Electronic Supplementary Information

4-Vinylbenzodioxinones as A New Type of Precursor for Palladium-Catalyzed (4+3) Cycloaddition of Azomethine Imines

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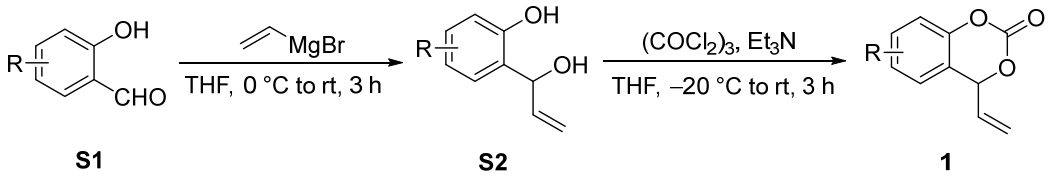
Contents

General Information

All reactions were performed under an Argon atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator or oil pump. Reactions were monitored through thin-layer chromatography (TLC) on silica gel–precoated glass plates. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker 300 MHz, 400 MHz and 500 MHz of NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; dd = doublet of doublets; td = triplet of doublets; dt = doublet of triplets; dq = doublet of quartets; ddd = doublet of doublet of doublets; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. HRMS analyses were carried out on a Thermo Q-Exactive high resolution mass spectrometer (Thermo Scientific, Waltham, MA, USA) apparatus. The type of mass analyzer used for HRMS measurement is TOF. Data were analyzed using instrument-supplied software Xcalibur Qual Browser. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 173.15 K. In addition, unless noted otherwise, in the reactions that need heating, the heat source is oil bath.

General Procedure for Preparation of Substrates

Preparation of 4-Vinylbenzodioxinones 1



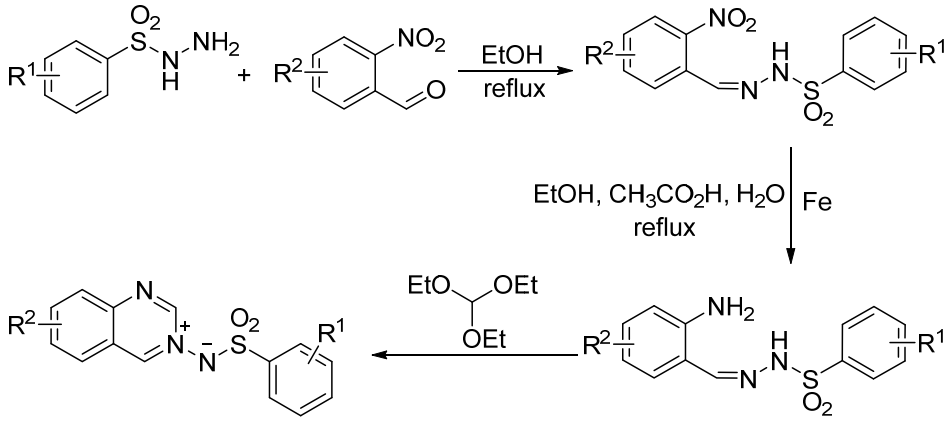
S1 **S2** **1**

To a solution of Substituted 2-hydroxybenzaldehyde **S1** (1 equiv., 8 mmol) in THF (16 mL) was added vinylmagnesium bromide (1.0 M in THF, 2.0 equiv.) at 0 ℃. The reaction mixture was stirred at room temperature under Ar atmosphere for 3 h, and then the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was transferred to the separating funnel and separated. The obtained aqueous layer was extracted with ethyl acetate (5 mL×3) for three times. The combined organic layers were washed by brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford corresponding diols **S2**.

To a solution of diol **S2** (1 equiv.) and Et_3N (3 equiv.) in THF (0.5 M) was added triphosgene (0.67 equiv, 0.5 M in THF) at -20 °C. The reaction was stirred under Ar atmosphere at room temperature for 3 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with ethyl acetate (5 mL×3) for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford corresponding product **1a–1q** in 8–76% yield. The ^1H, ^{13}C-NMR spectra of the products were in accordance with the Supporting Information

Preparation of C, N-Cyclic Aomethine Imines 2

The C, N-cyclic aomethine imines were synthesized using known literature procedures.[1]

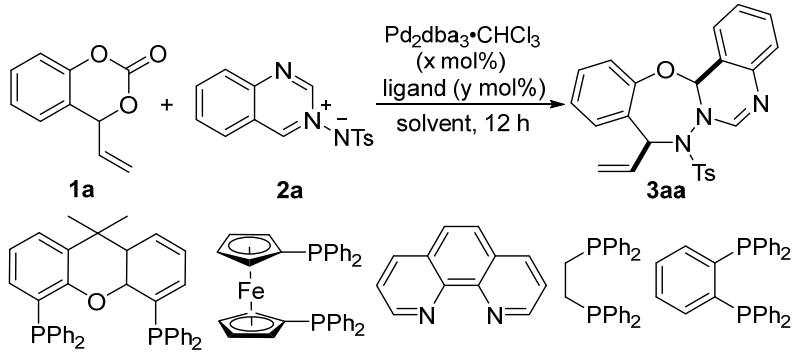


1 (a) T. Wang, J. Luo, C. Gu, R. Li, X. Tang, D. Yu, J. Li, CN 103172575A. (b) T. Wang, A.-L. Shao, H.-Y. Feng, S.-W. Yang, M. Gao, J. Tian, A.-W. Lei, *Tetrahedron*, 2015, **71**, 4473–4477. (c) X. Zhang, C. Yuan, C. Zhang, X. Gao, B. Wang, Z. Sun, Y. Xiao, H. Guo, *Tetrahedron*, 2016, **72**, 8274-8281. (d) X. Wang, Z. Li, C. Feng, Q. Zhen, M. Guo, Y. Yao, X. Zou, P Wang, Y. Hou, P. Gong, *Synlett*, 2021, **32**, 2090-2096.

Optimization of Reaction Conditions for Diastereoselective and Enantioselective (4+3) Cycloaddition

Initially, the reaction of 4-vinylbenzodioxinone **1a** and C, N-cyclic azomethine imine **2a** was chosen as the model reaction for optimization of the reaction conditions (Table S1). With the use of $Pd_2(dba)_3{\cdot}CHCl_3$ as the catalyst, various ligands were first screened. Except 1,10-phen (entry 6), other monophosphine and diphosphine ligands exhibited certain catalytic activities, leading to (4+3) cycloaddition product **3aa** in 33−91% yields with 5:1 to >20:1 dr (entries 1−5). According to the results, XantPhos was a nice choice in terms of diastereoselectivity (entry 2). Using XantPhos as the ligand, we next tried to increase yield of the reaction through screening the ratio of palladium catalyst to ligand, reaction time and solvent (entries 7−14). Reducing the amount of ligand could increase the yield to 65% and the dr value was still >20:1 (entry 8 vs entries 2 and 7). Lengthening the reaction time from 12 hours to 24 hours slightly increased the yield from 65% to 69% (entry 9). Subsequently, several solvents such as $CHCl_3$, 1,2-dichloroethane (DCE), toluene, THF and 1,4-dioxane were screened (entries 10−14). Among these solvents, DCE showed the best compatibility, resulting in the product **3aa** in 88% yield with >20:1 dr (entry 14). When the reaction was performed at 2 mmol of scale, the product still was generated in 73% yield with >20:1 dr under standard reaction conditions.

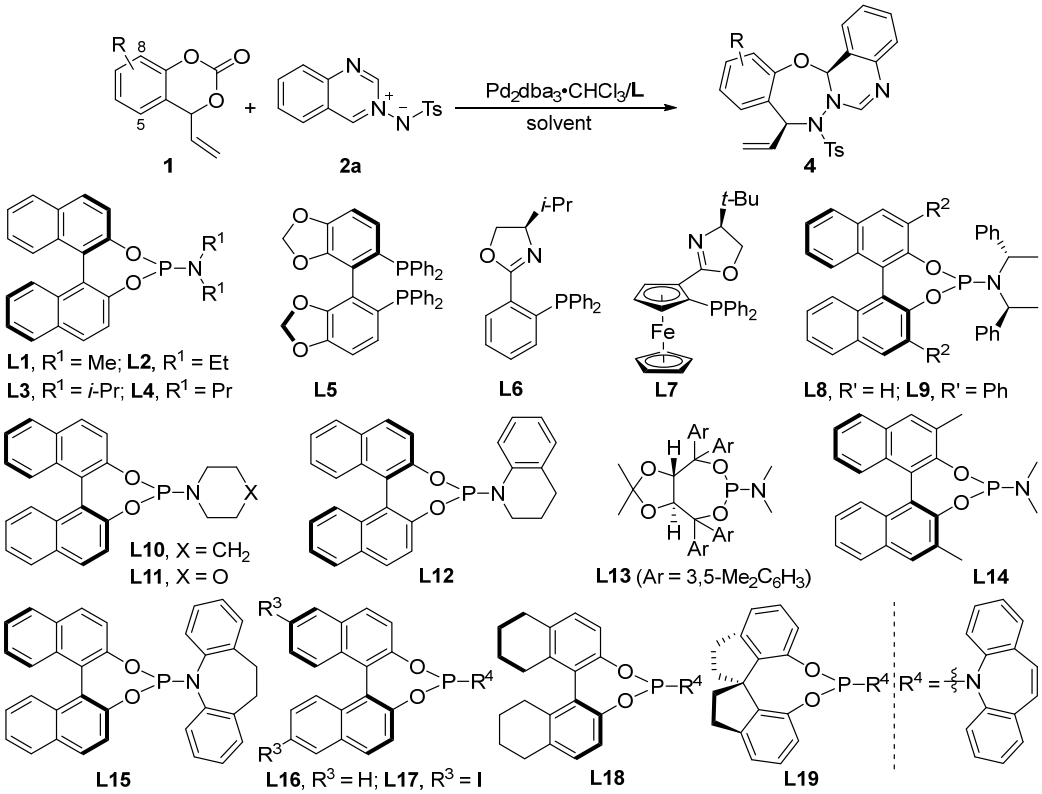
Table S1. Optimization of Reaction Conditions for Diastereoselective (4+3) Cycloaddition[a]



entry	ligand	x:y	solvent	yield (%)[b]	dr[c]
1	PPh_3	2.5:10	CH_2Cl_2	91	5:1
2	XantPhos	2.5:10	CH_2Cl_2	54	>20:1
3	dppf	2.5:10	CH_2Cl_2	33	6:1
4	dppbz	2.5:10	CH_2Cl_2	47	8:1
5	dppe	2.5:10	CH_2Cl_2	48	6:1
6	1,10-phen	2.5:10	CH_2Cl_2	trace	—
7	XantPhos	5.0:10	CH_2Cl_2	42	>20:1
8	XantPhos	2.5:5.0	CH_2Cl_2	65	>20:1
9[d]	XantPhos	2.5:5.0	CH_2Cl_2	69	>20:1
10[d]	XantPhos	2.5:5.0	toluene	38	3:1
11[d]	XantPhos	2.5:5.0	THF	56	6:1
12[d]	XantPhos	2.5:5.0	1,4-dioxane	trace	—
13[d]	XantPhos	2.5:5.0	$CHCl_3$	82	>20:1
14[d]	XantPhos	2.5:5.0	DCE	88	>20:1

[a] Unless otherwise stated, reactions of **1a** (0.12 mmol) and **2a** (0.1 mmol) were performed at 25 °C in the presence of $Pd_2dba_3{\cdot}CHCl_3$ and ligand in 1 mL of solvent for 12 h. [b] Isolated yield. [c] Determined by ^{1}HNMR analysis. [d] The reaction was carried out for 24 h.

Table S2. Exploration of Reaction Conditions for Enantioselective (4+3) Cycloaddition[a]

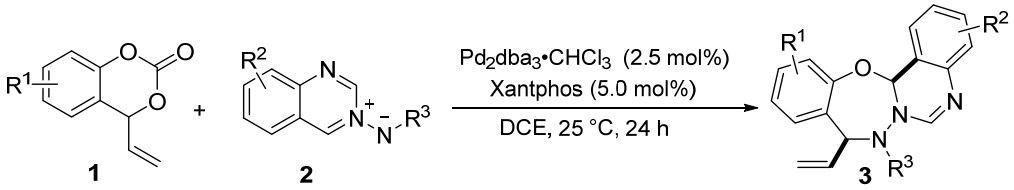


entry	R in **1**	ligand	solvent	T/°C	*t*/h	**3aa** yield (%)[b]	ee (%)[c]
1	H	**L1**	CH_2Cl_2	25	12	88	5
2	H	**L2**	CH_2Cl_2	25	12	56	20
3	H	**L3**	CH_2Cl_2	25	12	46	21
4	H	**L4**	CH_2Cl_2	25	12	32	–10
5	H	**L5**	CH_2Cl_2	25	12	trace	/
6	H	**L6**	CH_2Cl_2	25	12	trace	/
7	H	**L7**	CH_2Cl_2	25	12	trace	/
8	H	**L8**	CH_2Cl_2	25	12	43	20
9	H	**L9**	CH_2Cl_2	25	12	18	–11
10	H	**L10**	CH_2Cl_2	25	12	31	7
11	H	**L11**	CH_2Cl_2	25	12	25	8
12	H	**L12**	CH_2Cl_2	25	12	35	–19
13	H	**L13**	CH_2Cl_2	25	12	46	4
14	H	**L14**	CH_2Cl_2	25	12	35	–11
15	H	**L15**	CH_2Cl_2	25	12	76	58
16	H	**L16**	CH_2Cl_2	25	12	trace	/
17	H	**L17**	CH_2Cl_2	25	12	83	59
18	H	**L18**	CH_2Cl_2	25	12	40	33
19	H	**L19**	CH_2Cl_2	25	12	trace	/
20	H	**L17**	DCE	25	12	83	67
21	H	**L17**	$CHCl_3$	25	12	95	36
22	H	**L17**	toluene	25	12	messy	/
23	H	**L17**	THF	25	12	messy	/
24	H	**L17**	DCE	0	24	85	73
25	8-OEt	**L17**	DCE	0	24	90	92
26	8-OEt	**L17**	DCE	–20	24	98	94

[a] Unless noted otherwise, the reaction of **1** (0.12 mmol), **2a** (0.1 mmol), Pd_2dba_3•$CHCl_3$ (5 mol%) and ligand (10 mol% for phosphoramidite, 5.0 mol% for diphosphines) was performed in 1.0 mL of solvent under indicated reaction conditions. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

General Procedure for (4+3) Cycloaddition Reaction

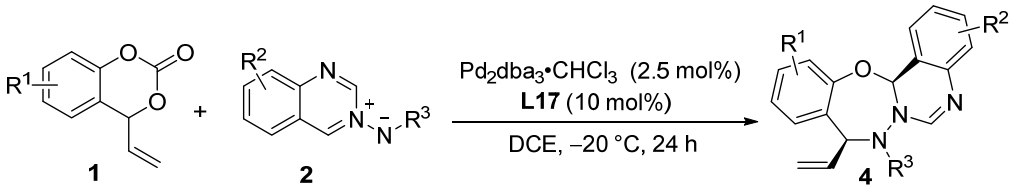
General Procedure for Diastereoselective (4+3) Cycloaddition Reactions



1 2 3

An oven-dried 10 mL of Schlenk tube was charged with 4-vinylbenzodioxinones **1** (0.12 mmol), azomethine imines **2** (0.1 mmol), Pd_2dba_3•$CHCl_3$ (0.025 equiv., 2.6 mg), Xantphos (0.05 equiv., 2.9 mg) in 1 mL of DCE under Ar atmosphere at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **3** (petroleum ether/EtOAc as the eluent).

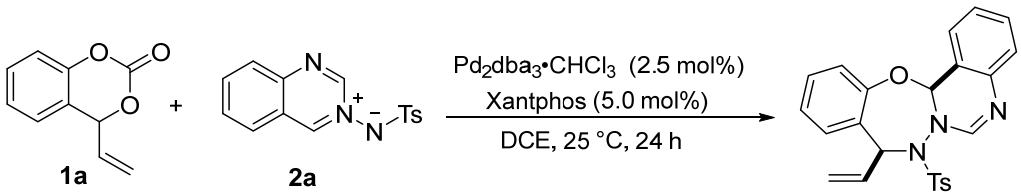
General Procedure for enantioselective (4+3) Cycloaddition Reactions



1 2 4

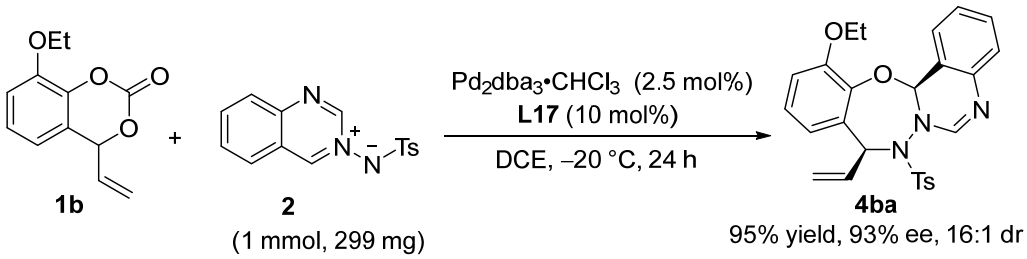
An oven-dried 10 mL of Schlenk tube was charged with 4-vinylbenzodioxinones **1** (0.12 mmol), azomethine imines **2** (0.1 mmol), Pd_2dba_3•$CHCl_3$ (0.025 equiv, 2.6 mg), **L17** (0.1 equiv., 7.6 mg) in 1 mL of DCE under Ar atmosphere at –20 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **4** (petroleum ether/EtOAc as the eluent).

The Scaled-up Reaction



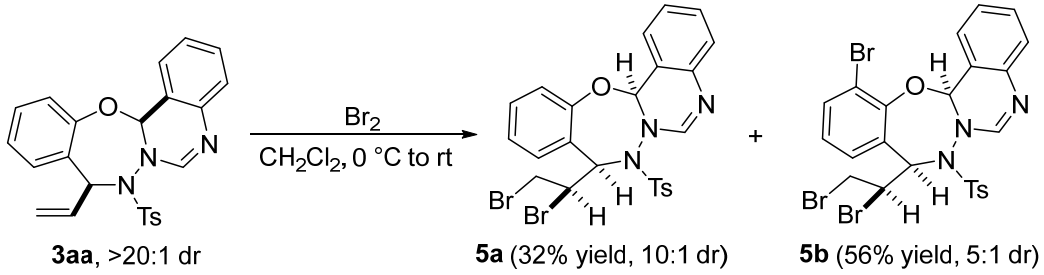
1a **2a** (2 mmol, 598 mg) **3aa**, 73% yield, >20:1 dr

An oven-dried 100 mL of Schlenk tube was charged with 4-vinylbenzodioxinone **1a** (423 mg 2.4 mmol), azomethine imines **2a** (598 mg, 2.0 mmol), Pd_2dba_3•$CHCl_3$ (0.025 equiv, 52 mg), Xantphos (0.05 equiv, 58 mg) in 20 mL of DCE under Ar atmosphere at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (petroleum ether/EtOAc as the eluent) to afford the product **3aa** (630 mg, 73% yield, >20:1 dr).

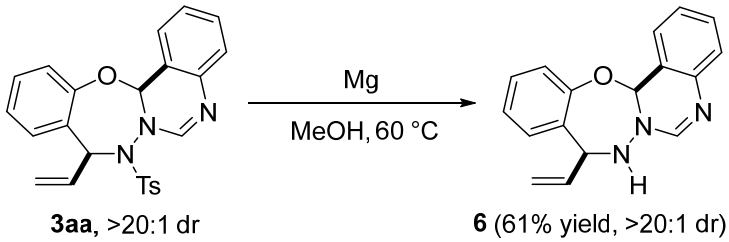


An oven-dried 100 mL of Schlenk tube was charged with 4-vinylbenzodioxinones **1b** (264 mg, 1.2 mmol), azomethine imine **2a** (299 mg, 1.0 mmol), Pd_2dba_3•$CHCl_3$ (0.025 equiv., 26 mg), **L17** (0.1 equiv., 76 mg) in 10 mL of DCE under Ar atmosphere at –20 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (petroleum ether/EtOAc as the eluent) to afford the product **4ba** (452 mg, 95% yield, 93% ee, 16:1 dr).

Further Transformation of the Product 3aa



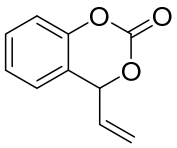
An oven-dried 10 mL of Schlenk tube was charged with the product **3aa** (43.1 mg, 0.1 mmol), at 0 ℃, a solution of Br_2 in DCM (0.6 M in DCM, 5.0 equiv) was added. The reaction was stirred at ambient temperature for 2 h. Upon full conversion, the mixture was concentrated and then purified through flash column chromatography (20% EtOAc/PE) to afford the corresponding product **5a** as a white solid (18.9 mg, 32% yield, 10:1 dr) and **5b** as a white solid (37.4 mg, 56% yield, 5:1 dr).



An oven-dried 10 mL of Schlenk tube was charged with the product **3aa** (43.1 mg, 0.1 mmol, > 20:1 dr), Mg (240 mg, 10 mmol, 200-300 mesh), and anhydrous MeOH (3 mL) under argon atmosphere. The resulting solution was heated at 60 ℃ for 1 h. Then NH_4Cl (2 mL) was added to the reaction mixture to quench excess magnesium powder. The aqueous phase was extracted with ethyl acetate (3×3 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Then the mixture was purified through flash column chromatography (74% EtOAc/PE) to afford the corresponding product **6** as a light yellow solid (16.9 mg, 61% yield, > 20:1 dr).

Characterization Data for New Substrates and All Products

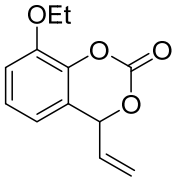
4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1a)



1a

Prepared according to the general procedure as described above in 53% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (td, *J* = 7.8, 1.6 Hz, 1H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.05 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.89 (d, *J* = 6.6 Hz, 1H), 5.49 (d, *J* = 10.3 Hz, 1H), 5.42 (dd, *J* = 17.0, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 146.5, 133.1, 130.2, 125.3, 125.1, 121.0, 119.8, 116.3, 80.2; IR (thin film) ν_{max} 1766, 1489, 1458, 1274, 1261, 1216, 1153, 1032, 942, 751, 468 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_9O_3^+$ $[M + H]^+$ 177.0546, found 177.0547.

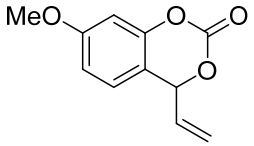
8-ethoxy-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1b)



1b

Prepared according to the general procedure as described above in 56% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a red solid. Melting point: 46–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.69 (d, *J* = 7.6 Hz,1H), 6.03 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.84 (d, *J* = 6.5 Hz, 1H), 5.46 (d, *J* = 10.3 Hz, 1H), 5.41 (dd, *J* = 17.0, 1.2 Hz, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.60, 146.42, 138.23, 133.13, 125.37, 120.98, 120.70, 116.02, 113.90, 80.13, 64.92, 14.70; IR (thin film) ν_{max} 1769, 1489, 1473, 1279, 1221, 1151, 1113, 1081, 1022, 944, 749 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{13}O_4^+$ $[M + H]^+$ 221.0808, found 221.0805.

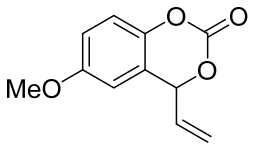
7-methoxy-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1c)



1c

Prepared according to the general procedure as described above in 76% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a brown solid. Melting point: 35–36 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.56 (dd, *J* = 2.9, 0.8 Hz, 1H), 5.96 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.76 (d, *J* = 6.6 Hz, 1H), 5.42 (dt, *J* = 10.2, 0.8 Hz, 1H), 5.36 (dt, *J* = 16.9, 0.9 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 145.7, 141.5, 131.9, 120.0, 119.6, 116.2, 114.3, 108.9, 79.2, 54.8; IR (thin film) ν_{max} 1770, 1497, 1433, 1259, 1225, 1163, 1034, 817, 764 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{11}O_4^+$ $[M + H]^+$ 207.0652, found 207.0652.

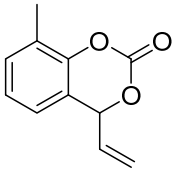
6-methoxy-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1d)



1d

Prepared according to the general procedure as described above in 68% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a brown solid. Melting point: 33–34 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.9 Hz, 0H), 6.89 (dd, *J* = 9.0, 2.9 Hz, 0H), 6.64 (d, *J* = 2.9 Hz, 0H), 6.04 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 0H), 5.83 (d, *J* = 6.6 Hz, 0H), 5.49 (d, *J* = 10.3 Hz, 0H), 5.44 (d, *J* = 17.2 Hz, 0H), 3.80 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 145.3, 143.5, 137.2, 134.6, 131.7, 130.6, 128.9, 128.8, 128.0, 127.6, 127.6, 127.5, 127.5, 123.5, 121.7, 118.3, 97.6, 83.8; IR (thin film) ν_{max} 1768, 1496, 1432, 1259, 1224, 1162, 1033, 817, 765 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{11}O_4^+$ $[M + H]^+$ 207.0652, found 207.0653.

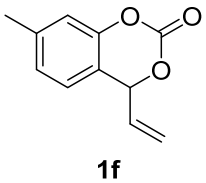
8-methyl-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1e)



1e

Prepared according to the general procedure as described above in 27% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 78–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.85 (m, 1H), 5.97 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.77 (d, *J* = 6.5 Hz, 1H), 5.39 (dt, *J* = 10.4, 0.9 Hz, 1H), 5.33 (dt, *J* = 17.0, 0.9 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 145.8, 132.2, 130.6, 125.0, 123.8, 121.4, 119.6, 118.6, 79.1, 14.0; IR (thin film) ν_{max} 1770, 1473, 1219, 1162, 1089, 1027, 943, 790, 755 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{11}O_3^+$ $[M + H]^+$ 191.0703, found 191.0702.

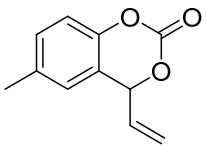
7-methyl-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1f)



1f

Prepared according to the general procedure as described above in 20% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 – 6.90 (m, 2H), 6.85 (s, 1H), 6.06 – 5.88 (m, 1H), 5.77 (d, *J* = 6.6 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 5.33 (d, *J* = 17.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 146.7, 140.9, 133.3, 126.0, 124.7, 120.7, 116.7, 116.6, 80.3, 21.3; IR (thin film) ν_{max} 1780, 1415, 1259, 1155, 1016, 984, 807, 764, 750 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{11}O_3^+$ $[M + H]^+$ 191.0703, found 191.0699.

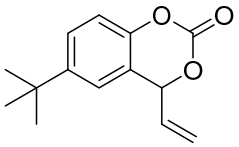
6-methyl-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1g)



1g

Prepared according to the general procedure as described above in 40% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 44–45 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 5.93 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.74 (d, *J* = 6.7 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 145.6, 134.2, 132.2, 129.6, 124.3, 119.7, 118.4, 114.9, 79.3, 19.8; IR (thin film) ν_{max} 1769, 1496, 1227, 1167, 1152, 1126, 1027, 815, 764 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{10}O_3^+$ $[M + H]^+$ 191.0703, found 191.0702.

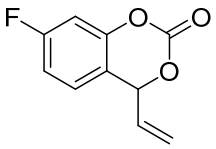
6-(tert-butyl)-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1h)



1h

Prepared according to the general procedure as described above in 68% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 5.97 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.79 (d, *J* = 6.6 Hz, 1H), 5.40 (d, *J* = 10.3 Hz, 1H), 5.35 (dd, *J* = 17.0, 1.1 Hz, 1H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 146.8, 146.6, 133.3, 127.2, 121.7, 120.8, 119.1, 115.7, 80.6, 34.6, 31.4; IR (thin film) ν_{max} 2961, 1771, 1498, 1273, 1235, 1158, 1131, 1025, 823, 763 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{17}O_3^+$ $[M + H]^+$ 233.1172, found 233.1171.

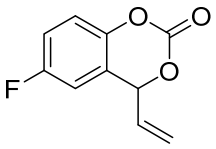
7-fluoro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1i)



1i

Prepared according to the general procedure as described above in 21% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.5, 5.7 Hz, 1H), 6.88 (td, *J* = 8.4, 2.5 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.96 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.79 (d, *J* = 6.7 Hz, 1H), 5.44 (d, *J* = 10.3 Hz, 1H), 5.36 (dd, *J* = 17.1, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (C-F, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 149.7 (C-F, $^{2}J_{C\text{-}F}$ = 12.4 Hz), 145.8, 132.8, 126.4 (C-F, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 121.4, 115.8 (C-F, $^{1}J_{C\text{-}F}$ = 3.4 Hz), 112.6 (C-F, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 104.5 (C-F, $^{2}J_{C\text{-}F}$ = 26.0 Hz)., 80.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.28; IR (thin film) ν_{max} 1599, 1497, 1274, 1261, 1152, 1099, 972, 835, 764, 749 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8FO_3^+$ $[M + H]^+$ 195.0452, found 195.0451.

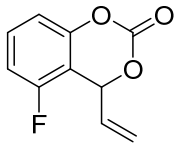
6-fluoro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1j)



1j

Prepared according to the general procedure as described above in 26% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 37–38 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.78 (d, *J* = 6.8 Hz, 1H), 5.47 (d, *J* = 10.3 Hz, 1H), 5.39 (d, *J* = 17.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4 (C-F, $^{1}J_{C\text{-}F}$ = 245.8 Hz), 146.1, 144.8 (C-F, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 132.4, 121.7, 121.4 (C-F, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 117.9 (C-F, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 117.1 (C-F, $^{2}J_{C\text{-}F}$ = 23.8 Hz), 112.0 (C-F, $^{2}J_{C\text{-}F}$ = 25.5 Hz), 79.8 (C-F, $^{3}J_{C\text{-}F}$ = 2.3 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.78; IR (thin film) ν_{max} 1770, 1482, 1259, 1213, 1158, 1109, 1030, 820, 761 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8FO_3^+$ $[M + H]^+$ 195.0452, found 195.0453.

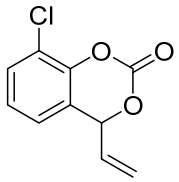
5-fluoro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1k)



1k

Prepared according to the general procedure as described above in 35% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (td, *J* = 8.4, 6.1 Hz, 1H), 6.87 (dd, *J* = 18.4, 8.8 Hz, 2H), 6.11 – 5.85 (m, 2H), 5.35 – 5.28 (m, 1H), 5.29 – 5.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7 (C-F, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 149.5 (C-F, $^{3}J_{C\text{-}F}$ 6.0 Hz), 145.6, 132.5, 131.0 (C-F, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 119.5, 112.2 (C-F, $^{2}J_{C\text{-}F}$ = 14.8 Hz), 112.1 (C-F, $^{3}J_{C\text{-}F}$ = 1.2 Hz), 108.3 (C-F, $^{2}J_{C\text{-}F}$ = 20.8 Hz), 75.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.15; IR (thin film) ν_{max} 1777, 1604, 1468, 1241, 1148, 1046, 942, 787, 765, 747 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8FO_3^+$ $[M + H]^+$ 195.0452, found 195.0452.

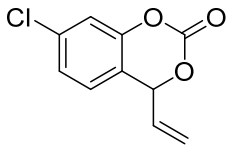
8-chloro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1l)



1l

Prepared according to the general procedure as described above in 10% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 46–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.99 (dt, *J* = 7.7, 1.2 Hz, 1H), 5.96 (ddd, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.81 (d, *J* = 6.5 Hz, 1H), 5.44 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.37 (dd, *J* = 17.0, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.46, 144.9, 132.5, 130.9, 125.7, 123.4, 121.7, 121.6, 121.5, 80.1; IR (thin film) ν_{max} 1774, 1457, 1236, 1162, 1140, 1028, 986, 785, 747 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8ClO_3^+$ $[M + H]^+$ 211.0156, found 211.0155.

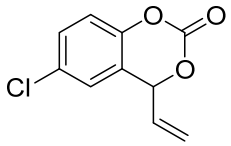
7-chloro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1m)



1m

Prepared according to the general procedure as described above in 19% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.79 (d, *J* = 6.7 Hz, 1H), 5.44 (d, *J* = 10.3 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 145.7, 135.8, 132.6, 126.1, 125.6, 121.6, 118.4, 116.9, 80.0; IR (thin film) ν_{max} 1594, 1484, 1408, 1263, 1229, 982, 934, 900, 734, 703 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8ClO_3^+$ $[M + H]^+$ 211.0156, found 211.0156.

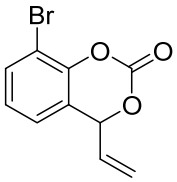
6-chloro-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1n)



1n

Prepared according to the general procedure as described above in 34% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 6.97 (m, 2H), 6.80 (dd, *J* = 7.6, 2.5 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.79 (d, *J* = 6.7 Hz, 1H), 5.46 (d, *J* = 10.3 Hz, 1H), 5.39 (dd, *J* = 17.0, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 145.8, 133.2, 132.33, 128.0, 121.9, 121.8, 118.1, 117.9, 79.7; IR (thin film) ν_{max} 1774, 1492, 1436, 1250, 1220, 1152, 1029, 824, 764 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8ClO_3^+$ $[M + H]^+$ 211.0156, found 211.0153.

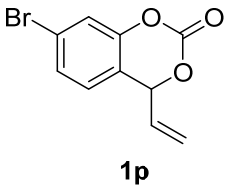
8-bromo-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1o)



1o

Prepared according to the general procedure as described above in 8% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 78–79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 1H), 7.07 – 6.99 (m, 2H), 5.96 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.80 (dt, *J* = 6.6, 1.1 Hz, 1H), 5.44 (dd, *J* = 10.4, 1.0 Hz, 1H), 5.37 (dd, *J* = 17.1, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 145.6, 134.0, 132.5, 126.1, 124.1, 121.7, 121.5, 110.1, 80.1; IR (thin film) ν_{max} 1777, 1453, 1235, 1203, 1161, 1136, 1029, 986, 749, cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8BrO_3^+$ $[M + H]^+$ 254.9651, found 254.9650.

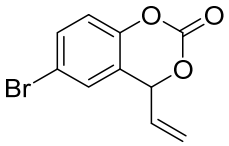
7-bromo-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1p)



1p

Prepared according to the general procedure as described above in 12% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a light yellow solid. Melting point: 48–49 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 6.95 (dd, *J* = 8.1, 0.8 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.77 (dd, *J* = 6.8, 1.3 Hz, 1H), 5.44 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.36 (dd, *J* = 17.1, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 144.7, 131.5, 127.5, 125.3, 122.2, 120.5, 118.7, 117.9, 79.0; IR (thin film) ν_{max} 1774, 1586, 1484, 1408, 1218, 1161, 1066, 1028, 947, 758 cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8BrO_3^+$ $[M + H]^+$ 254.9651, found 254.9652.

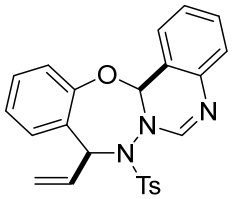
6-bromo-4-vinyl-4H-benzo[d][1,3]dioxin-2-one (1q)



1q

Prepared according to the general procedure as described above in 13% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 50–51 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.21 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 5.94 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.79 (d, *J* = 6.8 Hz, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 5.39 (d, *J* = 17.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 144.8, 131.3, 129.6, 129.3, 124.1, 120.7, 120.5, 116.8, 78.8; IR (thin film) ν_{max} 1769, 1479, 1260, 1148, 1124, 1108, 1027, 946, 817, 756, cm^{-1}; HRMS (ESI) calculated for $C_{10}H_8BrO_3^+$ $[M + H]^+$ 254.9651, found 254.9651.

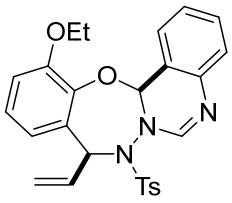
8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3aa)



3aa

Prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography (20% EtOAc/PE) to afford a white solid. Melting point: 100–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.35 (ddd, *J* = 8.4, 6.8, 1.9 Hz, 1H), 7.28 (ddd, *J* = 17.7, 7.7, 1.4 Hz, 2H), 7.23 – 7.17 (m, 3H), 7.14 – 7.02 (m, 3H), 6.96 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 6.05 (ddd, *J* = 16.7, 10.2, 6.1 Hz, 1H), 5.97 (dt, *J* = 6.1, 1.5 Hz, 1H), 5.93 (d, *J* = 1.6 Hz, 1H), 5.24 (dt, *J* = 10.0, 1.0 Hz, 1H), 5.05 (dt, *J* = 16.9, 1.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 148.3, 145.1, 139.7, 134.6, 132.3, 130.9, 130.6, 130.1, 130.1, 123.0, 128.3, 128.2, 126.4, 126.1, 125.2, 122.2, 121.9, 121.4, 86.1, 67.3, 21.7; IR (thin film) ν_{max} 1766, 1489, 1458, 1274, 1261, 1153, 1032, 942, 751 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{22}N_3O_3S^+$ $[M + H]^+$ 432.1376, found 432.1376.

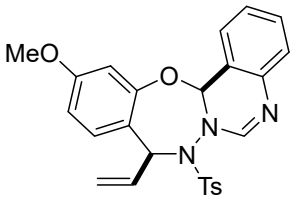
13-ethoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino [3,2-c]quinazoline (3ba)



3ba

Prepared according to the general procedure as described above in 81% yield (38.4 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a white solid. Melting point: 130–131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.35 (ddt, *J* = 5.7, 4.1, 1.9 Hz, 2H), 7.29 – 7.18 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.82 (d, *J* = 1.4 Hz, 0H), 6.11 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 5.93 (dt, *J* = 6.3, 1.4 Hz, 1H), 5.27 (dt, *J* = 10.1, 1.1 Hz, 1H), 5.19 (dt, *J* = 17.1, 1.2 Hz, 1H), 4.06 – 3.91 (m, 2H), 2.32 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 147.2, 146.4, 144.0, 138.6, 133.5, 132.1, 130.8, 129.4, 128.9, 127.8, 127.2, 125.2, 125.0, 124.5, 121.1, 120.3, 120.0, 112.8, 85.1, 66.3, 63.4, 20.6, 13.9; IR (thin film) ν_{max} 1604, 1261, 1204, 1165, 1089, 931, 765, 751, 669 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{26}N_3O_4S^+$ $[M + H]^+$ 476.1639, found 476.1638.

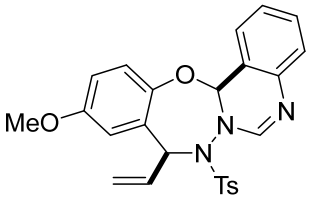
12-methoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ca)



3ca

Prepared according to the general procedure as described above in 98% yield (45.1 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.42 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.73 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.04 (ddd, *J* = 16.8, 10.2, 6.1 Hz, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.89 (dt, *J* = 6.3, 1.5 Hz, 1H), 5.28 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.11 (dt, *J* = 17.0, 1.1 Hz, 1H), 3.76 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 150.5, 147.5, 144.3, 137.5 133.4, 130.9, 130.7, 129.6, 129.0, 127.3, 127.1, 125.6, 124.4, 121.9, 121.3, 120.2, 113.9, 113.7, 85.3, 66.1, 54.7, 20.7; IR (thin film) ν_{max} 1620, 1275, 1261, 1165, 930, 764, 750, 704, 663 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_4S^+$ $[M + H]^+$ 462.1482, found 462.1483.

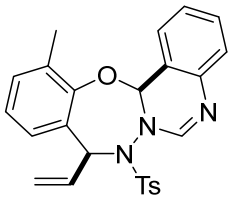
11-methoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3da)



3da (10:1 dr)

Prepared according to the general procedure as described above in 98% yield (45.1 mg, 10:1 dr). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.36 (ddd, *J* = 8.5, 6.7, 2.1 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.73 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.05 (ddd, *J* = 16.9, 10.2, 6.2 Hz, 1H), 5.94 (d, *J* = 1.5 Hz, 1H), 5.90 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.27 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.11 (dt, *J* = 17.1, 1.2 Hz, 1H), 3.76 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 151.7, 148.4, 145.1, 139.6, 134.6, 132.1, 131.8, 130.5, 123.0, 128.3, 128.2, 126.3, 126.1, 123.0, 122.0, 121.5, 114.9, 114.7, 86.2, 67.2, 55.8, 21.7; IR (thin film) ν_{max} 1605, 1495, 1203, 1176, 1165, 937, 764, 751, 667, 549 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_4S^+$ $[M + H]^+$ 462.1482, found 462.1481.

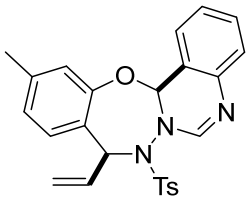
13-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ea)



3ea

Prepared according to the general procedure as described above in 94% yield (41.8 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 152–153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.57 – 7.48 (m, 2H), 7.38 (ddd, *J* = 8.4, 6.9, 1.8 Hz, 2H), 7.28 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.15 (dd, *J* = 7.4, 1.7 Hz, 4H), 7.11 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 1.5 Hz, 1H), 6.08 (ddd, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.95 (dd, *J* = 5.7, 1.6 Hz, 1H), 5.25 (dt, *J* = 10.1, 1.1 Hz, 1H), 5.11 (t, *J* = 1.2 Hz, 1H), 2.31 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 148.4, 145.1, 139.8, 134.6, 132.5, 131.6, 131.0, 130.9, 130.5, 129.9, 128.3, 128.2, 128.2, 127.7, 126.3, 126.2, 124.8, 121.8, 121.4, 86.0, 67.4, 21.7, 16.7; IR (thin film) ν_{max} 557, 667, 703, 733, 749, 764, 1166, 1264, 1491, 1619 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1533.

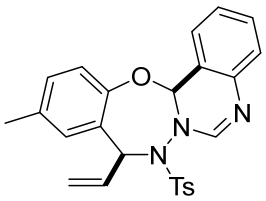
12-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3fa)



3fa

Prepared according to the general procedure as described above in 82% yield (36.5 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 138–139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.37 (ddd, *J* = 7.9, 5.3, 3.4 Hz, 1H), 7.30 – 7.16 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.89 (m, 1H), 6.86 (d, *J* = 1.5 Hz, 1H), 6.80 (d, *J* = 1.7 Hz, 1H), 6.04 (ddd, *J* = 17.0, 10.2, 6.1 Hz, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.94 (dt, *J* = 6.0, 1.5 Hz, 1H), 5.24 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.06 (dt, *J* = 17.0, 1.1 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 145.3, 143.5, 137.2, 134.6, 131.7, 130.6, 128.9, 128.8, 128.0, 127.6, 127.6, 127.5, 127.5, 123.5, 121.7, 118.3, 97.6, 83.8; IR (thin film) ν_{max} 549, 597, 666, 703, 733, 764, 1165, 1263, 1605, 1618 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1533.

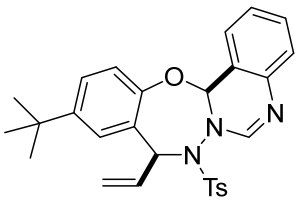
11-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ga)



3ga

Prepared according to the general procedure as described above in 87% yield (38.7 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid, Melting point: 100–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.36 (ddd, *J* = 8.1, 5.9, 2.8 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.14 – 7.07 (m, 3H), 7.04 – 6.99 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 1.5 Hz, 1H), 6.05 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.91 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.25 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.08 (dt, *J* = 17.1, 1.2 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 147.3, 144.0, 138.6, 133.8, 133.5, 131.4, 129.5, 129.5, 129.4, 128.9, 127.3, 127.2, 125.3, 125.0, 120.9, 120.8, 120.5, 85.1, 66.2, 20.6, 19.7; IR (thin film) ν_{max} 1915, 1605, 1177, 1165, 934, 765, 754, 667, 624, 557 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1532.

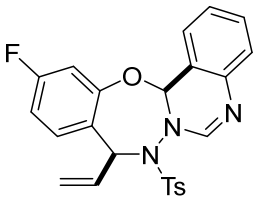
13-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ha)



3ha

Prepared according to the general procedure as described above in 75% yield (36.5 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid; Melting point: 148–149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.36 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.31 – 7.19 (m, 4H), 7.14 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.08 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 5.96 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.77 (d, *J* = 1.5 Hz, 1H), 5.27 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.10 (dt, *J* = 17.0, 1.1 Hz, 1H), 2.30 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 147.5, 147.2, 143.9, 138.7, 133.9, 131.5, 129.5, 129.0, 128.8, 127.2, 127.1, 125.8, 125.2, 125.1, 120.8, 120.5, 120.4, 85.0, 66.8, 33.5, 30.4, 20.6; IR (thin film) ν_{max} 1619, 1274, 1262, 1167, 764, 749, 703, 668, 622, 551 cm^{-1}; HRMS (ESI) calculated for $C_{28}H_{30}N_3O_3S^+$ $[M + H]^+$ 488.2002, found 488.2003.

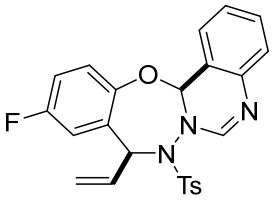
12-fluoro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ia)



3ia

Prepared according to the general procedure as described above in 62% yield (27.8 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.39 (ddd, *J* = 8.5, 6.9, 1.8 Hz, 1H), 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.18 – 7.12 (m, 3H), 6.95 – 6.84 (m, 2H), 6.78 (dt, *J* = 8.1, 1.1 Hz, 1H), 6.50 (dq, *J* = 6.2, 1.4 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 6.02 (ddd, *J* = 16.7, 10.2, 6.1 Hz, 1H), 5.28 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.11 (dd, *J* = 17.1, 1.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 158.4 (C-F, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 157.91, 147.0, 144.2, 138.6, 133.7, 130.3, 129.7, 129.3 (C-F, $^{2}J_{C\text{-}F}$ = 10.3 Hz), 129.0, 127.2, 127.0, 125.3 (C-F, $^{2}J_{C\text{-}F}$ = 25.5 Hz), 120.9, 120.0, 118.3 (C-F, $^{2}J_{C\text{-}F}$ = 15.1 Hz), 116.8 (C-F, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 111.0 (C-F, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 85.4, 57.5 (C-F, $^{3}J_{C\text{-}F}$ = 6.5 Hz), 20.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.59; IR (thin film) ν_{max} 1619 1263, 1167, 1007, 910, 764, 747, 732, 703, 667,550 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}FN_3O_3S^+$ $[M + H]^+$ 450.1282, found 450.1281.

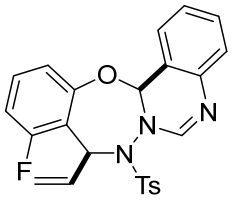
11-fluoro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ja)



3ja

Prepared according to the general procedure as described above in 43% yield (19.3 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 135–136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.38 (ddd, *J* = 8.4, 6.8, 1.9 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.03 (dd, *J* = 8.2, 2.9 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.83 (d, *J* = 1.5 Hz, 1H), 6.13 – 5.98 (m, 2H), 5.89 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.11 (dd, *J* = 17.1, 1.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 157.3, 153.1 (C-F, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 147.0, 144.3, 138.5, 133.3, 131.6 (C-F, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 130.6, 129.6, 129.0, 127.3, 127.1, 122.6 (C-F, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 121.3, 120.1, 115.6, 115.4 (C-F, $^{3}J_{C\text{-}F}$ = 23.3, 17.7 Hz), 115.3, 85.3, 65.6, 20.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.41; IR (thin film) ν_{max} 1619, 1606, 1264, 1166, 934, 733, 666, 654, 592, 550 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}FN_3O_3S^+$ $[M + H]^+$ 450.1282, found 450.1284.

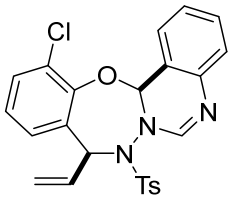
10-fluoro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ka)



3ka

Prepared according to the general procedure as described above in 54% yield (24.3 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.39 (ddd, *J* = 8.0, 7.2, 1.7 Hz, 1H), 7.34 – 7.20 (m, 4H), 7.17 – 7.11 (m, 2H), 6.93 – 6.79 (m, 2H), 6.72 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 6.06 – 6.00 (m, 1H), 5.97 (dt, *J* = 6.0, 1.4 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 5.05 (d, *J* = 17.3 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 161.0, 158.3 (C-F, $^{2}J_{C\text{-}F}$ = 11.2 Hz), 147.0, 144.3, 138.5, 133.4, 131.2, 130.1 (C-F, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 129.7, 129.0, 127.2, 127.2, 126.0 (C-F, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 125.5, 125.2, 120.9, 119.9, 111.0 (C-F, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 109.0 (C-F, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 85.5, 66.0, 20.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.59; IR (thin film) ν_{max} 1617, 1605, 1263, 1166, 764, 747, 734, 703, 666, 549 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}FN_3O_3S^+$ $[M + H]^+$ 450.1282, found 450.1283.

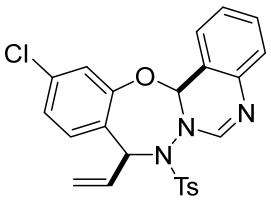
13-chloro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3la)



3la

Prepared according to the general procedure as described above in 75% yield (34.8 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.32 (m, 3H), 7.30 – 7.22 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 1.5 Hz, 1H), 6.13 (s, 1H), 5.96 (d, *J* = 6.4 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.14 (dd, *J* = 17.0, 1.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 147.8, 145.4, 139.6, 134.2, 133.5, 131.6, 130.8, 130.7, 130.0, 129.2, 128.3, 128.3, 128.2, 127.8, 126.5, 126.2, 125.8, 122.4, 120.6, 86.8, 67.0, 21.7; IR (thin film) ν_{max} 1622, 1606, 1456, 1275, 1260, 1166, 764, 750, 704, 667 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}ClN_3O_3S^+$ $[M + H]^+$ 466.0987, found 466.0985.

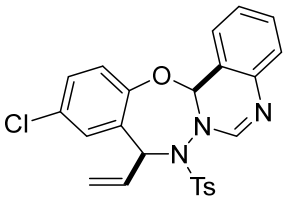
12-chloro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ma)



3ma

Prepared according to the general procedure as described above in 67% yield (31.2mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.40 (ddd, *J* = 8.3, 6.8, 2.0 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.17 – 7.09 (m, 3H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.83 (d, *J* = 1.5 Hz, 1H), 6.09 (d, *J* = 1.5 Hz, 1H), 6.02 (ddd, *J* = 16.7, 10.1, 6.0 Hz, 1H), 5.99 – 5.93 (m, 1H), 5.46 – 5.14 (m, 1H), 5.06 (dd, *J* = 17.0, 1.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 148.0, 145.4, 139.5, 135.2, 134.3, 131.9, 130.9, 130.8, 130.1, 129.6, 128.3, 128.2, 126.5, 126.2, 125.4, 122.8, 122.1, 121.0, 86.5, 66.6, 21.7; IR (thin film) ν_{max} 1622, 1274, 1263, 1167, 937, 764, 748, 703, 666, 550, cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}ClN_3O_3S^+$ $[M + H]^+$ 466.0987, found 466.0986.

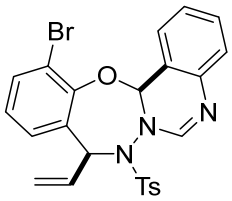
11-chloro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3na)



3na

Prepared according to the general procedure as described above in 75% yield (34.9 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 152–153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.38 (ddd, *J* = 8.4, 6.8, 2.0 Hz, 1H), 7.31 – 7.17 (m, 5H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 6.02 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 5.90 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.5 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 148.0, 145.4, 139.5, 134.3, 132.6, 131.6, 130.7, 130.2, 130.1, 123.0, 129.8, 128.3, 128.2, 126.5, 126.2, 123.7, 122.4, 121.1, 86.4, 66.6, 21.7; IR (thin film) ν_{max} 554, 1618, 1605, 1275, 1260, 1165, 935, 763, 749, 668 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21}ClN_3O_3S^+$ $[M + H]^+$ 466.0987, found 466.0985.

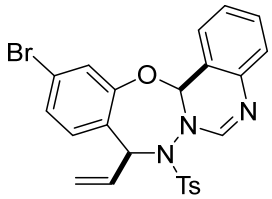
13-bromo-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3oa)



3oa

Prepared according to the general procedure as described above in 51% yield (26 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 4H), 7.39 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.12 (d, *J* = 1.5 Hz, 1H), 6.07 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 5.96 (dt, *J* = 6.3, 1.5 Hz, 1H), 5.29 (dt, *J* = 10.2, 1.0 Hz, 1H), 5.18 – 5.08 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 146.8, 144.3, 138.6, 133.2, 132.7, 132.3, 130.6, 129.7, 129.0, 128.4, 128.1, 127.2, 125.4, 125.2, 125.1, 121.4, 119.5, 116.3, 85.8, 66.0, 20.7; IR (thin film) ν_{max} 1621, 1605, 1488, 1275, 1260, 1165, 764, 750, 666, 545 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21Br}N_3O_3S^+$ $[M + H]^+$ 510.0482, found 510.0482.

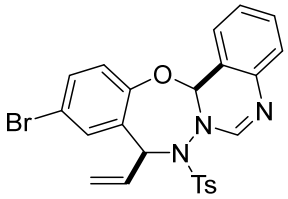
12-bromo-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3pa)



3pa

Prepared according to the general procedure as described above in 61% yield (31.1 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 89–90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.39 (ddd, *J* = 8.1, 6.5, 2.3 Hz, 1H), 7.32 – 7.20 (m, 4H), 7.20 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 6.83 (d, *J* = 1.5 Hz, 1H), 6.09 (d, *J* = 1.5 Hz, 1H), 6.02 (ddd, *J* = 16.9, 10.1, 6.1 Hz, 1H), 5.95 (dt, *J* = 6.1, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.06 (dd, *J* = 16.9, 1.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 146.9, 144.4, 138.5, 133.3, 130.8, 130.1, 129.7, 129.1, 129.0, 127.3, 127.3, 127.1, 125.5, 125.1, 124.7, 121.9, 121.1, 119.9, 85.5, 65.7, 20.7; IR (thin film) ν_{max} 1618,1605,1495,1203, 1164, 765, 752, 734, 667, 548, cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21Br}N_3O_3S^+$ $[M + H]^+$ 510.0482, found 510.0482.

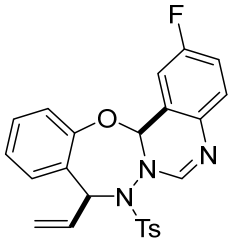
11-chloro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3qa)



3qa

Prepared according to the general procedure as described above in 49% yield (24.9 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 138–139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 2H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.38 (ddd, *J* = 8.6, 6.9, 1.8 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 6.01 (ddd, *J* = 16.8, 10.2, 6.1 Hz, 1H), 5.89 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.09 (dd, *J* = 17.0, 1.4 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 146.9, 144.4, 138.4, 133.3, 132.0, 131.9, 131.6, 130.6, 129.7, 129.0, 127.3, 127.2, 125.5, 125.1, 123.0, 121.3, 120.0, 116.8, 85.4, 65.5, 20.7; IR (thin film) ν_{max} 1618, 1605, 1478, 1261, 1165, 804, 765, 751, 663, 549 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{21Br}N_3O_3S^+$ $[M + H]^+$ 510.0482, found 510.0482.

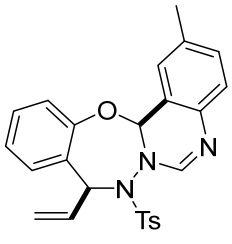
2-fluoro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ab)



3ab

Prepared according to the general procedure as described above in 99% yield (44.4 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 146–147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.16 – 7.04 (m, 4H), 6.97 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.04 (ddd, *J* = 16.6, 10.1, 6.0 Hz, 1H), 5.98 (dt, *J* = 6.1, 1.4 Hz, 1H), 5.89 (d, *J* = 1.5 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 5.10 – 5.00 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5 (C-F, $^{1}J_{C\text{-}F}$ = 246.1 Hz), 157.9, 147.7 (C-F, $^{3}J_{C\text{-}F}$ = 2.1 Hz), 145.2, 136.2 (C-F, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 134.5, 132.3, 130.8, 130.2, 130.1, 130.0, 128.2, 128.0 (C-F, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 127.9, 125.4, 122.5 (C-F, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 122.1, 122.0, 118.0 (C-F, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 114.3 (C-F, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 85.6 (C-F, $^{1}J_{C\text{-}F}$ = 2.1 Hz), 67.3, 21.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.97; IR (thin film) ν_{max} 1615, 1489, 1164, 857, 764, 749, 719, 667, 550 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{22}N_3O_4S^+$ $[M + H]^+$ 448.1326, found 448.1326.

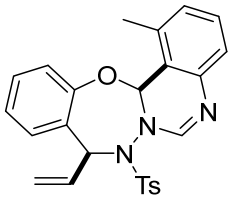
2-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ac)



3ac

Prepared according to the general procedure as described above in 49% yield (21.8 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 2H), 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.18 – 7.09 (m, 5H), 7.03 – 6.99 (m, 2H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.06 (ddd, *J* = 16.7, 10.2, 6.1 Hz, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.97 (dt, *J* = 6.1, 1.4 Hz, 1H), 5.26 (dt, *J* = 10.0, 1.1 Hz, 1H), 5.07 (dt, *J* = 16.9, 1.1 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 146.6, 144.0, 136.3, 135.3, 133.6, 131.3, 130.5, 130.0, 129.0, 129.0, 128.9, 127.4, 127.1, 124.9, 124.1, 121.2, 120.8, 120.1, 85.2, 66.2, 20.6, 20.1; IR (thin film) ν_{max} 1610, 1275, 1261, 1165, 933, 764, 749, 669, 551 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1533.

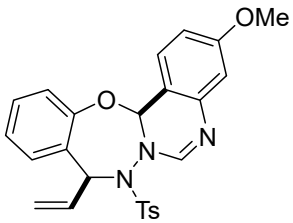
1-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ad)



3ad

Prepared according to the general procedure as described above in 65% yield (28.9 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a light yellow solid. Melting point: 128–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.23 (td, *J* = 7.7, 1.7 Hz, 1H), 7.18 – 7.08 (m, 5H), 7.01 (dd, *J* = 8.2, 1.4 Hz, 2H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.06 (ddd, *J* = 16.7, 10.2, 6.2 Hz, 1H), 6.00 – 5.92 (m, 2H), 5.25 (d, *J* = 10.1 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 158.1, 147.7, 145.1, 137.3, 136.3, 134.6, 132.3, 131.6, 131.0, 130.07, 130.04, 129.9, 128.4, 128.2, 125.9, 125.2, 122.3, 121.9, 121.1, 86.2, 67.2, 21.7, 21.2 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1533.

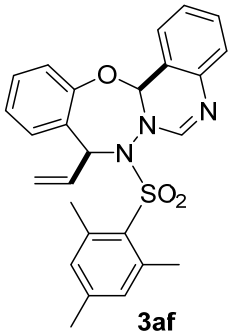
3-methoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ae)



3ae

Prepared according to the general procedure as described above in 83% yield (38.3 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a light yellow solid. Melting point: 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.57 – 7.44 (m, 2H), 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.23 (td, *J* = 7.7, 1.7 Hz, 1H), 7.14 – 7.06 (m, 4H), 6.96 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.89 (d, *J* = 1.5 Hz, 1H), 6.83 – 6.72 (m, 2H), 6.06 (ddd, *J* = 16.8, 10.2, 6.1 Hz, 1H), 5.97 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.89 (d, *J* = 1.5 Hz, 1H), 5.26 (d, *J* = 9.9 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 3.76 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 158.0, 148.7, 145.1, 141.0, 134.6, 132.3, 130.9, 130.1, 130.0, 129.9, 129.2, 128.2, 125.1, 122.3, 121.9, 114.1, 114.0, 109.2, 86.0, 67.2, 55.5, 21.7; IR (thin film) ν_{max} 1609, 1275, 1263, 1165, 764, 748, 733, 703, 669, 571 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{23}N_3O_4S^+$ $[M + H]^+$ 462.1482, found 462.1482.

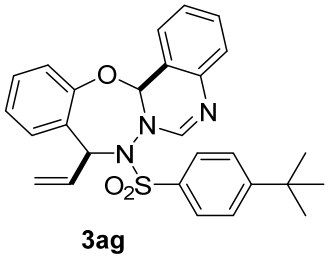
8-(mesitylsulfonyl)-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3af)



3af

Prepared according to the general procedure as described above in 60% yield (27.6 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. Melting point: 131–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.29 – 7.20 (m, 3H), 7.12 (td, *J* = 7.4, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.82 (s, 2H), 6.70 (d, *J* = 1.5 Hz, 1H), 6.55 (d, *J* = 1.5 Hz, 1H), 6.12 (ddd, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.97 (d, *J* = 6.6 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 2.39 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 147.7, 144.1, 140.8, 139.4, 132.3, 132.0, 131.4, 130.5, 130.3, 130.1, 129.9, 128.4, 126.5, 126.0, 125.4, 122.1, 121.8, 121.5, 86.5, 66.57, 22.8, 21.1; IR (thin film) ν_{max} 1603, 1275, 1261, 1177, 1163, 930, 764, 750, 668, 627 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{25}N_3O_3S^+$ $[M + H]^+$ 460.1689, found 460.1689.

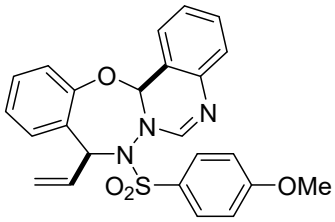
8-((4-(tert-butyl)phenyl)sulfonyl)-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (3ag)



3ag

Prepared according to the general procedure as described above in 83% yield (39.3 mg). It was purified by flash chromatography (20% EtOAc/PE) to afford a white solid. Melting point: 156–157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 2H), 7.37 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.21 (tdd, *J* = 7.4, 4.6, 1.5 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.98 (s, 1H), 6.94 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.07 (ddd, *J* = 16.8, 10.2, 6.1 Hz, 1H), 5.97 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.77 (d, *J* = 1.5 Hz, 1H), 5.26 (dt, *J* = 10.1, 1.1 Hz, 1H), 5.07 (dt, *J* = 17.0, 1.0 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 157.0, 147.3, 138.6, 133.4, 131.3, 129.8, 129.5, 129.1, 129.0, 127.1, 126.9, 125.3, 125.2, 125.1, 124.2, 121.1, 120.9, 120.3, 85.0, 66.4, 34.2, 30.0; IR (thin film) ν_{max} 1620, 1604, 1275, 1261, 1169, 931, 764, 750, 630, 547 cm^{-1}; HRMS (ESI) calculated for $C_{27}H_{28}N_3O_3S^+$ $[M + H]^+$ 474.1846, found 474.1847

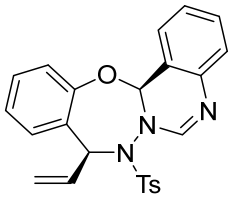
8-((4-(methoxy)phenyl)sulfonyl)-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiaze-pino[3,2-c]quinazoline (3ah)



3ah

Prepared according to the general procedure as described above in 77% yield (34.4 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a light yellow solid. Melting point: 100–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.37 (ddd, *J* = 8.5, 6.6, 2.1 Hz, 1H), 7.33 – 7.19 (m, 5H), 7.11 (td, *J* = 7.4, 1.3 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.92 (d, *J* = 1.5 Hz, 1H), 6.80 – 6.68 (m, 2H), 6.06 (ddd, *J* = 16.7, 10.2, 6.1 Hz, 1H), 5.97 (dt, *J* = 6.1, 1.5 Hz, 1H), 5.94 (d, *J* = 1.5 Hz, 1H), 5.26 (dt, *J* = 10.2, 1.0 Hz, 1H), 5.06 (dt, *J* = 16.9, 1.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 158.1, 148.4, 139.7, 132.4, 130.9, 130.6, 130.4, 130.13, 130.09, 128.7, 128.3, 126.3, 126.1, 125.2, 122.2, 121.9, 121.3, 114.5, 85.9, 67.2, 55.7; IR (thin film) ν_{max} 1621, 1605, 1274, 1262, 764, 748, 730, 702, 672, 556 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{22}N_3O_4S^+$ $[M + H]^+$ 448.1326, found 448.1326.

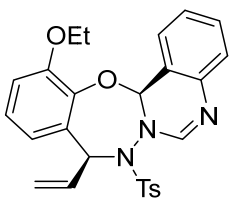
(9S,14aS)-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-]quina-zoline (4aa)



4aa (8:1 dr)

Prepared according to the general procedure as described above in 51% yield (22.0 mg, 8:1 dr). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. Melting point: 98–99°C; $[\alpha]^{25}_{D}$ = +72 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.47 – 7.27 (m, 6H), 7.23 – 7.16 (m, 3H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.14 (ddd, *J* = 16.6, 10.1, 6.1 Hz, 1H), 6.07 – 5.99 (m, 2H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.14 (dd, *J* = 17.1, 1.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 148.3, 145.1, 139.6, 134.6, 132.3, 130.9, 130.6, 130.1, 130.0, 129.9, 128.3, 128.2, 126.3, 126.1, 125.2, 122.2, 121.9, 121.4, 86.1, 67.3, 21.7; IR (thin film) ν_{max} 1766, 1489, 1458, 1274, 1261, 1153, 1032, 942, 751 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{22}N_3O_3S^+$ $[M + H]^+$ 432.1376, found 432.1376.; HPLC analysis: **4aa**, 75% ee (IE, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =22.0 min (major), 24.1 min (minor).

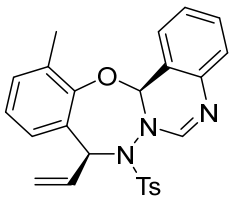
(9S,14aS)-13-ethoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepine-[3,2-c]quinazoline (4ba)



4ba (16:1 dr)

Prepared according to the general procedure as described above in 98% yield (48.5 mg, 16:1 dr). It was purified by flash chromatography (30% EtOAc/PE) to afford a white solid. Melting point: 128–129 °C; $[\alpha]^{25}_{D}$ = +104 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.42 (ddd, *J* = 7.2, 4.0, 2.3 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.14 (dd, *J* = 37.6, 8.0 Hz, 3H), 7.03 – 6.83 (m, 3H), 6.18 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 6.06 (d, *J* = 1.5 Hz, 1H), 6.00 (dt, *J* = 6.4, 1.5 Hz, 1H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.26 (dd, *J* = 17.1, 1.3 Hz, 1H), 4.21 – 3.94 (m, 2H), 2.38 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 148.2, 147.4, 145.0, 139.7, 134.6, 133.1, 131.9, 130.5, 129.9, 128.8, 128.2, 126.2, 126.0, 125.6, 122.1, 121.4, 121.1, 113.9, 86.1, 67.3, 64.4, 21.7, 14.9; IR (film) ν_{max} 1604, 1261, 1204, 1165, 1089, 931, 765, 751, 669 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{26}N_3O_4S^+$ $[M + H]^+$ 476.1639, found 476.1638; HPLC analysis: **4ba**, 94% ee (IE, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =25.6 min (major), 28.1 min (minor).

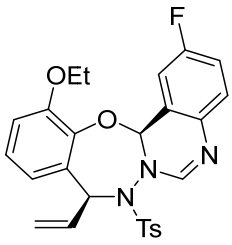
(9S,14aS)-13-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino-[3,2-c]quinazoline (4ea)



4ea (6:1 dr)

Prepared according to the general procedure as described above in 83% yield (36.9 mg, 6:1 dr). It was purified by flash chromatography (25% EtOAc/PE) to afford a light yellow solid. Melting point: 146–147 °C; $[\alpha]^{25}_{D}$ = +40 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.04 (m, 10H), 6.98 – 6.89 (m, 1H), 6.15 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 6.10 – 5.91 (m, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 2.38 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 148.45, 145.06, 134.6, 132.5, 131.5, 131.0, 130.9, 130.5, 129.93, 129.91, 128.3, 128.2, 127.7, 126.3, 126.2, 124.8, 121.8, 121.4, 86.0, 67.4, 21.7, 16.7; IR (film) ν_{max} 1619, 1491, 1264, 1166, 764, 749, 733, 703, 667, 557 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}N_3O_3S^+$ $[M + H]^+$ 446.1533, found 446.1533; HPLC analysis: **4ea**, 82% ee (IE, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =20.5 min (major), 24.0 min (minor).

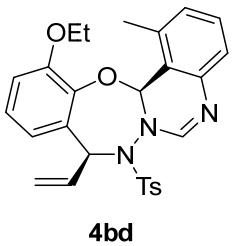
(9S,14aS)-13-ethoxy-2-fluoro-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (4bb)



4bb

Prepared according to the general procedure as described above in 93% yield (45.9 mg). It was purified by flash chromatography (30% EtOAc/PE) to afford a light yellow solid. Melting point: 131–132 °C; $[\alpha]^{25}_{D}$ = +64 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.05 (m, 6H), 7.04 – 6.83 (m, 3H), 6.16 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 6.03 – 6.01 (m, 1H), 6.01 – 5.97 (m, 1H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 4.06 (h, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6 (C-F, $^1J_{C\text{-}F}$ = 245.9 Hz), 151.6, 147.5 (C-F, $^3J_{C\text{-}F}$ = 2.1 Hz), 147.1, 145.2, 136.2 (C-F, $^3J_{C\text{-}F}$ = 2.7 Hz), 134.5, 133.0, 131.8, 129.9, 128.2, 127.8 (C-F, $^2J_{C\text{-}F}$ = 8.4 Hz), 125.8, 122.6 (C-F, $^3J_{C\text{-}F}$ = 8.4 Hz), 122.1, 121.0, 117.9 (C-F, $^2J_{C\text{-}F}$ = 22.7 Hz), 114.8 (C-F, $^2J_{C\text{-}F}$ = 23.7 Hz), 113.7, 85.6 (C-F, $^3J_{C\text{-}F}$ = 2.0 Hz), 67.3, 64.4, 21.7, 14.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.46; IR (film) ν_{max} 1617, 1491, 1346, 1277, 1205, 1166, 1091, 946, 868 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{25}FN_3O_4S$ [M + H] 494.1550, found 494.1543. HPLC analysis: **4bb**, 95% ee (IC, isopropanol : hexane=30 : 70, 1 mL/min, UV: 254 nm), t_R =9.4 min (major), 13.1 min (minor).

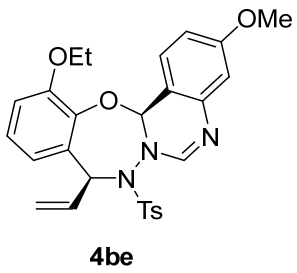
(9S,14aS)-13-ethoxy-1-methyl-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepine[3,2-c]quinazoline (4bd)



4bd

Prepared according to the general procedure as described above in 85% yield (41.6 mg). It was purified by flash chromatography (30% EtOAc/PE) to afford a light yellow solid. Melting point: 136–137 °C; $[\alpha]^{25}_{D}$ = +96 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.45 (m, 2H), 7.28 – 6.98 (m, 6H), 6.87 (ddd, *J* = 25.9, 8.0, 1.4 Hz, 2H), 6.74 (d, *J* = 1.4 Hz, 1H), 6.10 (ddd, *J* = 16.9, 10.2, 6.3 Hz, 1H), 6.03 (d, *J* = 1.4 Hz, 1H), 5.91 (dt, *J* = 6.5, 1.5 Hz, 1H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 17.0 Hz,1H), 4.05 – 3.93 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 1.42 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 146.5, 146.3, 144.0, 136.4, 135.0, 133.6, 132.2, 130.8, 130.3, 128.9, 128.0, 127.2, 124.8, 124.5, 121.0, 120.12, 119.98, 112.6, 85.2, 66.2, 63.3, 20.6, 20.1, 13.9; IR (film) ν_{max} 1610, 1496, 1276, 1196, 1164, 1089, 1016, 935, 801 cm^{-1}; HRMS (ESI) calculated for $C_{27}H_{28}N_3O_4S$ [M + H] 490.1801, found 490.1804; HPLC analysis: **4bd**, 94% ee (IC, isopropanol : hexane=30 : 70, 1 mL/min, UV: 254 nm), t_R =13.8 min (major), 17.0 min (minor).

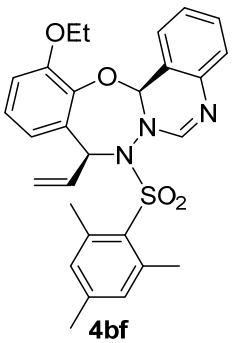
(9S,14aS)-13-ethoxy-3-methoxy-8-tosyl-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (4be)



4be

Prepared according to the general procedure as described above in 46% yield (23.3 mg). It was purified by flash chromatography (30% EtOAc/PE) to afford a light yellow solid. Melting point: 144–145 °C; $[\alpha]^{25}_{D}$ = +24 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 77.68 – 7.52 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 41.9, 7.9 Hz, 3H), 7.01 – 6.76 (m, 5H), 6.18 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 6.05 – 5.93 (m, 2H), 5.41 – 5.31 (m, 1H), 5.31 – 5.22 (m, 1H), 4.09 – 4.00 (m, 2H), 3.83 (s, 3H), 2.39 (s, 3H), 1.44 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 151.7, 148.5, 147.3, 145.0, 141.1, 134.6, 133.1, 131.9, 129.9, 129.7, 128.2, 125.5, 122.1, 121.1, 114.0, 113.9, 109.1, 86.1, 67.3, 64.4, 55.5, 21.7, 14.9; IR (film) ν_{max} 1609, 1498, 1469, 1279, 1164, 1088, 1015, 933, 798 cm^{-1}; HRMS (ESI) calculated for $C_{27}H_{28}N_3O_5S$ [M + H] 506.1750, found 506.1750; HPLC analysis: **4be**, 90% ee (ID, isopropanol : hexane=60 : 40, 1 mL/min, UV: 254 nm), t_R =21.8 min (major), 45.7 min (minor).

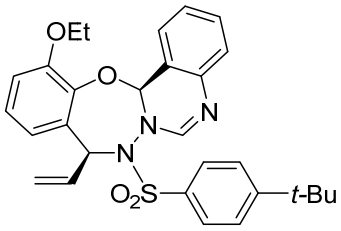
(9S,14aS)-13-ethoxy-8-(mesitylsulfonyl)-9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (4bf)



4bf

Prepared according to the general procedure as described above in 98% yield (49.5 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. Melting point: 168–169 °C; $[\alpha]^{25}_{D}$ = +160 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.42 – 7.15 (m, 3H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.96 – 6.78 (m, 4H), 6.70 (d, *J* = 1.4 Hz, 1H), 6.49 (d, *J* = 1.4 Hz, 1H), 6.18 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.91 (dd, *J* = 6.8, 1.3 Hz, 1H), 5.35 – 5.10 (m, 2H), 4.02 (dtt, *J* = 16.0, 9.1, 7.0 Hz, 2H), 2.41 (s, 6H), 2.20 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 146.6, 146.4, 143.0, 139.8, 138.5, 132.4, 131.3, 130.6, 129.4, 127.9, 125.2, 124.8, 124.7, 120.9, 120.4, 119.8, 112.6, 85.6, 65.7, 63.2, 21.7, 20.1, 13.9; IR (film) ν_{max} 1620, 1604, 1486, 1332, 1205, 1177, 931, 863 cm^{-1}; HRMS (ESI) calculated for $C_{28}H_{30}N_3O_4S$ [M + H] 504.1957, found 504.1961; HPLC analysis: **4bf**, 92% ee (IE, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =7.5 min (major), 8.5 min (minor).

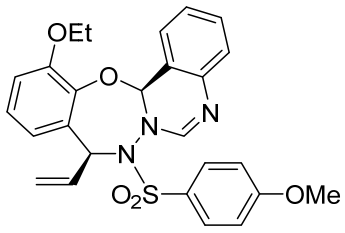
(9S,14aS)-8-((4-(tert-butyl)phenyl)sulfonyl)-13-ethoxy-9-vinyl-8,9-dihydro-14aH-benzo-[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (4bg)



4bg (18:1 dr)

Prepared according to the general procedure as described above in 92% yield (47.6 mg, 18:1 dr). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. Melting point: 142–143 °C; $[\alpha]^{25}_{D}$ = +24 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.47 – 7.21 (m, 6H), 7.17 – 6.83 (m, 4H), 6.20 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 5.99 (dt, *J* = 6.3, 1.5 Hz, 1H), 5.69 (d, *J* = 1.4 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 5.26 (dt, *J* = 17.1, 1.1 Hz, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 151.7, 148.4, 147.3, 139.8, 134.5, 133.0, 131.9, 130.5, 128.7, 128.0, 126.2, 126.1, 126.0, 125.5, 122.1, 121.3, 121.2, 113.6, 85.9, 67.6, 64.3, 35.2, 31.0, 14.9; IR (film) ν_{max} 1620, 1605, 1486, 1361, 1204, 1173, 1086, 931, 862, cm^{-1}; HRMS (ESI) calculated for $C_{29}H_{32}N_3O_4S$ [M + H] 518.2114, found 518.2112; HPLC analysis: **4bg**, 94% ee (IC, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =9.2 min (major), 11.3 min (minor)

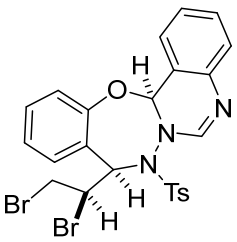
(9S,14aS)-13-ethoxy-8-((4-methoxyphenyl)sulfonyl)-9-vinyl-8,9-dihydro-14aH-benzo-[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (4bh)



4bh

Prepared according to the general procedure as described above in 72% yield (35.4 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a light yellow solid. Melting point: 138–139 °C; $[\alpha]^{25}_{D}$ = +56 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.49 (m, 2H), 7.40 – 7.19 (m, 4H), 7.09 – 6.68 (m, 5H), 6.11 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 5.98 (d, *J* = 1.4 Hz, 1H), 5.92 (dt, *J* = 6.2, 1.5 Hz, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 17.0 Hz, 1H), 3.98 (dtt, *J* = 16.1, 9.2, 7.0 Hz, 2H), 3.75 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 150.6, 147.3, 146.4, 138.7, 132.0, 130.9, 129.4, 127.8, 127.7, 125.1, 125.0, 124.5, 121.0, 120.3, 120.0, 113.4, 112.8, 85.0, 66.3, 63.4, 54.7, 13.8; IR (film) ν_{max} 1604, 1486, 1356, 1205, 1161, 1092, 932, 835 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{26}N_3O_5S$ [M + H] 492.1593, found 492.1591; HPLC analysis: **4bh**, 94% ee (IC, isopropanol : hexane=40 : 60, 1 mL/min, UV: 254 nm), t_R =10.9 min (major), 13.6 min (minor).

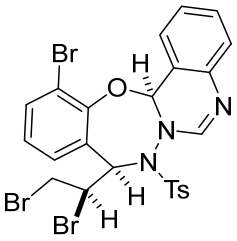
9-(1,2-dibromoethyl)-8-tosyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (5a)



5a (10:1 dr)

Prepared according to the general procedure as described above in 32% yield (18.9 mg, 10:1 dr). It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. Melting point: 172–173 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 3H), 7.61 (dd, *J* = 7.6, 1.7 Hz, 7H), 7.40 (ddd, *J* = 8.3, 6.9, 1.9 Hz, 2H), 7.34 – 7.20 (m, 1H), 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.67 (d, *J* = 10.5 Hz, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 3.50 (dd, *J* = 12.0, 3.3 Hz, 1H), 2.98 (dd, *J* = 11.9, 3.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 145.7, 144.5, 138.3, 132.8, 130.6, 130.3, 129.8, 129.0, 127.6, 127.4, 127.2, 125.6, 125.3, 124.5, 121.2, 119.9, 86.4, 68.4, 48.5, 36.2, 20.7; HRMS (ESI) calculated for $C_{24}H_{22}Br_2N_3O_3S^+$ $[M + H]^+$ 589.9743, found 589.9749.

13-bromo-9-1,2-dibromoethyl)-8-tosyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepine-[3,2-c]quinazoline (5b)

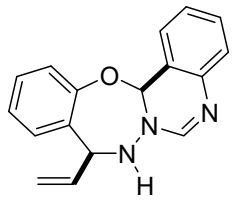


5b (5:1 dr)

Prepared according to the general procedure as described above in 56% yield (37.3 mg, 5:1 dr). It was purified by flash chromatography (20% EtOAc/PE) to afford a white solid. Melting point: 138–139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.39 (m, 2H), 7.39 – 7.18 (m, 7H), 7.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.89 (d, *J* = 1.4 Hz, 1H), 6.22 (d, *J* = 1.4 Hz, 1H), 5.89 (d, *J* = 9.4 Hz, 1H), 4.87 – 4.62 (m, 1H), 4.04 – 3.78 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 146.0, 145.9, 139.2, 133.7, 132.4, 130.9, 130.8, 130.2, 129.5, 128.6, 128.4, 126.8, 126.3, 124.9, 121.8, 121.0, 87.2, 66.9, 49.6, 36.5, 21.8; HRMS (ESI) calculated for $C_{24}H_{22}Br_3N_3O_3S^+$ $[M + H]^+$ 667.8848, found 667.8840.

9-vinyl-8,9-dihydro-14aH-benzo[6,7][1,3,4]oxadiazepino[3,2-c]quinazoline (6)

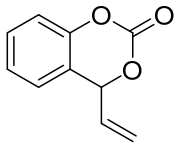
Prepared according to the general procedure as described above in 61% yield (16.9 mg). It was purified by flash chromatography (75% EtOAc/PE) to afford a light yellow solid. Melting point: 191–192 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.24 (s, 1H), 7.83 (s, 1H), 7.60 – 7.47 (m, 1H), 7.23 – 6.99 (m, 6H), 6.86 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.78 – 6.67 (m, 2H), 6.39 (ddd, *J* = 17.3, 10.3, 8.9 Hz, 1H), 5.81 – 5.51 (m, 1H), 5.45 (dd, *J* = 17.3, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.1, 148.8, 142.1, 139.7, 134.5, 129.6, 128.6, 128.3, 127.6, 127.3, 127.0, 126.2, 125.7, 124.1, 120.6, 116.1, 52.0; HRMS (ESI) calculated for $C_{17}H_{15}N_3O$ [M + H] 278.1293, found 278.1292..



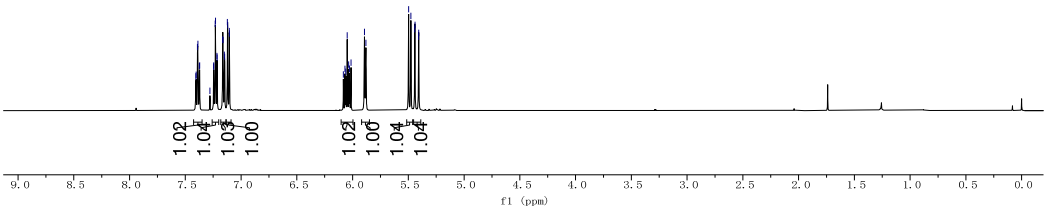
6

^{1}H and ^{13}C NMR Spectra of New Substrates

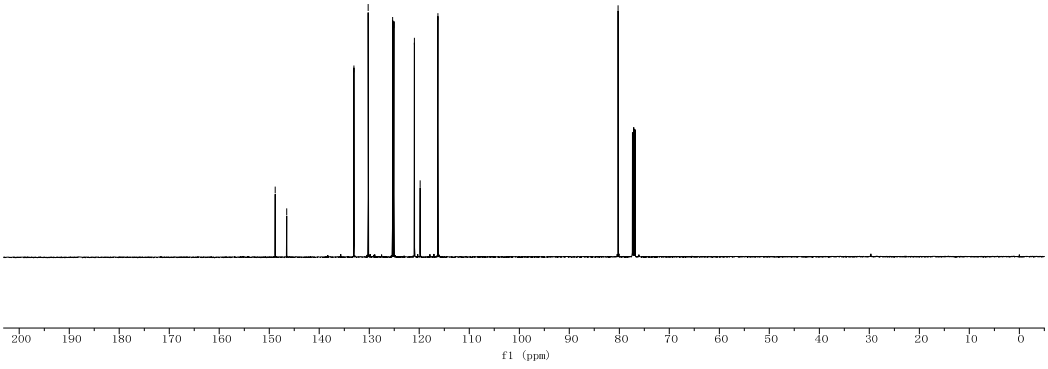
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



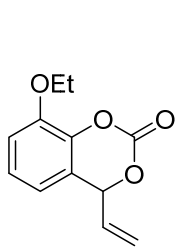
1a



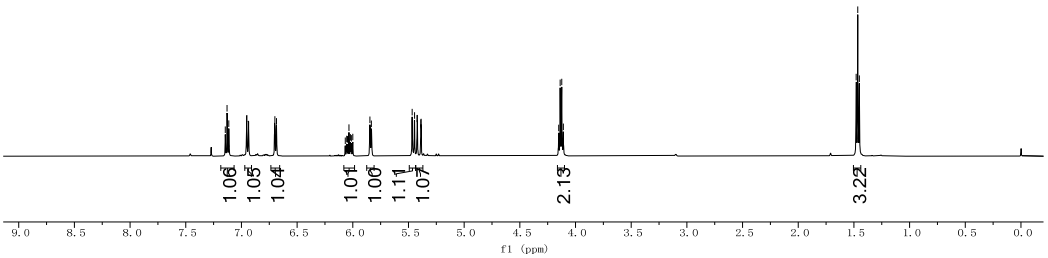
^{13}C NMR (126 MHz, $CDCl_3$)



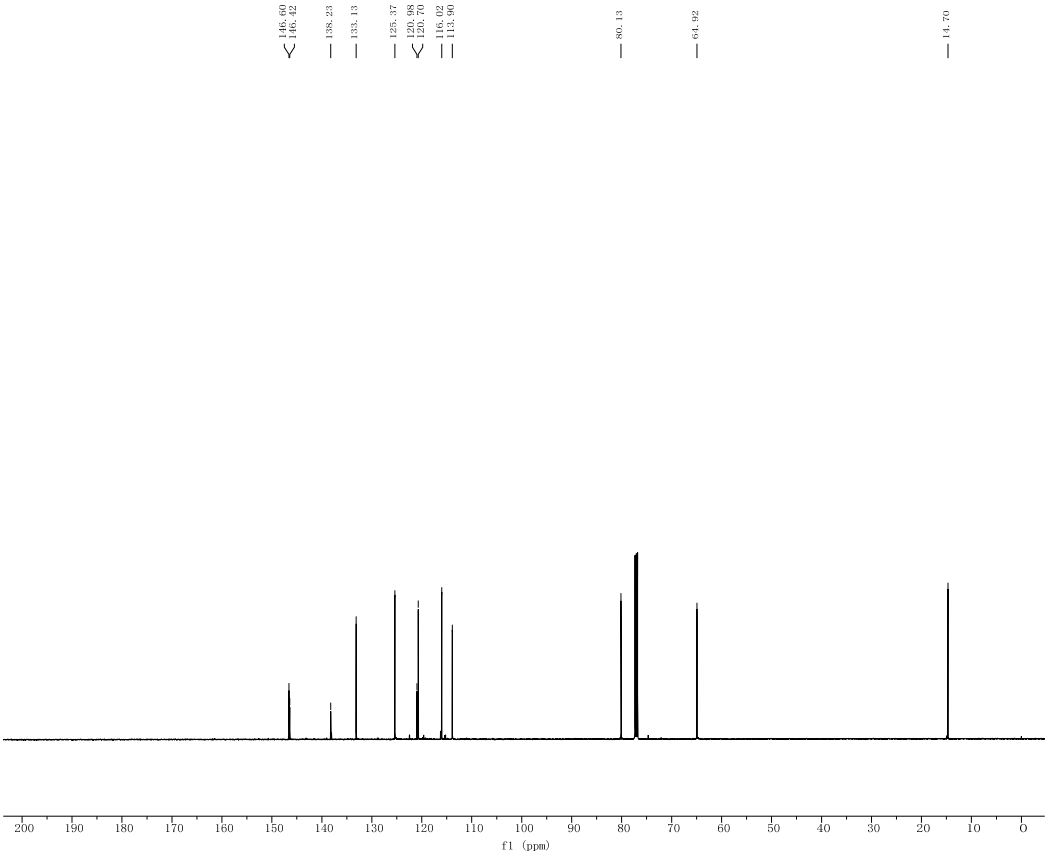
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



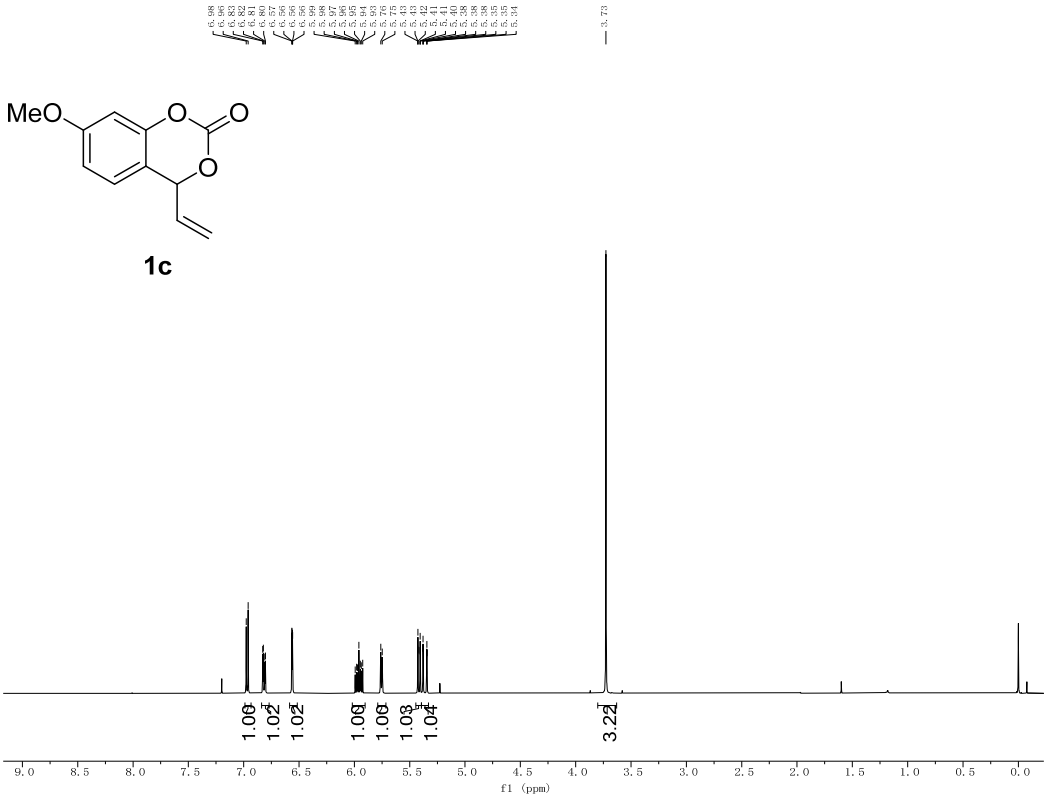
1b



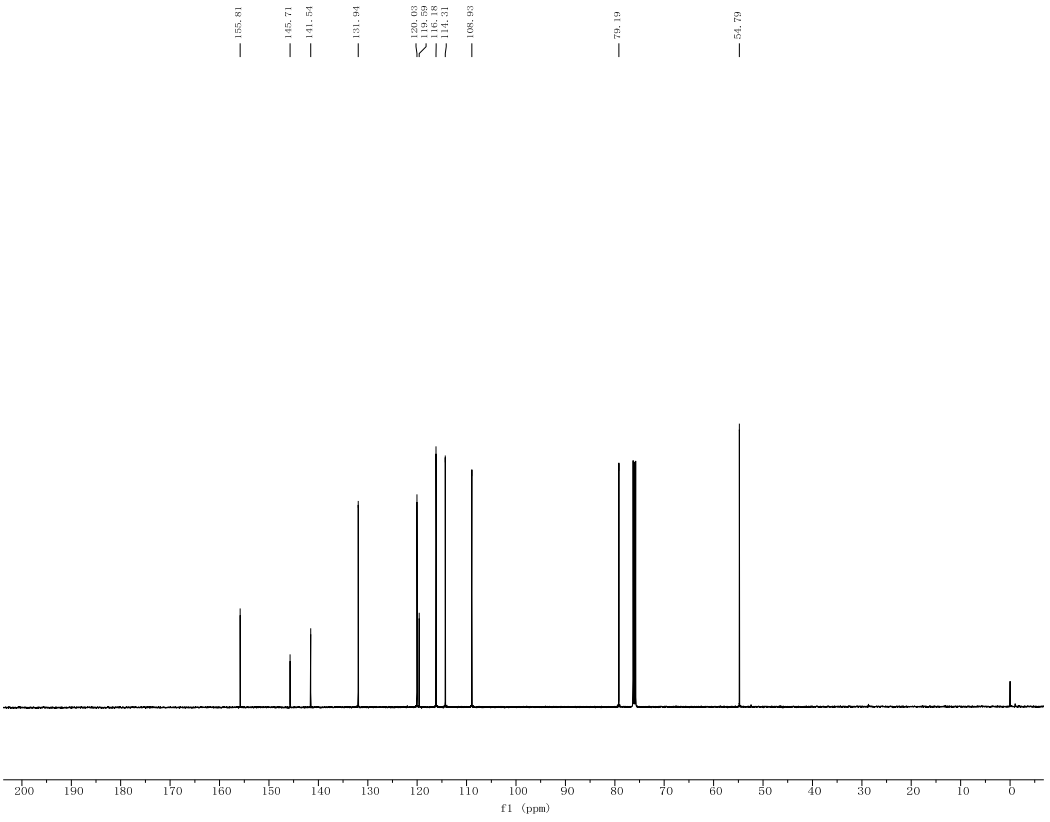
^{13}C NMR (126 MHz, $CDCl_3$)



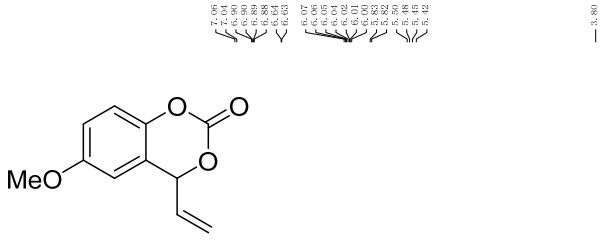
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



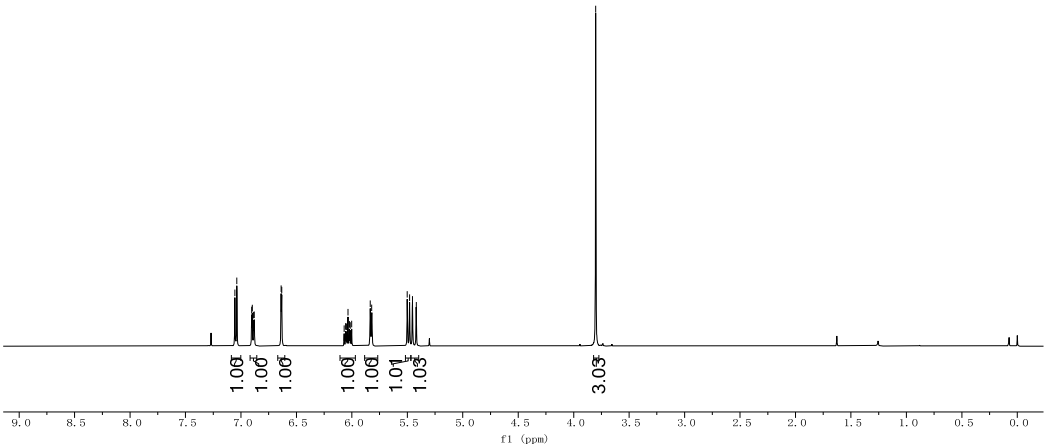
^{13}C NMR (126 MHz, $CDCl_3$)



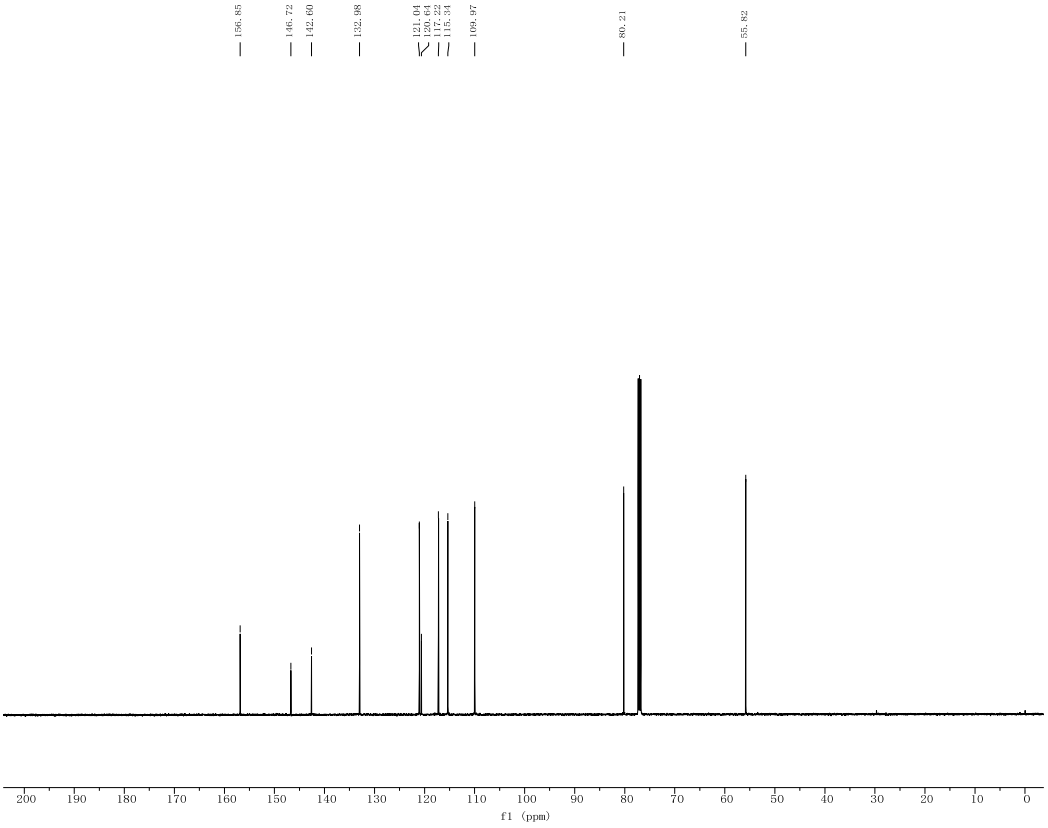
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



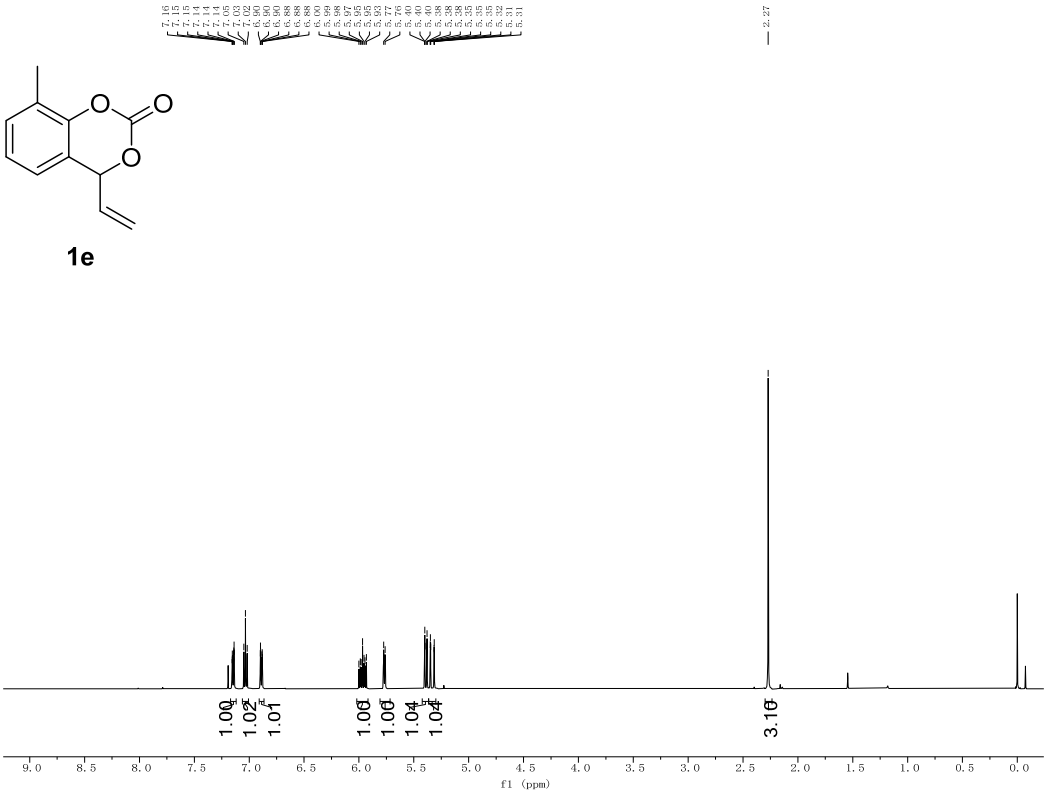
1d



^{13}C NMR (126 MHz, $CDCl_3$)

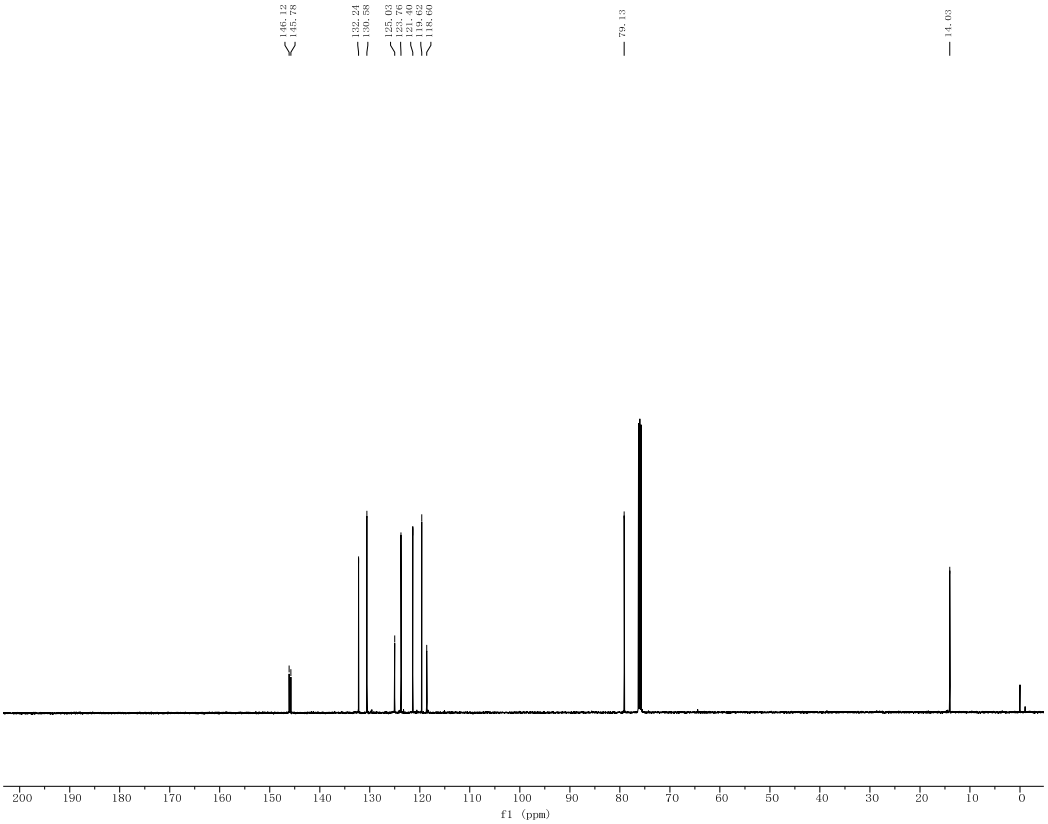


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

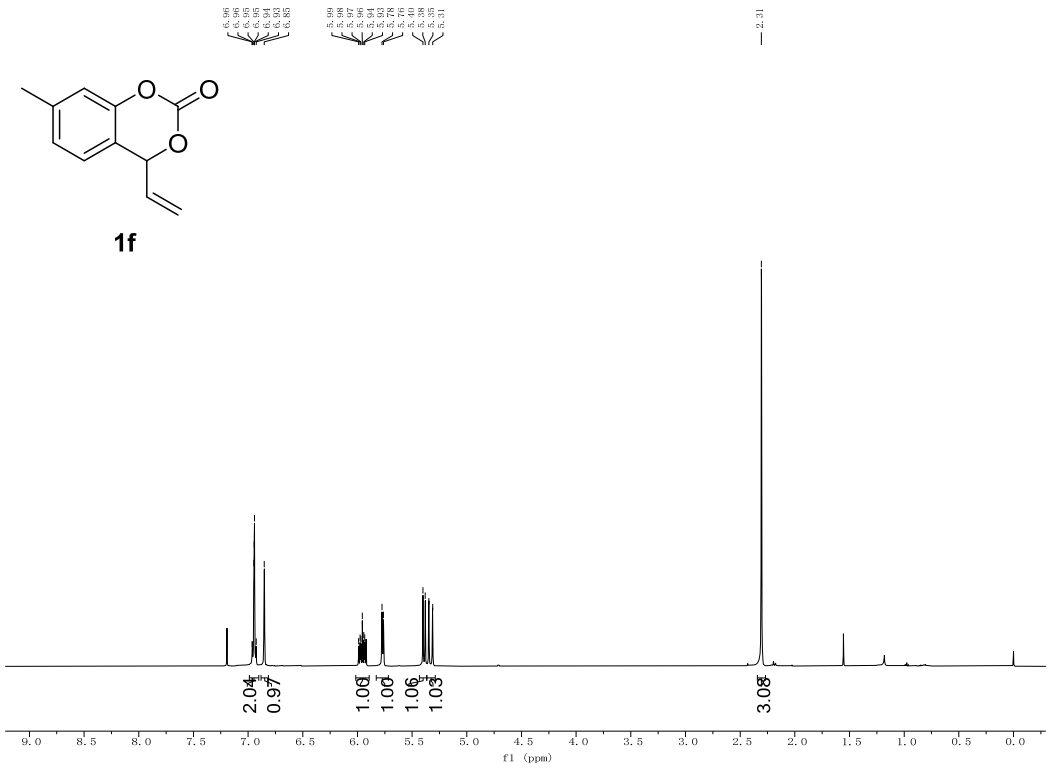


1e

^{13}C NMR (126 MHz, $CDCl_3$)

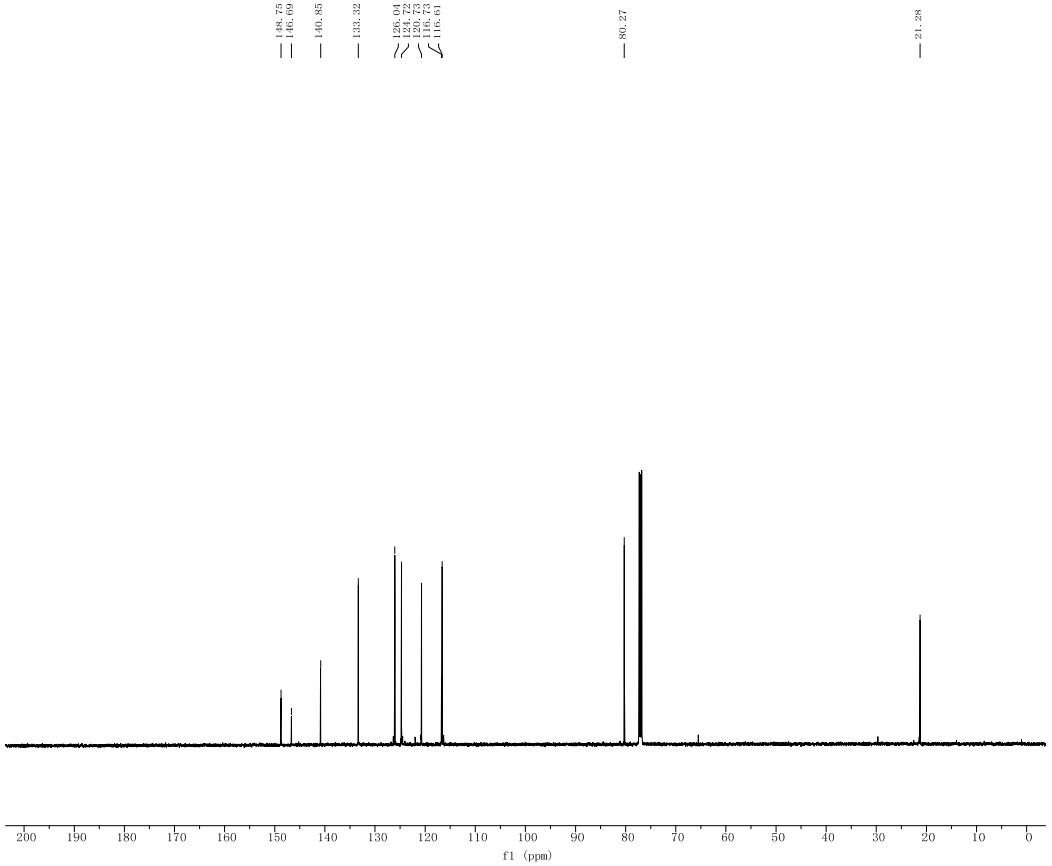


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

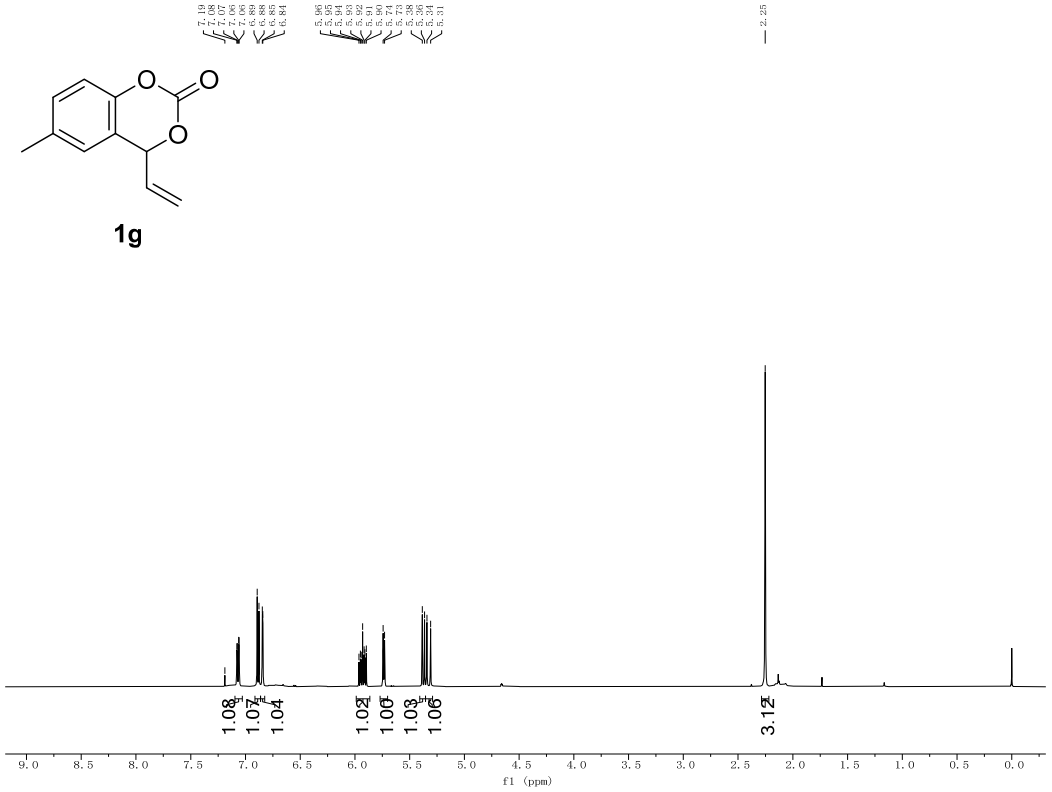


1f

^{13}C NMR (126 MHz, $CDCl_3$)

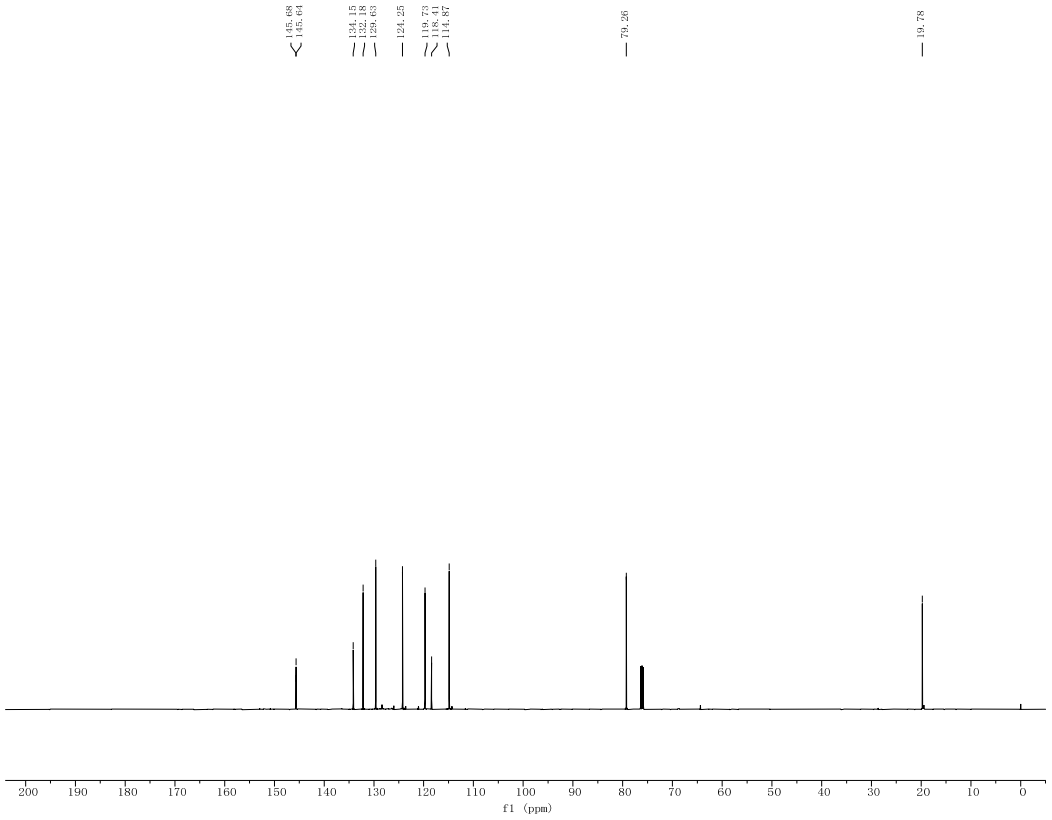


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

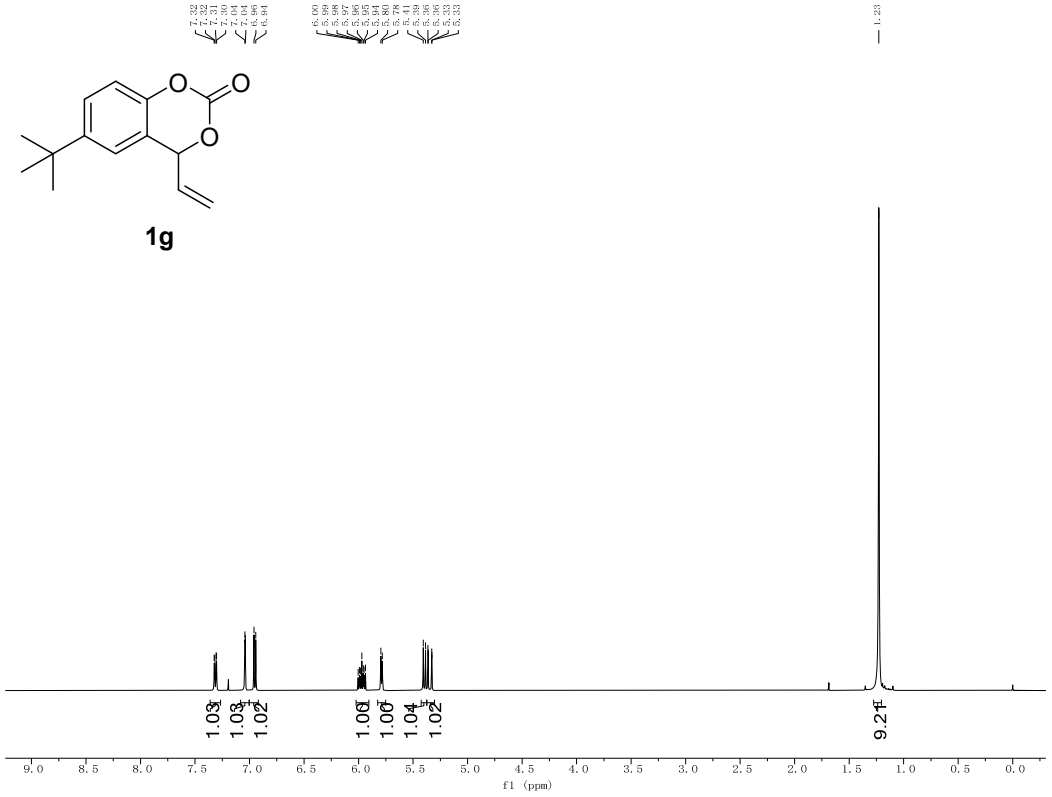


1g

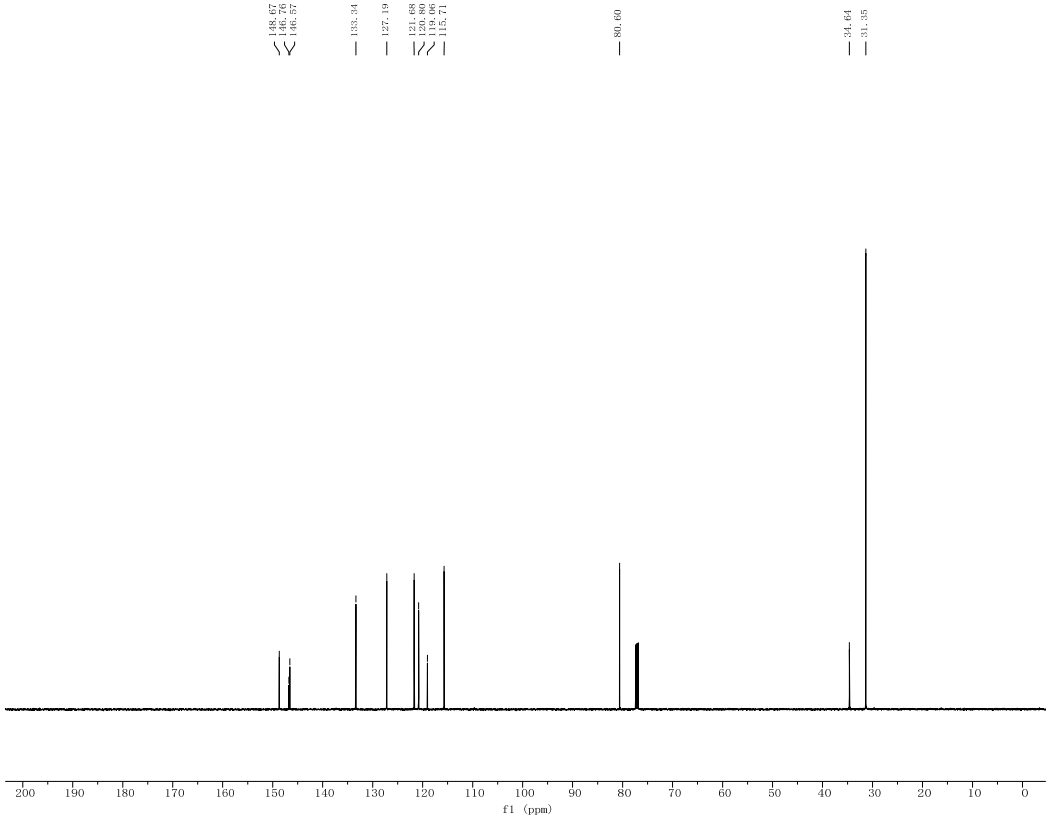
^{13}C NMR (126 MHz, $CDCl_3$)



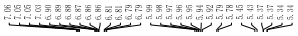
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

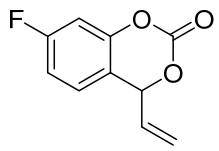


^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)





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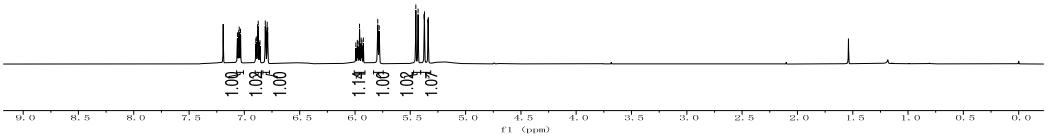
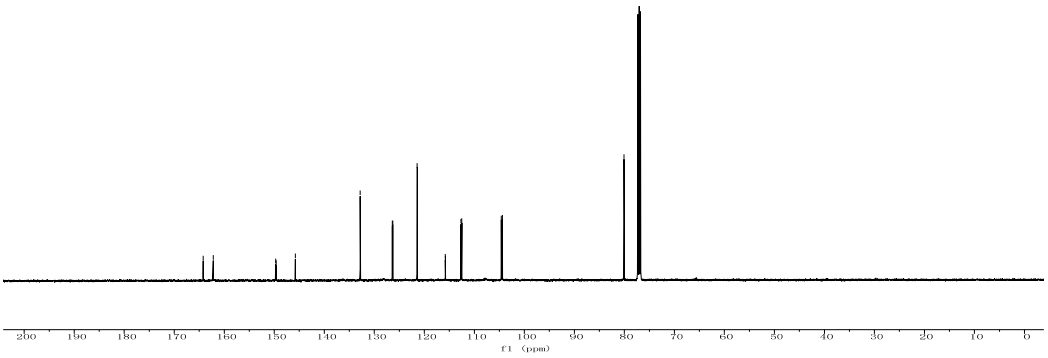
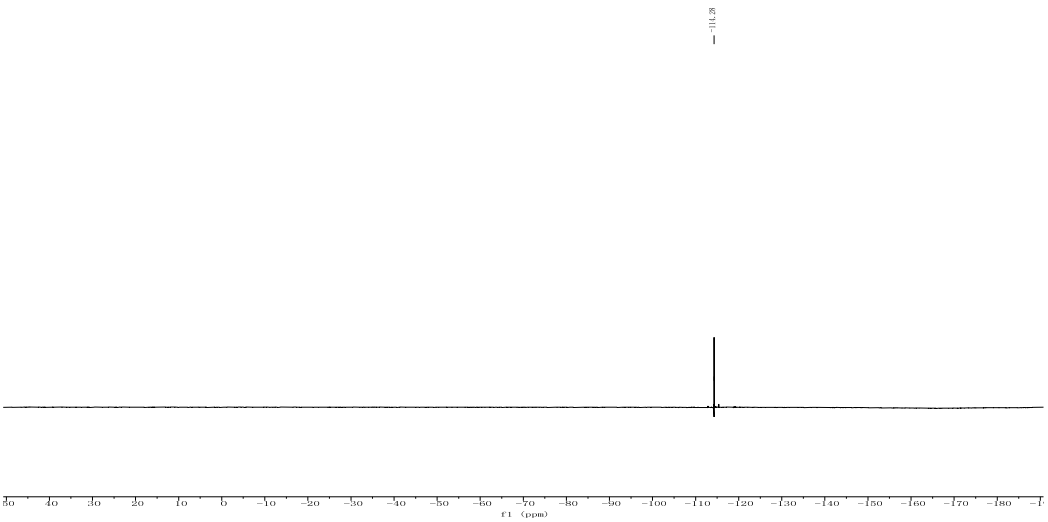


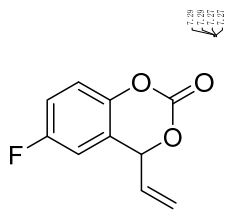
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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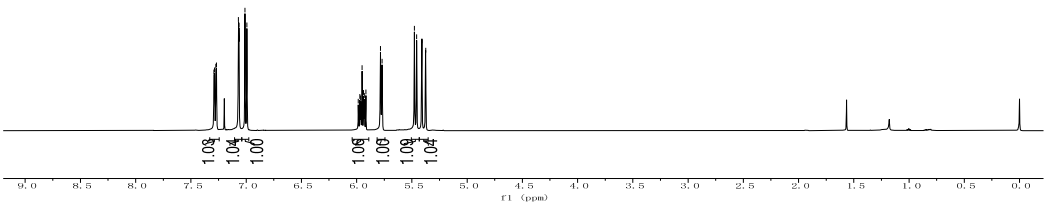
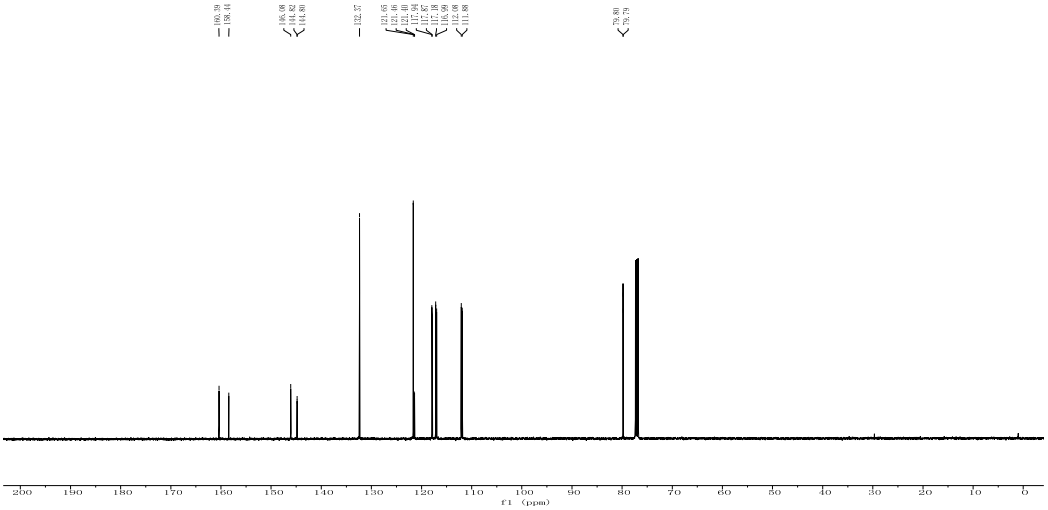
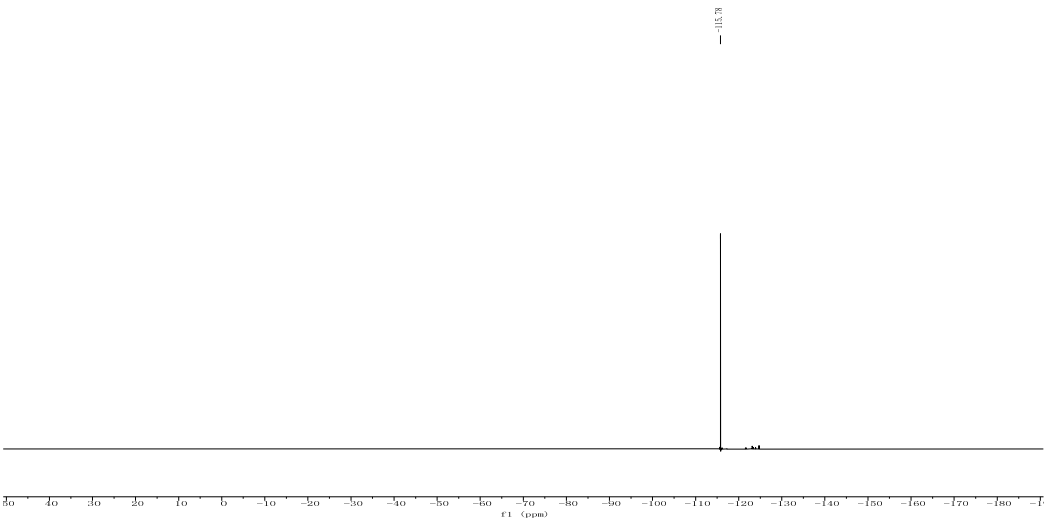


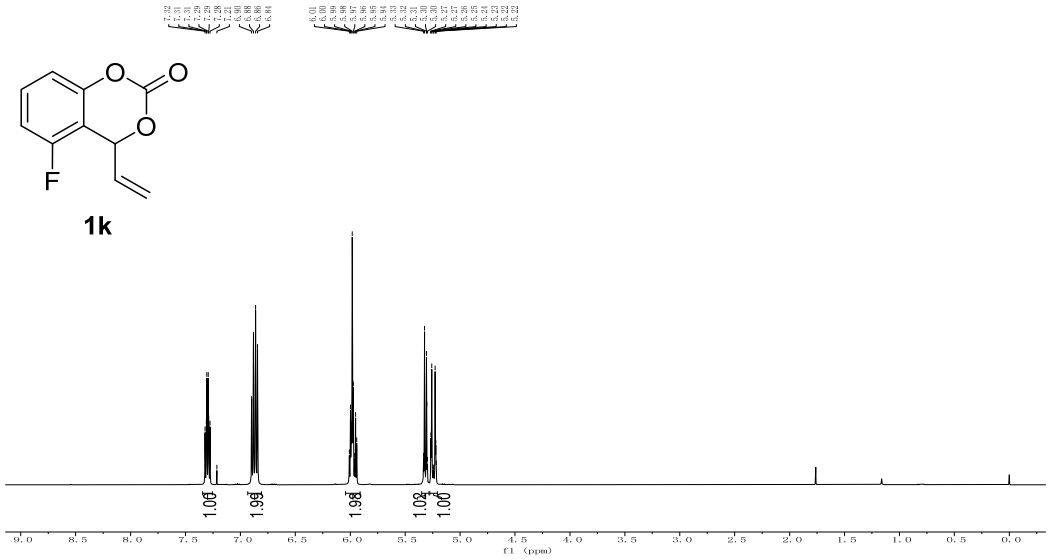
^{13}C NMR (126 MHz, $CDCl_3$)



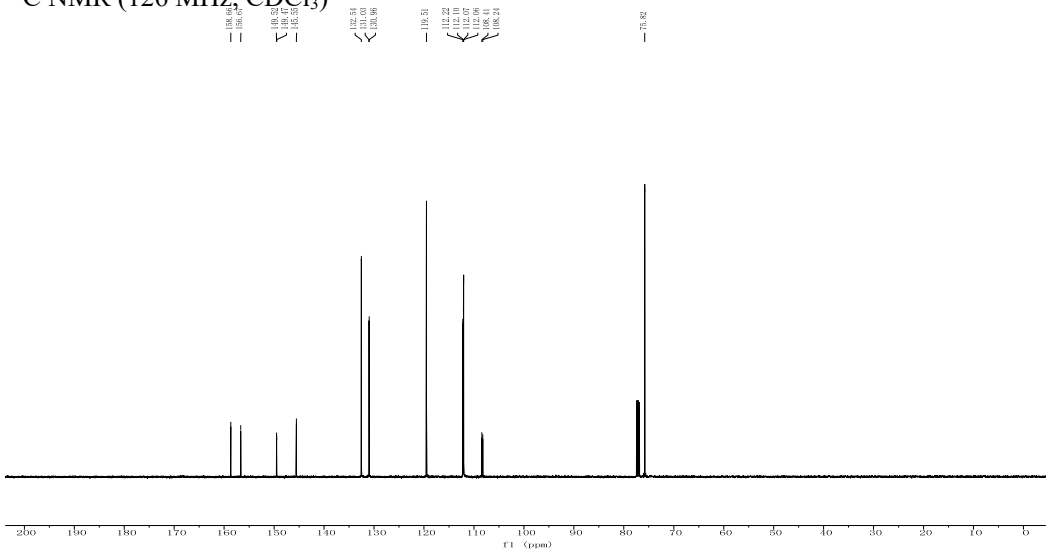
^{19}F NMR (471 MHz, $CDCl_3$)



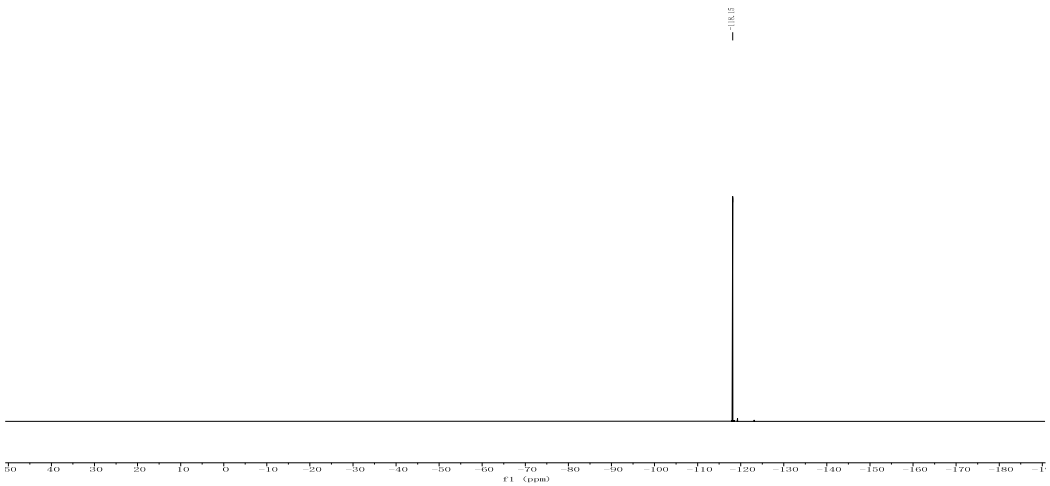
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



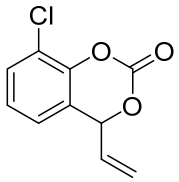
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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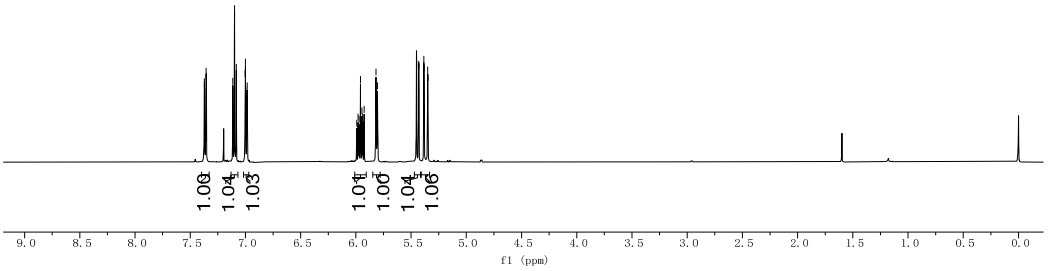
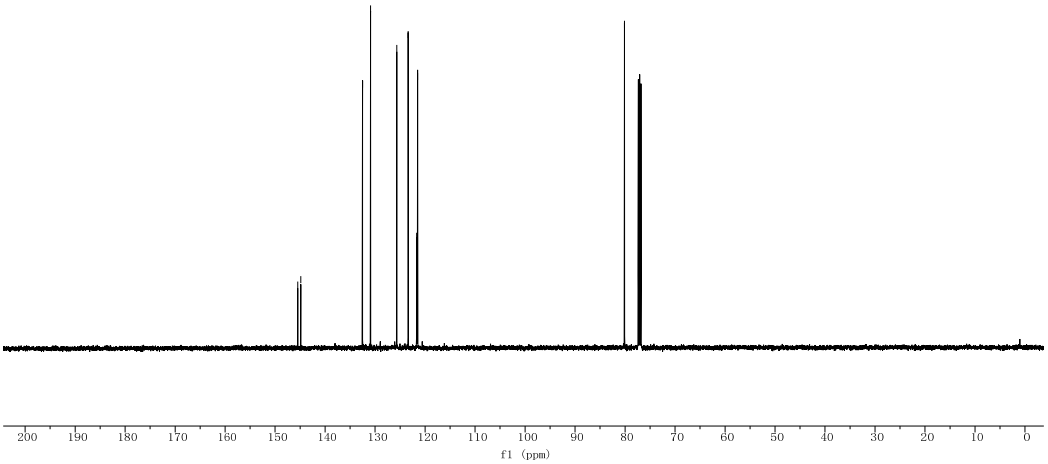
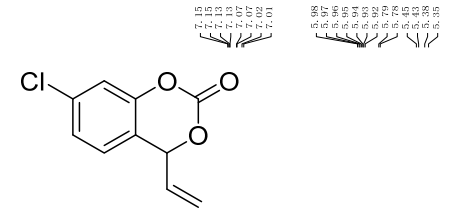


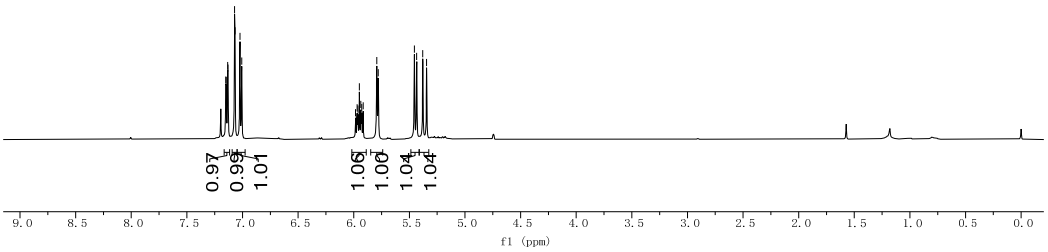
^{13}C NMR (126 MHz, $CDCl_3$)



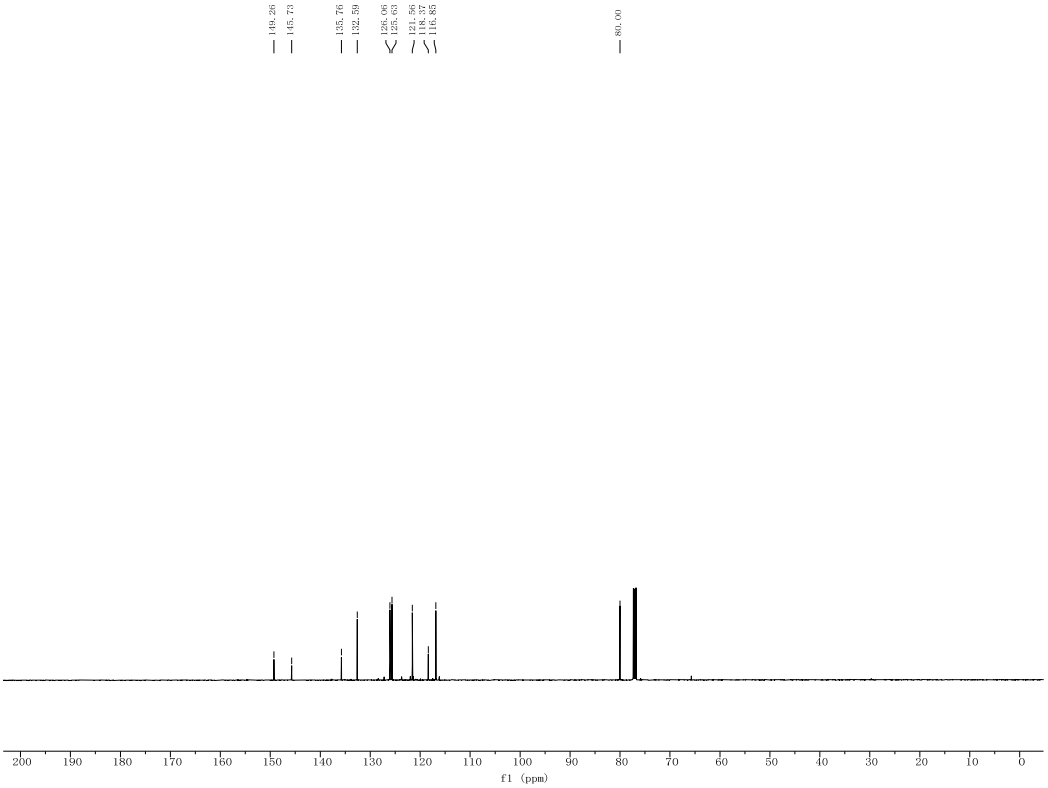
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



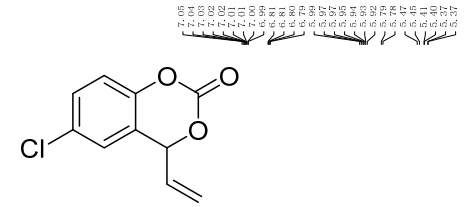
1m



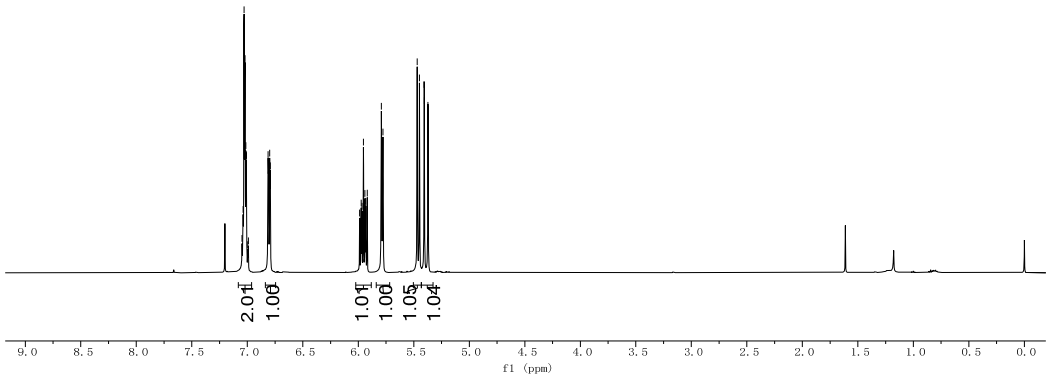
^{13}C NMR (126 MHz, $CDCl_3$)



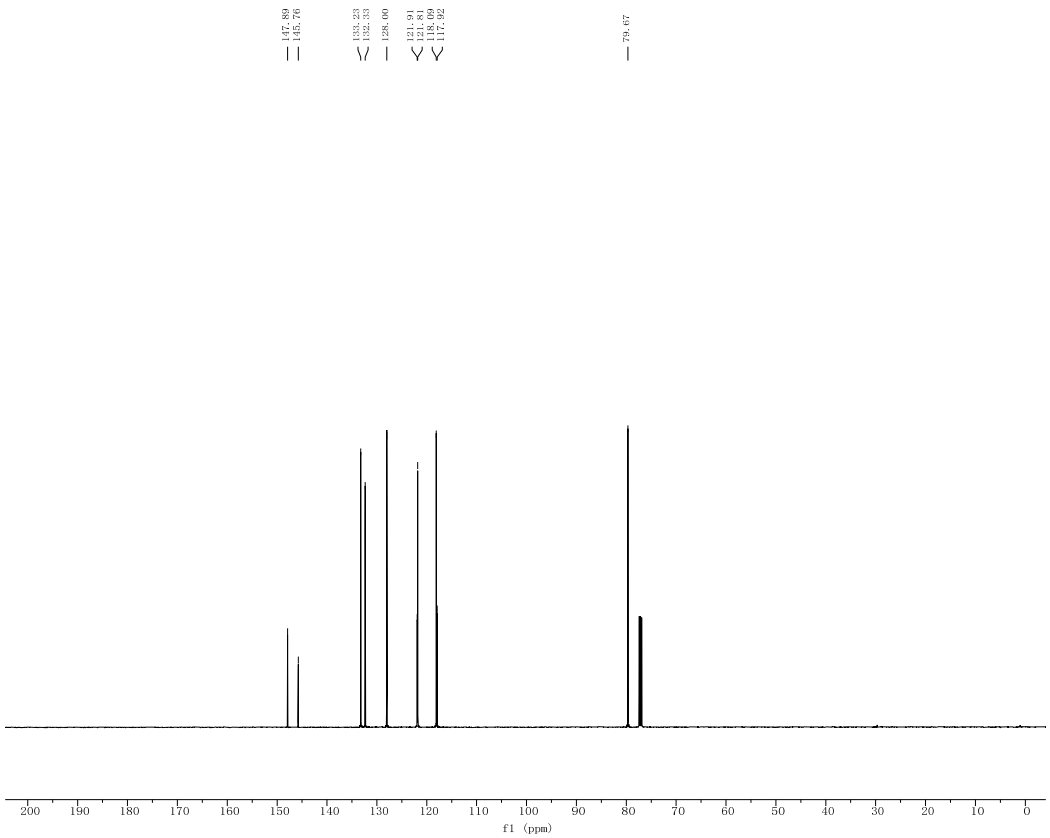
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



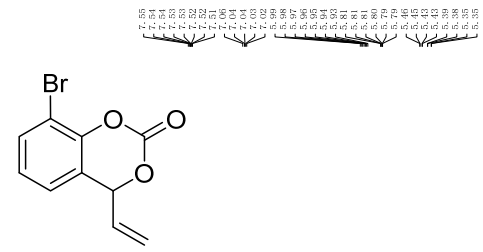
1n



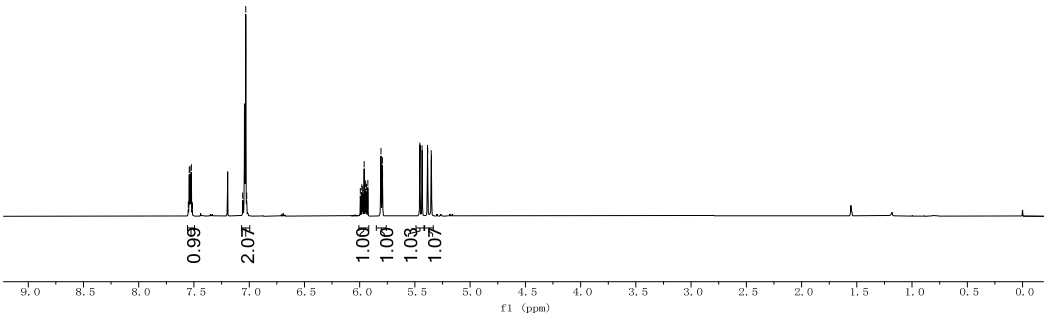
^{13}C NMR (126 MHz, $CDCl_3$)



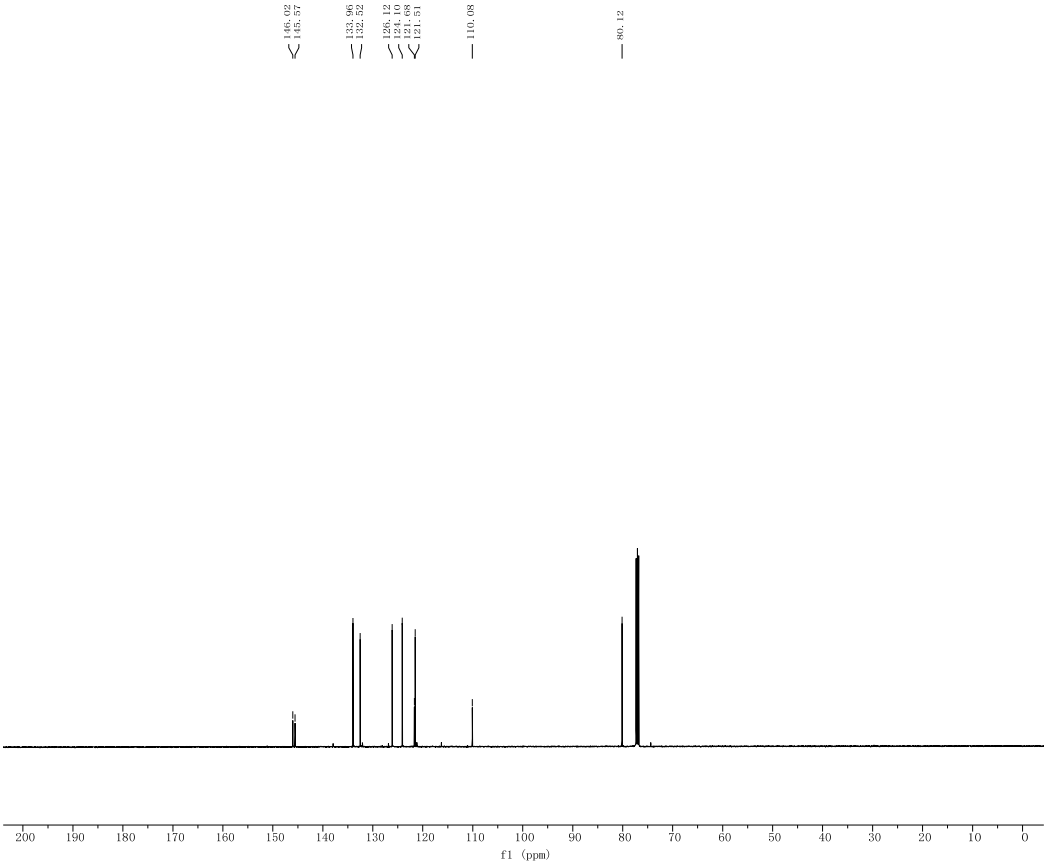
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



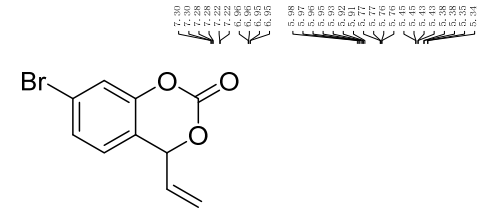
1o



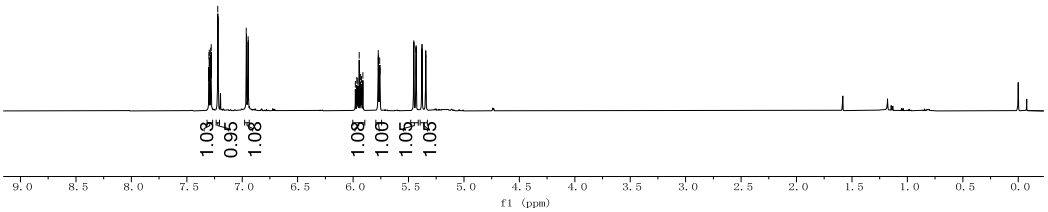
^{13}C NMR (126 MHz, $CDCl_3$)



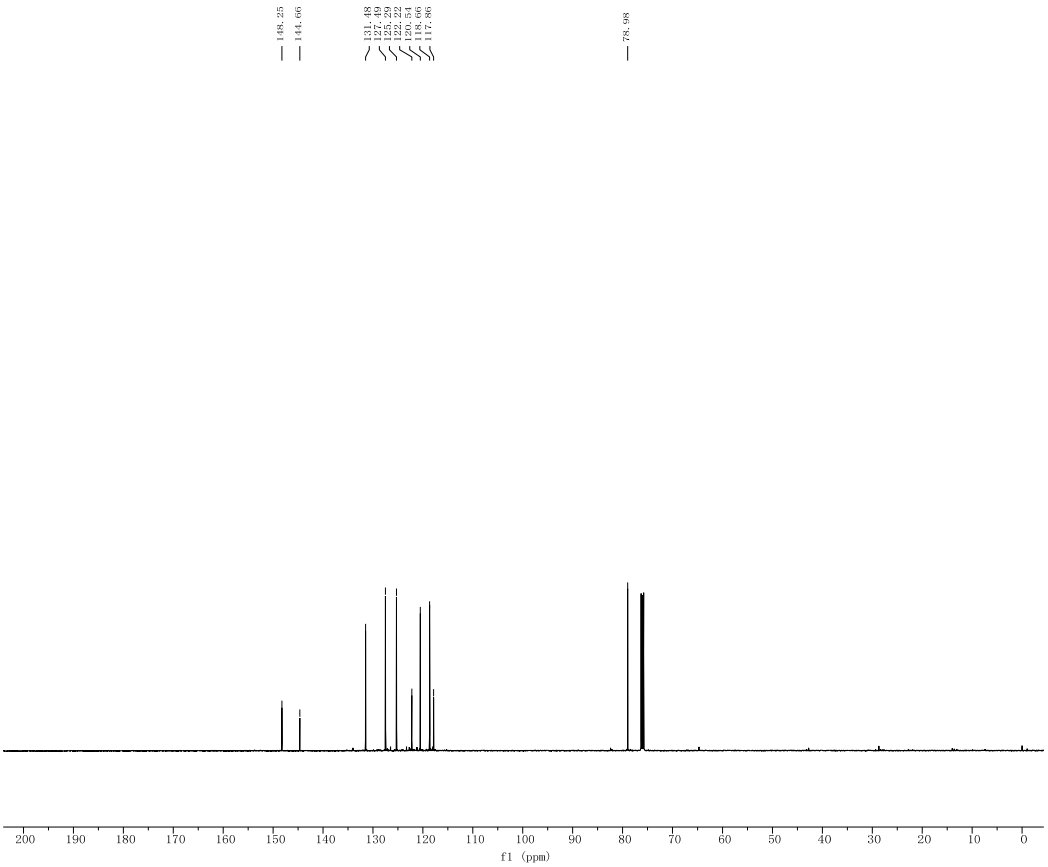
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



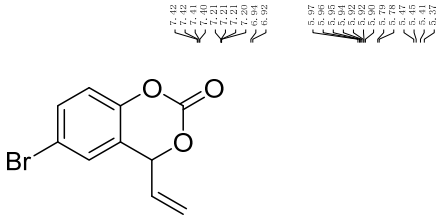
1p



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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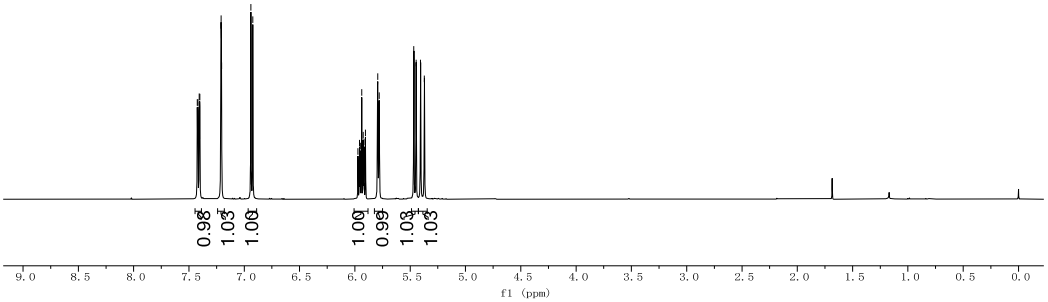
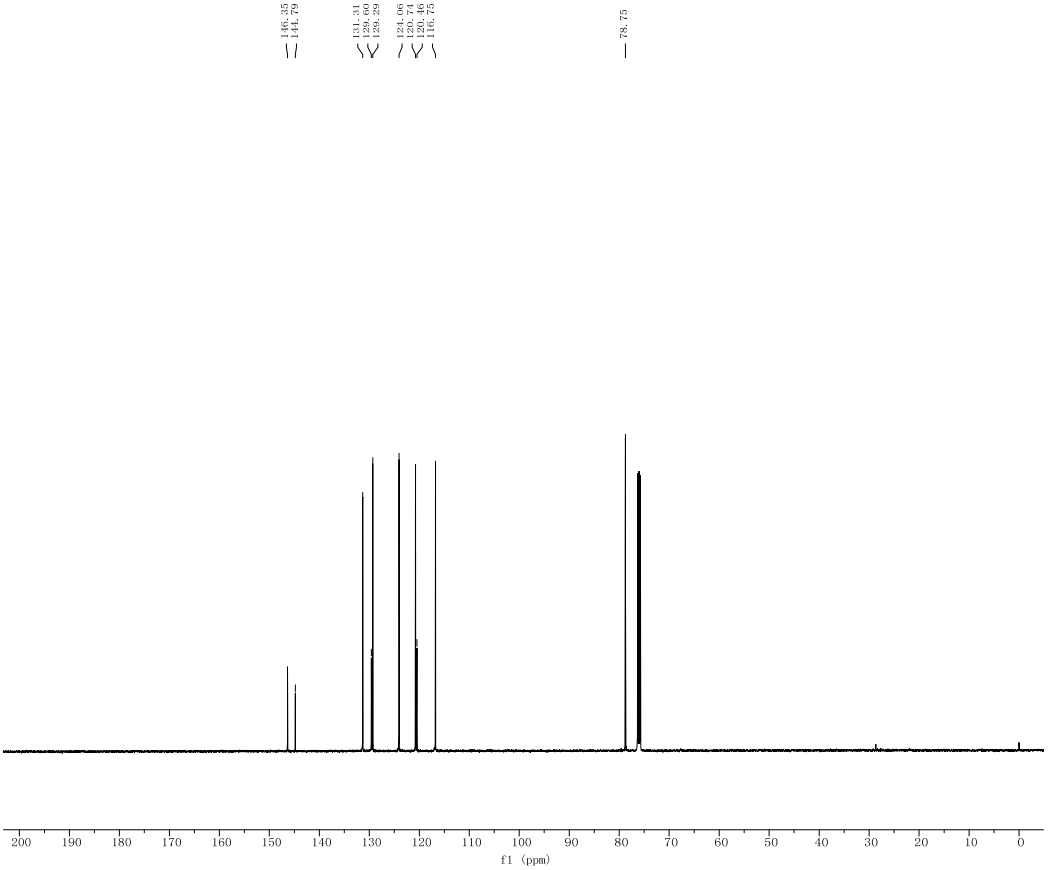
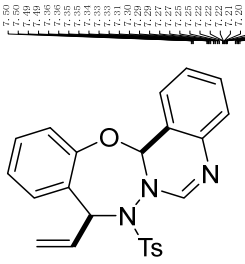


^{13}C NMR spectrum (126 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR Spectra of All Products

^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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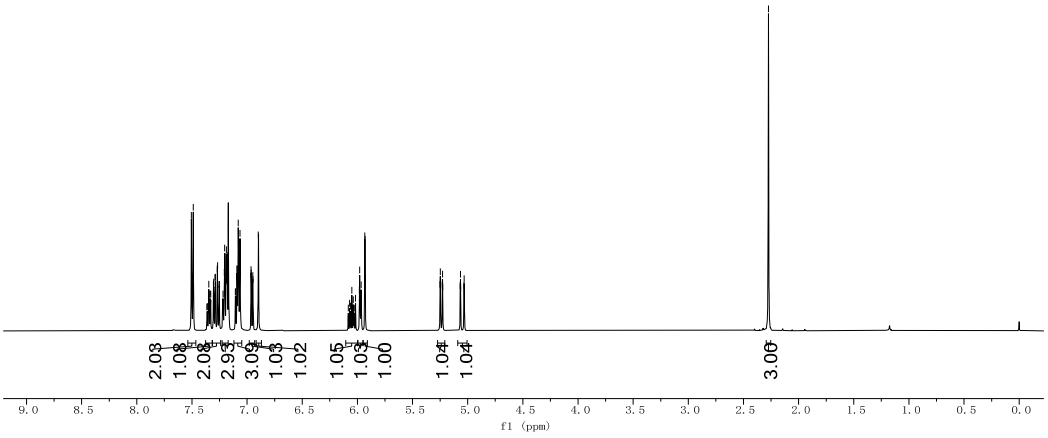
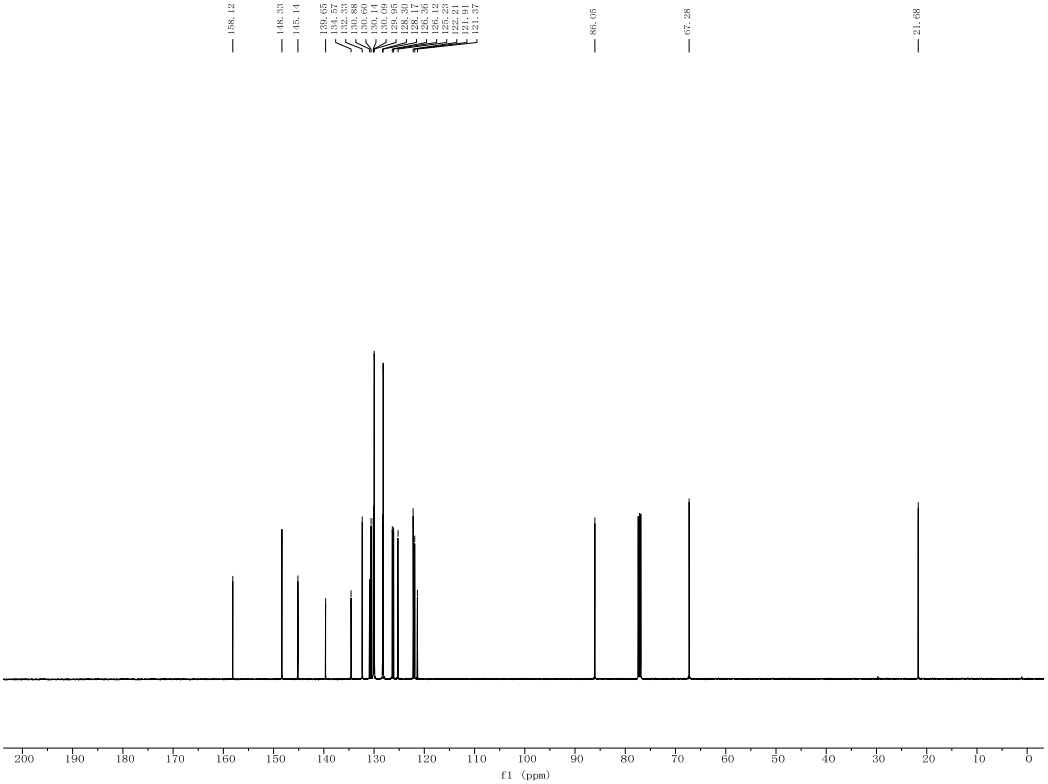
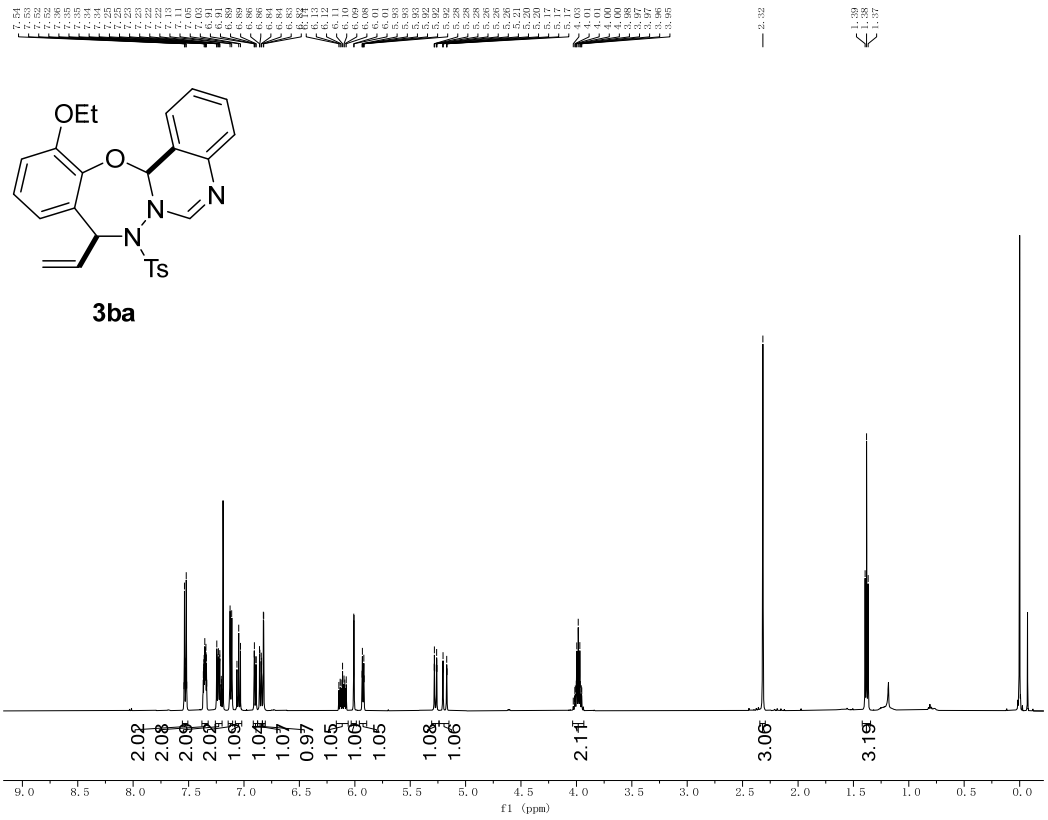


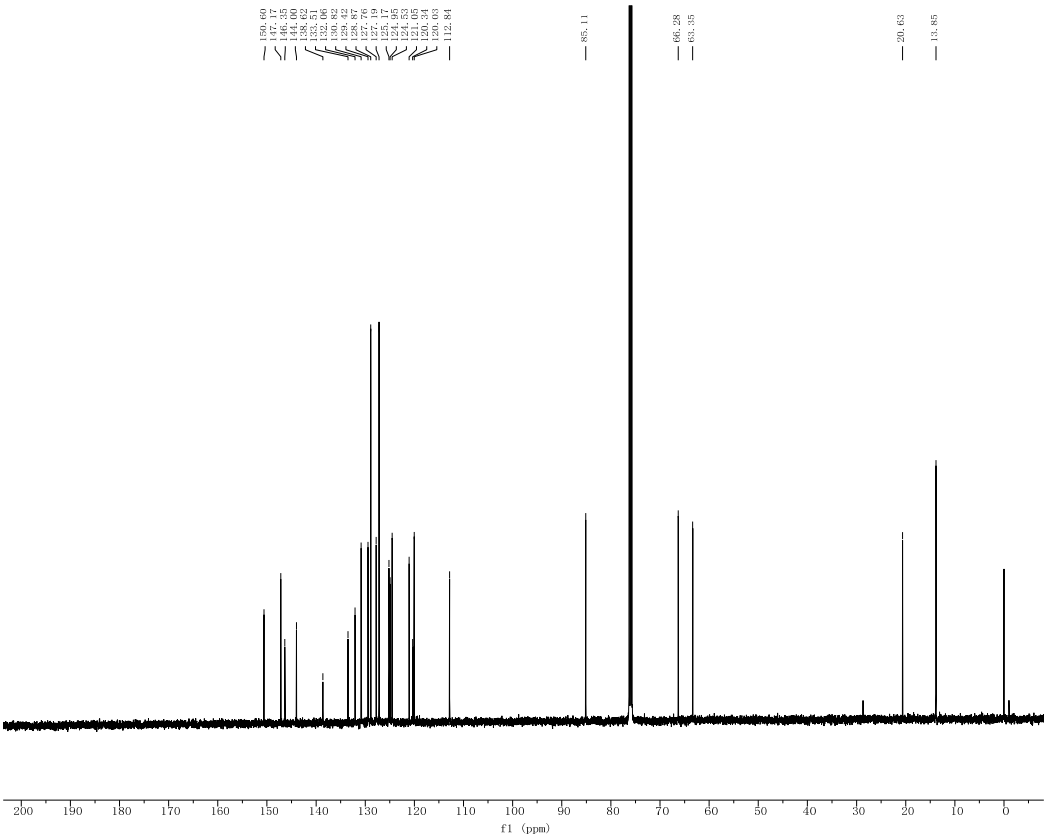
^{13}C NMR (126 MHz, $CDCl_3$)



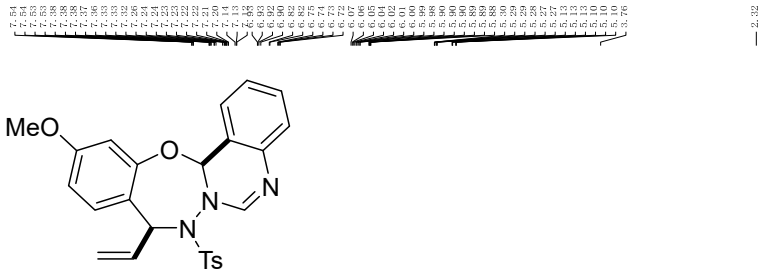
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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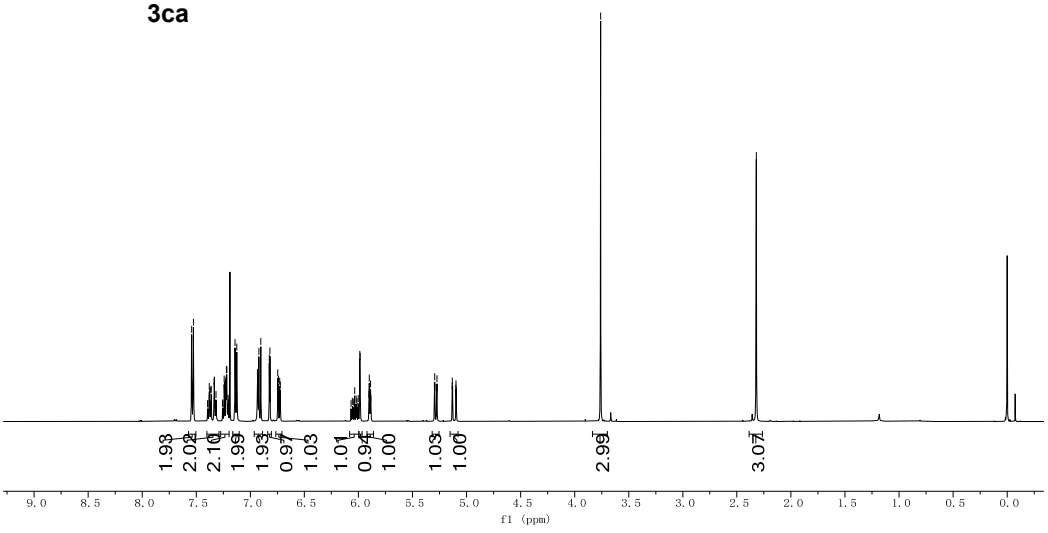
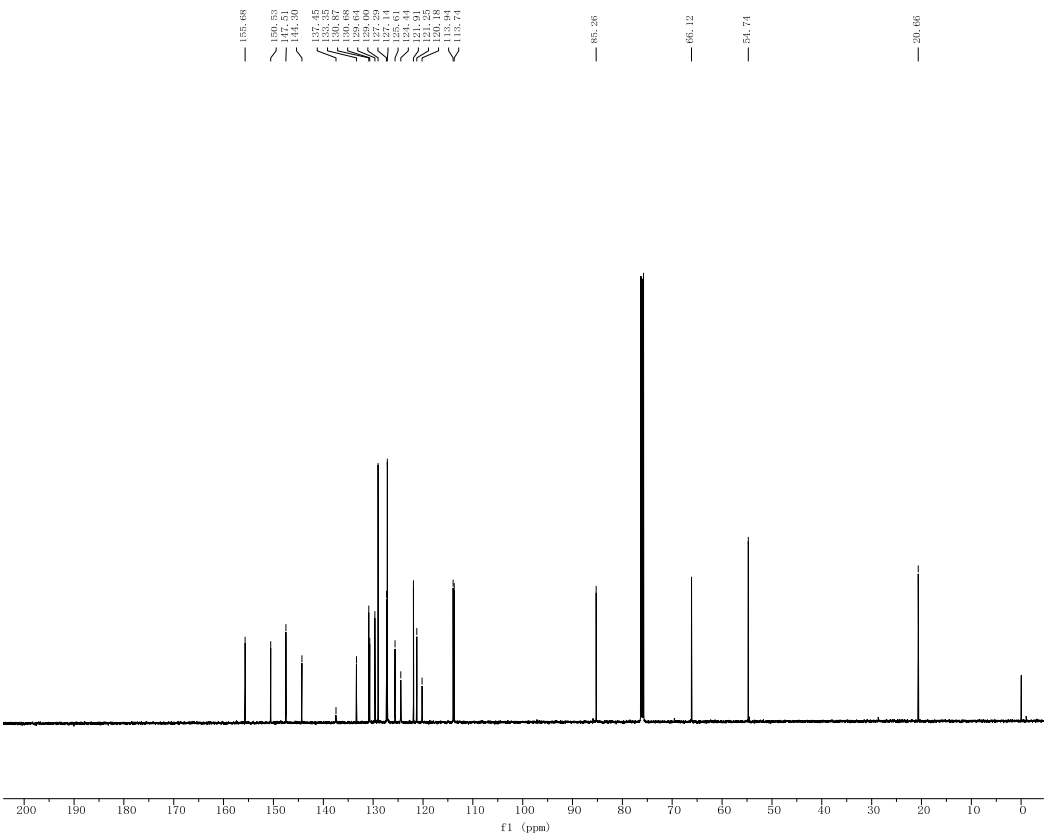
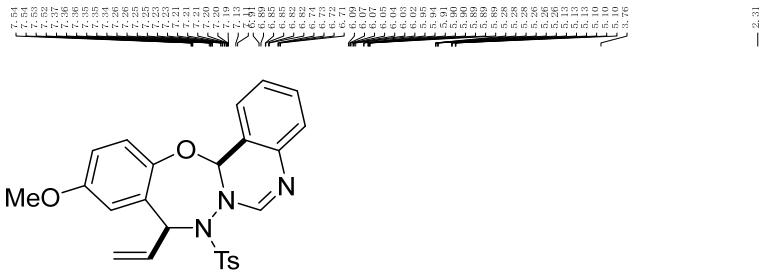


^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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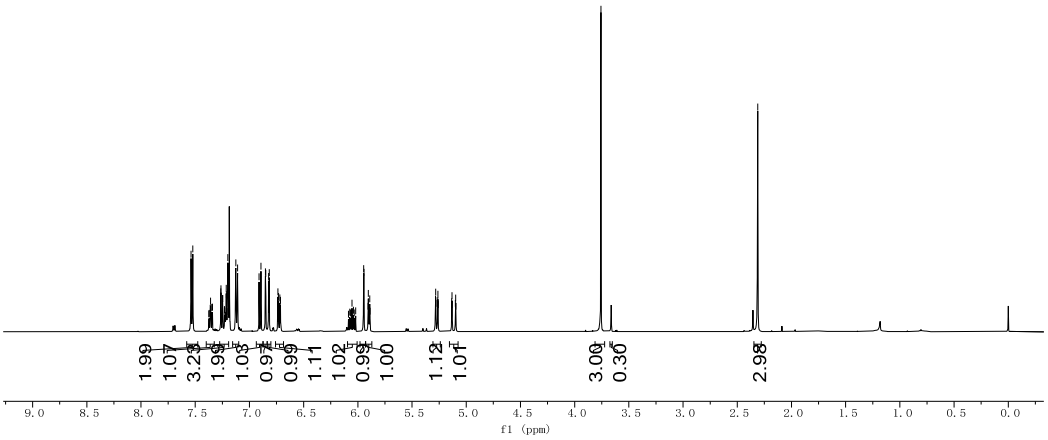
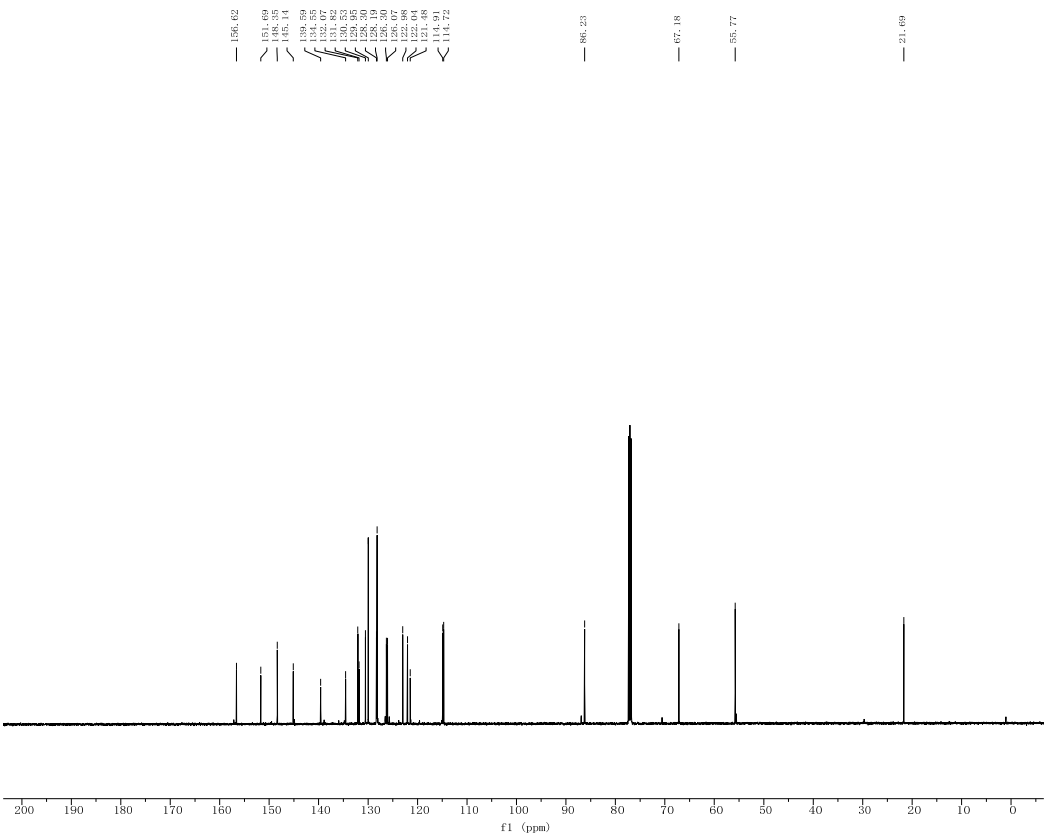
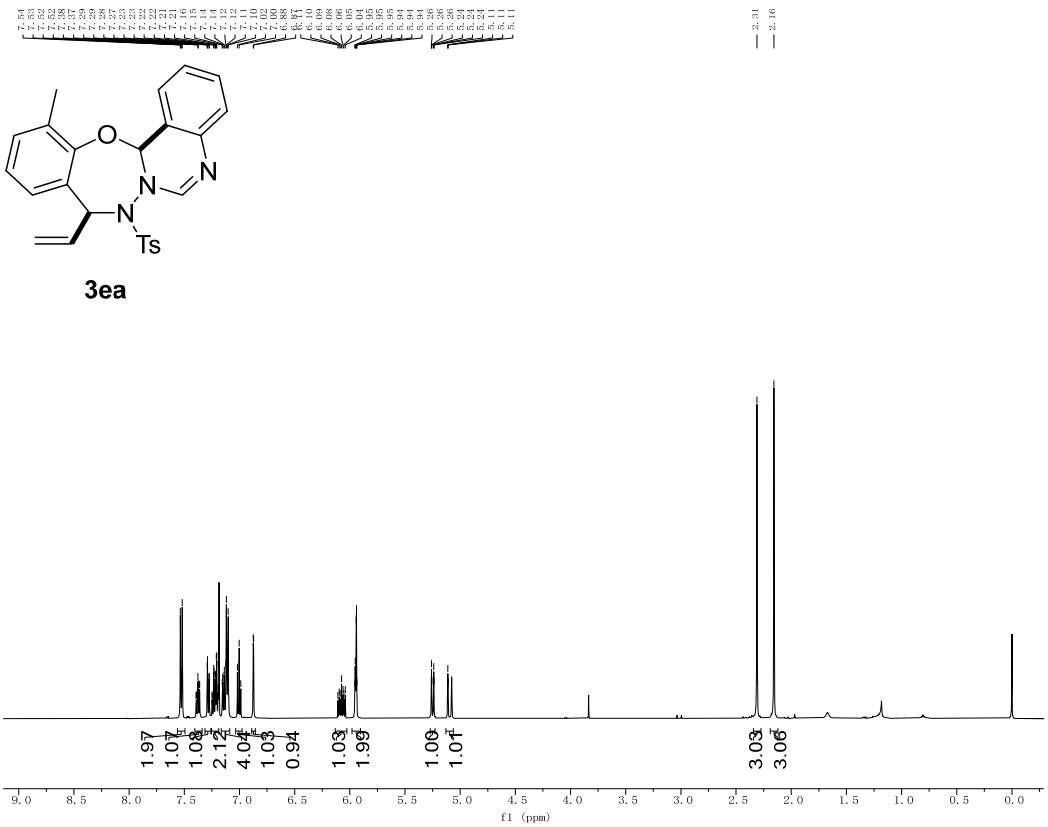


^{13}C NMR (126 MHz, $CDCl_3$)

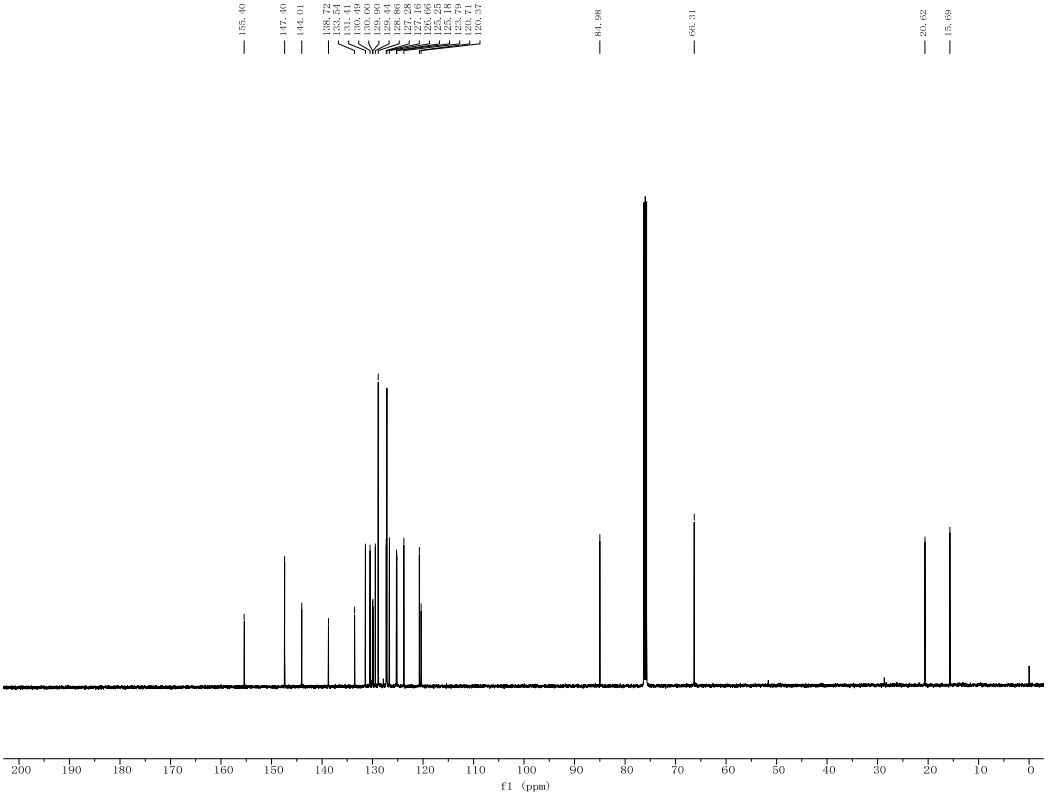


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

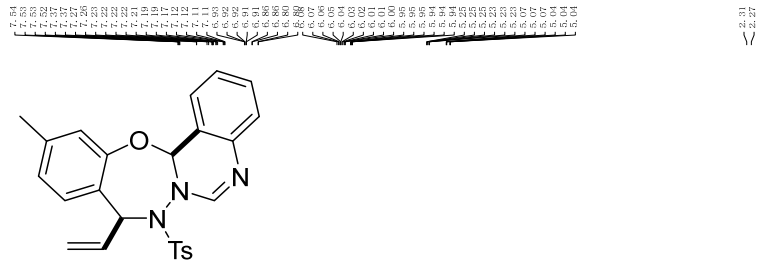


3ea

^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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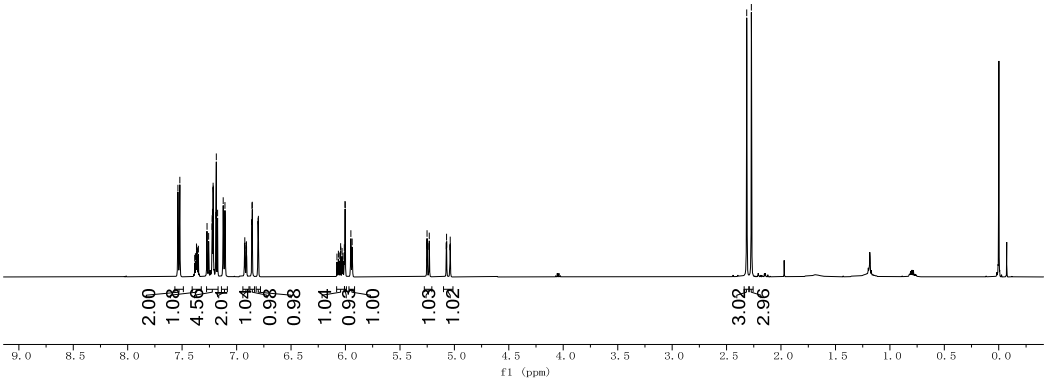
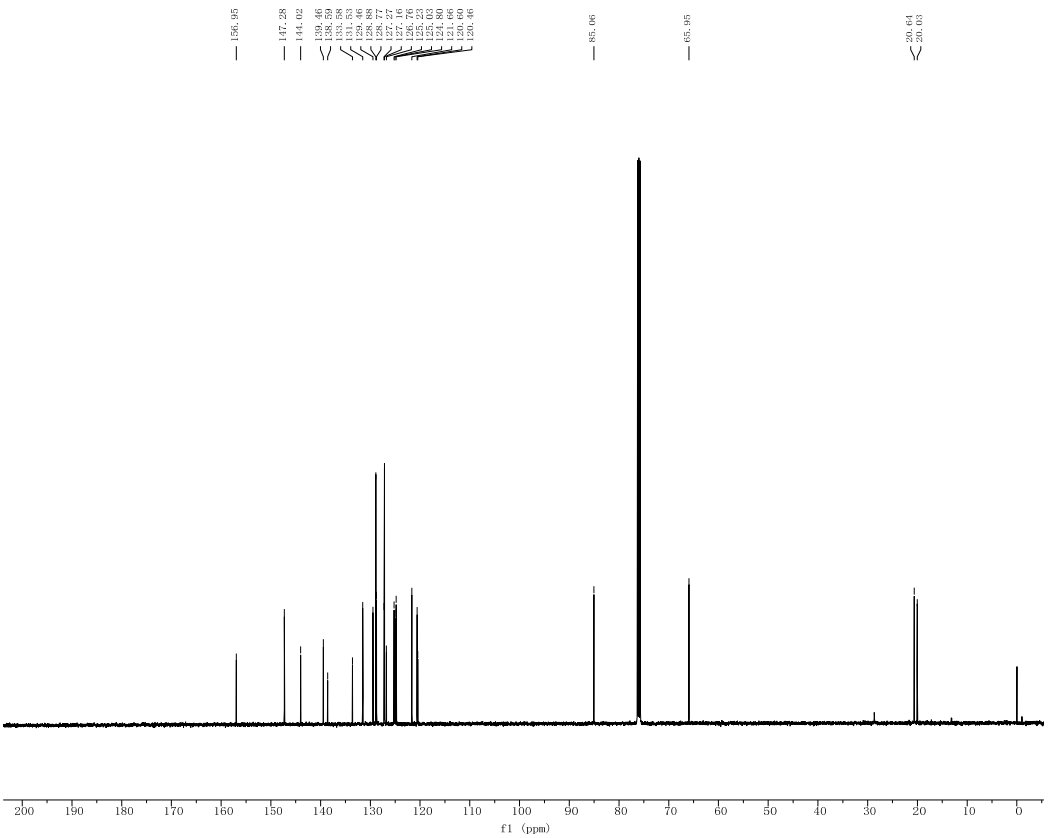
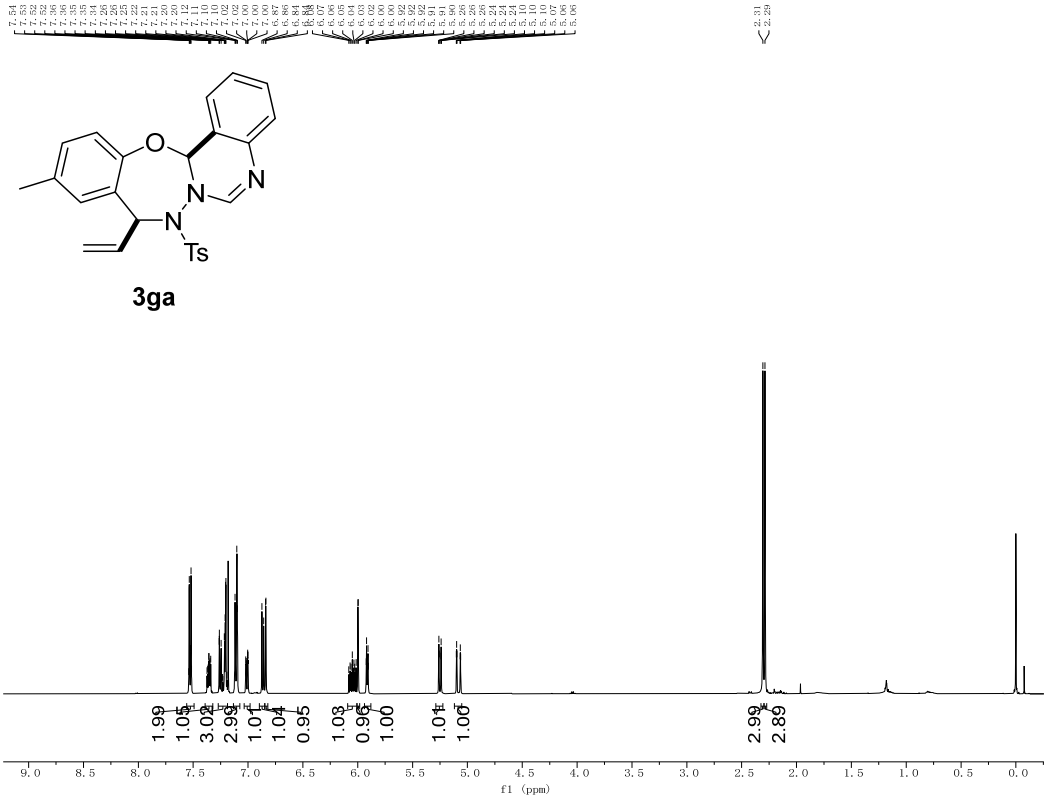


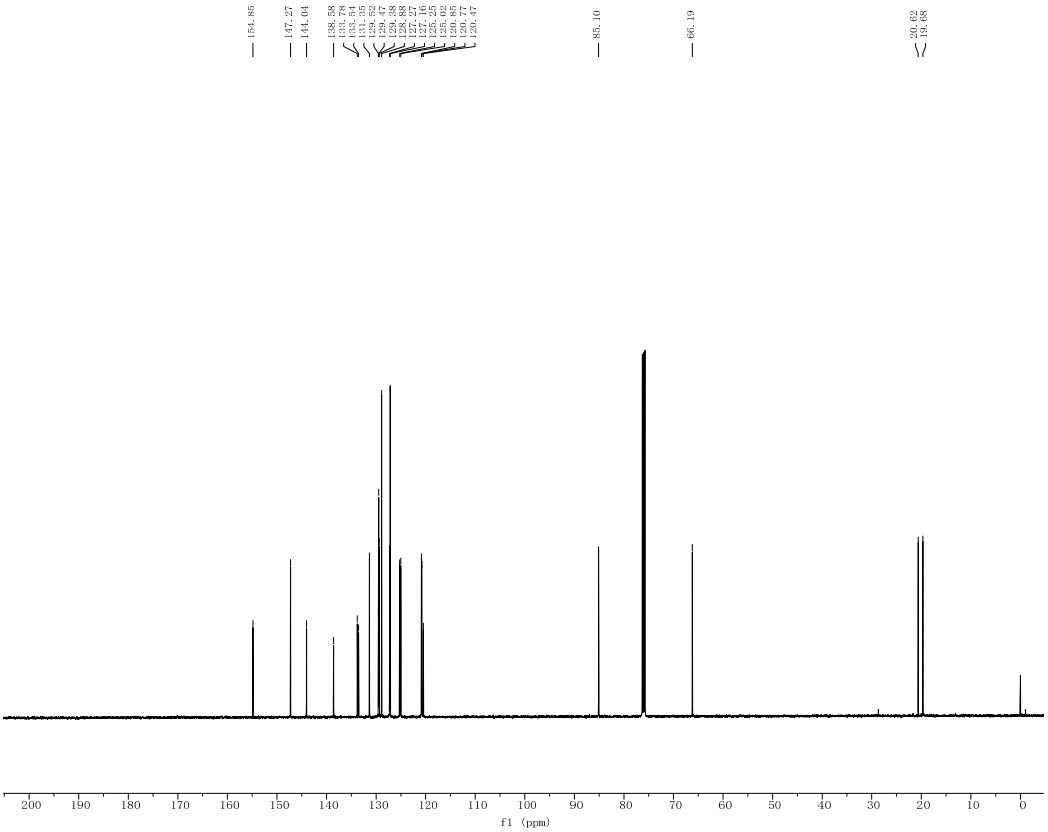
^{13}C NMR (126 MHz, $CDCl_3$)



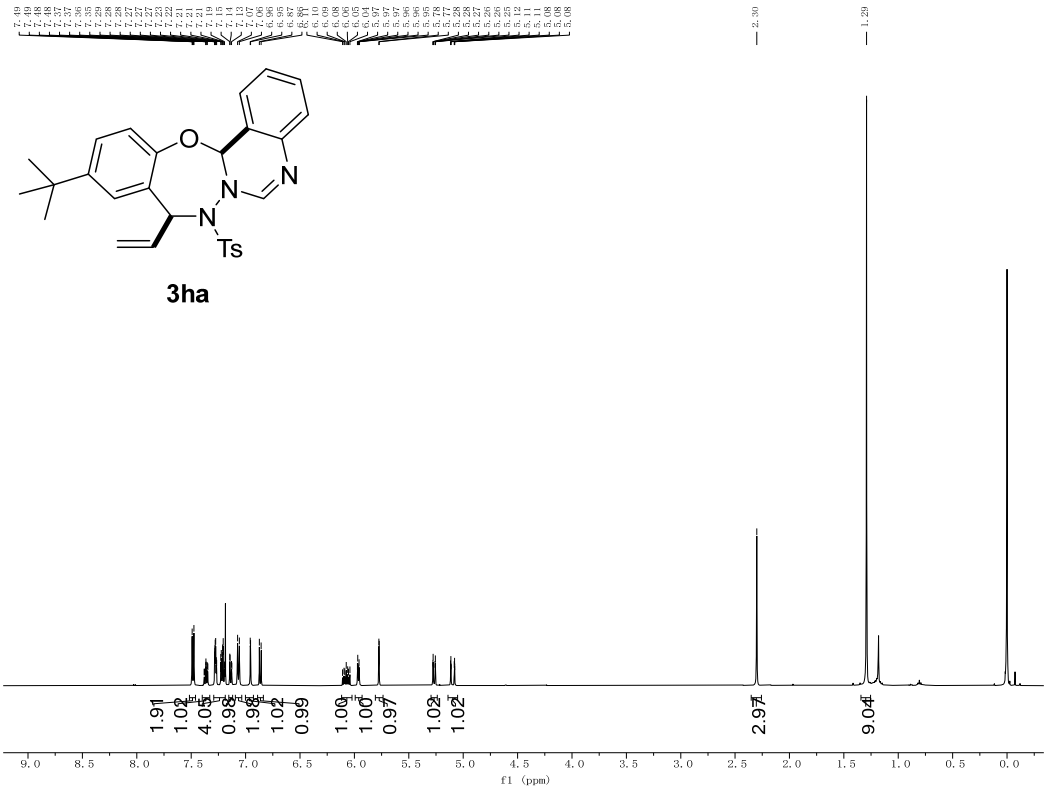
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



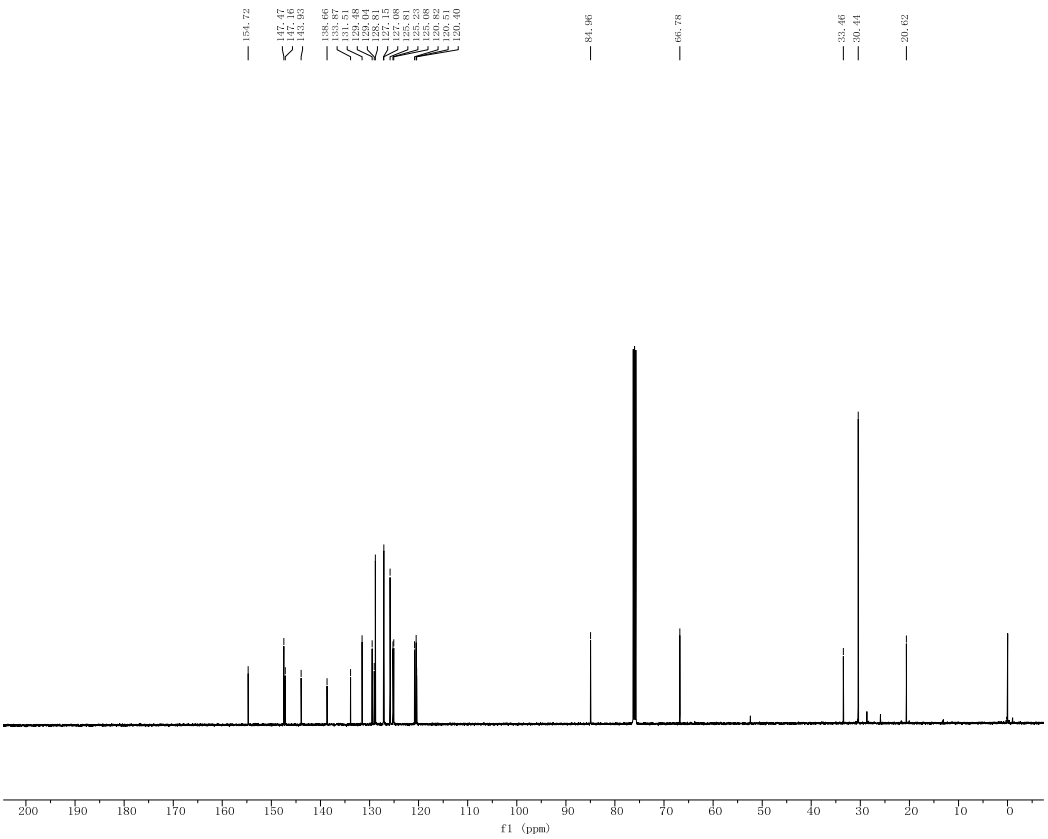
^{13}C NMR (126 MHz, $CDCl_3$)



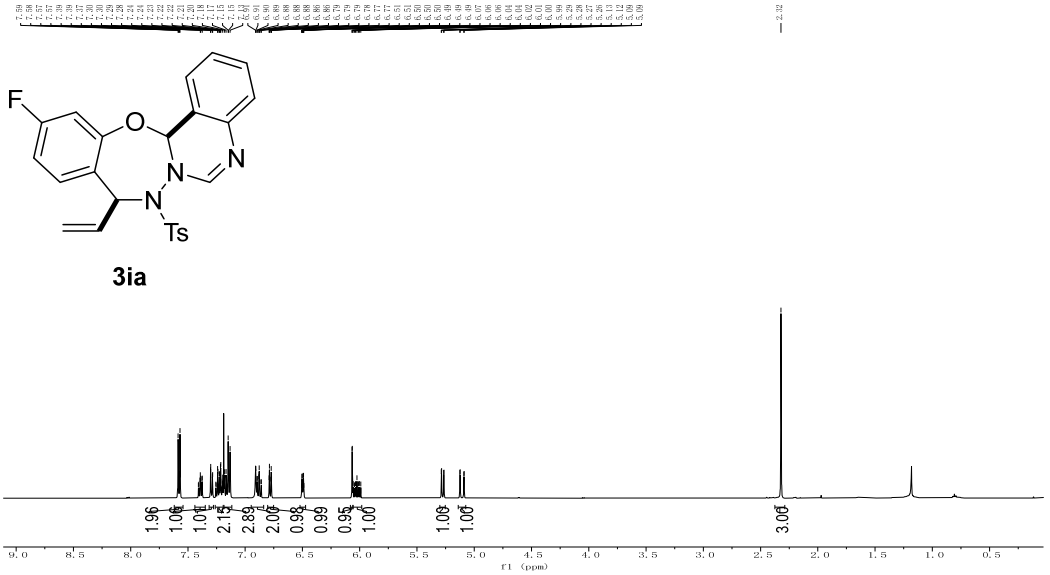
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

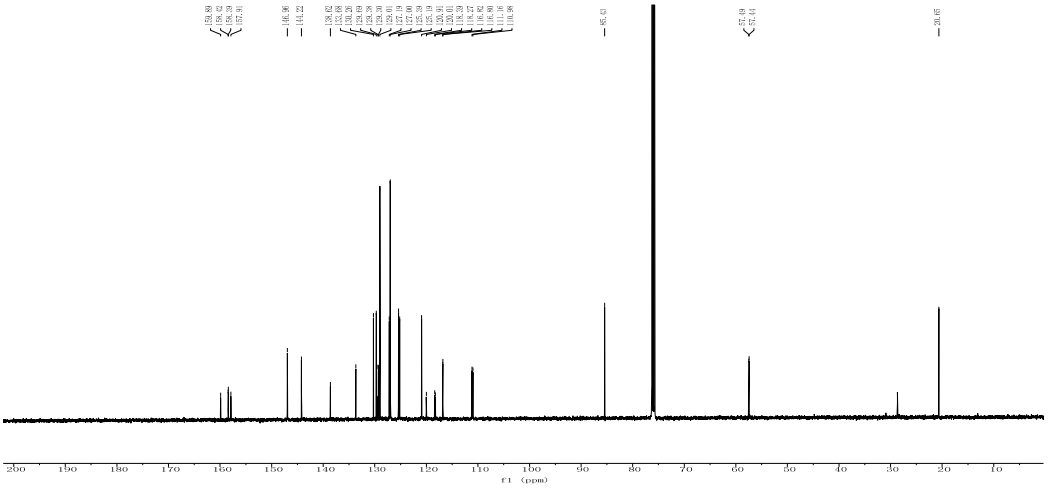


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

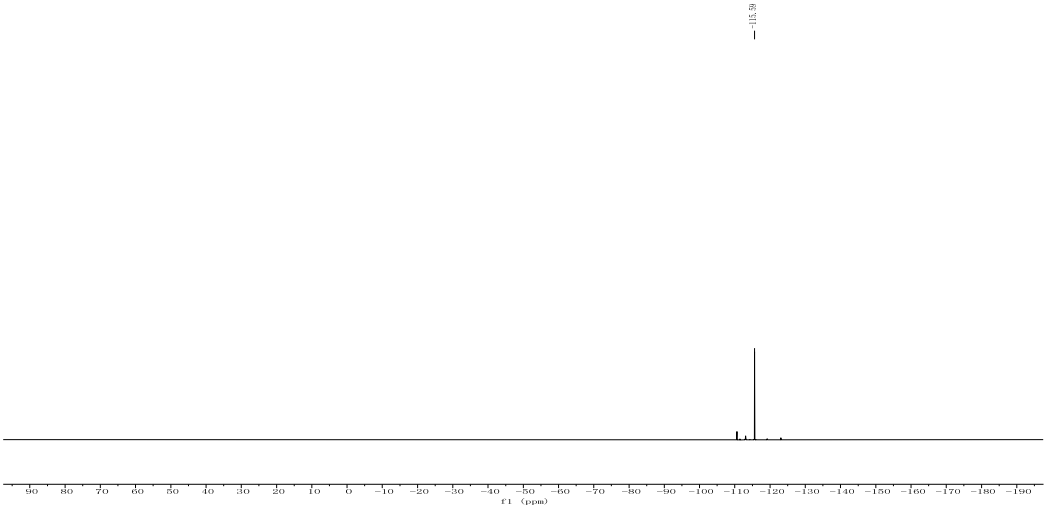


3ia

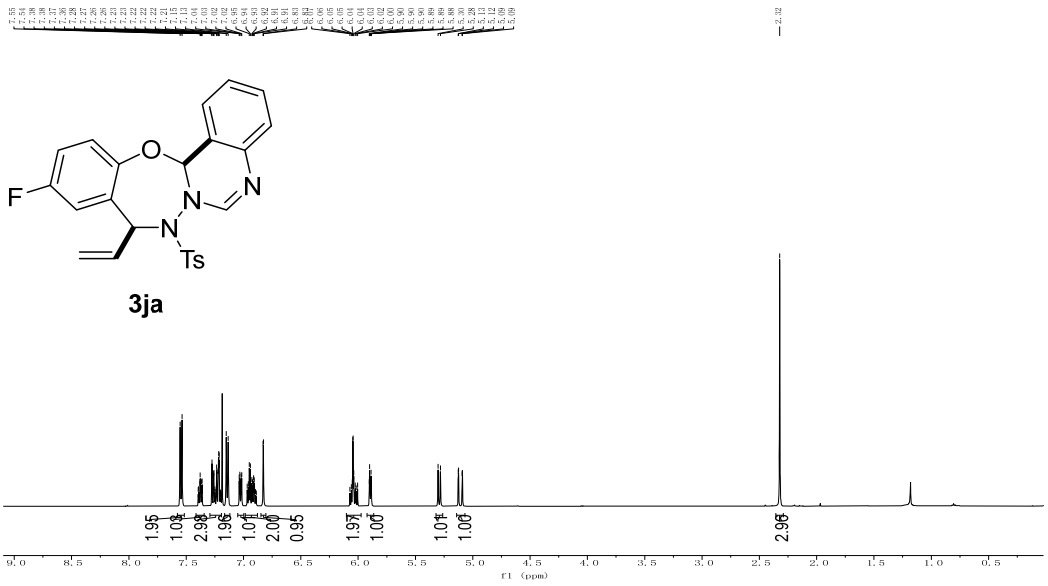
^{13}C NMR (126 MHz, $CDCl_3$)



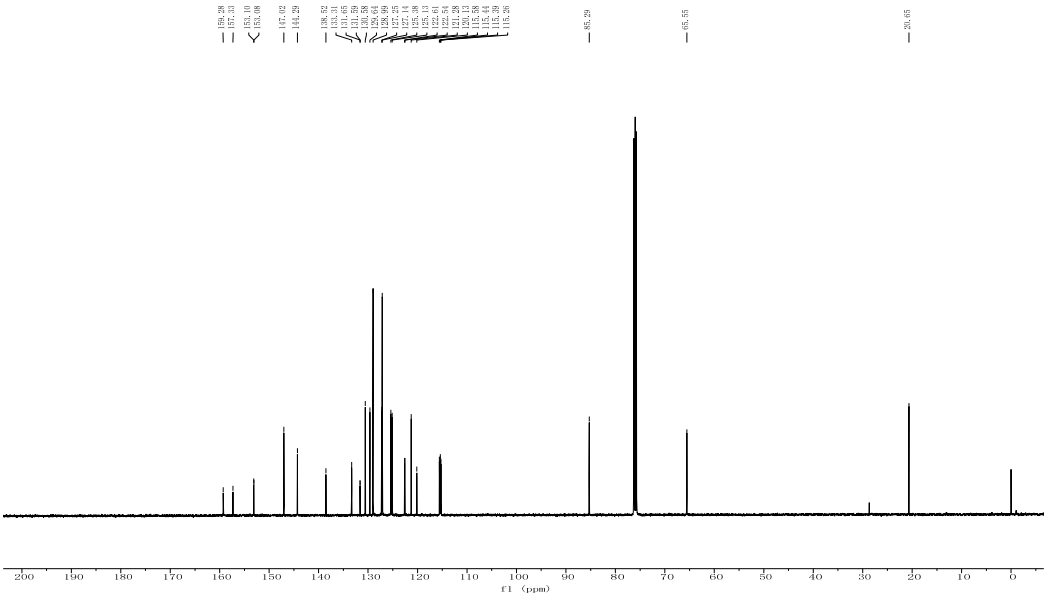
^{19}F NMR (471 MHz, $CDCl_3$)



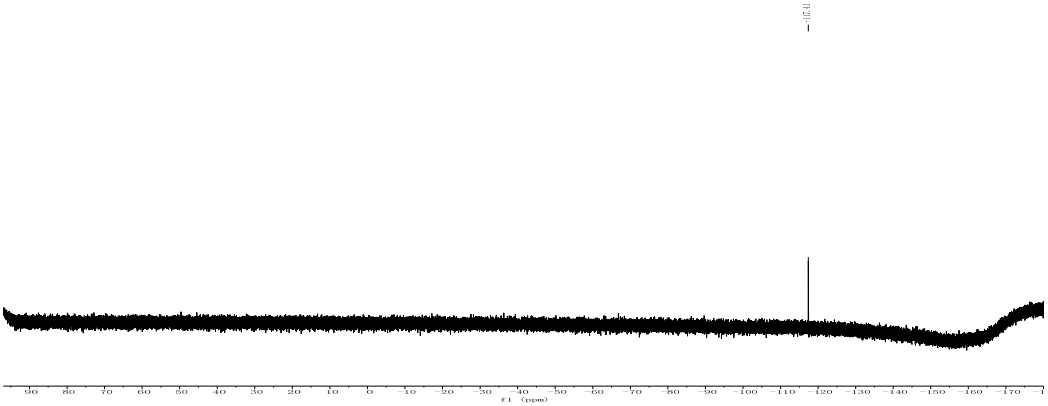
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



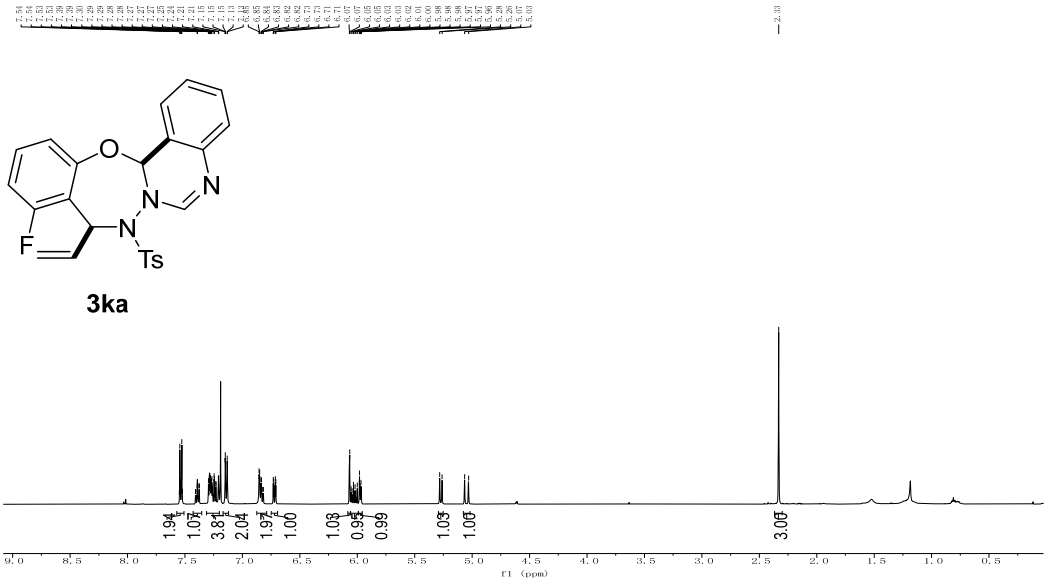
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

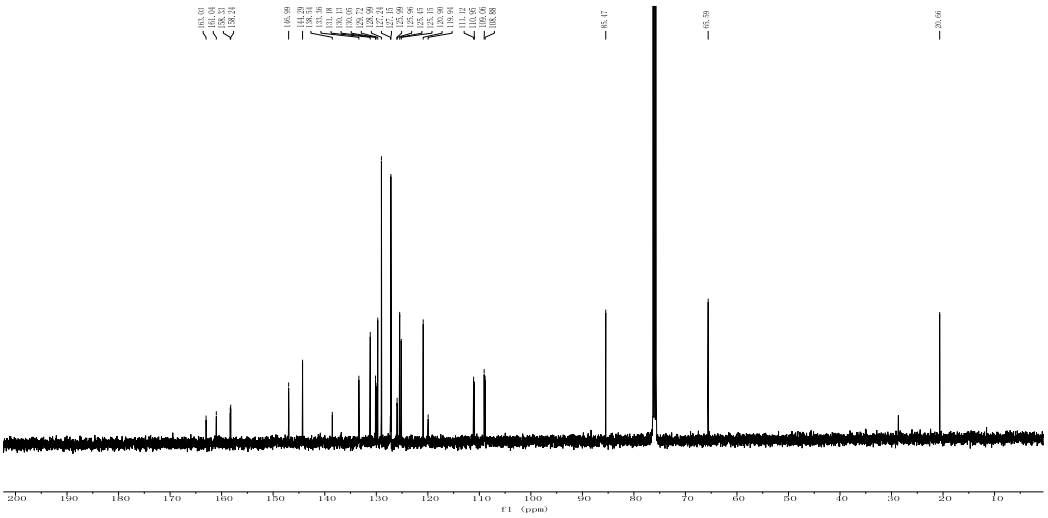


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

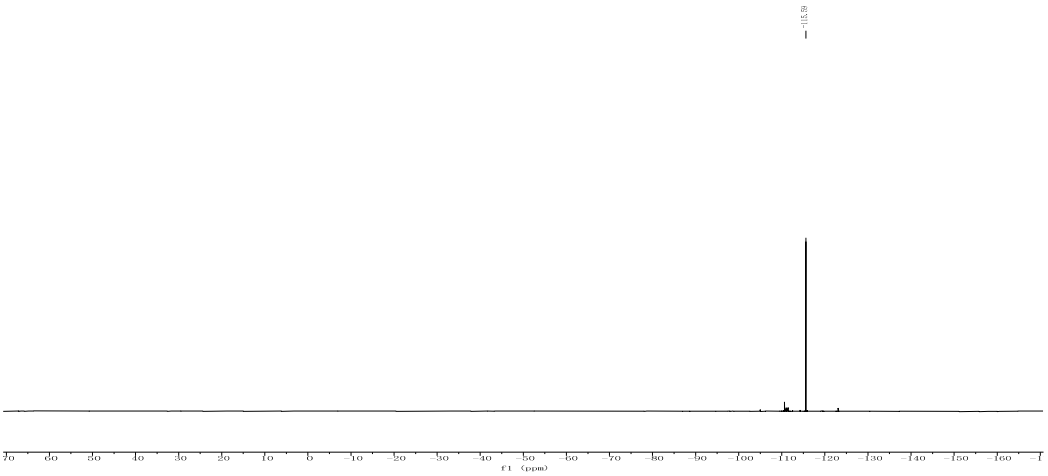


3ka

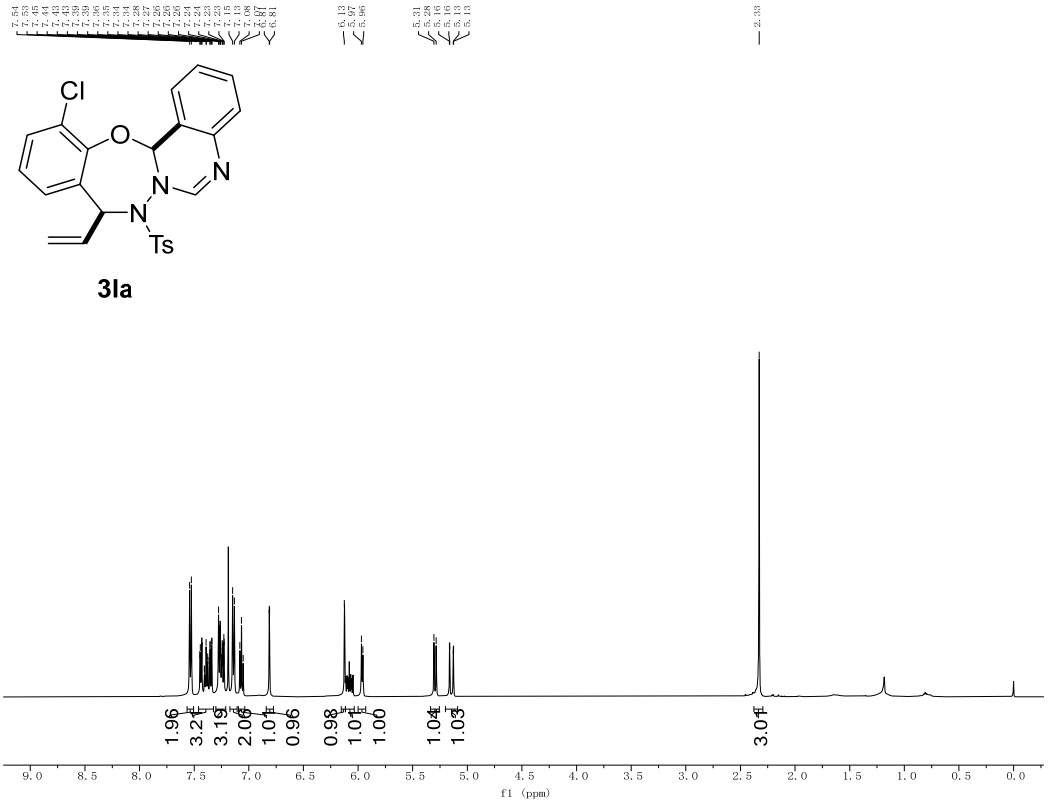
^{13}C NMR (126 MHz, $CDCl_3$)



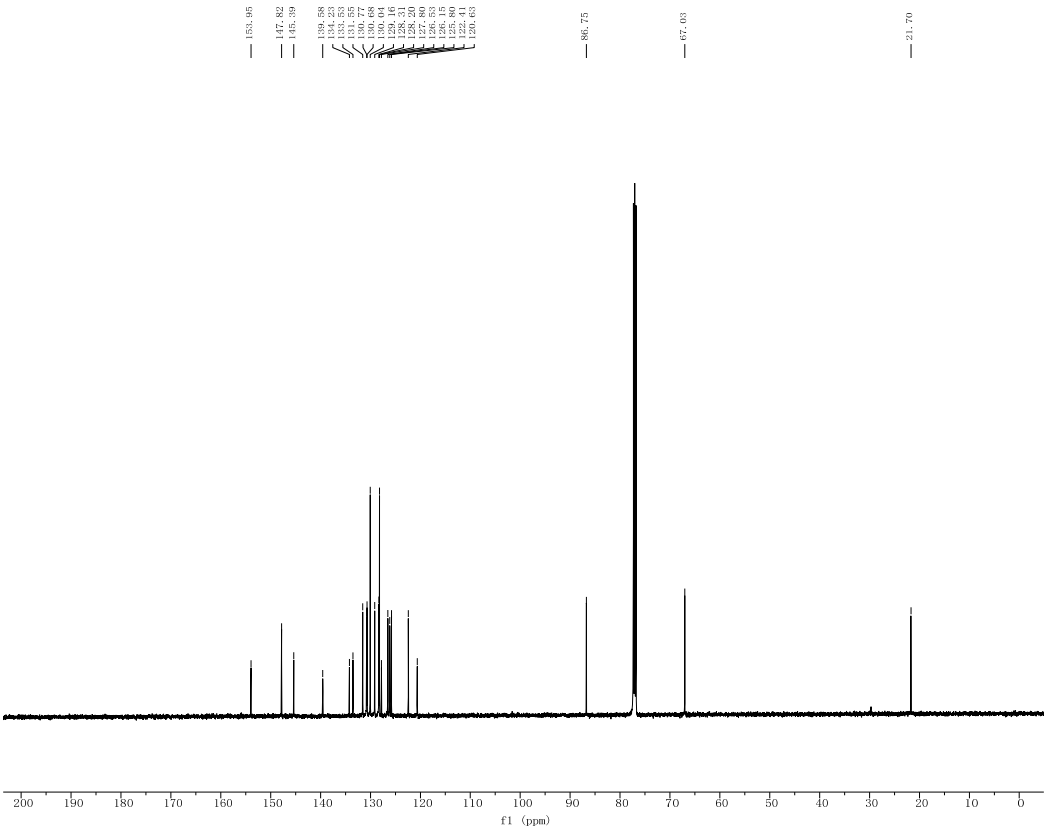
^{19}F NMR (471 MHz, $CDCl_3$)



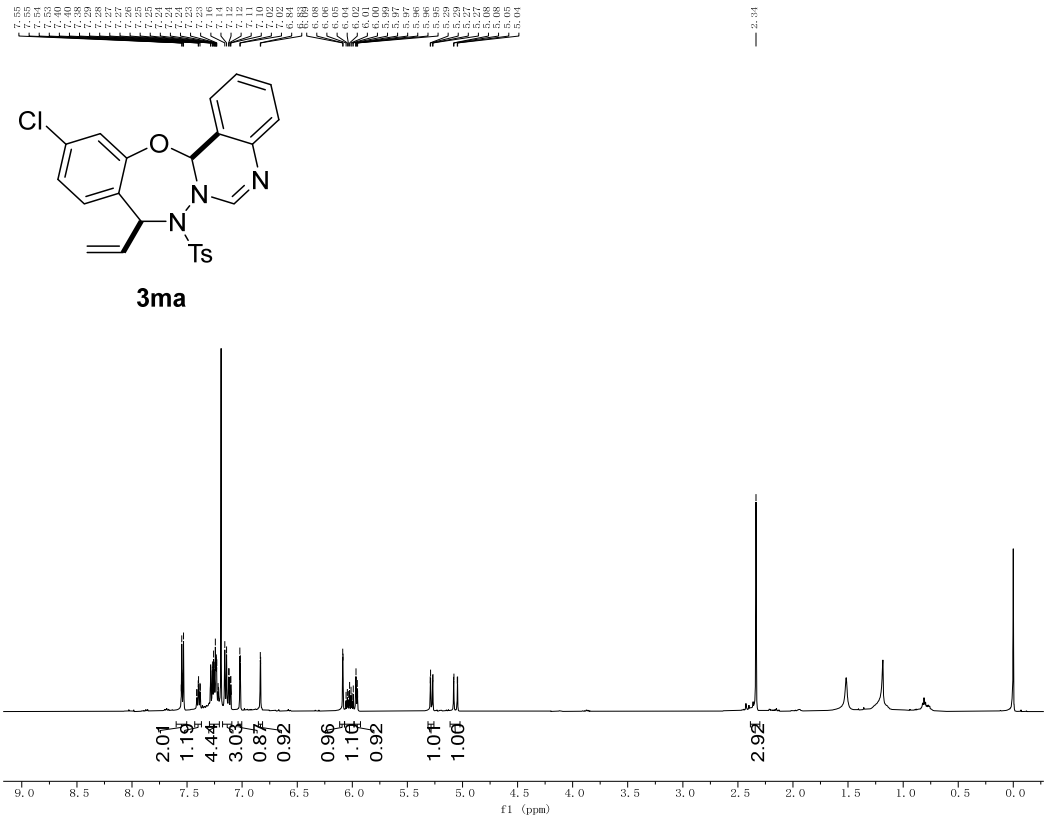
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



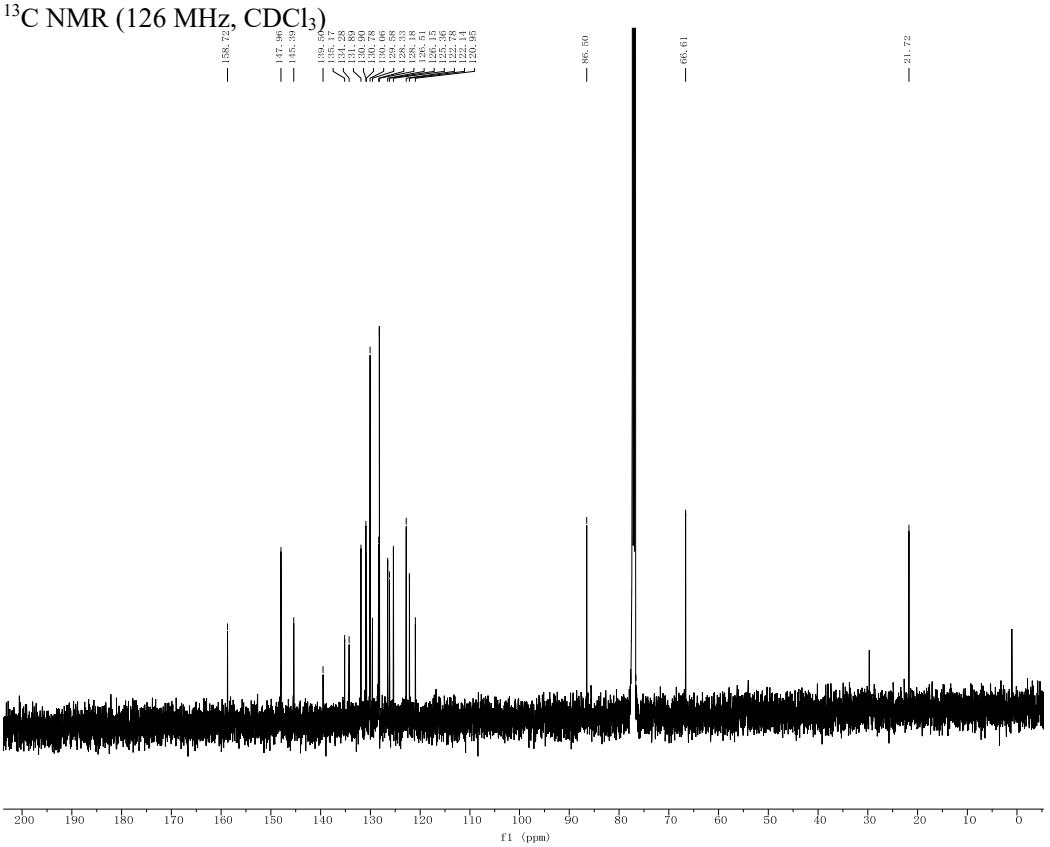
^{13}C NMR (126 MHz, $CDCl_3$)



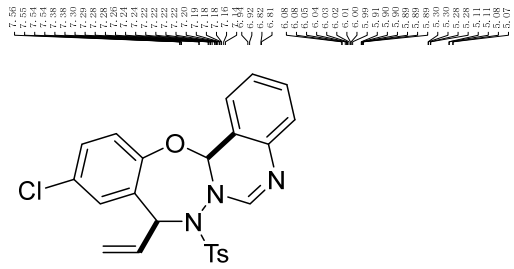
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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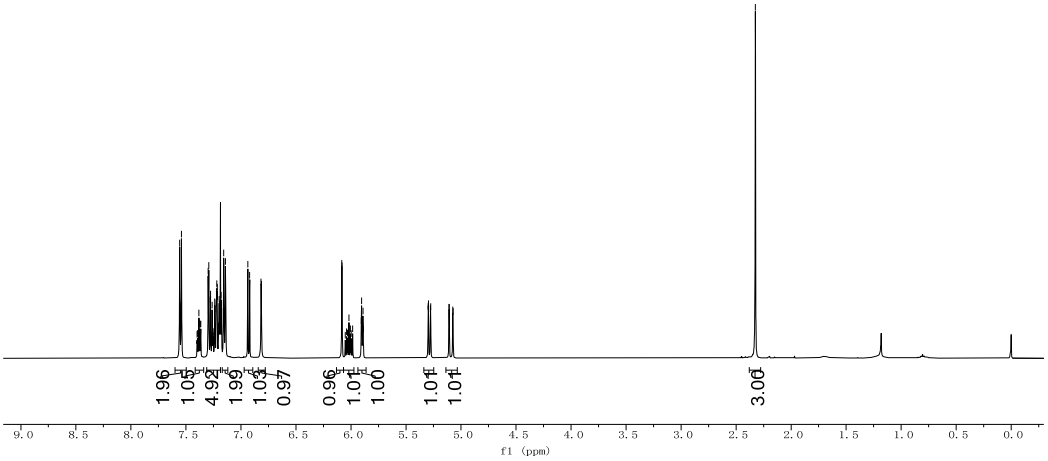
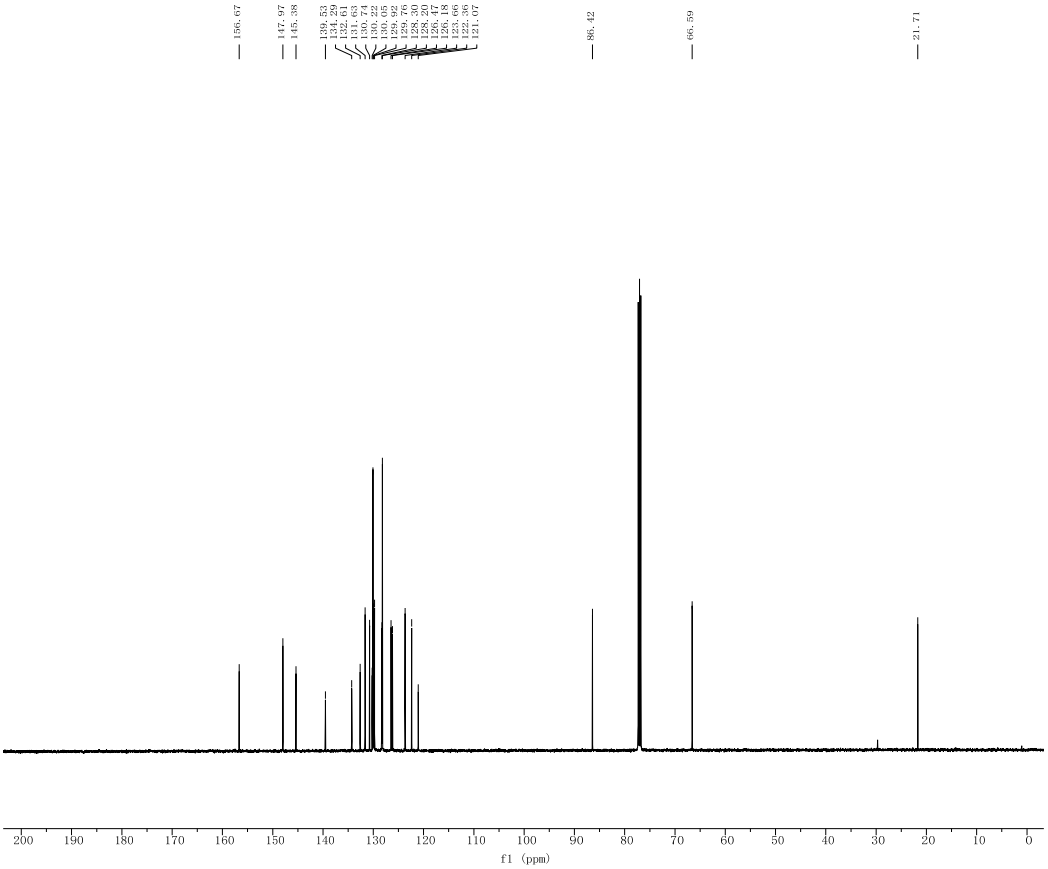
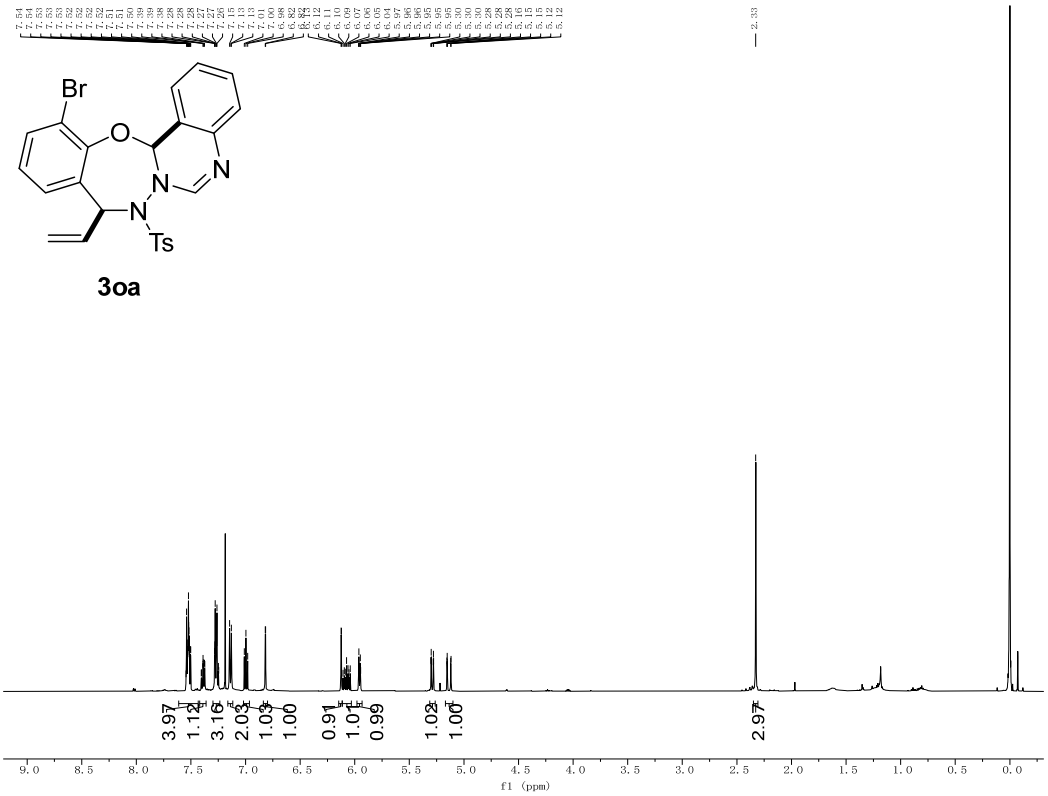


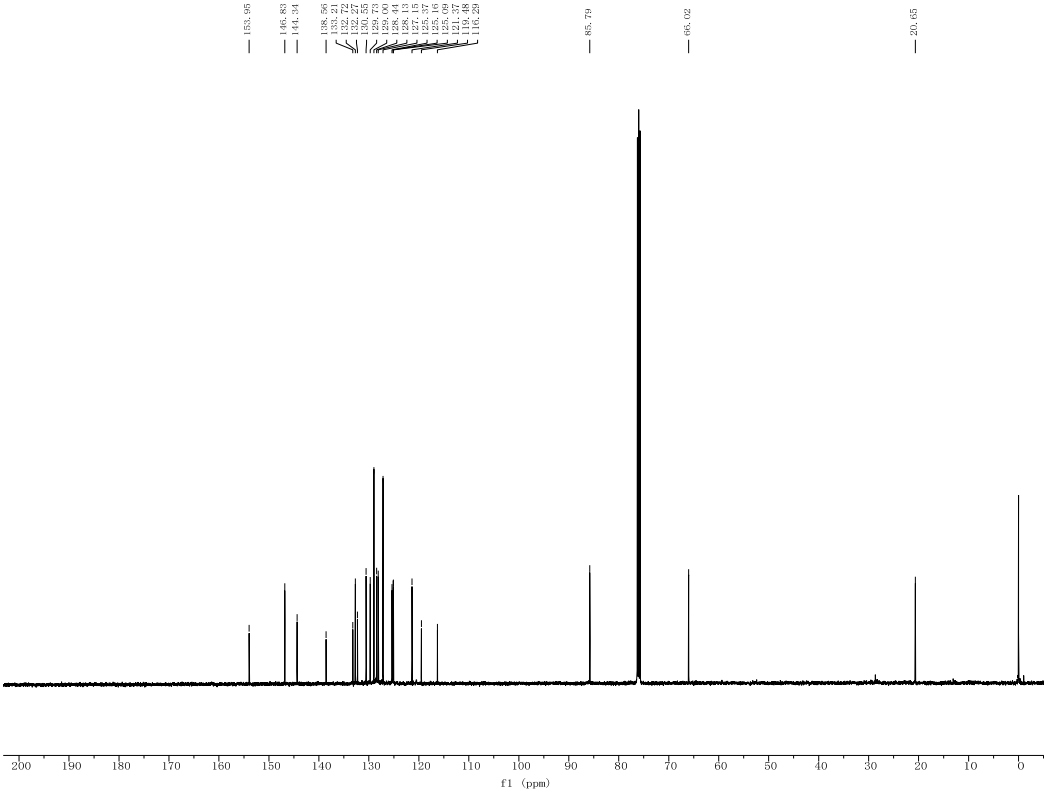
^{13}C NMR (126 MHz, $CDCl_3$)



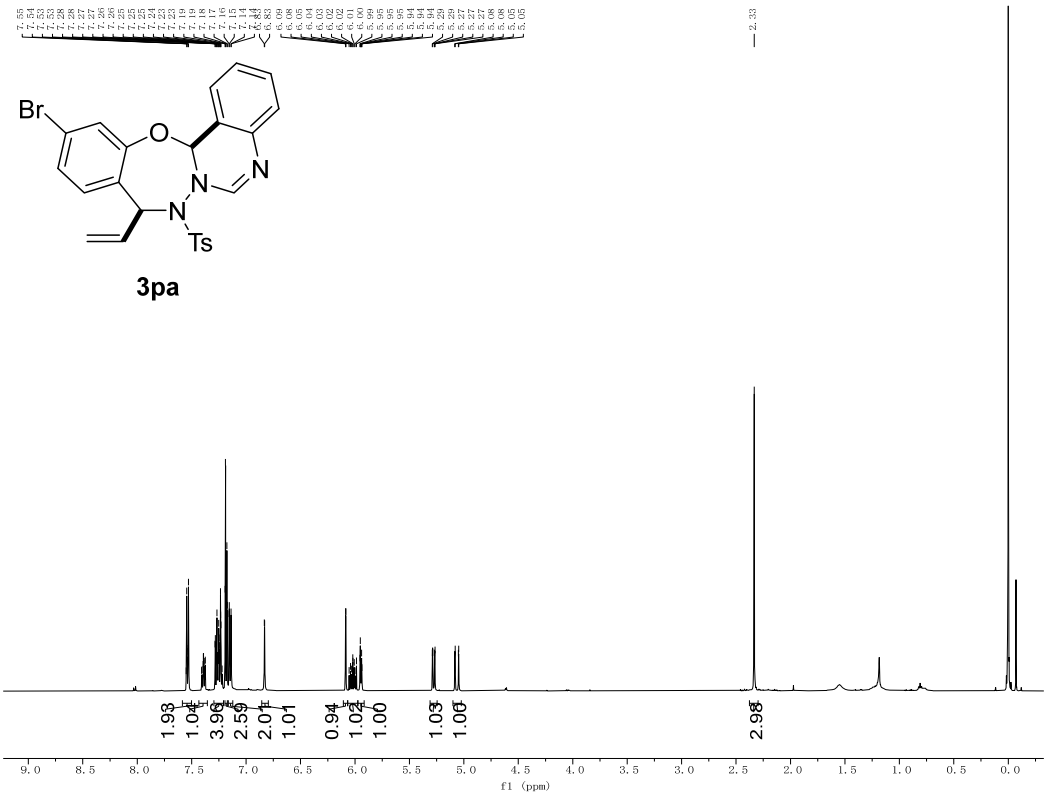
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



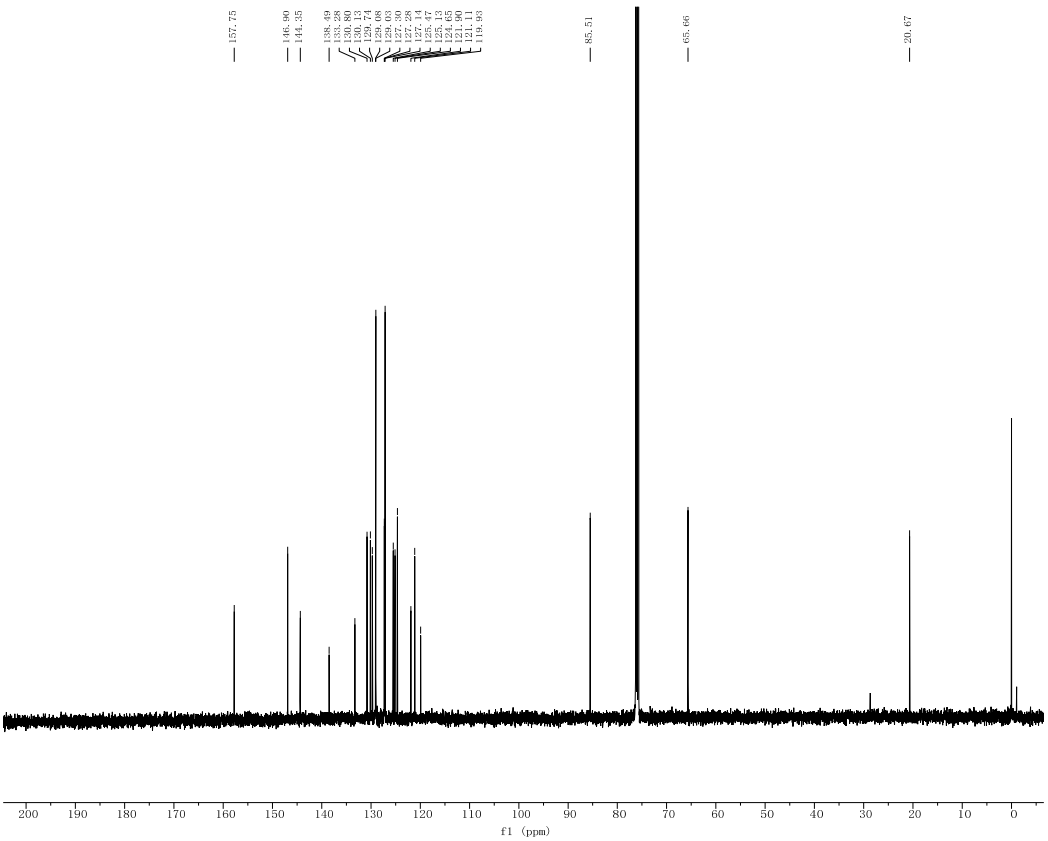
^{13}C NMR (126 MHz, $CDCl_3$)



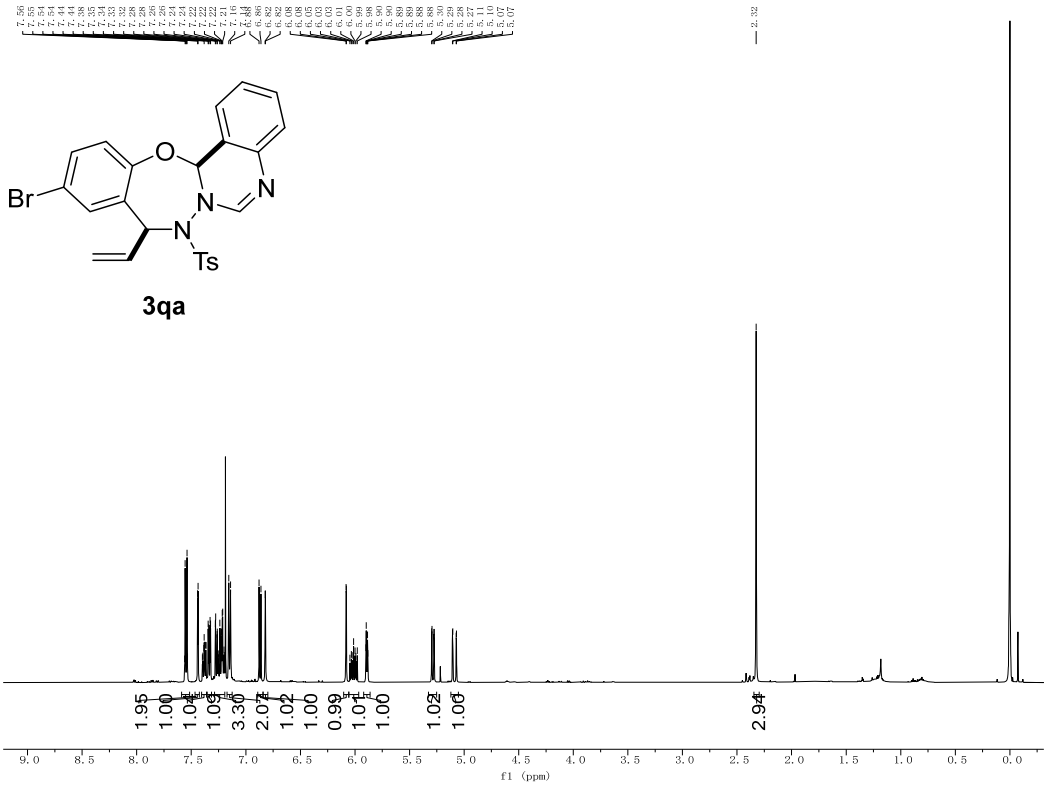
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



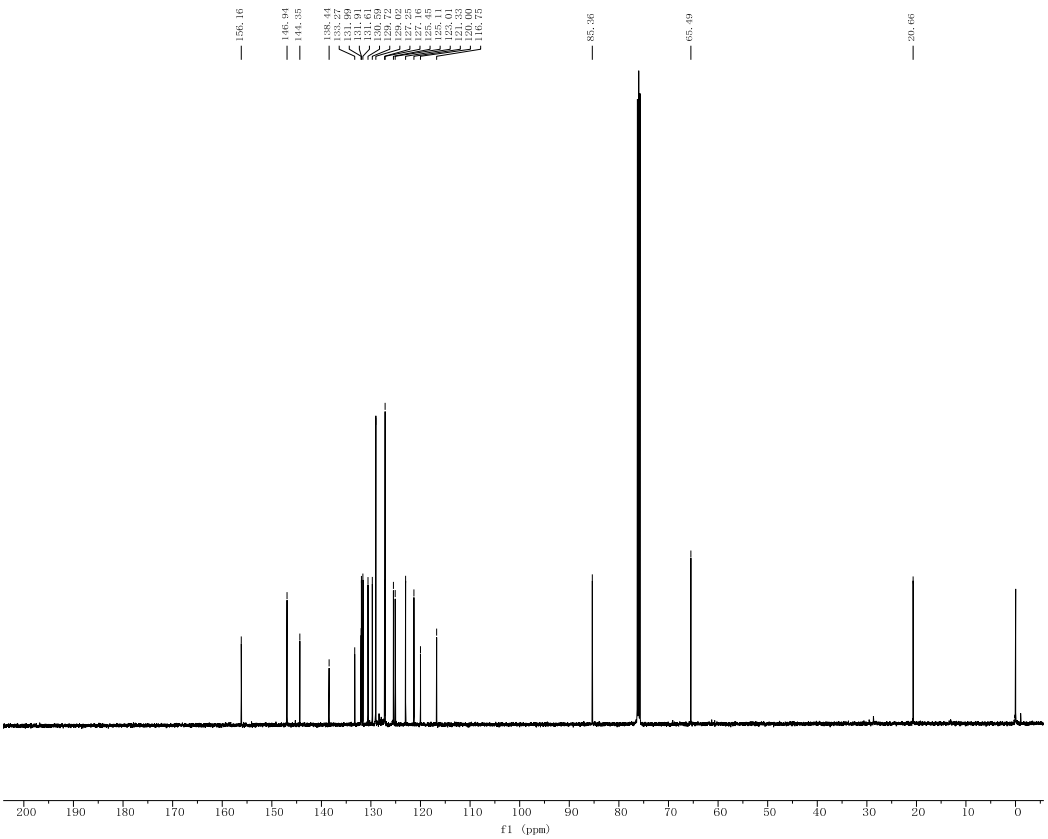
^{13}C NMR (126 MHz, $CDCl_3$)



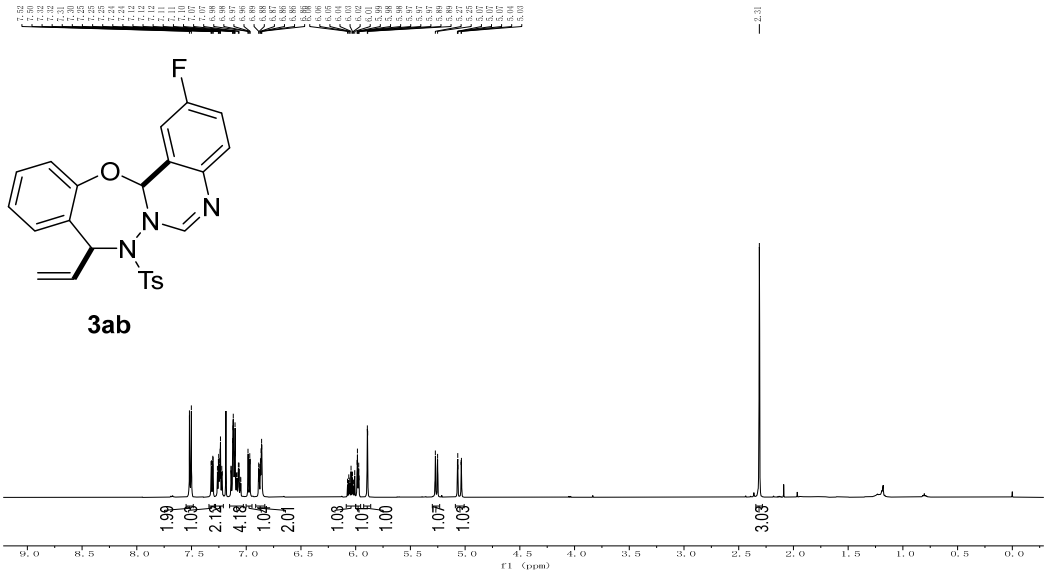
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



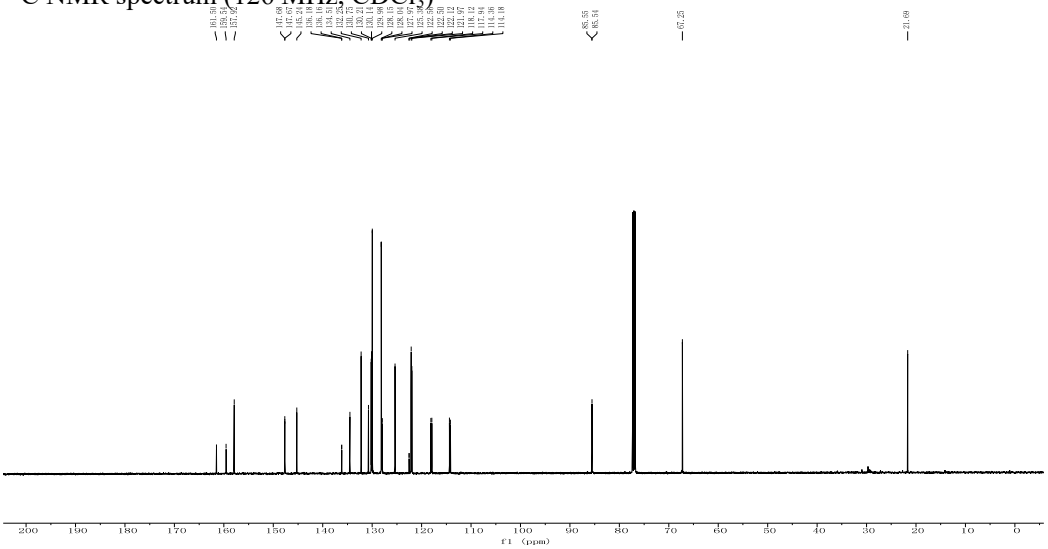
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



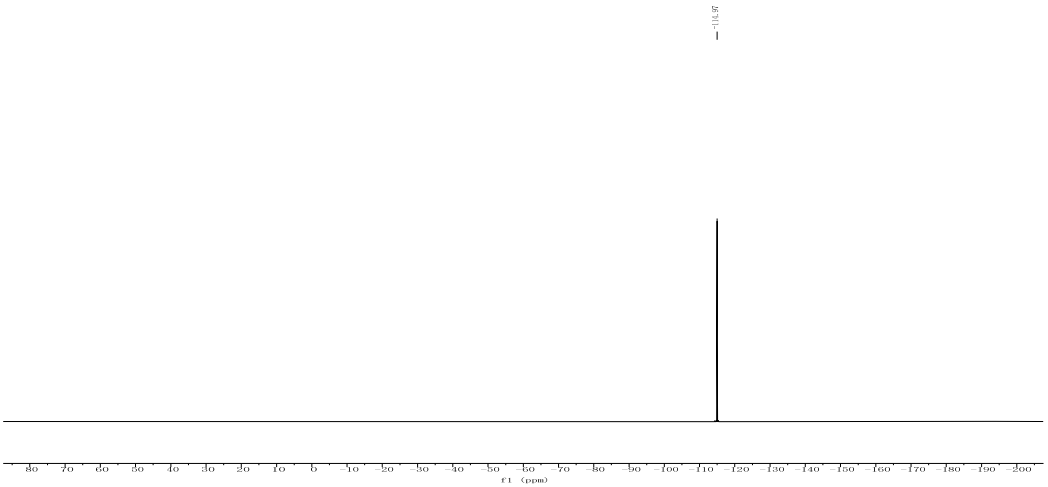
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



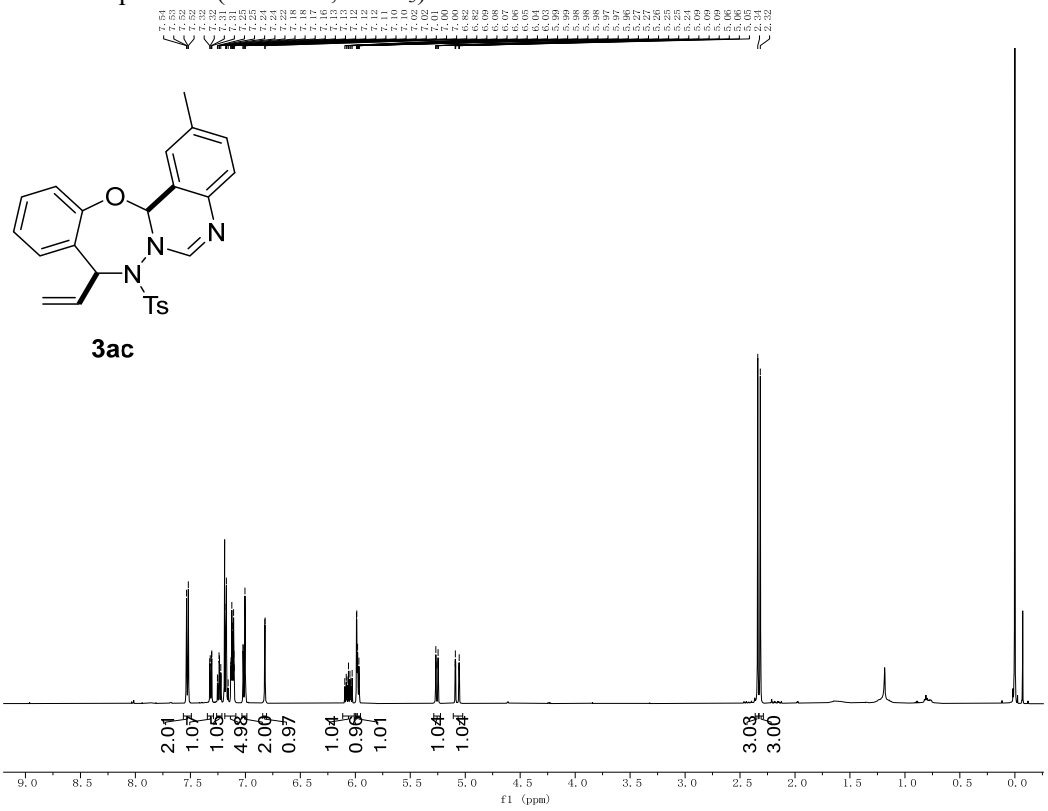
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



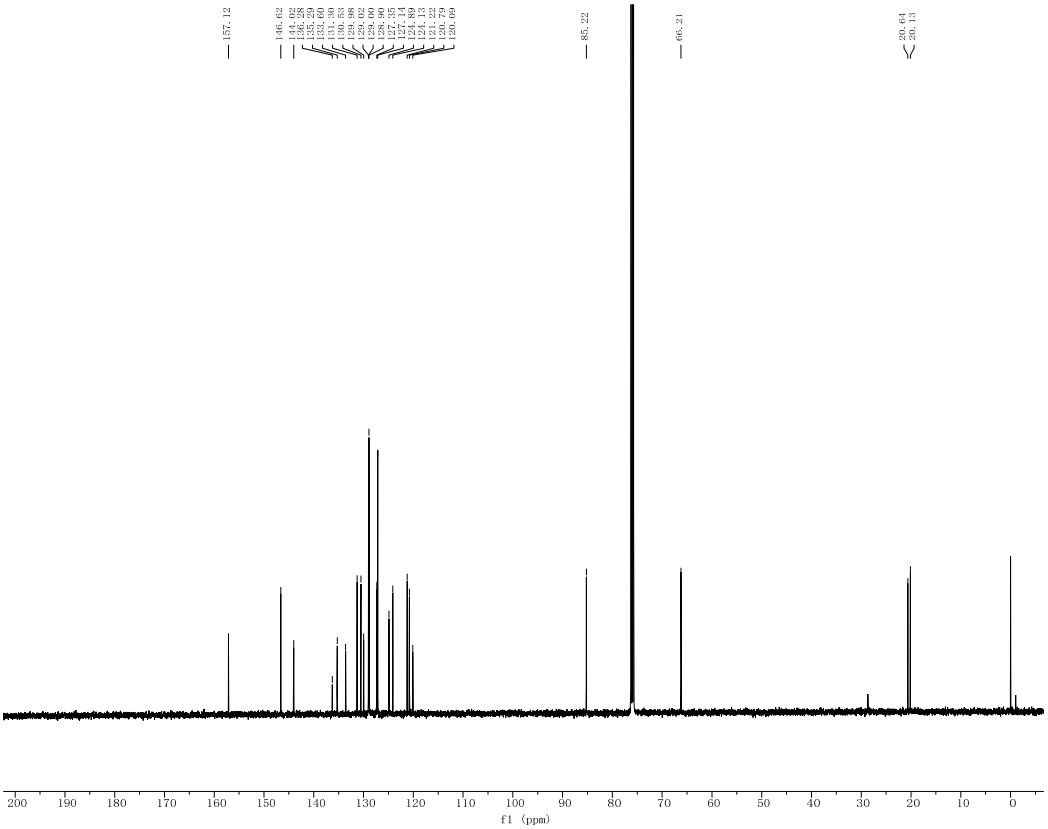
^{19}F NMR (471 MHz, $CDCl_3$)



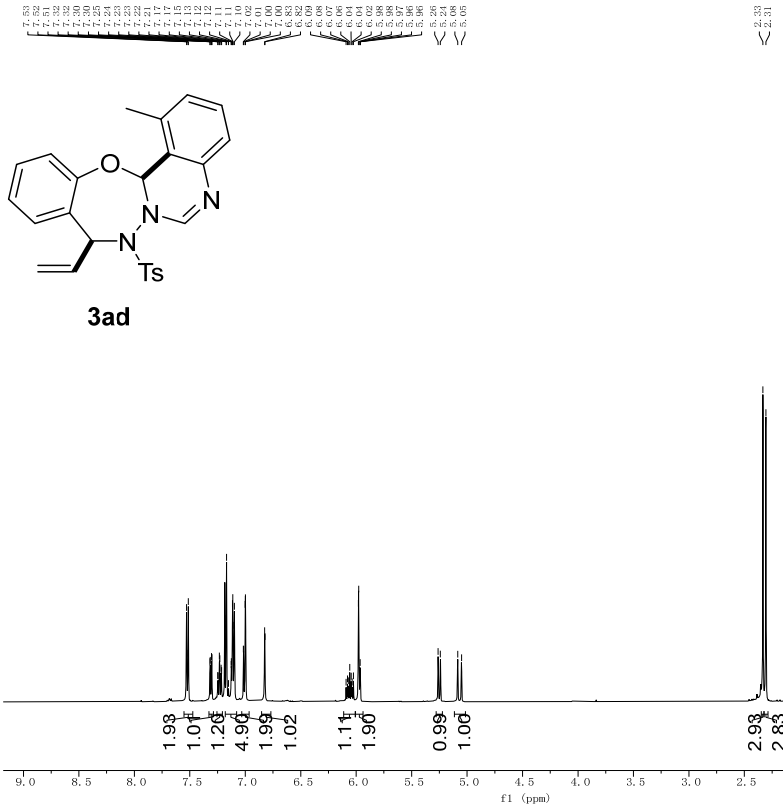
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR spectrum (126 MHz, $CDCl_3$)

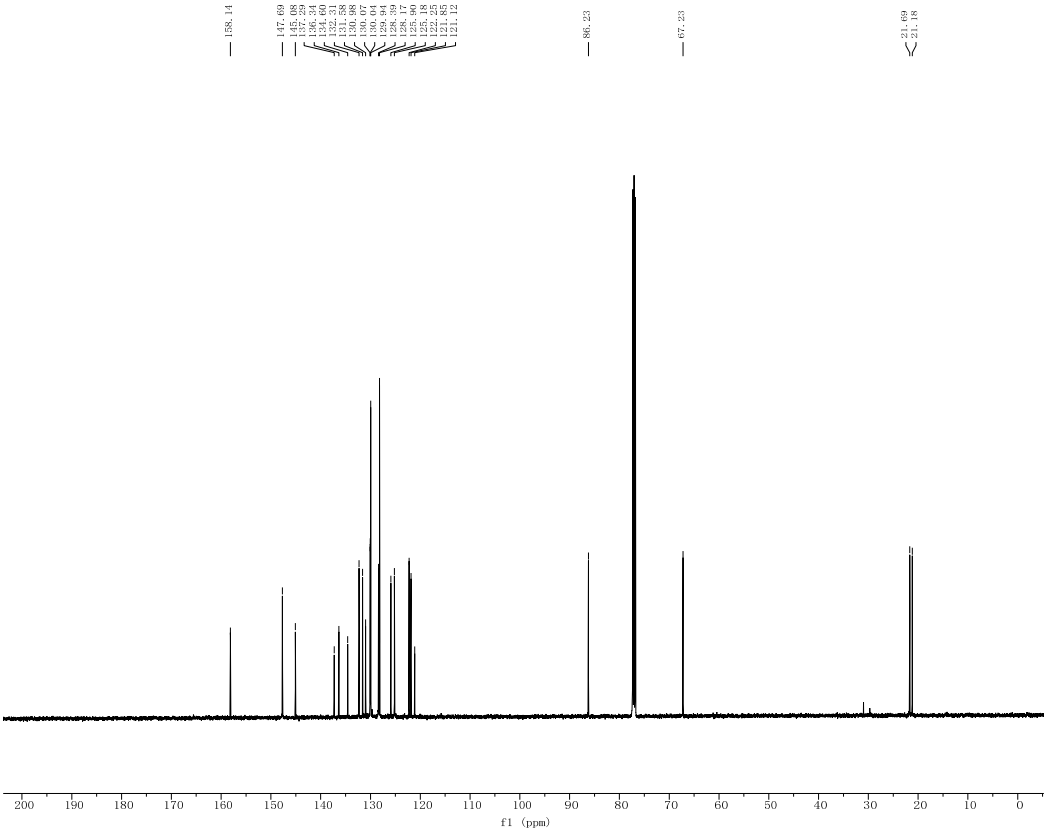


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

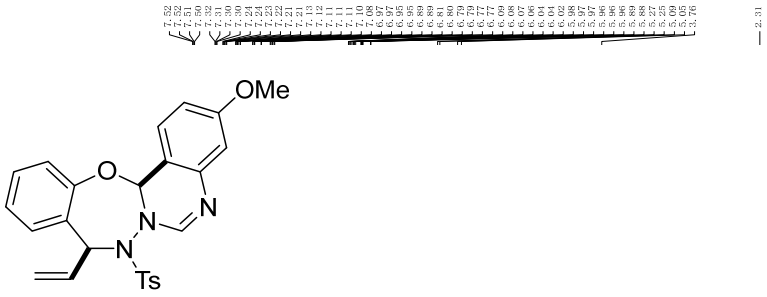


3ad

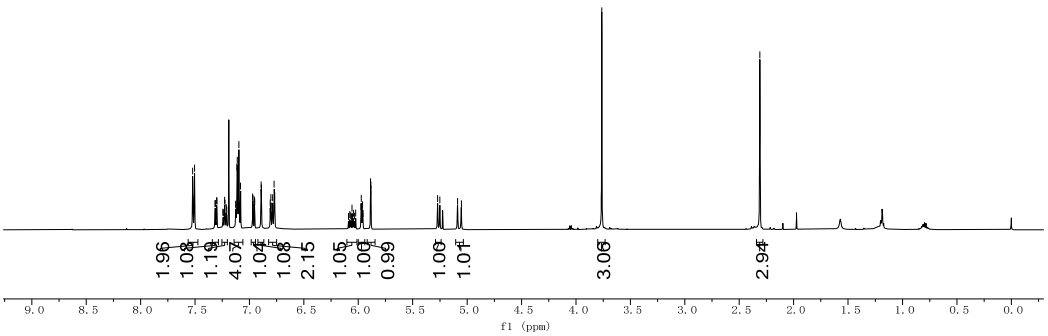
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



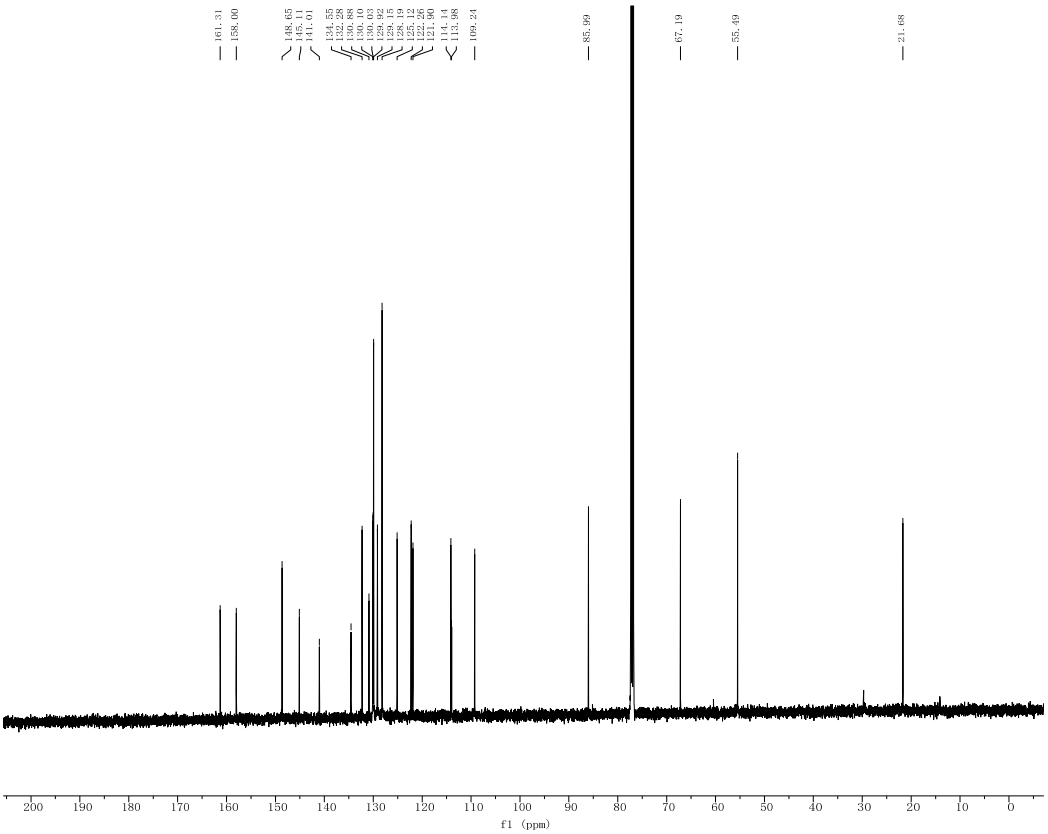
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



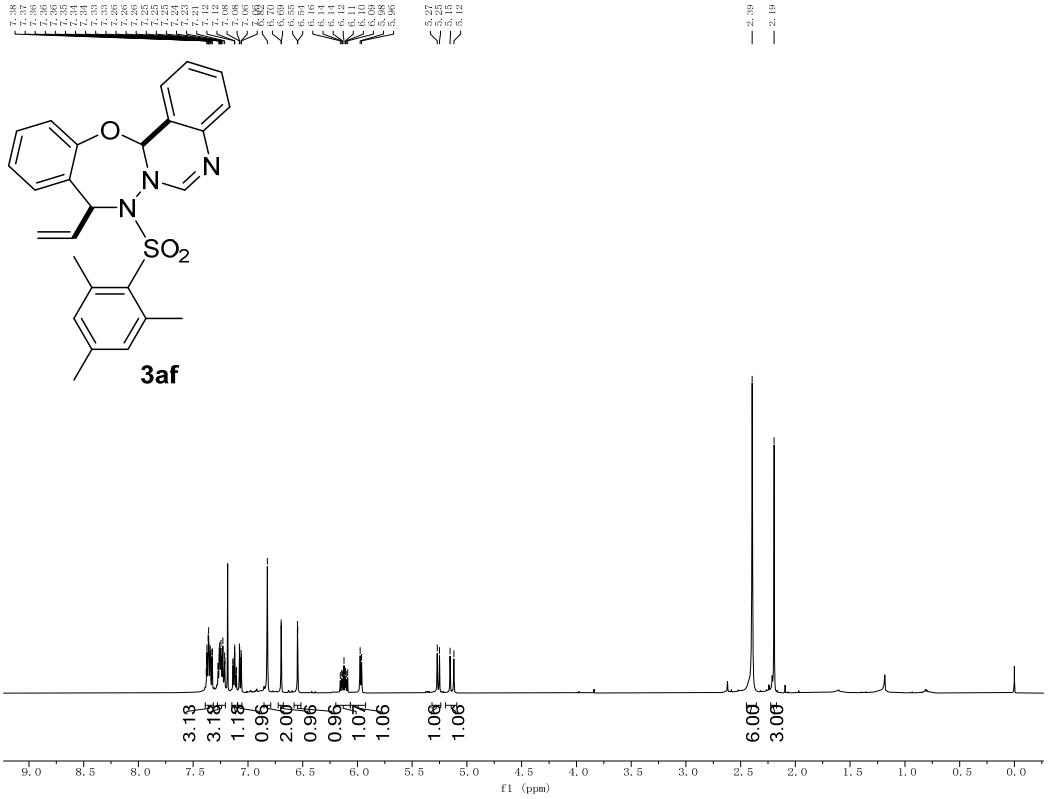
3ae



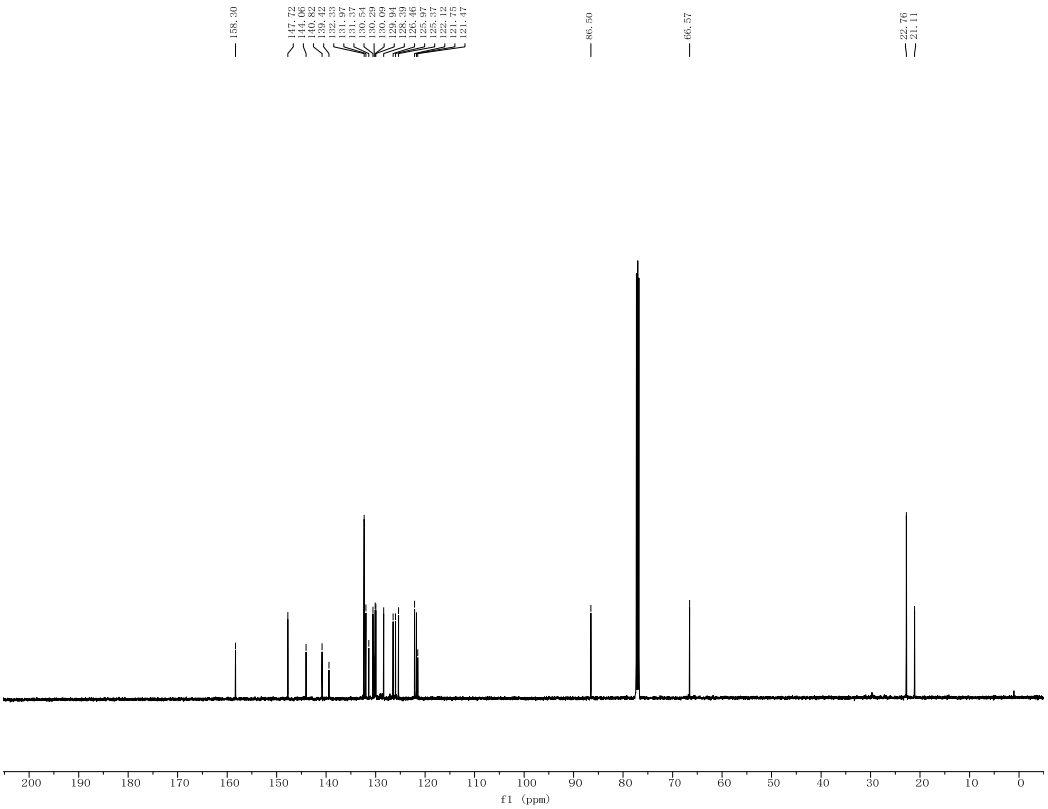
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



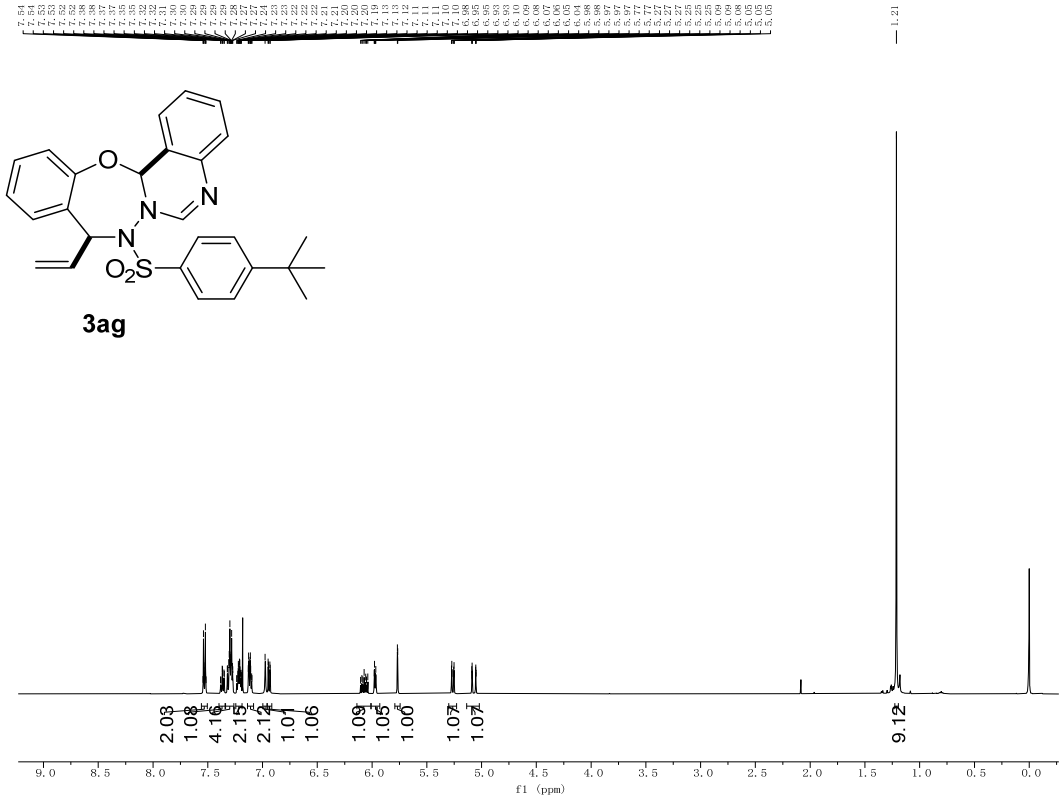
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



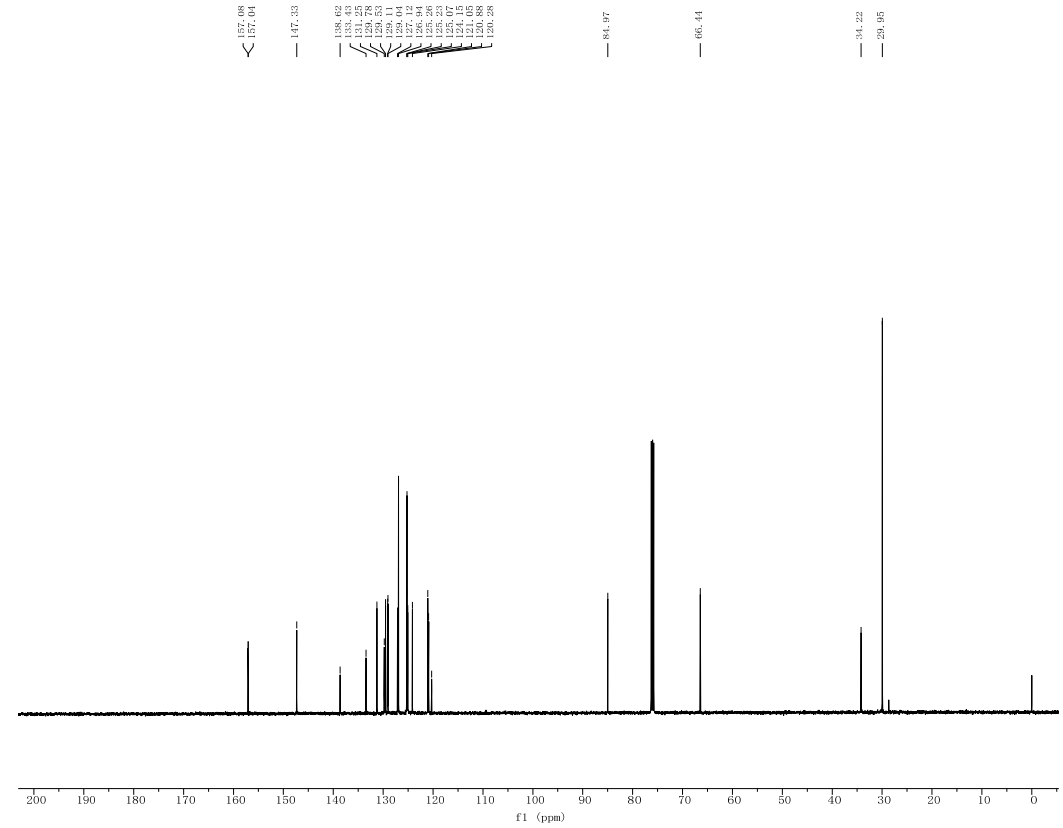
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



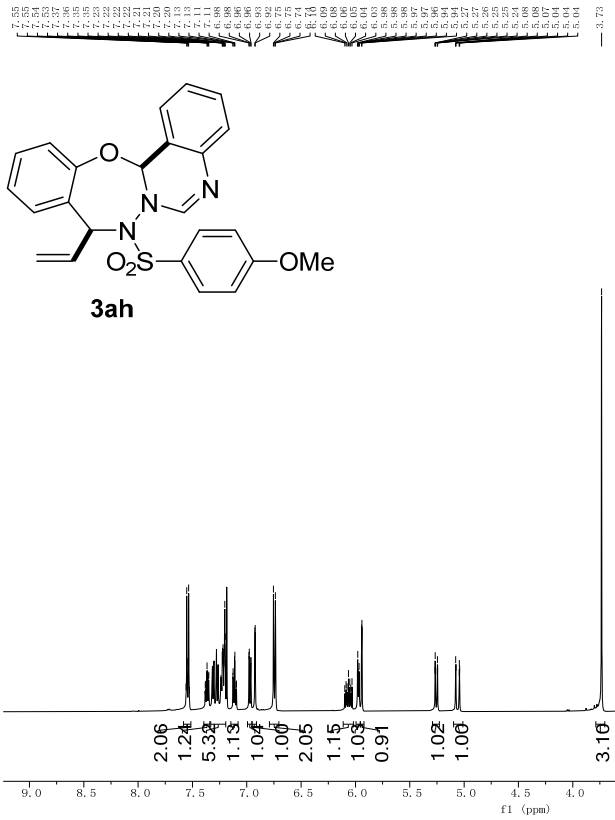
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



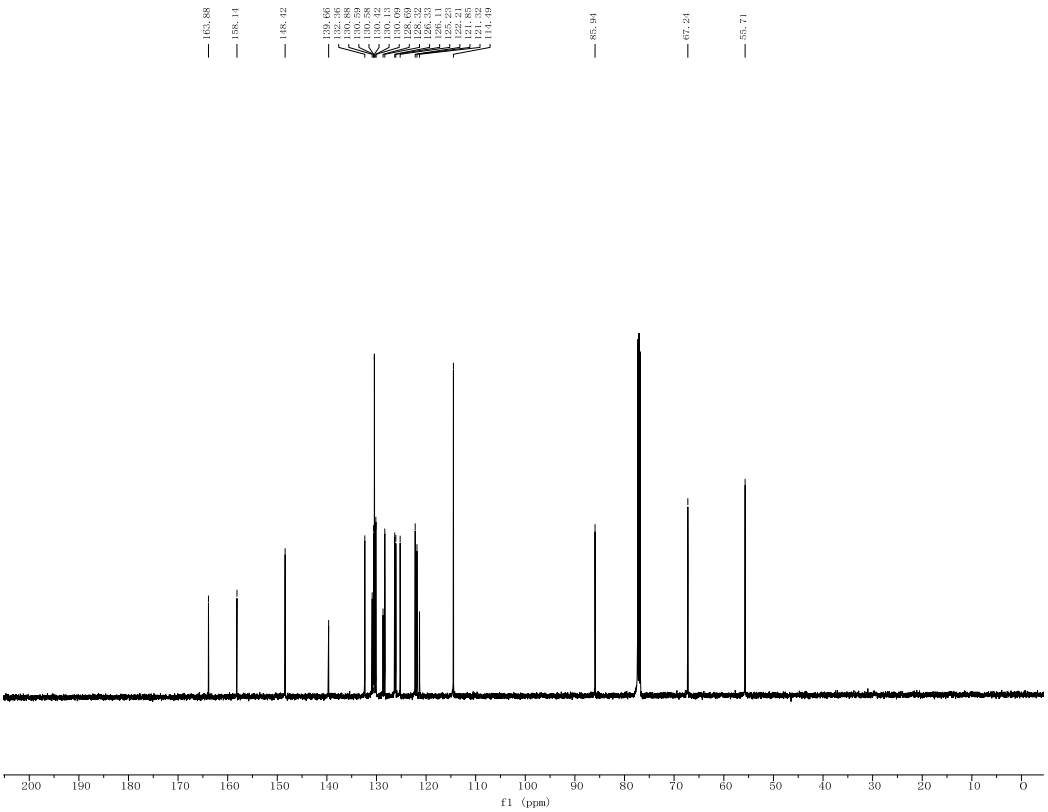
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



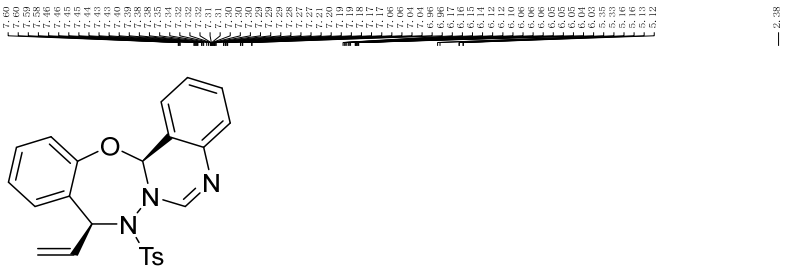
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



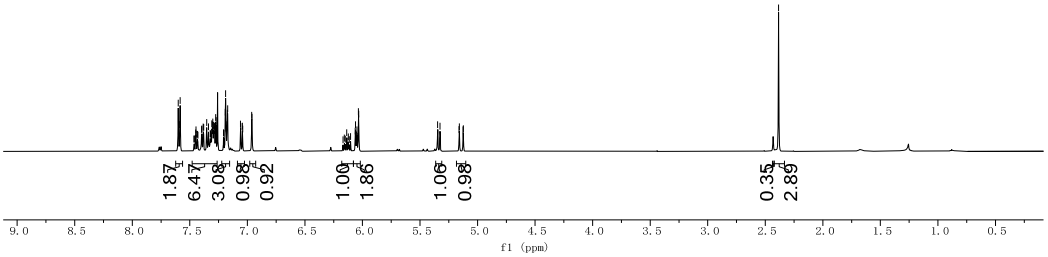
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



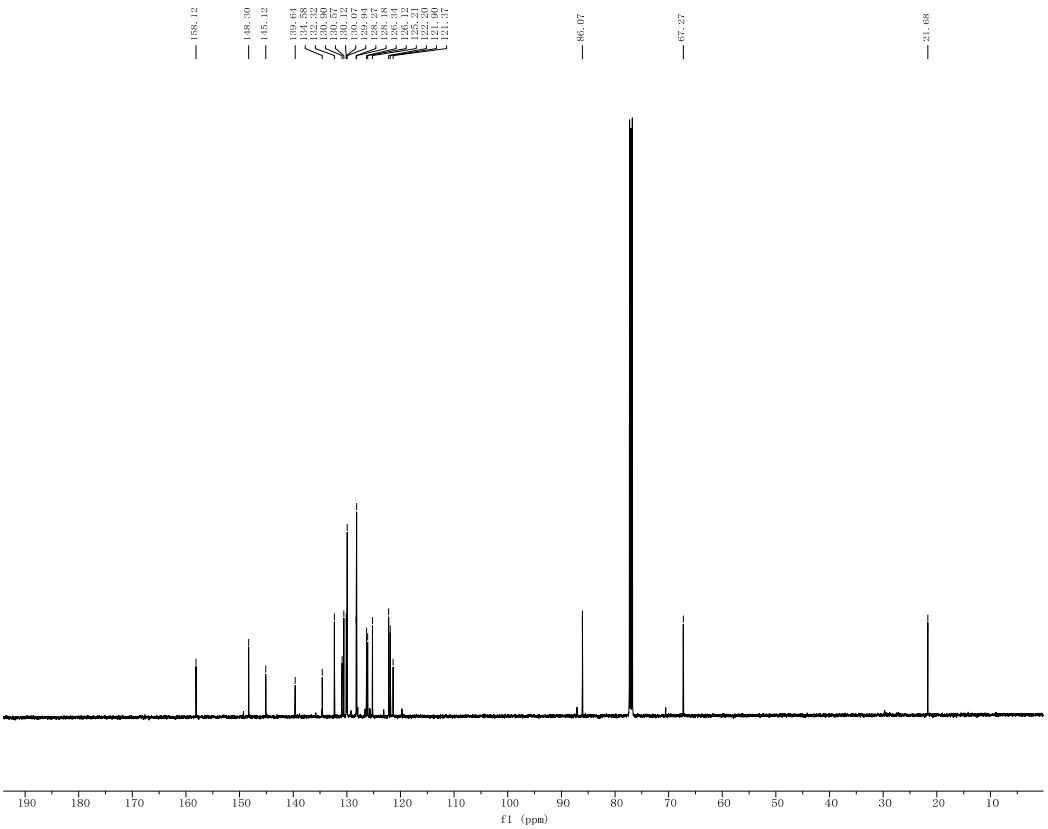
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



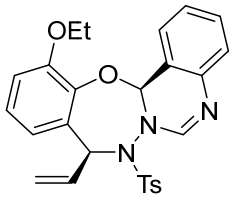
4aa (8:1 dr)



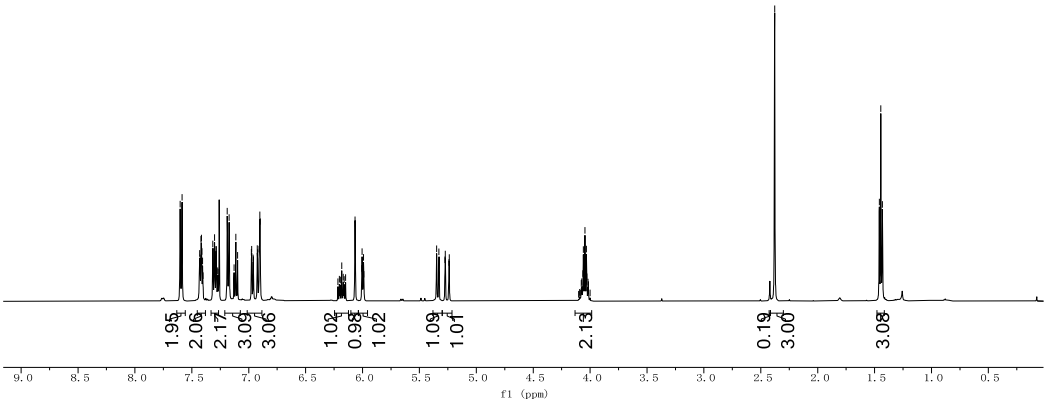
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



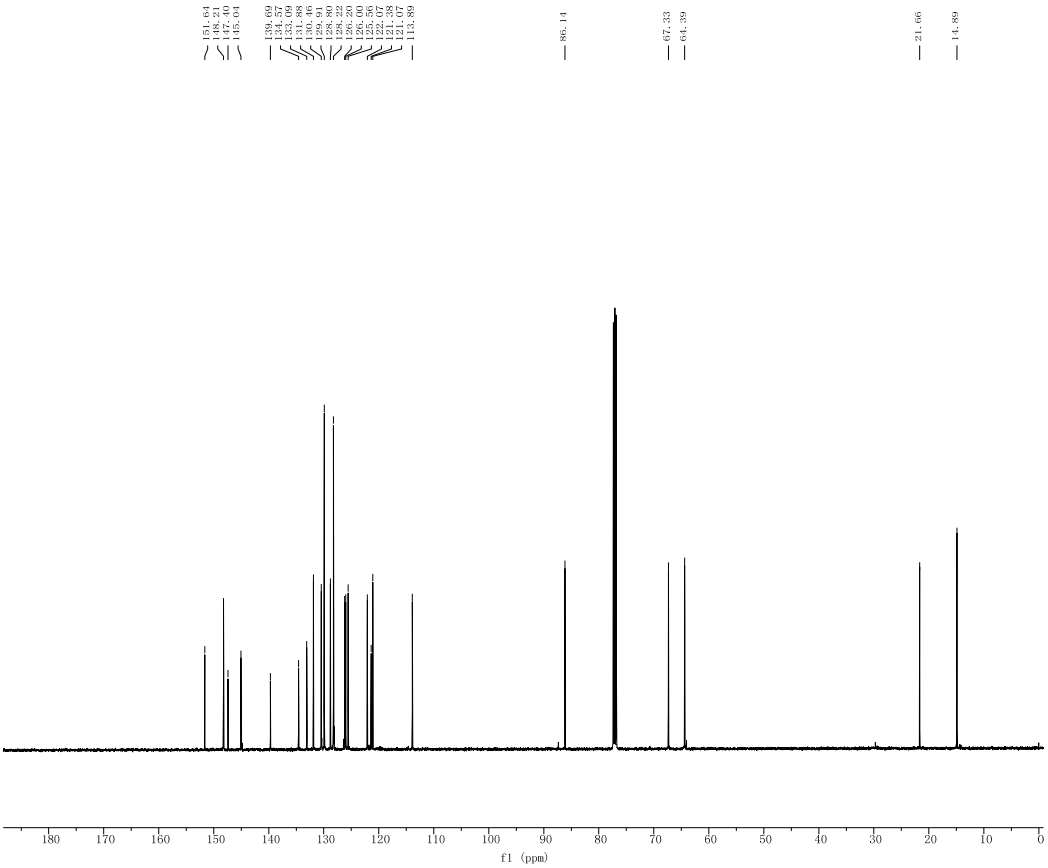
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



4ba (16:1 dr)

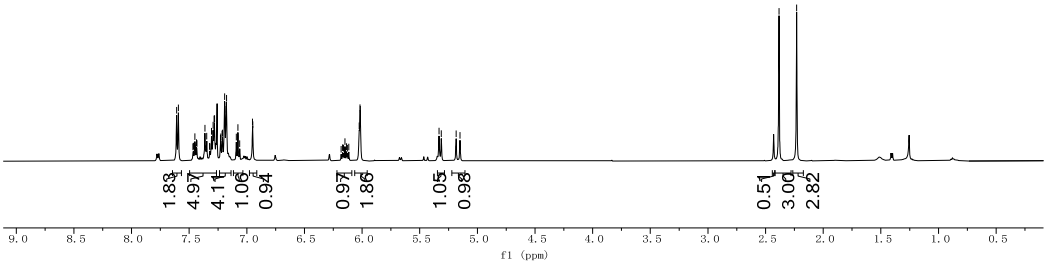


^{13}C NMR spectrum (126 MHz, $CDCl_3$)

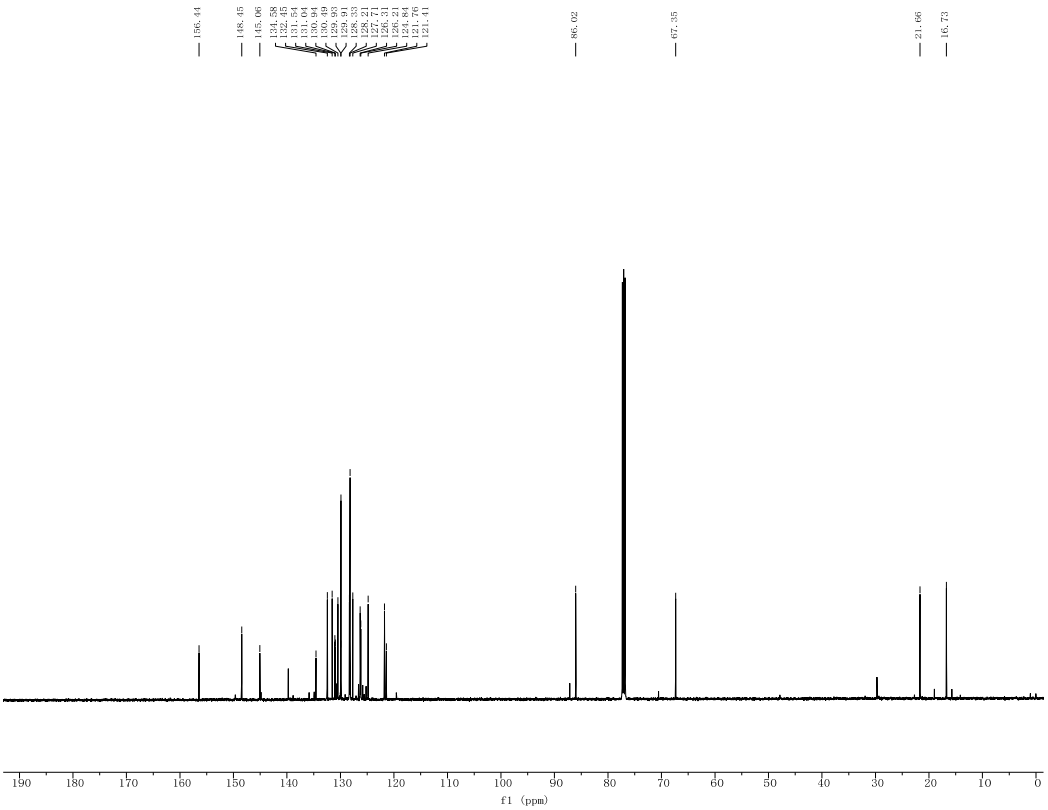


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

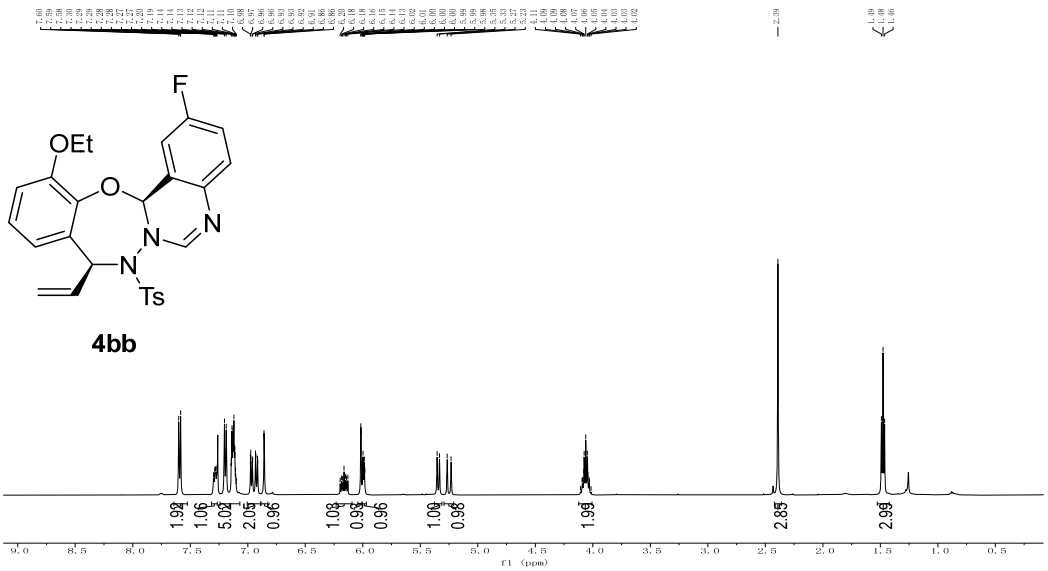
4ea (6:1 dr)



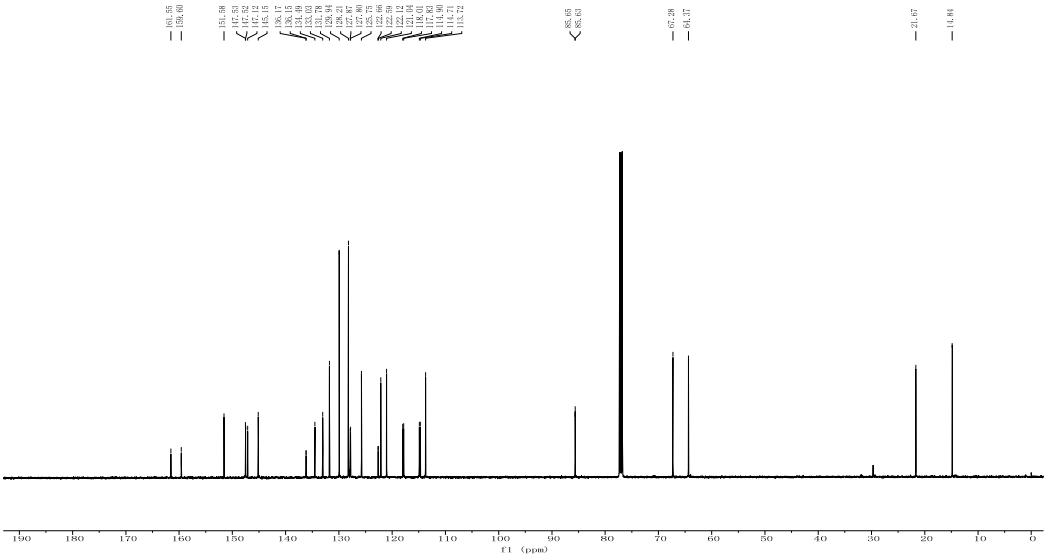
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



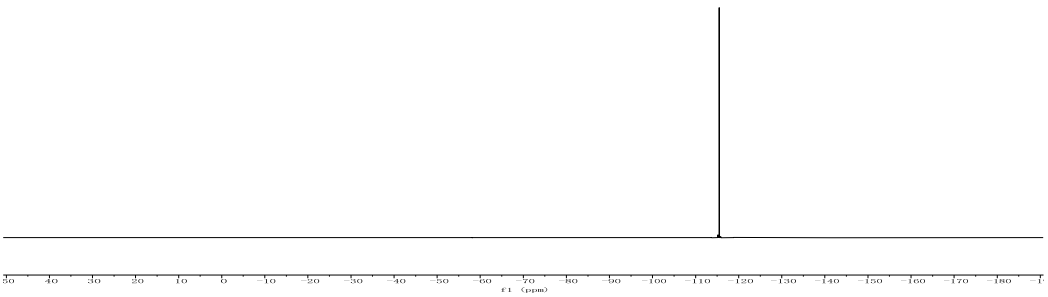
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



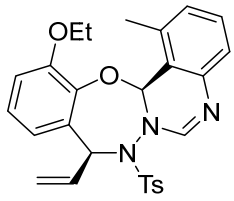
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



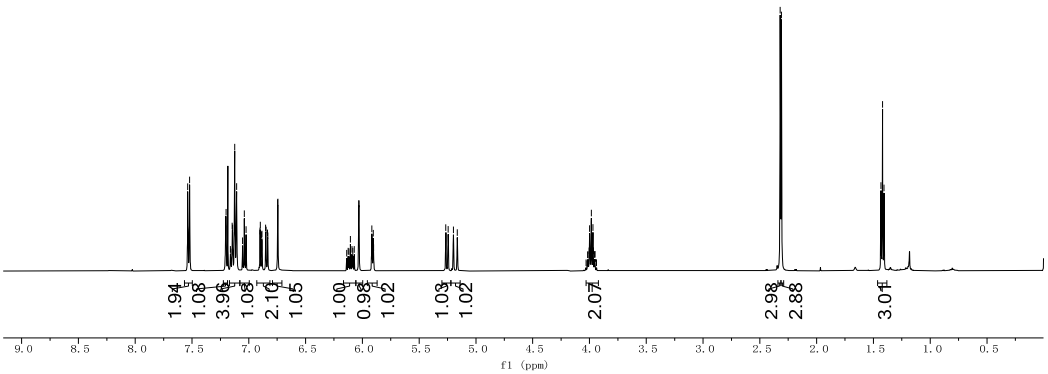
^{19}F NMR (471 MHz, $CDCl_3$) δ -115.46.



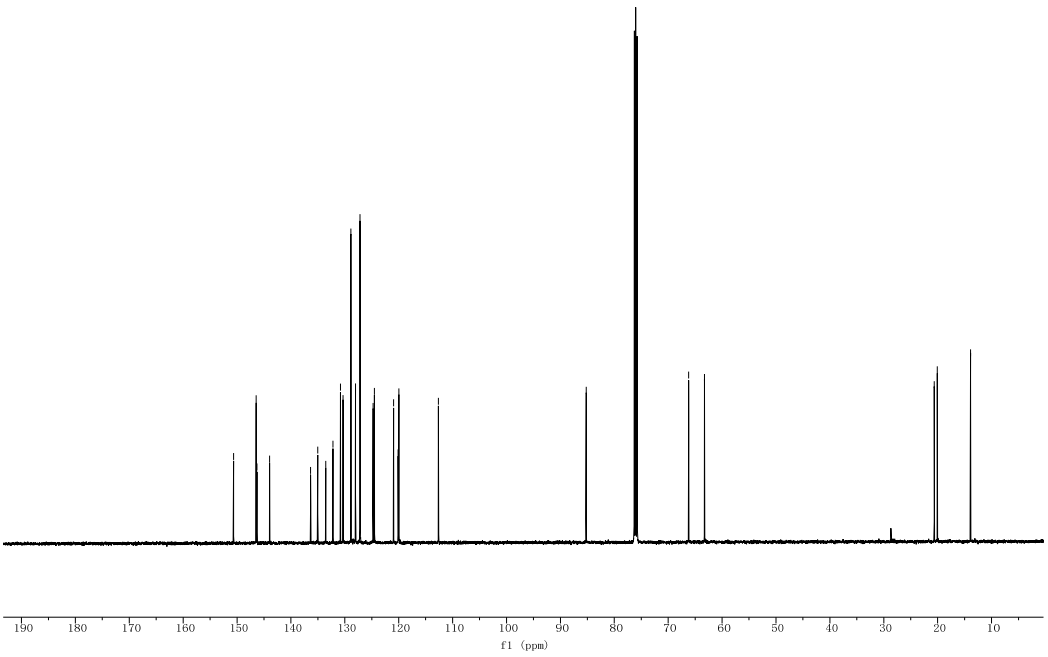
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



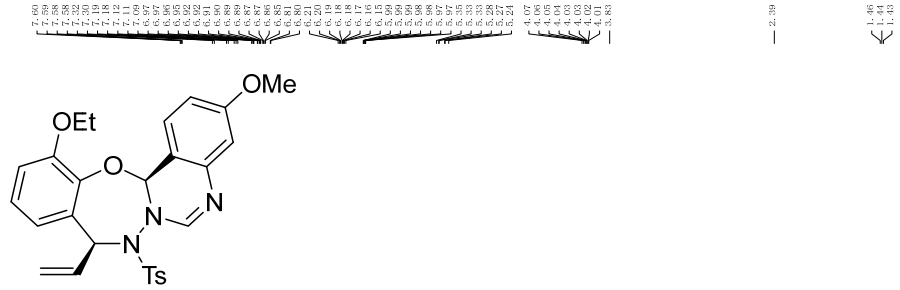
4bd



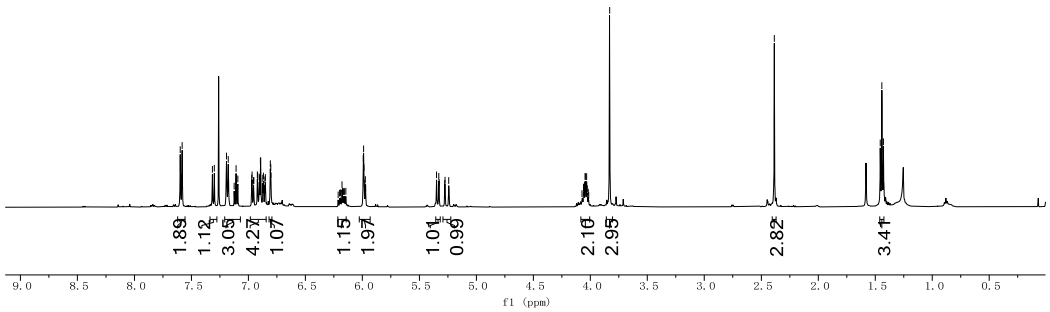
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



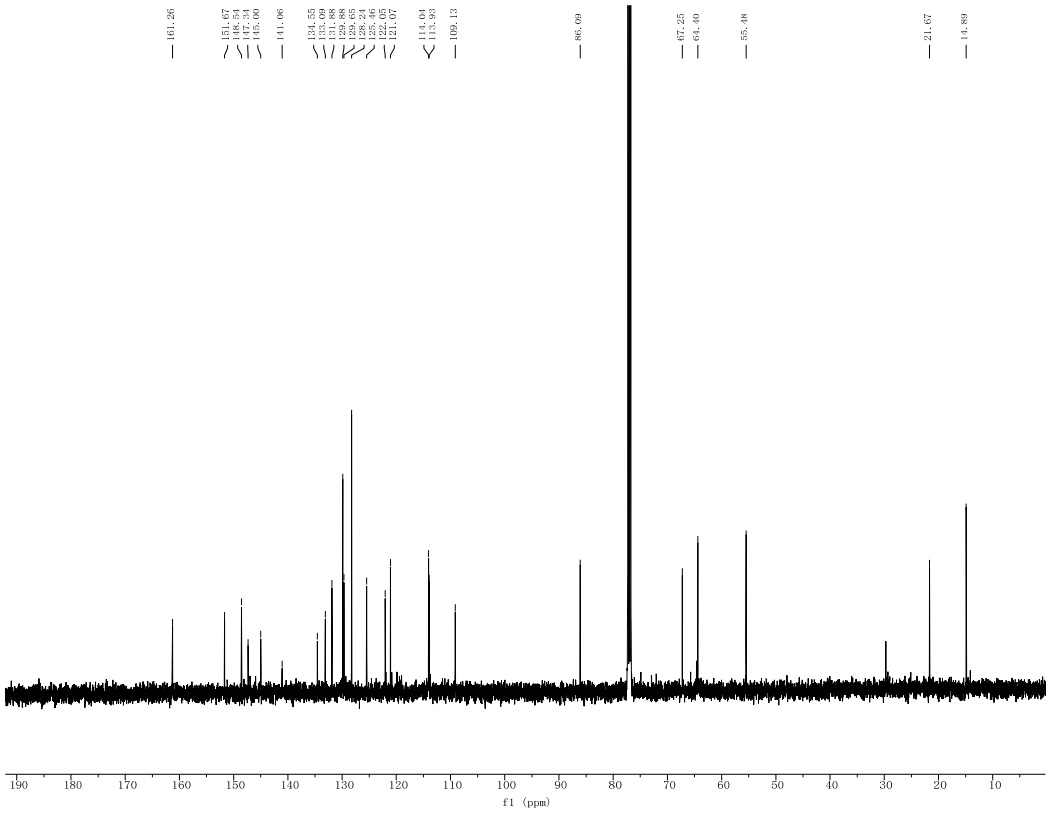
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



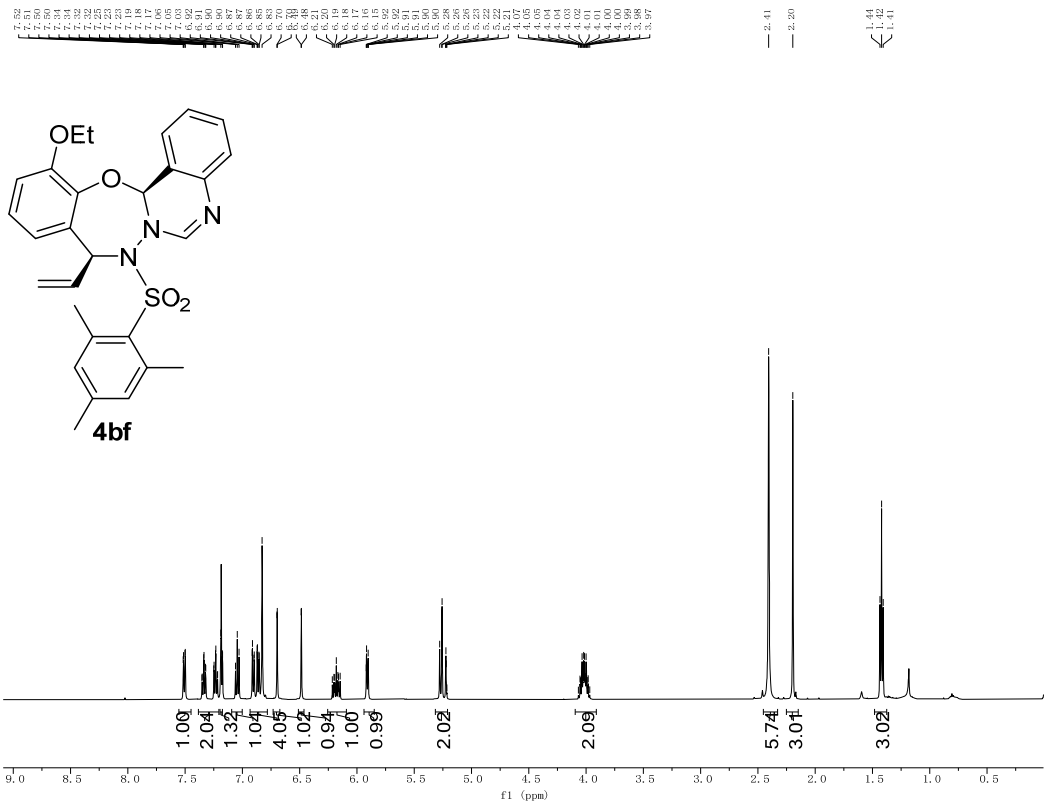
4be



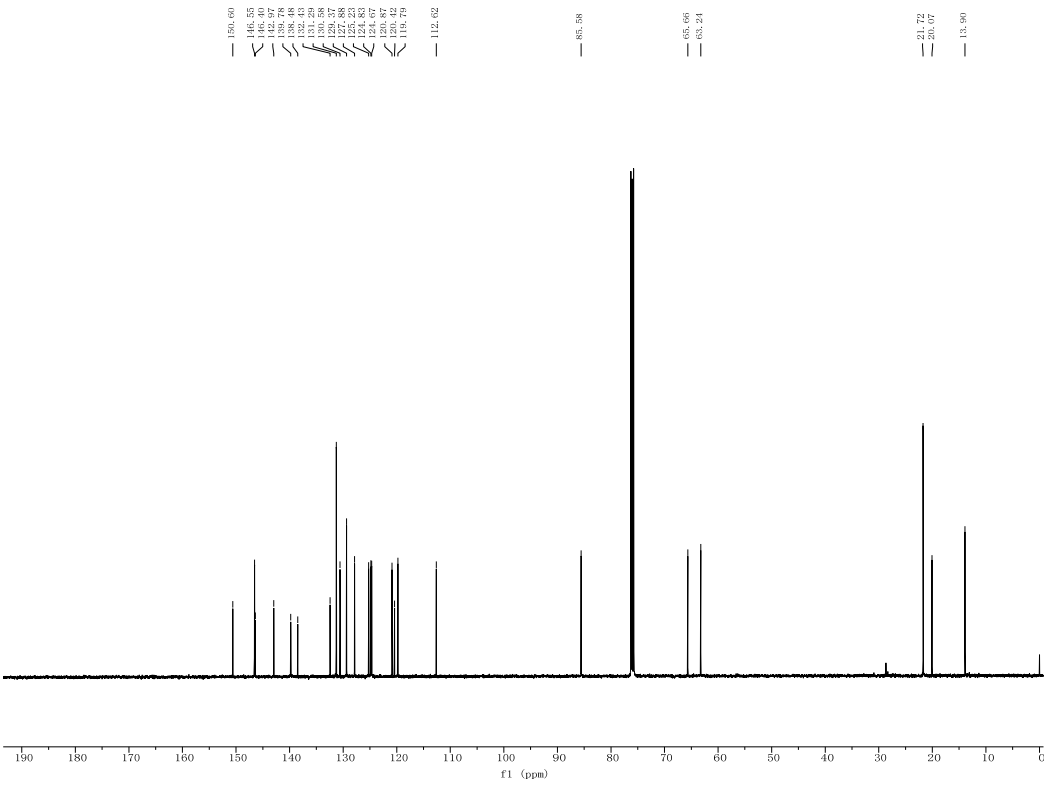
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



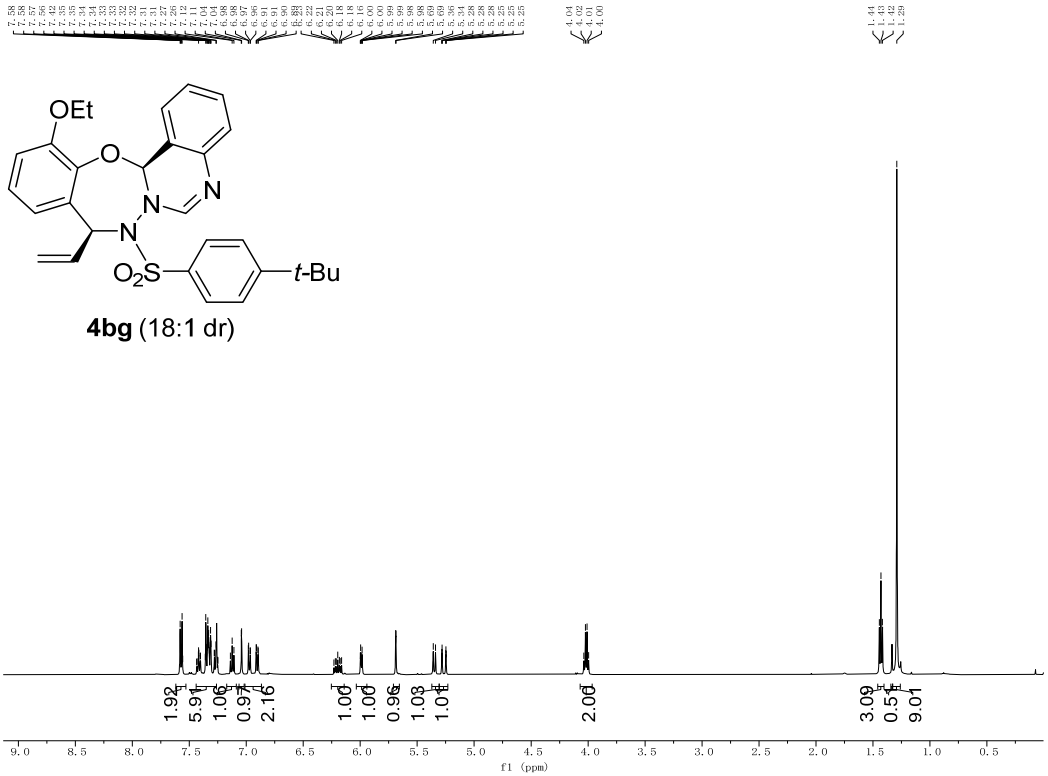
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



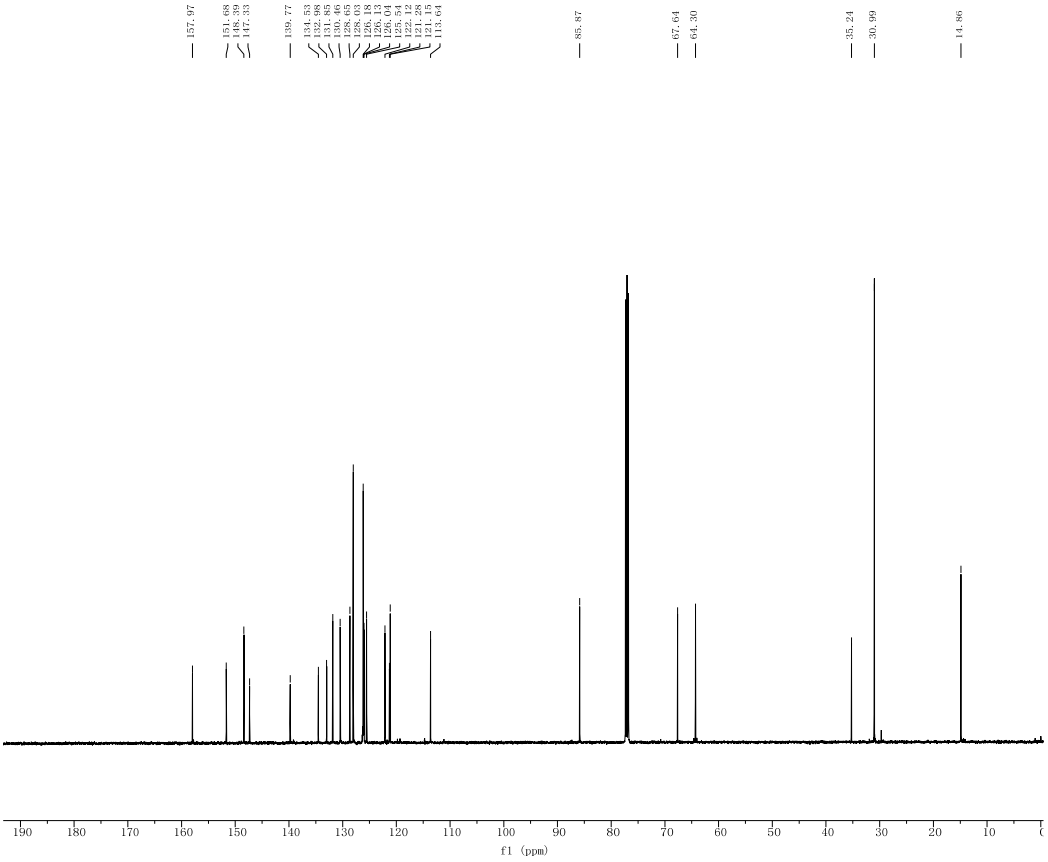
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



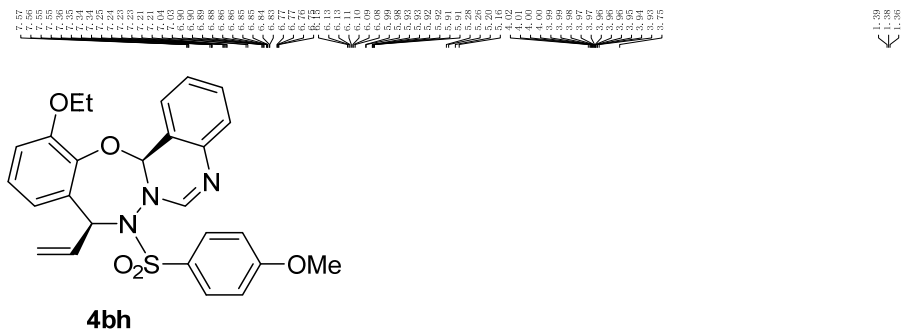
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



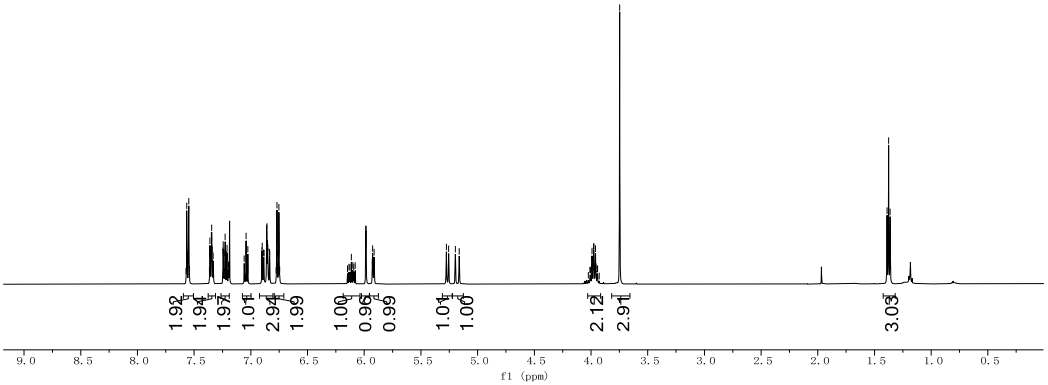
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



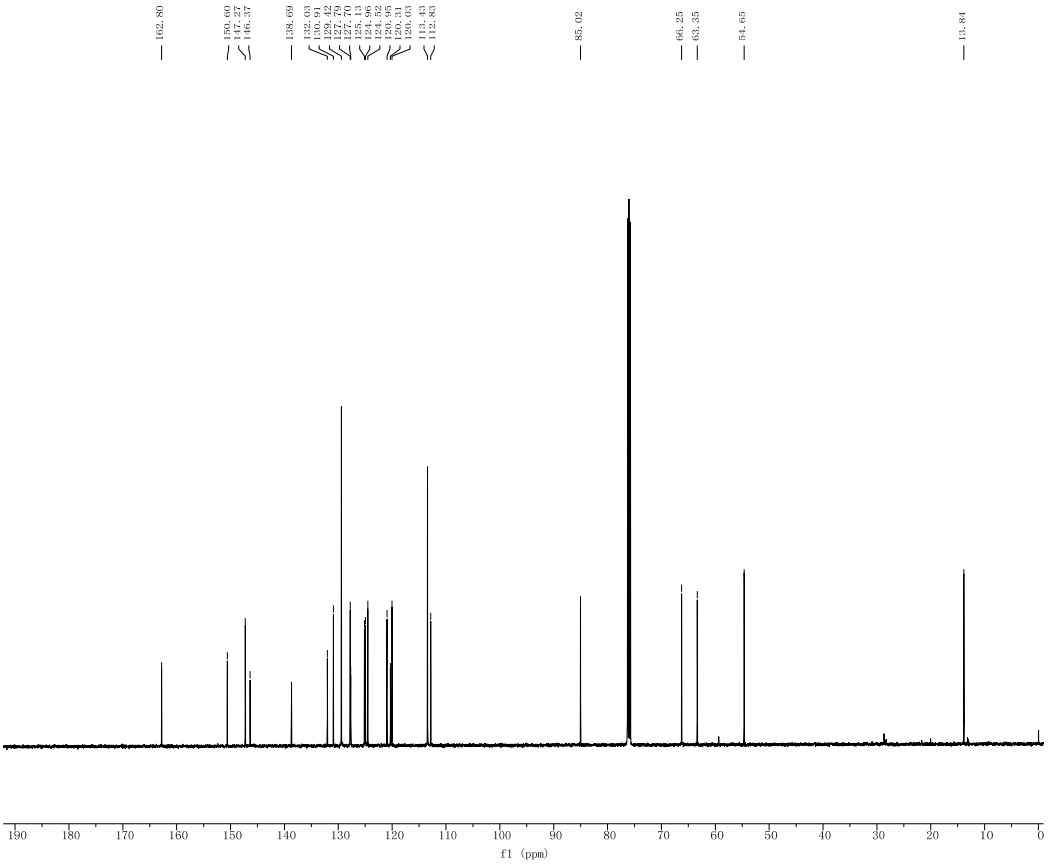
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



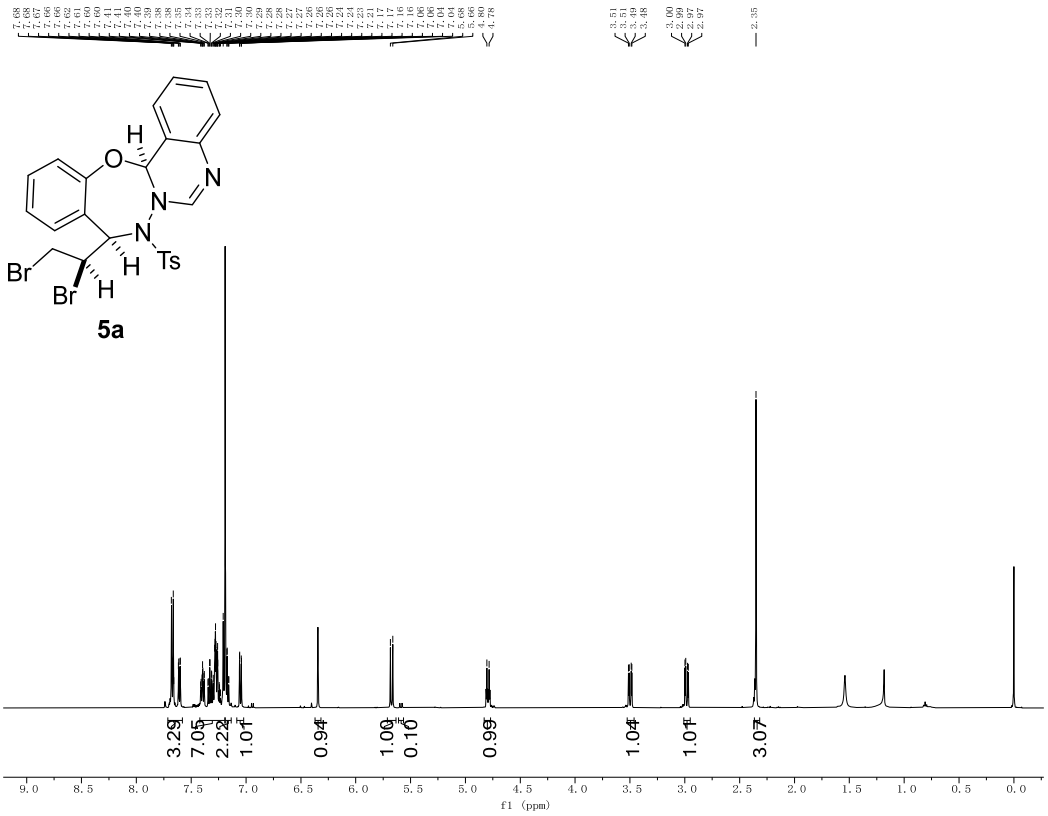
4bh



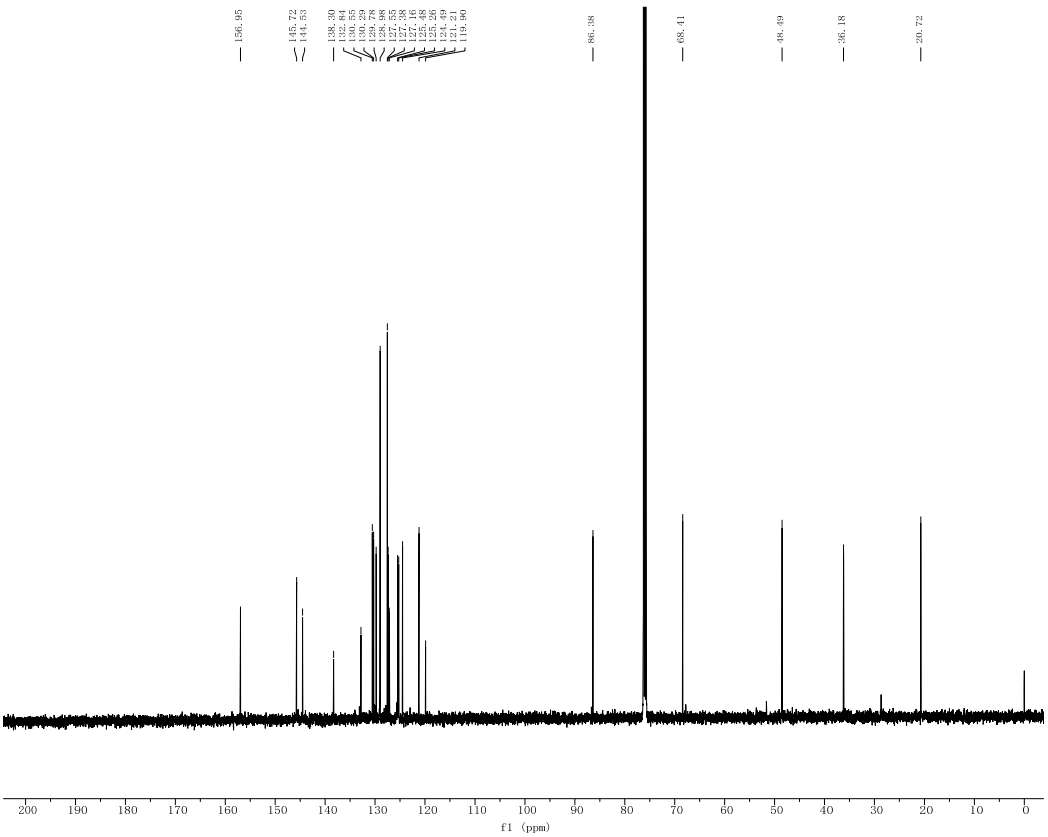
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



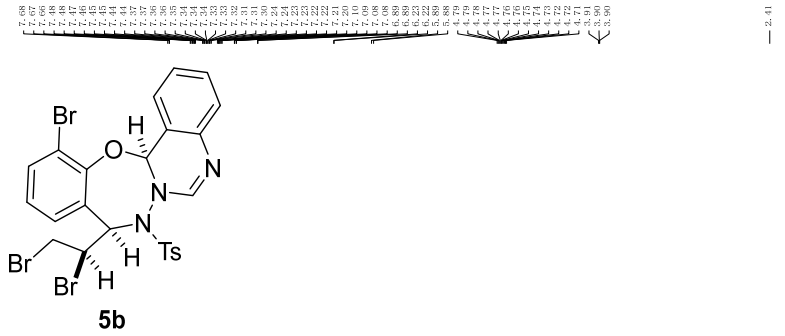
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



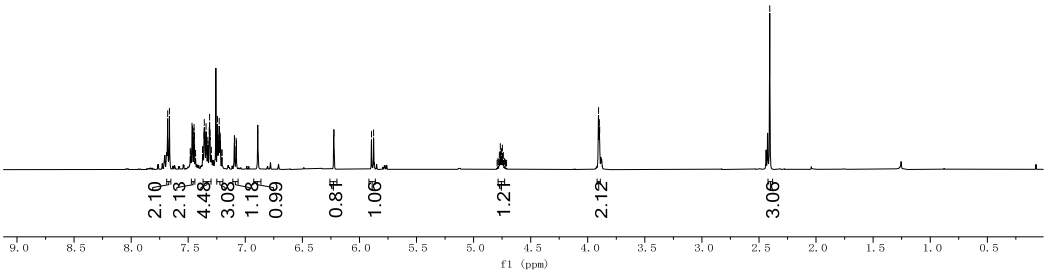
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



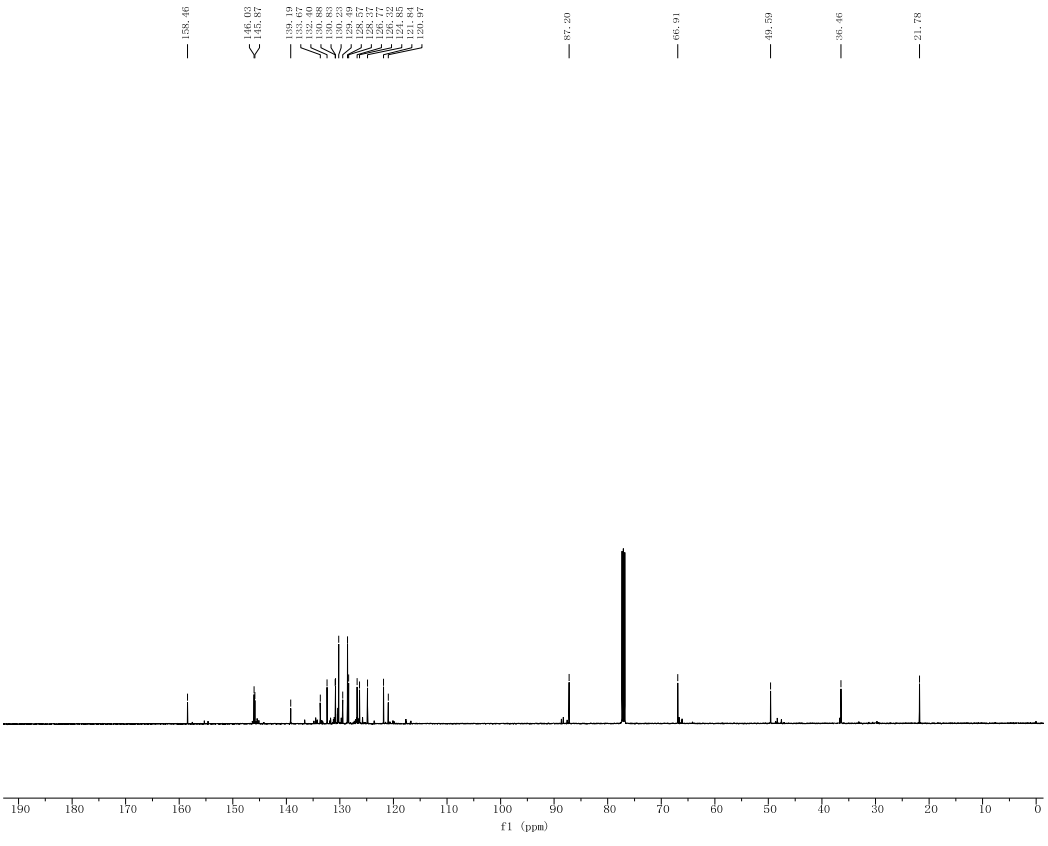
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



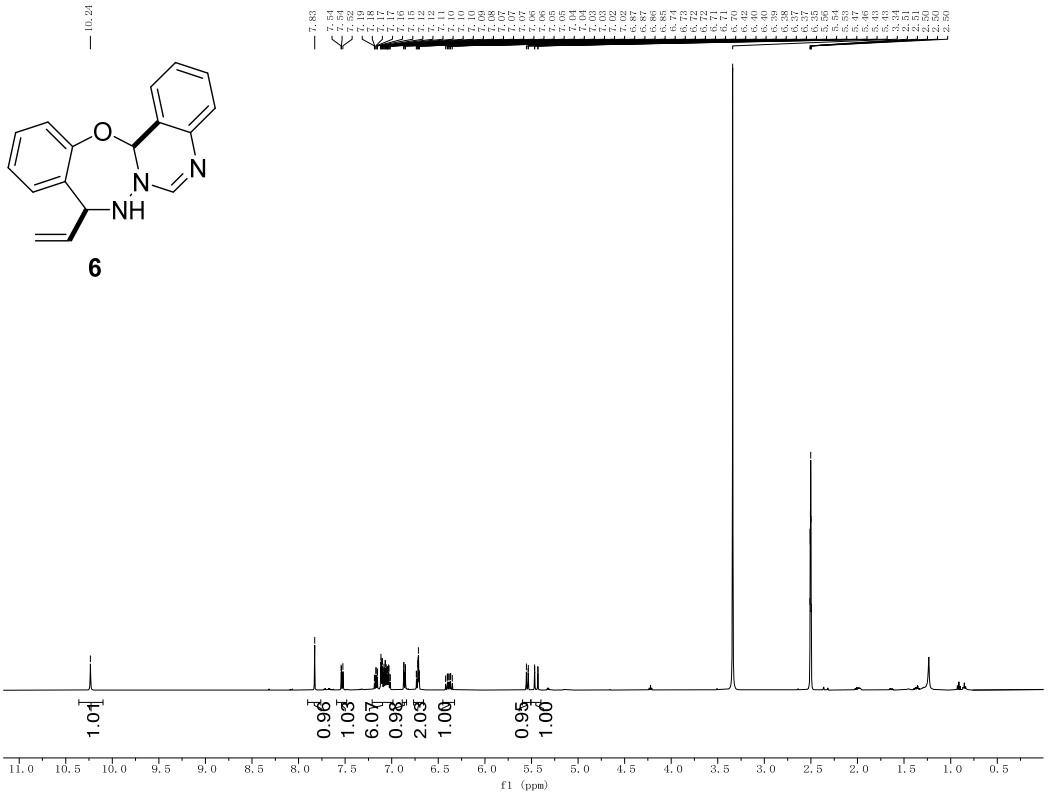
5b



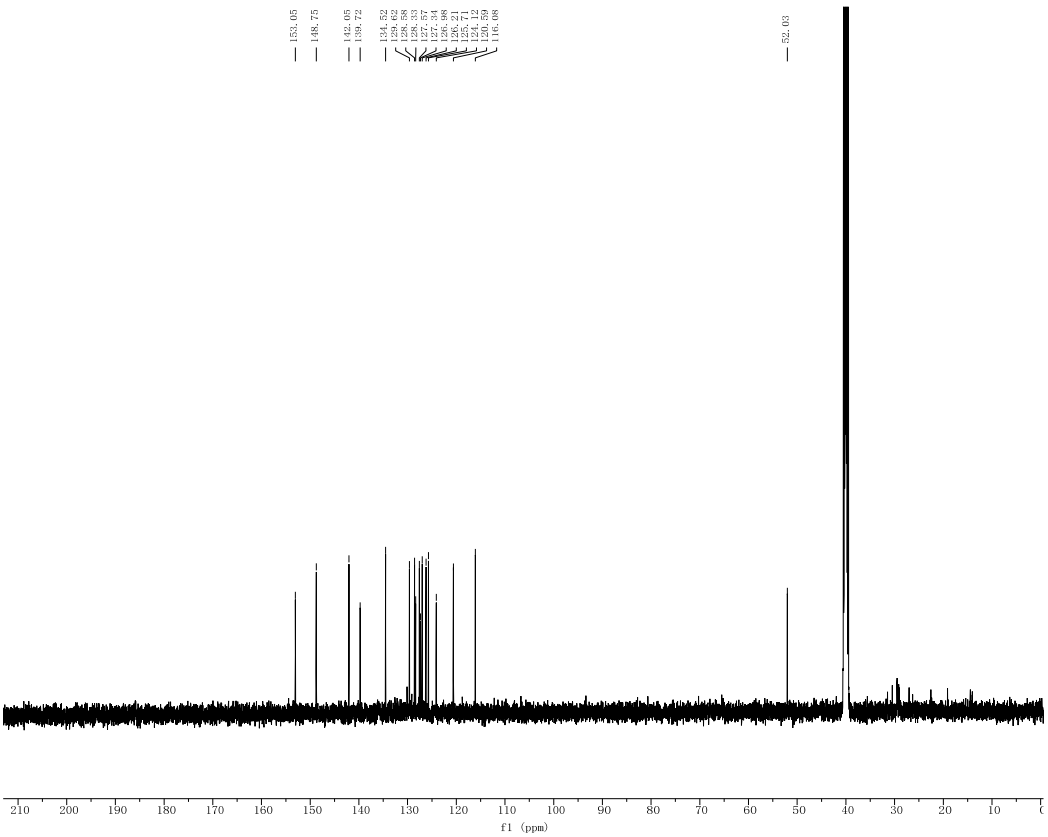
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, DMSO-d_6)

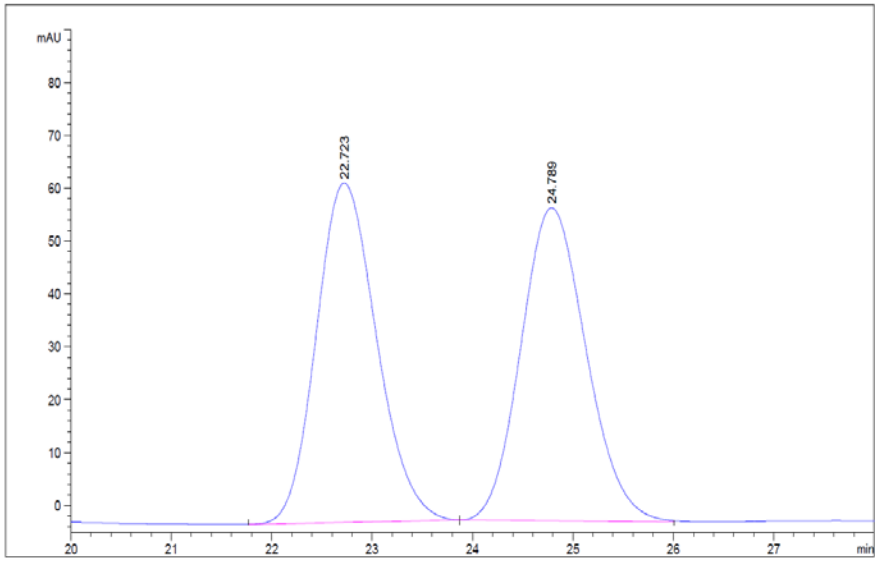


^{13}C NMR spectrum (126 MHz, DMSO-d_6)



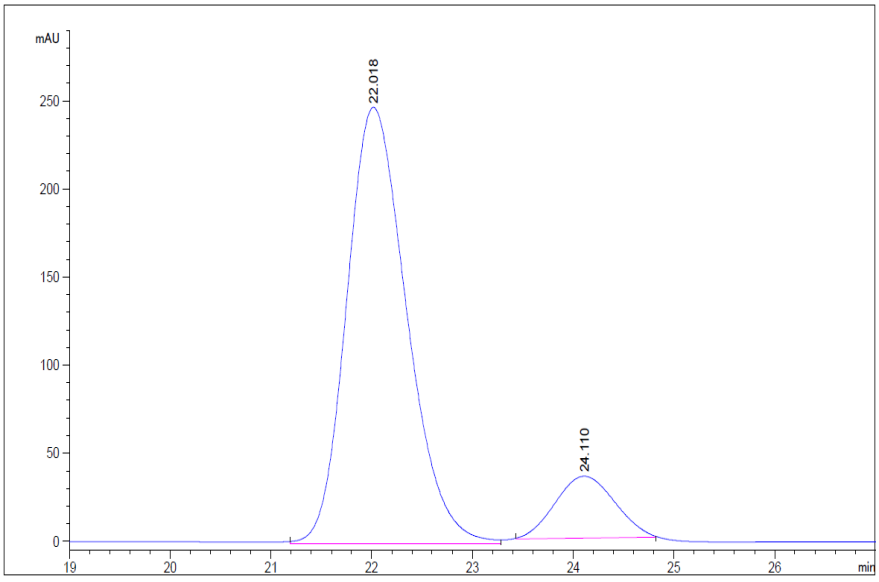
HPLC Chromatograms of All Products

HPLC chromatogram of racemic product **3aa**



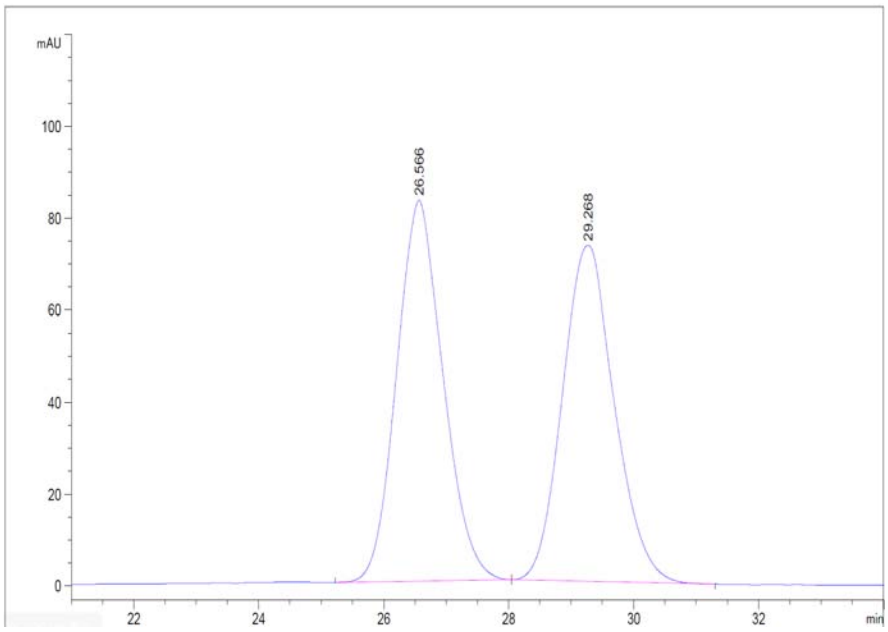
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.723	BB	0.6479	2678.49487	64.17604	50.0655
2	24.789	MF R	0.7523	2671.49121	59.18179	49.9345

HPLC chromatogram of chiral product **4aa**



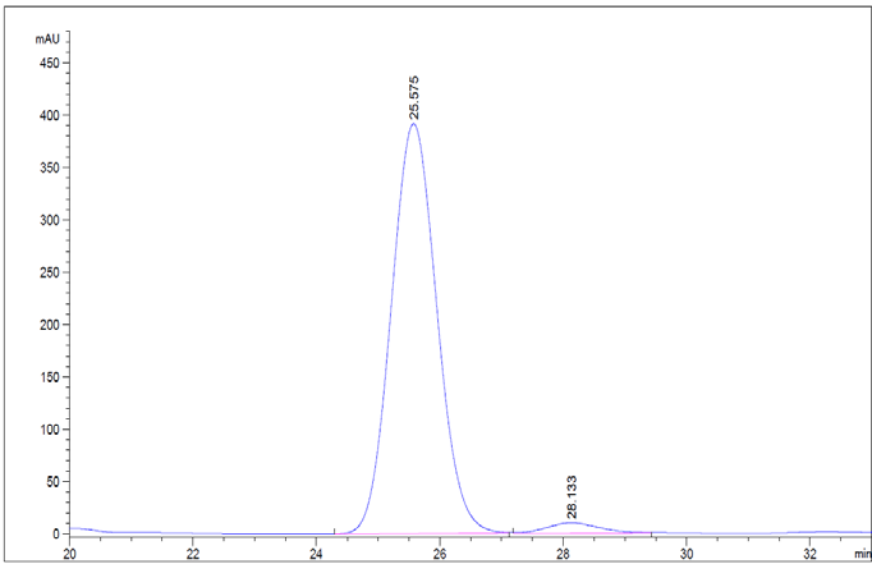
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.018	MM R	0.6511	1.02281	247.74037	87.5946
2	24.110	MM R	0.6866	1448.53503	35.16076	12.4054

HPLC chromatogram of racemic product **3ba**



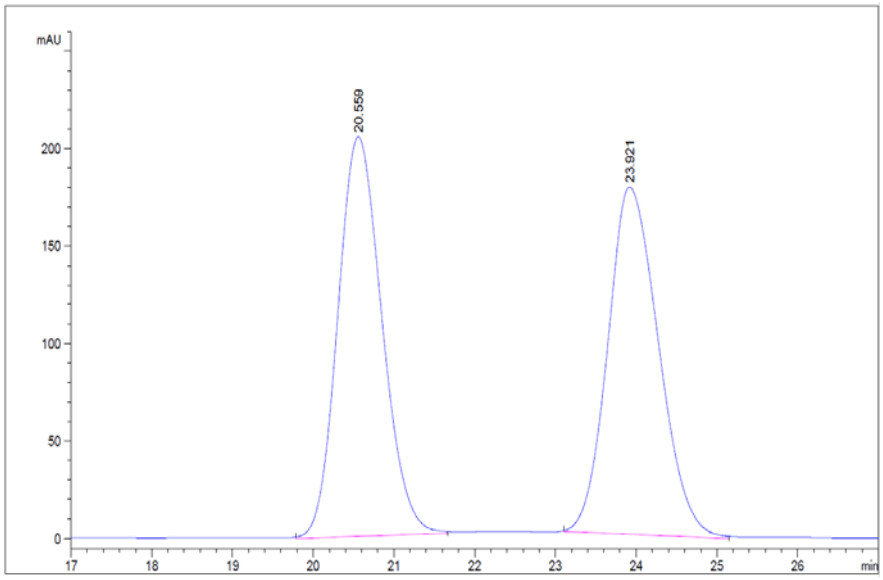
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.566	BB	0.8011	4265.23486	82.78930	50.2802
2	29.268	BB	0.8624	4217.69141	73.07430	49.7198

HPLC chromatogram of chiral product **4ba**



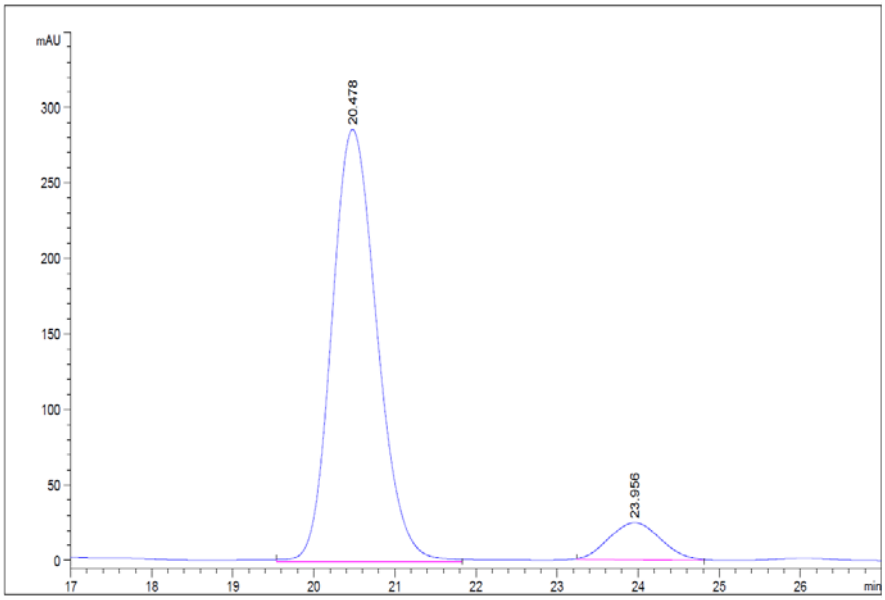
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.575	MM R	0.8541	2.00571	391.37234	97.0873
2	28.133	MM R	1.0031	601.73303	9.99827	2.9127

HPLC chromatogram of racemic product **3ea**



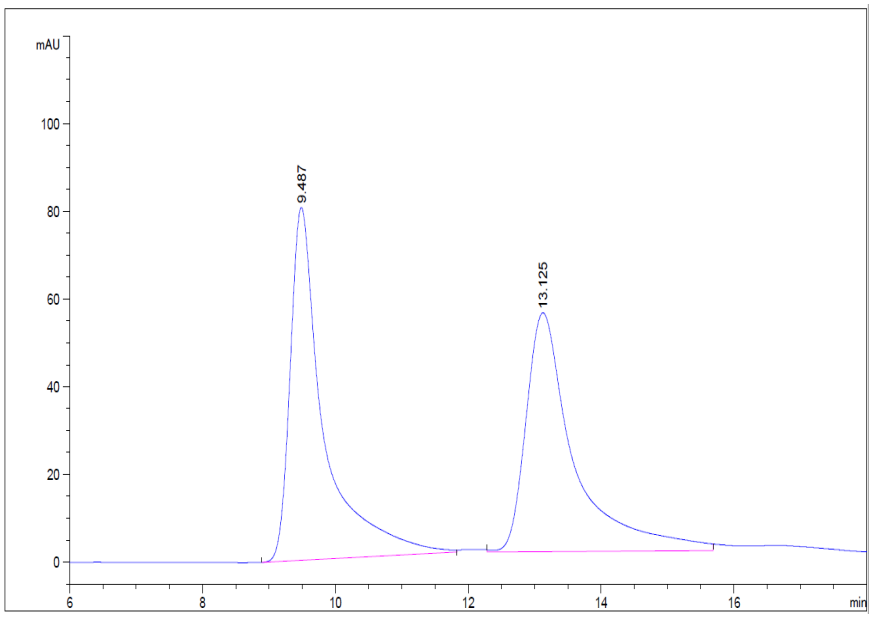
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.559	MM R	0.6316	7766.18994	204.93684	49.9866
2	23.921	MM R	0.7271	7770.35352	178.10362	50.0134

HPLC chromatogram of chiral product **4ea**



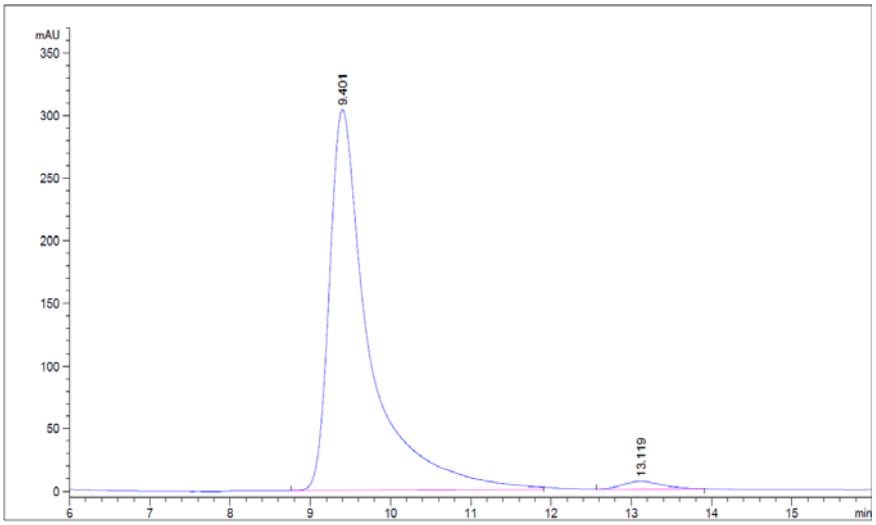
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.478	MM R	0.6437	1.10426e4	285.93152	91.0105
2	23.956	MM R	0.7363	1090.72668	24.69032	8.9895

HPLC chromatogram of racemic product **4bb**



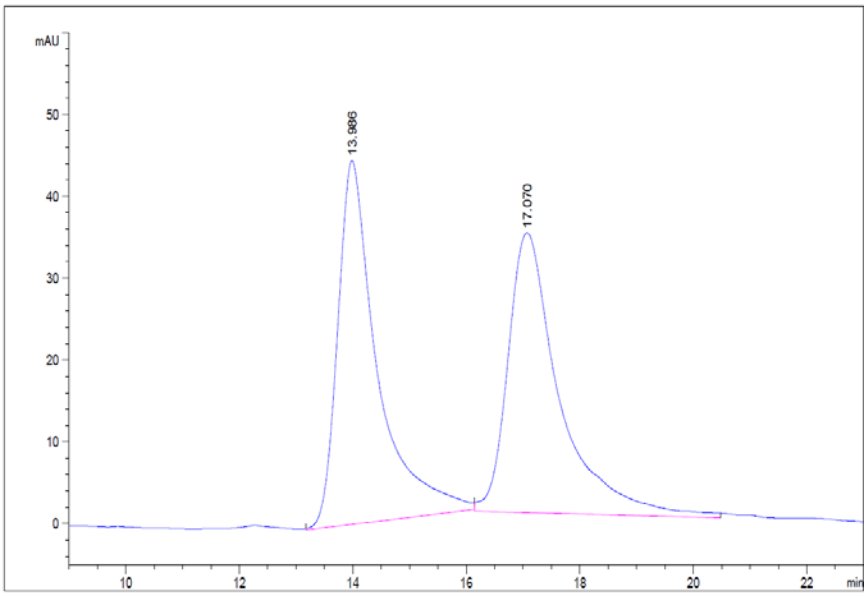
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.487	MM R	0.5864	2832.74561	80.50751	50.7375
2	13.125	MF R	0.8418	2750.39478	54.45171	49.2625

HPLC chromatogram of chiral product **4bb**



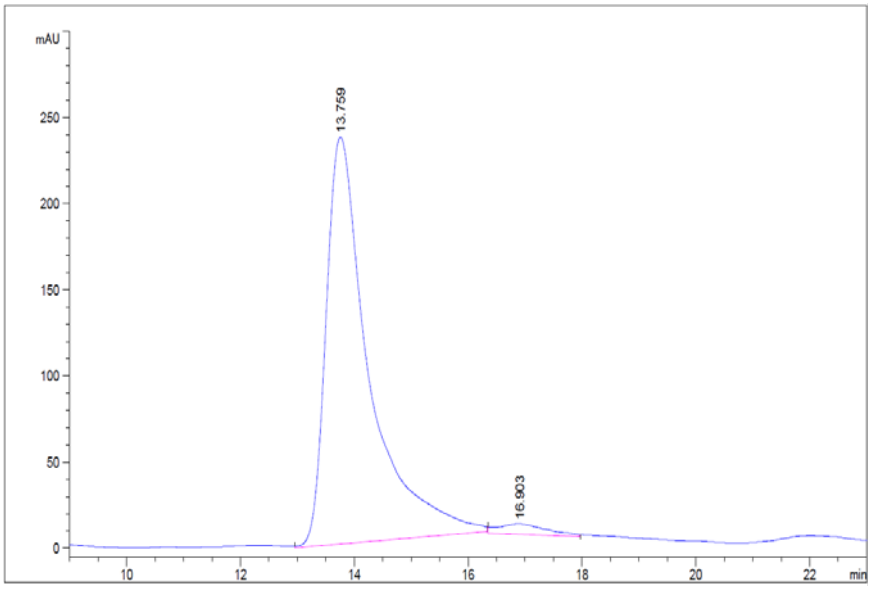
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.401	MF R	0.5761	1.05173e4	304.28091	97.7340
2	13.119	MM R	0.5983	243.84918	6.79263	2.2660

HPLC chromatogram of racemic product **4bd**



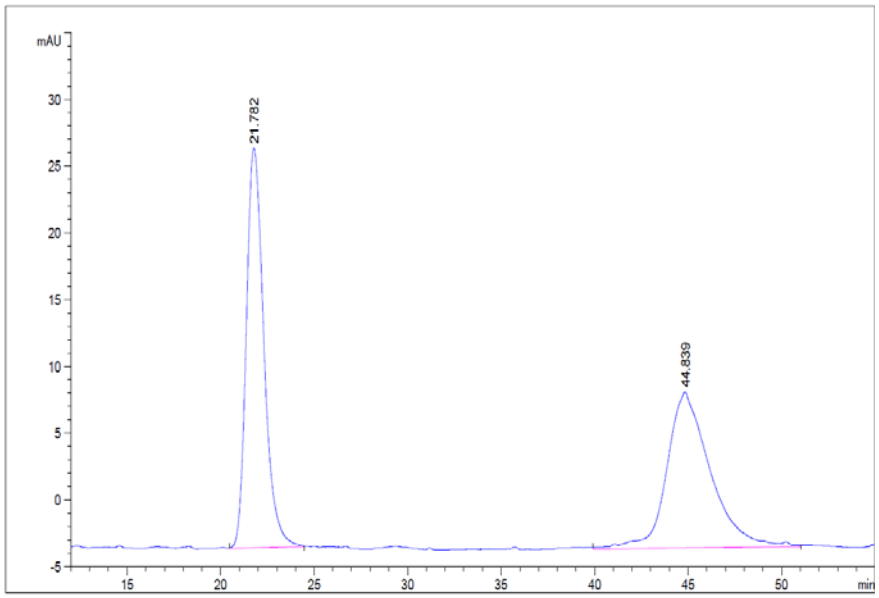
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.986	MM R	0.8079	2156.36377	44.48328	50.1075
2	17.070	MM R	1.0479	2147.10791	34.14918	49.8925

HPLC chromatogram of chiral product **4bd**



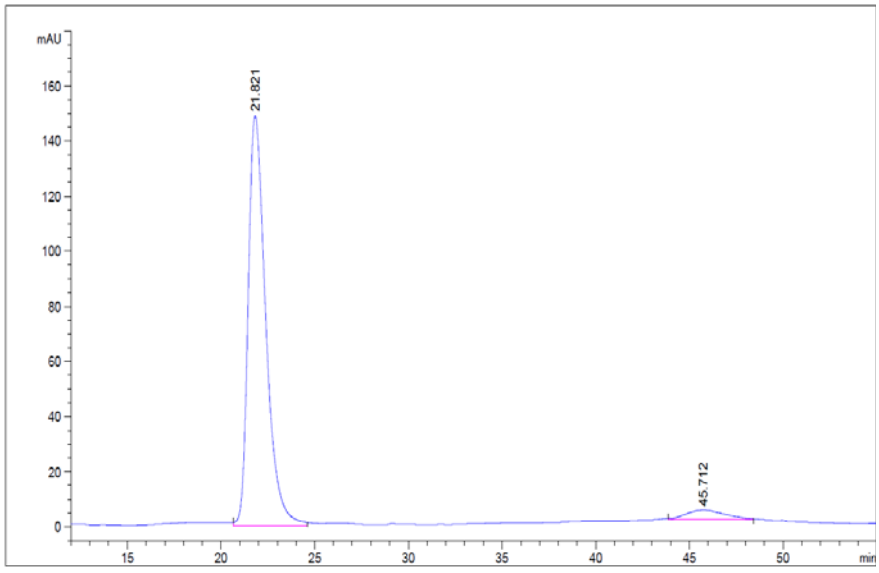
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.759	MM R	0.8752	1.23932e4	236.01077	97.1160
2	16.903	MM R	0.9999	368.03125	6.13428	2.8840

HPLC chromatogram of racemic product **4be**



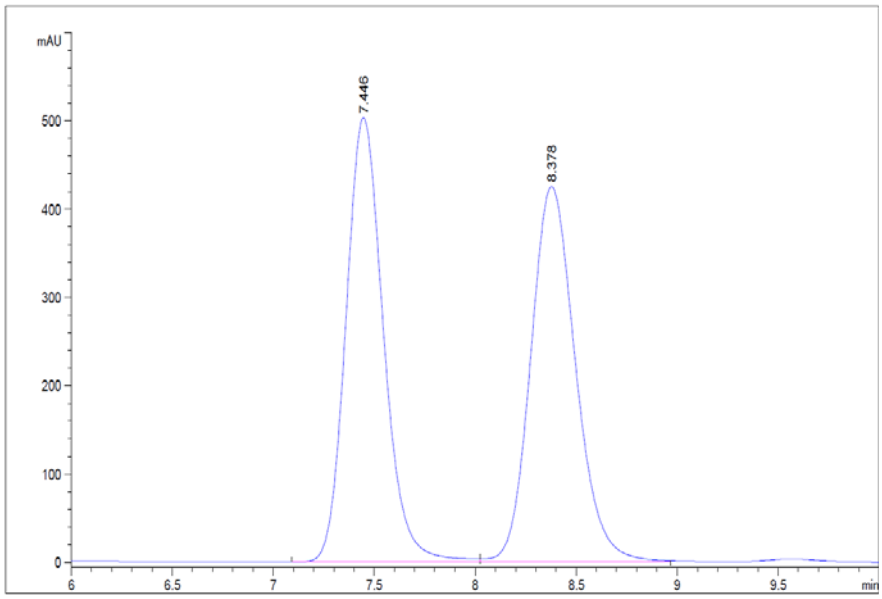
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.782	MM R	1.0876	1956.32544	29.98030	50.7708
2	44.839	MM R	2.6998	1896.92639	11.71021	49.2292

HPLC chromatogram of chiral product **4be**



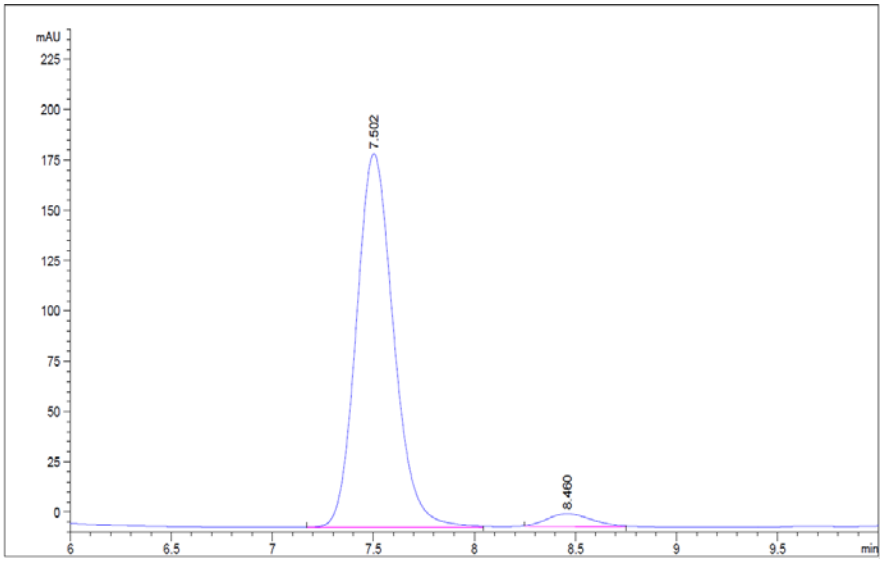
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.821	MM R	1.0836	9664.59473	148.64738	95.0148
2	45.712	MM R	2.4580	507.08252	3.43827	4.9852

HPLC chromatogram of racemic product **4bf**



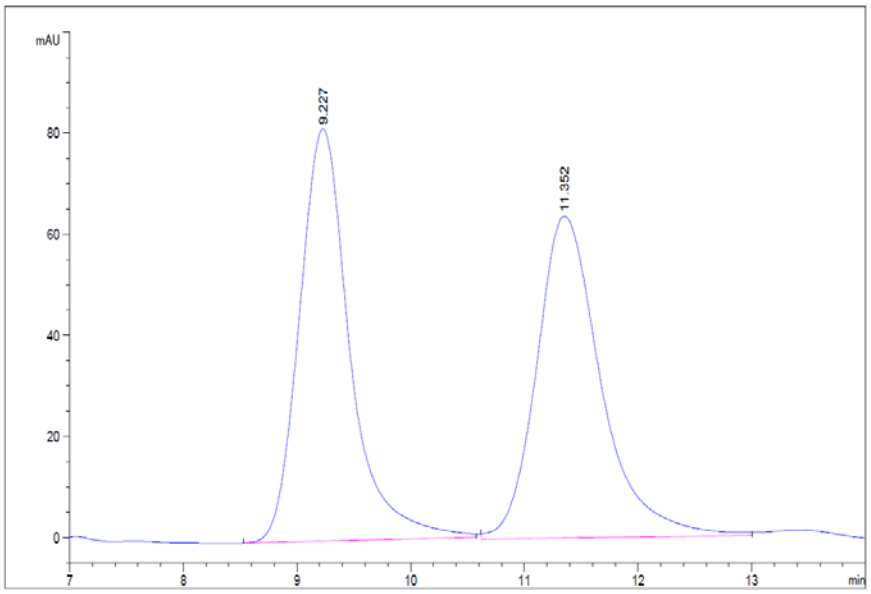
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.446	BV	0.1984	6475.07471	502.34210	49.7771
2	8.378	MF R	0.2563	6533.07764	424.82959	50.2229

HPLC chromatogram of chiral product **4bf**



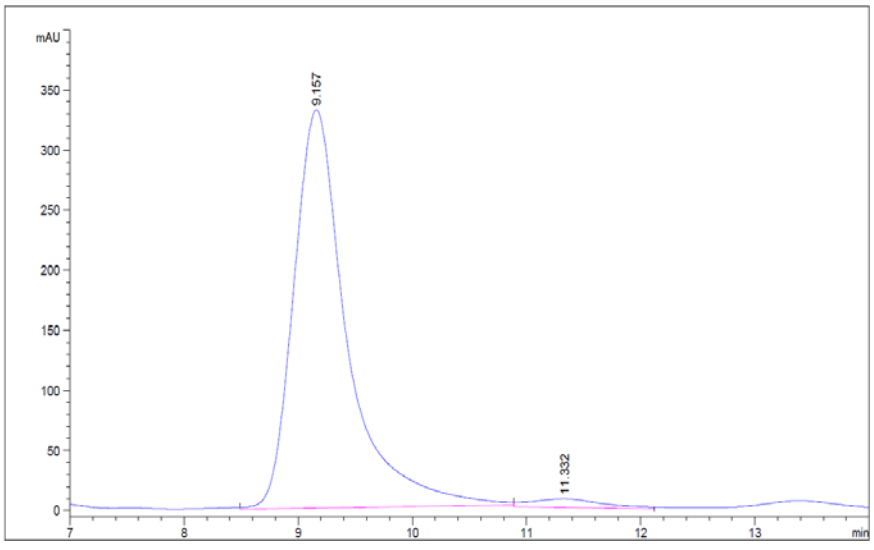
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.502	MM R	0.2139	2387.36035	186.04926	96.0679
2	8.460	MM R	0.2549	97.71642	6.39007	3.9321

HPLC chromatogram of racemic product **4bg**



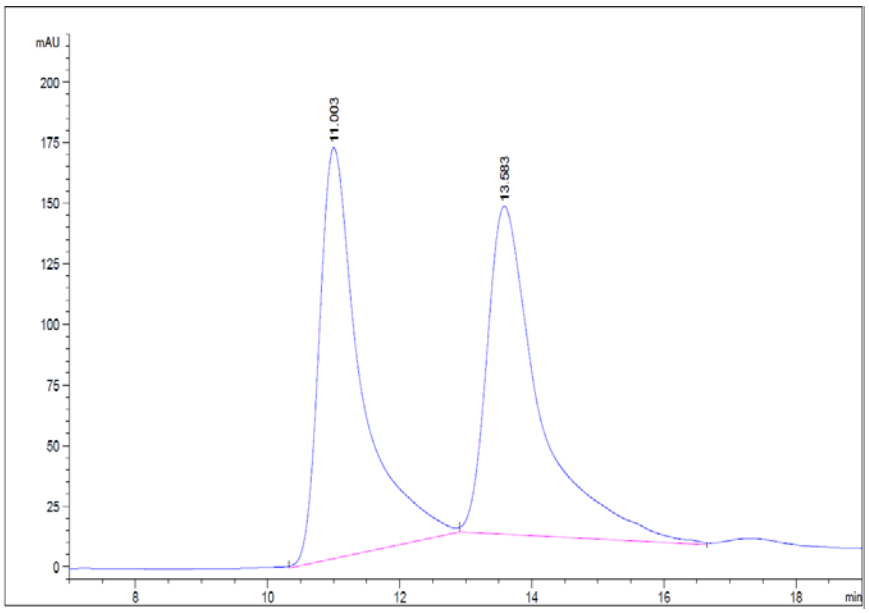
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.227	MM R	0.5144	2516.26147	81.53439	50.0469
2	11.352	MM R	0.6569	2511.54663	63.72014	49.9531

HPLC chromatogram of chiral product **4bg**



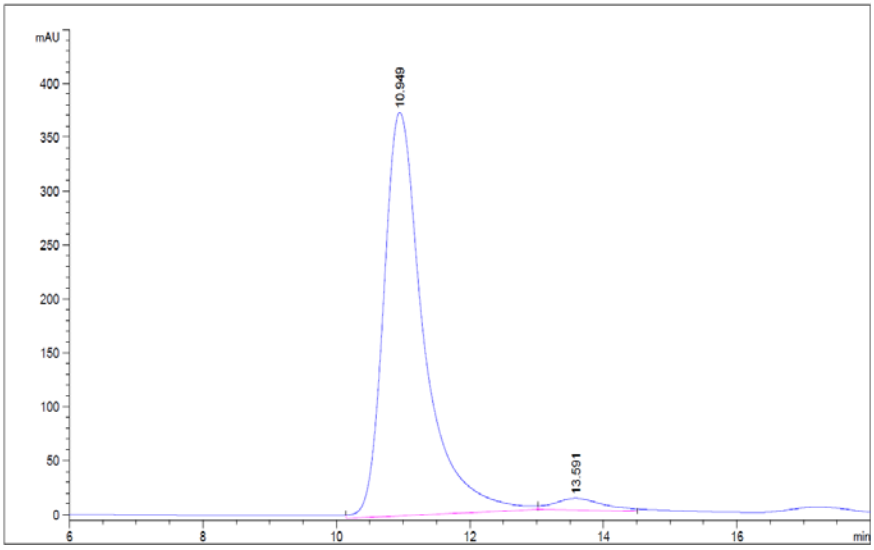
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.157	MM R	0.5423	1.07812e4	331.33960	97.1263
2	11.332	MM R	0.7347	318.98666	7.23658	2.8737

HPLC chromatogram of racemic product **4bh**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.003	MM R	0.7355	7485.40674	169.63321	50.0263
2	13.583	MM R	0.9202	7477.54004	135.43274	49.9737

HPLC chromatogram of chiral product **4bh**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.949	MM R	0.6953	1.56092e4	374.14340	96.4782
2	13.591	MM R	0.8548	569.79614	11.10919	3.5218

X-Ray Crystallographic Data

X-Ray Crystallography Data Crystallographic data for the product **3aa** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2264459. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of the product **3aa** were obtained by slow evaporation of a solution containing **3aa** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **3aa** are listed in the Table S3.

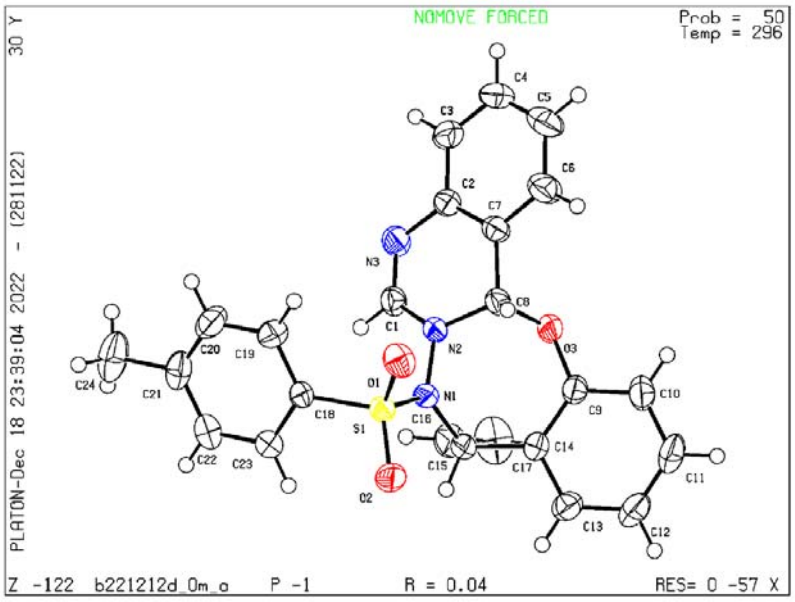


Figure S1. ORTEP view of the compound **3aa** with thermal ellipsoids drawn at the 50% probability level

Table S3. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**
Empirical formula	$C_{24}H_{21}N_3O_3S$
Formula weight	431.50
Temperature/K	296(2)

Crystal system	triclinic
Space group	P-1
a/Å	8.0853(5)
b/Å	10.9301(7)
c/Å	13.3531(8)
α/°	104.791(2)
β/°	92.638(2)
γ/°	111.152(2)
Volume/Å^3	1051.52(11)
Z	2
Density (calculated)	1.363
Absorption coefficient	0.186
F(000)	452.0
Theta range for data collection	0.58 × 0.5 × 0.45
Index ranges	MoKα (λ = 0.71073)
Reflections collected	4.178 to 55.1
Independent reflections	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Completeness to theta = 25.242°	32847
Max. and min. transmission	4845 [Rint = 0.0401, Rsigma = 0.0242]
Data/restraints/parameters	4845/0/281
Goodness-of-fit on F^2	1.103
Final R indexes [I>2sigma(I)]	R1= 0.0404, wR2= 0.1186
Final R indexes [all data]	R1 = 0.0505, wR2 = 0.1269
Largest diff. peak/hole / e Å^{-3}	0.37/-0.43

X-Ray Crystallography Data Crystallographic data for the product **4ba** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2311978. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of the product **4ba** were obtained by slow evaporation of a solution containing **4ba** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **4ba** are listed in the Table S4.

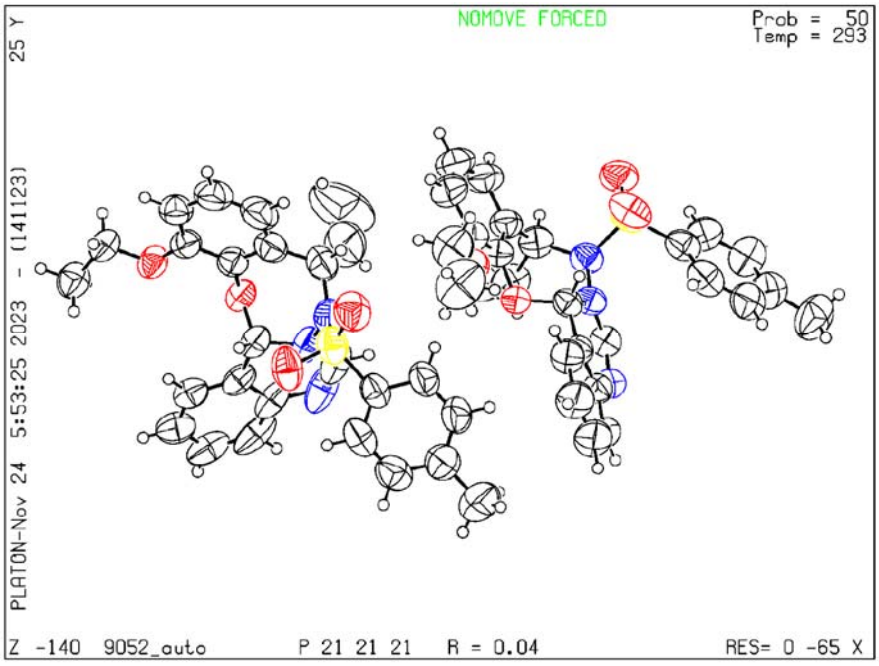


Figure S2. ORTEP view of the compound **4ba** with thermal ellipsoids drawn at the 50% probability level

Table S4. Crystal data and structure refinement for **4ba**.

Identification code	**4ba**
Empirical formula	$C_{26}H_{25}N_3O_4S$
Formula weight	475.55

Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.53610(10)
b/Å	17.8100(2)
c/Å	26.2442(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4924.67(9)
Z	8
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	1.472
F(000)	2000.0
Crystal size/mm^3	0.15 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.736 to 153.512
Index ranges	$-12 \le h \le 13$, $-22 \le k \le 22$, $-33 \le l \le 33$
Reflections collected	148366
Independent reflections	10285 [R_{int} = 0.0684, R_{sigma} = 0.0237]
Data/restraints/parameters	10285/9/617
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1235
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.1342
Largest diff. peak/hole / e Å^{-3}	0.35/-0.24
Flack parameter	-0.002(6)

X-Ray Crystallography Data Crystallographic data for the product **5b** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2270182. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of the product **5b** were obtained by slow evaporation of a solution containing **5b** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **5b** are listed in the Table S5.

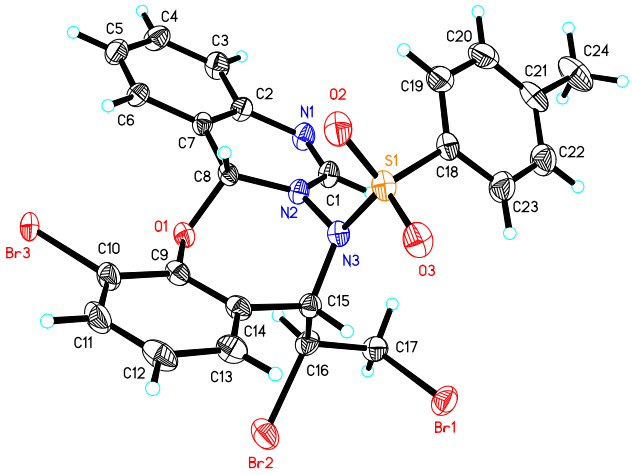


Figure S5. ORTEP view of the compound **5b** with thermal ellipsoids drawn at the 50% probability level

Table S5. Crystal data and structure refinement for **5b**.

Identification code	**5b**
Empirical formula	$C_{24}H_{20}Br_3N_3O_3S$
Formula weight	670.22
Temperature	213(2) K
Wavelength	0.71073

Crystal system	Triclinic
Space group	P -1
a/Å	a = 10.8989(7)
b/Å	b = 11.4714(7)
c/Å	c = 11.6523(8)
α/°	1246.00(14)
β/°	2
γ/°	1.786 Mg/m^3
Absorption coefficient	4.972 mm^{-1}
F(000)	660
Crystal size	0.180 x 0.150 x 0.130 mm^3
Theta range for data collection	3.059 to 25.496?
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14
Reflections collected	22982
Independent reflections	4620 [R(int) = 0.0698]
Completeness to theta = 25.242?	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4091
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4620 / 0 / 317
Goodness-of-fit on F^2	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1368
R indices (all data)	R1 = 0.0823, wR2 = 0.1502