Supporting Information

Construction of C-X (X=N, O) bonds from Benzyl Alcohols via Cu-BTC-Catalyzed Oxidative Coupling

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1. Experimental procedures

1.1 Materials

All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received.

Synthesis of Cu-BTC: Weigh 3.0 g of 1,3,5- homobenzenetric acid was dissolved in 30 mL of N, N-dimethylformamide and 60 mL of anhydrous ethanol, weigh 6.0 g of Cu $(NO_3)_2$-$3H_2O$ was dissolved in 60 mL of deionized water, and the two solutions were mixed and stirred until clarified. The mixture was transferred to a PTFE-lined stainless steel reactor, and the reaction was crystallized at 85 °C. After 20 h of constant temperature reaction, it was removed, left to stand, naturally cooled to room temperature, centrifuged and washed several times, and the blue crystals obtained after drying were Cu-BTC [1].

Synthesis of Cu-BDC: Similar to the synthesis of Cu-BTC, only 1,3,5-

homobenzenetricarboxylic acid needs to be replaced with 1,2-benzenedicarboxylic acid [2].

Synthesis of Cu-BTeC: Similar to the synthesis of Cu-BTC, only 1,3,5-homobenzenetricarboxylic acid was exchanged for 1,2,4,5-homobenzenetetraacetic acid [3].

Synthesis of copper benzoate: Weigh the molar ratio of 1:3 copper oxide and benzoic acid (in order to make the reaction of copper oxide complete, benzoic acid should be excessive), the copper oxide and benzoic acid were placed in a mortar and grind, and then loaded into a three-necked flask, add a small amount of distilled water into a paste, three-necked flasks on the mouth of a condensate tube, a mouth of the installation of an electric stirrer, the other mouth with a grinding mouth plug tightly put into a constant-temperature bath, control the temperature in the 95~97℃, open the stirrer, after 6~8h of reaction will be transferred to a small beaker, add appropriate amount of acetone, heated to a slight boil, while hot, the filter cake was washed with anhydrous pressure extraction, and the product with a reduced pressure filtration. Stirrer, after 6~8h reaction, the product was transferred to a small beaker, add appropriate amount of acetone, heated to a slight boil, while hot, filtration under reduced pressure, the filter cake was washed with anhydrous ethanol, the product was put into the oven at 80 ℃ in the drying of 5 h to get light blue copper benzoate powder.

Synthesis of Co-BTC, Zn-BTC, Ni-BTC, Fe-BTC, Mn-BTC: These MOFs materials were synthesized in a similar way [4] , with the only difference being the

replacement of $Cu(NO_3)_2$-$3H_2O$ with $Co(NO_3)_2$-$6H_2O$, $Zn(NO_3)_2$-$6H_2O$, $Ni(NO_3)_2$-$6H_2O$, $Fe(NO_3)_3$-$9H_2O$, and $Mn(NO_3)_2$-$4H_2O$, respectively.

1.2 Methods

Powder X-ray diffraction (PXRD) Analysis.

Approximately 20 mg of crystalline sample was 50 °C dried before PXRD analysis. PXRD data were collected at ambient temperature on a Puxi DX-3 diffractometer at 40 kV, 40 mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 2°/min, a step size of 0.02° in 2θ, and a 2θ range of 4-45°.

Scanning Electron Microscope（SEM）Analysis.

Cu-BTC single crystals were imaged using an Olympus BX60 optical microscope equipped with a ProgRes C5 camera. Optical microscopic images were captured and analyzed with ProgRes® CapturePro 2.8.8 software. SEM images of Cu-BTC crystals were obtained with FEI Phenom® Bench-top SEM. Crystals were mounted on conductive carbon taps and sputter-coated with 5-10 nm of Au-Pd before imaging.

N_2 Sorption Analysis.

BET surface area (cm^2/g) were tested by autosorb iQ/AsiQwin analyzer (Quantachrome) at liquid nitrogen temperature (77K). Approximately 30-50 mg of activated samples were evacuated on a vacuum line overnight, then transferred to a pre-weighed sample tube and degassed at 100 °C for approximately 24 h or until the outgas rate was < 5 μm Hg.

^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopy (NMR).

The obtained products (3a-3s、4a-4q) was dissolved in $CDCl_3$, DMSO-d_6 or acetone-d_6 (according to their solubility). The ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded by Bruker Advance-III 400/500MHz NMR spectrometers.

High-Resolution Mass Spectroscopy (HRMS).

The solution of obtained products (3a-3s、4a-4q) in methanol were injected into Agilent 6540 Liquid Chromatography-Electrospray Ionisation Quadrupole-TOF mass spectrometer respectively to measure their high-resolution mass spectrum.

2. Supporting information

2.1 Catalyst characterization information

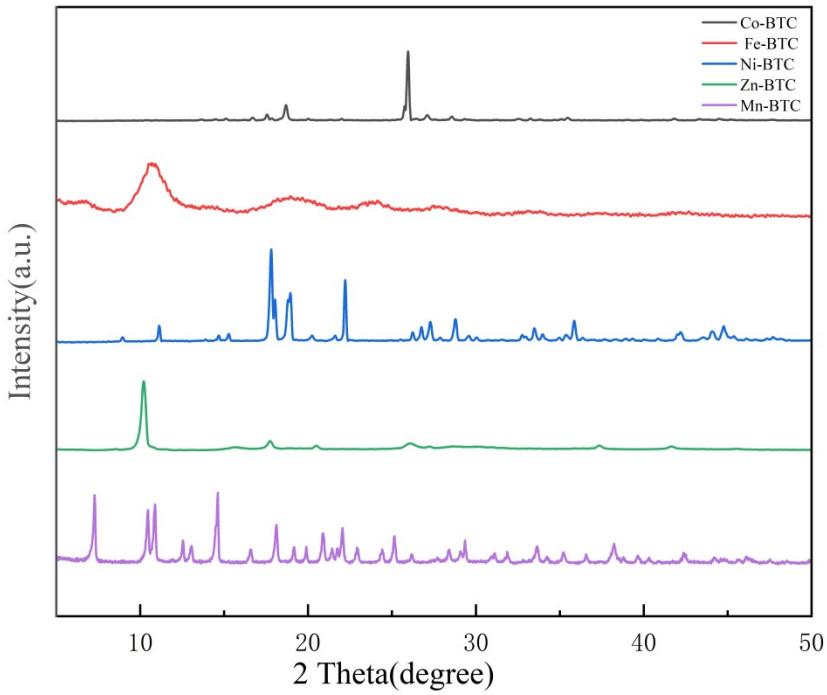


Figure S1. XRD spectra of different metals

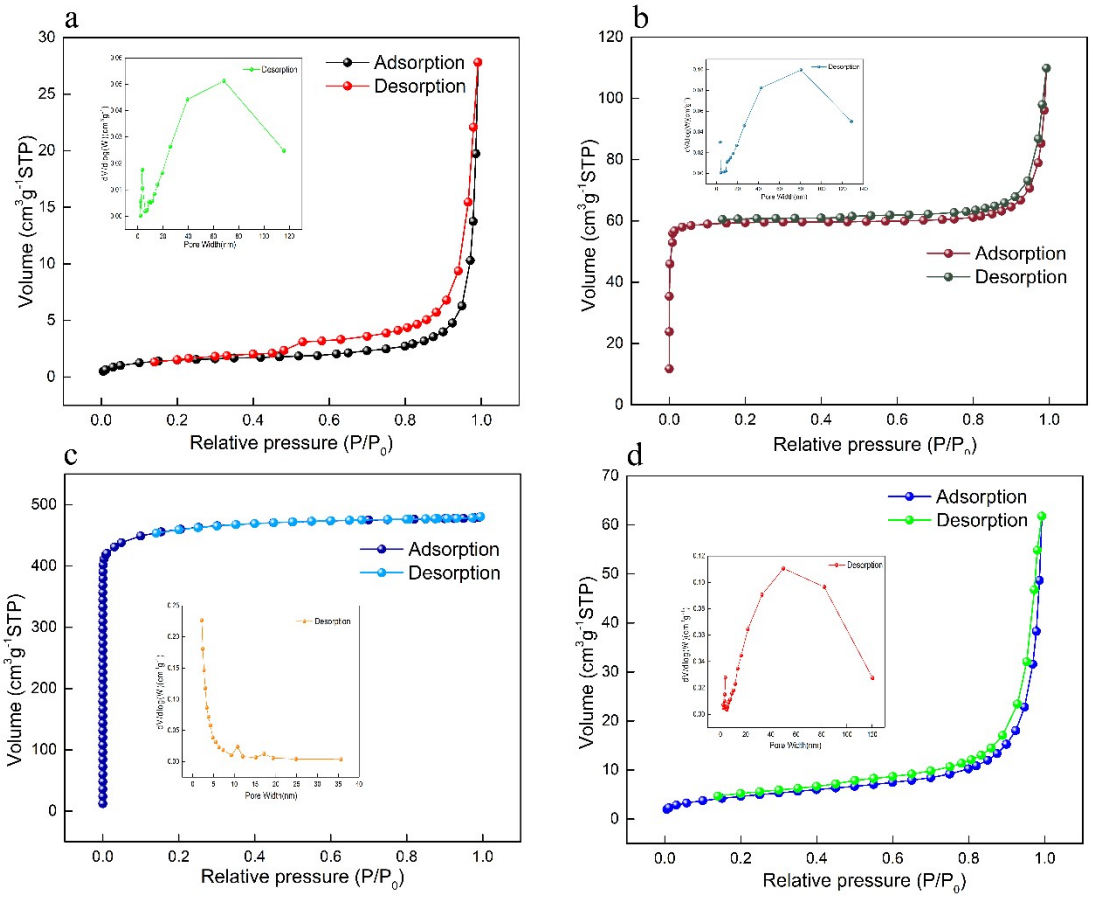


Figure S2. Surface area and porosity analysis of (a) Copper benzoate (b) Cu-BDC (c) Cu-BTC (d) Cu-BTeC

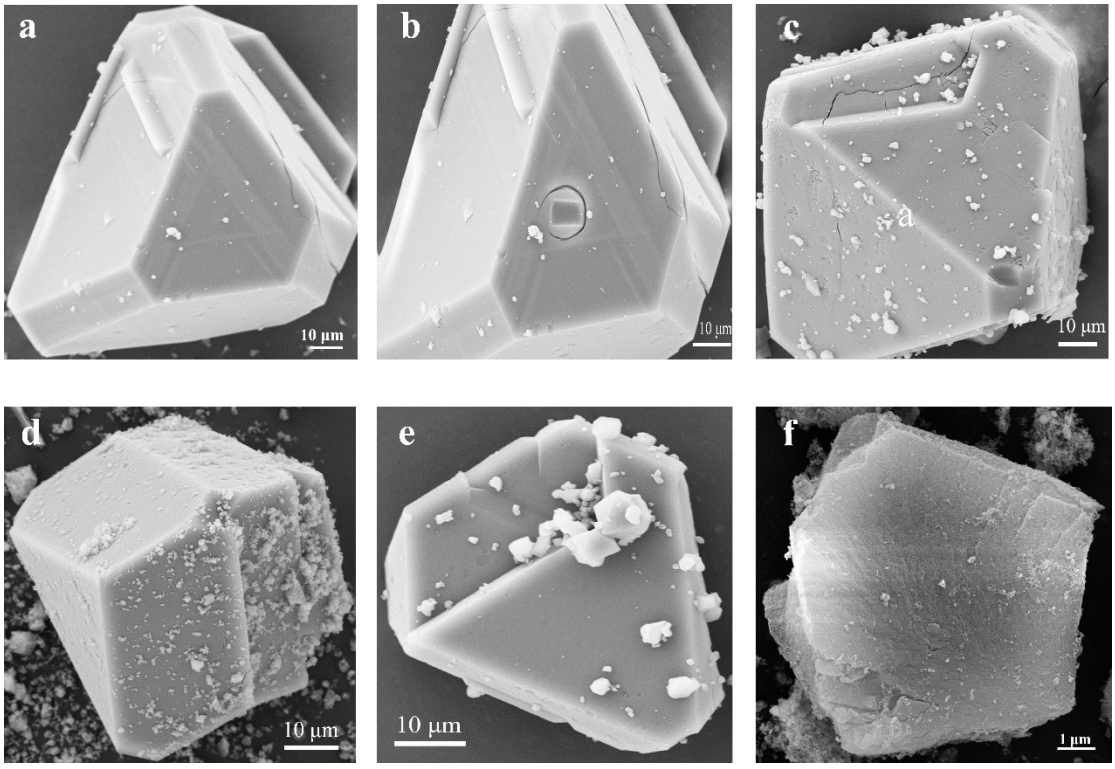


Figure S3. SEM images of catalysts after successive cycling experiments (a) fresh Cu-BTC (b) first cycle (c) second cycle (d) third cycle (e) fourth cycle (f) fifth cycle

2.2 Evaluation of catalyst performance

NMR and GC/MS analysis

^{1}H and ^{13}C NMR spectra for quinazolinones of Table-2 were assigned and reproduced from the corresponding literature. ^{1}H and ^{13}C NMR spectra were recorded using at ambient temperature on JEOL-ECX 600 operating at 600.17 and 150.92 MHz, respectively with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks 77.00 ppm chloroform, 40.45 ppm dimethylsulfoxide, respectively. Abbreviations used in the NMR experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. LC-MS spectra was taken by AGILENT 1100.

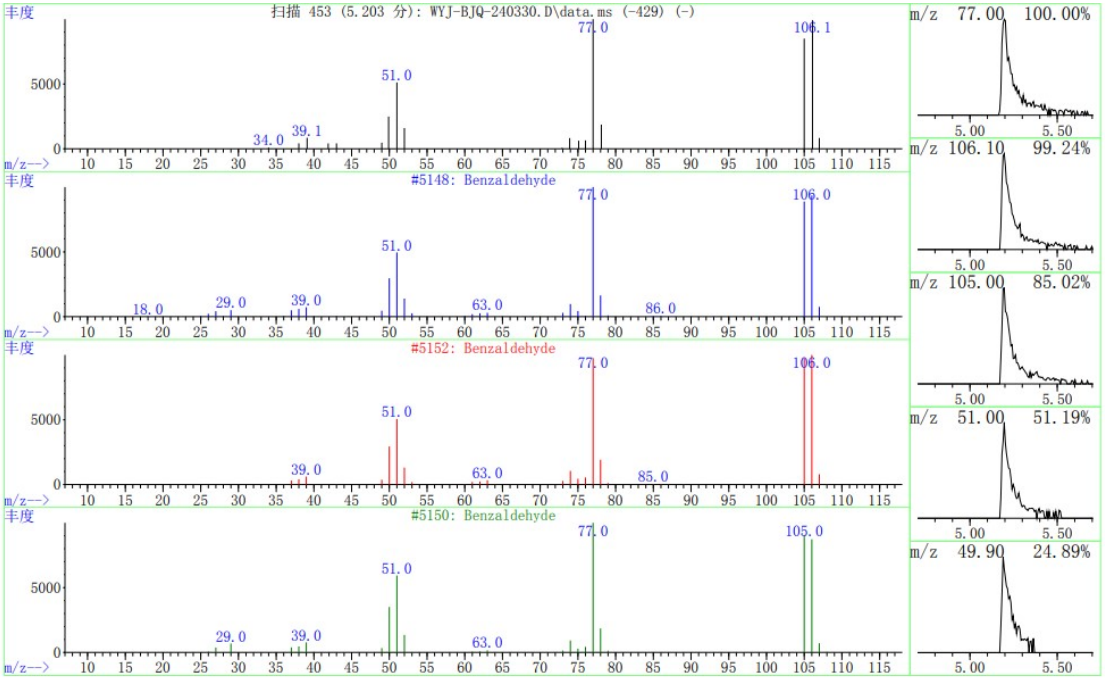


Figure S4. Oxidation of benzyl alcohol to benzaldehyde in other solvents

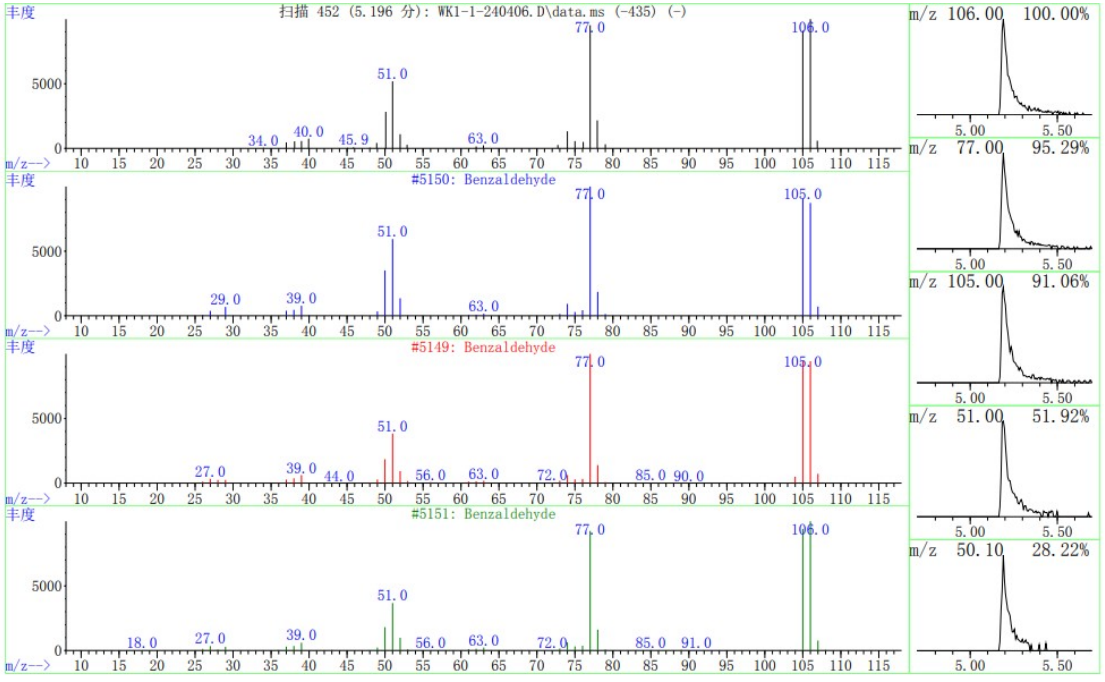
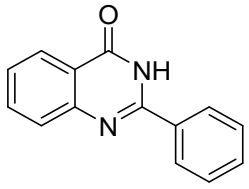
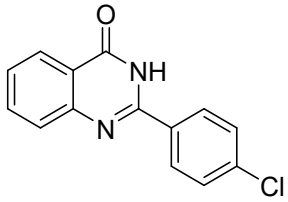


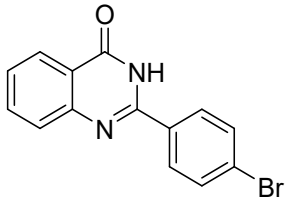
Figure S5. Oxidation of benzyl alcohol to benzaldehyde in the presence of Cu-BTC



2-Phenyl-3*H*-quinazolin-4-one(3a): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.54 (s, 1H), 8.17 (dd, J = 9.6, 7.4 Hz, 3H), 7.84 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.62 – 7.49 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.74, 152.83, 135.08, 133.21, 131.87, 129.08, 128.24, 127.06, 126.33, 121.45; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 223.0793; obtained mass: 223.0790.

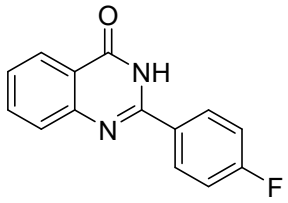


2-(4-Chloro-phenyl)-3*H*-quinazolin-4-one(3b): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.60 (s, 1H), 8.22 – 8.18 (m, 2H), 8.16 (dd, J = 7.9, 1.5 Hz, 1H), 7.85 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.54 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.63, 151.84, 149.06, 136.78, 135.16, 132.04, 130.11, 129.17, 128.24, 128.01, 127.27, 126.35, 121.48; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 257.0403; obtained mass: 257.0403.

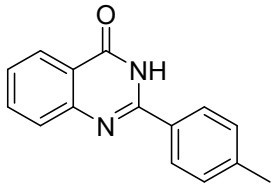


2-(4-bromophenyl)quinazolin-4(3H)-one (3c): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.54 (s, 1H), 8.20 – 8.17 (m, 2H), 8.16 – 8.11 (m, 1H), 7.88 – 7.83 (m, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.61 – 7.51 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.70, 152.79, 149.22, 135.17, 135.10, 133.20, 132.41, 132.10, 131.87, 130.29, 129.09,

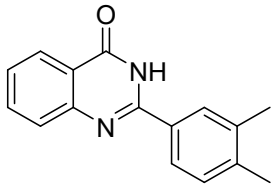
128.24, 127.99, 127.08, 126.36, 126.33, 125.71, 121.47; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 300.9898; obtained mass: 300.9899.



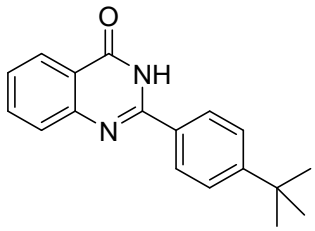
2-(4-Fluoro-phenyl)-3*H*-quinazolin-4-one(3d): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.75 (s, 1H), 8.32 (dt, *J* = 7.9, 1.2 Hz, 1H), 8.22 – 8.18 (m, 2H), 7.83 – 7.80 (m, 2H), 7.52 (ddd, *J* = 8.1, 4.4, 3.5 Hz, 1H), 7.31 – 7.26 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.19, 149.44, 148.27, 134.03, 128.47, 128.38, 127.95, 126.95, 125.97, 125.42, 119.75, 115.43, 115.21; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 241.0699; obtained mass: 241.0699.



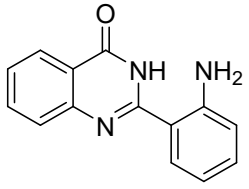
2-*p*-Tolyl-3*H*-quinazolin-4-one(3e)： ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.38 (s, 1H), 8.33 – 8.30 (m, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.49 (ddd, *J* = 8.2, 6.4, 1.9 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.00, 150.40, 148.49, 141.32, 133.84, 128.93, 128.89, 128.18, 126.91, 125.91, 125.67, 125.42, 119.88, 20.51; HRMS (APCI) m/z: $[M+H]^+$: exact mass:237.09503; obtained mass: 237.0951.



2-(3,4-dimethylphenyl)quinazolin-4(3H)-one(3f): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 7.91 (s, 1H), 7.84 – 7.77 (m, 3H), 7.49 (ddd, *J* = 8.1, 6.6, 1.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.79, 150.48, 148.50, 140.08, 136.73, 133.81, 129.43, 129.20, 127.05, 126.90, 125.62, 125.41, 123.20, 18.89, 18.86; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 251.1106; obtained mass: 251.1107.

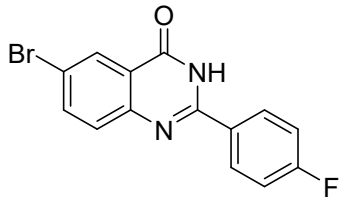


2-(4-(tert-butyl)phenyl)quinazolin-4(3H)-one(3g): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.17 – 8.12 (m, 3H), 7.83 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.48 (m, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.80, 152.69, 149.30, 135.04, 132.05, 130.42, 129.13, 128.04, 126.88, 126.32, 125.90, 121.39, 35.16, 31.39;HRMS (APCI) m/z: $[M+H]^+$: exact mass: 278.1419; obtained mass: 278.1420.

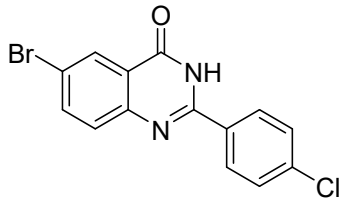


2-(2-aminophenyl)quinazolin-4(3H)-one(3h): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 8.30 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.79 – 7.70 (m, 3H), 7.58 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.84 – 6.79 (m, 2H), 6.25 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.45, 152.15, 148.63, 148.52, 134.83, 132.55, 127.19, 126.87, 126.69, 126.51, 120.59, 117.79, 117.39,

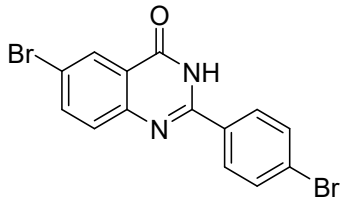
113.21; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 238.0902; obtained mass: 238.0902.



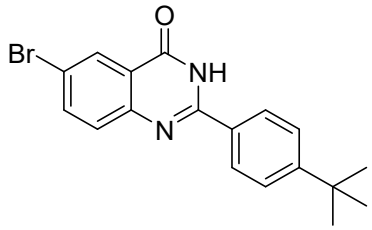
6-bromo-2-(4-fluorophenyl)quinazolin-4(3H)-one(3i): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.56 (s, 1H), 8.26 (dd, J = 8.9, 5.4 Hz, 2H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.84 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.38 (d, J = 8.9 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.76, 163.28, 151.98, 149.11, 135.09, 130.85 (d, J = 9.0 Hz), 129.78, 127.86, 127.06, 126.33, 121.36, 116.21, 115.99; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 318.9804; obtained mass: 318.9804.



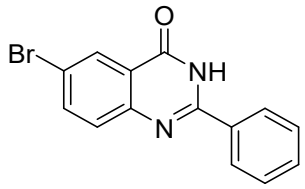
6-bromo-2-(4-chlorophenyl)quinazolin-4(3H)-one (3j): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 8.20 (d, J = 8.7 Hz, 2H), 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.56 – 7.51 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.75, 135.12, 132.13, 130.11, 129.16, 127.23, 126.35, 121.47; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 334.9509; obtained mass: 334.9504.



6-bromo-2-(4-bromophenyl)quinazolin-4(3H)-one(3k): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.23 (d, J = 2.4 Hz, 1H), 8.19 – 8.15 (m, 2H), 7.98 (dd, J = 8.7, 2.4 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.60 – 7.53 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.87, 133.03, 132.08, 129.12, 128.48, 128.33, 119.36; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 380.8983; obtained mass: 380.8985.

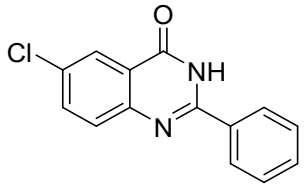


6-bromo-2-(4-(tert-butyl)phenyl)quinazolin-4(3H)-one(3l): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 8.13 (d, J = 8.5 Hz, 2H), 7.83 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.6 Hz, 2H), 7.53 – 7.49 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.77, 154.81, 152.70, 135.05, 130.43, 128.04, 127.90, 126.89, 126.32, 125.91, 121.39, 35.16, 31.39; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 357.0524; obtained mass: 357.0524.

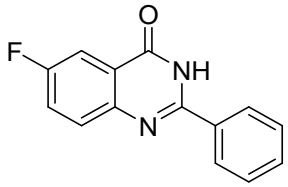


6-bromo-2-phenylquinazolin-4(3H)-one(3m): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.53 (s, 1H), 8.20 – 8.14 (m, 3H), 7.84 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.58 – 7.52 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 135.06, 131.85,

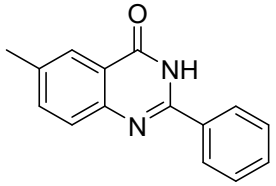
129.08, 128.24, 127.04, 126.33; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 300.9899 obtained mass: 300.9898.



6-chloro-2-phenylquinazolin-4(3H)-one(3n): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.18 (d, J = 7.5 Hz, 2H), 8.09 (d, J = 2.5 Hz, 1H), 7.86 (dd, J = 8.7, 2.6 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.57 (dt, J = 14.3, 6.9 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.86, 153.40, 147.93, 135.16, 132.97, 132.07, 131.22, 130.15, 129.11, 128.33, 125.36, 122.71; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 257.0403 obtained mass: 257.0403.

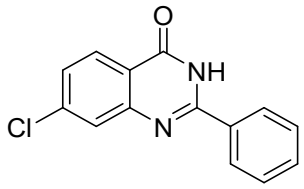


6-fluoro-2-phenylquinazolin-4(3H)-one(3o): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.65 (s, 1H), 8.17 (d, J = 7.3 Hz, 2H), 7.85 – 7.80 (m, 2H), 7.73 (td, J = 8.7, 3.0 Hz, 1H), 7.62 – 7.53 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.24, 161.68, 159.25, 152.45, 133.10, 131.89, 129.09, 128.23, 123.65, 123.41, 122.72, 122.64, 111.11, 110.87; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 241.0699 obtained mass: 241.0699.

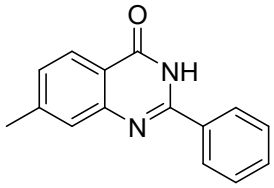


6-methyl-2-phenylquinazolin-4(3H)-one(3p): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.20 (dd, J = 8.1, 1.6 Hz, 2H), 7.99 (s, 1H), 7.70 (d, J = 2.0 Hz, 2H),

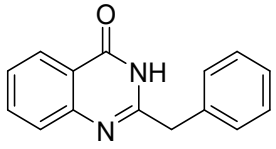
7.64 – 7.55 (m, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.82, 162.64, 151.97, 136.79, 136.36, 133.26, 131.71, 129.06, 128.11, 127.85, 125.71, 121.19, 21.22; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 237.0950 obtained mass: 237.0951.



7-chloro-2-phenylquinazolin-4(3H)-one(3q): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.20 – 8.13 (m, 3H), 7.80 (d, J = 2.0 Hz, 1H), 7.62 – 7.54 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.19, 139.64, 132.90, 132.19, 129.12, 128.44, 128.40, 127.27, 120.31; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 257.0403 obtained mass: 257.0405.

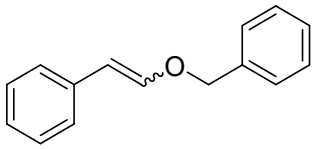


7-methyl-2-phenylquinazolin-4(3H)-one(3r): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 8.21 – 8.17 (m, 2H), 8.06 (d, J = 8.0 Hz, 1H), 7.62 – 7.56 (m, 4H), 7.37 (dd, J = 8.2, 1.7 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.64, 152.86, 145.55, 133.28, 131.81, 129.07, 128.50, 128.18, 126.20, 119.06, 21.84; HRMS (APCI) m/z: $[M+H]^+$: exact mass: 237.0950 obtained mass: 237.0952.

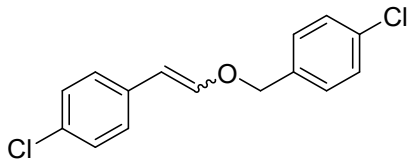


Glycosminine (3s): ^{1}H NMR (400 MHz, Chloroform-d) δ 10.67 (s, 1H), 8.33 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 3.9 Hz, 2H), 7.86 – 7.79 (m, 2H), 7.60 (s, 2H), 7.52 (d, J =

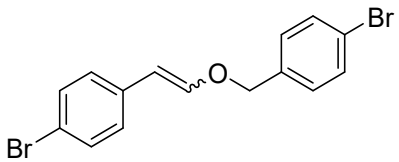
8.0 Hz, 1H), 7.26 (d, *J* = 1.3 Hz, 1H), 4.16 – 4.08 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.48, 133.93, 131.70, 130.77, 128.17, 126.98, 126.12, 125.91, 125.43, 119.91, 40.33; $[M+H]^+$: exact mass: 236.0950 obtained mass: 236.0951.



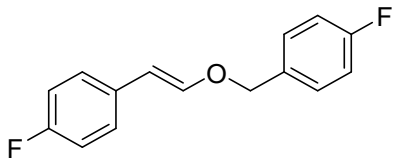
(2-(benzyloxy)vinyl)benzene(4a, E/Z=98/2): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (d, *J* = 6.8 Hz, 4H), 7.38 – 7.34 (m, 1H), 7.28 (dd, *J* = 13.0, 5.5 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 5.95 (d, *J* = 12.9 Hz, 1H), 4.94 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.83, 137.53, 136.65, 129.00, 128.91, 128.40, 128.24, 125.92, 125.32, 106.77, 71.83; $[M+H]^+$: exact mass: 210.1045 obtained mass: 210.1040.



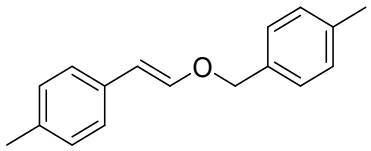
1-chloro-4-(2-((4-chlorobenzyl)oxy)vinyl)benzene(4b, E/Z=79/21): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.09 (s, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 12.9 Hz, 1H), 5.76 (d, *J* = 12.9 Hz, 1H), 4.81 (s, 1H), 4.72 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.79, 145.30, 134.02, 133.54, 133.00, 130.32, 128.51, 127.84, 127.80, 127.70, 127.61, 127.31, 125.32, 105.16, 73.24, 70.14; $[M+H]^+$: exact mass: 278.0265 obtained mass: 278.0265.



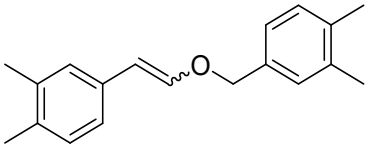
1-bromo-4-(2-((4-bromobenzyl)oxy)vinyl)benzene(4c, E/Z=94/6): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 6.0 Hz, 4H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.98 – 6.94 (m, 1H), 5.80 (d, *J* = 12.9 Hz, 1H), 4.77 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.84, 134.00, 130.63, 128.13, 127.60, 125.68, 121.12, 121.01, 105.21, 70.17; $[M+H]^{+}$: exact mass: 367.9234 obtained mass: 367.9235.



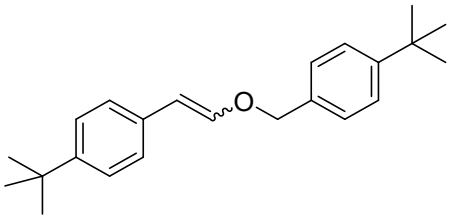
(E)-1-fluoro-4-(2-((4-fluorobenzyl)oxy)vinyl)benzene (4d): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 8.5, 5.6 Hz, 4H), 6.90 (t, *J* = 8.7 Hz, 5H), 4.48 (s, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.47, 160.03, 135.60, 135.57, 127.75, 127.66, 114.40, 114.19, 63.43; $[M+H]^{+}$: exact mass: 246.0856 obtained mass: 246.0855.



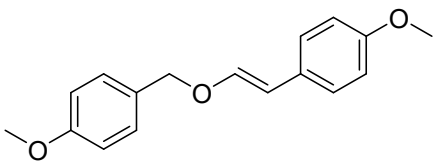
(E)-1-methyl-4-(2-((4-methylbenzyl)oxy)vinyl)benzene (4e): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 1H), 7.03 (d, *J* = 4.9 Hz, 1H), 5.92 (d, *J* = 12.9 Hz, 1H), 4.83 (s, 2H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.08, 136.84, 134.31, 128.24, 126.73, 124.03, 105.68, 70.81, 20.02; $[M+H]^{+}$: exact mass: 238.1358 obtained mass: 238.1357.



4-(2-((3,4-dimethylbenzyl)oxy)vinyl)-1,2-dimethylbenzene (4f, E/Z=94/6): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.09 (m, 3H), 7.02 (dd, *J* = 10.4, 2.5 Hz, 3H), 6.97 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 12.9 Hz, 1H), 4.81 (s, 2H), 2.27 (d, *J* = 4.7 Hz, 6H), 2.22 (d, *J* = 4.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.04, 135.81, 133.19, 128.81, 128.77, 128.11, 125.50, 124.27, 121.54, 105.65, 70.89, 18.76, 18.73, 18.49, 18.32; $[M+H]^+$: exact mass: 266.2671 obtained mass: 266.1670.

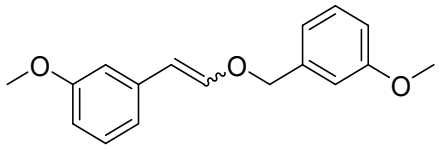


1-(tert-butyl)-4-(2-((4-(tert-butyl)benzyl)oxy)vinyl)benzene (4g, E/Z=94/6): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 1.8 Hz, 1H), 7.40 (s, 1H), 7.33 (s, 1H), 7.32 – 7.29 (m, 2H), 7.28 (s, 1H), 7.18 – 7.16 (m, 2H), 7.05 (d, *J* = 12.9 Hz, 1H), 5.95 (d, *J* = 12.9 Hz, 1H), 4.86 (s, 2H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.15, 147.36, 133.80, 133.43, 129.33, 127.55, 126.93, 125.98, 125.54, 125.51, 124.88, 106.53, 71.76, 34.61, 34.41, 31.37, 31.34, 31.32; $[M+H]^+$: exact mass: 322.2297 obtained mass: 322.2298.

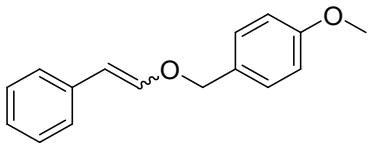


(E)-1-methoxy-4-(2-((4-methoxybenzyl)oxy)vinyl)benzene (4h): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.7 Hz, 4H), 4.54 (s, 4H),

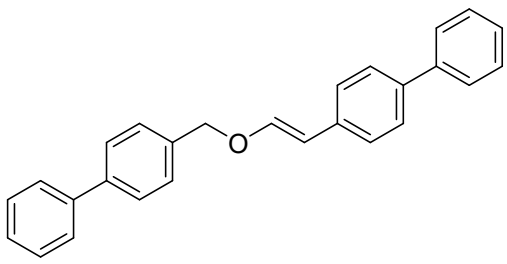
3.76 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.11, 132.15, 127.60, 112.89, 63.85, 63.84, 54.25; $[M+H]^+$: exact mass: 270.1256 obtained mass: 270.1256.



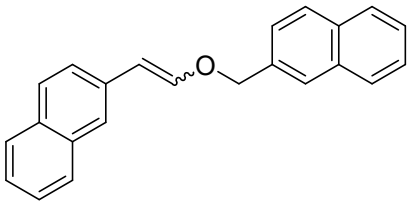
1-methoxy-3-(2-((3-methoxybenzyl)oxy)vinyl)benzene (4i, E/Z=94/6): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 12.9 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.90 – 6.81 (m, 2H), 6.77 (t, *J* = 2.1 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.94 (d, *J* = 12.8 Hz, 1H), 4.88 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.84, 158.82, 146.91, 137.24, 136.68, 128.63, 128.52, 118.72, 116.77, 112.71, 111.91, 110.19, 109.83, 105.85, 70.77, 54.24, 54.22, 54.15; $[M+H]^+$: exact mass: 270.1256 obtained mass: 270.1255.



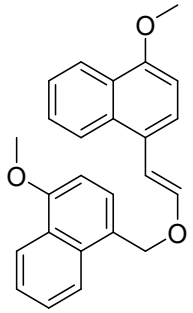
1-methoxy-4-((styryloxy)methyl)benzene (4j, E/Z=96/4): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.16 (dd, *J* = 8.4, 6.1 Hz, 3H), 7.10 – 6.97 (m, 2H), 6.88 – 6.72 (m, 1H), 5.94 – 5.83 (m, 1H), 5.04 (s, 2H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.72, 147.51, 135.76, 129.20, 128.42, 128.40, 128.08, 127.43, 113.85, 106.73, 71.73, 66.14, 55.12; $[M+H]^+$: exact mass: 240.1150 obtained mass: 240.1151.



(E)-4-(((2-([1,1'-biphenyl]-4-yl)vinyl)oxy)methyl)-1,1'-biphenyl (4k): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 8H), 7.47 – 7.42 (m, 8H), 7.35 (t, *J* = 7.3 Hz, 2H), 4.75 (s, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.85, 140.69, 139.89, 128.80, 127.48, 127.36, 127.34, 127.12, 65.15; $[M+H]^{+}$: exact mass: 362.1671 obtained mass: 362.1670.

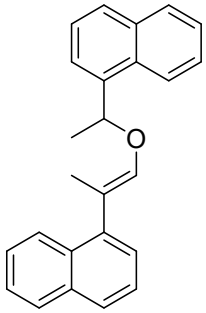


2-(((2-(naphthalen-2-yl)vinyl)oxy)methyl)naphthalene (4l, E/Z=91/9): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.81 (m, 4H), 7.74 (dd, *J* = 13.3, 8.1 Hz, 3H), 7.59 (s, 1H), 7.54 – 7.48 (m, 3H), 7.45 – 7.33 (m, 3H), 7.28 (s, 1H), 6.18 (d, *J* = 12.8 Hz, 1H), 5.12 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.07, 133.17, 132.87, 132.68, 132.27, 131.04, 127.47, 127.13, 126.97, 126.74, 126.59, 126.41, 125.54, 125.30, 125.17, 125.15, 124.32, 124.01, 122.87, 122.26, 106.36, 71.22; $[M+H]^{+}$: exact mass: 310.1358 obtained mass: 310.1355.

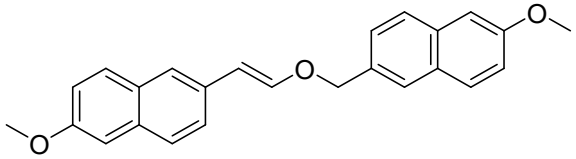


(E)-1-methoxy-4-(2-((4-methoxynaphthalen-1-yl)methoxy)vinyl)naphthalene (4m): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.10 – 7.98 (m, 2H), 7.58 – 7.45 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 12.6 Hz, 1H), 6.77 (dd, *J* = 18.0, 7.9 Hz, 1H), 6.64 – 6.57 (m, 1H), 6.36 (d, *J* = 12.7

Hz, 1H), 4.14 (s, 1H), 4.11 (d, *J* = 7.1 Hz, 6H), 4.08 (s, 1H), 3.97 (d, *J* = 14.5 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.14, 153.23, 152.64, 134.01, 132.85, 131.85, 127.06, 125.55, 125.38, 124.81, 123.97, 123.26, 122.84, 122.34, 121.58, 121.21, 106.06, 102.34, 59.38; $[M+H]^+$: exact mass: 370.1569 obtained mass: 370.1568.

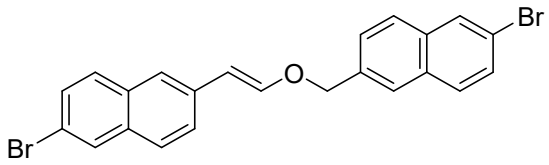


(E)-1-(1-(1-(naphthalen-1-yl)ethoxy)prop-1-en-2-yl)naphthalene (4n): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.0 Hz, 2H), 7.52 (dd, *J* = 11.5, 7.0 Hz, 4H), 5.11 (s, 1H), 4.06 (t, *J* = 6.9 Hz, 1H), 2.75 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.74, 134.60, 134.47, 132.97, 132.03, 130.08, 129.27, 129.13, 128.47, 128.21, 127.65, 127.39, 127.06, 125.43, 125.00, 123.31, 120.09, 66.75, 28.69, 13.11; $[M+H]^+$: exact mass: 338.1671 obtained mass: 338.1670.

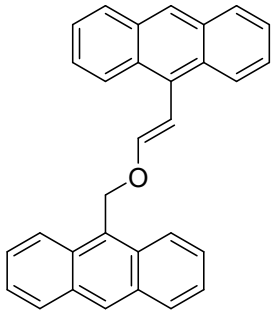


(E)-2-methoxy-6-(2-((6-methoxynaphthalen-2-yl)methoxy)vinyl)naphthalene (4o): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.74 – 7.61 (m, 5H), 7.57 (s, 2H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.09 (d, *J* = 3.4 Hz, 2H), 6.86 (s, 1H), 6.56 – 6.42 (m, 2H), 6.23 (d, *J* = 10.8 Hz, 1H), 3.91 (d, *J* = 2.7 Hz, 6H); ^{13}C

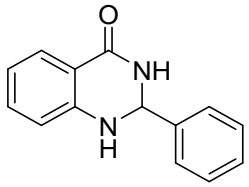
NMR (151 MHz, Chloroform-*d*) δ 156.49, 132.55, 131.56, 128.31, 128.12, 126.11, 124.07, 123.97, 123.49, 122.65, 117.99, 104.85, 54.30; $[M+H]^+$: exact mass: 370.1569 obtained mass: 370.1568.



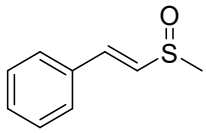
(E)-2-bromo-6-(2-((6-bromonaphthalen-2-yl)methoxy)vinyl)naphthalene (4p): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 7.99 (m, 1H), 7.94 (dd, *J* = 19.1, 6.3 Hz, 1H), 7.86 – 7.68 (m, 4H), 7.67 – 7.52 (m, 3H), 7.51 – 7.31 (m, 3H), 5.13 (d, *J* = 36.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.94, 128.82, 128.72, 128.66, 128.60, 128.53, 128.05, 127.17, 126.59, 126.56, 126.41, 126.26, 125.38, 125.30, 125.19, 125.16, 125.09, 123.28, 106.47, 70.90; $[M+H]^+$: exact mass: 467.9547 obtained mass:467.9548.



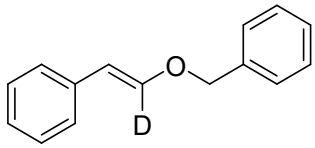
(E)-9-(((2-(anthracen-9-yl)vinyl)oxy)methyl)anthracene (4q): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.28 – 8.20 (m, 2H), 7.94 (d, *J* = 9.6 Hz, 3H), 7.47 – 7.38 (m, 4H), 7.28 – 7.19 (m, 4H), 7.14 (d, *J* = 8.8 Hz, 4H), 3.88 (s, 2H), 3.03 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.61, 130.62, 130.42, 129.06, 128.00, 127.10, 126.32, 125.02, 124.27, 123.75, 35.09, 12.87; $[M+H]^+$: exact mass: 410.1671 obtained mass:410.1670.



2-phenyl-2,3-dihydroquinazolin-4(1H)-one(IV): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.69 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 2H), 7.89 – 7.79 (m, 2H), 7.60 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.55 – 7.49 (m, 1H), 7.26 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.07, 151.54, 135.01, 132.63, 131.85, 129.22, 127.96, 127.17, 126.98, 126.47, 120.91; exact mass: 224.0950 obtained mass:224.0951.



(E)-(2-(methylsulfinyl)vinyl)benzene(A): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H), 7.39 – 7.32 (m, 3H), 7.23 (d, *J* = 15.4 Hz, 1H), 6.88 (d, *J* = 15.5 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.10, 136.32, 133.73, 132.28, 129.74, 128.94, 127.65, 60.36, 40.95, 21.02, 14.19; exact mass: 166.0452 obtained mass:166.0452.



d-4a: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 4.1 Hz, 4H), 7.35 – 7.33 (m, 1H), 7.25 – 7.20 (m, 4H), 7.13 (t, *J* = 6.8 Hz, 1H), 5.95 (s, 1H), 4.90 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.66, 135.70, 128.60, 127.57, 127.34, 127.08, 126.67, 126.58, 124.74, 124.13, 105.66; exact mass: 211.1107 obtained mass:211.1107.

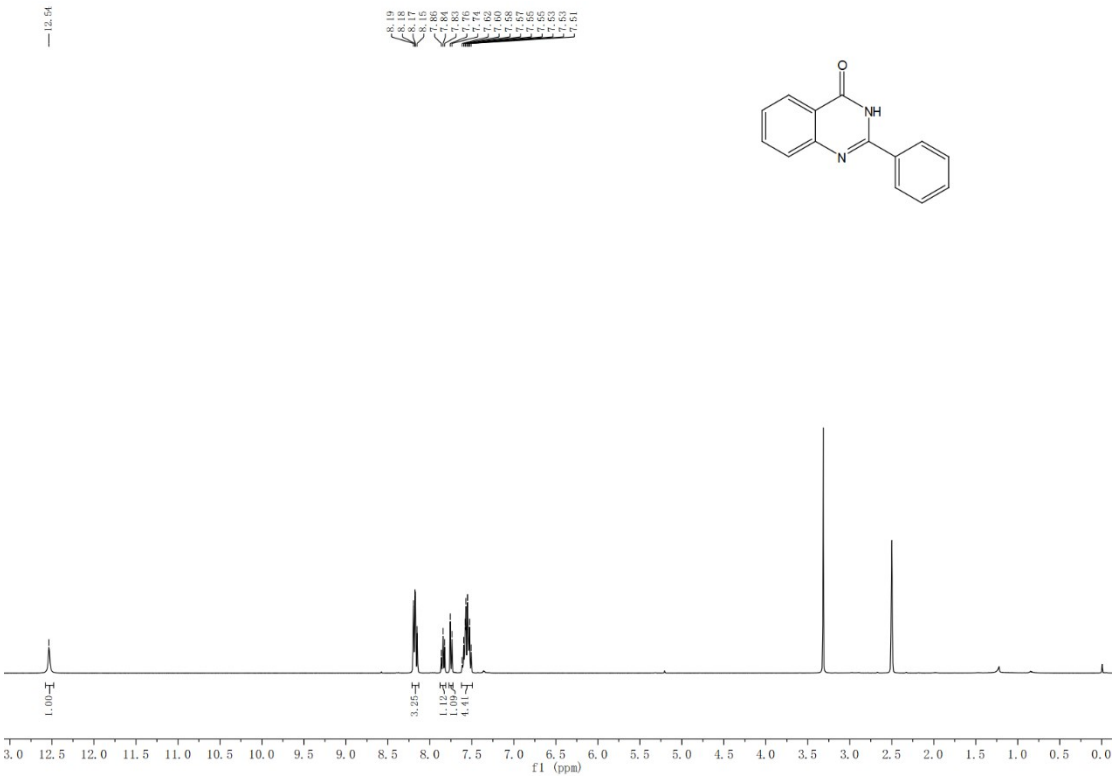


Figure S6. ^{1}H NMR spectrum of compound **3a**

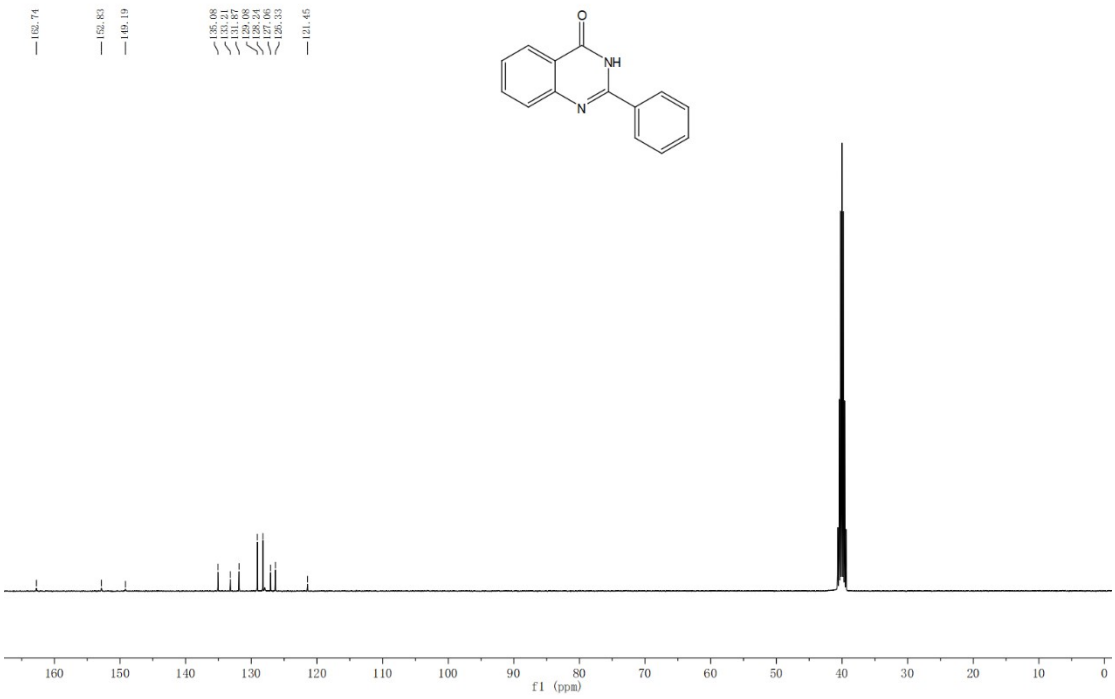


Figure S7. ^{13}C NMR spectrum of compound **3a**

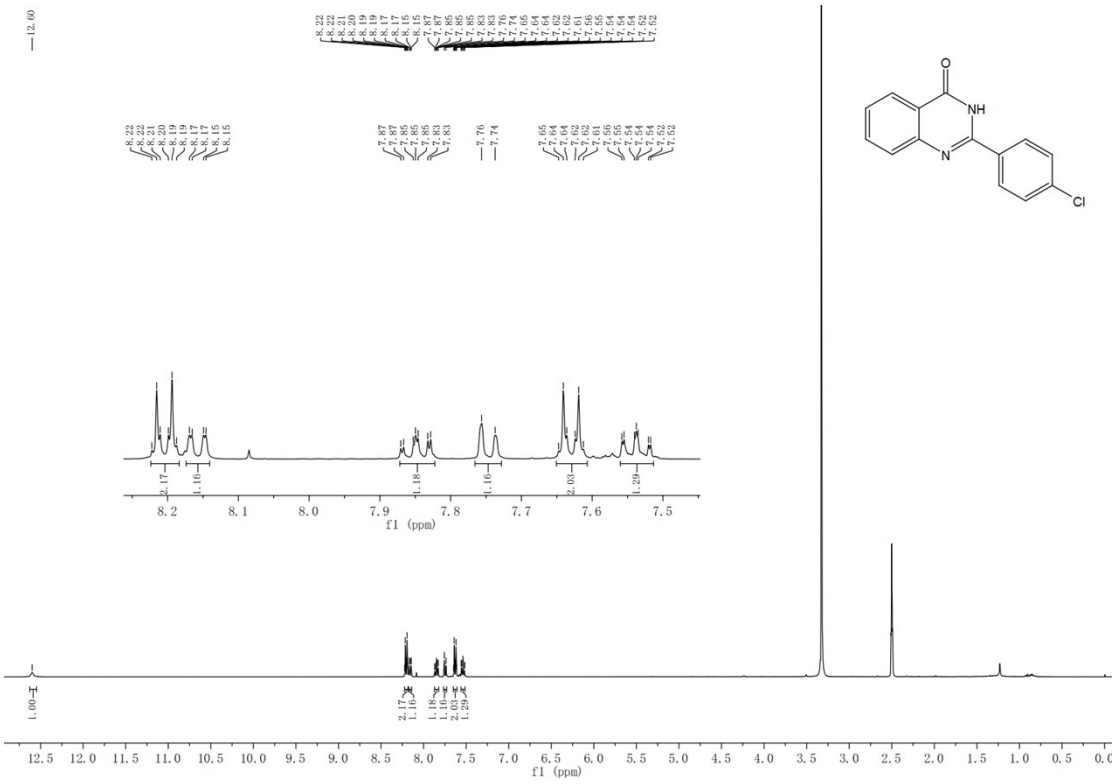


Figure S8. ^{1}H NMR spectrum of compound **3b**

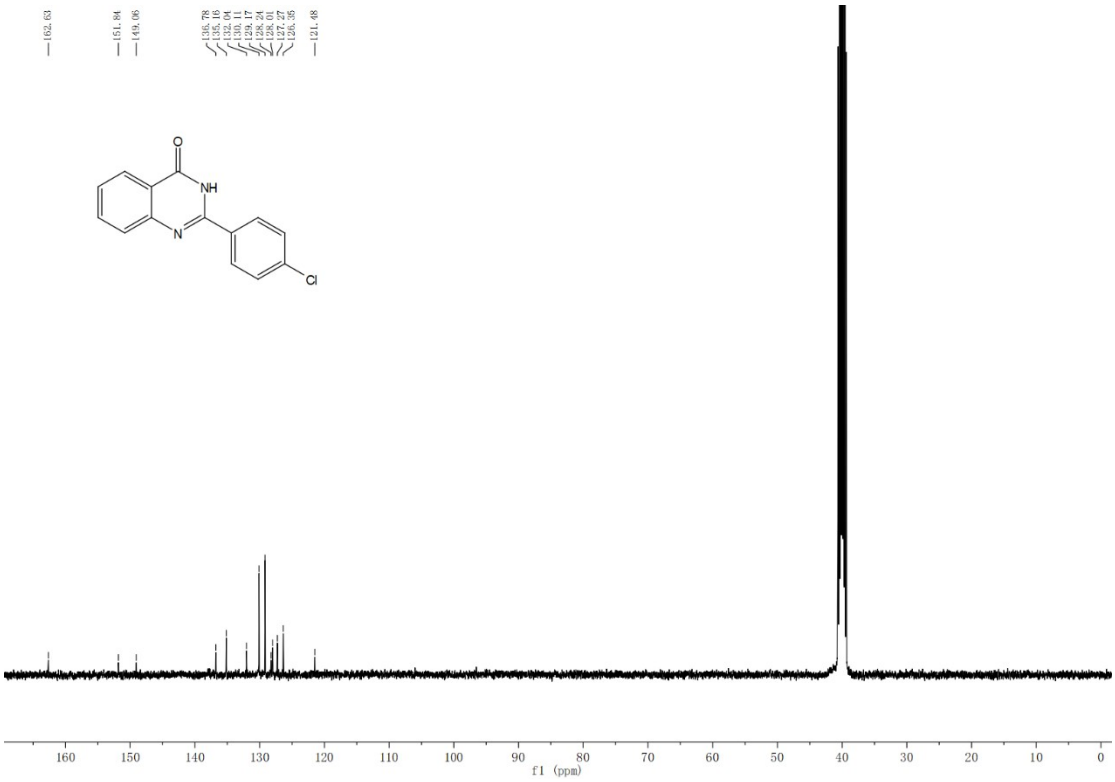


Figure S9. ^{13}C NMR spectrum of compound **3b**

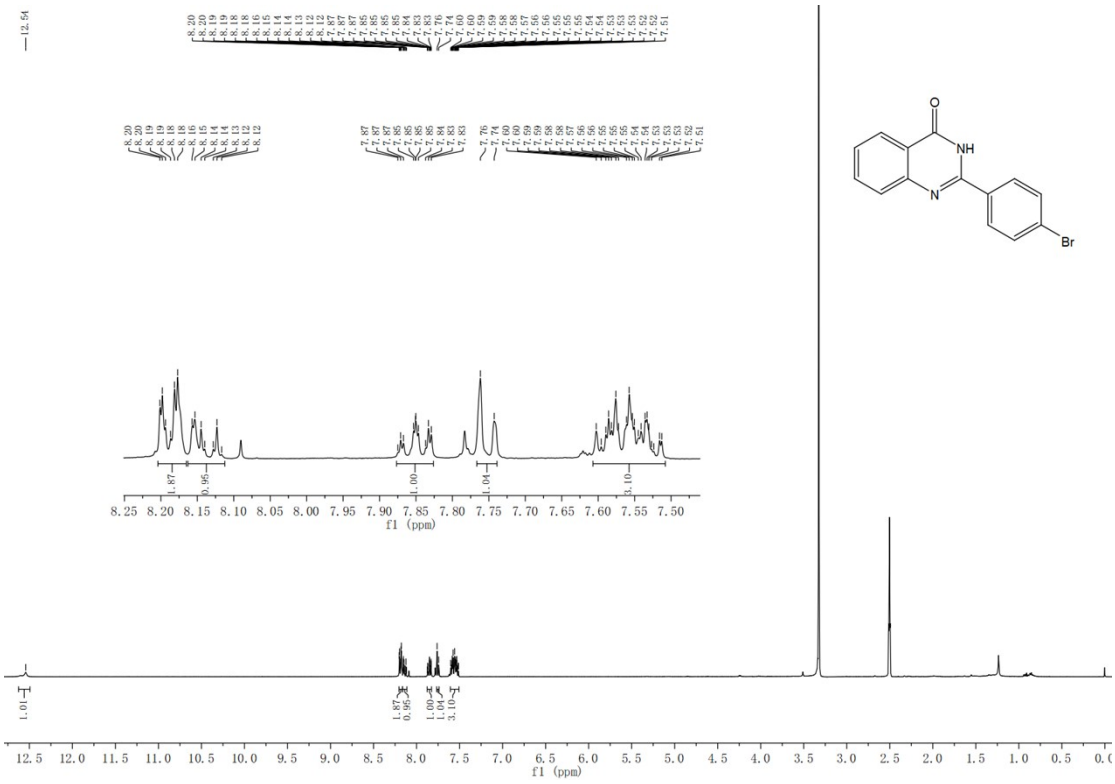


Figure S10. ^{1}H NMR spectrum of compound **3c**

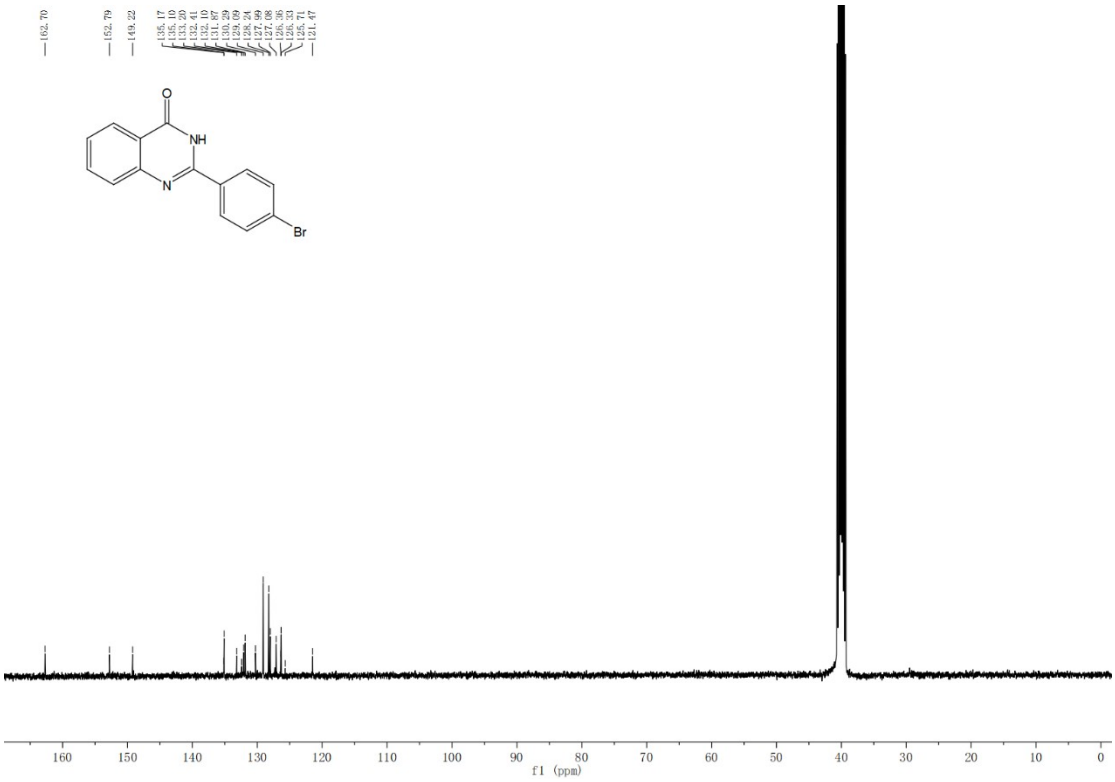


Figure S11. ^{13}C NMR spectrum of compound **3c**

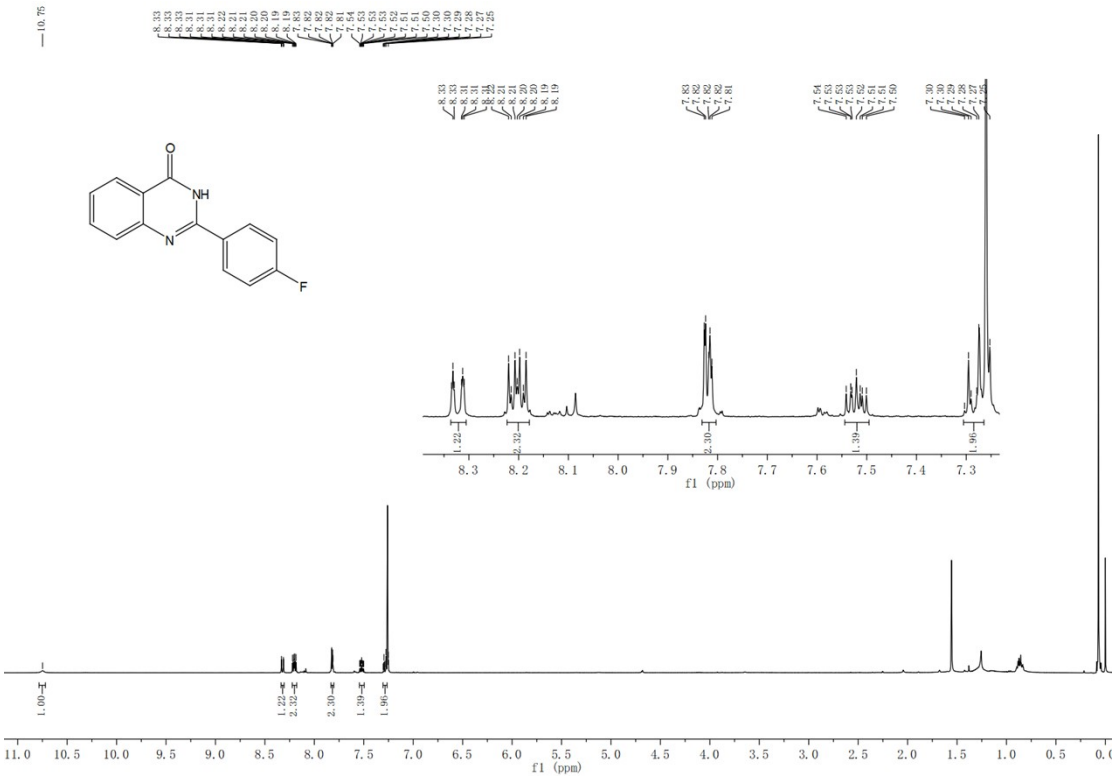


Figure S12. ^{1}H NMR spectrum of compound **3d**

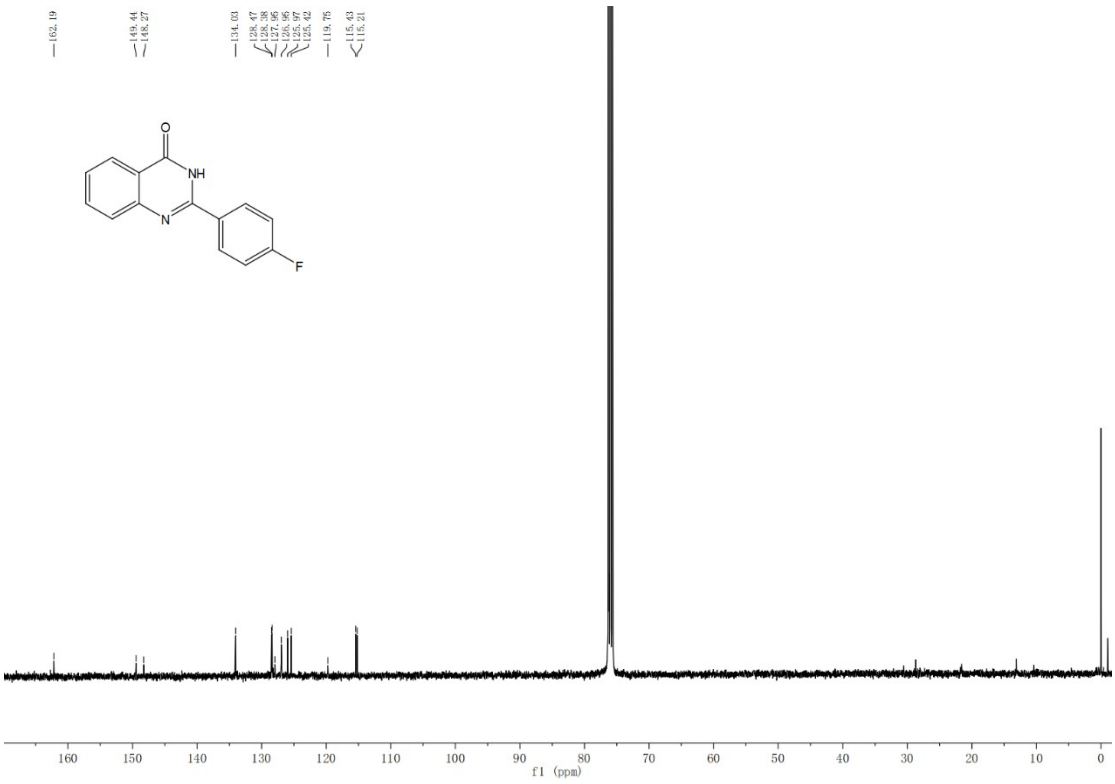


Figure S13. ^{13}C NMR spectrum of compound **3d**

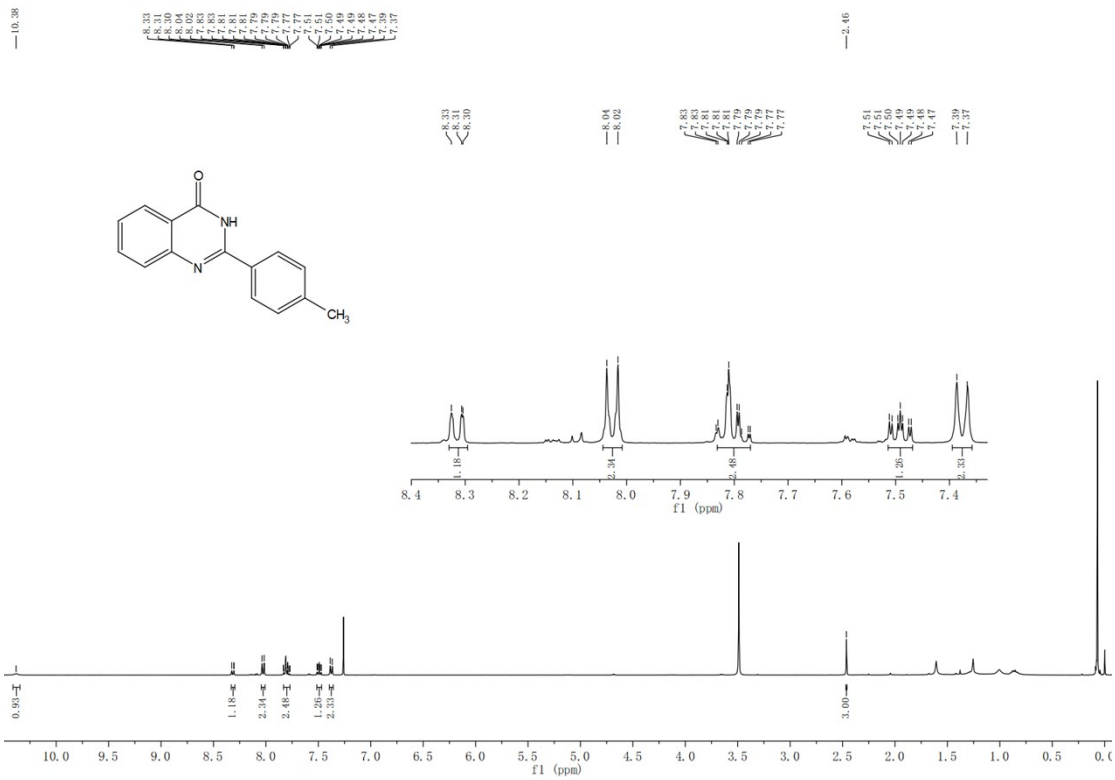


Figure S14. ^{1}H NMR spectrum of compound **3e**

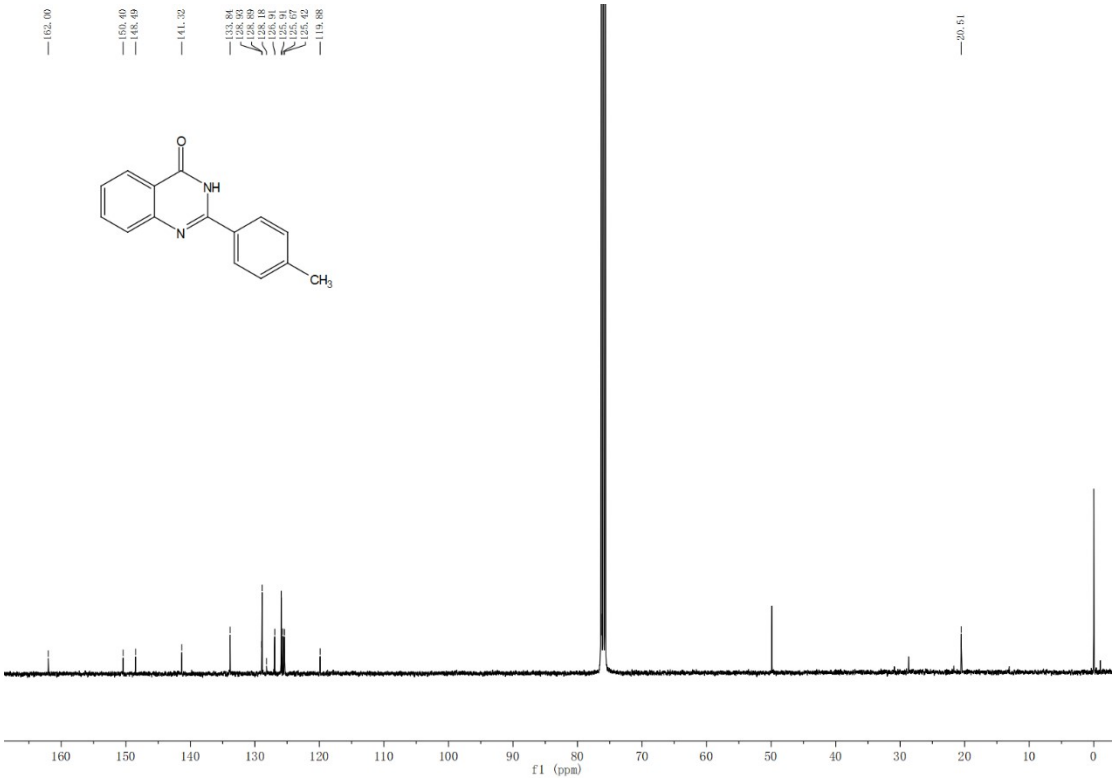


Figure S15. ^{13}C NMR spectrum of compound **3e**

Figure S16. ^{1}H NMR spectrum of compound **3f**

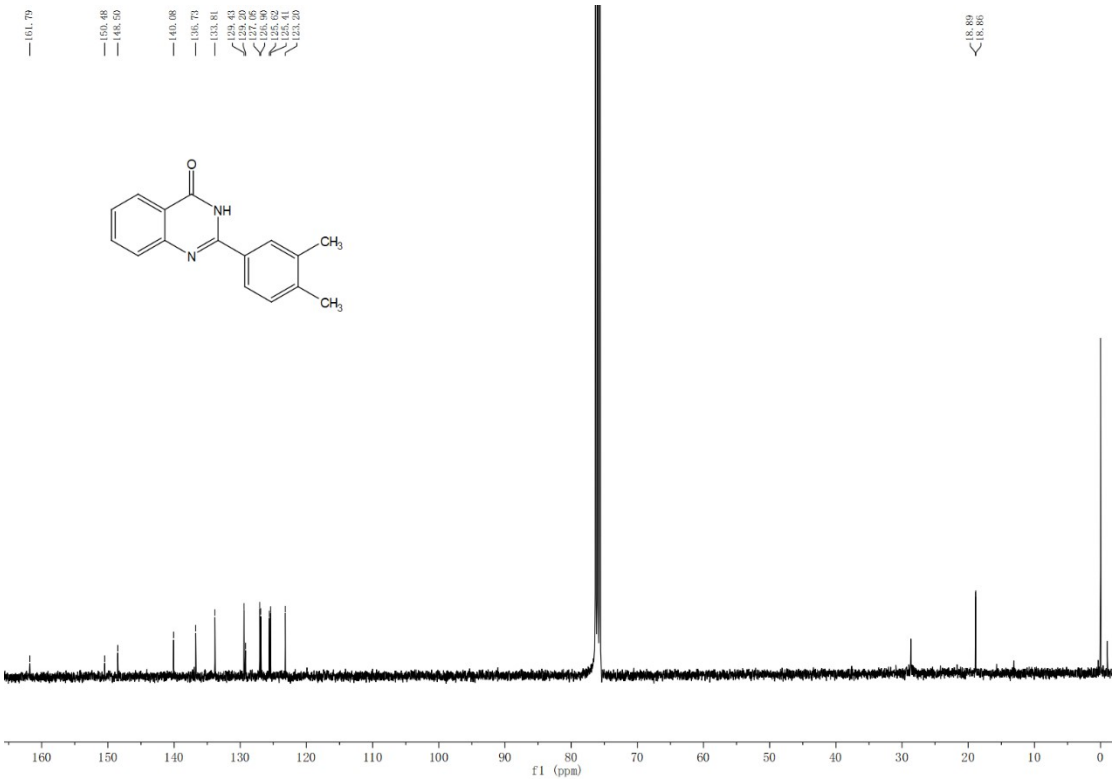


Figure S17. ^{13}C NMR spectrum of compound **3f**

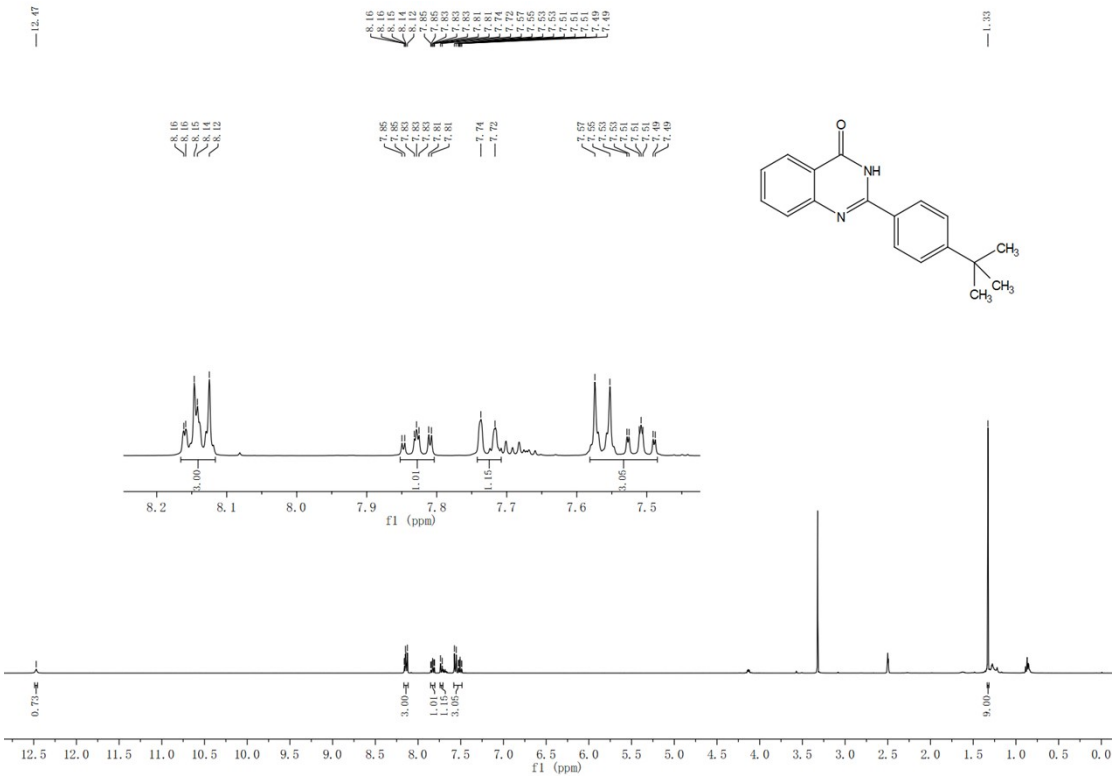


Figure S18. ^{1}H NMR spectrum of compound **3g**

Figure S19. ^{13}C NMR spectrum of compound **3g**

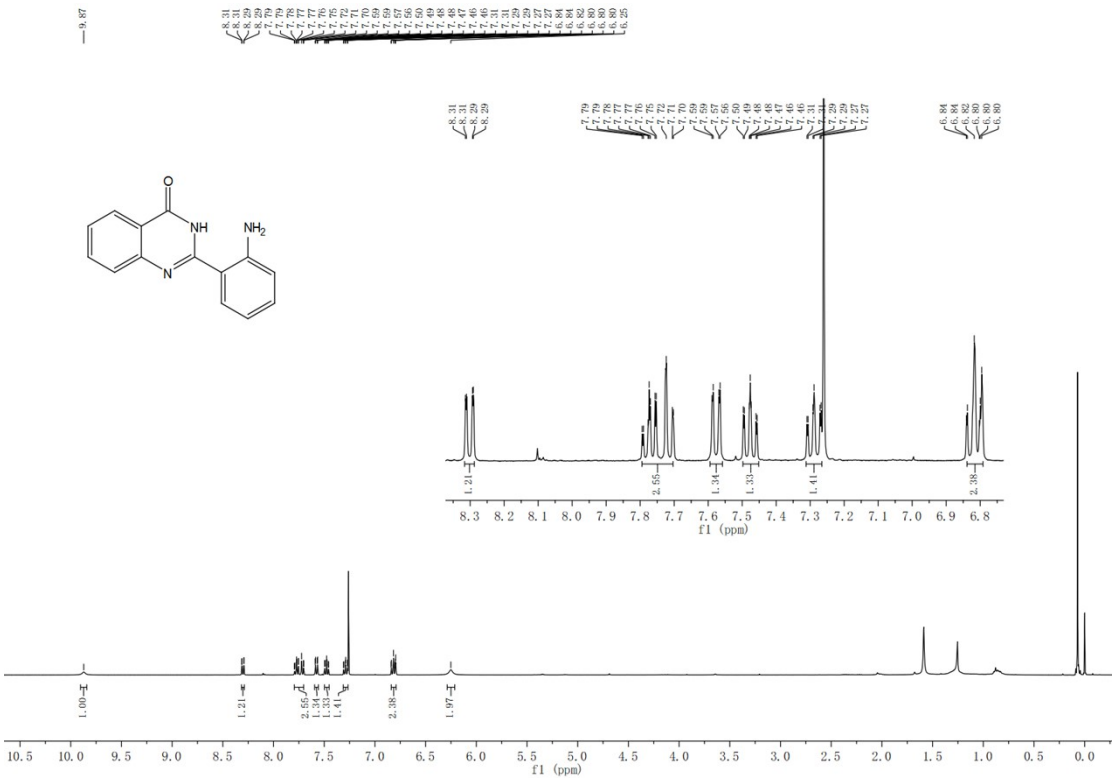


Figure S20. ^{1}H NMR spectrum of compound **3h**

Figure S21. ^{13}C NMR spectrum of compound **3h**

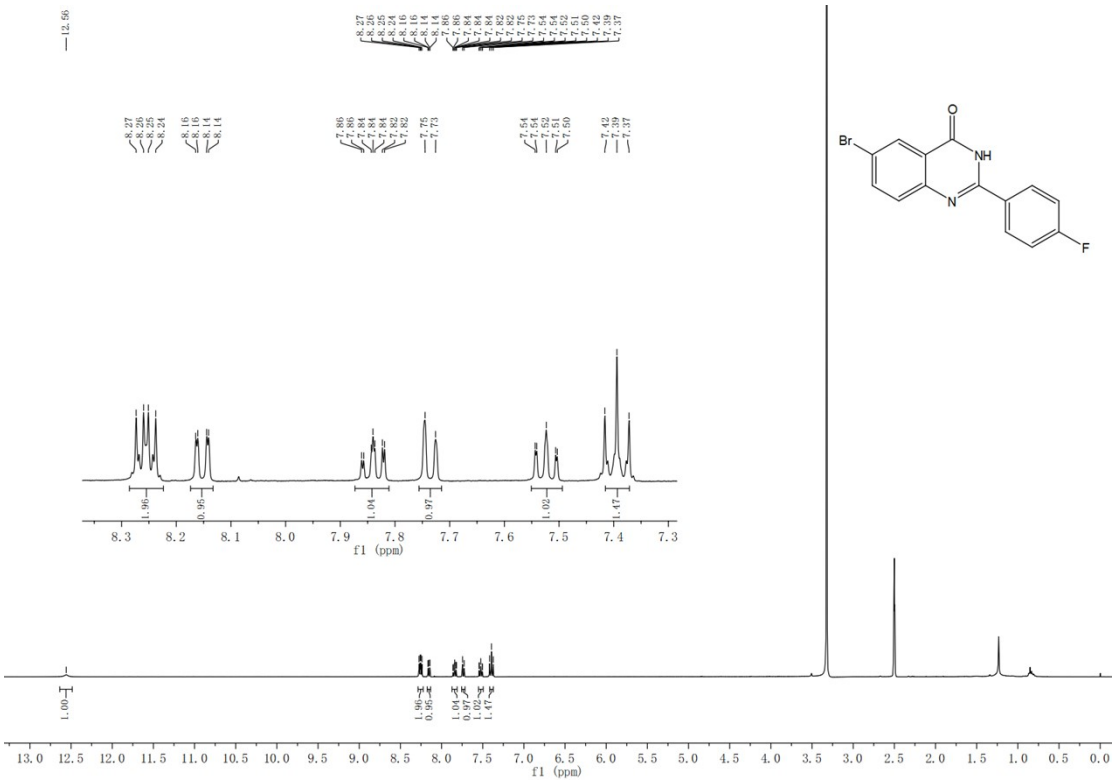


Figure S22. ^{1}H NMR spectrum of compound **3i**

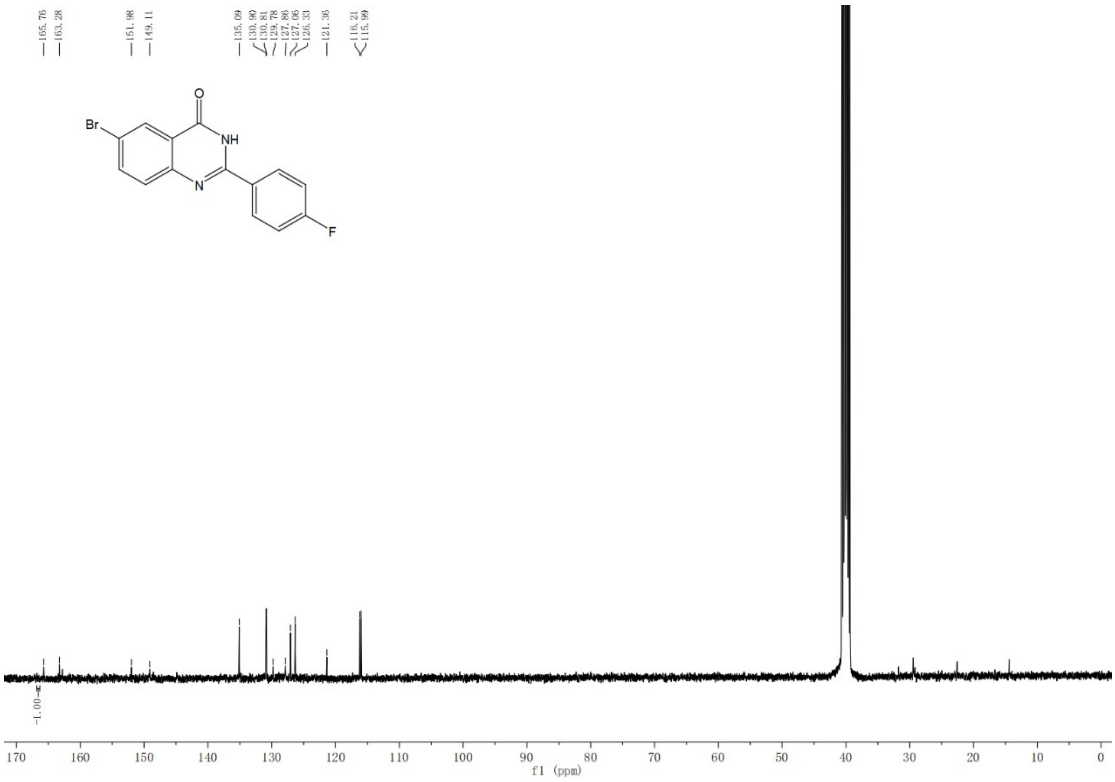


Figure S23. ^{13}C NMR spectrum of compound **3i**

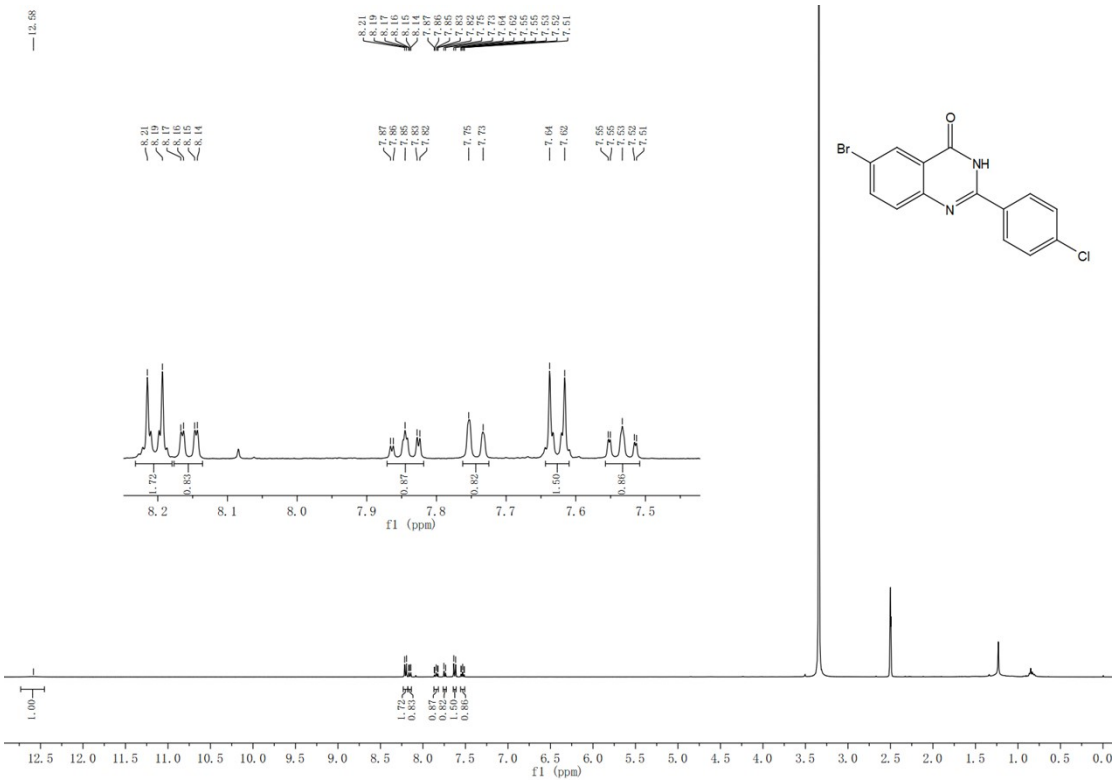


Figure S24. ^{1}H NMR spectrum of compound **3j**

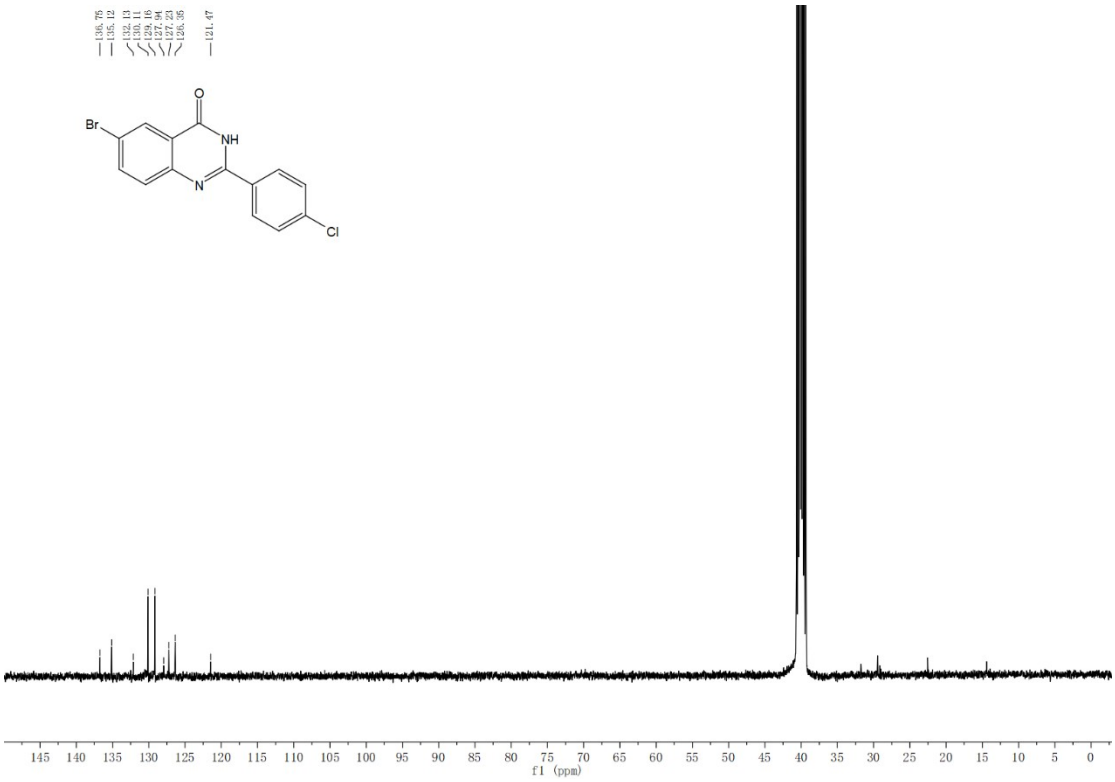


Figure S25. ^{13}C NMR spectrum of compound **3j**

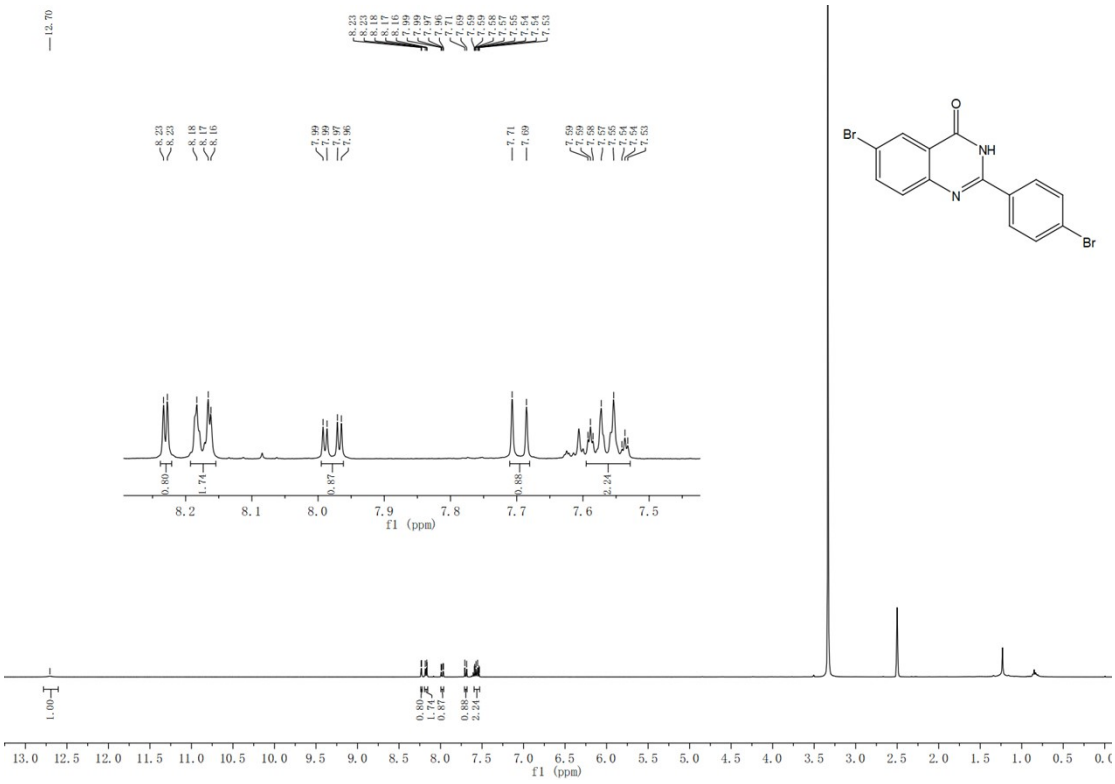


Figure S26. ^{1}H NMR spectrum of compound **3k**

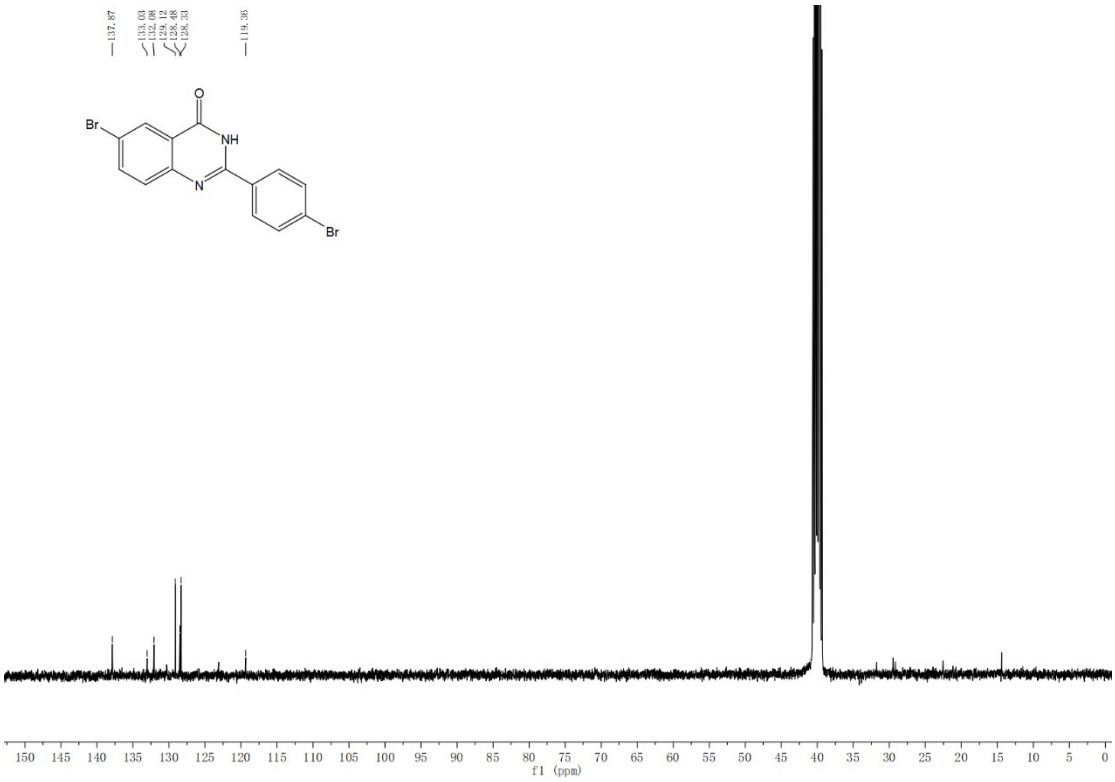


Figure S27. ^{13}C NMR spectrum of compound **3k**

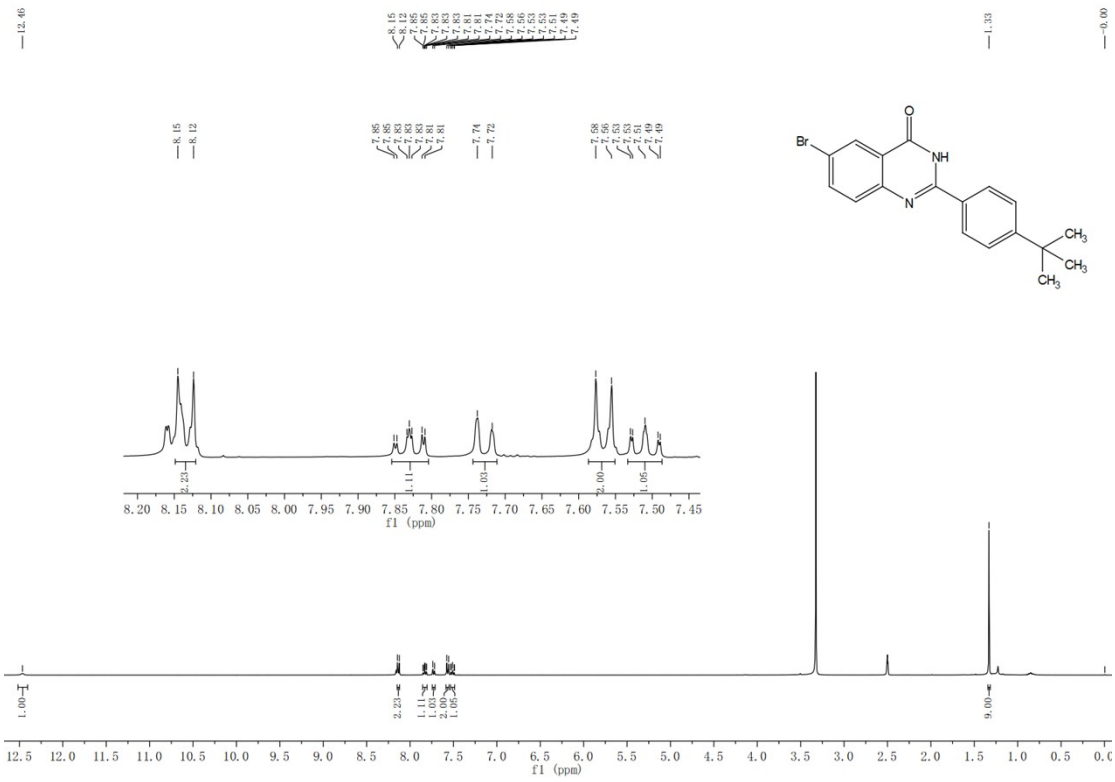


Figure S28. ^{1}H NMR spectrum of compound **3l**

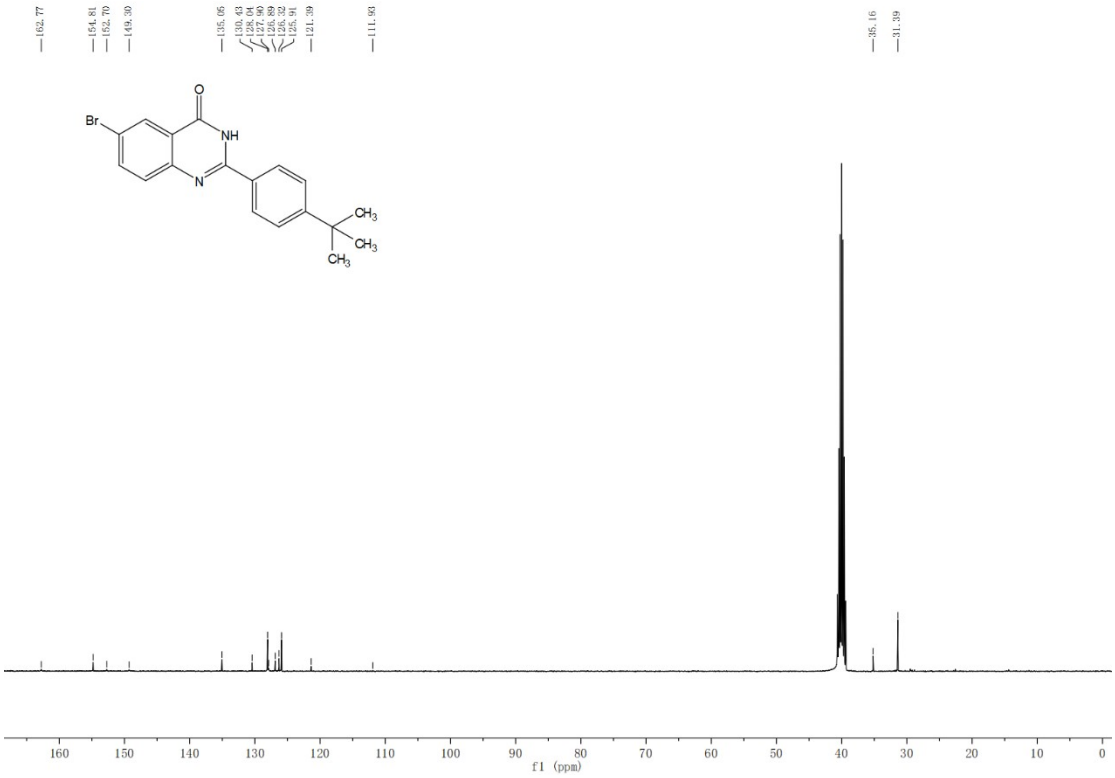


Figure S29. ^{13}C NMR spectrum of compound **3l**

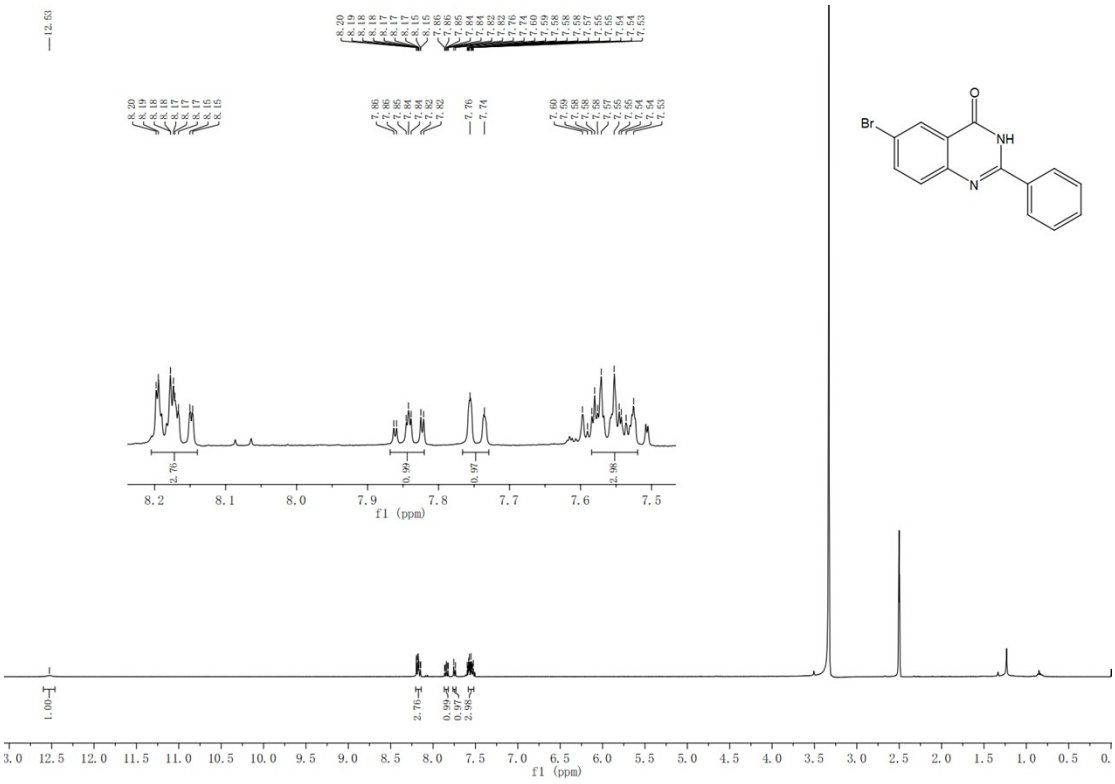


Figure S30. ^{1}H NMR spectrum of compound **3m**

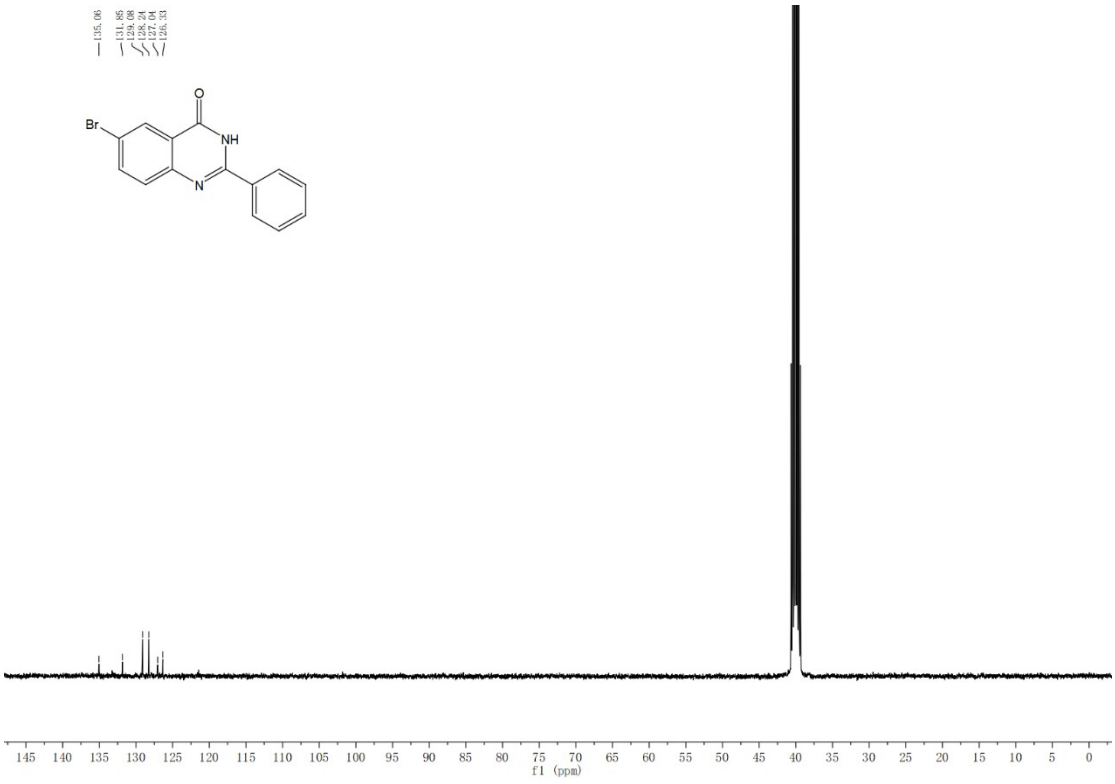


Figure S31. ^{13}C NMR spectrum of compound **3m**

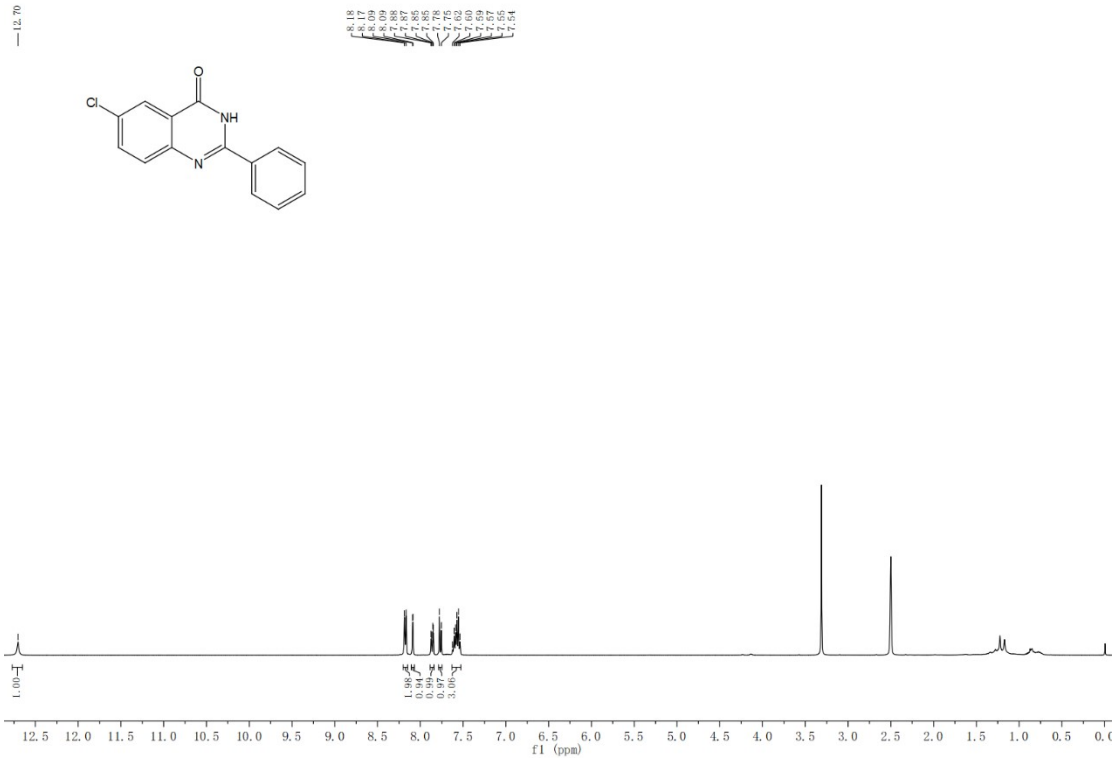


Figure S32. ^{1}H NMR spectrum of compound **3n**

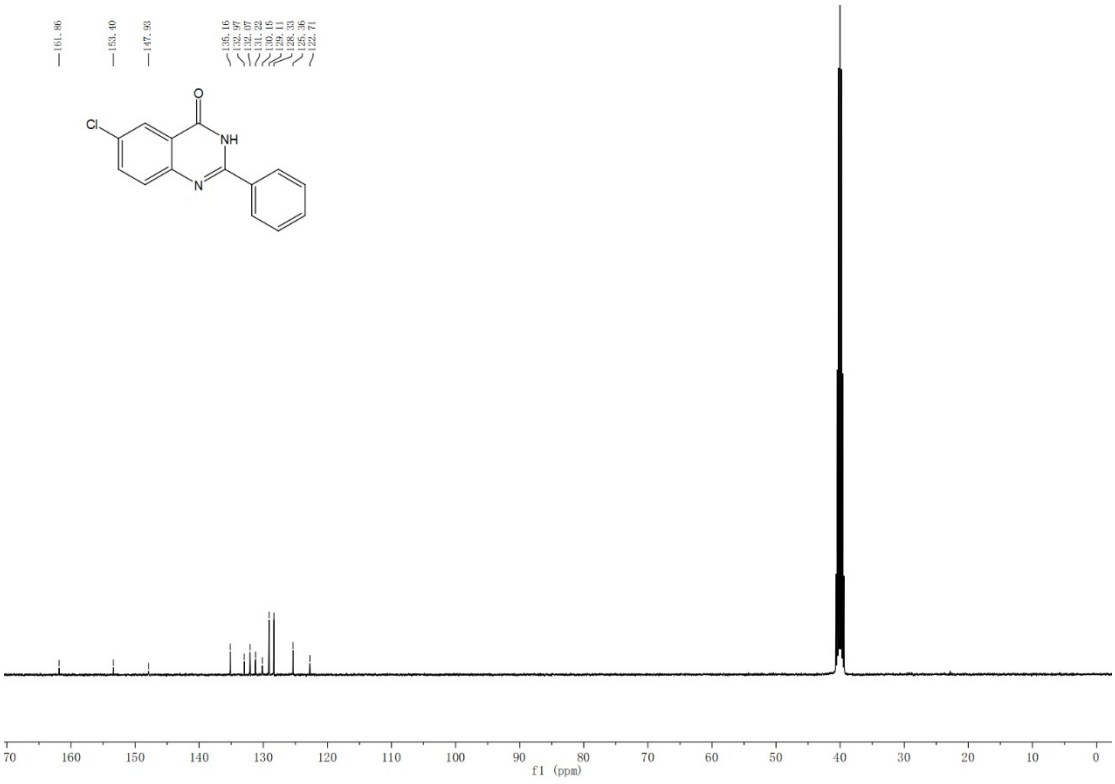


Figure S33. ^{13}C NMR spectrum of compound **3n**

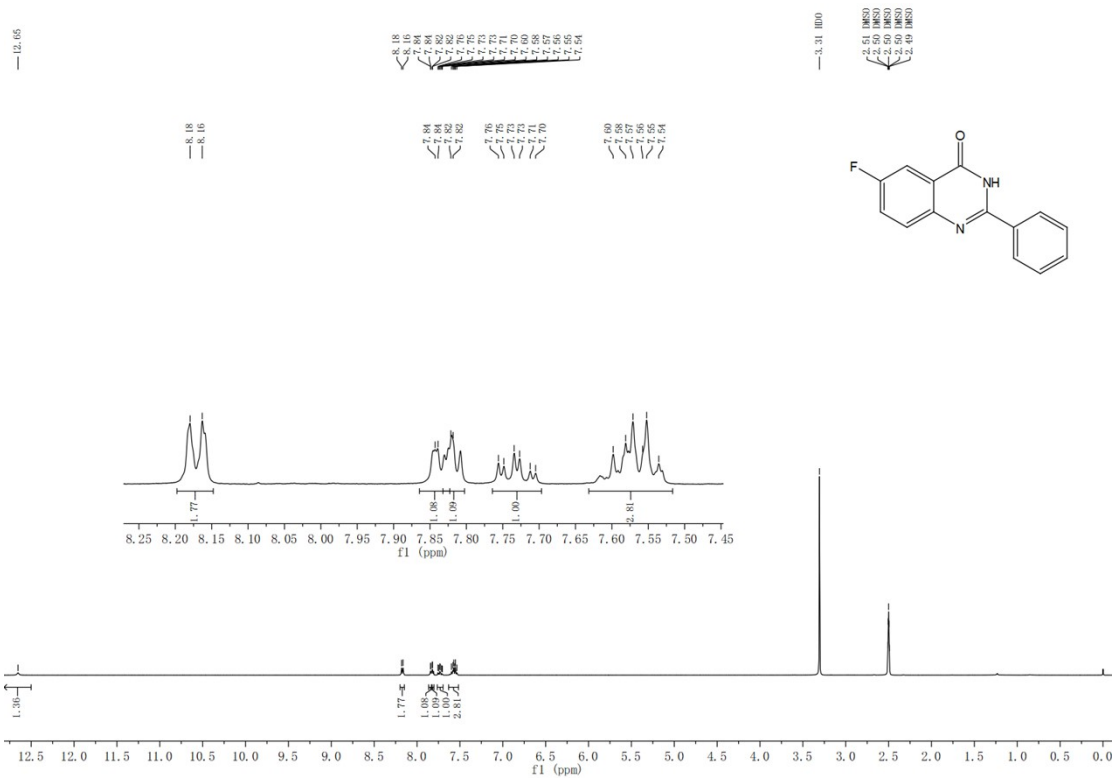


Figure S34. ^{1}H NMR spectrum of compound **3o**

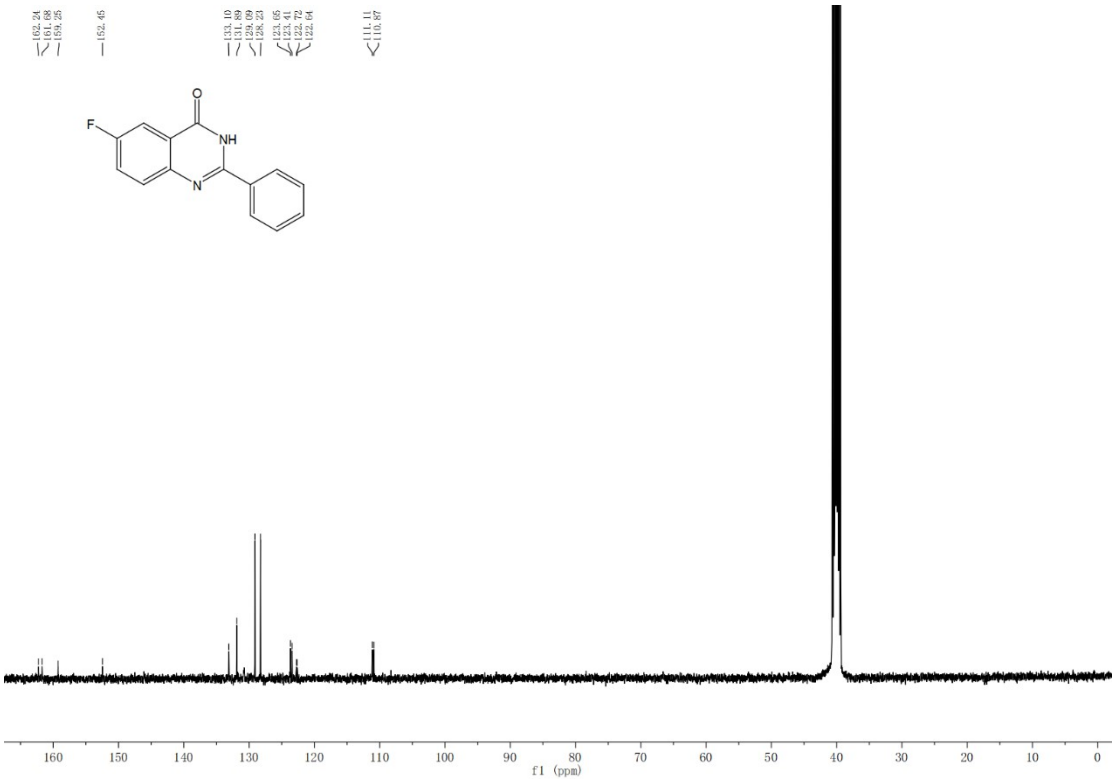


Figure S35. ^{13}C NMR spectrum of compound **3o**

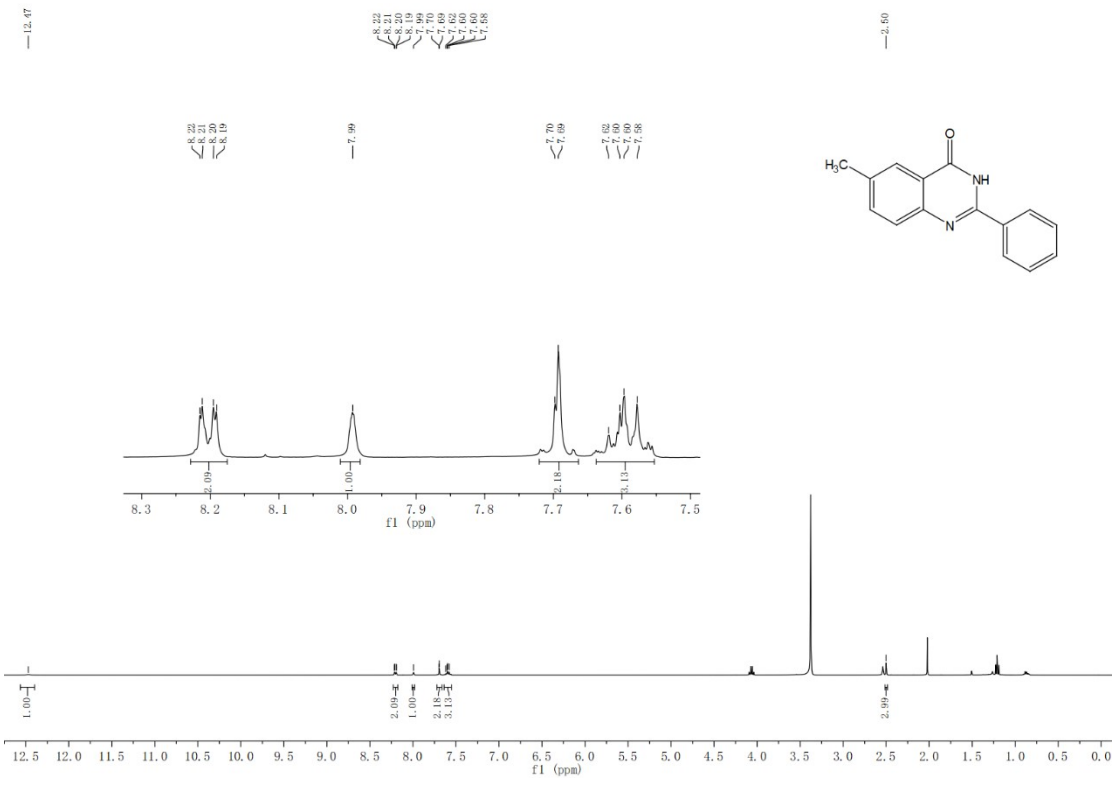


Figure S36. ^{1}H NMR spectrum of compound **3p**

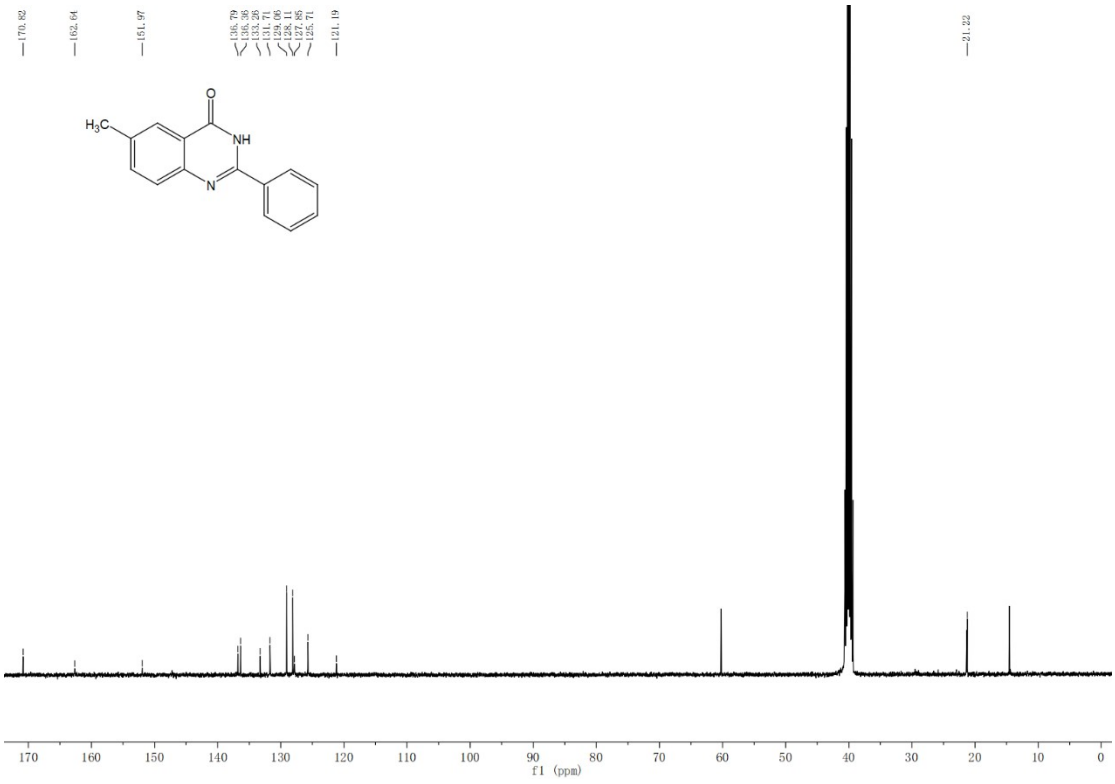


Figure S37. ^{13}C NMR spectrum of compound **3p**

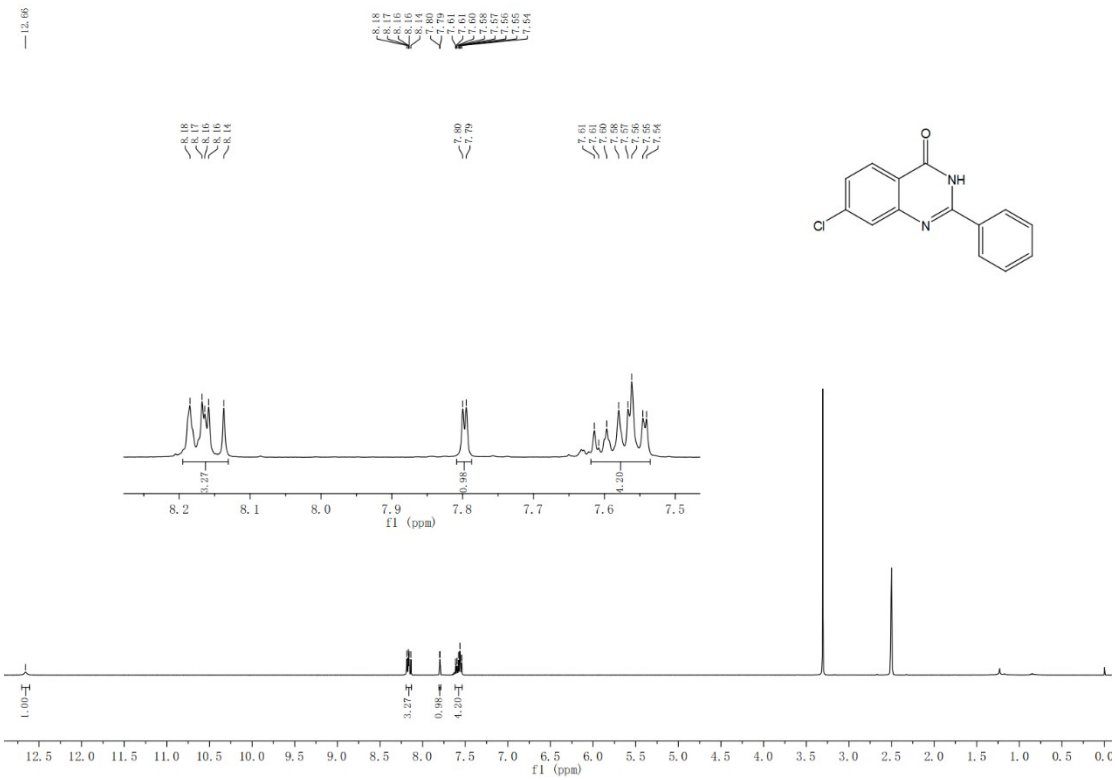


Figure S38. ^{1}H NMR spectrum of compound **3q**

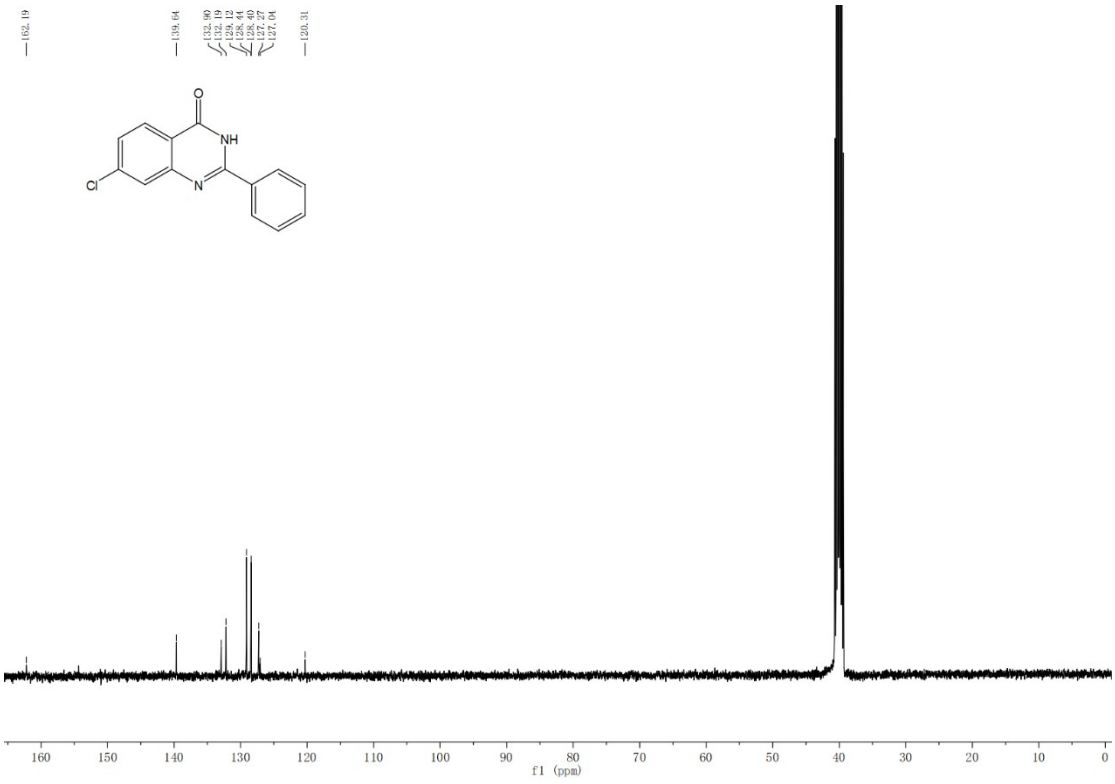


Figure S39. ^{13}C NMR spectrum of compound **3q**

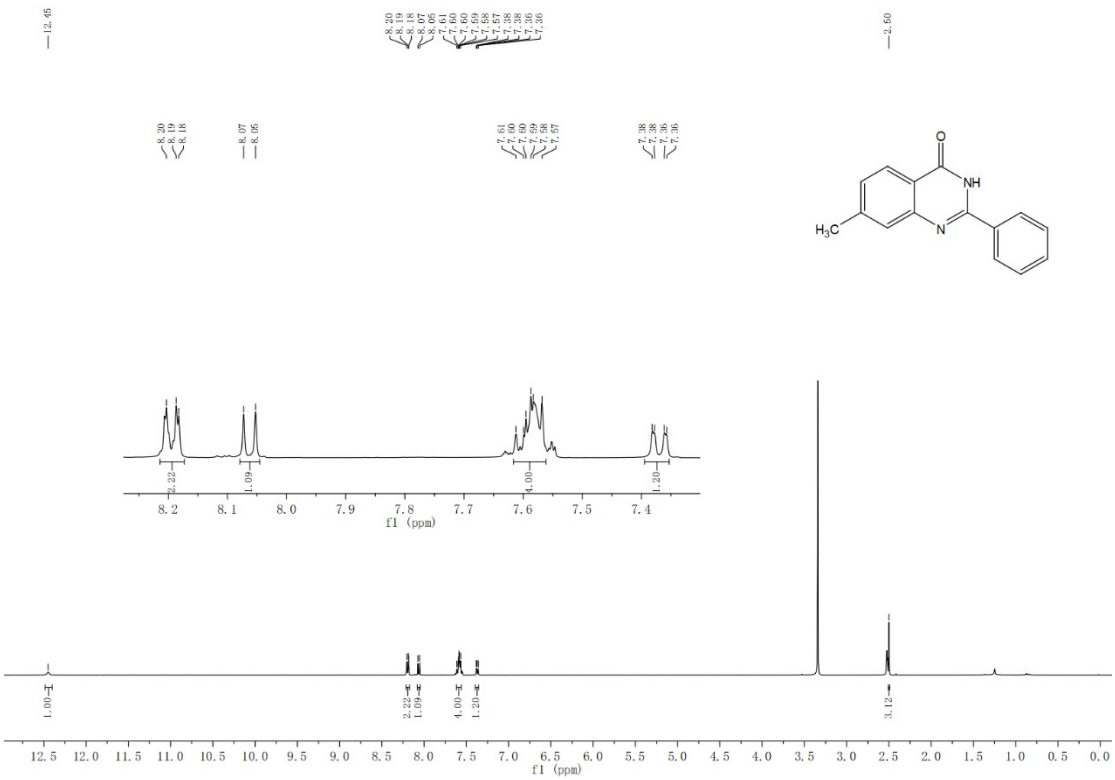


Figure S40. ^{1}H NMR spectrum of compound **3r**

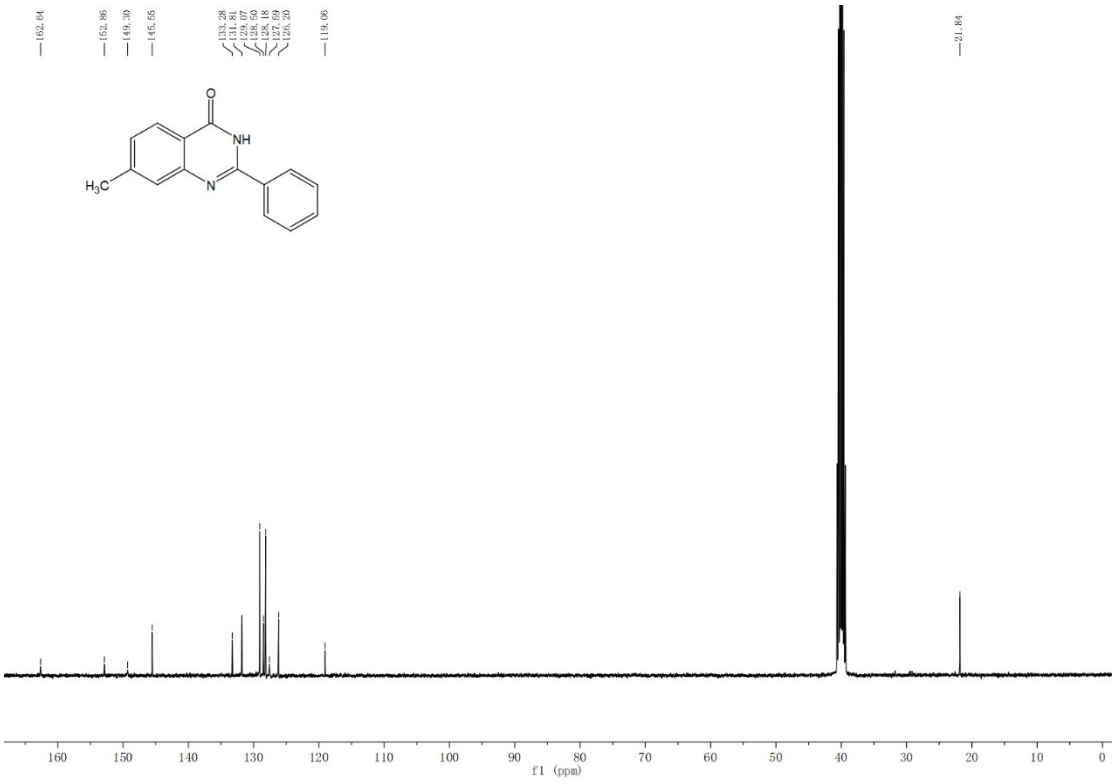


Figure S41. ^{13}C NMR spectrum of compound **3r**

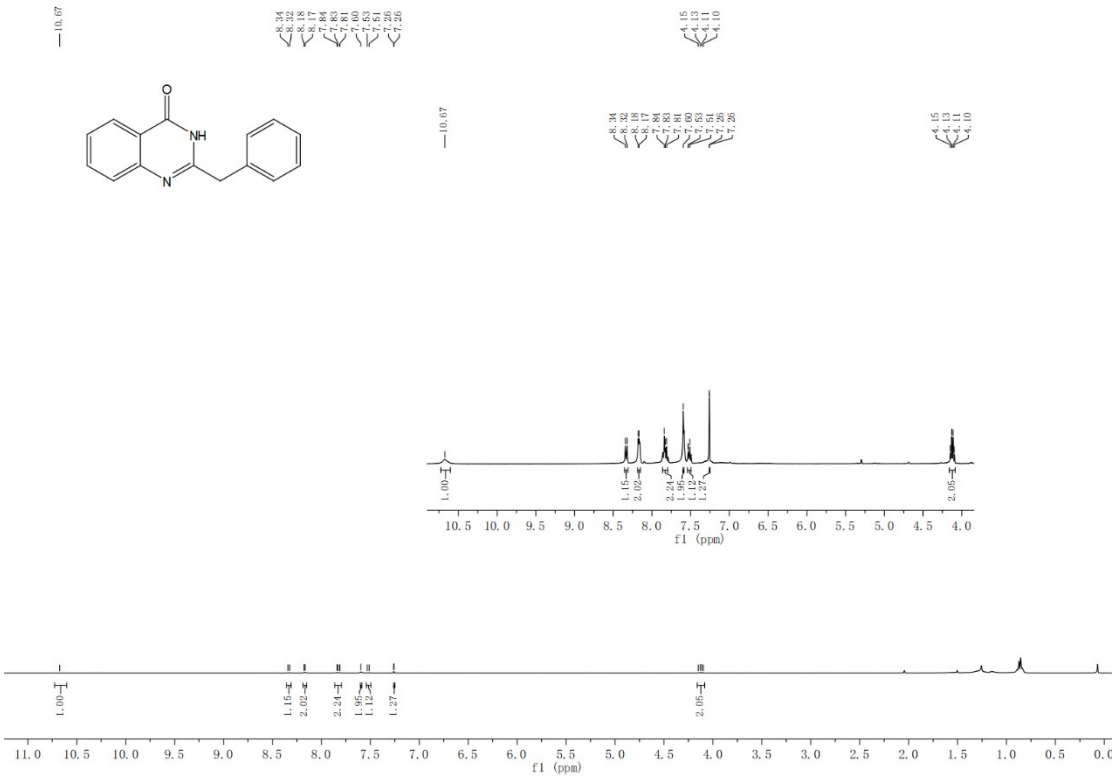


Figure S42. ^{1}H NMR spectrum of compound **3s**

Figure S43. ^{13}C NMR spectrum of compound **3s**

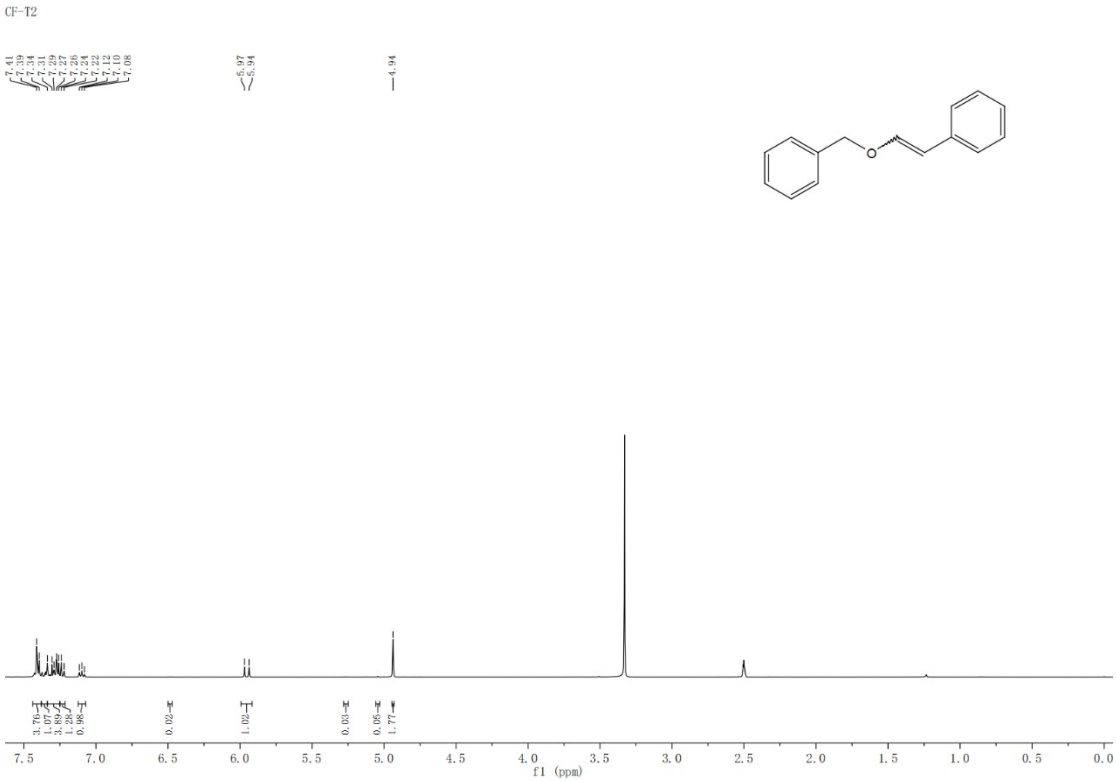


Figure S44. ^{1}H NMR spectrum of compound **4a**

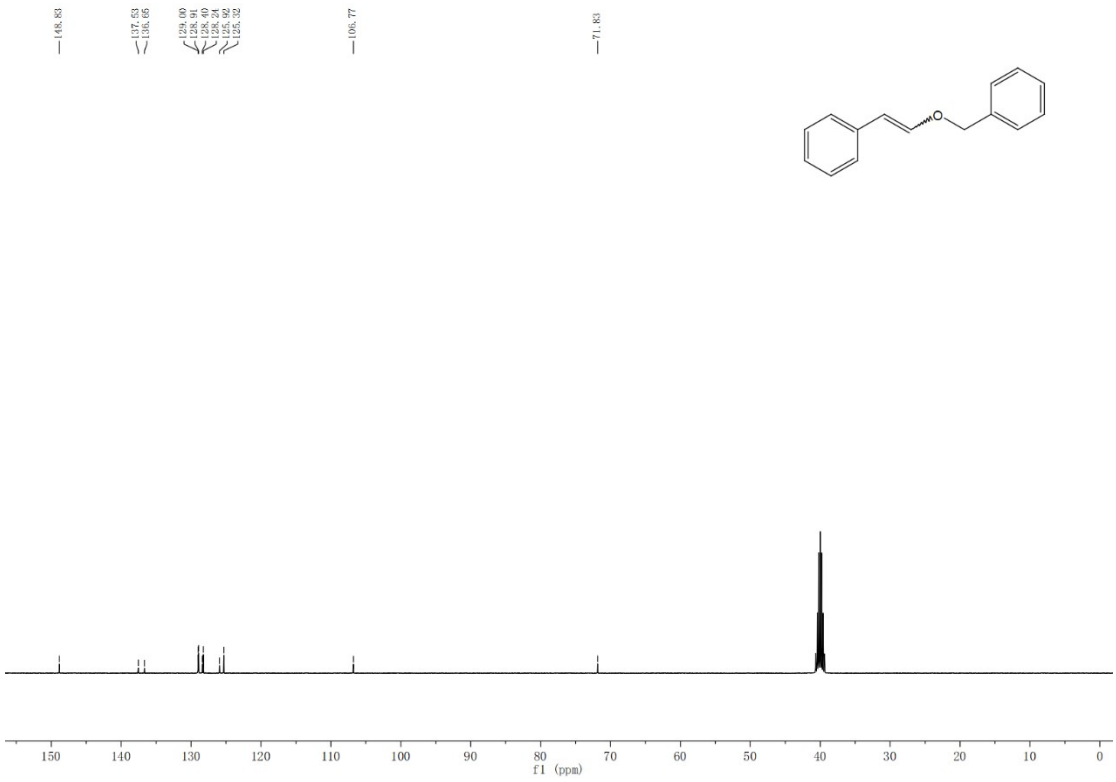


Figure S45. ^{13}C NMR spectrum of compound **4a**

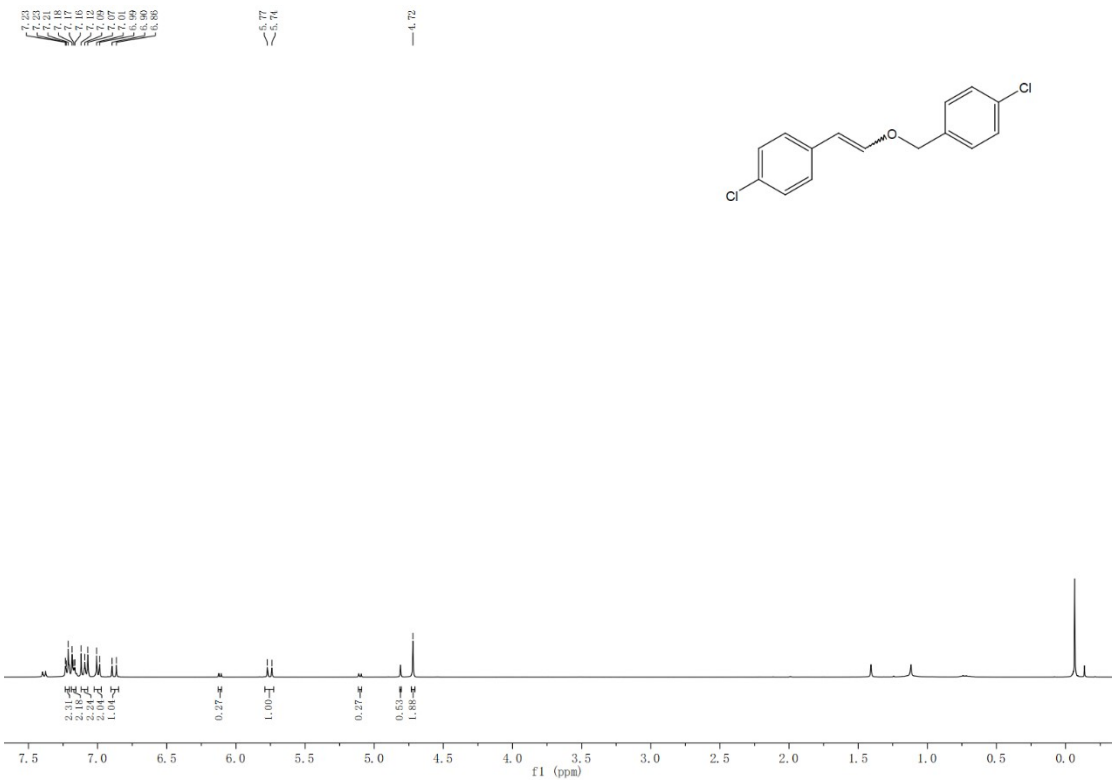


Figure S46. ^{1}H NMR spectrum of compound **4b**

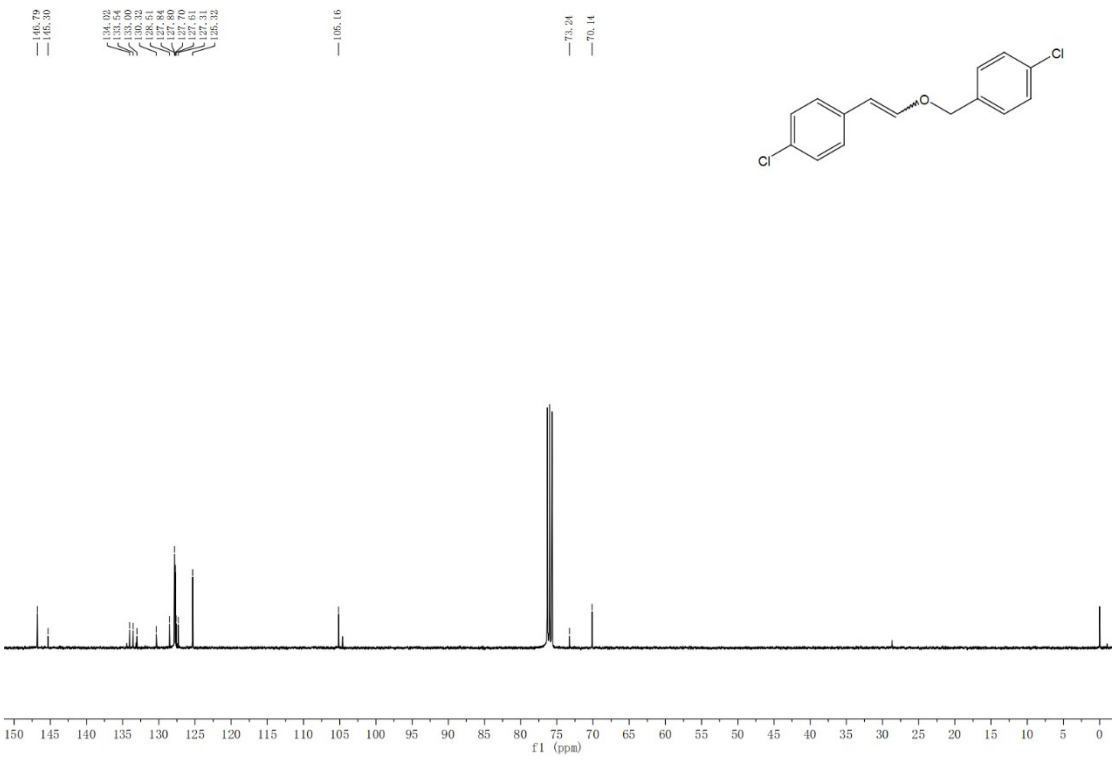


Figure S47. ^{13}C NMR spectrum of compound **4b**

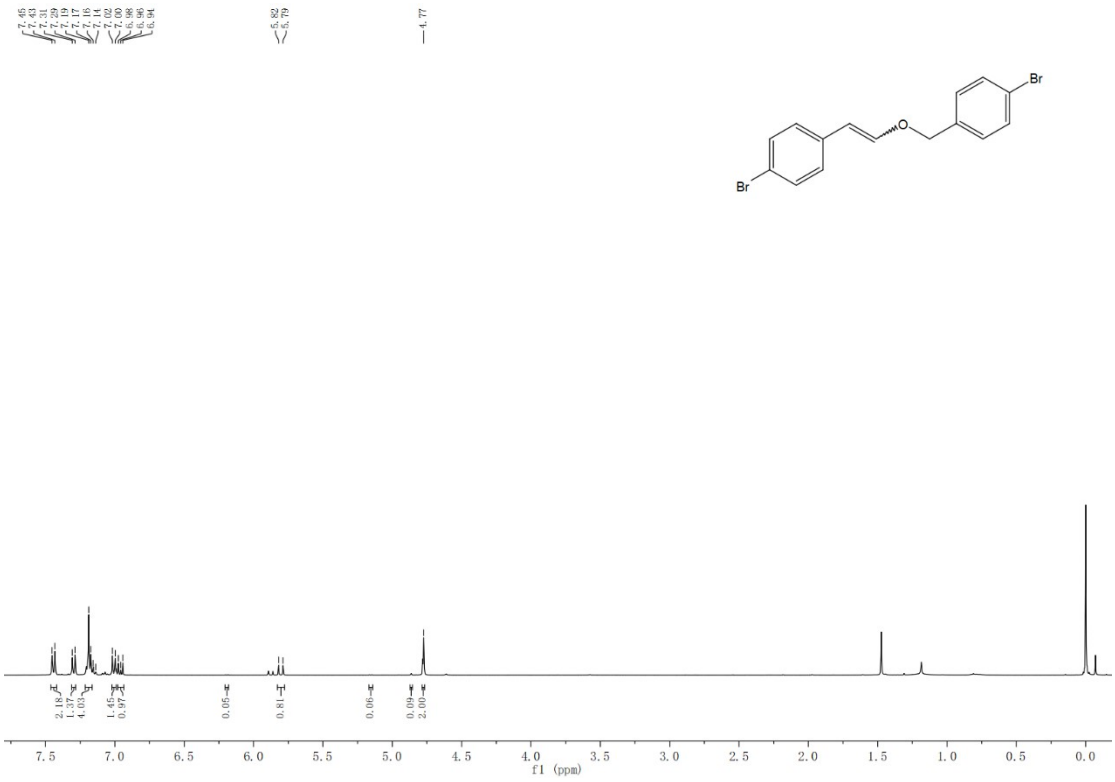


Figure S48. ^{1}H NMR spectrum of compound **4c**

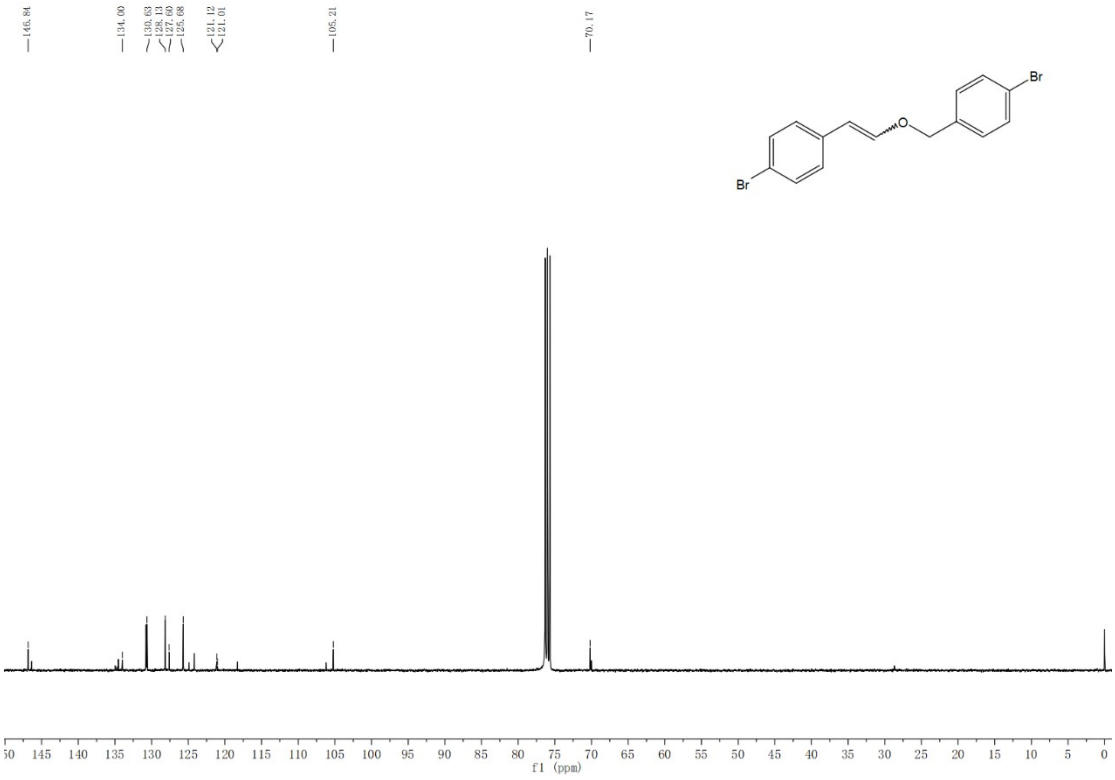


Figure S49. ^{13}C NMR spectrum of compound **4c**

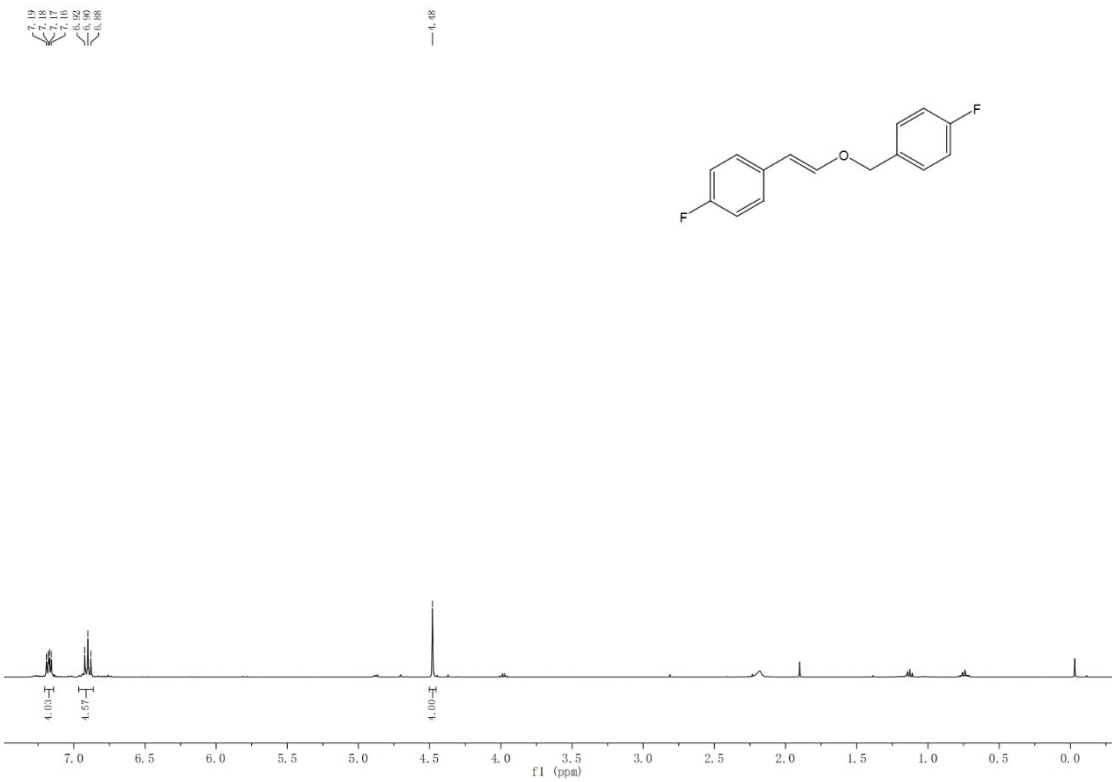


Figure S50. ^{1}H NMR spectrum of compound **4d**

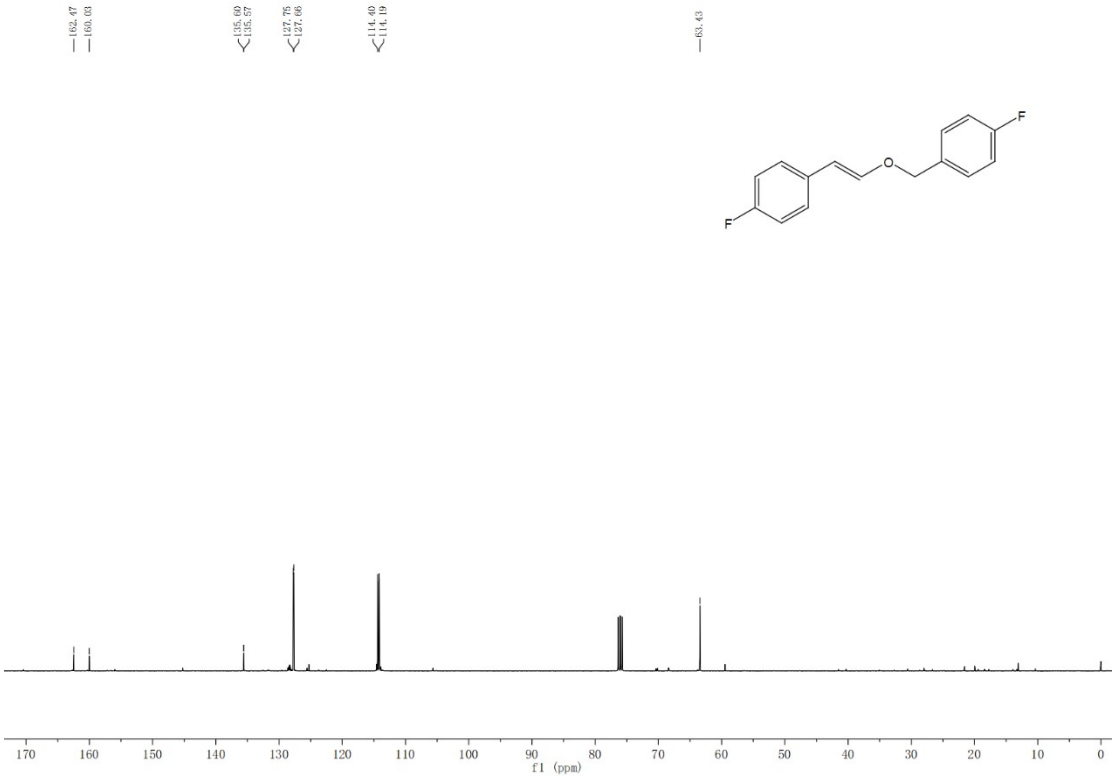


Figure S51. ^{13}C NMR spectrum of compound **4d**

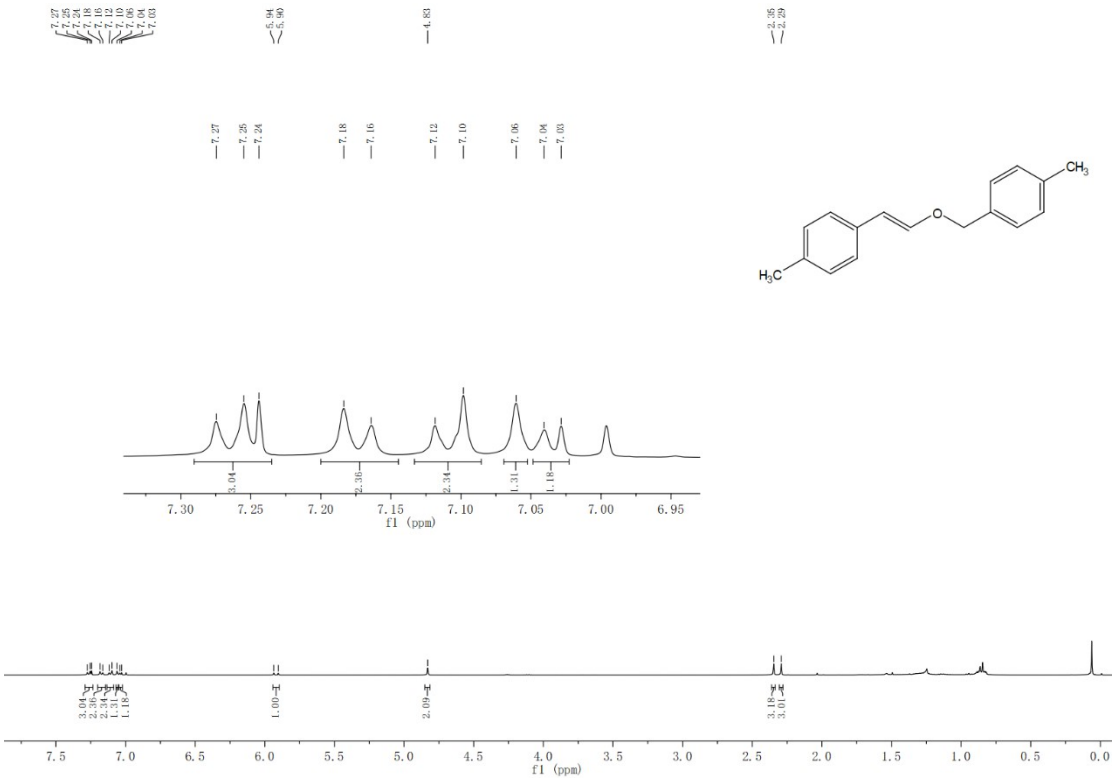


Figure S52. ^{1}H NMR spectrum of compound **4e**

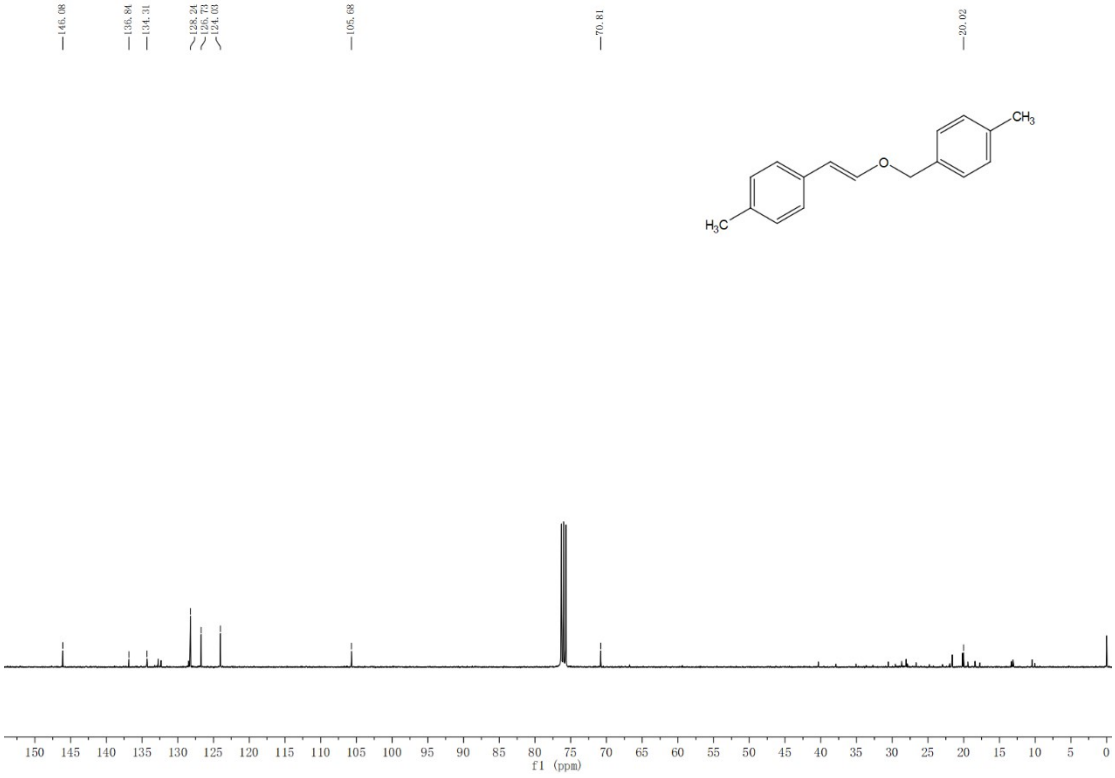


Figure S53. ^{13}C NMR spectrum of compound **4e**

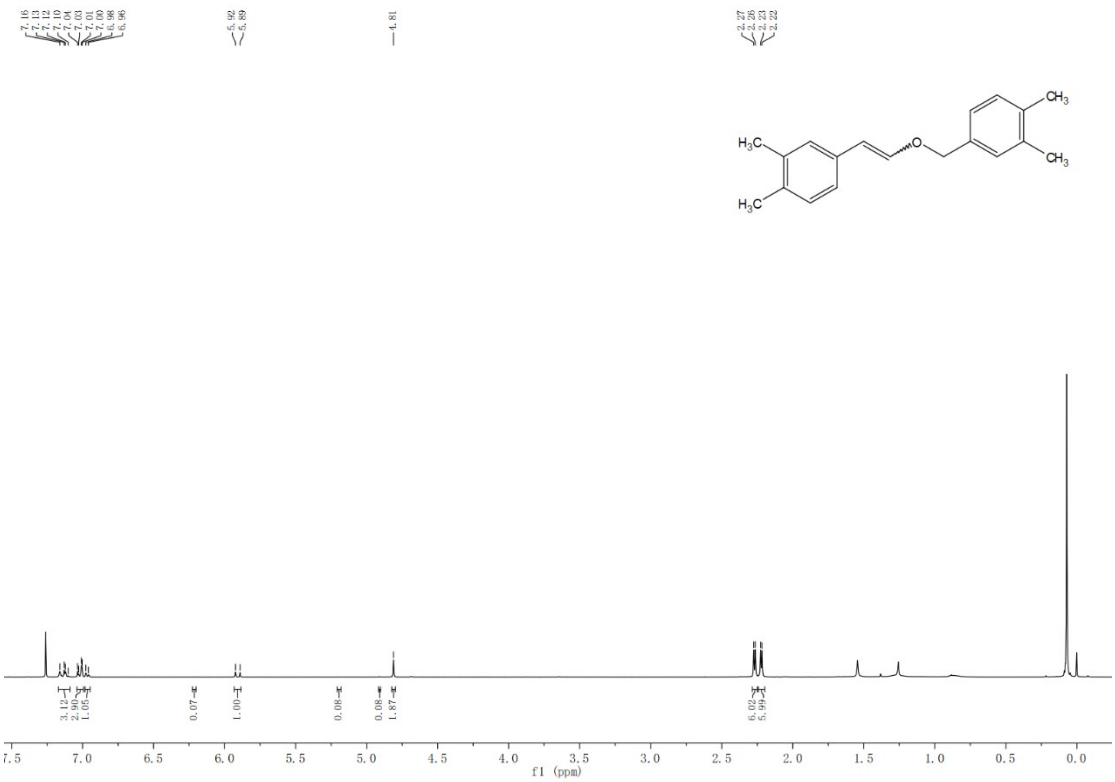


Figure S54. ^{1}H NMR spectrum of compound **4f**

Figure S55. ^{13}C NMR spectrum of compound **4f**

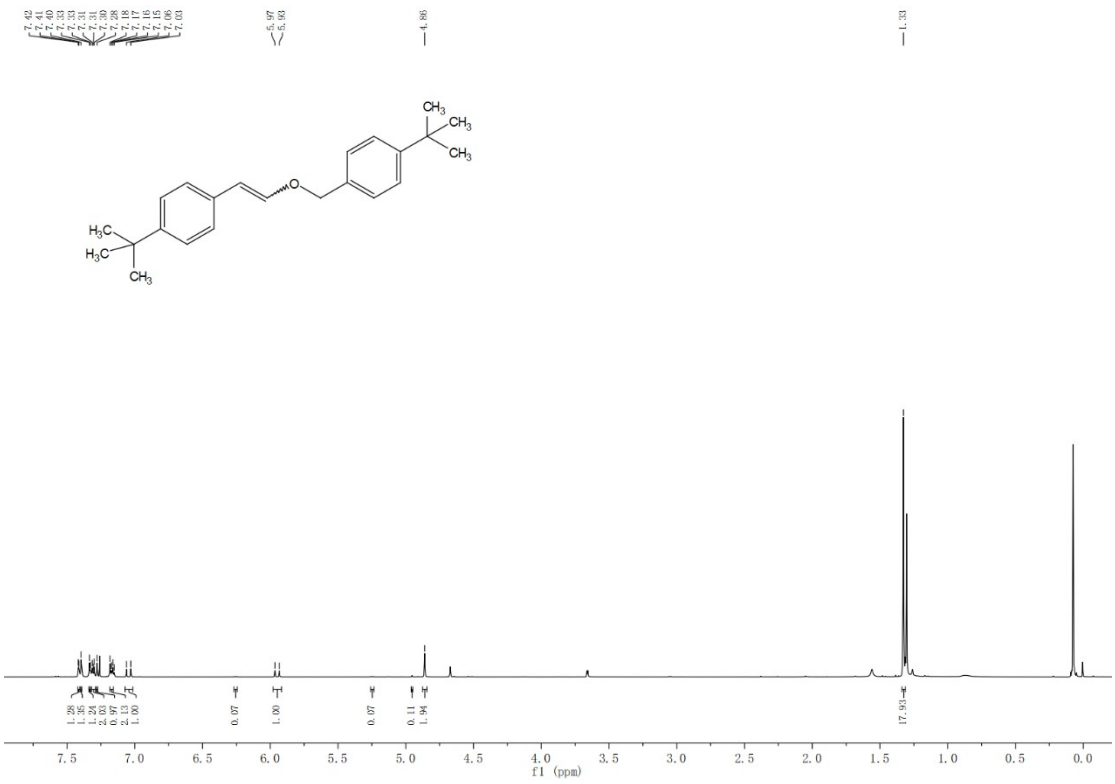


Figure S56. ^{1}H NMR spectrum of compound **4g**

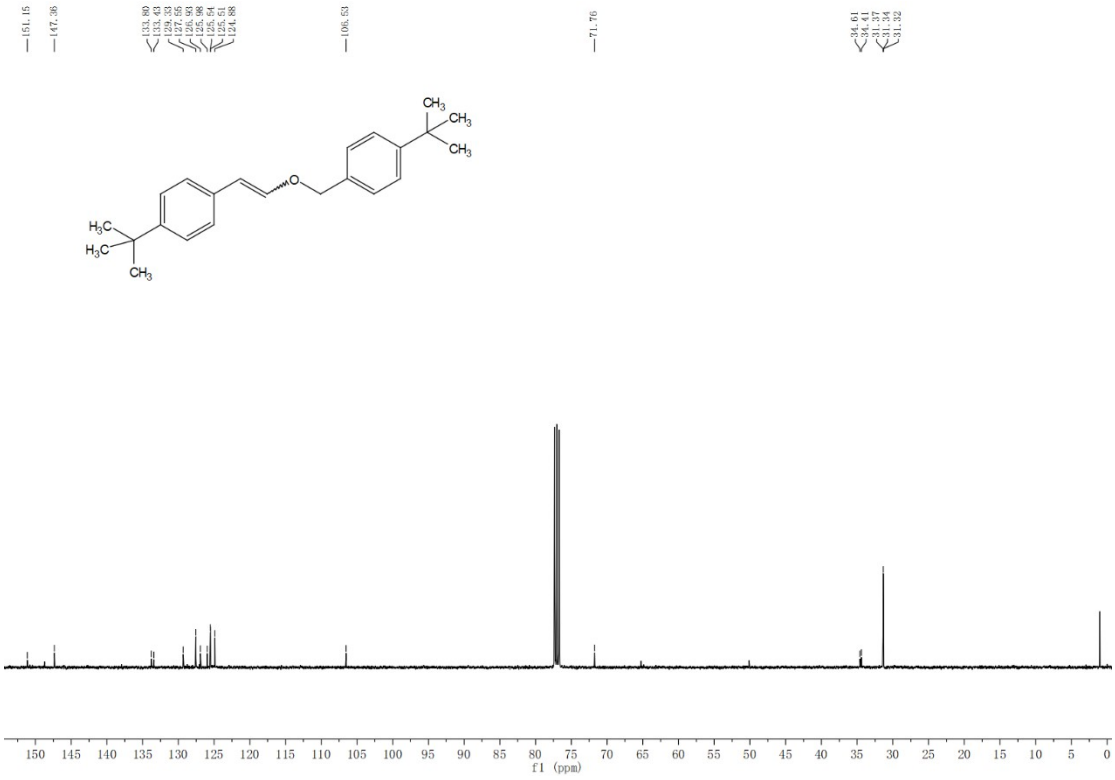


Figure S57. ^{13}C NMR spectrum of compound **4g**

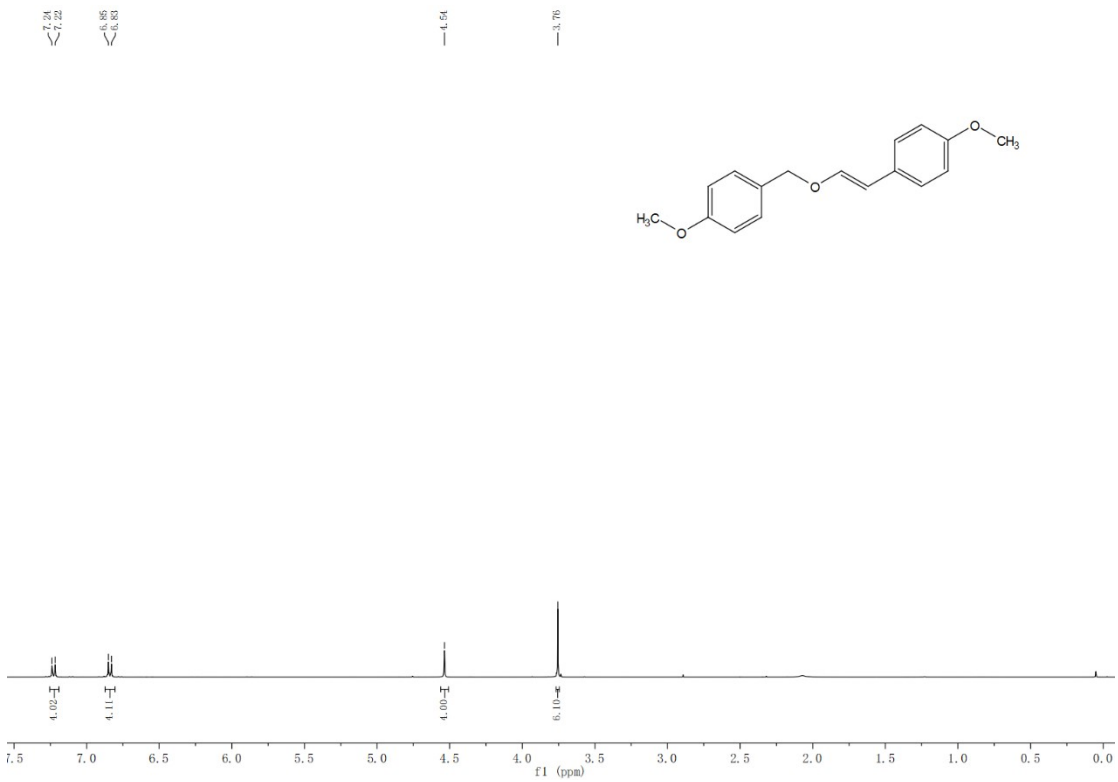


Figure S58. ^{1}H NMR spectrum of compound **4h**

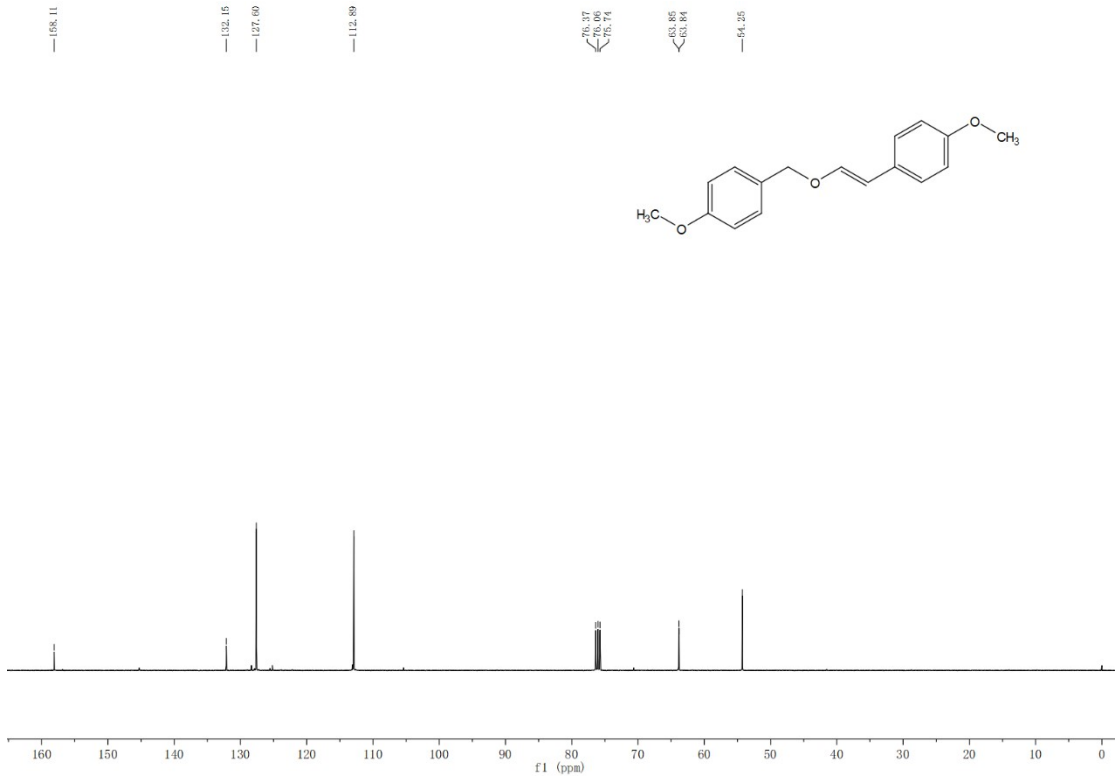


Figure S59. ^{13}C NMR spectrum of compound **4h**

Figure S60. ^{1}H NMR spectrum of compound **4i**

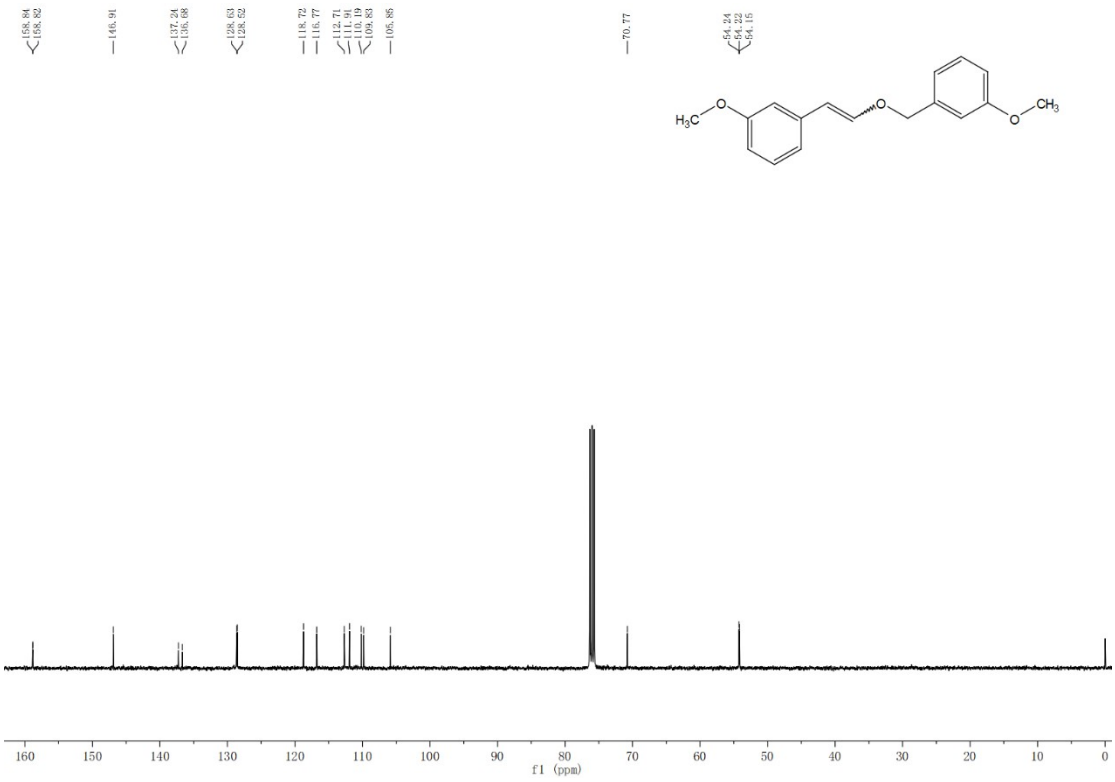


Figure S61. ^{13}C NMR spectrum of compound **4i**

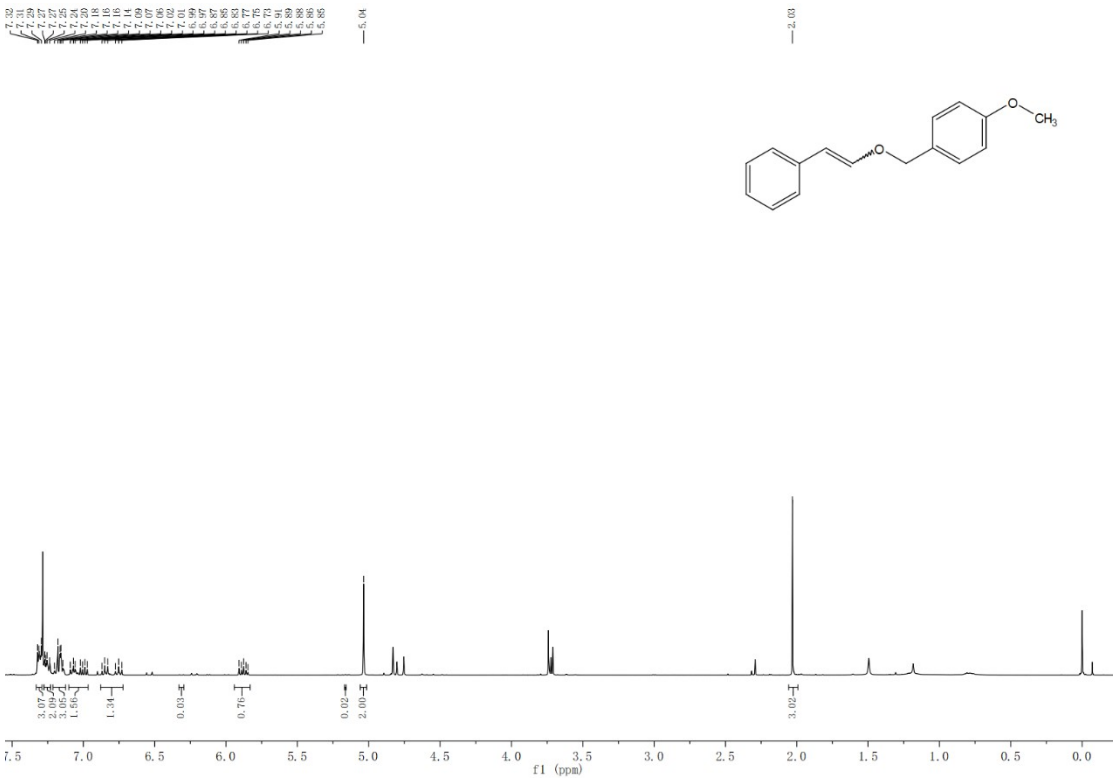


Figure S62. ^{1}H NMR spectrum of compound **4j**

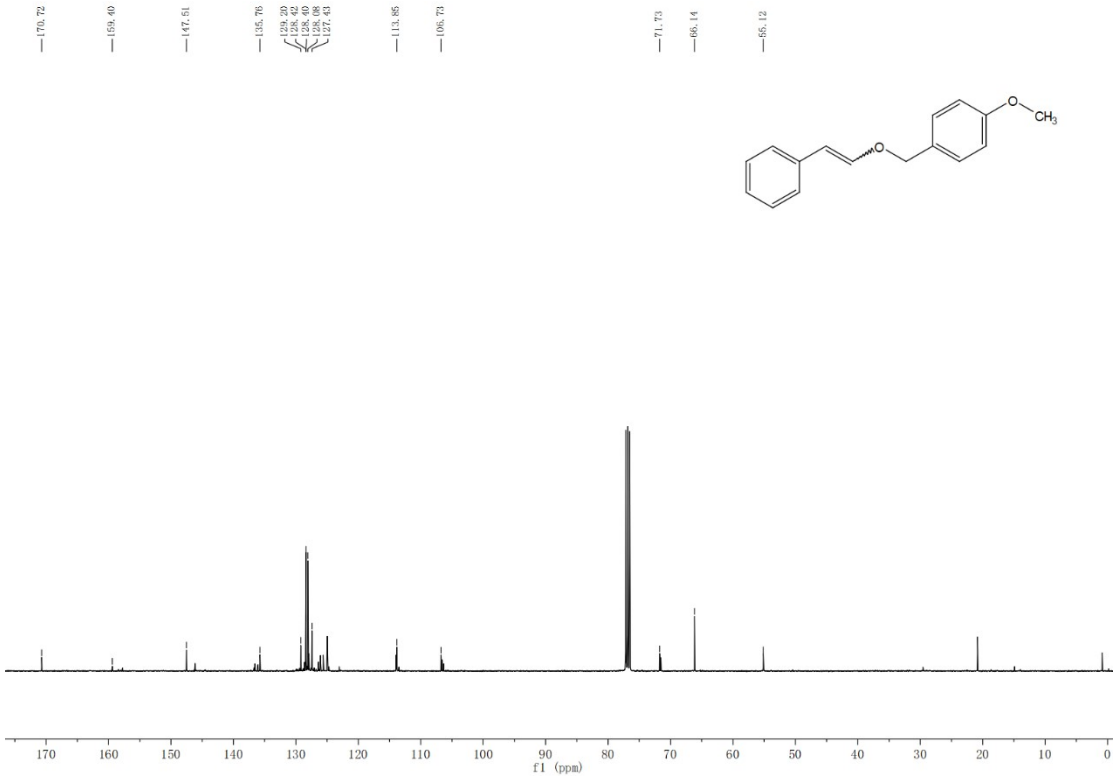


Figure S63. ^{13}C NMR spectrum of compound **4j**

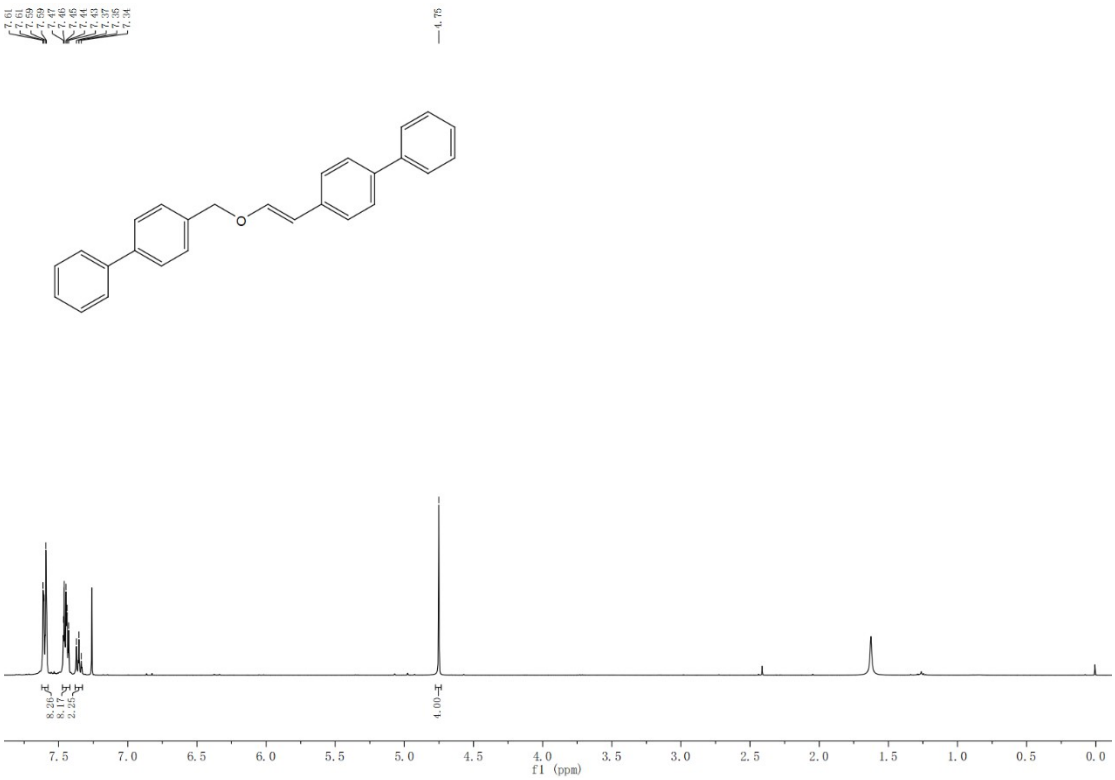


Figure S64. ^{1}H NMR spectrum of compound **4k**

Figure S65. ^{13}C NMR spectrum of compound **4k**

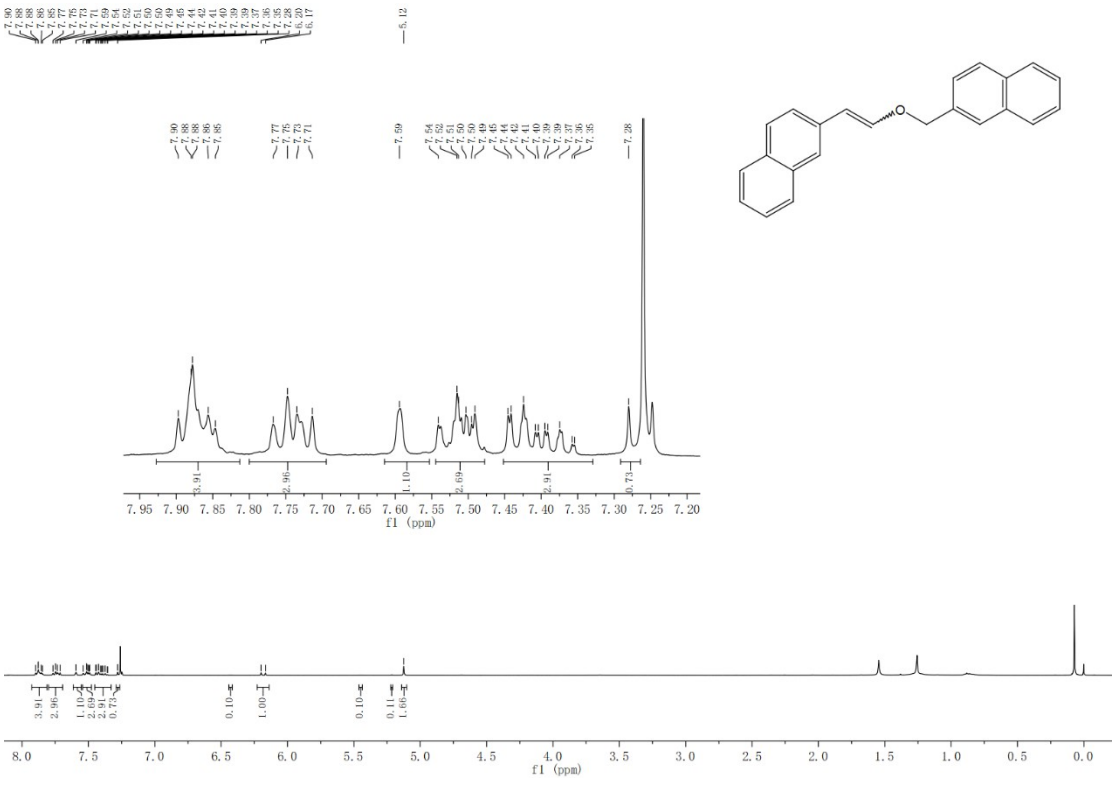


Figure S66. ^{1}H NMR spectrum of compound **4l**

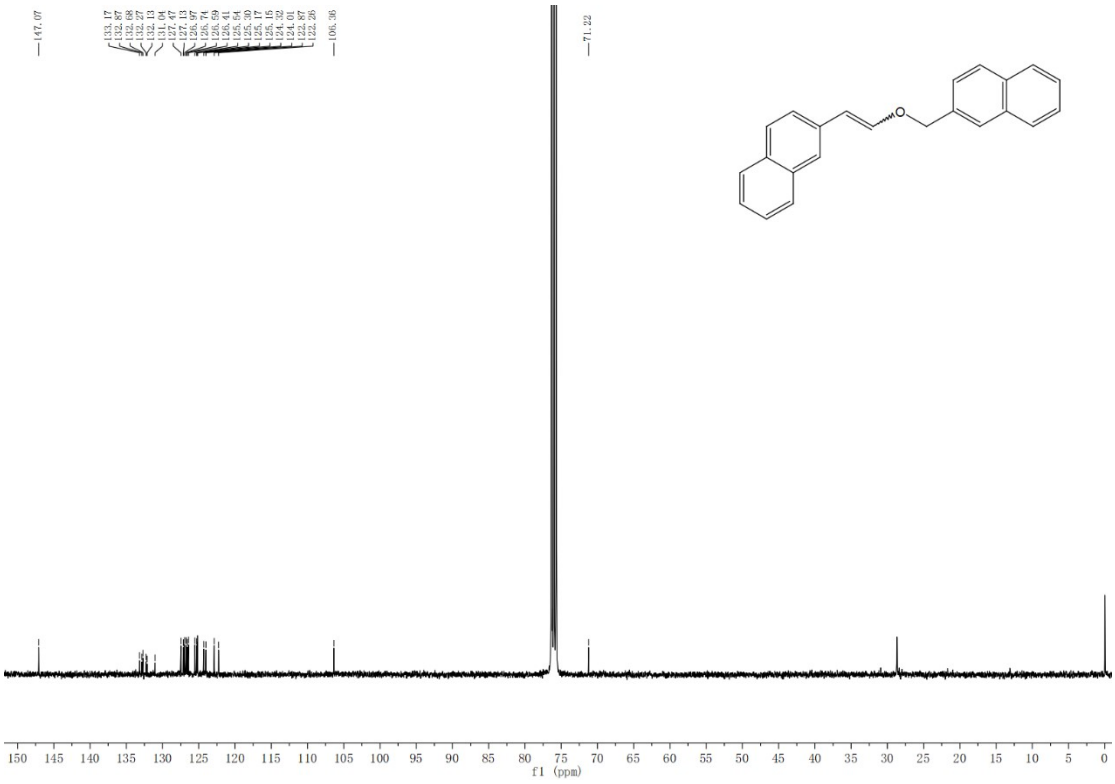


Figure S67. ^{13}C NMR spectrum of compound **4l**

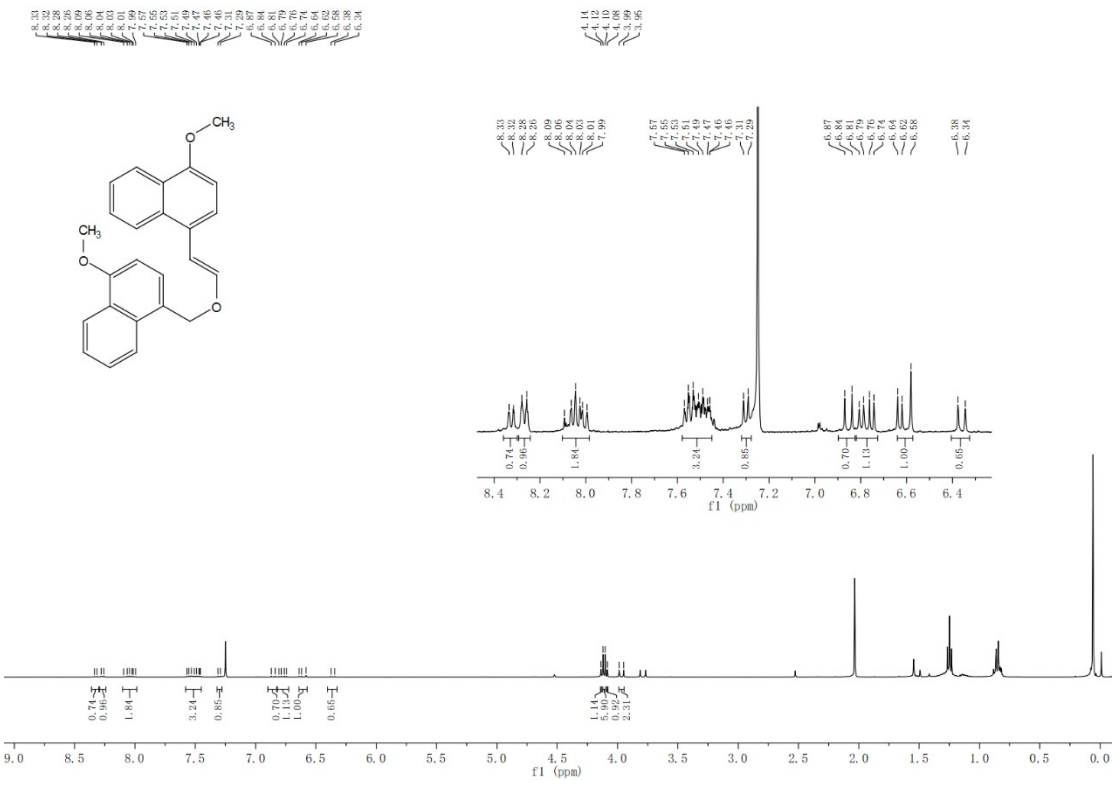


Figure S68. ^{1}H NMR spectrum of compound **4m**

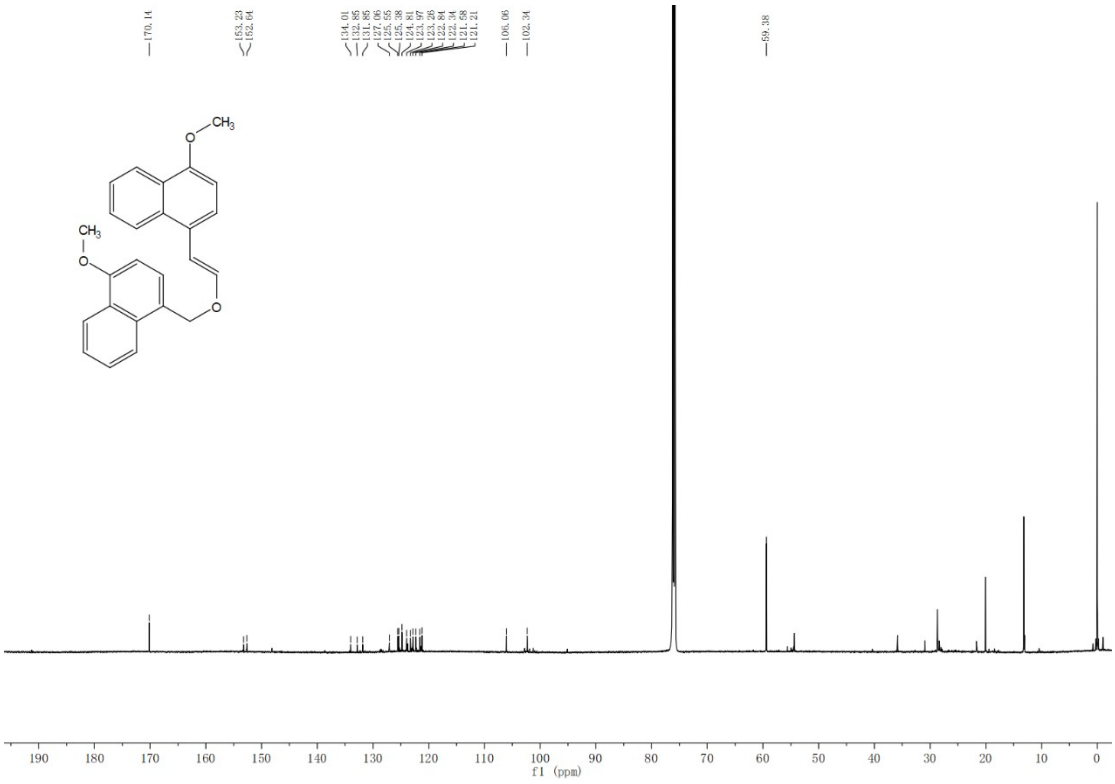


Figure S69. ^{13}C NMR spectrum of compound **4m**

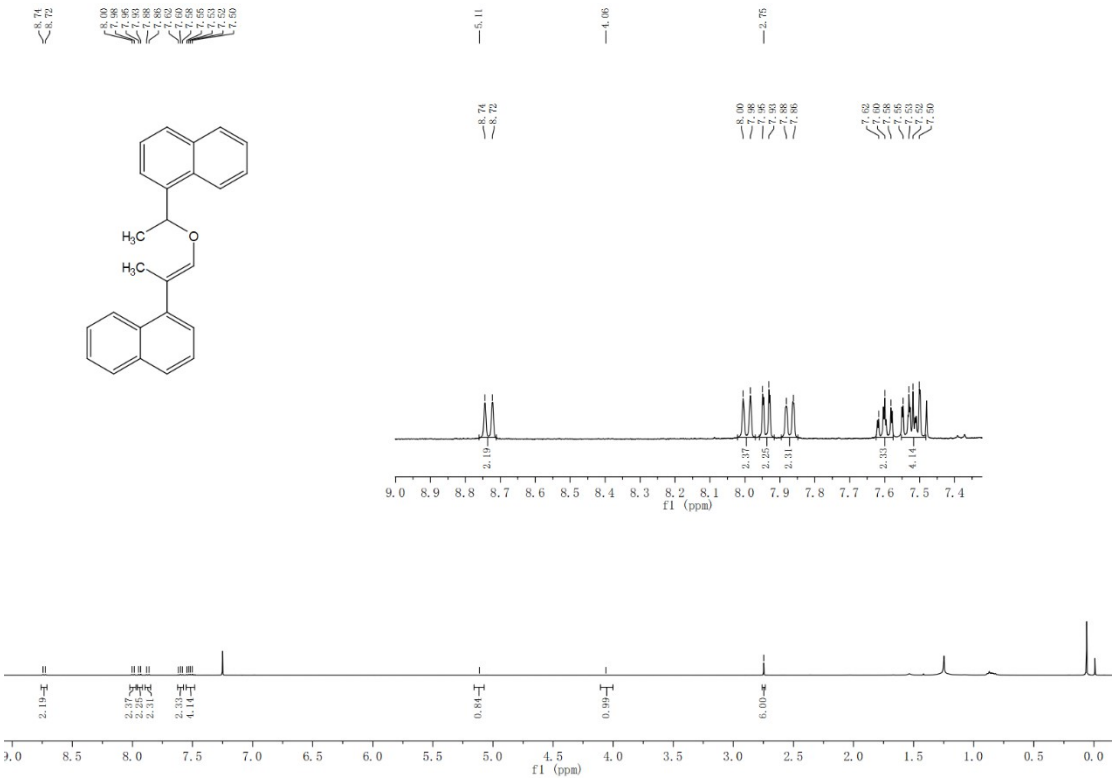


Figure S70. ^{1}H NMR spectrum of compound **4n**

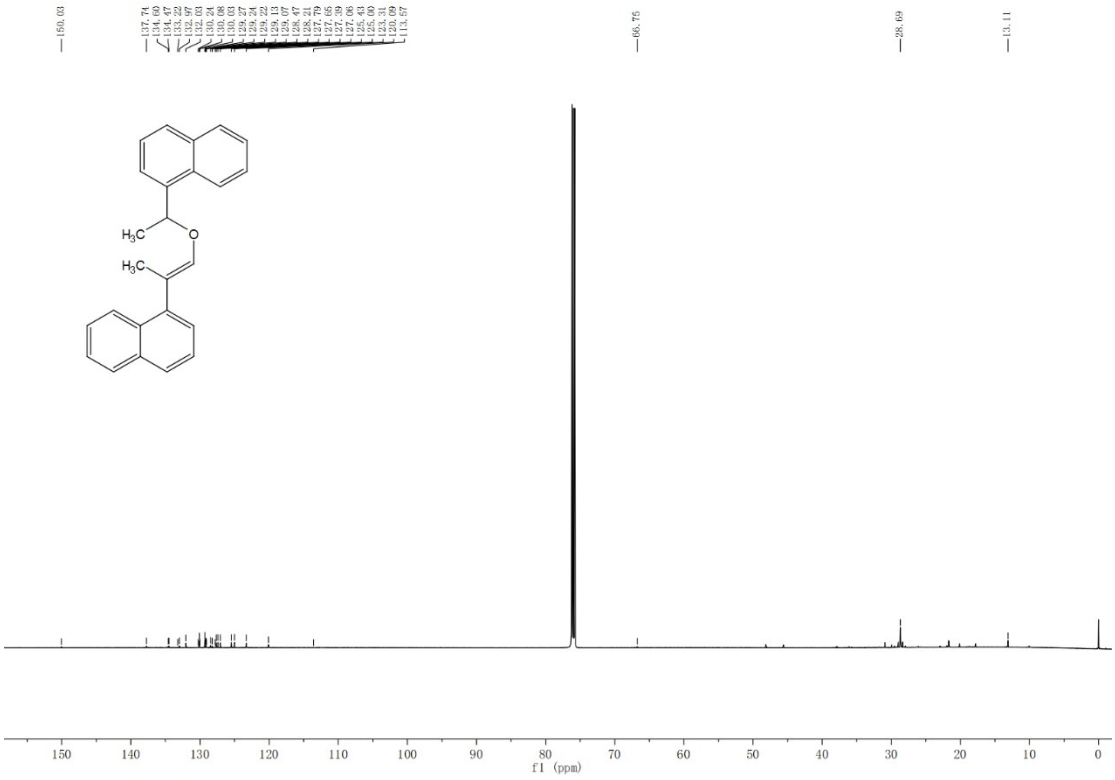


Figure S71. ^{13}C NMR spectrum of compound **4n**

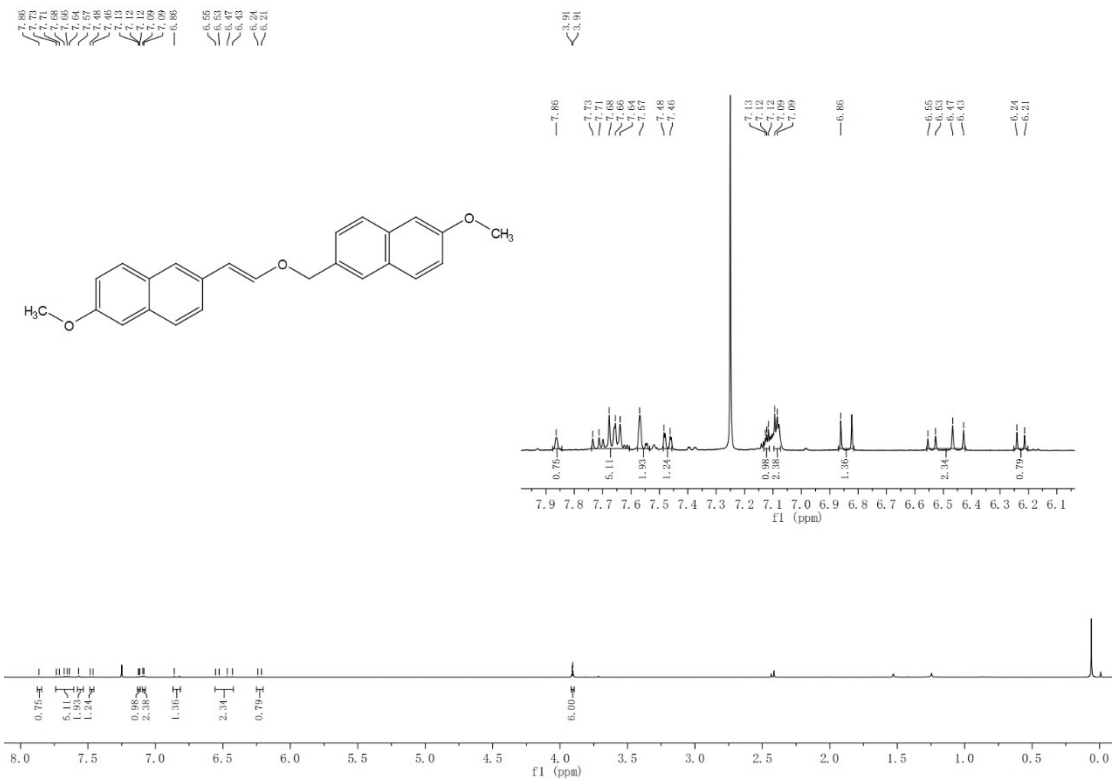


Figure S72. ^{1}H NMR spectrum of compound **4o**

Figure S73. ^{13}C NMR spectrum of compound **4o**

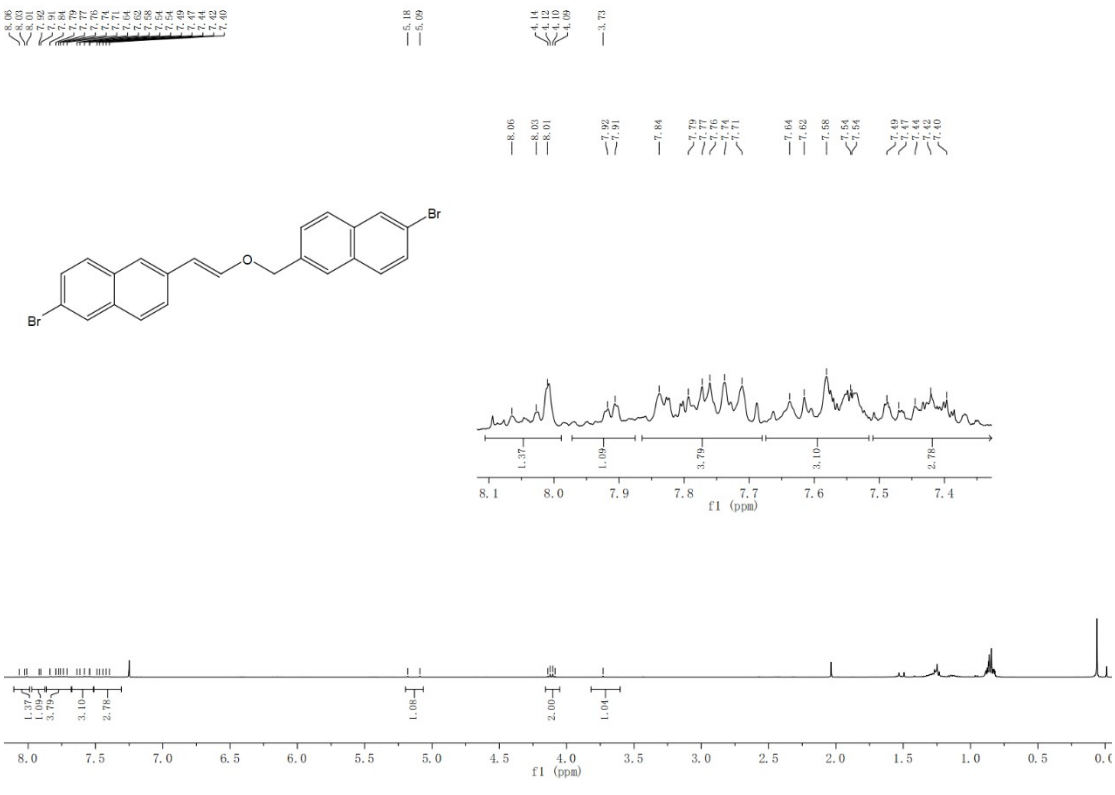


Figure S74. ^{1}H NMR spectrum of compound **4p**

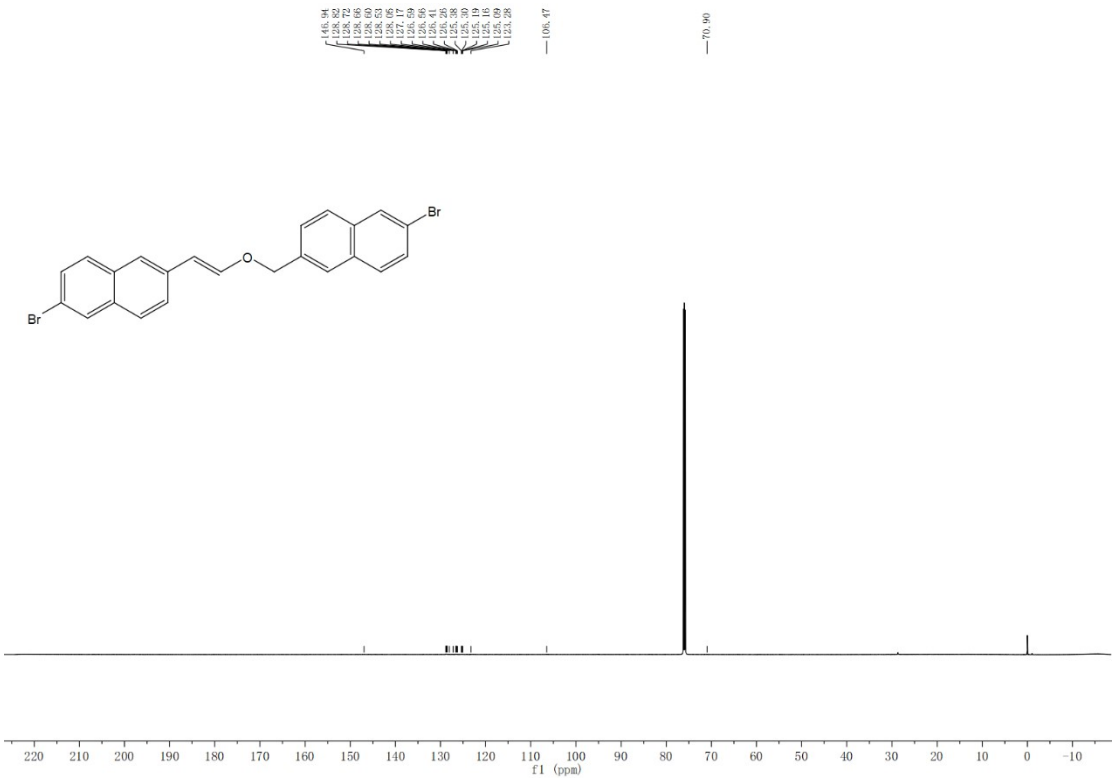


Figure S75. ^{13}C NMR spectrum of compound **4p**

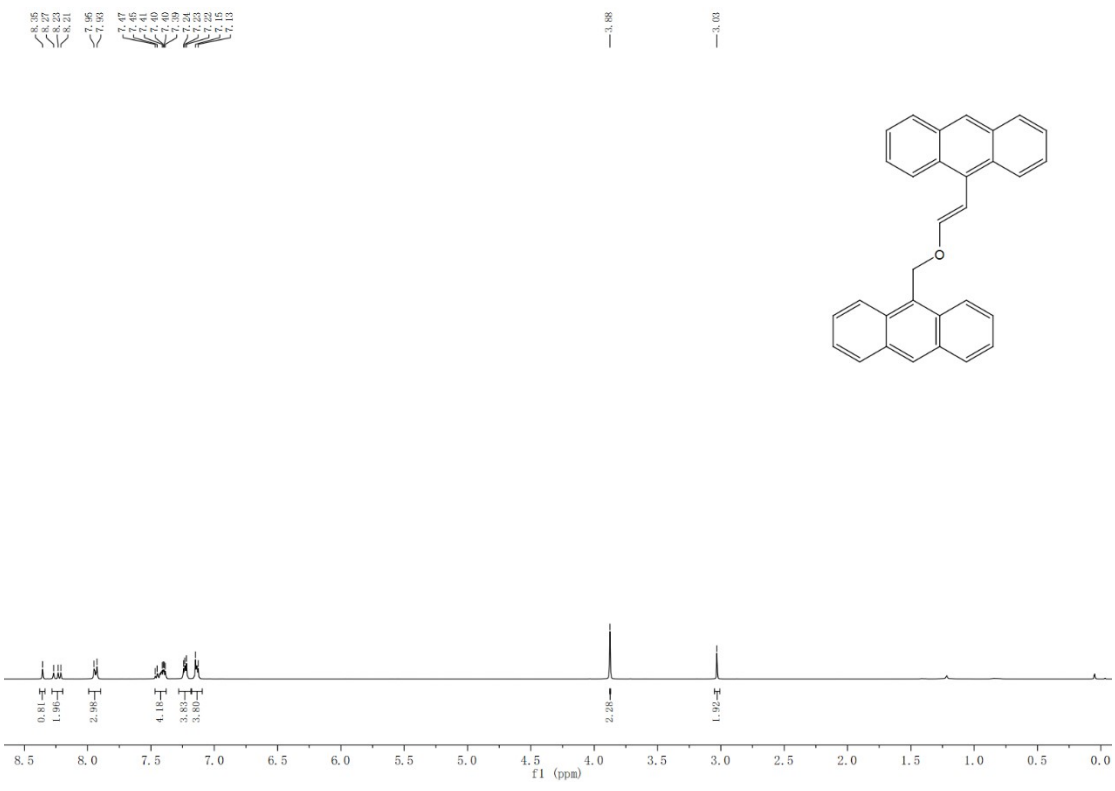


Figure S76. ^{1}H NMR spectrum of compound **4q**

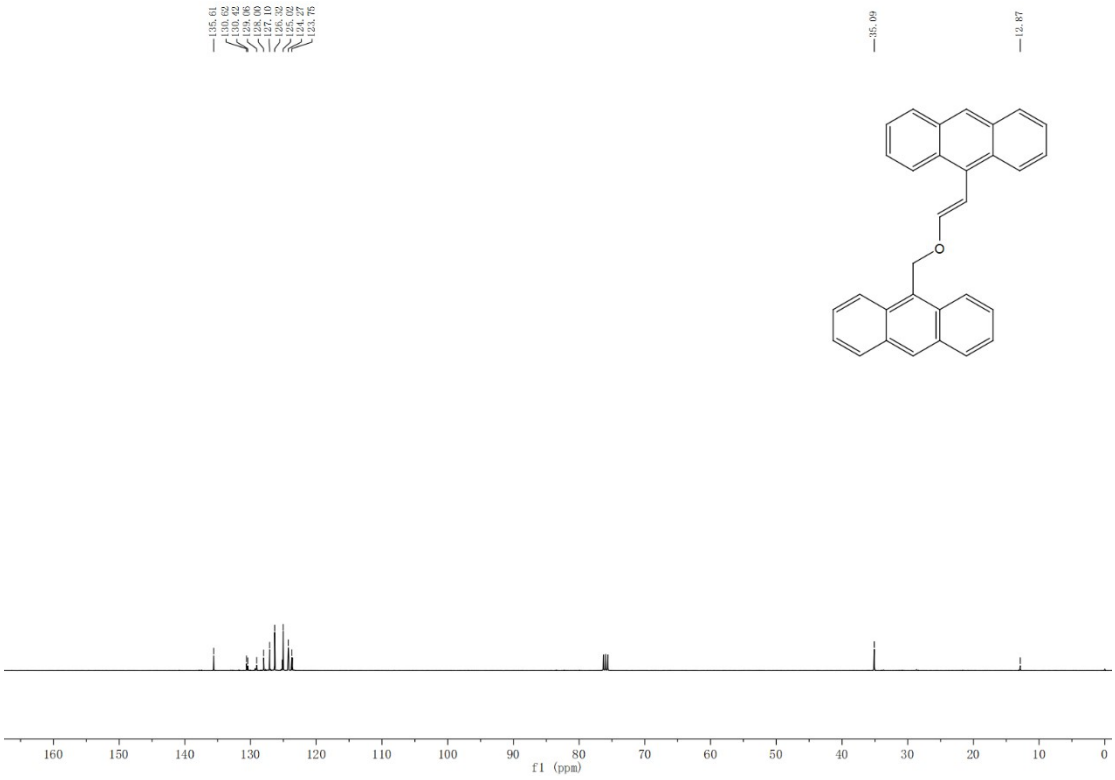


Figure S77. ^{13}C NMR spectrum of compound **4q**

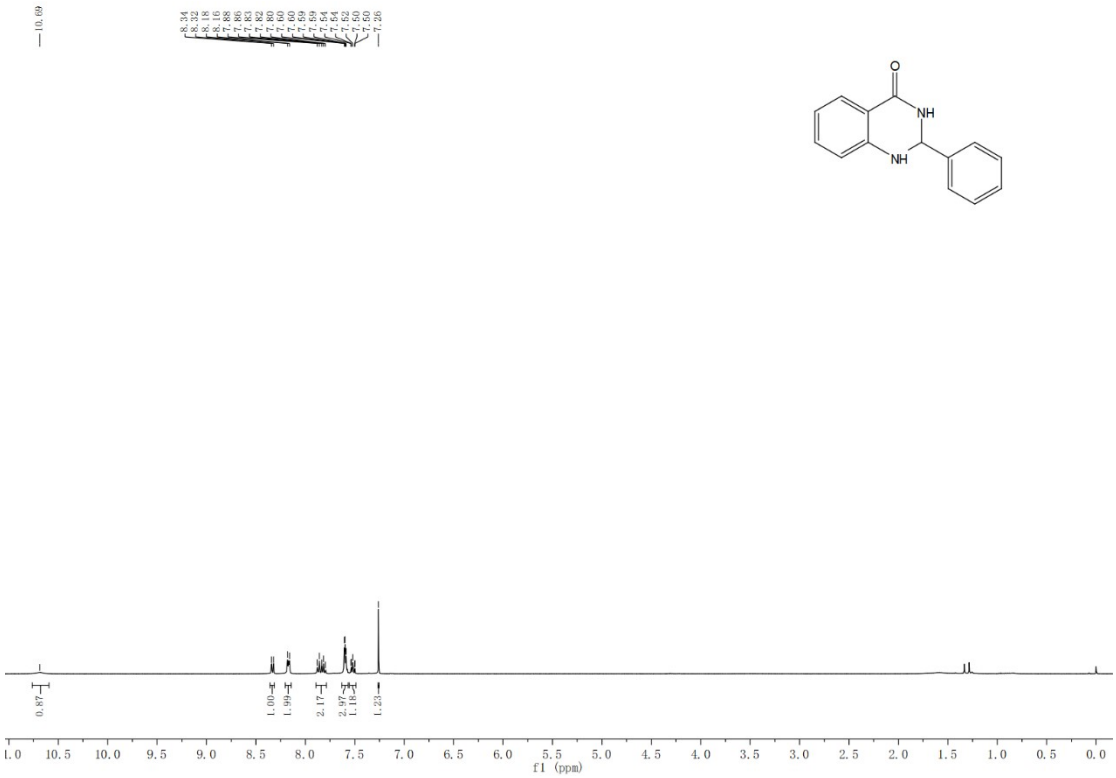


Figure S78. ^{1}H NMR spectrum of compound **IV**

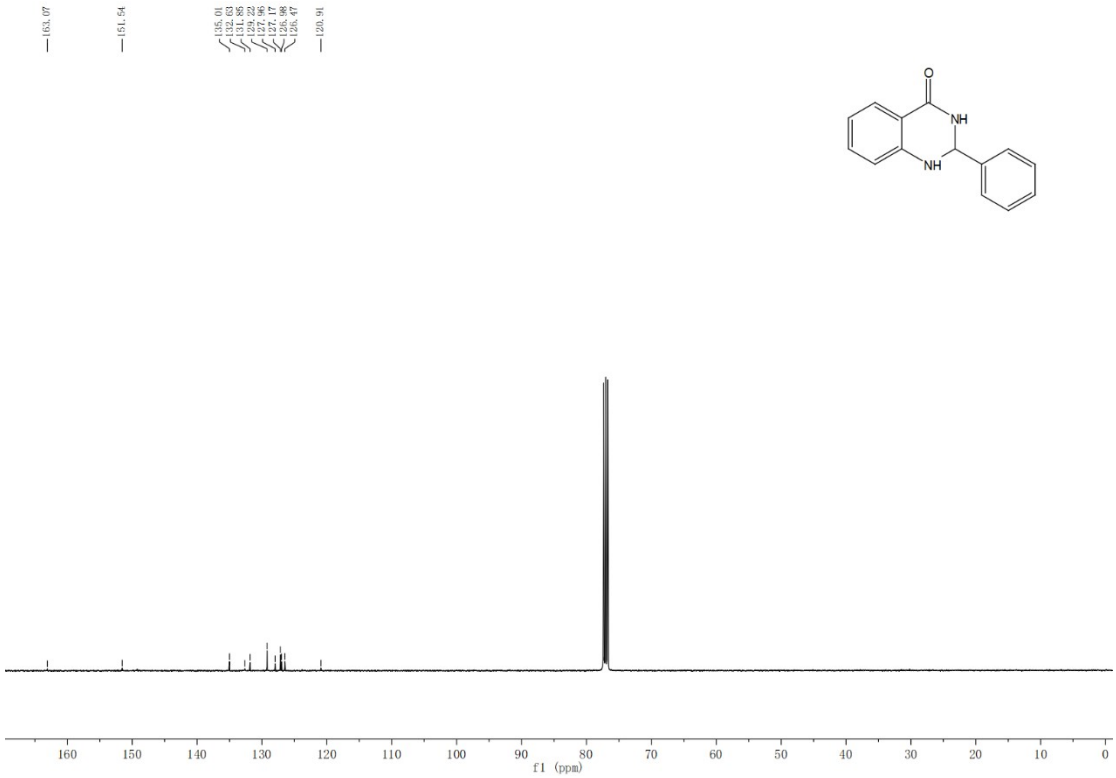


Figure S79. ^{13}C NMR spectrum of compound **IV**

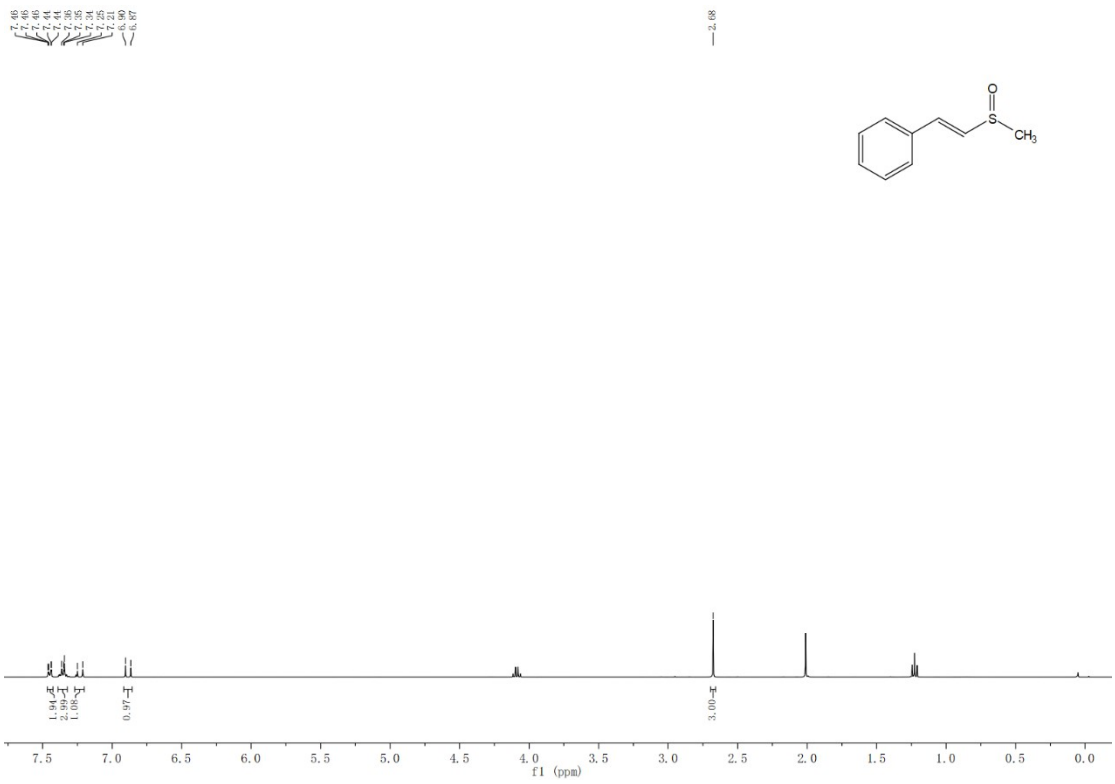


Figure S80. ^{1}H NMR spectrum of compound **A**

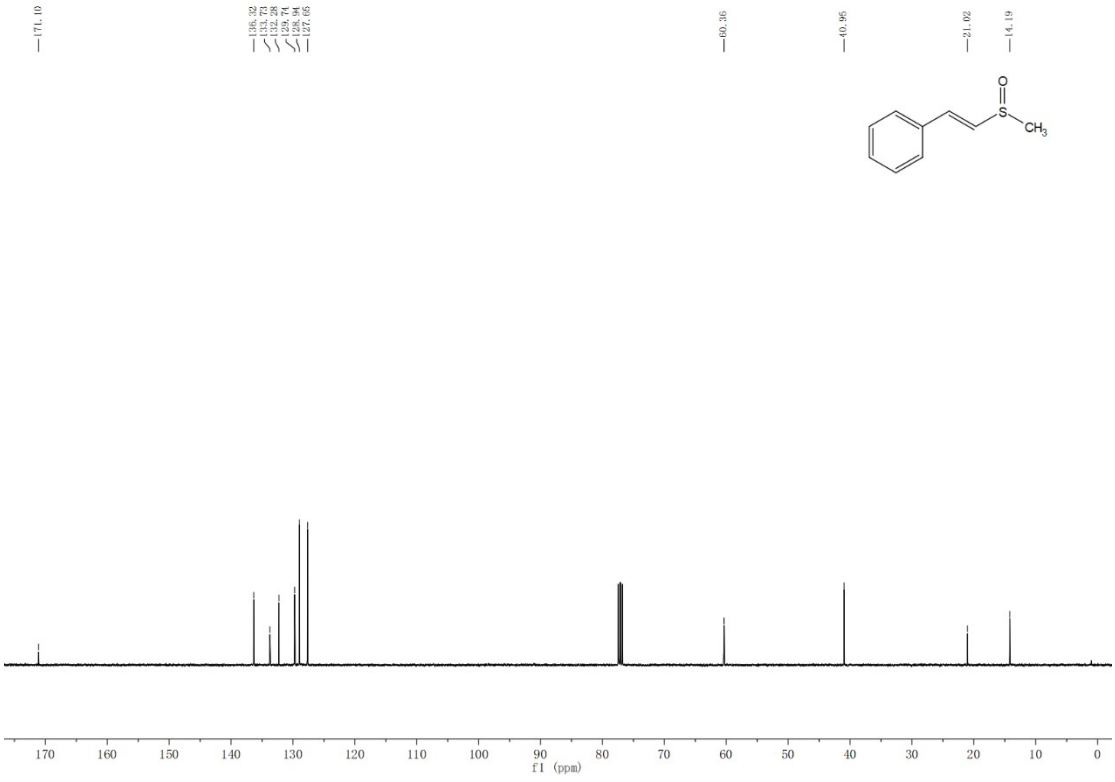


Figure S81. ^{13}C NMR spectrum of compound **A**

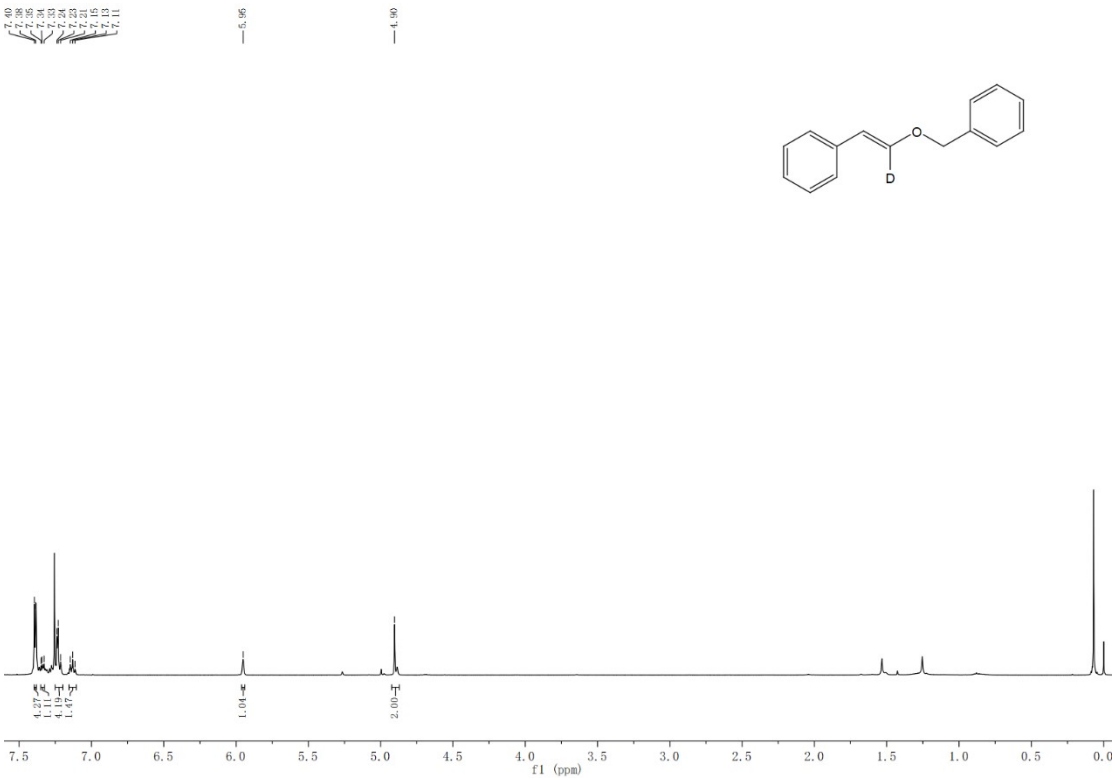


Figure S82. ^{1}H NMR spectrum of compound **d-4a**

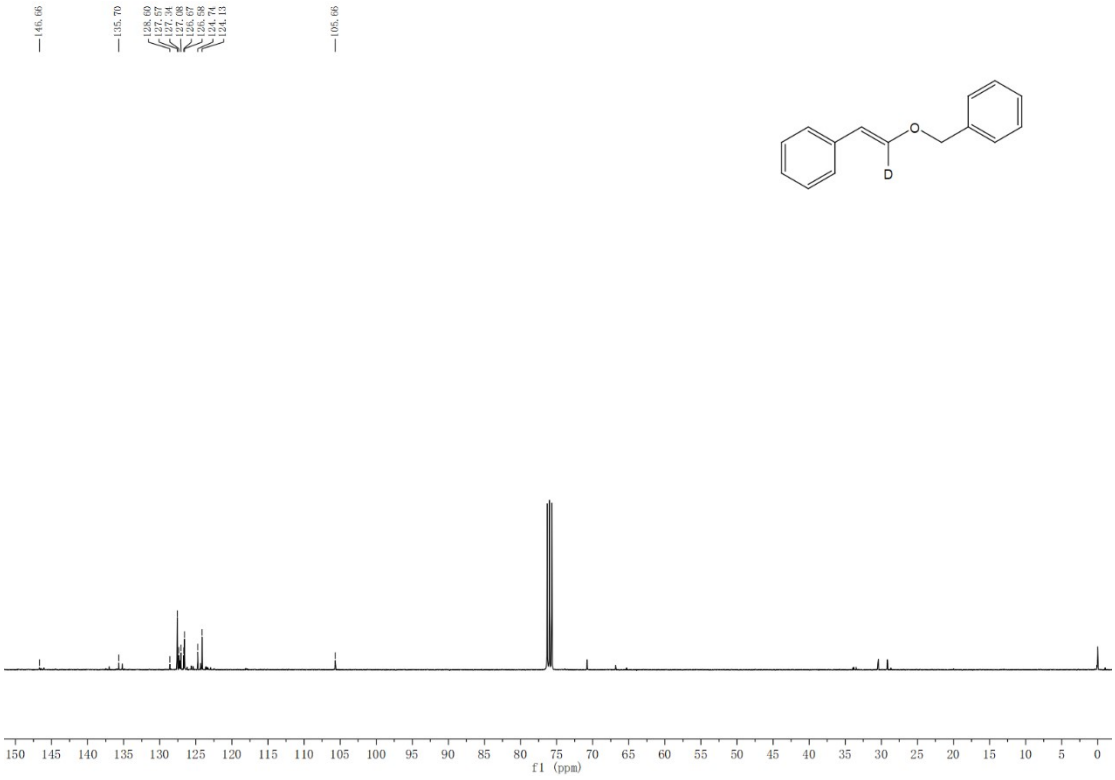


Figure S83. ^{13}C NMR spectrum of compound**d-4a**

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[2] Y. Wang, Y. Qin, W. Li, Y. Wang, L. Zhu, M. Zhao, Y. Yu, *Transactions of Tianjin University* **2023**, *29*, 275-283.

[3] Y. Yue, A. J. Binder, R. Song, Y. Cui, J. Chen, D. K. Hensley, S. Dai, *Dalton Trans.* **2014**, *43*, 17893-17898.

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