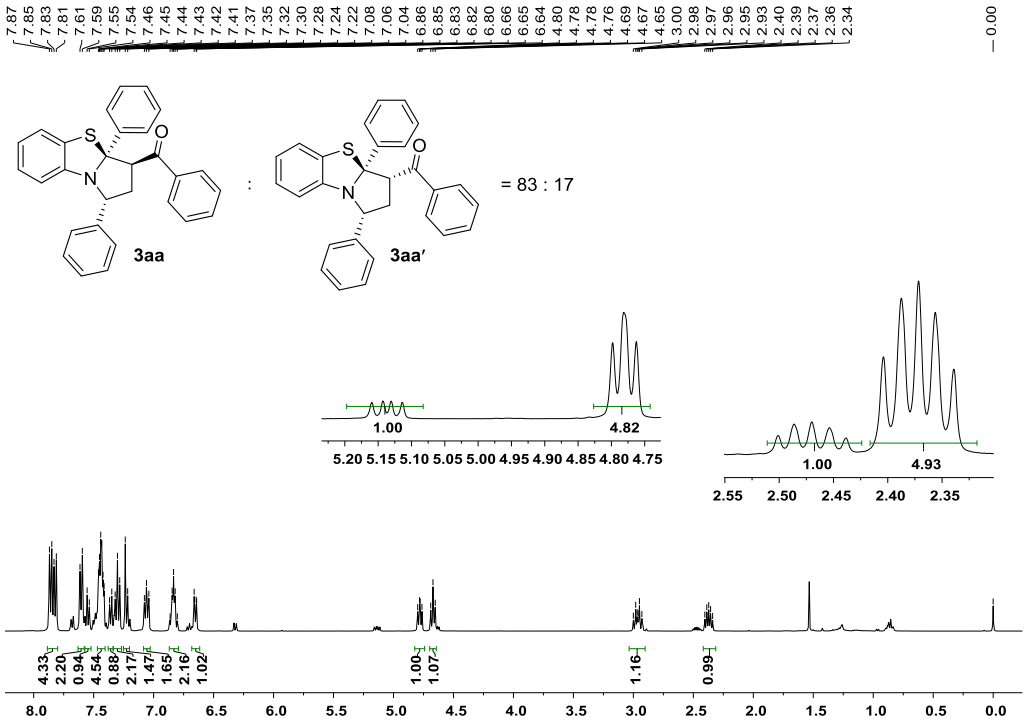


	Retention Time	Area	% Area
1	12.434	3634274	97.93
2	14.069	76644	2.07

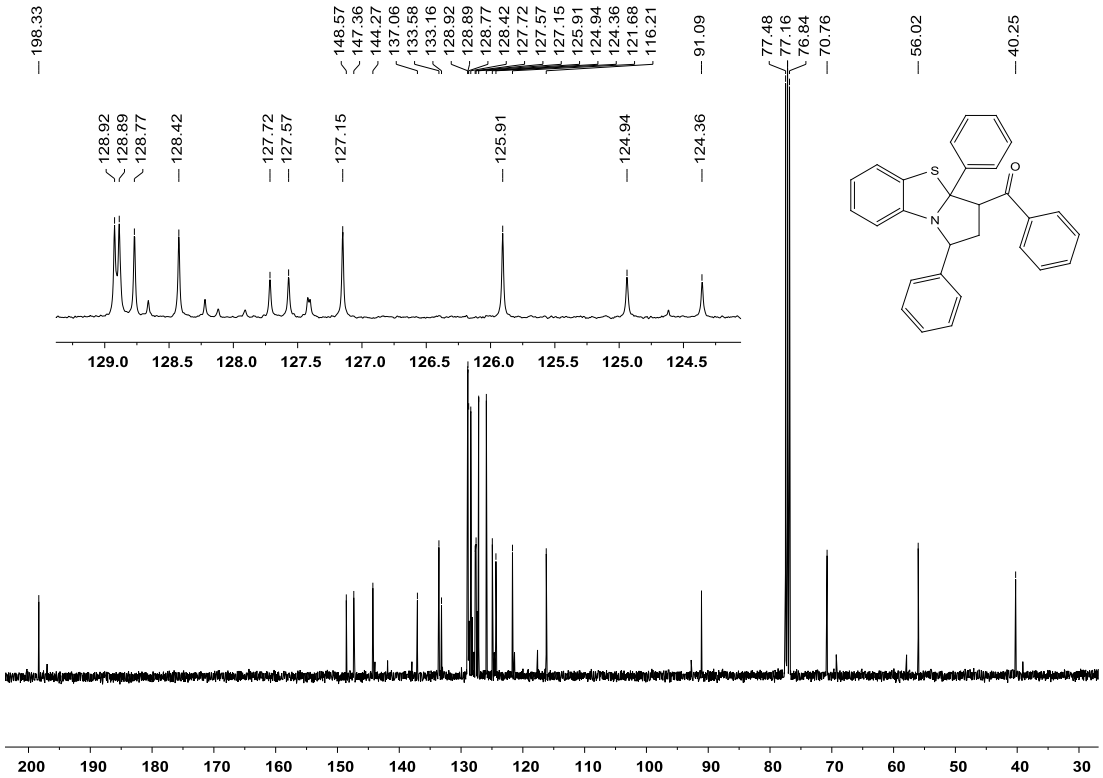
(L) Copies of NMR Spectra.

Compound **3aa:**

^{1}H NMR (400 MHz, $CDCl_3$)

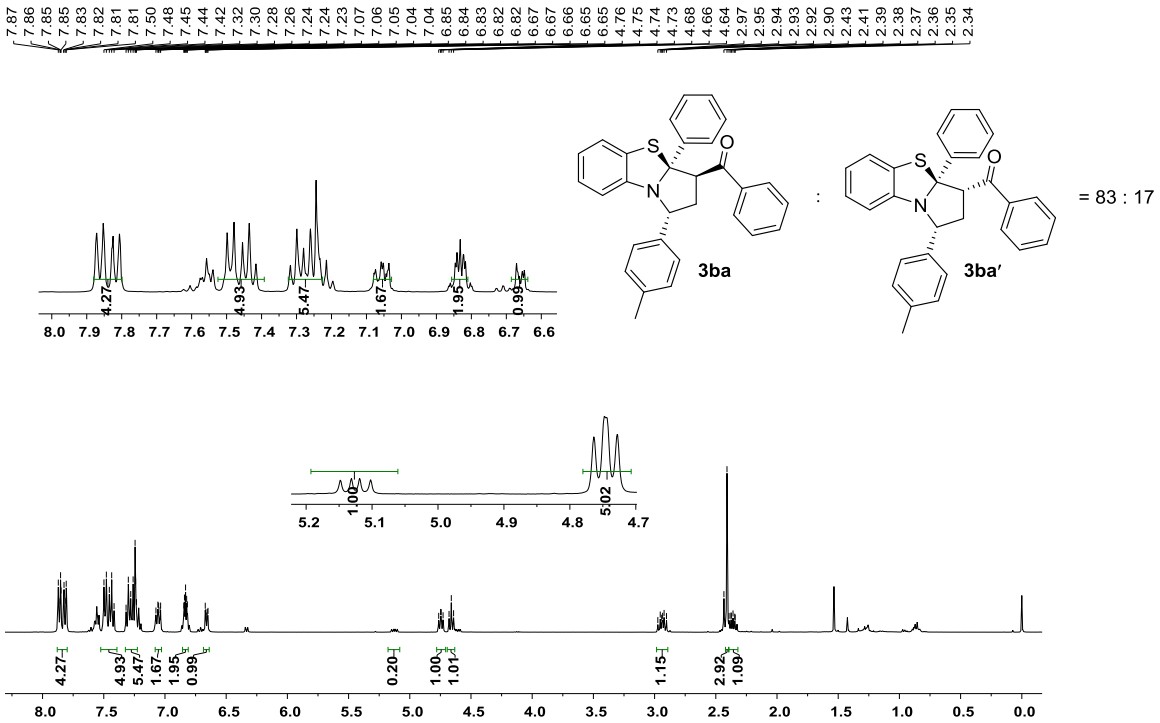


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

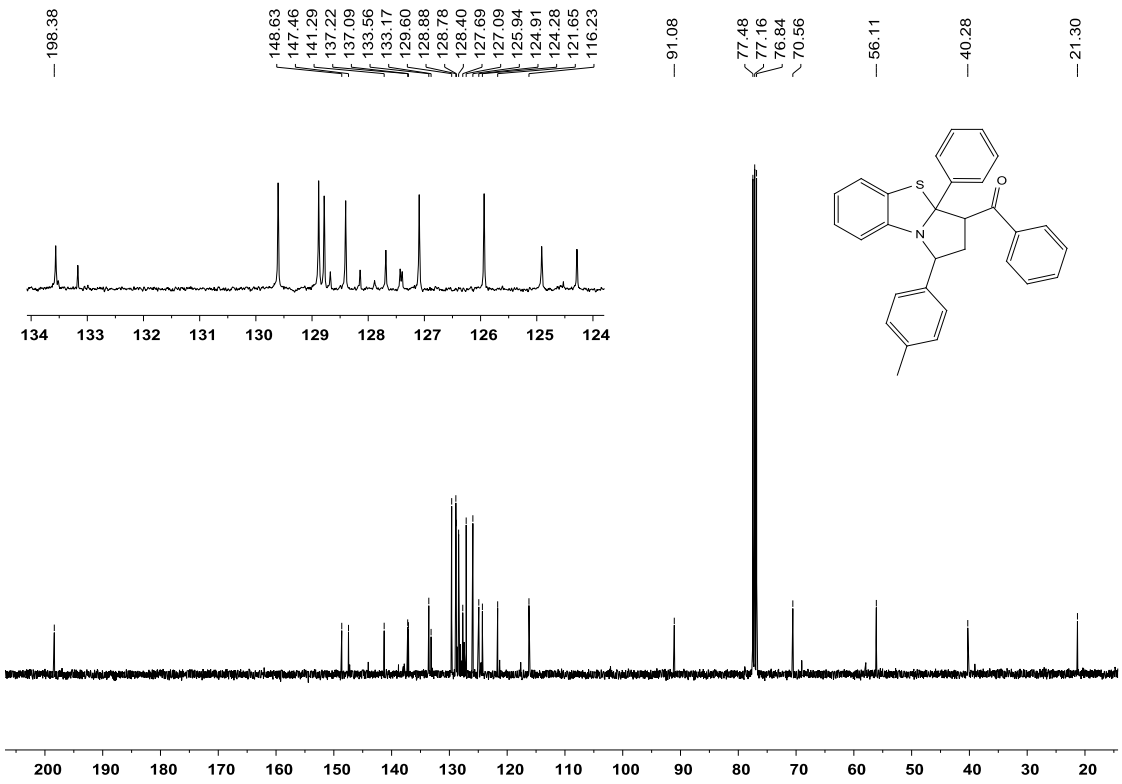


Compound **3ba:**

^{1}H NMR (400 MHz, $CDCl_3$)

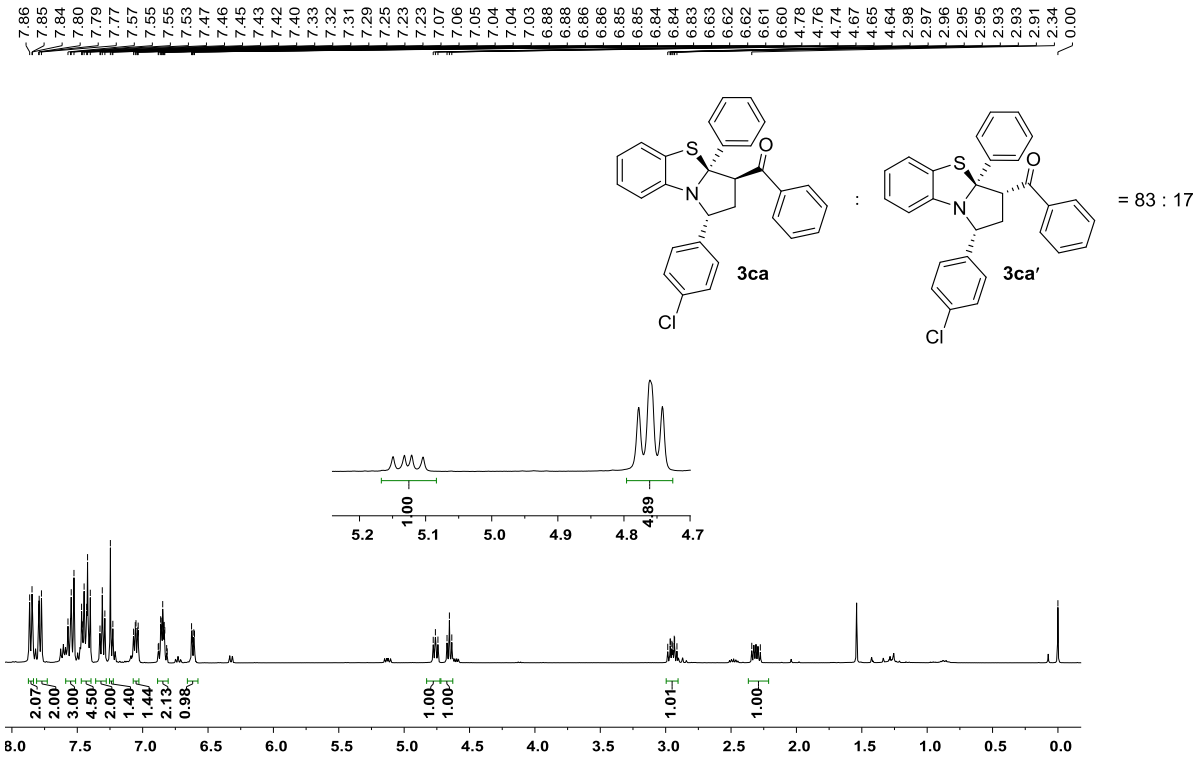


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

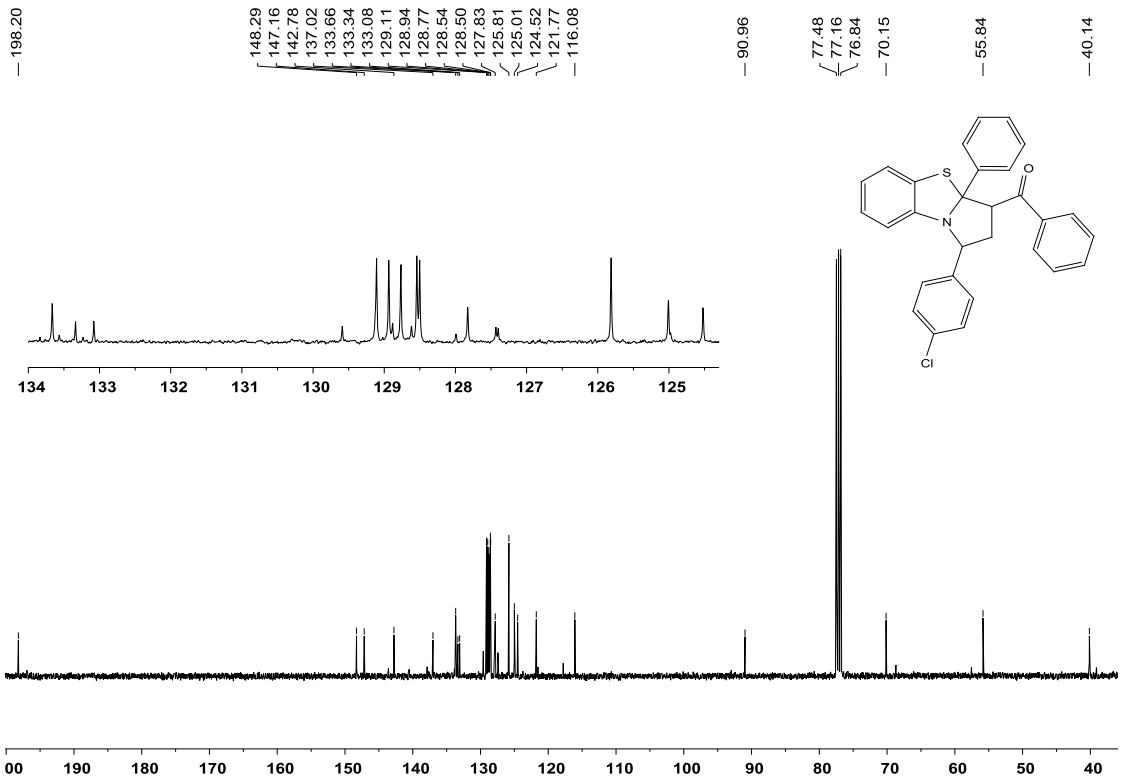


Compound **3ca:**

^{1}H NMR (400 MHz, $CDCl_3$)

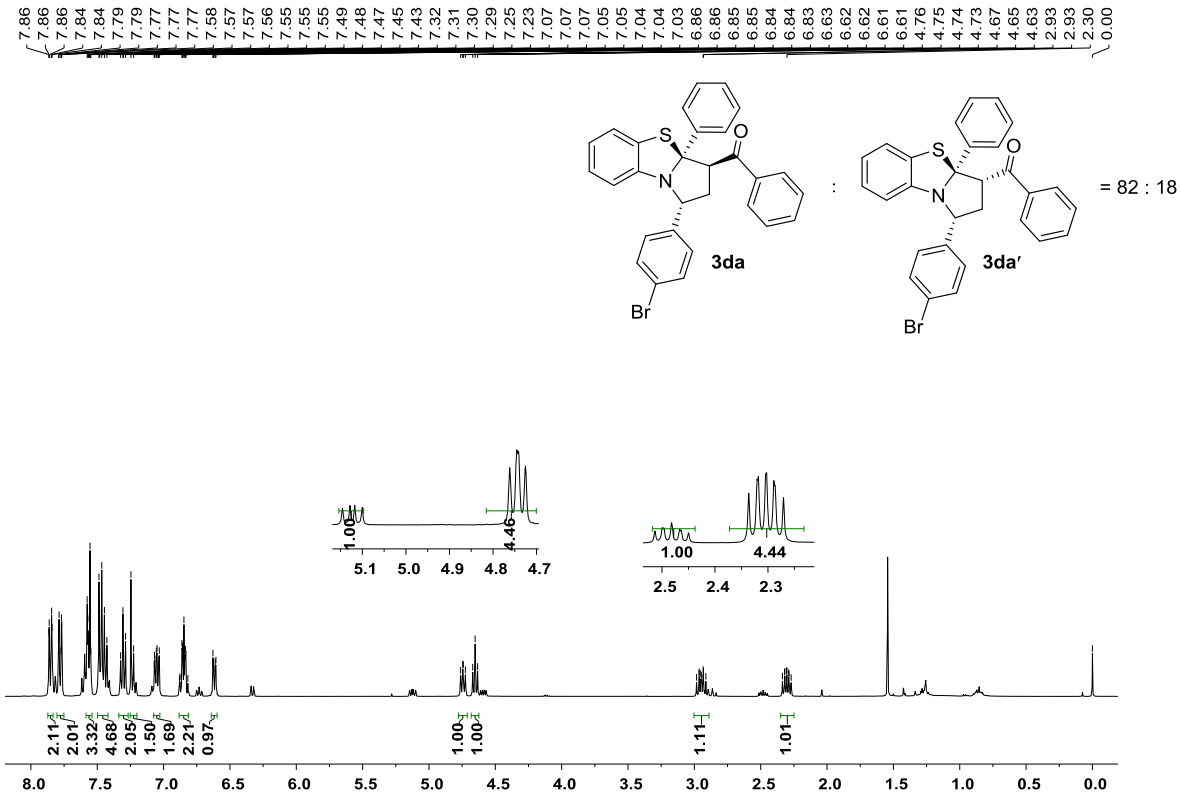


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

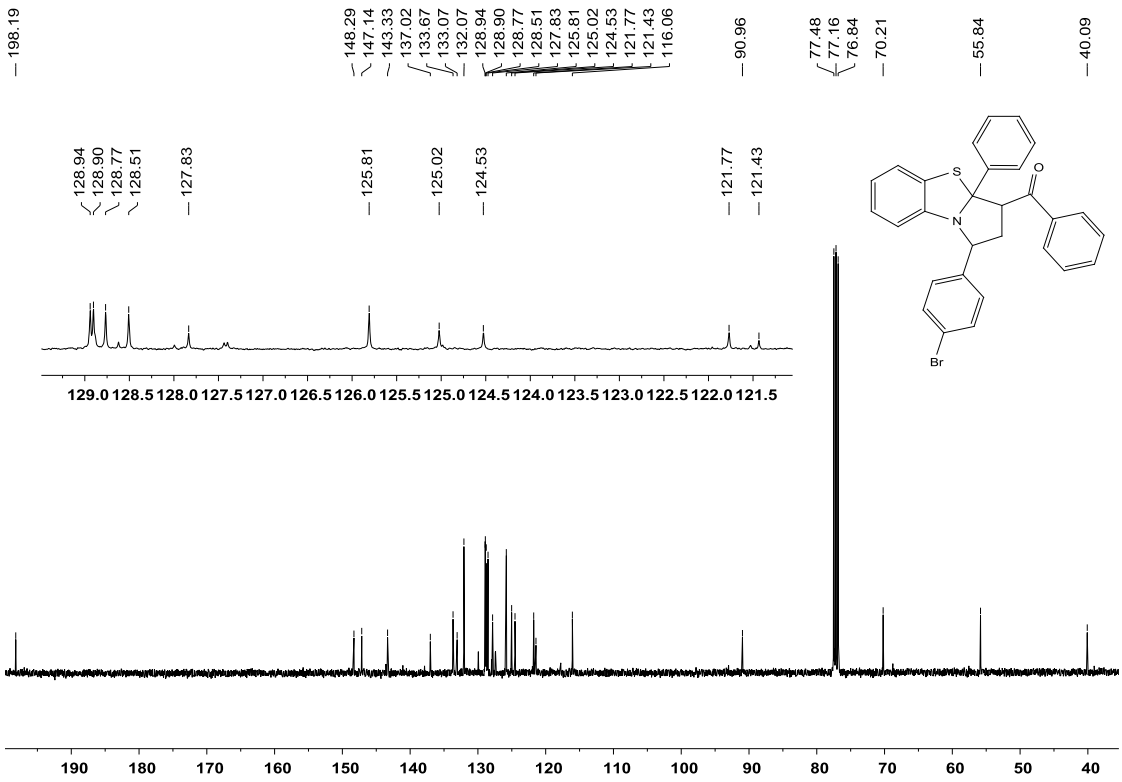


Compound **3da:**

^{1}H NMR (400 MHz, $CDCl_3$)

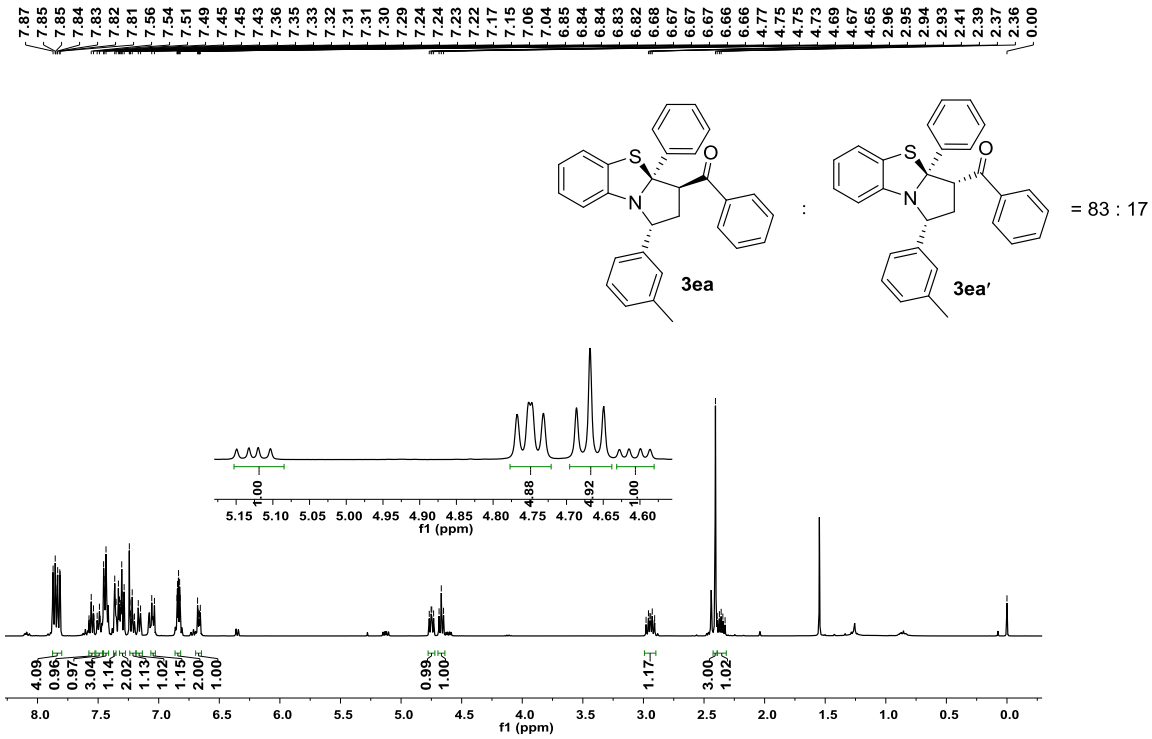


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

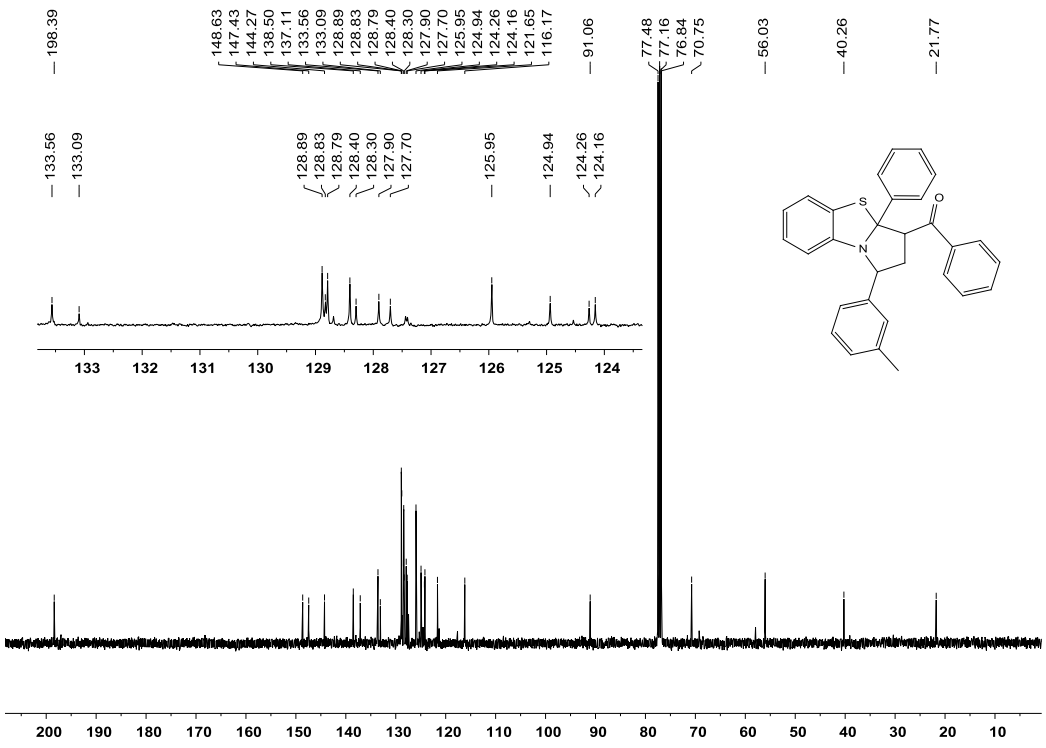


Compound **3ea:**

^{1}H NMR (400 MHz, $CDCl_3$)

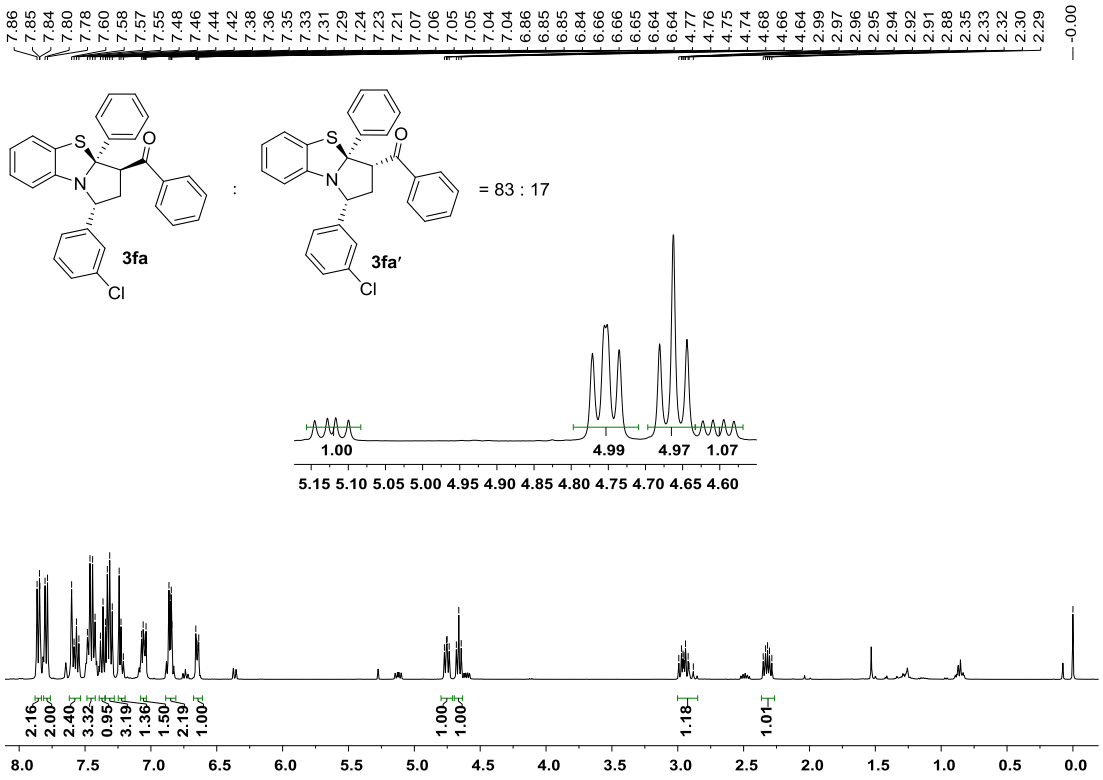


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

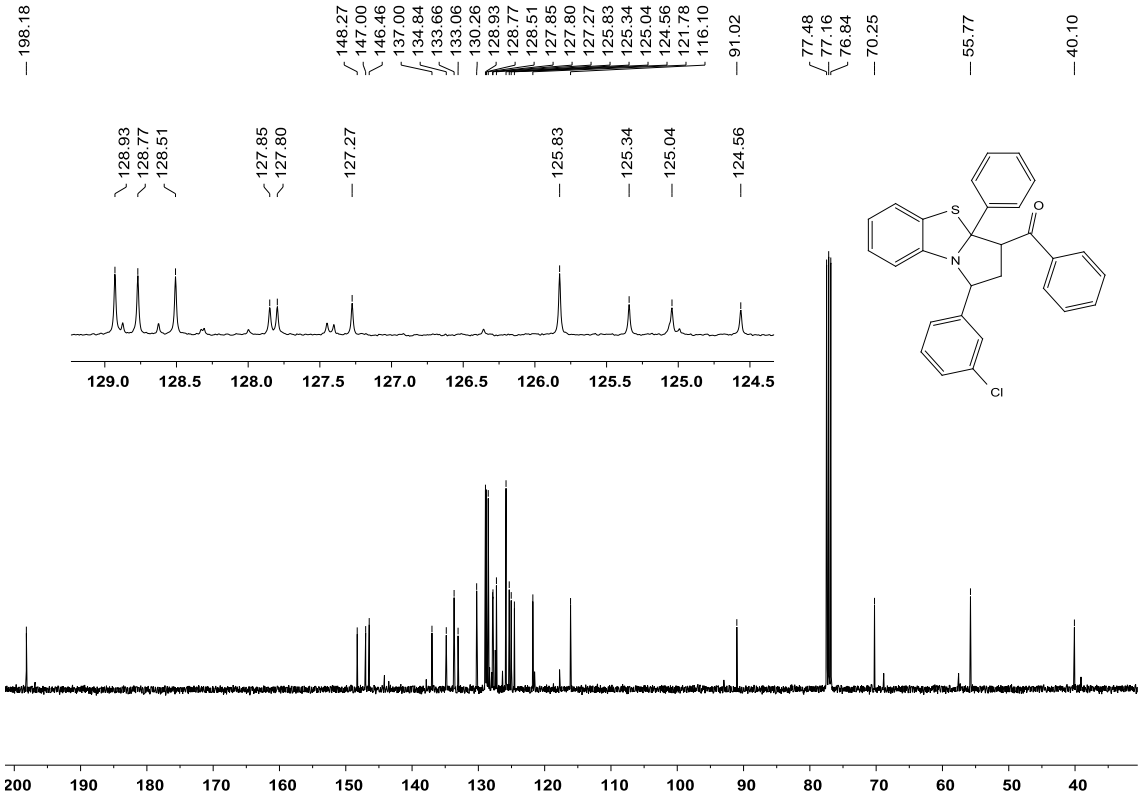


Compound **3fa:**

^{1}H NMR (400 MHz, $CDCl_3$)

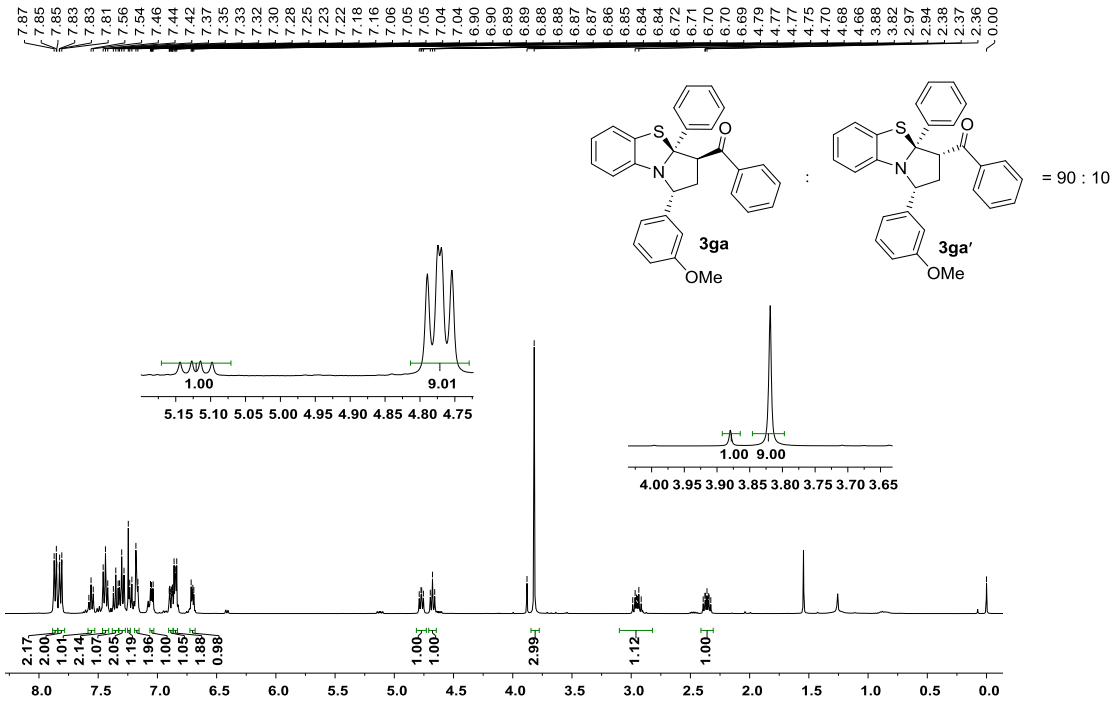


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

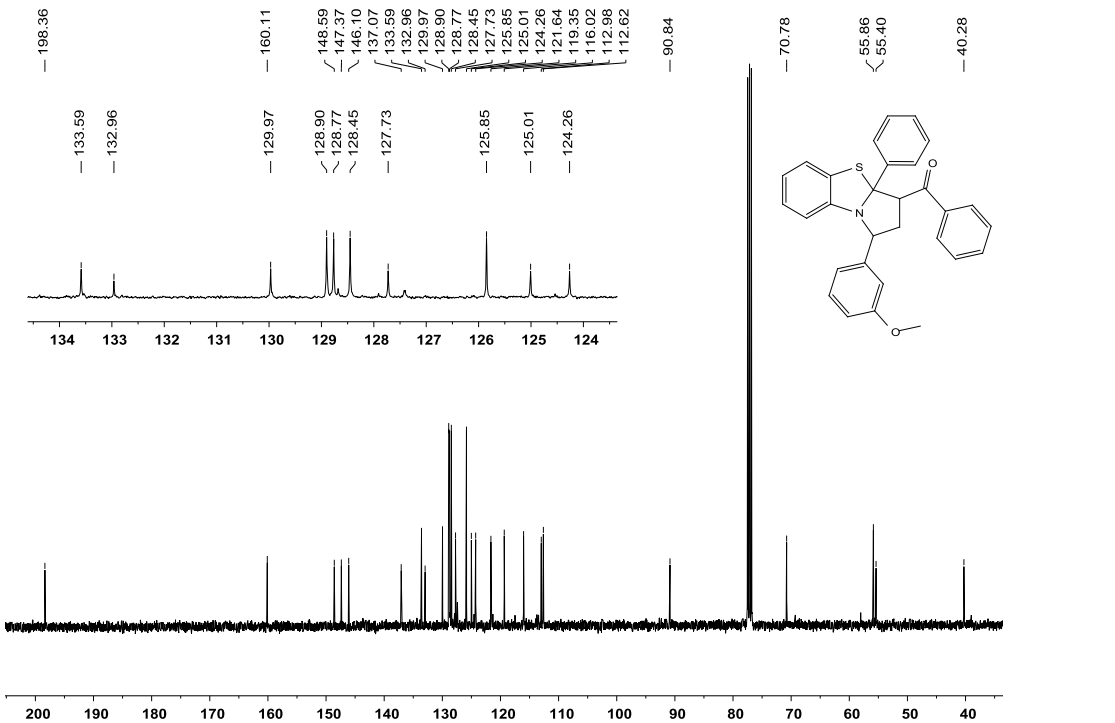


Compound **3ga:**

^{1}H NMR (400 MHz, $CDCl_3$)

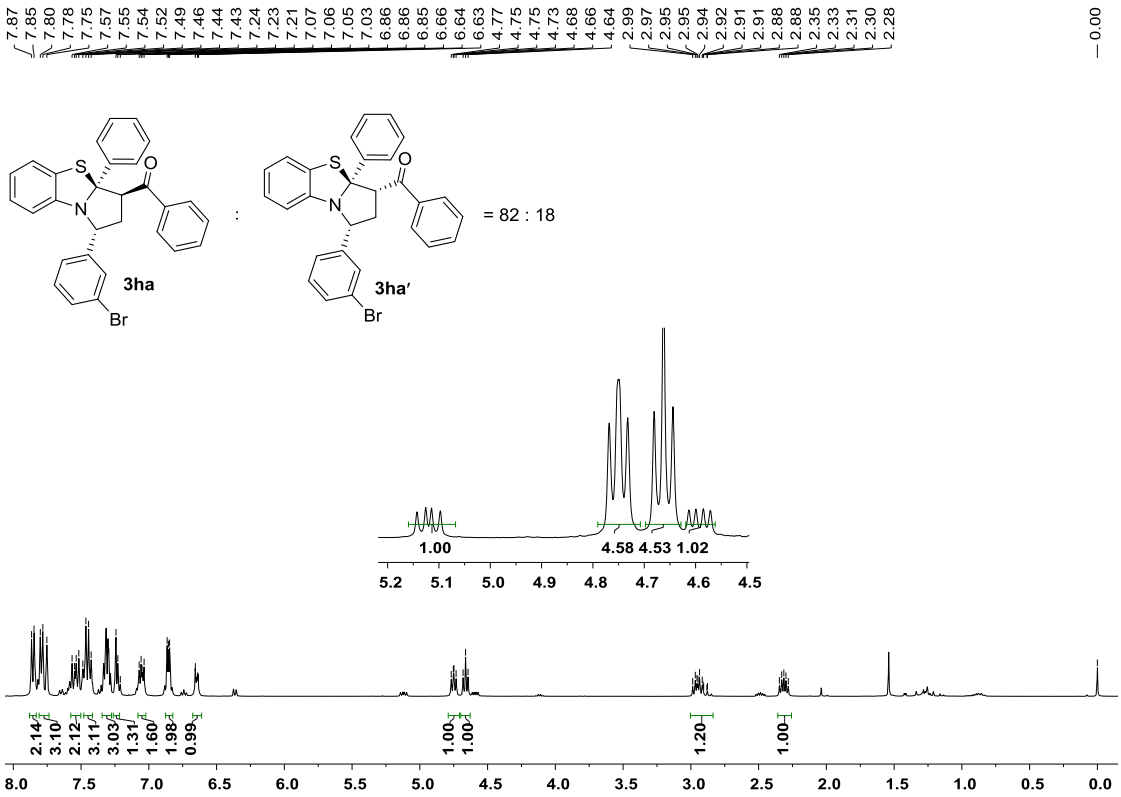


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

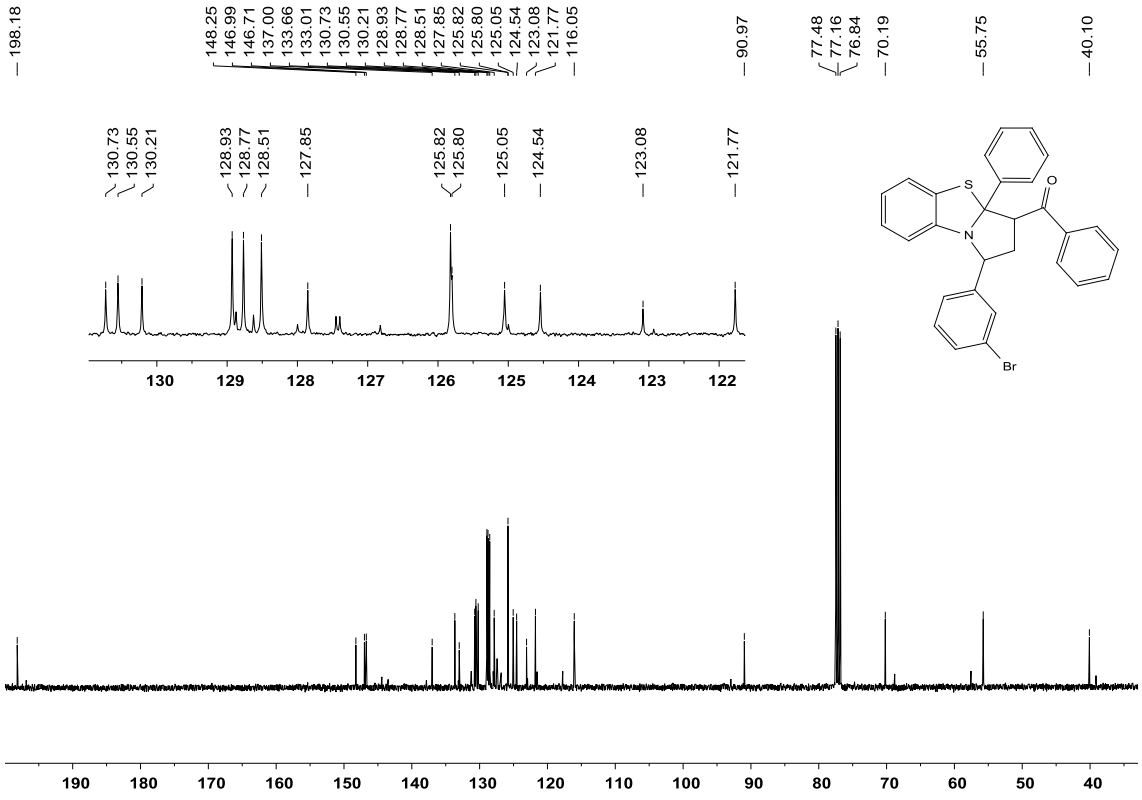


Compound **3ha:**

^{1}H NMR (400 MHz, $CDCl_3$)

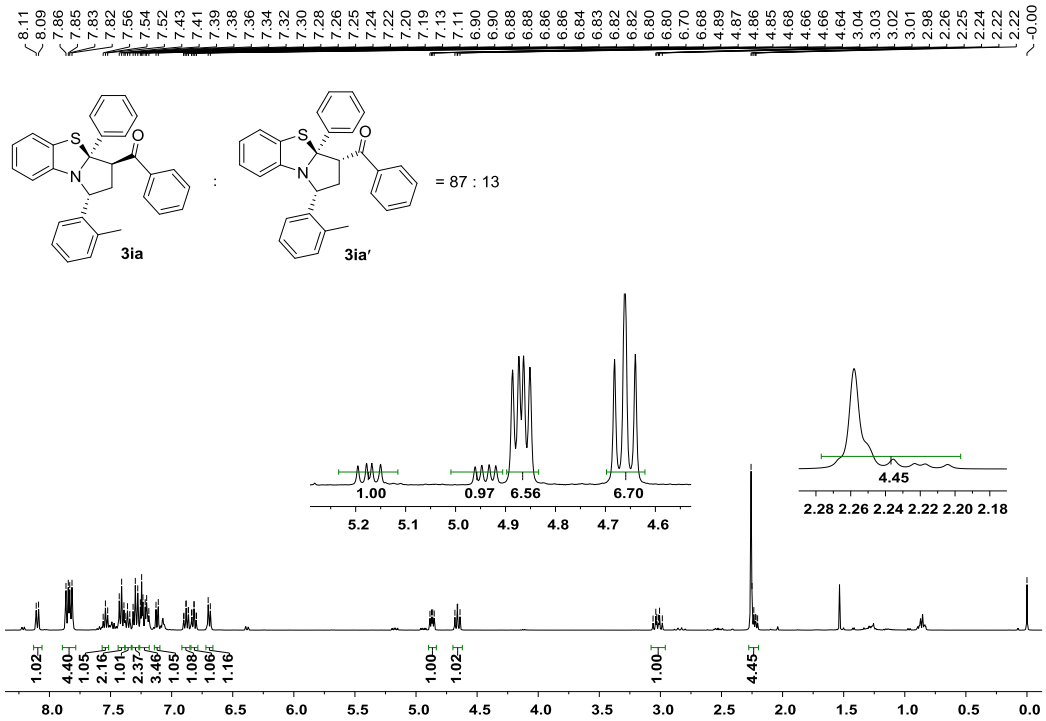


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

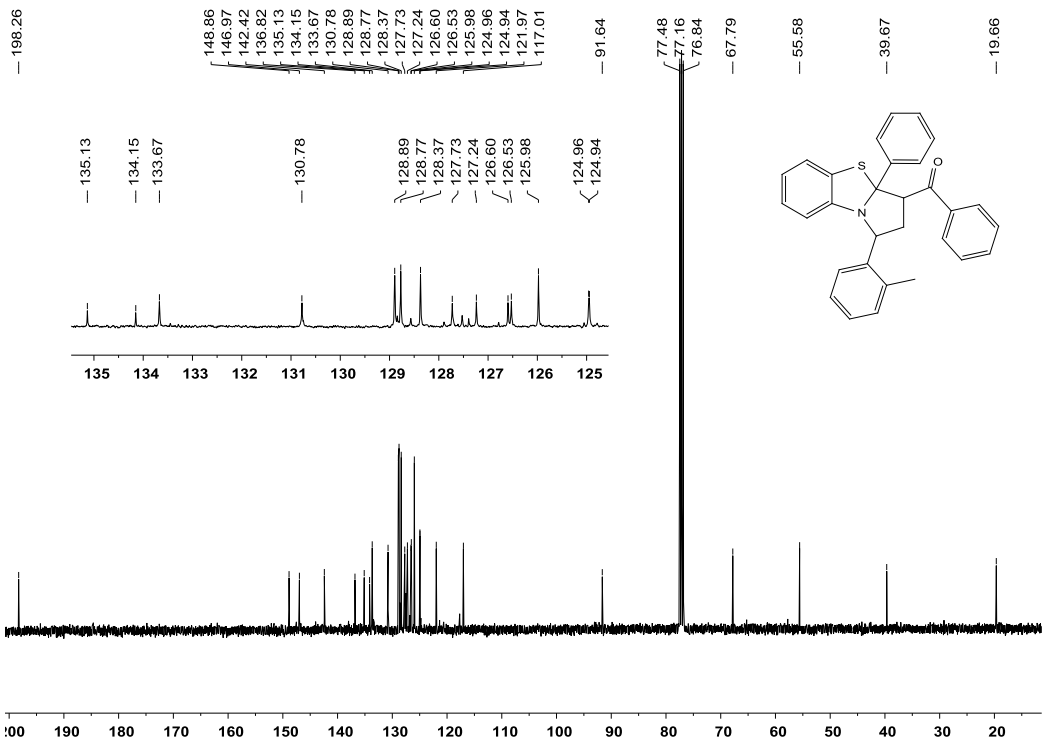


Compound **3ia:**

^{1}H NMR (400 MHz, $CDCl_3$)

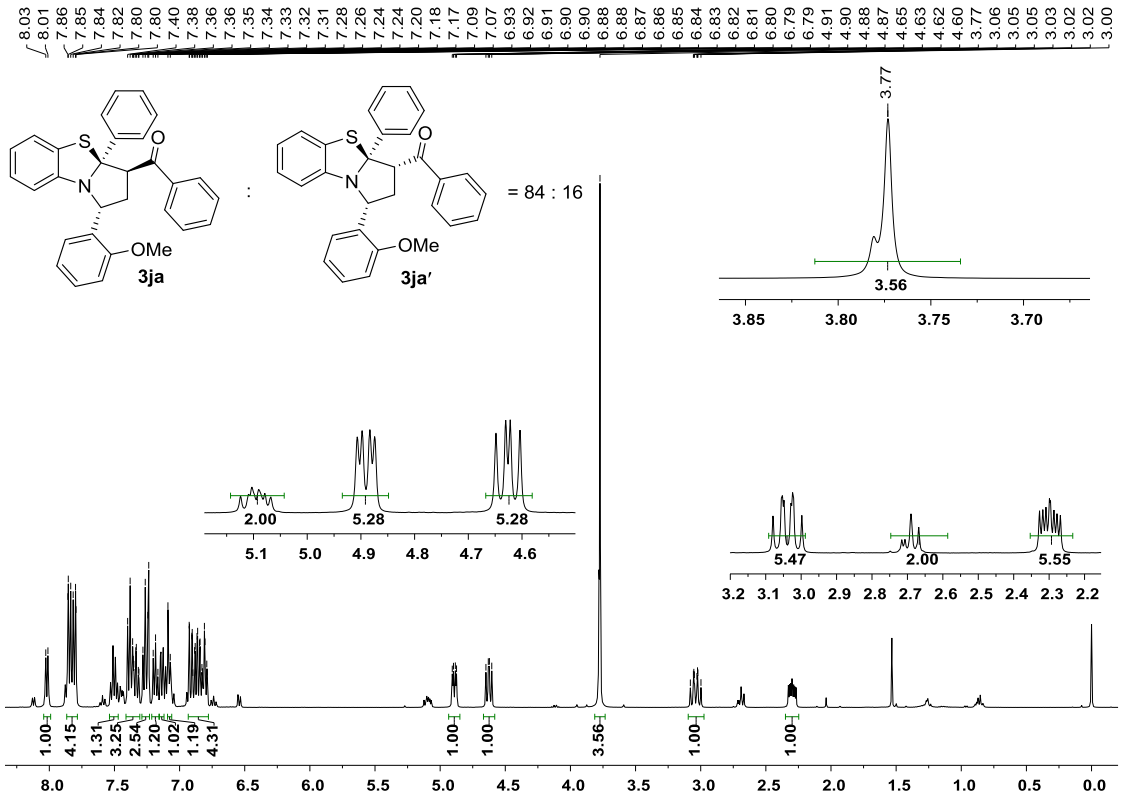


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

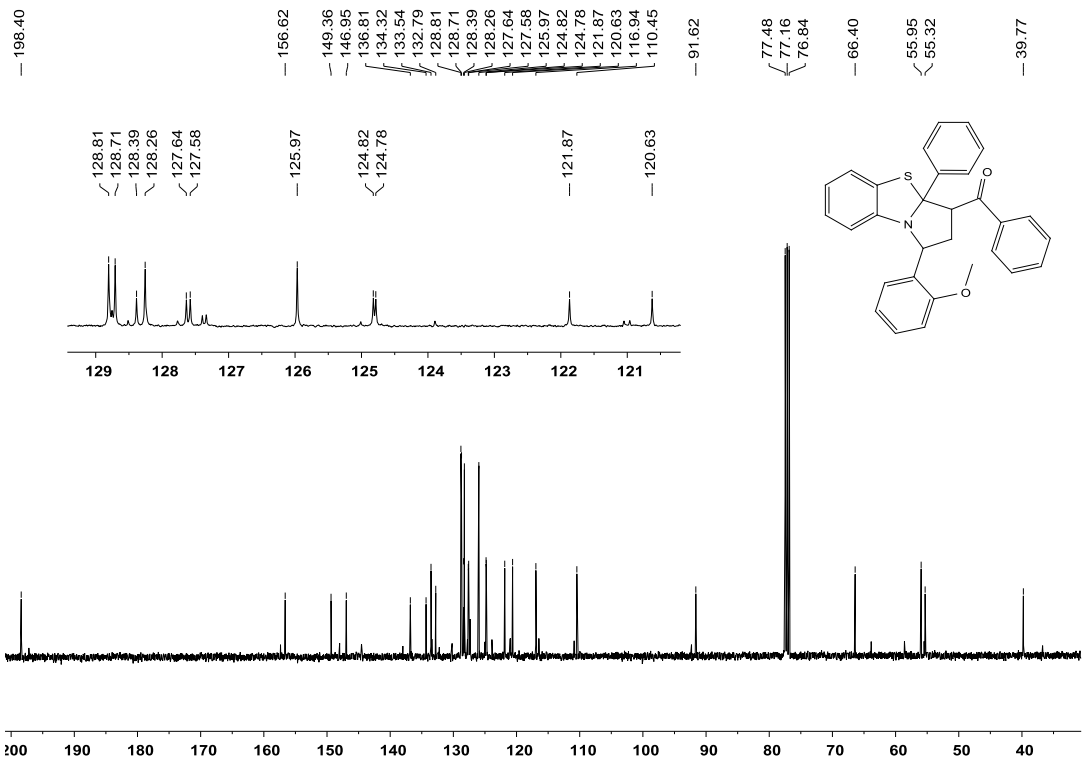


Compound **3ja:**

^{1}H NMR (400 MHz, $CDCl_3$)

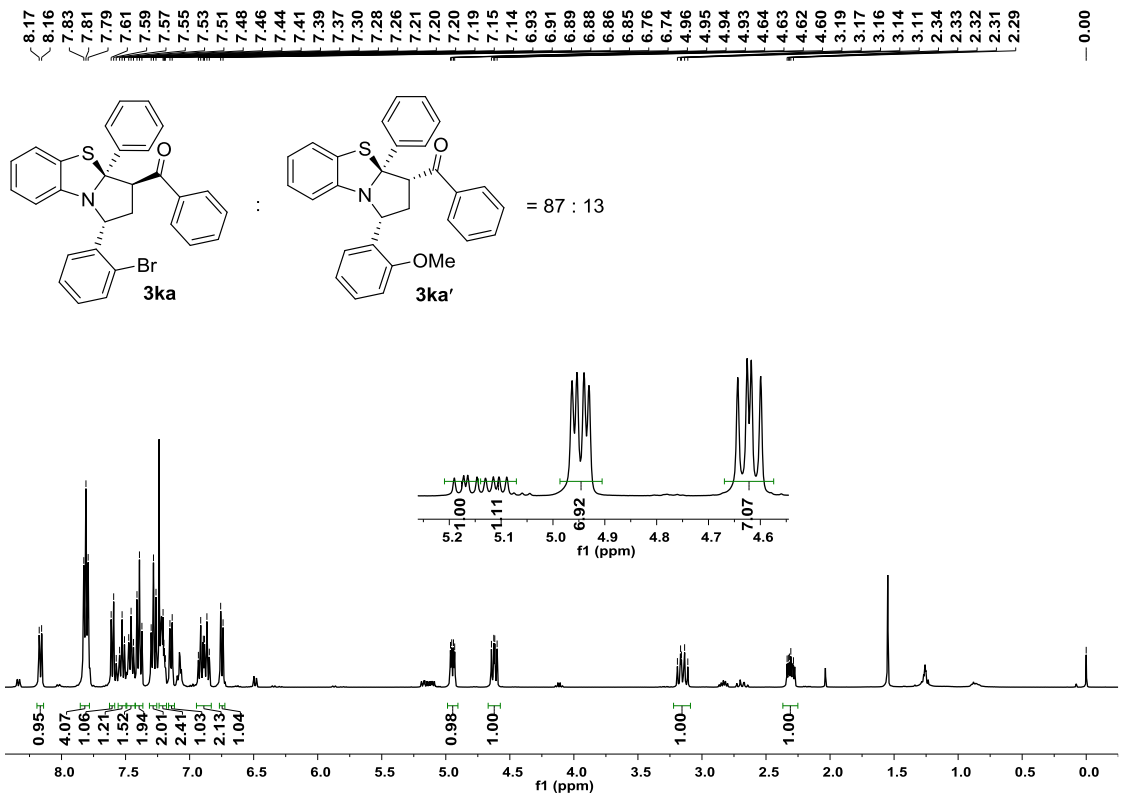


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

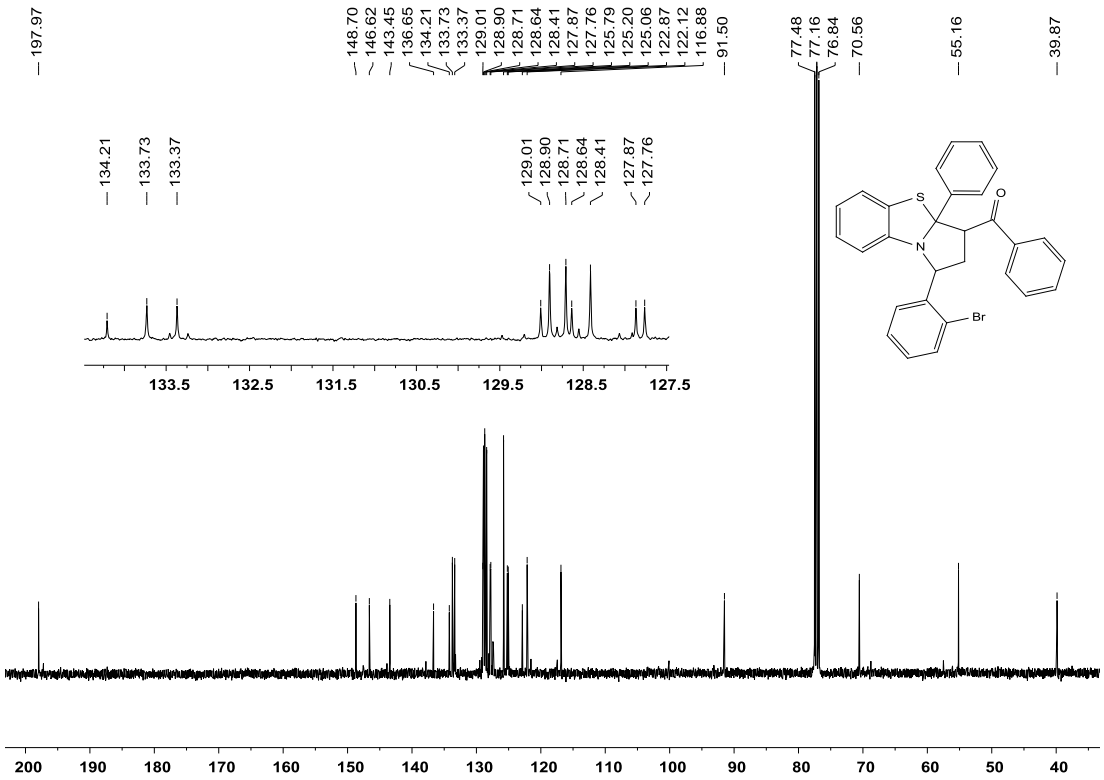


Compound **3ka:**

^{1}H NMR (400 MHz, $CDCl_3$)

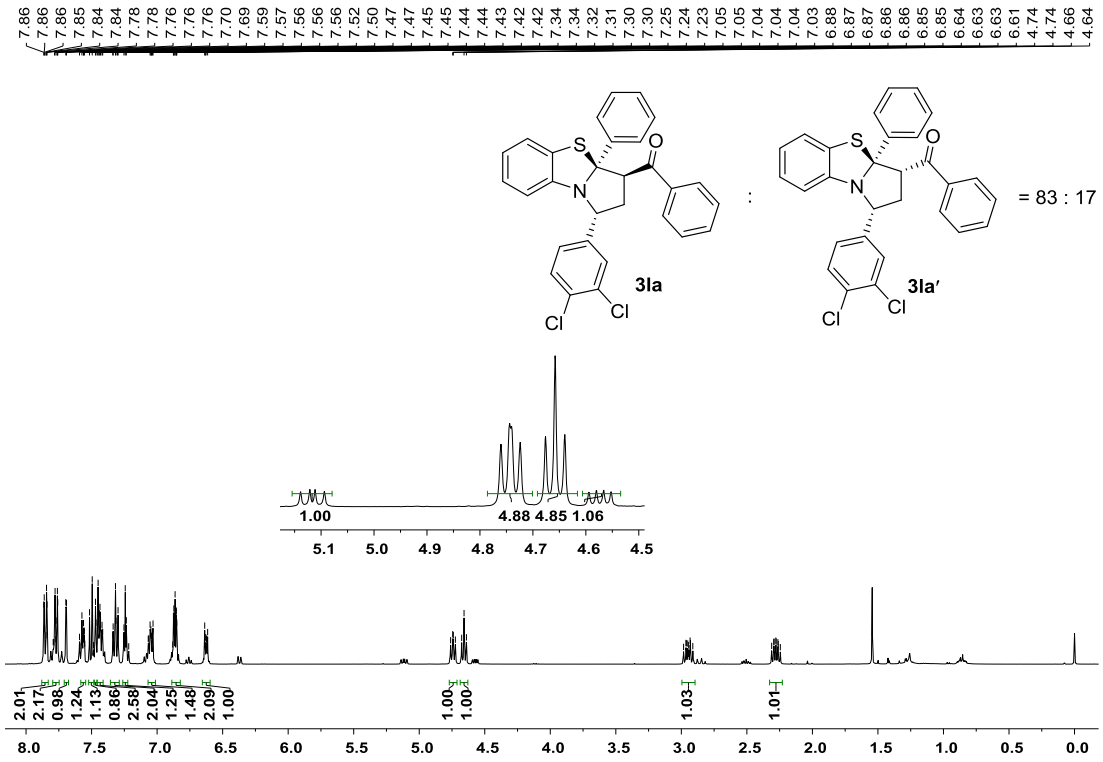


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

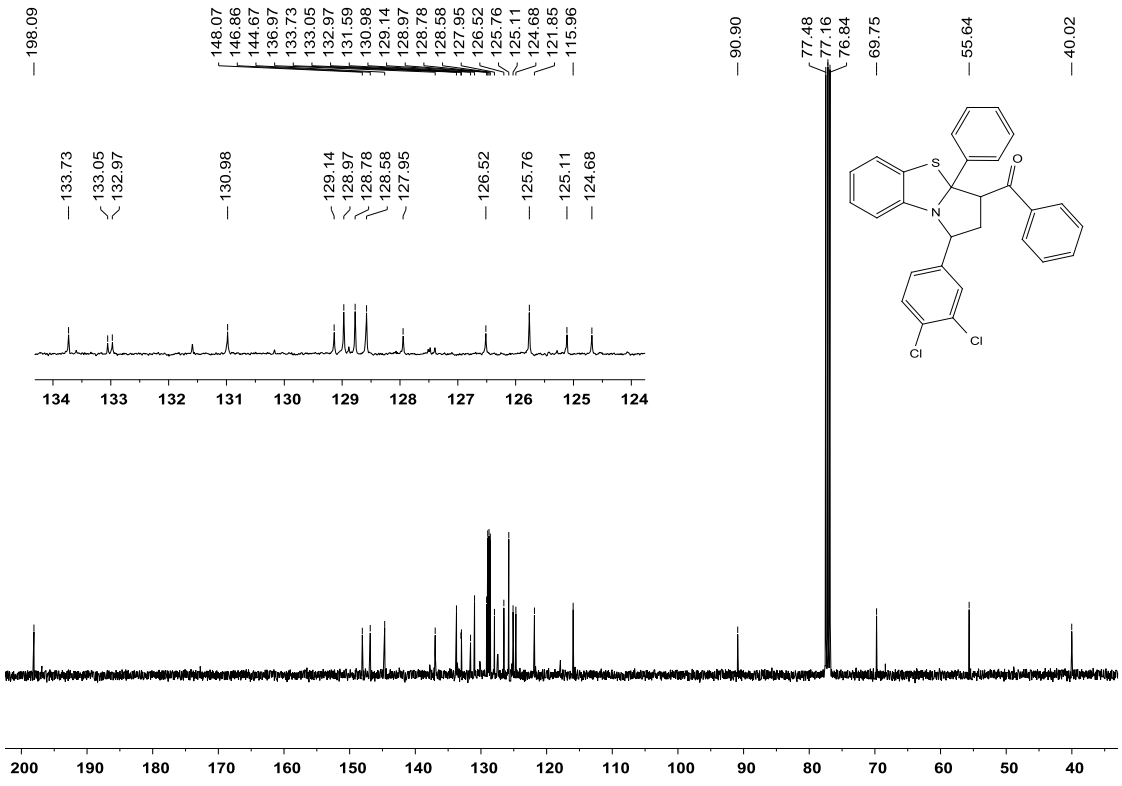


Compound **3la:**

^{1}H NMR (400 MHz, $CDCl_3$)

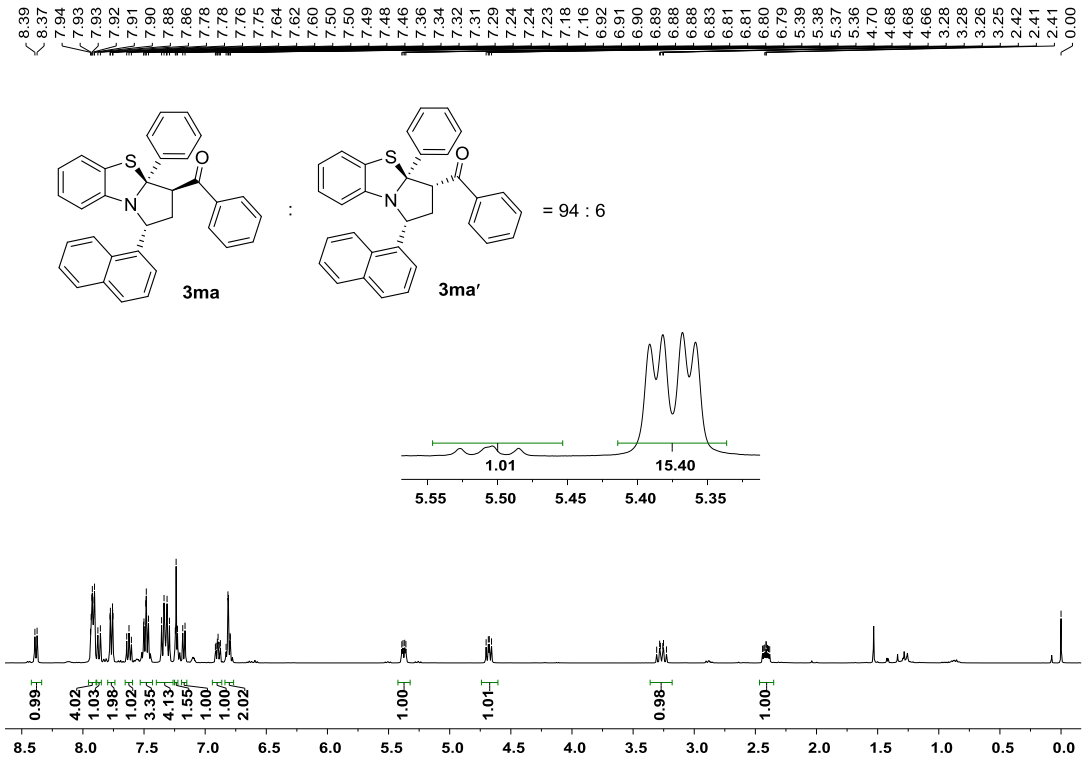


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

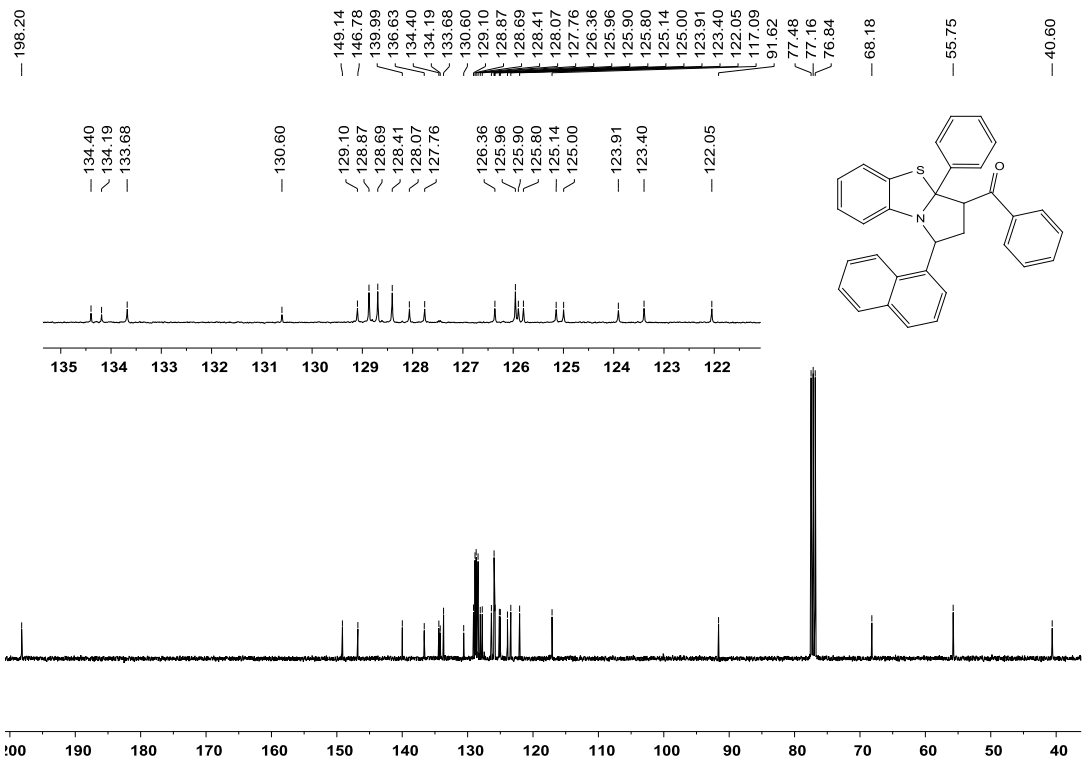


Compound **3ma:**

^{1}H NMR (400 MHz, $CDCl_3$)

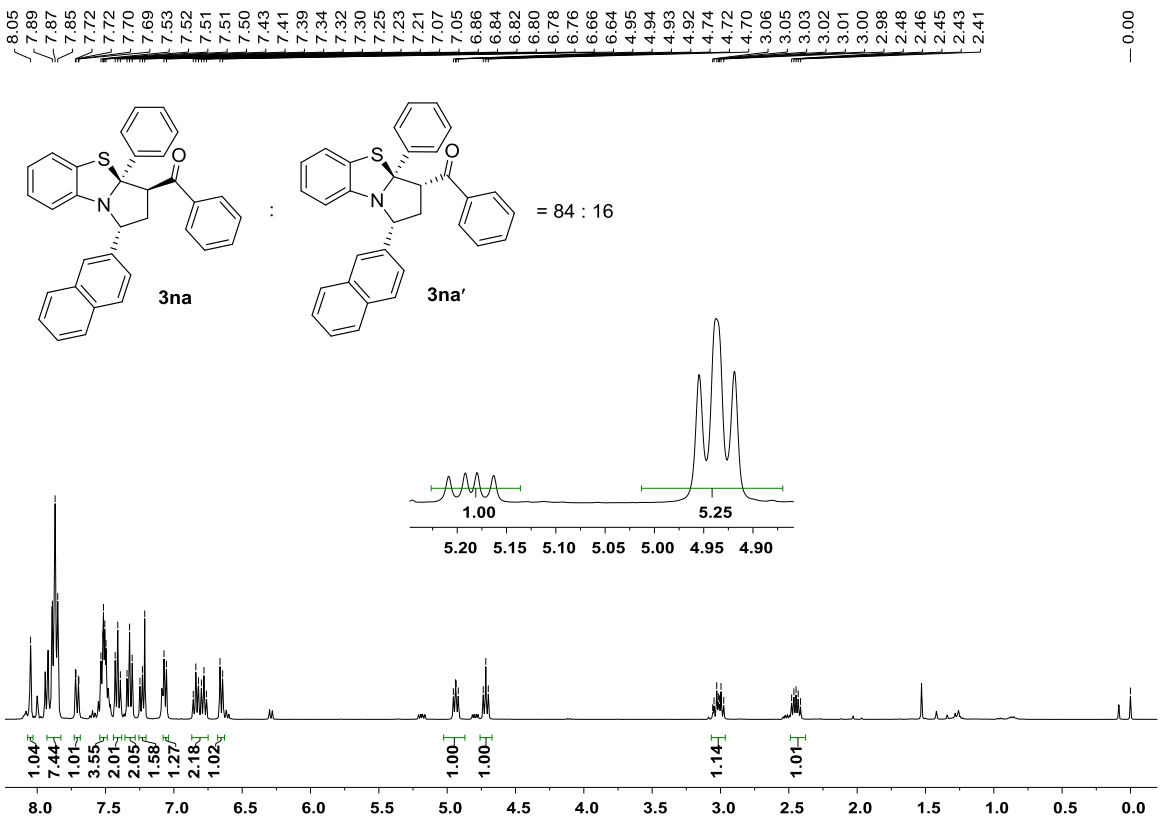


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

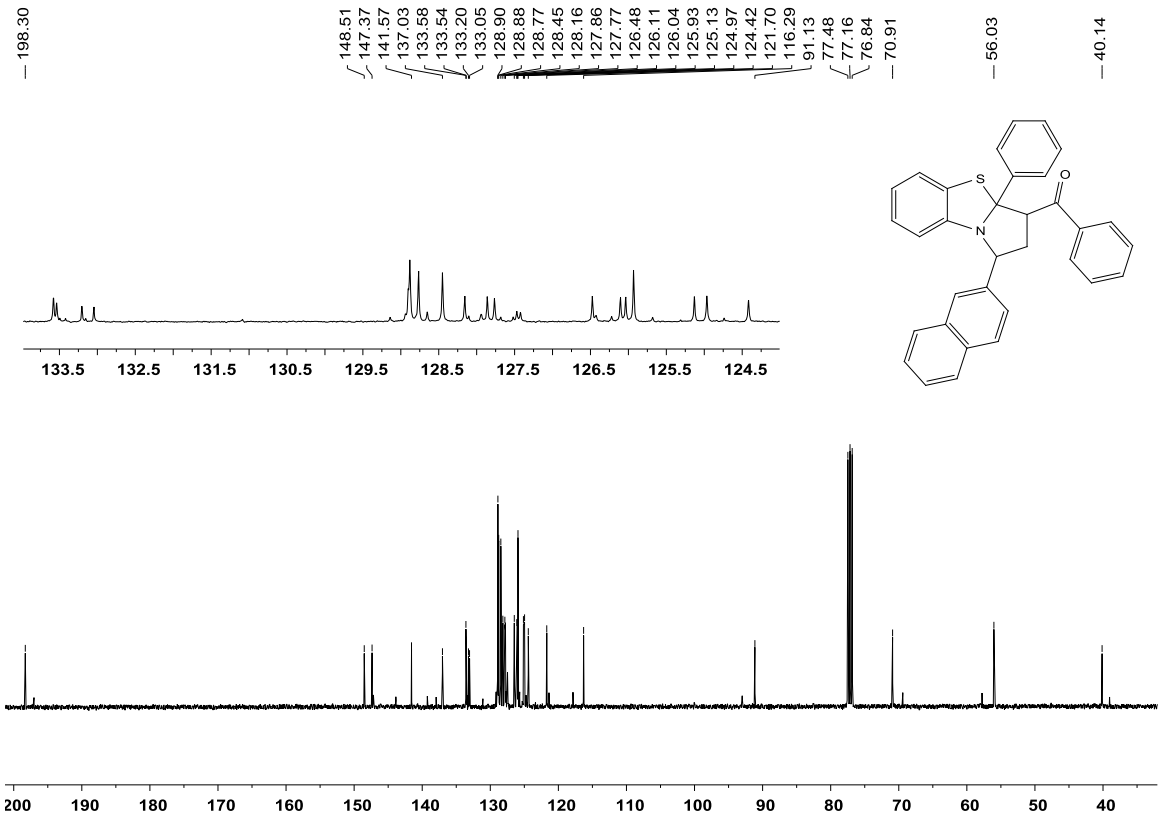


Compound **3na:**

^{1}H NMR (400 MHz, $CDCl_3$)

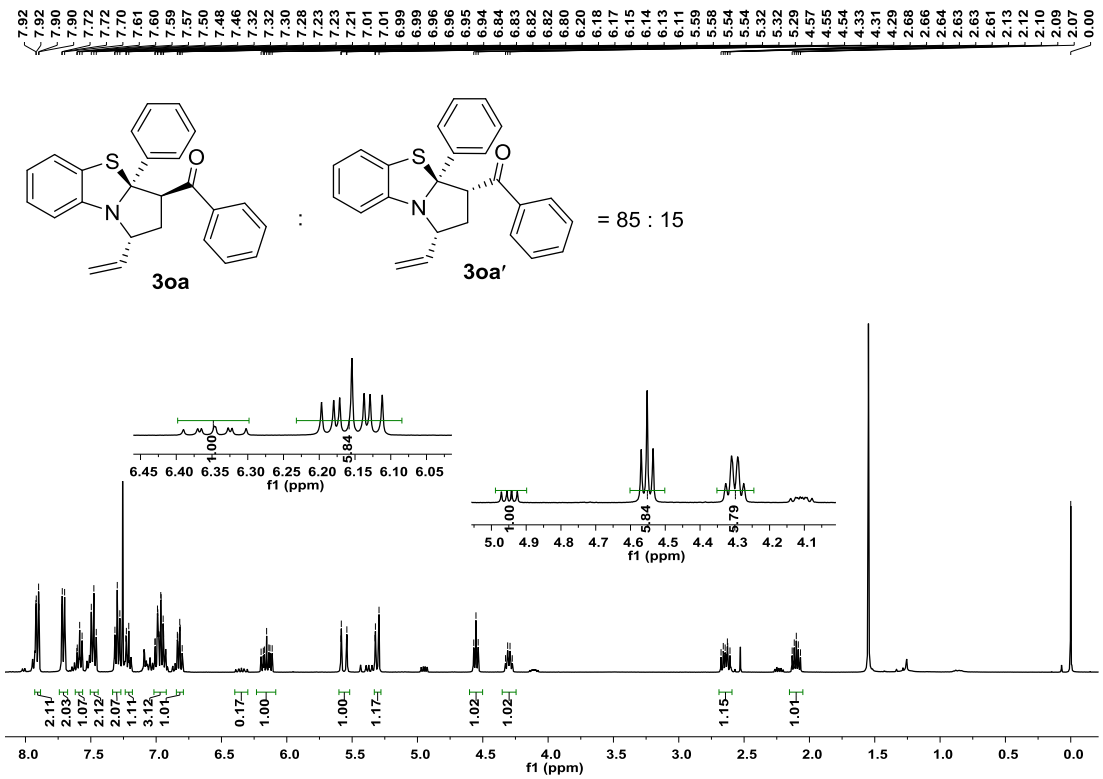


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

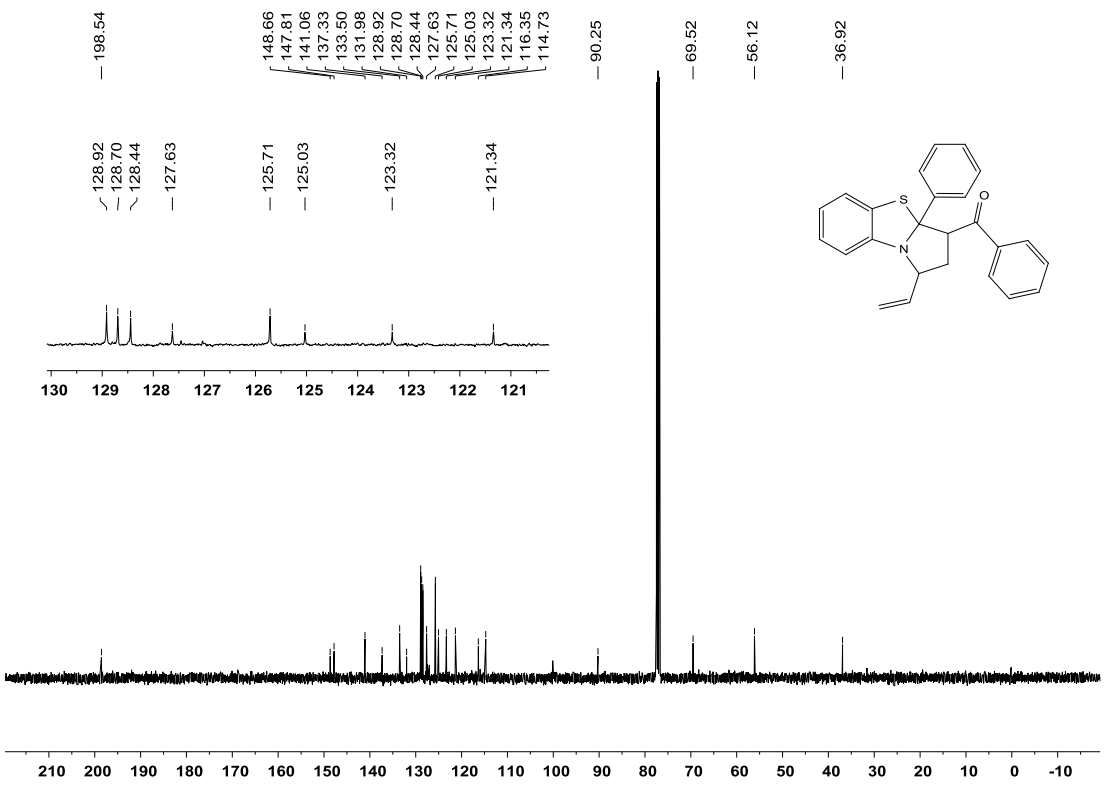


Compound **3oa:**

^{1}H NMR (400 MHz, $CDCl_3$)

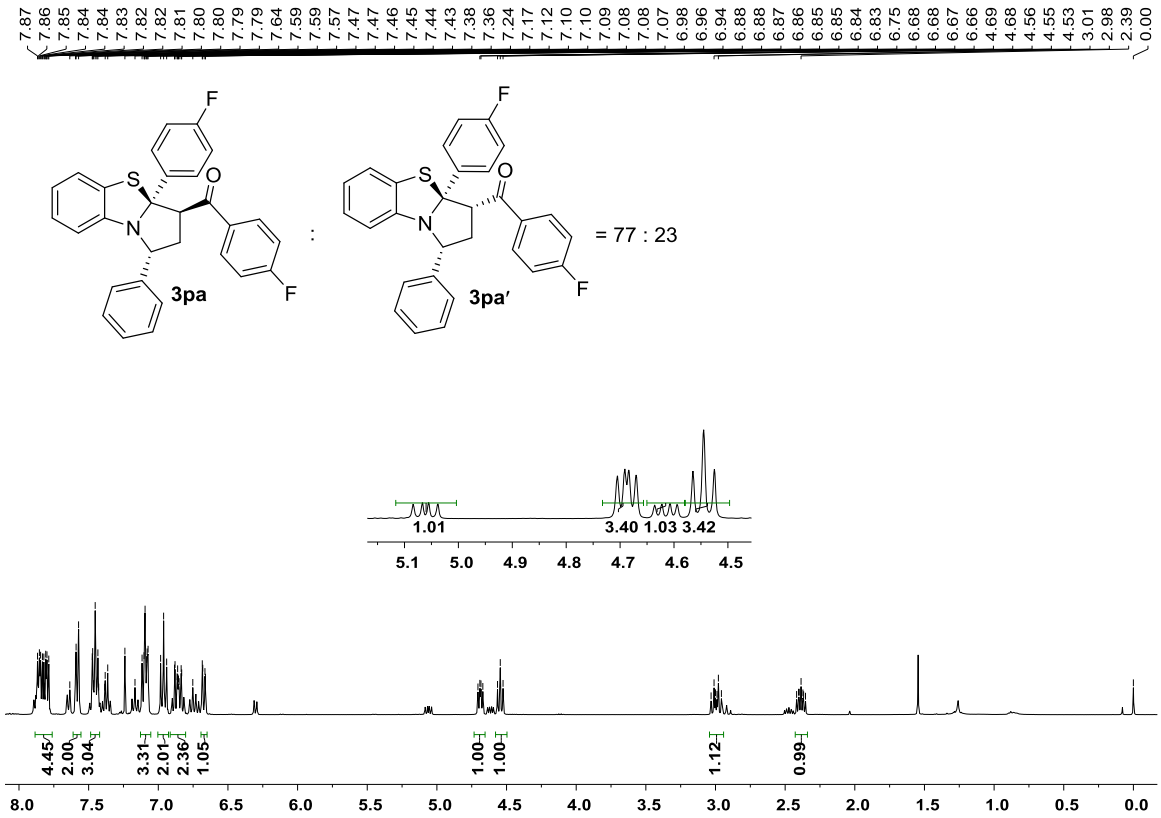


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

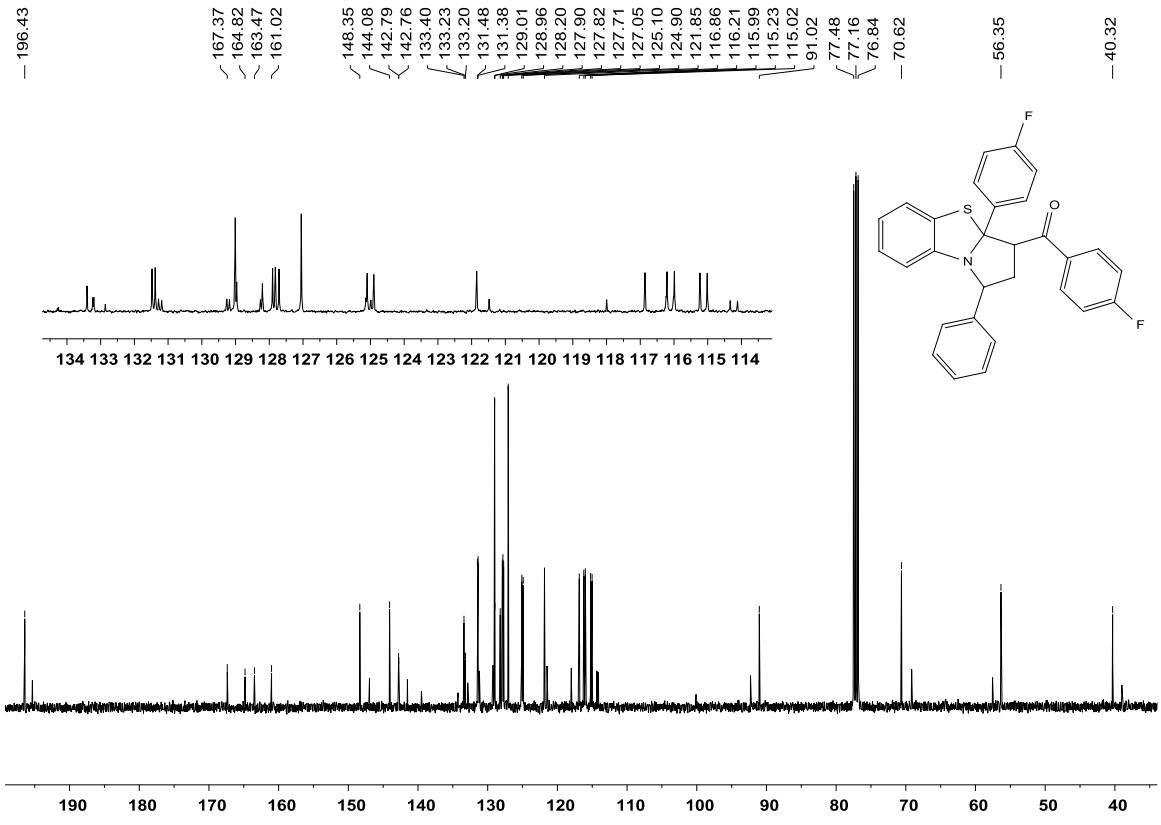


Compound **3pa:**

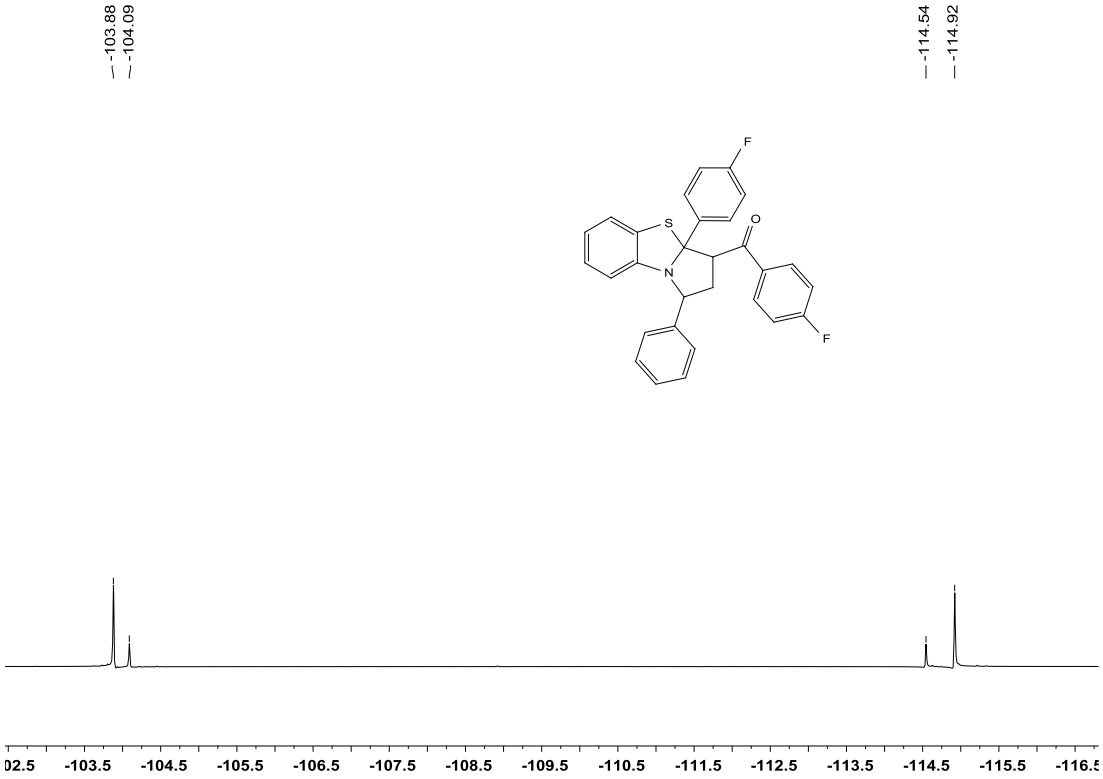
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

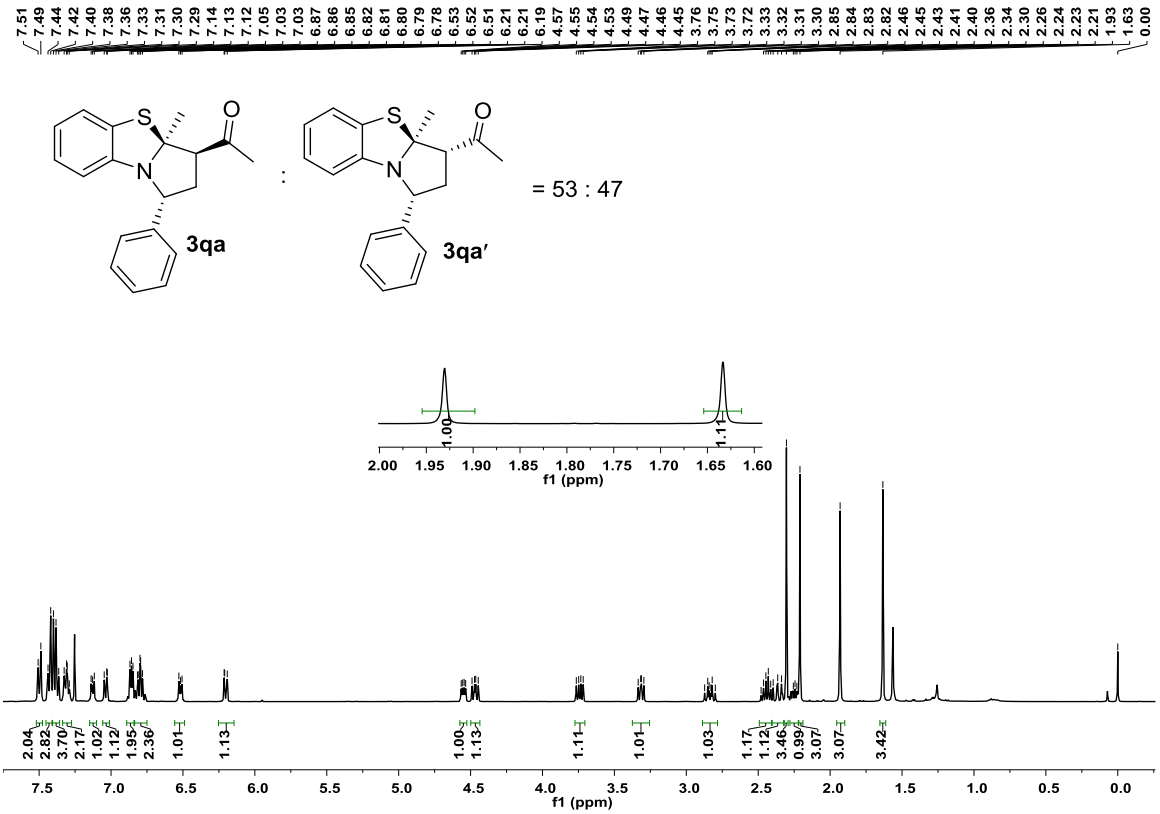


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

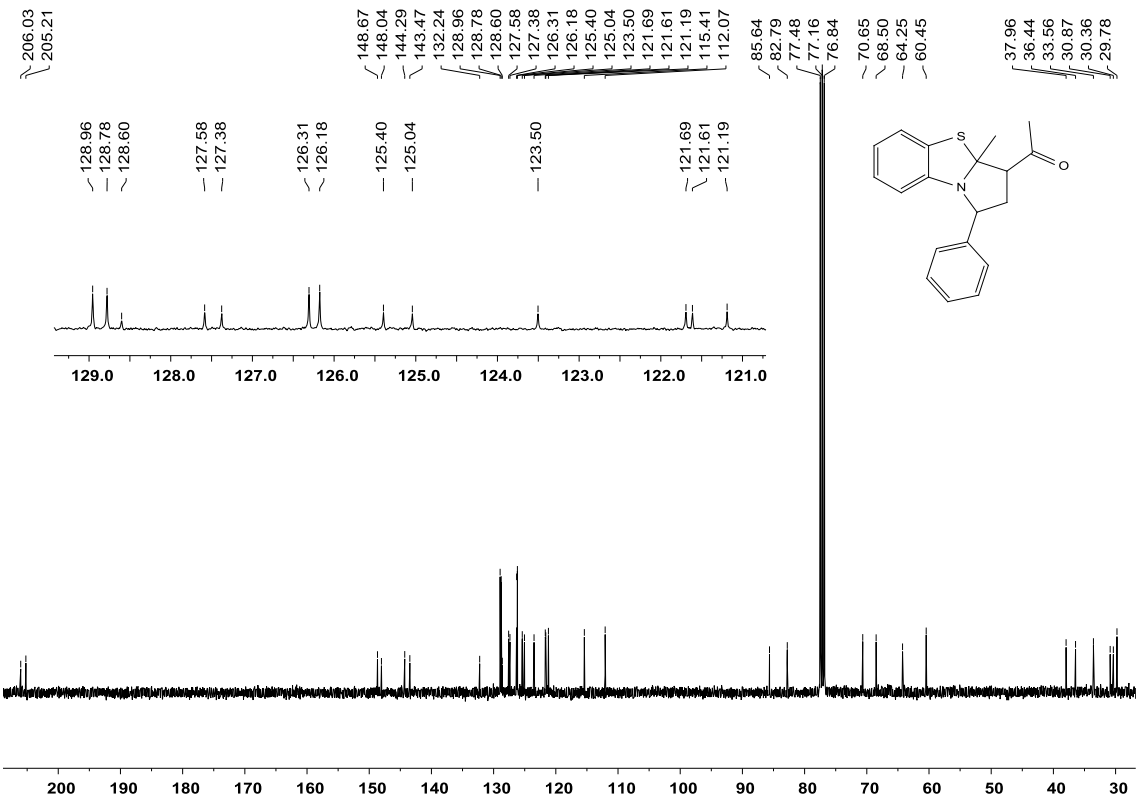


Compound **3qa:**

^{1}H NMR (400 MHz, $CDCl_3$)

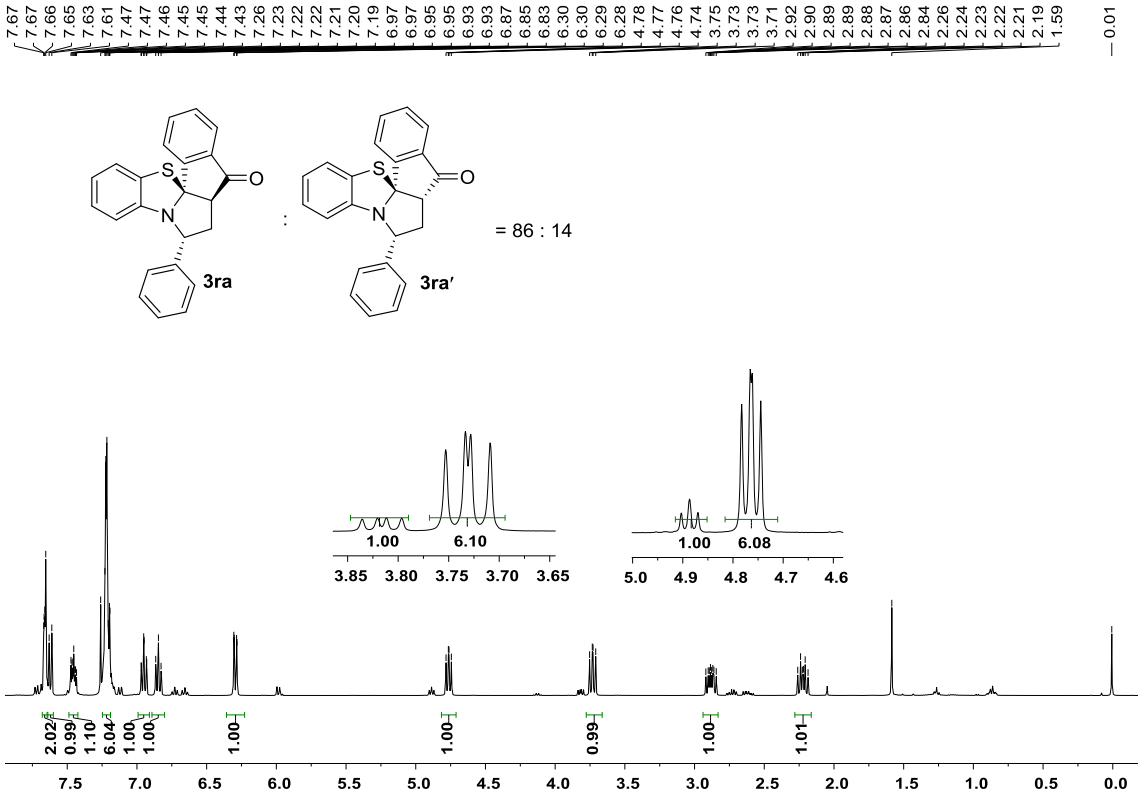


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

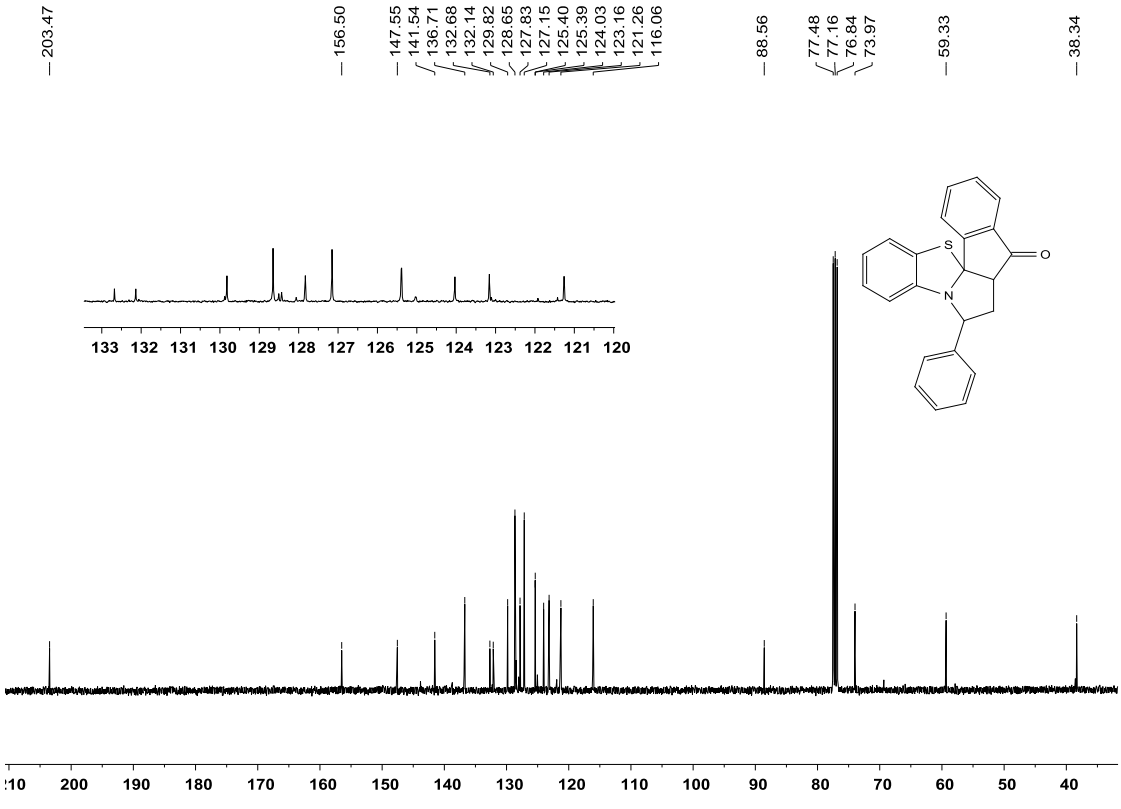


Compound **3ra:**

^{1}H NMR (400 MHz, $CDCl_3$)

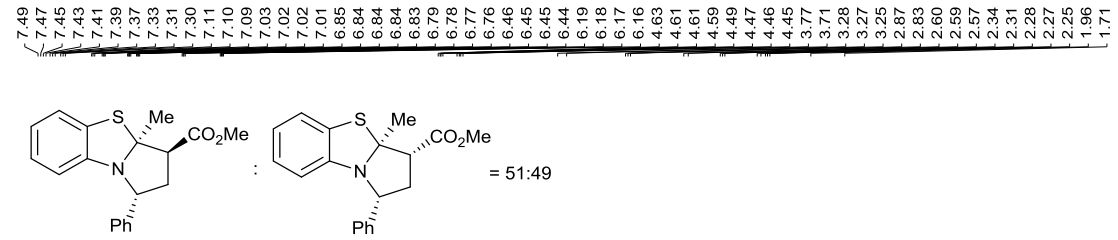


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

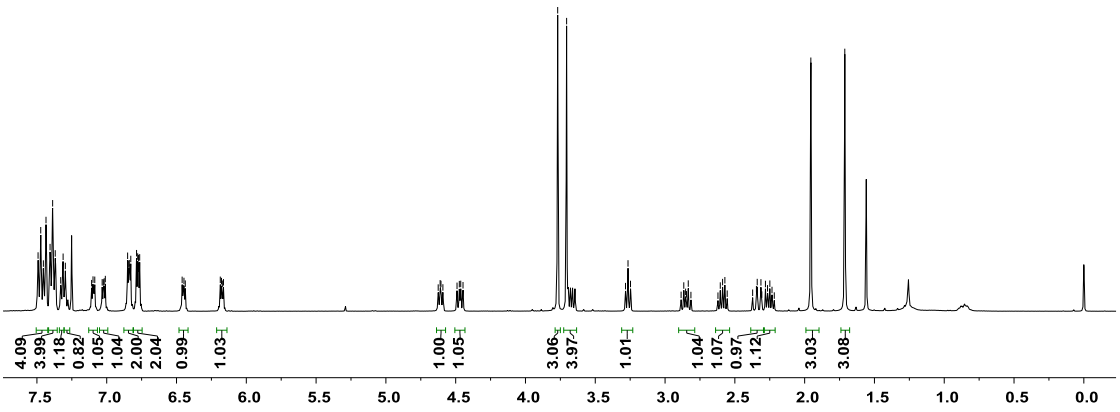


Compound **3sa:**

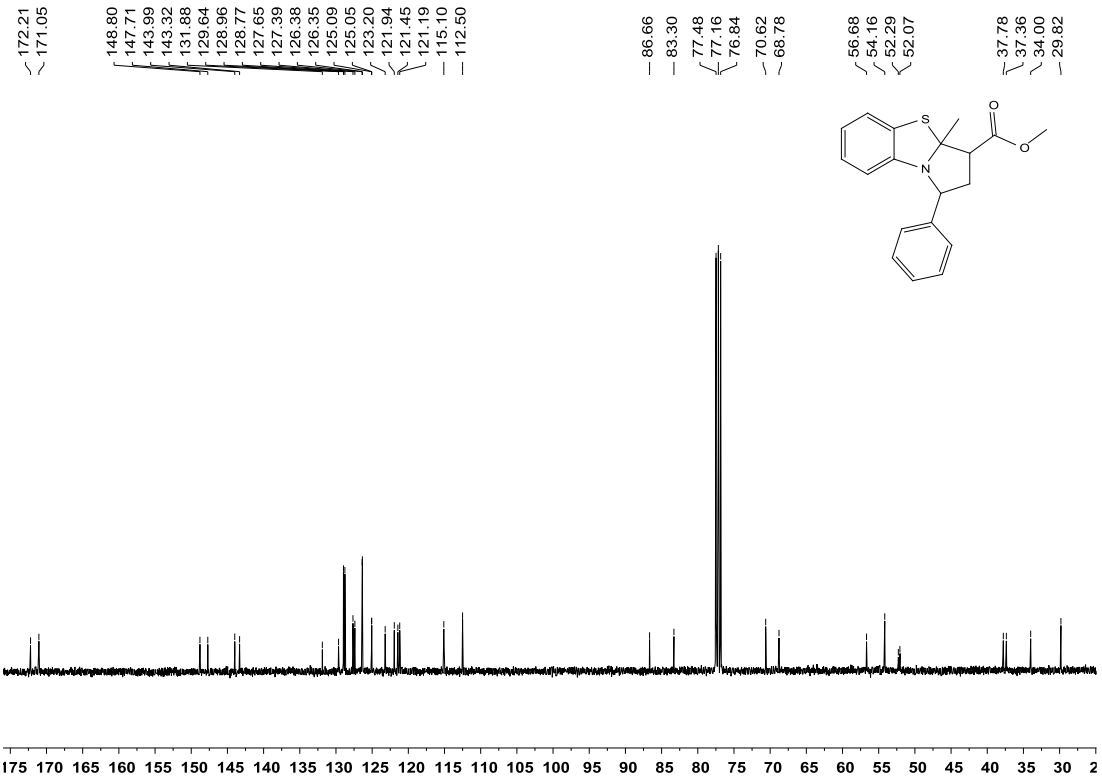
^{1}H NMR (400 MHz, $CDCl_3$)



= 51:49

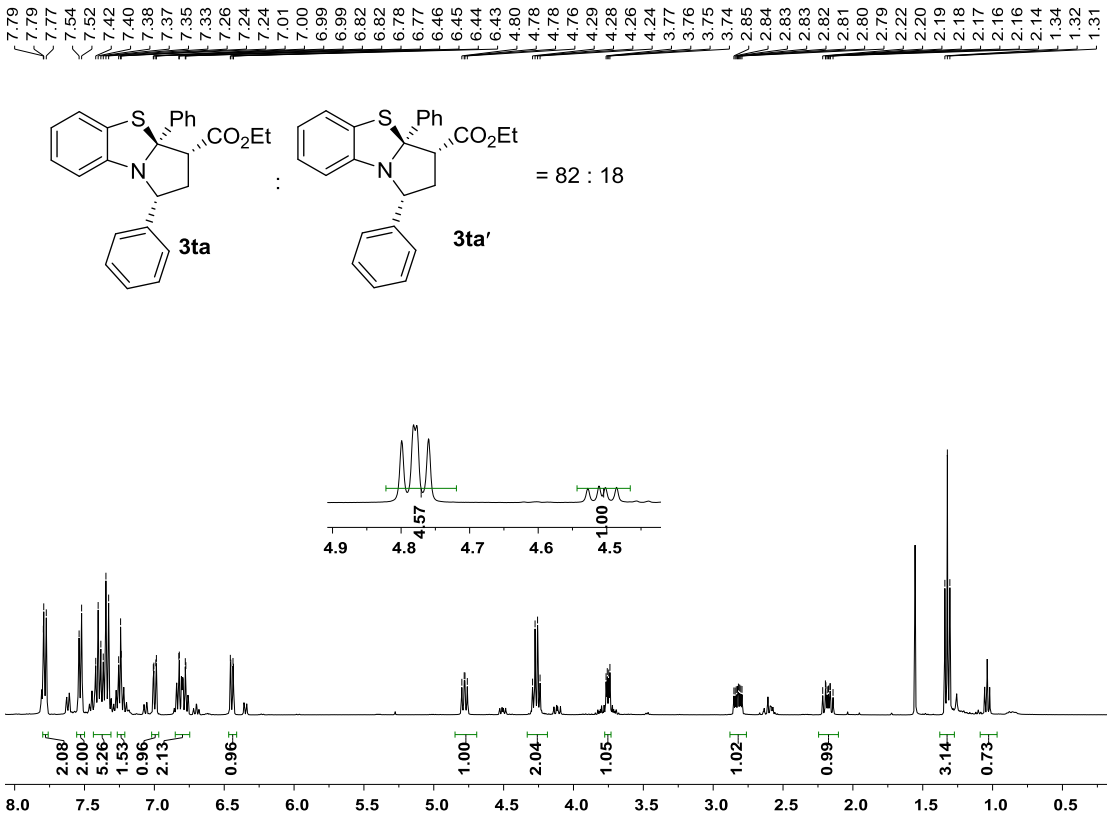


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

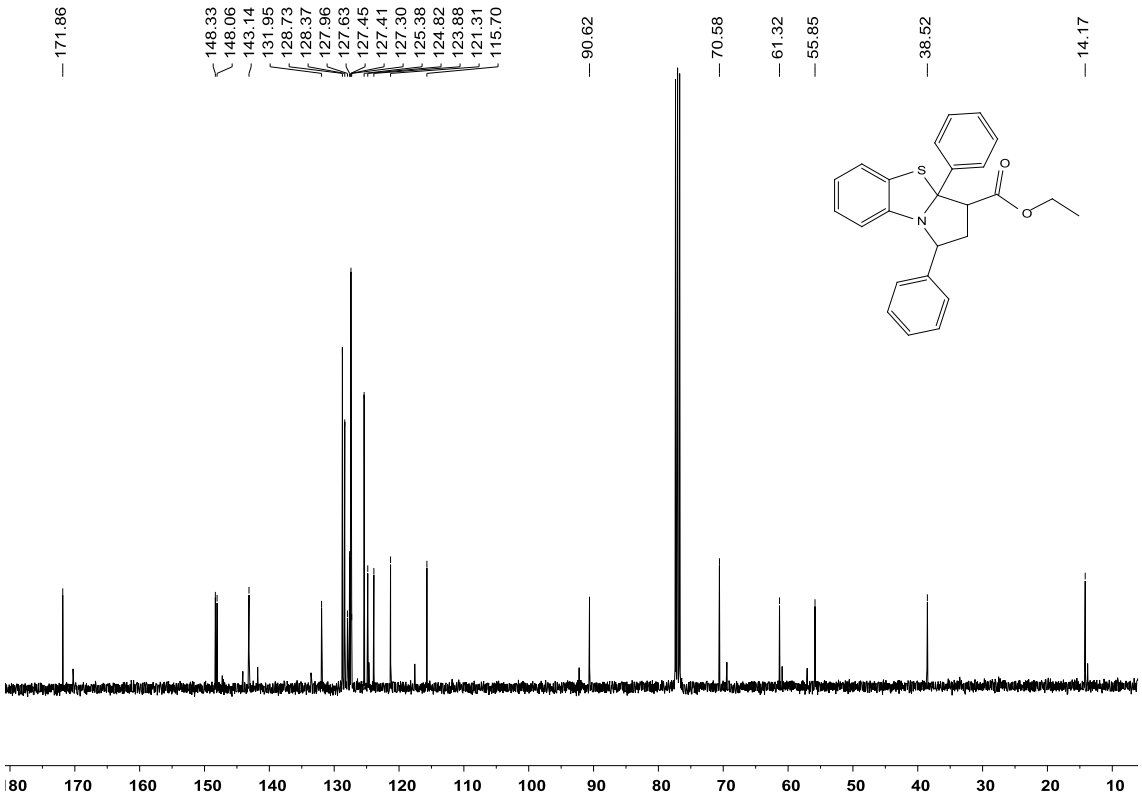


Compound **3ta:**

^{1}H NMR (400 MHz, $CDCl_3$)

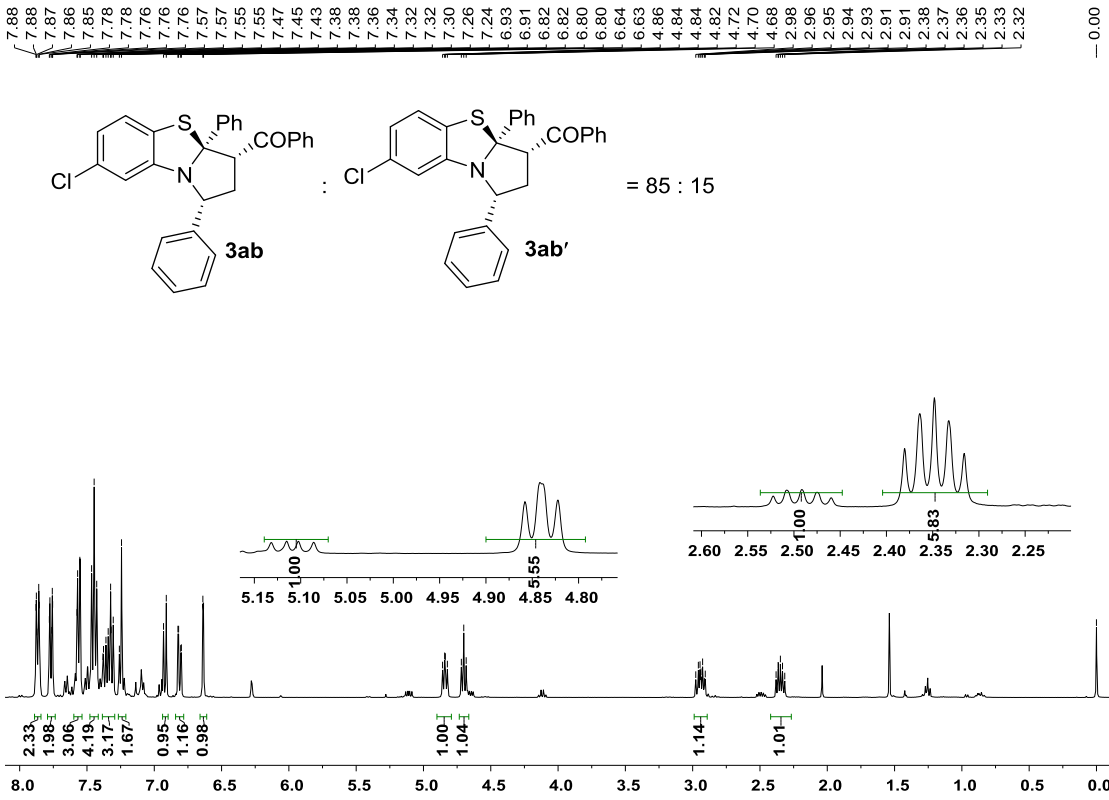


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

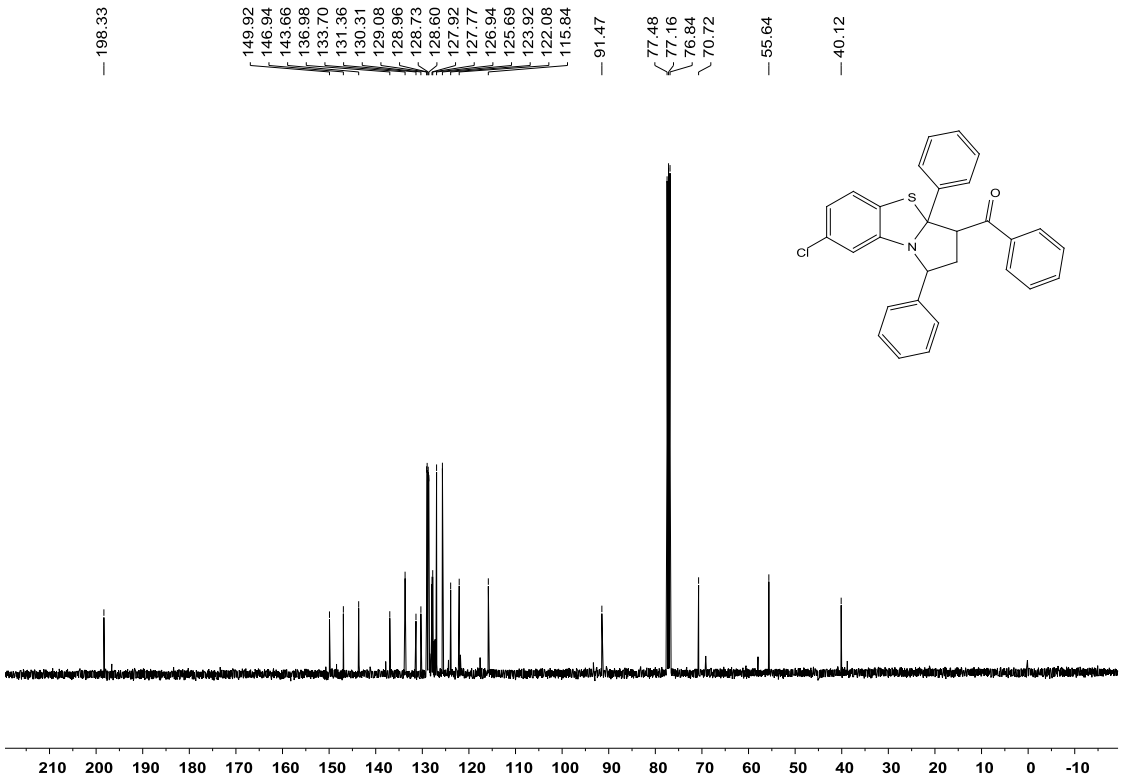


Compound **3ab:**

^{1}H NMR (400 MHz, $CDCl_3$)

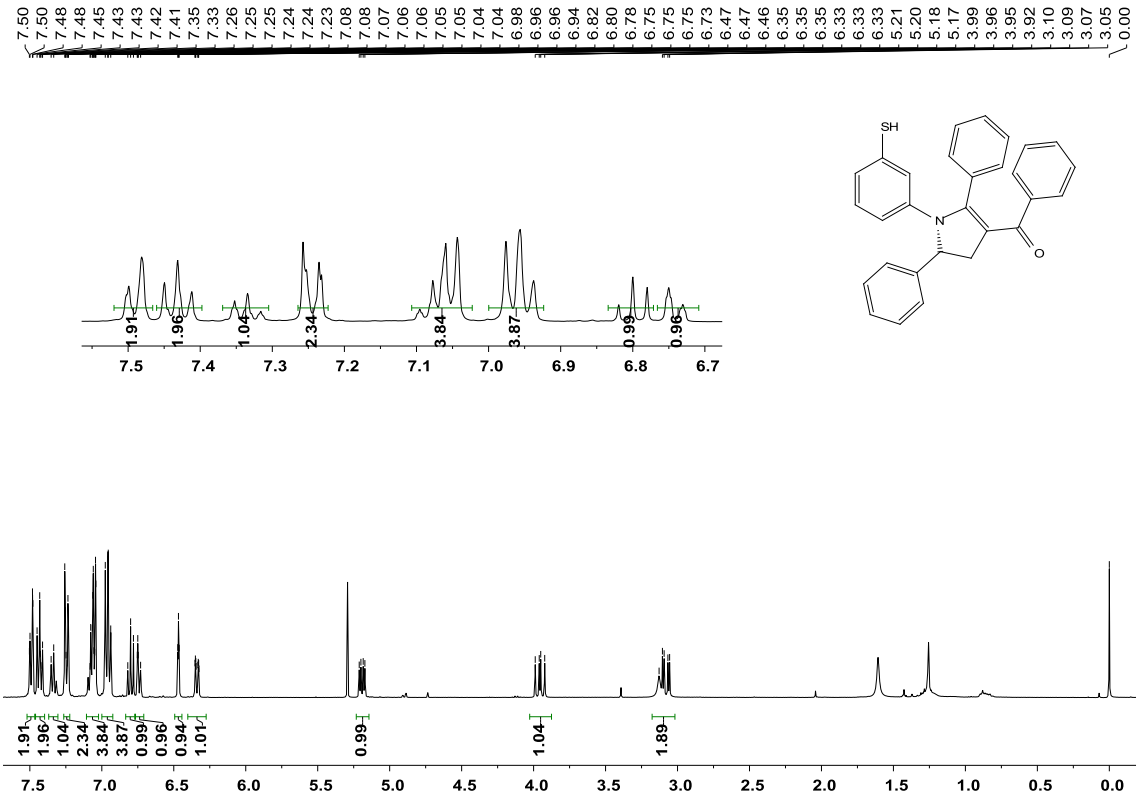


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

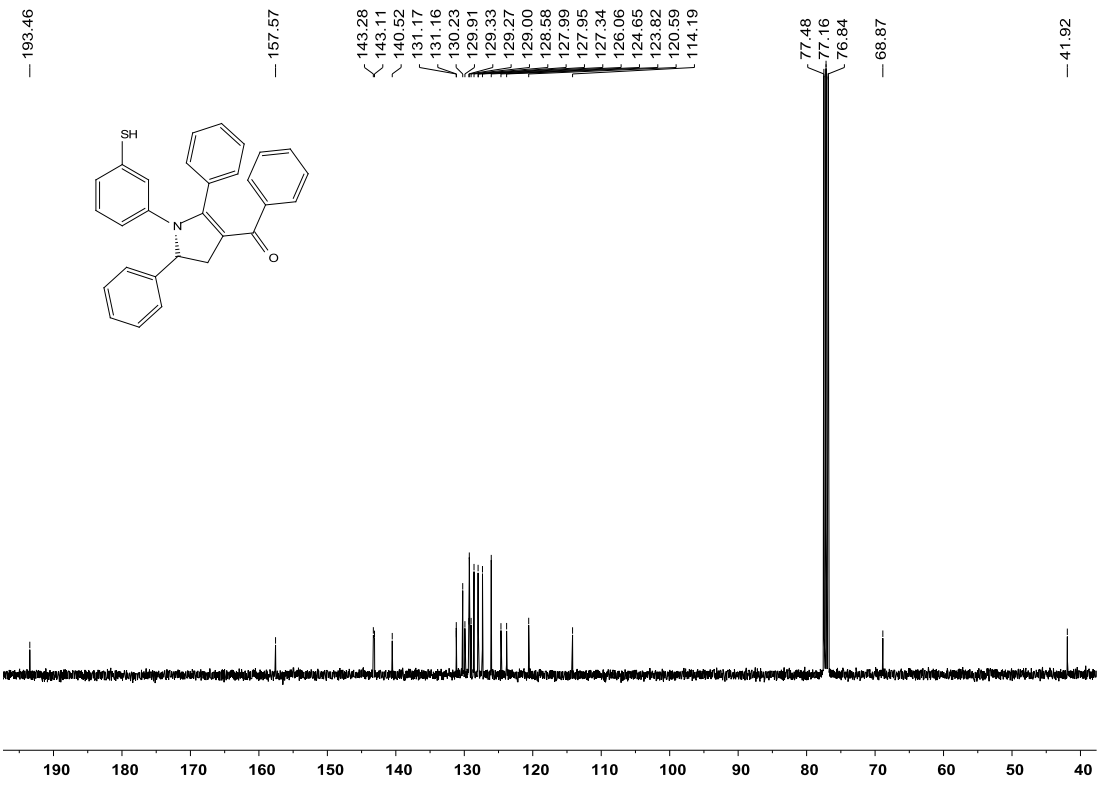


Compound **3ac:**

^{1}H NMR (400 MHz, $CDCl_3$)

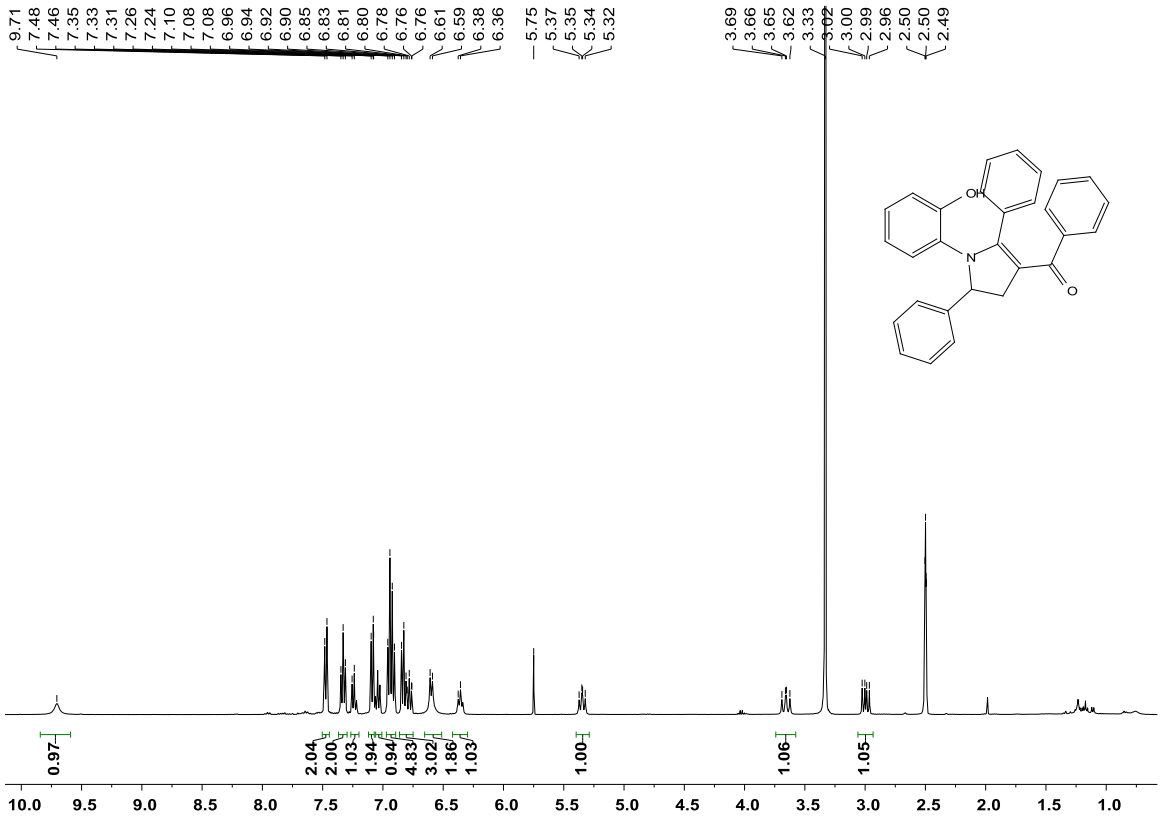


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

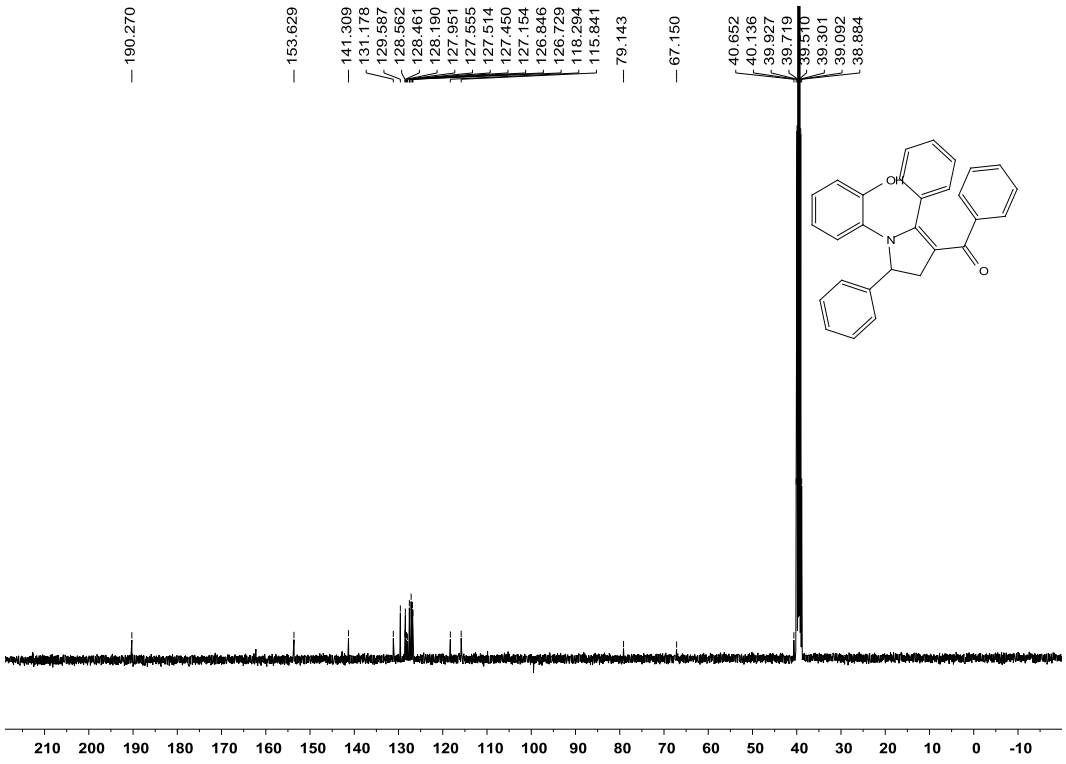


Compound **3ad:**

^{1}H NMR (400 MHz, d_6-DMSO)

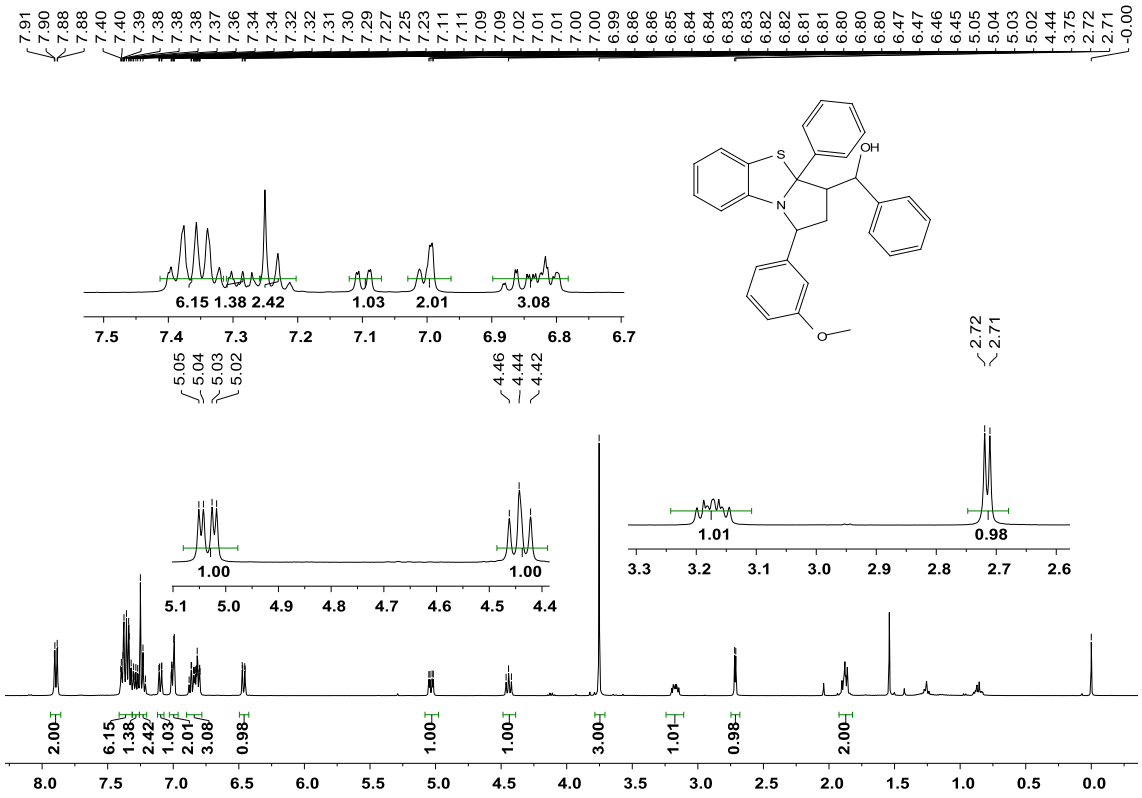


^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO)

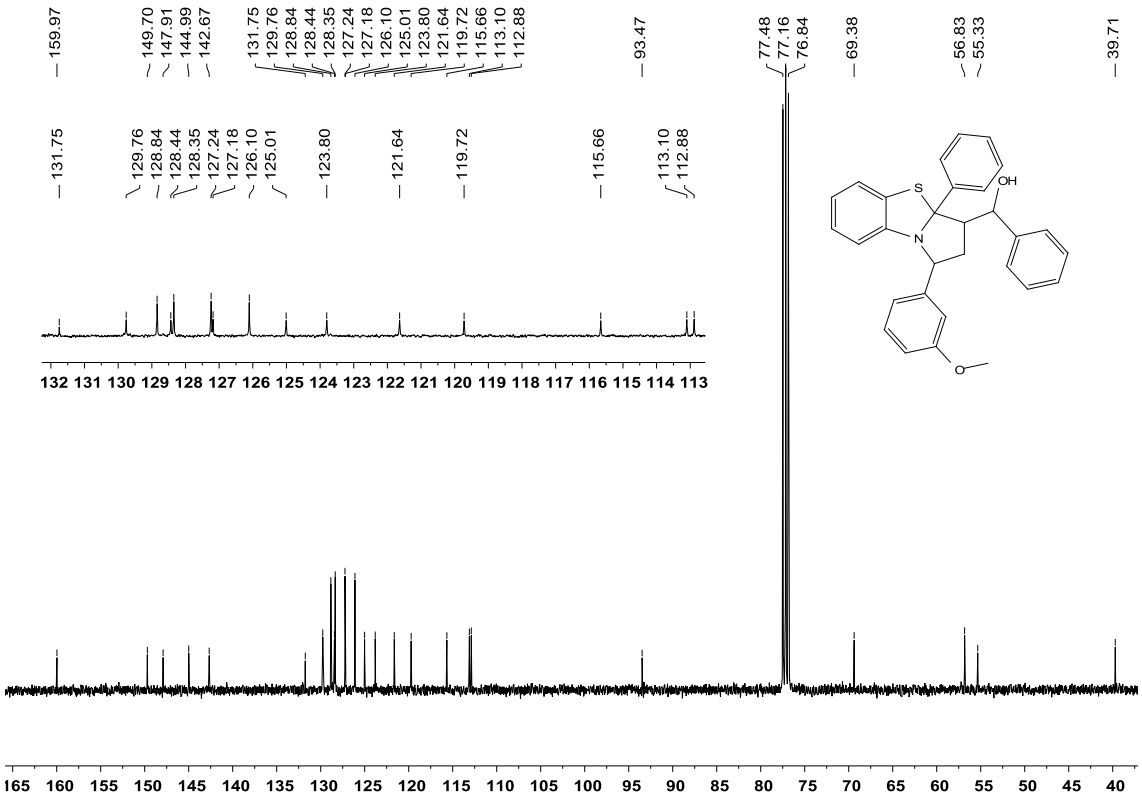


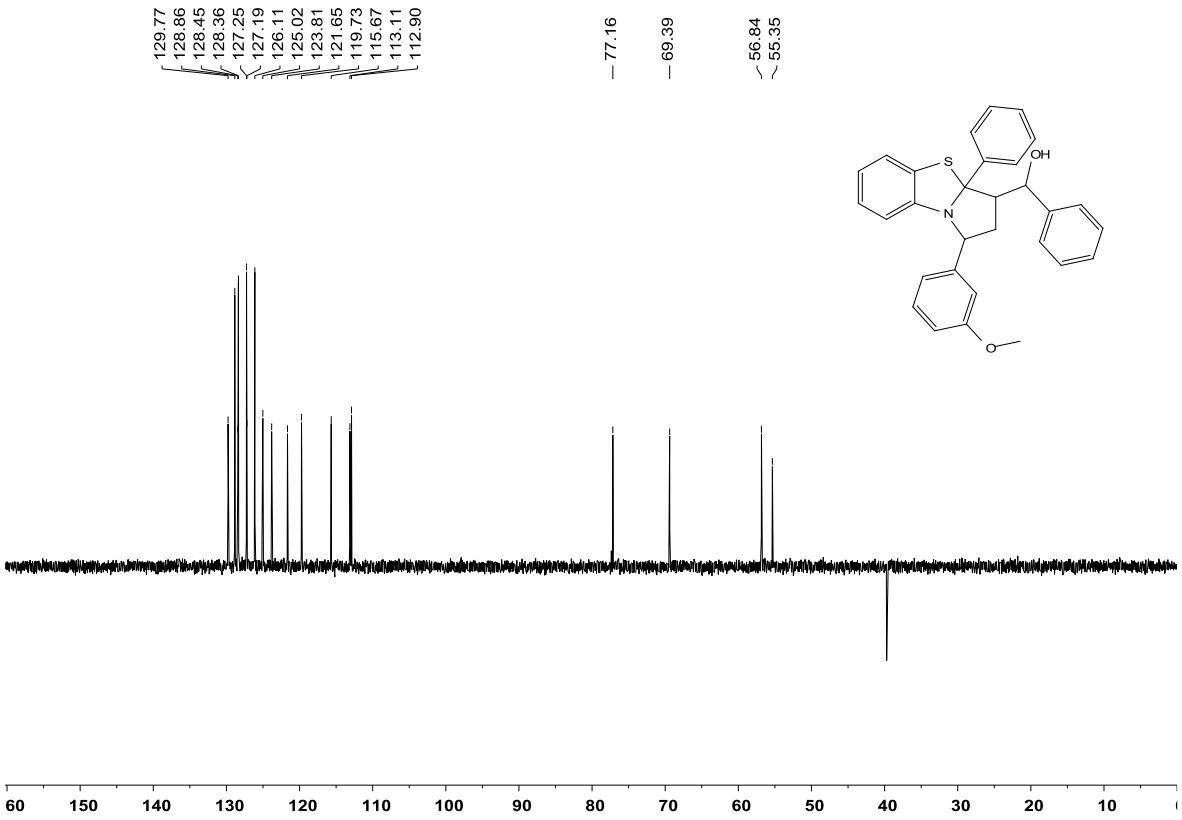
Compound **4:**

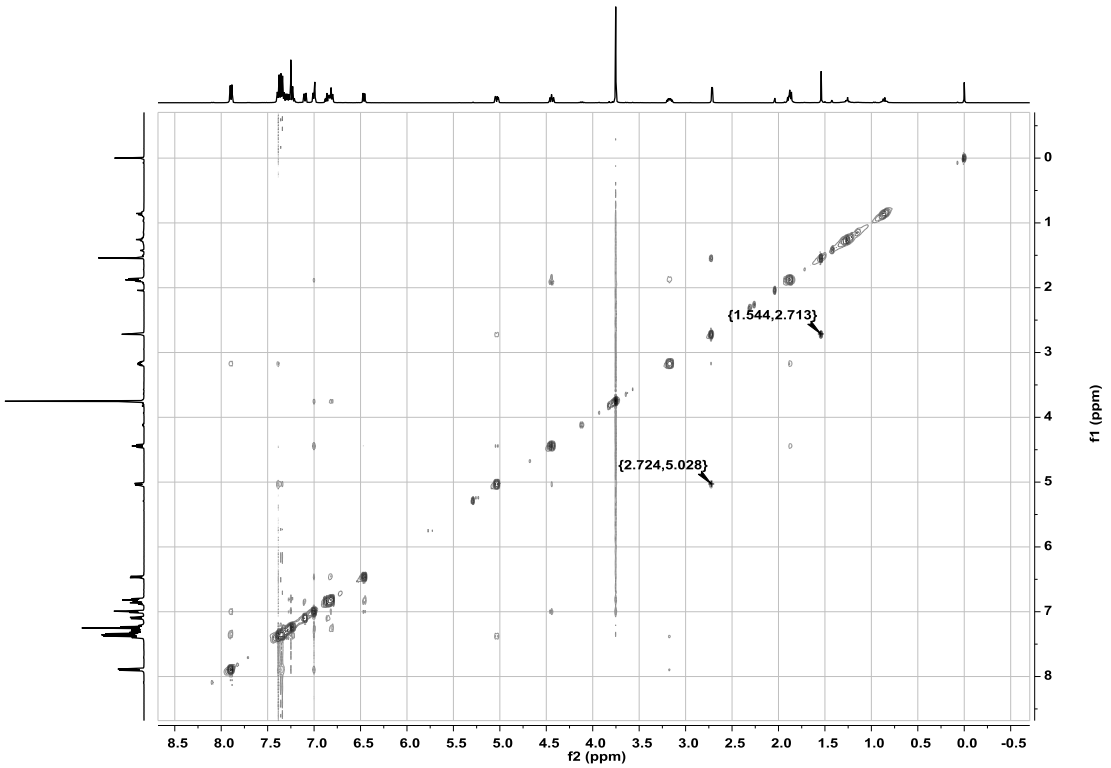
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

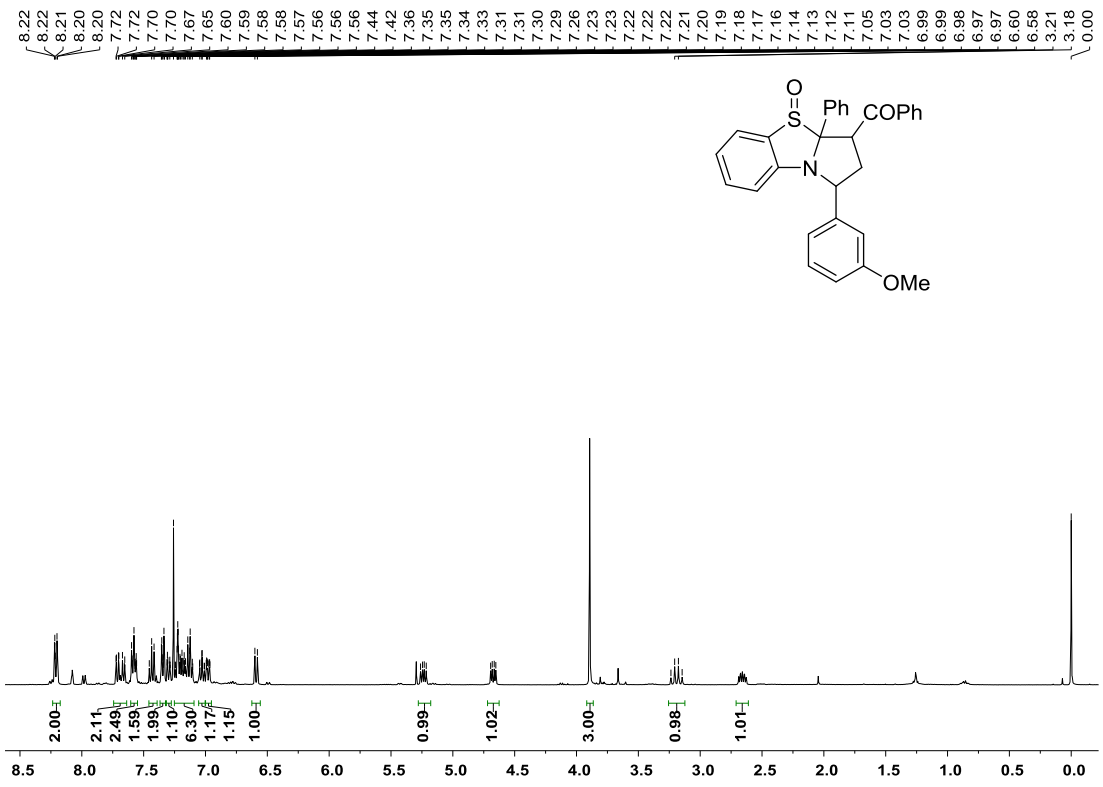



129.77
128.86
128.45
128.36
127.25
127.19
126.11
125.02
123.81
121.65
119.73
115.67
113.11
112.90
77.16
69.39
56.84
55.35
S
N
OH
O
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

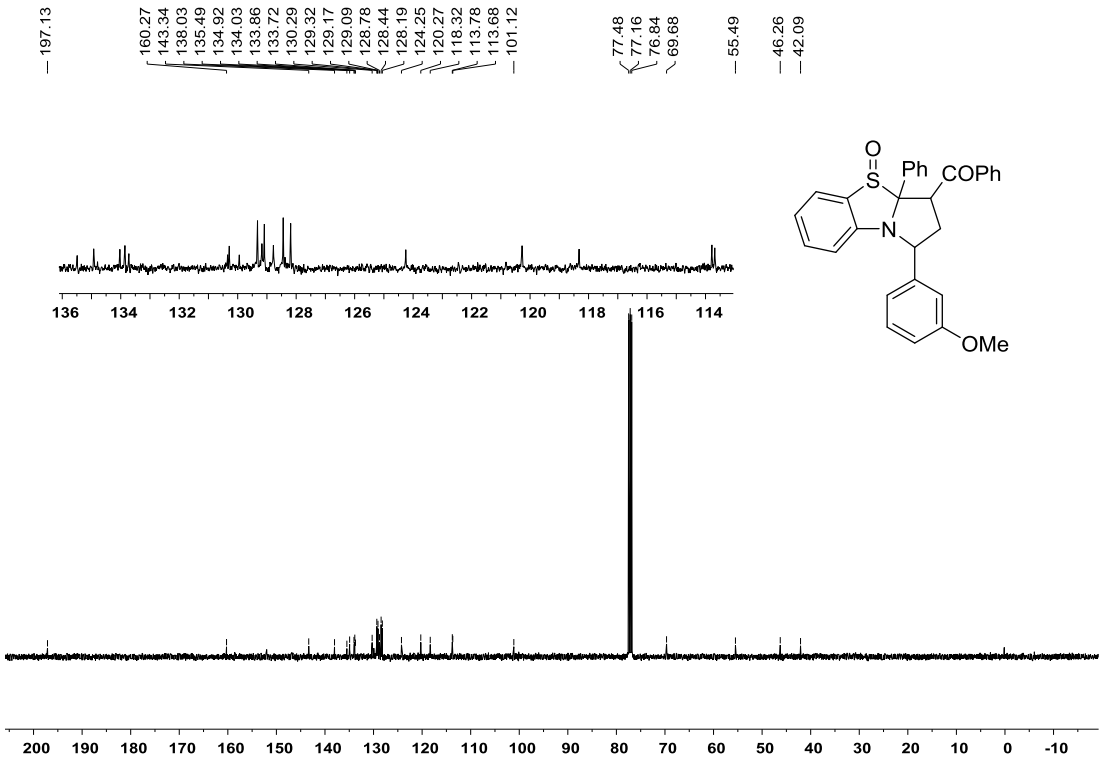

{1.544,2.713}
{2.724,5.028}
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7
8

Compound **5:**

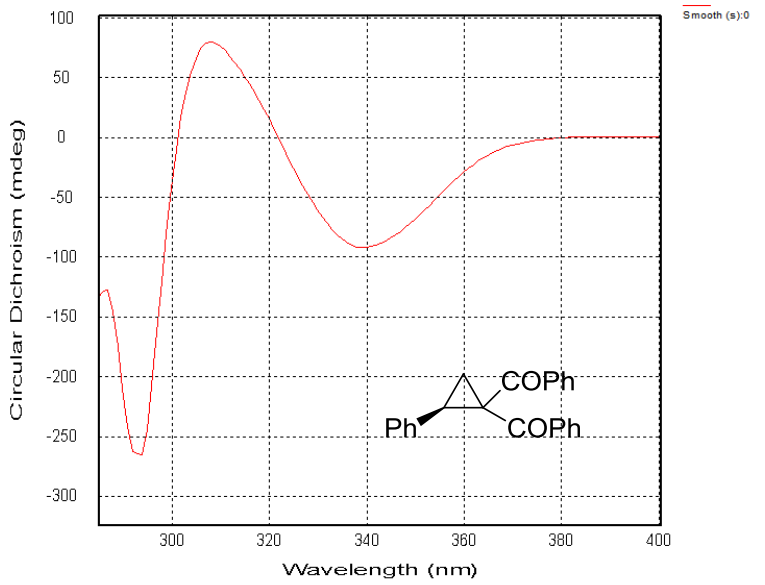
^{1}H NMR (400 MHz, $CDCl_3$)

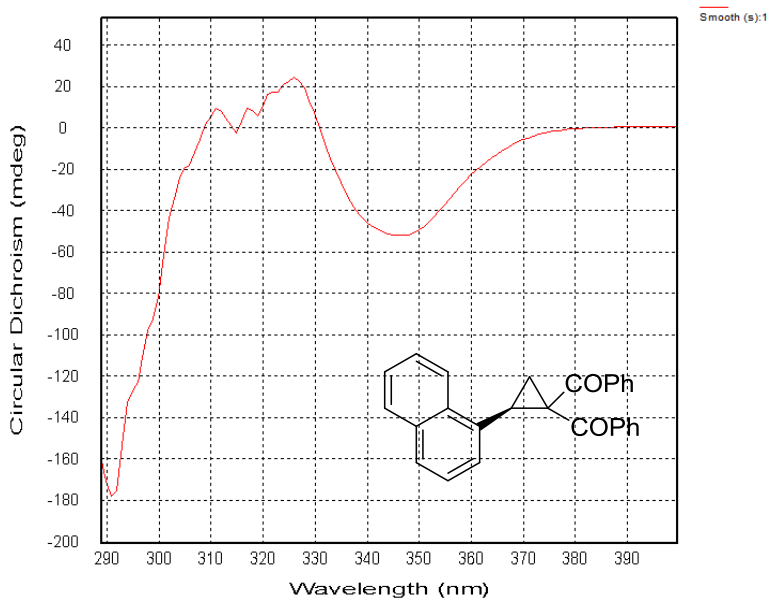


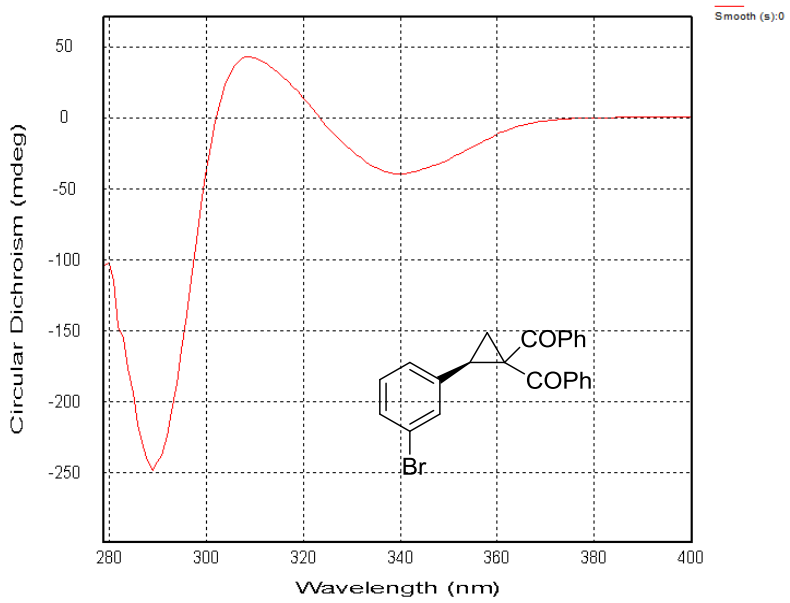
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

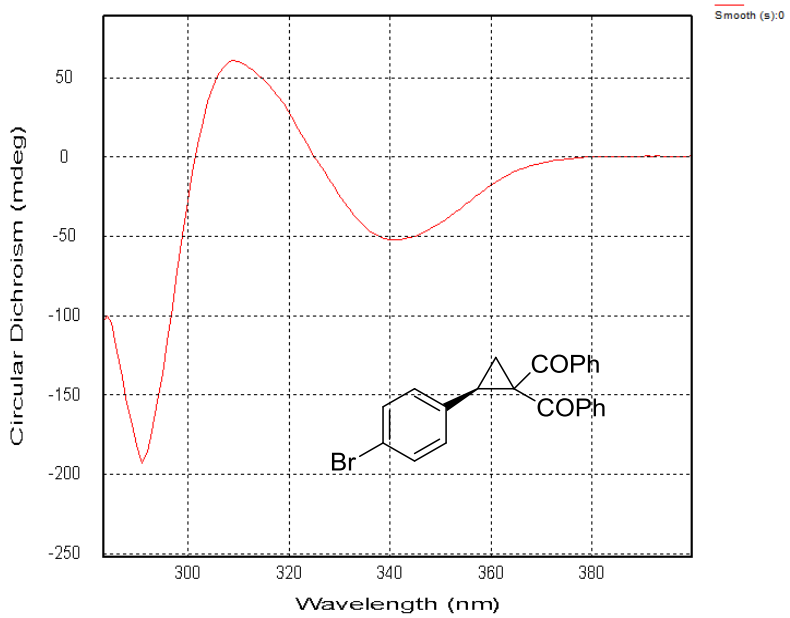


(M) Copies of CD Spectra for Recovered D-A Cyclopropanes






Smooth (s):0
50
0
-50
-100
-150
-200
-250
Circular Dichroism (mdeg)
280
300
320
340
360
380
400
Wavelength (nm)
COPh
COPh
Br


Smooth (s):0
50
0
-50
-100
-150
-200
-250
Circular Dichroism (mdeg)
300
320
340
360
380
Wavelength (nm)
COPh
COPh
Br