Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplemental Information

Metal-free visible-light-induced cross-dehydrogenative coupling of benzocyclic imines with water/P(O)H compounds : efficent access to functionalized benzazepines/ones

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1. General information

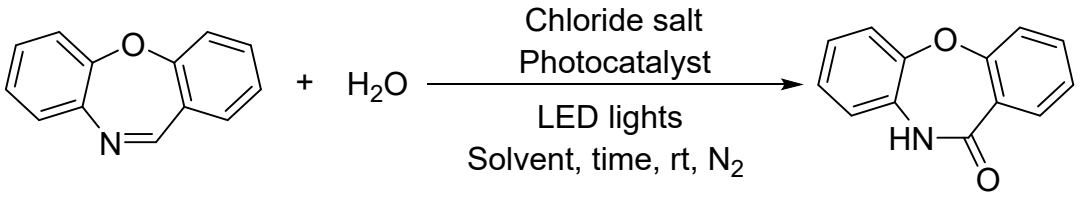
All reactions were carried out under inert atmospheres employing standard techniques unless otherwise noted. All reagents and materials were commercially available and used as received, unless otherwise noted. Diglycidyl ether of bisphenol A (DGEBA) with epoxy resin value of 0.44 mol/100 g was purchased from Nantong Xingchen Synthetic Material Co., Ltd., China. 4,4-diaminodiphenyl methane (DDM), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were purchased from Titan Technology Co., Ltd., China. All solvent was in ultra-dry and anhydrous storage and its purity ≥ 99.9%.

The products were purified on column chromatography with silica gel (200–300 mesh). Thin-layer chromatography (TLC) separations were performed on silica gel GF254 plates with a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluent, and the plates were visualized with UV light. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker AMX 400 NMR spectrometer with TMS as an internal standard in $CDCl_3$ or DMSO-d_6 solution. Chemical shifts for ^{1}H NMR were reported in terms of chemical shift in reference to TMS at 0.00 ppm, residual $CHCl_3$ at 7.26 ppm, or residual DMSO-d_6 at 2.50 ppm (δ ppm). The following abbreviations were used to illustrate the diversities: δ = chemical shifts, *J* = coupling constant, s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. Chemical shifts for ^{13}C NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm, middle peak) and the DMSO-d_6 solvent signal (39.50 ppm, middle peak).

RLR-18CF continuous flow photo reactor is supported by Beijing Bibby scientific Co., Ltd., China. Melting points were obtained on a Yanaco M500 melting point apparatus and are uncorrected. High resolution mass spectra were obtained via an Agilent LC/MSD TOF 6500 series mass spectrometer. According to GB/T 2406.2-2009 standard, the limiting oxygen index (LOI) values were evaluated using the JF-3 oxygen index instrument (Jiangning, China) with sample's dimension of 130 mm × 6.5 mm × 3.2 mm. The limiting oxygen index of each sample was the average of five parallel tests. According to GB/T 2408-2008 standard, the vertical burning (UL-94) tests were assessed using the CZF-3 instrument (Jiangning, China) with sample's dimension of 130 mm × 13 mm × 3.2 mm. The burning time of each sample was the average of five parallel tests.

2. Optimization of condition

Table S1 Reaction Conditions Optimizations for 3a

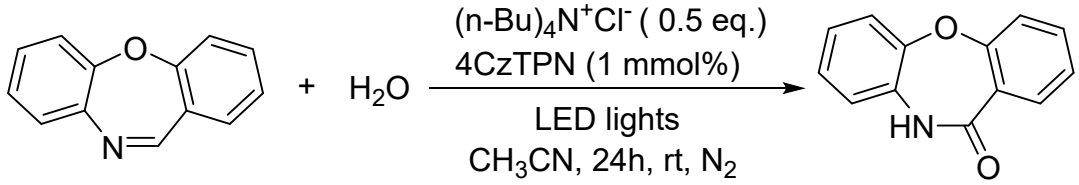


1 **3a**

entry	chloride salt	photocatalyst	solvent	LED lights	time	3a[b]
1	NaCl	$Ir(ppy)_2(bpy)PF_6$	DCM	30W blue LEDs	48	45%
2	KCl	$Ir(ppy)_2(bpy)PF_6$	DCM	30W blue LEDs	48	38%
3	LiCl	$Ir(ppy)_2(bpy)PF_6$	DCM	30W blue LEDs	48	10%
4	$MgCl_2$	$Ir(ppy)_2(bpy)PF_6$	DCM	30W blue LEDs	48	25%
5	$NiCl_2$	$Ir(ppy)_2(bpy)PF_6$	DCM	30W blue LEDs	48	35%
6	$(n\text{-}Bu)_4N^+Cl^-$	$Ir(ppy)_2(bpy)PF_6$	DCM	50W blue LEDs	24	64%
7	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	DCM	50W blue LEDs	24	74%
8	$(n\text{-}Bu)_4N^+Cl^-$	4CzIPN	DCM	50W blue LEDs	24	67%
9	$(n\text{-}Bu)_4N^+Cl^-$	Eosin-Y	DCM	50W blue LEDs	24	38%
10	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	CH_3CN	50W blue LEDs	24	98%
11	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	$CHCl_3$	50W blue LEDs	24	64%
12	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	DMF	50W blue LEDs	24	5%
13	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	PhCl	50W blue LEDs	24	62%
14	$(n\text{-}Bu)_4N^+Cl^-$	4CzTPN	EtOH	50W blue LEDs	24	NR

[a]Conditions: **1a** (0.2 mmol), photocatalyst (1 mol %), HAT agents tetrabutyl ammonium chloride (0.5 equiv), and 10 uL of water in solvent (2 mL) under a nitrogen atmosphere irradiation using blue LEDs at room temperature. [b]Isolated yields were shown.

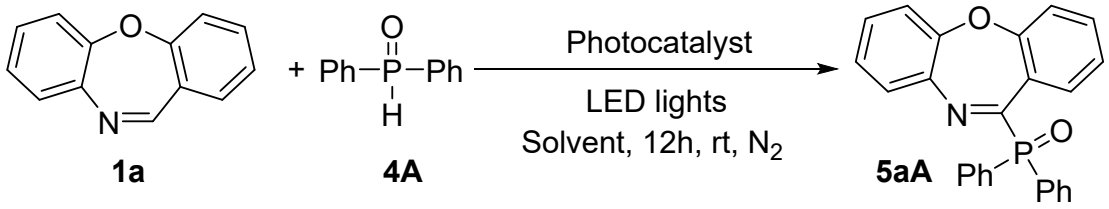
Table S2 Control experiment



entry	Conditions[a]	3a[b]
1	No water	trace
2	No $(n\text{-}Bu)_4N^+Cl^-$	45%
3	No photocatalyst	trace
4[c]	No light	N.D.
5[c]	No light, 60°C	N.D.

[a]Conditions: **1a** (0.2 mmol), 4CzTPN (1 mol %), tetrabutyl ammonium chloride (0.5 equiv), and 10 uL of water in CH_3CN (2 mL) under a nitrogen atmosphere irradiation using 50W blue LEDs at room temperature. [b]Isolated yields were shown. [c] N.D. = not detected.

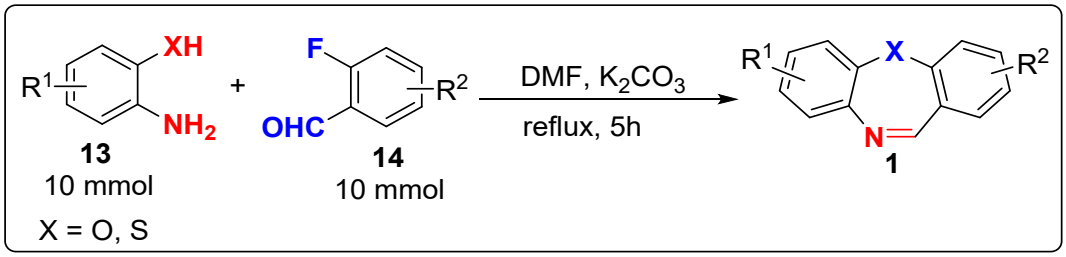
Table S3 Reaction Conditions Optimizations for 5aA



entry	photocatalyst	solvent	LED lights	time	3a[b]
1	$Ir(ppy)_2(bpy)PF_6$	DCM	15W blue LEDs	6	54%
2	4CzTPN	DCM	15W blue LEDs	6	58%
3	Eosin Y	DCM	15W blue LEDs	6	trace
4[c]	4CzTPN	CH_3CN	15W blue LEDs	6	N.D.
5	4CzTPN	THF	15W blue LEDs	6	trace
6	4CzTPN	PhCl	15W blue LEDs	6	trace
7	4CzTPN	DMF	15W blue LEDs	6	trace
8	4CzTPN	DCM	20W blue LEDs	8	51%
9	4CzTPN	DCM	50W blue LEDs	12	76%

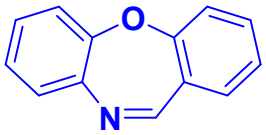
[a] Conditions: the reaction was conducted on a 0.2 mmol scale. **1a** (0.2 mmol), **4a** (0.2 mmol), photocatalyst (5 mmol %) in solvent (2 mL) under a nitrogen atmosphere irradiation using LED lights at room temperature. [b] Isolated yields. [c] N.D. = not detected.

3. General procedure for the preparation of benzocyclic imine 1

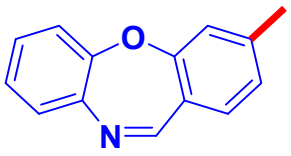


2-Aminophenol or 2-aminobenzenethiol **13** (10.0 mmol), 2-fluorobenzaldehyde **14** (10.0 mmol), and potassium carbonate (15.0 mmol, 2.07 g) were stirred in 20 mL DMF solvent and refluxed at 150 °C for 5 h. After cooled to room temperature, the reaction mixture were directly purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 5/1, *v*/*v*) to afford the desired product **1.**

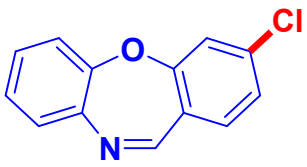
4. Characterization data of compounds 1a-1o [1,2,7]



dibenzo[b,f][1,4]oxazepine (1a). Lit.[1]. Yellow solid (1.17 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.52 (s, 1H), 7.44 (ddd, *J* = 8.1, 7.5, 1.7 Hz, 1H), 7.35 (ddd, *J* = 13.4, 7.6, 1.8 Hz, 2H), 7.27 – 7.10 (m, 5H). ^{13}C NMR (101 MHz, CDCl3): 160.8, 160.6, 152.8, 140.6, 133.5, 130.2, 129.3, 128.9, 127.5, 125.8, 125.2, 121.5, 120.8.

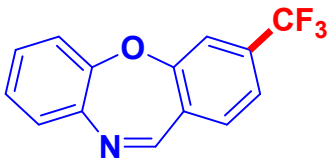


3-methyldibenzo[b,f][1,4]oxazepine (1b). Lit.[1] Brown solid (1.8g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H), 7.36 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.24 – 7.14 (m, 1H), 7.11 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 (s, 1H), 2.36 (s, 1H). ^{13}C NMR (101MHz, $CDCl_3$): 160.8, 160.5, 152.8, 144.8, 140.7, 130.2, 129.3, 128.8, 125.9, 125.8, 124.8, 121.5, 121.3, 21.5.

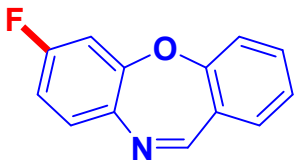


3-chlorodibenzo[b,f][1,4]oxazepine (1c). Lit.[1] Yellow solid (0.79g,

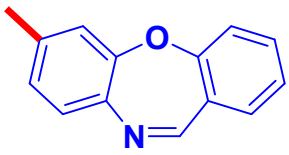
34%). ^{11}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H), 7.37 (dd, J = 7.5, 1.9 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.11 (dd, J = 7.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.9, 159.6, 152.4, 140.3, 139.3, 131.0, 129.5, 129.2, 126.2, 125.9, 125.6, 121.5, 121.5.



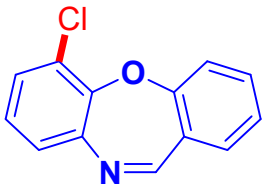
3-(trifluoromethyl)dibenzo[b,f][1,4]oxazepine (1d). Lit.[1] Yellow solid (1.1g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.55 (s, 1H), 7.49 – 7.35 (m, 4H), 7.30 – 7.18 (m, 2H), 7.15 (dd, J = 7.8, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.5, 159.2, 152.3, 140.2, 135.0 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.7, 130.2, 129.6, 129.5, 126.3, 123.3 (q, $J_{C\text{-}F}$ = 272.8 Hz), 122.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 121.5, 118.3 (q, $J_{C\text{-}F}$ = 3.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): -63.05.



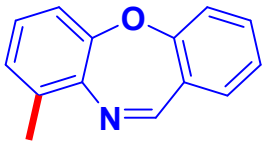
7-fluorodibenzo[b,f][1,4]oxazepine **(1e).** Lit.[2] **.** Yellow solid (1.9 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H), 7.37 (dd, J = 7.5, 1.9 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.25 – 7.15 (m, 4H), 7.11 (dd, J = 7.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 163.9 161.4, 160.1 (d, $J_{C\text{-}F}$ = 1.4 Hz), 159.8, 153.2 (d, $J_{C\text{-}F}$ = 11.3 Hz), 137.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 133.6, 130.3 (t, $J_{C\text{-}F}$ = 4.8 Hz), 127.2, 125.6, 120.8, 112.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 109.1 (d, $J_{C\text{-}F}$ = 24.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): 112.79.



7-methyldibenzo[b,f][1,4]oxazepine (1f). Lit.[1] Yellow solid(0.96 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H), 7.44 (td, J = 7.8, 1.7 Hz, 1H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 – 7.11 (m, 3H), 7.01 – 6.93 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.4, 159.9, 152.4, 139.6, 138.0, 133.4, 130.2, 129.1, 127.5, 126.5, 125.1, 121.9, 120.8, 21.0.

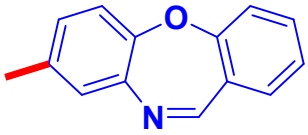


6-chlorodibenzo[b,f][1,4]oxazepine (1g). Lit.[1] Yellow solid (1.40 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.58 (s, 1H), 7.50 (td, J = 8.0, 1.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 (d, J = 7.5 Hz, 1H), 7.10 (t, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.3, 156.0, 148.1, 142.0, 133.7, 130.0, 129.0, 127.5, 127.3, 126.7, 125.9, 125.7, 121.6.

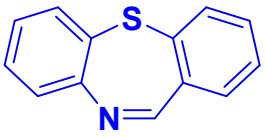


9-methyldibenzo[*b,f*][1,4]oxazepine (1h). Lit.[1] Yellow solid (1.04 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.62 (s, 1H), 7.44 (td, J = 7.9, 1.6 Hz, 1H), 7.35 (dd, J = 7.6, 1.6 Hz, 1H), 7.20 (td, J = 7.5, 0.8 Hz, 1H), 7.13 (dd, J = 16.5, 8.3 Hz, 2H), 7.02 (dd, J = 18.5, 7.6

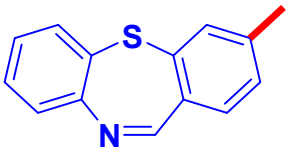
Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.7, 160.7, 150.6, 140.1, 135.5, 133.4, 130.2, 129.6, 129.5, 127.4, 125.1, 121.1, 120.7, 20.7.



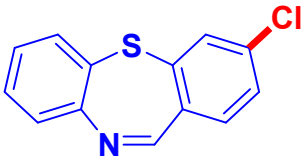
8-methyldibenzo[b,f][1,4]oxazepine (1i). Lit.[1] Yellow solid (0.83 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.51 (s, 1H), 7.44 (td, J = 8.0, 1.7 Hz, 1H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.22 – 7.09 (m, 3H), 7.02 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.7, 160.7, 150.6, 140.1, 135.5, 133.4, 130.2, 129.6, 129.5, 127.4, 125.1, 121.1, 120.7, 20.7.



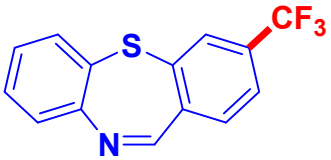
dibenzo[b,f][1,4]thiazepine (1j). Lit.[1] White solid (1.68 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.90 (s, 1H), 7.47 – 7.30 (m, 7H), 7.21 – 7.13 (m, 1H). ^{13}C NMR (101 MHz, CDCl3): 162.3, 148.6, 139.4, 137.3, 132.8, 131.7, 131.5, 129.5, 129.3, 128.9, 128.3, 127.3, 126.9.



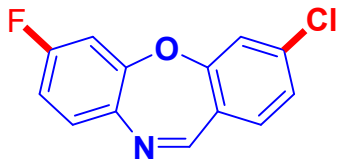
3-methyldibenzo[b,f][1,4]thiazepine (1k). Lit.[2] Yellow solid (1.8 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.68 (s, 1H), 7.24 (dd, J = 7.8, 1.1 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.07 – 7.03 (m, 2H), 6.95 (ddd, J = 17.5, 11.7, 4.8 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.1, 148.6, 142.1, 138.9, 134.4, 132.6, 131.9, 129.3, 129.1, 128.8, 128.7, 126.9, 126.85, 21.0.



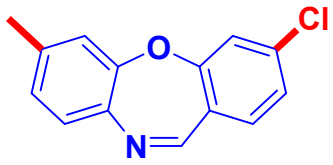
3-chlorodibenzo[b,f][1,4]thiazepine (1l). Lit.[1] Brown solid (2.3 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.75 (s, 1H), 7.37 – 7.30 (m, 2H), 7.28 – 7.20 (m, 4H), 7.12 – 7.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.2, 148.5, 141.0, 137.8, 135.6, 133.0, 131.5, 130.4, 129.7, 128.6, 128.1, 127.6, 127.1. ^{19}F NMR (376 MHz, $CDCl_3$): -62.96.



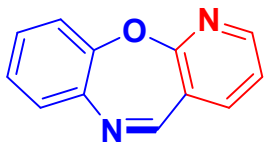
3-(trifluoromethyl)dibenzo[b,f][1,4]thiazepine (1m). Lit.[1] Yellow solid (2.4 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.80 (s, 1H), 7.58 (s, 1H), 7.47 (dd, J = 8.0, 0.9 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.19 (m, 2H), 7.08 (ddd, J = 7.9, 6.7, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.9, 148.4, 140.6, 140.1, 133.3 (q, $J_{C\text{-}F}$ = 33.2 Hz), 133.0, 129.8, 129.7, 128.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 127.9, 127.8, 127.2, 125.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.40 (q, $J_{C\text{-}F}$ = 272.9 Hz).



3-chloro-7-fluorodibenzo[b,f][1,4]oxazepine (1n). Lit.[2] Yellow solid (1.8 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.40 (s, 1H), 7.33 (dd, J = 8.8, 6.2 Hz, 1H), 7.28 (d, J = 2.6 Hz, 1H), 7.22 (dd, J = 8.2, 1.9 Hz, 1H), 7.15 (d, J = 1.8 Hz, 1H), 6.92 (ddd, J = 8.8, 7.7, 2.8 Hz, 1H), 6.84 (dd, J = 8.7, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.7 (d, $J_{C\text{-}F}$ = 250.0 Hz), 159.9, 158.7 (d, $J_{C\text{-}F}$ = 1.7 Hz), 152.6 (d, $J_{C\text{-}F}$ = 11.1 Hz), 139.2, 136.9 (d, $J_{C\text{-}F}$ = 3.7 Hz), 130.9, 130.5 (d, $J_{C\text{-}F}$ = 9.9 Hz), 125.9, 125.7, 121.4, 113.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 109.1 (d, $J_{C\text{-}F}$ = 24.4 Hz).



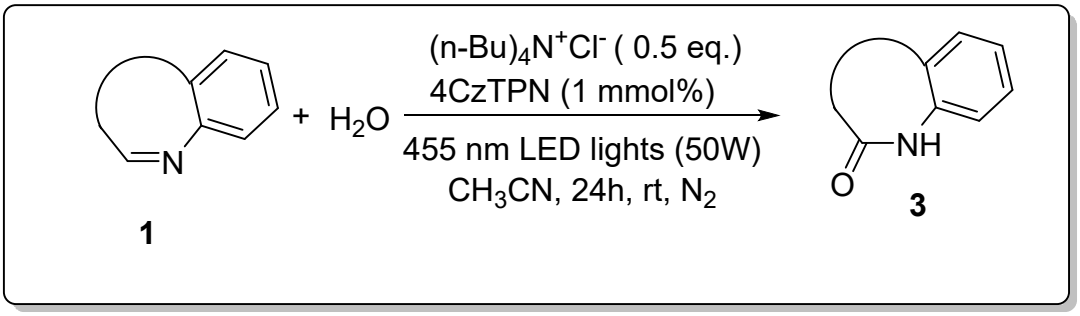
3-chloro-7-methyldibenzo[b,f][1,4]oxazepine (1o). Lit.[2] White solid (1.2g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.33 (s, 1H), 7.19 – 7.15 (m, 2H), 7.12 – 7.06 (m, 2H), 6.92 (dd, J = 8.0, 1.2 Hz, 1H), 6.84 (d, J = 1.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.65, 158.7, 151.9, 139.9, 138.9, 137.9, 130.9, 129.3, 126.8, 126.1, 125.5, 121.9, 121.5, 20.9.



benzo[b]pyrido[3,2-f][1,4]oxazepine (1p). Lit.[7] Yellow solid (0.36g, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.43 (s, 1H), 8.39 (dd, J = 4.9, 1.9 Hz, 1H), 7.75 (dd, J = 7.5, 2.0 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): 163.8, 157.8, 151.6, 150.6, 140.0, 139.5, 129.7, 129.4, 126.3, 122.4, 121.8, 121.7.

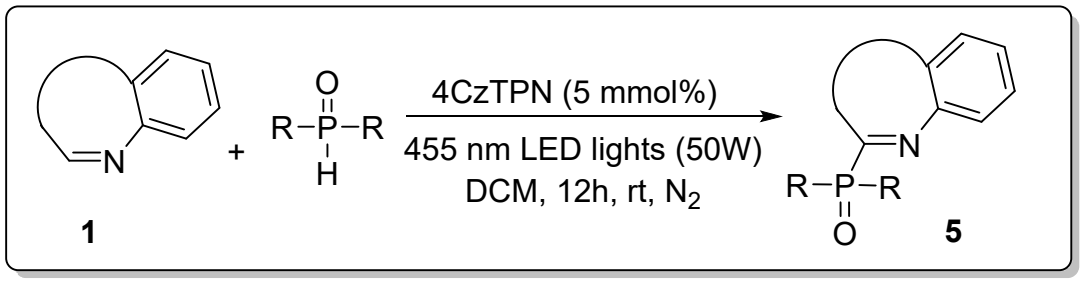
5. General procedure for the synthesis of benzozepinones 3 and 5

Standard Procedure for 3



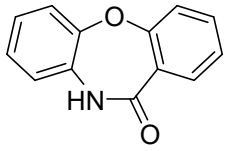
Benzocyclic imine **1** (0.2 mmol), 4CzTPN (1.6 mg, 0.002 mmol, 1 mmol%), and tetrabutyl ammonium chloride (27.8 mg, 0.1 mmol) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), water (10 uL) and CH_3CN (2.0 mL) was added, the vial was sealed and exposed to blue LEDs (50 W LED light) at room temperature for 12 h. The reaction mixture was diluted with H_2O (15 mL) and washed with dichloromethane (3 x 10 mL). The organic phase was dried over anhydrous sodium sulfate and purified directly by column chromatography to afford the product **3**.

Standard Procedure for 5

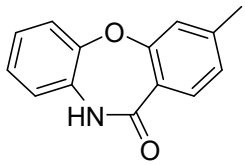


Benzocyclic imine **1** (0.2 mmol), 4CzTPN (8.0 mg, 0.010 mmol, 5 mmol%), and P(O)H compound (0.2 mmol) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), DCM (2.0 mL) was added, the vial was sealed and exposed to blue LEDs (50 W LED light) at room temperature for 12 h. The reaction mixture was diluted with H_2O (15 mL) and washed with dichloromethane (3 x 10 mL). The organic phase was dried over anhydrous sodium sulfate and purified directly by column chromatography to afford the product **5**.

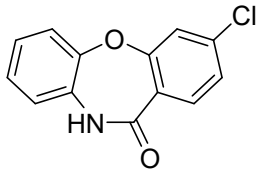
6. Characterization data of compounds 3 and 5 [3-6]



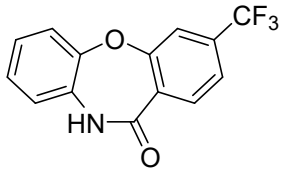
dibenzo[*b,f*][1,4]oxazepin-11(10H)-one (**3a**). lit[5]. White solid. M.p.: 118-120 °C, 41mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (s, 1H), 6.76 – 6.66 (m, 1H), 6.32 – 6.21 (m, 1H), 6.05 – 5.96 (m, 3H), 5.94 – 5.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.8, 159.8, 151.0, 134.6, 132.1, 130.7, 125.9, 125.3, 121.8, 121.4, 120.9. HRMS (ESI) calcd. for $C_{13}H_{10}NO_2^+$ (M + H^+) *m/z* 212.0707, found 212.0704.



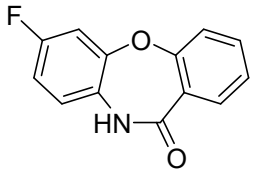
3-methyldibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3b). White solid. M.p.: 138-140 °C, 23mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.95 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.33 – 7.19 (m, 5H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 158.7, 149.9, 144.9, 130.9, 129.9, 125.2, 124.9, 124.8, 121.3, 120.8, 120.4, 120.3, 20.5. HRMS (ESI) calcd. for $C_{14}H_{12}NO_2^+$ (M + H^+) *m/z* 226.0863, found 226.0863.



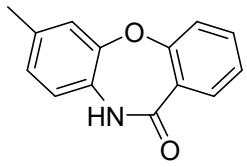
3-chlorodibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3c). Yellow oil. 42mg, 86% yield. ^{1}H NMR (400 MHz, DMSO): 10.61 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.23 – 7.12 (m, 3H). ^{13}C NMR (101 MHz, DMSO): 164.8, 159.2, 149.9, 138.1, 132.9, 130.9, 126.3, 125.8, 125.4, 124.7, 121.7, 121.4, 120.9. HRMS (ESI) calcd. for $C_{13}H_9ClNO_2^+$ (M + H^+) *m/z* 246.0316, found 246.0318.



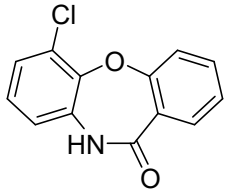
3-(trifluoromethyl)dibenzo[*b,f*][1,4]oxazepin-11(10H)-one (**3d**). White solid, M.p: 181-182 °C, 23mg, 41% yield for 24 h (54% yield for 48 h). ^{1}H NMR (400 MHz, $CDCl_3$): 9.16 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.22 – 7.12 (m, 3H). ^{13}C NMR (101 MHz, DMSO): 1, 158.9, 150.1, 133.9 (q, $J_{C\text{-}F}$ = 32.6 Hz), 132.9, 130.7, 129.6, 126.4, 125.5, 123.1 (q, $J_{C\text{-}F}$ = 272.8 Hz). 122.1 (q, $J_{C\text{-}F}$ = 3.6 Hz) 121.9, 121.5, 118.1 (q, $J_{C\text{-}F}$ = 3.5 Hz). HRMS (ESI) calcd. for $C_{14}H_9F_3NO_2^+$ (M + H^+) m/z 280.0580, found 280.0582.



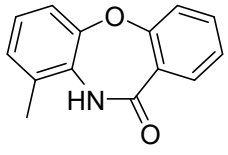
7-fluorodibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3e). White solid, M.p.: 204 - 206 °C. 26 mg, 57% yield. ^{19}F-NMR (69Hz, $CDCl_3$) = 115.5. ^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (s, 1H), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 (td, *J* = 8.0, 1.6 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 2H), 6.94 (dt, *J* = 8.5, 4.0 Hz, 2H), 6.85 – 6.77 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 170.6, 163.7, 163.9 (d, J_{C-F} = 243.1 Hz), 156.2 (d, J_{C-F} = 11.3 Hz), 138.1 (d, J_{C-F} = 300.9 Hz), 133.1 (d, J_{C-F} = 3.4 Hz), 130.9, 130.7, 127.7 (d, J_{C-F} = 9.7 Hz), 125.8, 117.9 (d, J_{C-F} = 22.4 Hz), 114.1 (d, J_{C-F} = 24.6 Hz), 84.2 (t, J_{C-F} = 33.2 Hz). HRMS (ESI) calcd. for $C_{13}H_9FNO_2^+$ (M + H^+) m/z 230.0612, found 230.0614.



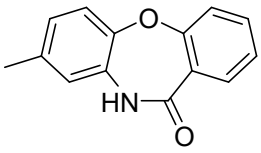
7-methyldibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3f). White solid. M.p.: 170-175°C, 27mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.57 (s, 1H), 7.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 (td, *J* = 7.8, 1.7 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.08 (s, 1H), 7.00 – 6.89 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.5, 159.8, 151.0), 136.3, 134.5, 132.1, 128.0, 126.6, 125.3, 122.2, 121.1, 120.9, 20.8. HRMS (ESI) calcd. for $C_{14}H_{12}NO_2^+$ (M + H^+) *m/z* 226.0863, found 226.0863.



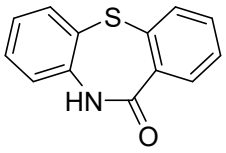
6-chlorodibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3g). White solid. M.p.: 225-226°C, 38mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 8.45 (s, 1H), 7.94 (d, *J* = 5.8 Hz, 1H), 7.75 – 7.39 (m, 3H), 7.16 – 6.89 (m, 2H). ^{13}C NMR (101 MHz, DMSO): 159.9, 152.7, 140.3, 129.1, 127.6, 126.0, 121.0, 120.5, 120.2, 120.1, 119.8, 115.3, 115.0. HRMS (ESI) calcd. for $C_{13}H_9ClNO_2^+$ (M + H^+) m/z 246.0317, found 246.0318.



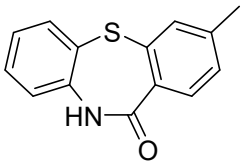
9-methyldibenzo[*b,f*][1,4]oxazepin-11(10H)-one (trans:cis = 58:42) (**3h**). Yellow oil, 31mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.62 (s, 1H), 7.91 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.75 (s, 1H), 7.51 (td, *J* = 7.8, 1.7 Hz, 1H), 7.44 (td, *J* = 8.0, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.17 – 7.07 (m, 3H), 7.06 – 6.96 (m, 4H), 2.42 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.0, 156.0, 151.8, 134.6, 131.9, 129.5, 129.2, 127.6, 125.7, 125.5, 125.4, 120.9, 119.6, 17.9. HRMS (ESI) calcd. for $C_{14}H_{12}NO_2^+$ (M + H^+) *m/z* 226.0863, found 226.0863.



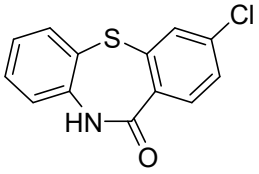
8-methyldibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3i). Yellow oil, 37mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 9.25 (s, 1H), 7.95 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 (td, *J* = 7.9, 1.7 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 6.96 – 6.88 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.8, 156.0, 149.0, 136.0, 134.5, 132.1, 130.3, 126.5, 125.3, 125.2, 121.8, 121.4, 120.9, 20.9. HRMS (ESI) calcd. for $C_{14}H_{12}NO_2^+$ (M + H^+) *m/z* 226.0863, found 226.0863.



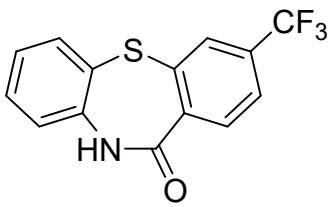
dibenzo[*b,f*][1,4]thiazepin-11(10H)-one (3j). White solid. M.p.: 202 – 205°C. 44mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.76 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.54 (dd, *J* = 24.0, 7.4 Hz, 2H), 7.45 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.22 – 7.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): 169.8, 139.4, 137.5, 137.0, 133.2, 132.4, 132.0, 131.99, 130.4, 129.9, 128.9, 126.2, 122.7. HRMS (ESI) calcd. for $C_{13}H_{10}NOS^+$ (M + H^+) *m/z* 228.0478, found 228.0492.



3-methyldibenzo[*b,f*][1,4]thiazepin-11(10H)-one (3k). White solid. M.p.320-321 °C, 29mg, 58% yield. ^{1}H NMR (400 MHz, DMSO): 10.60 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.23 (td, *J* = 8.1, 1.1 Hz, 2H), 7.13 (td, *J* = 7.5, 1.4 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO): 167.9, 141.9, 139.5, 135.5, 134.4, 131.9, 131.2, 130.8, 129.3, 129.0, 128.3, 124.8, 122.6, 20.0. HRMS (ESI) calcd. for $C_{14}H_{12}NOS^+$ (M + H^+) *m/z* 242.0634, found 242.0640.



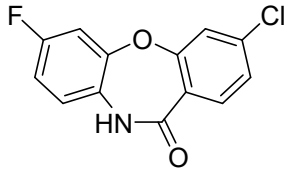
3-chlorodibenzo[*b,f*][1,4]thiazepin-11(10H)-one (3l). White solid. M.p. 104-106 °C, 48mg, 92% yield. ^{1}H NMR (400 MHz, DMSO): 10.77 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.38 (td, *J* = 7.9, 1.5 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.16 (td, *J* = 7.6, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 171.9, 144.3, 142.6, 141.0, 140.7, 137.4, 137.2, 135.1, 134.6, 133.5, 132.7, 130.1, 127.8. HRMS (ESI) calcd. for $C_{13}H_9ClNOS^+$ (M + H^+) *m/z* 262.0688, found 242.0698.



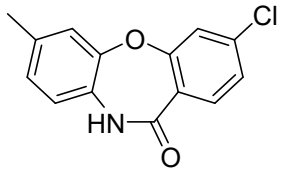
3-(trifluoromethyl)dibenzo[*b,f*][1,4]thiazepin-11(10H)-one (**3m**)

White solid. M.p. 207-209 °C. 34mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 9.03 (s, 1H), 7.95

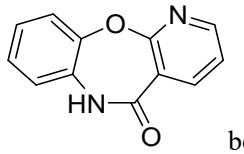
(d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.60 (dd, *J* = 11.0, 4.0 Hz, 2H), 7.35 (td, *J* = 8.0, 1.1 Hz, 1H), 7.24 – 7.14 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$): 169.1, 140.4, 139.2, 138.7, 134.2, 133.8, 133.4, 132.5, 130.3, 129.5, 128.8 (dd, J_{C-F} = 7.3, 3.6 Hz), 126.6, 125.6 (q, J_{C-F} = 3.4 Hz), 123.1. HRMS (ESI) calcd. for $C_{14}H_9F_3NOS^+$ (M + H^+) *m/z* 296.0352, found 296.0354.



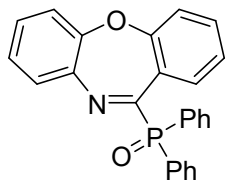
3-chloro-7-fluorodibenzo[*b,f*][1,4]oxazepin-11(10H)-one (3n). White solid. M.p. 225-227 °C. 31mg, 59% yield. ^{1}H NMR (400 MHz, DMSO): 10.61 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.43 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.34 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.19 (dd, *J* = 8.9, 5.9 Hz, 1H), 7.10 (td, *J* = 8.5, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO): 164.9, 159.3 (d, *J* = 243.4 Hz), 159.2, 150.9 (d, *J* = 11.5 Hz), 138.6, 133.4, 128.1 (d, *J* = 3.2 Hz), 126.6, 124.9, 123.2 (d, *J* = 9.6 Hz), 121.5, 113.7 (d, *J* = 22.5 Hz), 109.6 (d, *J* = 24.8 Hz). HRMS (ESI) calcd. for $C_{13}H_8ClFNO_2$+ (M + H^+) *m/z* 264.0223, found 264.0222.



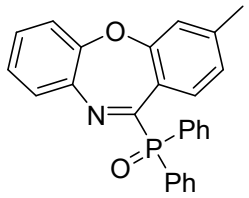
3-chloro-7-methyldibenzo[*b,f*][1,4]oxazepin-11(10H)-one (**3o**). White solid. M.p. 192-195 °C. 45mg, 86% yield. ^{1}H NMR (400 MHz, DMSO): 10.52 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.18 (d, *J* = 1.0 Hz, 1H), 7.02 (dt, *J* = 8.1, 4.6 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 170.6, 164.5, 155.0, 143.7, 140.3, 137.6, 133.0, 131.5, 130.2, 129.5, 126.5, 126.4, 125.8, 25.4. HRMS (ESI) calcd. for $C_{14}H_{11}ClNO_2^+$ (M + H^+) *m/z* 260.0473, found 260.0475.



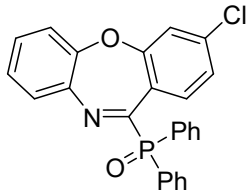
benzo[*b*]pyrido[*3,2-f*][1,4]oxazepin-5(6H)-one (**3p**) [8]. Yellow solid. M.p. 128-129 °C. 35mg, 83% yield. ^{1}H NMR (400 MHz, DMSO): 10.74 (s, 1H), 8.50 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.26 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.45 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.10 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.0, 162.9, 152.9, 148.6, 142.9, 126.9, 126.1, 123.0, 122.4, 122.2, 120.6. HRMS (ESI) calcd. for $C_{12}H_9N_2O_2$+ (M + H^+) *m/z* 213.0659, found 213.0660.



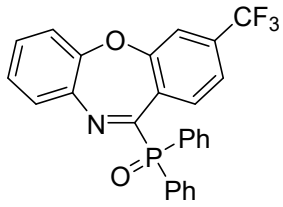
dibenzo[*b,f*][1,4]oxazepin-11-yldiphenylphosphine oxide (5aA) White solid. M.p. 167-169 °C. 62mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 8.17 (d, *J* = 7.5 Hz, 1H), 8.03 – 7.91 (m, 4H), 7.56 – 7.39 (m, 7H), 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 168.4, 167.2, 160.5 (d, J_{C-P} = 7.2 Hz), 151.3, 139.6 (d, J_{C-P} = 27.2 Hz), 132.7, 131.6, 131.4, 131.3, 131.1 (d, J_{C-P} = 2.8 Hz), 130.6, 129.6, 128.9, 127.7 (d, J_{C-P} = 1.3 Hz), 127.5, 127.4, 125.74 (d, J_{C-P} = 27.2 Hz), 124.8, 124.3, 120.2, 119.9. ^{31}P NMR (162 MHz, $CDCl_3$) 26.26. HRMS (ESI) calcd. for $C_{25}H_{19}NO_2P^+$ (M + H^+) *m/z* 396.1148, found 396.1149.



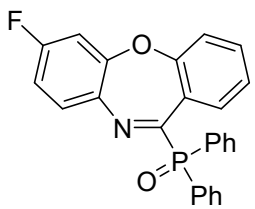
(3-methyldibenzo[*b*,*f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5bA). White solid. M.p. 169-170 °C. 38mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (d, *J* = 8.4 Hz, 1H), 7.99 – 7.89 (m, 4H), 7.57 – 7.42 (m, 6H), 7.25 – 7.12 (m, 2H), 7.00 – 6.94 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 168.6 (d, *J* = 125.2 Hz), 161.5 (d, *J* = 7.3 Hz), 152.3, 145.0, 140.7 (d, *J* = 27.7 Hz), 132.7, 132.3, 132.3, 132.0, 132.0, 131.6, 130.4, 129.7, 128.6 (d, *J* = 1.3 Hz), 128.5, 128.4, 126.1, 125.7, 124.0 (d, *J* = 27.5 Hz), 121.4, 121.1, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) 26.34. HRMS (ESI) calcd. for $C_{26}H_{21}NO_2P^+$ (M + H^+) *m/z* 410.1305, found 410.1306.



(3-chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5cA). White solid. M.p. 157-159 °C. 18mg, 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.85 (m, 4H), 7.58 – 7.44 (m, 6H), 7.29 – 7.26 (m, 1H), 7.25 – 7.13 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): 160.8 (d, *J* = 189.8 Hz), 151.8, 140.2 (d, *J* = 9.3 Hz), 139.5, 133.2, 132.3, 132.2, 132.2, 131.5, 131.2, 130.1, 128.8, 128.6, 128.5, 126.4, 126.2, 125.8, 125.8, 121.9, 121.4 (d, *J* = 12.3 Hz), 121.4 (d, *J* = 36.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 26.56. HRMS (ESI) calcd. for $C_{25}H_{18}ClNO_2P^+$ (M + H^+) *m/z* 430.0759, found 430.0763.

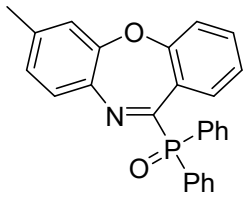


diphenyl(3-(trifluoromethyl)dibenzo[*b*,*f*][1,4]oxazepin-11-yl)phosphine oxide (5dA). White solid. M.p. 100-102 °C. 12mg, 13% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.32 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.90 (m, 4H), 7.60 – 7.39 (m, 8H), 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.9 (d, *J* = 124.5 Hz), 161.4 (d, *J* = 7.0 Hz), 151.7, 140.2 (d, *J* = 26.4 Hz), 135.1 (d, *J* = 33.3 Hz), 132.6, 132.32, 132.31, 132.2, 132.0, 131.4, 131.0, 130.4, 129.6 (d, *J* = 26.9 Hz), 129.57 (dd, *J* = 321.4, 294.5 Hz).128.9 (d, *J* = 1.3 Hz), 128.7, 128.6, 126.3, 122.2 (dd, *J* = 7.2, 3.6 Hz), 121.2, 118.3(dd, *J* = 7.2, 3.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 26.45. HRMS (ESI) calcd. for $C_{26}H_{18}F_3NO_2P^+$ (M + H^+) *m/z* 464.1022, found 464.1029.

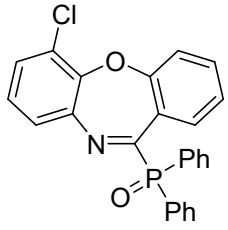


(7-fluorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5eA). White solid. M.p. 189-192 °C. 50mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (d, *J* = 7.9 Hz, 1H), 7.97 – 7.89 (m, 4H), 7.58 – 7.37 (m, 7H), 7.24 – 7.11 (m, 3H), 6.92 – 6.82 (m, 2H). ^{13}C NMR (101 MHz, CDCl3): 168.2 (dd, *J* = 125.1, 1.5 Hz), 164.5, 162.0, 160.8 (d, *J* = 7.1 Hz),

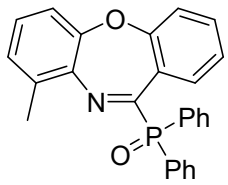
152.7 (d, J = 11.3 Hz), 137.1 (dd, J = 28.1, 3.6 Hz), 133.8, 132.4, 132.3, 132.2, 132.1 (d, J = 2.6 Hz), 131.4, 130.7, 129.8 (dd, J = 10.1, 1.3 Hz), 128.5 (d, J = 12.3 Hz), 126.7, 126.5, 125.7, 120.9, 112.9 (d, J = 22.3 Hz), 108.8 (d, J = 24.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 26.58. HRMS (ESI) calcd. for $C_{25}H_{18}FNO_2P^+$ (M + H^+) *m/z* 414.1054, found 414.1055.



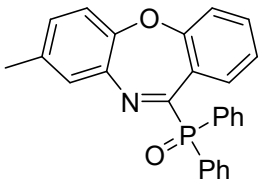
(7-methyldibenzo[*b,f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5fA). White solid. M.p. 165-167 °C. 35mg, 43% yield. ^{1}H NMR (400 MHz, CDCl3): 8.15 (d, J = 7.9 Hz, 1H), 7.96 (dd, J = 11.6, 7.0 Hz, 4H), 7.57 – 7.38 (m, 7H), 7.21 – 7.10 (m, 3H), 6.96 (d, J = 7.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 167.3, 166.1, 160.3 (d, J_{C-P} = 7.3 Hz), 150.9, 139.8, 137.1 (d, J_{C-P} = 27.7 Hz), 132.5, 131.8, 131.3, 131.3, 130.9 (d, J_{C-P} = 2.5 Hz), 130.7, 129.6, 127.5, 127.4, 126.0, 125.7, 125.5, 124.2, 120.6, 119.9, 20.2. ^{31}P NMR (162 MHz, $CDCl_3$) 26.19. HRMS (ESI) calcd. for $C_{26}H_{21}NO_2P$+ (M + H^+) *m/z* 410.1305, found 410.1306.



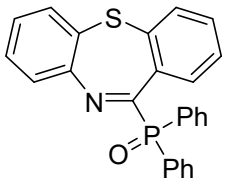
(6-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5gA). White solid. M.p. 201-203 °C. 46mg, 54% yield. ^{1}H NMR (400 MHz, CDCl3): 8.20 (dd, J = 7.8, 1.1 Hz, 1H), 7.98 – 7.85 (m, 4H), 7.57 – 7.43 (m, 7H), 7.40 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 7.15 – 7.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): 169.8 (d, J = 123.5 Hz), 161.0 (d, J = 7.1 Hz), 147.5, 141.8 (d, J = 27.5 Hz), 133.9, 132.3, 132.21, 132.19, 132.17, 131.1, 130.6, 129.6, 128.6, 128.5, 128.5, 128.4, 126.8 (d, J = 1.3 Hz), 126.7, 126.5 (d, J = 1.6 Hz), 125.7 (d, J = 2.9 Hz), 121.5. ^{31}P NMR (162 MHz, $CDCl_3$) 26.91. HRMS (ESI) calcd. for $C_{25}H_{18}ClNO_2P^+$ (M + H^+) *m/z* 430.0759, found 430.0763.



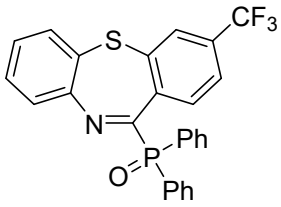
(9-methyldibenzo[*b,f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5hA). White solid. M.p. 177-179 °C. 52mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) : 8.26 (dd, J = 7.8, 1.0 Hz, 1H), 8.01 – 7.79 (m, 4H), 7.61 – 7.33 (m, 7H), 7.16 (dt, J = 17.8, 8.2 Hz, 3H), 6.98 (t, J = 7.0 Hz, 2H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 166.7, 165.5, 160.5 (d, J_{C-P} = 7.0 Hz), 151.6, 138.0 (d, J_{C-P} = 26.7 Hz), 136.5 (d, J_{C-P} = 1.3 Hz), 132.6, 131.4, 131.3, 131.1 (d, J_{C-P} = 2.8 Hz), 130.3, 129.5, 128.5, 127.5, 127.4, 126.4, 126.2, 125.9, 124.4, 119.8, 117.5, 17.2. ^{31}P NMR (162 MHz, $CDCl_3$) 29.31. HRMS (ESI) calcd. for $C_{26}H_{21}NO_2P^+$ (M + H^+) *m/z* 410.1305, found 410.1306.



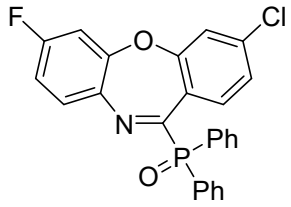
(8-methyldibenzo[*b,f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5iA). White solid. M.p. 120-122 °C. 53mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.99 – 7.90 (m, 4H), 7.63 – 7.37 (m, 7H), 7.24 – 7.10 (m, 3H), 7.04 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 168.7 (d, *J* = 125.1 Hz), 161.6 (d, *J* = 7.0 Hz), 150.1, 140.1 (d, *J* = 27.5 Hz), 135.6, 133.6, 132.6, 132.33, 132.31, 132.0 (d, *J* = 2.6 Hz), 131.8, 131.7, 131.6, 130.5 (d, *J* = 11.5 Hz), 128.8 (d, *J* = 1.3 Hz), 128.7, 128.6, 128.5, 128.4, 125.2, 120.8 (d, *J* = 7.6 Hz), 20.7. ^{31}P NMR (162 MHz, $CDCl_3$) 26.29. HRMS (ESI) calcd. for $C_{26}H_{21}NO_2P$+ (M + H^+) *m/z* 410.1305, found 410.1313.



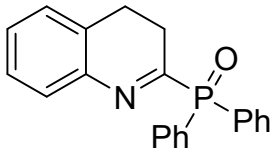
dibenzo[*b,f*][1,4]thiazepin-11-yldiphenylphosphine oxide (**5jA**). White solid. M.p. 168-170 °C. 83mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$)： 7.98 – 7.88 (m, 2H), 7.79 – 7.67 (m, 3H), 7.54 – 7.35 (m, 7H), 7.20 – 7.05 (m, 3H), 6.94 – 6.88 (m, 1H), 6.60 (td, *J* = 7.7, 1.3 Hz, 1H), 6.49 (dd, *J* = 8.1, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 145.0 (d, *J* = 11.4 Hz), 140.2 (d, *J* = 3.7 Hz), 137.2 (d, *J* = 13.3 Hz), 132.8 (d, *J* = 5.6 Hz), 132.1, 131.9 (d, *J* = 2.8 Hz), 131.8, 131.6, 131.5, 131.2, 131.2, 131.0, 130.9, 130.5, 128.9, 128.8 (d, *J* = 1.9 Hz), 128.7 (d, *J* = 3.6 Hz), 128.6 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 4.7 Hz), 119.8 (d, *J* = 26.5 Hz), 117.7. ^{31}P NMR (162 MHz, $CDCl_3$) 31.53. HRMS (ESI) calcd. for $C_{25}H_{19}NOPS^+$ (M + H^+) *m/z* 412.0920, found 412.0924.



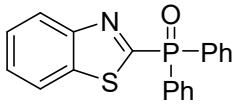
diphenyl(3-(trifluoromethyl)dibenzo[*b,f*][1,4]thiazepin-11-yl)phosphine oxide (**5mA**) White solid. M.p. 168-170 °C. 83mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 9.50 (s, 1H), 8.17 – 7.91 (m, 3H), 7.79 (s, 1H), 7.72 – 7.41 (m, 7H), 7.39 – 7.28 (m, 2H), 7.25 – 7.10 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.4 (d, *J* = 7.0 Hz), 151.7, 140.2 (d, *J* = 26.5 Hz), 135.1 (d, *J* = 33.4 Hz), 132.4, 132.3, 132.3, 132.2, 132.0, 131.4, 130.9, 130.4, 129.6 (q, *J* = 294.5 Hz), 129.4 (d, *J* = 1.3 Hz), 128.9 (d, *J* = 1.2 Hz), 128.7, 128.6, 126.5, 126.3, 124.6, 122.2 (dd, *J* = 6.5, 3.1 Hz), 121.2, 118.3 (d, *J* = 3.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 26.76. HRMS (ESI) calcd. for $C_{26}H_{18}F_3NOPS^+$ (M + H^+) *m/z* 480.0794, found 480.0780.



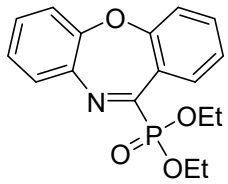
(3-chloro-7-fluorodibenzo[*b,f*][1,4]oxazepin-11-yl)diphenylphosphine oxide (5nA). White solid. M.p. 179-181 °C. 31mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, J = 8.4 Hz, 1H), 7.96 – 7.87 (m, 4H), 7.60 – 7.43 (m, 6H), 7.22 – 7.14 (m, 3H), 6.94 – 6.85 (m, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) 26.90. ^{13}C NMR (101 MHz, $CDCl_3$): 164.6, 162.1, 161.1 (d, $J_{P\text{-}C}$ = 6.7 Hz), 152.2 (d, $J_{P\text{-}C}$ = 11.2 Hz), 139.6, 132.3, 132.3, 132.2, 132.1, 131.5, 131.1, 123.0 (d, $J_{P\text{-}C}$ = 9.0 Hz), 128.7, 128.5, 126.1, 121.5, 113.4 (d, $J_{P\text{-}C}$ = 22.2 Hz), 108.9 (d, $J_{P\text{-}C}$ = 24.6 Hz). HRMS (ESI) calcd. for $C_{25}H_{17}ClFNO_2P^+$ (M + H^+) *m/z* 448.0664, found 448.0669.



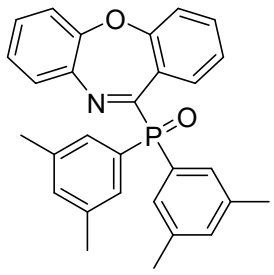
(3,4-dihydroquinolin-2-yl)diphenylphosphine oxide (5qA). Yellow liquid. ^{31}P NMR (162 MHz, $CDCl_3$) 31.57. HRMS (ESI) calcd. for $C_{21}H_{19}NOP^+$ (M + H^+) *m/z* 332.1199, found 332.1200.



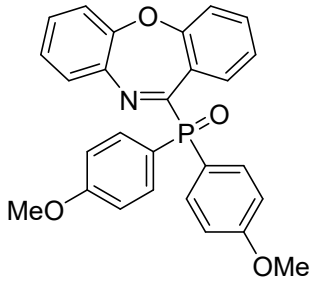
benzo[d]thiazol-2-yldiphenylphosphine oxide (5rA). lit [3].Yellow solid. M.p. 175-178 °C. 43mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (d, J = 8.1 Hz, 1H), 8.05 – 7.89 (m, 5H), 7.61 – 7.42 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): 154.5 (d, $J_{C\text{-}P}$ = 21.2 Hz), 135.9, 131.8 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.4 (d, $J_{C\text{-}P}$= 2.1 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.6, 129.5, 127.8 (d, $J_{C\text{-}P}$ = 12.8 Hz), 125.8 (d, $J_{C\text{-}P}$ = 4.8 Hz), 123.9, 121.2. ^{31}P NMR (162 MHz, $CDCl_3$) 20.08. HRMS (ESI) calcd. for $C_{19}H_{15}NOPS^+$ (M + H^+) *m/z* 336.0606, found 336.0612.



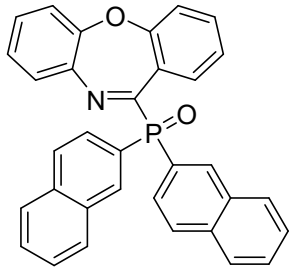
diethyl dibenzo[*b,f*][1,4]oxazepin-11-ylphosphonate (5aB). White solid. M.p. 61-63 °C. 30mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (dd, J = 7.8, 1.1 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.32 (dd, J = 7.7, 1.4 Hz, 1H), 7.23 – 7.03 (m, 5H), 4.25 (p, J = 7.2 Hz, 4H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 164.0 (d, J = 221.5 Hz), 160.6 (d, $J_{C\text{-}P}$ = 9.9 Hz), 151.5, 139.4 (d, $J_{C\text{-}P}$ = 33.2 Hz), 132.6, 129.1, 128.8, 127.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 125.3 (d, $J_{C\text{-}P}$ = 34.7 Hz), 124.9, 124.3, 120.1 (d, $J_{C\text{-}P}$ = 0.9 Hz), 119.9 (d, $J_{C\text{-}P}$ = 1.2 Hz), 63.0 (d, $J_{C\text{-}P}$ = 6.9 Hz), 15.4 (d, $J_{C\text{-}P}$ = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 6.67. HRMS (ESI) calcd. for $C_{17}H_{19}NO_4P^+$ (M + H^+) *m/z* 332.1047, found 332.1051.



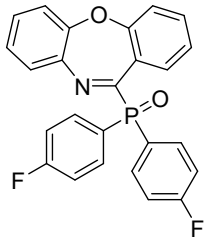
dibenzo[*b*,*f*][1,4]oxazepin-11-ylbis(3,5-dimethylphenyl)phosphine oxide (**5aC**). White solid. M.p. 161-163 °C. 46mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 12.1 Hz, 4H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 15.4, 7.3 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 6H), 2.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 169.2 (d, *J* = 123.6 Hz), 161.5 (d, J = 7.1 Hz), 152.3, 140.7 (d, *J* = 27.2 Hz), 138.1, 137.9, 133.8 (d, *J* = 2.8 Hz), 133.5, 132.3, 131.3, 130.7, 129.8, 129.8, 129.6, 128.5 (d, *J* = 0.9 Hz), 126.9, 126.7, 125.7, 125.2, 121.1, 120.7, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) 27.26. HRMS (ESI) calcd. for $C_{29}H_{27}NO_2P^+$ (M + H^+) *m/z* 452.1774, found 452.1767.



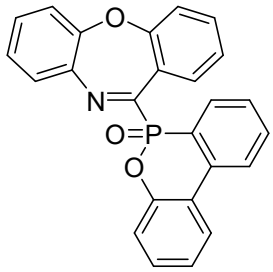
dibenzo[*b*,*f*][1,4]oxazepin-11-ylbis(4-methoxyphenyl)phosphine oxide (**5aD**). White solid. M.p. 151-153 °C. 28mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.90 – 7.81 (m, 4H), 7.42 (td, *J* = 7.8, 1.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.12 (m, 4H), 6.97 (dd, *J* = 8.9, 2.3 Hz, 4H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 169.5 (d, *J* = 125.1 Hz), 162.6 (d, *J* = 2.8 Hz), 161.5 (d, *J* = 7.3 Hz), 152.3, 140.7 (d, *J* = 27.2 Hz), 134.2, 134.1, 133.5, 130.7, 129.7, 128.6 (d, *J* = 1.0 Hz), 126.9, 126.7, 125.8, 125.3, 124.1, 124.0, 123.6, 122.9, 120.9 (d, *J* = 28.6 Hz), 116.1, 114.2, 114.0. ^{31}P NMR (162 MHz, $CDCl_3$) 26.72. HRMS (ESI) calcd. for $C_{27}H_{23}NO_4P^+$ (M + H^+) *m/z* 456.1359, found 456.1360.



dibenzo[*b*,*f*][1,4]oxazepin-11-yldi(naphthalen-2-yl)phosphine oxide (**5aE**). Yellow oil. 41mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.50 (d, *J* = 14.0 Hz, 2H), 8.17 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.96 – 7.86 (m, 2H), 7.82 (dd, *J* = 8.3, 3.2 Hz, 4H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.39 (m, 4H), 7.38 – 7.28 (m, 1H), 7.21 – 7.11 (m, 2H), 7.10 – 7.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 168.9 (d, *J* = 125.8 Hz), 161.6 (d, *J* = 7.2 Hz), 152.3, 140.6 (d, *J* = 27.5 Hz), 134.9 (d, *J* = 2.2 Hz), 134.5, 134.1 (d, *J* = 8.9 Hz), 133.7, 132.6, 132.5, 132.1, 130.6, 129.8 (d, *J* = 5.5 Hz), 129.2, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.9, 127.3, 127.3, 127.2, 126.9 (d, *J* = 4.7 Hz), 126.7, 125.9, 125.8, 125.3, 125.3, 125.2, 121.7, 121.4, 121.0 (d, *J* = 26.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 26.97. HRMS (ESI) calcd. for $C_{33}H_{23}NO_2P^+$ (M + H^+) *m/z* 496.1461, found 496.1468.



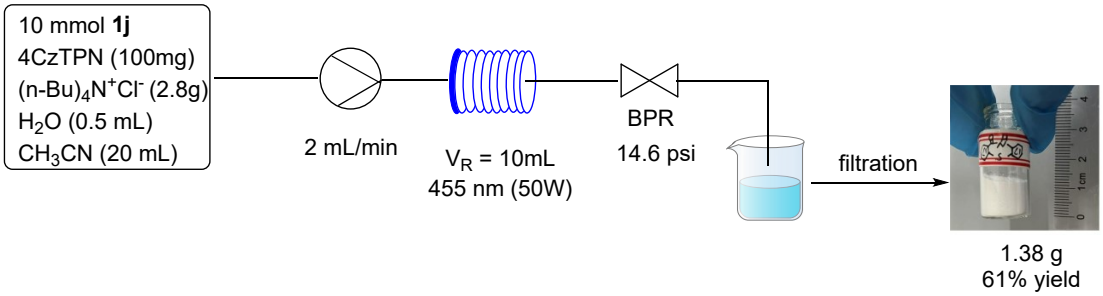
dibenzo[*b*,*f*][1,4]oxazepin-11-ylbis(4-fluorophenyl)phosphine oxide (**5aF**).Yellow oil. 26mg, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, *J* = 7.9 Hz, 1H), 7.92 – 7.80 (m, 4H), 7.38 (td, *J* = 7.9, 1.5 Hz, 1H), 7.23 – 7.01 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): 168.5 (d, *J* = 127.2 Hz), 166.6 (d, *J* = 3.4 Hz), 164.1 (d, *J* = 3.4 Hz), 161.5 (d, *J* = 7.3 Hz), 152.2, 140.4 (d, *J* = 27.7 Hz), 134.8 (dd, *J* = 10.4, 9.1 Hz), 133.9, 130.3 (d, *J* = 39.2 Hz), 128.6 (d, *J* = 1.3 Hz), 128.3 (d, *J* = 3.4 Hz), 127.3 (d, *J* = 3.4 Hz), 126.5 (d, *J* = 27.7 Hz), 125.7 (d, *J* = 53.0 Hz), 121.1 (d, *J* = 25.1 Hz), 116.0 (dd, *J* = 21.5, 13.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 24.69. HRMS (ESI) calcd. for $C_{25}H_{17}F_2NO_2P^+$ (M + H^+) *m/z* 432.0960, found 432.0990.



6-(dibenzo[*b*,*f*][1,4]oxazepin-11-yl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5aG**). White solid. M.p. 291-293 °C. 37mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.32 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.09 (dd, *J* = 12.5, 7.6 Hz, 1H), 7.91 (ddd, *J* = 9.3, 7.8, 3.6 Hz, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.50 (ddd, *J* = 15.9, 8.2, 2.2 Hz, 2H), 7.37 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.08 (m, 2H), 7.03 (dd, *J* = 15.9, 7.6 Hz, 3H), 6.89 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 166.4 (d, *J* = 165.9 Hz), 161.5 (d, *J* = 8.7 Hz), 152.1, 149.5 (d, *J* = 8.3 Hz), 140.3 (d, *J* = 32.7 Hz), 137.3 (d, *J* = 6.5 Hz), 133.9, 133.7 (d, *J* = 2.3 Hz), 131.9 (d, *J* = 9.5 Hz), 130.4, 129.9 (d, *J* = 4.5 Hz), 128.8 (d, *J* = 1.6 Hz), 128.4 (d, *J* = 13.8 Hz), 125.7, 125.4, 125.4, 125.3, 124.8, 124.4, 123.8 (d, *J* = 10.6 Hz), 123.4, 123.3, 123.1, 121.0, 120.3 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 22.82. HRMS (ESI) calcd. for $C_{25}H_{17}NO_3P^+$ (M + H^+) *m/z* 410.0941, found 410.0938.

7.Scale up reaction and application

1) Scale up reaction of 3j using continuous flow reactor



To a 250 mL solution bottle was added dibenzo[*b*,*f*][1,4]thiazepine **1j** (10 mmol, 2.11 g), photocatalyst 4CzTPN (0.1 mmol, 100 mg), and tetrabutyl ammonium chloride (10 mmol, 2.8 g) , Consequently, the reactants were dissolved in 20 mL CH_3CN and 0.5 mL water, then charged with N_2 atmosphere. It was moved into a 10 mL coiled tubing loaded by a peristaltic pump. The reaction mixture was passed to a micro flow reactor which was illuminated with eight 50 W, 455 nm RLR-18CF blue LEDs. A circulating water system used to keep the reactor's temperature be constant. And the reaction was keeping the flow rate of 2 mL per min and underwent continuous rection for 12 h. The obtained yellow mixture was filtered and dried, the white product **3j** was gave in 61% yield.

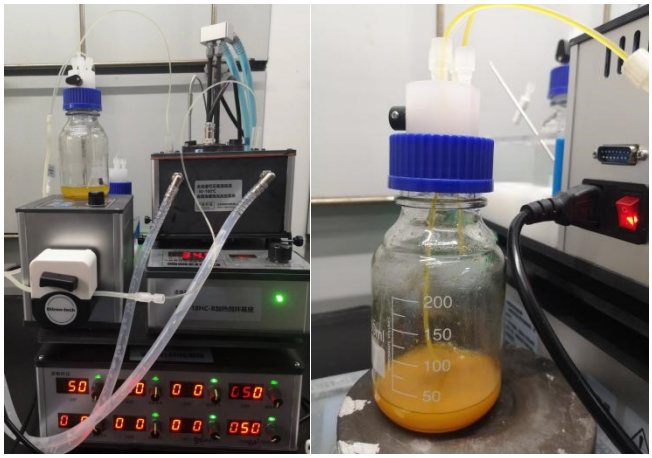
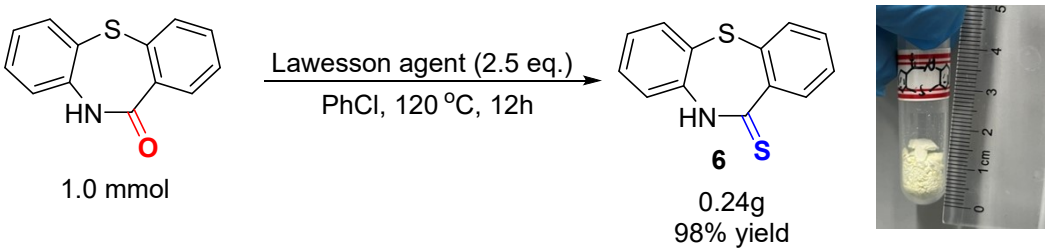


Figure S1 Scale up reaction of **3j** using continuous flow reactor.

2) Synthetic transformations of 3j



To a 10 mL Schlenk tube containing a stir bar were charged with dibenzo[*b*,*f*][1,4]thiazepin-11(10H)-one 3j (227 mg, 1 mmol), Lawesson's Reagent (1.01 g, 2.5 mmol, 2.5 equiv), and PhCl (3 mL). The resulting solution was stirred at 120 °C for 12 h. The obtained light yellow mixture was filtered and dried, the yellow product **3j** was gave in 98% yield. M.p. 112.5-114.7 °C. ^{1}H NMR (400 MHz, DMSO): 12.85 (s, 1H), 7.88 – 7.83 (m, 1H), 7.57 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.35 – 7.30 (m, 1H), 7.23 (td, *J* = 7.6, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO): 199.9, 142.5, 139.9, 134.1, 132.5, 132.1, 132.1, 131.2, 130.9, 129.4, 128.3, 126.6, 123.4. HRMS (ESI) calcd. for $C_{13}H_{10}NS_2^+$ (M + H^+) *m/z* 244.0250, found 244.0255.

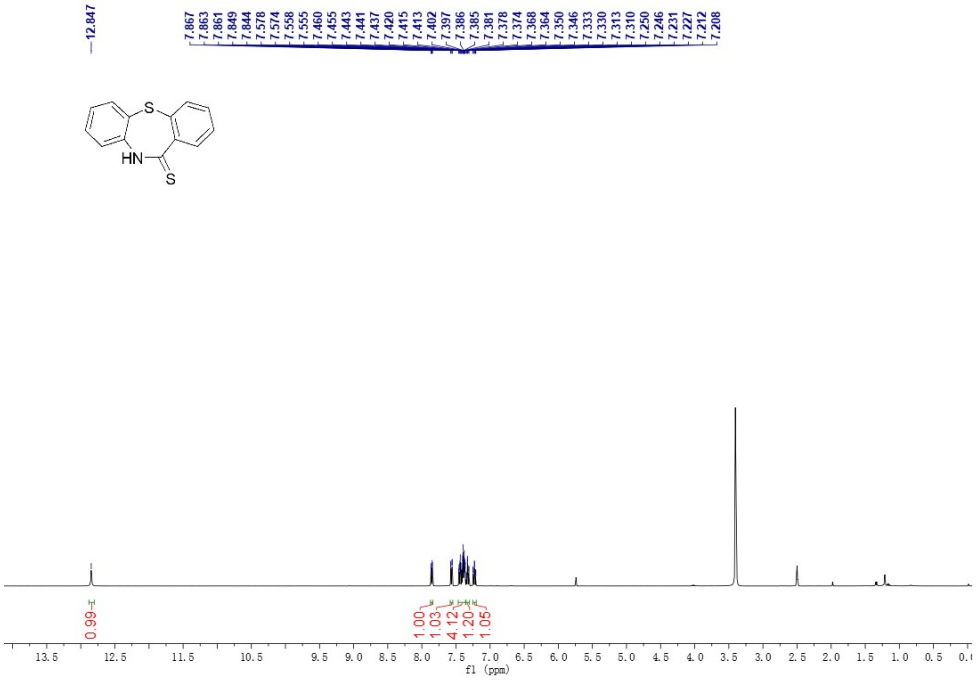


Figure S2 ^{1}H NMR Spectrum of Compound **6**

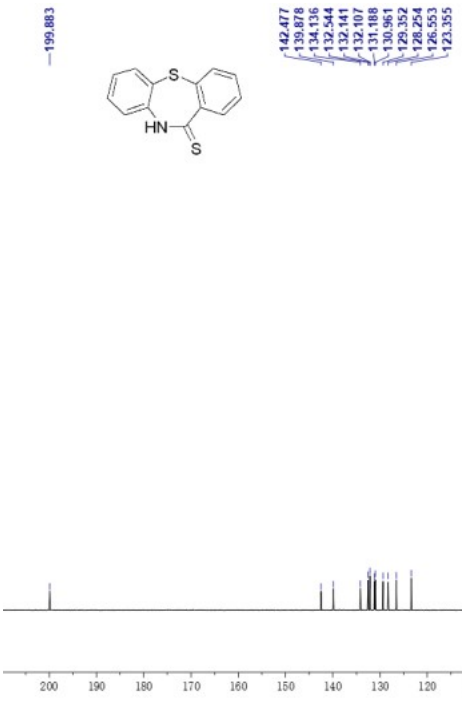
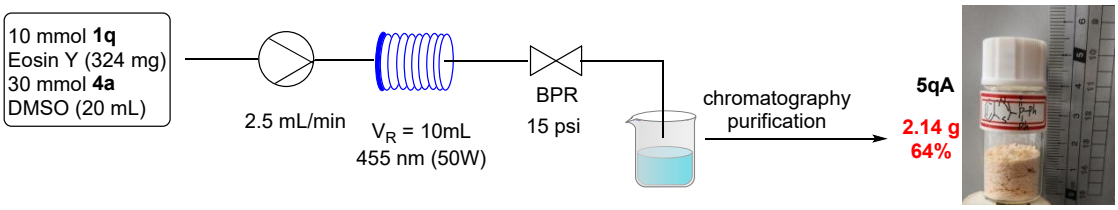


Figure S3 ^{13}C NMR Spectrum of Compound **6**

3) Scale up reaction of 5qA in continuous flow



To a 250 mL solution bottle was added benzo[d]thiazole **1q** (10 mmol, 1.35 g), photocatalyst Eosin Y (0.5 mmol, 324 mg), and diphenylphosphine oxide (30 mmol, 6.0 g) , Consequently, the reactants were dissolved in 20 mL DMSO and charged with N_2 atmosphere. It was moved into a 10 mL coiled tubing loaded by a peristaltic pump. The reaction mixture was passed to a micro flow reactor which was illuminated with eight 50 W, 455 nm RLR-18CF blue LEDs. A circulating water system used to keep the reactor's temperature be constant. And the reaction was keeping the flow rate of 2.5 mL per min and underwent continuous rection for 6 h. The result mixture was added with brine water (100 mL), then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers dried over $NaSO_4$. After removal of the solvent in vacuum the residue was purified by flash chromatography (silica gel, 20% EtOAc in PE) to give 2.14 g (64%) of the desired product **5qA**.

4) Flame retardancy of 5qA in epoxy resin

To a 500 mL breaker was added the flame retardant **5qA** (5.0 g) and bisphenol-A diglycidyl ether type epoxy resin (DGEBA) (76.0 g), and the white uniform mixture were mechanically stirred at 90 °C for 30 min. Then the curing agent 4,4-diaminodiphenylmethane (DDM) (19.0 g) was added to the resulting mixture and mechanically stirred for 5 min, and poured into a preheated stainless steel mold and film fixation rapidly. Finally, put it into an air blast oven for curing at 100 °C for 2 h, and heated to 150 °C for curing for 2 h to obtain a flame retardant epoxy resin. The cured epoxy

resins containing 5 wt% **5qA** were denoted as **EP-NS$_{5\%}$**.

According to GB/T 2406.2-2009 standard, the limiting oxygen index (LOI) values were evaluated using the JF-3 oxygen index instrument (Jiangning, China) with sample's dimension of 130 mm × 6.5 mm × 3.2 mm. The limiting oxygen index of each sample was the average of five parallel tests. According to GB/T 2408-2008 standard, the vertical burning (UL-94) tests were assessed using the CZF-3 instrument (Jiangning, China) with sample's dimension of 130 mm × 13 mm × 3.2 mm. The burning time of each sample was the average of five parallel tests.

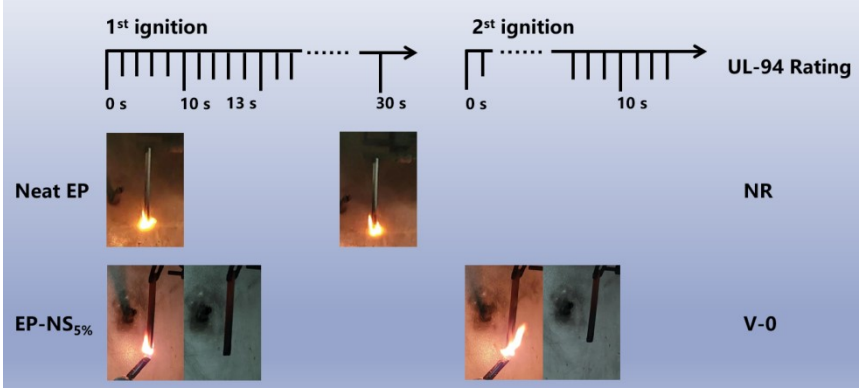
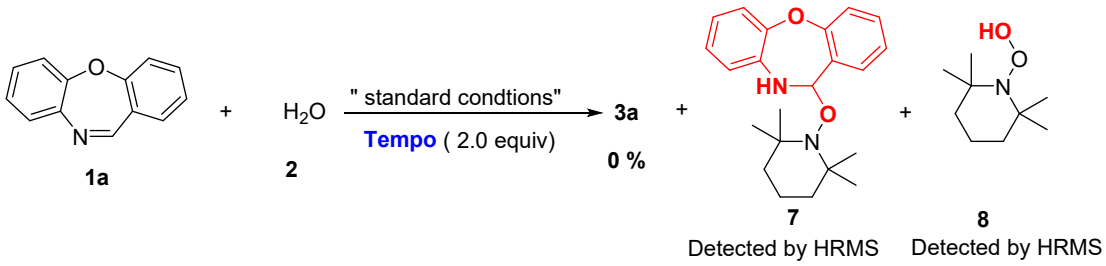


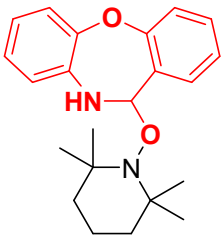
Figure S4 The vertical burning (UL-94) tests of EP-NS$_{5\%}$

8. Mechanistic Investigation

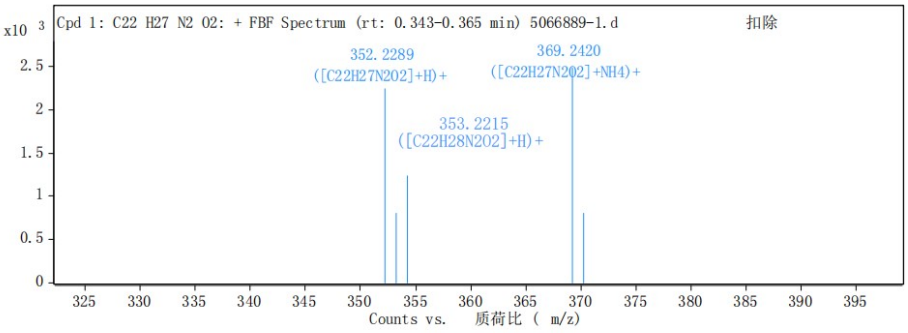
Radical Trap Experiments



Following the standard procedure, the reaction of dibenzo[*b*,*f*][1,4]oxazepine **1a** (0.2 mmol), 4CzTPN (1.6 mg, 0.002 mmol, 1 mmol%), tetrabutyl ammonium chloride (27.8 mg, 0.1 mmol), and TEMPO (62.5 mg, 0.40 mmol, 2.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), water (10 uL) and CH_3CN (2.0 mL) was added, the vial was sealed and exposed to blue LEDs (50 W LED light) at room temperature for 12 h. No product **3a** was observed. The compound **7** and and **8** was detected by HRMS.



11-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine **7**. HRMS (ESI) calcd. for $C_{22}H_{29}N_2O_2^+$ ($M + H^+$) *m/z* 353.2224, found 353.2215.

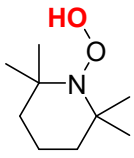


MS 质谱图峰列表

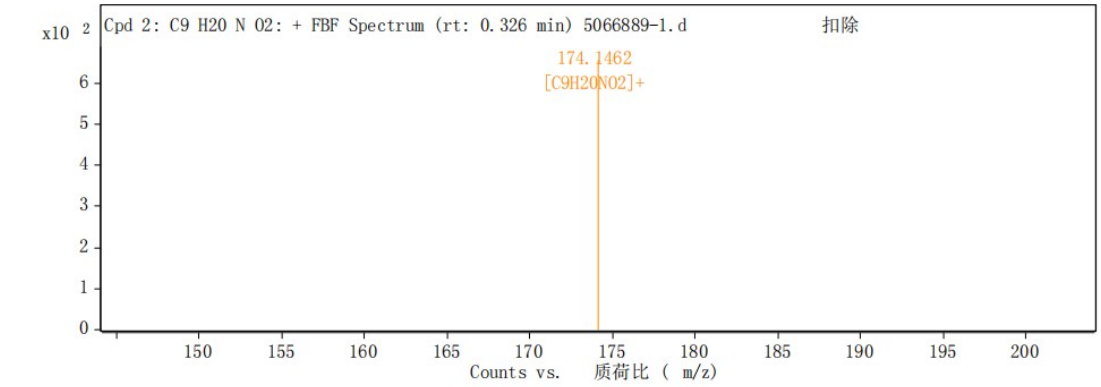
m/z	z	丰度	分子式	离子
352.2289	1	2242.52	C22H27N2O2	(M+H)+
353.2215	1	803.18	C22H27N2O2	(M+H)+
354.2169	1	1243.08	C22H27N2O2	(M+H)+
369.242	1	2489.04	C22H27N2O2	(M+NH4)+
370.2459	1	807.57	C22H27N2O2	(M+NH4)+

--- 报告结束 ---

Figure S5 The HRMS spectrum of compound **7**



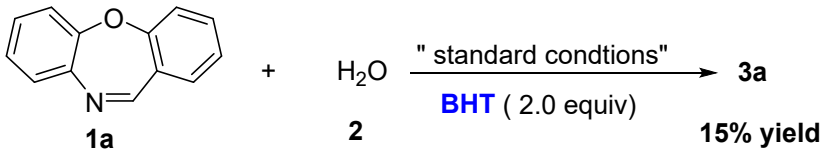
1-hydroperoxy-2,2,6,6-tetramethylpiperidine **8**. HRMS (ESI) calcd. for $C_9H_{20}NO_2$+ (M + H+) m/z 174.1468, found 174.1462.



MS 质谱图峰列表

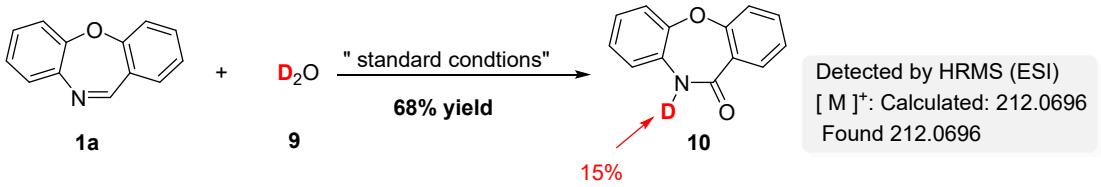
m/z	z	丰度	分子式	离子
174.1462	1	655.08	C9H20NO2	M+

Figure S6 HRMS spectrum of compound **8**



Following the standard procedure, the reaction of dibenzo[*b*,*f*][1,4]oxazepine **1a** (0.2 mmol), 4CzTPN (1.6 mg, 0.002 mmol, 1 mmol%), tetrabutyl ammonium chloride (27.8 mg, 0.1 mmol), and BHT (88 mg, 0.40 mmol, 2.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), water (10 uL) and CH_3CN (2.0 mL) was added, the vial was sealed and exposed to blue LEDs (50 W LED light) at room temperature for 12 h. product **3a** was observed in 15% yield.

Isotope labeling experiment



Following the standard procedure. When 10 uL D_2O was added to replace H_2O, the desired deuterated-3a **10** was obtained in 68% yield with 15% deuteration. And the compound 10 was detected by HRMS as well. ^1H NMR (400 MHz, $CDCl_3$): 9.00 (s, 1H), 7.96 (dd, J = 8.1, 1.7 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.29 – 7.21 (m, 3H), 7.16 – 7.09 (m, 3H).

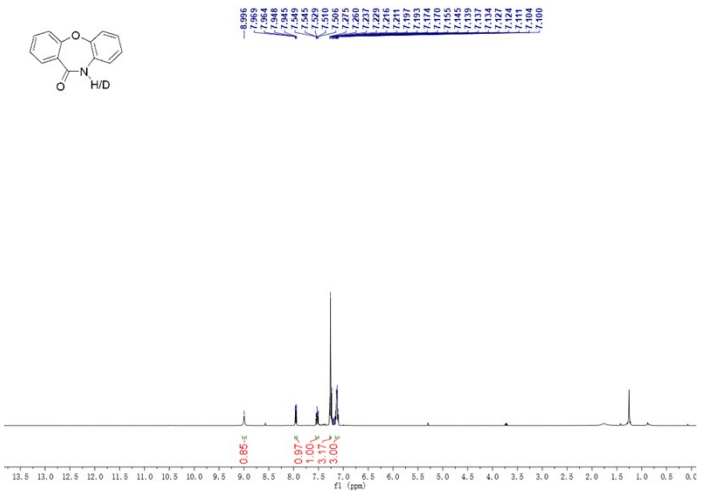
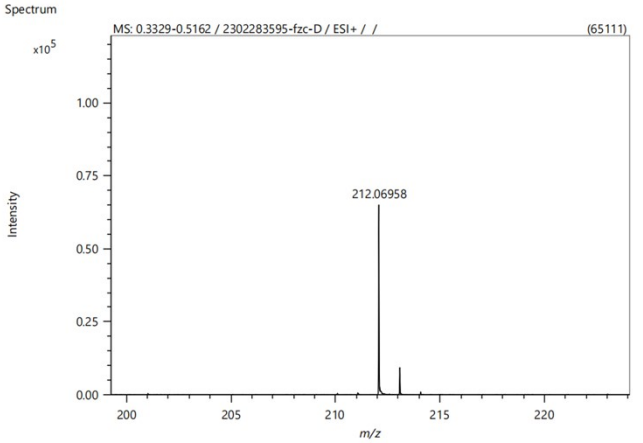


Figure S7 ^1H NMR spectrum of compound **10**



Elemental Composition

Parameters	
Tolerance:	±5.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-1.5 - 100.0

Elements Set 1:

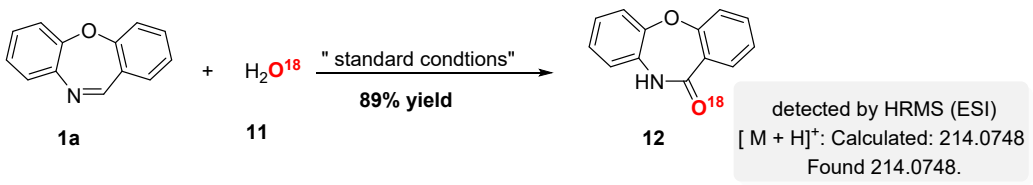
Symbol	C	H	O	N	Na	S	Cl	Br
Min	0	0	0	0	0	0	0	0
Max	200	200	8	3	0	0	0	0

Symbol	F	P	D
Min	0	0	1
Max	0	0	1

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
212.06958	65111.00	C13 H8 N O2 D	212.06905	0.53	2.49	10.0

Figure S8 HRMS spectra of compound **10**



Following the standard procedure. When 10 uL H_2O^{18} was added to replace H_2O, the desired **12** was obtained in 89% yield and detected by HRMS as well.

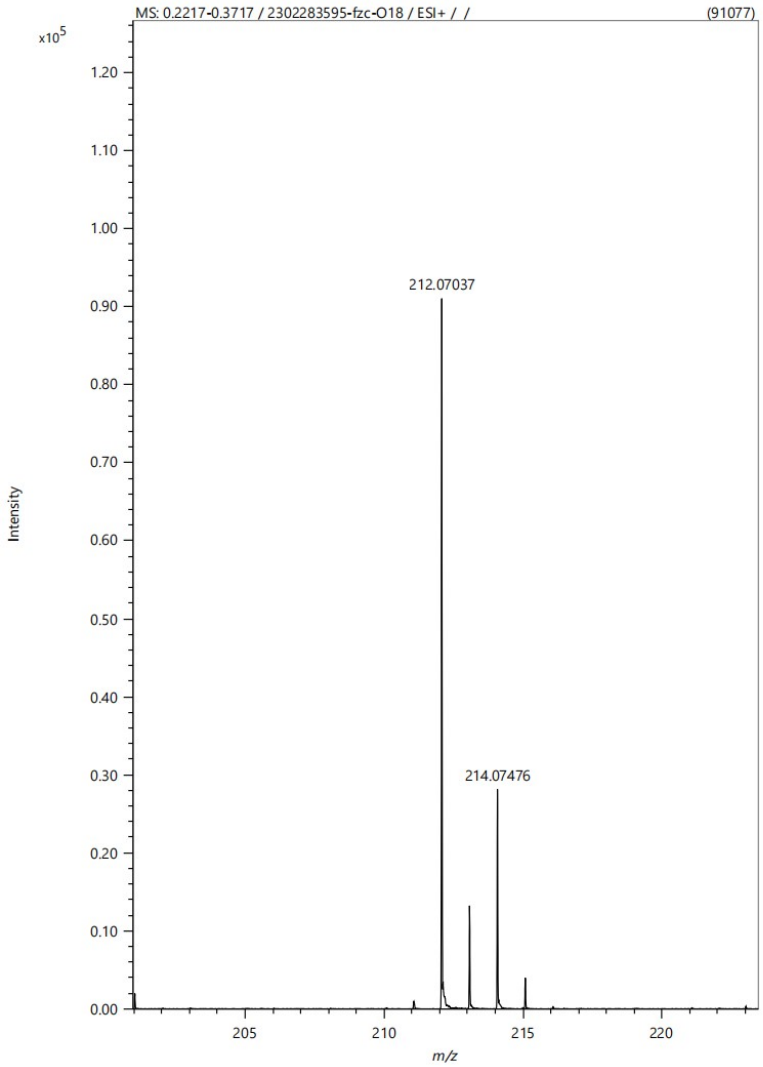
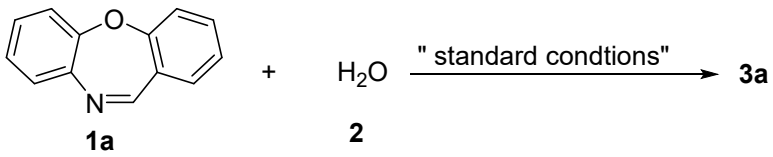


Figure S9 HRMS spectra of compound **12**

The Light On-Off Experiment



Following the standard procedure. Yield was determined by ^{1}H NMR of the crude mixture using 1,3,5- trimethoxybenzene (3.7 mg, 0.022 mmol) as internal standard.

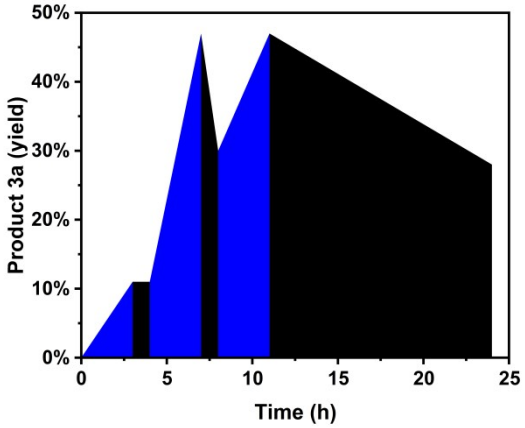


Figure S10 The light on-off experiment

The EPR Experiment

Following the standard procedure. Dibenzo[*b,f*][1,4]oxazepine **1a** (0.2 mmol), 4CzTPN (1.6 mg, 0.002 mmol, 1 mmol%), tetrabutyl ammonium chloride (27.8 mg, 0.1 mmol), and BHT (88 mg, 0.40 mmol, 2.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), water (10 uL) and CH_3CN (2.0 mL) was added, the vial was sealed and exposed to blue LEDs (50 W LED light) at room temperature for 4 h. Then, to the resulted mixture was added radical scavenger 5,5-Dimethyl -1-pyrroline N-oxide (DMPO) (226 mg, 2 mmol) and followed by detecting the EPR signal.

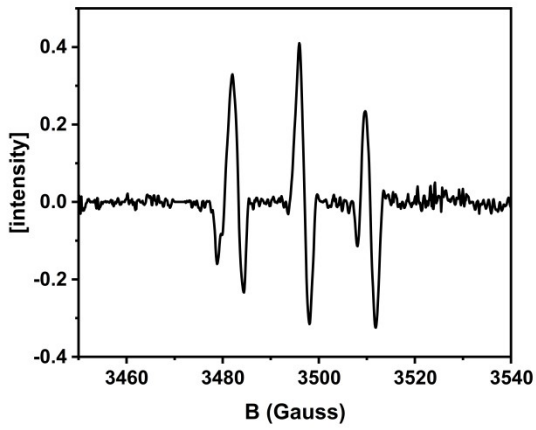


Figure S11 EPR spectra of the reaction mixture.

9. Supplemental References

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2. Z. C. Fu, Y. L. Lei, F. Sun and J. Xu. *Org. Chem. Front.*, **202**2, 9, 2464–2470.
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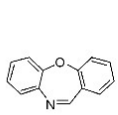
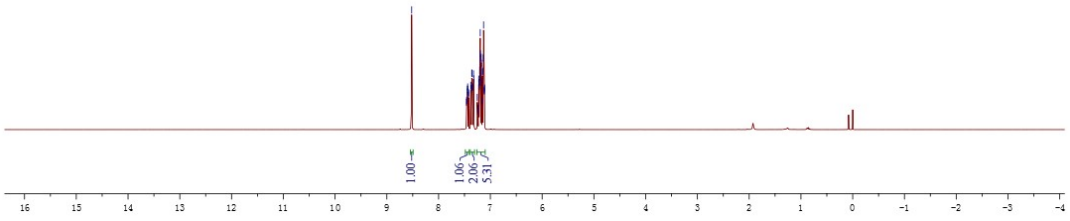
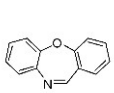
10. Copies of NMR Spectra of Compounds1, 3 and 5

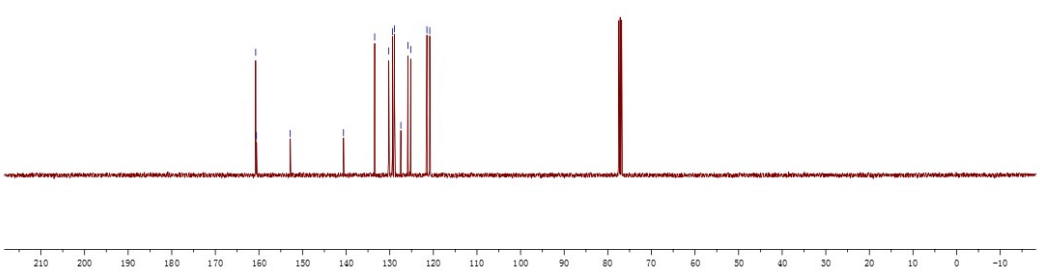
Copies of ^{1}H (400 MHz), ^{31}P (167 MHz) and ^{13}C (101 MHz) spectra of products 1a-1o in $CDCl_3$ or DMSO-d6



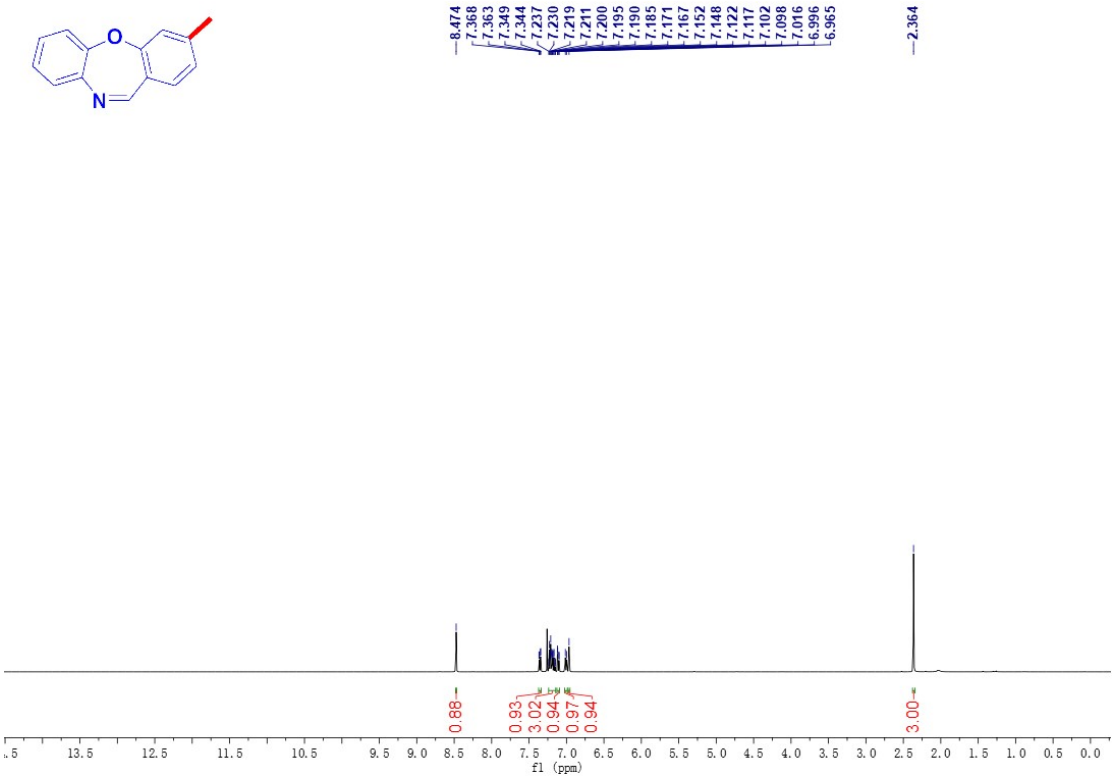


^{1}H NMR Spectrum of Compound **1a**

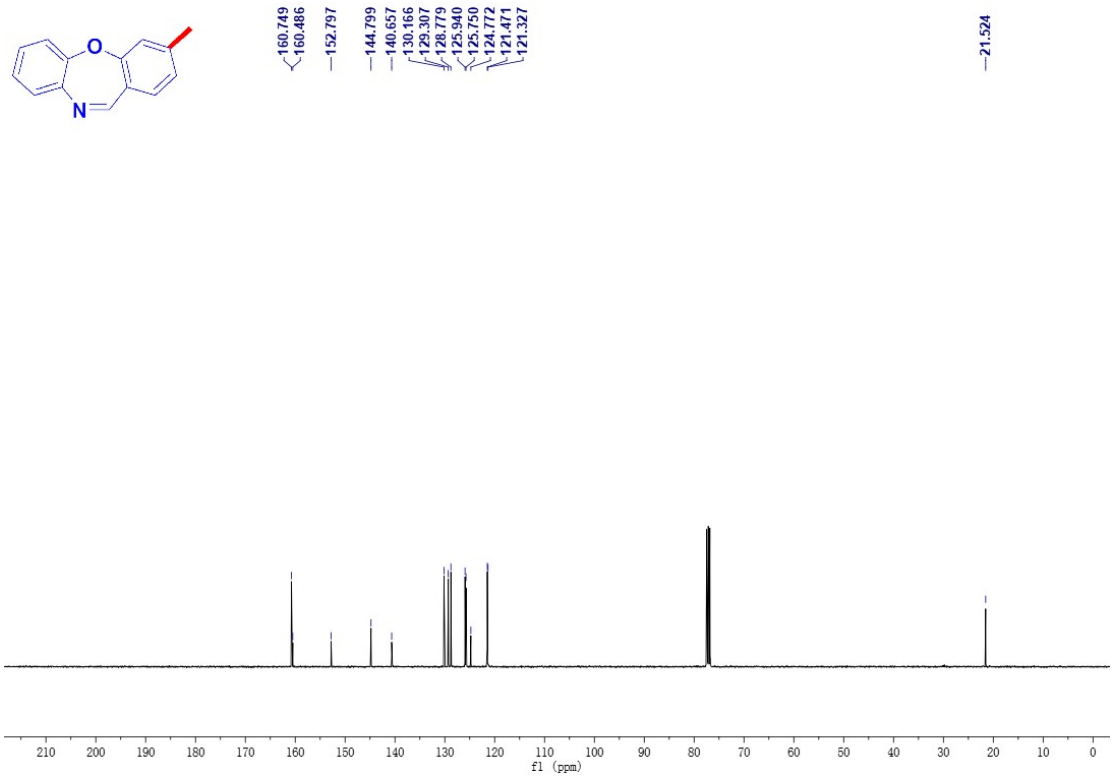




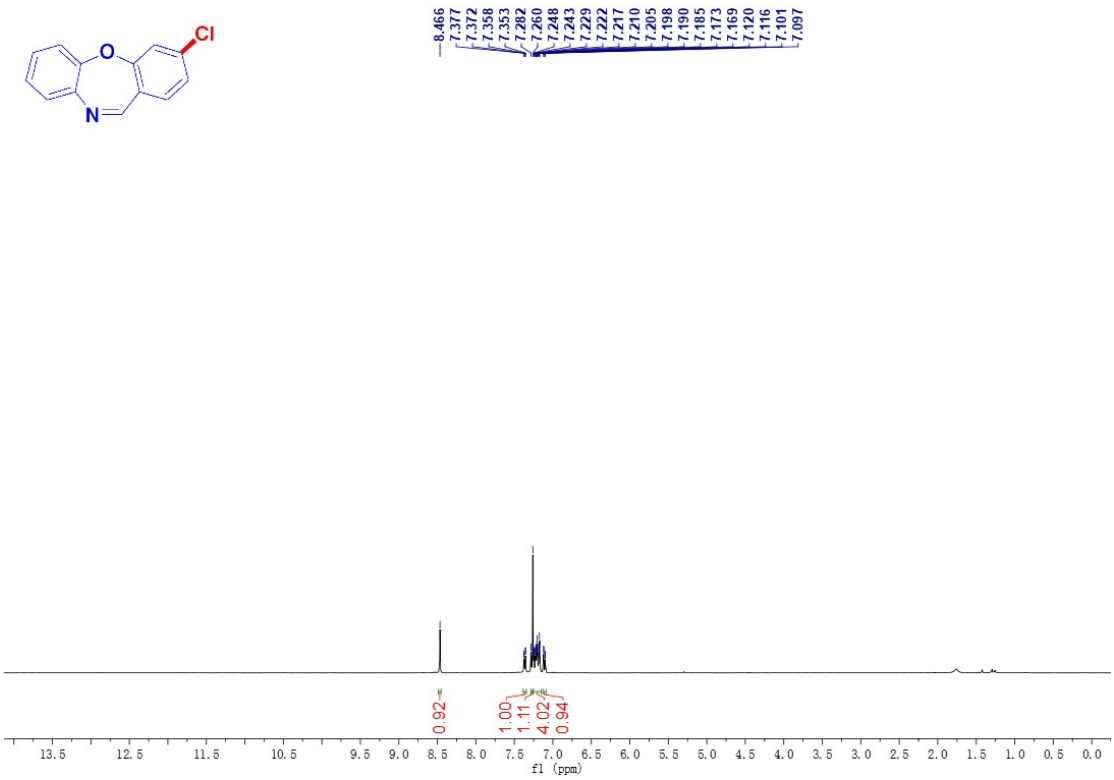
^{13}C NMR Spectrum of Compound **1a**



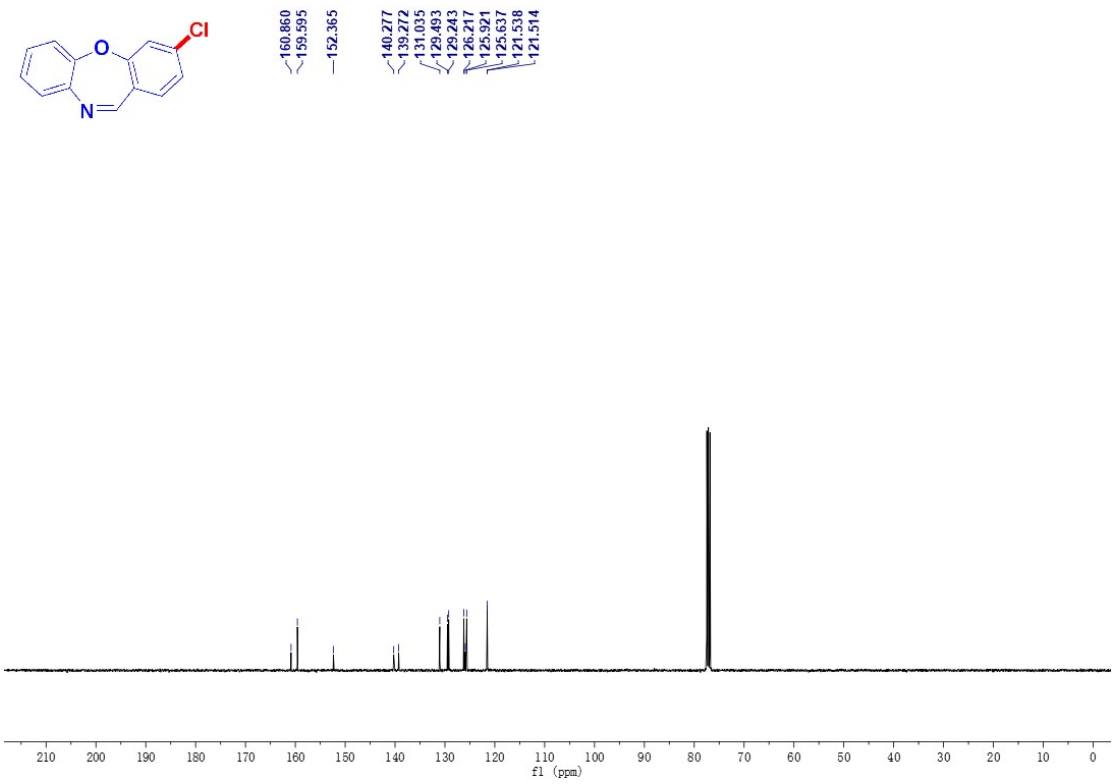
^{1}H NMR Spectrum of Compound **1b**



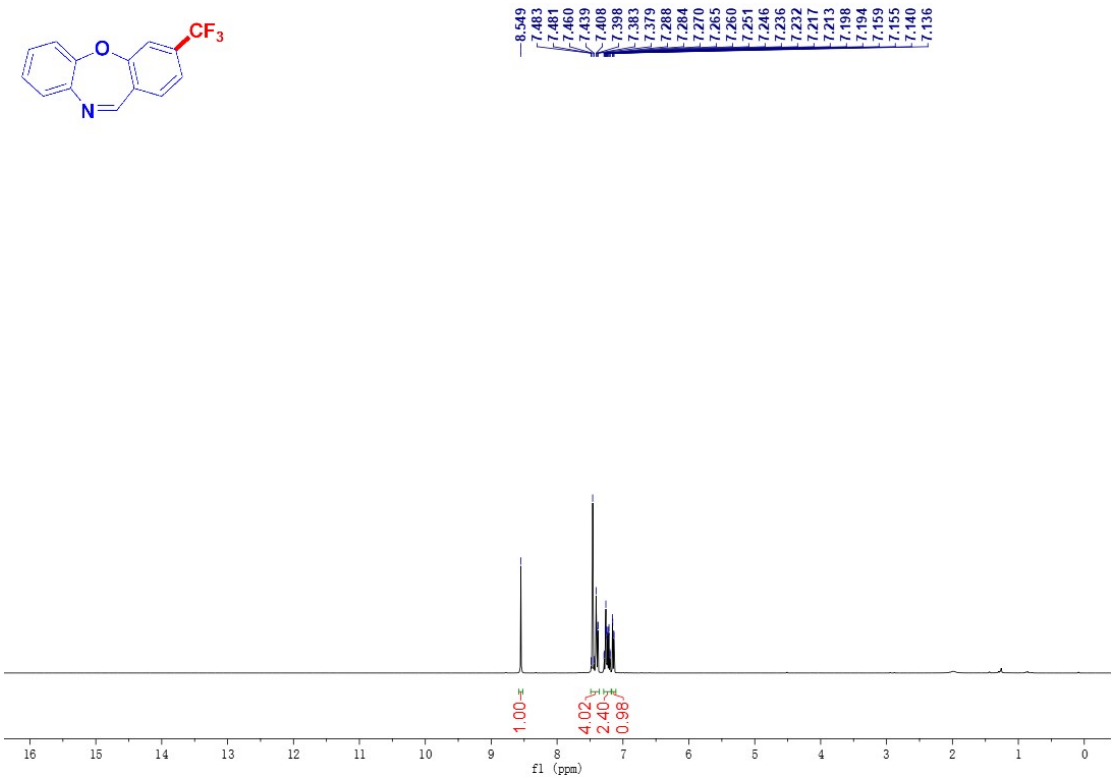
^{13}C NMR Spectrum of Compound **1b**



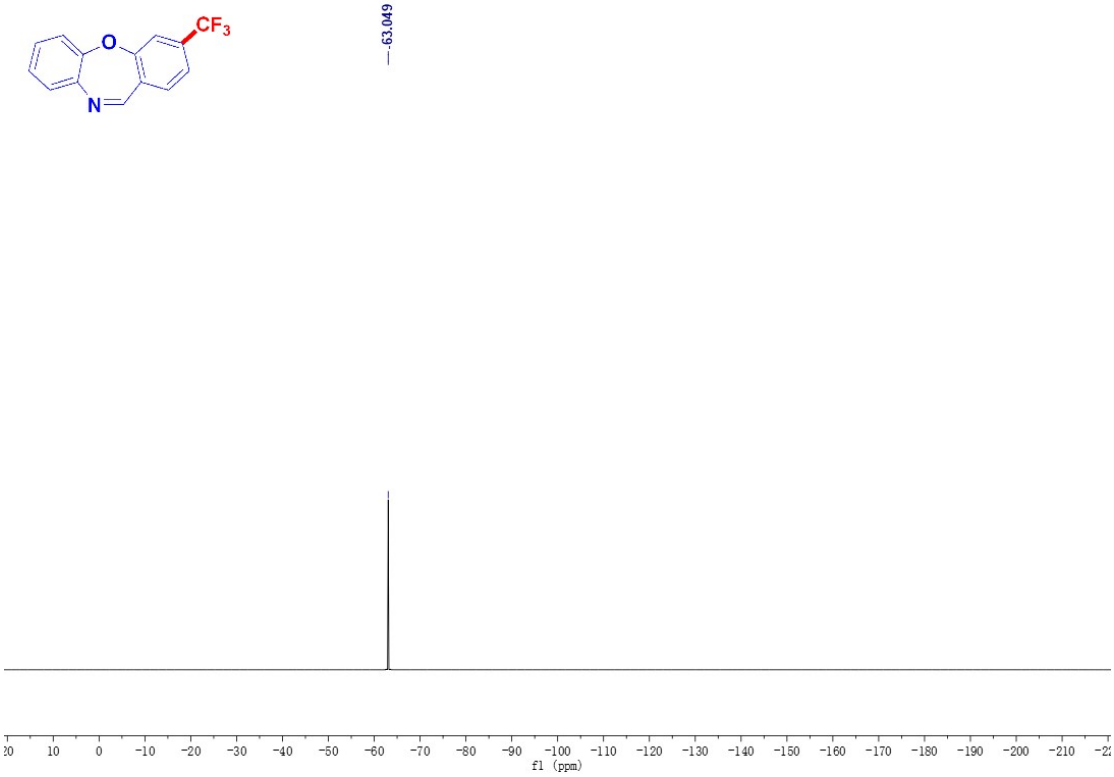
^{1}H NMR Spectrum of Compound **1c**



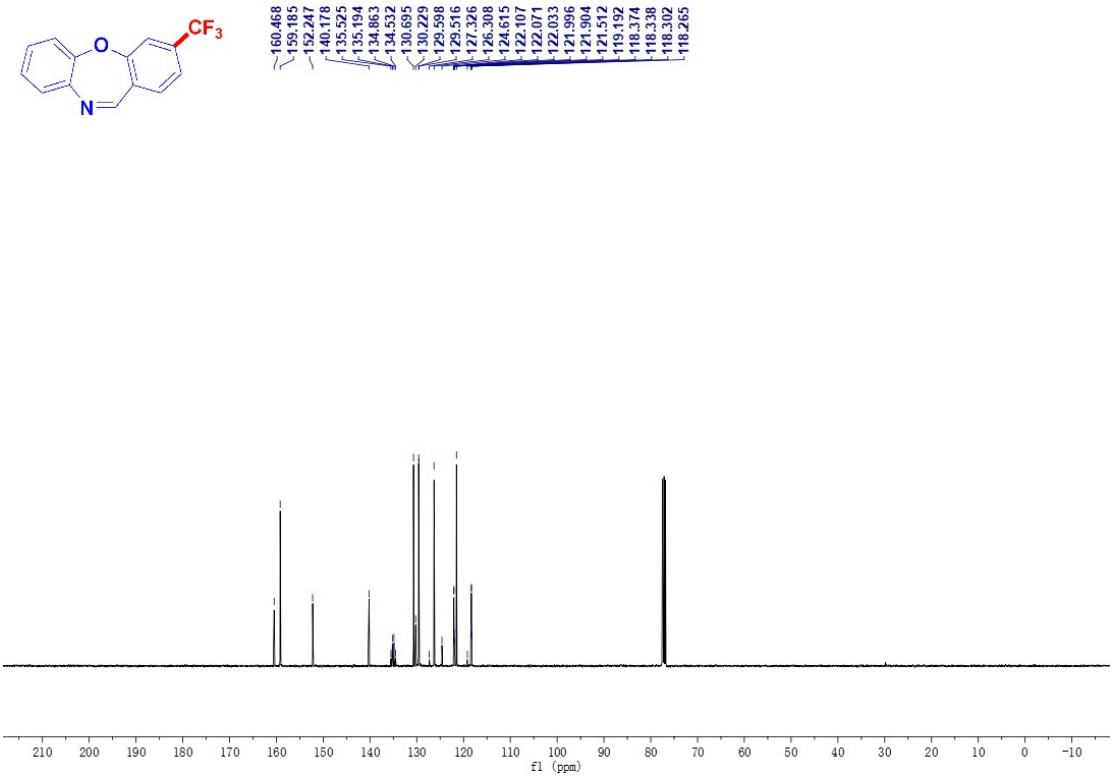
^{13}C NMR Spectrum of Compound **1c**



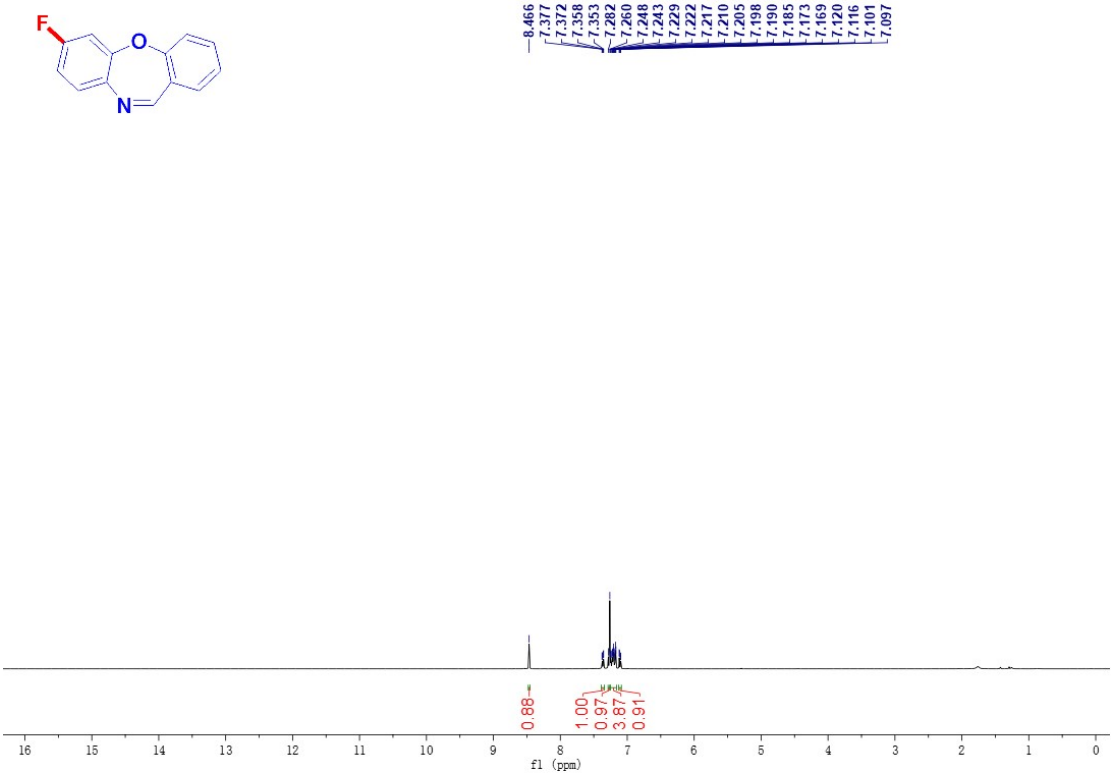
^{1}H NMR Spectrum of Compound **1d**



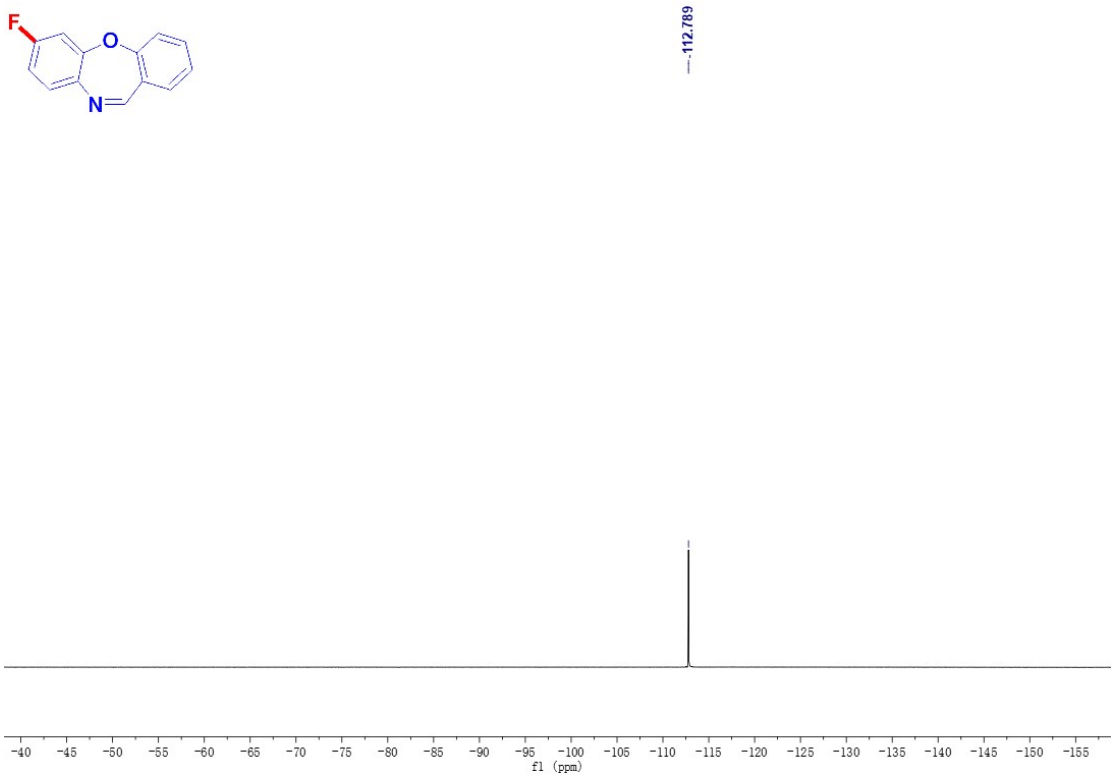
^{19}F NMR Spectrum of Compound **1d**



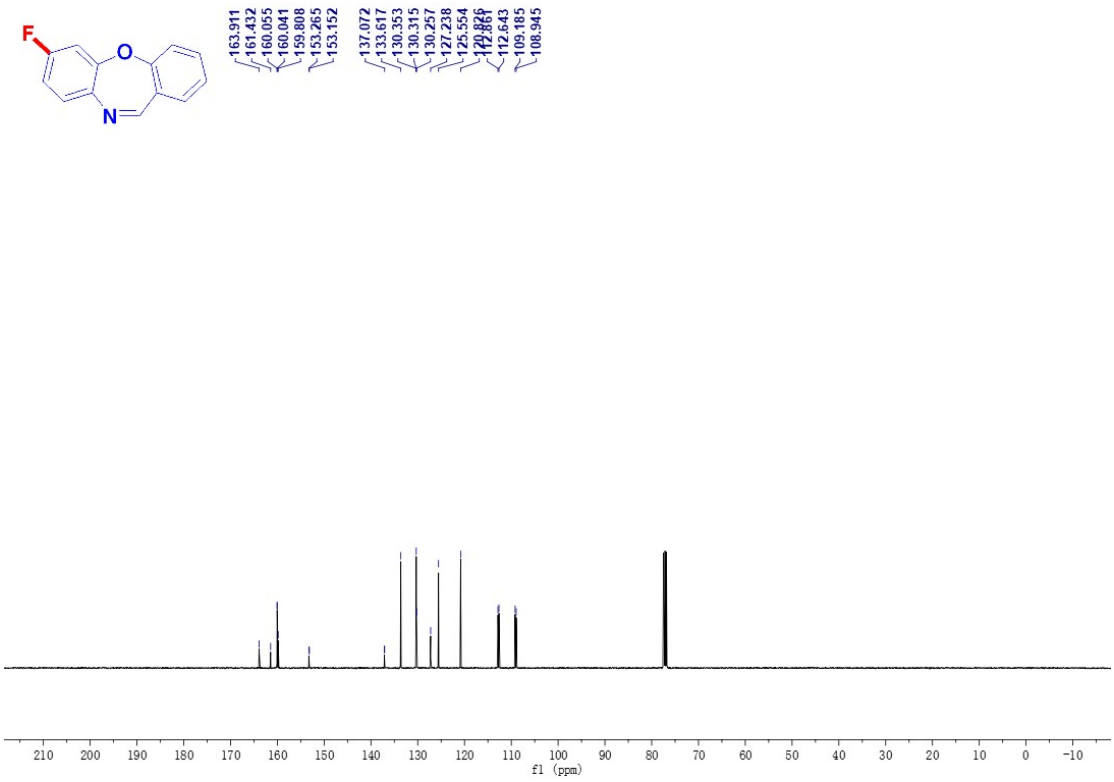
^{13}C NMR Spectrum of Compound **1d**



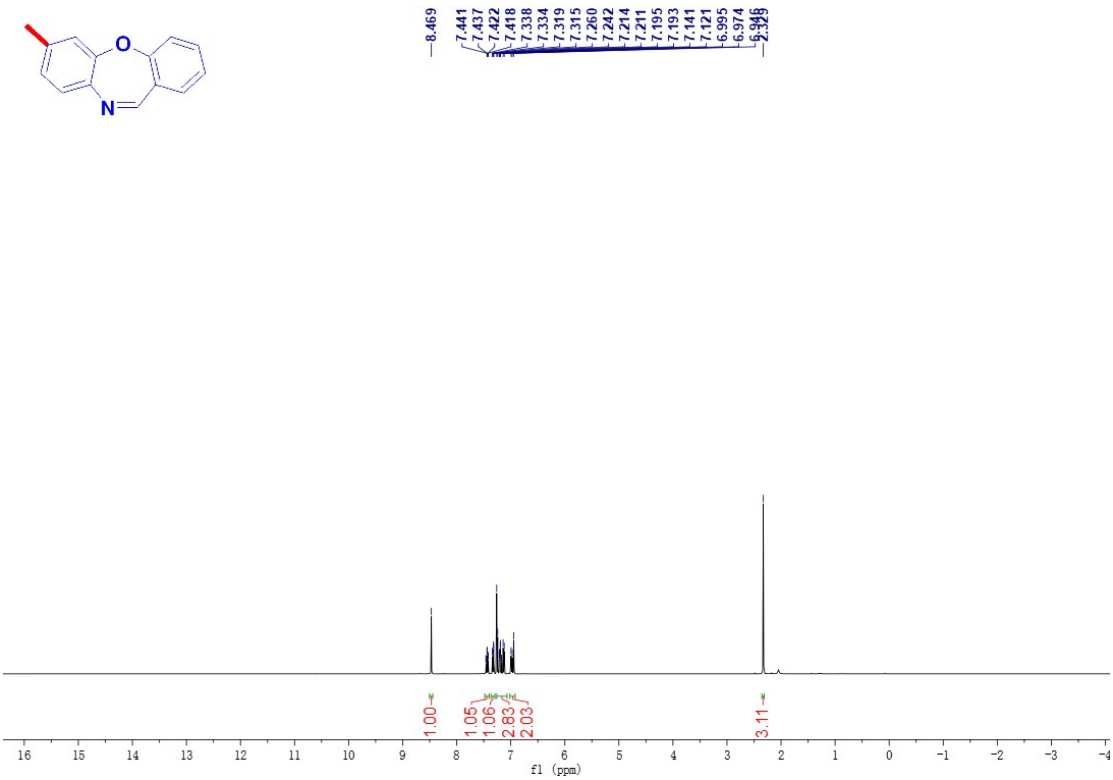
^{1}H NMR Spectrum of Compound **1e**



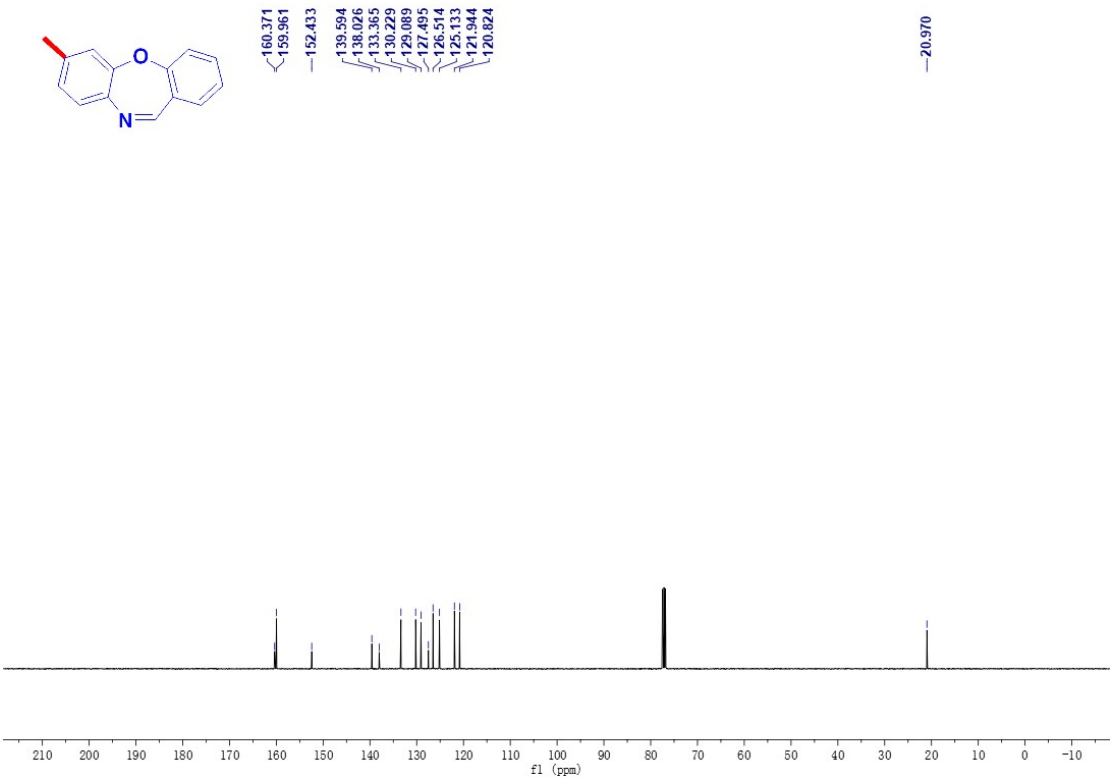
^{19}F NMR Spectrum of Compound **1e**



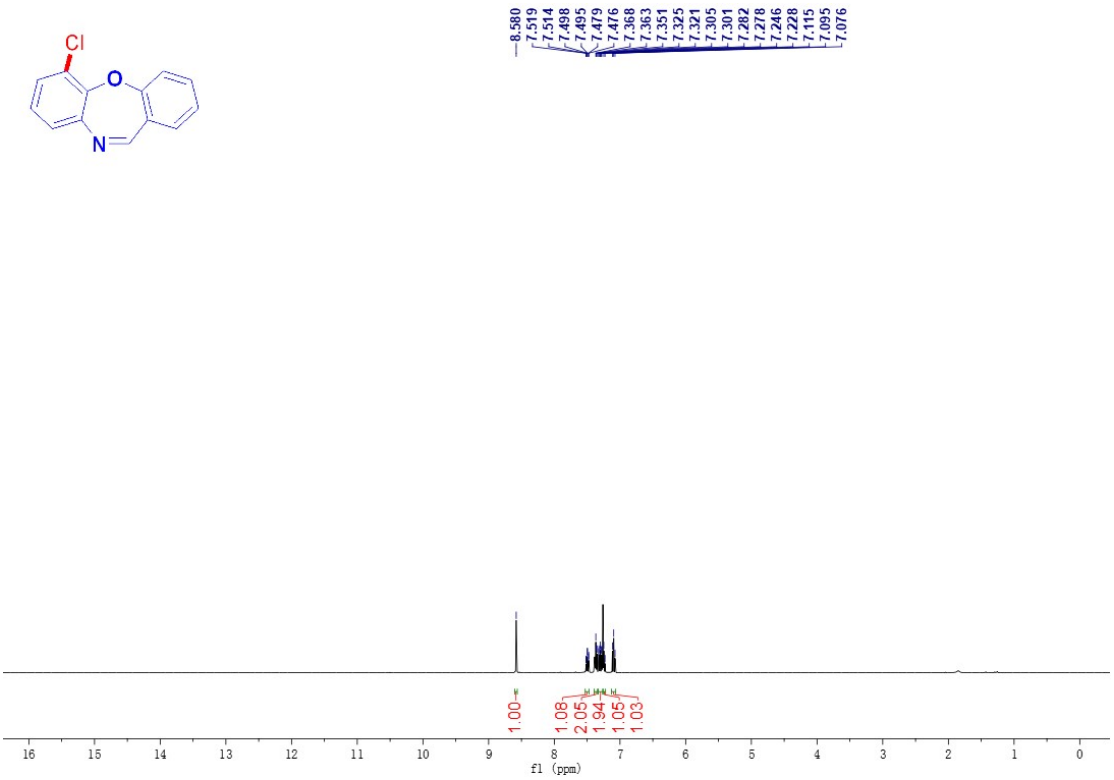
^{13}C NMR Spectrum of Compound **1e**



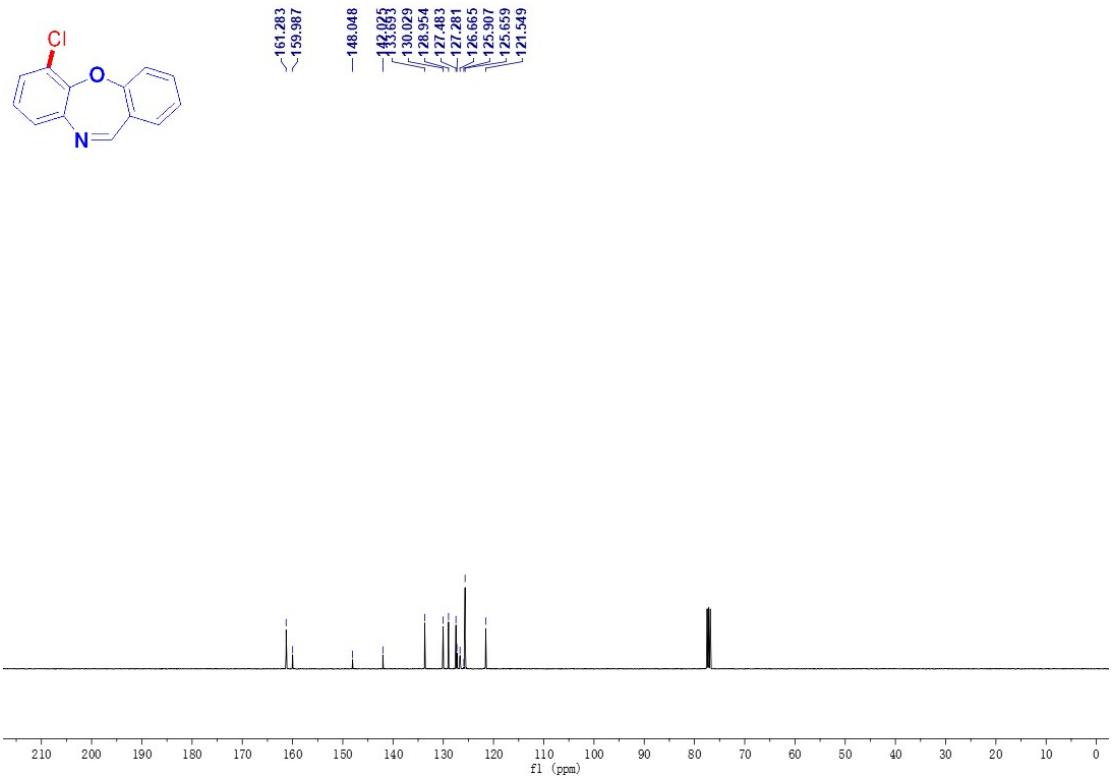
^{1}H NMR Spectrum of Compound **1f**



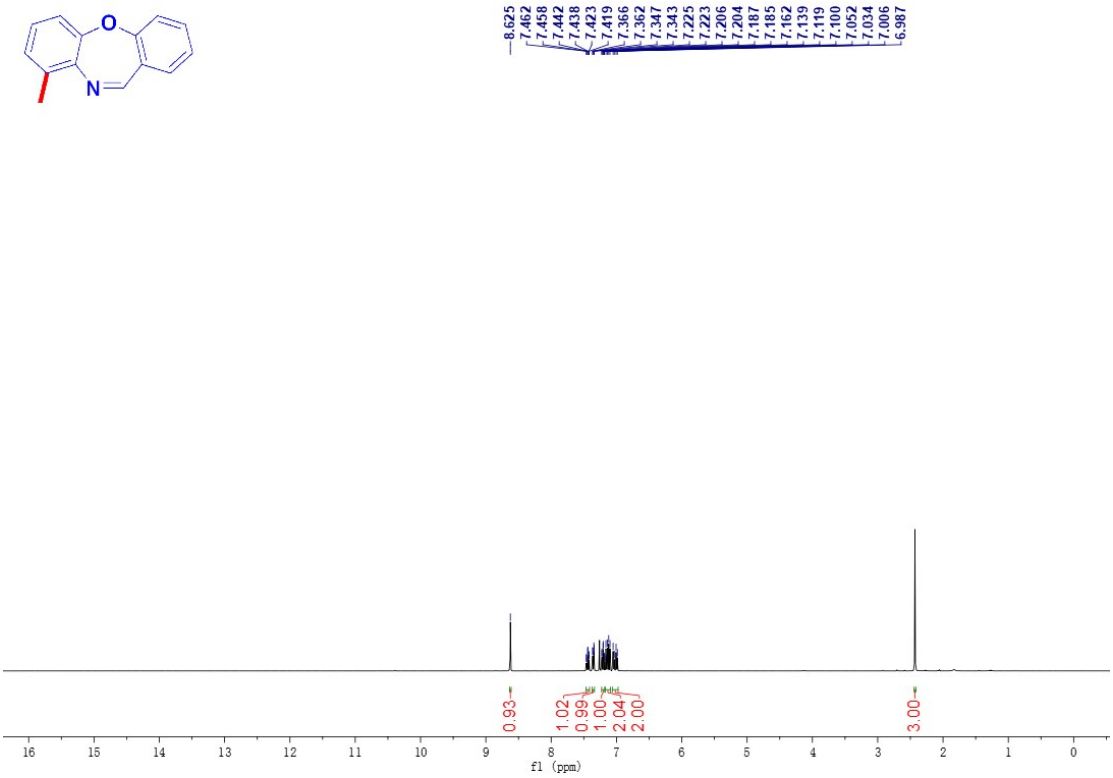
^{13}C NMR Spectrum of Compound **1f**



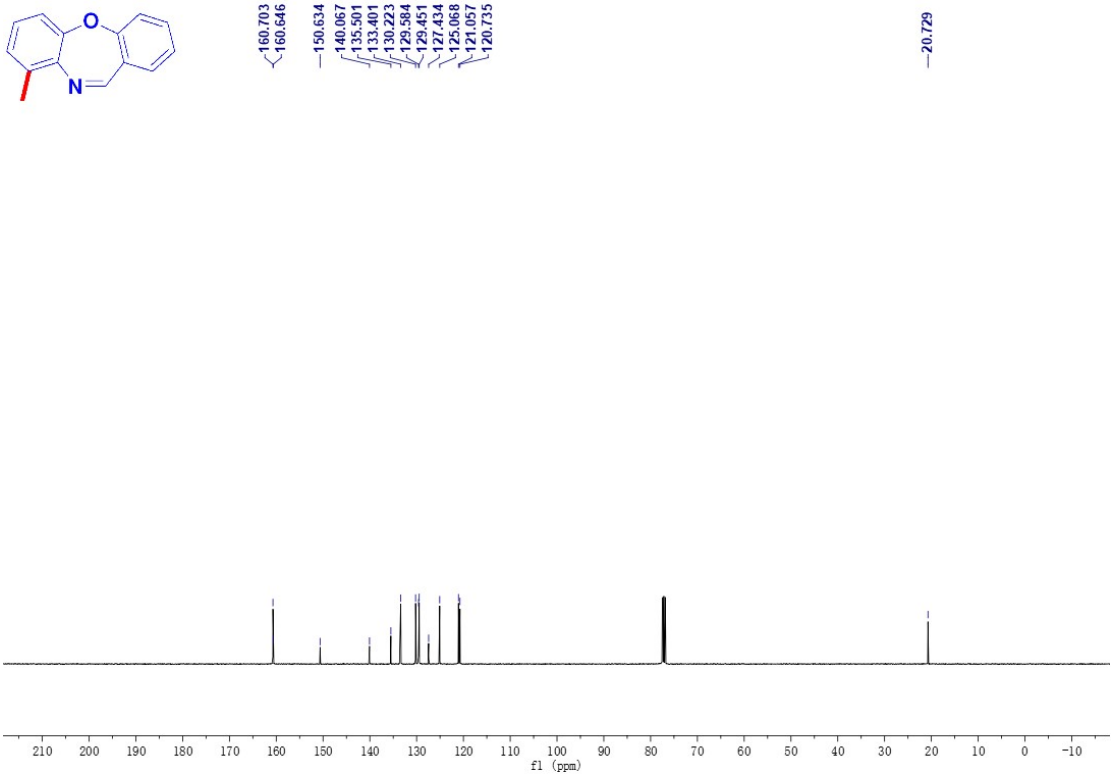
^{1}H NMR Spectrum of Compound **1g**



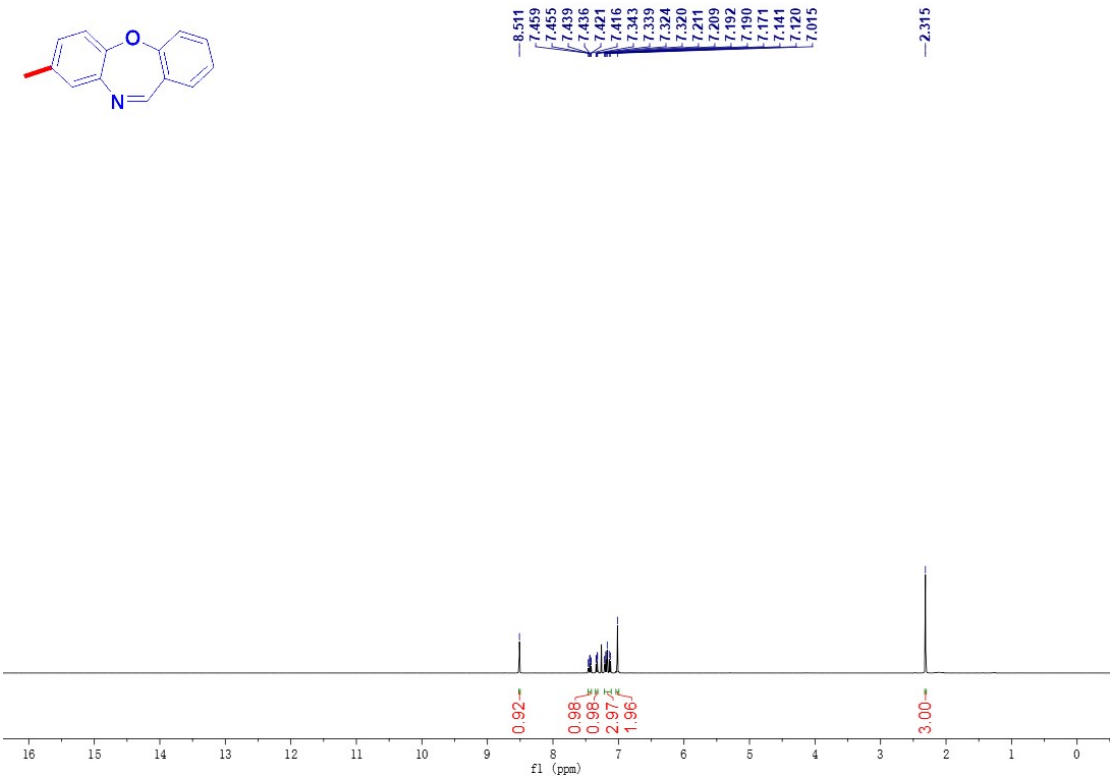
^{13}C NMR Spectrum of Compound **1g**



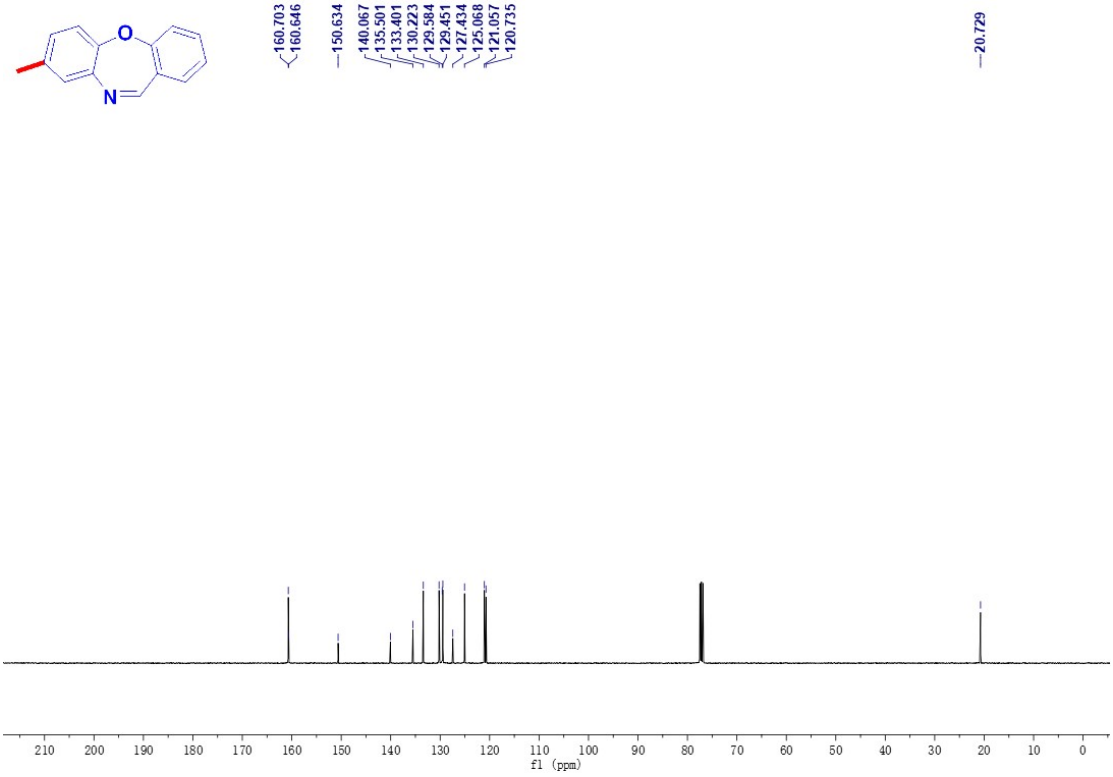
^{1}H NMR Spectrum of Compound **1h**



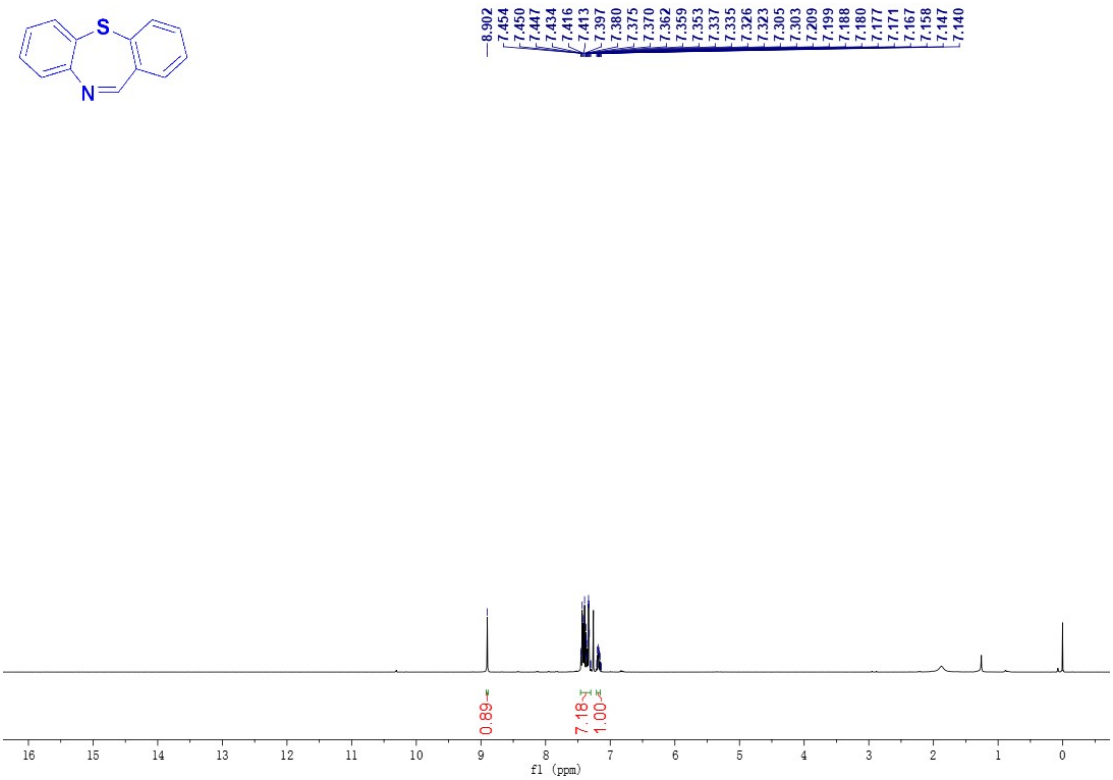
^{13}C NMR Spectrum of Compound **1h**



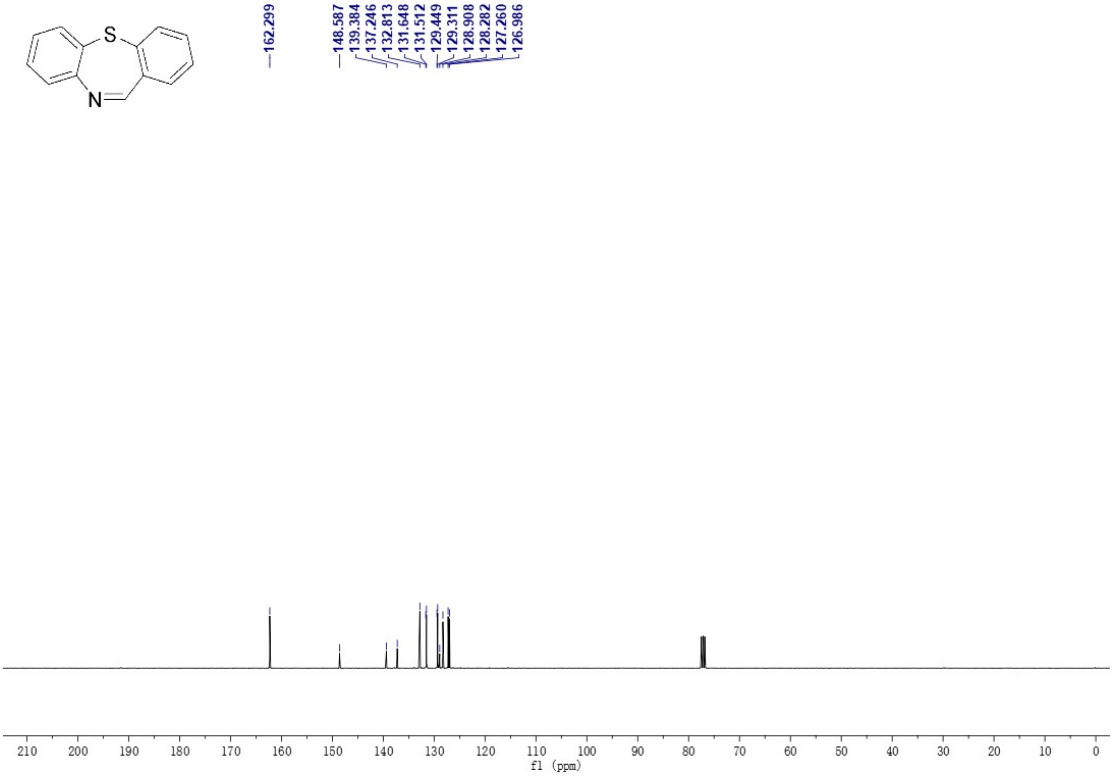
^{1}H NMR Spectrum of Compound **1i**



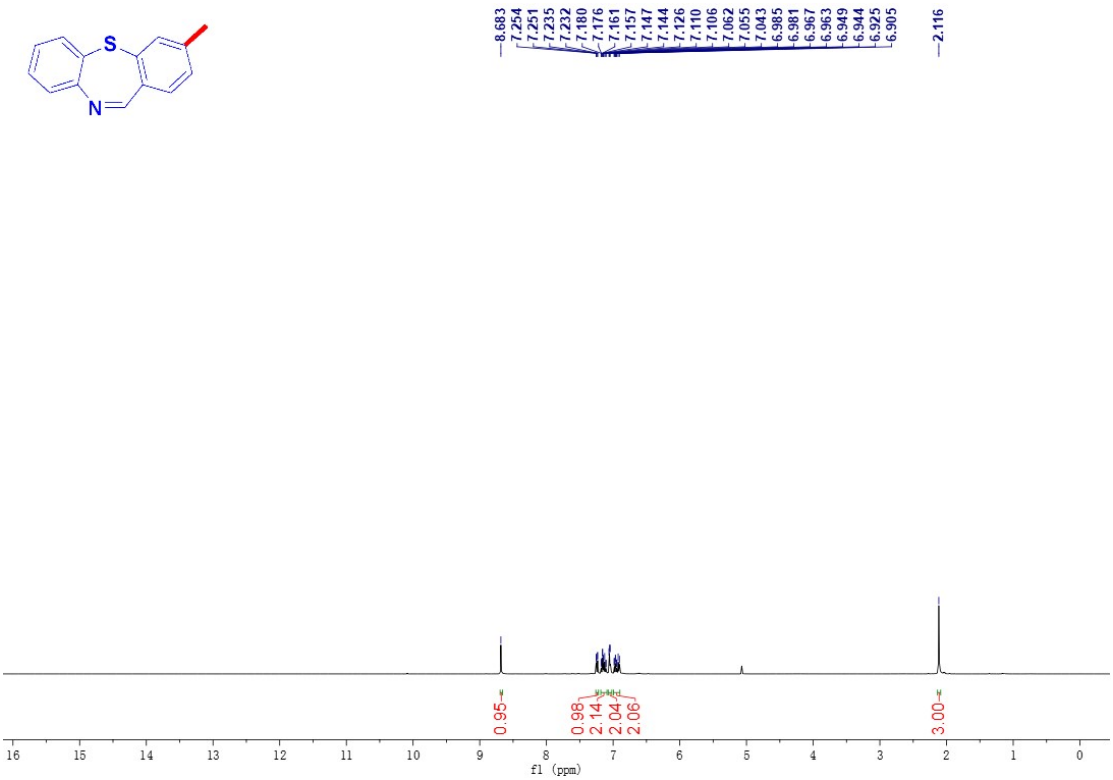
^{13}C NMR Spectrum of Compound **1i**



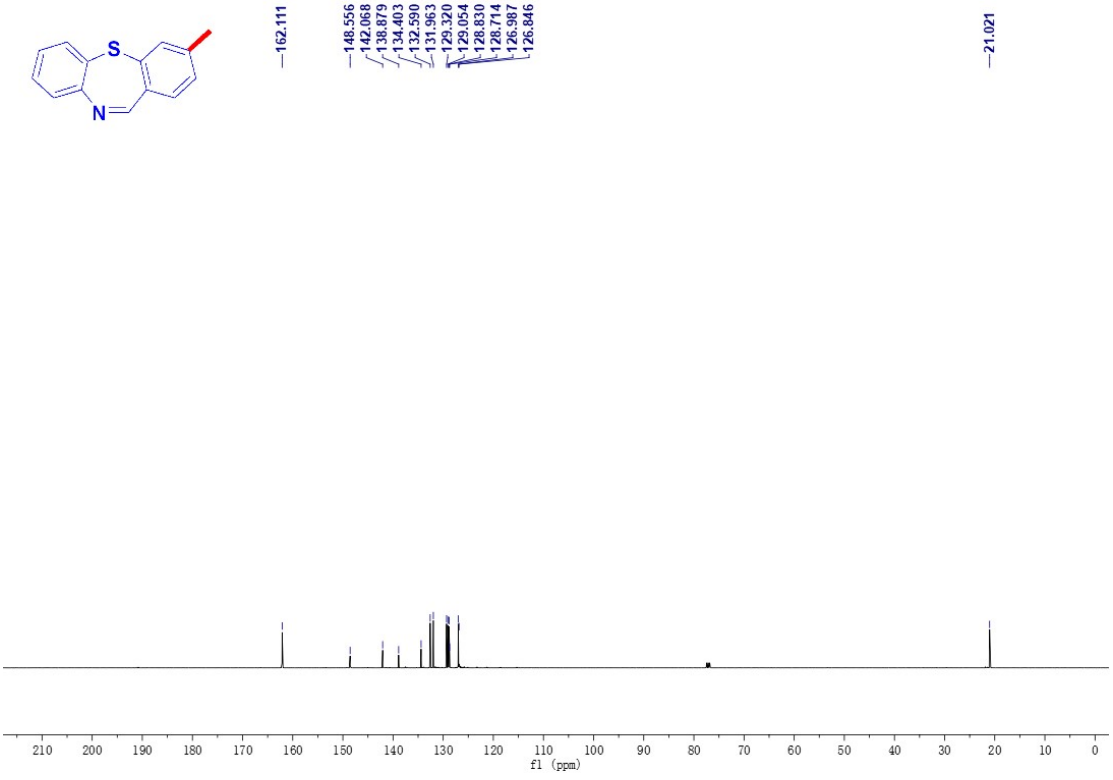
^{1}H NMR Spectrum of Compound **1j**



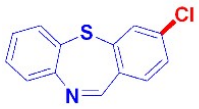
^{13}C NMR Spectrum of Compound **1j**

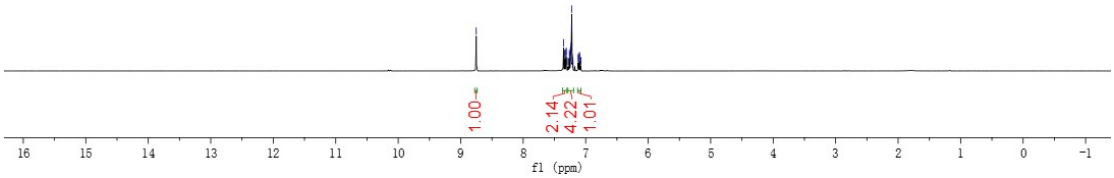


^{1}H NMR Spectrum of Compound **1k**

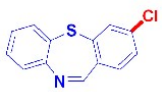


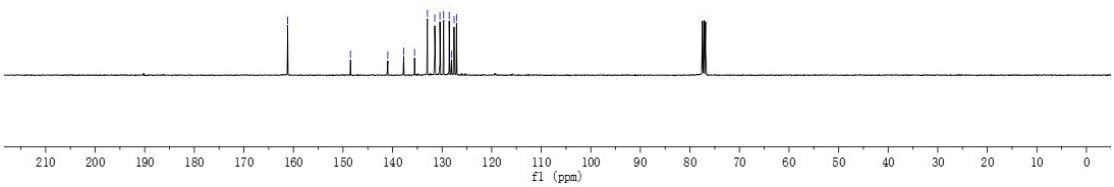
^{13}C NMR Spectrum of Compound **1k**



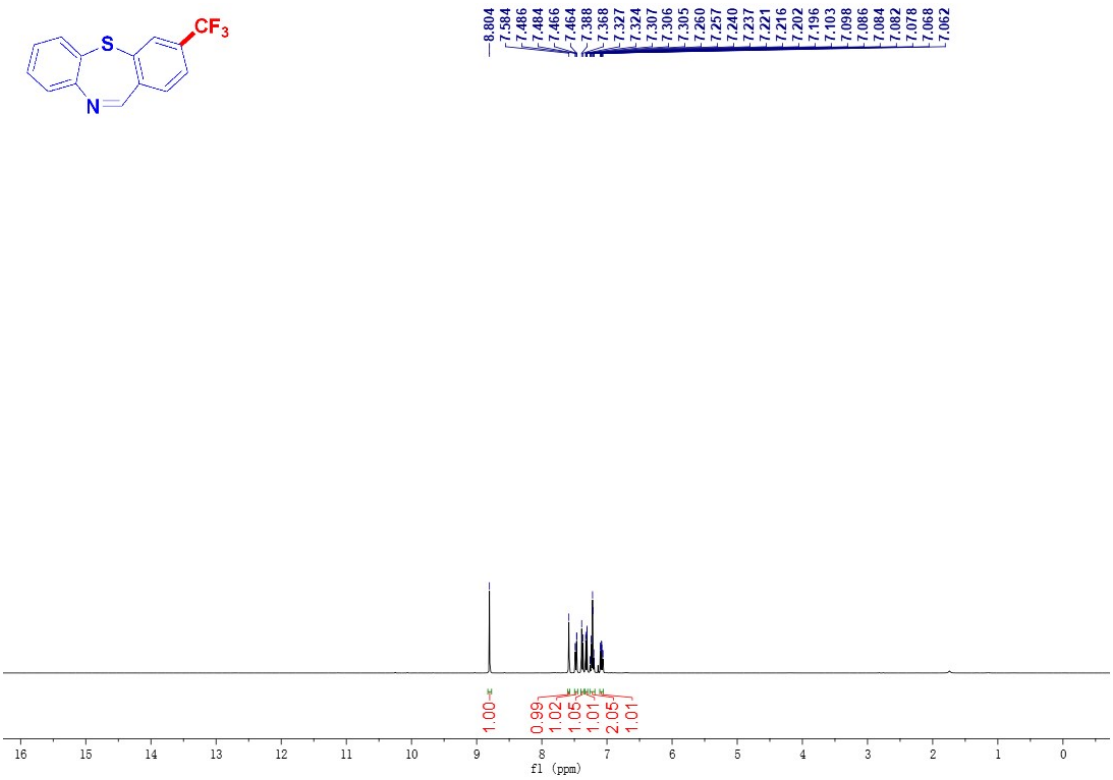


^{1}H NMR Spectrum of Compound **1l**

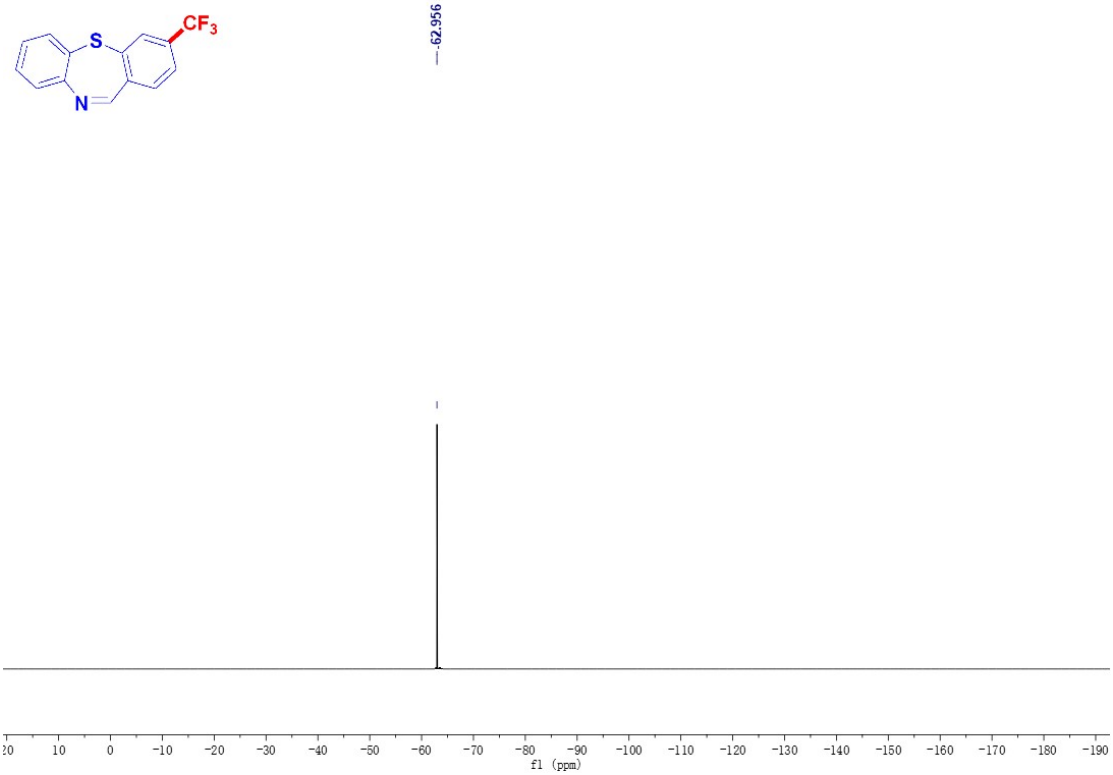




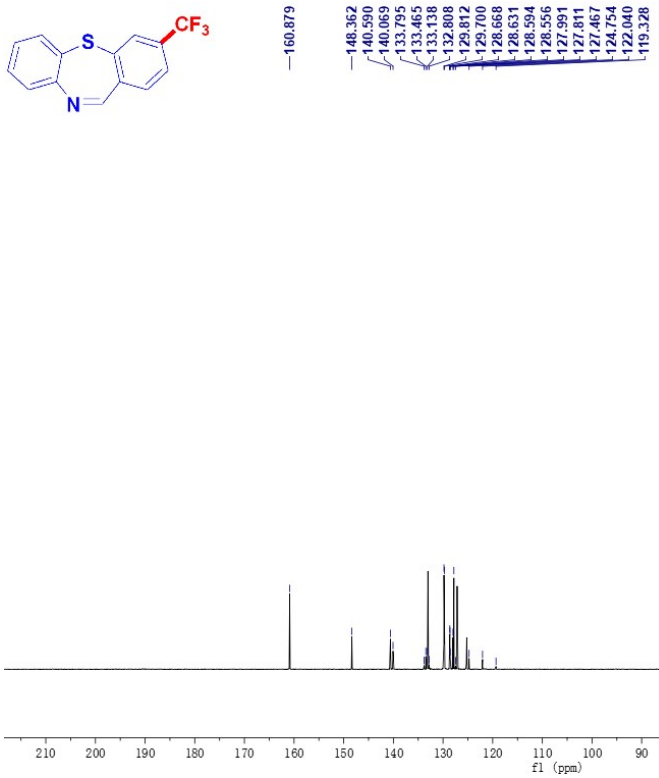
^{13}C NMR Spectrum of Compound **1l**



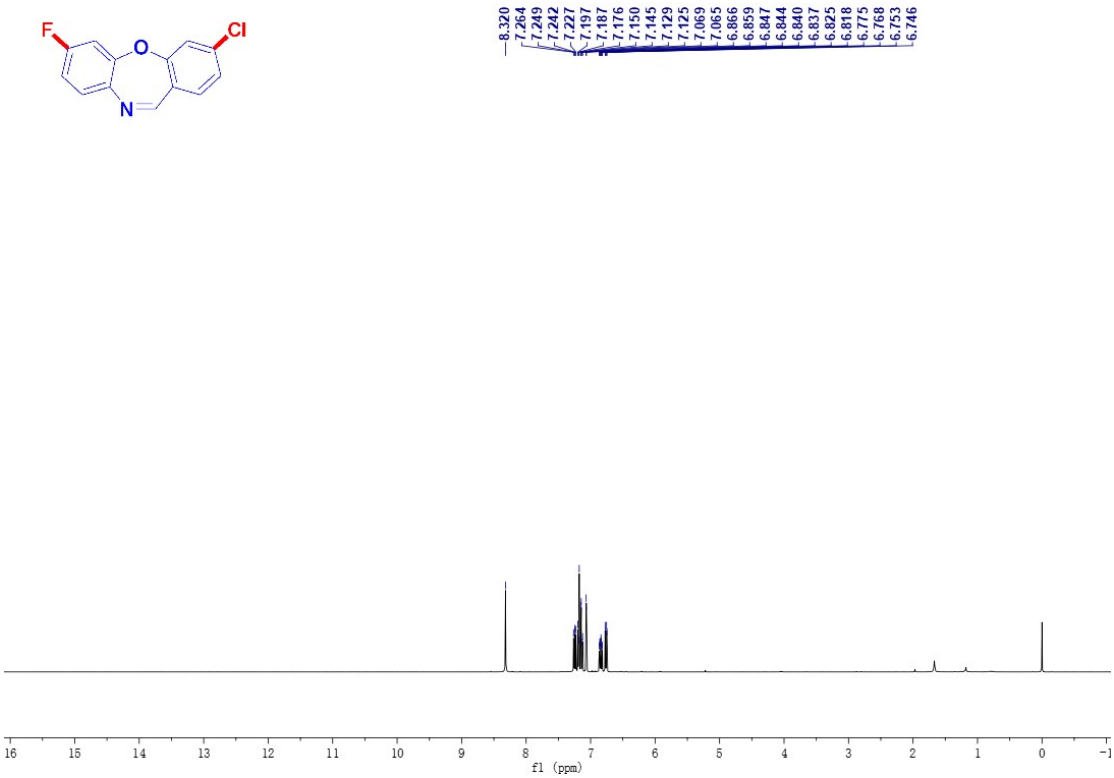
^{1}H NMR Spectrum of Compound **1m**



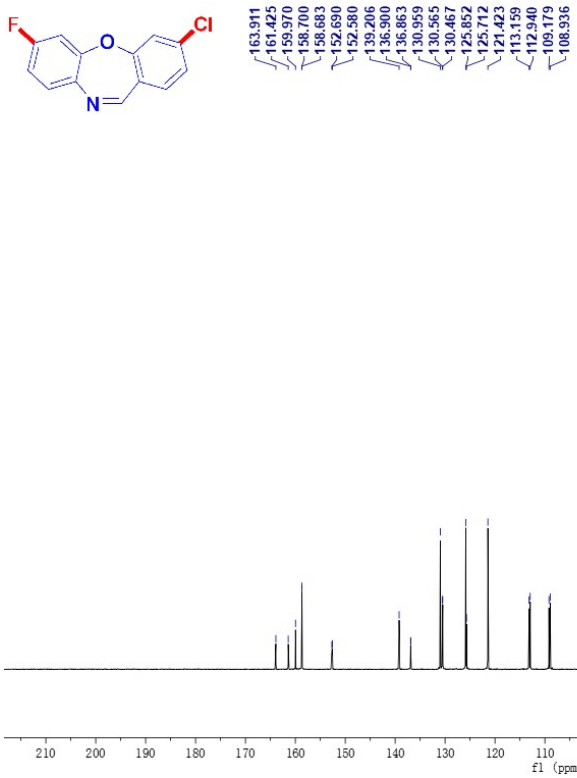
^{19}F NMR Spectrum of Compound **1m**



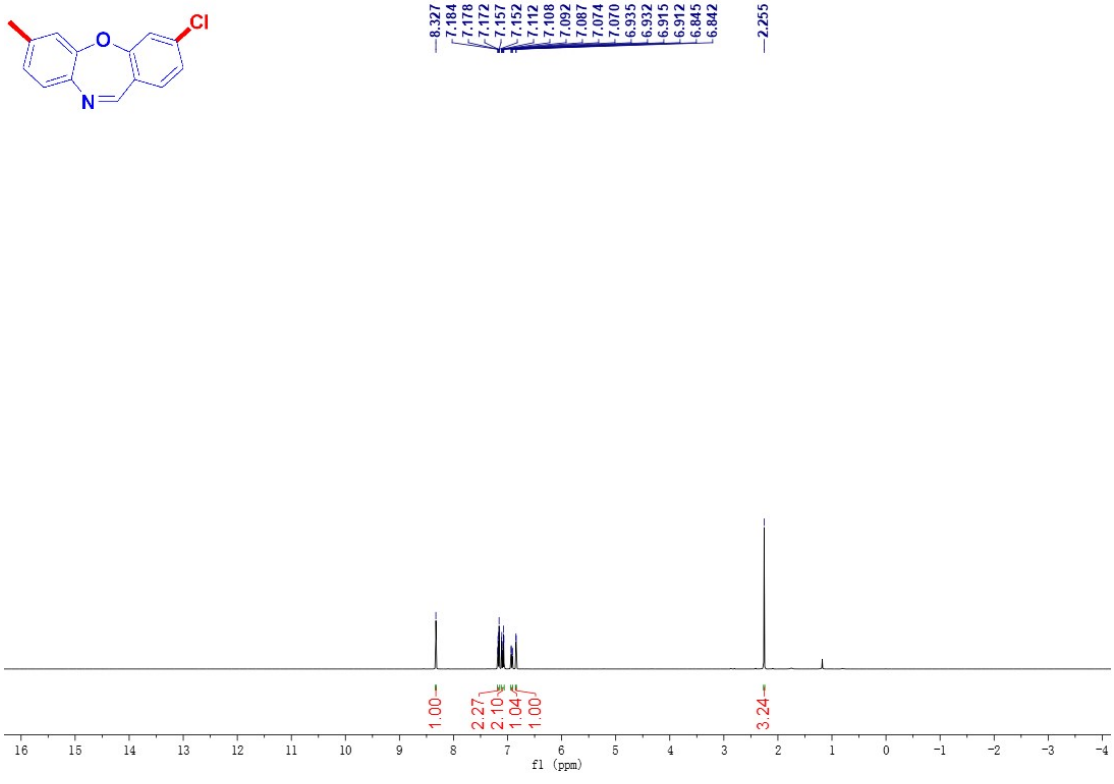
^{13}C NMR Spectrum of Compound **1m**



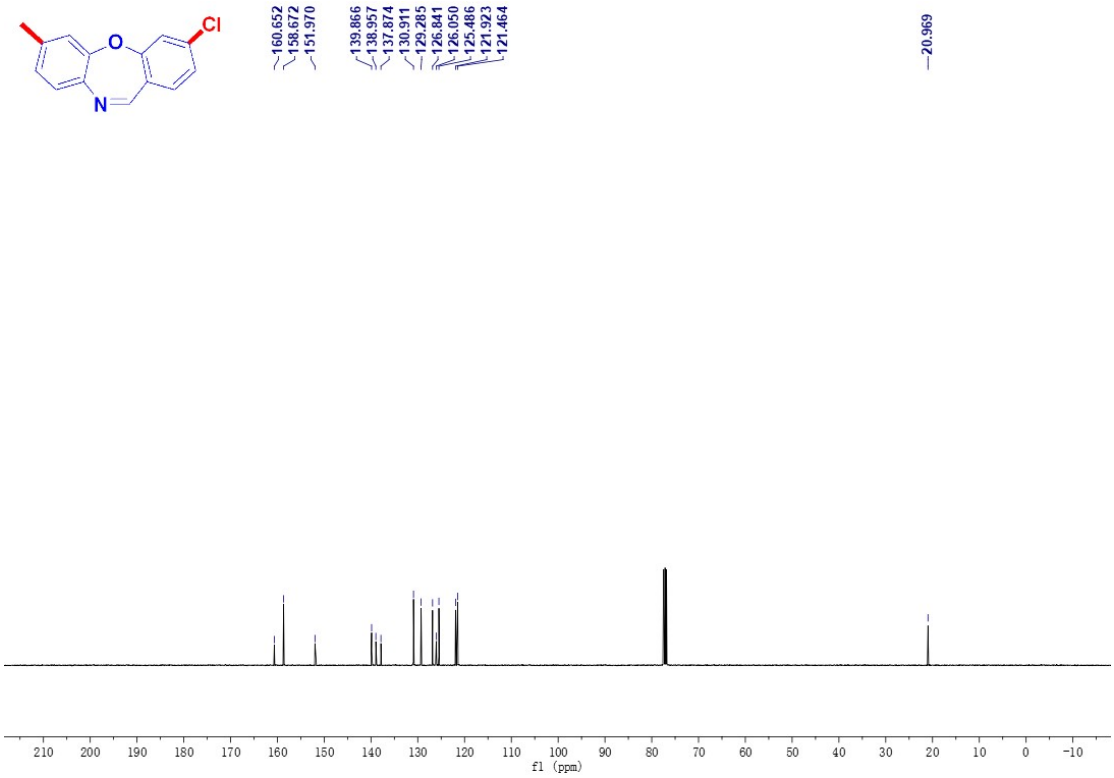
^{1}H NMR Spectrum of Compound **1n**



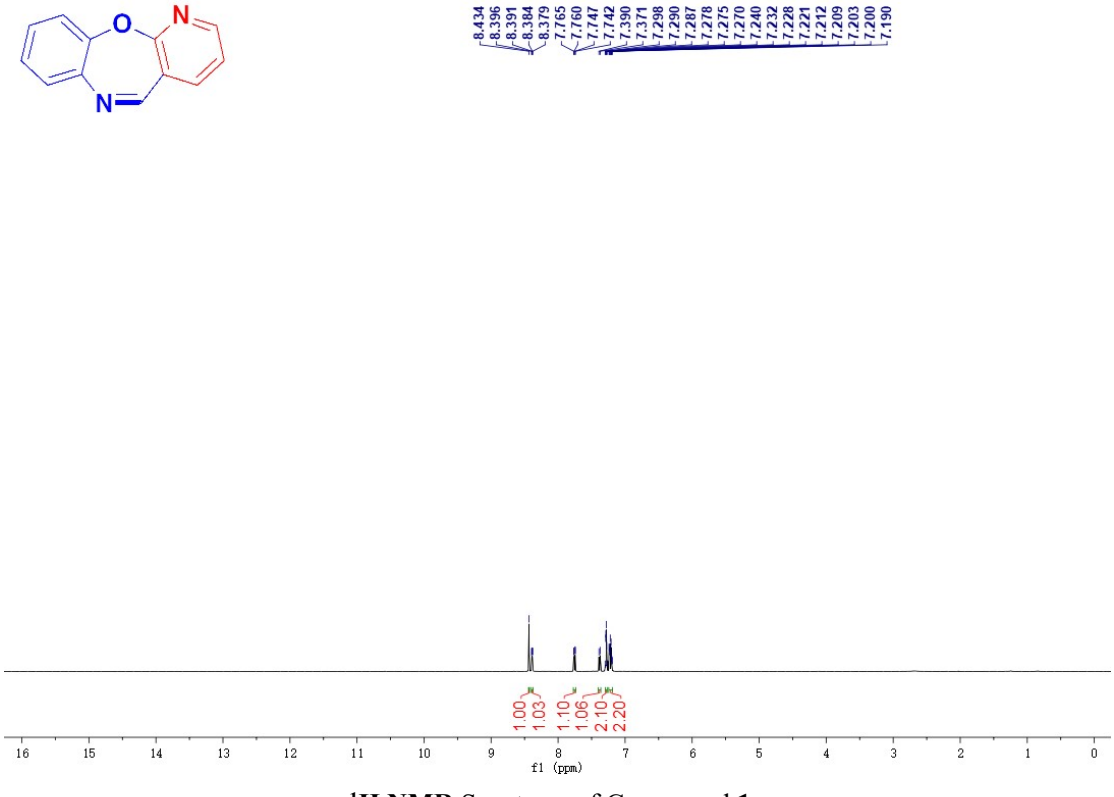
^{13}C NMR Spectrum of Compound **1n**



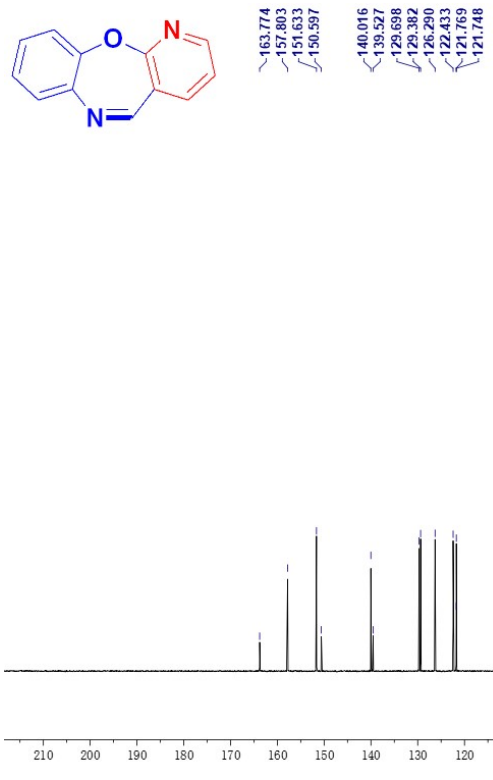
^{1}H NMR Spectrum of Compound **1o**



^{13}C NMR Spectrum of Compound **1o**

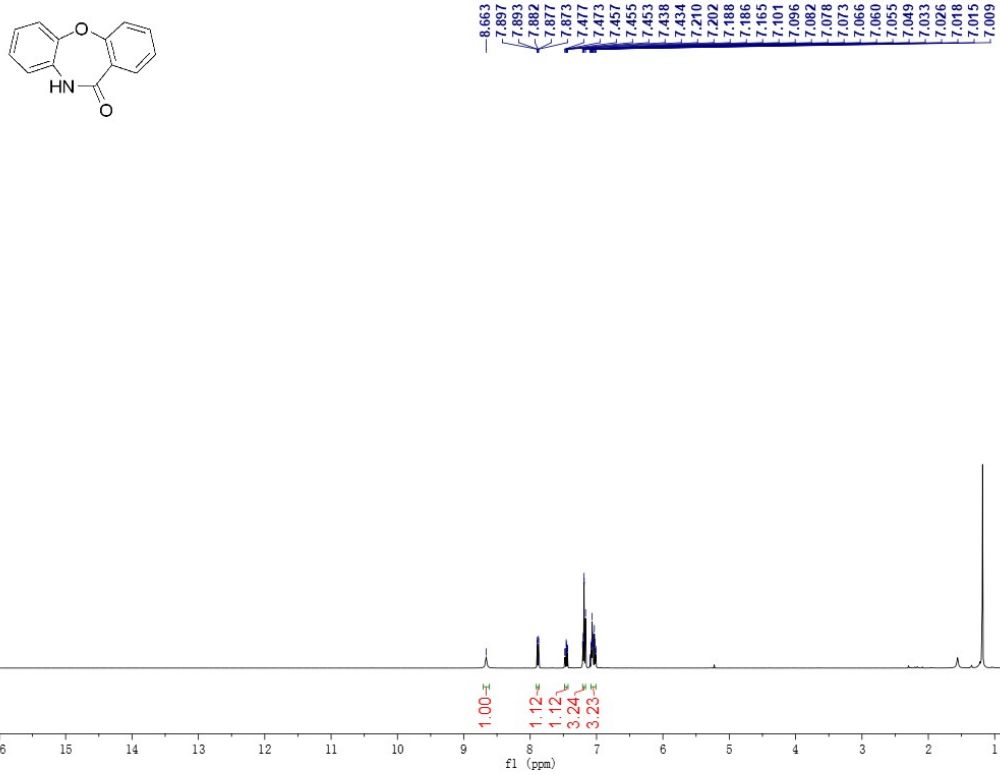


^{1}H NMR Spectrum of Compound **1p**

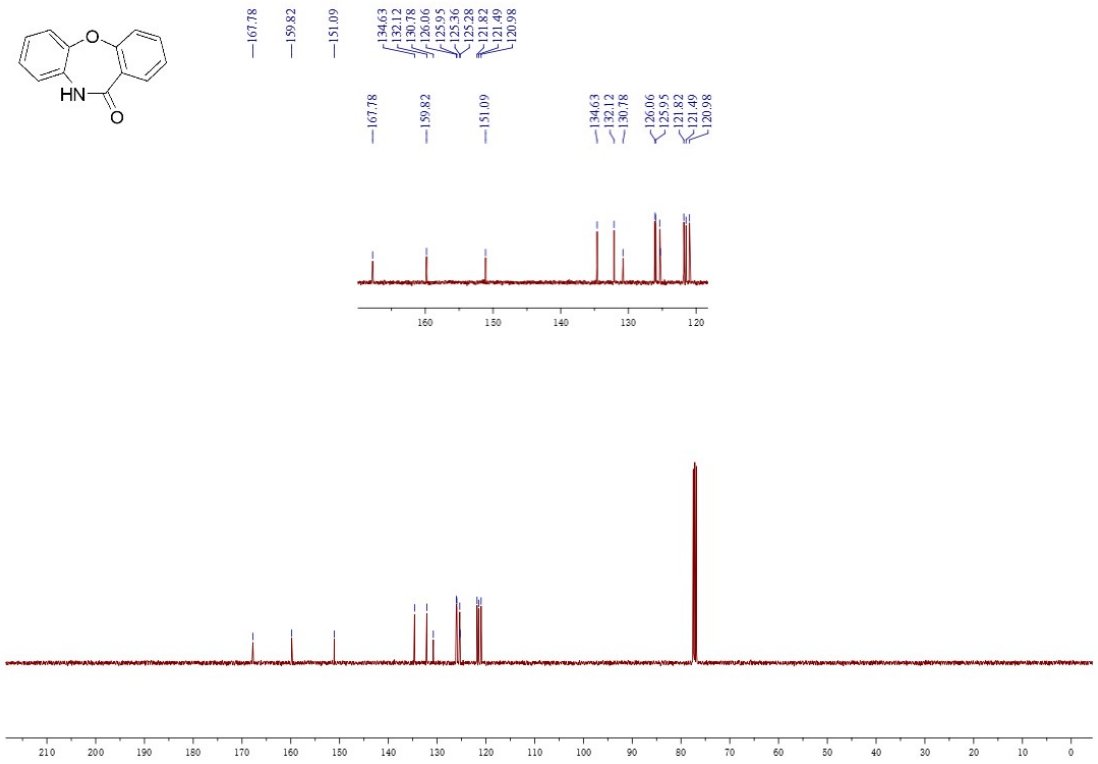


^{13}C NMR Spectrum of Compound **1p**

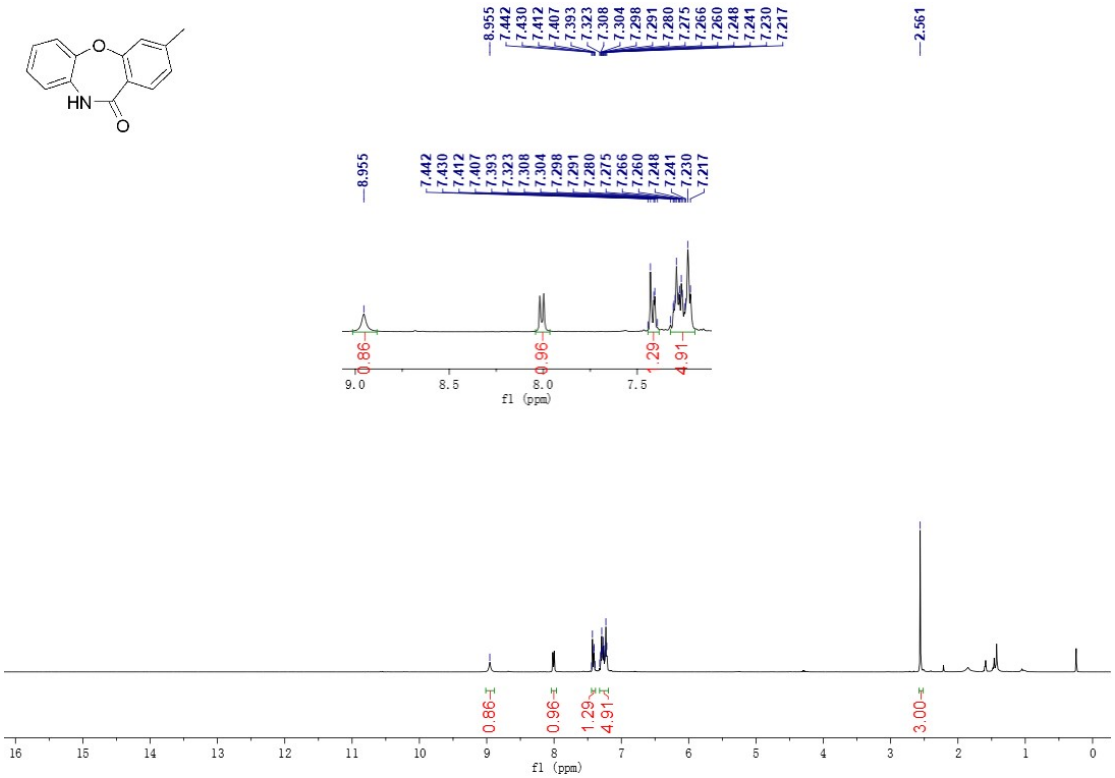
Copies of ^{1}H (400 MHz), ^{19}F (67 MHz) and ^{13}C (101 MHz) spectra of products 3a-3q in $CDCl_3$ or DMSO-d6



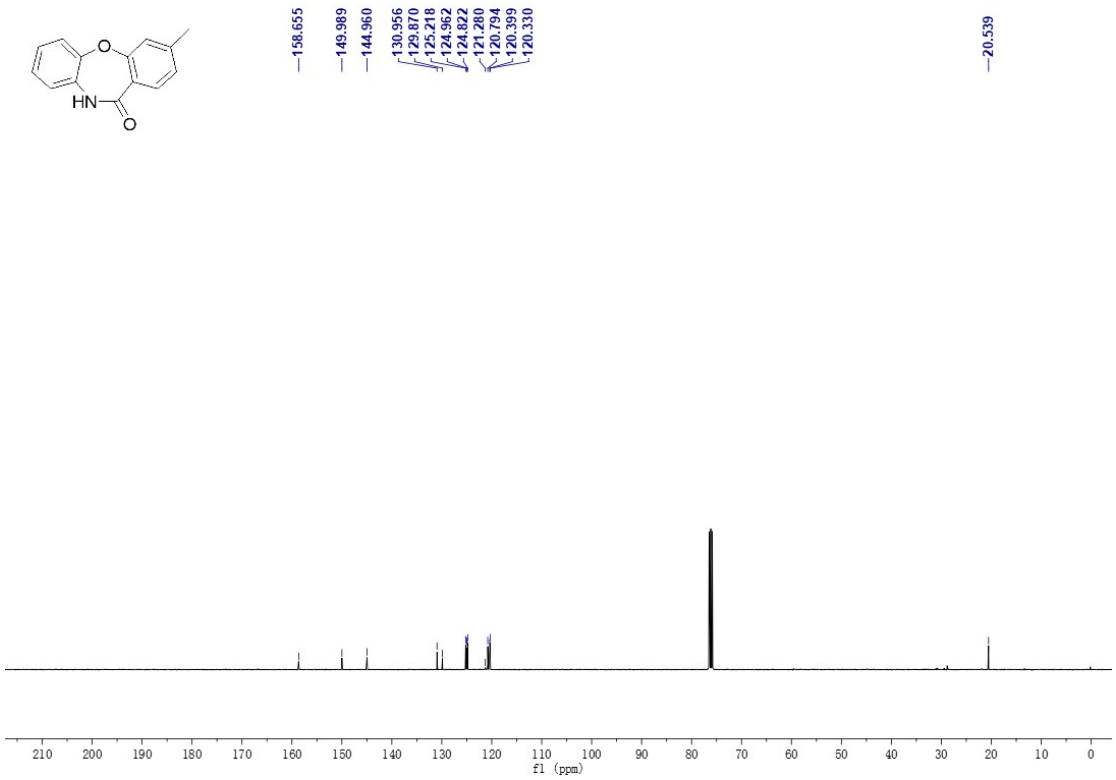
^{1}H NMR Spectrum of Compound **3a**



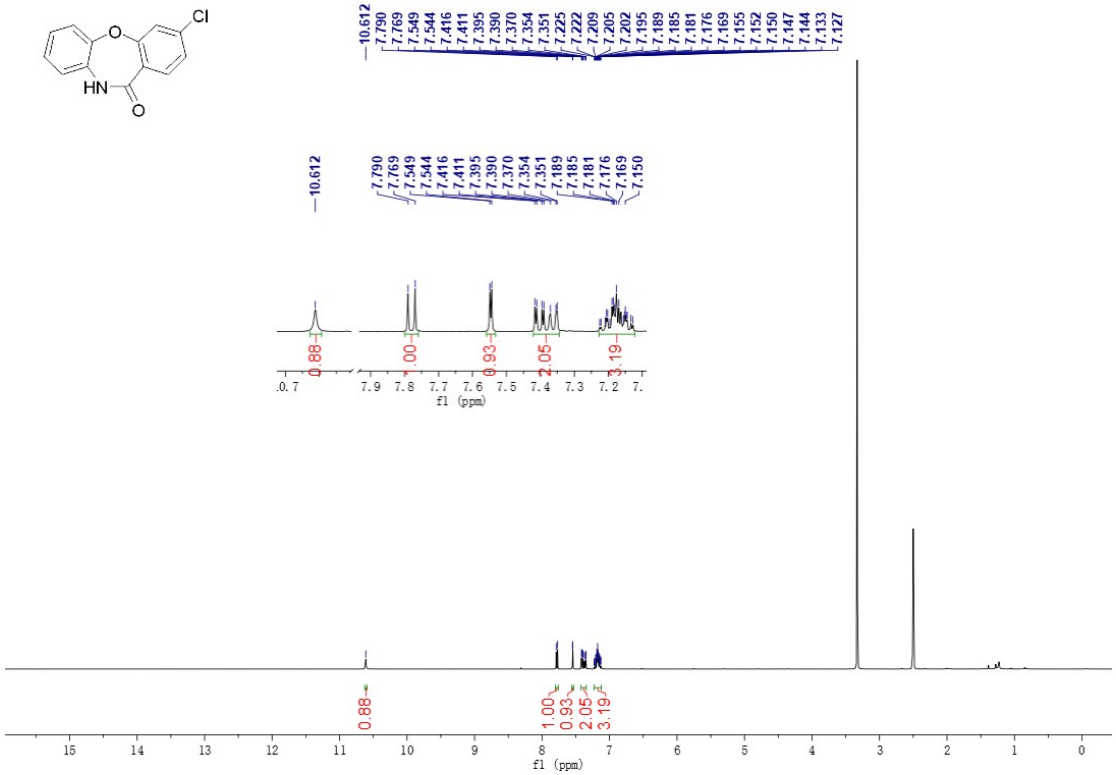
^{13}C NMR Spectrum of Compound **3a**



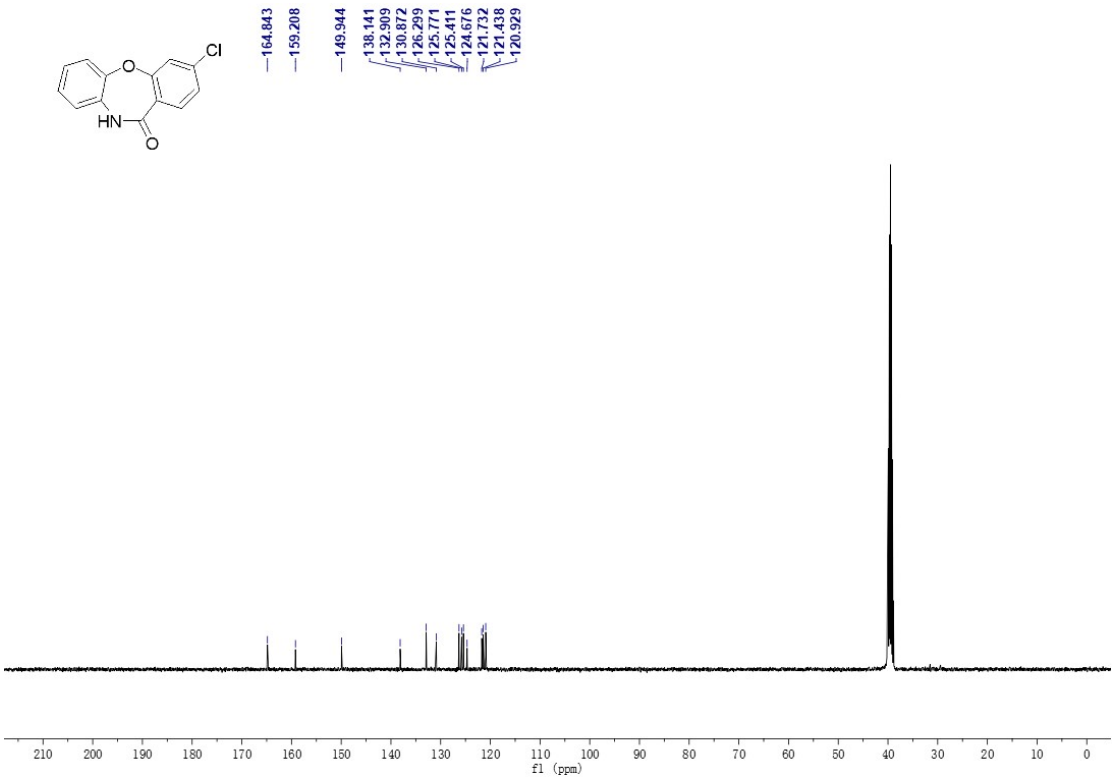
^{1}H NMR Spectrum of Compound **3b**



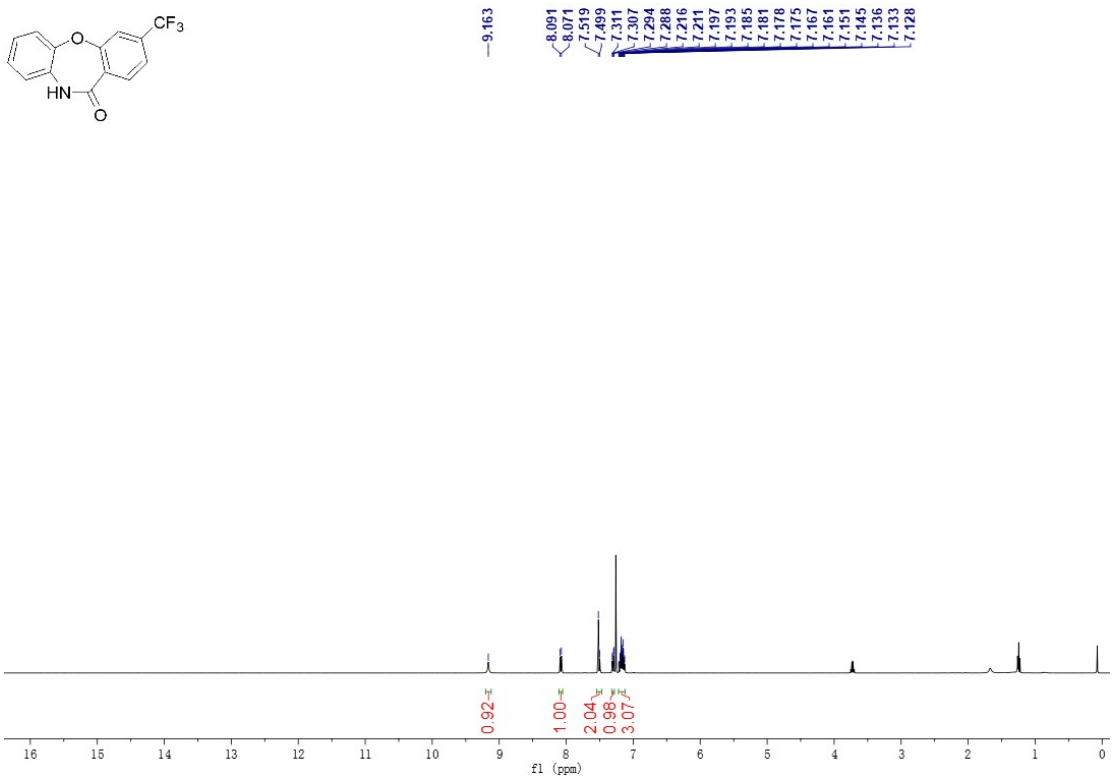
^{13}C NMR Spectrum of Compound **3b**



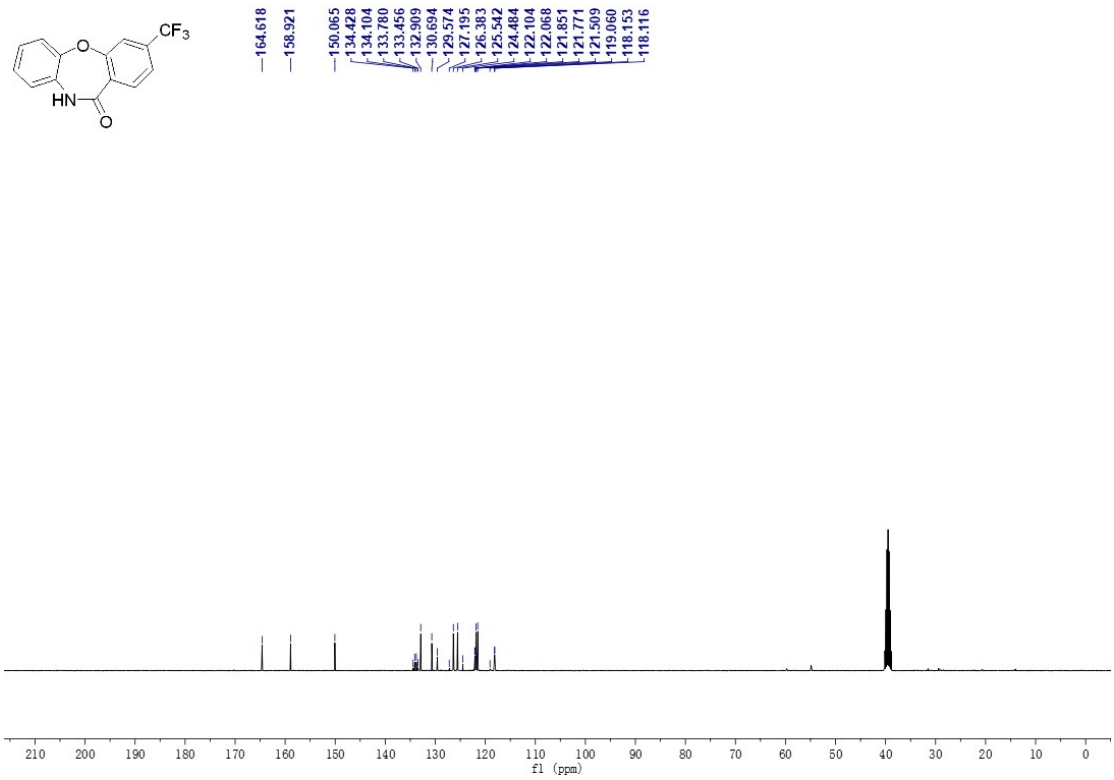
^{1}H NMR Spectrum of Compound **3c**



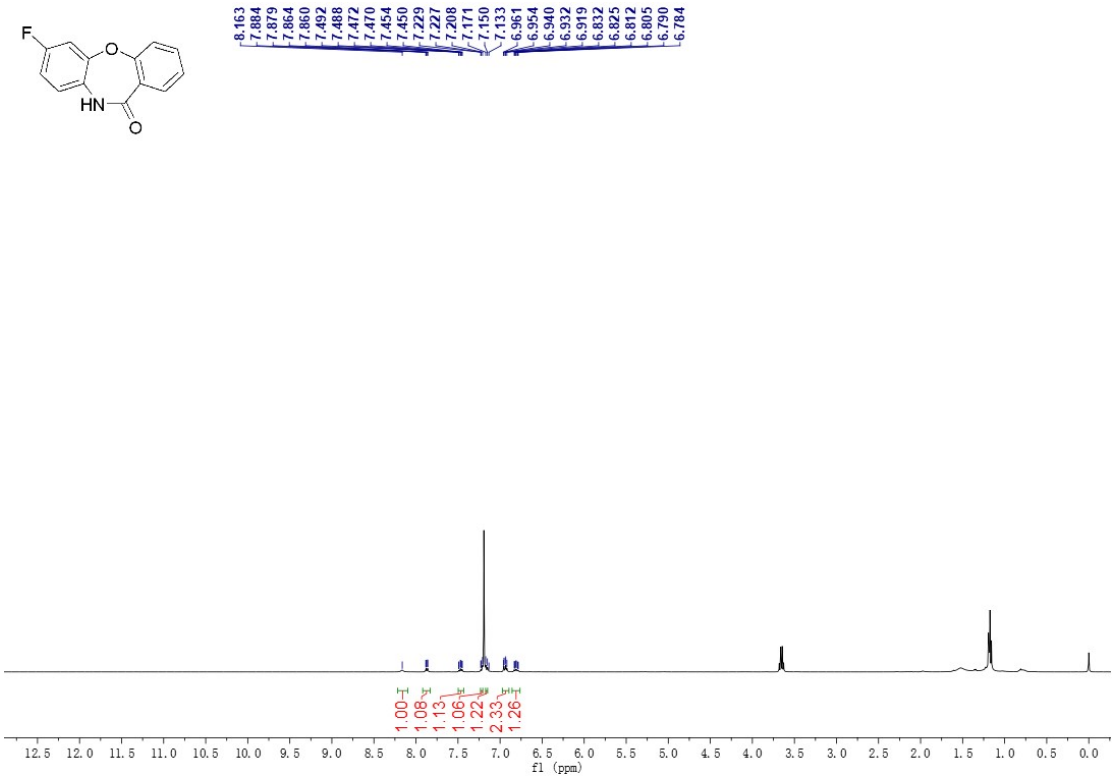
^{13}C NMR Spectrum of Compound **3c**



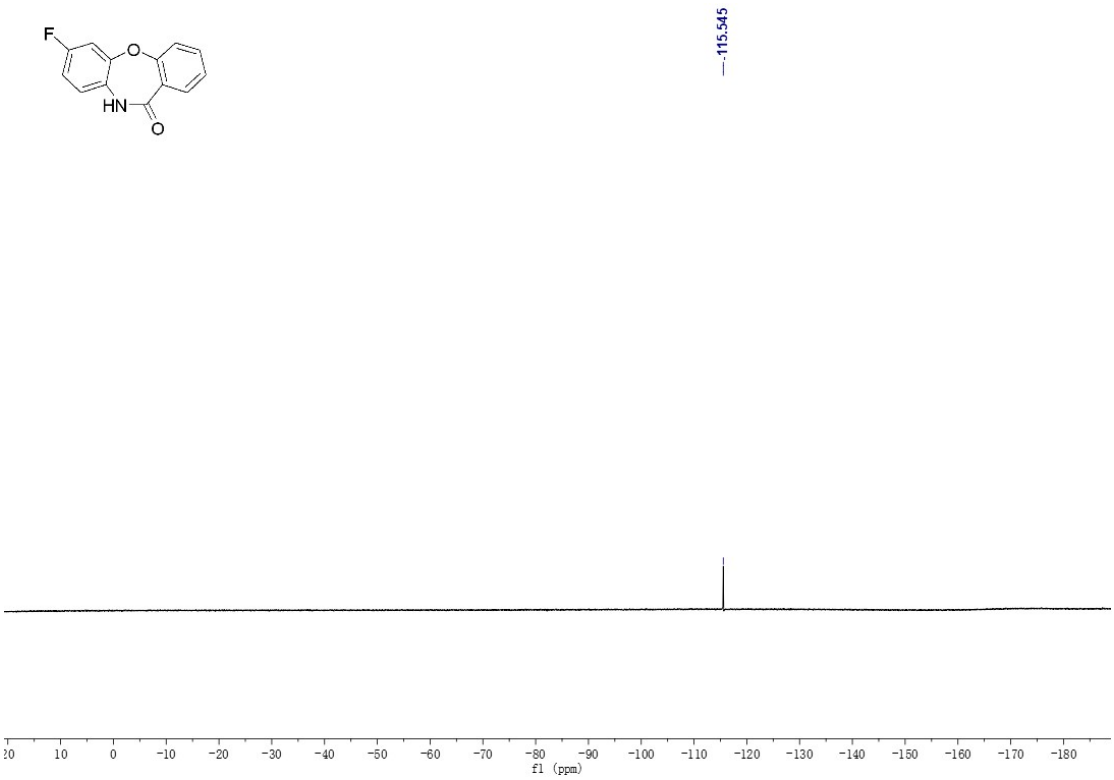
^{1}H NMR Spectrum of Compound **3d**



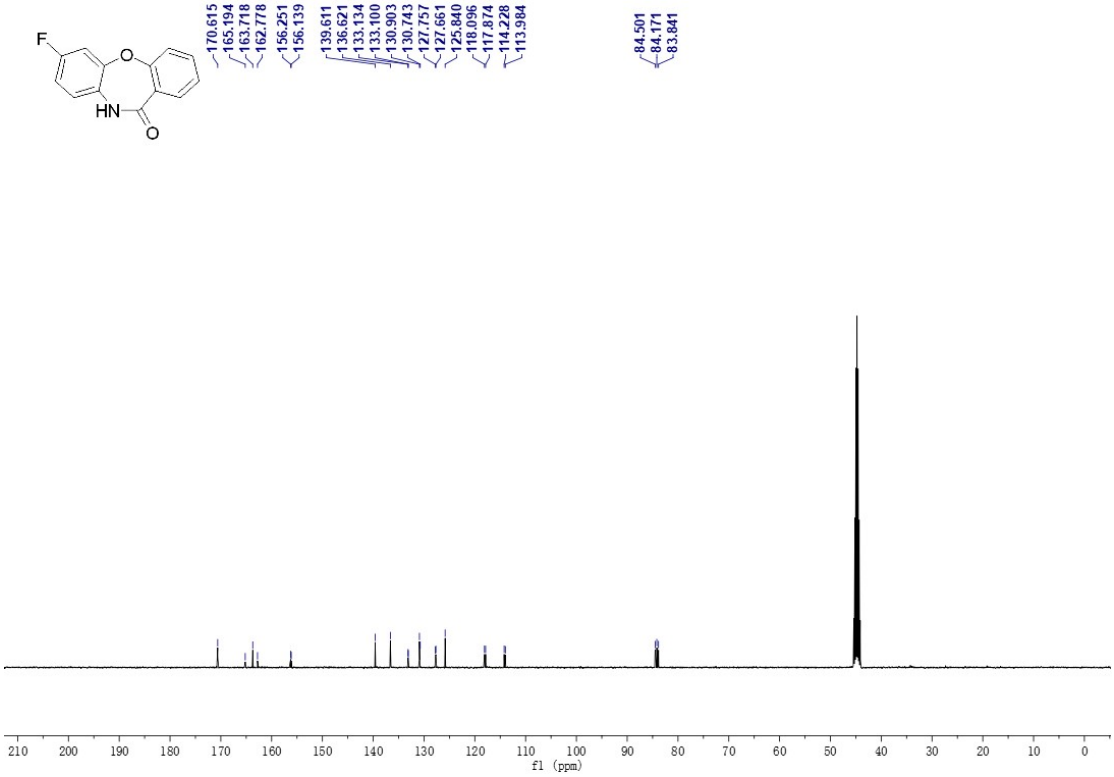
^{13}C NMR Spectrum of Compound **3d**



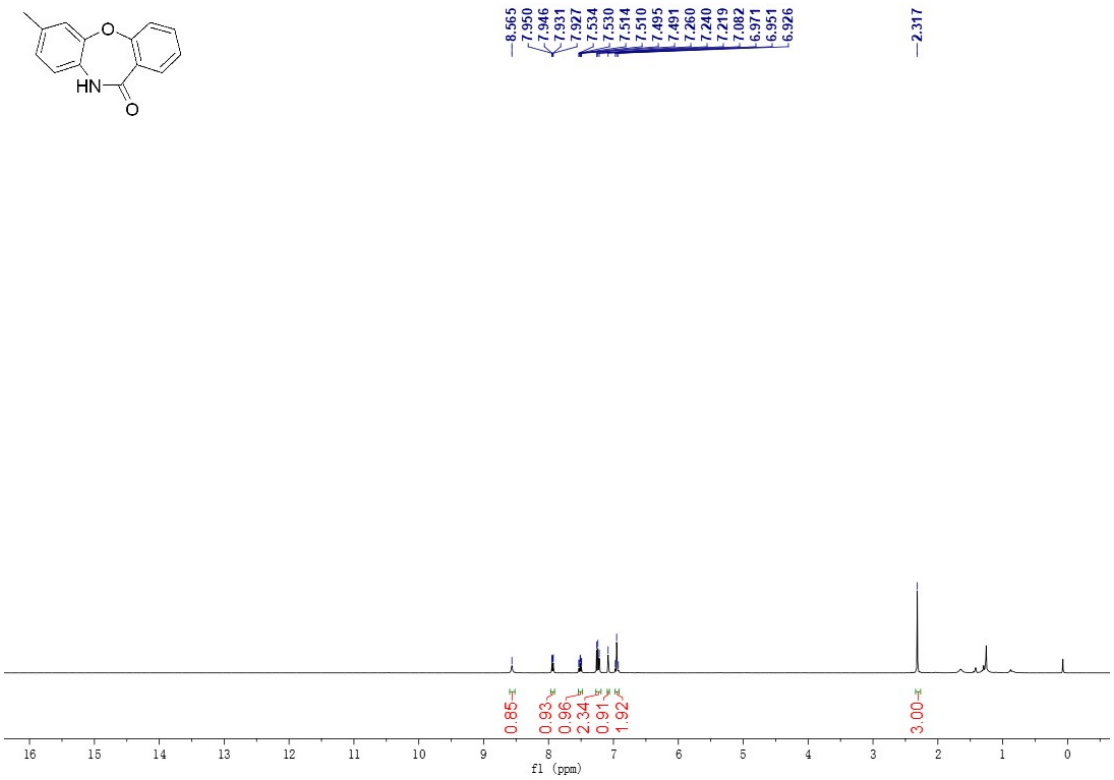
^{1}H NMR Spectrum of Compound **3e**



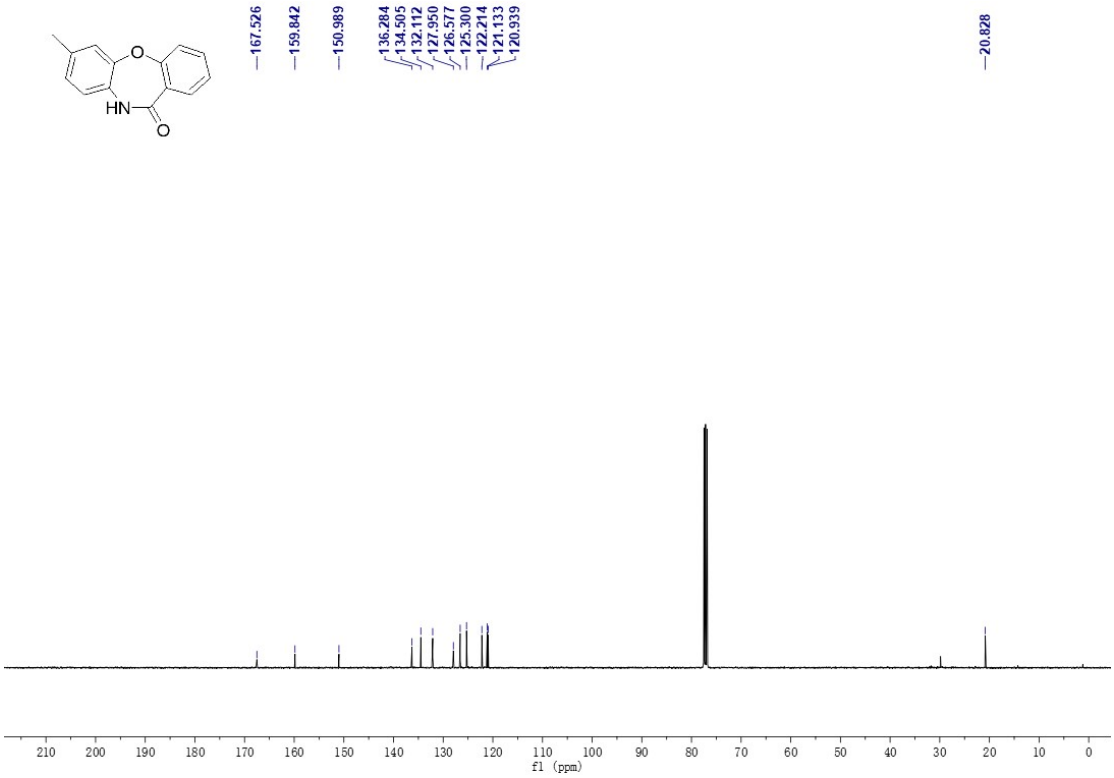
^{19}F NMR Spectrum of Compound **3e**



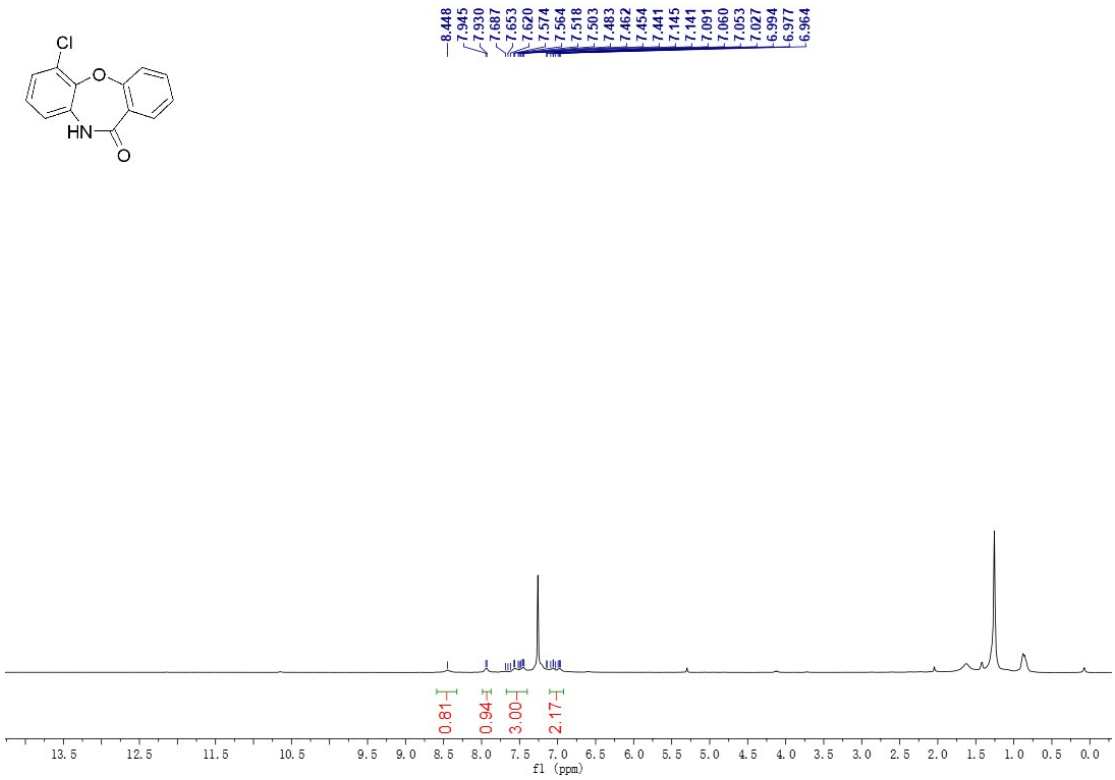
^{13}C NMR Spectrum of Compound **3e**



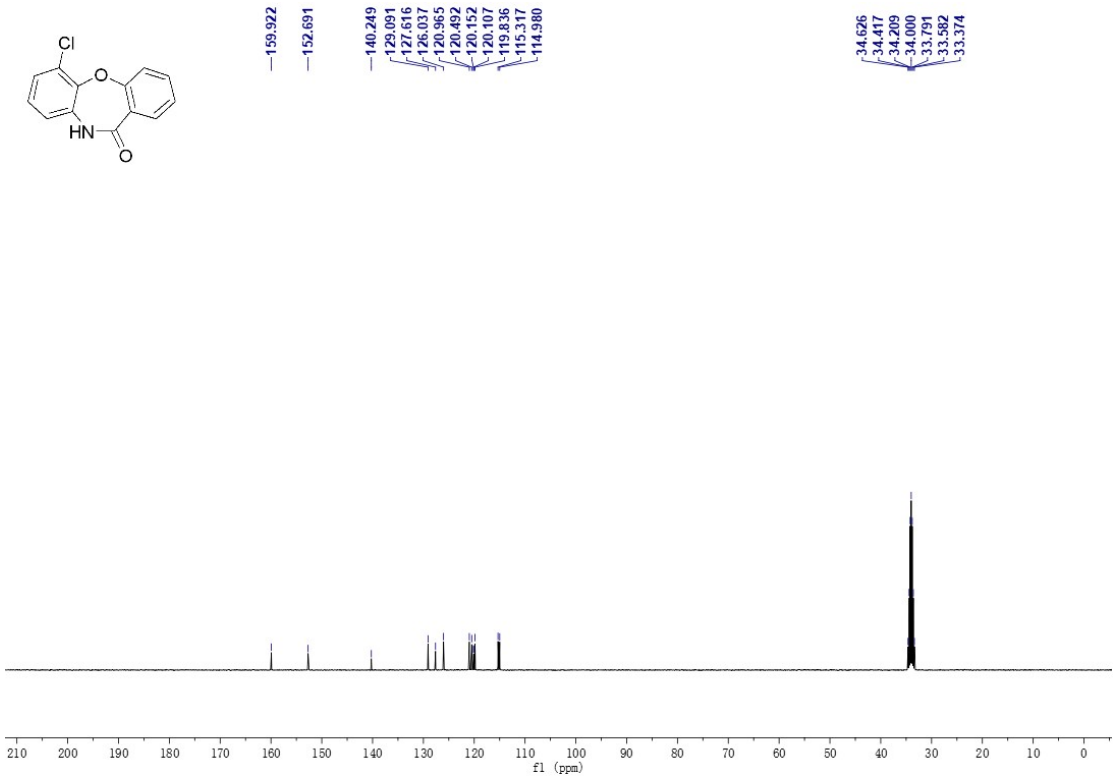
^{1}H NMR Spectrum of Compound **3f**



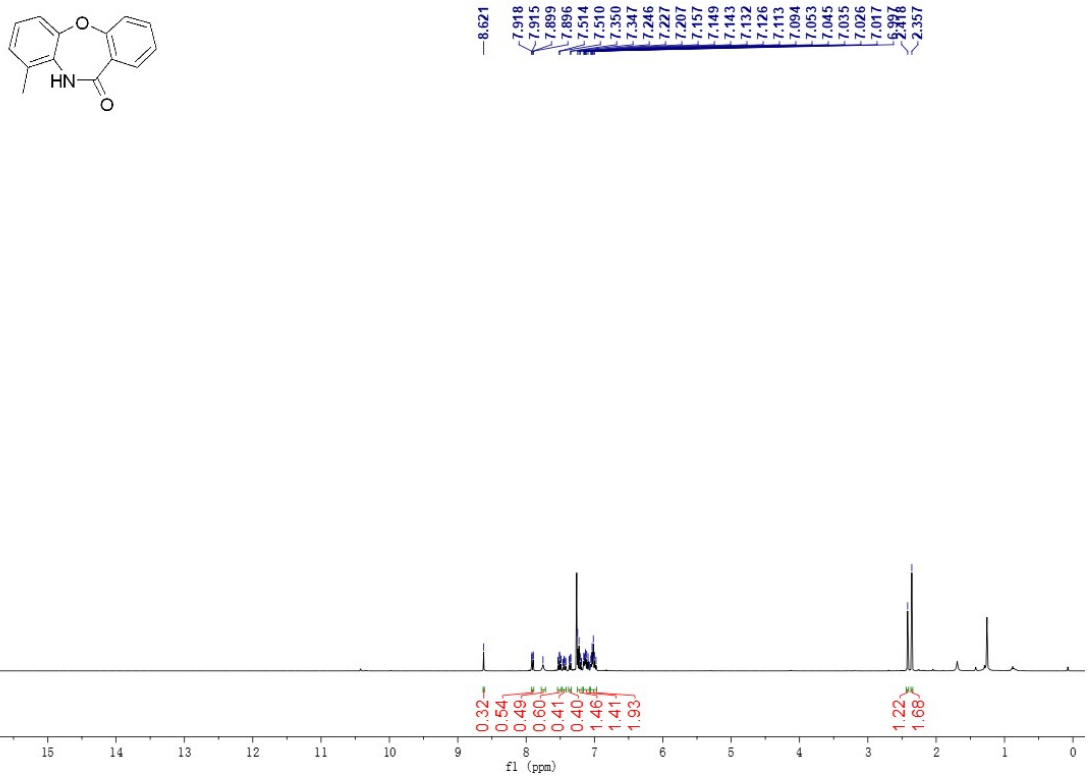
^{13}C NMR Spectrum of Compound **3f**



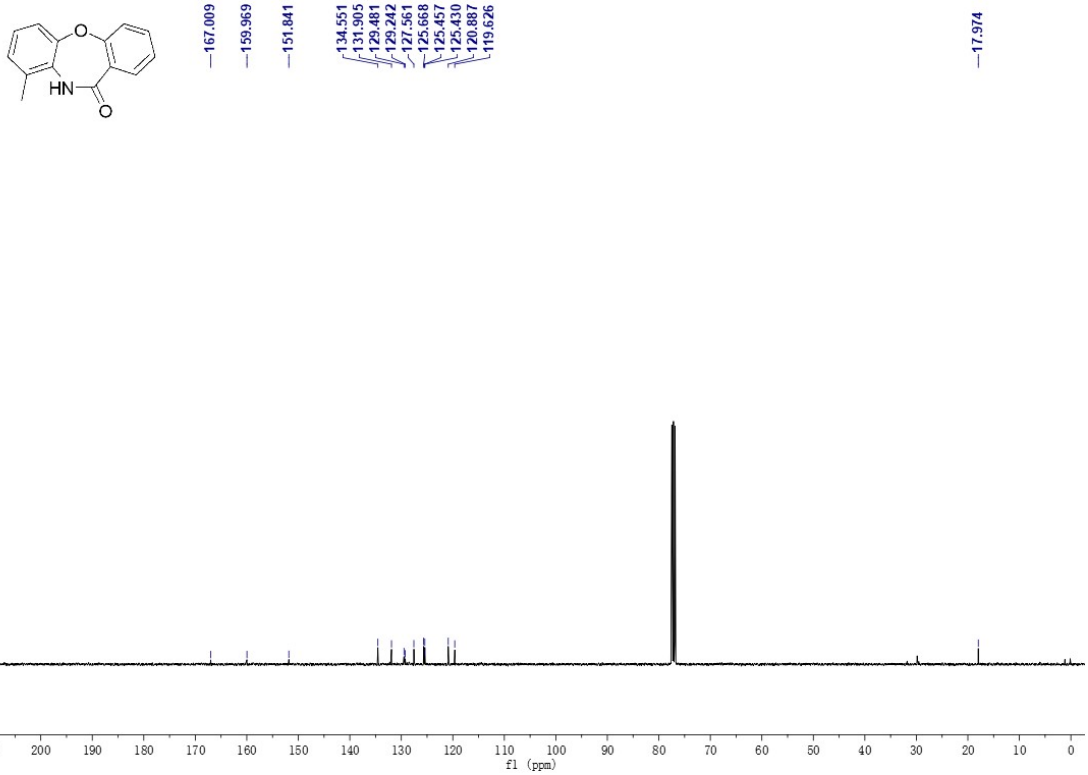
^{1}H NMR Spectrum of Compound **3g**



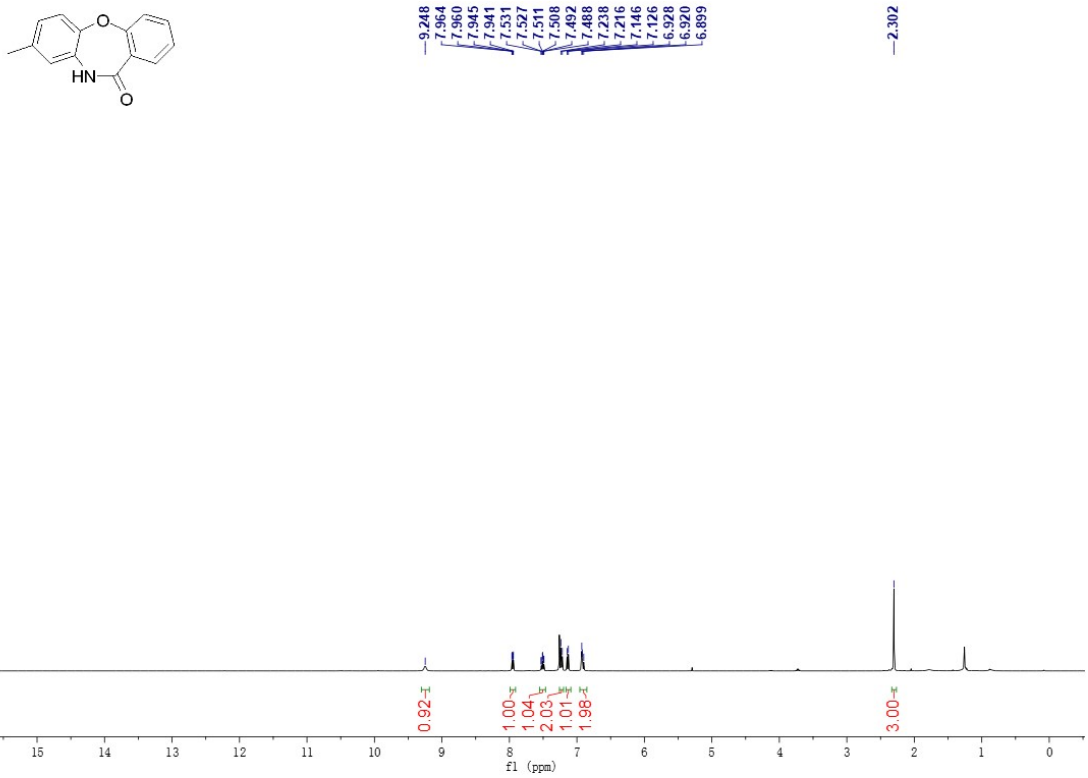
^{13}C NMR Spectrum of Compound **3g**



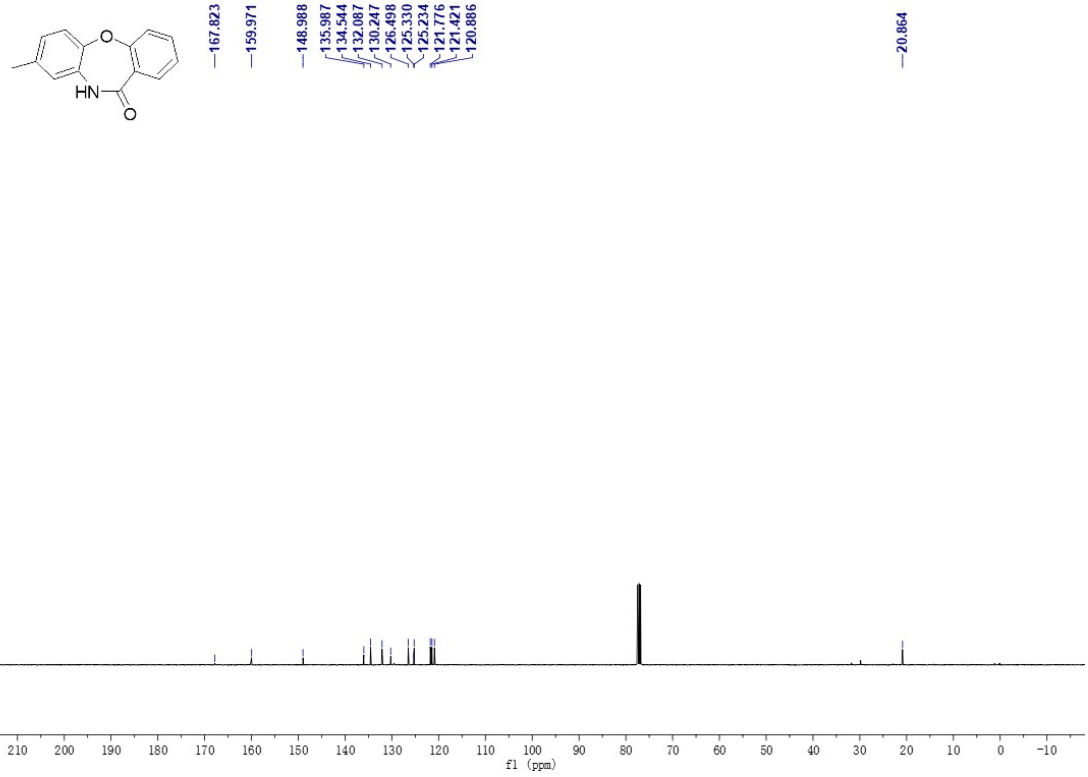
^{1}H NMR Spectrum of Compound **3h**



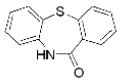
^{13}C NMR Spectrum of Compound **3h**

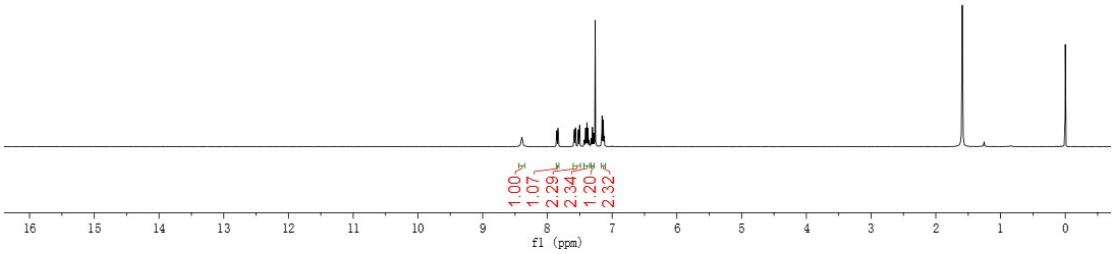


^{1}H NMR Spectrum of Compound **3i**

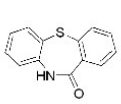


^{13}C NMR Spectrum of Compound **3i**

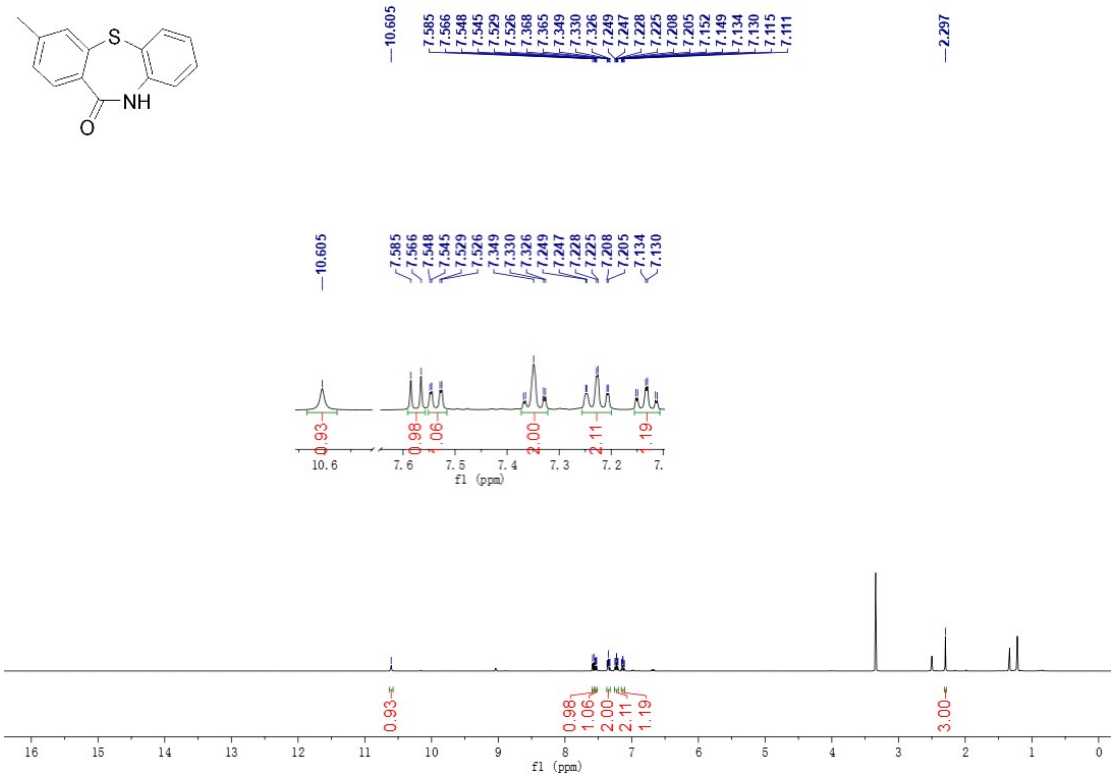




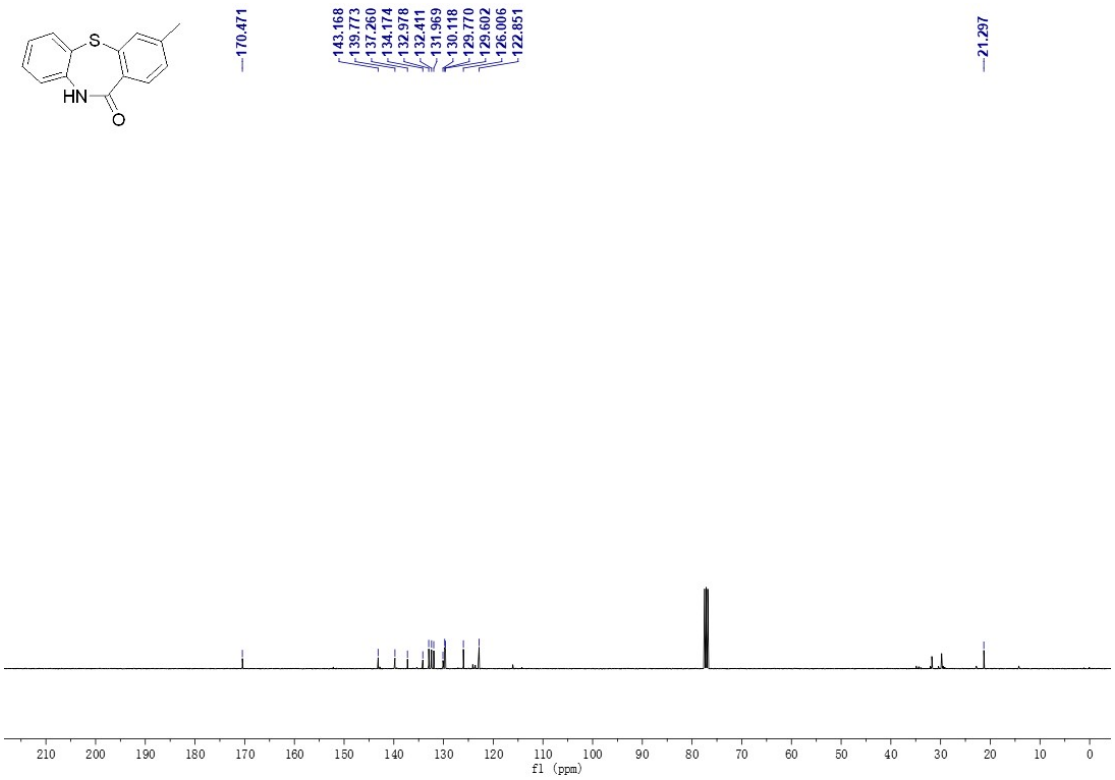
^{1}H NMR Spectrum of Compound **3j**



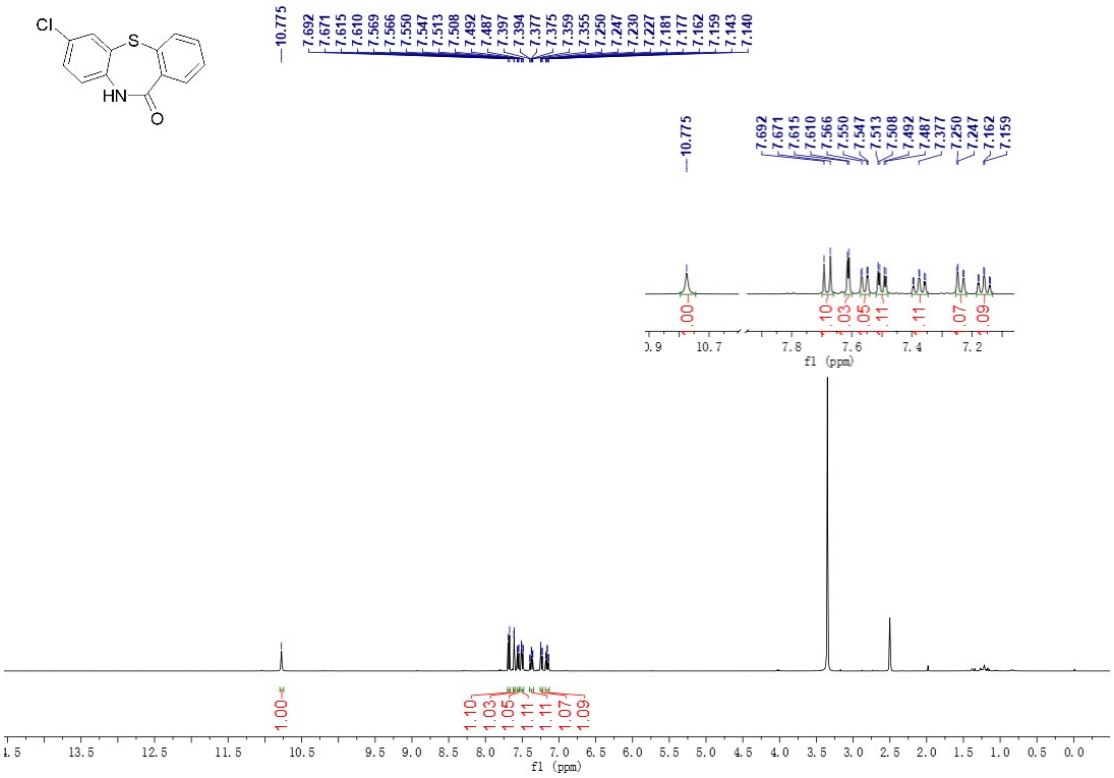
^{13}C NMR Spectrum of Compound **3j**



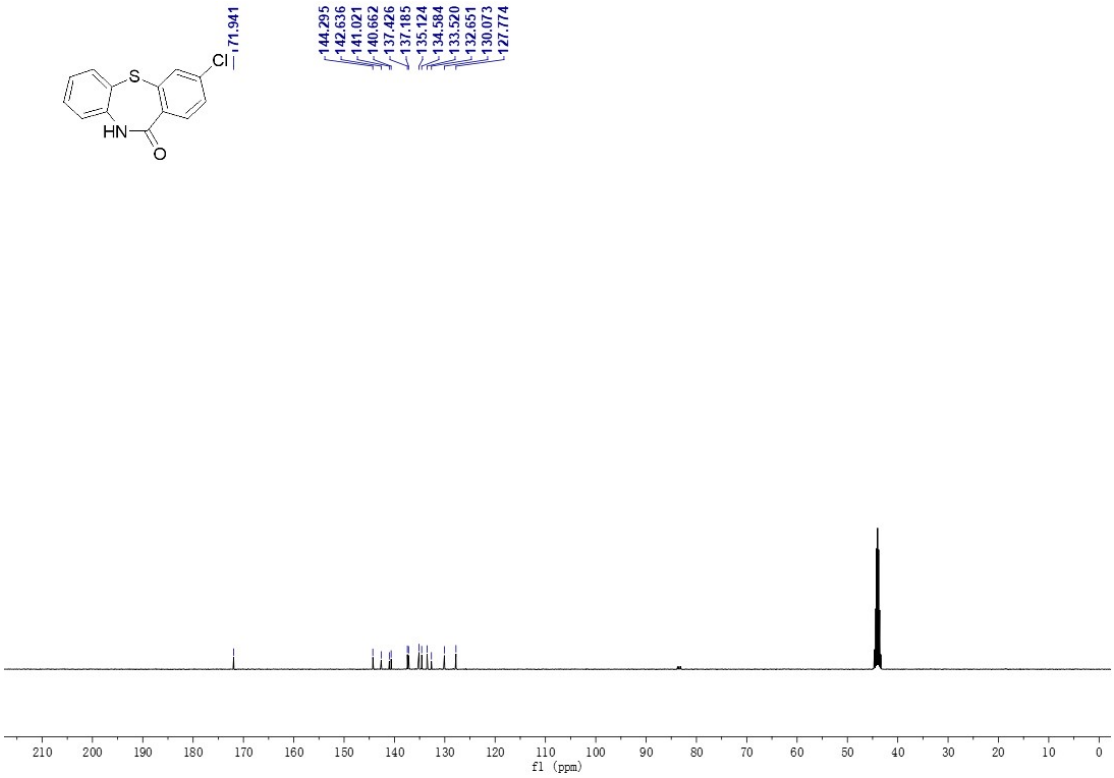
^{1}H NMR Spectrum of Compound **3k**



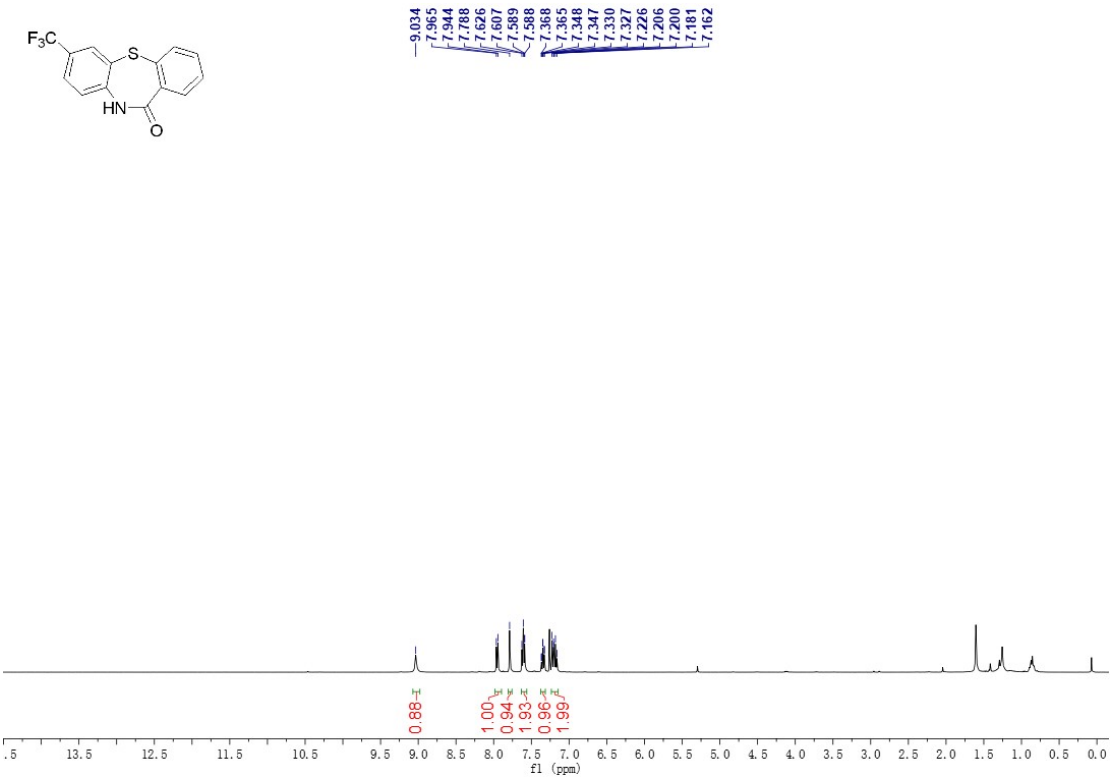
^{13}C NMR Spectrum of Compound **3k**



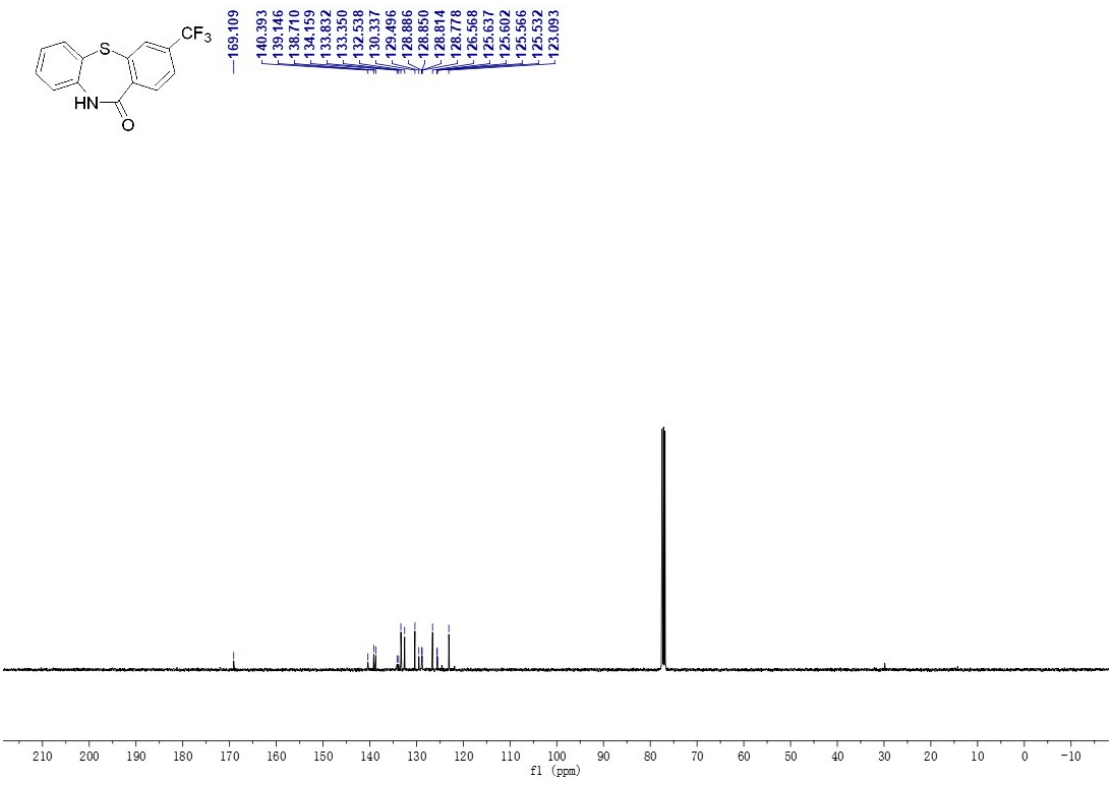
^{1}H NMR Spectrum of Compound **3l**



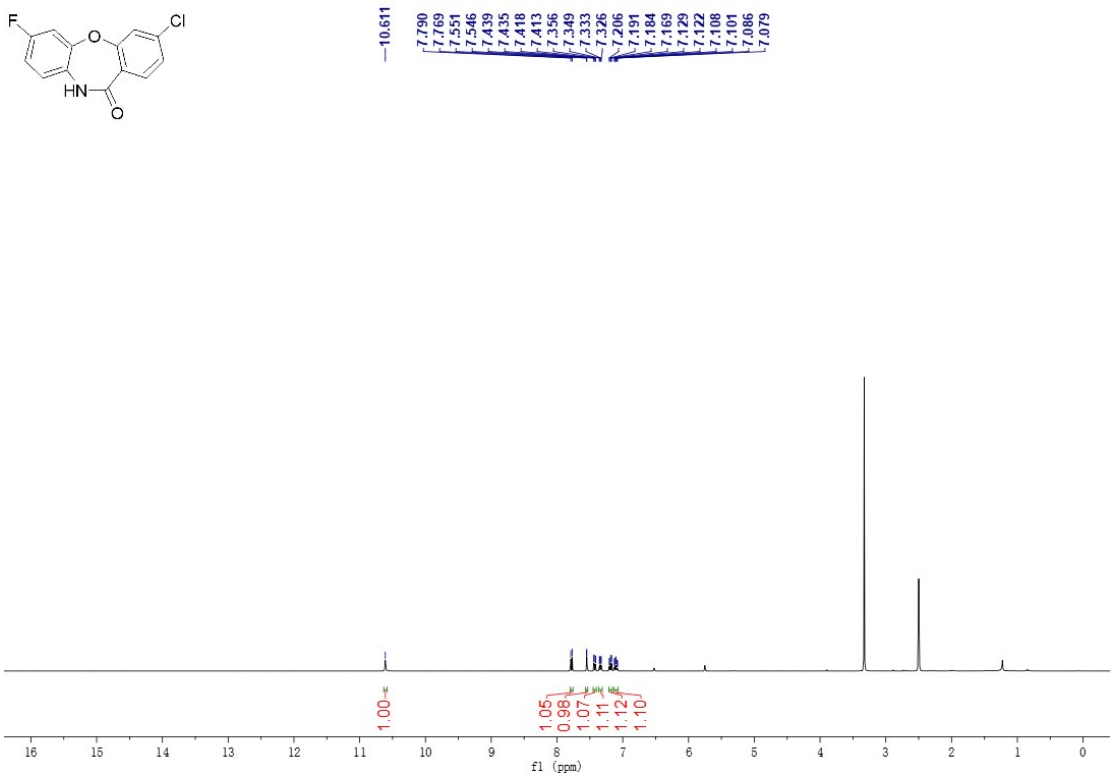
^{13}C NMR Spectrum of Compound **3l**



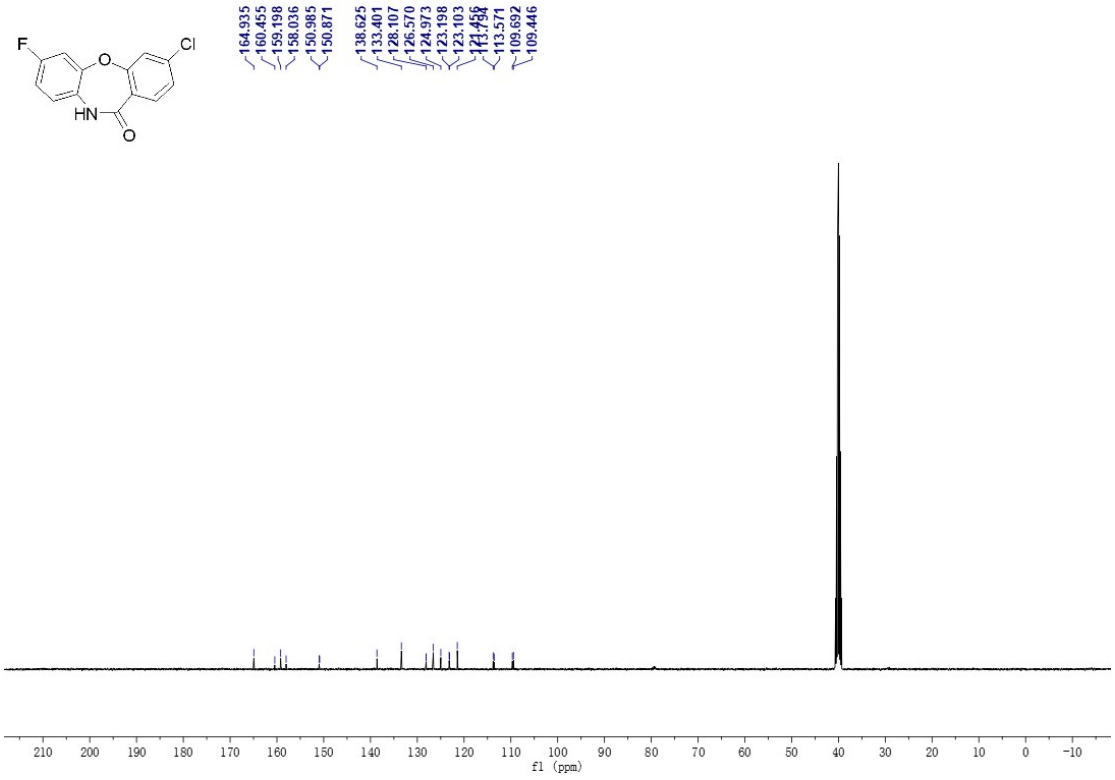
^{1}H NMR Spectrum of Compound **3m**



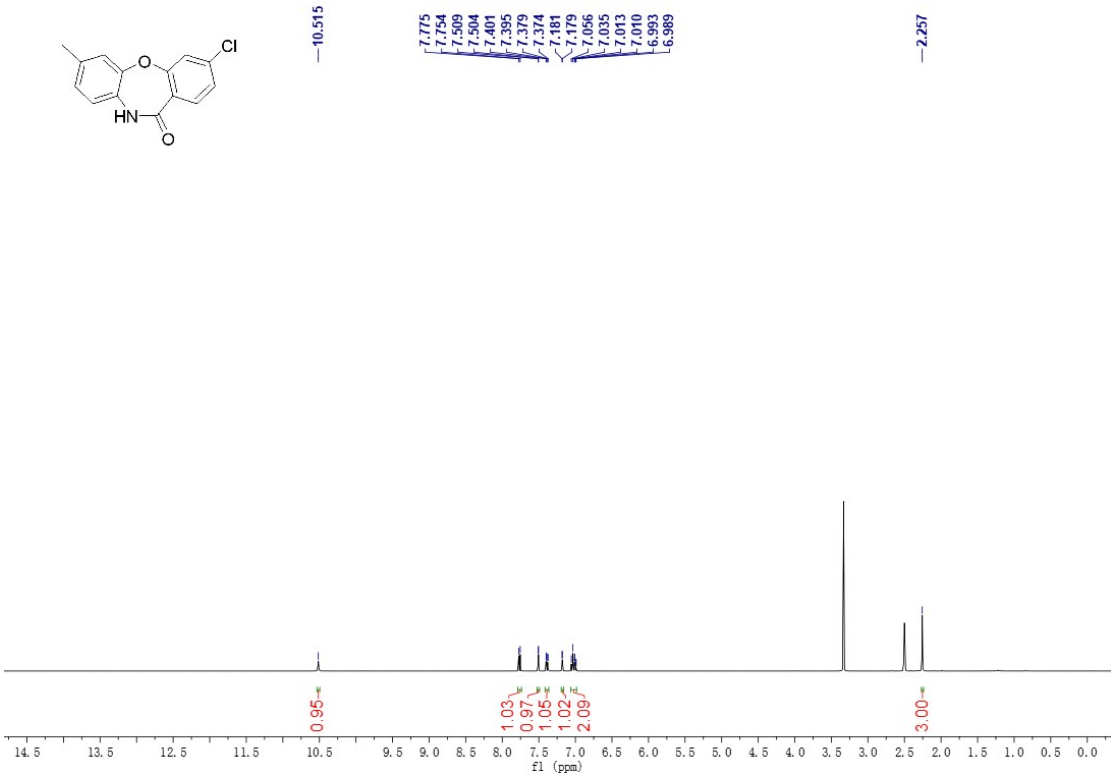
^{13}C NMR Spectrum of Compound **3m**



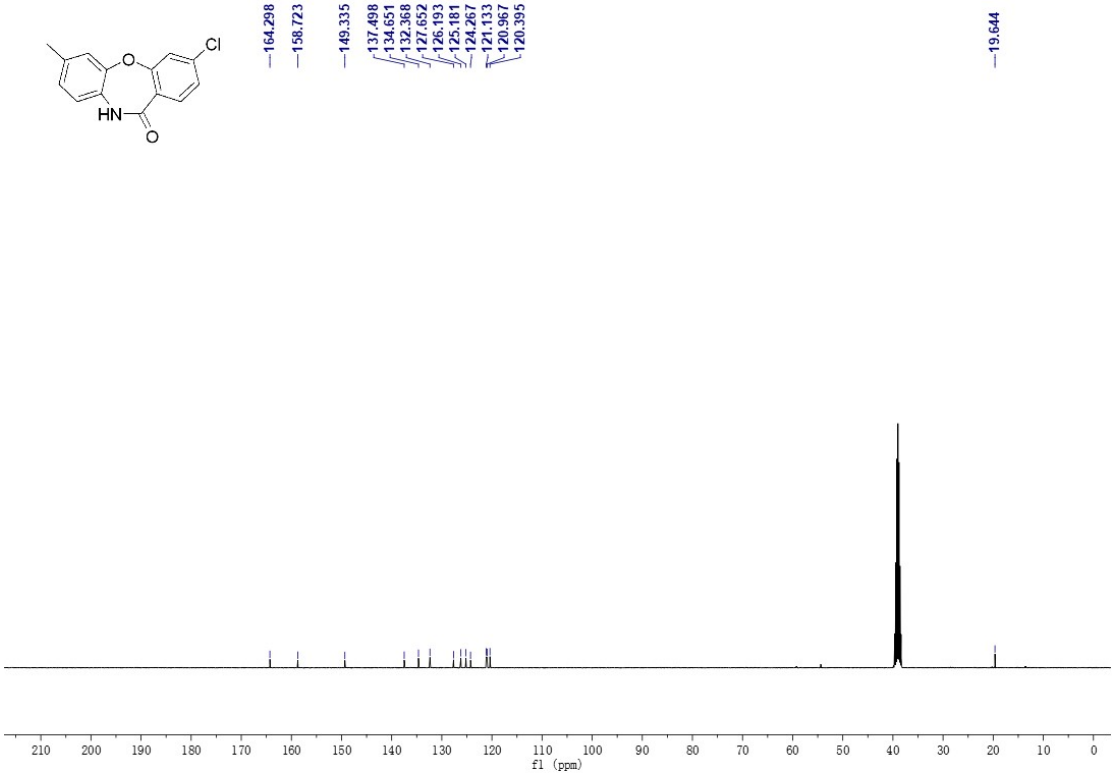
^{1}H NMR Spectrum of Compound **3n**



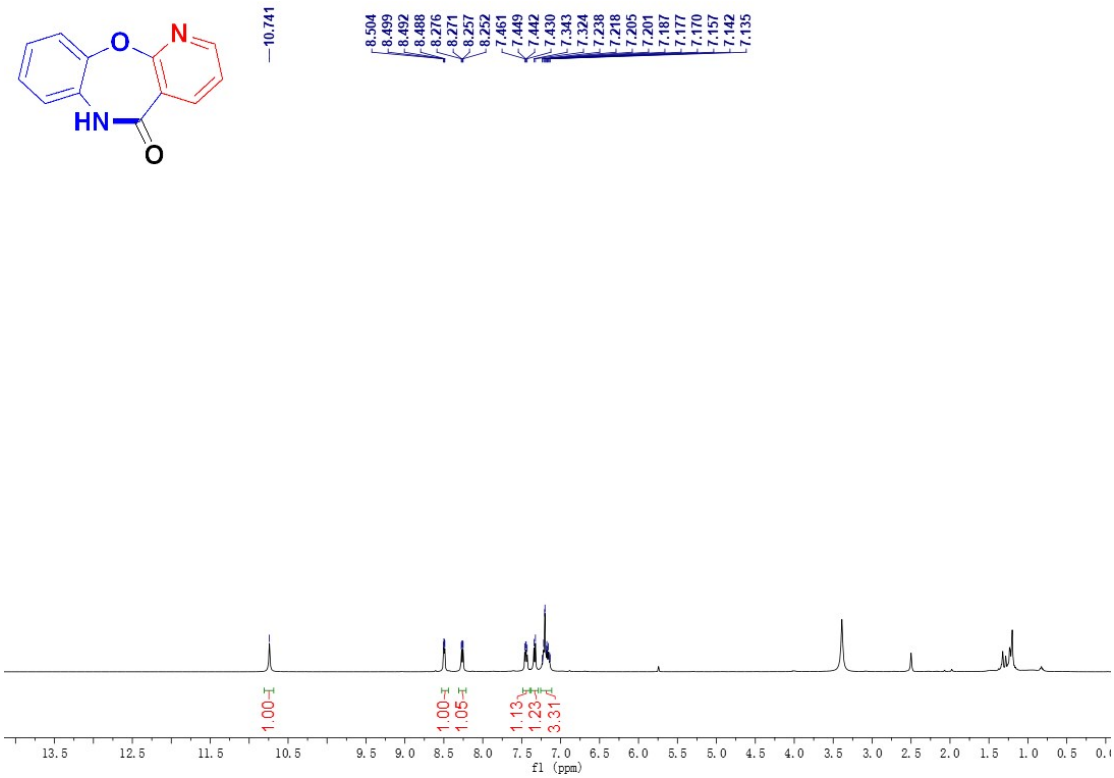
^{13}C NMR Spectrum of Compound **3n**



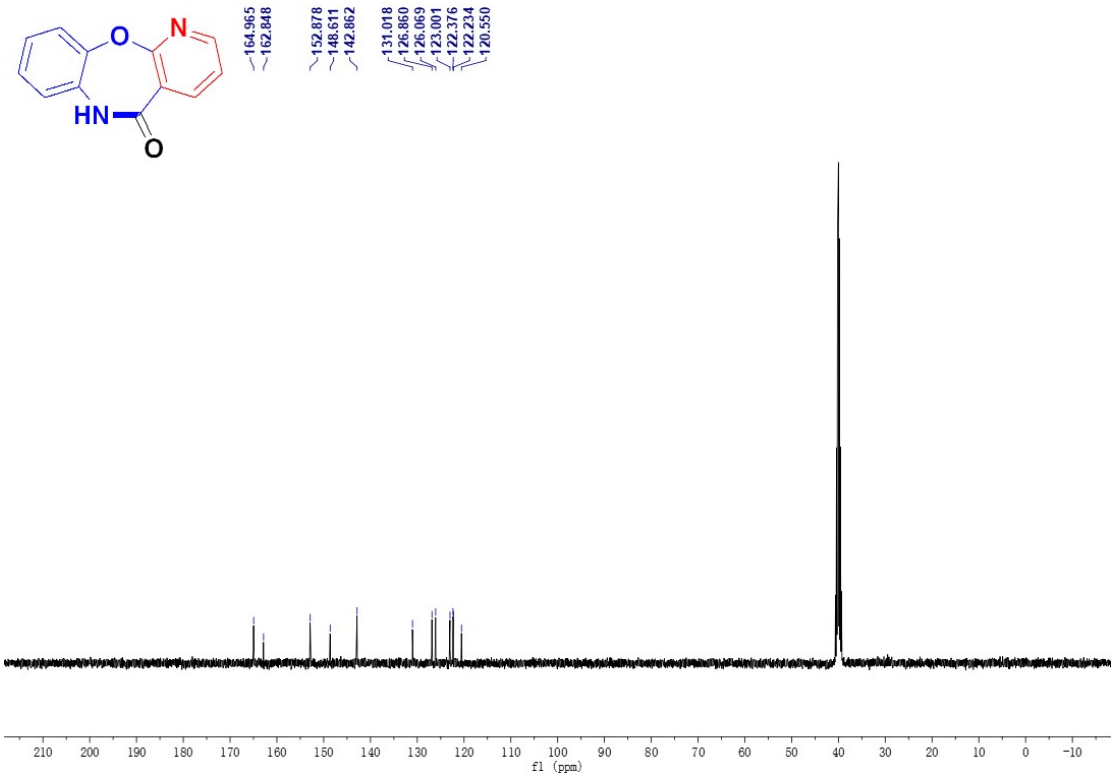
^{1}H NMR Spectrum of Compound **3o**



^{13}C NMR Spectrum of Compound **3o**

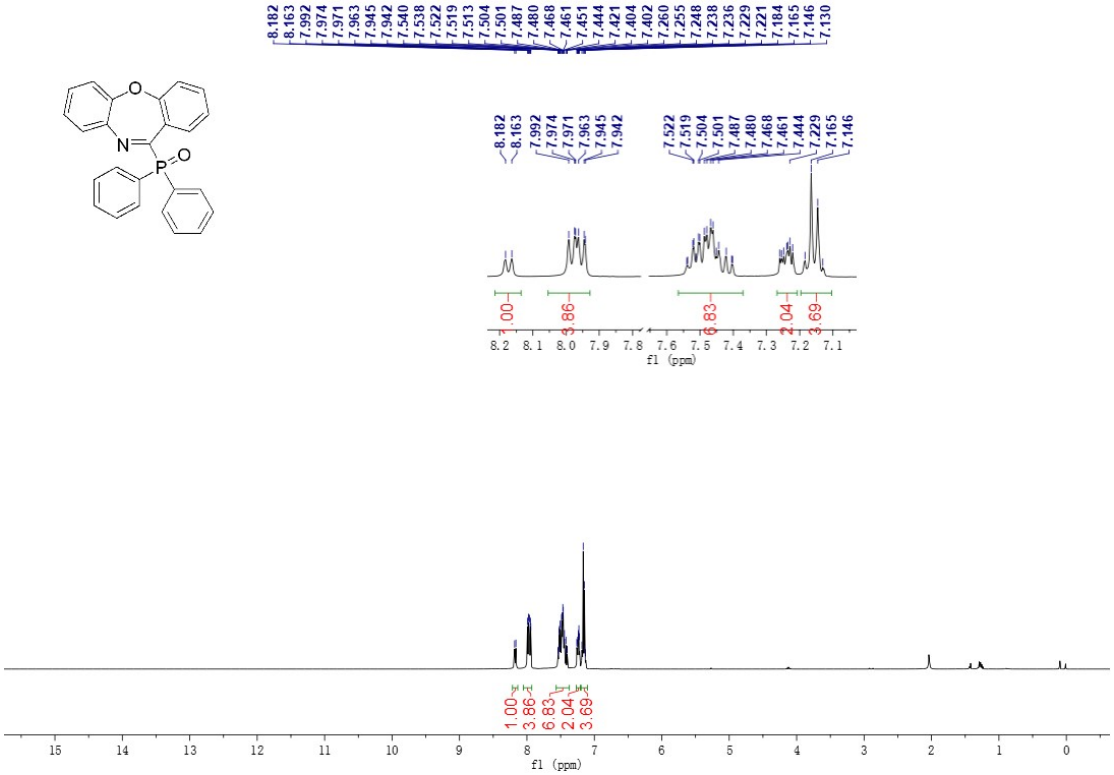


^{1}H NMR Spectrum of Compound **3p**

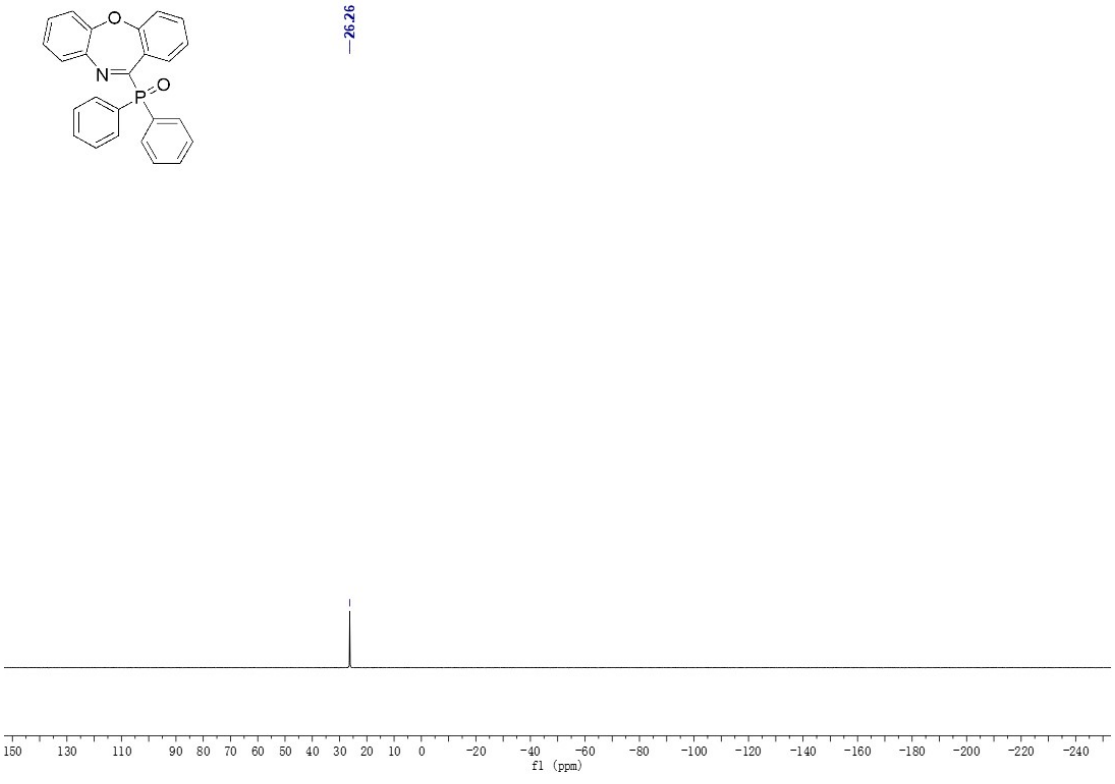


^{13}C NMR Spectrum of Compound **3p**

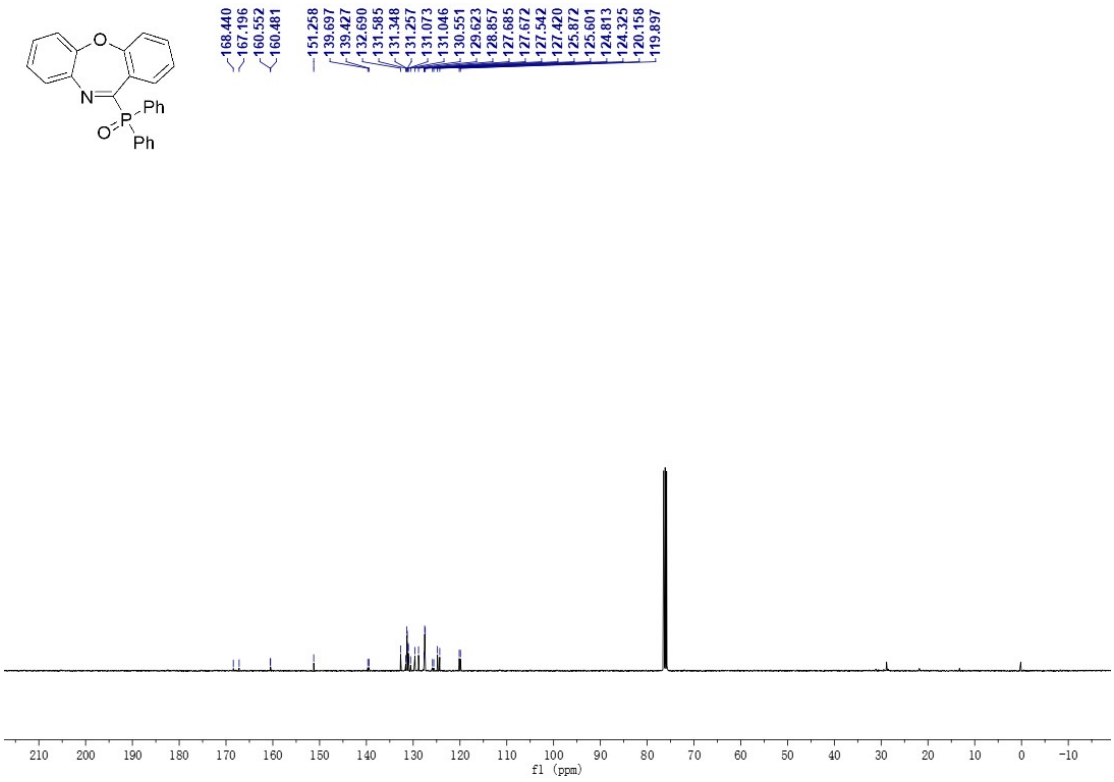
Copies of ^{1}H (400 MHz), ^{31}P (377 MHz) and ^{13}C (101 MHz) spectra of products 5aA-5aG in $CDCl_3$ or DMSO-d6



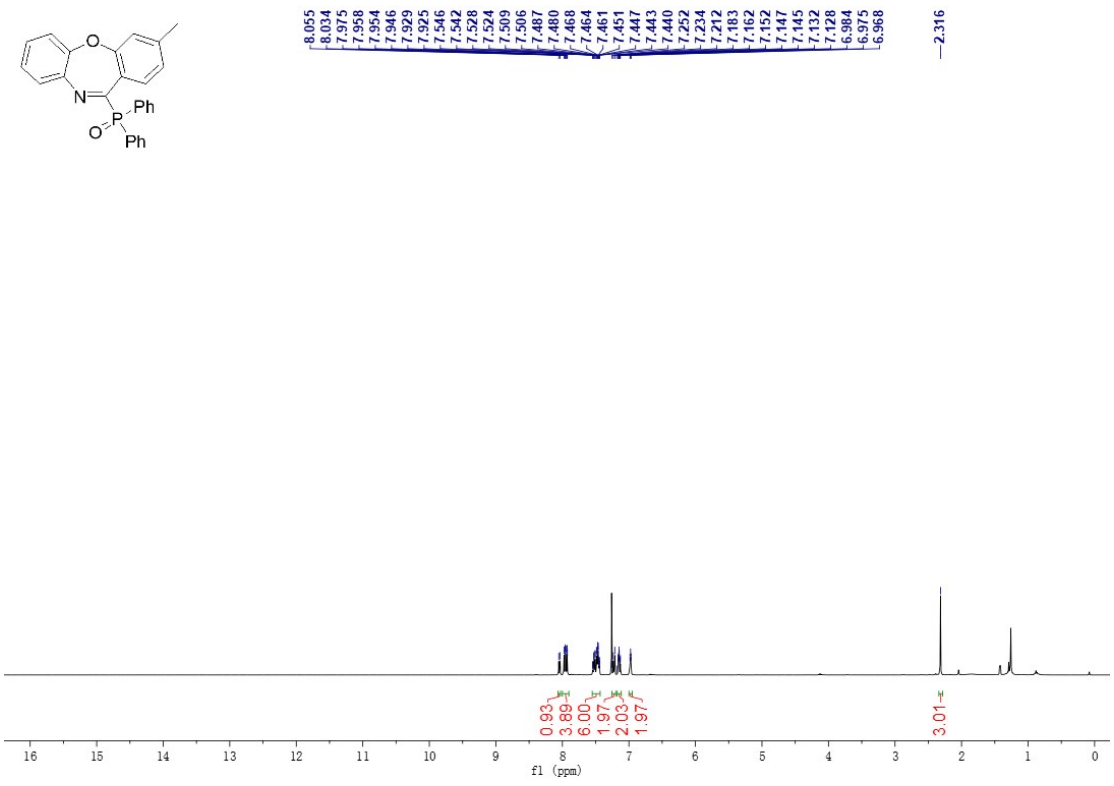
^{1}H NMR Spectrum of Compound **5aA**



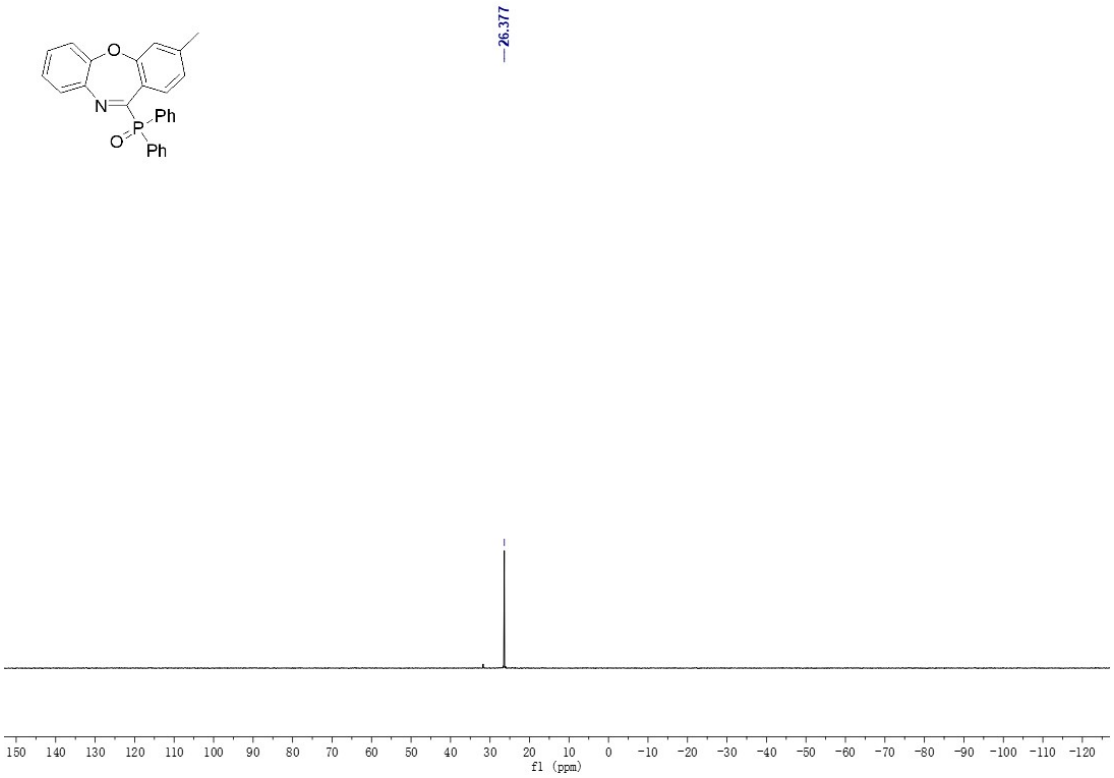
^{31}P NMR Spectrum of Compound **5aA**



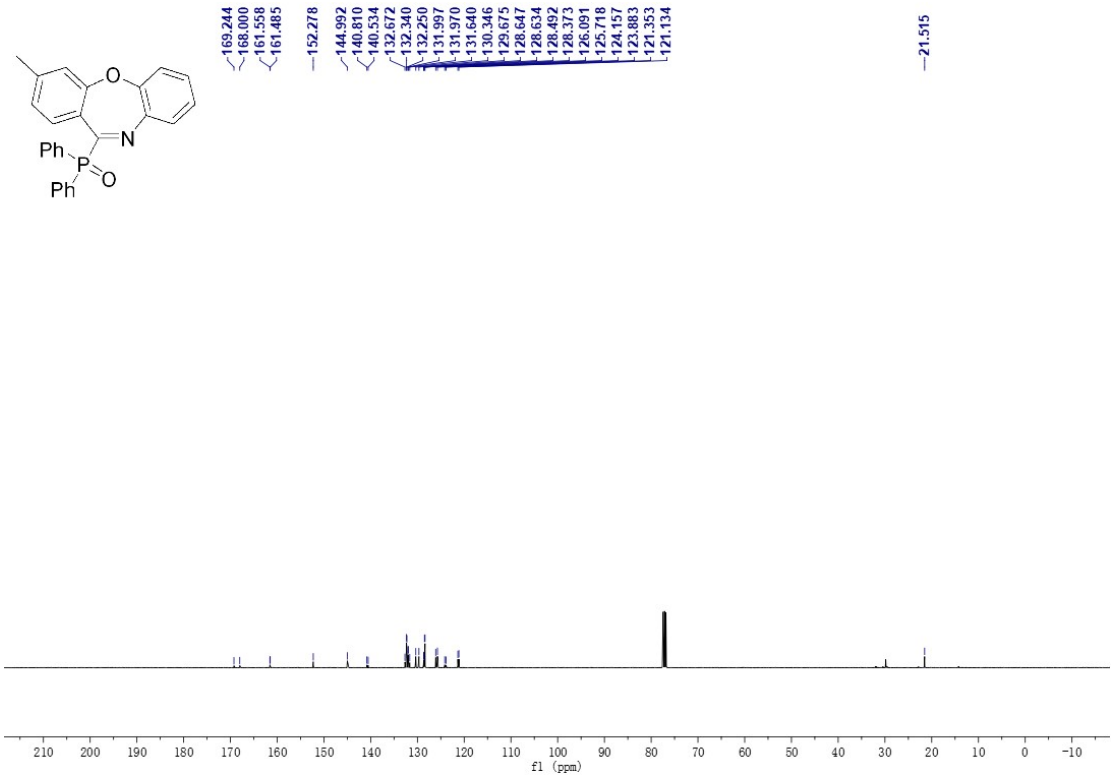
^{13}C NMR Spectrum of Compound **5aA**



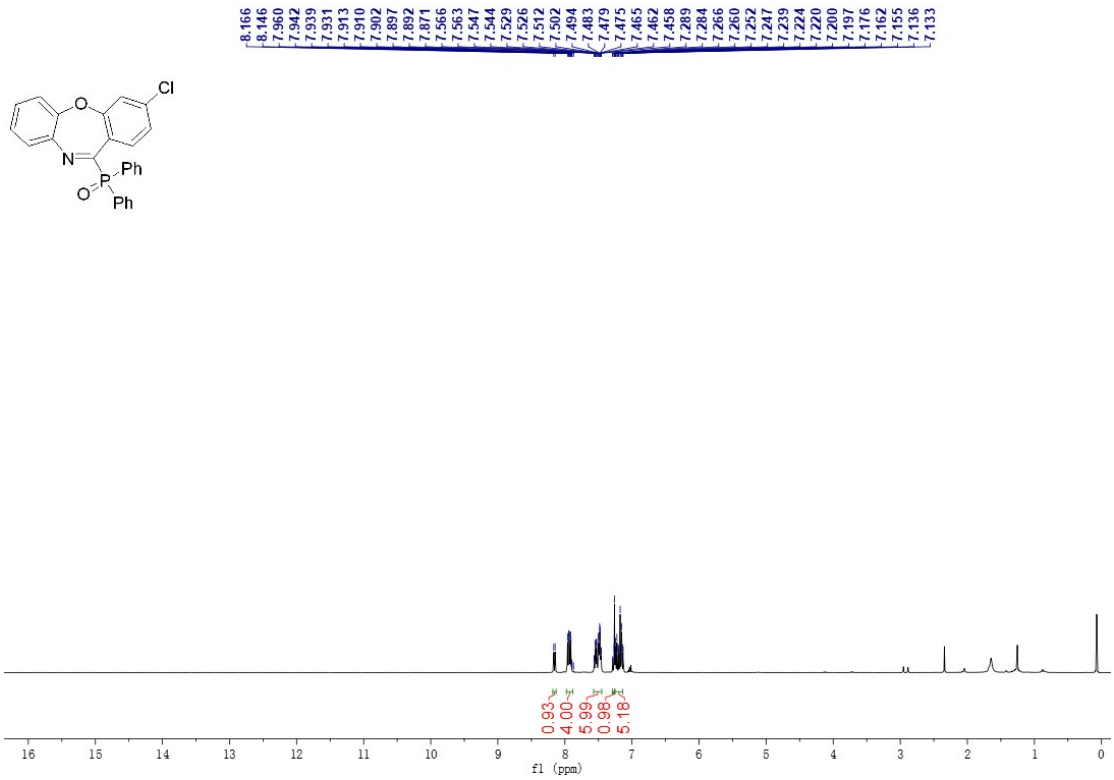
^{1}H NMR Spectrum of Compound **5bA**



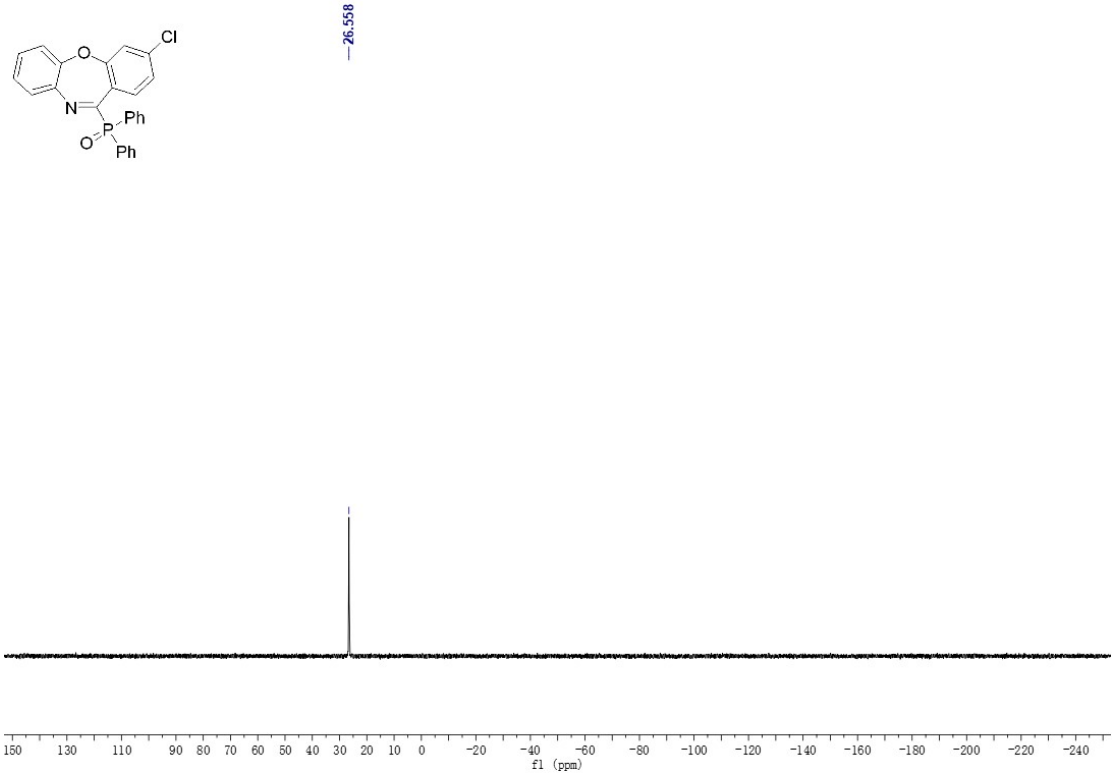
^{31}P NMR Spectrum of Compound **5bA**



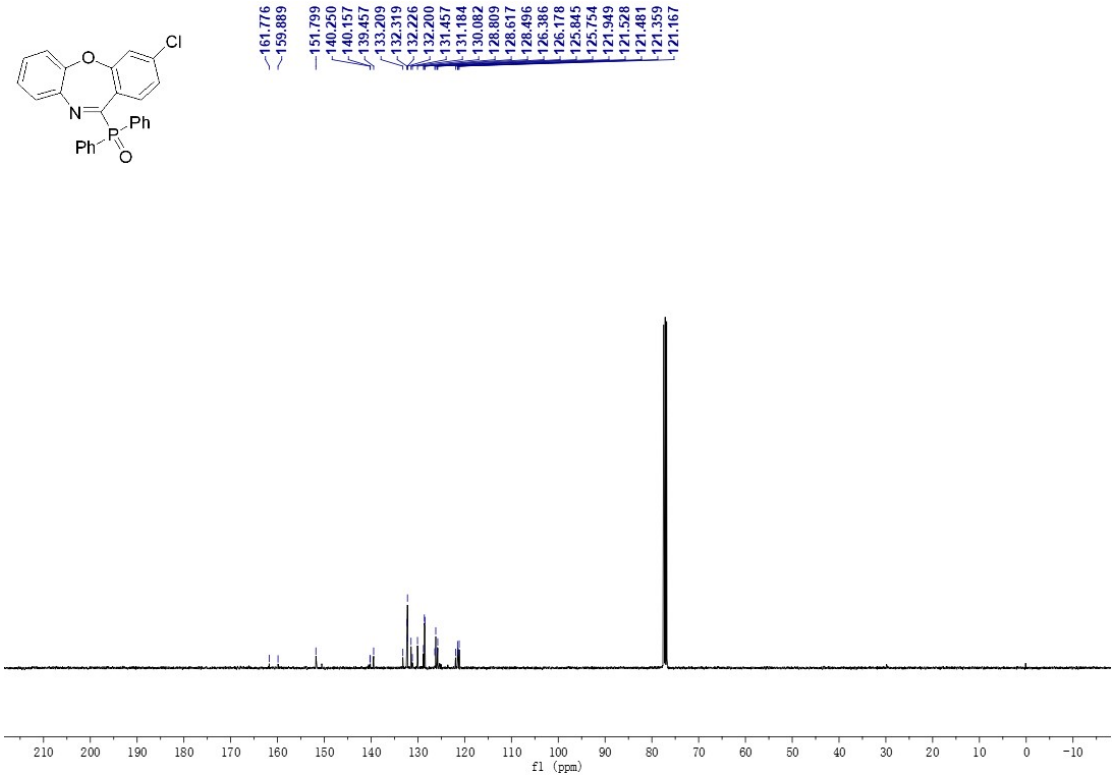
^{13}C NMR Spectrum of Compound **5bA**



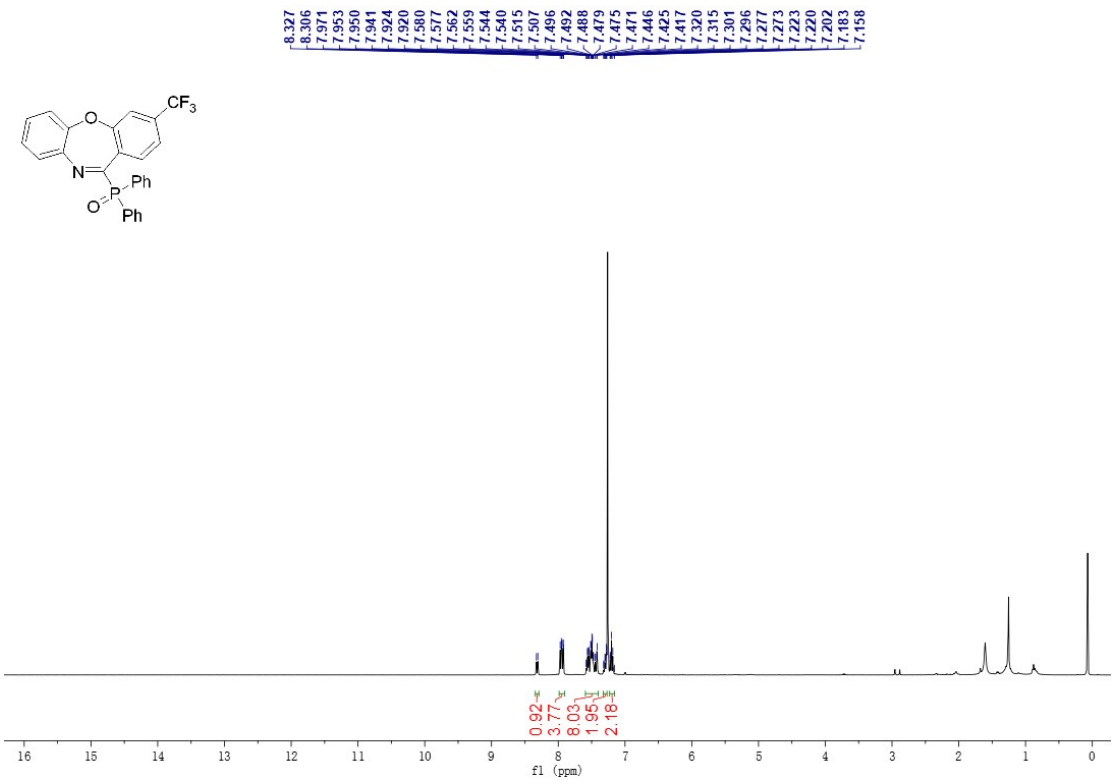
^{1}H NMR Spectrum of Compound **5cA**



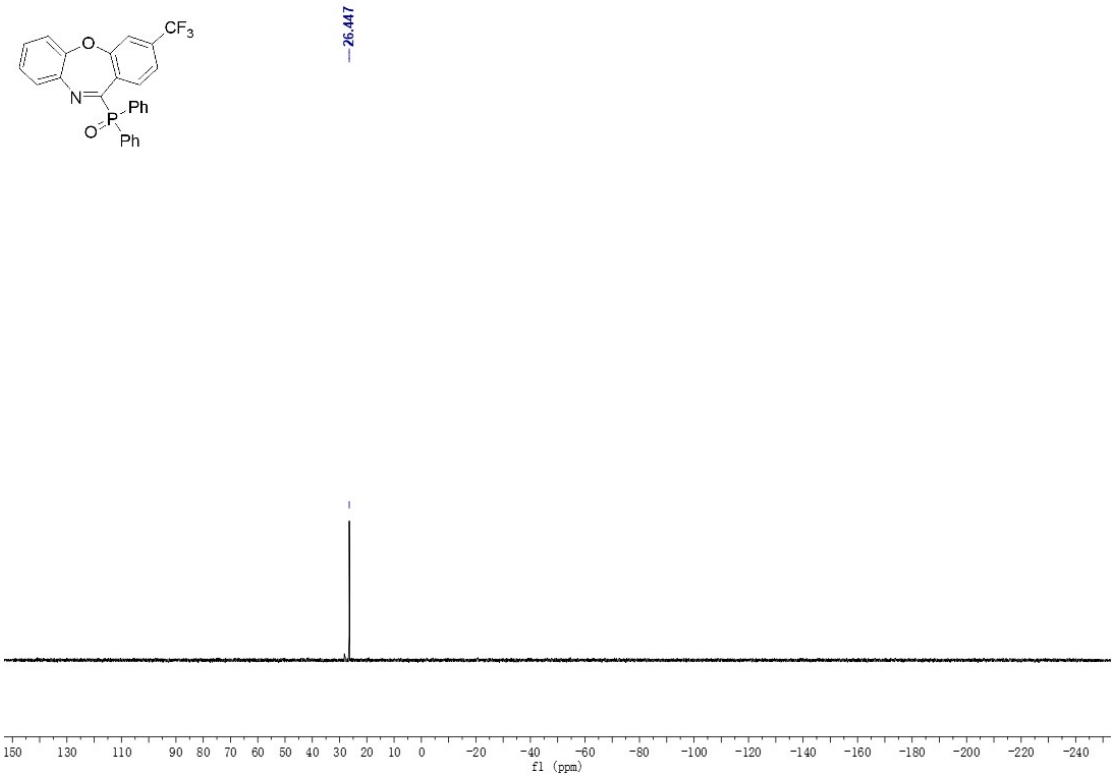
^{31}P NMR Spectrum of Compound **5cA**



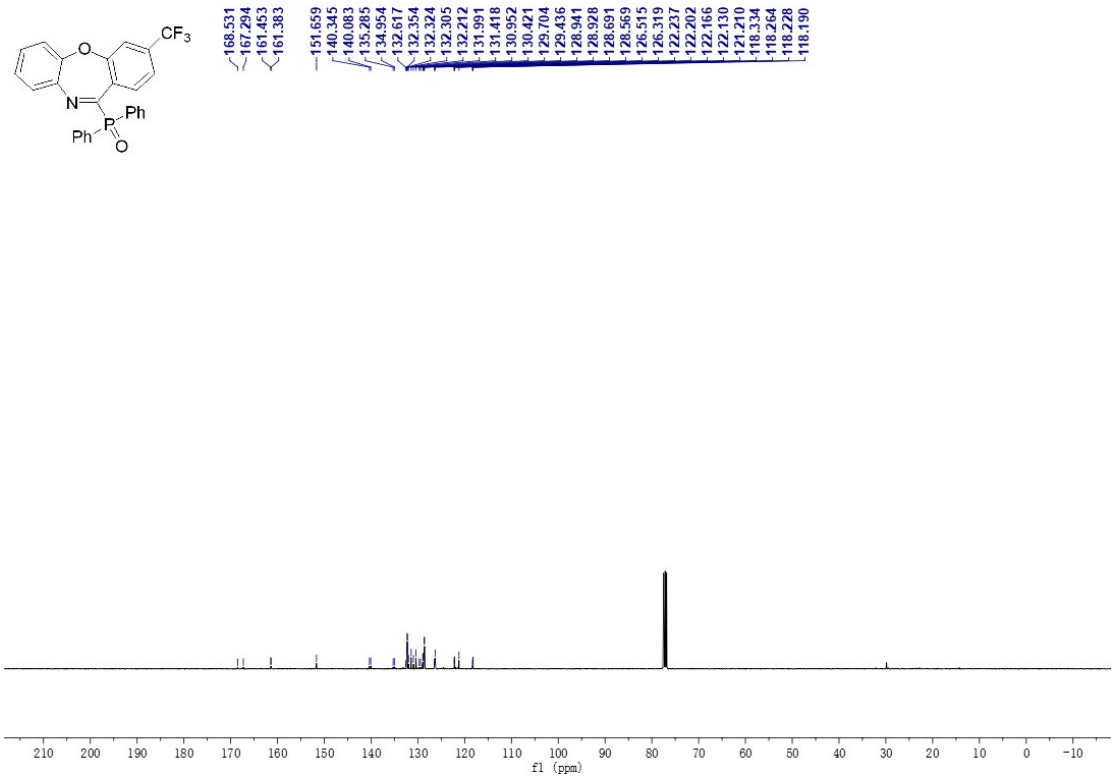
^{13}C NMR Spectrum of Compound **5cA**



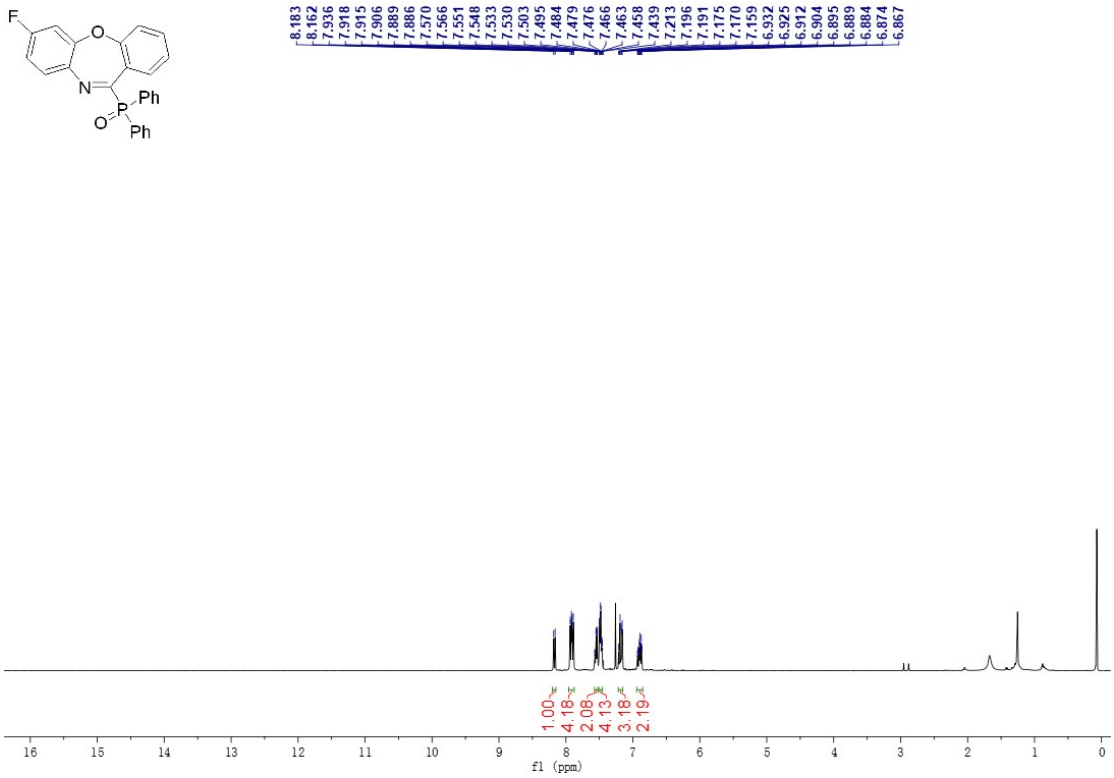
^{1}H NMR Spectrum of Compound **5dA**



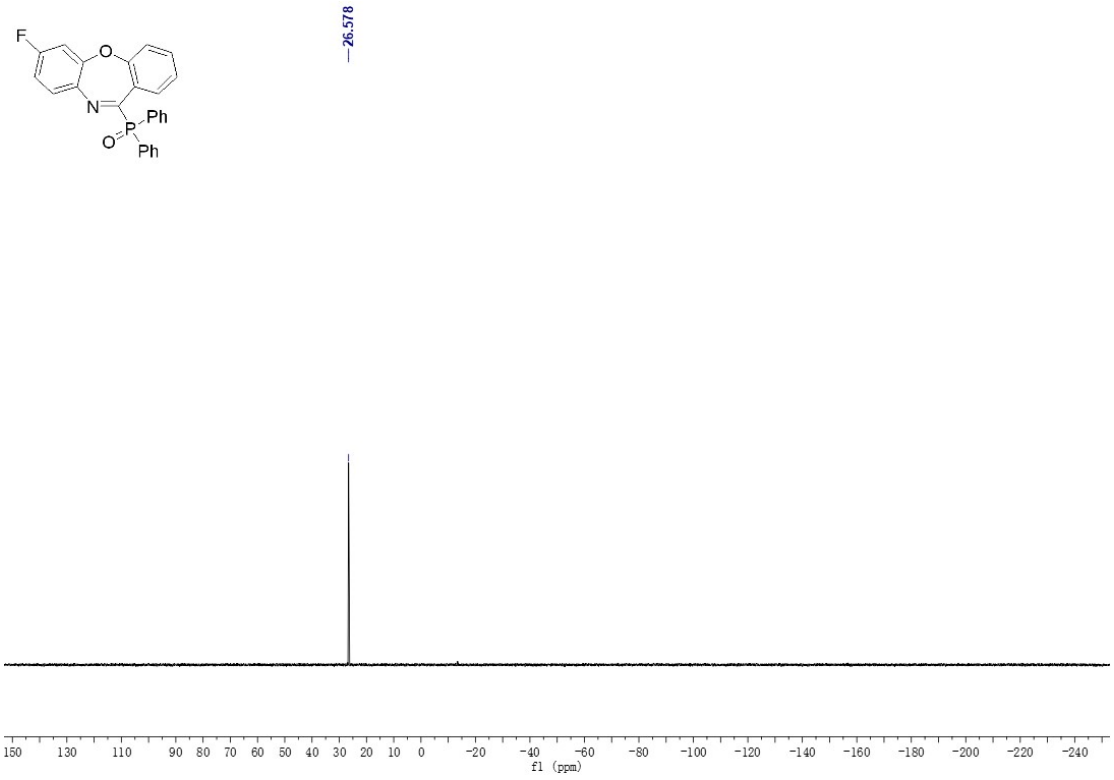
^{31}P NMR Spectrum of Compound **5dA**



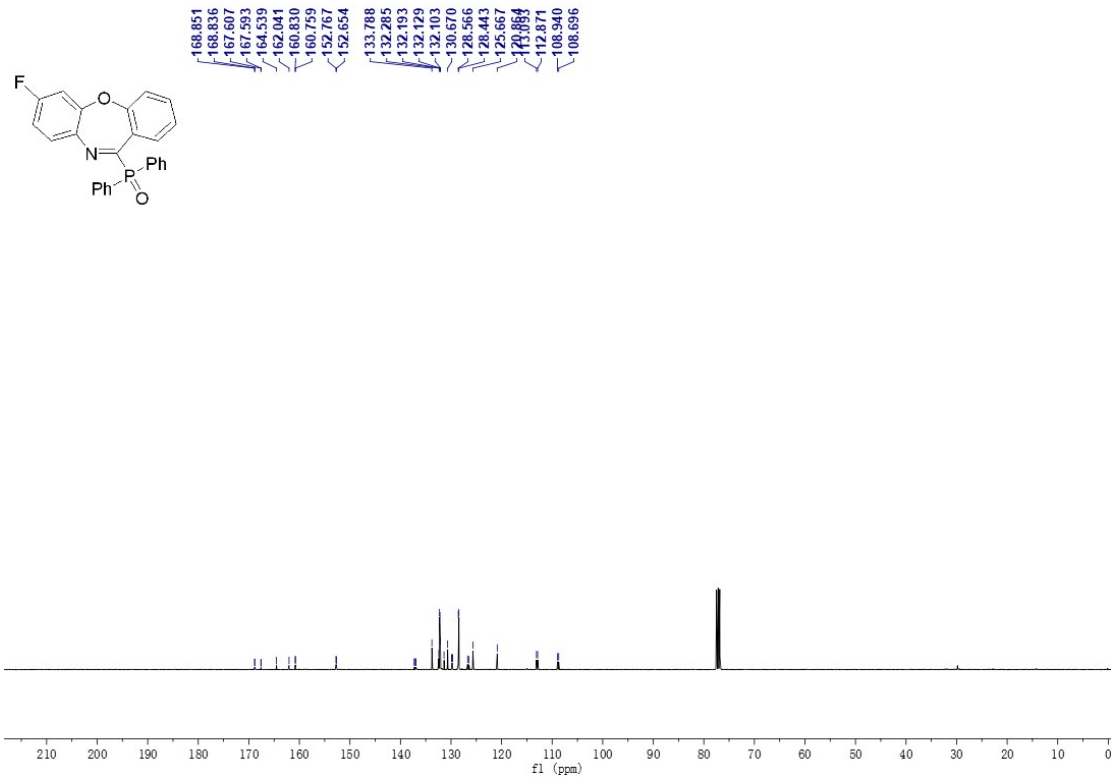
^{13}C NMR Spectrum of Compound **5dA**



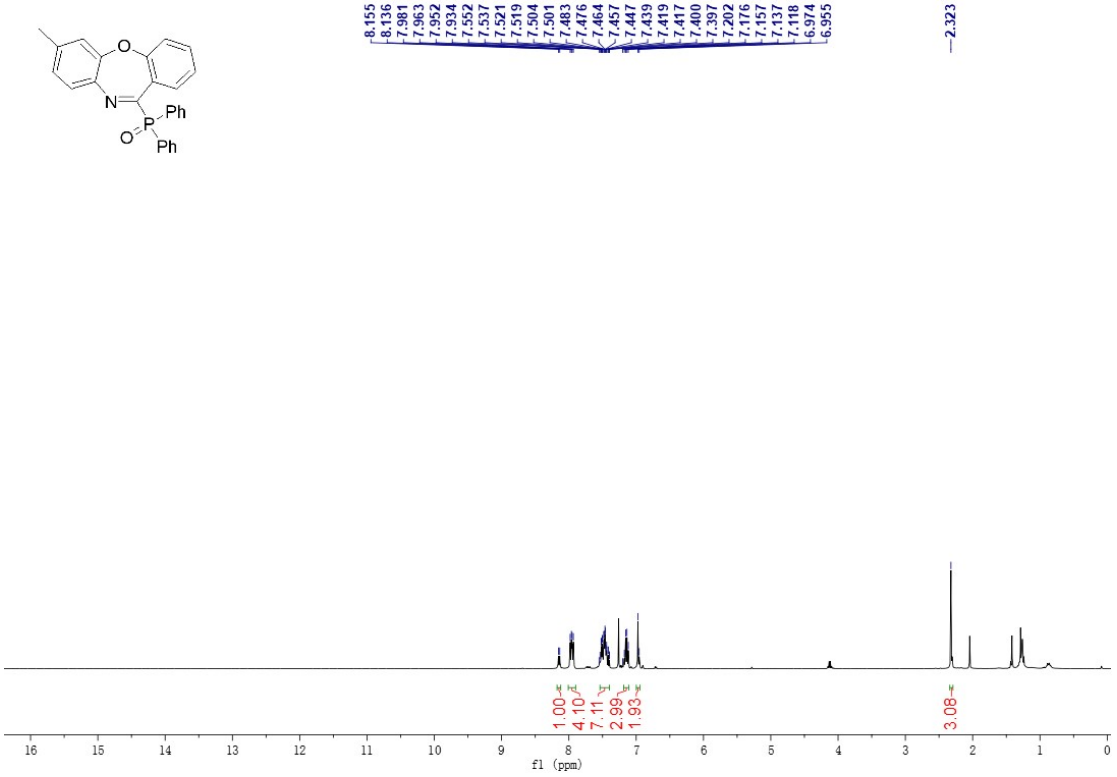
^{1}H NMR Spectrum of Compound **5eA**



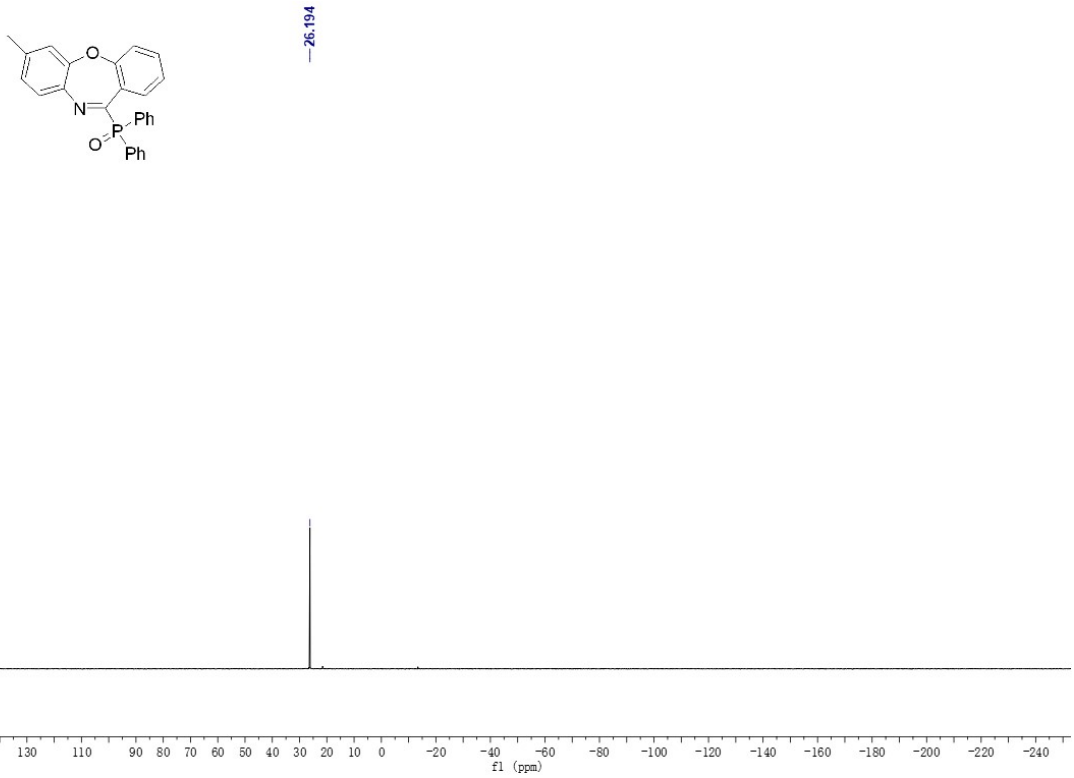
^{31}P NMR Spectrum of Compound **5eA**



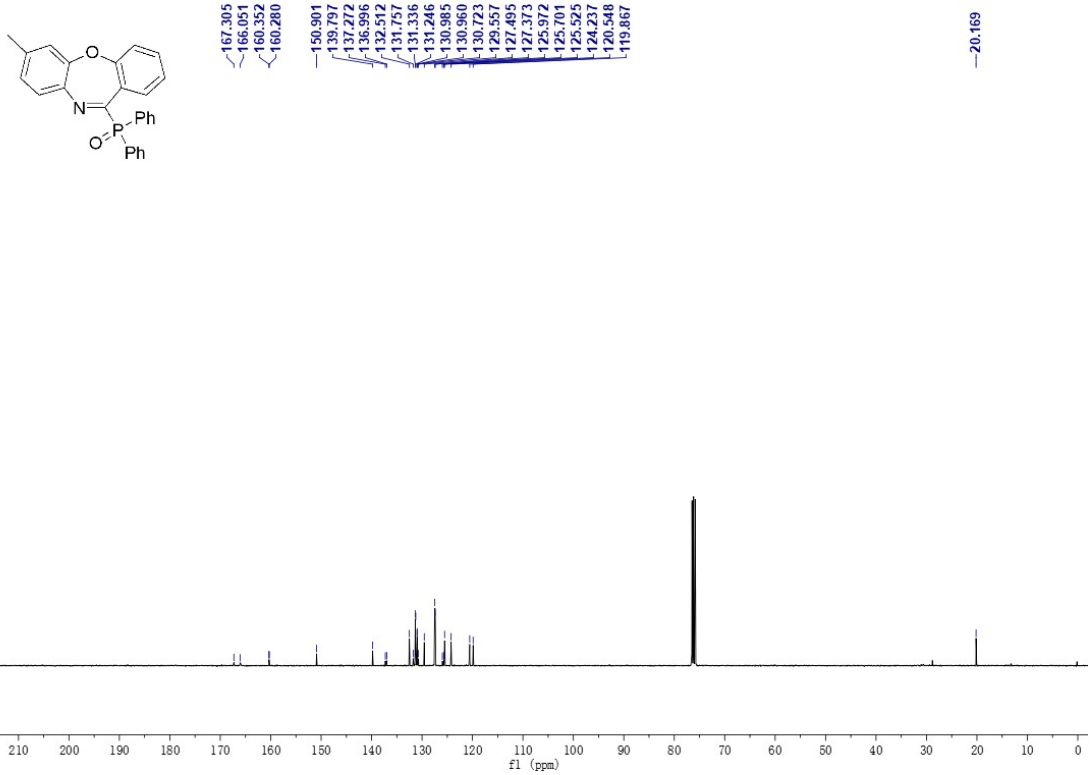
^{13}C NMR Spectrum of Compound **5eA**



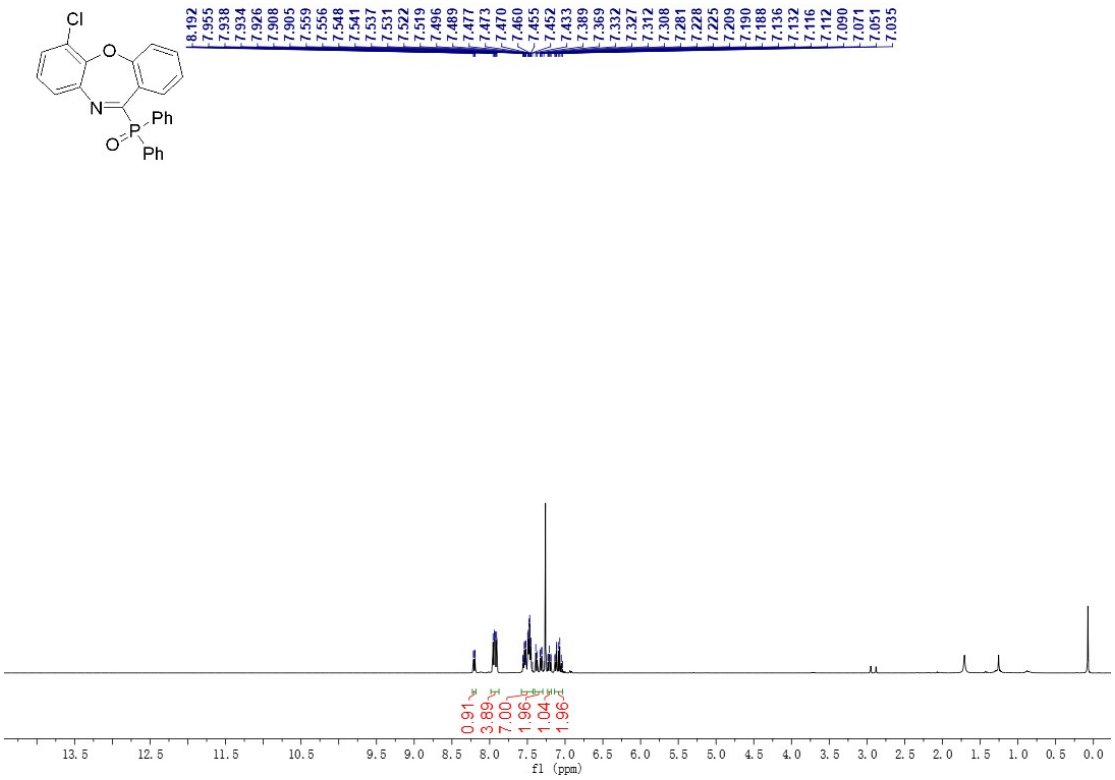
^{1}H NMR Spectrum of Compound **5fA**



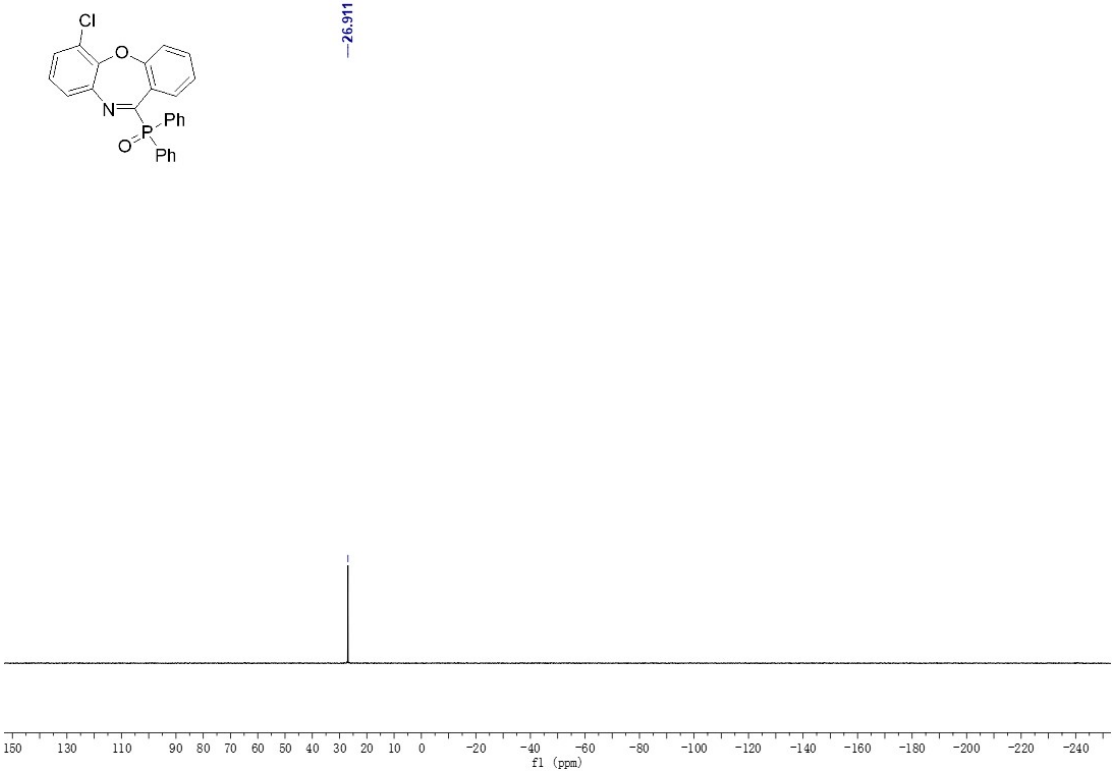
^{31}P NMR Spectrum of Compound **5fA**



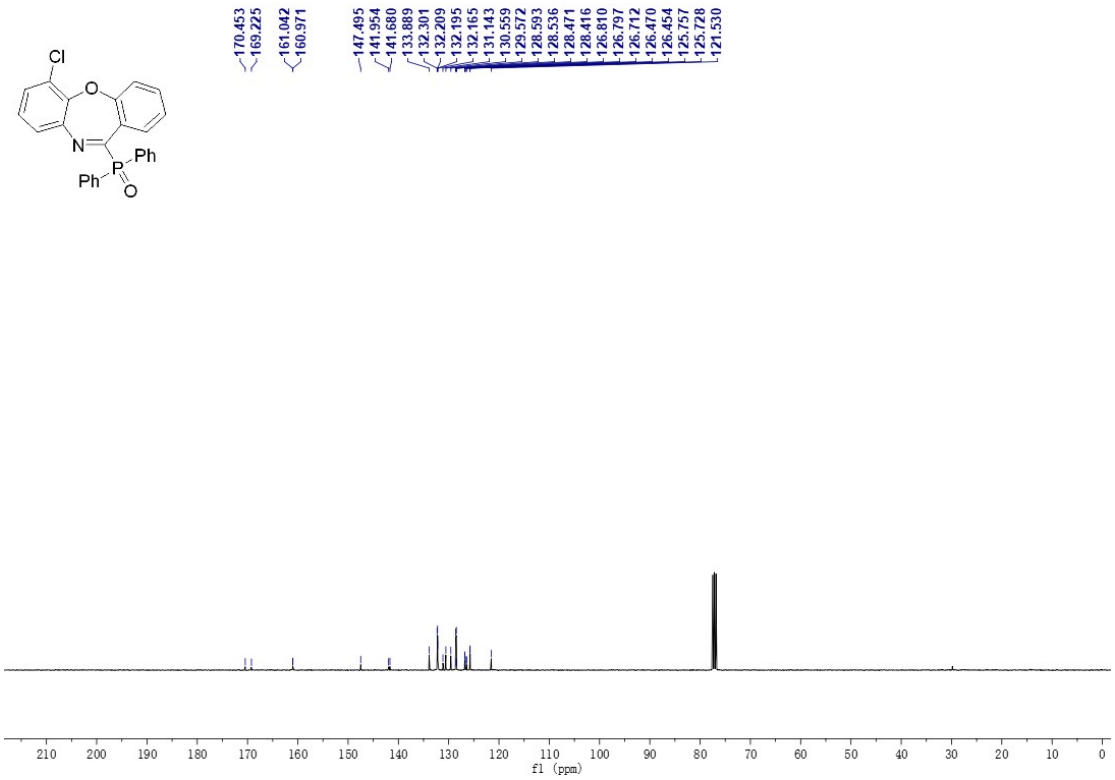
^{13}C NMR Spectrum of Compound **5fA**



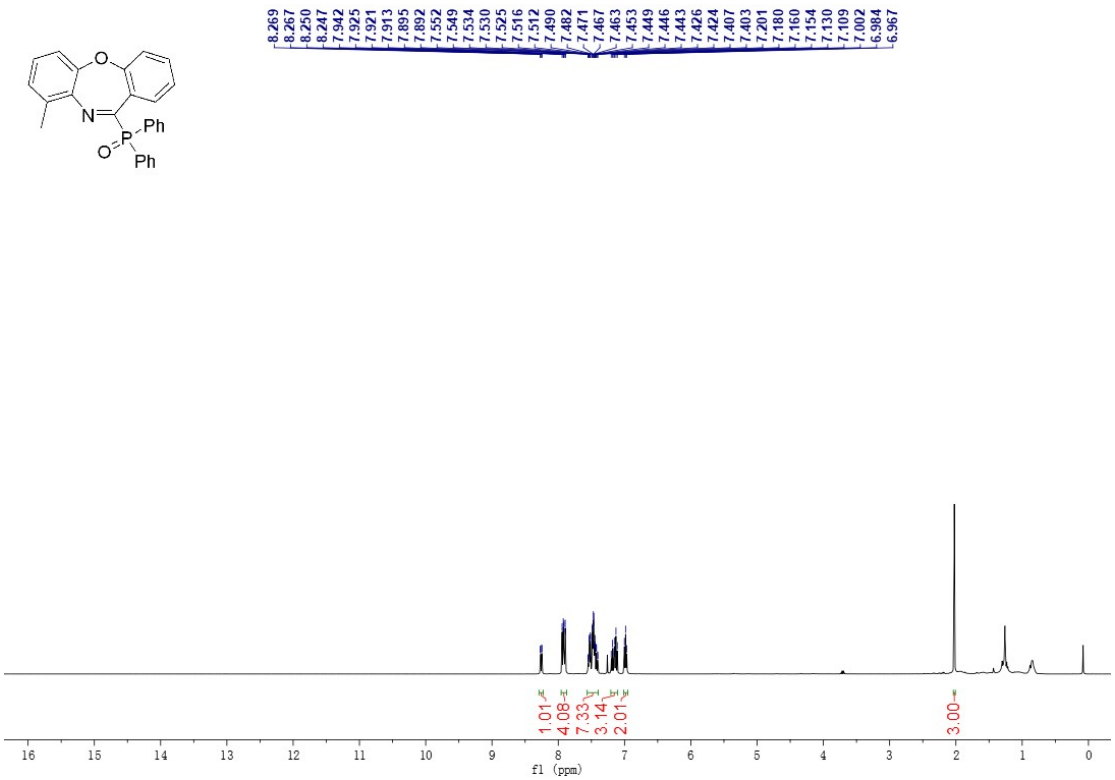
^{1}H NMR Spectrum of Compound **5gA**



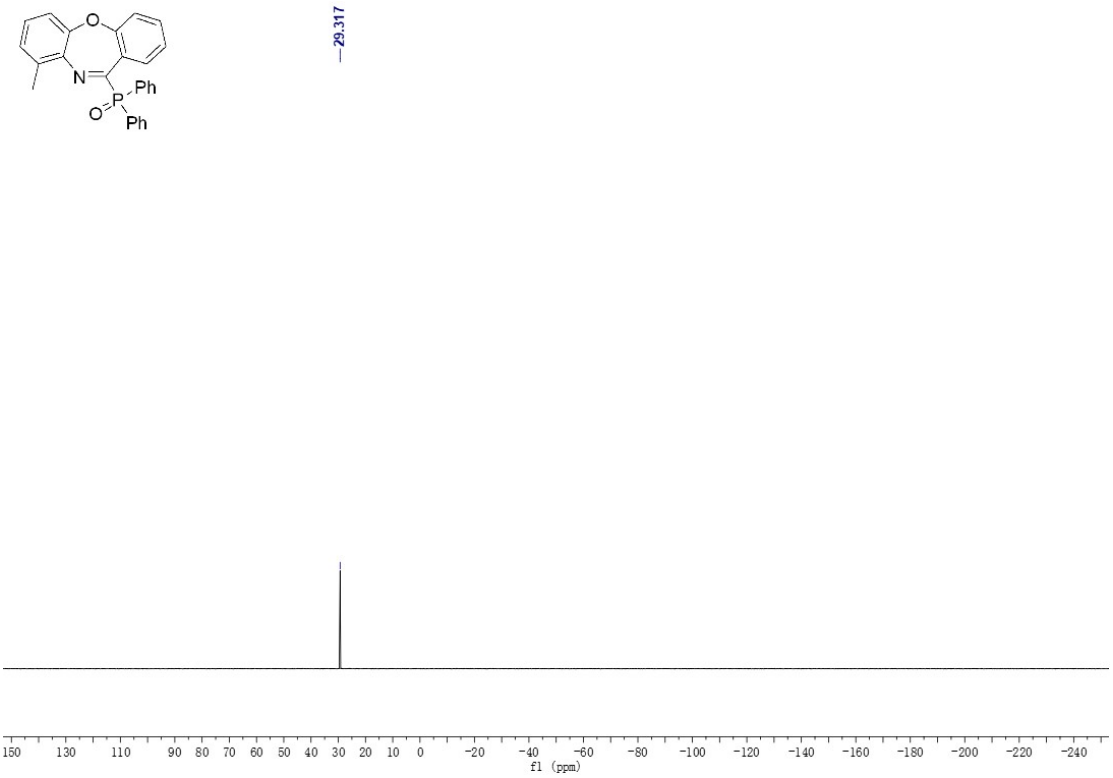
^{31}P NMR Spectrum of Compound **5gA**



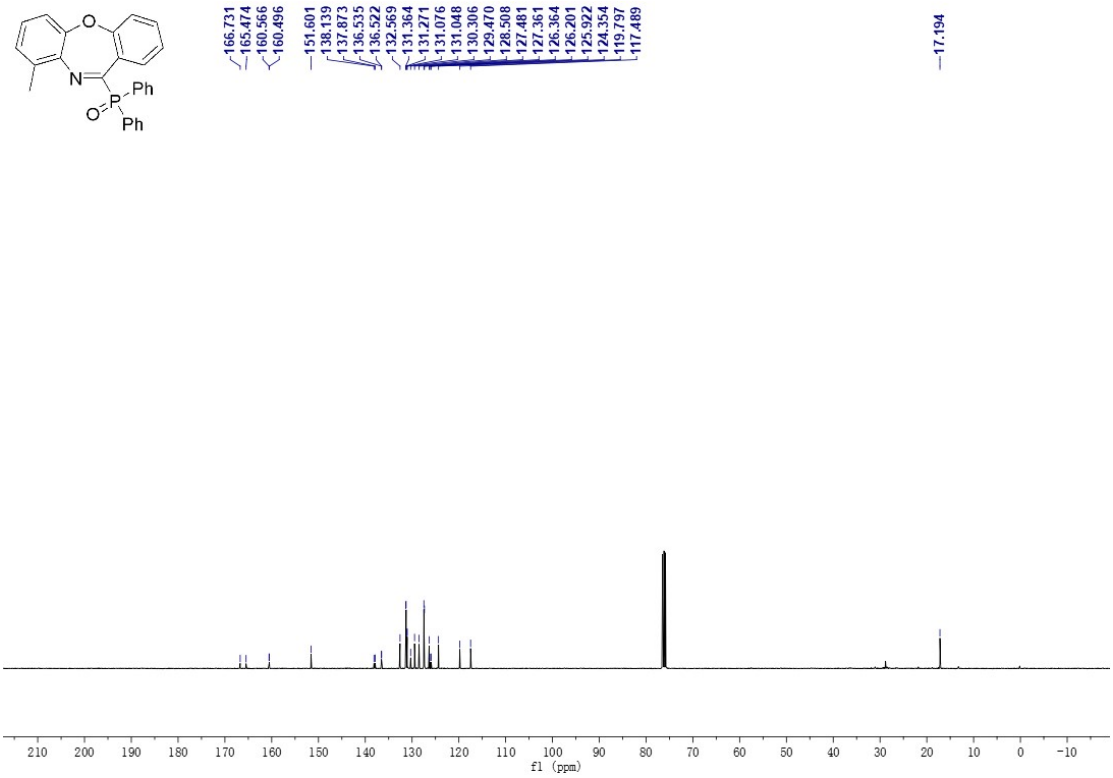
^{13}C NMR Spectrum of Compound **5gA**



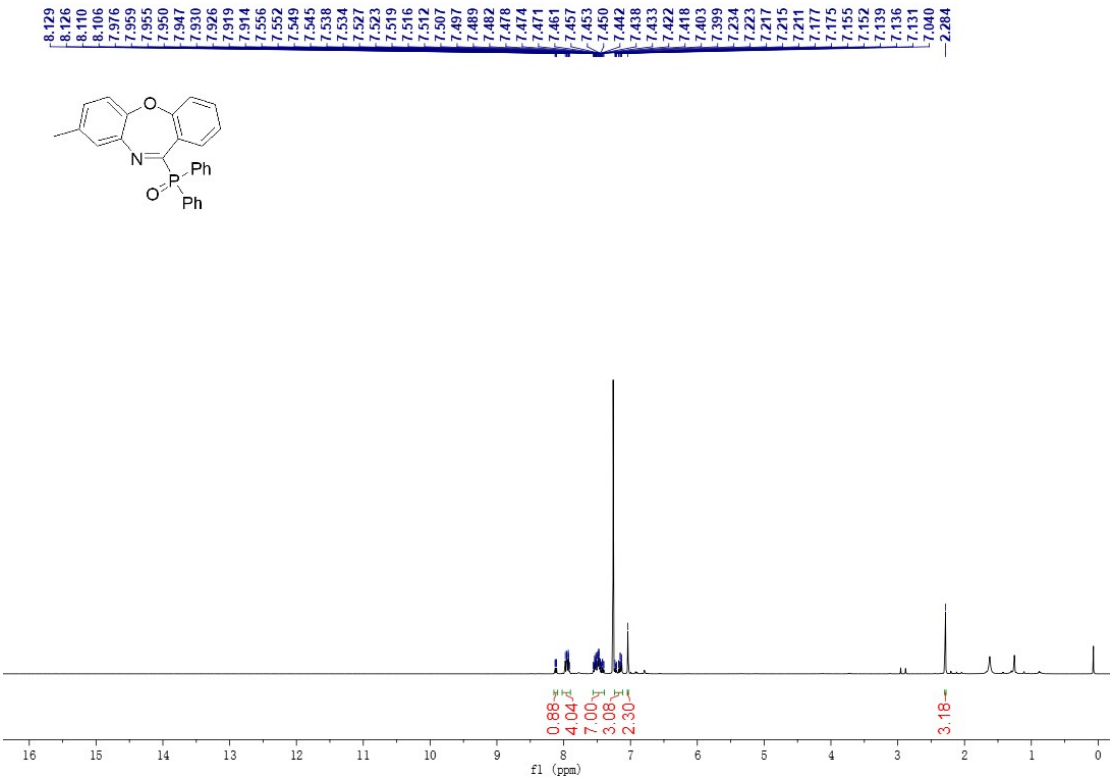
^{1}H NMR Spectrum of Compound **5hA**



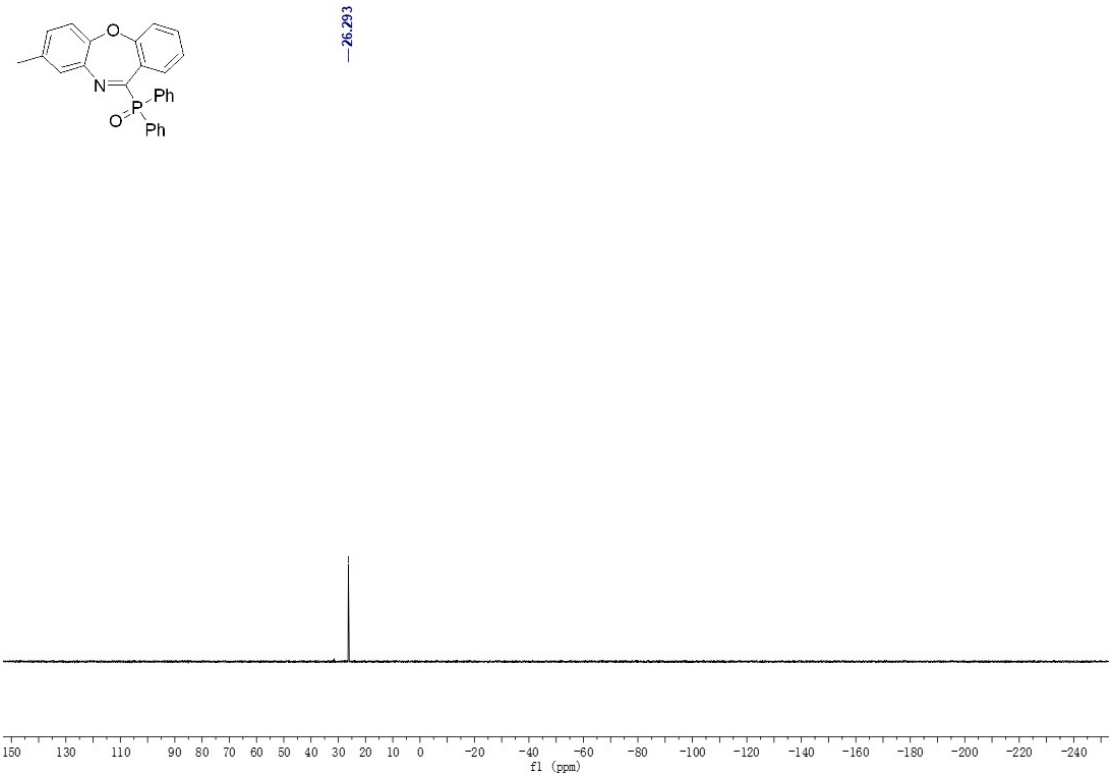
^{31}P NMR Spectrum of Compound **5hA**



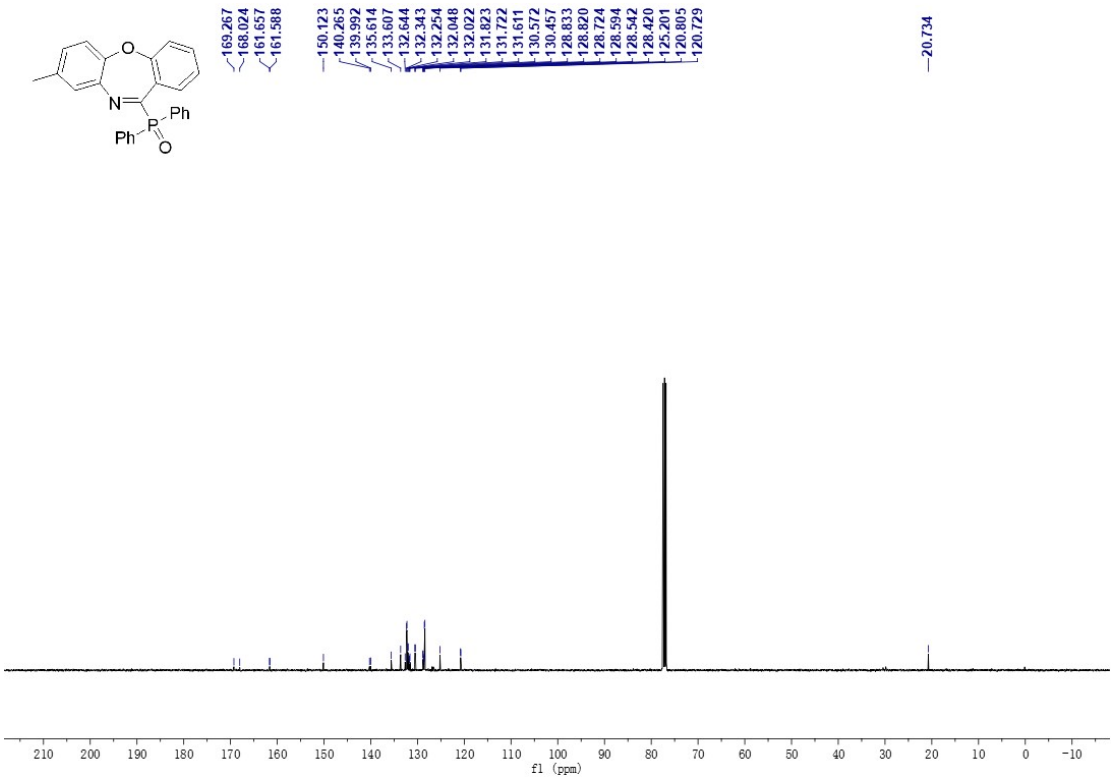
^{13}C NMR Spectrum of Compound **5hA**



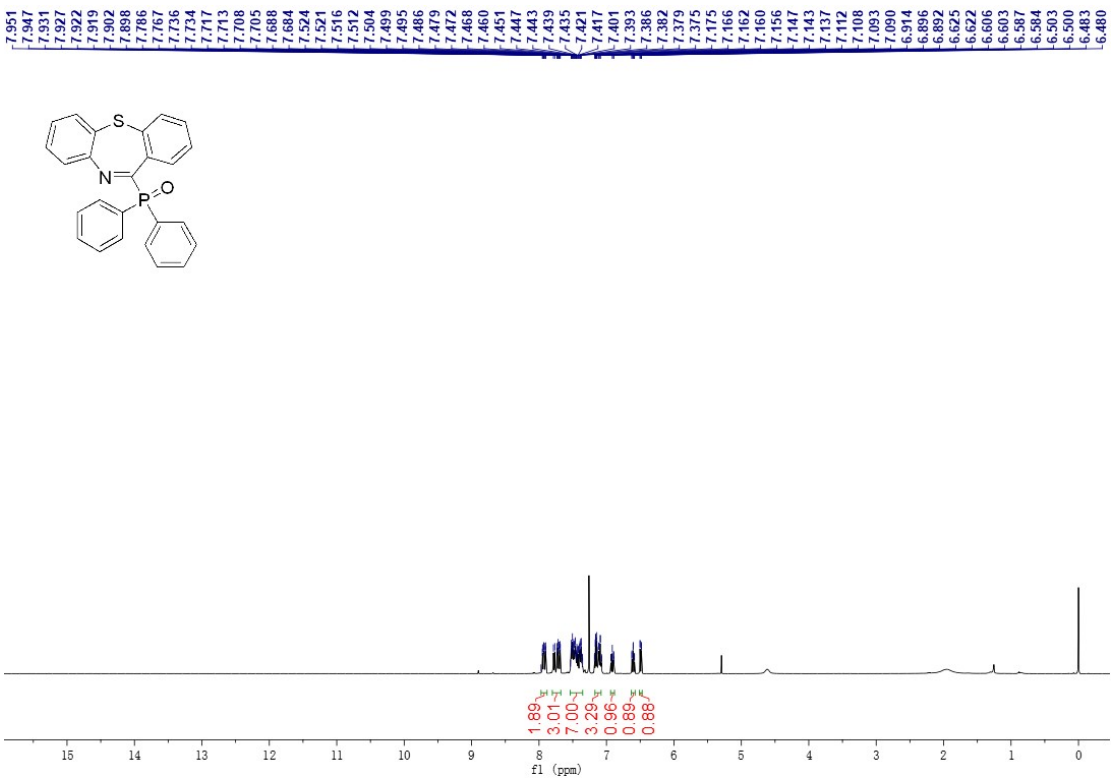
^{1}H NMR Spectrum of Compound **5iA**



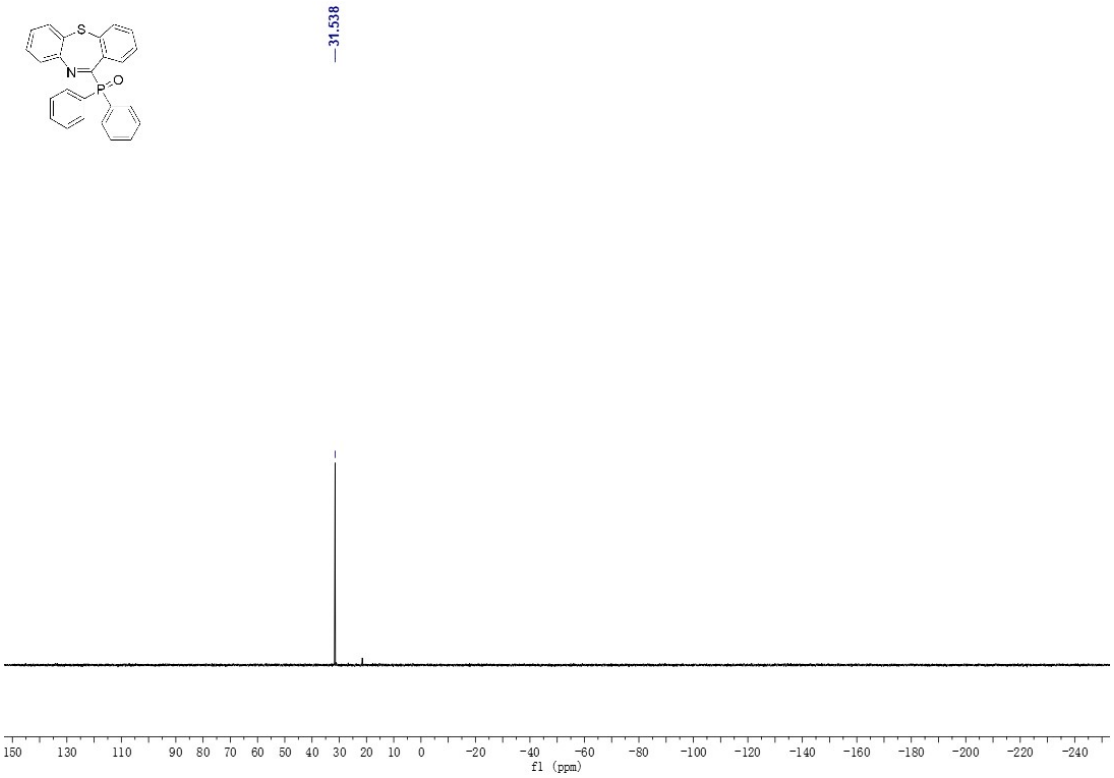
^{31}P NMR Spectrum of Compound **5iA**



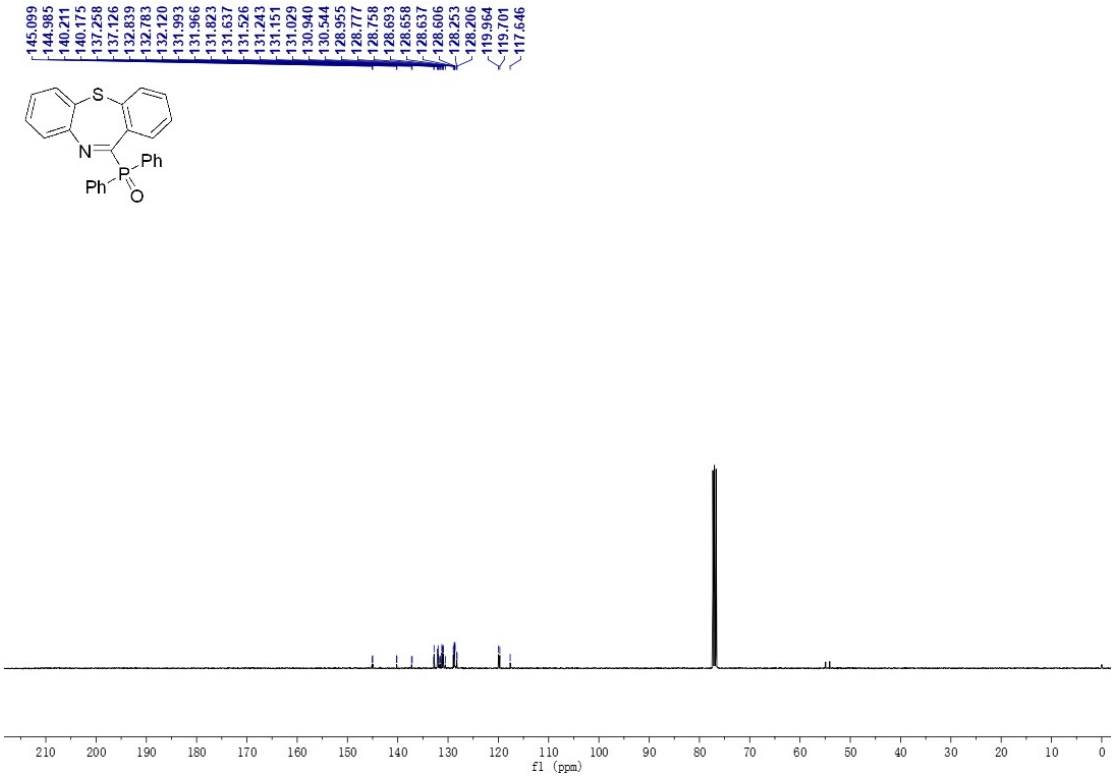
^{13}C NMR Spectrum of Compound **5iA**



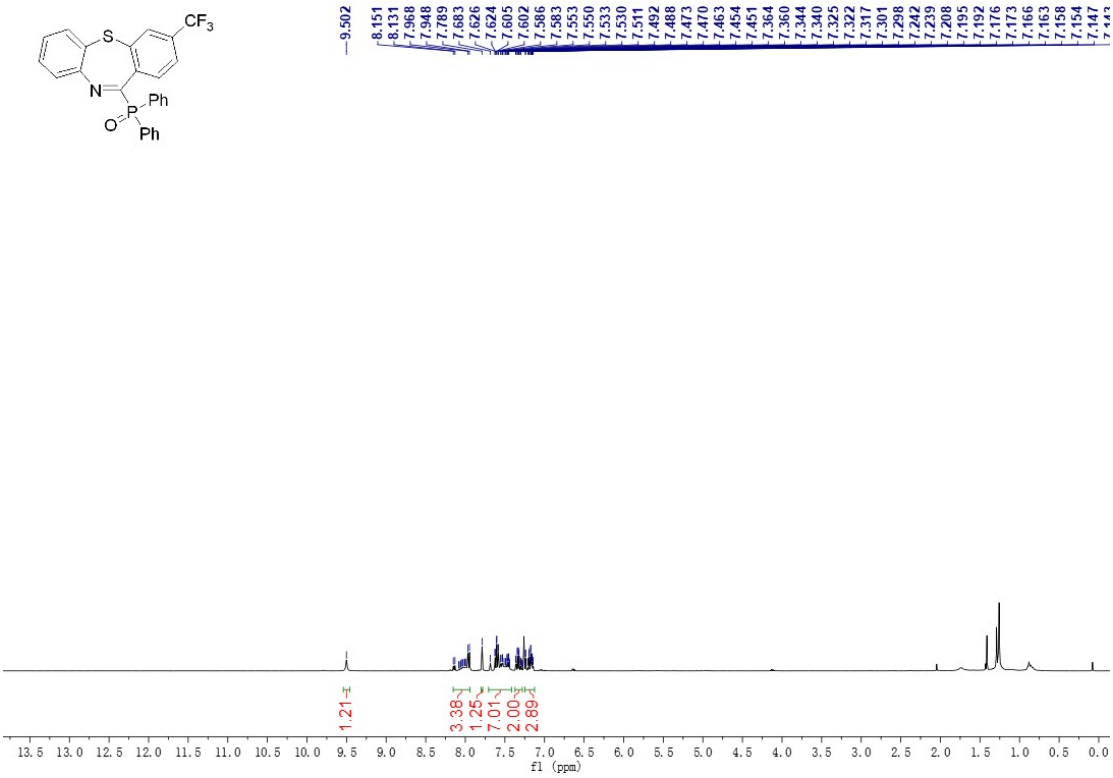
^{1}H NMR Spectrum of Compound **5jA**



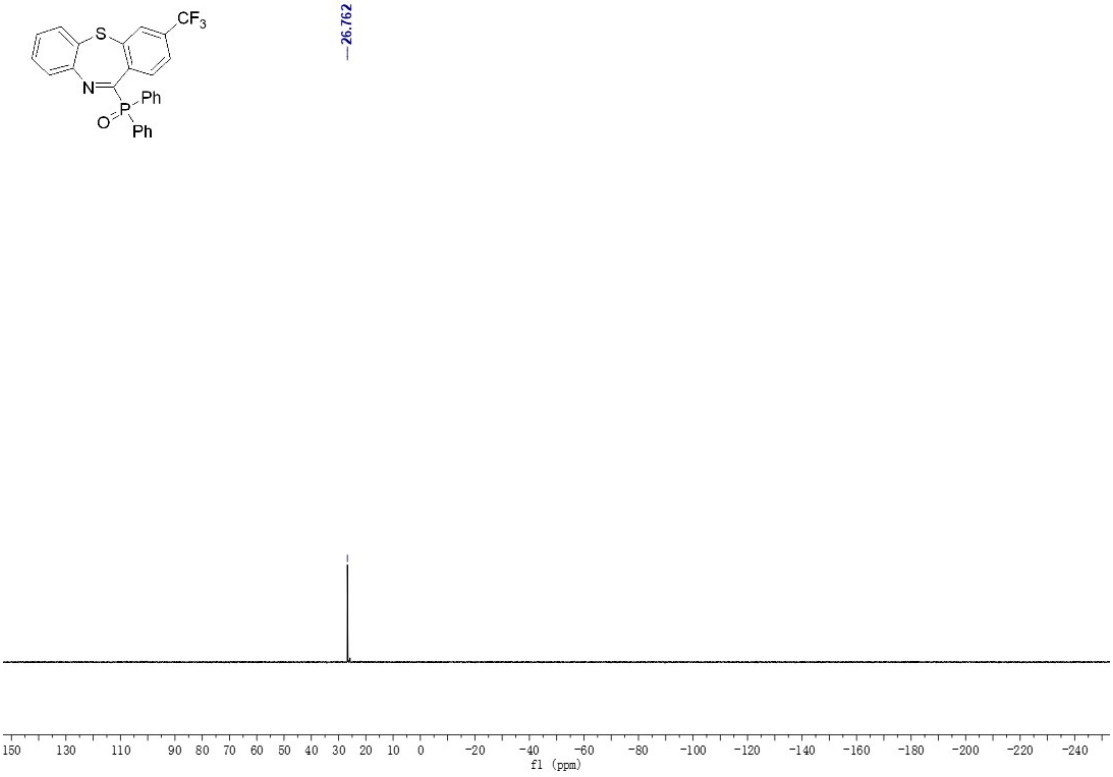
^{31}P NMR Spectrum of Compound **5jA**



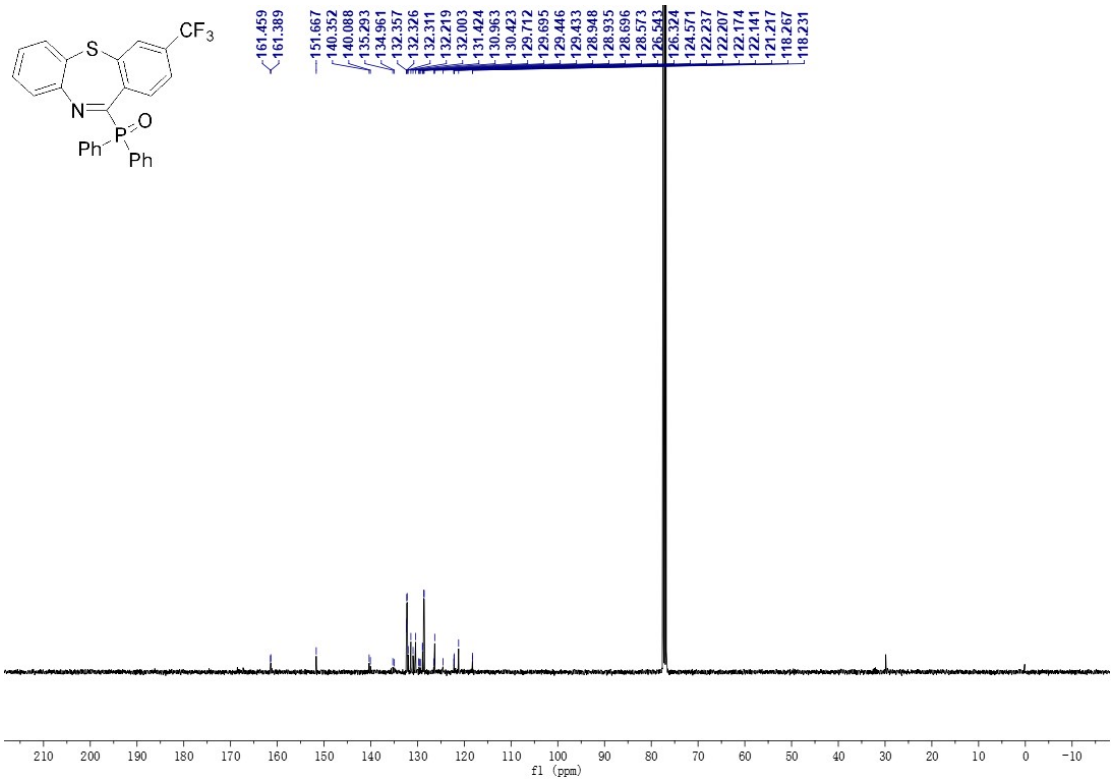
^{13}C NMR Spectrum of Compound **5jA**



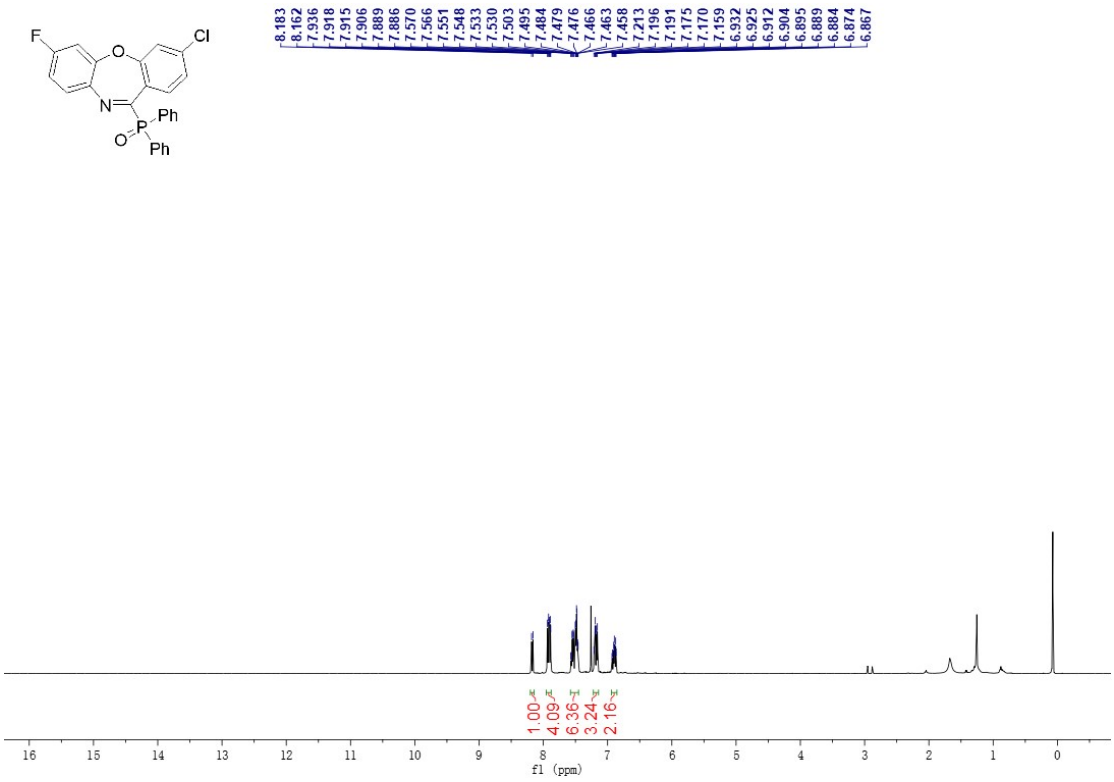
^{1}H NMR Spectrum of Compound **5mA**



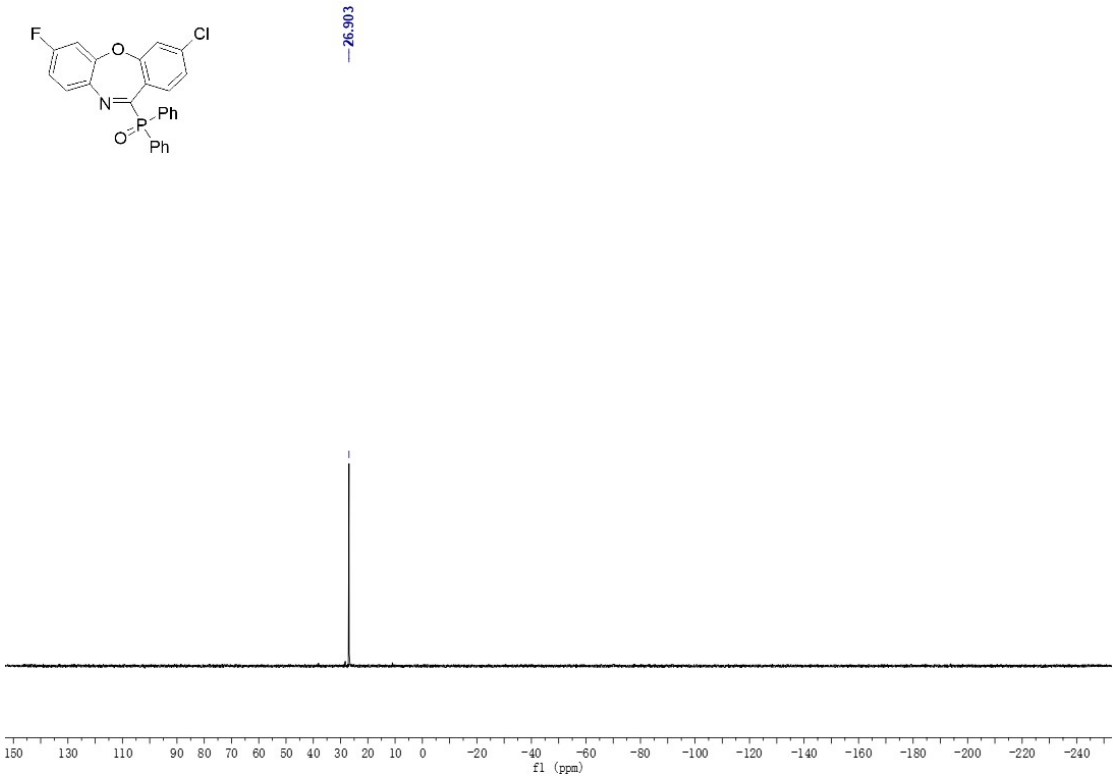
^{31}P NMR Spectrum of Compound **5mA**



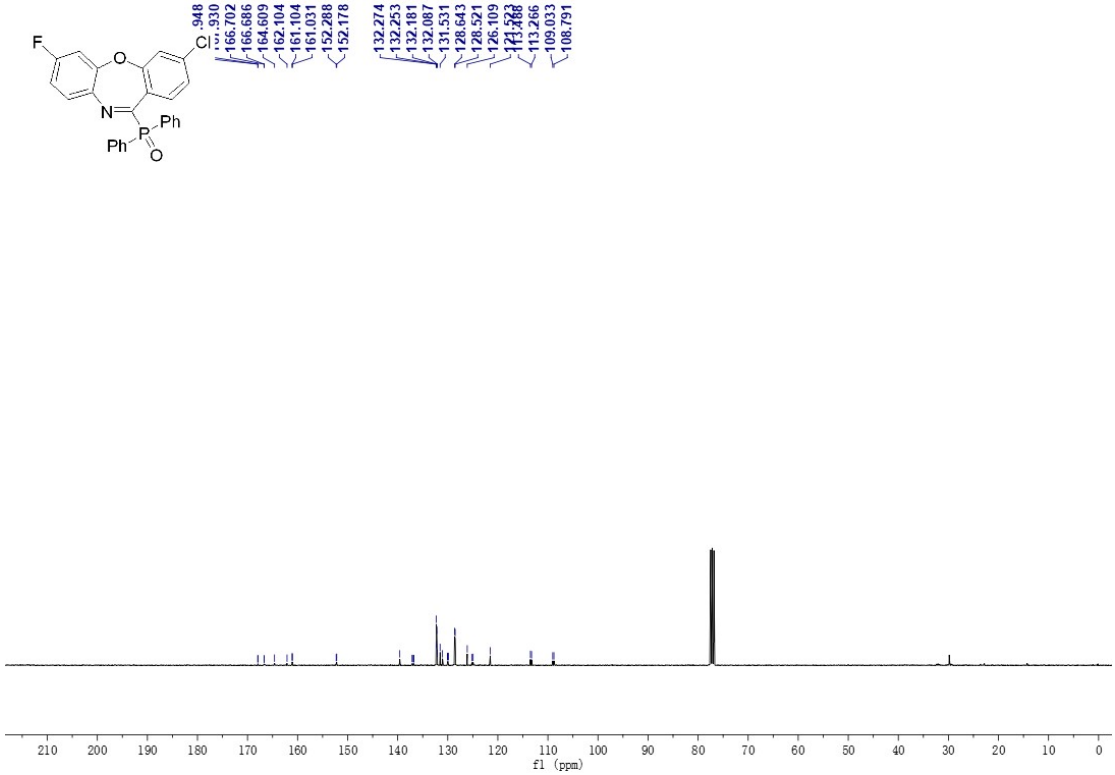
^{13}C NMR Spectrum of Compound **5mA**



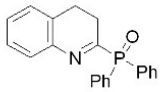
^{1}H NMR Spectrum of Compound **5nA**



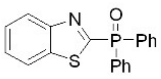
^{31}P NMR Spectrum of Compound **5nA**



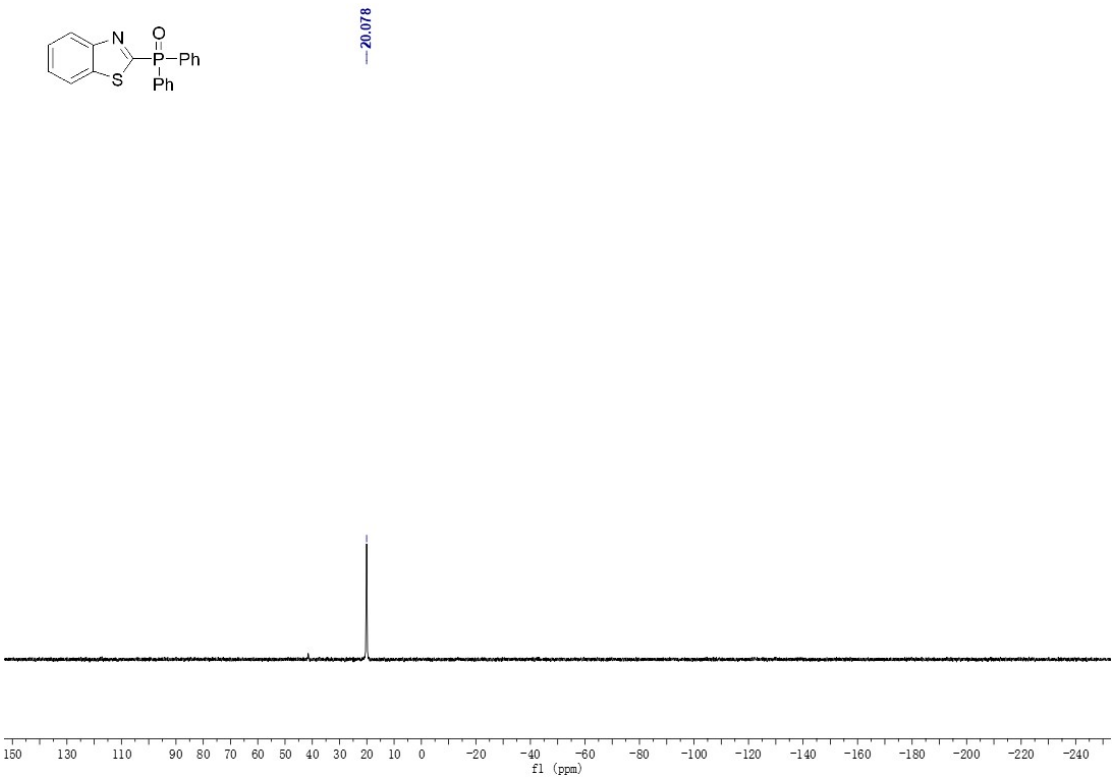
^{13}C NMR Spectrum of Compound **5nA**



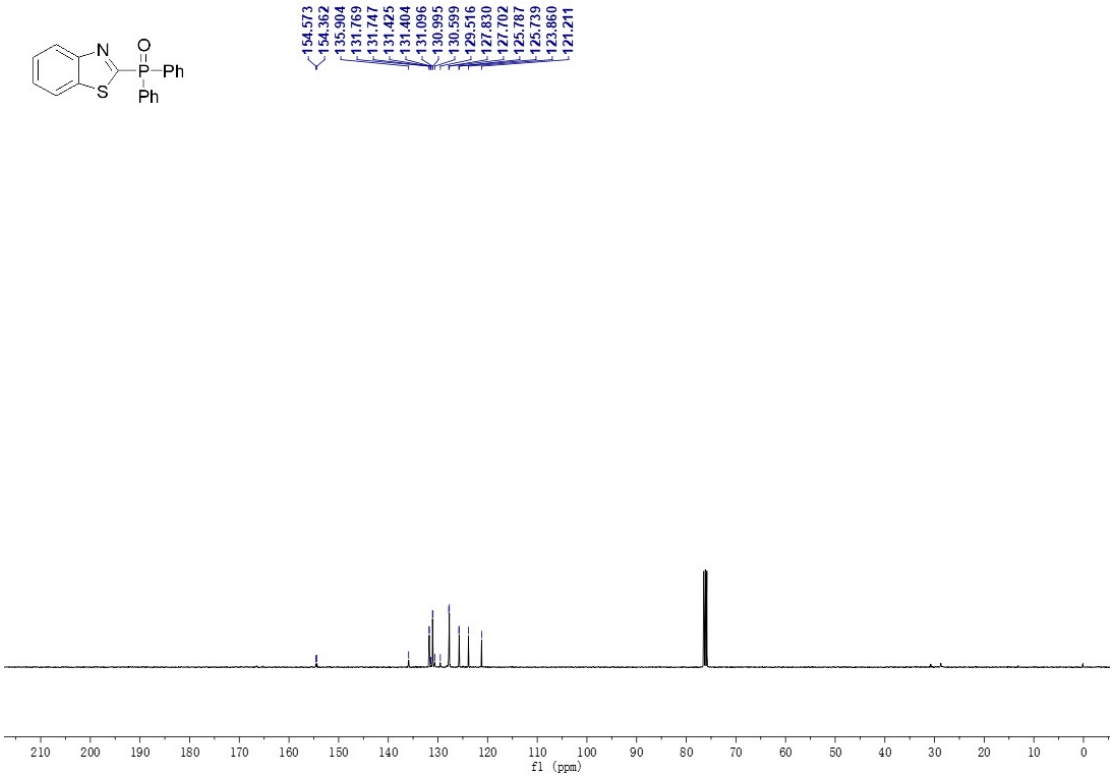
^{31}P NMR Spectrum of Compound **5pA**



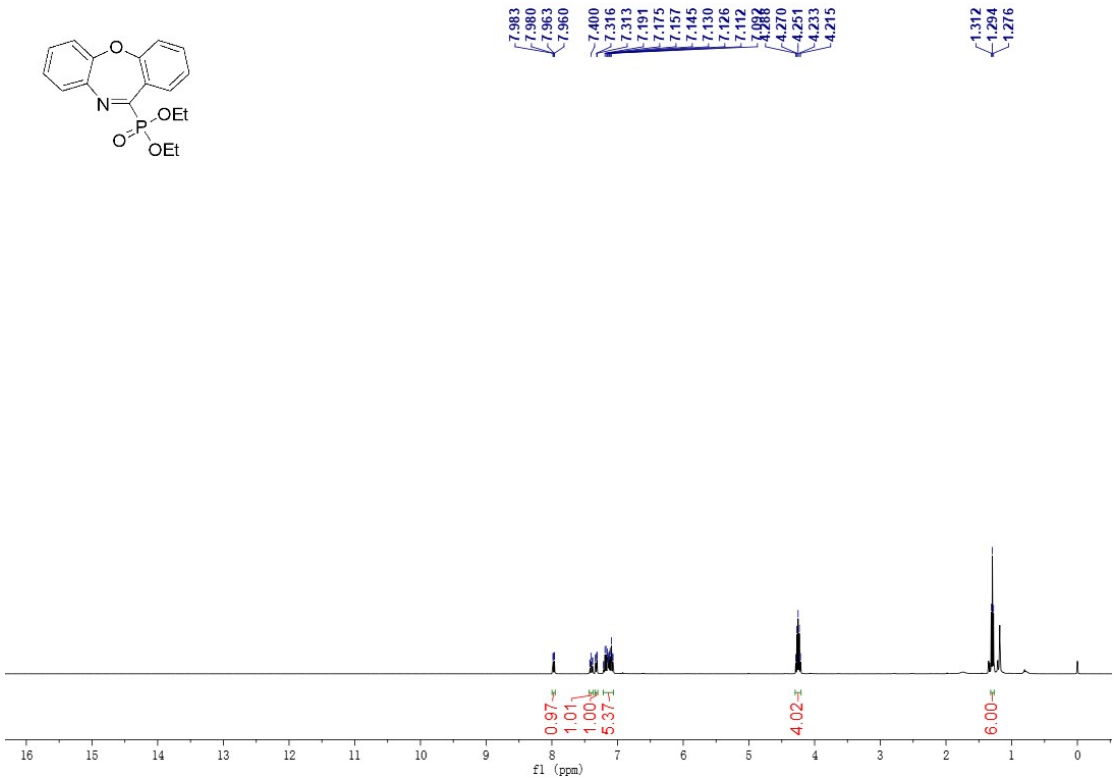
^{1}H NMR Spectrum of Compound **5qA**



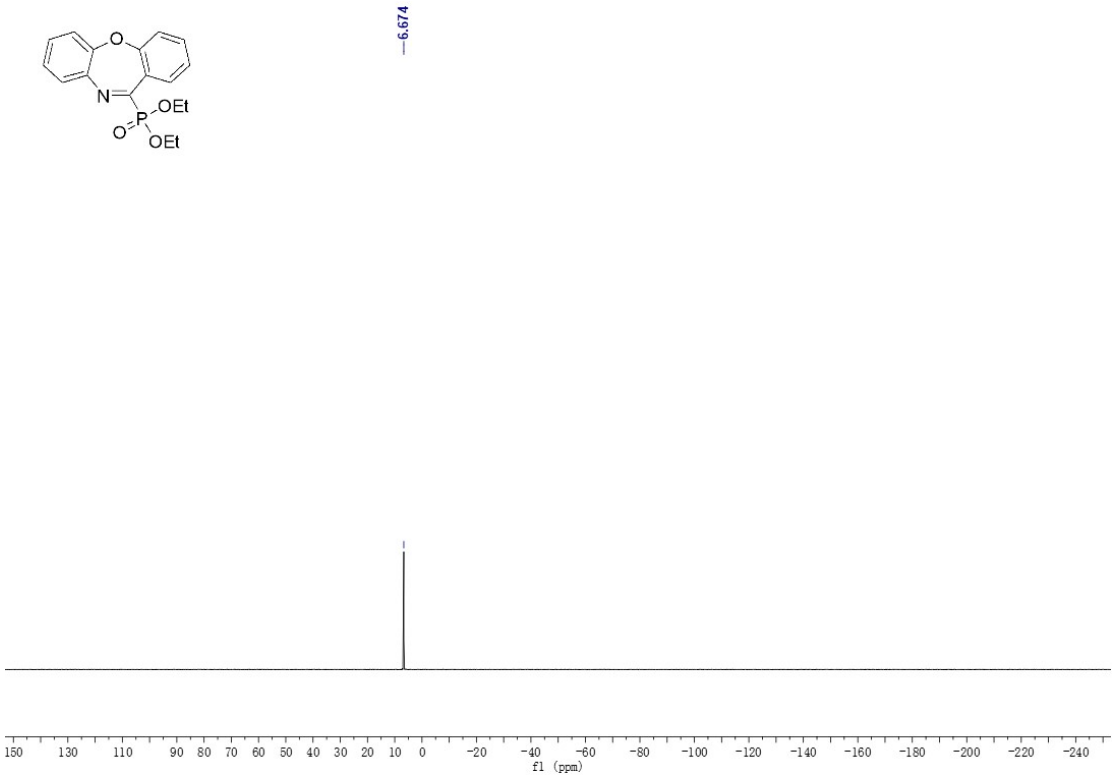
^{31}P NMR Spectrum of Compound **5qA**



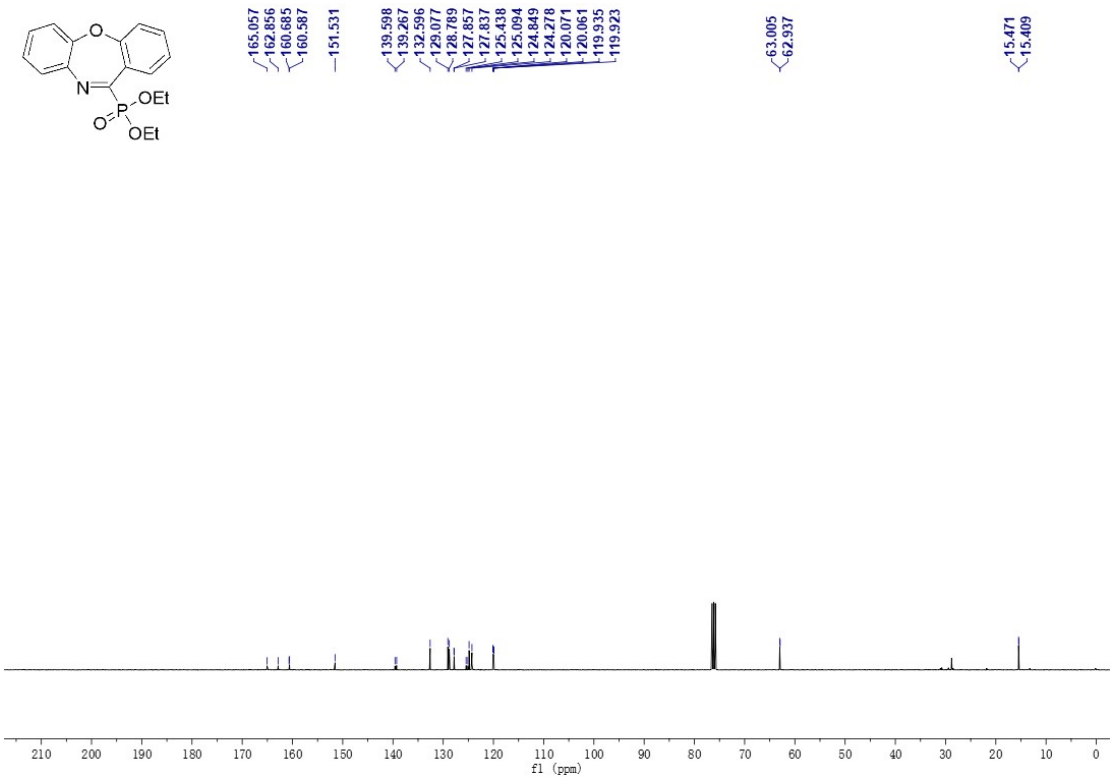
^{13}C NMR Spectrum of Compound **5qA**



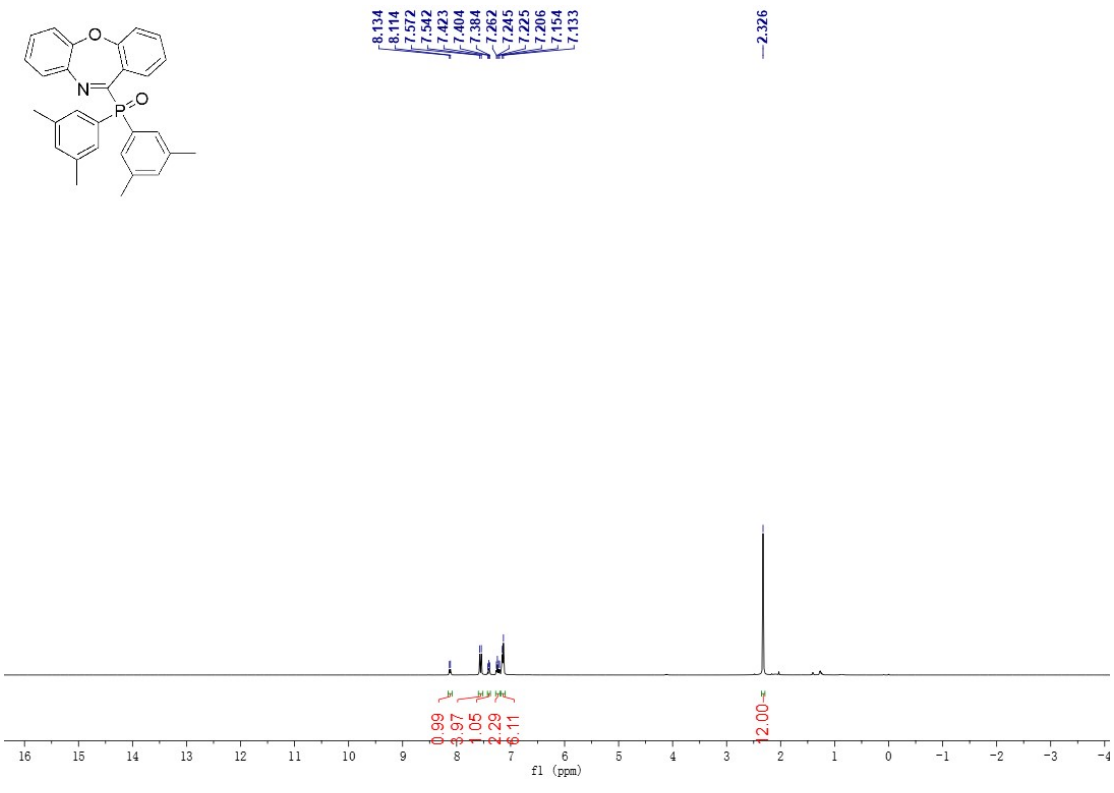
^{1}H NMR Spectrum of Compound **5aB**



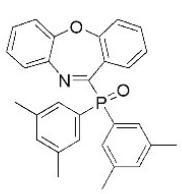
^{31}P NMR Spectrum of Compound **5aB**



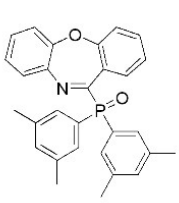
^{13}C NMR Spectrum of Compound **5aB**



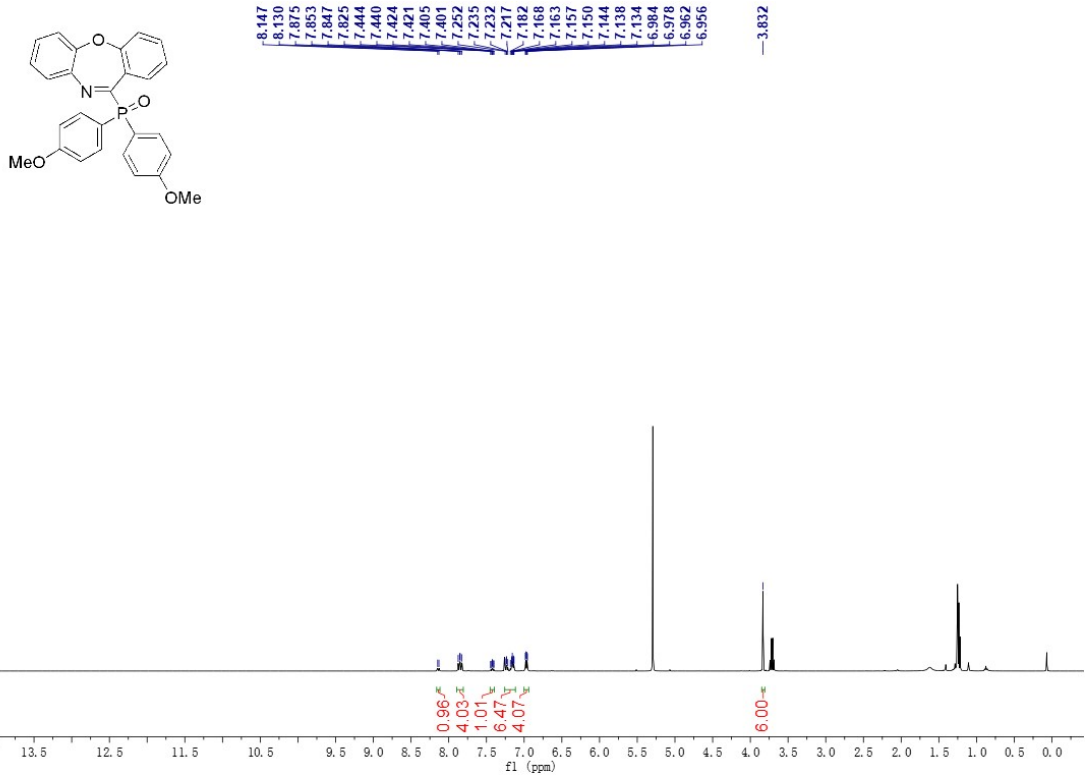
^{1}H NMR Spectrum of Compound **5aC**



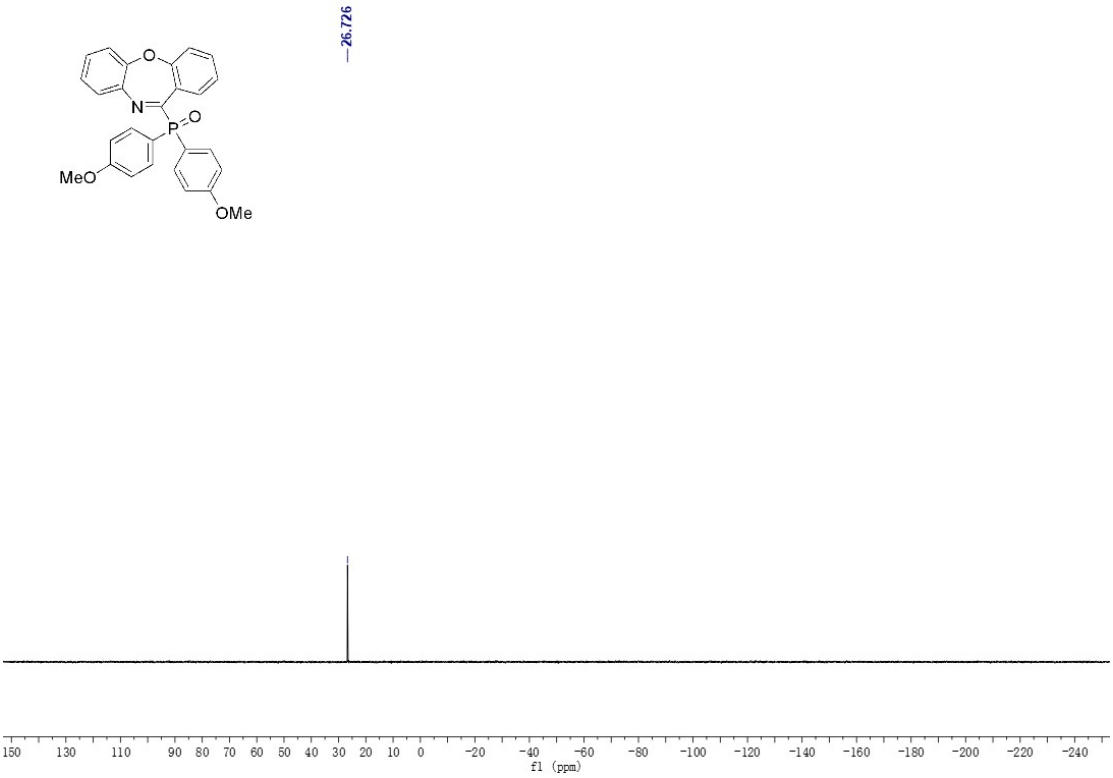
^{31}P NMR Spectrum of Compound **5aC**



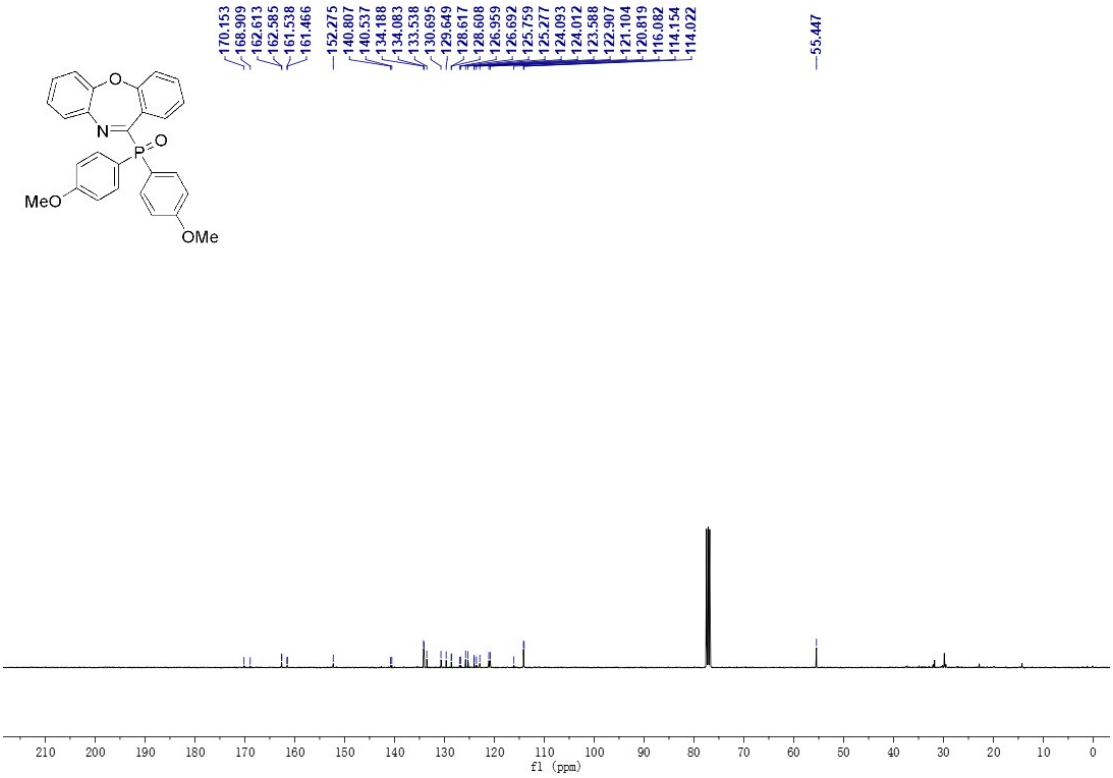
^{13}C NMR Spectrum of Compound **5aC**



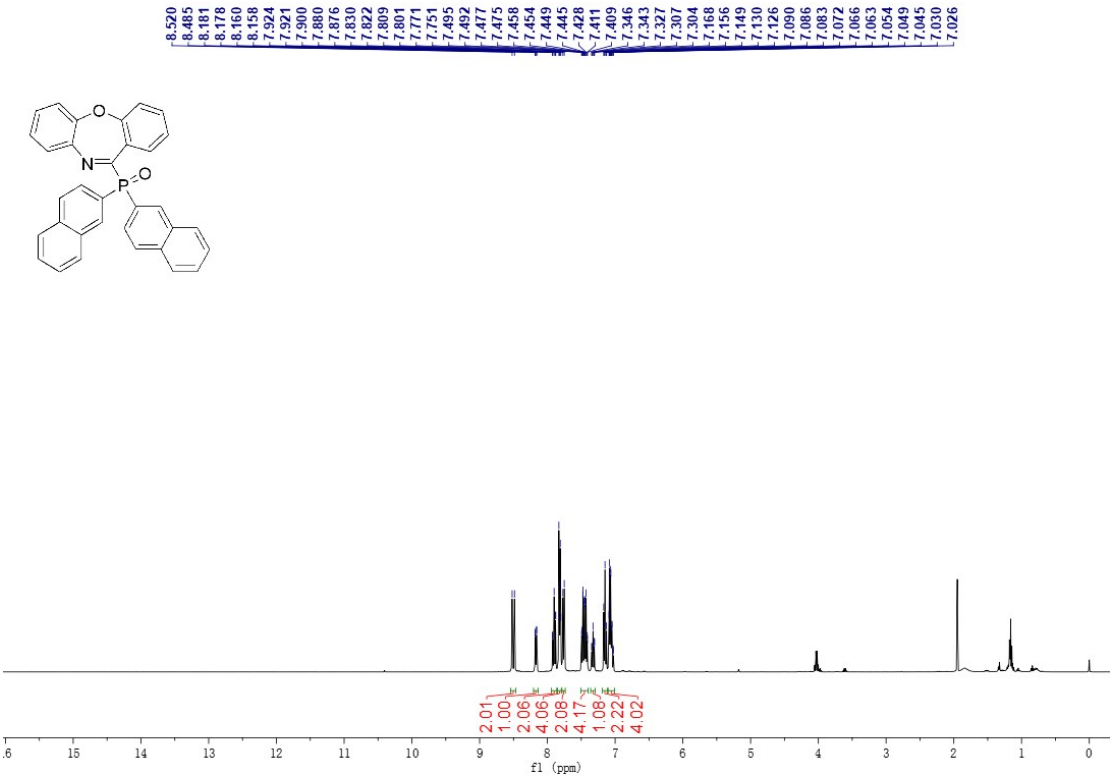
^{1}H NMR Spectrum of Compound **5aD**



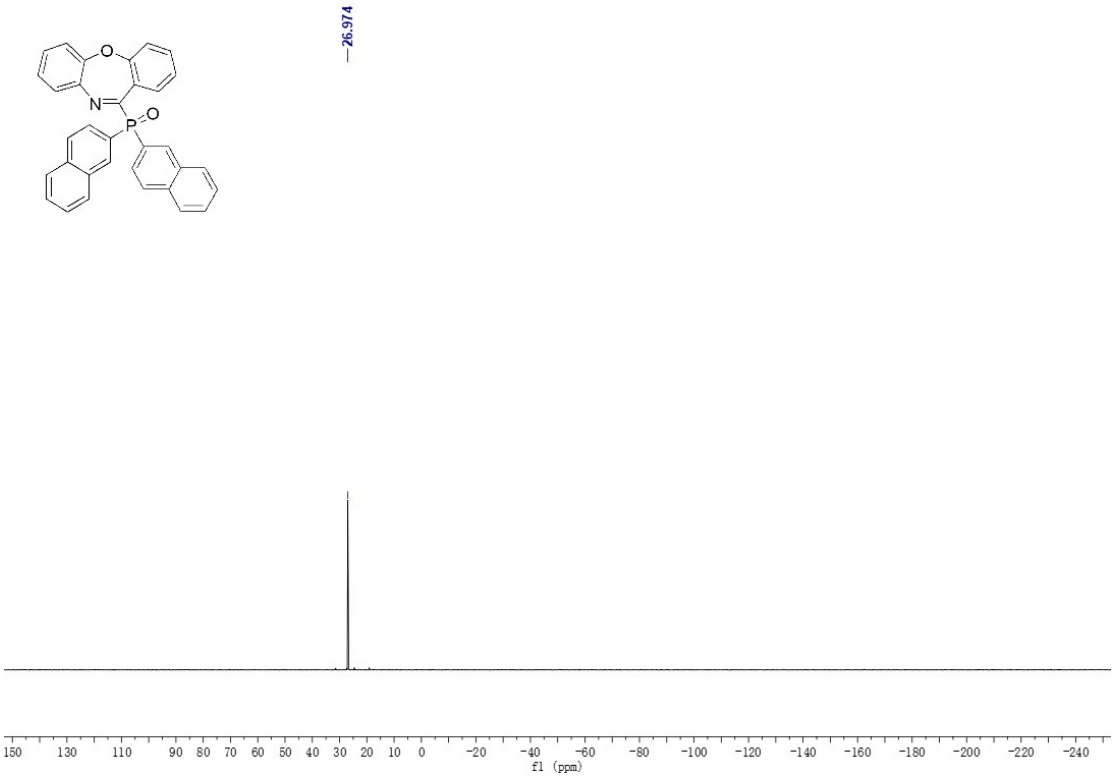
^{31}P NMR Spectrum of Compound **5aD**



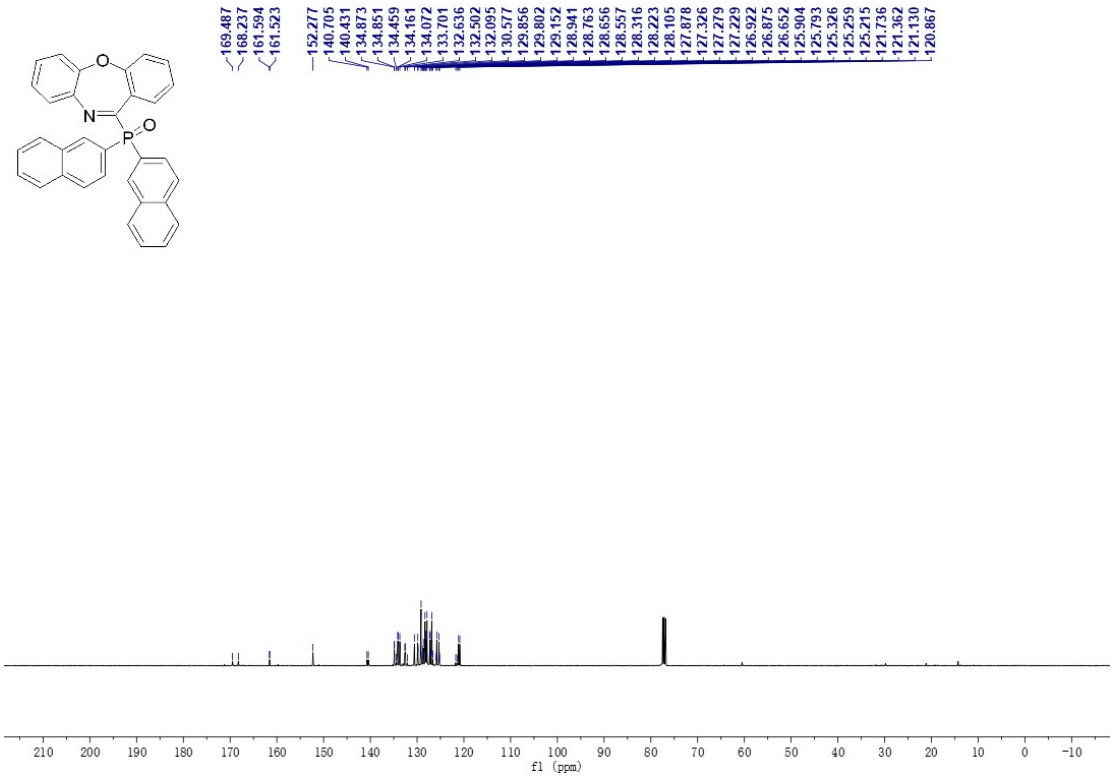
^{13}C NMR Spectrum of Compound **5aD**



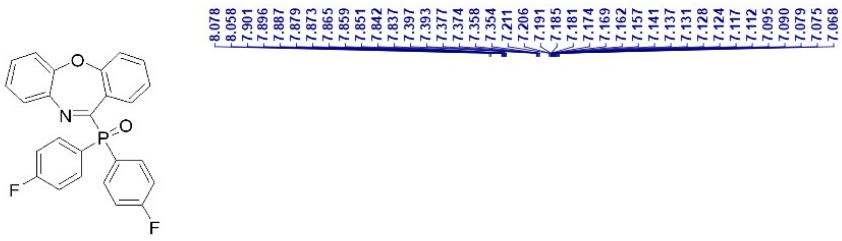
^{1}H NMR Spectrum of Compound **5aE**

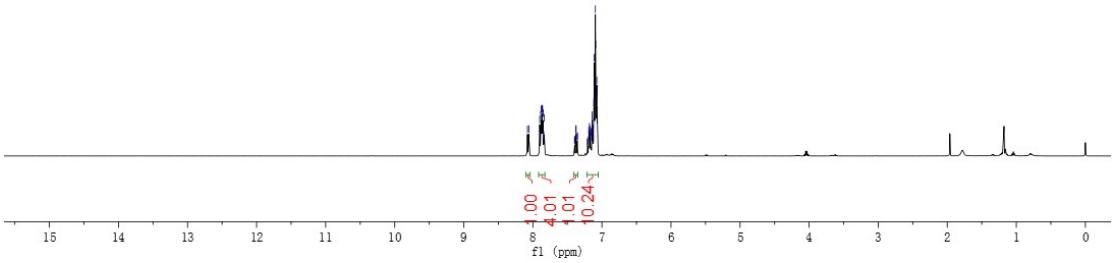


^{31}P NMR Spectrum of Compound **5aE**

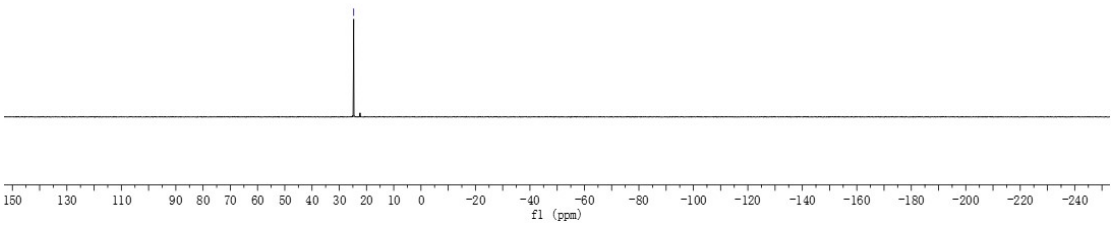


^{13}C NMR Spectrum of Compound **5aE**

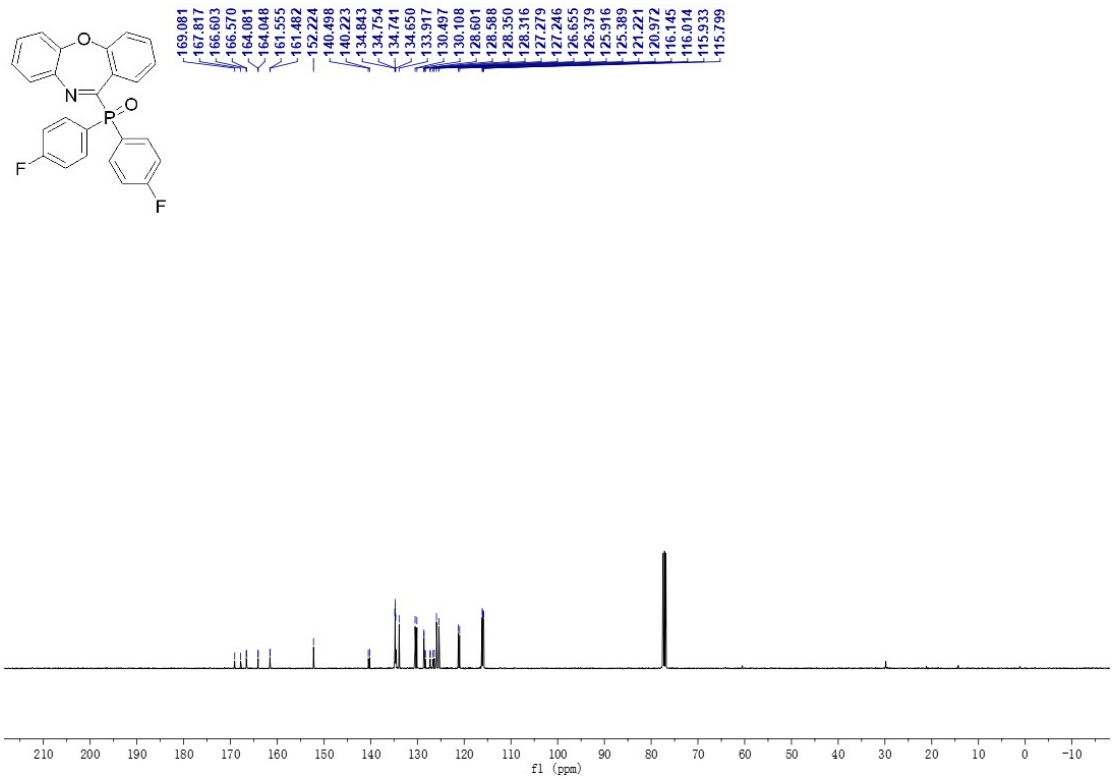




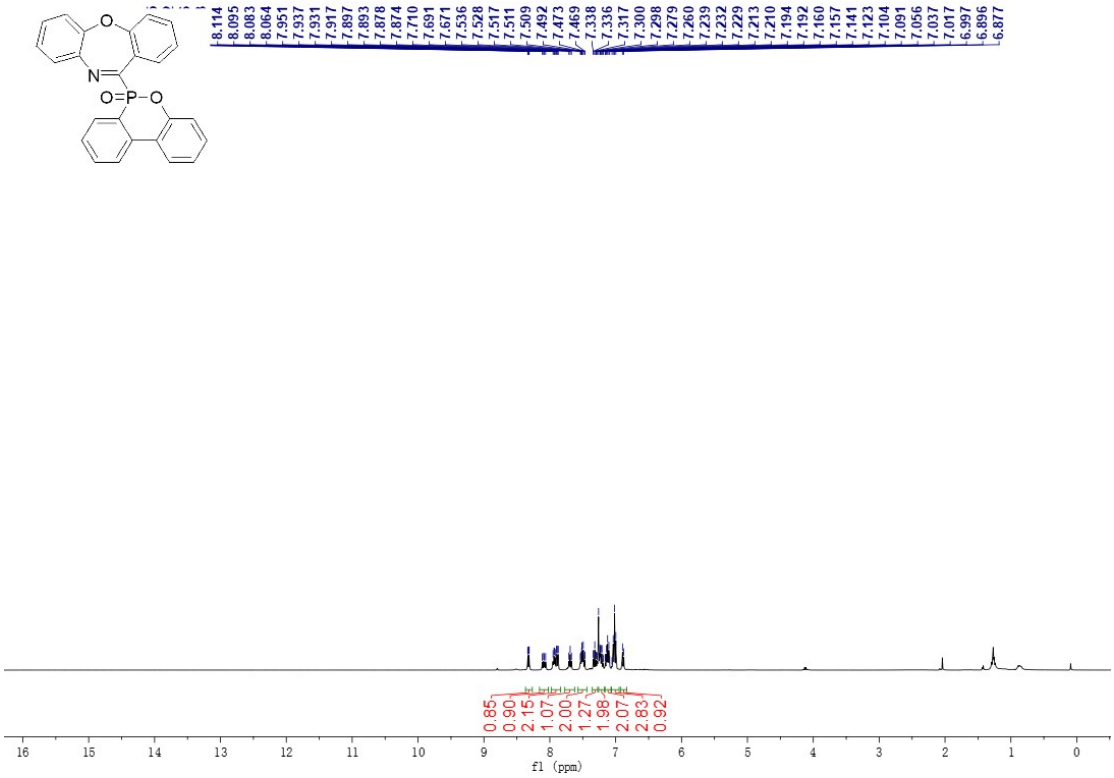
^{1}H NMR Spectrum of Compound **5aF**



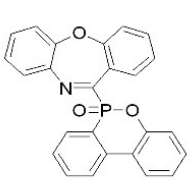
^{31}P NMR Spectrum of Compound **5aF**



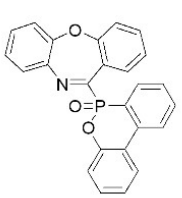
^{13}C NMR Spectrum of Compound **5aF**



^{1}H NMR Spectrum of Compound **5aG**

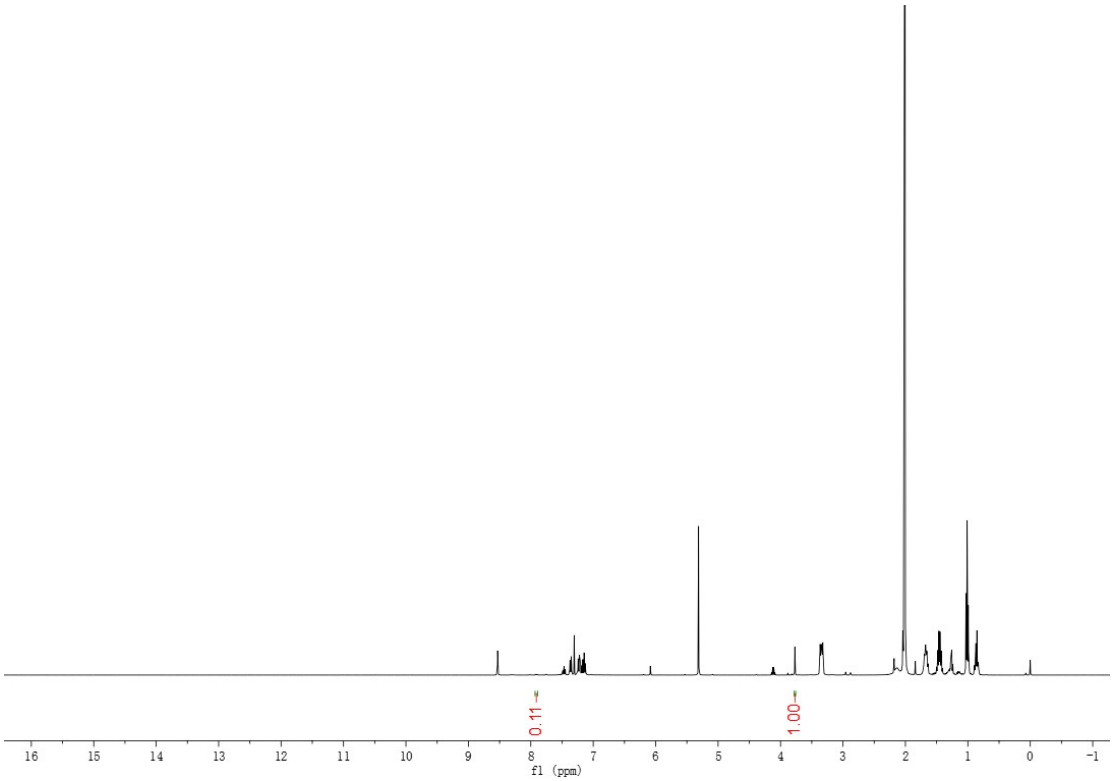


^{31}P NMR Spectrum of Compound **5aG**

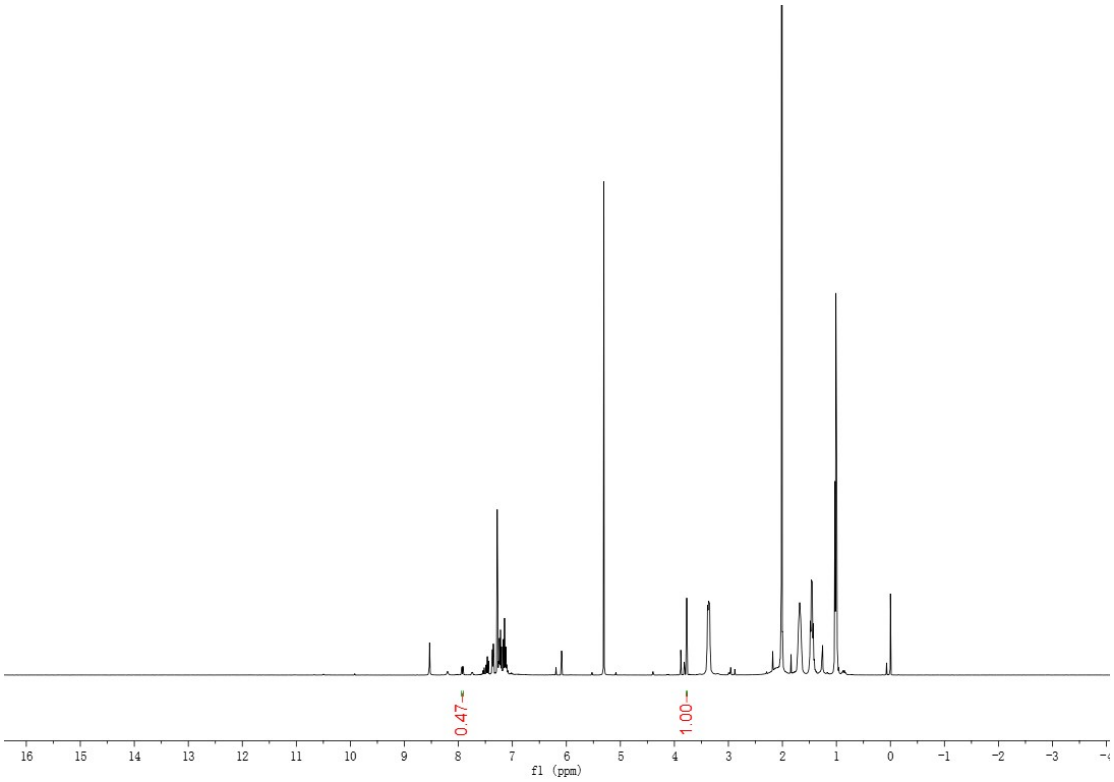


^{13}C NMR Spectrum of Compound **5aG**

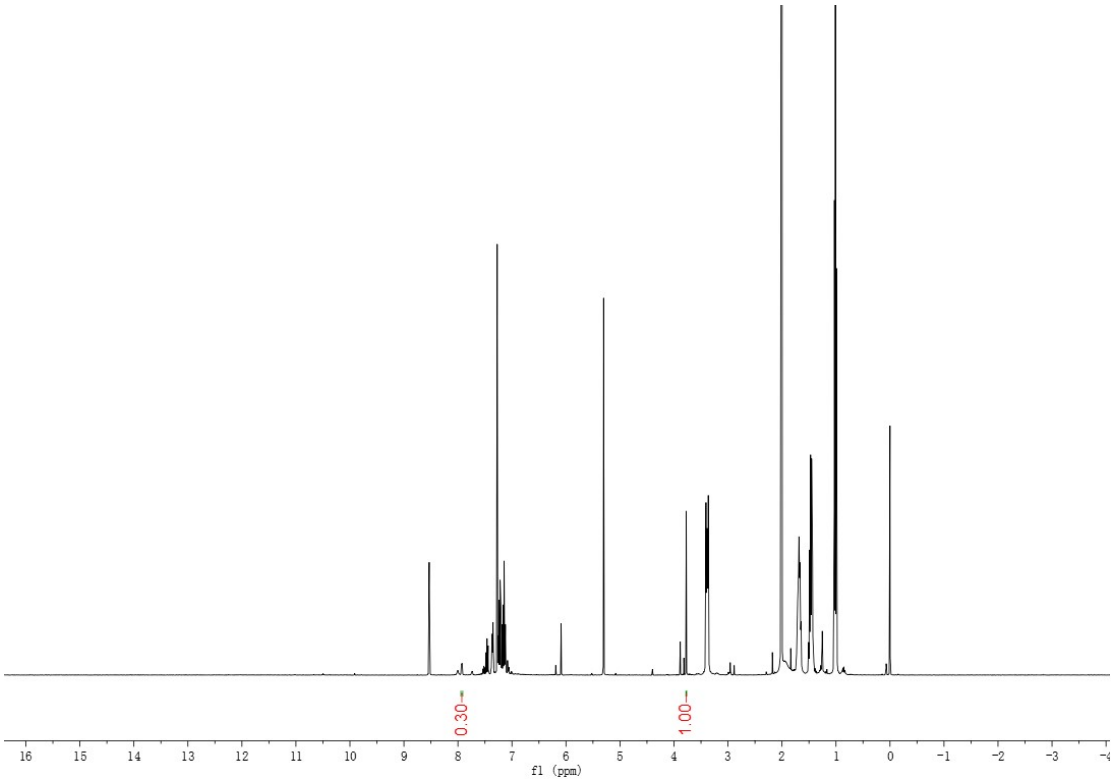
Copies of ^{1}H (400 MHz) in $CDCl_3$ of the light on-off experiments



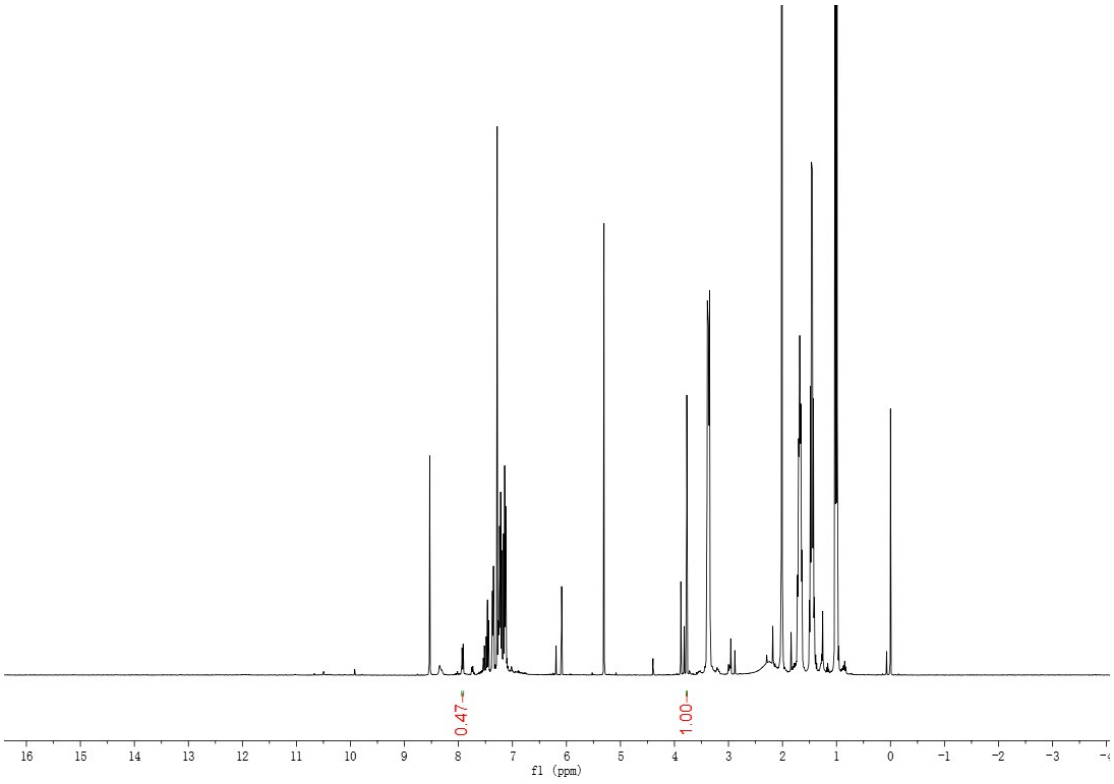
^{1}H NMR Spectrum of 3h



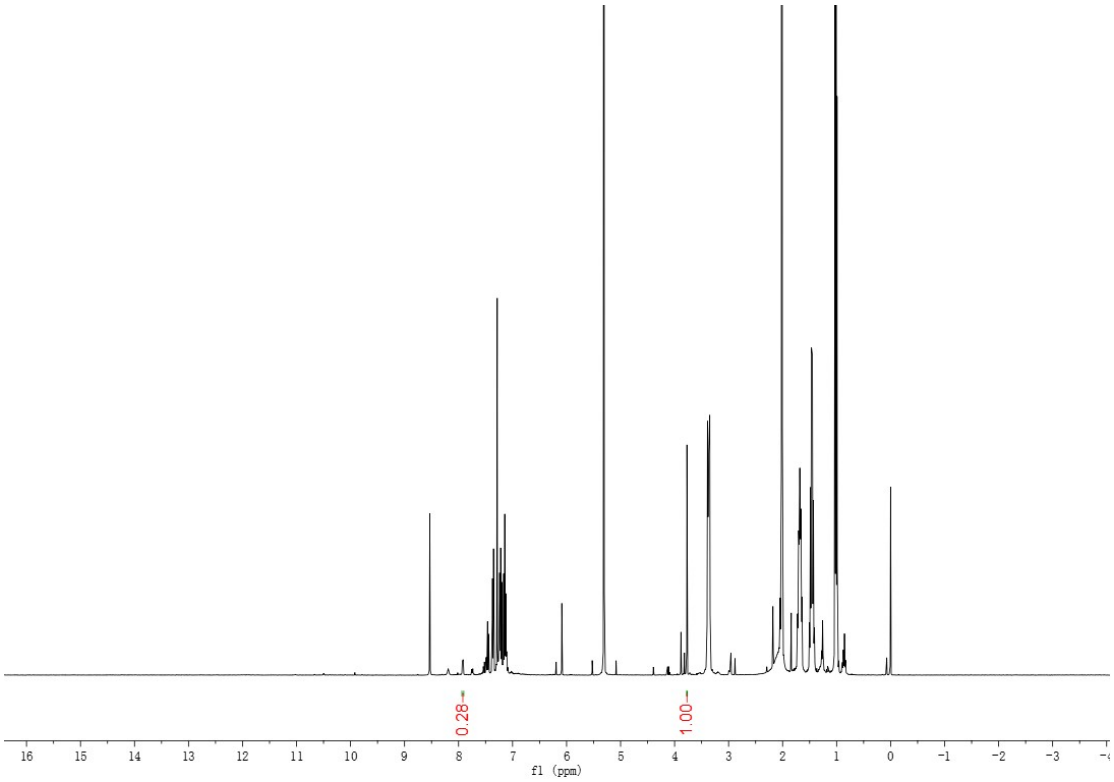
^{1}H NMR Spectrum of 6h



^{1}H NMR Spectrum of 9h



^{1}H NMR Spectrum of 12h



^{1}H NMR Spectrum of 24h