

Supporting Information

Silver or Cerium-Promoted Free Radical Cascade Difunctionalization of *o*-Vinylanilides with Sodium Aryl- or Alkylsulfonates

Jilai Wu,^a Yuanyuan Zong,^a Chunxia Zhao,^a Qinqin Yan,^a Lixian Sun,^a Yiming Li,^a Jincan Zhao,^a Yaxin

Ge^a and Zejiang Li^{*,a,b,c}

^aCollege of Chemistry & Environmental Science, Hebei University, Baoding, Hebei, 071002, P. R. China; ^bKey Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, Hebei University, Baoding, Hebei, 071002, P. R. China; ^cKey Laboratory of Chemical Biology of Hebei Province, Hebei University, Baoding, Hebei, 071002, P. R. China.

E-mail: lizejiang898@126.com

General Information.....	1
Typical procedure for the reaction.....	1
The modification of the cascade reaction conditions.....	2
Mechanistic study.....	3
Physical data and references for the following products.....	4-16
Copies of the ¹ H NMR, ¹³ C NMR.....	17-44

General Information

¹H and ¹³C NMR spectra were recorded on a Bruker advance III 600 spectrometer in CDCl₃ with TMS as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by ¹H and ¹³C NMR, HRMS. The starting materials were purchased from Energy, J&K Chemicals or Aldrich and used without further purification.

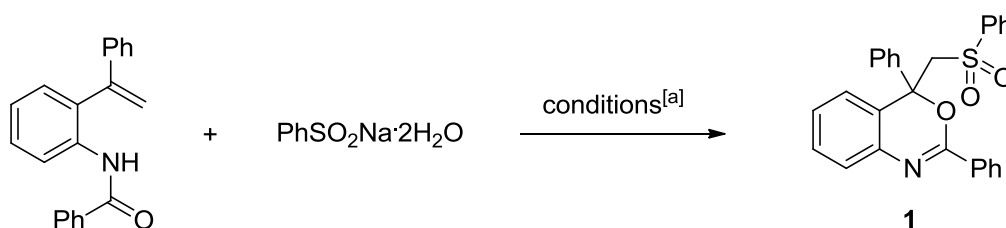
Typical procedure for the reaction

Conditions 1: A mixture of *o*-vinylanilides (1 equiv, 0.2 mmol), sodium salts (2 equiv, 0.4 mmol), AgNO₃ (3 equiv, 0.6 mmol) and EtOH (2 mL) was stirred at 80 °C in a sealed tube

(15 mL) under nitrogen for 11 h. When the reaction was finished, the mixture was condensed under vacuum and purified by column chromatography to afford the final product.

Conditions 2: A mixture of *o*-vinylanilides (1 equiv, 0.2 mmol), sodium salts (2.5 equiv, 0.5 mmol), CAN (1.5 equiv, 0.3 mmol) and CH₃CN (2 mL) was stirred at 80 °C in a sealed tube (15 mL) under nitrogen for 11 h. When the reactions were finished, the final products were isolated via the same work-up procedure.

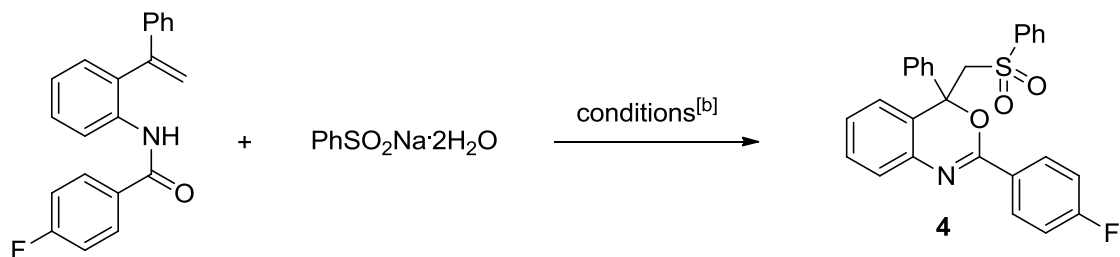
The modification of the cascade reaction conditions 1.



Entry	PhSO ₂ Na·2H ₂ O (equivalent)	Ag(I) (equivalent)	Solvent (mL)	Yield ^b (%)
1	2.0	AgNO ₃ (0.5)	EtOH (2.0)	Trace
2	2.0	AgNO ₃ (1.0)	EtOH (2.0)	47
3	2.0	AgNO ₃ (2.0)	EtOH (2.0)	63
4	2.0	AgNO ₃ (2.5)	EtOH (2.0)	71
5	2.0	AgNO ₃ (3.0)	EtOH (2.0)	95
6	2.0	AgCl (3.0)	EtOH (2.0)	Trace
7	2.0	AgOAc (3.0)	EtOH (2.0)	23
8	1.0	AgNO ₃ (3.0)	EtOH (2.0)	58
9	1.5	AgNO ₃ (3.0)	EtOH (2.0)	65
10	2.5	AgNO ₃ (3.0)	EtOH (2.0)	93
11 ^c	2.0	AgNO ₃ (3.0)	EtOH (2.0)	82
12 ^d	2.0	AgNO ₃ (3.0)	EtOH (2.0)	66
13 ^e	2.0	AgNO ₃ (3.0)	EtOH (2.0)	Trace
14 ^f	2.0	AgNO ₃ (3.0)	EtOH (2.0)	60
15	2.0	AgNO ₃ (3.0)	EtOH (0.5)	55
16	2.0	AgNO ₃ (3.0)	EtOH (1.0)	67
17	2.0	AgNO ₃ (3.0)	EtOH (3.0)	80
18	2.0	AgNO ₃ (3.0)	DCE (2.0)	Trace
19	2.0	AgNO ₃ (3.0)	CH ₃ CN (2.0)	21
20	2.0	AgNO ₃ (3.0)	cyclohexane (2.0)	60
21	2.0	AgNO ₃ (3.0)	DMF (2.0)	Trace
22	2.0	AgNO ₃ (3.0)	DMSO (2.0)	Trace
23 ^g	2.0	AgNO ₃ (3.0)	EtOH (2.0)	65

^aReaction conditions 1: *N*-(2-(1-phenylvinyl)phenyl)benzamide (1 equiv, 0.2 mmol), PhSO₂Na·2H₂O (2 equiv, 0.4 mmol), AgNO₃ (3 equiv, 0.6 mmol), EtOH (2 mL), N₂, 11h. ^bIsolated yields. ^c6 h. ^d18 h. ^e60 °C. ^f100 °C. ^gair.

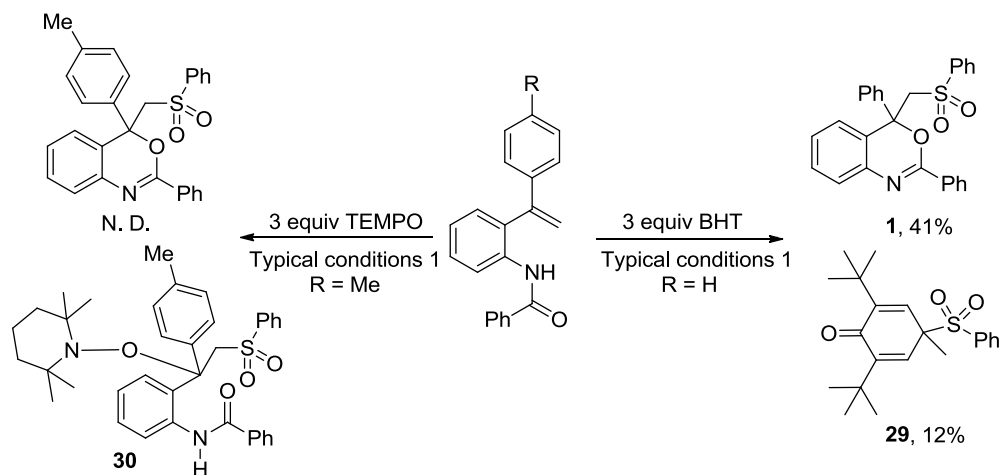
The modification of the cascade reaction conditions 2.



Entry	PhSO ₂ Na·2H ₂ O (equivalent)	CAN (equivalent)	Solvent (mL)	Yield (%)
1	2.5	CAN (0.5)	CH ₃ CN (2.0)	15
2	2.5	CAN (1.0)	CH ₃ CN (2.0)	20
3	2.5	CAN (1.5)	CH ₃ CN (2.0)	72
4	2.5	CAN (2.0)	CH ₃ CN (2.0)	60
5	2.5	CAN (2.5)	CH ₃ CN (2.0)	25

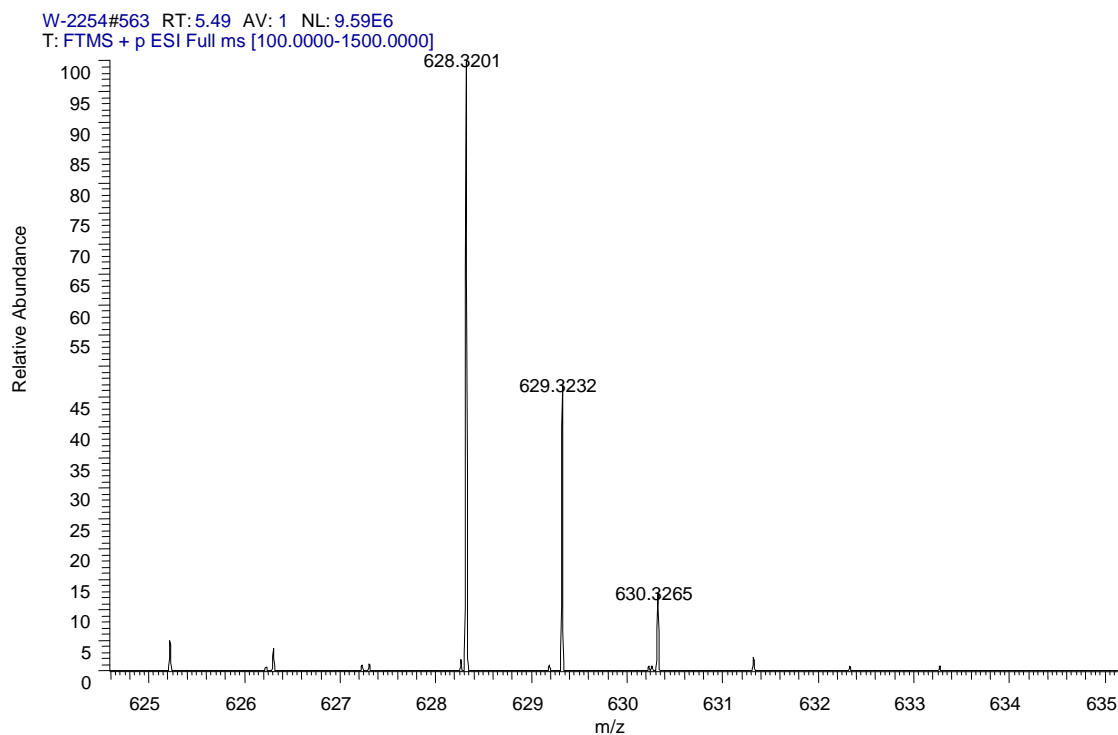
^bReaction conditions 2: *o*-vinylanilides (1 equiv, 0.2 mmol), sodium salts (2.5 equiv, 0.5 mmol), CAN (1.5 equiv, 0.3 mmol), CH₃CN (2 mL), 80 °C, N₂, 11 h, isolated yields.

Mechanistic study



HRMS of product 30

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
W-2254	C ₃₇ H ₄₂ N ₂ O ₄ S	[M+NH ₄] ⁺	628.3201	628.3204	-0.48



Physical data and references for the following products

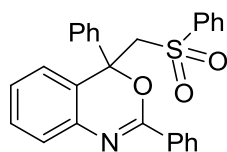
References:

1. T. Liu, D. Zheng, Z. Li and J. Wu, *Adv. Synth. Catal.*, 2018, **360**, 865.
2. M. Chaitanya and P. Anbarasan, *Org. Lett.*, 2018, **20**, 1183.
3. J. Wang, R. Sang, X. Chong, Y. Zhao, W. Fan, Z. J. Li and J. C. Zhao, *Chem. Commun.*, 2017, **53**, 7961.

Physical data for the following products:

1. 2,4-diphenyl-4-enylsulfonylmethyl-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 127-128 °C.



$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.85 (d, $J = 7.8$ Hz, 2H), 7.60 (d, $J = 7.8$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.33 – 7.27 (m, 4H), 7.24 – 7.18 (m, 5H), 7.15 (s, 5H), 4.23 (q, $J = 15.6$ Hz,

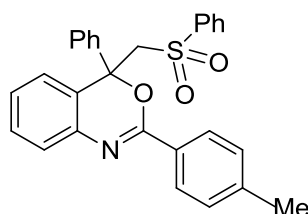
2H).

¹³C NMR (150 MHz, CDCl₃): δ 154.7, 141.7, 140.8, 138.8, 133.2, 131.7, 131.5, 129.6, 128.9, 128.7, 128.6, 128.2, 128.1, 127.9, 126.4, 126.0, 125.3, 124.1, 80.9, 64.6.

HRMS (ESI, m/z): Calculated for C₂₇H₂₂NO₃S (M+H)⁺ 440.1315, found 440.1307.

2. 4-phenyl-4-((phenylsulfonyl)methyl)-2-(p-tolyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 156-158 °C.



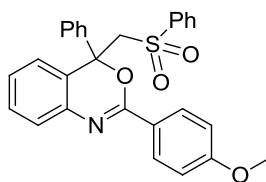
¹H NMR (600 MHz, CDCl₃): δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 5.4 Hz, 2H), 7.41 (s, 1H), 7.35 (s, 1H), 7.30 – 7.26 (m, 4H), 7.22 (s, 6H), 7.18 (d, *J* = 7.2 Hz, 2H), 4.29 (q, *J* = 15.0 Hz, 2H), 2.41 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 154.9, 142.0, 141.6, 140.8, 138.9, 133.2, 129.6, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 126.1, 125.8, 125.2, 125.1, 124.2, 80.8, 64.6, 21.6.

HRMS (ESI, m/z): Calculated for C₂₈H₂₄NO₃S (M+H)⁺ 454.1471, found 454.1462.

3. 2-(4-methoxyphenyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 199-200 °C.



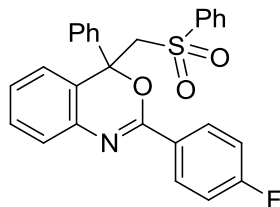
¹H NMR (600 MHz, CDCl₃): δ 7.90 – 7.88 (m, 2H), 7.68 – 7.66 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 3H), 7.26 – 7.24 (m, 1H), 7.23 – 7.20 (m, 6H), 6.89 – 6.87 (m, 2H), 4.29 (dd, *J* = 35.4, 15.6 Hz, 2H), 3.87 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 162.5, 154.7, 141.6, 140.8, 139.0, 133.2, 129.8, 129.6, 128.9, 128.6, 128.5, 128.2, 125.9, 125.6, 125.3, 125.1, 124.1, 124.1, 113.6, 80.8, 64.5, 55.4.

HRMS (ESI, m/z): Calculated for C₂₈H₂₄NO₄S (M+H)⁺ 470.1421, found 470.1418.

4. 2-(4-fluorophenyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 147-148 °C.



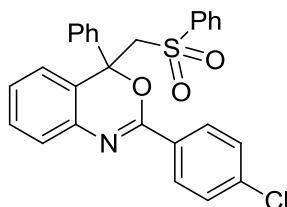
¹H NMR (600 MHz, CDCl₃): δ 7.81 – 7.79 (m, 2H), 7.67 (dd, J = 8.4, 1.2 Hz, 2H), 7.52 – 7.50 (m, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.36 (td, J = 7.8, 1.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.19 (m, 2H), 4.29 (q, J = 15.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 165.8, 164.1, 153.8, 141.5, 140.8, 138.6, 133.3, 130.2, 130.1, 129.7, 128.9, 128.7, 128.1, 127.8, 126.4, 125.9, 125.2, 125.1, 124.0, 115.4, 115.2, 81.0, 64.3.

HRMS (ESI, m/z): Calculated for C₂₇H₂₁FNO₃S (M+H)⁺ 458.1221, found 458.1214.

5. 2-(4-chlorophenyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



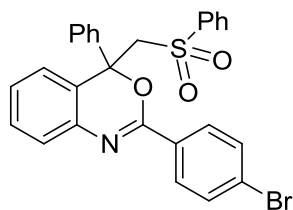
¹H NMR (600 MHz, CDCl₃): δ 7.88 – 7.87 (m, 2H), 7.68 – 7.67 (m, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.32 – 7.27 (m, 4H), 7.25 – 7.20 (m, 6H), 4.29 (q, J = 15.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 153.8, 141.5, 140.8, 138.5, 137.8, 133.3, 130.2, 129.7, 129.2, 129.0, 128.7, 128.5, 128.1, 126.6, 126.0, 125.2, 124.1, 81.1, 64.4.

HRMS (ESI, m/z): Calculated for C₂₇H₂₁ClNO₃S (M+H)⁺ 474.0925, found 474.0921.

6. 2-(4-bromophenyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 133-135 °C.



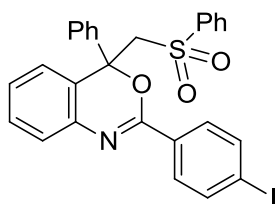
^1H NMR (600 MHz, CDCl_3): δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.43 (t, $J = 7.2$ Hz, 1H), 7.37 – 7.34 (m, 1H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.28 – 7.25 (m, 3H), 7.23 (d, $J = 7.2$ Hz, 3H), 7.21 – 7.19 (m, 2H), 4.28 (q, $J = 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 153.9, 141.4, 140.8, 138.4, 133.3, 131.4, 130.6, 129.7, 129.3, 129.0, 128.7, 128.1, 126.6, 126.4, 126.0, 125.2, 125.1, 124.1, 81.1, 64.3.

HRMS (ESI, m/z): Calculated for $\text{C}_{27}\text{H}_{21}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 518.0420, found 518.0419.

7. 2-(4-iodophenyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 143-145 $^\circ\text{C}$.



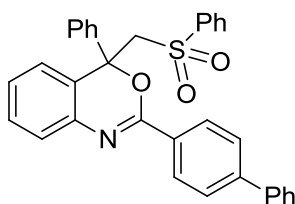
^1H NMR (600 MHz, CDCl_3): δ 7.73– 7.72 (m, 2H), 7.67 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.65 – 7.64 (m, 2H), 7.43 (t, $J = 7.2$ Hz, 1H), 7.35 (td, $J = 7.8, 1.8$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.28 – 7.26 (m, 2H), 7.26 – 7.24 (m, 1H), 7.24 – 7.22 (m, 3H), 7.20 – 7.19 (m, 2H), 4.28 (q, $J = 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 154.1, 141.4, 140.8, 138.4, 137.4, 133.3, 131.3, 129.7, 129.3, 129.0, 128.7, 128.1, 126.7, 126.0, 125.3, 125.2, 124.2, 98.8, 81.1, 64.4.

HRMS (ESI, m/z): Calculated for $\text{C}_{27}\text{H}_{21}\text{INO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 566.0281, found 566.0273.

8. 2-([1,1'-biphenyl]-4-yl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 152-154 $^\circ\text{C}$.



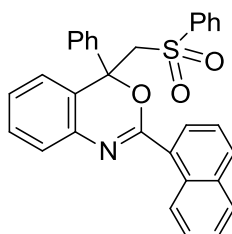
¹H NMR (600 MHz, CDCl₃): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.35 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.26 – 7.22 (m, 6H), 4.32 (q, *J* = 15.0 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 154.6, 144.2, 141.7, 140.8, 140.2, 138.8, 133.3, 130.5, 129.6, 128.9, 128.9, 128.7, 128.6, 128.4, 128.2, 127.9, 127.2, 126.8, 126.4, 126.0, 125.3, 125.2, 124.2, 81.0, 77.2, 77.0, 76.8, 64.6.

HRMS (ESI, *m/z*): Calculated for C₃₃H₂₆NO₃S (M+H)⁺ 516.1628, found 516.1626.

9. 2-(naphthalen-1-yl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



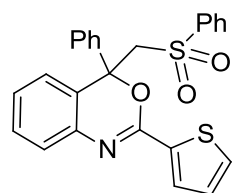
¹H NMR (600 MHz, CDCl₃): δ 8.21 (s, 1H), 8.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.72 (m, 2H), 7.58 – 7.53 (m, 2H), 7.41 – 7.38 (m, 2H), 7.36 – 7.34 (m, 1H), 7.33 – 7.32 (m, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.24 (m, 4H), 7.23 – 7.20 (m, 3H), 4.36 (q, *J* = 15.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 154.6, 141.7, 140.9, 138.8, 134.9, 133.2, 132.5, 129.7, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.9, 127.7, 127.6, 126.5, 126.4, 126.0, 125.3, 125.2, 124.4, 124.3, 81.0, 64.4.

HRMS (ESI, *m/z*): Calculated for C₃₁H₂₄NO₃S (M+H)⁺ 490.1471, found 490.1465.

10. 4-phenyl-4-((phenylsulfonyl)methyl)-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 150-152 °C.



¹H NMR (600 MHz, CDCl₃): δ 7.69 – 7.67 (m, 2H), 7.46 (ddd, *J* = 7.8, 4.2, 1.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.32 – 7.30 (m, 3H), 7.26 – 7.22 (m, 7H), 7.04

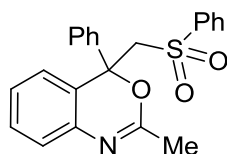
(dd, $J = 4.8, 4.2$ Hz, 1H), 4.27 (dd, $J = 36.6, 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 151.4, 141.5, 140.8, 138.7, 136.0, 133.2, 130.6, 130.2, 129.7, 128.9, 128.7, 128.2, 127.6, 126.2, 125.7, 125.5, 125.3, 123.9, 81.2, 64.6.

HRMS (ESI, m/z): Calculated for $\text{C}_{25}\text{H}_{20}\text{NO}_3\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 446.0879, found 446.0873.

11. 2-methyl-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



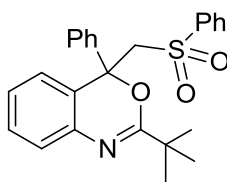
^1H NMR (600 MHz, CDCl_3): δ 7.68 (d, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.31 – 7.26 (m, 4H), 7.23 – 7.22 (m, 2H), 7.11 (dd, $J = 16.8, 8.4$ Hz, 2H), 7.04 – 7.03 (m, 1H), 4.14 (q, $J = 15.6$ Hz, 2H), 1.97 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 158.4, 141.7, 140.6, 138.1, 133.4, 129.6, 128.9, 128.6, 128.3, 126.2, 125.5, 125.4, 125.0, 123.4, 80.4, 64.3, 21.4.

HRMS (ESI, m/z): Calculated for $\text{C}_{22}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 378.1158, found 378.1152.

12. 2-(tert-butyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



^1H NMR (600 MHz, CDCl_3): δ 7.61 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.52 – 7.50 (m, 1H), 7.37 (dd, $J = 8.4, 7.8$ Hz, 2H), 7.27 – 7.25 (m, 4H), 7.18 – 7.16 (m, 3H), 6.99 (td, $J = 7.8, 1.2$ Hz, 1H), 6.93 (d, $J = 1.2$ Hz, 1H), 4.27 (d, $J = 15.0$ Hz, 1H), 4.20 (d, $J = 15.0$ Hz, 1H), 1.14 (s, 9H).

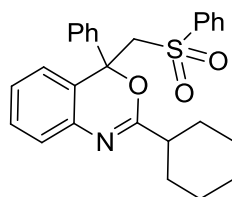
^{13}C NMR (150 MHz, CDCl_3): δ 166.1, 142.4, 140.8, 139.0, 133.3, 129.4, 129.0, 128.7, 128.4, 128.1, 126.0, 125.6, 125.6, 125.5, 122.3, 80.2, 64.8, 37.2, 27.6.

HRMS (ESI, m/z): Calculated for $\text{C}_{25}\text{H}_{26}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 420.1628, found 420.1622.

13. 2-cyclohexyl-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp

146-148 °C.



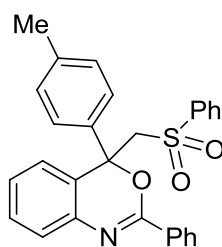
¹H NMR (600 MHz, CDCl₃): δ 7.64 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54 – 7.52 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.24 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.14 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.02 (td, *J* = 7.8, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.22 – 4.17 (m, 2H), 2.10 – 2.04 (m, 1H), 1.84 – 1.80 (m, 2H), 1.78 – 1.73 (m, 2H), 1.68 – 1.64 (m, 2H), 1.39 (qd, *J* = 12.0, 2.4 Hz, 1H), 1.32 (ddd, *J* = 24.0, 12.0, 3.0 Hz, 1H), 1.26 – 1.14 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 163.8, 142.2, 140.8, 138.5, 133.2, 129.4, 128.9, 128.6, 128.5, 128.1, 125.8, 125.7, 125.5, 125.3, 123.1, 80.0, 64.5, 43.3, 29.5, 29.3, 25.8, 25.7, 25.6.

HRMS (ESI, *m/z*): Calculated for C₂₇H₂₈NO₃S (M+H)⁺ 446.1784, found 446.1779.

14. 2-phenyl-4-((phenylsulfonyl)methyl)-4-(*p*-tolyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 154-156 °C.



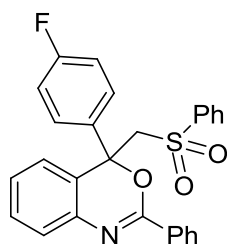
¹H NMR (600 MHz, CDCl₃): δ 7.91 (d, *J* = 6.6 Hz, 2H), 7.66 (d, *J* = 6.6 Hz, 2H), 7.46 (s, 1H), 7.37 – 7.34 (m, 4H), 7.27 (s, 4H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.32 – 4.26 (m, 2H), 2.24 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 154.7, 140.8, 138.8, 138.7, 138.5, 133.2, 131.7, 131.5, 129.5, 129.3, 128.8, 128.2, 128.1, 127.8, 126.3, 125.9, 125.2, 124.2, 80.8, 64.6, 20.9.

HRMS (ESI, *m/z*): Calculated for C₂₈H₂₄NO₃S (M+H)⁺ 454.1471, found 454.1462.

15. 4-(4-fluorophenyl)-2-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



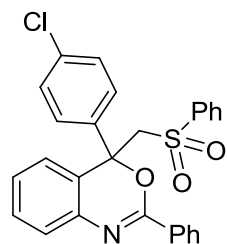
^1H NMR (600 MHz, CDCl_3): δ 7.94 – 7.92 (m, 2H), 7.68 – 7.66 (m, 2H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.39 – 7.35 (m, 3H), 7.29 (dd, $J = 13.8, 6.0$ Hz, 4H), 7.25 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 6.92 – 6.89 (m, 2H), 4.28 (q, $J = 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 162.5 (d, $J = 247.4$ Hz), 154.6, 140.7, 138.7, 137.3 (d, $J = 3.2$ Hz), 133.3, 131.6, 131.5, 129.8, 128.9, 128.2, 128.1, 127.8, 127.4 (d, $J = 8.4$ Hz), 126.5, 126.0, 125.0, 124.1, 115.6 (d, $J = 21.8$ Hz), 80.5, 64.4.

HRMS (ESI, m/z): Calculated for $\text{C}_{27}\text{H}_{21}\text{FNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 458.1221, found 458.1215.

16. 4-(4-chlorophenyl)-2-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 156-157 $^\circ\text{C}$.



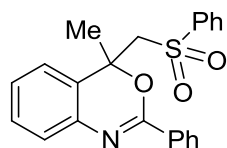
^1H NMR (600 MHz, CDCl_3): δ 7.95 – 7.94 (m, 2H), 7.67 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.42 – 7.35 (m, 4H), 7.30 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 4H), 4.27 (q, $J = 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 154.6, 140.7, 139.9, 138.6, 134.7, 133.3, 131.7, 131.4, 129.8, 129.0, 128.8, 128.2, 128.1, 127.8, 126.9, 126.6, 126.1, 124.9, 124.0, 80.5, 64.2.

HRMS (ESI, m/z): Calculated for $\text{C}_{27}\text{H}_{21}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 474.0925, found 474.0922.

18. 4-methyl-2-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 108-110 $^\circ\text{C}$.



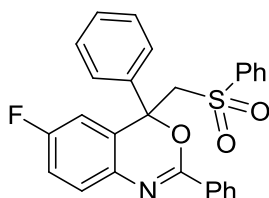
¹H NMR (600 MHz, CDCl₃): δ 8.06 – 8.04 (m, 2H), 7.72 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.83 (d, *J* = 15.0 Hz, 1H), 3.63 (d, *J* = 14.4 Hz, 1H), 2.09 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 155.6, 140.6, 138.3, 133.4, 132.0, 131.5, 129.5, 129.1, 128.2, 128.1, 127.7, 127.0, 125.6, 123.2, 77.9, 64.0, 27.0.

HRMS (ESI, m/z): Calculated for C₂₂H₂₀NO₃S (M+H)⁺ 378.1158, found 378.1153.

19. 6-fluoro-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



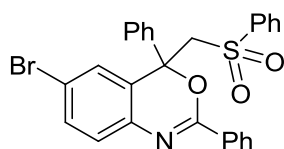
¹H NMR (600 MHz, CDCl₃): δ 7.93 – 7.92 (m, 2H), 7.70 – 7.69 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.22 (m, 5H), 7.04 (td, *J* = 8.4, 3.0 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.28 – 4.23 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 160.7 (d, *J* = 245.2 Hz), 154.1, 141.2, 140.7, 135.1, 133.4, 131.6, 131.4, 129.0, 128.8, 128.2, 128.1, 127.8, 127.6 (d, *J* = 8.2 Hz), 125.8 (d, *J* = 7.2 Hz), 125.1, 116.4 (d, *J* = 21.9 Hz), 112.4 (d, *J* = 24.6 Hz), 80.6, 64.3.

HRMS (ESI, m/z): Calculated for C₂₇H₂₁FNO₃S (M+H)⁺ 458.1221, found 458.1216.

20. 6-bromo-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 127-128 °C.



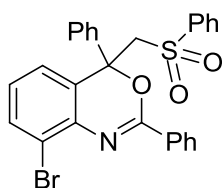
¹H NMR (600 MHz, CDCl₃): δ 7.98 – 7.96 (m, 2H), 7.69 – 7.68 (m, 2H), 7.51 – 7.47 (m, 1H), 7.44 – 7.42 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.27 – 7.24 (m, 3H), 7.22 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.26 (s, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 155.2, 141.2, 140.6, 137.9, 133.5, 132.7, 131.8, 131.4, 130.1, 129.0, 128.9, 128.9, 128.4, 128.3, 128.1, 128.1, 128.0, 127.5, 125.9, 125.2, 119.3, 80.5, 64.2.

HRMS (ESI, m/z): Calculated for C₂₇H₂₁BrNO₃S (M+H)⁺ 518.0420, found 518.0416.

21. 8-bromo-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine.

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



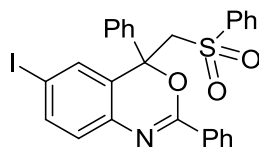
¹H NMR (600 MHz, CDCl₃): δ 7.99 – 7.97 (m, 2H), 7.68 – 7.67 (m, 2H), 7.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.20 (d, *J* = 9.0 Hz, 5H), 7.08 (t, *J* = 7.8 Hz, 1H), 4.29 (q, *J* = 15.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 155.6, 141.0, 140.6, 137.0, 133.5, 133.4, 132.0, 131.2, 128.9, 128.8, 128.2, 128.3, 128.2, 128.1, 126.8, 126.0, 125.2, 124.6, 121.7, 81.0, 64.3

HRMS (ESI, m/z): Calculated for C₂₇H₂₁BrNO₃S (M+H)⁺ 518.0420, found 518.0420.

22. 6-iodo-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 126-128 °C.



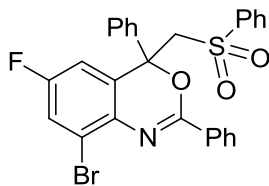
¹H NMR (600 MHz, CDCl₃): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.29 (d, *J* = 2.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.20 (m, 5H), 4.31 (q, *J* = 15.6 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 154.6, 141.6, 140.8, 138.7, 133.2, 131.6, 131.5, 129.6, 128.8, 128.6, 128.6, 128.1, 127.8, 126.3, 125.9, 125.2, 124.1, 80.9, 64.5.

HRMS (ESI, m/z): Calculated for C₂₇H₁₉INO₃S [M-H]⁻ 564.0136, found 564.0145.

23. 8-bromo-6-fluoro-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 172-174 °C.



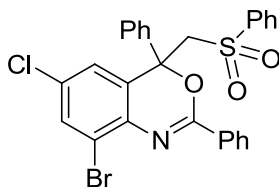
¹H NMR (600 MHz, CDCl₃): δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.35 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.25 (dd, *J* = 5.4, 1.8 Hz, 3H), 7.22 (dd, *J* = 7.8, 3.0 Hz, 2H), 6.99 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.28 – 4.22 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 159.7 (d, *J* = 249.2 Hz), 155.0, 140.6 (d, *J* = 7.6 Hz), 133.7 (d, *J* = 3.2 Hz), 133.5, 132.0, 131.0, 129.1, 129.0, 128.9, 128.2, 128.2, 128.1, 127.0 (d, *J* = 7.6 Hz), 125.1, 122.2, 122.1, 120.7 (d, *J* = 24.8 Hz), 112.0 (d, *J* = 24.3 Hz), 80.8, 64.0.

HRMS (ESI, *m/z*): Calculated for C₂₇H₂₀FBrNO₃S (M+H)⁺ 536.0326, found 536.0327.

24. 8-bromo-6-chloro-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 167-168 °C.



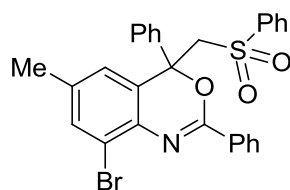
¹H NMR (600 MHz, CDCl₃): δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.25 (m, 3H), 7.22 – 7.21 (m, 2H), 7.14 (d, *J* = 1.8 Hz, 1H), 4.28 – 4.22 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 155.9, 140.6, 140.5, 135.9, 133.6, 133.1, 132.2, 131.5, 131.0, 129.1, 129.0, 129.0, 128.4, 128.3, 128.1, 126.8, 125.1, 124.6, 122.2, 80.8, 64.0.

HRMS (ESI, *m/z*): Calculated for C₂₇H₂₀ClBrNO₃S (M+H)⁺ 552.0030, found 552.0029.

25. 8-bromo-6-methyl-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 168-169 °C.



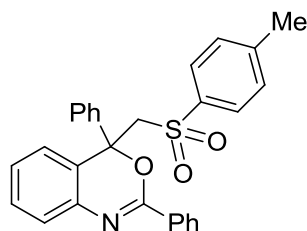
¹H NMR (600 MHz, CDCl₃): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.21 (s, 5H), 6.98 (s, 1H), 4.28 (q, *J* = 15.6 Hz, 1H), 2.31 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 154.9, 141.2, 140.6, 137.1, 134.6, 133.9, 133.3, 131.7, 131.3, 128.8, 128.7, 128.7, 128.1, 128.1, 128.1, 125.5, 125.2, 125.1, 121.4, 80.9, 64.2, 21.0.

HRMS (ESI, *m/z*): Calculated for C₂₈H₂₃BrNO₃S (M+H)⁺ 532.0577, found 532.0576.

26. 2,4-diphenyl-4-(tosylmethyl)-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



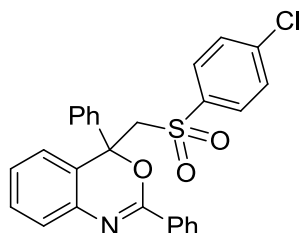
¹H NMR (600 MHz, CDCl₃): δ 7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.46 (m, 1H), 7.38 – 7.35 (m, 3H), 7.31 (ddd, *J* = 17.4, 7.8, 1.2 Hz, 3H), 7.25 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.23 – 7.22 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.27 (q, *J* = 15.0 Hz, 2H), 2.21 (s, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 154.6, 144.3, 141.9, 138.7, 137.8, 131.7, 131.4, 129.5, 129.5, 128.7, 128.6, 128.2, 128.0, 127.8, 126.3, 125.9, 125.5, 125.2, 123.9, 80.9, 64.6, 21.4.

HRMS (ESI, *m/z*): Calculated for C₂₈H₂₄NO₃S (M+H)⁺ 454.1471, found 454.1465.

27. 4-(((4-chlorophenyl)sulfonyl)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



¹H NMR (600 MHz, CDCl₃): δ 7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.57 – 7.56 (m, 2H), 7.51 – 7.48 (m, 1H), 7.41 – 7.39 (m, 2H), 7.37 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.26 –

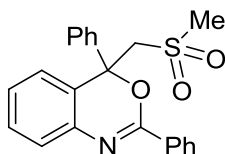
7.24 (m, 1H), 7.24 – 7.22 (m, 5H), 7.20 – 7.18 (m, 2H), 4.30 (dd, $J = 36.6, 15.6$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3): δ 154.5, 141.6, 140.2, 139.0, 138.7, 131.7, 131.4, 129.7, 129.6, 129.2, 128.7, 128.6, 128.2, 127.7, 126.4, 126.0, 125.3, 125.2, 123.8, 80.8 64.7.

HRMS (ESI, m/z): Calculated for $\text{C}_{27}\text{H}_{21}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$)⁺ 474.0925, found 474.0921.

28. 4-((methylsulfonyl)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 186-188 °C.



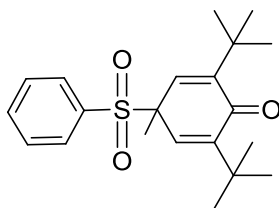
^1H NMR (600 MHz, CDCl_3): δ 8.27 – 8.26 (m, 2H), 7.56 – 7.53 (m, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.42 (td, $J = 7.8, 1.2$ Hz, 1H), 7.38 – 7.36 (m, 4H), 7.34 – 7.28 (m, 4H), 4.19 – 4.13 (m, 2H), 2.80 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 154.7, 141.0, 138.7, 131.9, 131.7, 129.9, 128.8, 128.8, 128.6, 128.0, 126.8, 126.2, 125.5, 125.0, 124.8, 80.9, 63.5, 43.9.

HRMS (ESI, m/z): Calculated for $\text{C}_{22}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺ 378.1158, found 378.1153.

29. 2,6-di-tert-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dienone

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), mp 150-152 °C.



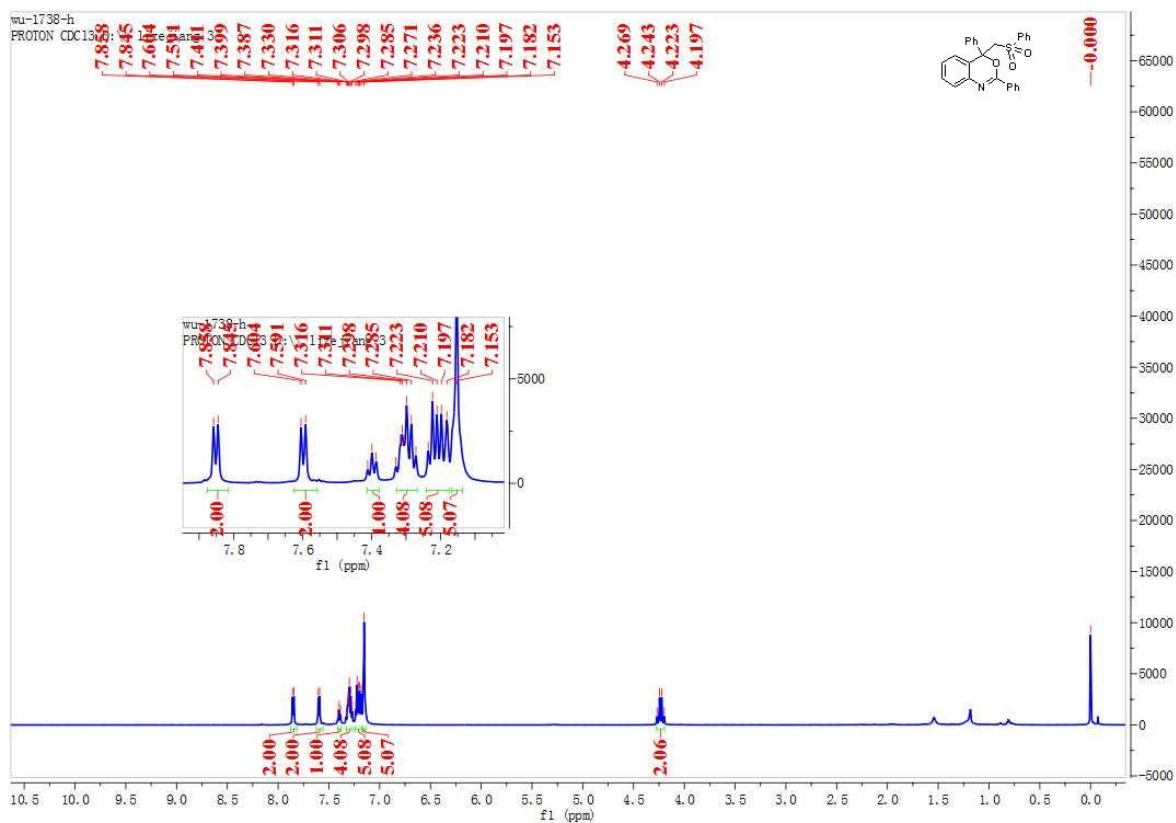
^1H NMR (600 MHz, CDCl_3): δ 7.64 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 6.65 (s, 2H), 1.83 (s, 3H), 1.10 (s, 18H).

^{13}C NMR (150 MHz, CDCl_3): δ 183.6, 151.4, 135.5, 134.1, 133.6, 130.3, 128.2, 65.8, 35.19, 29.0, 18.4.

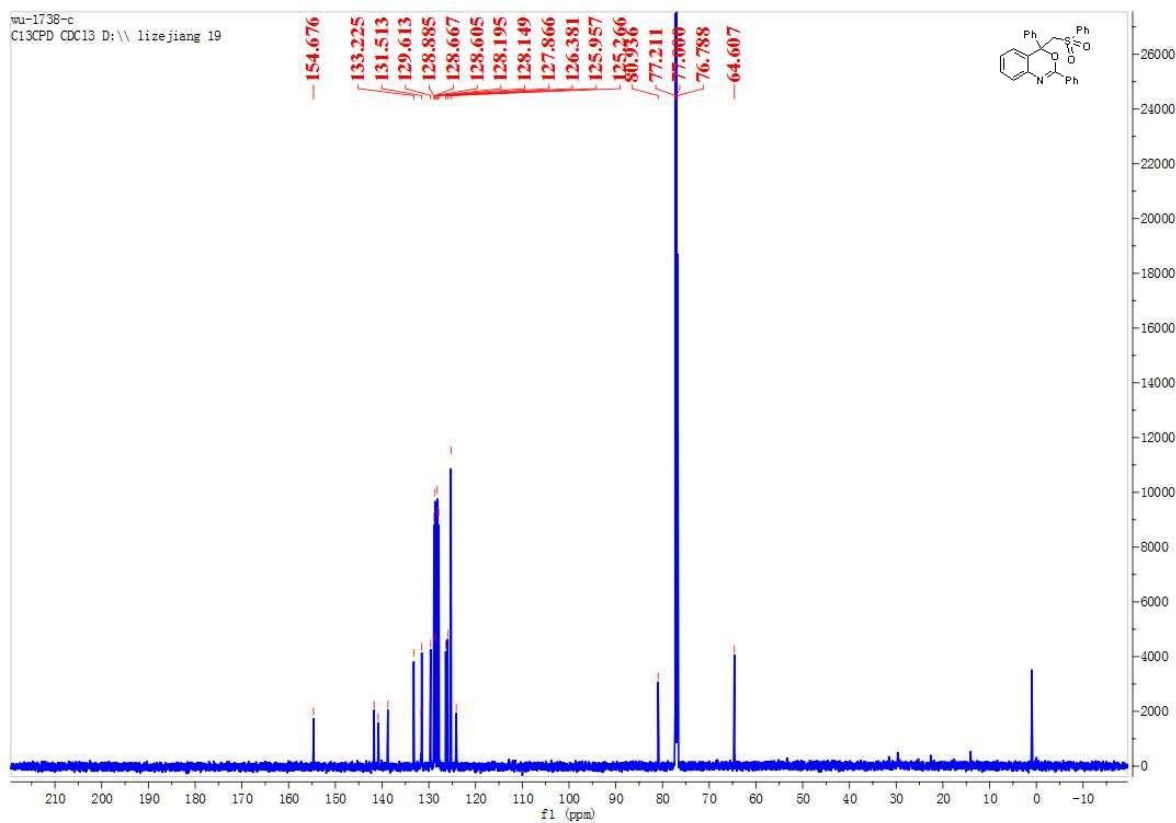
HRMS (ESI, m/z): Calculated for $\text{C}_{21}\text{H}_{27}\text{O}_3\text{S}$ ($\text{M}-\text{H}$)⁻ 359.1686, found 359.1692.

Copies of the ^1H NMR, ^{13}C NMR

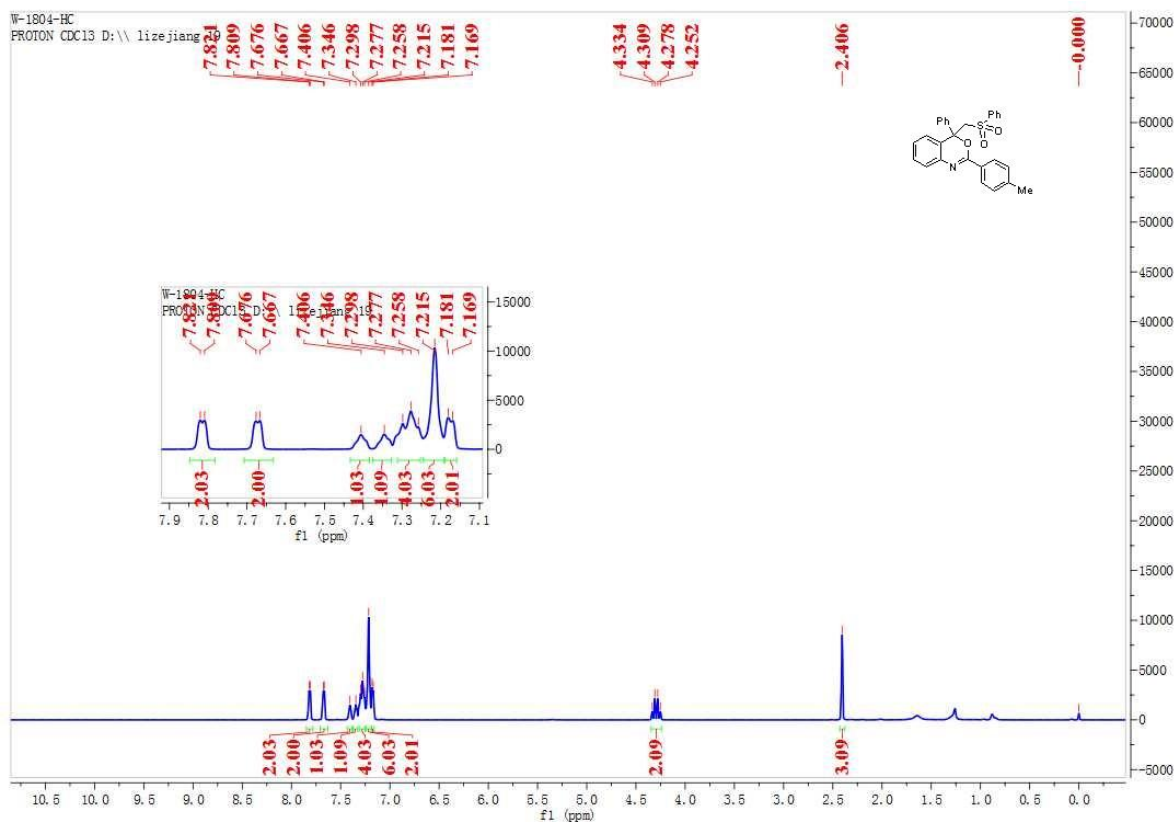
1- ^1H NMR



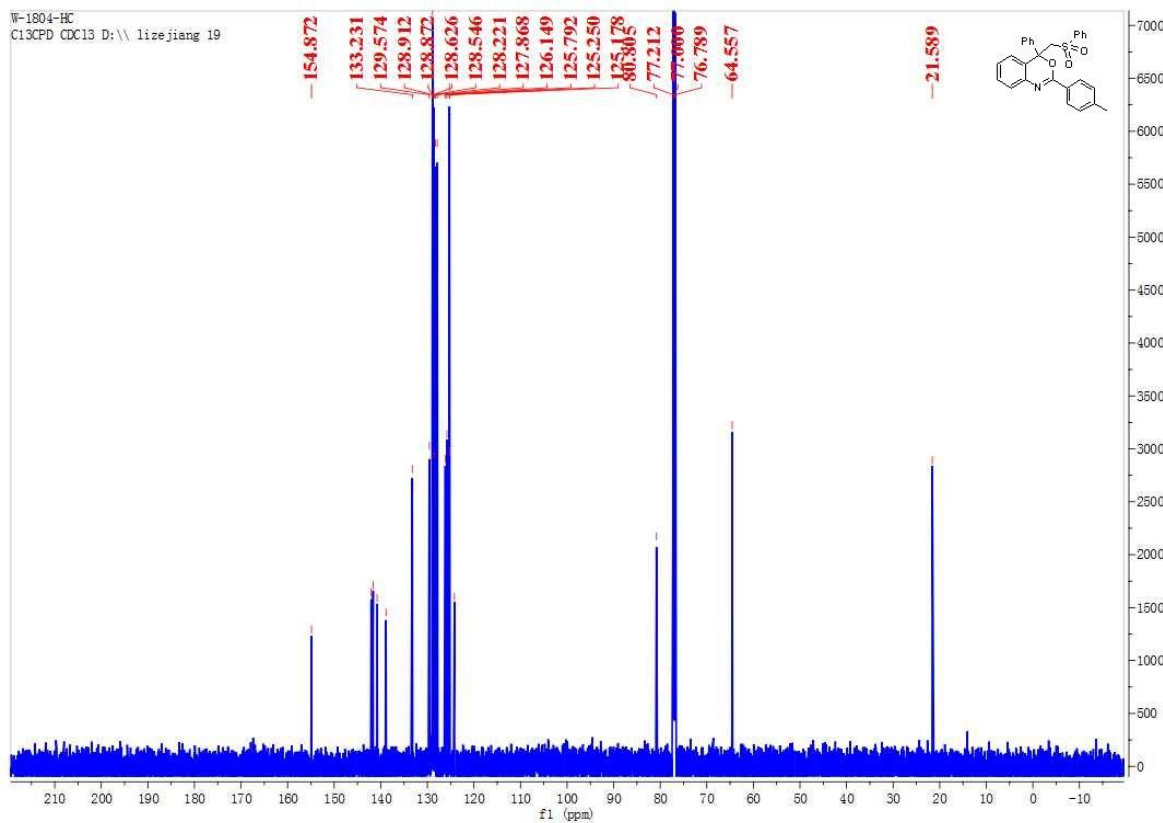
1- ^{13}C NMR



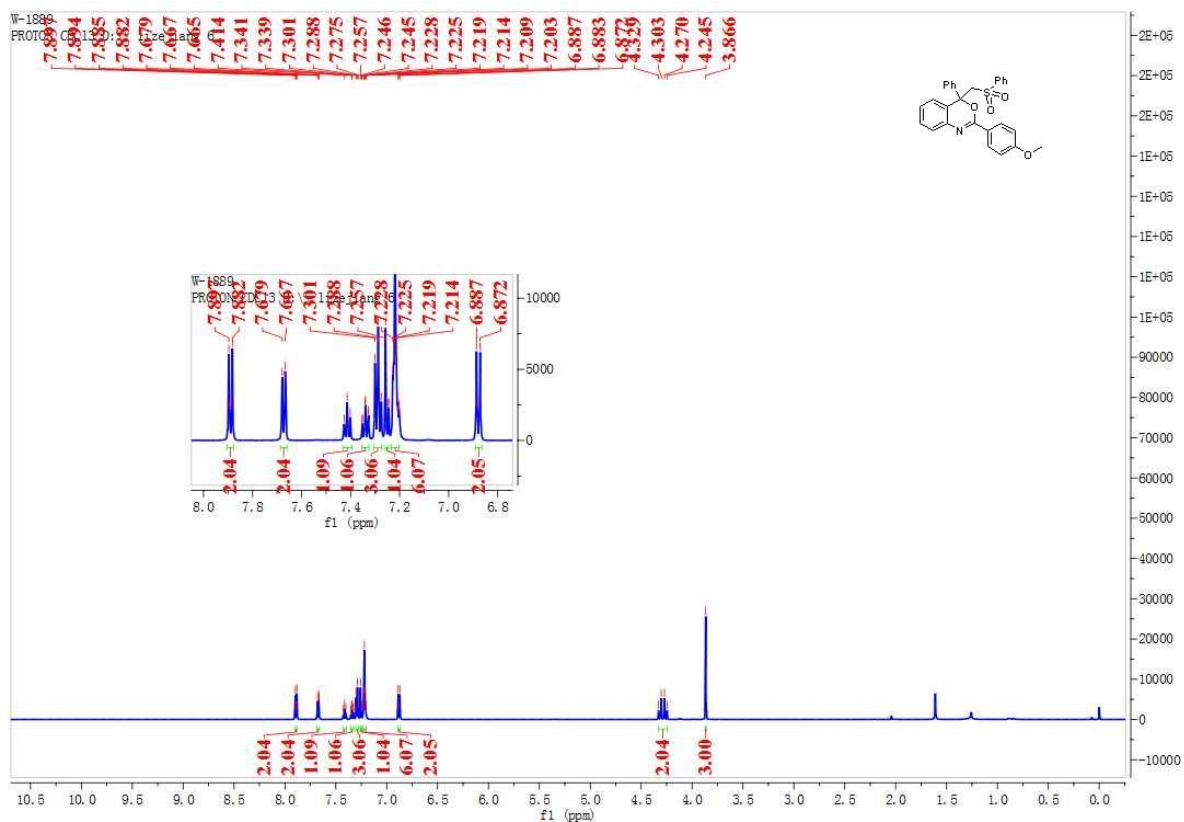
2-¹H NMR



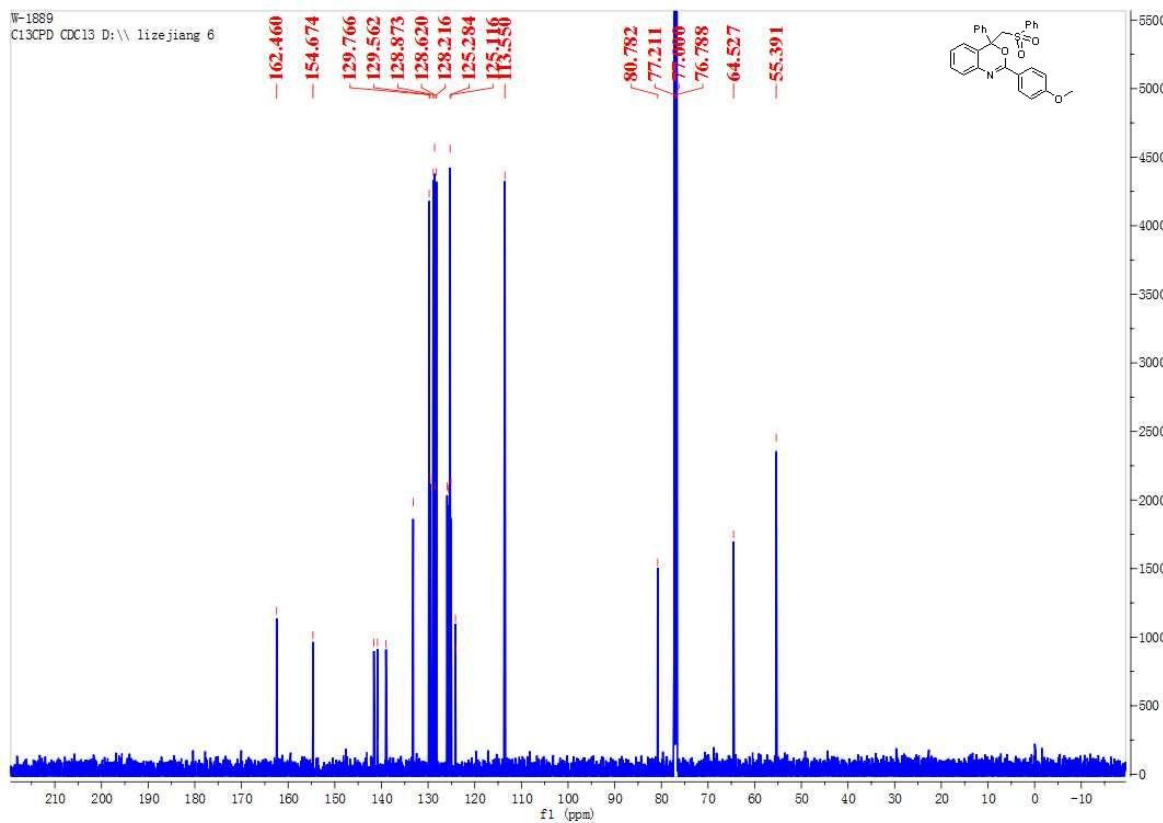
2-¹³C NMR



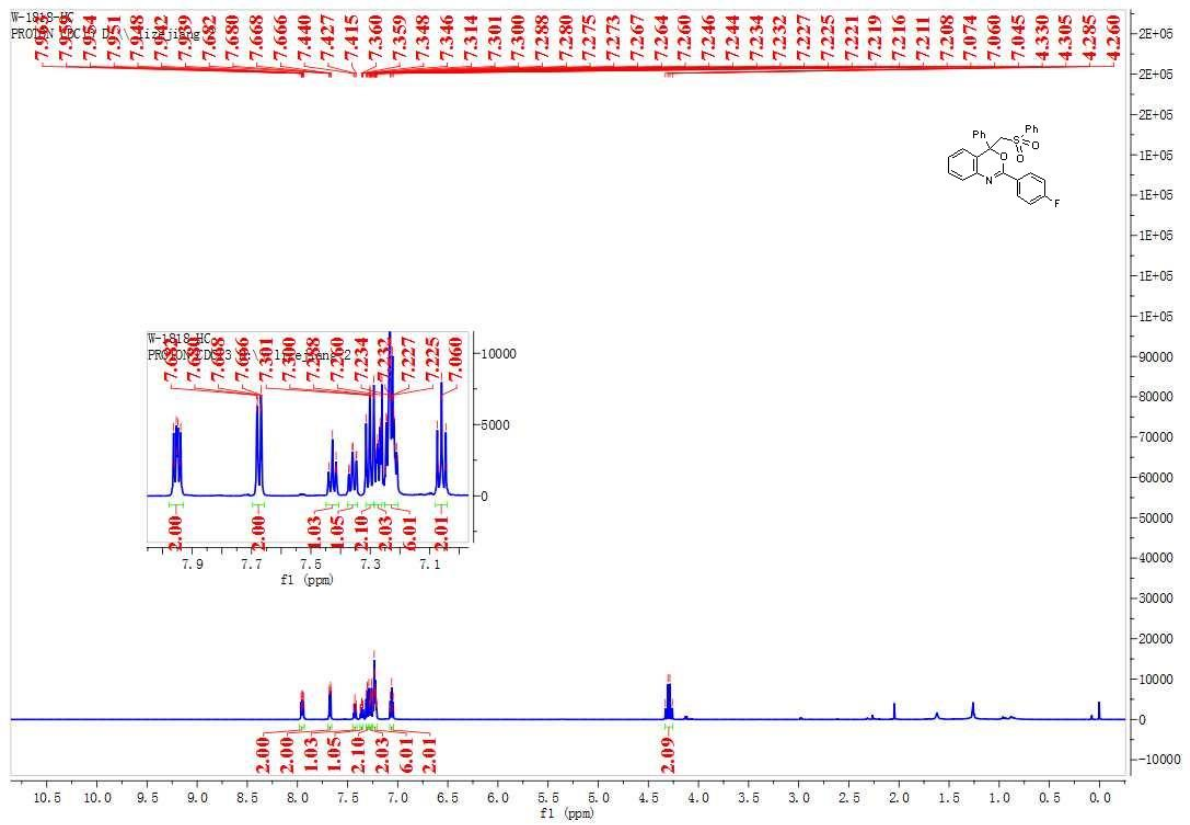
3-¹H NMR



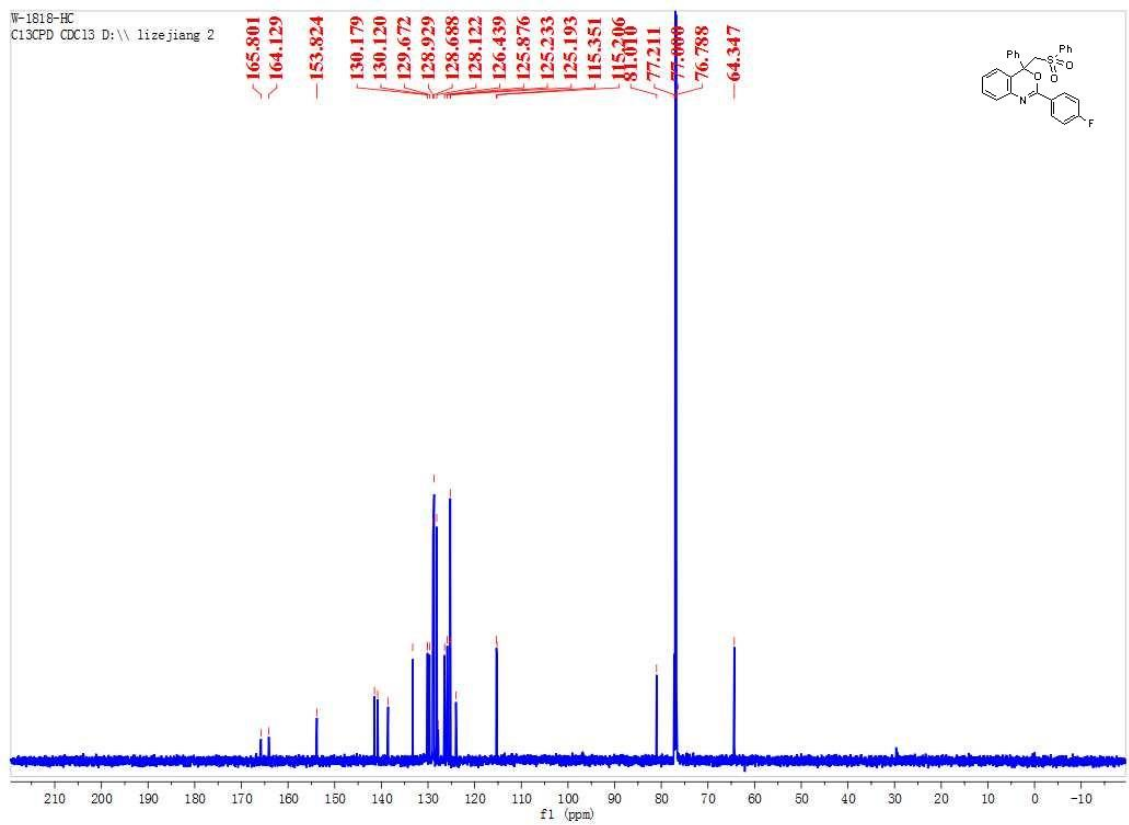
3-¹³C NMR



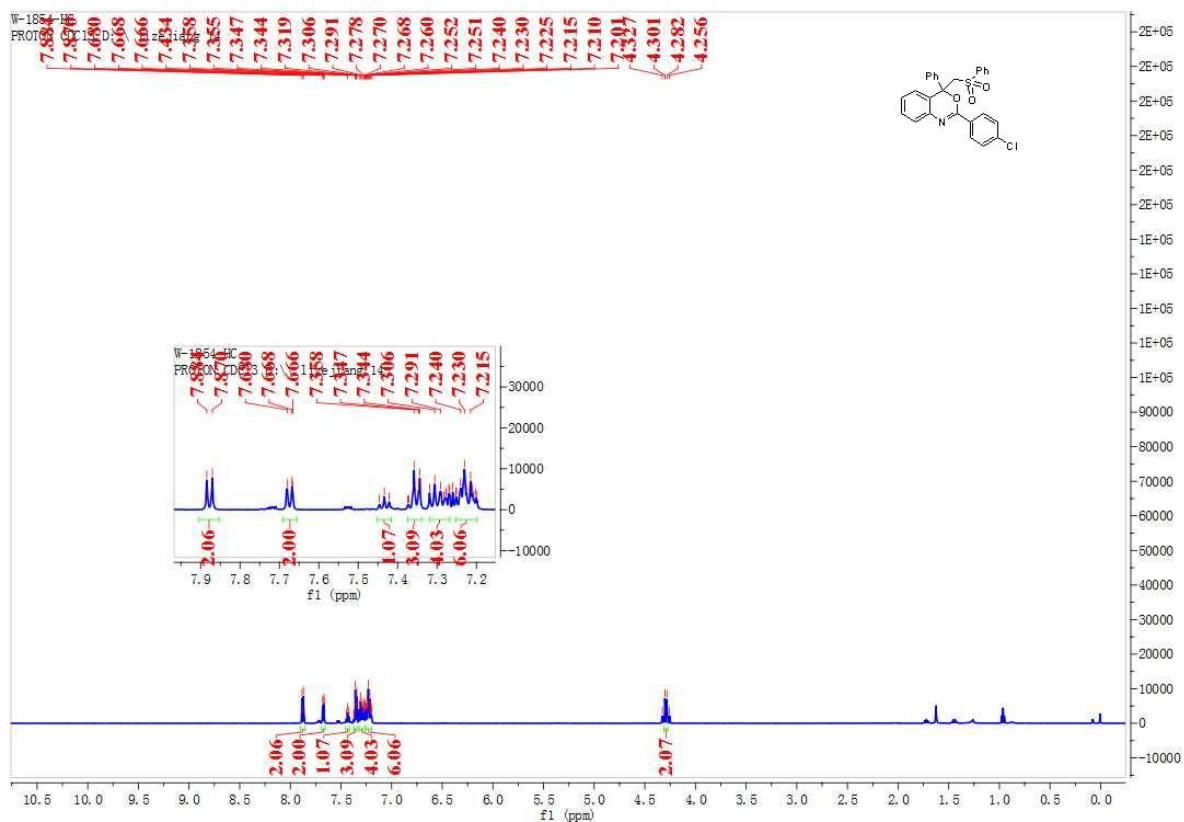
4-¹H NMR



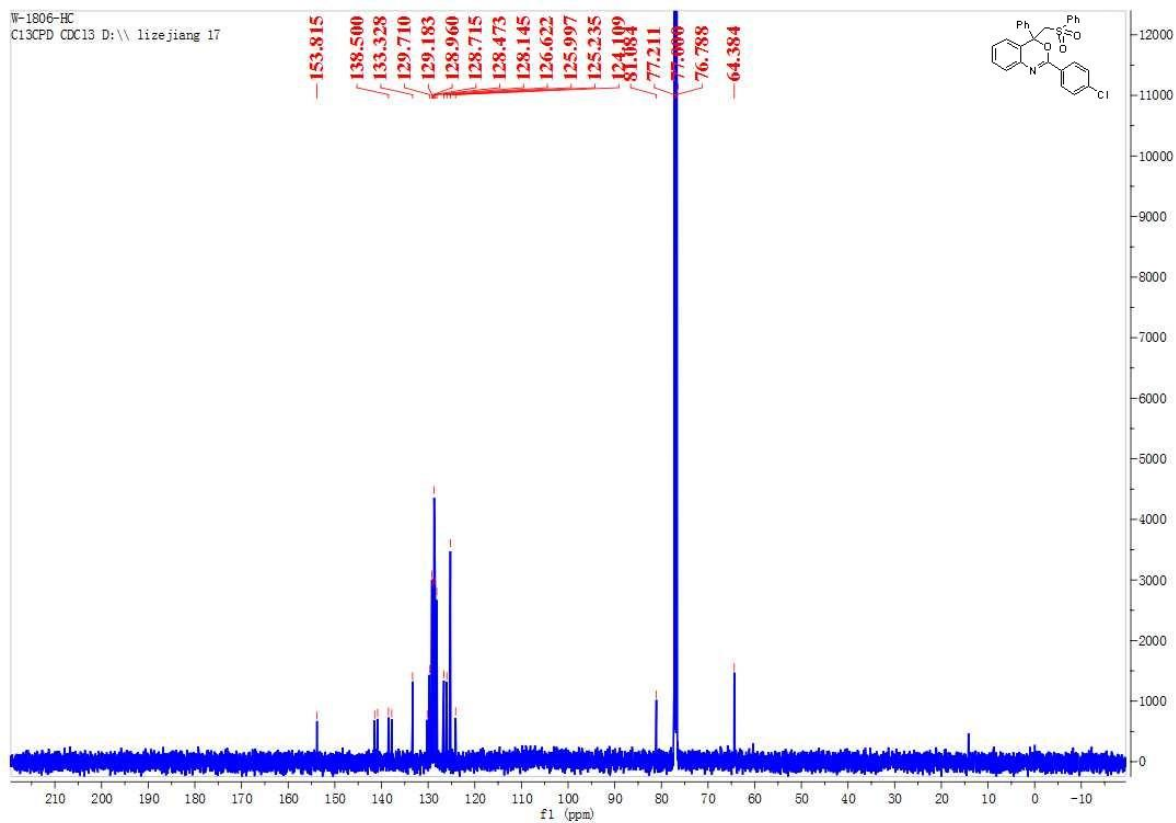
4-¹³C NMR



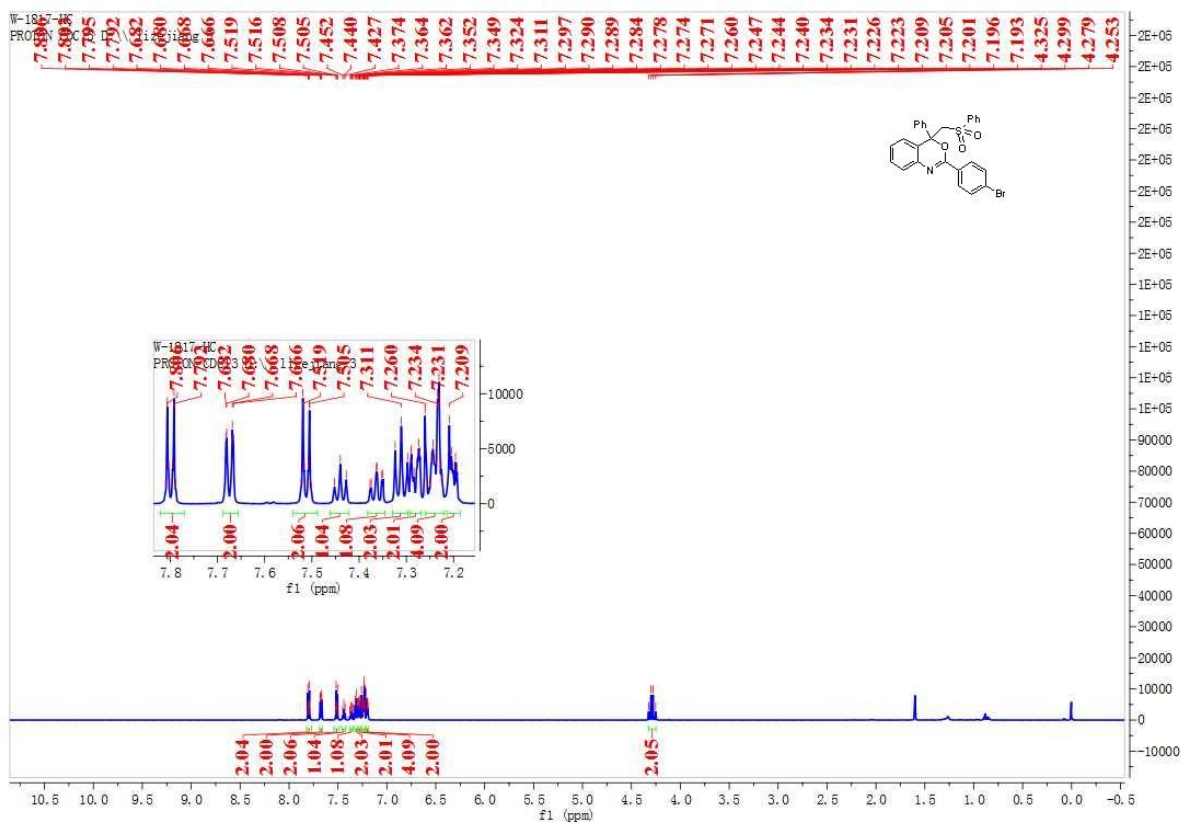
5-¹H NMR



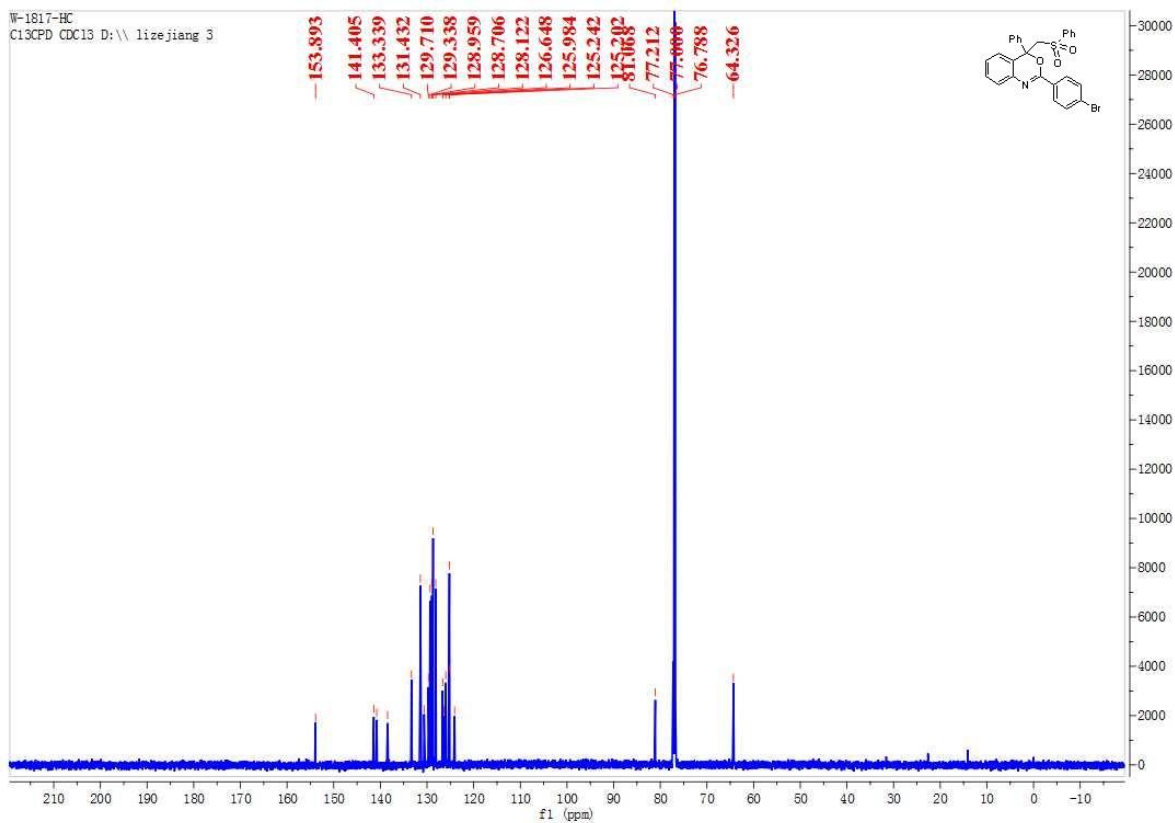
5-¹³C NMR



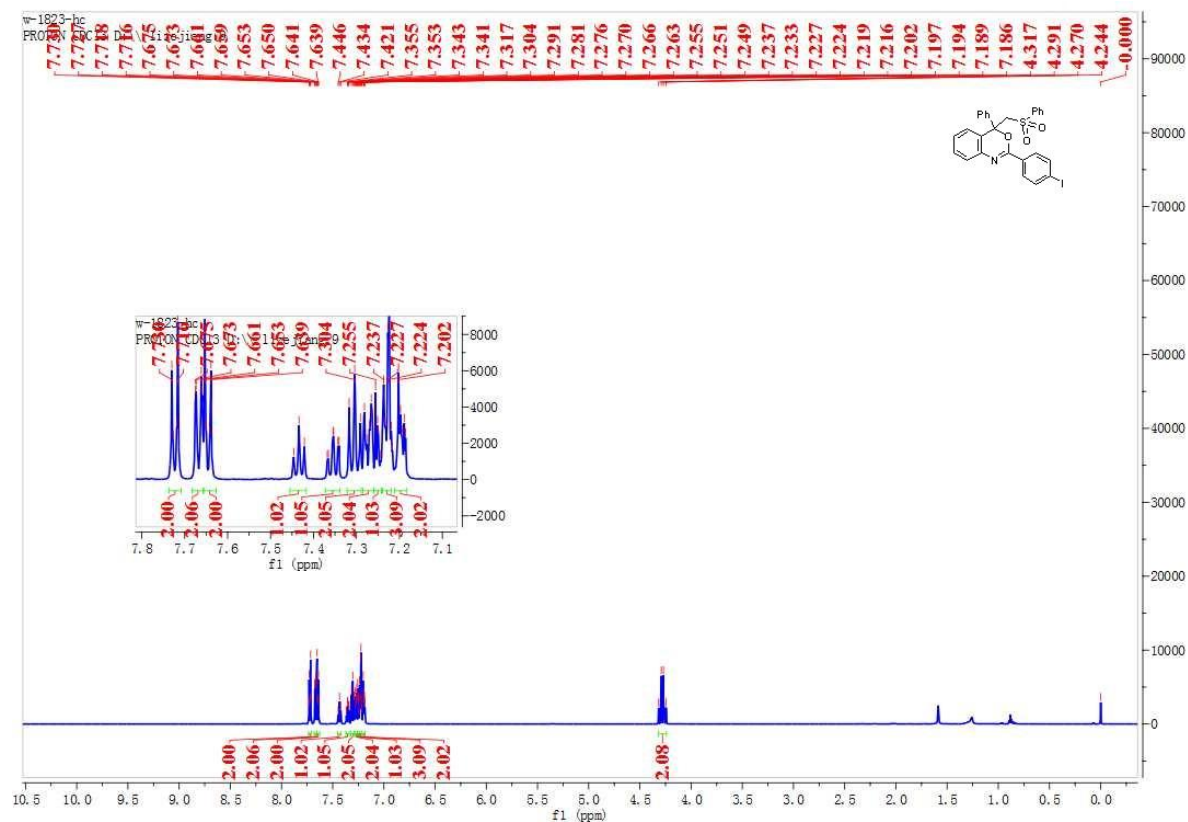
6-¹H NMR



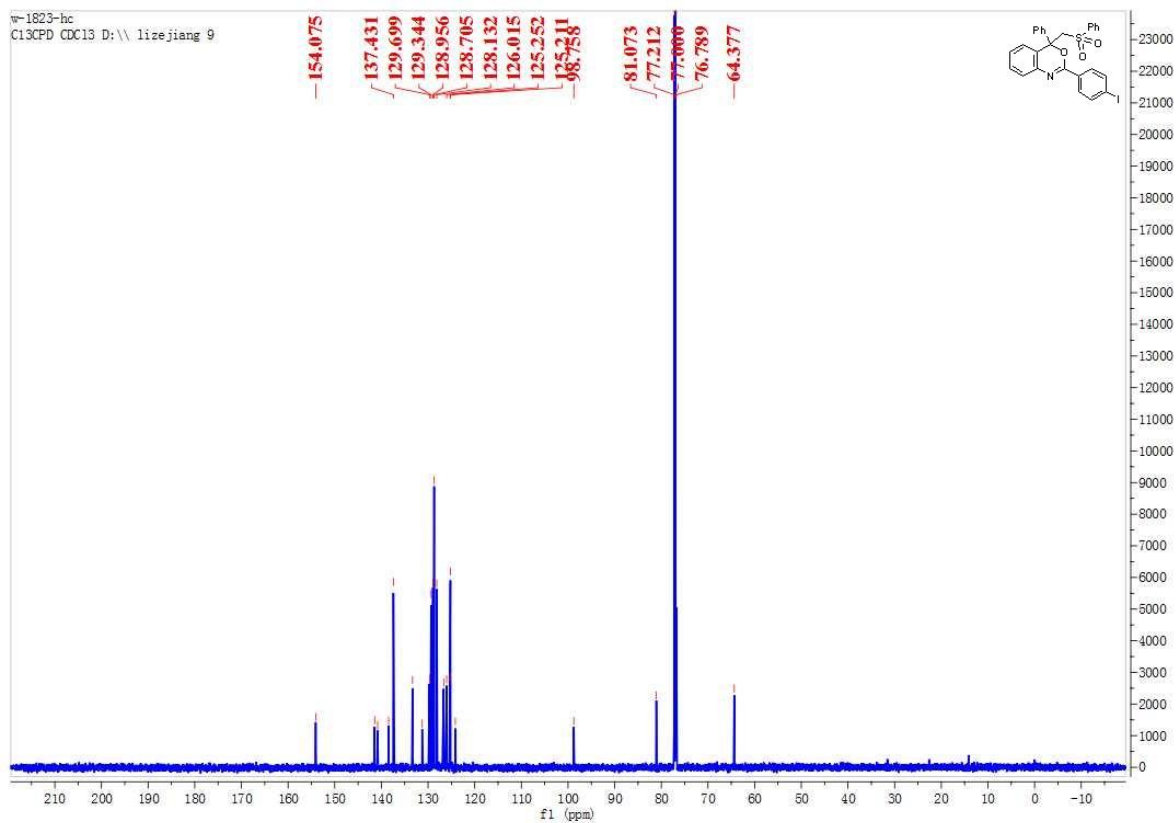
6-¹³C NMR



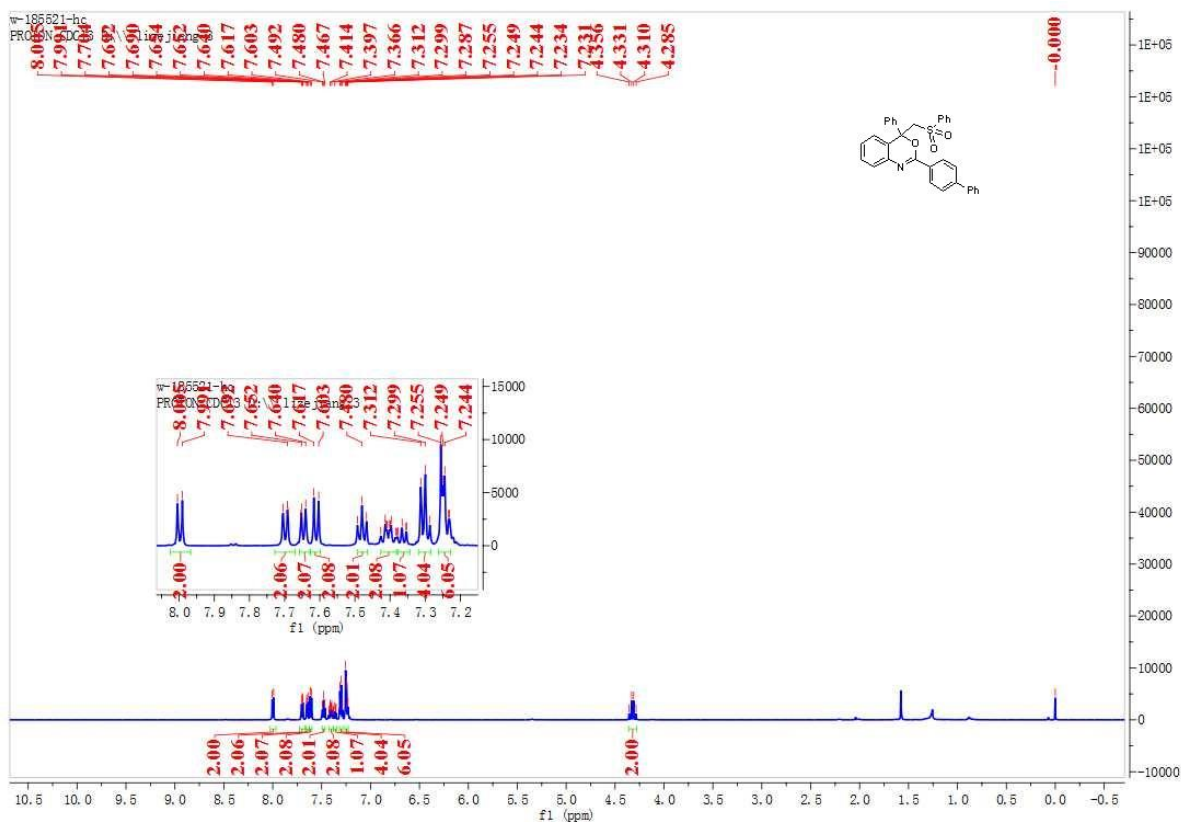
7-¹H NMR



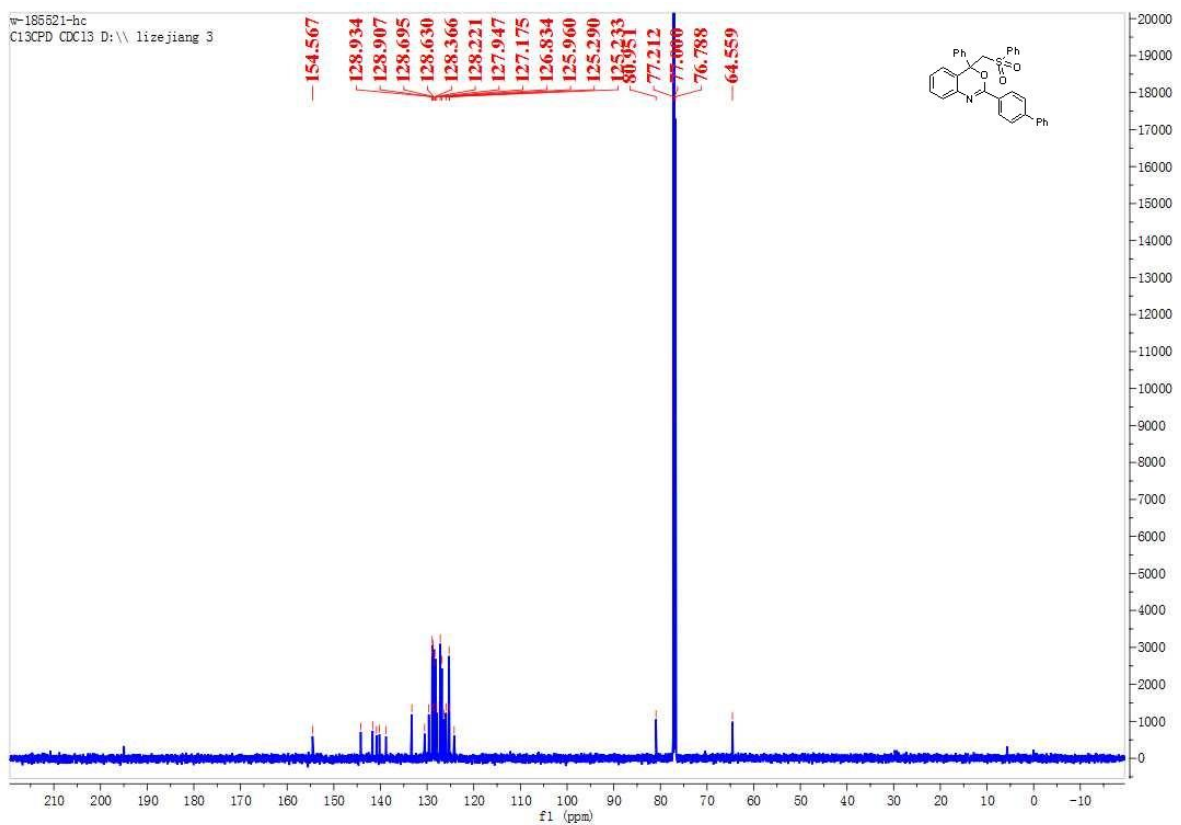
7-¹³C NMR



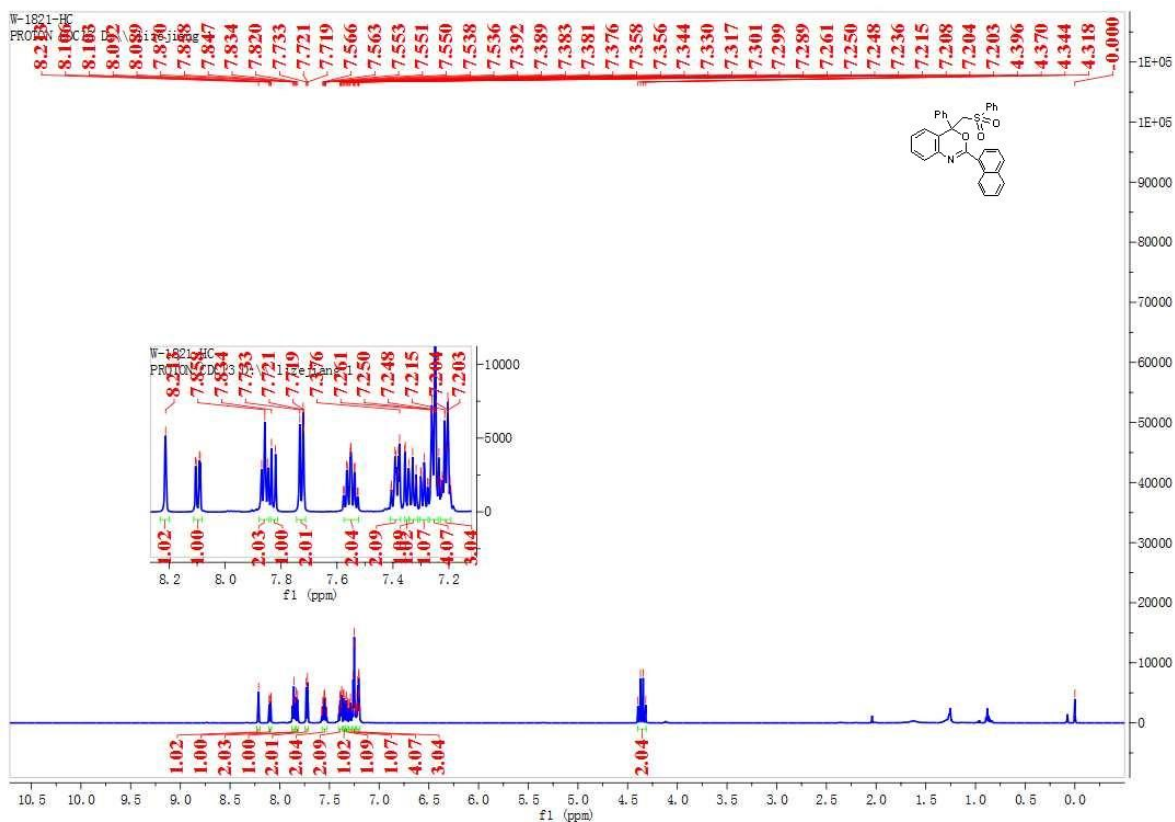
8-¹H NMR



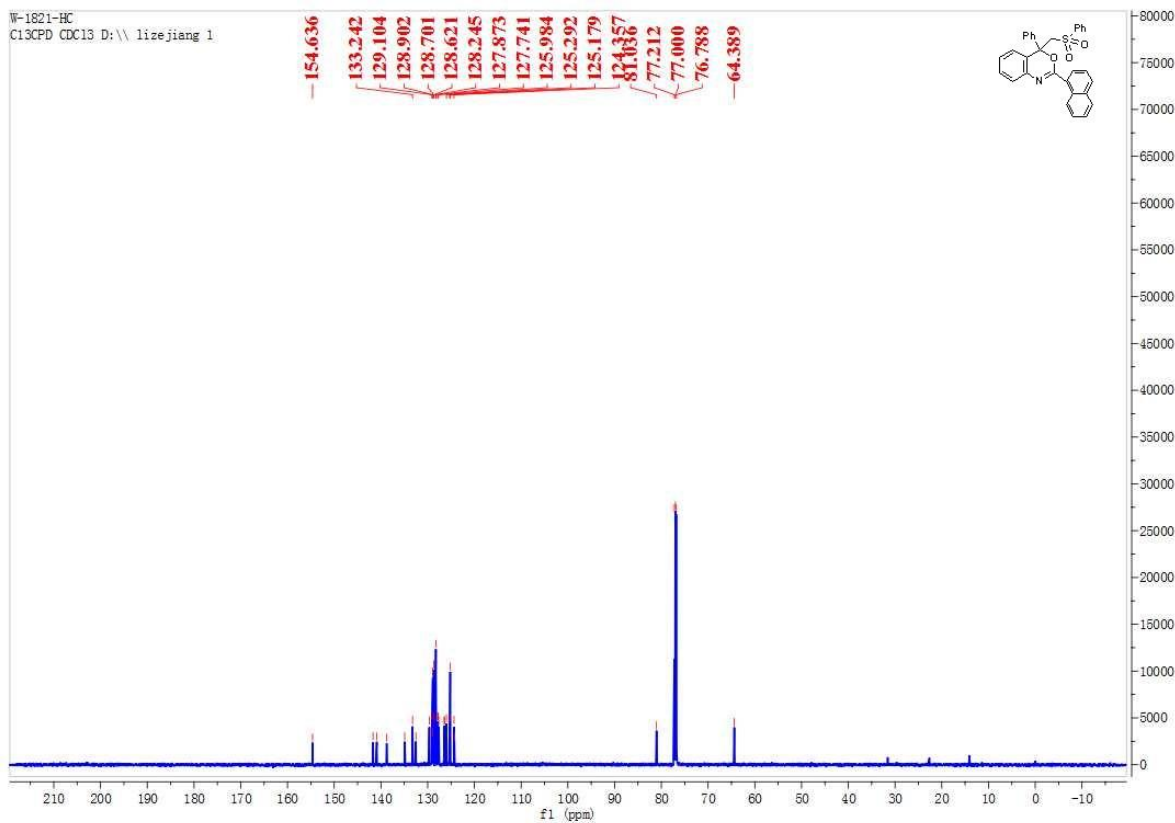
8-¹³C NMR



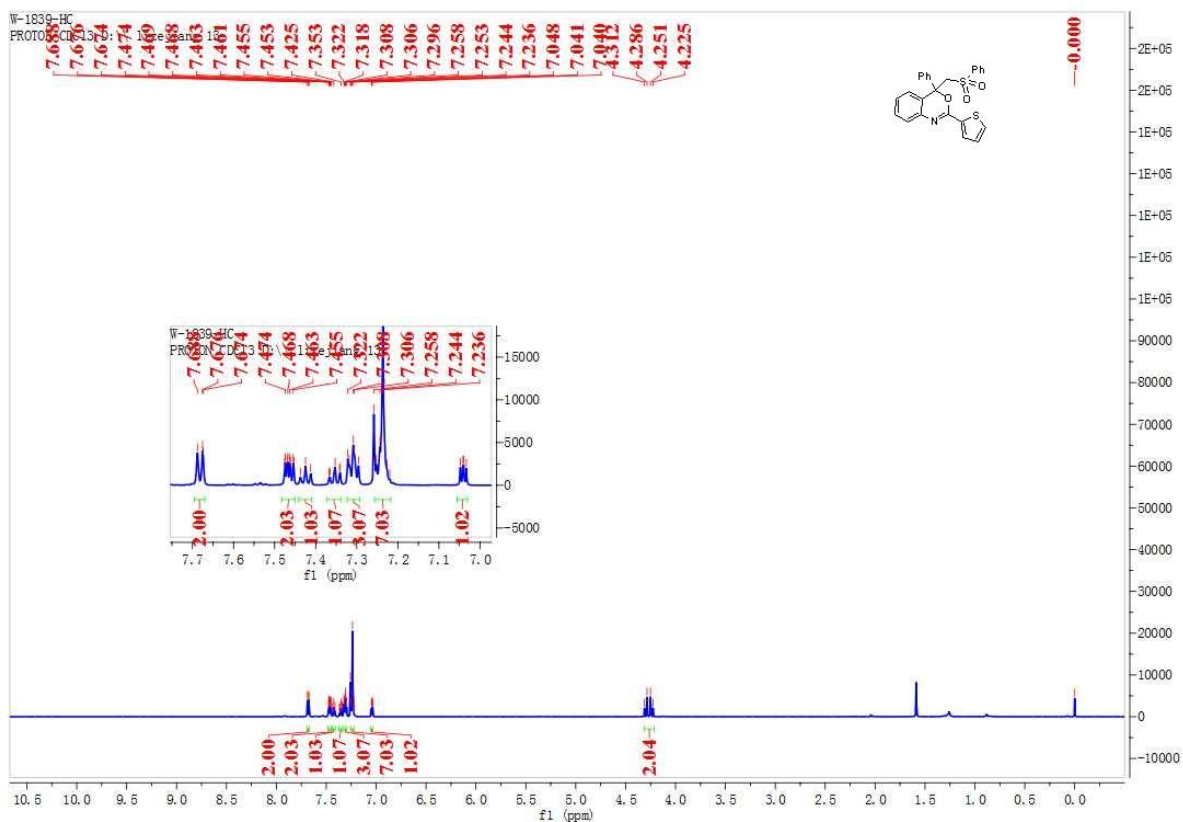
9-¹H NMR



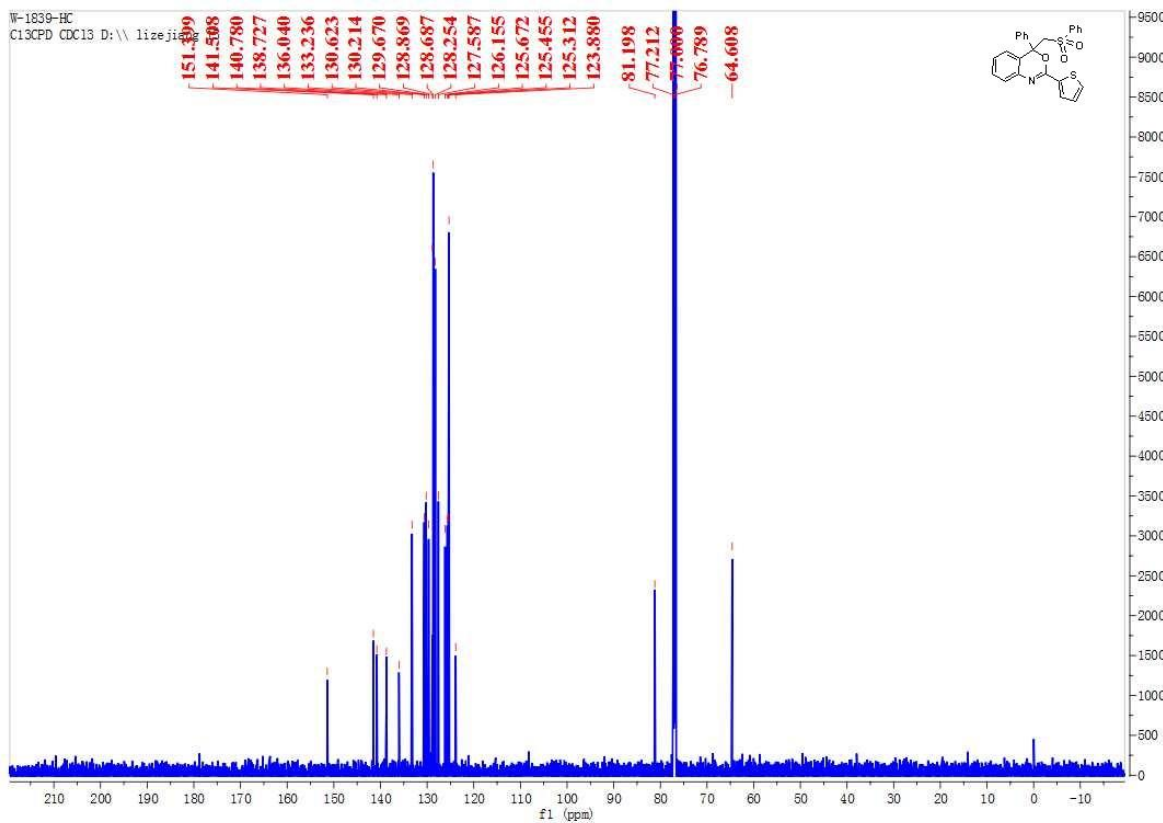
9-¹³C NMR



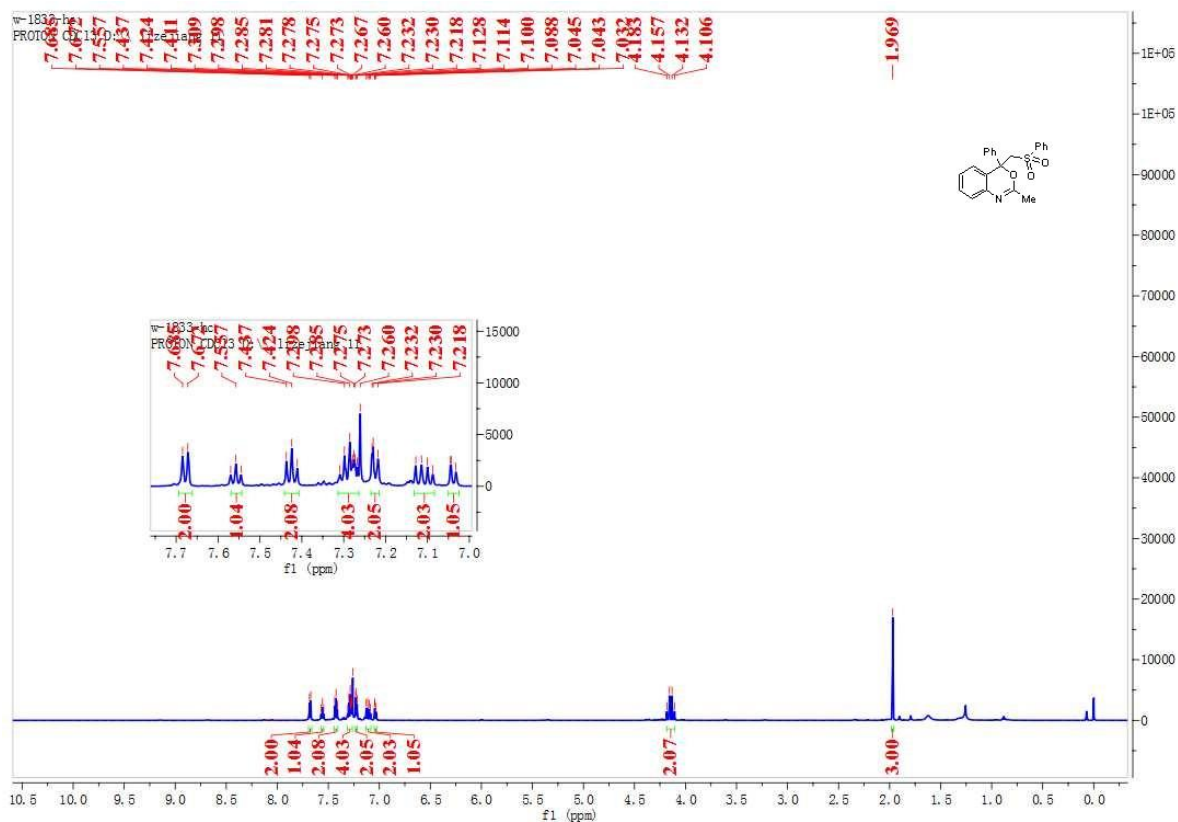
10-¹H NMR



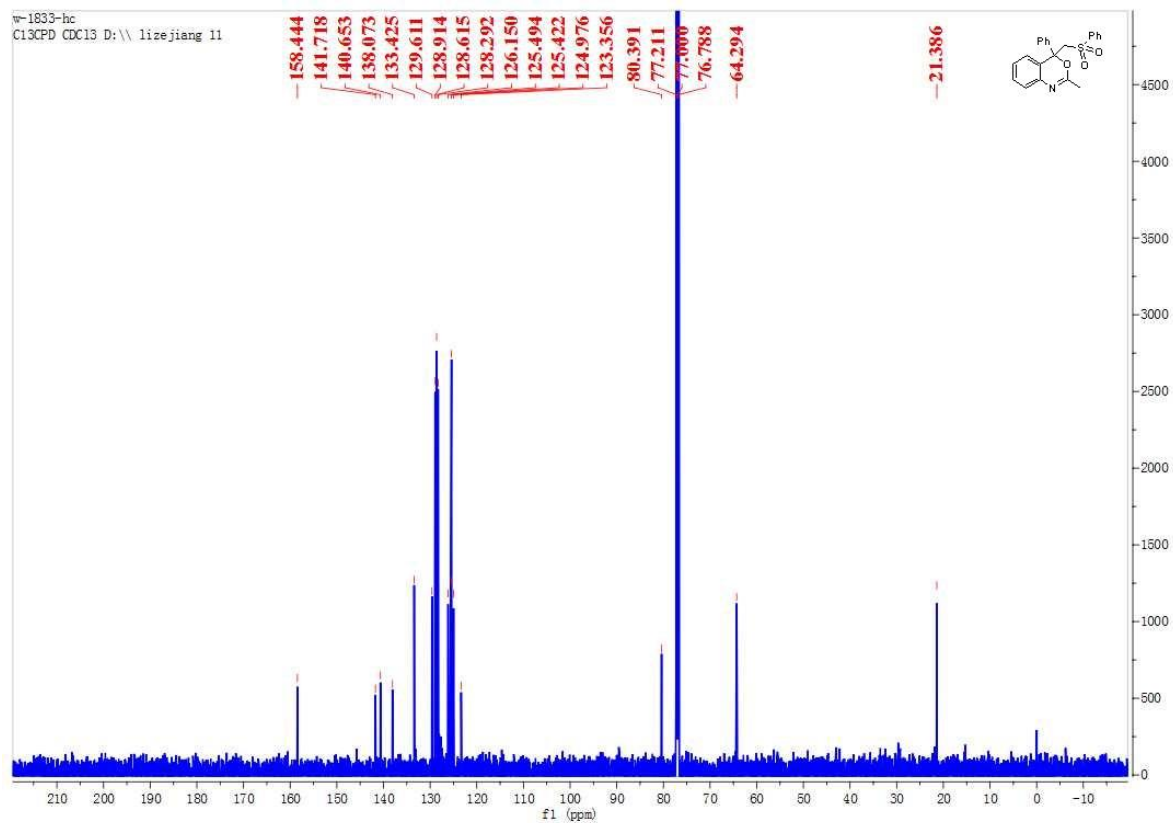
10-¹³C NMR



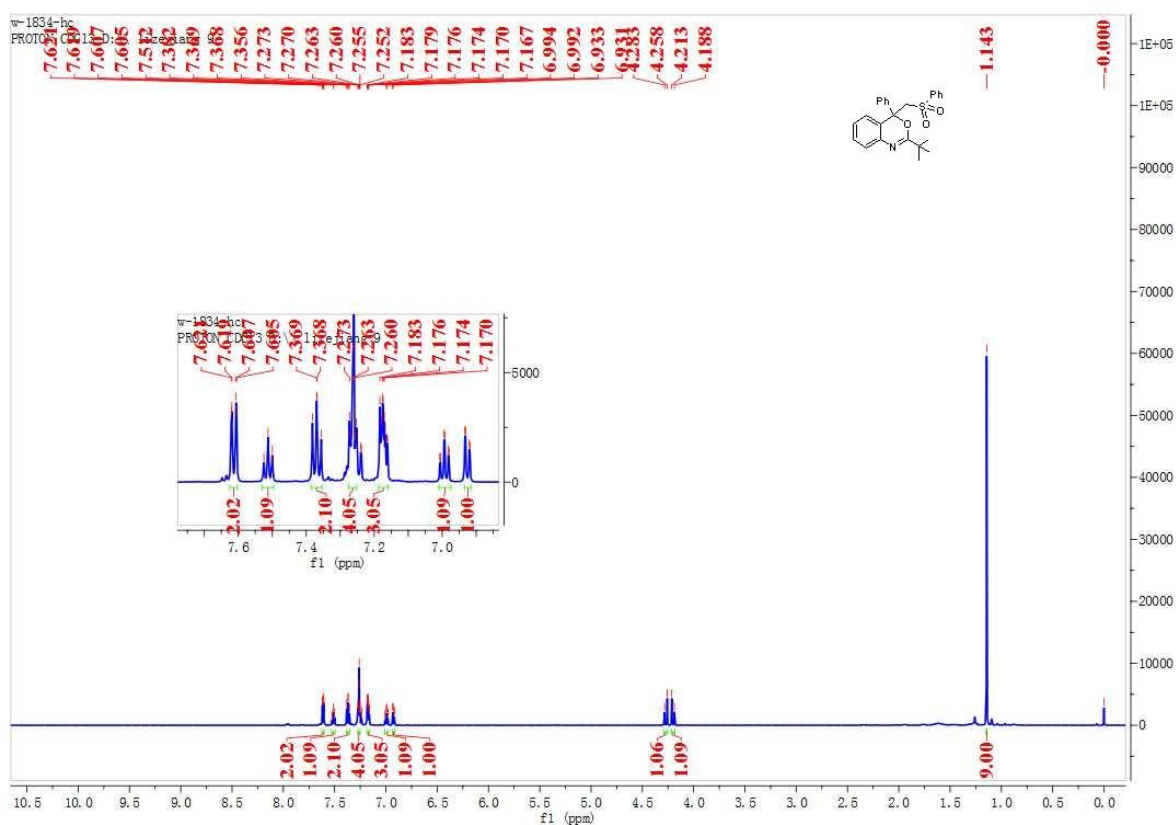
11-¹H NMR



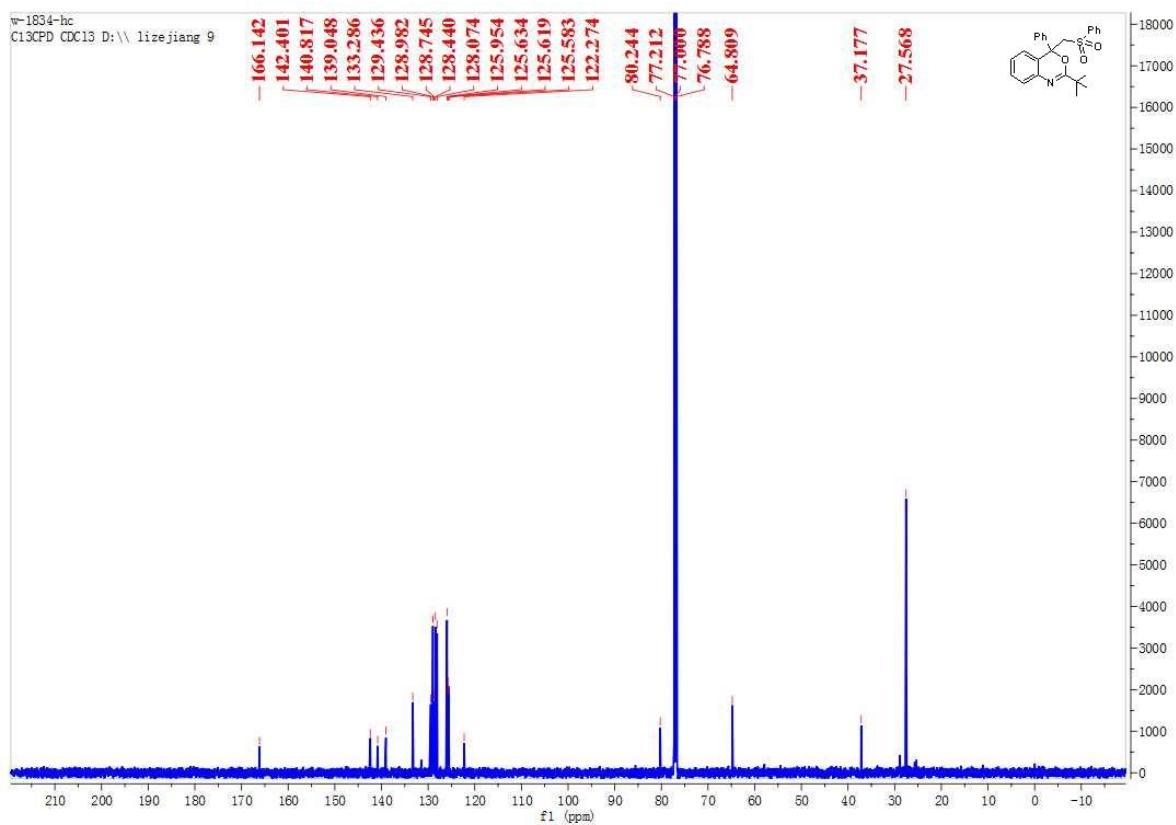
11-¹³C NMR



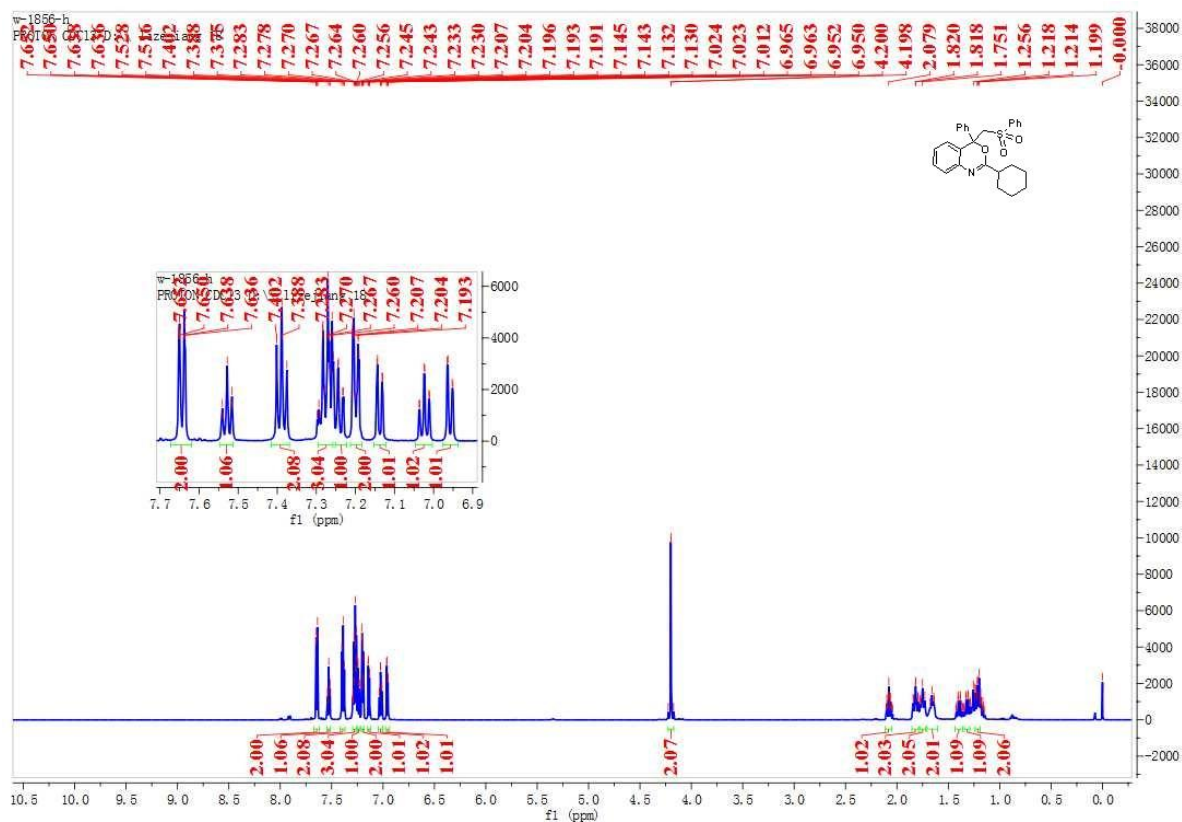
12-¹H NMR



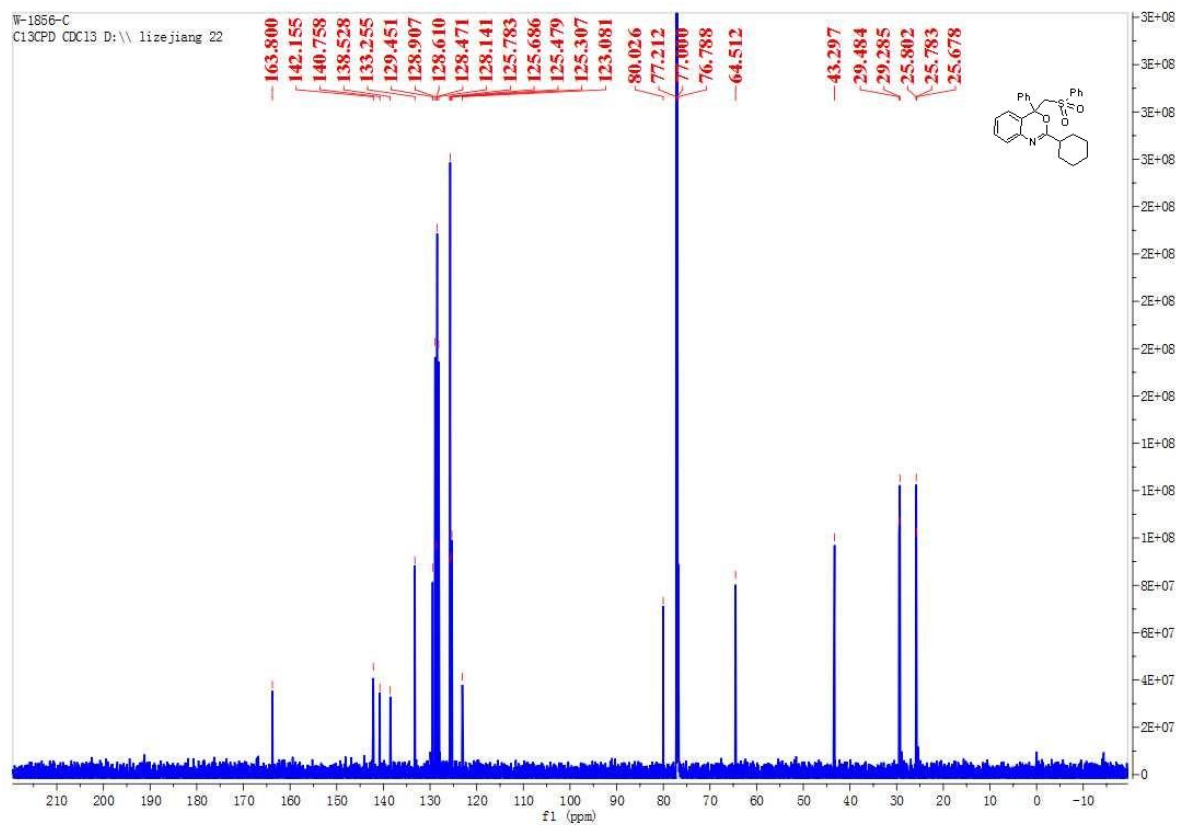
12-¹³C NMR



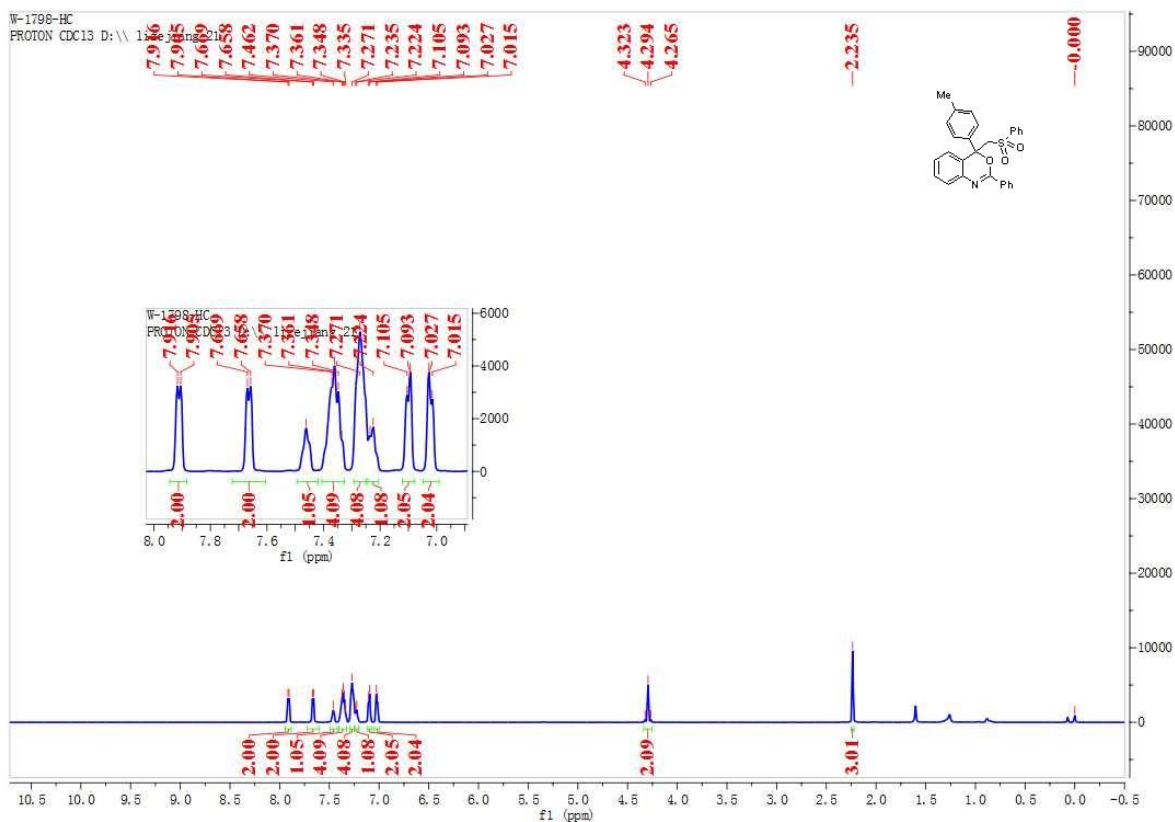
13-¹H NMR



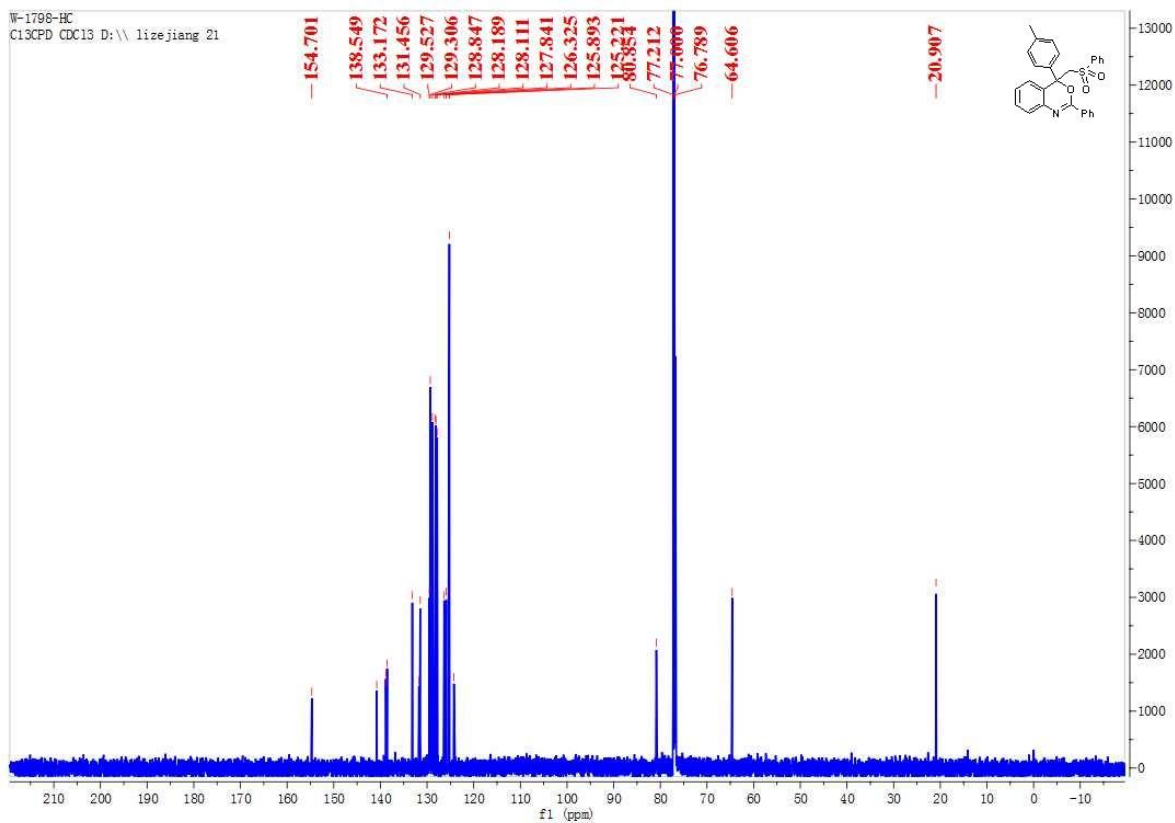
13-¹³C NMR



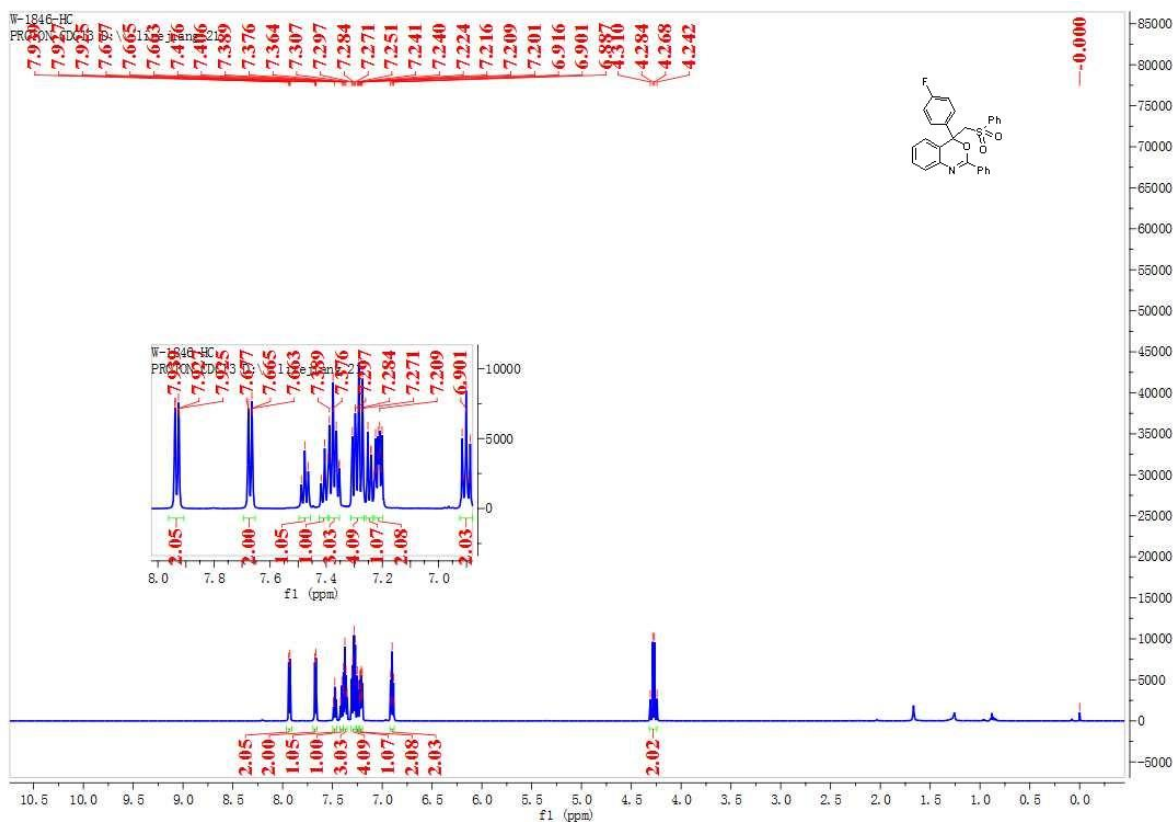
14-¹H NMR



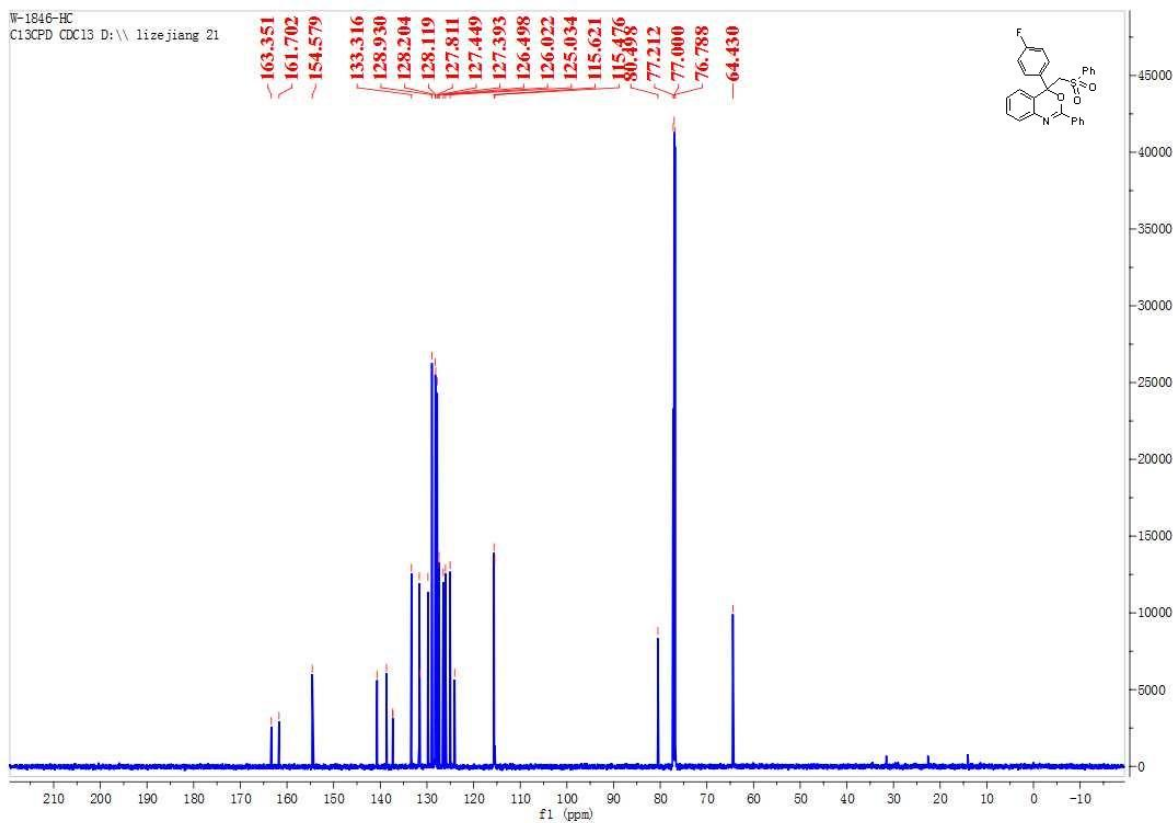
14-¹³C NMR



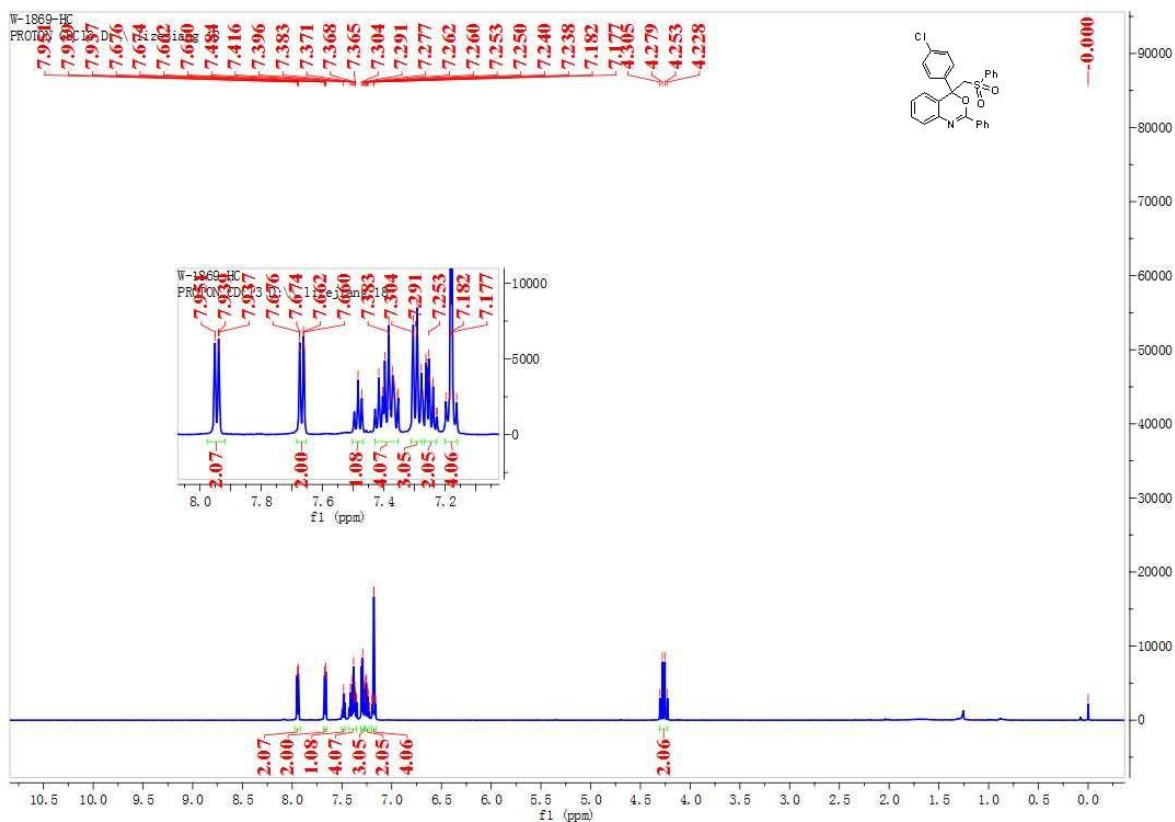
15-¹H NMR



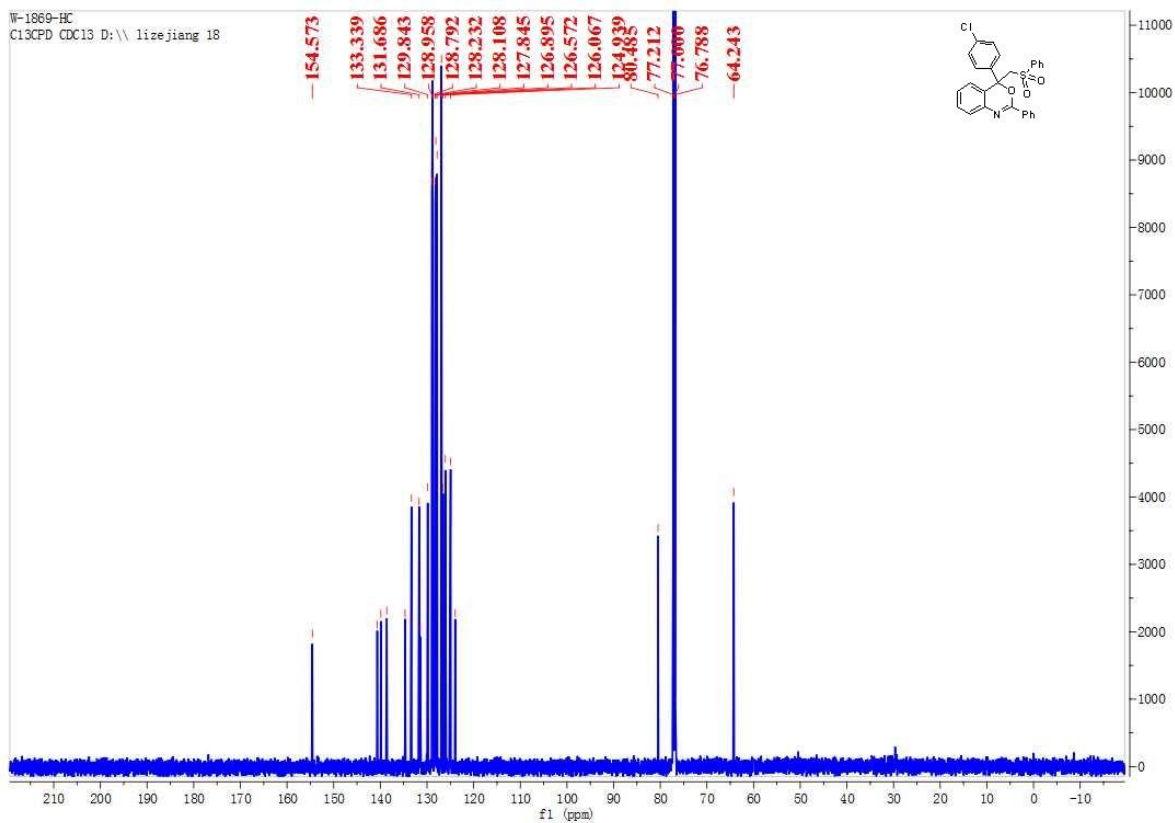
15-¹³C NMR



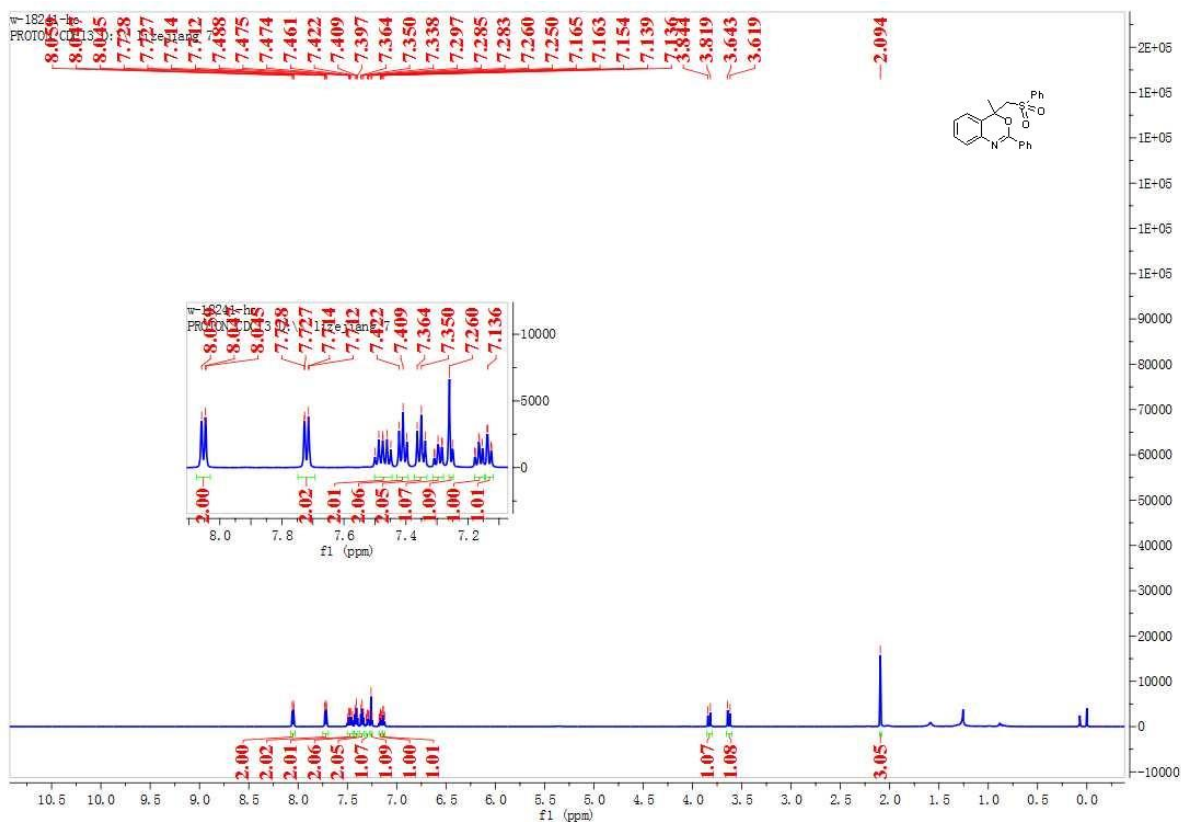
16-¹H NMR



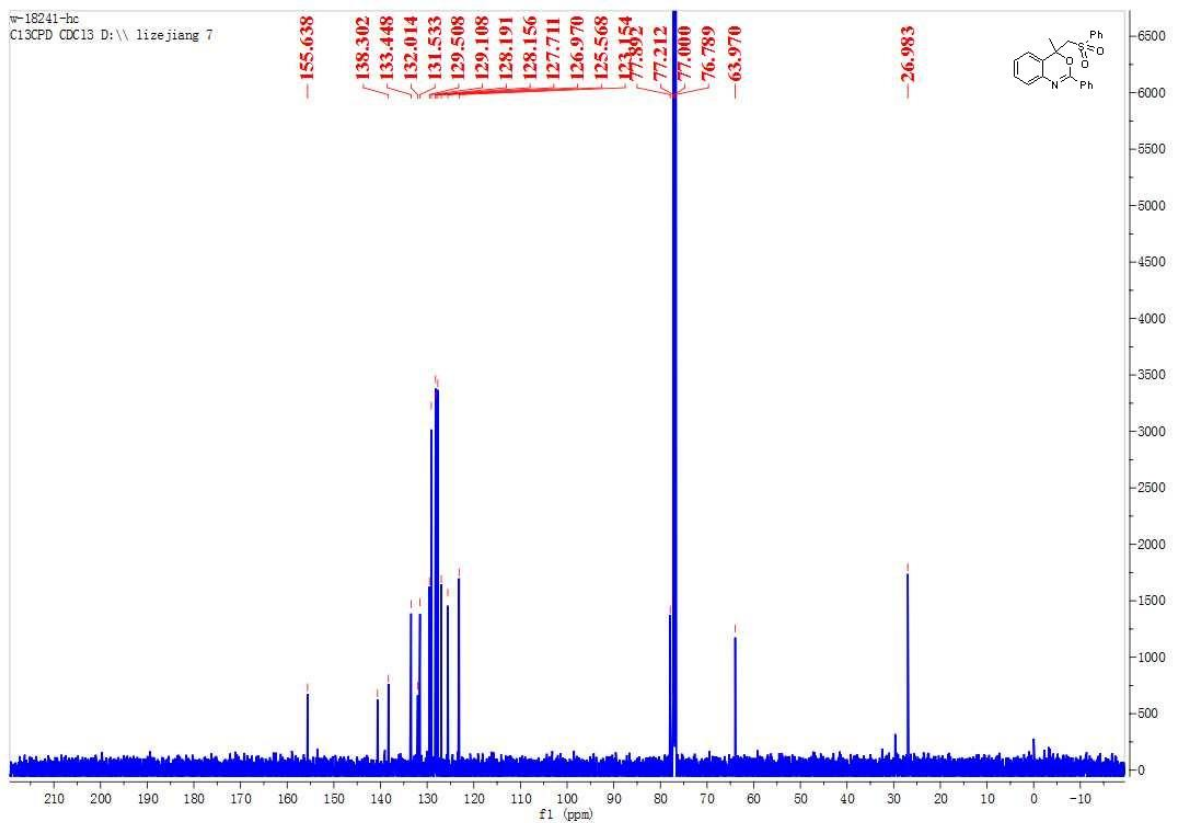
16-¹³C NMR



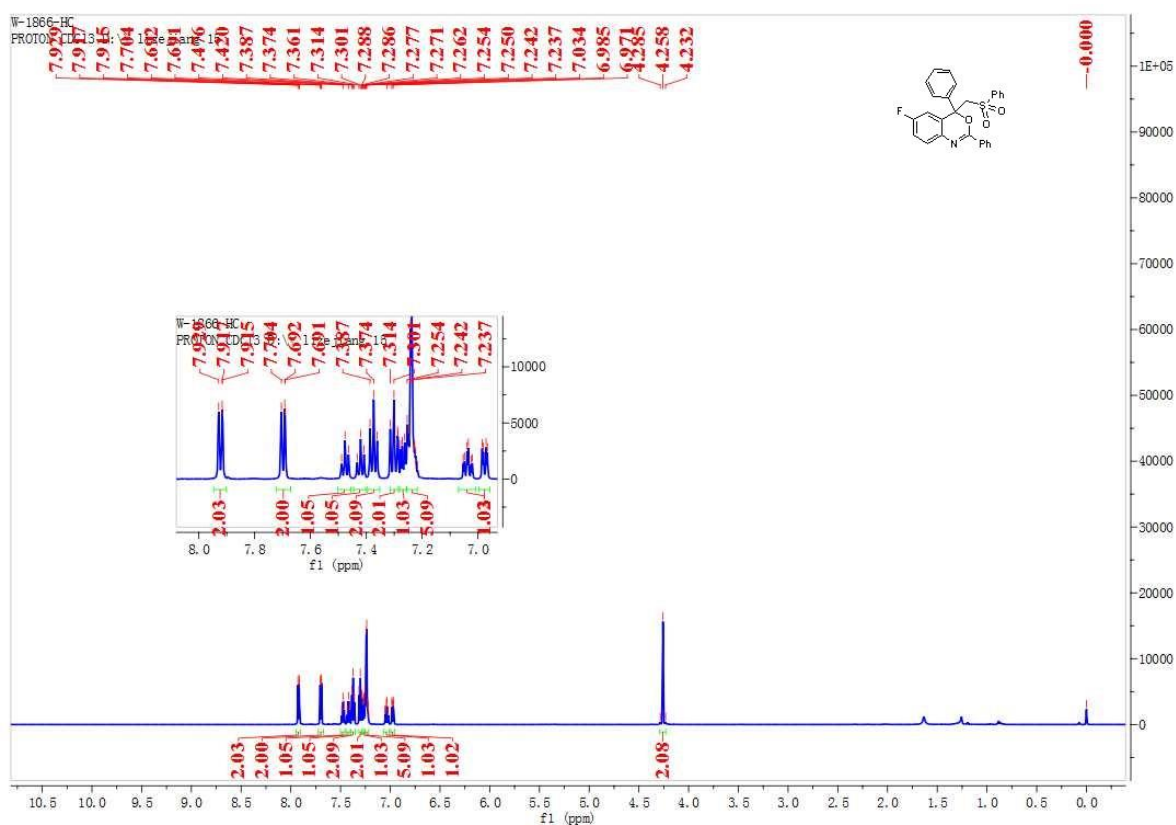
18-¹H NMR



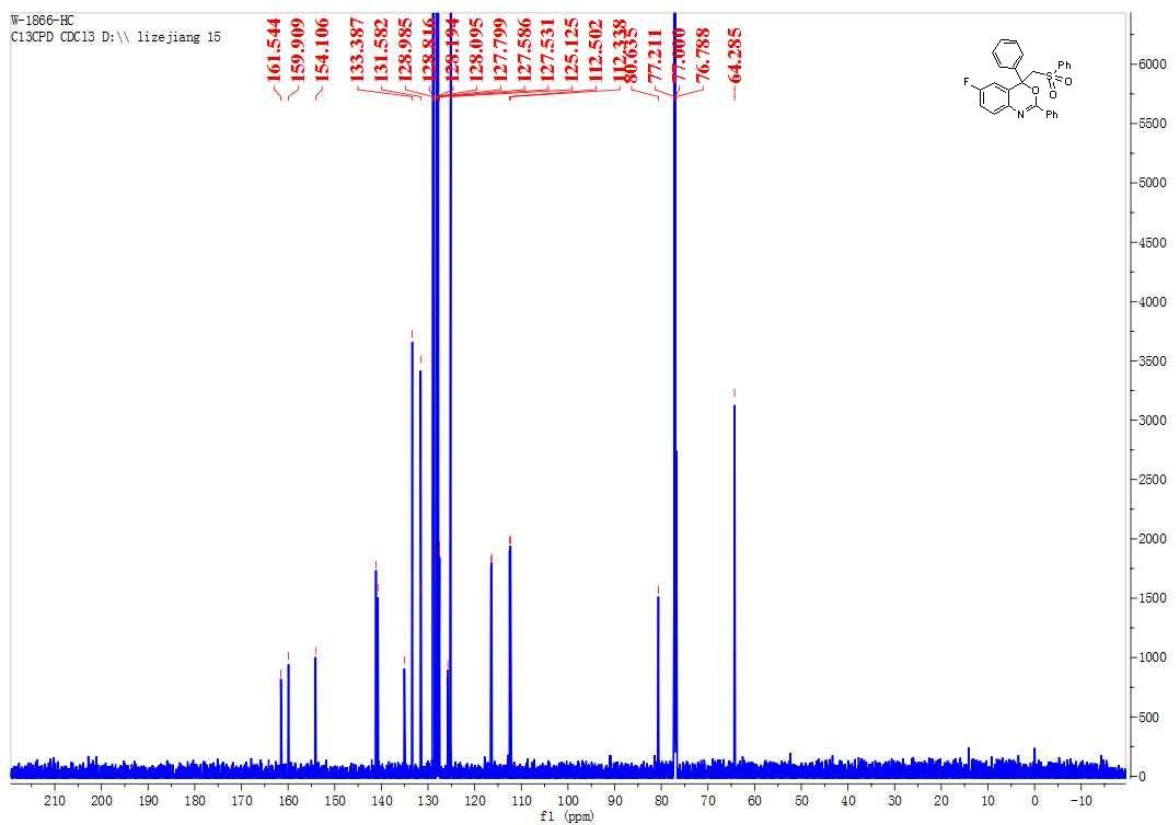
18-¹³C NMR



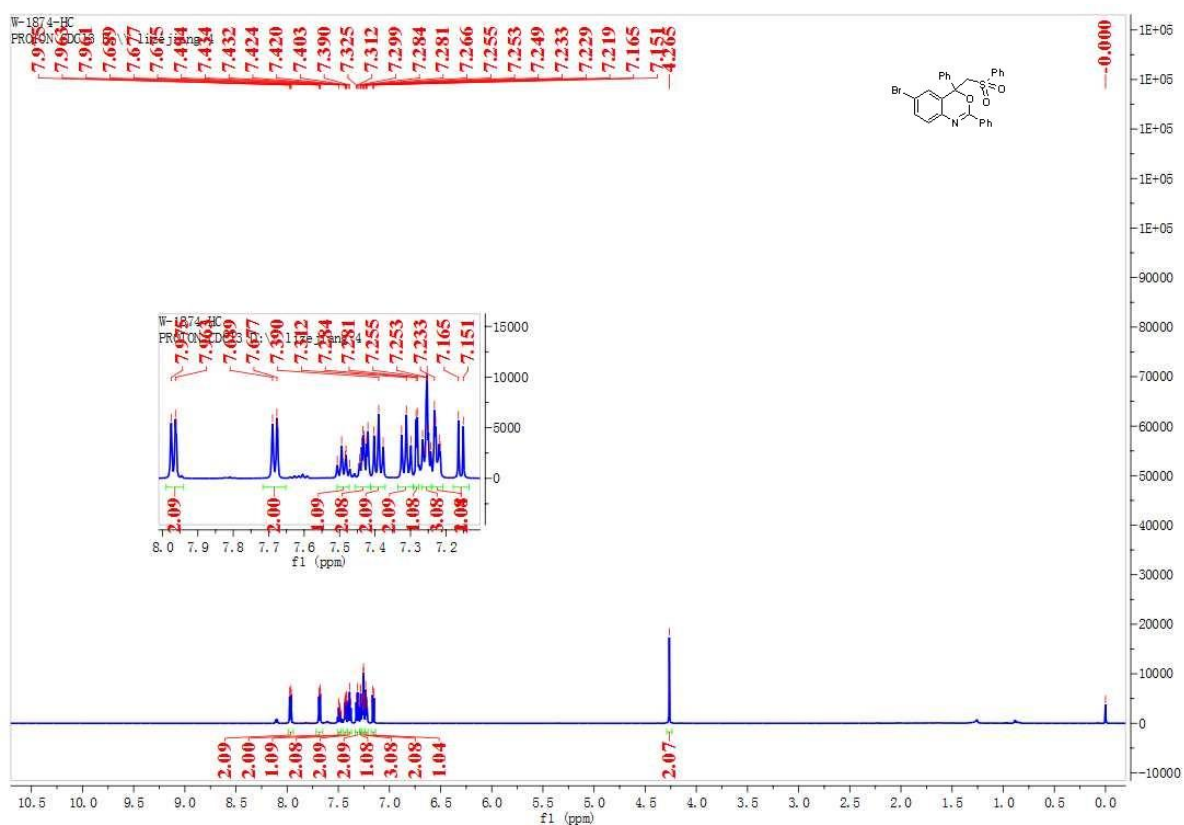
19-¹H NMR



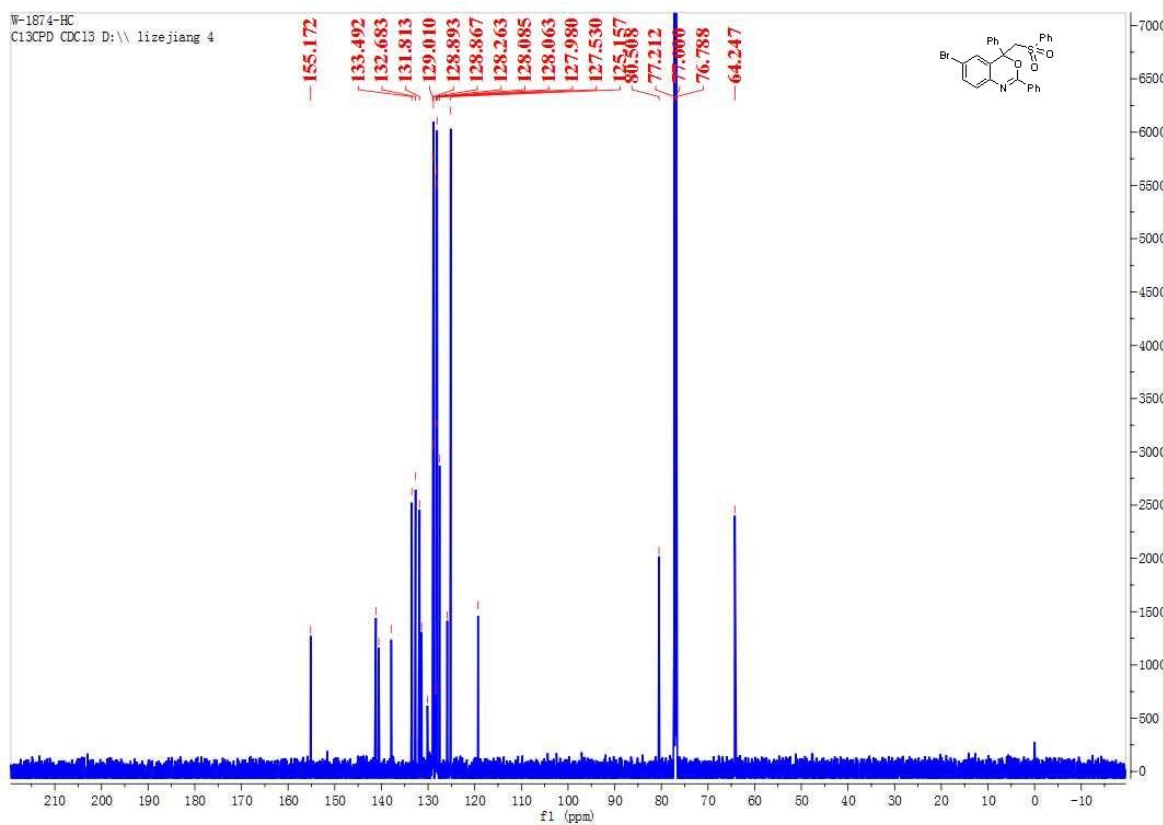
19-¹³C NMR



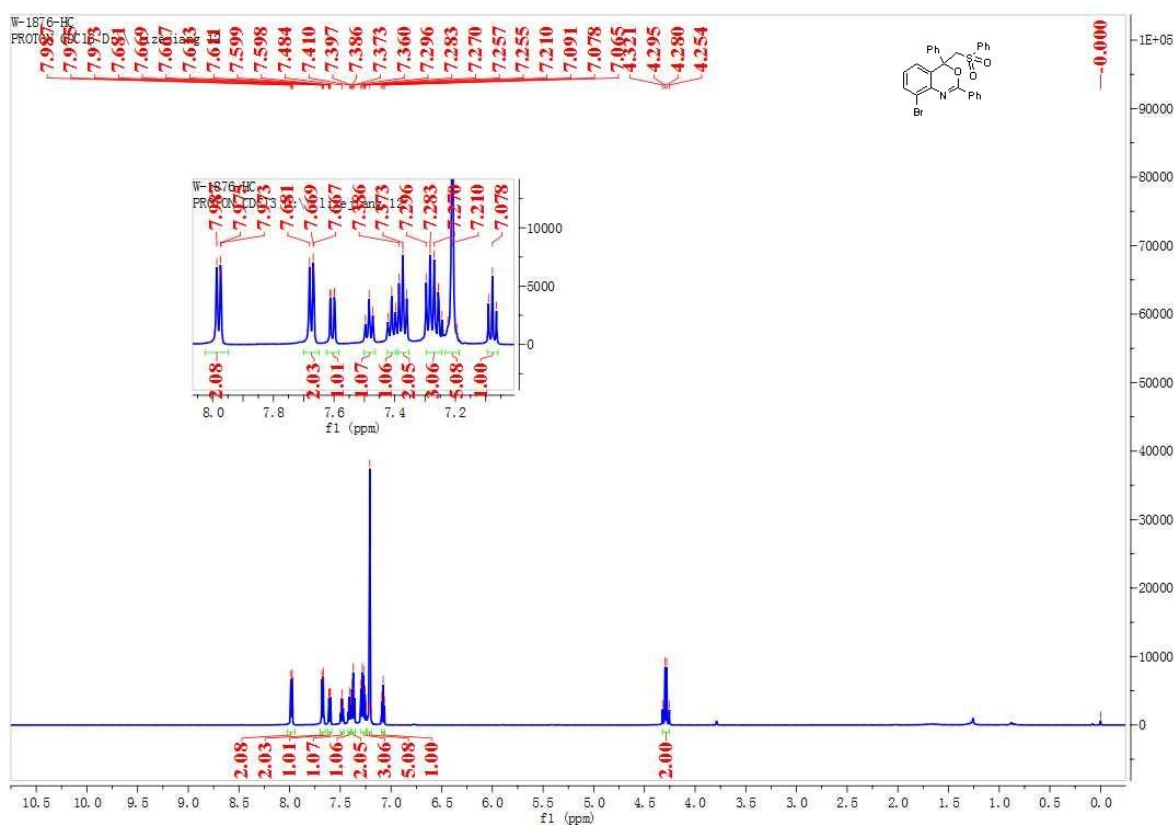
20-¹H NMR



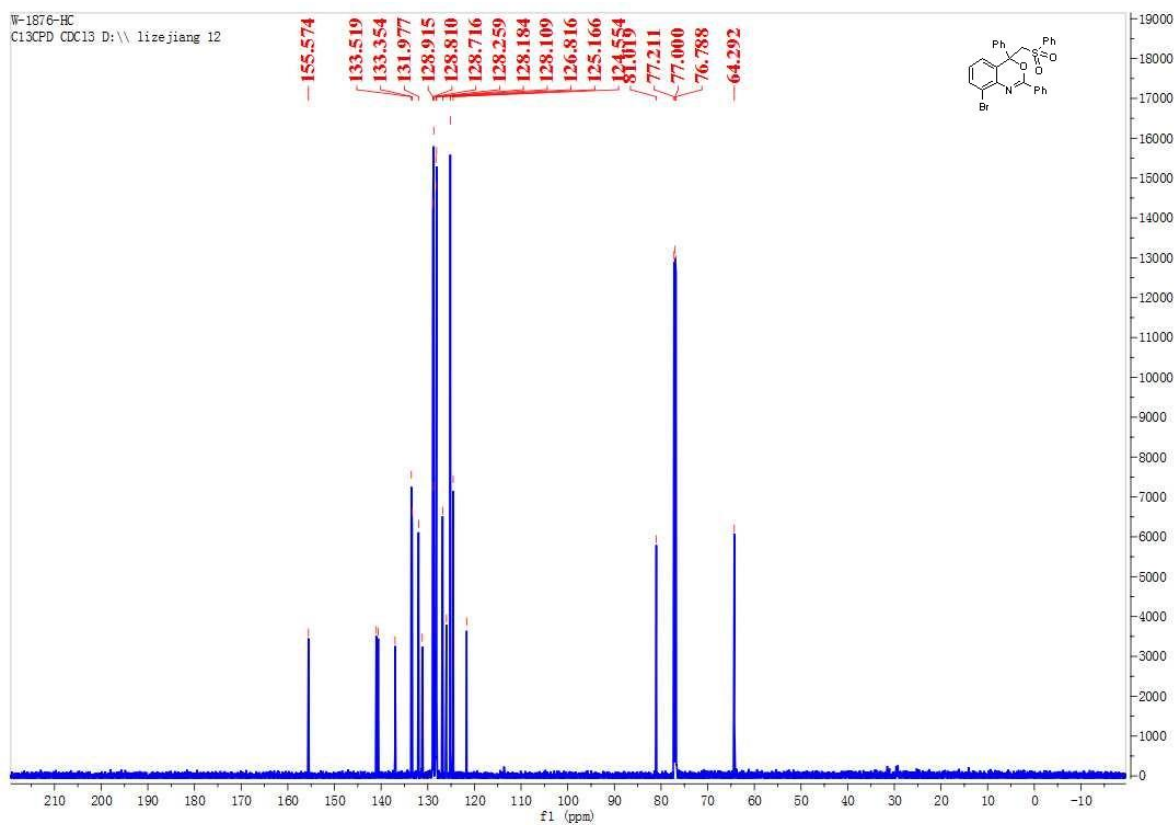
20-¹³C NMR



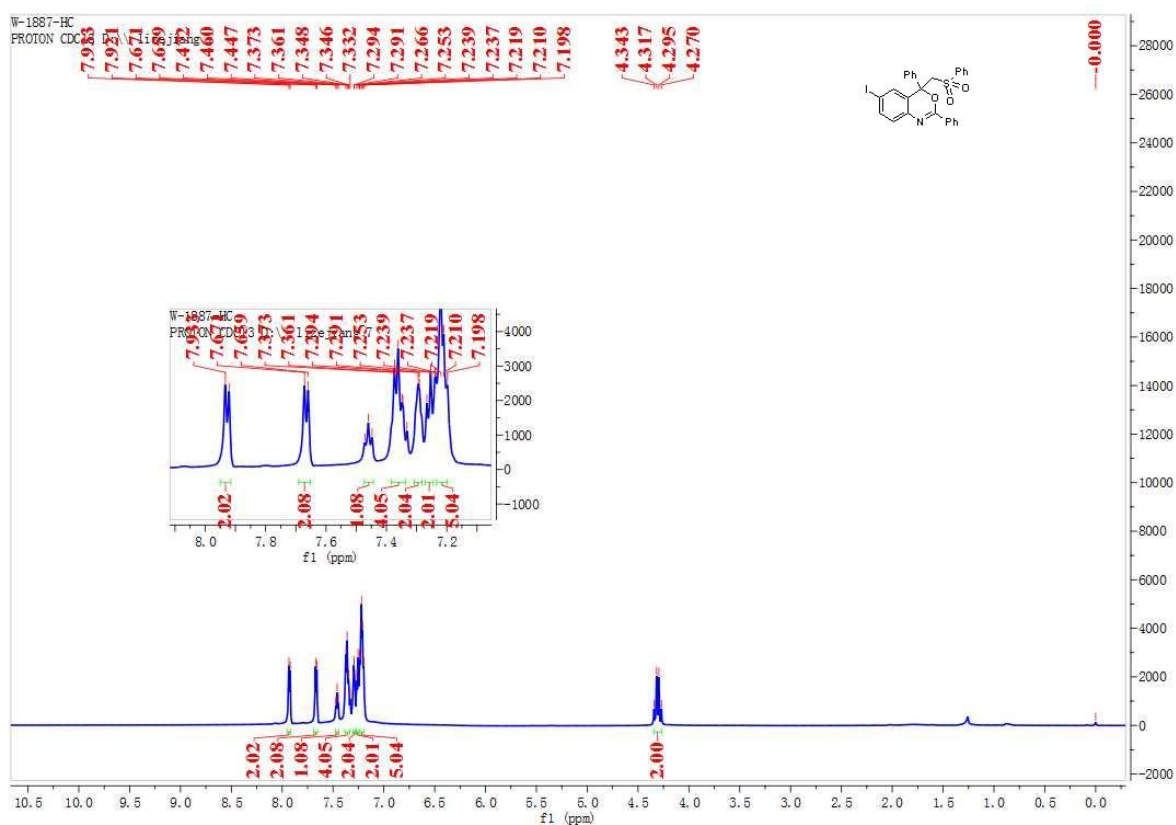
21-¹H NMR



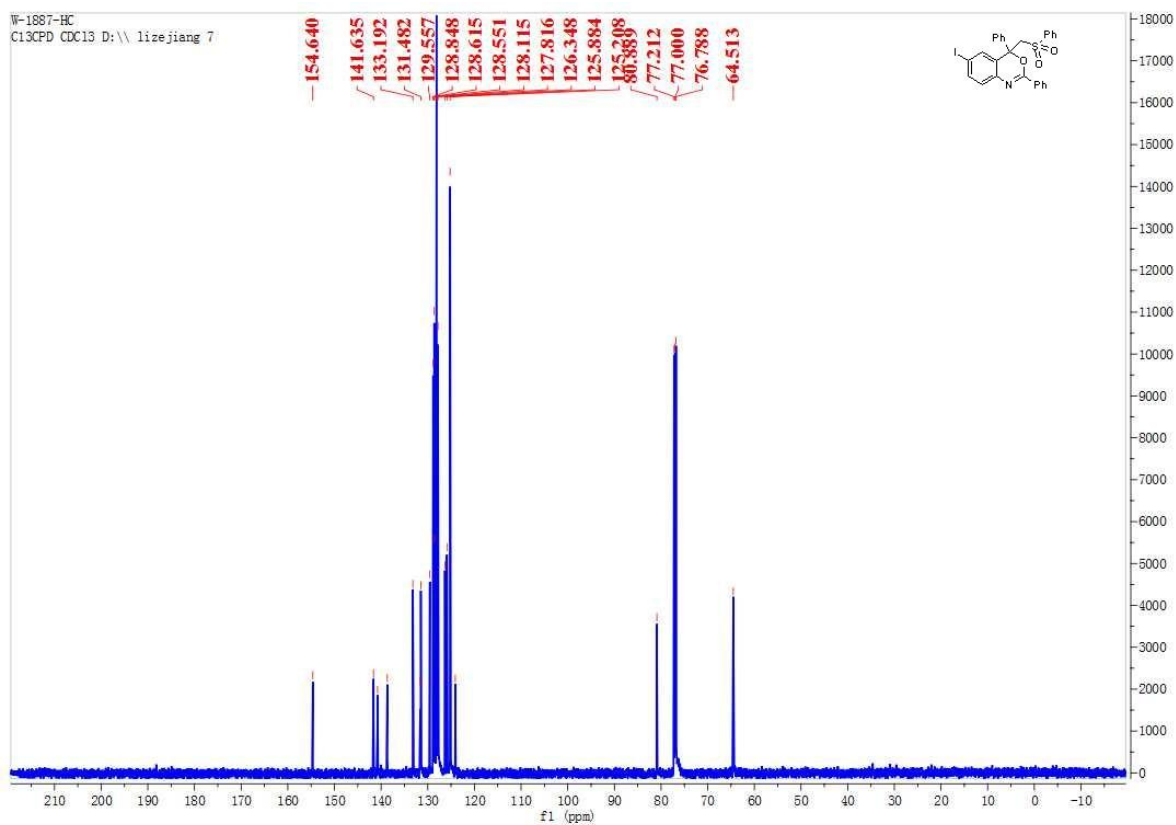
21-¹³C NMR



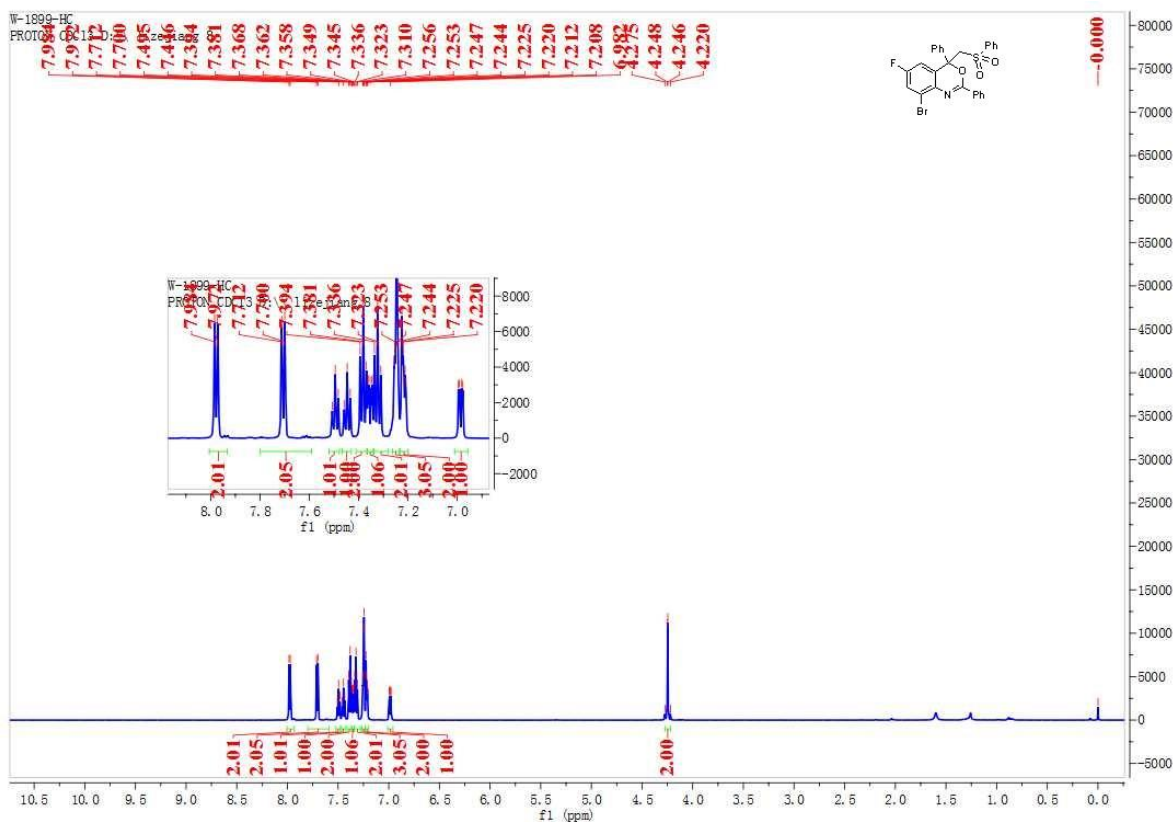
22-¹H NMR



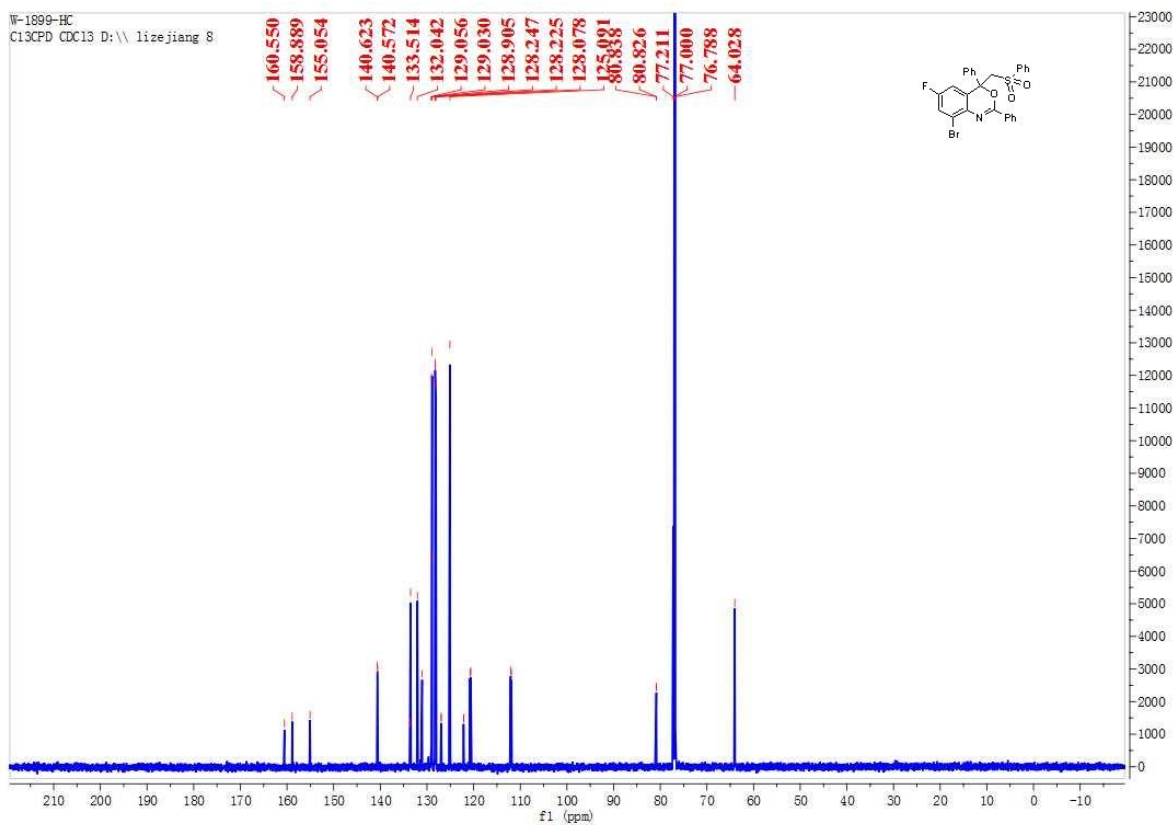
22-¹³C NMR



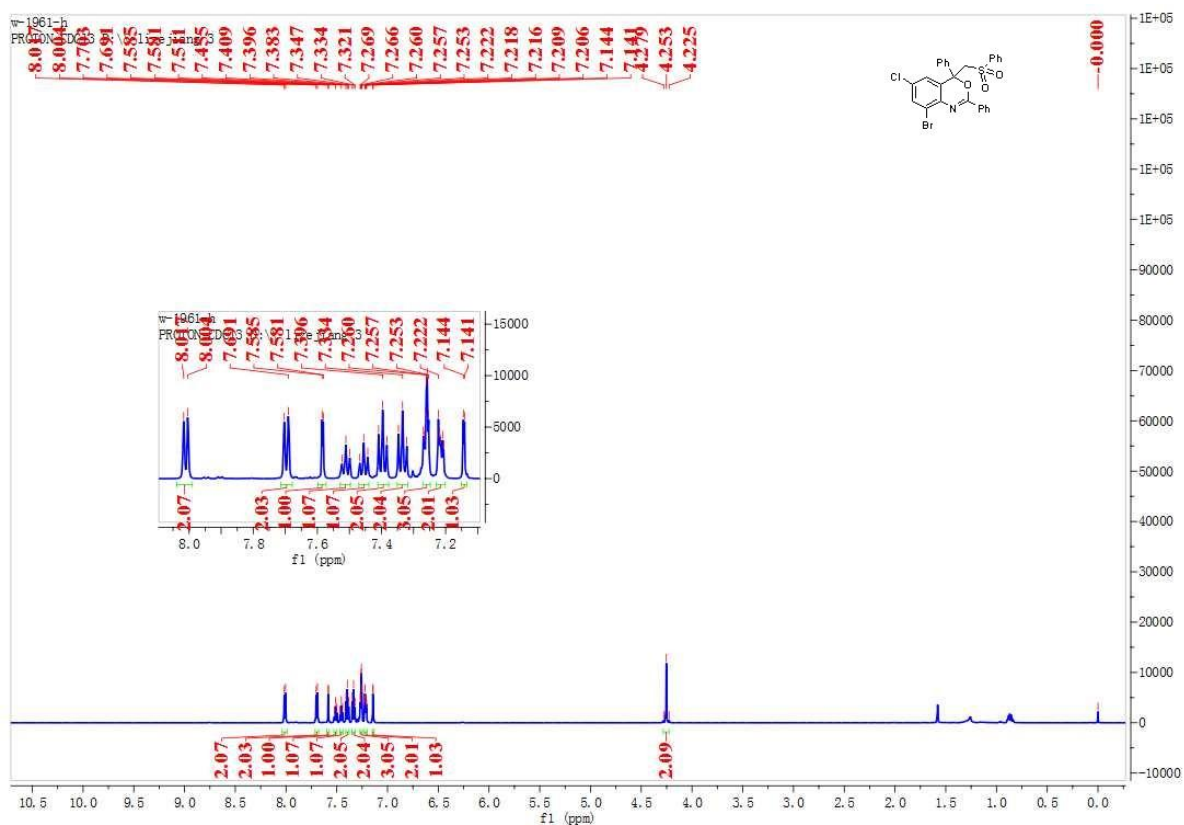
23-¹H NMR



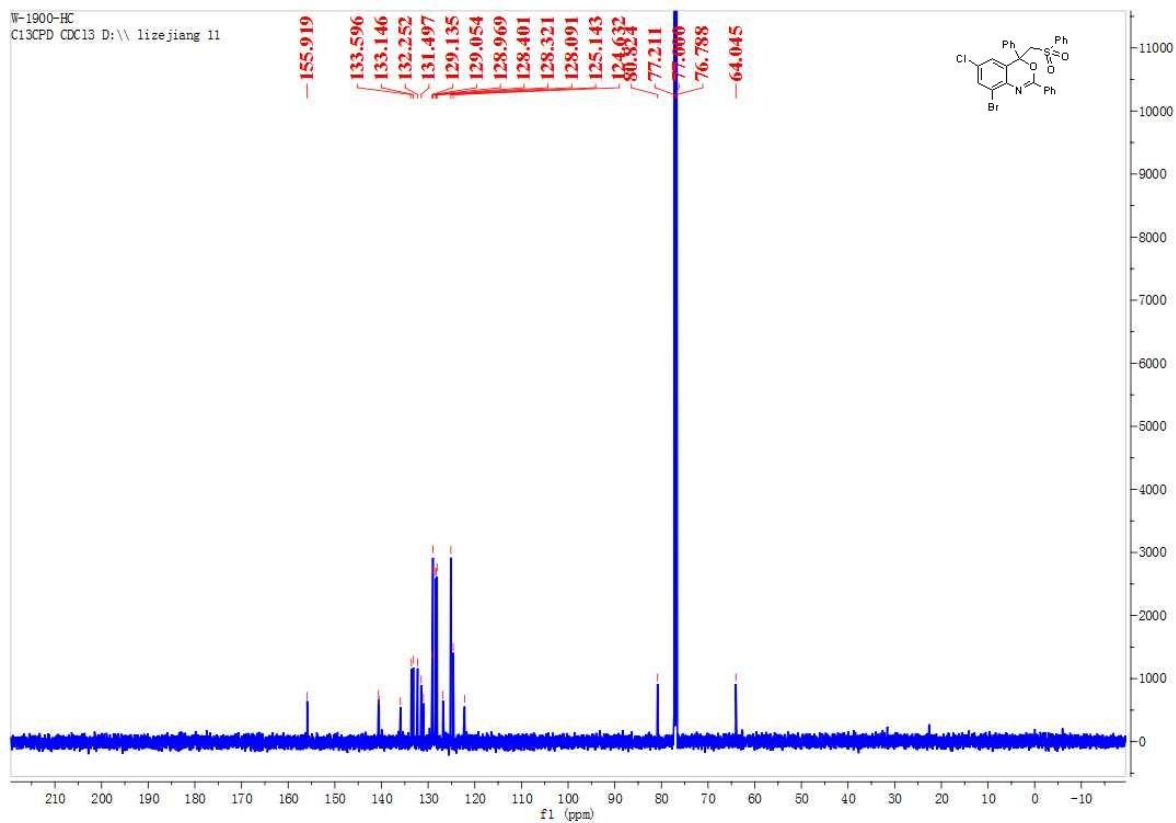
23-¹³C NMR



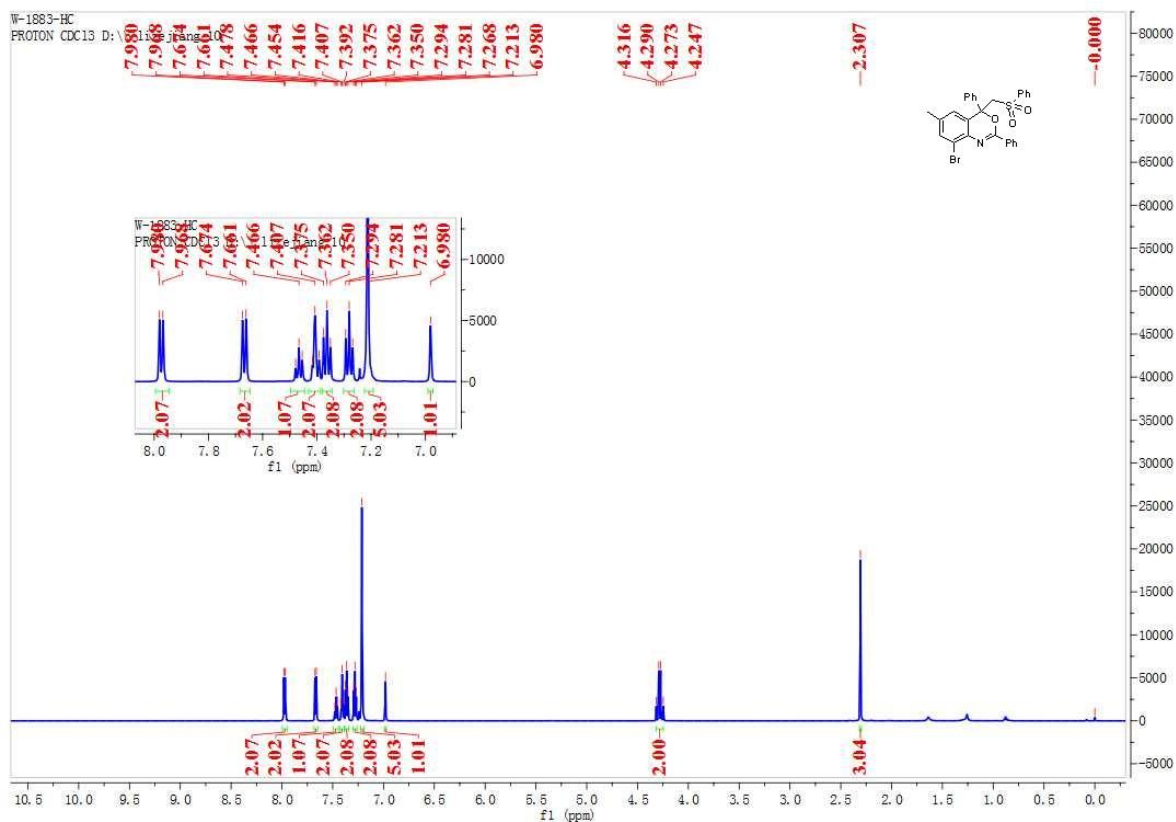
24-¹H NMR



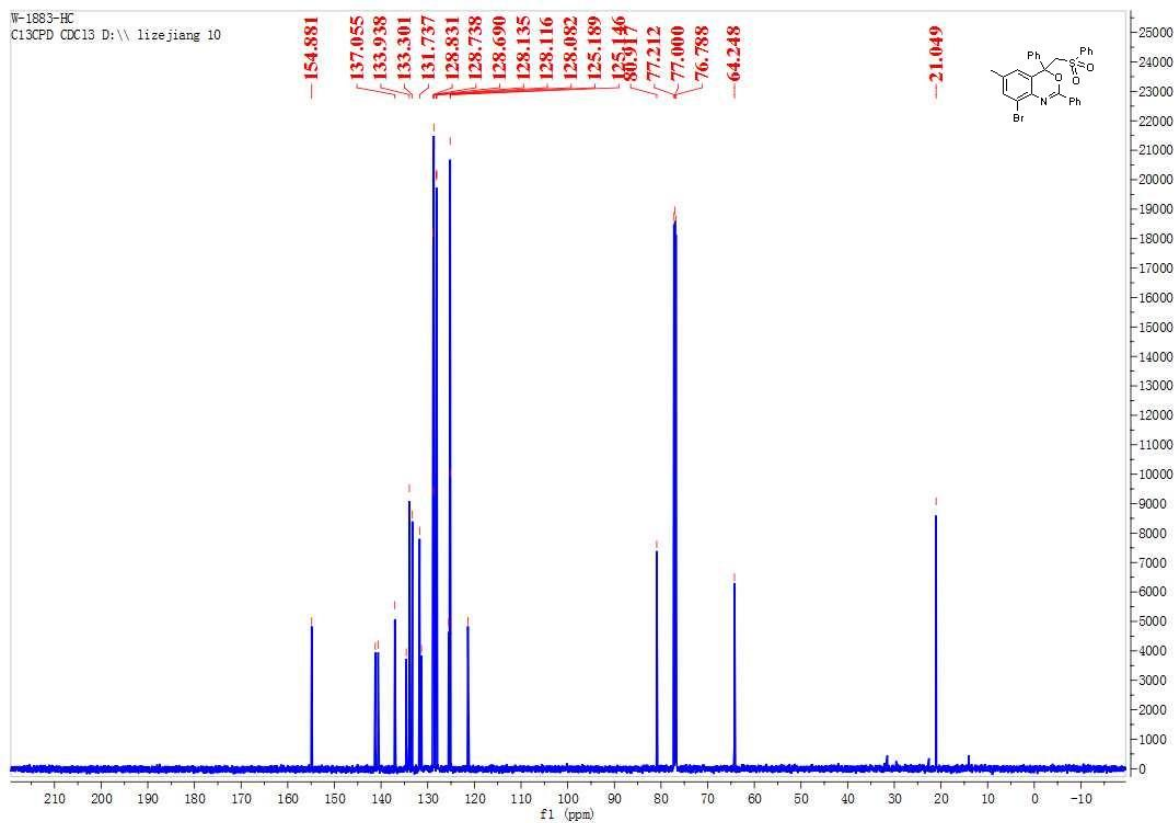
24-¹³C NMR



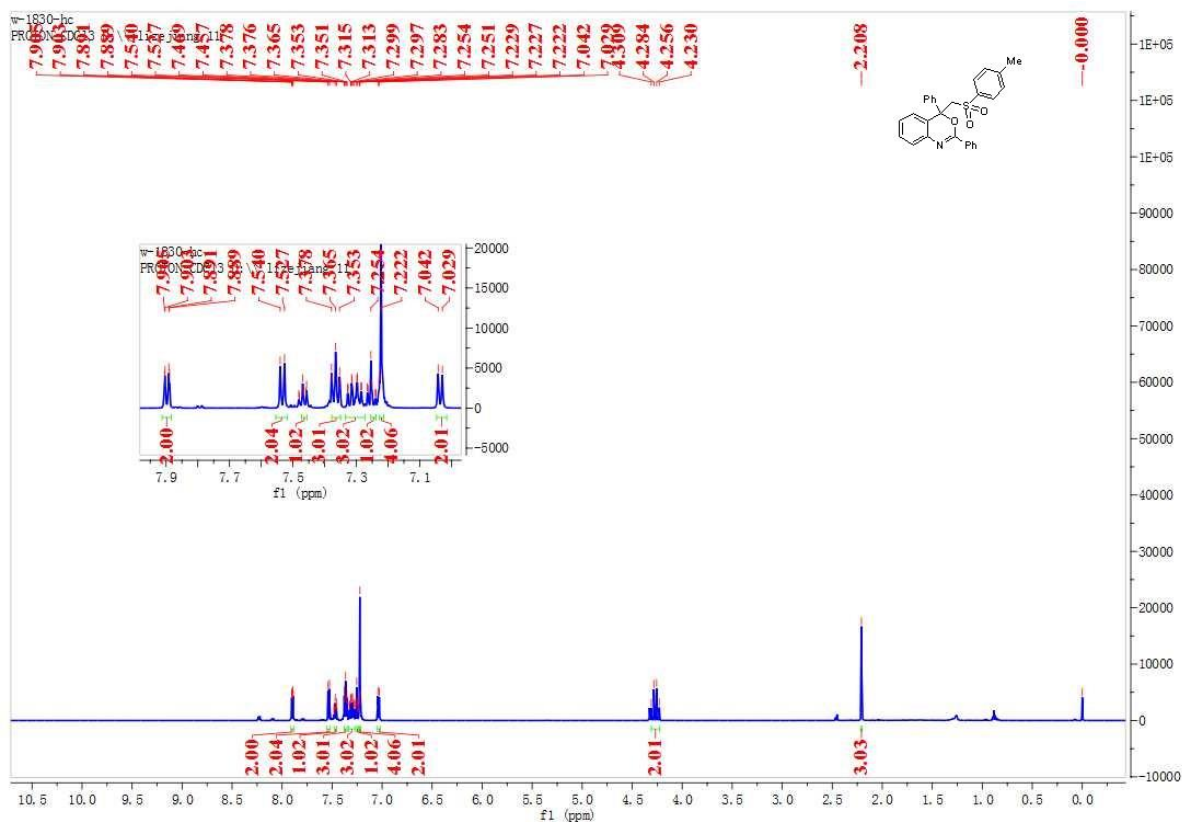
25-¹H NMR



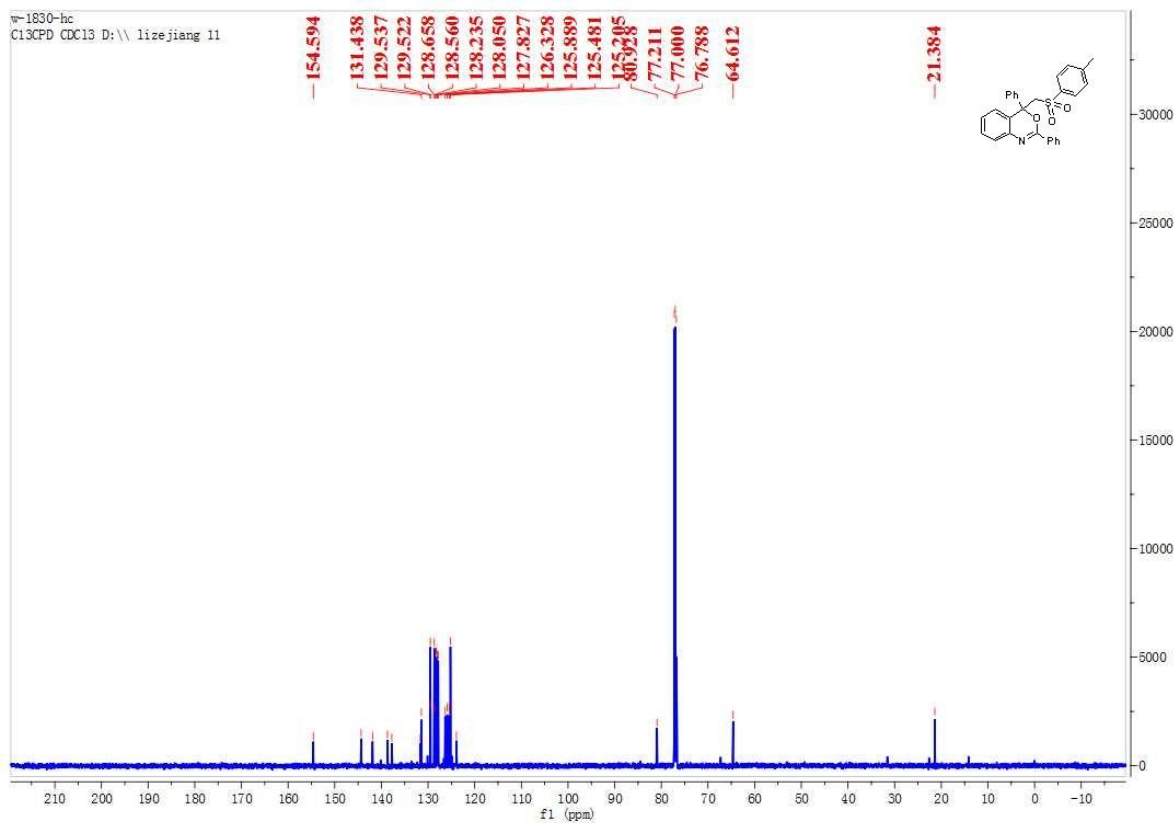
25-¹³C NMR



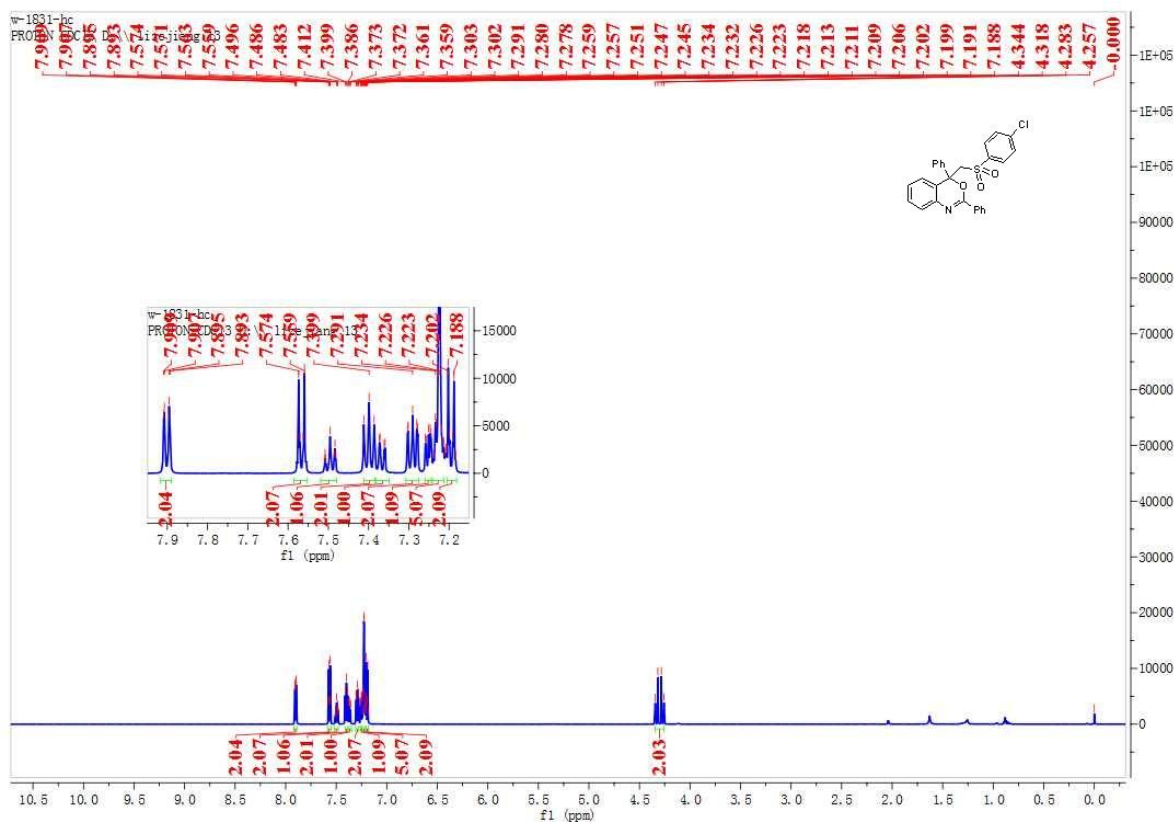
26-¹H NMR



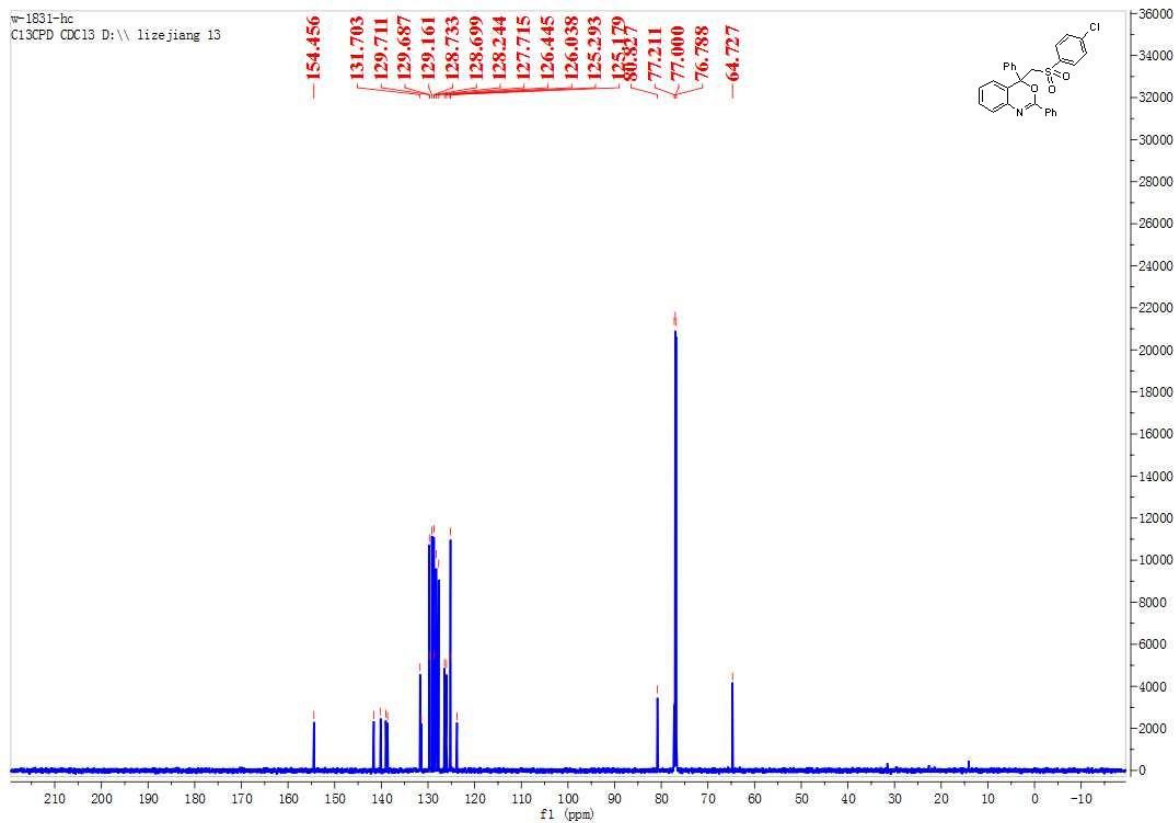
26-¹³C NMR



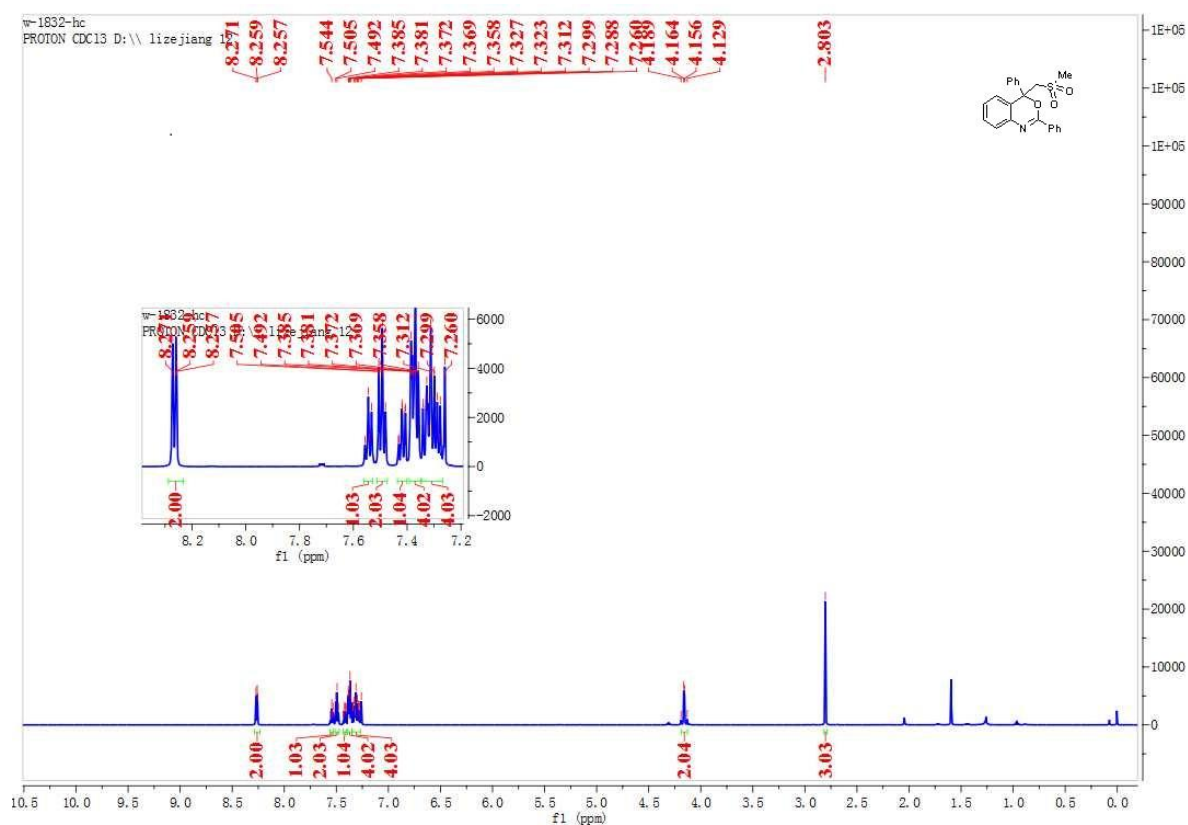
27-¹H NMR



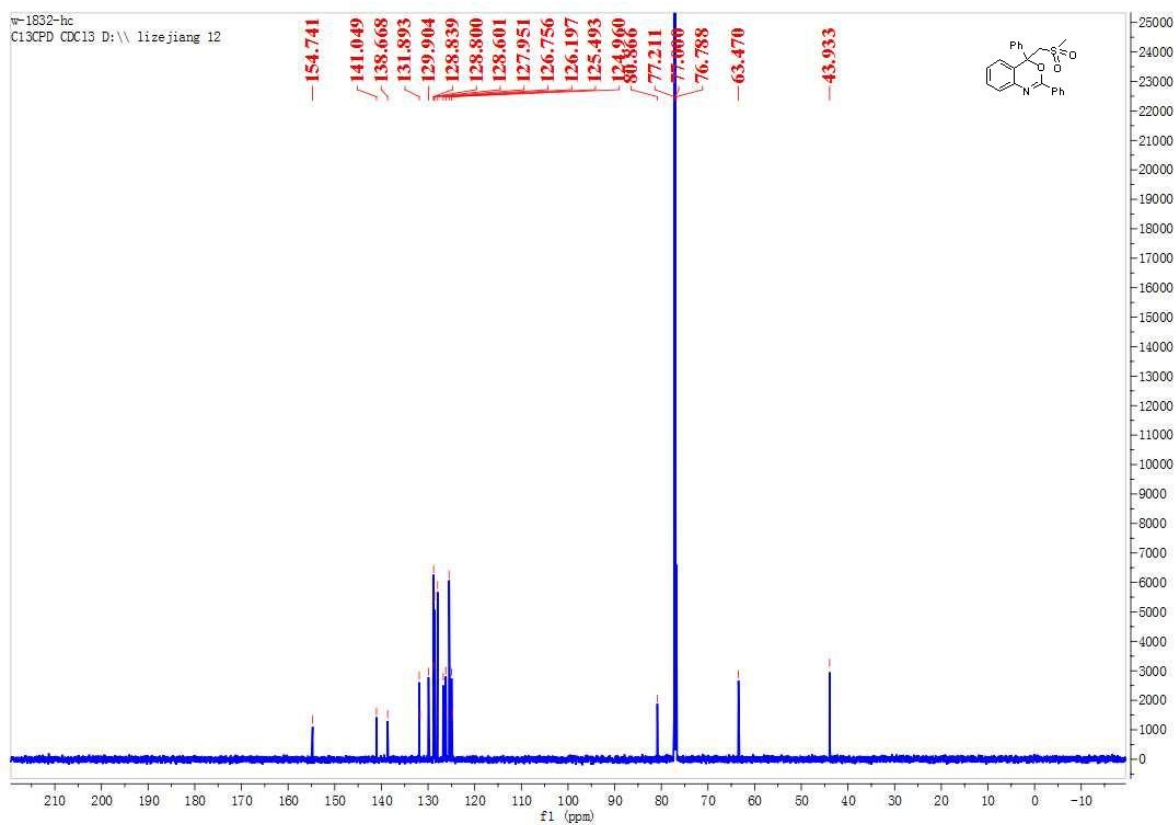
27-¹³C NMR



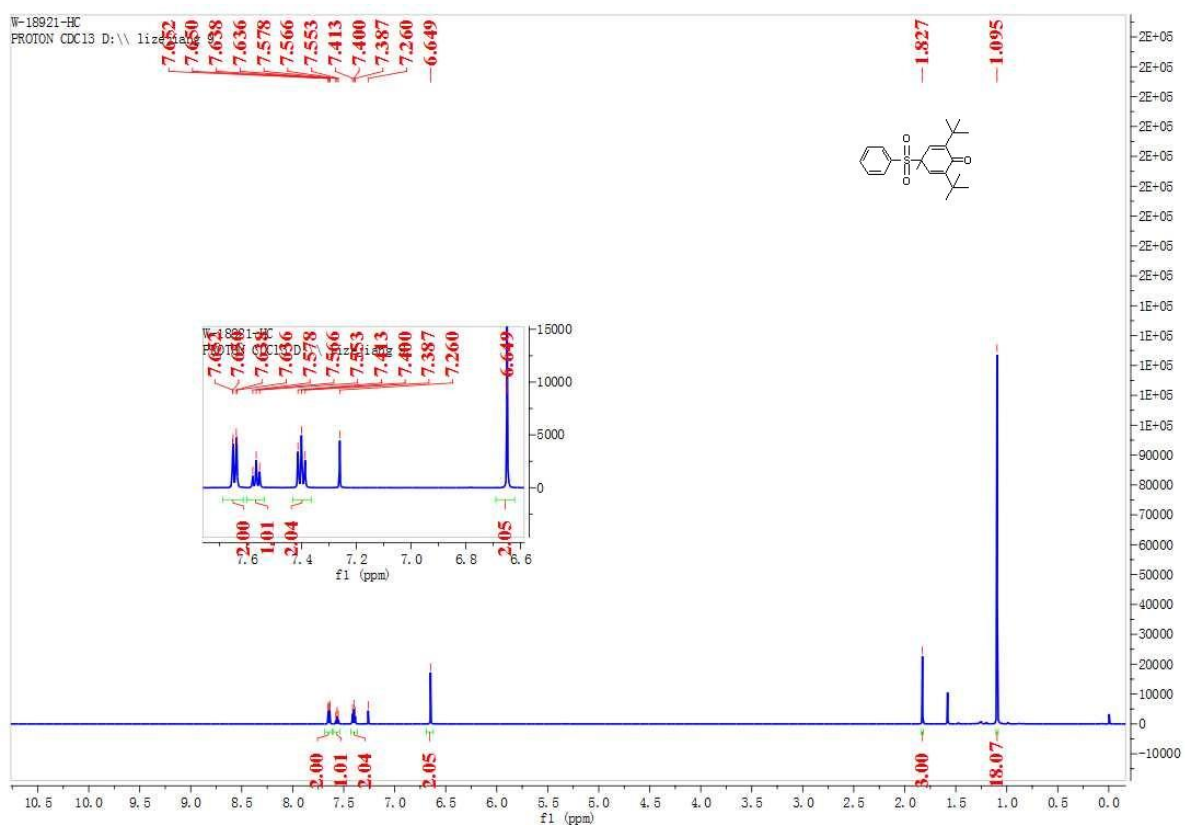
28-¹H NMR



28-¹³C NMR



29-¹H NMR



29-¹³C NMR

