

Supplementary Information

Old Dye Safranine as an Organic Photocatalyst for the Synthesis of Substituted Quinazolinones

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1. General

Air and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stirring bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

Synthetic reagents were purchased from Bidepharm, Macklin, and Meryer and used without further purification, unless otherwise indicated. THF, DCM, CHCl_3 , EA, PE (60–90 °C), MeOH and EtOH (AR grade) were used directly without purification. 1,4-Dioxane (SuperDry, with molecular sieves) was purchased from Macklin and used directly.

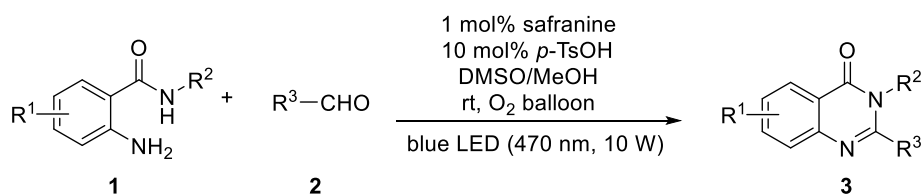
NMR spectra were measured on Bruker ARX 500 (^1H at 400 MHz, ^{13}C at 101 MHz) nuclear magnetic resonance spectrometers. ^1H -NMR spectra are reported relative to Me_4Si (0.00 ppm) or residual solvent signals (d^6 -DMSO: 2.50 ppm, D_2O : 4.79 ppm). Data for ^1H -NMR spectra are reported as follows: chemical shift (ppm, s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C -NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl_3 : 77.00 ppm, d^6 -DMSO: 39.52 ppm). Melting points were determined on RY-1G melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were measured on Agilent 1260/6530 (ESI).

Photoirradiation experiments were conducted with blue LEDs (OSRAM Oslon SSL80 Blue 470 nm SMD, GB CS8PM1.13-HXHY-35, $\lambda_{\text{max}} = 470$ nm, $U = 3.2$ V, $I = 800$ mA, 2.5 W*4). The reaction tube was placed at a distance of 5 mm above the blue LEDs.

Abbreviations:

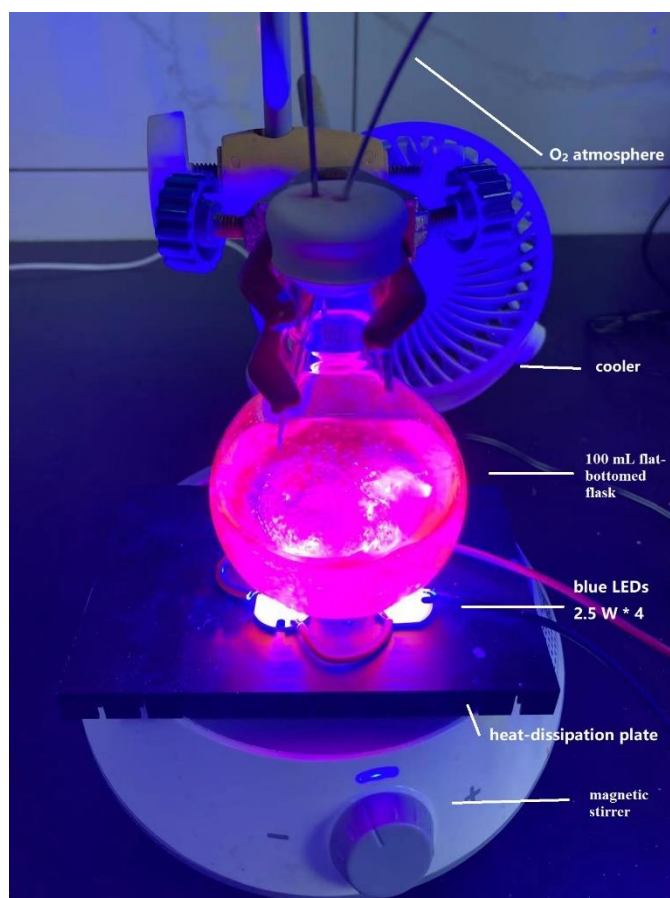
Ts = toluenesulfonyl
m.p. = melting point
DMSO = dimethyl sulfoxide
DCM = dichloromethane
EA = ethyl acetate
PE = petroleum ether
TLC = thin layer chromatography
THF = tetrahydrofuran

2. General procedure for the synthesis of quinazolinones.

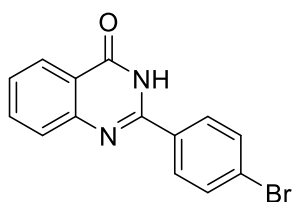


General procedure: To an oven-dried 100 mL flat-bottomed flask with a magnetic stirrer were added *o*-aminobenzamide (**1**, 1.0 mmol), aldehyde (**2**, 1.1 mmol), safranine (3.5 mg, 1 mol%), *p*-TsOH (17.0 mg, 10 mol%) and DMSO/MeOH (10 mL, v/v = 1:1), and bubbled with O₂ gas for 5 min at room temperature. The reaction system was then stirred and irradiated by blue LEDs ($\lambda_{\text{max}} = 470 \text{ nm}$, $U = 3.2 \text{ V}$, $I = 800 \text{ mA}$, $2.5 \text{ W} \times 4$) at room temperature under balloon pressured O₂. When TLC indicated the disappearance of the starting material, 50 mL H₂O was added to the reaction system. The precipitated solid was then filtered and washed with cold 50% EtOH (10 mL). The solid was pure enough and no further purification was needed.

For product **3c** and **3q-t**, after added H₂O, the resultant mixture was extracted with EA (3 × 50 mL). The combined organic layers were dried by Na₂SO₄ and then concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the corresponding product (eluted with PE/EA 2:1).



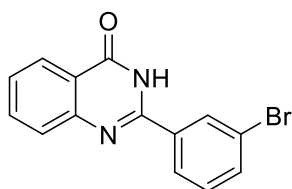
Product 3a



278.8 mg. Yield: 92%, 2 h.

White solid, m. p. = 308 °C, TLC R_f = 0.72 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.64 (s, 1H), 8.21 – 8.09 (m, 3H), 7.90 – 7.81 (m, 1H), 7.80 – 7.72 (m, 3H), 7.59 – 7.50 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 162.87, 152.17, 148.75, 134.36, 132.53, 131.53, 129.81, 127.34, 126.45, 125.87, 125.01, 121.08. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

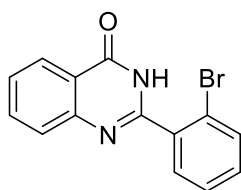
Product 3b



269.3 mg. Yield: 89%, 2 h.

White solid, m. p. = 300 °C, TLC R_f = 0.42 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.64 (s, 1H), 8.39 (s, 1H), 8.18 (dd, J = 12.3, 8.0 Hz, 2H), 7.90 – 7.83 (m, 1H), 7.83 – 7.74 (m, 2H), 7.54 (dd, J = 16.7, 8.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 162.23, 151.03, 148.42, 134.99, 134.68, 134.04, 130.77, 130.41, 127.53, 126.92, 126.81, 125.89, 121.90, 121.12. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

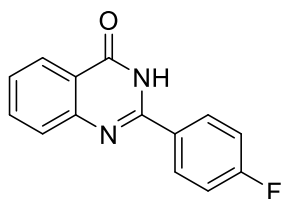
Product 3c



259.7 mg. Yield: 86%, 12 h.

Off-white solid, m. p. = 172 °C, TLC R_f = 0.39 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.62 (s, 1H), 8.19 (d, J = 7.4 Hz, 1H), 7.85 (t, J = 6.9 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 6.8 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 161.42, 153.33, 148.55, 135.87, 134.58, 132.63, 131.66, 130.78, 127.67, 127.47, 127.04, 125.84, 121.27, 120.97. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[2]

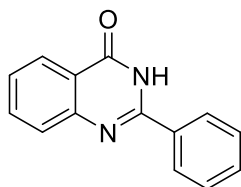
Product 3d



207.3 mg. Yield: 86%, 2 h.

White solid, m. p. = 278 °C, TLC R_f = 0.60 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.56 (s, 1H), 8.25 (dd, J = 8.4, 5.6 Hz, 2H), 8.15 (d, J = 7.7 Hz, 1H), 7.83 (t, J = 7.5 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.04 (d, J = 249.4 Hz), 162.20, 151.35, 148.65, 134.63, 130.37 (d, J = 9.0 Hz), 129.23, 127.46, 126.60, 125.85, 120.89, 115.62 (d, J = 21.9 Hz). ^{19}F NMR (376 MHz, DMSO) δ -109.07. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

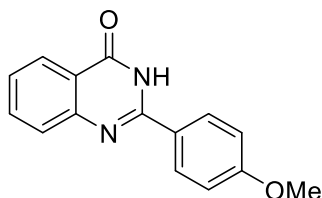
Product 3e



188.0 mg. Yield: 84%, 4 h.

White solid, m. p. = 238 °C, TLC R_f = 0.75 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.54 (s, 1H), 8.24 – 8.12 (m, 3H), 7.89 – 7.79 (m, 1H), 7.78 – 7.68 (m, 1H), 7.64 – 7.45 (m, 4H). ^{13}C NMR (126 MHz, DMSO) δ 162.24, 152.30, 148.75, 134.59, 132.72, 131.38, 128.60, 127.77, 127.51, 126.57, 125.85, 121.00. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

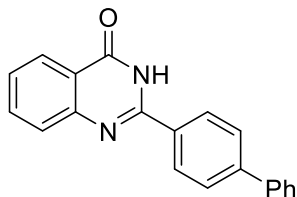
Product 3f



226.2 mg. Yield: 90%, 2 h.

White solid, m. p. = 248 °C, TLC R_f = 0.50 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.41 (s, 1H), 8.19 (d, J = 8.7 Hz, 2H), 8.13 (d, J = 7.6 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 162.33, 161.85, 151.88, 148.85, 134.50, 129.44, 127.20, 126.09, 125.81, 124.76, 120.65, 113.97, 55.43. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

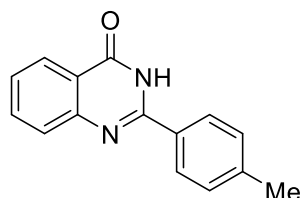
Product 3g



259.5 mg. Yield: 87%, 4 h.

White solid, m. p. = 292 °C, TLC R_f = 0.56 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.62 (s, 1H), 8.36 – 8.25 (m, 2H), 8.23 – 8.12 (m, 1H), 7.95 – 7.84 (m, 3H), 7.82 – 7.71 (m, 3H), 7.60 – 7.48 (m, 3H), 7.46 – 7.39 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 162.50, 152.17, 148.99, 143.07, 139.19, 134.84, 131.79, 129.30, 128.61, 128.41, 127.73, 127.08, 126.97, 126.80, 126.10, 121.22. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[3]

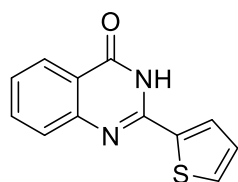
Product 3h



207.4 mg. Yield: 88%, 3 h.

White solid, m. p. = 238 °C, TLC R_f = 0.61 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.45 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 7.9 Hz, 2H), 7.81 (t, J = 7.3 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 162.25, 152.20, 148.84, 141.42, 134.54, 129.89, 129.17, 127.67, 127.42, 126.36, 125.83, 120.91, 20.98. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

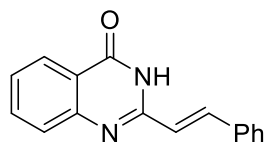
Product 3i



200.8 mg. Yield: 88%, 6 h.

Off-white solid, m. p. = 280 °C, TLC R_f = 0.50 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.65 (s, 1H), 8.23 (d, J = 2.9 Hz, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.86 (d, J = 4.6 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.29 – 7.20 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 161.79, 148.59, 147.83, 137.35, 134.66, 132.14, 129.38, 128.49, 126.90, 126.30, 125.97, 120.86. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

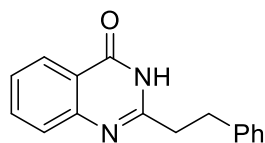
Product 3j



161.6 mg. Yield: 65%, 4 h.

White solid, m. p. = 250 °C, TLC R_f = 0.50 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.34 (s, 1H), 8.11 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 16.2 Hz, 1H), 7.80 (t, J = 7.1 Hz, 1H), 7.72 – 7.60 (m, 3H), 7.53 – 7.34 (m, 4H), 7.01 (d, J = 16.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 161.75, 151.43, 148.90, 138.30, 134.99, 134.49, 129.77, 129.06, 127.63, 127.05, 126.21, 125.87, 121.10, 121.04. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

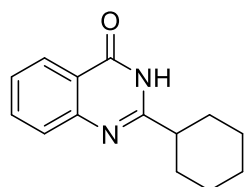
Product 3k



217.7 mg. Yield: 87%, 5 h.

White solid, m. p. = 210 °C, TLC R_f = 0.62 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 12.26 (s, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.77 (t, J = 7.3 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.35 – 7.22 (m, 4H), 7.21 – 7.14 (m, 1H), 3.13 – 2.97 (m, 2H), 2.97 – 2.80 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 161.80, 156.60, 148.83, 140.76, 134.31, 128.36, 128.35, 126.79, 126.08, 126.02, 125.71, 120.84, 36.33, 32.47. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

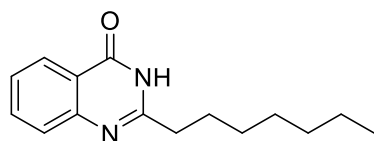
Product 3l



193.0 mg. Yield: 84%, 4 h.

White solid, m. p. = 222 °C, TLC R_f = 0.66 (PE/EA 2:1). ^1H NMR (500 MHz, DMSO) δ 12.08 (s, 1H), 8.07 (d, J = 7.4 Hz, 1H), 7.75 (t, J = 7.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 2.57 (t, J = 11.8 Hz, 1H), 1.89 (d, J = 12.2 Hz, 2H), 1.78 (d, J = 12.7 Hz, 2H), 1.63 – 1.49 (m, 3H), 1.36 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.93, 160.77, 148.90, 134.19, 126.92, 125.88, 125.65, 120.94, 42.82, 30.18, 25.50, 25.33. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

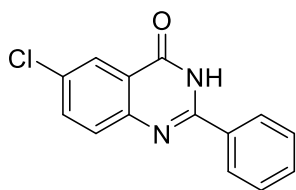
Product 3m



221.6 mg. Yield: 84%, 5 h.

White solid, m. p. = 138 °C, TLC R_f = 0.56 (PE/EA 2:1). ^1H NMR (500 MHz, DMSO) δ 12.16 (s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 2.58 (t, J = 7.6 Hz, 2H), 1.76 – 1.65 (m, 2H), 1.35 – 1.20 (m, 8H), 0.88 – 0.79 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.81, 157.50, 148.97, 134.23, 126.78, 125.86, 125.66, 120.77, 34.49, 31.11, 28.48, 28.36, 26.77, 22.04, 13.92. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[4]

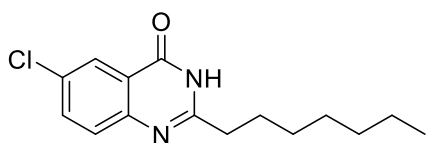
Product 3n



220.2 mg. Yield: 86%, 3 h.

White solid, m. p. = 294 °C, TLC R_f = 0.71 (PE/EA 2:1). ^1H NMR (500 MHz, DMSO) δ 12.73 (s, 1H), 8.17 (d, J = 7.9 Hz, 2H), 8.09 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.57 (dt, J = 14.7, 7.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 162.87, 152.17, 148.75, 134.36, 132.53, 131.53, 129.81, 127.34, 126.45, 125.87, 125.01, 121.08. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[5]

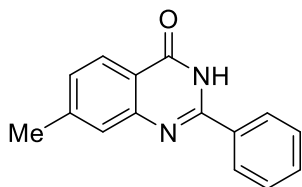
Product 3o



262.7 mg. Yield: 85%, 5 h.

White solid, m. p. = 194 °C, TLC R_f = 0.80 (PE/EA 2:1). ^1H NMR (500 MHz, DMSO) δ 12.21 (s, 1H), 8.00 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 2.59 (t, J = 7.6 Hz, 2H), 1.78 – 1.65 (m, 2H), 1.37 – 1.21 (m, 8H), 0.92 – 0.80 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 160.59, 157.97, 134.04, 129.89, 128.81, 124.45, 121.86, 34.29, 30.83, 28.20, 28.05, 26.39, 21.73, 13.58. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 279.1259, found 279.1265.

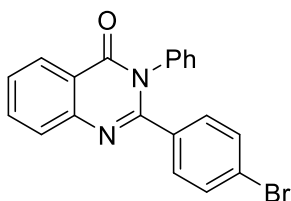
Product 3p



180.4 mg. Yield: 76%, 2 h.

White solid, m. p. = 244 °C, TLC R_f = 0.50 (PE/EA 2:1). ^1H NMR (500 MHz, DMSO) δ 12.45 (s, 1H), 8.17 (d, J = 7.4 Hz, 2H), 8.04 (d, J = 8.1 Hz, 1H), 7.62 – 7.50 (m, 4H), 7.34 (d, J = 7.7 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 162.11, 152.30, 148.86, 145.06, 132.78, 131.32, 128.59, 128.01, 127.70, 127.16, 125.71, 118.60, 21.37. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[1]

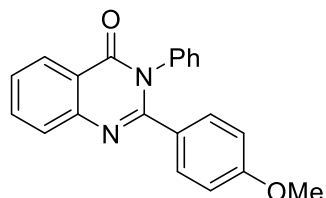
Product 3q



350.7 mg. Yield: 93%, 12 h.

White solid, m. p. = 192°C, TLC R_f = 0.71 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 8.20 (d, J = 7.7 Hz, 1H), 7.90 (t, J = 7.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.38 – 7.25 (m, 7H). ^{13}C NMR (126 MHz, DMSO) δ 161.27, 154.22, 147.15, 137.65, 134.87, 134.81, 131.02, 130.53, 129.47, 128.69, 128.34, 127.42, 127.30, 126.46, 122.45, 120.81. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[6]

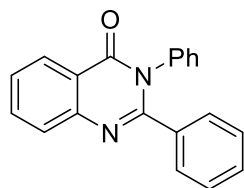
Product 3r



298.6 mg. Yield: 91%, 12 h.

White solid, m. p. = 150 °C, TLC R_f = 0.44 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 8.18 (d, J = 7.8 Hz, 1H), 7.88 (dd, J = 11.2, 4.1 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.42 – 7.22 (m, 7H), 6.76 (d, J = 8.7 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.50, 159.47, 154.92, 147.33, 138.07, 134.73, 130.70, 129.47, 128.61, 128.10, 127.91, 127.32, 126.93, 126.44, 120.52, 112.86, 55.11. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[7]

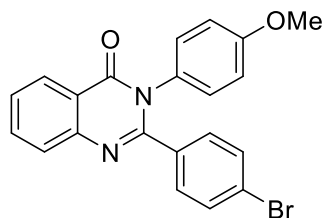
Product 3s



234.8 mg. Yield: 79%, 12 h.

White solid, m. p. = 158 °C, TLC R_f = 0.70 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 8.20 (d, J = 7.9 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.17 (m, 8H). ^{13}C NMR (126 MHz, DMSO) δ 161.38, 155.18, 147.26, 137.83, 135.62, 134.79, 129.51, 128.89, 128.86, 128.56, 128.15, 127.48, 127.41, 127.17, 126.46, 120.75. The ^1H NMR & ^{13}C NMR spectra are consistent with the literature.^[11]

Product 3t

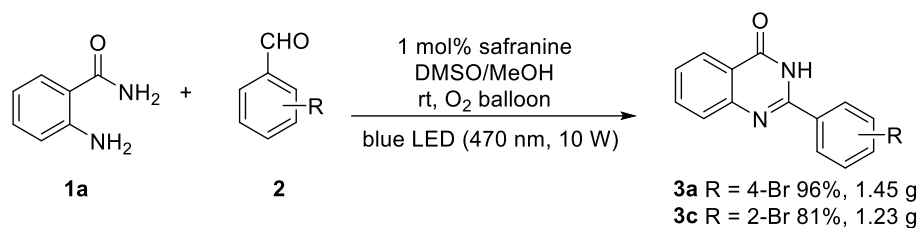


283.1 mg. Yield: 70%, 24 h.

White solid, m. p. = 196 °C, TLC R_f = 0.66 (PE/EA = 2:1). ^1H NMR (500 MHz, DMSO) δ 8.19 (d, J = 7.9 Hz, 1H), 7.90 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 3.73

(s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.52, 158.69, 154.59, 147.16, 135.09, 134.73, 131.02, 130.58, 130.50, 130.21, 127.38, 127.22, 126.47, 122.39, 120.81, 113.86, 55.25. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{16}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 407.0390, found 407.0395.

3. Gram-scale synthesis of 3a and 3c



3a: To an oven-dried 100 mL flat-bottomed flask with a magnetic stirrer were added *o*-aminobenzamide (680.7 mg, 5.0 mmol), 4-bromobenzaldehyde (1.017 g, 5.5 mmol), safranine (17.5 mg, 1 mol%), *p*-TsOH (86 mg, 10 mol%) and DMSO/MeOH (50 mL, v/v 1:1), and bubbled with O₂ gas for 5 min at room temperature. The reaction system was then stirred and irradiated by blue LEDs ($\lambda_{\text{max}} = 470 \text{ nm}$, $U = 3.2 \text{ V}$, $I = 800 \text{ mA}$, $2.5 \text{ W} \times 4$) at room temperature under balloon pressured O₂. When TLC indicated the disappearance of the starting material (after 3 h), 250 mL H₂O was added to the reaction system. The precipitated solid was then filtered and washed with cold 50% EtOH (30 mL) to afford the desired product **3a** (1.45 g, 96%).

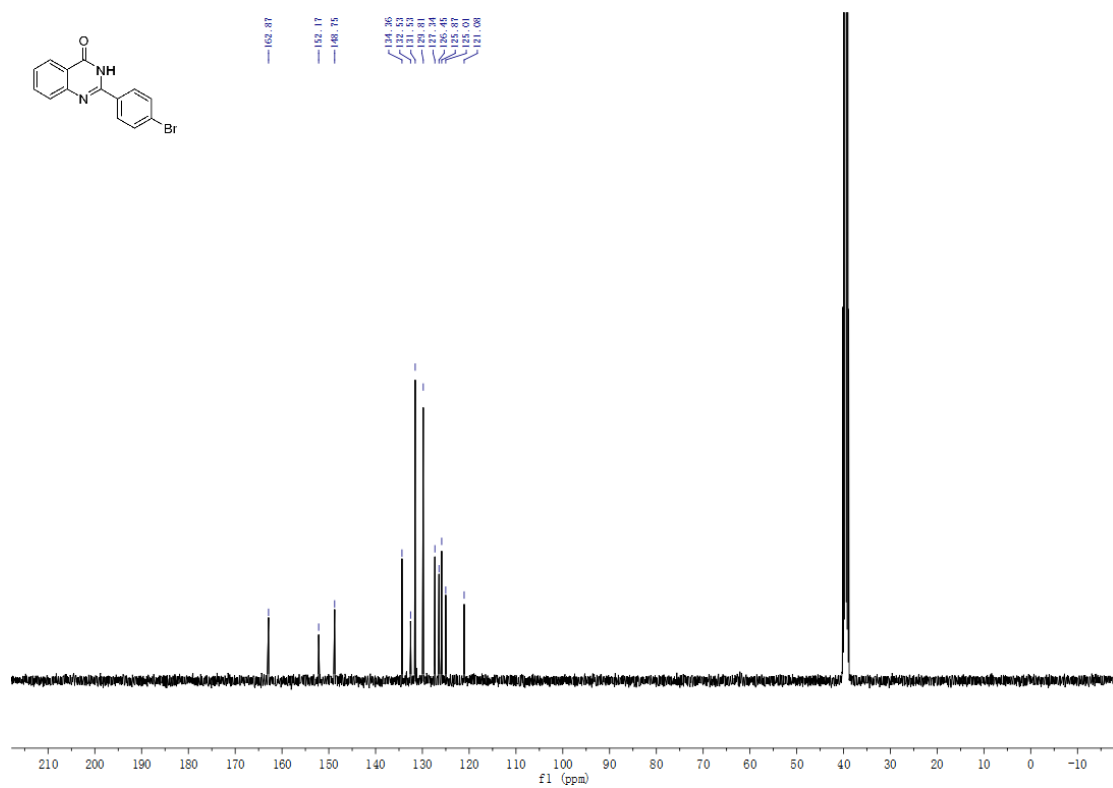
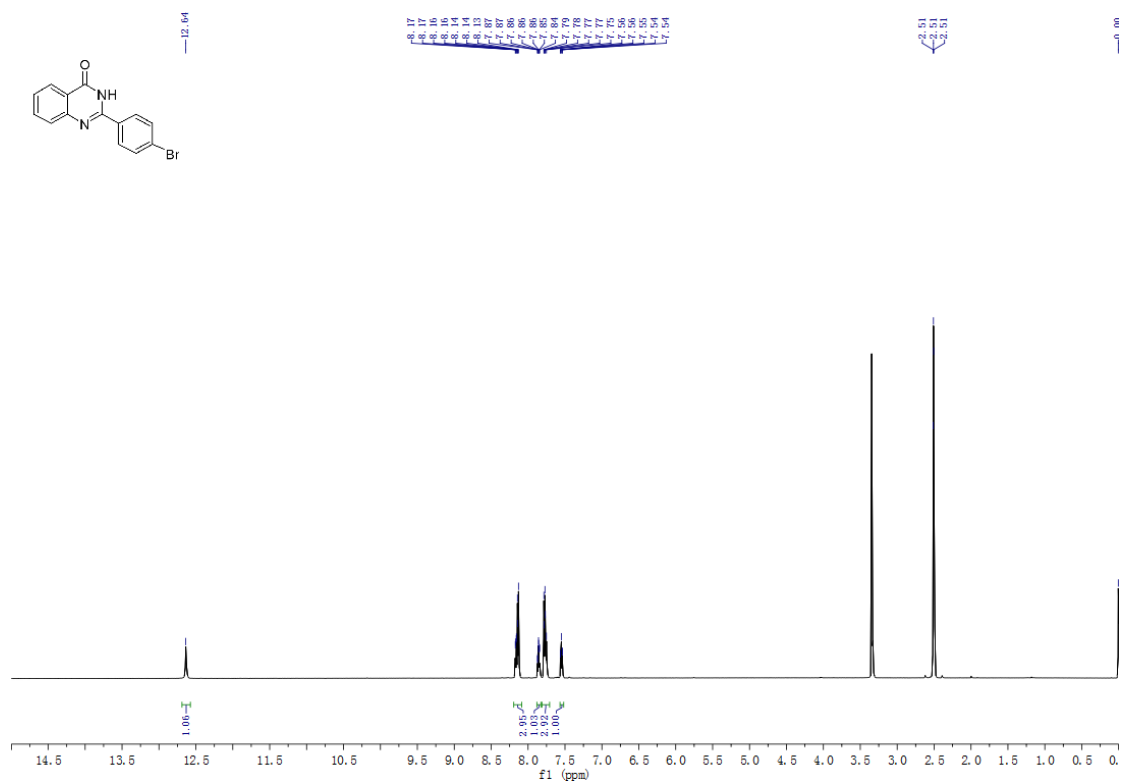
3c: To an oven-dried 100 mL flat-bottomed flask with a magnetic stirrer were added *o*-aminobenzamide (680.7 mg, 5.0 mmol), 2-bromobenzaldehyde (1.017 g, 5.5 mmol), safranine (17.5 mg, 1 mol%), *p*-TsOH (86 mg, 10 mol%) and DMSO/MeOH (50 mL, v/v 1:1), and bubbled with O₂ gas for 5 min at room temperature. The reaction system was then stirred and irradiated by blue LEDs ($\lambda_{\text{max}} = 470 \text{ nm}$, $U = 3.2 \text{ V}$, $I = 800 \text{ mA}$, $2.5 \text{ W} \times 4$) at room temperature under balloon pressured O₂. When TLC indicated the disappearance of the starting material (after 30 h), 250 mL H₂O was added to the reaction system. The precipitated solid was then filtered and further purified by flash column chromatography on silica gel (eluted with PE/EA 2:1) to afford the corresponding product **3c** (1.23 g, 81%).

4. References

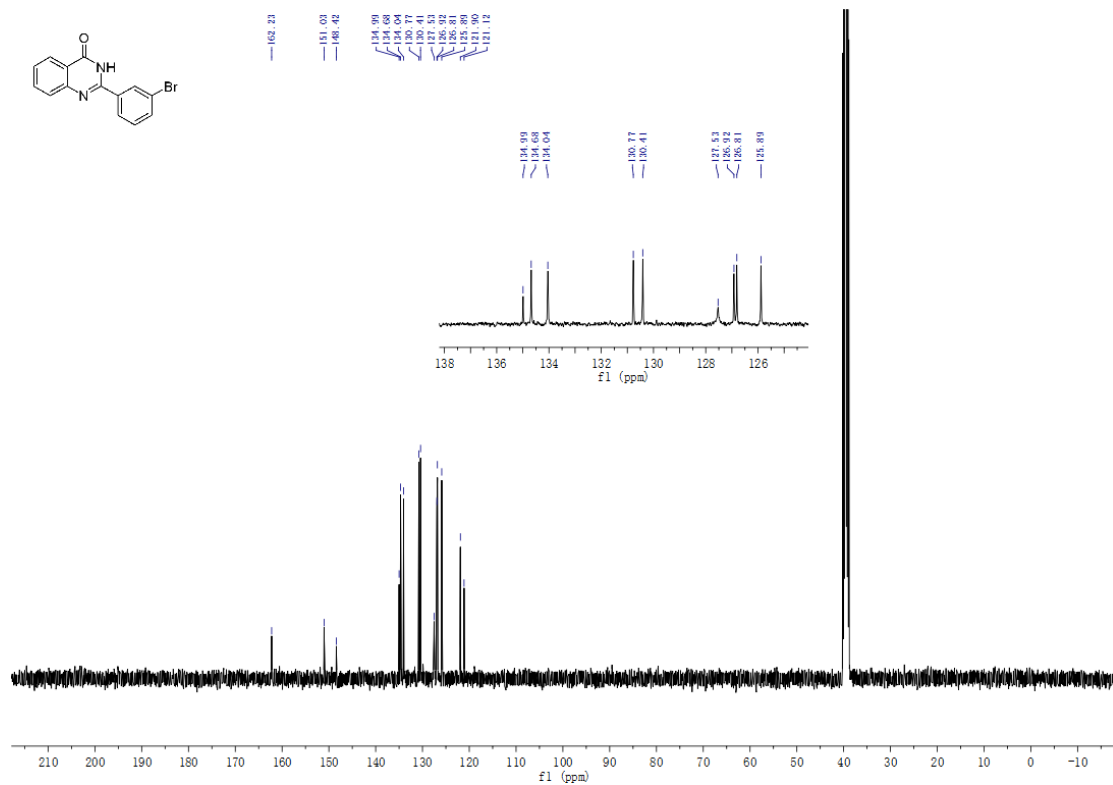
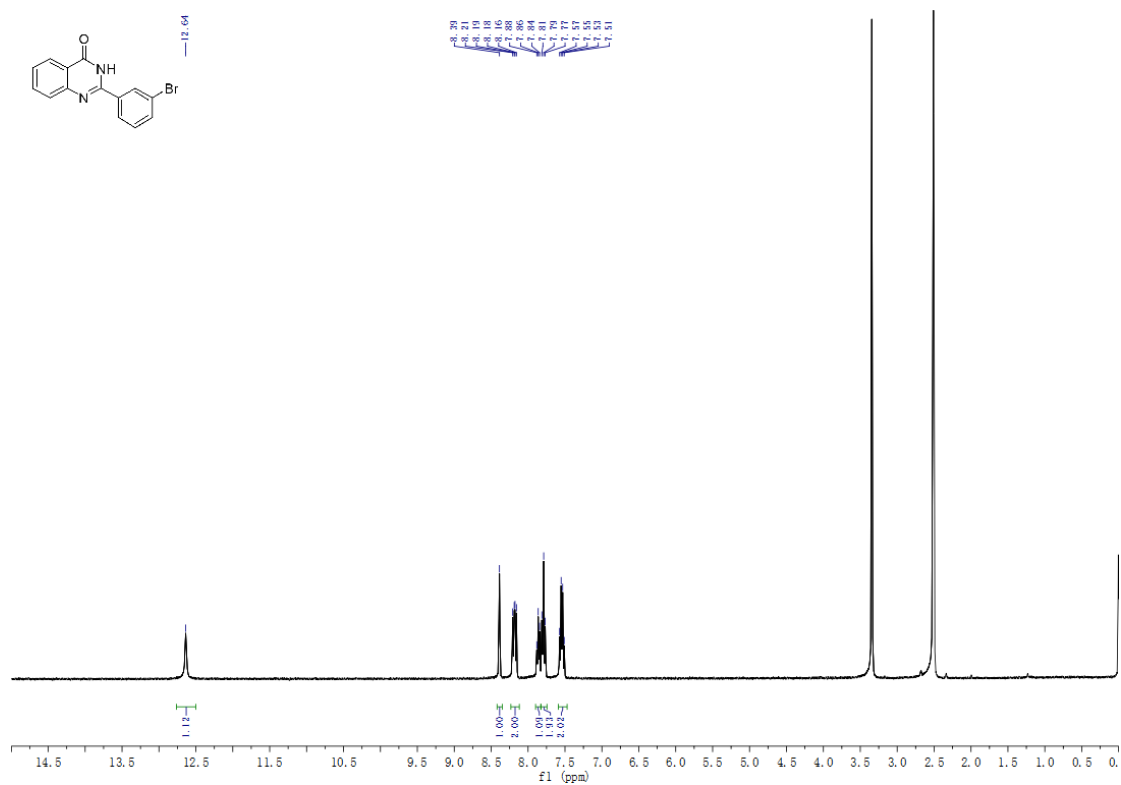
- (1) Wang, R.; Liu, S.; Li, L.; Song, A.; Yu, S.; Zhuo, S.; Xing, L.-B. Metal-Free Catalyst for the Visible-Light-Induced Photocatalytic Synthesis of Quinazolinones. *Mol. Catal.* **2021**, *509*, 111668. <https://doi.org/10.1016/j.mcat.2021.111668>.
- (2) Das, S.; Sinha, S.; Samanta, D.; Mondal, R.; Chakraborty, G.; Brandaõ, P.; Paul, N. D. Metal–Ligand Cooperative Approach To Achieve Dehydrogenative Functionalization of Alcohols to Quinolines and Quinazolin-4(3*H*)-Ones under Mild Aerobic Conditions. *J. Org. Chem.* **2019**, *84* (16), 10160–10171. <https://doi.org/10.1021/acs.joc.9b01343>.
- (3) Liu, C.-H.; Wang, J.-j., Xu, Z.; Li, D.; Wang, Q. New Application of an Old Dye: Bay-Annulated Indigo (BAI) as an Organic Photocatalyst for the Oxidation of Organic Sulfides. *Mol. Catal.* **2023**, *541*, 113109. <https://doi.org/10.1016/j.mcat.2023.113109>.
- (4) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. Ruthenium-Catalysed Oxidative Synthesis of Heterocycles from Alcohols. *Org. Biomol. Chem.* **2012**, *10* (2), 240–243. <https://doi.org/10.1039/C1OB06516E>.
- (5) Jia, F.-C.; Zhou, Z.-W.; Xu, C.; Wu, Y.-D.; Wu, A.-X. Divergent Synthesis of Quinazolin-4(3*H*)-Ones and Tryptanthrins Enabled by a *Tert*-Butyl Hydroperoxide/ K_3PO_4 -Promoted Oxidative Cyclization of Isatins at Room Temperature. *Org. Lett.* **2016**, *18* (12), 2942–2945. <https://doi.org/10.1021/acs.orglett.6b01291>.
- (6) Raghavendra, G. M.; Pavan Kumar, C. S.; Suresha, G. P.; Rangappa, K. S.; Mantelingu, K. T3P Catalyzed One Pot Three-Component Synthesis of 2,3-Disubstituted 3*H*-Quinazolin-4-Ones. *Chin. Chem. Lett.* **2015**, *26* (8), 963–968. <https://doi.org/10.1016/j.ccl.2015.03.037>.
- (7) Hwang, H. S.; Cho, E. J. Complementary Reactivity in Selective Radical Processes: Electrochemistry of Oxadiazolines to Quinazolinones. *Org. Lett.* **2021**, *23* (13), 5148–5152. <https://doi.org/10.1021/acs.orglett.1c01676>.

5. ¹H and ¹³C-NMR Spectra

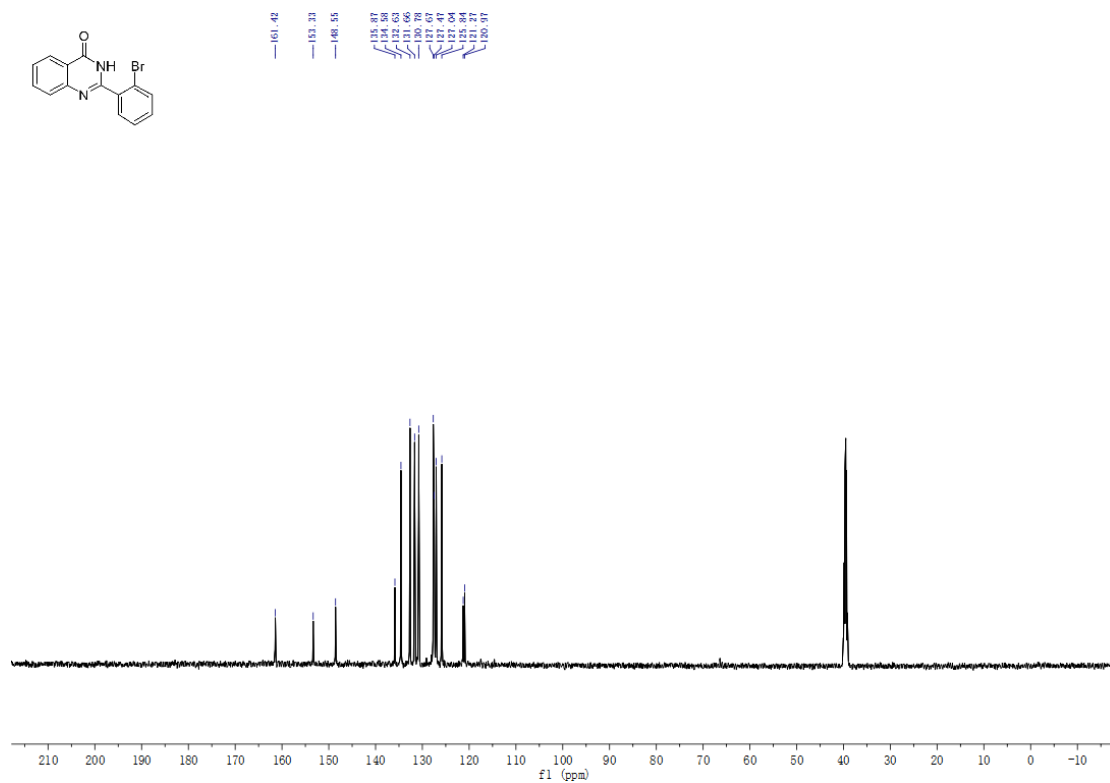
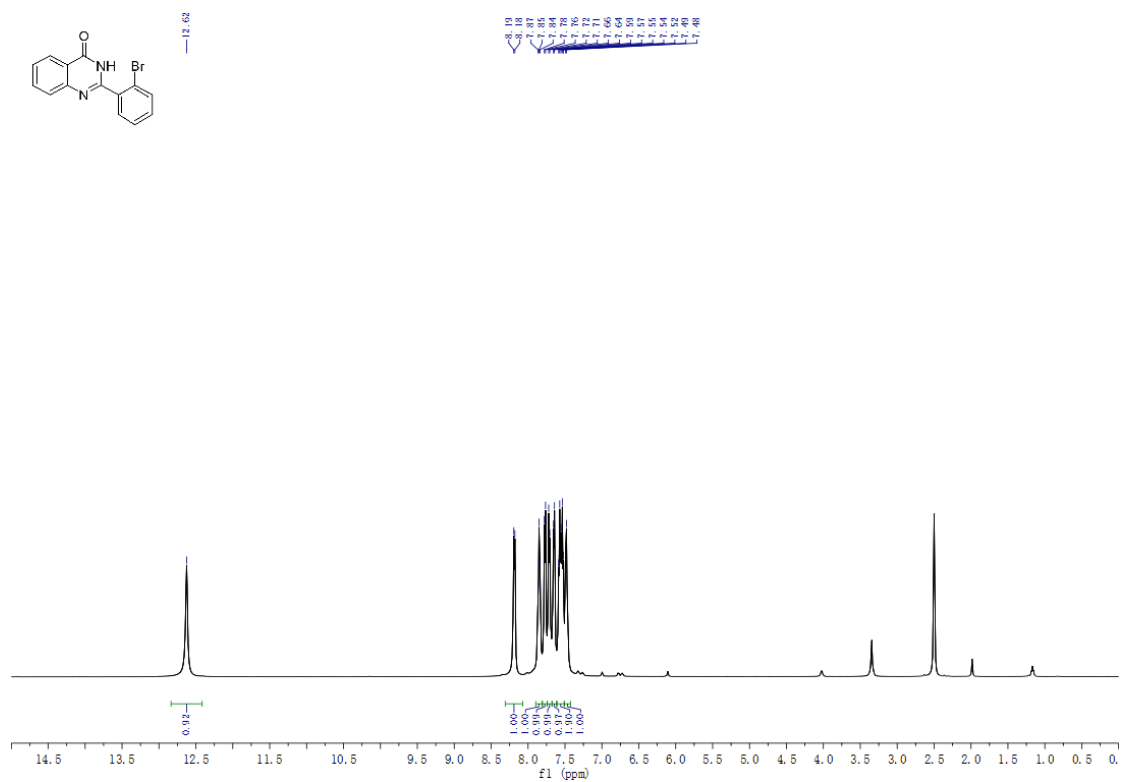
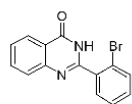
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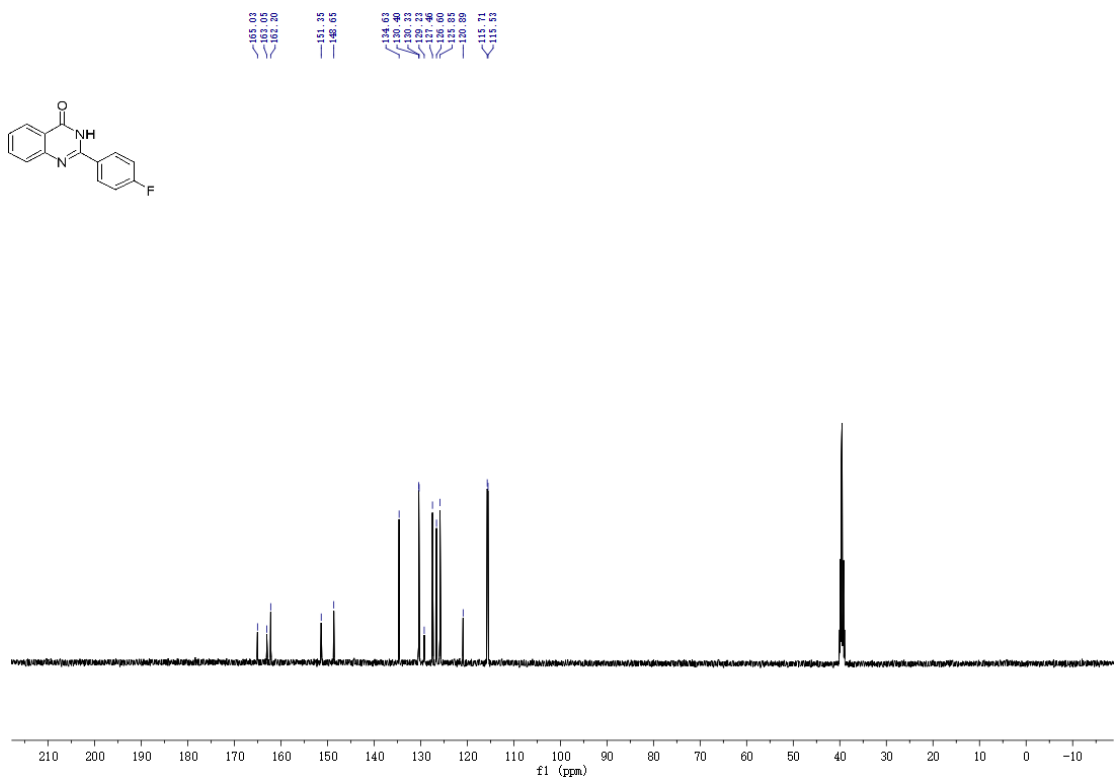
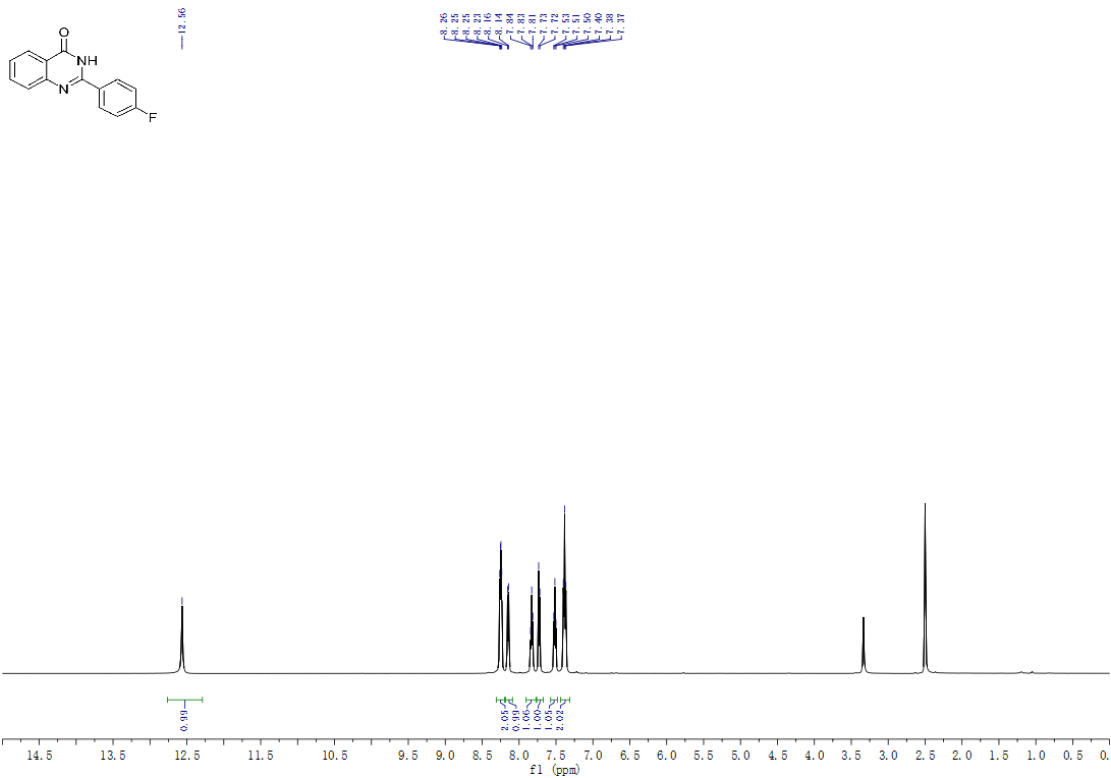
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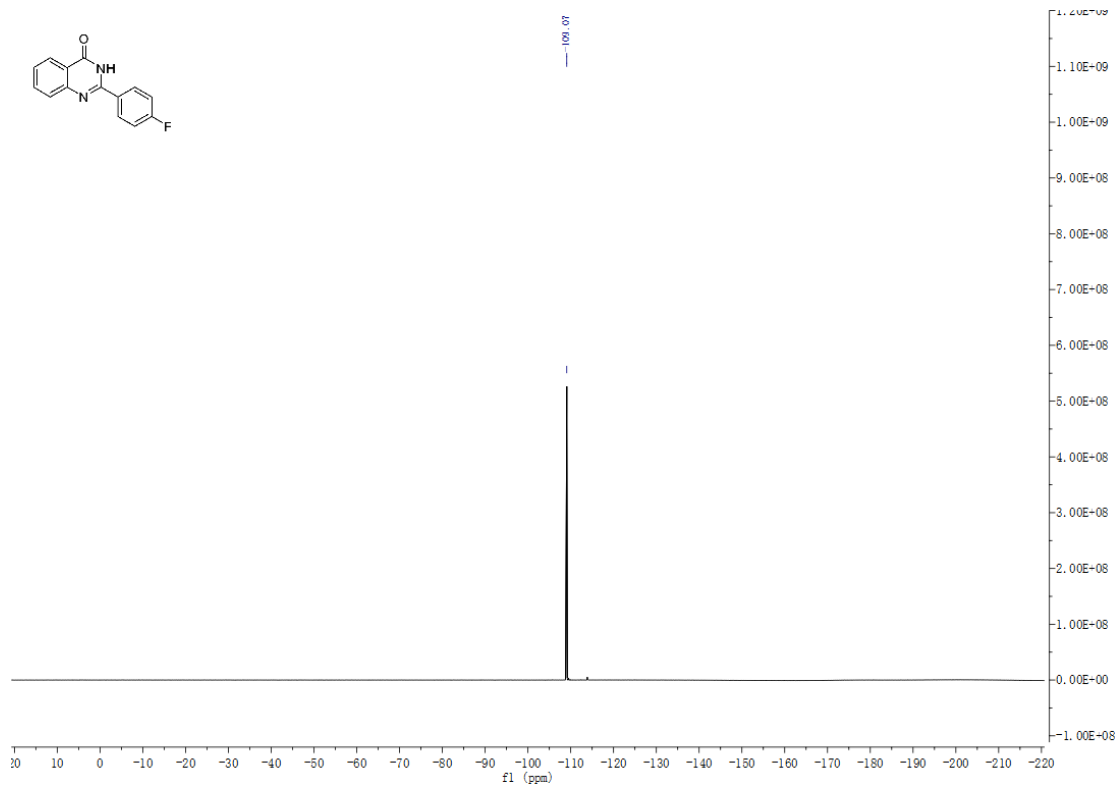


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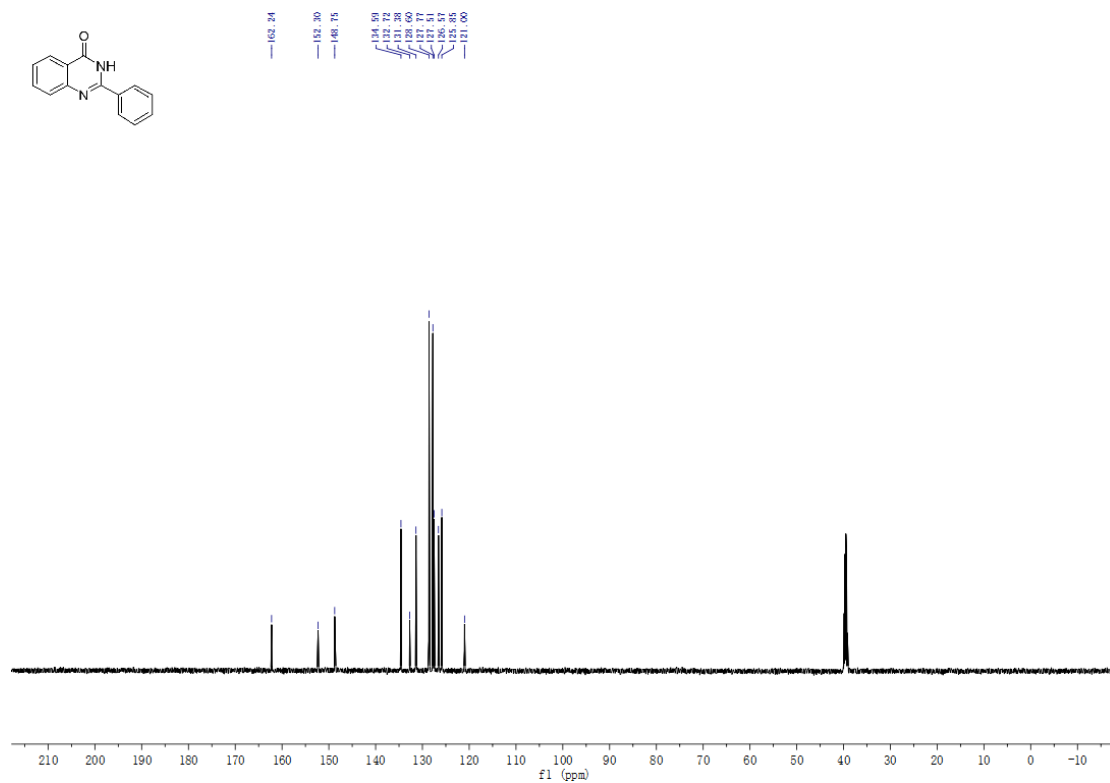
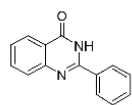
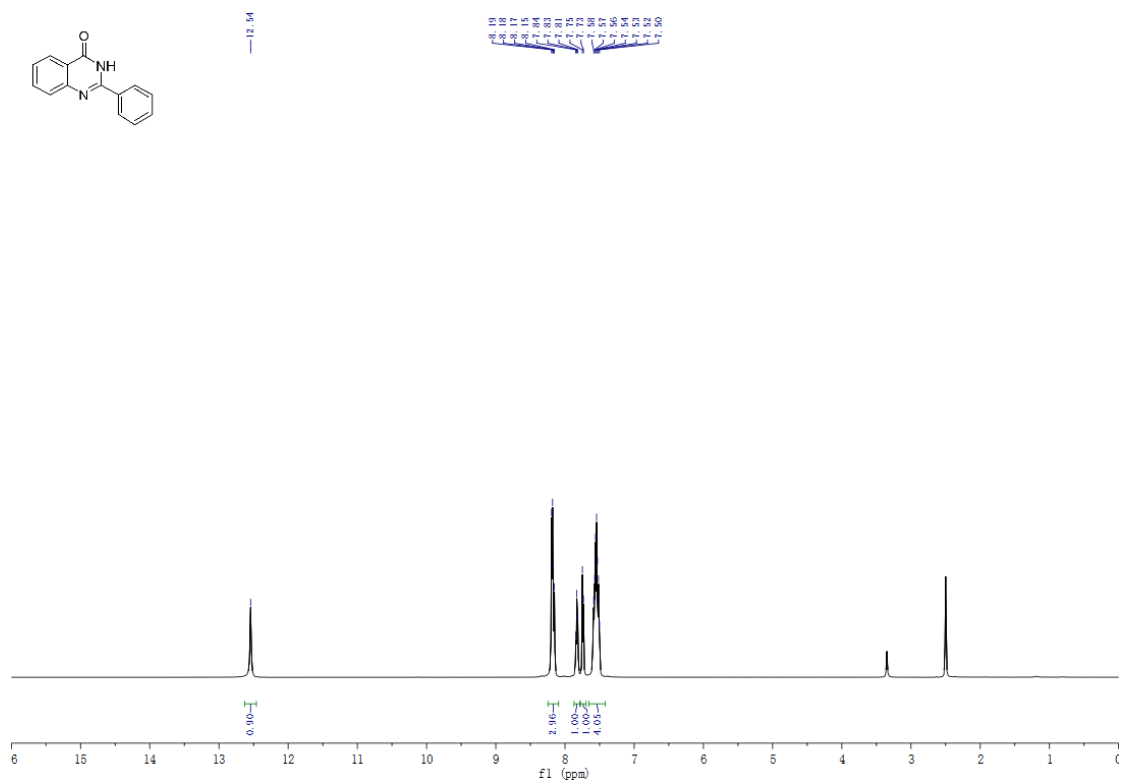
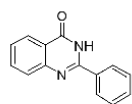


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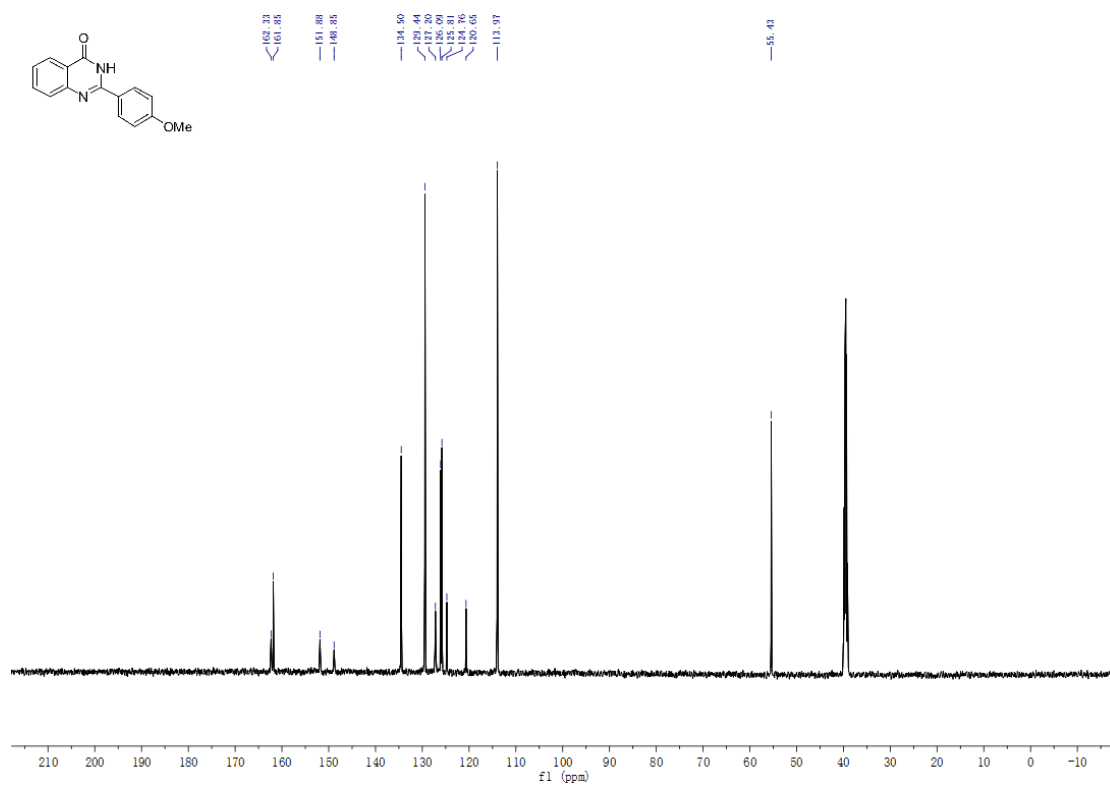
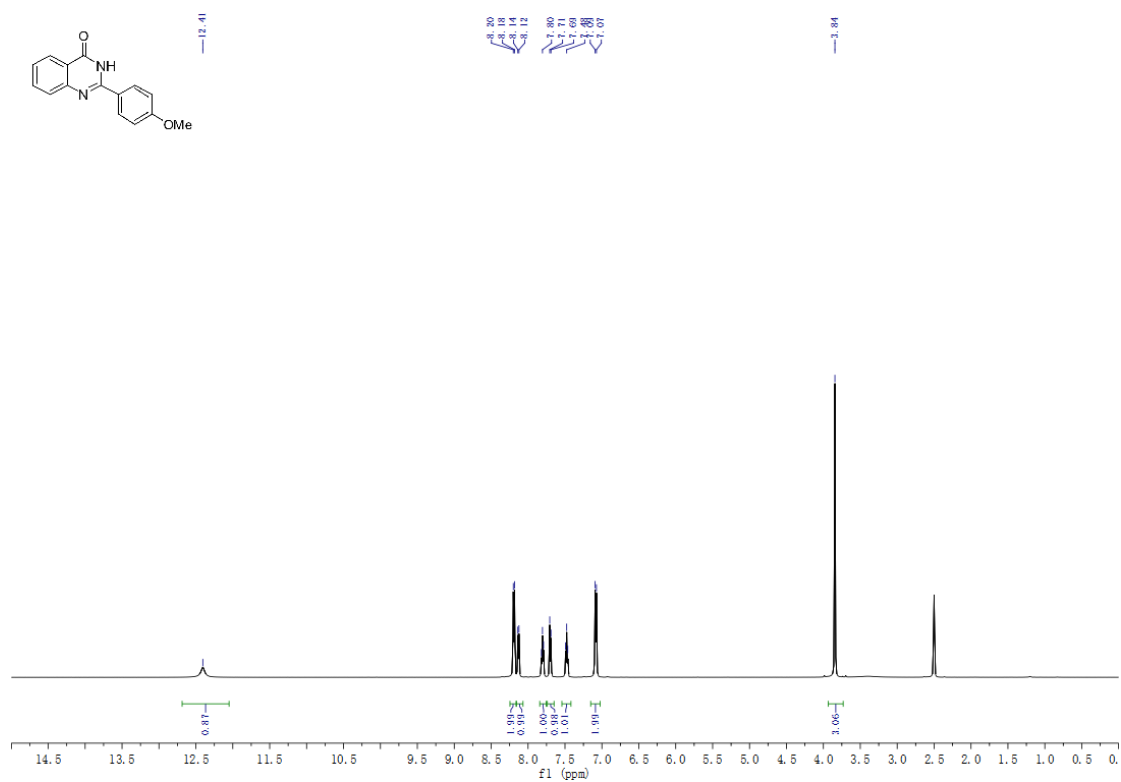




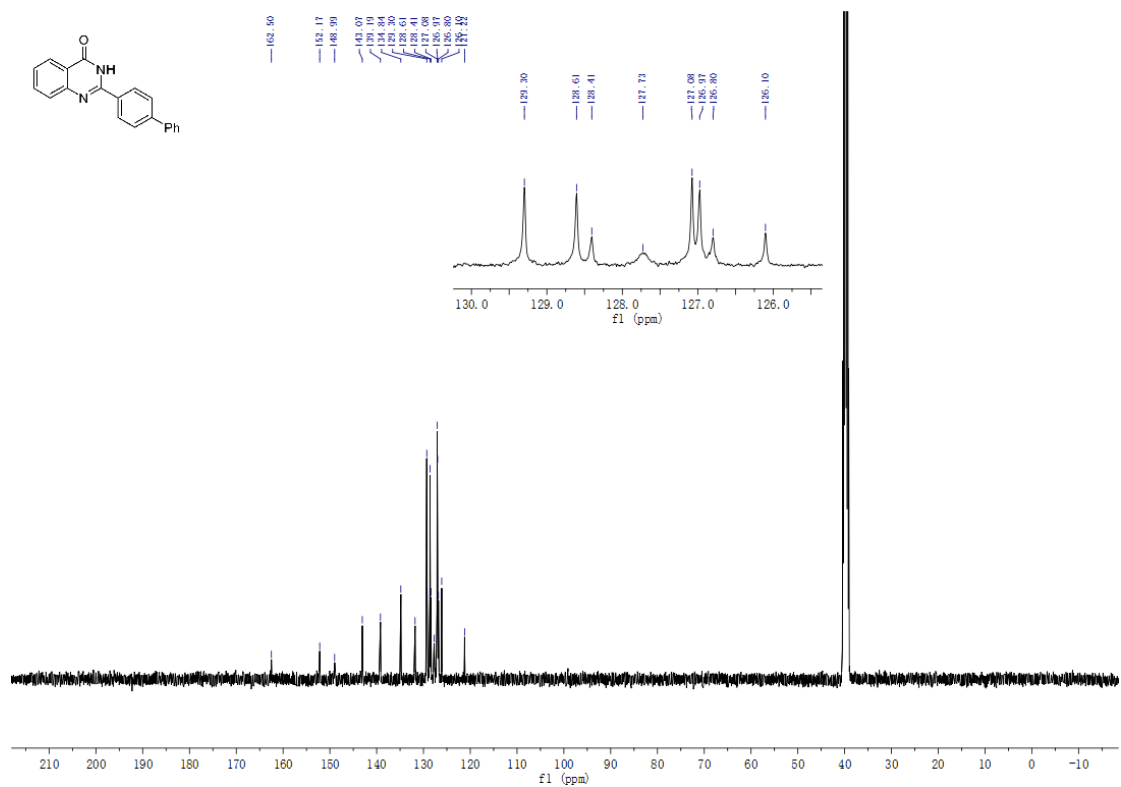
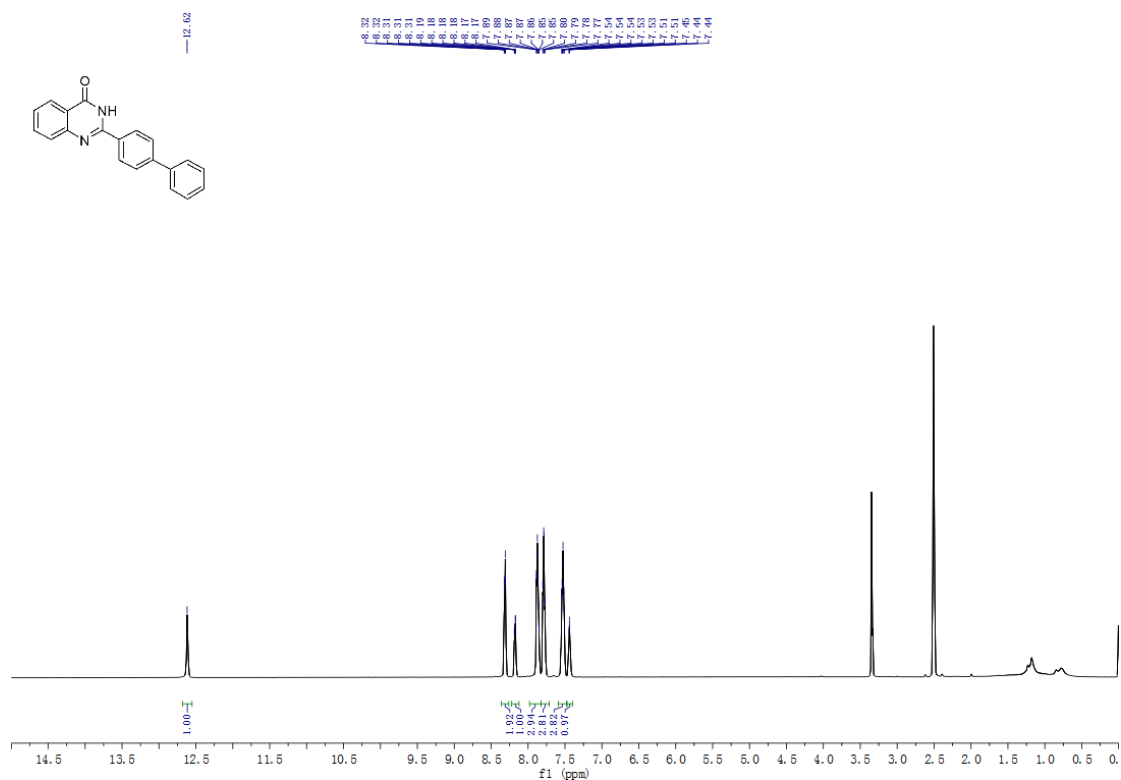
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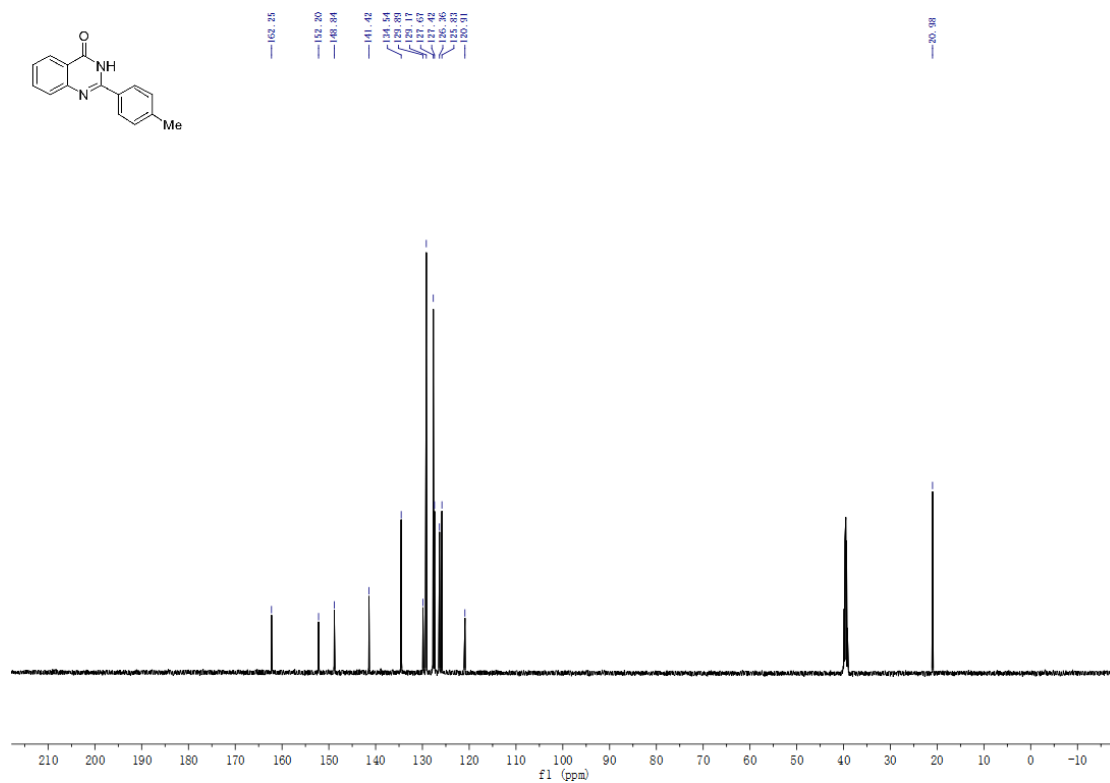
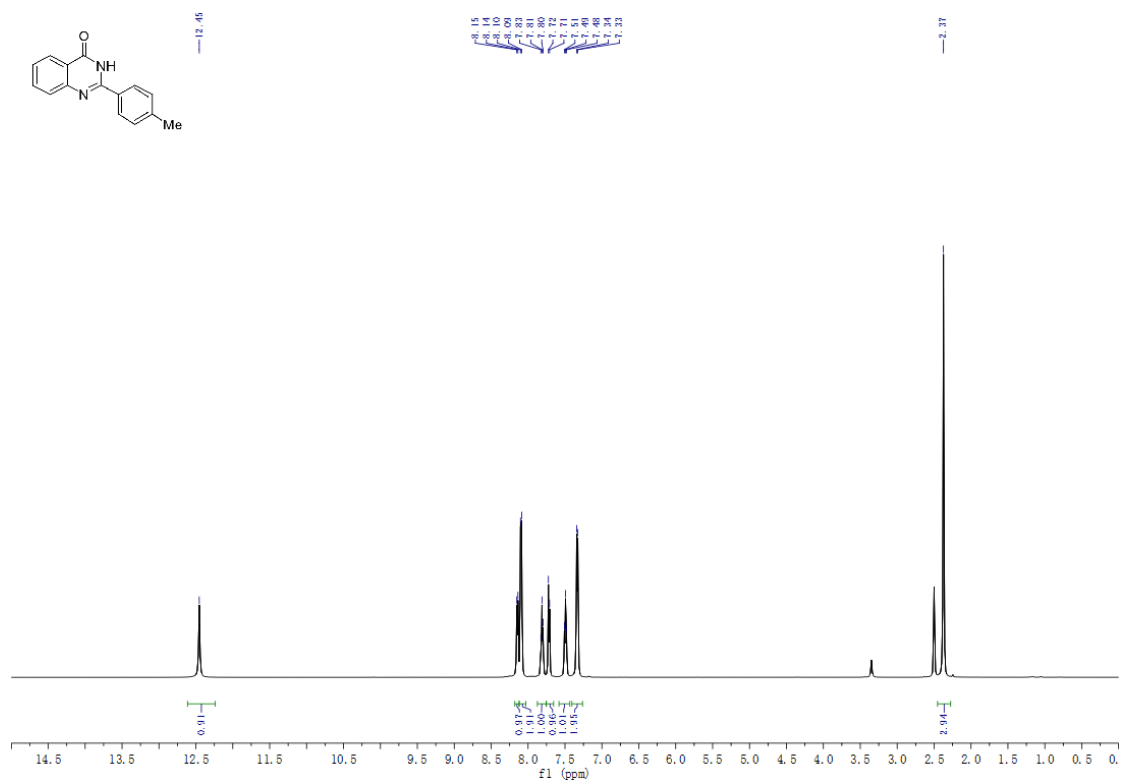
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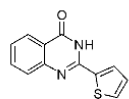
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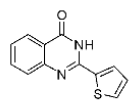
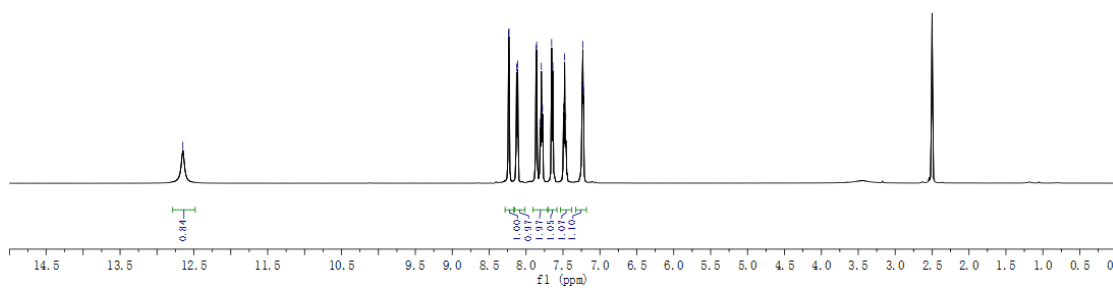


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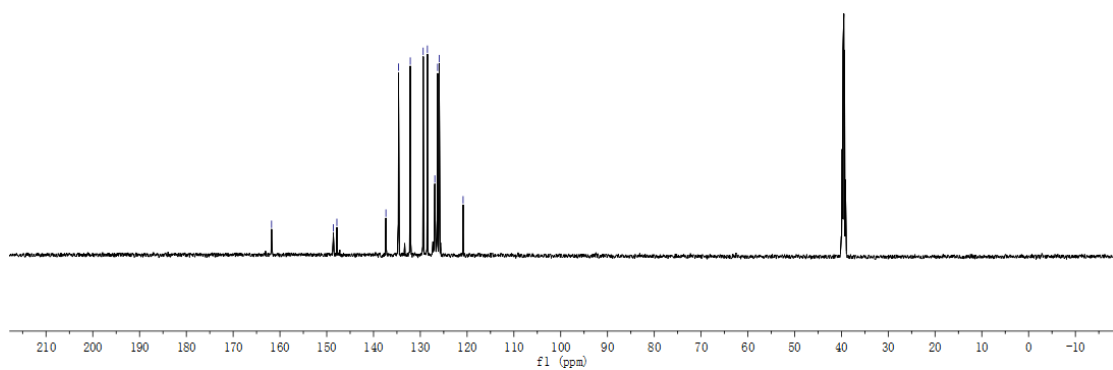
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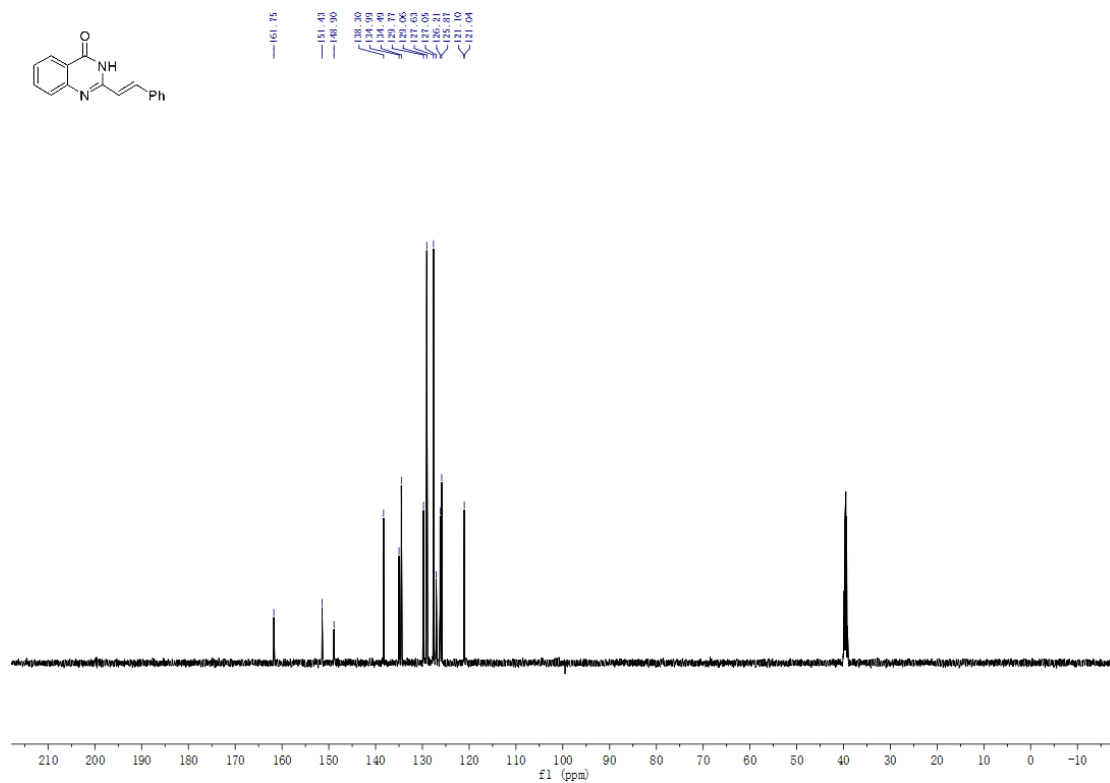
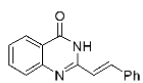
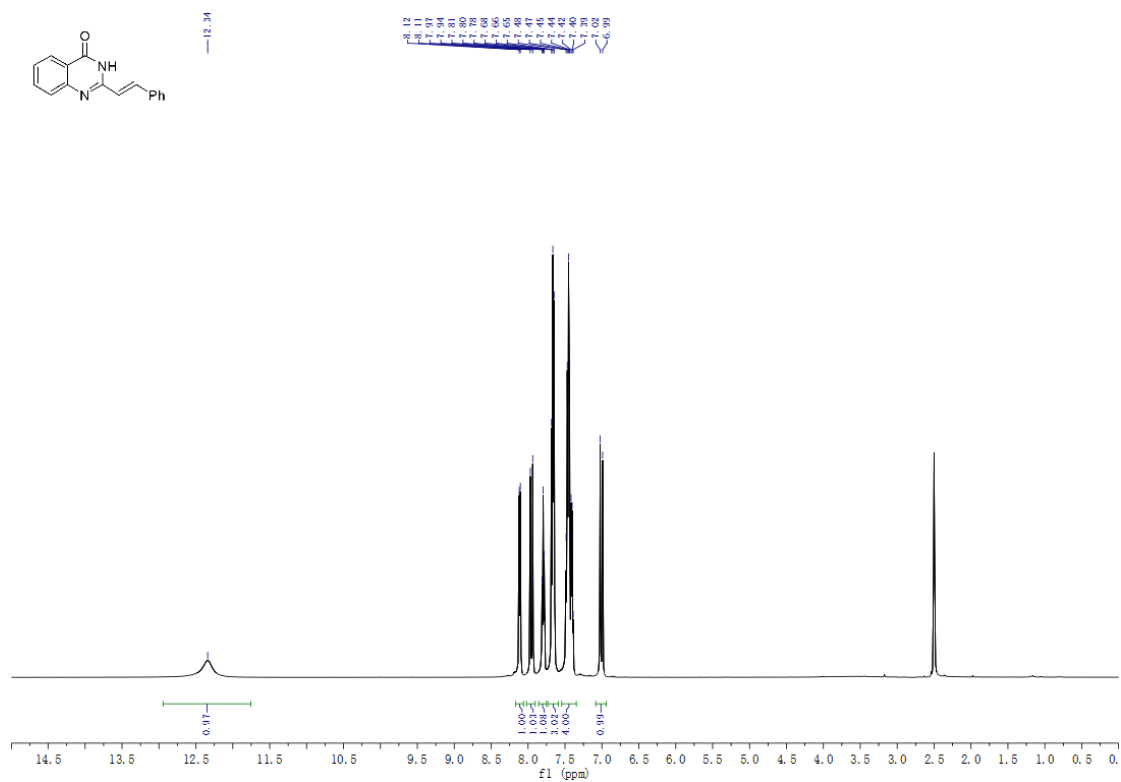
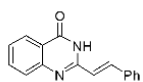


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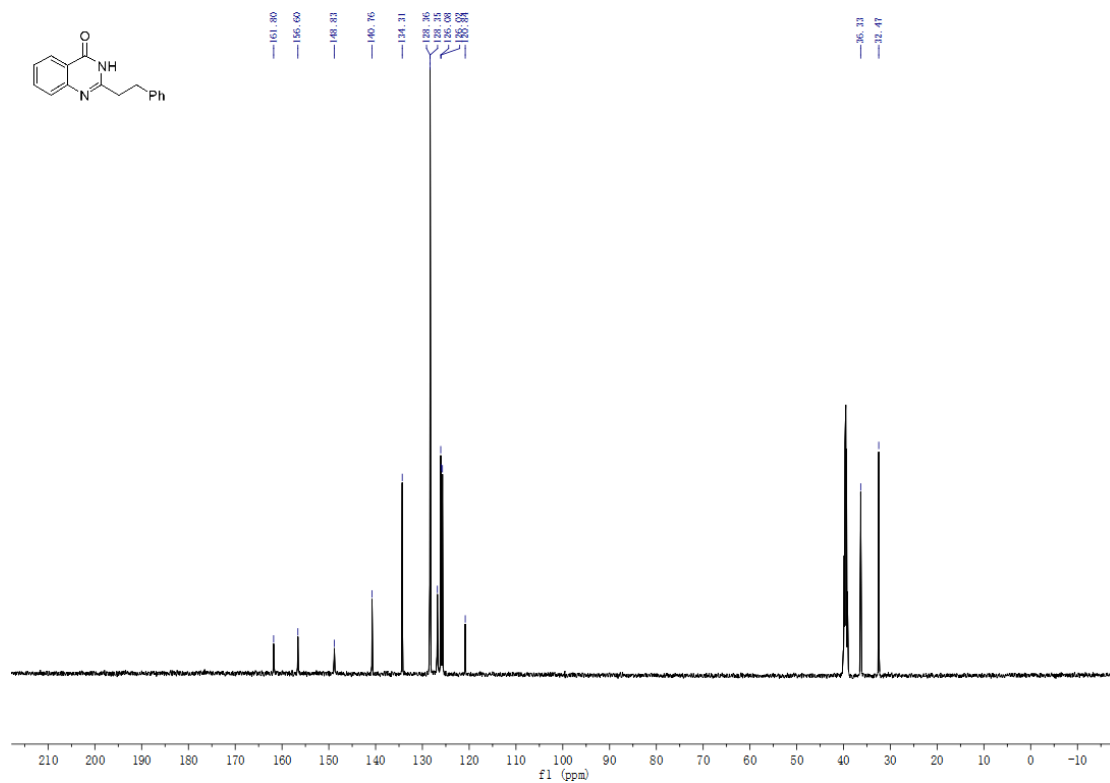
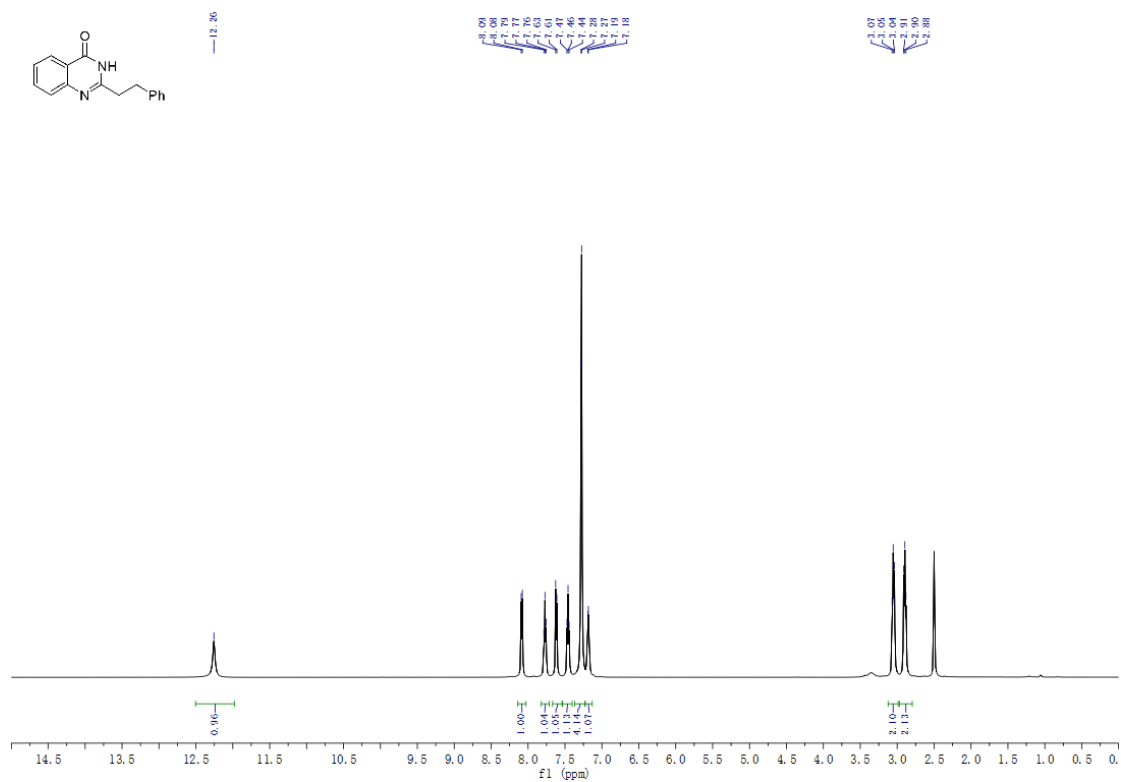
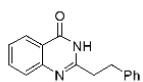
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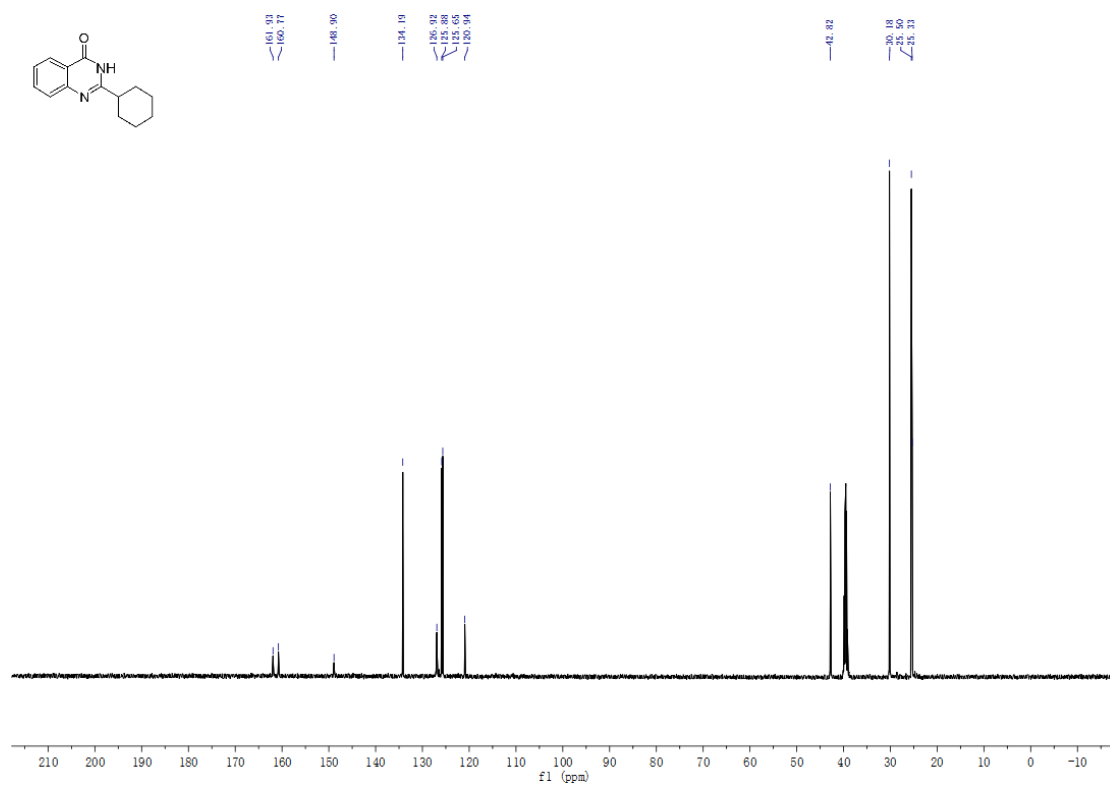
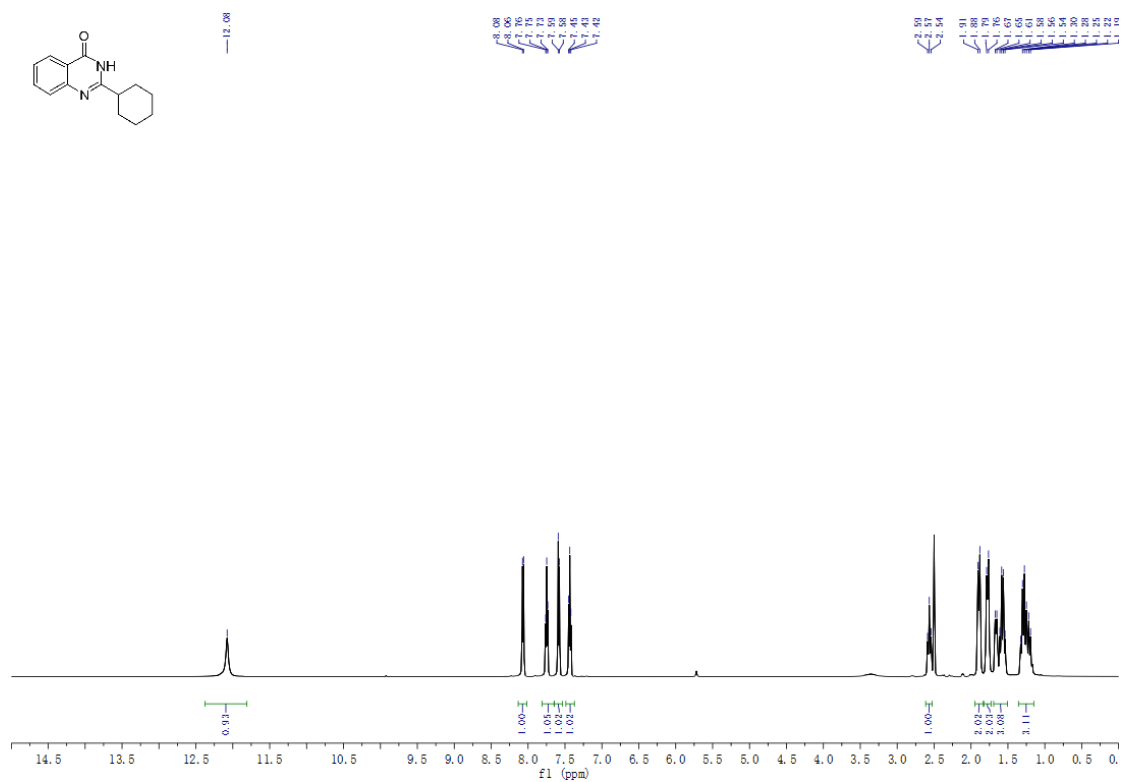
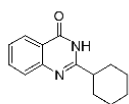
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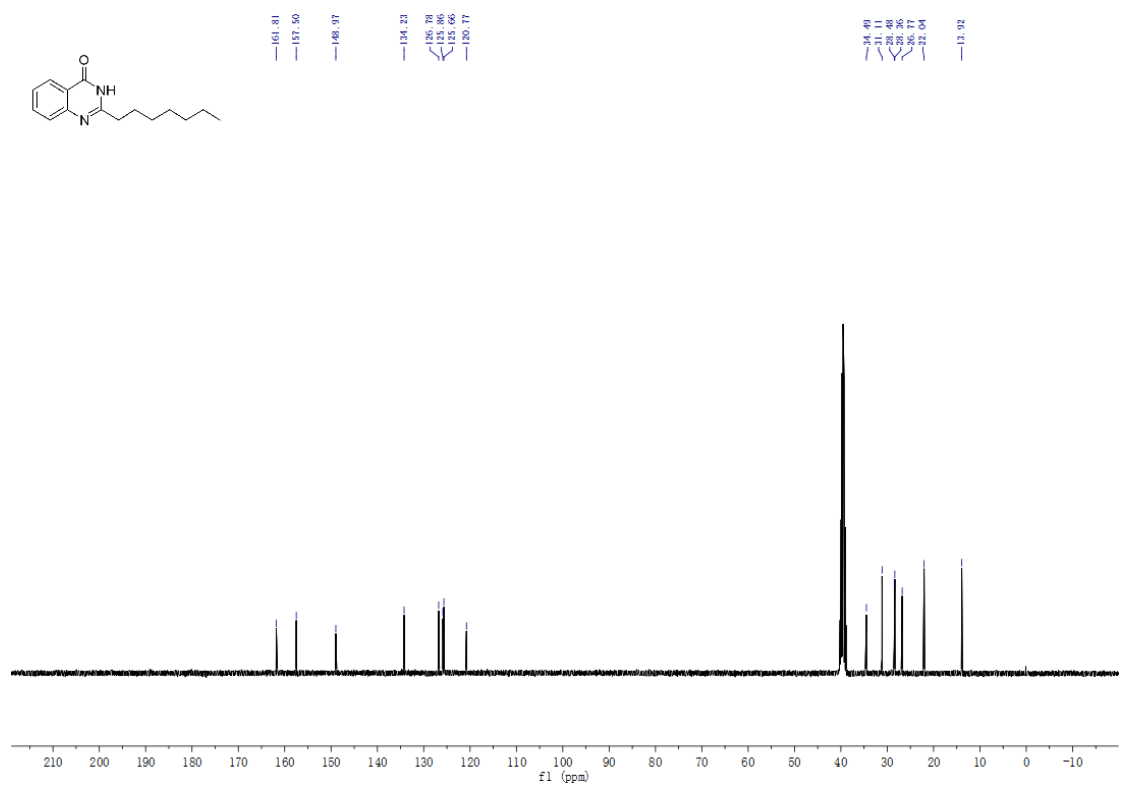
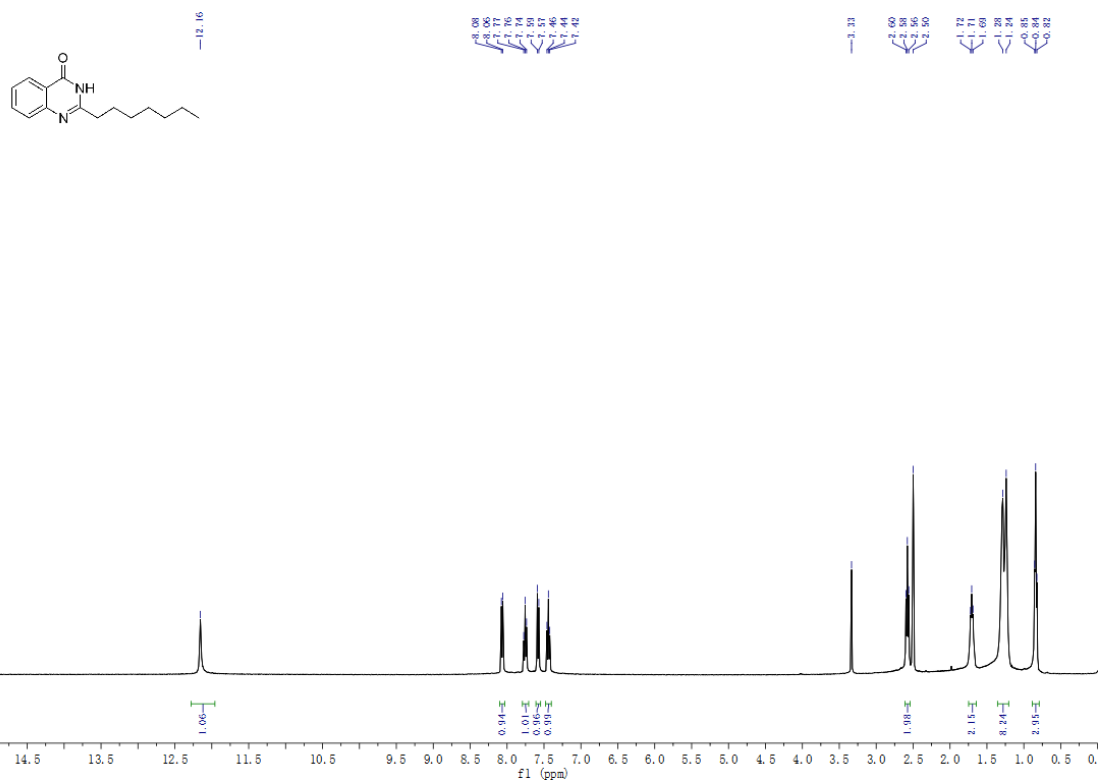
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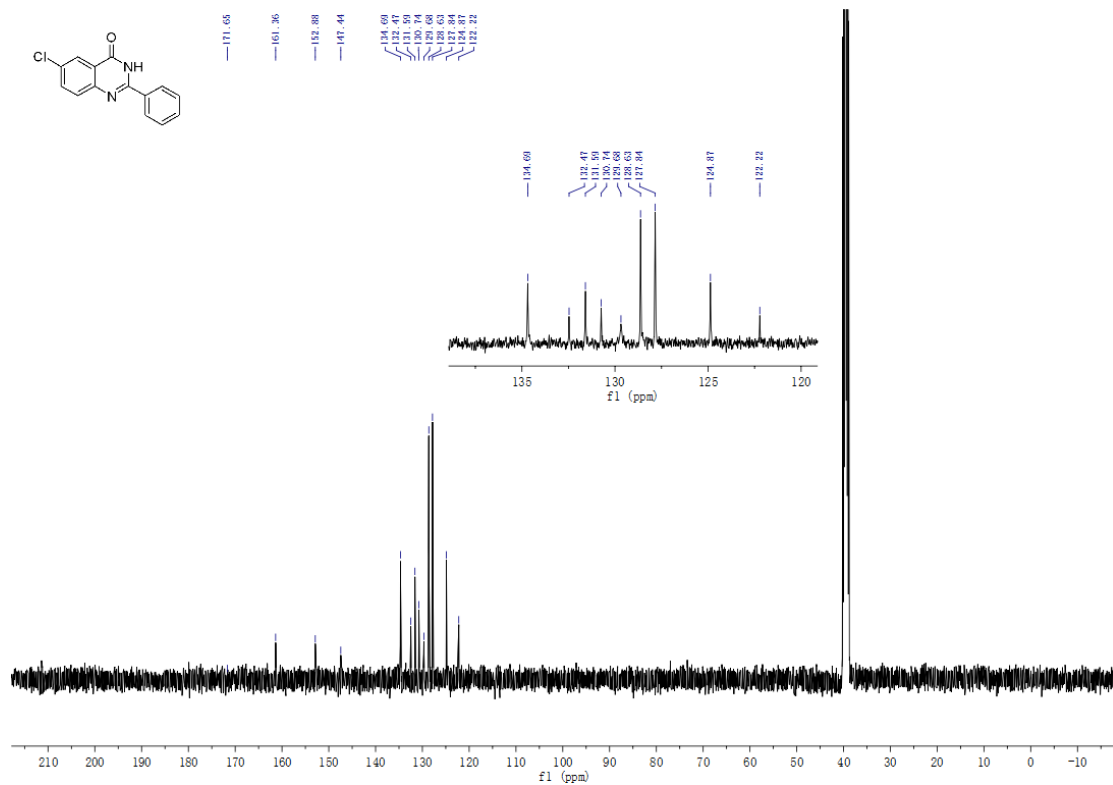
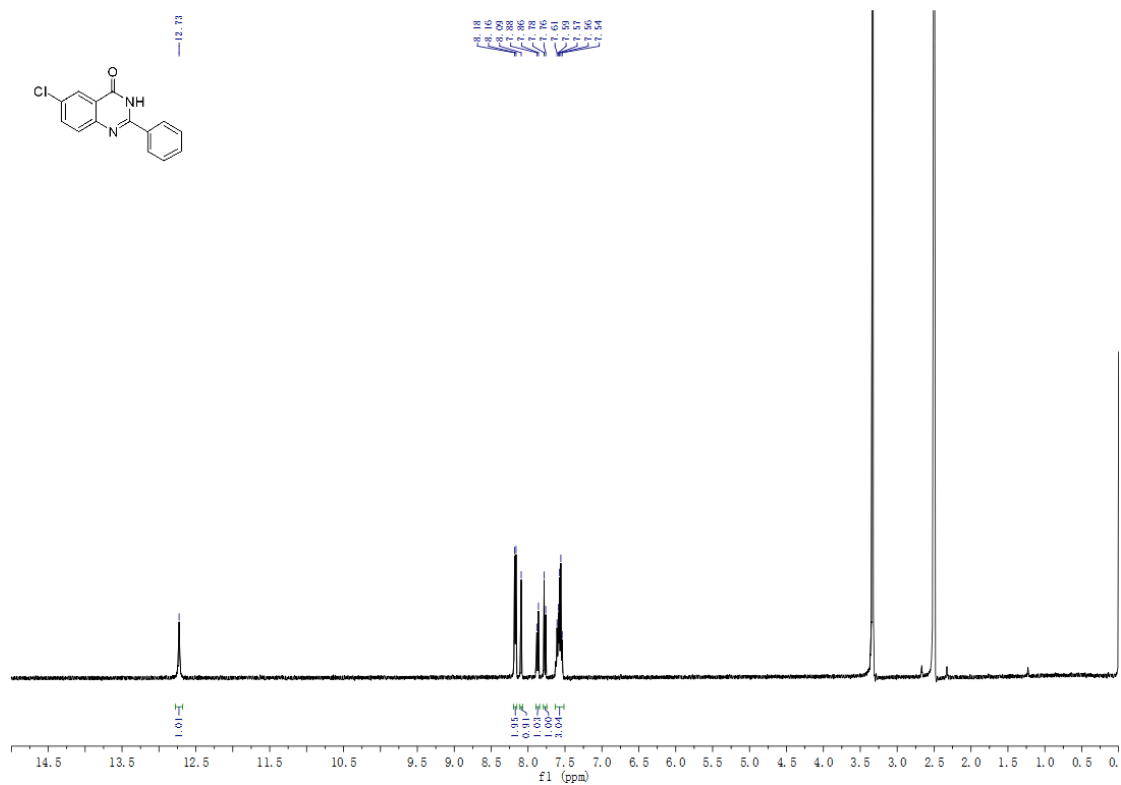
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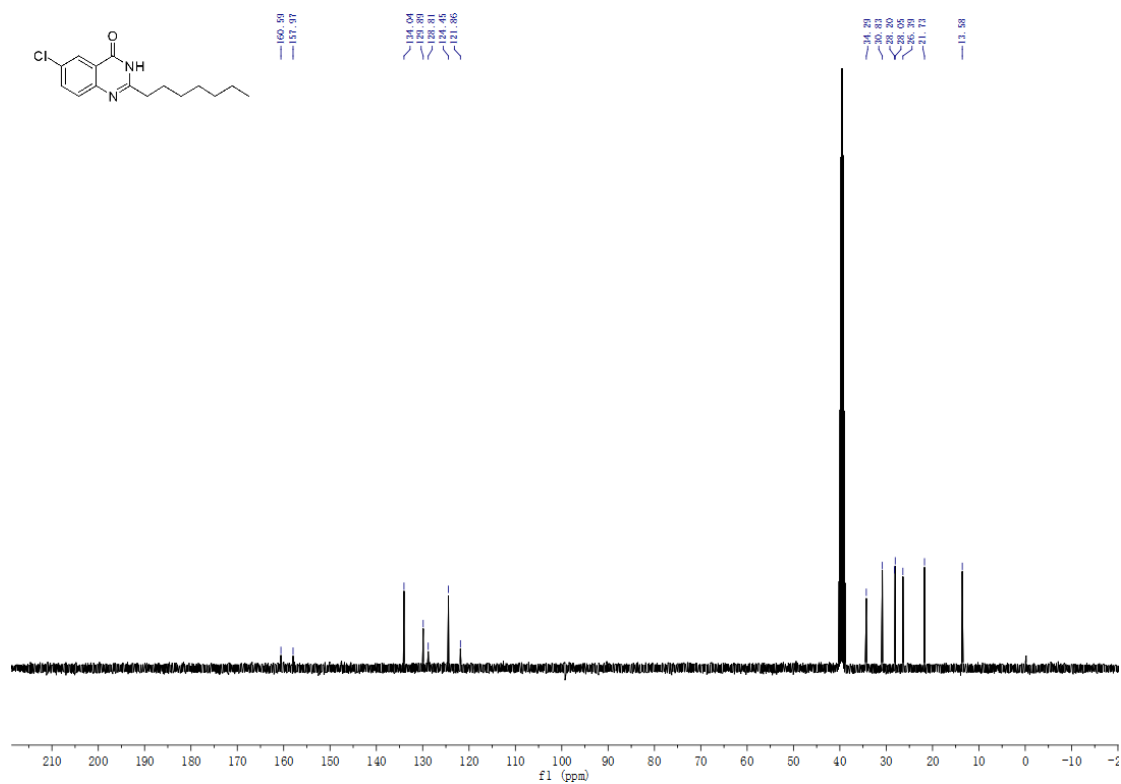
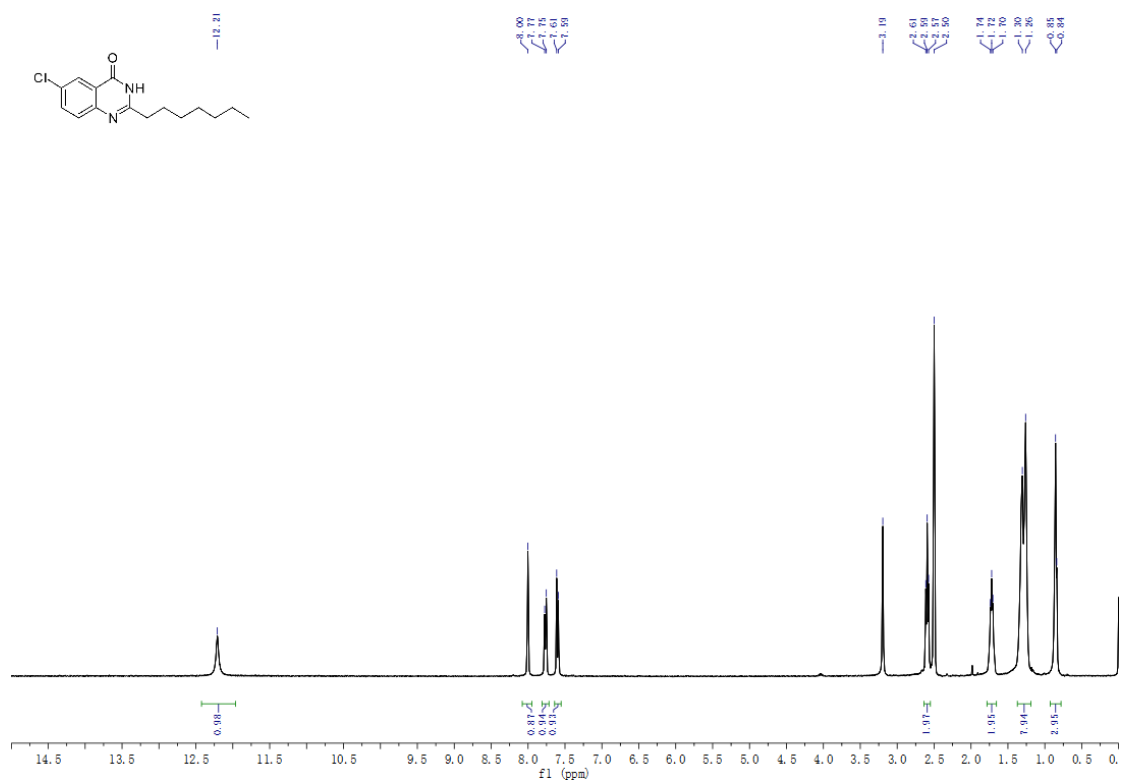
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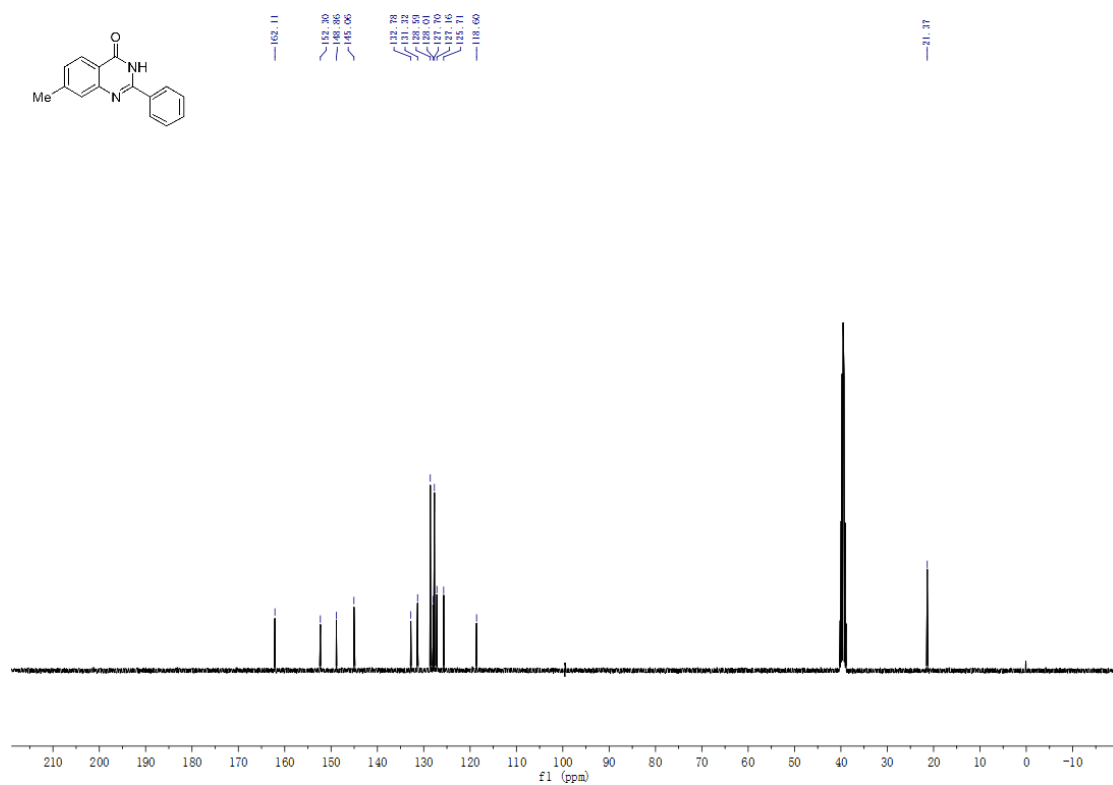
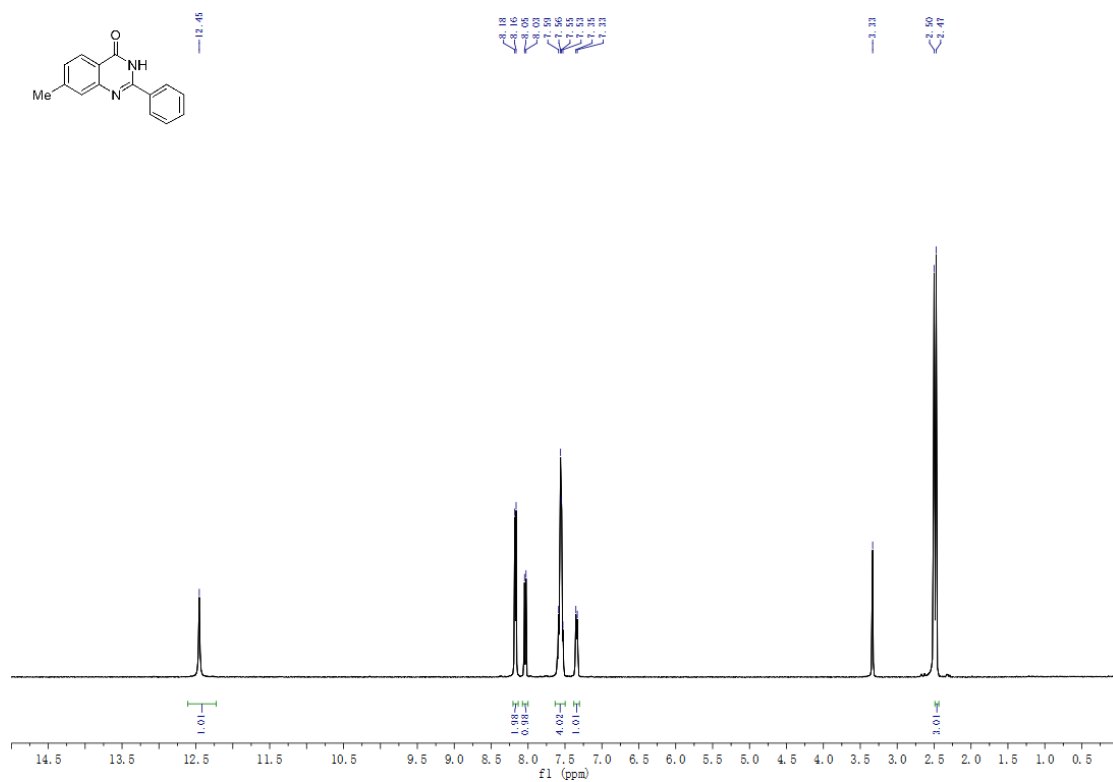
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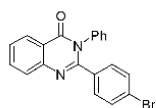
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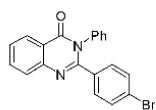
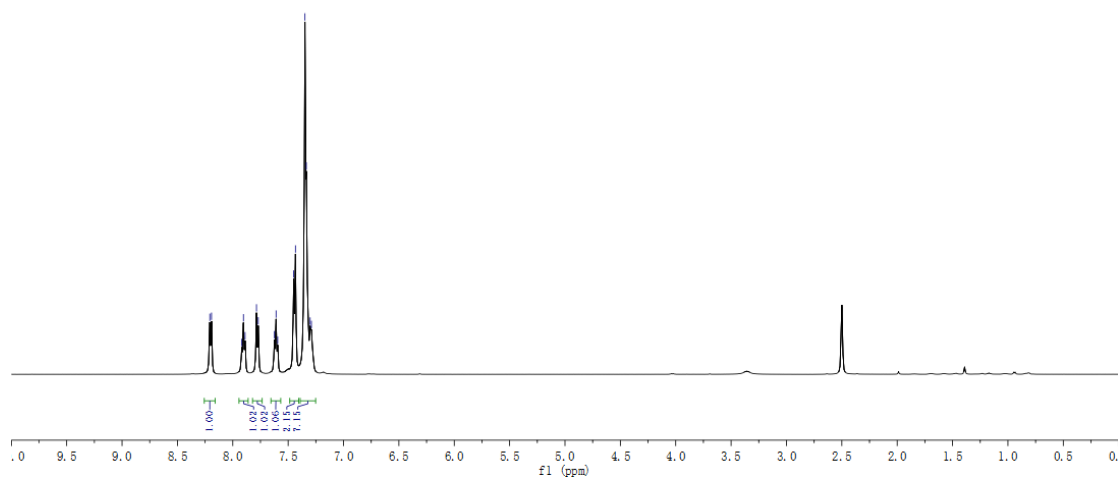
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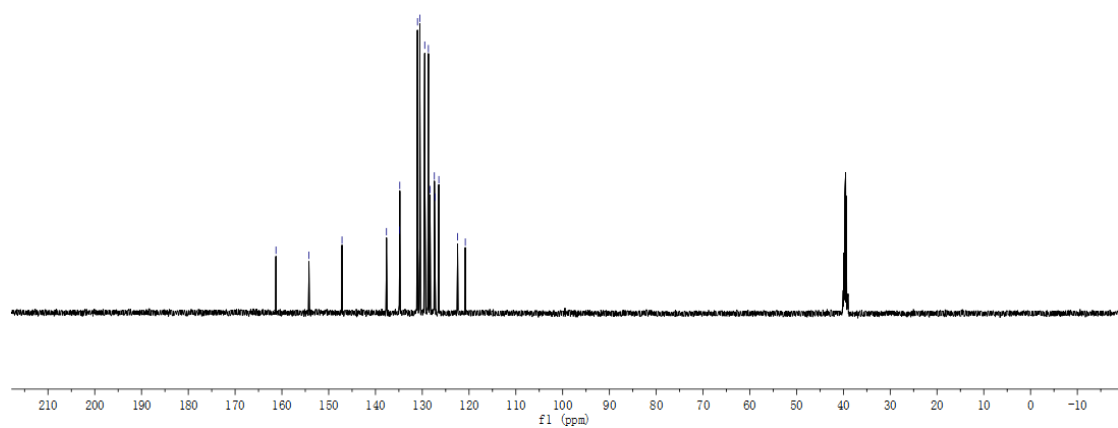
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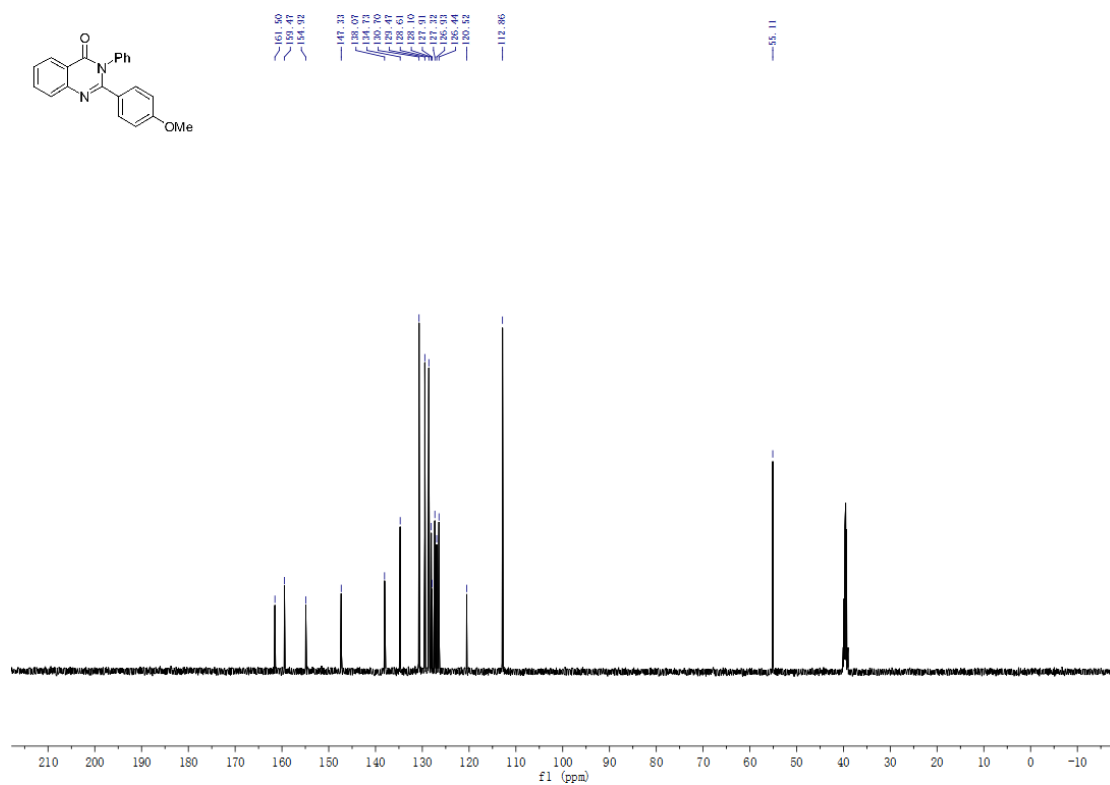
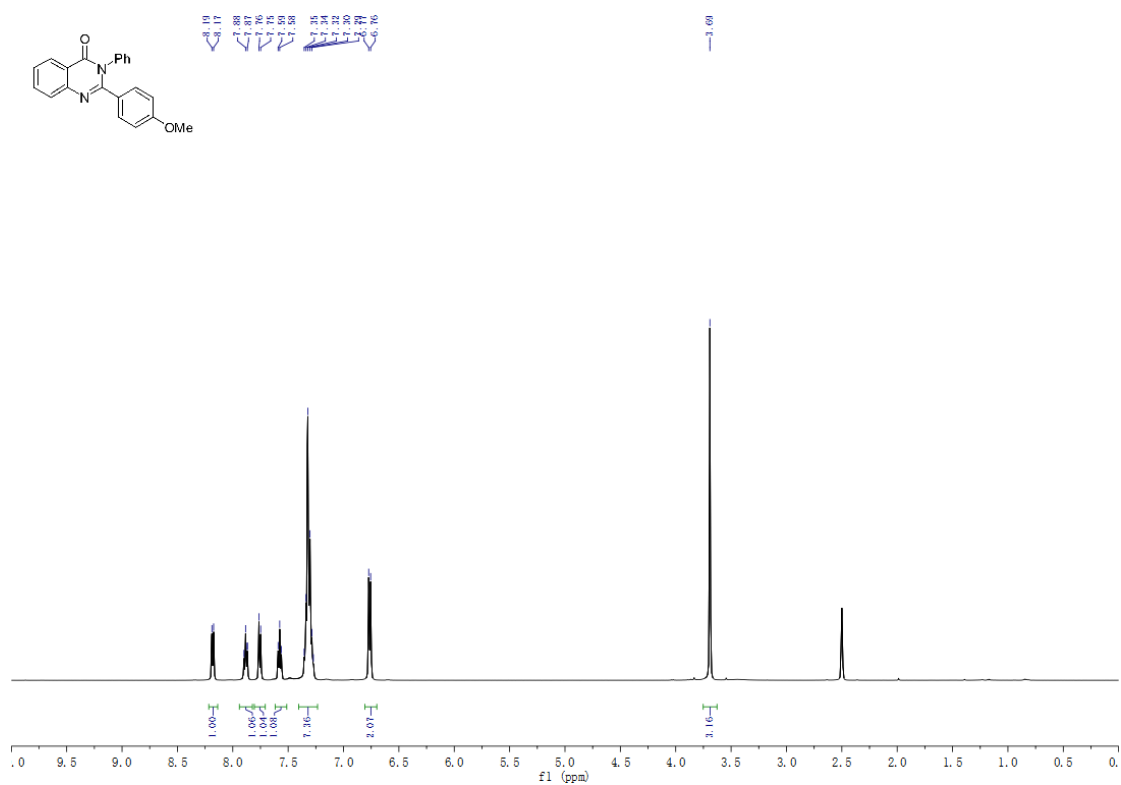
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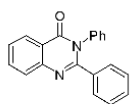
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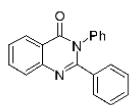
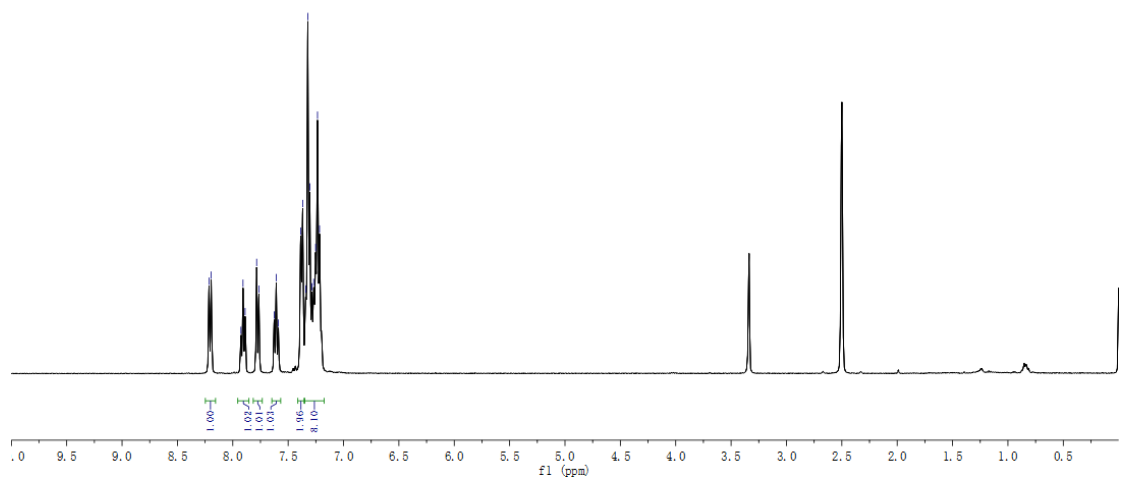
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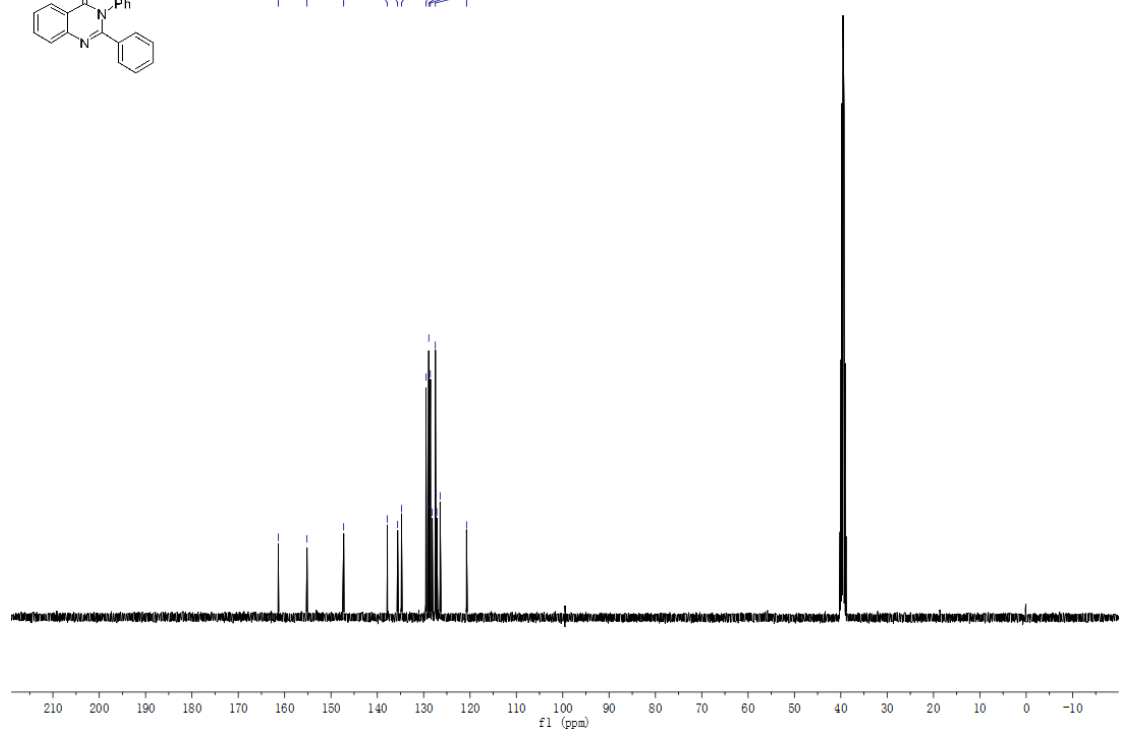
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Product 3t

