

# Supporting Information

## An Unexpected $\text{NH}_4\text{HSO}_4$ -Catalyzed C3-H Alkenylation of Quinoxalin-2(1H)-ones with Allenes

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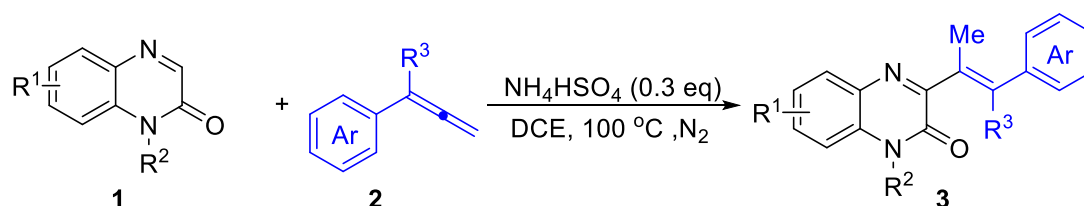
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## 1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra were recorded at 400, 101, 162 and 376 MHz, respectively. Chemical shifts were quoted in ppm relative to  $\text{CDCl}_3$  ( $\delta_{\text{H}} = 7.26$ ,  $\delta_{\text{C}} = 77.0$  ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. The reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Mass spectra were performed on a spectrometer operating on ESI-TOF. Melting points were measured on a melting point apparatus and were uncorrected.

## 2. Experimental Section

### General procedure for the synthesis of product 3



To a 10 mL sealed pressure tube equipped with a stirring bar was added quinoxalin-2(1H)-ones **1** (0.3 mmol, 1 eq), allene **2** (0.45 mmol, 1.5 eq) and  $\text{NH}_4\text{HSO}_4$  (0.09 mmol, 0.3 eq) in DCE (3 mL). The reaction mixture was stirred at  $100\text{ }^\circ\text{C}$  for about 12 h under a  $\text{N}_2$  atmosphere. After completion,  $\text{H}_2\text{O}$  (10 mL) was added to the mixture, followed by extraction with DCM three times (10 mL  $\times$  3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was further purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 8:1-4:1) to afford the purified product **3**. The investigated unsuccessful substrates are summarized in Figure S1.

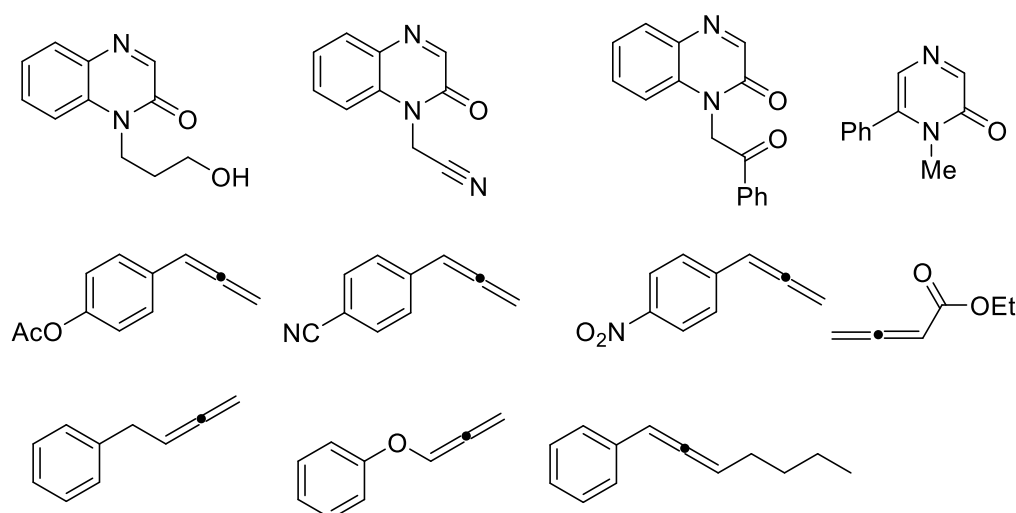
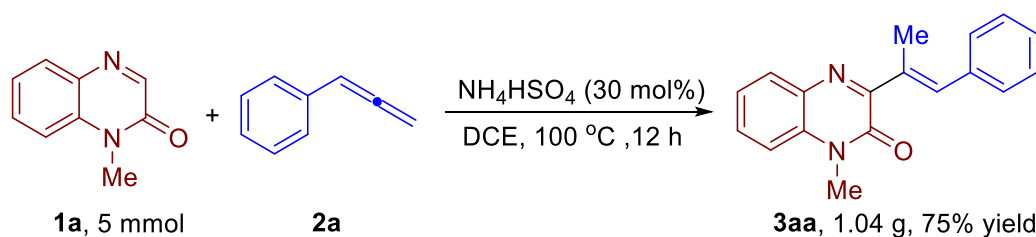


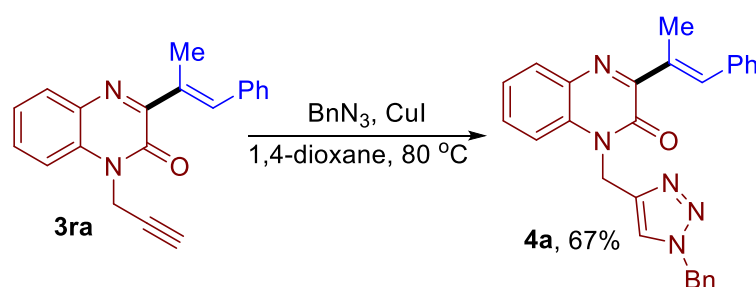
Figure S1 Unsuccessful substrates

## Gram-scale synthesis of 3aa



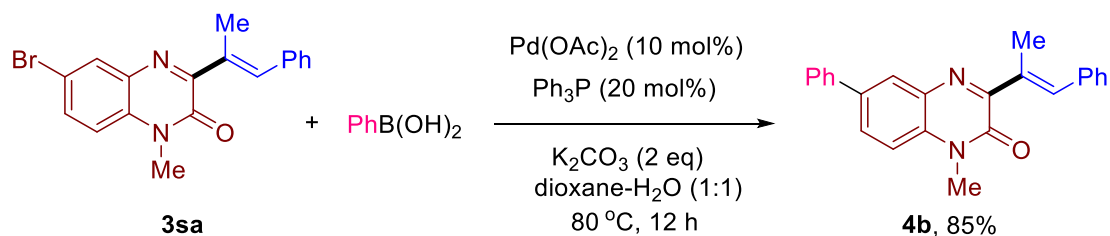
To a 100 mL round-bottom flask equipped with a stirring bar was added 1-methylquinoxalin-2(1*H*)-one **1a** (5 mmol, 0.80 g), phenylallene **2a** (7.5 mmol, 0.99 g) and  $\text{NH}_4\text{HSO}_4$  (1.5 mmol, 0.17 g) in DCE (50 mL). The reaction mixture was stirred at 100 °C for about 12 h under a  $\text{N}_2$  atmosphere. After completion,  $\text{H}_2\text{O}$  (30 mL) was added to the mixture, followed by extraction with DCM three times (30 mL  $\times$  3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was further purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 8:1-4:1) to afford the purified product 1.04 g of **3aa** in 75% isolated yield.

## Synthesis of 4a via copper-catalyzed click reaction of 3ra with $\text{BnN}_3$



To a solution of compound **3ra** (0.5 mmol) and  $\text{PhCH}_2\text{N}_3$  (0.6 mmol) in 1,4-dioxane (5 mL) was added  $\text{CuI}$  (0.15 mmol), the reaction mixture was stirred at 80 °C for about 2 h. After completion, the reaction was allowed to cool to room temperature, then,  $\text{H}_2\text{O}$  (5 mL) was added to the mixture, which was further extracted with DCM for three times (10 mL  $\times$  3). The organic phase was then dried with anhydrous sodium sulfate, concentrated under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA 6:1- 2:1) to give 0.145 g of **4a** in 67% isolated yield.

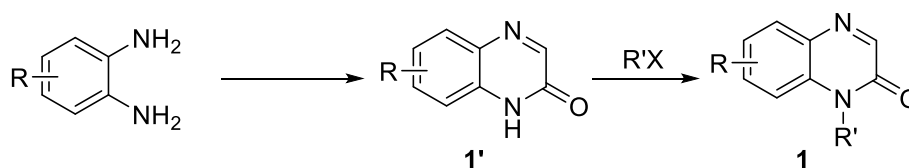
## Synthesis of 4b via Suzuki reaction



An oven-dried reaction tube was charged with a magnetic stir bar and  $\text{Pd}(\text{OAc})_2$  (10 mol%, 0.02 mmol, 5 mg),  $\text{PPh}_3$  (0.04 mmol, 11 mg) and compound **3sa** (0.2 mmol, 71 mg) under nitrogen atmosphere. Then, phenyl boronic acid (0.5 mmol, 61 mg),  $\text{K}_2\text{CO}_3$  (0.4 mmol, 55 mg) and 1,4-dioxane/ $\text{H}_2\text{O}$  (2 mL (1/1),  $\text{N}_2$  purged) were added to the reaction tube under nitrogen atmosphere. The resulting mixture was then stirred at 80 °C 12 h. After completion of reaction (monitored by TLC), the reaction mixture

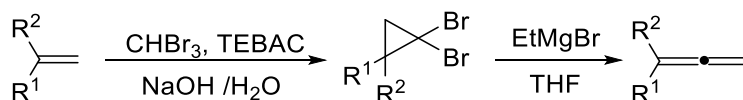
was concentrated in vacuo and isolated the product by silica gel flash column chromatography using (PE/EA, 4/1) to afford desired compound **4b** (60 mg, 85%).

### General procedures for the preparation of quinoxalin-2(1*H*)-ones <sup>1</sup>



To a suspension of o-arylenediamine (1 equiv.) in ethanol (1 mol/L) was added ethyl 2-oxoacetate (1.1 equiv.). The mixture was stirred at reflux for 1h, then at room temperature overnight. The precipitated solid was filtered and washed with ethanol, then dried to give quinoxalinone **1'**. To a suspension of quinoxalinone **1'** (1 equiv.) in DMF was added potassium carbonate (1.2 equiv.) and the corresponding halogenoalkane (1.6 equiv.). The mixture was stirred at room temperature overnight. Ethyl acetate and water were added. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with a saturated solution of NH<sub>4</sub>Cl then brine, dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue is purified by flash chromatography over silica gel to afford the desired product **1**.

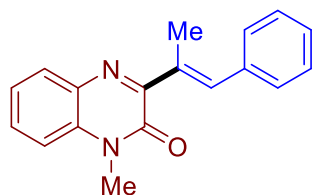
### General procedure for the synthesis of allenes <sup>2</sup>



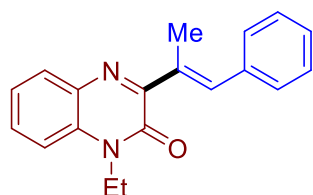
Step 1: To a solution of alkene (5.0 mmol, 1.0 equiv), bromoform (1.8955 g, 7.5 mmol, 1.5 equiv) and BnNEt<sub>3</sub>Cl (11.4 mg, 0.05 mmol, 1 mol%) was added dropwise a solution of 50% NaOH, and the mixture was stirred at room temperature for 60 min, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water and DCM were added and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic phases were washed with saturated NaCl solution, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography afforded dibromocyclopropane derivatives.

Step 2: EtMgBr (3.0 M in ether, 1.5 equiv) was added dropwise to a pre-cooled (icebath) solution of dibromocyclopropane derivatives (5 mmol, 1.0 equiv) in dry THF (1.0 mL/mmol) under nitrogen atmosphere. After EtMgBr was added the mixture was then slowly warmed to room temperature, and stirred at room temperature for an additional 2 hours. Then the reaction was quenched by HCl (0.5 N, 10.0 ml) solution, water was added, and the mixture extracted with ether (3 x 50 mL). The combined organic layers were washed with brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After removing the S-6 solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford allenes.

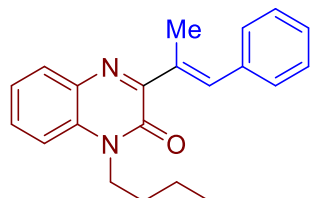
### 3. Characterization data of products



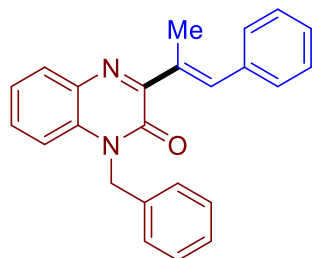
**(E)-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3aa):** TLC (PE/EtOAc, 6:1),  $R_f = 0.43$ ; colorless liquid (64.7 mg, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 - 7.89 (m, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.50 - 7.46 (m, 1H), 7.42 - 7.40 (m, 2H), 7.34 - 7.29 (m, 3H), 7.24 - 7.18 (m, 2H), 3.68 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 154.7, 137.8, 136.3, 135.2, 133.2, 133.0, 130.4, 130.2, 129.8, 128.3, 127.4, 123.8, 113.6, 29.4, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}$ : 277.1335; found: 277.1335.



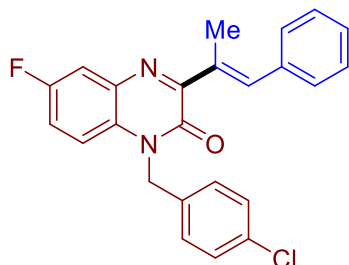
**(E)-1-ethyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ba):** TLC (PE/EtOAc, 6:1),  $R_f = 0.53$ ; colorless liquid (67.1 mg, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 - 7.91 (m, 1H), 7.83 (d,  $J = 8.1$  Hz, 1H), 7.49 - 7.45 (m, 1H), 7.42 - 7.40 (m, 2H), 7.35 - 7.24 (m, 4H), 7.20 - 7.18 (m, 1H), 4.30 (q,  $J = 7.1$  Hz, 2H), 2.34 (s, 3H), 1.34 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 154.2, 137.8, 136.4, 135.2, 133.3, 132.1, 130.6, 130.1, 129.8, 128.2, 127.4, 123.6, 113.5, 37.7, 16.7, 12.6. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$ : 291.1492; found: 291.1495.



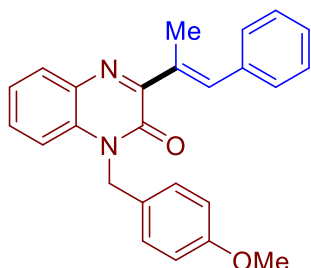
**(E)-1-butyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ca):** TLC (PE/EtOAc, 10:1),  $R_f = 0.74$ ; colorless liquid (70.7 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 - 7.93 (m, 1H), 7.83 (d,  $J = 7.9$  Hz, 1H), 7.49 - 7.40 (m, 3H), 7.34 - 7.29 (m, 2H), 7.27 - 7.26 (m, 1H), 7.24 - 7.18 (m, 2H), 4.26 - 4.19 (m, 2H), 2.35 (s, 3H), 1.77 - 1.66 (m, 2H), 1.51 - 1.41 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 154.4, 137.8, 136.3, 135.2, 133.2, 132.3, 130.6, 130.1, 129.8, 128.2, 127.4, 123.5, 113.6, 42.5, 29.4, 20.5, 16.7, 14.0. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ : 319.1805; found: 319.1814.



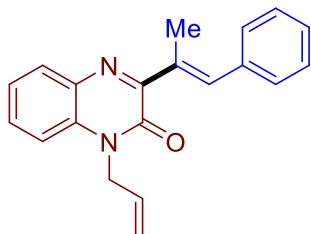
**(E)-1-benzyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3da)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.70; colorless liquid (70.8 mg, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 - 8.02 (m, 1H), 7.81 (d,  $J$  = 7.9 Hz, 1H), 7.41 - 7.39 (m, 2H), 7.34 - 7.28 (m, 3H), 7.25 - 7.20 (m, 3H), 7.20 - 7.14 (m, 5H), 5.46 (s, 2H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 154.7, 137.8, 136.8, 135.5, 135.1, 133.2, 132.5, 130.4, 130.1, 129.9, 129.1, 128.2, 127.7, 127.4, 126.9, 123.8, 114.4, 46.2, 16.8. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}$ : 353.1648; found: 353.1647.



**(E)-1-(4-chlorobenzyl)-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ea)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.71; colorless liquid (94.5 mg, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 - 8.07 (m, 1H), 7.87 - 7.83 (m, 1H), 7.46 - 7.44 (m, 2H), 7.39 - 7.35 (m, 2H), 7.31 - 7.22 (m, 3H), 7.20 - 7.18 (m, 2H), 7.06 - 6.97 (m, 1H), 6.90 - 6.80 (m, 1H), 5.41 (s, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (d,  $J_{\text{C-F}}$  = 252.0 Hz), 155.1, 154.5, 137.7, 137.1, 134.8, 133.9, 133.5, 132.5, 132.4, 129.8, 129.4, 128.5, 128.3, 127.6, 112.0 (d,  $J_{\text{C-F}}$  = 23.5 Hz), 101.0 (d,  $J_{\text{C-F}}$  = 28.3 Hz), 45.9, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{19}\text{ClFN}_2\text{O}$ : 405.1164; found: 405.1158.

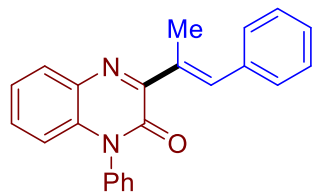


**(E)-1-(4-methoxybenzyl)-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3fa)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.56; white solid (73.4 mg, 64%), melting point: 87-88 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 - 7.99 (m, 1H), 7.79 (d,  $J$  = 7.5 Hz, 1H), 7.40 - 7.38 (m, 2H), 7.34 - 7.27 (m, 3H), 7.22 - 7.18 (m, 3H), 7.15 - 7.12 (m, 2H), 6.76 - 6.73 (m, 2H), 5.38 (s, 2H), 3.65 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 156.5, 154.7, 137.8, 136.7, 135.1, 133.1, 132.5, 130.4, 130.1, 129.8, 128.5, 128.2, 127.6, 127.4, 123.8, 114.4, 114.4, 55.4, 45.6, 16.8. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_2$ : 383.1754; found: 383.1749.

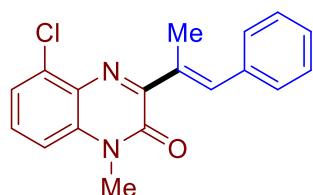


**(E)-1-allyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ga)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.69; colorless liquid (67.1 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.84 (d,  $J$  = 8.0 Hz, 1H), 7.47 - 7.41 (m, 3H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.27 - 7.16 (m, 3H), 5.97 - 5.87 (m, 1H), 5.24 - 5.12 (m, 2H), 4.89 (d,  $J$  = 4.6 Hz, 2H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 154.3, 137.8, 136.7,

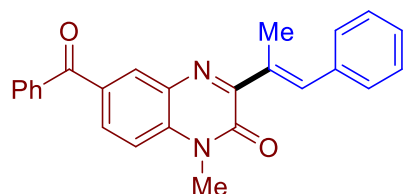
135.1, 133.1, 132.4, 130.9, 130.4, 130.1, 129.8, 128.2, 127.4, 123.8, 118.1, 114.1, 44.8, 16.7. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{20}H_{19}N_2O$ : 303.1492; found: 303.1492.



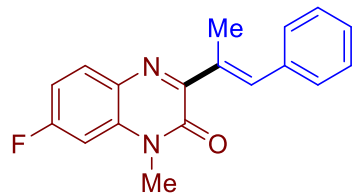
**(E)-1-phenyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ha)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.69; white solid (77.2 mg, 76%). melting point: 116-117 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.20 (s, 1H), 7.91 - 7.89 (m, 1H), 7.62 - 7.59 (m, 2H), 7.55 - 7.51 (m, 1H), 7.43 (d,  $J$  = 7.6 Hz, 2H), 7.37 - 7.27 (m, 6H), 7.25 (d,  $J$  = 7.2 Hz, 1H), 6.62 - 6.60 (m, 1H), 2.42 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  156.6, 154.6, 137.8, 137.3, 136.4, 134.9, 133.9, 132.9, 130.5, 129.9, 129.8, 129.5, 128.4, 128.2, 127.4, 124.0, 115.4, 16.7. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{23}H_{19}N_2O$ : 339.1492; found: 339.1487.



**(E)-5-chloro-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ia)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.40; colorless liquid (75.5 mg, 81%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.3 - 8.24 (m, 1H), 7.41 - 7.39 (m, 2H), 7.35 - 7.30 (m, 4H), 7.21 (d,  $J$  = 7.2 Hz, 1H), 7.11 - 7.09 (m, 1H), 3.63 (s, 3H), 2.37 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  155.4, 154.3, 138.2, 137.8, 135.2, 135.1, 134.3, 129.9, 129.9, 129.5, 128.3, 127.6, 124.5, 112.4, 29.8, 16.52. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{18}H_{16}ClN_2O$ : 311.0946; found: 311.0947.

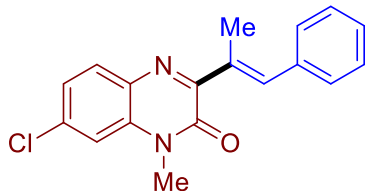


**(E)-6-benzoyl-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ja)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.49; colorless liquid (75.3 mg, 66%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.11 (s, 1H), 7.89 (d,  $J$  = 8.2 Hz, 1H), 7.79 - 7.14 (m, 3H), 7.63 (d,  $J$  = 8.2 Hz, 1H), 7.58 - 7.56 (m, 1H), 7.48 - 7.47 (m, 2H), 7.44 - 7.42 (m, 2H), 7.36 - 7.32 (m, 2H), 7.24 (d,  $J$  = 7.3 Hz, 1H), 3.71 (s, 3H), 2.36 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  195.9, 158.4, 138.3, 138.0, 137.6, 137.3, 135.3, 135.0, 133.1, 130.2, 130.0, 129.9, 128.7, 128.3, 127.7, 125.3, 115.5, 29.6, 16.7. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{25}H_{21}N_2O_2$ : 381.1598; found: 381.1601.

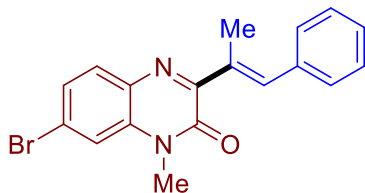


**(E)-7-fluoro-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ka)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.66; white solid (67.1 mg, 76%), melting point: 77-78 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.81 (s, 1H), 7.65 - 7.62 (m, 1H), 7.27 - 7.25 (m, 2H), 7.20 - 7.16 (m, 2H), 7.09 - 7.04 (m, 1H), 6.87 - 6.82 (m,

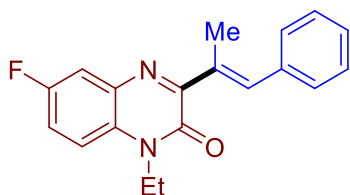
1H), 6.78 - 6.75 (m, 1H), 3.47 (s, 3H), 2.18 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.3 (d, *J*<sub>C-F</sub> = 251.5 Hz), 155.2 (d, *J*<sub>C-F</sub> = 3.5 Hz), 154.5, 137.7, 136.4, 134.8, 134.5 (d, *J*<sub>C-F</sub> = 11.6 Hz), 132.1 (d, *J*<sub>C-F</sub> = 10.5 Hz), 129.8, 129.6 (d, *J*<sub>C-F</sub> = 2.1 Hz), 128.2, 127.4, 111.6 (d, *J*<sub>C-F</sub> = 23.6 Hz), 100.5 (d, *J*<sub>C-F</sub> = 27.9 Hz), 29.5, 16.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -107.47. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>FN<sub>2</sub>O: 295.1241; found: 295.1241.



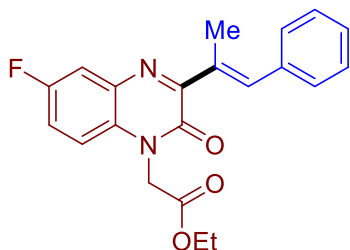
**(E)-7-chloro-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3la)**: TLC (PE/EtOAc, 6:1), *R*<sub>f</sub> = 0.64; white solid (68.1 mg, 73%), melting point: 91-92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 7.52 - 7.31 (m, 6H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 1.2 Hz, 1H), 3.68 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.2, 154.2, 138.8, 137.7, 135.9, 135.5, 135.0, 134.8, 130.0, 128.3, 128.3, 127.7, 124.7, 112.6, 30.0, 16.5. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>ClN<sub>2</sub>O: 311.0946; found: 311.0955.



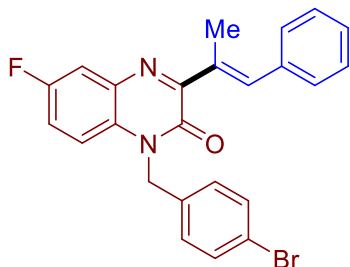
**(E)-7-bromo-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3ma)**: TLC (PE/EtOAc, 6:1), *R*<sub>f</sub> = 0.67; white solid (81.0 mg, 76%), melting point: 76-77 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.46 - 7.40 (m, 4H), 7.38 - 7.34 (m, 2H), 7.22 (s, 1H), 3.67 (s, 3H), 2.35 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.6, 154.4, 137.6, 137.0, 134.9, 134.1, 131.8, 131.5, 129.8, 128.3, 127.6, 127.0, 124.1, 116.7, 29.5, 16.6. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>BrN<sub>2</sub>O: 355.0441; found: 355.0442.



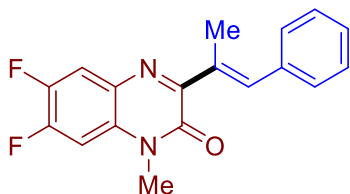
**(E)-1-ethyl-6-fluoro-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3na)**: TLC (PE/EtOAc, 6:1), *R*<sub>f</sub> = 0.61; white solid (74.0 mg, 80%), melting point: 131 - 132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.41 - 7.39 (m, 2H), 7.33 - 7.30 (m, 2H), 7.23 - 7.19 (m, 3H), 4.33 - 4.21 (m, 2H), 2.32 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.7 (d, *J*<sub>C-F</sub> = 243.8 Hz), 153.8, 137.7, 137.3, 134.9, 133.9 (d, *J*<sub>C-F</sub> = 11.4 Hz), 129.9, 128.6 (d, *J*<sub>C-F</sub> = 1.7 Hz), 128.3, 128.2, 127.5, 117.9 (d, *J*<sub>C-F</sub> = 24.2 Hz), 115.7 (d, *J*<sub>C-F</sub> = 22.2 Hz), 114.5 (d, *J*<sub>C-F</sub> = 8.8 Hz), 37.9, 16.6, 12.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -119.42. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>18</sub>FN<sub>2</sub>O: 309.1398; found: 309.1396.



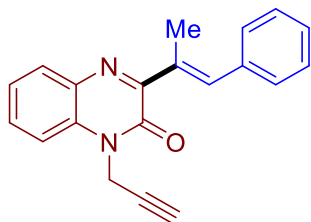
**Ethyl (E)-2-(6-fluoro-2-oxo-3-(1-phenylprop-1-en-2-yl)quinoxalin-1(2H)-yl)acetate (30a):** TLC (PE/EtOAc, 6:1),  $R_f = 0.45$ ; white solid (82.4 mg, 75%), melting point: 123-124 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (s, 1H), 7.55 - 7.52 (m, 1H), 7.41 - 7.39 (m, 2H), 7.34 - 7.31 (m, 2H), 7.26 - 7.19 (m, 2H), 6.98 - 6.94 (m, 1H), 4.98 (s, 2H), 4.20 (q,  $J = 7.1$  Hz, 2H), 2.33 (s, 3H), 1.23 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 159.0 (d,  $J_{\text{C-F}} = 244.7$  Hz), 157.1, 154.0, 138.0, 137.6, 134.7, 133.7 (d,  $J_{\text{C-F}} = 11.5$  Hz), 129.9, 128.9, 128.3, 127.7, 117.9 (d,  $J_{\text{C-F}} = 24.4$  Hz), 115.9 (d,  $J_{\text{C-F}} = 22.3$  Hz), 114.2 (d,  $J_{\text{C-F}} = 8.9$  Hz), 62.3, 44.1, 16.5, 14.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.80. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{20}\text{FN}_2\text{O}_3$ : 367.1452; found: 367.1451.



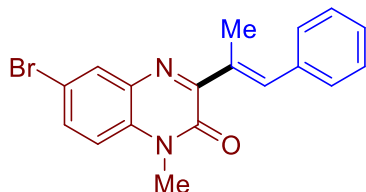
**(E)-1-(4-bromobenzyl)-6-fluoro-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3pa):** TLC (PE/EtOAc, 10:1),  $R_f = 0.65$ ; colorless liquid (83.6 mg, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 7.53 - 7.51 (m, 1H), 7.42 - 7.37 (m, 4H), 7.35 - 7.31 (m, 2H), 7.22 - 7.18 (m, 1H), 7.10 - 7.05 (m, 4H), 5.40 (s, 2H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9 (d,  $J_{\text{C-F}} = 244.9$  Hz), 157.3, 154.3, 137.9, 137.6, 134.8, 134.4, 133.9 (d,  $J_{\text{C-F}} = 11.5$  Hz), 132.3, 132.2, 129.9, 128.7, 128.3, 127.7, 121.9, 117.9 (d,  $J_{\text{C-F}} = 24.2$  Hz), 115.8 (d,  $J_{\text{C-F}} = 22.3$  Hz), 115.2 (d,  $J_{\text{C-F}} = 8.8$  Hz), 45.9, 16.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.68. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{19}\text{BrFN}_2\text{O}$ : 449.0659; found: 449.0658.



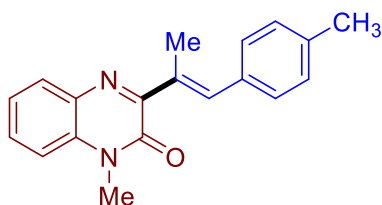
**(E)-6,7-difluoro-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3qa):** TLC (PE/EtOAc, 6:1),  $R_f = 0.65$ ; white solid (67.5 mg, 72%), melting point: 144-145 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.71 - 7.62 (m, 1H), 7.44 - 7.42 (m, 2H), 7.38 - 7.34 (m, 2H), 7.27 (d,  $J = 7.2$  Hz, 1H), 7.09 - 7.05 (m, 1H), 3.66 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4 (d,  $J_{\text{C-F}} = 3.7$  Hz), 154.1, 151.3 (dd,  $J_{\text{C-F}} = 254.1$  Hz, 14.4 Hz), 146.7 (dd,  $J_{\text{C-F}} = 247.8$  Hz, 14.0 Hz), 137.4, 137.1, 134.5, 130.1 (dd,  $J_{\text{C-F}} = 9.2$  Hz, 1.5 Hz), 129.7, 129.0 (dd,  $J_{\text{C-F}} = 9.2$  Hz, 2.9 Hz), 128.1, 127.4, 117.5 (dd,  $J_{\text{C-F}} = 18.0$  Hz, 2.2 Hz), 102.0 (d,  $J_{\text{C-F}} = 23.2$  Hz), 29.7, 16.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -131.04, -131.09, -142.21, -142.27. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_2\text{N}_2\text{O}$ : 313.1147; found: 313.1150.



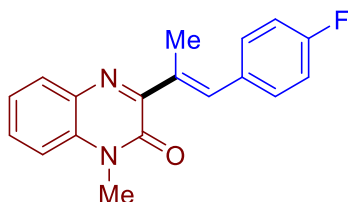
**(E)-3-(1-phenylprop-1-en-2-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3ra):** TLC (PE/EtOAc, 6:1),  $R_f = 0.61$ ; white solid (65.8 mg, 73%), melting point: 94-95 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 - 8.03 (m, 1H), 7.87 (d,  $J = 8.1$  Hz, 1H), 7.56 - 7.52 (m, 1H), 7.45 - 7.41 (m, 3H), 7.38 - 7.34 (m, 3H), 7.25 - 7.22 (m, 2H), 5.07 (s, 2H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 153.7, 137.7, 137.0, 134.9, 133.2, 131.6, 130.5, 130.3, 129.9, 129.5, 128.3, 127.5, 124.2, 114.0, 73.2, 31.8, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$ : 301.1335; found: 301.1333.



**(E)-6-bromo-1-methyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (3sa):** TLC (PE/EtOAc, 6:1),  $R_f = 0.54$ ; white solid (82.1 mg, 77%), melting point: 148 - 149 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (s, 1H), 8.01 - 7.97 (m, 1H), 7.57 (d,  $J = 8.8$  Hz, 1H), 7.43 - 7.41 (m, 2H), 7.37 - 7.33 (m, 2H), 7.24 - 7.21 (m, 1H), 7.13 (d,  $J = 8.9$  Hz, 1H), 3.67 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 154.3, 137.5, 137.4, 134.7, 133.7, 132.6, 132.5, 132.1, 129.8, 128.2, 127.5, 116.2, 114.9, 29.4, 16.5. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{O}$ : 355.0441; found: 355.0445.

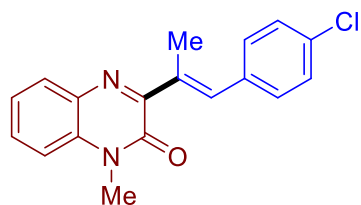


**(E)-1-methyl-3-(1-(p-tolyl)prop-1-en-2-yl)quinoxalin-2(1H)-one (3ab):** TLC (PE/EtOAc, 6:1),  $R_f = 0.55$ ; colorless liquid (70.6 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 - 7.87 (m, 1H), 7.80 (d,  $J = 7.9$  Hz, 1H), 7.46 - 7.42 (m, 1H), 7.31 - 7.29 (m, 2H), 7.26 - 7.24 (m, 1H), 7.21 (d,  $J = 8.4$  Hz, 1H), 7.12 - 7.10 (m, 2H), 3.65 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 154.5, 137.1, 136.2, 134.6, 134.2, 132.9, 132.7, 130.0, 129.8, 128.8, 123.5, 113.4, 29.2, 21.2, 16.5. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$ : 291.1492; found: 291.1488.

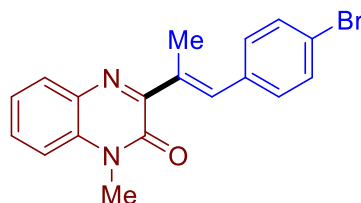


**(E)-3-(1-(4-fluorophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ac):** TLC (PE/EtOAc, 6:1),  $R_f = 0.41$ ; colorless liquid (69.8 mg, 79%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (s, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.52 - 7.48 (m, 1H), 7.41 - 7.38 (m, 2H), 7.33 - 7.25 (m, 2H), 7.05 - 7.00 (m, 2H), 3.69 (s, 3H),

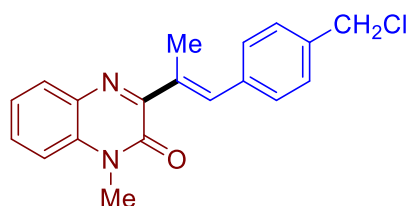
2.33 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (d,  $J_{\text{C-F}} = 248.4$  Hz), 156.5, 154.7, 135.1, 135.0, 133.8 (d,  $J_{\text{C-F}} = 3.4$  Hz), 133.1, 132.9, 131.5 (d,  $J_{\text{C-F}} = 8.0$  Hz), 130.3, 130.2, 123.8, 115.2 (d,  $J_{\text{C-F}} = 21.5$  Hz), 113.6, 29.4, 16.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.28. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{FN}_2\text{O}$ : 295.1241; found: 295.1235.



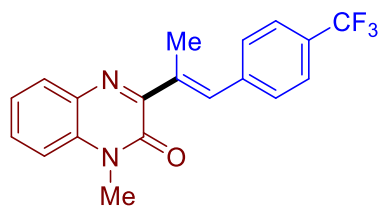
**(E)-3-(1-(4-chlorophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ad)**: TLC (PE/EtOAc, 6:1),  $R_f = 0.49$ ; white solid (70.9 mg, 76%), melting point: 107-108°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 - 7.88 (m, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.54 - 7.50 (m, 1H), 7.38 - 7.33 (m, 4H), 7.31-7.30 (m, 1H), 7.23 (s, 1H), 3.71 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 154.7, 136.2, 135.8, 135.0, 133.2, 132.9, 131.1, 130.4, 130.3, 129.7, 128.5, 123.9, 113.7, 29.4, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}$ : 311.0946; found: 311.0949.



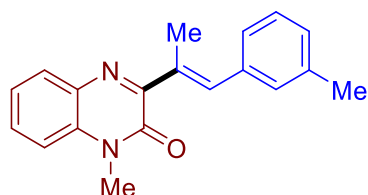
**(E)-3-(1-(4-bromophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ae)**: TLC (PE/EtOAc, 6:1),  $R_f = 0.50$ ; colorless liquid (85.3 mg, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 - 7.83 (m, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.49 - 7.41 (m, 3H), 7.29 - 7.23 (m, 4H), 3.65 (s, 3H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 154.6, 136.6, 135.8, 135.0, 133.1, 132.9, 131.4, 131.3, 130.4, 130.3, 123.8, 121.4, 113.6, 29.3, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{O}$ : 355.0441; found: 355.0437.



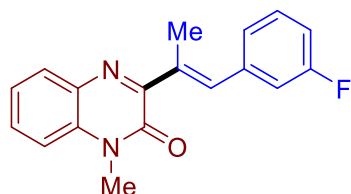
**(E)-3-(1-(4-(chloromethyl)phenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3af)**: TLC (PE/EtOAc, 6:1),  $R_f = 0.58$ ; white solid (75.0 mg, 77%), melting point: 102-103 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 - 7.89 (m, 1H), 7.82 (d,  $J = 7.9$  Hz, 1H), 7.50 - 7.46 (m, 1H), 7.41 - 7.39 (m, 2H), 7.35 - 7.33 (m, 2H), 7.30 - 7.28 (m, 1H), 7.25 - 7.23 (m, 1H), 4.54 (s, 2H), 3.67 (s, 3H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 154.7, 138.0, 136.4, 135.8, 135.6, 133.2, 132.9, 130.4, 130.3, 130.2, 128.5, 123.8, 113.6, 46.3, 29.4, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{18}\text{ClN}_2\text{O}$ : 325.1102; found: 325.1100.



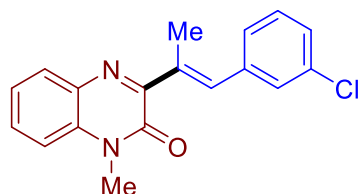
**(E)-1-methyl-3-(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)quinoxalin-2(1H)-one (3ag):** TLC (PE/EtOAc, 6:1),  $R_f = 0.47$ ; colorless liquid (67.1 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 - 7.91 (m, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.58 - 7.56 (m, 2H), 7.50 - 7.48 (m, 3H), 7.32 - 7.30 (m, 1H), 7.27 - 7.25 (m, 1H), 3.68 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 154.6, 141.4, 137.1, 134.7, 133.2, 132.9, 130.5, 130.5, 129.9, 129.1 (q,  $J_{\text{C-F}} = 32.6$  Hz), 125.2 (q,  $J_{\text{C-F}} = 3.8$  Hz), 124.4 (q,  $J_{\text{C-F}} = 273.0$  Hz), 123.9, 113.7, 29.4, 16.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.47. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ : 345.1209; found: 345.1203.



**(E)-1-methyl-3-(1-(m-tolyl)prop-1-en-2-yl)quinoxalin-2(1H)-one (3ah):** TLC (PE/EtOAc, 6:1),  $R_f = 0.43$ ; colorless liquid (67.1 mg, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 1H), 7.86 (d,  $J = 7.9$  Hz, 1H), 7.53 - 7.49 (m, 1H), 7.34 - 7.24 (m, 5H), 7.09 - 7.03 (m, 1H), 3.71 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 154.7, 137.8, 137.7, 136.7, 135.0, 133.2, 133.0, 130.6, 130.3, 130.1, 128.2, 128.1, 126.9, 123.8, 113.6, 29.4, 21.6, 16.8. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$ : 291.1492; found: 291.1486.

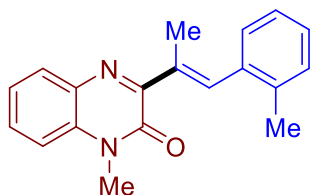


**(E)-3-(1-(3-fluorophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ai):** TLC (PE/EtOAc, 6:1),  $R_f = 0.49$ ; colorless liquid (65.3 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 - 7.83 (m, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.48 - 7.44 (m, 1H), 7.30 - 7.21 (m, 3H), 7.17 - 7.15 (m, 1H), 7.09 (d,  $J = 10.1$  Hz, 1H), 6.91 - 6.87 (m, 1H), 3.65 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J_{\text{C-F}} = 246.1$  Hz), 156.3, 154.6, 139.9 (d,  $J_{\text{C-F}} = 7.8$  Hz), 136.3, 134.9 (d,  $J_{\text{C-F}} = 2.2$  Hz), 133.2, 132.9, 130.4 (d,  $J_{\text{C-F}} = 5.4$  Hz), 129.7 (d,  $J_{\text{C-F}} = 8.4$  Hz), 125.6 (d,  $J_{\text{C-F}} = 2.8$  Hz), 123.8, 116.3 (d,  $J_{\text{C-F}} = 21.7$  Hz), 114.2 (d,  $J_{\text{C-F}} = 21.3$  Hz), 113.6, 29.4, 16.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.57. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{FN}_2\text{O}$ : 295.1241; found: 295.1240.

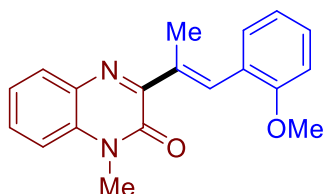


**(E)-3-(1-(3-chlorophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3aj):** TLC (PE/EtOAc, 6:1),  $R_f = 0.56$ ; colorless liquid (68.1 mg, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 - 7.84 (m, 1H), 7.81 (d,

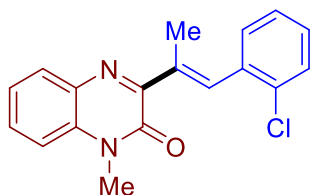
$J = 8.0$  Hz, 1H), 7.5 - 7.46 (m, 1H), 7.38 (s, 1H), 7.31 - 7.22 (m, 4H), 7.18 (s, 1H), 3.66 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 154.6, 139.6, 136.4, 134.7, 134.1, 133.2, 132.9, 130.4, 129.6, 129.5, 127.9, 127.4, 123.8, 113.6, 29.4, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}$ : 311.0946; found: 311.0941.



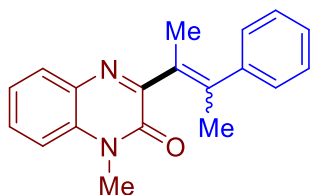
**(E)-1-methyl-3-(1-(*o*-tolyl)prop-1-en-2-yl)quinoxalin-2(1H)-one (3ak):** TLC (PE/EtOAc, 3:1),  $R_f = 0.54$ ; colorless liquid (66.2 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 - 8.08 (m, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.49 - 7.45 (m, 1H), 7.30 - 7.25 (m, 3H), 7.16 - 7.11 (m, 3H), 3.68 (s, 3H), 2.29 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 154.8, 137.2, 137.1, 136.4, 135.0, 133.1, 132.9, 130.4, 130.1, 130.0, 129.3, 127.5, 125.4, 123.7, 113.6, 29.4, 20.2, 16.4. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$ : 291.1492; found: 291.1490.



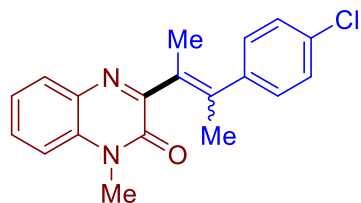
**(E)-3-(1-(2-methoxyphenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3al):** TLC (PE/EtOAc, 3:1),  $R_f = 0.54$ ; colorless liquid (51.5 mg, 56%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 - 8.07 (m, 1H), 7.79 (d,  $J = 7.9$  Hz, 1H), 7.45 - 7.42 (m, 1H), 7.34 (d,  $J = 7.5$  Hz, 1H), 7.26 - 7.21 (m, 2H), 7.18 - 7.15 (m, 1H), 6.91 - 6.88 (m, 1H), 6.82 (d,  $J = 8.2$  Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 156.3, 154.8, 135.0, 133.1, 133.0, 132.7, 130.7, 130.4, 130.0, 129.0, 126.8, 123.6, 120.1, 113.5, 110.5, 55.7, 29.4, 16.7. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2$ : 307.1441; found: 307.1437.



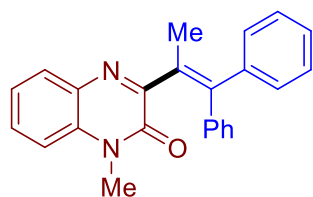
**(E)-3-(1-(2-chlorophenyl)prop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3am):** TLC (PE/EtOAc, 3:1),  $R_f = 0.54$ ; colorless liquid (63.4 mg, 68%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 - 8.09 (m, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.49 - 7.45 (m, 1H), 7.39 (d,  $J = 7.5$  Hz, 1H), 7.35 (d,  $J = 7.7$  Hz, 1H), 7.28 (d,  $J = 7.7$  Hz, 1H), 7.23 - 7.12 (m, 3H), 3.67 (s, 3H), 2.22 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 154.7, 136.4, 136.3, 134.3, 134.0, 133.2, 132.9, 131.0, 130.5, 130.4, 129.5, 128.7, 126.3, 123.7, 113.6, 29.4, 16.5. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}$ : 311.0946; found: 311.0954.



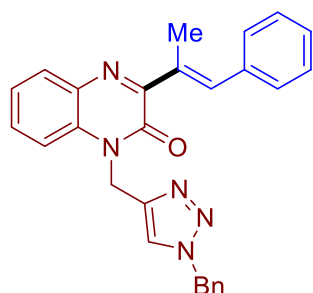
**(E)-1-methyl-3-(3-phenylbut-2-en-2-yl)quinoxalin-2(1H)-one (3an):** A mixture of *Z* and *E* isomers, E/Z = 7: 1. TLC (PE/EtOAc, 6:1),  $R_f = 0.37$ ; colorless liquid (40.1 mg, 46%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.9$  Hz, 1H), 7.55 - 7.51 (m, 1H), 7.35 - 7.28 (m, 6H), 7.20 (s, 1H), 3.70 (s, 3H), 1.90 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 154.1, 143.0, 137.6, 133.4, 132.8, 130.3, 130.1, 129.0, 128.3, 128.1, 126.7, 123.7, 113.7, 29.2, 22.3, 18.9. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{19}\text{NO}$ : 291.1492; found: 291.1500.



**3-(3-(4-chlorophenyl)but-2-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ao):** A mixture of *Z* and *E* isomers, E/Z = 5: 3. TLC (PE/EtOAc, 6:1),  $R_f = 0.34$ ; colorless liquid (56.5 mg, 58%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 7.9$  Hz, 1H), 7.64 - 7.49 (m, 2H), 7.36 - 7.17 (m, 8H), 6.99 (s, 2H), 3.69 (s, 3H), 3.52 (s, 2H), 2.12 (d,  $J = 11.3$  Hz, 4H), 1.87 (d,  $J = 10.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 160.6, 154.0, 142.3, 141.3, 137.0, 136.3, 133.3, 133.0, 132.7, 132.5, 132.5, 132.0, 130.4, 130.3, 130.1, 130.0, 129.8, 129.7, 129.6, 129.3, 128.3, 128.0, 123.7, 123.5, 113.7, 113.5, 29.2, 29.1, 22.1, 20.9, 18.9, 18.3. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{18}\text{ClN}_2\text{O}$ : 325.1102; found: 325.1107.

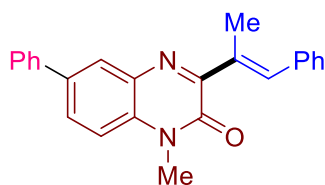


**3-(1,1-diphenylprop-1-en-2-yl)-1-methylquinoxalin-2(1H)-one (3ap):** TLC (PE/EtOAc, 6:1),  $R_f = 0.31$ ; colorless liquid (49.7 mg, 47%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.0$  Hz, 1H), 7.48 - 7.44 (m, 1H), 7.32 - 7.31 (m, 4H), 7.26 (d,  $J = 7.3$  Hz, 2H), 7.19 (d,  $J = 8.4$  Hz, 1H), 7.02 - 6.97 (m, 5H), 3.52 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 153.7, 143.6, 142.6, 141.7, 133.2, 132.7, 131.6, 130.1, 130.0, 129.9, 129.6, 128.0, 127.7, 127.1, 126.6, 123.5, 113.5, 29.1, 20.2. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}$ : 353.1648; found: 353.1645.



**(E)-1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (4a):** TLC (PE/EtOAc, 3:1),  $R_f = 0.32$ ; colorless liquid (87.1 mg, 67%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 - 7.97 (m, 1H), 7.88 - 7.82 (m, 2H), 7.60 (s, 1H), 7.55 - 7.51 (m, 1H), 7.45 - 7.43 (m, 2H), 7.40 - 7.29 (m, 7H), 7.23 - 7.21 (m, 2H), 5.53 (s, 2H), 5.43 (s, 2H), 2.37 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 154.5, 143.1, 137.7, 136.5, 135.0, 134.4, 133.1, 132.2, 130.5, 130.3, 129.9, 129.3, 129.0, 128.3, 128.3,

127.5, 124.1, 123.8, 114.8, 54.5, 38.5, 16.7. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{27}H_{24}N_5O$ : 434.1975; found: 434.1966.

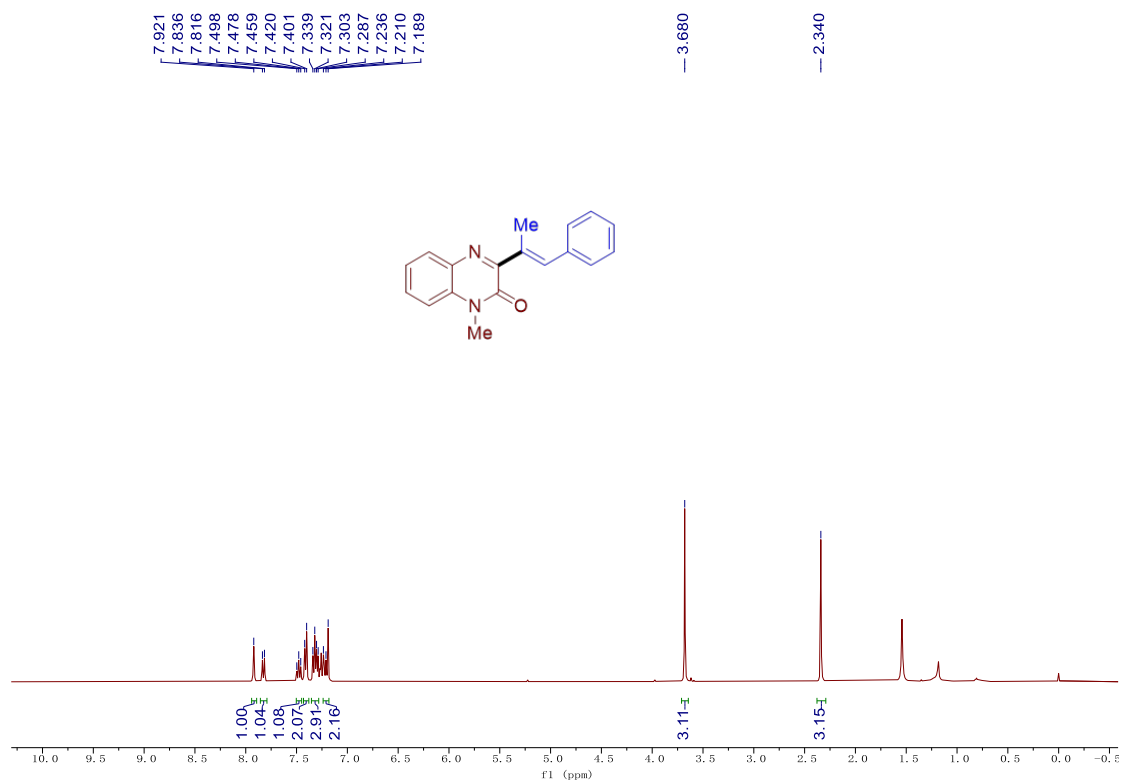


**(E)-1-methyl-6-phenyl-3-(1-phenylprop-1-en-2-yl)quinoxalin-2(1H)-one (4b)**: TLC (PE/EtOAc, 6:1),  $R_f$  = 0.39; colorless liquid (89.9 mg, 85%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.09 (s, 1H), 7.98 (s, 1H), 7.77 - 7.72 (m, 1H), 7.63 (d,  $J$  = 7.8 Hz, 2H), 7.43 (d,  $J$  = 7.6 Hz, 4H), 7.36 - 7.31 (m, 4H), 7.24 (d,  $J$  = 7.3 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  157.0, 154.6, 139.6, 137.7, 136.9, 136.5, 135.2, 133.2, 132.4, 129.9, 129.1, 129.0, 128.3, 128.3, 127.7, 127.5, 127.1, 114.04, 29.48, 16.7. HRMS (ESI):  $m/z$   $[M+H]^+$  calcd for  $C_{24}H_{21}N_2O$ : 353.1648; found: 353.1641.

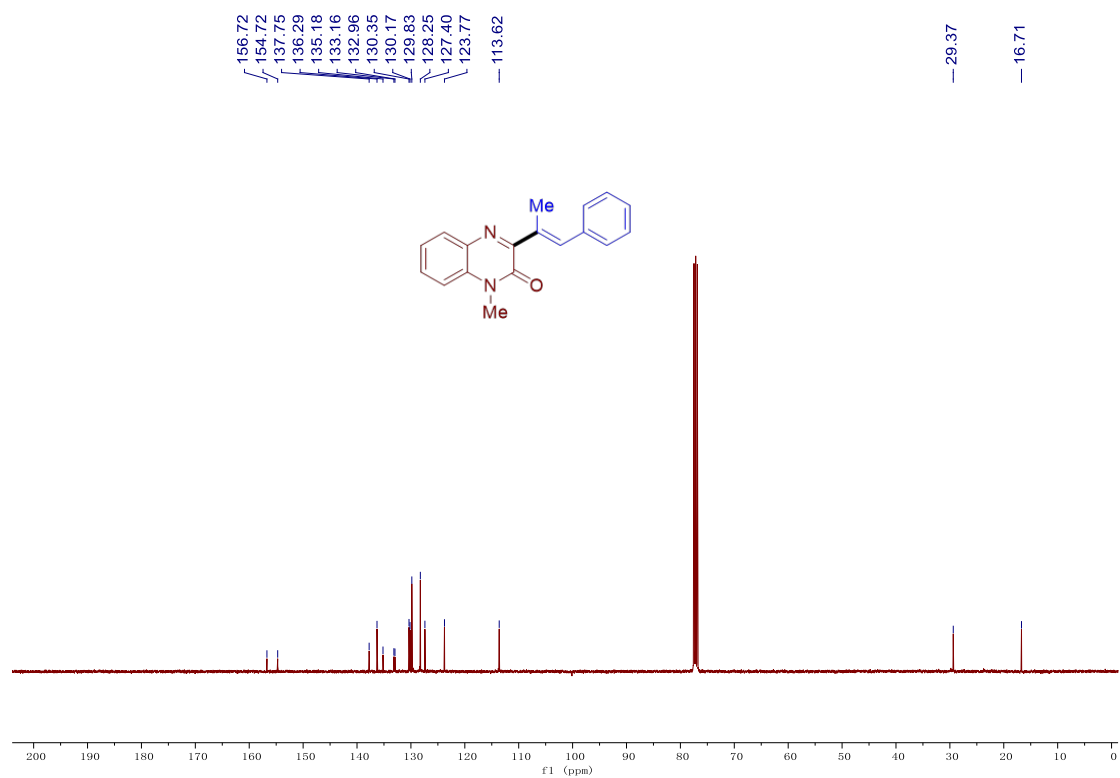
#### 4. References

1. Carr  $\ddot{a}$ , A.; Brion, J.-D.; Messaoudi, S.; Alami, M., Palladium(II)-Catalyzed Oxidative Arylation of Quinoxalin-2(1H)-ones with Arylboronic Acids. *Org. Lett.* **2013**, *15*, 5606-5609.
2. Chanthamath, S.; Chua, H. W.; Kimura, S.; Shibatomi, K.; Iwasa, S., Highly Regio- and Stereoselective Synthesis of Alkylidenecyclopropanes via Ru(II)-Pheox Catalyzed Asymmetric Inter- and Intramolecular Cyclopropanation of Allenes. *Org. Lett.* **2014**, *16*, 3408-3411.

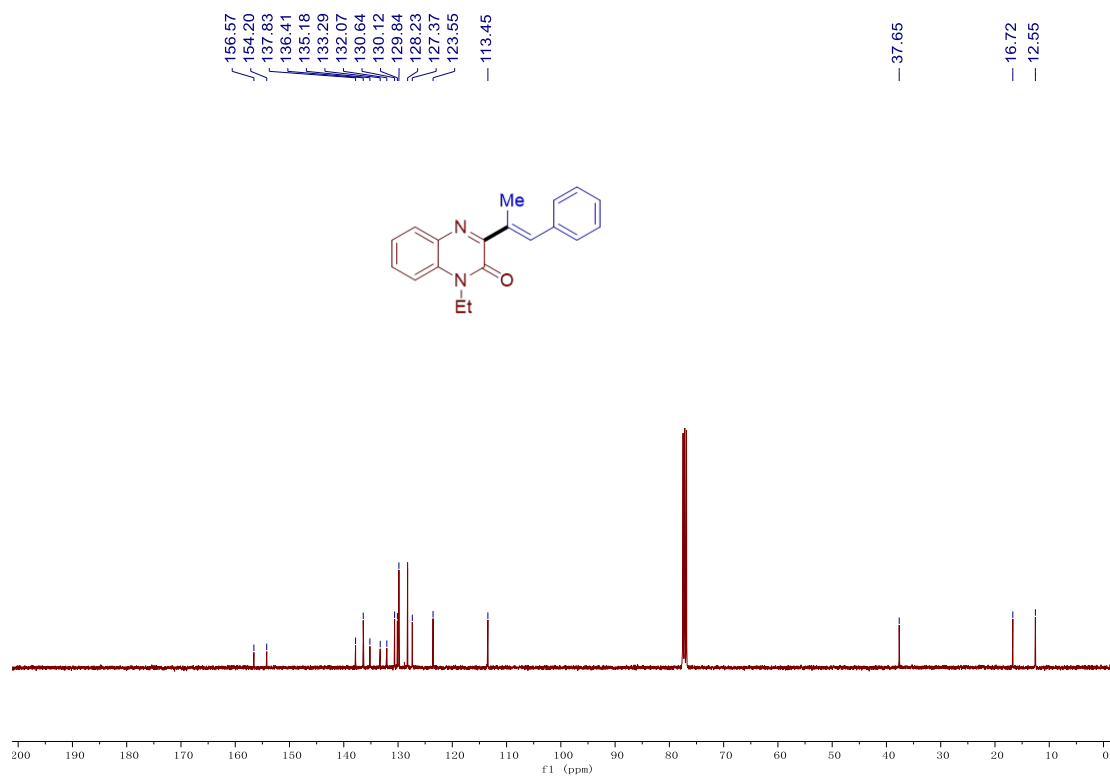
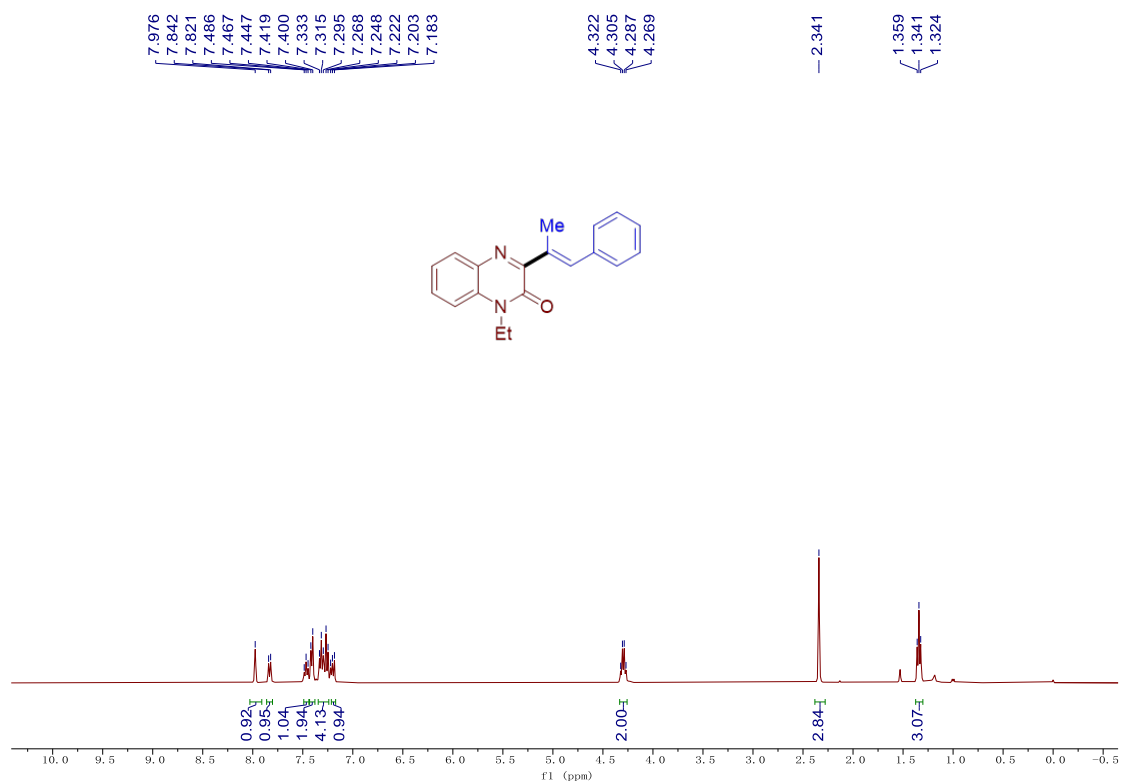
## 5. NMR spectra of products

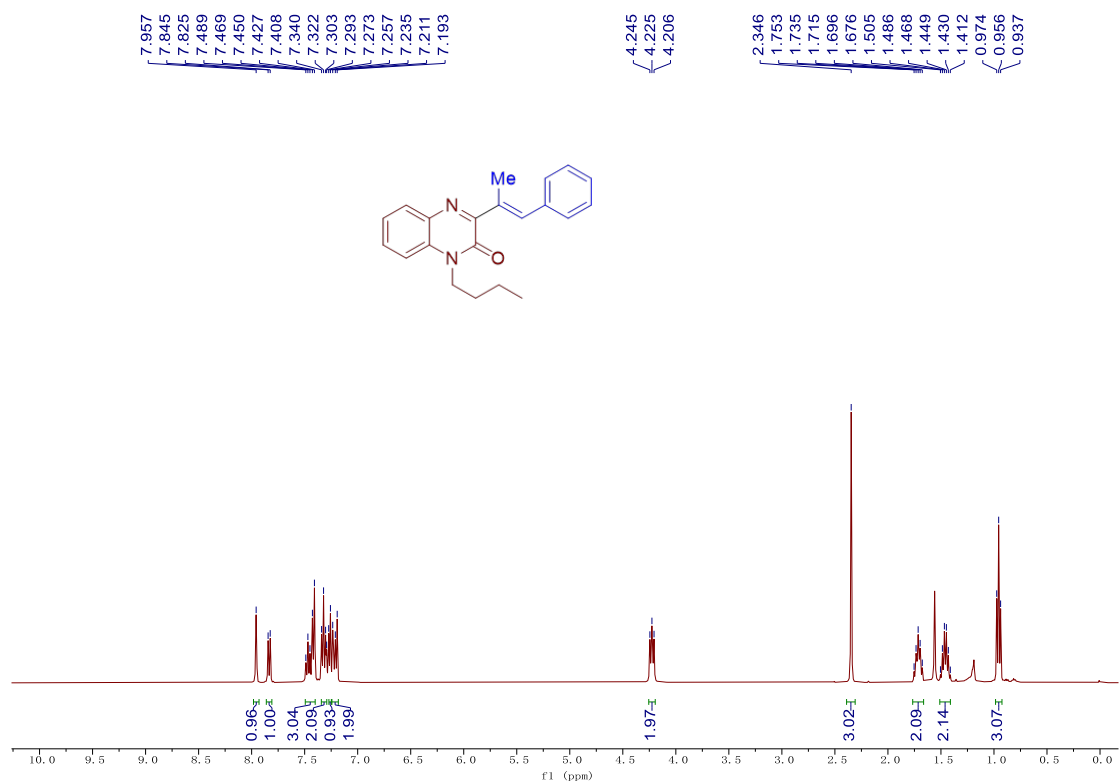


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3aa**

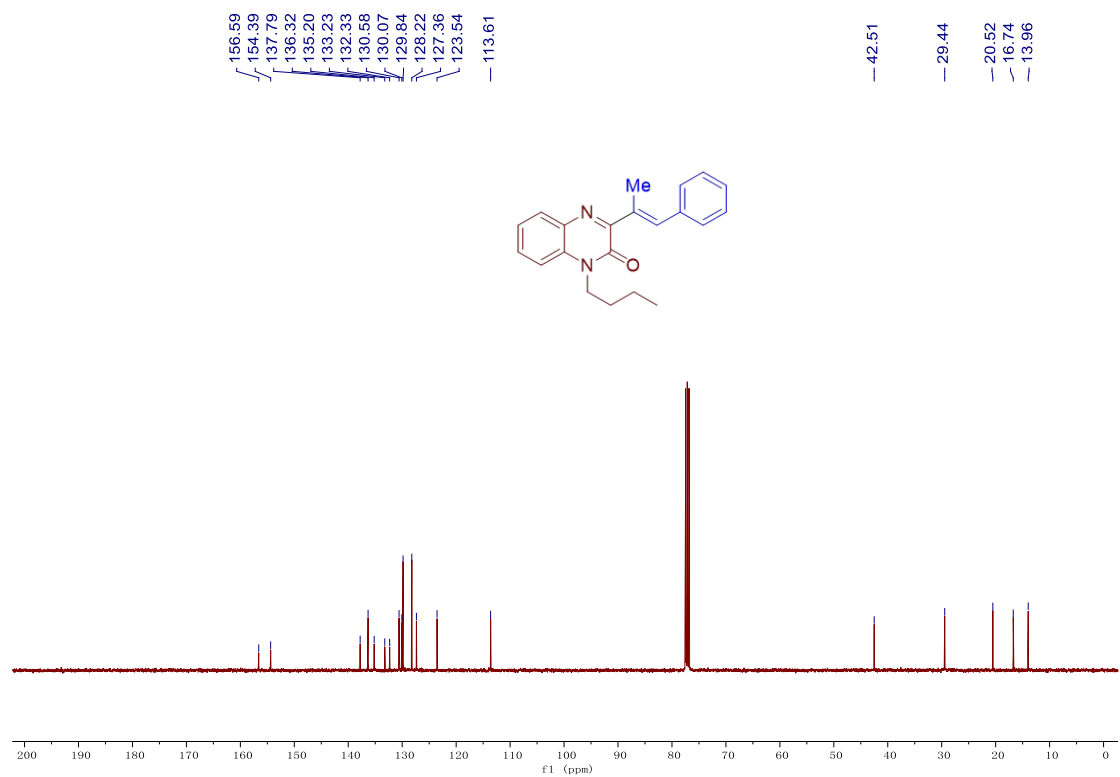


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3aa**

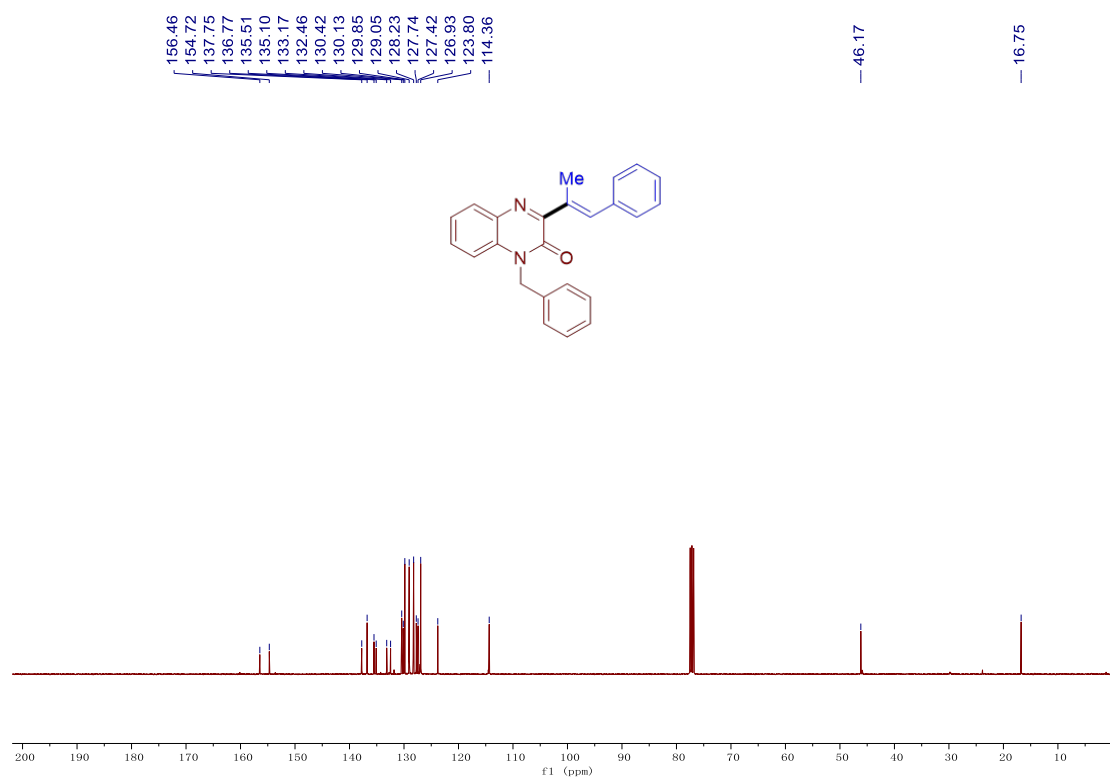
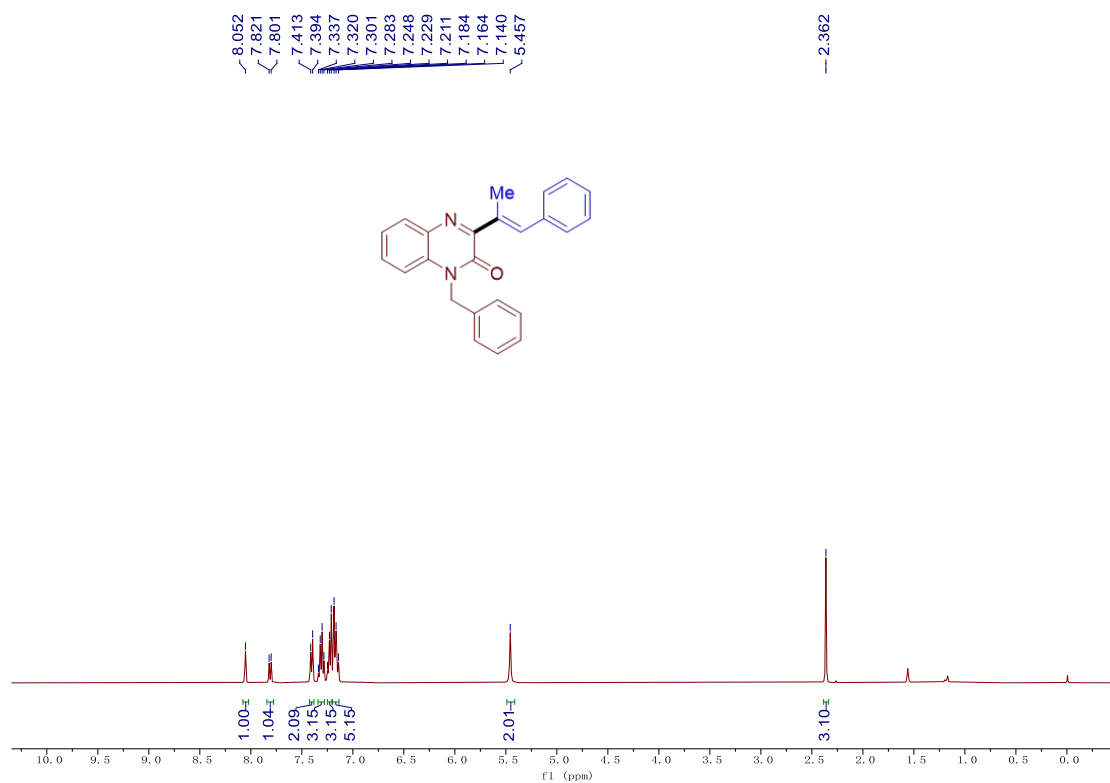


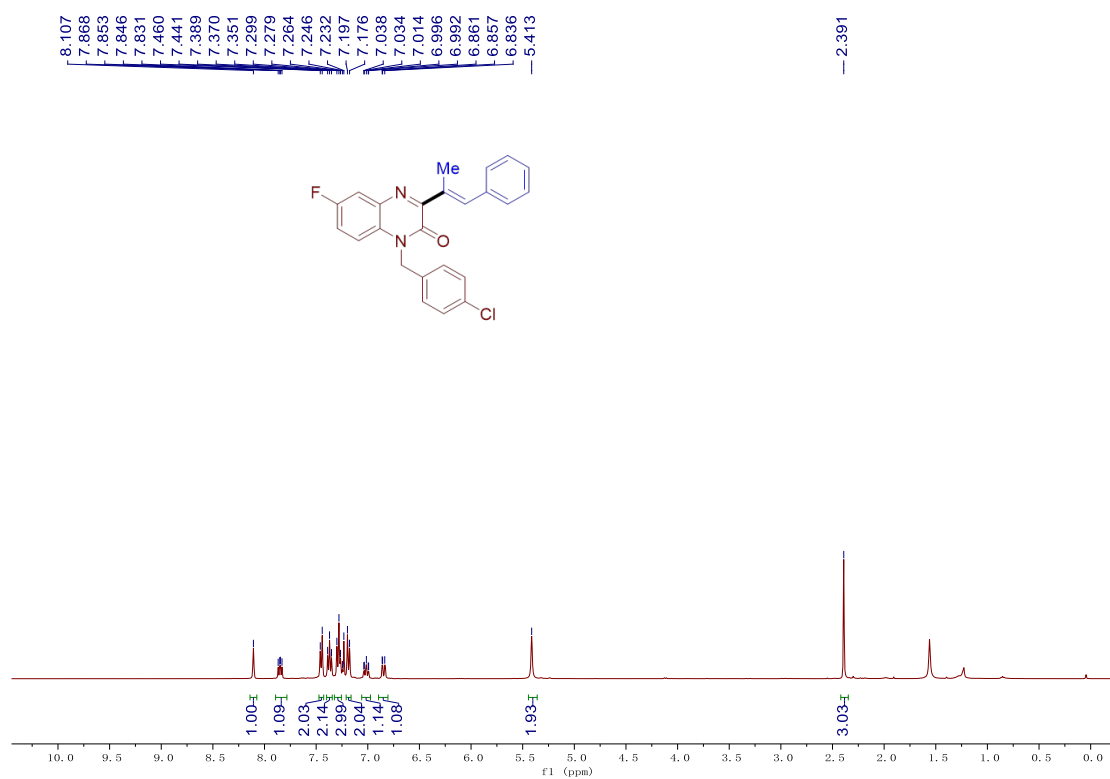


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ca**

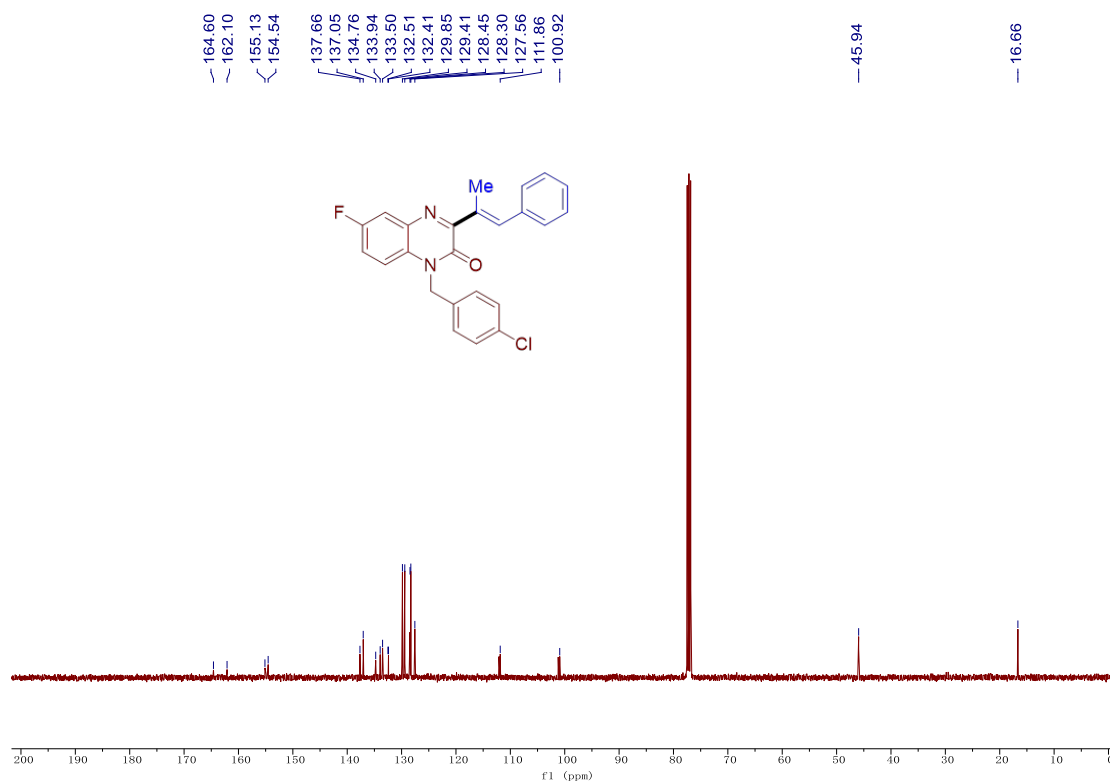


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ca**

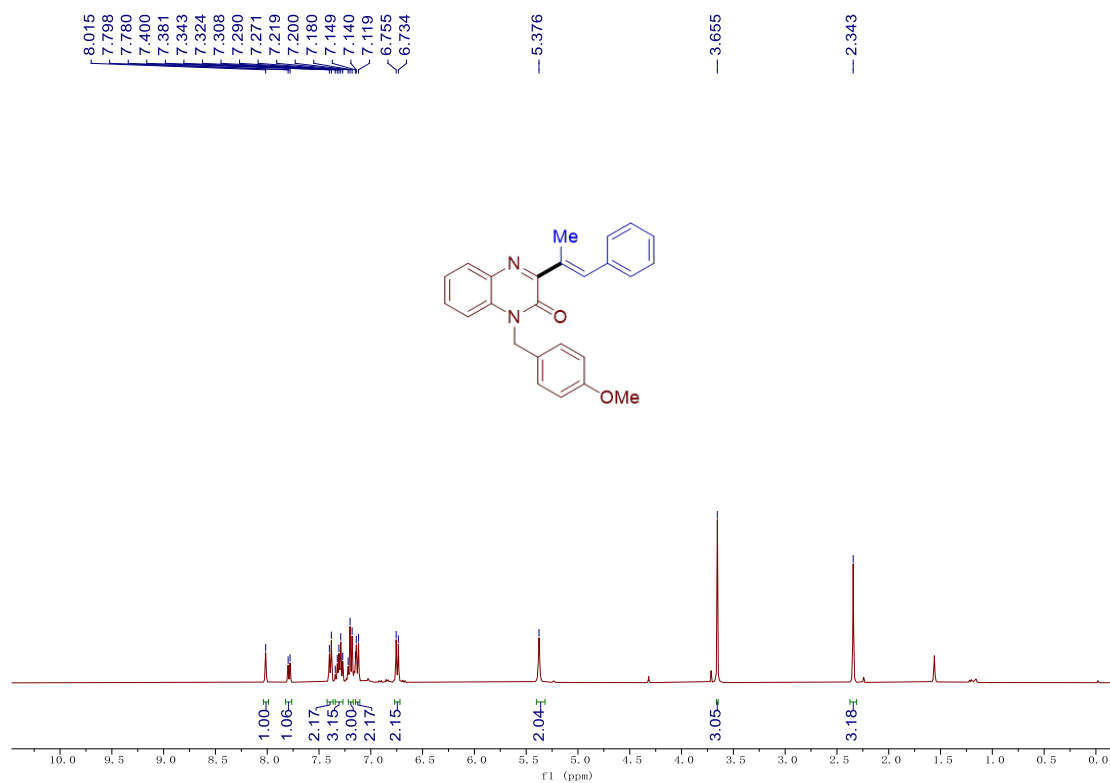




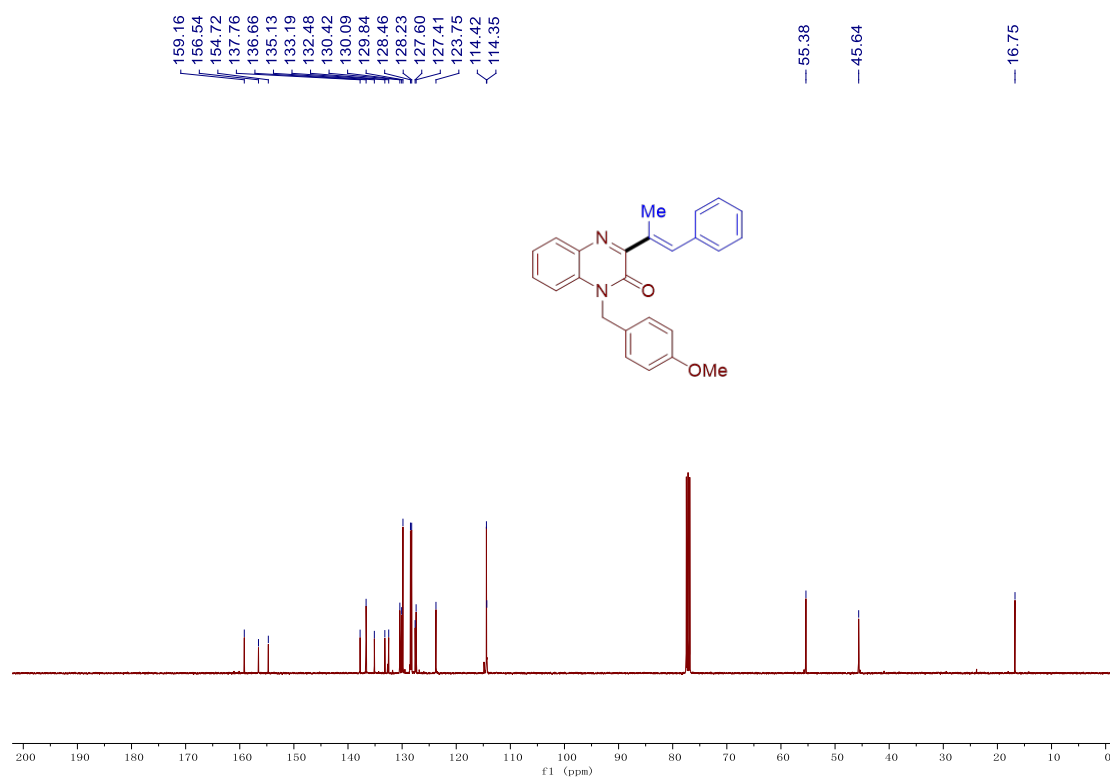
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ea**



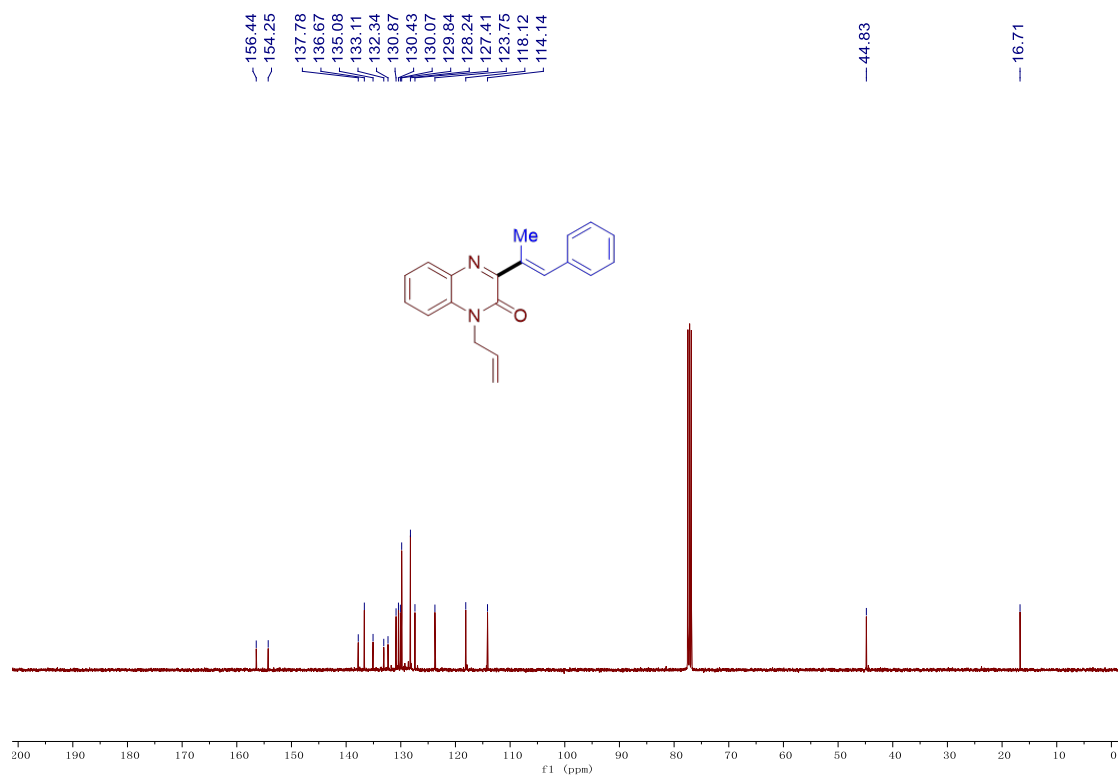
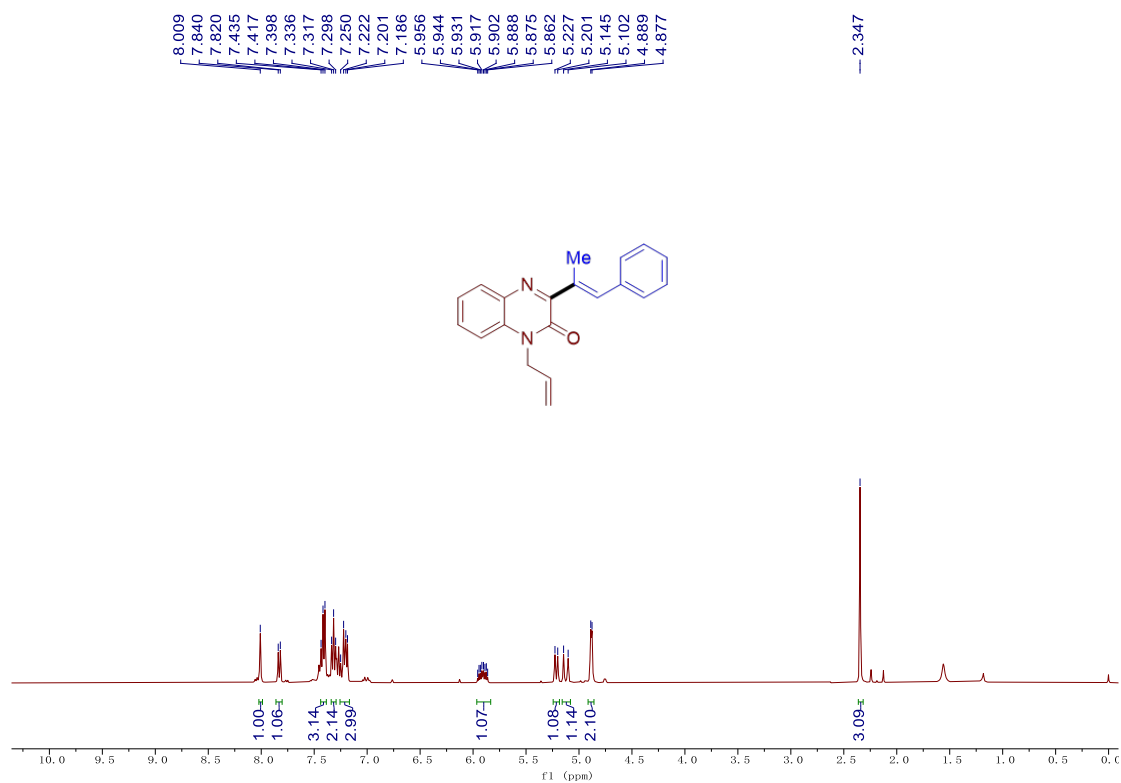
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ea**

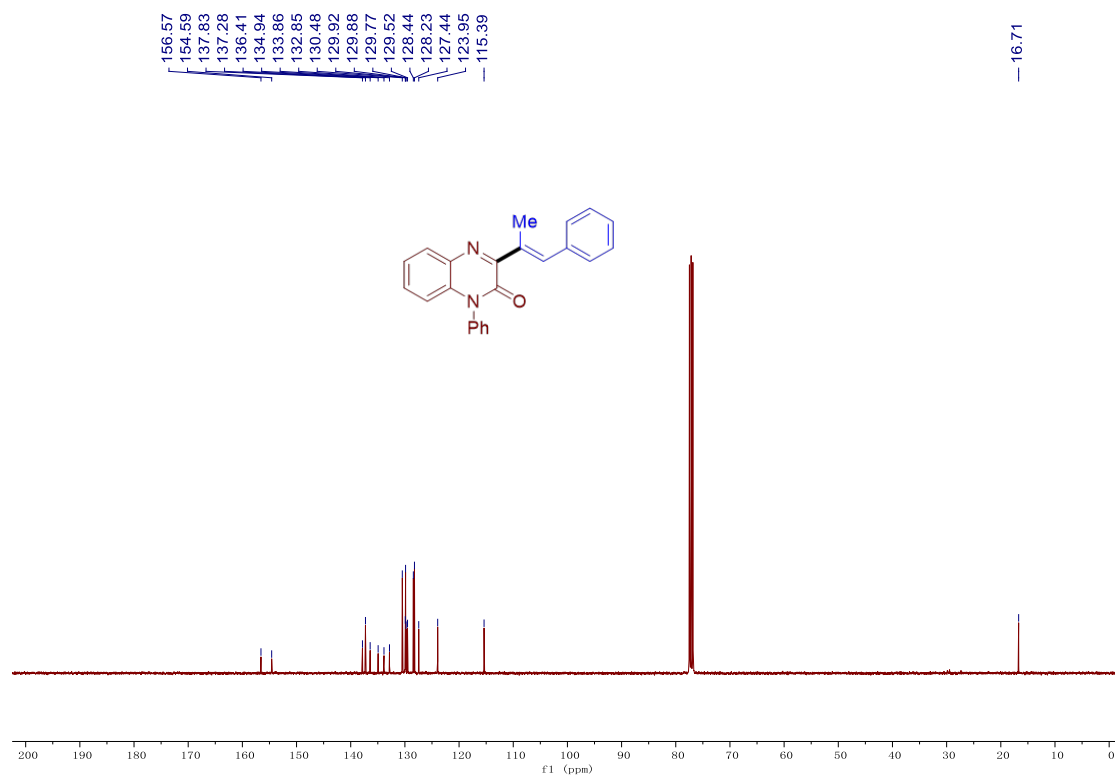
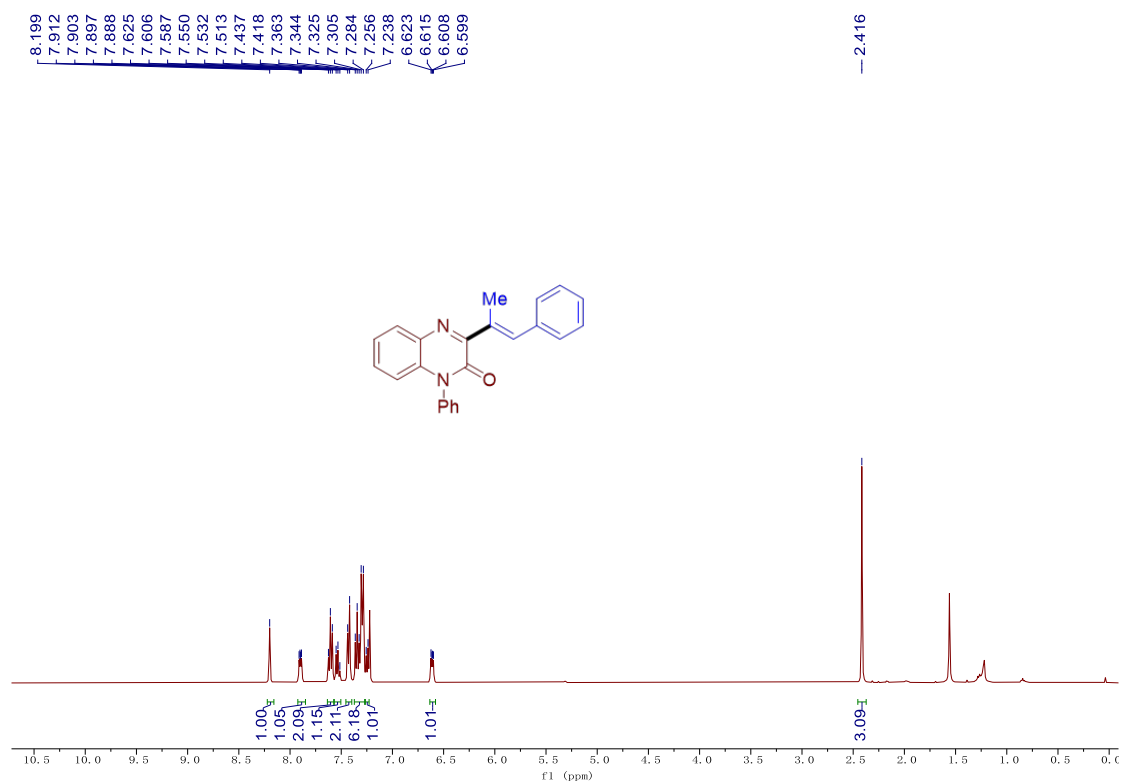


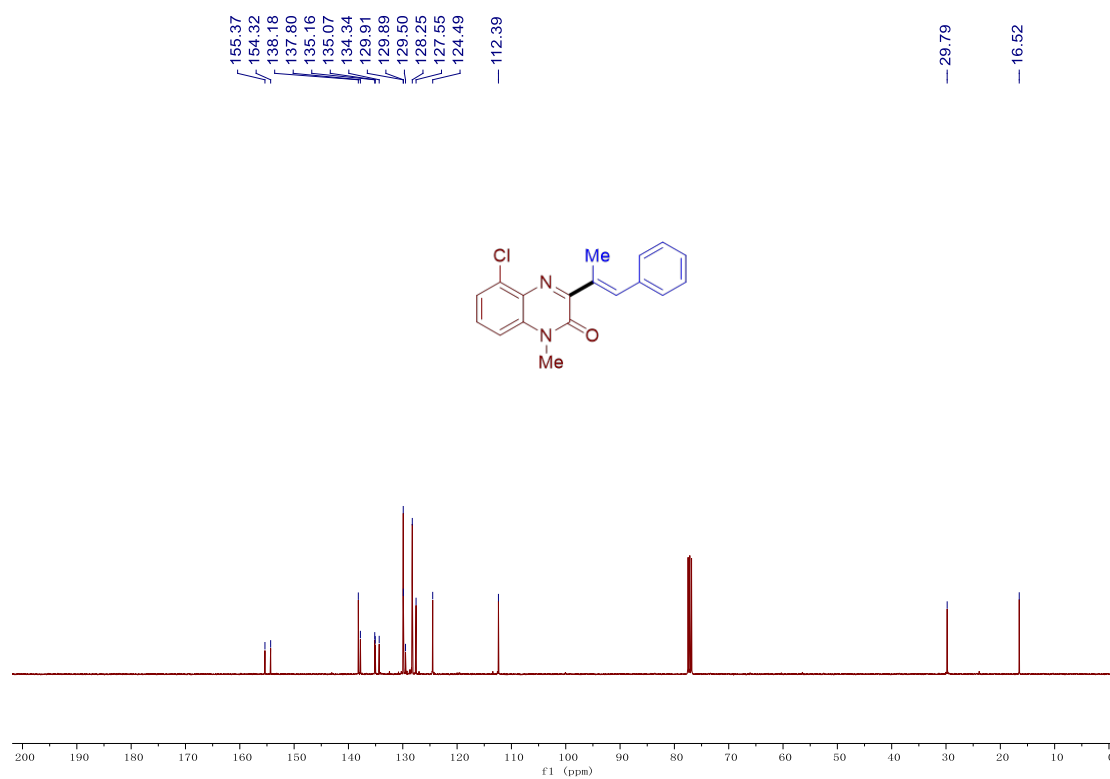
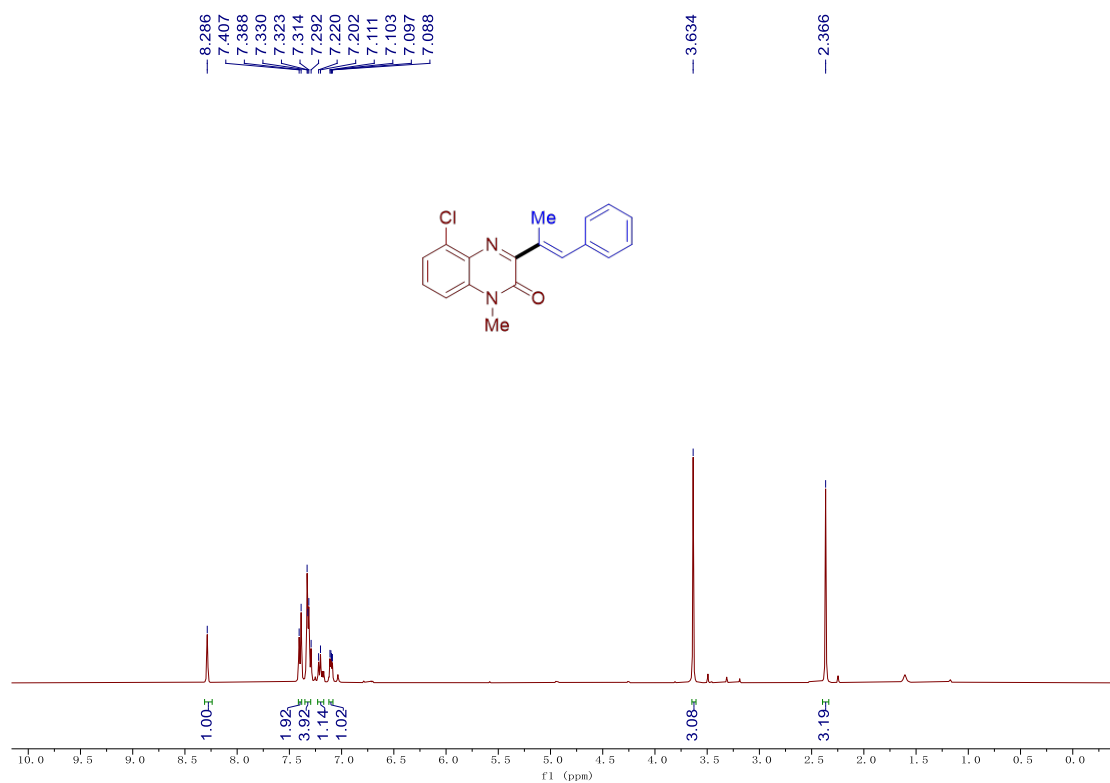
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3fa**

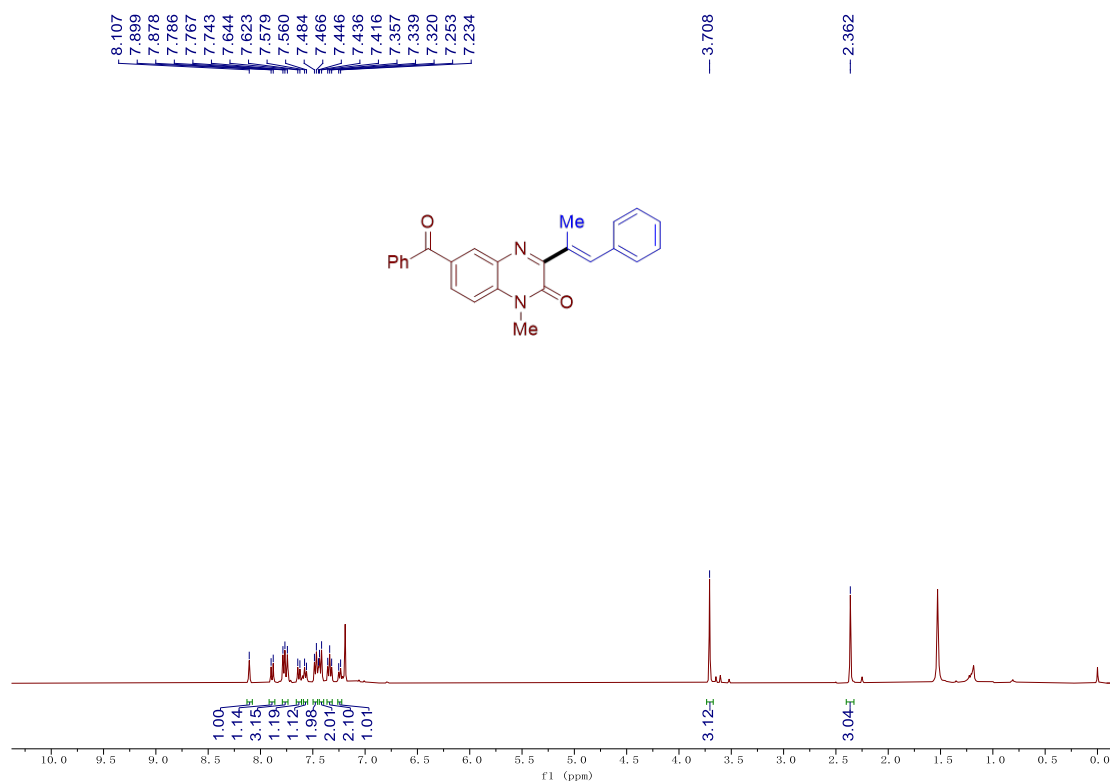


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3fa**

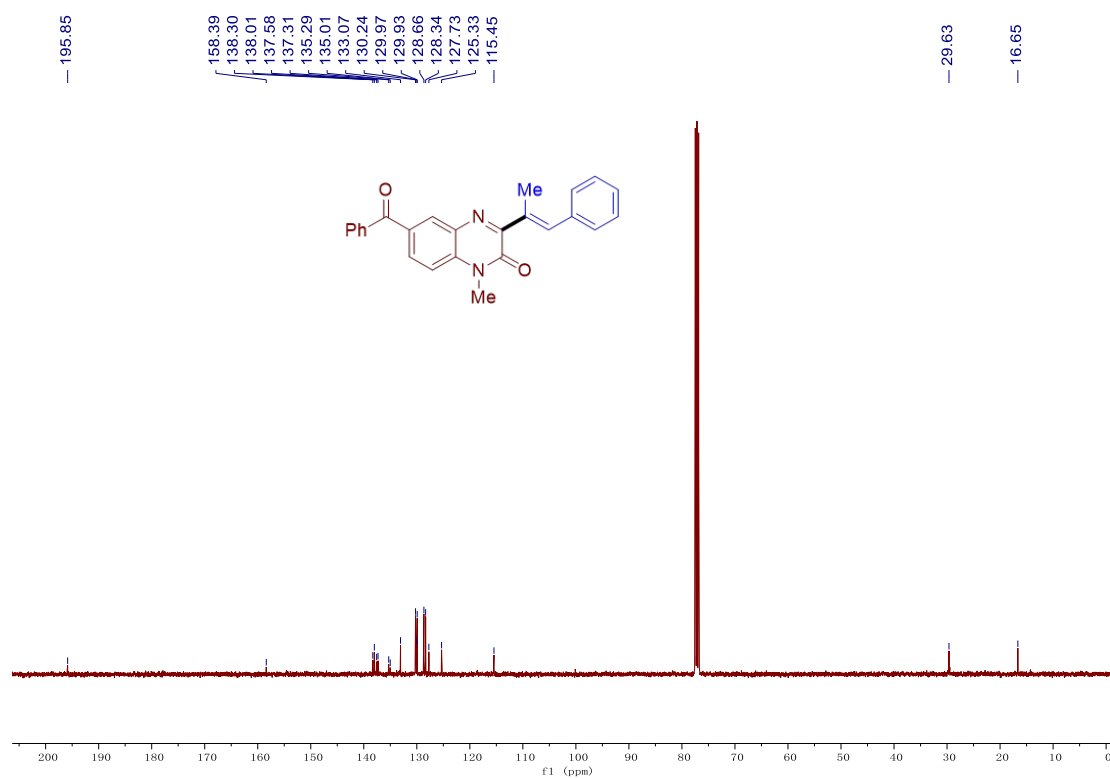




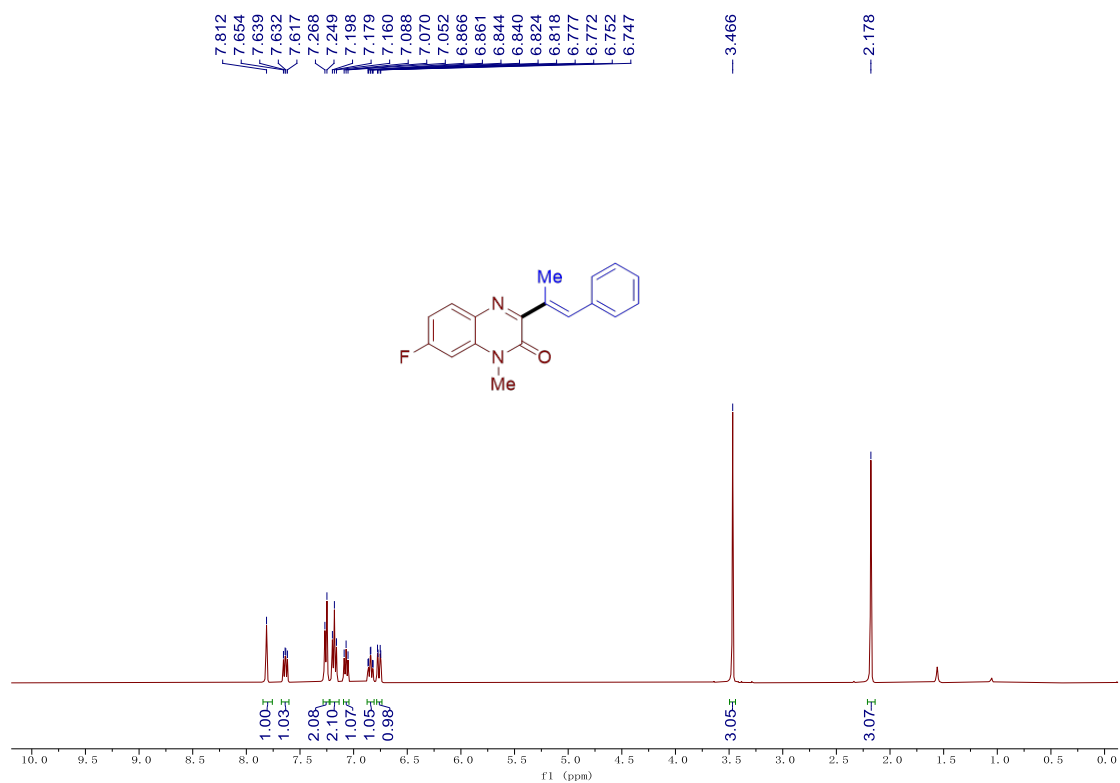




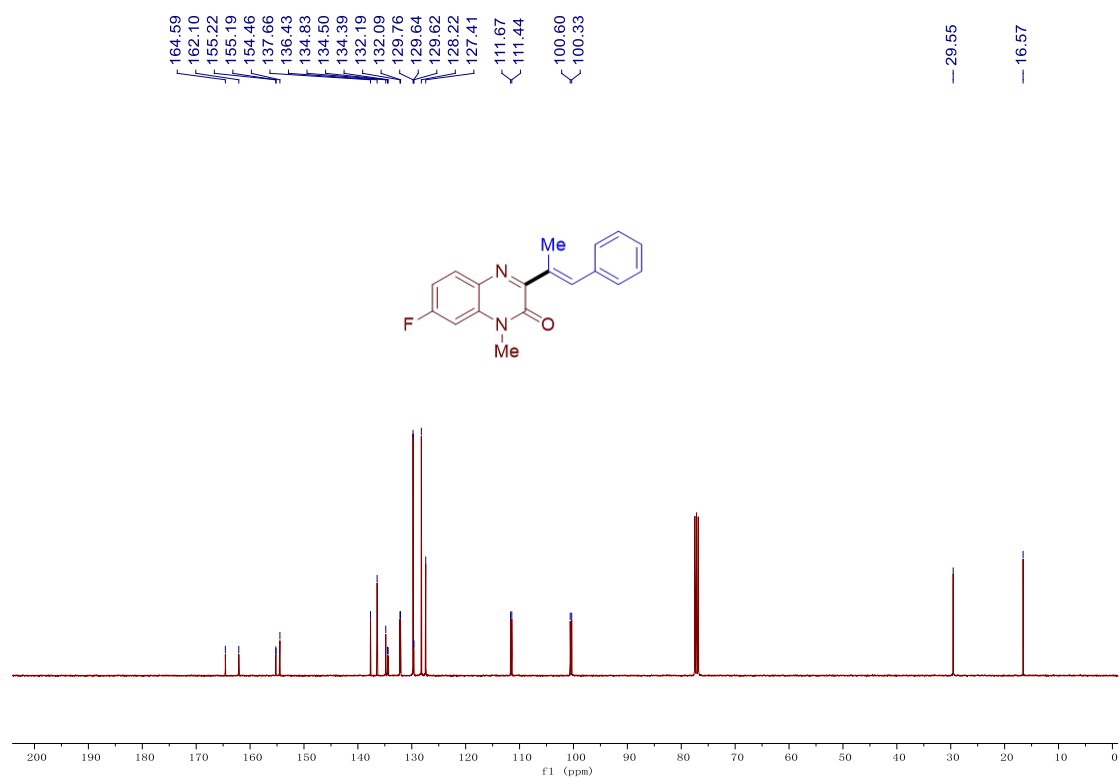
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ja**



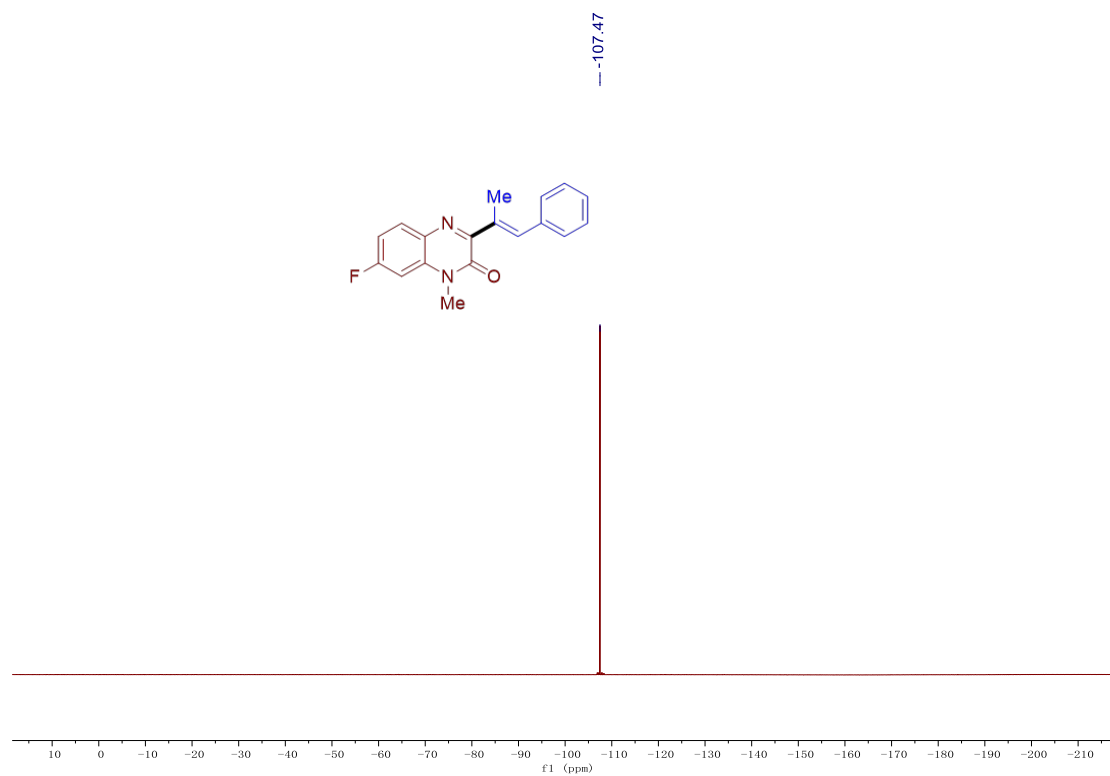
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ja**



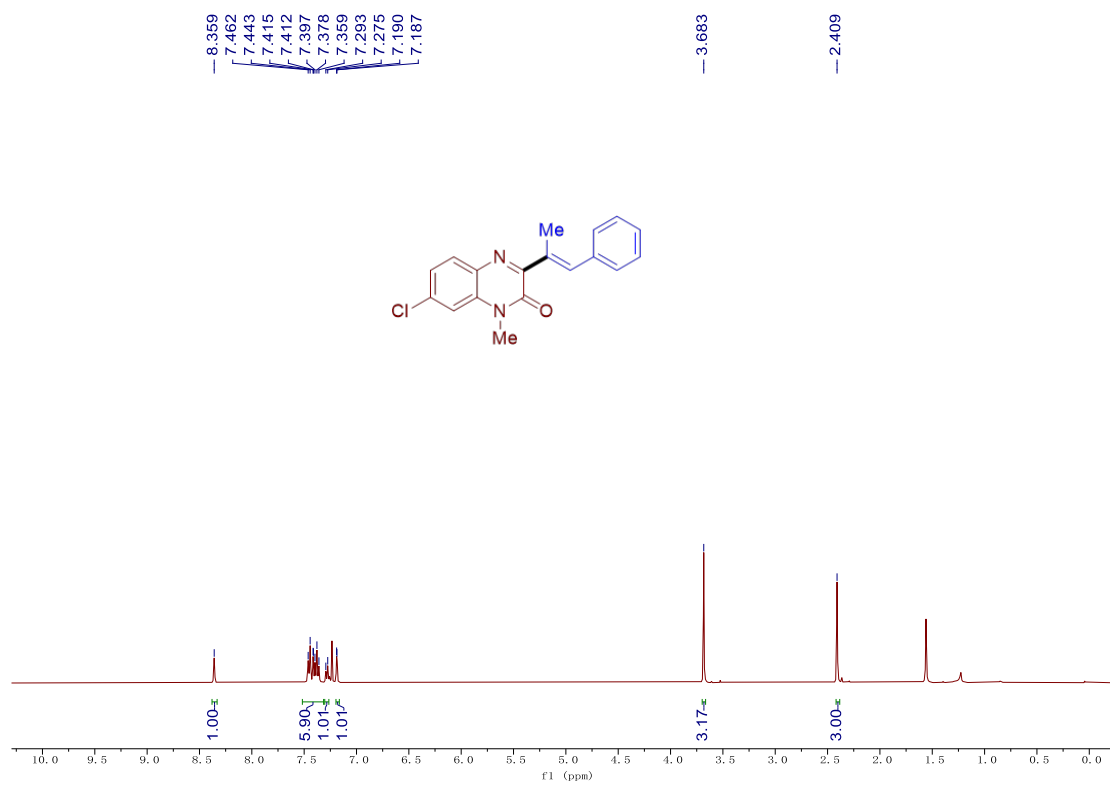
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ka**



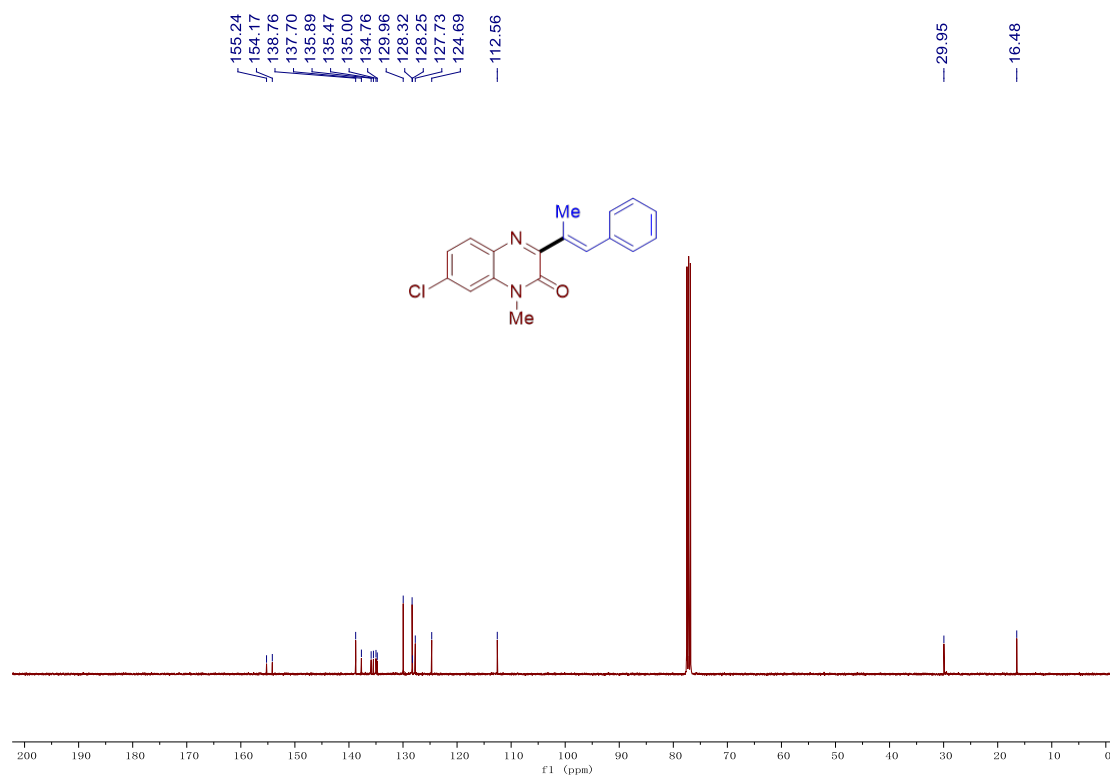
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ka**



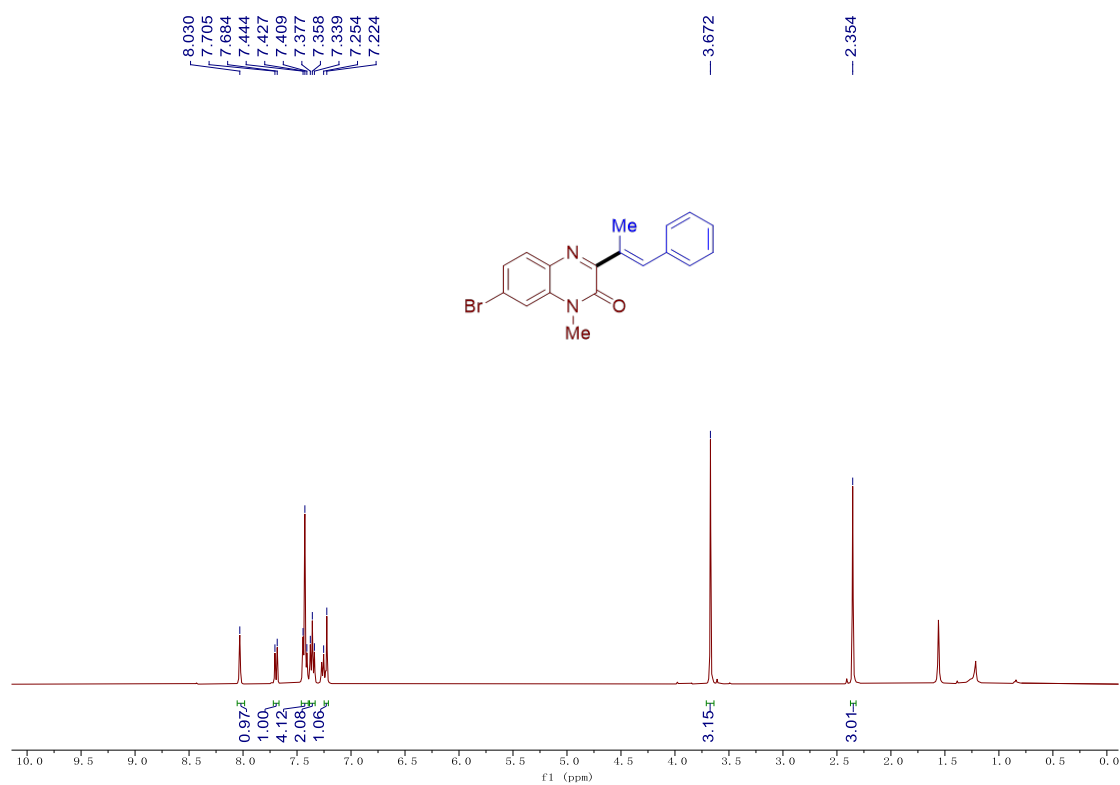
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra of **3ka**



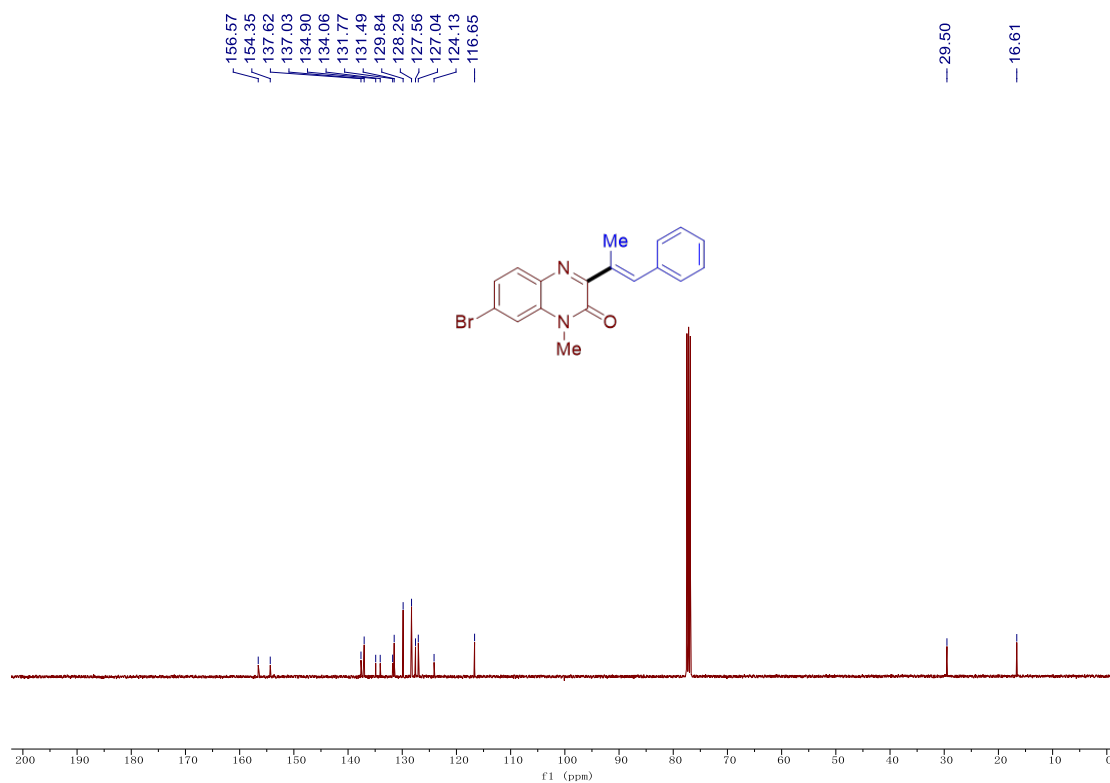
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **3la**



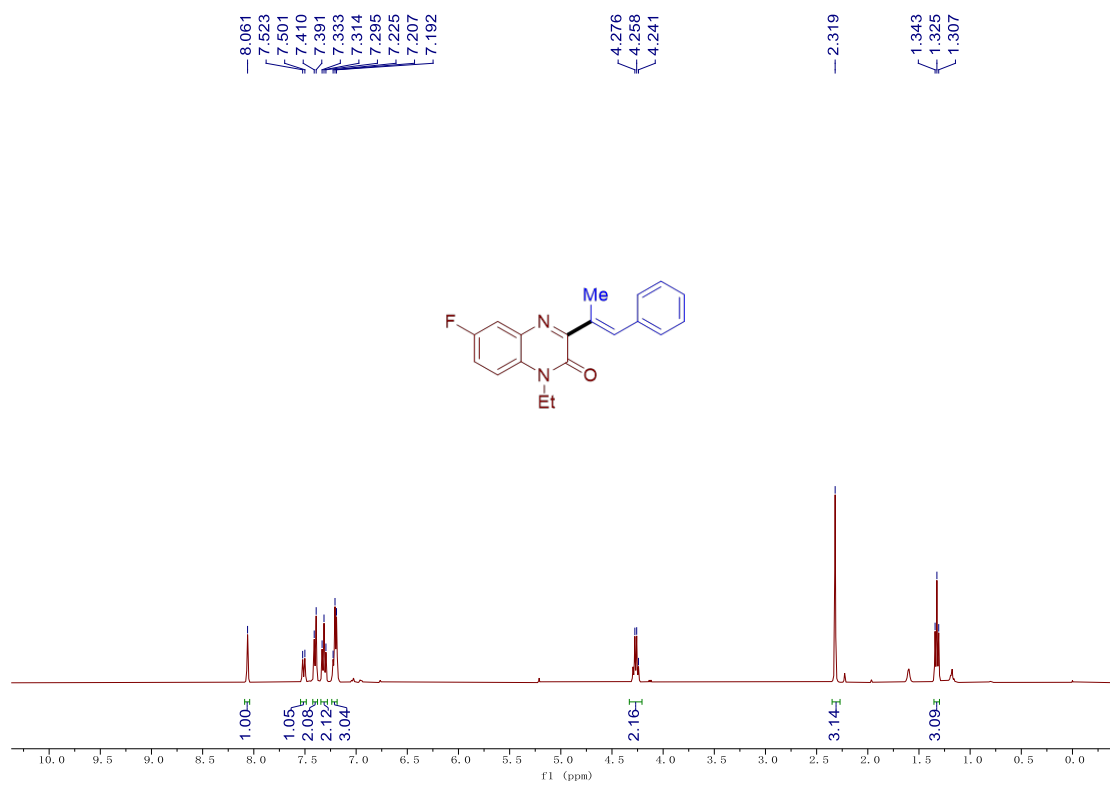
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3la**



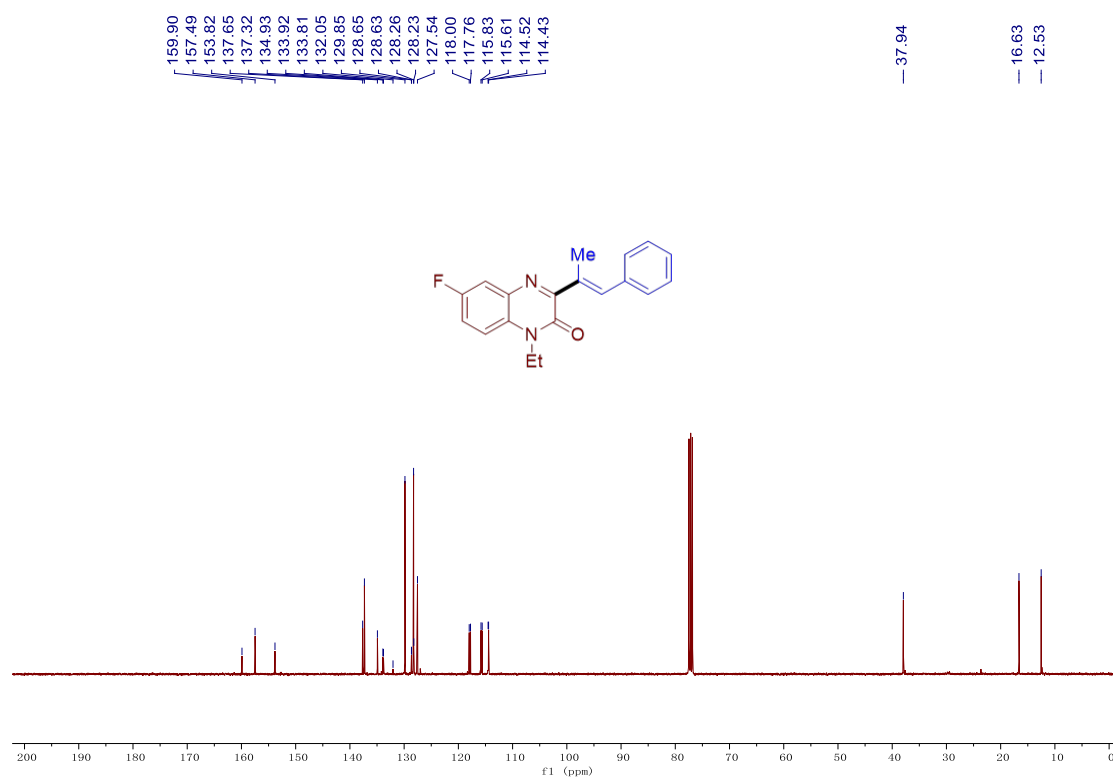
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ma**



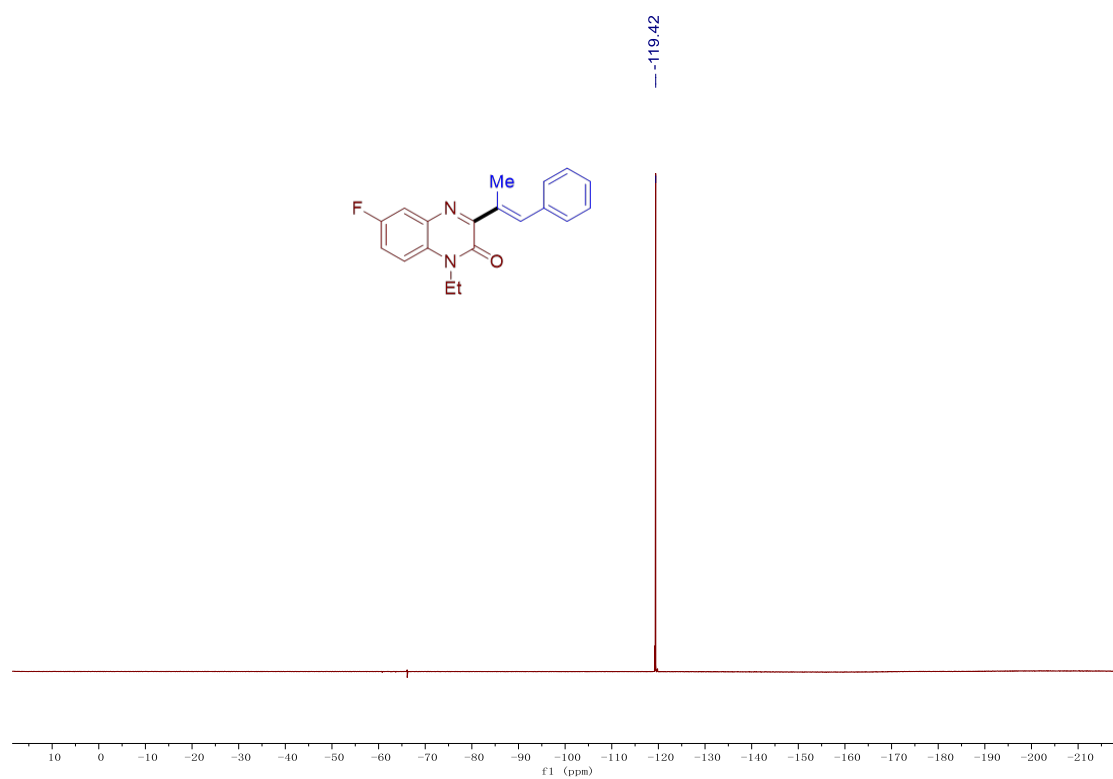
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ma**



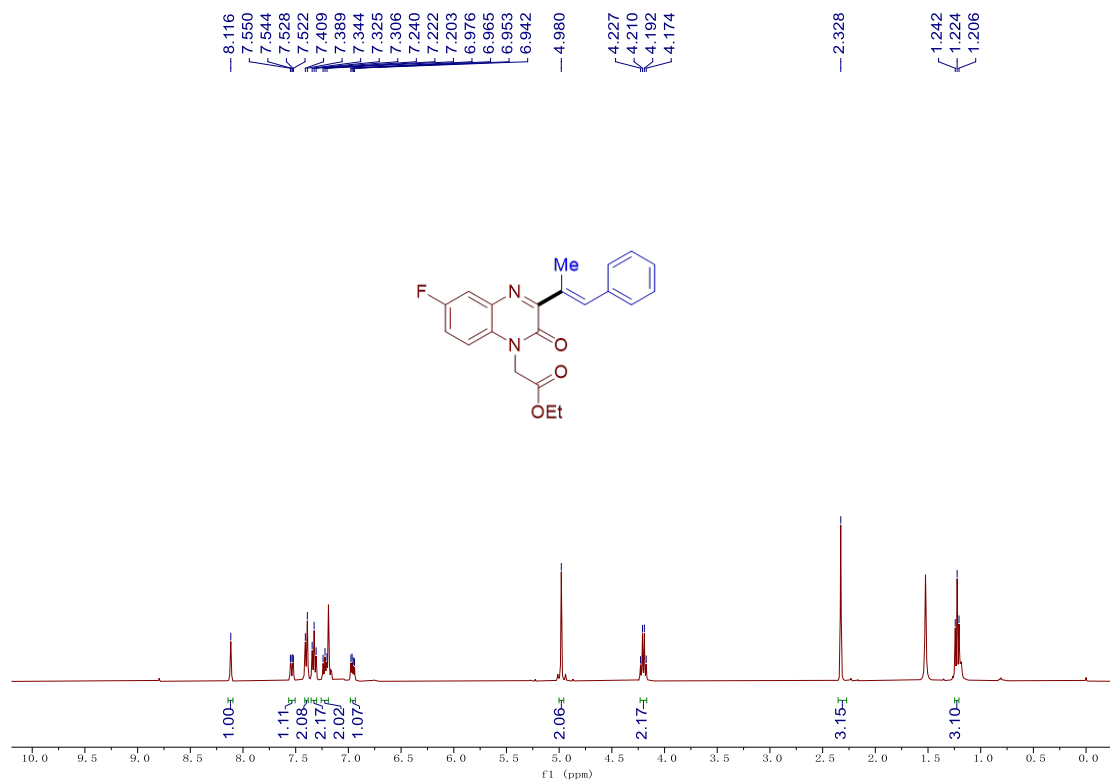
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3na**



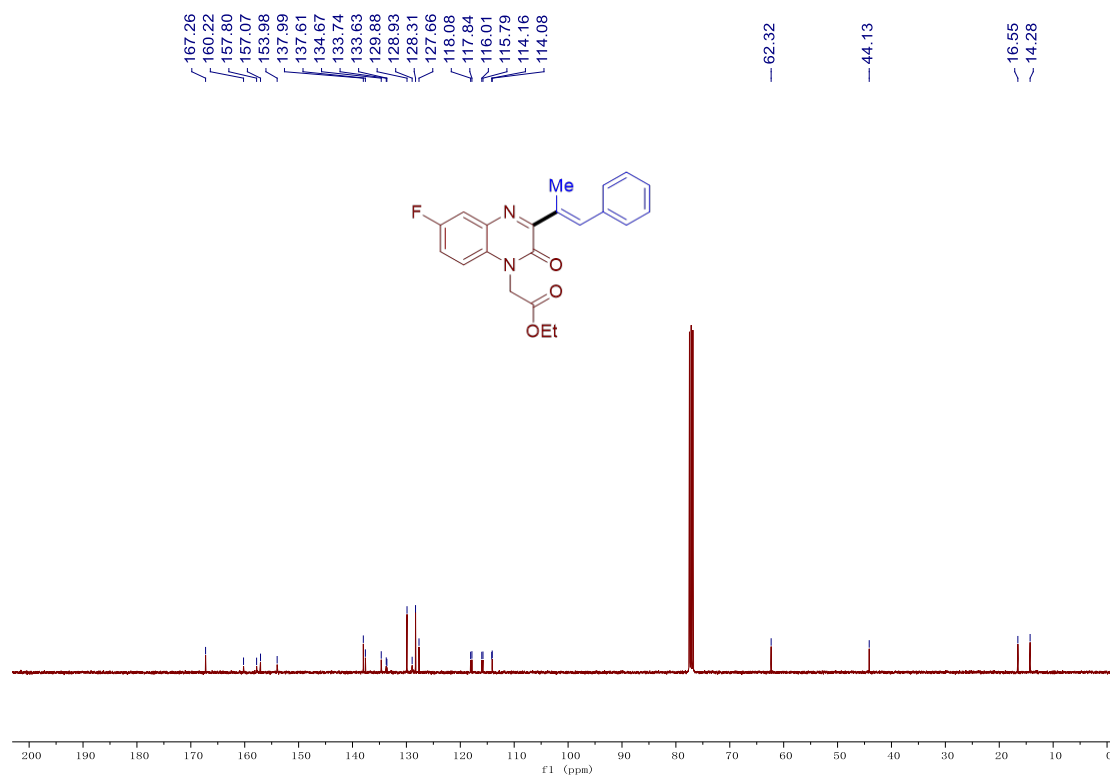
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3na**



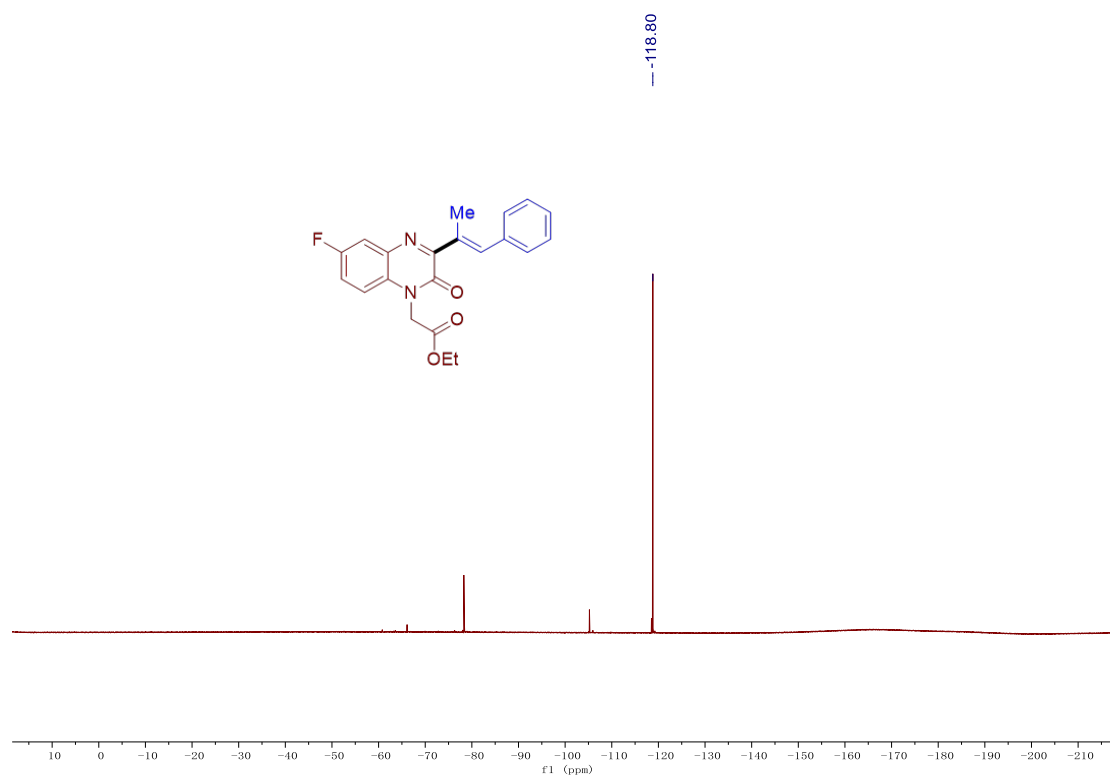
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of **3na**



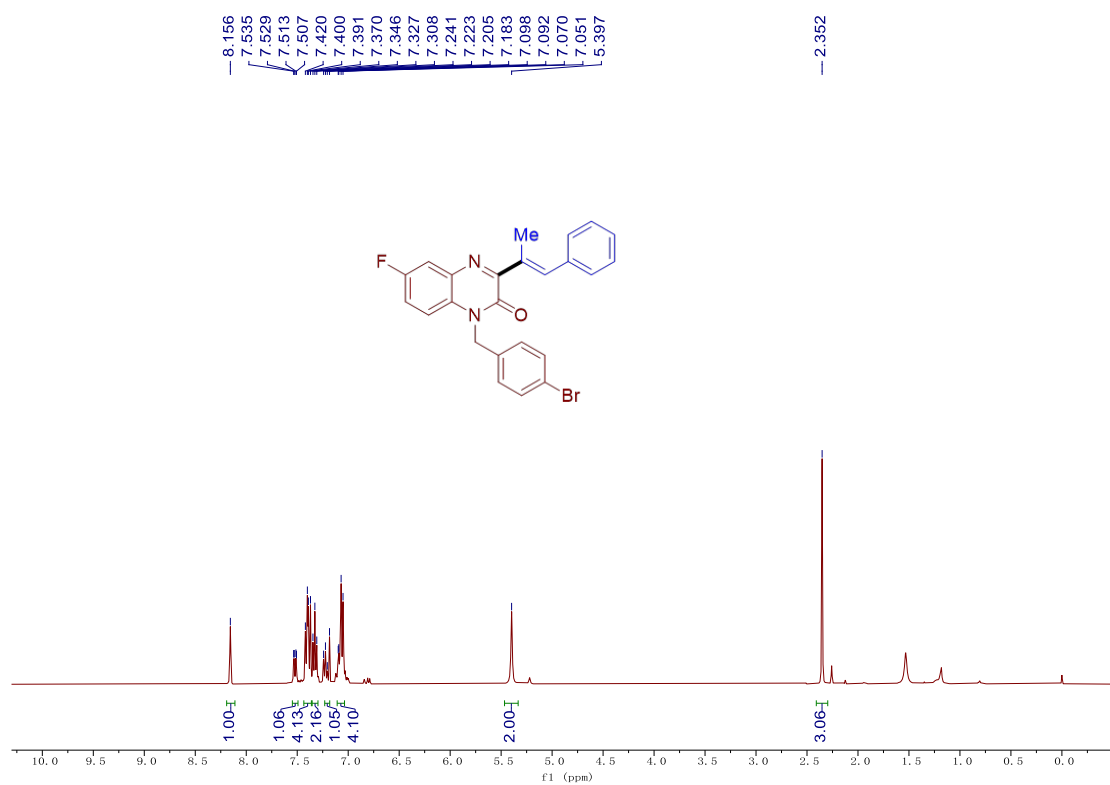
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **30a**



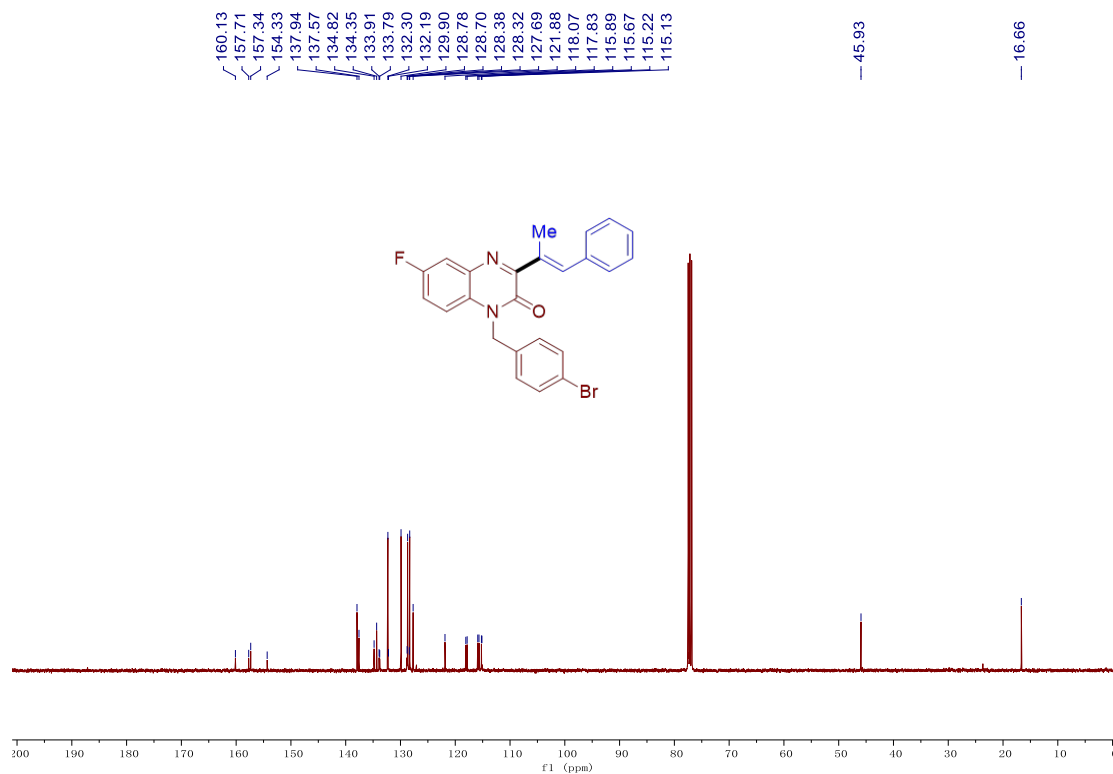
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **30a**



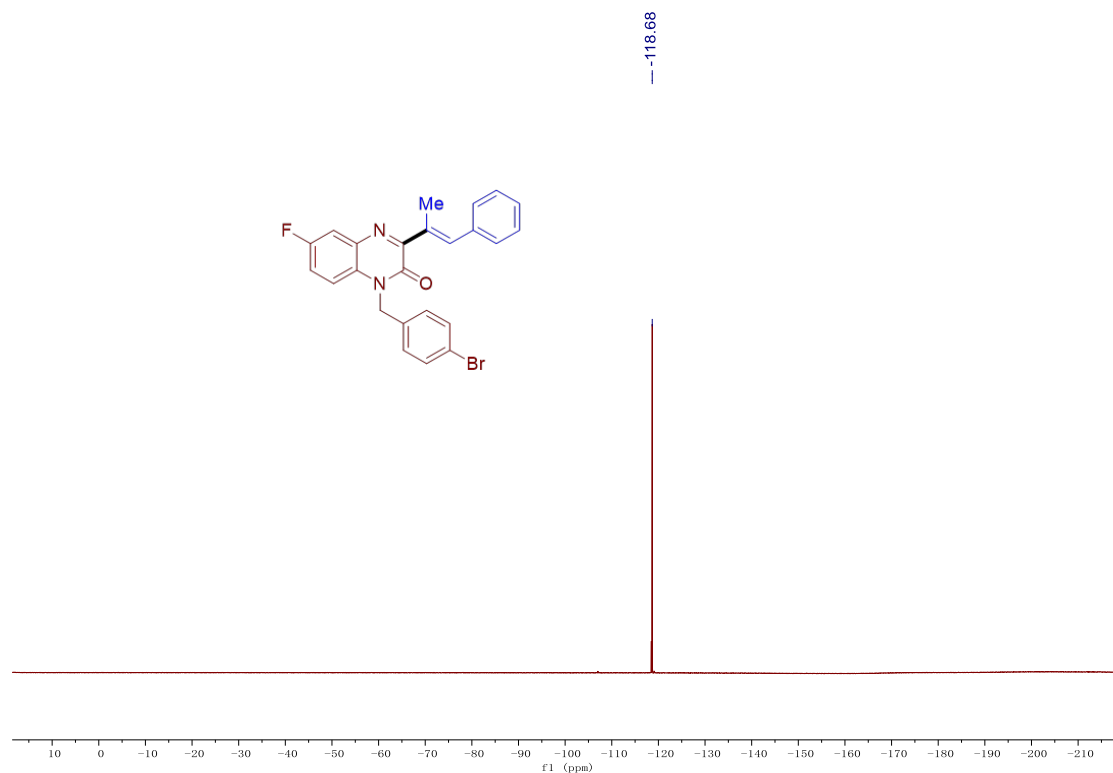
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of **3oa**



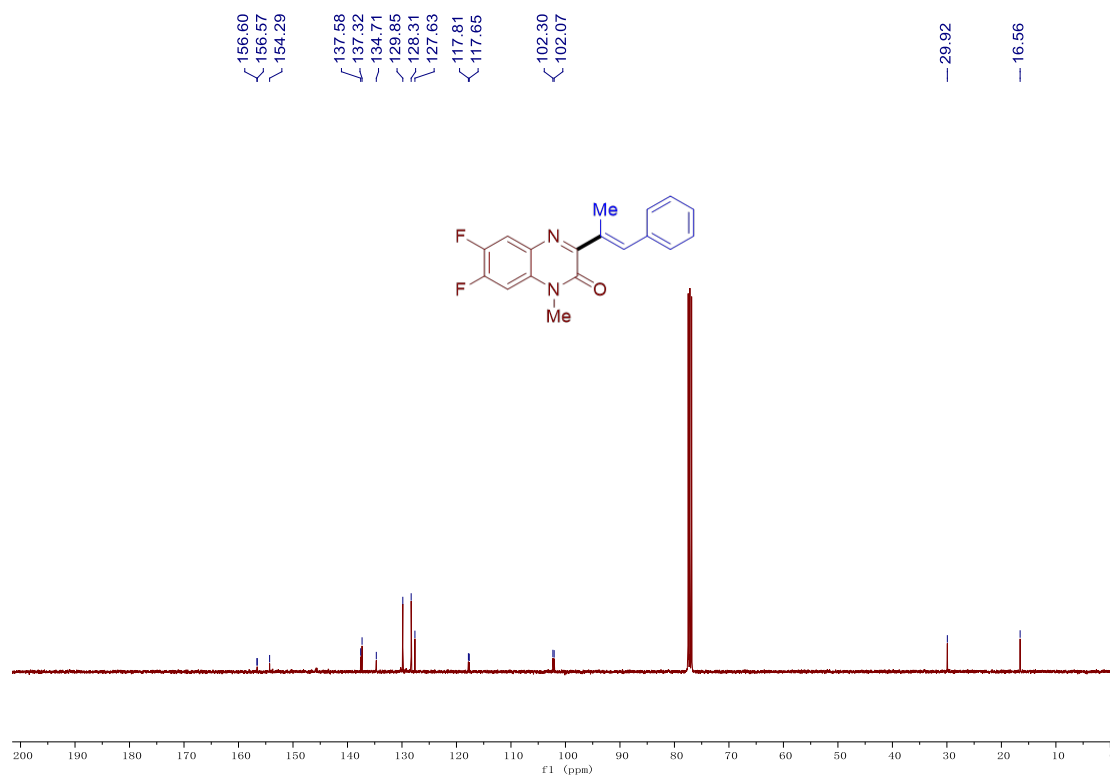
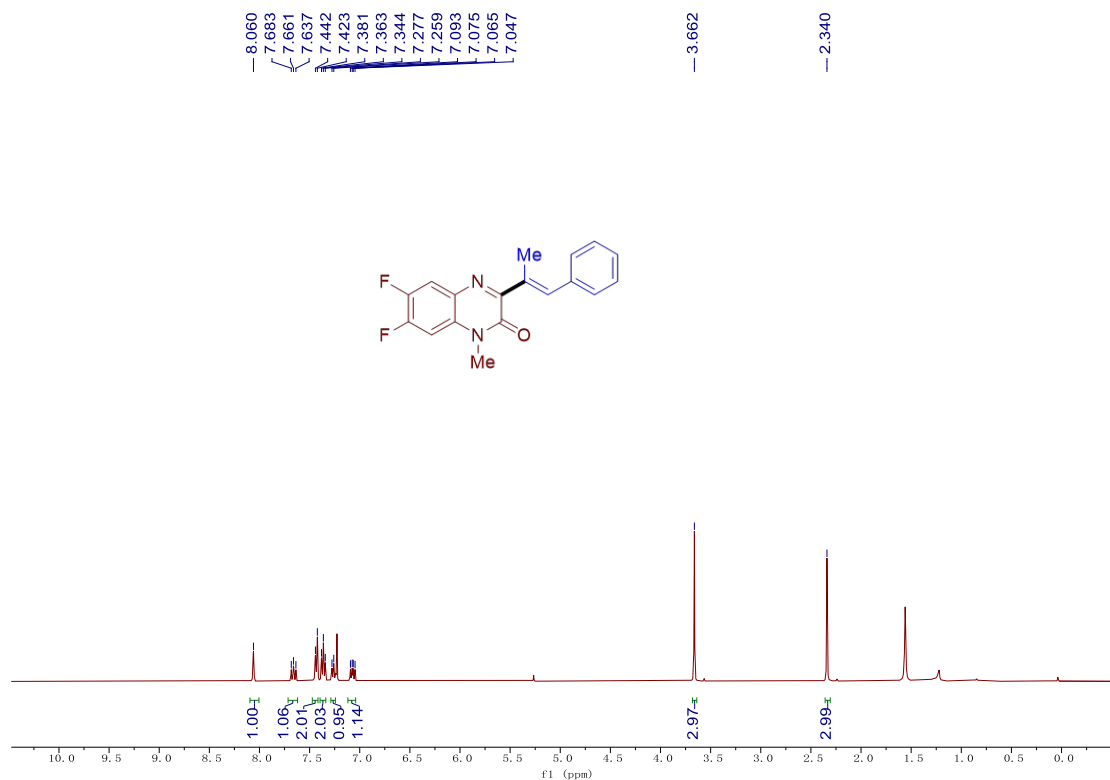
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3pa**

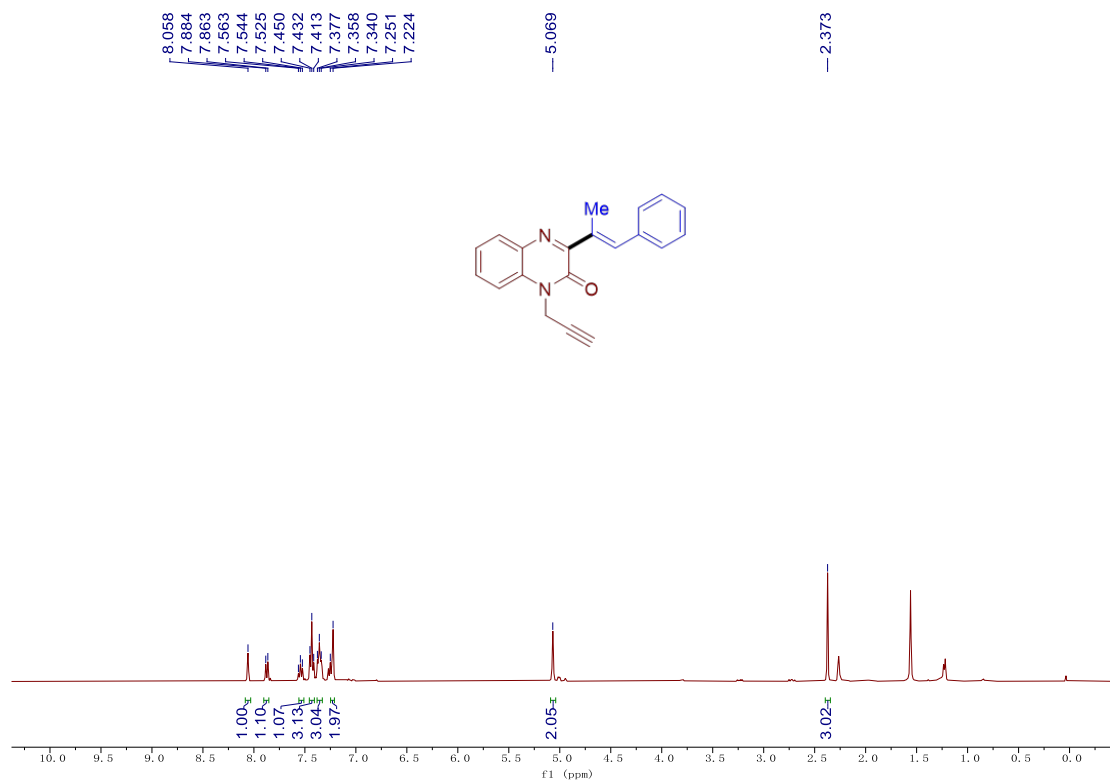


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3pa**

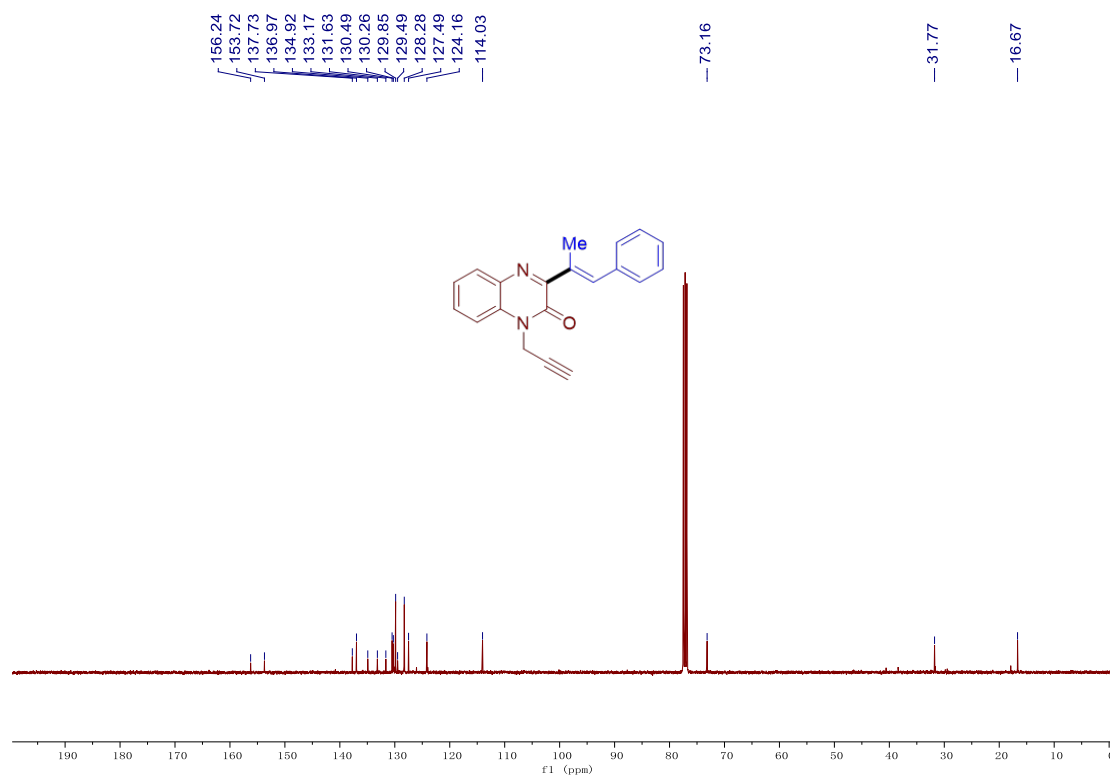


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of **3pa**

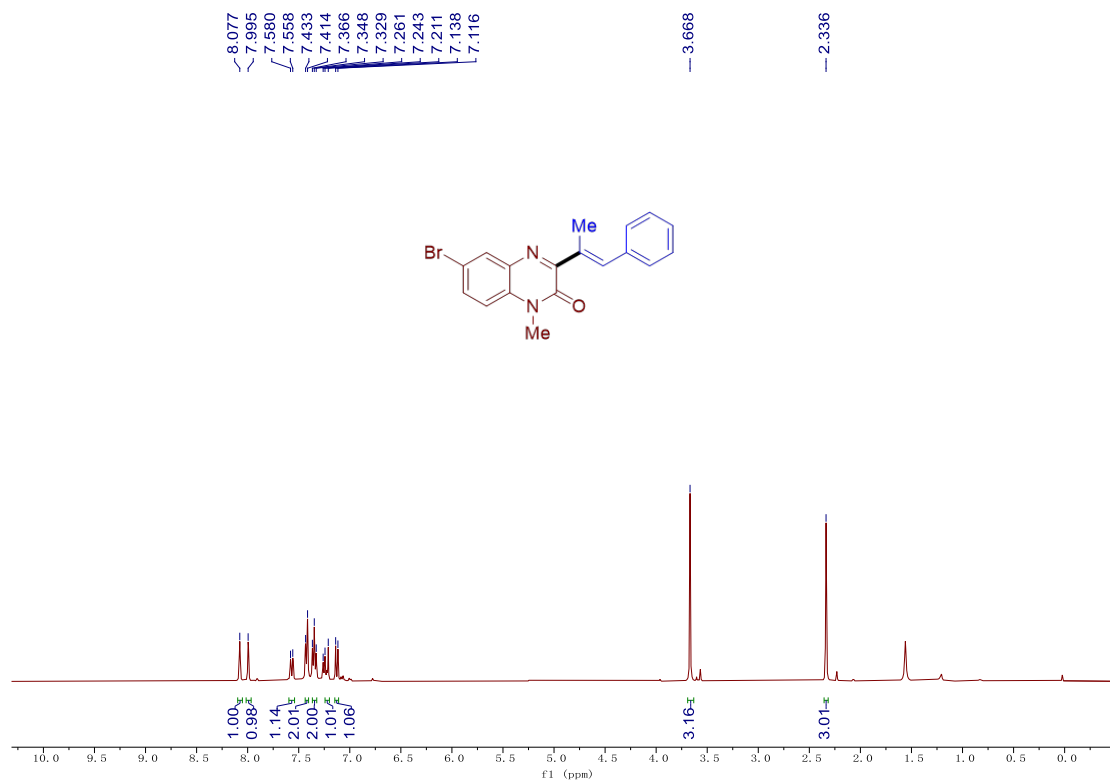




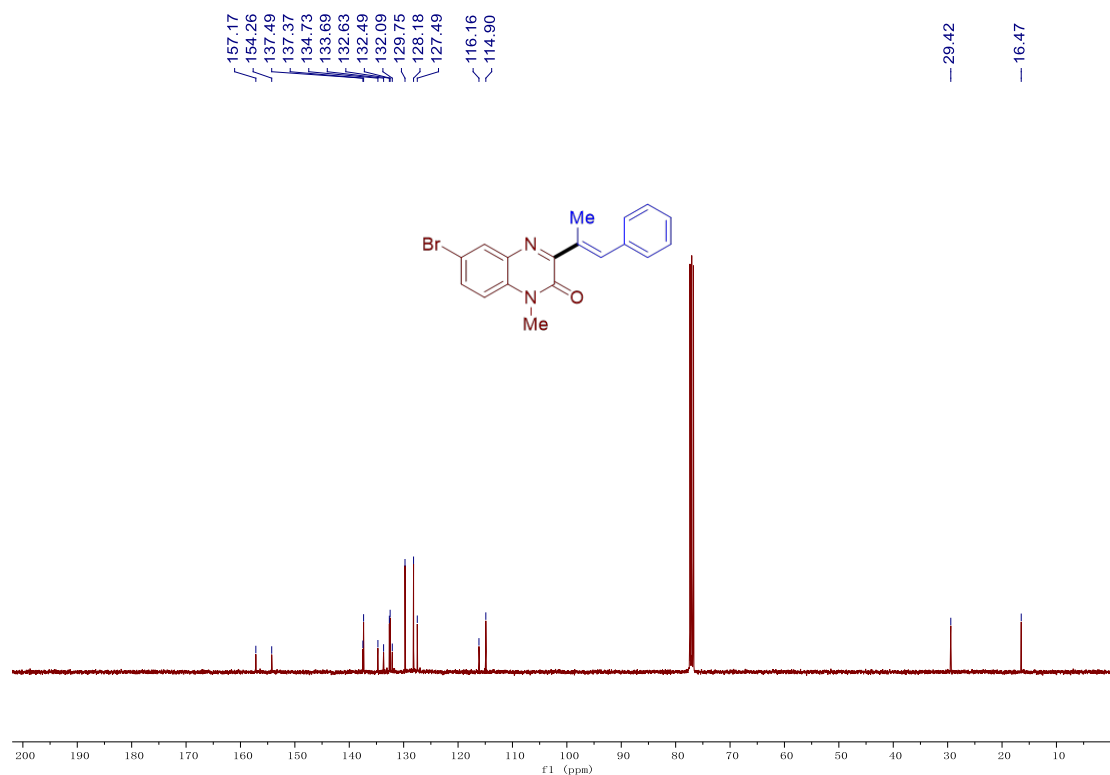
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ra**



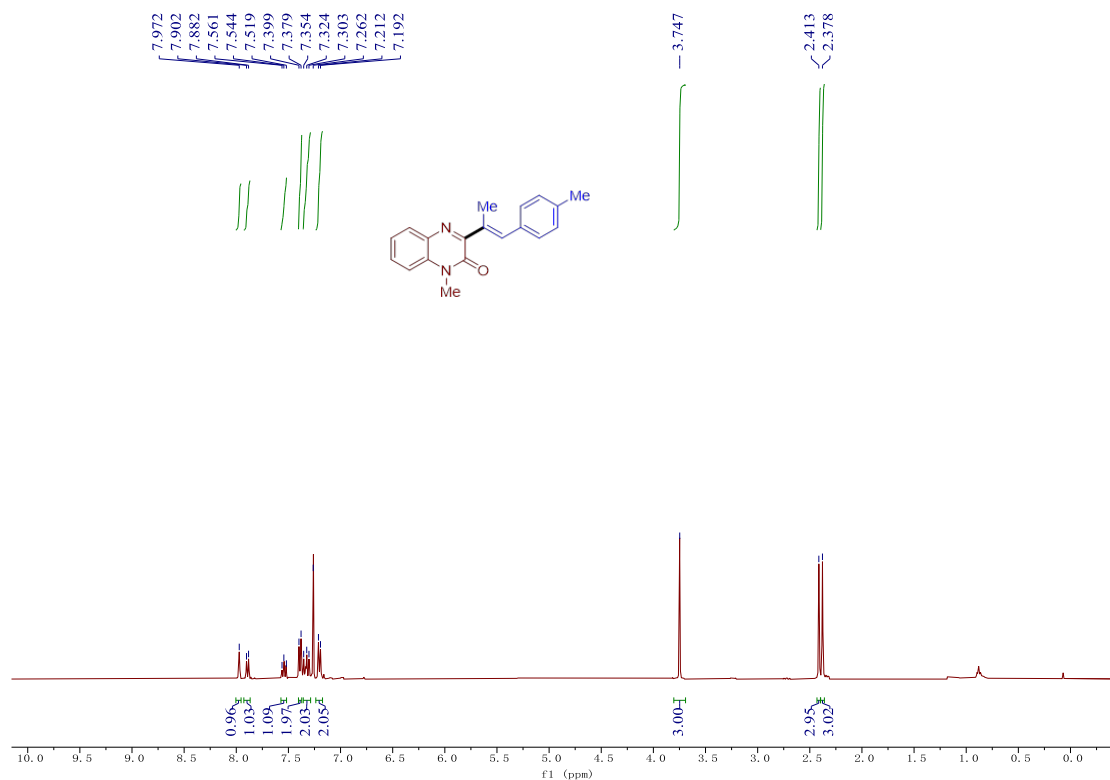
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ra**



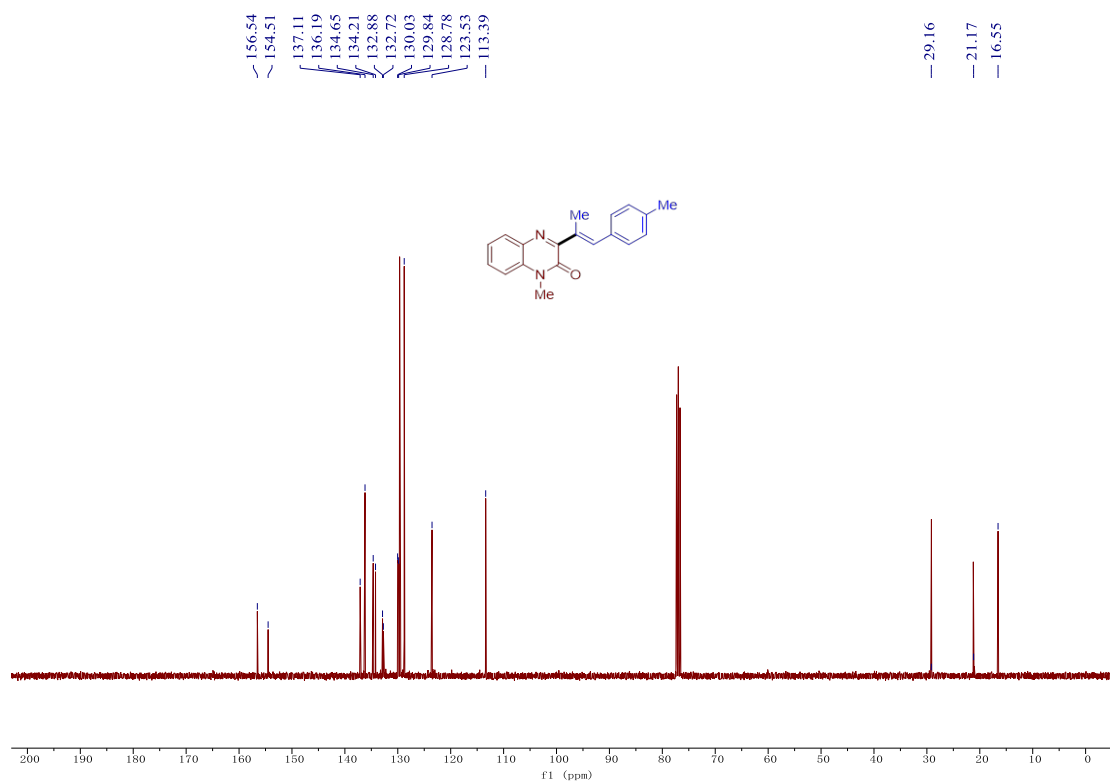
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3sa**



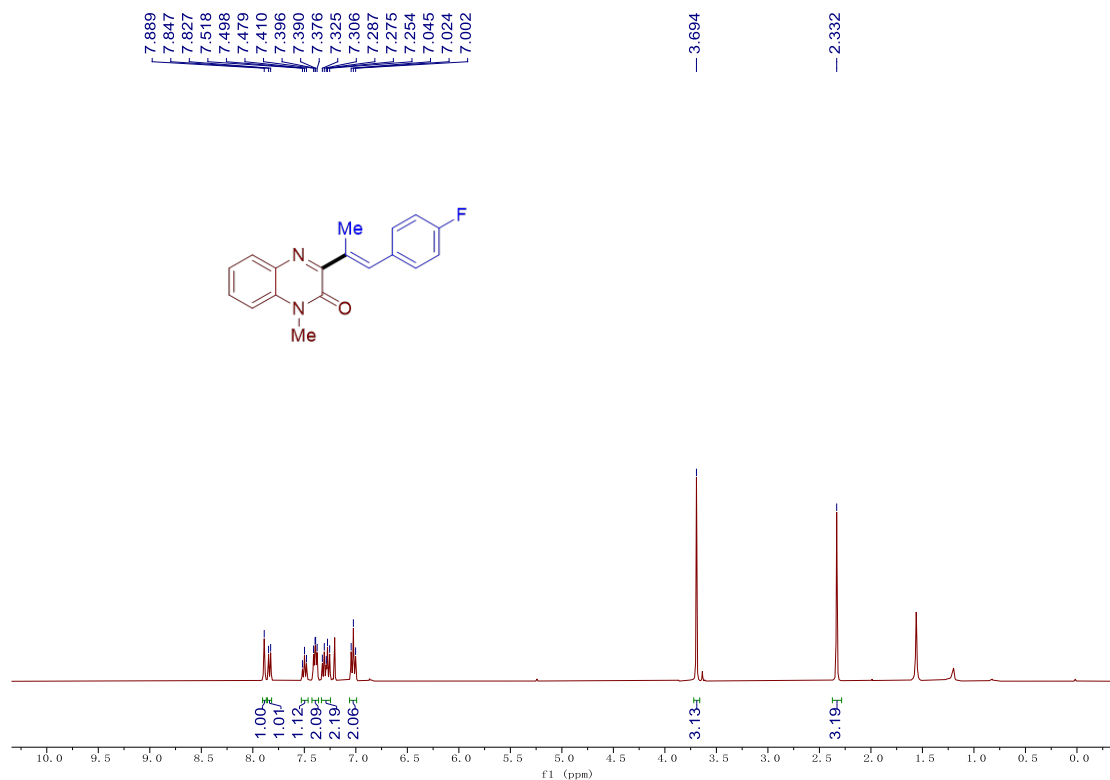
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3sa**



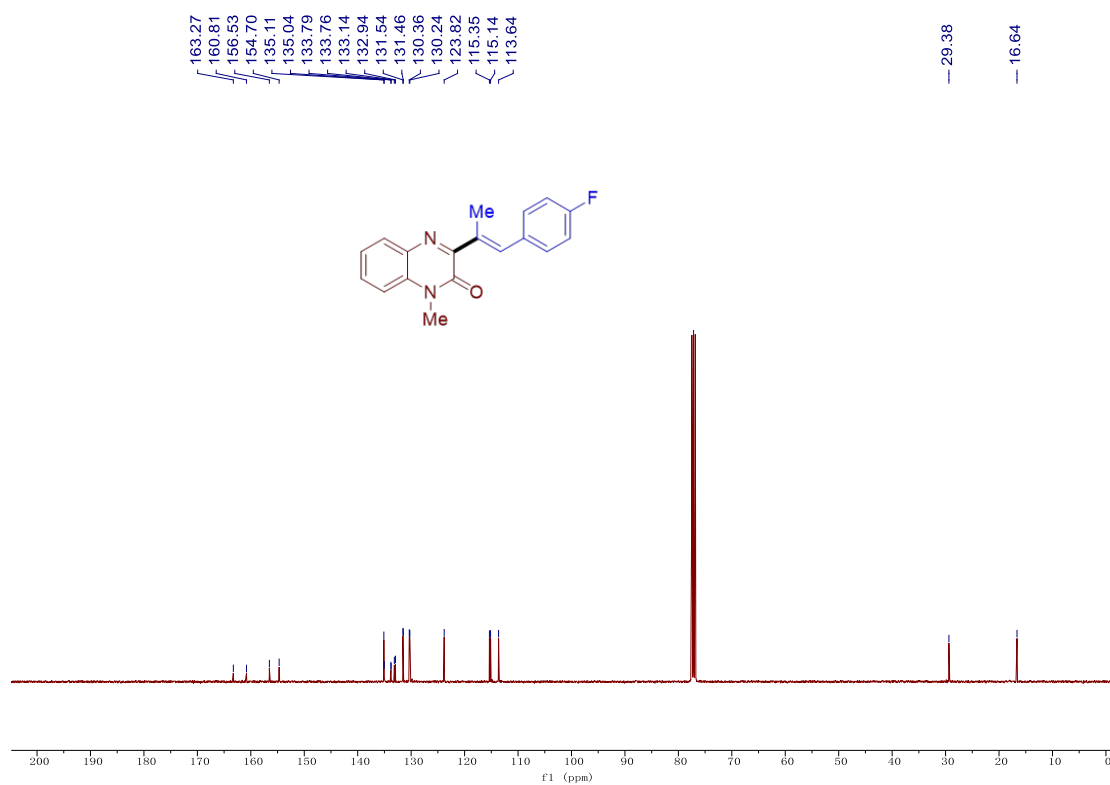
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ab**



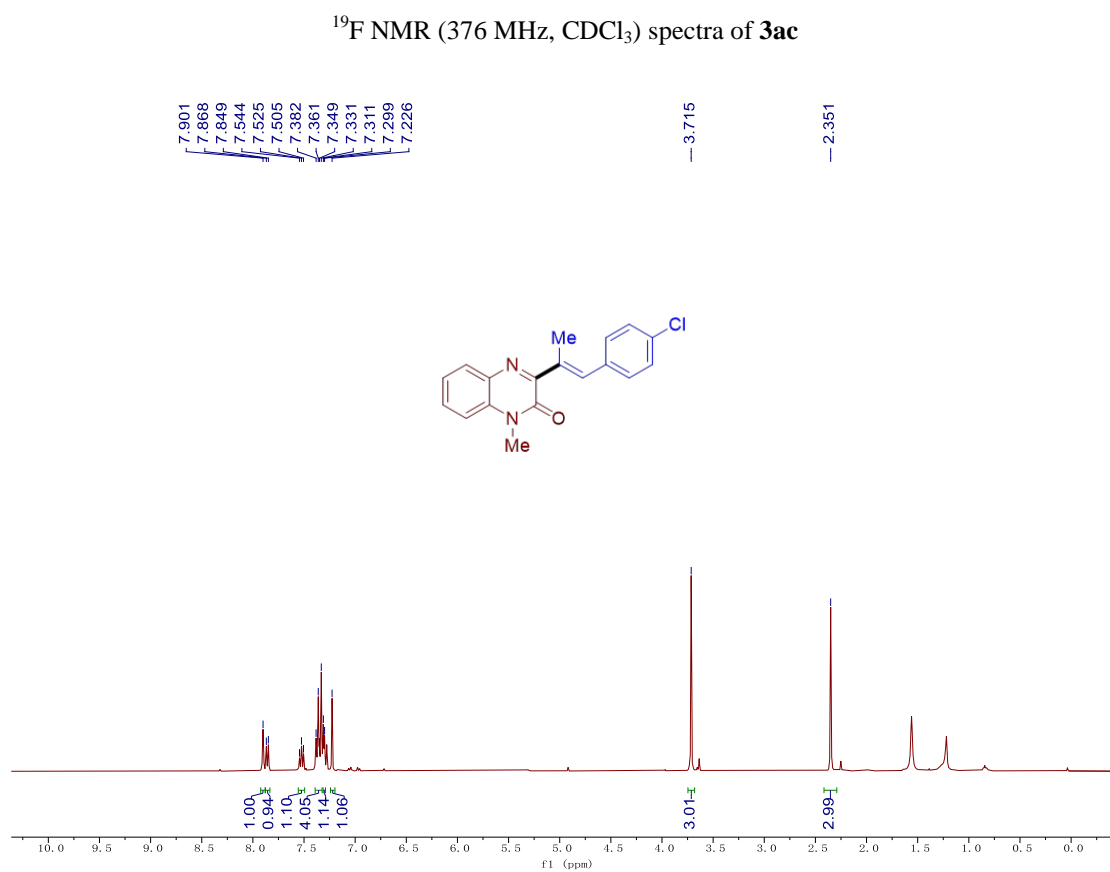
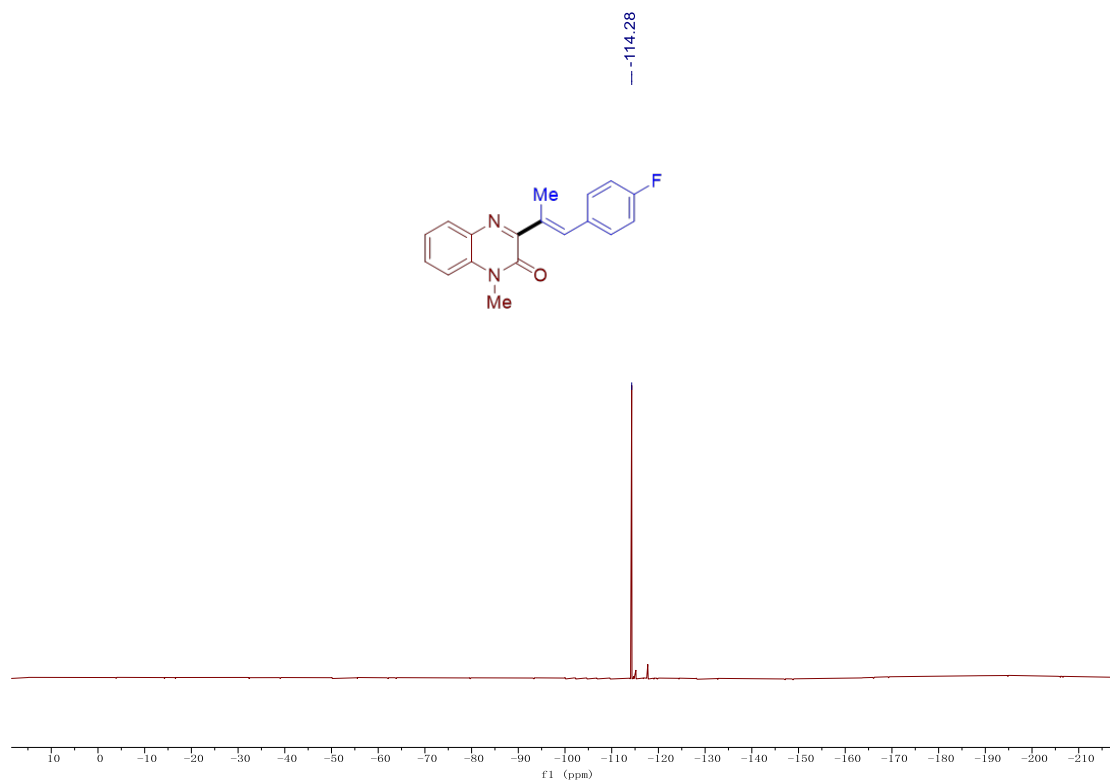
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ab**

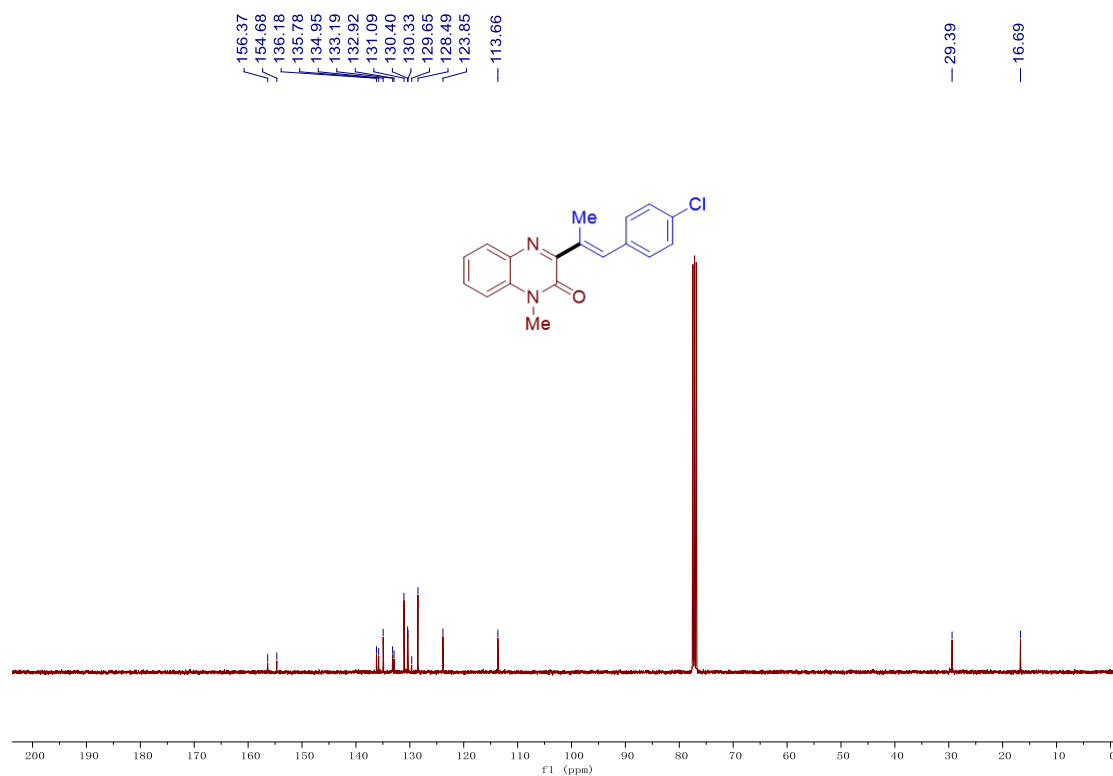


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ac**

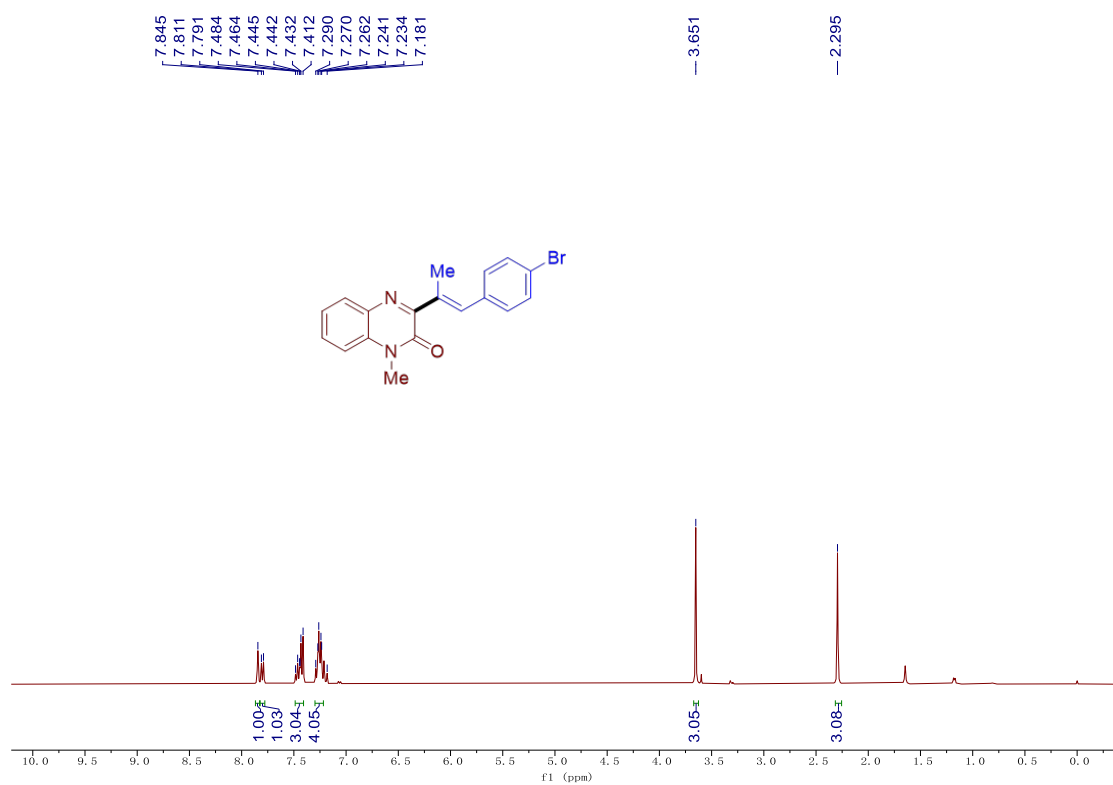


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ac**

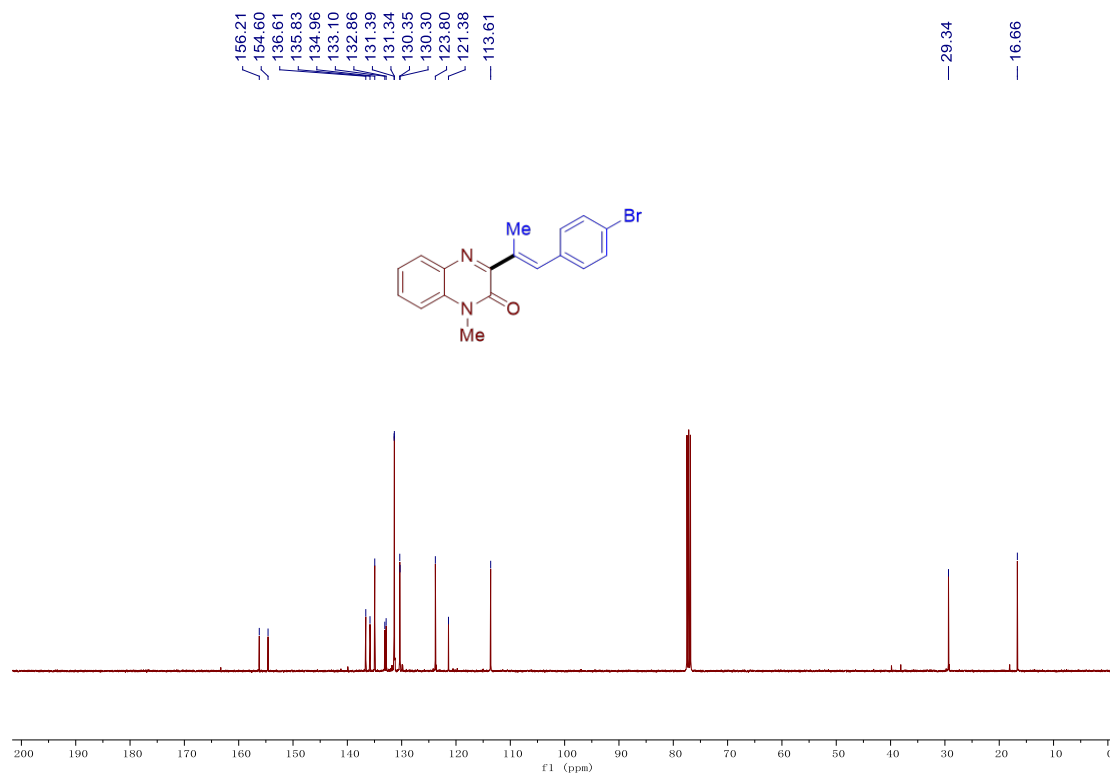




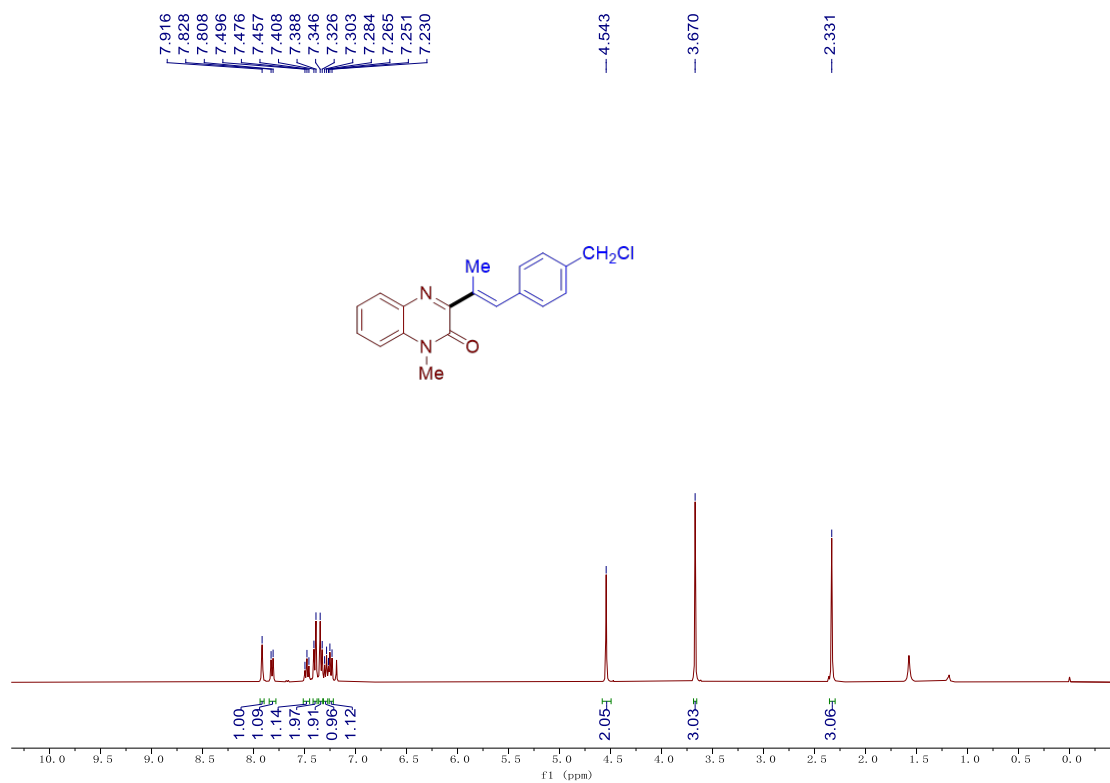
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **3ad**



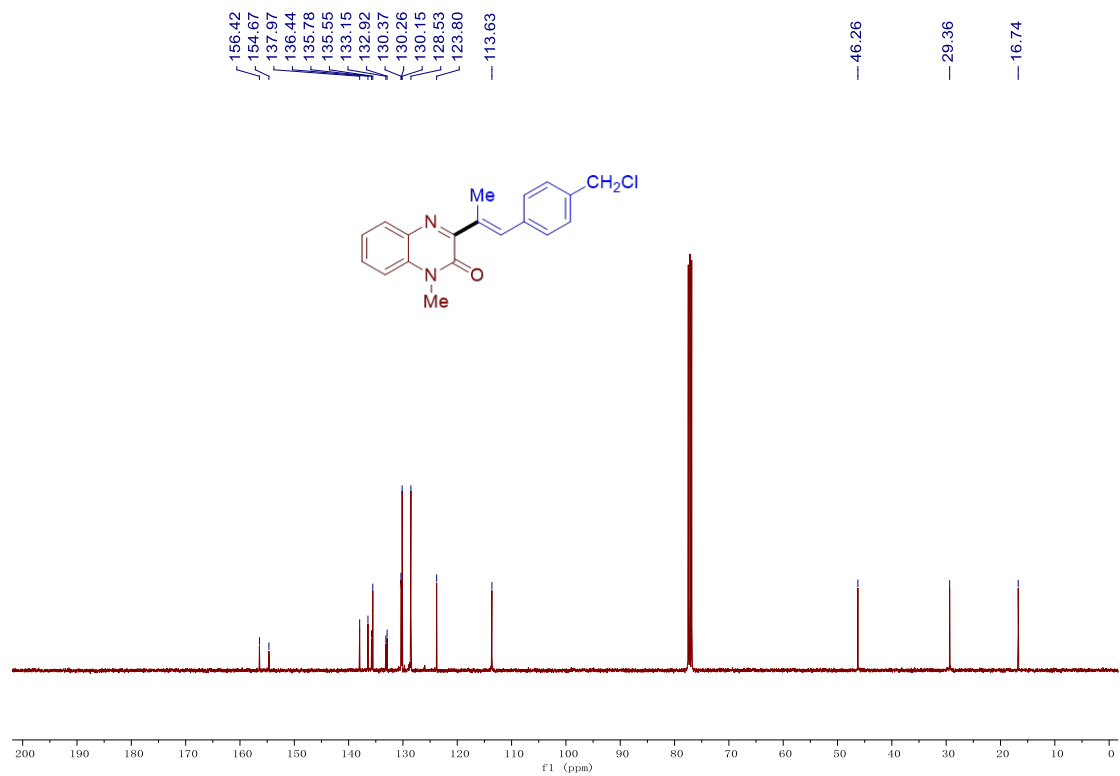
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **3ae**



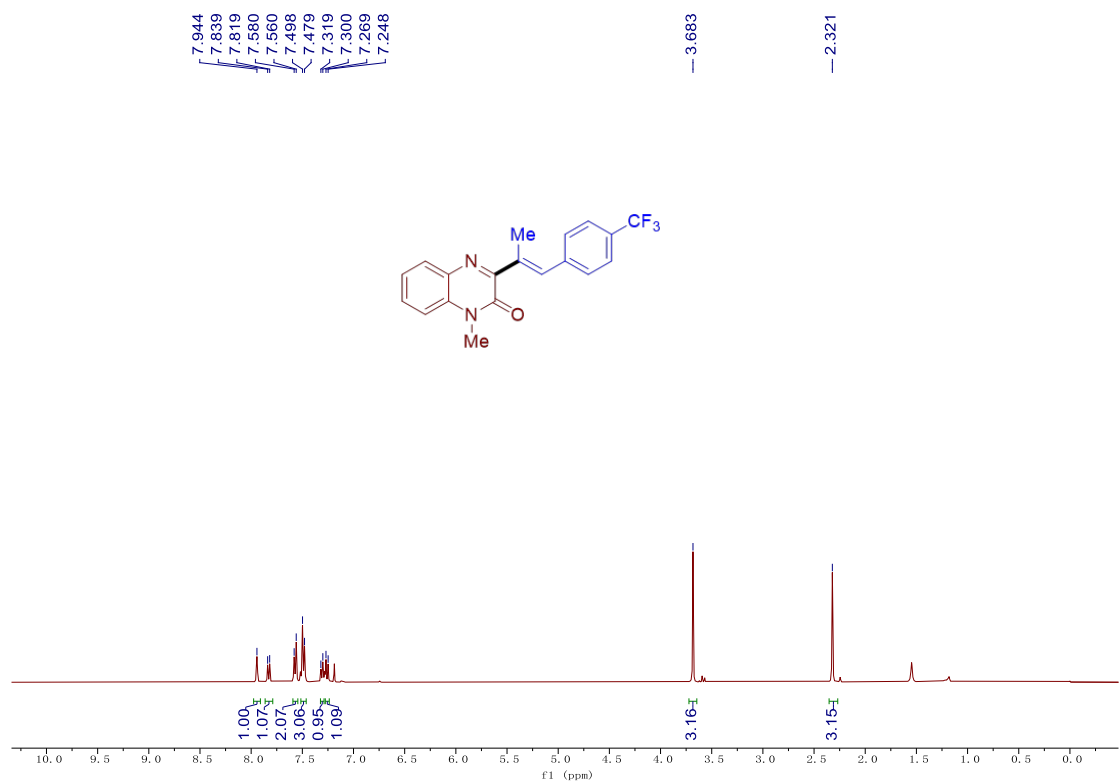
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ae**



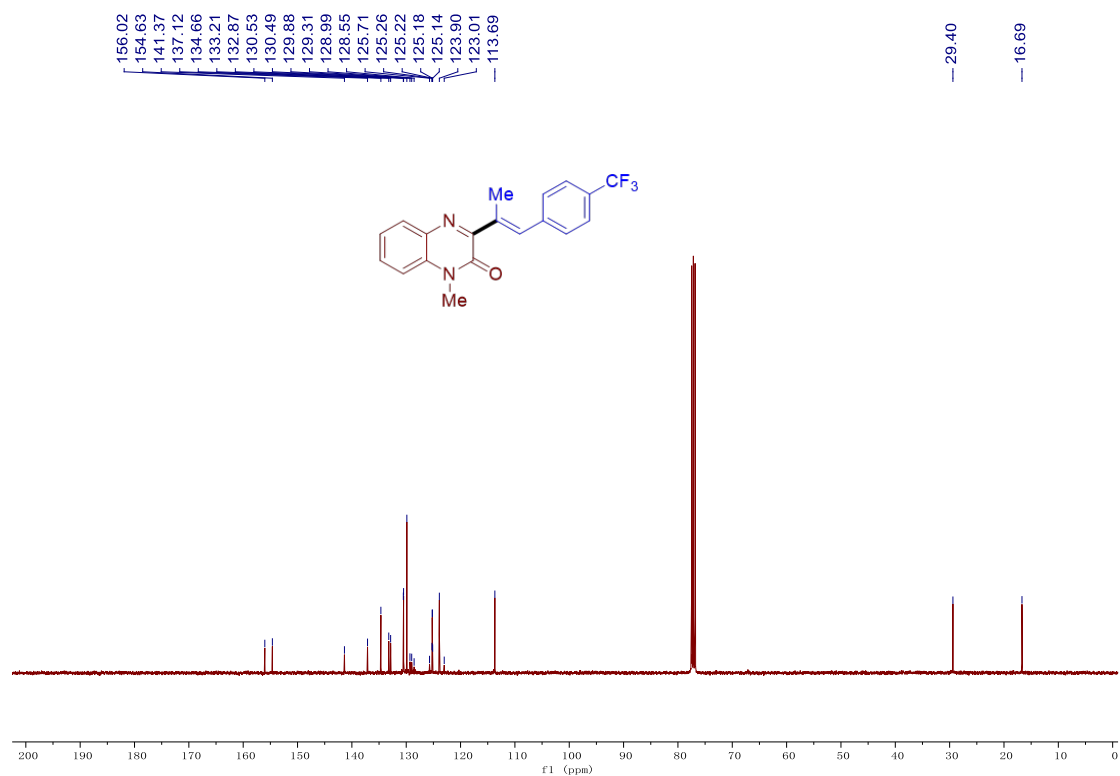
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3af**



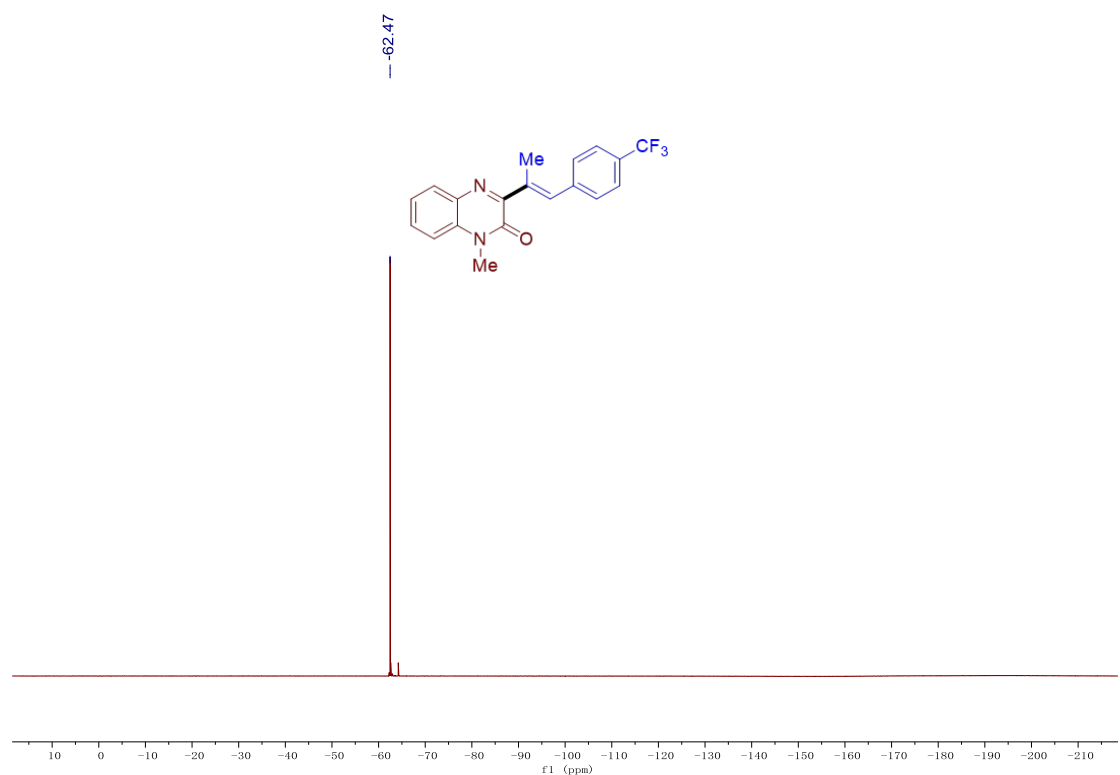
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3af**



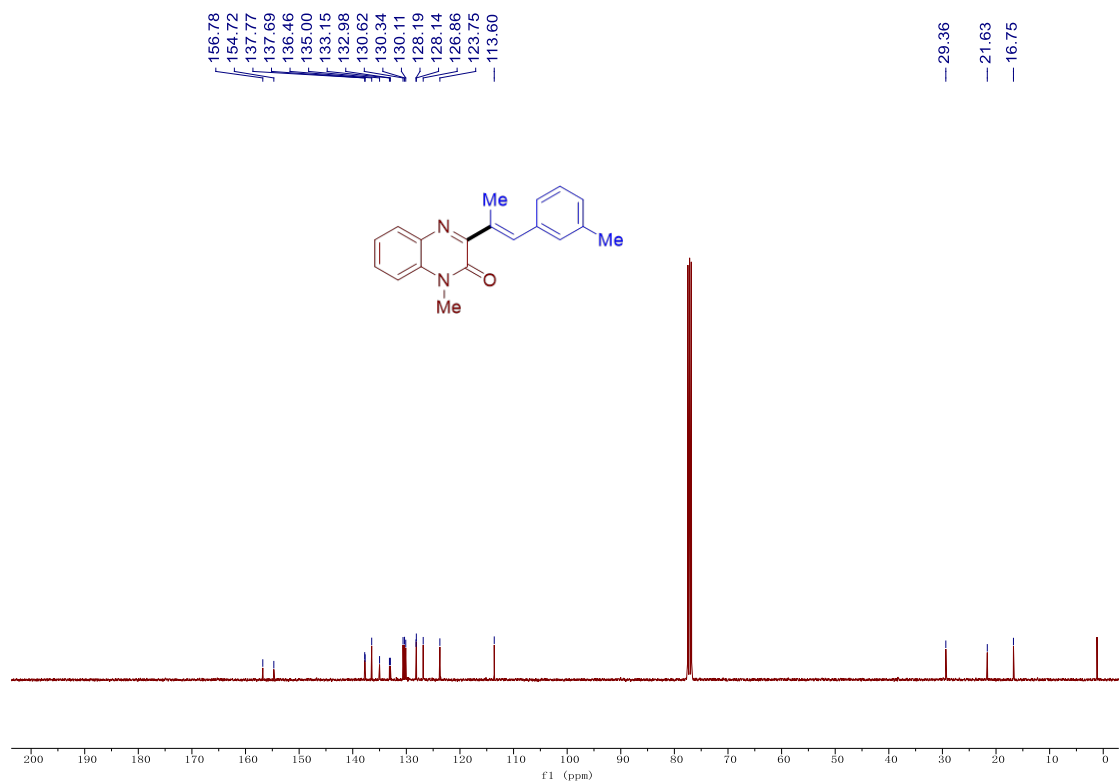
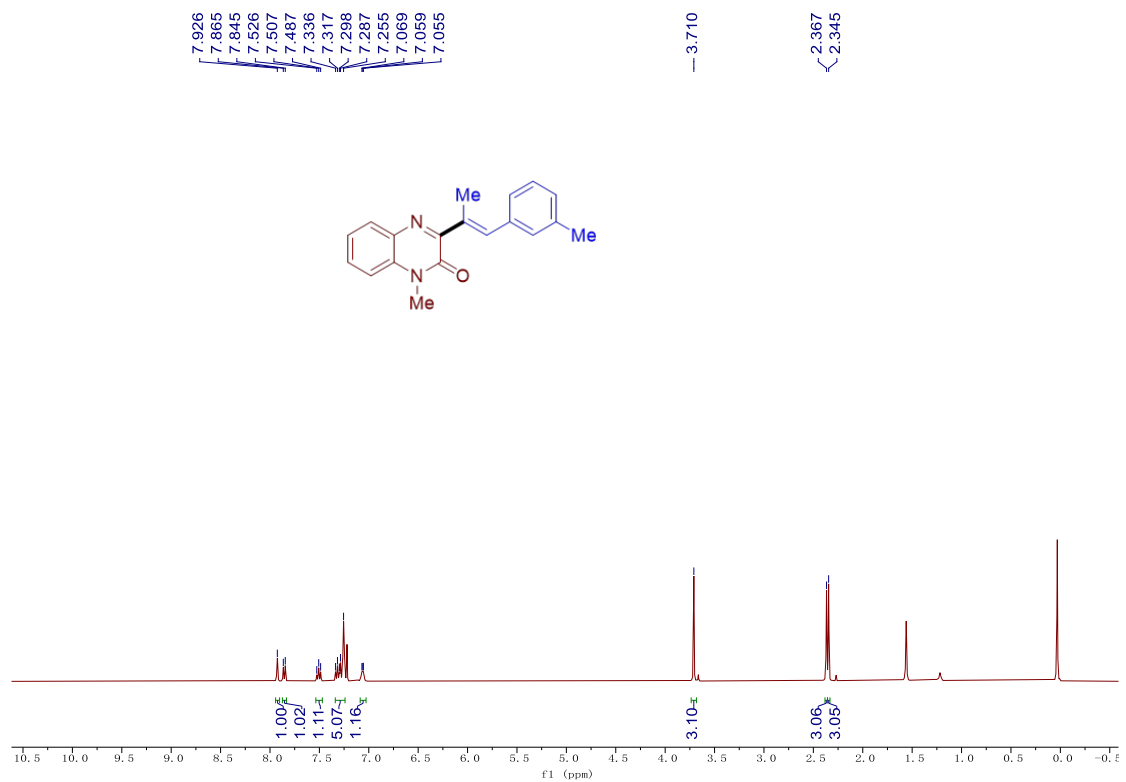
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ag**

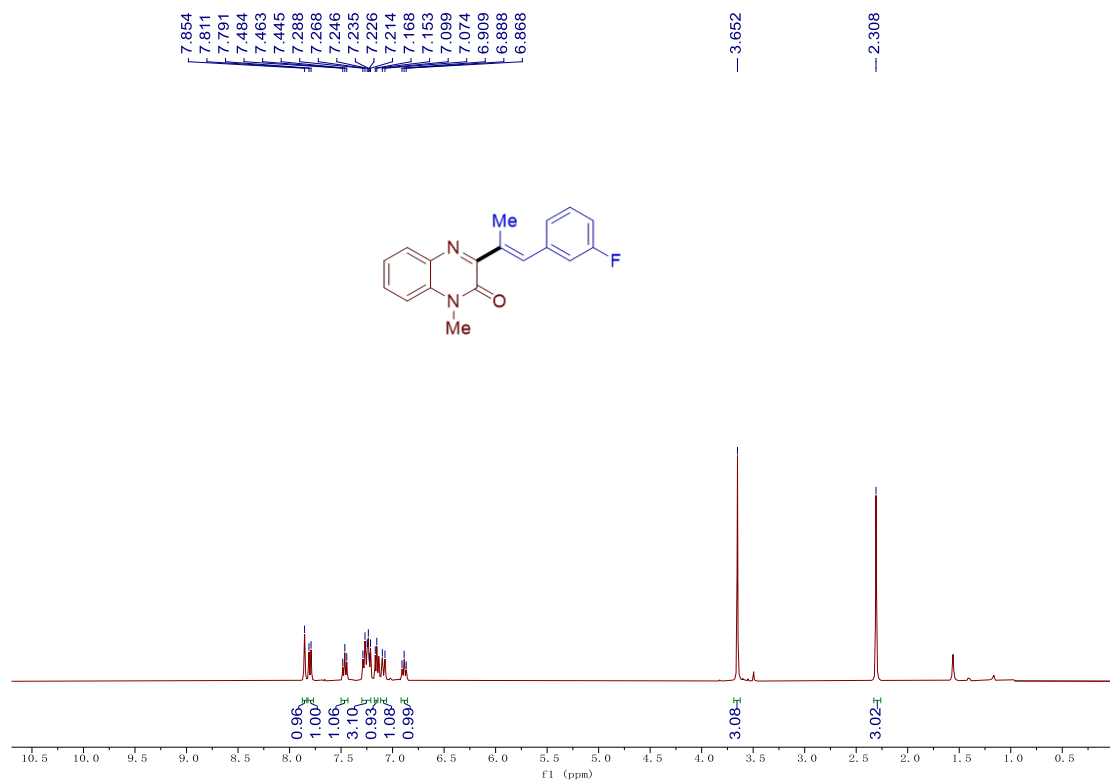


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ag**

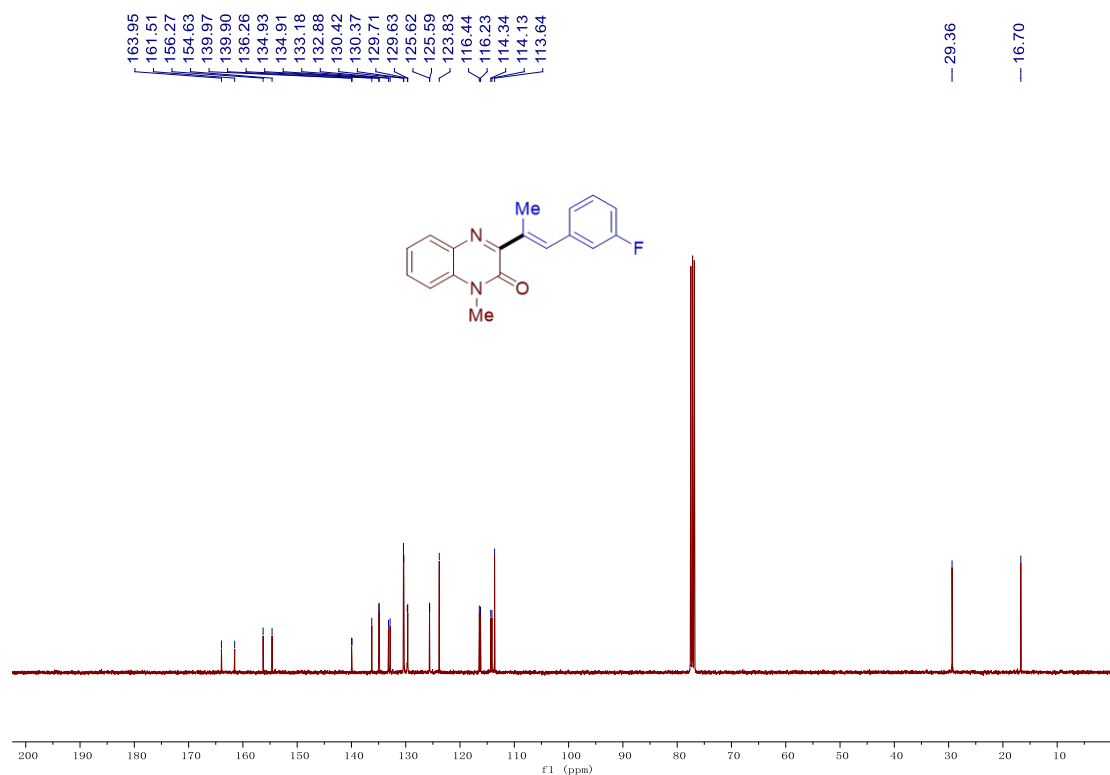


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of **3ag**

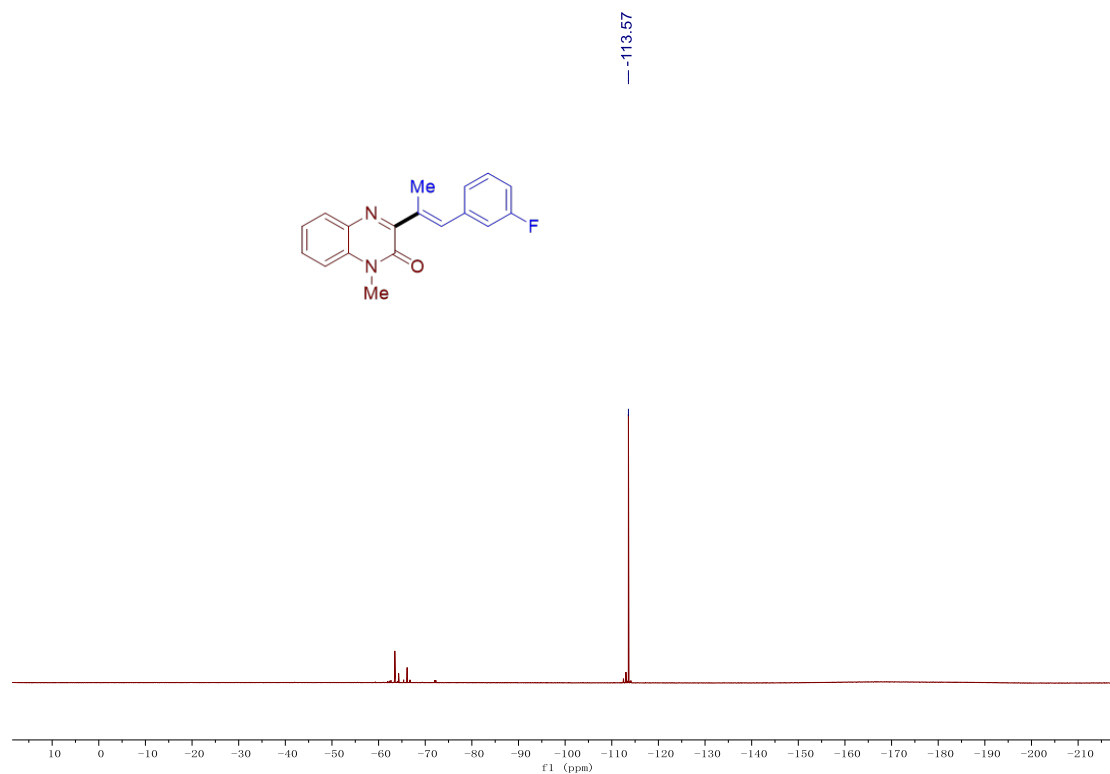




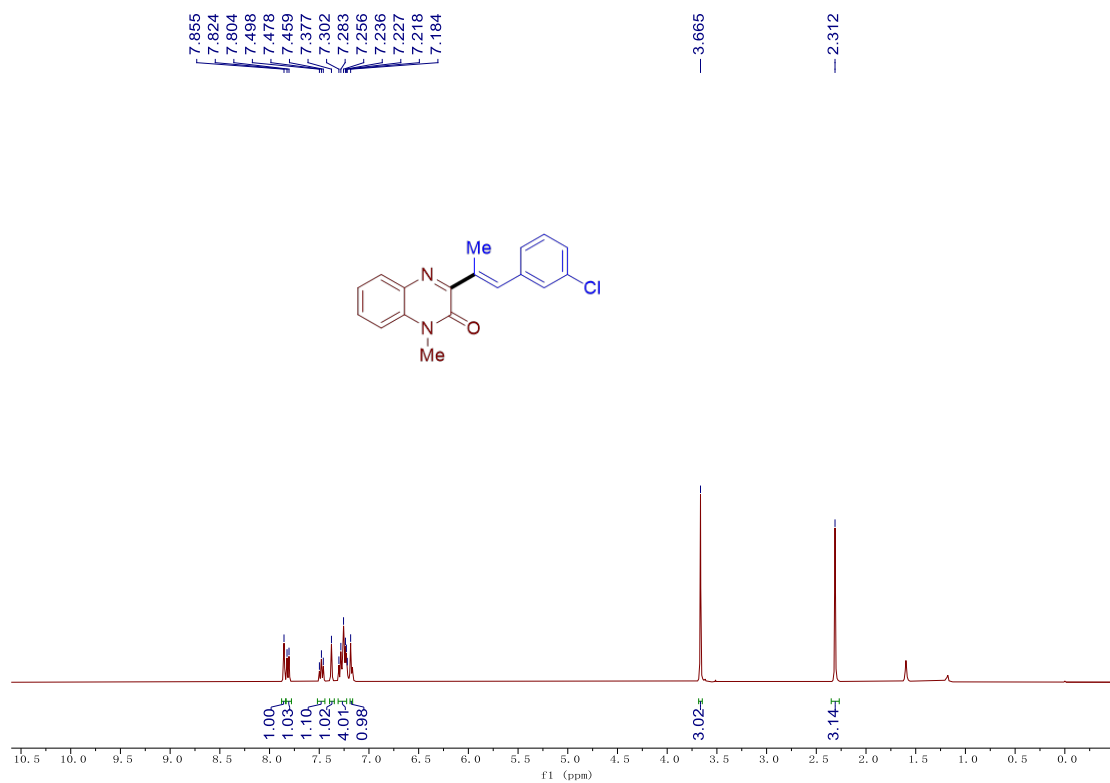
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ai**



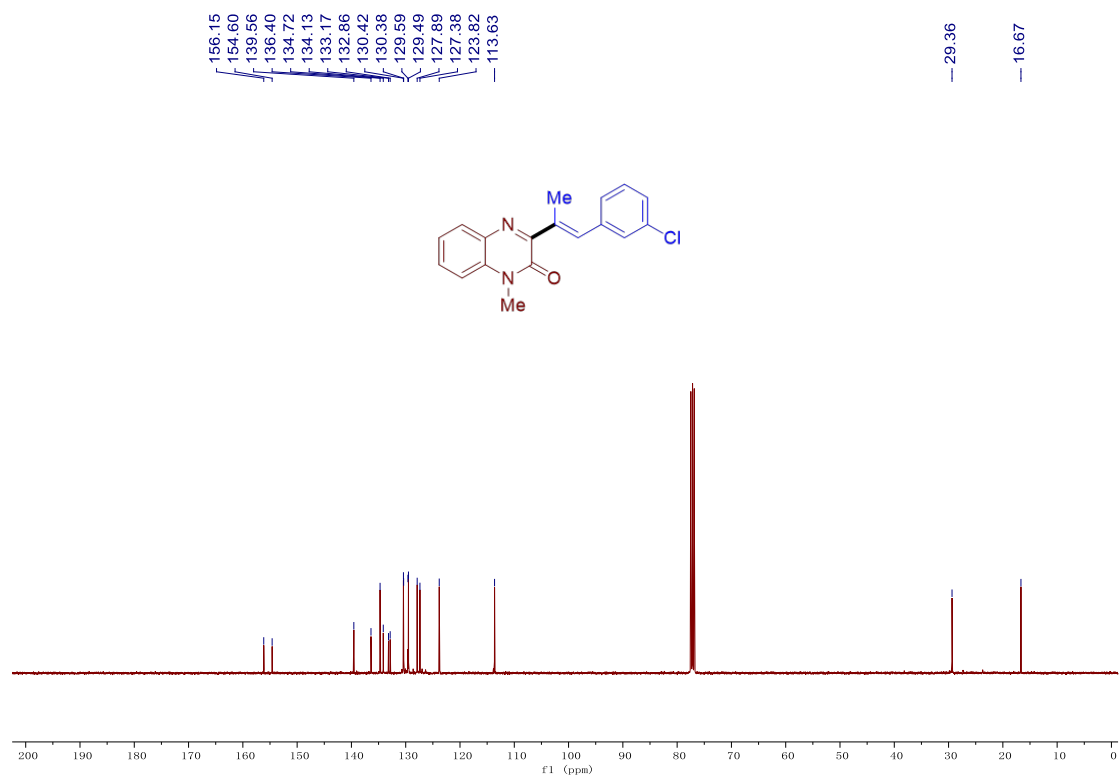
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ai**



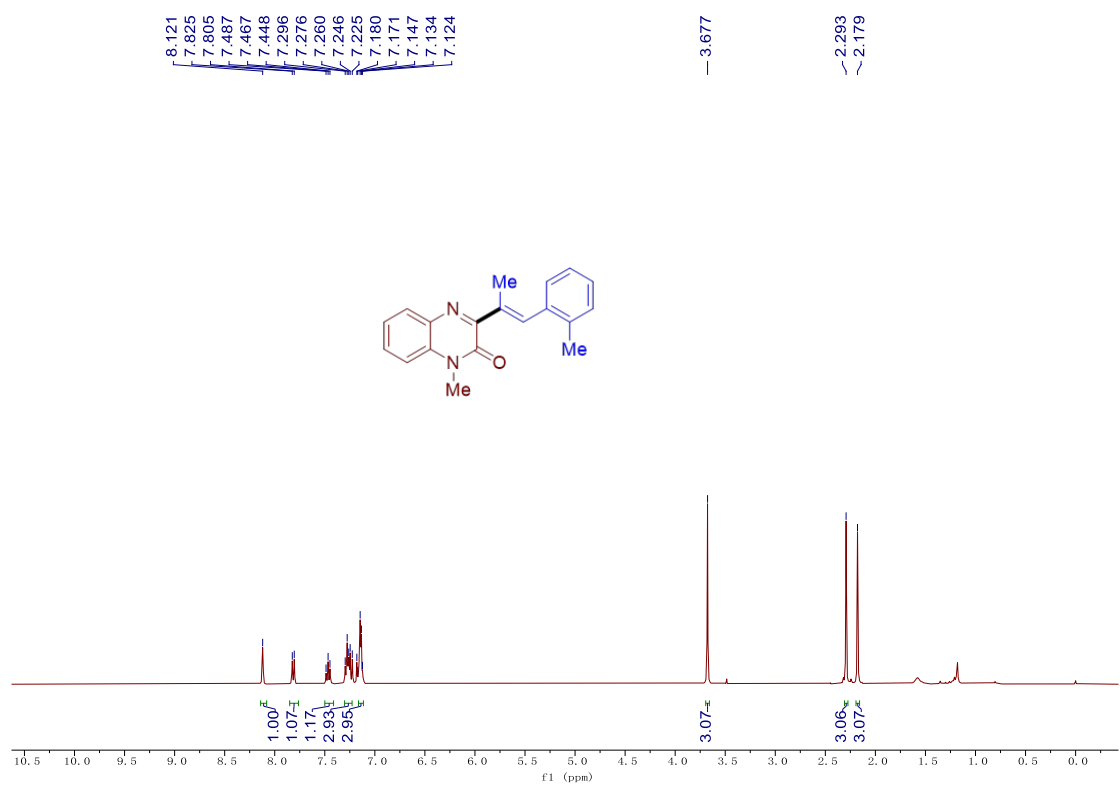
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra of 3ai



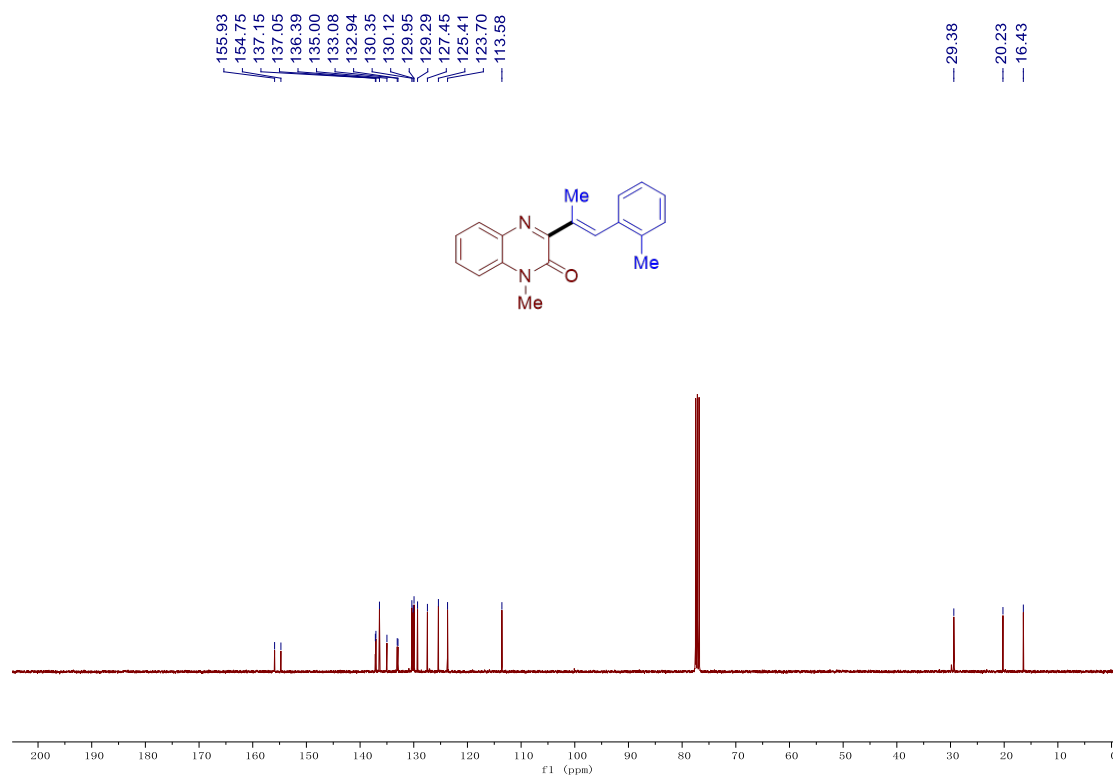
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of 3aj



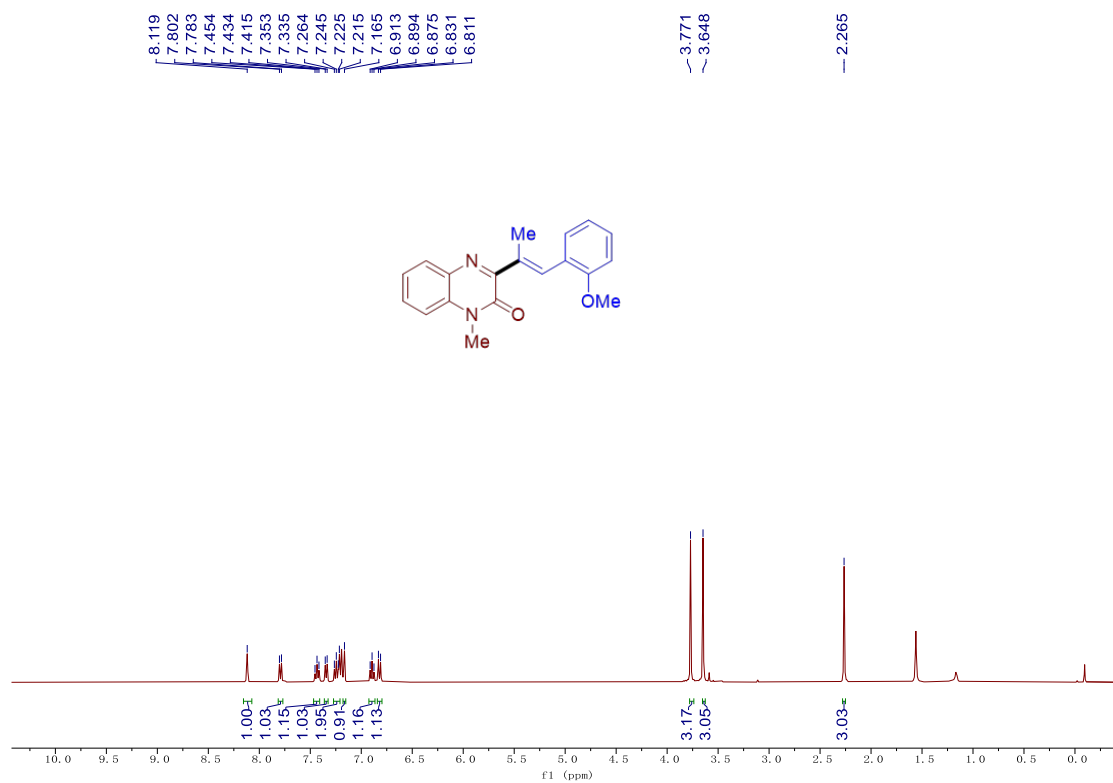
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3aj**



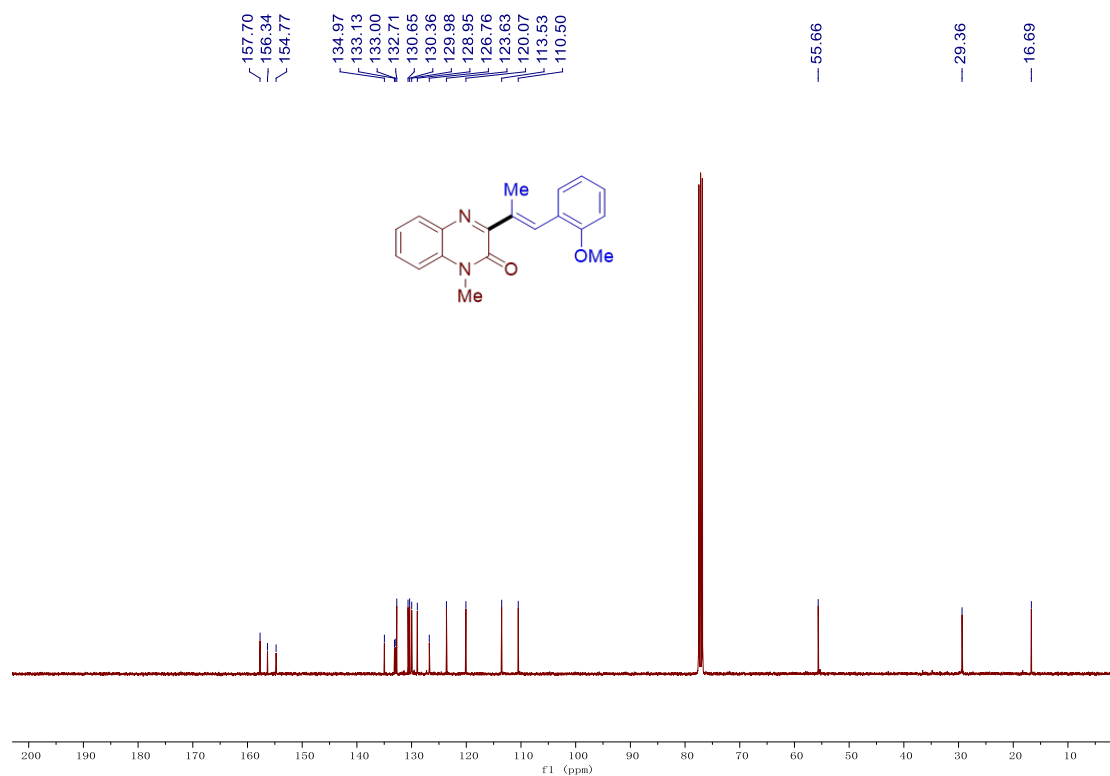
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3ak**



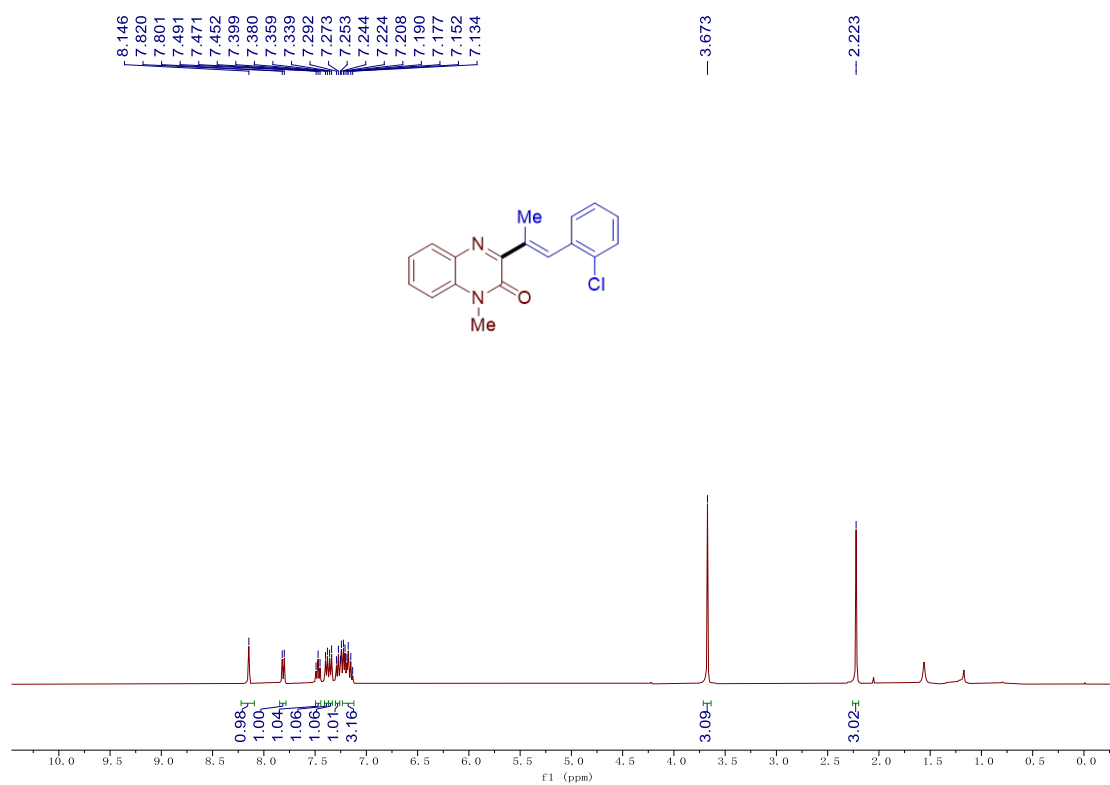
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **3ak**



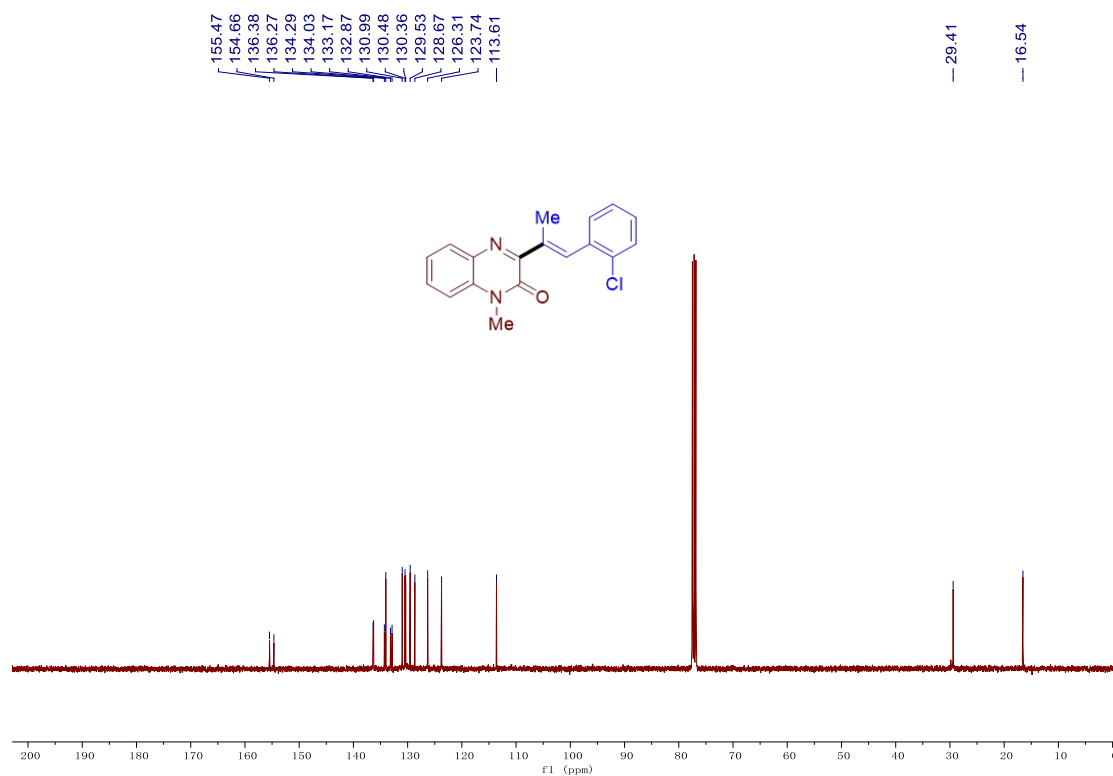
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **3al**



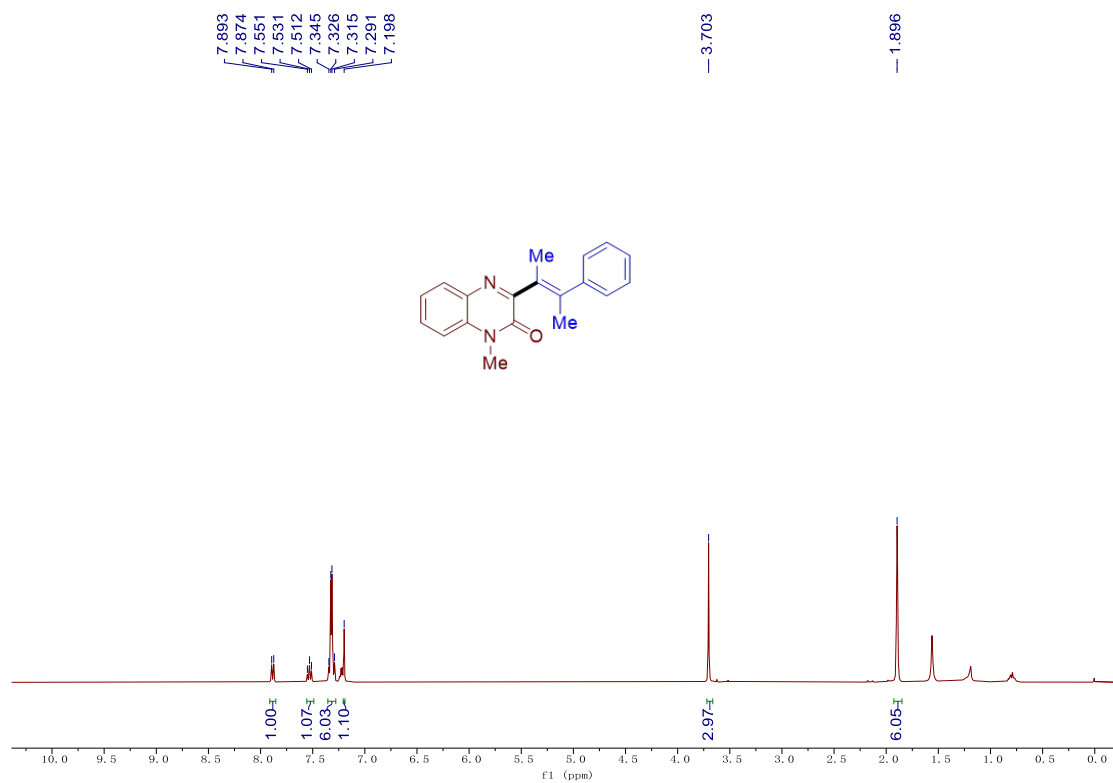
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3al**



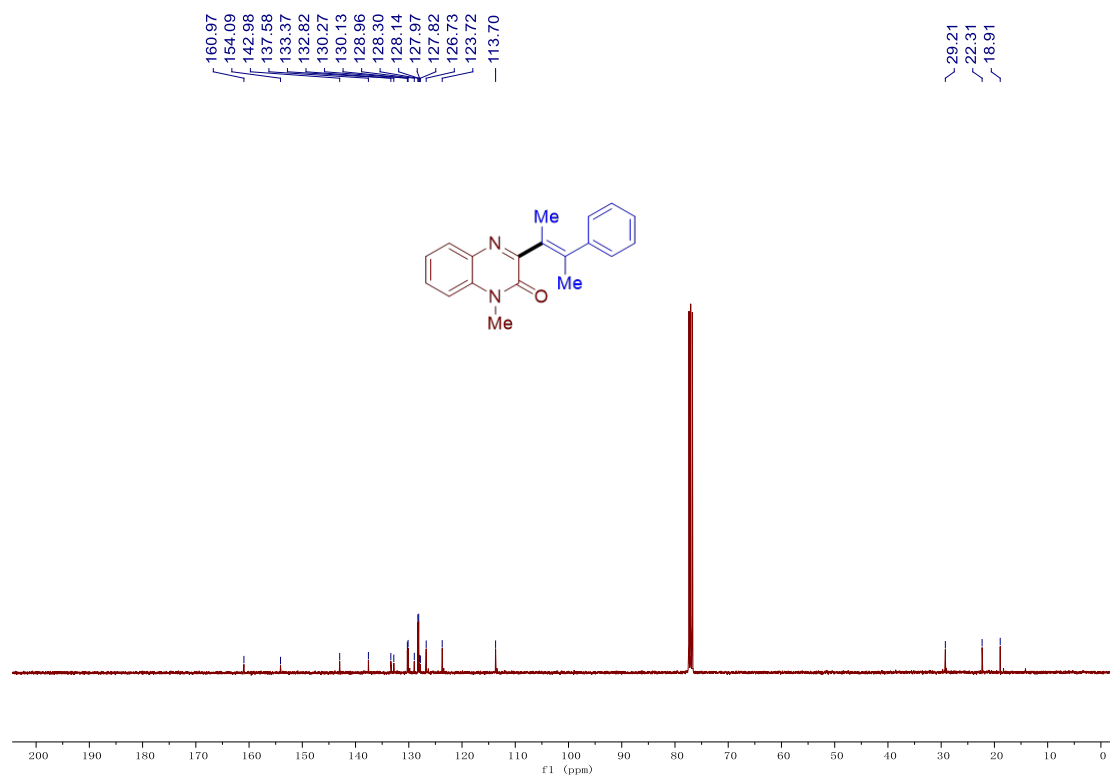
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3am**



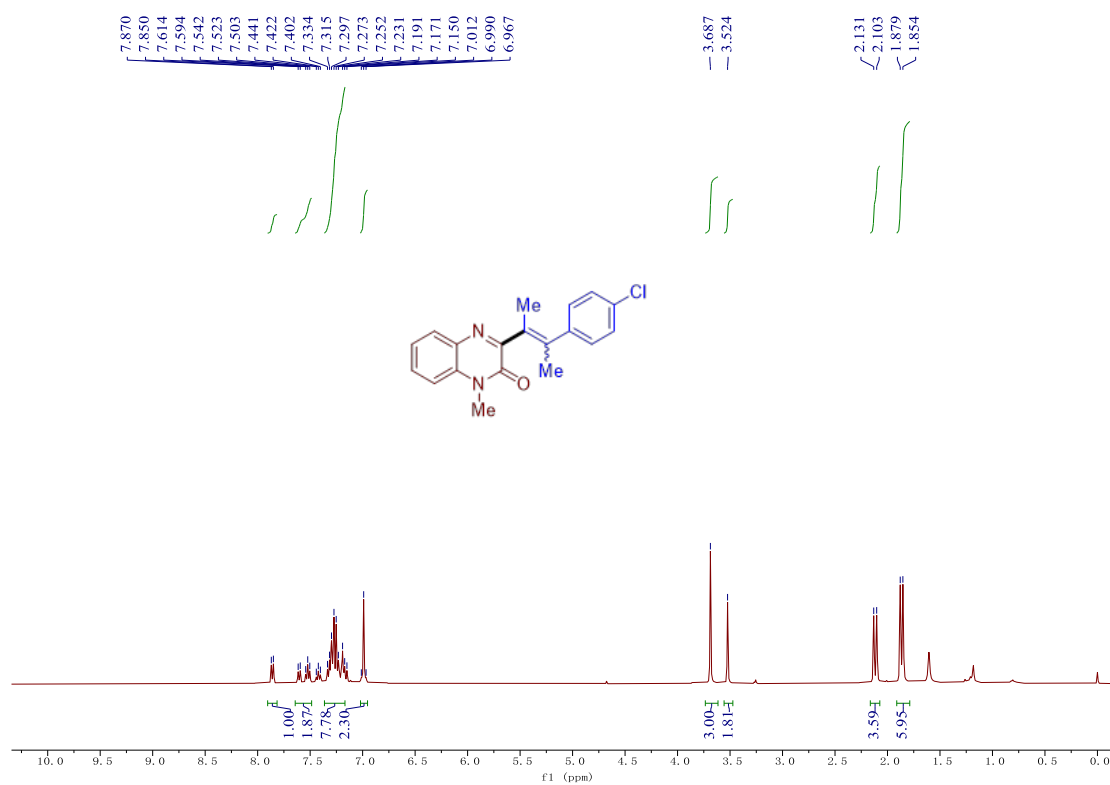
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3am**



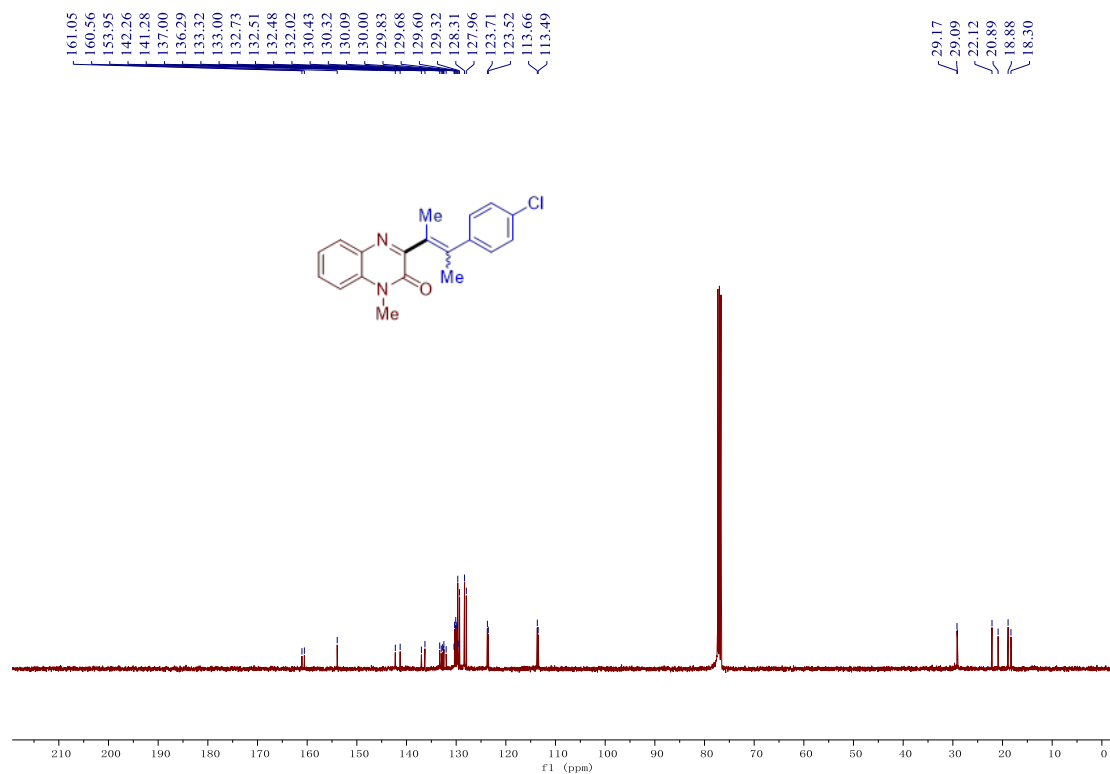
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **3am**



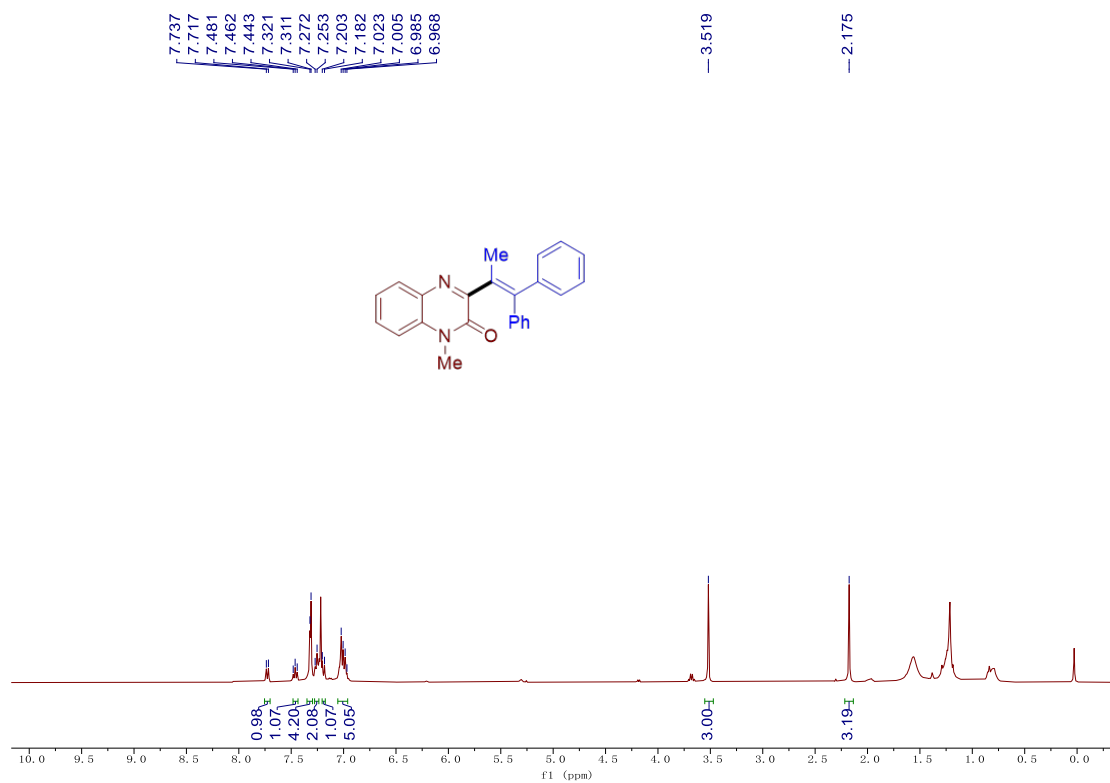
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **3an**



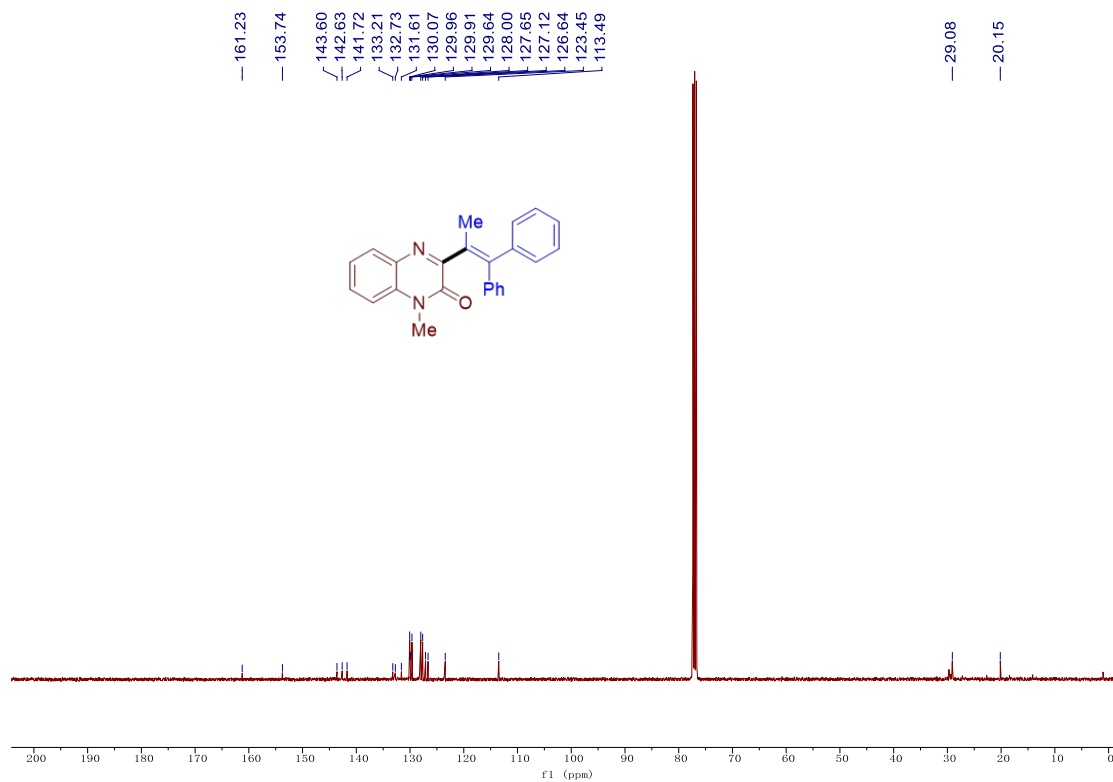
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **3ao**



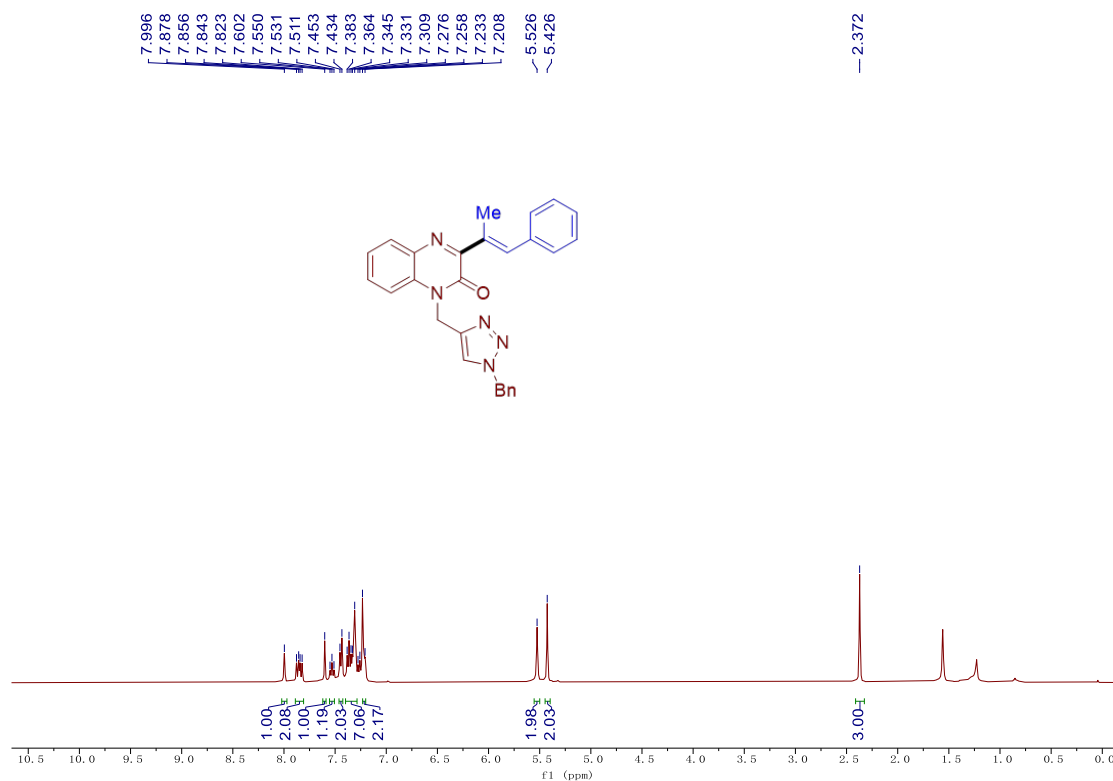
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **3ao**



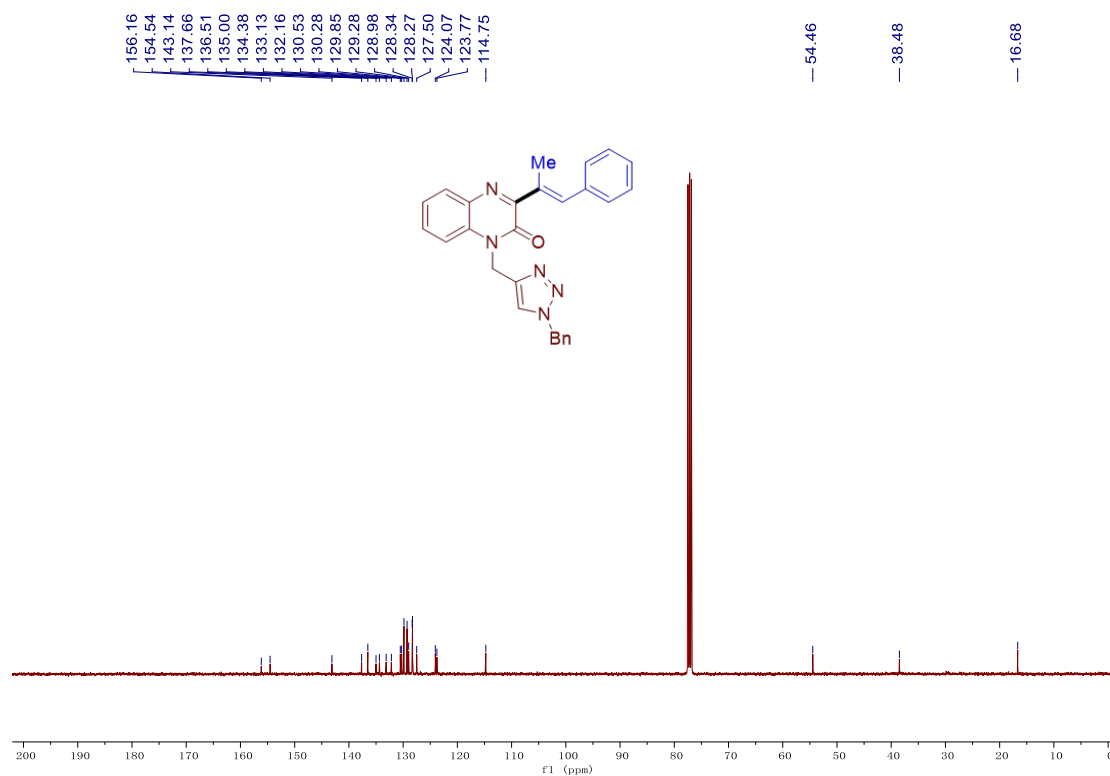
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **3ap**



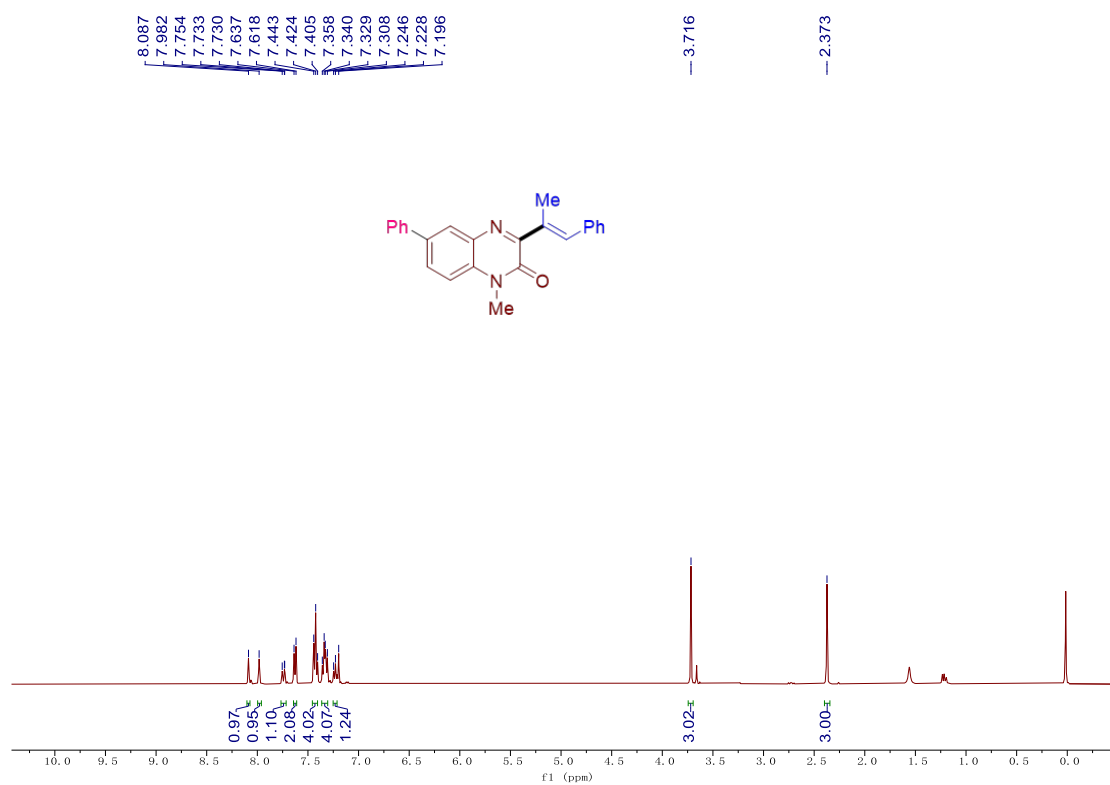
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of **3ap**



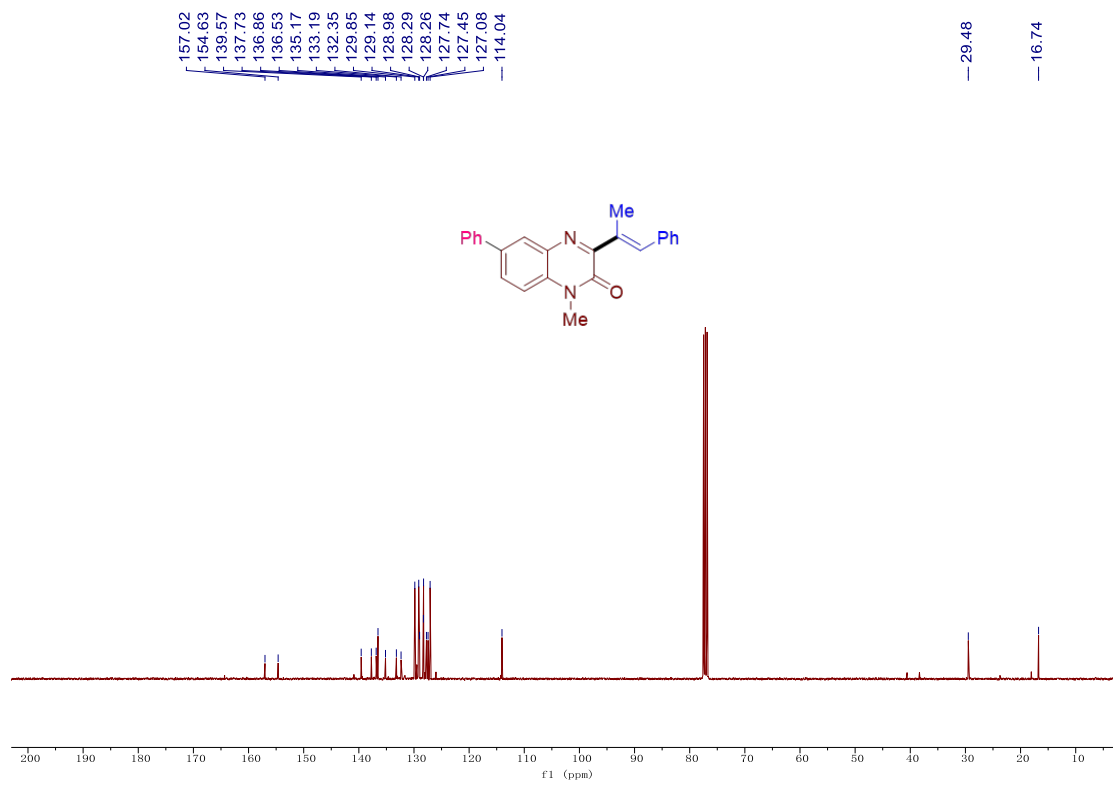
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of **4a**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of **4a**

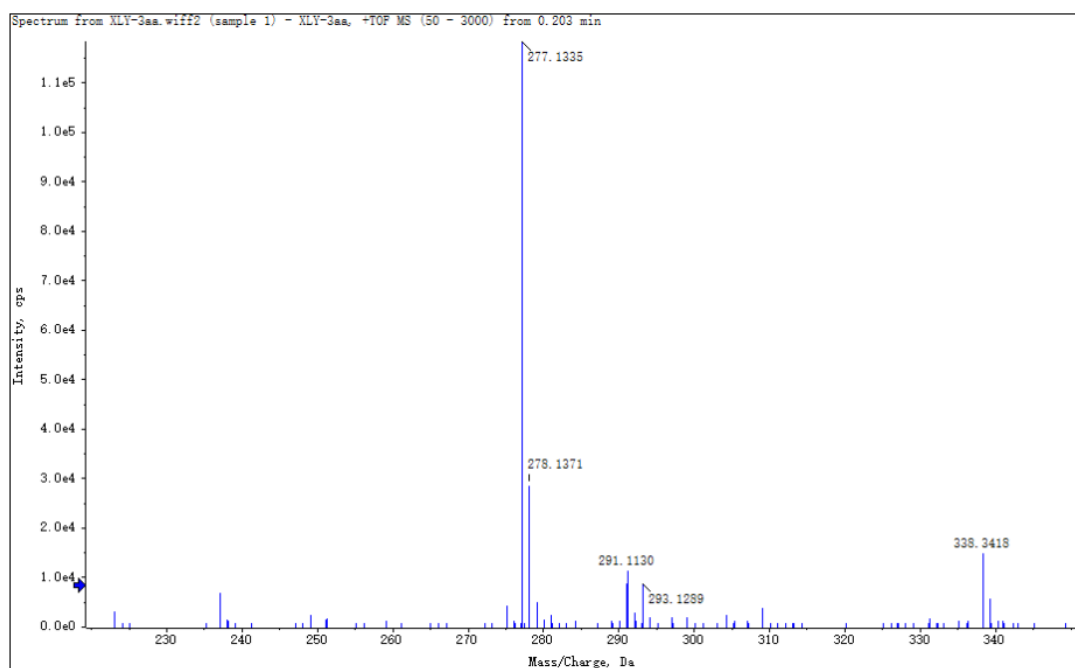


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of **4b**

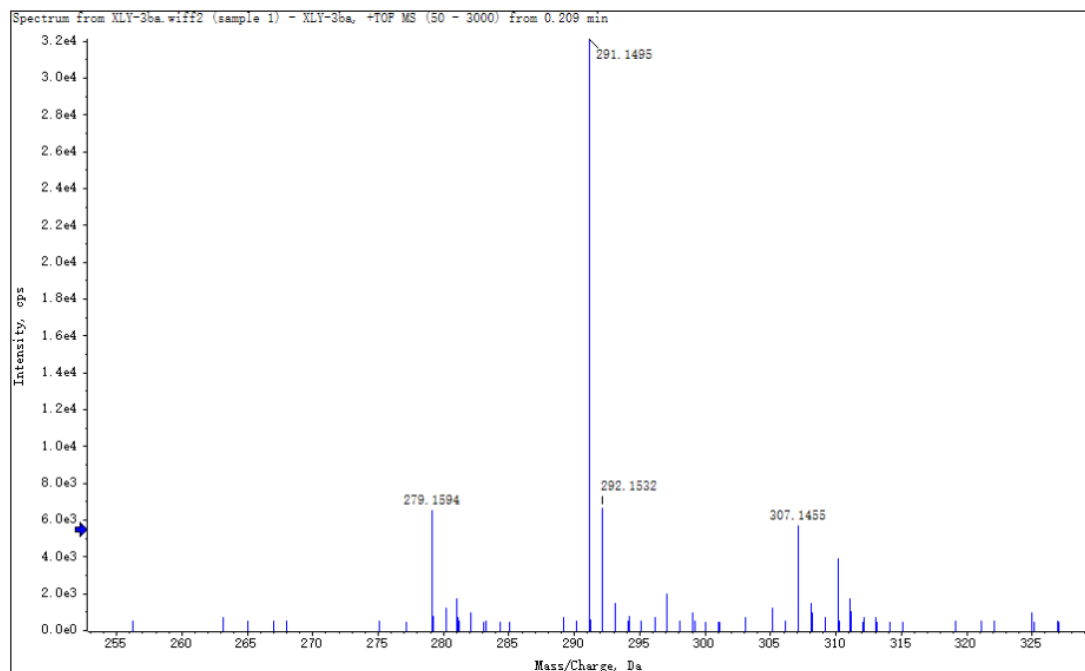


<sup>13</sup>CNMR (101 MHz, CDCl<sub>3</sub>) spectra of **4b**

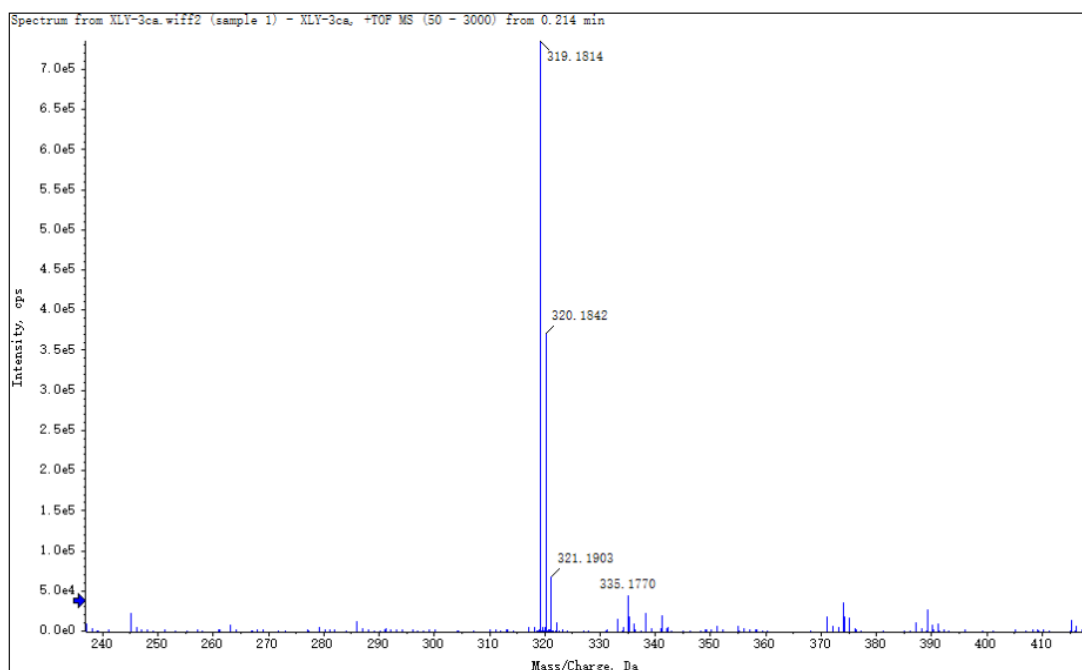
## 6. HRMS spectra of products



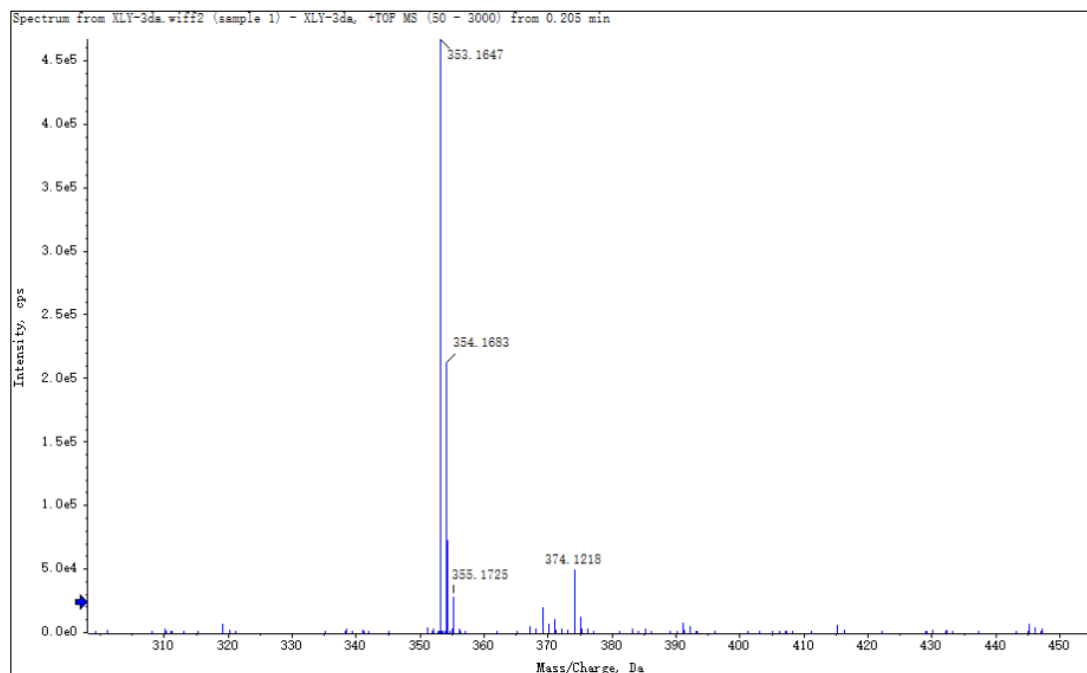
HRMS spectra of compound **3aa**



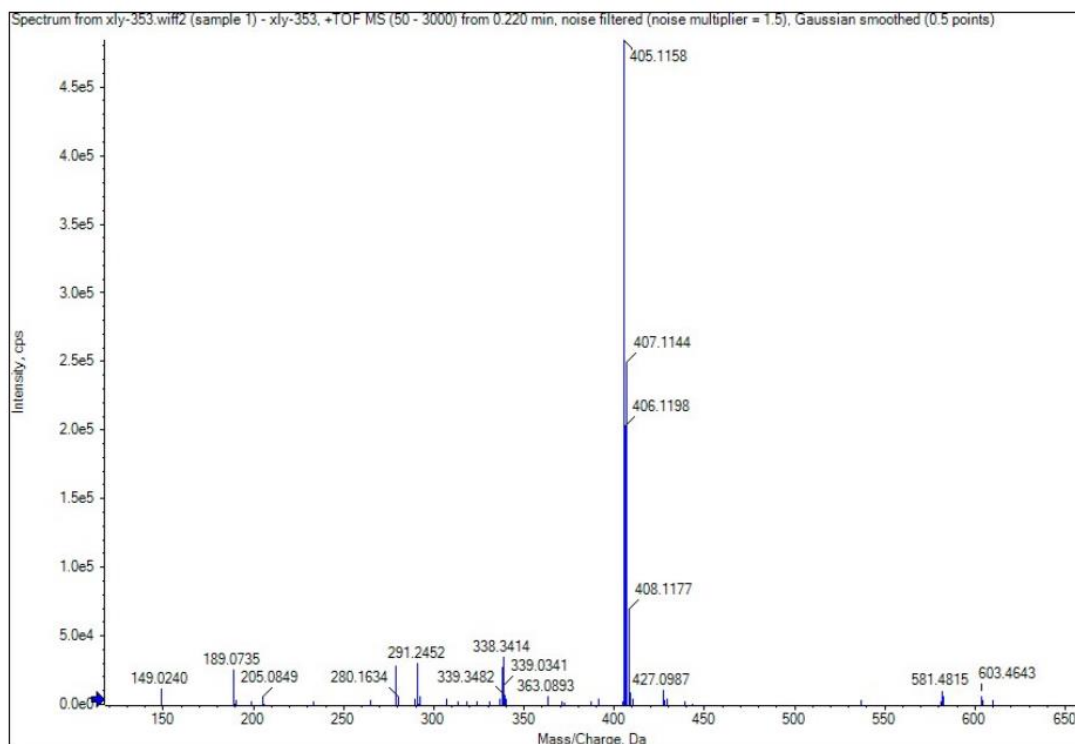
HRMS spectra of compound **3ba**



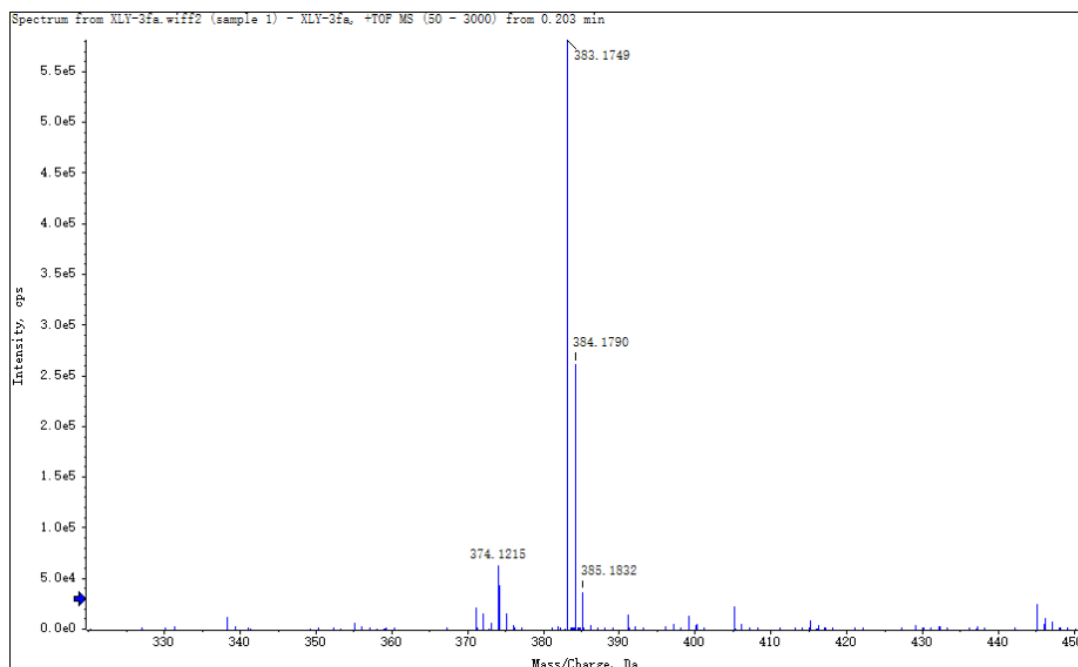
HRMS spectra of compound **3ca**



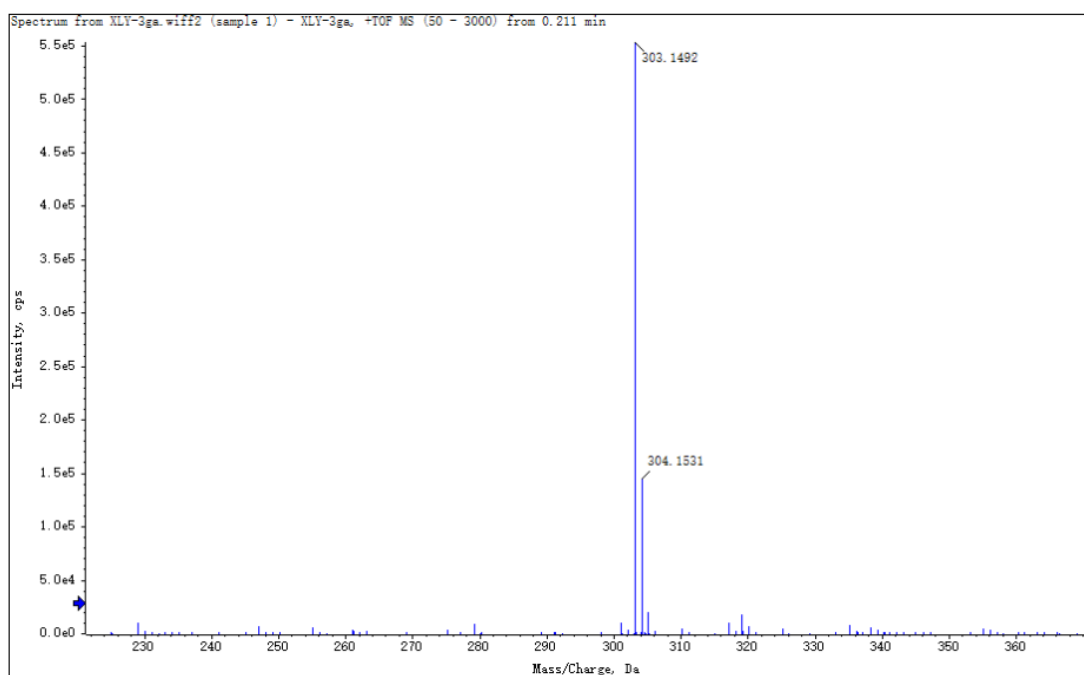
HRMS spectra of compound **3da**



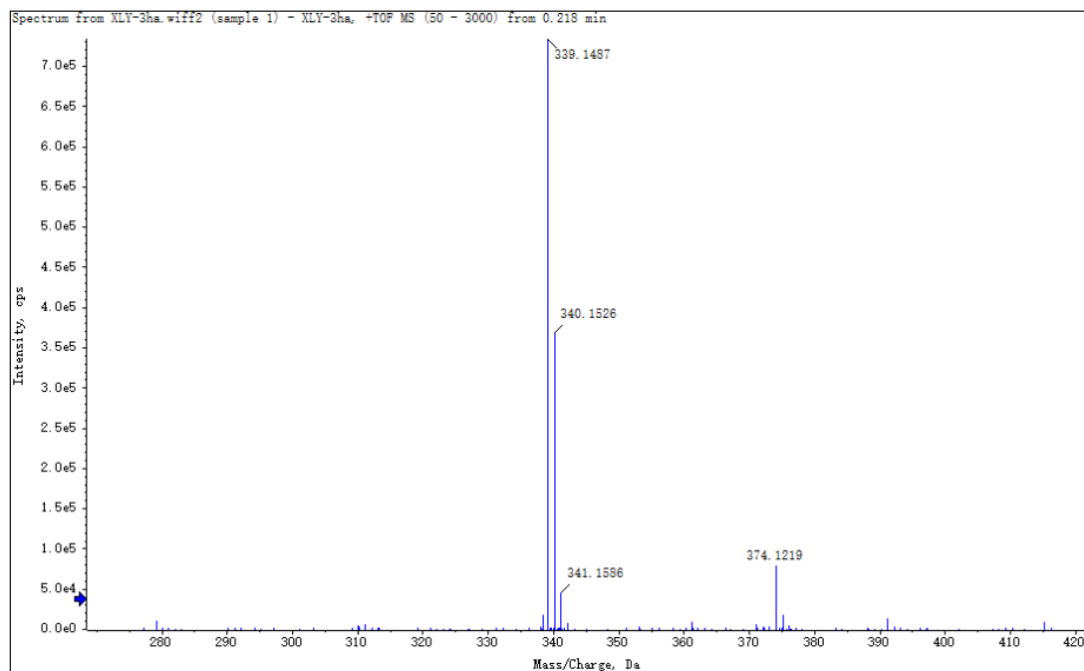
HRMS spectra of compound **3ea**



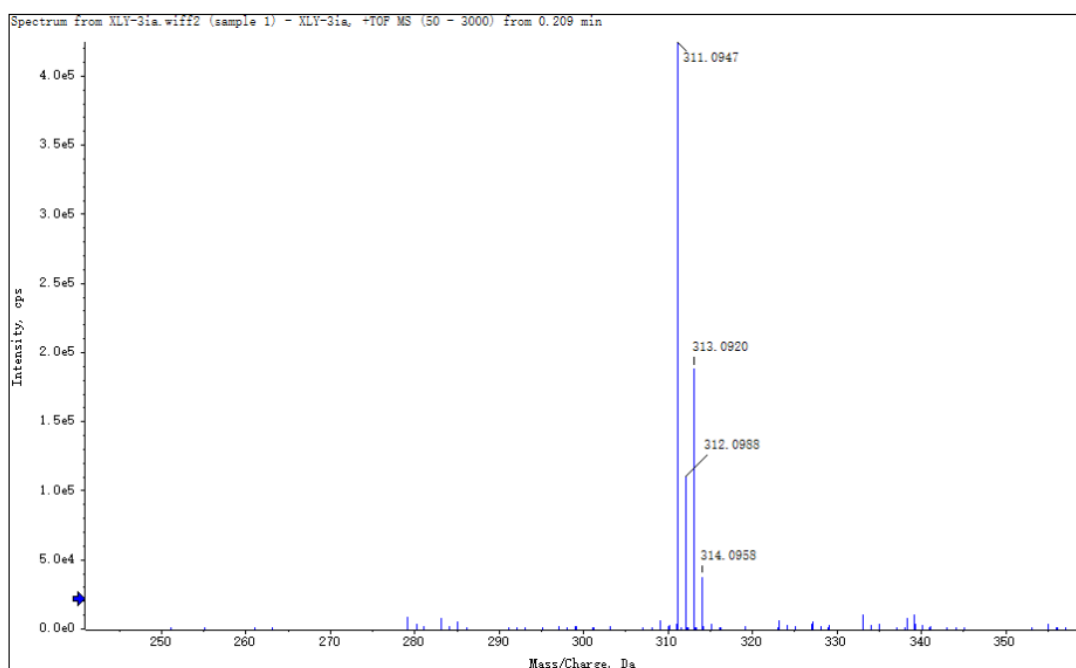
HRMS spectra of compound **3fa**



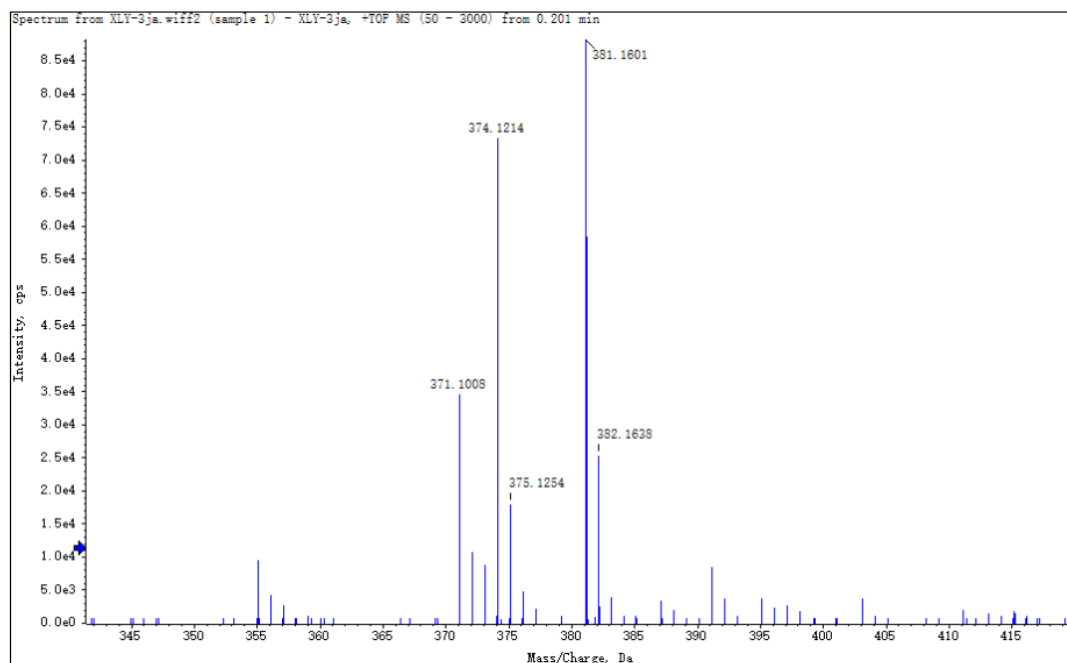
HRMS spectra of compound **3ga**



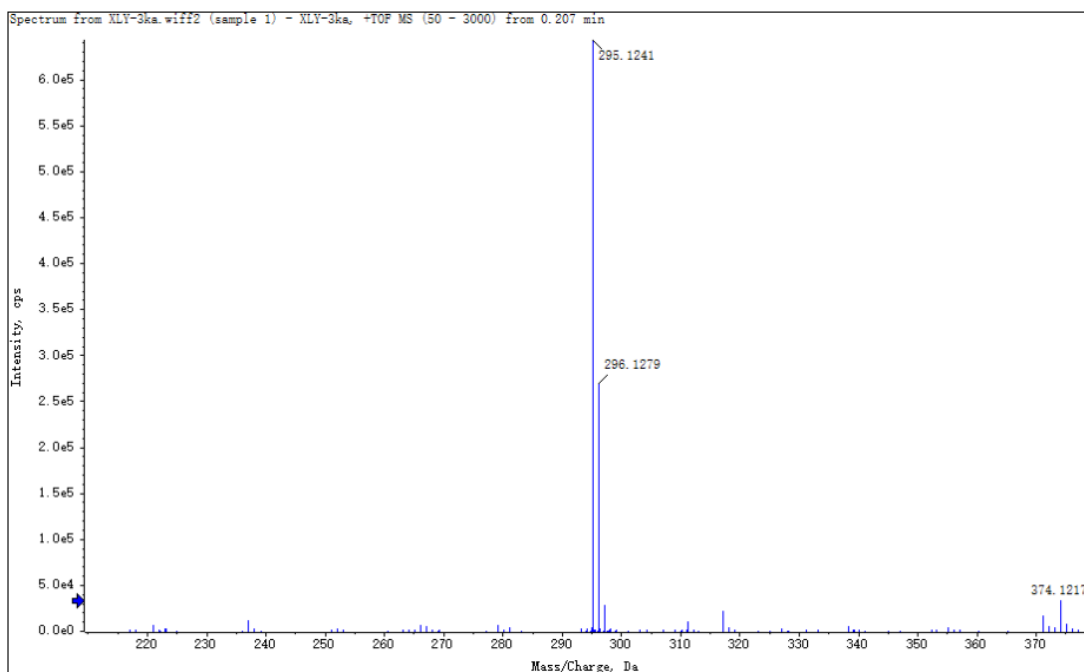
HRMS spectra of compound **3ha**



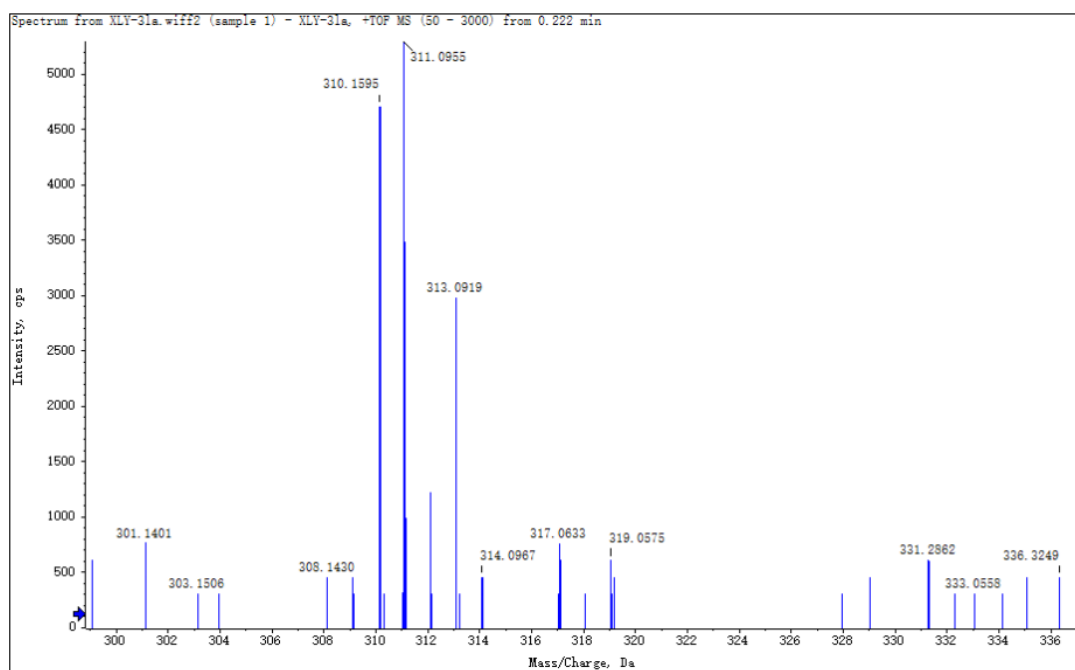
HRMS spectra of compound **3ia**



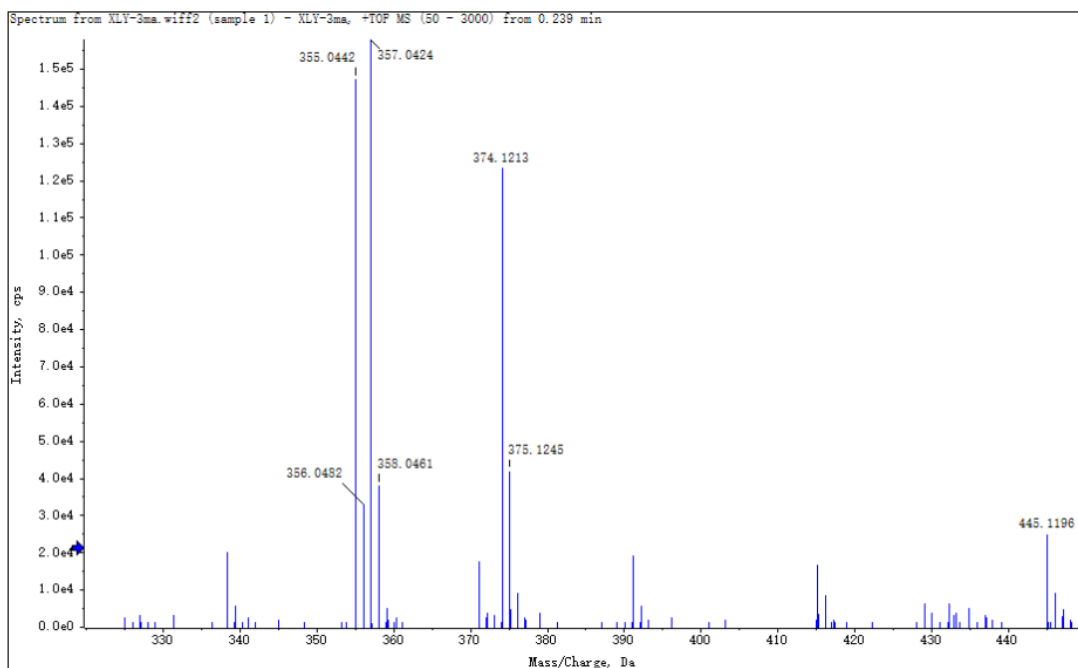
HRMS spectra of compound **3ja**



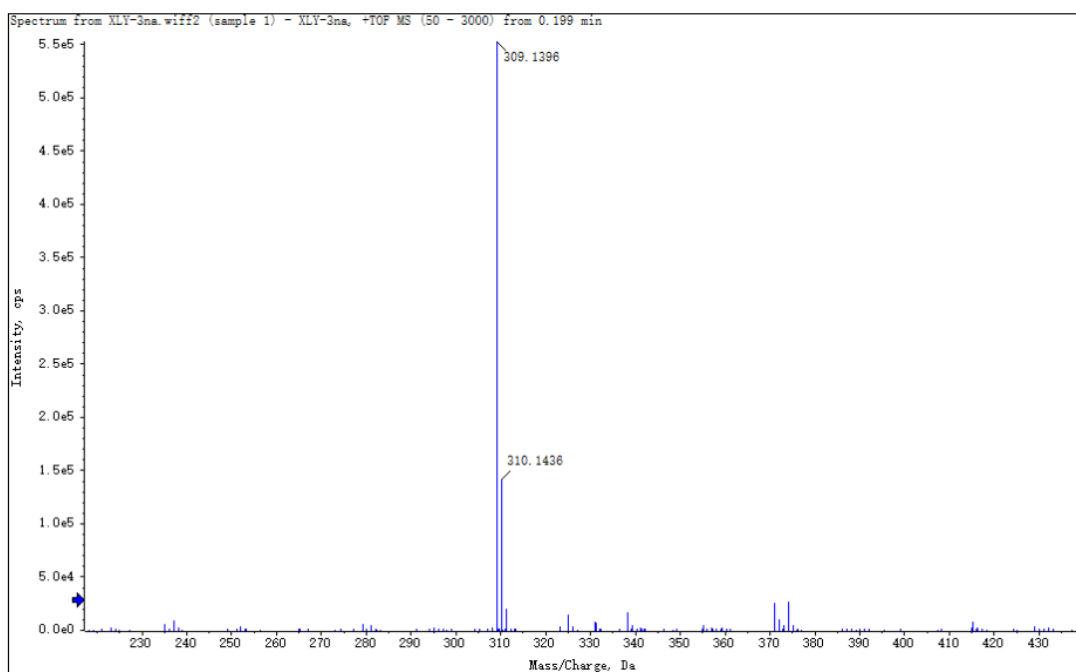
HRMS spectra of compound **3ka**



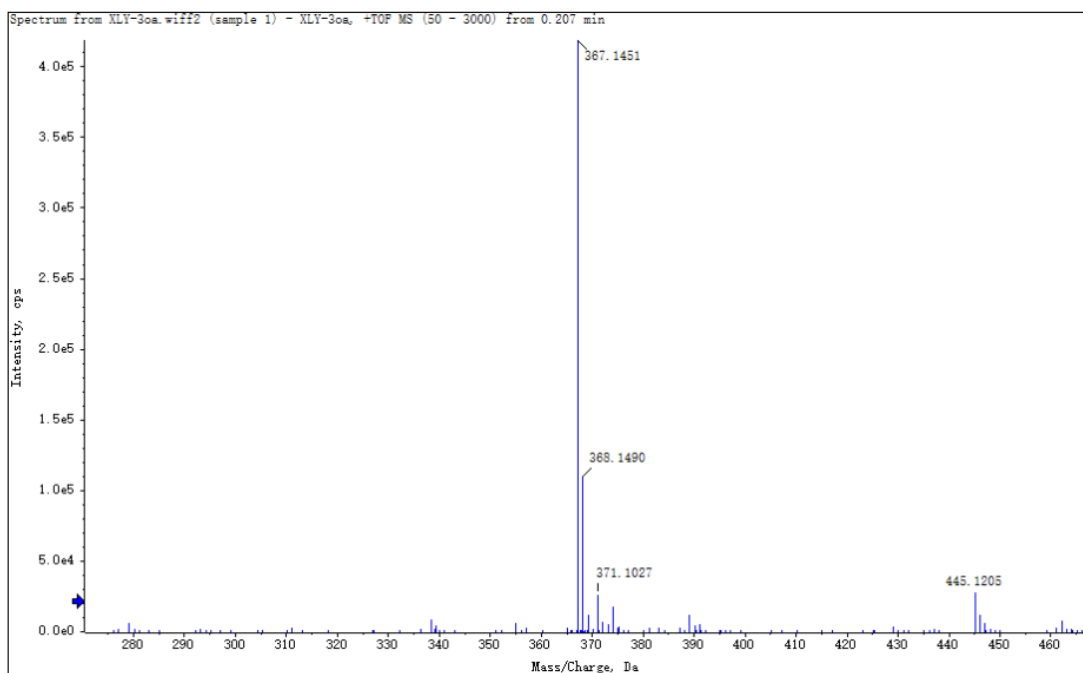
HRMS spectra of compound **3la**



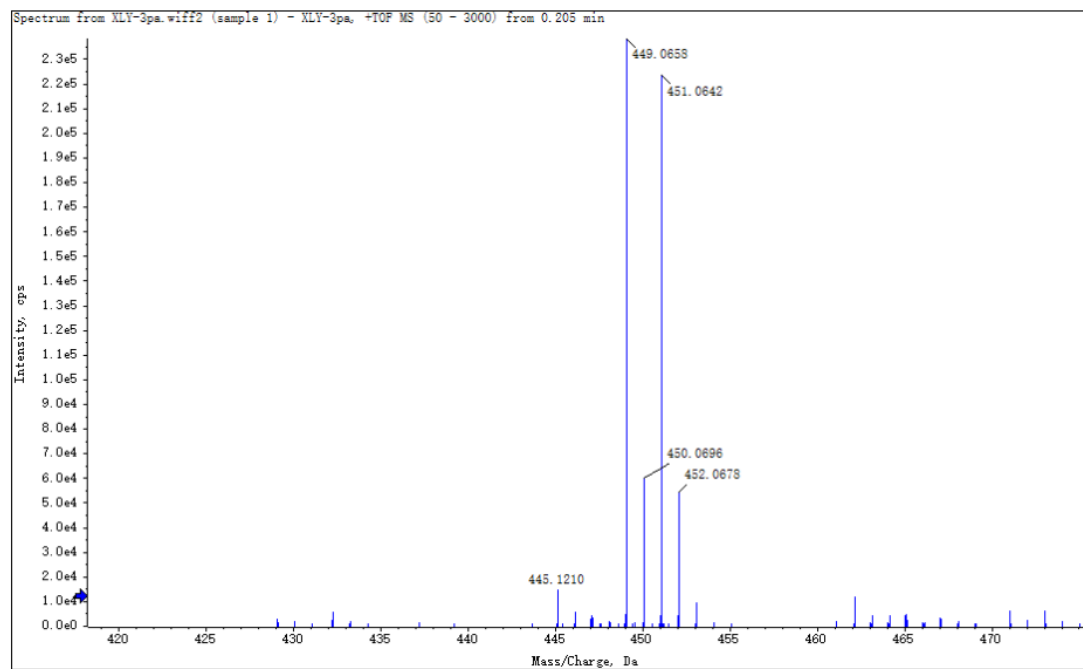
HRMS spectra of compound **3ma**



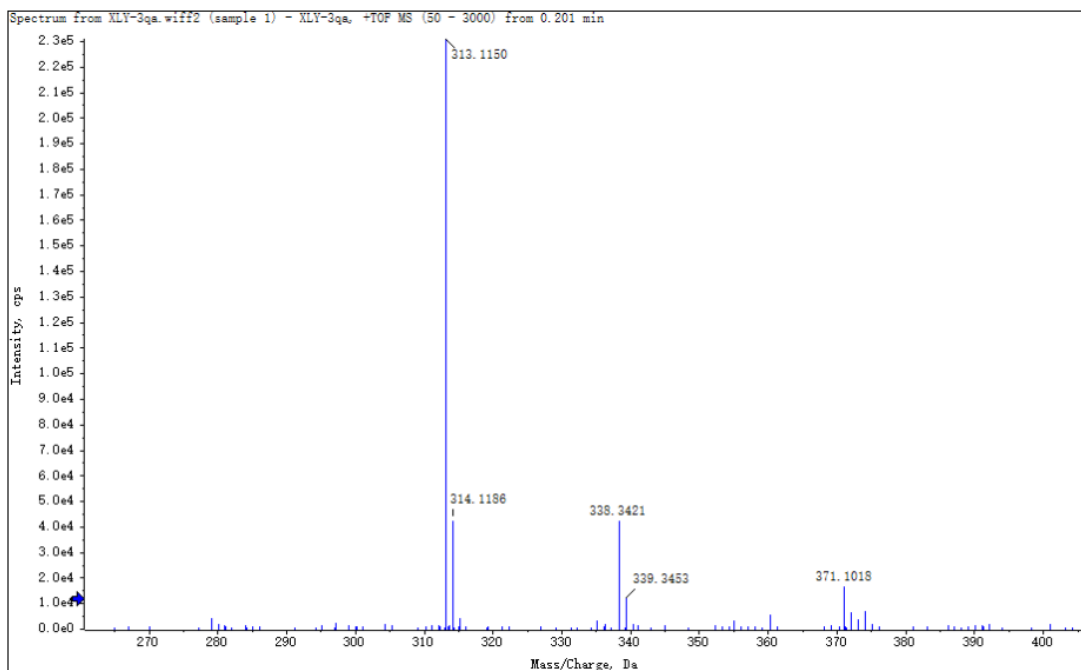
HRMS spectra of compound **3na**



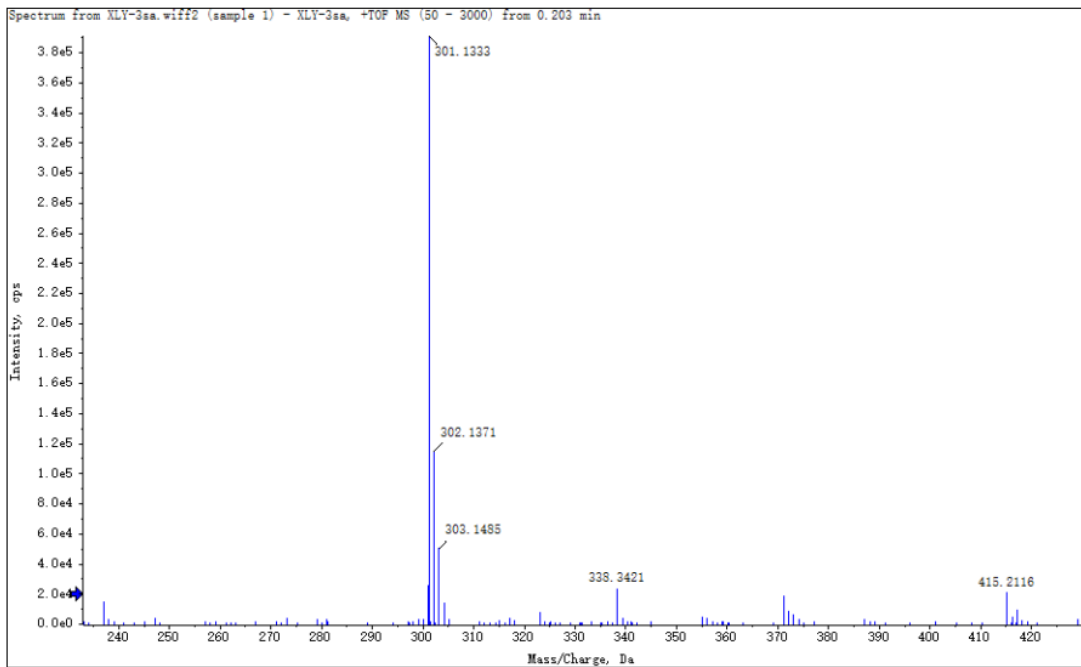
HRMS spectra of compound **30a**



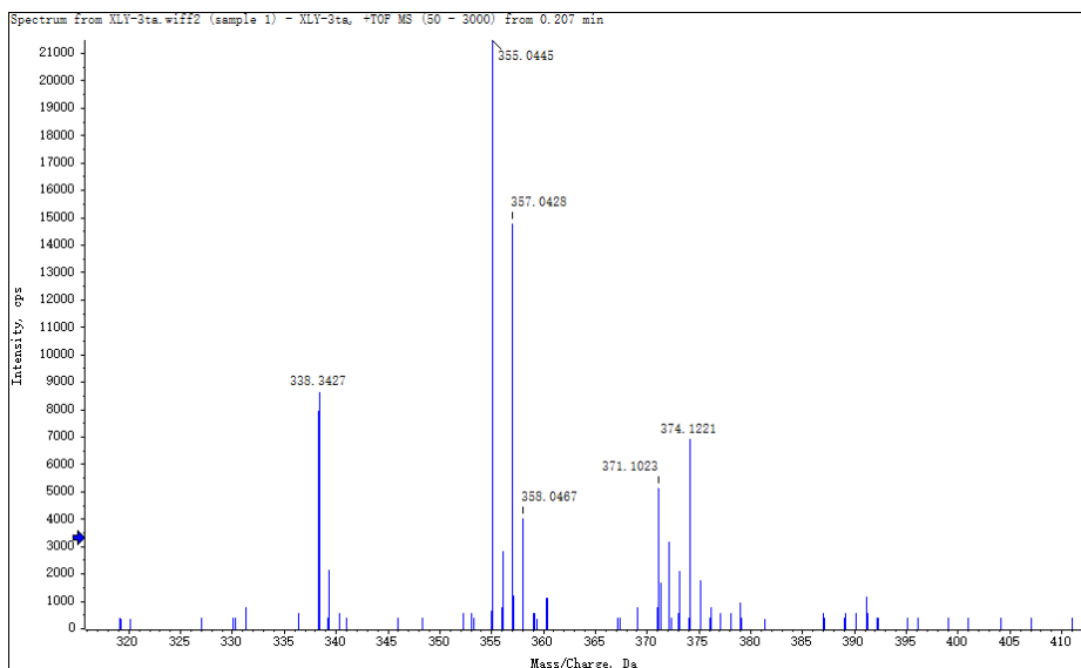
HRMS spectra of compound **3pa**



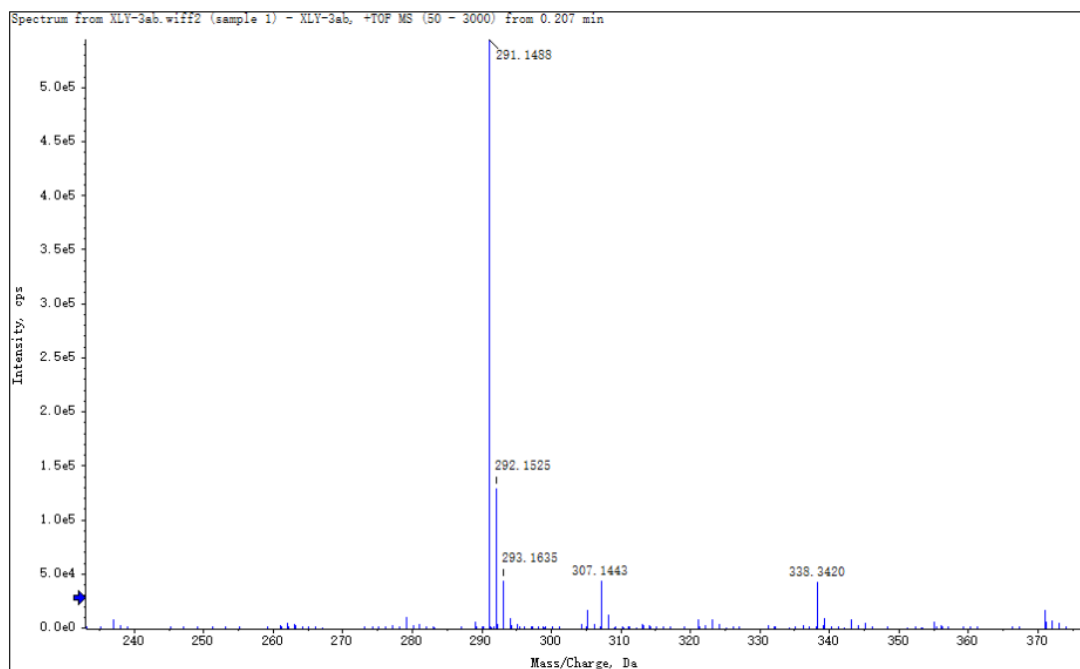
HRMS spectra of compound **3qa**



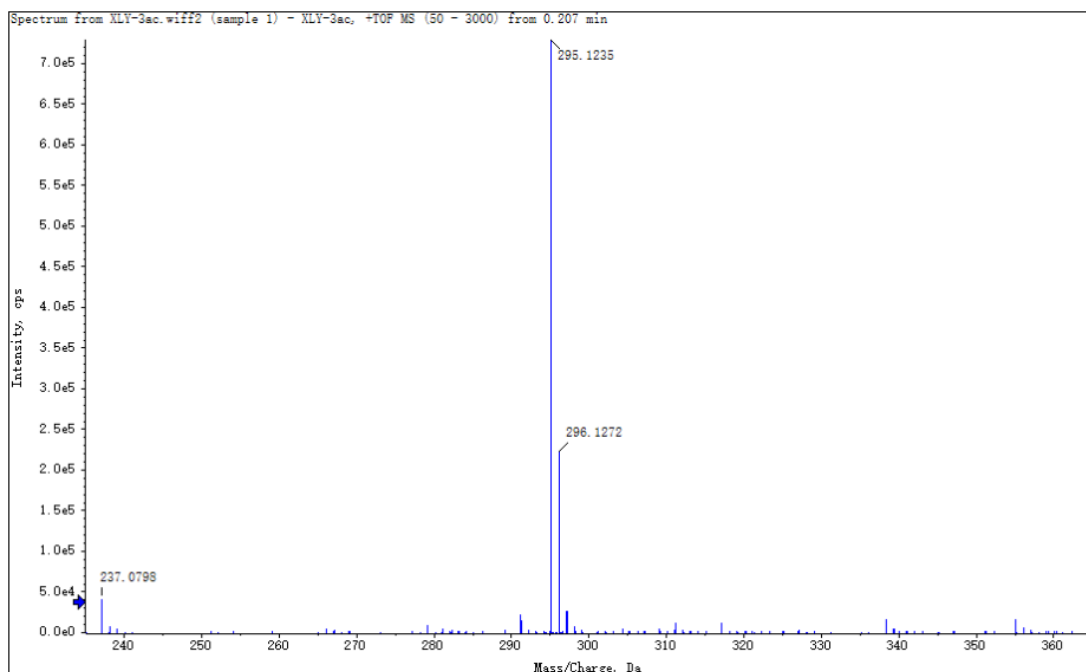
HRMS spectra of compound **3ra**



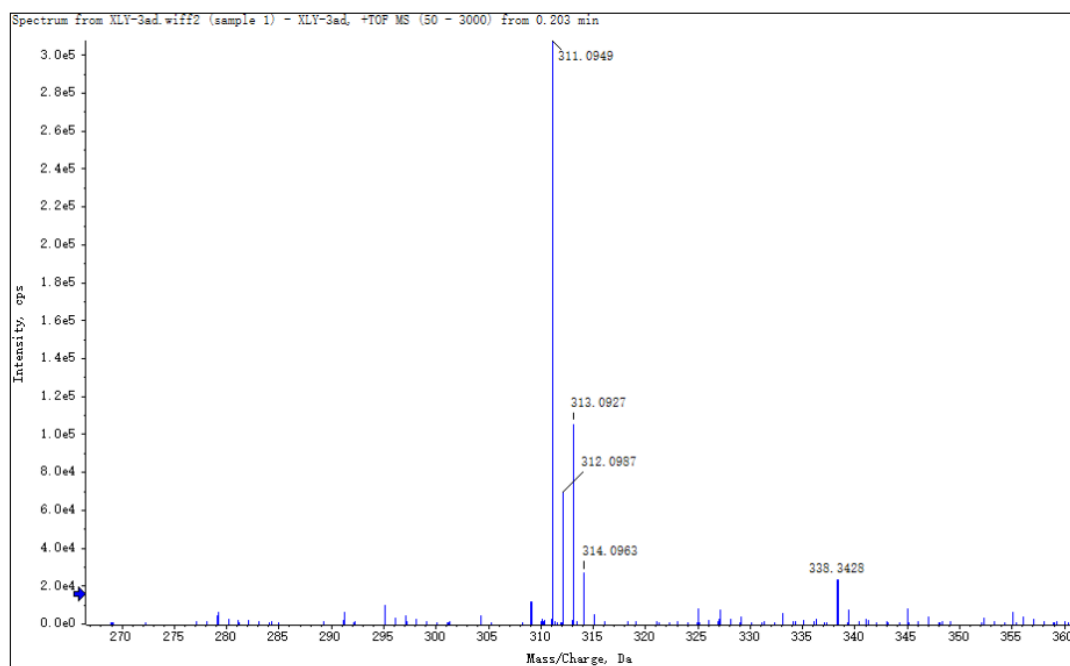
HRMS spectra of compound **3sa**



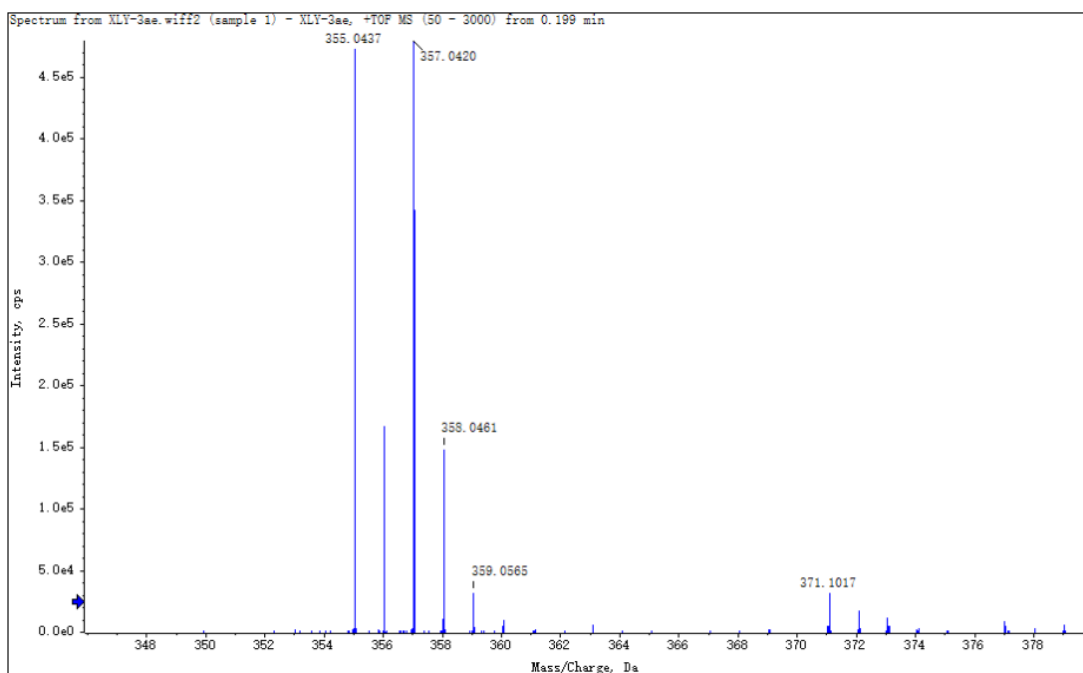
HRMS spectra of compound **3ab**



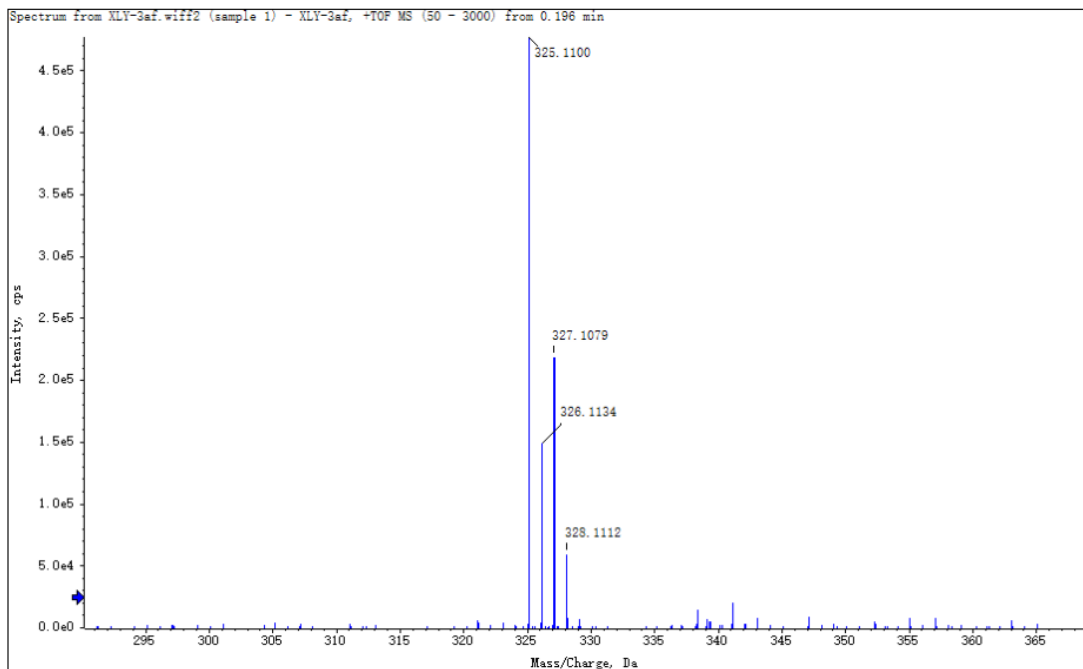
HRMS spectra of compound **3ac**



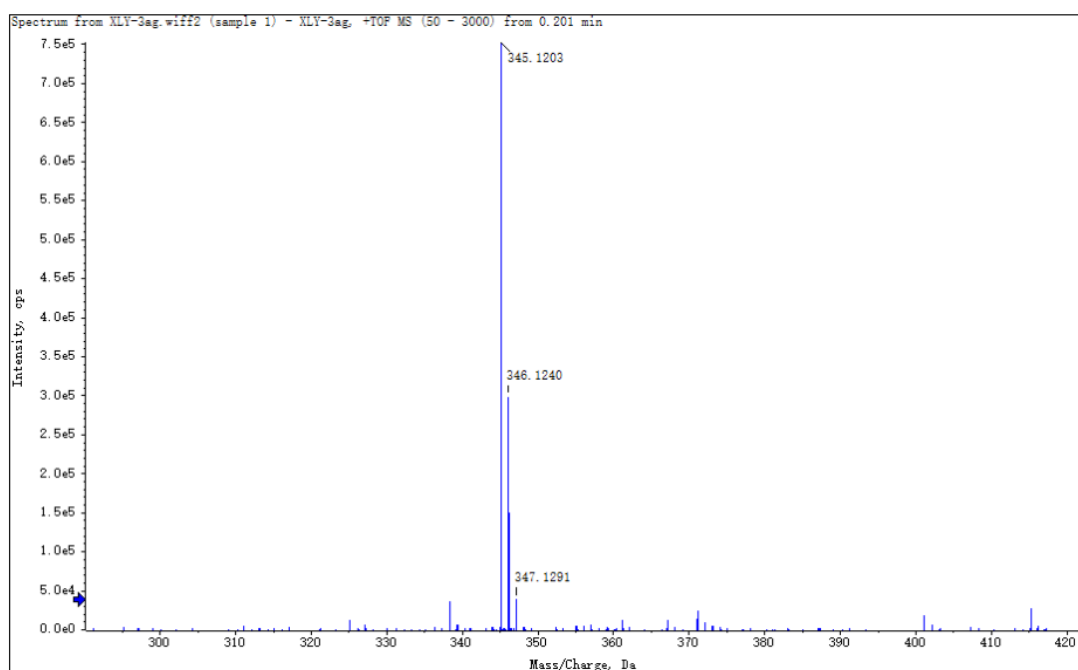
HRMS spectra of compound **3ad**



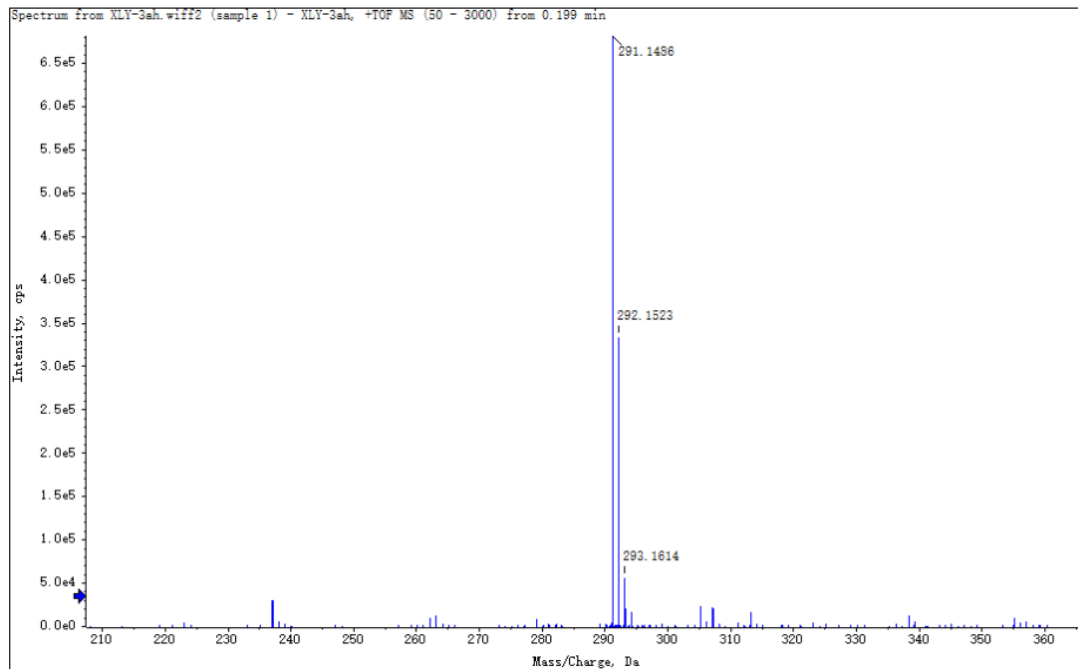
HRMS spectra of compound **3ae**



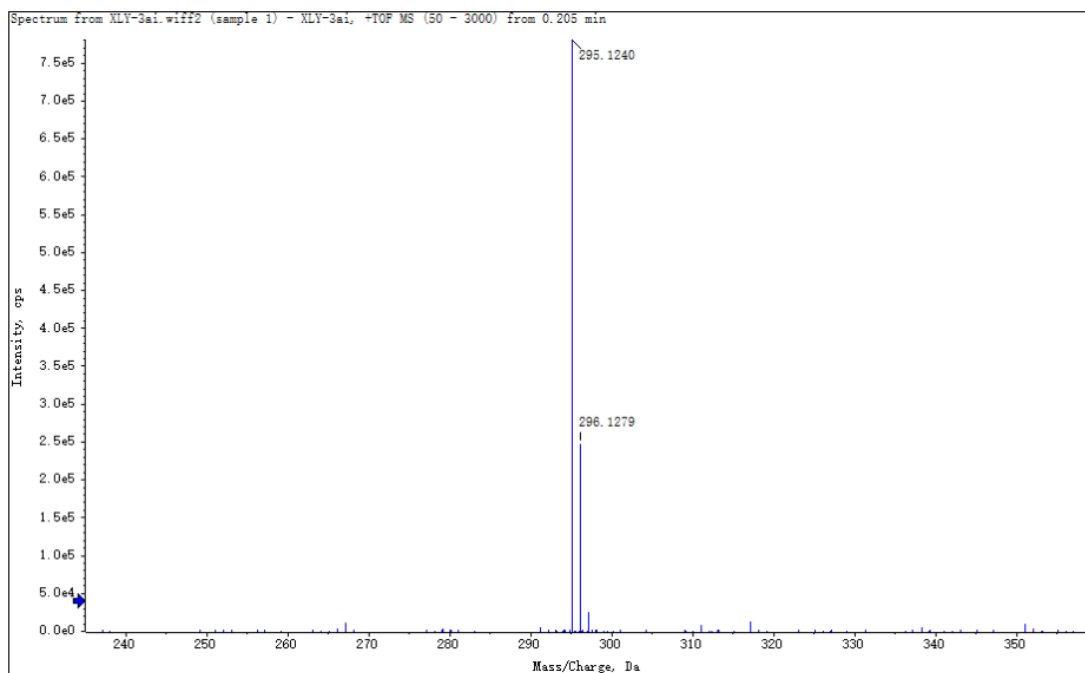
HRMS spectra of compound **3af**



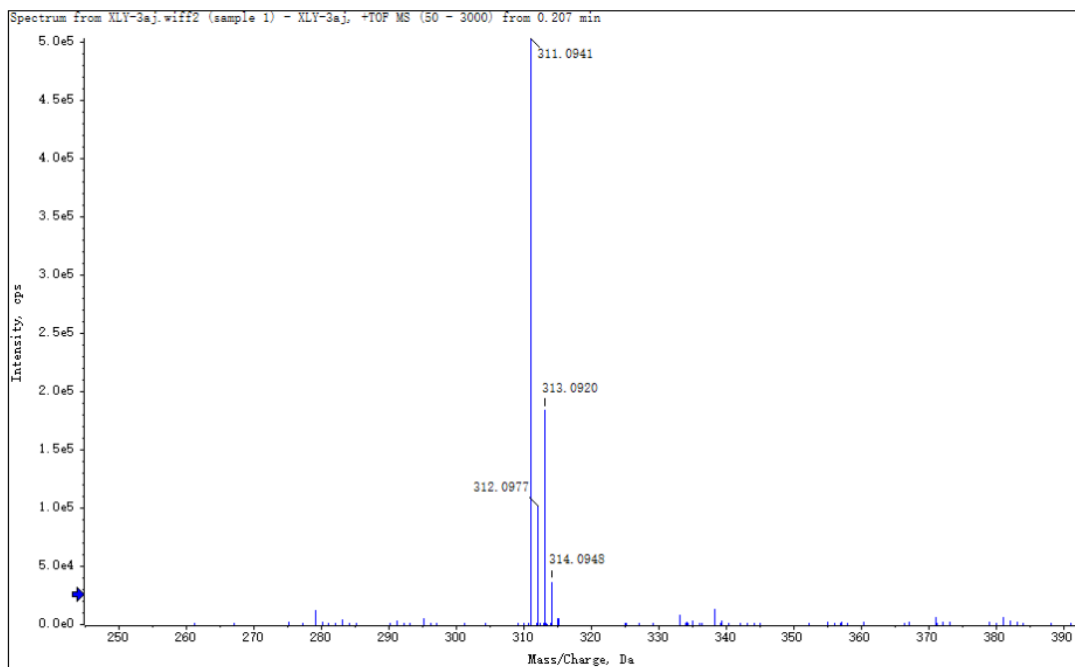
HRMS spectra of compound **3ag**



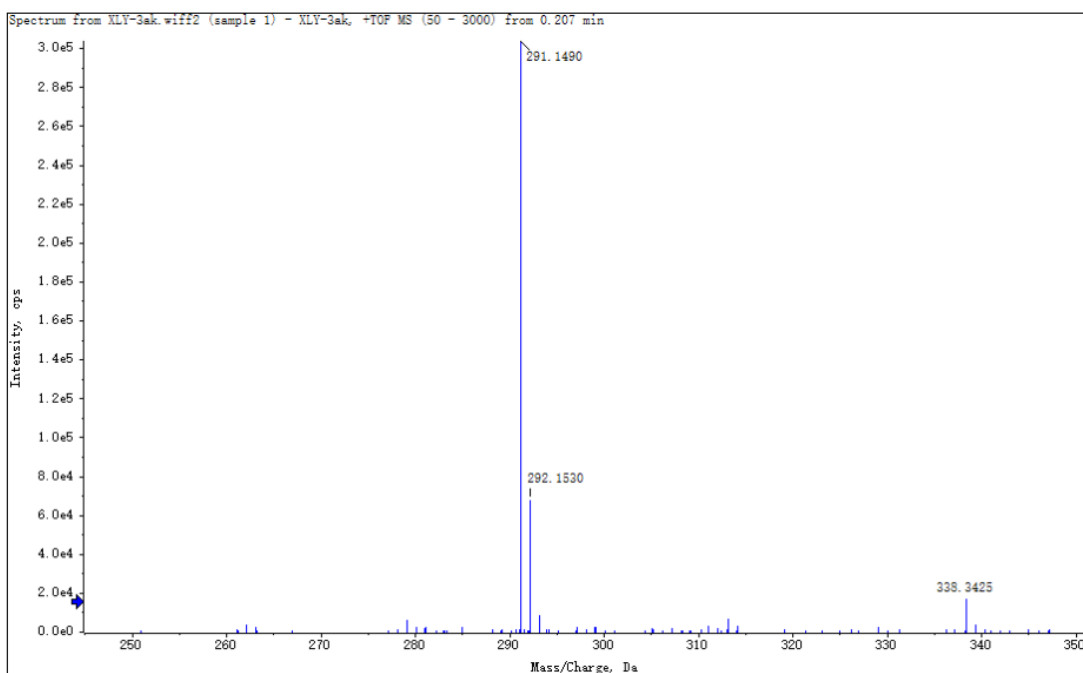
HRMS spectra of compound **3ah**



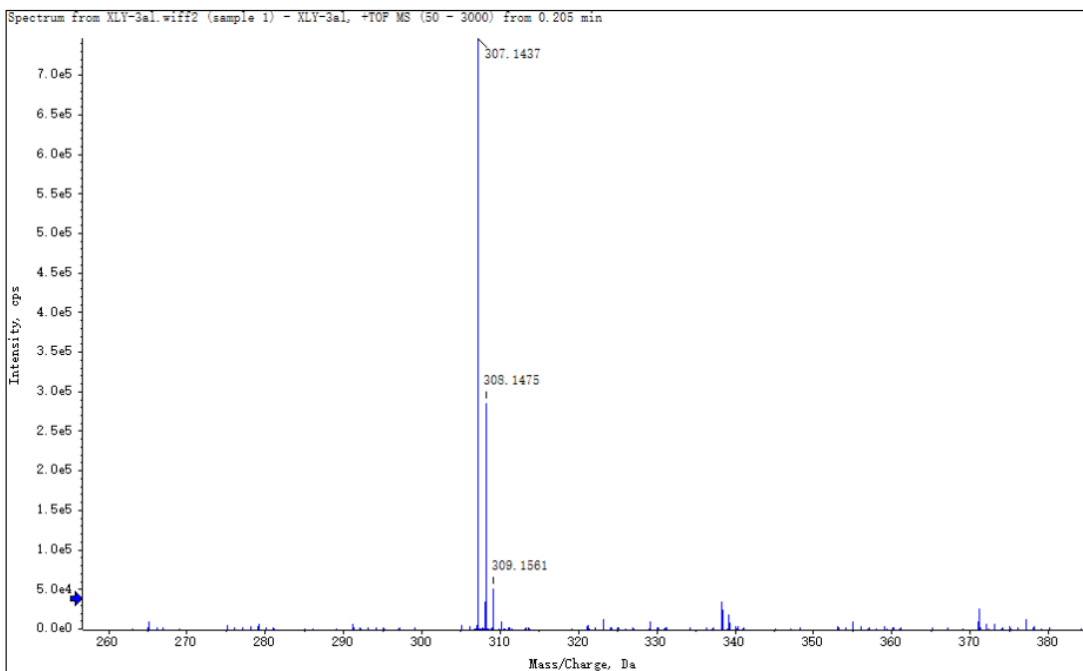
HRMS spectra of compound **3ai**



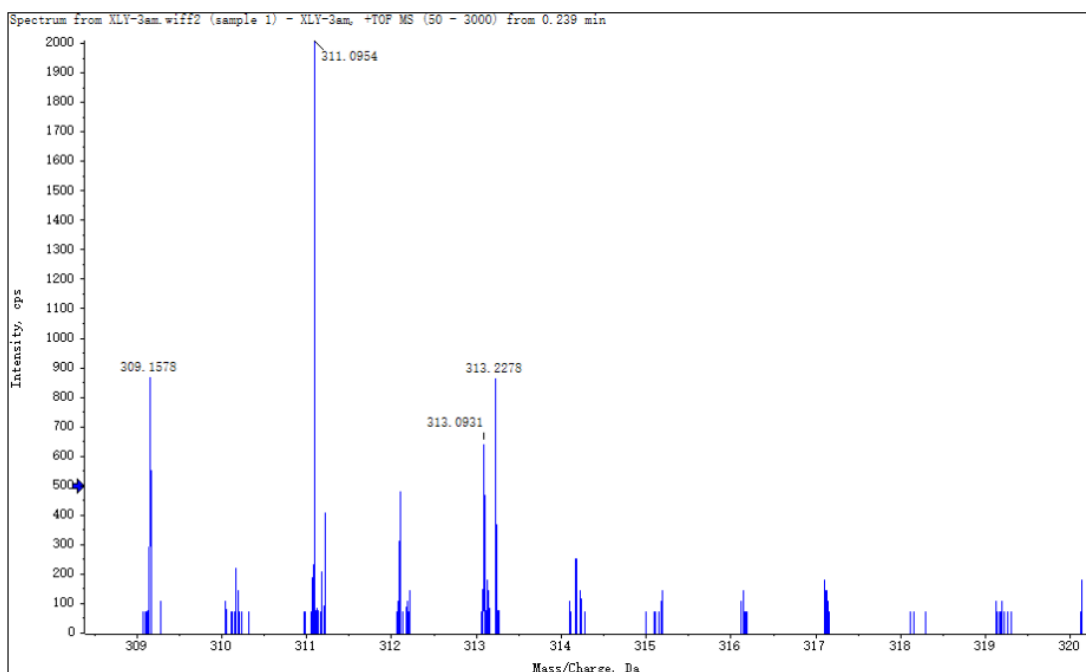
HRMS spectra of compound **3aj**



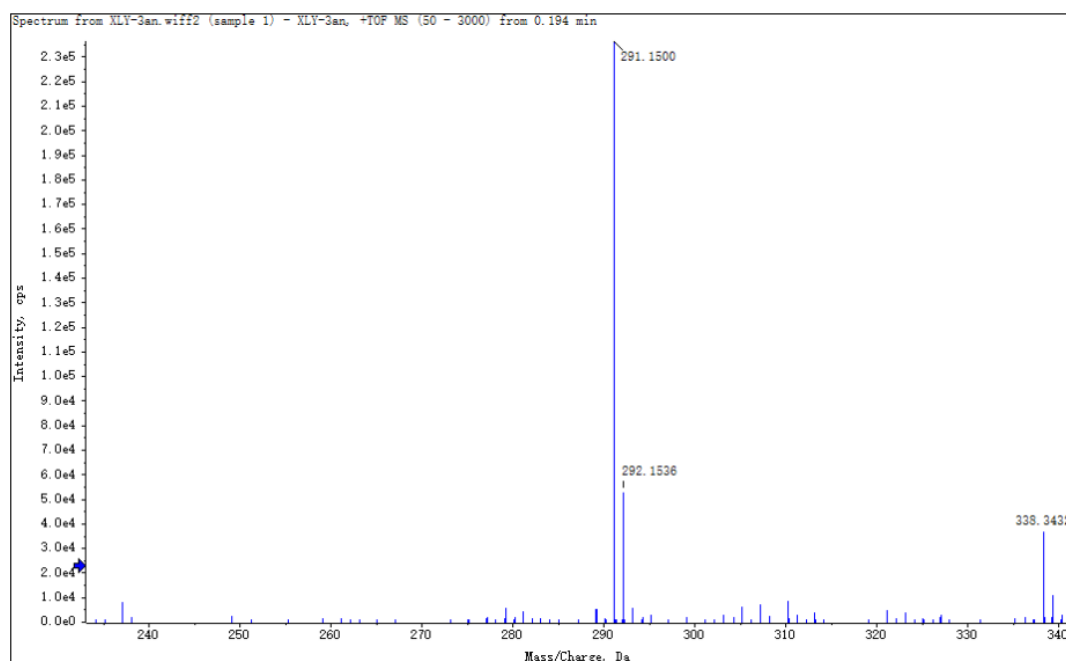
HRMS spectra of compound **3ak**



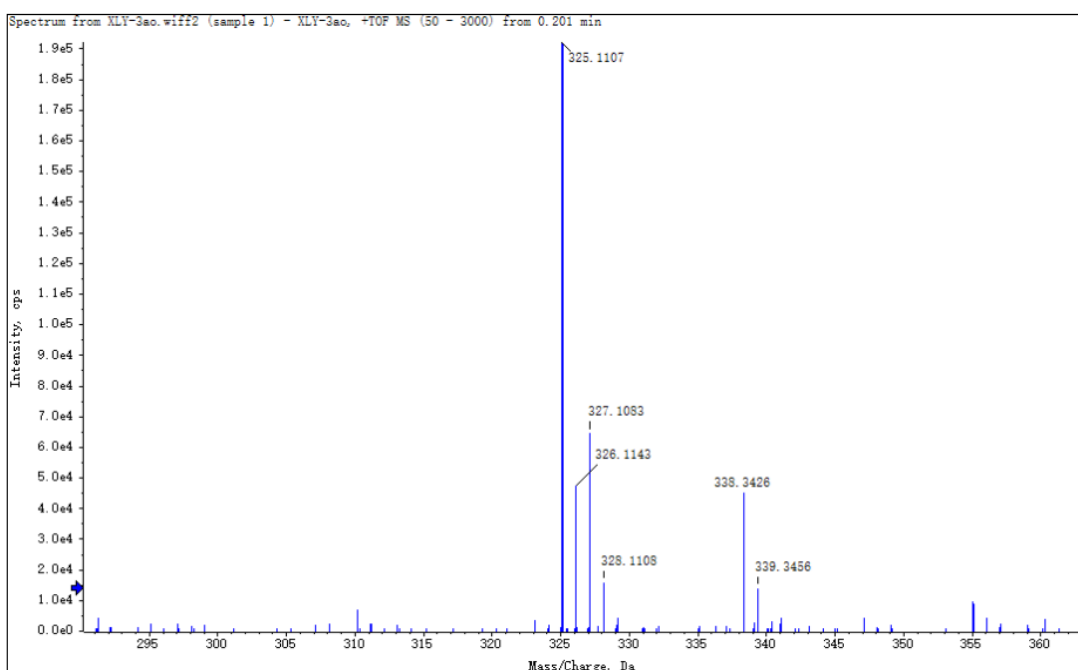
HRMS spectra of compound **3al**



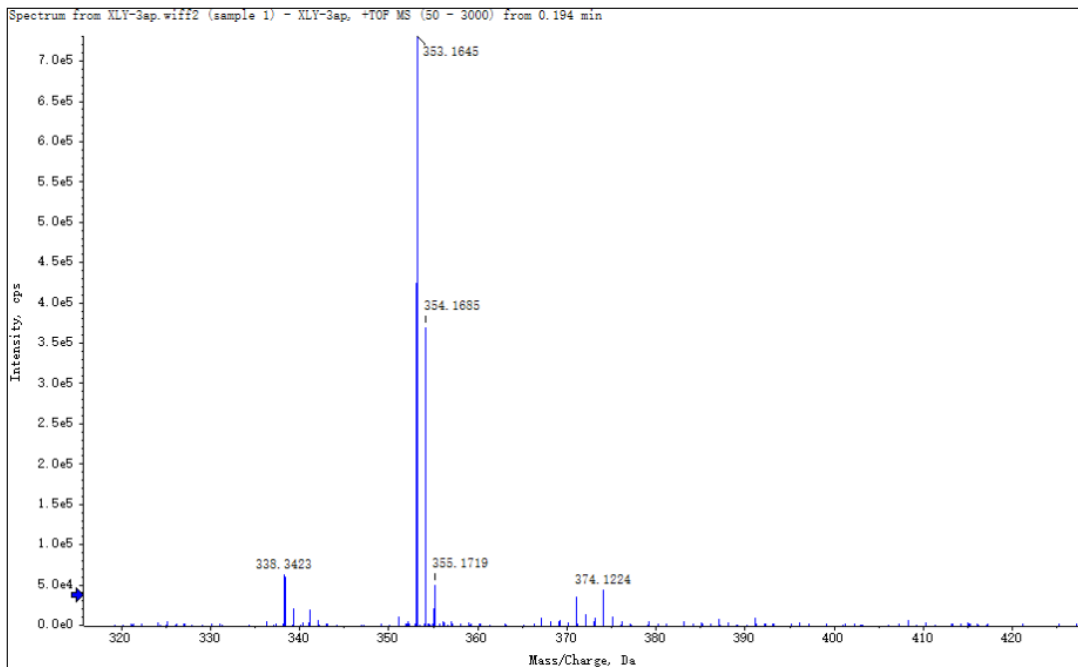
HRMS spectra of compound **3an**



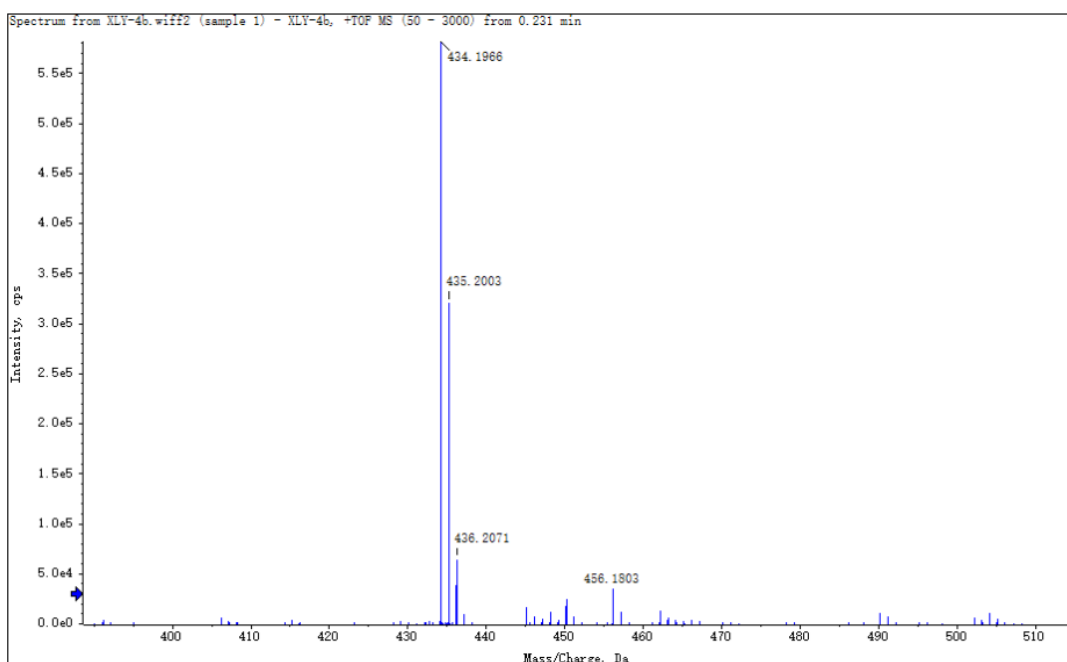
HRMS spectra of compound **3an**



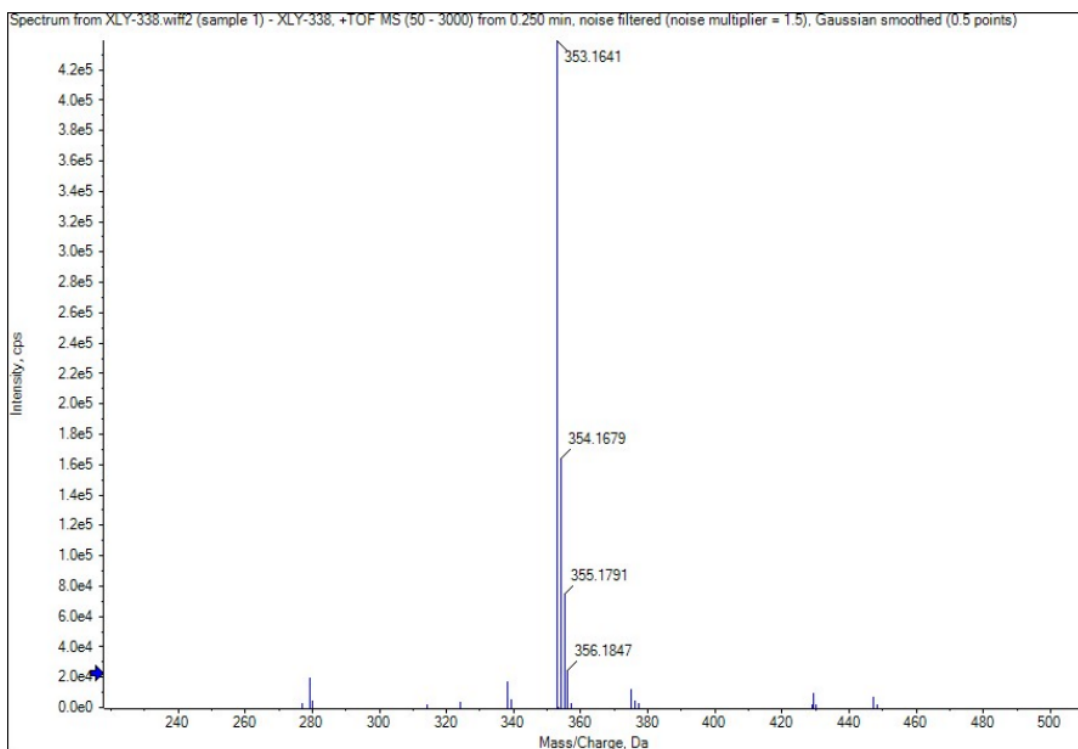
HRMS spectra of compound **3ao**



HRMS spectra of compound **3ap**



HRMS spectra of compound **4a**



HRMS spectra of compound **4b**