Supporting Information

C-H Benzylation of Quinoxalin-2(1*H*)-ones via Visible-Light Riboflavin Photocatalysis

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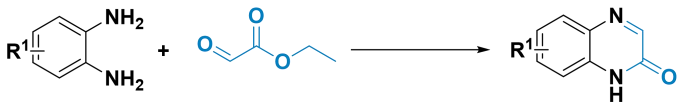
I. General considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200~300 mesh). ^{1}H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in DMSO-d_6 or in $CDCl_3$. Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer. The fluorescenceemission intensity of reaction solution was recorded on a HITACHI F-2700 spectrofluorimeter. The reactor was 3.0 cm from 10W blue LED.

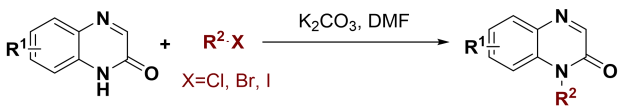
II. Experimental procedures

1. Preparation of quinoxalin-2 (1*H*)-one[1]



Ethyl-2-oxoacetate (22.1 mL, 111.11 mmol) was added to a solution of 1,2-diaminobenzene (10.0 g, 92.59 mmol) in ethanol (200 mL). The mixture was heated and maintained at 45 °C for 8 h. The resulting precipitate was filtered, thoroughly washed with water and dried under vacuum to afford quinoxalin-2 (1*H*) -ones.

Quinoxalin-2(1*H*)-one derivatives were prepared according to the reported methods[1]



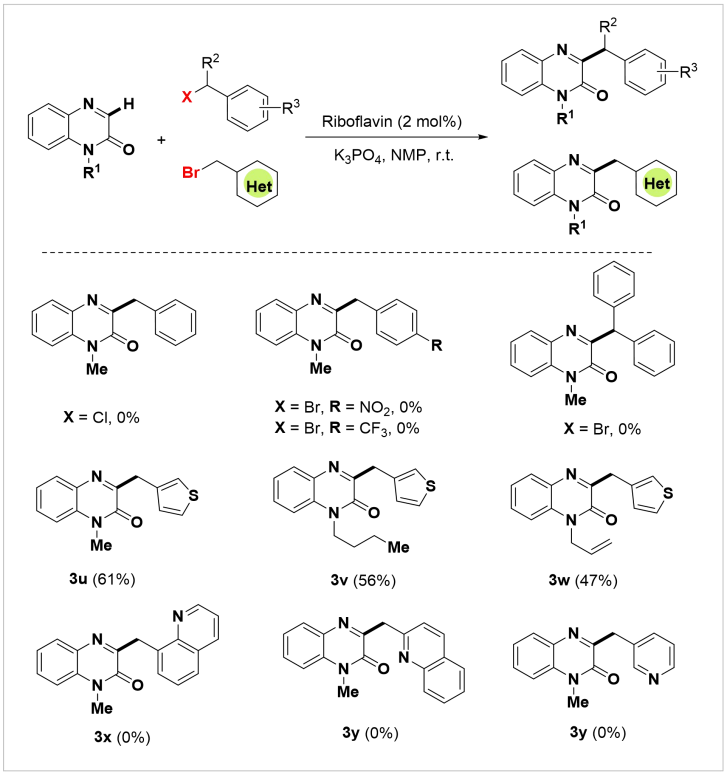
General procedure: To a 100 mL round-bottomed flask with a stir bar was added quinoxalin-2(1*H*)-one (5.0 mmol), DMF (15.0 mL), then was added potassium carbonate (828 mg, 6.0 mmol), followed by the dropwise addition of R_2-X (8.0 mmol). The reaction mixture was then stirred for 1~12h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over Na_2SO_4,

filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired quinoxalin-2(1*H*)-ones.

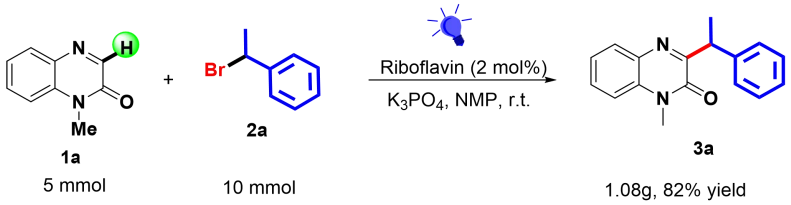
2. General procedure for synthesis of quinoxalin-2(1*H*)-ones

General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added quinoxalin-2(1*H*)-ones **1** (0.2 mmol), benzyl bromides **2** (0.4 mmol), K_3PO_4 (2.0 equiv.) and VB_2 (0.004 mmol, 2 mol%) in NMP (2.0 mL). The tube was evacuated and backfilled with nitrogen (three times), Then the mixture was stirred and irradiated by the a 10 W blue LED at room temperature for 24 h. The residue was added water (10 mL) and extracted with ethyl acetate (5 mL × 3). The combined organic phase was dried over Na_2SO_4. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.

3. Other alkylation reagents scope investigation

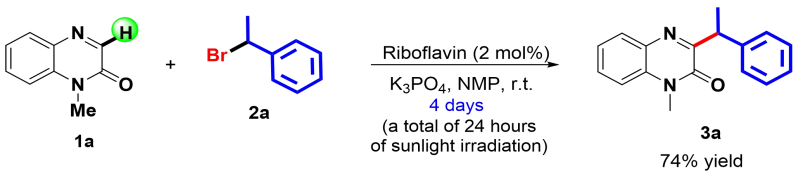


4. Gram scale



General procedure: To an oven-dried 50 mL Schlenk Tube with a stirring bar was added quinoxalin-2(1*H*)-ones **1a** (5.0 mmol), followed by the addition of benzyl bromide **2a** (10.0 mmol), K_3PO_4 (2.0 equiv.) and VB_2 (2 mol%). Then, air was withdrawn and backfilled with N_2 (three times) NMP (25 mL) was added and the mixture was irradiated under two 10W blue LEDs for 24 h. When the reaction is completed, The residue was added water and extracted with CH_2Cl_2, washed with brine, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography to afford the product **3a** (1.08 g, 82%).

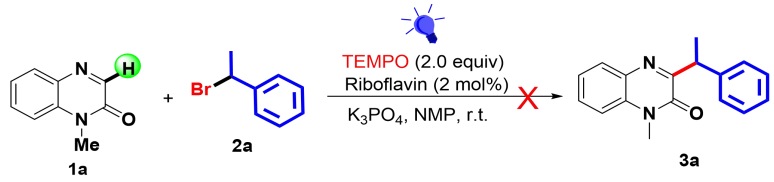
5. Sunlight-driven experiment



General procedure: 1a (0.20 mmol), **2a** (0.40 mmol), VB_2 (2 mol %), K_3PO_4 (2.0 equiv.) and a magnetic stir bar were added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL NMP was then added to the mixture in the presence of a flow of nitrogen. The solution was stirred under solar light for three days (A total of 24 hours of sunlight irradiation, Location: 36°8′54″ N, 120°23′3″ E). Afterward, the residue was added water (10 mL) and extracted with ethyl acetate (5 mL × 3). The combined organic phase was dried over Na_2SO_4, The resulting crude residue was purified via column chromatography on silica gel to afford **3a** in 74% yield.

III. Mechanistic studies

1. Investigation on the effect of TEMPO



The reaction was completely suppressed in the presence of TEMPO (2,2,6,6-tetra-methyl-1-piperidinyloxy, a well-known radical inhibitor), indicating a radical process might be involved in the present transformation.

2. Fluorescence quenching experiments

The fluorescence emission intensities were recorded on a HITACHI F-2700 spectrofluorimeter. The excitation wavelength was fixed at 446 nm. The samples were prepared by mixing Riboflavin (10^{-4} mol/L) and different amount of quencher in NMP in a light path quartz fluorescence cuvette. The concentration of quencher is 10^{-4} mol/L in NMP. For each quenching experiment, 0.02 ml of quencher solution was titrated to a mixed solution of Riboflavin. Then the emission intensity was collected and the results were presented in Figure S1 and Figure S2.

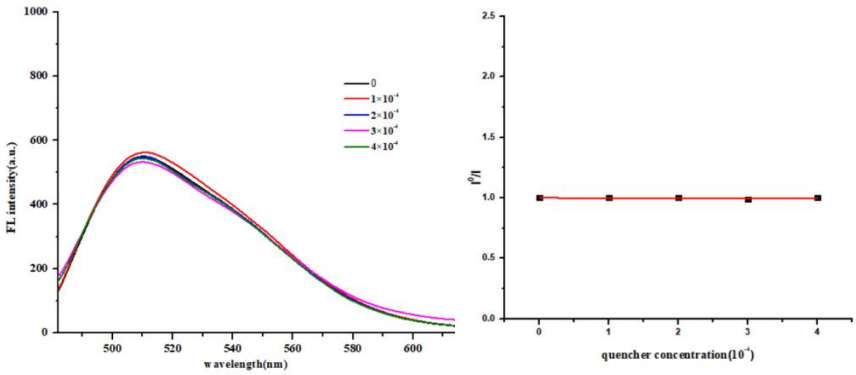


Figure S1. The emission quenching of Riboflavin in NMP by various concentrations of quencher **1a**.

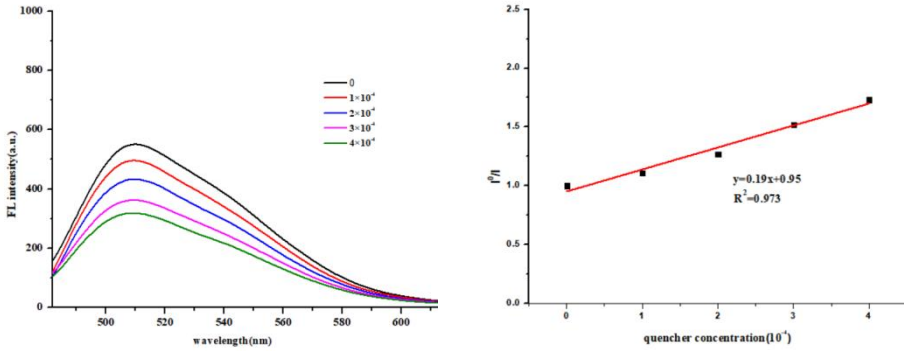


Figure S2. The emission quenching of Riboflavin in NMP by various concentrations of quencher **2a**.

3. Effect of Visible Light Irradiation

The reaction between **1a** and **2a** was conducted under the standard conditions on a 0.2mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (10 W blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with chromatography column on silica gel (EtOAc: petroleum ether=10:1) to give the corresponding products **3a**. The yield of **3a** was measured by weight of the product.

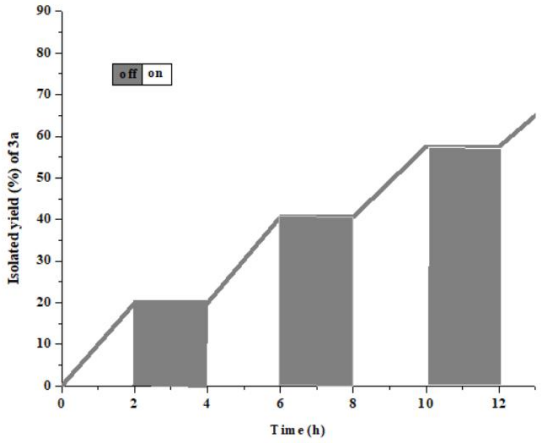
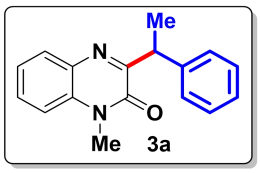


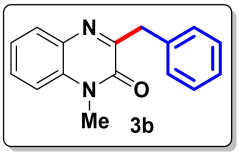
Figure S3. Visible light irradiation on/off experiment

IV. Characterization of products

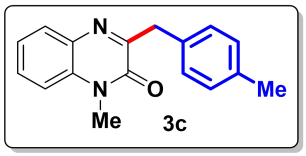


(*S*)-1-Methyl-3-(1-phenylethyl)quinoxalin-2(1*H*)-one (3a):[2] Eluent petroleum ether/ethyl acetate (10:1). 42.4 mg, 80% yield. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 7.9, 6.2 Hz, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 4.84 (q, *J* = 7.1 Hz, 1H), 3.64 (s, 3H), 1.70 (d, *J*

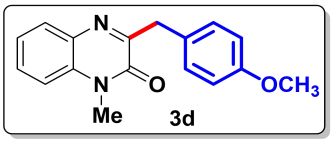
= 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 154.49, 143.19, 133.1, 132.7, 130.1, 129.7, 128.3, 128.1, 126.5, 123.4, 113.5, 41.8, 29.1, 19.6.HRMS calcd for $C_{17}H_{17}N_2O^+$ $[M+H]^+$: 265.1335; found 265.1340.



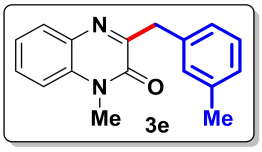
3-Benzyl-1-methylquinoxalin-2(1*H*)-one (3b):[3] Eluent petroleum ether/ethyl acetate (5:1). 35.1 mg, 70%. White solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.86 (dd, J = 8.1, 1.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.36-7.26 (m, 4H), 7.21 (t, J = 7.4 Hz, 1H), 4.27 (s, 2H), 3.66 (s, 3H).^{13}C NMR (125 MHz, CDCl3) δ 159.3, 154.7, 137.0, 133.3, 132.7, 129.9, 129.9, 129.5, 128.4, 126.6, 123.6, 113.5, 40.7, 29.1.HRMS calcd for $C_{16}H_{15}N_2O^+$ [M+H]+: 251.1179; found 251.1181.



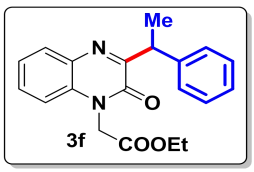
1-Methyl-3-(4-methylbenzyl)quinoxalin-2(1*H*)-one (3c):[3] Eluent petroleum ether/ethyl acetate (10:1). 45.1 mg, 85%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.3 Hz, 1H), 7.52 (s, 1H), 7.36 (s, 3H), 7.27 (s, 1H), 7.12 (s, 2H), 4.24 (s, 2H), 3.65 (s, 3H), 2.30 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 154.7, 136.1, 133.9, 133.3, 132.7, 129.9, 129.8, 129.4, 129.1, 123.5, 113.5, 40.3, 29.06, 21.02. HRMS calcd for $C_{17}H_{17}N_2O^+$ $[M+H]^+$: 265.1335; found 265.1338.



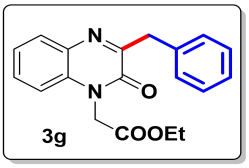
3-(4-Methoxybenzyl)-1-methylquinoxalin-2(1*H*)-one (3d):[4] Eluent petroleum ether/ethyl acetate (5:1). 37.7mg, 67%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.19 (s, 2H), 3.75 (s, 3H), 3.65 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 158.4, 133.4, 132.8, 130.5, 130.3, 129.9, 129.8, 129.0, 123.5, 113.8, 113.5, 55.2, 39.9, 29.1.HRMS calcd for $C_{17}H_{17}N_2O_2^+$ $[M+H]^+$: 281.1285; found 281.1281.



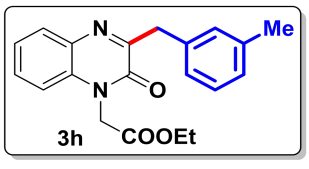
1-Methyl-3-(3-methylbenzyl)quinoxalin-2(1*H*)-one (3e):[3] Eluent petroleum ether/ethyl acetate (10:1). 41.9 mg, 79%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.35 (s, 1H), 7.27 (d, *J* = 6.5 Hz, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 4.23 (s, 2H), 3.66 (s, 3H), 2.32 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 154.8, 137.9, 136.9, 133.4, 132.8, 130.2, 130.0, 129.8, 128.3, 127.3, 126.5, 123.5, 113.5, 40.7, 29.1, 21.4.HRMS calcd for $C_{17}H_{17}N_2O^+$ $[M+H]^+$: 265.1335; found 265.1338.



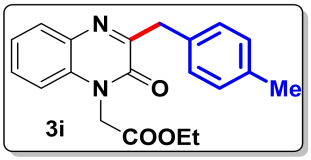
Ethyl (*S*)-2-(2-oxo-3-(1-phenylethyl)quinoxalin-1(2H)-yl)acetate (3f): Eluent petroleum ether/ethyl acetate (5:1). 40.4 mg, 60%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.07 (d, *J* = 17.3 Hz, 1H), 4.84-4.79 (m, 2H), 4.20 (dd, *J* = 9.7, 3.8 Hz, 2H), 1.69 (d, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 161.7, 154.0, 142.9, 132.8, 132.2, 130.5, 129.9, 128.4, 128.1, 126.5, 123.7, 112.9, , 61.9, 43.6, 41.9, 19.7, 14.0.HRMS calcd for $C_{20}H_{21}N_2O_3^+$ $[M+H]^+$:337.1547; found 337.1549.



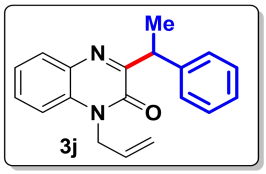
Ethyl 2-(3-benzyl-2-oxoquinoxalin-1(2H)-yl)acetate (3g):[2] Eluent petroleum ether/ethyl acetate (5:1). 55.2mg, 80%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.47 (dd, *J* = 16.0, 7.3 Hz, 3H), 7.30 (dd, *J* = 16.5, 9.1 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 4.98 (s, 2H), 4.28 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 159.1, 154.3, 136.8, 132.7, 132.4, 130.2, 129.9, 129.5, 128.4, 126.6, 123.8, 112.9, 62.0, 43.5, 40.6, 14.1.HRMS calcd for $C_{19}H_{18}N_2NaO_3^+$ $[M+Na]^+$: 345.1210 ; found 345.1211.



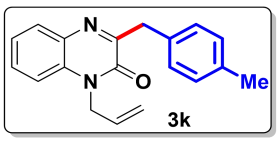
Ethyl 2-(3-(3-methylbenzyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (3h): Eluent petroleum ether/ethyl acetate (5:1). 56.0 mg, 83%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 6.3 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 2H), 4.98 (s, 2H), 4.24 (s, 2H), 4.22 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.24 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 159.2, 154.4, 137.9, 136.7, 132.8, 132.5, 130.3, 130.2, 129.9, 128.3, 127.4, 126.5, 123.8, 112.9, 62.0, 43.6, 40.5, 21.4, 14.1.HRMS calcd for $C_{20}H_{21}N_2O_3^+$ $[M+H]^+$: 337.1547; found 337.1542.



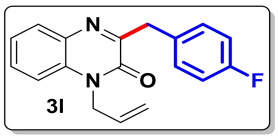
Ethyl 2-(3-(4-methylbenzyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (3i): Eluent petroleum ether/ethyl acetate (5:1). 48.6 mg, 72%. White solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.11 (s, 2H), 2.24 (s, 3H), 1.19 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 167.4, 158.7, 153.8, 135.4, 133.9, 132.4, 131.9, 131.7, 130.2, 128.9, 128.9, 128.5, 126.4, 123.7, 114.5, 61.3, 43.7, 39.2, 38.9, 20.6, 13.9.HRMS calcd for $C_{20}H_{21}N_2O_3^+$ $[M+H]^+$: 337.1547; found 337.1543.



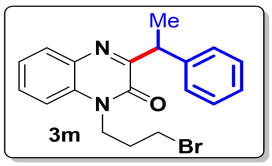
***(S)* -1-allyl-3-(1-phenylethyl)quinoxalin-2(1H)-one (3j):** Eluent petroleum ether/ethyl acetate (5:1). 43.4mg, 73%. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.52 -7.46 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* = 14.4, 6.0 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.95-5.86 (m, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.14 (d, *J* = 17.3 Hz, 1H), 4.98-4.93 (m, 1H), 4.87 (q, *J* = 7.1 Hz, 1H), 4.79-4.74 (m, 1H), 1.72 (d, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 154.0, 143.2, 132.9, 132.3, 130.8, 130.2, 129.6, 128.4, 128.1, 126.5, 123.4, 118.0, 114.0, 44.6, 41.8, 19.7.HRMS calcd for $C_{19}H_{19}N_2O^+$ $[M+H]^+$: 291.1492; found 291.1495.



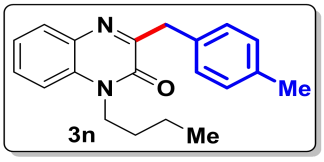
1-Allyl-3-(4-methylbenzyl)quinoxalin-2(1*H*)-one (3k): Eluent petroleum ether/ethyl acetate (5:1). 47.7 mg, 82%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 3.8 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 5.97-5.88 (m, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.88 (d, *J* = 5.0 Hz, 2H), 4.27 (s, 2H), 2.32 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 154.3, 136.1, 133.9, 132.9, 132.5, 130.7, 130.0, 129.7, 129.4, 129.1, 123.5, 118.1, 114.1, 44.6, 40.2, 21.0.HRMS calcd for $C_{19}H_{19}N_2O^+$ $[M+H]^+$: 291.1492; found 291.1495.



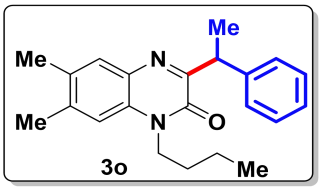
1-Allyl-3-(4-fluorobenzyl)quinoxalin-2(1*H*)-one (3l): Eluent petroleum ether/ethyl acetate (5:1). 44.9 mg, 76%. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.83 (m, 1H), 7.51-7.47 (m, 1H), 7.42 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26-7.24 (m, 1H), 6.97 (t, *J* = 8.7 Hz, 2H), 5.90 (m, *J* = 5.1 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 17.3 Hz, 1H), 4.88-4.85 (m, 2H), 4.24 (s, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 160.8, 159.1, 154.2, 132.9, 132.6, 132.5, 131.0, 130.5, 130.0, 129.9, 123.6, 118.1, 115.2, 115.1, 114.1, 44.6, 39.8.HRMS calcd for $C_{18}H_{16}FN_2O^+$ $[M+H]^+$: 295.1241; found 295.1249.



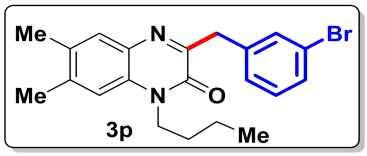
(*S*)-1-(3-bromopropyl)-3-(1-phenylethyl)quinoxalin-2(1*H*)-one (3m): Eluent petroleum ether/ethyl acetate (5:1). 60.1 mg, 81%. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.93 (m, 1H), 7.56-7.51 (m, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38-7.34 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.82 (q, *J* = 7.1 Hz, 1H), 4.41-4.34 (m, 1H), 4.32-4.26 (m, 1H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.26 (m, 2H), 1.69 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 154.2, 143.1, 133.0, 132.1, 130.5, 129.9, 128.4, 128.1, 126.5, 123.5, 113.2, 41.7, 41.2, 30.4, 29.9, 19.7.HRMS calcd for $C_{19}H_{20}BrN_2O^+$ $[M+H]^+$: 371.0754; found 371.0760.



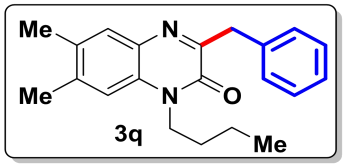
1-Butyl-3-(4-methylbenzyl)quinoxalin-2(1*H*)-one (3n): Eluent petroleum ether/ethyl acetate (10:1). 44.2 mg, 72%. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.82 (m, 1H), 7.48 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.21 (s, 2H), 4.20-4.17 (m, 2H), 2.29 (s, 3H), 1.68 (dd, *J* = 15.5, 7.9 Hz, 2H), 1.45 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.96 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 154.4, 136.0, 134.0, 133.0, 132.5, 130.1, 129.7, 129.4, 129.1, 123.3, 113.5, 42.2, 40.3, 29.2, 21.0, 20.3, 13.7.HRMS calcd for $C_{20}H_{23}N_2O^+$ $[M+H]^+$: 307.1805; found 307.1801.



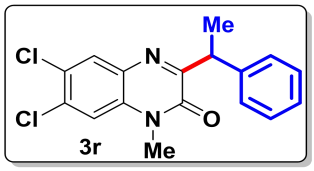
(*S*)-1-Butyl-6,7-dimethyl-3-(1-phenylethyl)quinoxalin-2(1*H*)-one (3o): Eluent petroleum ether/ethyl acetate (10:1). 53.6 mg, 75%. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 4.85 (q, *J* = 7.1 Hz, 1H), 4.29-4.23 (m, 1H), 4.12-4.06 (m, 1H), 2.44 (s, 3H), 2.39 (s, 3H), 1.71 (d, *J* = 6.9 Hz, 3H), 1.69 (s, 2H), 1.46 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 154.2, 143.5, 139.2, 132.1, 131.4, 130.4, 130.2, 128.3, 128.0, 126.3, 113.9, 42.0, 41.6, 29.3, 20.6, 20.2, 19.8, 19.0, 13.7. HRMS calcd for $C_{22}H_{26}N_2NaO^+$ $[M+Na]^+$: 357.1937; found 357.1938.



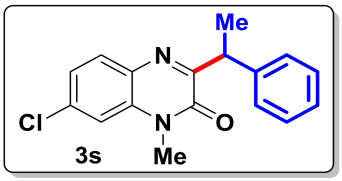
3-(3-Bromobenzyl)-1-butyl-6,7-dimethylquinoxalin-2(1*H*)-one (3p): Eluent petroleum ether/ethyl acetate (10:1). 53.6 mg, 66%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.57 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 4.18 (d, *J* = 12.4 Hz, 4H), 2.41 (s, 3H), 2.34 (s, 3H), 1.72 -1.68 (m, 2H), 1.45 (d, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 154.4, 139.8, 139.7, 132.4, 132.3, 131.4, 130.5, 130.3, 129.8, 129.6, 128.2, 122.3, 114.1, 42.1, 40.1, 29.3, 20.6, 20.3, 19.1, 13.8. HRMS calcd for $C_{21}H_{24}BrN_2O^+$ $[M+H]^+$: 399.1067; found 399.1064.



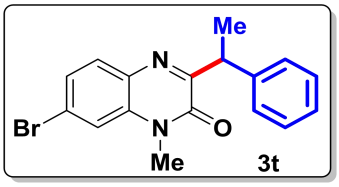
3-Benzyl-1-butyl-6,7-dimethylquinoxalin-2(1*H*)-one (3q): Eluent petroleum ether/ethyl acetate (10:1). 40.5 mg, 63%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 4.27 (s, 2H), 4.23-4.19 (m, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 1.73 (t, *J* = 7.7 Hz, 2H), 1.48 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 154.5, 139.5, 137.5, 132.3, 131.4, 130.6, 130.2, 129.5, 128.3, 126.4, 114.1, 42.1, 40.6, 29.3, 20.6, 20.3, 19.1, 13.8. HRMS calcd for $C_{21}H_{25}N_2O^+$ $[M+H]^+$: 321.1961; found 321.1967.



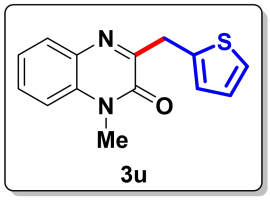
(*S*)-6,7-Dichloro-1-methyl-3-(1-phenylethyl)quinoxalin-2(1H)-one (3r): Eluent petroleum ether/ethyl acetate (10:1). 40.6 mg, 61%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.20 (dd, *J* = 12.4, 4.6 Hz, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.72 (q, *J* = 7.1 Hz, 1H), 3.49 (s, 3H), 1.58 (d, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 153.8, 142.5, 133.7, 132.5, 131.8, 130.9, 128.5, 128.1, 127.2, 126.8, 114.9, 41.9, 29.4, 19.5.HRMS calcd for $C_{17}H_{15}Cl_2N_2O^+$ $[M+H]^+$: 333.0556; found 333.0561.



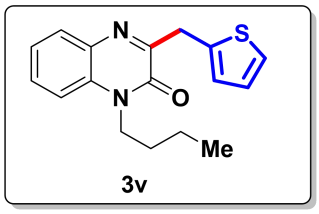
(*S*)-7-Chloro-1-methyl-3-(1-phenylethyl)quinoxalin-2(1*H*)-one (3s): Eluent petroleum ether/ethyl acetate (5:1). 46.7 mg, 78%. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.47-7.42 (m, 3H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20-7.16 (m, 2H), 4.82 (m, *J* = 7.1 Hz, 1H), 3.60 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 154.1, 142.7, 133.2, 131.7, 129.6, 129.4, 128.7, 128.4, 128.1, 126.6, 114.6, 41.9, 29.2, 19.5. HRMS calcd for $C_{17}H_{16}ClN_2O^+$ $[M+H]^+$: 299.0946; found 299.0952.



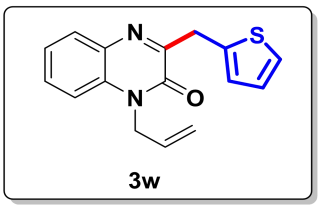
(*S*)-7-Bromo-1-methyl-3-(1-phenylethyl)quinoxalin-2(1*H*)-one (3t): Eluent petroleum ether/ethyl acetate (5:1). 48.7 mg, 71%. White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.1 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 4.91 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 154.1, 142.7,133.5, 132.5, 132.4, 132.2, 128.4, 128.1, 126.6, 115.9, 114.9, 41.9, 29.2, 19.5. HRMS calcd for $C_{17}H_{16}BrN_2O^+$ $[M+H]^+$: 343.0441; found 343.0441.



Methyl-3-(thiophen-2-ylmethyl)quinoxalin-2(1H)-one (3u): Eluent petroleum ether/ethyl acetate (10:1). 31.3mg, 61%. white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.22 (dt, *J* = 7.8, 3.5 Hz, 3H), 7.16 (d, *J* = 4.7 Hz, 1H), 4.27 (s, 2H), 3.66 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 154.7, 136.7, 133.3, 132.7, 129.9, 129.8, 129.0, 125.1, 123.6, 122.6, 113.6, 35.3, 29.1.



1-Butyl-6,7-dimethyl-3-(thiophen-2-ylmethyl)quinoxalin-2(1H)-one (3v): Eluent petroleum ether/ethyl acetate (10:1). 36.6 mg, 56%. white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.22 (d, *J* = 4.9 Hz, 2H), 7.17 (d, *J* = 4.6 Hz, 1H), 7.03 (s, 1H), 4.26 (s, 2H), 4.22- 4.18 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 1.71 (t, *J* = 7.6 Hz, 2H), 1.46 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (125 MHz, CDCl3) δ 157.4, 154.5, 139.5, 137.1, 132.3, 131.4, 130.5, 130.1, 129.0, 125.0, 122.4, 114.0,42.0, 35.1, 29.3, 20.6, 20.2, 19.1, 13.8.



3w

Allyl-3-(thiophen-2-ylmethyl)quinoxalin-2(1H)-one (3w): Eluent petroleum ether/ethyl acetate (10:1). 26.5 mg, 47%. white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 8.8, 4.0 Hz, 3H), 7.21 (d, *J* = 4.7 Hz, 1H), 5.97-5.90 (m, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.3 Hz, 1H), 4.92-4.90 (m, 2H), 4.33 (s, 2H).^{13}C NMR (125 MHz, CDCl3) δ 158.7, 154.3, 136.6, 132.8, 132.5, 130.6, 130.0, 129.8, 129.0, 125.1, 123.6, 122.6, 118.1, 114.1, 44.6, 35.2.

V. References

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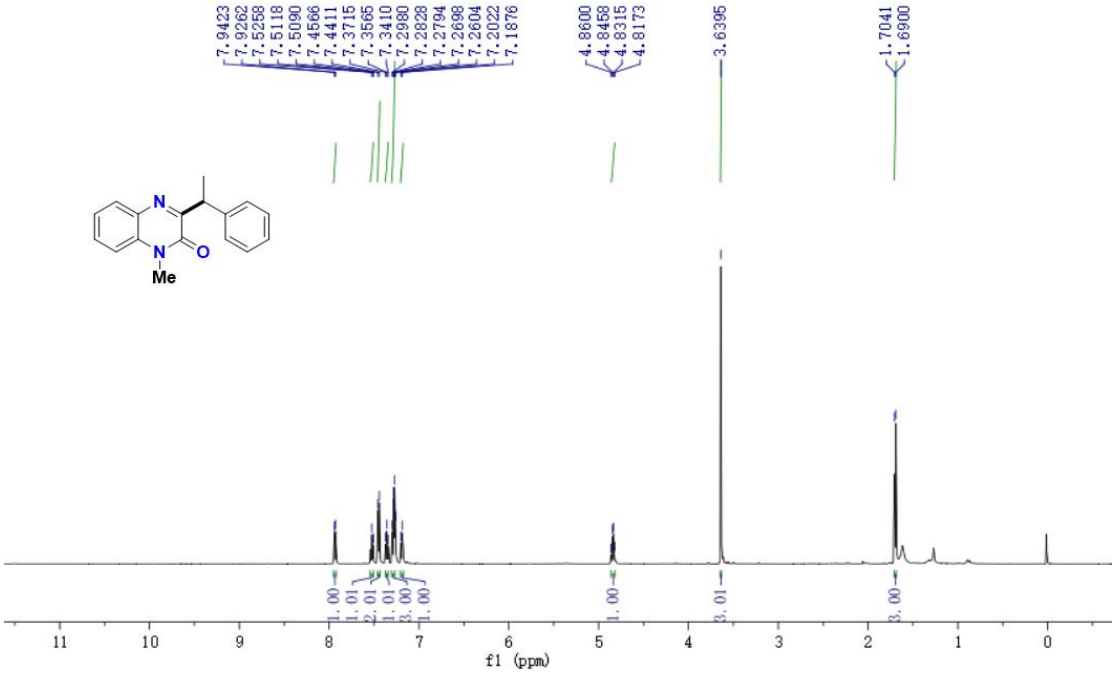
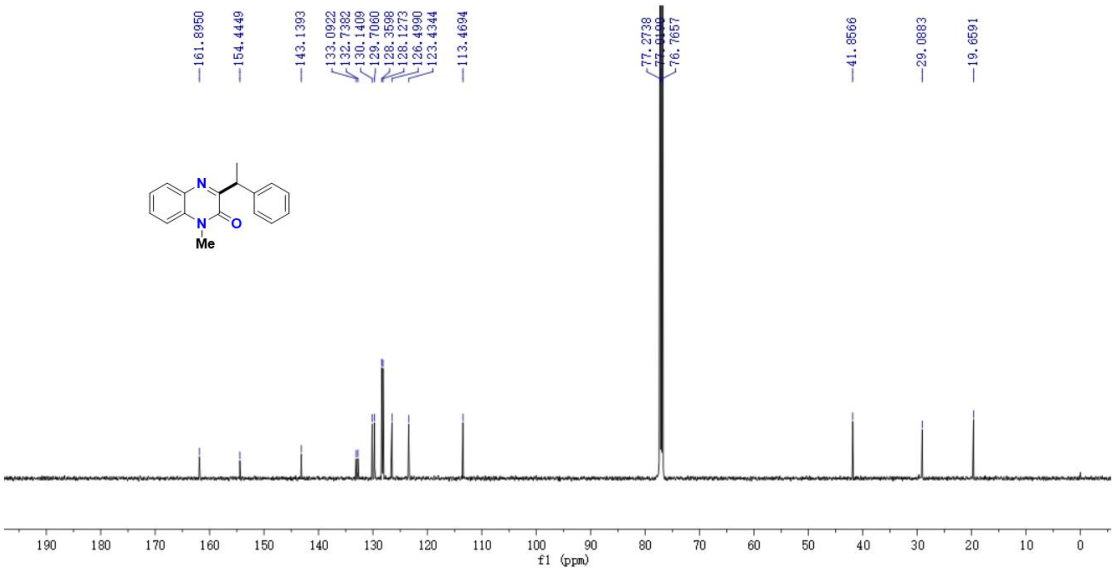
[4] C. Jin,W. Su, J. Yang, X. Zhuang, B. Sun, Z. Yan and X. Zhang, Construction of $C(sp^2) - C(sp^3)$ Bond between Quinoxalin-2(1H)-ones and N-Hydroxyphthalimide Esters via Photocatalytic Decarboxylative Coupling, *Asian Journal of Organic Chemistry.,* 2019, **14**, 3344-3349.

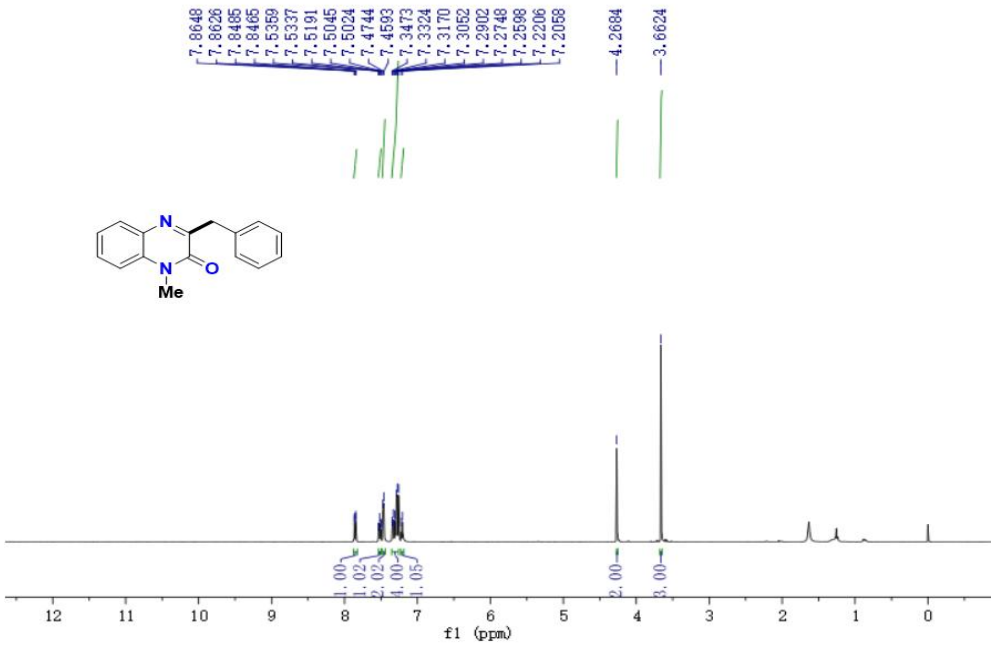
VI. NMR spectra of the products

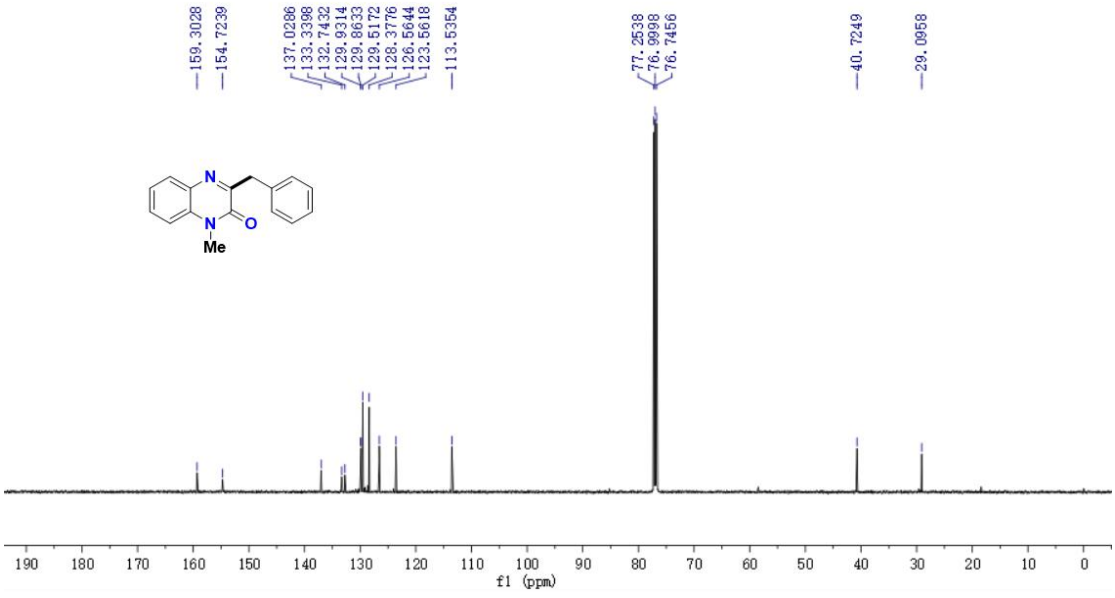
3a: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



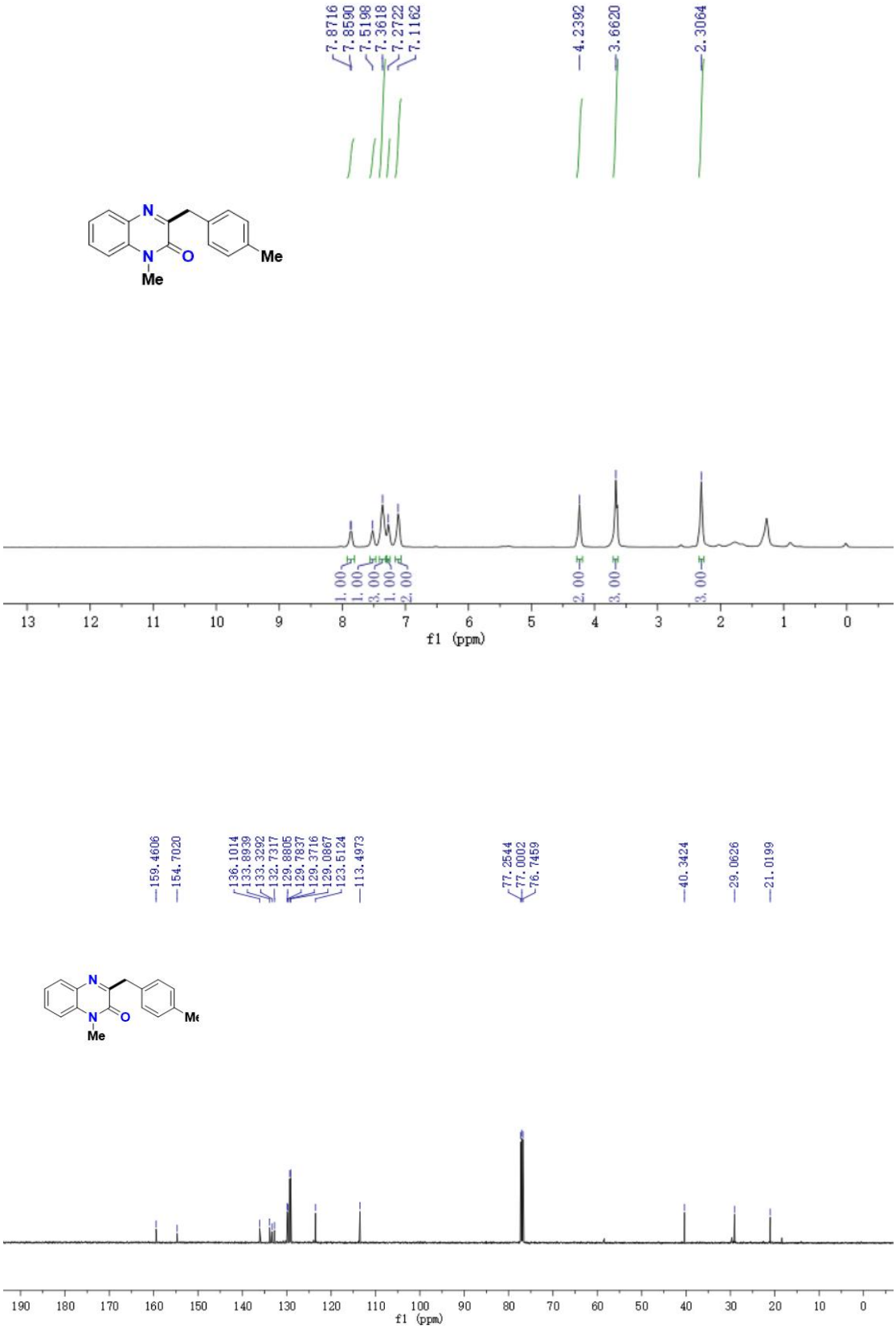


3b: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$

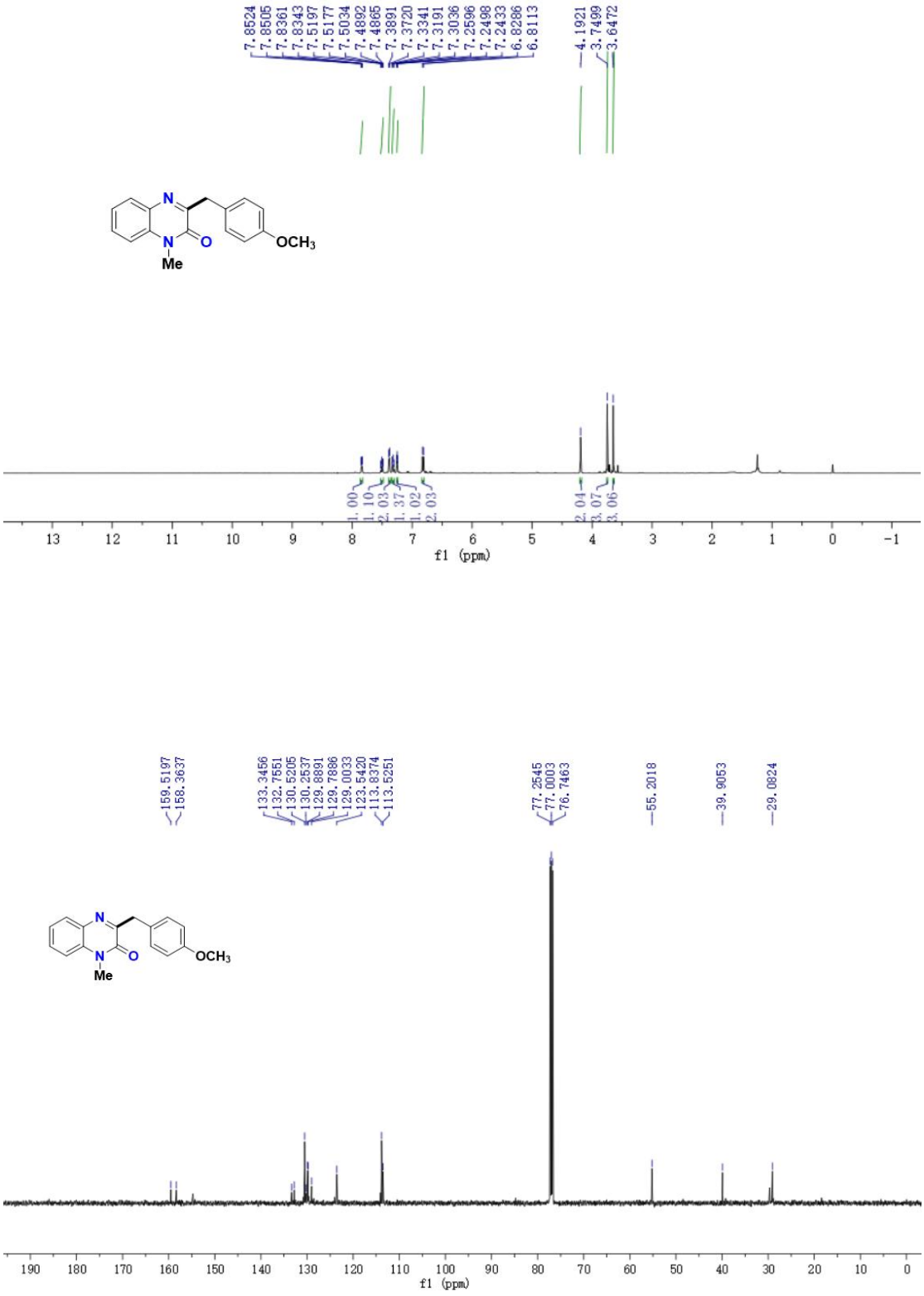




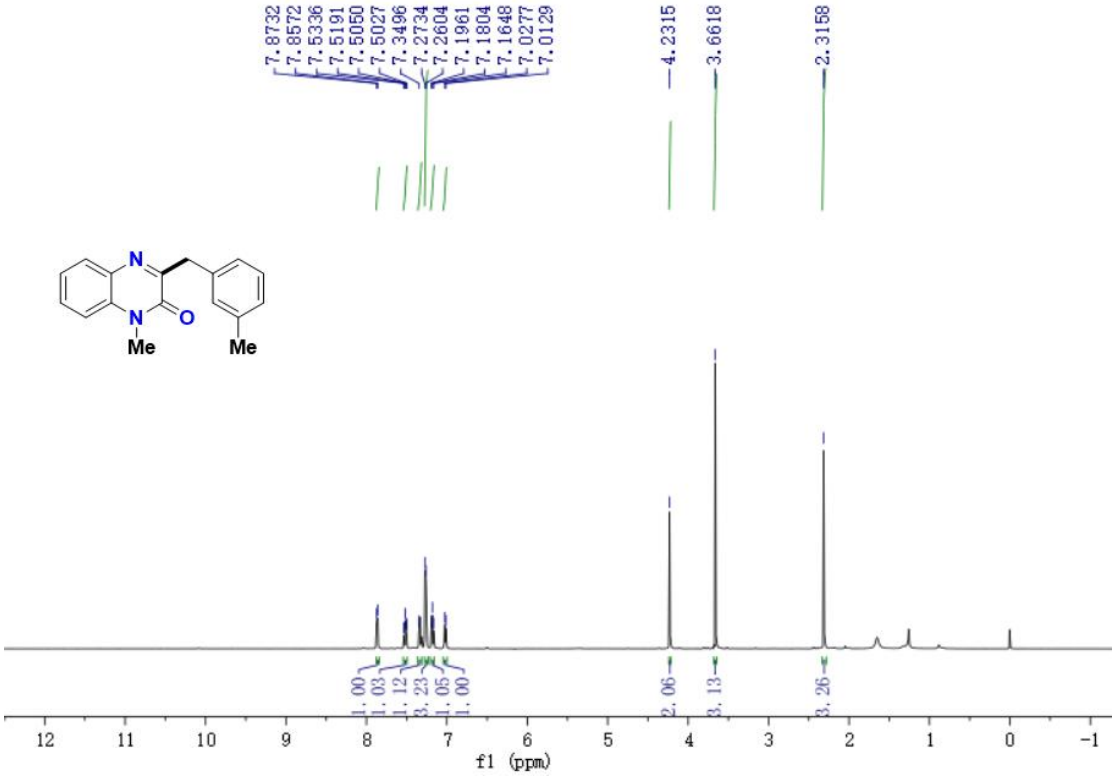
3c: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$

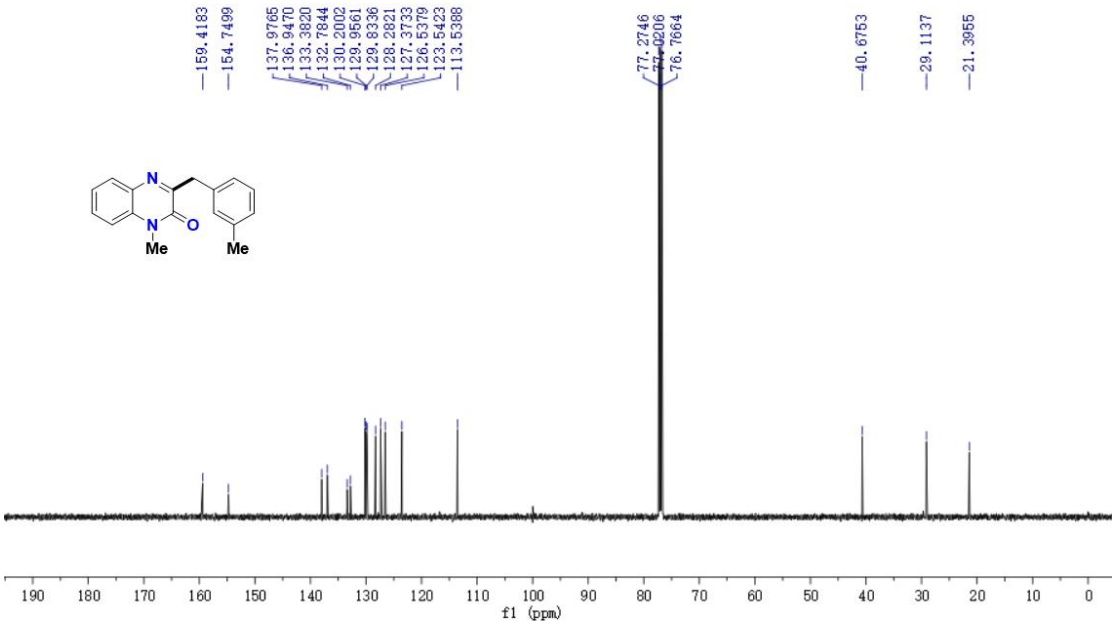


3d: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$

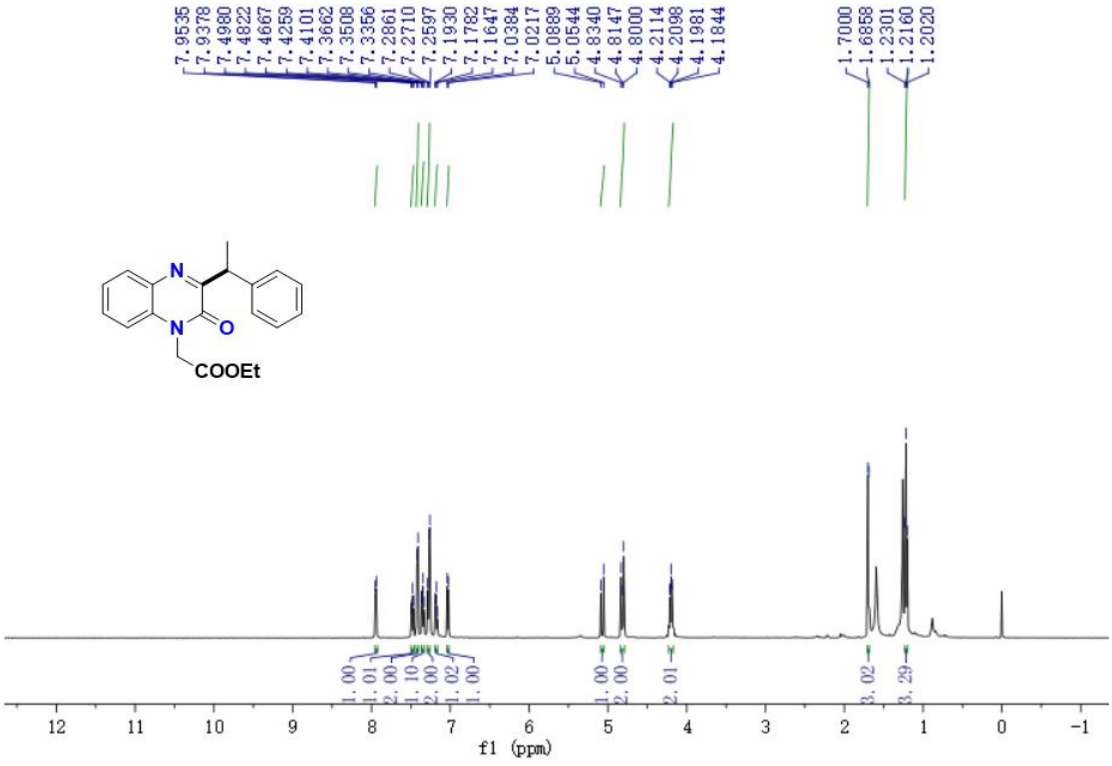


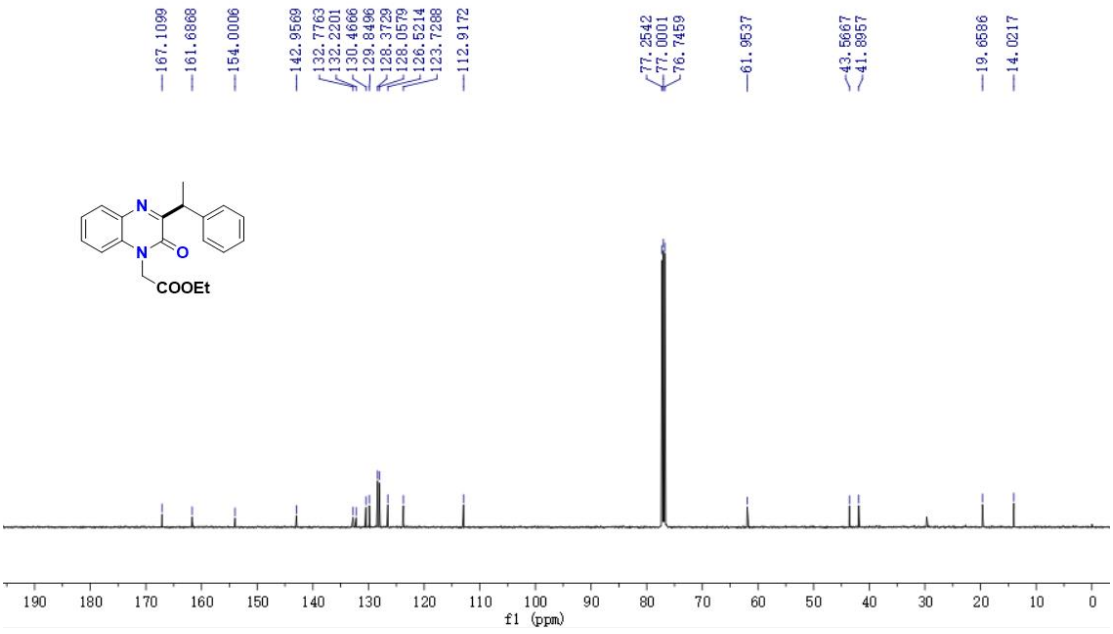
3e: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



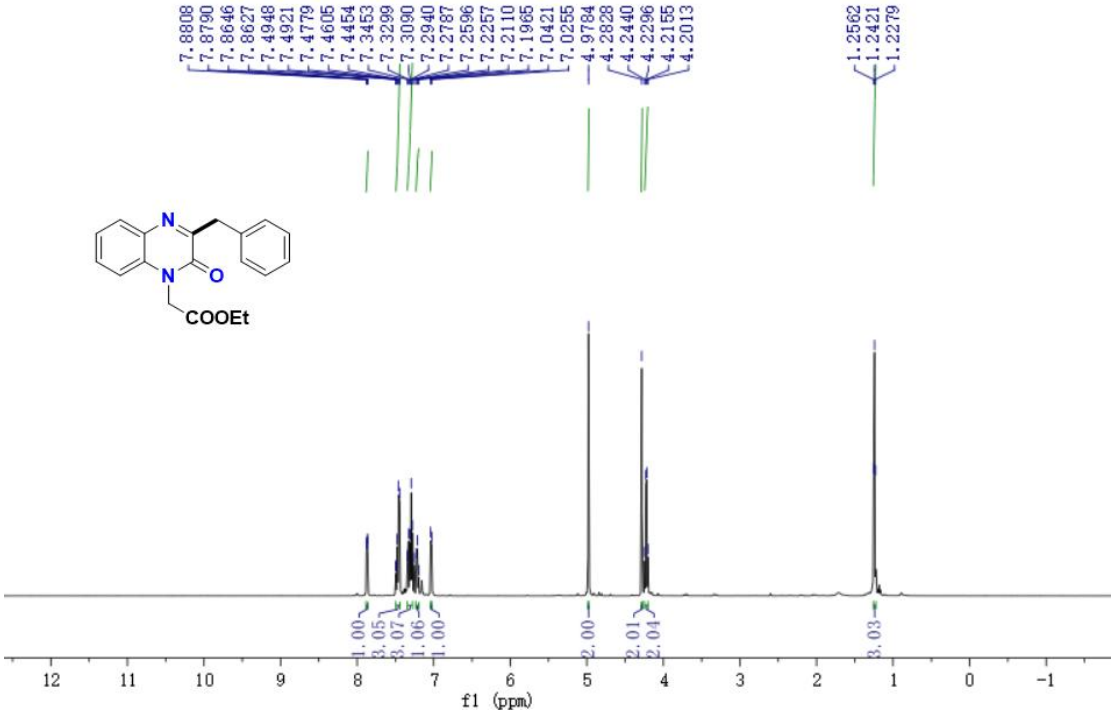


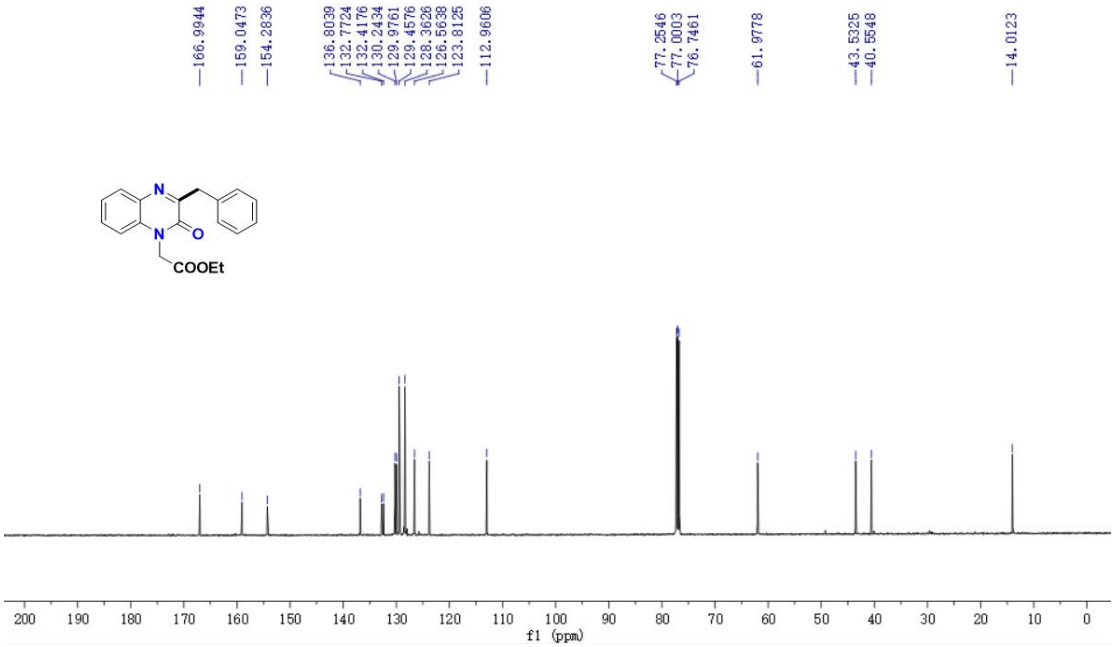
3f: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



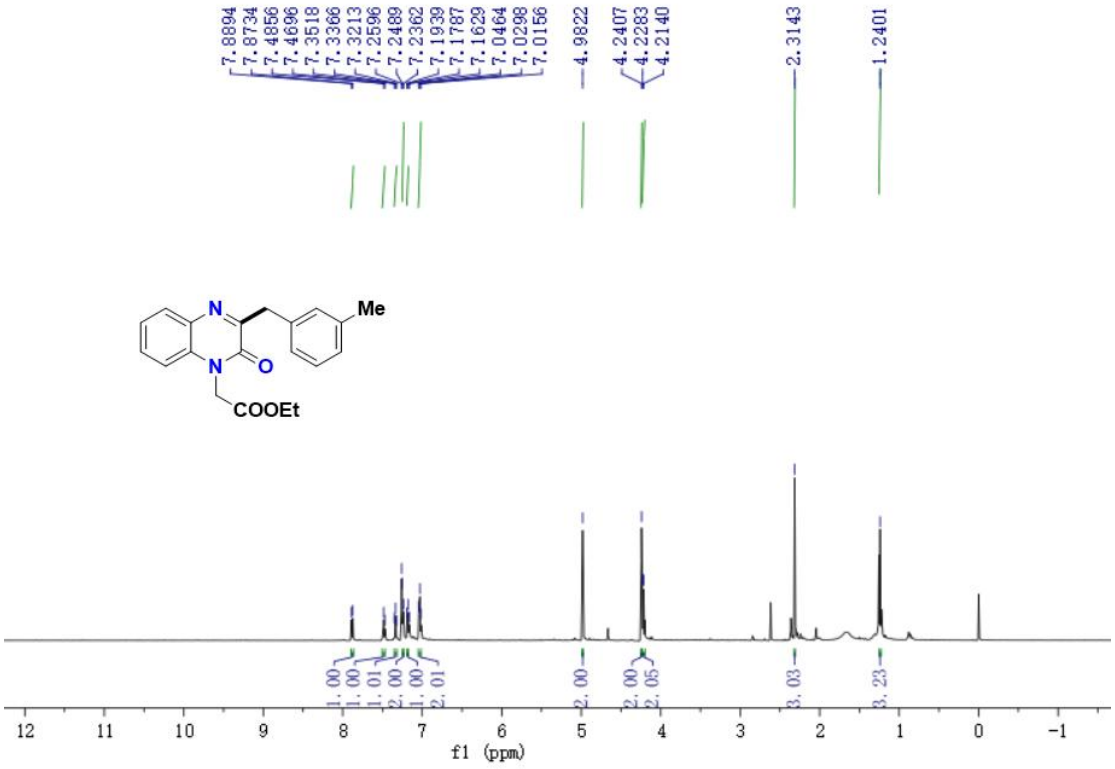


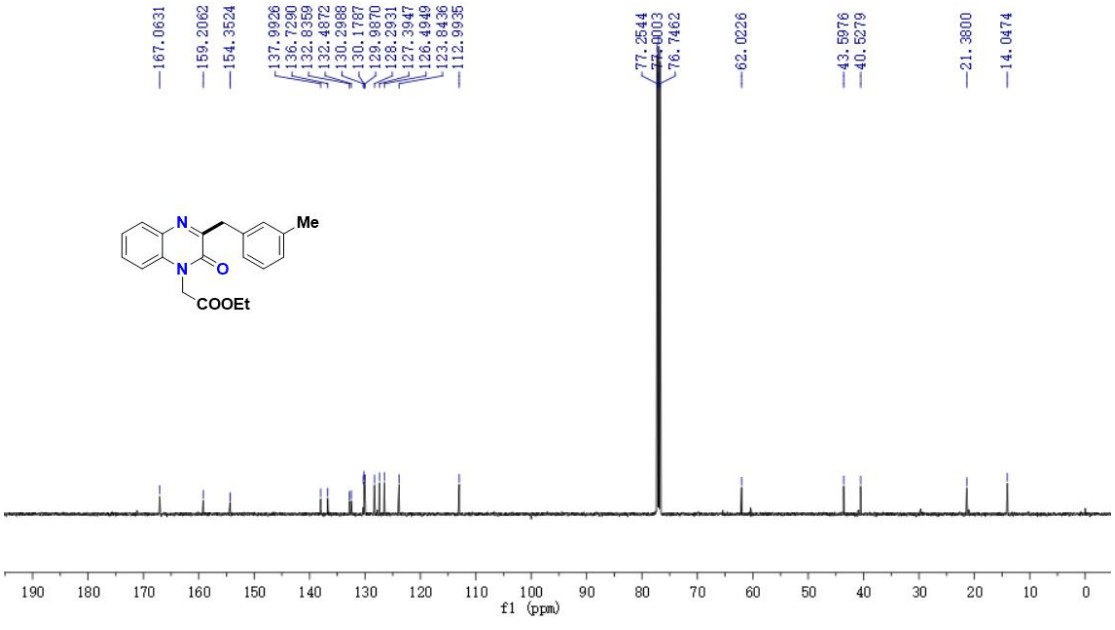
3g: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



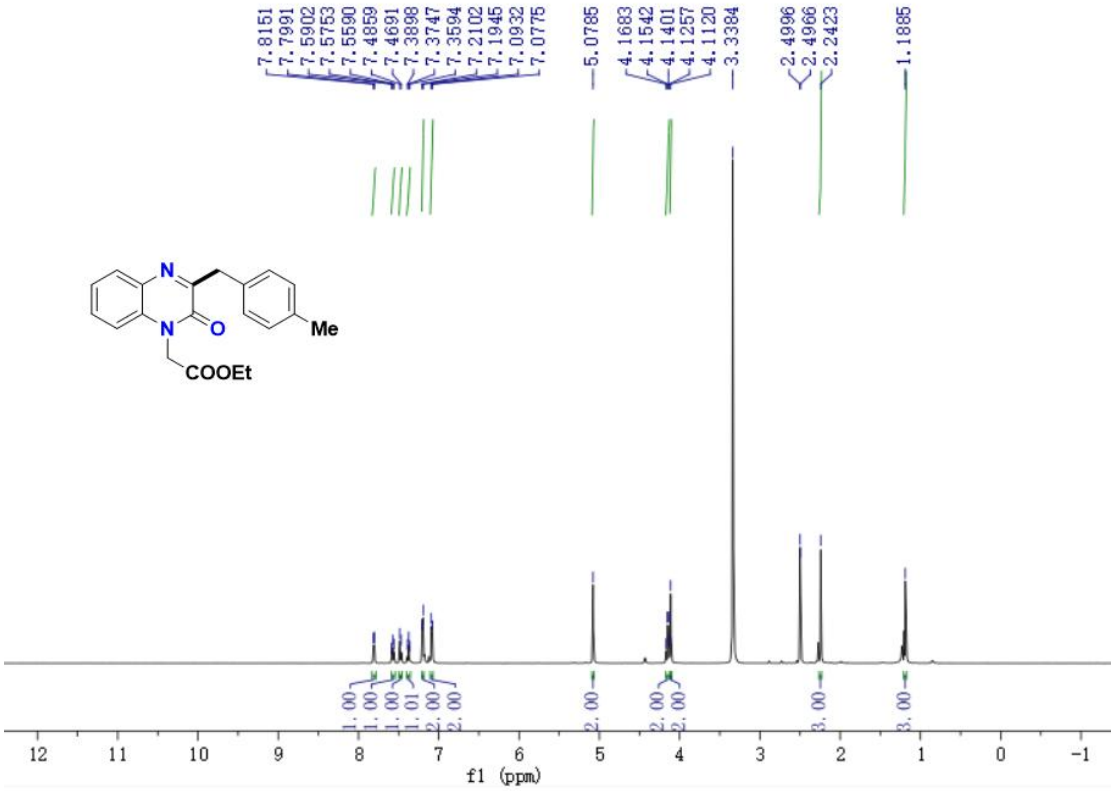


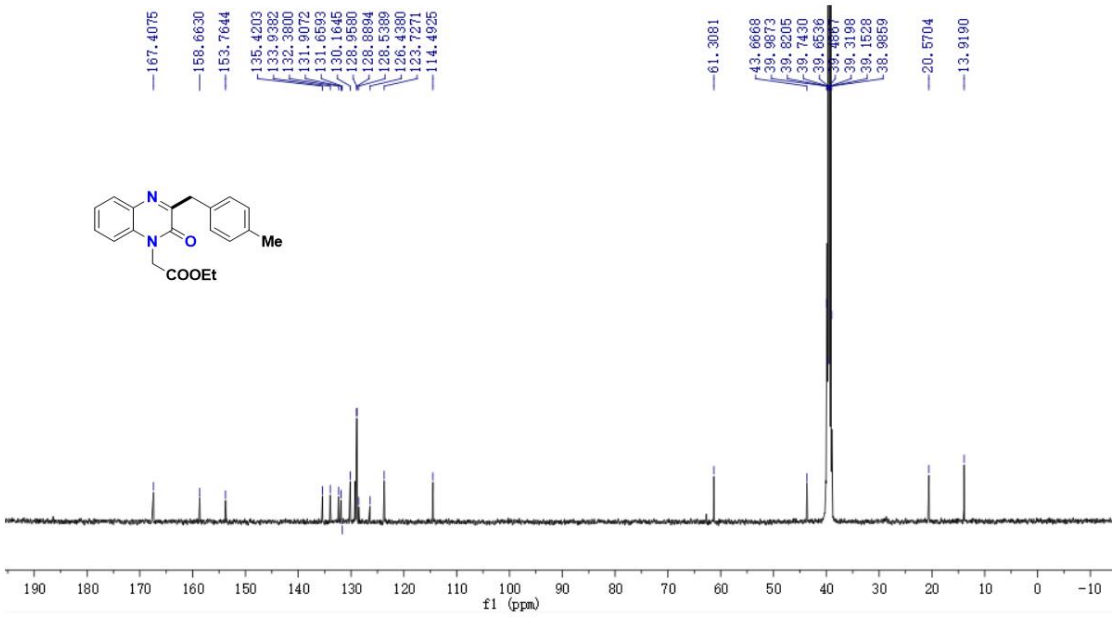
3h: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



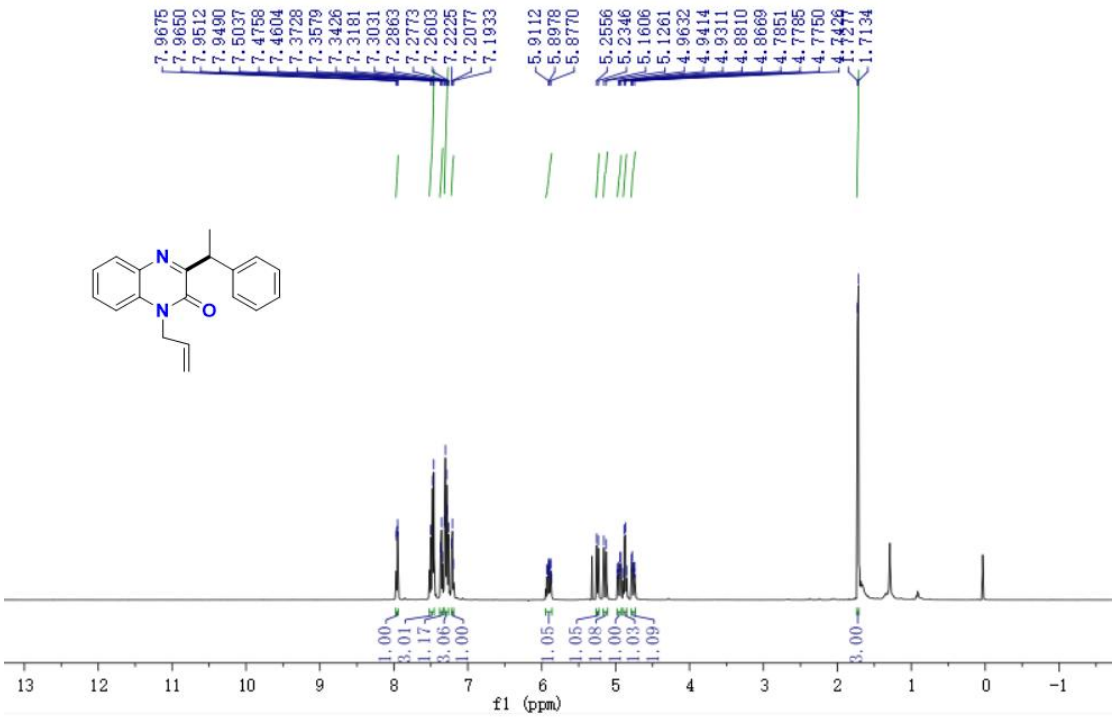


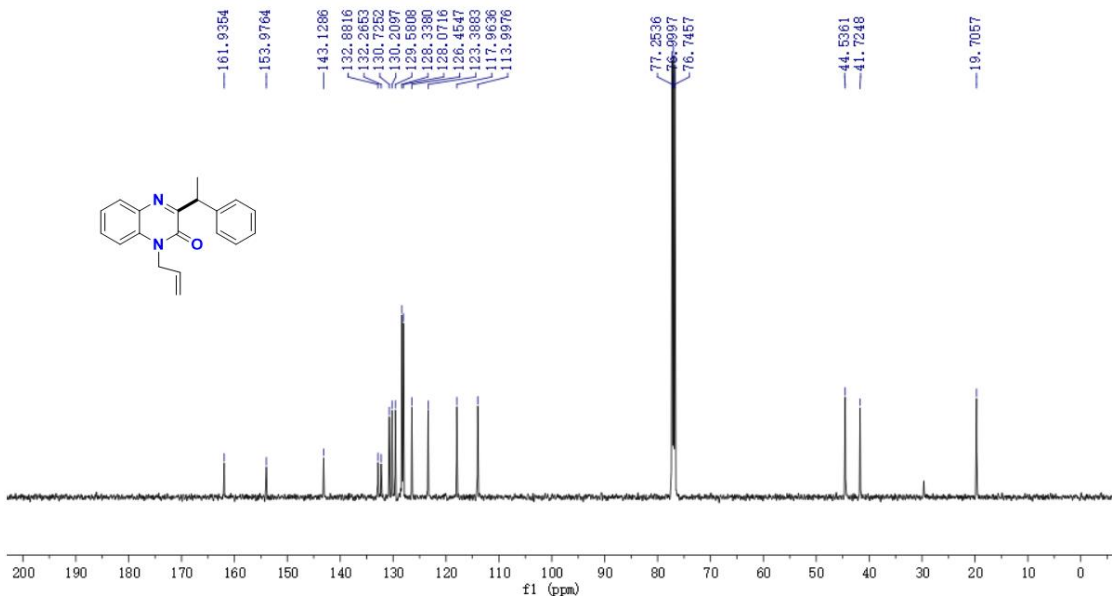
3i:^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), DMSO-d$_6$



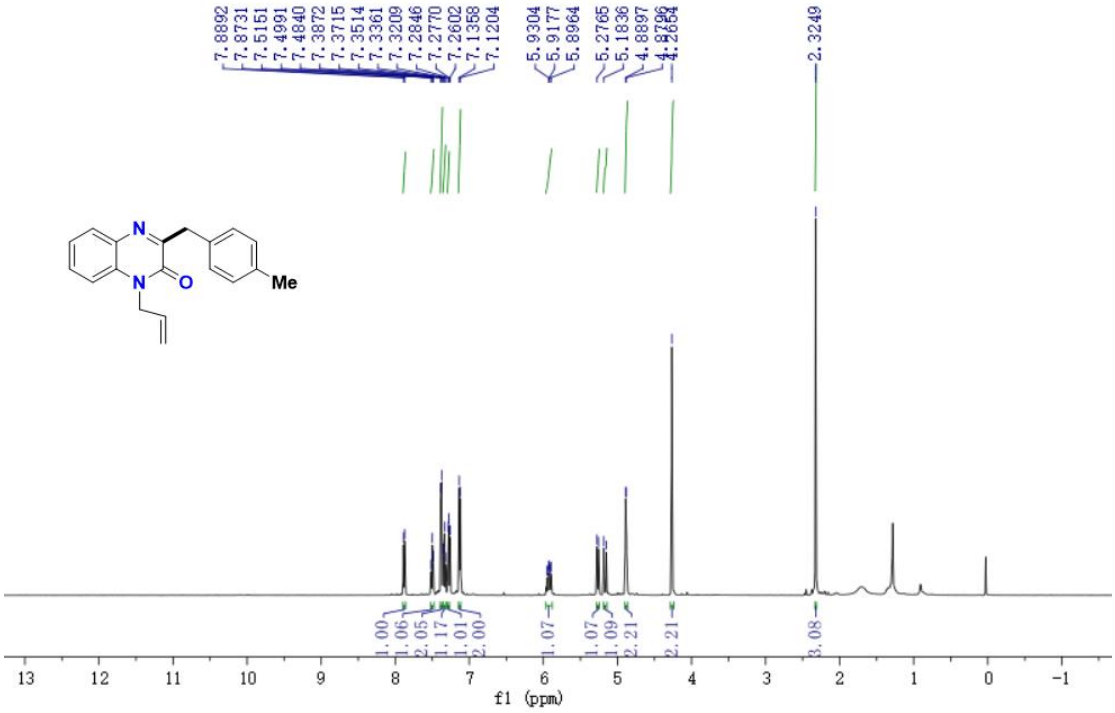


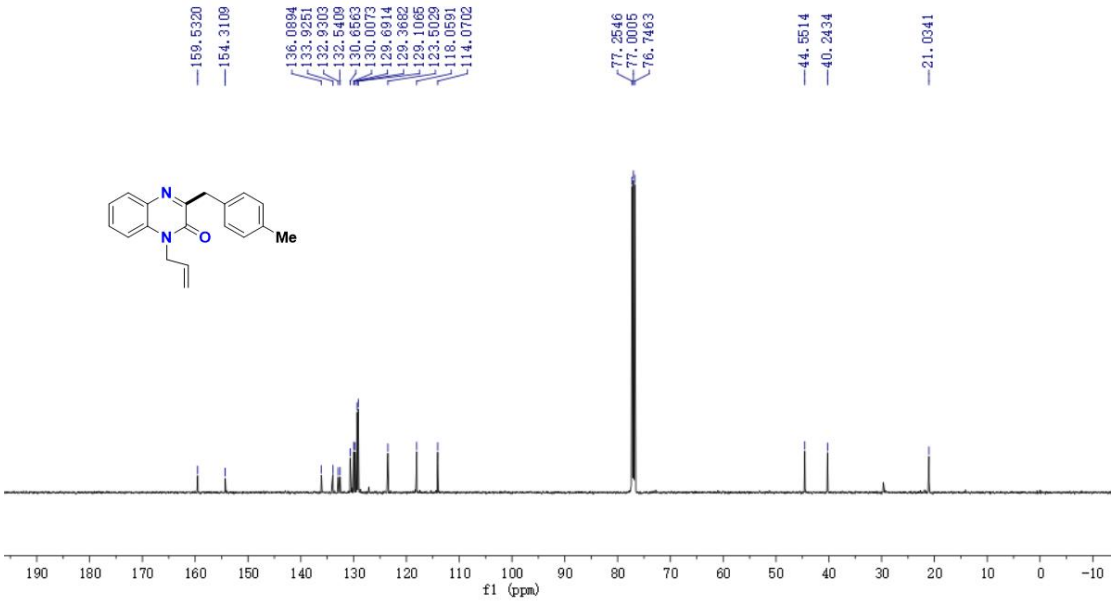
3j: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



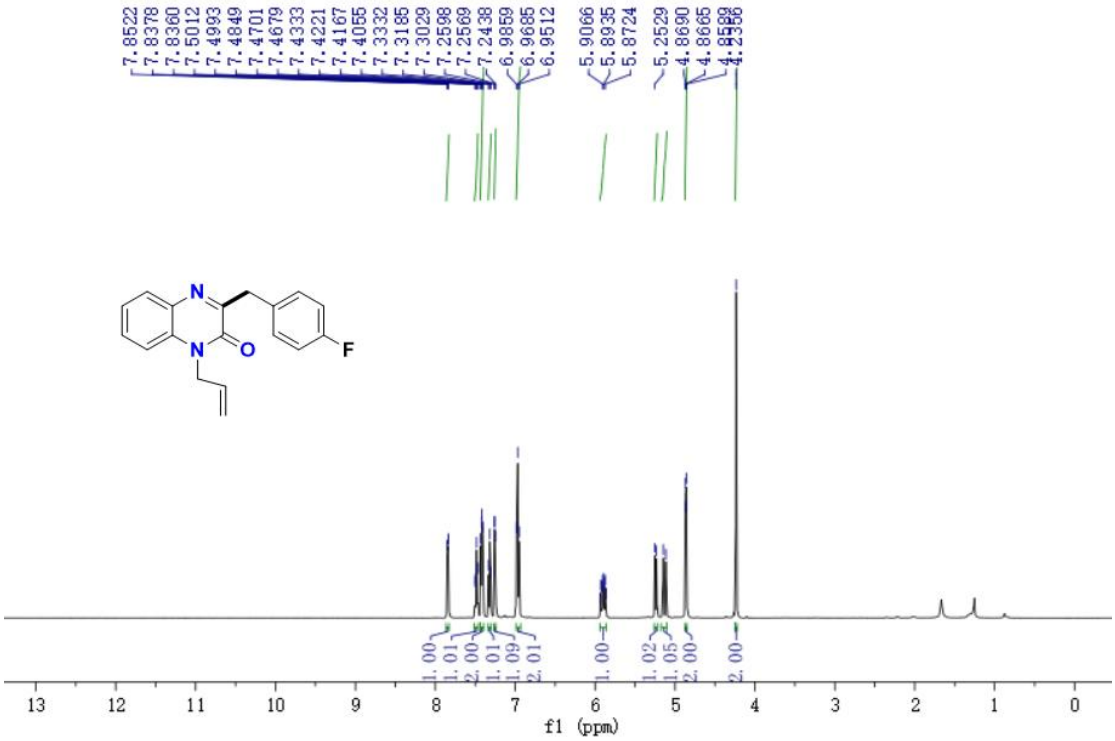


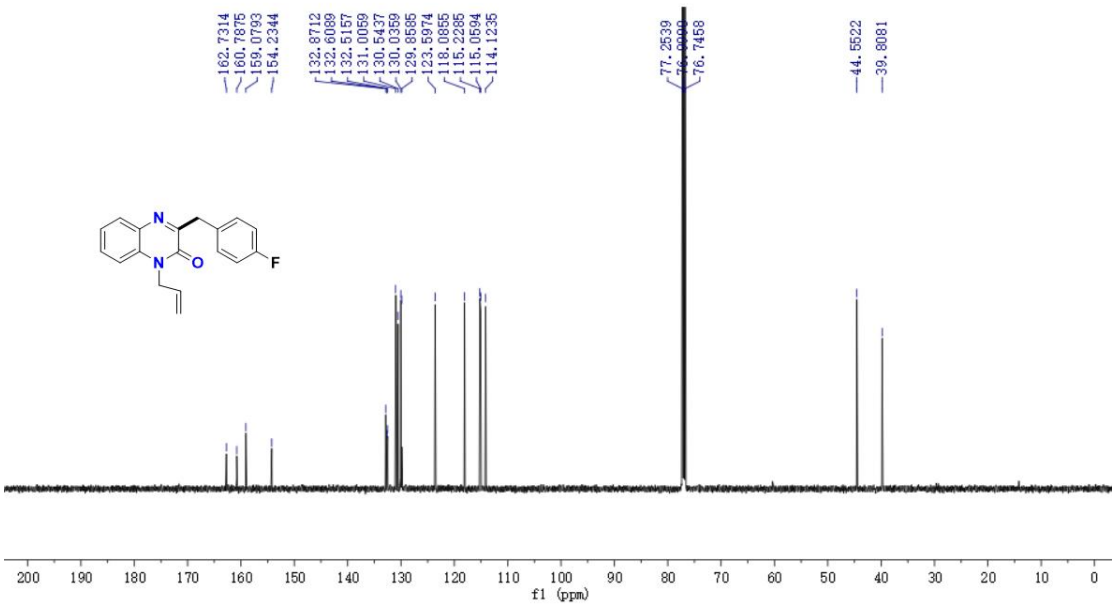
3k: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



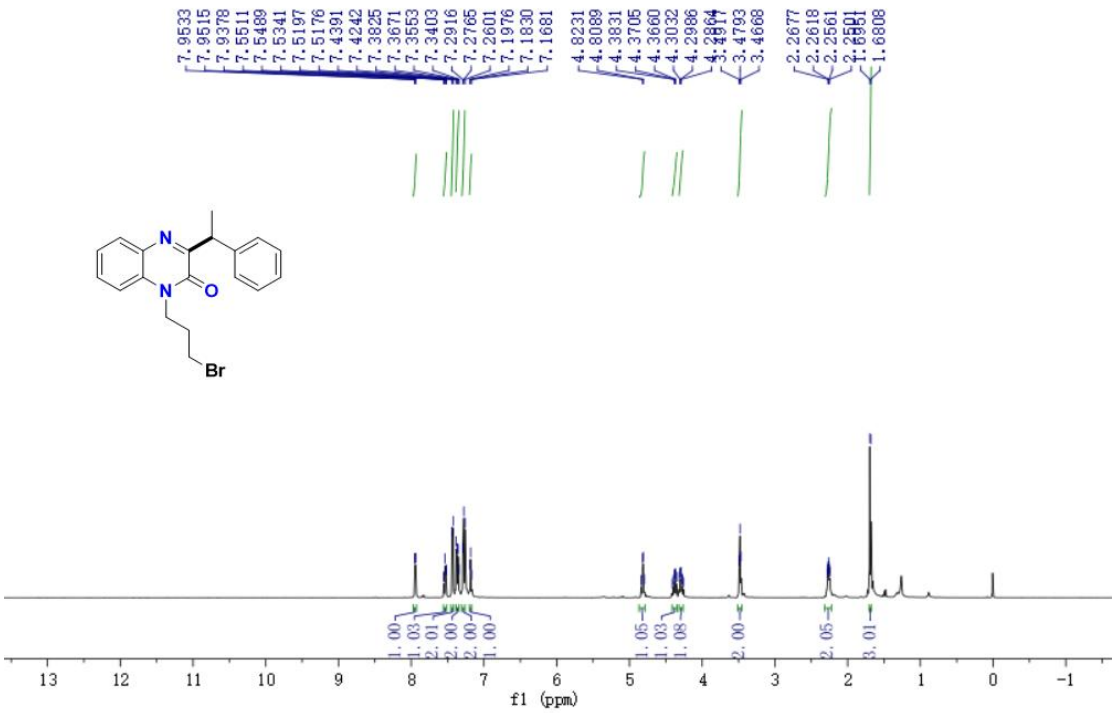


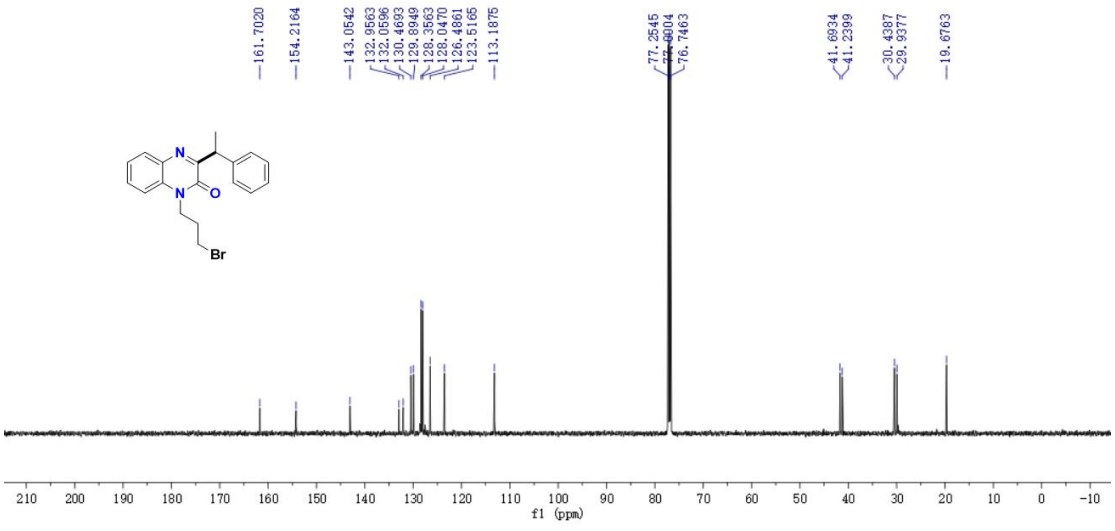
3l: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



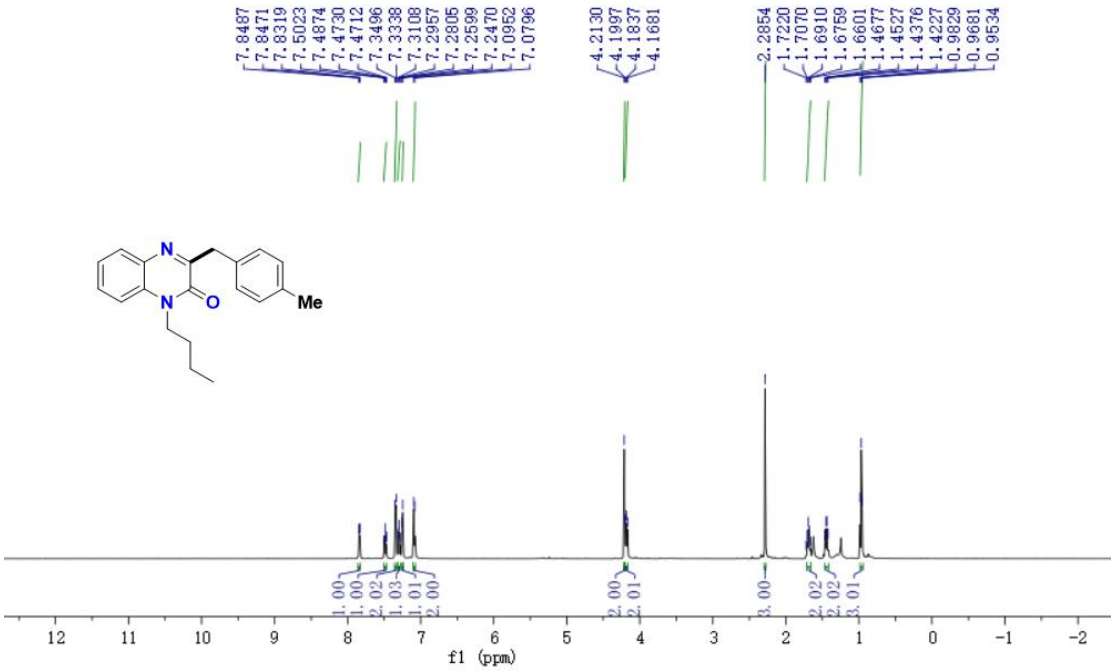


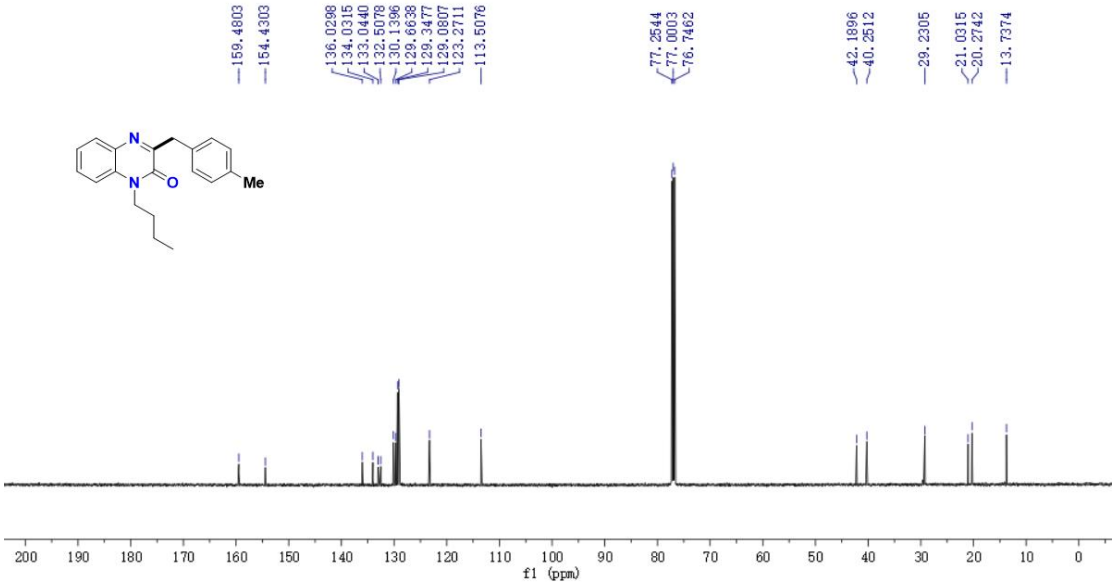
3m: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



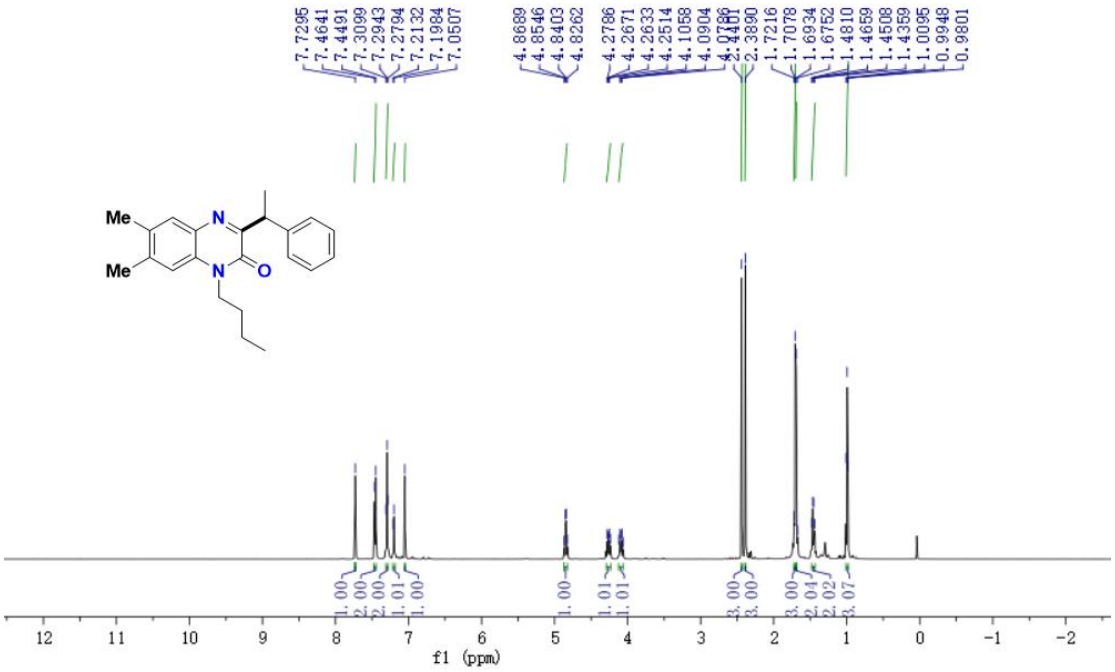


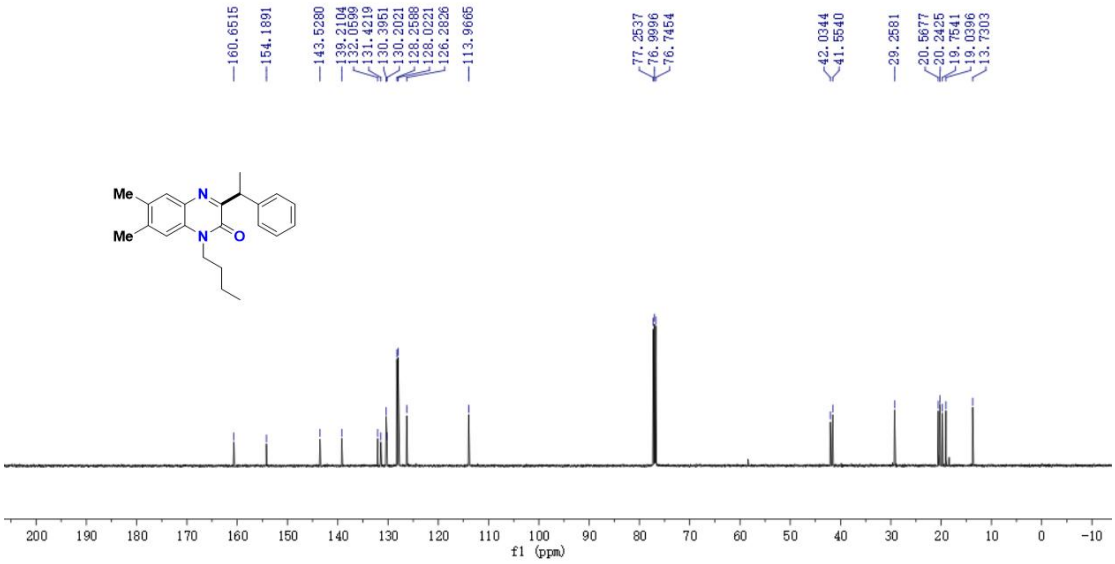
3n: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



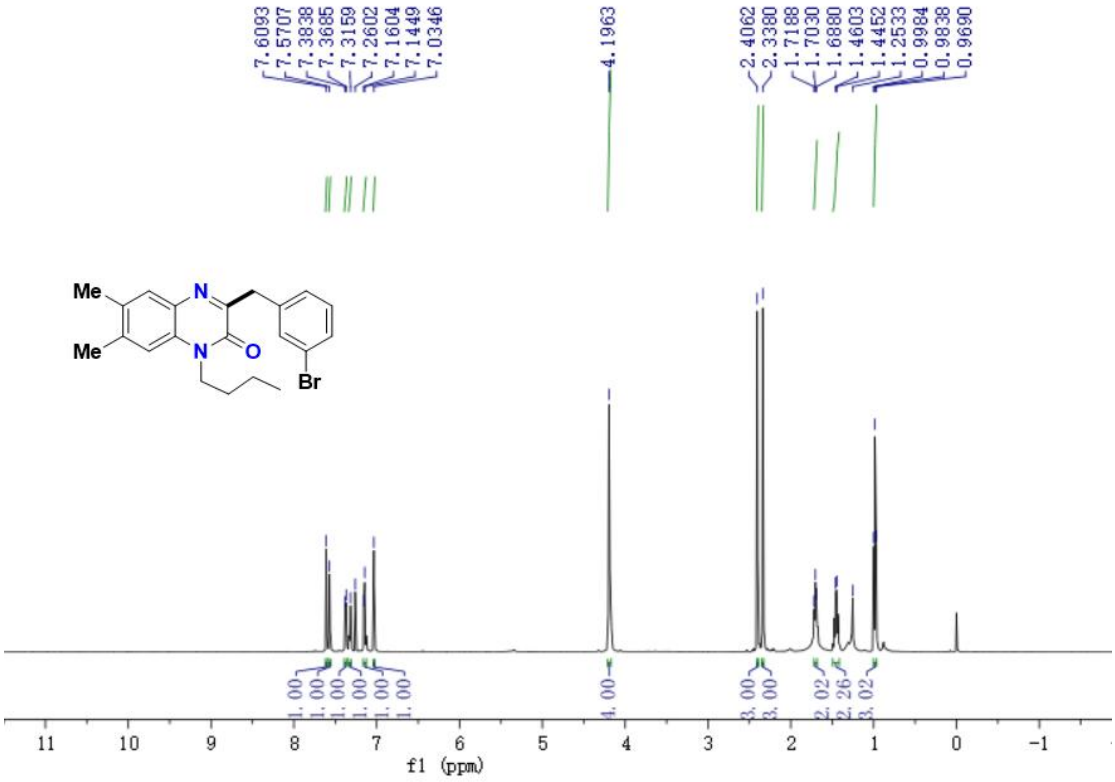


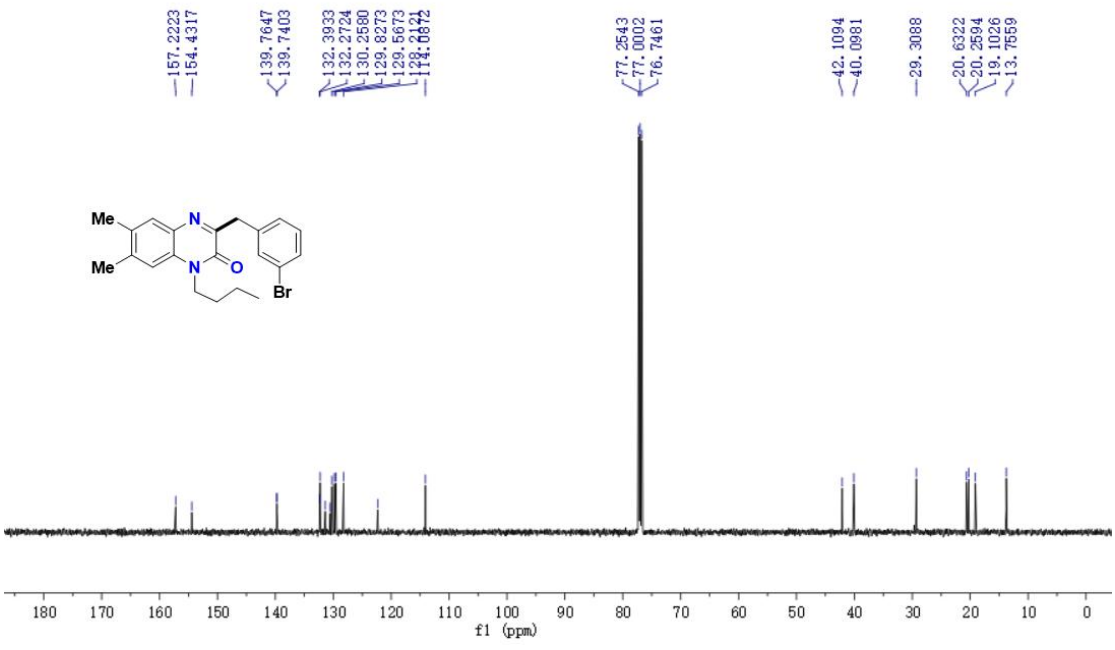
3o: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



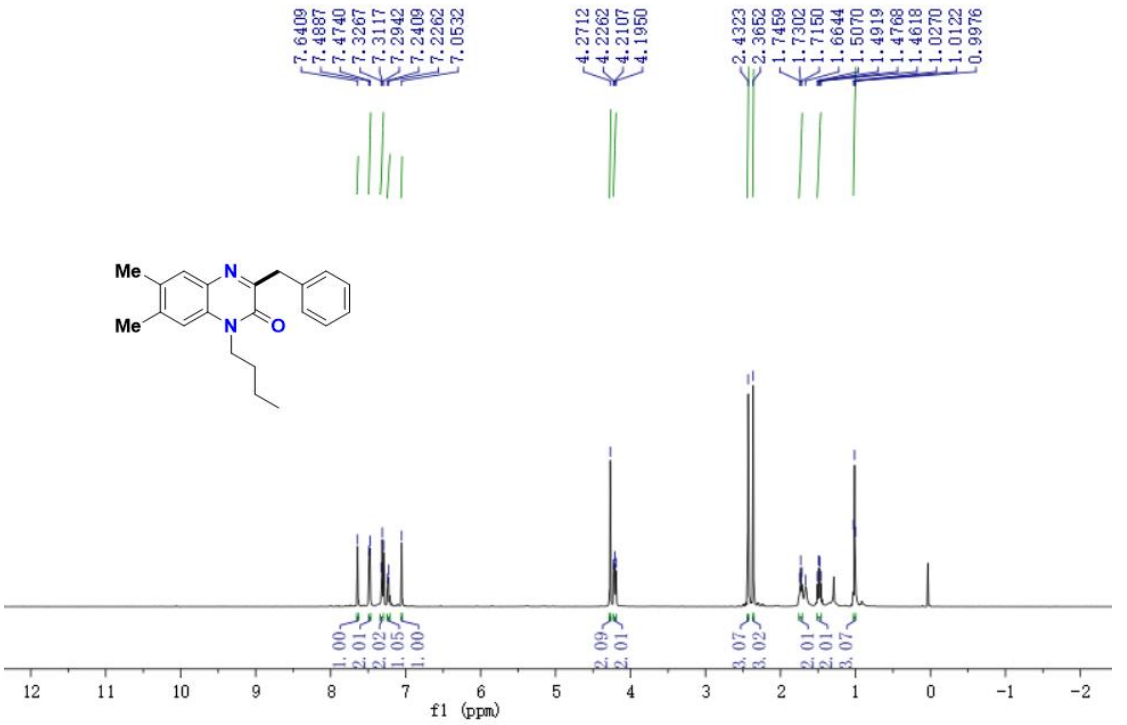


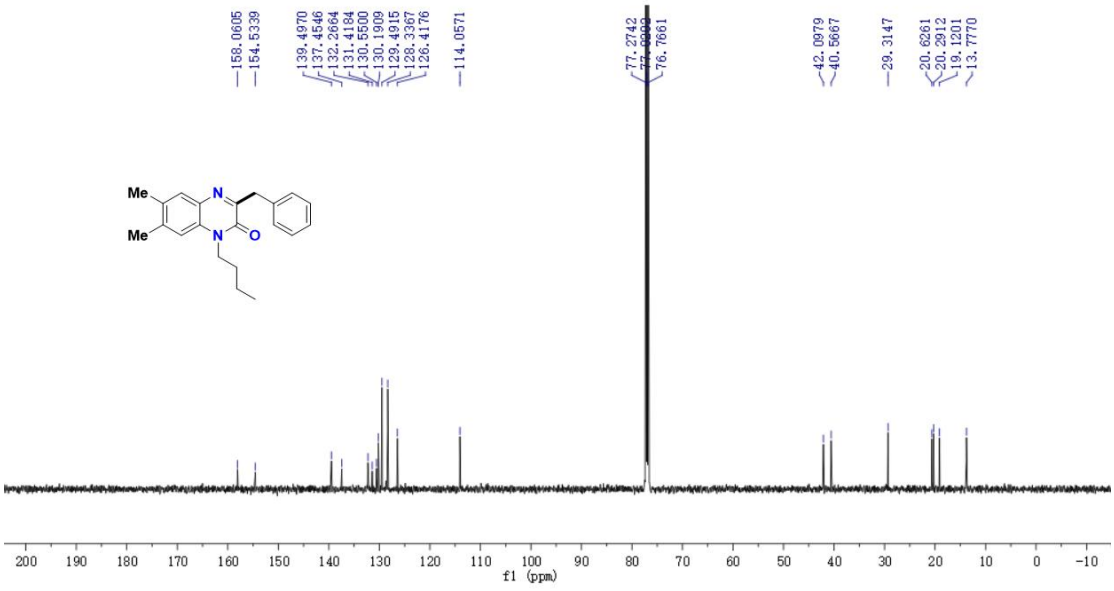
3p: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



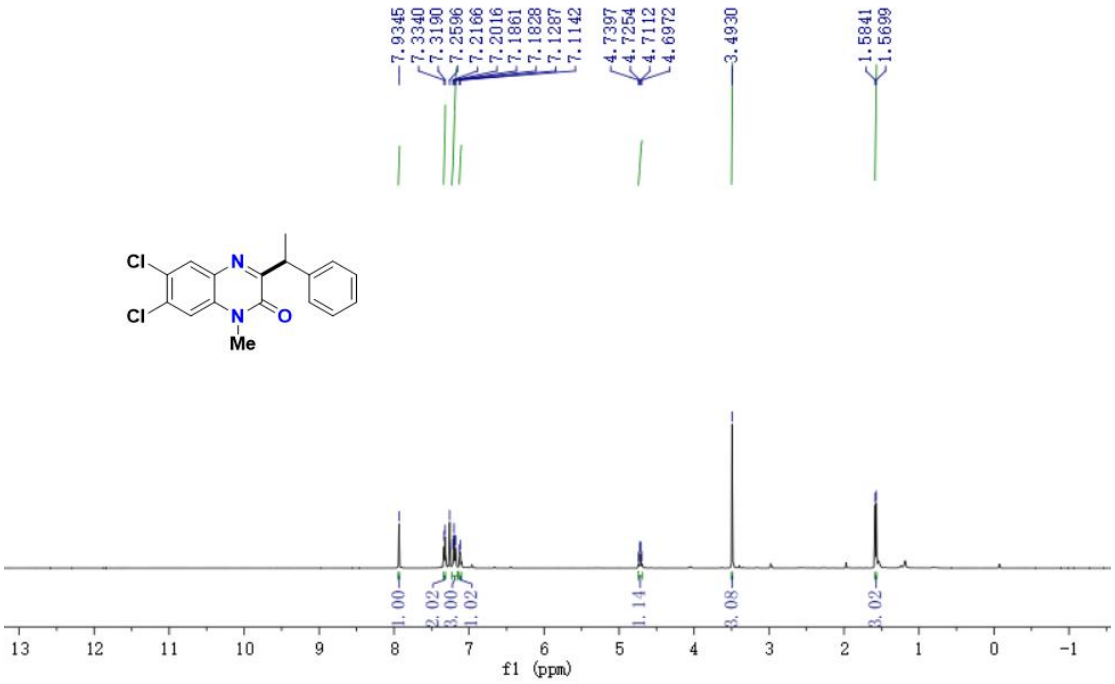


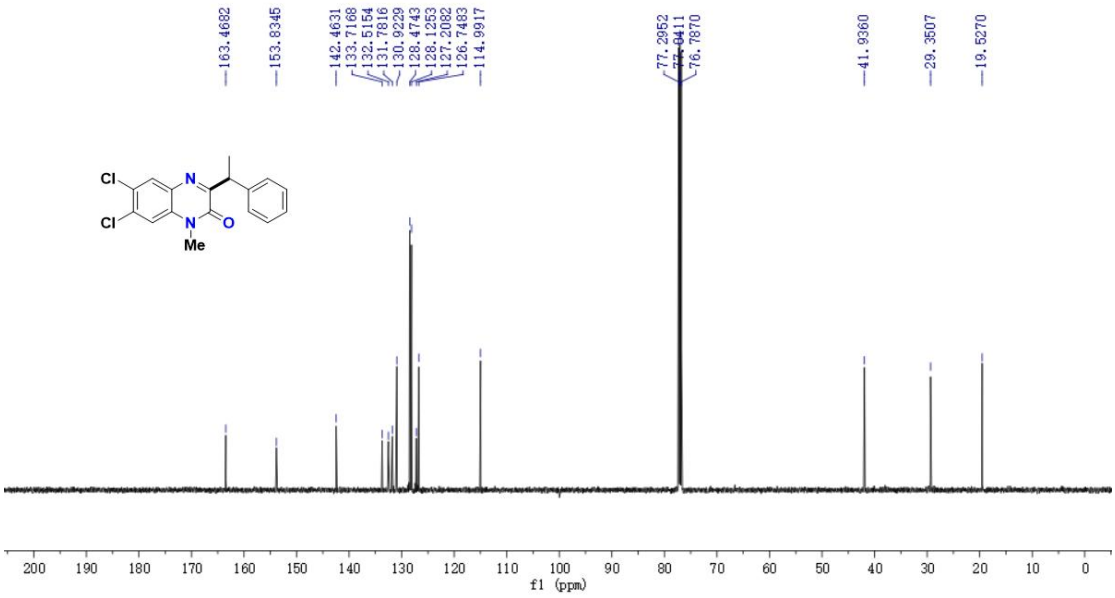
3q: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



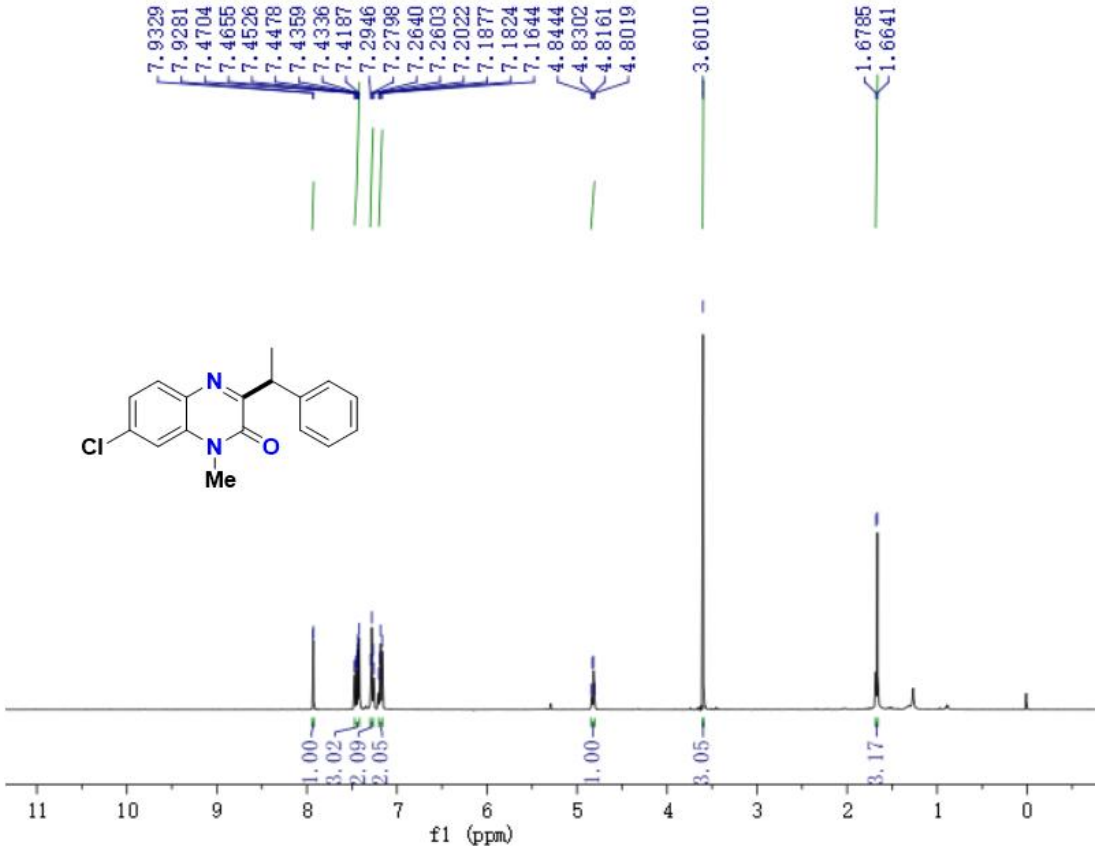


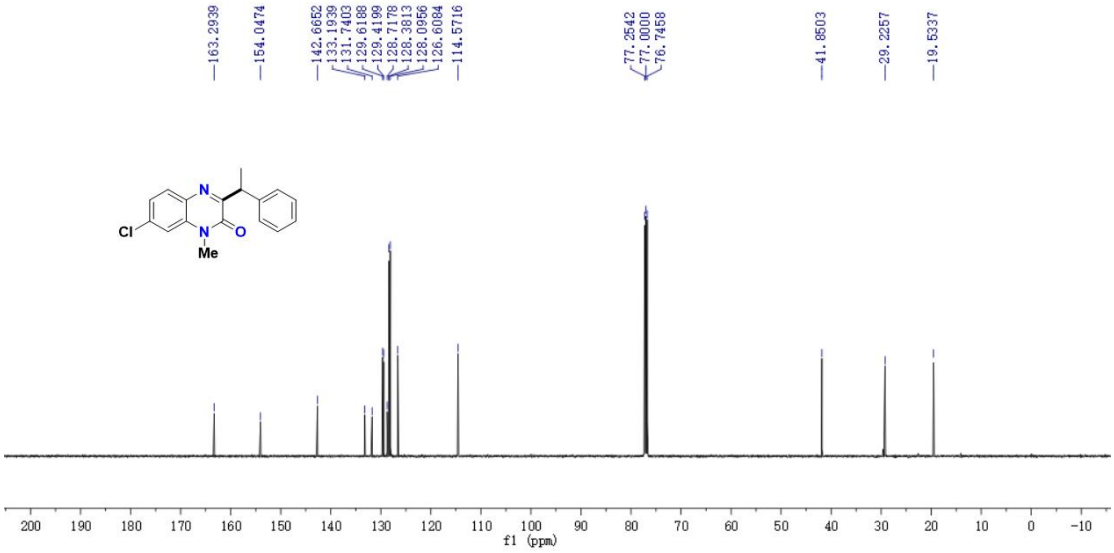
3r: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



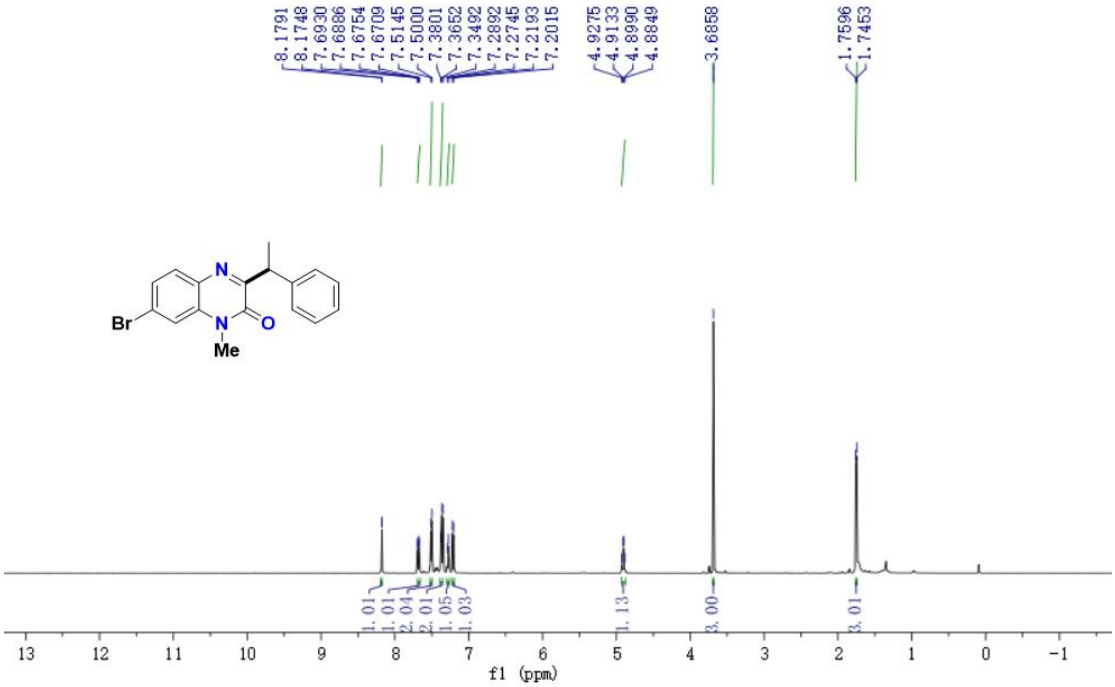


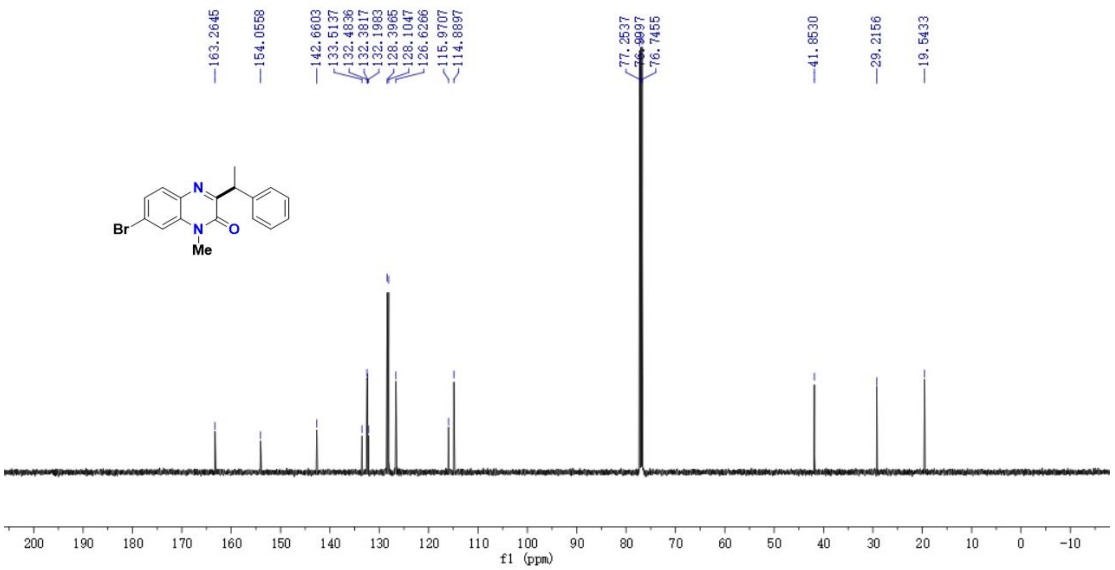
3s: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



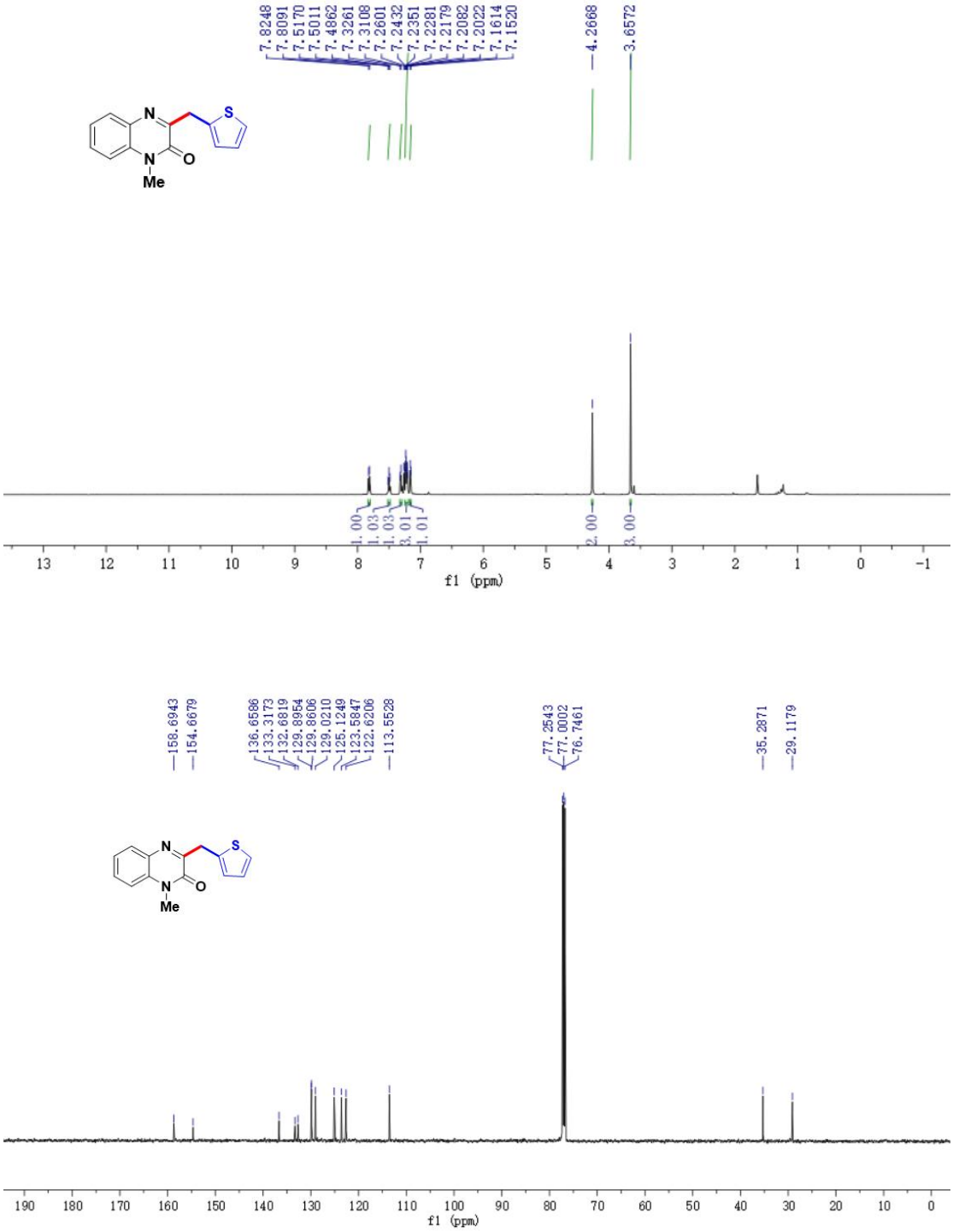


3t: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$

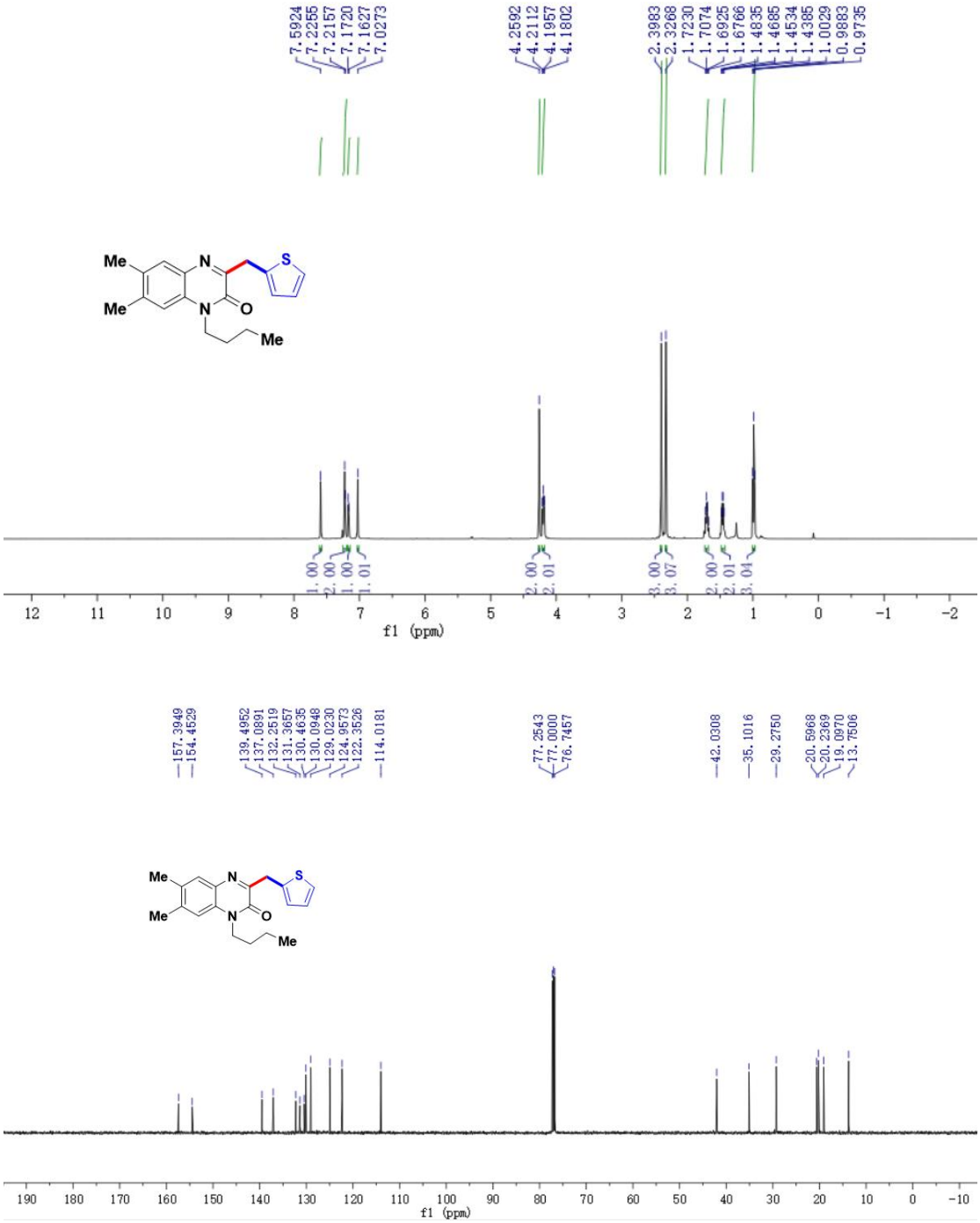




3u: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



3v: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$



3w: ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz), $CDCl_3$