Supplementary Information

Amides as key intermediates for the synthesis of 2,4-disubstituted quinazolines via acceptorless dehydrogenative coupling of alcohols

Yongfei Zhang,[a,b,c] Xing Liu,[a] Haiyang Jin,[a] Yingying Qiu,[a] Qing Yan,[a] Yonghai Hui,*[a] Zhifeng Ma[d] and Weiwei Jin*[c]

[a] College of Chemistry and Chemical Engineering, Lingnan Normal University, Zhanjiang, 524048, China.

[b] GuangDong Engineering Technology Research Center of Protection and utilization of blue carbon resources, Zhanjiang, 524048, China

[c] College of Life Sciences, China Jiliang University, Hangzhou, 310018, China.

[d] School of Chemistry&Environment, Yunnan Minzu University, Kunming, 650500, China.

hyhai97@126.com (Yonghai Hui, Corresponding Author)

wwjin0722@cjlu.edu.cn (Weiwei Jin, Corresponding Author)

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1. Experimental

General remarks

o-Aminobenzhydrol and its derivatives were obtained from Energy Chemical. *o*-Aminobenzophenone, benzyl alcohol and its derivatives and all the other chemicals were purchased from Adama-beta. All chemicals were used as received without further purification.

The reaction was monitored by thin layer chromatography (TLC) and NMR. 2,4-Disubstituted quinazolines were characterized by ^{1}H NMR and ^{13}C NMR spectra using an INOVA-400 spectrometer. The mass analysis was carried out using an LCMS-8045. The FT-IR spectrum was obtained on a Bruker Equinox 55 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (XRD) patterns were recorded at a scan rate of $6^{o}\cdot min^{-1}$ on an ESCALAB 250Xi X-ray diffractometer with 2θ ranging from 5^{o} to 80^{o} with Cu Kα radiation (λ = 0.154056 nm). The chemical states of the elements were investigated by X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS Supra+).Scanning electron microscopy (SEM) was performed on a LEO1430VP instrument. The N_2 isotherms were performed with a NOVA 4000e surface area analyzer. The specific surface areas of materials were evaluated with the BET method.

Computational Methods

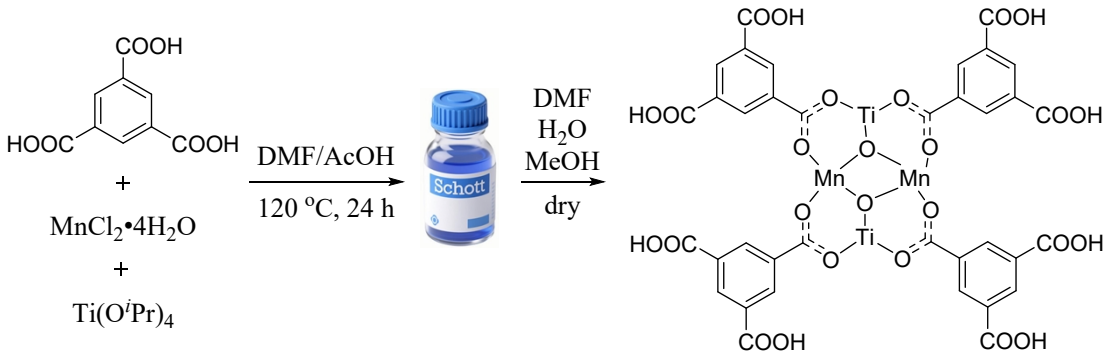
All density functional theory (DFT) calculations were performed to understand the nucleophilicity of the organic molecules, B3LYP-D3 method combined with a Def2-SVP basis set for all atoms were used to fully optimize all structures in the gas-phase. Then, vibrational frequency calculations on these optimized geometries were carried out at the same level of theory to confirm no imaginary frequency for all local minima. All DFT calculations were carried out by Gaussian16 program.

Synthesis of MUV-10(Mn)

MUV-10(Mn) was synthesized based on a modified procedure [1]. Benzene-1,3,5-tricarboxylic acid (BTC, 595 μmol), $MnCl_2\cdot 4H_2O$ (120~360 μmol), DMF (12 mL) and AcOH (3.5 mL) in a 25 ml Schott bottle. Then, $Ti(OiPr)_4$ (120 μmol) were added to the clear solution. The bottle was sealed and hold at 120 ºC for 48 h. After cooling

to room temperature, the product was recovered by centrifugation and washed several times with DMF, water and MeOH.

These samples, synthesized based on the molar ratios of $MnCl_2 \cdot 4H_2O$ and $Ti(OiPr)_4$ of 1:1, 2:1, and 3:1, were designated as MUV-10(Mn)-1, MUV-10(Mn)-2, and MUV-10(Mn)-3, respectively.



Scheme S1. Preparation of MUV-10(Mn).

General procedure for the acceptorless single dehydrogenation coupling reaction

General procedure for the synthesis of 2,4-diphenylquinazoline (5a). The reaction was carried out in a glass tube. In a typical procedure, 3 mg MUV-10(Mn)-1, 0.1 mmol ^{t}BuOK, 0.1 mmol *o*-aminobenzophenone and 0.3 mmol NH_4OAc and 0.3 mL benzyl alcohol were added into the tube and stirred at 130 °C for 16 h. After the reaction, the catalyst was separated from the reaction mixture via centrifugation, and the residue was purified by chromatography to afford the product 5a and confirmed by NMR.

General procedure for the acceptorless double dehydrogenation coupling reaction

General procedure for the synthesis of 2,4-disubstituted quinazolines (with 5a as an example). The reaction was carried out in a glass tube. In a typical procedure, 3 mg MUV-10(Mn)-1, 0.1 mmol ^{t}BuOK and 0.1 mmol *o*-aminobenzhydrol were added into the tube and stirred at 80 °C for 12 h. Then, 0.1 mmol ^{t}BuOK, 0.3 mmol NH_4OAc and 0.3 mL benzyl alcohol were added into the tube and stirred at 130 °C for another 16 h. After the reaction, the catalyst was separated from the reaction mixture via centrifugation, and the product was separated and purified by chromatography.

2. Supplementary characterization data of the catalyst

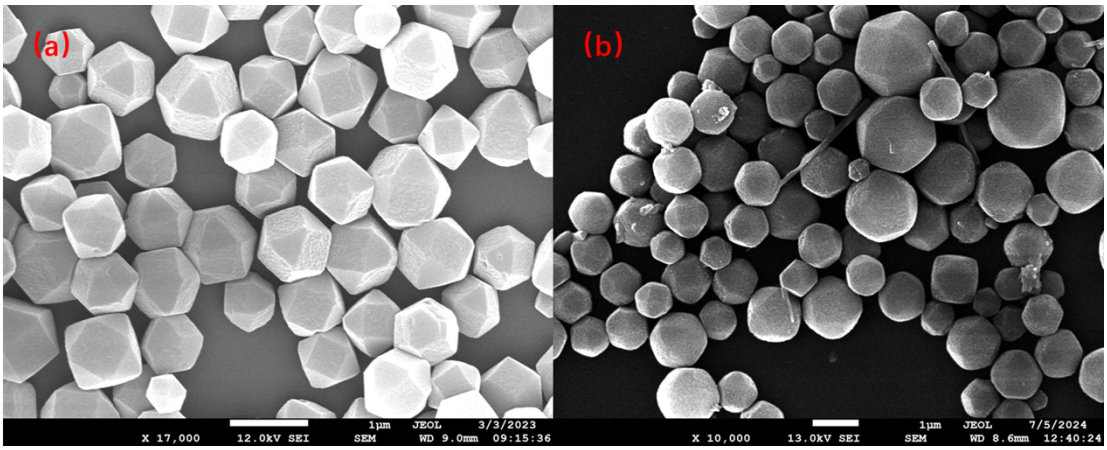


Fig. S1 Scanning electron micrograph of (a) MUV-10(Mn)-2 and (b) MUV-10(Mn)-3.

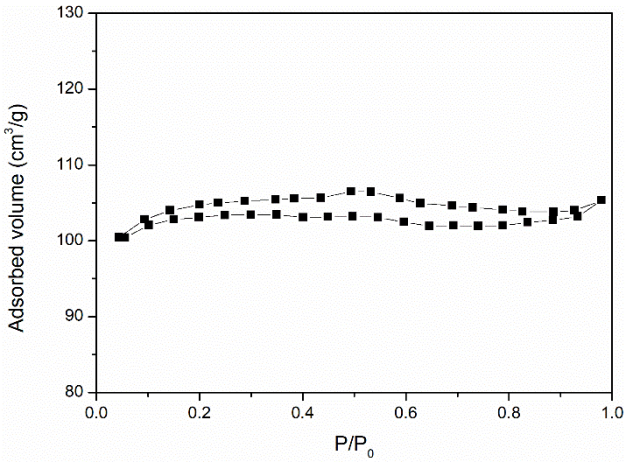


Fig. S2 Nitrogen sorption and desorption isotherms of MUV-10(Mn)-1.

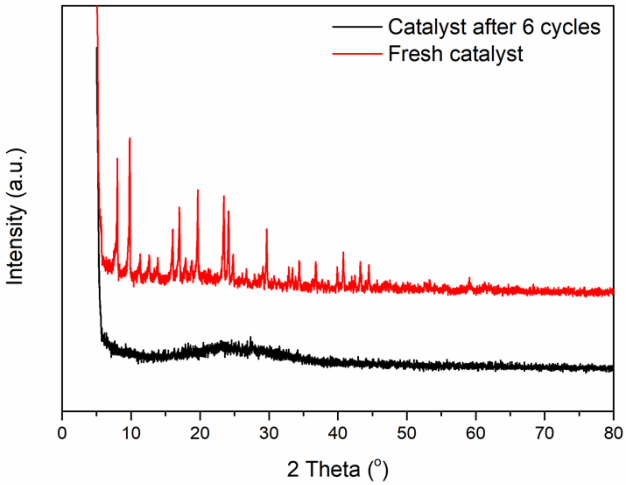


Fig. S3. The wide-angle XRD patterns of the fresh and spent (after 6 cycles) catalysts.

3. Reaction time versus yield curve

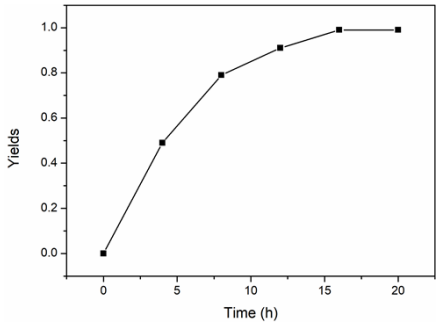


Fig. S4 A representative time course of the acceptorless single dehydrogenative coupling reaction, monitored by ^{1}H NMR. Reaction conditions: **2a** (0.1 mmol), **3a** (0.3 mL), **4a** (0.3 mmol), ^{t}BuOK (0.1 mmol) and MUV-10(Mn)-1 (3 mg) at 130 ºC for the parallel experiments with different reaction times.

4. The NMR data

2,4-Diphenylquinazoline (5a). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.62-8.59 (m, 2H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.05-8.01 (m, 1H), 7.90-7.87 (m, 2H), 7.72-7.64 (m, 4H), 7.59-7.55 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.1, 159.0, 151.2, 137.5, 137.0, 134.5, 130.9, 130.2, 130.0, 128.8, 128.7, 128.7, 128.2, 128.0, 126.9, 121.1. Analysis calc. for $C_{20}H_{14}N_2$ (282.12): C, 85.08; H, 5.00; N, 9.92. Found: C, 85.10; H, 4.99; N, 9.91.

2-(4-Fluorophenyl)-4-phenylquinazoline (5b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.68 (m, 2H), 8.14 (t, *J* = 8.6Hz, 2H), 7.92-7.86 (m, 3H), 7.62-7.54 (m, 4H), 7.23-7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 164.7 (d, $^{1}J_{C\text{-}F}$= 248 Hz, 1C), 159.3, 151.8, 137.5, 134.3 (d, $^{4}J_{C\text{-}F}$= 3.0 Hz, 1C), 133.7, 130.8 (d, $^{3}J_{C\text{-}F}$= 9 Hz, 2C), 130.2, 130.0, 129.0, 128.6, 127.1, 121.6, 115.5 (d, $^{2}J_{C\text{-}F}$= 21.0 Hz, 2C). Analysis calc. for $C_{20}H_{13}FN_2$ (300.11): C, 79.98; H, 4.36; N, 9.33. Found: C, 79.96; H, 4.37; N, 9.34.

2-(4-Chlorophenyl)-4-phenylquinazoline (5c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 6.7 Hz, 2H), 8.17(d, *J* = 8.4 Hz, 1H), 8.14 (dd, J_1 =8.4 Hz, J_2 =1.4 Hz, 1H), 7.93-7.87 (m, 3H), 7.62-7.55 (m, 4H), 7.49 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 159.2, 151.7, 137.5, 136.8, 136.5, 133.8, 130.2, 130.1, 130.1, 129.0,

128.8, 128.6, 127.3, 127.1, 121.7. Analysis calc. for $C_{20}H_{13}ClN_2$ (316.08): C, 75.83; H, 4.14; N, 8.84. Found: C, 75.81; H, 4.15; Cl, 11.21; N, 8.85.

2-(4-Bromophenyl)-4-phenylquinazoline (5d). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (dt, J_1 =8.7 Hz, J_2 = 2.4 Hz, 2H), 8.15 (t, J= 8.4 Hz, 2H), 7.93-7.87 (m, 3H), 7.66 (dt, J_1 = 8.5 Hz, J_2 = 2.6 Hz, 2H), 7.63-7.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 159.3, 151.8, 137.5, 137.1, 133.8, 131.7, 130.3, 130.2, 130.1, 129.1, 128.6, 127.3, 127.1, 125.3, 121.7. Analysis calc. for $C_{20}H_{13}BrN_2$ (360.03): C, 66.50; H, 3.63; N, 7.75. Found: C, 66.52; H, 3.64; N, 7.77.

2-(4-Nitrophenyl)-4-phenylquinazoline (5e). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (d, J = 8.4 Hz, 2H), 8.37 (d, J = 8.4 Hz, 2H), 8.19 (t, J = 8.8 Hz, 2H), 7.96 (t, J = 6.8 Hz, 1H), 7.91-7.88 (m, 2H), 7.66-7.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 158.0, 151.8, 149.2, 144.0, 137.2, 134.1, 130.3, 130.2, 129.5, 129.4, 128.7, 128.1, 127.2, 123.7, 122.0. Analysis calc. for $C_{20}H_{13}N_3O_2$ (327.10): C, 73.38; H, 4.00; N, 12.84. Found: C, 73.40; H, 4.00; N, 12.82.

2-(3-Chlorophenyl)-4-phenylquinazoline (5f). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71-8.70 (m, 1H), 8.62-8.59 (m, 1H), 8.20 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.94-7.88 (m, 3H), 7.63-7.57 (m, 4H), 7.49-7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 158.8, 151.7, 139.9, 137.4, 134.7, 133.9, 130.6, 130.2, 130.1, 129.8, 129.0, 128.7, 128.6, 127.5, 127.1, 126.8, 121.8. Analysis calc. for $C_{20}H_{13}ClN_2$ (316.08): C, 75.83; H, 4.14; N, 8.84. Found: C, 75.86; H, 4.13; Cl, 11.20; N, 8.82.

2-(3-Bromophenyl)-4-phenylquinazoline (5g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (t, J = 1.7 Hz, 1H), 8.66 (dt, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.16 (dd, J_1 = 8.4 Hz, J_2 = 1.7 Hz, 1H), 7.95-7.88 (m, 3H), 7.65-7.59 (m, 5H), 7.41 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 158.7, 151.5, 140.0, 137.3, 133.9, 133.5, 131.7, 130.2, 130.2, 130.1, 129.0, 128.6, 127.5, 127.3, 127.1, 122.9, 121.8. Analysis calc. for $C_{20}H_{13}BrN_2$ (360.03): C, 66.50; H, 3.63; N, 7.75. Found: C, 66.48; H, 3.64; N, 7.76.

2-(2-Chlorophenyl)-4-phenylquinazoline (5h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J_1 = 8.1 Hz, J_2 = 3.3 Hz, 2H), 7.97-7.87 (m, 4H), 7.67-7.63 (m, 1H), 7.62-7.52 (m, 3H), 7.44-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 161.3, 151.5, 138.4,

137.2, 133.9, 133.1, 131.9, 130.6, 130.3, 130.3, 130.1, 129.1, 128.7, 127.9, 127.1, 126.9, 121.4. Analysis calc. for $C_{20}H_{13}ClN_2$ (316.08): C, 75.83; H, 4.14; N, 8.84. Found: C, 75.80; H, 4.15; N, 8.86.

2-(2-Nitrophenyl)-4-phenylquinazoline (5i). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.16 (m, 3H), 7.97-7.89 (m, 2H), 7.83-7.80 (m, 2H), 7.72 (td, J_1 = 7.3 Hz, J_2 = 1.2 Hz, 1H), 7.67-7.57 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 158.9, 151.6, 150.1, 136.9, 134.1, 133.9, 132.3, 131.8, 130.3, 130.1, 129.1, 128.7, 128.1, 127.2, 124.2, 121.6. Analysis calc. for $C_{20}H_{13}N_3O_2$ (327.10): C, 73.38; H, 4.00; N, 12.84. Found: C, 73.35; H, 4.01; N, 12.86.

4-Phenyl-2-(p-tolyl)quinazoline (5j). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.51 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 8.0 Hz, 1H), 8.09 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.05-8.01 (m, 1H), 7.90-7.88 (m, 2H), 7.72-7.65 (m, 4H), 7.39 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 159.6, 151.7, 141.2, 137.5, 135.3, 134.9, 130.6, 130.5, 129.8, 129.1, 129.1, 128.6, 128.2, 127.3, 121.5, 21.6. Analysis calc. for $C_{21}H_{16}N_2$ (296.13): C, 85.11; H, 5.44; N, 9.45. Found: C, 85.09; H, 5.45; N, 9.46.

4-Phenyl-2-(m-tolyl)quinazoline (5k). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 8.9 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 8.13 (dd, J_1 = 8.4 Hz, J_2 = 1.7 Hz, 1H), 7.91-7.87 (m, 3H), 7.62-7.58 (m, 3H), 7.57-7.53 (m, 1H), 7.43 (td, J_1 =7.3 Hz, J_2 =0.7 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 160.4, 151.9, 138.2, 138.0, 137.7, 133.6, 131.4, 130.2, 130.0, 129.2, 129.1, 128.6, 128.5, 127.1, 127.0, 126.0, 121.7, 21.6. Analysis calc. for $C_{21}H_{16}N_2$ (296.13): C, 85.11; H, 5.44; N, 9.45. Found: C, 85.08; H, 5.46; N, 9.46.

4-Phenyl-2-(o-tolyl)quinazoline (5l). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (m, 2H), 7.99-7.97 (m, 1H), 7.94-7.90 (m, 1H), 7.88-7.85 (m, 2H), 7.63-7.56 (m, 4H), 7.37-7.33 (m, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 163.4, 151.6, 138.8, 137.5, 137.4, 133.7, 131.3, 130.7, 130.2, 129.9, 129.3, 129.1, 128.6, 127.3, 127.0, 126.0, 121.0, 21.3. Analysis calc. for $C_{21}H_{16}N_2$ (296.13): C, 85.11; H, 5.44; N, 9.45. Found: C, 85.09; H, 5.45; N, 9.46.

2-(4-Methoxyphenyl)-4-phenylquinazoline (5m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66-8.64 (m, 2H), 8.13 (d, J = 8.4 Hz, 1H), 8.10 (dd, J_1 = 9.0 Hz, J_2 = 2.1 Hz, 1H), 7.89-7.84 (m, 3H), 7.61-7.58 (m, 3H), 7.53-7.49 (m, 1H), 7.06-7.02 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 161.8, 160.0, 151.9, 137.8, 133.6, 130.8, 130.4, 130.2, 129.9, 128.9, 128.5, 127.1, 126.6, 121.4, 113.9, 55.4. Analysis calc. for $C_{21}H_{16}N_2O$ (312.13): C, 80.75; H, 5.16; N, 8.97. Found: C, 80.78; H, 5.16; N, 8.94.

2-(Naphthalen-2-yl)-4-phenylquinazoline (5n). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.82 (dd, J_1 = 8.6 Hz, J_2 = 1.7 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 8.16 (dd, J_1 = 8.3 Hz, J_2 = 2.0 Hz, 1H), 8.06-8.04 (m, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.96-7.89 (m, 4H), 7.67-7.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 160.2, 151.9, 137.7, 135.5, 134.7, 133.7, 133.4, 130.2, 130.0, 129.3, 129.1, 129.0, 128.6, 128.2, 127.7, 127.1, 127.0, 126.1, 125.6, 121.8. Analysis calc. for $C_{24}H_{16}N_2$ (332.13): C, 86.72; H, 4.85; N, 8.43. Found: C, 86.70; H, 4.86; N, 8.44.

4-Phenyl-2-(pyridin-4-yl)quinazoline (5o). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 2H), 8.54 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 2H), 8.22-8.17 (m, 2H), 7.97-7.93 (m, 1H), 7.91-7.88 (m, 2H), 7.66-7.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 158.1, 151.8, 150.4, 145.6, 137.2, 134.0, 130.2, 130.2, 129.4, 128.7, 128.1, 127.1, 122.4, 122.3. Analysis calc. for $C_{19}H_{13}N_3$ (283.11): C, 80.54; H, 4.62; N, 14.83. Found: C, 80.56; H, 4.61; N, 14.82.

2-(Naphthalen-1-yl)-4-phenylquinazoline (5p). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 8.7 Hz, 1H), 8.27-8.21 (m, 3H), 8.00-7.90 (m, 5H), 7.67-7.51 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 162.7, 151.6, 137.4, 136.4, 134.2, 133.9, 131.3, 130.3, 130.2, 130.0, 129.7, 129.1, 128.6, 128.5, 127.6, 127.1, 126.8, 126.0, 125.8, 125.3, 121.3. Analysis calc. for $C_{24}H_{16}N_2$ (332.13): C, 86.72; H, 4.85; N, 8.43. Found: C, 86.69; H, 4.87; N, 8.44.

6-Chloro-2,4-diphenylquinazoline (5q). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.66 (m, 2H), 8.12 (d, J = 6.4 Hz, 1H), 8.10 (s, 1H), 7.88-7.86 (m, 2H), 7.83 (dd, J_1 = 9.2 Hz, J_2 = 7.2 Hz, 1H), 7.64-7.62 (m, 3H), 7.54-7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 160.5, 150.5, 137.8, 137.1, 134.5, 132.6, 130.9, 130.8, 130.2, 130.1,

128.8, 128.7, 128.6, 125.8, 122.2. Analysis calc. for $C_{20}H_{13}ClN_2$ (316.08): C, 75.83; H, 4.14; N, 8.84. Found: C, 75.81; H, 4.15; N, 8.85.

2-(4-Bromophenyl)-6-chloro-4-phenylquinazoline (5r). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 8.4 Hz, 2H), 8.10-8.08 (m, 2H), 7.87-7.82 (m, 3H), 7.66-7.62 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.5, 149.4, 135.9, 135.7, 133.7, 131.9, 130.7, 129.8, 129.3, 129.2, 129.0, 127.8, 124.8, 124.6, 121.2. Analysis calc. for $C_{20}H_{12}BrClN_2$ (393.99): C, 60.71; H, 3.06; N, 7.08. Found: C, 60.73; H, 3.05; N, 7.07.

6-Chloro-4-phenyl-2-(p-tolyl)quinazoline (5s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 8.0 Hz, 2H), 8.10-8.08 (m, 2H), 7.88-7.85 (m, 2H), 7.81 (dd, J_1 = 9.2 Hz, J_2 =6.8 Hz, 1H), 7.63-7.61 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 160.6, 150.5, 141.1, 137.2, 135.0, 134.4, 132.3, 130.8, 130.2, 130.1, 129.4, 128.7, 128.7, 125.8, 122.1, 21.6. Analysis calc. for $C_{21}H_{15}ClN_2$ (330.09): C, 76.25; H, 4.57; N, 8.47. Found: C, 76.22; H, 4.58; N, 8.49.

4-Methyl-2-phenylquinazoline (5t). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63-8.60 (m, 2H), 8.12-8.08 (m, 2H), 7.90-7.85 (m, 1H), 7.62-7.58 (m, 1H), 7.56-7.50 (m, 3H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 133.6, 130.4, 129.2, 128.6, 128.6, 128.3, 126.9, 125.0, 123.0, 29.7. Analysis calc. for $C_{15}H_{12}N_2$ (220.10): C, 81.79; H, 5.49; N, 12.72. Found: C, 81.76; H, 5.50; N, 12.74.

4-(4-fluorophenyl)-2-phenylquinazoline (5u). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.67 (m, 2H), 8.17 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.92-7.88 (m, 3H), 7.58-7.50 (m, 4H), 7.31-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 164.0 (d, $^1J_{C\text{-}F}$=249 Hz, 1C), 160.2, 152.0, 138.0, 133.8 (d, $^4J_{C\text{-}F}$=3 Hz, 1C), 133.7, 132.2 (d, $^3J_{C\text{-}F}$=8 Hz, 2C), 130.6, 129.3, 128.7, 128.6, 128.3, 127.2, 126.7, 121.6, 115.7 (d, $^2J_{C\text{-}F}$=21 Hz, 2C). Analysis calc. for $C_{20}H_{13}FN_2$ (300.11): C, 79.98; H, 4.36; N, 9.33. Found: C, 79.96; H, 4.37; N, 9.34.

4-(4-chlorophenyl)-2-phenylquinazoline (5v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.67 (m, 2H), 8.19 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.93-7.89 (m, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.60-7.51 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 160.2, 151.9., 137.9, 136.4, 136.1, 133.8, 131.5, 130.7, 129.2, 128.9, 128.7, 128.6,

128.3, 127.3, 126.6, 121.5. Analysis calc. for $C_{20}H_{13}ClN_2$ (316.08): C, 75.83; H, 4.14; N, 8.84. Found: C, 75.82; H, 4.13; N, 8.86.

4-(4-bromophenyl)-2-phenylquinazoline (5w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.66 (m, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.92-7.88 (m, 1H), 7.79-7.73 (m, 4H), 7.58-7.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 160.2, 152.0, 137.9, 136.5, 133.8, 131.8, 131.8, 130.7, 129.3, 128.7, 128.6, 127.3, 126.6, 124.7, 121.5. Analysis calc. for $C_{20}H_{13}BrN_2$ (360.03): C, 66.50; H, 3.63; N, 7.75. Found: C, 66.47; H, 3.64; N, 7.77.

***N*-(2-Bsenzoylphenyl)benzamide (IV).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.98 (s, 1H), 8.90 (d, *J* = 8, 1H), 8.09-8.06 (m, 2H), 7.74-7.72 (m, 2H), 7.68-7.59 (m, 3H), 7.56-7.49 (m, 5H), 7.16-7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 164.9, 140.1, 137.8, 133.7, 133.5, 133.1, 131.4, 131.0, 128.8, 127.8, 127.3, 126.4, 122.1, 121.2, 120.4. Analysis calc. for $C_{20}H_{15}NO_2$ (301.11): C, 79.72; H, 5.02; N, 4.65. Found: C, 79.69; H, 5.03; N, 4.67. MS: m/z 301.95 $[M+H]^+$

References

1 J. Castells-Gil, N. M. Padial, N. Almora-Barrios, J. Albero, A. R. RuizSalvador, J. González-Platas, H. García and C. Martí-Gastaldo, *Angew. Chem. Int. Ed.*, 2018, **57**, 8453-8457.

5. The NMR spectra

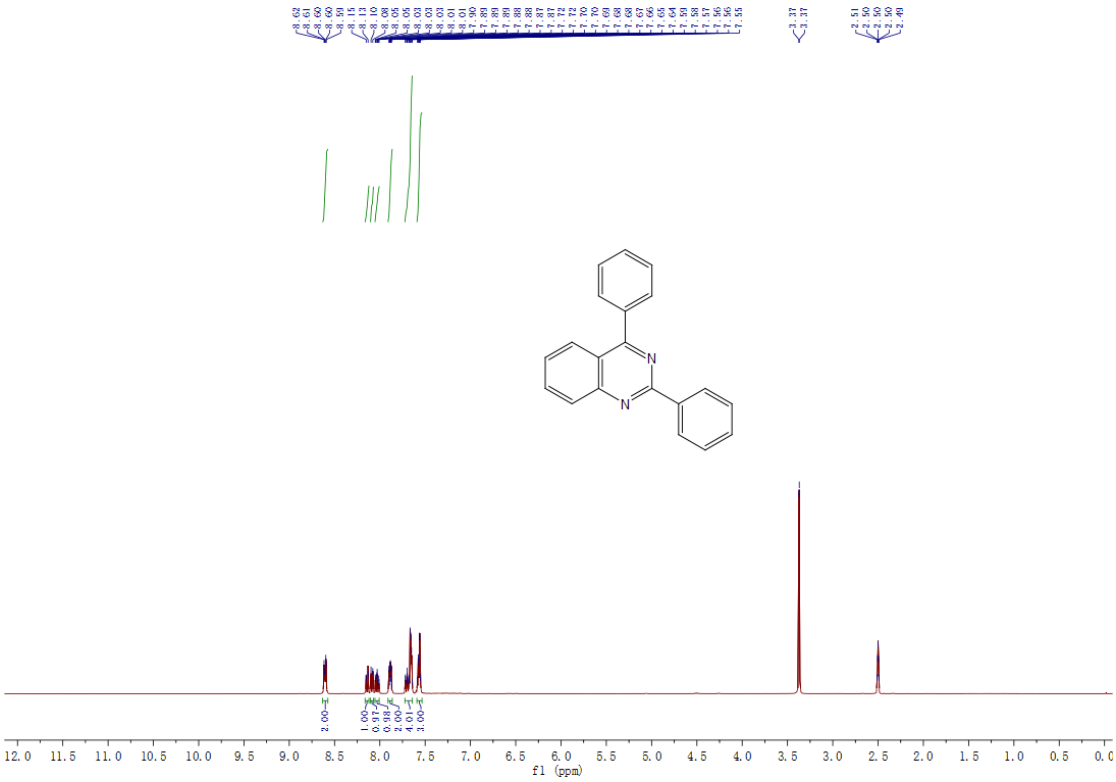


Fig. S5 ^{1}H NMR spectrum of **5a**

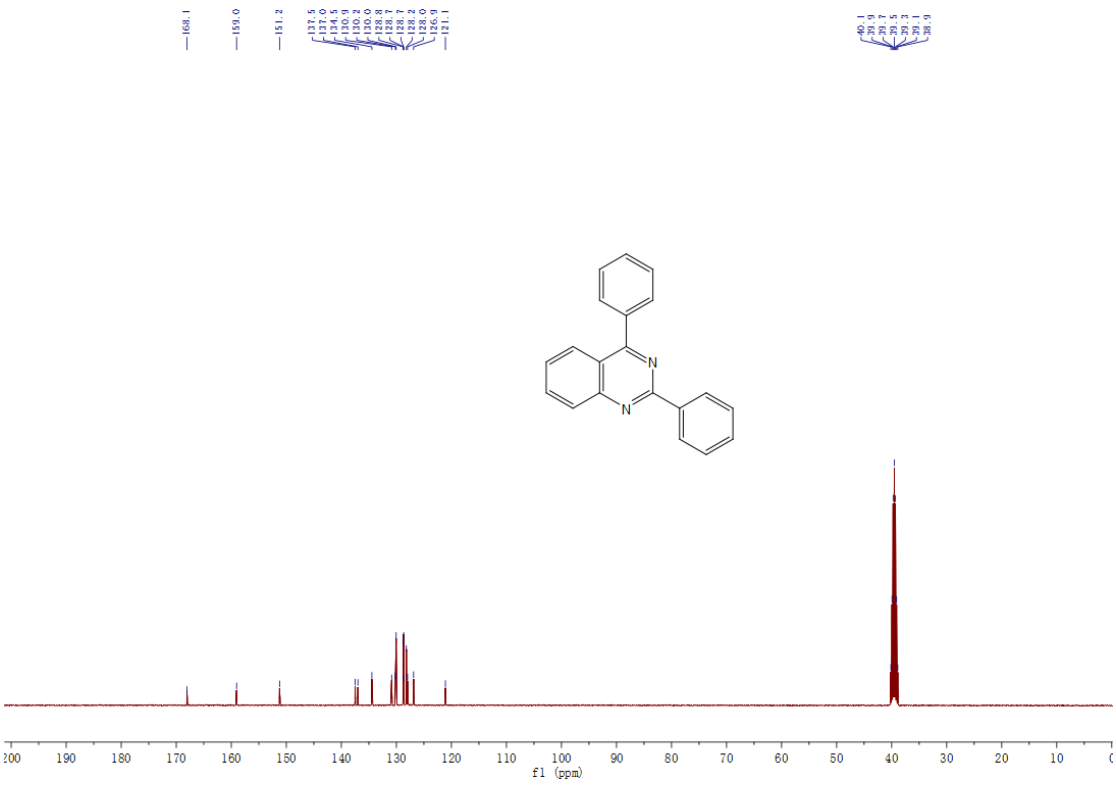


Fig. S6 ^{13}C NMR spectrum of **5a**

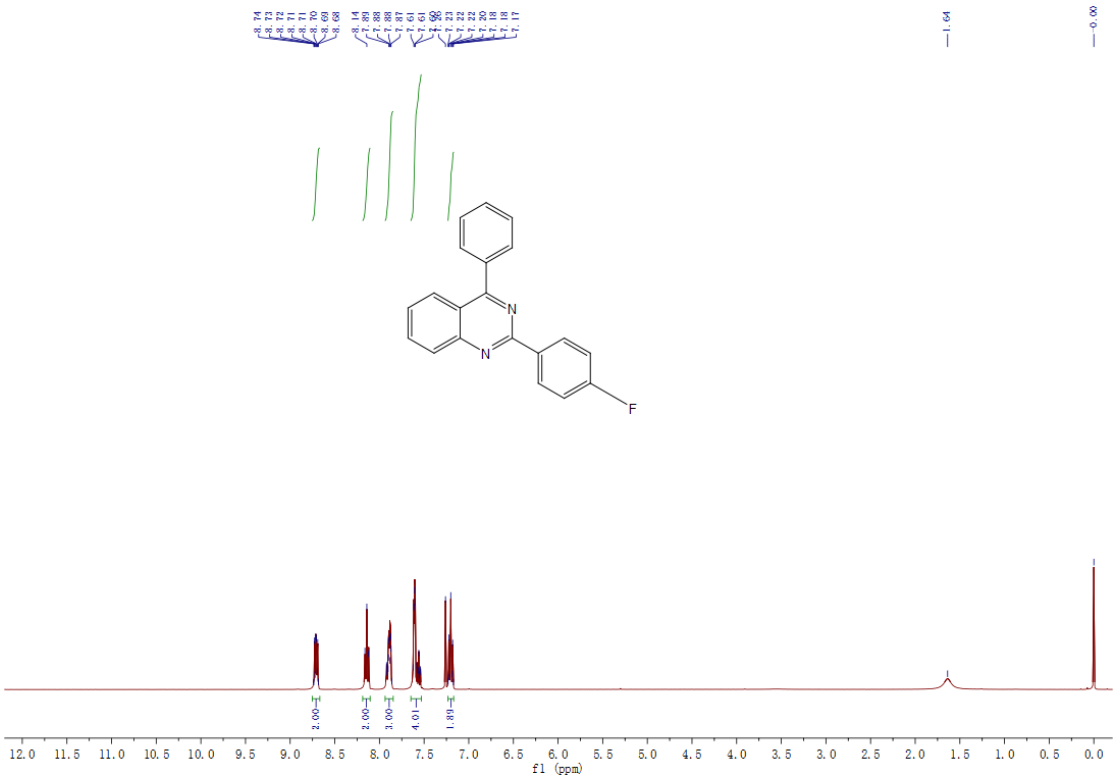


Fig. S7 ^{1}H NMR spectrum of **5b**

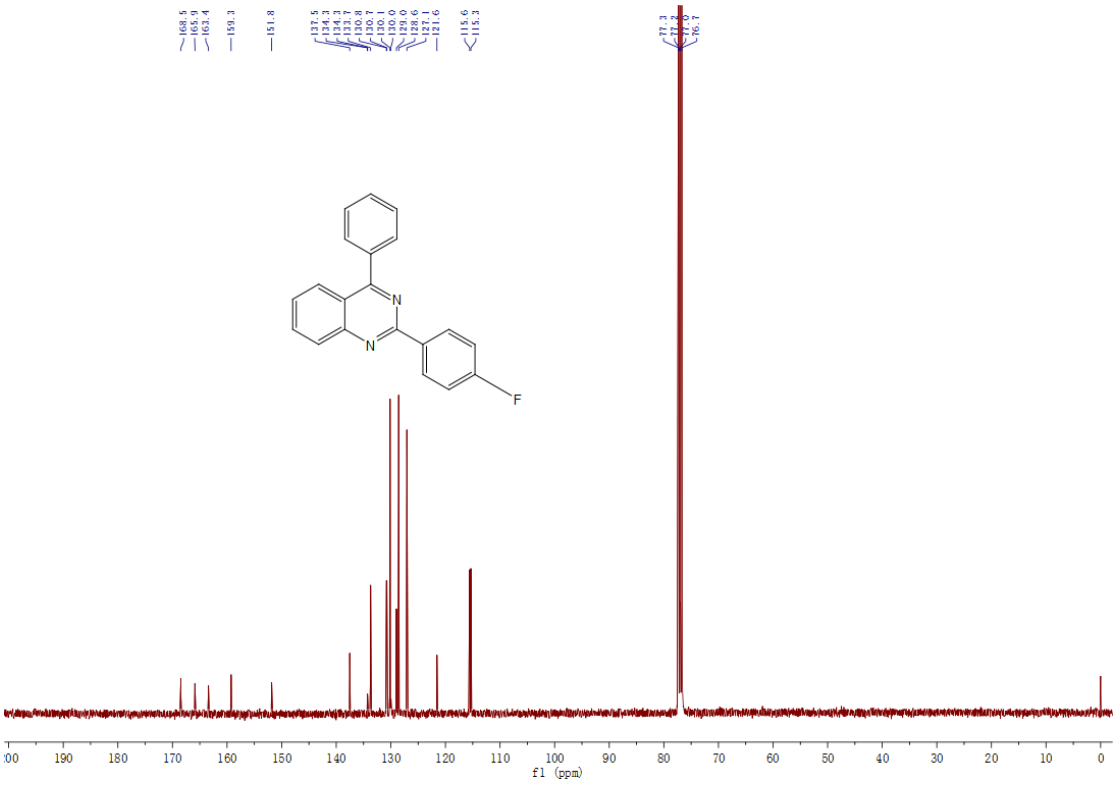


Fig. S8 ^{13}C NMR spectrum of **5b**

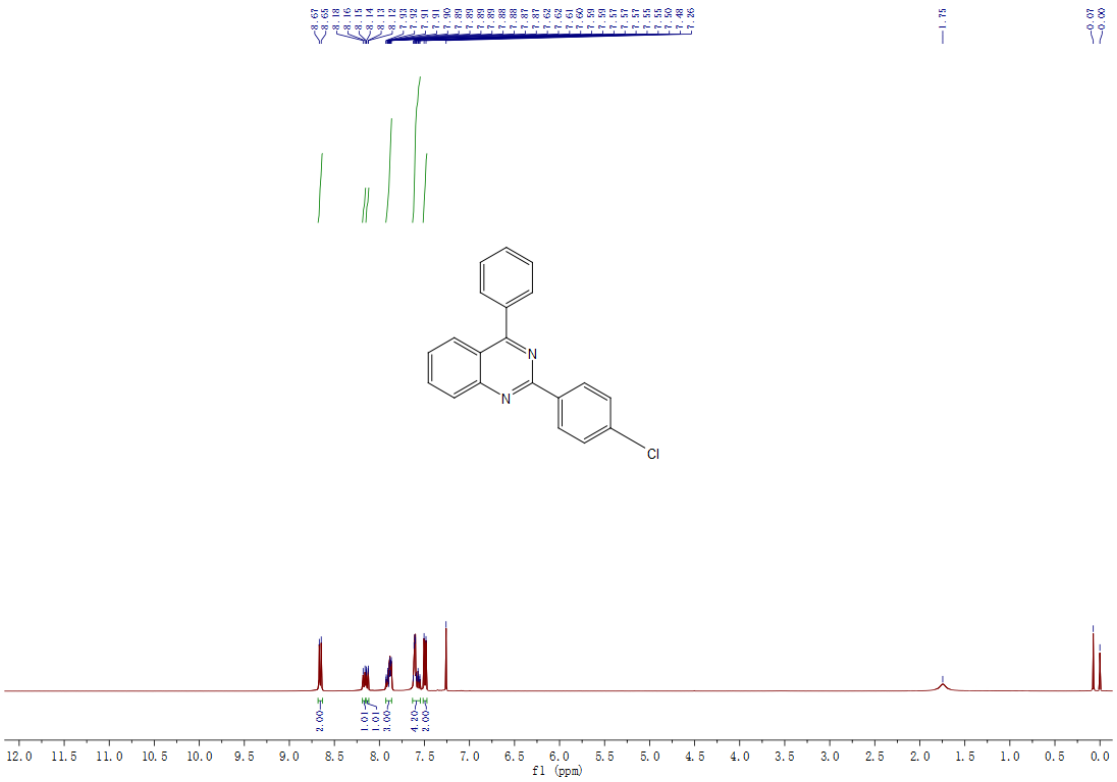


Fig. S9 ^{1}H NMR spectrum of **5c**

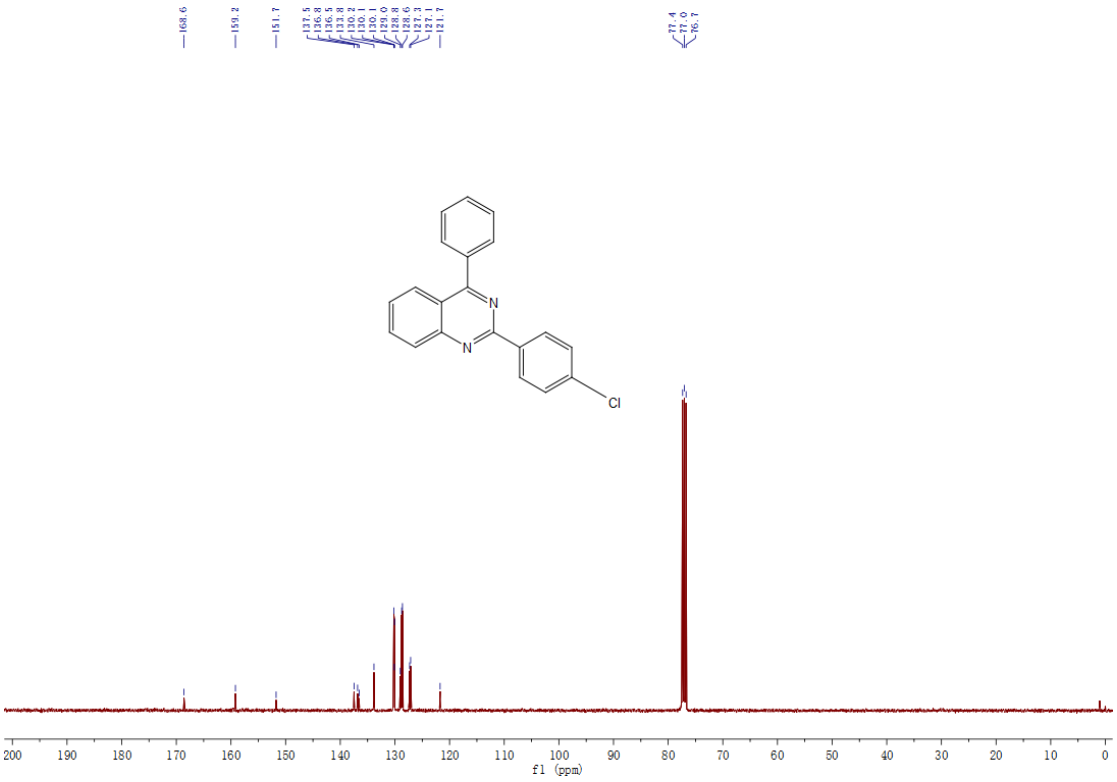


Fig. S10 ^{13}C NMR spectrum of **5c**

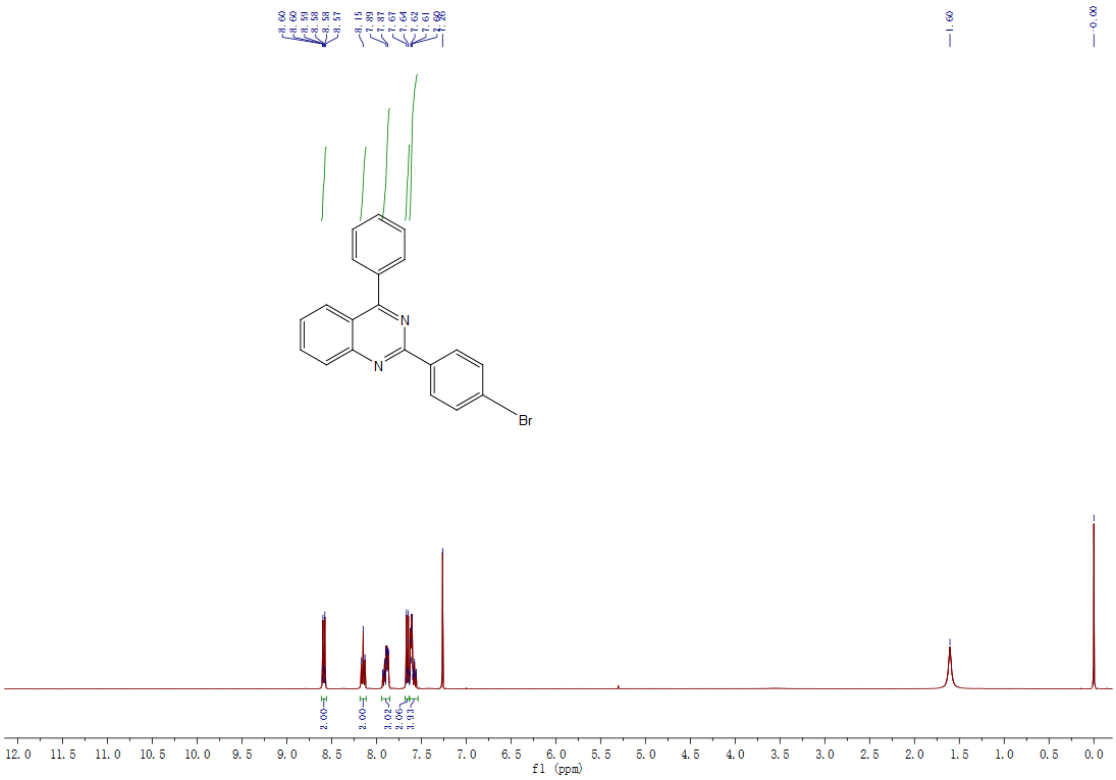


Fig. S11 ^{1}H NMR spectrum of **5d**

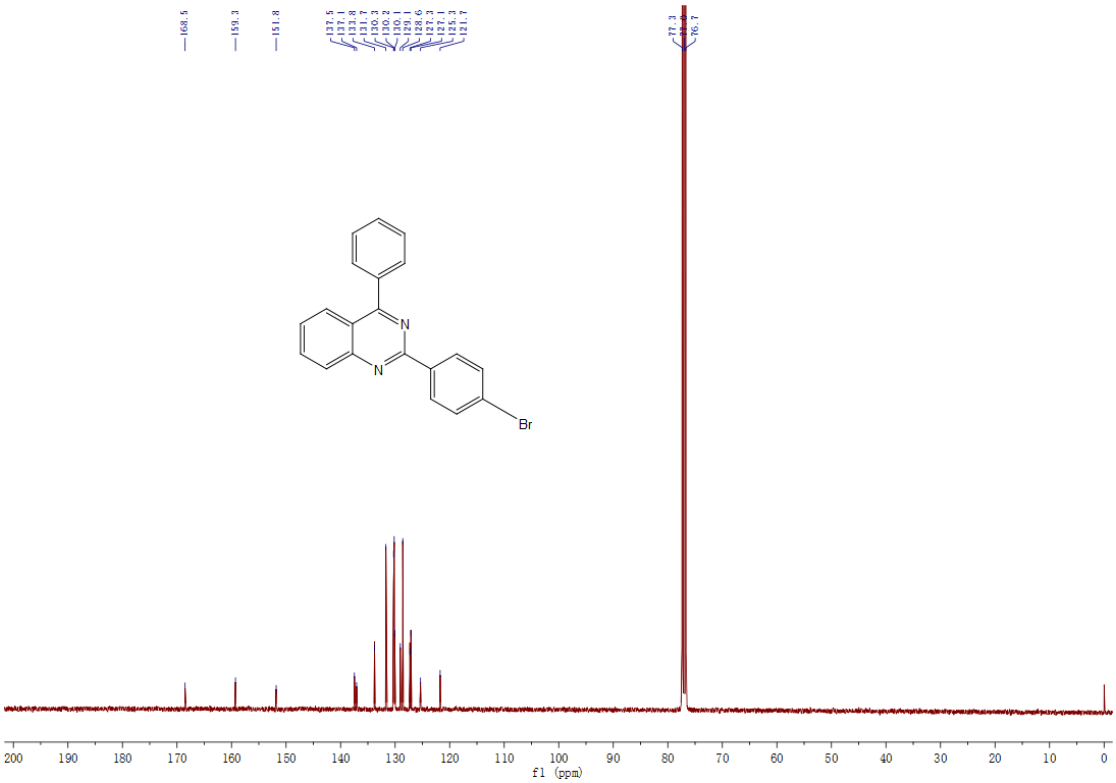


Fig. S12 ^{13}C NMR spectrum of **5d**

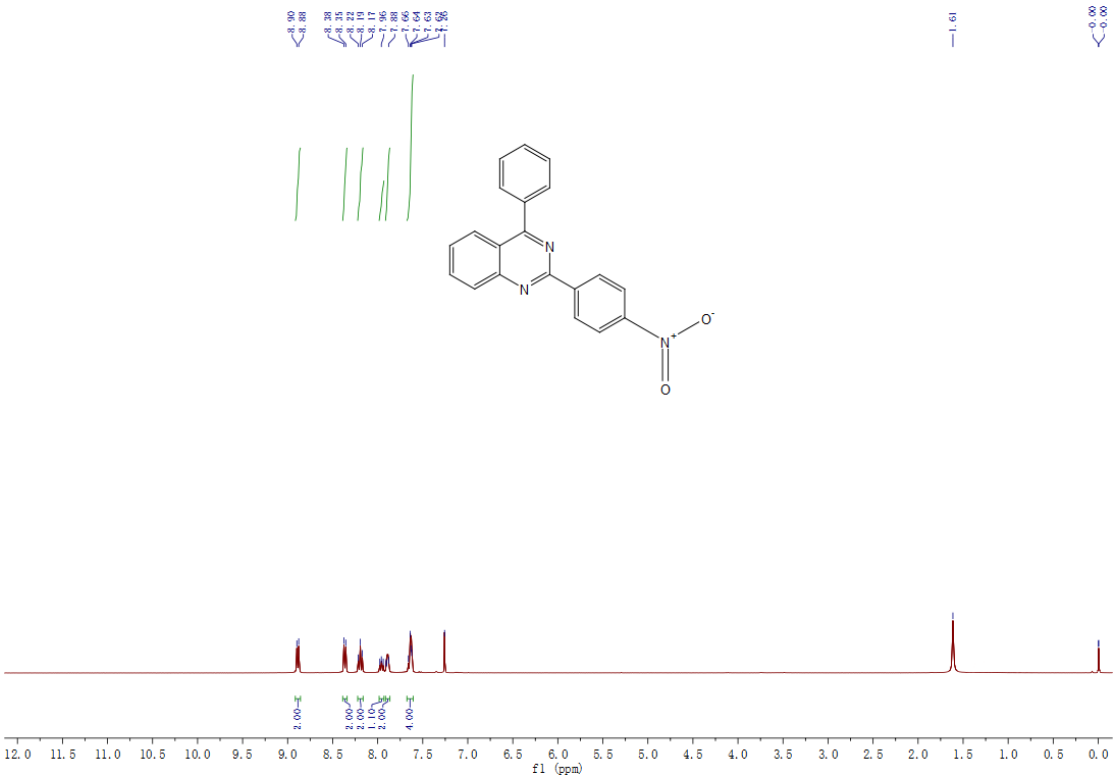


Fig. S13 ^{1}H NMR spectrum of **5e**

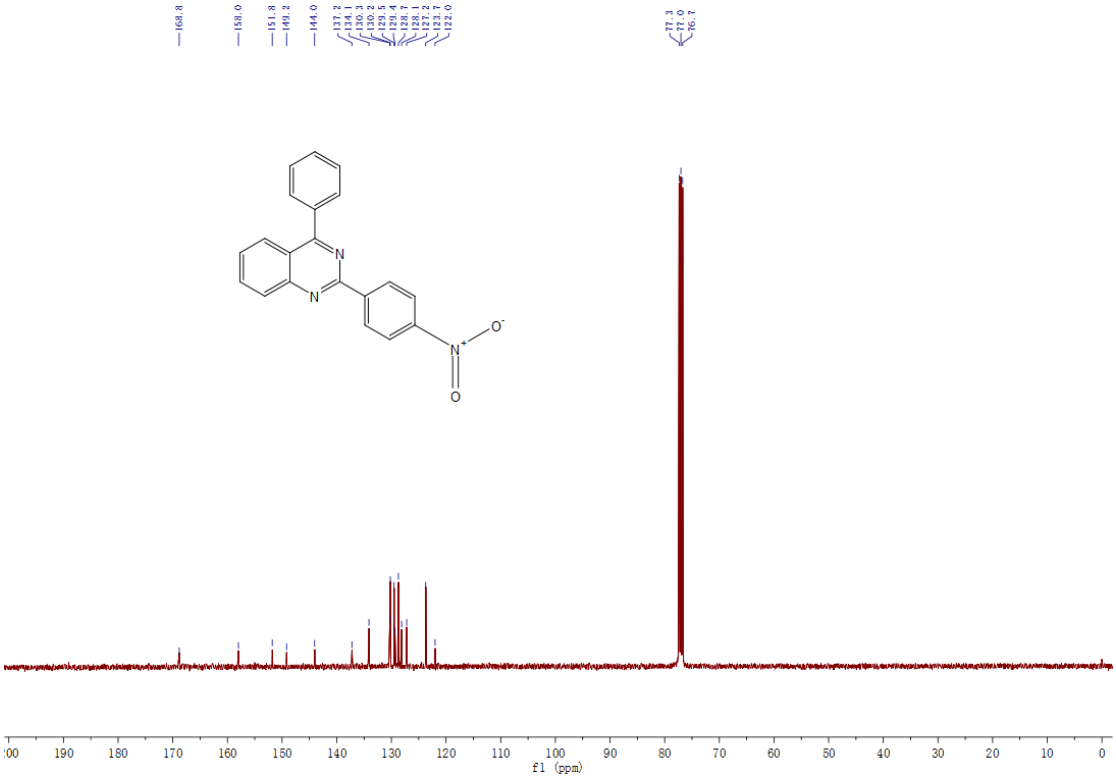


Fig. S14 ^{13}C NMR spectrum of **5e**

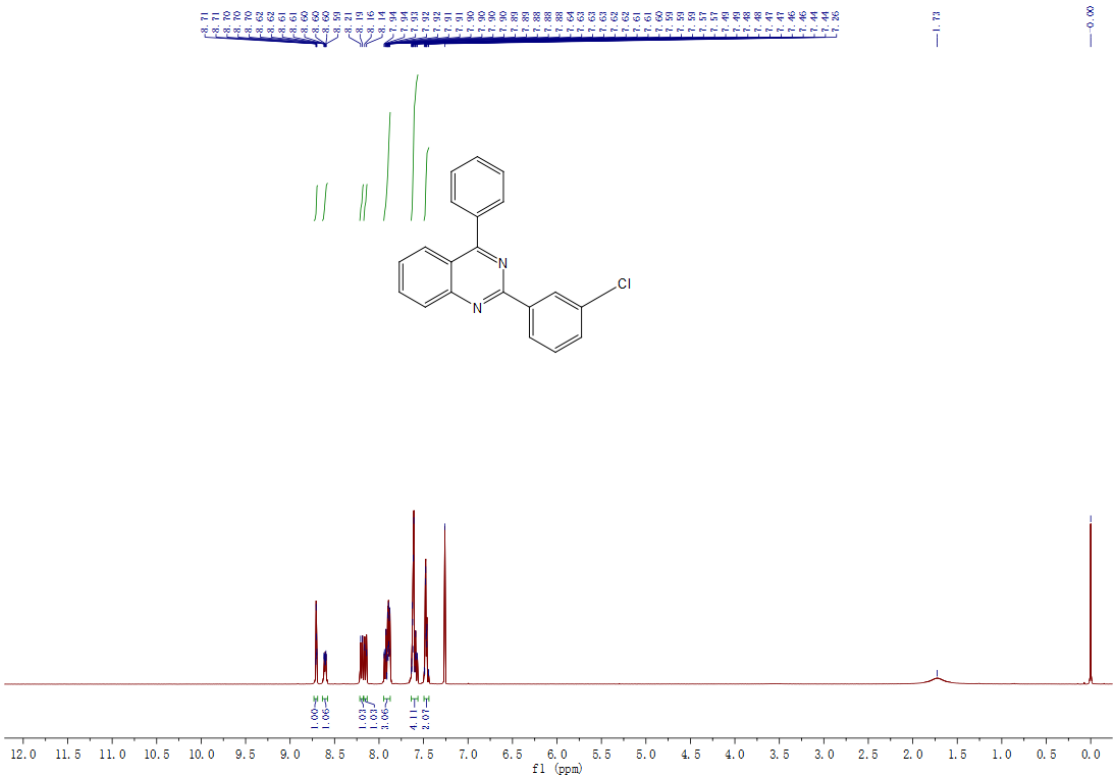


Fig. S15 ^{1}H NMR spectrum of **5f**

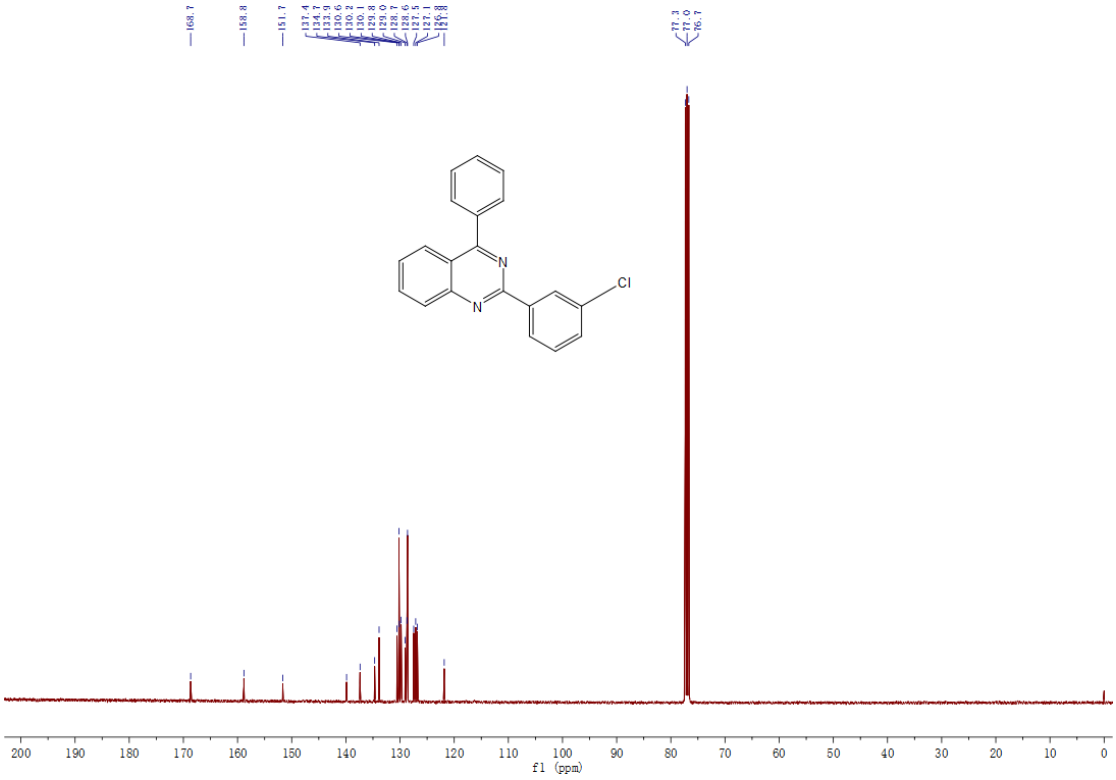


Fig. S16 ^{13}C NMR spectrum of **5f**

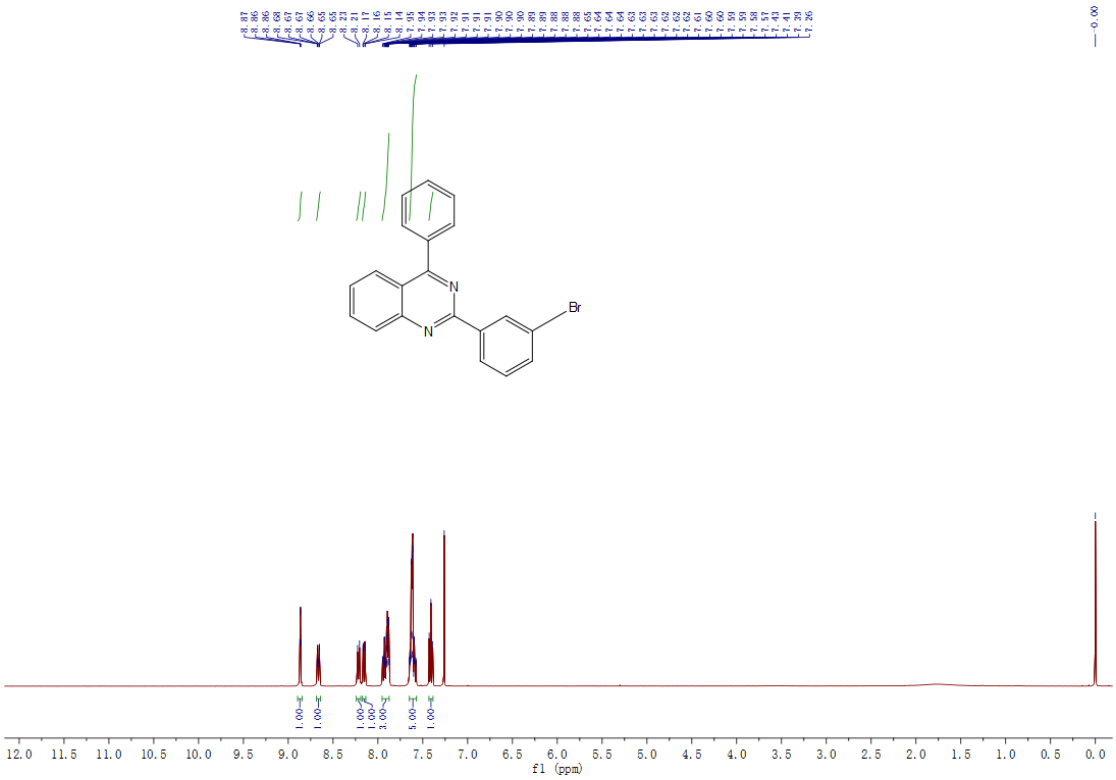


Fig. S17 ^{1}H NMR spectrum of **5g**

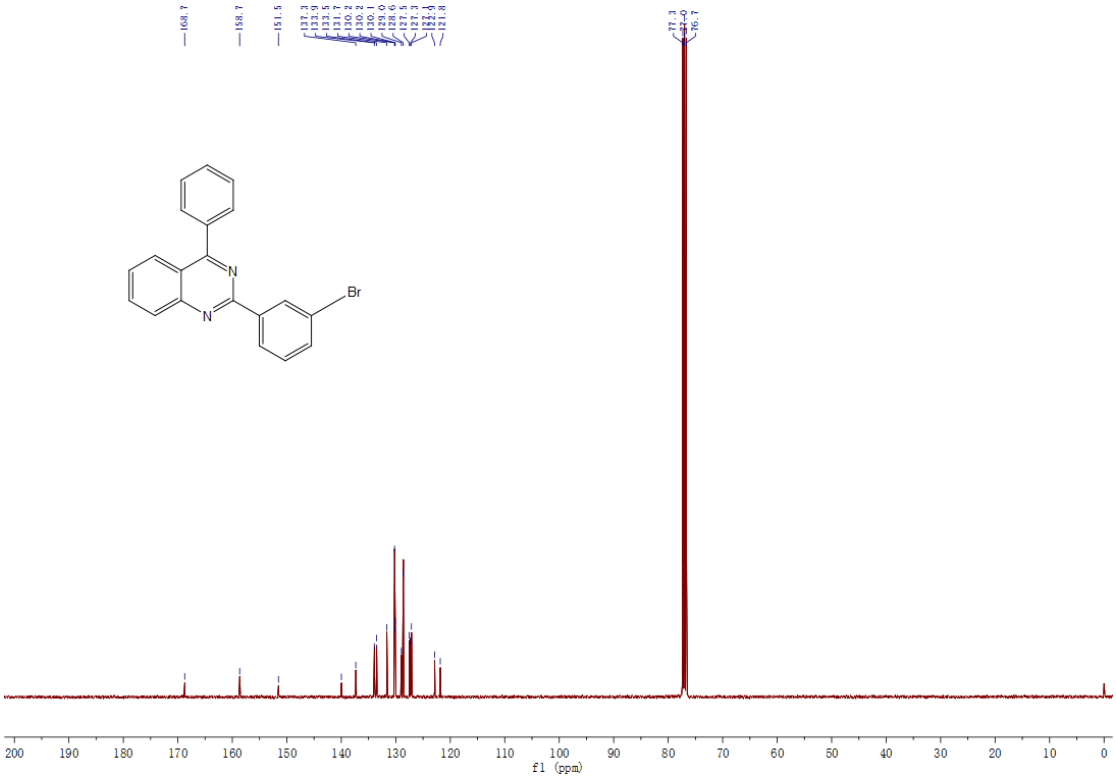


Fig. S18 ^{13}C NMR spectrum of **5g**

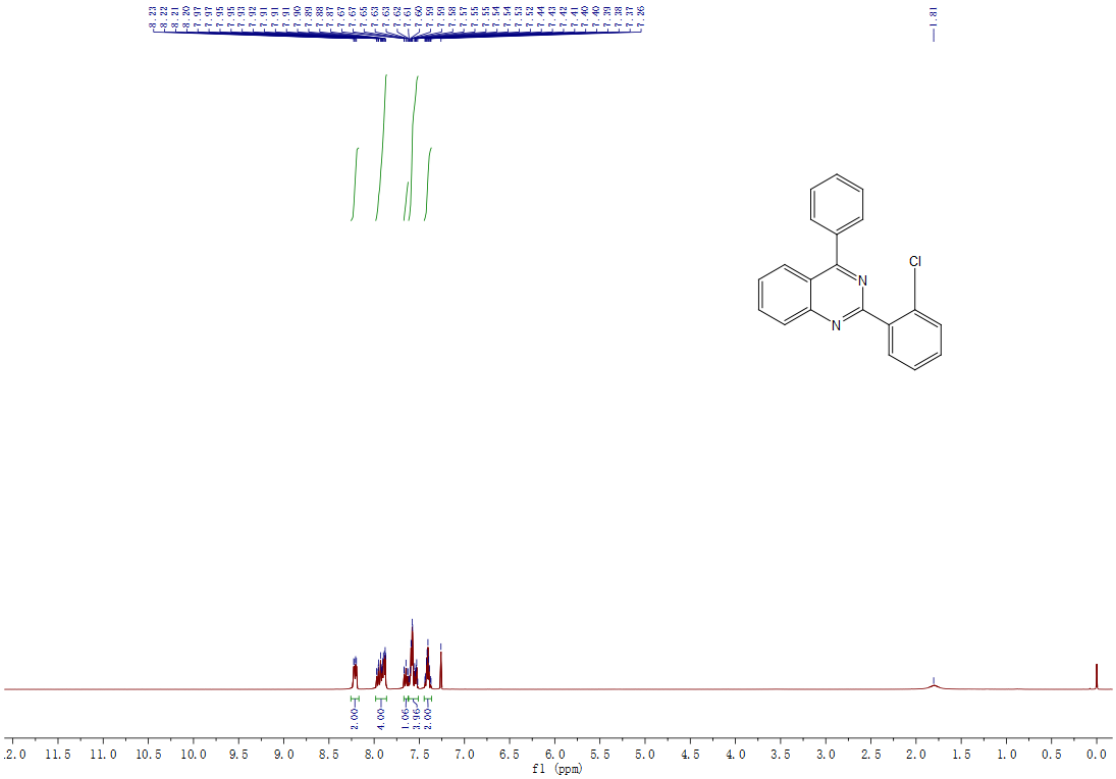


Fig. S19 ^{1}H NMR spectrum of **5h**

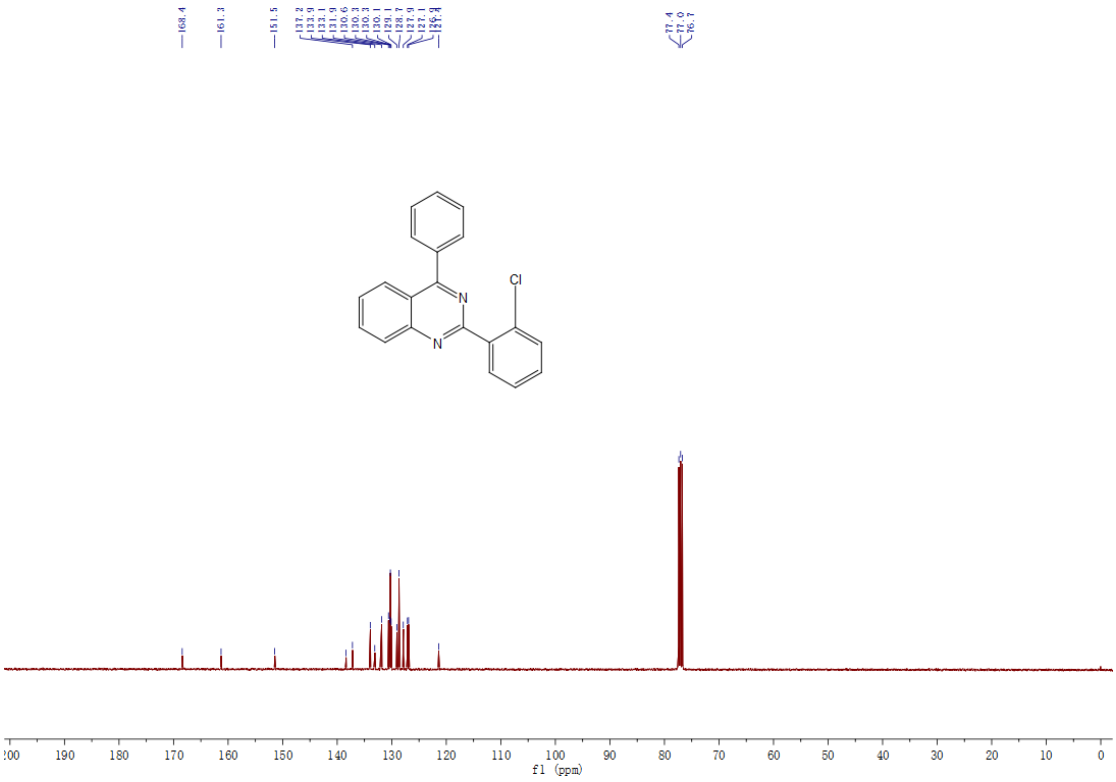


Fig. S20 ^{13}C NMR spectrum of **5h**

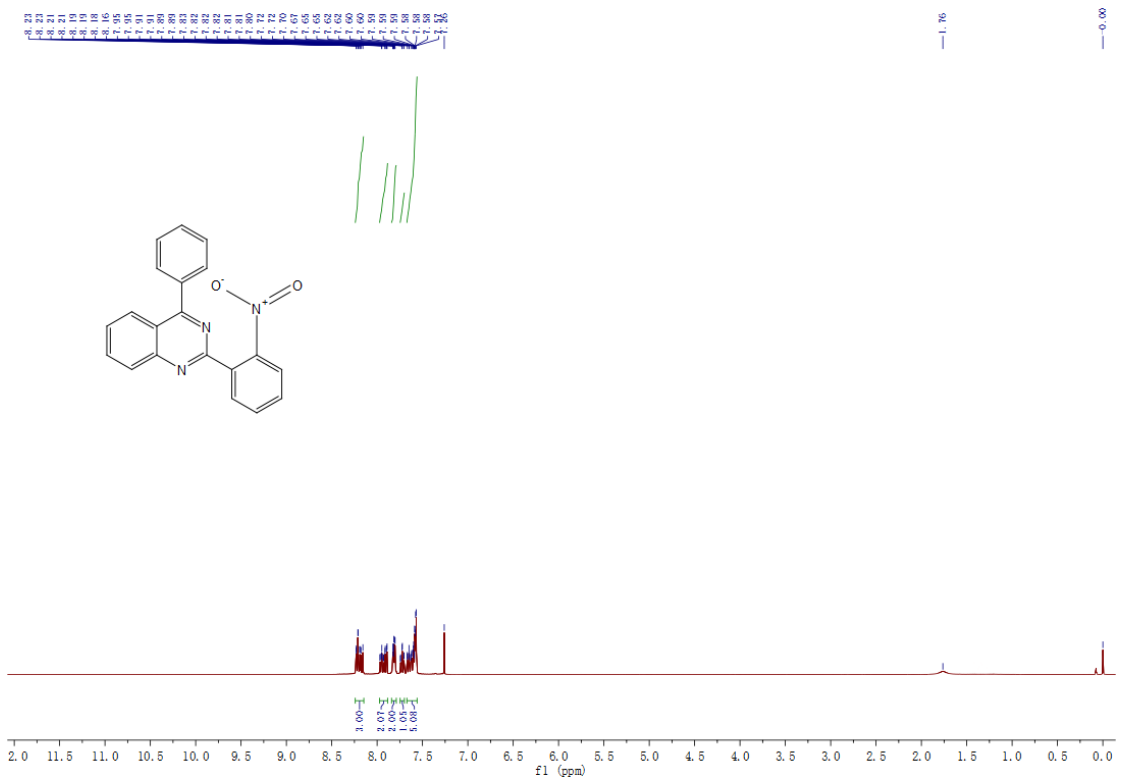


Fig. S21 ^{1}H NMR spectrum of **5i**

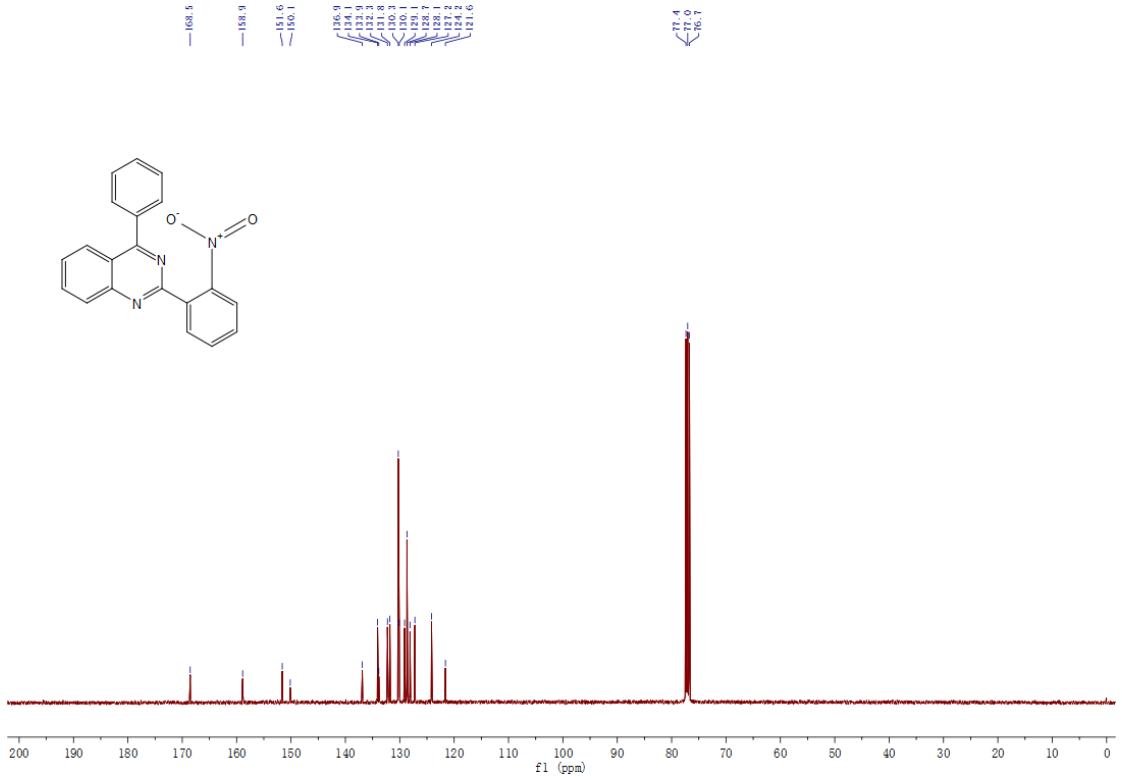


Fig. S22 ^{13}C NMR spectrum of **5i**

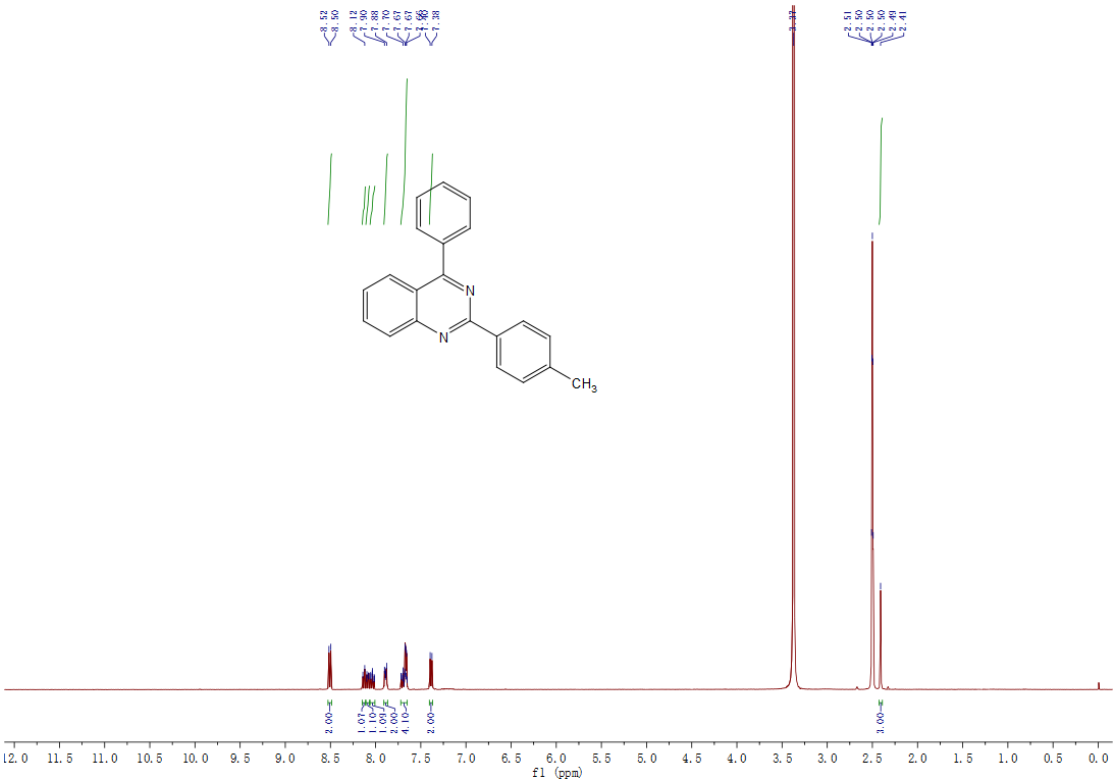


Fig. S23 ^{1}H NMR spectrum of **5j**

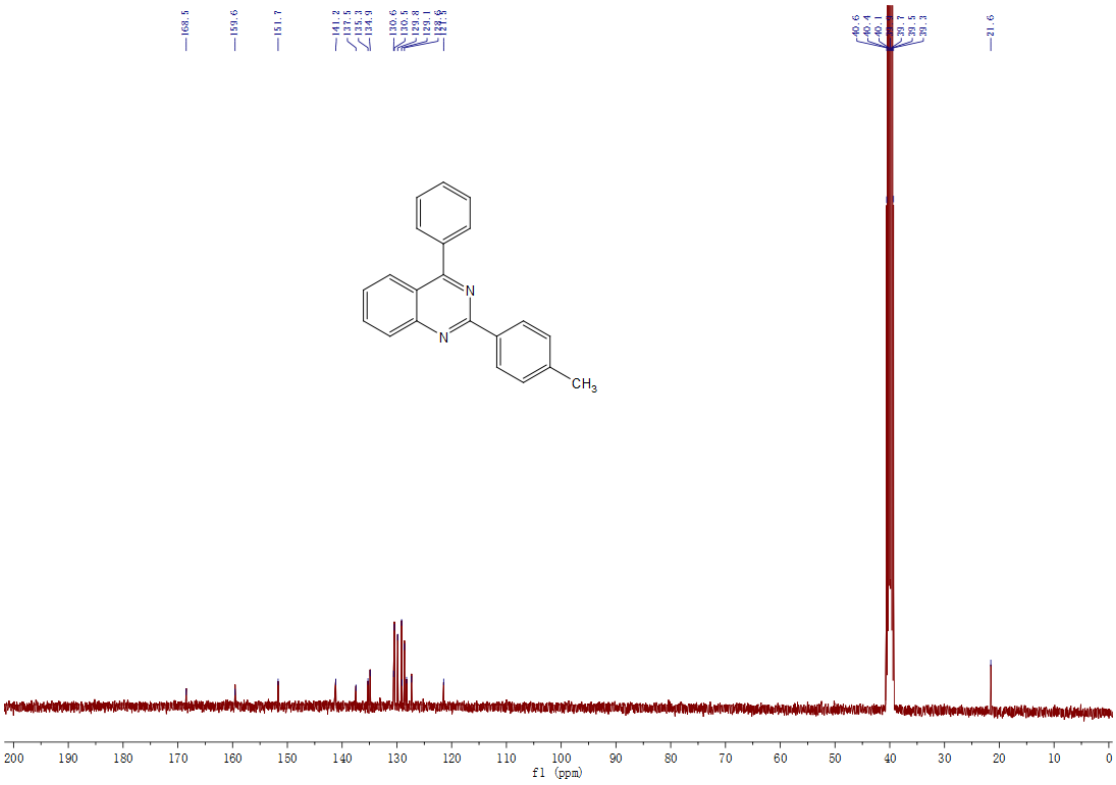


Fig. S24 ^{13}C NMR spectrum of **5j**

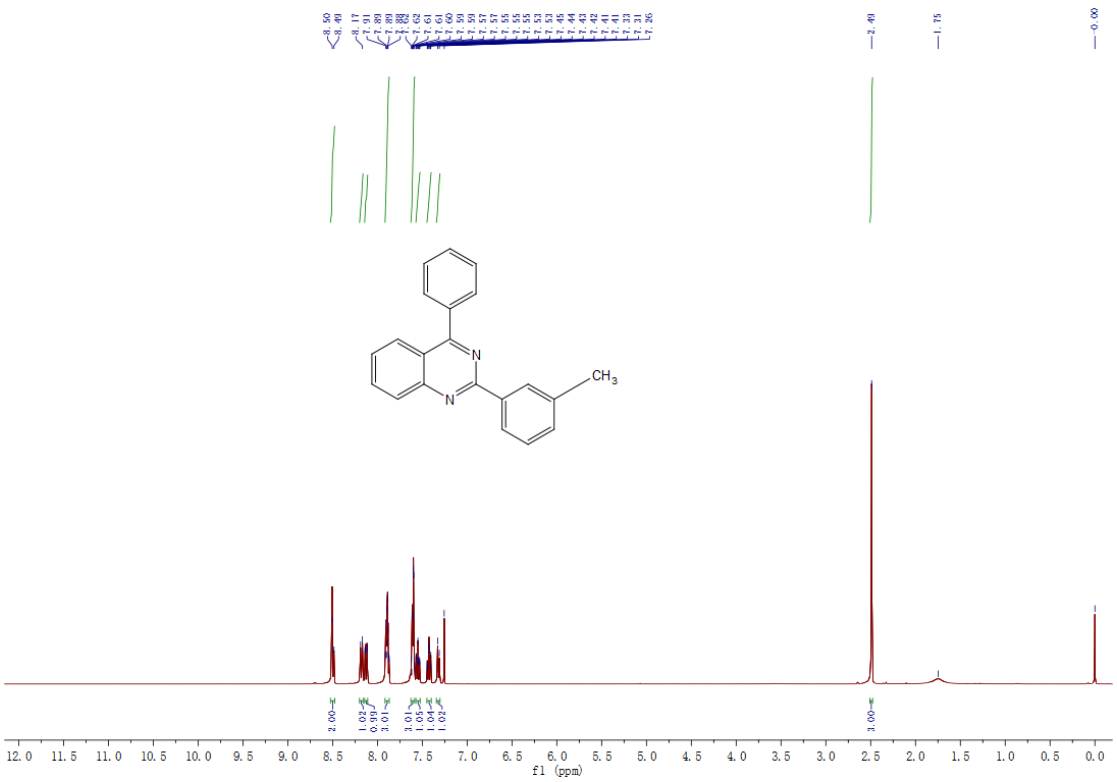


Fig. S25 ^{1}H NMR spectrum of **5k**

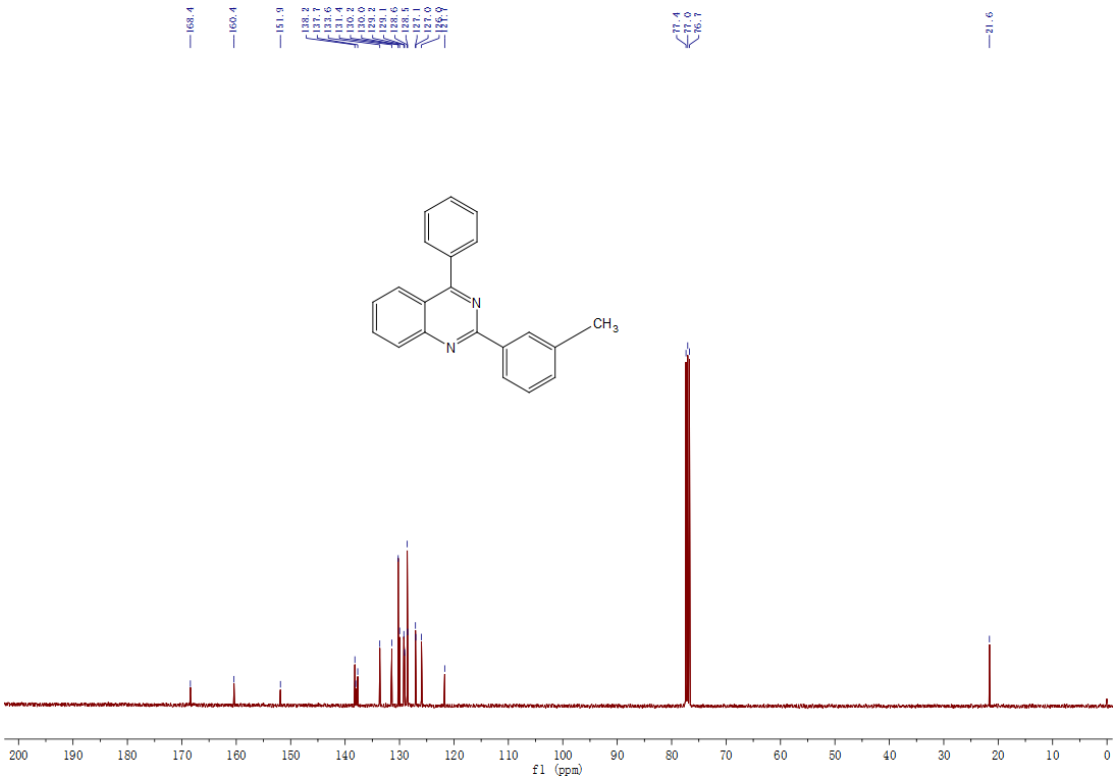


Fig. S26 ^{13}C NMR spectrum of **5k**

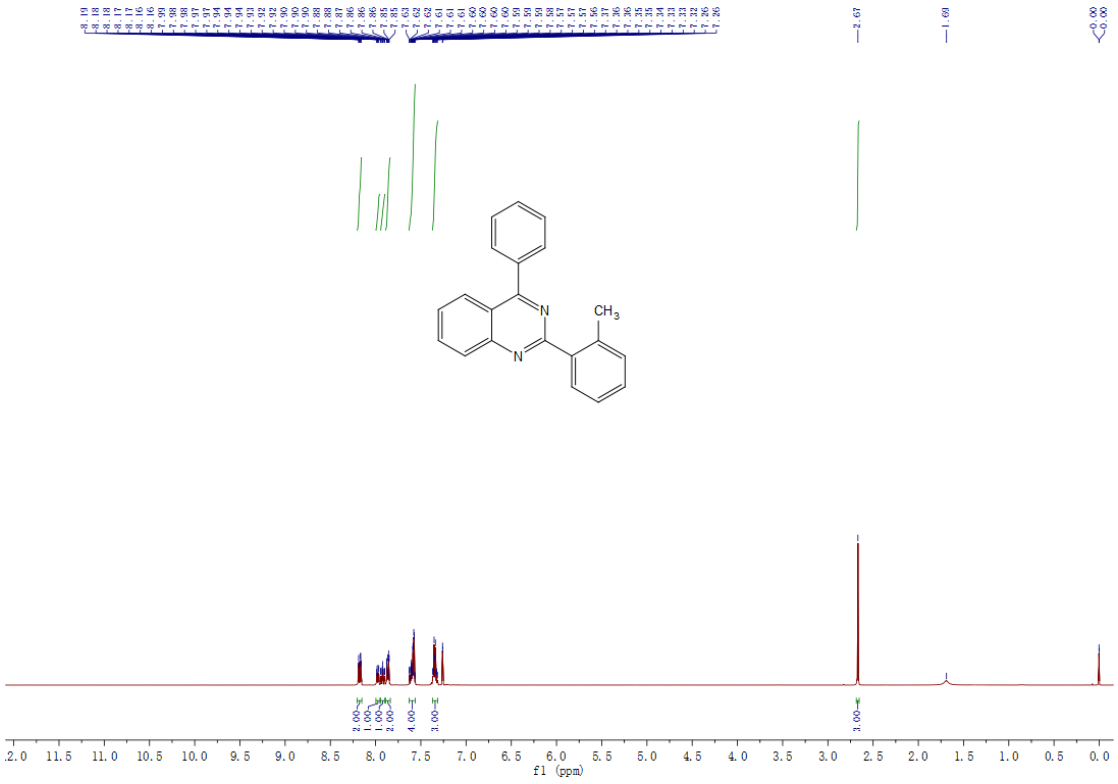


Fig. S27 ^{1}H NMR spectrum of **5l**

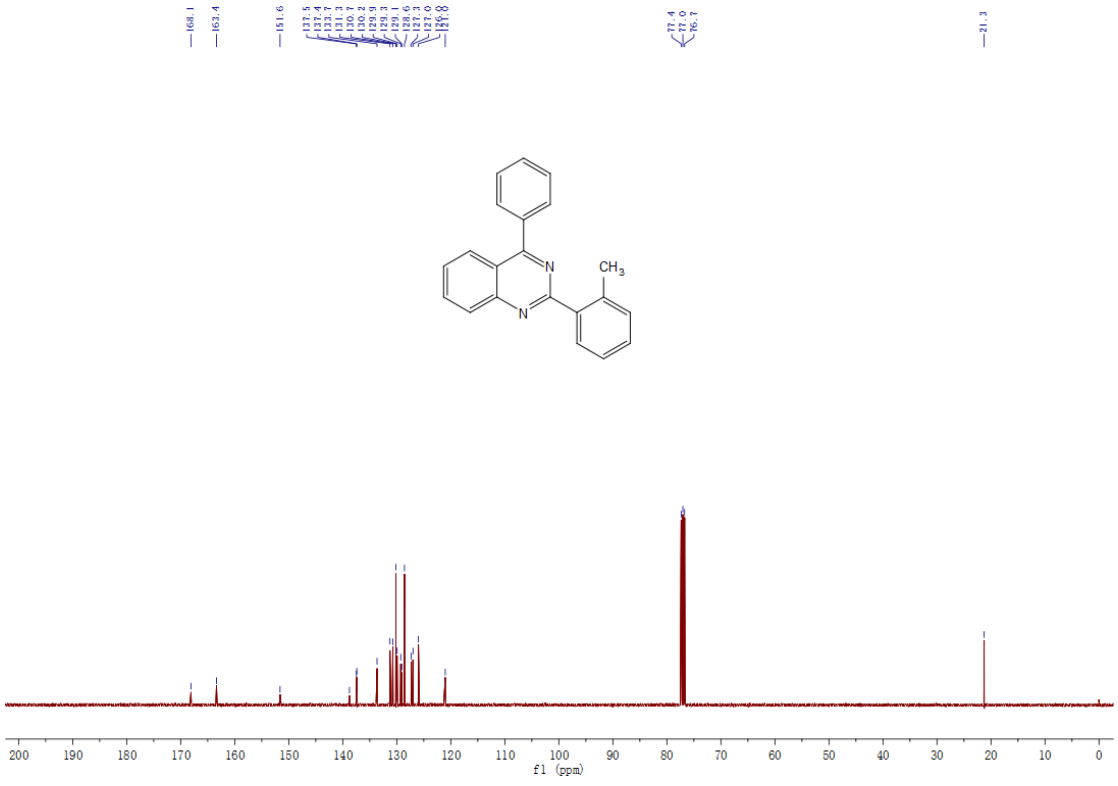


Fig. S28 ^{13}C NMR spectrum of **5l**

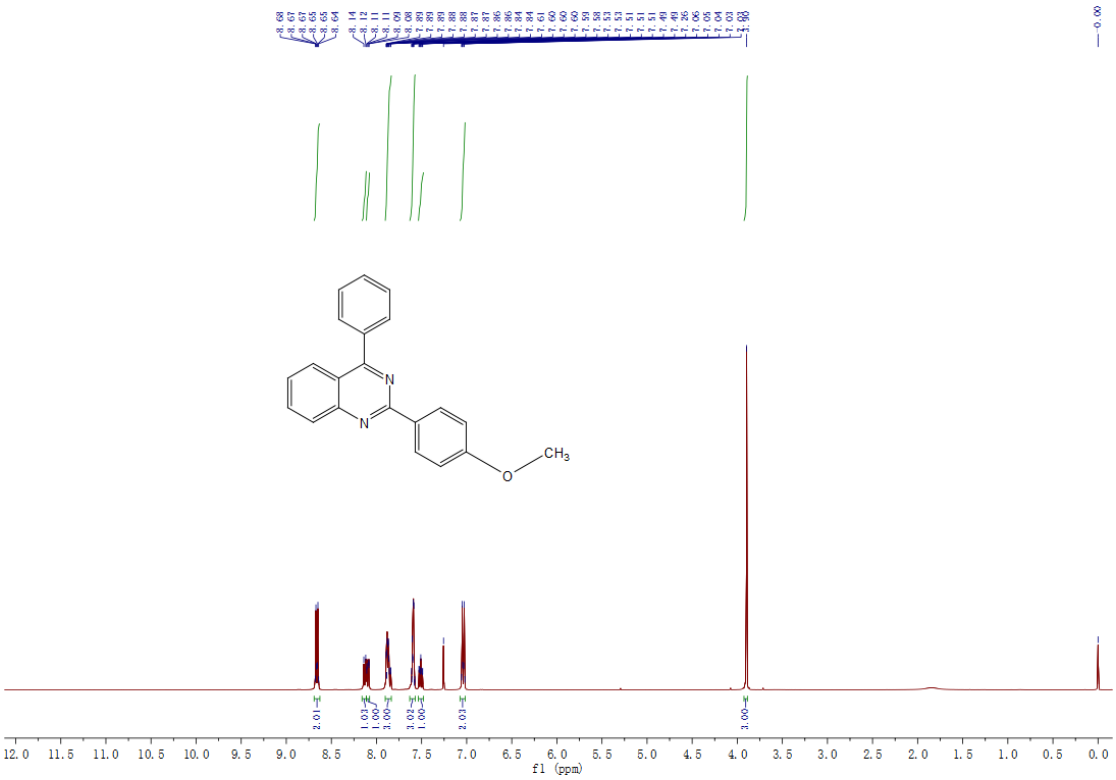


Fig. S29 ^{1}H NMR spectrum of **5m**

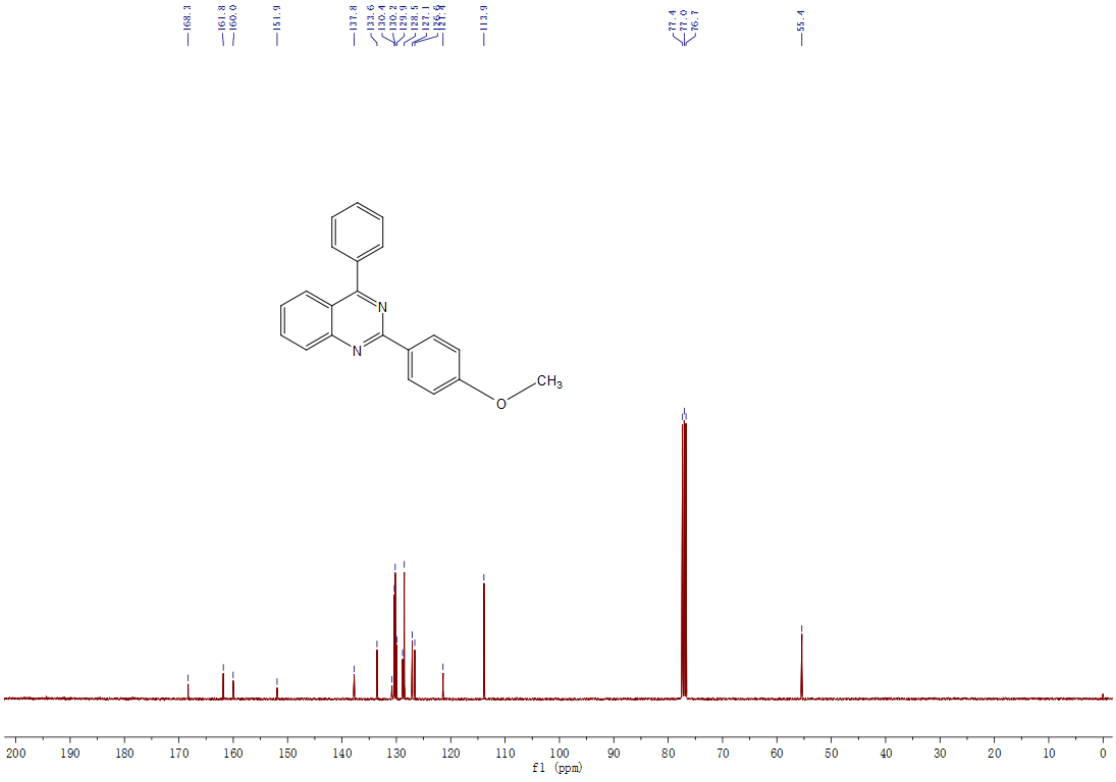


Fig. S30 ^{13}C NMR spectrum of **5m**

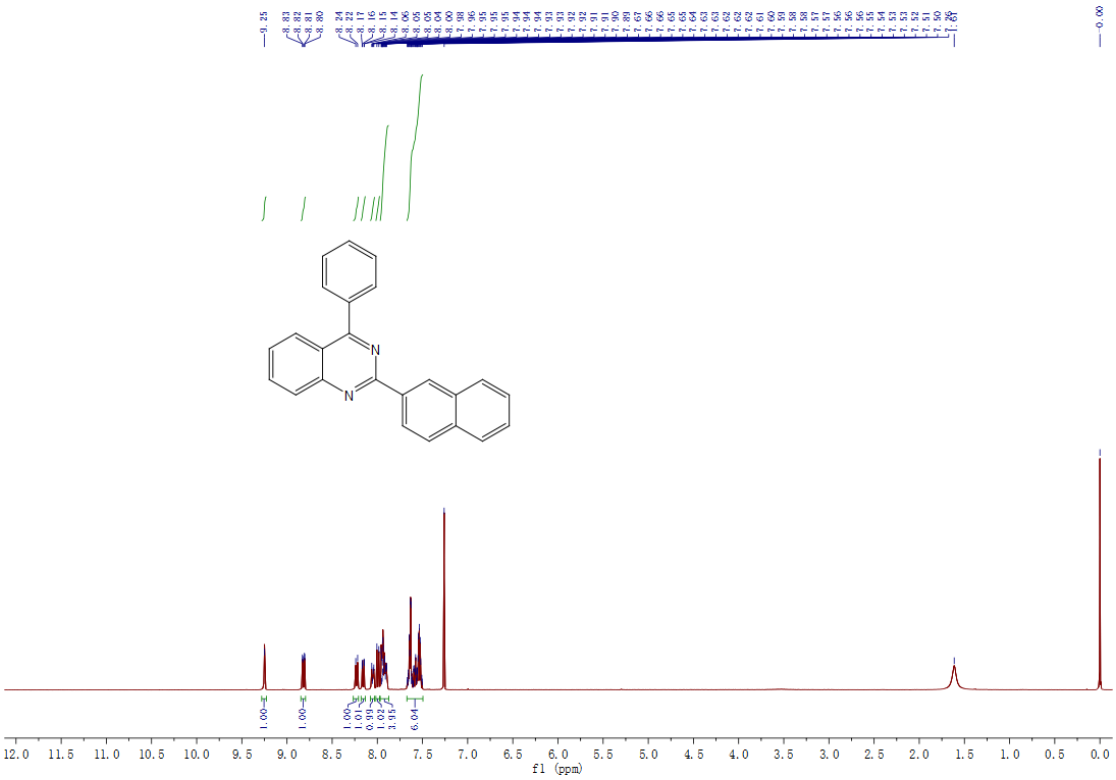


Fig. S31 ^{1}H NMR spectrum of **5n**

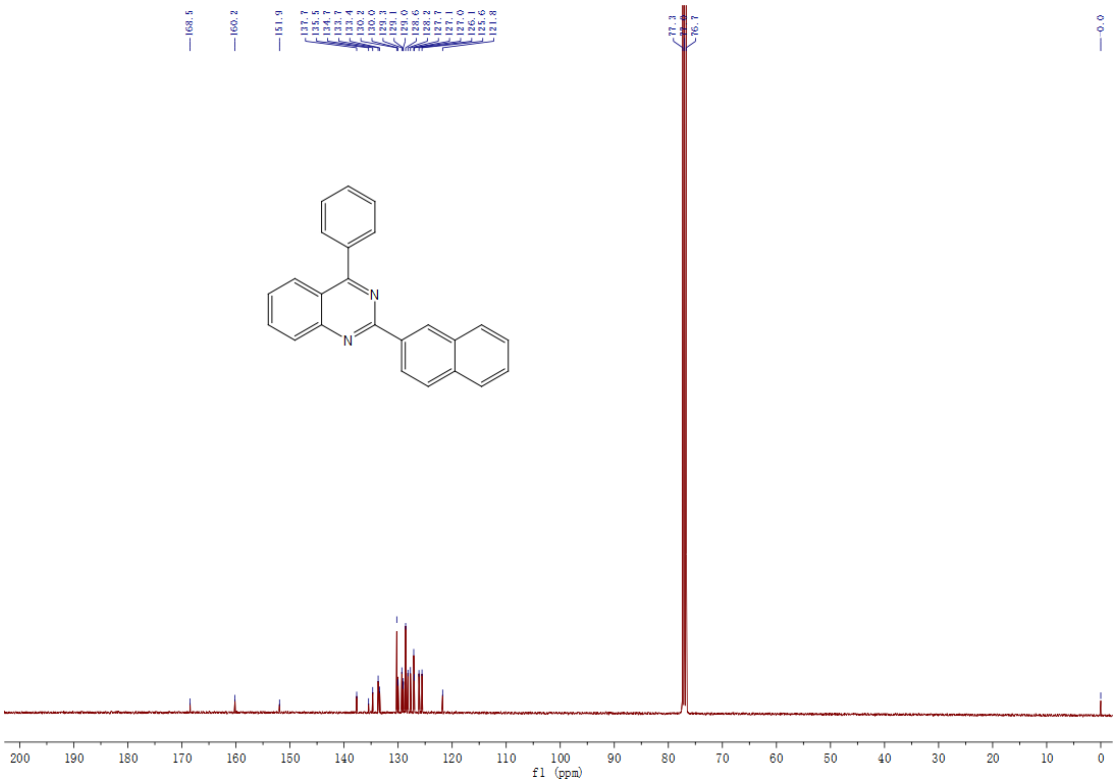


Fig. S32 ^{13}C NMR spectrum of **5n**

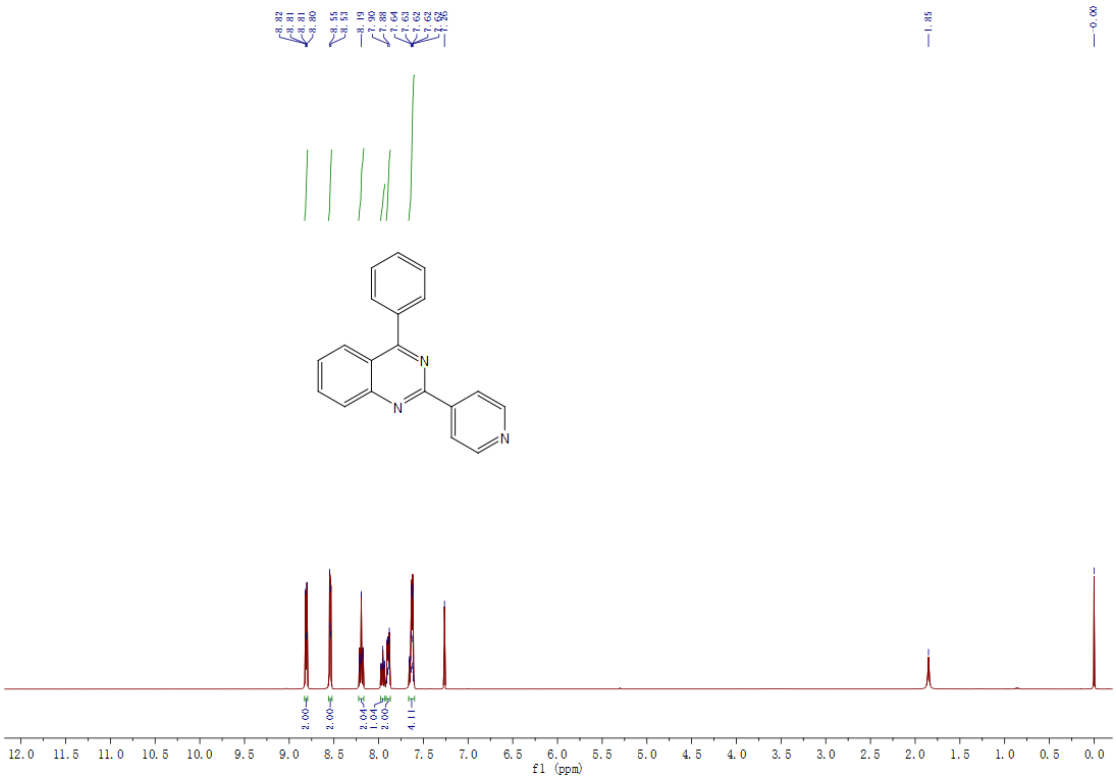


Fig. S33 ^{1}H NMR spectrum of **5o**

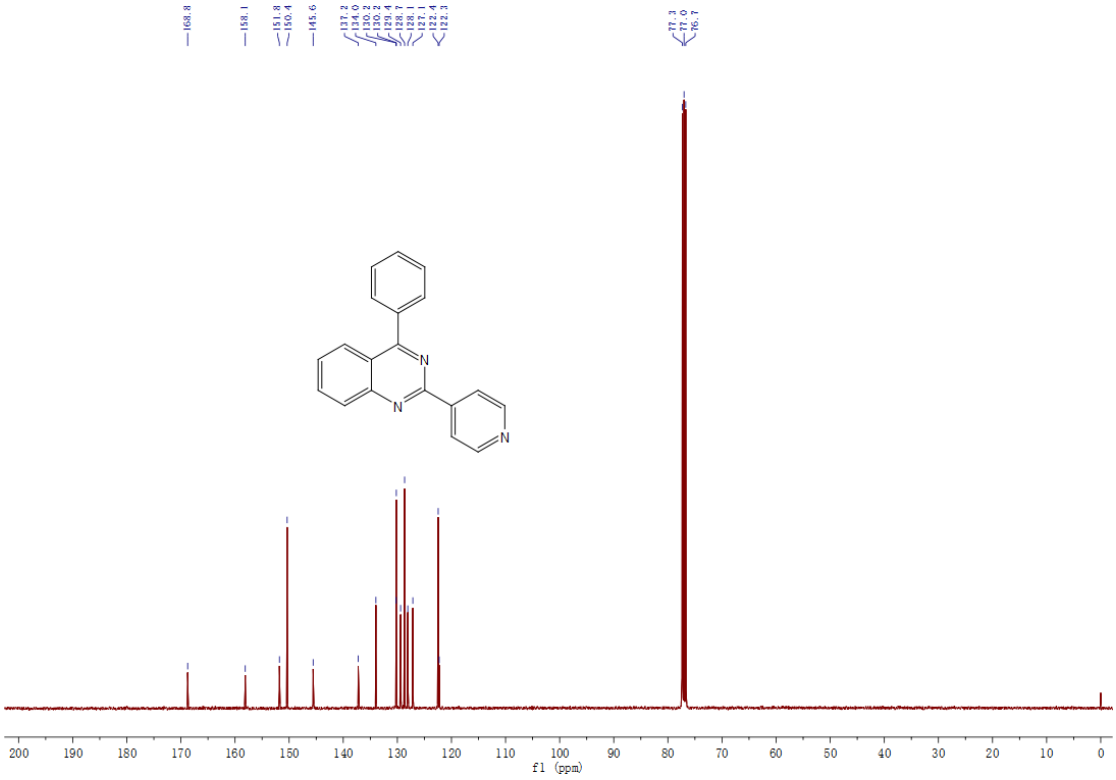


Fig. S34 ^{13}C NMR spectrum of **5o**

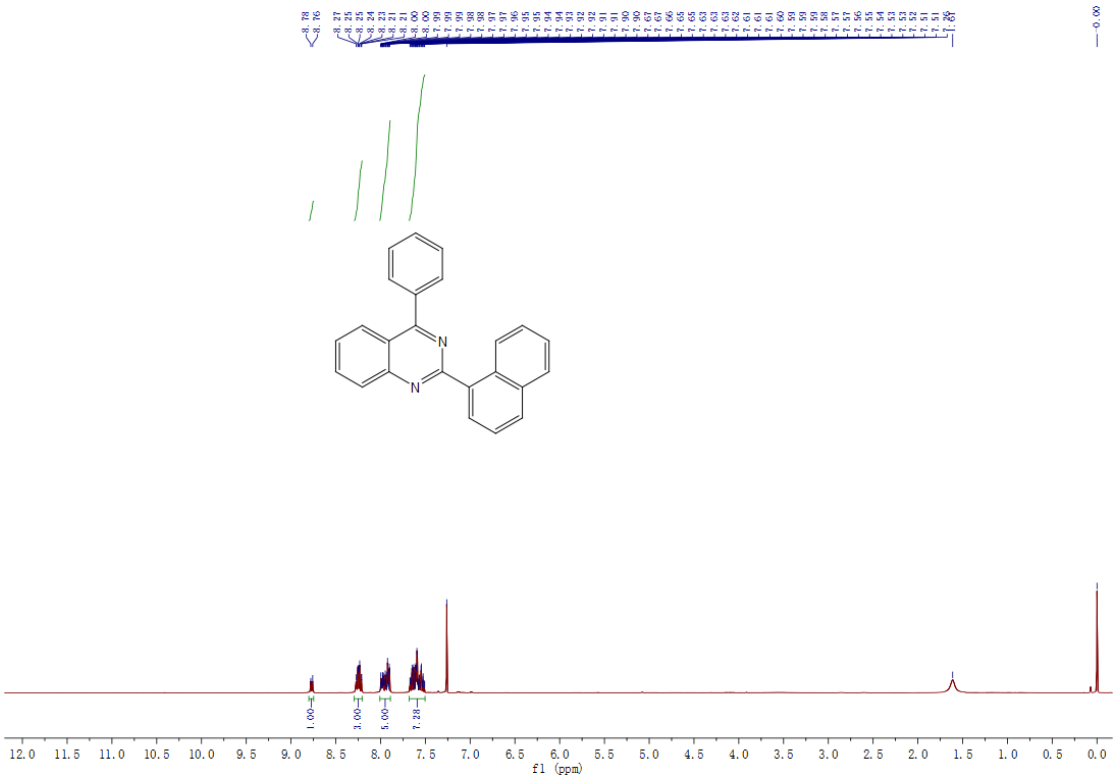


Fig. S35 ^{1}H NMR spectrum of **5p**

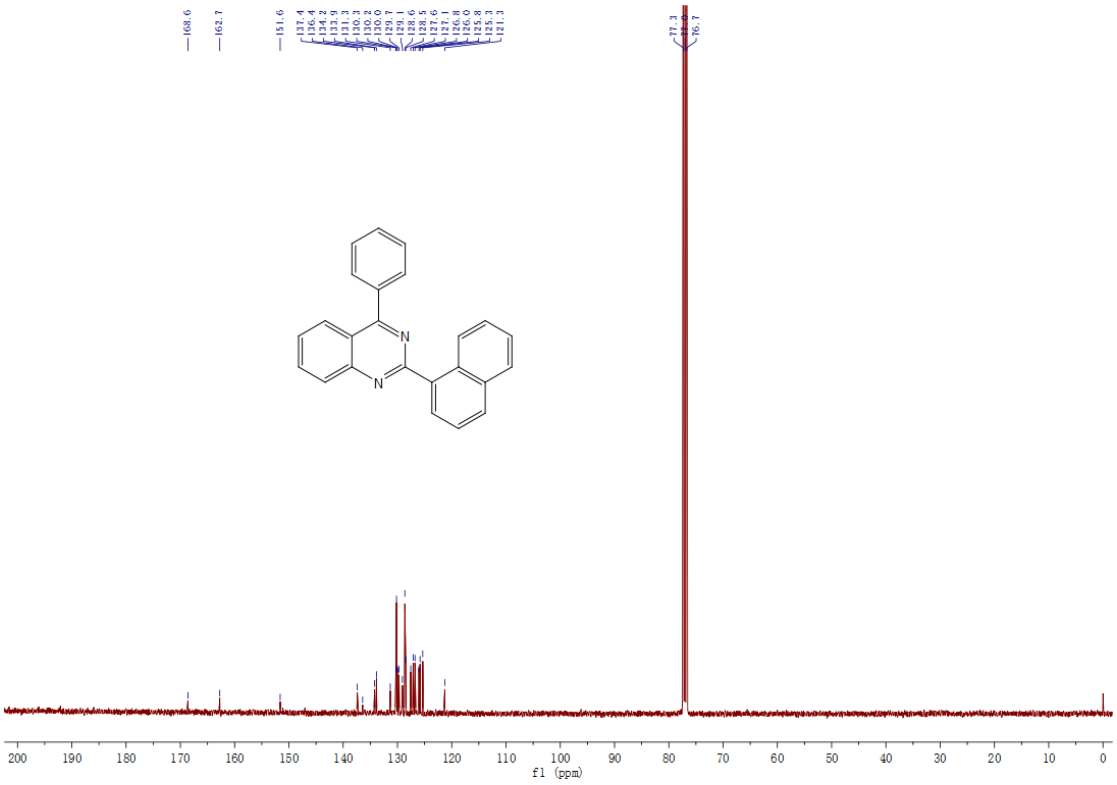


Fig. S36 ^{13}C NMR spectrum of **5p**

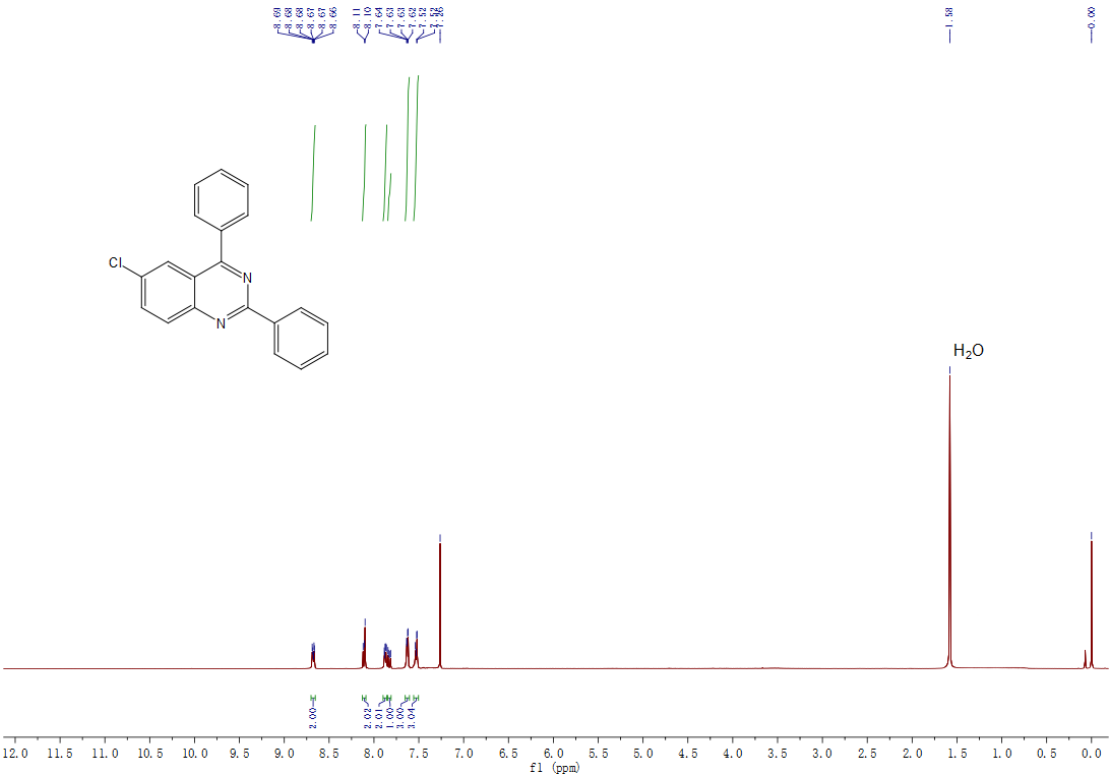


Fig. S37 ^{1}H NMR spectrum of **5q**

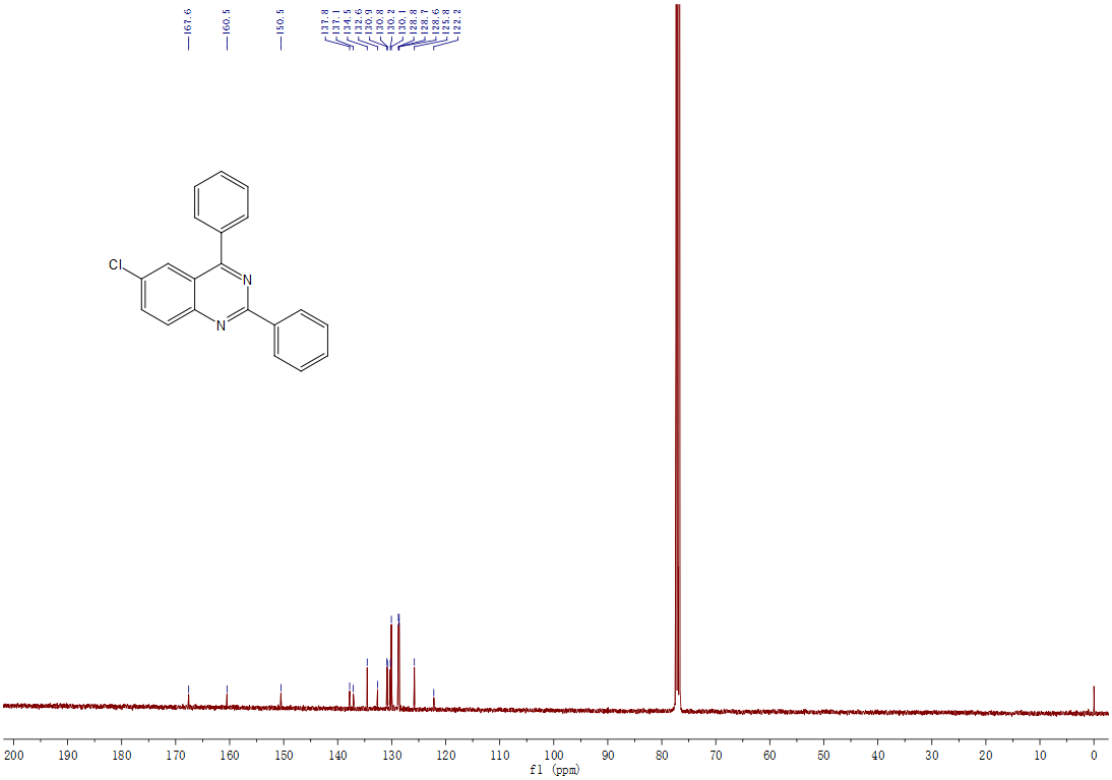


Fig. S38 ^{13}C NMR spectrum of **5q**

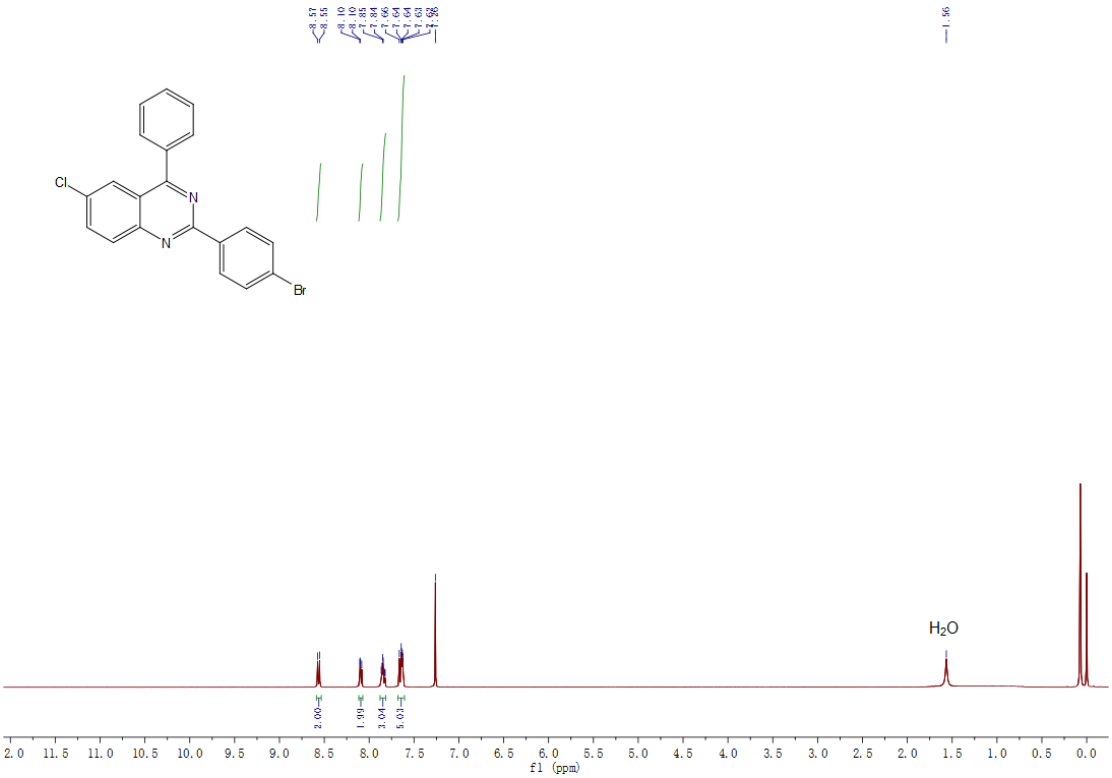


Fig. S39 ^{1}H NMR spectrum of **5r**

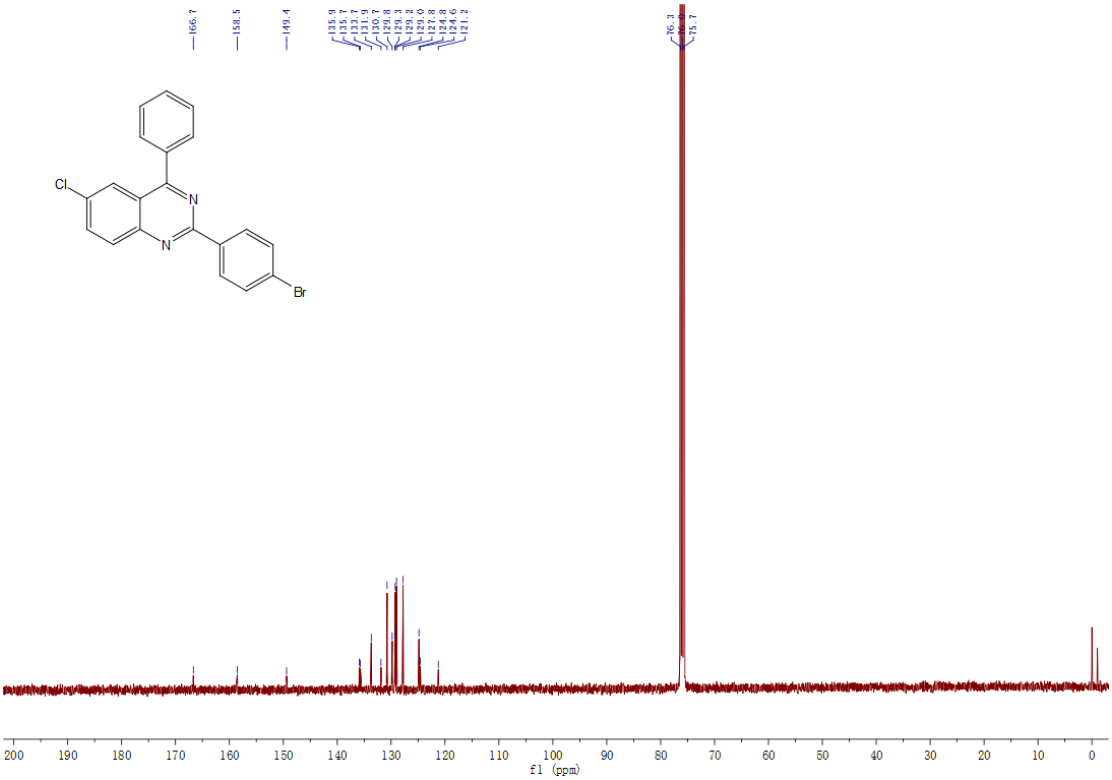


Fig. S40 ^{13}C NMR spectrum of **5r**

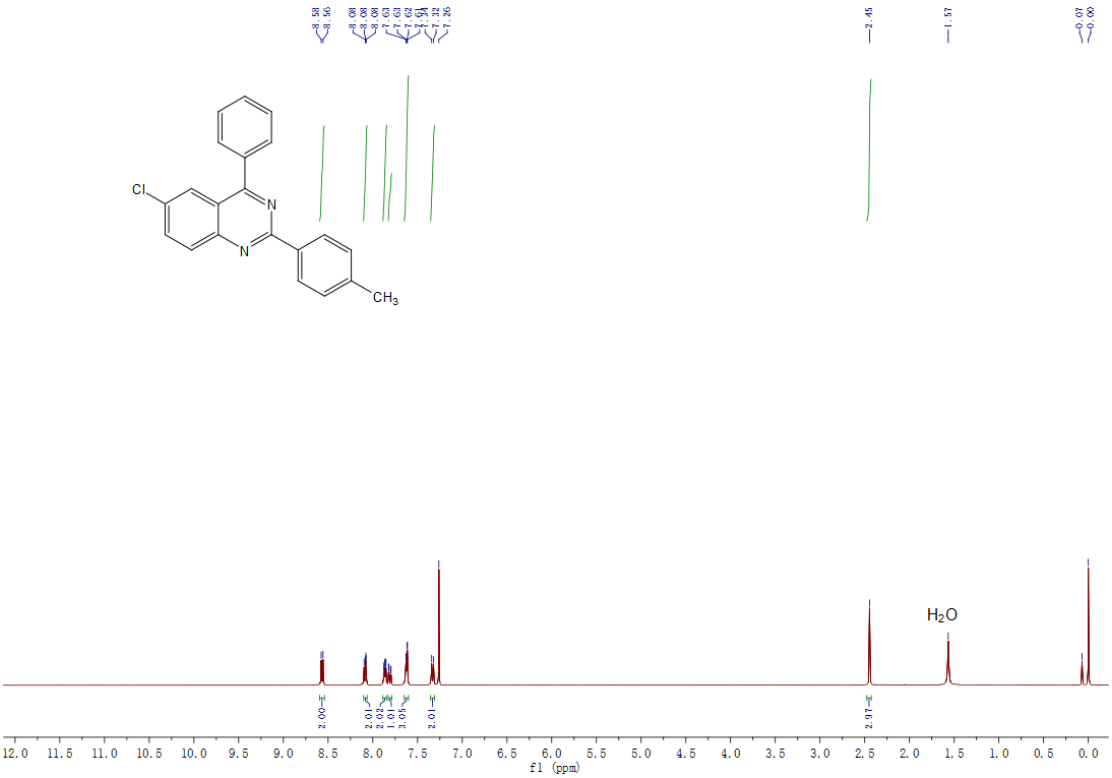


Fig. S41 ^{1}H NMR spectrum of **5s**

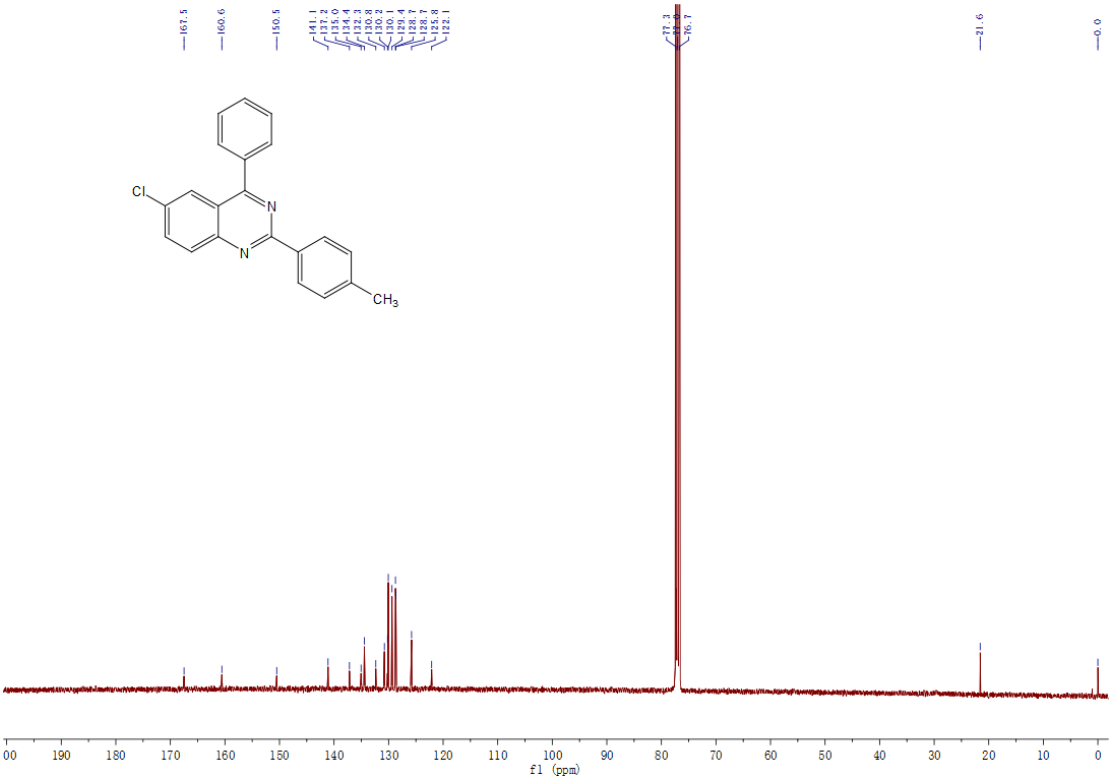


Fig. S42 ^{13}C NMR spectrum of **5s**

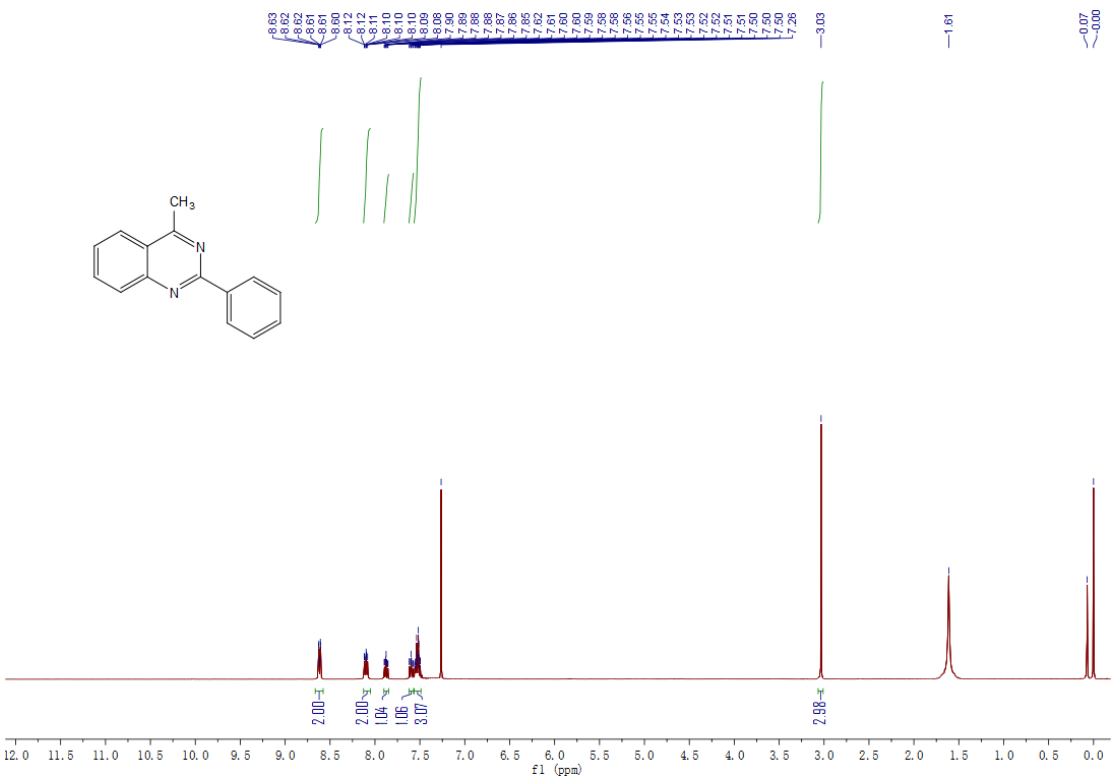


Fig. S43 ^{1}H NMR spectrum of **5t**

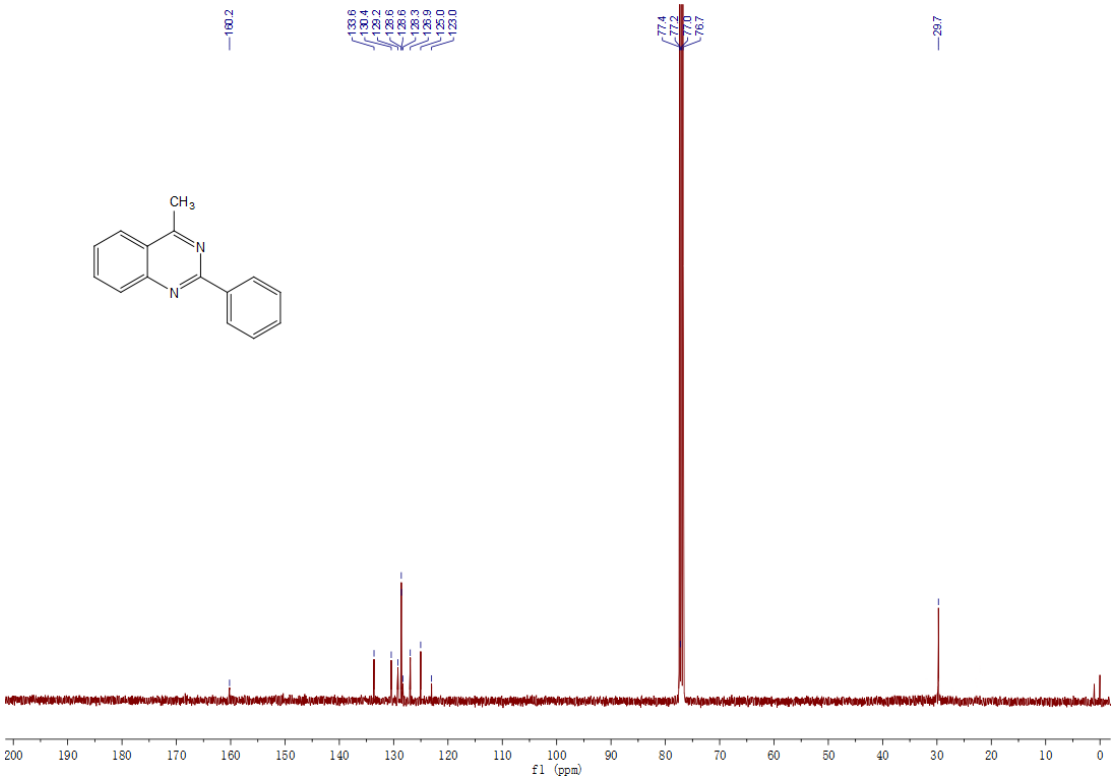


Fig. S44 ^{13}C NMR spectrum of **5t**

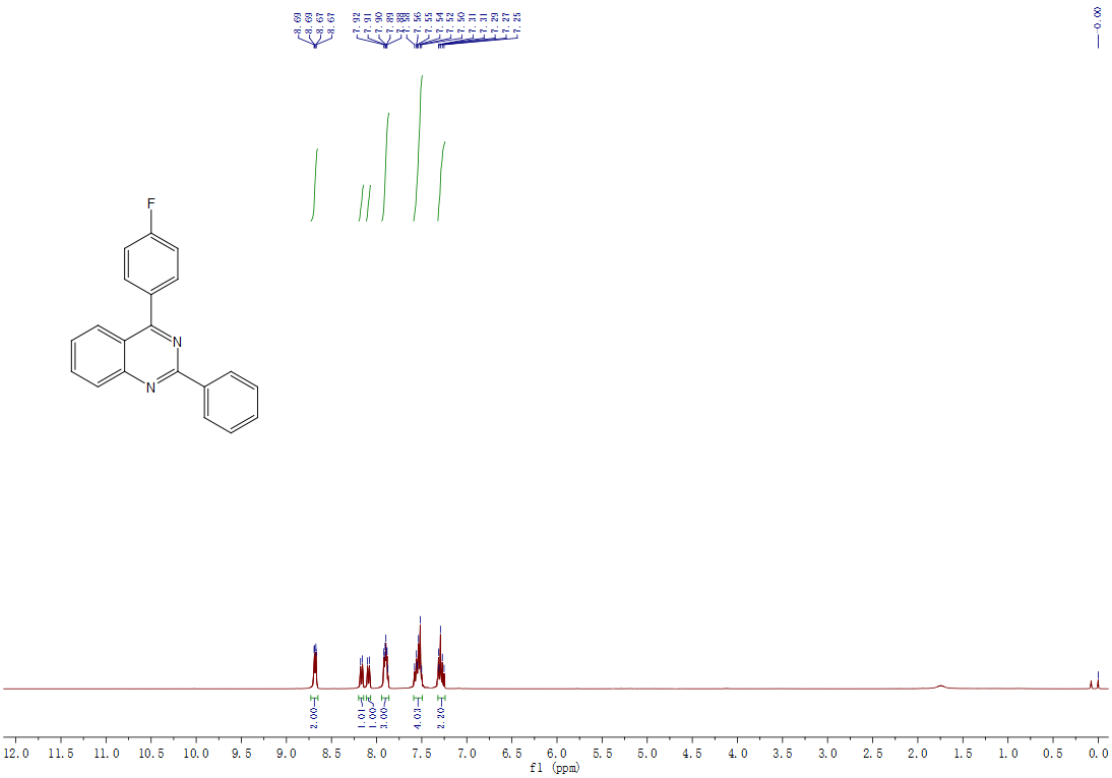


Fig. S45 ^{1}H NMR spectrum of **5u**

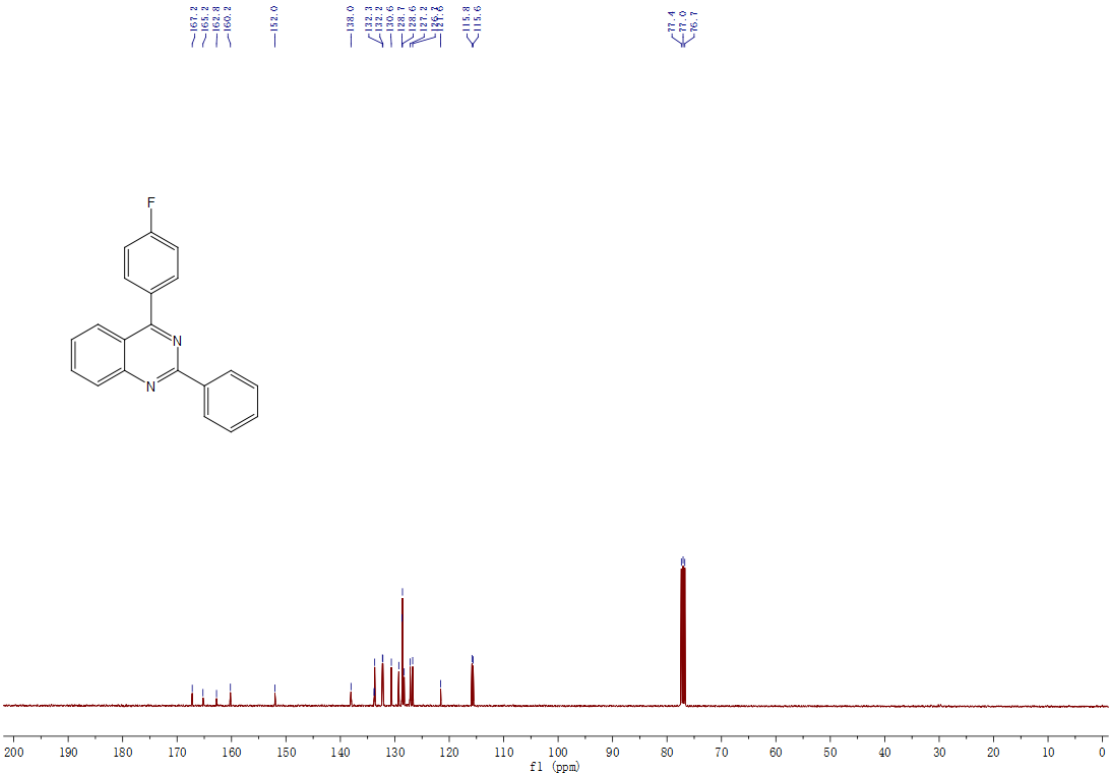


Fig. S46 ^{13}C NMR spectrum of **5u**

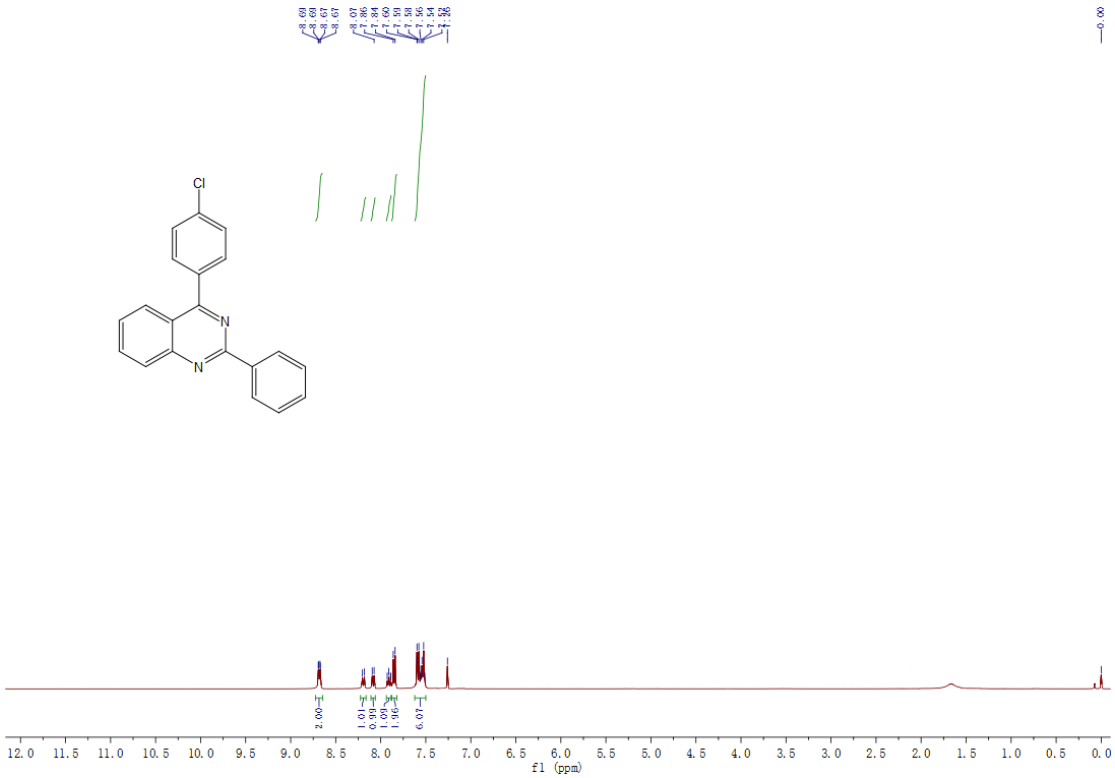


Fig. S47 ^{1}H NMR spectrum of **5v**

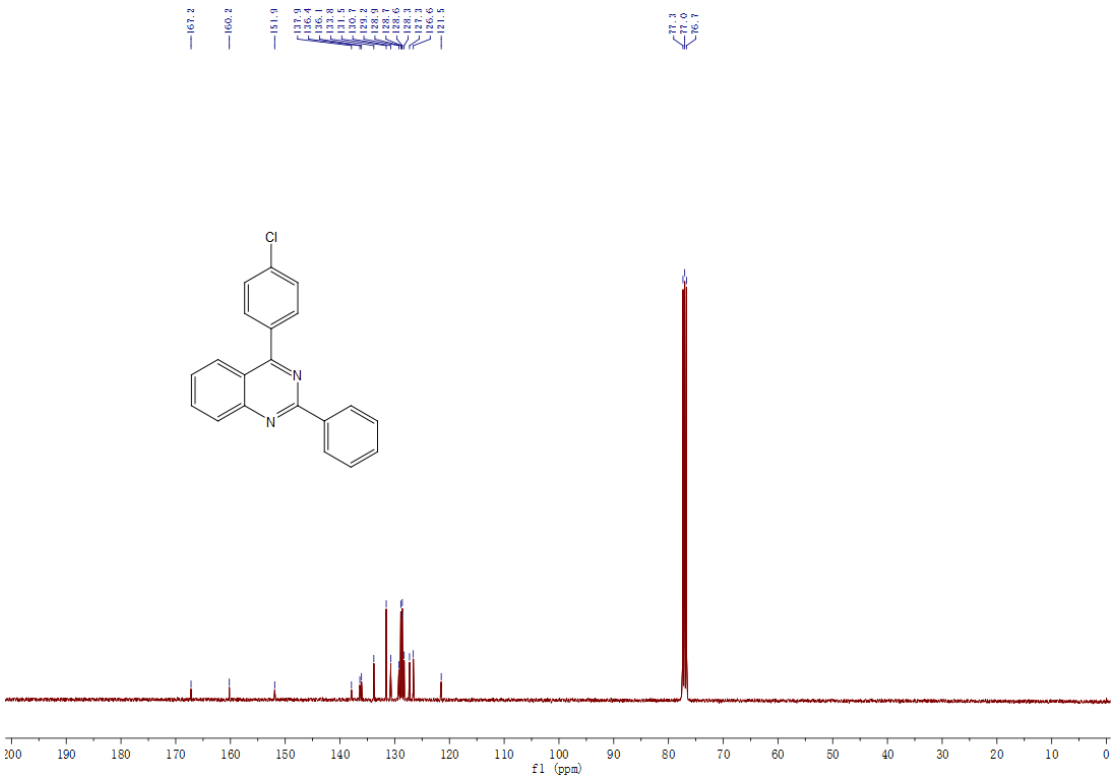


Fig. S48 ^{13}C NMR spectrum of **5v**

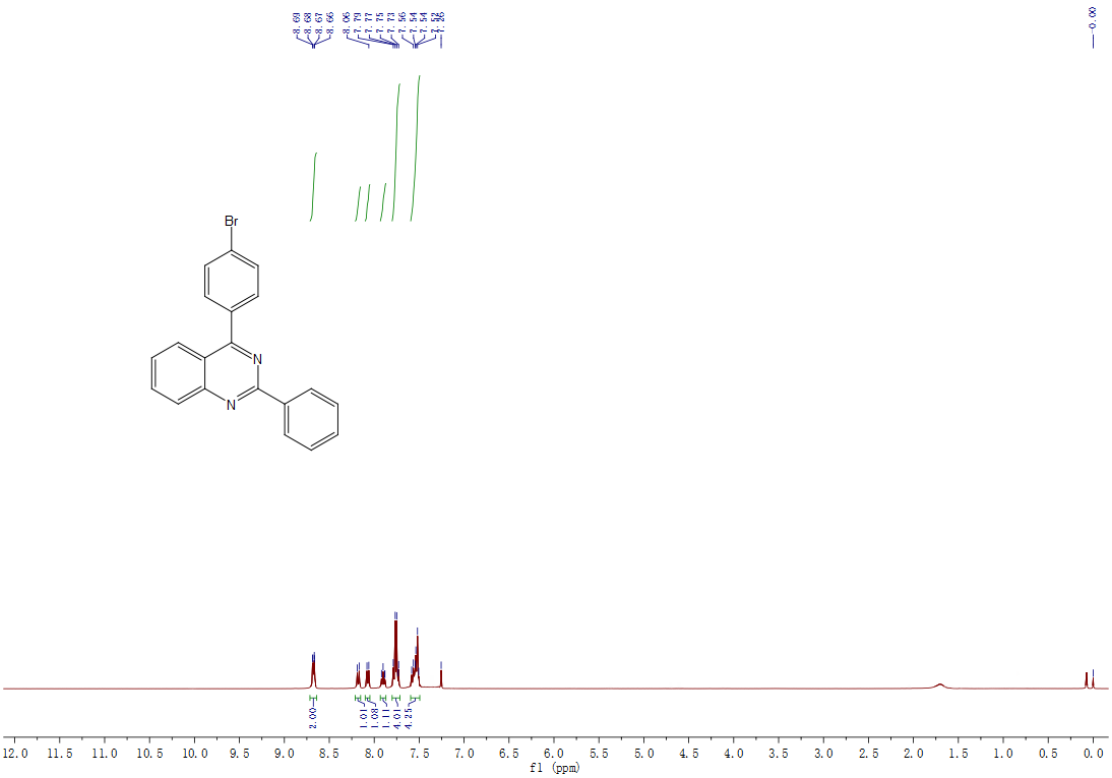


Fig. S49 ^{1}H NMR spectrum of **5w**

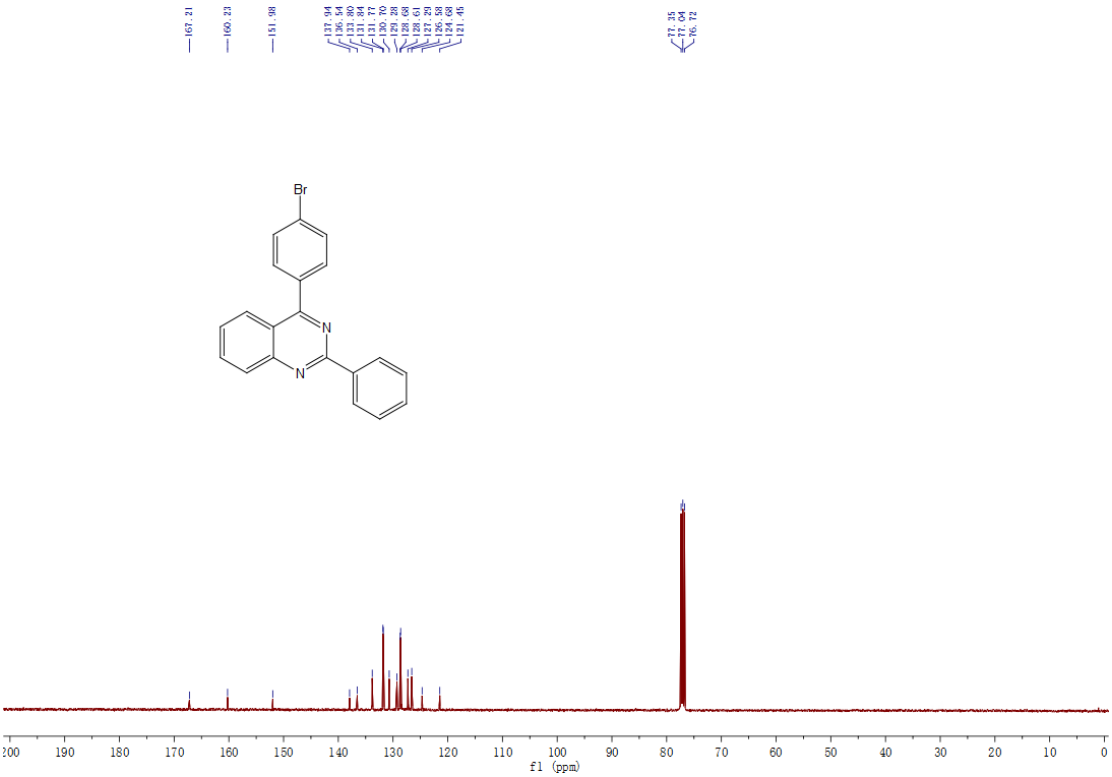


Fig. S50 ^{13}C NMR spectrum of **5w**

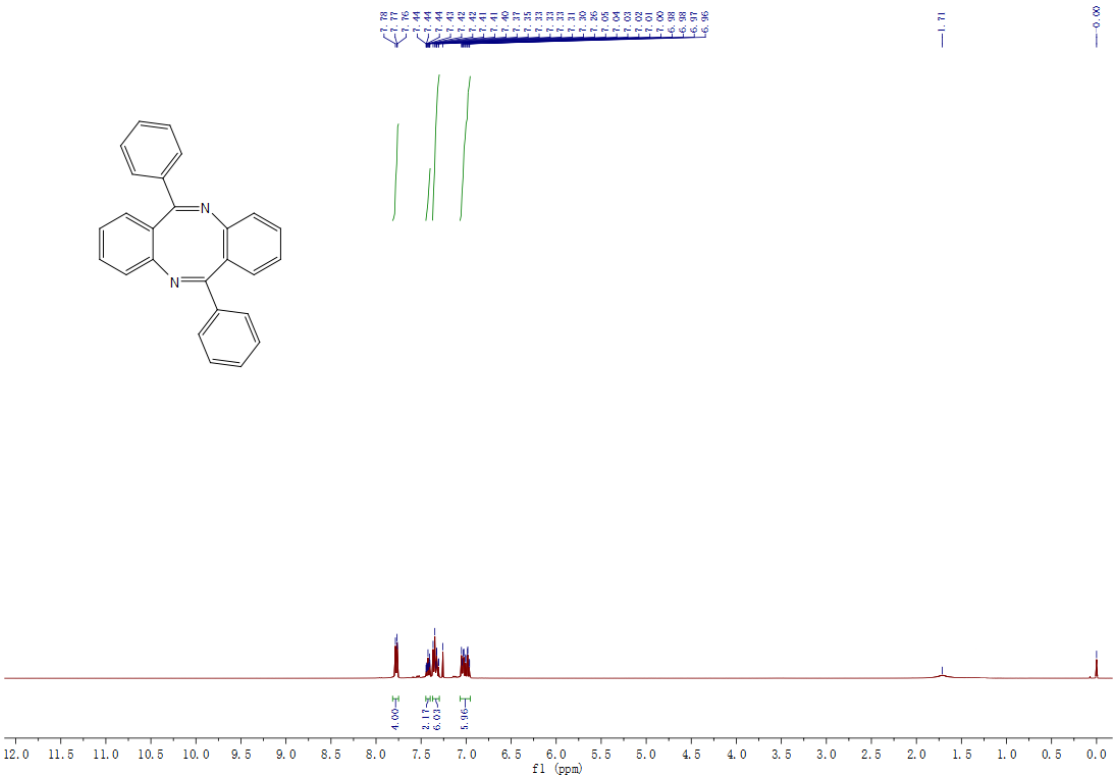


Fig. S51 ^{1}H NMR spectrum of compound **6**

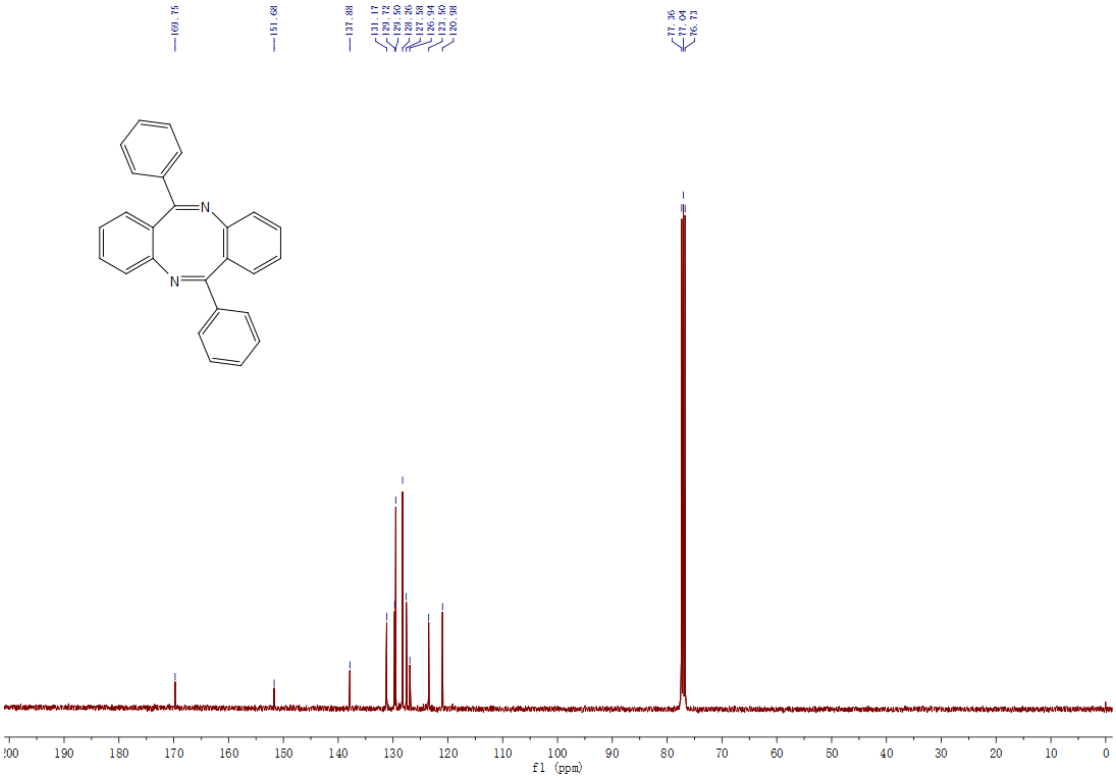


Fig. S52 ^{13}C NMR spectrum of compound **6**

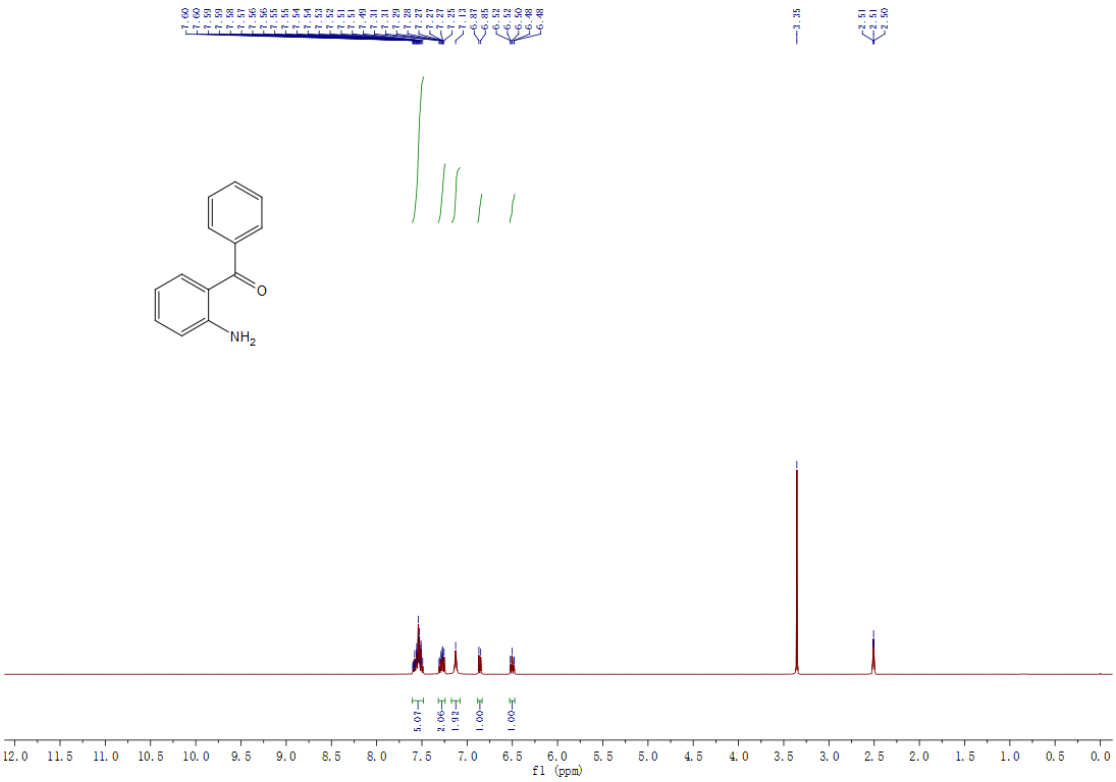


Fig. S53 ^{1}H NMR spectrum of **2a**

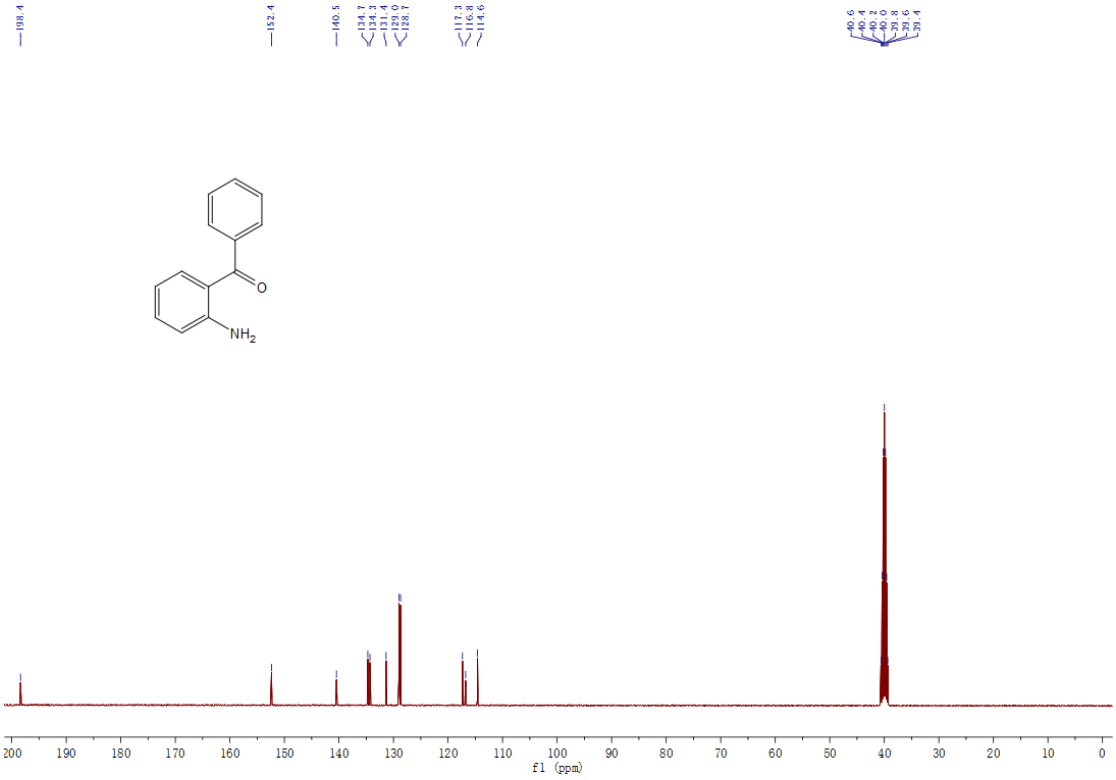


Fig. S54 ^{13}C NMR spectrum of **2a**

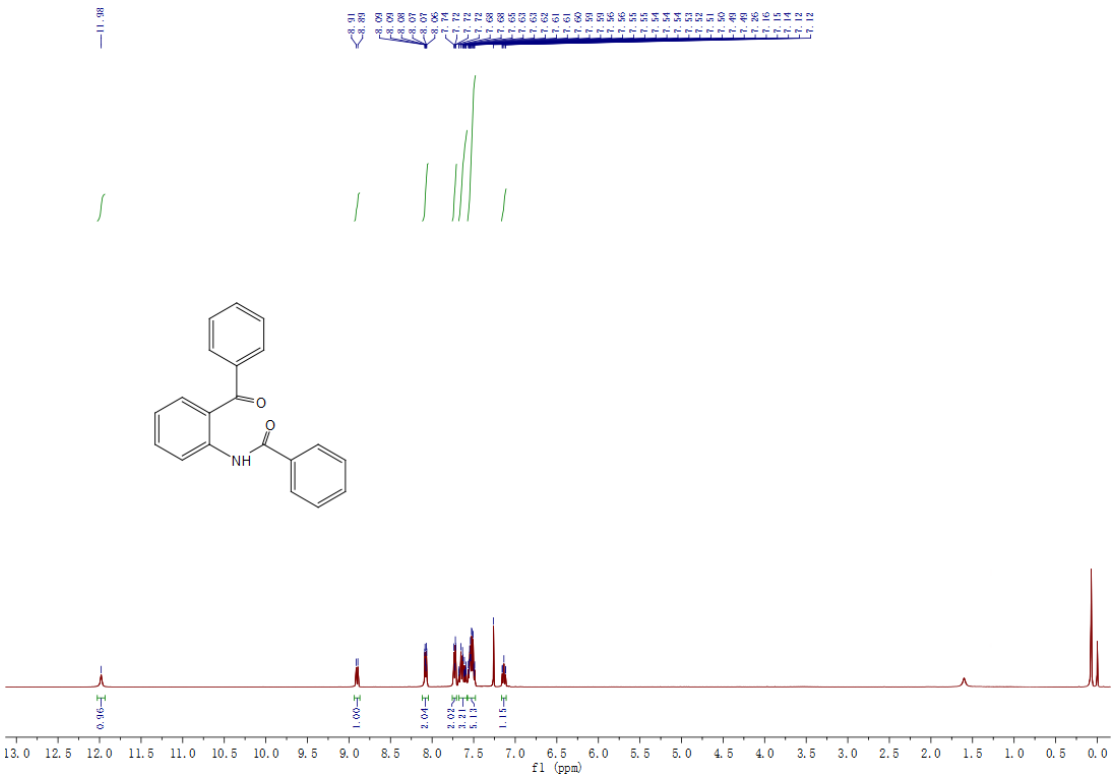


Fig. S55 ^{1}H NMR spectrum of intermediate **IV**

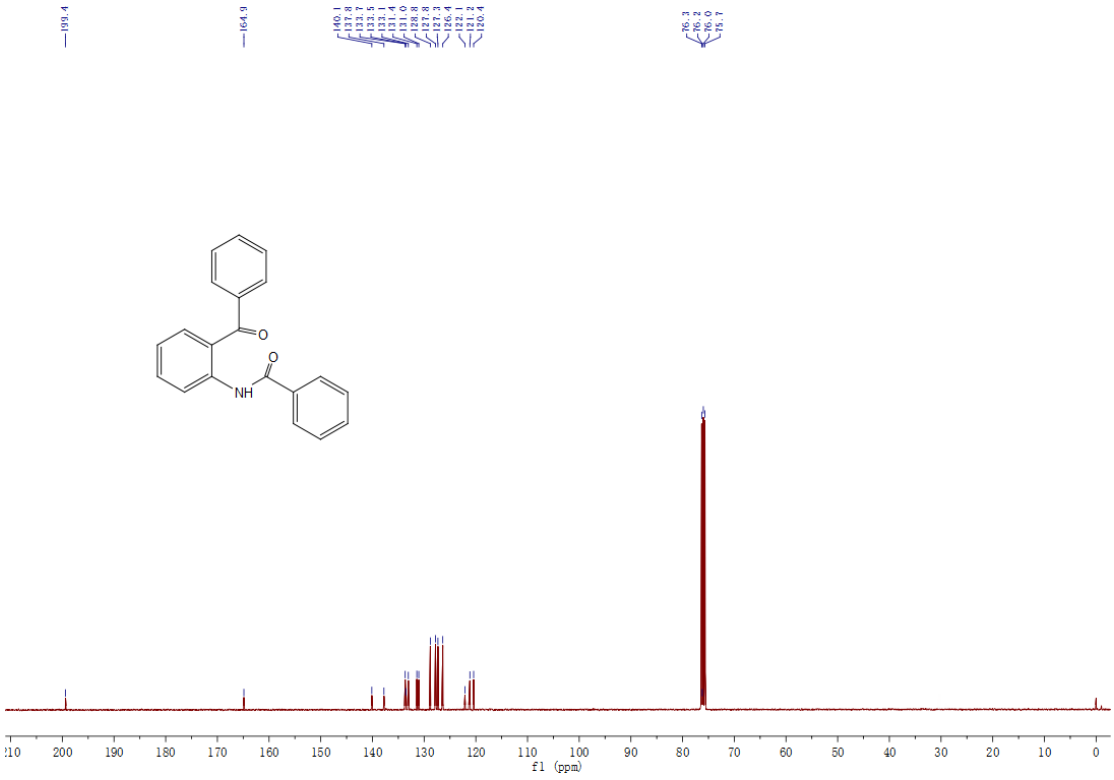


Fig. S56 ^{13}C NMR spectrum of intermediate **IV**