

Supplementary Information

Rh(III)-Catalyzed chemo-, regio- and stereoselective carboamination of sulfonyl allenes with *N*-phenoxy amides or *N*-enoxy imides

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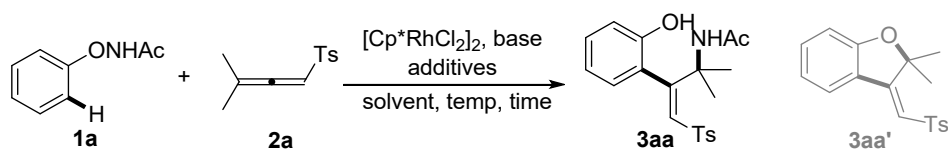
I. General

NMR spectra were recorded on JEOL 400 NMR (^1H 400 MHz; ^{13}C 100 MHz) in either CDCl_3 or $\text{DMSO}-d_6$. Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm; d_6 -DMSO: $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.52$ ppm). Mass spectra and high-resolution mass spectra were measured on an agilent TOF-G6230B mass spectrometer and Thermo-DFS mass spectrometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) and preparative TLC (200x200 mm, 0.2-0.25 mm in thickness) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography. $[\text{Cp}^*\text{IrCl}_2]_2$, $[\text{Cp}^*\text{RhCl}_2]_2$, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ and CsOAc were purchased from Aldrich and used without further purification. *N*-phenoxy amides,^{S1} *N*-enoxy imides^{S2} and the allene substrates^{S3} were synthesized according to published procedures. Other chemicals were purchased from commercial suppliers and were dried and purified when necessary. No attempts were made to optimize yields for substrate synthesis.

II. Experimental Information and Characterization Data

Optimization studies:

The mixture of *N*-phenoxy amide **1a** (0.1 mmol, 1.0 equiv), sulfonyl allene **2a** (0.1 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and base (1 equiv) in the solvent was stirred in an oil bath without exclusion of air or moisture. Afterwards, it was diluted with EtOAc and filtered through a short silica gel column to remove the metal residues. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 3/1) to afford the corresponding product **3aa**.

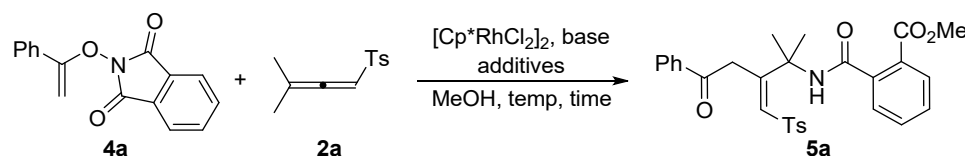
Table S1. Conditions Screening for the Synthesis of **3aa**.^a

#	solvent	Temp (°C)	base	additive	Time (h)	Yield (%) ^b	
						3aa	3aa'
<i>solvent screening</i>							
1	MeCN	40	NaOAc	/	12	24	trace
2	DCE	40	NaOAc	/	12	27	trace
3	Dioxane	40	NaOAc	/	12	74	nd
4	DMF	40	NaOAc	/	12	trace	nd
5	Toluene	40	NaOAc	/	12	53	trace
6	Acetone	40	NaOAc	/	12	39	trace
7	HFIP	40	NaOAc	/	12	trace	nd
8	DMSO	40	NaOAc	/	12	nd	nd
9	THF	40	NaOAc	/	12	74	nd
<i>reaction temperature screening</i>							
10	THF	rt	NaOAc	/	12	57	nd
11	THF	60	NaOAc	/	12	66	nd
12	THF	80	NaOAc	/	12	63	nd
<i>additive screening</i>							
13	THF	rt	NaOAc	HOAc	12	36	11
14	THF	rt	NaOAc	PivOH	12	28	trace
15	THF	rt	NaOAc	4ÅMS	12	53	trace
16	THF	rt	NaOAc	Amberlite IRA-400	12	50	nd
17	THF	rt	NaOAc	Amberlite IR-120	12	38	nd
<i>base screening</i>							
18	THF	rt	KOAc	/	12	37	nd
19	THF	rt	CsOAc	/	12	22	nd
20	THF	rt	Zn(OAc) ₂	/	12	<10	nd
21	THF	rt	Mn(OAc) ₂	/	12	30	nd
22	THF	rt	K ₂ CO ₃	/		28	nd
23	THF	rt	KOPiv	/	12	25	nd
24	THF	rt	K ₃ PO ₄	/	12	nd	nd
<i>Reaction time screening</i>							
25	THF	rt	NaOAc	/	8	50	nd
26	THF	rt	NaOAc	/	12	53	nd
27	THF	rt	NaOAc	/	16	52	nd
28	THF	rt	NaOAc	/	24	53	nd

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %), base (1.0 equiv), solvent (0.5 mL), temperature, time, under air. ^bIsolated yields. nd: not detected.

The mixture of *N*-enoxy imide **4a** (0.1 mmol, 1.0 equiv), sulfonyl allene **2a** (0.1 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (2.5 mol %) and base (1 equiv) in the solvent was stirred in an oil bath without exclusion of air or moisture. Afterwards, it was diluted with EtOAc and filtered through a short silica gel column to remove the metal residues. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 2/1) to afford the corresponding product **5a**.

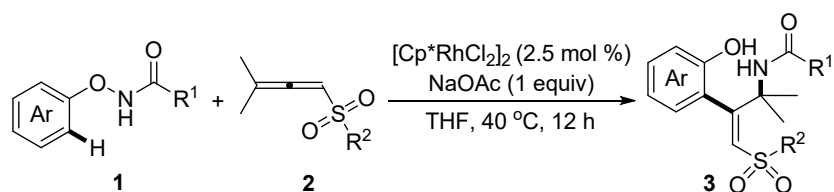
Table S2. Conditions Screening for the Synthesis of **5a**.^a



#	base	Temp/°C	additive	4a:2a	Time/h	yield(%) ^b
<i>base screening</i>						
1	KOAc	40	/	1:1	12	18
2	CsOAc	40	/	1:1	12	22
3	Zn(OAc) ₂	40	/	1:1	12	trace
4	K ₂ CO ₃	40	/	1:1	12	trace
5	KOPiv	40	/	1:1	12	25
6	Cs ₂ CO ₃	40	/	1:1	12	12
7	NaOAc	40	/	1:1	12	12
<i>additive screening</i>						
8	KOPiv	40	HOAc	1:1	12	<10
9	KOPiv	40	PivOH	1:1	12	12
10	KOPiv	40	4ÅMS	1:1	12	22
11	KOPiv	40	Amberlite IRA-400	1:1	12	15
12	KOPiv	40	Amberlite IR-120	1:1	12	trace
13	KOPiv	40	AgSbF ₆	1:1	12	ND
<i>other parameters screening</i>						
14	KOPiv	40	/	1.5:1	12	31
15	KOPiv	40	/	2:1	12	51
16	KOPiv	40	/	2:1	6	33
17	KOPiv	40	/	2:1	8	36
18	KOPiv	40	/	2:1	24	21
19	KOPiv	rt	/	2:1	12	46
20	KOPiv	60	/	2:1	12	15
21	KOPiv	80	/	2:1	12	<10

^aReaction Conditions: **1a**, **2a** (0.1 mmol), [Cp*RhCl₂]₂ (2.5 mol %), base (1.0 equiv), solvent (0.5 mL), temperature, time, under air. ^bIsolated yields. ND: not detected.

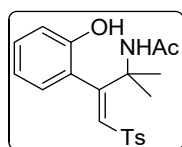
General procedure for the carboamination of *N*-phenoxy amides with sulfonyl allenes:



The mixture of *N*-phenoxy amide **1** (0.2 mmol, 1.0 equiv), sulfonyl allene **2** (0.2 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and NaOAc (0.2 mmol, 1.0 equiv) in THF (2.0 mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC to afford the corresponding allylamine derivatives **3**.

Characterization of products:

(*Z*)-*N*-(3-(2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3aa**)**



This compound was obtained in 74% yield (55.2 mg) as light yellow solid, m.p.: 186-187 °C. Eluent: PE/EA = 2/1, R_f = 0.7.

¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.02 (brs, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.78-6.71 (m, 2H), 6.09 (s, 1H), 2.41 (s, 3H), 2.14 (s, 3H), 1.82 (s, 3H), 1.35 (s, 3H).

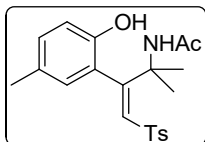
¹³C NMR (100 MHz, CDCl₃): δ 171.6, 157.4, 154.3, 144.7, 138.8, 130.2, 130.1, 130.0, 127.8, 127.3, 126.1, 118.7, 117.2, 55.3, 28.0, 26.2, 24.2, 21.7.

HRMS (ESI) calculated for C₂₀H₂₄NO₄S ($[\text{M}+\text{H}]^+$): 374.1421; found: 374.1417.

Scale-up synthesis of **3aa:** The mixture of *N*-phenoxyacetamide **1a** (2.0 mmol, 1.0 equiv), sulfonyl allene **2a** (2.0 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and NaOAc (2.0 mmol, 1.0 equiv) in THF (10.0 mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the resulted mixture was purified by silica

gel column chromatography to afford the corresponding allylamine derivatives **3aa** in 73% (0.544 g) isolated yield.

(Z)-N-(3-(2-hydroxy-5-methylphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ba)



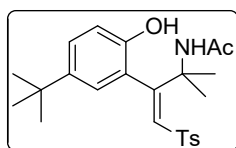
This compound was obtained in 75% yield (58.0 mg) as light yellow solid, m.p.: 185-187 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

^1H NMR (400 MHz, CDCl_3): δ 9.56 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.3 Hz, 1H), 6.87-6.78 (m, 2H), 6.55 (s, 1H), 6.08 (s, 1H), 2.42 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H), 1.81 (s, 4H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 157.6, 152.0, 144.7, 138.9, 130.7, 130.2, 130.0, 128.0, 127.9, 127.4, 125.8, 117.1, 55.3, 28.1, 26.3, 24.3, 21.7, 20.4.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 388.1577; found: 388.1571.

(Z)-N-(3-(5-(tert-butyl)-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ca)



This compound was obtained in 65% yield (57.0 mg) as light yellow oil. Eluent: PE/EA = 2/1, R_f = 0.8.

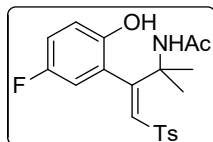
^1H NMR (400 MHz, CDCl_3): δ 9.50 (s, 1H), 7.80 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.6 Hz, 1H), 6.86-6.83 (m, 2H), 6.72 (s, 1H), 6.14 (s, 1H), 2.42 (s, 3H), 2.12 (s, 3H), 1.82 (s, 3H), 1.32 (s, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 157.9, 151.8, 144.7, 141.6, 138.9, 130.1, 130.0, 127.4, 127.0, 125.4, 124.1, 116.8, 55.4, 34.0, 31.6, 28.3, 26.5, 24.3, 21.7.

HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{32}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 392.1327; found: 392.1321.

(Z)-N-(3-(5-fluoro-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide

(3da)



This compound was obtained in 81% yield (63.3 mg) as light yellow solid, m.p.: 136-138 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

^1H NMR (400 MHz, CDCl_3): δ 9.72 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.92-6.81 (m, 3H), 6.51 (dd, J = 8.3, 2.8 Hz, 1H), 6.09 (s, 1H), 2.43 (s, 3H), 2.14 (s, 3H), 1.81 (s, 3H), 1.36 (s, 3H).

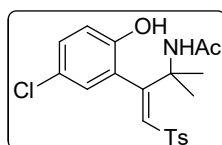
^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 156.0, 155.5 (d, J = 238.1 Hz), 150.5, 145.0, 138.6, 130.9, 130.1, 126.2 (d, J = 7.3 Hz), 118.3 (d, J = 8.0 Hz), 116.6 (d, J = 22.5 Hz), 114.1 (d, J = 23.6 Hz), 55.1, 28.1, 26.3, 24.2, 21.7.

^{19}F NMR (376 MHz, CDCl_3): δ -126.13.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{FNO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 392.1327; found: 392.1322.

(Z)-N-(3-(5-chloro-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide

(3ea)



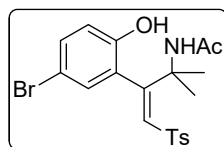
This compound was obtained in 78% yield (65.1 mg) as light yellow solid, m.p.: 187-188 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

^1H NMR (400 MHz, CDCl_3): δ 10.02 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 8.7, 2.3 Hz, 1H), 6.91 (brs, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.74 (d, J = 2.3 Hz, 1H), 6.08 (s, 1H), 2.43 (s, 3H), 2.15 (s, 3H), 1.81 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 155.8, 153.3, 145.0, 138.5, 131.0, 130.2, 130.0, 127.4, 127.3, 127.2, 123.3, 118.8, 55.2, 28.0, 26.2, 24.2, 21.7.

HRMS (ESI) calculated for C₂₀H₂₃ClNO₄S ([M+H]⁺): 408.1031; found: 408.1026.

(Z)-N-(3-(5-bromo-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3fa)



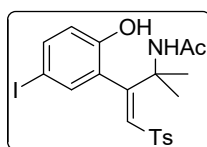
This compound was obtained in 80% yield (71.6 mg) as light yellow solid, m.p.: 168-170 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

¹H NMR (400 MHz, CDCl₃): δ 10.07 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.93 (brs, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.08 (s, 1H), 2.43 (s, 3H), 2.15 (s, 3H), 1.81 (s, 3H), 1.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.8, 155.7, 153.8, 145.0, 138.5, 132.9, 131.0, 130.2, 130.0, 127.8, 127.4, 119.3, 110.4, 55.2, 28.0, 26.2, 24.2, 21.7.

HRMS (ESI) calculated for C₂₀H₂₃BrNO₄S ([M+H]⁺): 452.0526; found: 452.0522.

(Z)-N-(3-(2-hydroxy-5-iodophenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ga)



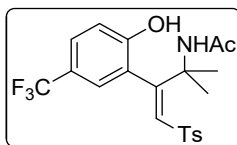
This compound was obtained in 72% yield (72.0 mg) as light yellow solid, m.p.: 182-183 °C. Eluent: PE/EA = 2/1, R_f = 0.7.

¹H NMR (400 MHz, CDCl₃): δ 10.10 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 6.90 (brs, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.07 (s, 1H), 2.43 (s, 3H), 2.14 (s, 3H), 1.80 (s, 3H), 1.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.8, 155.6, 154.6, 145.0, 138.9, 138.5, 135.7, 131.0, 130.2, 128.6, 127.4, 119.8, 79.9, 55.2, 28.0, 26.2, 24.2, 21.7.

HRMS (ESI) calculated for C₂₀H₂₃INO₄S ([M+H]⁺): 500.0387; found: 500.0383.

(Z)-N-(3-(2-hydroxy-5-(trifluoromethyl)phenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ha)



This compound was obtained in 86% yield (75.6 mg) as light yellow solid, m.p.: 179-181 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

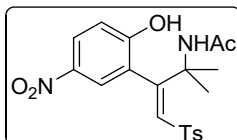
^1H NMR (400 MHz, CDCl_3): δ 10.55 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.01 (s, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.92 (s, 1H), 6.10 (s, 1H), 2.43 (s, 3H), 2.17 (s, 3H), 1.84 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 157.6, 155.7, 145.1, 138.4, 131.4, 130.2, 127.5, 126.1, 125.1 (q, J = 3.6 Hz), 124.4 (q, J = 270.9 Hz), 121.1 (q, J = 32.9 Hz), 117.8, 55.2, 28.1, 26.3, 24.3, 21.7.

^{19}F NMR (376 MHz, CDCl_3): δ -61.02.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 442.1295; found: 442.1288.

(Z)-N-(3-(2-hydroxy-5-nitrophenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ia)



This compound was obtained in 90% yield (75.2 mg) as light yellow oil. Eluent: PE/EA = 2/1, R_f = 0.7.

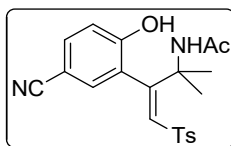
^1H NMR (400 MHz, CDCl_3): δ 11.37 (s, 1H), 8.10 (d, J = 9.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.74 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.12 (s, 1H), 6.97 (d, J = 9.1 Hz, 1H), 6.12 (s, 1H), 2.44 (s, 3H), 2.20 (s, 3H), 1.87 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 161.0, 154.4, 145.3, 139.7, 138.1, 132.0, 130.3, 127.5, 126.5, 126.1, 124.4, 117.9, 55.1, 27.9, 26.1, 24.1, 21.7.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 419.1272; found: 419.1267.

(Z)-N-(3-(5-cyano-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide

(3ja)



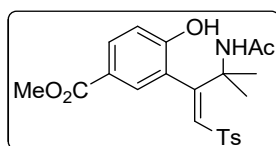
This compound was obtained in 57% yield (45.3 mg) as light yellow solid, m.p.: 192-193 °C. Eluent: PE/EA = 2/1, R_f = 0.7.

^1H NMR (400 MHz, CDCl_3): δ 10.97 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 6.96 (d, J = 8.6 Hz, 1H), 6.91 (brs, 1H), 6.06 (s, 1H), 2.44 (s, 3H), 2.17 (s, 3H), 1.82 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.1, 158.9, 154.7, 145.3, 138.3, 134.3, 132.3, 131.8, 130.3, 127.5, 127.1, 119.1, 118.6, 102.1, 55.2, 28.0, 26.2, 24.2, 21.8.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 399.1373; found: 399.1369.

methyl (Z)-3-(3-acetamido-3-methyl-1-tosylbut-1-en-2-yl)-4-hydroxybenzoate (3ka)



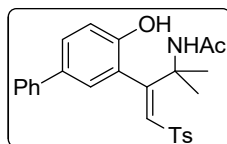
This compound was obtained in 58% yield (50.0 mg) as light yellow solid, m.p.: 191-192 °C. Eluent: PE/EA = 3/1, R_f = 0.4.

^1H NMR (400 MHz, CDCl_3): δ 10.65 (s, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.49 (s, 1H), 7.34 (d, J = 8.1 Hz, 2H), 6.94-6.91 (m, 2H), 6.08 (s, 1H), 3.85 (s, 3H), 2.43 (s, 3H), 2.17 (s, 3H), 1.84 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 166.7, 159.1, 156.0, 145.0, 138.5, 132.1, 131.2, 130.2, 130.0, 127.5, 126.0, 120.8, 117.3, 55.3, 52.0, 28.0, 26.2, 24.2, 21.7.

HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{26}\text{NO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 432.1476; found: 432.1475.

(Z)-N-(3-(4-hydroxy-[1,1'-biphenyl]-3-yl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3la)



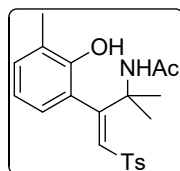
This compound was obtained in 72% yield (64.9 mg) as light yellow solid, m.p.: 175-177 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

^1H NMR (400 MHz, CDCl_3): δ 9.96 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.50-7.41 (m, 3H), 7.38 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.33-7.25 (m, 1H), 7.01-6.96 (m, 2H), 6.93 (s, 1H), 6.17 (s, 1H), 2.41 (s, 3H), 2.16 (s, 3H), 1.86 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 157.2, 154.1, 144.8, 140.4, 138.7, 132.0, 130.6, 130.1, 128.9, 127.4, 126.9, 126.7, 126.4, 126.3, 117.8, 55.4, 28.2, 26.4, 24.3, 21.7.

HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{28}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 450.1734; found: 450.1729.

(Z)-N-(3-(2-hydroxy-3-methylphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ma)



This compound was obtained in 64% yield (49.8 mg) as light yellow solid, m.p.: 205-207 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

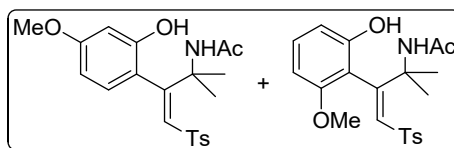
^1H NMR (400 MHz, CDCl_3): δ 9.81 (s, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 6.6 Hz, 1H), 6.93 (brs, 1H), 6.66-6.57 (m, 2H), 6.09 (s, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 2.14 (s, 3H), 1.82 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 157.7, 152.3, 144.7, 138.9, 131.0, 130.2, 130.0, 127.3, 126.4, 125.6, 125.3, 118.3, 55.3, 28.1, 26.3, 24.2, 21.7, 16.4.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 388.1577; found: 388.1572.

(Z)-N-(3-(2-hydroxy-4-methoxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3na) & (Z)-N-(3-(2-hydroxy-6-methoxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)

acetamide (**3na'**)



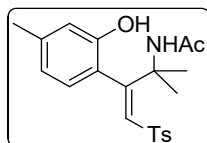
This compound was obtained in 54% yield (43.4 mg) as light yellow oil. Eluent: PE/EA = 2/1, R_f = 0.7. An inseparable mixture of two regio isomers was obtained, and the ratio was determined to be **3na/3na'** = 5/1 by $^1\text{H-NMR}$ analysis.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.89 (s, 0.83H), 9.84 (s, 0.17H), 7.77 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.09 (t, J = 8.2 Hz, 0.17H), 7.02 (brs, 0.83H), 6.93 (brs, 0.17H), 6.65 (d, J = 8.4 Hz, 0.83H), 6.59-6.53 (m, 0.17H), 6.47 (s, 0.83H), 6.33-6.29 (m, 1H), 6.08 (s, 6H), 3.74 (s, 2.49H), 3.71 (s, 0.51H), 2.41 (s, 3H), 2.13 (s, 2.49H), 2.12 (s, 0.51H), 1.91 (s, 0.51H), 1.79 (s, 2.49H), 1.35 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.7, 171.5, 161.3, 157.5, 156.6, 155.7, 155.6, 153.4, 144.7, 144.5, 138.9, 138.8, 131.0, 130.5, 130.0, 129.9, 129.8, 128.5, 127.3, 127.2, 118.9, 115.9, 110.5, 105.5, 101.9, 101.3, 55.5, 55.3, 28.3, 28.0, 26.7, 26.2, 24.20, 24.15, 21.6.

HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 404.1526; found: 404.1521.

(*Z*)-*N*-(3-(2-hydroxy-4-methylphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (**3oa**)



This compound was obtained in 62% yield (47.3 mg) as light yellow oil. Eluent: PE/EA = 2/1, R_f = 0.8.

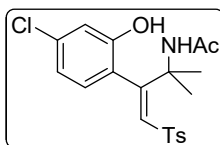
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.68 (s, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.88 (brs, 1H), 6.74 (s, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.07 (s, 1H), 2.41 (s, 3H), 2.25 (s, 3H), 2.13 (s, 3H), 1.80 (s, 3H), 1.36 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.6, 157.6, 154.2, 144.7, 140.4, 138.9, 130.3, 130.0, 127.6, 127.3, 123.4, 119.6, 117.8, 55.4, 28.1, 26.3, 24.2, 21.7, 21.3.

HRMS (ESI) calculated for C₂₁H₂₆NO₄S ([M+H]⁺): 388.1577; found: 388.1573.

(Z)-N-(3-(4-chloro-2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide

(3pa)



This compound was obtained in 82% yield (66.8 mg) as light yellow solid, m.p.: 174-176 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

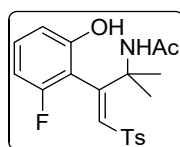
¹H NMR (400 MHz, CDCl₃): δ 10.17 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.93-6.91 (m, 2H), 6.73-6.66 (m, 2H), 6.07 (s, 1H), 2.42 (s, 3H), 2.14 (s, 3H), 1.80 (s, 3H), 1.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.8, 156.3, 155.4, 144.9, 138.6, 135.4, 130.9, 130.1, 128.7, 127.4, 124.7, 119.0, 117.6, 55.2, 28.1, 26.3, 24.2, 21.7.

HRMS (ESI) calculated for C₂₀H₂₃ClNO₄S ([M+H]⁺): 408.1031; found: 408.1027.

(Z)-N-(3-(2-fluoro-6-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide

(3qa)



This compound was obtained in 66% yield (51.6 mg) as light yellow solid, m.p.: 130-132 °C. Eluent: PE/EA = 2/1, R_f = 0.8.

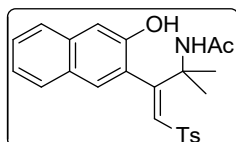
¹H NMR (400 MHz, CDCl₃): δ 10.12 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 15.2, 8.1 Hz, 1H), 6.94 (brs, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.49 (t, *J* = 8.7 Hz, 1H), 6.13 (s, 1H), 2.42 (s, 3H), 2.16 (s, 3H), 1.88 (s, 3H), 1.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.7, 158.9 (d, *J* = 242.8 Hz), 156.3 (d, *J* = 4.7 Hz), 150.5, 144.9, 138.6, 132.3, 130.2, 130.1, 127.4, 114.8 (d, *J* = 19.7 Hz), 113.1 (d, *J* = 1.9 Hz), 105.6 (d, *J* = 22.3 Hz), 55.3, 27.7, 26.7, 24.3, 21.7.

¹⁹F NMR (376 MHz, CDCl₃): δ -113.82.

HRMS (ESI) calculated for C₂₀H₂₃FNO₄S ([M+H]⁺): 392.1327; found: 392.1321.

(Z)-N-(3-(3-hydroxynaphthalen-2-yl)-2-methyl-4-tosylbut-3-en-2-yl)acetamide (3ra)



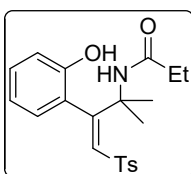
This compound was obtained in 47% yield (39.7 mg) as light yellow oil. Eluent: PE/EA = 2/1, R_f = 0.7.

¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29-7.22 (m, 3H), 6.89 (brs, 1H), 6.18 (s, 1H), 2.41 (s, 3H), 2.17 (s, 3H), 1.88 (s, 3H), 1.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.9, 157.0, 152.3, 144.9, 138.7, 135.2, 130.8, 130.1, 129.1, 127.4, 127.3, 127.1, 126.8, 126.5, 123.6, 111.5, 55.5, 28.2, 26.2, 24.3, 21.7.

HRMS (ESI) calculated for C₂₄H₂₆NO₄S ([M+H]⁺): 424.1577; found: 424.1571.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)propionamide (3sa)



This compound was obtained in 78% yield (60.4 mg) as light yellow oil. Eluent: PE/EA = 3/1, R_f = 0.7.

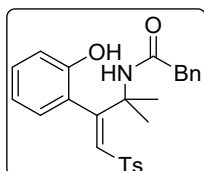
¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.81 (brs, 1H), 6.78-6.70 (m, 2H), 6.08 (s, 1H), 2.50-2.31 (m, 5H), 1.82 (s, 3H), 1.35 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 174.8, 157.5, 154.4, 144.7, 138.8, 130.3, 130.1, 130.0, 127.8, 127.3, 126.2, 118.7, 117.3, 55.1, 30.1, 28.2, 26.3, 21.7, 9.0.

HRMS (ESI) calculated for $C_{21}H_{26}NO_4S$ ($[M+H]^+$): 388.1577; found: 388.1572.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-tosylbut-3-en-2-yl)-2-phenylacetamide

(3ta)



This compound was obtained in 65% yield (54.7 mg) as white solid. Eluent: PE/EA = 3/1. $R_f = 0.7$.

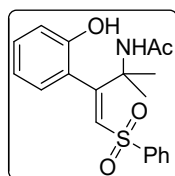
1H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.79 (d, $J = 7.9$ Hz, 2H), 7.42-7.28 (m, 7H), 7.19-7.16 (m, 1H), 6.91 (d, $J = 8.1$ Hz, 1H), 6.75-6.70 (m, 2H), 6.65 (s, 1H), 6.10 (s, 1H), 3.85-3.71 (m, 2H), 2.42 (s, 3H), 1.70 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 156.8, 154.3, 144.8, 138.8, 134.5, 130.5, 130.1, 130.0, 129.0, 127.8, 127.5, 127.4, 126.0, 118.7, 117.3, 55.4, 44.2, 27.7, 26.3, 21.7.

HRMS (ESI) calculated for $C_{26}H_{28}NO_4S$ ($[M+H]^+$):450.1734; found:450.1727.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-(phenylsulfonyl)but-3-en-2-yl)acetamide

(3ab)



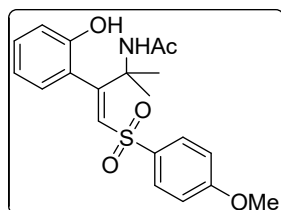
This compound was obtained in 65% yield (46.8 mg) as light yellow oil. Eluent: PE/EA = 3/1, $R_f = 0.4$.

1H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.91 (d, $J = 7.4$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.79-6.71 (m, 2H), 6.11 (s, 1H), 2.14 (s, 3H), 1.82 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 157.9, 154.3, 141.7, 133.8, 130.2, 130.0, 129.5, 127.8, 127.3, 126.0, 118.8, 117.4, 55.4, 28.0, 26.3, 24.3.

HRMS (ESI) calculated for C₁₉H₂₂NO₄S ([M+H]⁺): 360.1264; found: 360.1260.

(Z)-N-(3-(2-hydroxyphenyl)-4-((4-methoxyphenyl)sulfonyl)-2-methylbut-3-en-2-yl)acetamide (3ac)



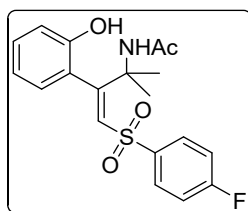
This compound was obtained in 70% yield (55.5 mg) as light yellow solid, m.p.: 120-122 °C. Eluent: PE/EA = 3/1, R_f = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.01-6.96 (m, 3H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.78-6.69 (m, 2H), 6.09 (s, 1H), 3.85 (s, 3H), 2.15 (s, 3H), 1.81 (s, 3H), 1.35 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.7, 163.7, 156.9, 154.3, 133.3, 130.6, 130.1, 129.5, 127.8, 126.1, 118.6, 117.3, 114.6, 55.8, 55.3, 28.0, 26.3, 24.2.

HRMS (ESI) calculated for C₂₀H₂₄NO₅S ([M+H]⁺): 390.1370; found: 390.1361.

(Z)-N-(4-((4-fluorophenyl)sulfonyl)-3-(2-hydroxyphenyl)-2-methylbut-3-en-2-yl)acetamide (3ad)



This compound was obtained in 54% yield (40.7 mg) as light yellow oil. Eluent: PE/EA = 3/1, R_f = 0.5.

¹H NMR (400 MHz, CDCl₃): δ 9.75 (s, 1H), 7.97-7.88 (m, 2H), 7.25-7.17 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.80 (brs, 1H), 6.78-6.74 (m, 2H), 6.09 (s, 1H), 2.15 (s, 3H), 1.81 (s, 3H), 1.36 (s, 3H).

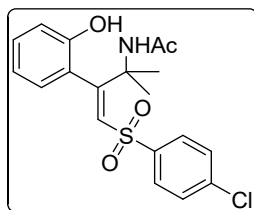
¹³C NMR (100 MHz, CDCl₃): δ 171.7, 165.8 (d, *J* = 256.4 Hz), 158.2, 154.3, 137.8 (d, *J* = 3.0 Hz), 130.33, 130.31, 130.24, 129.9, 127.7, 125.9, 118.9, 117.5, 116.8 (d, *J*

= 22.5 Hz), 55.4, 28.0, 26.3, 24.3.

¹⁹F NMR (376 MHz, CDCl₃): δ -103.31.

HRMS (ESI) calculated for C₁₉H₂₁FNO₄S ([M+H]⁺): 378.1170; found: 378.1167.

(Z)-N-(4-((4-chlorophenyl)sulfonyl)-3-(2-hydroxyphenyl)-2-methylbut-3-en-2-yl)acetamide (3ae)



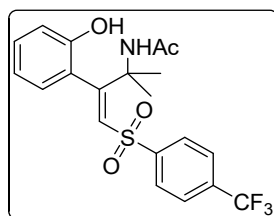
This compound was obtained in 77% yield (60.8 mg) as light yellow oil. Eluent: PE/EA = 3/1, R_f = 0.6.

¹H NMR (400 MHz, CDCl₃): δ 9.76 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.22-7.17 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.83 (s, 1H), 6.78-6.71 (m, 2H), 6.08 (s, 1H), 2.14 (s, 3H), 1.81 (s, 3H), 1.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.7, 158.5, 154.3, 140.5, 140.2, 130.3, 129.8, 129.6, 128.9, 127.7, 125.9, 118.9, 117.4, 55.4, 28.0, 26.3, 24.3.

HRMS (ESI) calculated for C₁₉H₂₁ClNO₄S ([M+H]⁺): 394.0875; found: 394.0873.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)but-3-en-2-yl)acetamide (3af)



This compound was obtained in 49% yield (41.8 mg) as light yellow oil. Eluent: PE/EA = 3/1, R_f = 0.6.

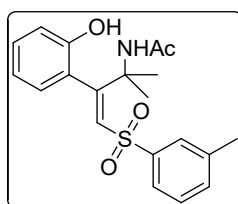
¹H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.24-7.16 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.82 (s, 1H), 6.79-6.72 (m, 2H), 6.08 (s, 1H), 2.15 (s, 3H), 1.83 (s, 3H), 1.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.7, 159.5, 154.2, 145.1, 135.5 (q, *J* = 33.4 Hz), 130.4, 129.0, 128.0, 127.6, 126.7 (q, *J* = 3.4 Hz), 125.7, 123.2 (q, *J* = 273.2 Hz), 118.9, 117.5, 55.5, 28.0, 26.3, 24.2.

¹⁹F NMR (376 MHz, CDCl₃): δ -63.13.

HRMS (ESI) calculated for C₂₀H₂₁F₃NO₄S ([M+H]⁺): 428.1138; found: 428.1131.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-(m-tolylsulfonyl)but-3-en-2-yl)acetamide (3ag)



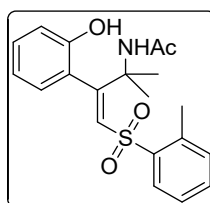
This compound was obtained in 64% yield (47.6 mg) as light yellow oil. Eluent: PE/EA = 3/1, R_f = 0.5.

¹H NMR (400 MHz, CDCl₃): δ 9.79 (s, 1H), 7.72-7.69 (m, 2H), 7.43-7.38 (m, 2H), 7.19 (t, *J* = 8.3 Hz, 1H), 6.93-6.88 (m, 2H), 6.82-6.71 (m, 2H), 6.11 (s, 1H), 2.42 (s, 3H), 2.15 (s, 3H), 1.82 (s, 3H), 1.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.7, 157.6, 154.4, 141.5, 139.8, 134.5, 130.2, 129.3, 127.8, 127.6, 126.1, 124.4, 118.8, 117.4, 55.3, 28.0, 26.3, 24.3, 21.4.

HRMS (ESI) calculated for C₂₀H₂₄NO₄S ([M+H]⁺): 374.1421; found: 374.1416.

(Z)-N-(3-(2-hydroxyphenyl)-2-methyl-4-(o-tolylsulfonyl)but-3-en-2-yl)acetamide (3ah)



This compound was obtained in 67% yield (49.8 mg) as light yellow solid, m.p.: 168-169 °C. Eluent: PE/EA = 3/1, R_f = 0.4.

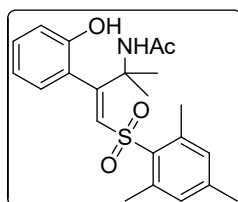
¹H NMR (400 MHz, CDCl₃): δ 9.78 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.4

Hz, 1H), 7.38-7.27 (m, 2H), 7.19 (t, $J = 7.7$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 6.88 (brs, 1H), 6.82-6.75 (m, 2H), 6.11 (s, 1H), 2.68 (s, 3H), 2.15 (s, 3H), 1.84 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 158.4, 154.4, 139.8, 137.5, 133.8, 132.6, 130.2, 129.9, 128.4, 127.4, 126.7, 126.1, 118.8, 117.4, 55.4, 27.3, 26.3, 24.3, 20.6.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 374.1421; found: 374.1418.

(Z)-N-(3-(2-hydroxyphenyl)-4-(mesitylsulfonyl)-2-methylbut-3-en-2-yl)acetamide (3ai)



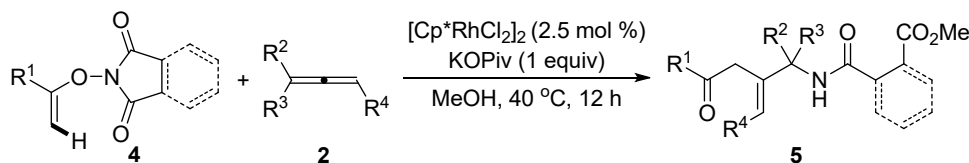
This compound was obtained in 60% yield (48.5 mg) as light yellow oil. Eluent: PE/EA = 3/1, $R_f = 0.55$.

^1H NMR (400 MHz, CDCl_3): δ 9.82 (s, 1H), 7.19 (t, $J = 7.7$ Hz, 1H), 6.94-6.91 (m, 3H), 6.85 (brs, 1H), 6.80 (d, $J = 7.3$ Hz, 1H), 6.75 (t, $J = 7.3$ Hz, 1H), 6.14 (s, 1H), 2.65 (s, 6H), 2.27 (s, 3H), 2.15 (s, 3H), 1.83 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 156.7, 154.5, 143.3, 139.3, 135.7, 132.2, 131.7, 130.0, 127.5, 126.3, 118.8, 117.4, 55.3, 27.2, 26.4, 24.4, 22.8, 21.0.

HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 402.1734; found: 402.1730.

General procedure for the carboamination of *N*-enoxy imides with sulfonyl allenes:

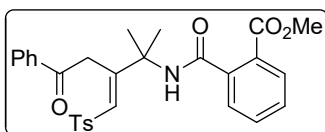


The mixture of *N*-enoxy imide **4** (0.4 mmol, 2.0 equiv), sulfonyl allene **2** (0.2 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and KOPIv (0.2 mmol, 1.0 equiv) in MeOH (2.0

mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC to afford the corresponding allylamine derivatives **5**.

Characterization of products:

(E)-methyl 2-((2-methyl-5-oxo-5-phenyl-3-(tosylmethylene)pentan-2-yl) carbamoyl)benzoate (5a)



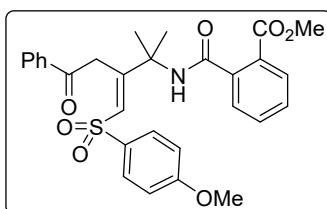
This compound was obtained in 51% yield (52.9 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.86 (brs, 1H), 7.94 (d, $J = 7.8$ Hz, 2H), 7.88-7.83 (m, 3H), 7.79 (d, $J = 7.7$ Hz, 1H), 7.59-7.53 (m, 2H), 7.50 (d, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 6.11 (s, 1H), 3.75 (s, 3H), 3.55 (s, 2H), 2.42 (s, 3H), 1.45 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 199.4, 167.3, 167.0, 156.1, 144.4, 138.4, 138.2, 137.5, 133.3, 132.4, 130.1, 129.8, 129.3, 128.7, 128.3, 127.9, 127.5, 118.1, 52.6, 48.1, 41.0, 28.1, 21.8.

HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{30}\text{NO}_6\text{S}$ ($[\text{M}^+\text{H}]^+$): 520.1788; found: 520.1793.

(E)-methyl 2-((3-(((4-methoxyphenyl)sulfonyl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)carbamoyl)benzoate (5b)



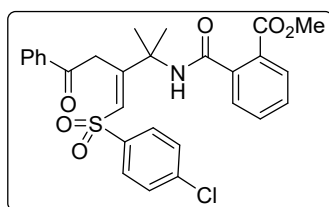
This compound was obtained in 47% yield (50.3 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

¹H NMR (400 MHz, CDCl₃): δ 8.80 (brs, 1H), 7.95-7.85 (m, 5H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60-7.53 (m, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.11 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.54 (s, 2H), 1.44 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 199.5, 167.3, 167.0, 163.6, 155.3, 138.2, 137.5, 133.4, 132.9, 132.4, 130.9, 130.1, 129.8, 129.4, 128.7, 128.3, 128.0, 118.8, 114.4, 55.7, 52.6, 48.1, 41.0, 28.0.

HRMS (ESI) calculated for C₂₉H₃₀NO₇S ([M+H]⁺): 536.1738; found: 536.1728.

(*E*)-methyl 2-((3-(((4-chlorophenyl)sulfonyl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)carbamoyl)benzoate (5c)



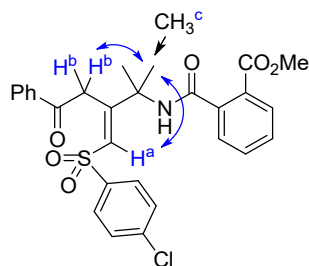
This compound was obtained in 42% yield (45.5 mg) as light yellow oil. Eluent: PE/EA = 2/1. *R_f* = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 8.76 (brs, 1H), 7.94-7.91 (m, 4H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.61-7.55 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.49-7.43 (m, 4H), 6.12 (s, 1H), 3.76 (s, 3H), 3.52 (s, 2H), 1.45 (s, 6H).

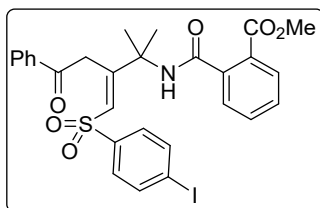
¹³C NMR (100 MHz, CDCl₃): δ 199.5, 167.4, 166.9, 156.4, 140.1, 139.7, 138.1, 137.3, 133.5, 132.5, 130.2, 130.1, 129.4, 129.2, 129.1, 128.7, 128.3, 128.0, 117.8, 52.6, 48.2, 41.2, 28.0.

HRMS (ESI) calculated for C₂₈H₂₇ClNO₆S ([M+H]⁺): 540.1242; found: 540.1235.

¹H-¹H NOESY:



(E)-methyl 2-((3-(((4-iodophenyl)sulfonyl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)carbamoyl)benzoate (5d)



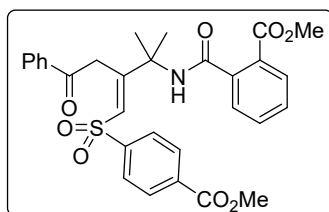
This compound was obtained in 39% yield (49.2 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.78 (brs, 1H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.89-7.85 (m, 3H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.60-7.55 (m, 2H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.48-7.43 (m, 2H), 6.10 (s, 1H), 3.76 (s, 3H), 3.52 (s, 2H), 1.45 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 199.5, 167.3, 166.9, 156.6, 140.9, 138.4, 138.1, 137.3, 133.5, 132.5, 131.3, 130.2, 130.1, 129.0, 128.8, 128.6, 128.3, 127.9, 125.2, 117.4, 101.4, 52.6, 48.2, 41.2, 28.0.

HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{27}\text{INO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 632.0598; found: 632.0592.

(E)-methyl 2-((3-(((4-(methoxycarbonyl)phenyl)sulfonyl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)carbamoyl)benzoate (5e)



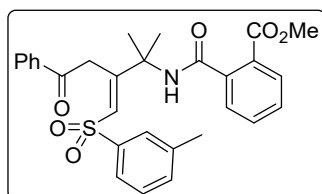
This compound was obtained in 52% yield (58.6 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.85 (brs, 1H), 8.16 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H), 7.93 (d, $J = 7.6$ Hz, 2H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 7.61-7.54 (m, 2H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.46-7.43 (m, 2H), 6.14 (s, 1H), 3.95 (s, 3H), 3.75 (s, 3H), 3.54 (s, 2H), 1.45 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 199.5, 167.3, 166.9, 165.8, 157.2, 145.1, 138.1, 137.2, 134.4, 133.5, 132.5, 130.3, 130.2, 130.1, 129.1, 128.9, 128.7, 128.3, 127.9, 127.6, 125.3, 117.0, 52.8, 52.6, 48.2, 41.2, 28.0.

HRMS (ESI) calculated for C₃₀H₃₀NO₈S ([M+H]⁺): 564.1687; found: 564.1683.

(E)-methyl 2-((2-methyl-5-oxo-5-phenyl-3-((m-tolylsulfonyl)methylene)pentan-2-yl)carbamoyl)benzoate (5f)



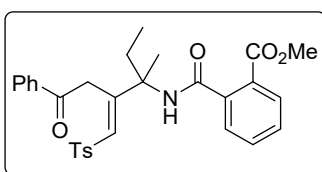
This compound was obtained in 43% yield (44.8 mg) as light yellow oil. Eluent: PE/EA = 2/1. R_f = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 8.92 (brs, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.79-7.74 (m, 3H), 7.70 (s, 1H), 7.58-7.53 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.40-7.39 (m, 1H), 6.10 (s, 1H), 3.74 (s, 3H), 3.58 (s, 2H), 2.41 (s, 3H), 1.46 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 199.5, 167.4, 166.9, 156.4, 140.1, 139.7, 138.1, 137.3, 133.5, 132.5, 130.2, 130.1, 129.4, 129.2, 129.1, 128.7, 128.3, 128.0, 117.8, 52.6, 48.2, 40.9, 28.1, 21.5.

HRMS (ESI) calculated for C₂₉H₃₀NO₆S ([M+H]⁺): 520.1788; found: 520.1784.

(E)-methyl 2-((3-methyl-6-oxo-6-phenyl-4-(tosylmethylene)hexan-3-yl)carbamoyl)benzoate (5g)



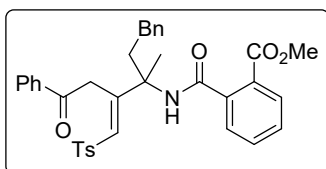
This compound was obtained in 65% yield (69.2 mg) as light yellow oil. Eluent: PE/EA = 2/1. R_f = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 8.68 (brs, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.87-7.81 (m, 4H), 7.59-7.53 (m, 2H), 7.50-7.42 (m, 3H), 7.30-7.26 (m, 2H), 6.08 (s, 1H), 3.75 (s, 3H), 3.67 (d, *J* = 17.3 Hz, 1H), 3.35 (d, *J* = 17.0 Hz, 1H), 2.41 (s, 3H), 2.10-2.03 (m, 1H), 1.79-1.74 (m, 1H), 1.31 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 199.7, 167.3, 167.0, 154.3, 144.4, 138.5, 138.3, 137.5, 133.4, 132.4, 130.0, 129.8, 129.2, 128.7, 128.3, 128.0, 127.5, 120.1, 52.5, 46.9, 44.7, 32.5, 23.8, 21.8, 8.8.

HRMS (ESI) calculated for C₃₀H₃₂NO₆S ([M+H]⁺): 534.1945; found: 534.1941.

(*E*)-methyl 2-((3-methyl-6-oxo-1,6-diphenyl-4-(tosylmethylene)hexan-3-yl)carbamoyl)benzoate (5h)



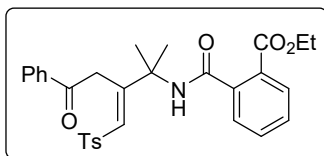
This compound was obtained in 59% yield (71.8 mg) as light yellow oil. Eluent: PE/EA = 2/1. R_f = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 8.61 (brs, 1H), 7.93-7.88 (m, 4H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.59-7.53 (m, 2H), 7.50-7.42 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.17-7.13 (m, 3H), 6.15 (s, 1H), 3.74-3.68 (m, 4H), 3.38 (d, *J* = 17.2 Hz, 1H), 2.69-2.61 (m, 1H), 2.57-2.49 (m, 1H), 2.40 (s, 3H), 2.37-2.30 (m, 1H), 2.03-1.95 (m, 1H), 1.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 199.5, 167.5, 167.0, 154.0, 144.5, 142.1, 138.4, 138.2, 137.5, 133.4, 132.4, 130.0, 129.9, 129.8, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 126.0, 120.8, 52.5, 47.2, 44.7, 42.0, 30.7, 24.3, 21.8.

HRMS (ESI) calculated for C₃₆H₃₆NO₆S ([M+H]⁺): 610.2258; found: 610.2251.

(*E*)-ethyl 2-((2-methyl-5-oxo-5-phenyl-3-(tosylmethylene)pentan-2-yl)carbamoyl)benzoate (5i)



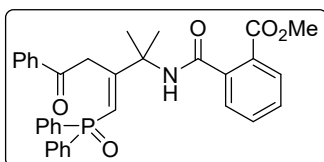
This compound was obtained in 53% yield (56.7 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

^1H NMR (400 MHz, DMSO- d_6): δ 9.51 (s, 1H), 7.91 (d, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.81-7.76 (m, 3H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.62-7.53 (m, 2H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 6.48 (s, 1H), 4.19 (q, $J = 7.3$ Hz, 2H), 3.39 (s, 2H), 2.39 (s, 3H), 1.25 (s, 6H), 1.22 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 167.4, 166.4, 156.3, 144.4, 138.4, 138.3, 137.5, 133.3, 132.2, 130.0, 129.8, 129.6, 128.8, 128.6, 128.3, 127.9, 127.5, 117.7, 61.5, 48.0, 41.0, 28.1, 21.8, 14.3.

HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{32}\text{NO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 534.1945; found: 534.1940.

(E)-methyl 2-((3-((diphenylphosphoryl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)carbamoyl)benzoate (5j)



This compound was obtained in 62% yield (70.0 mg) as white solid. Eluent: PE/EA = 1/2. $R_f = 0.5$.

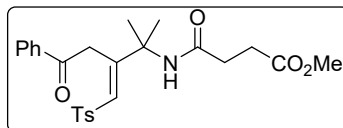
^1H NMR (400 MHz, CD_3OD): δ 8.02 (d, $J = 7.9$ Hz, 2H), 7.82-7.76 (m, 5H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.56-7.53 (m, 3H), 7.50-7.46 (m, 8H), 6.26-6.21 (m, 1H), 3.74 (s, 3H), 3.57 (s, 2H), 1.47 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 199.6, 167.4, 167.1, 164.9 (d, $J = 4.3$ Hz), 138.4, 138.1, 133.9, 132.9, 132.0, 131.9, 131.3, 131.2, 129.9, 129.6, 129.3, 128.8, 128.7, 128.5, 128.4, 128.3, 127.7, 125.8, 123.4, 105.8 (d, $J = 100.9$ Hz), 52.3, 47.8, 41.0 (d, $J = 11.1$ Hz), 28.9.

^{31}P NMR (162 MHz, CDCl_3): δ 27.37.

HRMS (ESI) calculated for $\text{C}_{34}\text{H}_{33}\text{NO}_5\text{P}$ ($[\text{M}+\text{H}]^+$): 566.2091; found: 566.2088.

(E)-methyl 4-((2-methyl-5-oxo-5-phenyl-3-(tosylmethylene)pentan-2-yl)amino)-4-oxobutanoate (5k)



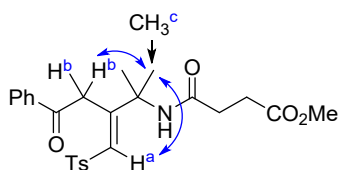
This compound was obtained in 52% yield (48.9 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.45 (brs, 1H), 7.88 (d, $J = 7.9$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.58-7.55 (m, 1H), 7.46-7.43 (m, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 6.06 (s, 1H), 3.64 (s, 3H), 3.32 (s, 2H), 2.69-2.63 (m, 4H), 2.43 (s, 3H), 1.32 (s, 6H).

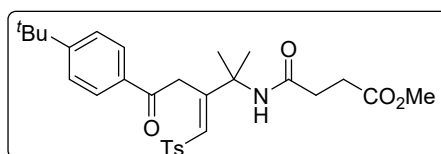
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 198.9, 173.3, 170.6, 156.1, 144.4, 138.4, 137.3, 133.5, 129.8, 128.7, 128.2, 127.4, 52.0, 48.4, 40.6, 31.8, 29.0, 27.8, 21.8.

HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{30}\text{NO}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 472.1788; found: 472.1789.

^1H - ^1H NOESY:



(E)-methyl 4-((5-(4-(tert-butyl)phenyl)-2-methyl-5-oxo-3-(tosylmethylene)pentan-2-yl)amino)-4-oxobutanoate (5l)



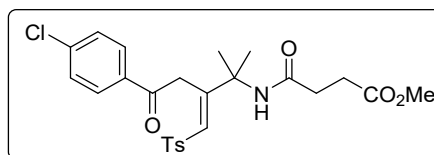
This compound was obtained in 48% yield (50.5 mg) as light yellow oil. Eluent: PE/EA = 2/1. $R_f = 0.4$.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.40 (brs, 1H), 7.84-7.79 (m, 4H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 6.07 (s, 1H), 3.64 (s, 3H), 3.28 (s, 2H), 2.70-2.65 (m, 4H), 2.43 (s, 3H), 1.34 (s, 9H), 1.31 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 198.7, 173.3, 170.6, 157.4, 156.1, 144.4, 138.5, 134.7, 129.8, 128.3, 127.5, 125.7, 52.0, 48.4, 40.7, 35.3, 31.8, 31.2, 29.1, 27.8, 21.8.

HRMS (ESI) calculated for C₂₉H₃₈NO₆S ([M+H]⁺): 528.2414; found: 528.2414.

(E)-methyl 4-((5-(4-chlorophenyl)-2-methyl-5-oxo-3-(tosylmethylene)pentan-2-yl)amino)-4-oxobutanoate (5m)



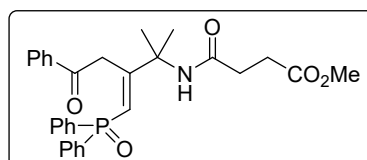
This compound was obtained in 67% yield (67.6 mg) as light yellow oil. Eluent: PE/EA = 2/1. R_f = 0.4.

¹H NMR (400 MHz, CDCl₃): δ 8.53 (brs, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.04 (s, 1H), 3.64 (s, 3H), 3.30 (s, 2H), 2.69-2.63 (m, 4H), 2.43 (s, 3H), 1.32 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 197.7, 173.3, 170.6, 156.3, 144.5, 139.9, 138.4, 135.7, 129.9, 129.7, 129.0, 127.4, 52.0, 48.2, 40.6, 31.8, 29.0, 27.9, 21.8.

HRMS (ESI) calculated for C₂₅H₂₉ClNO₆S ([M+H]⁺): 506.1399; found: 506.1403.

(E)-methyl 4-((3-((diphenylphosphoryl)methylene)-2-methyl-5-oxo-5-phenylpentan-2-yl)amino)-4-oxobutanoate (5n)



This compound was obtained in 55% yield (56.8 mg) as white solid. Eluent: PE/EA = 1/2. R_f = 0.5.

¹H NMR (400 MHz, CDCl₃): δ 9.59 (brs, 1H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.72-7.67 (m, 4H), 7.54-7.49 (m, 3H), 7.45-7.42 (m, 6H), 5.68 (d, *J* = 19.6 Hz, 1H), 3.56 (s, 3H), 3.51 (s, 2H), 2.48-2.44 (m, 4H), 1.45 (s, 6H).

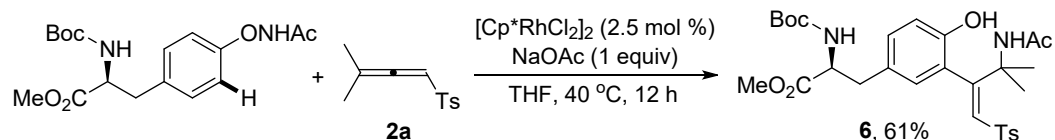
¹³C NMR (100 MHz, CDCl₃): δ 199.4, 173.1, 170.5, 164.6, 137.9, 133.9, 133.1, 132.9, 131.9, 131.2, 131.1, 128.8, 128.7, 128.6, 128.2, 106.1 (d, *J* = 101.8 Hz), 51.8, 48.0, 40.8 (d, *J* = 10.5 Hz), 31.7, 29.1, 28.7.

³¹P NMR (162 MHz, CDCl₃): δ 26.75.

HRMS (ESI) calculated for C₃₀H₃₃NO₅P ([M+H]⁺): 518.2091; found: 518.2088.

III. Synthetic Applications

Late-stage C-H modification of complex molecules:

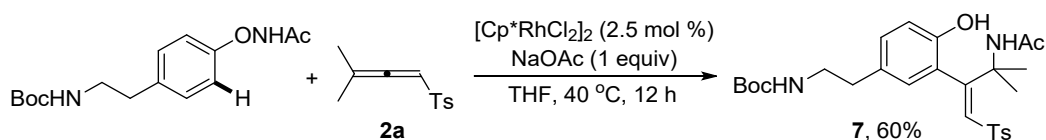


The mixture of tyrosine derivative (0.2 mmol, 1.0 equiv), sulfonfyl allene **2a** (0.2 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and NaOAc (0.2 mmol, 1.0 equiv) in THF (2.0 mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (Eluent: PE/EA = 2/1, $R_f = 0.4$) to afford the desired product **6** in 61% (71.6 mg) isolated yield as yellowish oil. NMR analysis showed that the tautomerization was observed in CDCl_3 .

^1H NMR (400 MHz, CDCl_3): δ 9.77-9.74 (m, 1H), 7.81-7.75 (m, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 6.93-6.81 (m, 3H), 6.51 (s, 1H), 6.10-6.05 (m, 1H), 4.95 (t, $J = 9.0$ Hz, 1H), 4.55-4.42 (m, 1H), 3.63-3.56 (m, 3H), 3.03-2.84 (m, 2H), 2.42 (s, 3H), 2.13 (s, 3H), 1.82-1.80 (m, 3H), 1.39 (s, 9H), 1.34-1.31 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 172.3, 171.7, 157.2, 155.1, 155.0, 153.5, 144.8, 138.8, 131.1, 131.0, 130.4, 130.3, 130.1, 128.6, 128.4, 127.4, 126.13, 126.07, 117.44, 117.36, 80.0, 55.29, 55.25, 54.7, 54.5, 52.2, 52.1, 37.44, 37.36, 28.4, 28.1, 26.3, 24.2, 21.7.

HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{39}\text{N}_2\text{O}_8\text{S}$ ($[\text{M}+\text{H}]^+$): 575.2422; found: 575.2421.



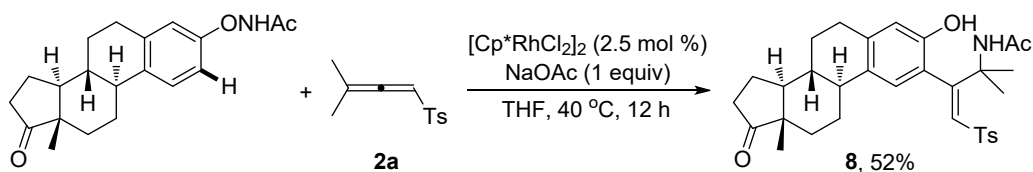
The mixture of dopamine derivative (0.2 mmol, 1.0 equiv), sulfonfyl allene **2a** (0.2 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and NaOAc (0.2 mmol, 1.0 equiv) in THF (2.0 mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted

mixture was purified by preparative TLC (Eluent: PE/EA = 2/1, R_f = 0.4) to afford the desired product **7** in 60% (61.8 mg) isolated yield as light yellow solid, m.p.: 118-121 °C.

^1H NMR (400 MHz, CDCl_3): δ 9.67 (s, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.77 (s, 1H), 6.58 (s, 1H), 6.09 (s, 1H), 4.52 (brs, 1H), 3.33-3.18 (m, 2H), 2.64 (t, J = 6.4 Hz, 2H), 2.43 (s, 3H), 2.14 (s, 3H), 1.81 (s, 3H), 1.41 (s, 9H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 157.2, 156.0, 152.8, 144.7, 138.8, 130.3, 130.2, 130.1, 129.1, 127.8, 127.4, 126.1, 117.4, 79.3, 55.3, 42.1, 35.2, 28.5, 28.1, 26.3, 24.2, 21.7.

HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_6\text{S}$ ($[\text{M}+\text{H}]^+$): 517.2367; found: 517.2366.



The mixture of estrone derivative (0.2 mmol, 1.0 equiv), sulfonfyl allene **2a** (0.2 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) and NaOAc (0.2 mmol, 1.0 equiv) in THF (2.0 mL) was stirred at 40 °C for 12 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (Eluent: PE/EA = 2/1, R_f = 0.5) to afford the desired product **8** in 52% (56.0 mg) isolated yield as light yellow solid, m.p.: 185-186 °C. NMR analysis showed that the tautomerization was observed in CDCl_3 .

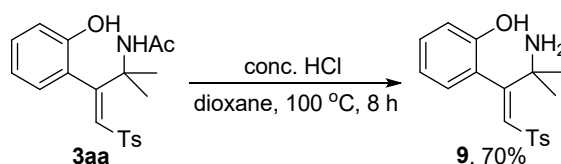
^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.86 (s, 1H), 8.82 (s, 1H), 7.75 (d, J = 7.7 Hz, 2H), 7.42 (s, 2H), 6.80 (s, 1H), 6.46 (s, 1H), 5.99 (s, 1H), 2.75-2.70 (m, 2H), 2.43-2.35 (m, 4H), 2.27-2.21 (m, 1H), 2.08-1.98 (m, 2H), 1.90-1.85 (m, 5H), 1.75-1.69 (m, 1H), 1.58-1.43 (m, 6H), 1.32-1.24 (m, 6H), 0.79 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 221.2, 171.6, 157.7, 157.6, 152.1, 152.0, 144.7, 138.90, 138.86, 138.6, 130.3, 130.2, 130.0, 127.4, 124.6, 124.2, 123.9, 117.0, 116.9,

55.34, 55.31, 50.5, 50.4, 48.1, 48.0, 43.9, 43.8, 31.6, 31.5, 29.31, 29.25, 28.20, 28.15, 26.54, 26.50, 26.46, 26.42, 14.0, 13.9.

HRMS (ESI) calculated for $C_{32}H_{40}NO_5S$ ($[M+H]^+$): 550.2622; found: 550.2619.

Derivatization of compound **3aa**:

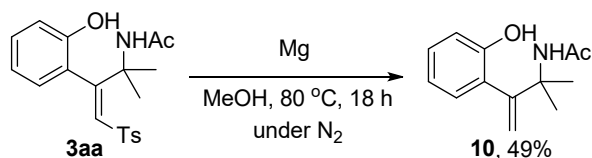


A sealed tube was charged with **3aa** (0.1 mmol, 1.0 equiv) in 1,4-dioxane (0.5 mL), followed by the addition of concentrated HCl solution (0.5 mL). The reaction mixture was stirred at 100 °C for 8 h. Afterwards, the resulted mixture was quenched with saturated NaHCO_3 and extracted by EA for three times. The combined extracts were washed with brine and dried over Na_2SO_4 . The solvent was evaporated, and the residue was purified by preparative TLC (Eluent: PE/EA = 1/1, R_f = 0.5) to afford the desired product **9** in 70% (23.3 mg) isolated yield as light yellow oil.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 7.83 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 7.7 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.3 Hz, 1H), 6.77-6.70 (m, 2H), 6.10 (s, 1H), 2.40 (s, 3H), 1.37 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 158.6, 154.8, 145.0, 138.7, 133.5, 130.1, 129.9, 128.7, 128.0, 127.6, 119.2, 116.9, 53.1, 31.6, 21.7.

HRMS (ESI) calculated for $C_{18}H_{22}NSO_3$ ($[M+H]^+$): 332.1315; found: 332.1316.

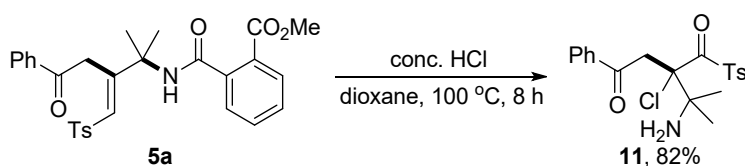


The mixture of **3aa** (0.2 mmol, 1.0 equiv) and Mg (2 mmol, 10 equiv) in MeOH (4.0 mL) was stirred at 80 °C for 18 h under an atmosphere of N_2 . Afterwards, the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and purified by preparative TLC (eluent: PE/EA = 2/1, R_f = 0.6) to give the target product in 49% isolated yield (21.5 mg) as light yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.96 (s, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.93-6.86 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.07 (brs, 1H), 5.51 (s, 1H), 5.15 (s, 1H), 2.03 (s, 3H), 1.38 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 170.1, 155.0, 150.4, 129.1, 129.0, 127.6, 118.8, 116.5, 116.2, 56.5, 29.8, 24.0.

HRMS (ESI) calculated for C₁₃H₁₈NO₂ ([M+H]⁺): 220.1332; found: 220.1331.



A sealed tube was charged with **5a** (0.1 mmol, 1.0 equiv) in 1,4-dioxane (0.5 mL), followed by the addition of concentrated HCl solution (0.5 mL). The reaction mixture was stirred at 100 °C for 8 h. Afterwards, the resulted mixture was quenched with saturated NaHCO₃ and extracted by EA for three times. The combined extracts were washed with brine and dried over Na₂SO₄. The solvent was evaporated, and the residue was purified by preparative TLC (Eluent: PE/EA = 2/1, R_f = 0.6) to afford the desired product **11** in 82% yield (33.3 mg) as light yellow oil.

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 4.83 (s, 2H), 3.47 (s, 2H), 2.40 (s, 3H), 1.09 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 203.7, 198.0, 145.0, 136.5, 136.1, 133.7, 129.8, 128.78, 128.77, 128.2, 62.8, 51.7, 45.9, 25.1, 21.8.

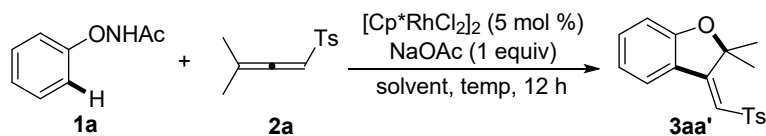
HRMS (ESI) calculated for C₂₀H₂₂Cl₂NSO₄ ([M+Cl]⁻): 442.0652; found: 442.0647.

Switchable assembly of compound **3aa'**:

The mixture of *N*-phenoxyacetamide **1a** (0.1 mmol, 1.0 equiv), sulfonyl allene **2a** (0.1 mmol, 1.0 equiv), [Cp**Rh*Cl₂]₂ (5 mol %) and NaOAc (1 equiv) in the solvent was stirred in an oil bath without exclusion of air or moisture. Afterwards, it was diluted with EtOAc and filtered through a short silica gel column to remove the metal

residues. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 3/1, $R_f = 0.6$) to afford the corresponding product **3aa'**.

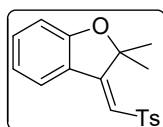
Table S3. Conditions Screening for the Synthesis of **3aa'**.^a



#	solvent	pH of PBS	1a:2a	Temp/°C	yield(%) ^b
1	THF/PBS = 1/1	4.2	1:1	40	19
2	THF/PBS = 1/1	7.0	1:1	40	20
3	THF/PBS = 1/1	9.4	1:1	40	20
4	PBS	7.0	1:1	40	15
5	dioxane/PBS = 1/1	7.0	1:1	40	13
6	MeOH/PBS = 1/1	7.0	1:1	40	25
7	MeOH/PBS = 1/1	7.0	1:1	80	31
8	MeOH/PBS = 1/1	7.0	1:1.5	80	55
9	MeOH/PBS = 1/1	7.0	1:2	80	61
10	MeOH/PBS = 2/1	7.0	1:2	80	60
11	MeOH/PBS = 4/1	7.0	1:2	80	72 (69) ^c
12	MeOH/PBS = 6/1	7.0	1:2	80	66

^aReaction Conditions: **1a** (0.1 mmol), **2a**, [Cp*RhCl₂]₂ (5 mol %), NaOAc (1.0 equiv), solvent (0.5 mL), temperature, 12 h, under air. ^b¹H-NMR yields using 1,3,5-trimethoxybenzene as an internal standard. ^cIsolated yield was reported in the parentheses.

2,2-dimethyl-3-(tosylmethylene)-2,3-dihydrobenzofuran (**3aa'**)

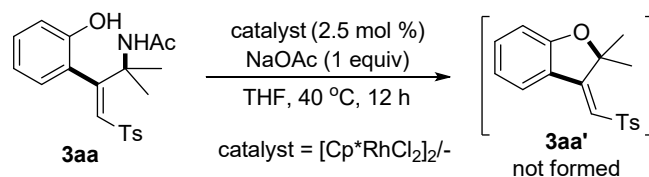


¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.7$ Hz, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.12-7.06 (m, 2H), 5.80 (s, 1H), 2.41 (s, 3H), 1.40 (s, 6H).

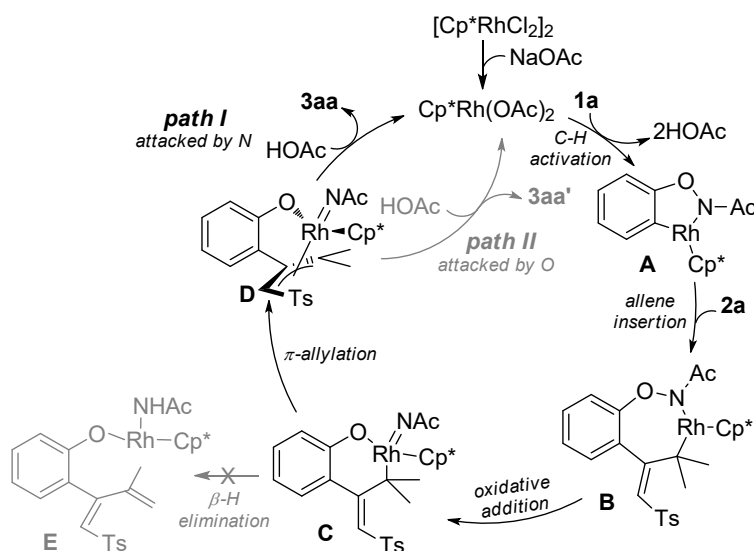
¹³C NMR (100 MHz, CDCl₃): δ 175.9, 155.4, 143.8, 140.0, 133.3, 129.5, 128.8, 127.4, 124.1, 122.5, 110.7, 102.3, 46.8, 29.0, 21.7.

HRMS (ESI) calculated for C₁₈H₁₉SO₃ ([M+H]⁺): 315.1050; found: 315.1050.

Conversion of compound **3aa** to **3aa'**:



Two batches of the mixture of compound **3aa** (0.1 mmol, 1.0 equiv) and NaOAc (1 equiv) in THF (0.1 M) was stirred in an oil bath in the presence or absence of $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %) without exclusion of air or moisture. Afterwards, the reaction was monitored by TLC and no corresponding dihydrobenzofuran product **3aa'** was formed.

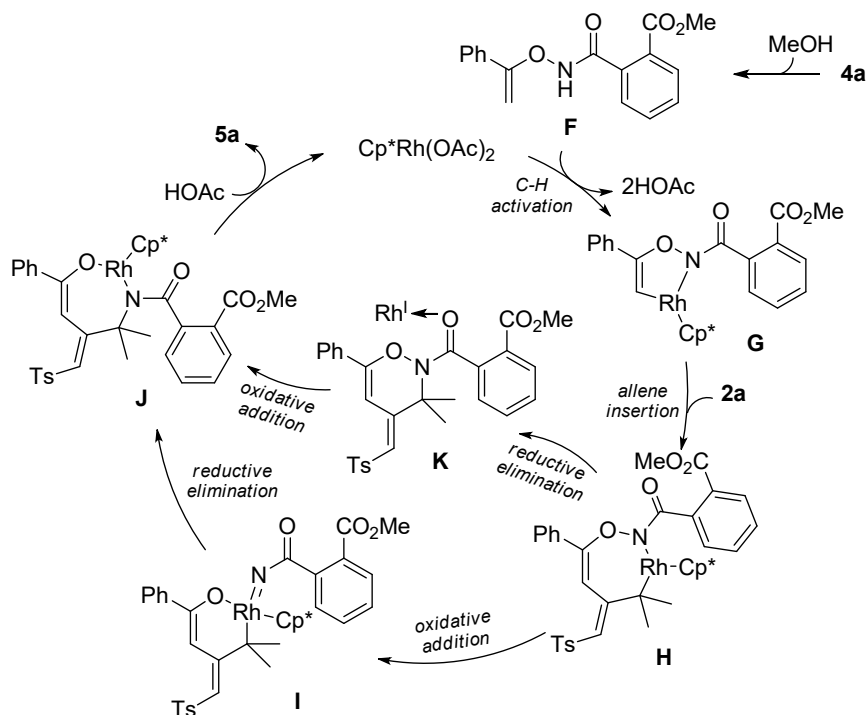


Scheme S1 Proposed Catalytic Cycle for the C-H Coupling of *N*-Phenoxyacetamide with Sulfonyl Allene

Proposed catalytic cycle for *N*-enoxyphthalimide substrate:

Initially, *N*-enoxyphthalimide **4a** converted into the active substrate **F** with the assistance of MeOH, which underwent the Rh(III)-catalyzed N-H/C-H bond cleavage to afford the intermediate **G**. Subsequent allene insertion from **G** delivered the seven-membered intermediate **H**, which underwent the oxidative addition followed by a C-N bond reductive elimination to give intermediate **J**. Alternatively, the direct C-N bond reductive elimination from **H** could also be involved to afford intermediate **K** along

with the generation of Rh(I) species, further O-N bond cleavage re-oxidized the Rh(I) to intermediate **J**. Finally, the protonolysis of intermediate **J** led to the release of desired carboamination product **5a** with the regeneration of active Cp*Rh(OAc)₂ catalyst.



Scheme S2 Proposed Catalytic Cycle for the C-H Coupling of *N*-Enoxyphthalimide with Sulfonyl Allene

IV. X-Ray Crystallographic Data

X-ray crystallographic data of compound **3aa**:

Single crystals of C₂₀H₂₃NO₄S [805-3B] were prepared using the mixed PE/EA solvent at room temperature. A suitable crystal was selected and on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection.

Crystal Data for C₂₀H₂₃NO₄S (*M* = 373.45 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 19.1418(19) Å, *b* = 11.1056(12) Å, *c* = 20.762(2) Å, β = 90.211(11)°, *V* = 4413.7(8) Å³, *Z* = 8, *T* = 149.99(10) K, μ(Mo Kα) = 0.168 mm⁻¹, *D*_{calc} = 1.124 g/cm³, 25767 reflections measured (3.924° ≤ 2θ ≤ 50°), 7719 unique (*R*_{int} =

0.0947, $R_{\text{sigma}} = 0.0922$) which were used in all calculations. The final R_1 was 0.0950 ($I > 2\sigma(I)$) and wR_2 was 0.2662 (all data).

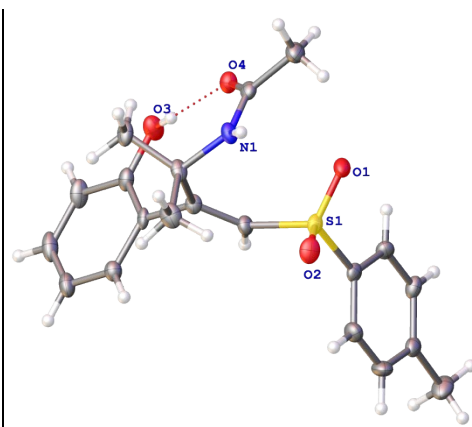


Table S4. Crystal data and structure refinement for 805-3B

Identification code	805-3B
Empirical formula	$C_{20}H_{23}NO_4S$
Formula weight	373.45
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.1418(19)
b/Å	11.1056(12)
c/Å	20.762(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90.211(11)
$\gamma/^\circ$	90
Volume/Å ³	4413.7(8)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.124
μ/mm^{-1}	0.168
F(000)	1584.0
Crystal size/mm ³	0.15 × 0.12 × 0.11
Radiation	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.924 to 50
Index ranges	-22 ≤ h ≤ 21, -13 ≤ k ≤ 13, -24 ≤ l ≤ 19
Reflections collected	25767
Independent reflections	7719 [$R_{\text{int}} = 0.0947$, $R_{\text{sigma}} = 0.0922$]
Data/restraints/parameters	7719/3/487
Goodness-of-fit on F ²	1.054
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0950$, $wR_2 = 0.2462$

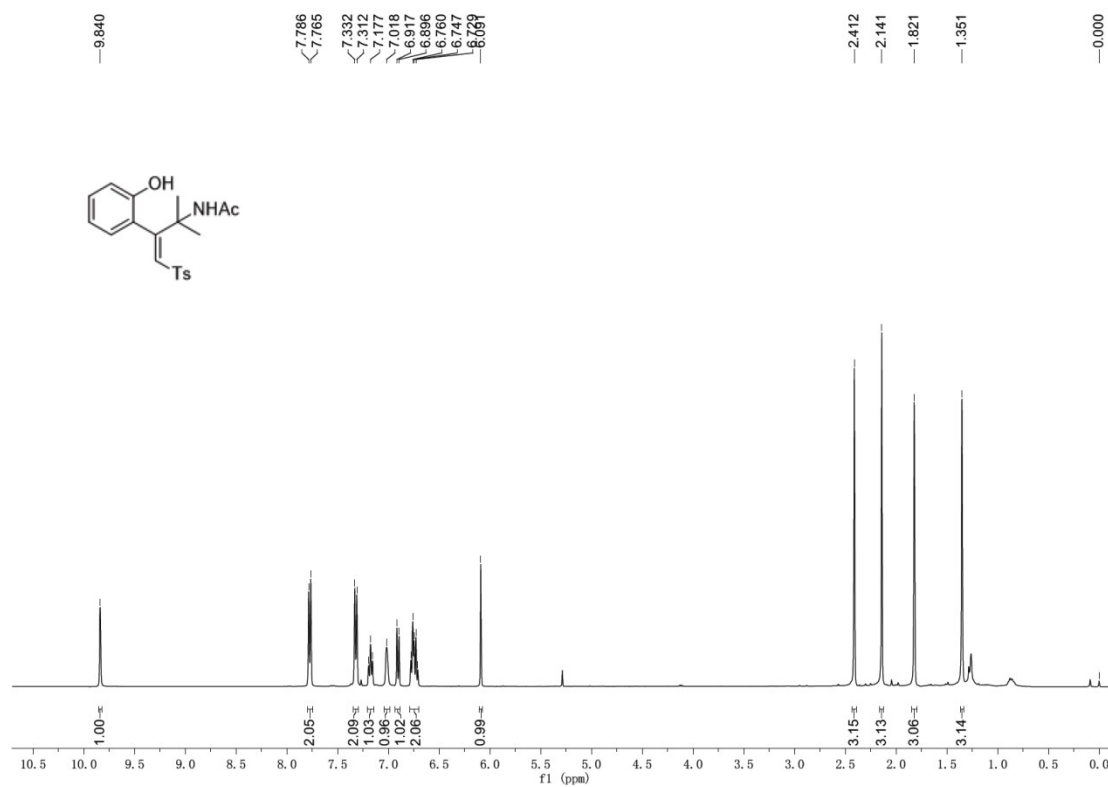
Final R indexes [all data]	$R_1 = 0.1213$, $wR_2 = 0.2662$
Largest diff. peak/hole / e Å ⁻³	0.56/-0.45

V. References

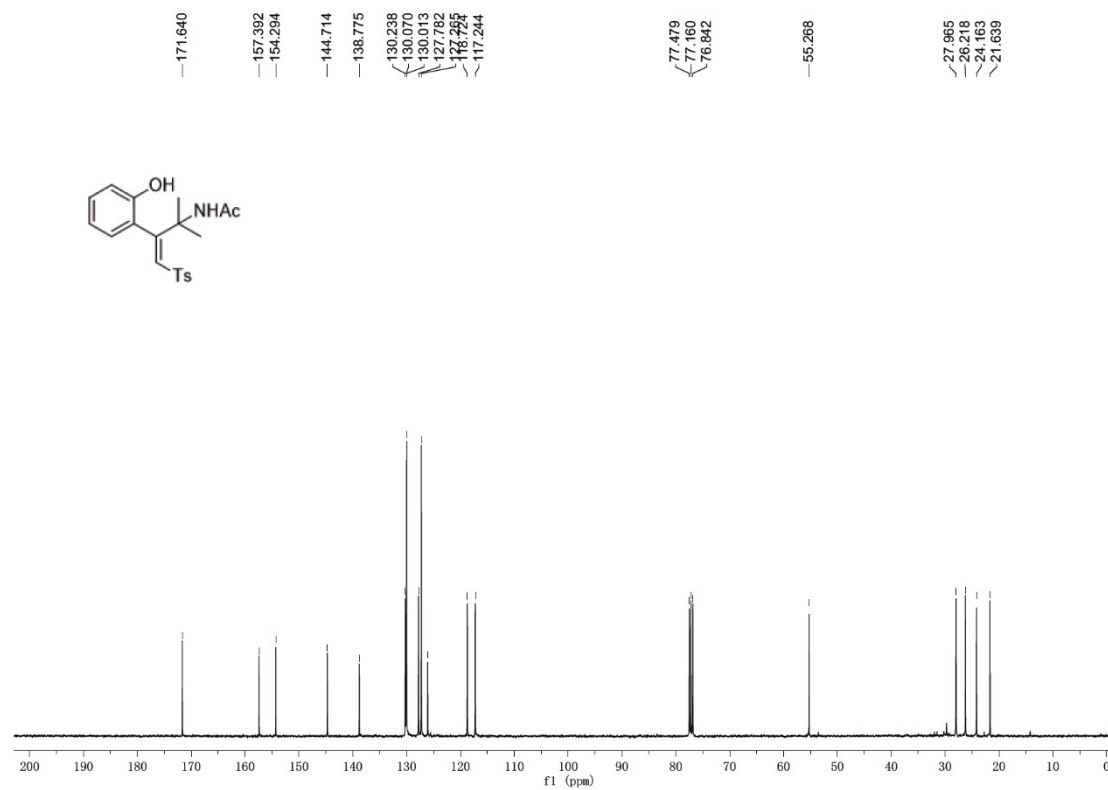
- [S1] (a) Liu, G.; Shen, Y.; Zhou, Z.; Lu, X. *Angew. Chem. Int. Ed.*, **2013**, *52*, 6033. (b) Li, B.; Lan, J.; Wu, D.; You, J. *Angew. Chem. Int. Ed.*, **2015**, *54*, 14008. (c) Wu, Y.; Chen, Z.; Yang, Y.; Zhu, W.; Zhou, B. *J. Am. Chem. Soc.* **2018**, *140*, 42.
- [S2] (a) Phipps, E. J. T.; Rovis, T. *J. Am. Chem. Soc.* **2019**, *141*, 6807. (b) Duchemin, C.; Cramer, N. *Org. Chem. Front.* **2019**, *6*, 209.
- [S3] Tata, R. R.; Hampton, C. S.; Harmata, M. *Adv. Synth. Catal.* **2017**, *359*, 1232.

VI. Copies of ^1H , ^{13}C and ^{19}F NMR spectra

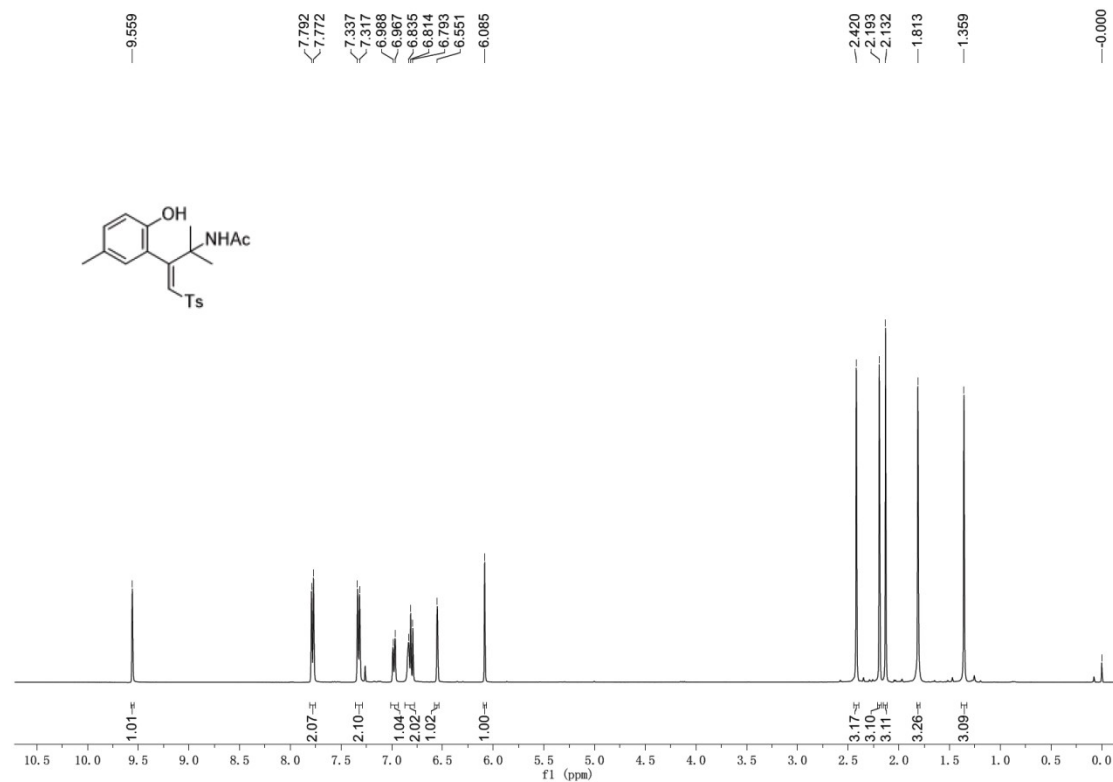
3aa- ^1H NMR (400 MHz, CDCl_3)



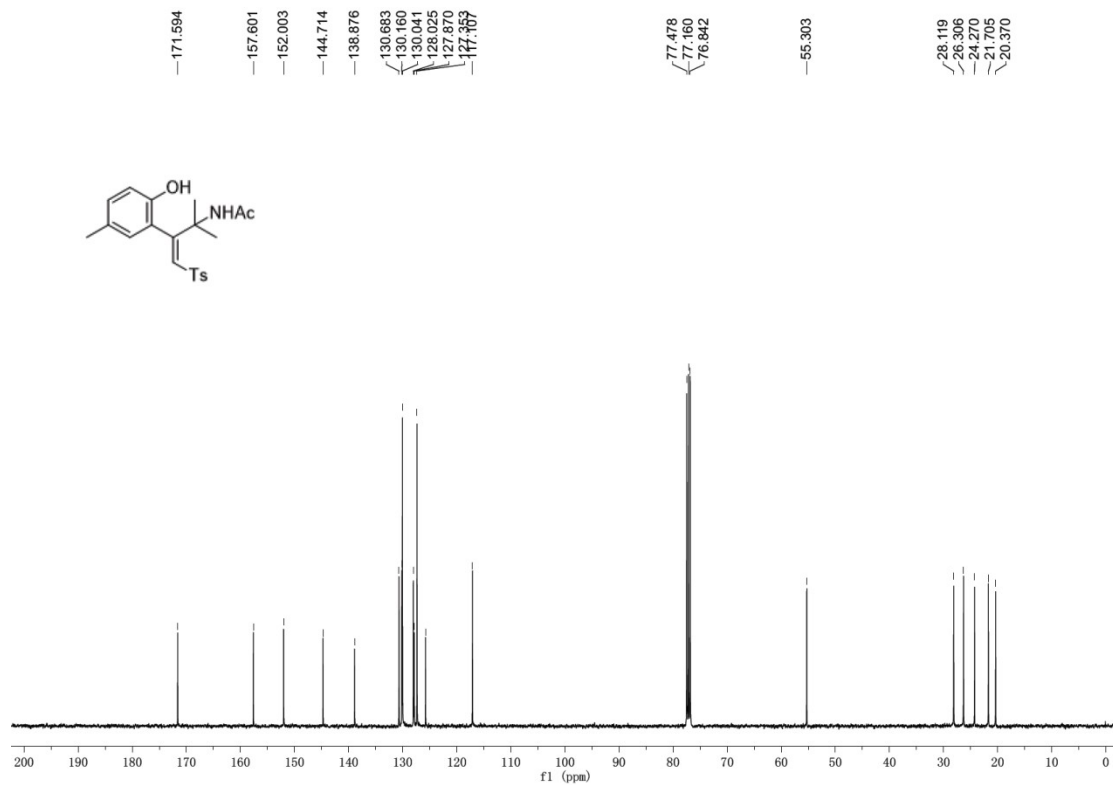
3aa- ^{13}C NMR (100 MHz, CDCl_3)



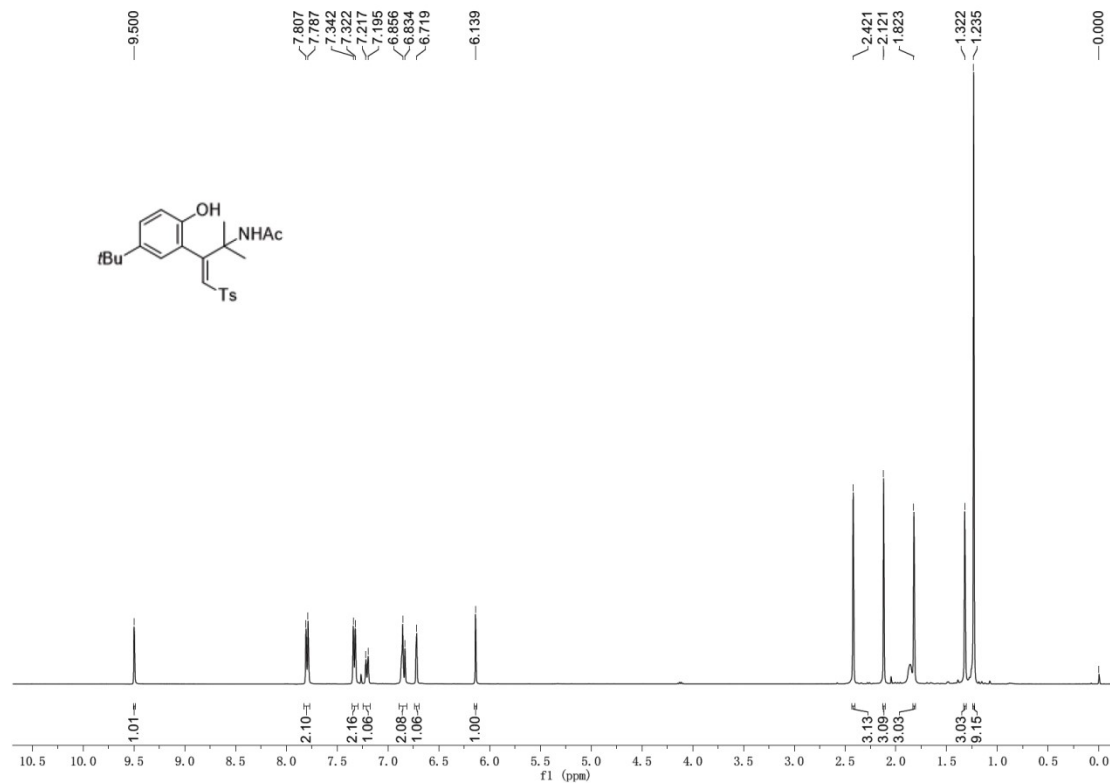
3ba-¹H NMR (400 MHz, CDCl₃)



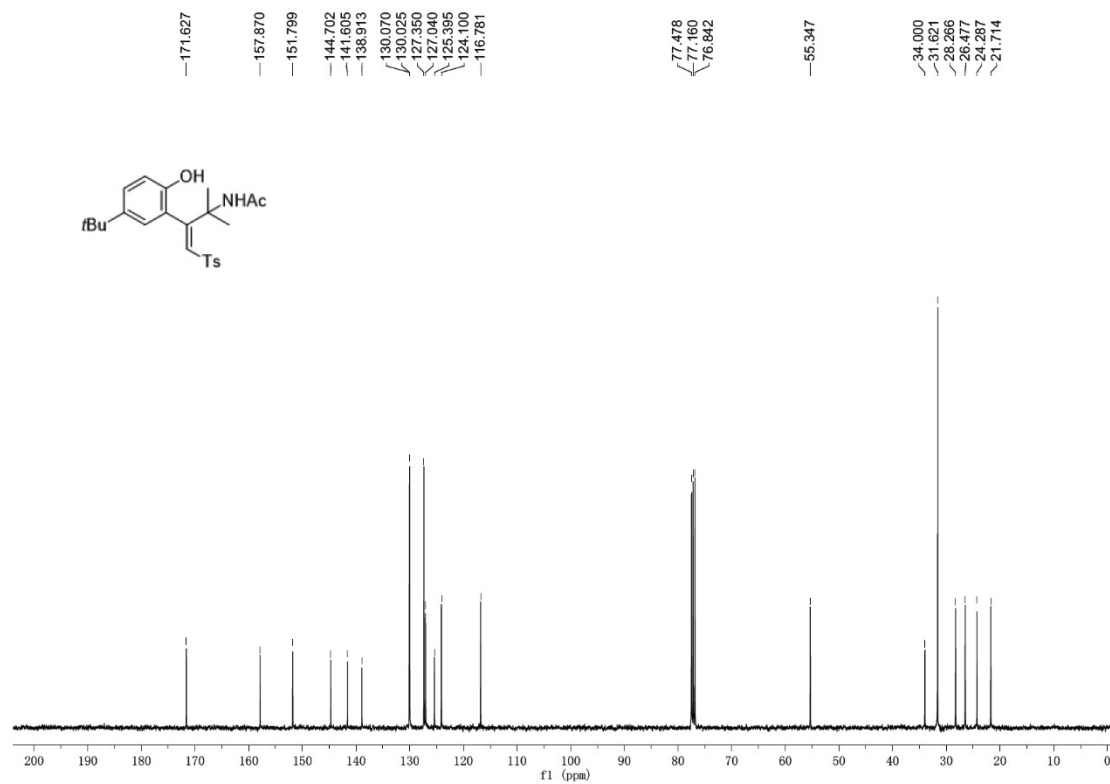
3ba-¹³C NMR (100 MHz, CDCl₃)



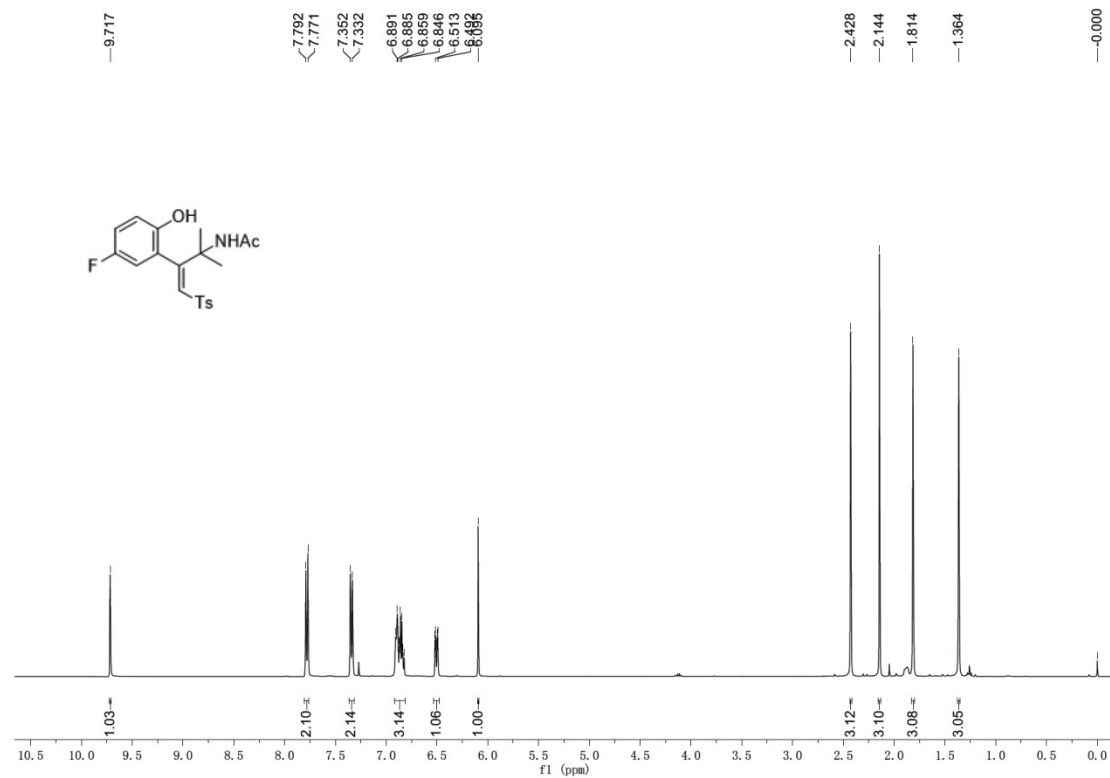
3ca-¹H NMR (400 MHz, CDCl₃)



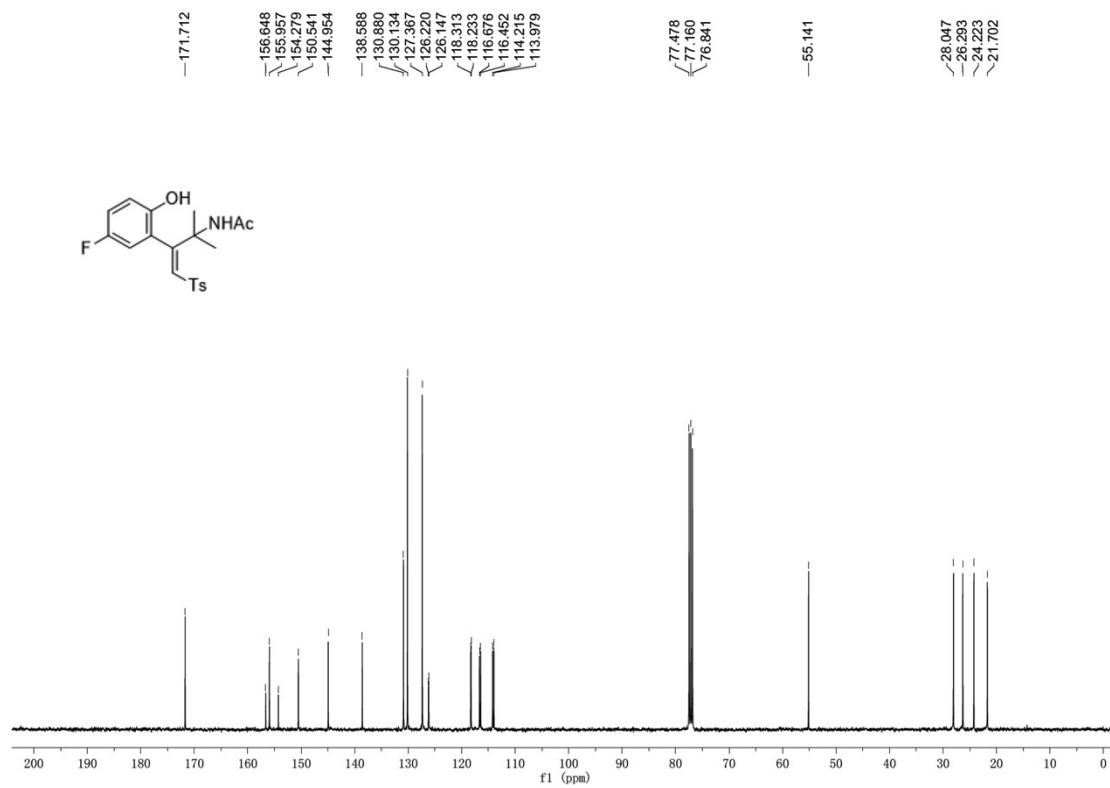
3ca-¹³C NMR (100 MHz, CDCl₃)



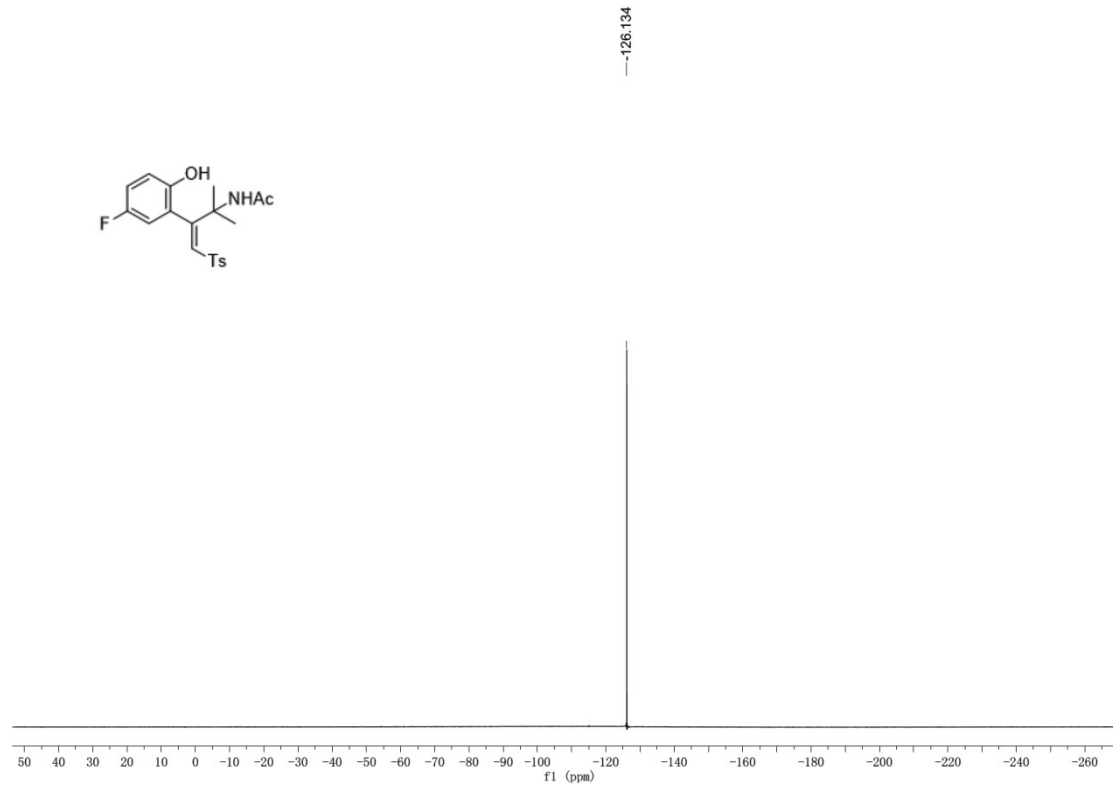
3da-¹H NMR (400 MHz, CDCl₃)



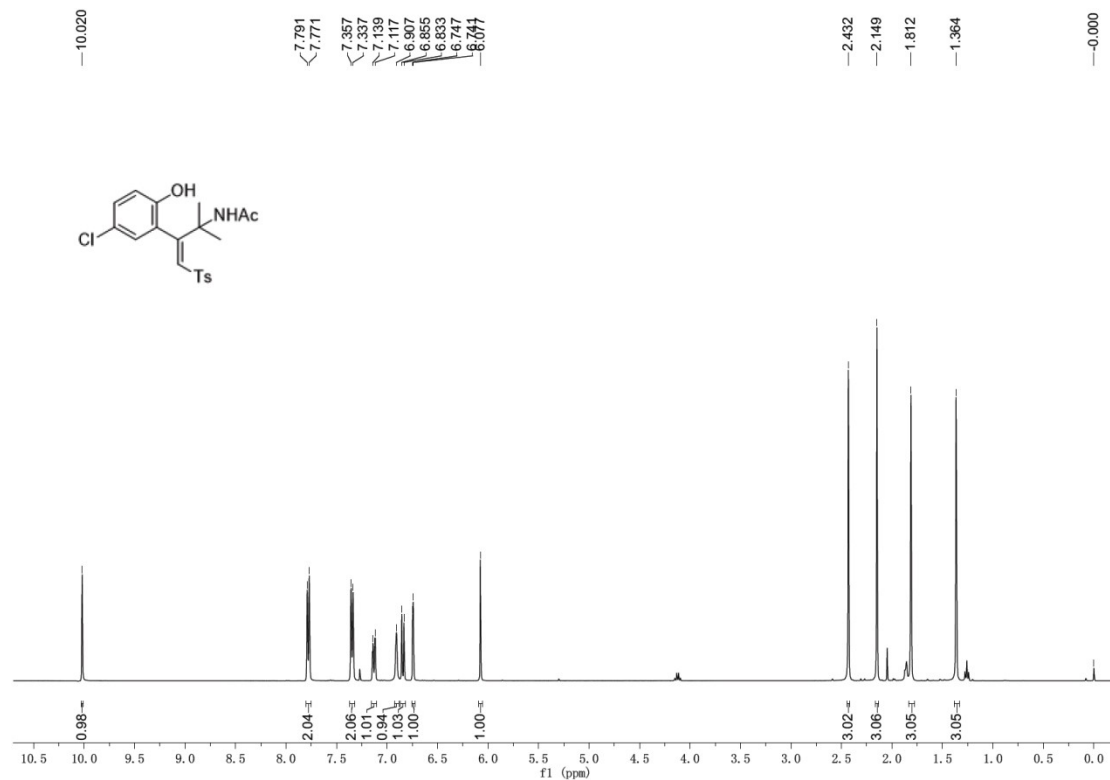
3da-¹³C NMR (100 MHz, CDCl₃)



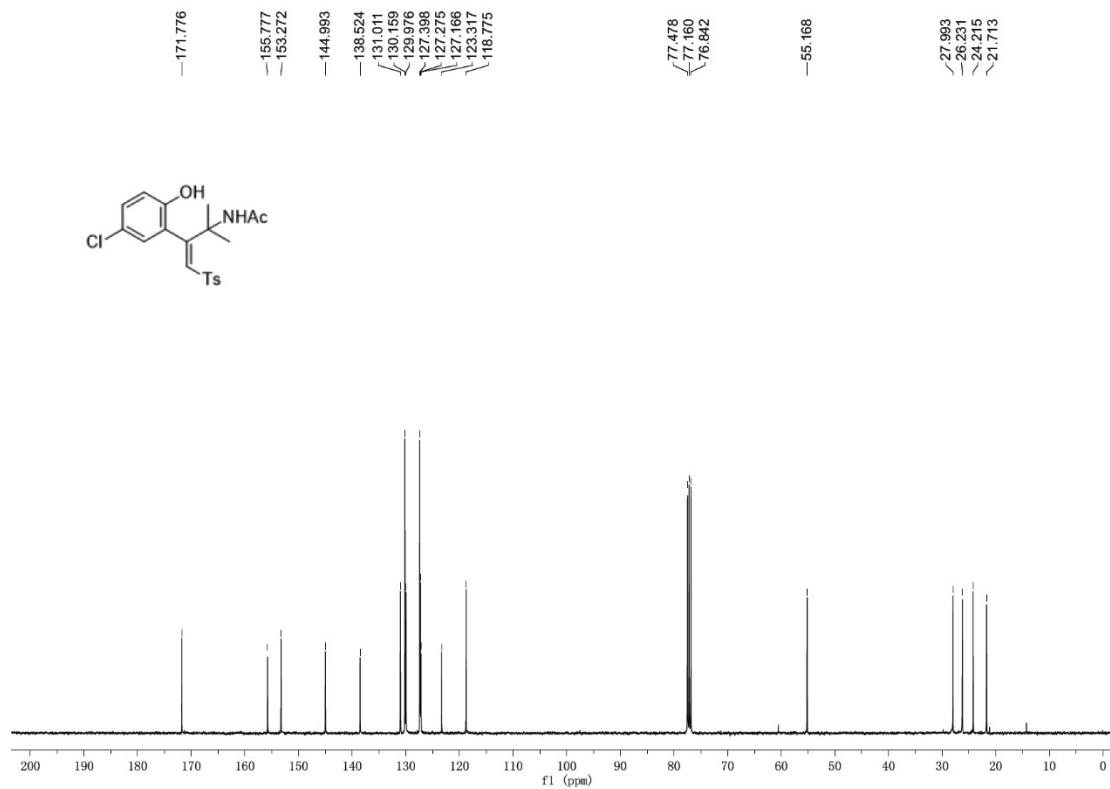
3da-¹⁹F NMR (376 MHz, CDCl₃)



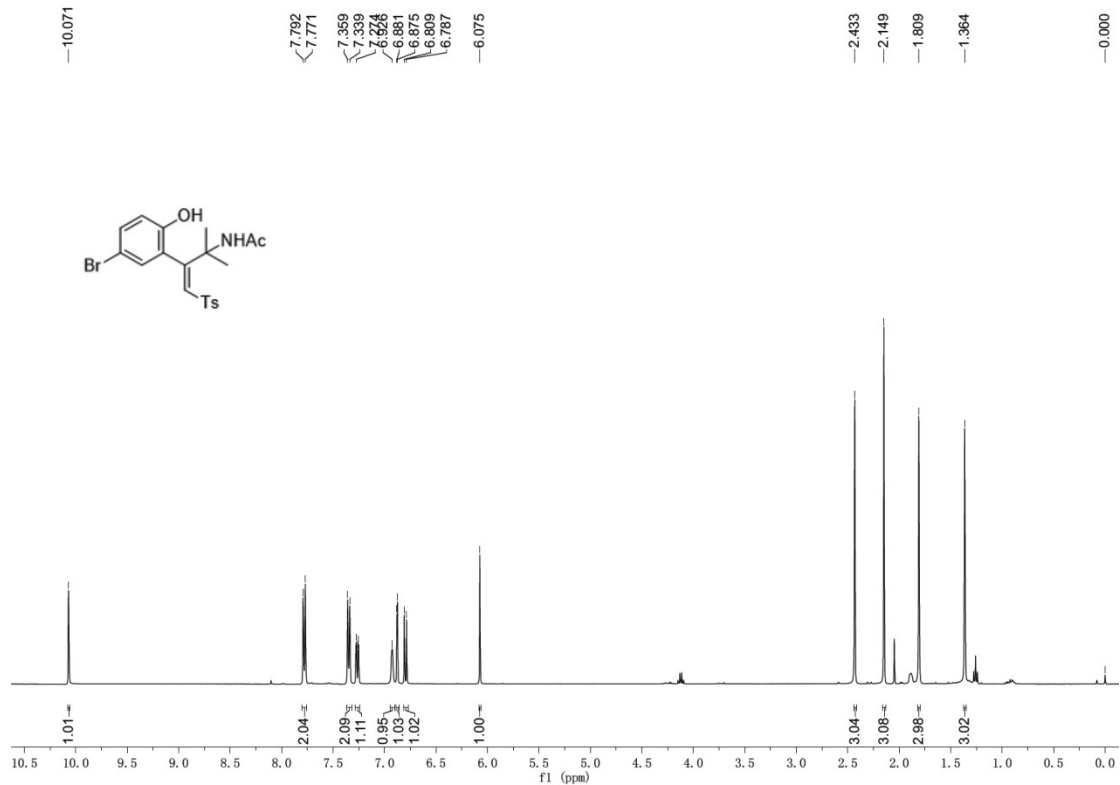
3ea-¹H NMR (400 MHz, CDCl₃)



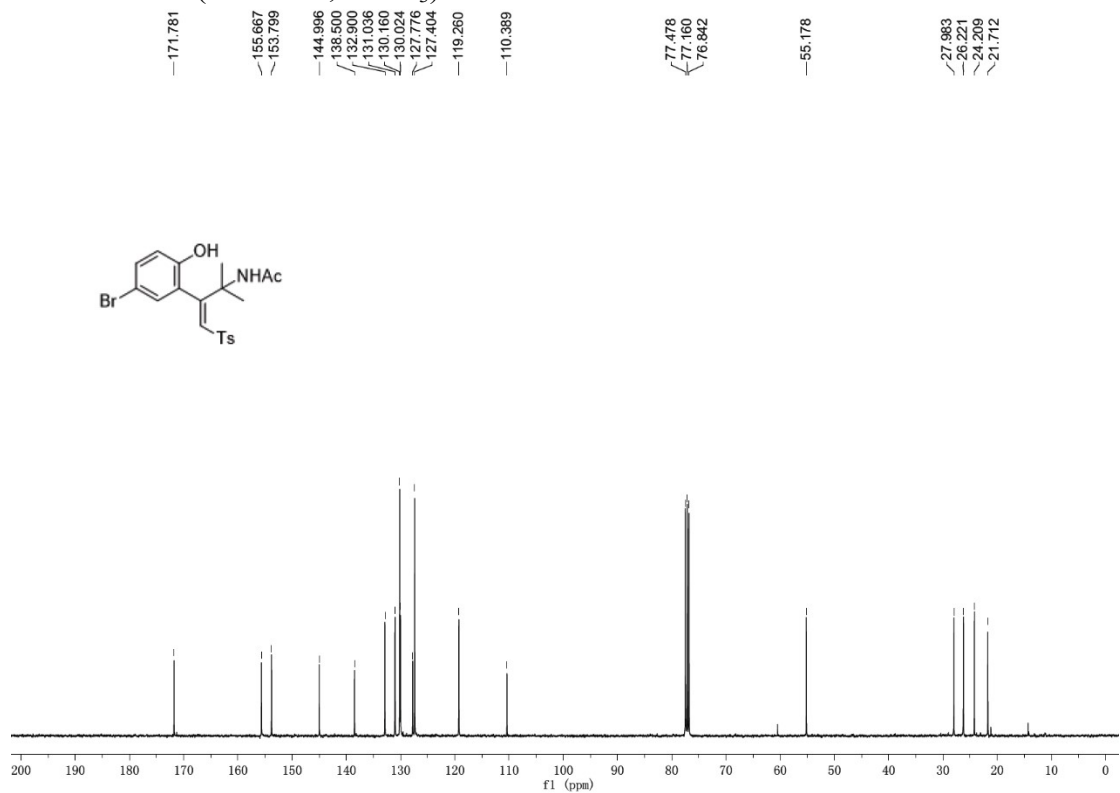
3ea-¹³C NMR (100 MHz, CDCl₃)



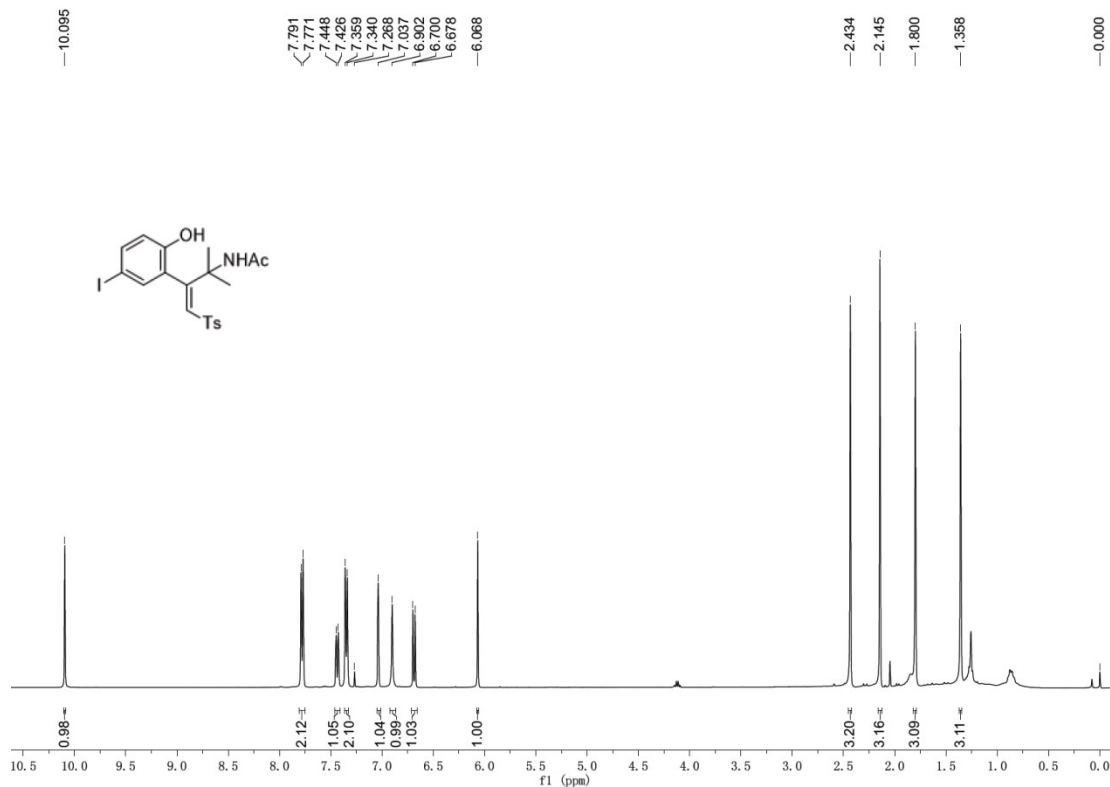
3fa-¹H NMR (400 MHz, CDCl₃)



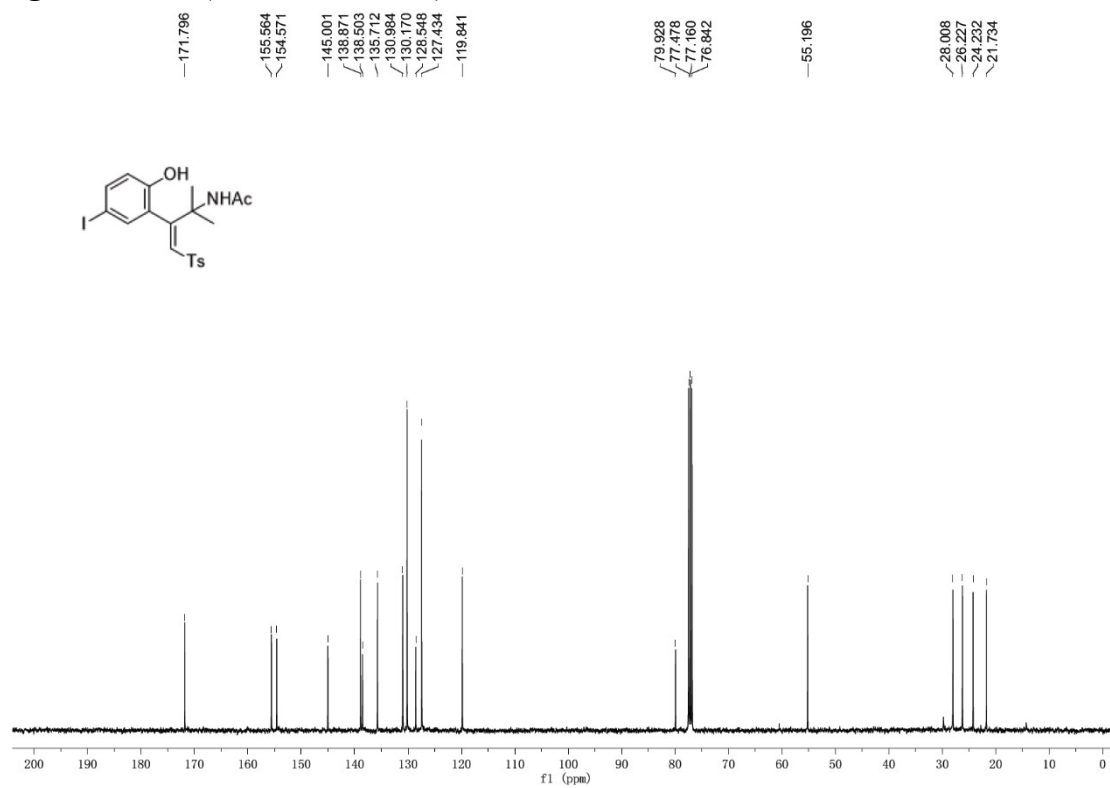
3fa-¹³C NMR (100 MHz, CDCl₃)



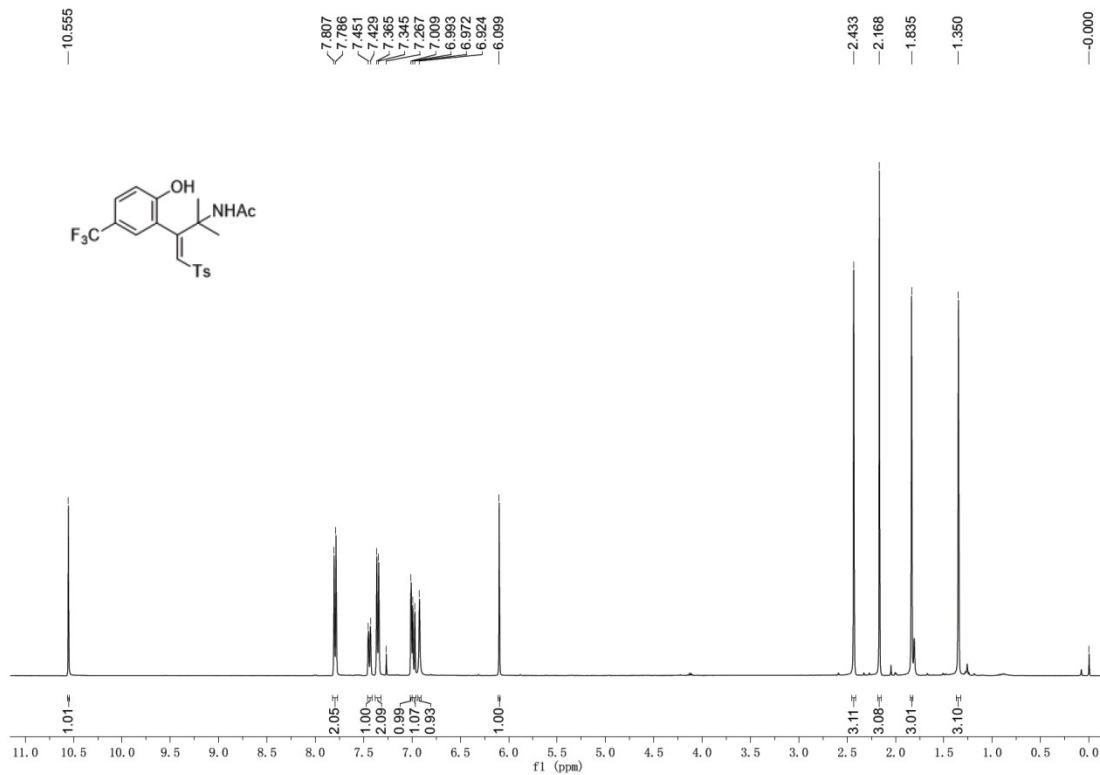
3ga-¹H NMR (400 MHz, CDCl₃)



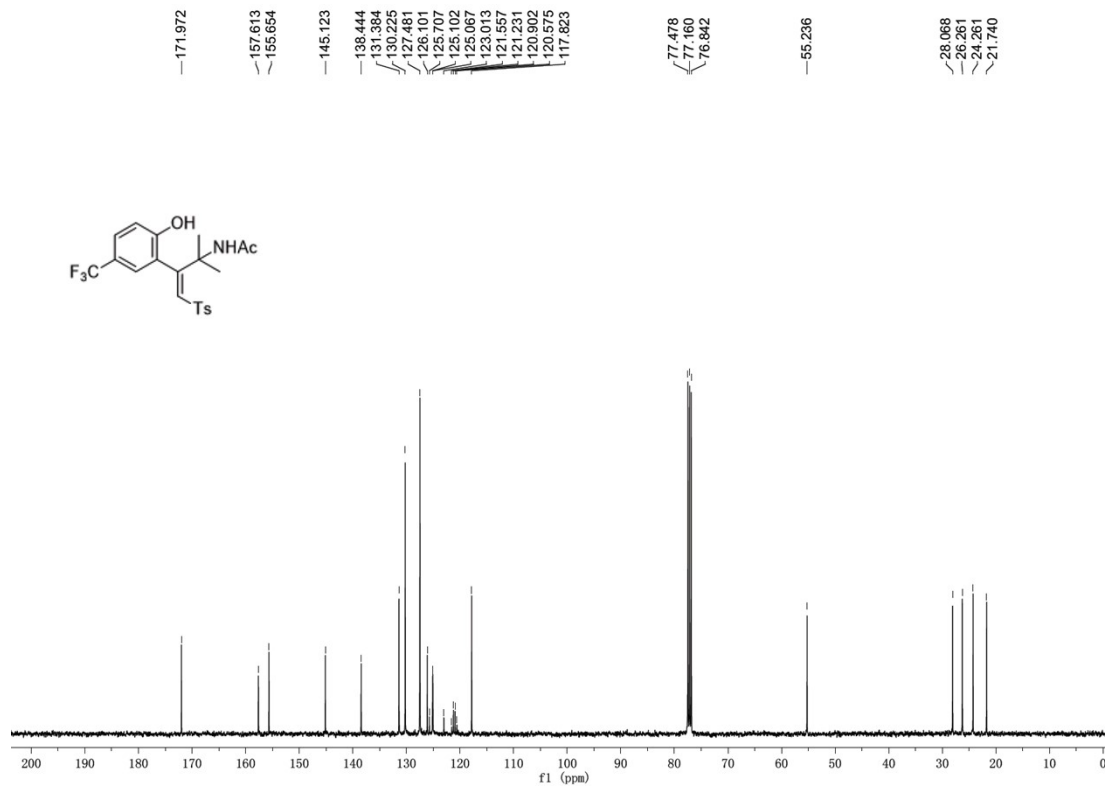
3ga-¹³C NMR (100 MHz, CDCl₃)



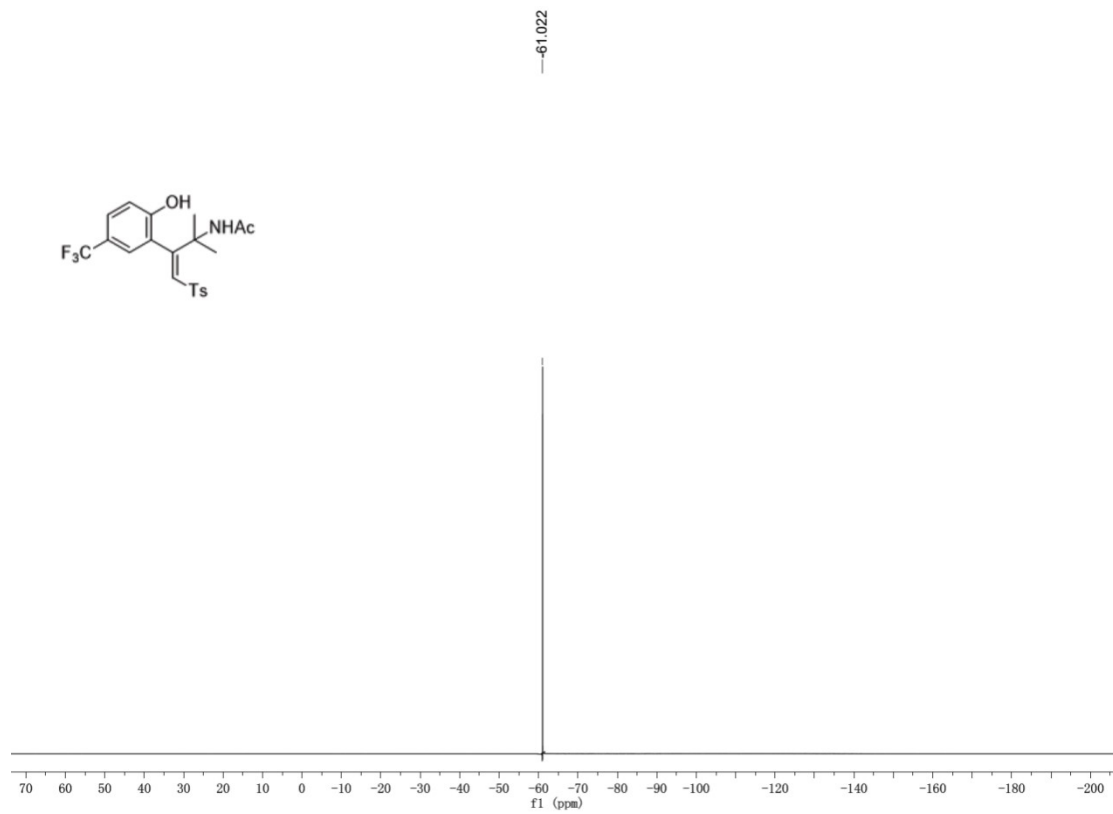
3ha-¹H NMR (400 MHz, CDCl₃)



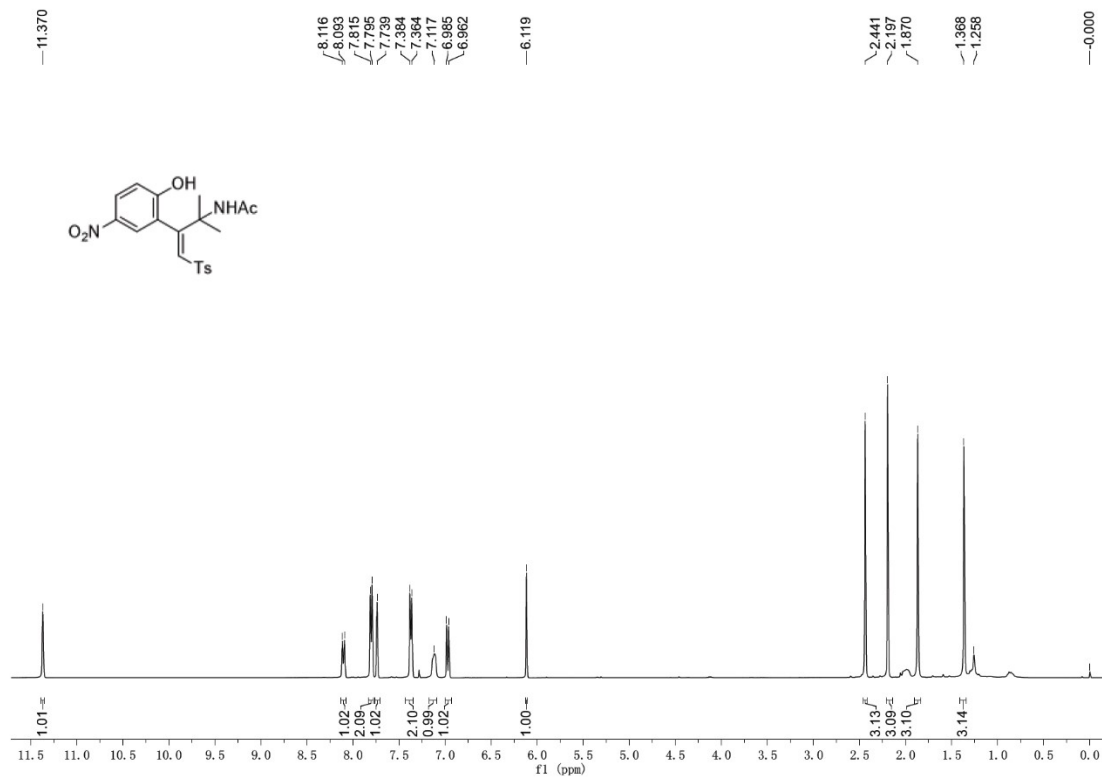
3ha-¹³C NMR (100 MHz, CDCl₃)



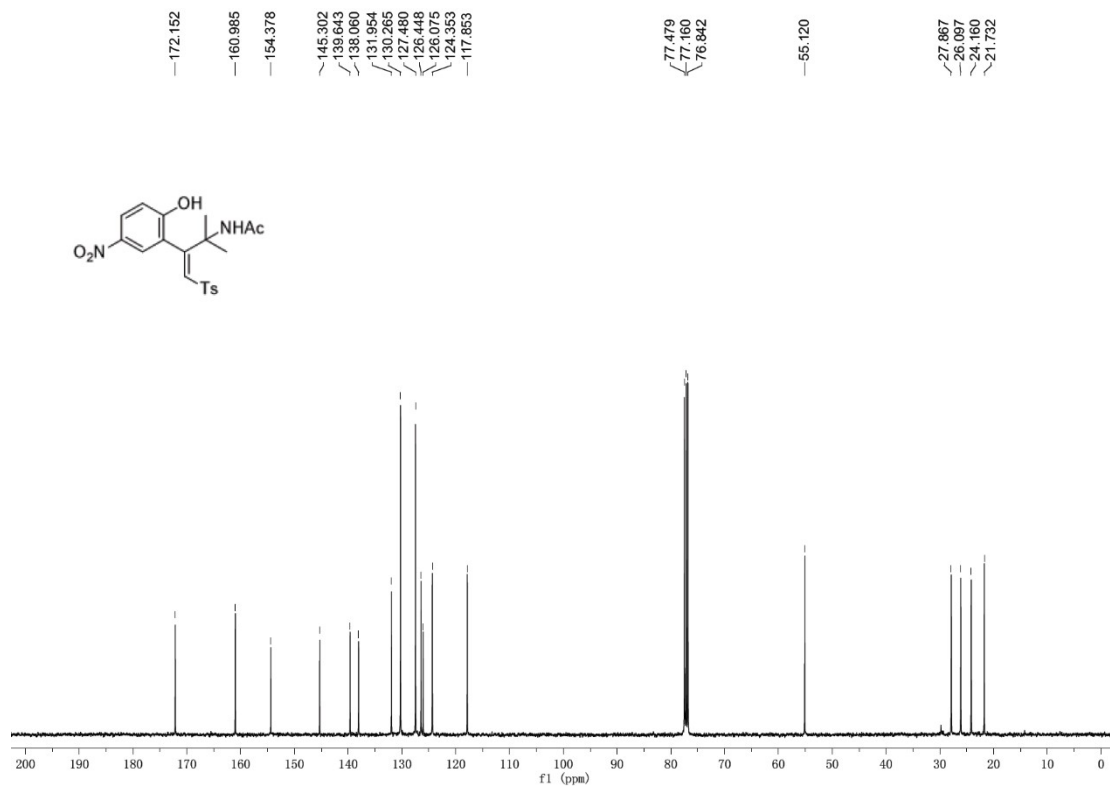
3ha-¹⁹F NMR (376 MHz, CDCl₃)



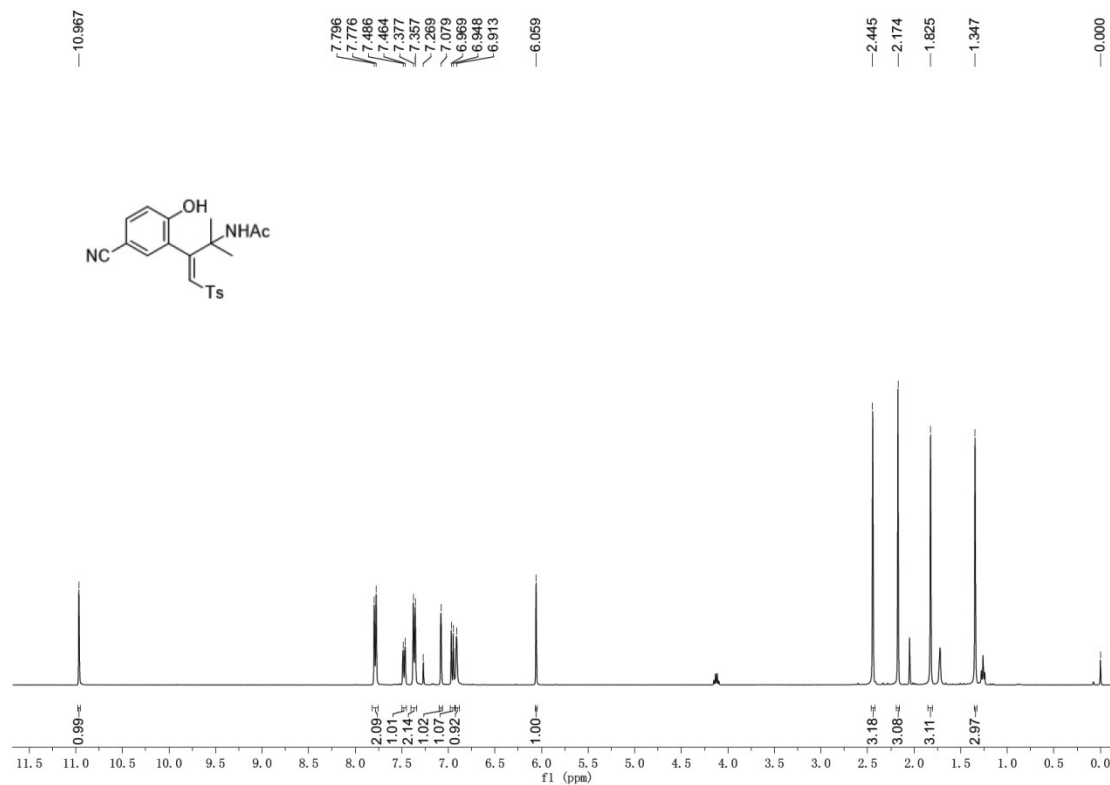
3ia-¹H NMR (400 MHz, CDCl₃)



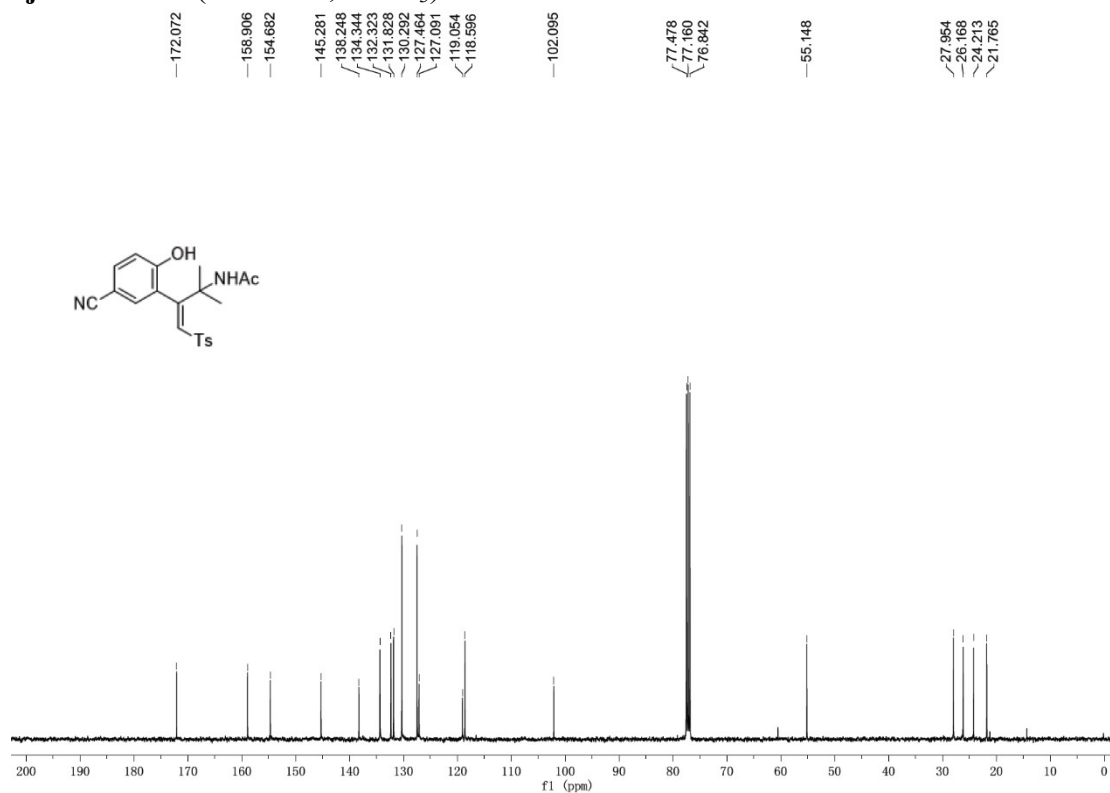
3ia-¹³C NMR (100 MHz, CDCl₃)



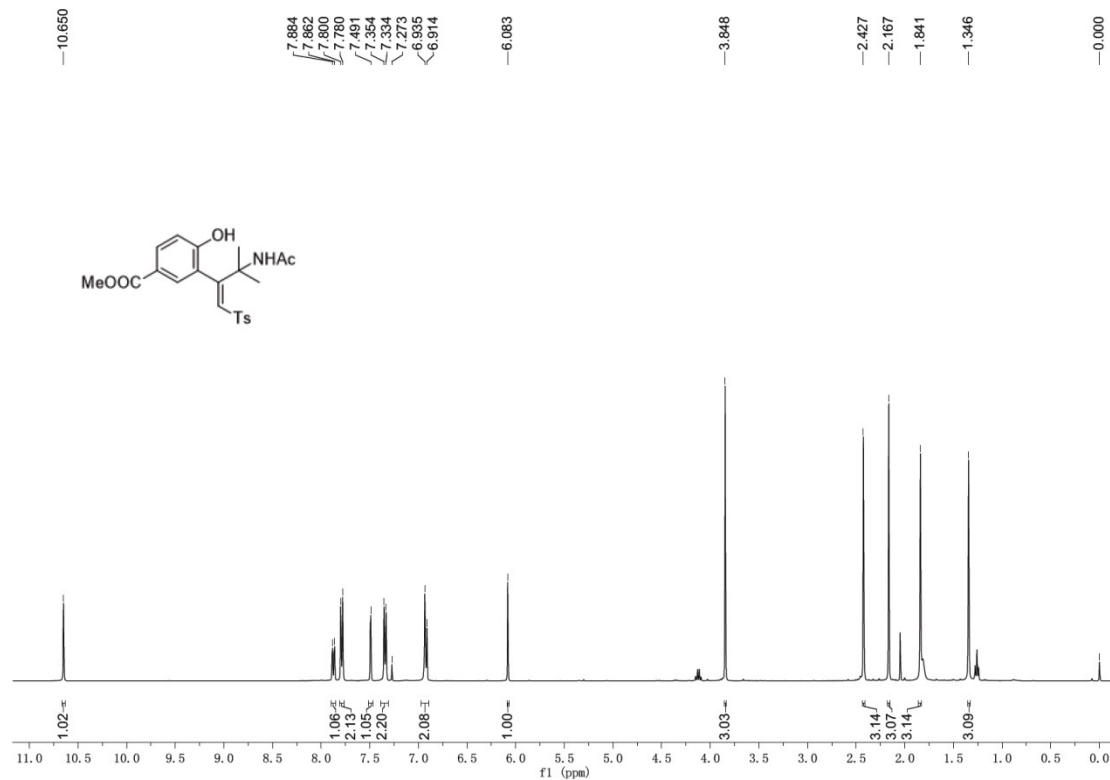
3ja-¹H NMR (400 MHz, CDCl₃)



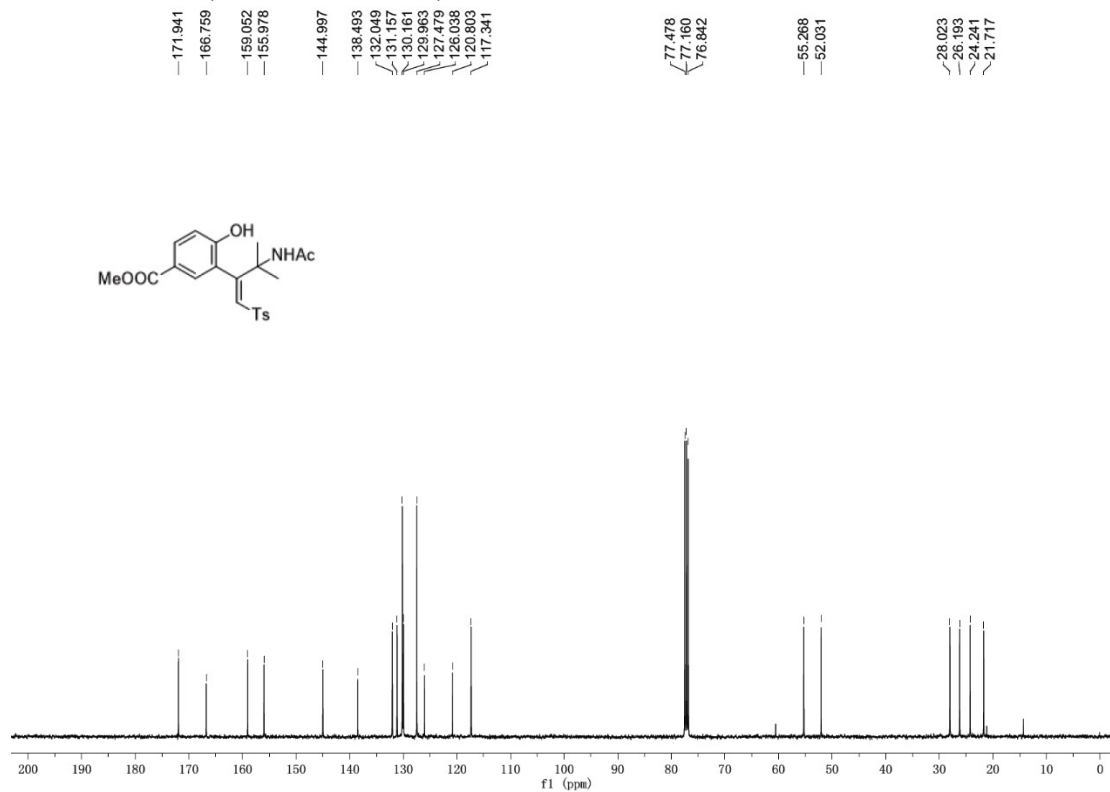
3ja-¹³C NMR (100 MHz, CDCl₃)



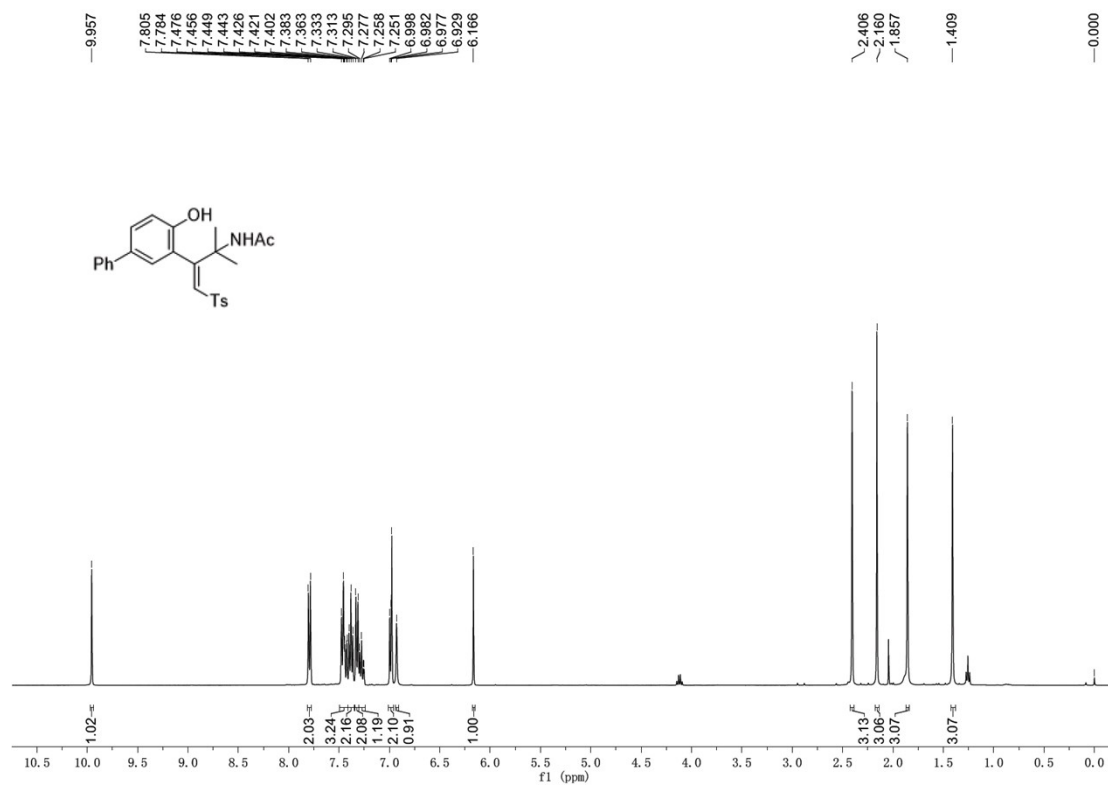
3ka-¹H NMR (400 MHz, CDCl₃)



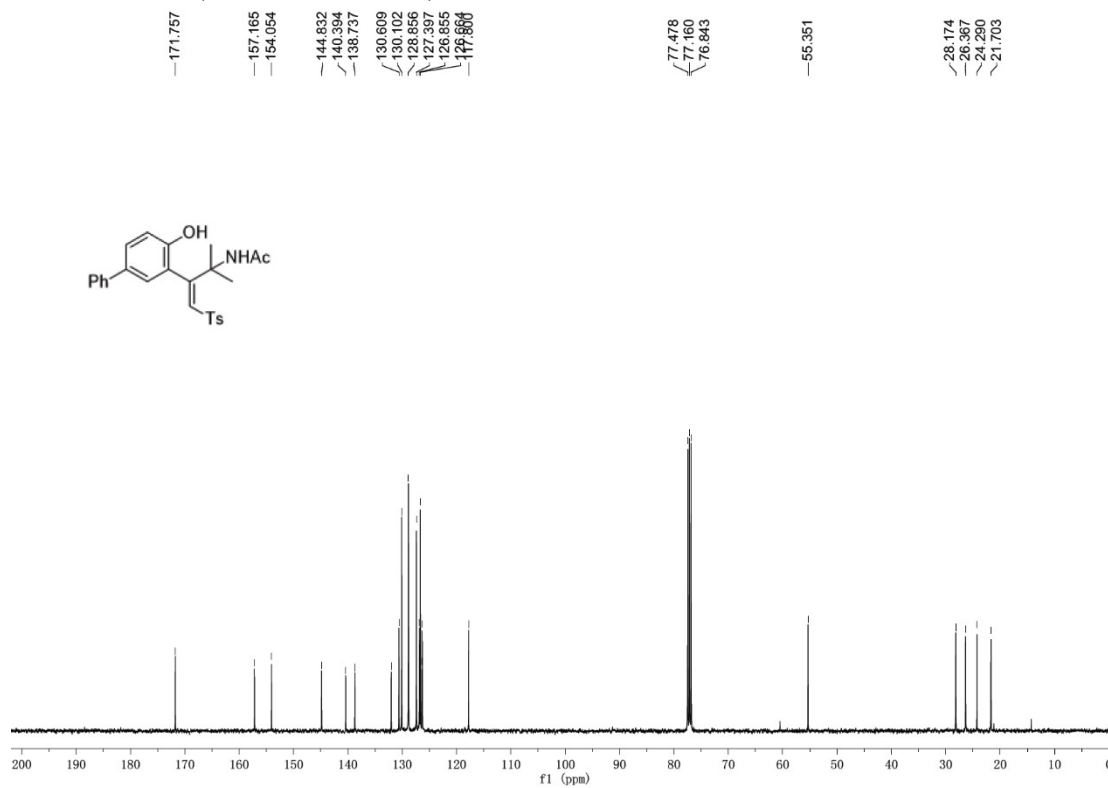
3ka-¹³C NMR (100 MHz, CDCl₃)



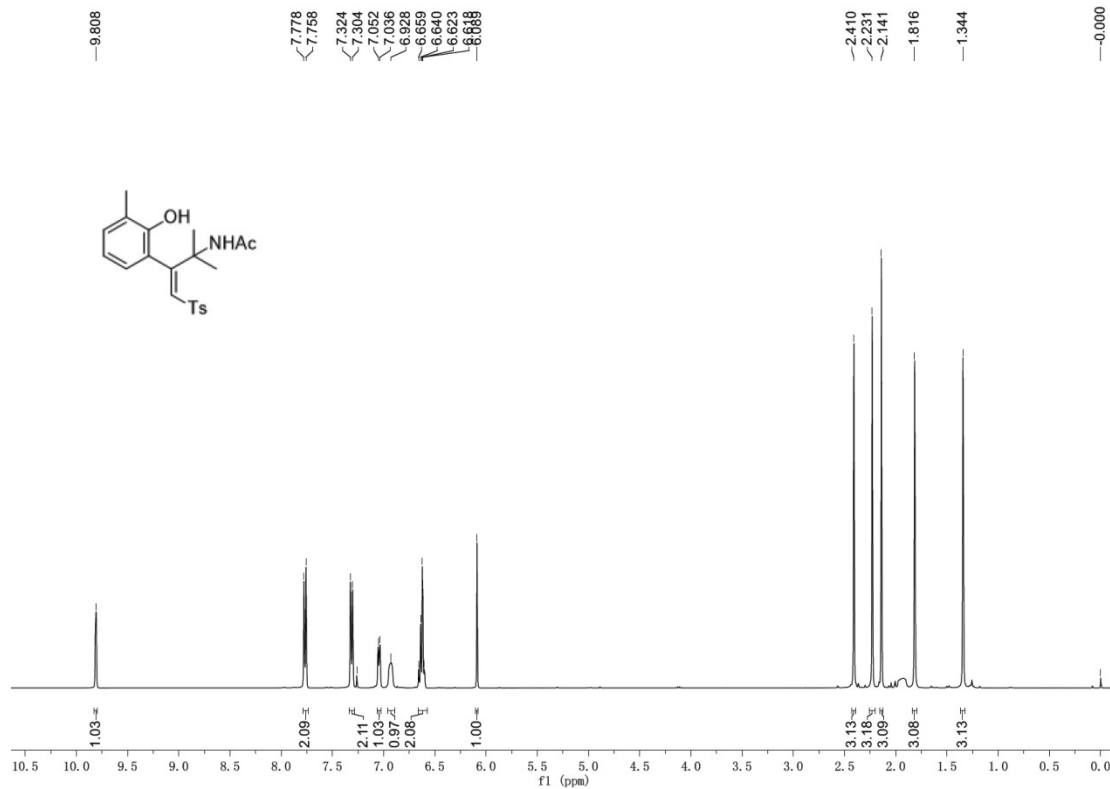
3la-¹H NMR (400 MHz, CDCl₃)



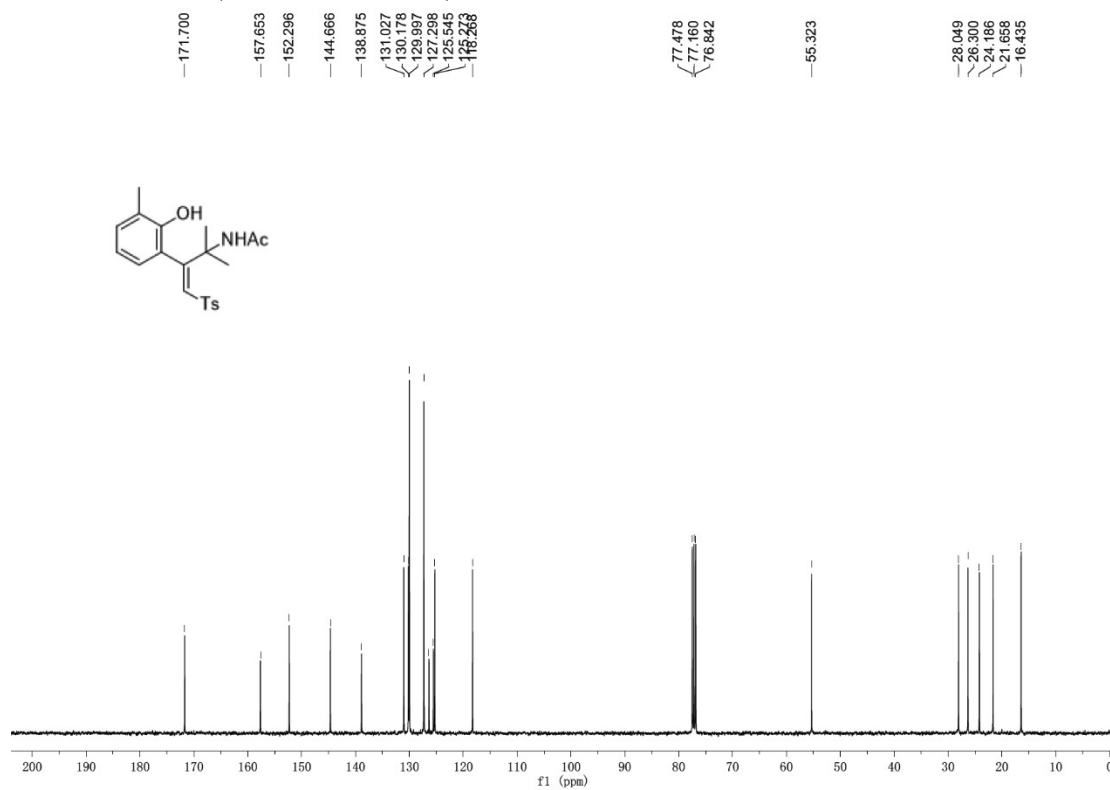
3la-¹³C NMR (100 MHz, CDCl₃)



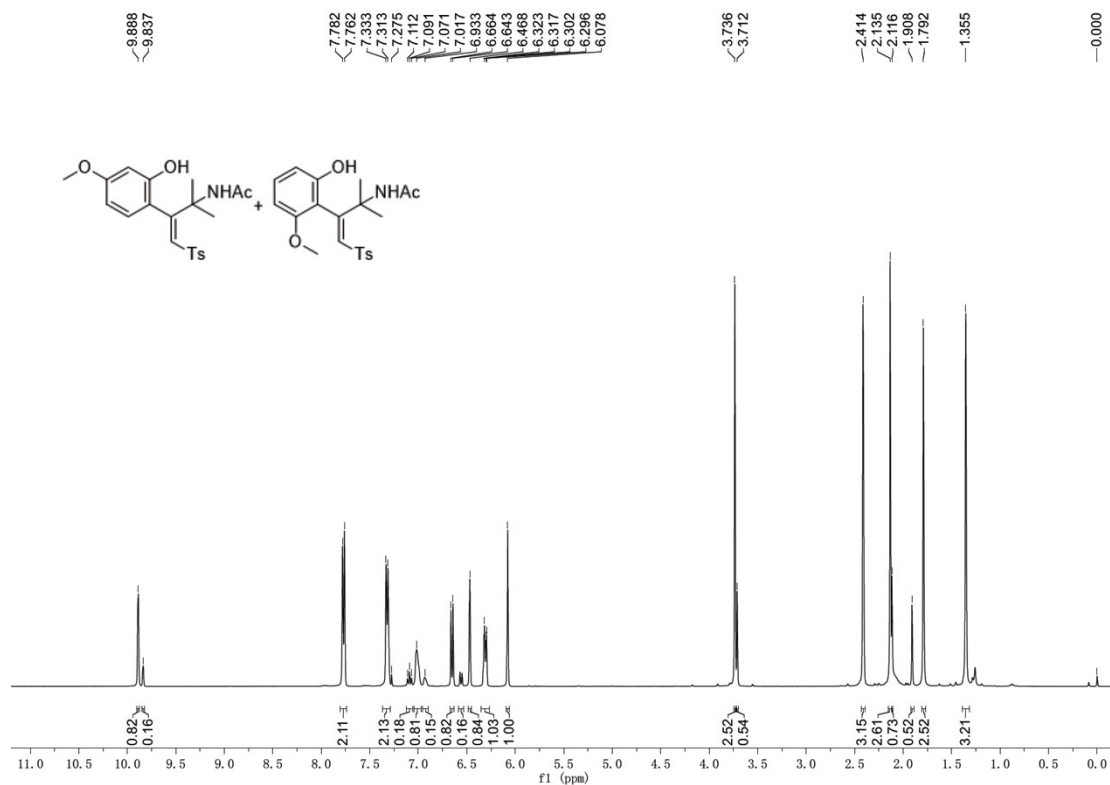
3ma-¹H NMR (400 MHz, CDCl₃)



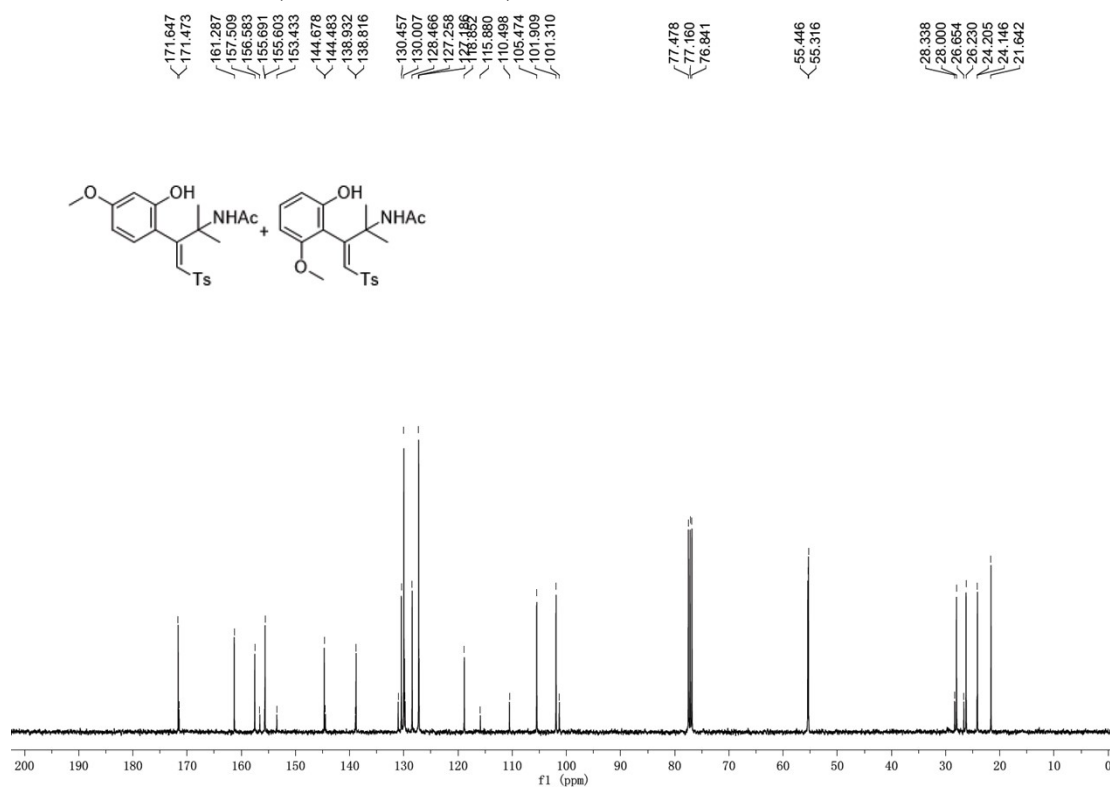
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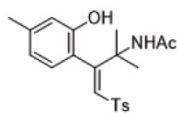
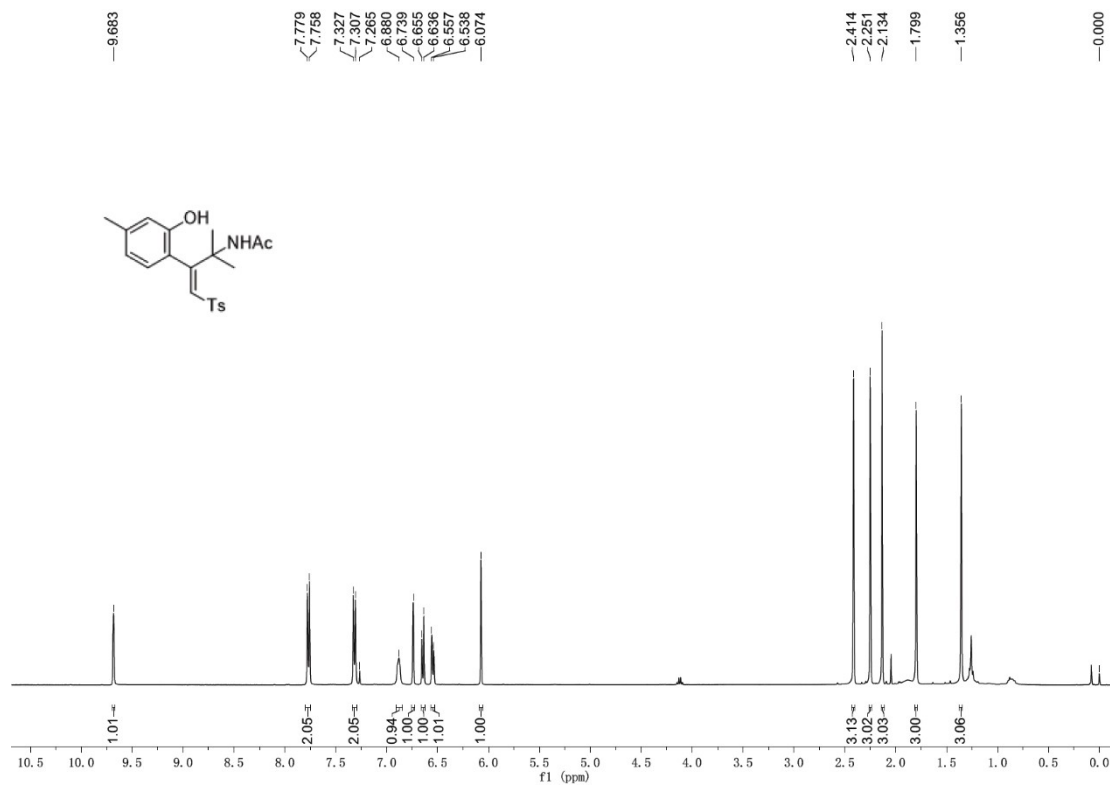
3na/3na' -¹H NMR (400 MHz, CDCl₃)



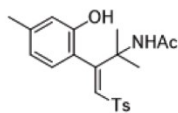
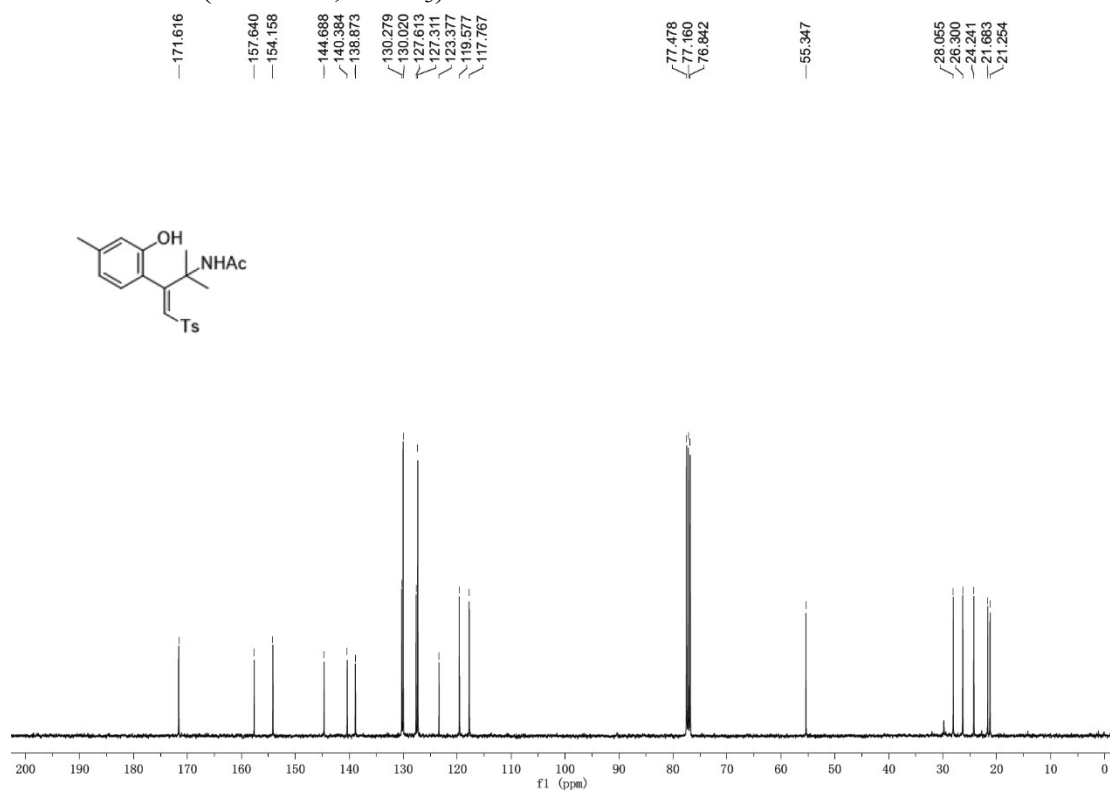
3na/3na' -¹³C NMR (100 MHz, CDCl₃)



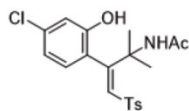
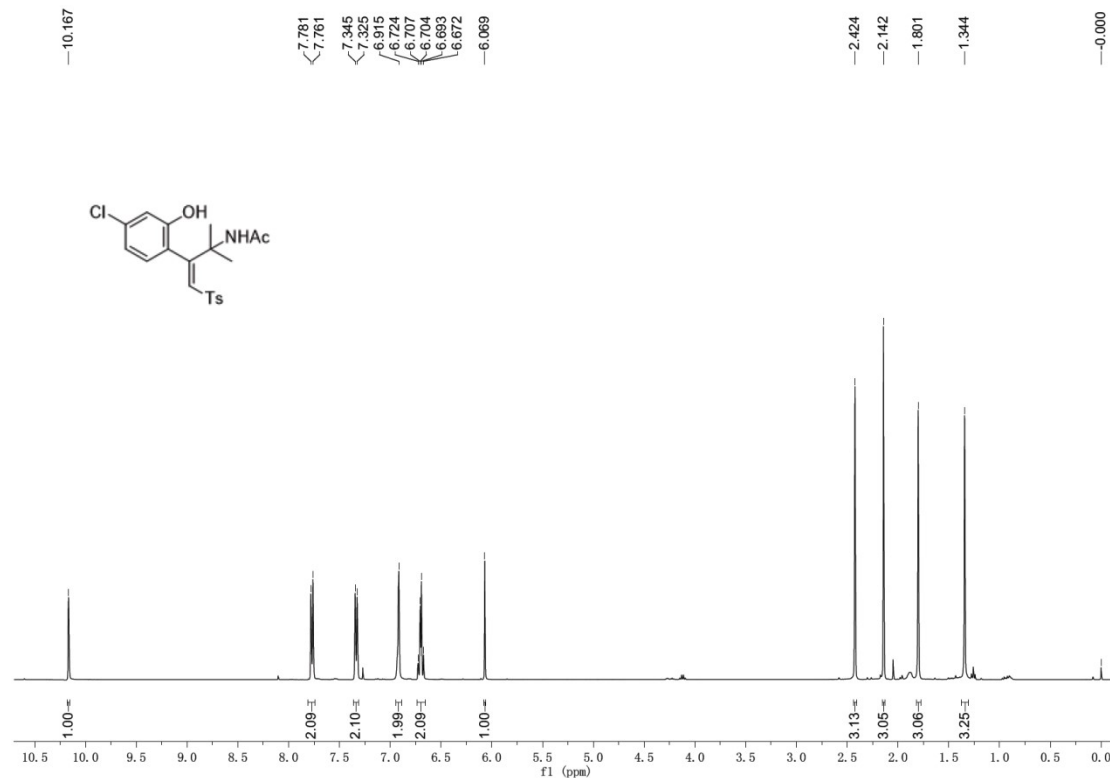
30a-¹H NMR (400 MHz, CDCl₃)



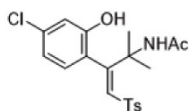
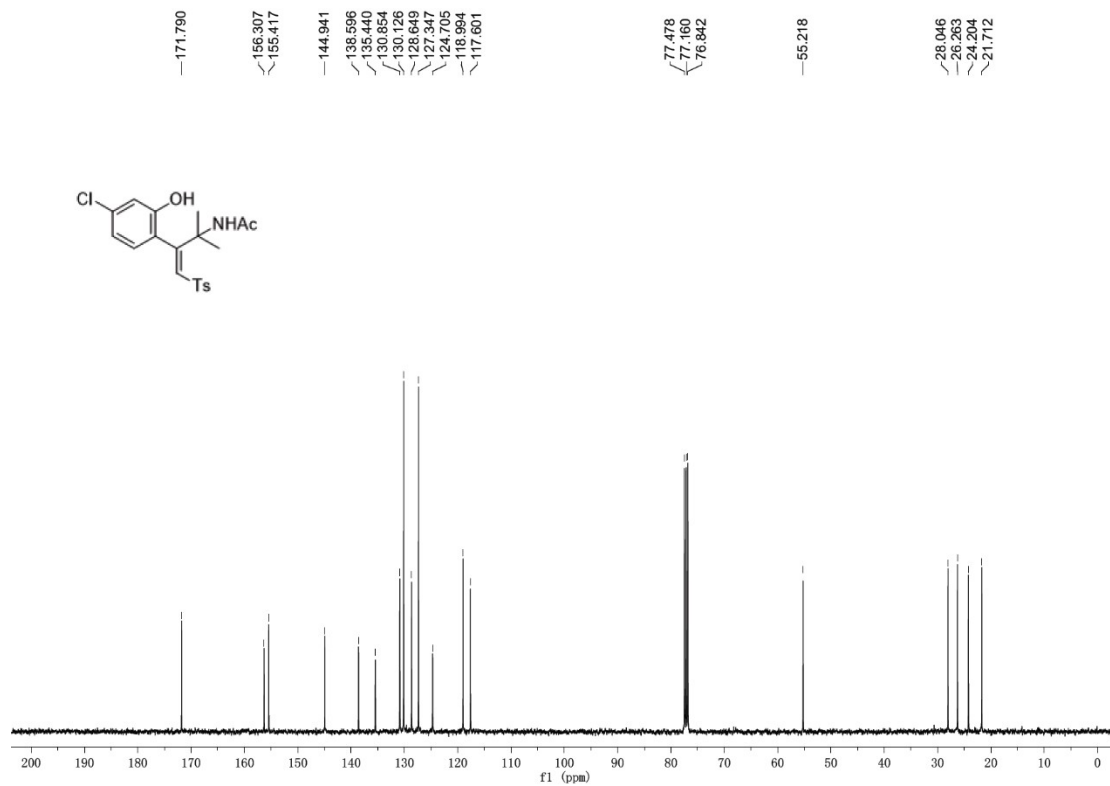
30a-¹³C NMR (100 MHz, CDCl₃)



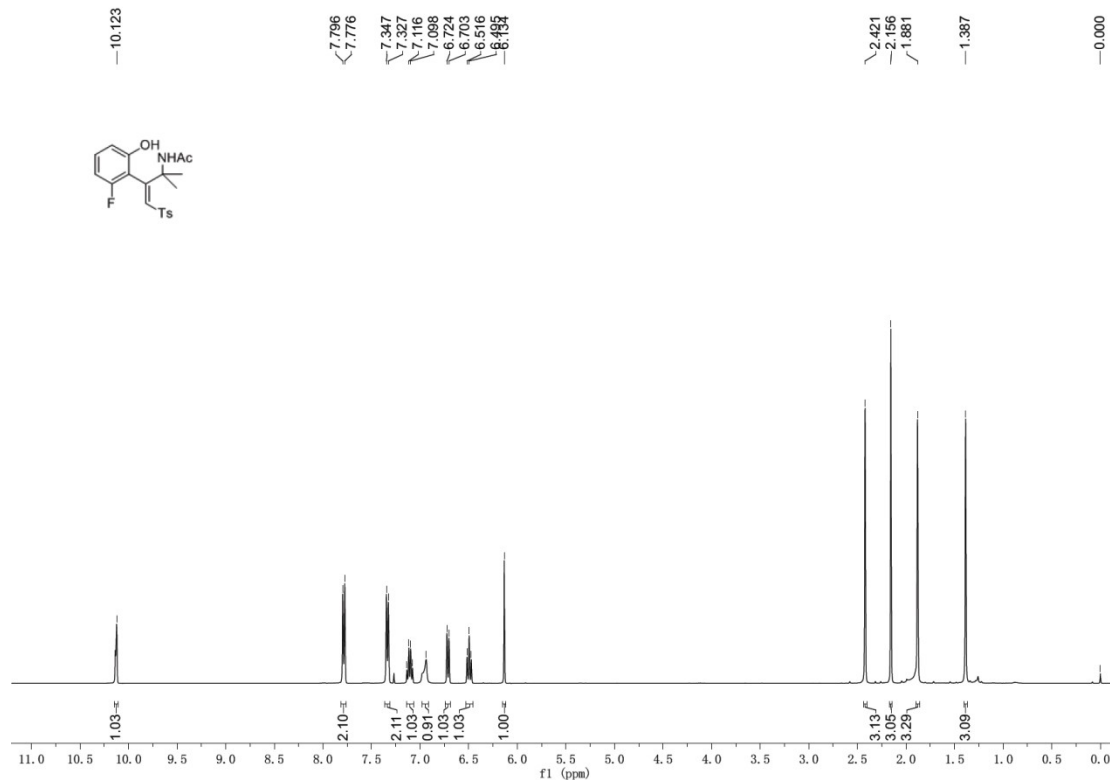
3pa-¹H NMR (400 MHz, CDCl₃)



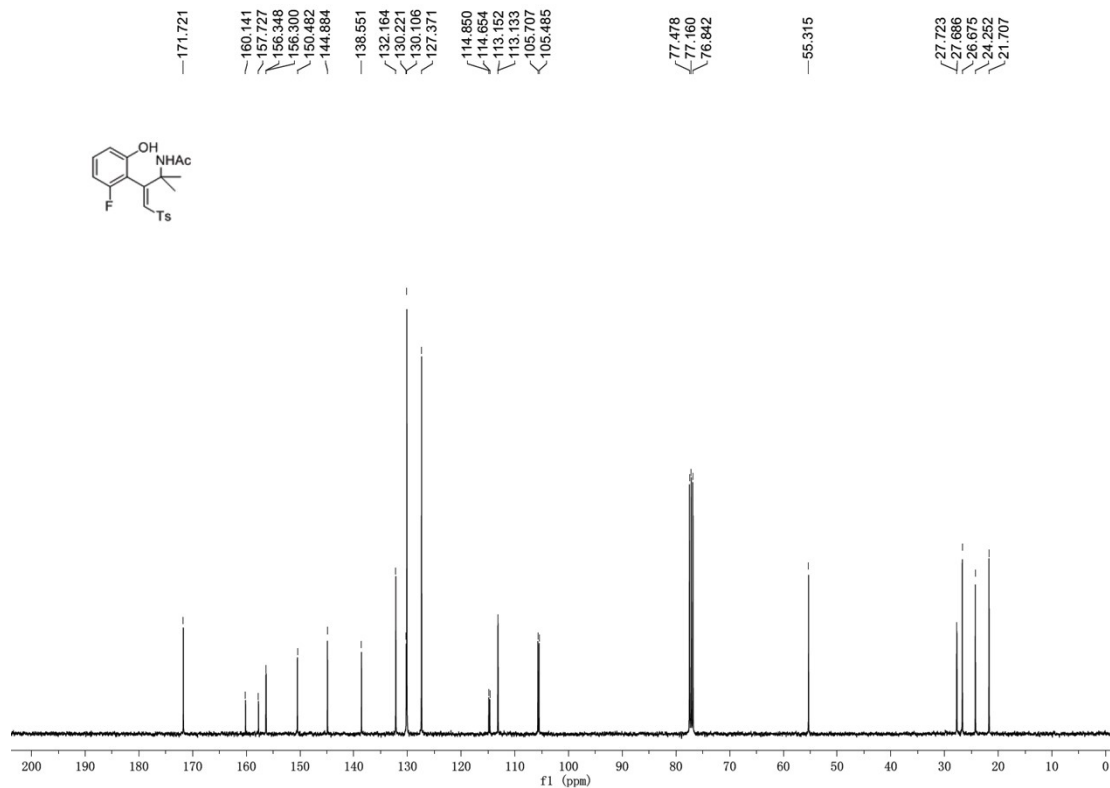
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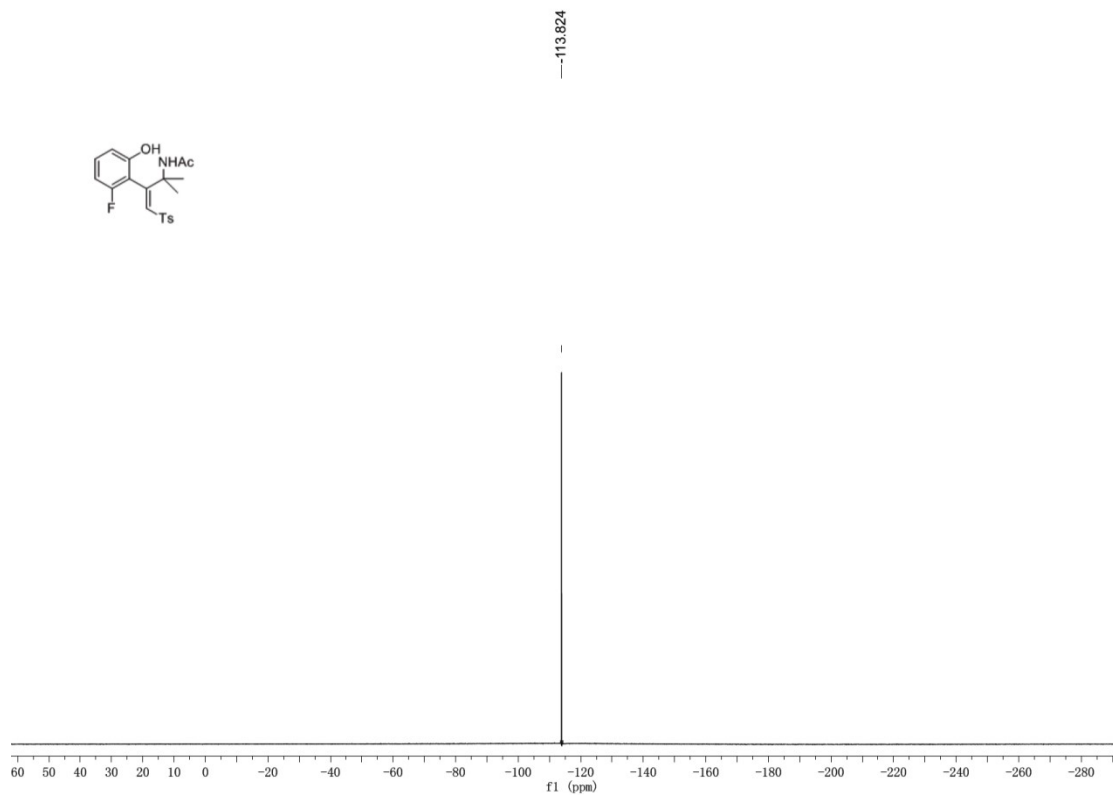
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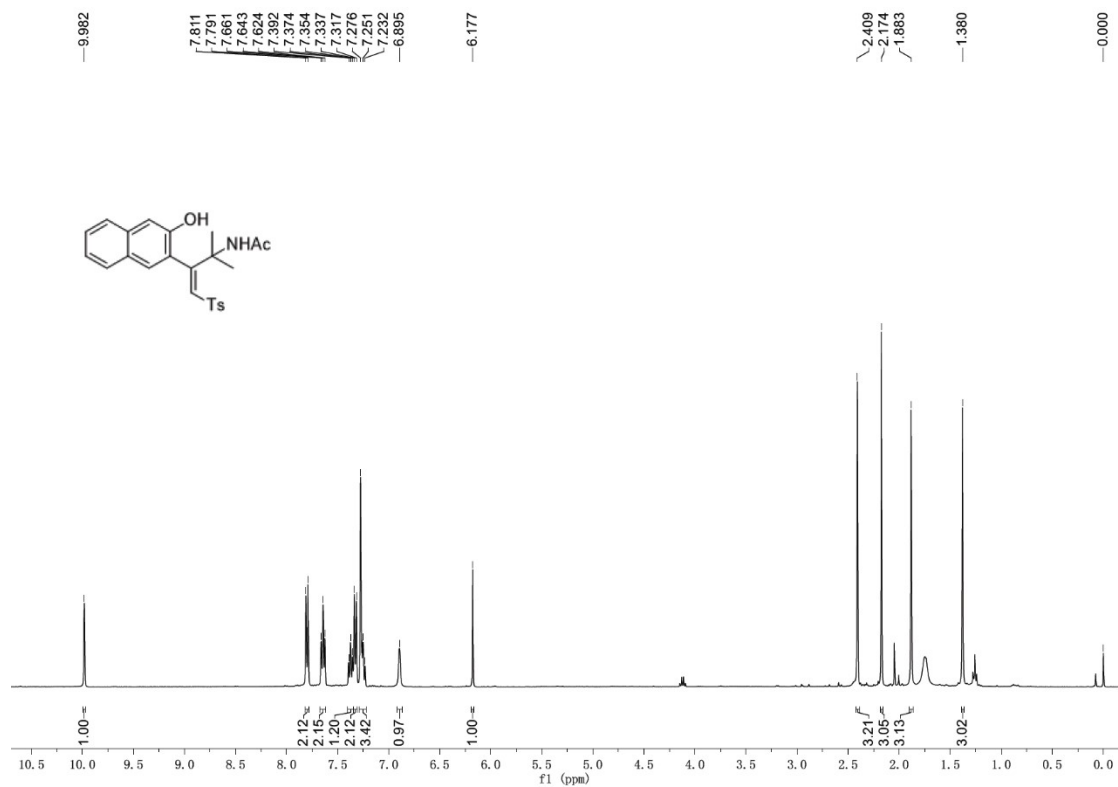
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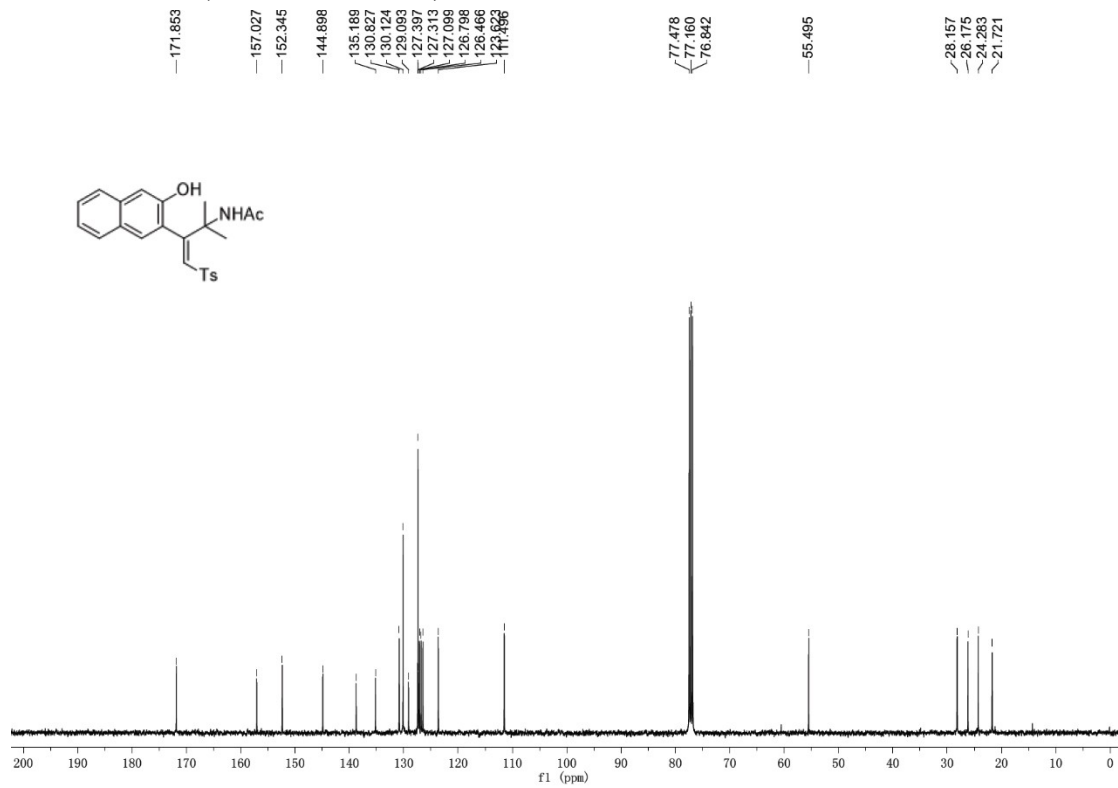
3qa-¹⁹F NMR (376 MHz, CDCl₃)



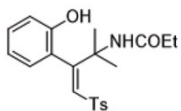
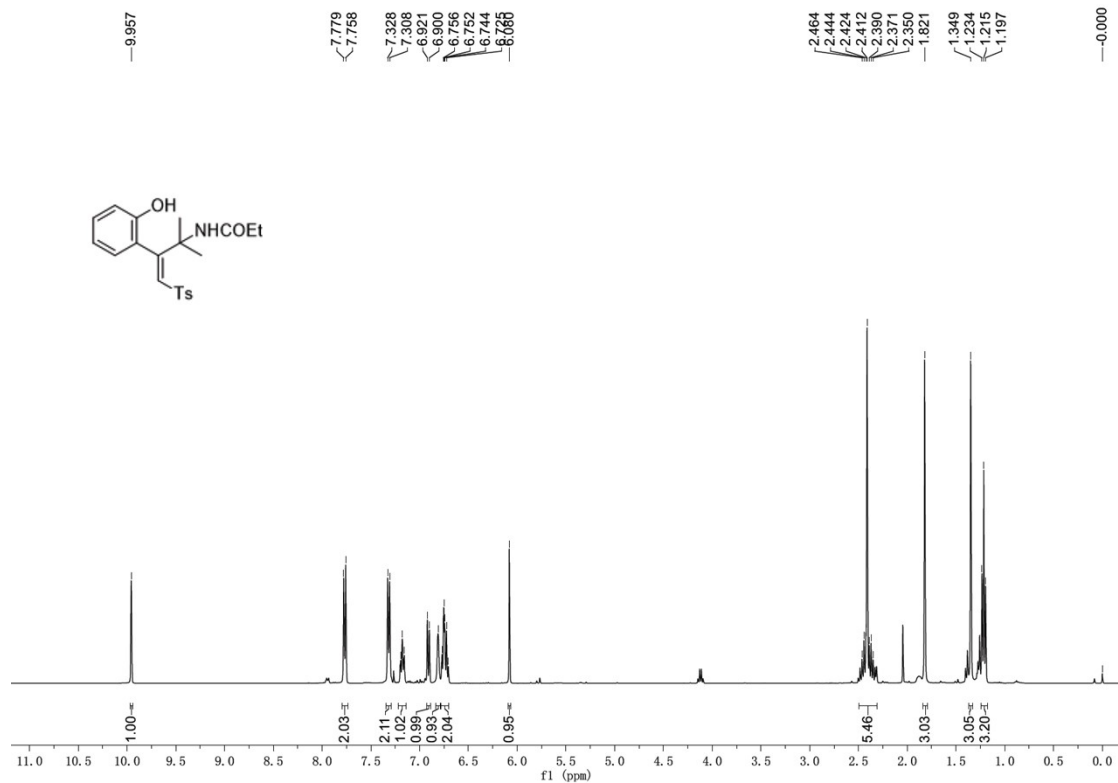
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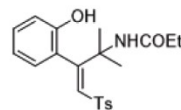
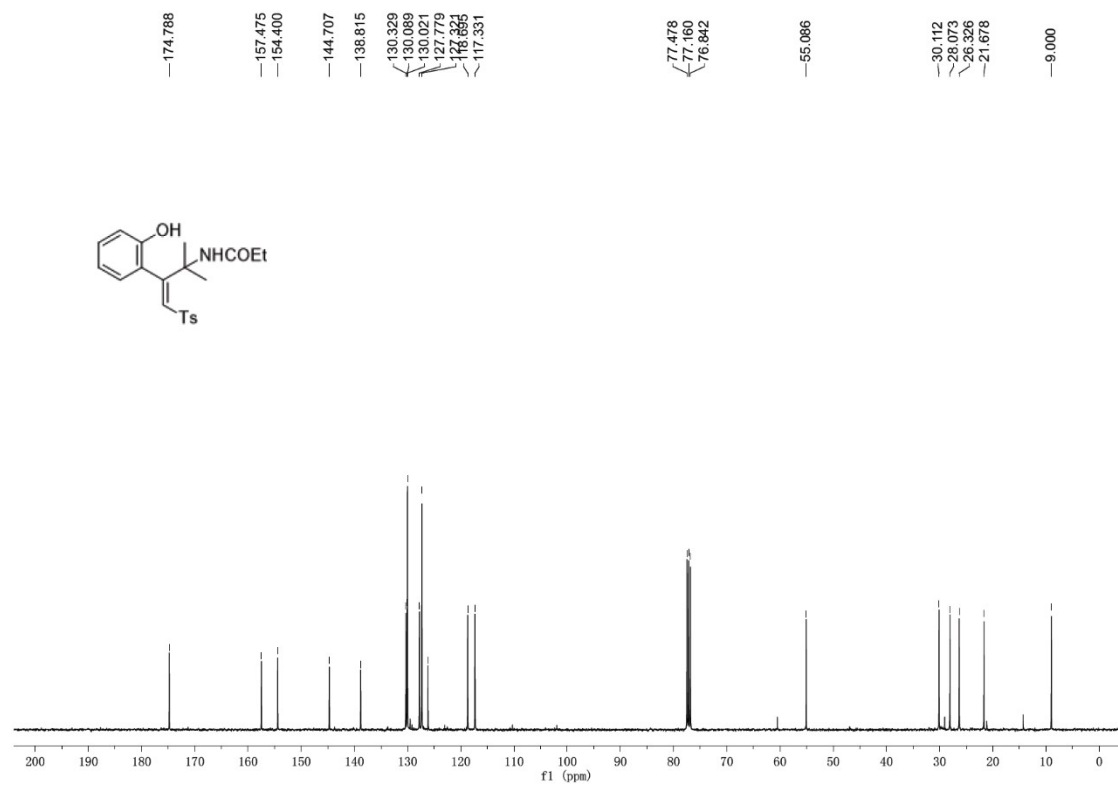
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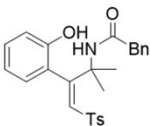
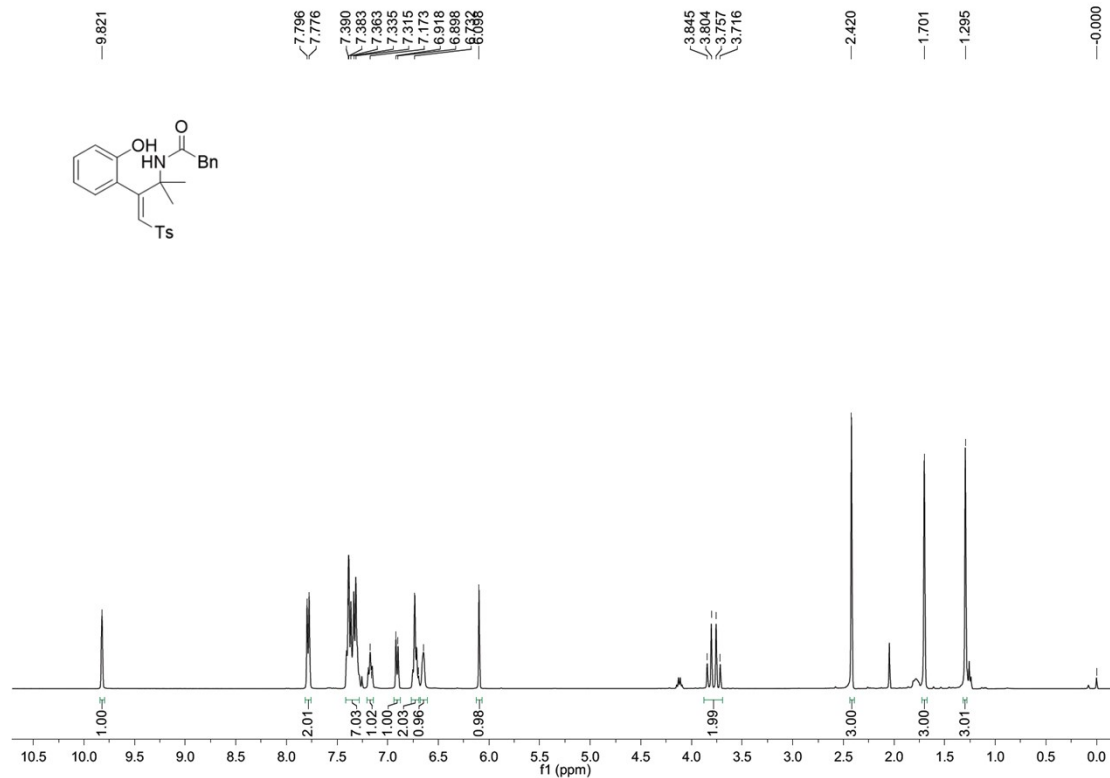
3sa-¹H NMR (400 MHz, CDCl₃)



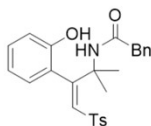
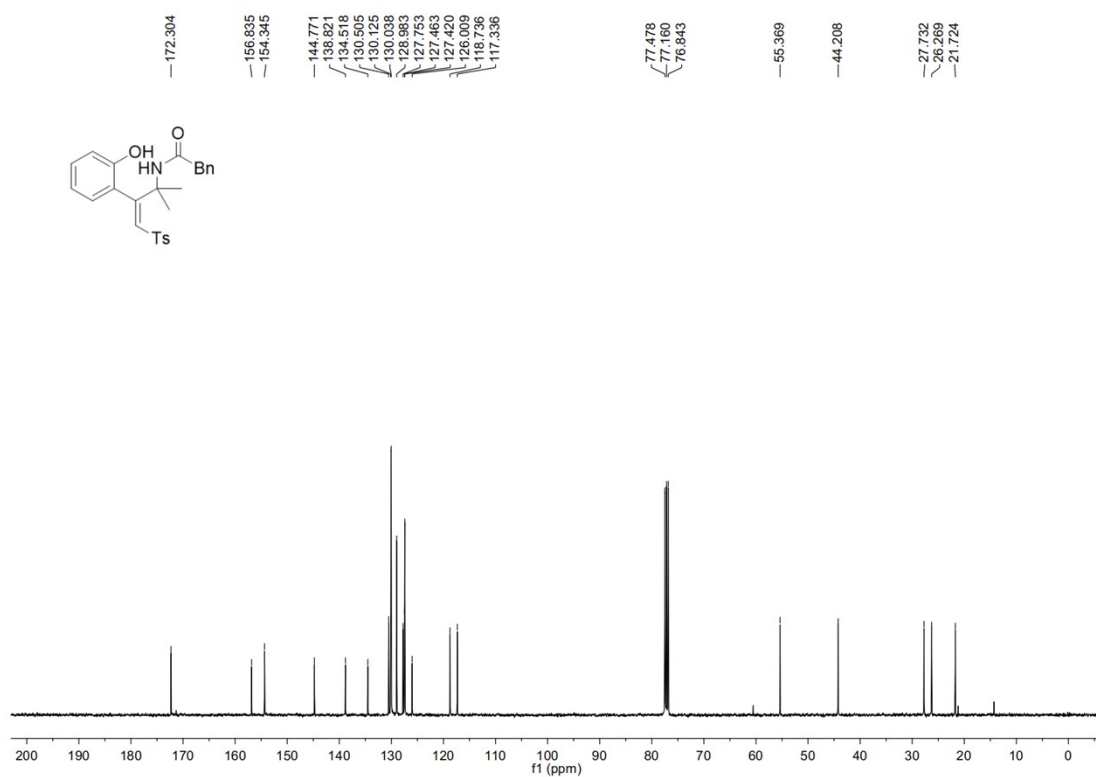
3sa-¹³C NMR (100 MHz, CDCl₃)



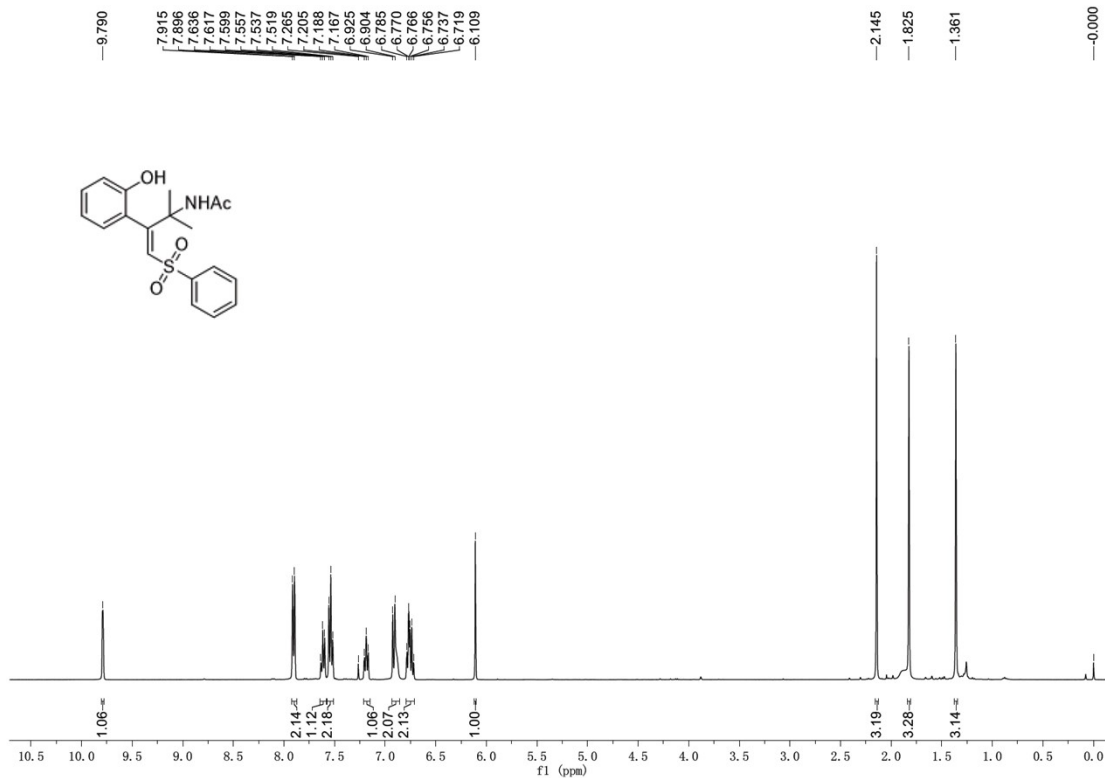
3ta-¹H NMR (400 MHz, CDCl₃)



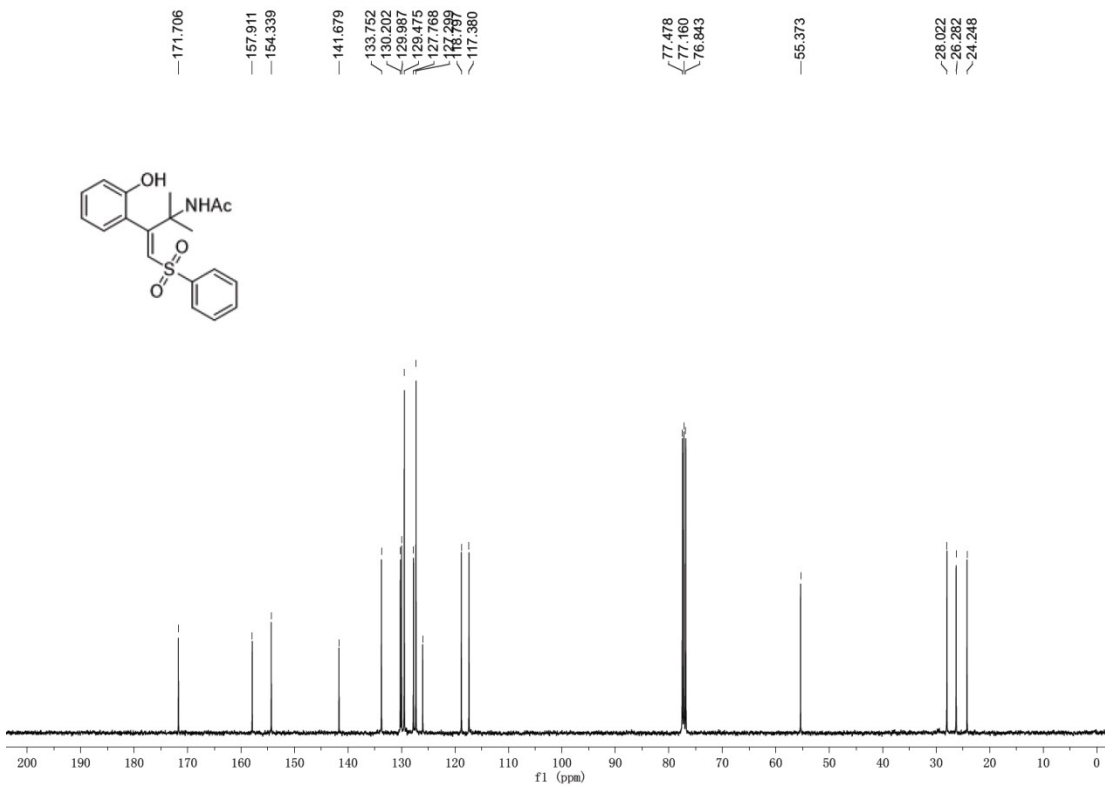
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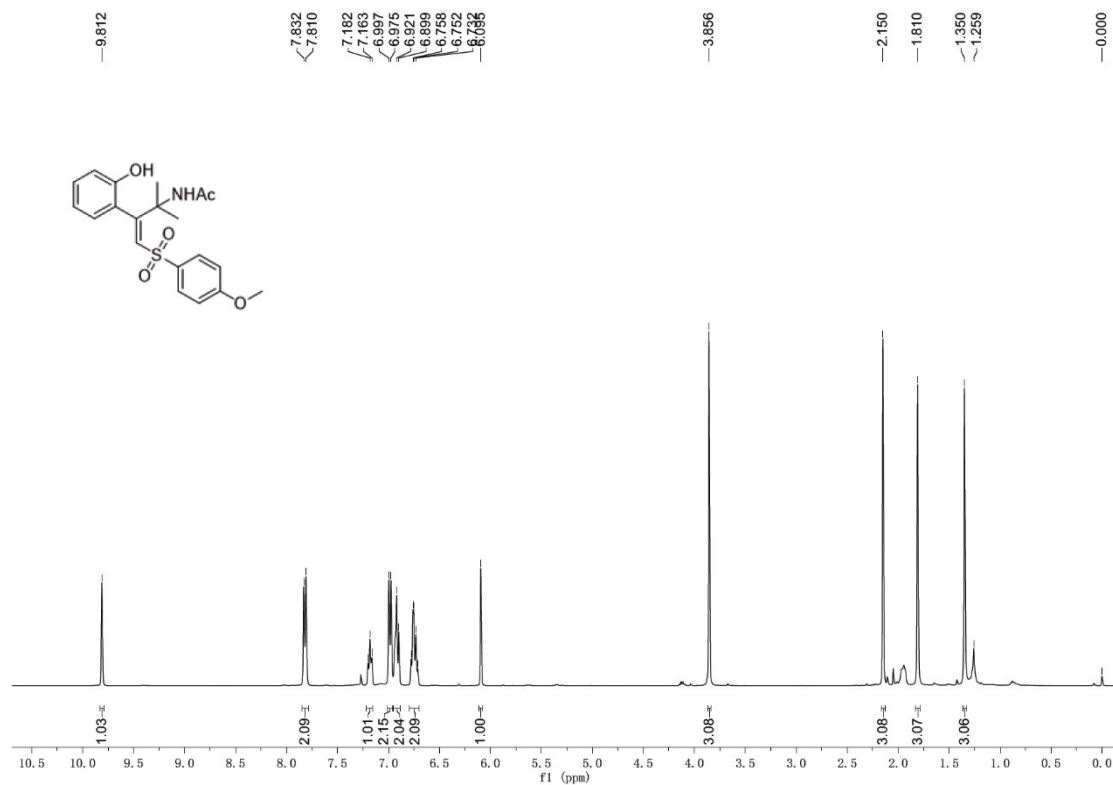
3ab-¹H NMR (400 MHz, CDCl₃)



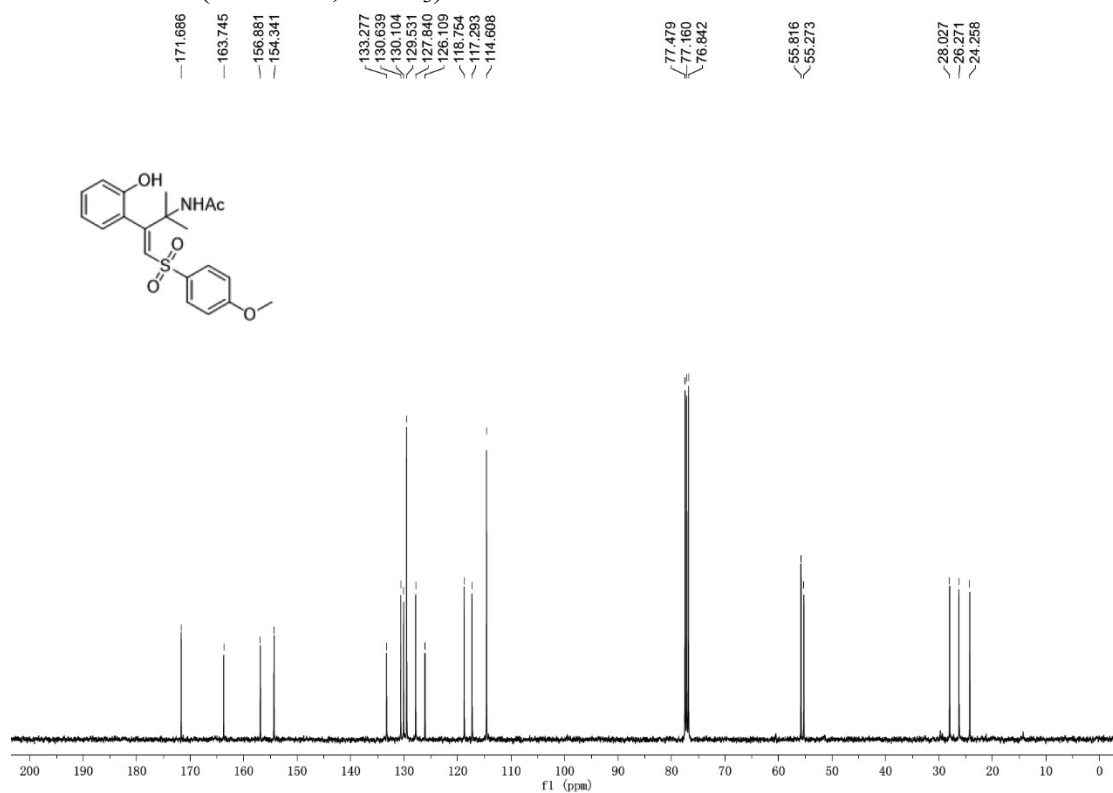
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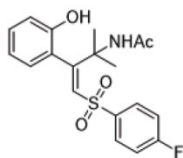
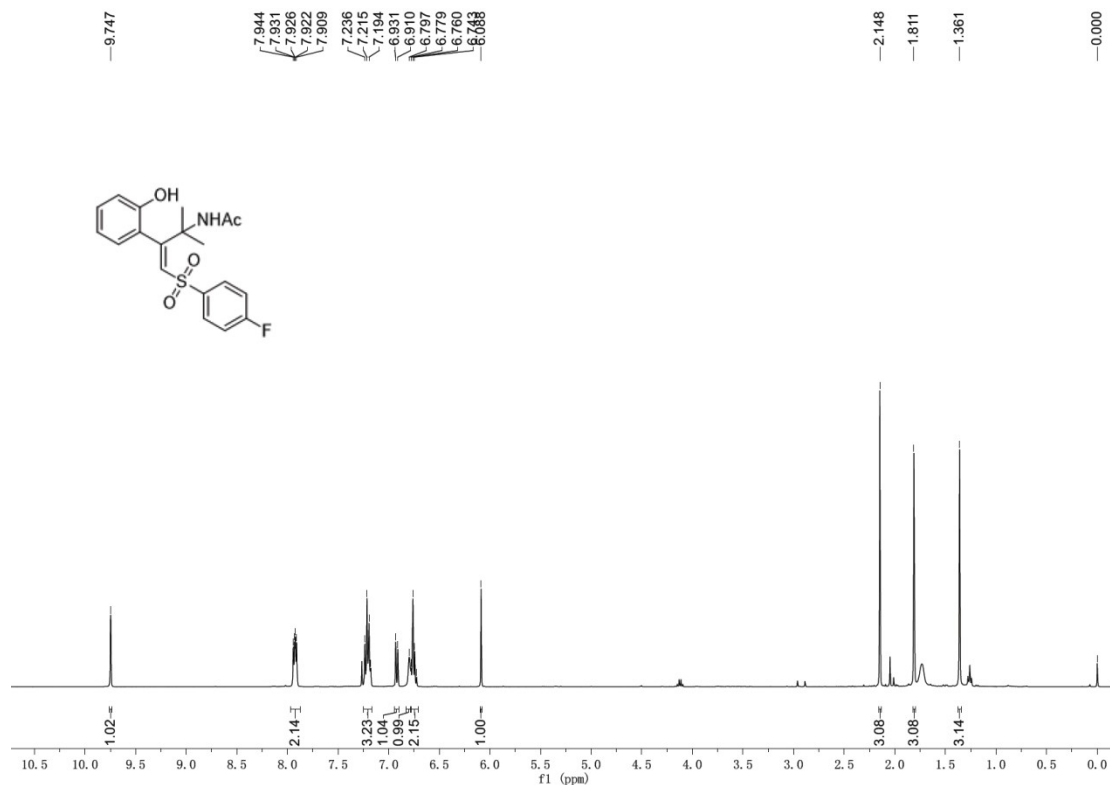
3ac-¹H NMR (400 MHz, CDCl₃)



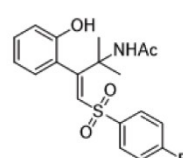
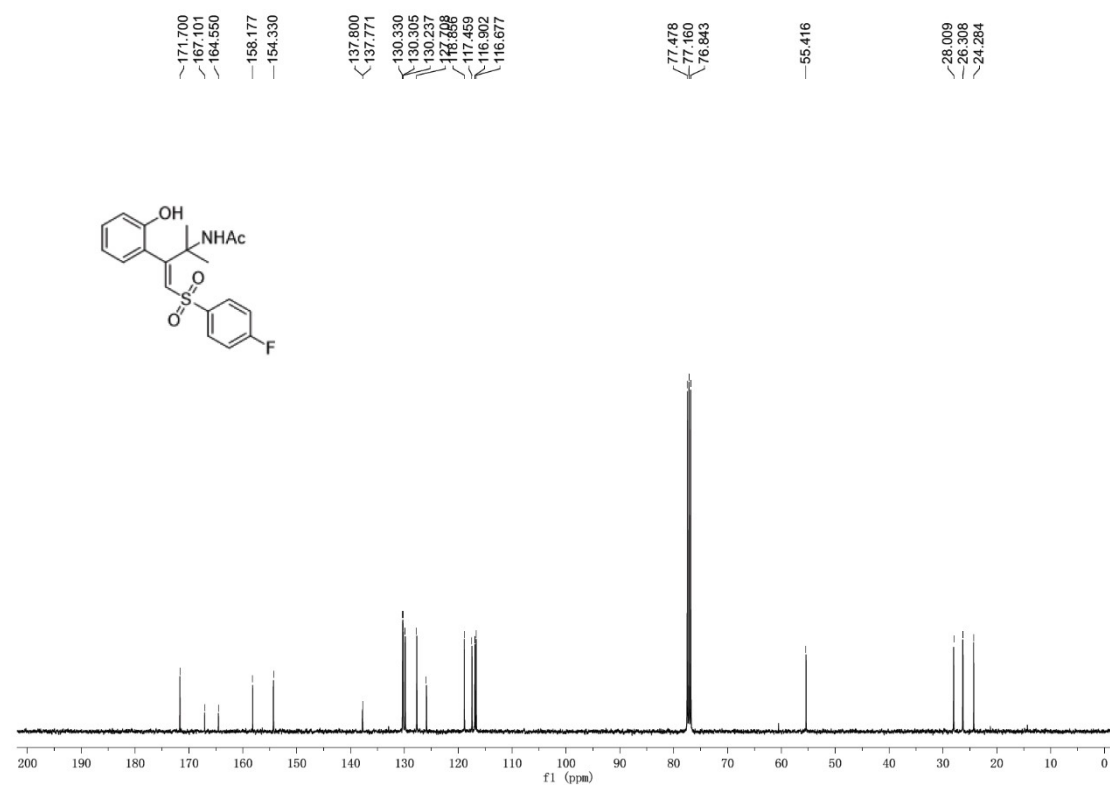
3ac-¹³C NMR (100 MHz, CDCl₃)



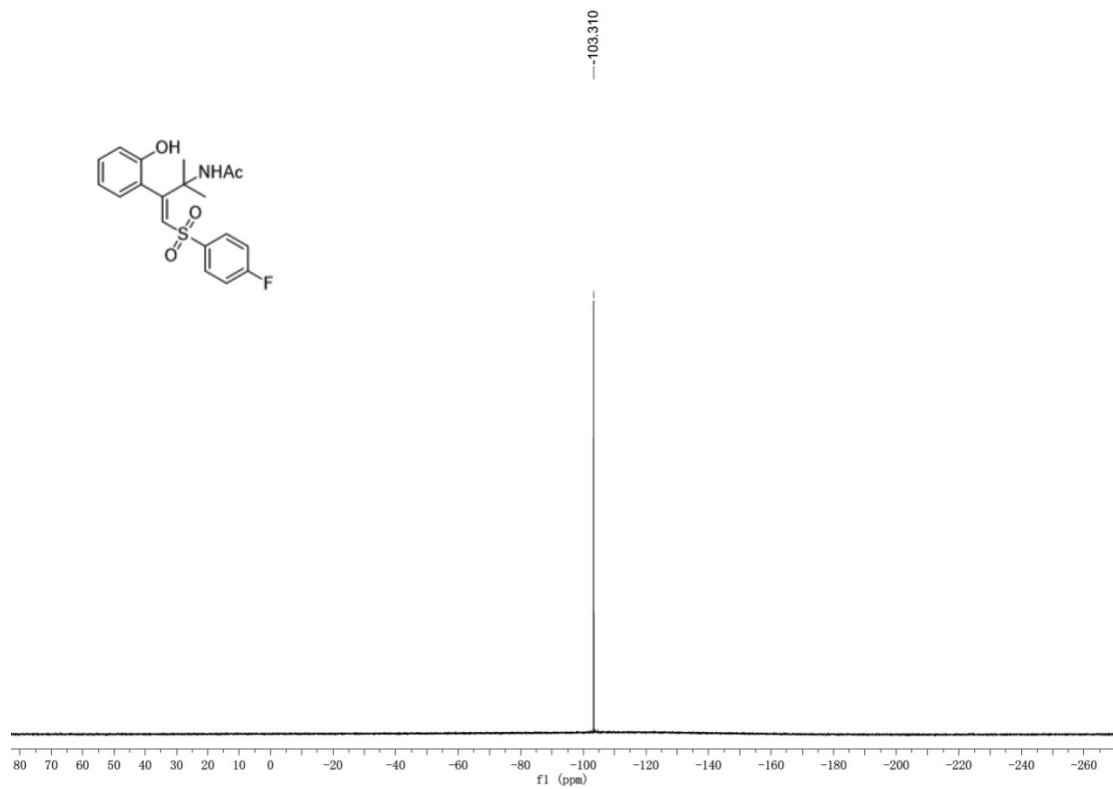
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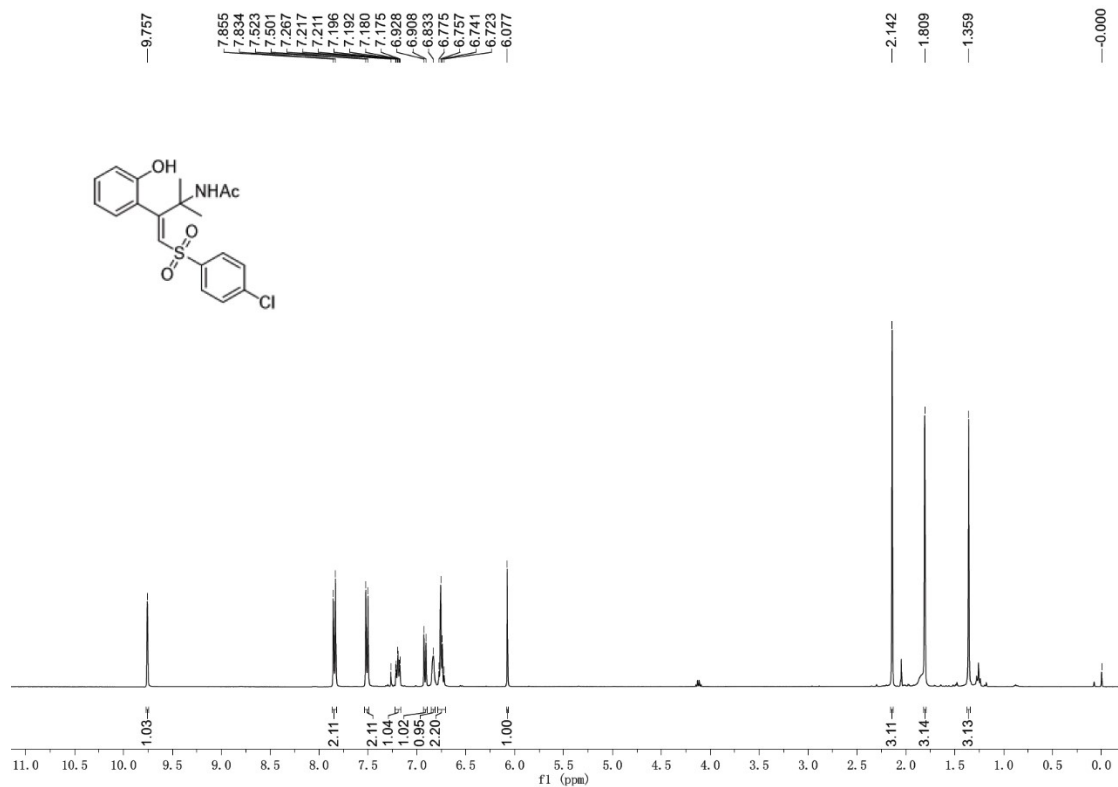
3ad-¹³C NMR (100 MHz, CDCl₃)



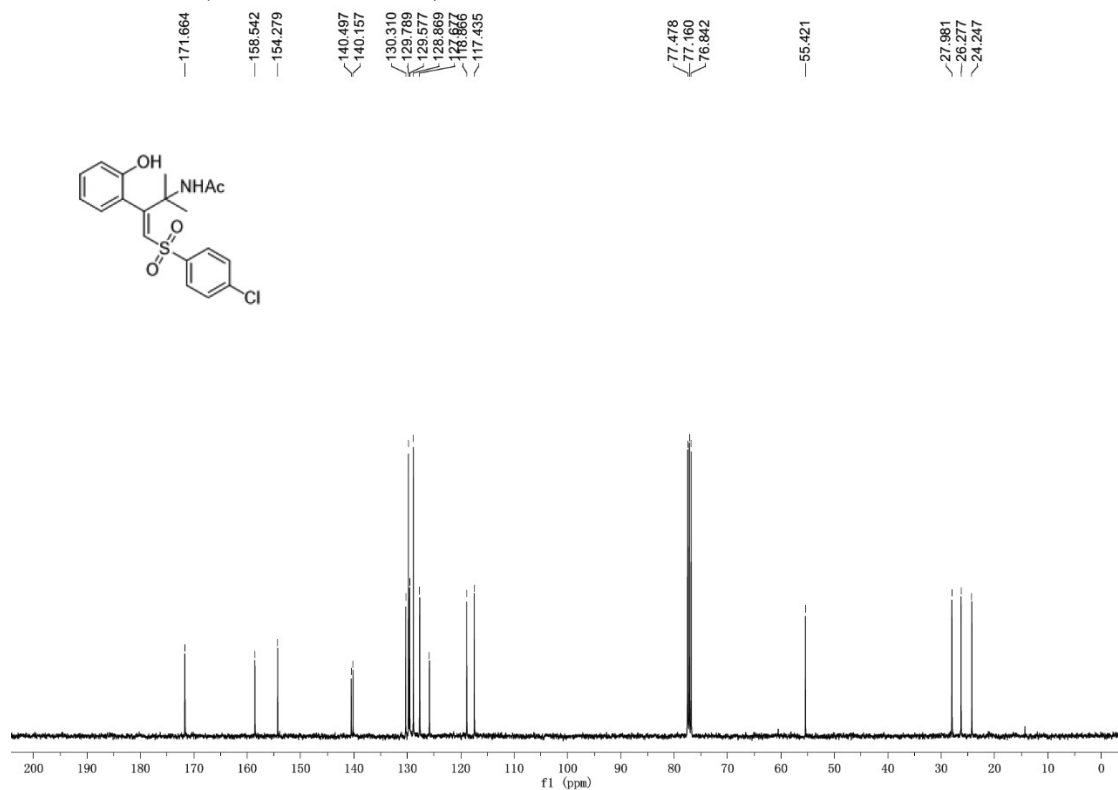
3ad-¹⁹F NMR (376 MHz, CDCl₃)



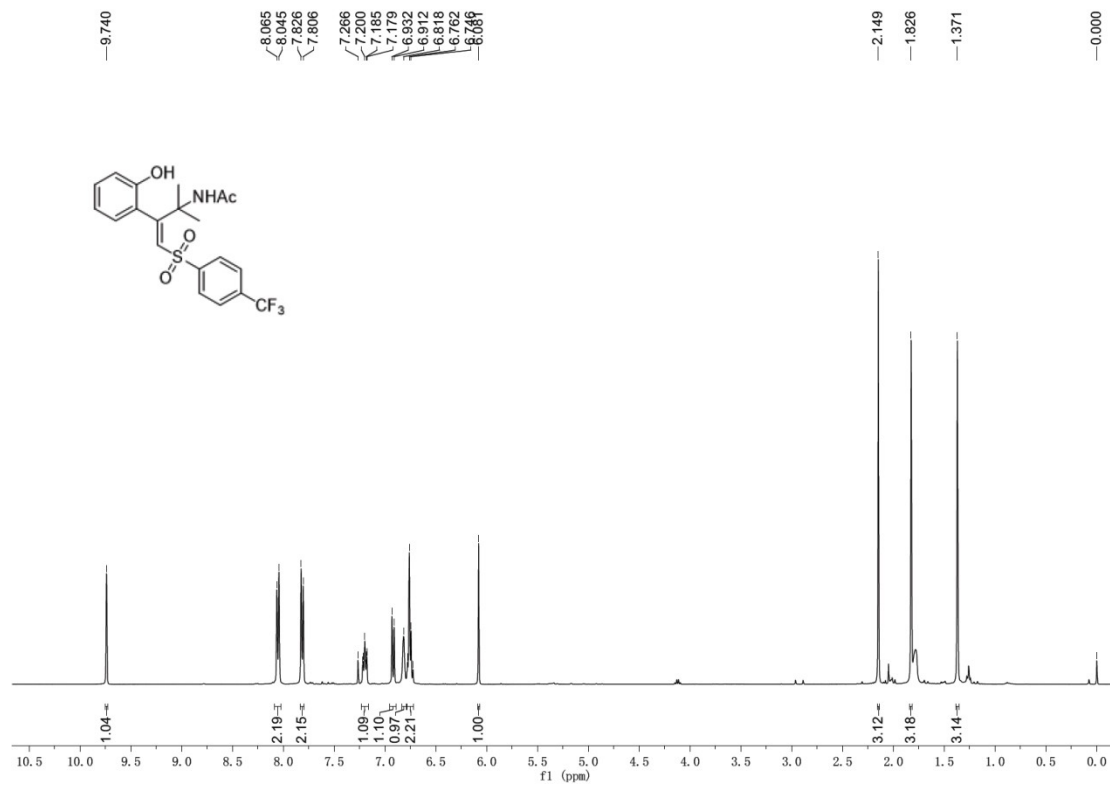
3ae-¹H NMR (400 MHz, CDCl₃)



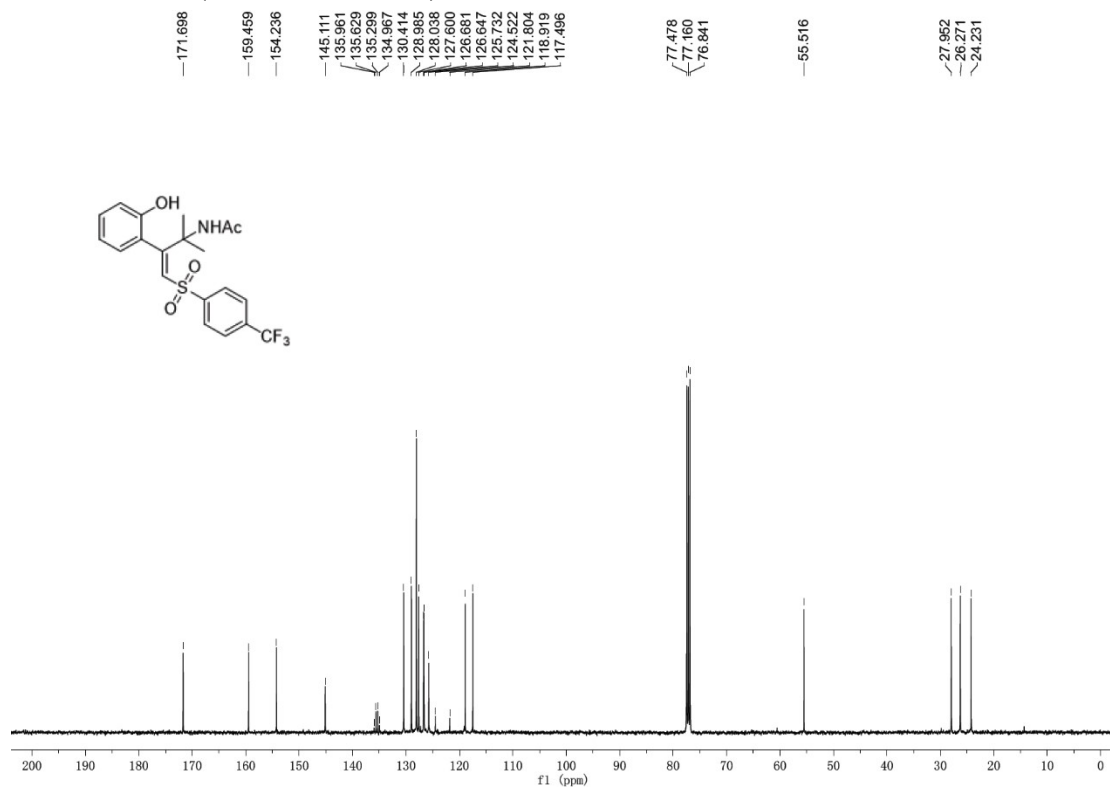
3ae-¹³C NMR (100 MHz, CDCl₃)



3af-¹H NMR (400 MHz, CDCl₃)

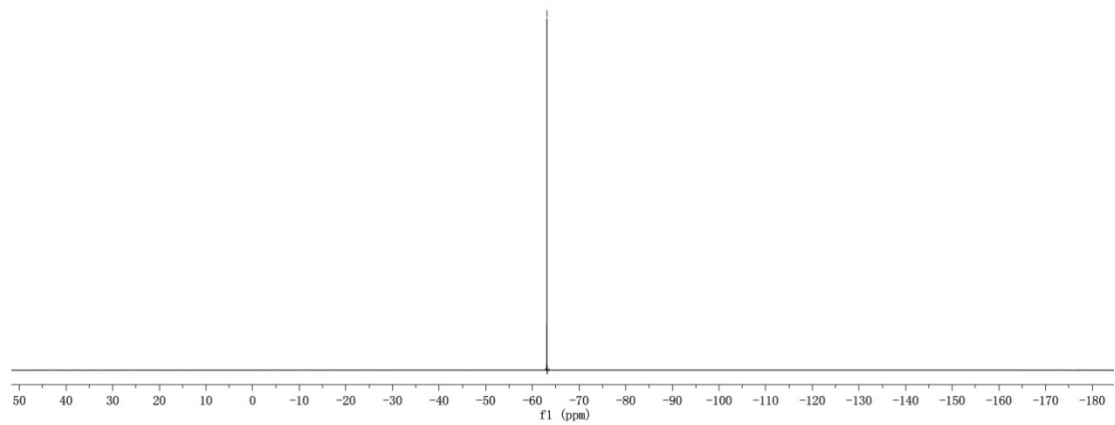
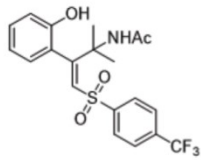


3af-¹³C NMR (100 MHz, CDCl₃)

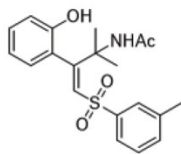
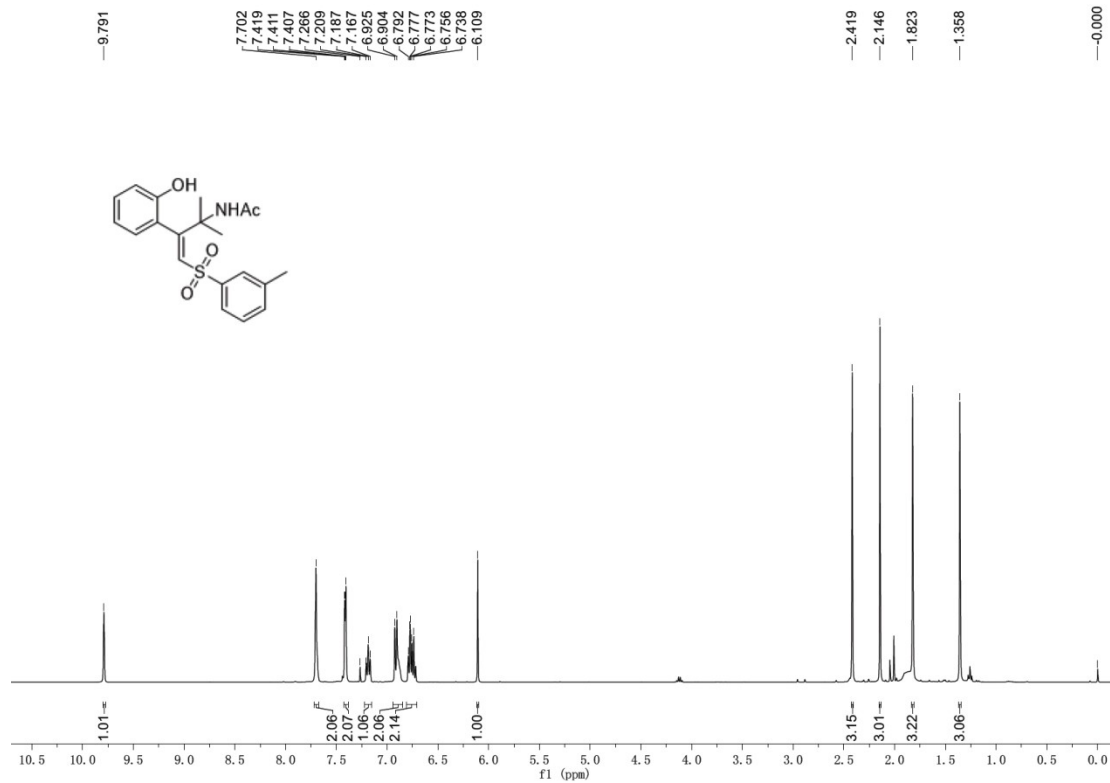


3af-¹⁹F NMR (376 MHz, CDCl₃)

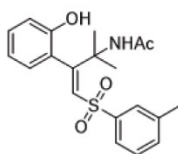
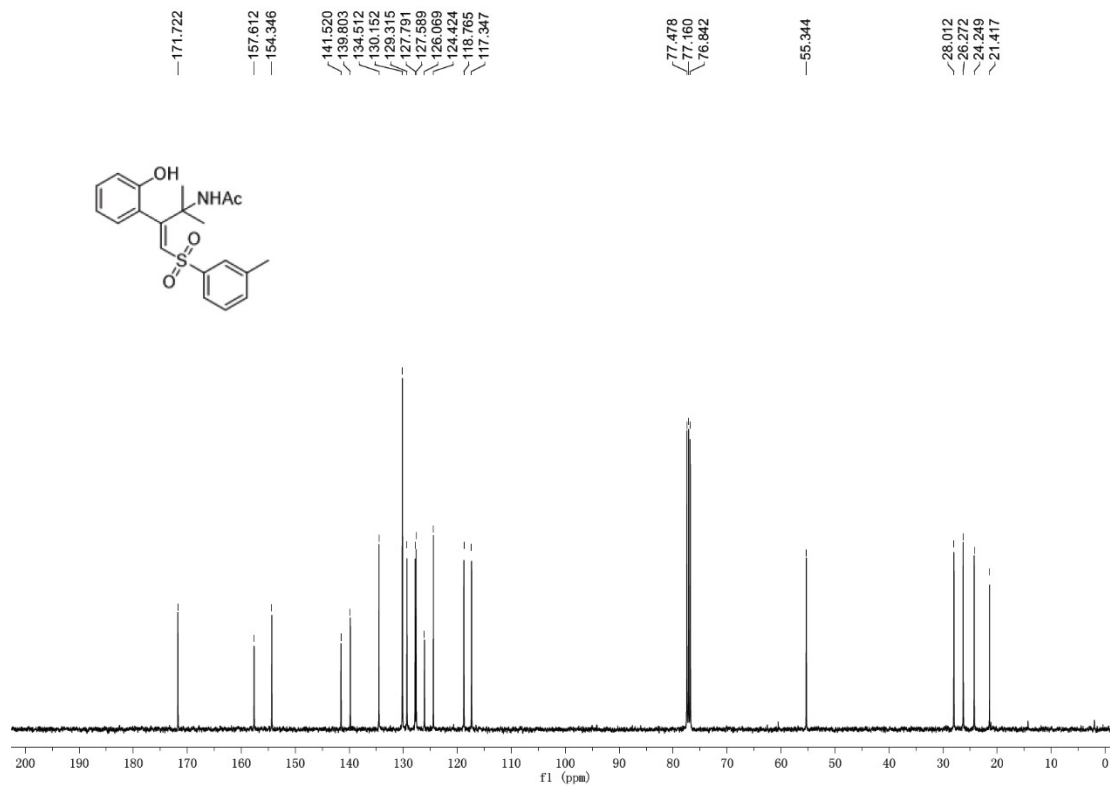
—63.130



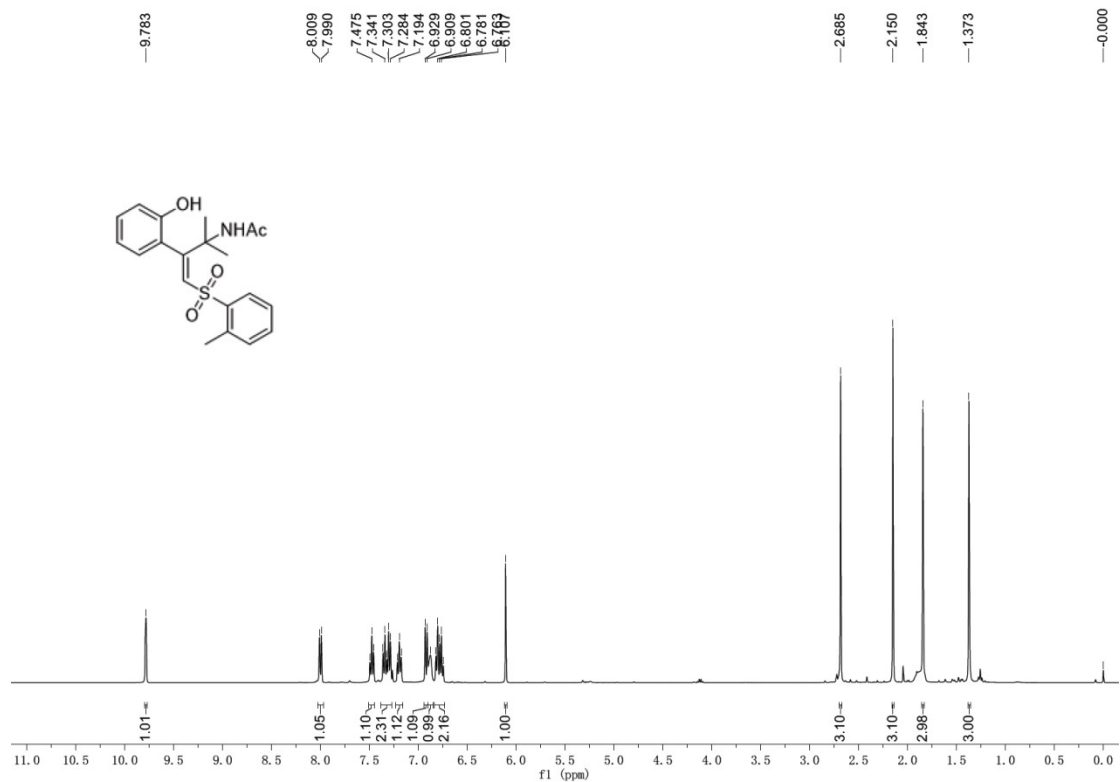
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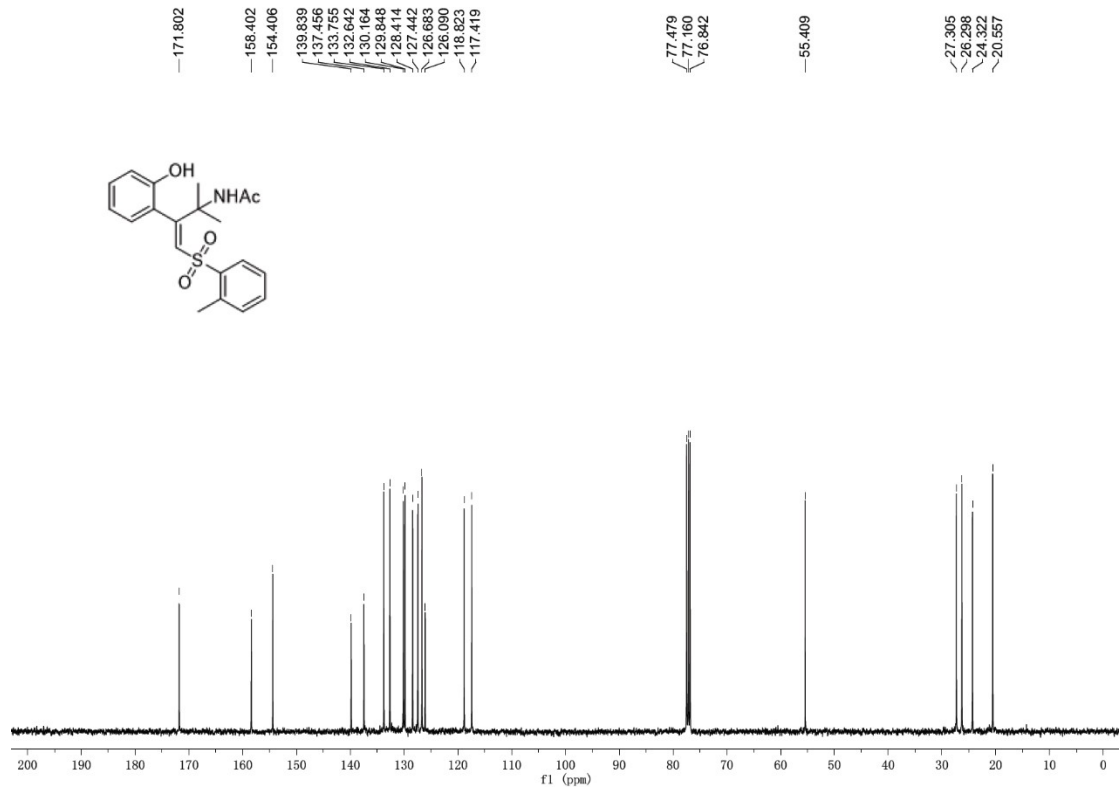
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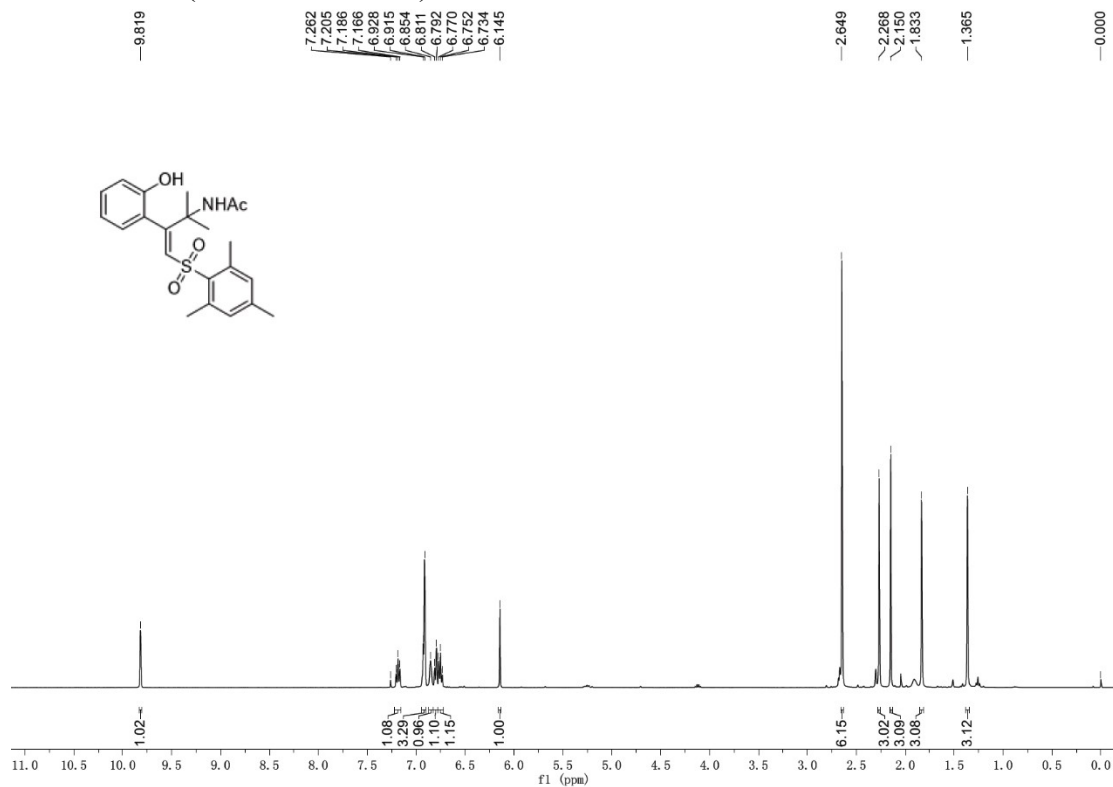
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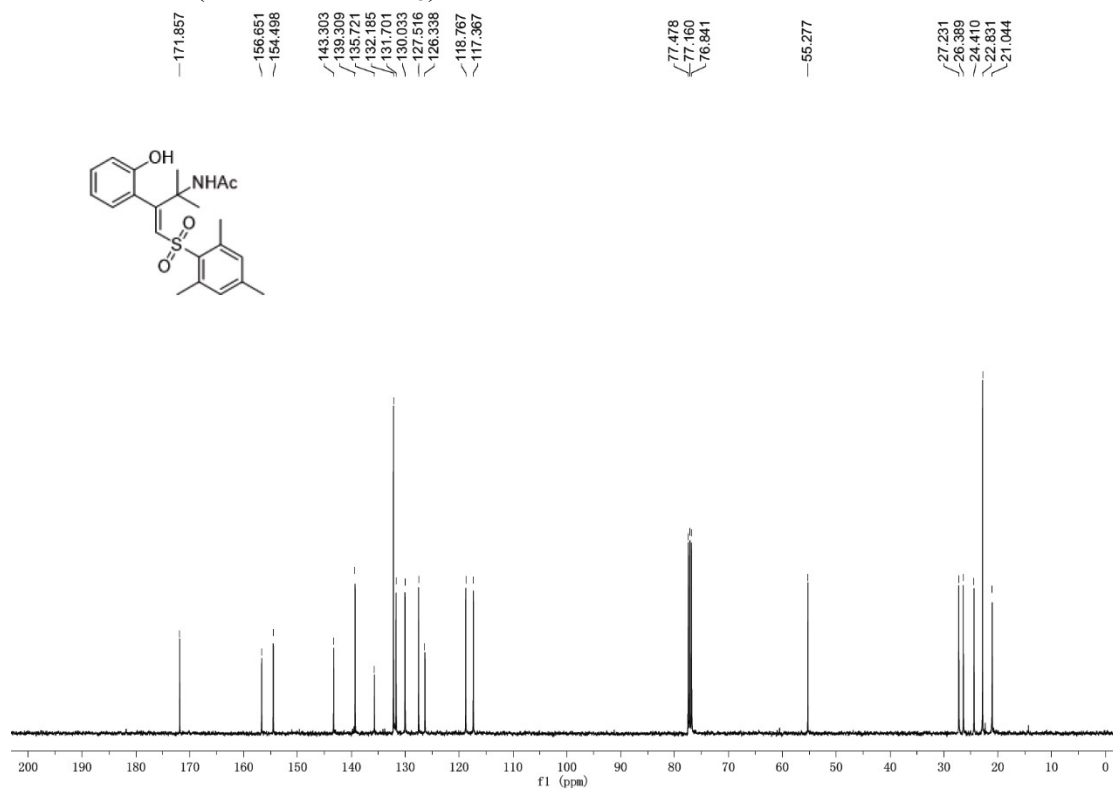
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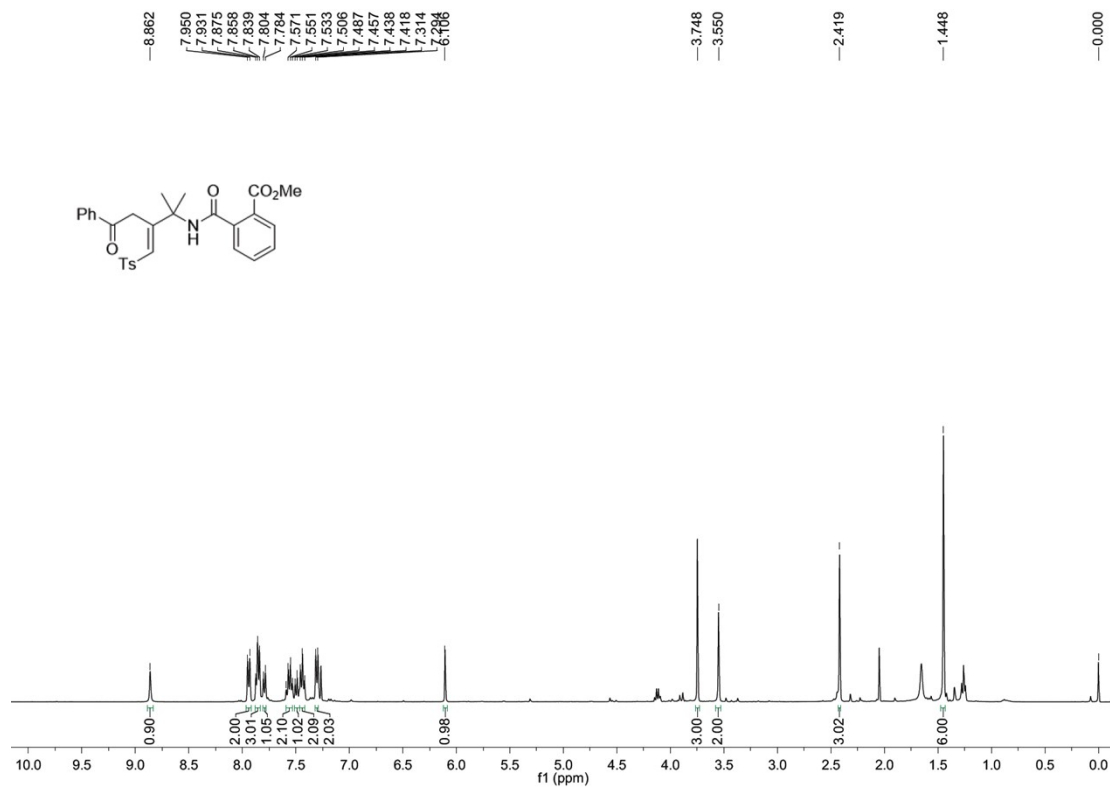
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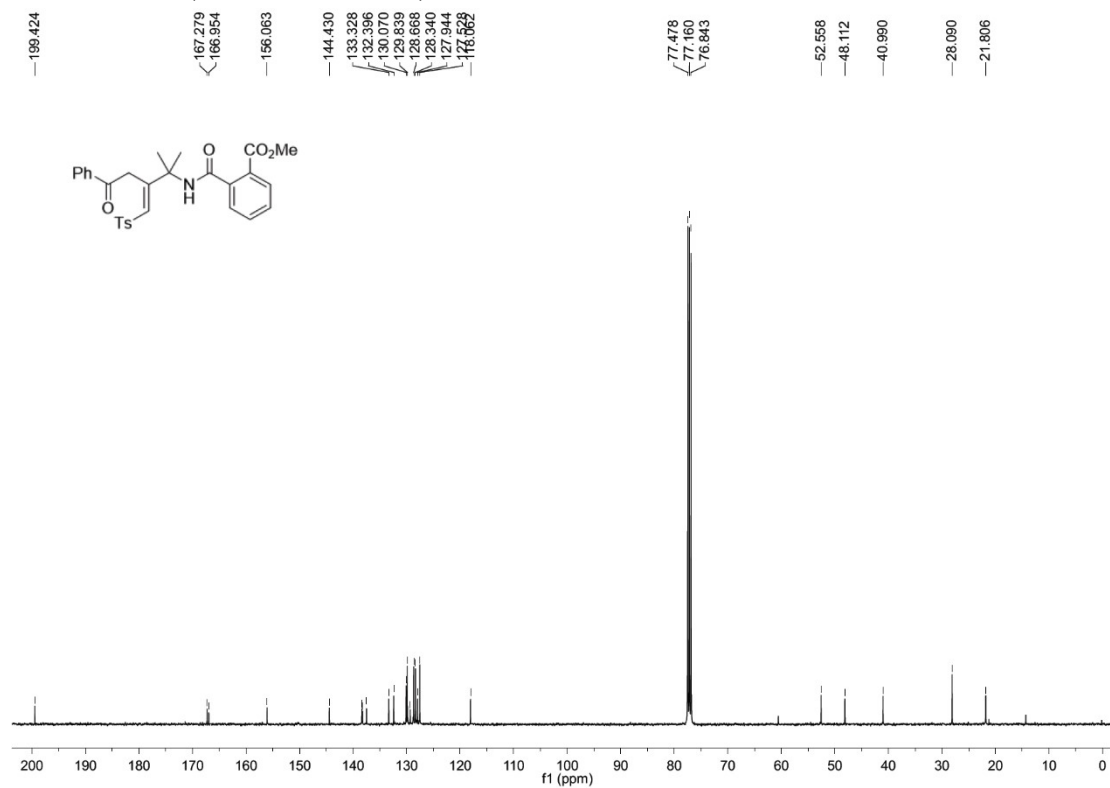
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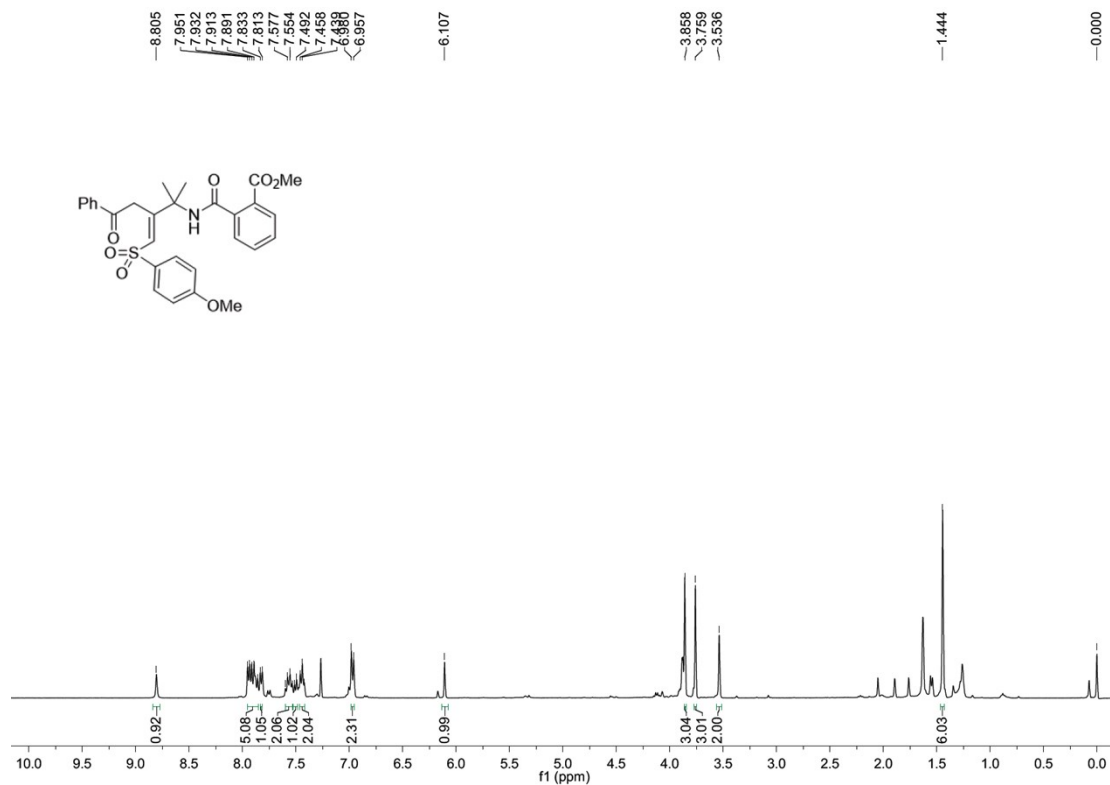
5a-¹H NMR (400 MHz, CDCl₃)



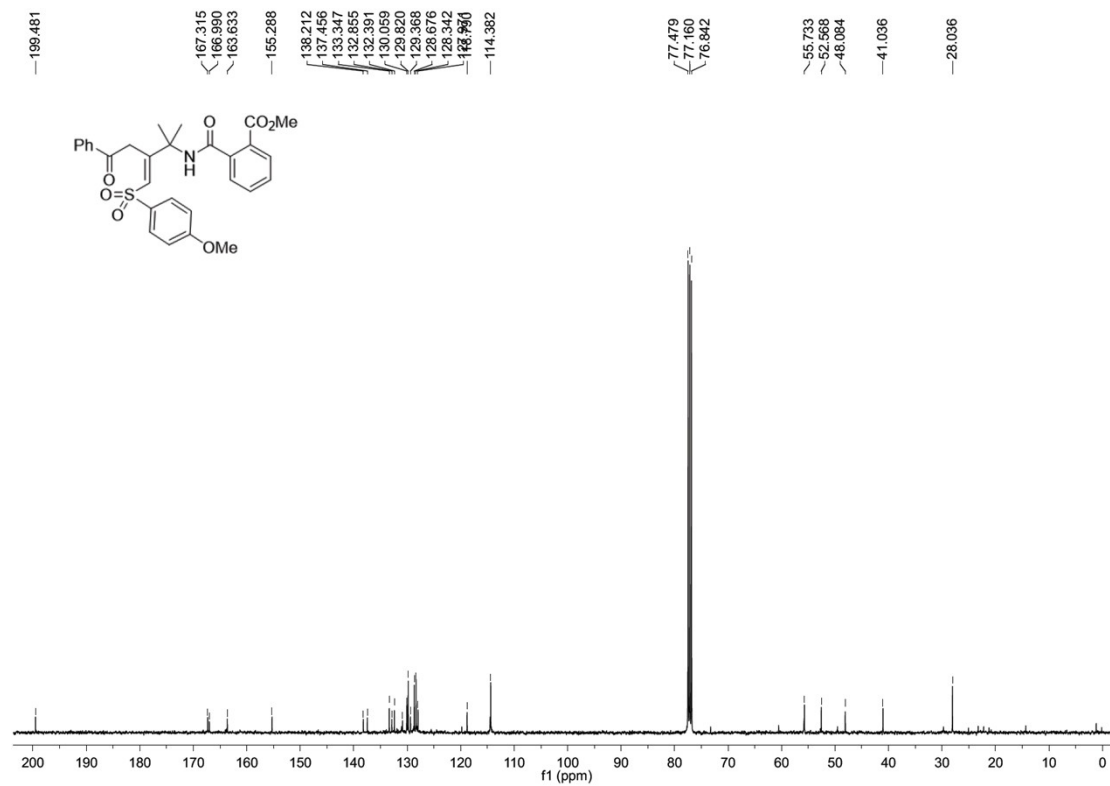
5a-¹³C NMR (100 MHz, CDCl₃)



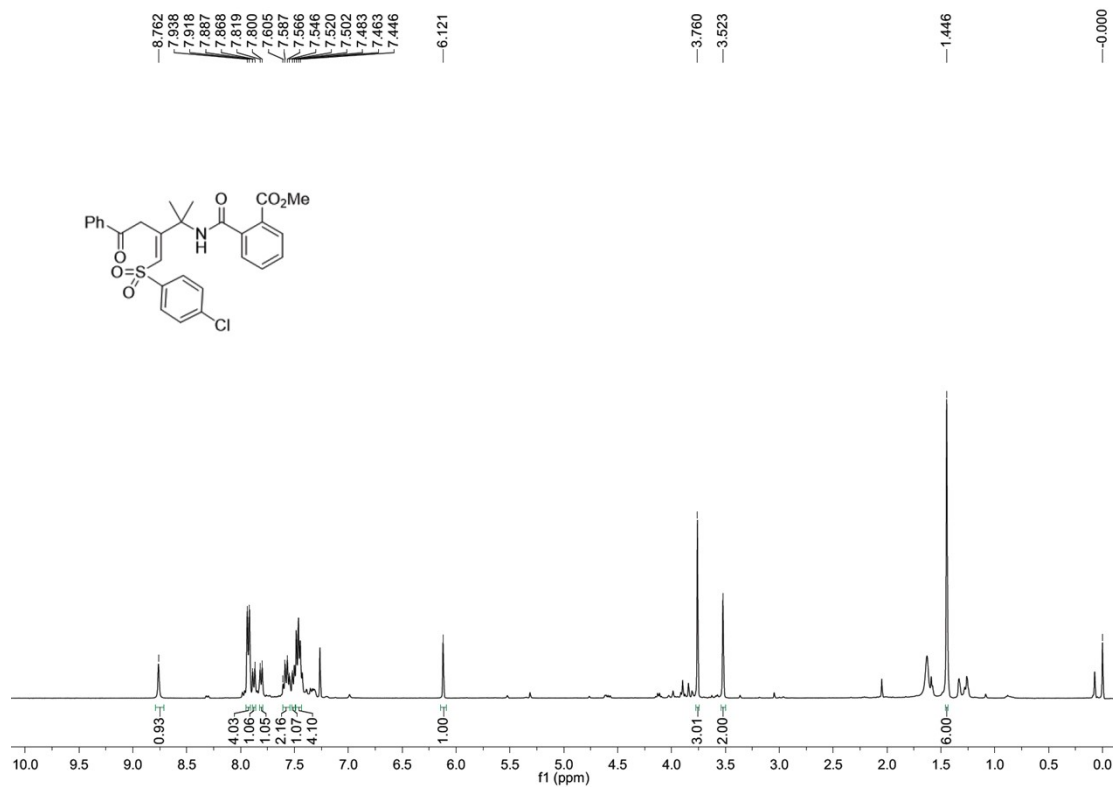
5b-¹H NMR (400 MHz, CDCl₃)



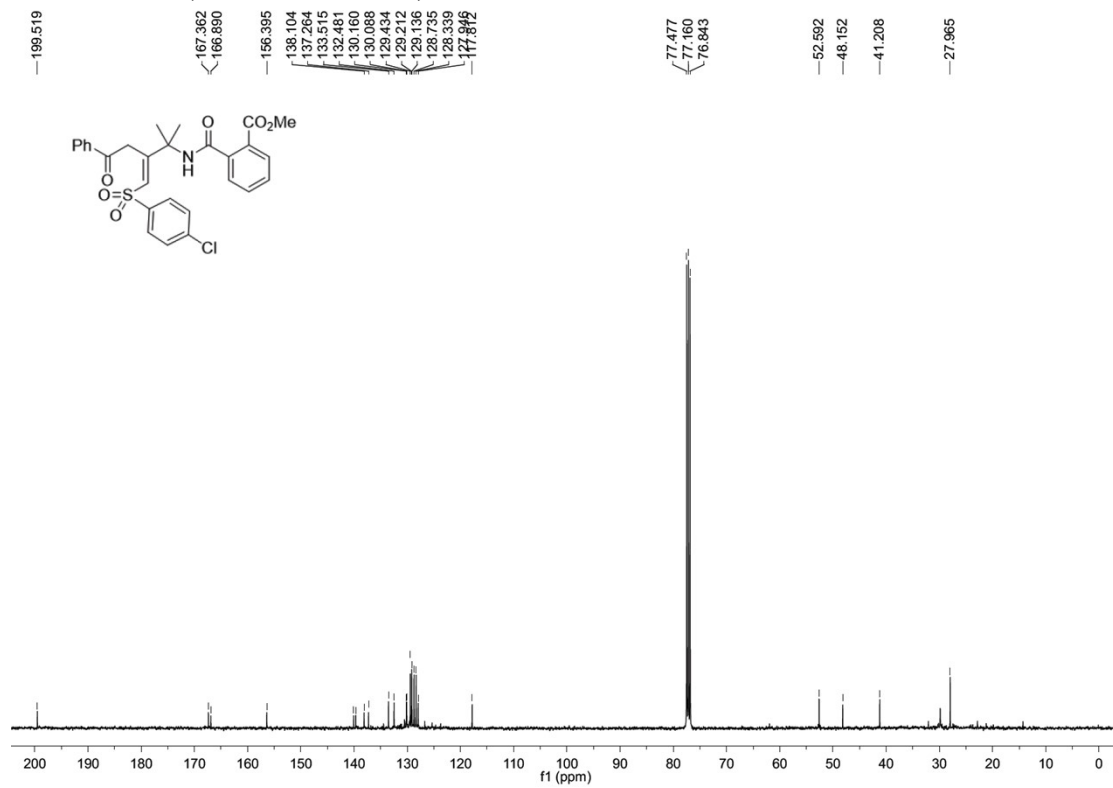
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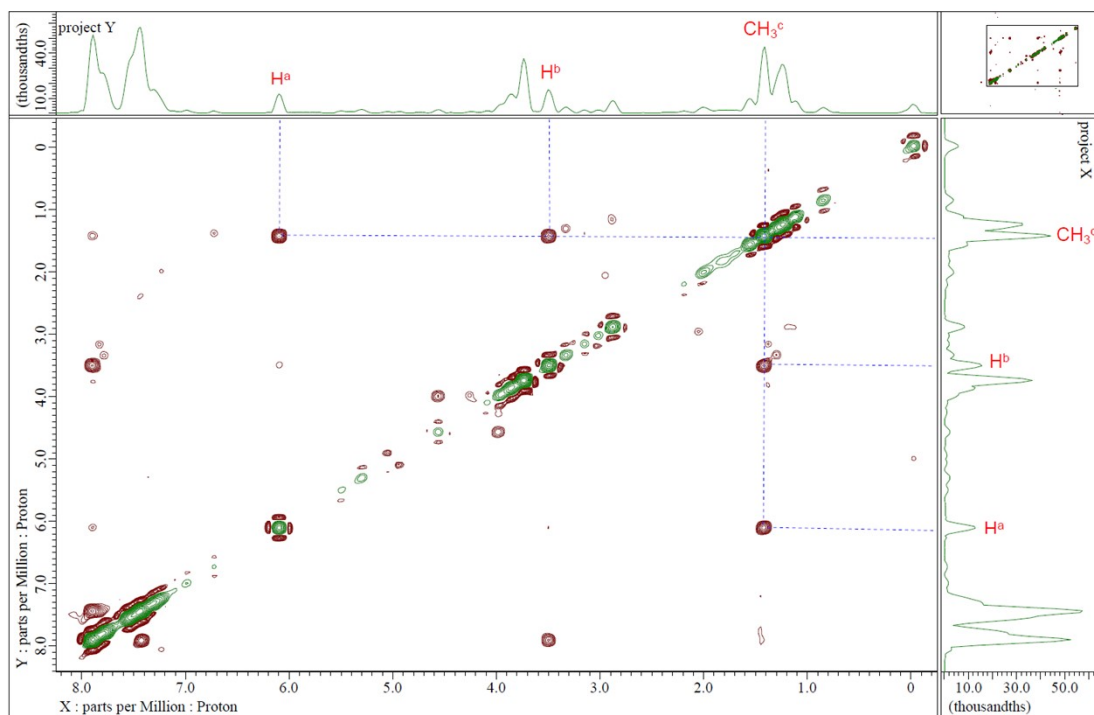
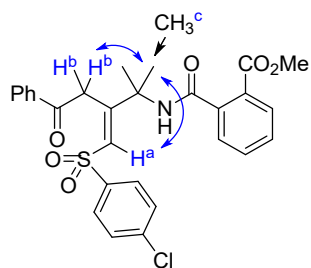
5c-¹H NMR (400 MHz, CDCl₃)



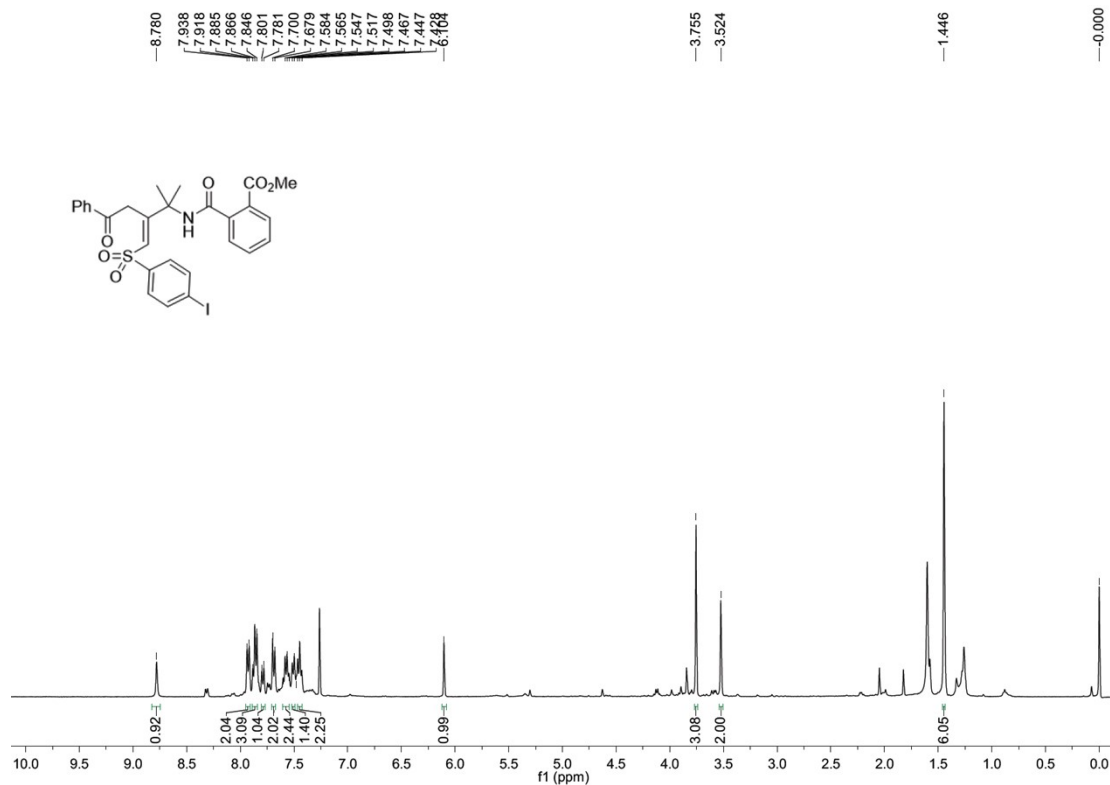
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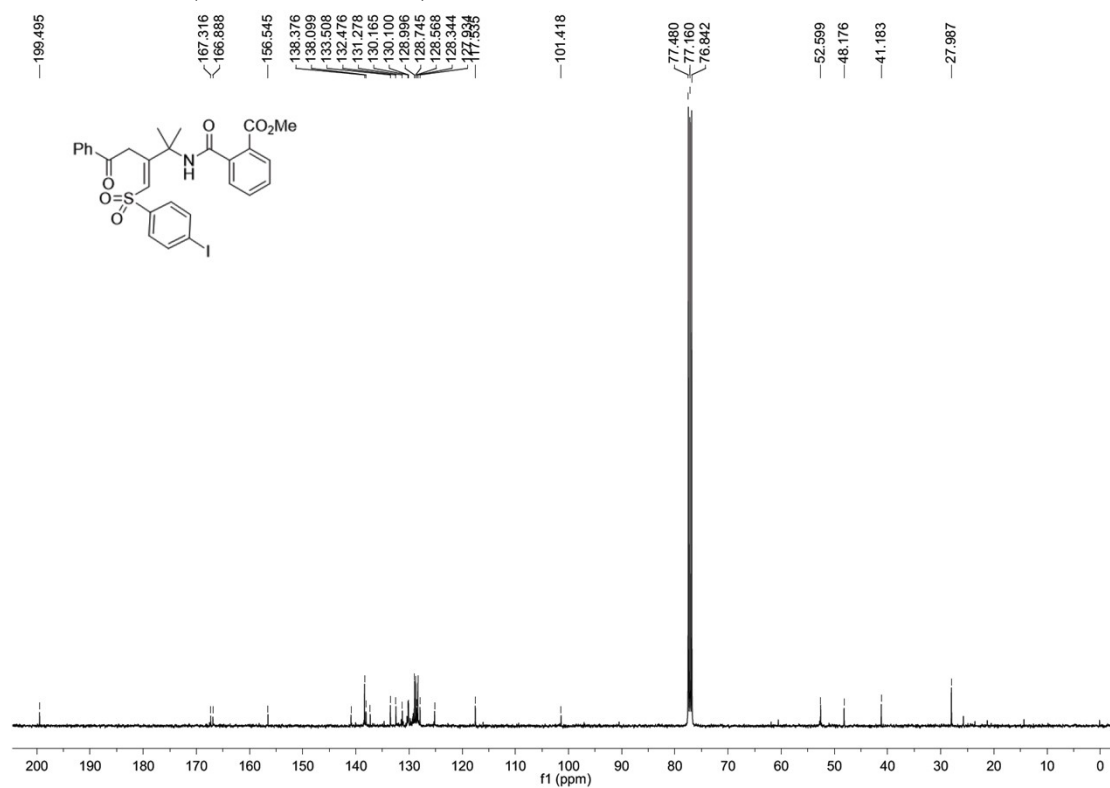
^1H - ^1H NOESY of 5c:



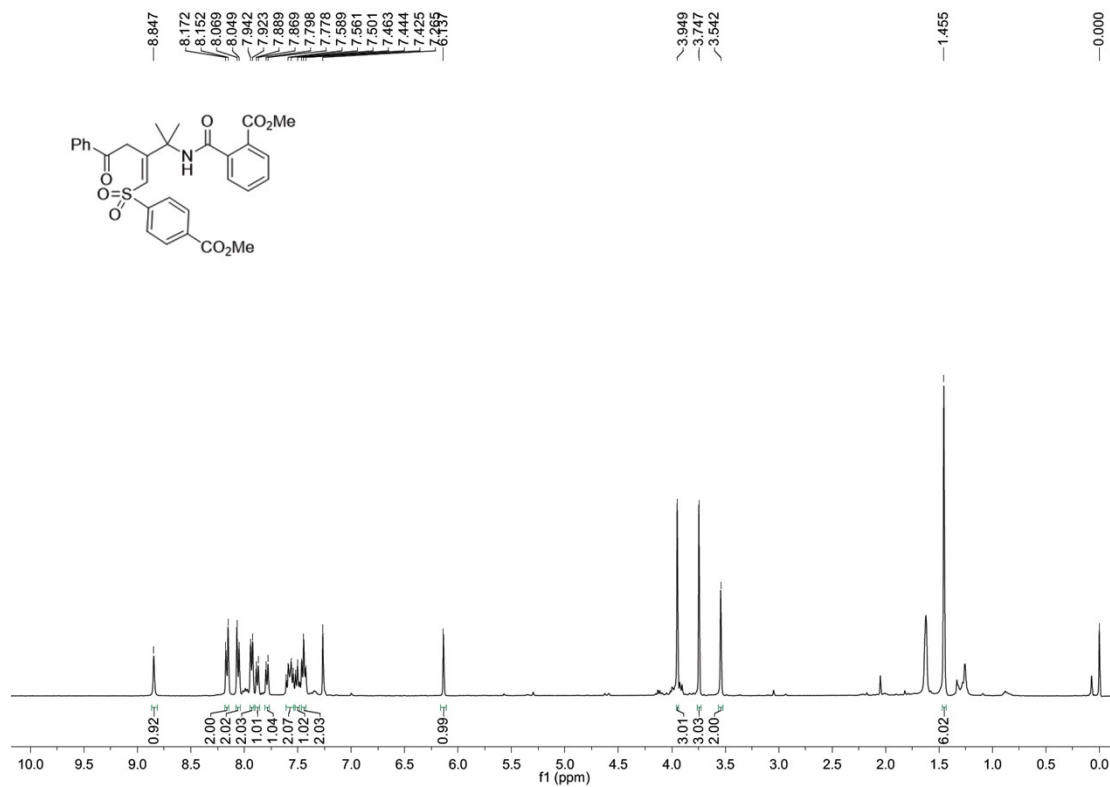
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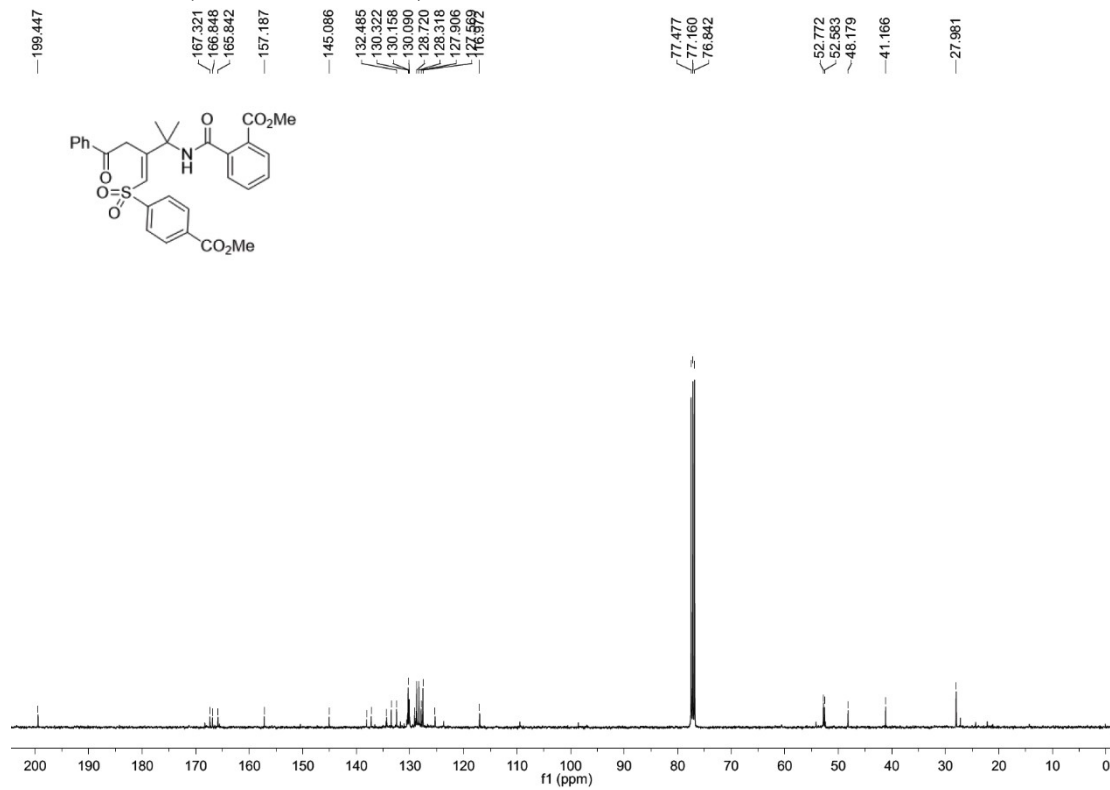
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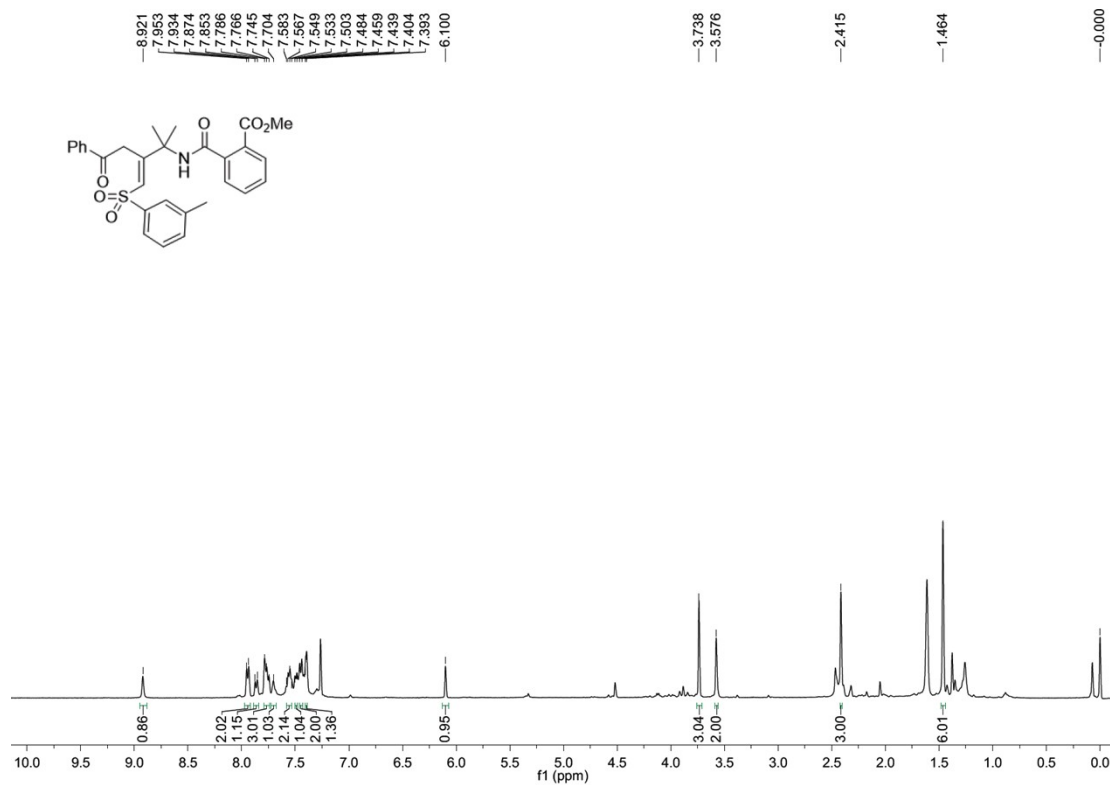
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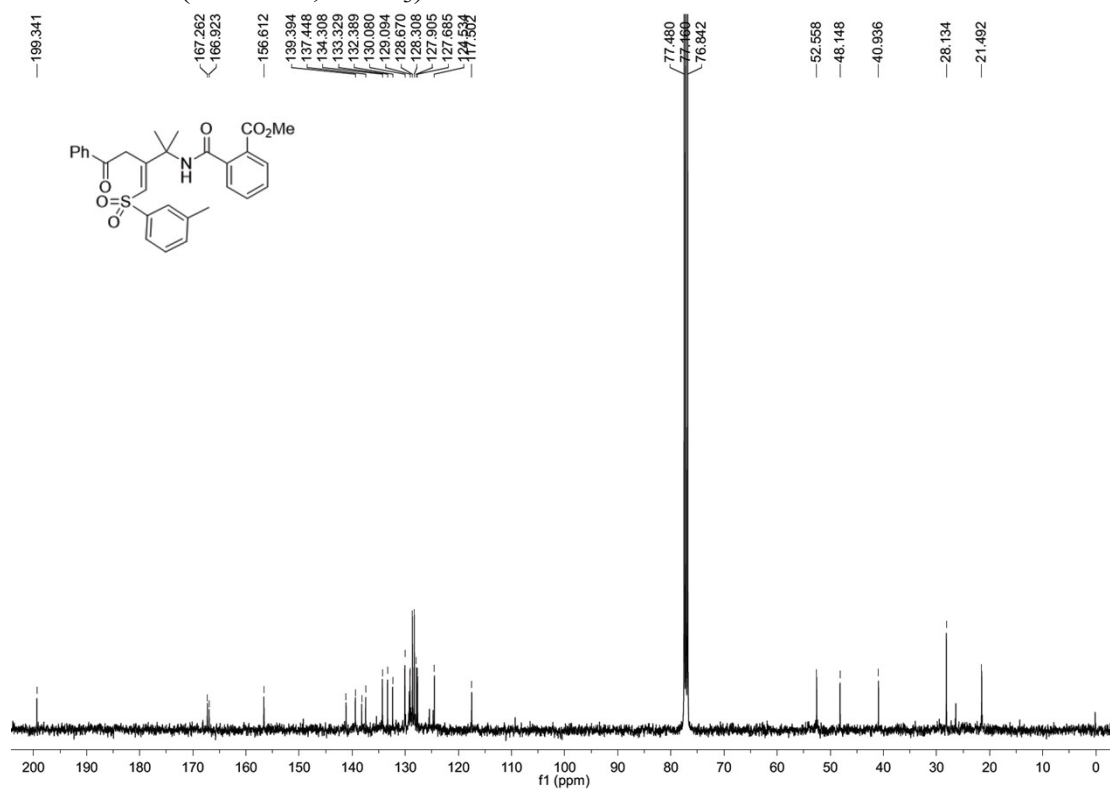
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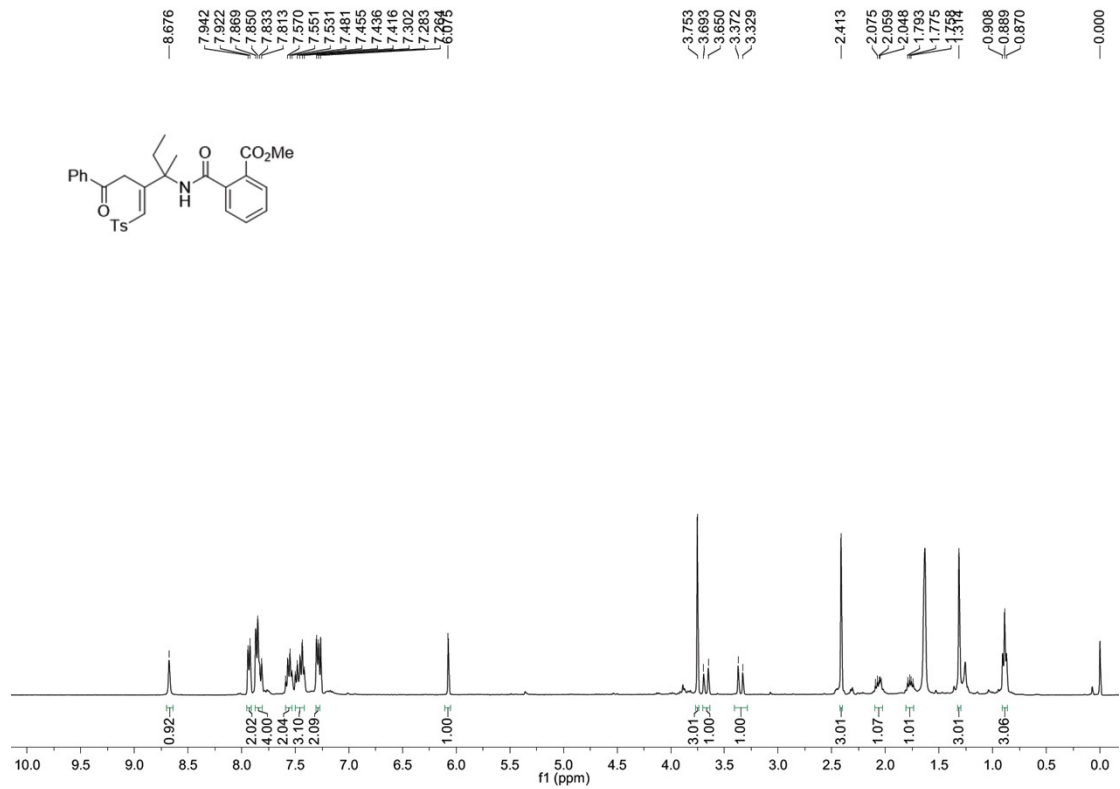
5f-¹H NMR (400 MHz, CDCl₃)



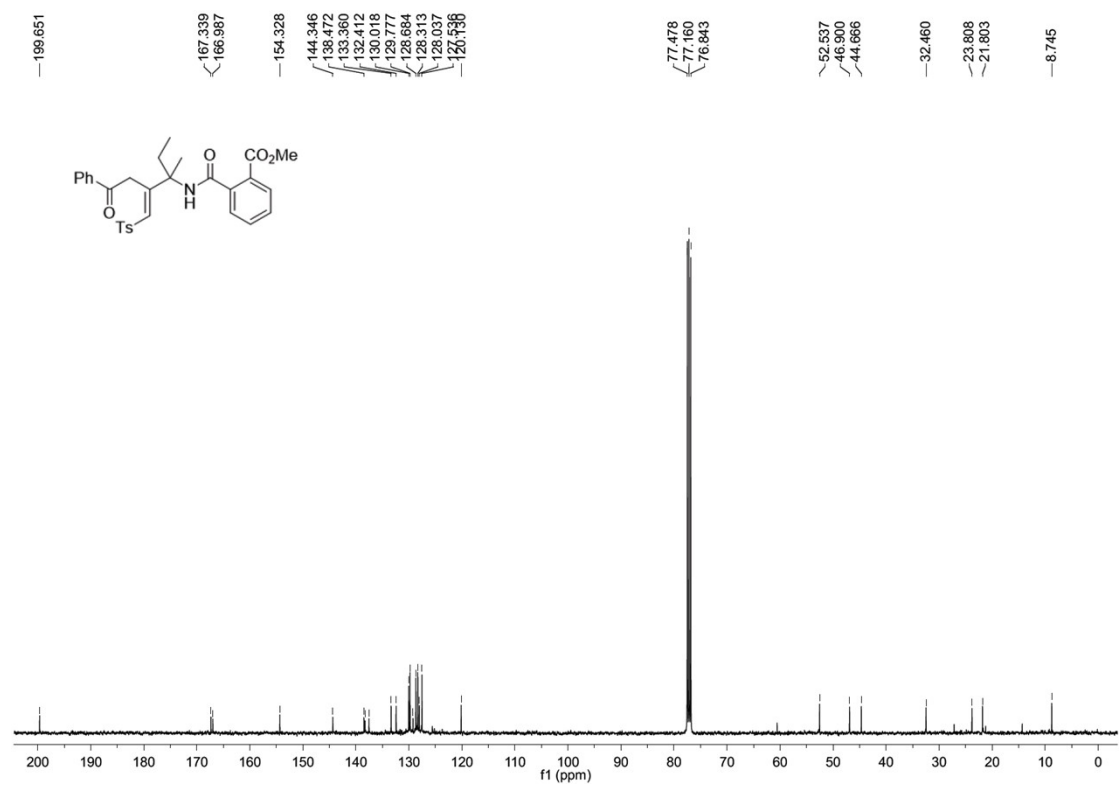
5f-¹³C NMR (100 MHz, CDCl₃)



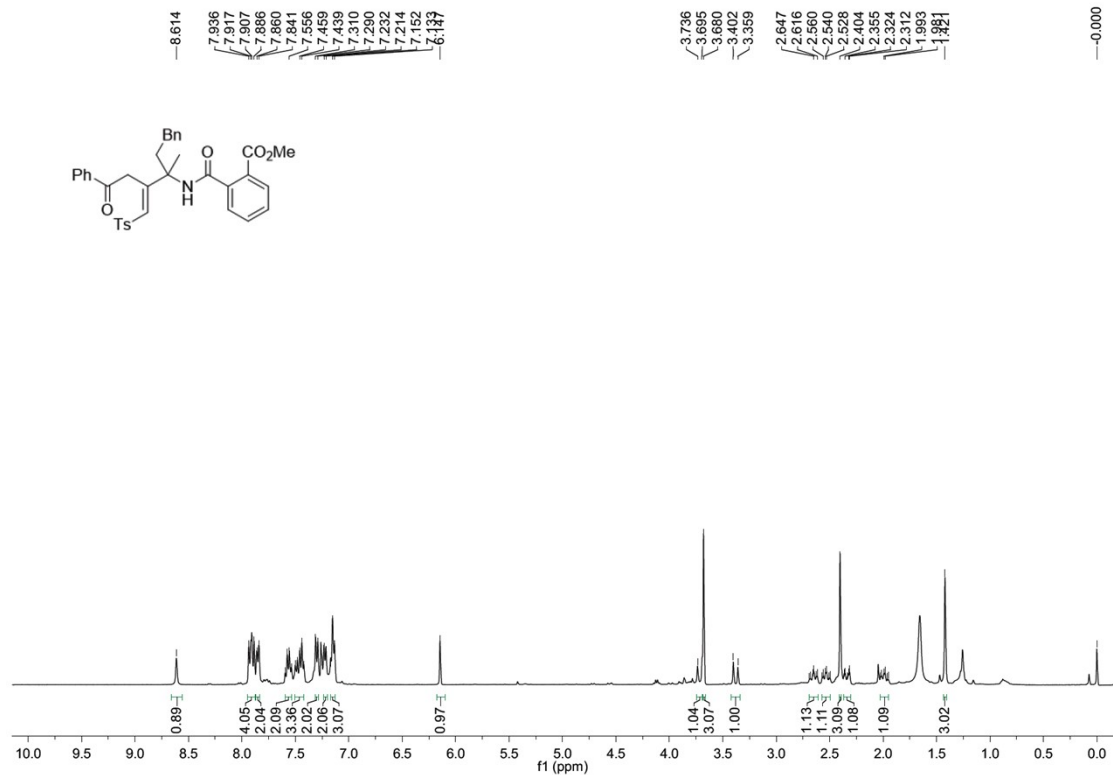
5g-¹H NMR (400 MHz, CDCl₃)



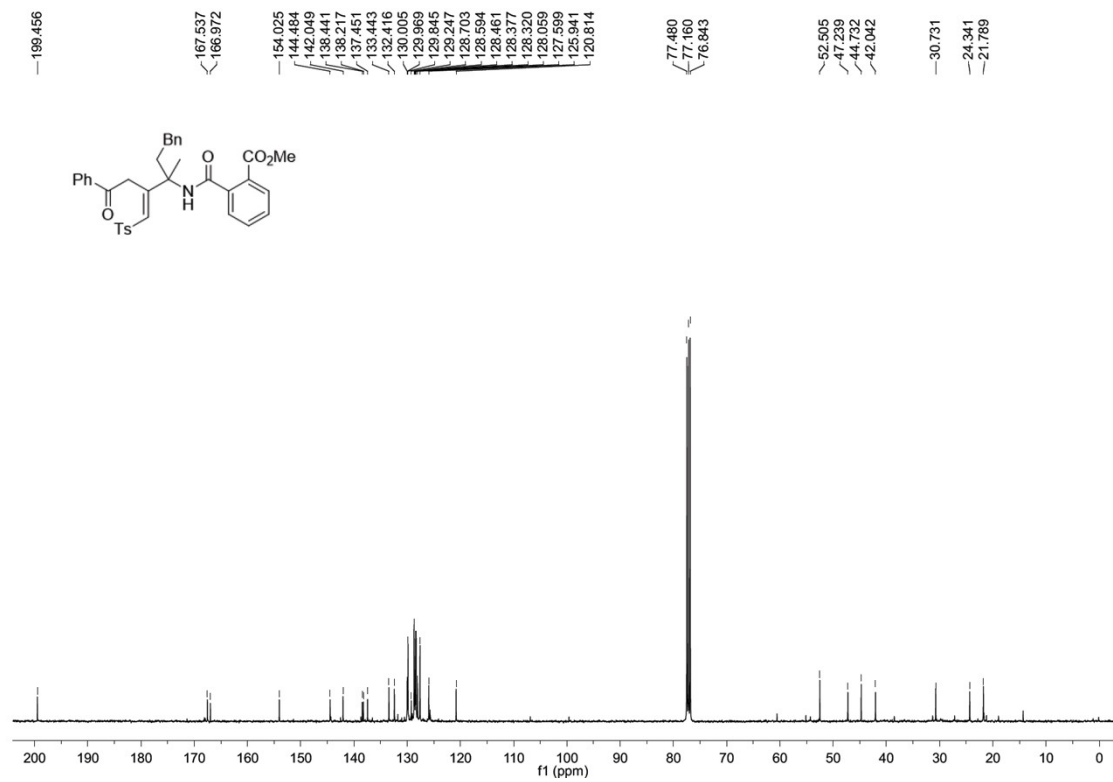
5g-¹³C NMR (100 MHz, CDCl₃)



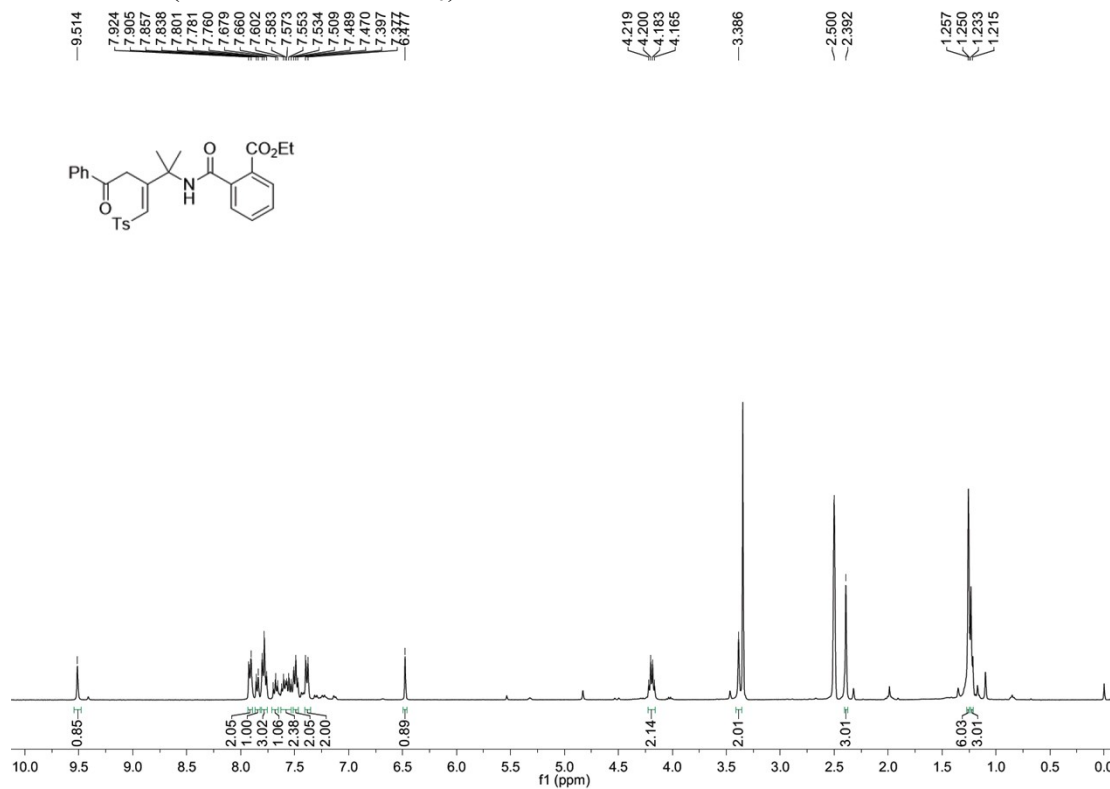
5h-¹H NMR (400 MHz, CDCl₃)



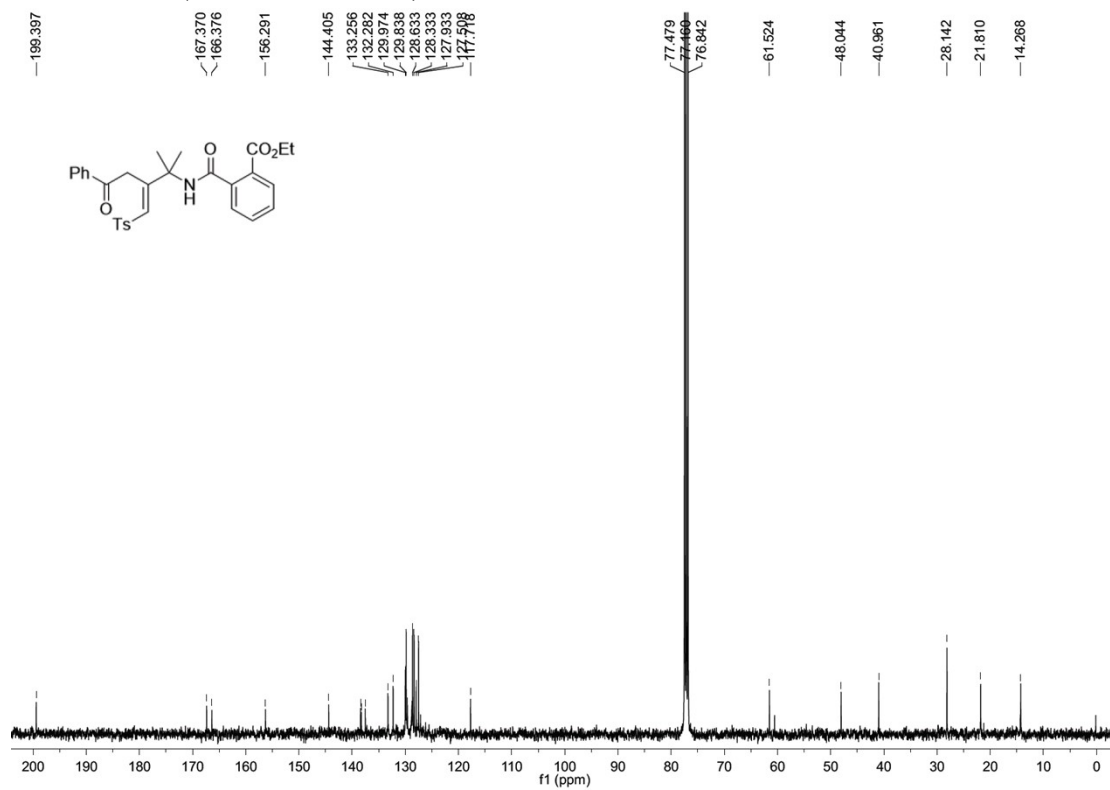
5h-¹³C NMR (100 MHz, CDCl₃)



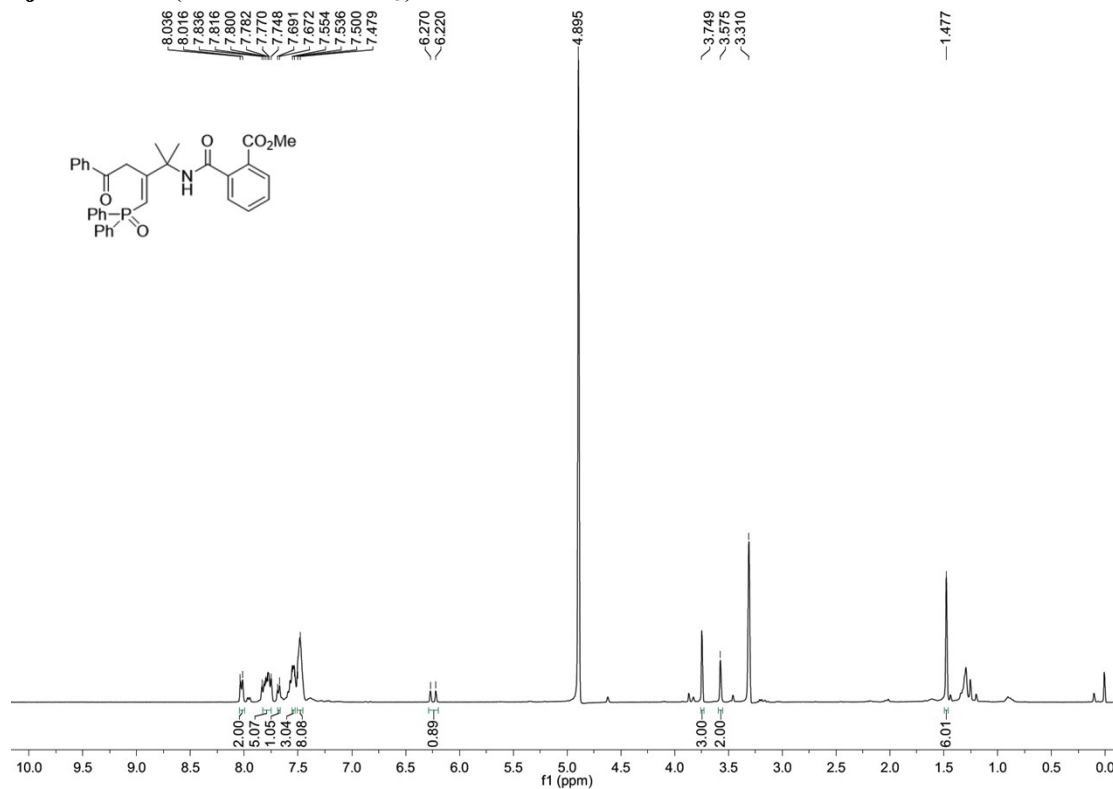
5i-¹H NMR (400 MHz, DMSO-*d*₆)



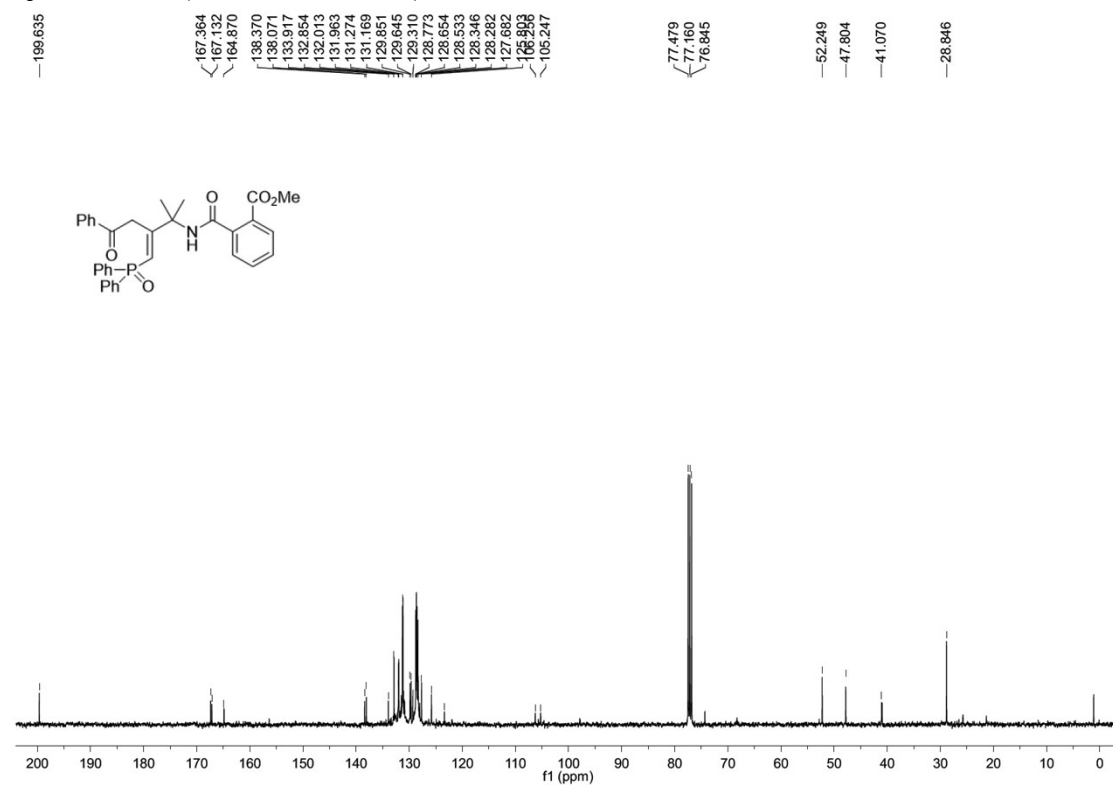
5i-¹³C NMR (100 MHz, CDCl₃)



5j-¹H NMR (400 MHz, CDCl₃)

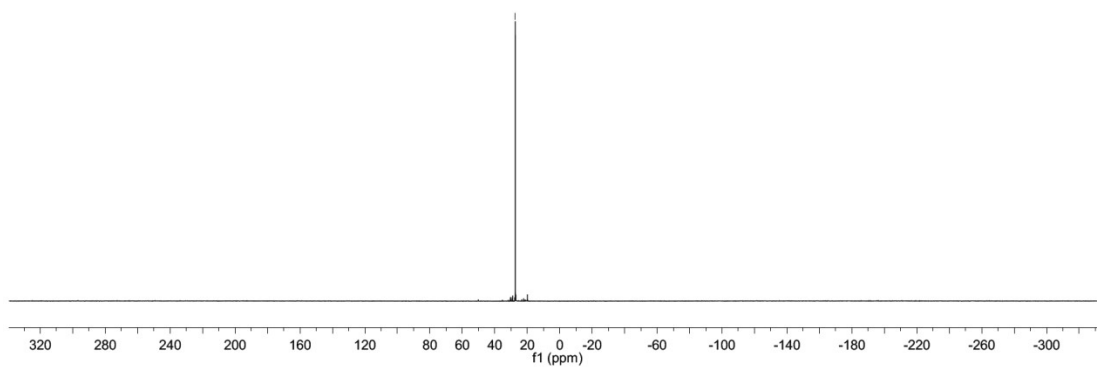
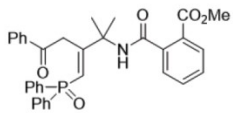


5j-¹³C NMR (100 MHz, CDCl₃)

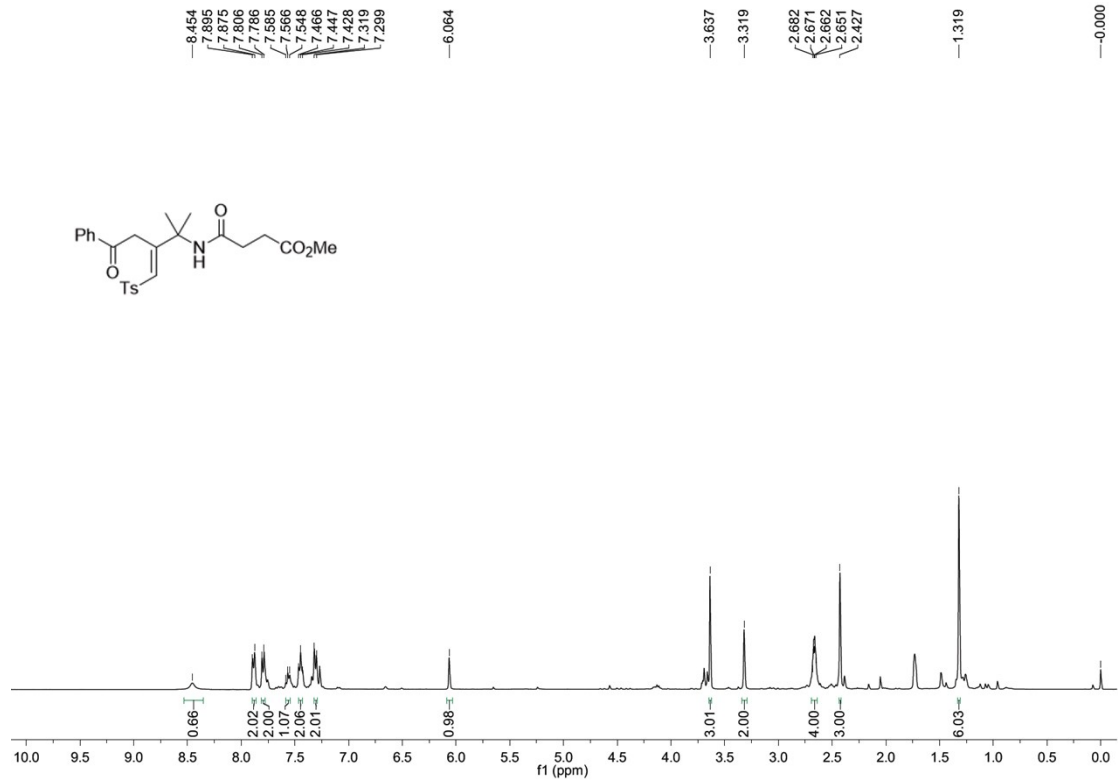


5j-³¹P NMR (162 MHz, CDCl₃)

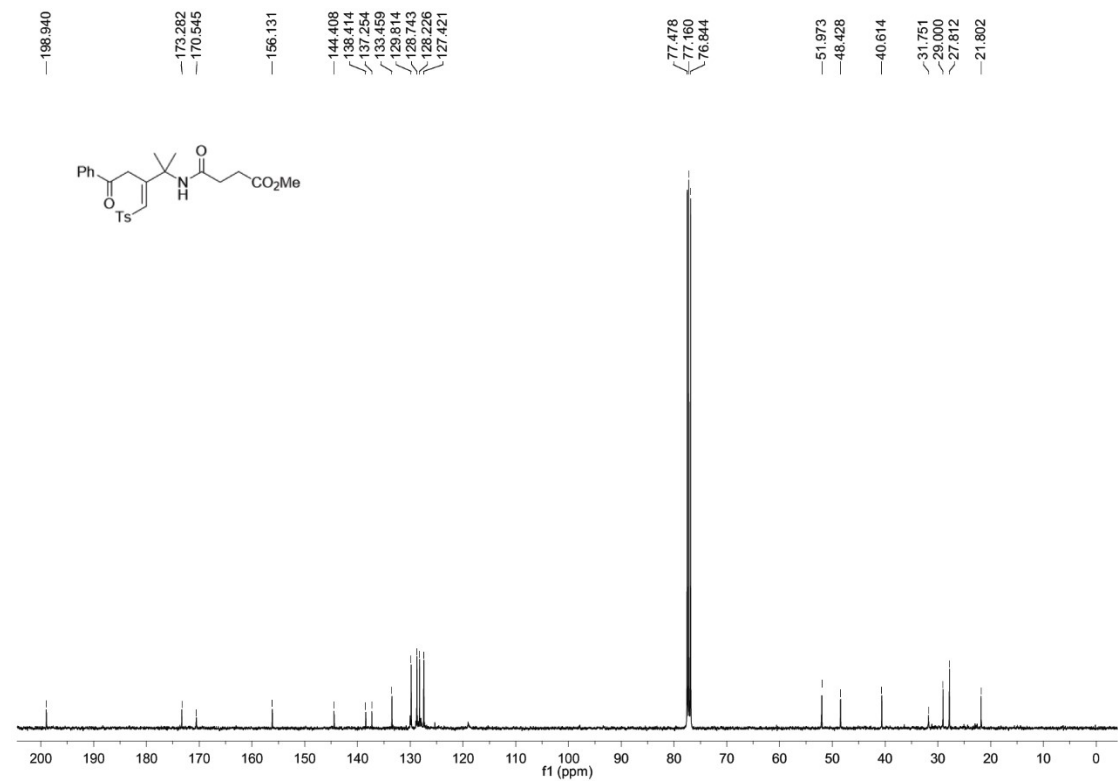
-27.374



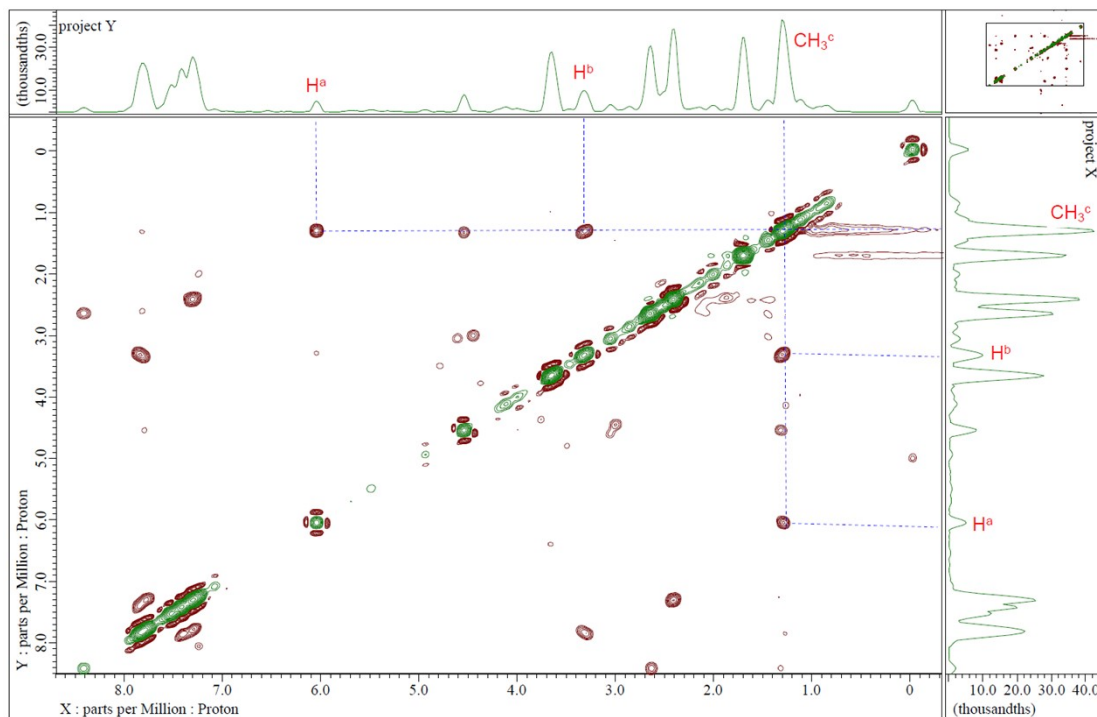
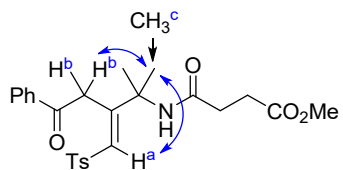
5k-¹H NMR (400 MHz, CDCl₃)



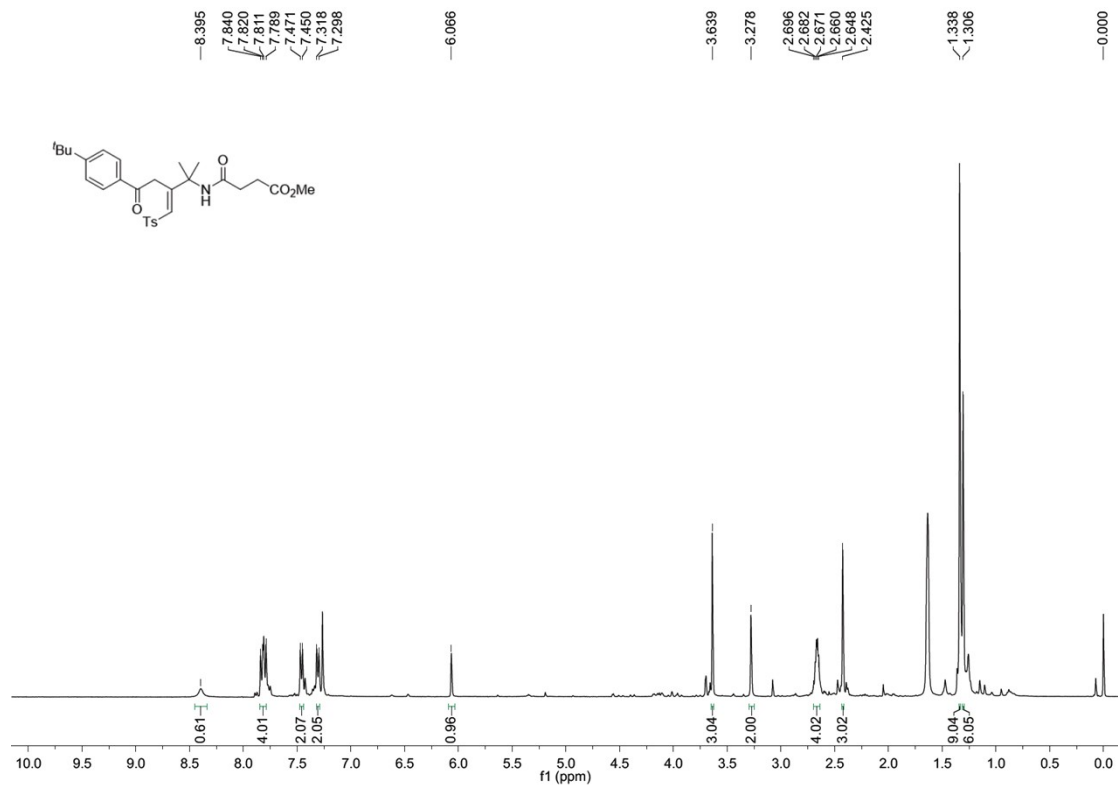
5k-¹³C NMR (100 MHz, CDCl₃)



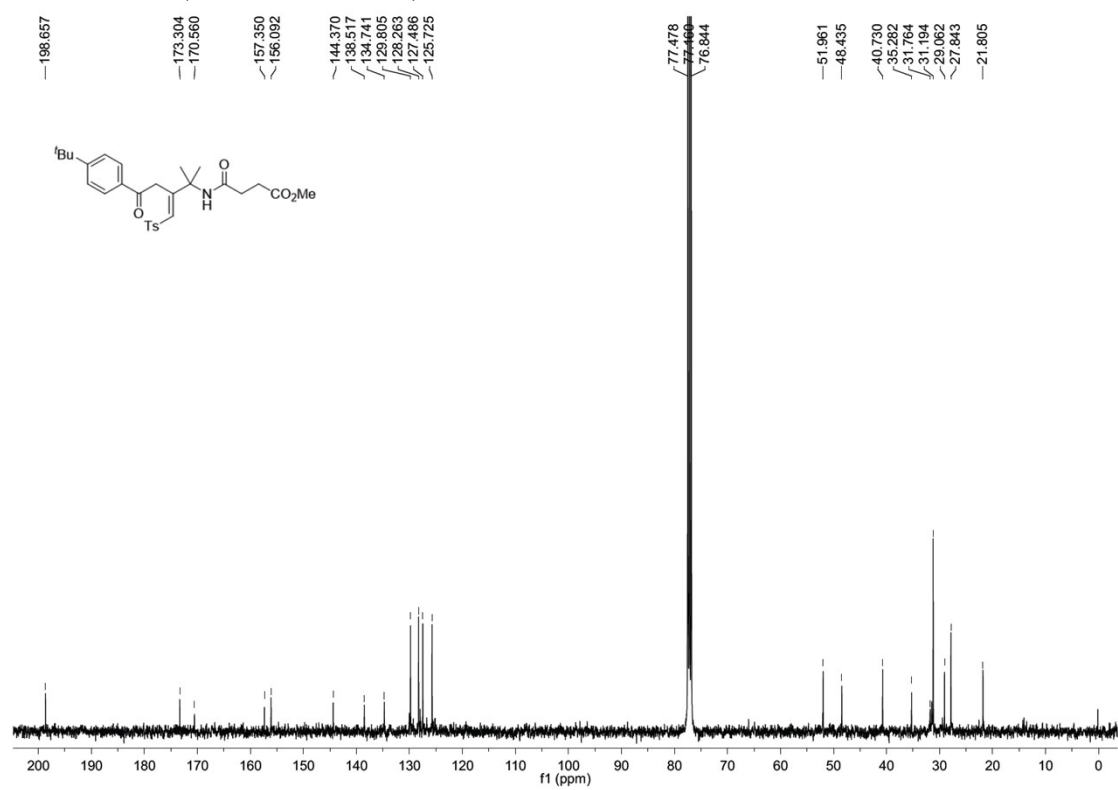
1H-1H NOESY of 5k:



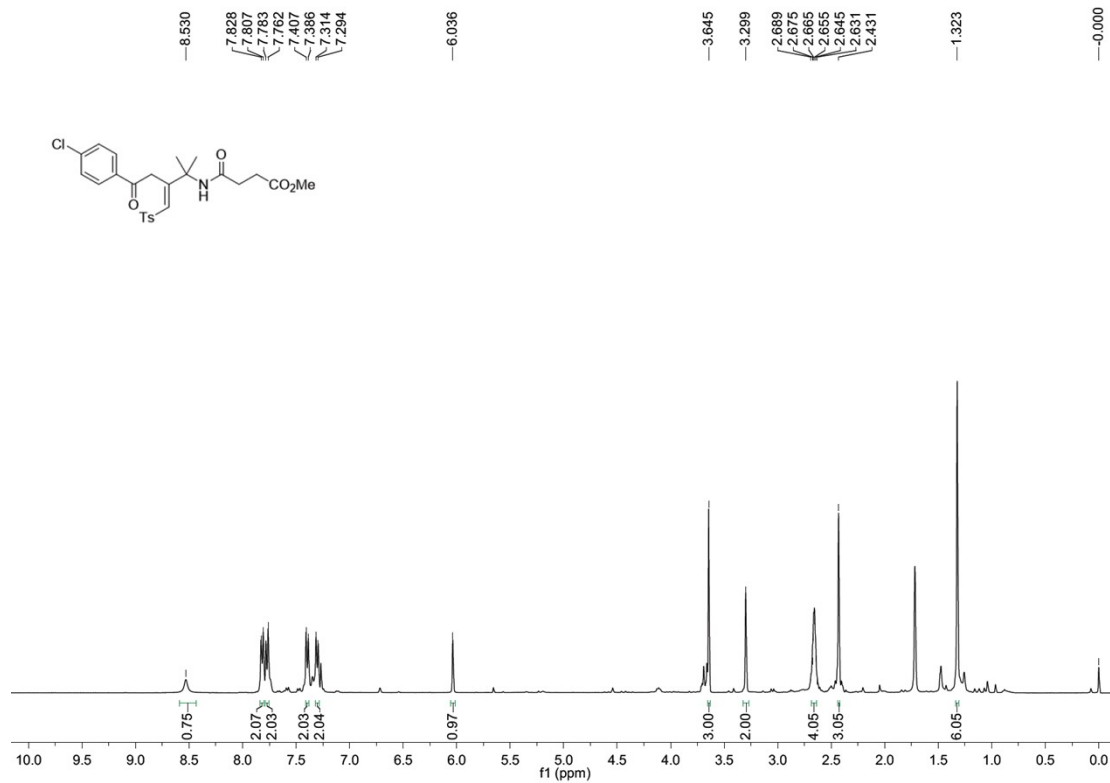
5I-¹H NMR (400 MHz, CDCl₃)



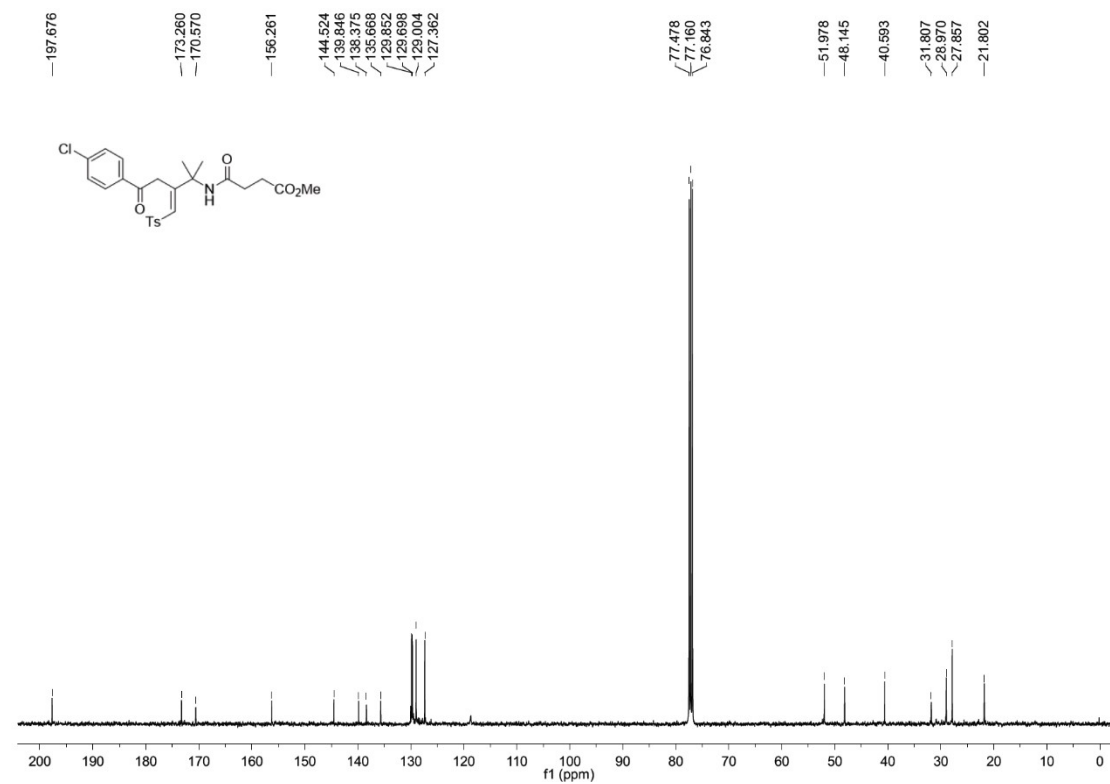
5I-¹³C NMR (100 MHz, CDCl₃)



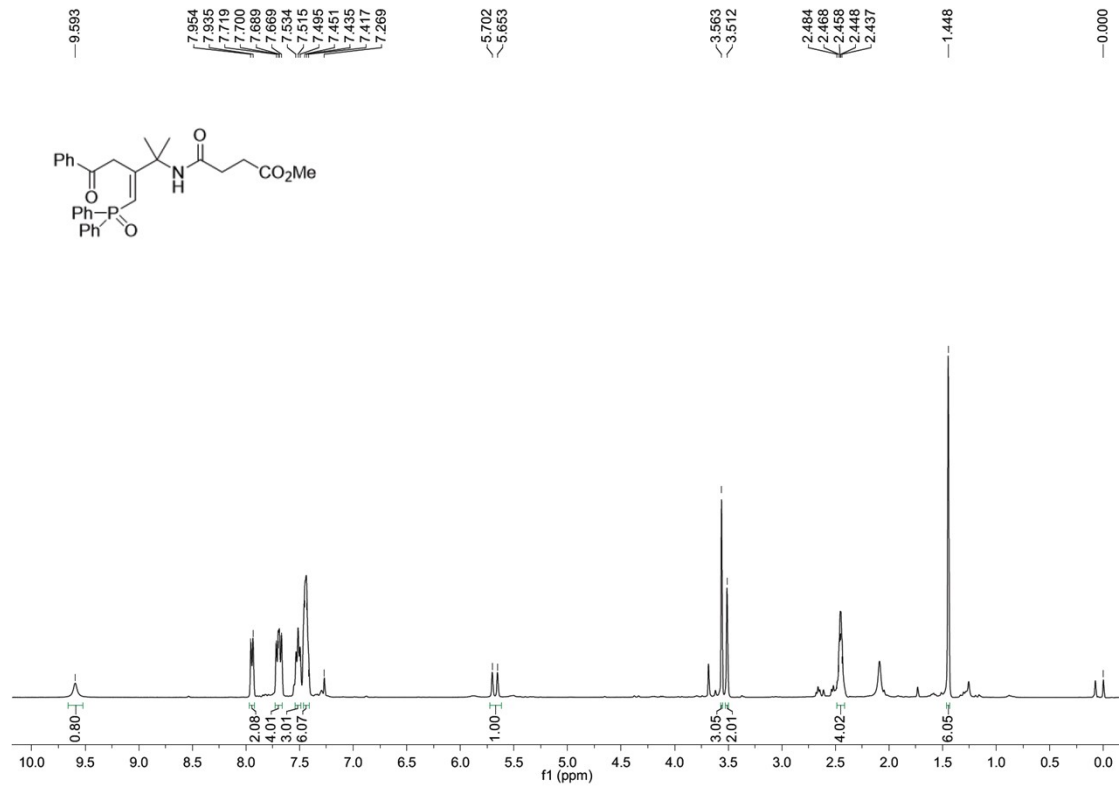
5m-¹H NMR (400 MHz, CDCl₃)



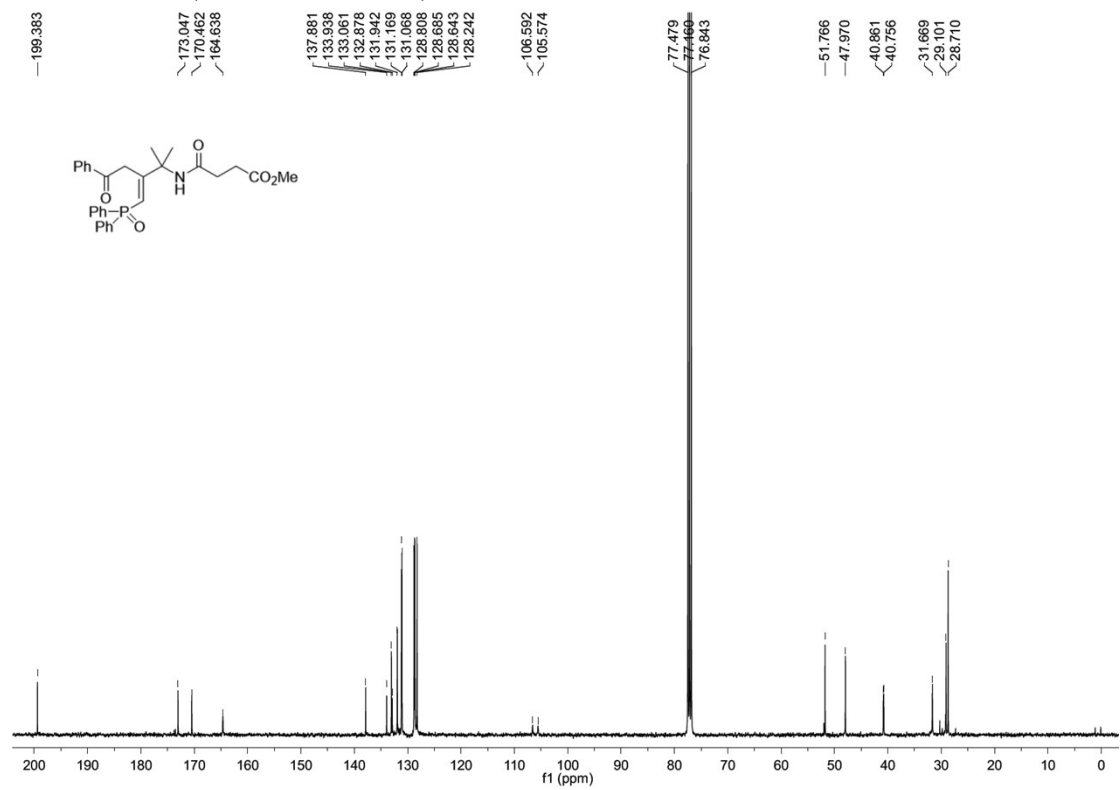
5m-¹³C NMR (100 MHz, CDCl₃)



5n-¹H NMR (400 MHz, CDCl₃)

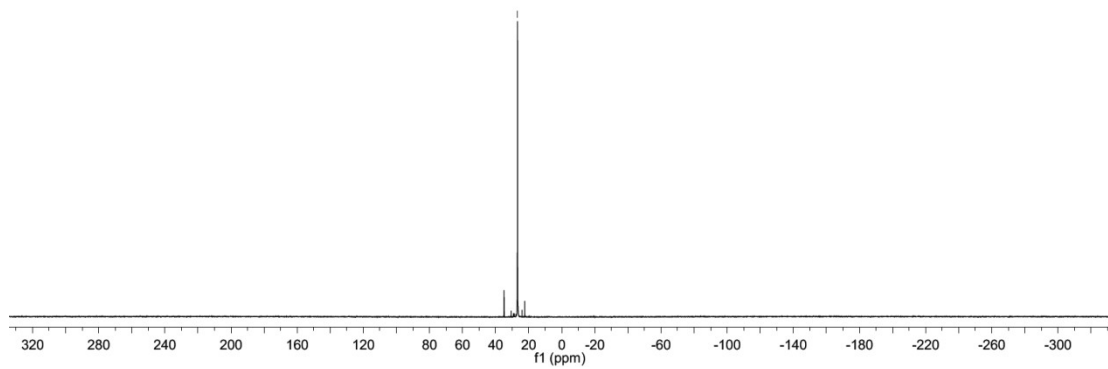
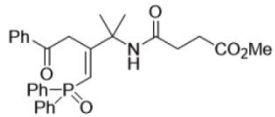


5n-¹³C NMR (100 MHz, CDCl₃)

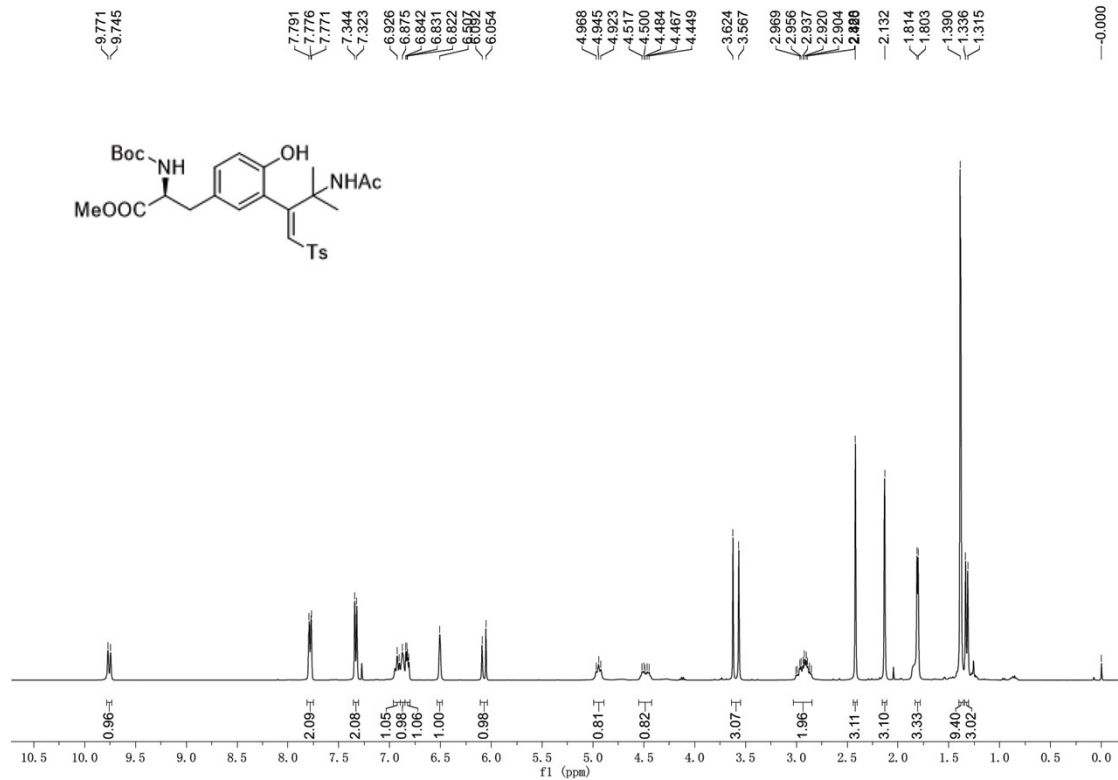


5n-³¹P NMR (162 MHz, CDCl₃)

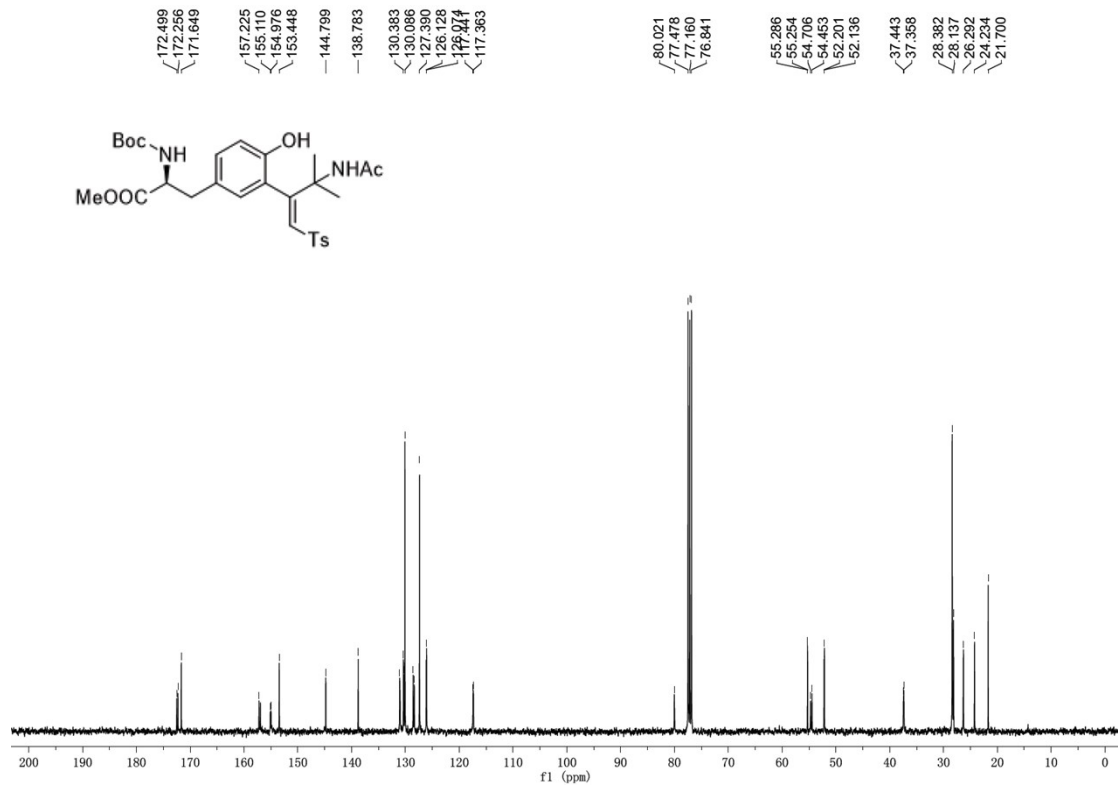
-26.754



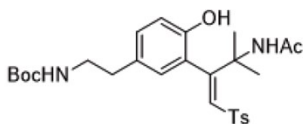
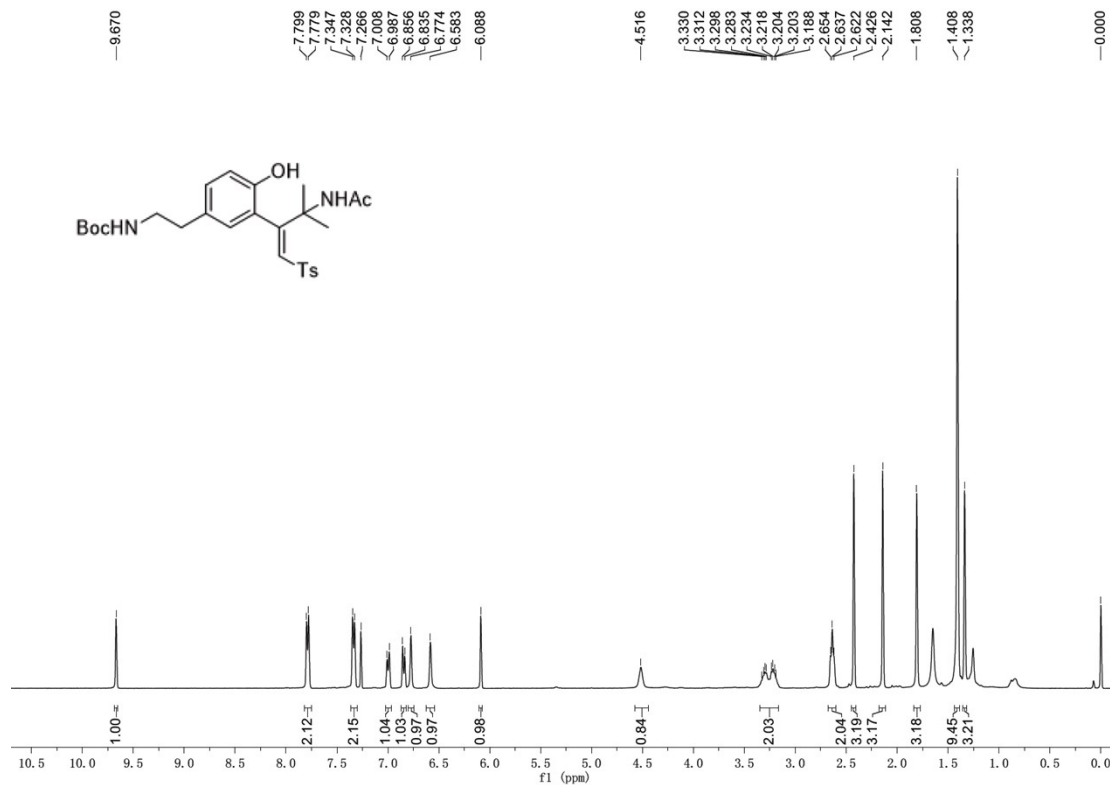
6-¹H NMR (400 MHz, CDCl₃)



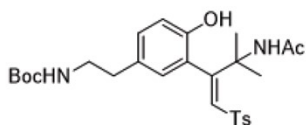
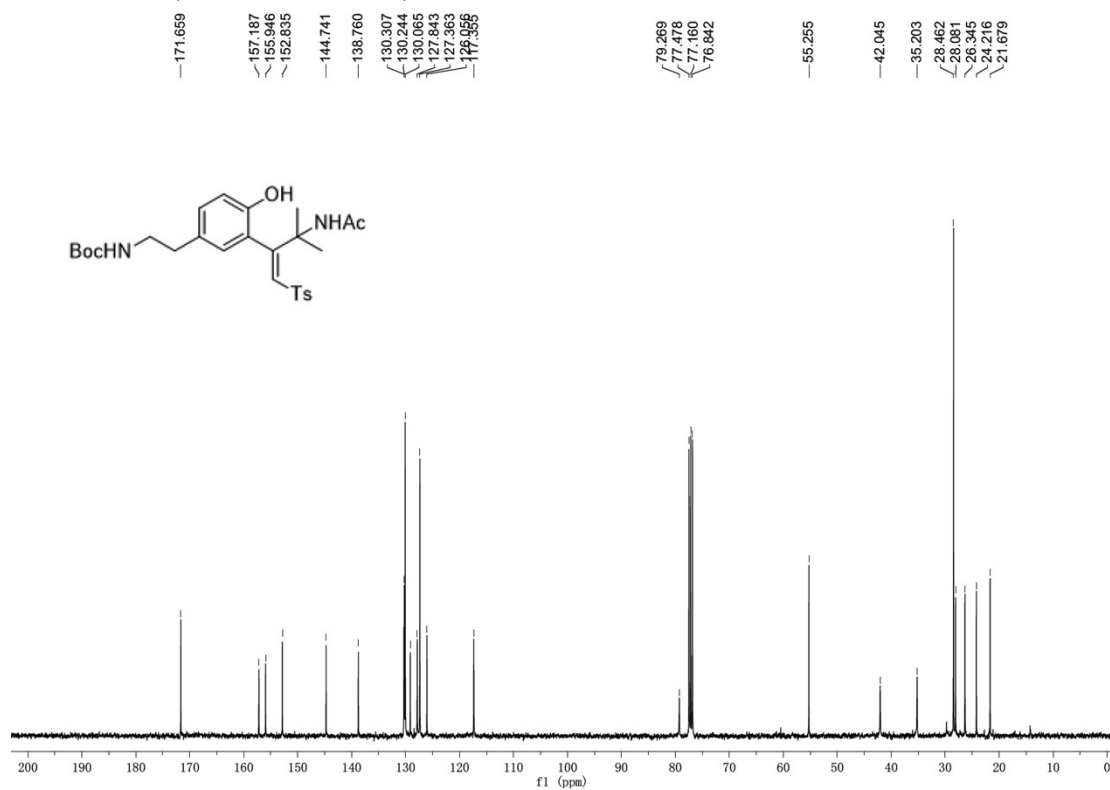
6-¹³C NMR (100 MHz, CDCl₃)



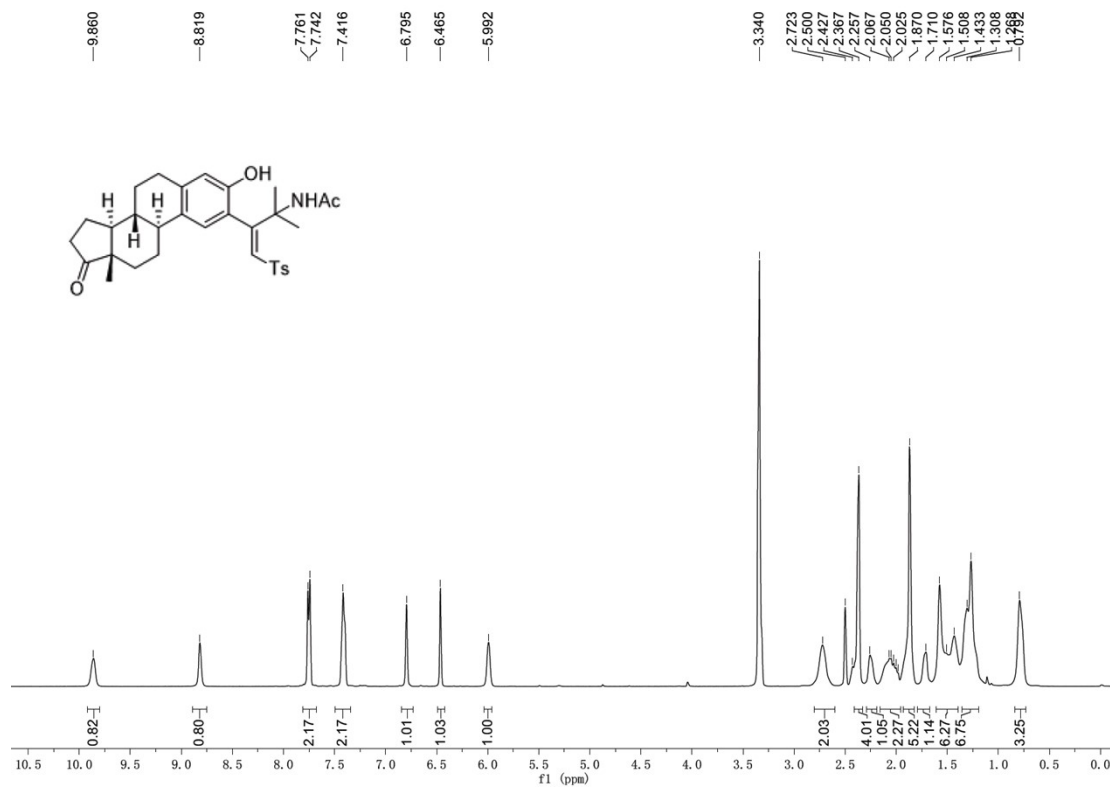
7-¹H NMR (400 MHz, CDCl₃)



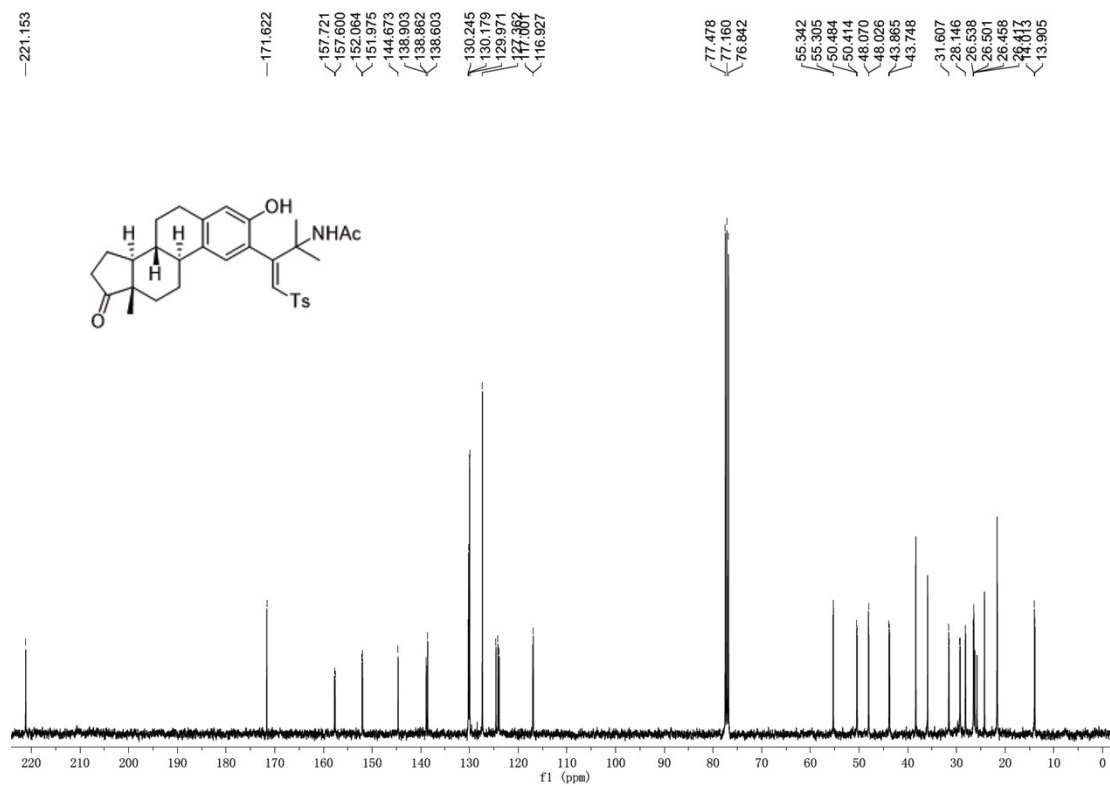
7-¹³C NMR (100 MHz, CDCl₃)



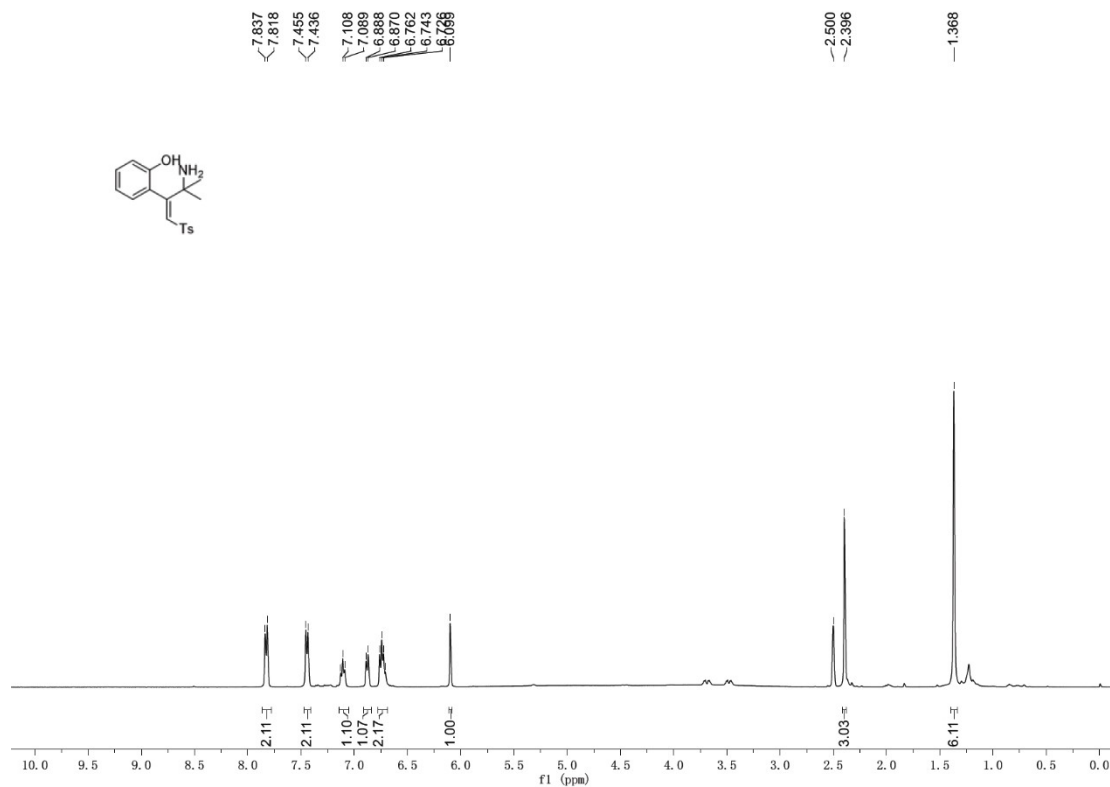
8-¹H NMR (400 MHz, CDCl₃)



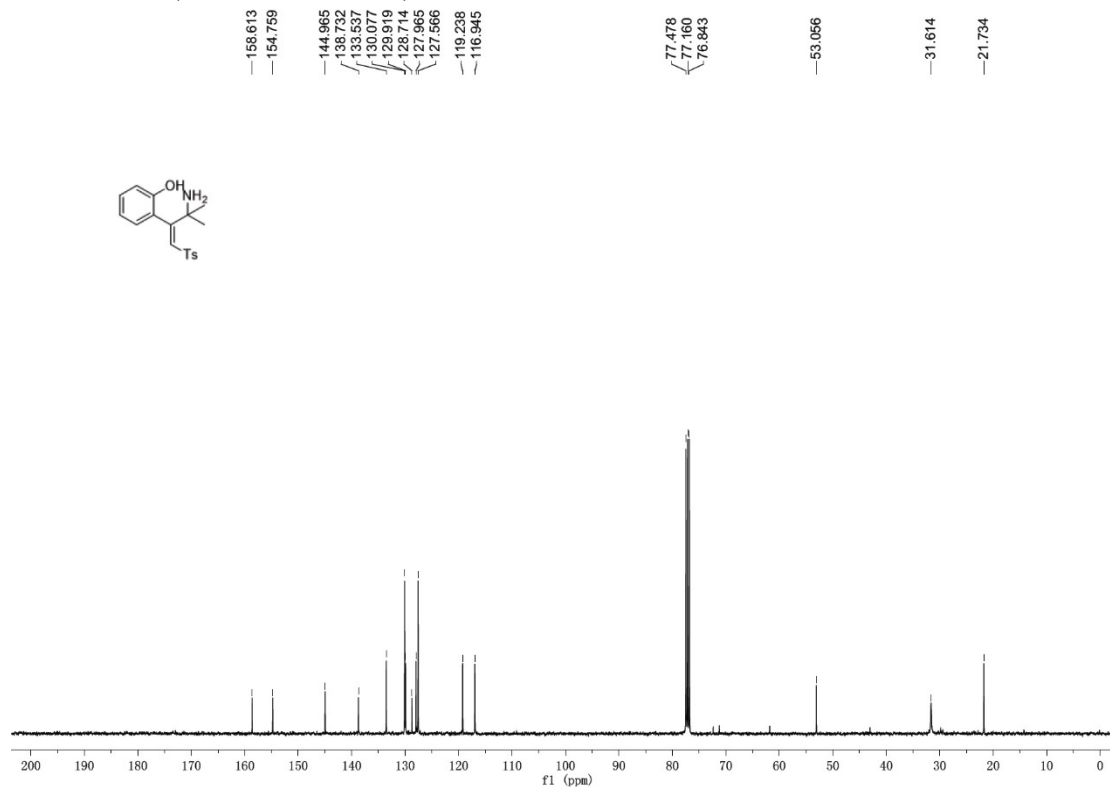
8-¹³C NMR (100 MHz, CDCl₃)



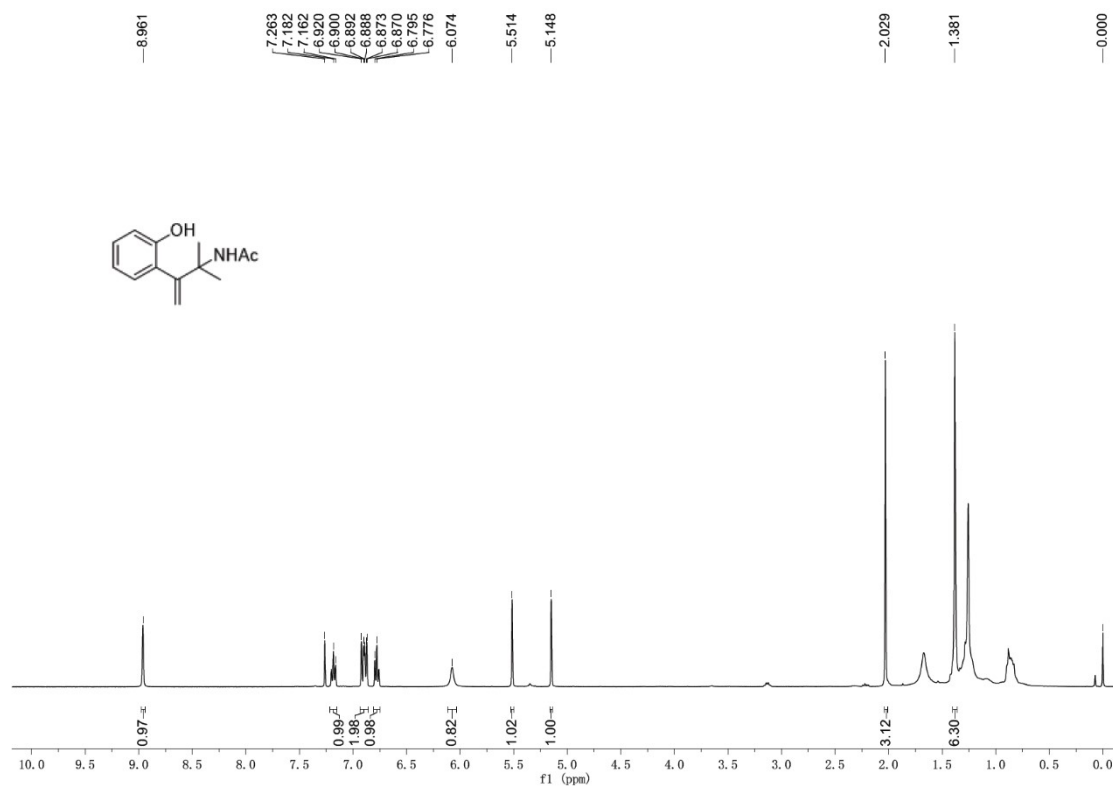
9-¹H NMR (400 MHz, CDCl₃)



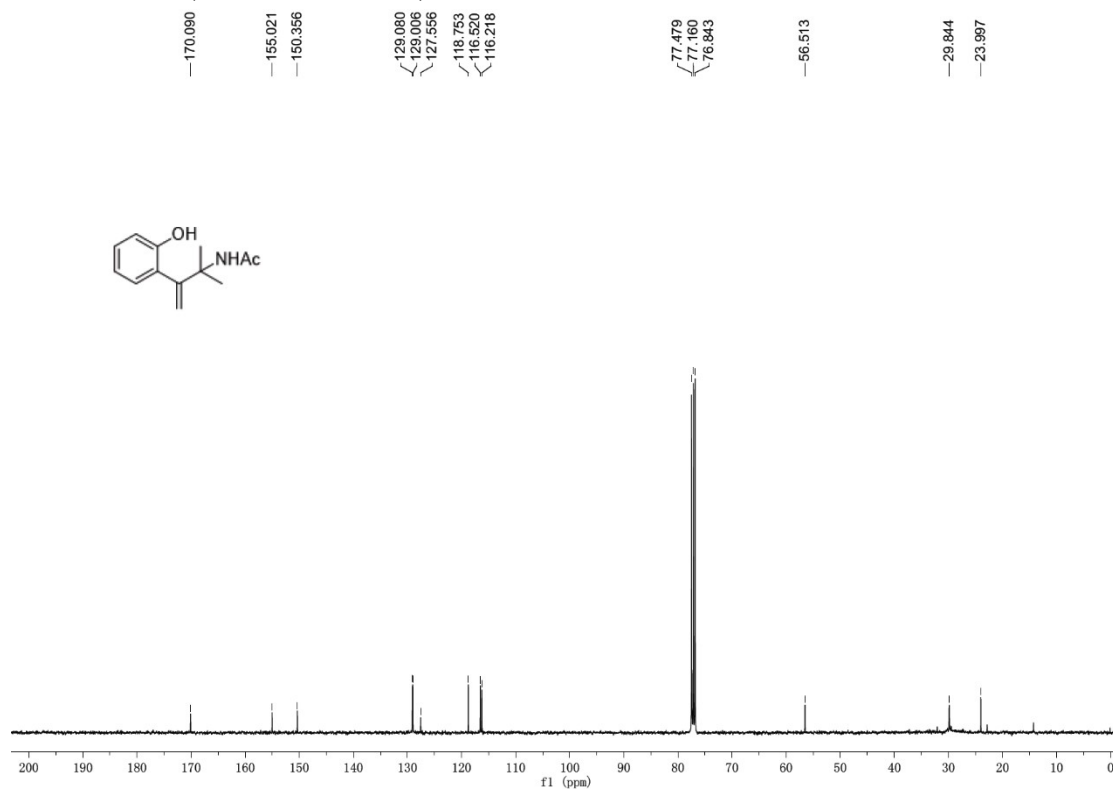
9-¹³C NMR (100 MHz, CDCl₃)



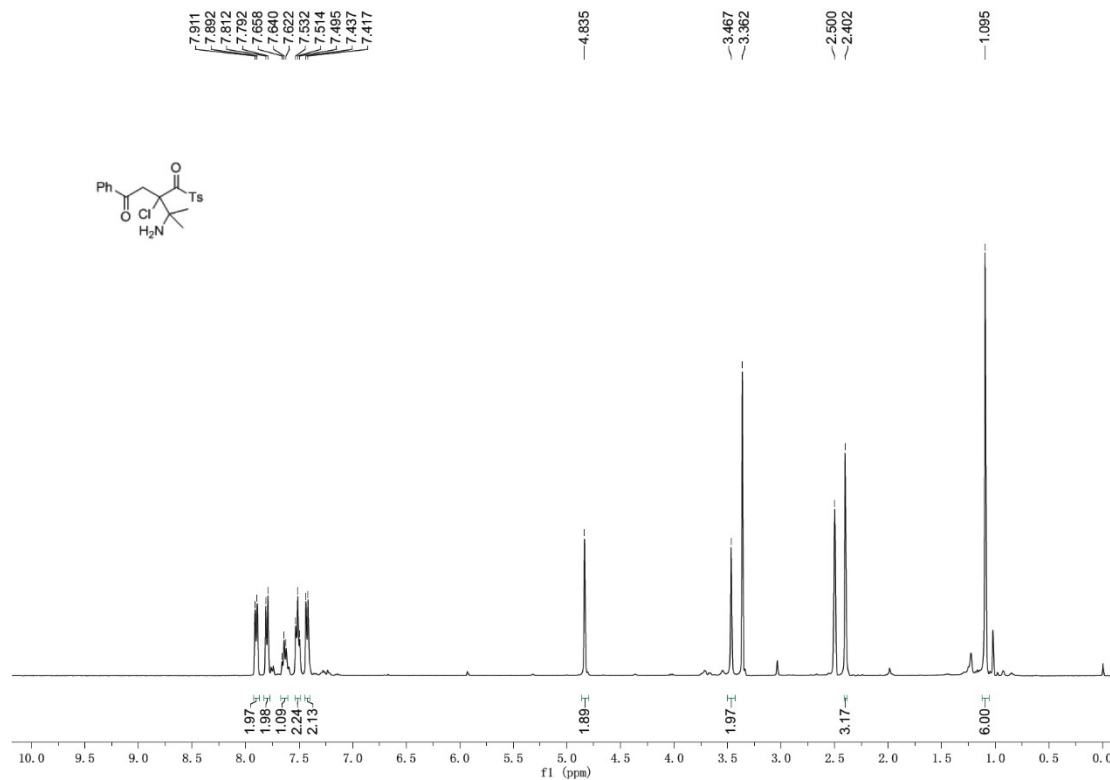
10-¹H NMR (400 MHz, CDCl₃)



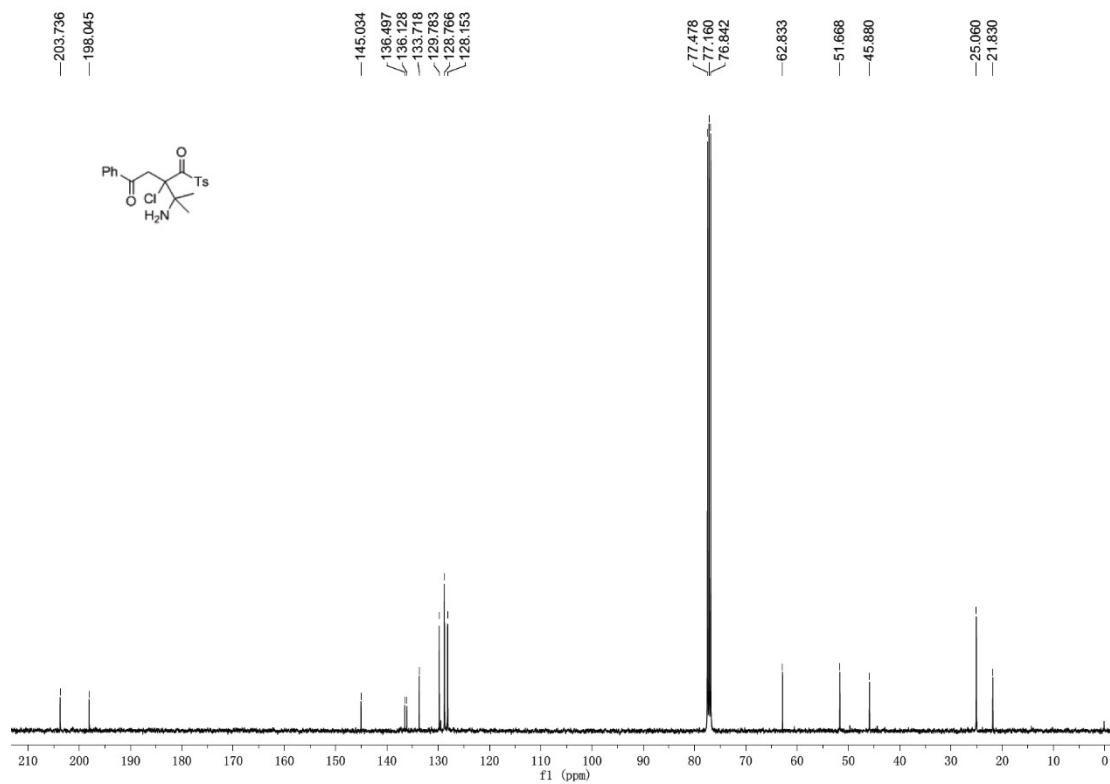
10-¹³C NMR (100 MHz, CDCl₃)



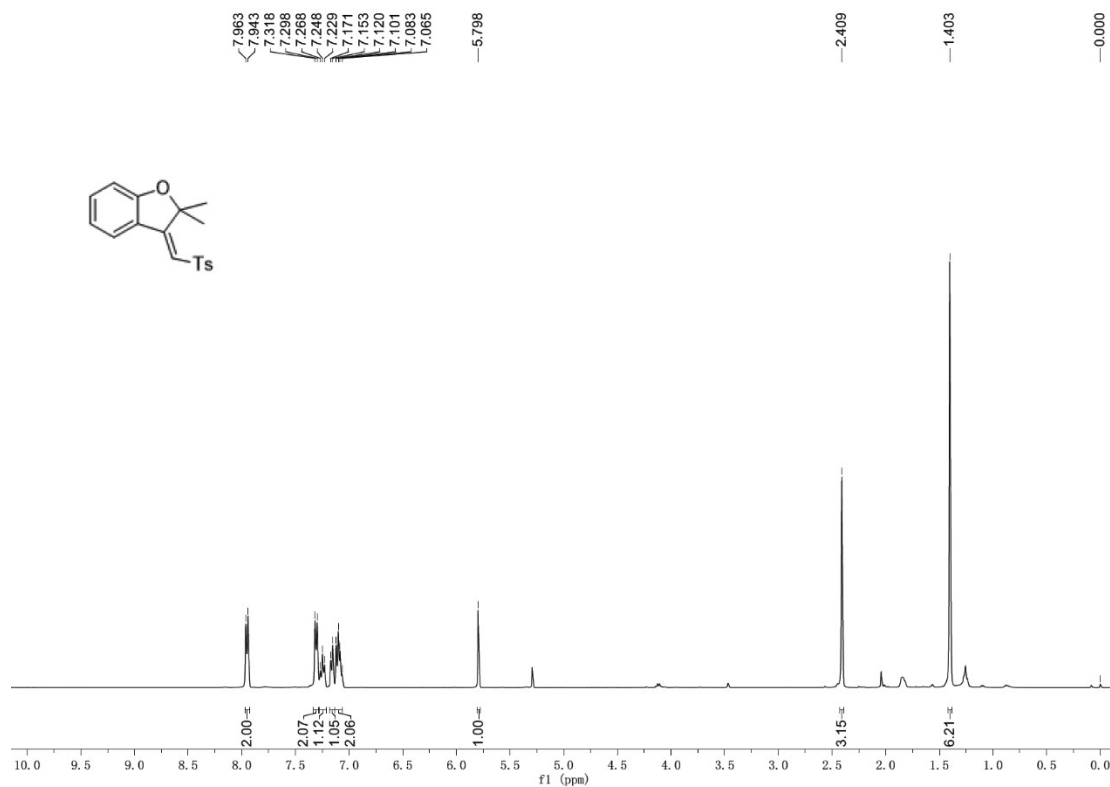
11-¹H NMR (400 MHz, DMSO-*d*₆)



11-¹³C NMR (100 MHz, CDCl₃)



3aa'-¹H NMR (400 MHz, CDCl₃)



3aa'-¹³C NMR (100 MHz, CDCl₃)

