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Supporting Information

Iridium-Catalyzed Highly Enantioselective and Chemodivergent Coupling Reaction of Vinyl Azides and Vinyl Benzoxazinones

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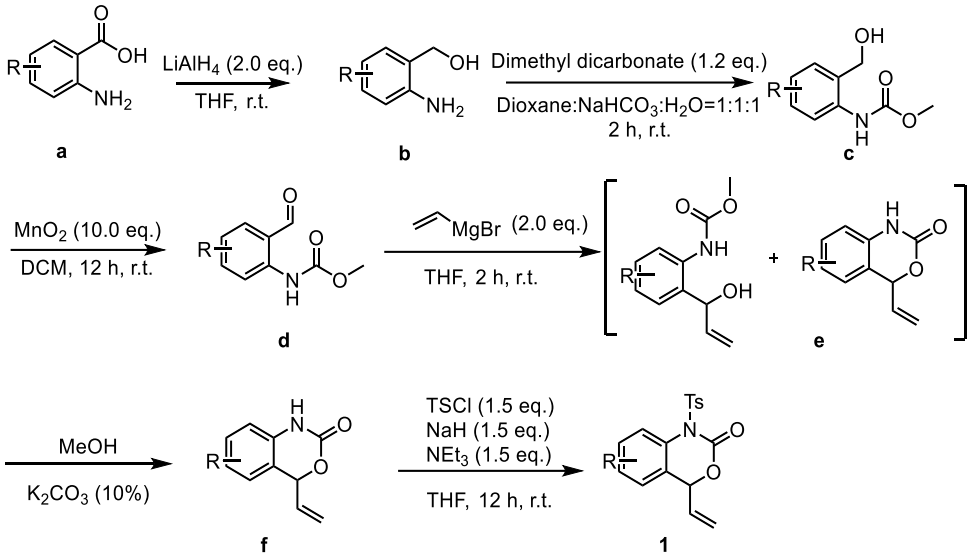
1. General Information

All reactions were generally performed in dried glassware filled with dry argon. TLC plates were stained using potassium permanganate or I_2. Chromatographic purification of products (column chromatography) was performed on the glass column filled in (300–400 Mesh) silica gel. Concentration of reaction product solutions and chromatography fractions under reduced pressure was performed by rotary evaporation at 30-40 °C at the appropriate pressure and then at rt, ca. 0.1 mmHg (vacuum pump) unless otherwise indicated. For reactions that require heating, oil bath is used as the heat source. NMR spectra were obtained on a Bruker 600 spectrometer, operating at 600 MHz for **^{1}H NMR**, 151 MHz for **^{13}C NMR**, 565 MHz for ^{19}F NMR. ^{1}H and ^{13}C positive chemical shifts (δ) are downfield from tetramethylsilane and are given in parts per million (ppm). Chemical shifts were reported in ppm relative to the central line of $CHCl_3$ (δ 7.26) for **^{1}H NMR**, for **^{13}C NMR**, the residual $CDCl_3$ (δ 77.16) were used as the internal standards. Coupling constants *(J)* are given in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, t = triplet, m = multiplet and brs = broad singlet. X-Ray structure analyses were performed with Rigaku Xtalab synergy. High resolution mass spectrometry (HRMS) were obtained on Xevo G2-Q TOF with ESI-HRMS (Electrospray ionization high-resolution mass spectra) and APCI-HRMS (atmospheric pressure chemical ionization high-resolution mass spectra) resource. Melting points range were determined in a X-4 micro melting point instrument (made in Shanghai, China). Optical rotation was recorded on PE polarmeter 341. Enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD, AD-H IA, IB column.

All commercial reagents were purchased from TCI, Leyan, Energy Chemical and used as received. Solvents used in catalytic reactions were dried and distilled in appropriate method. Solvent employed for column chromatography were purchased in technical grade quality without distillation before use.

2. Preparation of Alkenyl Benzoxazinanones



Vinyl oxazinone was synthesised based on relevant literature.[1,2] To a solution of **a** (10 mmol, 1.0 eq.) in THF (0.5 M, 20 mL) was added $LiAlH_4$ (20 mmol, 2.0 eq.) slowly at 0 °C. Then the reaction mixture was stirred to raise to r.t. slowly until the end monitored by TLC. For working up, the mixture was quenched by the dropwise addition of H_2O (1 mL) and 5% NaOH (aq.) (2 mL) slowly. After a few minutes, the suspension was filtered. The residue was washed with EtOAc, and the filtrate was washed by EtOAc, water and brine in turns, then dried over Na_2SO_4 and filtered. If needed, the crude product **b** should be purified by FCC.

To a stirring solution of o-amino benzyl alcohol **b** (10 mmol, 1.0 eq.) in a mixture of dioxane, sat. $NaHCO_3$ and water (1:1:1, 0.5 M, 20 mL) dimethyl dicarbonate (12 mmol, 1.2 eq.) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h and slowly allowing it to reach r.t. Upon full conversion, the reaction mixture was diluted with brine, extracted with CH_2Cl_2, and dried over $MgSO_4$. The crude product **c** was employed in the next step without further purification.

The crude mixture from **c** (10 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (0.3 M, 30 mL) and MnO_2 (100 mmol, 10.0 eq.) was added. The reaction was stirred at ambient temperature for 4 h. Upon full conversion, the reaction mixture was filtered through a plug of Celite to yield the desired product **d**.

Vinylmagnesium bromide (20 mmol, 2.0 eq., 1 M in THF) was added dropwise to a stirring solution of aldehyde **d** in dry THF (0.1 M, 50 mL) at −78 °C. The ice bath was removed and the reaction mixture was stirred for 2 h. Upon full conversion, additional Grignard reagent was quenched by addition of $NaHCO_3$ and the resulting suspension was extracted with Et_2O and dried over $MgSO_4$. The isolated crude was a mixture of intermediate and vinyl benzoxazinone.

The crude product **e** was dissolved in MeOH (0.2 M, 50 mL) and K_2CO_3 (10%, 10 mL) was added. The reaction was stirred at r.t. for 2 h. Upon full conv., the reaction mixture was neutralized by dropwise addition of HCl (3 M) and extracted with $MgSO_4$. The crude was purified by FC in silica (pentane/EtOAc 2:1) to yield the product **f.**

The product **f** (20 mmol) and Et_3N (30 mmol, 1.5 eq.) were stirred in THF (80 mL) at 0 °C. Then NaH (30 mmol,1.5 eq.) was added slowly to the mixture and stirred at r.t. for 1 h. The reaction mixture was added 4-toluenesulfonyl chloride (30 mmol, 1.5 eq.). After 12 h, the reaction was diluted with 100 mL of H_2O and extracted three times with dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude solid was purified by flash column to afford the compound **1**.

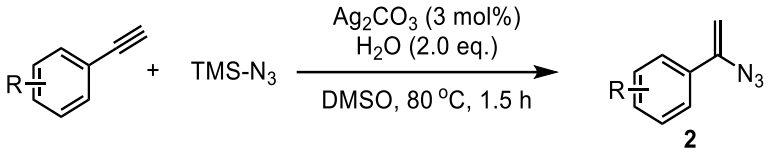
3. Preparation of Vinyl Azide

Sodium azide is toxic and can be absorbed through skin. Appropriate gloves are necessary when using it. It decomposes explosively upon heating to above 275 °C. Sodium azide is relatively safe in aqueous solution, unless acidified to form HN_3, which is volatile and highly toxic. Organic azides are potentially explosive substances that can decompose with the slight input of energy from external sources (heat, light, pressure, etc.). When designing the organic azides used for the project, we keep in mind the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group.

$$\frac{Nc+No}{N_N} \geqslant 3$$

Nc=Number of carbon atom
No=Number of atom about same size
N_N=Number of nitrogen atom

All organic azides prepared in this work are satisfied with the equation above. They are enough stable to be stored under –20 °C at least for 6 months. We have never experienced a safety problem with these materials.



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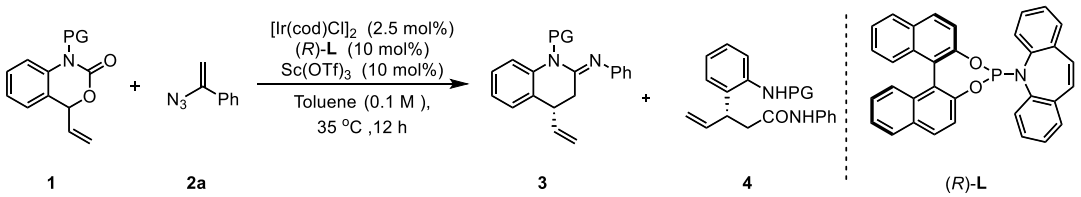
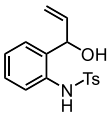
This procedure was slightly modified from Bi's method.[3] To a solution of Phenylacetylene (0.5 mL, 5 mmol), TMS-N_3 (1.4 mL, 10 mmol) and H_2O (0.18 mL, 10 mmol) in DMSO (15 mL) at 80 °C, Ag_2CO_3 (138 mg, 0.05 mmol) was added. The mixture was then stirred for 1.5 h until substrate consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 × 15 mL). The organic layer was washed with brine (3 × 40 mL), dried over Na_2SO_4 and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether) and concentrated in vacuo to afford **2**.

4. Reaction Conditions Optimization to Synthesis of 3

Table S1. Effect of leaving groups[a]

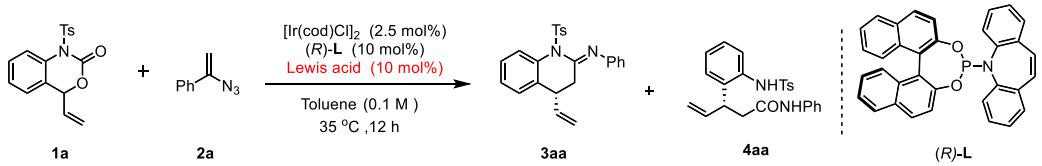


1 **2a** **3** **4** (*R*)-**L**

entry	PG	**3**/**4**[b]	yield of **3** (%)[c]	*ee* (%)[d]
1	H	-	N.D.	-
2	Ts	1:0.25	40	>99
3	Ms	-	trace	-
4	*p*-OMe-benzenesulfonyl	-	N.D.	-
5	*p*-F-benzenesulfonyl	-	N.D.	-
6	CO^{t}Bu	-	N.D.	-
7	COMe	-	N.D.	-
8	COAd	-	N.D.	-
9	*p*-Cl-benzoyl	-	N.D.	-
10		-	N.D.	-

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg) in toluene 2 mL was stirred for 15 minutes. $Sc(OTf)_3$ (10 mol%, 9.8 mg), **1** (0.2 mmol, 1.0 eq.), **2a** (0.3 mmol, 1.5 eq.) was added to the solution and then stirred at 35 °C for 12 h. [b] **^{1}H NMR** yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S2. Effect of Lewis acid[a]

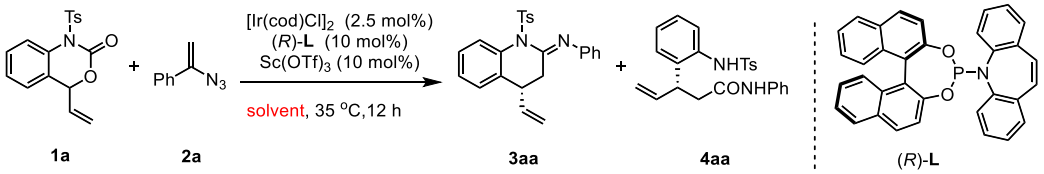


1a **2a** **3aa** **4aa** (*R*)-**L**

entry	Lewis acid	**3aa/4**[b]	yield of **3aa** (%)[c]	*ee* (%)[d]	entry	Lewis acid	**3aa/4aa**[b]	yield of **3aa** (%)[c]	*ee* (%)[d]
1	$Ho(OTf)_3$	1:1.02	35	91	16	$ZnBr_2$	-	N.R.	-
2	$Ce(OTf)_3$	1:0.51	37	93	17	$ZnCl_2$	-	N.R.	-
3	$Gd(OTf)_3$	-	N.D.	-	18	ZnI_2	-	N.R.	-
4	$Tb(OTf)_3$	1:0.40	24	97	19	$InBr_3$	-	N.R.	-
5	$Nb(OTf)_3$	-	N.D.	-	20	$InCl_3$	-	N.R.	-
6	$La(OTf)_3$	-	N.D.	-	21	$BiCl_3$	-	N.R.	-
7	$Sm(OTf)_3$	-	N.D.	-	22	$BF_3.Et_2O$	1:0.32	22	>99
8	$Eu(OTf)_3$	-	N.D.	-	23	$Ag(NTf_2)_2$	-	trace	-
9	$Yb(OTf)_3$	1:0.49	40	97	24	CH_3COOH	-	N.D.	-
10	$In(OTf)_3$	1:0.43	8	94	25	PhOH	-	N.D.	-
11	$Pr(OTf)_3$	-	N.D.	-	26	CF_3SO_3H	-	N.D.	-
12	$Y(OTf)_3$	1:0.31	18	95	27	PhCOOH	-	N.D.	-
13	$Zn(OTf)_2$	-	N.R.	-					
14	Ag(OTf)	-	N.R.	-					
15	$Sc(OTf)_3$	1:0.28	40	>99					

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg) in toluene 2 mL was stirred for 15 minutes. Lewis acid (10 mol%), **1** (0.2 mmol, 1.0 eq.), **2a** (0.3 mmol, 1.5 eq.) was added to the solution and then stirred at 35 °C for 12 h. [b] ^1H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S3. Effect of solvents[a]

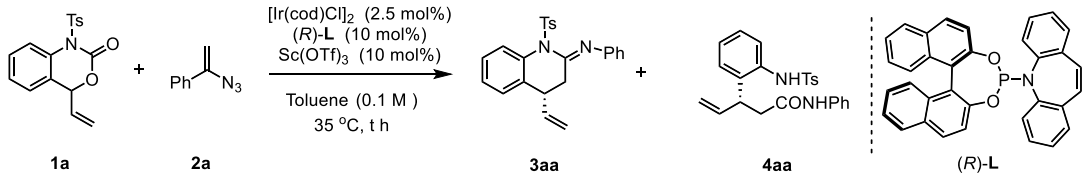


1a **2a** **3aa** **4aa** (*R*)-**L**

entry	solvent (2 mL)	**3aa/4aa**[b]	yield of **3aa** (%)[c]	*ee*(%)[d]
1	toluene	1:0.25	40	>99
2	Benzene	1:0.29	35	>99
3	Fluorobenzene	1:0.30	30	>99
4	Chlorobenzene	1:0.26	40	>99
5	Dlmethyl benzene	-	N.D.	-
6	1,3,5-trimethyl benzene	-	N.D.	-
7	THF	-	trace	-
8	Et_2O	-	trace	-
9	DCM	-	trace	-
10	MECN	-	trace	-
11	MEOH	-	N.D.	-

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg) in solvent 2 mL was stirred for 15 minutes. $Sc(OTf)_3$ (10 mol%, 9.8 mg), **1** (0.2 mmol, 1.0 eq.), **2a** (0.3 mmol, 1.5 eq.) was added to the solution and then stirred at 35 °C for 12 h.[b] ^1H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S4. Effect of reaction time and equivalent of **2a**[a]

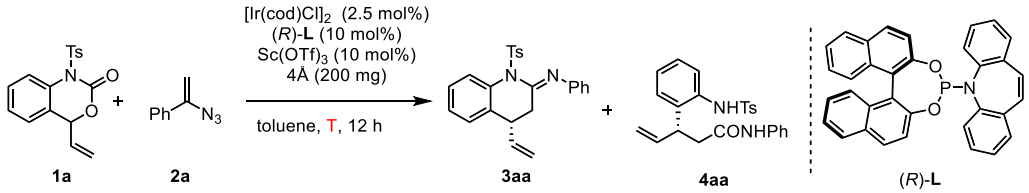


1a **2a** **3aa** **4aa** (*R*)-**L**

entry	t h	equivalent of **2a**	**3aa/4aa**[b]	yield (%)[c]	*ee* (%)[d]
1	5	1.5	1:0.29	12	>99
2	9	1.5	1:0.30	25	>99
3	12	1.5	1:0.25	40	>99
4	18	1.5	1:0.27	32	>99
5	24	1.5	1:0.30	24	>99
6	12	1.2	1:0.28	33	>99
7	12	1.8	1:0.25	38	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg) in toluene 2 mL was stirred for 15 minutes. $Sc(OTf)_3$ (10 mol%, 9.8 mg), **1** (0.2 mmol, 1.0 eq.), **2a** was added to the solution and then stirred at 35 °C for 12 h. [b] ^1H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S5. Effect of reaction temperature[a]

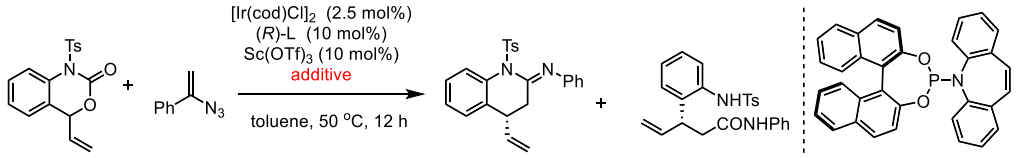


1a **2a** **3aa** **4aa** (*R*)-**L**

entry	T (°C)	**3aa/4aa**[b]	yield (%)[c]	*ee* (%)[d]
1	25	1:0.08	57	>99
2	35	1:0.11	60	>99
3	50	1:0.05	72	>99
4	80	1:0.06	48	60
5	100	1:0.09	26	40

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg) in toluene 0.5 mL were stirred for 15 minutes, while substrates **1a** (0.2 mmol, 1.0 eq.) and 4Å (200 mg) molecular sieves were complexed in 0.5 mL of toluene for 15 min. Two solutions are mixed, followed by the addition of **2a** (0.30 mmol, 1.5 eq.) and scandium trifluoromethanesulfonate. The reaction was stirred at certain temperature for 12 h afterward. [b] ^{1}H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S6. Effect of additives[a]

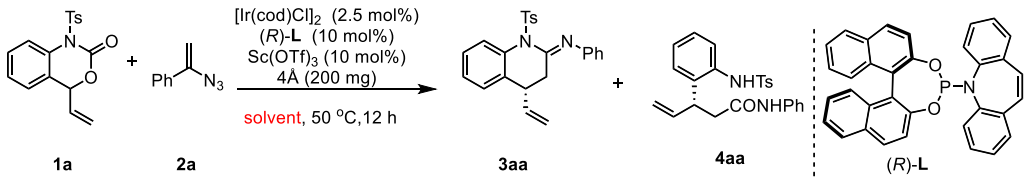


1a **2a** **3aa** **4aa** (*R*)-L

entry	additive	additive (mg)	**3aa/4aa**[b]	yield (%)[c]	*ee* (%)[d]
1	$MgSO_4$	200	1:0.62	47	>99
2	Na_2SO_4	200	1:0.40	15	>99
3	3Å	200	1:0.19	25	>99
4	4Å	200	1:0.05	70	>99
5	4Å	30	1:0.11	48	>99
6	4Å	50	1:0.06	49	>99
7	4Å	100	1:0.07	54	>99
8	4Å	300	1:0.10	63	>99
9	4Å	400	1:0.10	50	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg), toluene 0.5 mL, stir for 15 minutes. while substrates **1a** (0.2 mmol, 1.0 eq.) and additive molecular sieves were complexed in 0.5 mL of toluene for 15 min, and then the two solutions are mixed, followed by the addition of **2a** (0.30 mmol, 1.5 eq.) and scandium trifluoromethanesulfonate, and then the reaction was transferred to 50 °C for 12 h afterward. [b] ^{1}H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S7. Effect of solvents[a]

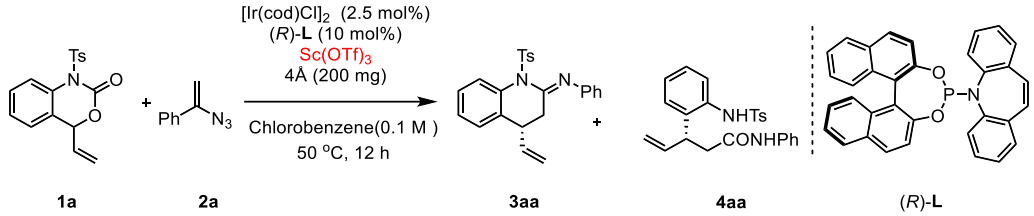


1a **2a** **3aa** **4aa** (*R*)-**L**

entry	solvent (2 mL)	**3aa/4aa**[b]	yield(%)[c]	*ee*(%)[d]
1	toluene	1:0.05	67	>99
2	Benzene	1:0.09	47	>99
3	Ethyl benzene	1:0.29	56	>99
4	Chlorobenzene	1:0.06	80	>99
5	Bromobenzene	1:0.14	43	>99
6	Iodobenzene	1:0.15	38	>99
7	(trifluoromethyl)benzene	1:0.11	65	>99
8	1,2-dichlorobenzene	1:0.12	73	>99
9	THF	1:1.5	23	>99
10	Et_2O	1:1.32	22	>99
11	DCM	1:0.91	17	>99
12	MeCN	1:0.86	21	>99
13	MEOH	-	N.D.	-

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg), solvent 0.5 mL, stir for 15 minutes. while substrates **1a** (0.2 mmol, 1.0 eq.) and 4Å （200 mg） molecular sieves were complexed in 0.5 mL of solvent for 15 min, and then the two solutions are mixed, followed by the addition of **2a** (0.30 mmol, 1.5 eq.) and scandium trifluoromethanesulfonate, and then the reaction was transferred to 50 °C for 12 h afterward. [b] ^1H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

Table S8. Effect of $Sc(OTf)_3$ loading[a]



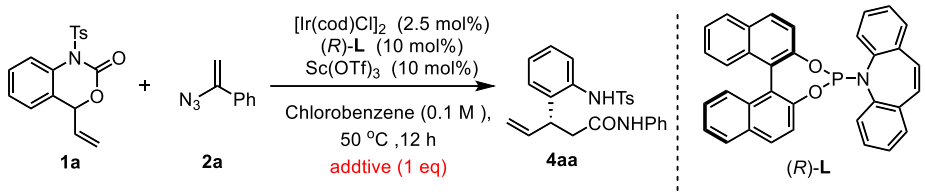
1a **2a** **3aa** **4aa** (*R*)-**L**

entry	$Sc(OTf)_3$ (mol%)	**3aa/4aa**[b]	yield(%)[c]	*ee*(%)[d]
1	5	1:0.08	58	>99
2	10	1:0.04	80	>99
3	20	1:0.06	44	>99
4	30	1:0.07	50	>99
5	50	1:0.12	44	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg), (*R*)-**L** (10 mol%, 10.1 mg), chlorobenzene 0.5 mL, stir for 15 minutes. while substrates **1a** (0.2 mmol, 1.0 eq.) and 4Å (200 mg) molecular sieves were complexed in 0.5 mL of chlorobenzene for 15 min, and then the two solutions are mixed, followed by the addition of **2a** (0.30 mmol,1.5 eq.) and $Sc(OTf)_3$, and then the reaction was transferred to 50 °C for 12 h afterward. [b] ^1H NMR yield ratio. [c] Isolated yield. [d] the *ee* was determined by chiral HPLC analysis.

5. Reaction Conditions Optimization to Synthesis of 4aa

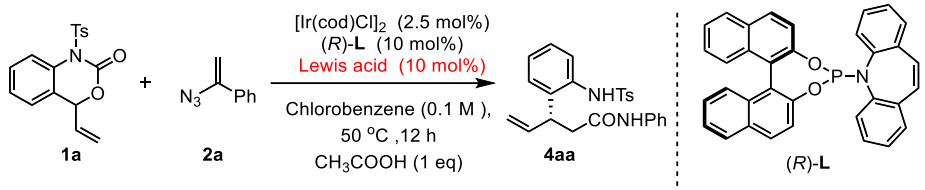
Table S9. Effect of additive[a]



entry	addtive	yield (%)[b]	ee (%)[c]
1	H_2O	23	>99
2	CF_3COOH	48	>99
3	CH_3COOH	56	>99
4	CF_3SO_3H	NR	-
5	HCOOH	trace	-
6	Phenol	36	>99
7	PhCOOH	43	>99
8	$NHTf_2$	NR	-
9	HBF_4	12	>99
10	*L*-Proline	NR	-
11	-	NR	-

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), chlorobenzene 0.5 mL, stir for 15 minutes., then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), $Sc(OTf)_3$, and additive and then the reaction was transferred to 50 °C for 12 h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

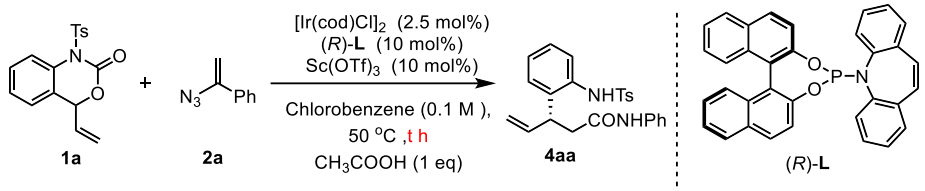
Table S10. Effect of Lewis acid[a]



entry	Lewis acid	yield (%)[b]	*ee* (%)[c]
1	$Ho(OTf)_3$	trace	-
2	$Ce(OTf)_3$	trace	-
3	$Yb(OTf)_3$	NR	-
4	$In(OTf)_3$	NR	-
5	$Sm(OTf)_3$	NR	-
6	$La(OTf)_3$	NR	-
7	$Cu(OTf)_2$	NR	-
8	$Fe(OTf)_3$	13	>99
9	$Sc(OTf)_3$	56	>99
10	$ZnBr_2$	trace	-
11	$BF_3.Et_2O$	NR	-
12	$InCl_3$	NR	-
13	ZnI_2	ND	-

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), chlorobenzene 0.5 mL, stir for 15 minutes., then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), Lewis acid, and CH_3COOH and then the reaction was transferred to 50 °C for 12 h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

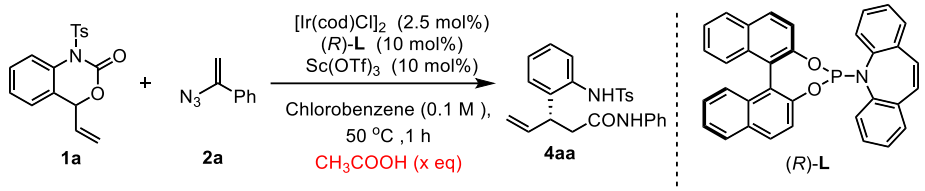
Table S11. Effect of reaction time[a]



entry	t (h)	yield (%)[b]	*ee* (%)[c]
1	0.5	37	>99
2	1	58	>99
3	3	56	>99
4	5	55	>99
5	9	57	>99
6	12	56	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), chlorobenzene 0.5 mL, stir for 15 minutes., then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), $Sc(OTf)_3$, and CH_3COOH and then the reaction was transferred to 50 °C for t h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

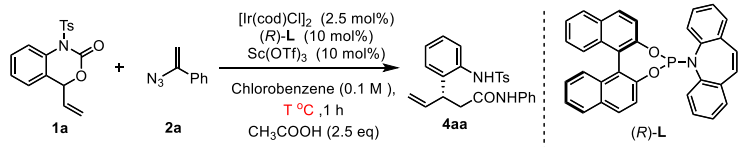
Table S12. Effect of equivalent of CH_3COOH[a]



entry	x (eq)	yield (%)[b]	*ee* (%)[c]
1	1	58	>99
2	2	85	>99
3	2.5	90	>99
4	3	76	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), chlorobenzene 0.5 mL, stir for 15 minutes., then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), $Sc(OTf)_3$, and CH_3COOH and then the reaction was transferred to 50 °C for 1 h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

Table S13. Effect of reaction temperature[a]

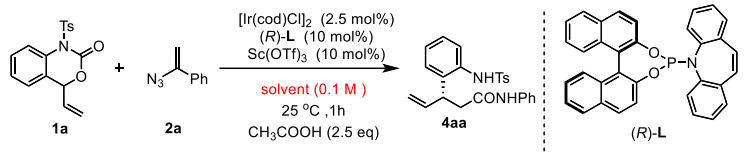


entry	T (°C)	yield (%)[b]	*ee* (%)[c]
1	10	74	>99
2	25	91	>99
3	40	81	>99
4	50	88	>99
5	65	70	>99

[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), chlorobenzene 0.5 mL, stir for 15 minutes.,

then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), $Sc(OTf)_3$, and CH_3COOH and then the reaction was stirred under certain temperature for 1 h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

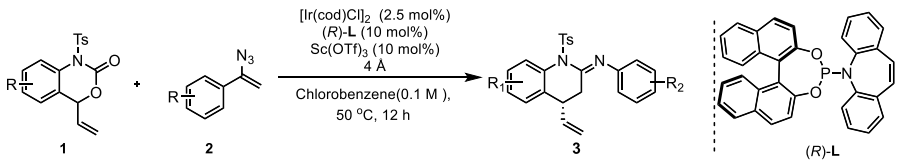
Table S14. Effect of solvent[a]



entry	solvent	yield (%)[b]	*ee* (%)[c]
1	THF	16	>99
2	DCM	trace	
3	DMF	NR	
4	MeCN	14	79
5	MeOH	NR	
6	chlorobenzene	93	>99
7	Tol	31	>99
8	1,2-dichlorobenzene	90	>99

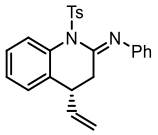
[a] Conditions and experimental procedures: Unless otherwise noted, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg), (*R*)-**L** (10 mol%, 5 mg), solvent 0.5 mL, stir for 15 minutes, then addition of substrates **1a** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol,1.5 eq.), $Sc(OTf)_3$, and CH_3COOH and then the reaction was stirred under 25 °C for 1 h afterward. [b] Isolated yield. [c] the *ee* was determined by chiral HPLC analysis.

6. General Procedure for the Synthesis of 3



In the glove box, $[Ir(cod)Cl]_2$ (2.5 mol%, 3.4 mg) and (*R*)-**L** (10 mol%, 10.1 mg) were added to a screw-capped glass vial fitted with a magnetic stirring bar, 0.5 mL of chlorobenzene was added and stirred for 15 min. The substrate **1** (0.2 mmol ,1.0 eq.), 4Å (200 mg) molecular sieves and 0.5 mL of chlorobenzene were stirred for 15 min in a test tube and then transferred to the screw-capped vial and washed with 1 mL of chlorobenzene. $Sc(OTf)_3$ (10 mol%, 9.8 mg), and substrate **2** (0.30 mmol, 1.5 eq.) were added sequentially and the reaction was transferred to 50 °C for 12 h with the stopper tightly closed. Then, the resulting mixture was filtered through celite, and concentrated in vacuo. The crude residue was purified via silica gel flash column chromatography to afford the product **3**.

Characterization of Amide (*R*,*E*)-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



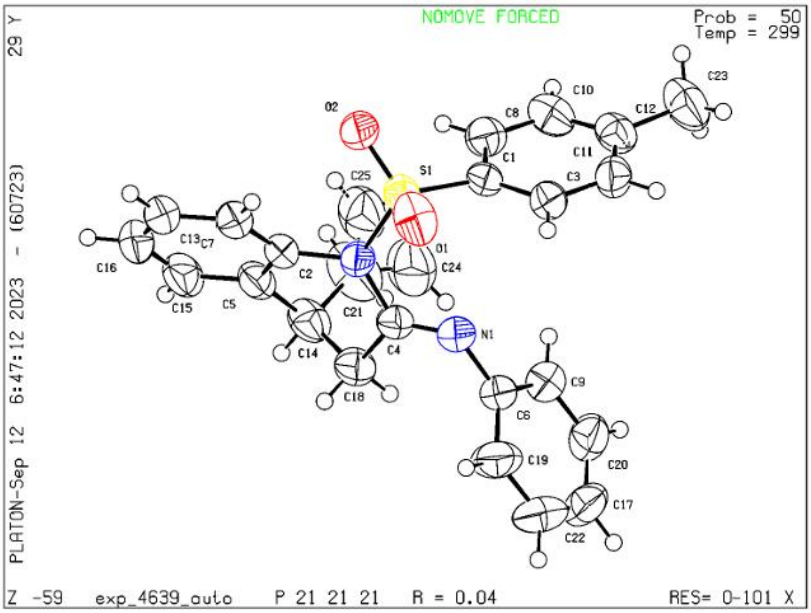
3aa

Prepared following general procedure the product **3aa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1) on silica gel to provide the title compound as a white solid (80% yield, 63.7 mg, 99% *ee*). m.p. 188 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.20 – 7.12 (m, 4H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.93 – 6.96 (m, 1H), 6.34 (d, *J* = 7.5 Hz, 2H), 5.64 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.95 (d, *J* = 17.1 Hz, 1H), 3.29 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.47 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.40 (s, 3H), 2.36 (dd, *J* = 16.8, 8.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.5, 148.2, 144.2, 137.6, 136.5, 135.7, 133.4, 129.7, 129.0, 127.2, 126.3, 125.2, 123.4, 120.1, 118.0, 39.8, 34.3, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{23}N_2O_2S^+$ 403.1475, found: 403.1497. $[\alpha]_D^{20}$ = -29.9 (c = 0.2, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 °C, 254 nm, t_{R1}: 14.9 min and t_{R2}: 28.9 min).

A colorless stick-shaped crystal of **3aa** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **3aa** in hexane/ 2-propanol (5:1).

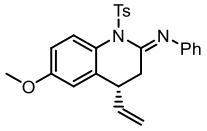
Figure S1. Crystal data and structure refinement for **3aa** (CCDC) is available from the Cambridge Crystallographic Data Centre (CCDC). Displacement ellipsoids are drawn at the 50% probability level.



Identification code	exp_4639_auto
Empirical formula	$C_{24}H_{22}N_2O_2S$
Formula weight	402.50
Temperature/K	299.14(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.1617(3)
b/Å	14.1664(6)
c/Å	18.0449(8)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	2086.39(15)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	1.552
F(000)	848.0
Crystal size/mm^3	0.18 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.934 to 153.446
Index ranges	-6 ≤ h ≤ 10, -17 ≤ k ≤ 17, -22 ≤ l ≤ 20
Reflections collected	11559
Independent reflections	4132 [R_{int} = 0.0366, R_{sigma} = 0.0383]
Data/restraints/parameters	4132/18/274
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	$_{R1}$ = 0.0395, wR_2 = 0.1034
Final R indexes [all data]	$_{R1}$ = 0.0138, wR_2 = 0.1091
Largest diff. peak/hole/e Å^{-3}	0.16/-0.31
Flack parameter	0.001(11)

(*R*,*E*)-6-methoxy-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



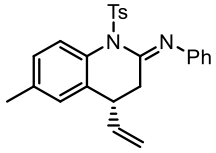
3ab

Prepared following general procedure the product **3ab** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a viscous liquid. (84% yield, 72.2mg, 99% *ee*）. m.p. 150 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.26 (m, 2H), 7.00 – 7.02 (m, 1H), 6.42 (d, *J* = 8.0

Hz, 2H), 5.75 – 5.64 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 2.51 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.39 (dd, *J* = 16.7, 4.5 Hz,1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.7, 148.2, 144.2, 137.5, 137.1, 136.8, 135.5, 130.3, 129.7, 129.0, 126.6, 126.1, 125.8, 123.3, 120.1, 117.8, 39.4, 34.4, 21.7, 21.4.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{24}N_2NaO_2S^+$ 455.1400; found: 455.1411. $[\alpha]_D^{20}$ = -24.3 (c =0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 32.2 min and t_{R2}: 68.0 min).

(*R*,*E*)-6-methyl-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

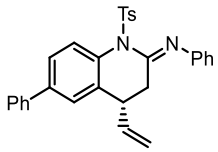


3ac

Prepared following general procedure the product **3ac** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (73% yield, 60.8 mg, 99% *ee*）. m.p. 136 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.31 (d, *J* = 8.0, 2H), 7.26 – 7.19 (m, 2H), 7.13 – 7.15 (m, 1H), 6.99 (d, *J* = 21.4 Hz, 2H), 6.45 – 6.37 (m, 2H), 5.69 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 3.30 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.50 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.46 (s, 3H), 2.40 (dd, *J* = 16.7, 4.5 Hz,1H), 2.35 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.7, 148.3, 144.2, 137.6, 136.7, 135.8, 133.2, 133.1, 129.7, 129.0, 127.7, 126.9, 125.1, 123.3, 120. 1, 117.9, 39.9, 34.4, 21.7, 21.0.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{25}N_2O_2S^+$ 417.1631; found: 417.1638. $[\alpha]_D^{20}$ = -24.1 (c =0.4, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 17.5 min and t_{R2}: 55.9 min).

(*R*,*E*)-N,6-diphenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

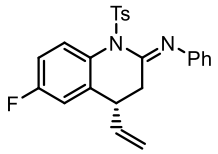


3ad

Prepared following general procedure the product **3ad** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (82% yield, 78 mg, 99% *ee*）· m.p. 163 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.63 (d, J = 8.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz , 1H), 7.27 – 7.20 (m, 4H), 7.14 – 7.18 (m , 2H), 7.03 – 6.99 (m, 1H), 6.93-6.96 (m, 1H), 6.34 (d, *J* = 7.8 Hz, 2H), 5.65 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 4.98 (d, *J* = 17.1 Hz, 1H), 3.31 (dd, *J* = 11.9, 8.0 Hz, 1H), 2.46 (dd, *J* = 16.7, 4.4 Hz, 1H), 2.40 (s, 3H), 2.37 (dd, *J* = 16.7, 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 148.1, 144.4, 143.4, 137.4, 136.3, 134.9, 133.8, 132.1, 129.8, 129.0, 129.0, 128.2, 125.6, 125.1, 124.7, 123.9, 123.5, 120.1, 118.3, 39.9, 34.1, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{30}H_{27}N_2O_2S^+$ 479.1788, found: 479.1771. $[\alpha]_D^{20}$ = -3.4 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 14.7 min and t_{R2}: 24.7 min).

(*R*,*E*)-6-fluoro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



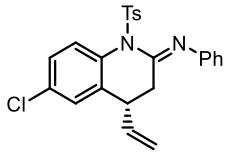
3ae

Prepared following general procedure the product **3ae** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (72% yield, 60.5 mg, 99% *ee*）. m.p. 132 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.65 (m, , 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.07 – 7.01 (m, 2H), 6.89 – 6.91 (m, 1H), 6.42 – 6.43 (m, 2H), 5.66 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H),

5.09 – 5.01 (d, *J* = 10.2 Hz, 1H), 3.32 (dd, *J* = 12.3, 8.0 Hz, 1H), 2.55 (dd, *J* = 16.8, 4.5 Hz, 1H), 2.48 (s, 3H), 2.38 (dd, *J* = 12.3, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.2 (d, *J* = 244.5 Hz), 153.2, 148.0, 144.4, 137.3, 135.9 (d, *J* = 7.5 Hz), 135.7, 131.6 (d, *J* = 3.0 Hz), 129.6, 129.1,129.0, 127.0 (d, *J* = 7.5 Hz), 123.5, 120.0, 118.8, 114.0 (d, *J* = 22.5 Hz), 113.3 (d, *J* = 22.5 Hz), 39.8, 34.2, 21.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.66.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}FN_2O_2S^+$ 421.1381; found: 421.1381. $[\alpha]_D^{20}$= -29.6 (c = 0.5, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 15.8 min and t_{R2}: 36.2 min).

(*R*,*E*)-6-chloro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

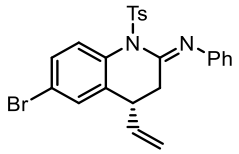


3af

Prepared following general procedure the product **3af** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (76% yield, 66.3 mg, 99% *ee*） .m.p. 163 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 – 6.95 (m, 1H), 6.40 – 6.42 (m, 2H), 5.66 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.00(d, *J* = 17.1 Hz, 1H), 3.32 (dd, *J* = 12.2, 7.7 Hz, 1H), 2.53 (dd, *J* = 16.8, 4.6 Hz, 1H), 2.48 (s, 3H), 2.40 (dd, *J* = 16.8, 8.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.9, 144.5, 137.2, 135.7, 135.2, 135.1, 134.3, 134.1, 131.4, 129.7, 129.1, 129.0, 127.21, 126.5, 126.4, 123.7, 123.5, 122.9, 120.0, 118.7, 118.4, 39.7, 34.0, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}ClN_2O_2S^+$ 437.1085; found: 437.1082. $[\alpha]_D^{20}$ = -20.0 (c = 0.5, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 15.9 min and t_{R2}: 44.3 min).

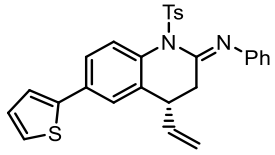
(*R*,*E*)-6-bromo-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



3ag

Prepared following general procedure the product **3ag** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (81% yield, 78 mg, 99% *ee*）. m.p. 175 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 – 6.95 (m, 1H), 6.40 – 6.42 (m, 2H), 5.66 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.00(d, *J* = 17.1 Hz, 1H), 3.32 (dd, *J* = 12.2, 7.7 Hz, 1H), 2.53 (dd, *J* = 16.8, 4.6 Hz, 1H), 2.48 (s, 3H), 2.40 (dd, *J* = 16.8, 8.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.9, 144.5, 137.2, 135.7, 135.2, 135.1, 134.3, 134.1, 131.4, 129.7, 129.1, 129.0, 127.2, 126.5, 126.4, 123.7, 123.5, 122.9, 120.0, 118.7, 118.4, 39.7, 34.0, 21.7. **HRMS (APCI)** (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}BrN_2O_2S^+$ 481.0586; found: 481.0596. $[\alpha]_D^{20}$= -12.3 (c = 0.4, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 17.7 min and t_{R2}: 55.6 min).

(*R*,*E*)-N-phenyl-6-(thiophen-2-yl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



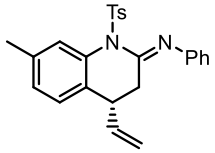
3ah

Prepared following general procedure the product **3ah** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (55% yield, 53.6 mg, 99% *ee*）. m.p. 157 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.52 (m, 3H), 7.36 – 7.38 (m, 2H), 7.32 – 7.25 (m, 4H), 7.14 – 7.18 (m, 2H), 6.94-6.96 (m, 1H), 6.35 (d, *J* = 7.8 Hz, 2H), 5.67 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H),

5.09 (d, *J* = 10.3 Hz, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 3.35 (dd, *J* = 12.1, 7.1 Hz, 1H), 2.50 (dd, *J* = 16.7, 4.6 Hz, 1H), 2.41 (s, 3H), 2.39 (dd, *J* = 16.7, 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.4, 148.1, 144.3, 140.2, 138.8, 137.4, 136.5, 135.0, 133.6, 129.8, 129.0, 128.9, 127.5, 127.1, 125.8, 125.5, 125.0, 123.4, 120.1, 118.2, 40.0, 34.2, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{28}H_{25}N_2O_2S_2^+$ 485.1352, found: 485.1330. $[\alpha]_D^{20}$ = -5.2 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 23.7 min and t_{R2}: 57.7 min).

(*R*,*E*)-7-methyl-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

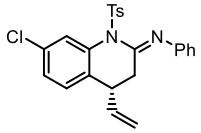


3ai

Prepared following general procedure the product **3ai** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid. (73% yield, 60.5 mg, 99% *ee*）. m.p. 146 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.26 (m, 2H), 7.00 – 7.02 (m, 1H), 6.42 (d, *J* = 8.0 Hz, 2H), 5.75 – 5.64 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 2.51 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.39 (dd, *J* = 16.7, 4.5 Hz,1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.7, 148.2, 144.2, 137.5, 137.1, 136.880, 135.5, 130.3, 129.7, 129.0, 126.6, 126.1, 125.8, 123.3, 120.1, 117.8, 39.4, 34.4, 21.7, 21.4.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{25}N_2O_2S^+$ 417.1631; found: 417.1638. $[\alpha]_D^{20}$ = -24.3 (c =0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}:16.2 min and t_{R2}: 28.8 min).

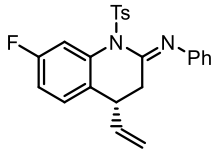
(*R*,*E*)-7-chloro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



3aj

Prepared following general procedure the product **3aj** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (43% yield, 37.3 mg, 99% *ee*） .m.p. 121 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.22–7.24 (m, 2H), 7.18 – 7.20 (m, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 2H), 5.67 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.34 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.53 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.48 (s, 3H), 2.42 (dd, *J* = 16.8, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.9, 144.5, 137.2, 136.6, 136.1, 132.70, 131.8, 129.7, 129.1, 129.0, 127.3, 125.9, 125.2, 123.5, 120.0, 118.4, 39.4, 34.1, 21.7.
HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}ClN_2O_2S^+$ 437.1085; found: 437.1082. $[\alpha]_D^{20}$ = -29.8 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 13.7min and t_{R2}: 21.4 min).

(*R*,*E*)-7-fluoro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



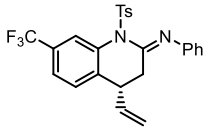
3ak

Prepared following general procedure the product **3ak** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (40% yield, 33.6 mg, 99% *ee*） . m.p. 151 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.46 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.26 (m, 2H), 7.10 – 7.13 (m, 1H), 7.02 – 7.04 (m, 1H), 6.90 – 6.94 (m, 1H), 6.41 – 6.43 (m, 2H), 5.68 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1,1H), 3.34 (dd, *J* = 12.4, 7.0 Hz, 1H), 2.53 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.48 (s, 3H), 2.43 (dd, *J* = 12.3, 8.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.5 Hz), 153.0, 147.9, 144.5, 137.3, 136.8 (d, *J* = 10.6 Hz), 136.4, 129.7, 129.1, 129.0, 128.9 (d, *J* = 3.0 Hz), 127.3 (d, *J* = 9.0 Hz). 123.5, 120.0, 118.1, 112.9 (d, *J* = 25.7 Hz), 112.6 (d, *J* = 21.1 Hz), 39.3, 34.2, 21.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.76.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{21}FN_2NaO_2S^+$ 443.1200; found: 443.1202. $[\alpha]_D^{20}$ = -15.3 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 16.7 min and t_{R2}: 36.4 min).

(*R*,*E*)-N-phenyl-1-tosyl-7-(trifluoromethyl)-4-vinyl-3,4-dihydroquinolin-2(1H)-imin

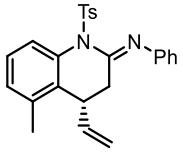


3al

Prepared following general procedure the product **3al** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (53% yield, 50.0 mg, 99% *ee*）. m.p. 134 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 3H), 7.47 (d, J = 7.9 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.26 (m, 2H), 7.03 – 7.05 (m, 1H), 6.43 (d, *J* = 7.3 Hz, 2H), 5.70 (ddd, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 3.42 (dd, *J* = 12.3, 7.0 Hz, 1H), 2.56 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.48 (s, 3H), 2.42 (dd, *J* = 16.8, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 147.8, 147.5, 144.6, 137.1, 137.0, 136.3, 136.2, 135.6, 129.8, 129.1, 126.9, 123.6, 122.5 (q, *J* = 4.5 Hz), 122.2, 120.0, 118.7, 39.8, 33.8, 21.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.40.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{22}F_3N_2O_2S^+$ 471.1349; found: 471.1378. $[\alpha]_D^{20}$ = -28.5 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 7.9 min and t_{R2}: 12.1 min).

(*R*,*E*)-5-methyl-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

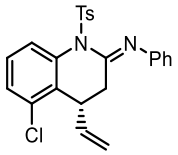


3am

Prepared following general procedure the product **3am** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (45% yield, 37.8 mg, 72% *ee*）. m.p. 117 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.13 (m, 5H), 6.96 – 7.02 (m, 2H), 6.35 (d, *J* = 7.6 Hz, 2H), 5.64 (ddd, *J* = 16.8, 10.2, 5.2 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 17.1 Hz, 1H), 3.52 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.70 (dd, *J* = 16.8, 1.8 Hz, 1H), 2.40 (s, 3H), 2.30 (dd, *J* = 16.8, 5.5 Hz, 1H), 2.23 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.3, 148.3, 144.1, 137.3, 136.2, 135.6, 135.3, 130.9, 130.3, 129.0, 128.7, 127.5, 126.6, 123.2, 123.0, 120.2, 117.0, 36.2, 33.2, 21.7, 18.9.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{25}N_2O_2S^+$ 417.1631; found: 417.1638. $[\alpha]_D^{20}$ = -7.8 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 72% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 17.1 min and t_{R2}: 20.9 min).

(*R*,*E*)-5-chloro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



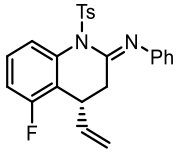
3an

Prepared following general procedure the product **3an** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (29% yield, 25 mg, 99% *ee*）. m.p. 60 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.22 – 7.20 (m, 3H), 7.18 – 7.20 (m, 2H), 6.94 – 6.97 (m, 1H), 6.32 (d, *J* = 7.5 Hz, 2H), 5.58 (ddd, *J* = 17.1, 10.3, 5.0 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.83 (d, *J* = 17.2 Hz, 1H), 3.85 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.71 (dd, *J* = 16.9, 2.0 Hz, 1H), 2.40 (s, 3H), 2.30 (dd, *J*

= 16.9, 5.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 148.0, 144.5, 136.9, 136.8, 135.2, 132.5, 130.5, 130.4, 129.0, 128.7, 127.6, 126.5, 123.8, 123.4, 120.1, 117.3, 36.6, 32.5, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}ClN_2O_2S^+$ 437.1085; found: 437.1082. $[\alpha]_D^{20}$ = -38.8 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 48.8 min and t_{R2}: 52.9 min).

(*R*,*E*)-5-fluoro-N-phenyl-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

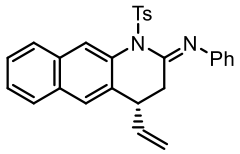


3ao

Prepared following general procedure the product **3ao** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (49% yield, 40.9 mg, 99% *ee*）. m.p. 162 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.27 – 7.21 (m, 2H), 7.02 – 7.04 (m, 1H), 6.95 – 6.98 (m, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 5.66 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.03 (d, *J* = 10.3 Hz, 1H), 4.90 (d, *J* = 17.2 Hz, 1H), 3.80 (dd, *J* = 12.3, 8.0 Hz, 1H), 2.77 (dd, *J* = 16.8, 4.5 Hz, 1H), 2.47 (s, 3H), 2.38 (dd, *J* = 12.3, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8 (d, *J* = 243.0 Hz), 158.2, 152.6, 147.9, 144.4, 137.0 (d, *J* = 9.0 Hz), 135.9, 130.3, 129.0, 128.7, 127.8 (d, *J* = 7.5 Hz), 123.4, 120.8 (d, *J* = 4.0 Hz), 120.1 (d, *J* = 19.5 Hz), 120.0, 117.2, 112.5 (d, *J* = 21.0 Hz), 32.5, 32.3, 32.3, 21.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -120.29.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}FN_2O_2S^+$ 421.1381; found: 421.1381. $[\alpha]_D^{20}$ = -36.9 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 17.9 min and t_{R2}: 18.9 min).

(*R*,*E*)-N-phenyl-1-tosyl-4-vinyl-3,4-dihydrobenzo[g]quinolin-2(1H)-imine

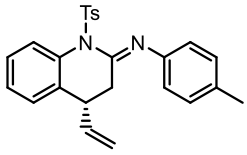


3ap

Prepared following general procedure the product **3ap** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (41% yield, 37.5 mg, 99% *ee*）. m.p. 141 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.39 – 7.44(m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.19 (m, 3H), 6.94 – 6.96 (m, 1H), 6.34 (d, *J* = 7.5 Hz, 2H), 5.72 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 3.42 (dd, *J* = 11.9, 8.0 Hz, 1H), 2.52 (dd, *J* = 16.7, 4.4 Hz, 1H), 2.42 (s, 3H), 2.36 (dd, *J* = 16.7, 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.4, 147.0, 143.3, 136.3, 135.7, 135.5, 131.9, 131.5, 131.3, 130.2, 128.7, 128.0, 127.1, 126.2, 125.3, 125.3, 124.0, 122.4, 122.3, 119.1, 117.3, 39.0, 33.2, 20.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{28}H_{25}N_2O_2S^+$ 453.1631; found: 453.1620. $[\alpha]_D^{20}$= -9.4 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 36.8 min and t_{R2}: 47.4 min).

(*R*,*E*)-N-(p-tolyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



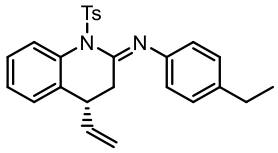
3ba

Prepared following general procedure the product **3ba** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (54% yield, 45.1 mg, 99% *ee*）. m.p. 173 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.28 (m, 3H), 7.18 – 7.08 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.24 (d, *J* = 8.2 Hz, 2H), 5.64 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 4.95 (d, *J* =

17.1 Hz, 1H), 3.28 (dd, *J* = 12.2, 7.4 Hz, 1H), 2.47 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.39 (s, 3H), 2.36 (dd, *J* = 16.8, 8.2 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.6, 145.60, 144.2, 137.6, 136.6, 135.8, 133.5, 132.8, 129.7, 129.5, 129.0, 127.1, 126.3, 125.8, 125.2, 120.0, 117.9, 39.8, 34.3, 21.7, 20.8.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{24}N_2NaO_2S^+$ 439.1451; found: 439.1462. $[\alpha]_D^{20}$ = -45.0 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 14.4 min and t_{R2}: 26.2 min).

(*R*,*E*)-N-(4-ethylphenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

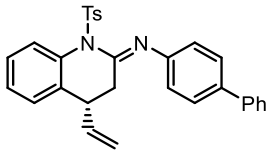


3ca

Prepared following general procedure the product **3ca** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (71% yield, 60.8 mg, 99% *ee*）. m.p. 107 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.71 (m, 1H), 7.36 – 7.29 (m, 3H), 7.22 – 7.15 (m, 2H), 7.05 – 7.07 (m, 2H), 6.34 (d, *J* = 8.0 Hz, 2H), 5.72 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 3.36 (dd, *J* = 12.2, 7.3 Hz, 1H), 2.61 – 2.56 (m, 2H), 2.54 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.46 (s, 3H), 2.44(dd, *J* = 16.8, 8.2 Hz, 1H), 1.20 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.5, 145.8, 144.2, 139.2, 137.6, 136.6, 135.8, 133.5, 129.7, 129.0, 128.3, 127.1, 126.3, 125.8, 125.2, 120.0, 118.0, 39.9, 34.3, 28.2, 21.7, 15.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{26}H_{27}N_2O_2S^+$ 431.1788, found: 431.1796. $[\alpha]_D^{20}$ = -26.9 (c = 0.7, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 19.2 min and t_{R2}: 32.4 min).

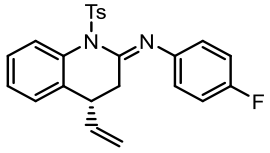
(*R*,*E*)-N-([1,1'-biphenyl]-4-yl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



3da

Prepared following general procedure the product **3da** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1) on silica gel to provide the title compound as a viscous liquid (73% yield, 69.8 mg, 99% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.42 (m, 2H), 7.30 – 7.37 (m, 4H), 7.24 – 7.17 (m, 2H), 6.49 (d, *J* = 8.3 Hz, 2H), 5.74 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 3.39 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.60 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.51(dd, *J* = 16.8, 8.1 Hz, 1H), 2.48 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.6, 147.4, 144.3, 140.7, 137.5, 136.5, 136.3, 135.7, 133.3, 129.7, 129.0, 128.8, 127.7, 127.2, 127.0, 126.8, 126.4, 125.9, 125.2, 120.5, 118.1, 39.8, 34.4, 21.7. **HRMS (APCI)** (m/z): $[M+H]^+$ Calcd. for $C_{30}H_{27}N_2O_2S^+$ 479.1788; found: 479.1771. $[\alpha]_D^{20}$ = -90.0 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 14.4 min and t_{R2}: 24.8 min).

(*R*,*E*)-N-(4-fluorophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



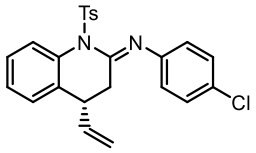
3ea

Prepared following general procedure the product **3ea** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1) on silica gel to provide the title compound as a white solid (66% yield, 55.1 mg, 99% *ee*). m.p. 149 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.30 – 7.23 (m, 3H), 7.12 (m, *J* = 19.4, 13.0, 3.8 Hz, 2H), 6.87 – 6.80 (m, 2H), 6.33 – 6.22 (m, 2H), 5.64 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 17.1 Hz, 1H), 3.29 (dd, *J* = 12.1, 7.3 Hz, 1H), 2.44 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.39

(s, 3H), 2.34 (dd, *J* = 16.8, 8.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.1 (d, *J* = 241.6 Hz), 153.2, 143.3 (d, *J* = 27.2 Hz), 136.5, 135.4, 134.5, 132.2, 128.6, 128.0(d, *J* = 9.1 Hz), 126.1, 125.3, 124.9, 124.1, 120.3 (d, *J* = 7.6 Hz), 117.0, 114.7 (d, *J* = 22.7 Hz)., 38.7, 33.3, 20.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -120.67.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{21}FN_2NaO_2S^+$ 443.1200; found: 443.1202. $[\alpha]_D^{20}$ = -33.0 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 21.4 min and t_{R2}: 37.5 min).

(*R*,*E*)-N-(4-chlorophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

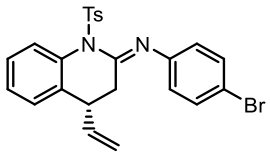


3fa

Prepared following general procedure the product **3fa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (57% yield, 49.6 mg, 99% *ee*）. m.p. 115 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.37 (m, 3H), 7.21 – 7.23 (m, 1H), 7.19 – 7.16 (m, 3H), 6.39 – 6.26 (m, 2H), 5.71 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.16 (d, *J* = 10.3 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 3.37 (dd, *J* = 12.2, 7.3 Hz, 1H), 2.51 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.47 (s, 3H), 2.42 (dd, *J* = 16.8, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.1, 146.7, 144.3, 137.4, 136.4, 135.5, 133.2, 132.7, 129.6, 129.1, 129.0, 128.7, 127.2, 126.4, 126.0, 125.1, 121.4, 118.1, 39.7, 34.3, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}lN_2O_2S^+$ 437.1085; found: 437.1082. $[\alpha]_D^{20}$ = -6.4 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 19.2 min and t_{R2}: 32.2 min).

(*R*,*E*)-N-(4-bromophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

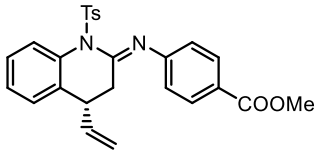


3ga

Prepared following general procedure the product **3ga** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (37% yield, 35.9 mg, 99% *ee*）. m.p. 179 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.38 – 7.31 (m, 5H), 7.21 – 7.24 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 6.31 – 6.23 (m, 2H), 5.71 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.16 (d, *J* = 10.3 Hz, 1H), 5.03 (d, *J* = 17.1, 1H), 3.37 (dd, *J* = 12.2, 7.3 Hz, 1H), 2.51 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.47 (s, 3H), 2.41 (dd, *J* = 16.8, 8.1 Hz, 1H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.0, 147.1, 144.4, 137.4, 136.3, 135.5, 133.1, 132.0, 129.6, 129.0, 127.2, 126.4, 126.0, 125.1, 121.8, 118.1, 116.3, 77.2, 77.0, 76.8, 39.7, 34.3, 21.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}BrN_2O_2S^+$ 481.0586; found: 481.0596. $[\alpha]_D^{20}$ = -4.7 (c = 0.2, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 21.3 min and t_{R2}: 33.9 min).

Methyl(*R*,*E*)-4-((1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-ylidene)amino)benzoate



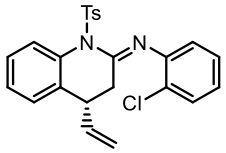
3ha

Prepared following general procedure the product **3ha** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (53% yield, 48.8 mg, 88% *ee*）. m.p. 162 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 12.6, 8.3 Hz, 4H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.21 – 7.07 (m, 2H), 6.35 (d, *J* = 8.3 Hz, 2H), 5.63 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.95 (d, *J* = 17.1 Hz, 1H), 3.80 (s, 3H), 3.30 (dd, *J* = 12.2, 7.0 Hz, 1H), 2.43 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.40 (s, 3H), 2.33

(dd, *J* = 16.8, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 153.5, 152.4, 144.5, 137.2, 136.3, 135.4, 133.0, 130.9, 129.7, 129.1, 127.3, 126.5, 126.1, 125.2, 125.1, 119.9, 118.2, 52.0, 39.7, 34.5, 21.7.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{24}FN_2NaO_2S^+$ 483.1349; found: 483.1346. $[\alpha]_D^{20}$ = -21.5 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 88% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 32.7 min and t_{R2}: 64.8 min).

(*R*,*E*)-N-(2-chlorophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

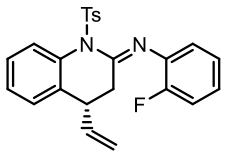


3ia

Prepared following general procedure the product **3ia** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (38% yield, 33.4 mg, 99% *ee*）. m.p. 189 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.24 – 7.20 (m, 3H), 7.19 – 7.12 (m, 2H), 7.04 – 7.07 (m, 1H), 6.87 – 6.89 (m, 1H), 6.38 (d, *J* = 7.4 Hz, 1H), 5.70 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.36 (dd, *J* = 11.8, 7.4 Hz, 1H), 2.43 (dd, *J* = 16.7, 4.4 Hz, 1H), 2.38 (s, 3H), 2.30 ((dd, *J* = 16.8, 8.1 Hz, 1H)). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.9, 144.3, 143.2, 136.6, 135.4, 134.7, 132.3, 128.8, 128.4, 128.1, 126.4, 126.1, 125.3, 124.8, 123.8, 123.4, 123.2, 120.4, 117.1, 38.6, 34.0, 20.6.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{21}ClN_2NaO_2S^+$ 459.0904, found: 459.0902. $[\alpha]_D^{20}$ = -5.6 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 20.5 min and t_{R2}: 34.8 min).

(*R*,*E*)-N-(2-fluorophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



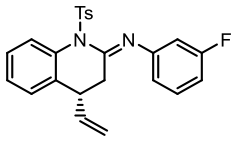
3ja

Prepared following general procedure the product **3ja** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (56% yield, 50.3 mg, 99% *ee*）. m.p. 105 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.28 (m, *J* = 8.0, 1.5 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.10 (d, *J* = 6.7 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.41 – 6.43(m, *J* = 12.1, 4.6 Hz, 1H), 5.65 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.96 (d, *J* = 17.1 Hz, 1H), 3.29 (dd, *J* = 12.1, 7.5 Hz, 1H), 2.45 (dd, *J* = 16.8, 4.5 Hz, 1H), 2.38 (s, 3H), 2.35 (dd, *J* = 16.8, 8.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 152.4 (d, *J* = 244.6 Hz), 143.3, 136.4, 135.4, 134.6 (d, *J* = 30.2 Hz), 134.5 (d, *J* = 13.6 Hz), 132.3, 128.5, 128.0, 126.1, 125.3, 124.9, 124.1, 123.5 (d, *J* = 7.5 Hz), 123.3 (d, *J* = 4.5 Hz), 121.9, 117.0, 115.0 (d, *J* = 19.6 Hz), 38.5, 33.7, 20.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -125.93.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{21}FN_2NaO_2S^+$ 443.1200; found: 443.1202. $[\alpha]_D^{20}$ = -126.0 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 12.8 min and t_{R2}: 19.6 min).

(*R*,*E*)-N-(3-fluorophenyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

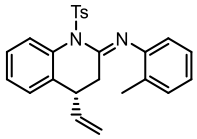


3ka

Prepared following general procedure the product **3ka** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (52% yield, 46.5 mg, 99% *ee*）. m.p. 117 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.12 (m, 1H), 7.12 – 7.06 (m, 2H), 6.62 – 6.65 (m,

1H), 6.12 – 6.13 (m, 1H), 5.98 – 6.00 (m, 1H), 5.64 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 4.96 (d, *J* = 17.1 Hz, 1H), 3.30 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.44 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.40 (s, 3H), 2.35 (dd, *J* = 16.8, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.6 Hz), 153.0, 148.8 (d, *J* = 9.1 Hz) 143.4, 136.3, 135.4, 134.5, 132.1, 129.2 (d, *J* = 9.1 Hz), 128.6, 128.0, 126.2, 125.4, 124.9, 124.1, 117.1, 114.8 (d, *J* = 1.5 Hz), 109.1 (d, *J* = 21.2 Hz), 106.4 (d, *J* = 22.9 Hz), 38.6, 33.3, 20.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.81. **HRMS (APCI)** (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}FN_2NaO_2S^+$ 421.1381; found: 421.1381. $[\alpha]_D^{20}$ = -19.4 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 12.0 min and t_{R2}: 22.0 min).

(*R*,*E*)-N-(o-tolyl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

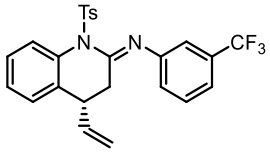


3la

Prepared following general procedure the product **3la** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (40% yield, 33.3 mg, 99% *ee*）. m.p. 61 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.35 (m, 3H), 7.23 – 7.12 (m, 3H), 7.04 – 7.07 (m, 1H), 6.96 (d, *J* = 10.2, 1H), 6.28 (d, *J* = 7.5 Hz, 1H), 5.81 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.21 (d, *J* = 10.2, 1H), 5.11 (d, *J* = 17.1, 1H), 3.45 (dd, *J* = 12.2, 7.3 Hz, 1H)), 2.50 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.44 (s, 3H), 2.38 (dd, *J* = 16.8, 8.1 Hz, 1H), 1.97 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 147.1, 144.0, 138.3, 136.5, 136.1, 133.7, 130.5, 129.2, 129.0, 128.2, 127.2, 126.5, 126.4, 125.8, 124.6, 123.4, 119.2, 118.1, 40.1, 35.0, 21.7, 17.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{25}N_2O_2S^+$ 417.1631; found: 417.1638. $[\alpha]_D^{20}$ = -18.5 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 15.1 min and t_{R2}: 21.2 min).

(*R*,*E*)-1-tosyl-N-(3-(trifluoromethyl)phenyl)-4-vinyl-3,4-dihydroquinolin-2(1H)-imi

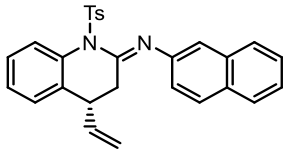


3ma

Prepared following general procedure the product **3ma** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (79% yield, 65.2 mg, 99% *ee*）. m.p. 117 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.22 – 7.27 (m, 2H), 7.19 (d, *J* = 7.1 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.42 (s, 1H), 5.72 (ddd, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.40 (dd, *J* = 12.3, 7.1 Hz, 1H), 2.52 – 2.49 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.48 (s, 3H), 2.41 (dd, *J* = 16.8, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.2, 148.4, 144.7, 137.2, 136.4, 135.4, 132.9, 129.7, 129.6, 129.1, 127.3, 126.5, 126.1, 125.1, 123.5, 120.1, 118.3, 117.0, 39.6, 34.3, 21.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.81.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{21}F_3N_2NaO_2S^+$ 493.1168; found: 493.1176. $[\alpha]_D^{20}$ = -24.6 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 9.2 min and t_{R2}: 15.5 min).

(*R*,*E*)-N-(naphthalen-2-yl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine



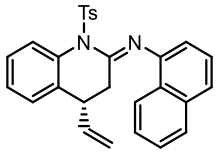
3na

Prepared following general procedure the product **3na** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (70% yield, 64.0 mg, 99% *ee*）. m.p. 174 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.43 (m, 1H), 7.33 – 7.37 (m, 4H), 7.20 – 7.24 (m, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.77 (s, 1H), 6.60 – 6.62 (m,

1H), 5.71 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.38 (d, *J* = 4.9 Hz, 1H), 2.57 (dd, *J* = 16.9, 4.7 Hz, 1H), 2.49 (s, 3H), 2.42 (dd, *J* = 16.8, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.9, 145.8, 144.3, 137.6, 136.5, 135.7, 134.0, 133.4, 130.4, 129.7, 129.1, 128.9, 127.8, 127.2, 127.2, 126.4, 126.4, 126.0, 125.1, 124.6, 121.1, 118.1, 116.0, 39.8, 34.6, 21.8.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{28}H_{24}N_2NaO_2S^+$ 475.1451; found: 475.1468. $[\alpha]_D^{20}$ = -18.6 (c = 0.5, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 20.0 min and t_{R2}: 33.3 min).

(*R*,*E*)-N-(naphthalen-1-yl)-1-tosyl-4-vinyl-3,4-dihydroquinolin-2(1H)-imine

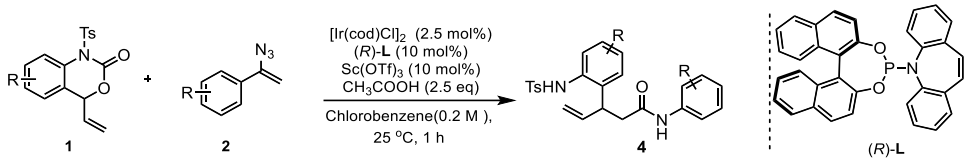


3oa

Prepared following general procedure the product **3oa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 20:1） on silica gel to provide the title compound as a white solid (51% yield, 46.4 mg, 99% *ee*）. m.p. 159 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.55 (m, 2H), 7.43 – 7.46(m, 1H), 7.38 – 7.30 (m, 3H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.22 (m, 1H), 7.16 (d, *J* = 6.9 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 1H), 5.74 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.42 (dd, *J* = 12.0, 6.7 Hz, 1H), 2.52 (dd, *J* = 16.9, 4.7 Hz, 1H), 2.46 (dd, *J* = 16.8, 8.1 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.3, 144.8, 144.2, 138.2, 136.4, 136.0, 134.2, 133.7, 129.3, 129.3, 127.7, 127.2, 126.6, 126.5, 126.3, 125.9, 125.8, 125.5, 124.6, 124.1, 123.5, 118.2, 114.6, 40.0, 35.0, 21.7.

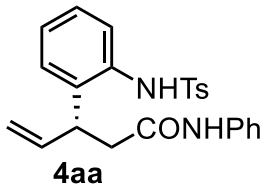
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{28}H_{24}N_2NaO_2S^+$ 475.1451; found: 475.1468. $[\alpha]_D^{20}$ = -47.0 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 10.2 min and t_{R2}: 13.2 min).

7. General Procedure for Synthesis of 4



In the glove box, $[Ir(cod)Cl]_2$ (2.5 mol%, 1.7 mg) and (*R*)-**L** (10 mol%, 5 mg) were added to a screw-capped glass vial fitted with a magnetic stirring bar, 0.5 mL of chlorobenzene was added and stirred for 15 min. To the mixture was added **1** (0.1 mmol ,1.0 eq.), $Sc(OTf)_3$ (10 mol%, 5 mg), **2** (0.15 mmol, 1.5 eq.） and CH_3COOH (15 uL, 0.25 mmol). The reaction was stirred at 25 °C for 1 h with the stopper tightly closed. The resulting mixture was filtered through celite, concentrated in vacuo and then purified via silica gel flash column chromatography to afford the product **4**.

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide

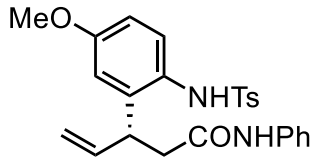


4aa

Prepared following general procedure the product **4aa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (93% yield, 39.1 mg, 99% *ee*）. m.p. 170 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.16 (m, 6H), 7.15 – 6.99 (m, 4H), 5.56 – 5.34 (m, 1H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 17.3 Hz, 1H), 4.01 – 3.79 (m, 1H), 2.91 (dd, *J* = 15.2, 4.3 Hz, 1H), 2.57 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.62, 140.96, 136.80, 134.86, 134.79, 134.75, 131.68, 127.13, 126.40, 126.07, 125.10, 124.69, 124.44, 121.99, 117.47, 111.87, 39.98, 36.02, 18.97.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}N_2O_3S^+$ 421.1580, found: 421.1591. $[\alpha]_D^{20}$ = + 113.3 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 19.1 min and t_{R2}: 21.7 min).

(*R*)-3-(5-methoxy-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide

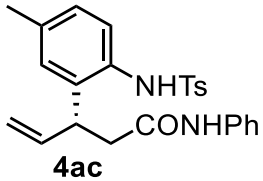


4ab

Prepared following general procedure the product **4ab** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (81% yield, 36.3 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.81 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.27 – 7.16 (m, 4H), 7.12 (d, *J* = 8.7, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.69 – 6.57 (m, 2H), 5.38 – 5.30 (m, 1H), 4.92 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 17.3 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.70 (s, 3H), 2.85 (dd, *J* = 15.2, 4.8 Hz, 1H), 2.55 (dd, *J* = 15.1, 10.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 158.6, 143.4, 140.3, 139.1, 137.6, 137.0, 129.7, 129.5, 128.9, 127.3, 126.6, 124.4, 120.0, 114.4, 114.0, 112.4, 55.35, 42.6, 38.7, 21.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{25}N_2NaO_4S^+$ 473.1505, found: 473.1513. $[\alpha]_D^{20}$ = + 186.1 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ^{o}C, 254 nm, t_{R1}: 22.0 min and t_{R2}: 23.9 min).

(*R*)-3-(5-methyl-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide



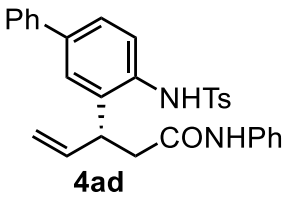
4ac

Prepared following general procedure the product **4ac** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (85% yield, 37.1 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.60 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.10 – 7.06 (m, 2H), 6.96 – 6.86 (m, 2H), 5.49 –

5.40 (m, 1H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 17.4 Hz, 1H), 3.93 – 3.82 (m, 1H), 2.88 (dd, *J* = 15.1, 4.7 Hz, 1H), 2.57 (dd, *J* = 15.1, 10.1 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 143.4, 139.5, 137.6, 137.5, 137.2, 137.0, 131.4, 129.7, 129.0, 128.9, 128.4, 127.3, 124.4, 120.0, 114.3, 42.5, 38.6, 21.5, 21.1.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{25}N_2NaO_3S^+$ 457.1556, found: 457.1551. $[\alpha]_D^{20}$ = + 142.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 16.6 min and t_{R2}: 18.6 min).

(*R*)-3-(4-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-3-yl)-N-phenylpent-4-enamide



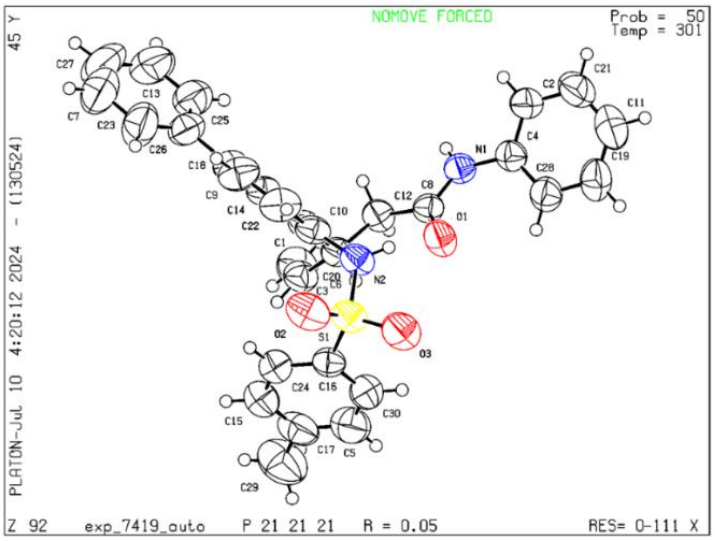
4ad

Prepared following general procedure the product **4ad** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (74% yield, 37.5 mg, 99% *ee*）. m.p. 138 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.28 (m, 8H), 7.28 – 7.18 (m, 4H), 7.06 (t, *J* = 7.4 Hz, 1H), 5.55 – 5.43 (m, 1H), 4.99 (d, *J* = 10.5 Hz, 1H), 4.89 (d, *J* = 17.4 Hz, 1H), 4.00 – 3.87 (m, 1H), 2.96 (dd, *J* = 15.3, 4.2 Hz, 1H), 2.62 (dd, *J* = 15.3, 10.4 Hz, 1H), 2.37 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 143.5, 140.1, 139.6, 139.3, 137.7, 137.4, 137.3, 133.5, 129.7, 129.0, 128.8, 127.5, 127.2, 127.0, 126.3, 124.6, 120.0, 114.5, 42.5, 38.4, 21.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{30}H_{28}N_2NaO_3S^+$ 519.1713, found: 519.1719. $[\alpha]_D^{20}$ = + 114.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 21.1 min and t_{R2}: 26.4 min).

A colorless stick-shaped crystal of **4ad** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **4ad** in hexane/ dichloromethane (3:1).

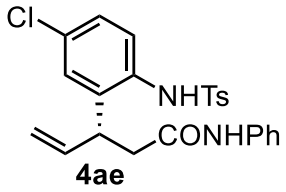
Figure S2. Crystal data and structure refinement for **4ad** (CCDC） is available from the Cambridge Crystallographic Data Centre (CCDC). Displacement ellipsoids are drawn at the 50% probability level.



Identification code	exp_7419_auto
Empirical formula	$C_{30}H_{28}N_2O_3S$
Formula weight	496.60
Temperature/K	301.1(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.59150(10)
b/Å	15.2029(3)
c/Å	23.0299(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3008.07(8)
Z	4

ρ_{calc}g/cm^3	1.097
μ/mm^{-1}	1.189
F(000)	1048.0
Crystal size/mm^3	0.25 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.678 to 151.412
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 19, -20 ≤ l ≤ 28
Reflections collected	17693
Independent reflections	5982 [R_{int} = 0.0294, R_{sigma} = 0.0333]
Data/restraints/parameters	5982/3/330
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1386
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.1423
Largest diff. peak/hole / e Å^{-3}	0.18/-0.17
Flack parameter	0.024(10)

(*R*)-3-(5-chloro-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide



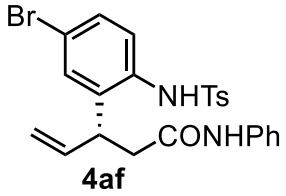
4ae

Prepared following general procedure the product **4ae** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (88% yield, 40.0 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.68 – 7.54 (m, 3H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.05 (m, 2H), 7.01 (d, *J* = 2.4 Hz, 1H), 5.35 – 5.20 (m, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 4.79 (d, *J* = 17.4 Hz, 1H), 3.86 – 3.66 (m, 1H), 2.92 (dd, *J* = 15.7, 3.8 Hz, 1H), 2.51 (dd, *J* = 15.7, 10.6 Hz, 1H), 2.36 (s,

3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 143.7, 139.5, 138.6, 137.3, 137.0, 132.9, 132.3, 129.8, 129.0, 128.5, 127.8, 127.1, 124.7, 120.1, 114.7, 42.3, 37.7, 21.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{23}ClN_2NaO_3S^+$ 477.1010, found: 477.1017. $[\alpha]_D^{20}$ = + 174.5 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 15.6 min and t_{R2}: 17.9 min).

(*R*)-3-(5-bromo-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide

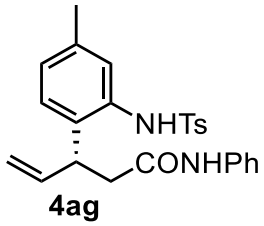


4af

Prepared following general procedure the product **4af** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (80% yield, 39.9 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.23 – 7.15 (m, 3H), 7.10 – 7.06 (m, 1H), 5.35 – 5.23 (m, 1H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.80 (d, *J* = 17.3 Hz, 1H), 3.82 – 3.71 (m, 1H), 2.93 (dd, *J* = 15.7, 3.8 Hz, 1H), 2.51 (dd, *J* = 15.7, 10.6 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.0, 143.7, 139.7, 138.6, 137.2, 137.0, 133.5, 131.4, 130.7, 129.8, 129.0, 128.7, 127.1, 124.7, 120.3, 120.1, 114.8, 42.3, 37.6, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}BrN_2O_3S^+$ 499.0686, found: 499.0678. $[\alpha]_D^{20}$ = + 145.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 16.1 min and t_{R2}: 18.6 min).

(*R*)-3-(4-methyl-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide

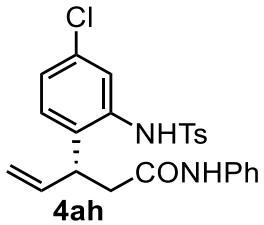


4ag

Prepared following general procedure the product **4ag** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (65% yield, 28.4 mg, 94% *ee*）. m.p. 189 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.49 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.16 (m, 5H), 7.09 – 7.04 (m, 2H), 6.98 – 6.90 (m, 2H), 5.48 – 5.31 (m, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 4.81 (d, *J* = 17.4 Hz, 1H), 3.89 – 3.75 (m, 1H), 2.89 (dd, *J* = 15.3, 4.3 Hz, 1H), 2.53 (dd, *J* = 15.2, 10.5 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 143.4, 139.5, 137.5, 137.3, 134.2, 133.9, 129.6, 128.9, 128.3, 127.9, 127.6, 127.2, 124.5, 120.0, 114.1, 42.5, 38.1, 21.5, 21.0.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{25}N_2NaO_3S^+$ 457.1556, found: 457.1551. $[\alpha]_D^{20}$ = + 143.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 94% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ºC, 254 nm, t_{R1}: 16.9 min and t_{R2}: 19.6 min).

(*R*)-3-(4-chloro-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide



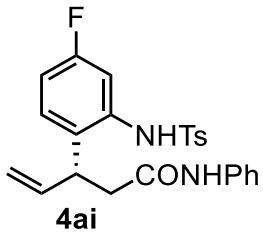
4ah

Prepared following general procedure the product **4ah** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (55% yield, 25.5 mg, 99% *ee*）. m.p. 145 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.40 – 7.35 (m, 3H), 7.27 – 7.24 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.13 – 7.03 (m,

2H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.40 – 5.27 (m, 1H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.80 (d, *J* = 17.4 Hz, 1H), 3.87 – 3.71 (m, 1H), 2.93 (dd, *J* = 15.6, 3.7 Hz, 1H), 2.51 (dd, *J* = 15.6, 10.8 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 143.7, 138.9, 137.2, 137.0, 135.5, 135.5, 132.9, 130.0, 129.7, 129.0, 127.2, 126.8, 126.4, 124.7, 120.0, 114.6, 42.3, 37.5, 21.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{23}ClN_2NaO_3S^+$ 477.1010, found: 477.1017. $[\alpha]_D^{20}$ = + 125.9 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 18.0 min and t_{R2}: 20.4 min).

(*R*)-3-(4-fluoro-2-((4-methylphenyl)sulfonamido)phenyl)-N-phenylpent-4-enamide

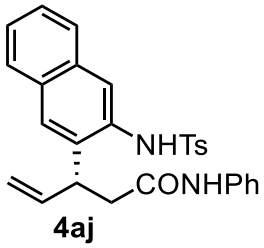


4ai

Prepared following general procedure the product **4ai** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (61% yield, 25.8 mg, 99% *ee*）. m.p. 172 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.05 (m, 2H), 7.03 – 6.99 (m, 2H), 6.82 – 6.77 (m, 2H), 5.44 – 5.32 (m, 1H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 17.4 Hz, 1H), 3.87 – 3.75 (m, 1H), 2.94 (dd, *J* = 15.5, 3.7 Hz, 1H), 2.52 (dd, *J* = 15.5, 10.8 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 161.4 (d, *J* = 246.3 Hz), 143.7, 139.2, 137.2, 137.0, 135.8 (d, *J* = 10.7 Hz), 132.3, 129.8, 129.0, 127.1, 124.7, 120.1, 114.4, 113.6 (d, *J* = 21.2 Hz), 113.0 (d, *J* = 24.1 Hz), 42.3, 37.4, 21.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.6.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{23}FN_2NaO_3S^+$ 461.1306, found: 461.1305. $[\alpha]_D^{20}$ = + 134.2 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 18.0 min and t_{R2}: 20.4 min).

(*R*)-3-(3-((4-methylphenyl)sulfonamido)naphthalen-2-yl)-N-phenylpent-4-enamide

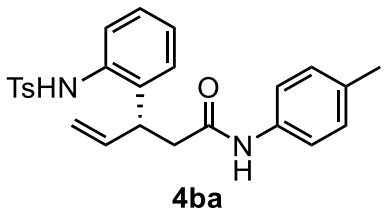


4aj

Prepared following general procedure the product **4aj** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (73% yield, 34.2 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.4 Hz, 1H), 7.77 (s, 1H), 7.72 – 7.59 (m, 5H), 7.55 (s, 1H), 7.41 – 7.36 (m, 4H), 7.23 – 7.12 (m, 4H), 7.04 – 7.01 (m, 1H), 5.60 – 5.44 (m, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.91 (d, *J* = 17.3 Hz, 1H), 4.03 – 3.96 (m, 1H), 3.01 (dd, *J* = 15.4, 4.3 Hz, 1H), 2.69 (dd, *J* = 15.4, 10.3 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.4, 143.5, 139.6, 137.4, 137.3, 136.2, 1325, 132.4, 131.8, 129.7, 128.9, 128.1, 127.6, 127.2, 126.3, 126.0, 124.6, 124.5, 120.1, 114.3, 42.9, 38.3, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{28}H_{27}N_2O_3S^+$ 471.1737, found: 471.1733. $[\alpha]_D^{20}$ = + 157.3 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 21.8 min and t_{R2}: 25.4 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(p-tolyl)pent-4-enamide



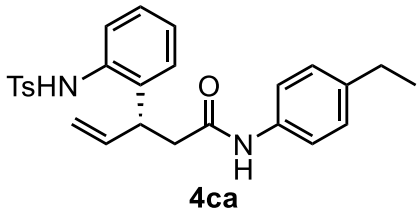
4ba

Prepared following general procedure the product **4ba** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (99% yield, 43.1 mg, 99% *ee*）. m.p.

182 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 1H), 7.29 – 7.25 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.03 (m, 5H), 5.50 – 5.37 (m, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* = 17.4 Hz, 1H), 3.92 – 3.83 (m, 1H), 2.90 (dd, *J* = 15.2, 4.2 Hz, 1H), 2.54 (dd, *J* = 15.1, 10.4 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 143.4, 139.4, 137.4, 134.8, 134.3, 134.2, 129.7, 129.4, 128.6, 127.6, 127.2, 127.0, 126.9, 120.2, 114.3, 425, 38.4, 21.5, 20.9.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{25}N_2NaO_3S^+$ 457.1556, found: 457.1551. $[\alpha]_D^{20}$ = + 89.7 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 17.4 min and t_{R2}: 20.9 min).

***(R)-N*-(4-ethylphenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

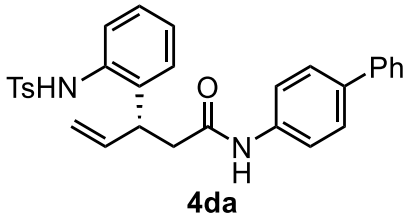


4ca

Prepared following general procedure the product **4ca** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (83% yield, 37.6 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.70 – 7.56 (m, 3H), 7.32 – 7.25 (m, 3H), 7.18 (d, *J* = 6.9 Hz, 2H), 7.15 – 7.01 (m, 5H), 5.50 – 5.34 (m, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.83 (d, *J* = 17.3 Hz, 1H), 3.87 (s, 1H), 2.90 (d, *J* = 15.0 Hz, 1H), 2.64 – 2.49 (m, 3H), 2.36 (s, 3H), 1.18 (t, *J* = 8.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 143.4, 140.6, 139.4, 137.4, 137.3, 135.1, 134.2, 129.7, 128.6, 128.2, 127.5, 127.2, 126.9, 120.3, 114.3, 42.4, 38.3, 28.3, 21.5, 15.7.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_3S^+$ 449.1893, found: 449.1908. $[\alpha]_D^{20}$ = + 147.6 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 15.3 min and t_{R2}: 19.1 min).

***(R)-N*-([1,1'-biphenyl]-4-yl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

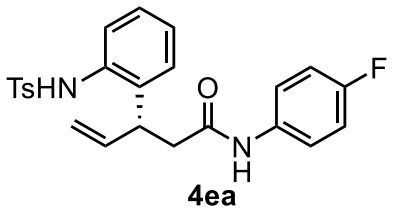


4da

Prepared following general procedure the product **4da** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (42% yield, 21.6 mg, 95% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.40 (m, 11H), 7.35 – 7.29 (m, 1H), 7.29 – 7.19 (m, 5H), 7.18 – 7.10 (m, 3H), 5.58 – 5.49 (m, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.90 (d, *J* = 17.4 Hz, 1H), 4.04 – 3.92 (m, 1H), 2.95 (dd, *J* = 14.9, 4.5 Hz, 1H), 2.62 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 143.5, 140.4, 139.3, 137.4, 137.3, 136.7, 134.2, 129.7, 128.8, 128.7, 127.7, 127.6, 127.3, 127.2, 127.1, 127.0, 126.9, 120.3, 114.6, 42.6, 38.9, 21.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{30}H_{28}N_2NaO_3S^+$ 519.1713, found: 519.1719. $[\alpha]_D^{20}$ = + 145.2 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 95% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ^{o}C, 254 nm, t_{R1}: 27.2 min and t_{R2}: 31.3 min).

***(R)-N*-(4-fluorophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**



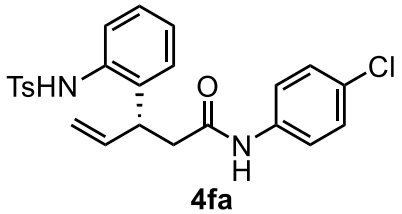
4ea

Prepared following general procedure the product **4ea** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel

to provide the title compound as a yellow liquid (91% yield, 40.2 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.72 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.25 – 7.17 (m, 3H), 7.15 – 7.04 (m, 3H), 6.93 – 6.89 (m, 2H), 5.50 – 5.42 (m, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 17.9 Hz, 1H), 3.93 – 3.88 (m, 1H), 2.89 (dd, *J* = 15.2, 4.6 Hz, 1H), 2.60 (dd, *J* = 15.2, 10.3 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 159.4 (d, *J* = 243.9 Hz), 143.6, 139.3, 137.3 (d, *J* = 51.1 Hz), 134.1, 133.5, 129.7, 128.7, 127.6, 127.2, 127.0 (d, *J* = 20.4 Hz), 121.9 (d, *J* = 7.7 Hz), 115.6, 115.4, 114.5, 42.3, 38.6, 21.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.8.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{23}FN_2NaO_3S^+$ 461.1306, found: 461.1305. $[\alpha]_D^{20}$ = + 164.1 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 17.6 min and t_{R2}: 19.2 min).

***(R)-N*-(4-chlorophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**



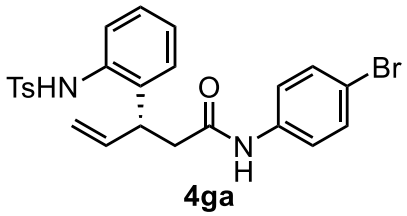
4fa

Prepared following general procedure the product **4fa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (73% yield, 32.8 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.82 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.14 (m, 5H), 7.13 – 7.07 (m, 3H), 5.57 – 5.41 (m, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 3.98 – 3.84 (m, 1H), 2.89 (dd, *J* = 15.2, 4.7 Hz, 1H), 2.62 (dd, *J* = 15.2, 10.1 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.4, 143.7, 139.2, 137.5, 137.1, 136.1, 134.1, 129.7, 129.4, 128.9, 128.7, 127.7, 127.2, 127.0, 121.2, 114.6, 42.4, 38.8, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}ClN_2O_3S^+$ 455.1191, found: 455.1193. $[\alpha]_D^{20}$ = + 87.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent,

hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 16.0 min and t_{R2}: 17.6 min).

***(R)-N*-(4-bromophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

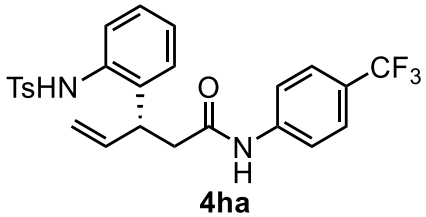


4ga

Prepared following general procedure the product **4ga** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (58% yield, 29.3 mg, 99% *ee*）.m.p.178 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 3H), 7.38 – 7.19 (m, 6H), 7.16 – 7.09 (m, 4H), 5.61 – 5.44 (m, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.89 (d, *J* = 17.3 Hz, 1H), 3.97 – 3.94 (m, 1H), 2.90 (dd, *J* = 15.1, 4.7 Hz, 1H), 2.63 (dd, *J* = 15.0, 10.1 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 143.7, 139.2, 137.5, 137.1, 136.6, 134.1, 131.9, 129.7, 128.8, 127.7, 127.2, 127.0, 121.5, 117.0, 114.7, 42.5, 39.1, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}BrN_2O_3S^+$ 499.0686, found: 499.0678. $[\alpha]_D^{20}$ = + 83.9 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 18.5 min and t_{R2}: 20.3 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(4-(trifluoromethyl)phenyl)pent-4-enamide

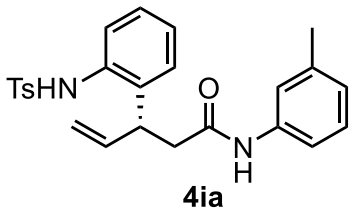


4ha

Prepared following general procedure the product **4ha** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (55% yield, 27.5 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.89 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.07 (m, 4H), 5.62 – 5.50 (m, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.92 (d, *J* = 17.4 Hz, 1H), 4.06 – 3.93 (m, 1H), 2.93 (dd, *J* = 14.9, 4.8 Hz, 1H), 2.71 (dd, *J* = 14.7, 10.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 143.9, 140.7, 139.1, 137.6, 137.0, 134.0, 13.0, 128.9, 127.7, 127.4, 127.3, 127.0, 126.1 (d, *J* = 3.5 Hz), 119.5, 114.9, 42.5, 39.3, 21.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.1.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}F_3N_2O_3S^+$ 489.1454, found: 489.1466. $[\alpha]_D^{20}$ = + 97.2 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ^{o}C, 254 nm, t_{R1}: 13.6 min and t_{R2}: 14.4 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(m-tolyl)pent-4-enamide

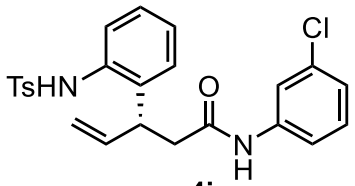


4ia

Prepared following general procedure the product **4ia** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (96% yield, 42.2 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.54 (s, 1H), 7.32 – 7.01 (m, 9H), 6.88 (d, *J* = 7.2 Hz, 1H), 5.49 – 5.38 (m, 1H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.84 (d, *J* = 17.3 Hz, 1H), 3.96 – 3.77 (m, 1H), 2.90 (dd, *J* = 15.3, 4.2 Hz, 1H), 2.56 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 143.5, 139.4, 138.8, 137.5, 137.4, 137.3, 134.2, 129.7, 128.7, 128.6, 127.6, 127.2, 127.0, 125.3, 120.66, 117.2, 114.3, 42.5, 38.3, 21.5, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{26}H_{26}N_2O_3S^+$ 435.1737, found: 435.1730. $[\alpha]_D^{20}$ = + 133.4 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 18.1 min and t_{R2}: 21.9 min).

***(R)-N*-(3-chlorophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

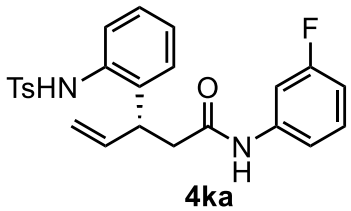


4ja

Prepared following general procedure the product **4ja** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (73% yield, 33.1 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 16.9 Hz, 1H), 7.85 (d, *J* = 14.9 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.28 – 7.20 (m, 3H), 7.16 – 7.09 (m, 5H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.60 – 5.41 (m, 1H), 4.99 (d, *J* = 10.5 Hz, 1H), 4.88 (d, *J* = 17.4 Hz, 1H), 3.95 – 3.94 (m, 1H), 2.90 (dd, *J* = 15.2, 4.9 Hz, 1H), 2.64 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.5, 143.7, 139.2, 138.7, 137.5, 137.1, 134.5, 134.1, 129.9, 129.8, 128.8, 127.7, 127.2, 127.0, 124.4, 120.0, 118.0, 114.7, 42.4, 39.0, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}ClN_2O_3S^+$ 455.1191, found: 455.1193. $[\alpha]_D^{20}$ = + 73.9 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 15.4 min and t_{R2}: 16.9 min).

***(R)-N*-(3-fluorophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

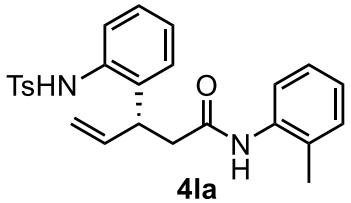


4ka

Prepared following general procedure the product **4ka** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (60% yield, 26.7 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.75 (s, 1H), 7.67 (d, *J* = 6.4 Hz, 2H), 7.35 (d, *J* = 10.8 Hz, 1H), 7.29 – 7.03 (m, 9H), 6.76 (t, *J* = 8.2 Hz, 1H), 5.62 – 5.47 (m, 1H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.90 (d, *J* = 17.5 Hz, 1H), 3.98 – 3.96 (m, 1H), 2.98 – 2.85 (m, 1H), 2.73 – 2.58 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 162.9 (d, *J* = 245.1 Hz), 143.7, 139.2, 139.1 (d, *J* = 10.9 Hz), 137.5, 137.1, 134.1, 130.0 (d, *J* = 9.1 Hz), 129.7, 128.8, 127.7, 127.2, 126.9, 115.1, 114.7, 111.1 (d, *J* = 21.0 Hz), 107.4 (d, *J* = 26.2 Hz), 42.5, 39.0, 21.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.5.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{25}H_{23}FN_2NaO_3S^+$ 461.1306, found: 461.1305. $[\alpha]_D^{20}$ = + 82.4 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ^{o}C, 254 nm, t_{R1}: 15.5 min and t_{R2}: 16.8 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(o-tolyl)pent-4-enamide



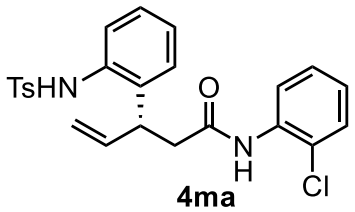
4la

Prepared following general procedure the product **4la** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (78% yield, 34.1 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.61 (d, *J* = 6.4 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.01 (m, 12H), 5.50 – 5.44 (m, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.88 (d, *J* = 17.3 Hz, 1H), 3.91 – 3.90 (m, 1H), 2.92 (d, *J* = 14.5 Hz, 1H), 2.68 – 2.55 (m, 1H), 2.36

(s, 3H), 1.94 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3, 143.4, 139.3, 137.4, 137.2, 135.0, 134.4, 130.5, 129.6, 128.6, 127.7, 127.3, 127.1, 127.0, 126.6, 125.8, 124.1, 42.30, 39.0, 21.5, 17.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{26}H_{26}N_2O_3S^+$ 435.1737, found: 435.1730. $[\alpha]_D^{20}$ = + 175.3 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 23.3 min and t_{R2}: 26.4 min).

***(R)-N*-(2-chlorophenyl)-3-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-enamide**

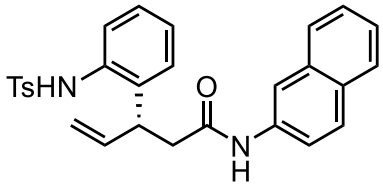


4ma

Prepared following general procedure the product **4ma** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a white solid (70% yield, 32.6 mg, 99% *ee*）.m.p.: 128 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 1H), 7.43 – 7.36 (m, 1H), 7.33 – 7.13 (m, 6H), 7.11 – 7.08 (m, 1H), 7.05 – 7.01 (m, 1H), 5.44 – 5.31 (m, 1H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 17.4 Hz, 1H), 3.90 – 3.79 (m, 1H), 2.98 (dd, *J* = 15.6, 4.1 Hz, 1H), 2.58 (dd, *J* = 15.6, 10.3 Hz, 1H), 2.36 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 143.4, 139.2, 137.3, 137.1, 134.3, 133.9, 129.6, 129.0, 128.3, 127.8, 127.7, 127.2, 126.9, 125.2, 122.9, 122.2, 114.3, 42.8, 37.7, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{25}H_{24}ClN_2O_3S^+$ 455.1191, found: 455.1193. $[\alpha]_D^{20}$ = + 84.7 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 16.2 min and t_{R2}: 17.0 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(naphthalen-2-yl)pent-4-enamide

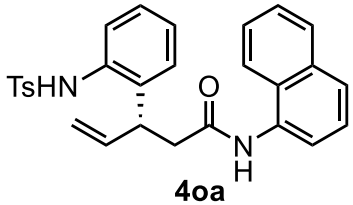


4na

Prepared following general procedure the product **4na** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a yellow liquid (92% yield, 43.2 mg, 99% *ee*）. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.06 (s, 1H), 7.95 (s, 1H), 7.76 – 7.58 (m, 5H), 7.45 – 7.30 (m, 3H), 7.26 – 7.25 (m, 1H), 7.19 – 7.03 (m, 5H), 5.57 – 5.32 (m, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 3.95 – 3.93 (m, 1H), 2.95 (dd, *J* = 15.3, 4.3 Hz, 1H), 2.65 (dd, *J* = 15.3, 10.2 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 143.6, 139.3, 137.6, 137.2, 135.0, 134.2, 133.7, 130.7, 129.7, 128.6, 127.7, 127.6, 127.5, 127.2, 127.0, 126.9, 126.4, 125.1, 120.0, 116.9, 114.5, 42.6, 38.5, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{28}H_{27}N_2O_3S^+$ 471.1737, found: 471.1733. $[\alpha]_D^{20}$ = + 113.8 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 ^{o}C, 254 nm, t_{R1}: 24.2 min and t_{R2}: 32.3 min).

(*R*)-3-(2-((4-methylphenyl)sulfonamido)phenyl)-N-(naphthalen-1-yl)pent-4-enamide



4oa

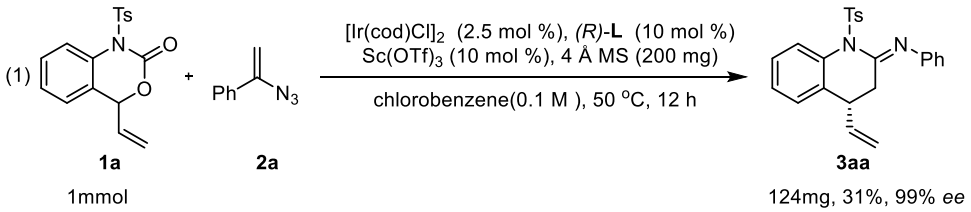
Prepared following general procedure the product **4oa** was obtained. The crude material was purified by column chromatography (petroleum ether/EtOAc = 2:1） on silica gel to provide the title compound as a viscous liquid (85% yield, 40.0 mg, 99% *ee*）. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.54 (m, 5H), 7.44 – 7.38 (m, 2H), 7.33 – 7.11 (m, 9H), 5.67 – 5.53 (m, 1H), 5.07 (d, *J* = 10.5 Hz, 1H), 4.97 (d, *J* = 17.4 Hz, 1H), 4.08 – 3.96 (m, 1H), 3.04 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.78 (dd, *J* = 13.9, 11.3 Hz, 1H), 2.34 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.0, 143.5, 139.3, 137.4, 137.2, 134.5, 1340, 129.6, 129.0, 128.5, 127.8, 127.2, 127.2, 127.0, 126.6, 126.3, 126.0, 125.6, 122.2, 121.1, 114.7, 42.3, 39.5, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{28}H_{27}N_2O_3S^+$ 471.1737, found: 471.1733. $[\alpha]_D^{20}$ = + 167.9 (c = 1.0, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 35 °C, 254 nm, t_{R1}: 43.6 min and t_{R2}: 59.9 min).

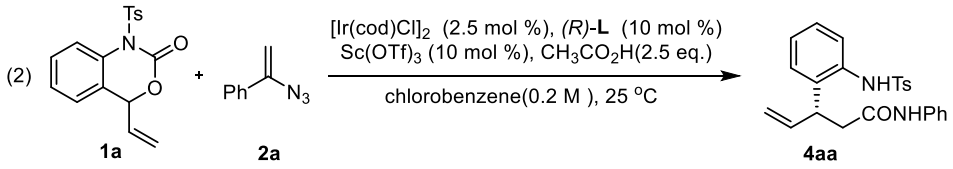
8. A 1mmol scale reaction of 1a

The procedure for preparing **3aa** is referred to the synthesis method of compound **3**



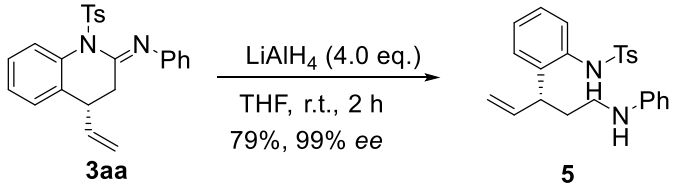
1a 1mmol **2a** **3aa** 124mg, 31%, 99% *ee*

The procedure for preparing **4aa** is referred to the synthesis method of compound **4**



1a 1mmol **2a** **4aa** 209mg, 50%, 99% *ee*

9. Synthetic Transformations of 3aa



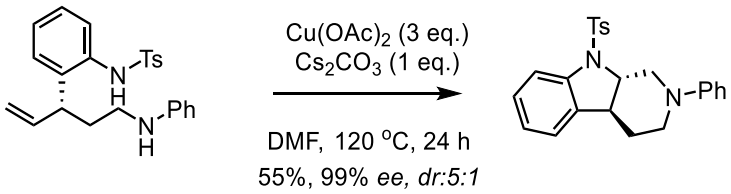
3aa **5**

According to the literature's procedure,[5] to a suspension of $LiAlH_4$ (30.4 mg, 0.8mmol) in anhydrous THF (2 mL) under argon was added solution of amidine (0.2 mmol, 80 mg) in CH_2Cl_2 (0.2 mL) at 0 °C. The mixture was stirred at room temperature

for 2 h. Then, water was dropwised, the mixture was extracted with EtOAc, organic layer was dried with anhydrous Na_2SO_4 and filtered with celite, concentrated in vacuo. Purification of the crude residue via silica gel flash column chromatography (eluent DCM to EtOAc) afforded the desired amine **5** (69.3 mg, 79%, 99% *ee*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.16 – 7.10 (m, 3H), 7.09 – 7.02 (m, 5H), 6.73 – 6.75 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 2H), 5.62 (ddd, *J* = 17.0, 10.3, 6.3 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.86 (d, *J* = 17.3 Hz, 1H), 3.49 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.72 – 2.65 (m, 1H), 2.25 (s, 3H), 2.00 – 1.93 (m, 1H), 1.66 – 1.72 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 143.4, 140.4, 137.5, 136.8, 135.1, 129.6, 129.6, 128.0, 127.3, 127.1, 126.6, 125.2, 119.2, 114.9, 114.5, 41.8, 39.60, 33.9, 21.5.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{26}N_2NaO_2S^+$ 429.1607, found: 429.1602. $[\alpha]_D^{20}$ = 59.3 (c = 0.2, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 25.4 min and t_{R2}: 38.1 min).



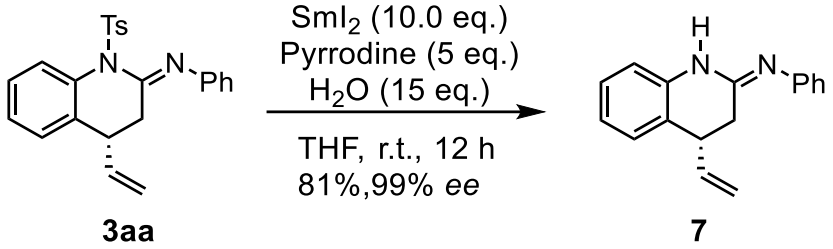
5 **6**

According to the literature's procedure,[6] **5** (56.6 mg, 0.1 mmol, 1.0 eq.) was dissolved in 1.9 mL DMF in a pressure tube equipped with a magnetic stir bar. Copper(II) acetate (60 mg, 0.3 mmol, 3.0 eq.) and cesium carbonate (33 mg, 0.1 mmol, 1.0 eq.) were added. The tube was sealed and heated to 120 ℃ for 24 h. After cooling, the mixture was diluted in ether and filtered through silica. The filtrate was concentrated to give the crude oil. This oil was purified by flash chromatography on silica gel (10% Et_2O in hexanes) to provide carboamination product **6** (30.0 mg, 53% yield, 99% *ee)*. m.p. 61 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.31 (m, 2H), 7.19 – 7.23 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.04 – 7.07 (m, 3H), 6.98 – 7.01 (m, 1H), 6.87 – 6.89 (m, 1H), 4.79 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.92 – 3.84 (m, 1H),

3.34 – 3.28 (m, 1H), 3.12 – 3.06 (m, 1H), 2.90 – 2.94 (m, 2H), 2.31 (s, 3H), 2.31 – 2.27 (m, 1H), 1.68 – 1.72 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.9, 144.5, 143.2, 132.8, 132.1, 129.8, 129.3, 128.0, 123.8, 122.1, 119.8, 117.0, 114.8, 67.7, 54.8, 49.4, 47.0, 26.3, 21.6.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{24}N_2NaO_2S^+$ 427.1451, found: 427.1454. $[\alpha]_D^{20}$ = -25.8 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 95%, *i*-propanol 5%, flow rate 0.5 mL/min, 25 ℃, 254 nm, t_{R1}: 17.3 min and t_{R2}: 35.7 min).

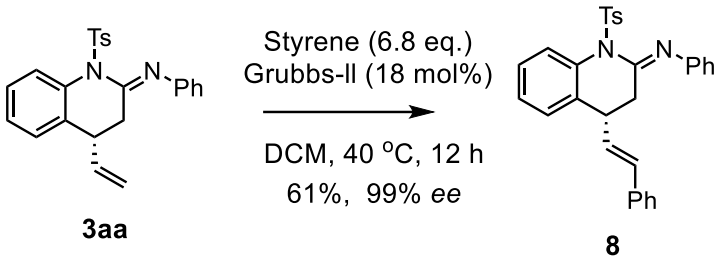


3aa **7**

According to the literature's procedure,[7] to a reaction tube was added 1 mL THF, **3aa** （40 mg, 0.1 mmol, 1.0 eq.）, samarium diiodide （10 mL, 10.0 eq.）, tetrahydropyridine（71 mg, 0.5 mmol, 5.0 eq.） and water （27 mg, 1.5 mmol, 15.0 eq.）at room temperature. The reaction was stirred for 12 hours and then quenched with sodium bicarbonate, extracted with EtOAc, dried over anhydrous sodium sulfate and concentrated. The residue was purified by flash chromatography on silica gel to get the product **7** (20.1 mg, 81% yield, 99% *ee*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.37 (m, 2H), 7.09 – 7.13 (m, 3H), 7.04 (d, *J* = 6.7 Hz, 2H), 6.92 – 6.94 (m, 1H), 6.66 (d, *J* = 4.8 Hz, 1H), 5.88 (dd, *J* = 17.0, 7.6 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 3.60 (d, *J* = 5.1 Hz, 1H), 2.73 (d, *J* = 44.3 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.2, 129.4, 127.9, 127.6, 125.5, 123.4, 122.1, 116.7, 40.0.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{16}N_2Na^+$ 271.1206, found: 271.1212. $[\alpha]_D^{20}$ = -15.0 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak AD-H, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 ℃, 254 nm, t_{R1}: 9.8 min and t_{R2}: 12.8 min).

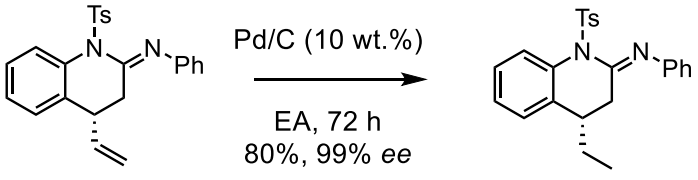


3aa **8**

Substrate **3aa** (40 mg, 0.1 mmol) and Grubbs-II (19.7 mg) were added to the test tube, followed by styrene and the reaction was carried out overnight at room temperature. After the reaction, it was filtered with celite and purified by flash chromatography on silica gel to obtain the product **8** (29.1 mg, 61% yield, 99% *ee*). m.p. 159 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.32 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.29 – 7.21 (m, 8H), 7.07 – 7.00 (m, 3H), 6.37 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.26 (dd, *J* = 16.0, 1.0 Hz, 1H), 6.05 (dd, *J* = 15.9, 6.5 Hz, 1H), 3.55 (q, *J* = 5.3 Hz, 1H), 2.59 (dd, *J* = 5.8, 4.4 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 148.1, 144.0, 137.2, 136.4, 135.7, 133.2, 132.5, 129.8, 129.0, 128.9, 128.6, 128.3, 127.8, 127.3, 126.8, 126.4, 125.9, 125.4, 123.4, 120.2, 39.1, 34.1, 21.7.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd. for $C_{30}H_{26}N_2NaO_2S^+$ 501.1607, found: 501.1630. $[\alpha]_D^{20}$ = 26.5 (c = 0.3, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 °C, 254 nm, t_{R1}: 39.2 min and t_{R2}: 49.5 min).



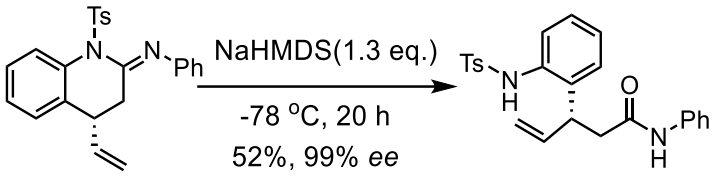
3aa **9**

To a vial was added **3aa** (80.5 mg, 0.2 mmol), Pd/C(10.5 mg, 10 wt.%), EA. The reaction was filled with hydrogen balloon and carried out at room temperature for 72 h. After the reaction was completed, it was filtered through silica gel and purified by flash

chromatography on silica gel to give the desired compound **9** (65 mg, 80% yield, 99% *ee*). m.p. 155 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.21–7.24 (m, 3H), 7.13 – 7.16 (m,2H), 7.08 – 7.11 (m, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.92 – 6.94 (m, 1H), 6.36 (d, *J* = 7.8 Hz, 2H), 2.49 – 2.42 (m, 1H), 2.37 (s, 3H), 2.36 – 2.27 (m, 2H), 1.51 – 1.40 (m, 1H), 1.26 (dt, *J* = 14.3, 7.2 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.3, 143.2, 136.4, 134.5, 133.7, 128.6, 127.9, 127.9, 125.9, 125.7, 124.6, 124.2, 122.2, 119.0, 37.0, 32.6, 24.3, 20.7, 10.9.

HRMS (APCI) (m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{24}N_2NaO_2S^+$ 427.1451, found: 427.1454. $[\alpha]_D^{20}$ = -15.3 (c = 0.1, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IA, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 30 ℃, 254 nm, t_{R1}: 8.7 min and t_{R2}: 11.5 min)



3aa **4aa**

Under argon atmosphere, to a bottle was added NaHMDS (2.0 mol/L in THF) and 1 mL of toluene. The bottle was cooled at -78 ºC and a solution of **3aa** (40 mg, 0.1 mmol) in THF was slowly added. The reaction was carried out at -78 ºC for 20 hours. The reaction was quenched with water, and the product was extracted by EA, dried over Na_2SO_4 and purified by a flash chromatography on silica gel to obtain **4aa** (22 mg, 52% yield, 99% *ee*). m.p. 175 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.49 (s, 1H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.24 – 7.27 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.14 (m, 2H), 7.11 – 7.06 (m, 2H), 5.46 (ddd, *J* = 17.2, 10.5, 5.3 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 3.89 – 3.93 (m, 1H), 2.92 (dd, *J* = 15.2, 4.4 Hz, 1H), 2.58 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 143.5, 139.3, 137.4, 134.2, 129.7, 128.9, 128.6, 127.6, 127.2, 126.9, 124.5, 120.0, 114.4, 42.5, 38.5, 21.5.

HRMS (APCI) (m/z): $[M+H]^+$ Calcd. for $C_{24}H_{25}N_2O_3S^+$ 421.1580, found: 421.1591. $[\alpha]_D^{20}$ = +92.6 (c = 0.2, CH_2Cl_2). **HPLC** analysis: 99% *ee* (Daicel ChiralPak IB, eluent, hexane 90%, *i*-propanol 10%, flow rate 1.0 mL/min, 25 °C, 254 nm, t_{R1}: 23.8 min and t_{R2}: 27.4 min)

9. References

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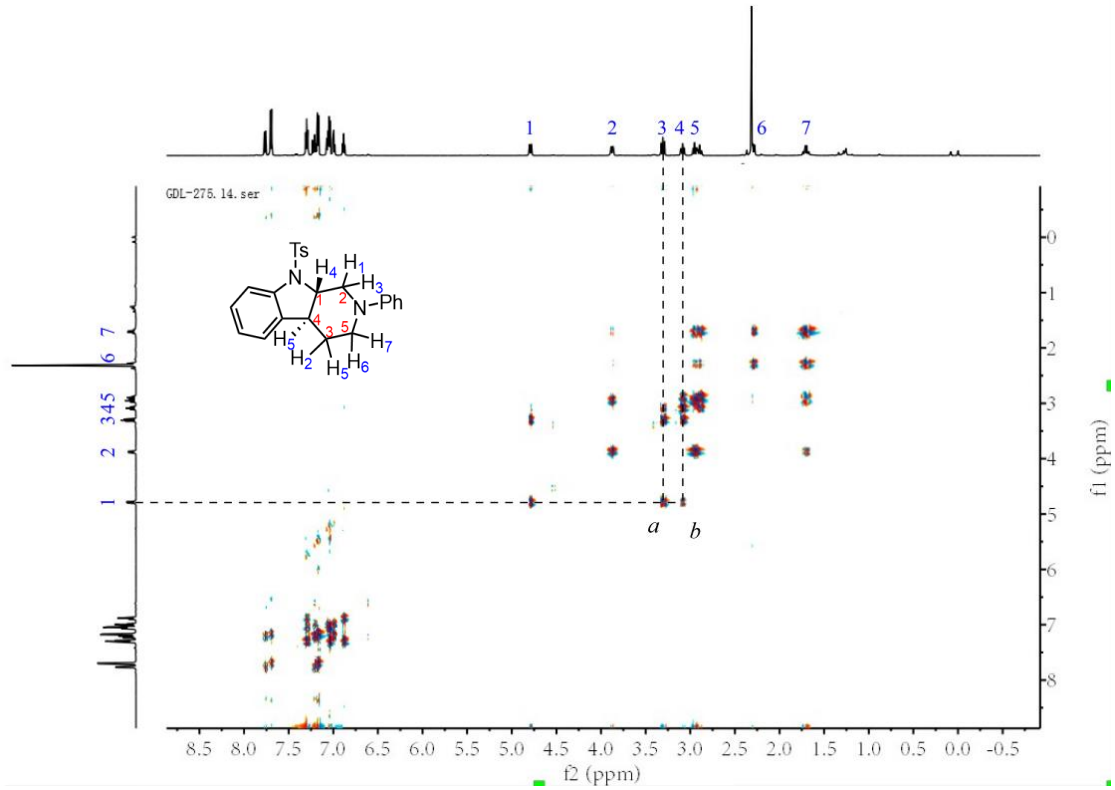
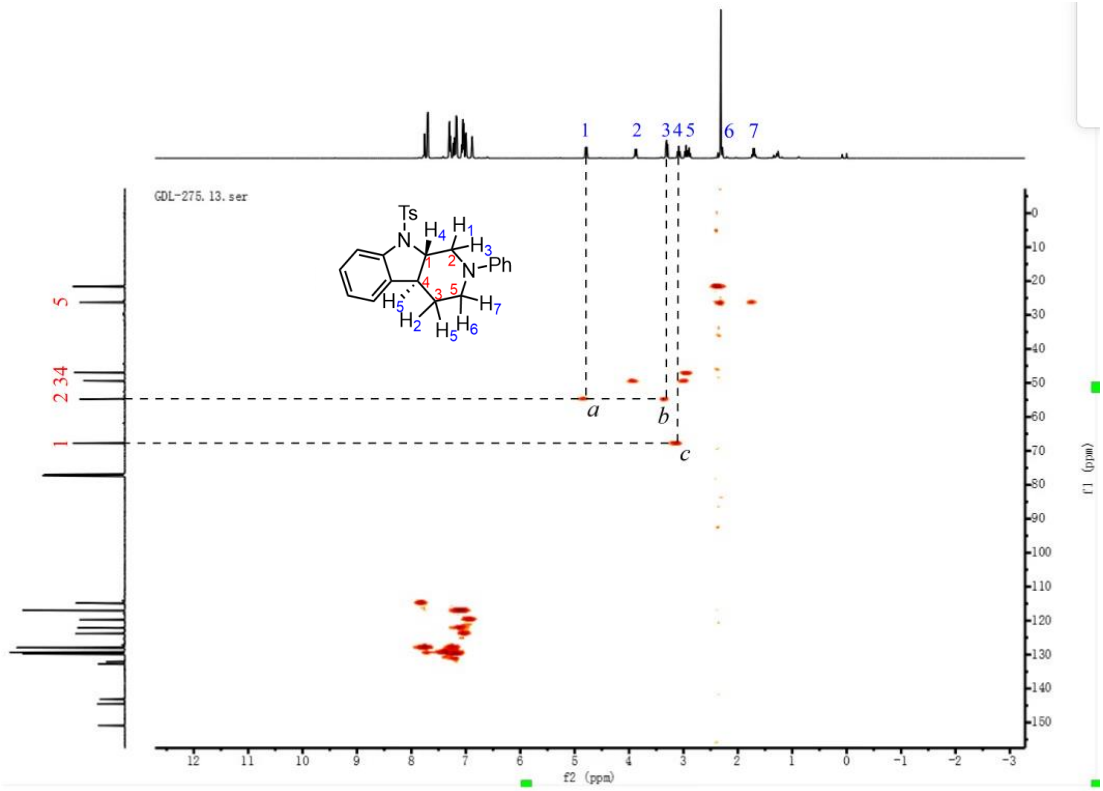
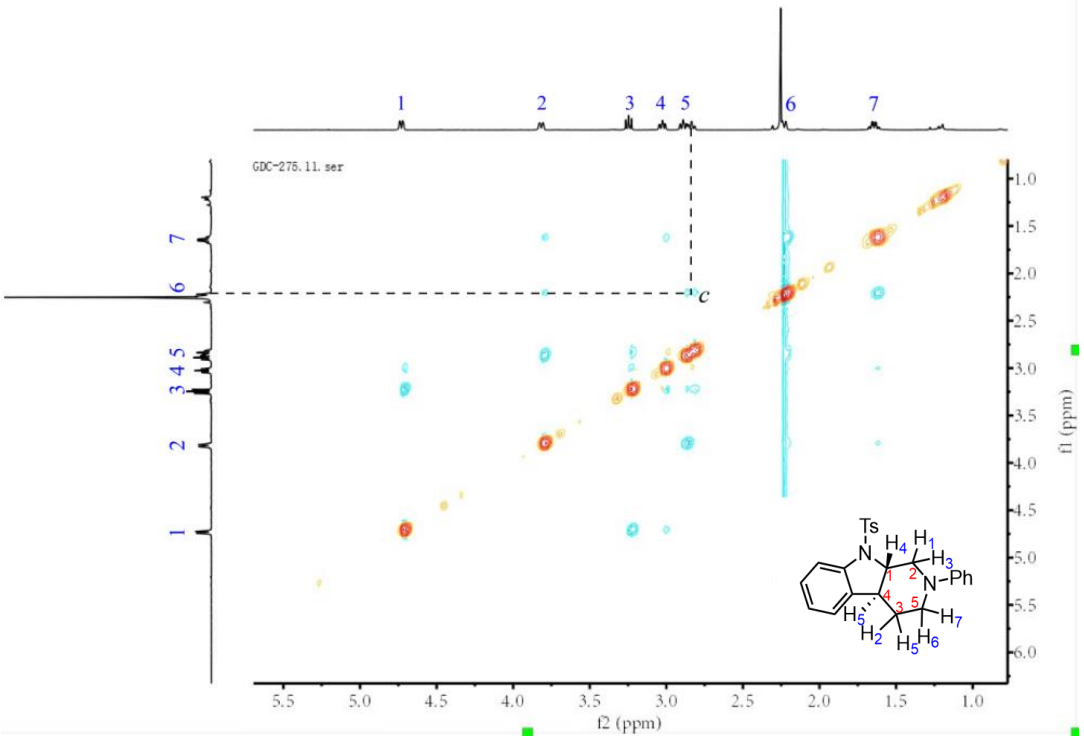
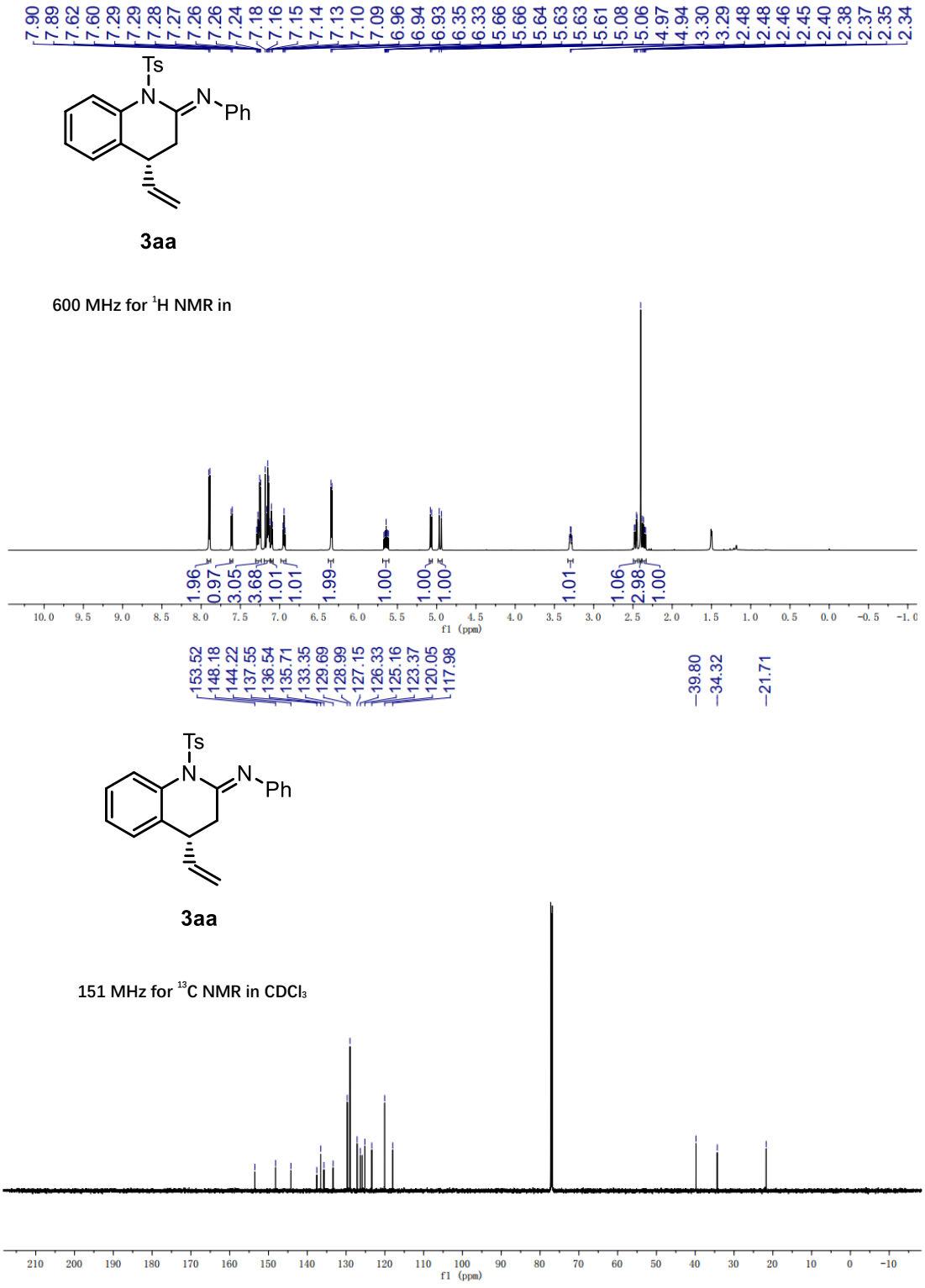
10. 2D spectrogram of 6

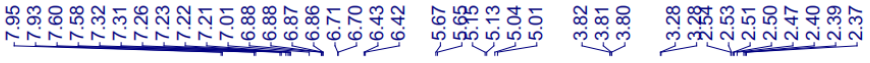


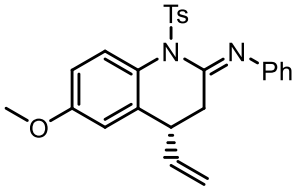



GDC-275.11.ser
1
2
3 4 5
6
7
f2 (ppm)
f1 (ppm)
Ts
N
Ph
H1
H2
H3
H4
H5
H6
H7

11. NMR Spectral Data

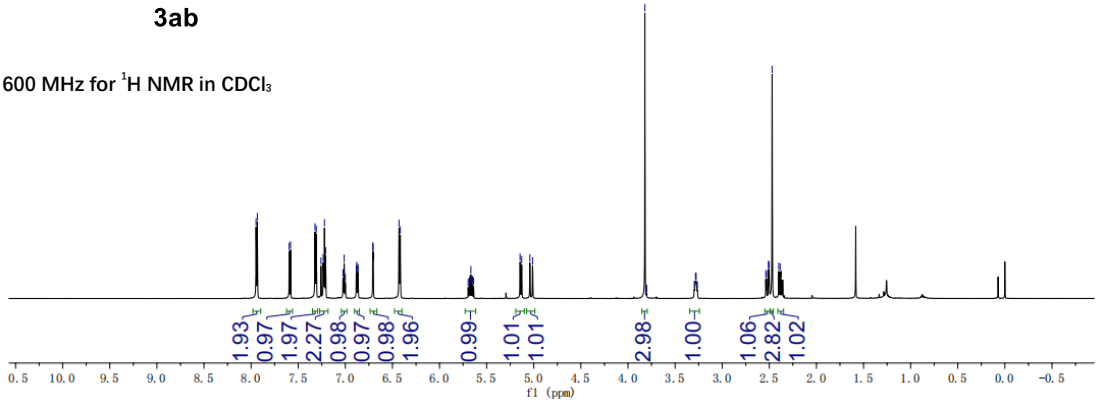


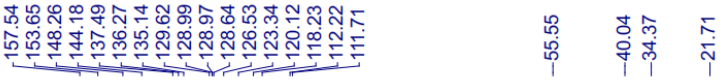


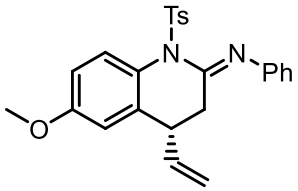


3ab

600 MHz for ^{1}H NMR in $CDCl_3$

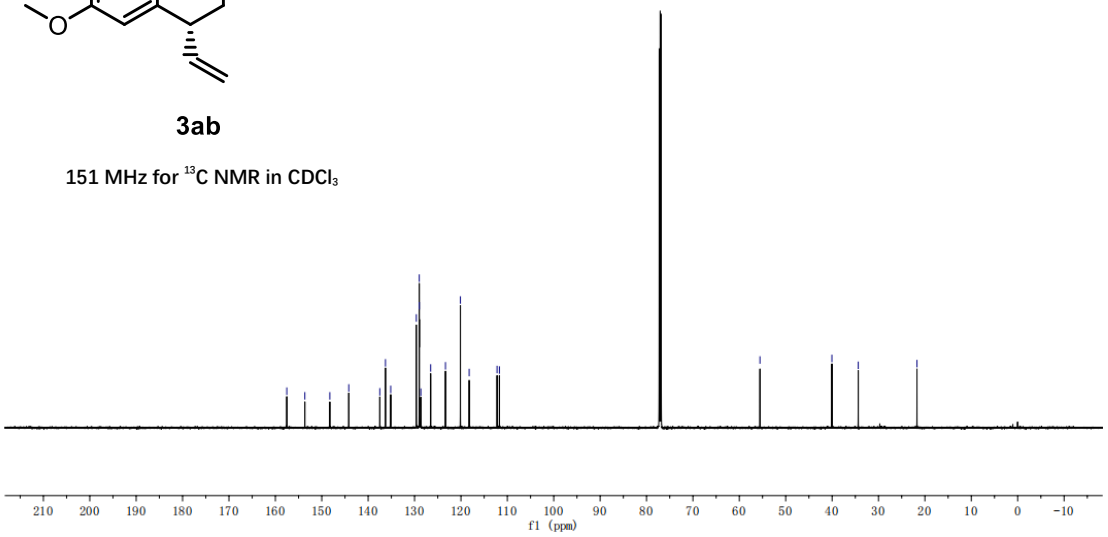


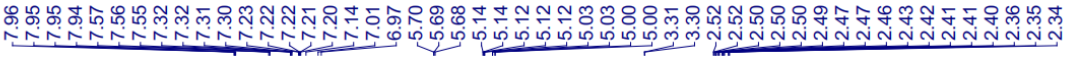


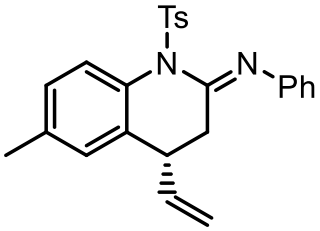


3ab

151 MHz for ^{13}C NMR in $CDCl_3$

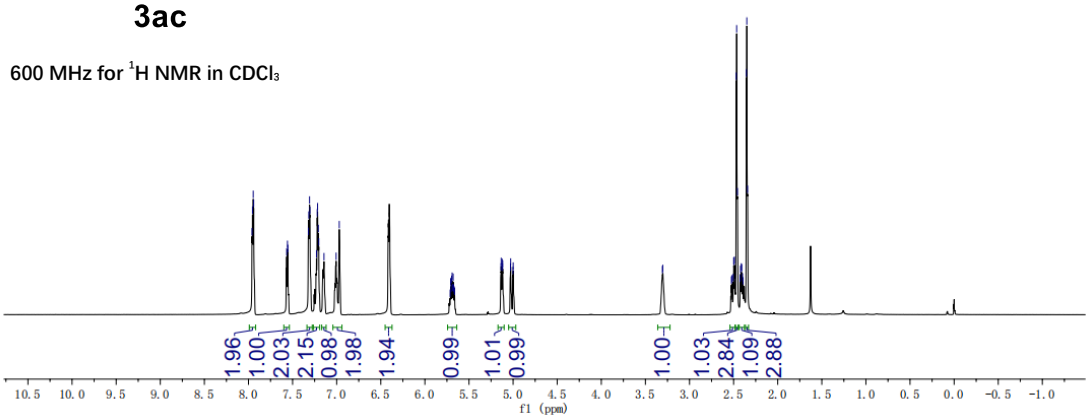


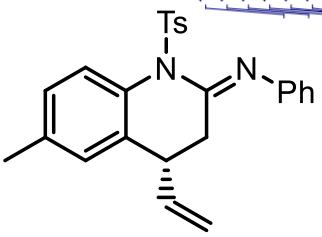




3ac

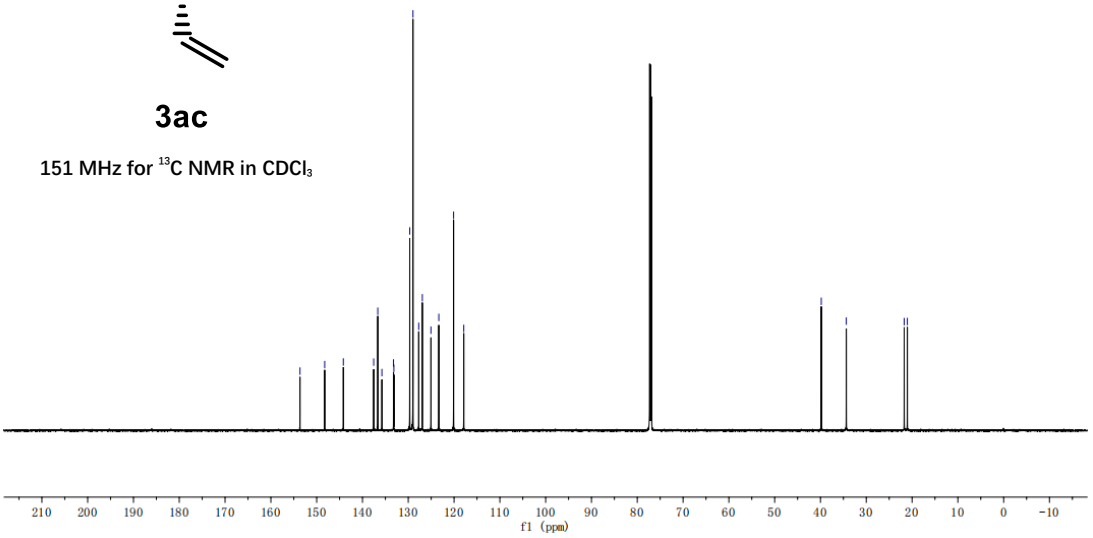
600 MHz for ^{1}H NMR in $CDCl_3$

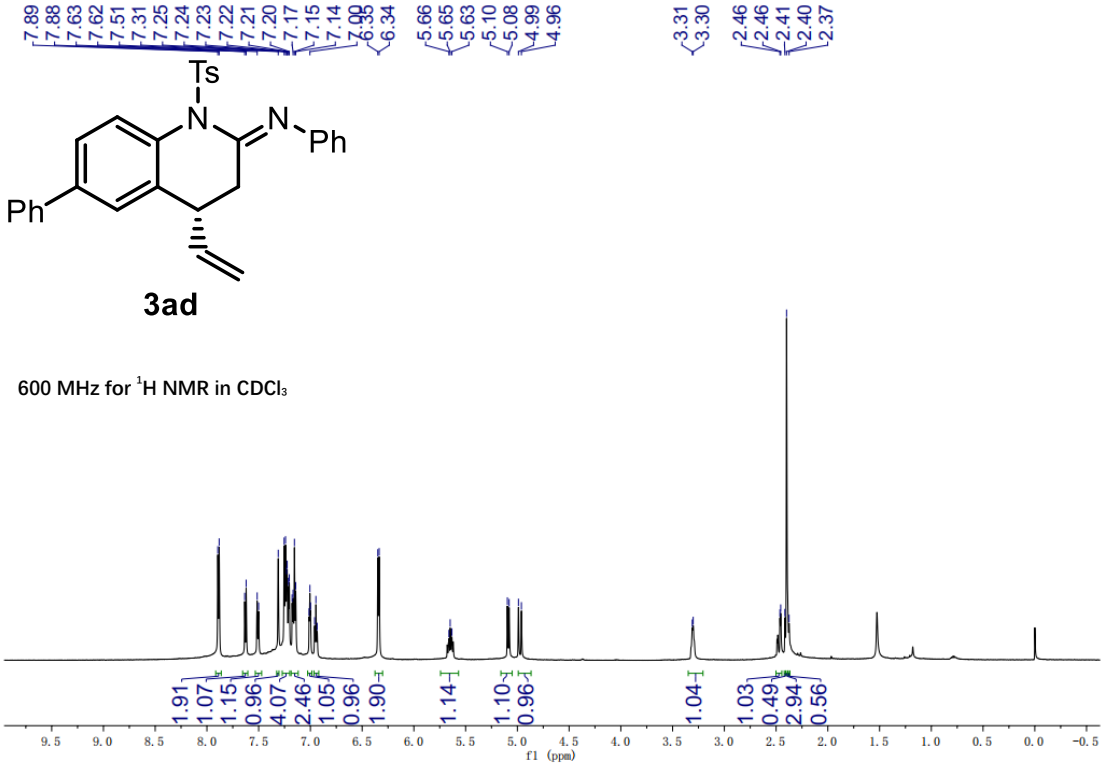


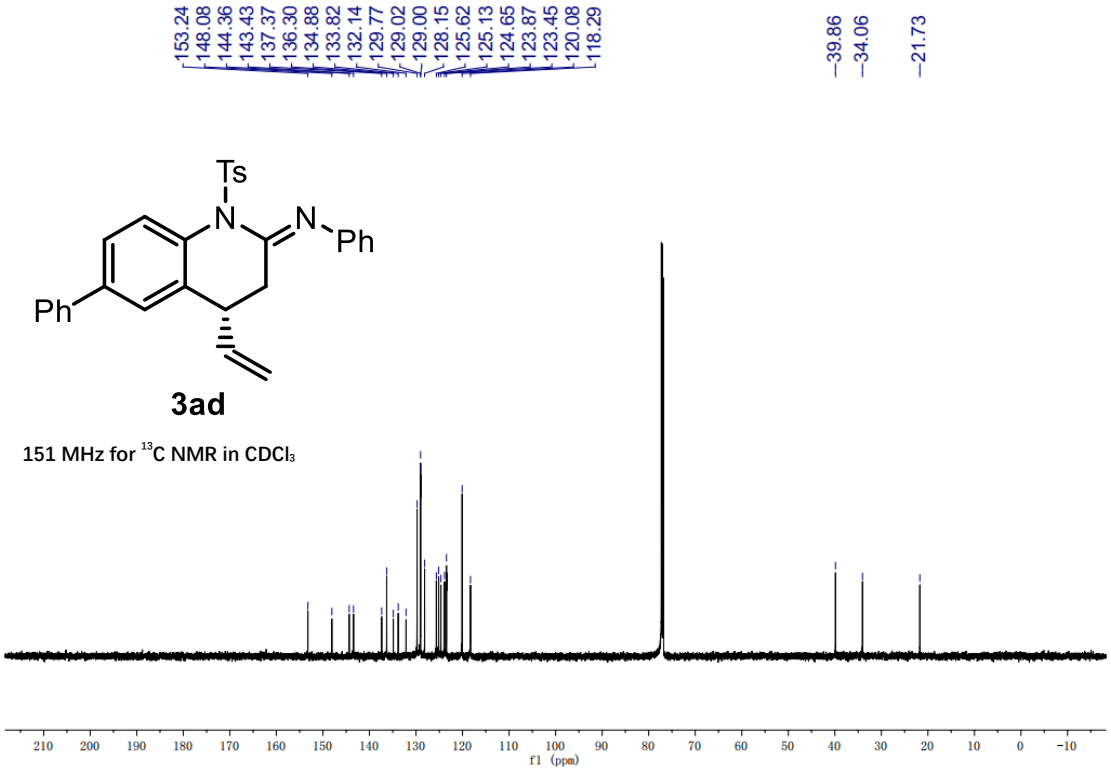


3ac

151 MHz for ^{13}C NMR in $CDCl_3$




7.89
7.88
7.63
7.62
7.51
7.31
7.25
7.24
7.23
7.22
7.21
7.20
7.17
7.15
7.14
7.00
6.35
6.34
5.66
5.65
5.63
5.10
5.08
4.99
4.96
3.31
3.30
2.46
2.46
2.41
2.40
2.37
Ts
N
N
Ph
Ph
3ad
600 MHz for 1H NMR in CDCl3
1.91
1.07
1.15
0.96
4.07
2.46
1.05
0.96
1.90
1.14
1.10
0.96
1.04
1.03
0.49
2.94
0.56
f1 (ppm)


153.24
148.08
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133.82
132.14
129.77
129.02
129.00
128.15
125.62
125.13
124.65
123.87
123.45
120.08
118.29
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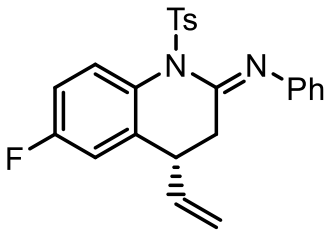
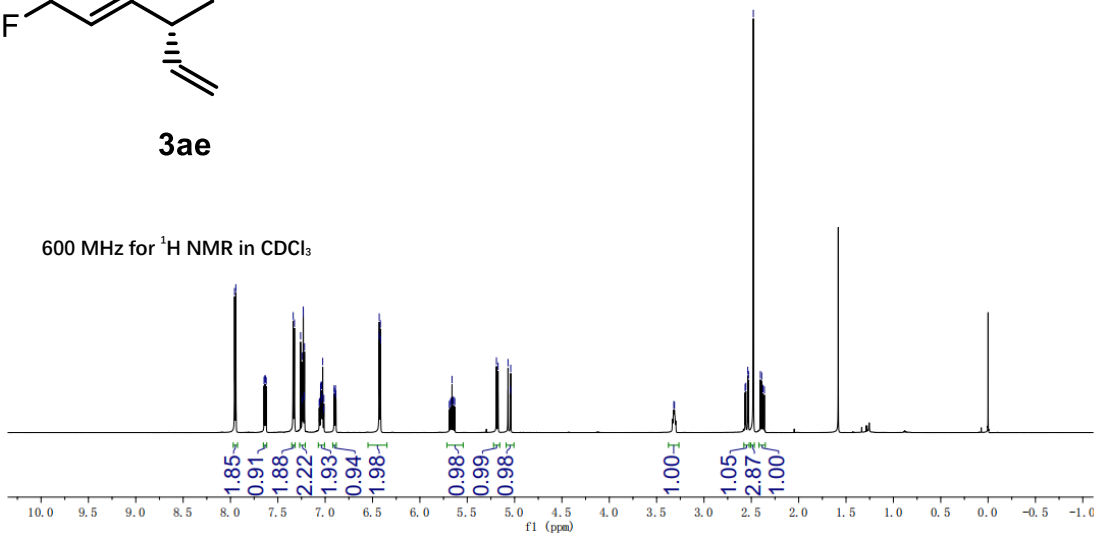
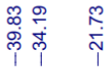
21.73
Ts
N
N
Ph
Ph
3ad
151 MHz for 13C NMR in CDCl3
f1 (ppm)

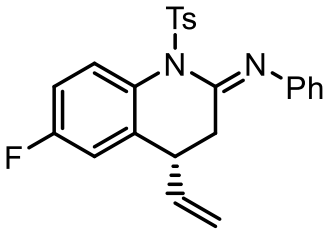


3ae

600 MHz for ^{1}H NMR in $CDCl_3$

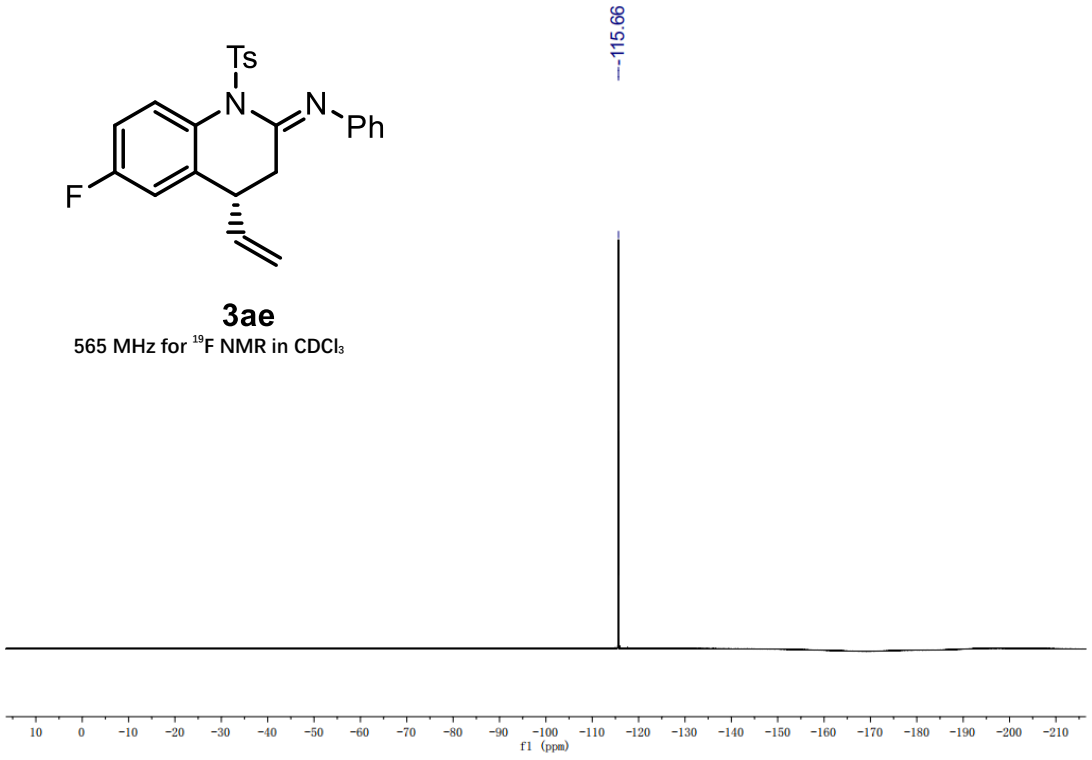






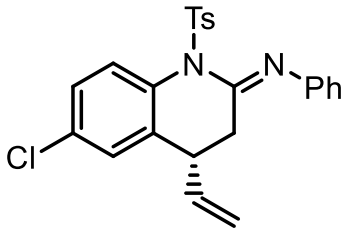
3ae

151 MHz for ^{13}C NMR in $CDCl_3$



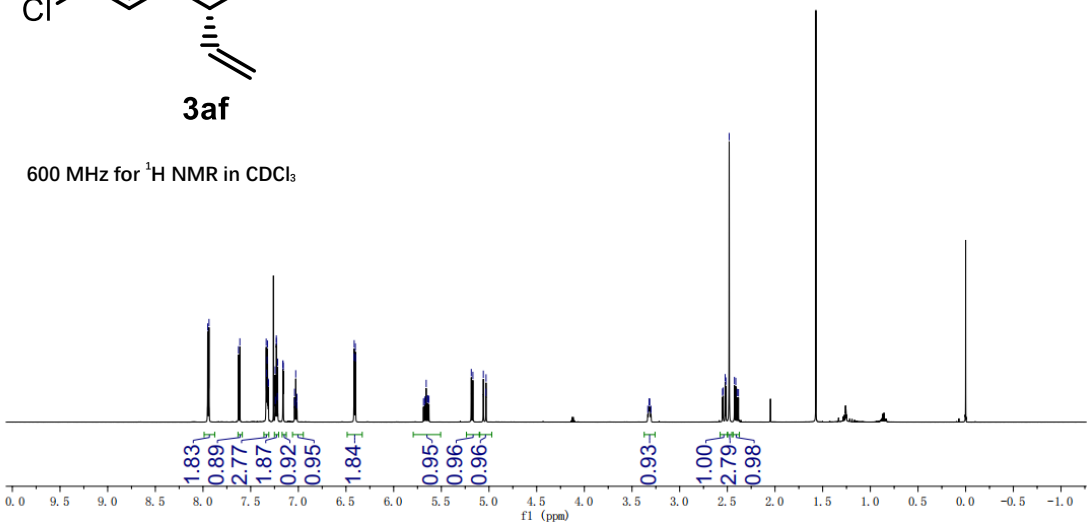
3ae

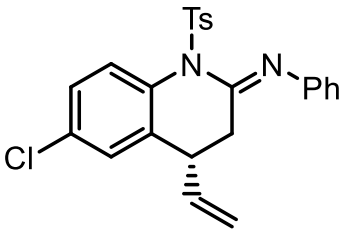
565 MHz for ^{19}F NMR in $CDCl_3$



3af

600 MHz for ^{1}H NMR in $CDCl_3$





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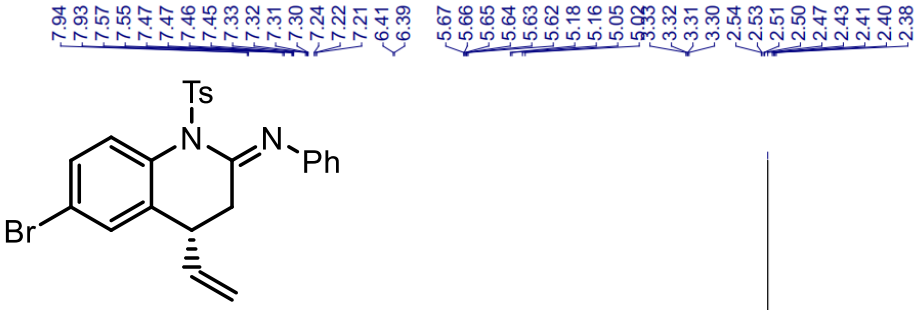
151 MHz for ^{13}C NMR in $CDCl_3$



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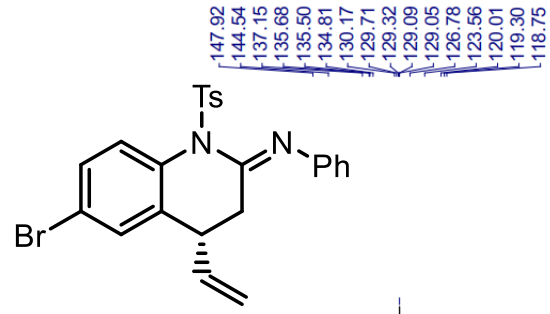
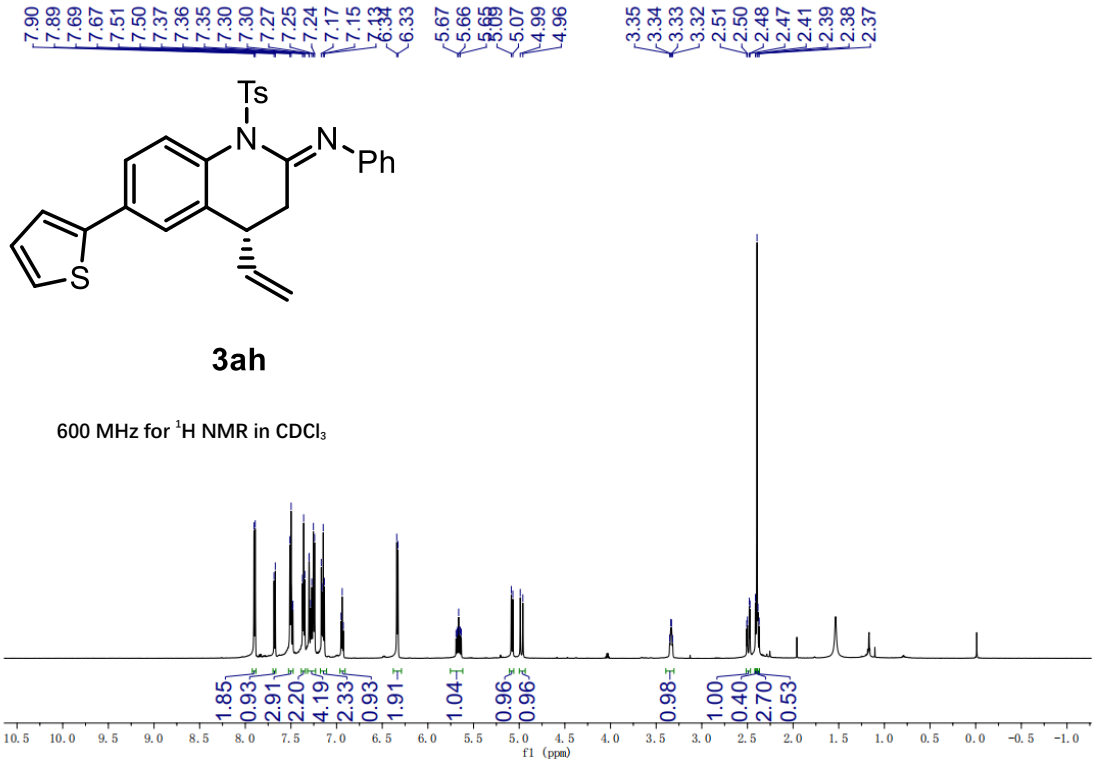
600 MHz for ^{1}H NMR in $CDCl_3$



3ag

151 MHz for ^{13}C NMR in $CDCl_3$


7.90
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7.50
7.37
7.36
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7.30
7.30
7.27
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7.17
7.15
7.13
6.34
6.33
5.67
5.66
5.65
5.09
5.07
4.99
4.96
3.35
3.34
3.33
3.32
2.51
2.50
2.48
2.47
2.41
2.39
2.38
2.37
Ts
N
N
Ph
S
3ah
600 MHz for ¹H NMR in CDCl₃
1.85
0.93
2.91
2.20
4.19
2.33
0.93
1.91
1.04
0.96
0.96
0.98
1.00
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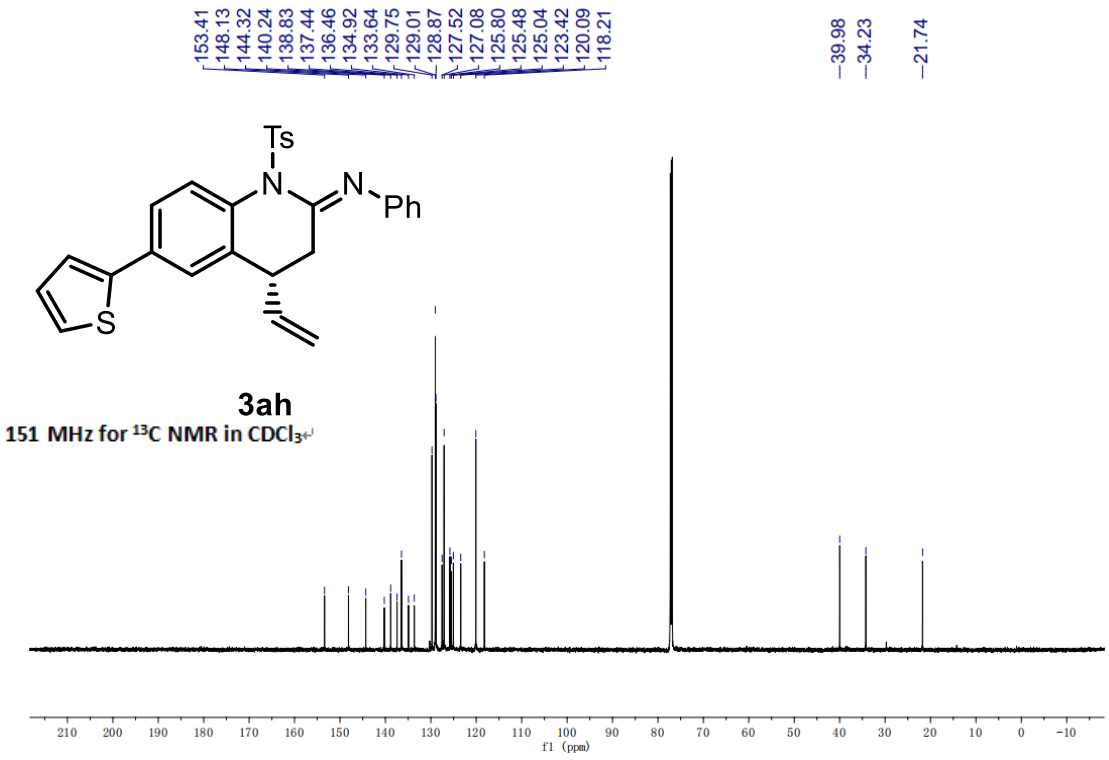
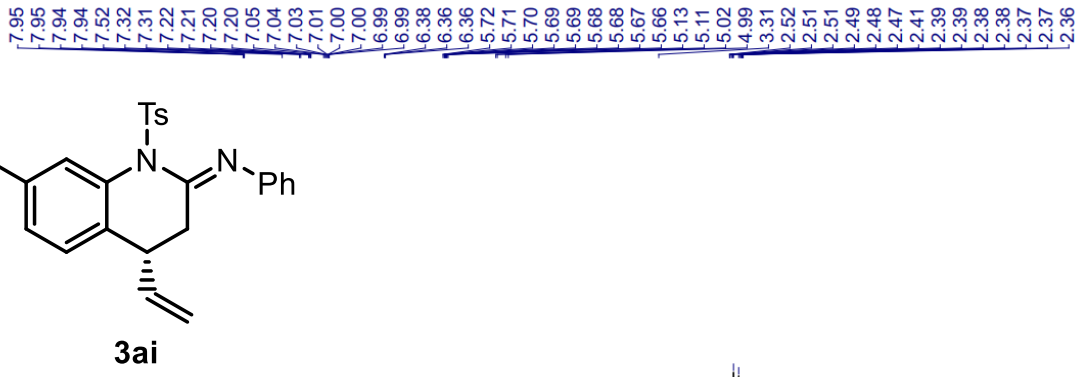
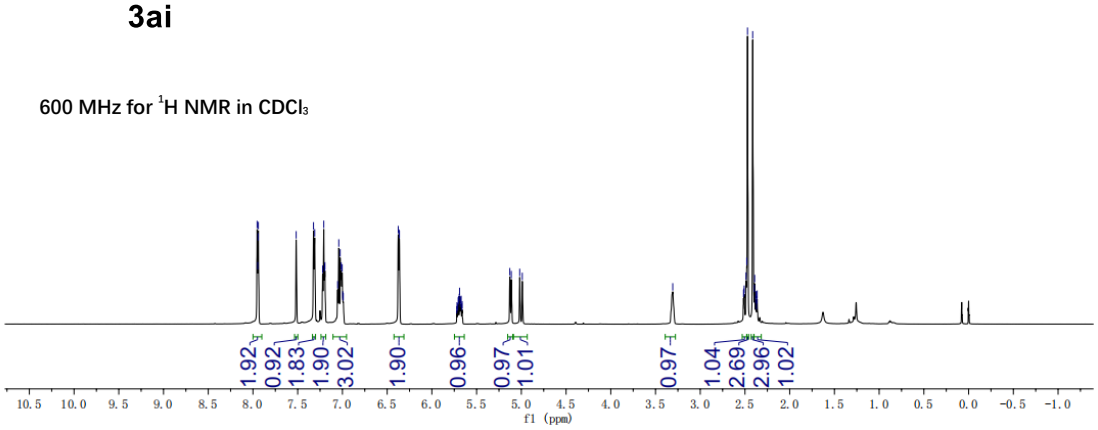
f1 (ppm)

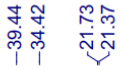

153.41
148.13
144.32
140.24
138.83
137.44
136.46
134.92
133.64
129.75
129.01
128.87
127.52
127.08
125.80
125.48
125.04
123.42
120.09
118.21
39.98
34.23
21.74
Ts
N
N
Ph
S
3ah
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

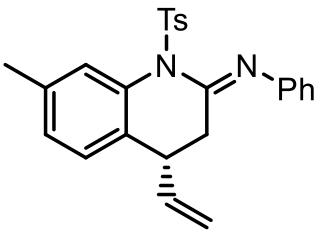


3ai

600 MHz for ^{1}H NMR in $CDCl_3$

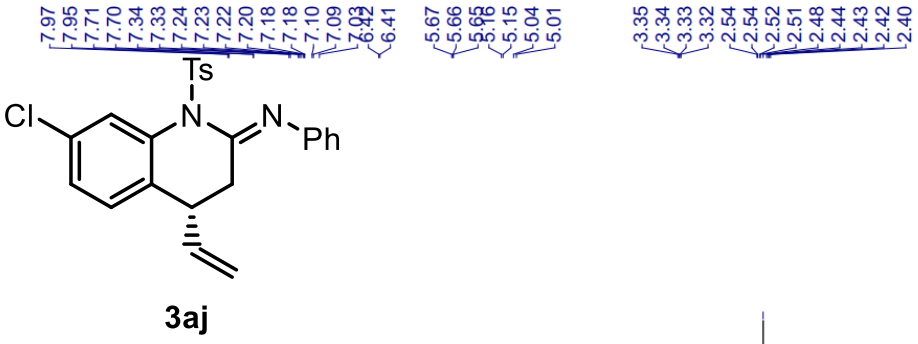






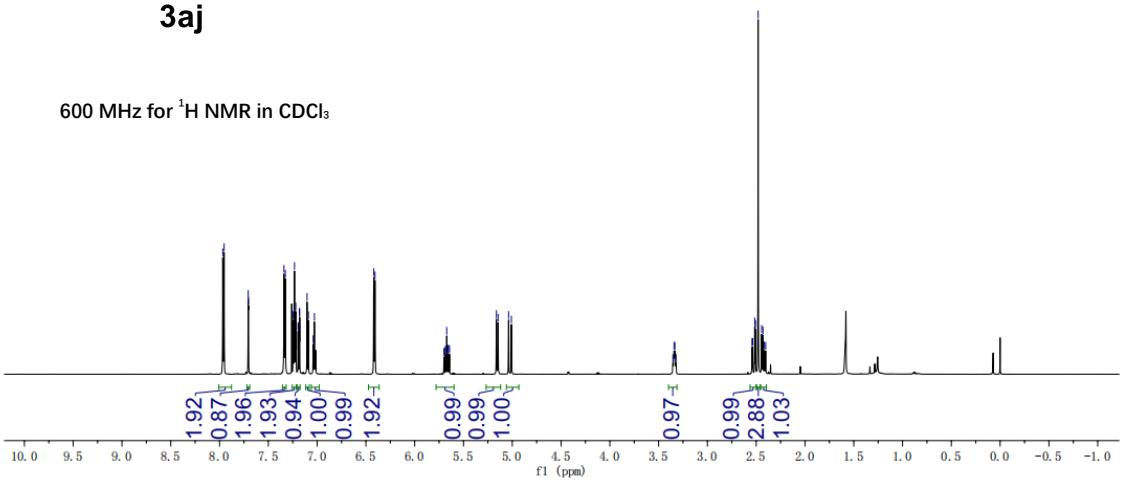
3ai

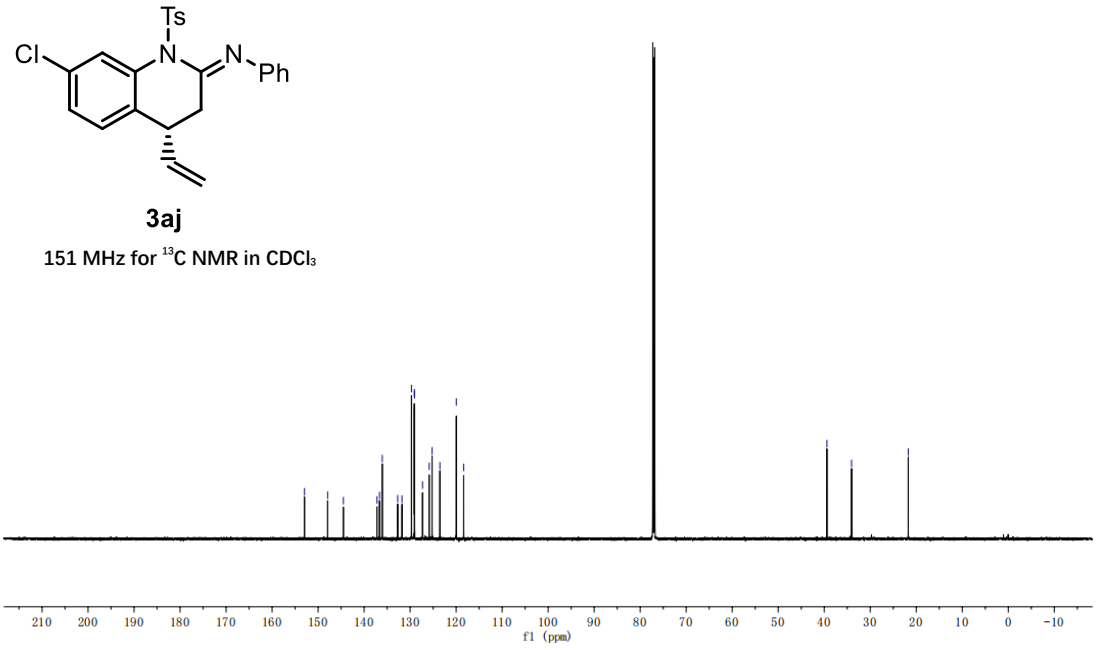
151 MHz for ^{13}C NMR in $CDCl_3$



3aj

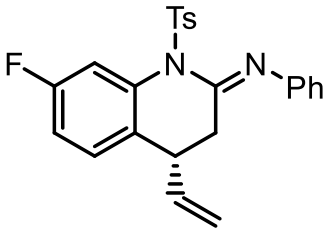
600 MHz for ^{1}H NMR in $CDCl_3$





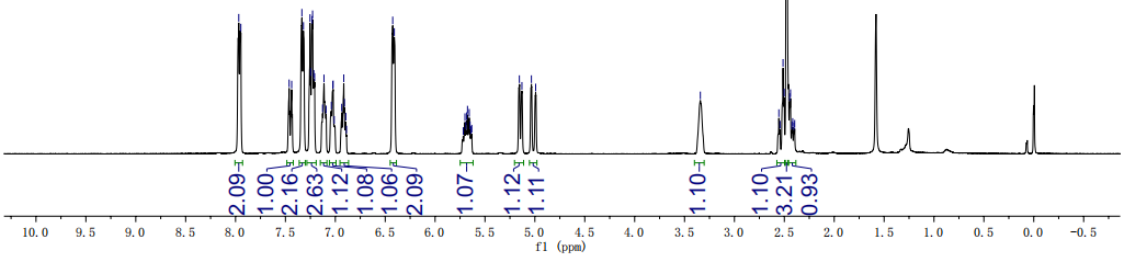
3aj

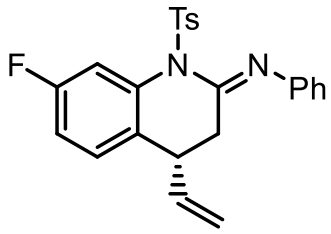
151 MHz for ^{13}C NMR in $CDCl_3$



3ak

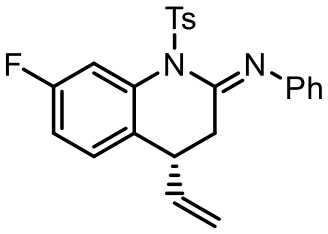
400 MHz for ^{1}H NMR in $CDCl_3$





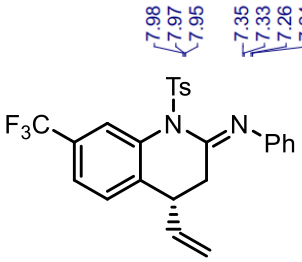
3ak

151 MHz for ^{13}C NMR in $CDCl_3$



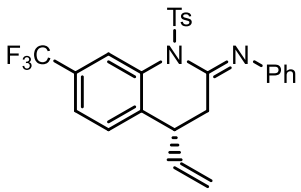
3ak

565 MHz for ^{19}F NMR in $CDCl_3$



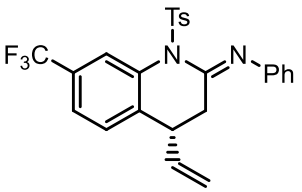
3al

600 MHz for ^{1}H NMR in $CDCl_3$



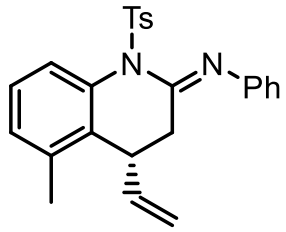
3al

151 MHz for ^{13}C NMR in $CDCl_3$



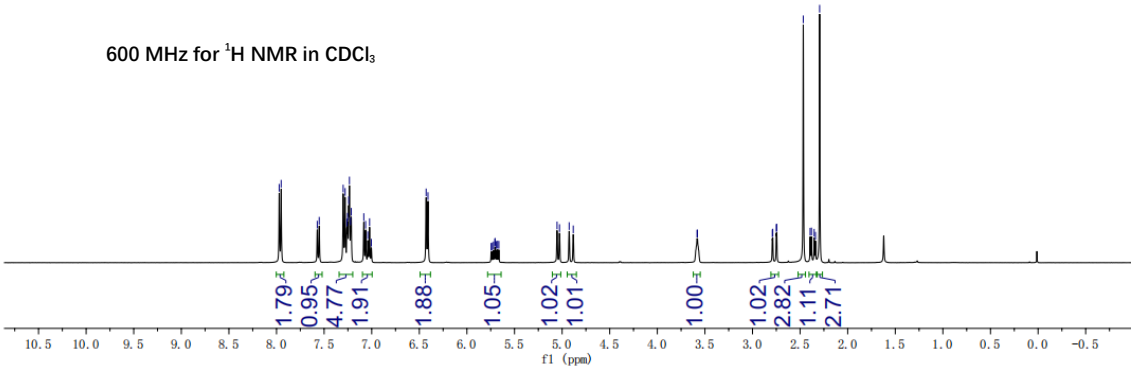
3al

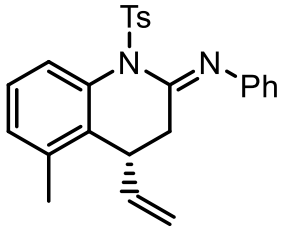
565 MHz for ^{19}F NMR in $CDCl_3$



3am

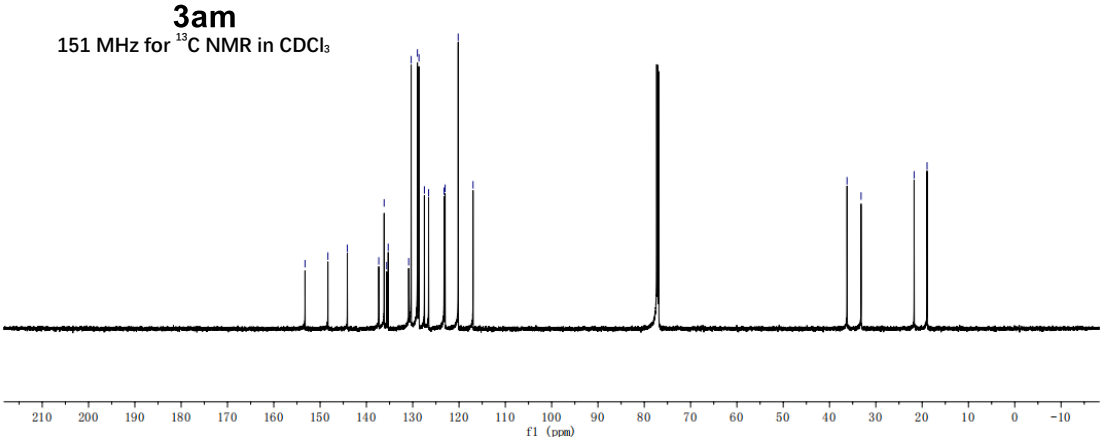
600 MHz for ^{1}H NMR in $CDCl_3$

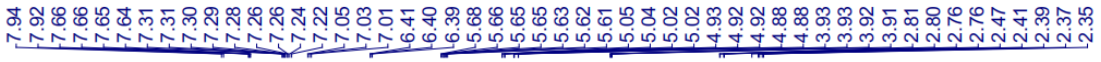


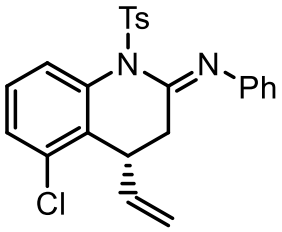


3am

151 MHz for ^{13}C NMR in $CDCl_3$

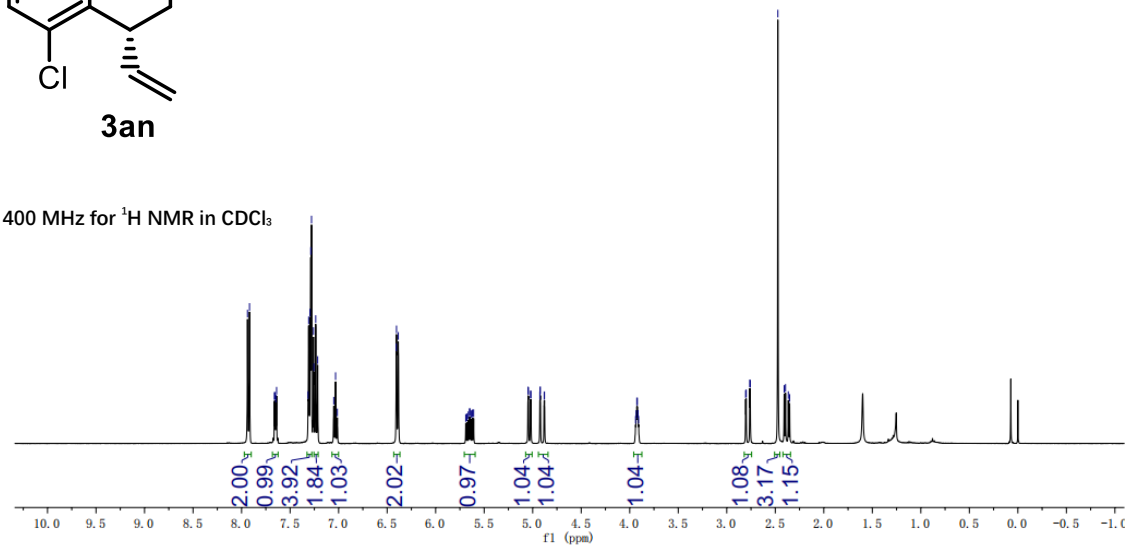


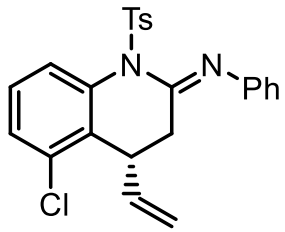




3an

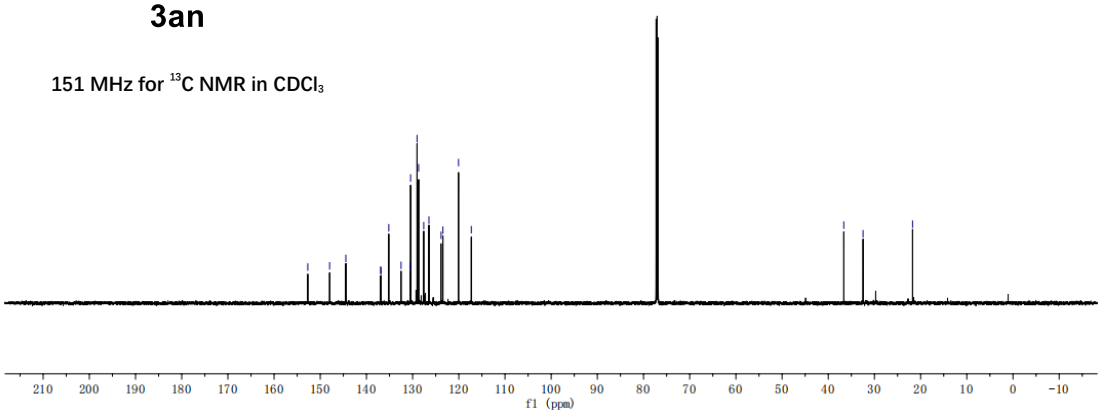
400 MHz for ^{1}H NMR in $CDCl_3$

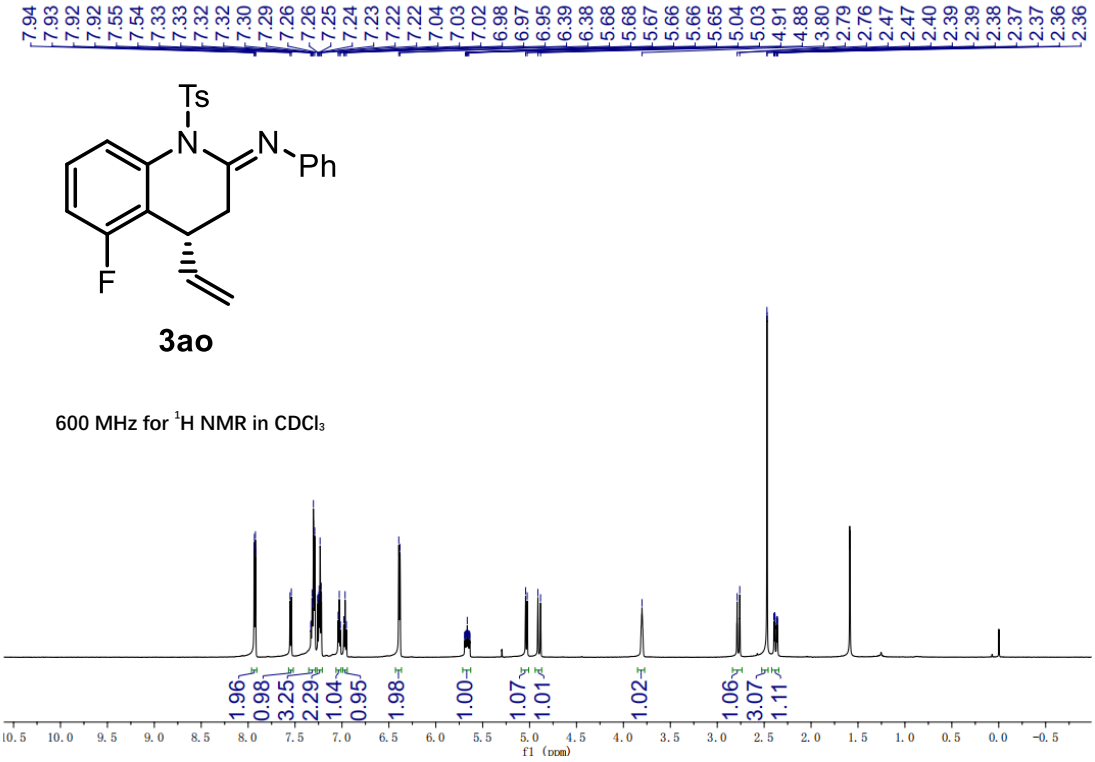


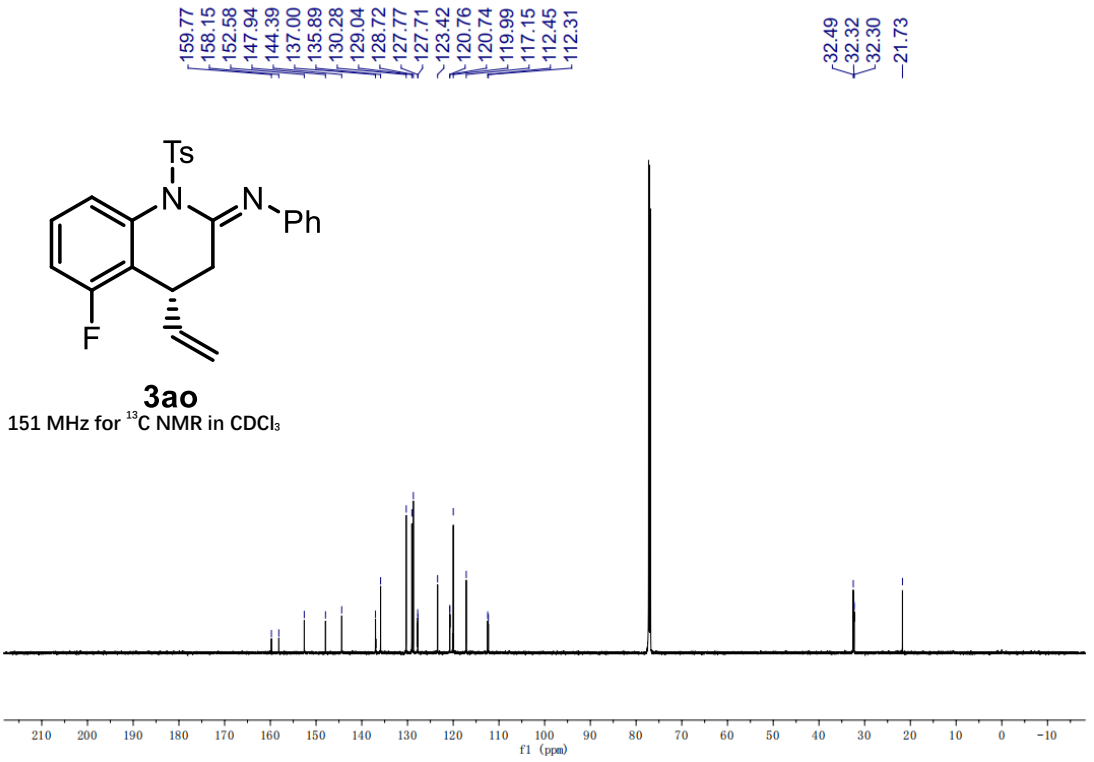


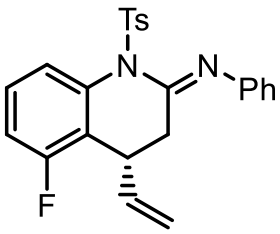
3an

151 MHz for ^{13}C NMR in $CDCl_3$



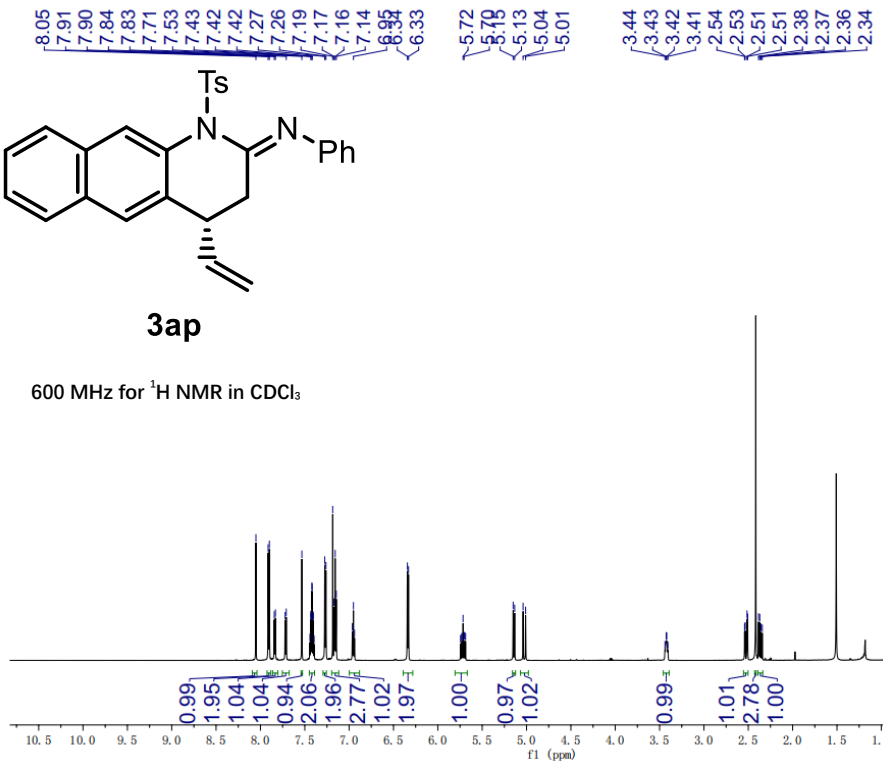

7.94
7.93
7.92
7.92
7.55
7.54
7.33
7.33
7.32
7.32
7.30
7.29
7.26
7.26
7.25
7.24
7.23
7.22
7.22
7.04
7.03
7.02
6.98
6.97
6.95
6.39
6.38
5.68
5.68
5.67
5.66
5.66
5.65
5.04
5.03
4.91
4.88
3.80
2.79
2.76
2.47
2.47
2.40
2.39
2.39
2.38
2.37
2.37
2.36
2.36
Ts
N
N
Ph
F
3ao
600 MHz for ^{1}H NMR in CDCl$_3$
1.96
0.98
3.25
2.29
1.04
0.95
1.98
1.00
1.07
1.01
1.02
1.06
3.07
1.11
f1 (ppm)


159.77
158.15
152.58
147.94
144.39
137.00
135.89
130.28
129.04
128.72
127.77
127.71
123.42
120.76
120.74
119.99
117.15
112.45
112.31
32.49
32.32
32.30
21.73
Ts
N
N
Ph
F
3ao
151 MHz for ^{13}C NMR in CDCl$_3$
f1 (ppm)



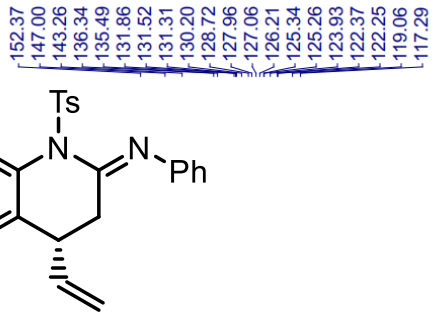
3ao

565 MHz for ^{19}F NMR in $CDCl_3$



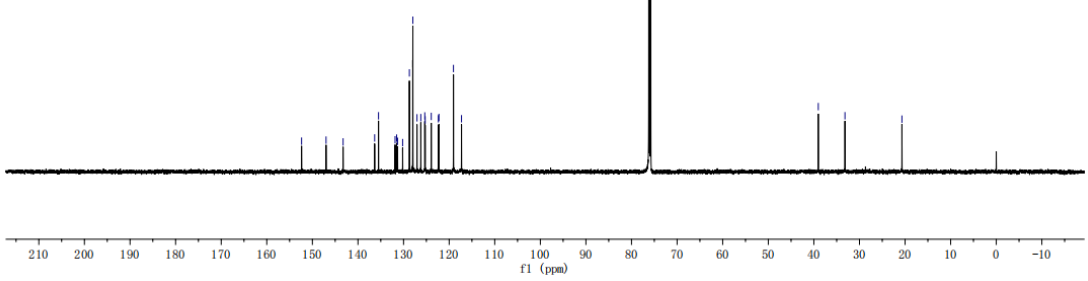
3ap

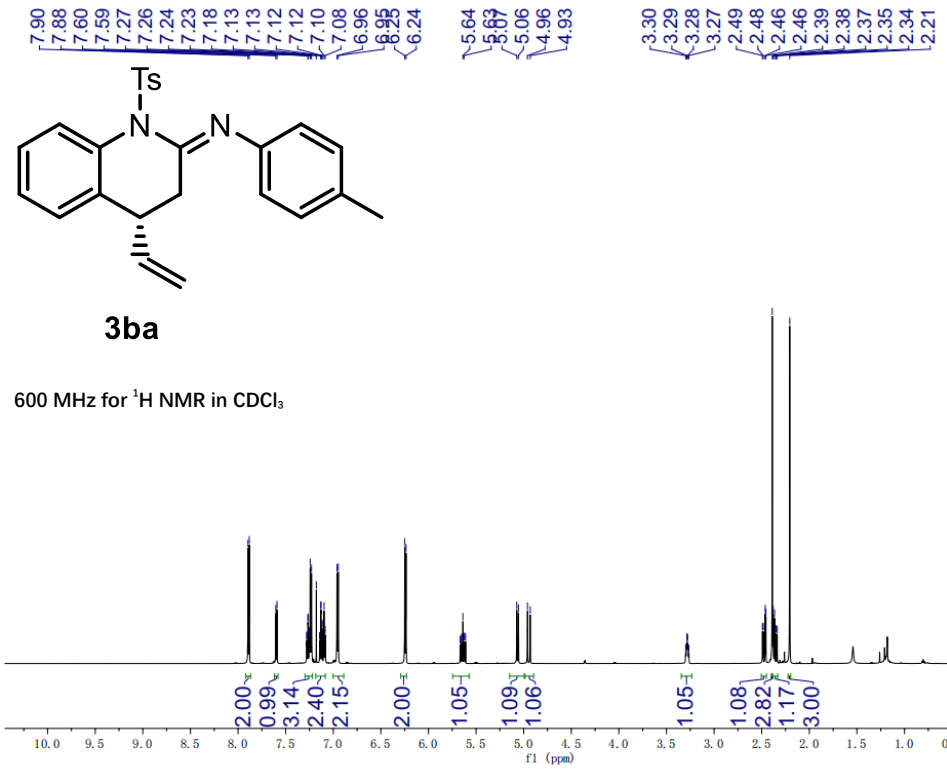
600 MHz for ^{1}H NMR in $CDCl_3$



3ap

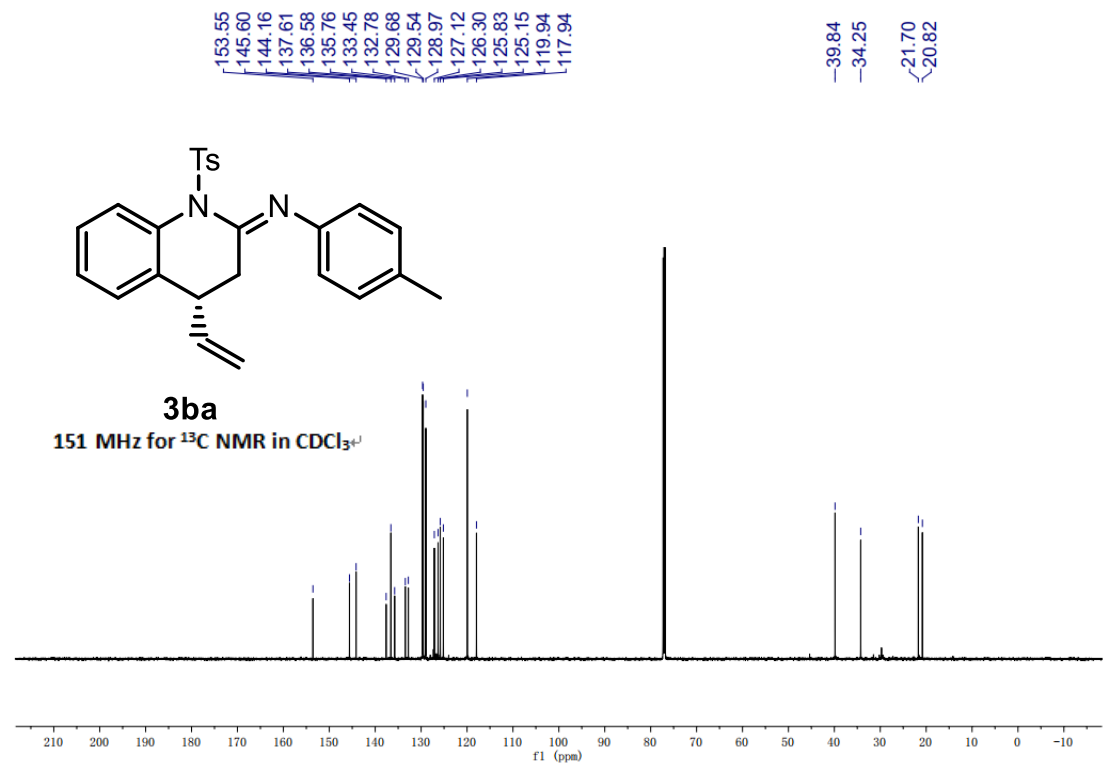
151 MHz for ^{13}C NMR in $CDCl_3$





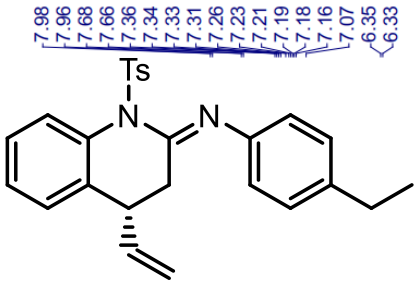
3ba

600 MHz for ^{1}H NMR in $CDCl_3$



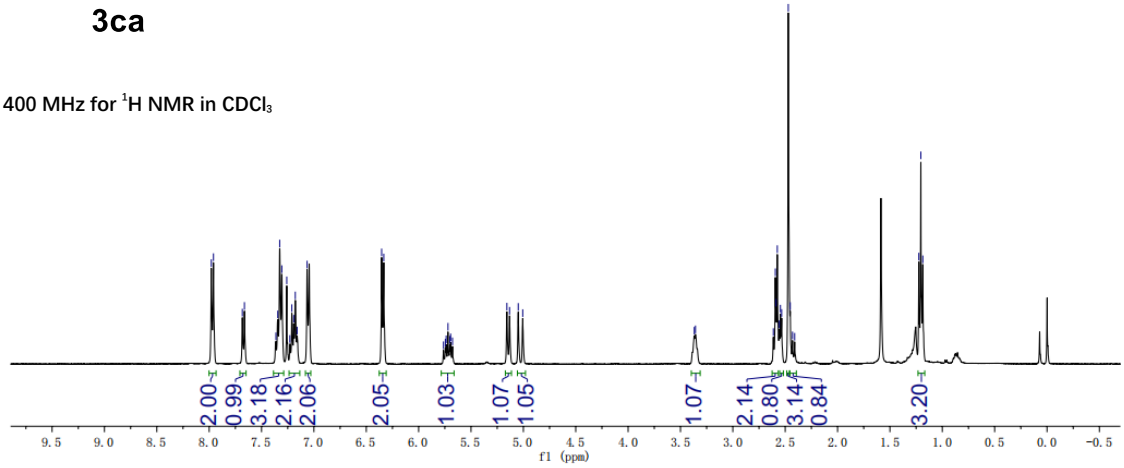
3ba

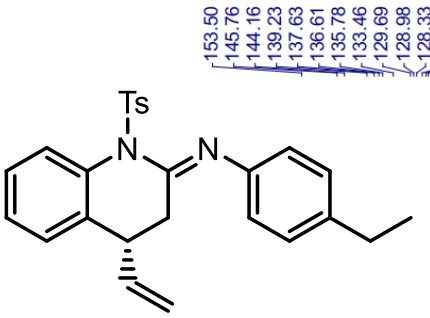
151 MHz for ^{13}C NMR in $CDCl_3$



3ca

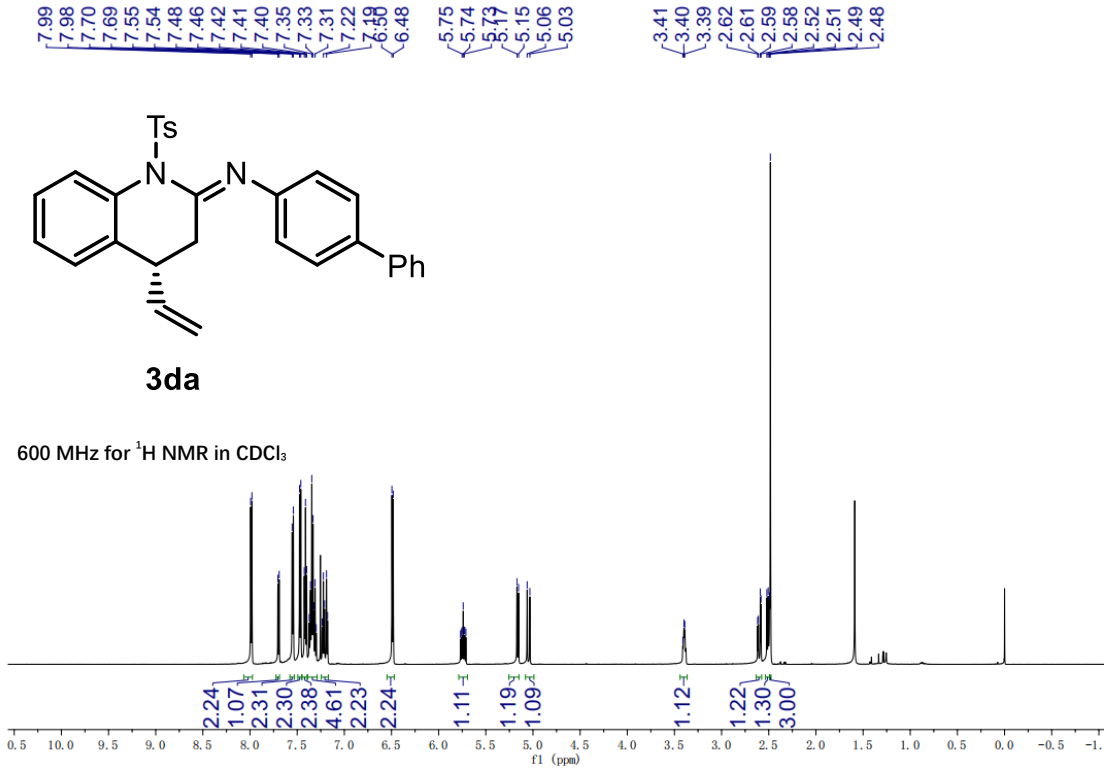
400 MHz for ^{1}H NMR in $CDCl_3$

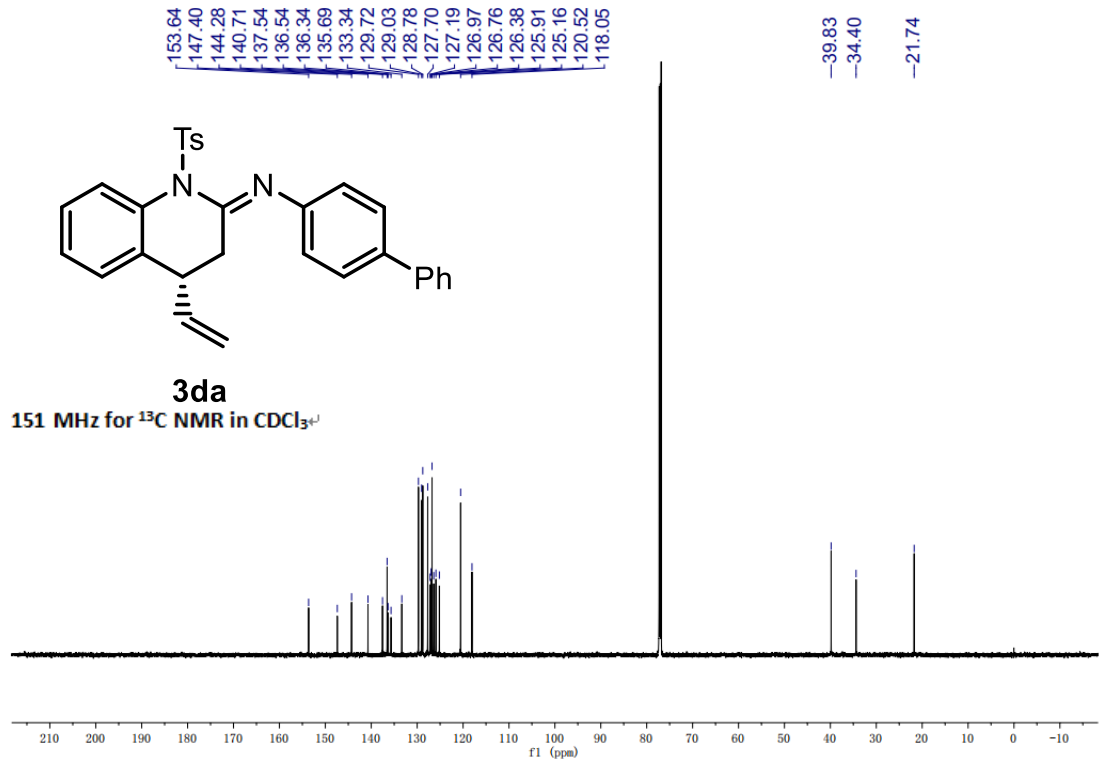


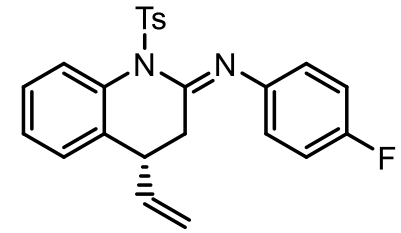


3ca

151 MHz for ^{13}C NMR in $CDCl_3$

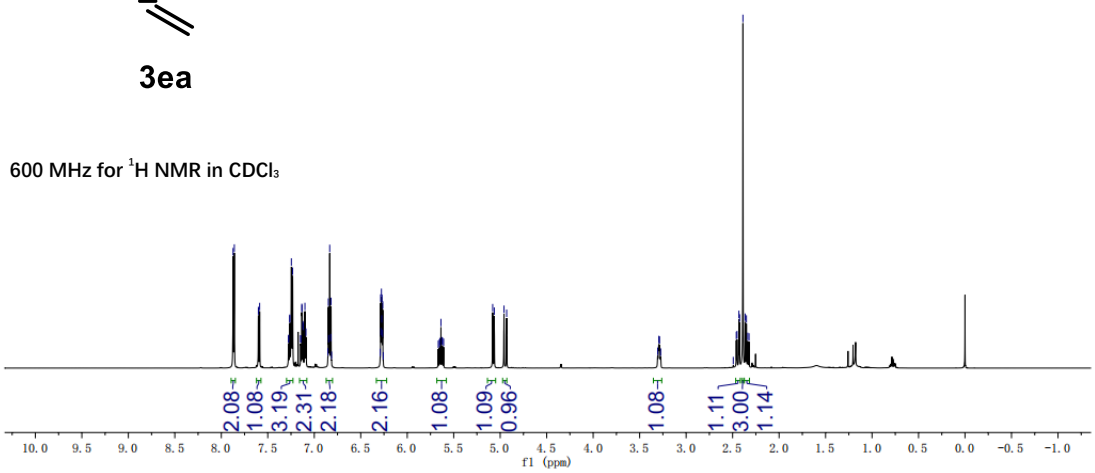

7.99
7.98
7.70
7.69
7.55
7.54
7.48
7.46
7.42
7.41
7.40
7.35
7.33
7.31
7.22
6.48
5.75
5.74
5.15
5.06
5.03
3.41
3.40
3.39
2.62
2.61
2.59
2.58
2.52
2.51
2.49
2.48
Ts
N
N
Ph
3da
600 MHz for ¹H NMR in CDCl₃
2.24
1.07
2.31
2.30
2.38
4.61
2.23
2.24
1.11
1.19
1.09
1.12
1.22
1.30
3.00
f1 (ppm)

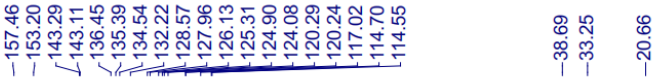

153.64
147.40
144.28
140.71
137.54
136.54
136.34
135.69
133.34
129.72
129.03
128.78
127.70
127.19
126.97
126.76
126.38
125.91
125.16
120.52
118.05
39.83
34.40
21.74
Ts
N
N
Ph
3da
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

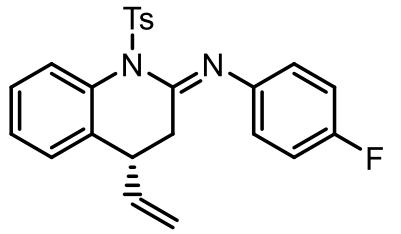


3ea

600 MHz for ^{1}H NMR in $CDCl_3$

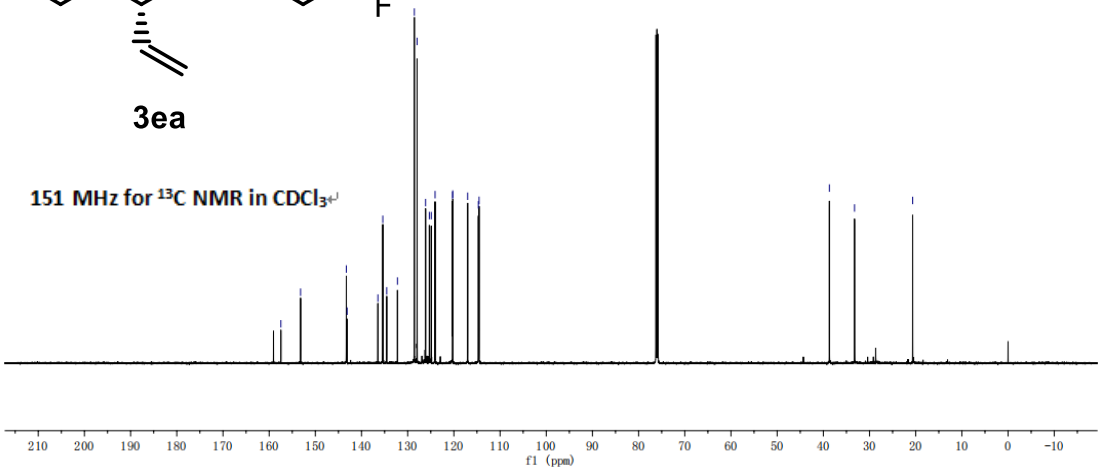


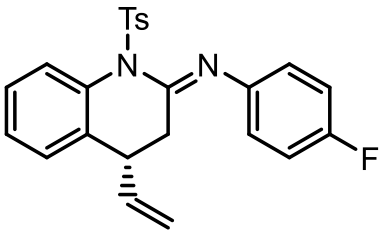




3ea

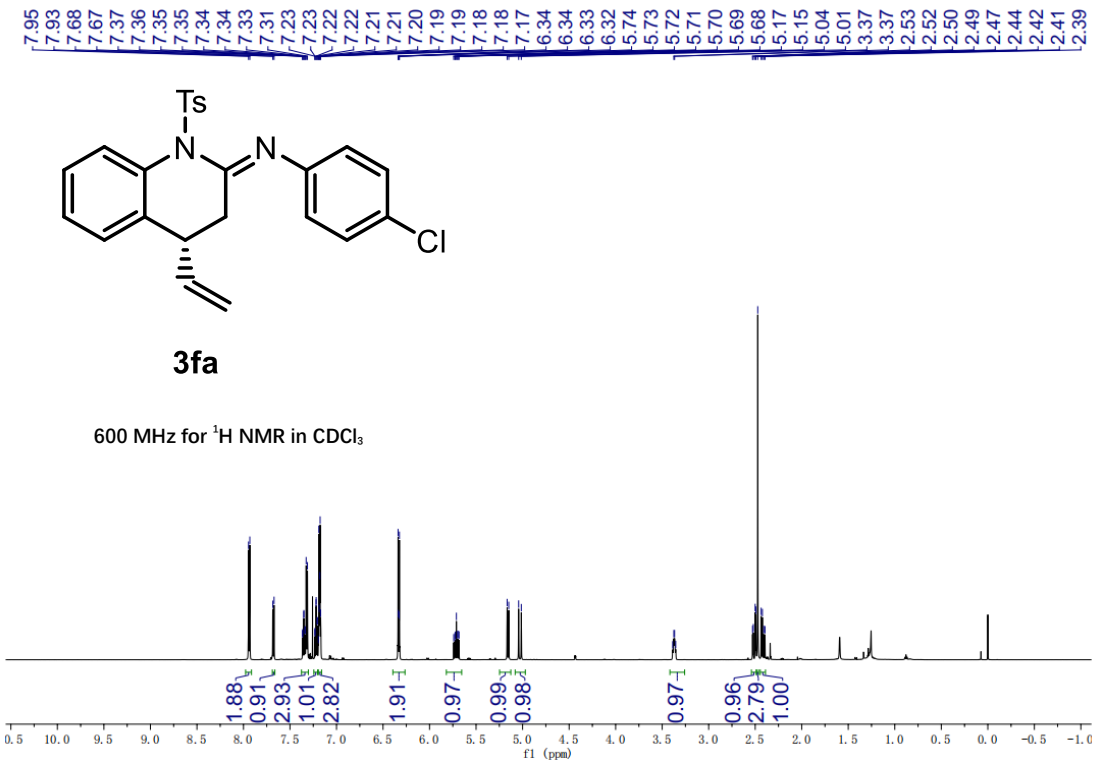
151 MHz for ^{13}C NMR in $CDCl_3$





3ea

565 MHz for ^{19}F NMR in $CDCl_3$


7.95
7.93
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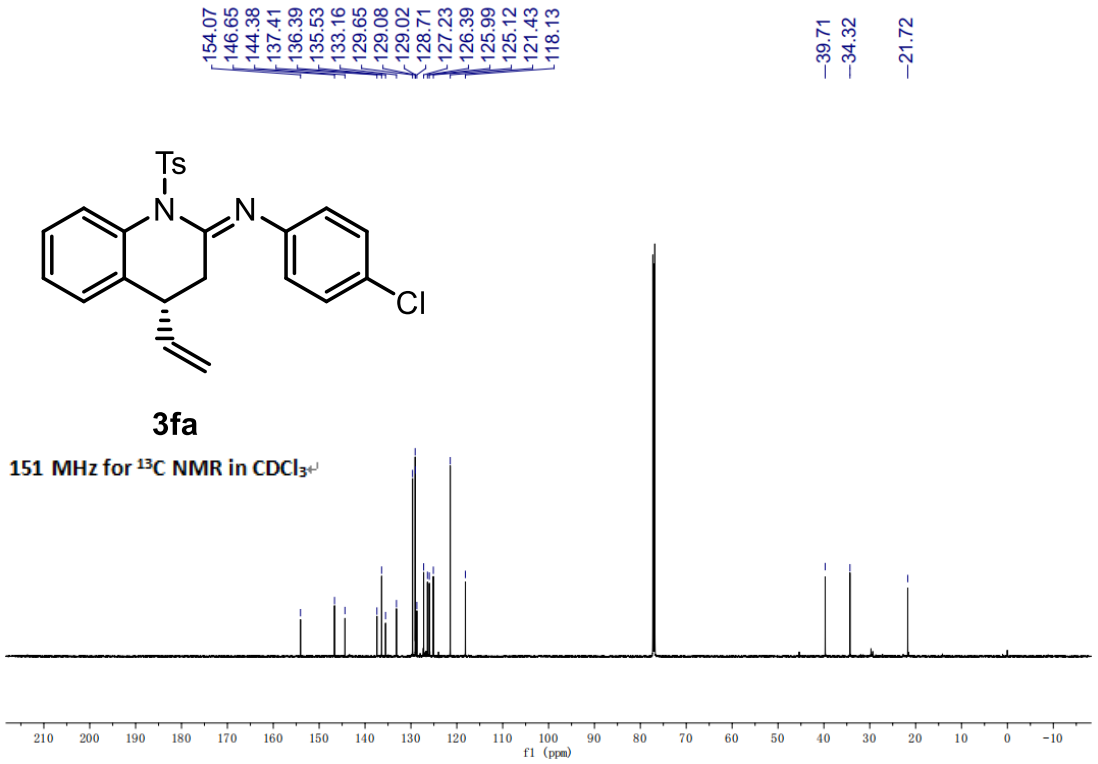
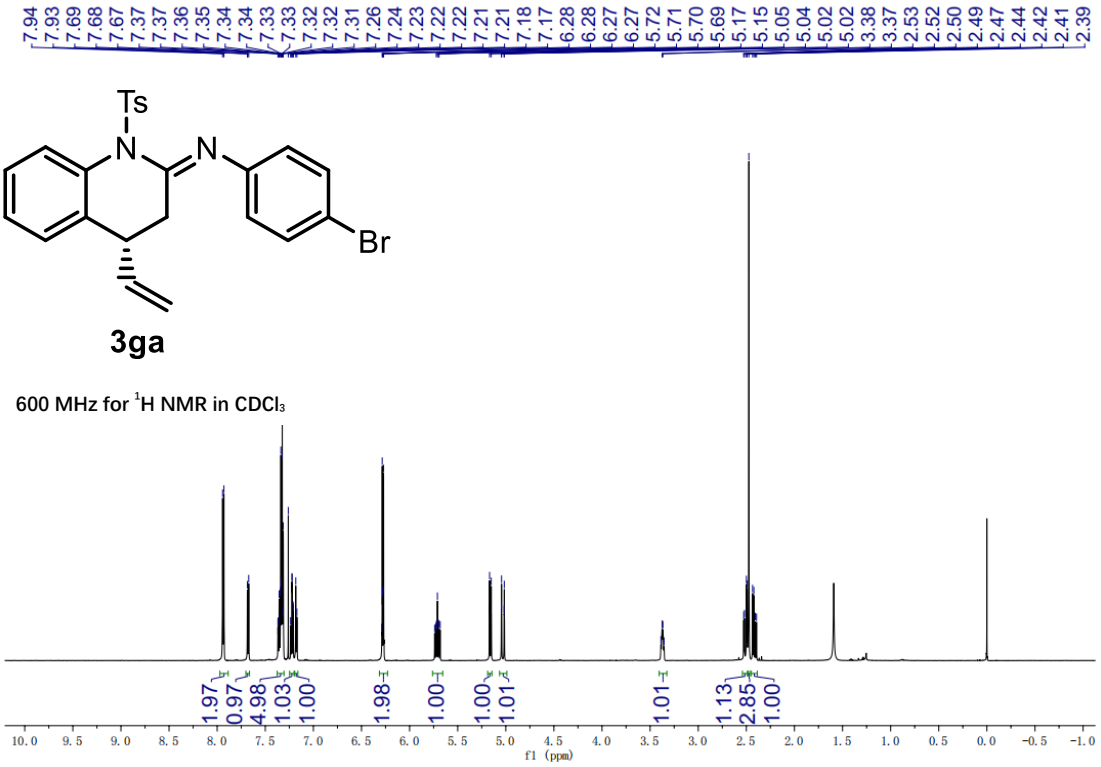
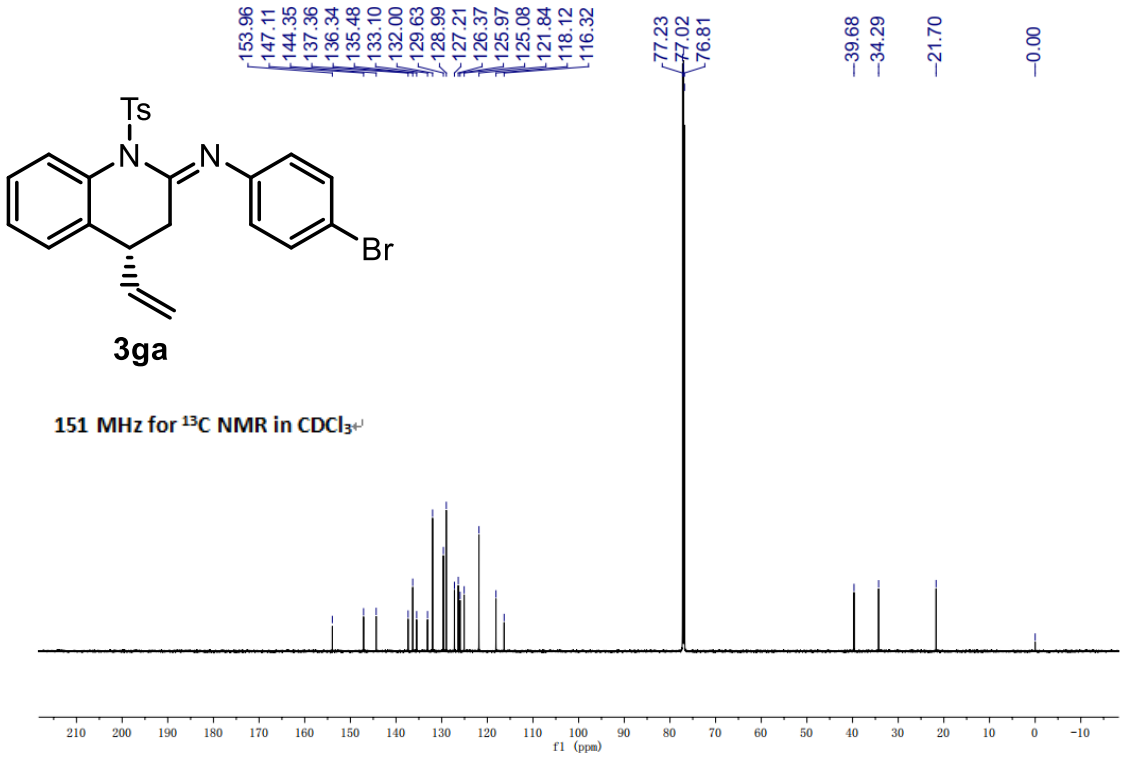
7.67
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
6.34
6.34
6.33
6.32
5.74
5.73
5.72
5.71
5.70
5.69
5.68
5.17
5.15
5.04
5.01
3.37
3.37
2.53
2.52
2.50
2.49
2.47
2.44
2.42
2.41
2.39
Ts
N
N
Cl
3fa
600 MHz for ^{1}H NMR in CDCl$_3$
1.88
0.91
2.93
1.01
2.82
1.91
0.97
0.99
0.98
0.97
0.96
2.79
1.00
f1 (ppm)


154.07
146.65
144.38
137.41
136.39
135.53
133.16
129.65
129.08
129.02
128.71
127.23
126.39
125.99
125.12
121.43
118.13
39.71
34.32
21.72
Ts
N
N
Cl
3fa
151 MHz for ^{13}C NMR in CDCl$_3$
f1 (ppm)


7.94
7.93
7.69
7.68
7.67
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.26
7.24
7.23
7.22
7.22
7.21
7.21
7.18
7.17
6.28
6.28
6.27
6.27
5.72
5.71
5.70
5.69
5.17
5.15
5.05
5.04
5.02
5.02
3.38
3.37
2.53
2.52
2.50
2.49
2.47
2.44
2.42
2.41
2.39
Ts
N
N
Br
3ga
600 MHz for ^{1}H NMR in CDCl$_3$
1.97
0.97
4.98
1.03
1.00
1.98
1.00
1.00
1.01
1.01
1.13
2.85
1.00
f1 (ppm)


153.96
147.11
144.35
137.36
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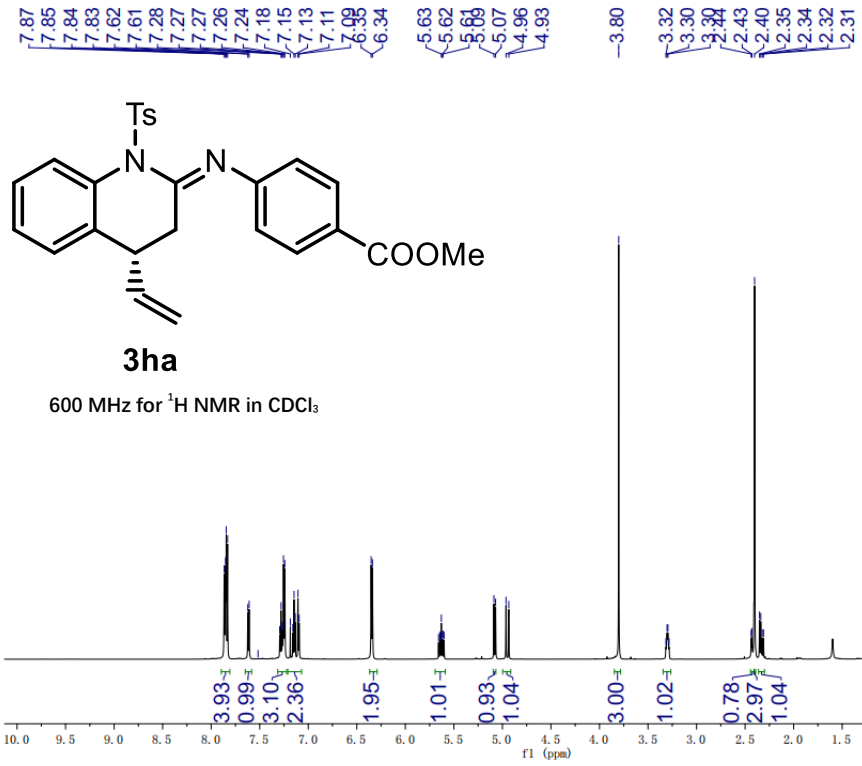
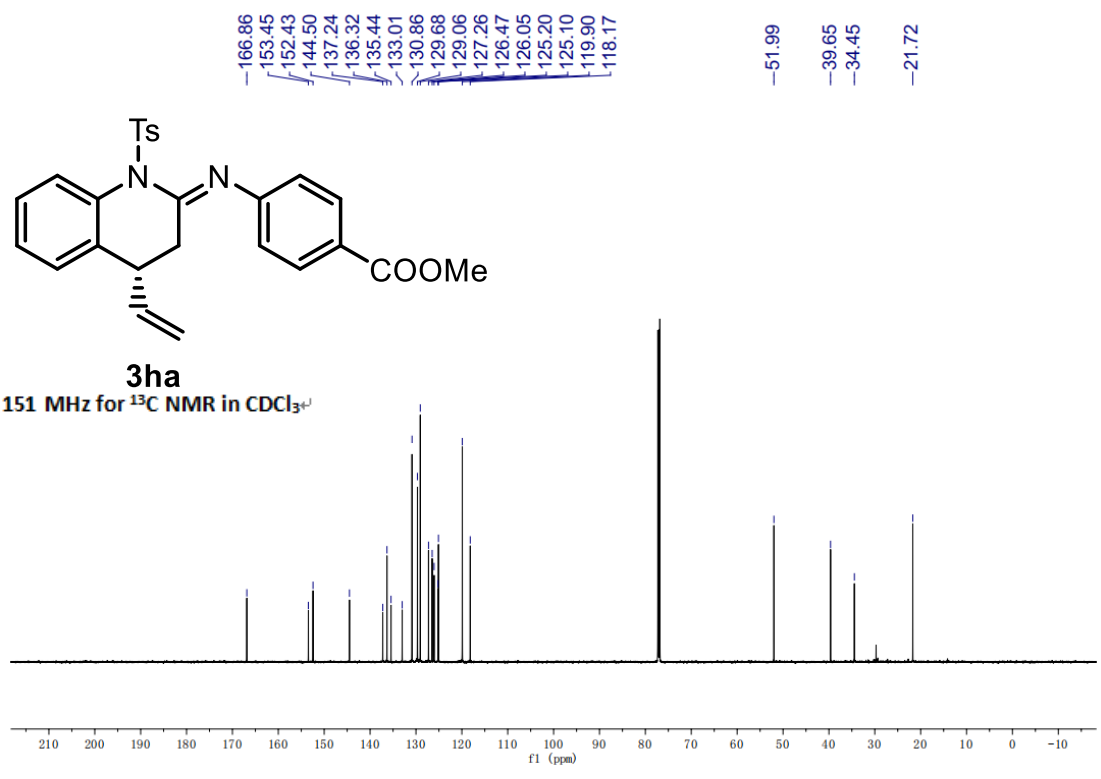
135.48
133.10
132.00
129.63
128.99
127.21
126.37
125.97
125.08
121.84
118.12
116.32
77.23
77.02
76.81
39.68
34.29
21.70
0.00
Ts
N
N
Br
3ga
151 MHz for ^{13}C NMR in CDCl$_3$
f1 (ppm)



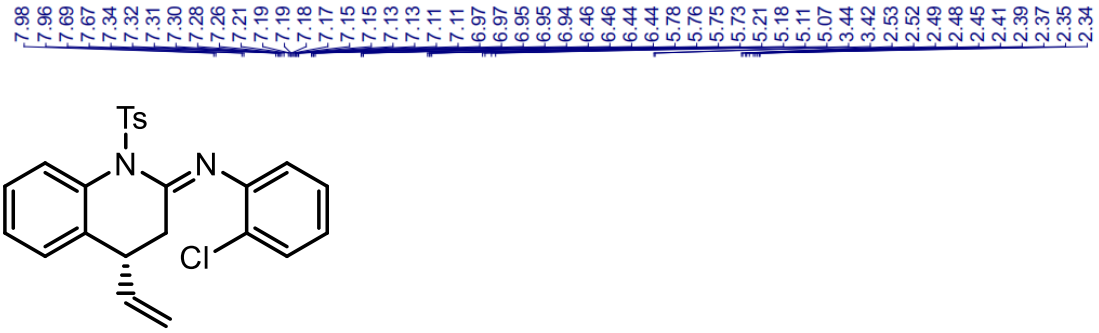
3ha

600 MHz for ^{1}H NMR in $CDCl_3$



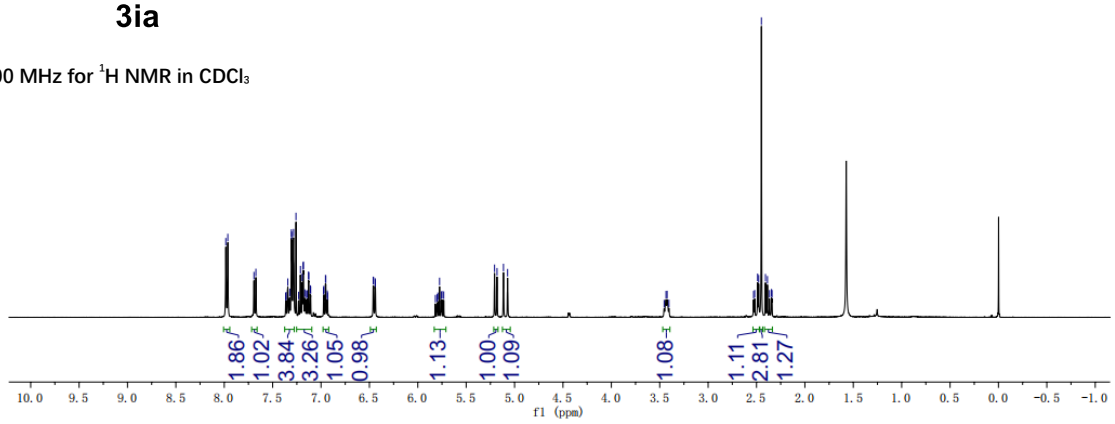
3ha

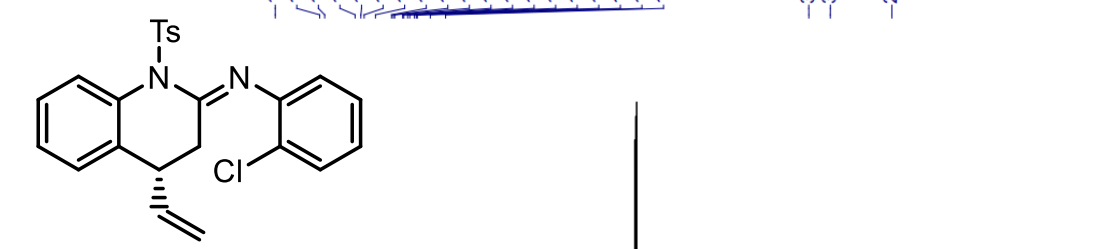
151 MHz for ^{13}C NMR in $CDCl_3$



3ia

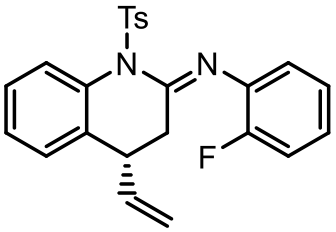
400 MHz for ^{1}H NMR in $CDCl_3$





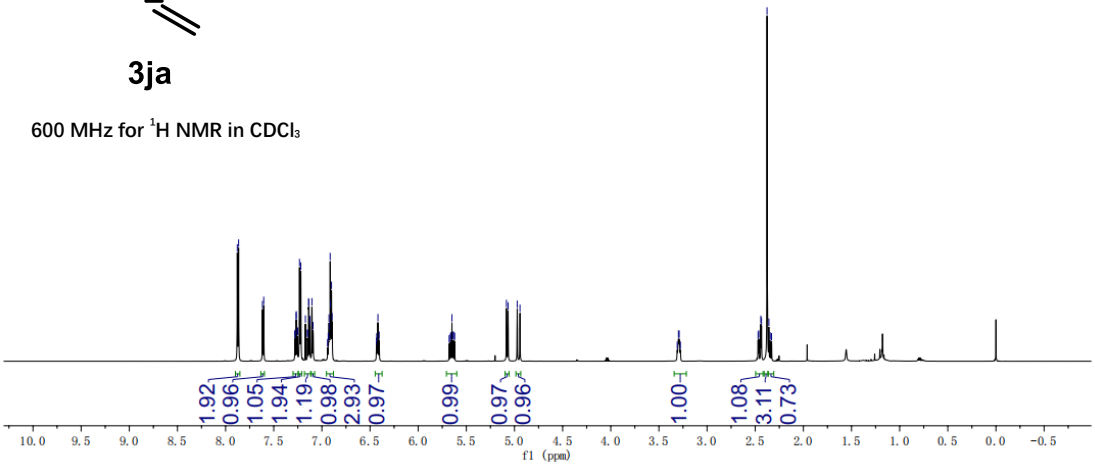
3ia

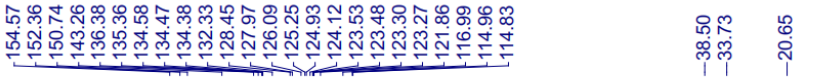
151 MHz for ^{13}C NMR in $CDCl_3$

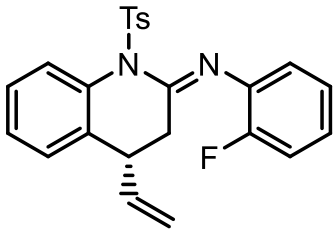


3ja

600 MHz for ^{1}H NMR in $CDCl_3$

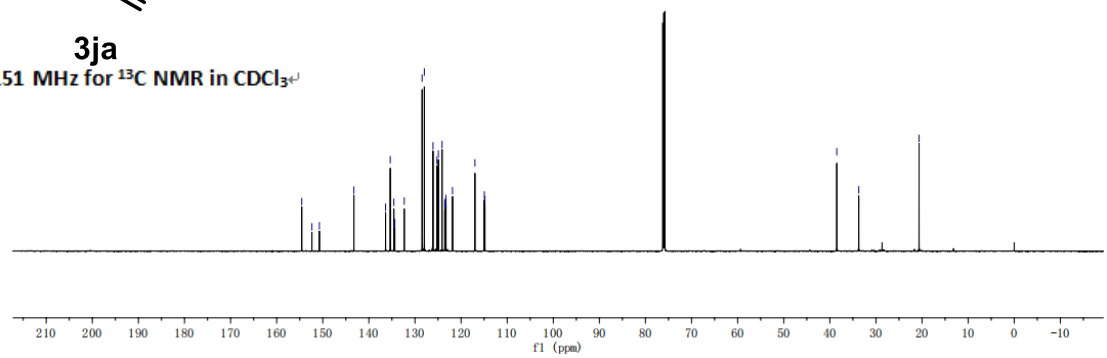


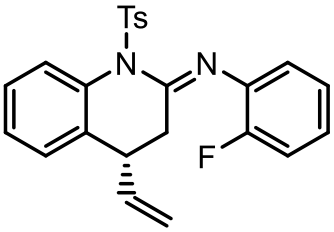




3ja

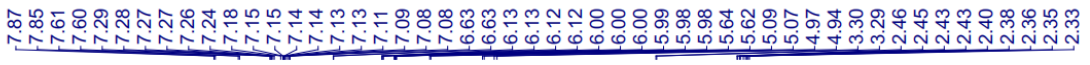
151 MHz for ^{13}C NMR in $CDCl_3$

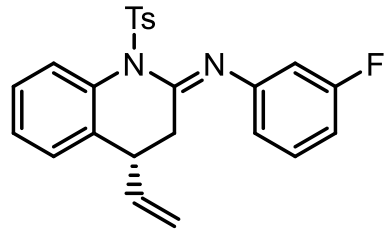




3ja

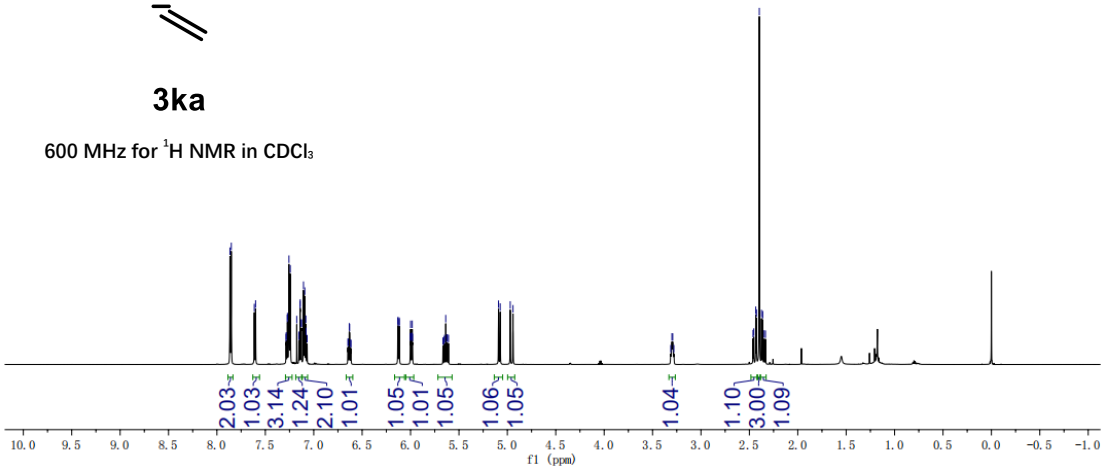
565 MHz for ^{19}F NMR in $CDCl_3$

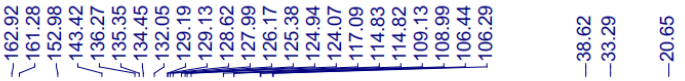


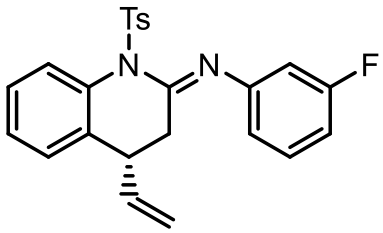


3ka

600 MHz for ^{1}H NMR in $CDCl_3$

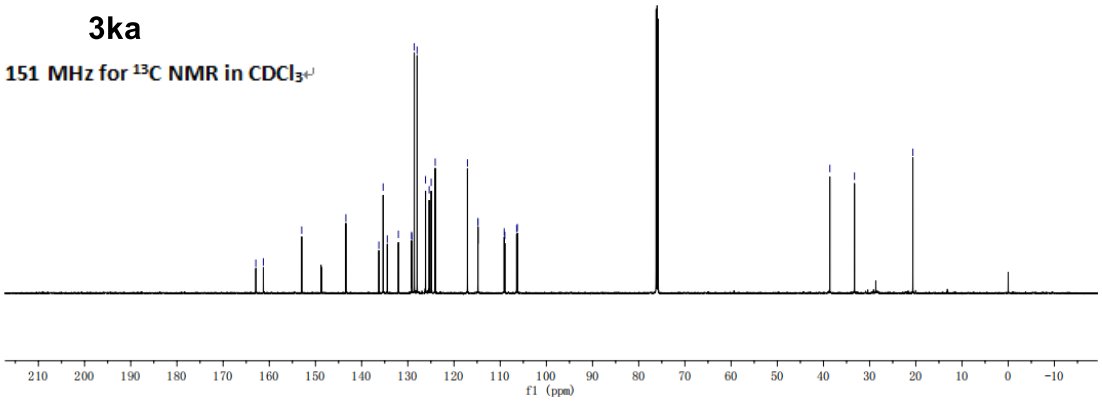


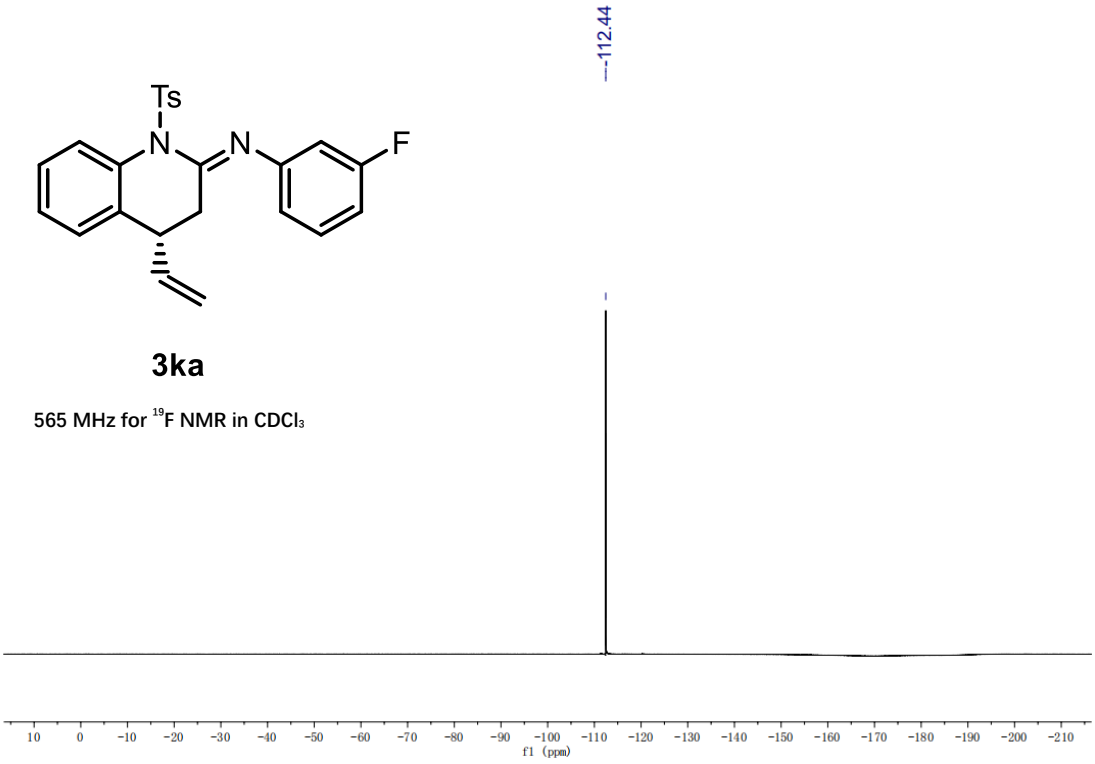




3ka

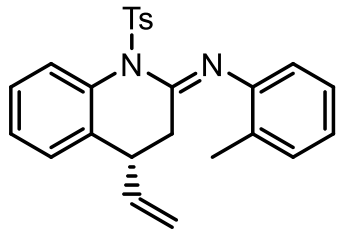
151 MHz for ^{13}C NMR in $CDCl_3$





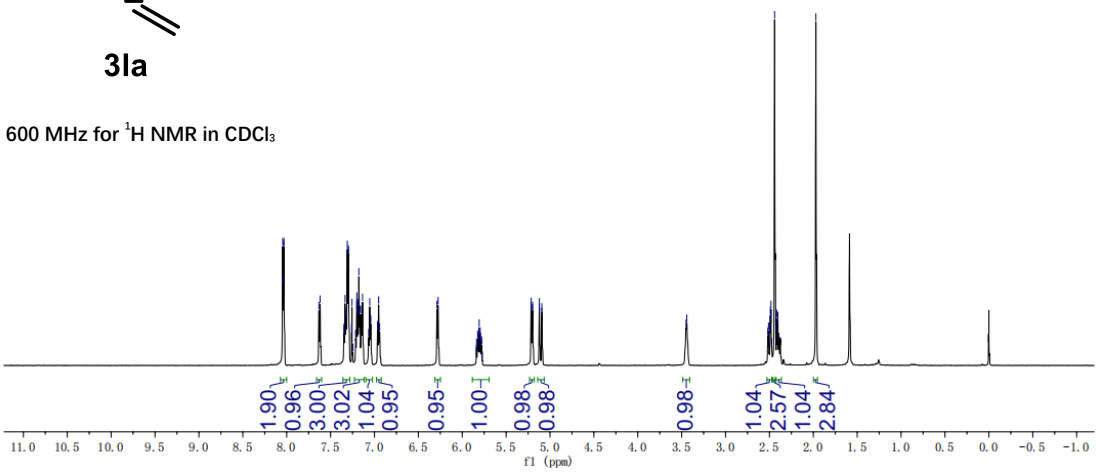
3ka

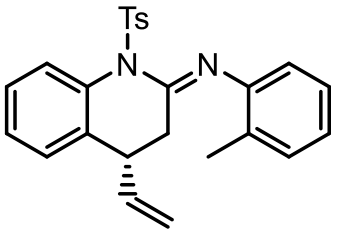
565 MHz for ^{19}F NMR in $CDCl_3$



3la

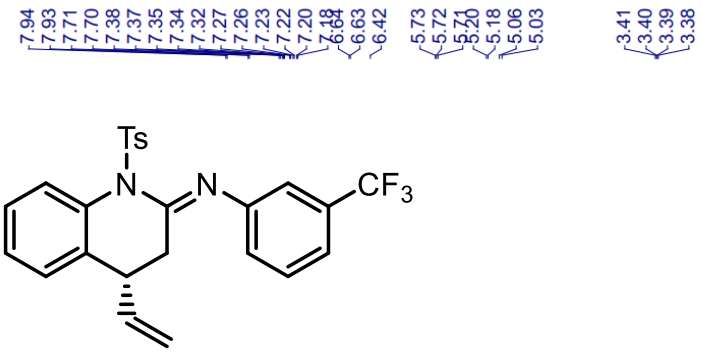
600 MHz for ^{1}H NMR in $CDCl_3$





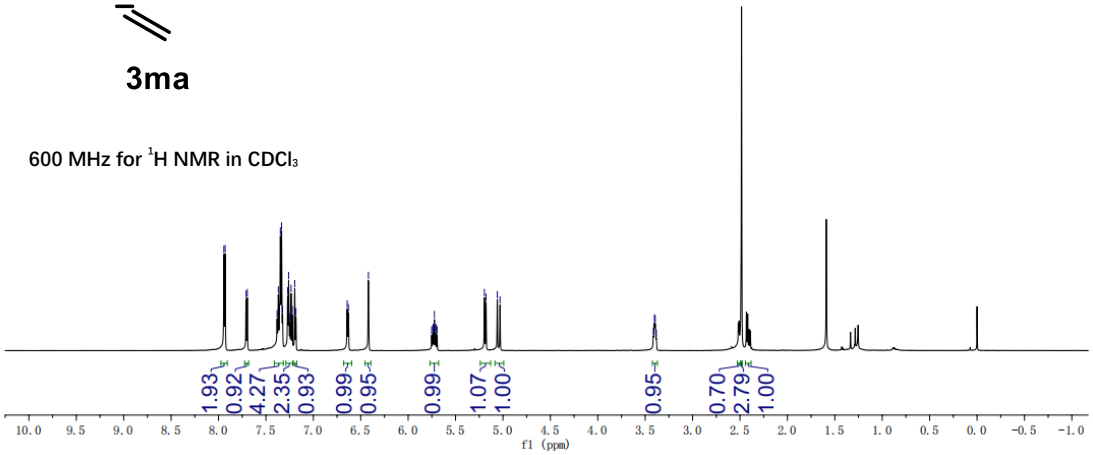
3la

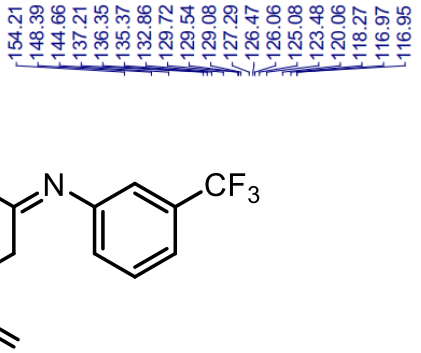
151 MHz for ^{13}C NMR in $CDCl_3$



3ma

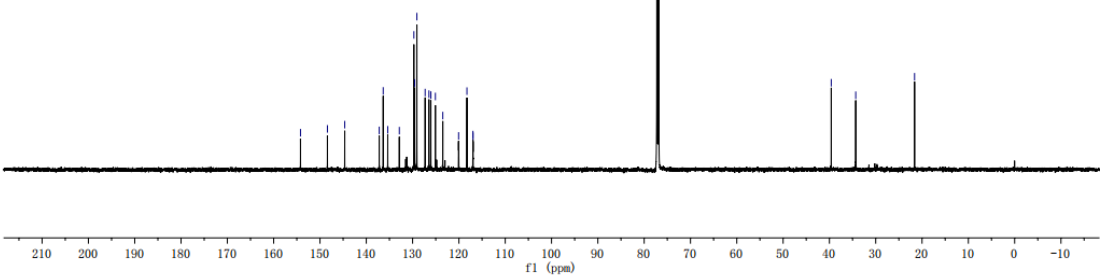
600 MHz for ^{1}H NMR in $CDCl_3$

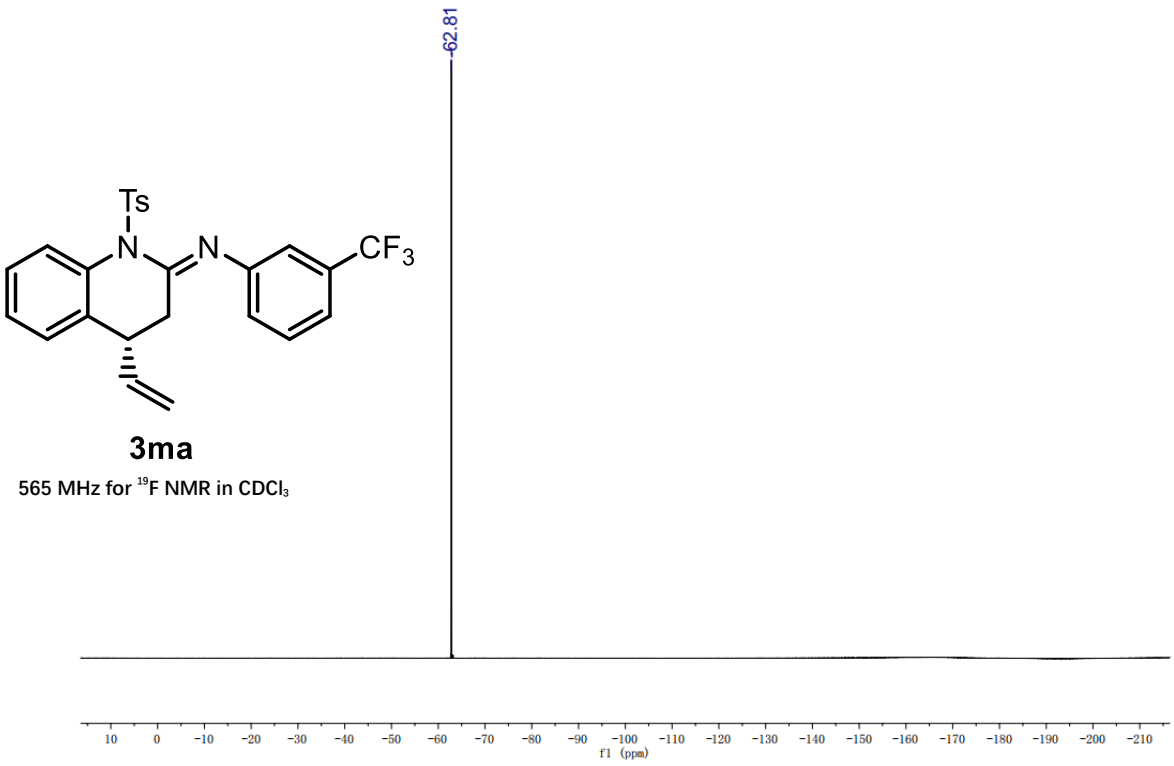




3ma

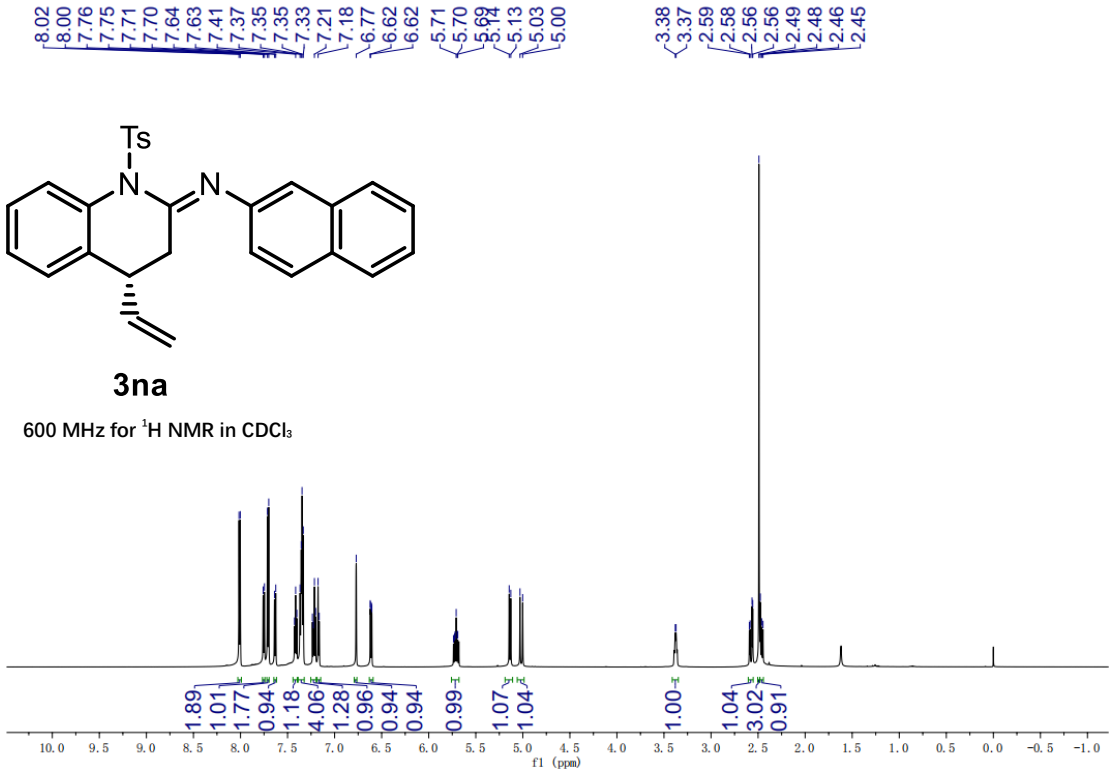
151 MHz for ^{13}C NMR in $CDCl_3$





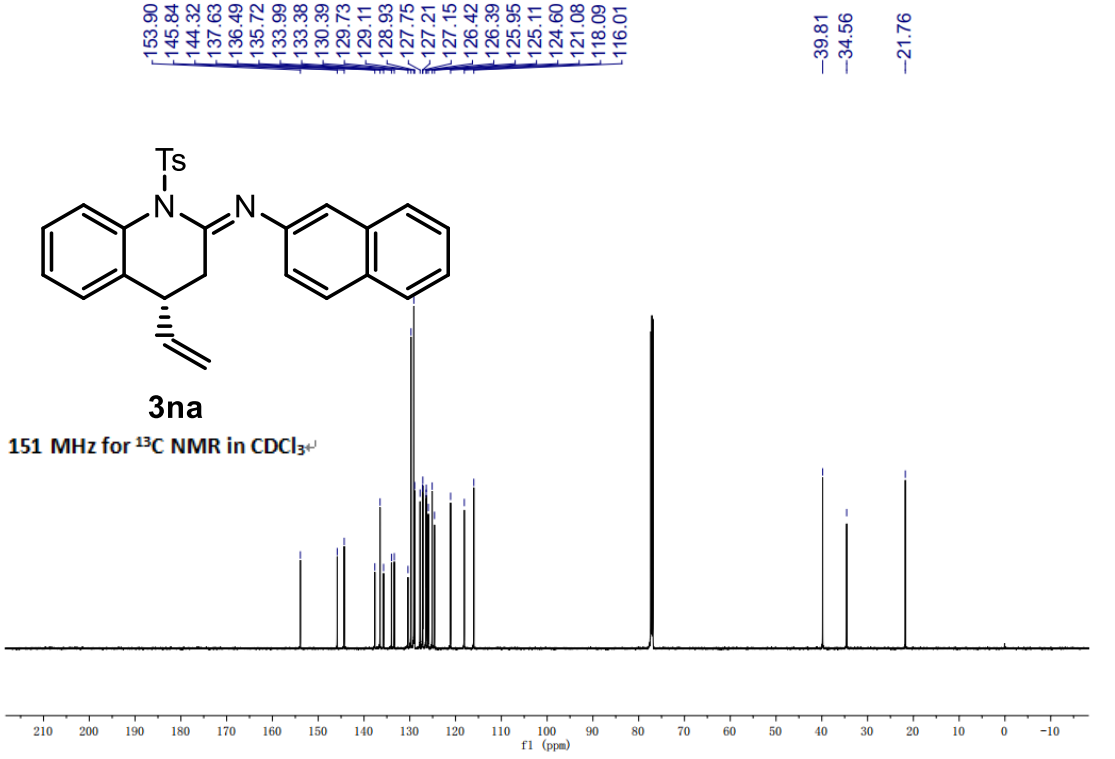
3ma

565 MHz for ^{19}F NMR in $CDCl_3$



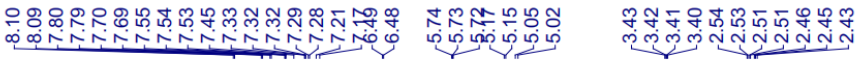
3na

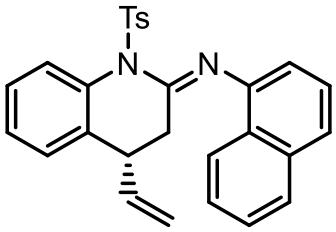
600 MHz for ^{1}H NMR in $CDCl_3$



3na

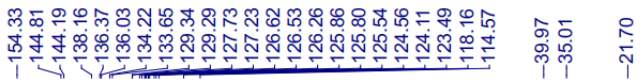
151 MHz for ^{13}C NMR in $CDCl_3$

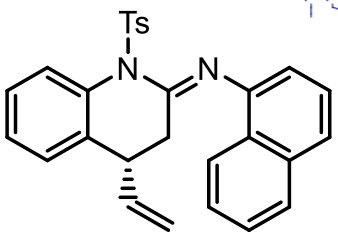




3oa

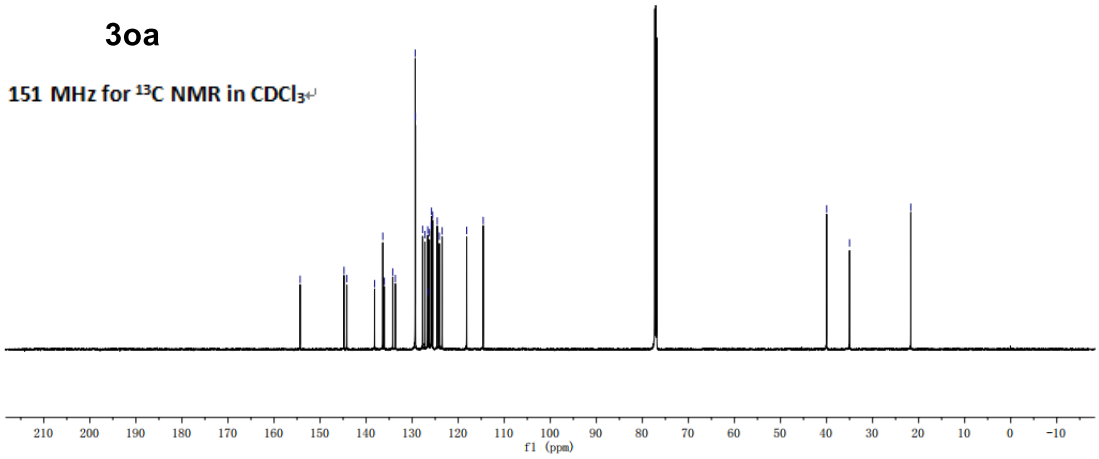
600 MHz for ^{1}H NMR in $CDCl_3$

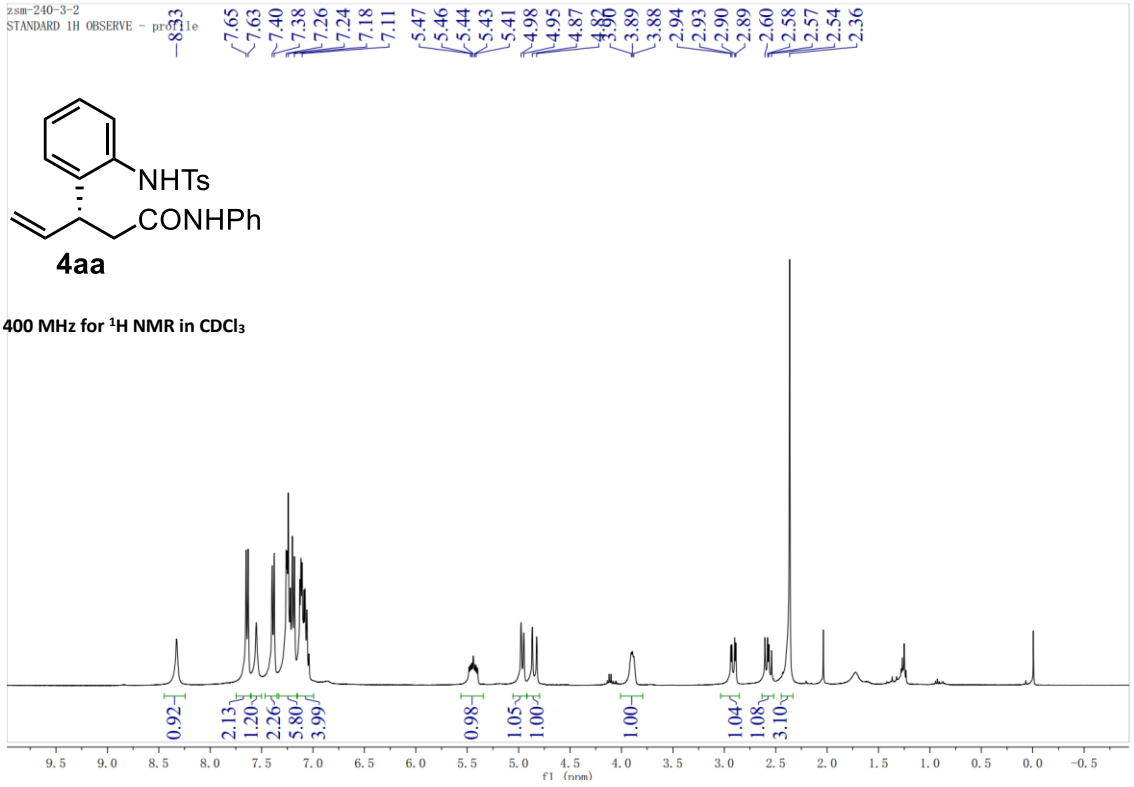




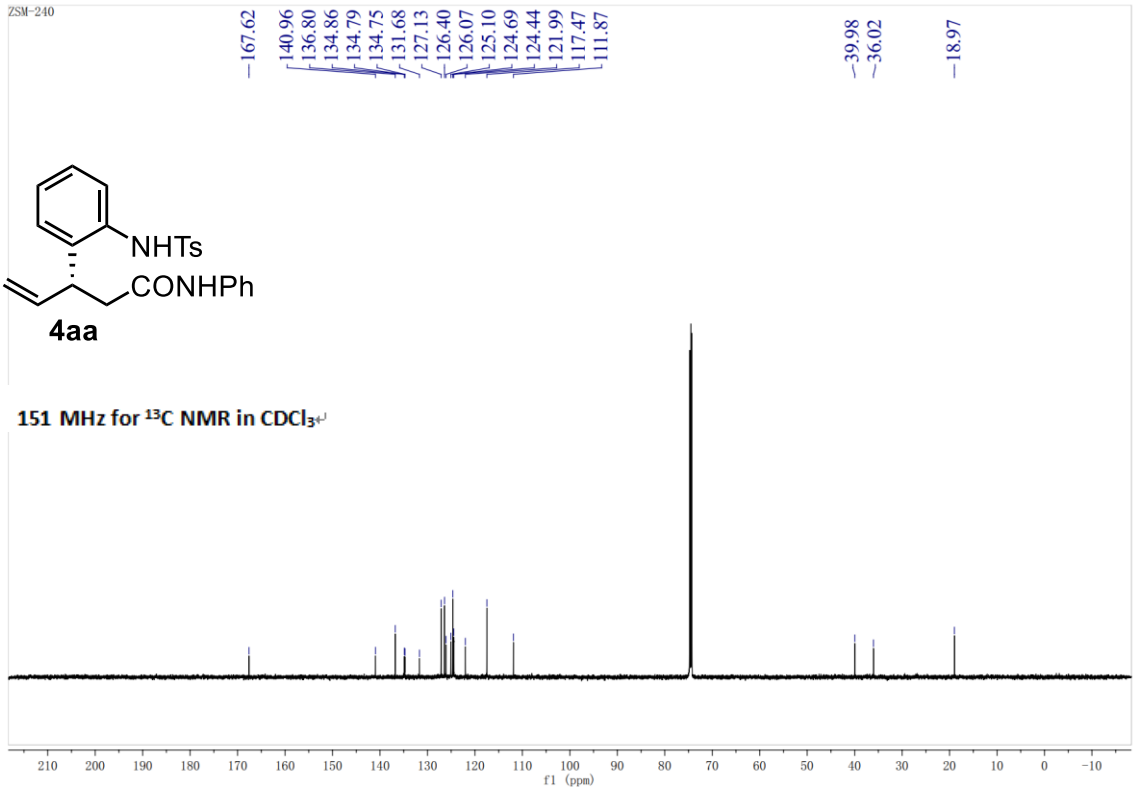
3oa

151 MHz for ^{13}C NMR in $CDCl_3$

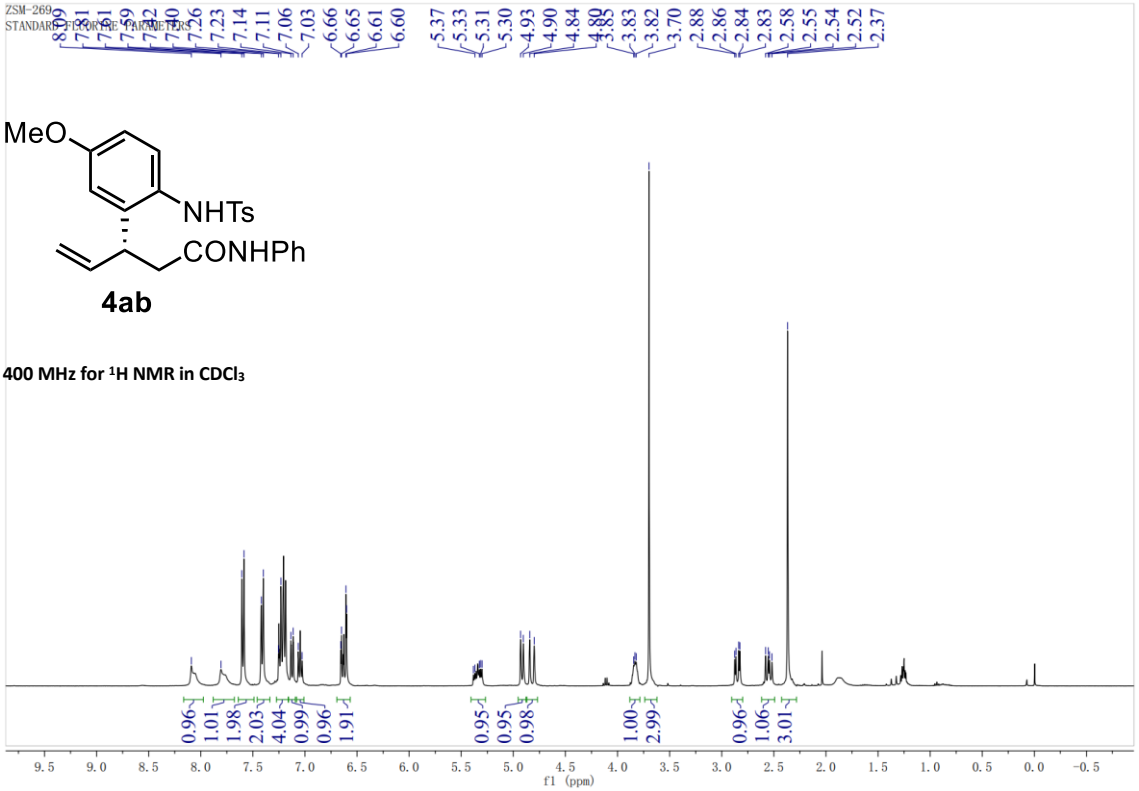


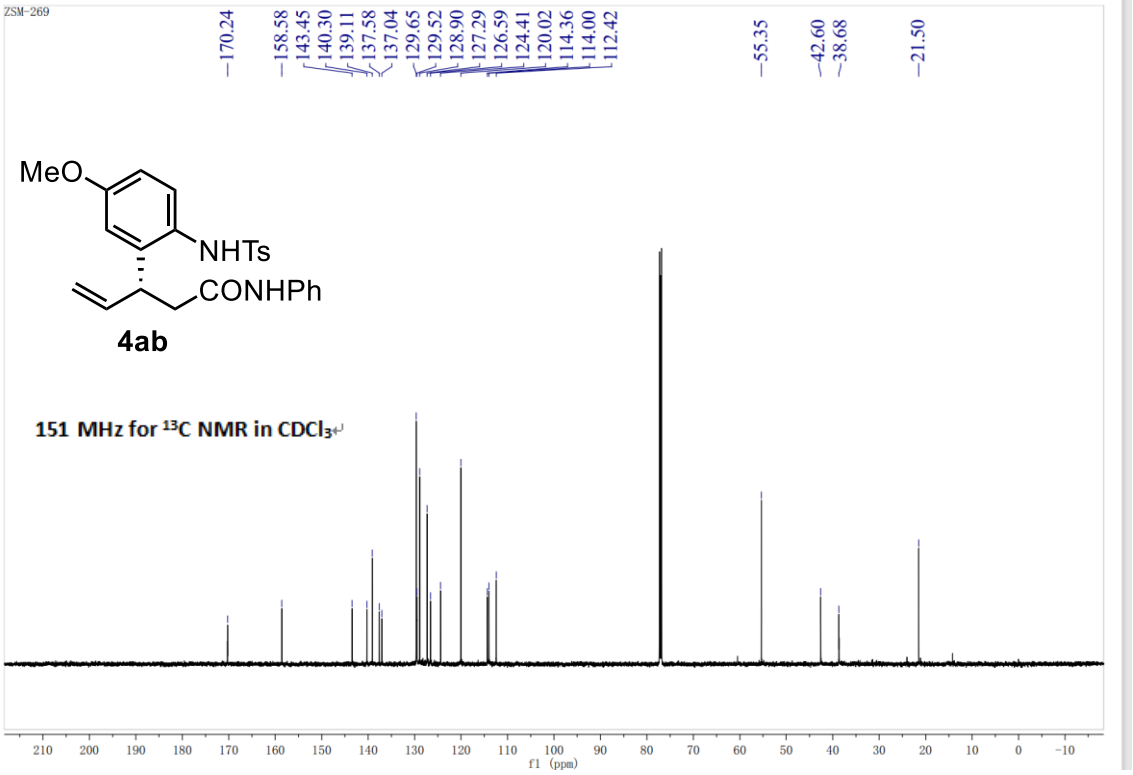


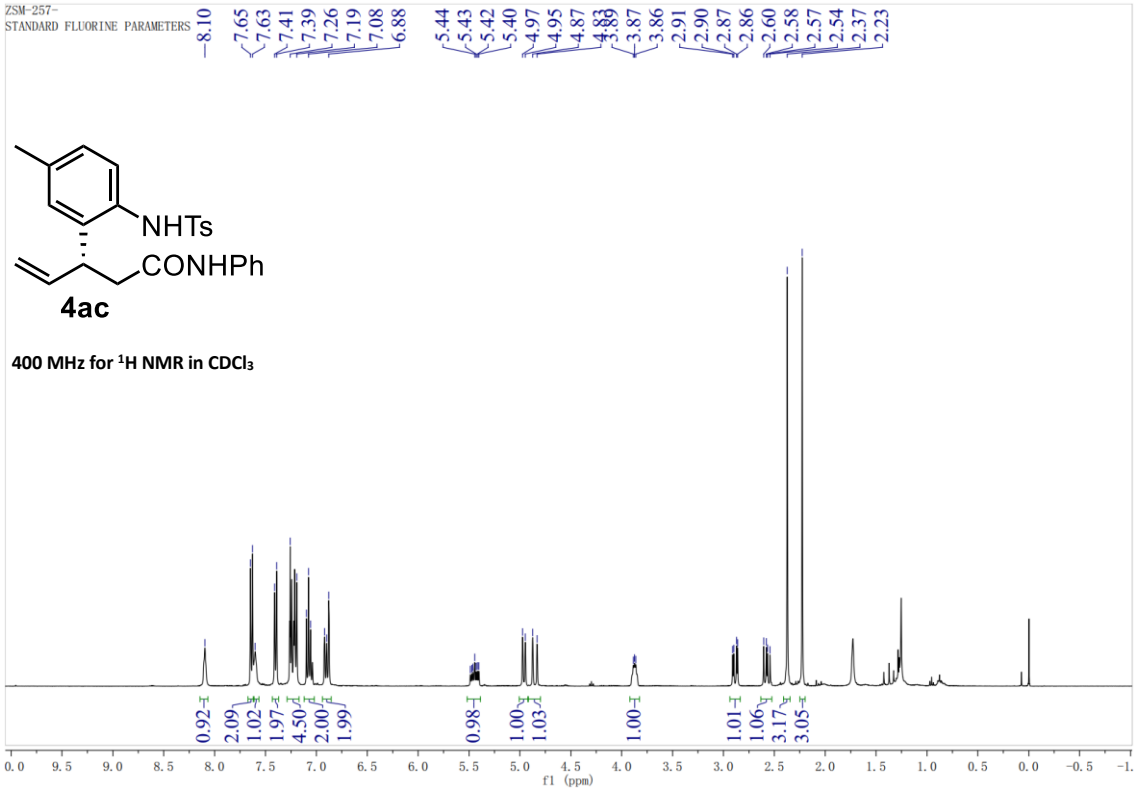
400 MHz for ^{1}H NMR in $CDCl_3$

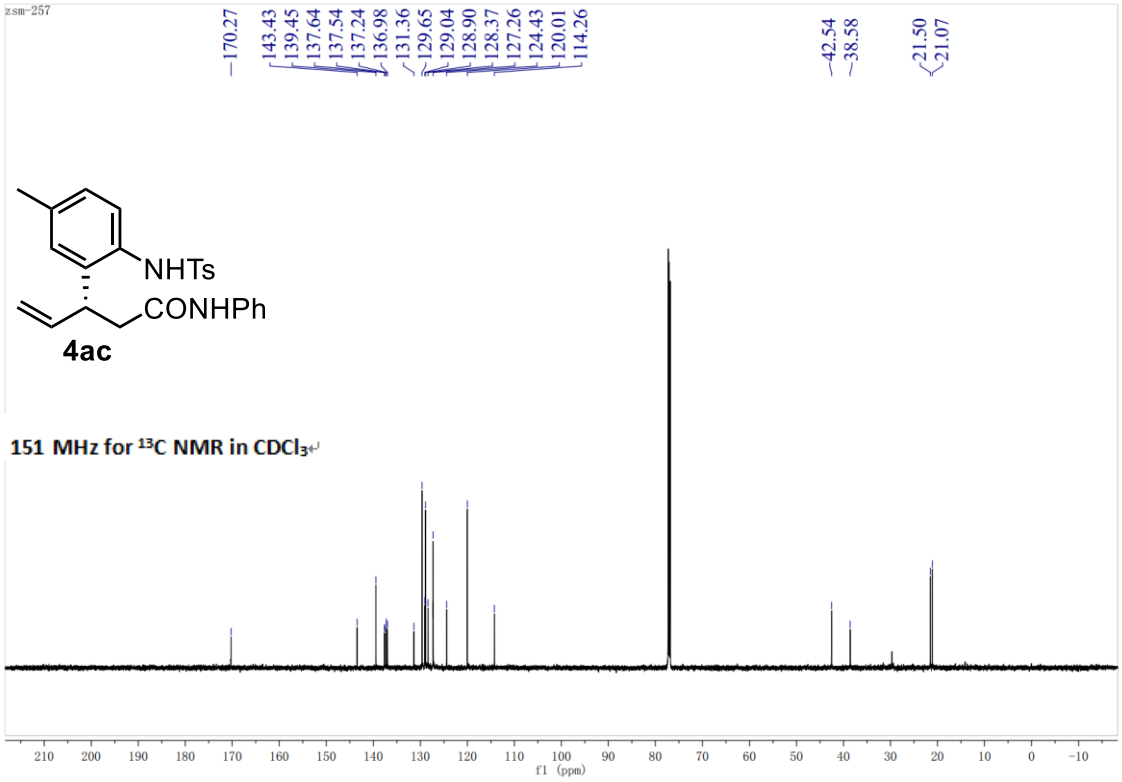


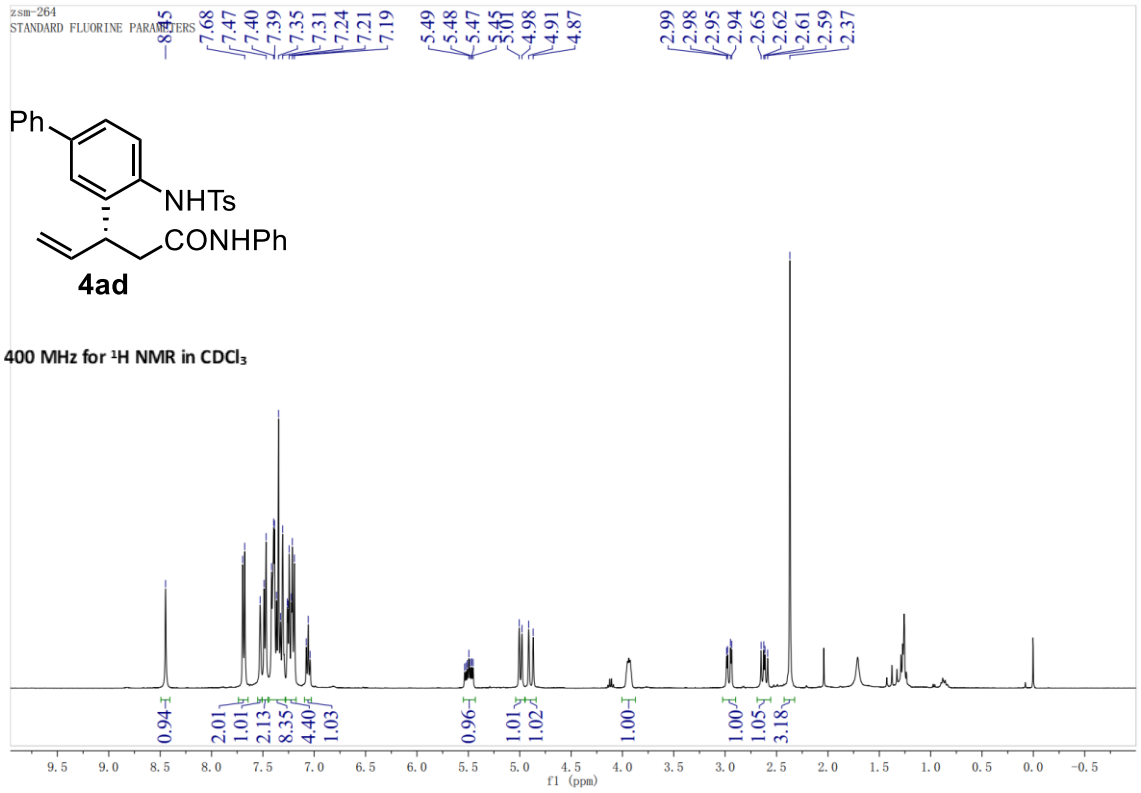
151 MHz for ^{13}C NMR in $CDCl_3$

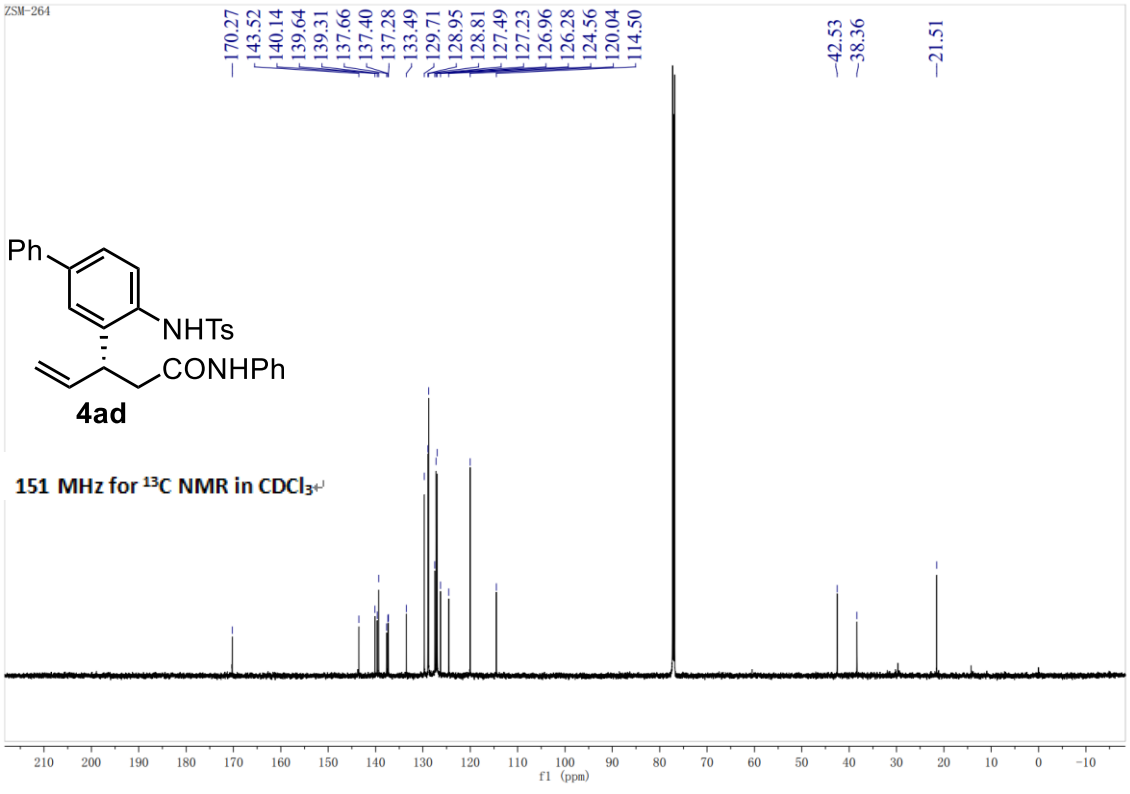

ZSM-269
MeO
NHTs
CONHPh
4ab
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)


ZSM-269
MeO
NHTs
CONHPh
4ab
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


ZSM-257-
STANDARD FLUORINE PARAMETERS
NHTs
CONHPh
4ac
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)


zsm-257
NHTs
CONHPh
4ac
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


zsm-264
STANDARD FLUORINE PARAMETERS
8.35
7.68
7.47
7.40
7.39
7.35
7.31
7.24
7.21
7.19
5.49
5.48
5.47
5.45
5.01
4.98
4.91
4.87
2.99
2.98
2.95
2.94
2.65
2.62
2.61
2.59
2.37
Ph
NHTs
CONHPh
4ad
400 MHz for ¹H NMR in CDCl₃
0.94
2.01
1.01
2.13
8.35
4.40
1.03
0.96
1.01
1.02
1.00
1.00
1.05
3.18
f1 (ppm)


ZSM-264
170.27
143.52
140.14
139.64
139.31
137.66
137.40
137.28
133.49
129.71
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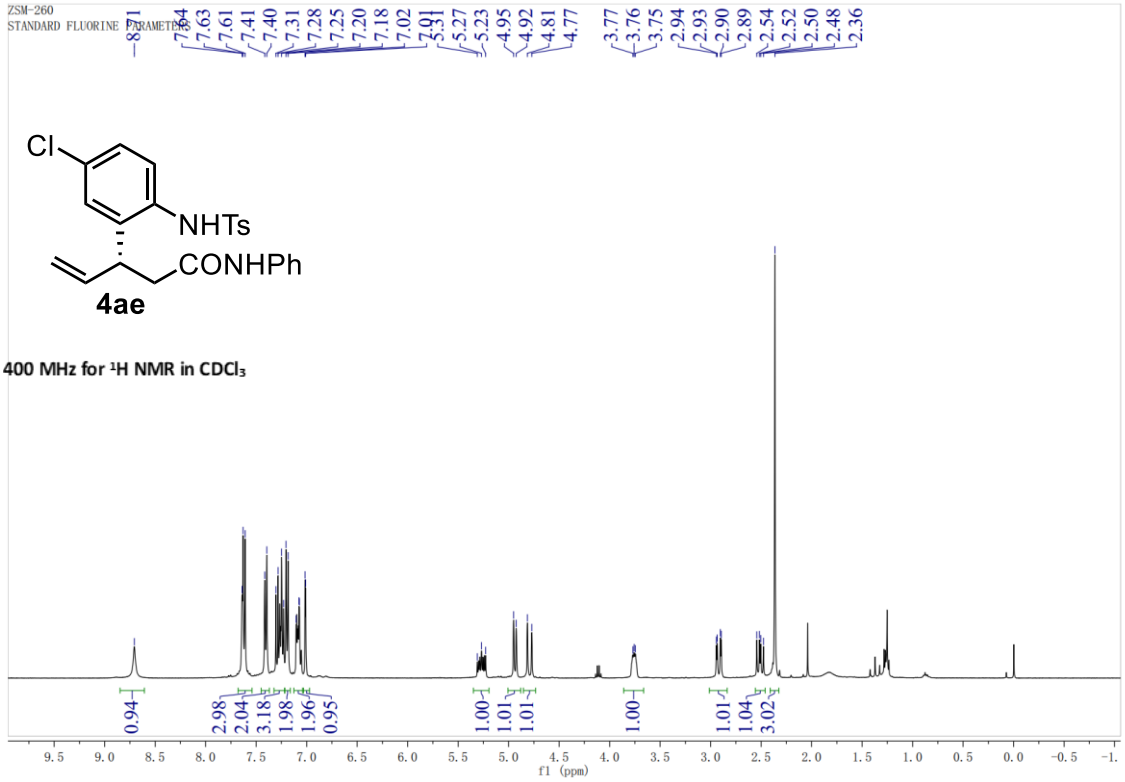
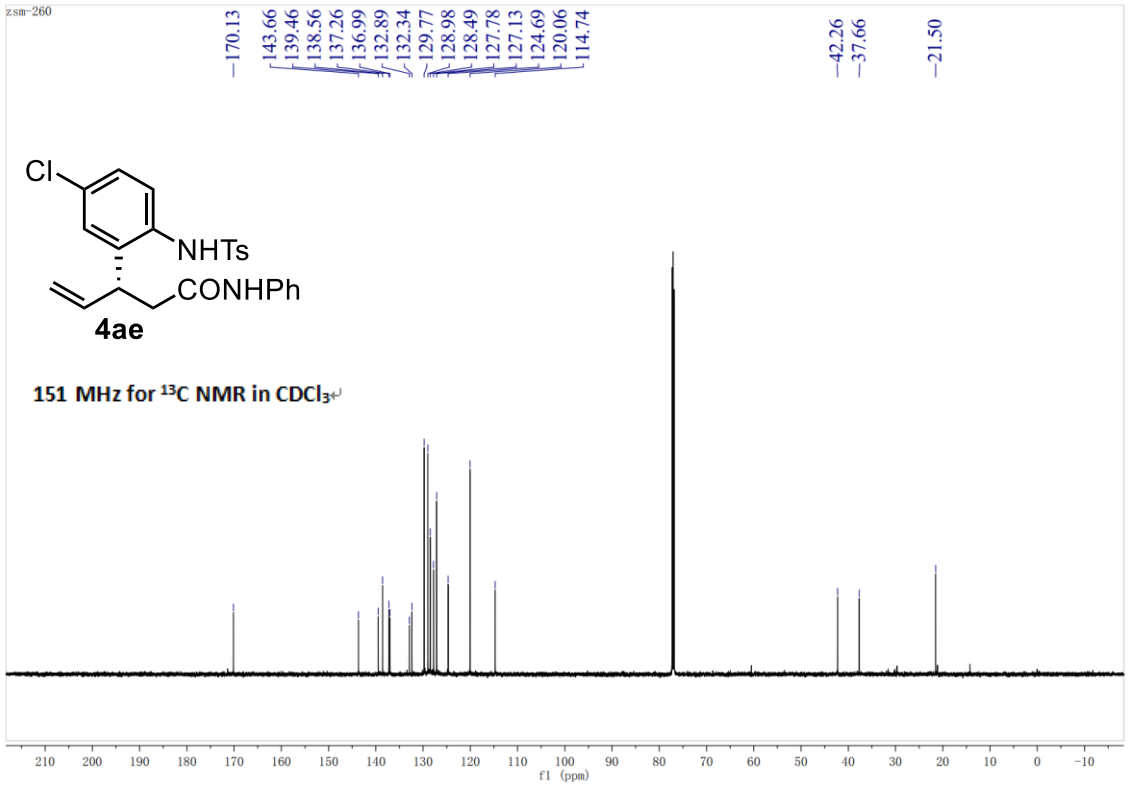
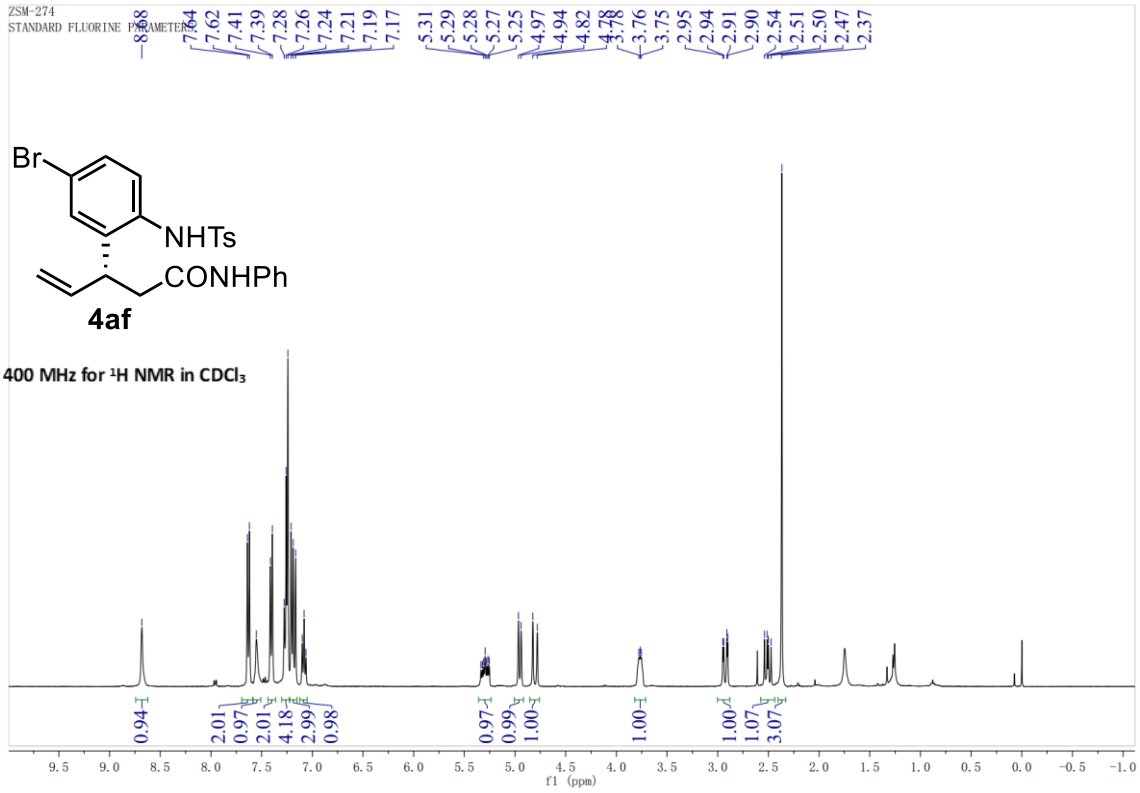
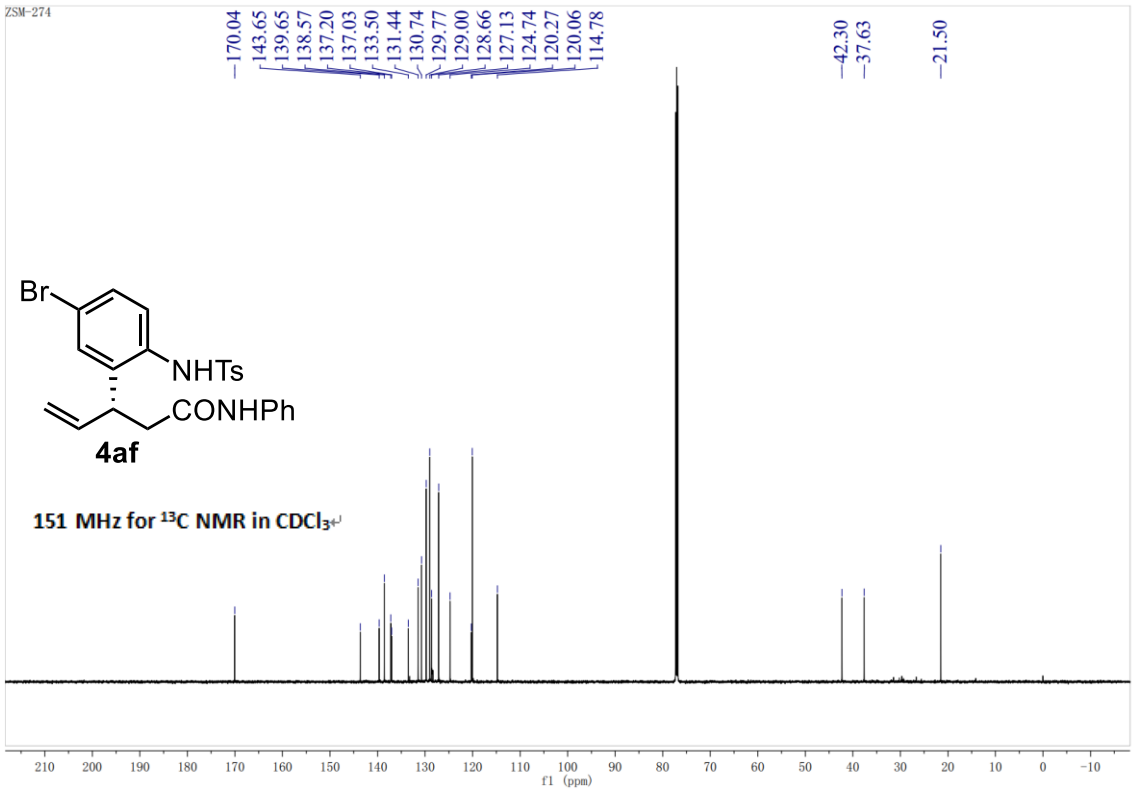
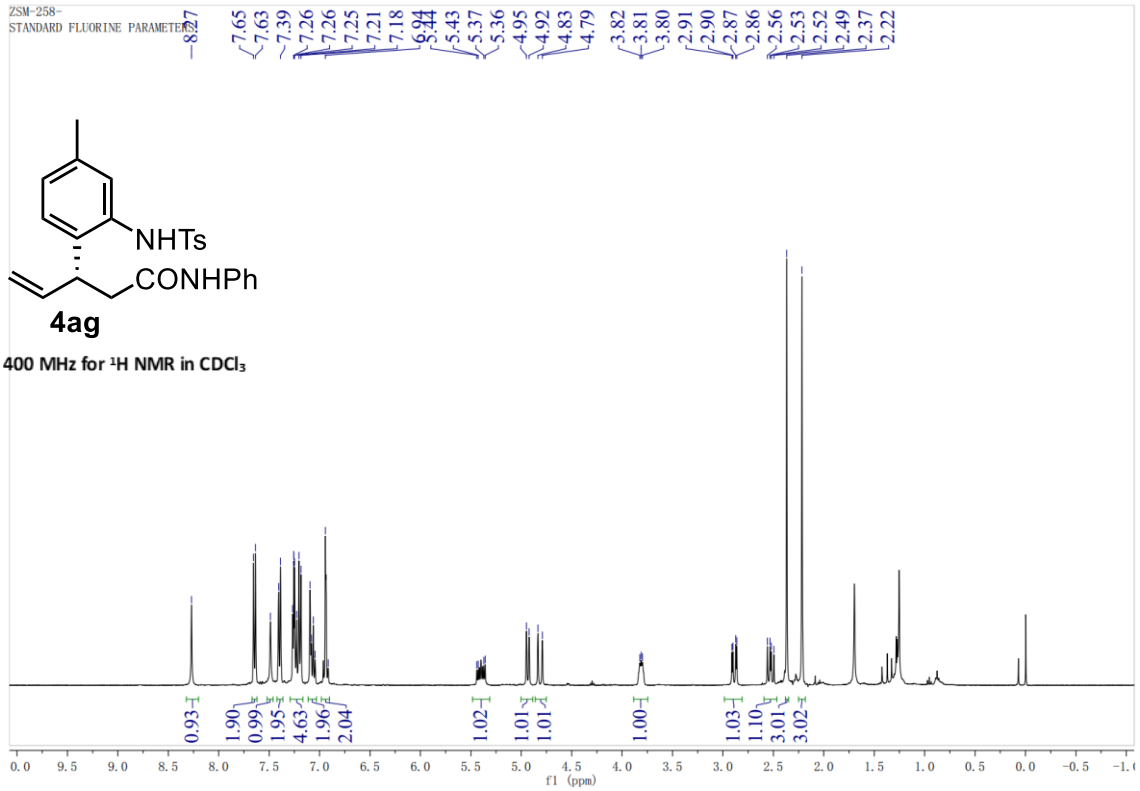
128.81
127.49
127.23
126.96
126.28
124.56
120.04
114.50
42.53
38.36
21.51
Ph
NHTs
CONHPh
4ad
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


ZSM-260
STANDARD FLUORINE PARAMETER
Cl
NHTs
CONHPh
4ae
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)


zsm-260
Cl
NHTs
CONHPh
4ae
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


ZSM-274
STANDARD FLUORINE PARAMETER
8.48
7.64
7.62
7.41
7.39
7.28
7.26
7.24
7.21
7.19
7.17
5.31
5.29
5.28
5.27
5.25
4.97
4.94
4.82
4.78
3.78
3.76
3.75
2.95
2.94
2.91
2.90
2.54
2.51
2.50
2.47
2.37
Br
NHTs
CONHPh
4af
400 MHz for ¹H NMR in CDCl₃
0.94
2.01
0.97
2.01
4.18
2.99
0.98
0.97
0.99
1.00
1.00
1.00
1.07
3.07
f1 (ppm)


ZSM-274
170.04
143.65
139.65
138.57
137.20
137.03
133.50
131.44
130.74
129.77
129.00
128.66
127.13
124.74
120.27
120.06
114.78
42.30
37.63
21.50
Br
NHTs
CONHPh
4af
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


ZSM-258-
STANDARD FLUORINE PARAMETER
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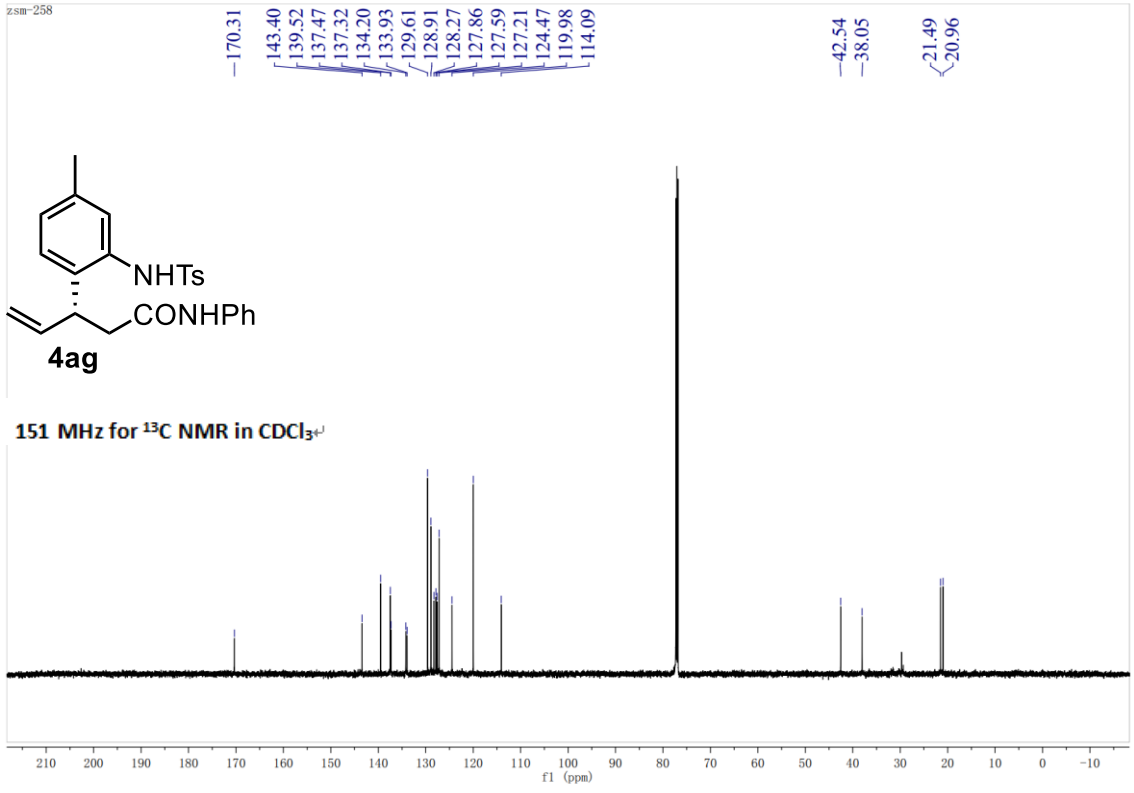
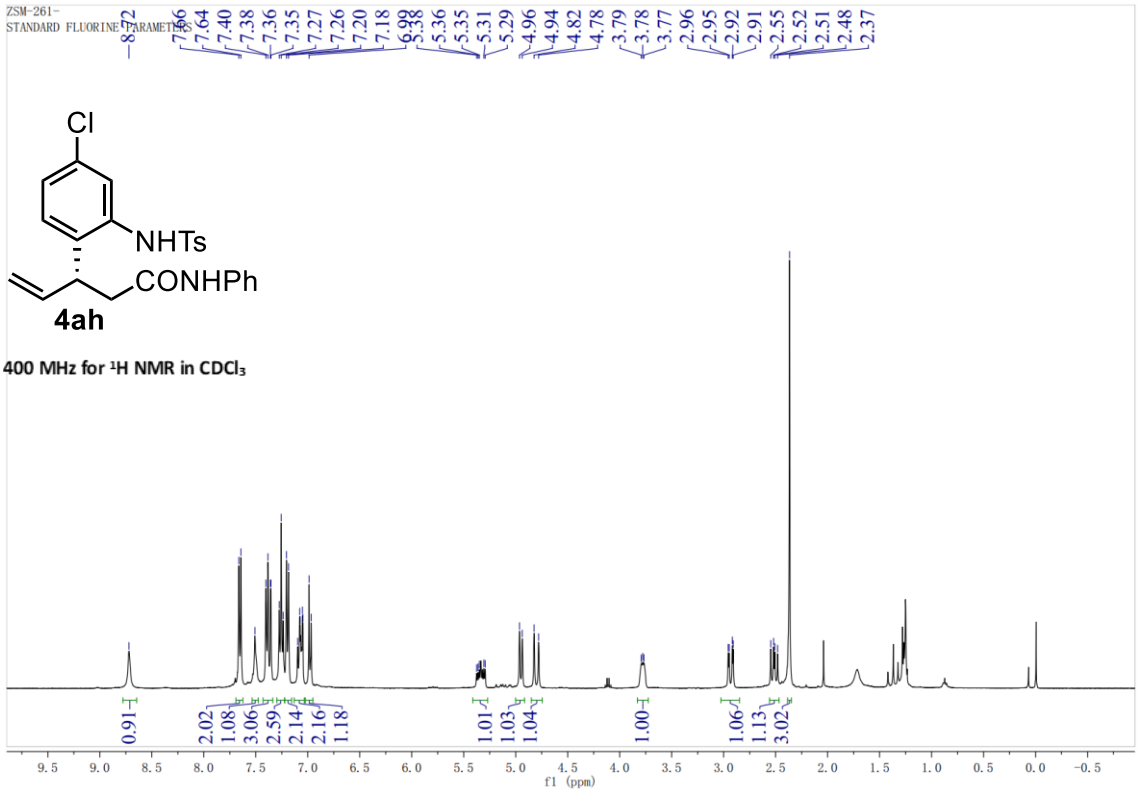
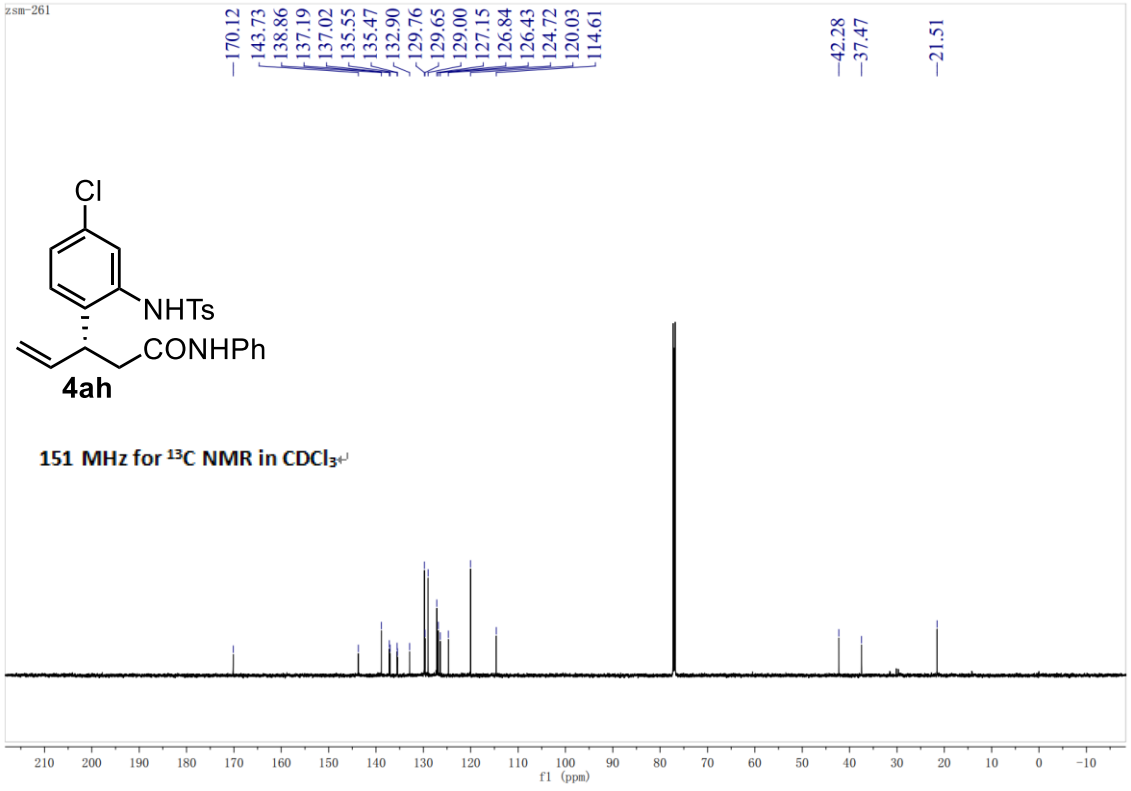
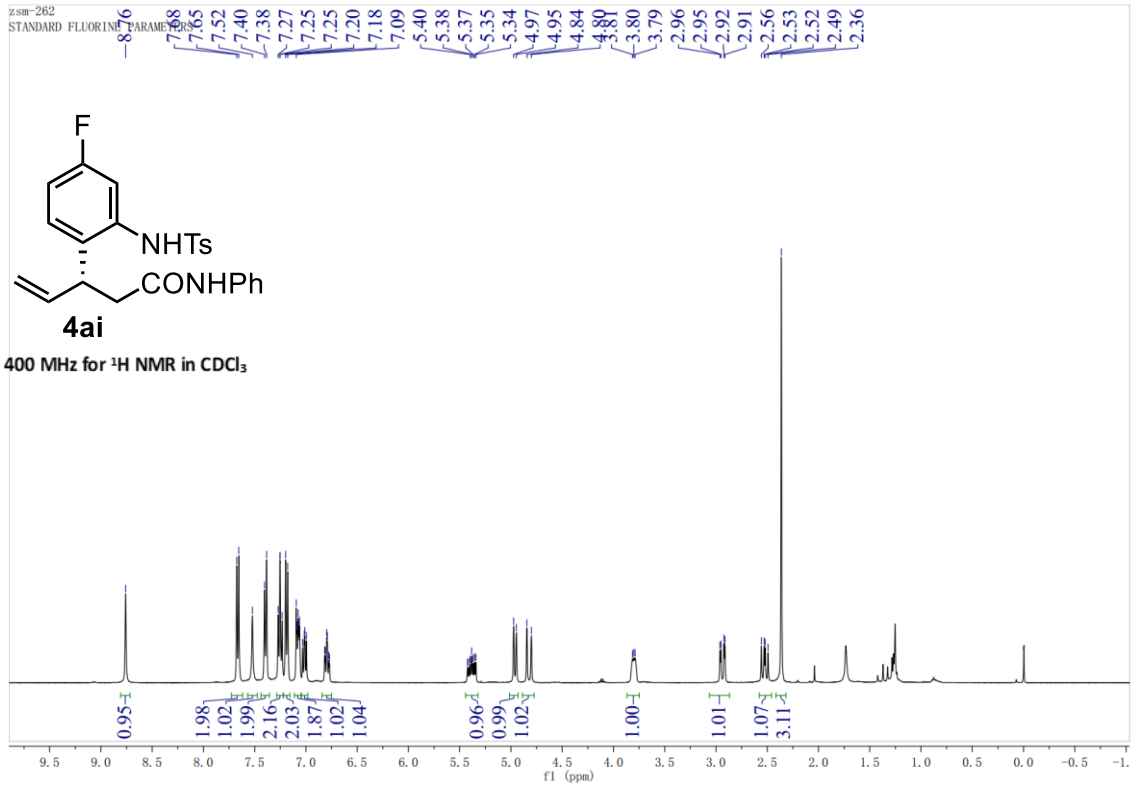
7.65
7.63
7.39
7.26
7.26
7.25
7.21
7.18
6.94
5.44
5.43
5.37
5.36
4.95
4.92
4.83
4.79
3.82
3.81
3.80
2.91
2.90
2.87
2.86
2.56
2.53
2.52
2.49
2.37
2.22
NHTs
CONHPh
4ag
400 MHz for ¹H NMR in CDCl₃
0.93
1.90
0.99
1.95
4.63
1.96
2.04
1.02
1.01
1.01
1.00
1.03
1.10
3.01
3.02
f1 (ppm)

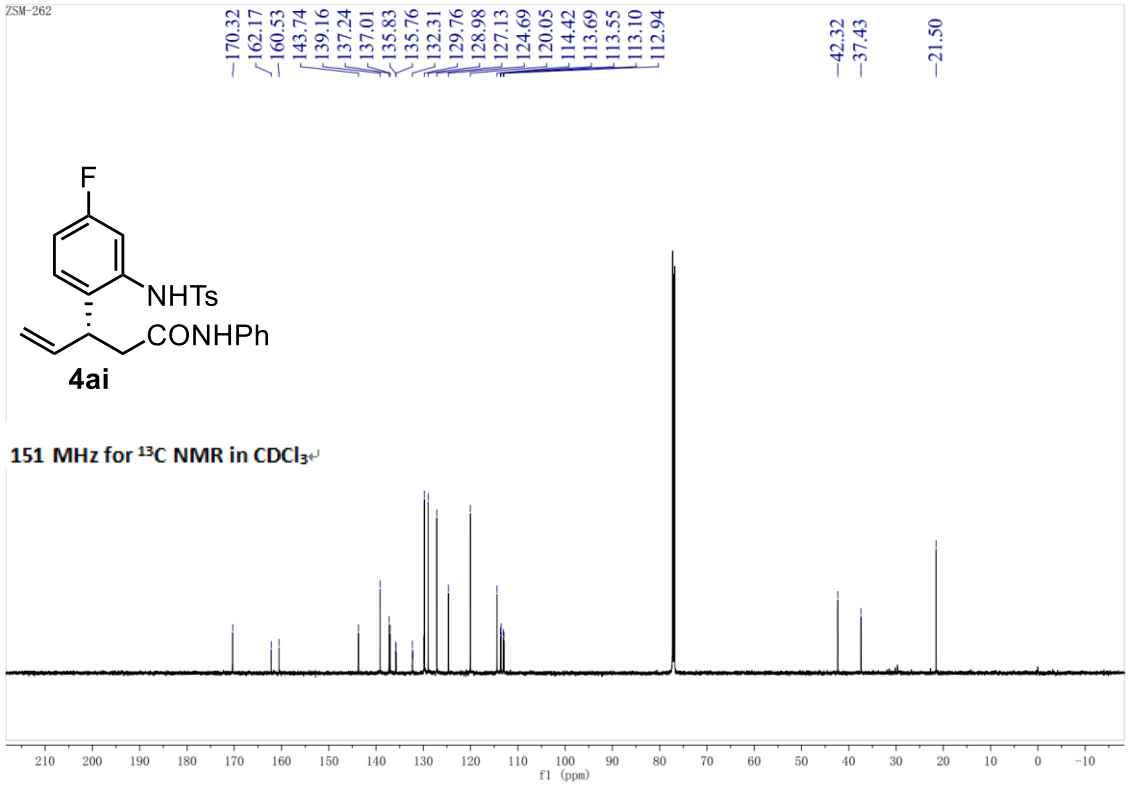

zsm-258
170.31
143.40
139.52
137.47
137.32
134.20
133.93
129.61
128.91
128.27
127.86
127.59
127.21
124.47
119.98
114.09
42.54
38.05
21.49
20.96
NHTs
CONHPh
4ag
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


ZSM-261-
STANDARD FLUORINE PARAMETERS
8.12
7.66
7.64
7.40
7.38
7.36
7.35
7.27
7.26
7.20
7.18
6.99
5.38
5.36
5.35
5.31
5.29
4.96
4.94
4.82
4.78
3.79
3.78
3.77
2.96
2.95
2.92
2.91
2.55
2.52
2.51
2.48
2.37
Cl
NHTs
CONHPh
4ah
400 MHz for ¹H NMR in CDCl₃
0.91
2.02
1.08
3.06
2.59
2.14
2.16
1.18
1.01
1.03
1.04
1.00
1.06
1.13
3.02
f1 (ppm)

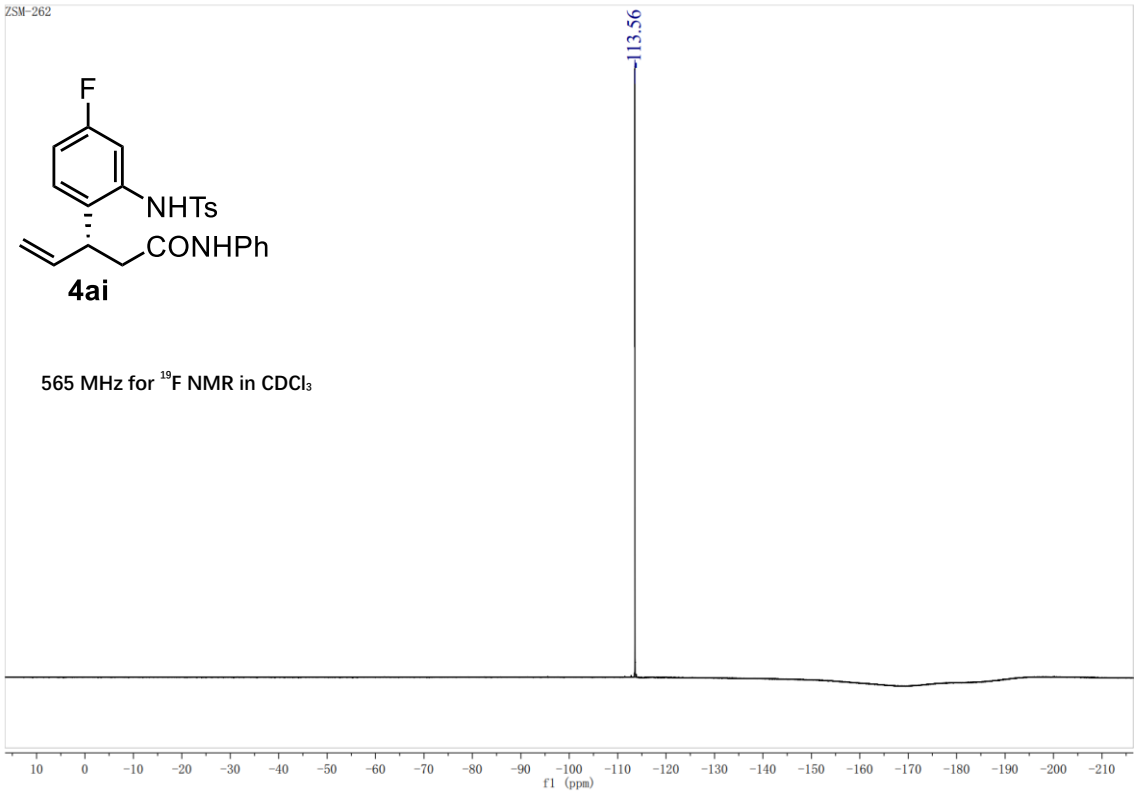

zsm-261
170.12
143.73
138.86
137.19
137.02
135.55
135.47
132.90
129.76
129.65
129.00
127.15
126.84
126.43
124.72
120.03
114.61
42.28
37.47
21.51
Cl
NHTs
CONHPh
4ah
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

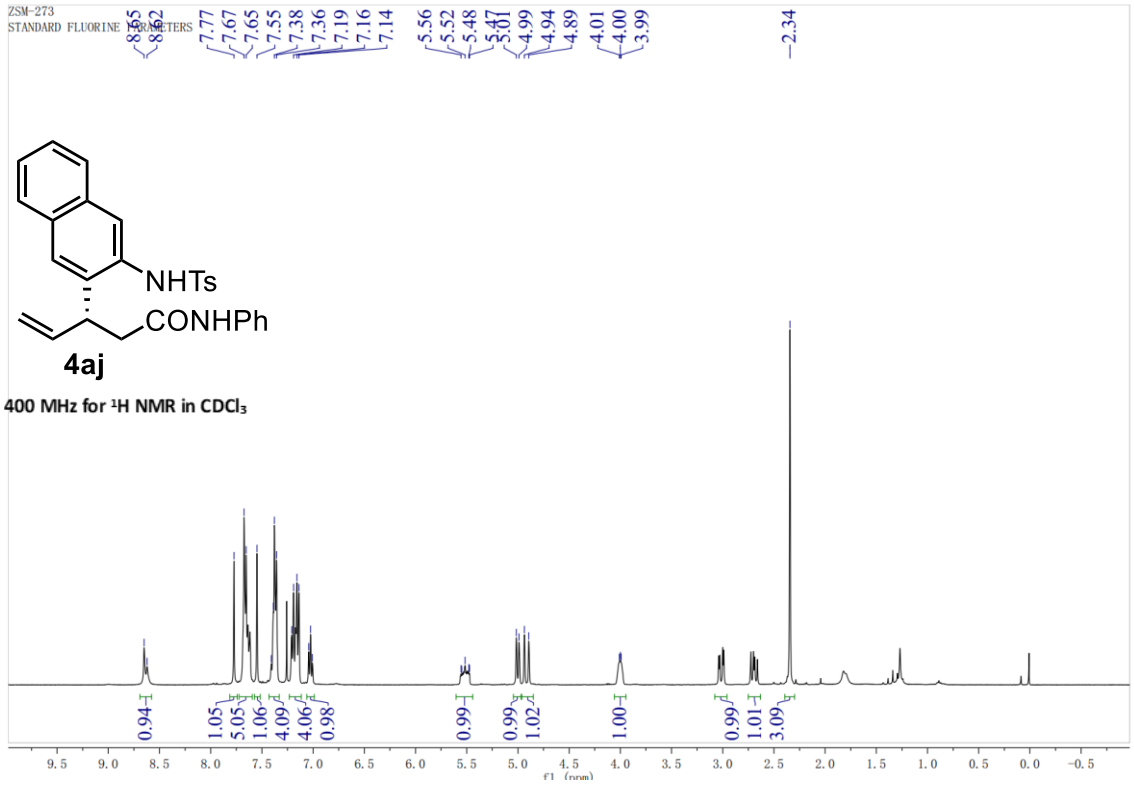


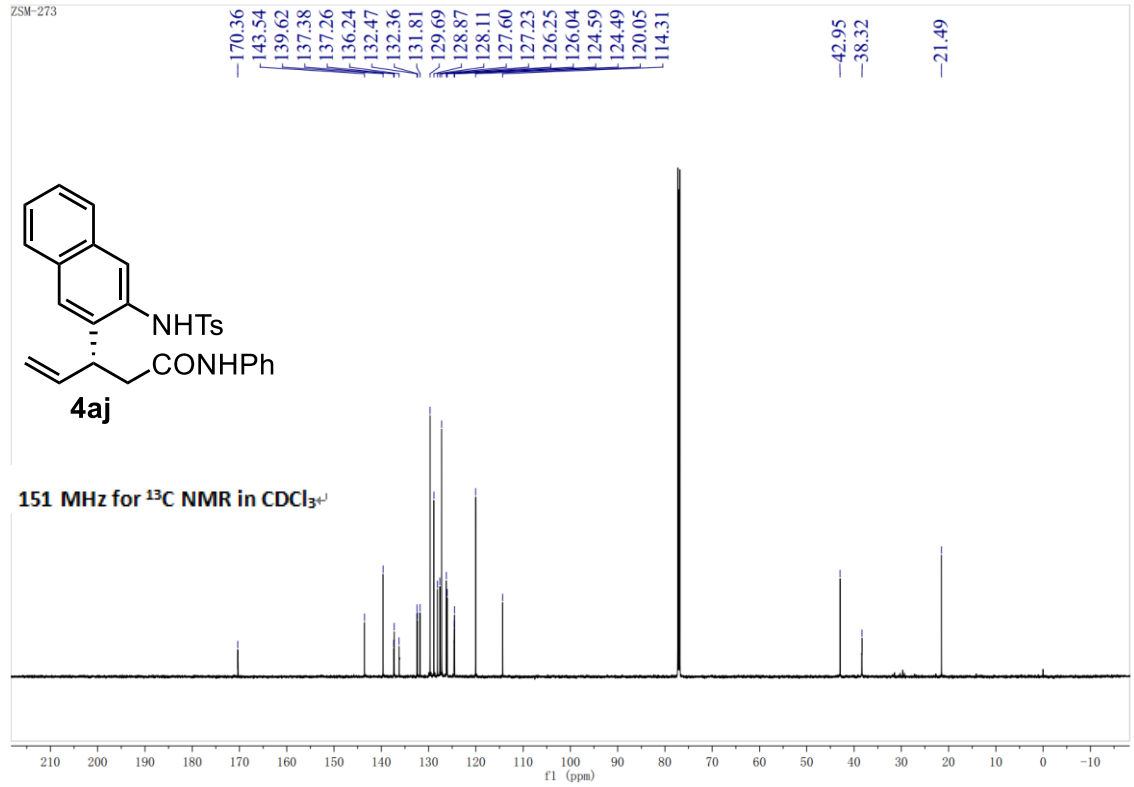
400 MHz for ^{1}H NMR in $CDCl_3$

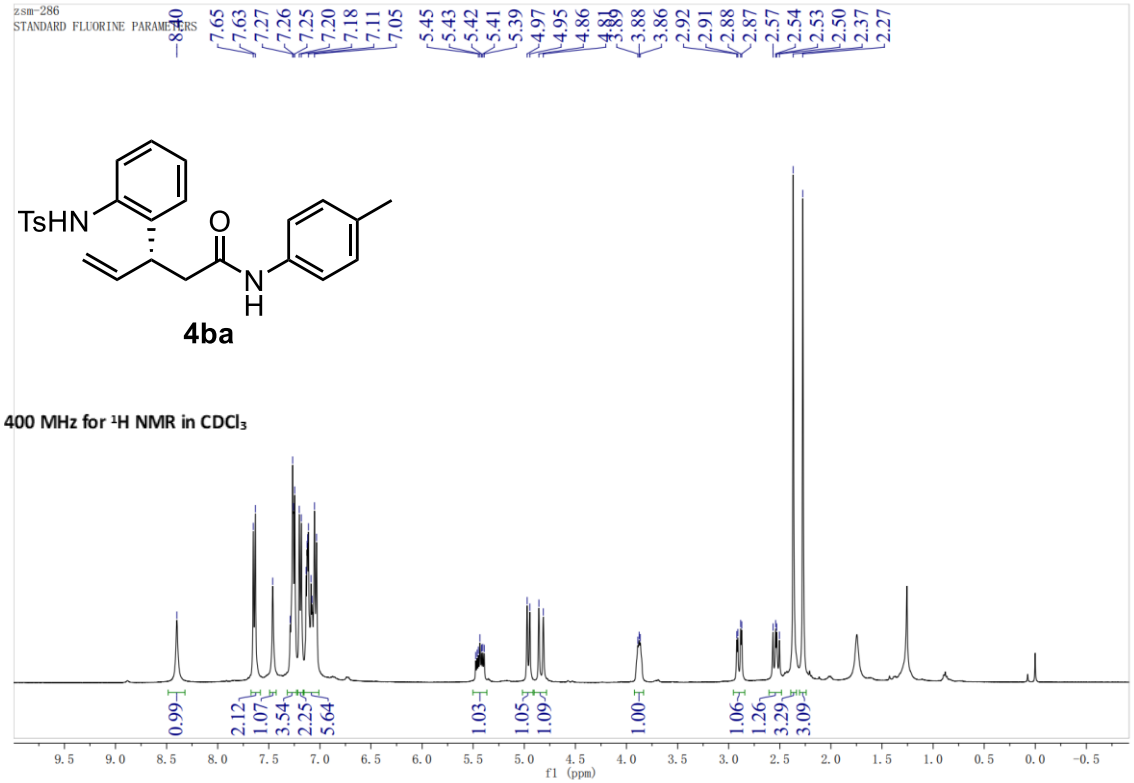


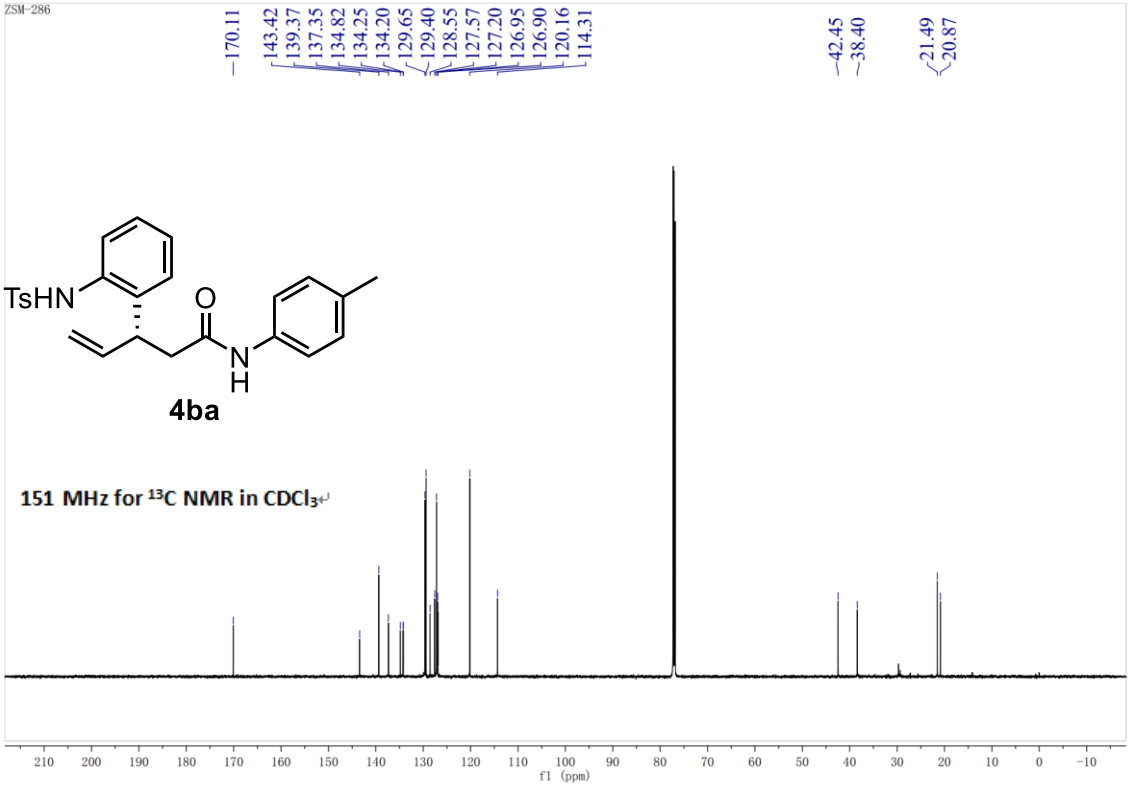
151 MHz for ^{13}C NMR in $CDCl_3$

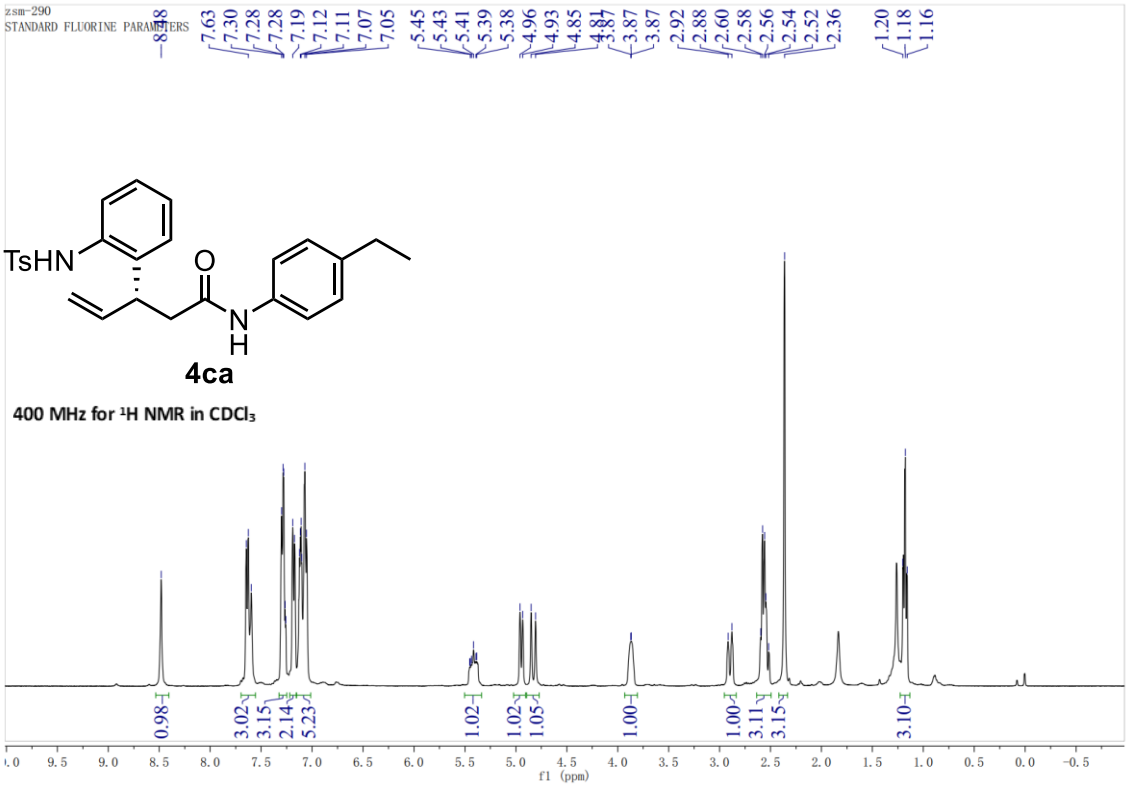

ZSM-262
113.56
F
NHTs
CONHPh
4ai
565 MHz for 19F NMR in CDCl3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

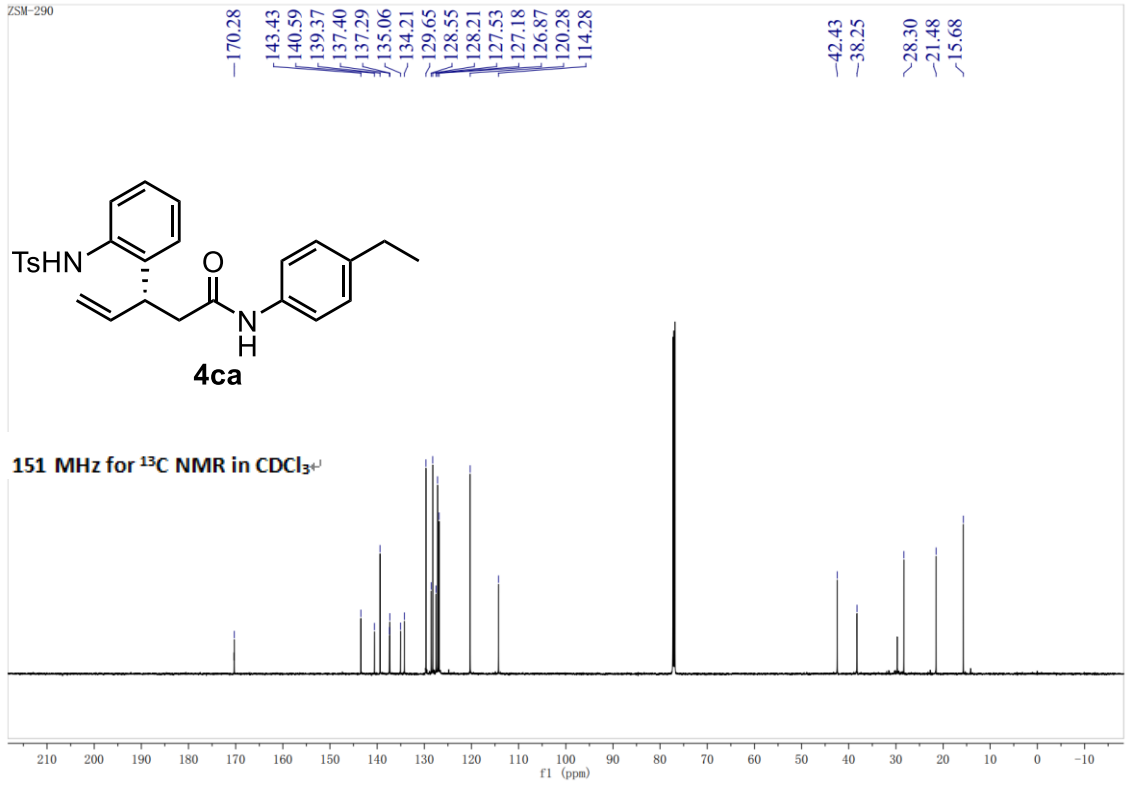

ZSM-273
STANDARD FLUORINE PARAMETERS
8.65
8.62
7.77
7.67
7.65
7.55
7.38
7.36
7.19
7.16
7.14
5.56
5.52
5.48
5.47
5.01
4.99
4.94
4.89
4.01
4.00
3.99
2.34
NHTs
CONHPh
4aj
400 MHz for ¹H NMR in CDCl₃
0.94
1.05
5.05
1.06
4.09
4.06
0.98
0.99
0.99
1.02
1.00
0.99
1.01
3.09
f1 (ppm)

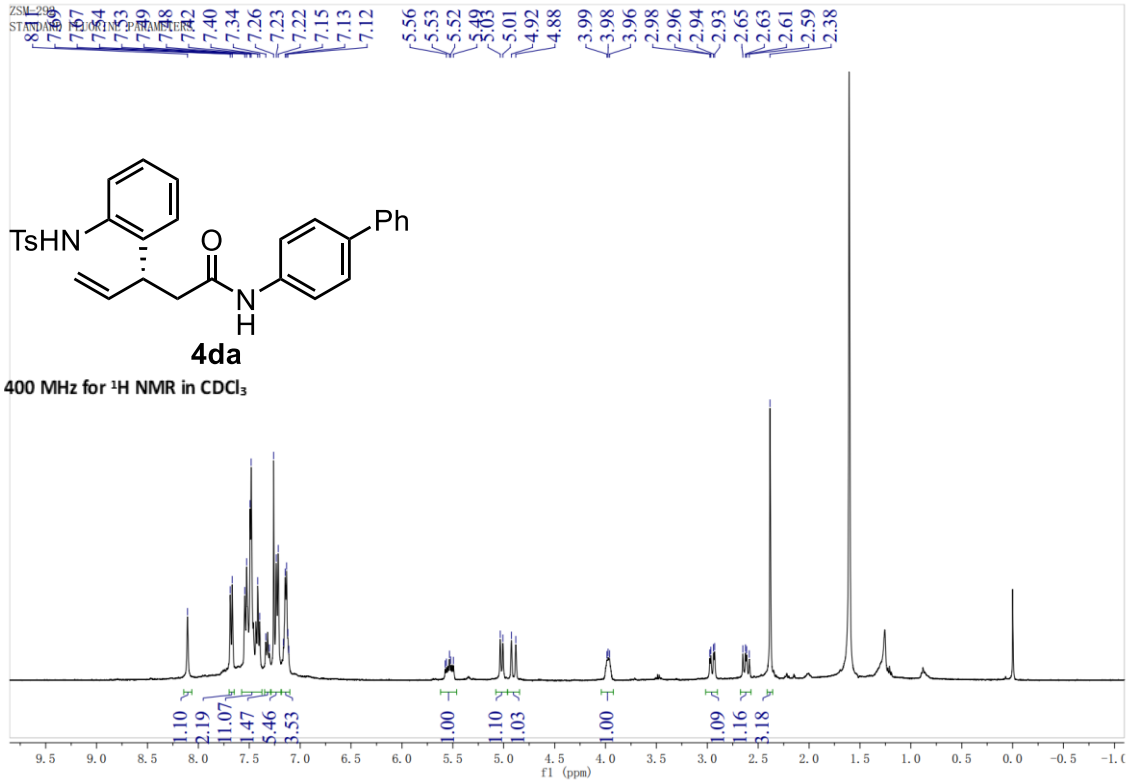

ZSM-273
170.36
143.54
139.62
137.38
137.26
136.24
132.47
132.36
131.81
129.69
128.87
128.11
127.60
127.23
126.25
126.04
124.59
124.49
120.05
114.31
42.95
38.32
21.49
NHTs
CONHPh
4aj
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

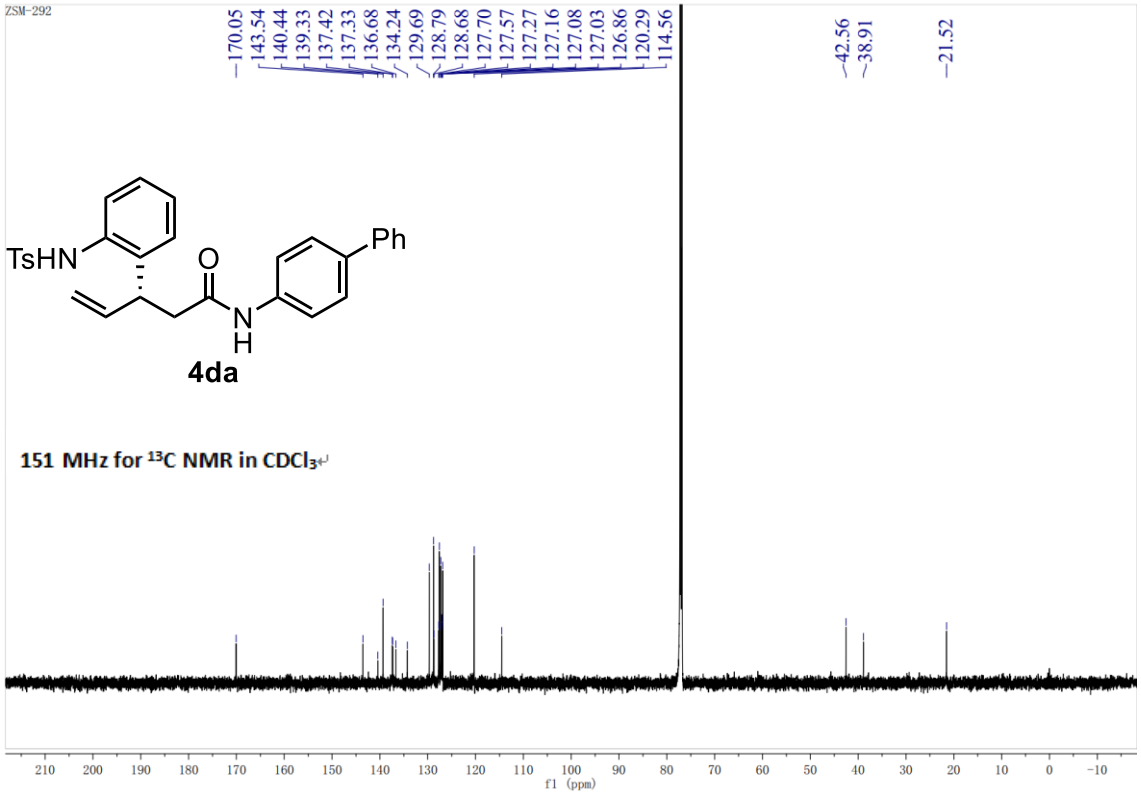

zsm-286
STANDARD FLUORINE PARAMETERS
8.40
7.65
7.63
7.27
7.26
7.25
7.20
7.18
7.11
7.05
5.45
5.43
5.42
5.41
5.39
4.97
4.95
4.86
4.81
3.89
3.88
3.86
2.92
2.91
2.88
2.87
2.57
2.54
2.53
2.50
2.37
2.27
TsHN
O
N
H
4ba
400 MHz for ¹H NMR in CDCl₃
0.99
2.12
1.07
3.54
2.25
5.64
1.03
1.05
1.09
1.00
1.06
1.26
3.29
3.09
f1 (ppm)

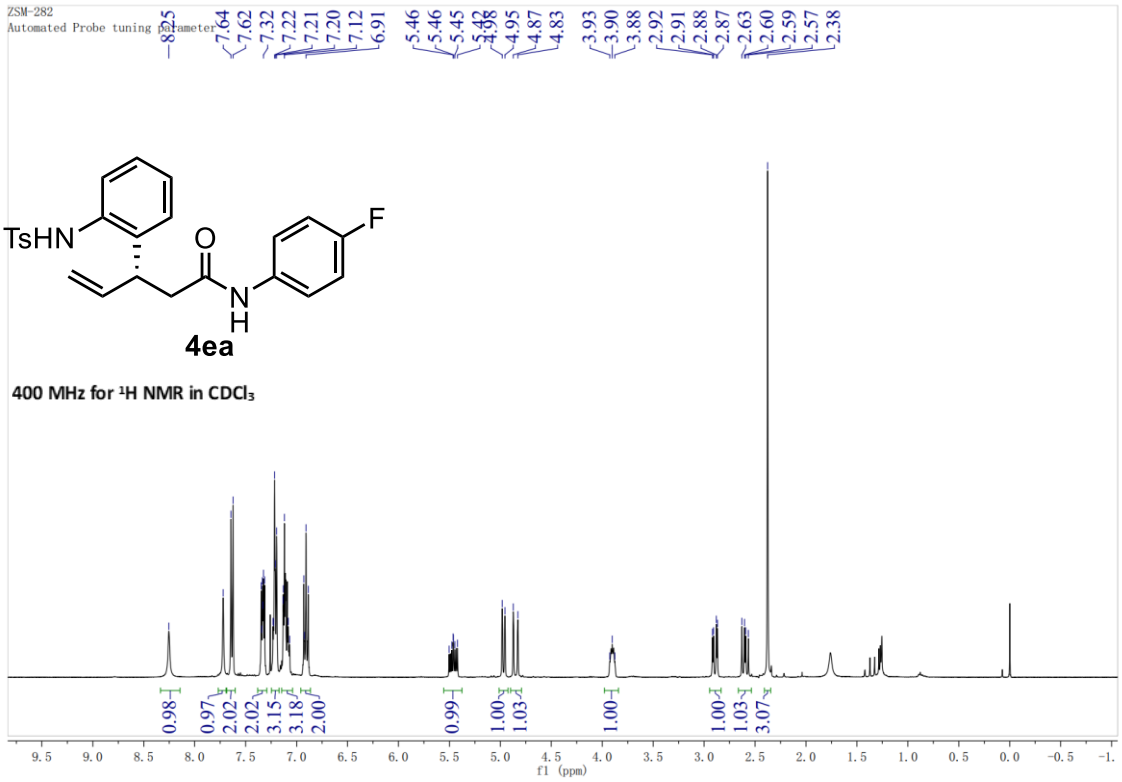

ZSM-286
170.11
143.42
139.37
137.35
134.82
134.25
134.20
129.65
129.40
128.55
127.57
127.20
126.95
126.90
120.16
114.31
42.45
38.40
21.49
20.87
TsHN
O
N
H
4ba
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

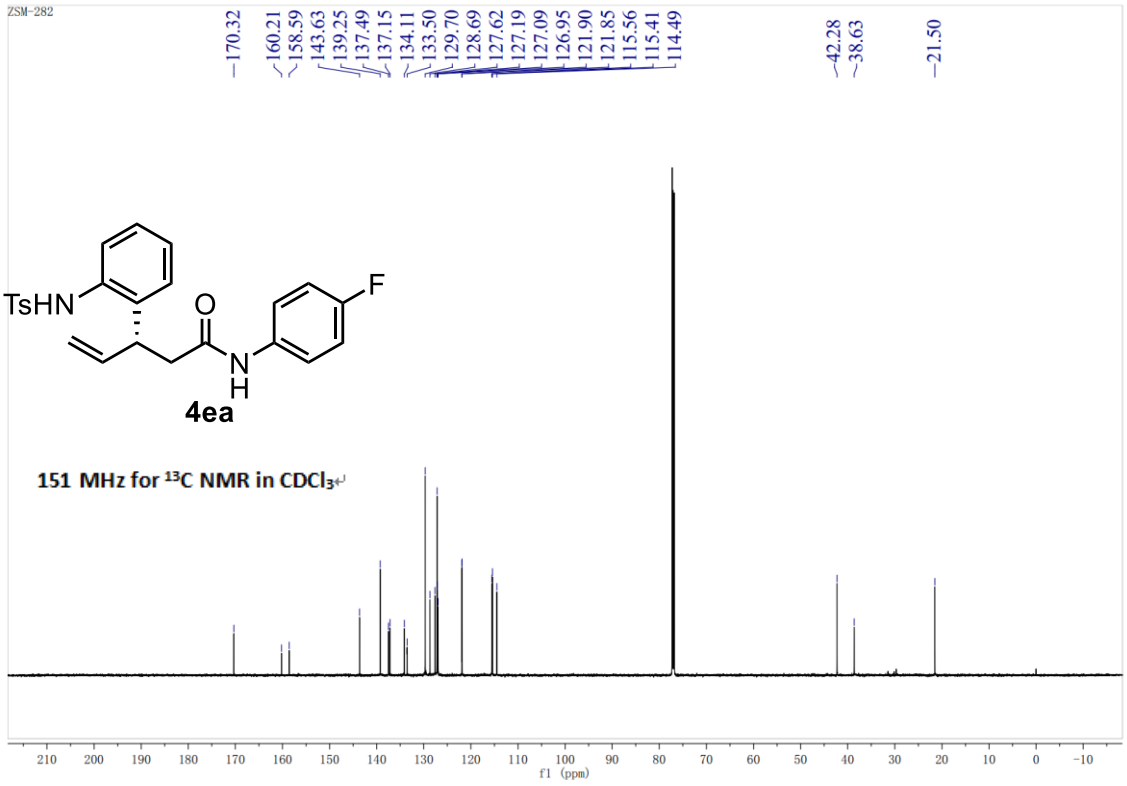

zsm-290
STANDARD FLUORINE PARAMETERS
TsHN
O
N
H
4ca
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)

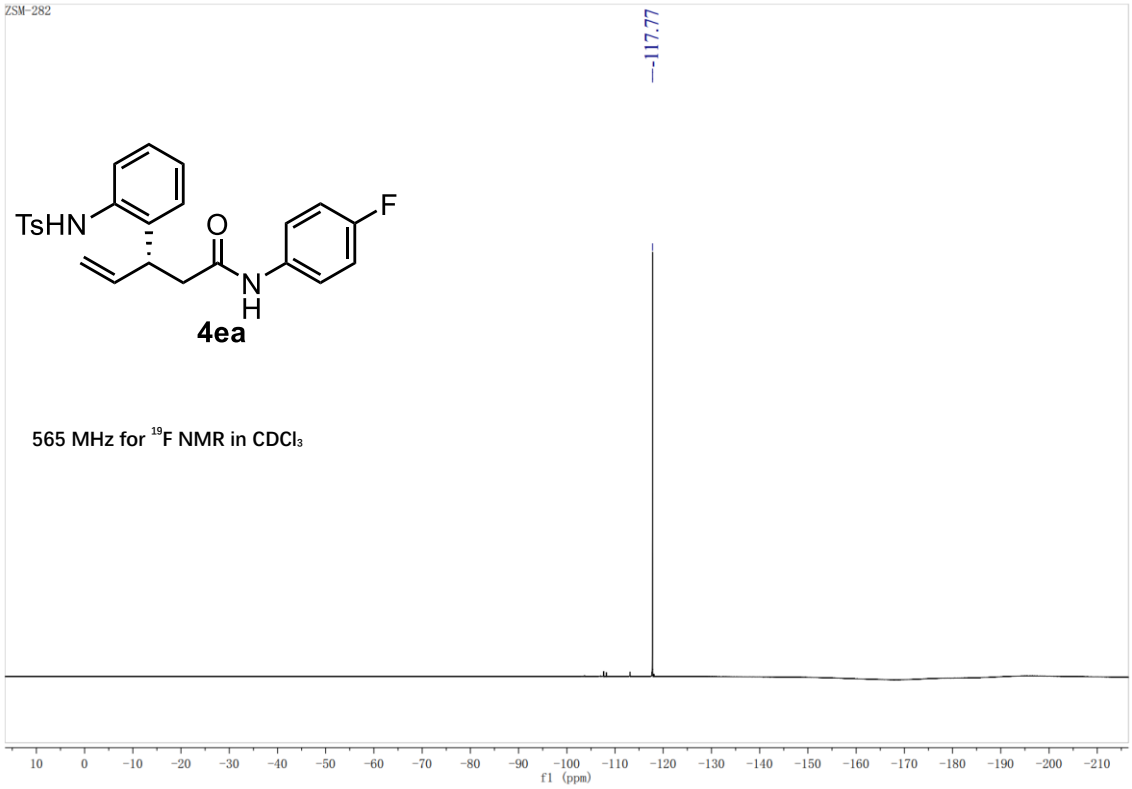

ZSM-290
TsHN
O
N
H
4ca
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

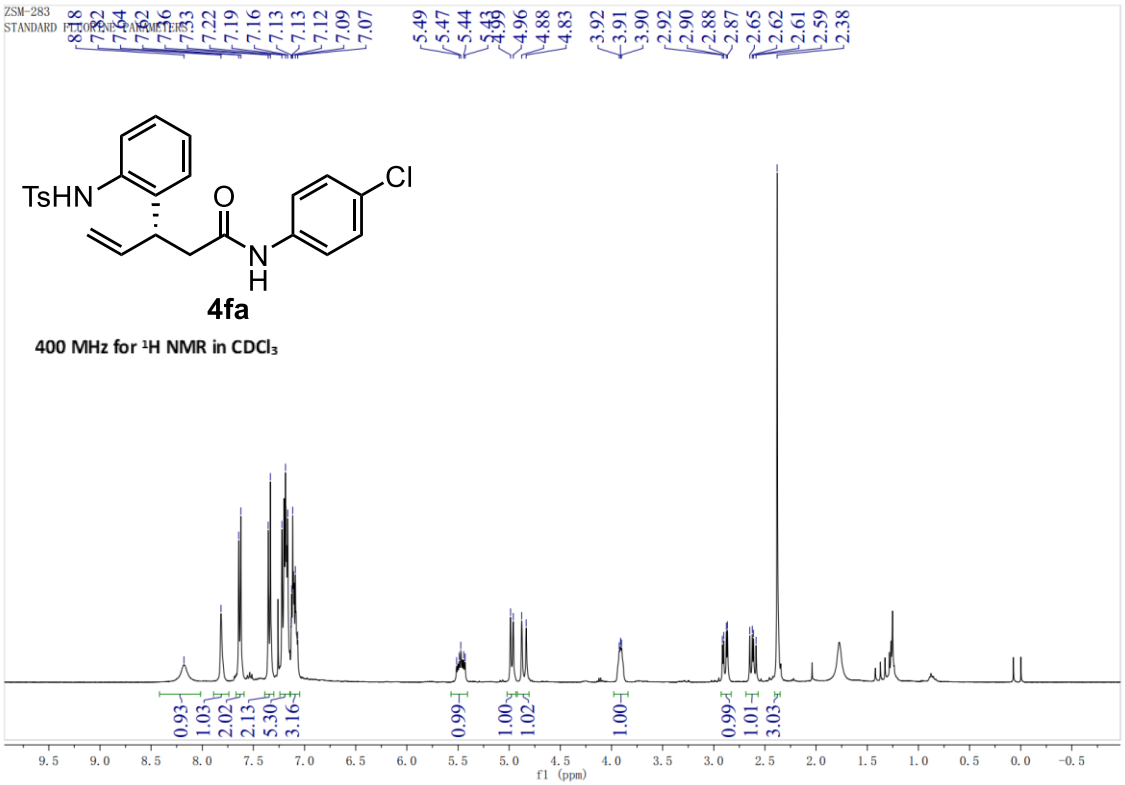

TsHN
O
N
H
Ph
4da
400 MHz for ¹H NMR in CDCl₃

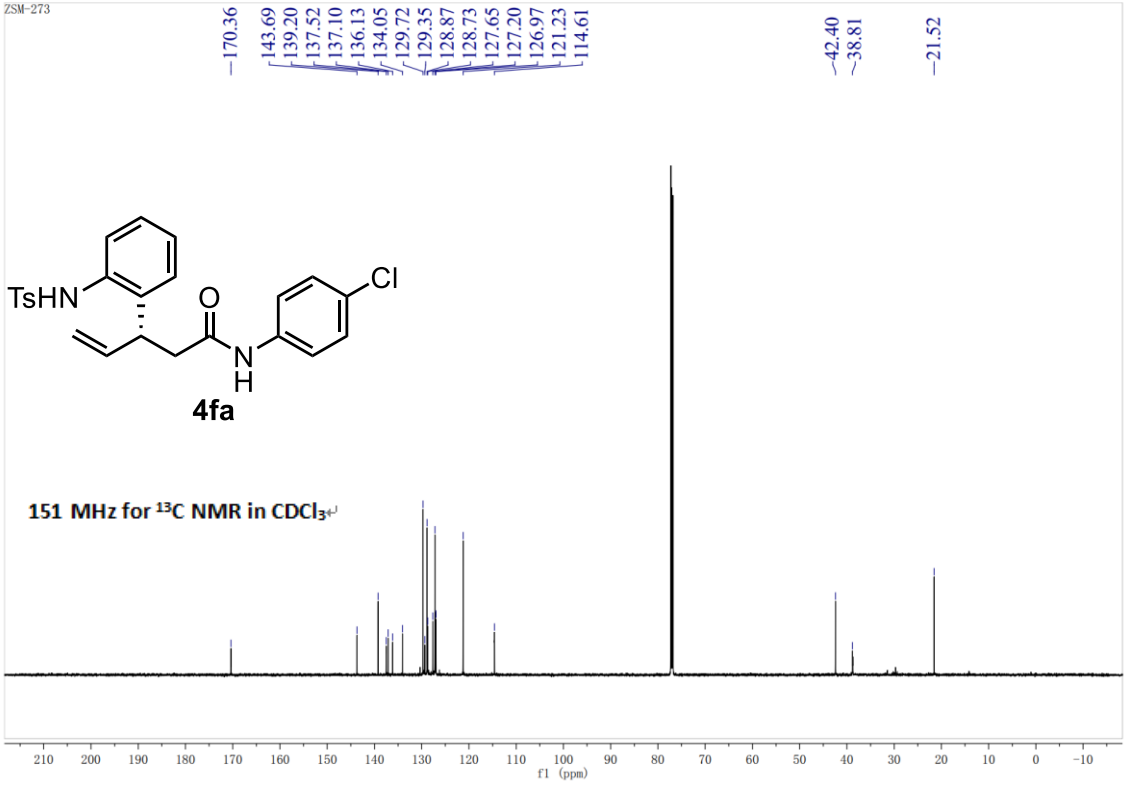

TsHN
O
N
H
Ph
4da
151 MHz for ¹³C NMR in CDCl₃

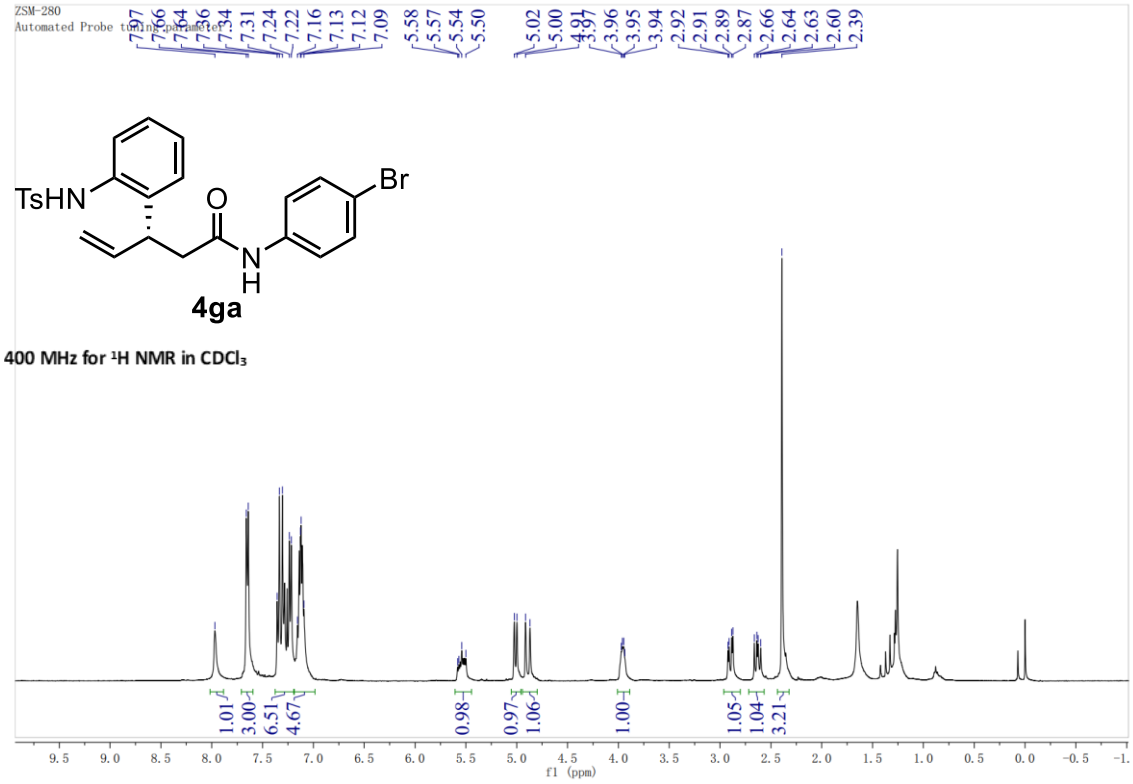

ZSM-282
Automated Probe tuning parameter
8.25
7.64
7.62
7.32
7.22
7.21
7.20
7.12
6.91
5.46
5.46
5.45
5.42
4.98
4.95
4.87
4.83
3.93
3.90
3.88
2.92
2.91
2.88
2.87
2.63
2.60
2.59
2.57
2.38
TsHN
O
N
H
F
4ea
400 MHz for ¹H NMR in CDCl₃
0.98
0.97
2.02
2.02
3.15
3.18
2.00
0.99
1.00
1.03
1.00
1.00
1.03
3.07
f1 (ppm)

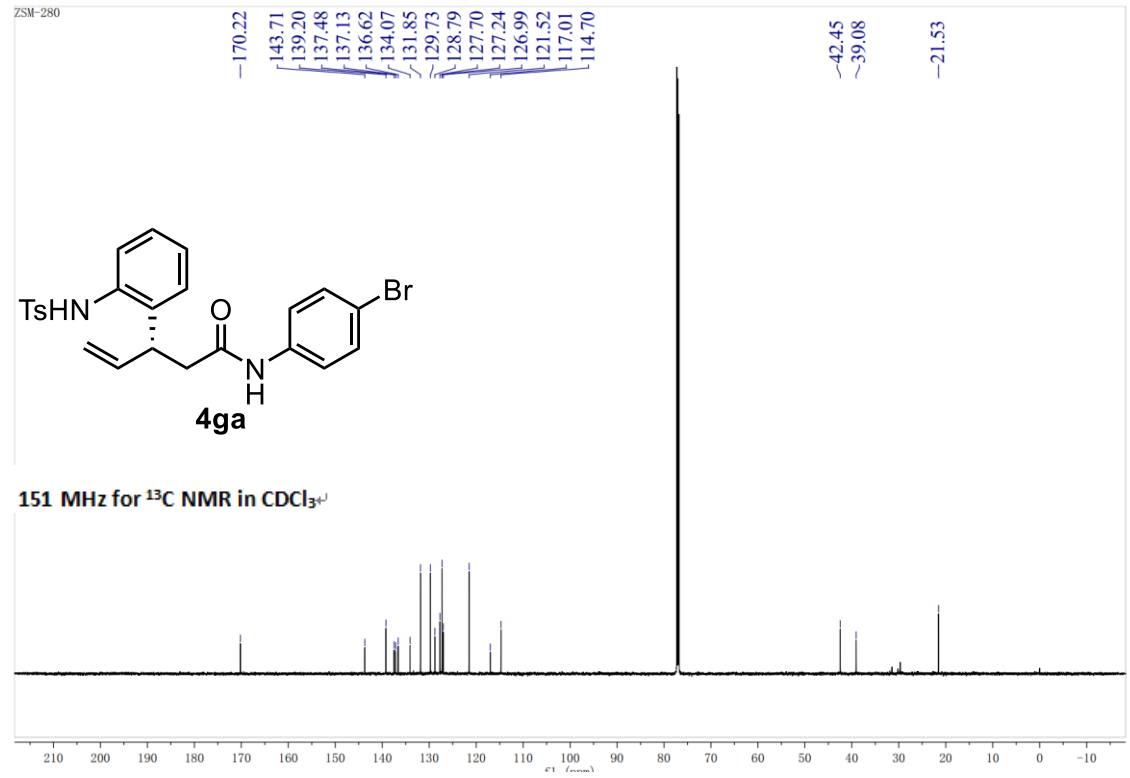

ZSM-282
170.32
160.21
158.59
143.63
139.25
137.49
137.15
134.11
133.50
129.70
128.69
127.62
127.19
127.09
126.95
121.90
121.85
115.56
115.41
114.49
42.28
38.63
21.50
TsHN
O
N
H
F
4ea
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

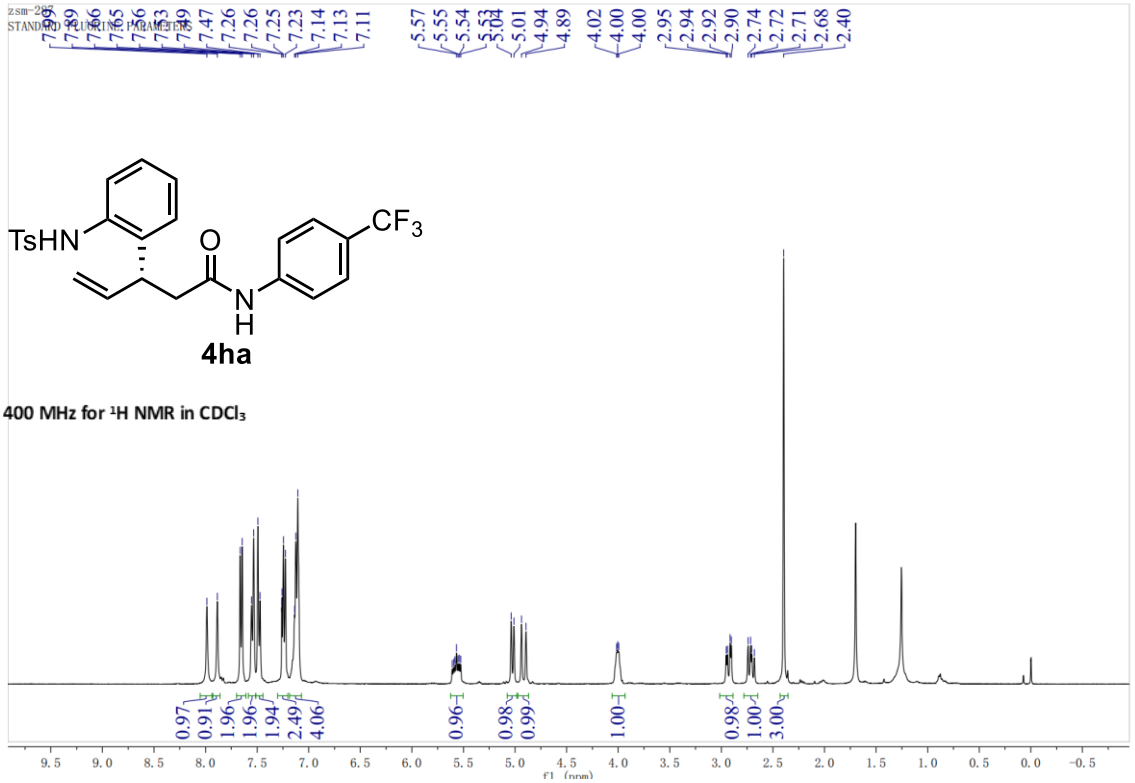

ZSM-282
-117.77
TsHN
O
N
H
F
4ea
565 MHz for 19F NMR in CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

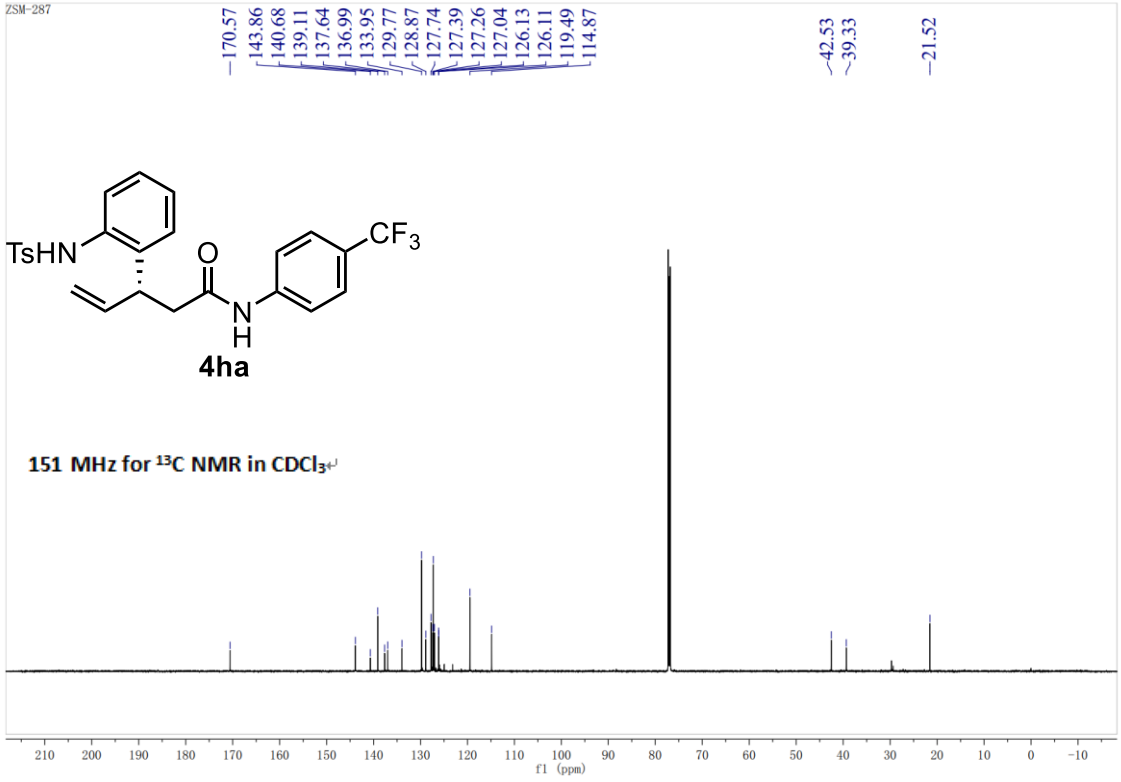

ZSM-283
TsHN
O
N
H
Cl
4fa
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)

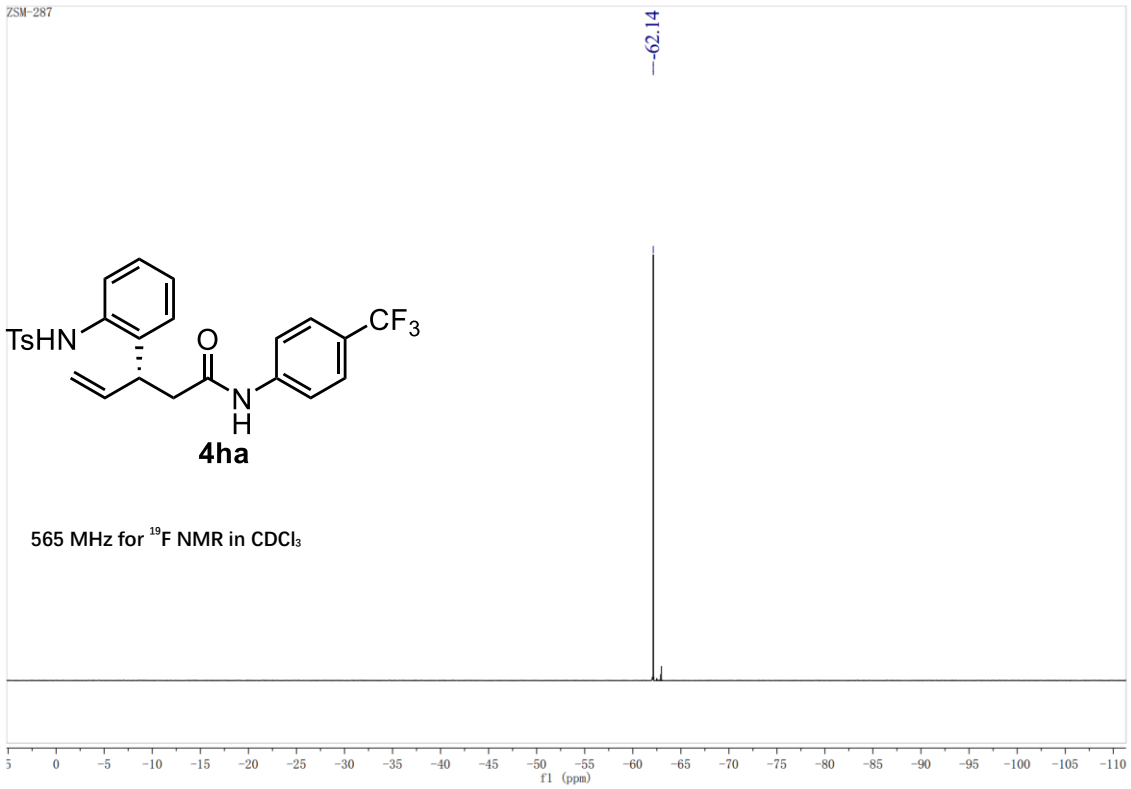

ZSM-273
TsHN
O
N
H
Cl
4fa
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

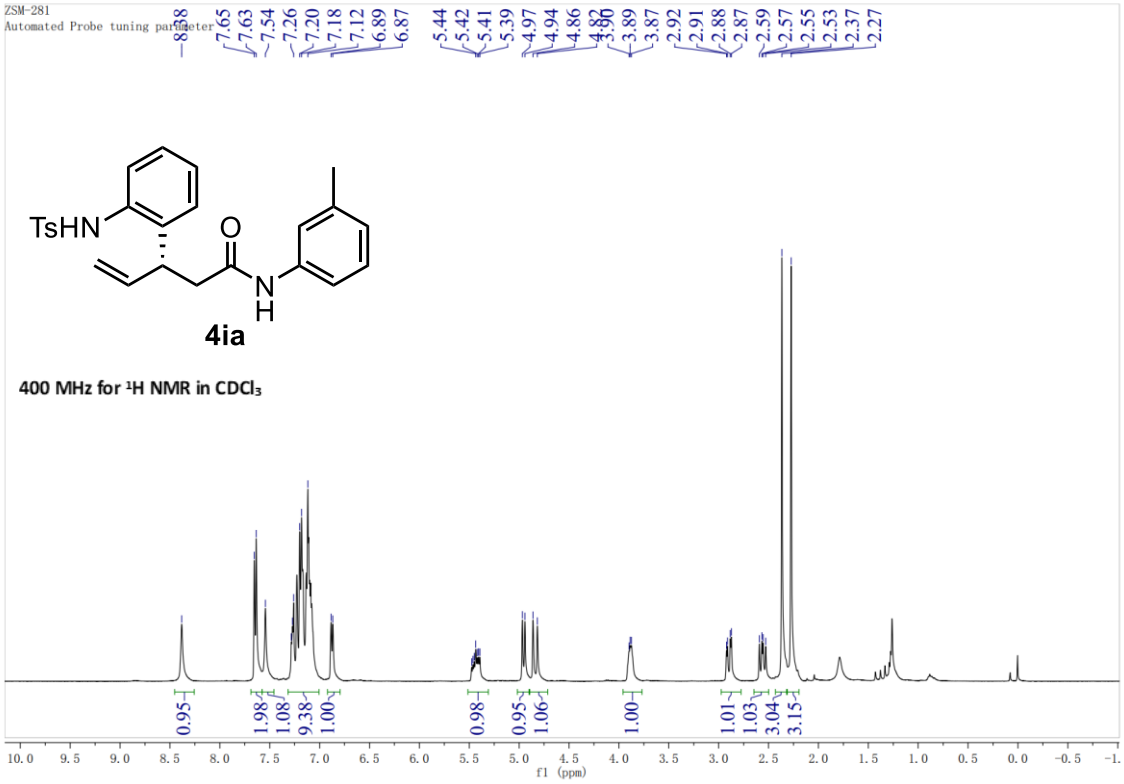

ZSM-280
7.97
7.66
7.64
7.36
7.34
7.31
7.24
7.22
7.16
7.13
7.12
7.09
5.58
5.57
5.54
5.50
5.02
5.00
4.97
4.97
3.96
3.95
3.94
2.92
2.91
2.89
2.87
2.66
2.64
2.63
2.60
2.39
TsHN
O
N
H
Br
4ga
400 MHz for ¹H NMR in CDCl₃
1.01
3.00
6.51
4.67
0.98
0.97
1.06
1.00
1.05
1.04
3.21
f1 (ppm)

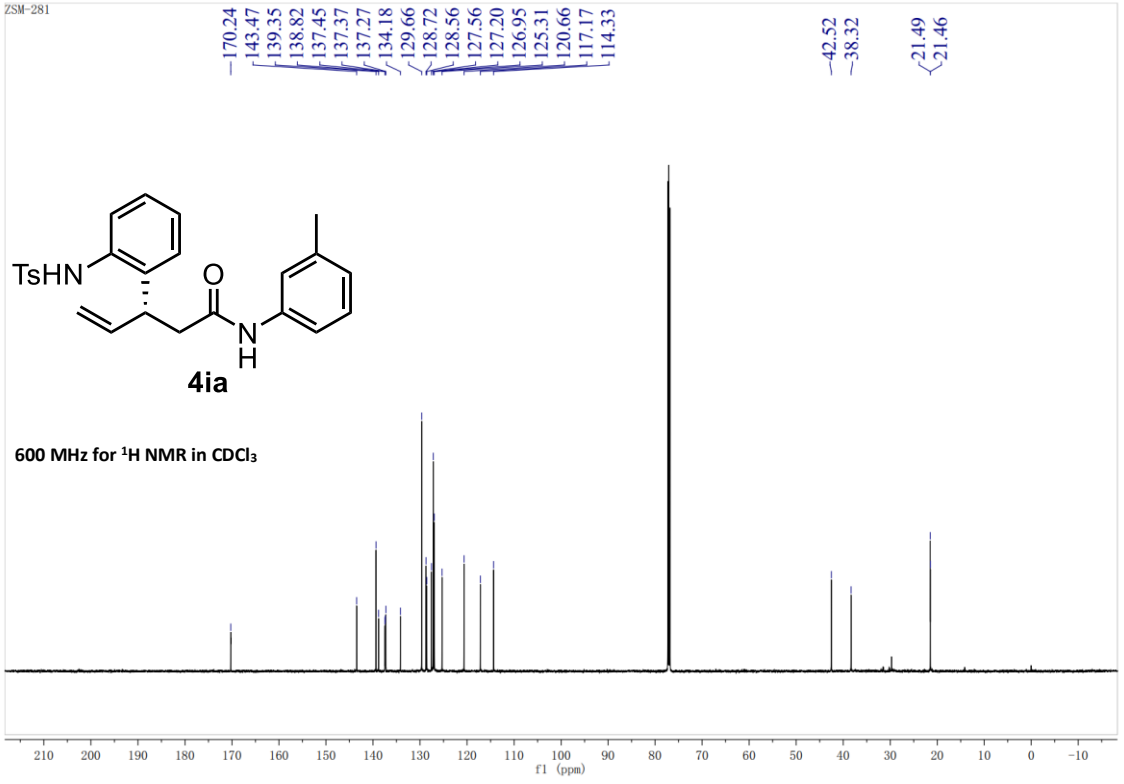

ZSM-280
170.22
143.71
139.20
137.48
137.13
136.62
134.07
131.85
129.73
128.79
127.70
127.24
126.99
121.52
117.01
114.70
42.45
39.08
21.53
TsHN
O
N
H
Br
4ga
151 MHz for ¹³C NMR in CDCl₃

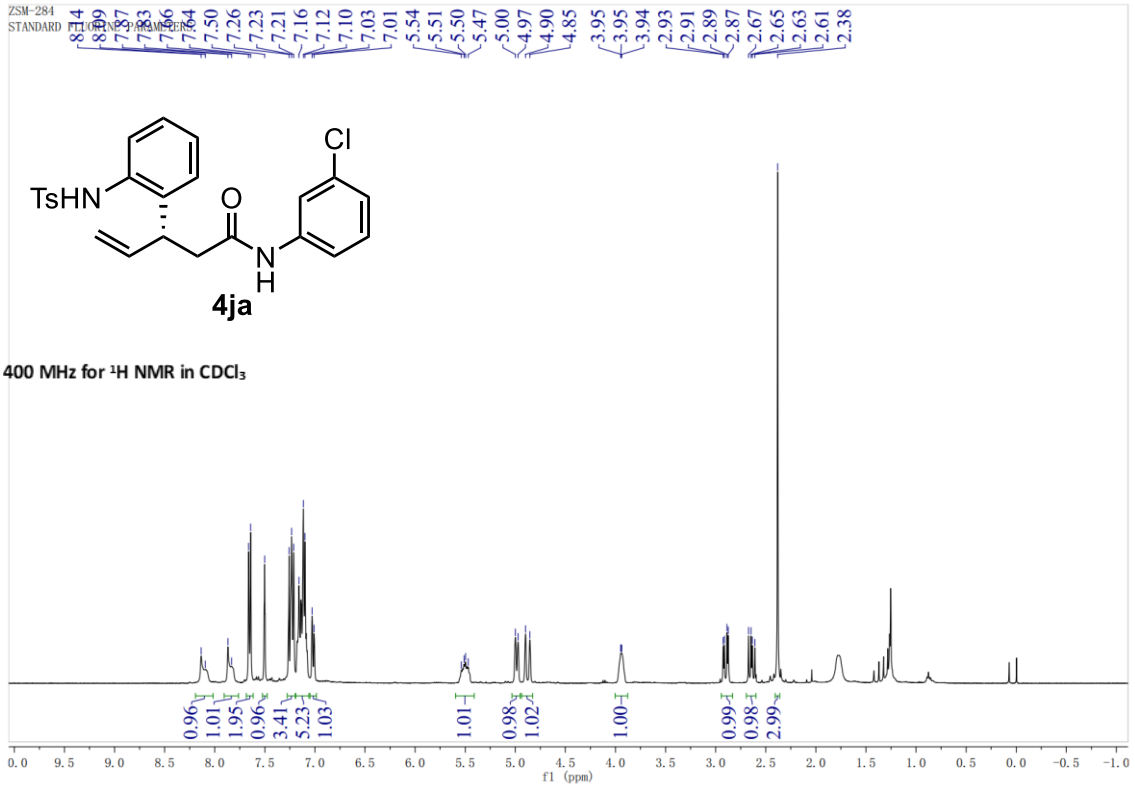

zsm-287
STANDARD PLUNRINT PARAMETERS
7.99
7.89
7.86
7.65
7.56
7.53
7.49
7.47
7.26
7.26
7.25
7.23
7.14
7.13
7.11
5.57
5.55
5.54
5.53
5.04
5.01
4.94
4.89
4.02
4.00
4.00
2.95
2.94
2.92
2.90
2.74
2.72
2.71
2.68
2.40
TsHN
O
N
H
CF3
4ha
400 MHz for ¹H NMR in CDCl₃
0.97
0.91
1.96
1.96
1.94
2.49
4.06
0.96
0.98
0.99
1.00
0.98
1.00
3.00
9.5
9.0
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
f1 (ppm)

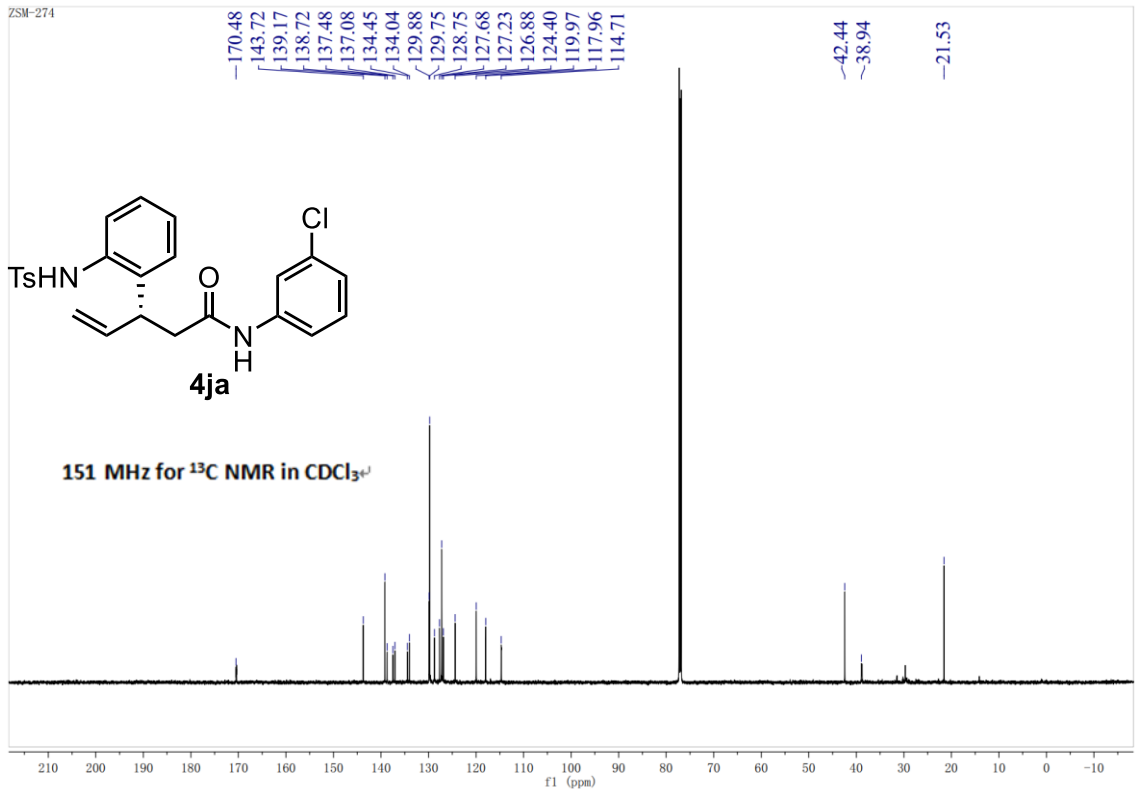

ZSM-287
170.57
143.86
140.68
139.11
137.64
136.99
133.95
129.77
128.87
127.74
127.39
127.26
127.04
126.13
126.11
119.49
114.87
42.53
39.33
21.52
TsHN
O
N
H
CF3
4ha
151 MHz for ¹³C NMR in CDCl₃
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

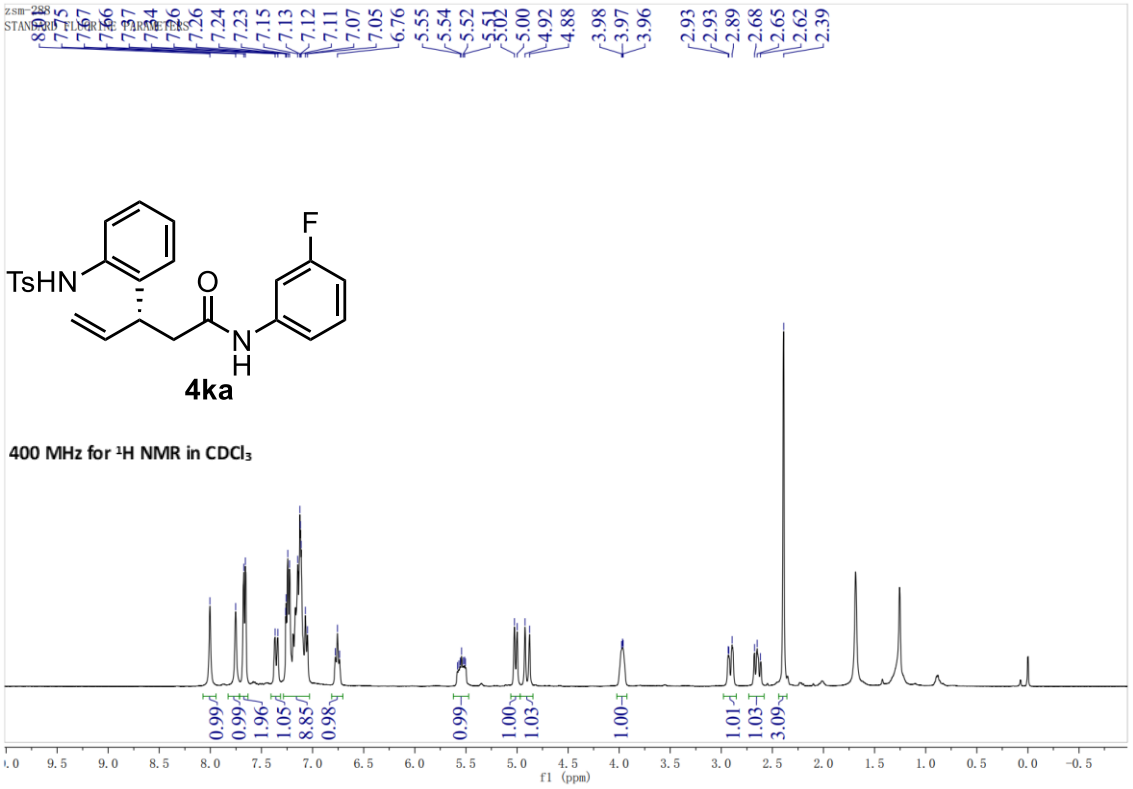

ZSM-287
-62.14
TsHN
O
N
H
CF3
4ha
565 MHz for 19F NMR in CDCl3
f1 (ppm)

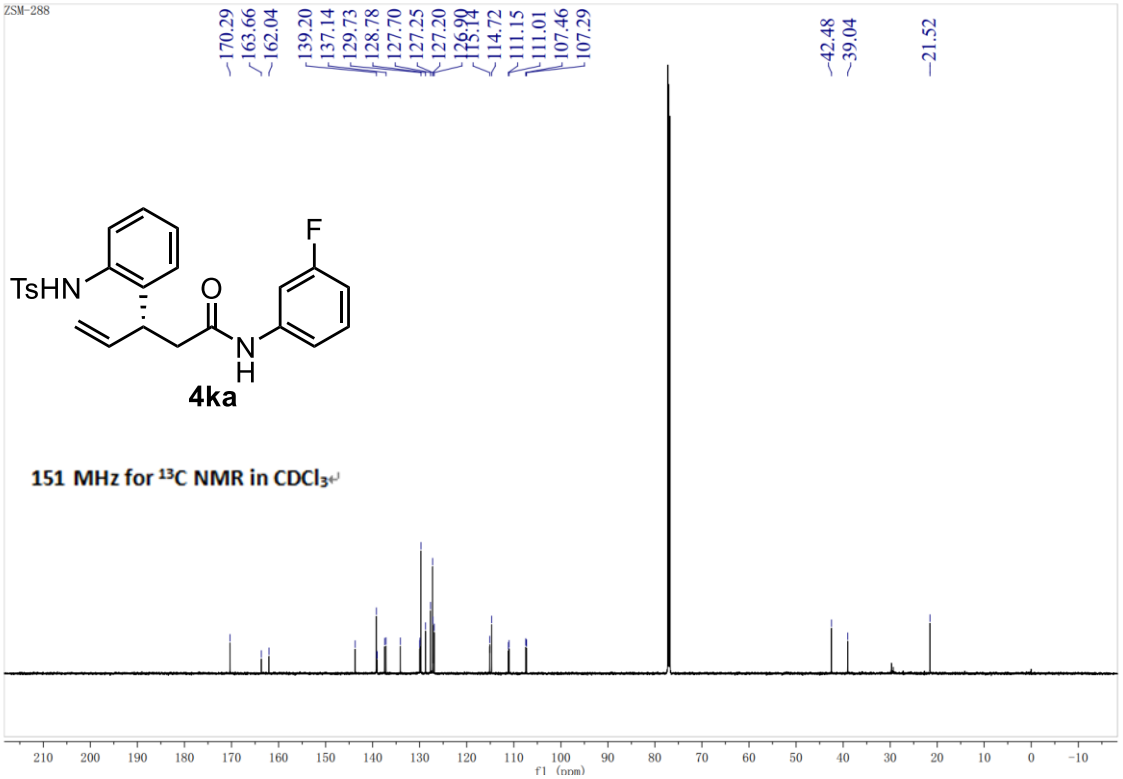

ZSM-281
Automated Probe tuning parameter
8.28
7.65
7.63
7.54
7.26
7.20
7.18
7.12
6.89
6.87
5.44
5.42
5.41
5.39
4.97
4.94
4.86
4.82
4.80
3.89
3.87
2.92
2.91
2.88
2.87
2.59
2.57
2.55
2.53
2.37
2.27
TsHN
O
N
H
4ia
400 MHz for ¹H NMR in CDCl₃
0.95
1.98
1.08
9.38
1.00
0.98
0.95
1.06
1.00
1.01
1.03
3.04
3.15
f1 (ppm)

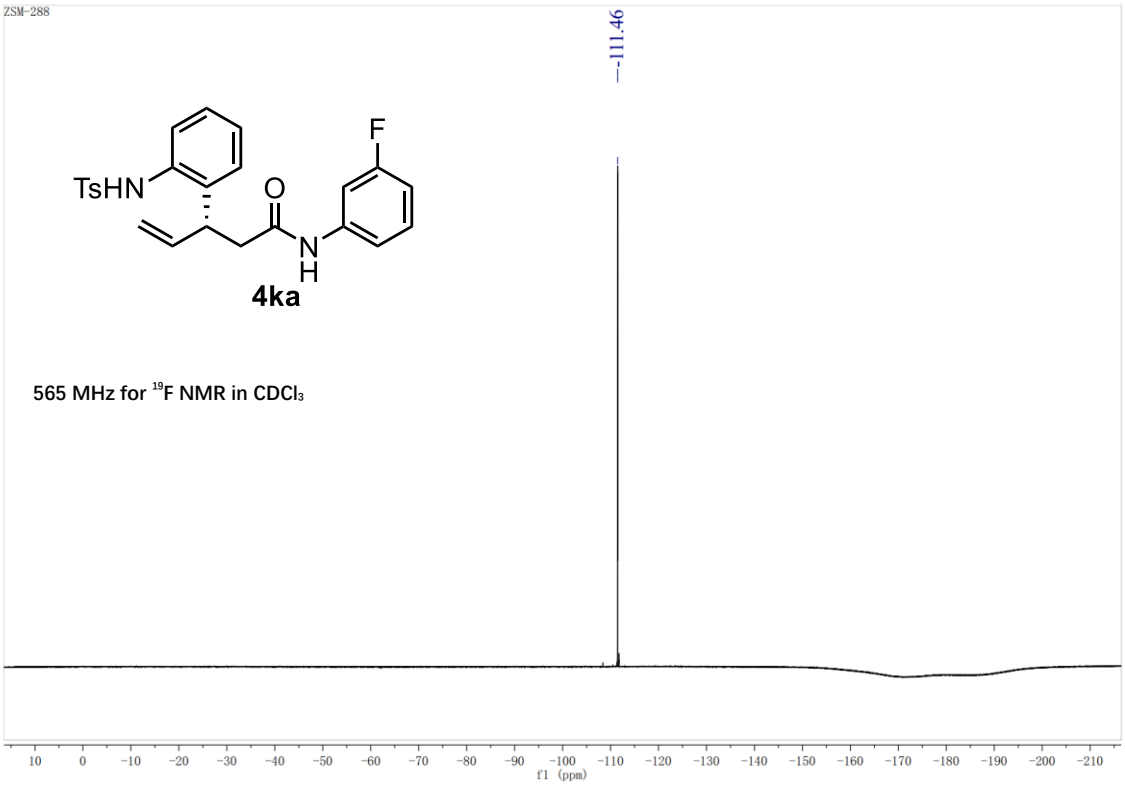

ZSM-281
170.24
143.47
139.35
138.82
137.45
137.37
137.27
134.18
129.66
128.72
128.56
127.56
127.20
126.95
125.31
120.66
117.17
114.33
42.52
38.32
21.49
21.46
TsHN
O
N
H
4ia
600 MHz for ¹H NMR in CDCl₃
f1 (ppm)

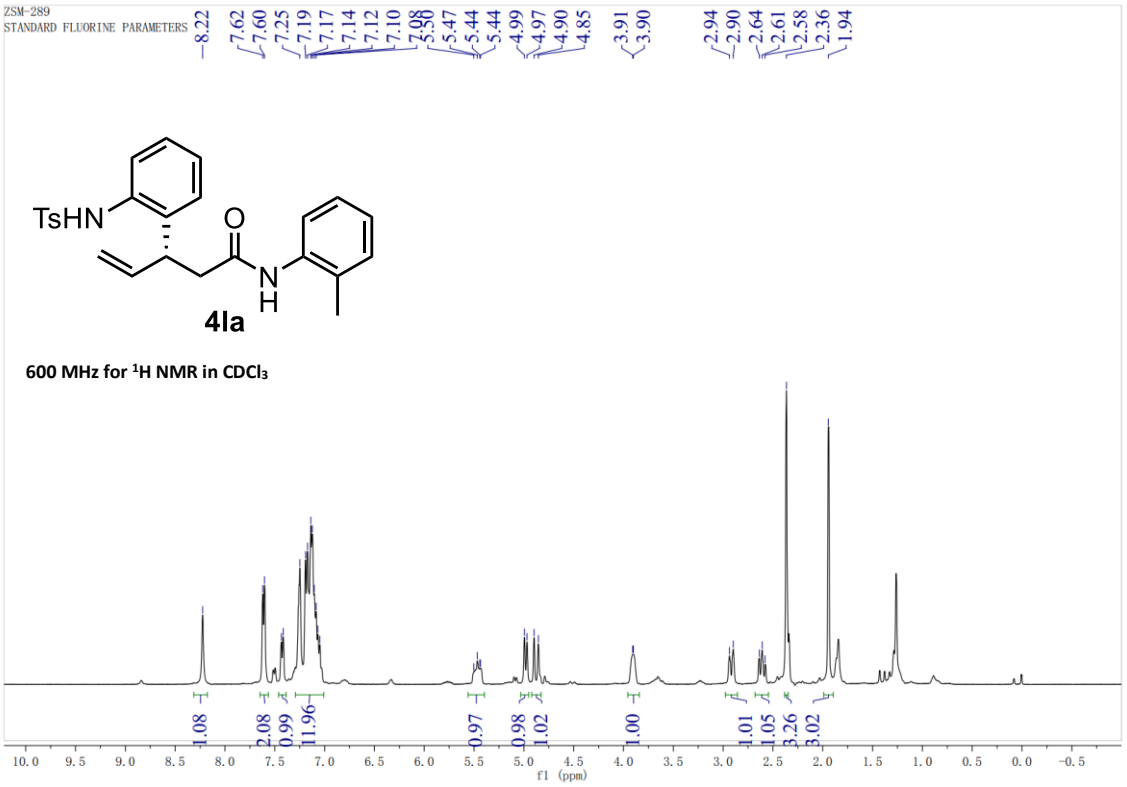

ZSM-284
STANDARD PROTON PARAMETERS
8.14
8.09
7.87
7.83
7.66
7.64
7.50
7.26
7.23
7.21
7.16
7.12
7.10
7.03
7.01
5.54
5.51
5.50
5.47
5.00
4.97
4.90
4.85
3.95
3.95
3.94
2.93
2.91
2.89
2.87
2.67
2.65
2.63
2.61
2.38
TsHN
O
N
H
Cl
4ja
400 MHz for ¹H NMR in CDCl₃
0.96
1.01
1.95
0.96
3.41
5.23
1.03
1.01
0.98
1.02
1.00
0.99
0.98
2.99
f1 (ppm)

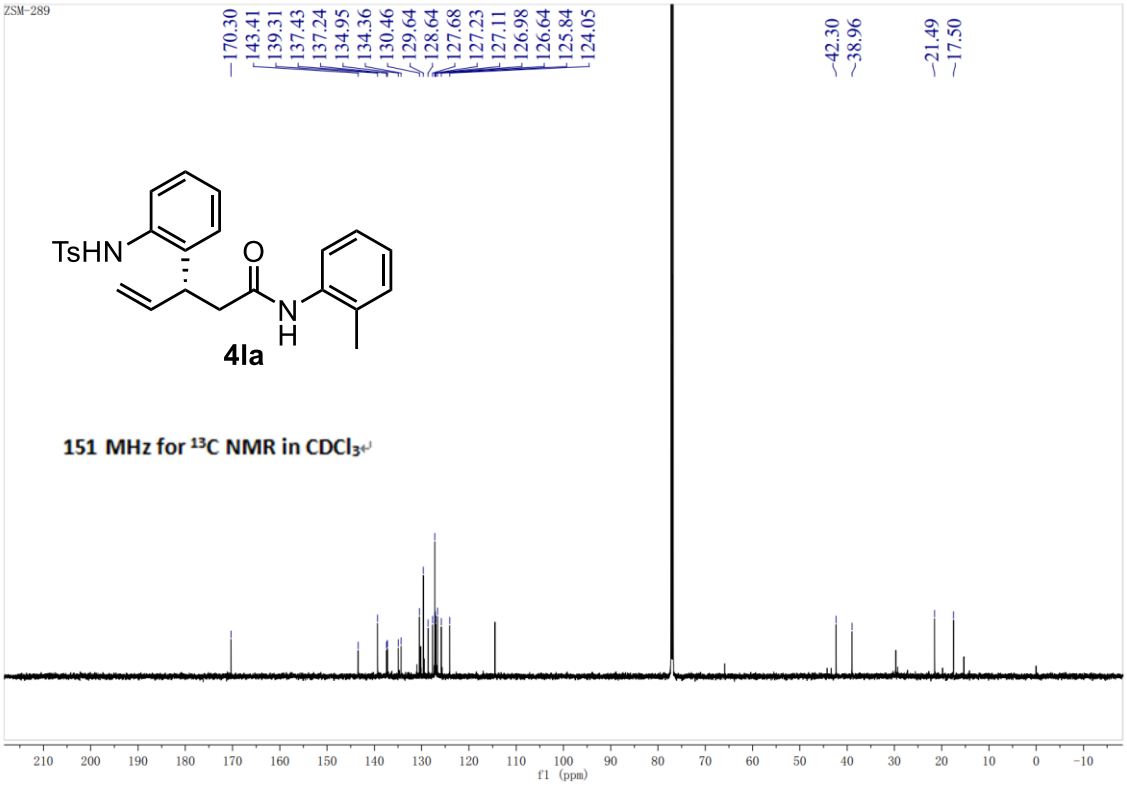

ZSM-274
170.48
143.72
139.17
138.72
137.48
137.08
134.45
134.04
129.88
129.75
128.75
127.68
127.23
126.88
124.40
119.97
117.96
114.71
42.44
38.94
21.53
TsHN
O
N
H
Cl
4ja
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

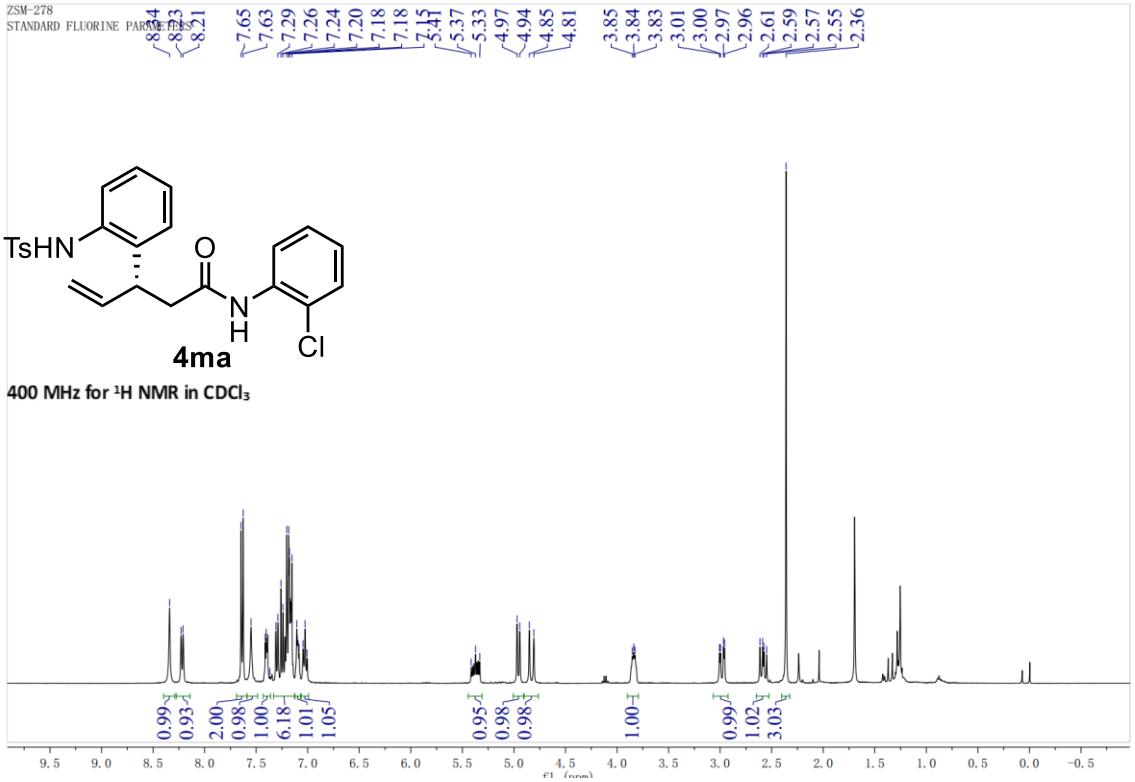

zsm-288
STANDARD ELUENT PARAMETERS
8.15
7.77
7.76
7.77
7.74
7.26
7.24
7.23
7.15
7.13
7.12
7.11
7.07
7.05
6.76
5.55
5.54
5.52
5.51
5.02
5.00
4.92
4.88
3.98
3.97
3.96
2.93
2.89
2.68
2.65
2.62
2.39
TsHN
O
N
H
F
4ka
400 MHz for ¹H NMR in CDCl₃
0.99
0.99
1.96
1.05
8.85
0.98
0.99
1.00
1.03
1.00
1.01
1.03
3.09
f1 (ppm)

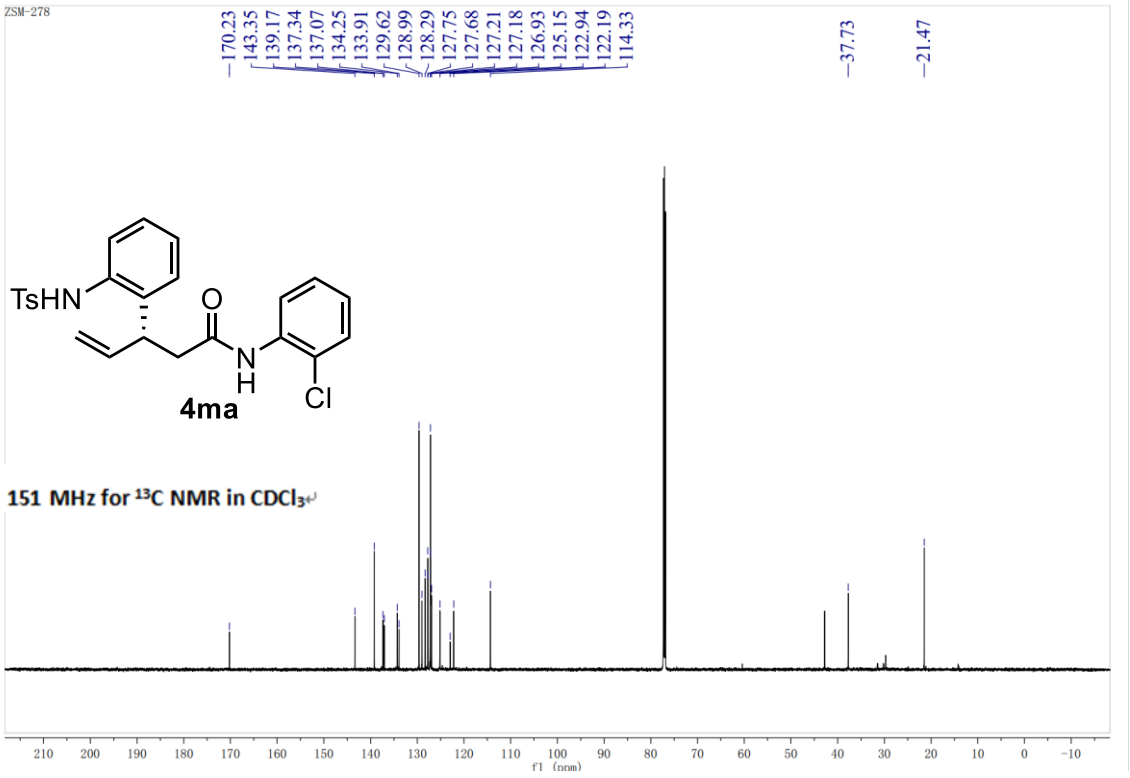

ZSM-288
170.29
163.66
162.04
139.20
137.14
129.73
128.78
127.70
127.25
127.20
126.90
115.14
114.72
111.15
111.01
107.46
107.29
42.48
39.04
21.52
TsHN
O
N
H
F
4ka
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

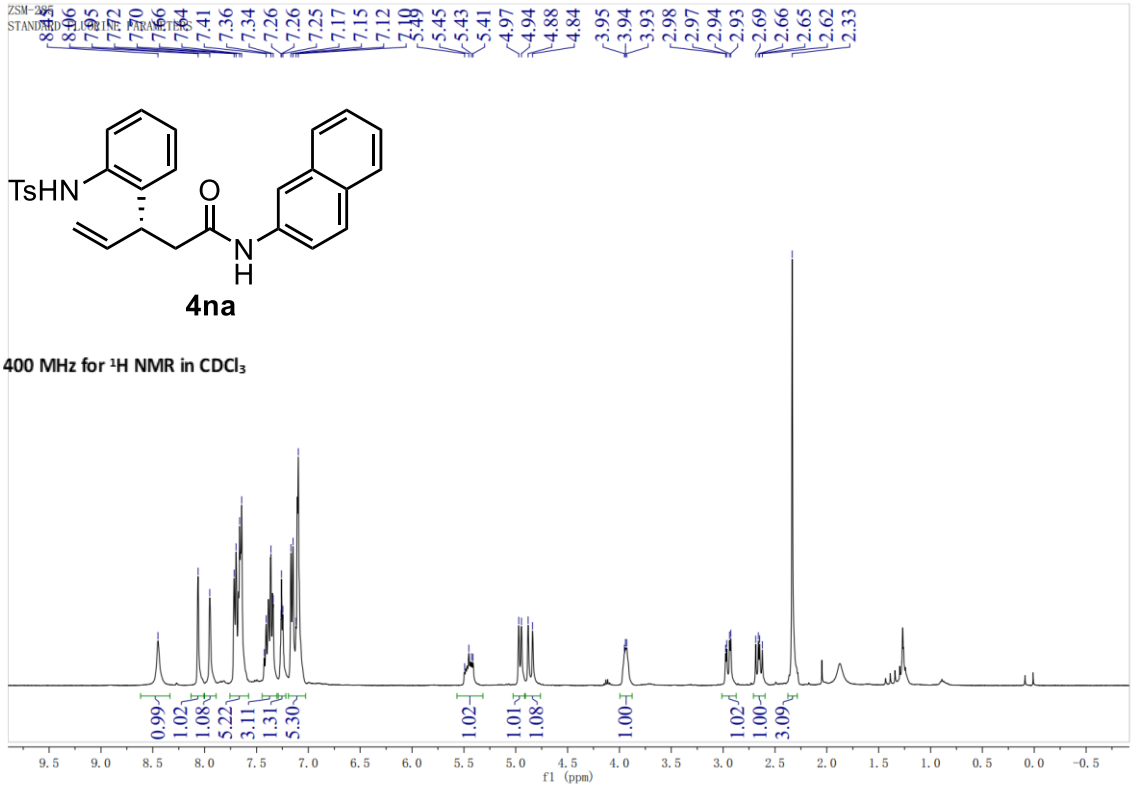

ZSM-288
-111.46
TsHN
O
F
N
H
4ka
565 MHz for 19F NMR in CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

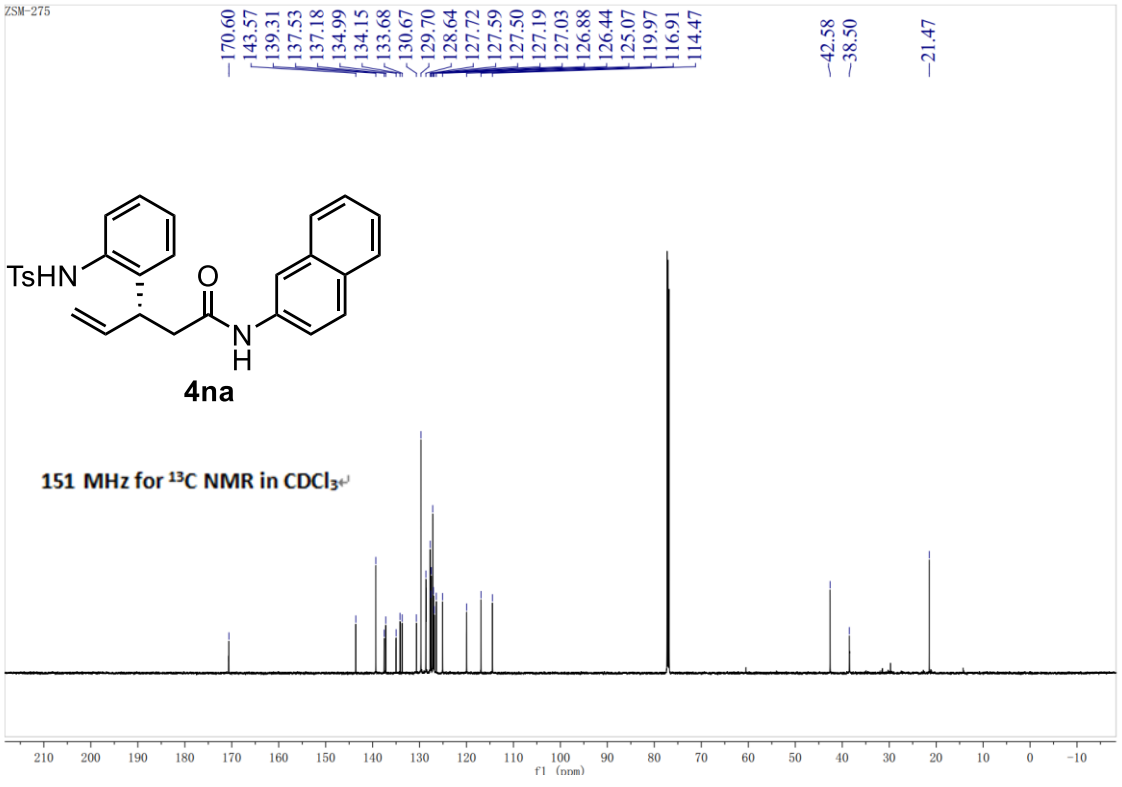

ZSM-289
STANDARD FLUORINE PARAMETERS
8.22
7.62
7.60
7.25
7.19
7.17
7.14
7.12
7.10
7.08
5.50
5.47
5.44
5.44
4.99
4.97
4.90
4.85
3.91
3.90
2.94
2.90
2.64
2.61
2.58
2.36
1.94
TsHN
O
N
H
4la
600 MHz for ¹H NMR in CDCl₃
1.08
2.08
0.99
11.96
0.97
0.98
1.02
1.00
1.01
1.05
3.26
3.02
f1 (ppm)

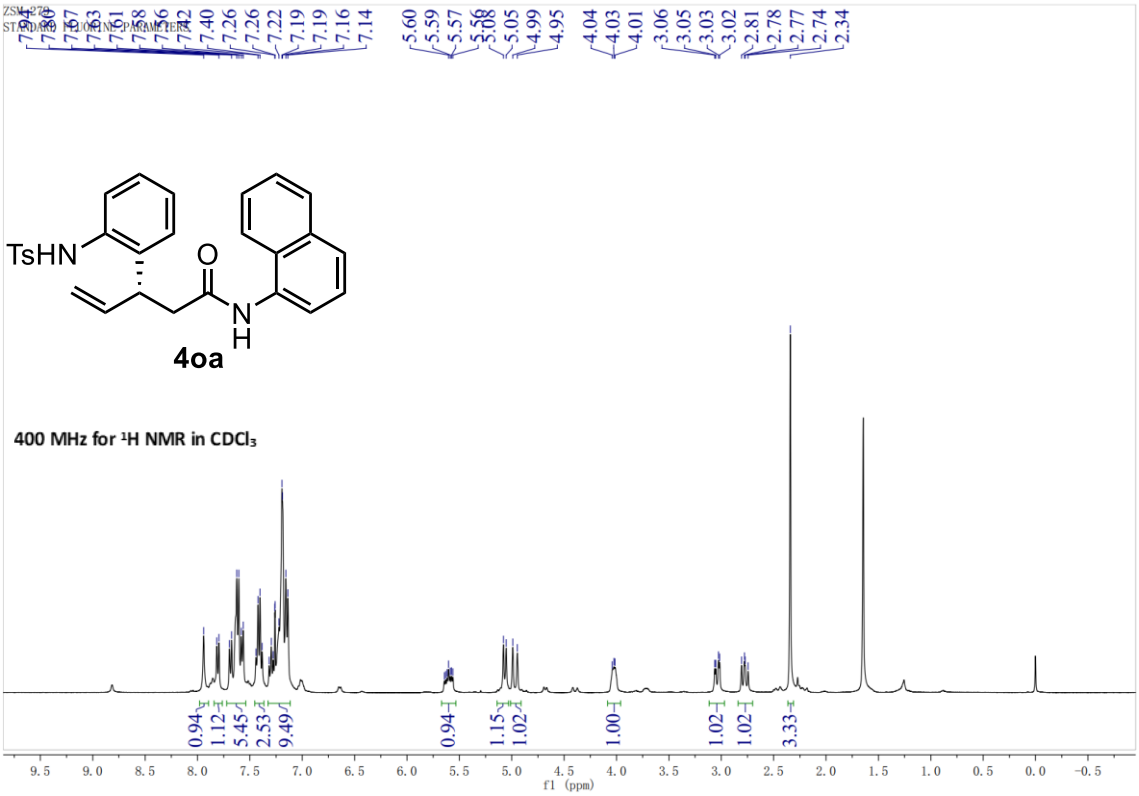

ZSM-289
170.30
143.41
139.31
137.43
137.24
134.95
134.36
130.46
129.64
128.64
127.68
127.23
127.11
126.98
126.64
125.84
124.05
42.30
38.96
21.49
17.50
TsHN
O
N
H
4la
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

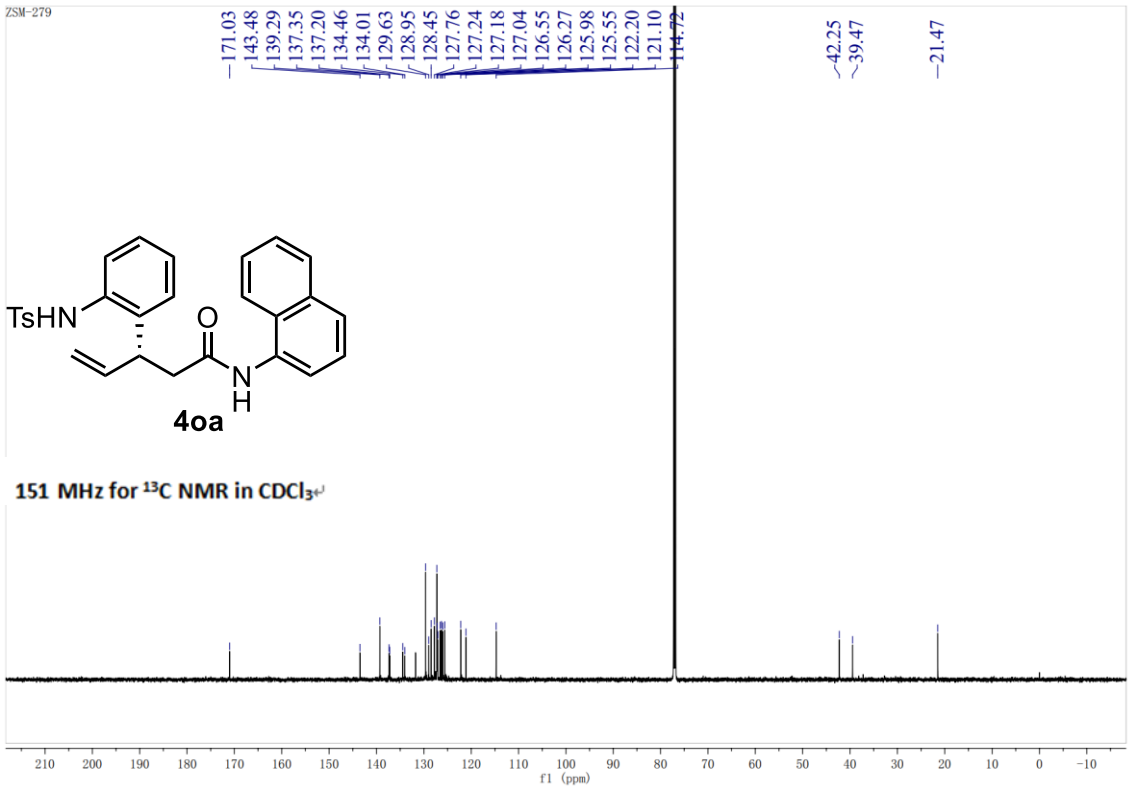

ZSM-278
STANDARD FLUORINE PARAMETERS
8.34
8.33
8.21
7.65
7.63
7.29
7.26
7.24
7.20
7.18
7.18
7.15
5.41
5.37
5.33
4.97
4.94
4.85
4.81
3.85
3.84
3.83
3.01
3.00
2.97
2.96
2.61
2.59
2.57
2.55
2.36
TsHN
O
N
H
Cl
4ma
400 MHz for ¹H NMR in CDCl₃
0.99
0.93
2.00
0.98
1.00
6.18
1.01
1.05
0.95
0.98
0.98
1.00
0.99
1.02
3.03
9.5 9.0 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
f1 (ppm)

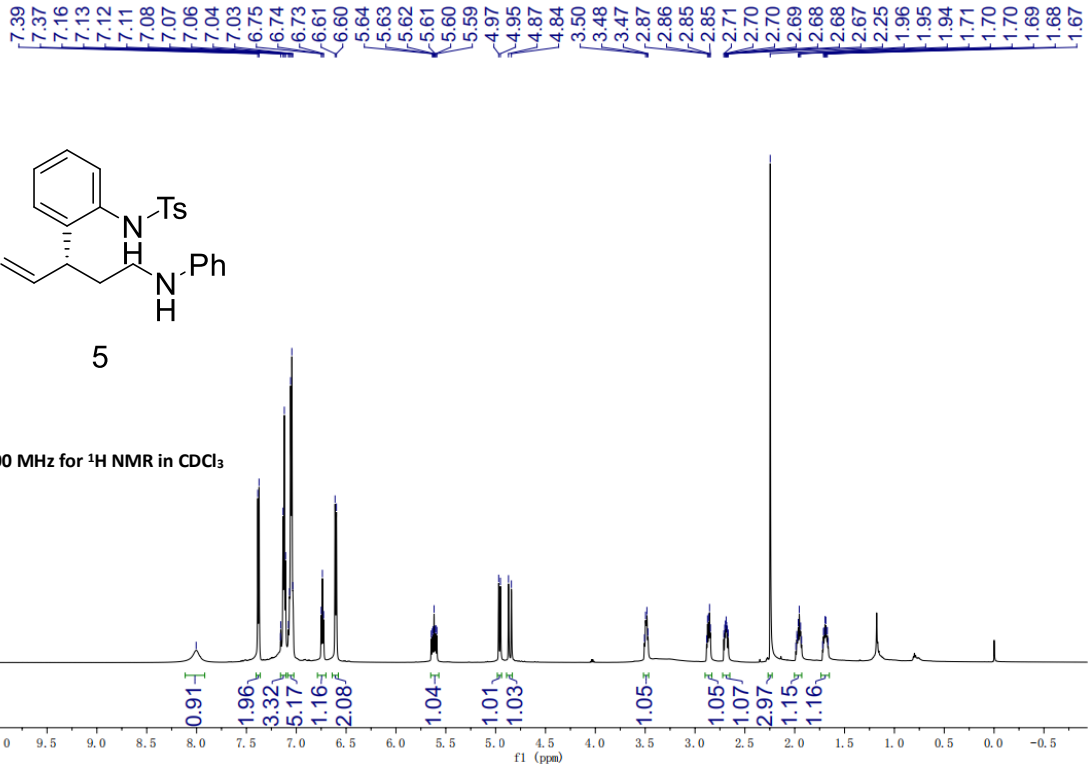

ZSM-278
170.23
143.35
139.17
137.34
137.07
134.25
133.91
129.62
128.99
128.29
127.75
127.68
127.21
127.18
126.93
125.15
122.94
122.19
114.33
37.73
21.47
TsHN
O
N
H
Cl
4ma
151 MHz for ¹³C NMR in CDCl₃
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

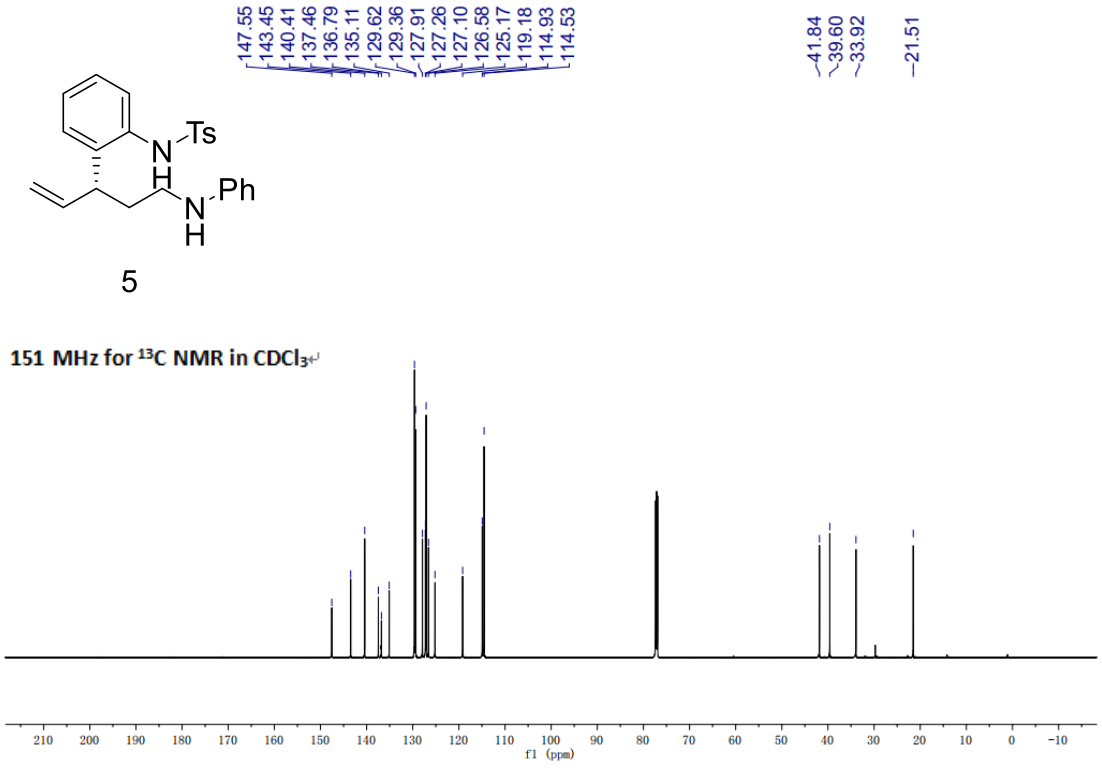

ZSM-295
STANDARD 1D PROTON PARAMETERS
8.46
7.95
7.72
7.70
7.66
7.64
7.41
7.36
7.34
7.26
7.26
7.25
7.17
7.15
7.12
5.45
5.43
5.41
4.97
4.94
4.88
4.84
3.95
3.94
3.93
2.98
2.97
2.94
2.93
2.69
2.66
2.65
2.62
2.33
TsHN
O
N
H
4na
400 MHz for ¹H NMR in CDCl₃
0.99
1.02
1.08
5.22
3.11
1.31
5.30
1.02
1.01
1.08
1.00
1.02
1.00
3.09
f1 (ppm)

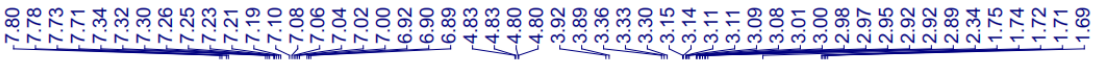

ZSM-275
170.60
143.57
139.31
137.53
137.18
134.99
134.15
133.68
130.67
129.70
128.64
127.72
127.59
127.50
127.19
127.03
126.88
126.44
125.07
119.97
116.91
114.47
42.58
38.50
21.47
TsHN
O
N
H
4na
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

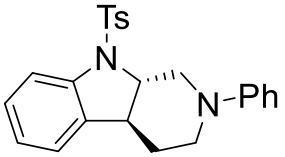

TsHN
O
N
H
4oa
400 MHz for ¹H NMR in CDCl₃
f1 (ppm)


ZSM-279
TsHN
O
N
H
4oa
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)


7.39
7.37
7.16
7.13
7.12
7.11
7.08
7.07
7.06
7.04
7.03
6.75
6.74
6.73
6.61
6.60
5.64
5.63
5.62
5.61
5.60
5.59
4.97
4.95
4.87
4.84
3.50
3.48
3.47
2.87
2.86
2.85
2.85
2.71
2.70
2.70
2.69
2.68
2.68
2.67
2.25
1.96
1.95
1.94
1.71
1.70
1.70
1.69
1.68
1.67
Ts
N
H
N
Ph
H
5
600 MHz for ¹H NMR in CDCl₃
0.91
1.96
3.32
5.17
1.16
2.08
1.04
1.01
1.03
1.05
1.05
1.07
2.97
1.15
1.16
f1 (ppm)

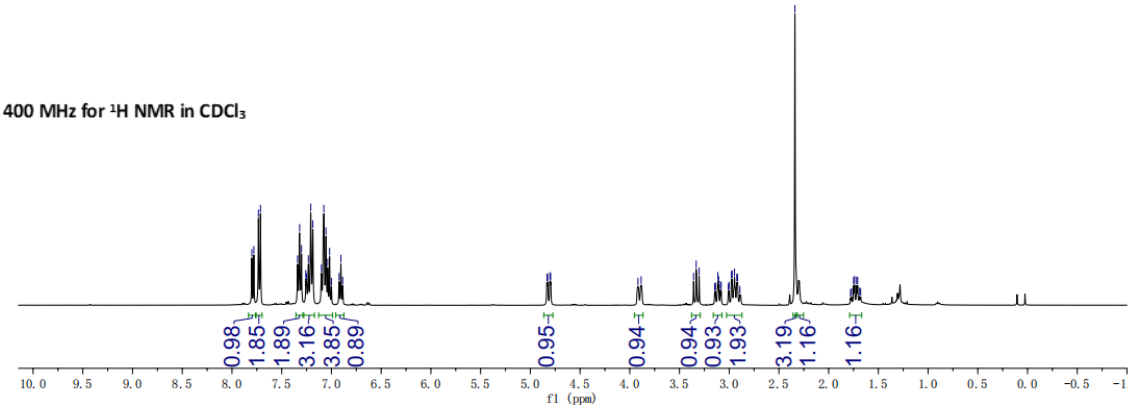

147.55
143.45
140.41
137.46
136.79
135.11
129.62
129.36
127.91
127.26
127.10
126.58
125.17
119.18
114.93
114.53
41.84
39.60
33.92
21.51
Ts
N
H
N
Ph
H
5
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

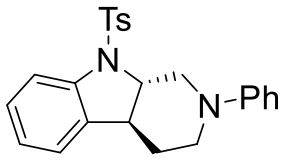




6

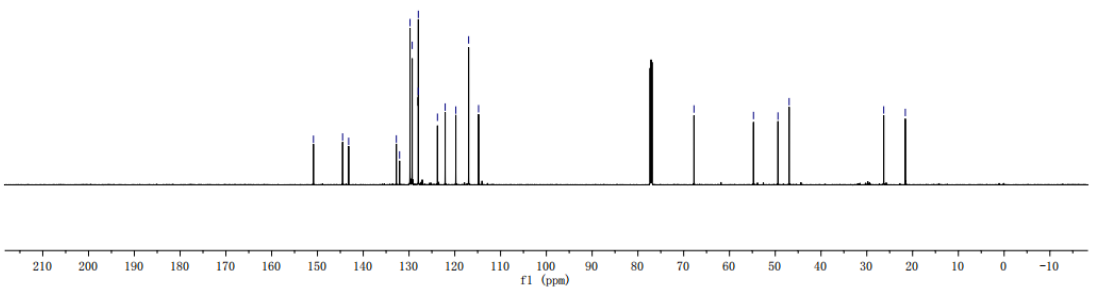
400 MHz for ^{1}H NMR in $CDCl_3$

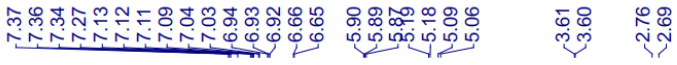


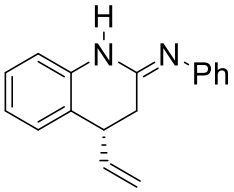


6

151 MHz for ^{13}C NMR in $CDCl_3$

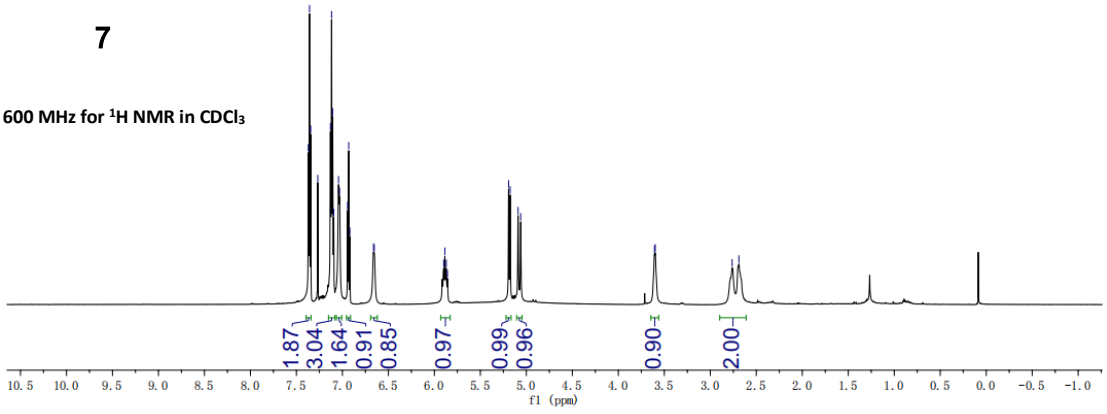


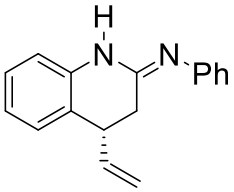


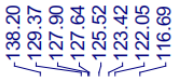


7

600 MHz for ^{1}H NMR in $CDCl_3$

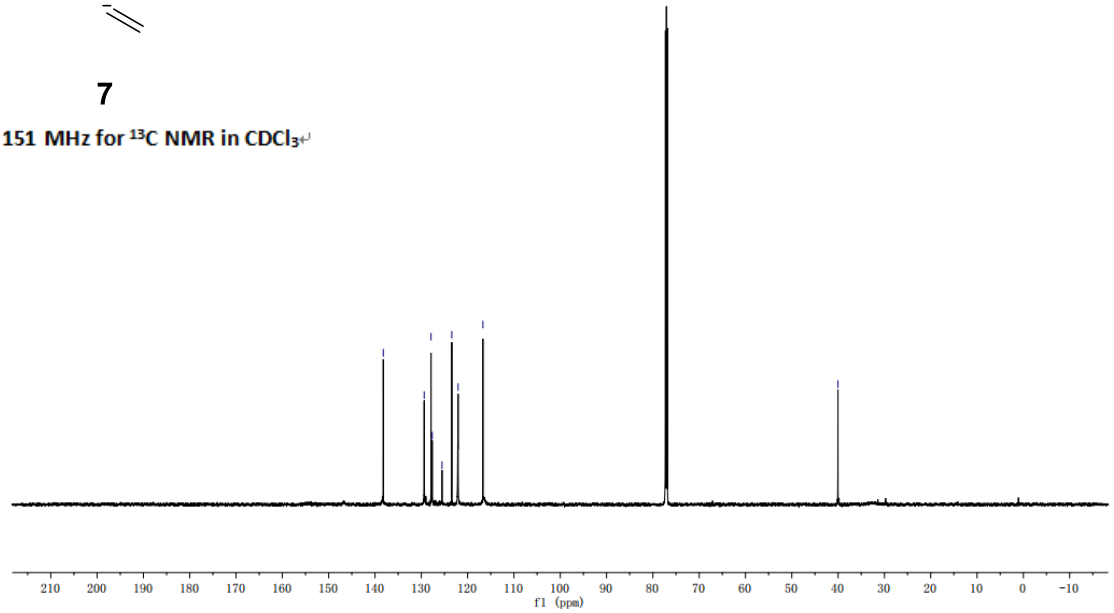


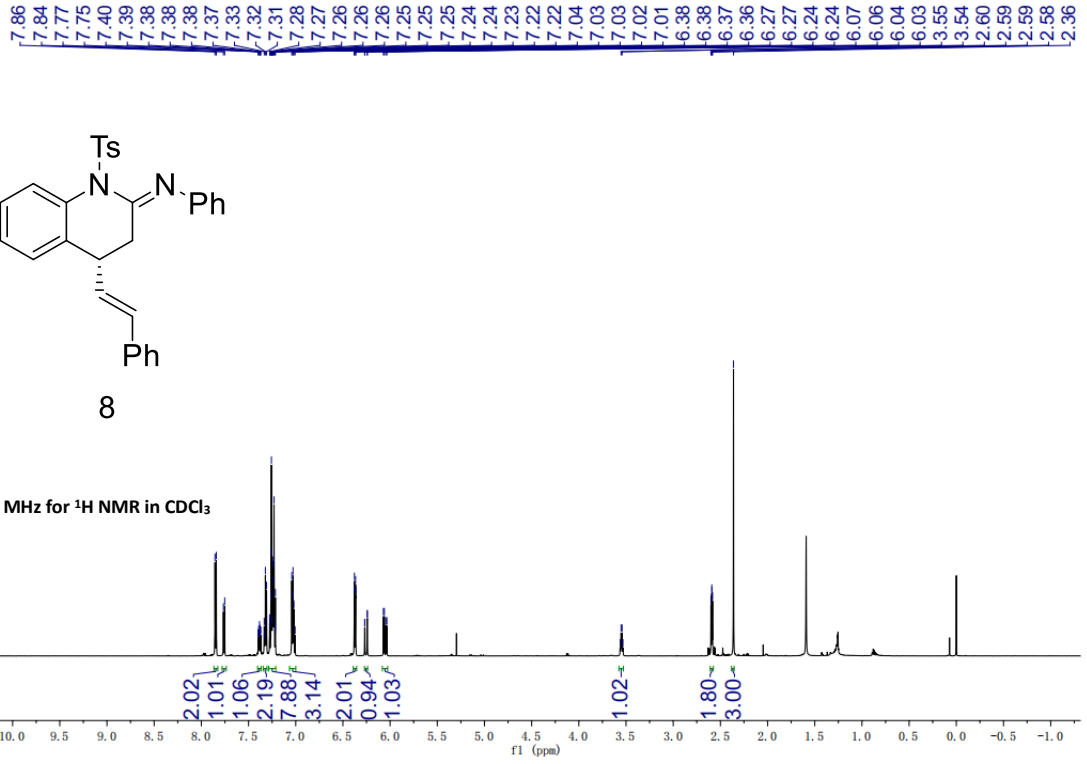


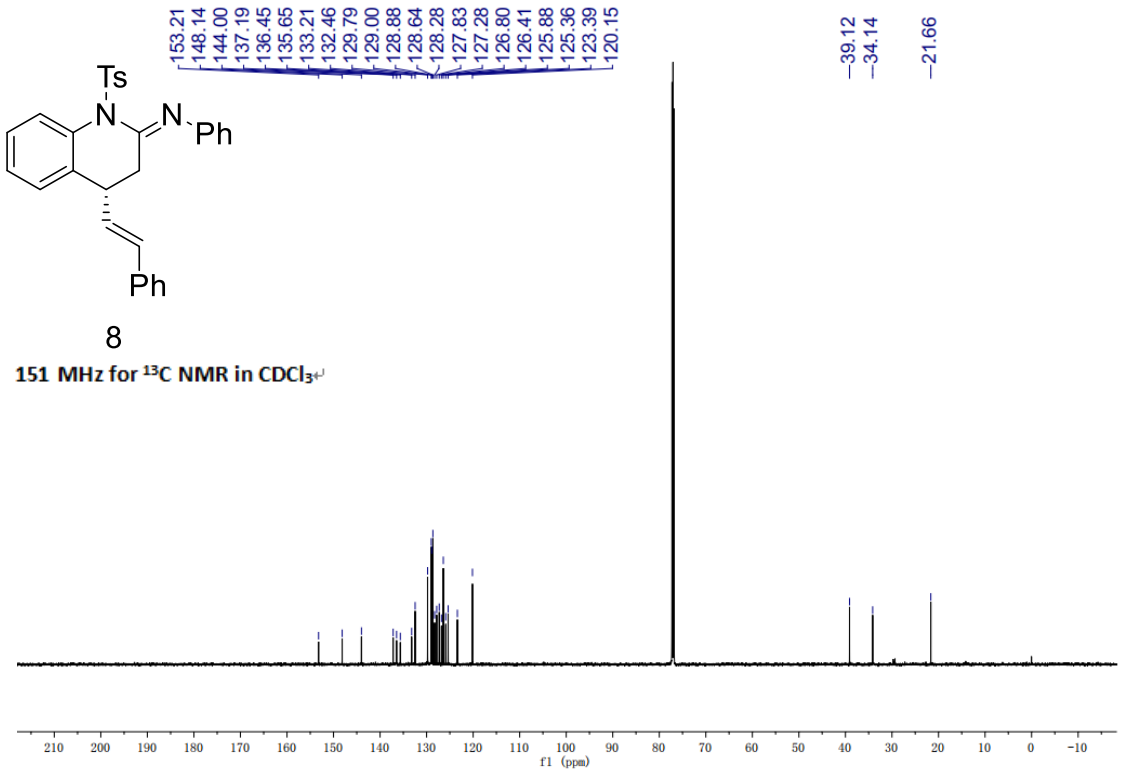


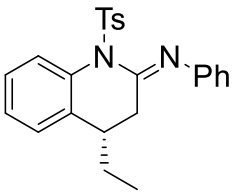
7

151 MHz for ^{13}C NMR in $CDCl_3$



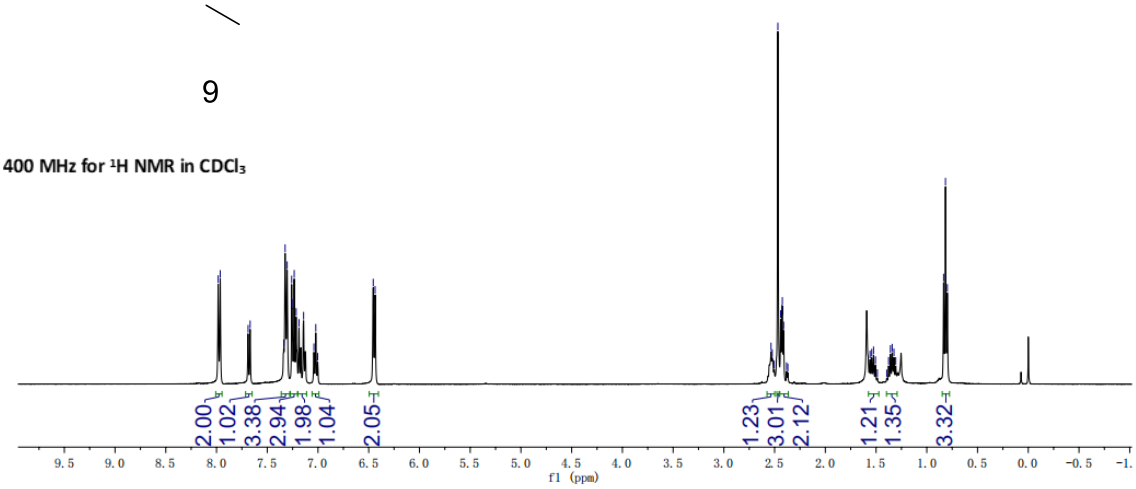

7.86
7.84
7.77
7.75
7.40
7.39
7.38
7.38
7.38
7.37
7.33
7.32
7.31
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.04
7.03
7.03
7.02
7.01
6.38
6.38
6.37
6.36
6.27
6.27
6.24
6.24
6.07
6.06
6.04
6.03
3.55
3.54
2.60
2.59
2.59
2.58
2.36
Ts
N
N
Ph
Ph
8
600 MHz for ¹H NMR in CDCl₃
2.02
1.01
1.06
2.19
7.88
3.14
2.01
0.94
1.03
1.02
1.80
3.00
10.0 9.5 9.0 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 −1.0
f1 (ppm)

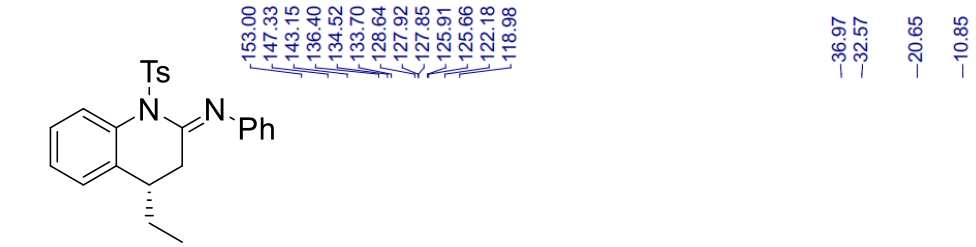

153.21
148.14
144.00
137.19
136.45
135.65
133.21
132.46
129.79
129.00
128.88
128.64
128.28
127.83
127.28
126.80
126.41
125.88
125.36
123.39
120.15
39.12
34.14
21.66
Ts
N
N
Ph
Ph
8
151 MHz for ¹³C NMR in CDCl₃
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



9

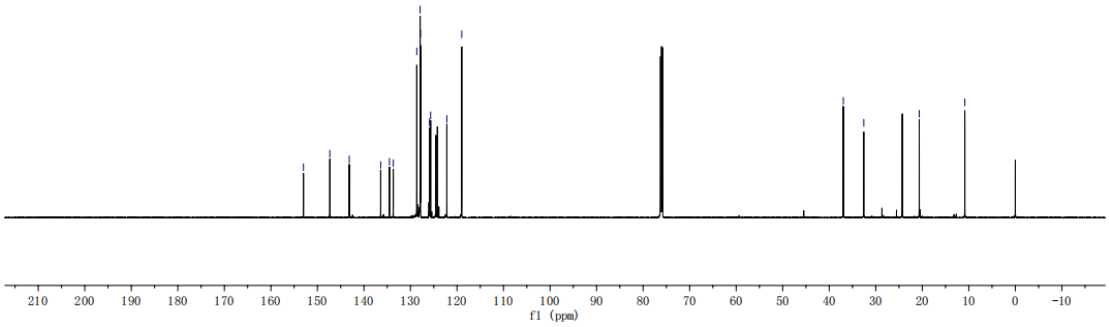
400 MHz for ^{1}H NMR in $CDCl_3$

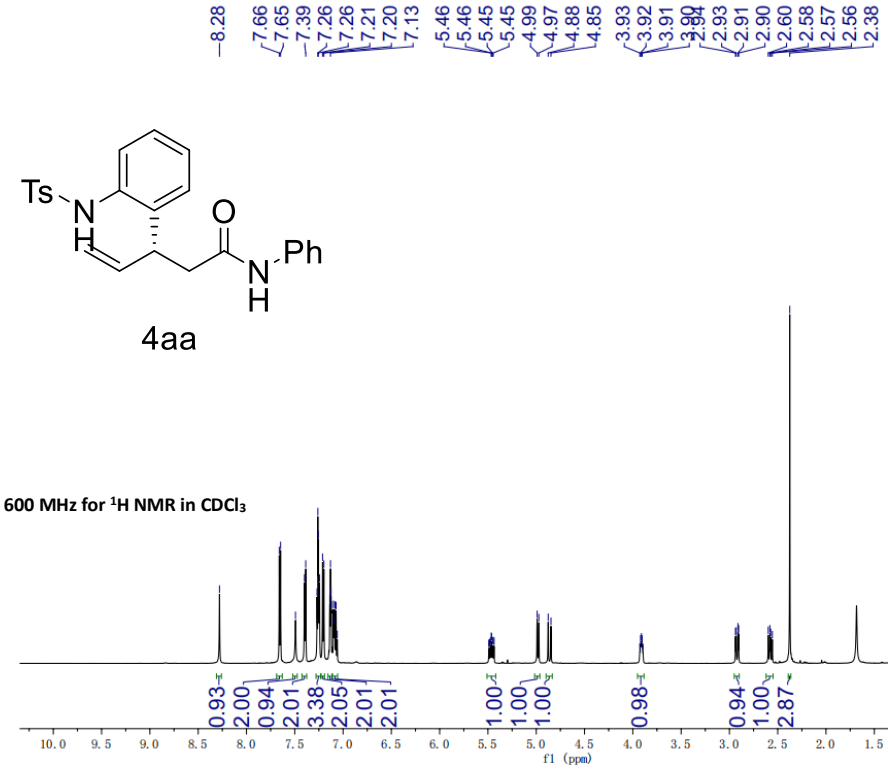


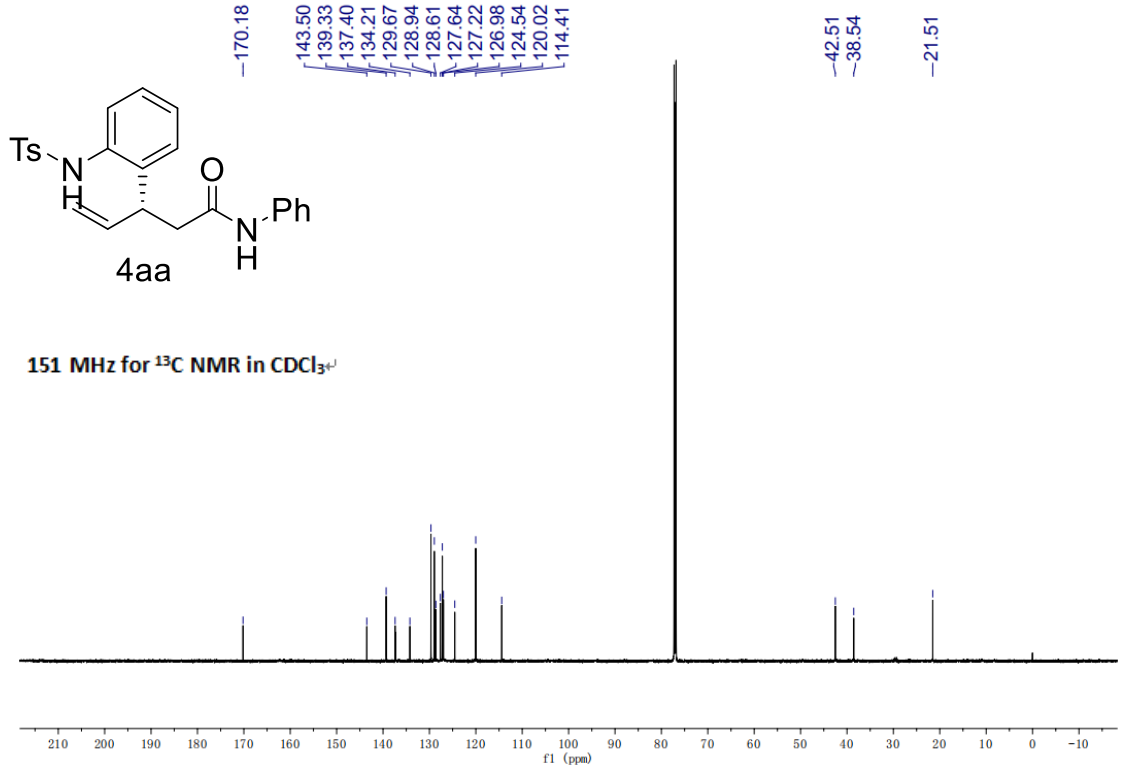


9

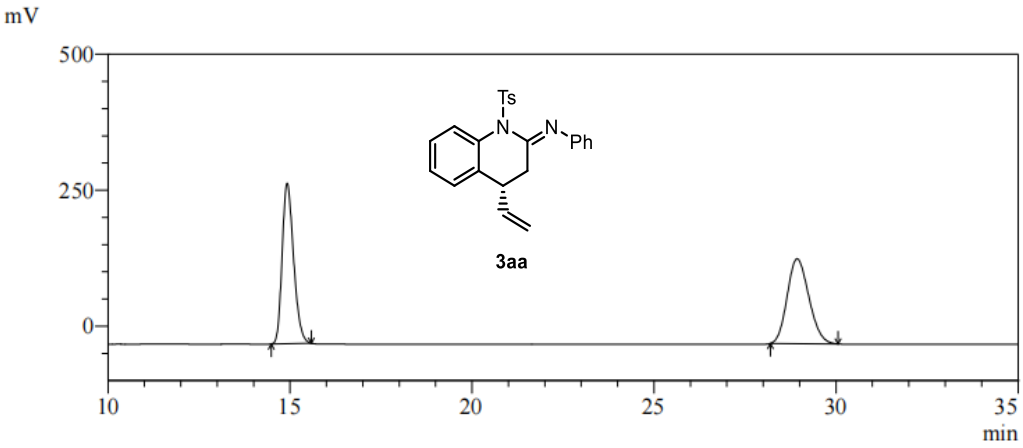
151 MHz for ^{13}C NMR in $CDCl_3$




8.28
7.66
7.65
7.39
7.26
7.26
7.21
7.20
7.13
5.46
5.46
5.45
5.45
4.99
4.97
4.88
4.85
3.93
3.92
3.91
3.90
2.94
2.93
2.91
2.90
2.60
2.58
2.57
2.56
2.38
Ts
N
H
O
N
H
Ph
4aa
600 MHz for ¹H NMR in CDCl₃
0.93
2.00
0.94
2.01
3.38
2.05
2.01
2.01
1.00
1.00
1.00
0.98
0.94
1.00
2.87
f1 (ppm)


170.18
143.50
139.33
137.40
134.21
129.67
128.94
128.61
127.64
127.22
126.98
124.54
120.02
114.41
42.51
38.54
21.51
Ts
N
H
O
N
H
Ph
4aa
151 MHz for ¹³C NMR in CDCl₃
f1 (ppm)

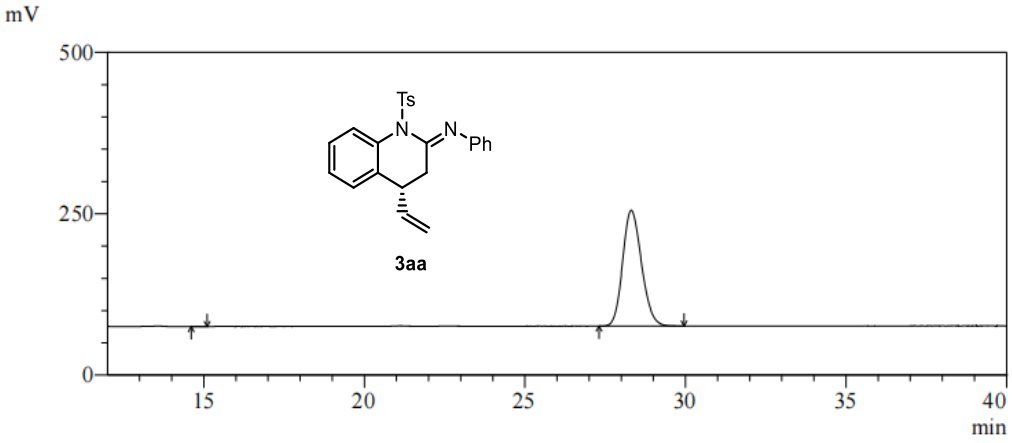
12.Copies of HPLC Analysis



Peak Table

Detector A 254nm

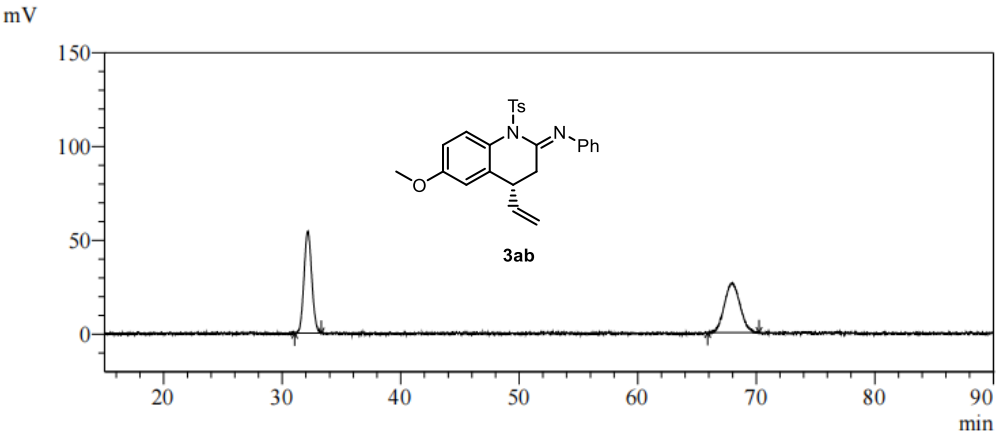
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.921	434.64	678.29	6452541	294807	49.971
2	28.933	230.04	678.29	6459978	156032	50.029
Total				12912519	450839	100.000



Peak Table

Detector A 254nm

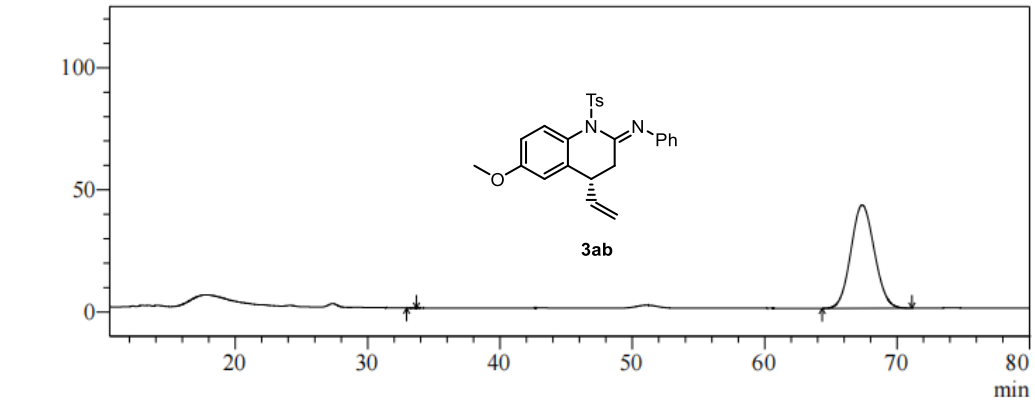
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.825	0.11	879.30	810	97	0.011
2	28.313	204.26	879.30	7341077	179607	99.989
Total				7341888	179704	100.000



Peak Table

Detector A 254nm

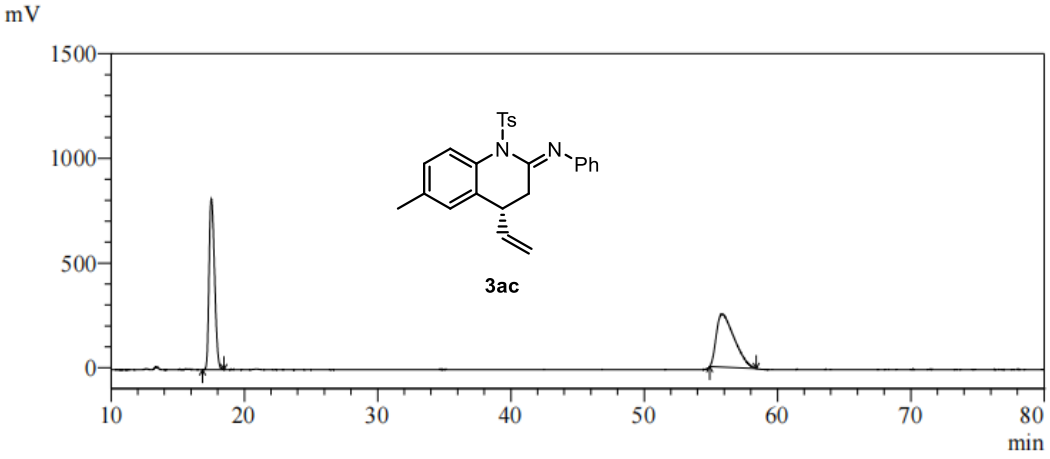
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	32.166	57.70	940.78	2473814	54285	50.584
2	68.016	28.17	940.78	2416713	26499	49.416
Total				4890526	80784	100.000



Peak Table

Detector A 254nm

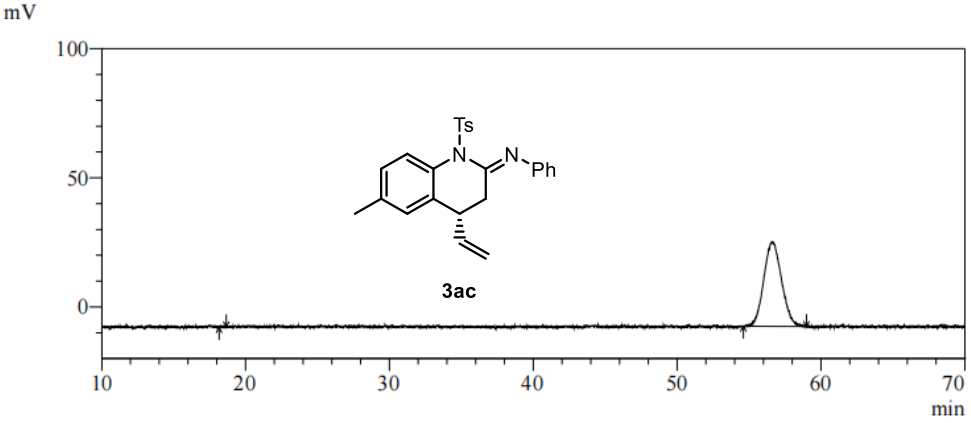
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	33.005	0.24	236.28	1749	56	0.033
2	67.354	179.03	236.28	5227844	42303	99.967
Total				5229594	42359	100.000



Peak Table

Detector A 254nm

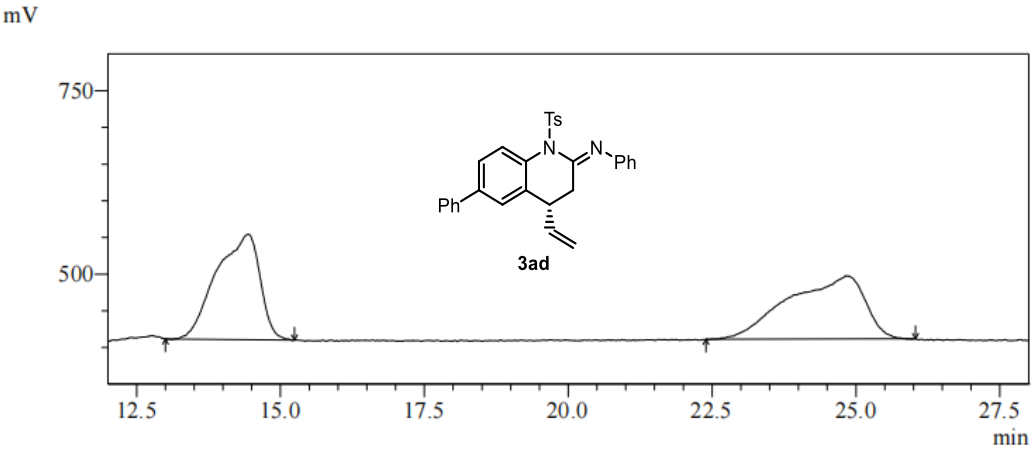
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.526	188.85	4315.95	23546748	815084	49.820
2	55.852	58.93	4315.95	23717146	254343	50.180
Total				47263894	1069426	100.000



Peak Table

Detector A 254nm

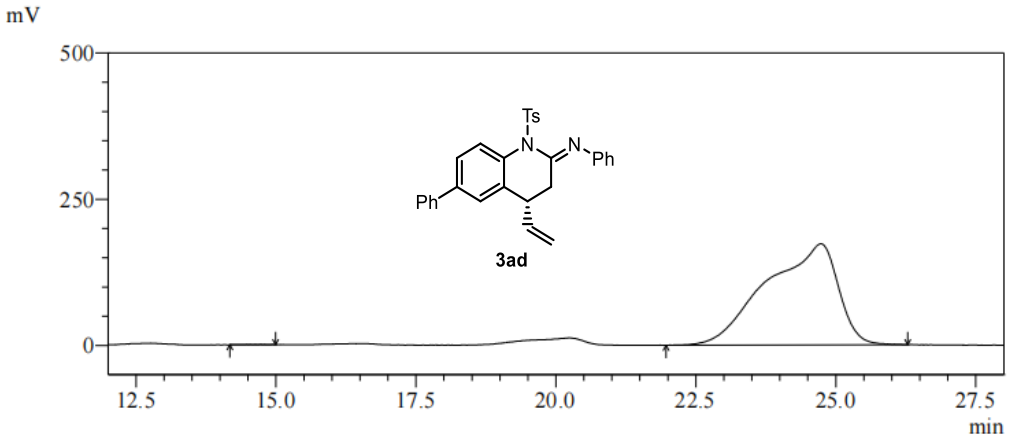
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	18.270	0.99	786.31	7004	779	0.248
2	56.583	41.58	786.31	2812677	32696	99.752
Total				2819682	33476	100.000



Peak Table

Detector A 210nm

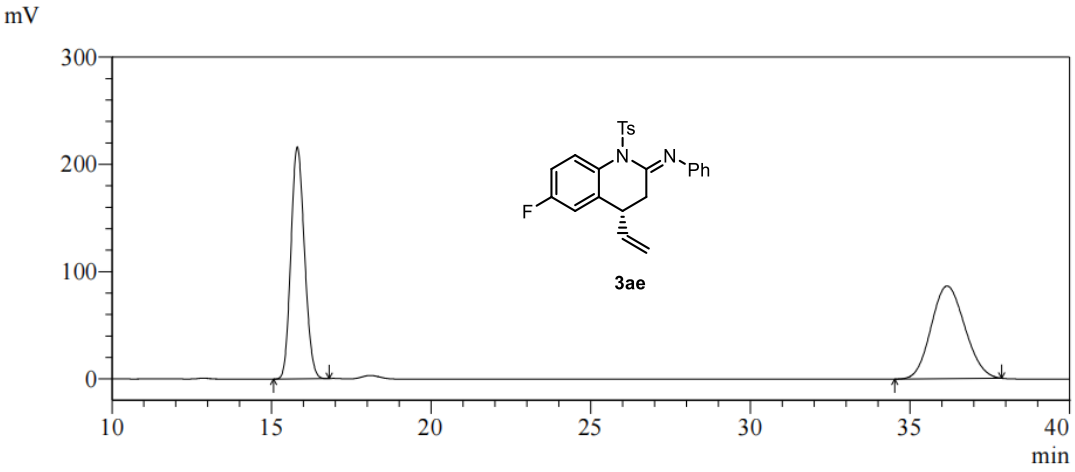
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.447	20.28	7088.85	7569576	143728	48.893
2	24.819	12.13	7088.85	7912342	86011	51.107
Total				15481918	229739	100.000



Peak Table

Detector A 254nm

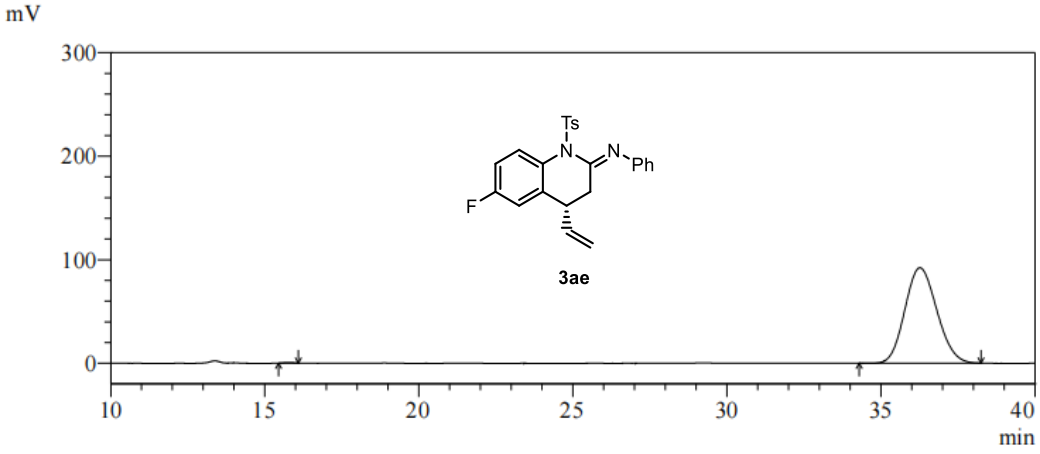
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.725	0.08	3558.85	4238	289	0.028
2	24.732	48.55	3558.85	15381205	172775	99.972
Total				15385444	173064	100.000



Peak Table

Detector A 254nm

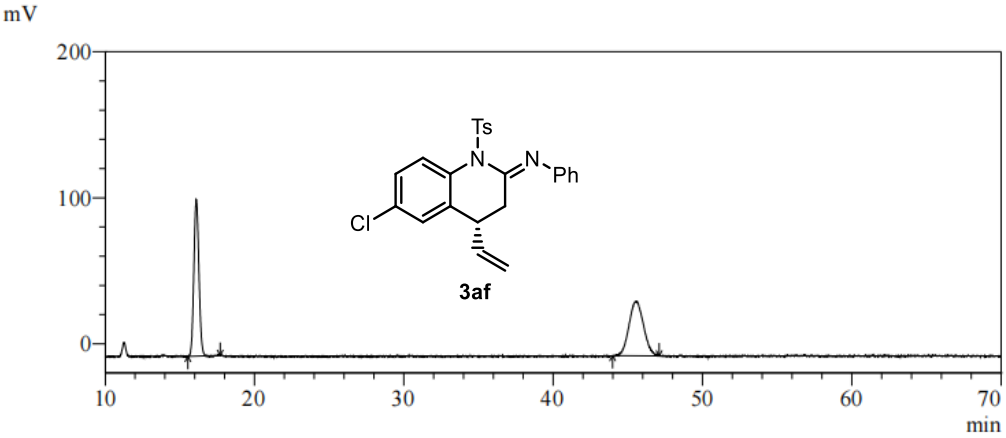
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	15.805	99.92	2164.09	6392246	216234	50.196
2	36.166	39.93	2164.09	6342283	86423	49.804
Total				12734529	302656	100.000



Peak Table

Detector A 254nm

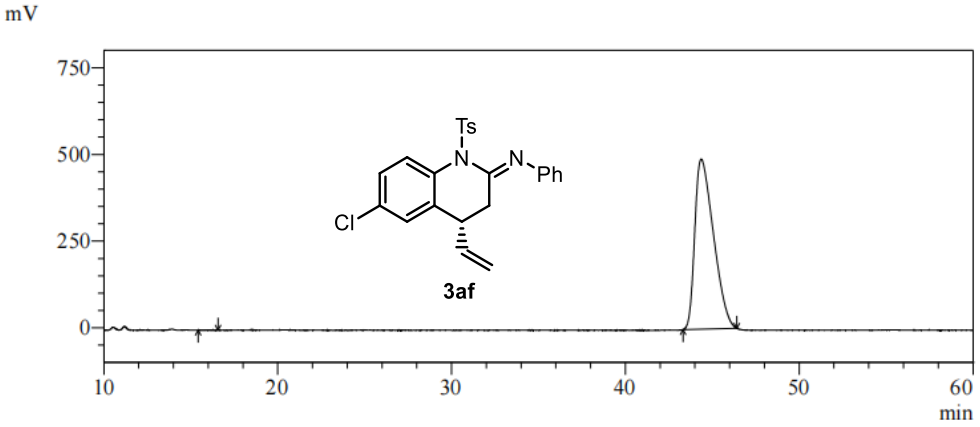
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	15.752	0.90	640.68	12450	575	0.186
2	36.268	144.03	640.68	6665028	92274	99.814
Total				6677478	92849	100.000



Peak Table

Detector A 254nm

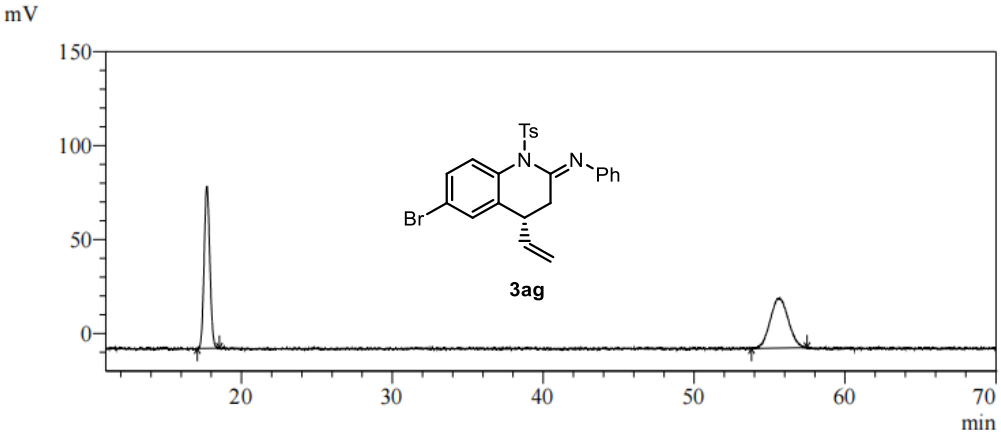
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.093	24.95	4304.85	2507643	107394	49.881
2	45.575	8.67	4304.85	2519630	37323	50.119
Total				5027274	144716	100.000



Peak Table

Detector A 254nm

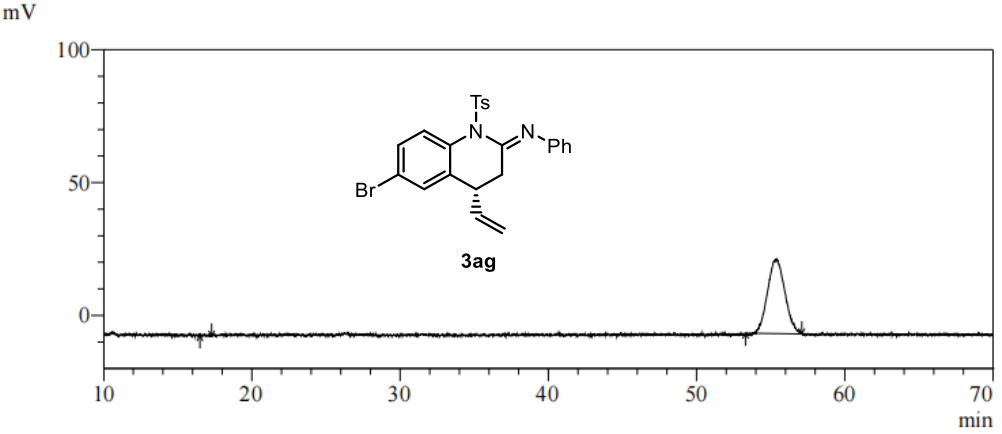
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	15.954	0.65	1074.29	8890	702	0.024
2	44.355	456.66	1074.29	36644150	490580	99.976
Total				36653040	491282	100.000



Peak Table

Detector A 254nm

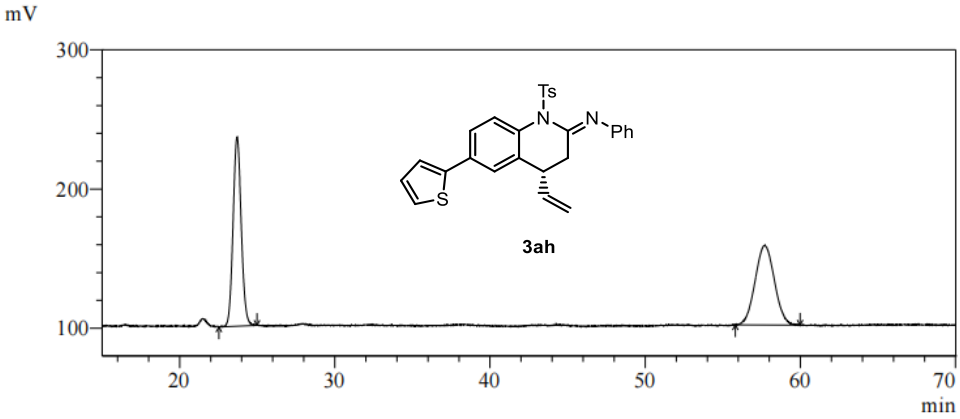
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.708	19.39	4449.54	2266827	86271	50.618
2	55.643	5.98	4449.54	2211467	26600	49.382
Total				4478293	112871	100.000



Peak Table

Detector A 254nm

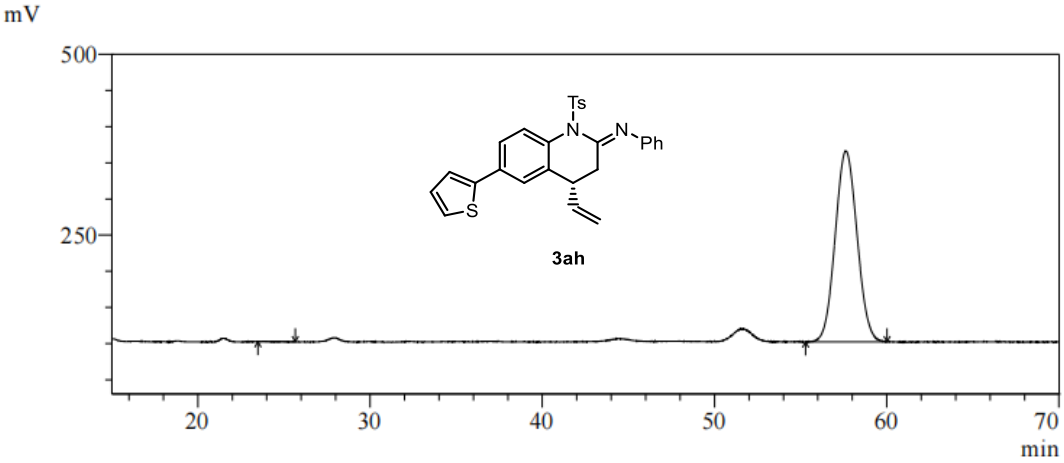
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.231	0.94	761.61	9142	714	0.400
2	55.374	36.96	761.61	2276208	28148	99.600
Total				2285351	28861	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	23.700	25.18	5397.61	4984937	135904	50.173
2	57.710	10.61	5397.61	4950468	57272	49.827
Total				9935404	193176	100.000

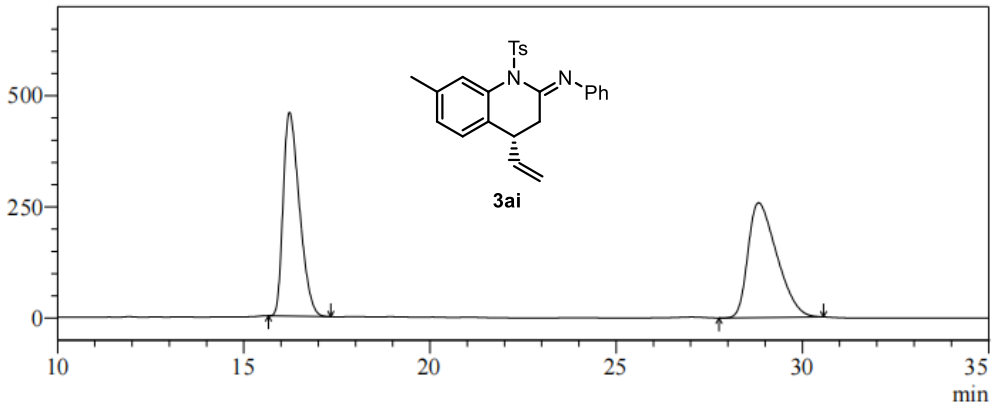


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	23.799	0.16	2501.87	17308	400	0.074
2	57.628	105.55	2501.87	23322166	264084	99.926
Total				23339474	264483	100.000

mV

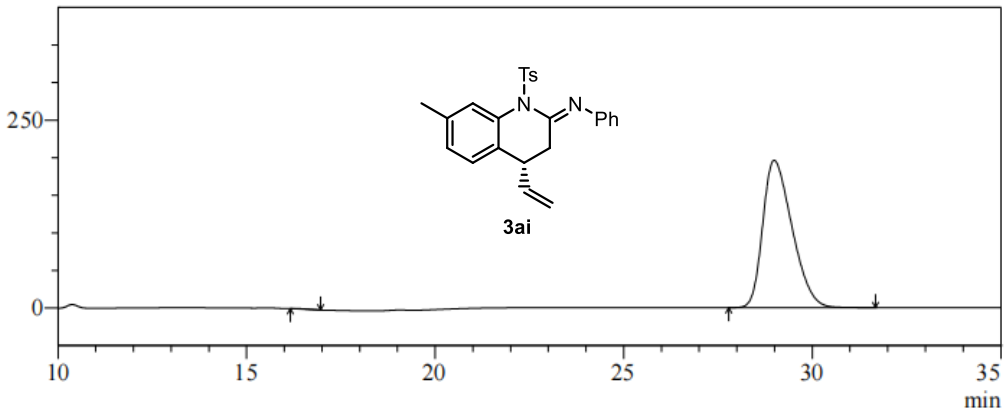


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.228	298.77	1533.76	13942144	458240	50.045
2	28.824	168.38	1533.76	13917200	258256	49.955
Total				27859344	716495	100.000

mV

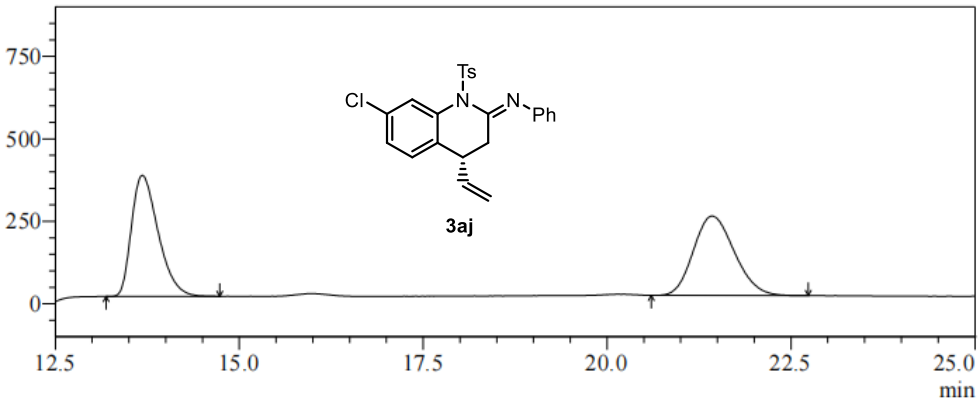


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.336	0.12	3831.20	14485	459	0.136
2	28.991	51.17	3831.20	10616490	196035	99.864
Total				10630975	196494	100.000

mV

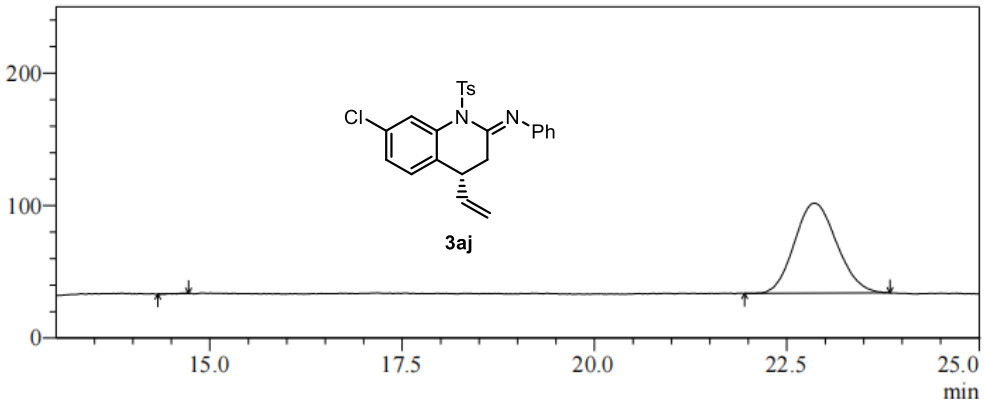


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	13.683	92.11	3987.23	9279374	367260	49.893
2	21.424	60.41	3987.23	9319265	240866	50.107
Total				18598639	608126	100.000

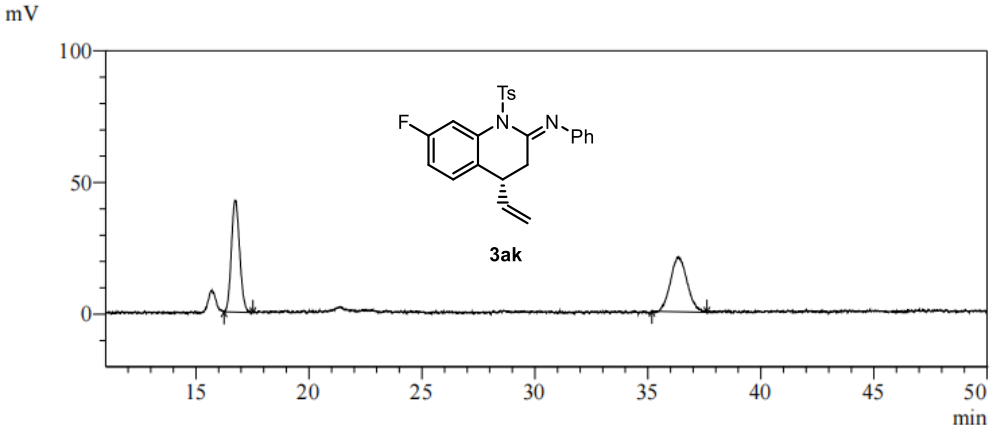
mV



Peak Table

Detector A 254nm

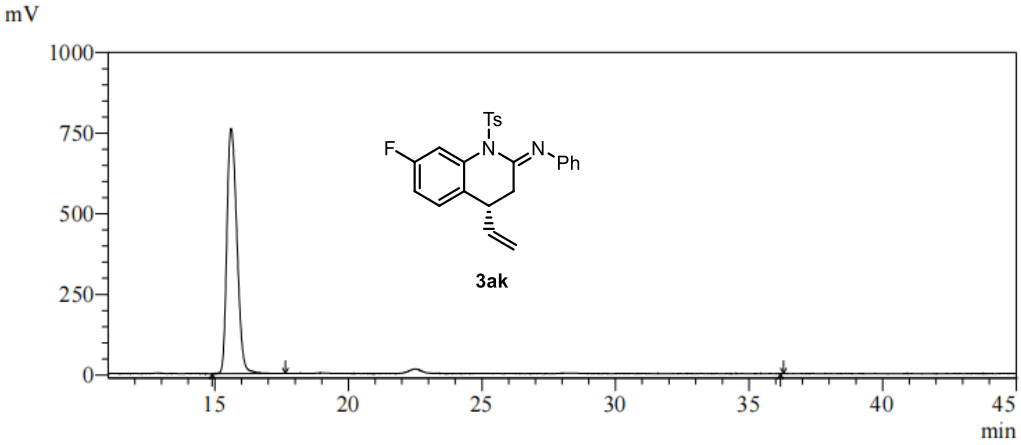
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.695	0.03	8723.14	106	278	0.004
2	22.870	7.78	8723.14	2602124	67838	99.996
Total				2602230	68116	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.725	44.64	949.02	1081127	42362	50.525
2	36.357	22.06	949.02	1058660	20935	49.475
Total				2139787	63297	100.000

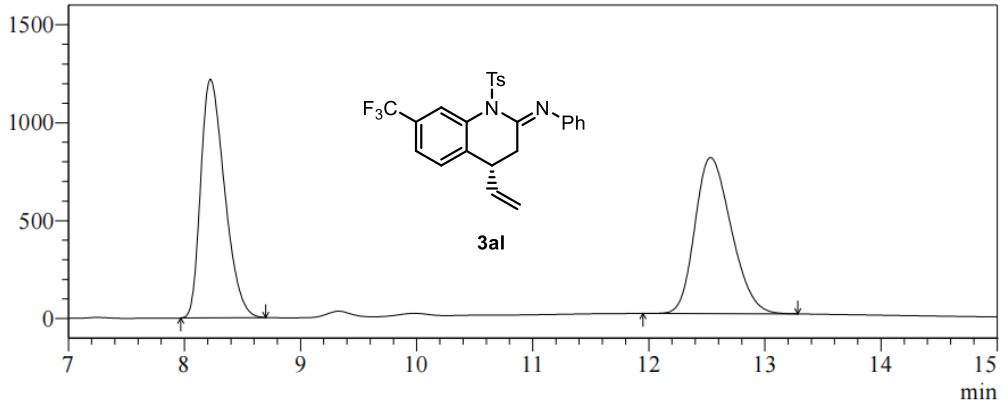


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	15.607	508.86	1494.15	19846927	760306	99.996
2	36.243	0.21	1494.15	734	307	0.004
Total				19847661	760613	100.000

mV

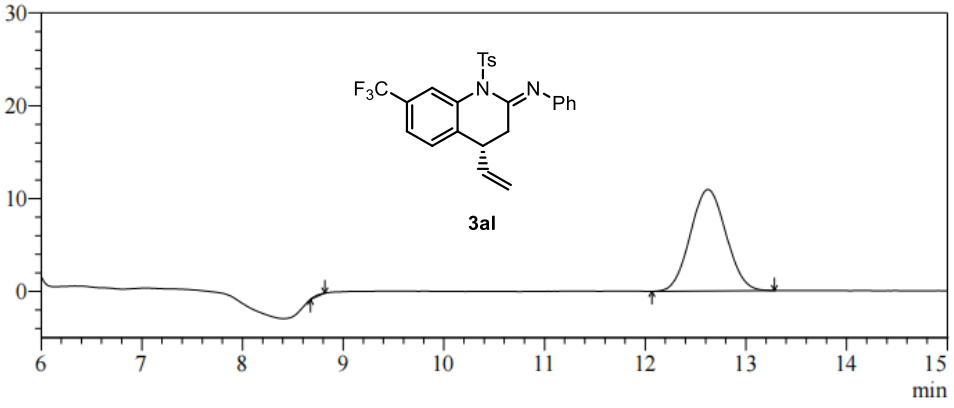


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	8.224	62.52	19480.41	17419350	1217913	50.101
2	12.531	40.92	19480.41	17349459	797046	49.899
Total				34768809	2014959	100.000

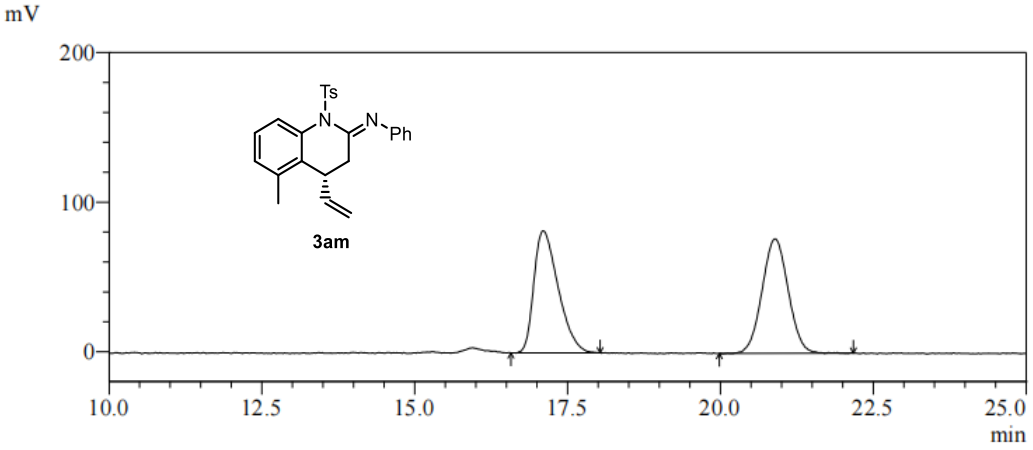
mV



Peak Table

Detector A 254nm

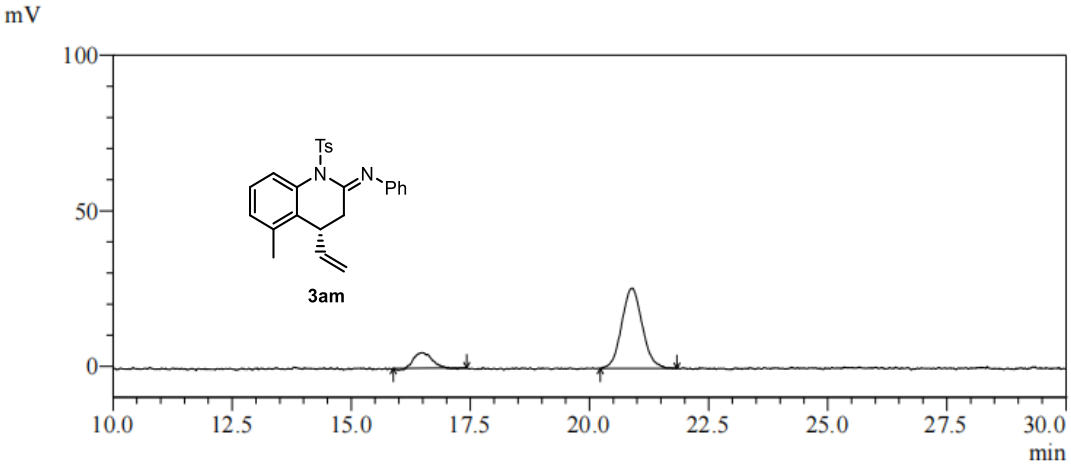
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	8.813	0.01	400.98	904	5	0.335
2	12.622	27.24	400.98	269207	10923	99.665
Total				270111	10928	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.101	100.60	811.77	2260772	81661	49.822
2	20.898	94.25	811.77	2276929	76511	50.178
Total				4537701	158171	100.000

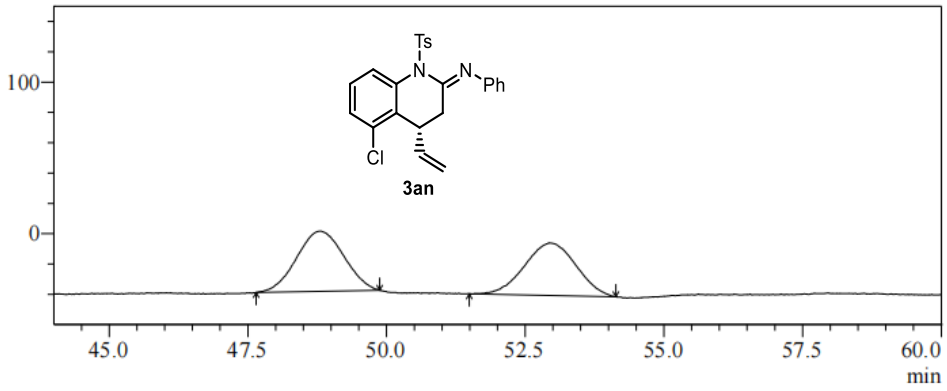


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.487	8.28	608.70	124871	5041	13.875
2	20.905	42.41	608.70	775093	25814	86.125
Total				899965	30855	100.000

mV

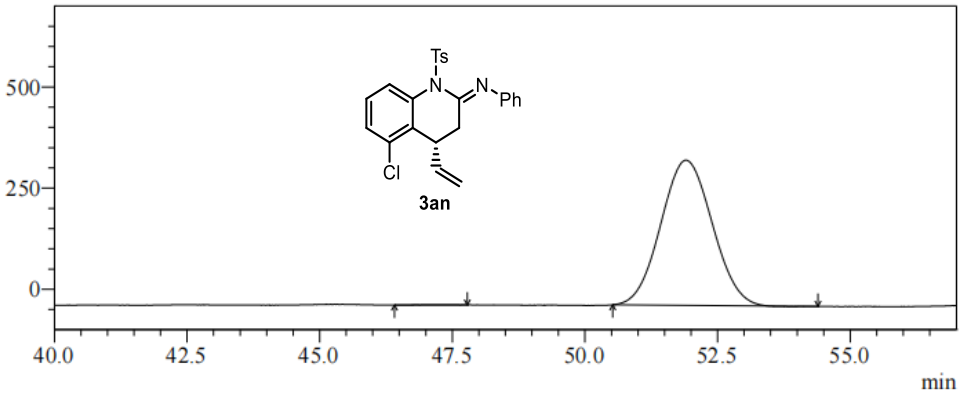


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	48.808	18.65	2130.98	2346551	39739	51.155
2	52.935	16.26	2130.98	2240600	34652	48.845
Total				4587151	74390	100.000

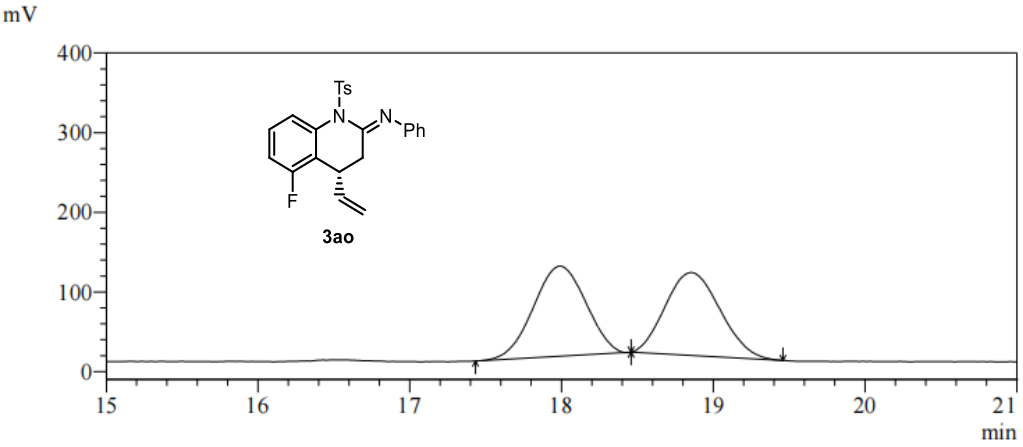
mV



Peak Table

Detector A 254nm

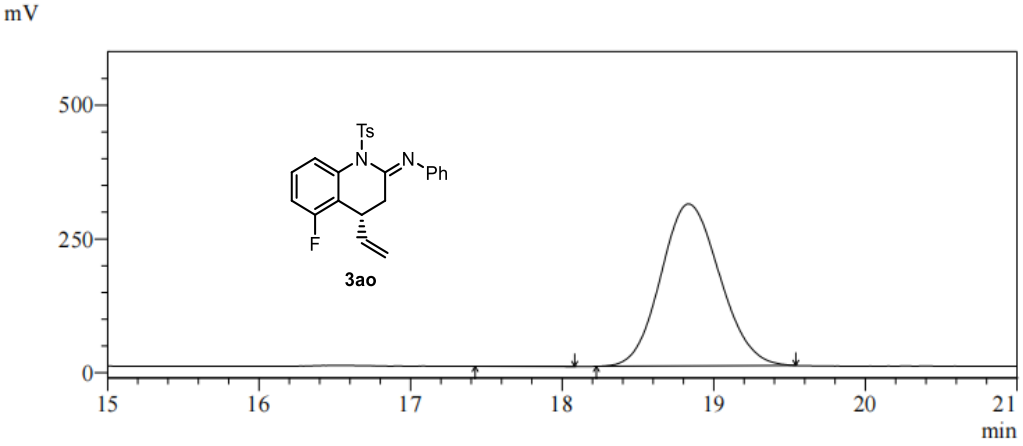
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	47.243	0.17	5015.90	30736	835	0.127
2	51.907	71.57	5015.90	24207188	359012	99.873
Total				24237924	359847	100.000



Peak Table

Detector A 254nm

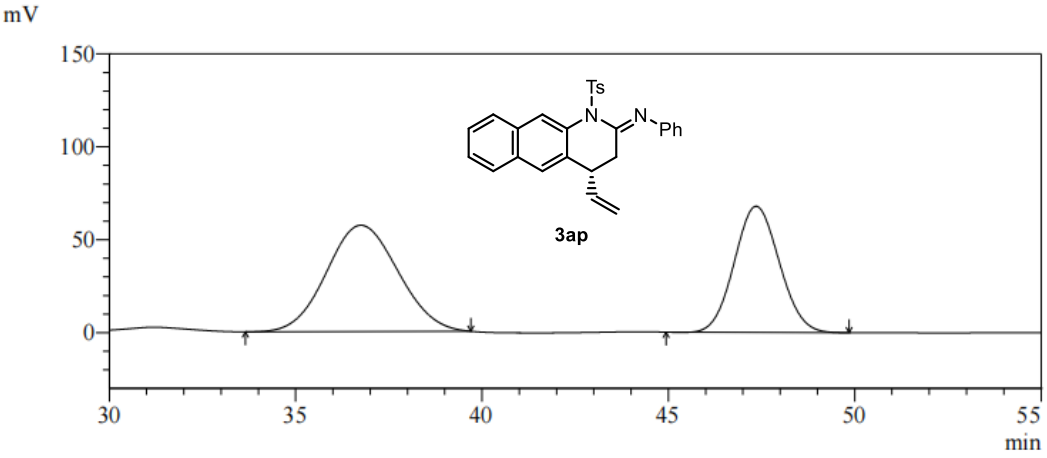
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.991	11.51	9824.99	2710835	113096	50.831
2	18.853	10.62	9824.99	2622251	104337	49.169
Total				5333087	217433	100.000



Peak Table

Detector A 254nm

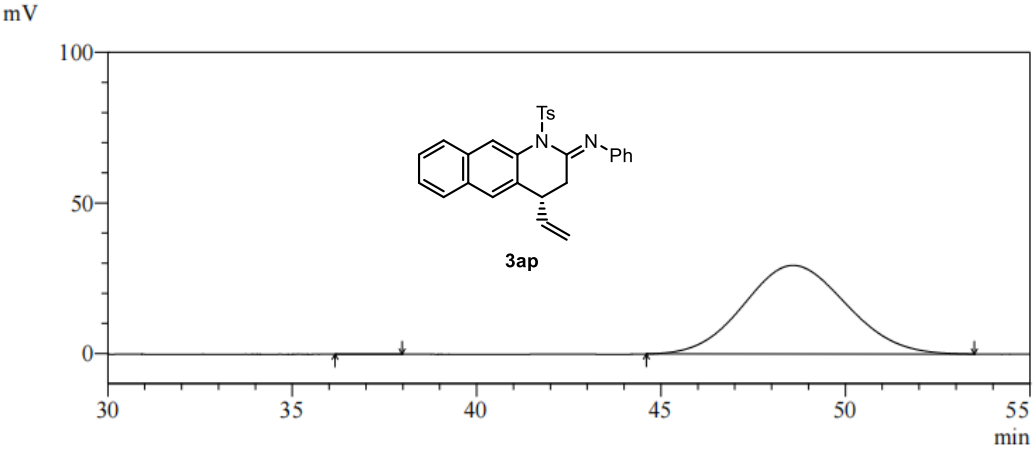
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.685	0.06	6774.17	6999	411	0.085
2	18.835	44.69	6774.17	8196025	302743	99.915
Total				8203023	303154	100.000



Peak Table

Detector A 254nm

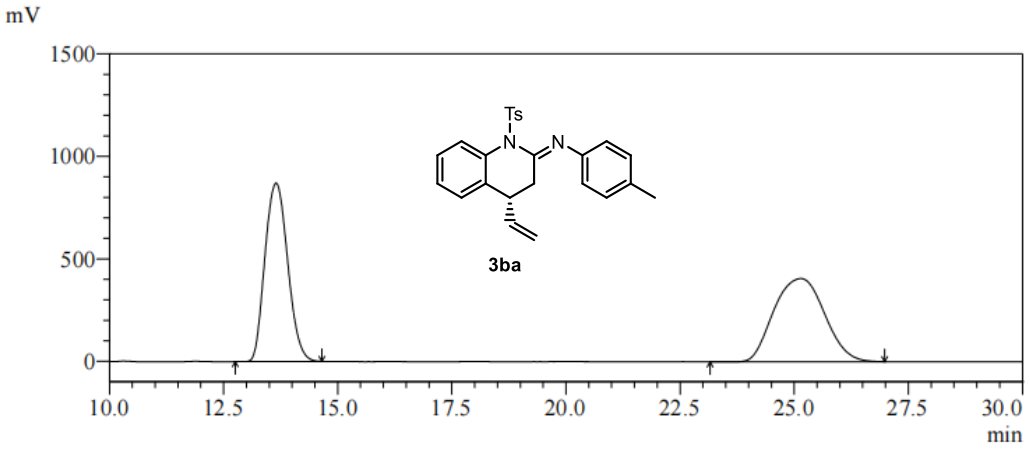
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	36.751	54.52	1049.39	7665893	57213	57.331
2	47.354	64.70	1049.39	5705429	67896	42.669
Total				13371321	125109	100.000



Peak Table

Detector A 254nm

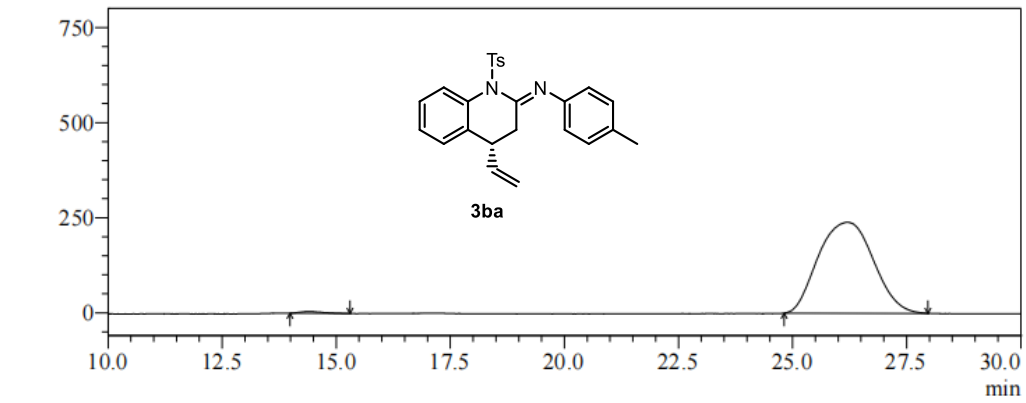
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	37.060	0.14	401.51	2721	56	0.048
2	48.568	73.29	401.51	5704723	29428	99.952
Total				5707445	29484	100.000



Peak Table

Detector A 254nm

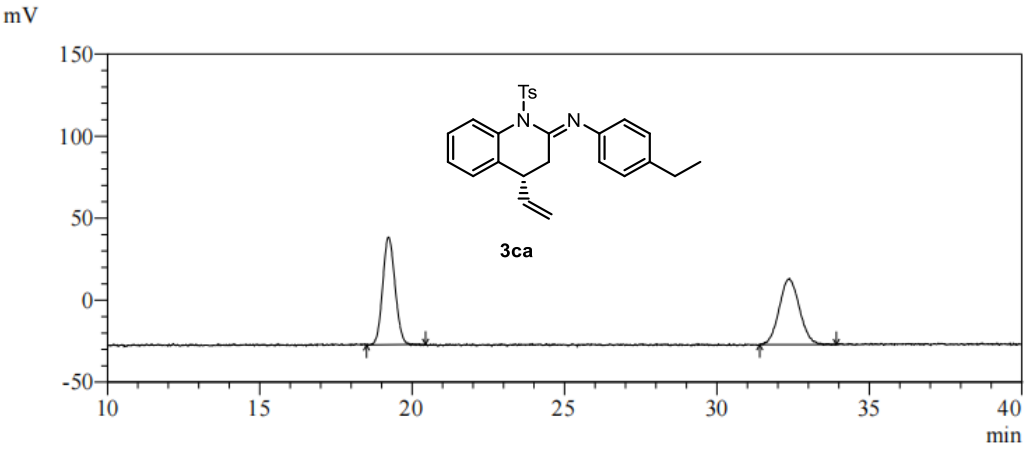
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	13.650	162.89	5348.20	30215336	871156	49.112
2	25.147	75.87	5348.20	31307747	405754	50.888
Total				61523083	1276909	100.000



Peak Table

Detector A 254nm

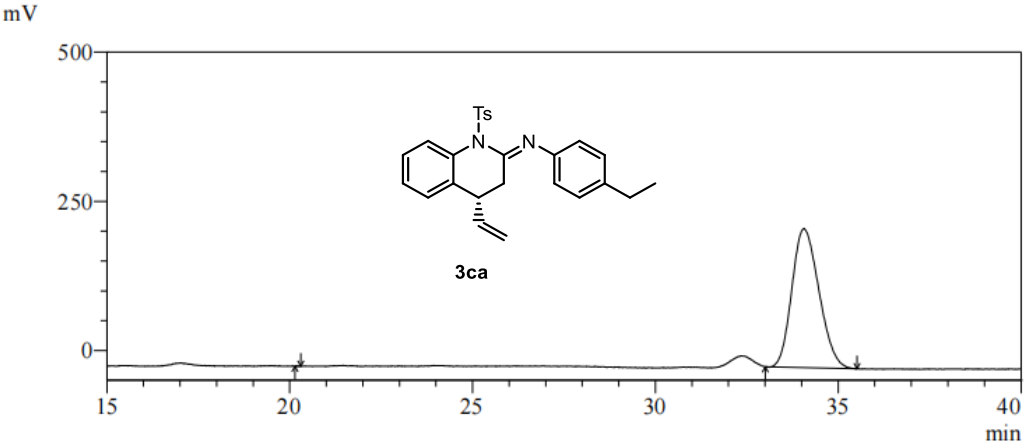
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	14.397	8.59	584.37	172430	5022	0.849
2	26.193	409.18	584.37	20145696	239112	99.151
Total				20318126	244133	100.000



Peak Table

Detector A 254nm

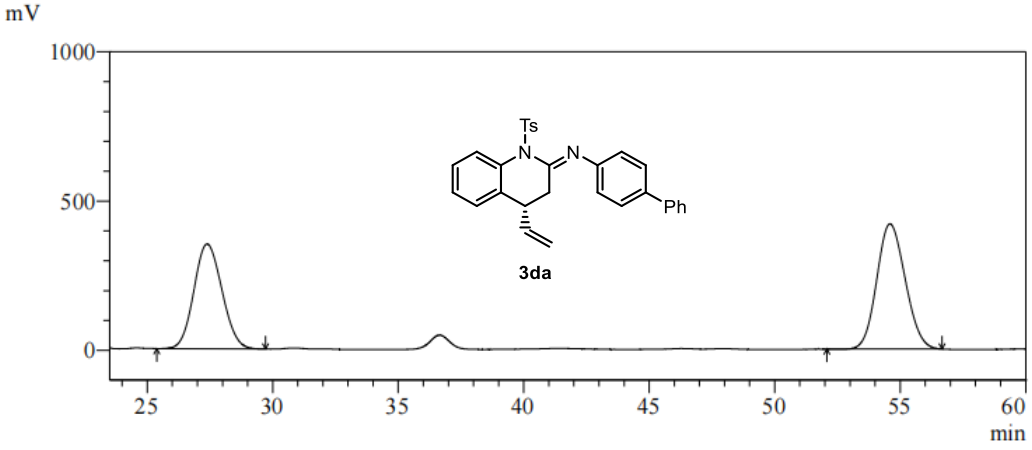
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	19.224	46.39	1410.93	1834934	65457	49.724
2	32.385	28.55	1410.93	1855270	40284	50.276
Total				3690204	105741	100.000



Peak Table

Detector A 254nm

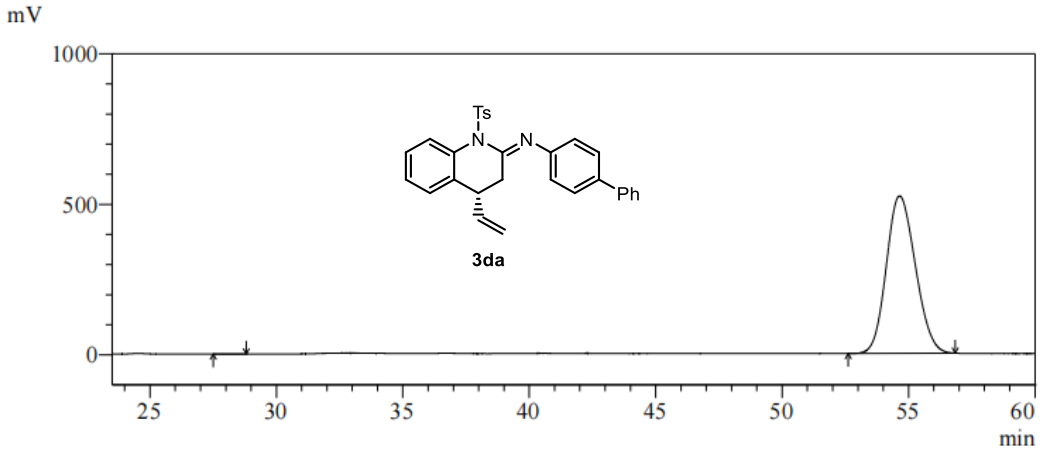
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	20.174	0.17	2212.50	916	372	0.008
2	34.065	105.24	2212.50	11991805	232842	99.992
Total				11992721	233213	100.000



Peak Table

Detector A 254nm

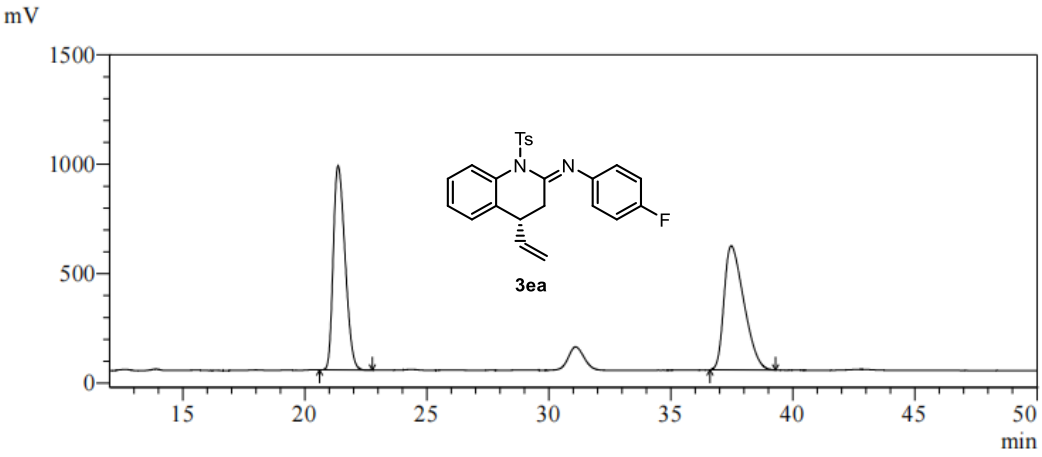
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	27.386	14.68	23909.00	27324584	351031	45.229
2	54.605	17.53	23909.00	33089815	419151	54.771
Total				60414399	770182	100.000



Peak Table

Detector A 254nm

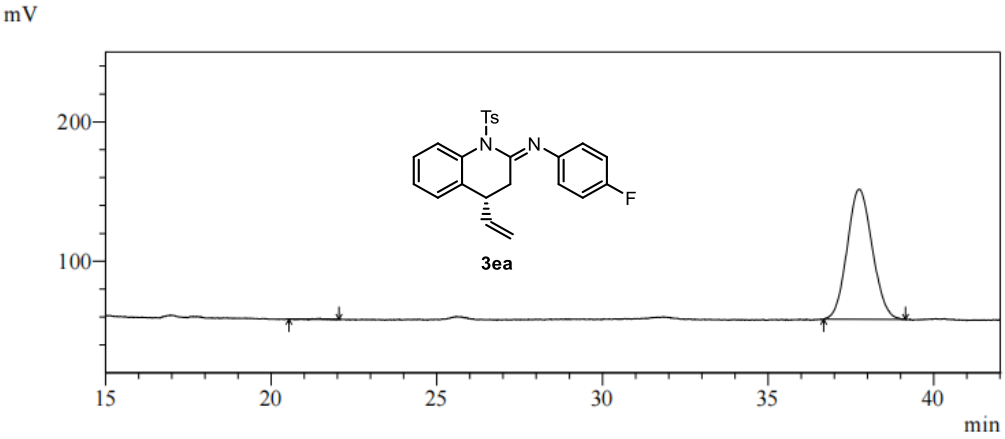
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	27.856	0.29	748.51	1719	215	0.004
2	54.645	699.15	748.51	41848454	523321	99.996
Total				41850173	523535	100.000



Peak Table

Detector A 254nm

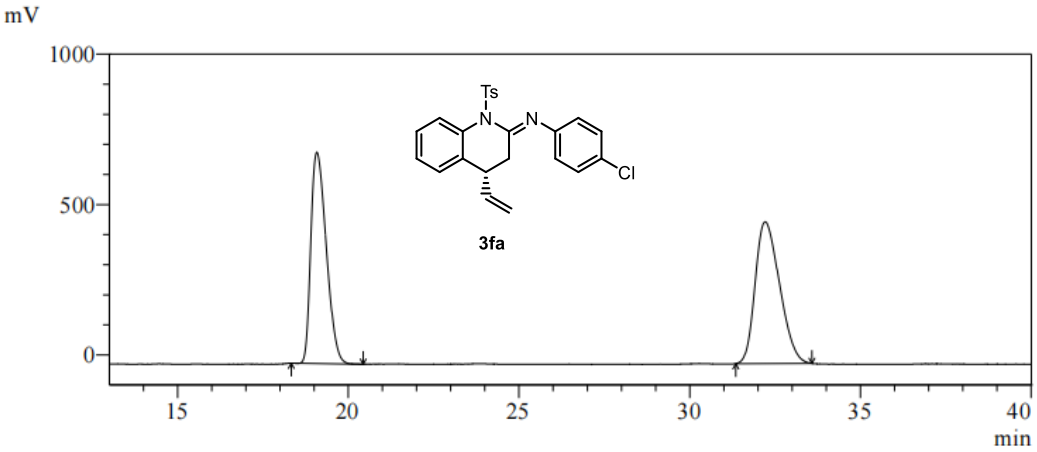
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	21.366	34.53	27024.67	31426278	933257	49.449
2	37.477	20.95	27024.67	32127118	566275	50.551
Total				63553397	1499532	100.000



Peak Table

Detector A 254nm

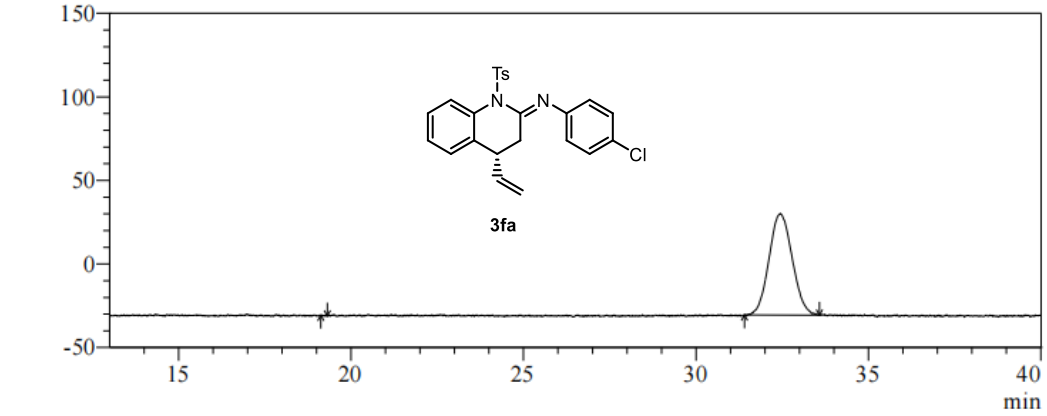
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	21.479	0.12	4449.01	7300	536	0.148
2	37.737	20.95	4449.01	4920555	93190	99.852
Total				4927855	93726	100.000



Peak Table

Detector A 254nm

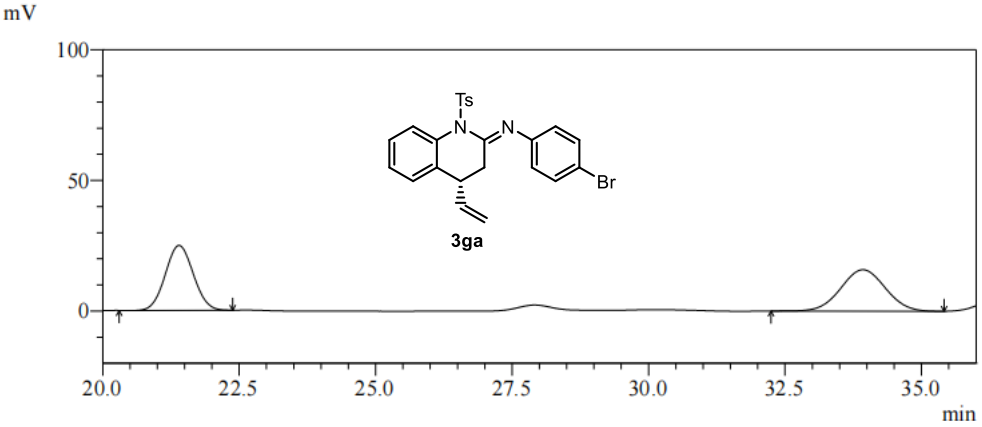
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	19.079	75.91	9250.24	22156155	702219	48.559
2	32.211	50.94	9250.24	23471241	471241	51.441
Total				45627396	1173460	100.000



Peak Table

Detector A 254nm

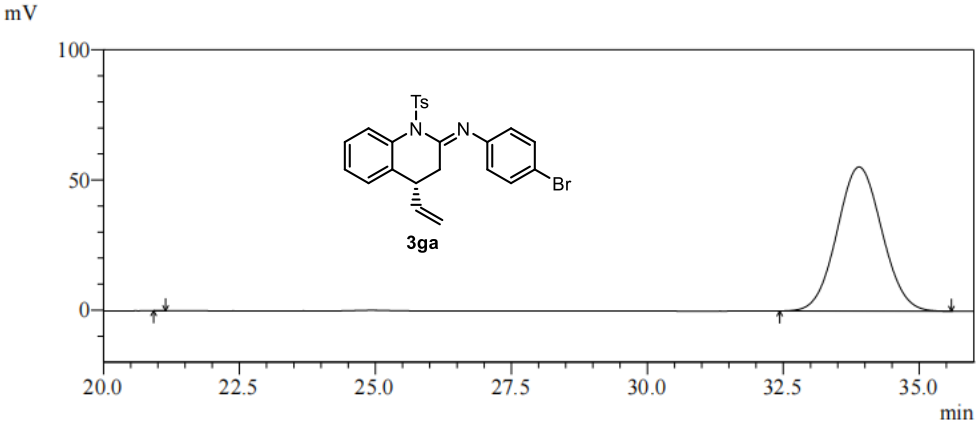
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	19.271	0.58	815.99	518	472	0.018
2	32.448	74.41	815.99	2834415	60719	99.982
Total				2834933	61190	100.000



Peak Table

Detector A 254nm

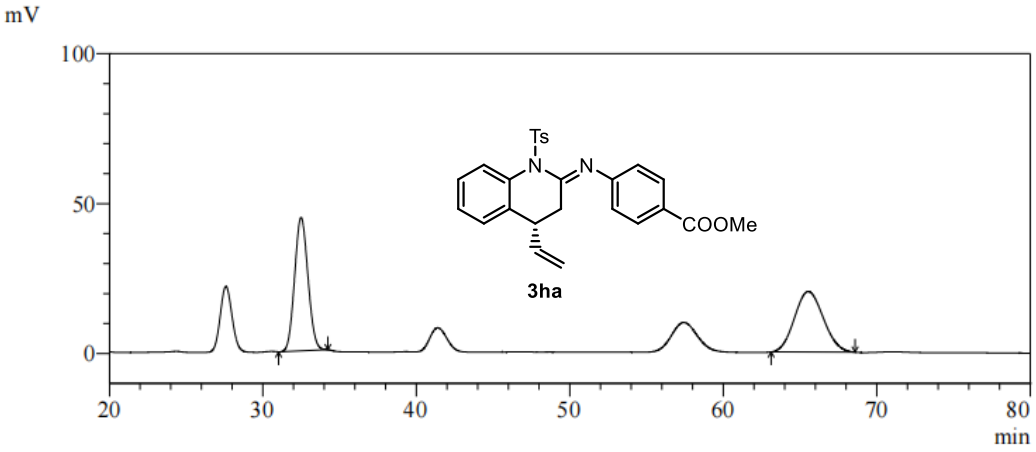
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	21.398	22.56	1101.05	885845	24843	49.559
2	33.926	14.41	1101.05	901621	15863	50.441
Total				1787466	40706	100.000



Peak Table

Detector A 254nm

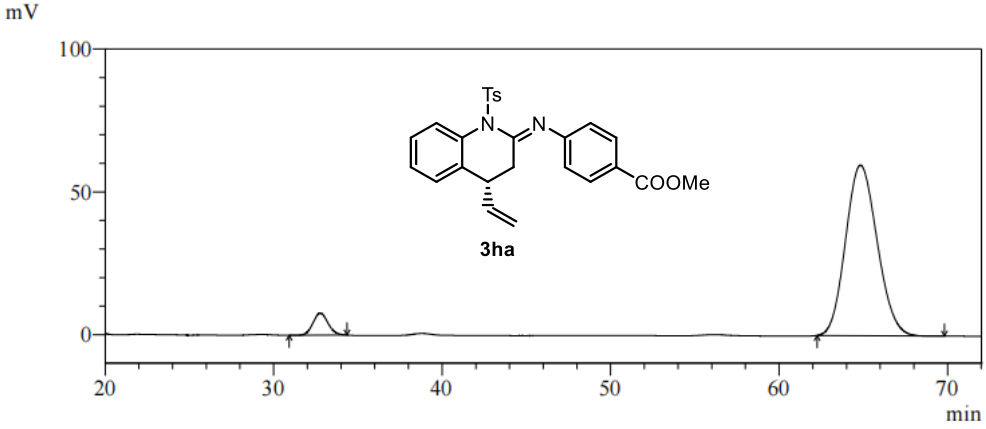
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	21.127	0.01	625.57	29	3	0.001
2	33.892	88.54	625.57	3187656	55386	99.999
Total				3187685	55389	100.000



Peak Table

Detector A 254nm

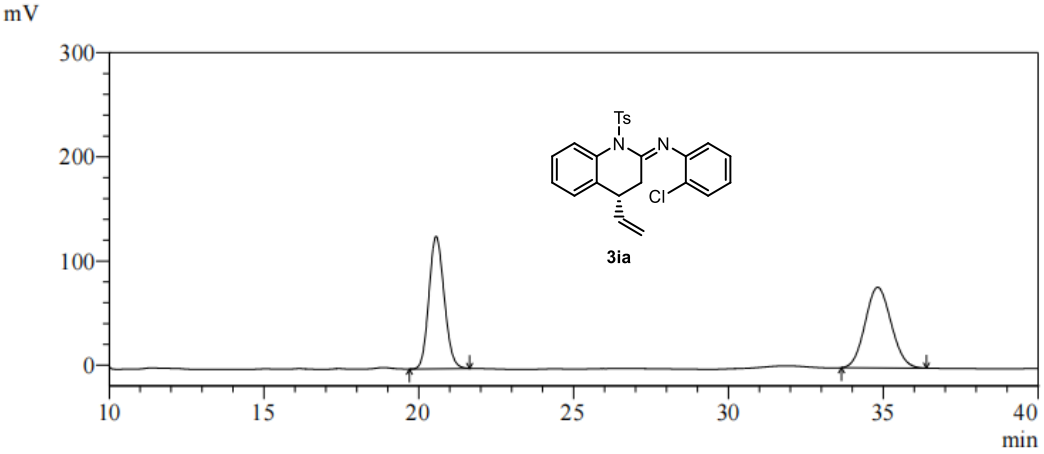
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	32.487	127.97	347.73	2690200	44498	50.403
2	65.527	58.16	347.73	2647138	20223	49.597
Total				5337338	64721	100.000



Peak Table

Detector A 254nm

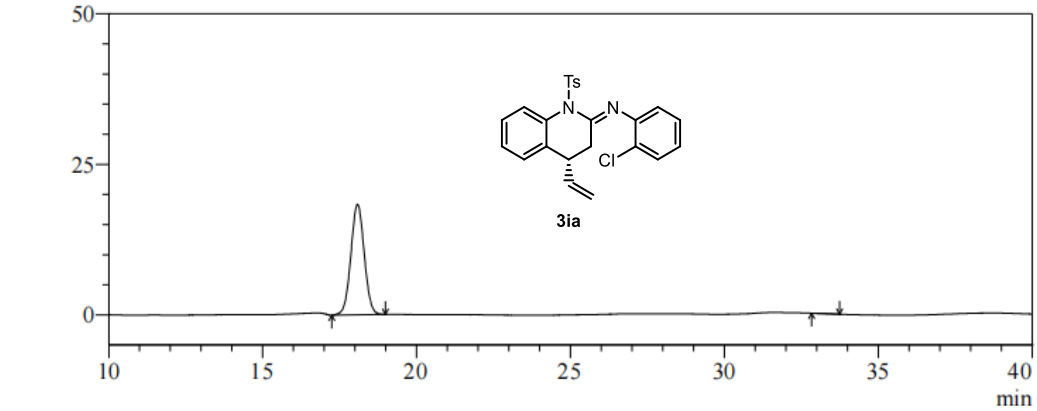
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	32.761	31.81	242.82	479302	7725	5.804
2	64.827	245.94	242.82	7779538	59720	94.196
Total				8258840	67445	100.000



Peak Table

Detector A 254nm

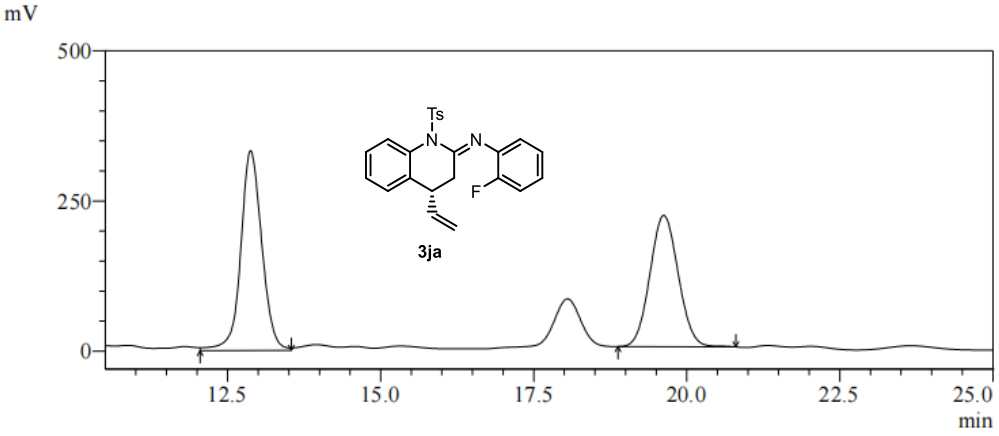
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	20.558	32.39	3922.55	4370165	127045	49.129
2	34.821	19.73	3922.55	4525057	77397	50.871
Total				8895222	204442	100.000



Peak Table

Detector A 254nm

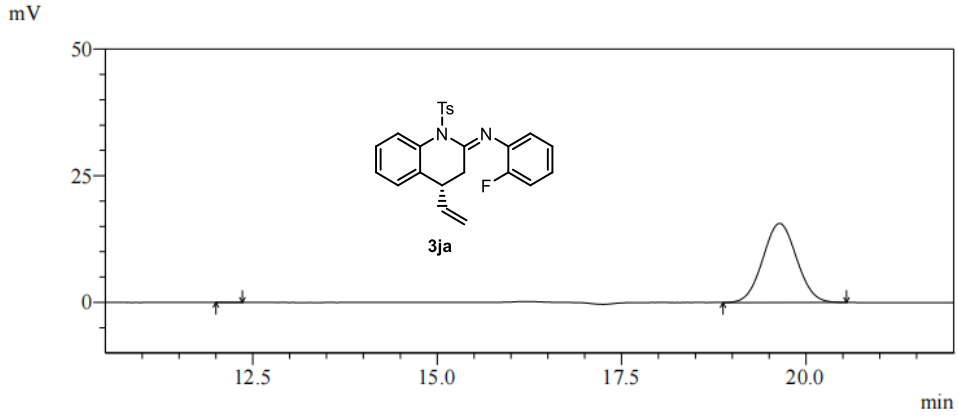
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	18.082	86.98	211.11	556835	18362	99.945
2	32.863	0.03	211.11	306	6	0.055
Total				557141	18368	100.000



Peak Table

Detector A 254nm

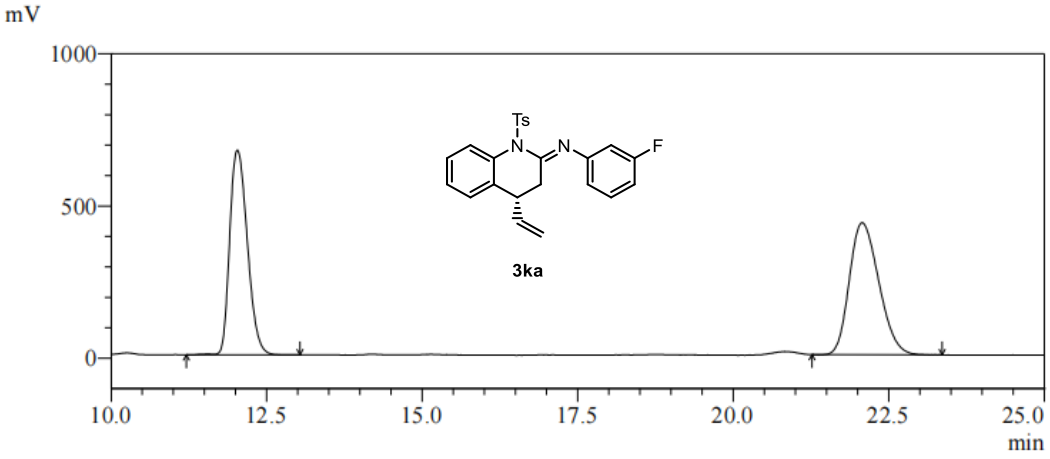
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	12.875	5.47	60791.94	7977575	332522	53.069
2	19.624	3.60	60791.94	7054886	218771	46.931
Total				15032462	551293	100.000



Peak Table

Detector A 254nm

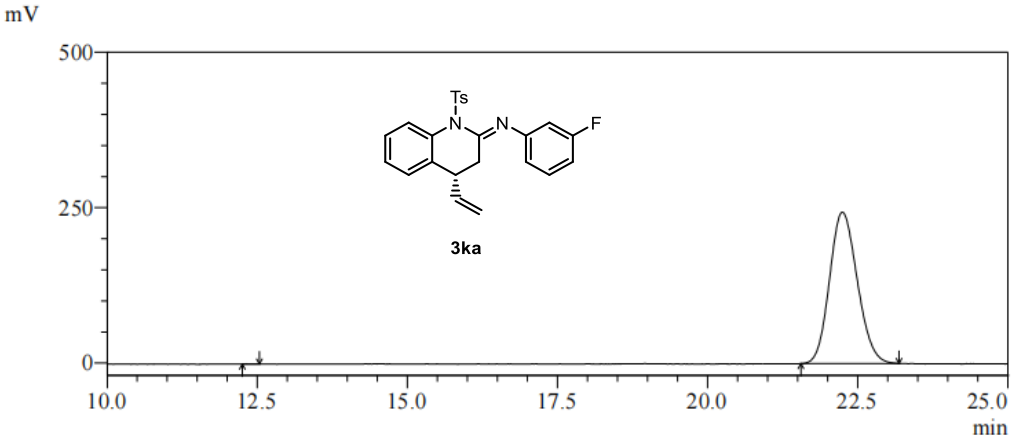
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	12.066	0.03	426.21	39	11	0.008
2	19.642	36.64	426.21	499100	15617	99.992
Total				499139	15628	100.000



Peak Table

Detector A 254nm

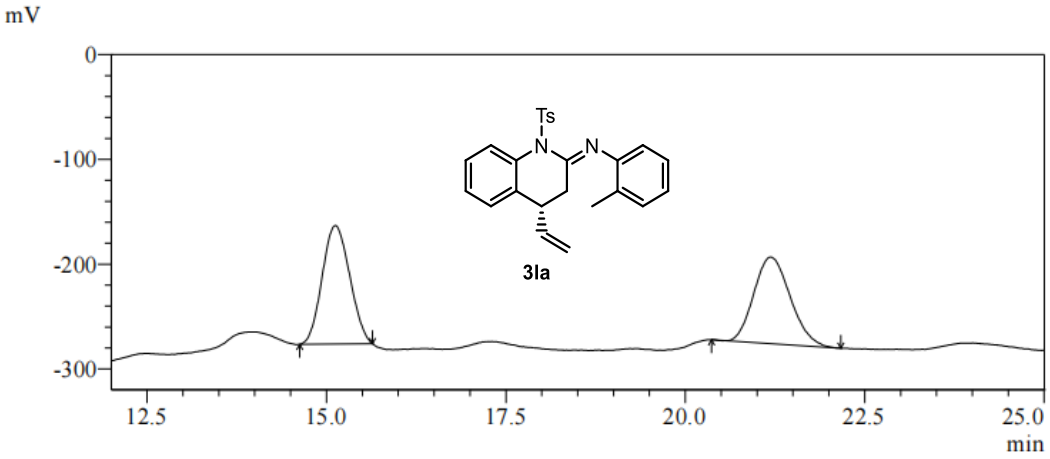
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	12.028	110.55	6083.14	13286596	672464	48.161
2	22.073	71.31	6083.14	14301176	433777	51.839
Total				27587772	1106240	100.000



Peak Table

Detector A 254nm

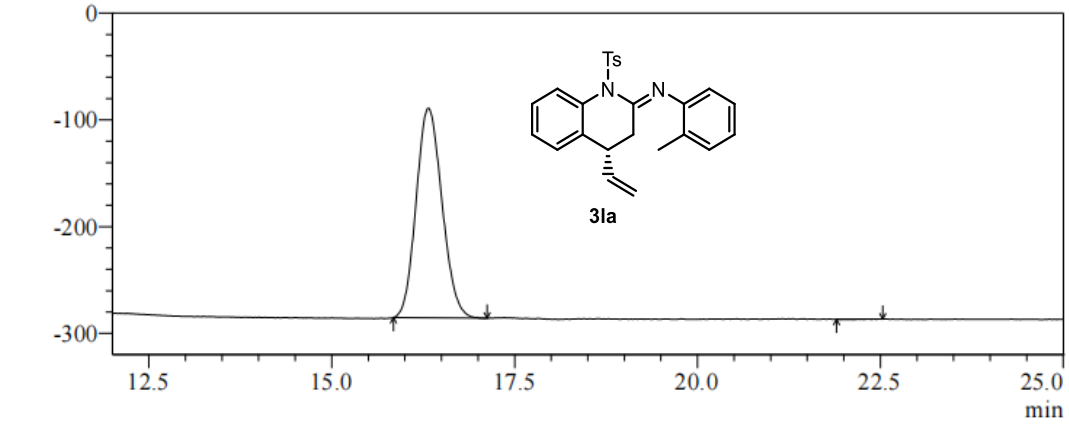
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	12.317	0.35	652.40	362	226	0.005
2	22.245	373.20	652.40	7831940	243477	99.995
Total				7832302	243703	100.000



Peak Table

Detector A 254nm

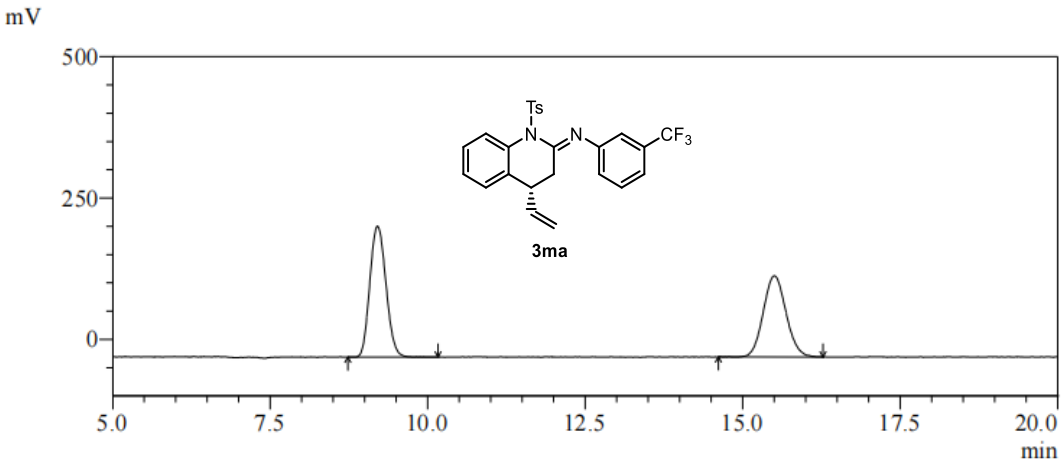
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	15.129	5.49	20613.49	3020036	113100	50.849
2	21.187	4.01	20613.49	2919235	82688	49.151
Total				5939271	195788	100.000



Peak Table

Detector A 254nm

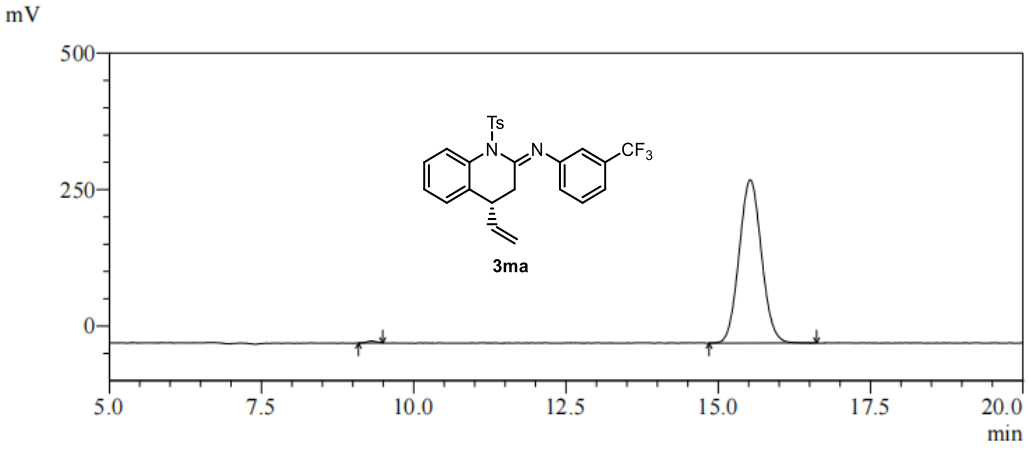
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	16.321	50.83	3863.73	4823195	196395	99.926
2	22.476	0.07	3863.73	3595	254	0.074
Total				4826790	196648	100.000



Peak Table

Detector A 254nm

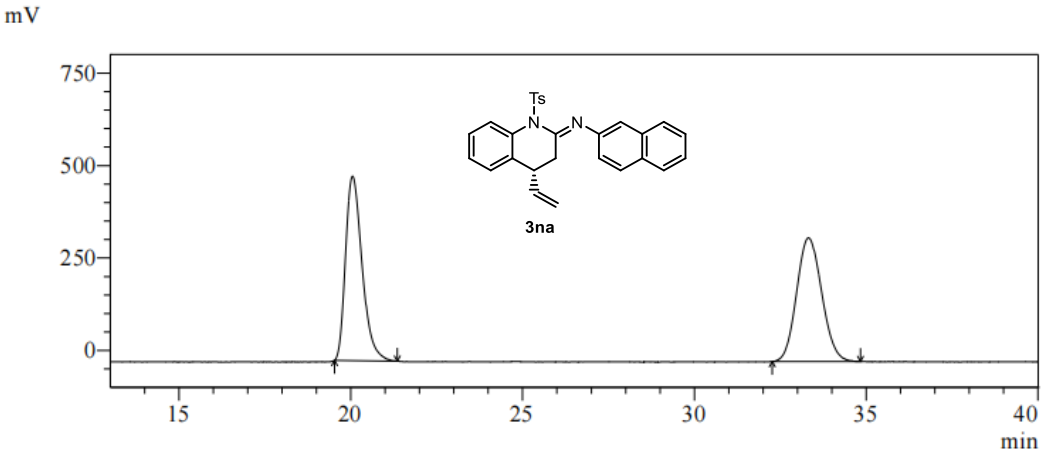
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	9.203	296.85	780.03	4116897	231552	53.270
2	15.504	184.02	780.03	3611453	143540	46.730
Total				7728350	375093	100.000



Peak Table

Detector A 254nm

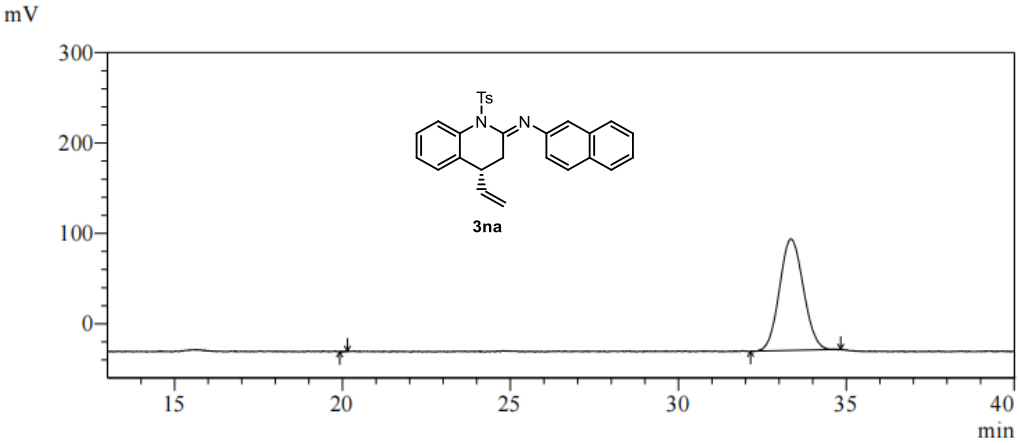
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	9.308	4.81	776.72	41973	3733	0.548
2	15.525	384.75	776.72	7614783	298840	99.452
Total				7656757	302573	100.000



Peak Table

Detector A 254nm

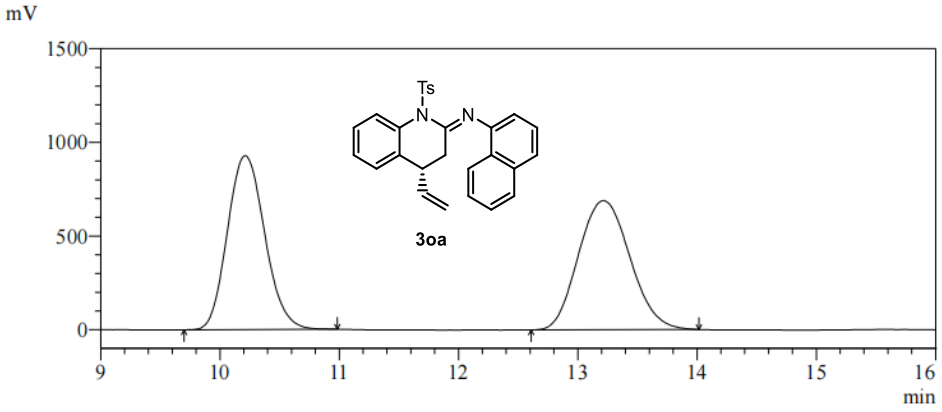
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	20.053	451.47	1103.31	16760512	498116	49.648
2	33.324	303.06	1103.31	16998455	334373	50.352
Total				33758967	832488	100.000



Peak Table

Detector A 254nm

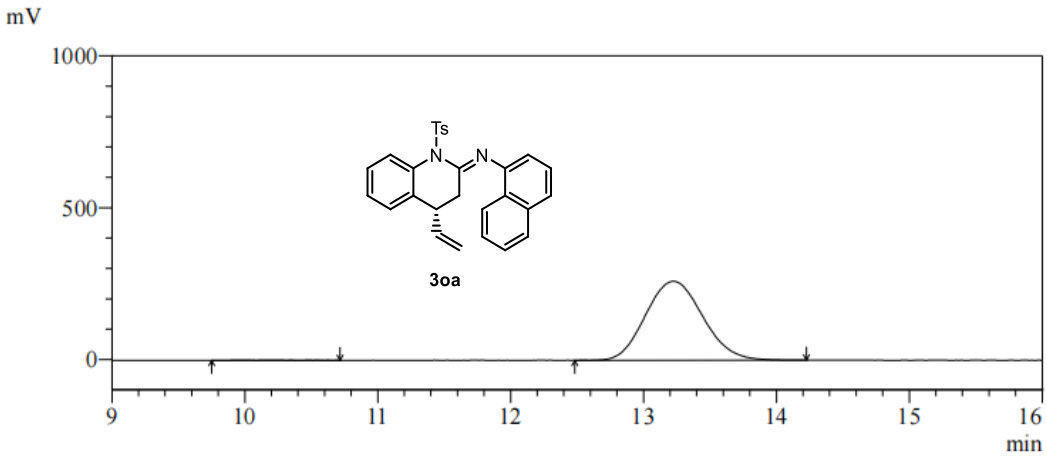
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	20.052	0.45	982.83	964	442	0.016
2	33.352	125.59	982.83	6108462	123432	99.984
Total				6109426	123874	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	10.212	32.54	28518.75	20239048	928034	49.397
2	13.216	24.17	28518.75	20733226	689336	50.603
Total				40972275	1617371	100.000

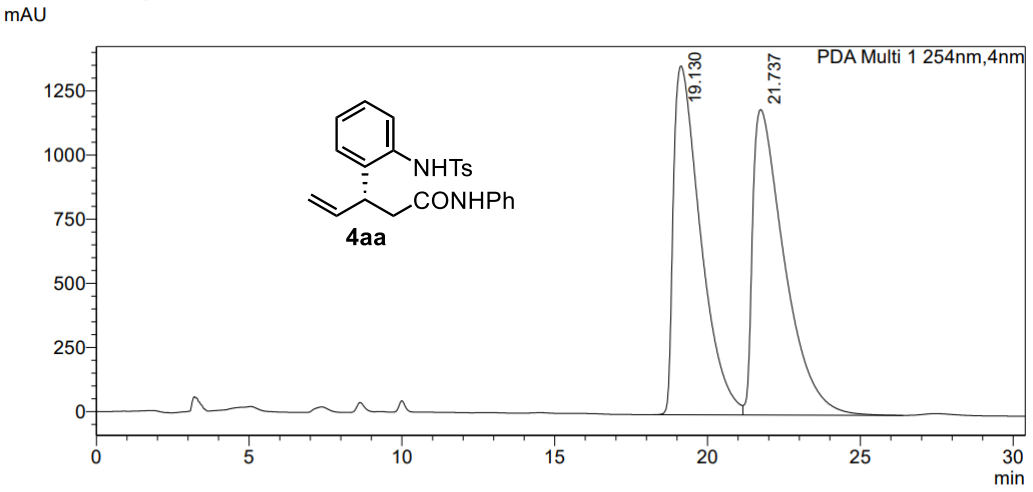


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	9.953	0.38	925.97	6041	354	0.078
2	13.224	280.69	925.97	7773012	259909	99.922
Total				7779054	260263	100.000

<Chromatogram>

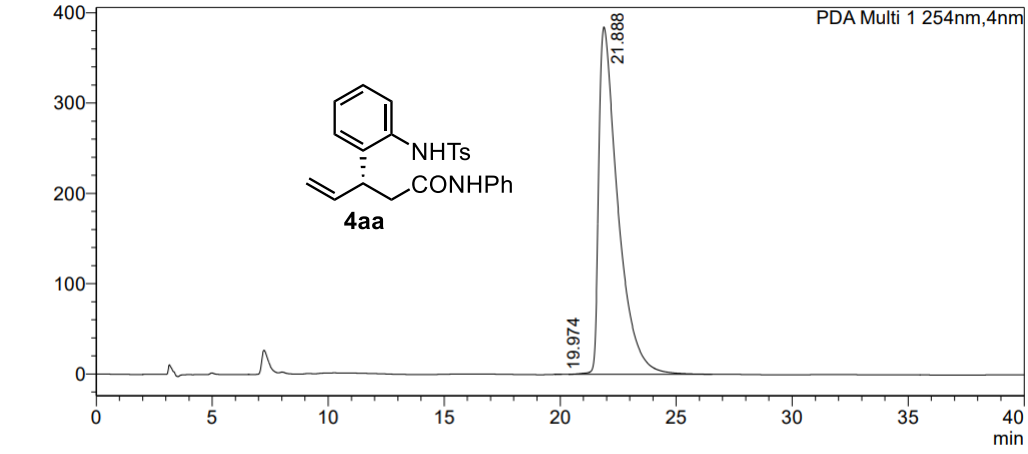


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.130	84086965	49.329
2	21.737	86373079	50.671
Total		170460043	100.000

<Chromatogram>

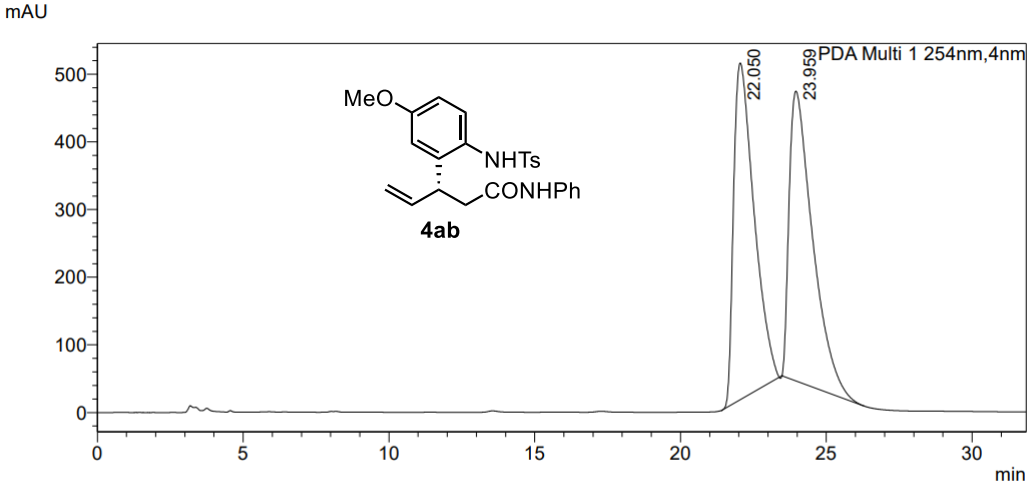


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.974	294	0.001
2	21.888	22071342	99.999
Total		22071635	100.000

<Chromatogram>

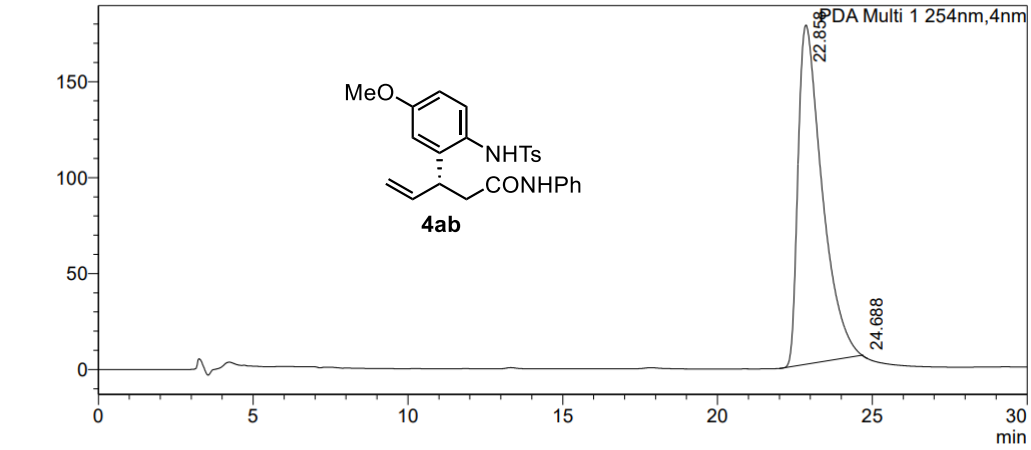


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.050	24270217	50.214
2	23.959	24062911	49.786
Total		48333128	100.000

<Chromatogram>

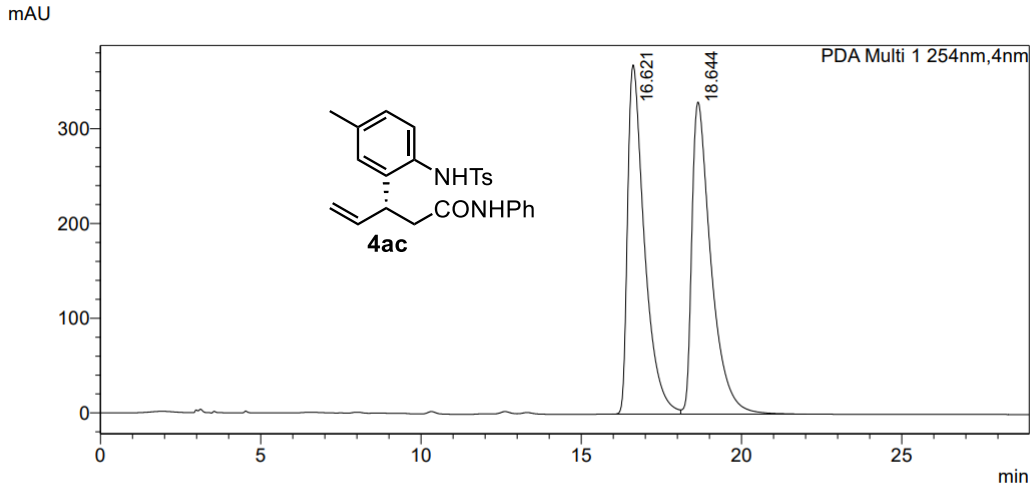


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.858	9570168	100.009
2	24.688	-868	-0.009
Total		9569300	100.000

<Chromatogram>

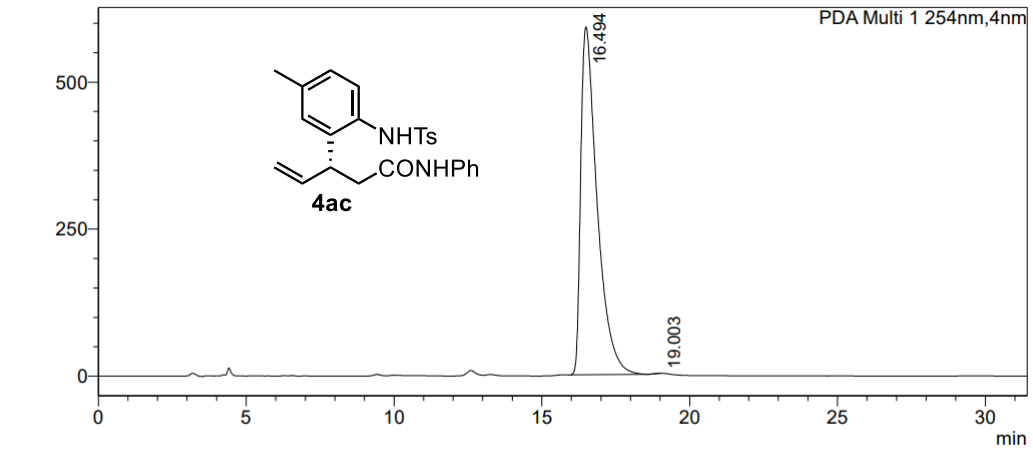


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.621	13507315	49.556
2	18.644	13749227	50.444
Total		27256542	100.000

<Chromatogram>

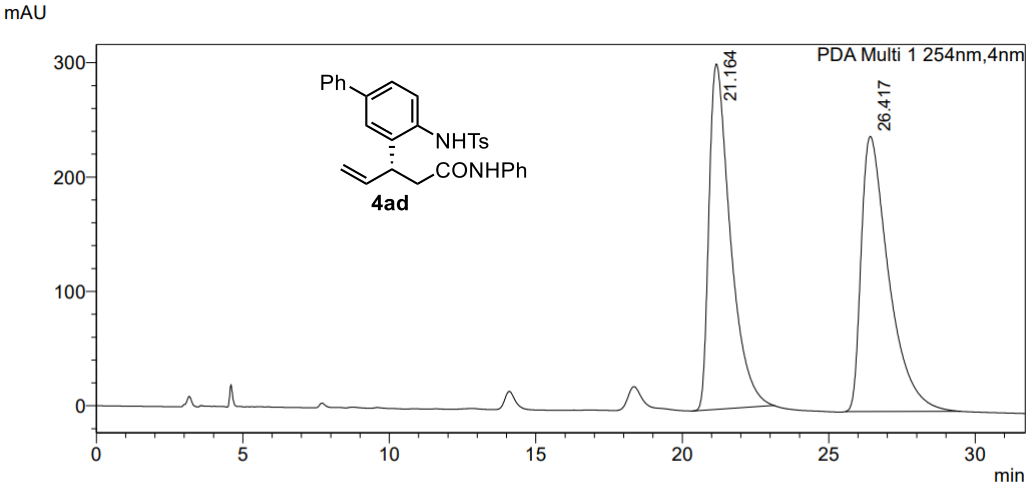


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.494	22806780	99.989
2	19.003	2410	0.011
Total		22809190	100.000

<Chromatogram>

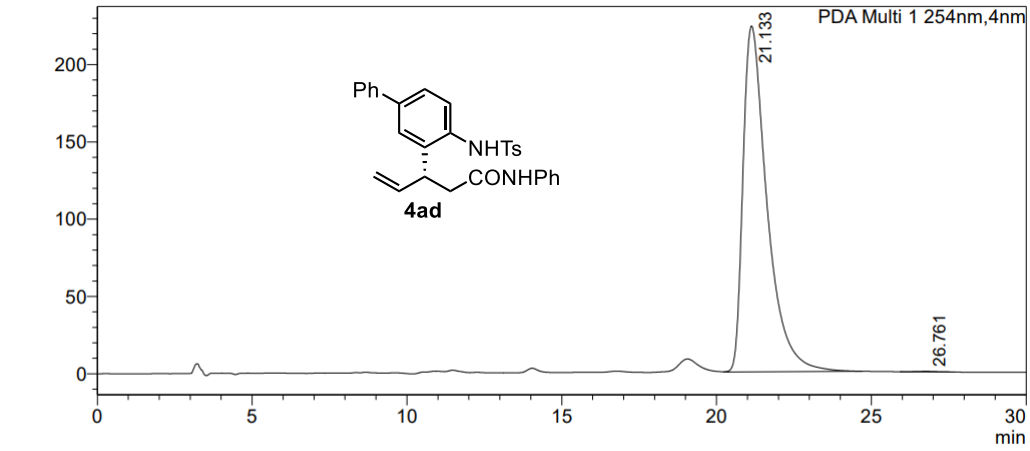


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.164	15329374	49.345
2	26.417	15736090	50.655
Total		31065464	100.000

<Chromatogram>

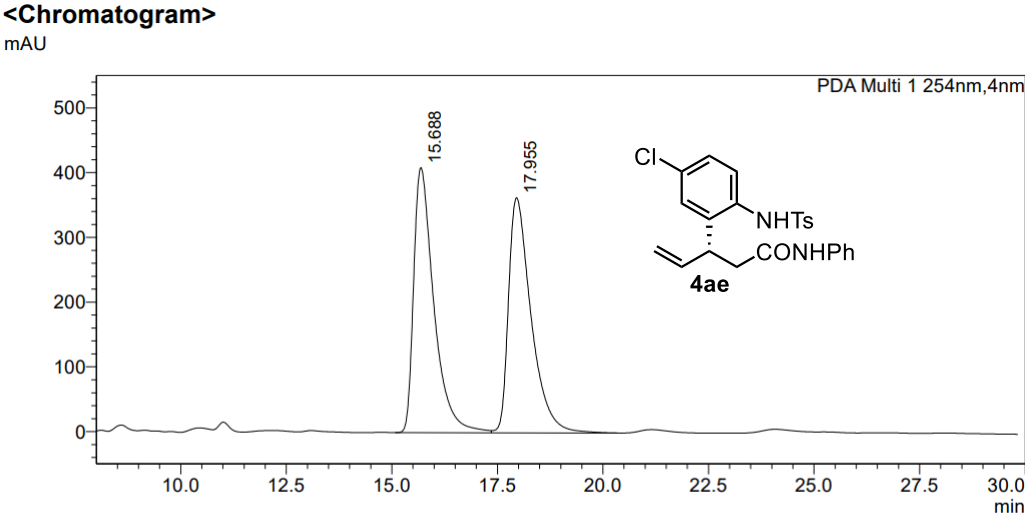


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.133	12113763	99.863
2	26.761	16626	0.137
Total		12130388	100.000

<Chromatogram>

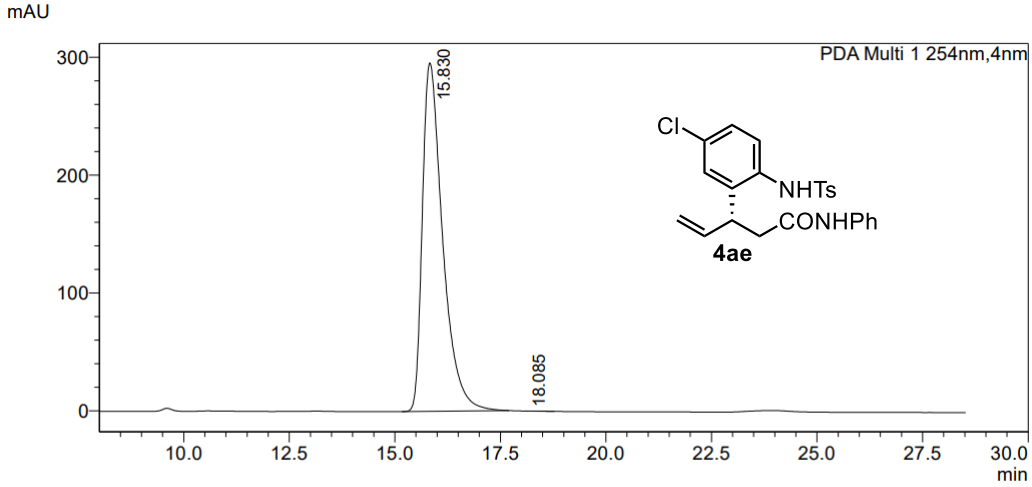


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.688	13655198	50.181
2	17.955	13556428	49.819
Total		27211627	100.000

<Chromatogram>

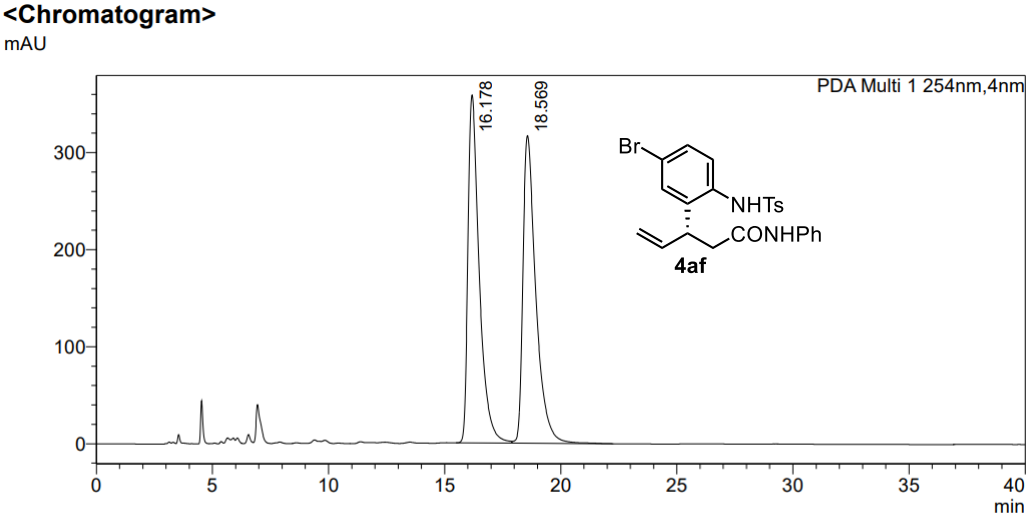


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.830	9896046	99.979
2	18.085	2119	0.021
Total		9898165	100.000

<Chromatogram>

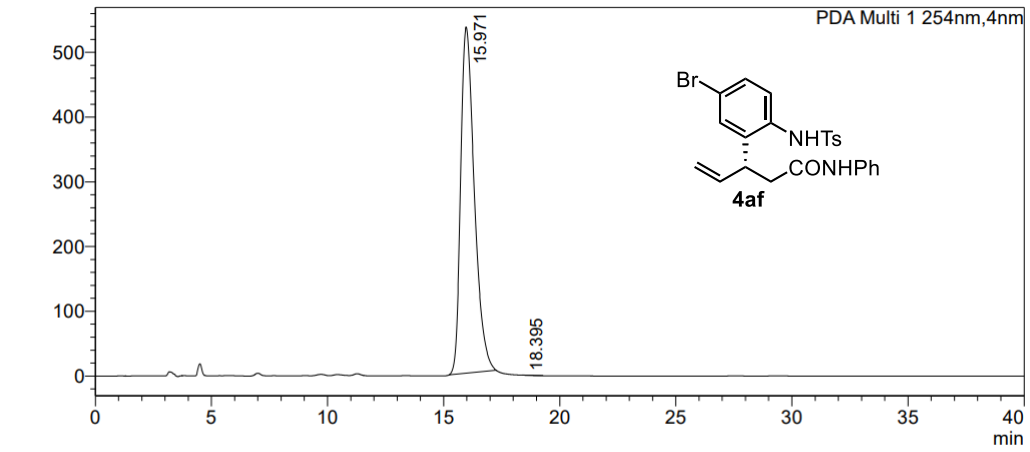


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.178	12154970	49.729
2	18.569	12287570	50.271
Total		24442540	100.000

<Chromatogram>

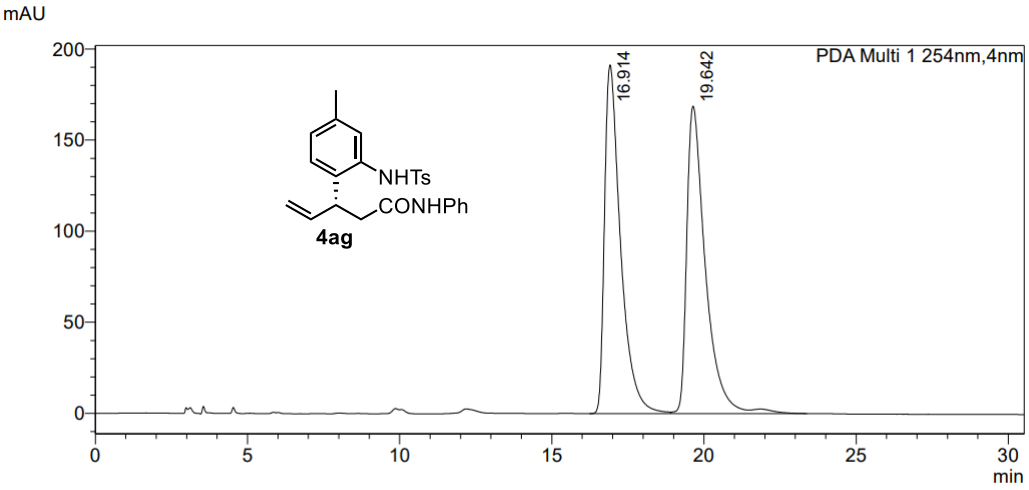


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.971	21920783	100.004
2	18.395	-984	-0.004
Total		21919799	100.000

<Chromatogram>

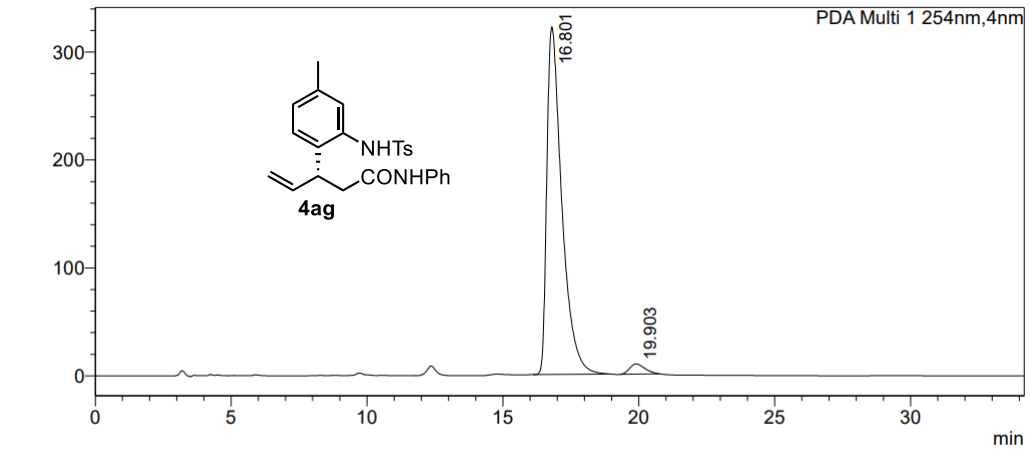


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.914	7040196	49.344
2	19.642	7227386	50.656
Total		14267582	100.000

<Chromatogram>



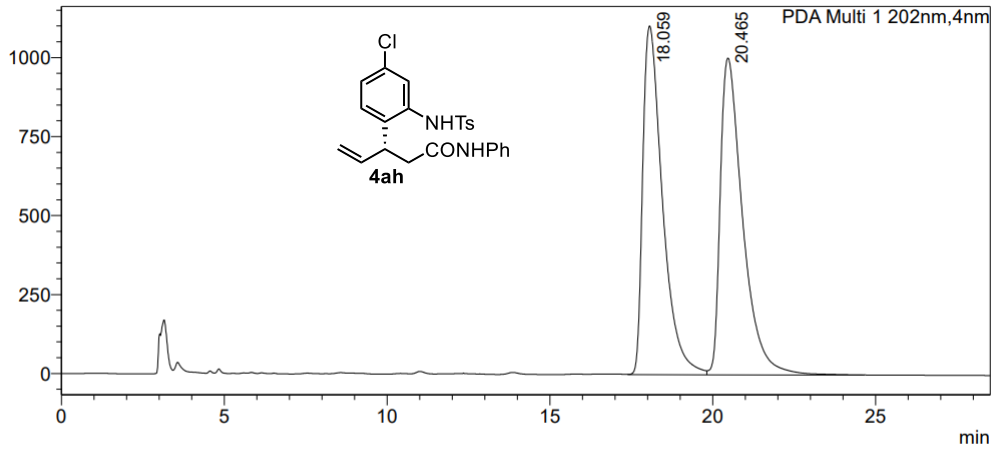
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.801	12355363	97.138
2	19.903	364002	2.862
Total		12719366	100.000

<Chromatogram>

mAU



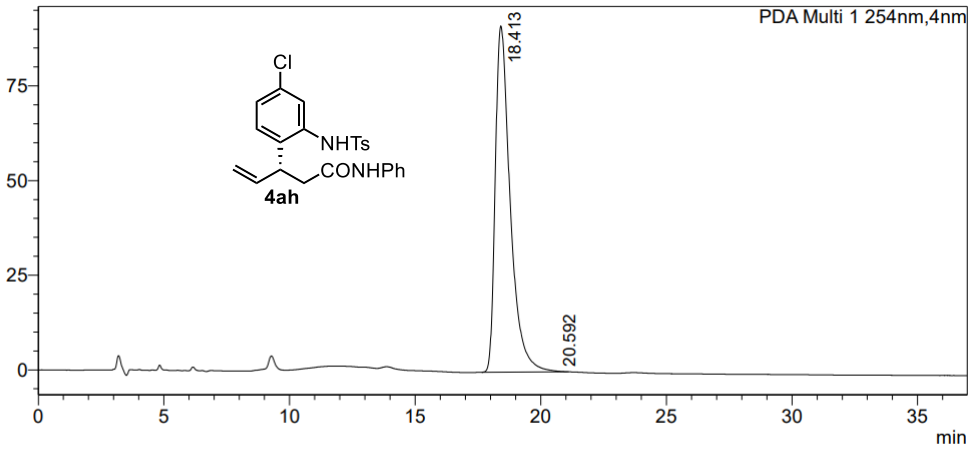
<Peak Table>

PDA Ch1 202nm

Peak#	Ret. Time	Area	Area%
1	18.059	46615042	49.225
2	20.465	48083413	50.775
Total		94698455	100.000

<Chromatogram>

mAU

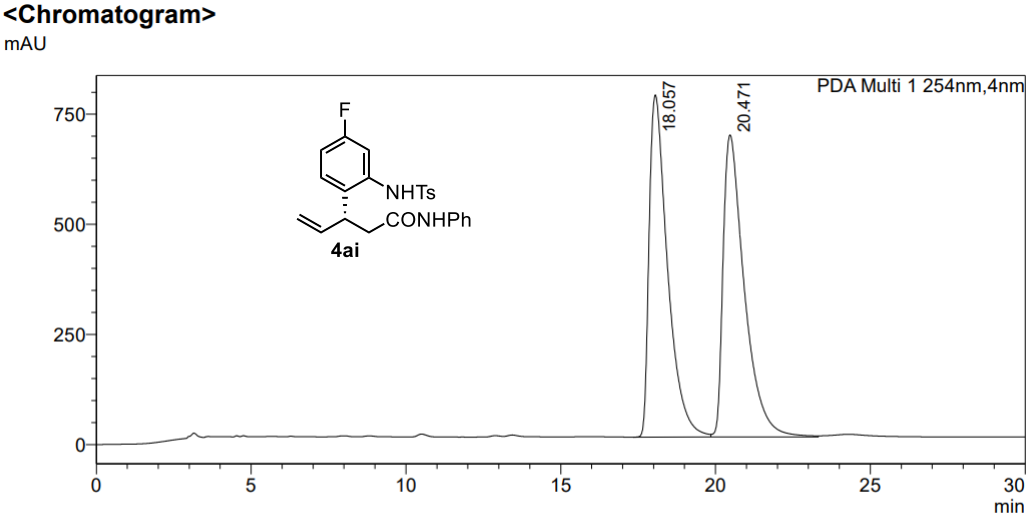


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.413	3791195	100.001
2	20.592	-33	-0.001
Total		3791162	100.000

<Chromatogram>

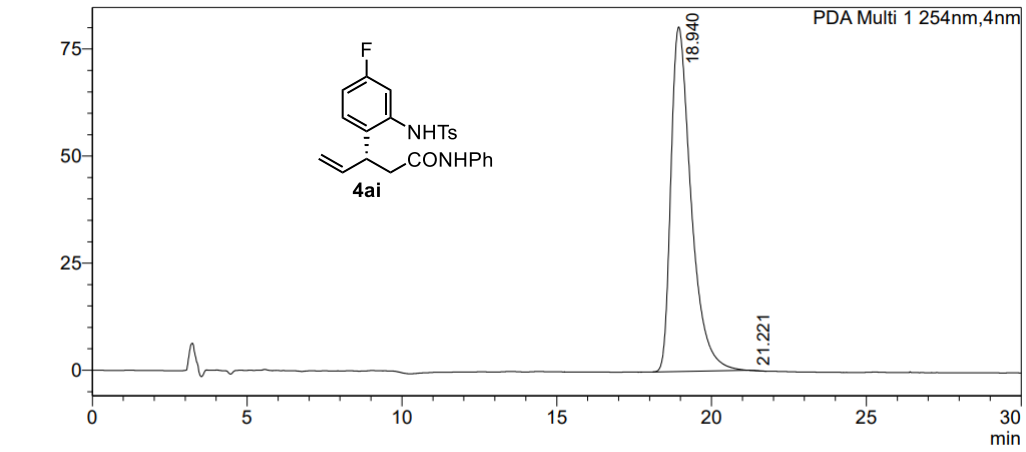


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.057	32204374	49.515
2	20.471	32835705	50.485
Total		65040079	100.000

<Chromatogram>

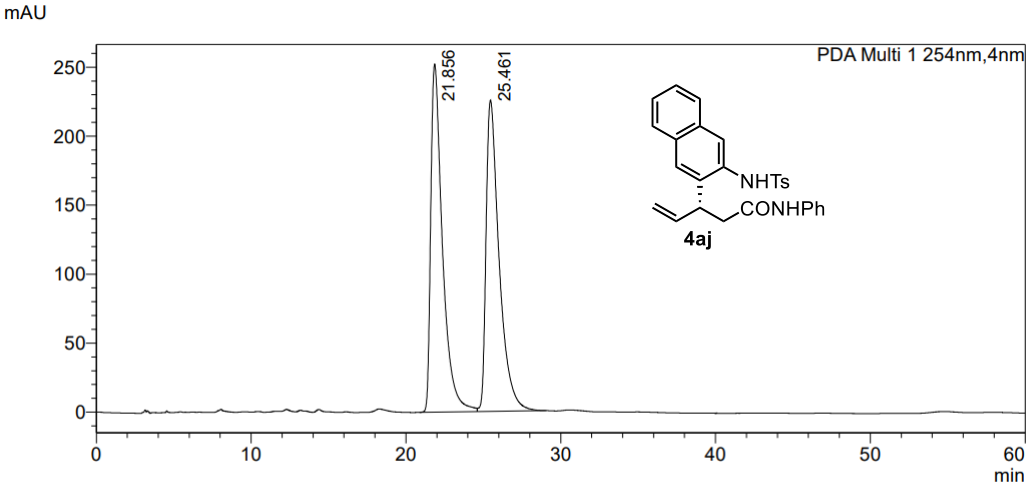


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.940	3656504	100.004
2	21.221	-143	-0.004
Total		3656361	100.000

<Chromatogram>

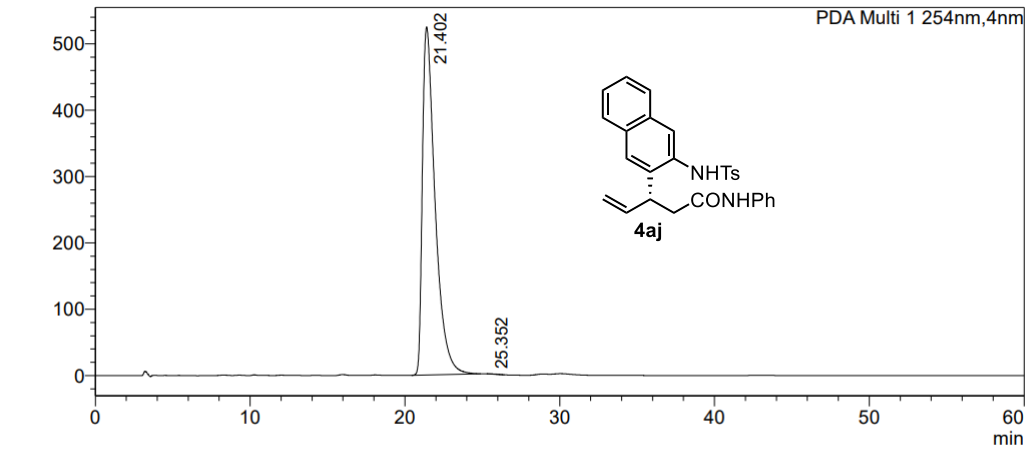


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.856	13279488	50.000
2	25.461	13279529	50.000
Total		26559017	100.000

<Chromatogram>

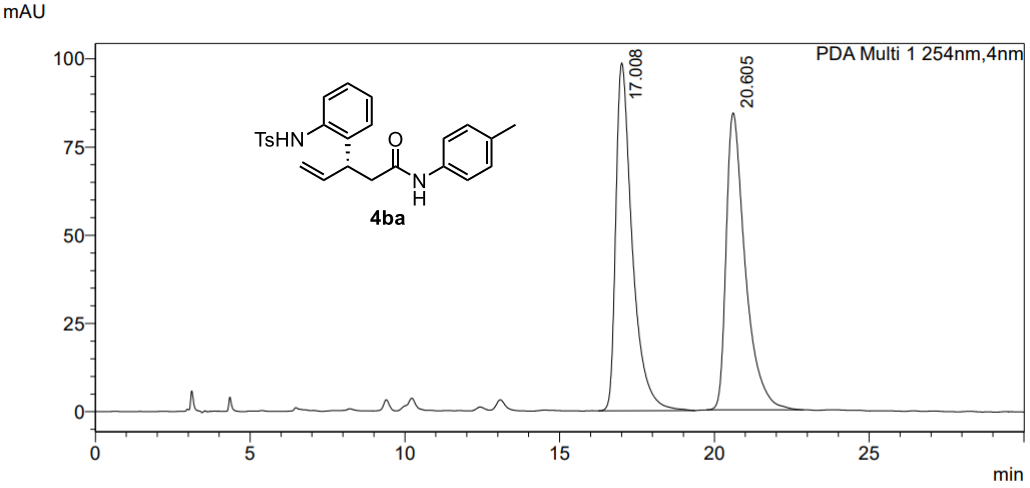


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.402	29967807	99.967
2	25.352	9812	0.033
Total		29977619	100.000

<Chromatogram>

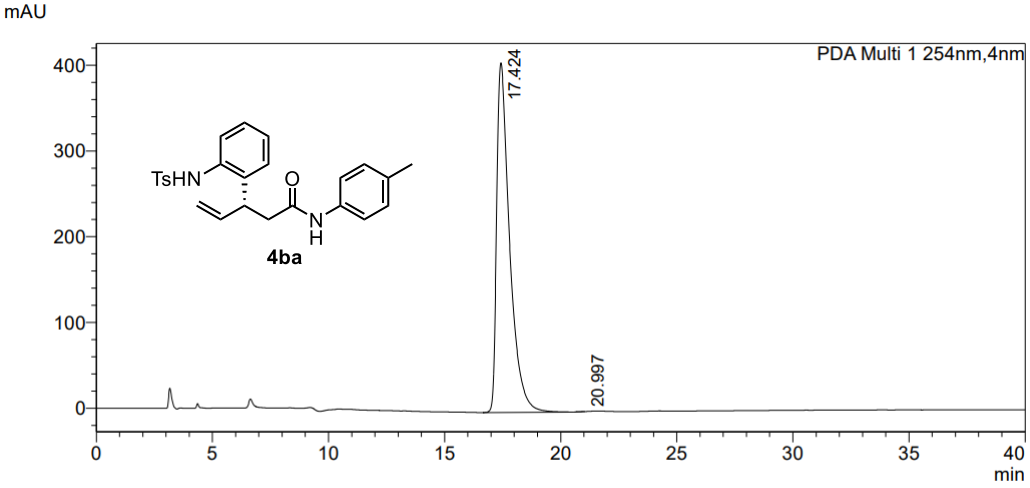


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.008	3642413	50.171
2	20.605	3617571	49.829
Total		7259984	100.000

<Chromatogram>

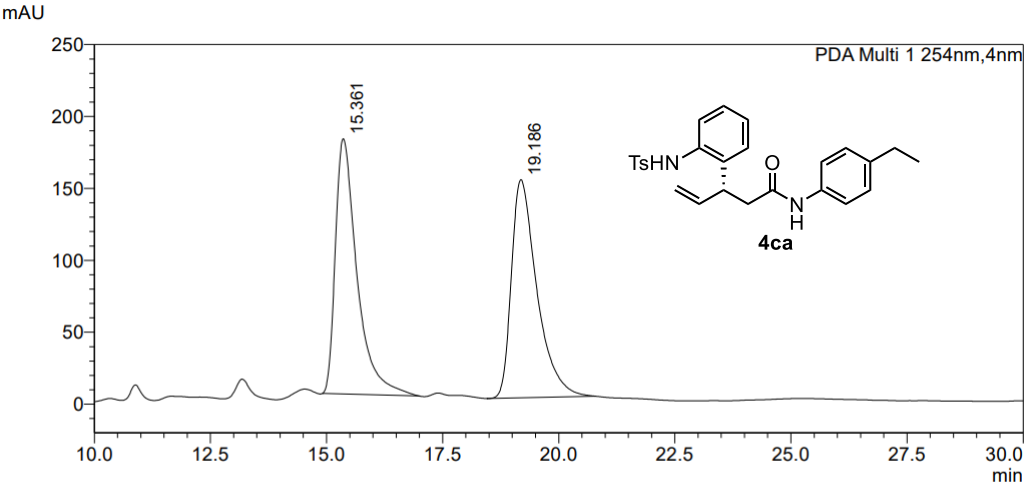


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.424	15813583	100.000
2	20.997	34	0.000
Total		15813616	100.000

<Chromatogram>

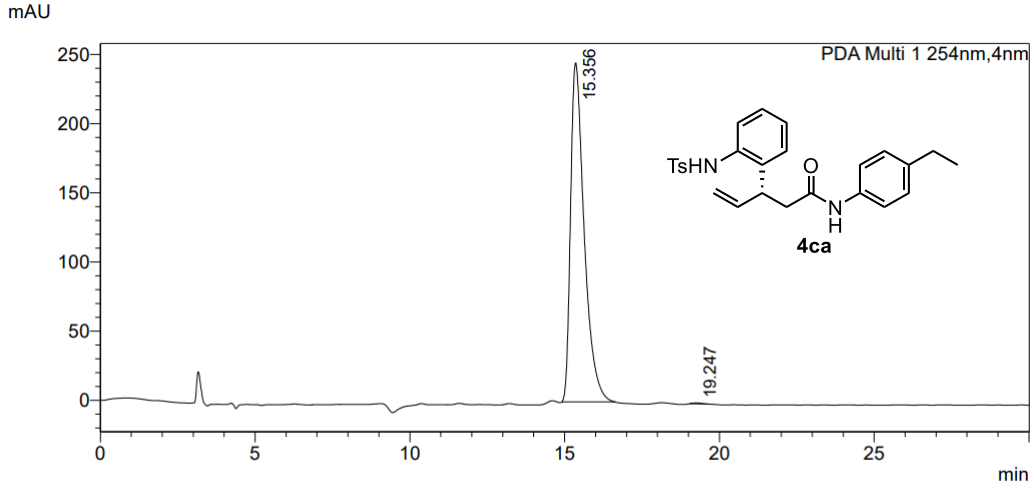


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.361	5760230	49.849
2	19.186	5795242	50.151
Total		11555473	100.000

<Chromatogram>

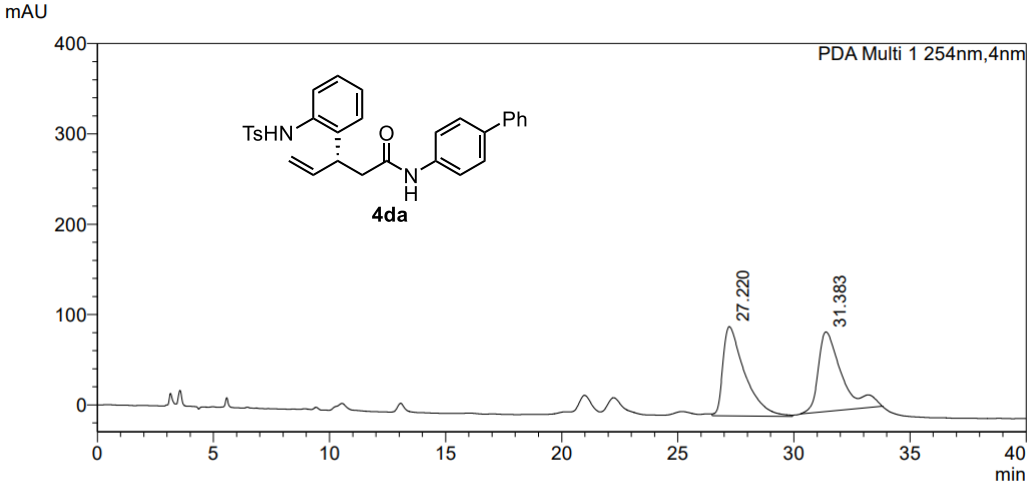


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.356	7503743	99.805
2	19.247	14629	0.195
Total		7518372	100.000

<Chromatogram>

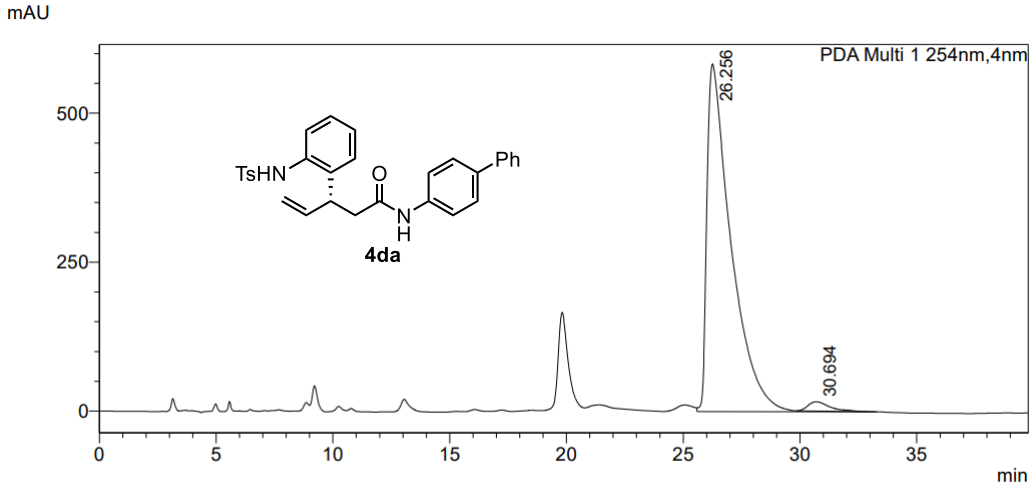


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.220	6445349	50.884
2	31.383	6221493	49.116
Total		12666842	100.000

<Chromatogram>

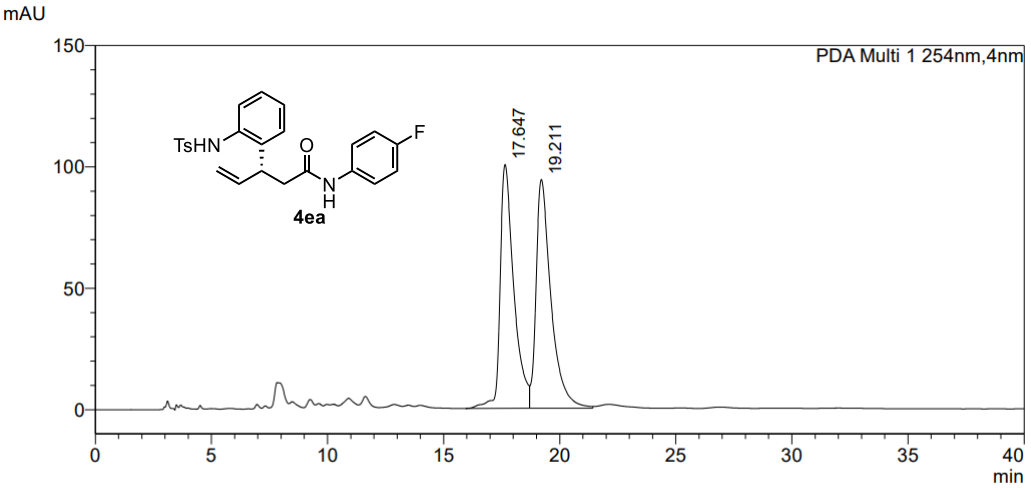


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.256	41882954	97.619
2	30.694	1021655	2.381
Total		42904609	100.000

<Chromatogram>

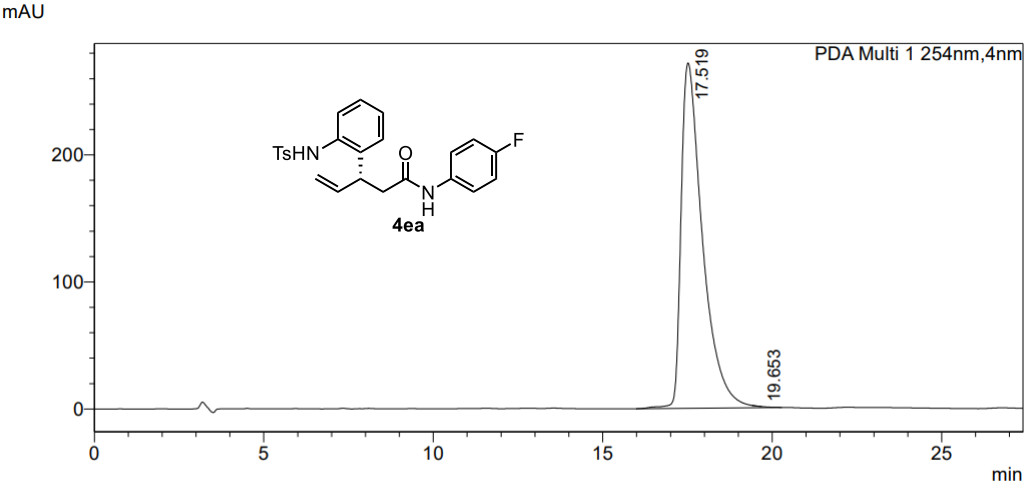


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.647	4135593	49.507
2	19.211	4217979	50.493
Total		8353571	100.000

<Chromatogram>

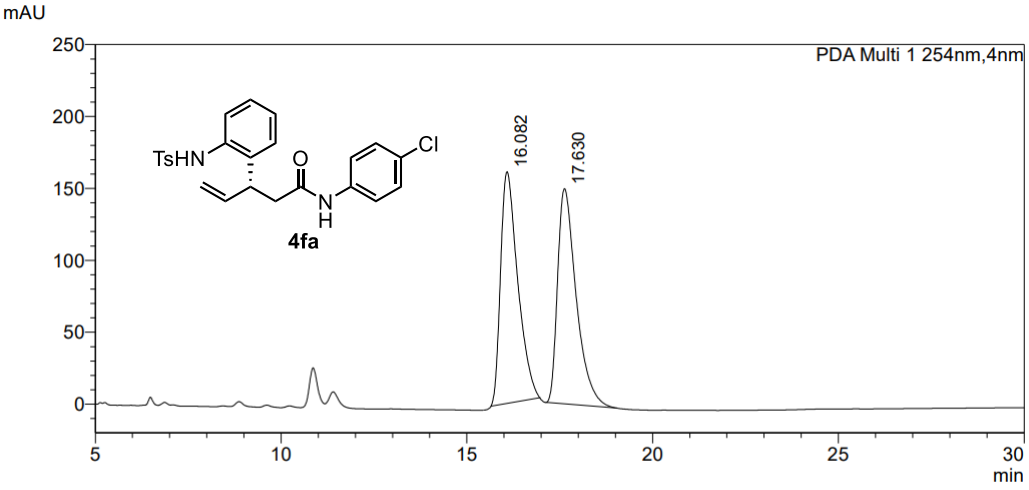


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.519	11977883	100.007
2	19.653	-867	-0.007
Total		11977016	100.000

<Chromatogram>

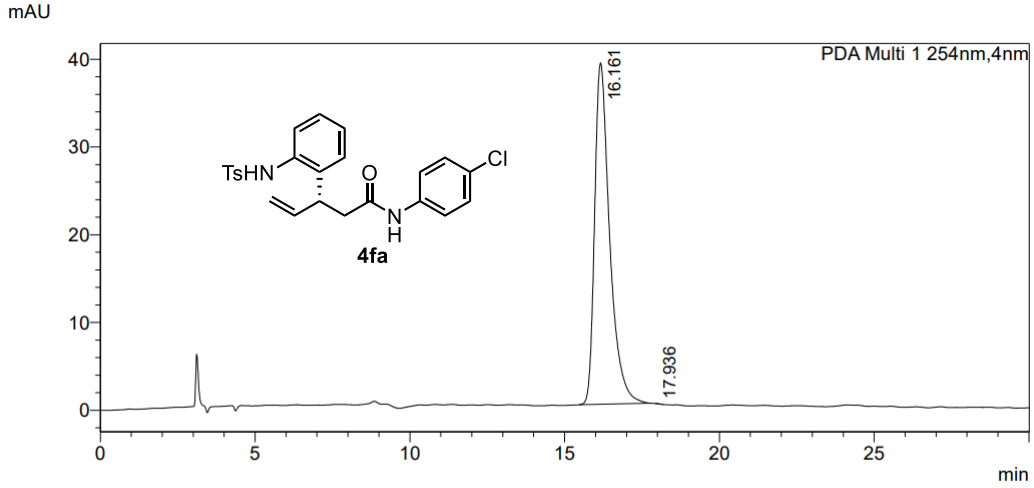


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.082	5176570	49.812
2	17.630	5215582	50.188
Total		10392152	100.000

<Chromatogram>

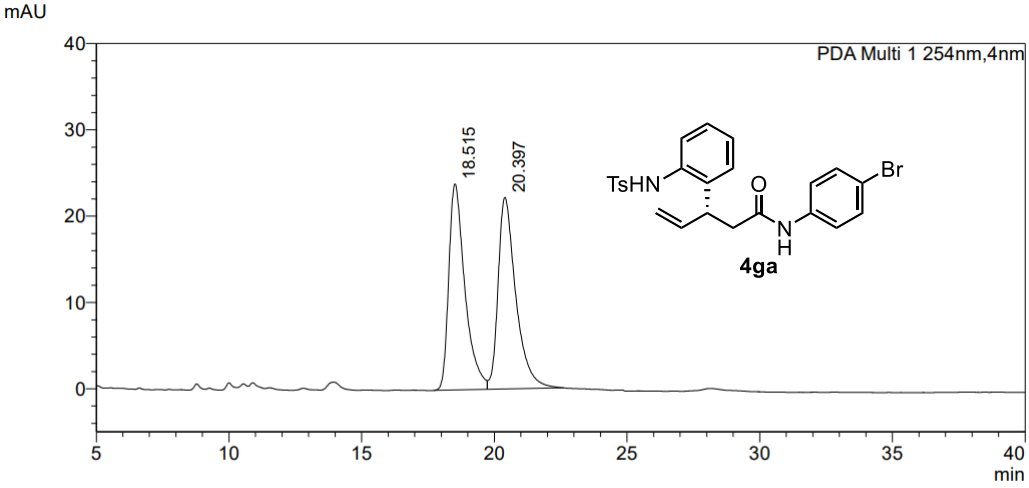


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.161	1314227	99.997
2	17.936	41	0.003
Total		1314268	100.000

<Chromatogram>

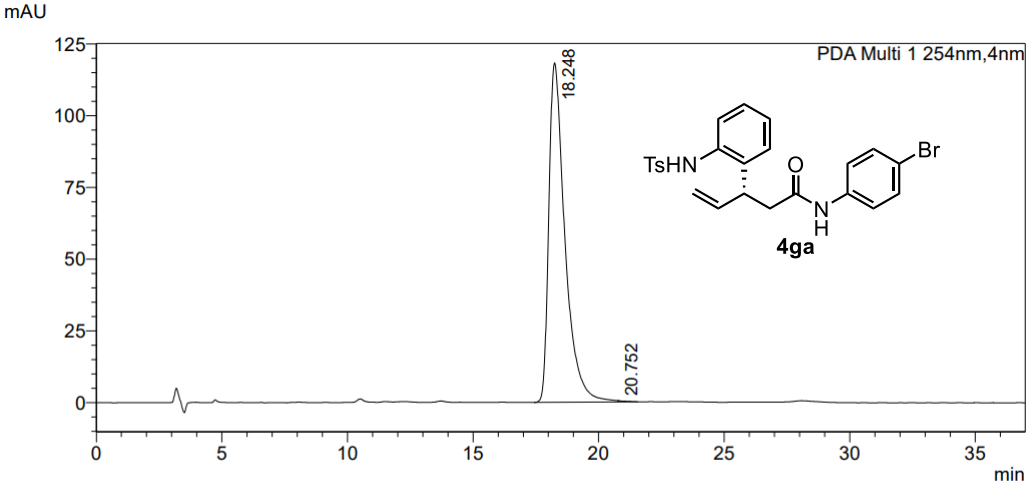


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.515	1010538	49.464
2	20.397	1032445	50.536
Total		2042983	100.000

<Chromatogram>

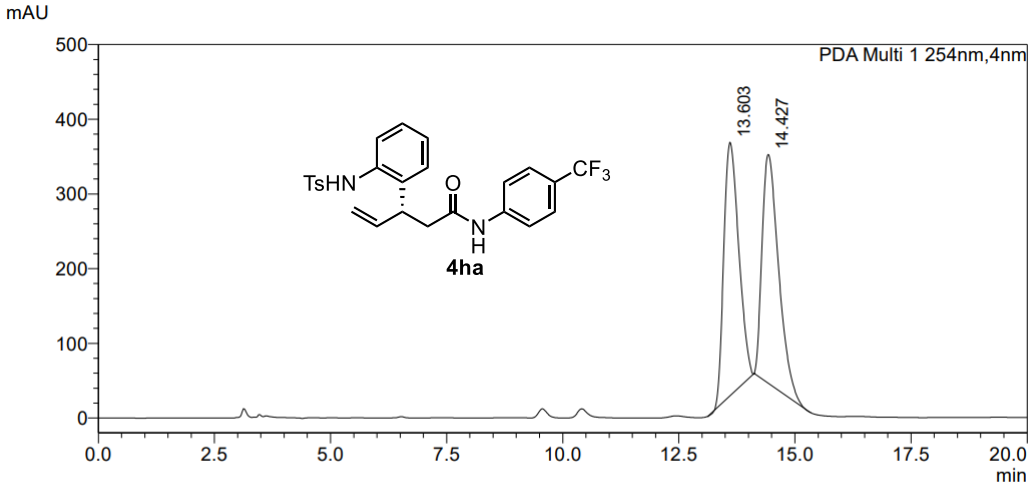


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.248	5287375	100.000
2	20.752	-23	-0.000
Total		5287352	100.000

<Chromatogram>

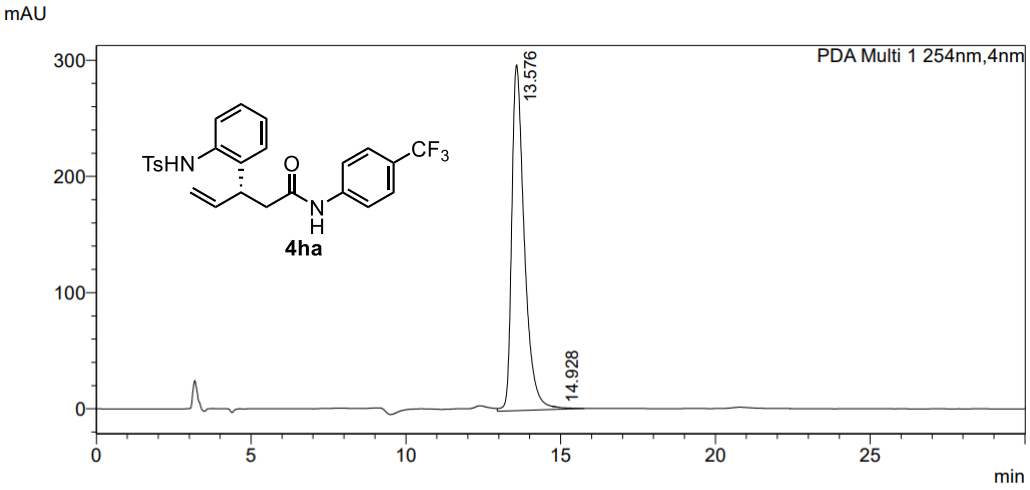


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.603	7588891	49.924
2	14.427	7612058	50.076
Total		15200949	100.000

<Chromatogram>

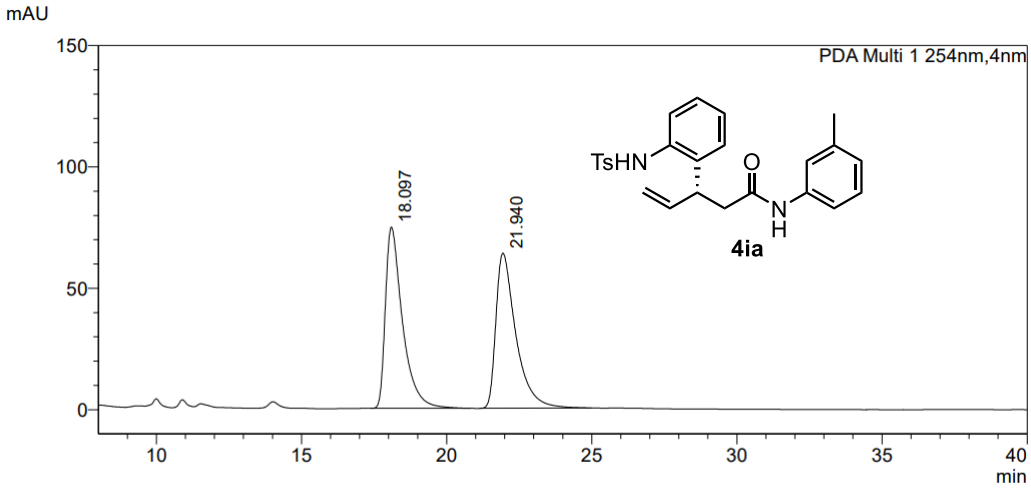


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.576	8462538	100.010
2	14.928	-833	-0.010
Total		8461705	100.000

<Chromatogram>

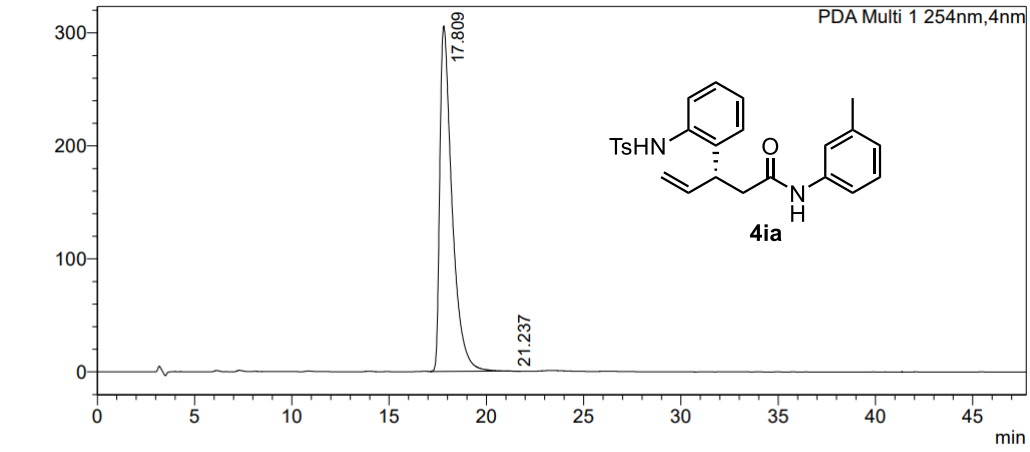


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.097	3062687	50.009
2	21.940	3061526	49.991
Total		6124213	100.000

<Chromatogram>

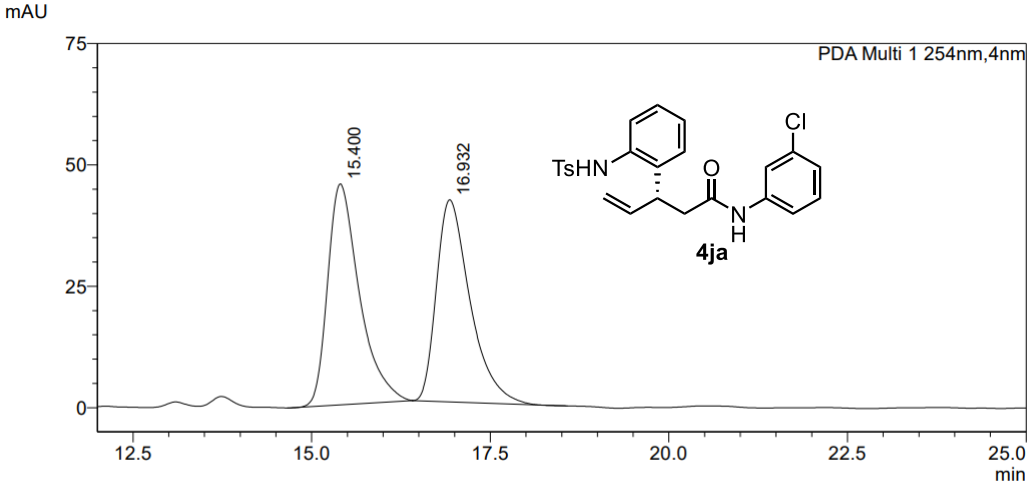


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.809	13365673	99.993
2	21.237	888	0.007
Total		13366560	100.000

<Chromatogram>

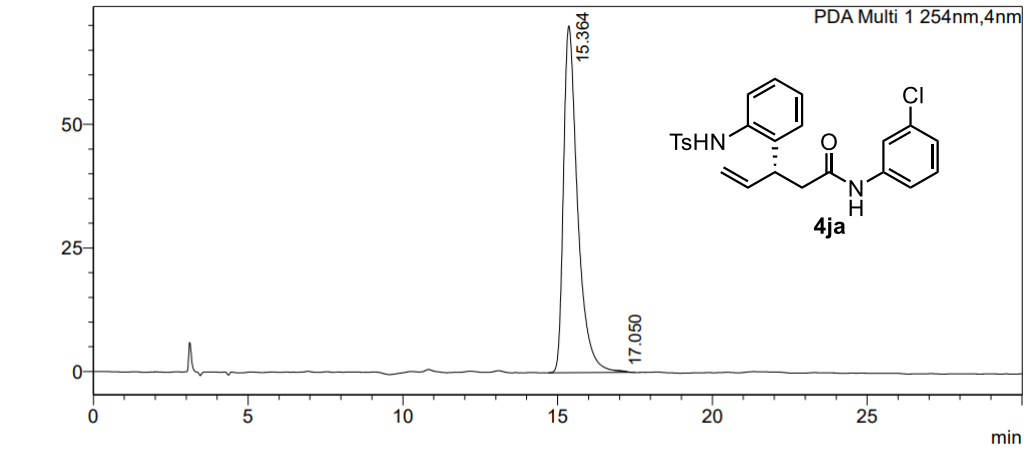


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.400	1404915	50.766
2	16.932	1362517	49.234
Total		2767432	100.000

<Chromatogram>

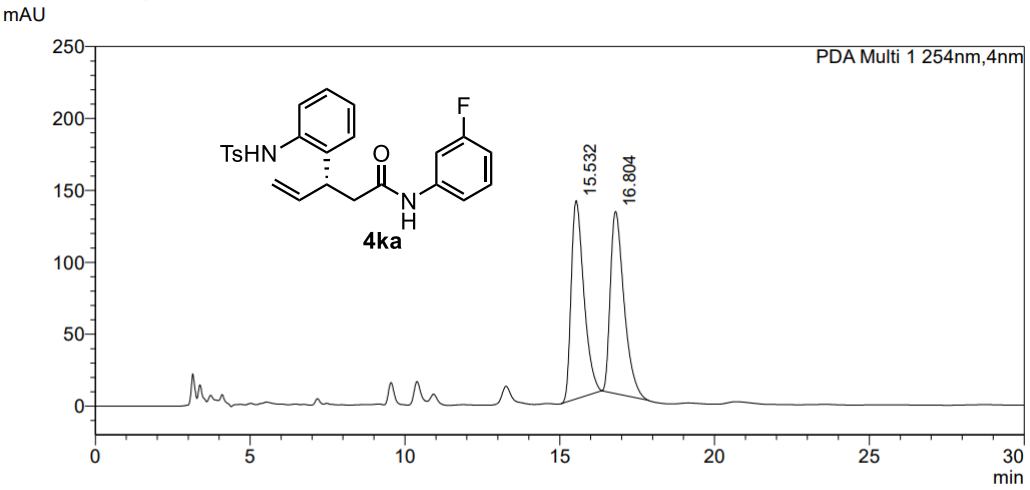


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.364	2235649	99.978
2	17.050	502	0.022
Total		2236151	100.000

<Chromatogram>

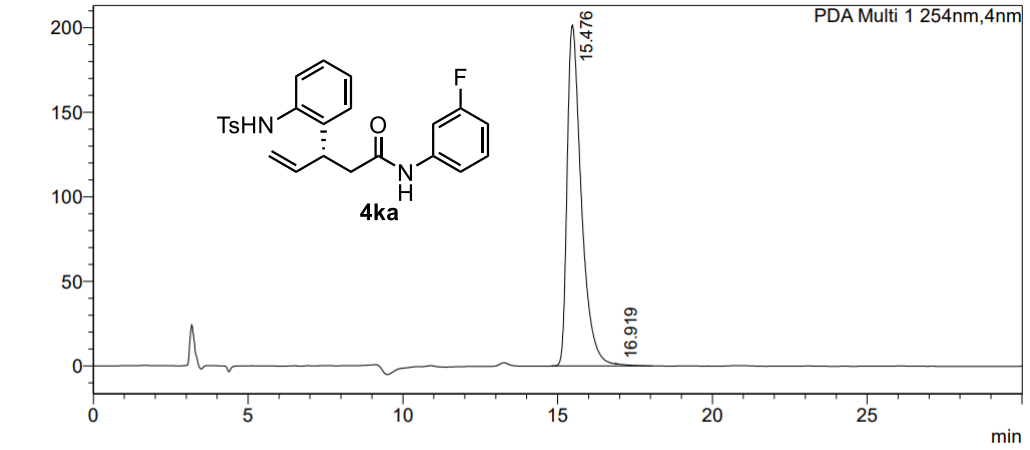


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.532	3945179	50.218
2	16.804	3910967	49.782
Total		7856146	100.000

<Chromatogram>

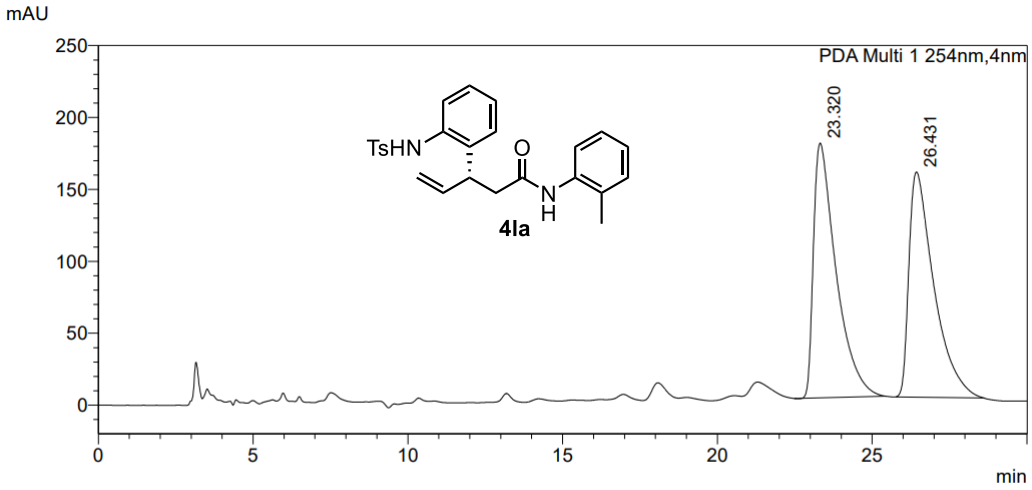


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.476	6453265	100.001
2	16.919	-85	-0.001
Total		6453180	100.000

<Chromatogram>

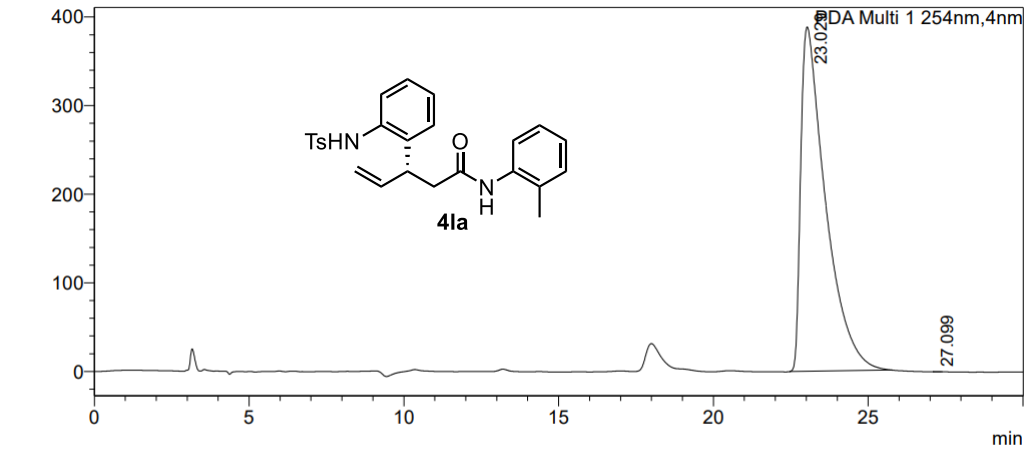


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.320	8985537	50.588
2	26.431	8776671	49.412
Total		17762208	100.000

<Chromatogram>

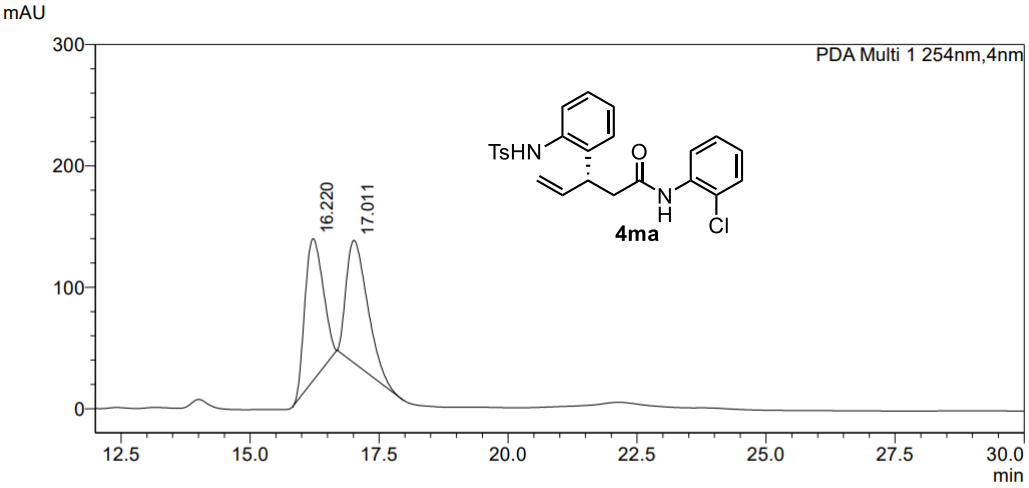


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.029	21637041	100.000
2	27.099	16	0.000
Total		21637057	100.000

<Chromatogram>

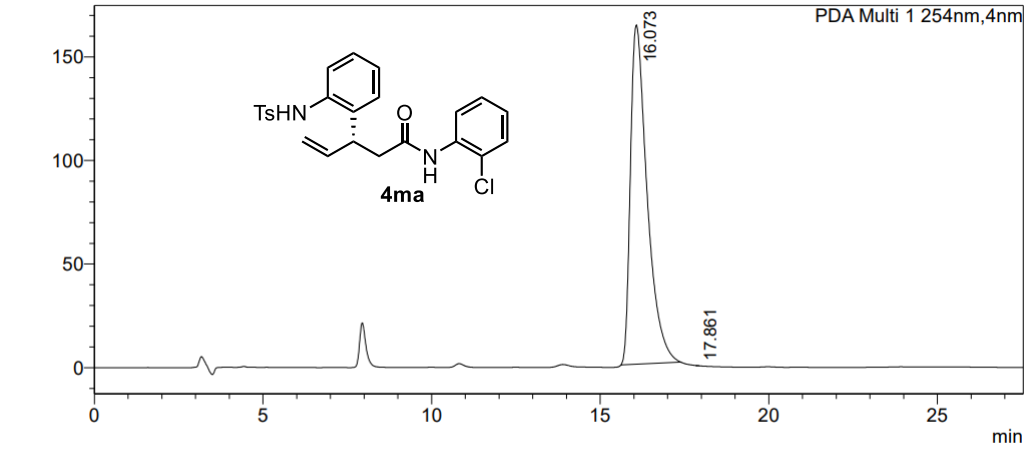


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area%
1	16.220	116827	49.391
2	17.011	100922	50.609
Total		217749	100.000

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.073	5641310	100.001
2	17.861	-39	-0.001
Total		5641271	100.000

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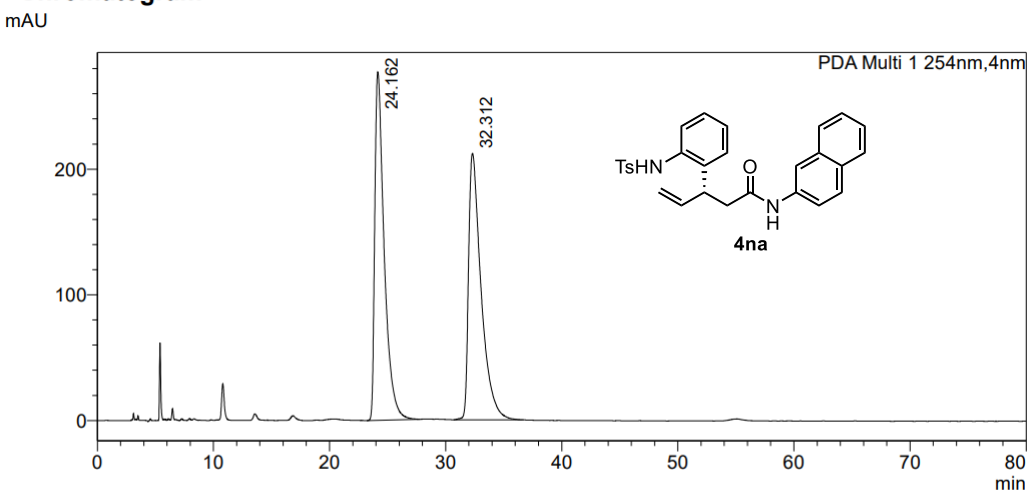
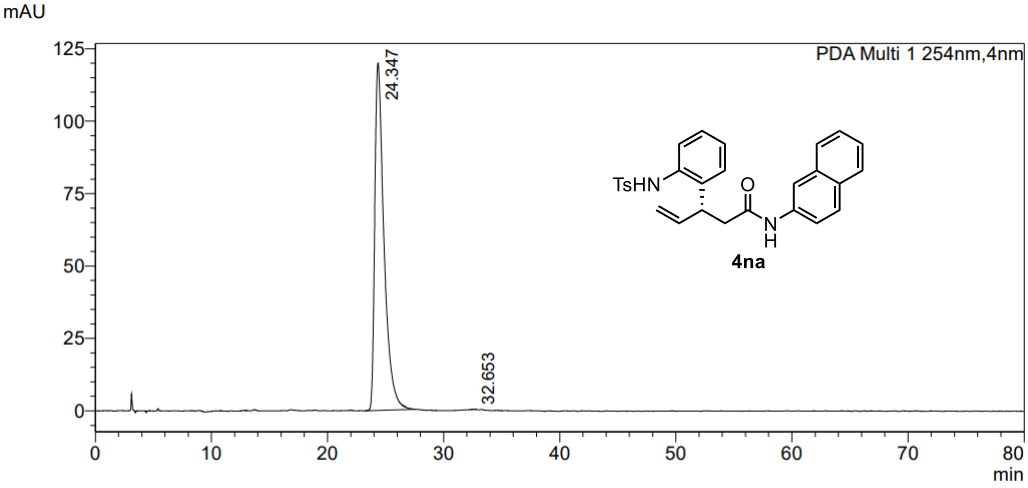


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.162	15695890	49.570
2	32.312	15968125	50.430
Total		31664015	100.000

<Chromatogram>

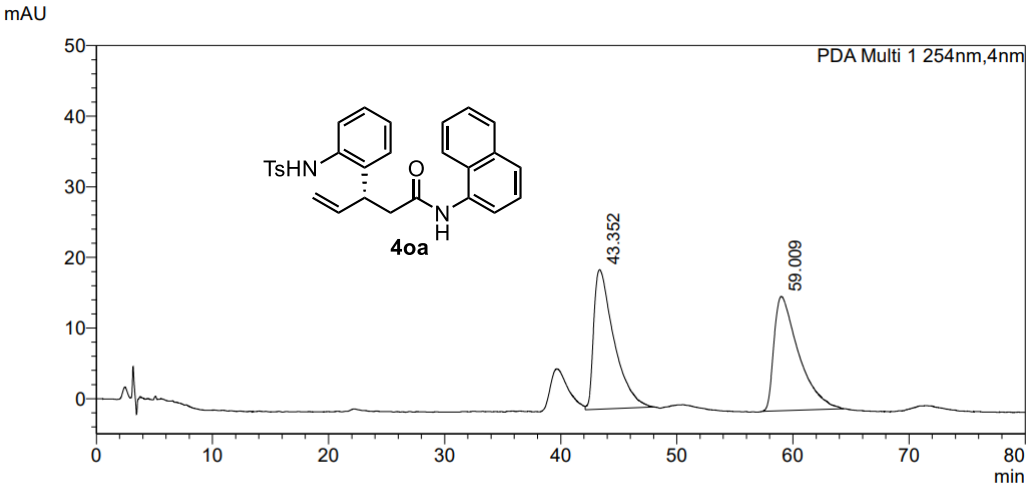


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.347	6650511	99.991
2	32.653	617	0.009
Total		6651128	100.000

<Chromatogram>

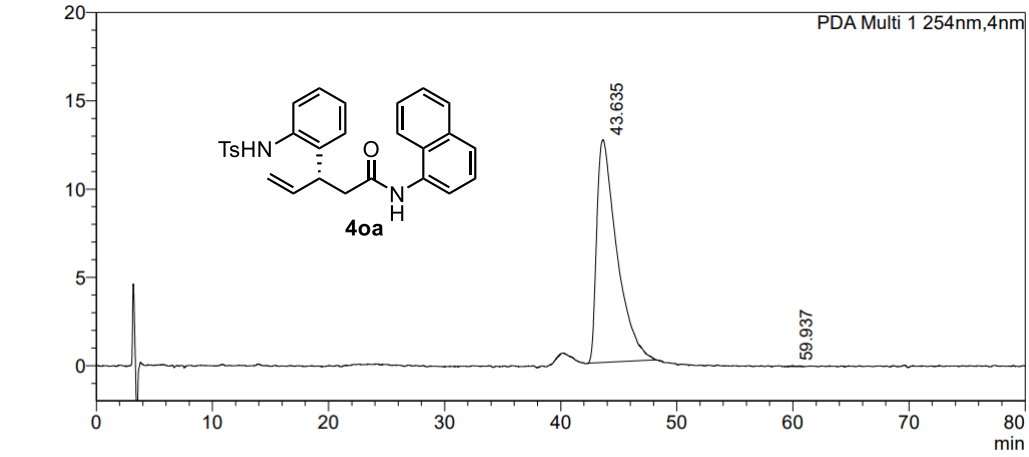


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	43.352	2400581	50.135
2	59.009	2387648	49.865
Total		4788229	100.000

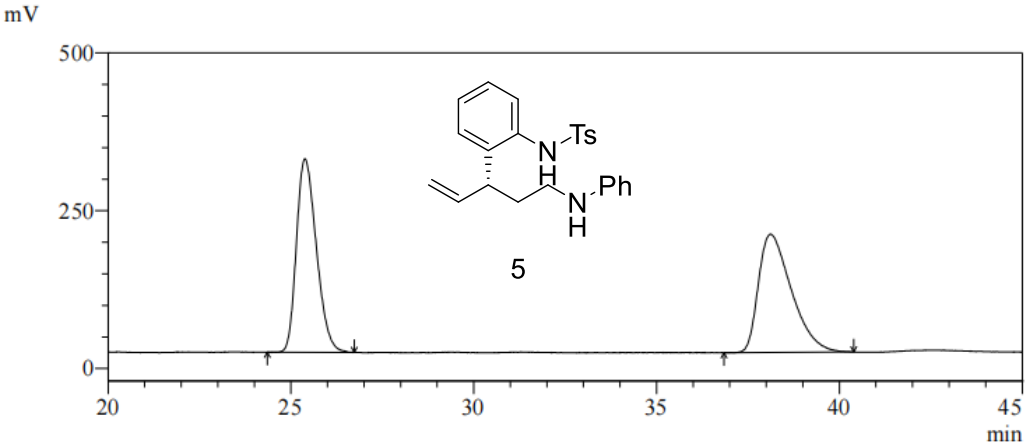
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

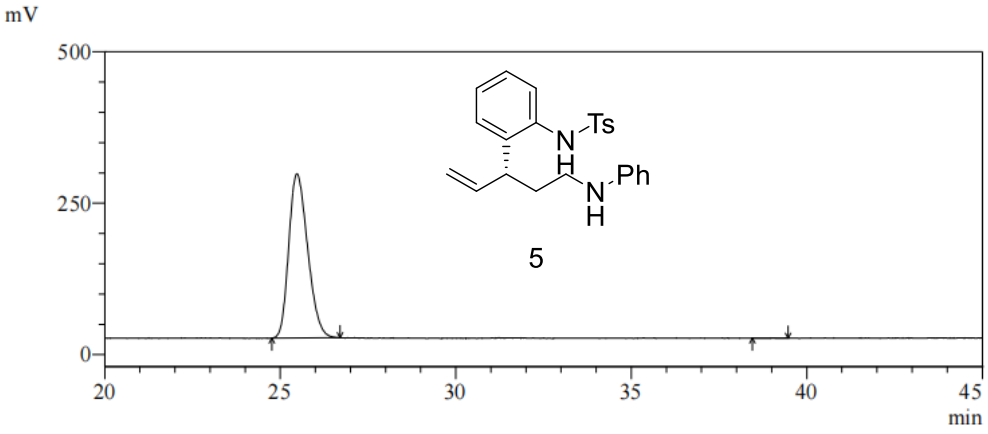
Peak#	Ret. Time	Area	Area%
1	43.635	1524573	99.868
2	59.937	2010	0.132
Total		1526582	100.000



Peak Table

Detector A 254nm

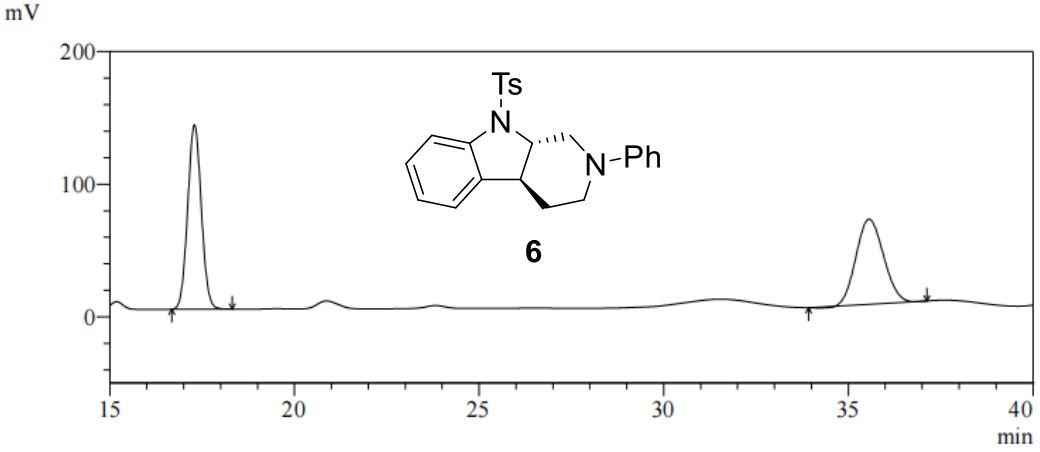
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	25.384	587.12	522.12	11624402	306544	49.809
2	38.122	358.59	522.12	11713346	187224	50.191
Total				23337748	493768	100.000



Peak Table

Detector A 254nm

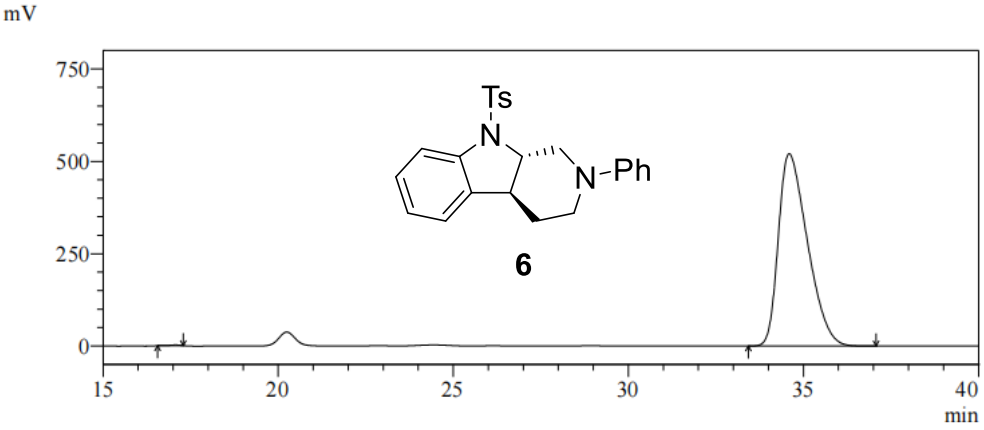
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	25.475	533.74	507.52	10116576	270887	99.876
2	39.023	1.29	507.52	12561	653	0.124
Total				10129137	271540	100.000



Peak Table

Detector A 254nm

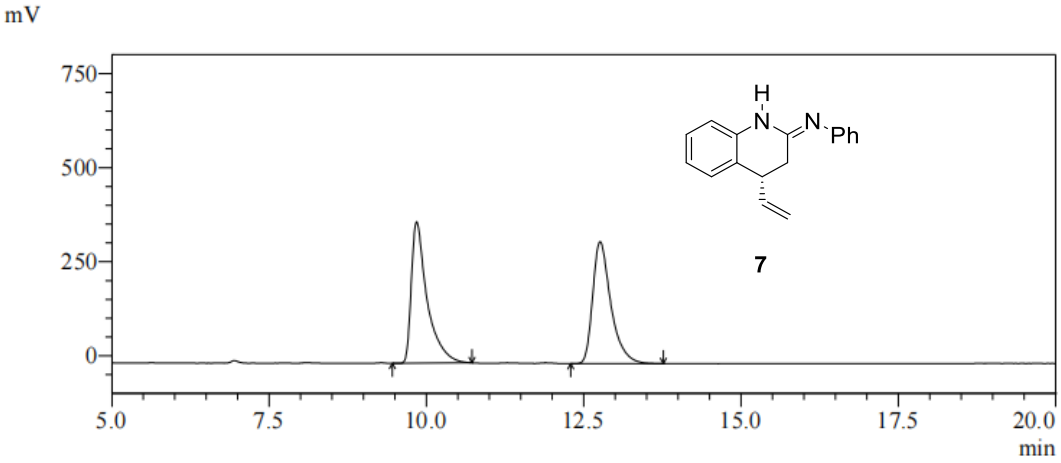
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.291	161.06	864.30	3574365	139204	51.843
2	35.564	74.36	864.30	3320281	64272	48.157
Total				6894646	203476	100.000



Peak Table

Detector A 254nm

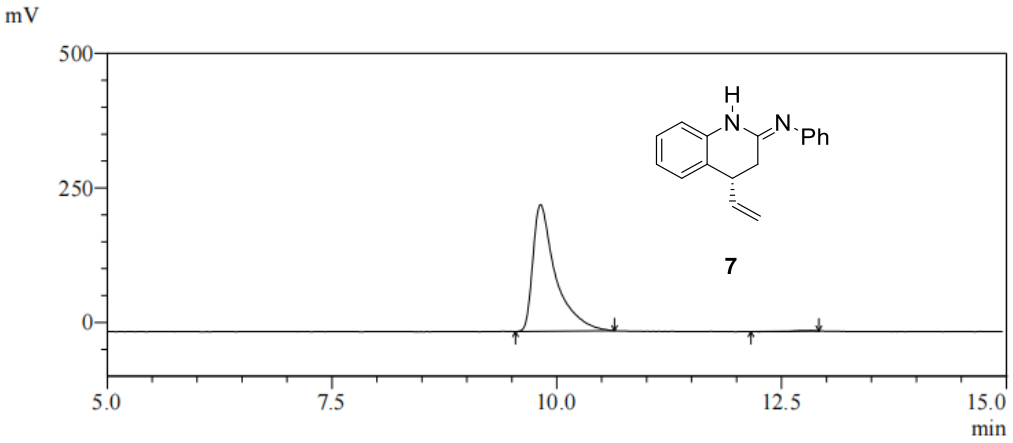
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	17.071	2.83	628.52	39196	1779	0.130
2	34.594	828.30	628.52	30065243	520602	99.870
Total				30104439	522382	100.000



Peak Table

Detector A 254nm

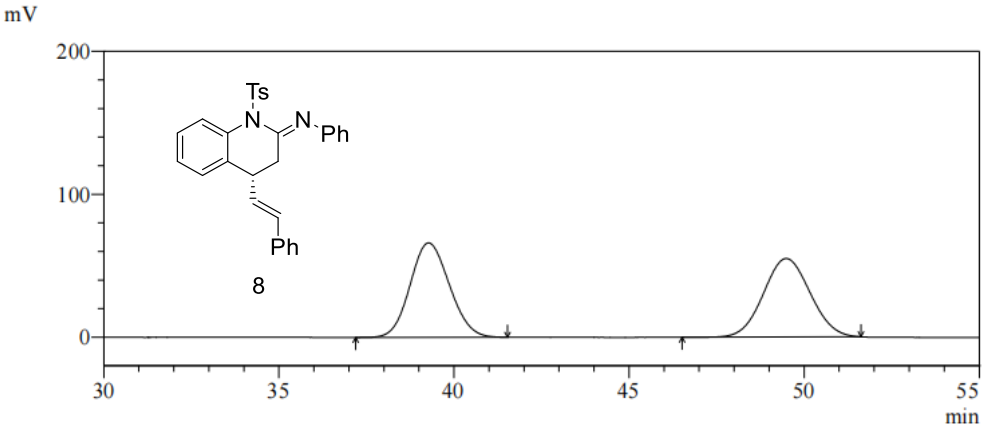
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	9.844	170.37	2207.09	6560800	376031	50.179
2	12.761	146.80	2207.09	6514067	324002	49.821
Total				13074867	700033	100.000



Peak Table

Detector A 254nm

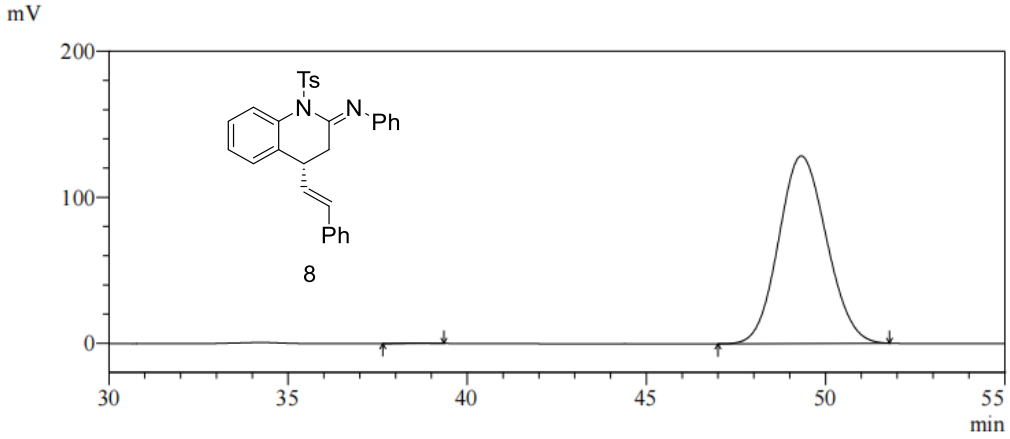
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	9.819	269.91	872.70	4149208	235554	99.898
2	12.823	1.26	872.70	4243	1103	0.102
Total				4153452	236657	100.000



Peak Table

Detector A 254nm

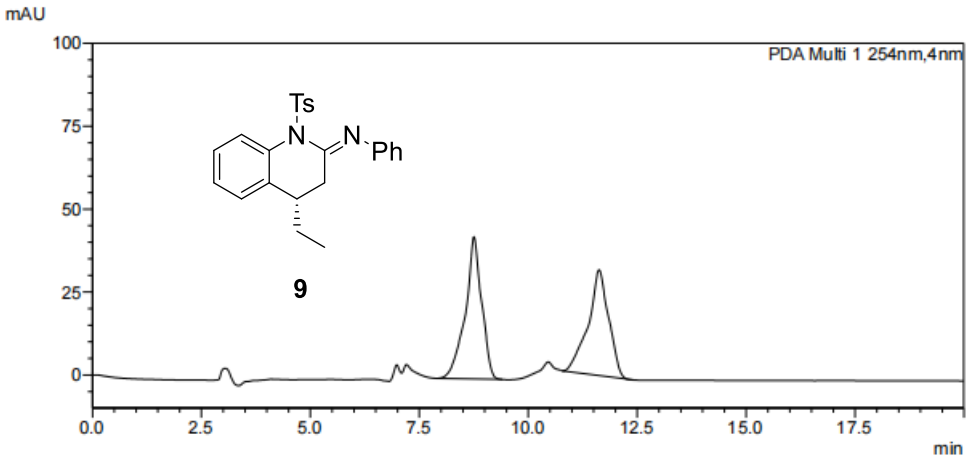
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	39.273	133.71	494.35	5156896	66099	50.265
2	49.486	111.10	494.35	5102468	54923	49.735
Total				10259364	121022	100.000



Peak Table

Detector A 254nm

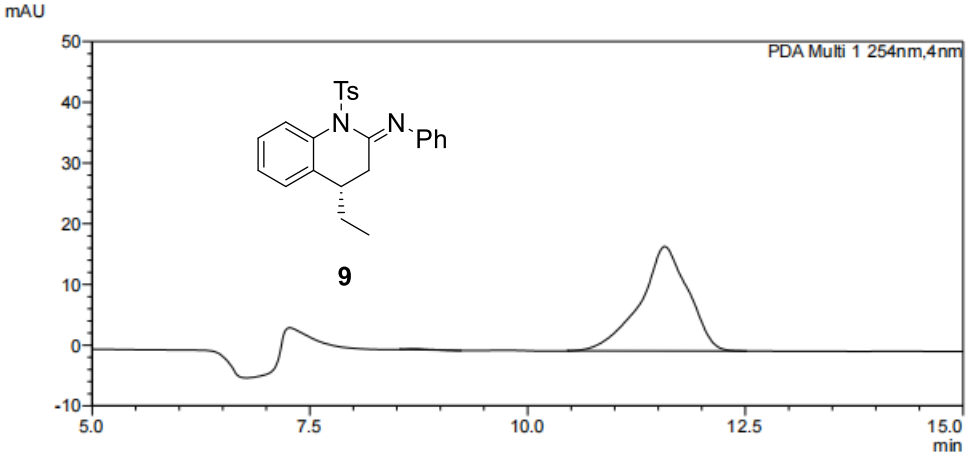
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	38.617	0.59	519.64	17863	305	0.149
2	49.324	247.16	519.64	11953325	128437	99.851
Total				11971189	128742	100.000



<Peak Table>

PDA Ch1 254nm

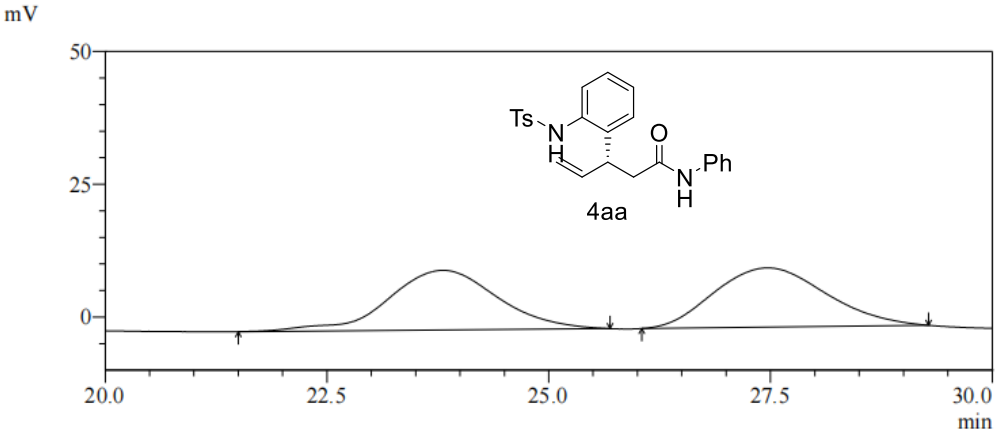
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	8.754	91.40	469.03	1121636	42870	51.803
2	11.625	67.94	469.03	1043555	31866	48.197
Total				2165190	74735	100.000



<Peak Table>

PDA Ch1 254nm

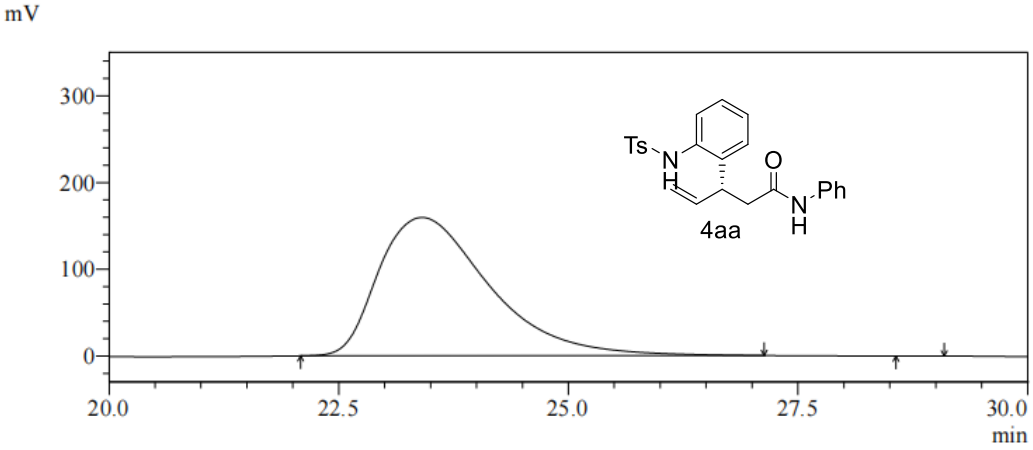
Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	8.703	0.22	699.63	2560	155	0.387
2	11.575	24.57	699.63	659460	17188	99.613
Total				662020	17343	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	23.804	6.37	1765.08	965681	11240	49.669
2	27.463	6.32	1765.08	978560	11148	50.331
Total				1944241	22389	100.000



Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	23.406	204.90	778.20	13396290	159457	99.995
2	28.955	0.06	778.20	656	43	0.005
Total				13396945	159500	100.000