Electro-Oxidation Induced O-S Cross-Coupling of Quinoxalinones with Sodium Sulfinates for Synthesizing 2-Sulfonyloxylated Quinoxalines

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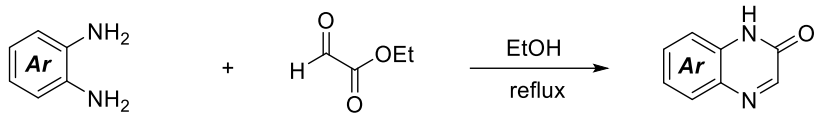
1. General information

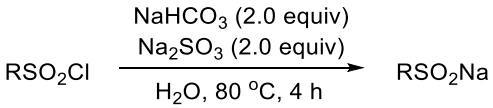
Chemicals and solvents were either purchased from commercial suppliers (Titan) or purified by standard techniques. The instrument for electrolysis is a DC regulated power supply (HSPY-200-01) (made in China). The anodic electrode was graphite plate (15 mm × 15 mm × 2 mm) and cathodic electrode was nickel foam (15 mm × 15 mm × 1 mm). Analytical thin-layer chromatography (TLC) was performed on silica gel plates with GF254 indicator (Yantai Jiangyou Silica gel Development Co., Ltd.) and compounds were visualized by irradiation with UV light at 254 nm. Flash chromatography was carried out utilizing silica gel 200-300 mesh (Qingdao Haiyang Chemical Co., Ltd.). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Plus-400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: TMS (0.00 ppm) or residual internal $CHCl_3$ (δ 7.26 ppm); ^{13}C: internal $CDCl_3$ (δ 77.2 ppm). Coupling constants were quoted in Hz (*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Cyclic Voltammetry were obtained on a Biologic sp300 potentiostat.

2. General procedure for the synthesis of quinoxalinones[1]



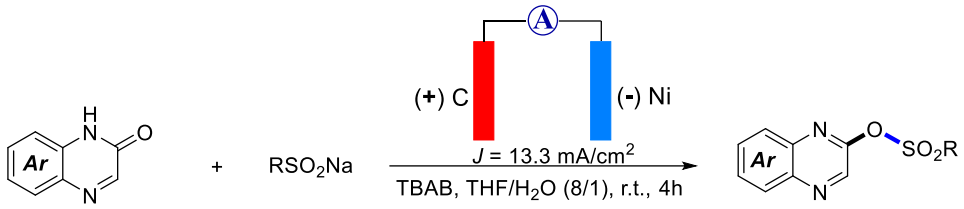
To a solution of 1,2-phenylenediamines (5 mmol, 1.0 equiv.) in ethanol (30 mL) was added ethyl glyoxalate (6 mmol, 1.2 equiv.). The reaction system was stirred and heated to reflux at 85 °C for 1 h, then stirred at room temperature for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with ethanol (3 × 5 ml), and finally dried to give quinoxalinones.

3. General procedure for the synthesis of sodium sulfinates[2]



Sulfonyl chlorides (5.00 mmol) were added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M) and heated at 80 °C for 4 h, after cooling to room temperature the volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid.

4. General procedure for electro-oxidation induced selective O-S cross-coupling



A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (2.0 equiv) and 10 mL of THF/H_2O (8/1). The mixture was electrolyzed using constant current conditions (~13.3 mA cm^{-2}) at room temperature under magnetic stirring for 4 h. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of quinoxalinone), the electrodes were removed and rinsed with EtOAc and the mixture was poured into a saturated aqueous solution of NaCl and the product was then extracted with ethyl acetate (3 × 10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired pure product.

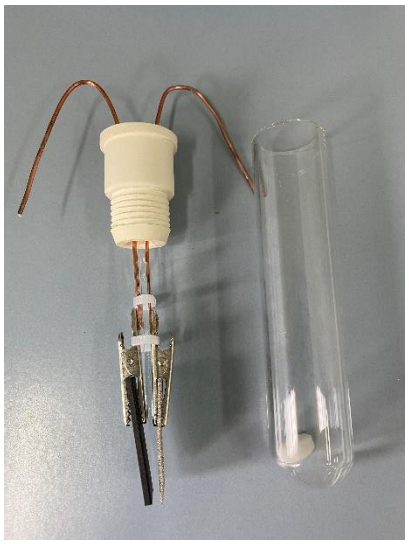
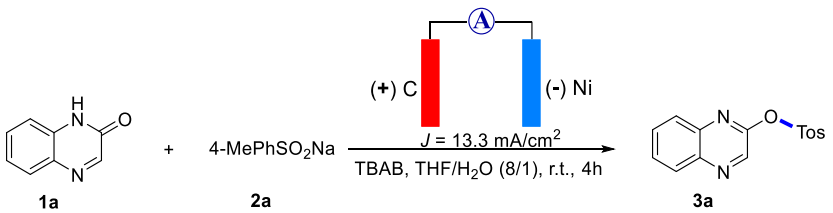


Figure S1. Reaction set-up parts

Figure S2. Assembled reaction set-up

5. Optimization of the reaction conditions

Table S1 Optimization of Reaction Condition[a]



Entry	Change from standard conditions	Yield(%)

1	none	82(75)[b]
2	without electricity	n.d.
3	without H_2O	trace
4	without TBAB	n.d.
5	HOAc instead of H_2O	trace
6	HFIP instead of H_2O	n.d.
7	1,4-dioxane instead of THF	65
8	CH3CN instead of THF	50
9	KBr instead of TBAB	50
10	TEAB instead of TBAB	30
11	TMAB instead of TBAB	20
12	20 mA, 6 h	62
13	40 mA, 3 h	63
14	+GF/-Ni	45
15	+CC/-Ni	61
16	+C/-Pt	64
17	+C/-SS	63
18	under Ar	81

[a]Reaction conditions: graphite plate anode (15 mm × 15 mm × 2 mm), nickel foam cathode (15 mm × 15 mm × 1 mm), constant current = 30 mA (J = 13.3 mA/cm^2), **1a** (0.50 mmol), **2a** (1.00 mmol), TBAB (2.0 equiv), THF/H_2O (8/1) (10 mL), room temperature, 4 h, undivided cell; The yield of **3a** was determined by ^{1}H NMR using 1,1,2,2-tetra-chloroethane as the internal standard; n.d. = not detected. [b]The yield of the isolated product is given within the parentheses.

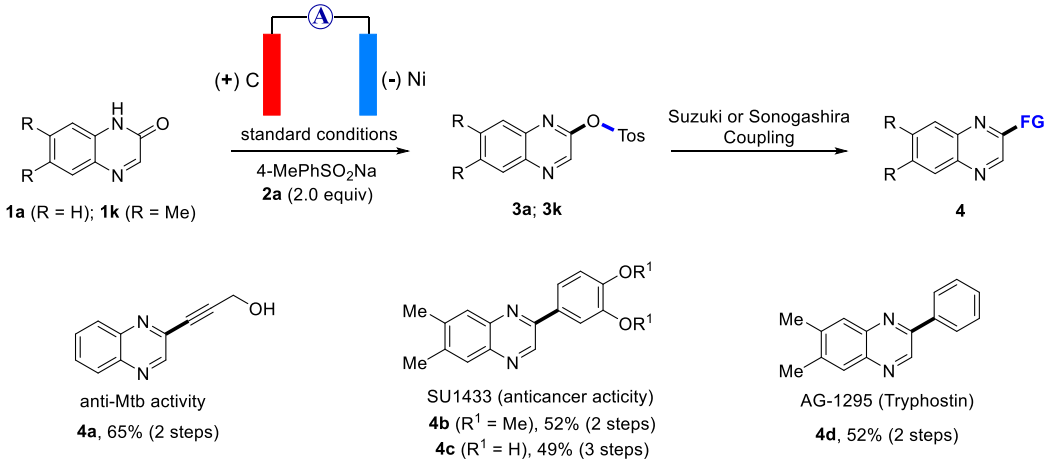
6. Synthetic Application to Preparation of Bioactive Molecules[3,4]

The preparation of 4a: To an oven dried two-necked flask equipped with a stirrer bar, was added **3a** (0.5 mmol), $PdCl_2(PPh_3)_2$ (5 mol %) and CuI (10 mol %), which was dissolved in 2 mL dry THF followed by an addition of Et_3N (2 equiv) and propargyl alcohol (1.2 equiv). The reaction mixture was refluxed at 50 °C and stirred for 18 h under nitrogen atmosphere. The reaction was quenched by adding ethyl acetate/water (3/1). The layers were separated, and the aqueous layer was washed with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude was purified by column chromatography.

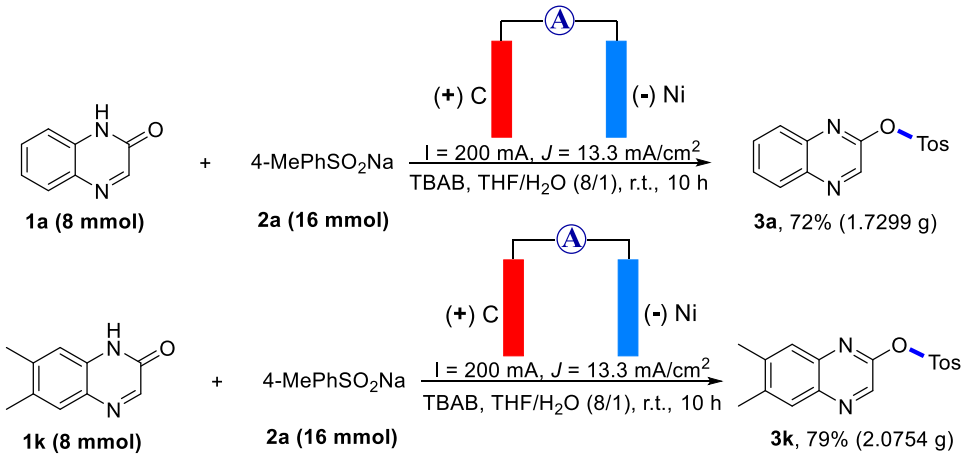
The preparation of 4b and 4d: An oven dried screw cap glass test tube (25 mL), which was equipped with magnetic stir bar, was charged with **3a** (1.0 mmol), $Pd(OAc)_2$ (2 mol %), BrettPhos (4 mol%), corresponding boronic acid (2.0 mmol) and $K_3PO_4 \cdot H_2O$ (3.0 mmol). The test tube was then tightly capped with a Teflon top plastic screw cap and evacuated and back

filled with argon; this process was repeated for a total of three times. The solvent was then added by a syringe under a positive flow of argon. And then the reaction mixture was stirred at room temperature for a few seconds to create a homogeneous slurry, and then transferred to a preheated oil bath (110 °C) and allowed to stir for 2 h. After the reaction was complete, the mixture was diluted with 3-5 mL of water and ~5 mL of ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and then purified using column chromatography.

The preparation of 4c: To a solution of **4a** (0.5 mmol) in dry CH_2Cl_2 (5 mL) was slowly added BBr_3 (1.2 mmol) at -20 °C. Upon warming to room temperature, the reaction mixture was stirred overnight. 1M HCl (2 mL) was added to quench the reaction at 0 °C. The product was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried over $NaSO_4$, filtered and concentrated under reduced pressure. The product may be purified with a silica gel column chromatography.



7. Gram-scale experiments



A 250 mL beaker with a stir bar was charged with quinoxalinone **1a** or **1k** (8.0 mmol, 1.0 equiv), 4-$MePhSO_2Na$ (2.8509 g, 16.0 mmol, 2.0 equiv) and $^nBu_4NBr$ (3.30 g, 16.0 mmol, 2.0 equiv)

and 160 mL of THF/H_2O (8/1). Graphite plate anode (50 mm × 30 mm × 2 mm) and nickel foam cathode (50 mm × 30 mm × 1 mm) were inserted into the mixture. Then, the reaction mixture was electrolyzed under a constant current of 200 mA (J = 13.3 mA/cm^2) at room temperature for 10 h. After the reaction, the electrodes were removed and rinsed with EtOAc. The mixture was poured into a saturated aqueous solution of NaCl and the product was then extracted with ethyl acetate (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The solvent was concentrated in vacuo and the crude material was purified by column chromatography to furnish the desired product as a white crystal.

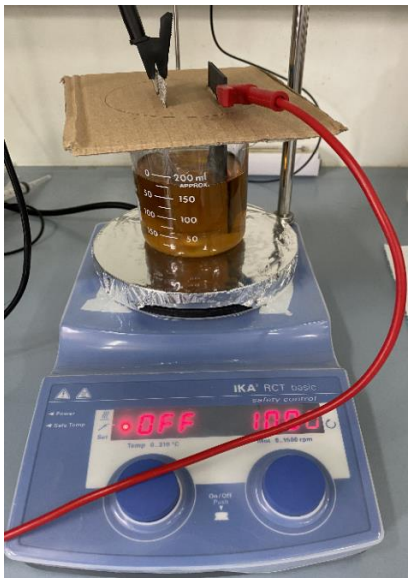


Figure S3. Setup for Gram-Scale Electrolysis

8. Mechanistic Experiments

Procedure for the Mechanistic Experiment (Scheme 6, a). A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), ^{n}Bu$_4$NBr (2.0 equiv), 10 mL of THF/H_2O (8/1) and TEMPO (2.0 equiv), BHT (4.0 equiv), respectively. The mixture was electrolyzed using constant current conditions (~13.3 mA cm^{-2}) at room temperature under magnetic stirring for 4 h. Only a tiny to trace amount of **3a** was afforded.

Procedure for the Mechanistic Experiment (Scheme 6, b). A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), ^{n}Bu$_4$NBr (2.0 equiv), 10 mL of THF/H_2O (8/1) and 4-*tert*-butylstyrene (2.0 equiv). The mixture was electrolyzed using constant current conditions (~13.3 mA cm^{-2}) at room temperature under magnetic stirring for 4 h. Vinyl sulfone **4** was produced in 18% isolated yield.

Procedure for the Mechanistic Experiment (Scheme 6, c). (1) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added

quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (2.0 equiv) and 10 mL of THF/H_2O (8/1). The mixture was electrolyzed using constant current conditions (~13.3 mA cm^{-2}) at room temperature under magnetic stirring for 4 h. No **3a** was detected. (2) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (2.0 equiv) and 10 mL of THF/H_2O (8/1). Then the electrolysis system was stirred at room temperature for 4 h (electric current was zero). Still, **3a** was not detected. (3) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), Na_2CO_3 (1.0 equiv), $^{n}Bu_4NBr$ (2.0 equiv) and 10 mL of THF/H_2O (8/1). Then the electrolysis system was stirred at room temperature for 4 h (electric current was zero). **3a** was obtained with 78% yield.

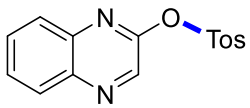
Procedure for the Mechanistic Experiment (Scheme 6, d). Several undivided cells were respectively equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (2.0 equiv) and 10 mL of THF/H_2O (8/1). Then the electrolysis system was stirred at room temperature for 1 h; 2 h (including turn-off 1h); 2 h; 3 h (including turn-off 1h); 3 h; 4 h (including turn-off 1h). The yield of **3a** was determined by isolated yield.

9. Cyclic voltammetry

Cyclic voltammetry was performed in a three-electrode cell at room temperature. The working electrode was a glassy carbon and the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated KCl solution. 10 mL of THF/H_2O (8/1) containing 0.1 M TBAB was poured into the electrochemical cell in all experiments. The CV of all substrates was measured at the concentration of 0.01 M. The scan rate is 50 mV/s, ranging from 0 to 2.2 V.

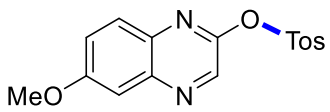
10. Detail descriptions for products

quinoxalin-2-yl 4-methylbenzenesulfonate (3a)



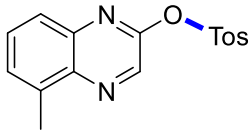
White solid, 68% yield, m.p. 90-91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.10 (d, *J* = 9.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 9.8 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ151.05, 146.06, 141.33, 139.84, 139.28, 133.45, 131.20, 129.90, 129.83, 129.27, 129.17, 128.60, 21.87. HRMS (ESI) Calcd for $C_{15}H_{12}N_2O_3S$ $(M+H)^+$: 301.0641, Found: 301.0628.

6-methoxyquinoxalin-2-yl 4-methylbenzenesulfonate (3b)



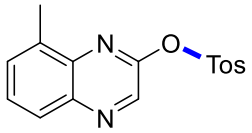
White solid, 86% yield, m.p. 116-117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.74 (m, 1H), 7.36 (m, 4H), 3.92 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.83, 149.61, 145.90, 143.04, 139.23, 135.53, 133.41, 129.87, 129.39, 128.96, 124.24, 106.93, 55.92, 21.81. HRMS (ESI) Calcd for $C_{16}H_{14}N_2O_4S$ $(M+H)^+$: 331.0753, Found: 331.0747.

5-methylquinoxalin-2-yl 4-methylbenzenesulfonate (3c)



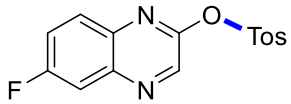
White solid, 73% yield, m.p. 103-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.66 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.89, 145.96, 140.54, 140.11, 137.86, 137.78, 133.50, 131.07, 129.95, 129.86, 129.13, 126.41, 21.84, 17.44, 17.44. HRMS (ESI) Calcd for $C_{16}H_{14}N_2O_3S$ $(M+H)^+$: 315.0798, Found: 315.0808.

8-methylquinoxalin-2-yl 4-methylbenzenesulfonate (3d)



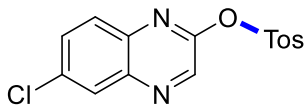
White solid, 71% yield, m.p. 99-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.37, 145.82, 141.53, 138.92, 138.72, 137.10, 133.90, 131.29, 129.79, 129.48, 129.17, 127.02, 21.85, 17.26.HRMS (ESI) Calcd for $C_{16}H_{14}N_2O_3S$ $(M+H)^+$: 315.0798, Found: 315.0804.

6-fluoroquinoxalin-2-yl 4-methylbenzenesulfonate (3e)



White solid, 50% yield, m.p. 67-68 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.90 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.73 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.60 – 7.48 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.60, (d, *J* = 250.8 Hz), 150.69 (d, *J* = 3.3 Hz), 146.16, 141.96 (d, *J* = 13.0 Hz), 140.21, 136.81, 136.80, 133.30, 130.48 (d, *J* = 9.9 Hz), 129.93, 129.08, 121.39 (d, *J* = 25.9 Hz), 113.11 (d, *J* = 21.9 Hz), 21.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.86. HRMS (ESI) Calcd for $C_{15}H_{11}FN_2O_3S$ $(M+H)^+$: 319.0547, Found: 319.0551.

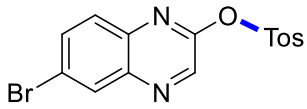
6-chloroquinoxalin-2-yl 4-methylbenzenesulfonate (3f)



White solid, 48% yield, m.p. 93-94 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.07 (d, *J* = 2.3 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.68 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.13, 146.20, 141.41,

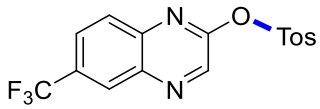
140.21, 138.29, 135.62, 133.25, 132.11, 129.92, 129.67, 129.12, 128.20, 21.85. HRMS (ESI) Calcd for $C_{15}H_{11}ClN_2O_3S$ $(M+H)^+$: 335.0252, Found: 335.0267.

6-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3g)



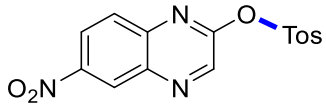
Off-white solid, 33% yield, m.p. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.26 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.82 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.22, 146.24, 141.75, 140.21, 138.63, 134.72, 133.29, 131.62, 129.96, 129.80, 129.17, 123.69, 21.90. HRMS (ESI) Calcd for $C_{15}H_{11}BrN_2O_3S$ $(M+H)^+$: 378.9747, Found: 378.9758.

6-(trifluoromethyl)quinoxalin-2-yl 4-methylbenzenesulfonate (3h)



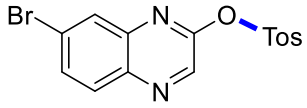
White solid, 33% yield, m.p. 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 8.19 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.92 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.03, 146.47, 142.21, 141.52, 139.04, 133.21, 133.09, 132.75, 130.62, 130.07, 129.28, 126.50 (q, *J* = 4.3 Hz), 125.56 (q, *J* = 3.2 Hz), 124.87, 122.16, 21.96. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74. HRMS (ESI) Calcd for $C_{16}H_{11}F_3N_2O_3S$ $(M+Na)^+$: 391.0335, Found: 391.0353.

6-nitroquinoxalin-2-yl 4-methylbenzenesulfonate (3i)



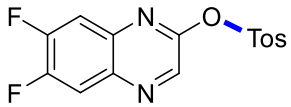
White solid, 20% yield, m.p. 145-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.99 (d, *J* = 2.5 Hz, 1H), 8.77 (s, 1H), 8.54 (dd, *J* = 9.2, 2.5 Hz, 1H), 8.06 (t, *J* = 8.8 Hz, 3H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.93, 147.72, 146.66, 142.79, 141.62, 139.88, 133.09, 130.07, 130.05, 129.38, 125.55, 124.70, 21.96. HRMS (ESI) Calcd for $C_{15}H_{11}N_3O_5S$ $(M+Na)^+$: 368.0312, Found: 368.0326.

7-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3j)



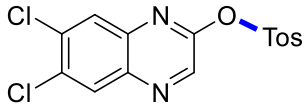
White solid, 47% yield, m.p. 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.12 – 7.99 (m, 3H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.69, 146.27, 140.49, 140.03, 139.56, 133.40, 130.88, 130.54, 130.00, 129.25, 125.48, 21.95. HRMS (ESI) Calcd for $C_{15}H_{11}BrN_2O_3S$ $(M+H)^+$: 378.9747, Found: 378.9736.

6,7-difluoroquinoxalin-2-yl 4-methylbenzenesulfonate (3k)



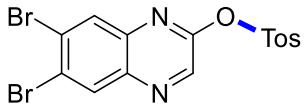
White solid, 50% yield, m.p. 133-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 (dd, *J* = 10.2, 8.1 Hz, 1H), 7.64 (dd, *J* = 10.3, 7.9 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.19 (dd, *J* = 257.0, 15.8 Hz), 152.16 (dd, *J* = 255.4, 15.7 Hz), 151.49 (d, *J* = 3.1 Hz), 146.32, 139.47 (d, *J* = 3.5 Hz), 138.52 (dd, *J* = 10.7, 1.6 Hz), 137.27 (dd, *J* = 11.2, 1.4 Hz), 133.29, 130.00, 129.14, 115.29 (dd, *J* = 17.7, 2.1 Hz), 114.48 (dd, *J* = 18.0, 1.8 Hz), 21.90. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.58 – -127.73 (m), -129.78 (m). HRMS (ESI) Calcd for $C_{15}H_{10}F_2N_2O_3S$ $(M+Na)^+$: 359.0272, Found: 359.0289.

6,7-dichloroquinoxalin-2-yl 4-methylbenzenesulfonate (3l)



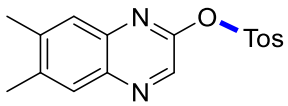
White solid, 67% yield, m.p. 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.20 (s, 1H), 8.08 – 7.94 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.80, 146.39, 140.40, 139.88, 138.60, 136.09, 134.50, 133.25, 130.03, 129.92, 129.23, 129.11, 21.94. HRMS (ESI) Calcd for $C_{15}H_{10}Cl_2N_2O_3S$ $(M+Na)^+$: 390.9681, Found: 390.9685.

6,7-dibromoquinoxalin-2-yl 4-methylbenzenesulfonate (3m)



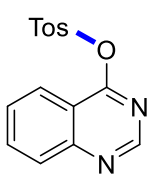
Off-white solid, 78% yield, m.p. 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.40 (s, 1H), 8.19 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.79, 146.41, 140.56, 140.39, 139.07, 133.31, 133.26, 132.53, 130.05, 129.25, 128.27, 126.47, 21.97.HRMS (ESI) Calcd for $C_{15}H_{10}Br_2N_2O_3S$ $(M+Na)^+$: 478.8671, Found: 478.8691.

6,7-dimethylquinoxalin-2-yl 4-methylbenzenesulfonate (3n)



White solid, 80% yield, m.p. 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 1H), 7.64 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.74, 145.89, 142.03, 140.50, 140.42, 138.72, 138.17, 133.59, 129.90, 129.10, 128.33, 127.74, 21.89, 20.48, 20.37. HRMS (ESI) Calcd for $C_{17}H_{16}N_2O_3S$ $(M+Na)^+$: 351.0774, Found: 351.0785.

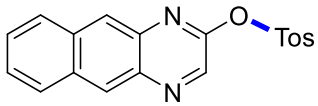
quinazolin-4-yl 4-methylbenzenesulfonate (3o)



White solid, 60% yield, m.p. 185-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.14 (d, *J* = 9.1 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.70 (m, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.62,

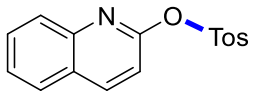
146.77, 140.54, 135.65, 133.50, 129.83, 128.33, 128.00, 127.19, 122.08, 21.85. HRMS (ESI) Calcd for $C_{15}H_{12}N_2O_3S$ $(M+H)^+$: 301.0641, Found: 301.0652.

benzo[g]quinoxalin-2-yl 4-methylbenzenesulfonate (3p)



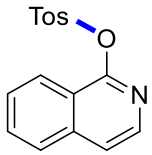
Yellow solid, 11% yield, m.p. 166-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.62 (s, 1H), 8.41 (s, 1H), 8.17 – 7.97 (m, 4H), 7.65 – 7.51 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.44, 146.12, 140.54, 137.69, 135.98, 134.40, 133.50, 129.92, 129.33, 128.75, 128.21, 128.13, 127.65, 127.08, 126.79, 21.90. HRMS (ESI) Calcd for $C_{19}H_{14}N_2O_3S$ $(M+H)^+$: 351.0799, Found: 351.0803.

quinolin-2-yl 4-methylbenzenesulfonate (3q)



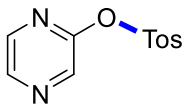
White solid, 58% yield, m.p. 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.32, 146.06, 145.40, 140.74, 134.08, 130.46, 129.64, 129.07, 128.57, 127.58, 127.11, 126.79, 114.27, 21.78. HRMS (ESI) Calcd for $C_{16}H_{13}NO_3S$ $(M+H)^+$: 300.0689, Found: 300.0701.

isoquinolin-1-yl 4-methylbenzenesulfonate (3r)



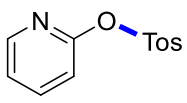
White solid, 67% yield, m.p. 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.61, 145.89, 136.80, 134.42, 134.00, 129.64, 129.62, 128.44, 127.88, 126.64, 126.38, 125.50, 107.46, 21.86. HRMS (ESI) Calcd for $C_{16}H_{13}NO_3S$ $(M+H)^+$: 300.0689, Found: 300.0697.

pyrazin-2-yl 4-methylbenzenesulfonate (3s)



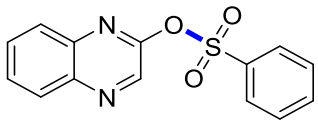
White solid, 40% yield, m.p. 60-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 12.1 Hz, 2H), 8.24 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.15, 146.06, 143.04, 142.19, 138.64, 133.28, 130.04, 128.82, 21.90. HRMS (ESI) Calcd for $C_{11}H_{10}N_2O_3S$ $(M+H)^+$: 251.0485, Found: 251.0493.

pyridin-2-yl 4-methylbenzenesulfonate (3u)



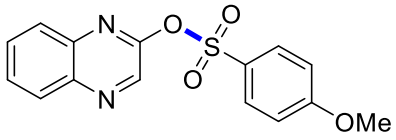
Off-white oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.21 (m, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.76 (ddd, *J* = 8.3, 7.3, 2.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.02, 148.36, 145.37, 140.15, 133.74, 129.76, 128.60, 122.70, 115.95, 21.75. HRMS (ESI) Calcd for $C_{12}H_{11}NO_3S$ $(M+H)^+$: 250.0532, Found: 250.0539.

quinoxalin-2-yl benzenesulfonate (3v)



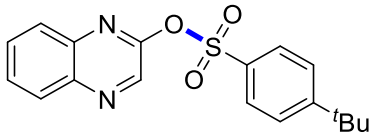
White solid, 60% yield, m.p. 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 8.09 (dd, *J* = 7.8, 2.3 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.77 – 7.67 (m, 3H), 7.63 – 7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.89, 141.28, 139.69, 139.12, 136.43, 134.70, 131.20, 129.84, 129.22, 129.19, 129.02, 128.47. HRMS (ESI) Calcd for $C_{14}H_{10}N_2O_3S$ $(M+H)^+$: 287.0485, Found: 287.0471.

quinoxalin-2-yl 4-methoxybenzenesulfonate (3w)



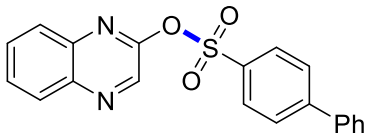
Off-white solid, 61% yield, m.p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.15 – 8.01 (m, 3H), 7.93 – 7.84 (m, 1H), 7.80 – 7.67 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.56, 151.02, 141.17, 139.72, 139.21, 131.46, 131.11, 129.70, 129.15, 128.47, 127.40, 114.41, 55.83. HRMS (ESI) Calcd for $C_{15}H_{12}N_2O_4S$ $(M+Na)^+$: 339.0410, Found: 339.0410.

quinoxalin-2-yl 4-(tert-butyl)benzenesulfonate (3x)



White solid, 58% yield, m.p. 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 3H), 7.95 – 7.85 (m, 1H), 7.82 – 7.67 (m, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.91, 150.99, 141.26, 139.80, 139.24, 133.29, 131.14, 129.76, 129.19, 128.96, 128.54, 126.28, 35.46, 31.04. HRMS (ESI) Calcd for $C_{18}H_{18}N_2O_3S$ $(M+Na)^+$: 343.1111, Found: 343.1096.

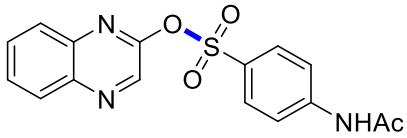
quinoxalin-2-yl [1,1'-biphenyl]-4-sulfonate (3y)



White solid, 56% yield, m.p. 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 2H), 8.14 – 8.05 (m, 1H), 7.95 – 7.85 (m, 1H), 7.84 – 7.68 (m, 4H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ150.97, 147.60, 141.28, 139.71,

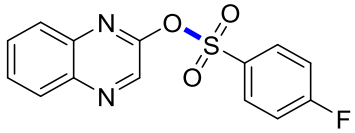
139.15, 138.79, 134.82, 131.19, 129.81, 129.63, 129.20, 129.16, 128.94, 128.48, 127.72, 127.42. HRMS (ESI) Calcd for $C_{20}H_{14}N_2O_3S$ $(M+Na)^+$: 385.0617, Found: 385.0636.

quinoxalin-2-yl 4-acetamidobenzenesulfonate (3z)



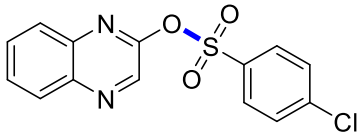
White solid, 60% yield, m.p. 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.34 (s, 1H), 8.12 – 8.01 (m, 3H), 7.89 – 7.82 (m, 1H), 7.82 – 7.70 (m, 4H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.34, 150.94, 144.17, 141.25, 139.69, 139.03, 131.36, 130.54, 130.19, 129.96, 129.21, 128.44, 119.17, 24.78. HRMS (ESI) Calcd for $C_{16}H_{13}N_3O_4S$ $(M+H)^+$: 344.0700, Found: 344.0710.

quinoxalin-2-yl 4-fluorobenzenesulfonate (3aa)



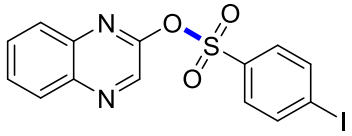
White solid, 73% yield, m.p. 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.26 – 8.15 (m, 2H), 8.14 – 8.05 (m, 1H), 7.92 – 7.82 (m, 1H), 7.80 – 7.70 (m, 2H), 7.33 – 7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.31 (d, J = 256.4 Hz), 150.89, 141.31, 139.57, 139.05, 132.45 (d, J = 3.4 Hz), 132.16 (d, J = 9.7 Hz), 131.28, 129.90, 129.25, 128.38, 116.60 (d, J = 22.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.38 (m). HRMS (ESI) Calcd for $C_{14}H_9FN_2O_3S$ $(M+H)^+$: 305.0390, Found: 305.0396.

quinoxalin-2-yl 4-chlorobenzenesulfonate (3ab)



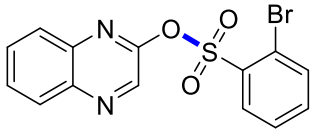
White solid, 61% yield, m.p. 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.16 – 8.05 (m, 3H), 7.90 – 7.82 (m, 1H), 7.76 (td, J = 6.4, 3.4 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.86, 141.48, 141.34, 139.55, 139.00, 134.97, 131.32, 130.60, 129.95, 129.54, 129.27, 128.39. HRMS (ESI) Calcd for $C_{14}H_9ClN_2O_3S$ $(M+H)^+$: 321.0095, Found: 321.0079.

quinoxalin-2-yl 4-iodobenzenesulfonate (3ac)



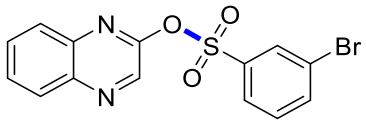
White solid, 50% yield, m.p. 121-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.15 – 8.07 (m, 1H), 7.96 (d, J = 8.6 Hz, 2H), 7.91 – 7.83 (m, 3H), 7.81 – 7.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.90, 141.40, 139.62, 139.04, 138.56, 136.26, 131.36, 130.37, 129.99, 129.33, 128.48, 102.94. HRMS (ESI) Calcd for $C_{14}H_9IN_2O_3S$ $(M+H)^+$: 412.9451, Found: 412.9466.

quinoxalin-2-yl 2-bromobenzenesulfonate (3ad)



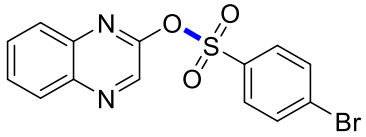
White solid, 82% yield, m.p. 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.27 (dt, *J* = 7.3, 1.7 Hz, 1H), 8.11 – 8.02 (m, 1H), 7.79 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.77 – 7.67 (m, 3H), 7.58 – 7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.68, 141.19, 139.42, 138.66, 136.75, 135.60, 135.27, 132.72, 131.15, 129.83, 129.07, 128.35, 127.66, 120.96. HRMS (ESI) Calcd for $C_{14}H_9BrN_2O_3S$ $(M+H)^+$: 364.9590, Found: 364.9572.

quinoxalin-2-yl 3-bromobenzenesulfonate (3ae)



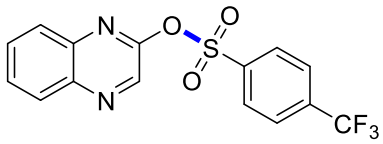
Off-white solid, 55% yield, m.p. 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.37 (s, 1H), 8.15 – 8.04 (m, 2H), 7.91 – 7.84 (m, 1H), 7.84 – 7.72 (m, 3H), 7.48 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.85, 141.37, 139.50, 138.85, 138.28, 137.66, 132.27, 131.39, 130.63, 129.98, 129.28, 128.41, 127.62, 122.93. HRMS (ESI) Calcd for $C_{14}H_9BrN_2O_3S$ $(M+H)^+$: 364.9590, Found: 364.9573.

quinoxalin-2-yl 4-bromobenzenesulfonate (3af)



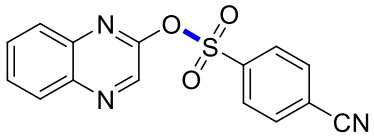
White solid, 63% yield, m.p. 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.12 – 8.06 (m, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.91 – 7.81 (m, 1H), 7.74 (dd, *J* = 8.5, 5.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.80, 141.27, 139.48, 138.93, 135.48, 132.49, 131.27, 130.56, 130.07, 129.89, 129.21, 128.34. HRMS (ESI) Calcd for $C_{14}H_9BrN_2O_3S$ $(M+H)^+$: 364.9590, Found: 364.9573.

quinoxalin-2-yl 4-(trifluoromethyl)benzenesulfonate (3ag)



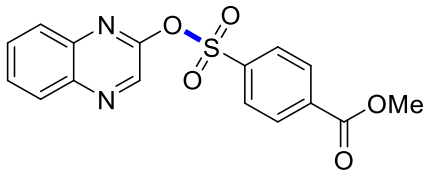
White solid, 41% yield, m.p. 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 2H), 8.12 – 8.01 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.80 – 7.75 (m, 1H), 7.75 – 7.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.90, 141.43, 140.22, 139.60, 138.97, 137.04 – 135.25 (q, *J* = 33.0 Hz), 131.59, 130.25, 129.86, 129.36, 128.47, 126.44 (q, *J* = 3.7 Hz), 124.46, 121.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.36. HRMS (ESI) Calcd for $C_{15}H_9F_3N_2O_3S$ $(M+H)^+$: 355.0359, Found: 355.0349.

quinoxalin-2-yl 4-cyanobenzenesulfonate (3ah)



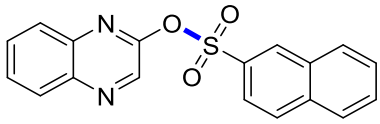
White solid, 61% yield, m.p. 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.18 – 8.06 (m, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.87 – 7.72 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.69, 141.45, 140.76, 139.35, 138.78, 132.91, 131.51, 130.18, 129.77, 129.32, 128.26, 118.26, 116.97. HRMS (ESI) Calcd for $C_{15}H_9N_3O_3S$ $(M+Na)^+$: 334.0257, Found: 334.0268.

methyl 4-((quinoxalin-2-yloxy)sulfonyl)benzoate (3ai)



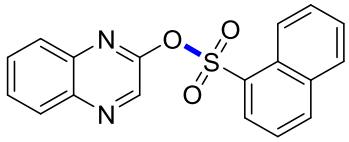
White solid, 36% yield, m.p. 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.23 (s, 4H), 8.14 – 8.07 (m, 1H), 7.83 (ddd, *J* = 7.9, 3.1, 1.4 Hz, 1H), 7.75 (ddd, *J* = 5.4, 4.7, 3.3 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.37, 150.88, 141.46, 140.45, 139.62, 139.02, 135.63, 131.40, 130.33, 130.07, 129.34, 129.23, 128.48, 52.92. HRMS (ESI) Calcd for $C_{16}H_{12}N_2O_5S$ $(M+Na)^+$: 367.0359, Found: 367.0376.

quinoxalin-2-yl naphthalene-2-sulfonate (3ak)



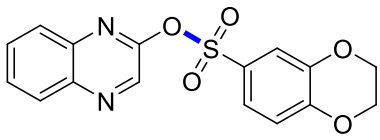
White solid, 66% yield, m.p. 77-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.67 (s, 1H), 8.11 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.98 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.89 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.73 – 7.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.94, 141.22, 139.65, 139.09, 135.64, 133.18, 131.84, 131.30, 131.14, 129.84, 129.76, 129.50, 129.45, 129.14, 128.42, 128.03, 127.92, 123.23. HRMS (ESI) Calcd for $C_{18}H_{12}N_2O_3S$ $(M+Na)^+$: 359.0461, Found: 359.0460.

quinoxalin-2-yl naphthalene-1-sulfonate (3al)



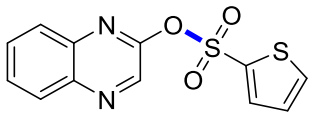
White solid, 50% yield, m.p. 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.7 Hz, 1H), 8.61 (s, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.07 – 7.99 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.94, 141.28, 139.76, 138.95, 136.21, 134.16, 132.17, 131.58, 131.11, 129.82, 129.17, 129.12, 128.60, 128.56, 127.43, 124.74, 124.07. HRMS (ESI) Calcd for $C_{18}H_{12}N_2O_3S$ $(M+H)^+$: 337.0641, Found: 337.0646.

quinoxalin-2-yl 2,3-dihydrobenzo[b][1,4]dioxine-6-sulfonate (3am)



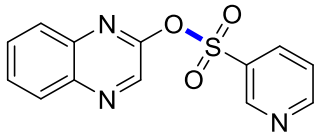
White solid, 50% yield, m.p. 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.13 – 8.04 (m, 1H), 7.95 – 7.86 (m, 1H), 7.74 (tt, *J* = 7.0, 5.1 Hz, 2H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 4.35 – 4.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.02, 149.28, 143.69, 141.25, 139.82, 139.21, 131.19, 129.78, 129.20, 128.58, 128.12, 123.03, 118.85, 117.88, 64.75, 64.17. HRMS (ESI) Calcd for $C_{16}H_{12}N_2O_5S$ $(M+H)^+$: 345.0540, Found: 345.0549.

quinoxalin-2-yl thiophene-2-sulfonate (3an)



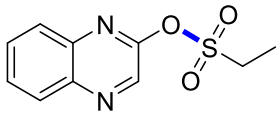
White solid, 70% yield, m.p. 117-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.18 – 8.09 (m, 1H), 8.03 – 7.93 (m, 2H), 7.85 – 7.73 (m, 3H), 7.17 (dd, *J* = 5.0, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.05, 141.47, 139.77, 139.07, 136.67, 135.73, 135.62, 131.37, 130.02, 129.38, 128.61, 127.65. HRMS (ESI) Calcd for $C_{12}H_8N_2O_3S_2$ $(M+Na)^+$: 314.9869, Found: 314.9883.

quinoxalin-2-yl pyridine-3-sulfonate (3ao)



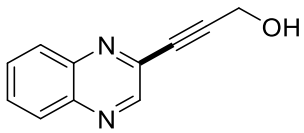
White solid, 60% yield, m.p. 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.93 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.71 (s, 1H), 8.48 (dt, *J* = 8.2, 1.9 Hz, 1H), 8.19 – 8.07 (m, 1H), 7.86 (dt, *J* = 8.1, 2.8 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.58 (dd, *J* = 8.1, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.92, 150.94, 150.09, 141.49, 139.46, 138.83, 136.89, 133.79, 131.51, 130.13, 129.38, 128.42, 123.75. HRMS (ESI) Calcd for $C_{13}H_9N_3O_3S$ $(M+Na)^+$: 310.0257, Found: 310.0256.

quinoxalin-2-yl ethanesulfonate (3ap)



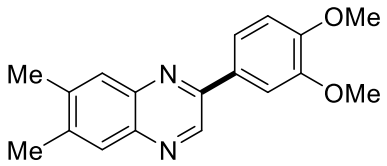
White solid, 12% yield, m.p. 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.16 (d, *J* = 9.4 Hz, 1H), 7.99 (d, *J* = 9.7 Hz, 1H), 7.87 – 7.74 (m, 2H), 3.83 (q, *J* = 7.4 Hz, 2H), 1.64 (d, *J* = 14.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.22, 141.50, 139.72, 139.53, 131.41, 130.03, 129.39, 128.52, 48.84, 8.37. HRMS (ESI) Calcd for $C_{10}H_{10}N_2O_3S$ $(M+H)^+$: 239.0485, Found: 239.0496.

3-(quinoxalin-2-yl)prop-2-yn-1-ol (4a)



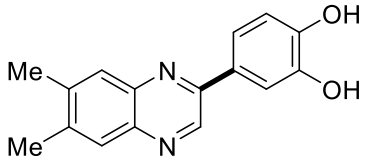
The title compound was known.[3] White solid, 65% yield (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.15 – 8.01 (m, 2H), 7.86 – 7.72 (m, 2H), 4.64 (s, 2H), 3.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.06, 142.08, 141.17, 138.93, 131.00, 130.87, 129.29, 129.22, 92.52, 83.05, 51.39. HRMS (ESI) Calcd for $C_{11}H_8N_2O$ $(M+H)^+$: 185.0709, Found: 185.0717.

2-(3,4-dimethoxyphenyl)-6,7-dimethylquinoxaline (4b)



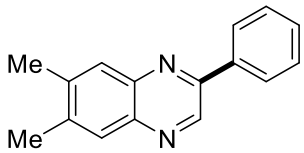
The title compound was known.[5] White solid, 52% yield (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.89 (s, 1H), 7.83 (s, 2H), 7.69 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.02, 150.61, 149.82, 142.16, 141.22, 140.86, 140.24, 139.81, 130.01, 128.53, 128.20, 120.31, 111.33, 110.26, 56.20, 56.14, 20.46, 20.40. HRMS (ESI) Calcd for $C_{18}H_{18}N_2O_2$ $(M+Na)^+$: 317.1261, Found: 317.1276.

4-(6,7-dimethylquinoxalin-2-yl)benzene-1,2-diol (4c)



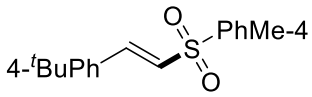
The title compound was known.[5] Orange solid, 49% yield (3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, DMSO) δ 9.29 (s, 1H), 7.80 (s, 2H), 7.75 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 150.29, 148.78, 146.30, 142.14, 140.37, 139.36, 138.92, 127.75, 127.66, 127.10, 118.95, 115.89, 113.95, 19.78, 19.65. HRMS (ESI) Calcd for $C_{16}H_{14}N_2O_2$ $(M+H)^+$: 267.1128, Found: 267.1128.

6,7-dimethyl-2-phenylquinoxaline (4d)



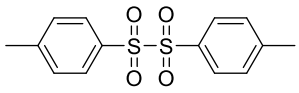
The title compound was known.[6] White solid, 52% yield (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.16 – 8.09 (m, 2H), 7.82 (d, *J* = 12.2 Hz, 2H), 7.54 – 7.41 (m, 3H), 2.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.93, 142.25, 141.27, 140.74, 140.47, 140.08, 137.11, 129.84, 129.05, 128.69, 128.12, 127.38, 20.35, 20.34, 20.32. HRMS (ESI) Calcd for $C_{16}H_{14}N_2$ $(M+H)^+$: 235.1230, Found: 235.1237.

(E)-1-(tert-butyl)-4-(2-tosylvinyl)benzene (5)



The title compound was known.[7] White solid, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.41 (s, 4H), 7.36 – 7.28 (m, 2H), 6.81 (d, *J* = 15.5 Hz, 1H), 2.42 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.96, 144.33, 142.04, 138.14, 130.02, 129.83, 128.51, 127.75, 126.78, 126.16, 35.09, 31.21, 21.71. HRMS (ESI) Calcd for $C_{19}H_{22}O_2S$ $(M+Na)^+$: 337.1233, Found: 337.1240.

4,4'-Dimethyldiphenyl disulfone (7)



The title compound was known.[8] White solid, 4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 4H), 7.43 (d, *J* = 8.4 Hz, 4H), 2.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.29, 131.65, 130.56, 128.02, 22.19. HRMS (ESI) Calcd for $C_{14}H_{14}O_4S_2$ $(M+Na)^+$: 333.0231, Found: 333.0227.

11. References

1. Dou, G.-Y.; Jiang, Y.-Y.; Xu, K.; Zeng, C.-C. *Org. Chem. Front.* **2019**, *6*, 2392.
2. Jiang, M.; Yuan, Y.; Wang, T.; Xiong, Y.; Li, J.; Guo, H.; Lei, A. *Chem. Commun.* **2019**, *55*, 13852.
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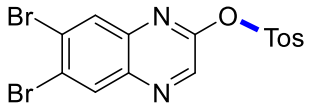
12. X-ray Crystal Structure of Compound 3n



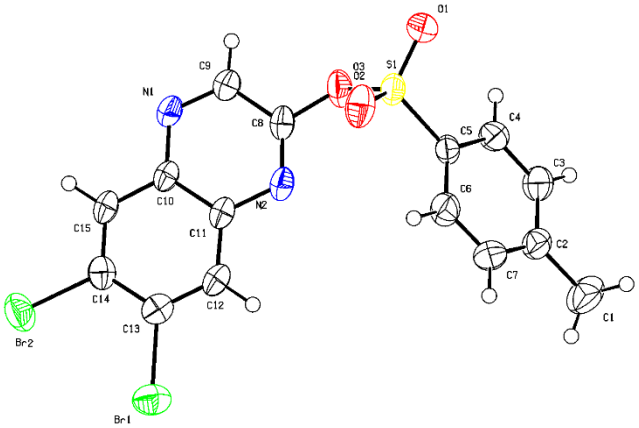


Table 1. Crystal data and structure refinement for CCDC 2162074.

Bond precision:	C-C = 0.0038 A	Wavelength = 0.71073	
Cell:	a = 6.2412(7)	b = 8.1065(9)	c = 16.0274(18)
	alpha = 88.586(4)	beta = 79.678(3)	gamma = 84.807(4)
Temperature:	293 K		
	Calculated	Reported	
Volume	794.47(15)	794.47(15)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{15}H_{10}Br_2N_2O_3S$	$C_{15}H_{10}Br_2N_2O_3S$	

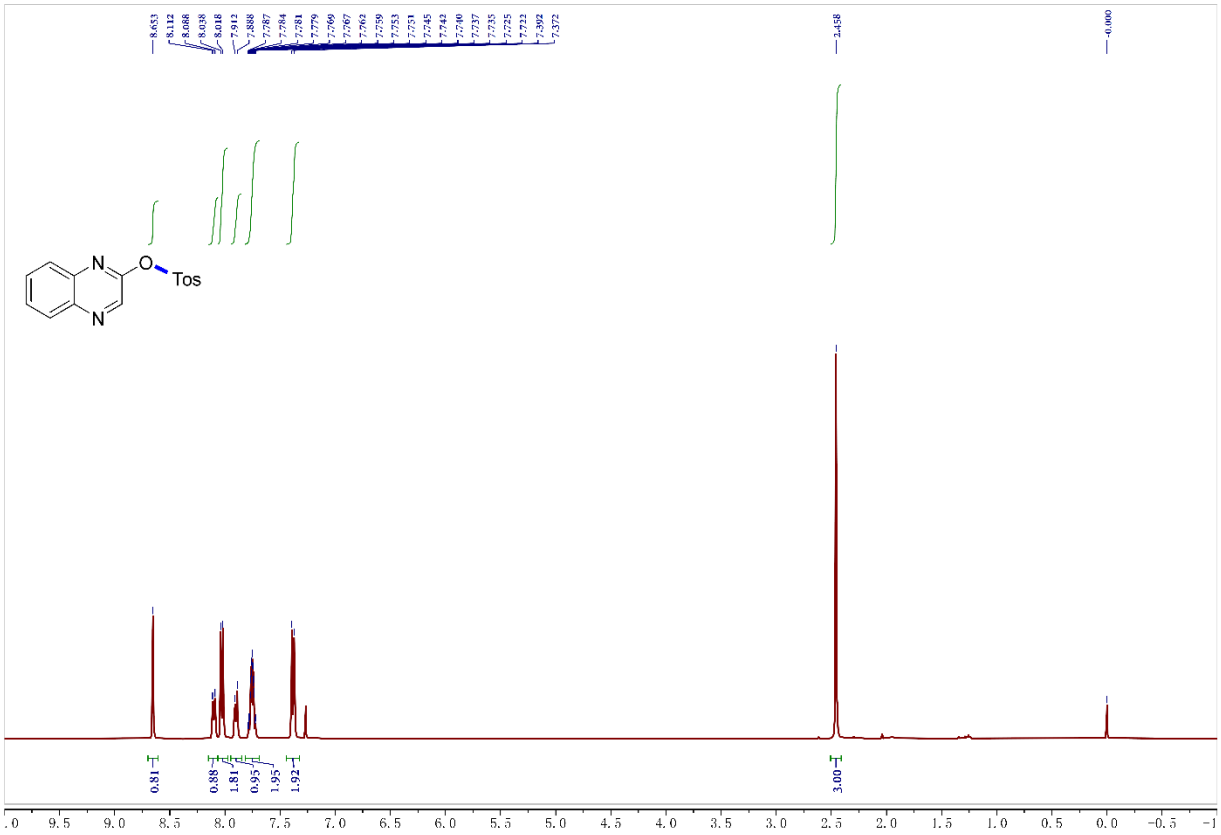
Sum formula	$C_{15}H_{10}Br_2N_2O_3S$	$C_{15}H_{10}Br_2N_2O_3S$
Mr	458.11	458.13
Dx, g cm^{-3}	1.915	1.915
Z	2	2
Mu (mm-1)	5.248	5.248
F000	448.0	448.0
F000’	447.31	
h,k,lmax	8,10,20	8,10,20
Nref	3661	3649
Tmin, Tmax	0.187, 0.332	0.554, 0.746
Tmin’ 0.139		

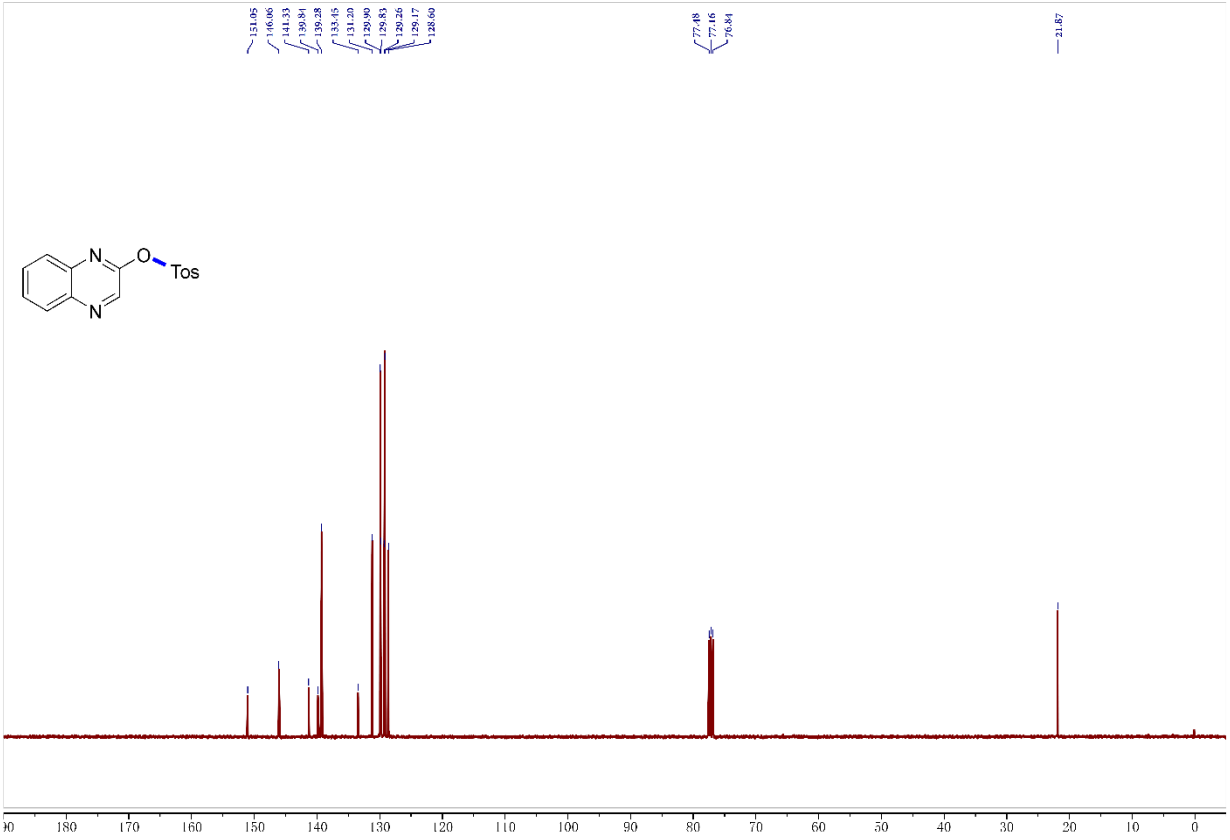
Correction method= # Reported T Limits: Tmin = 0.554 Tmax = 0.746

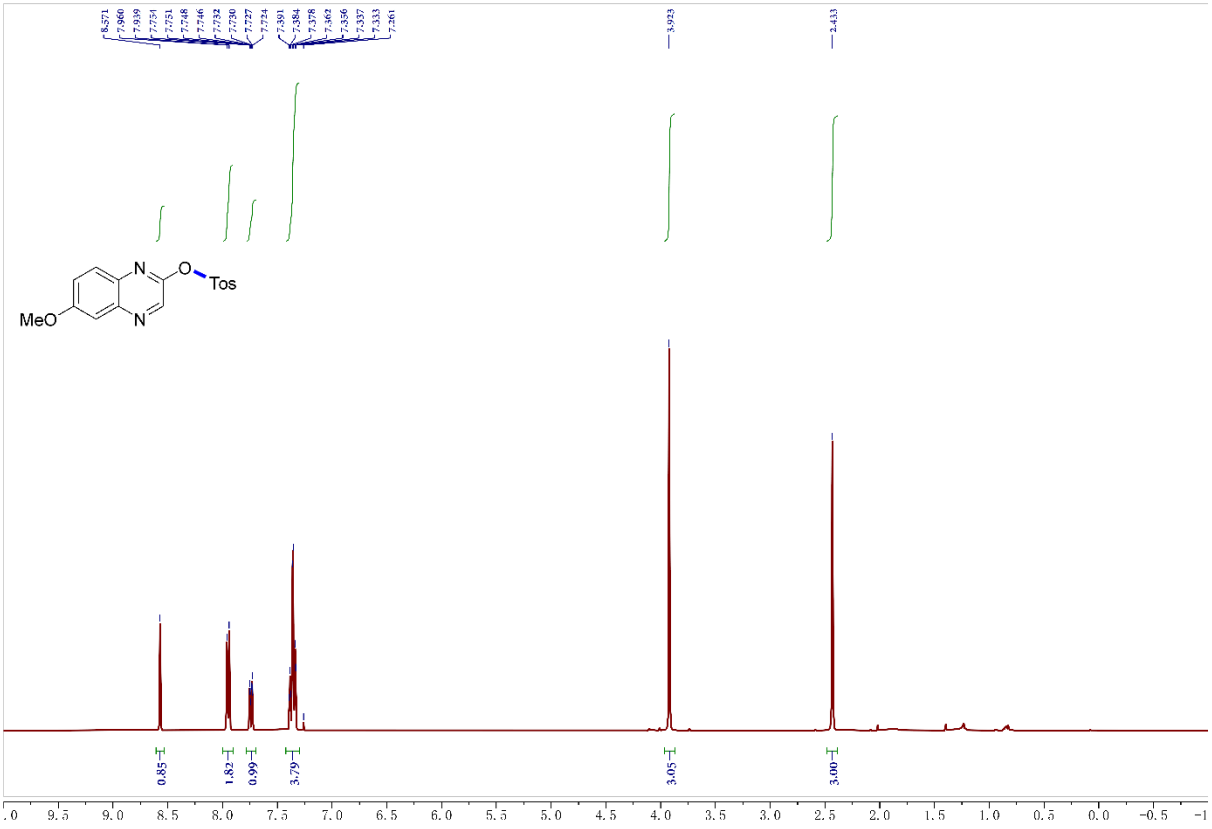
AbsCorr = MULTI-SCAN

Data completeness = 0.997	Theta(max) = 27.511
R(reflections) = 0.0302(2989)	wR2(reflections) = 0.0779(3649)
S = 1.027	Npar = 209

13. Copies of product NMR Spectra



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7.751
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7.746
7.732
7.730
7.727
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7.391
7.384
7.378
7.362
7.356
7.337
7.333
7.261
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O
Tos
MeO
N
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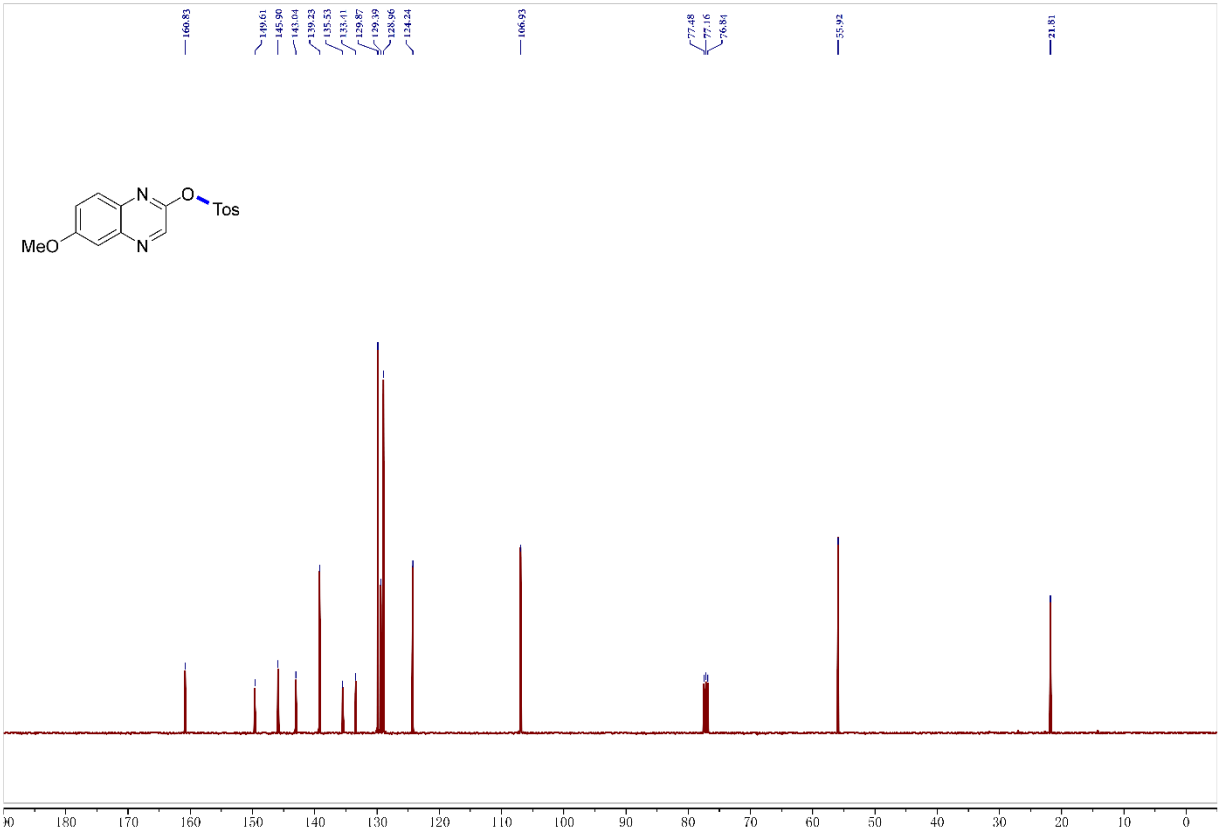
1.82
0.99
3.79
3.05
3.00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145.90
143.04
139.23
135.53
133.41
129.87
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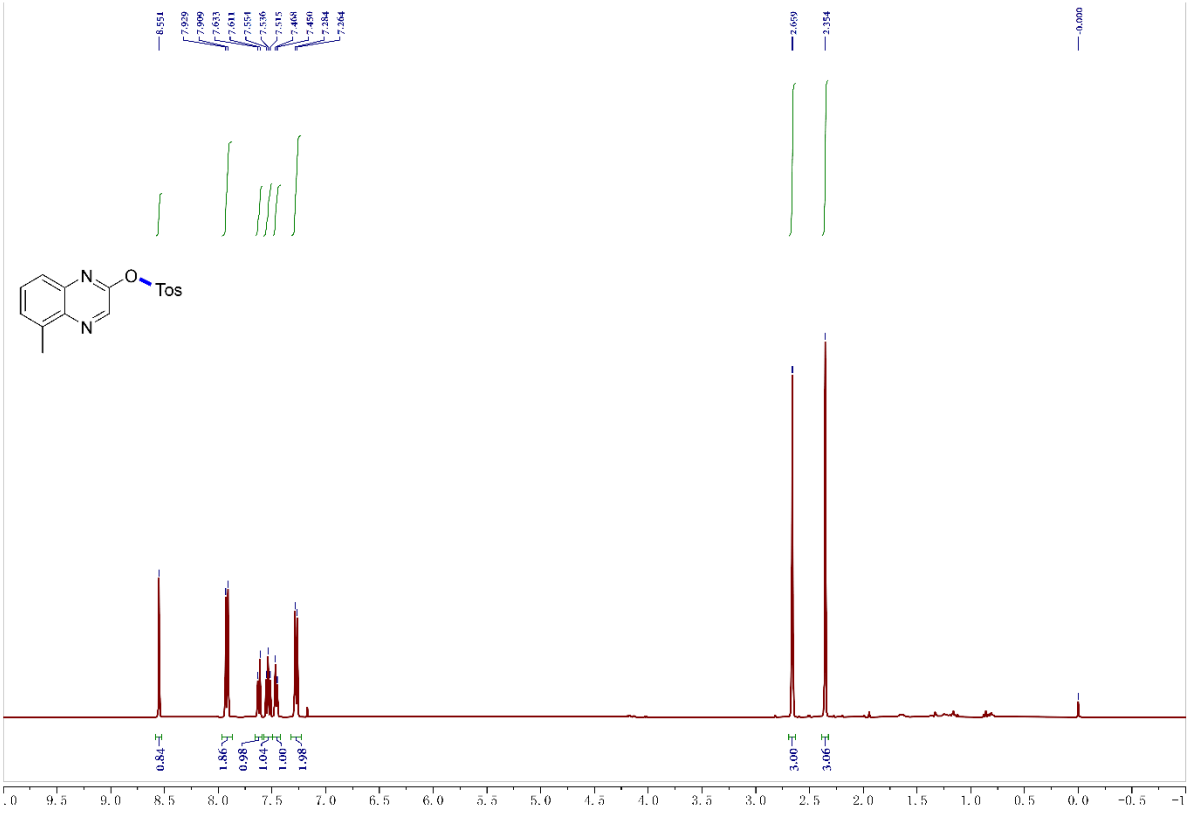
77.16
76.84
55.92
21.81
N
O
Tos
MeO
N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7.515
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7.450
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7.264
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0.000
Tos
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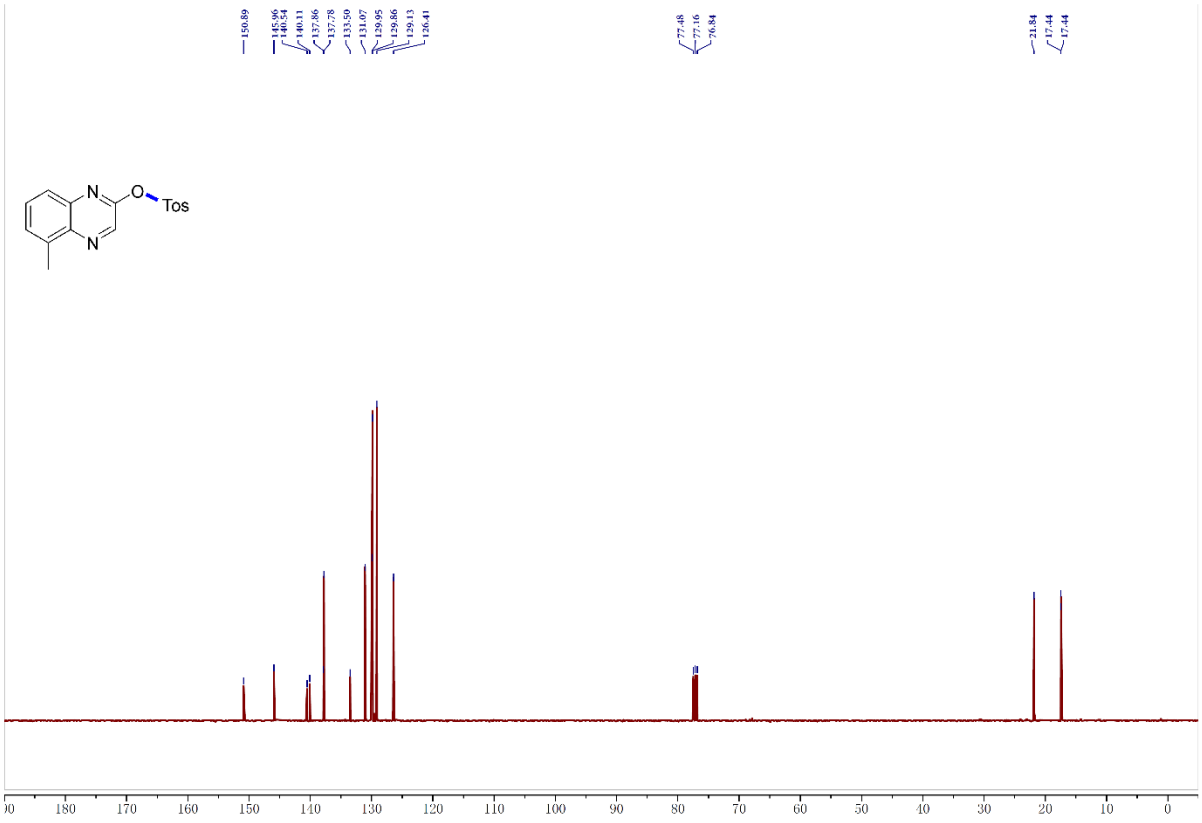
0.98
1.04
1.00
1.98
3.00
3.06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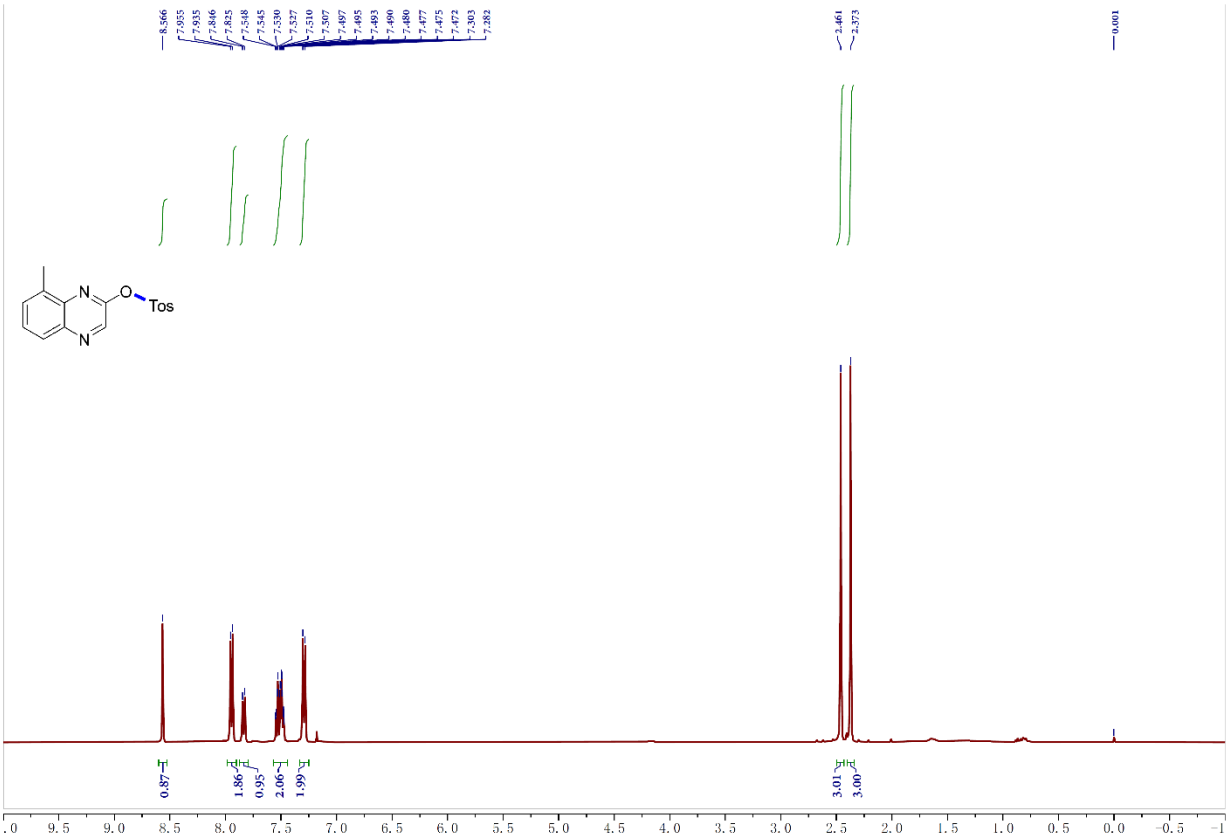
77.16
76.84
21.84
17.44
17.44
Tos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7.507
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7.493
7.490
7.480
7.477
7.475
7.472
7.303
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0.001
Tos
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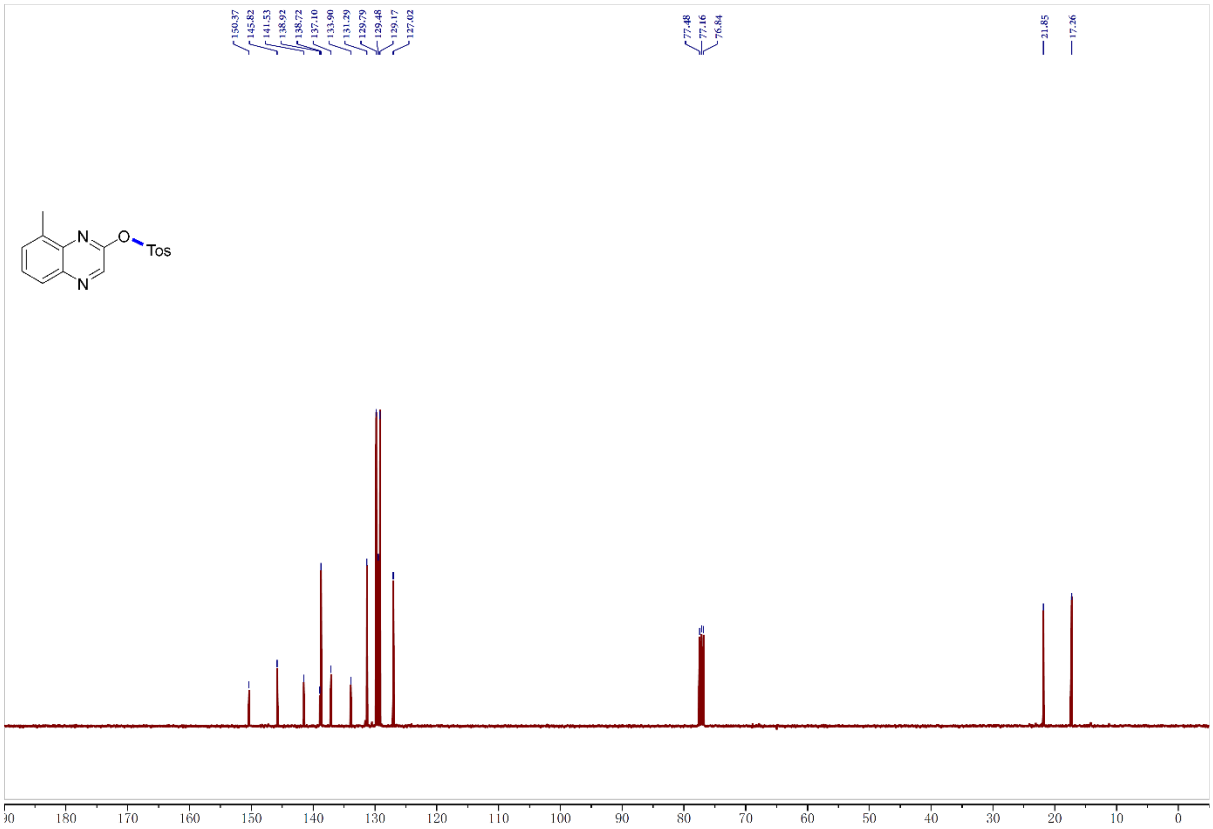
0.95
2.06
1.99
3.01
3.00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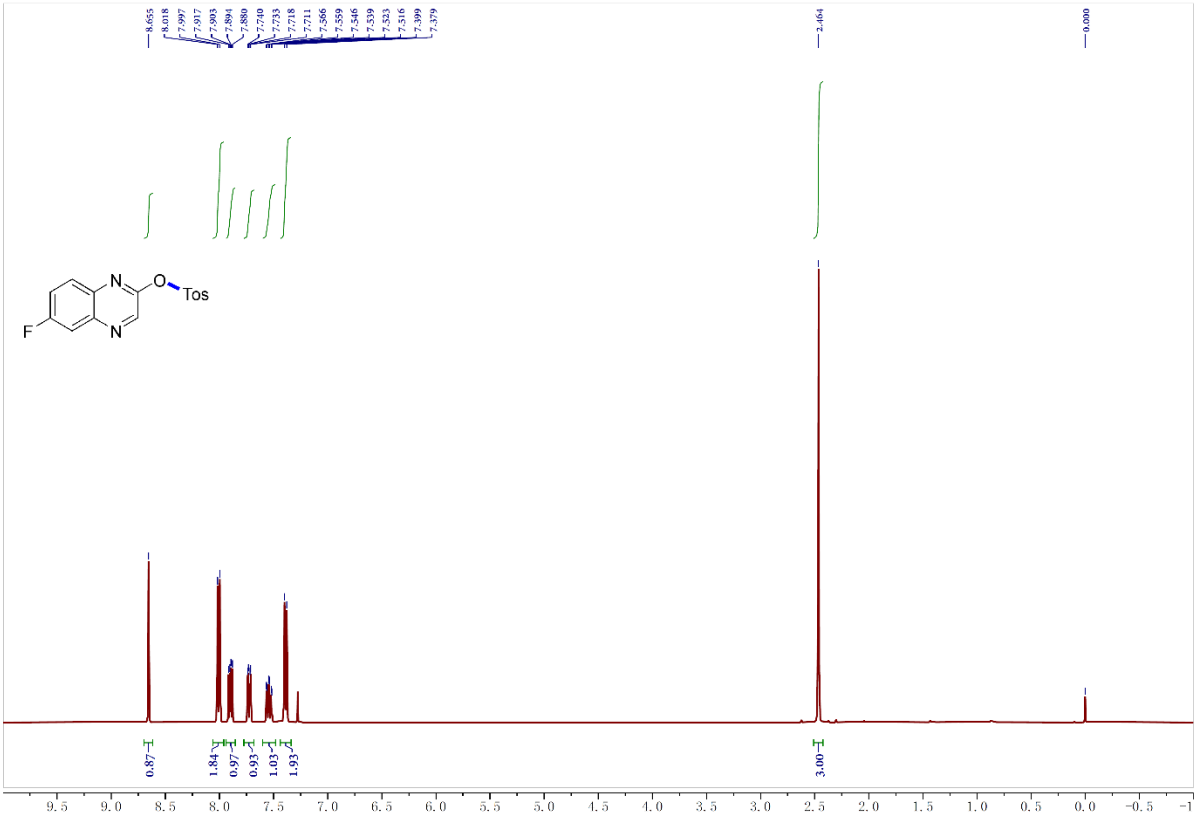
77.16
76.84
21.85
17.26
Tos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7.559
7.546
7.539
7.523
7.516
7.399
7.379
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Tos
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O
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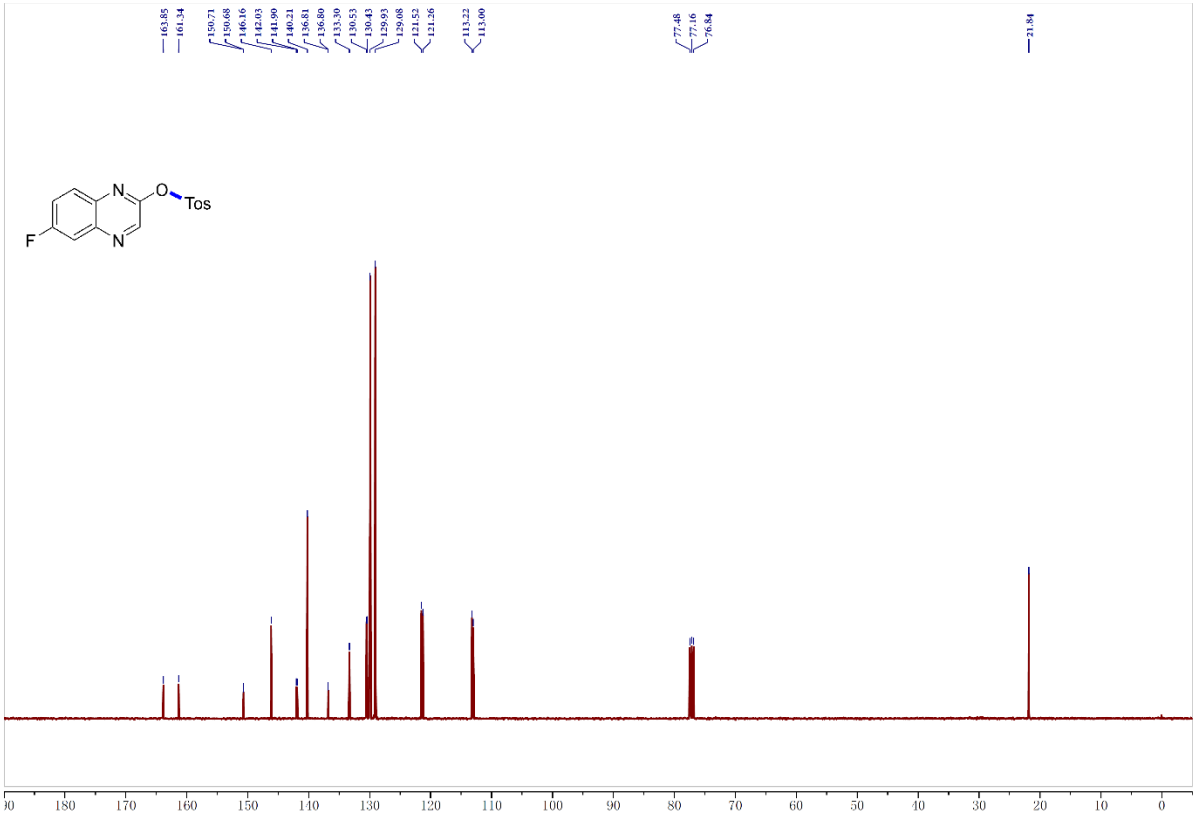
0.97
0.93
1.03
1.93
3.00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141.90
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133.30
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113.00
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76.84
21.84
Tos
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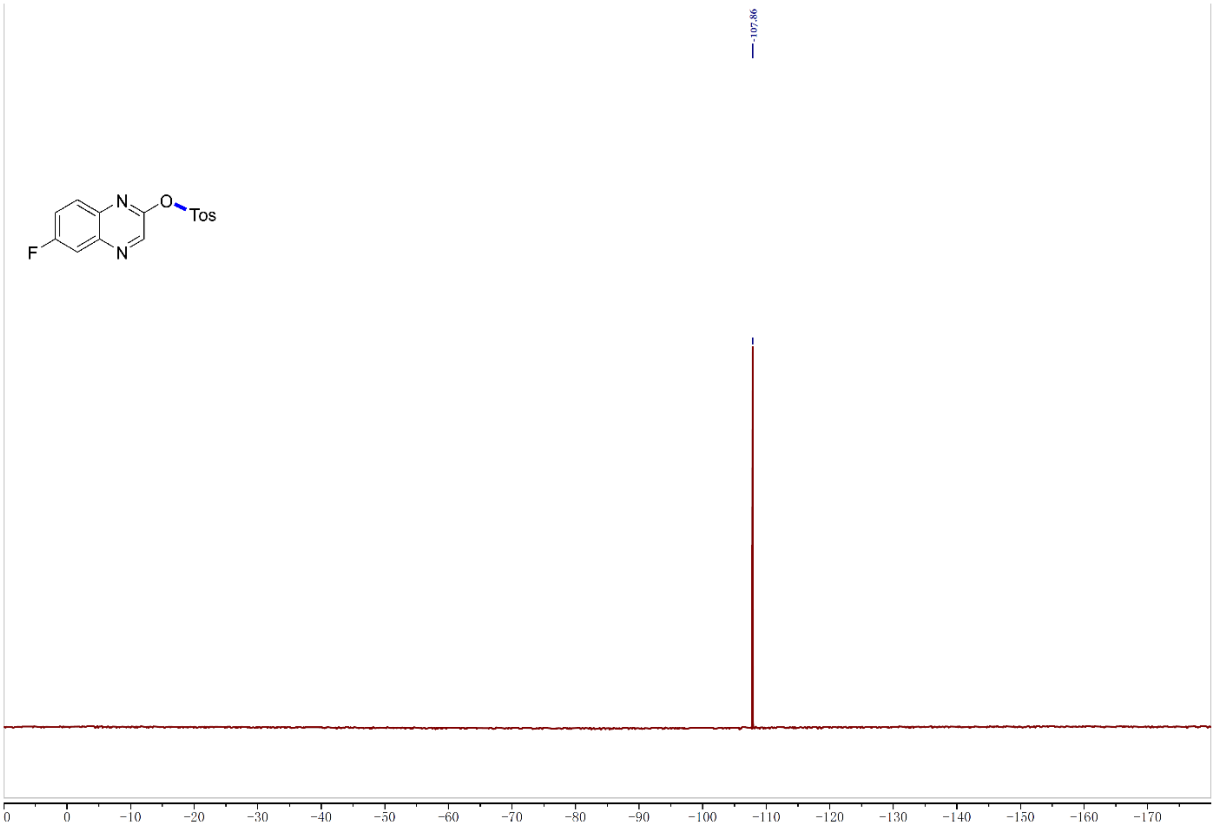
N
O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-150
-160
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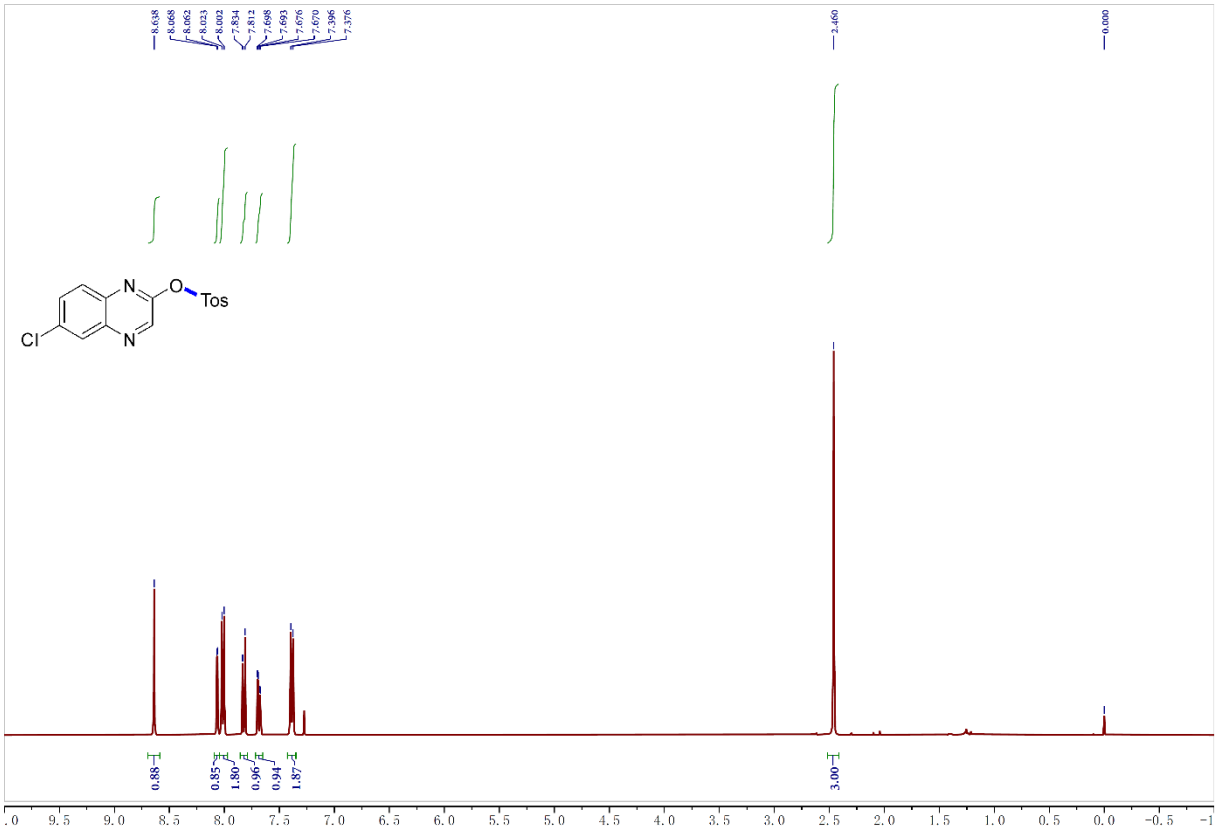
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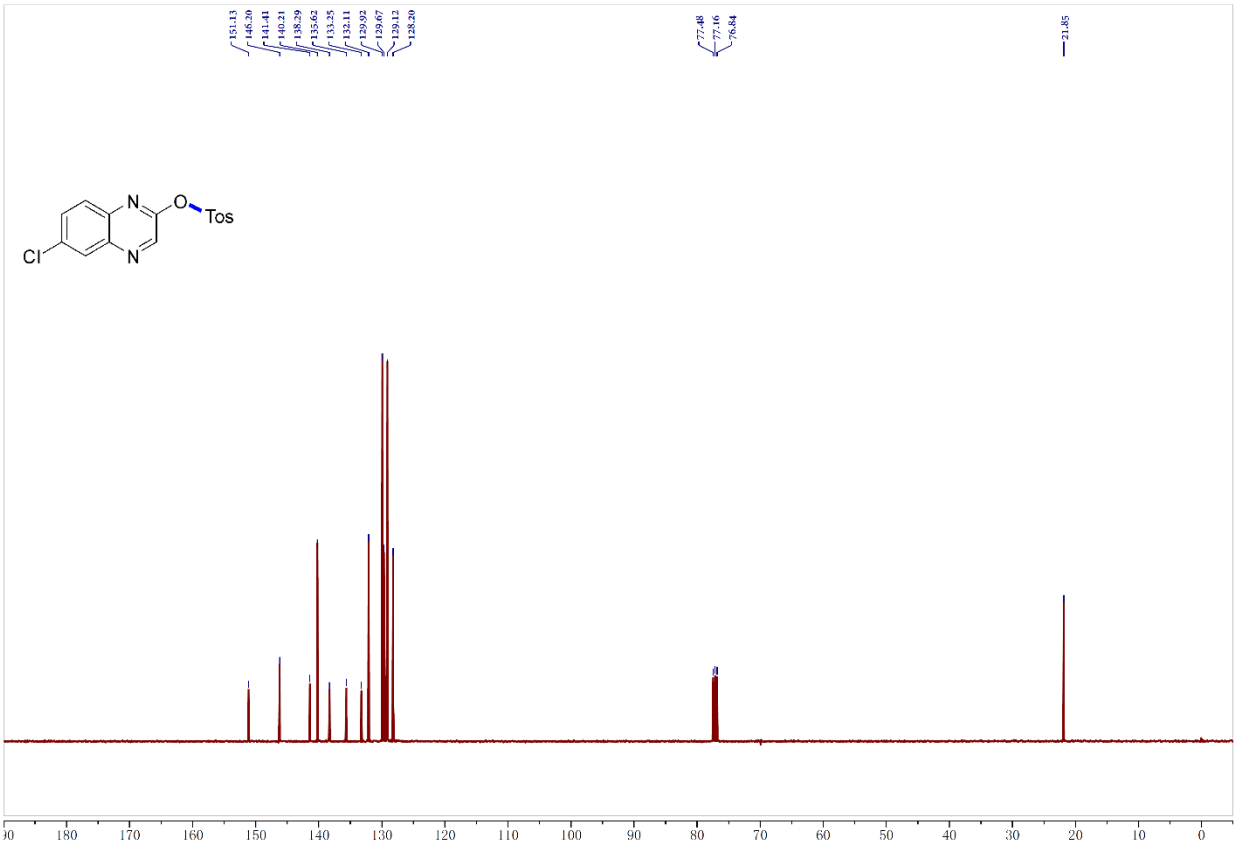
3.00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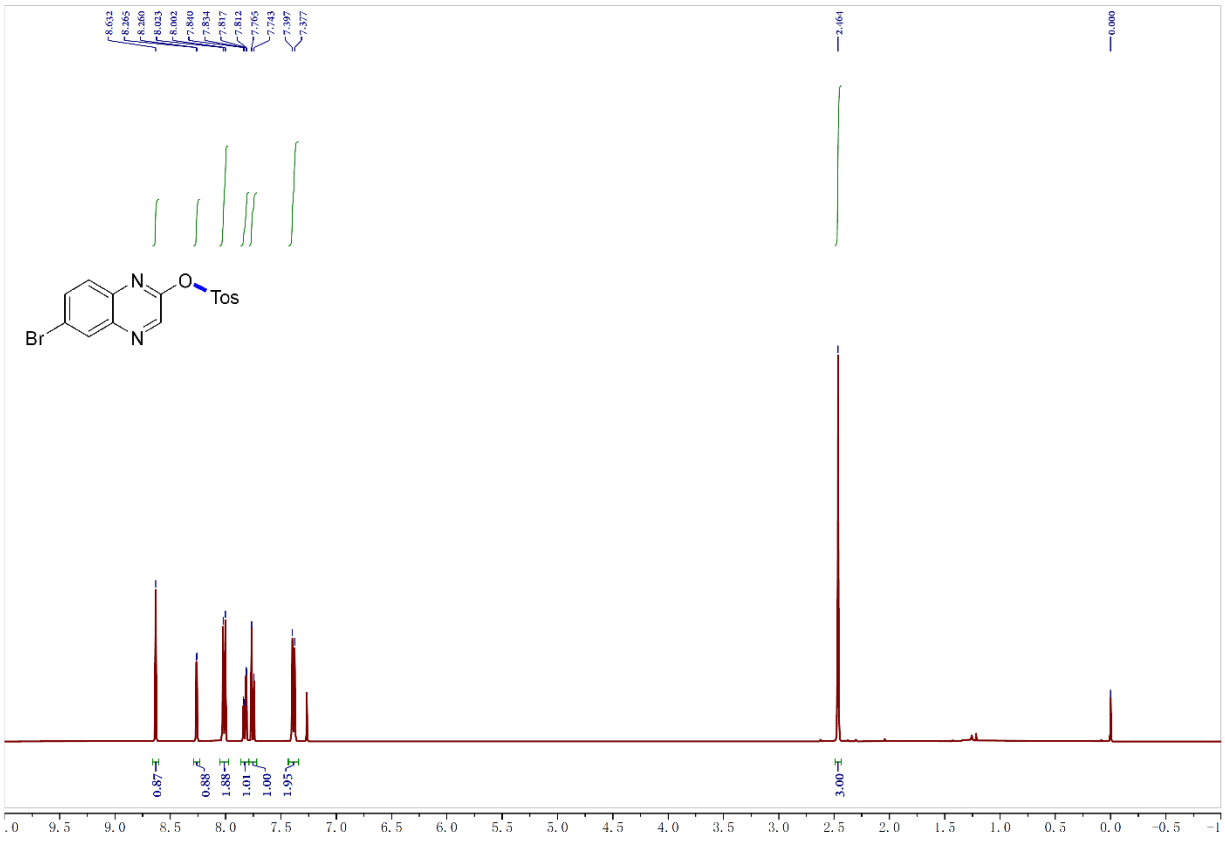
O
Tos
Cl
N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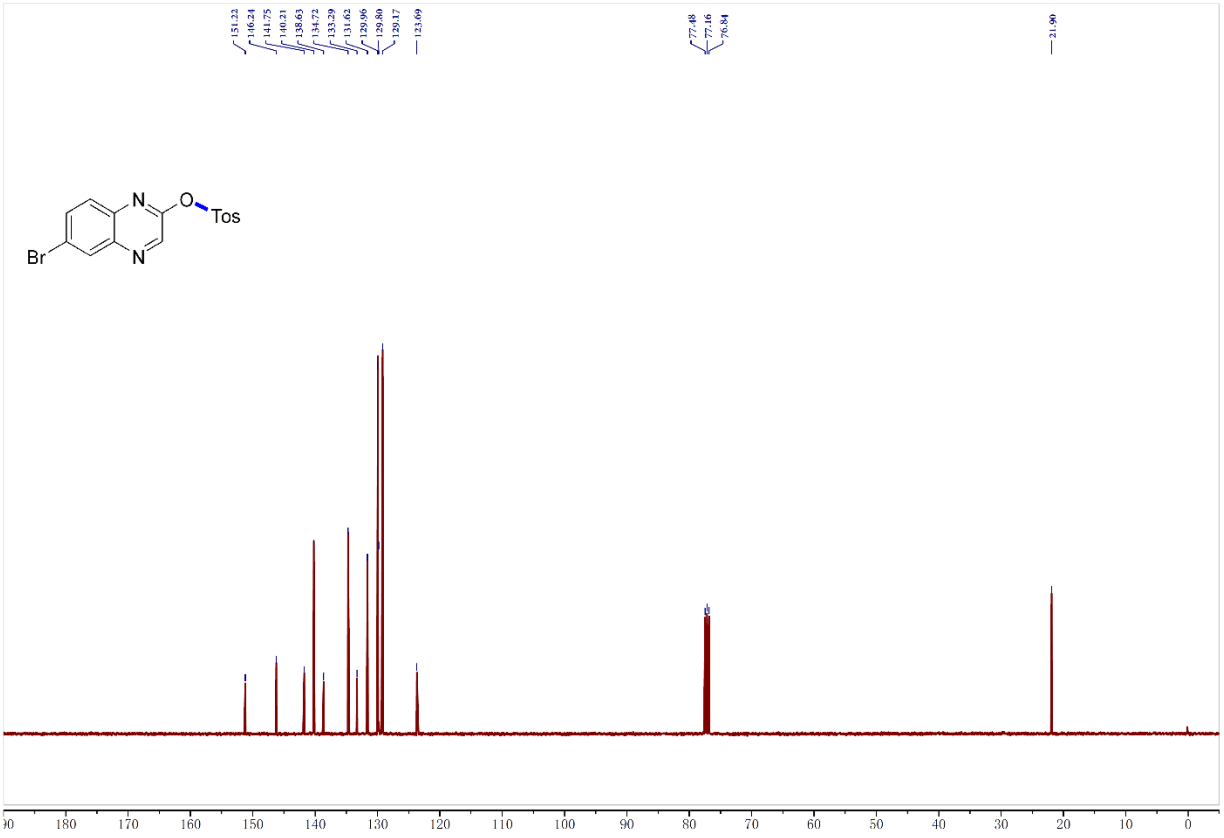
3.00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N
O
Tos
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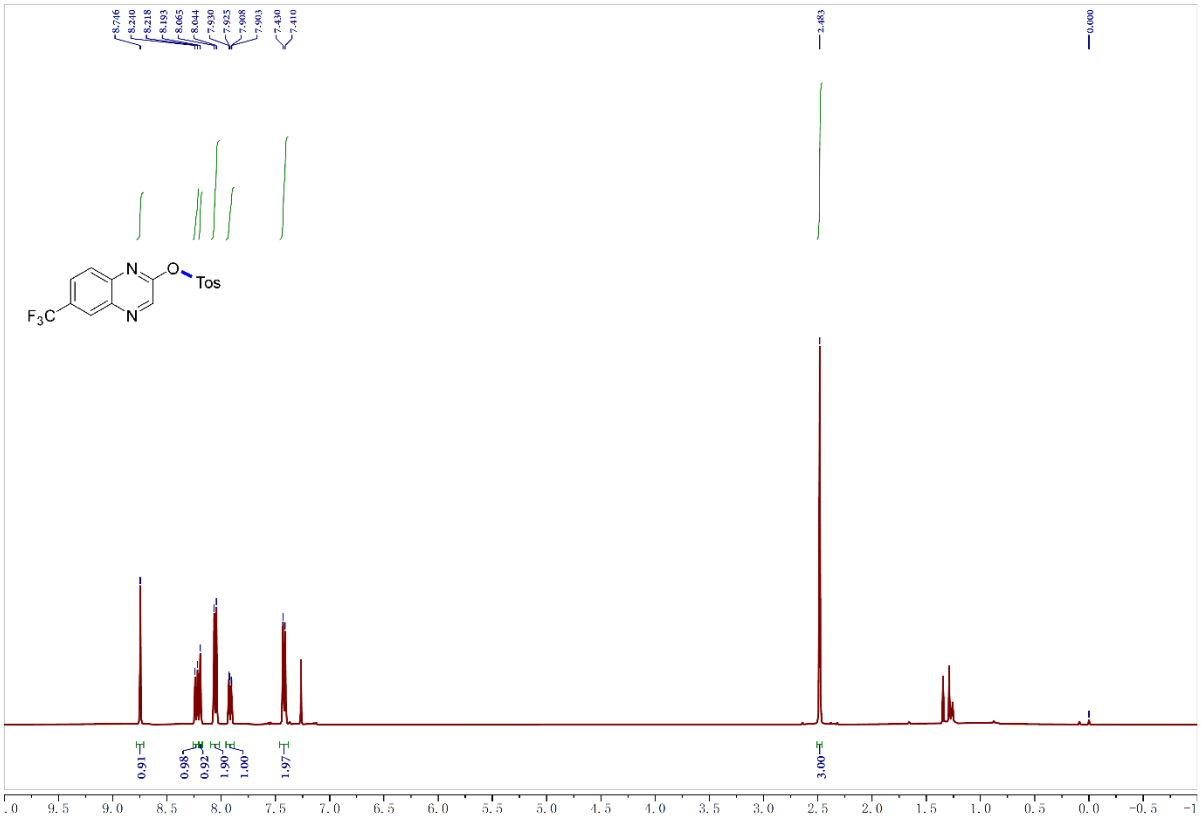
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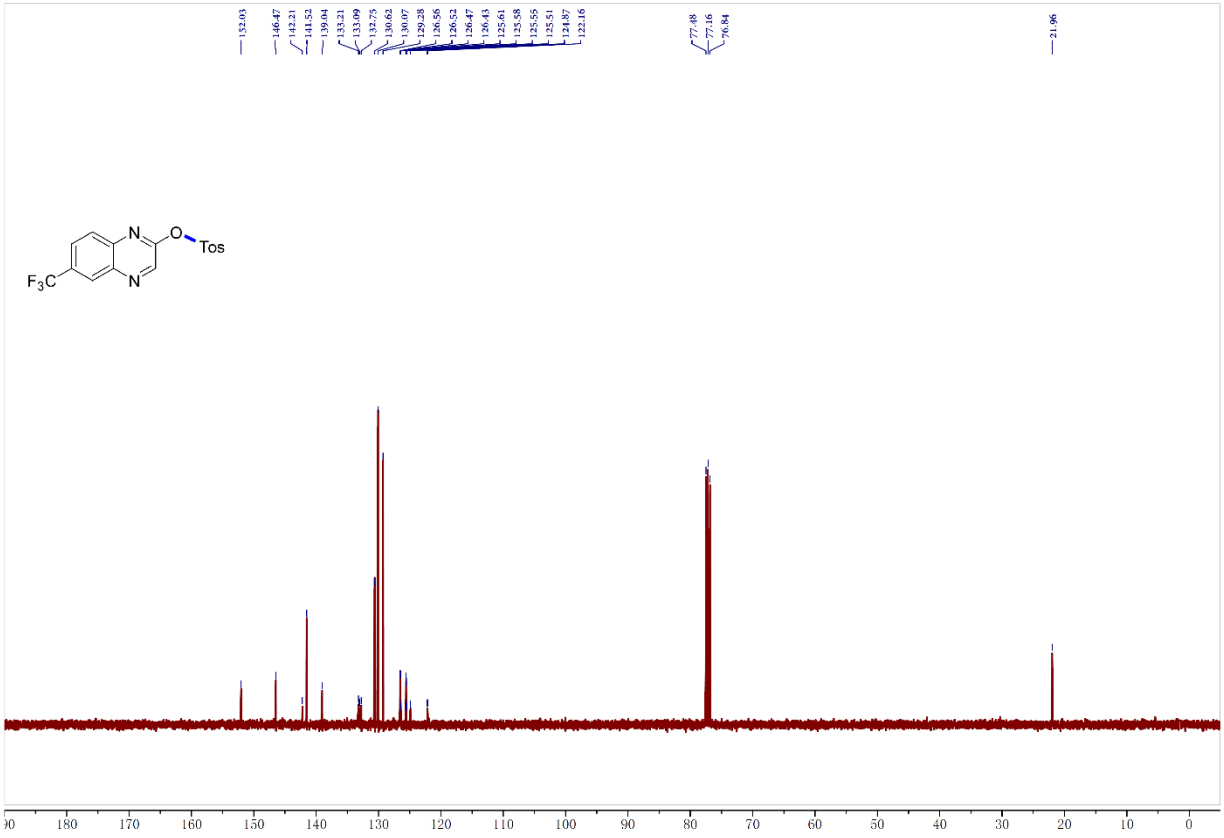
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126.52
126.47
126.43
125.61
125.58
125.55
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122.16
77.48
77.16
76.84
21.96
Tos
F3C
N
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30
20
10
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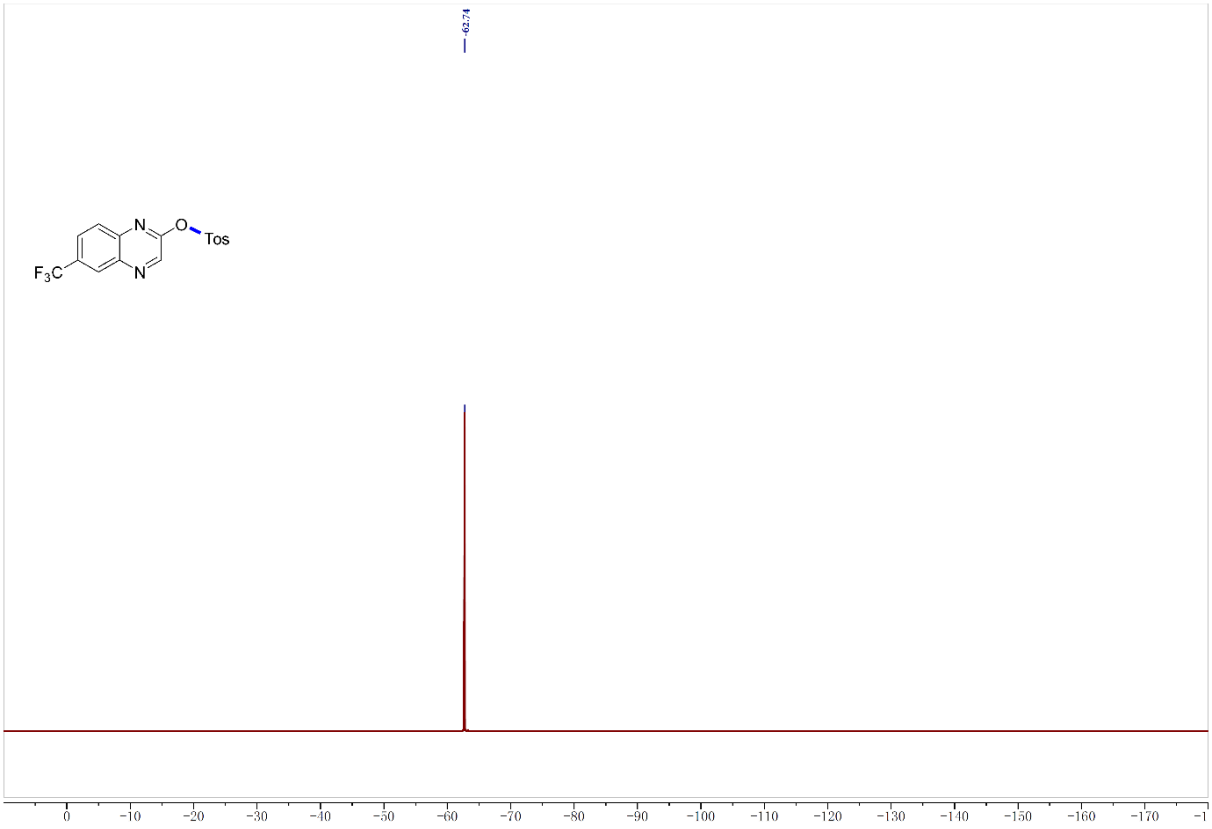
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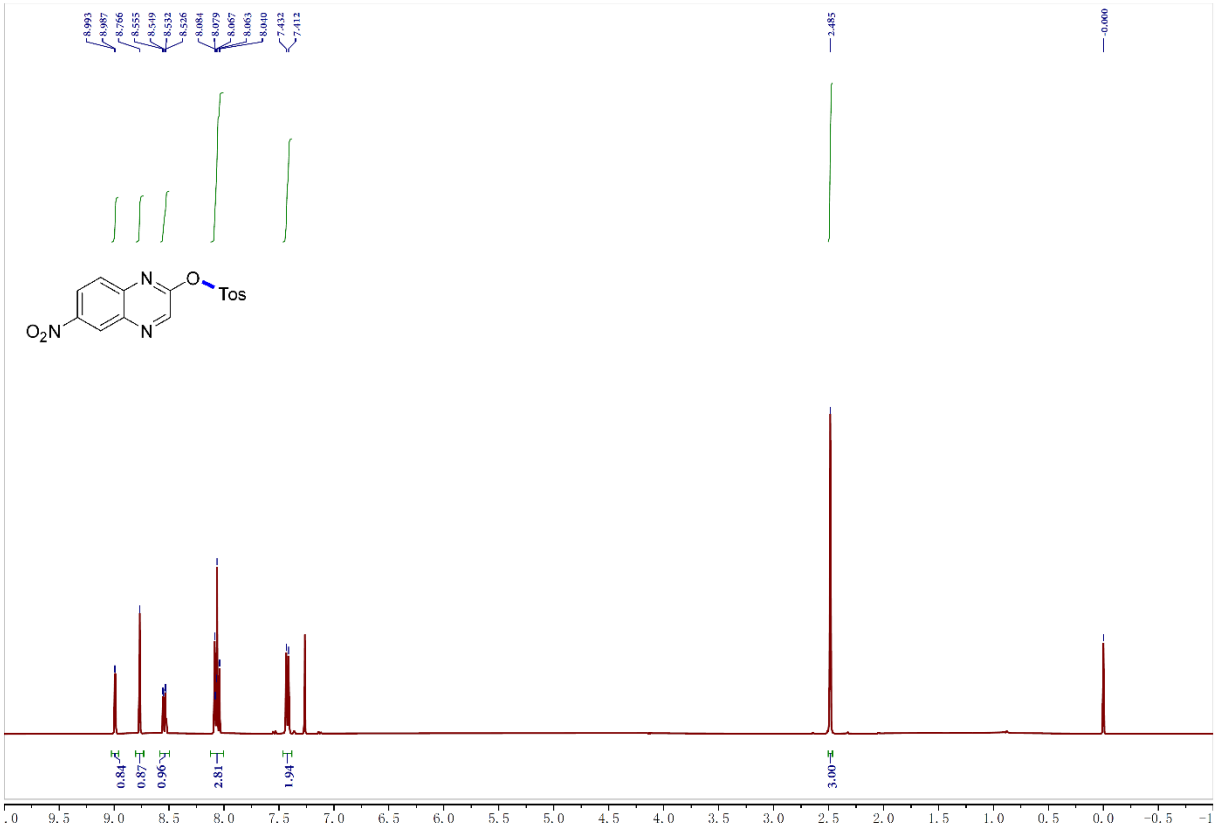
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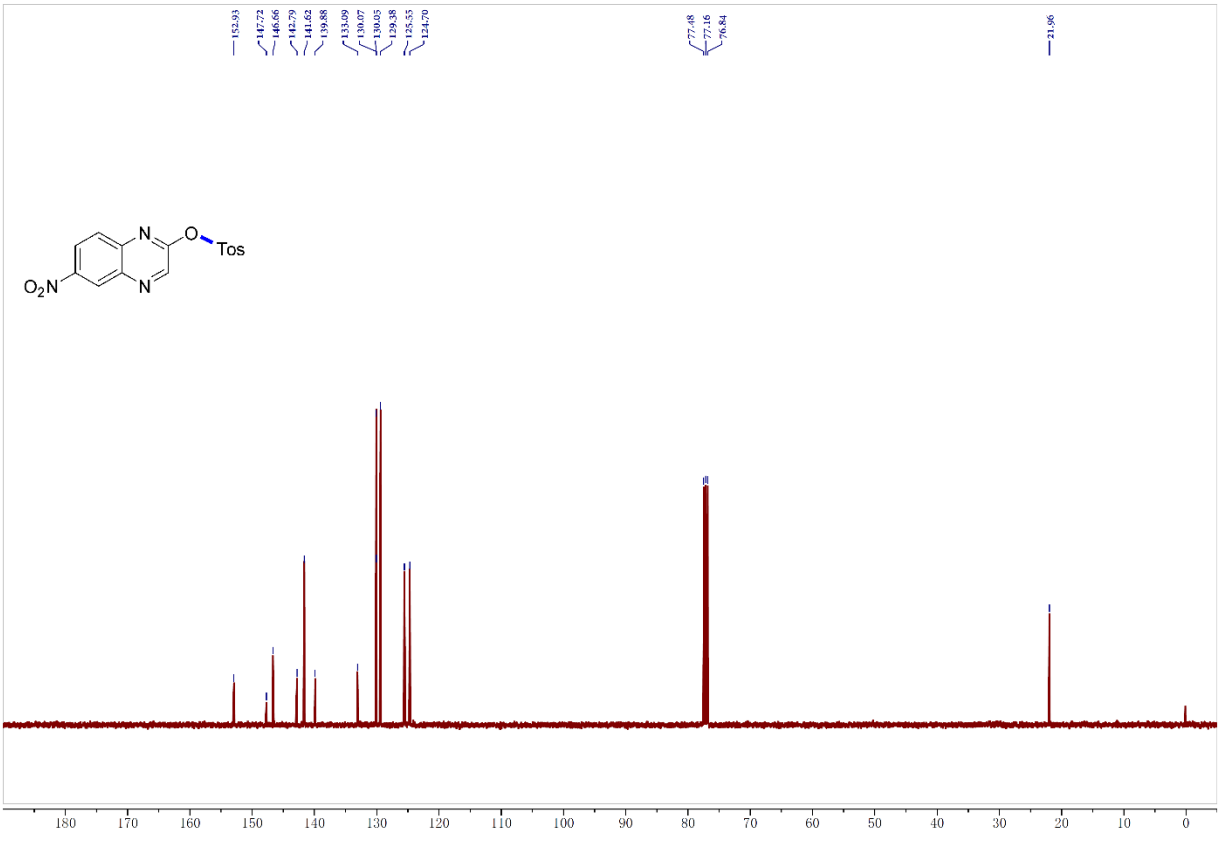
2.81
1.94
3.00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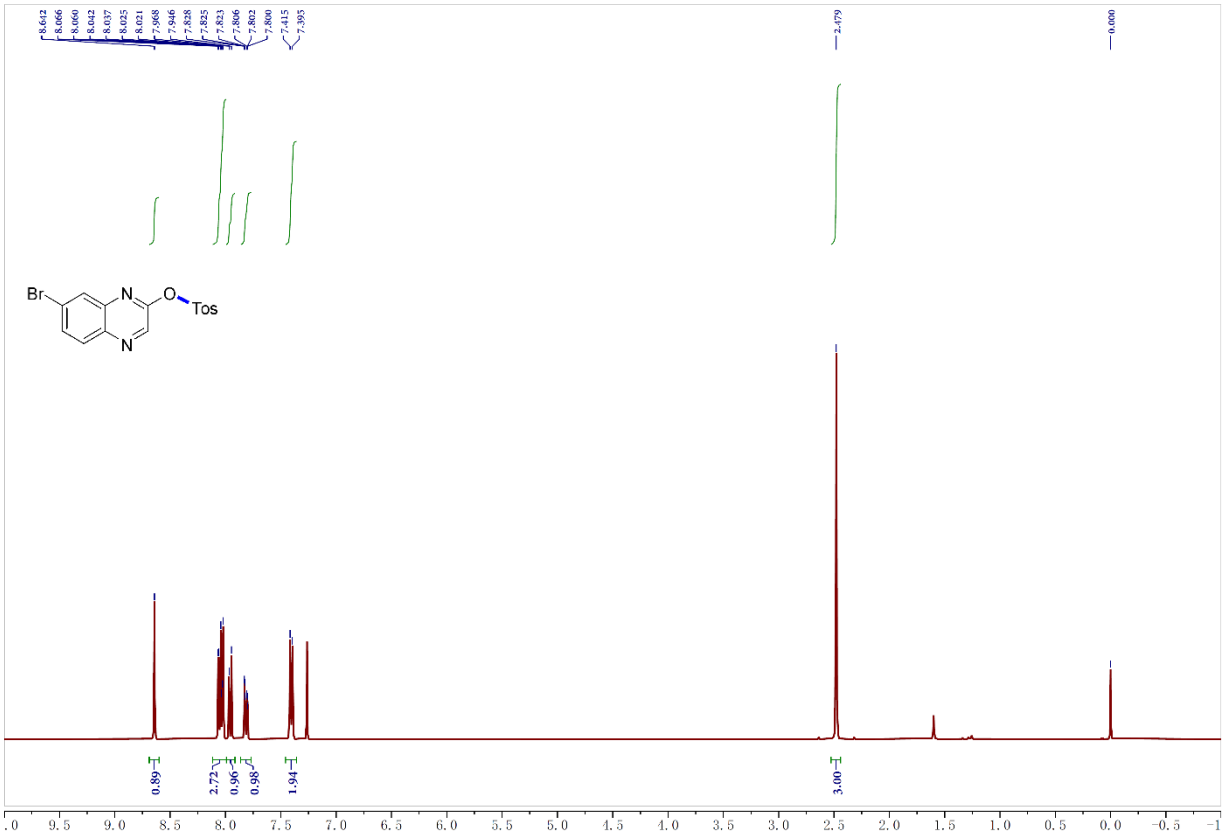
O_2N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7.806
7.802
7.800
7.415
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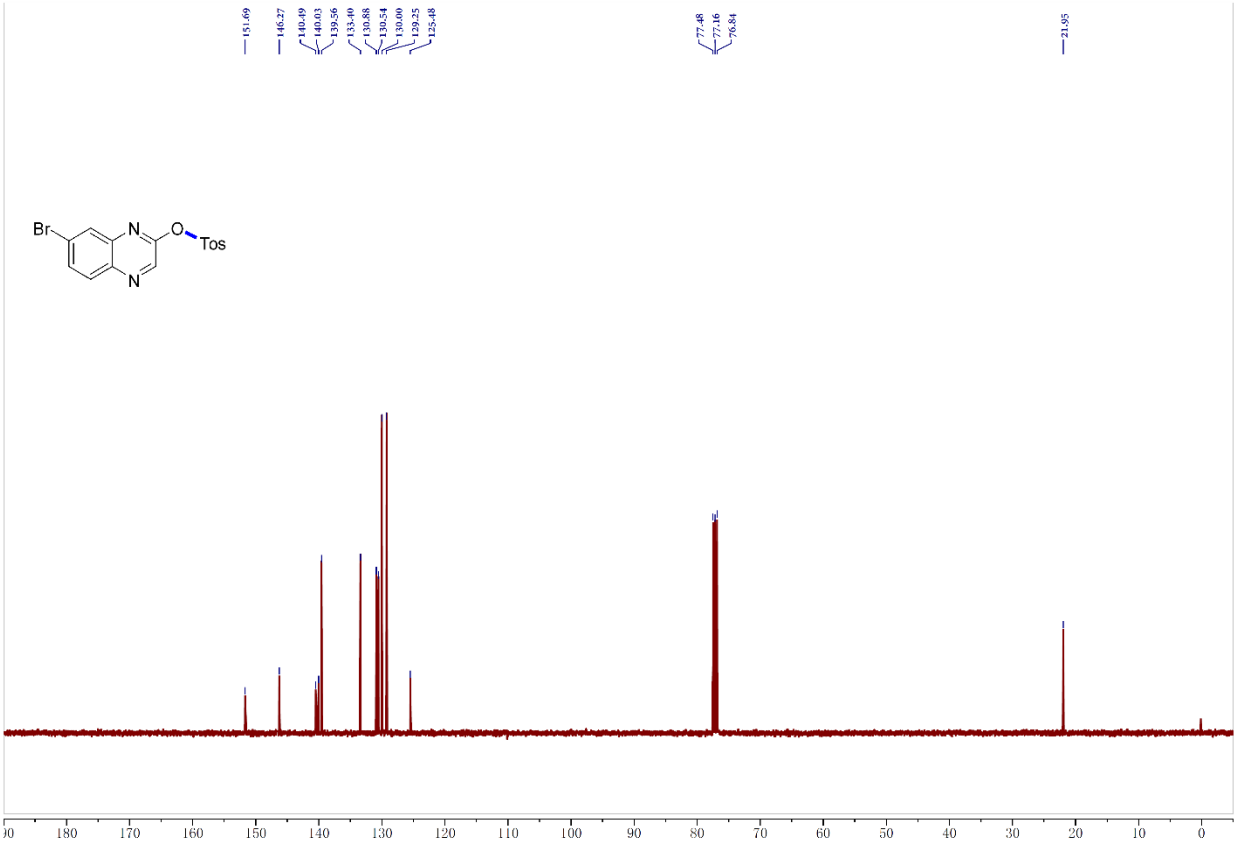
3.00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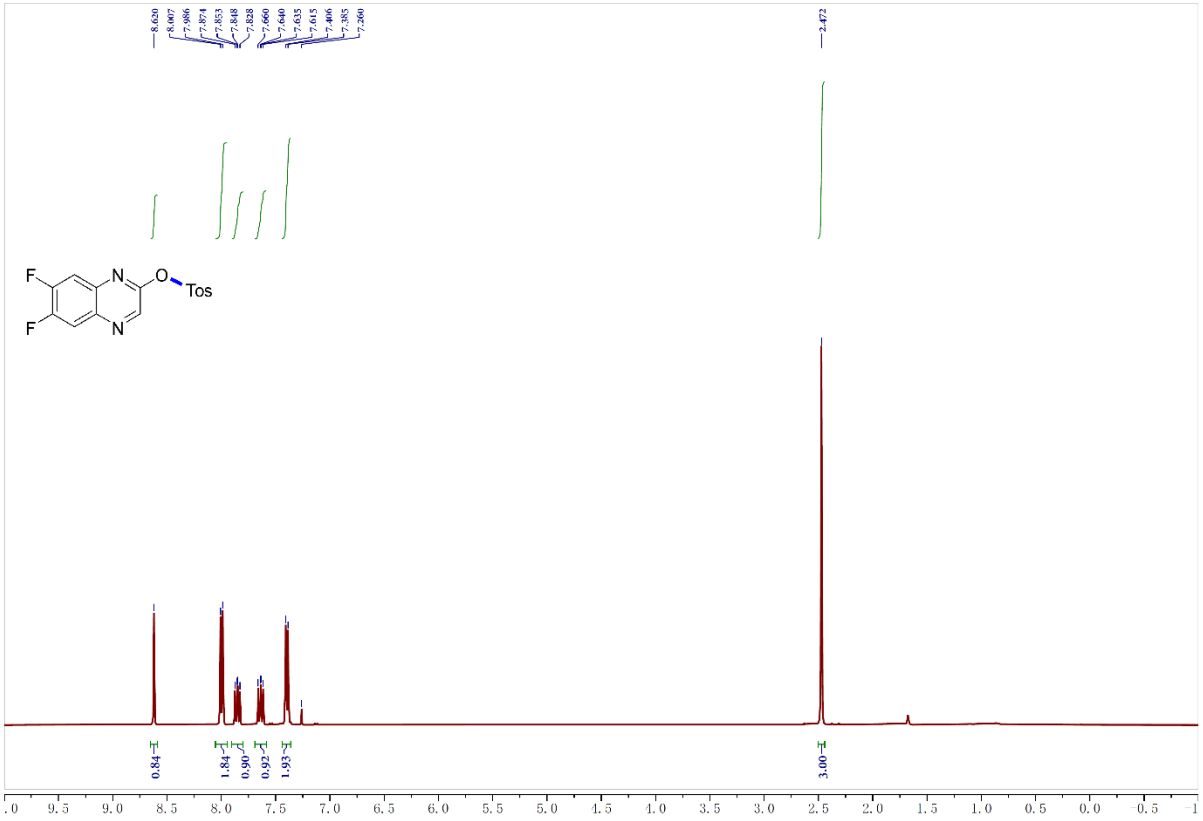
N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7.385
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N
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1.84
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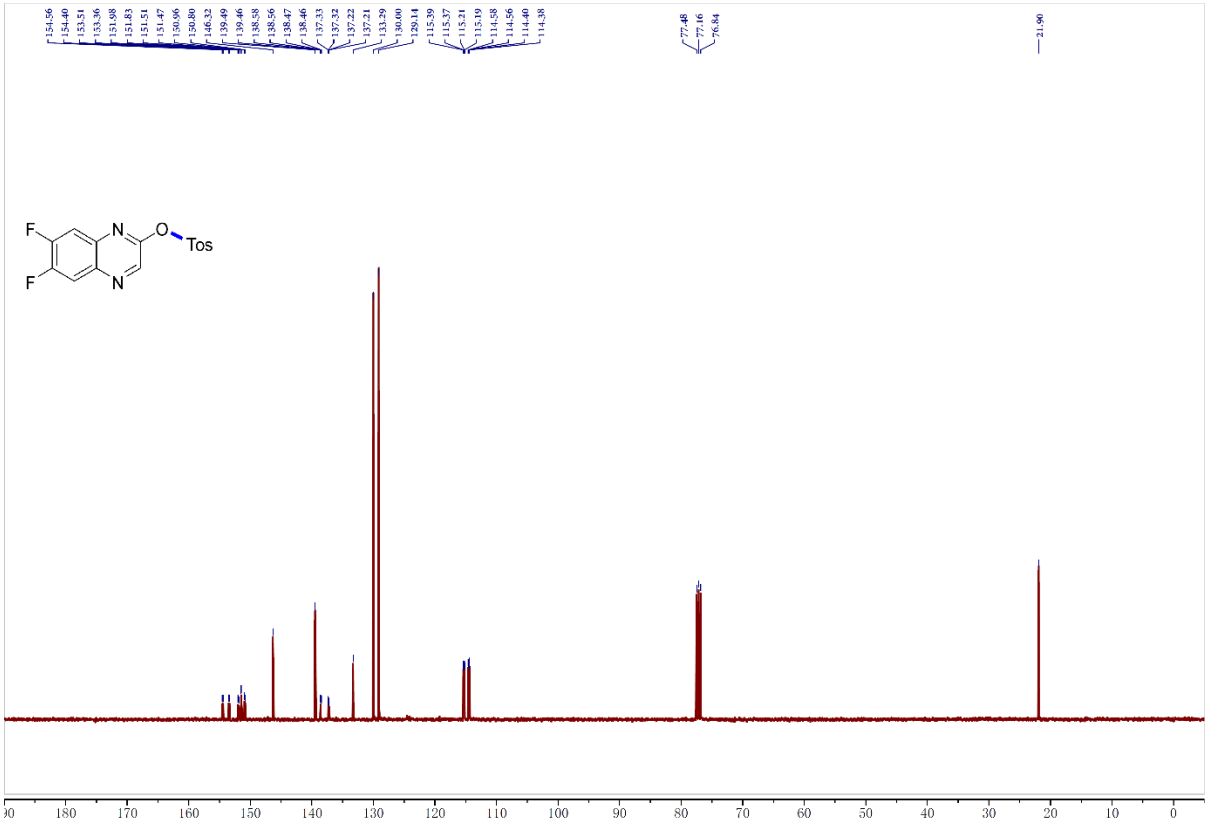
1.93
3.00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138.56
138.47
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137.21
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O
Tos
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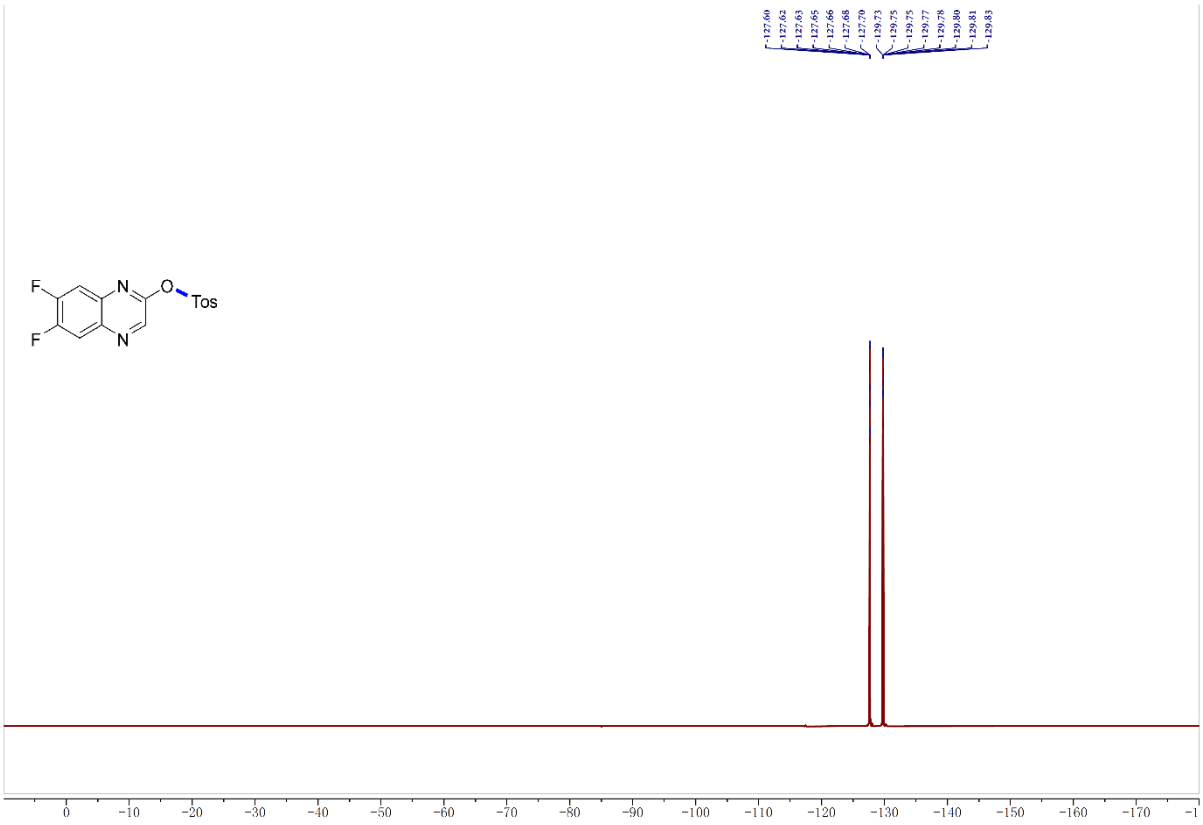
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F
N
O
Tos
F
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-20
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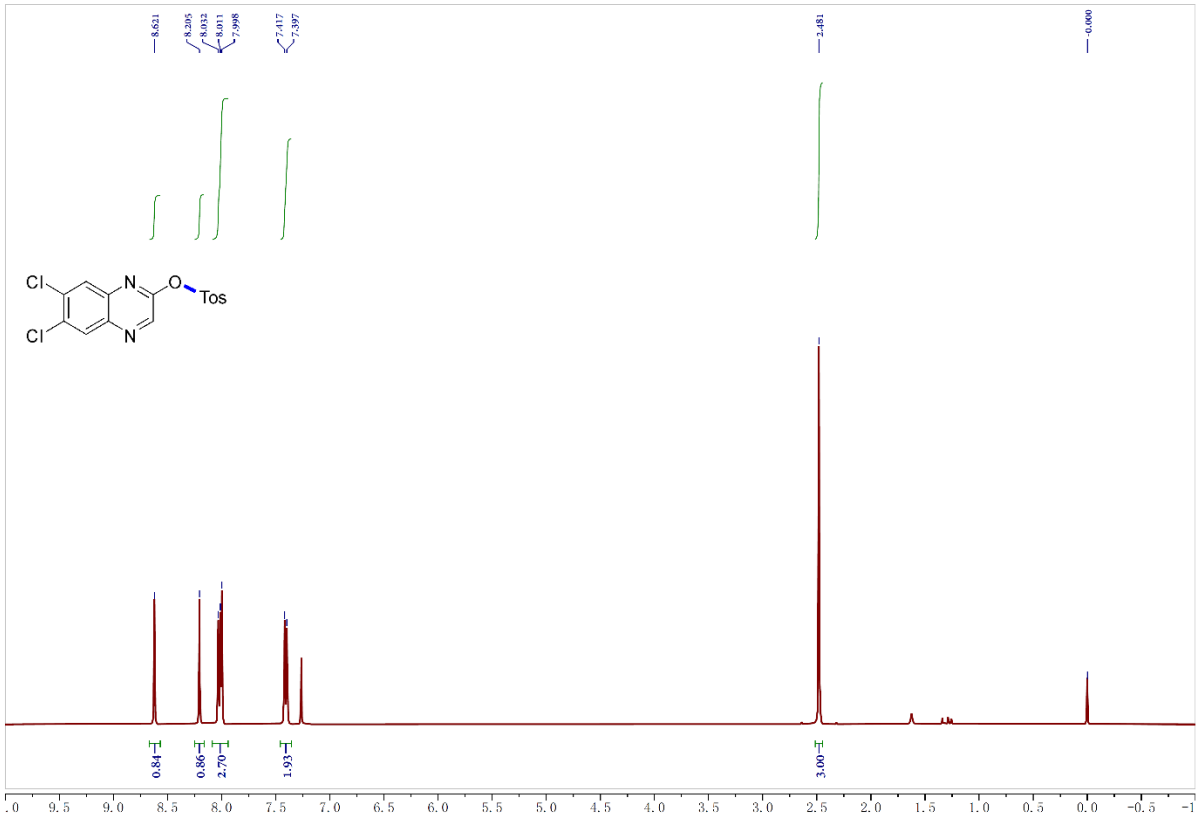
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Cl
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0.86
2.70
1.93
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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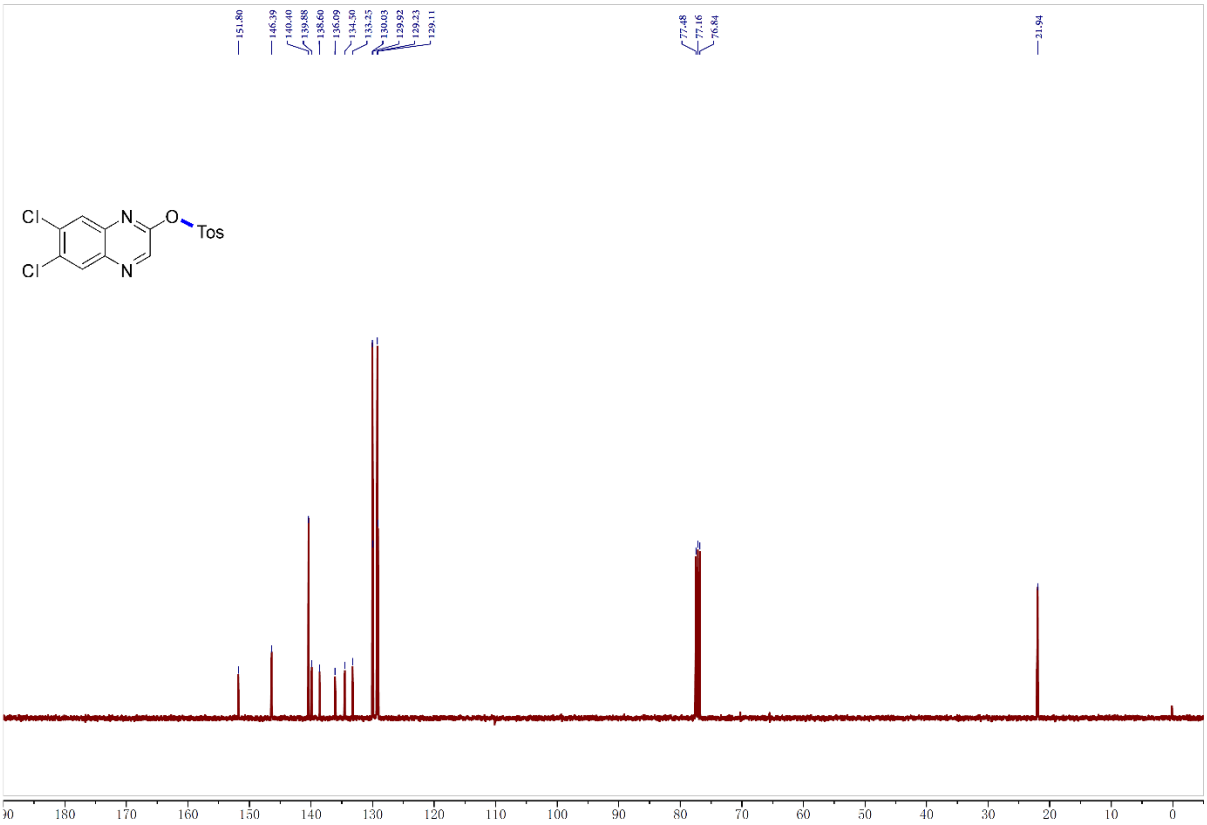
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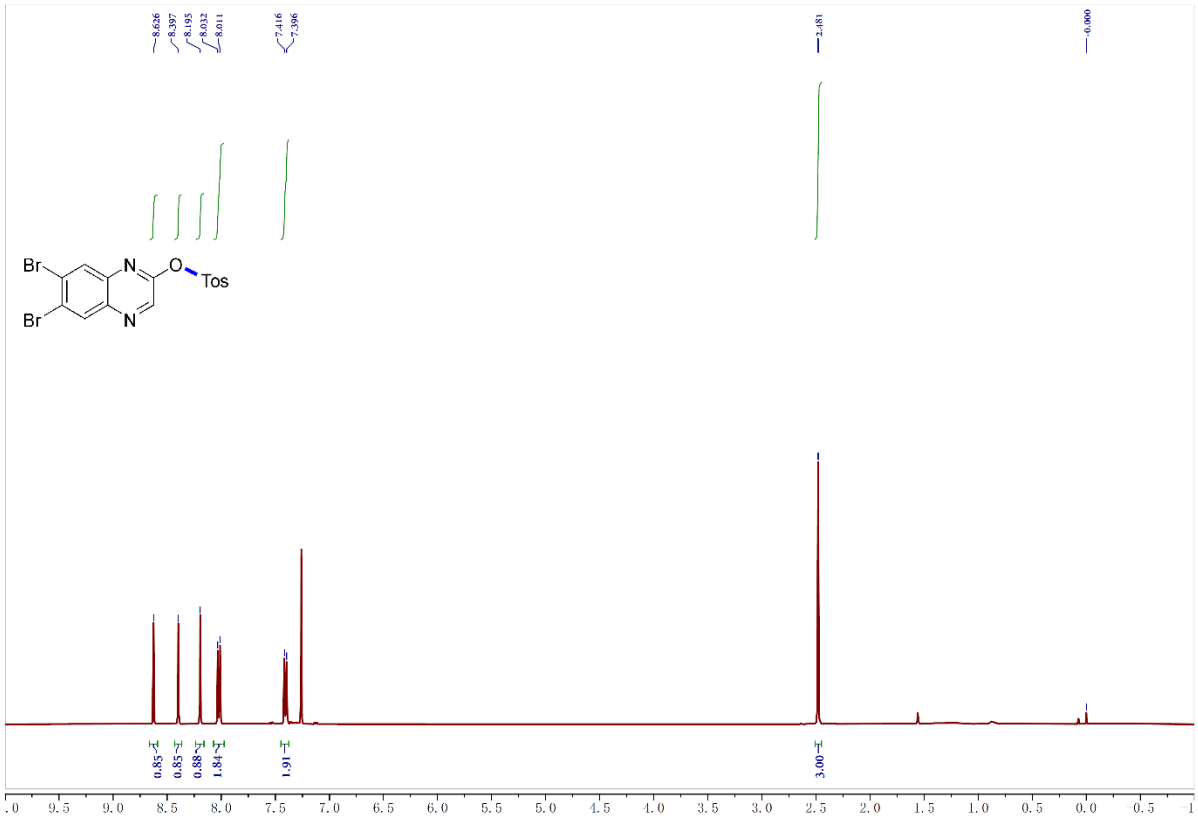
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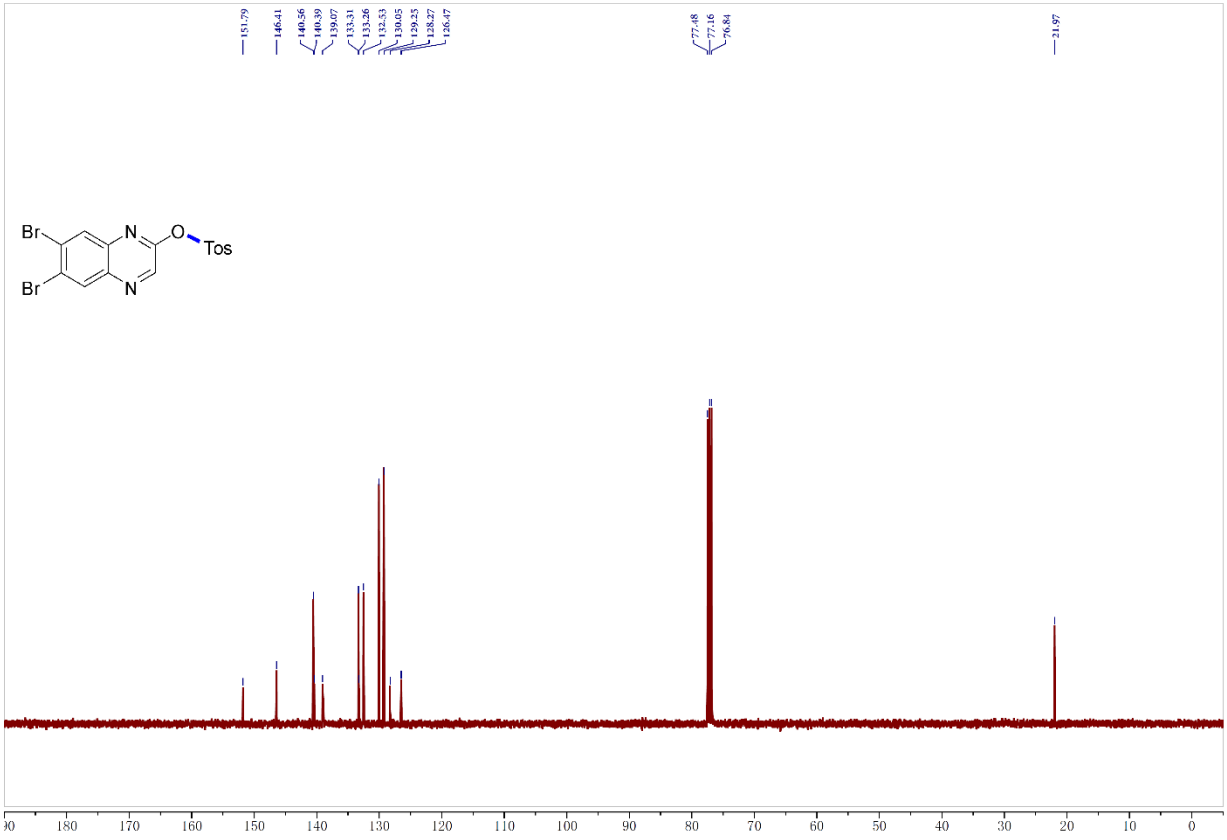
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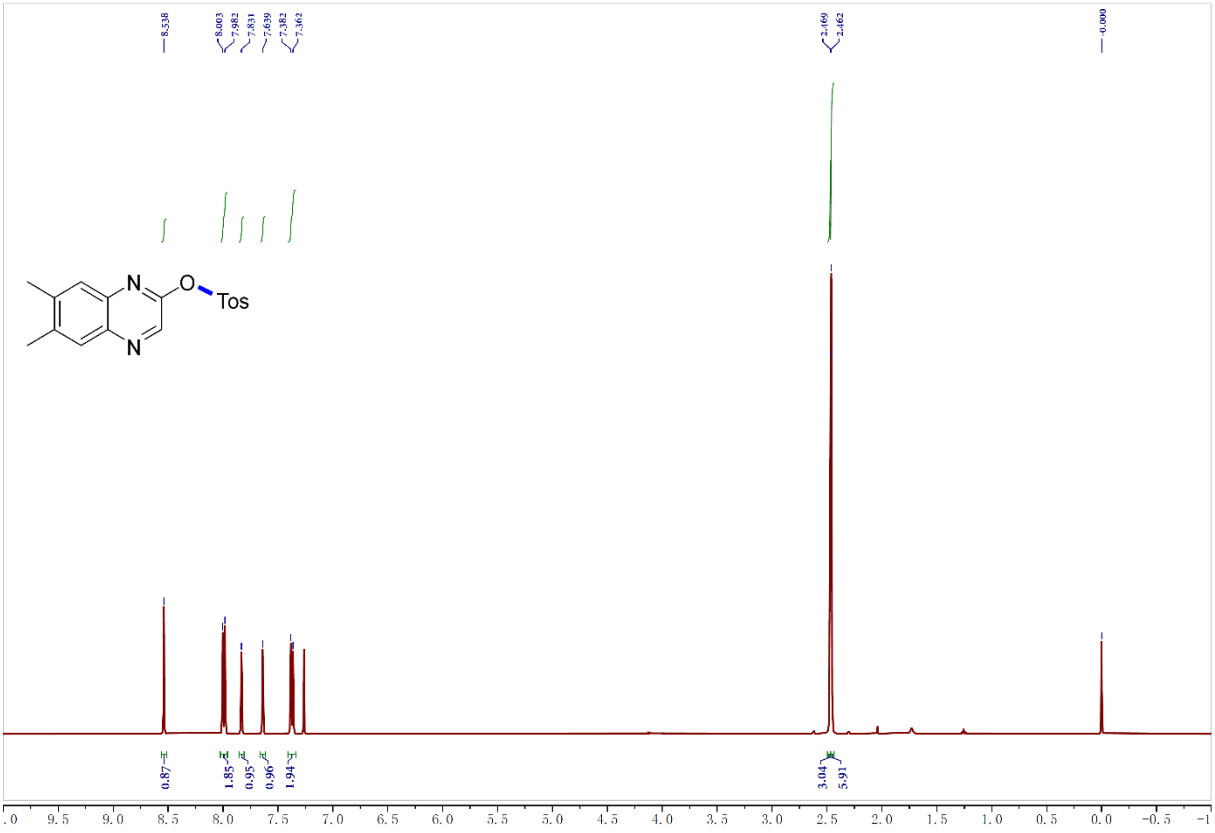
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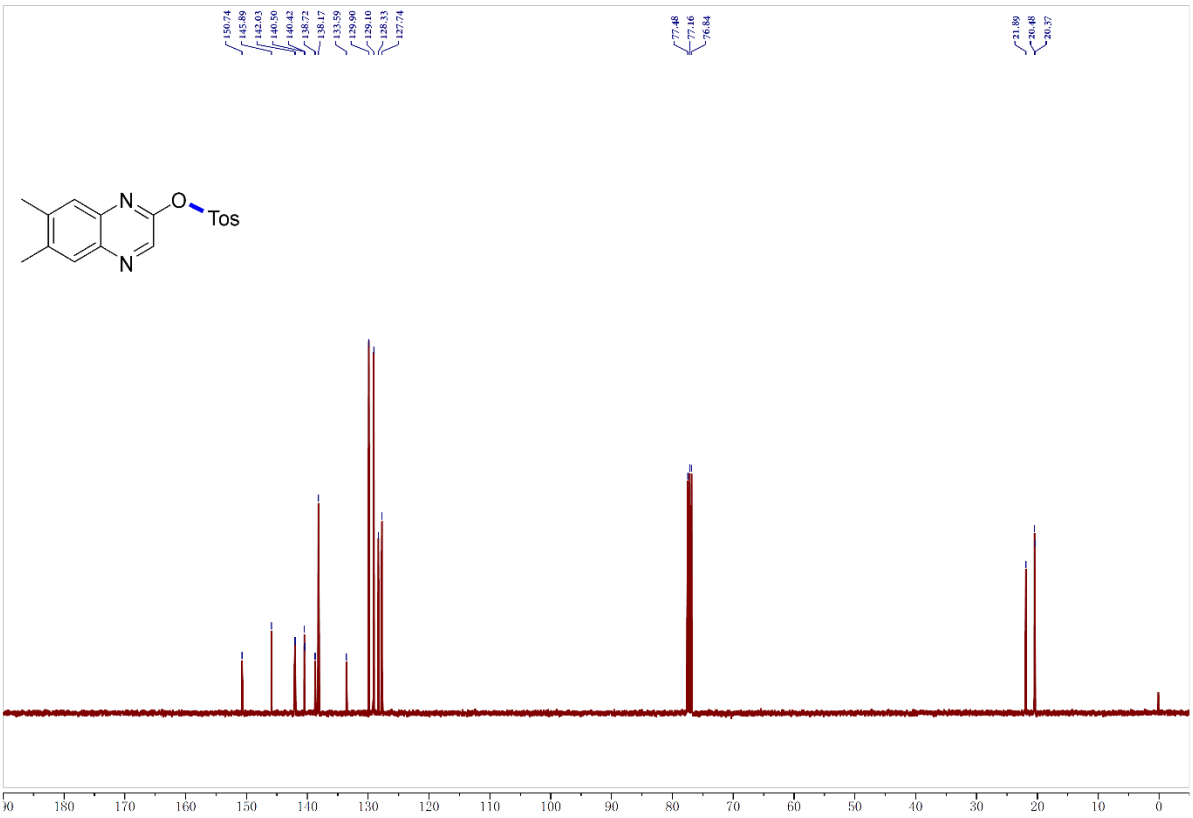
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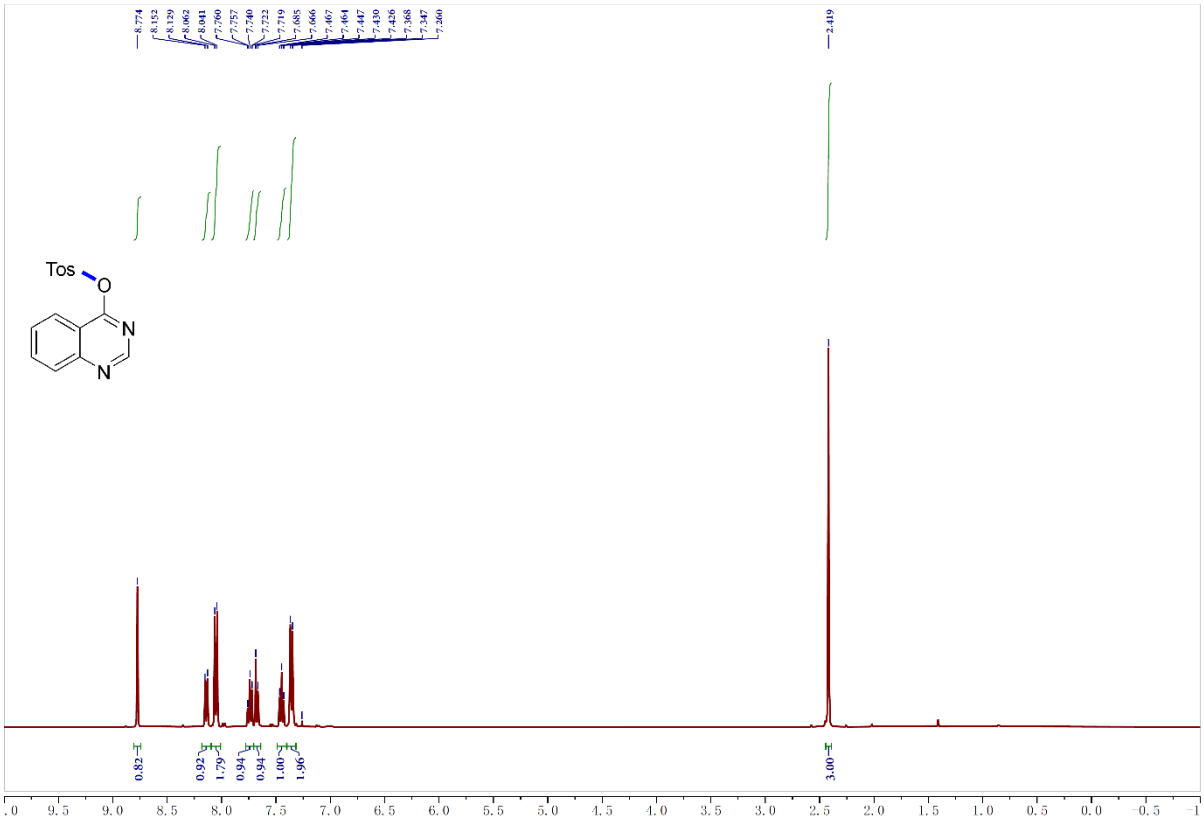
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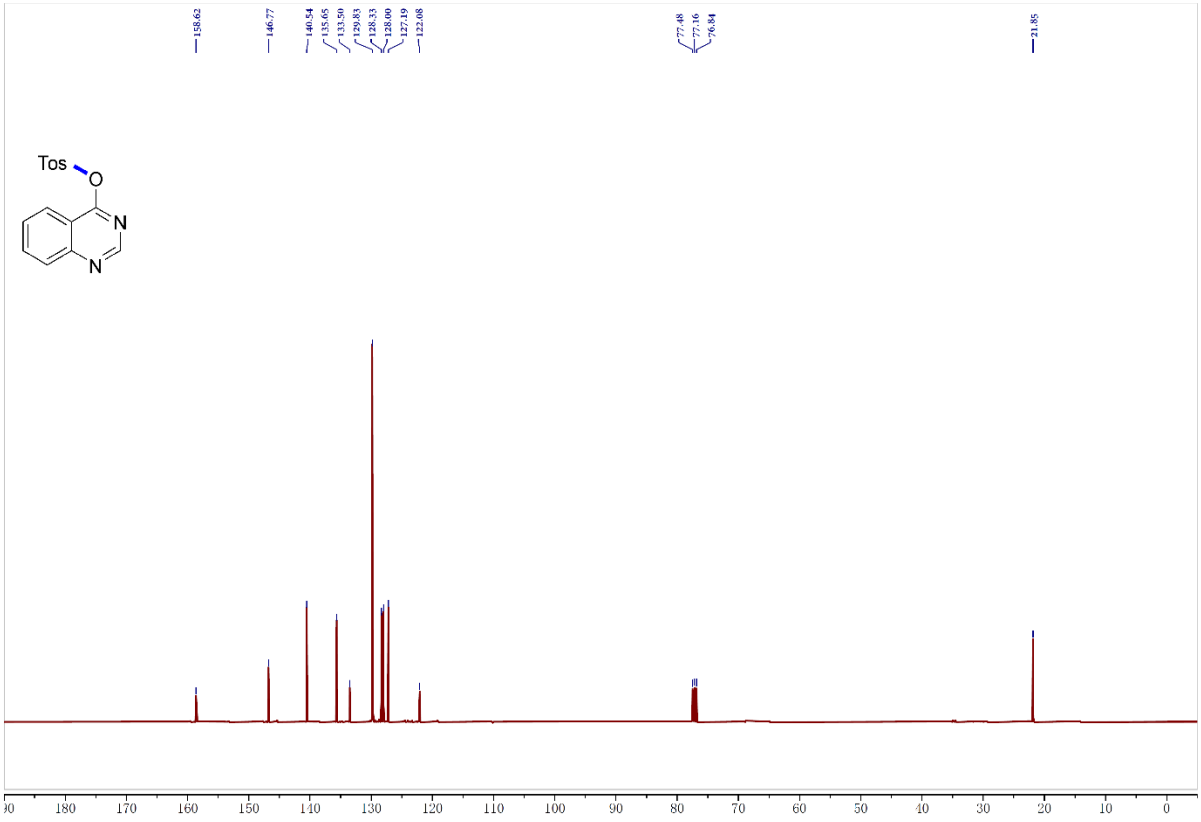
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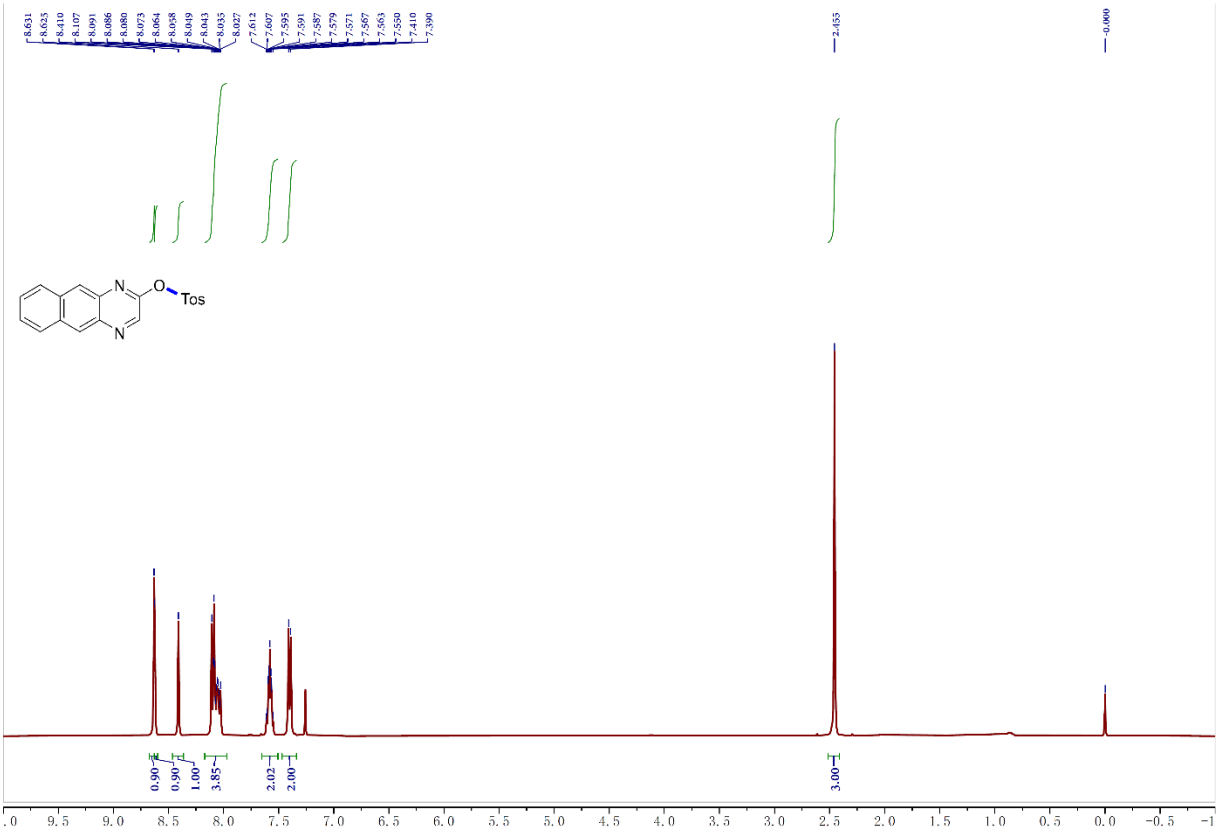
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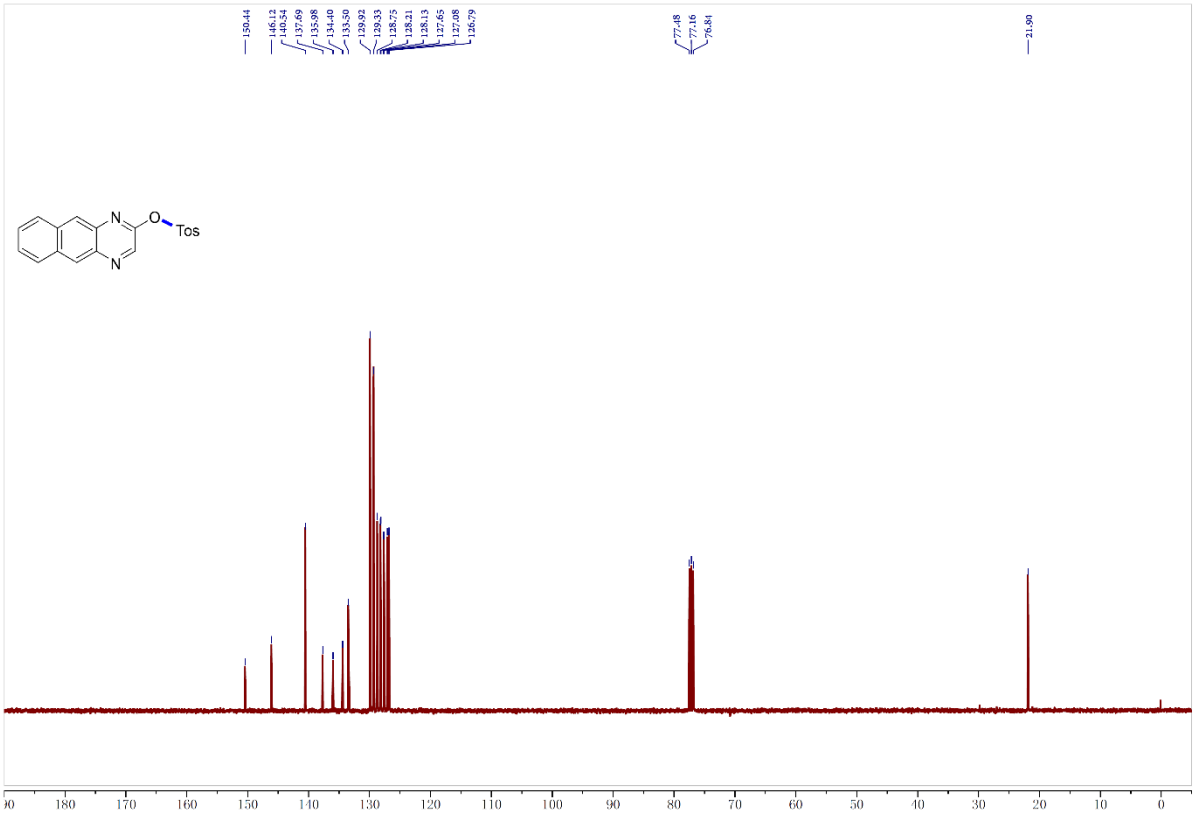
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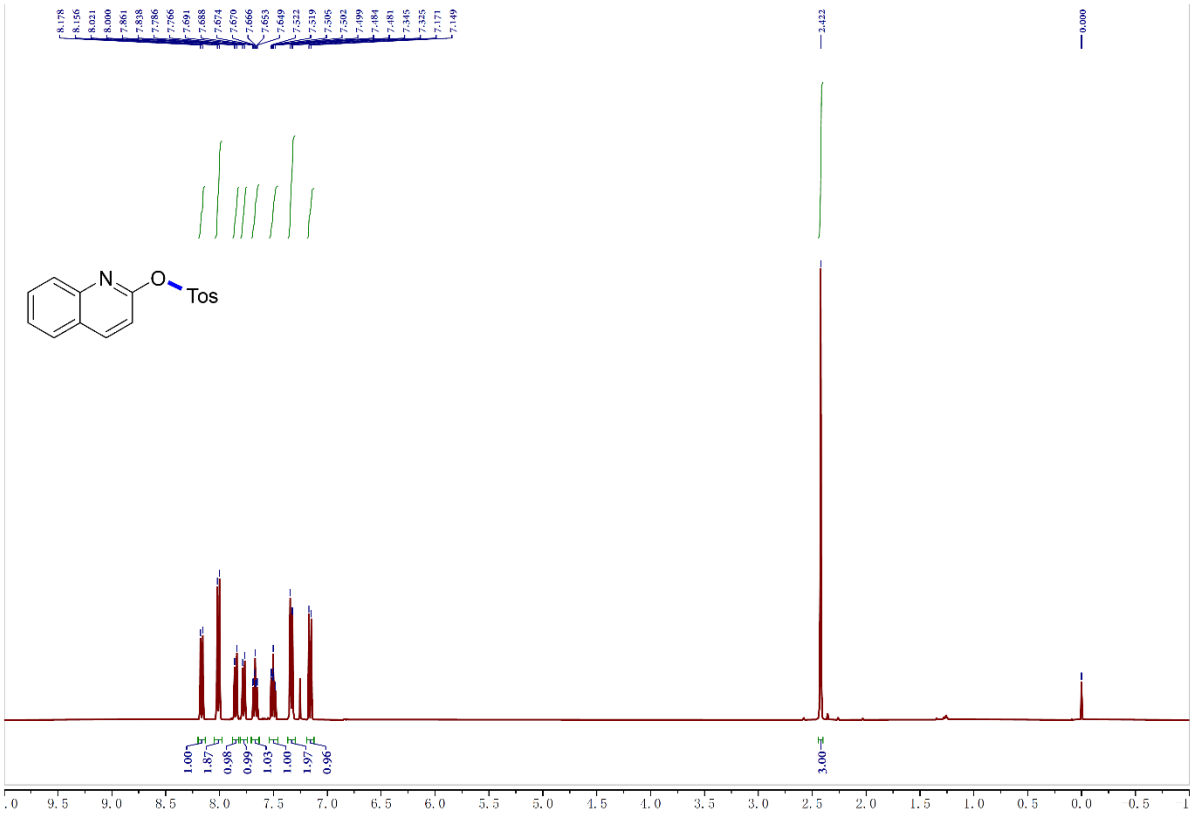
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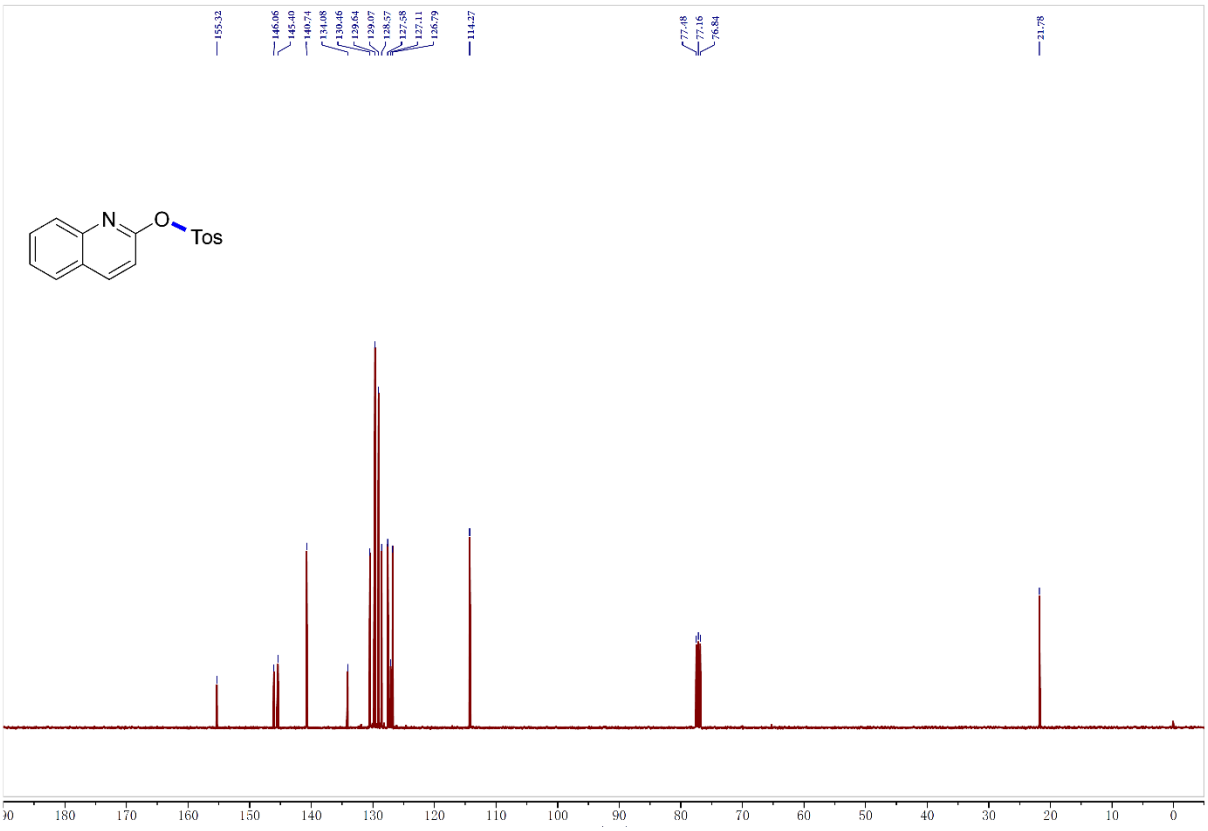
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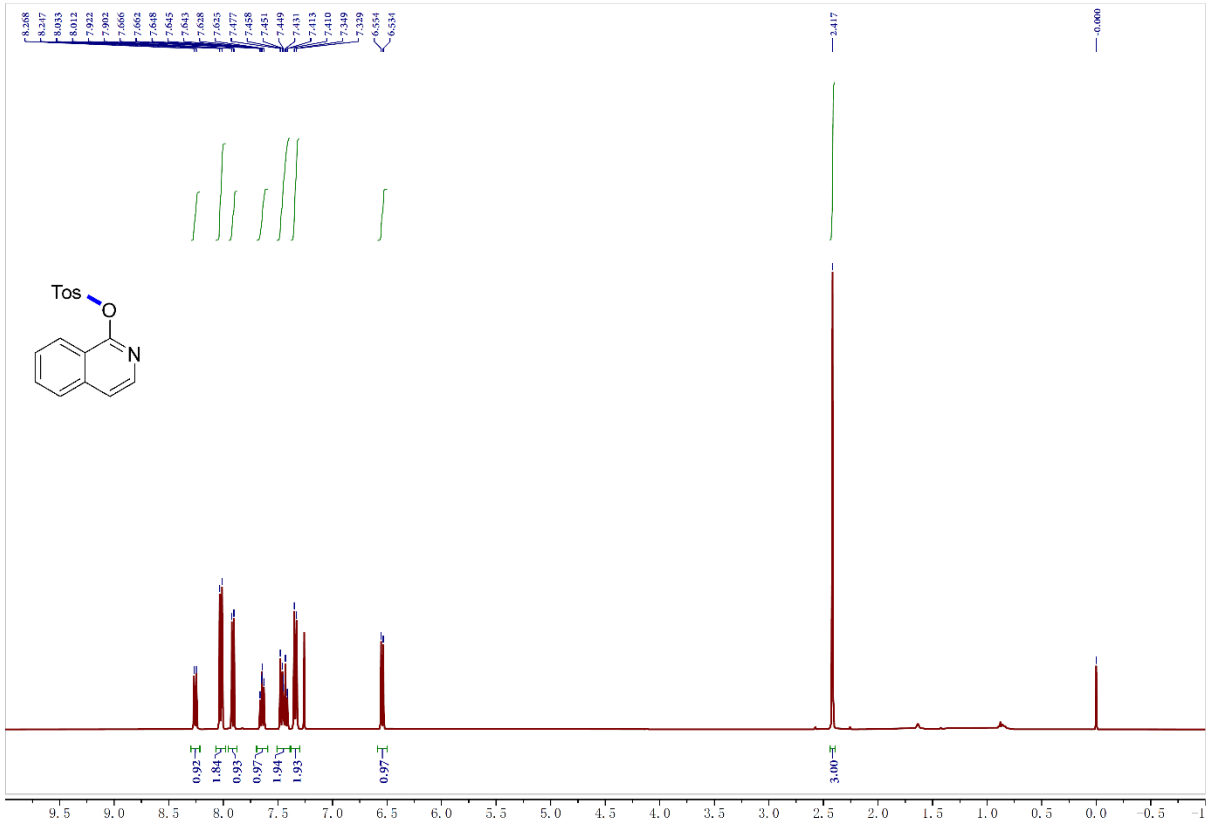
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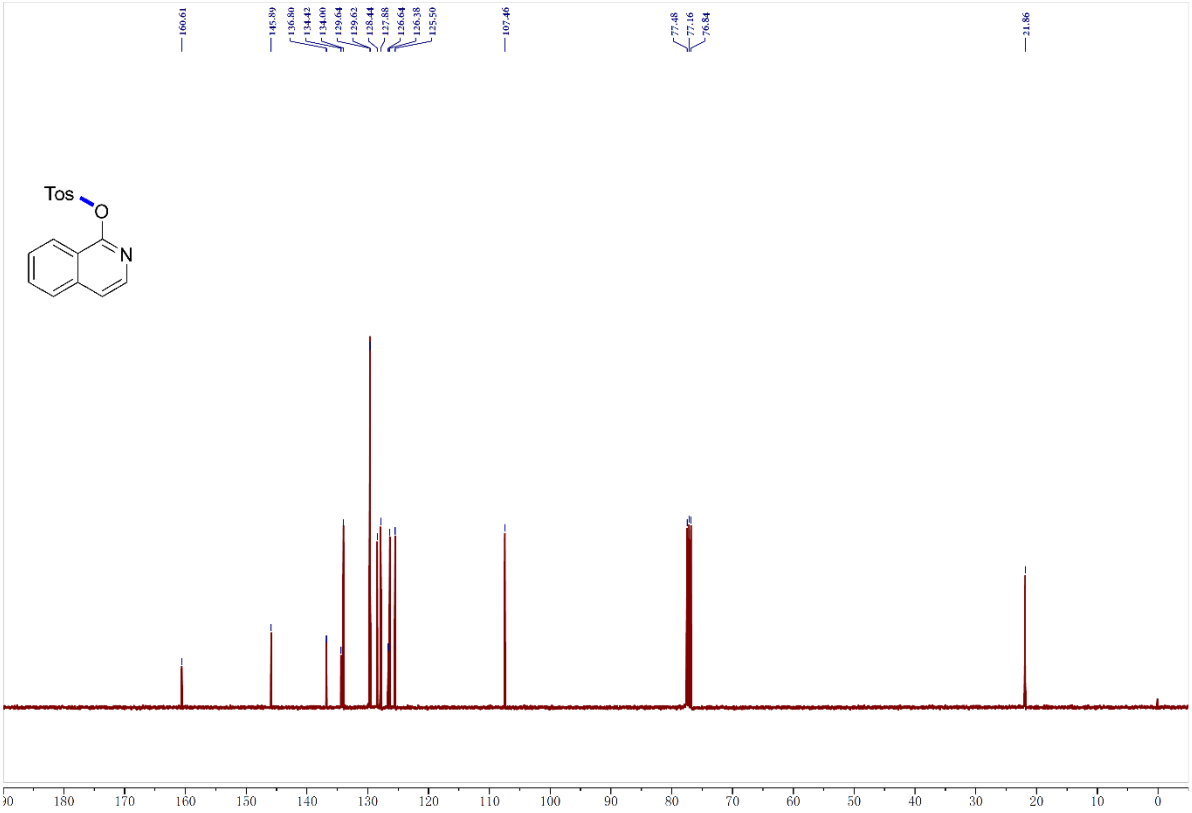
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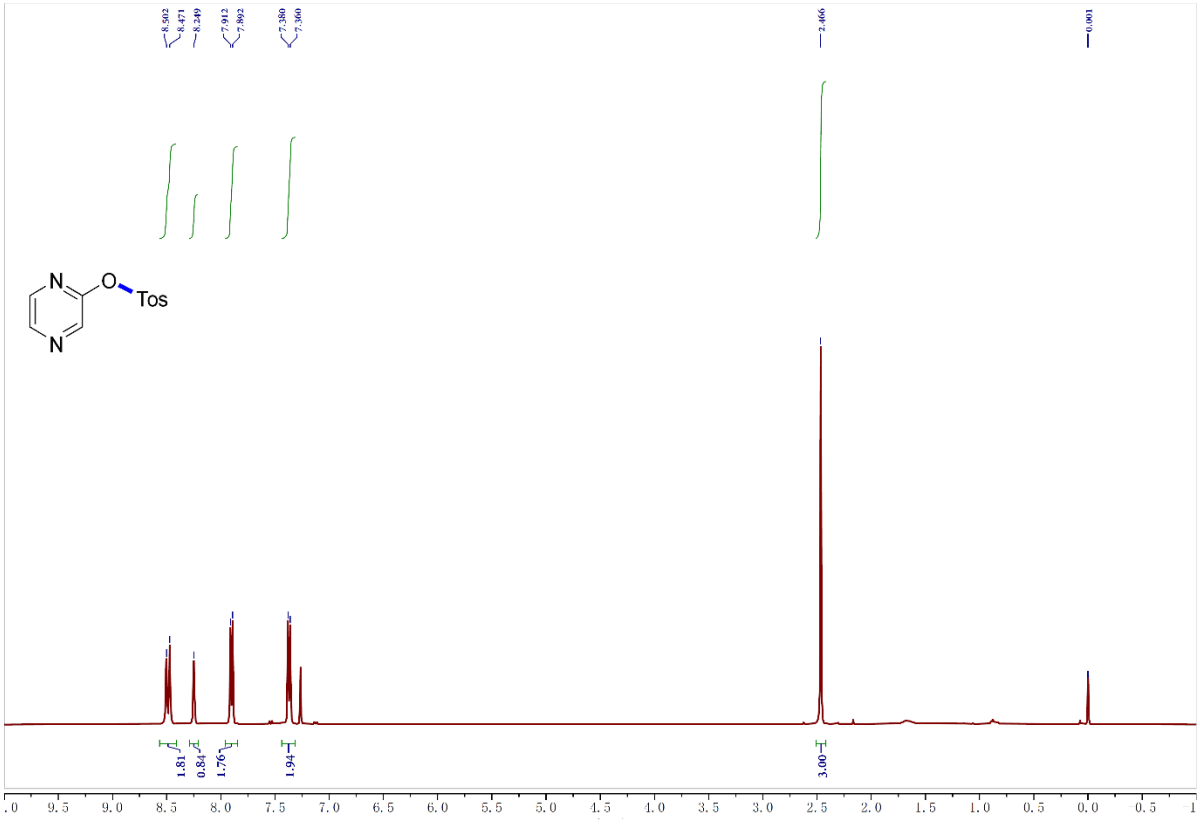
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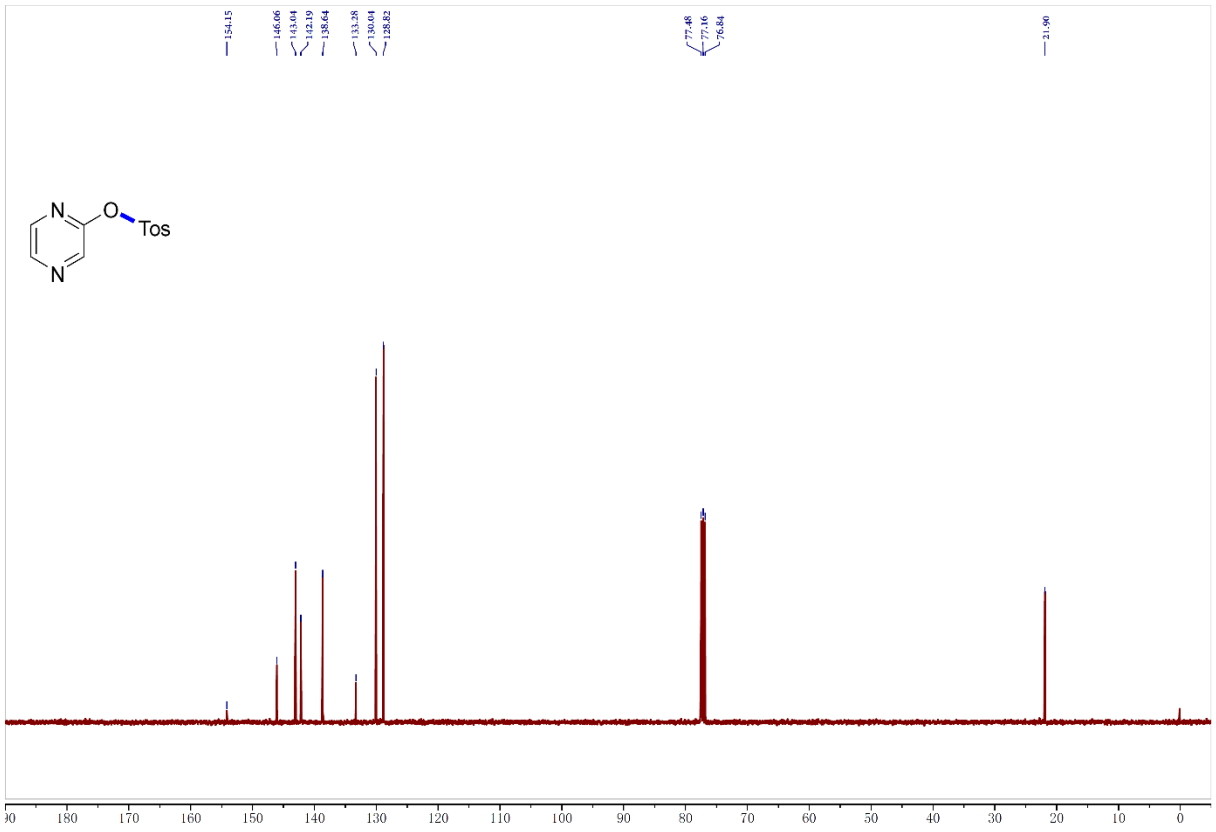
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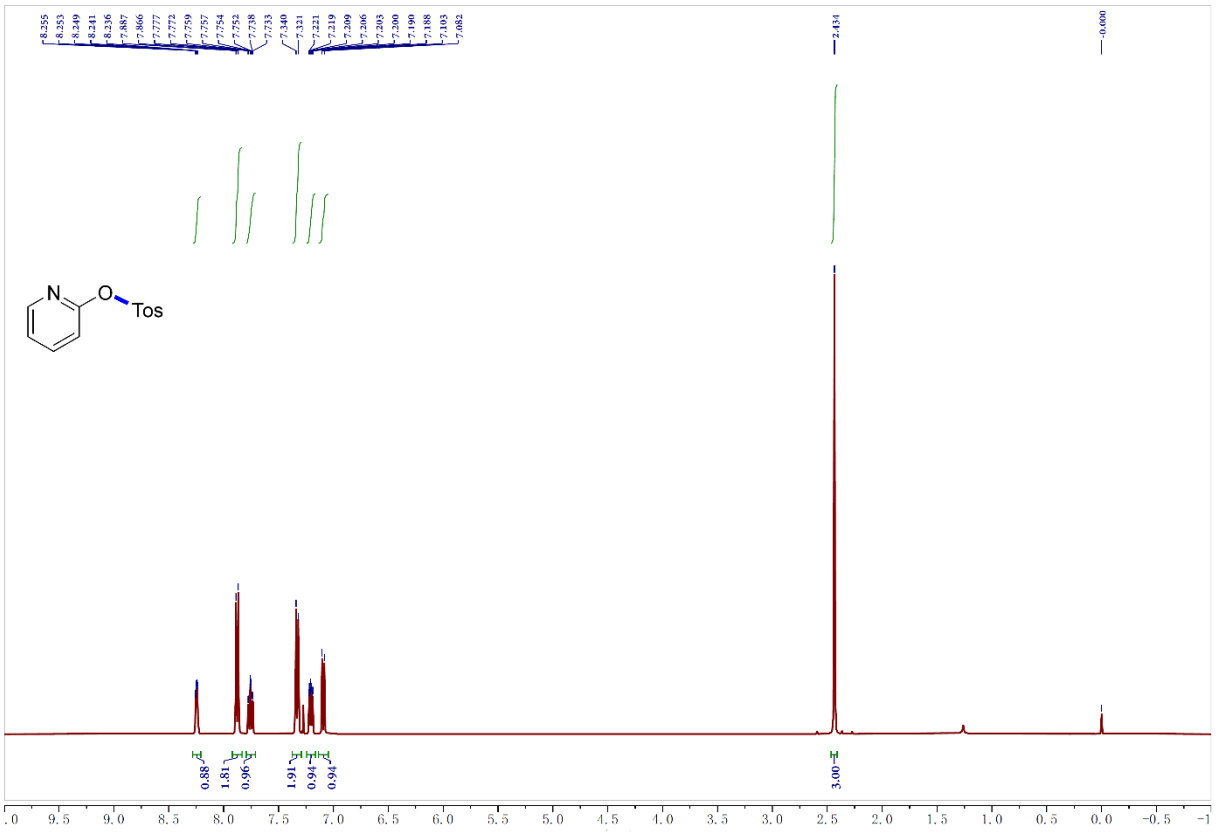
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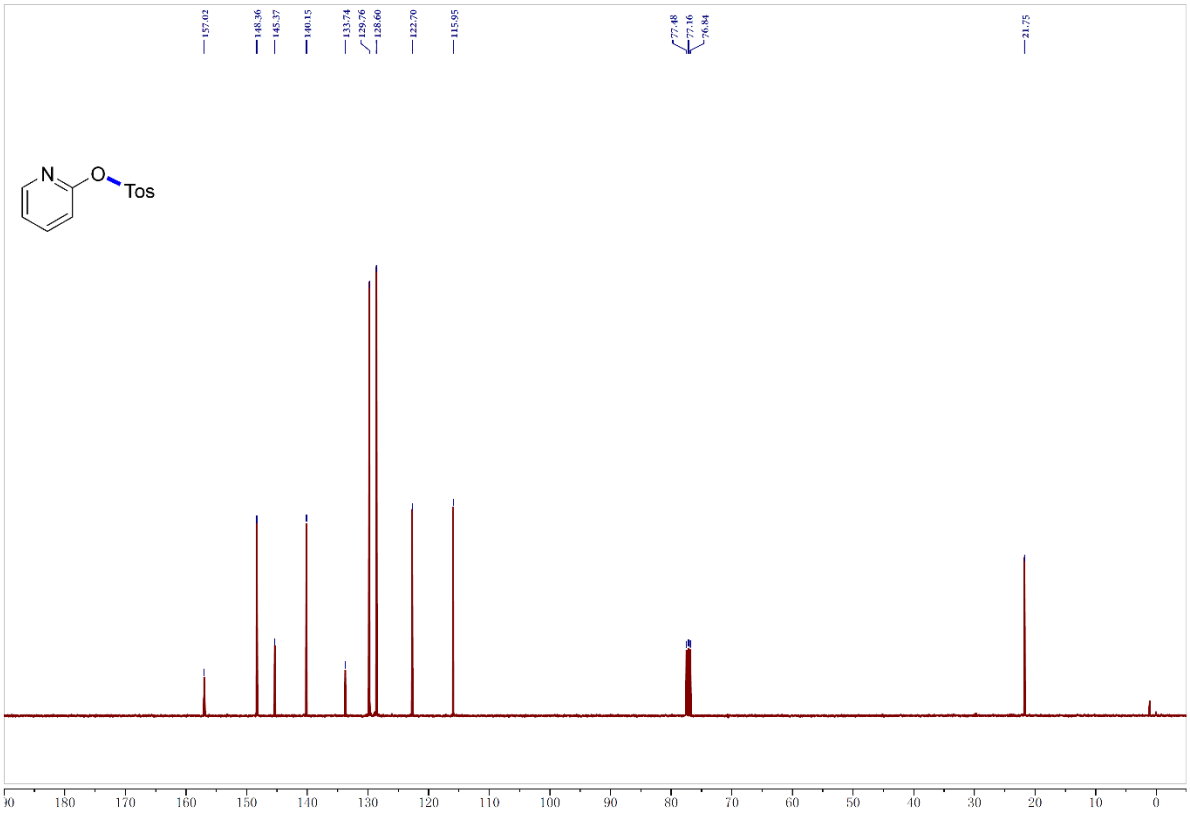
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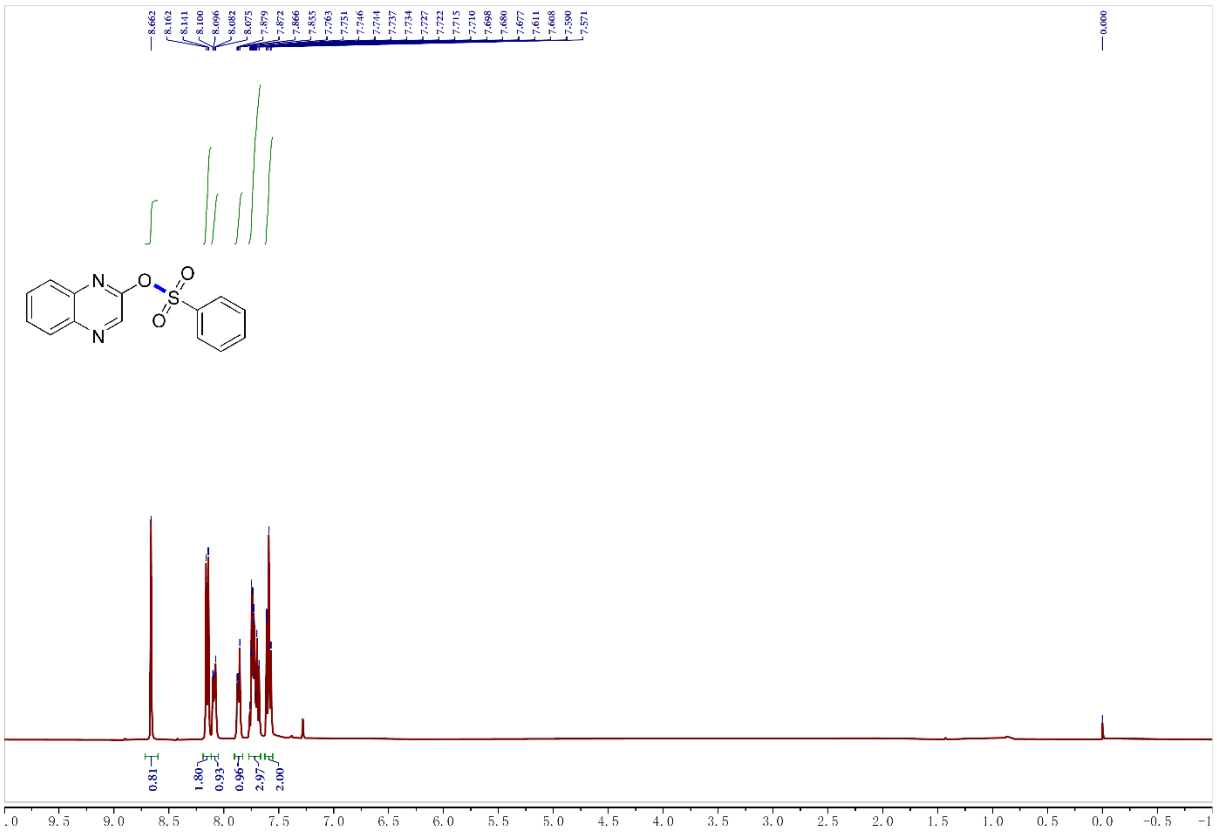
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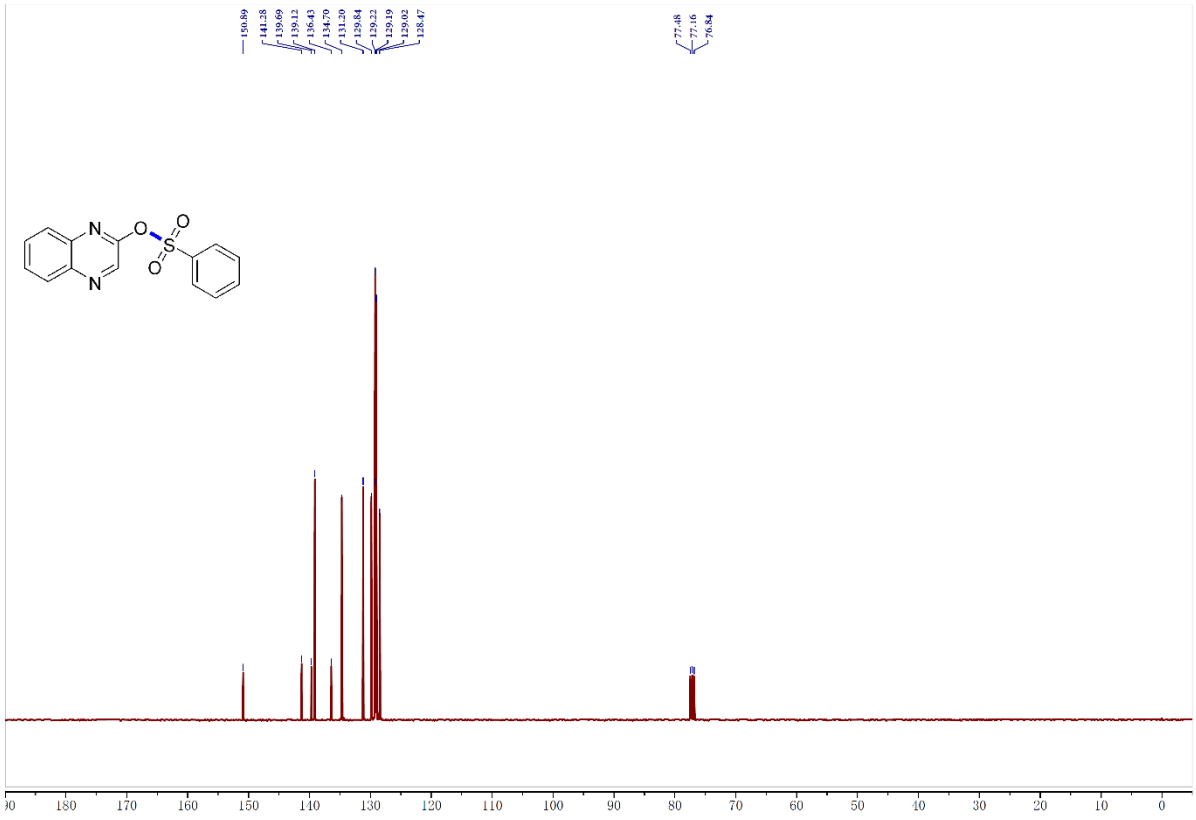
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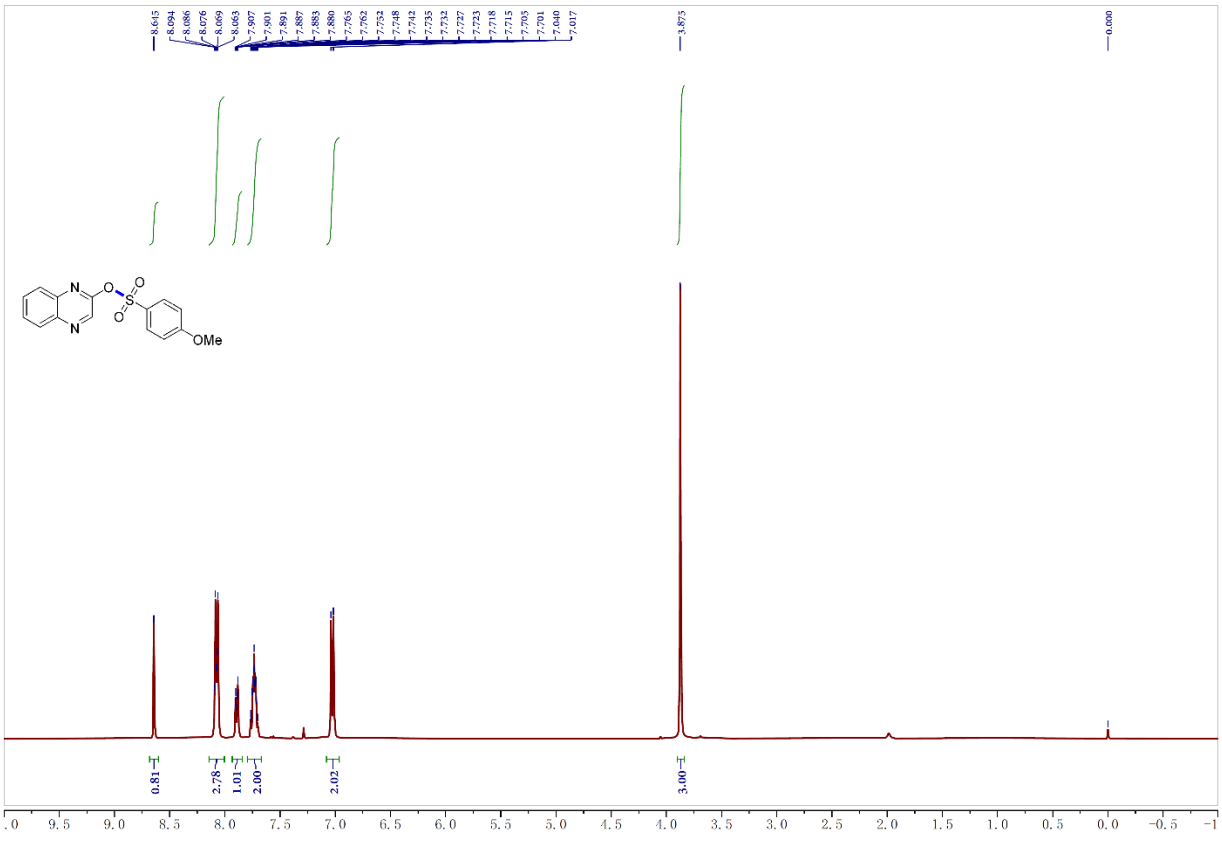
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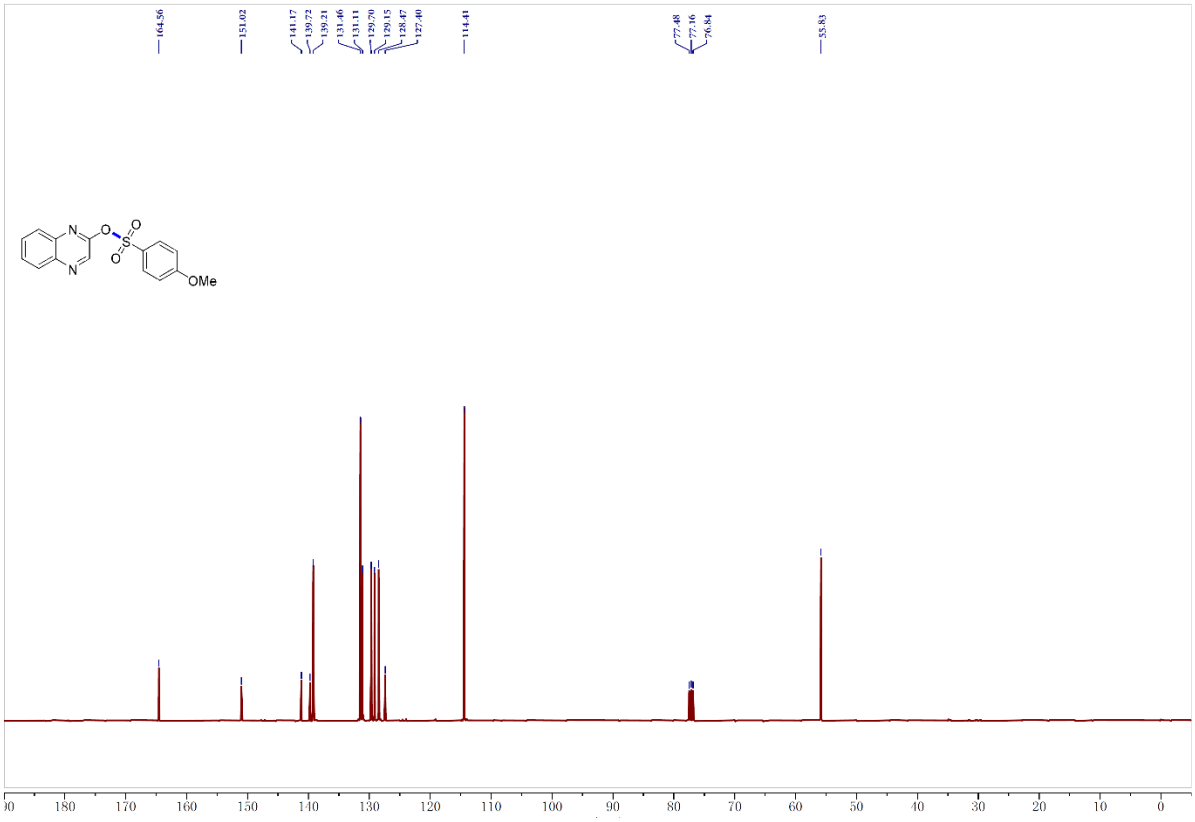
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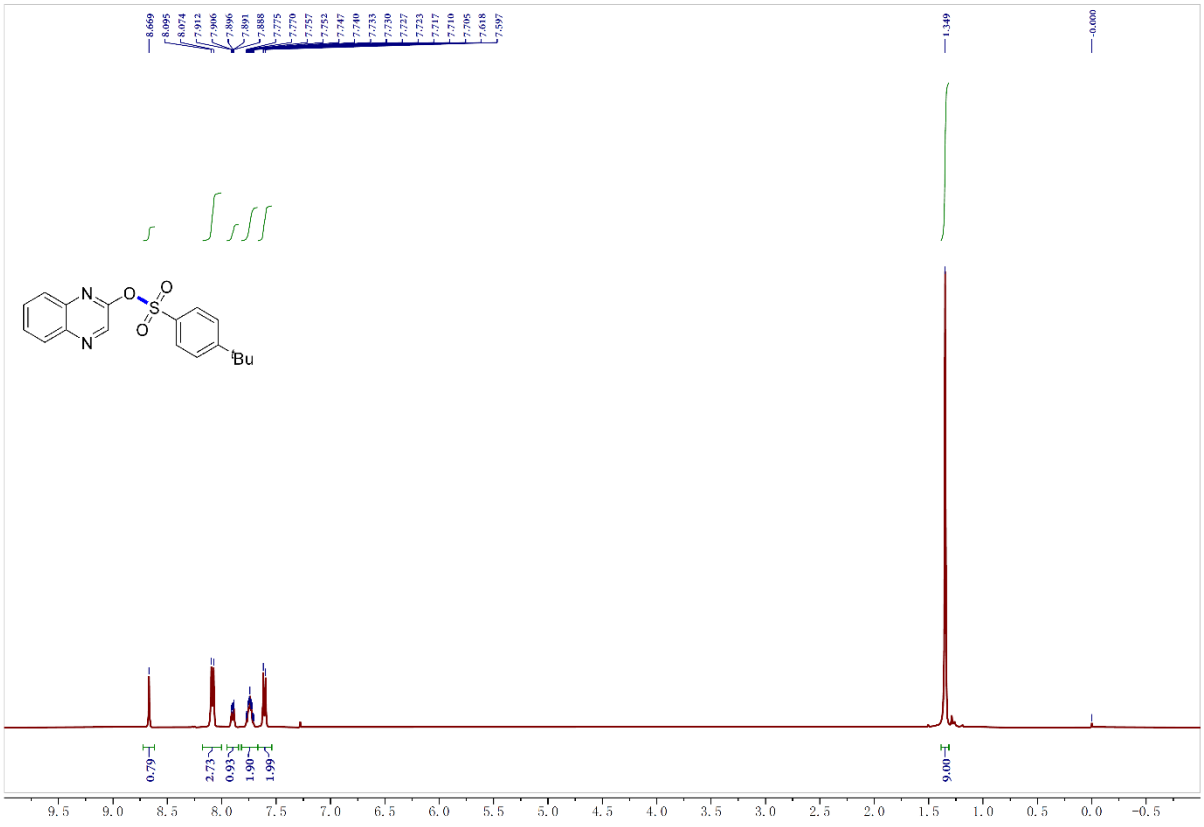
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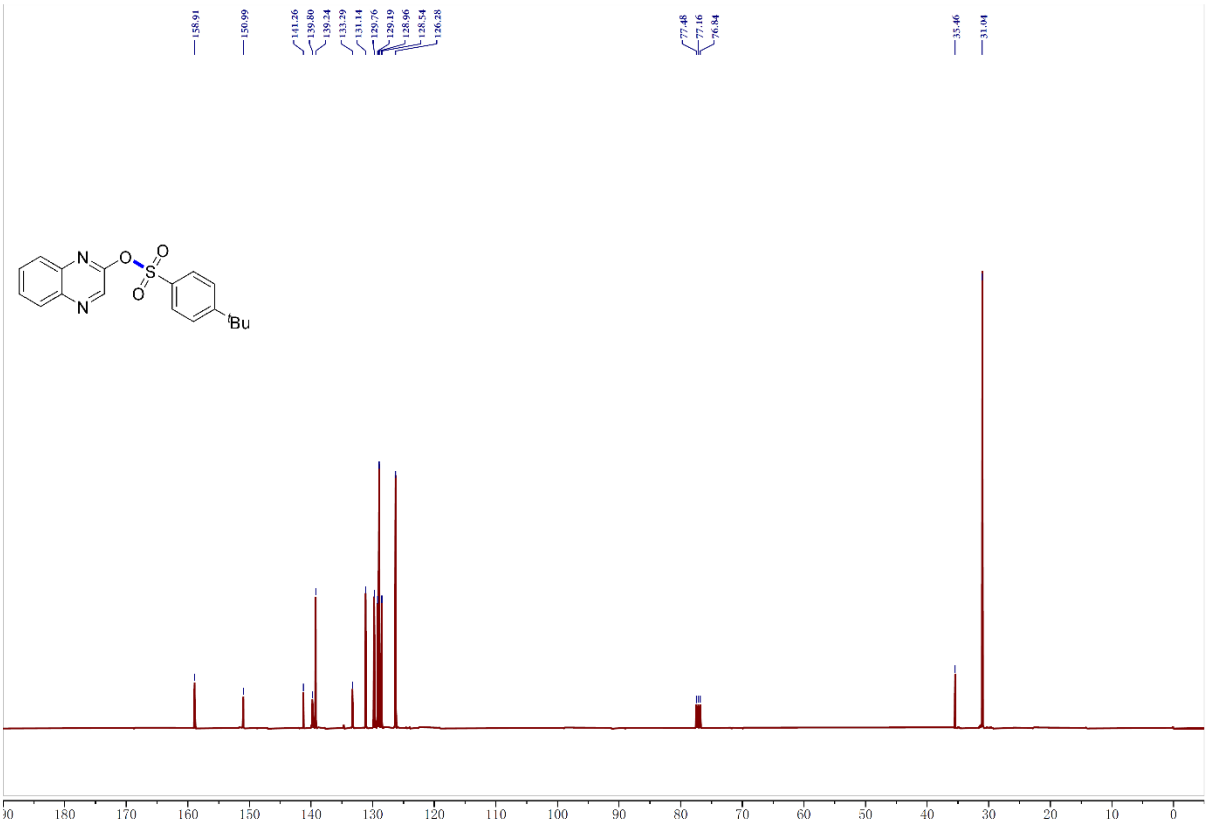
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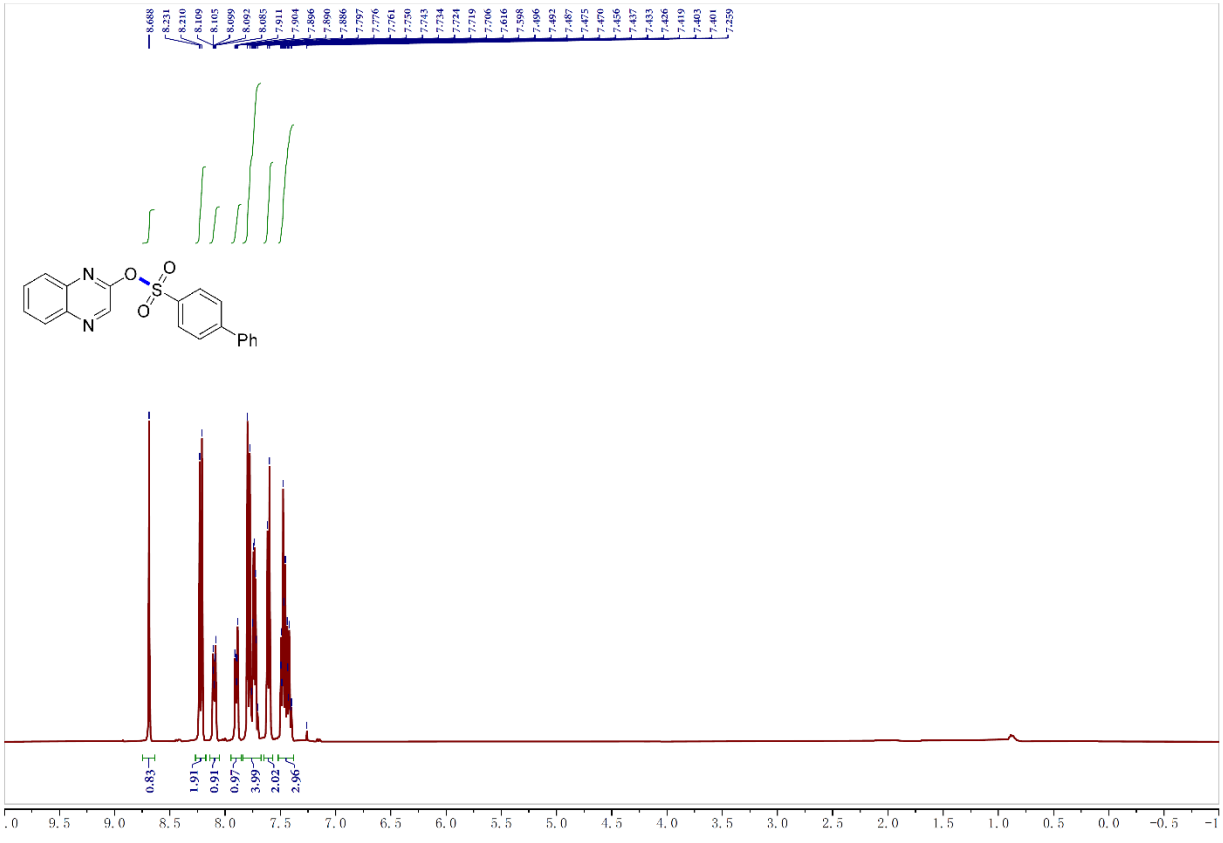
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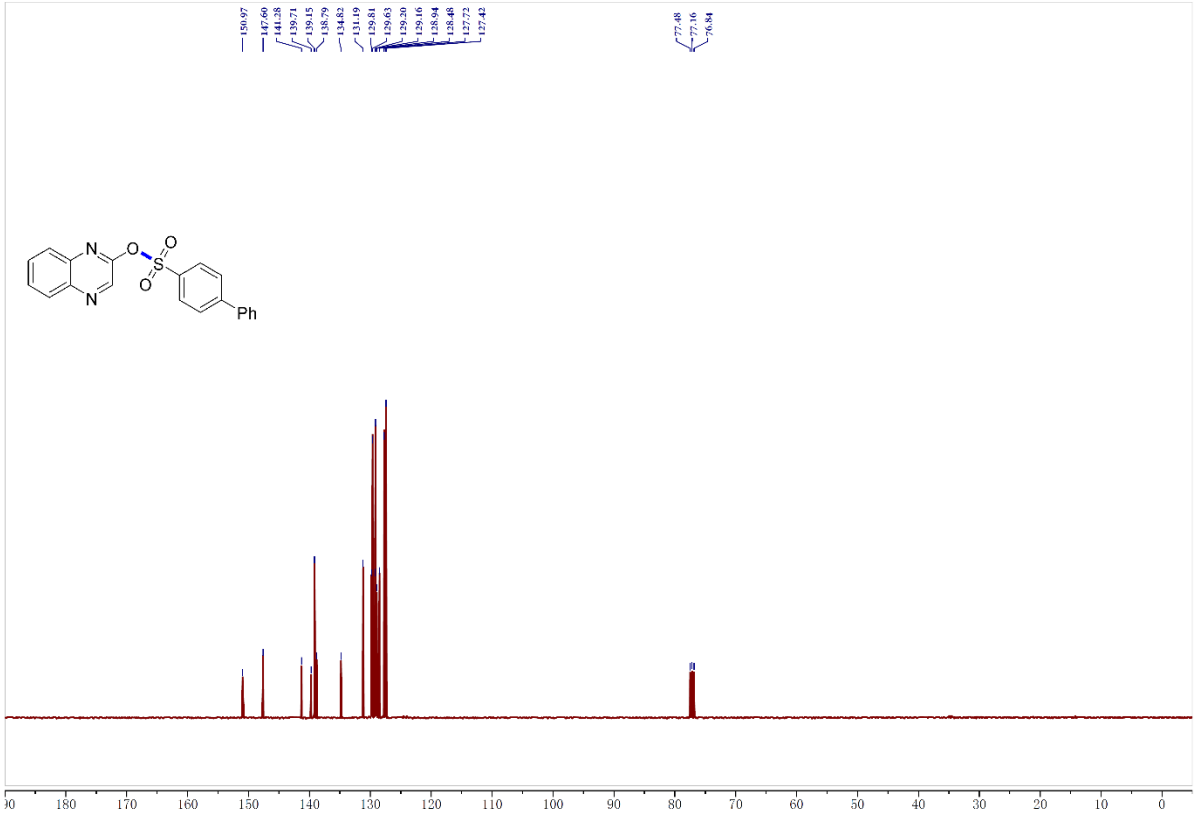
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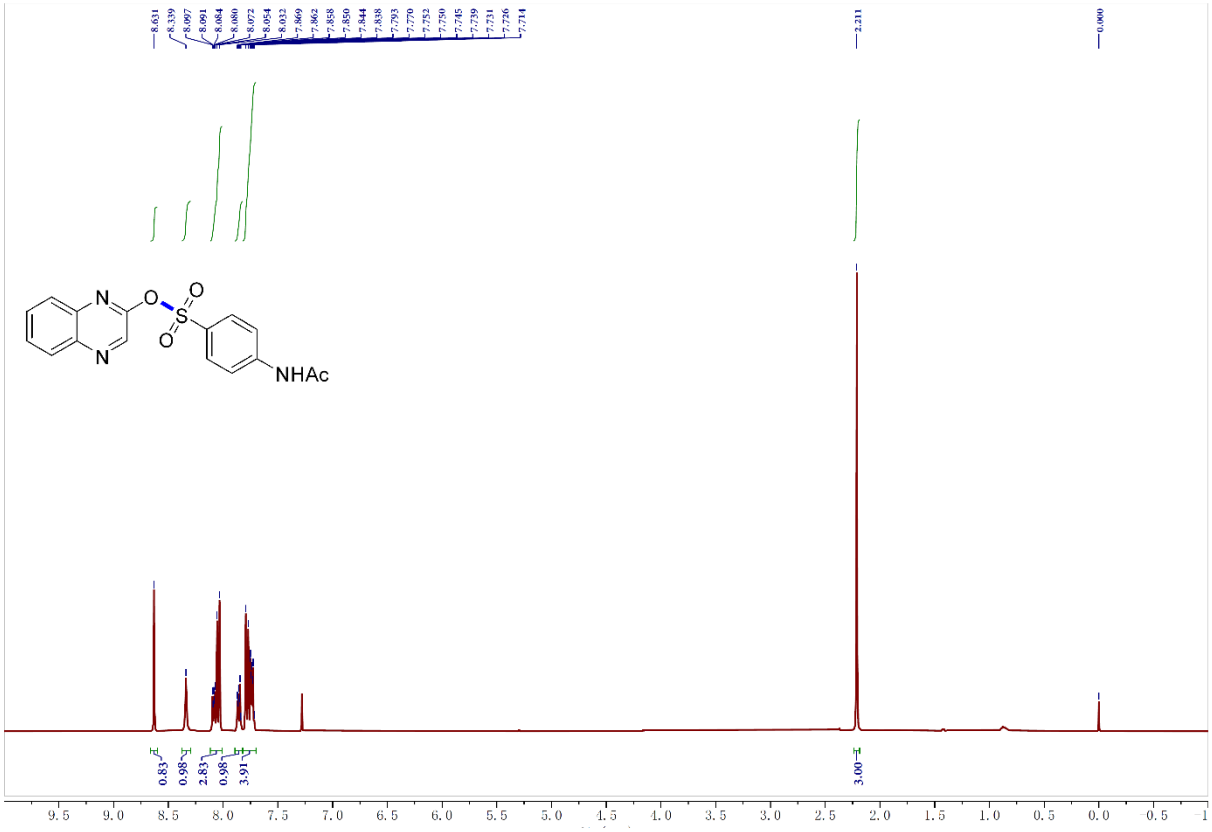
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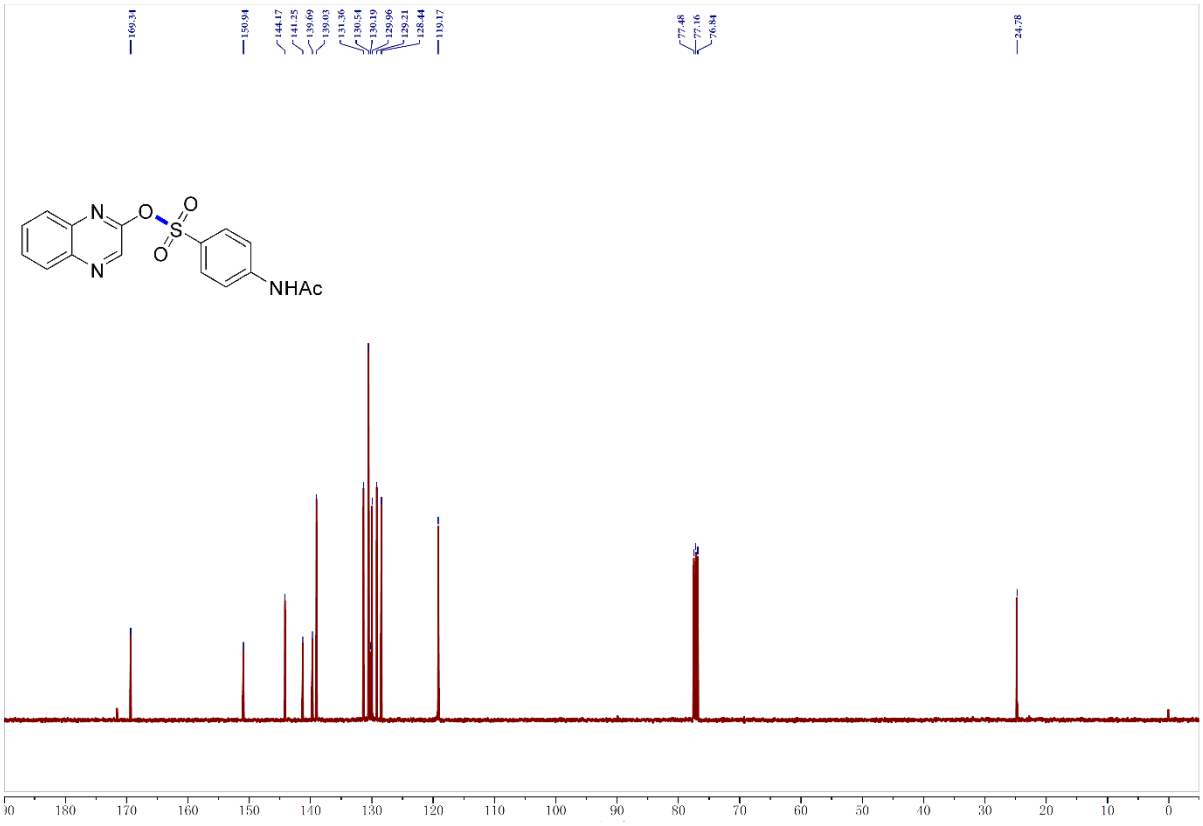
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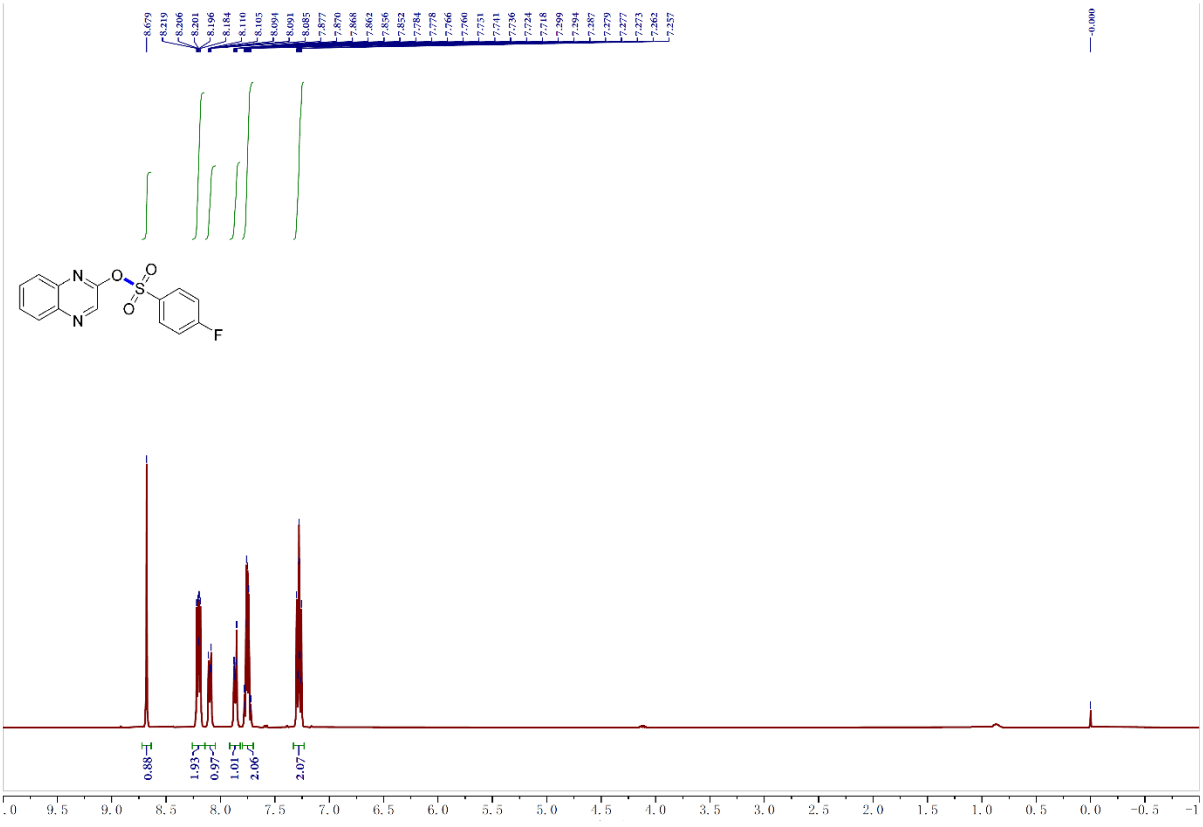
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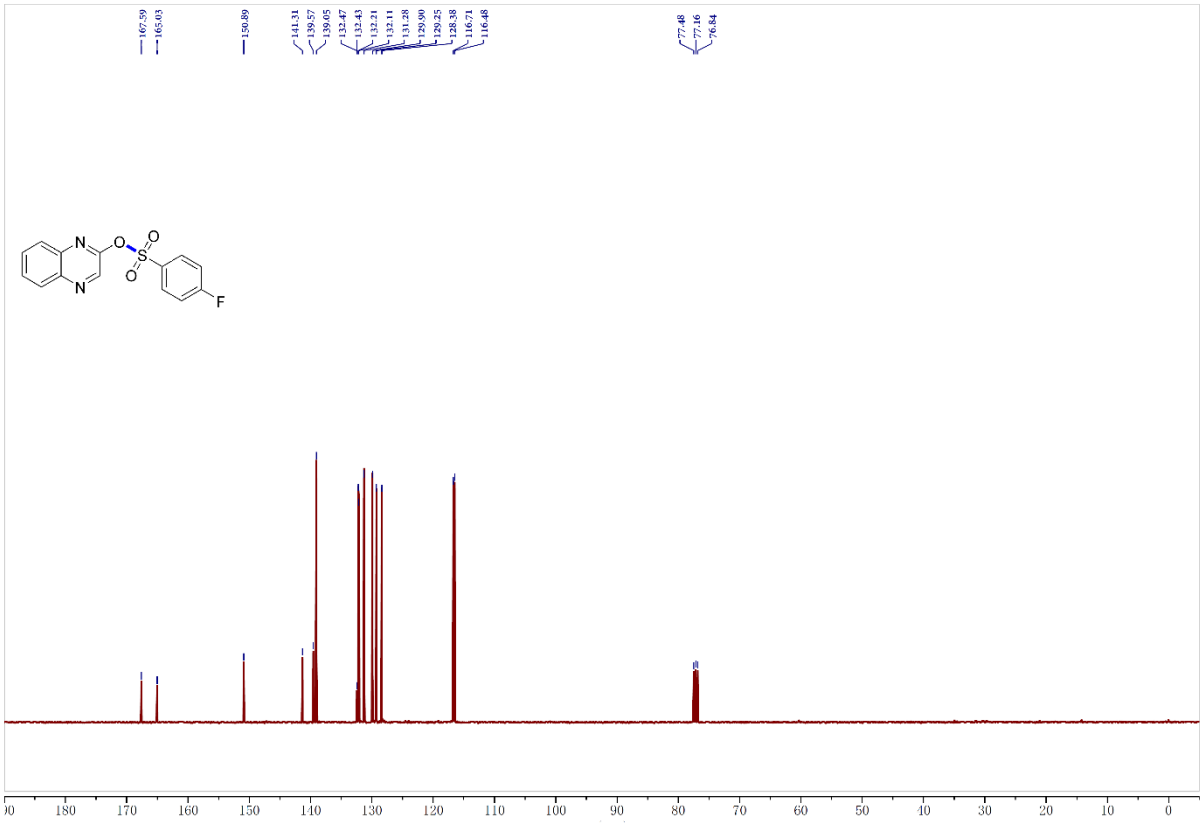
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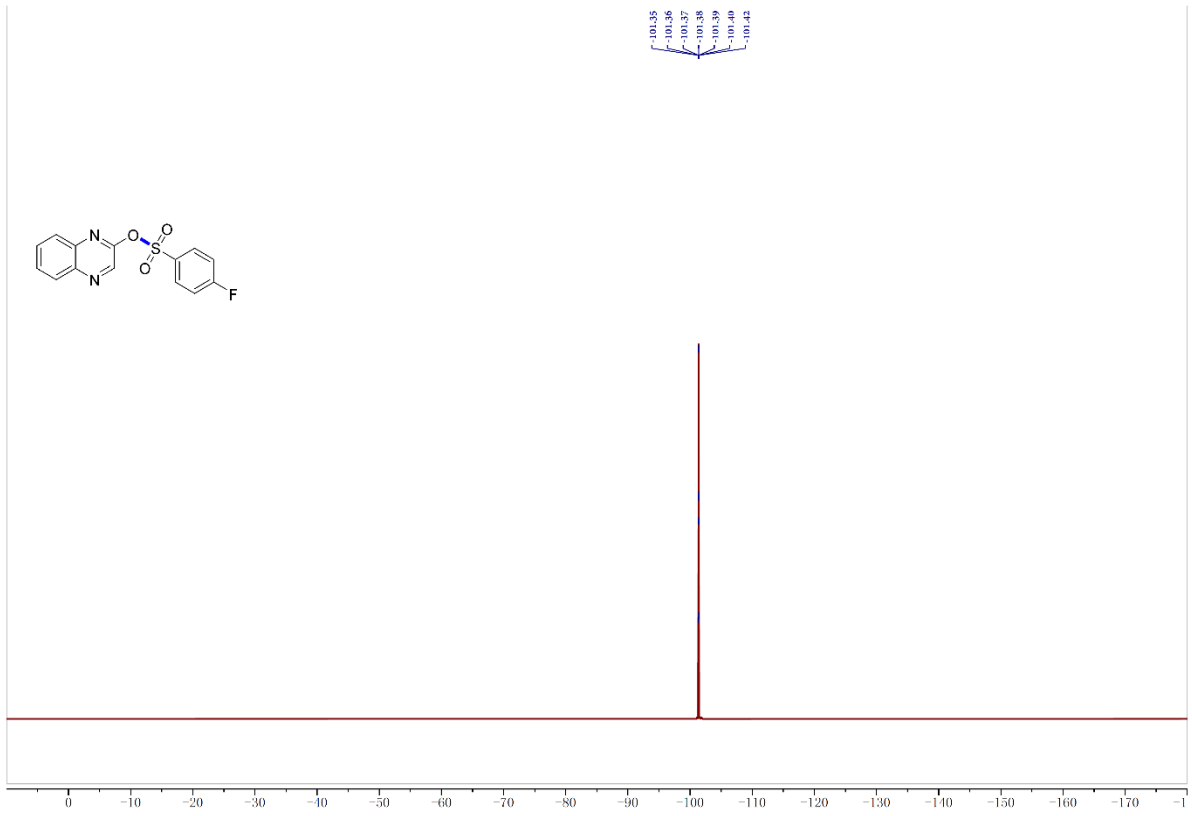
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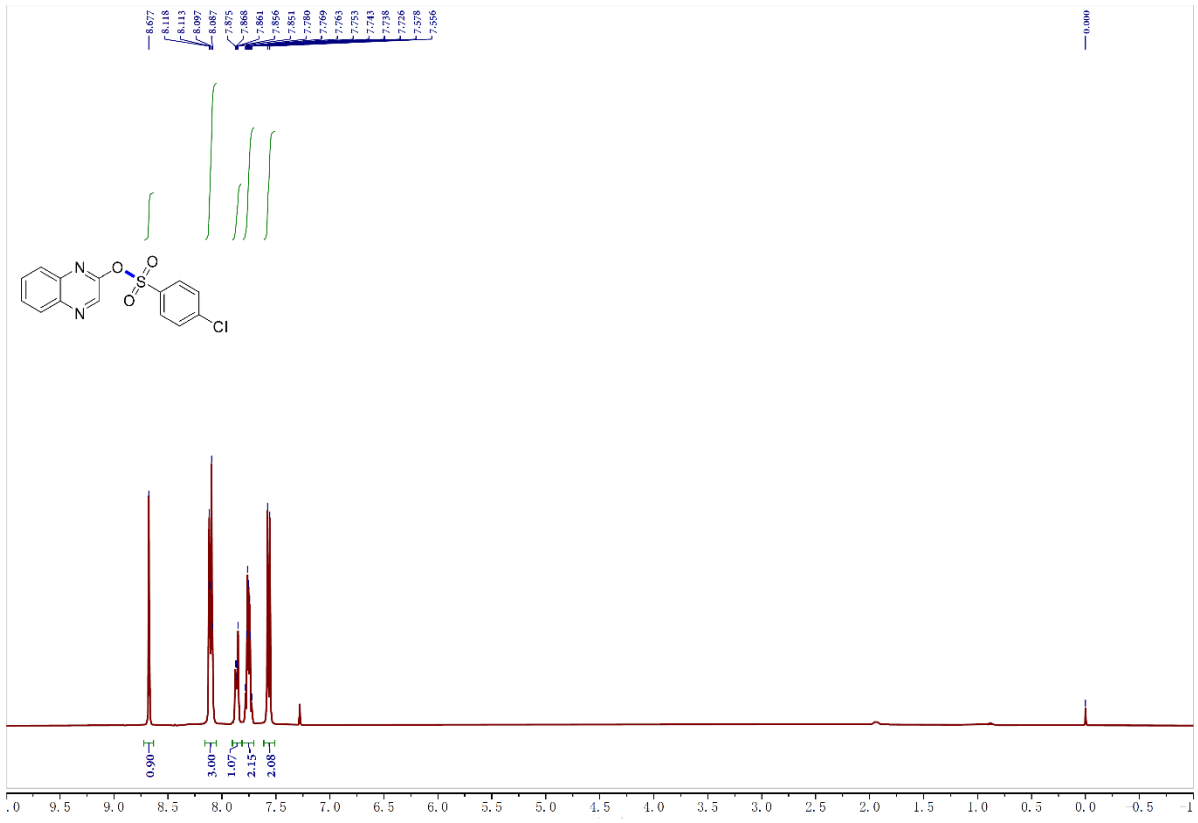
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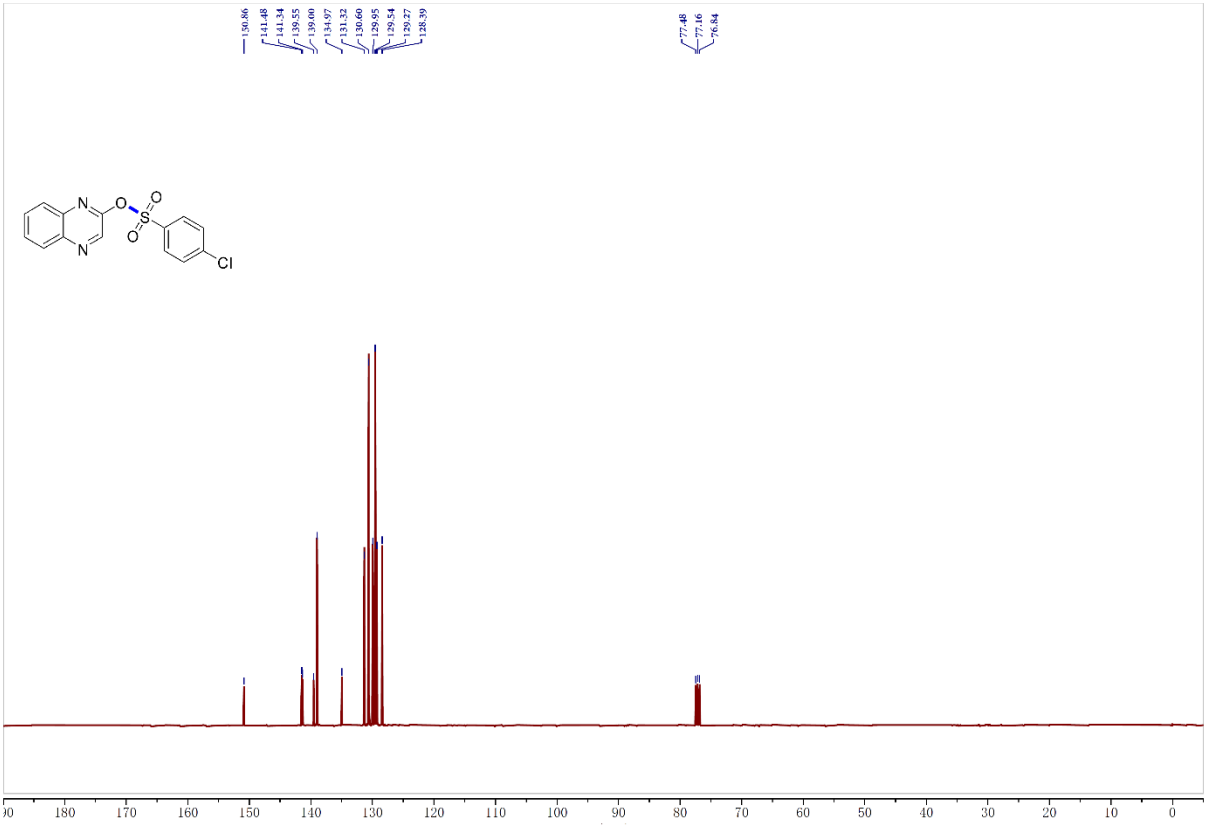
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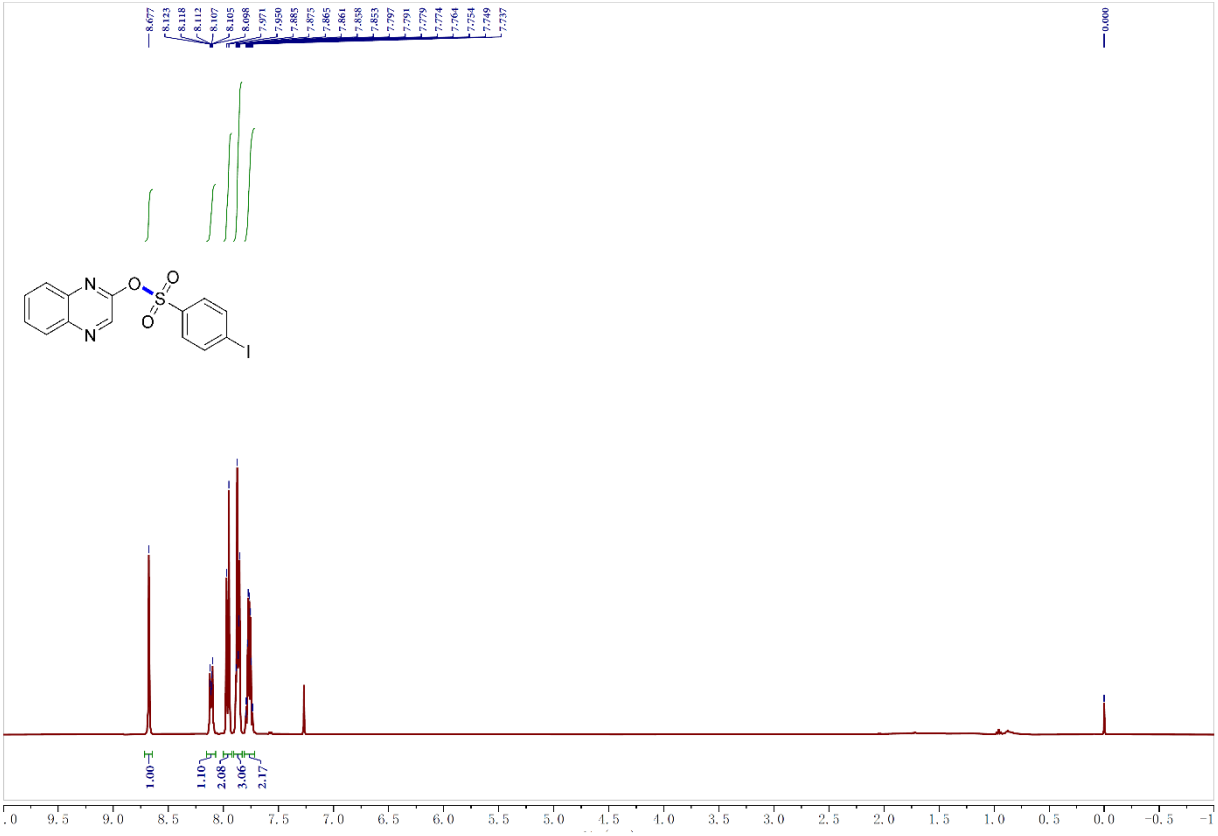
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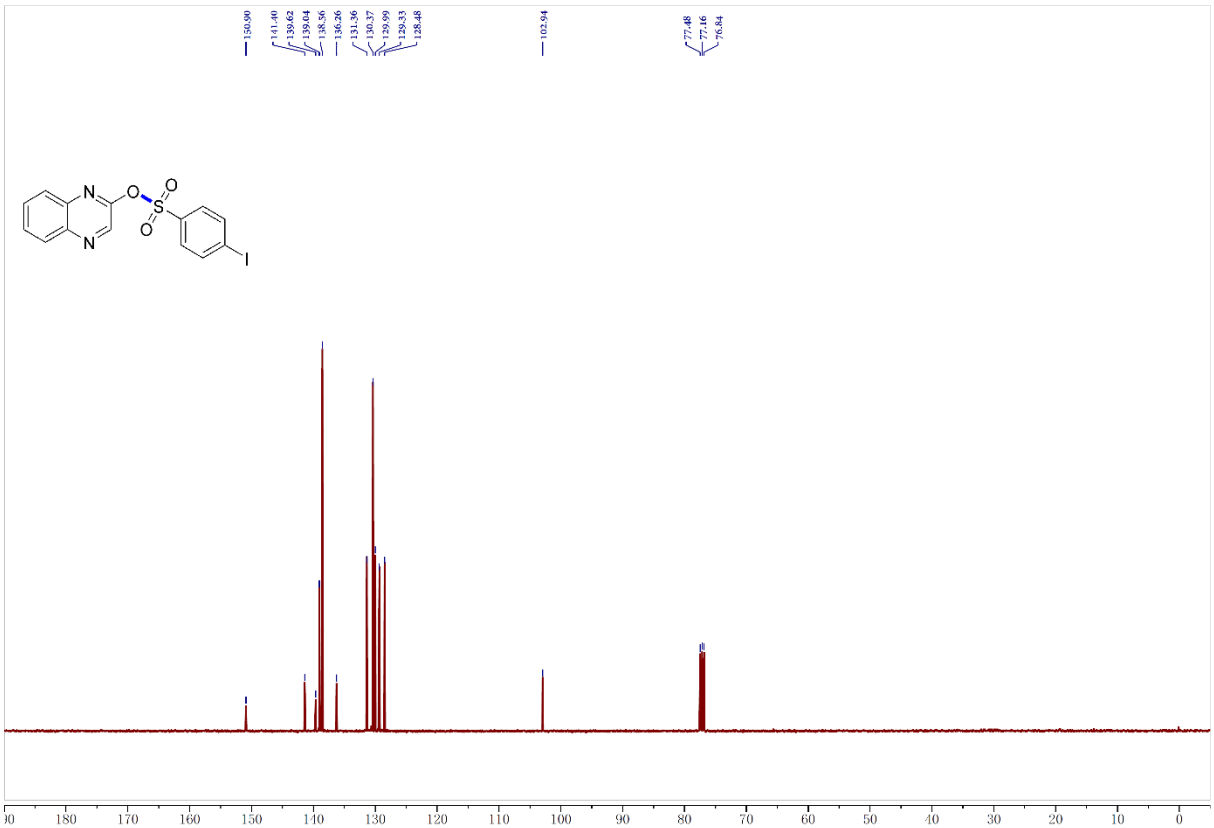
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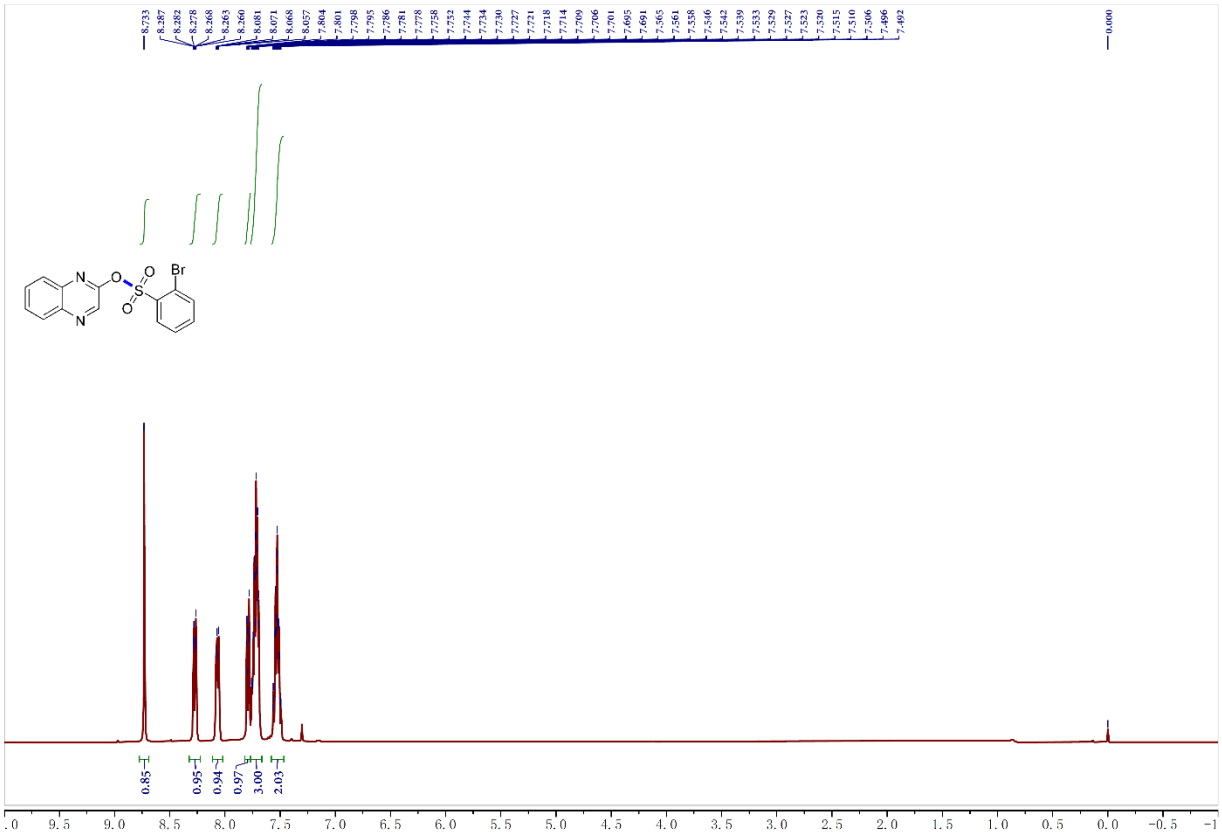
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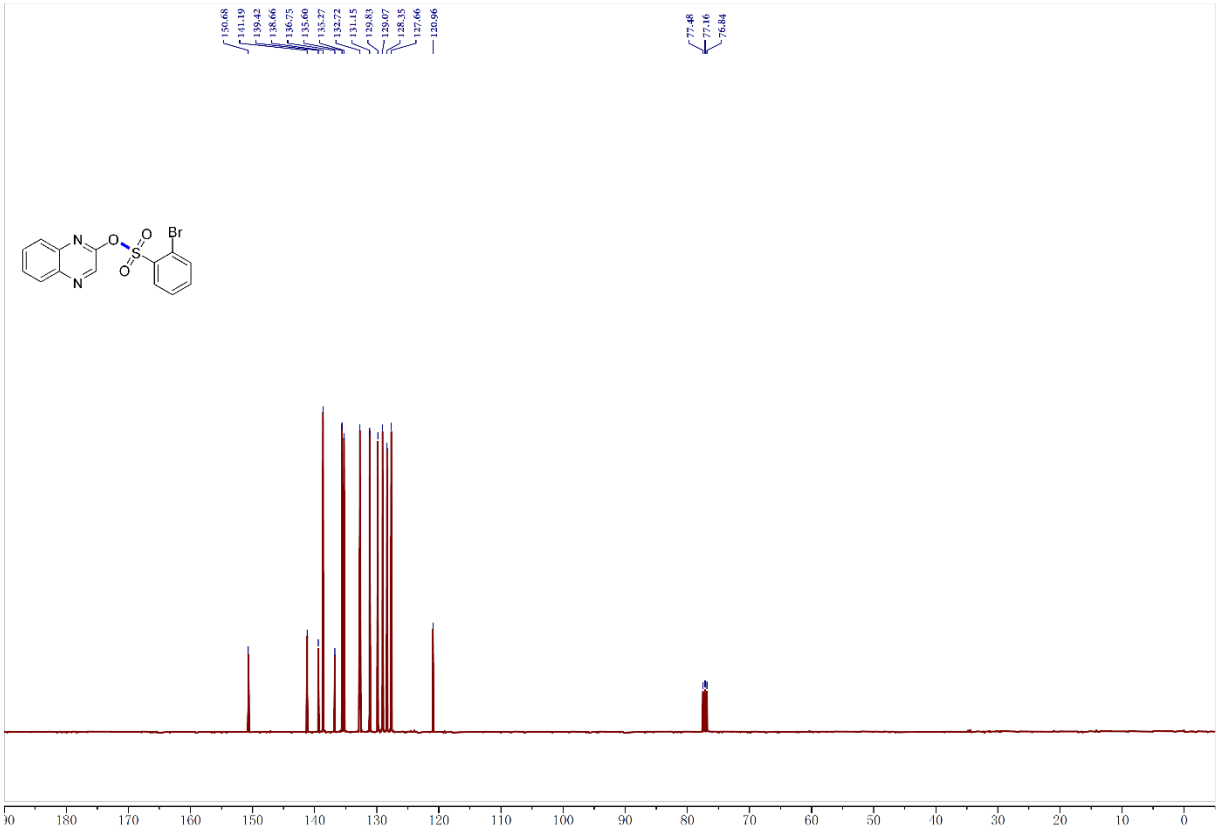
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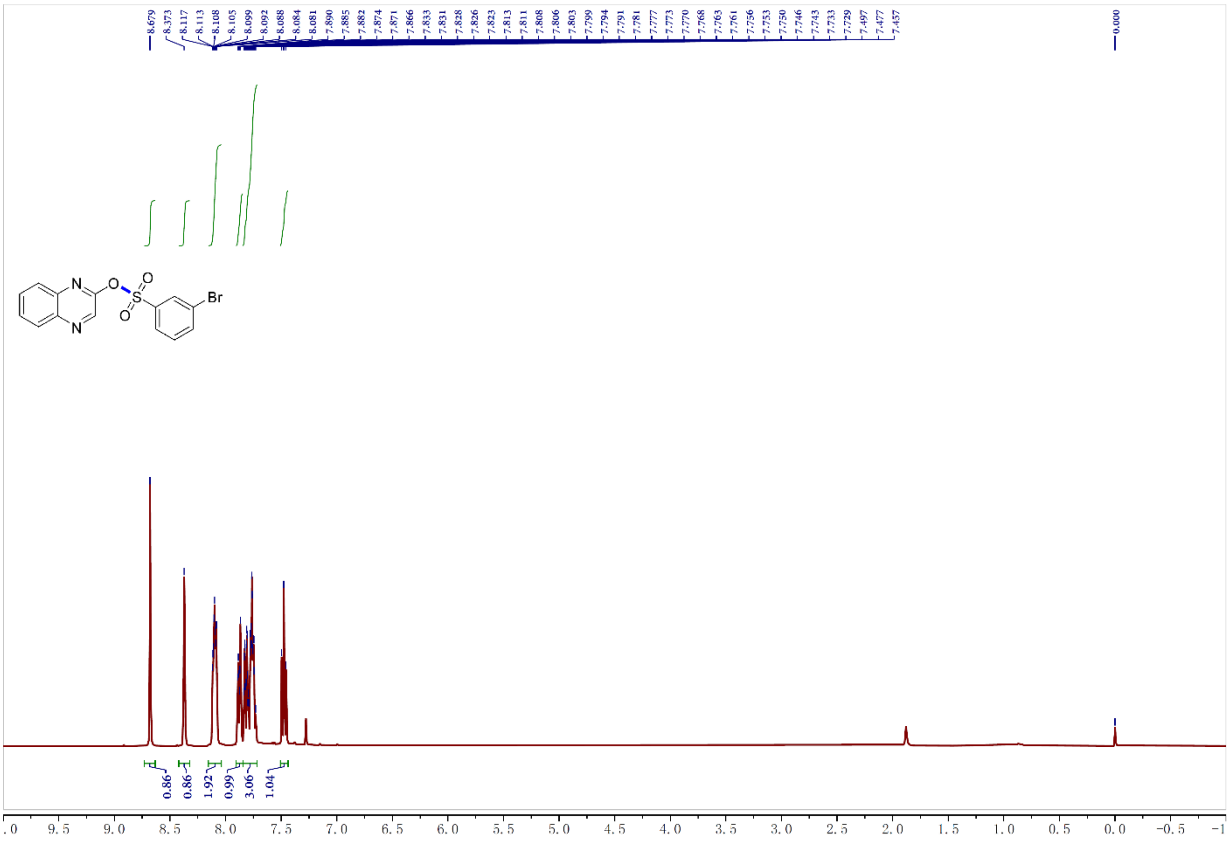
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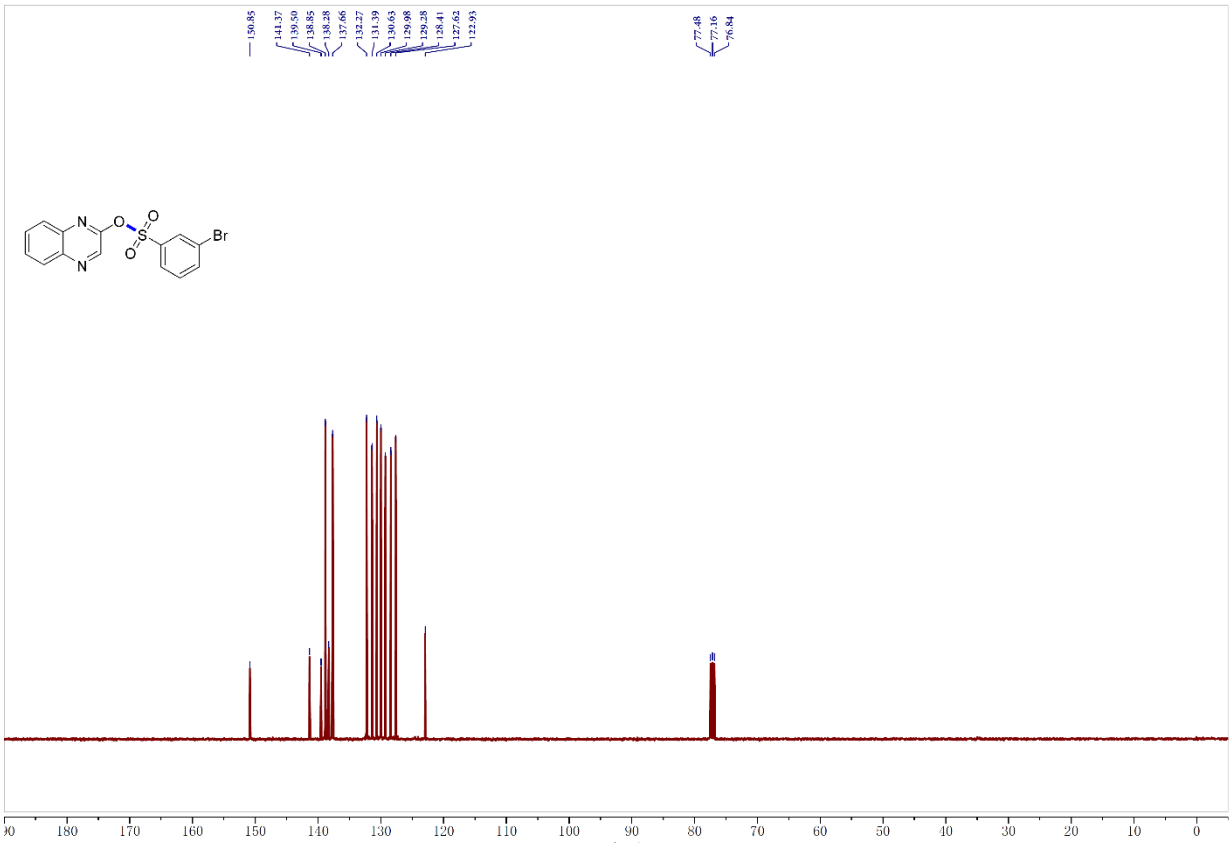
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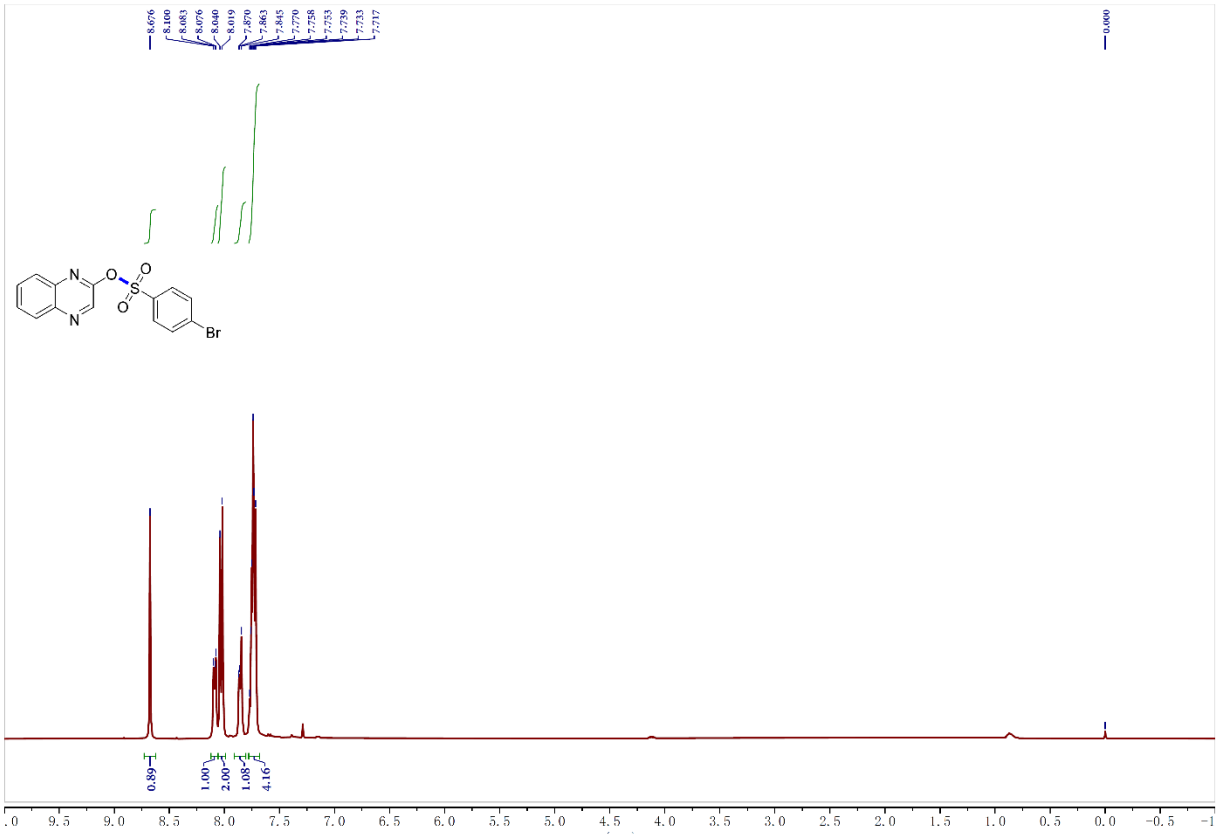
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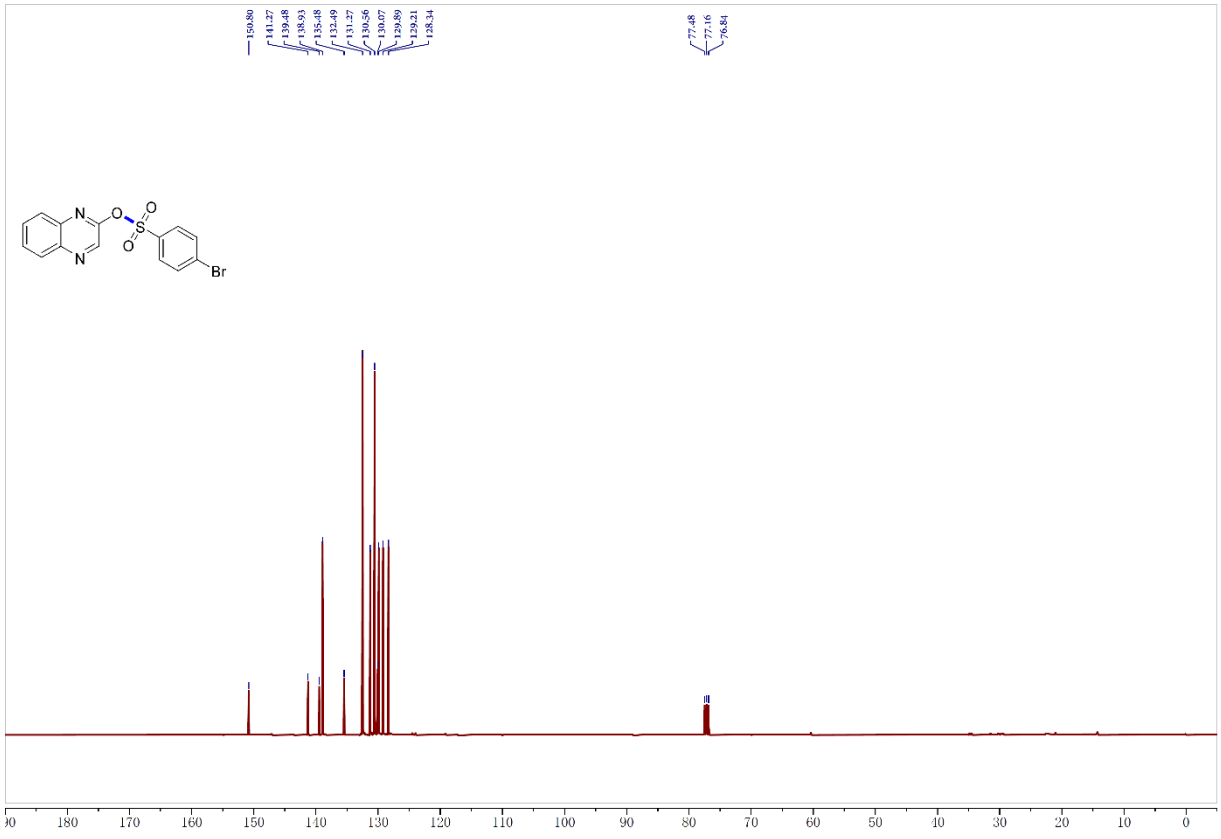
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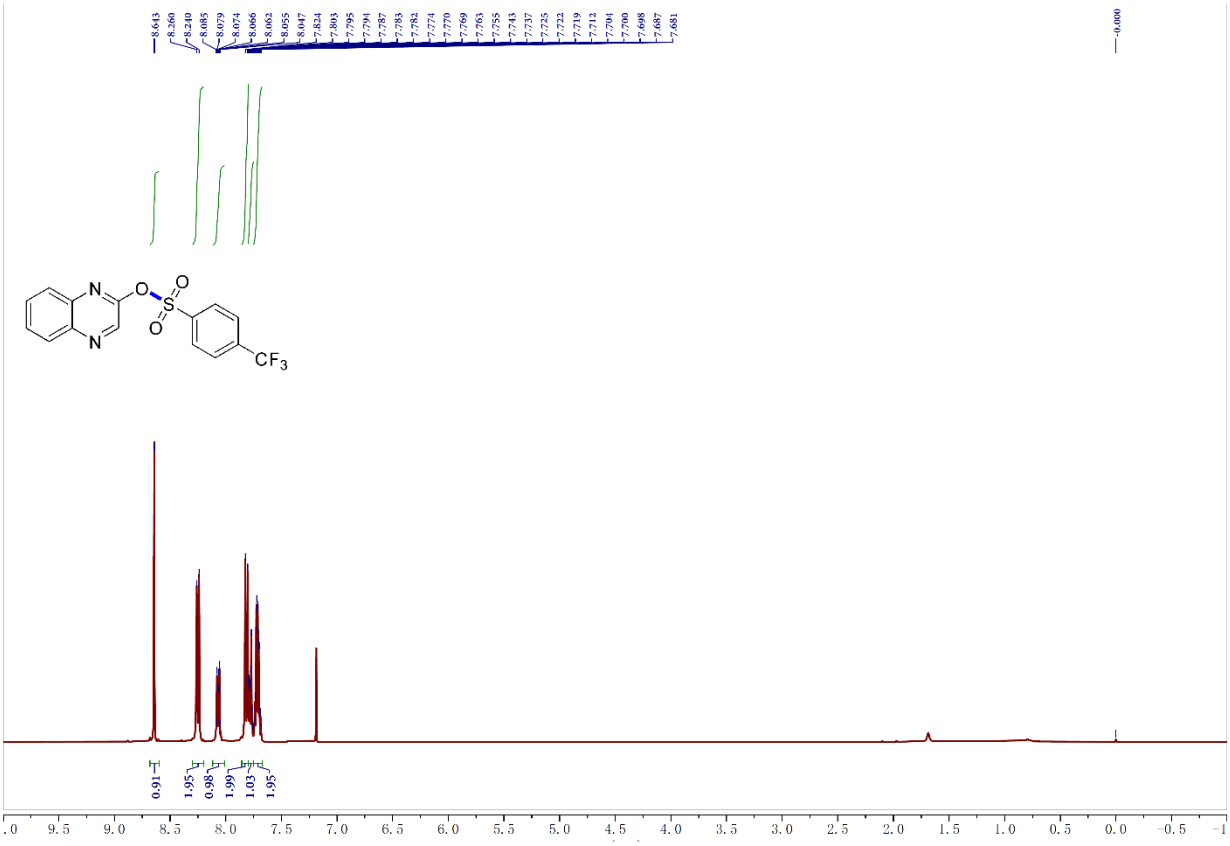
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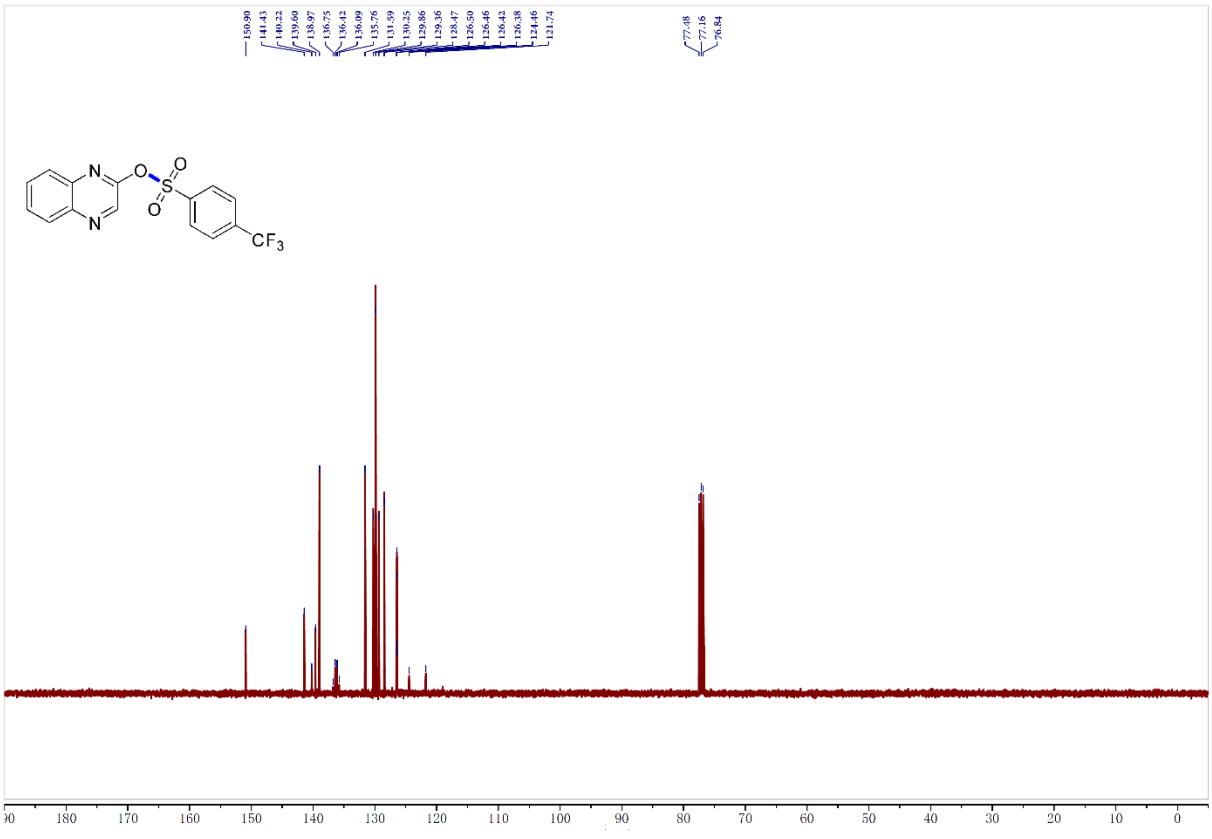
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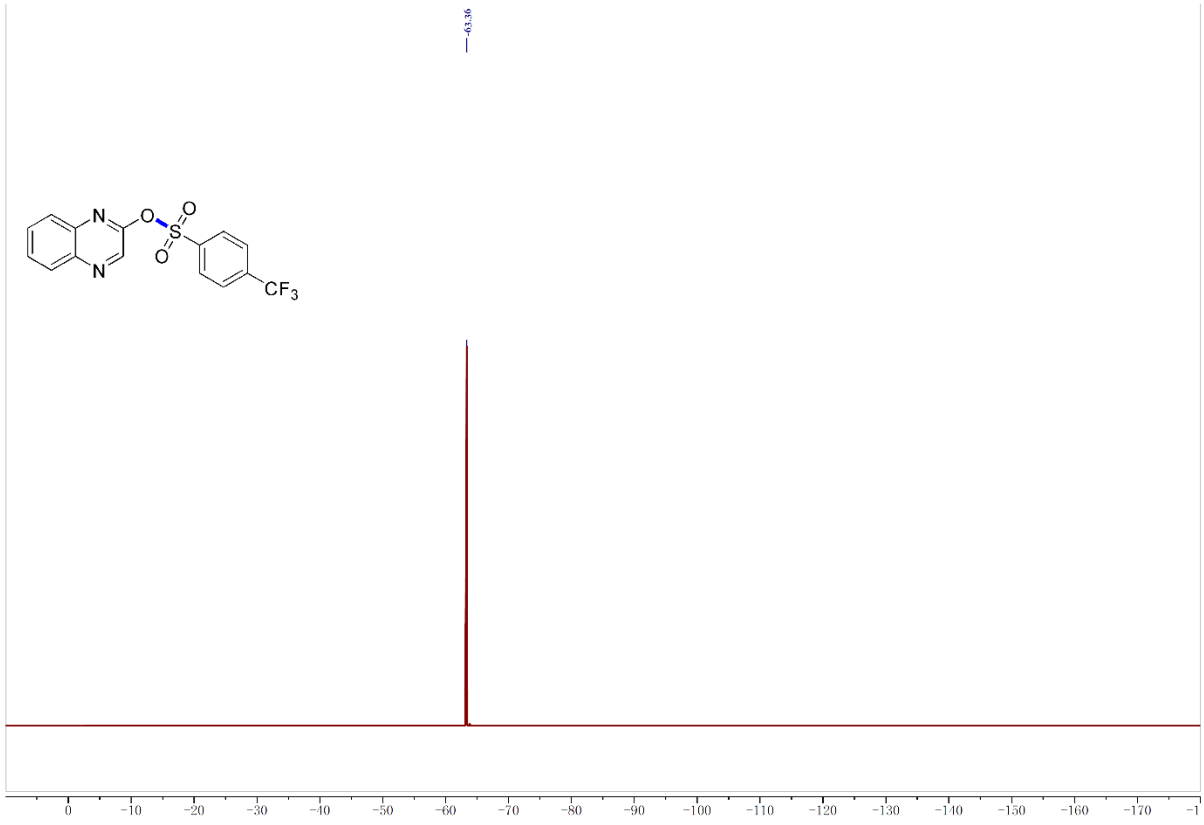
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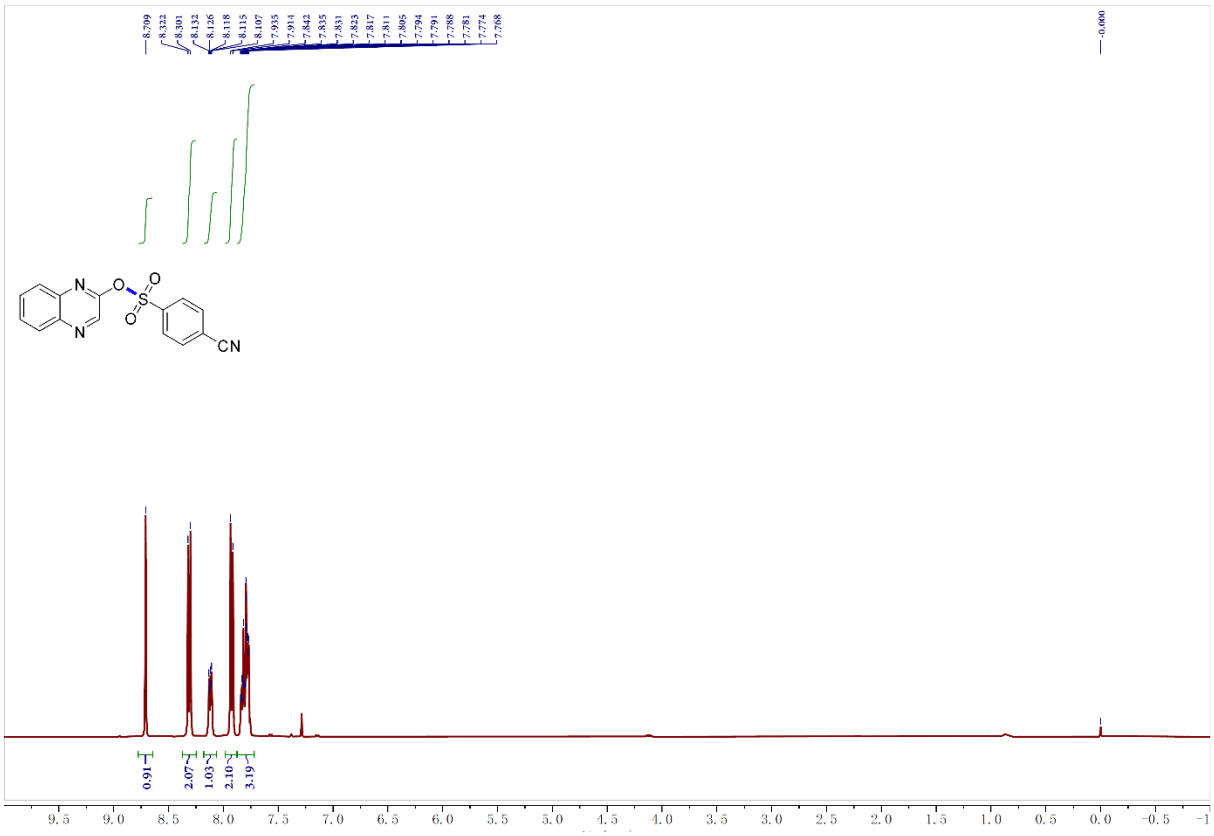
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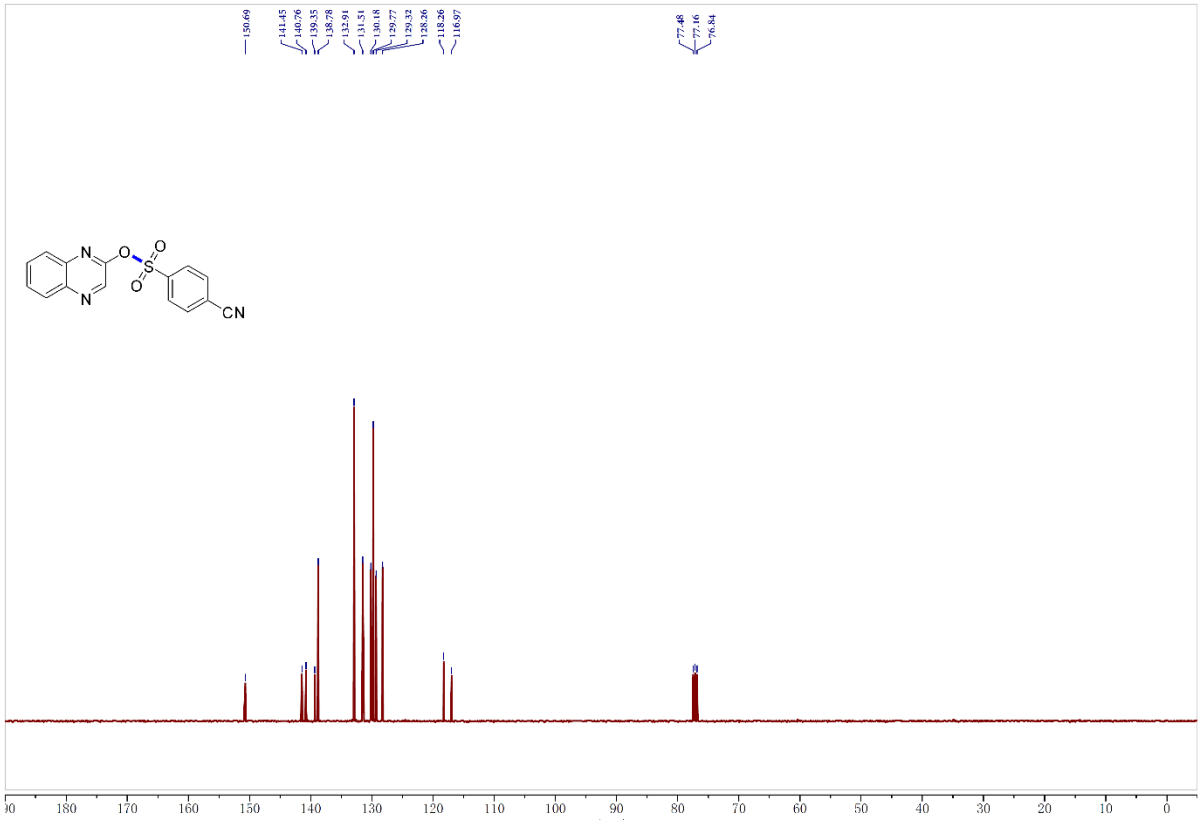
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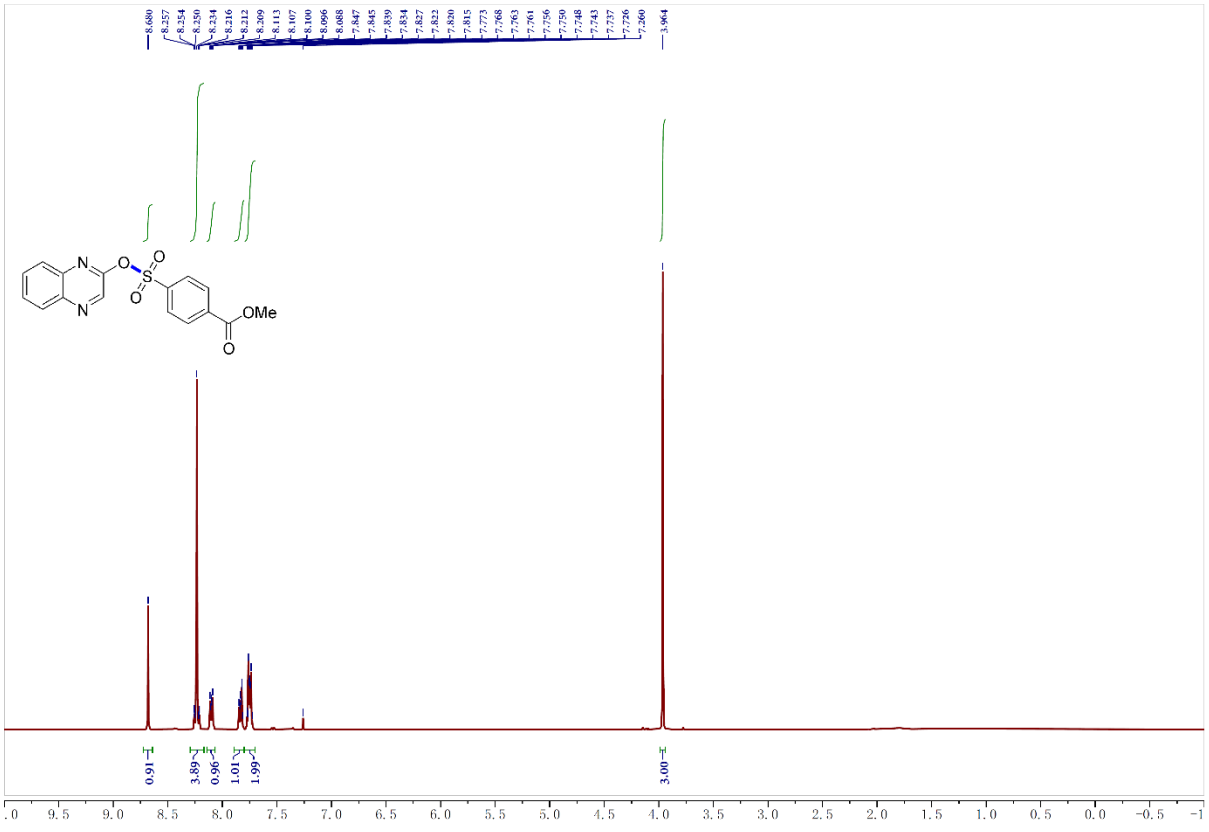
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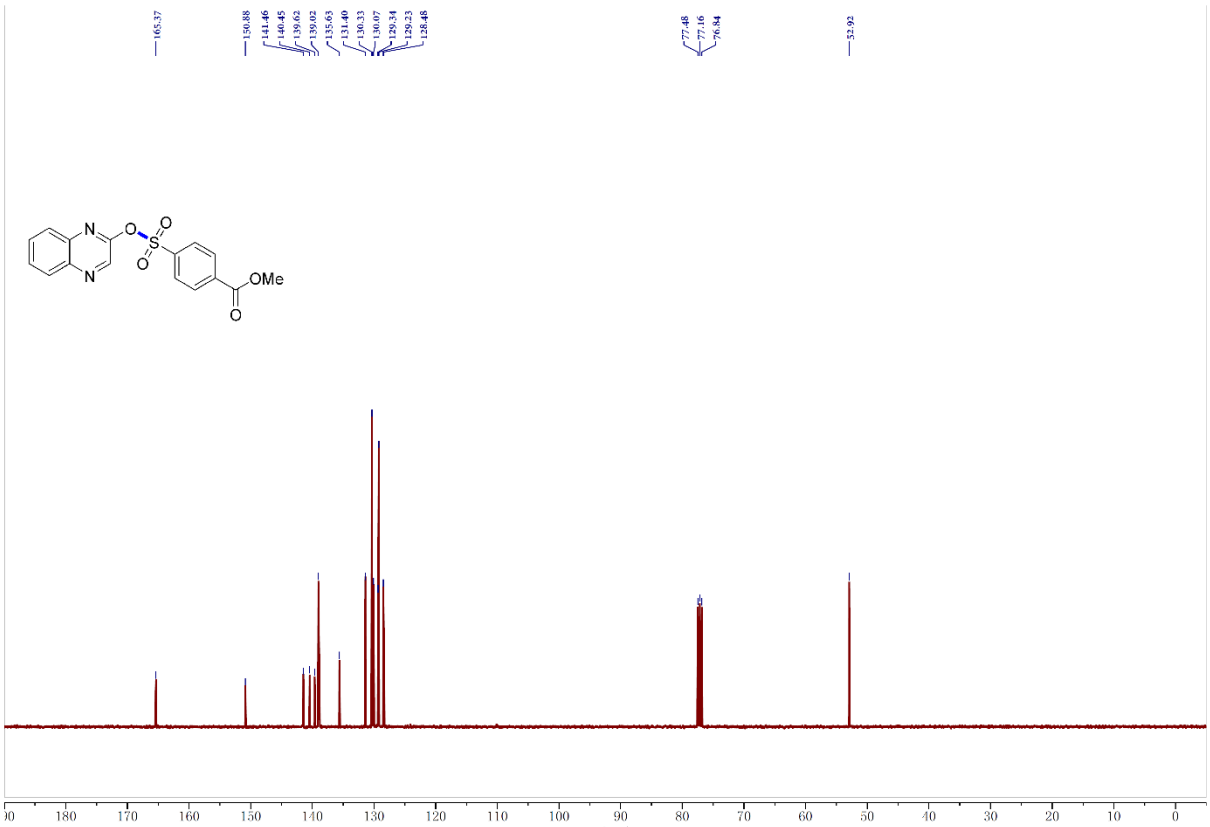
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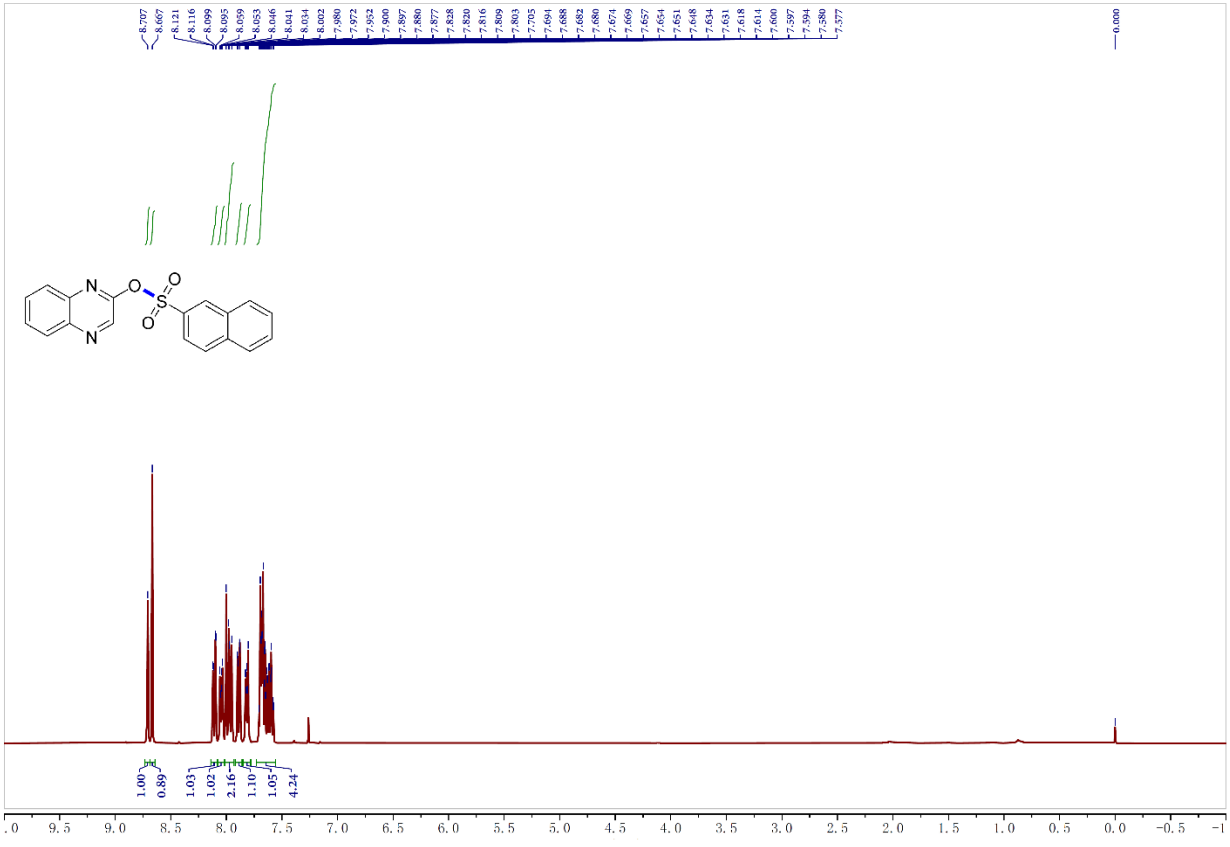
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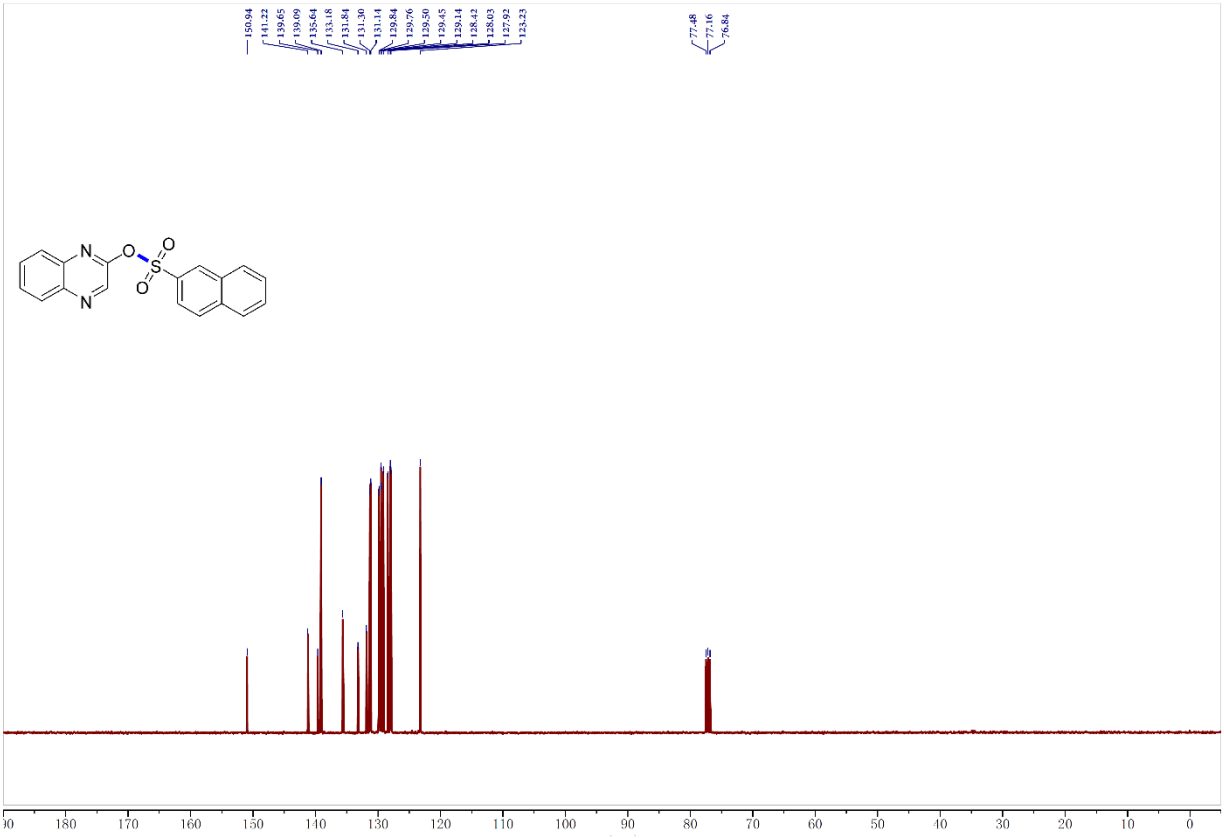
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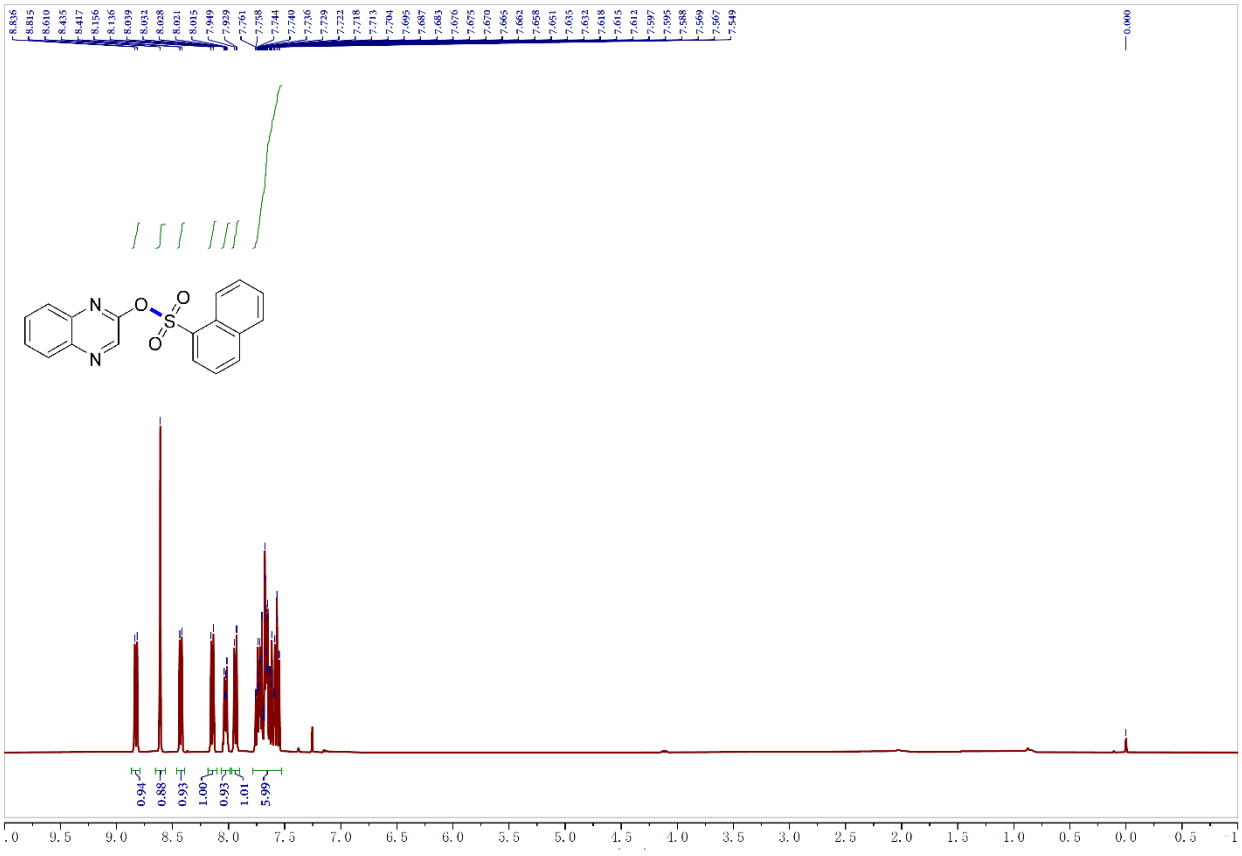
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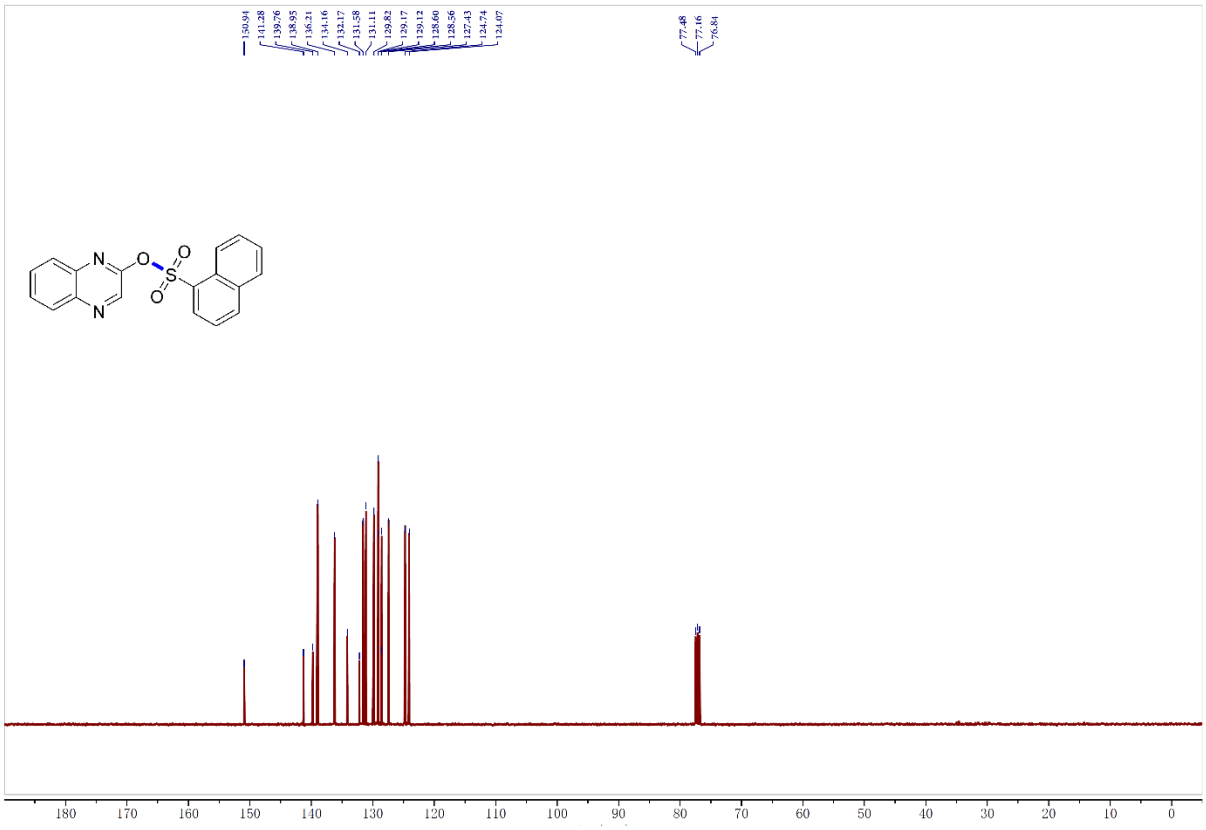
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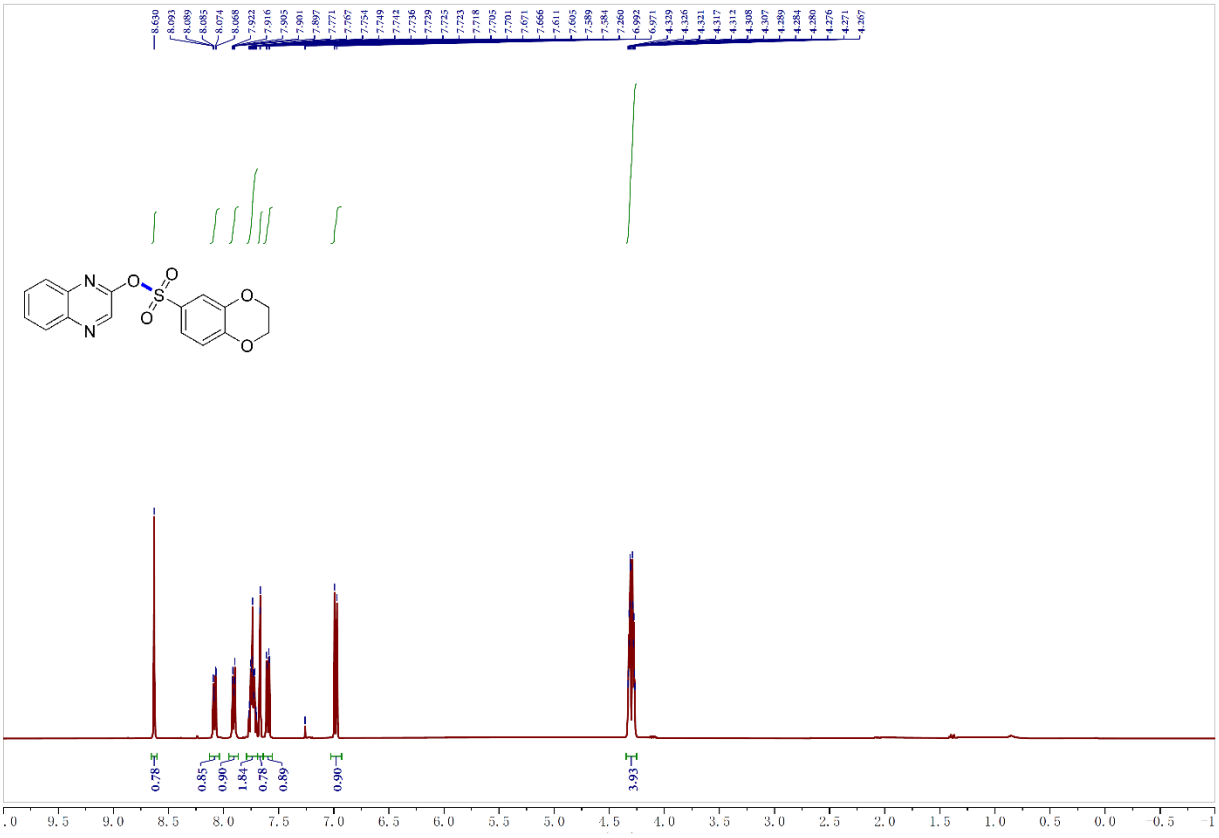
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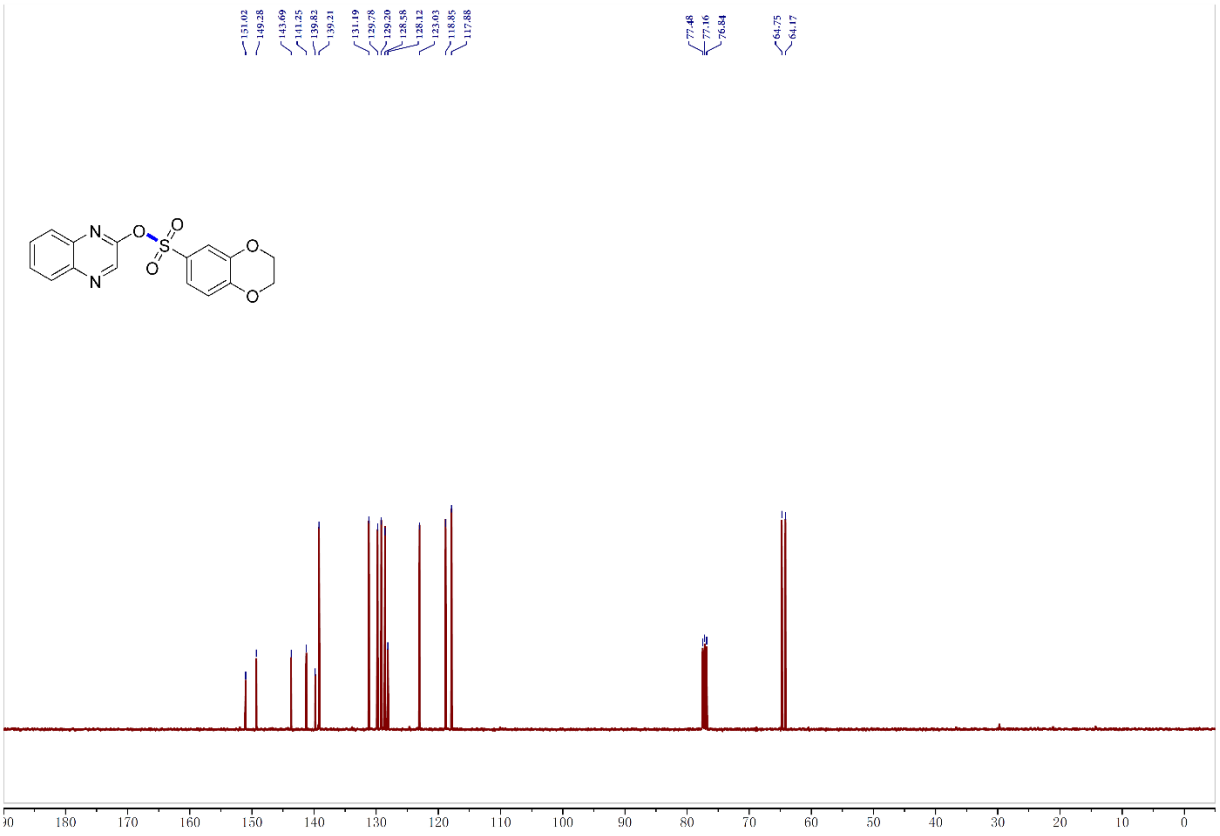
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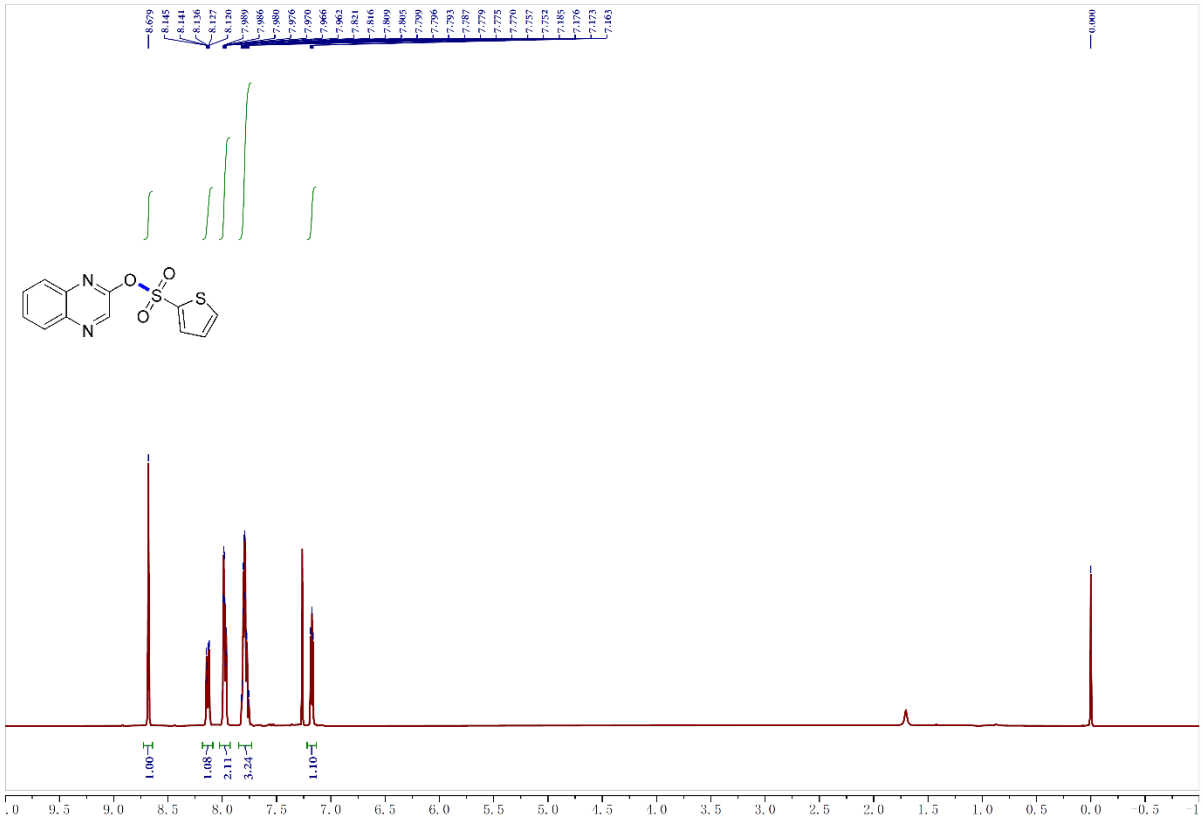
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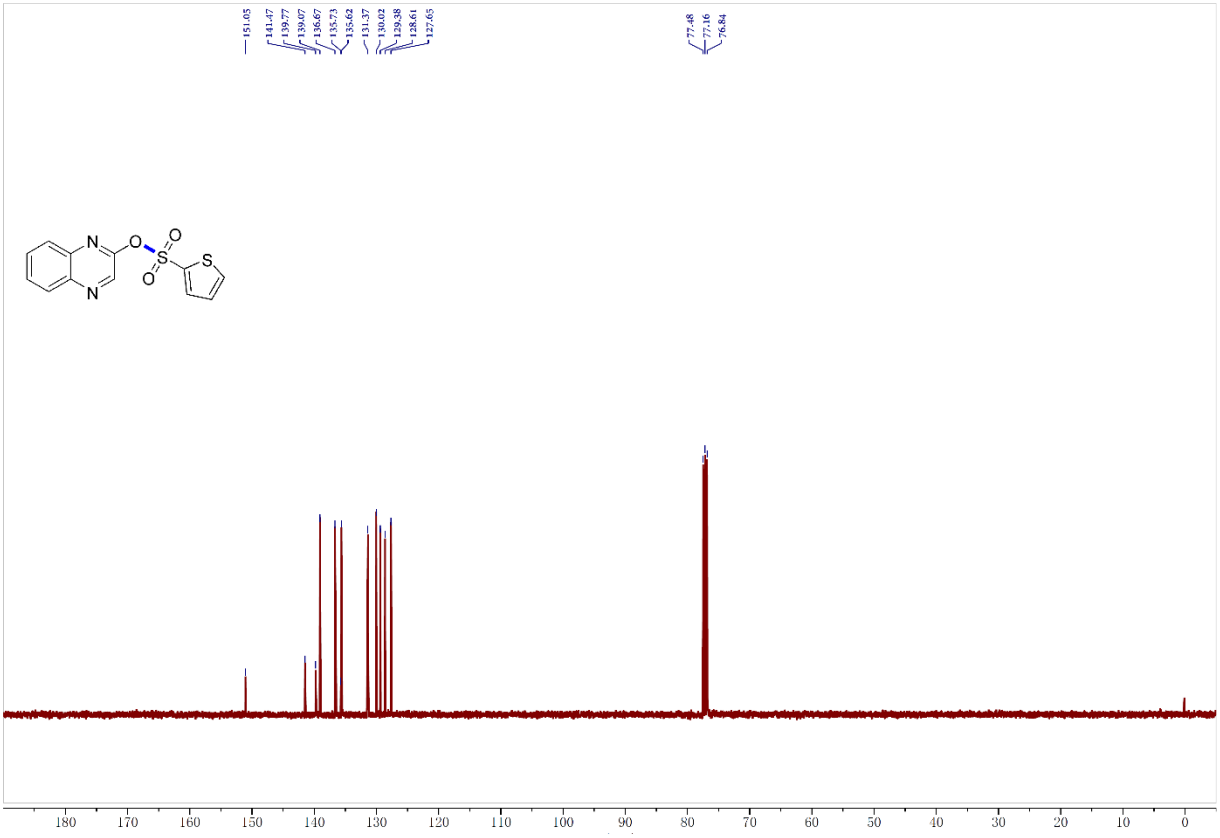
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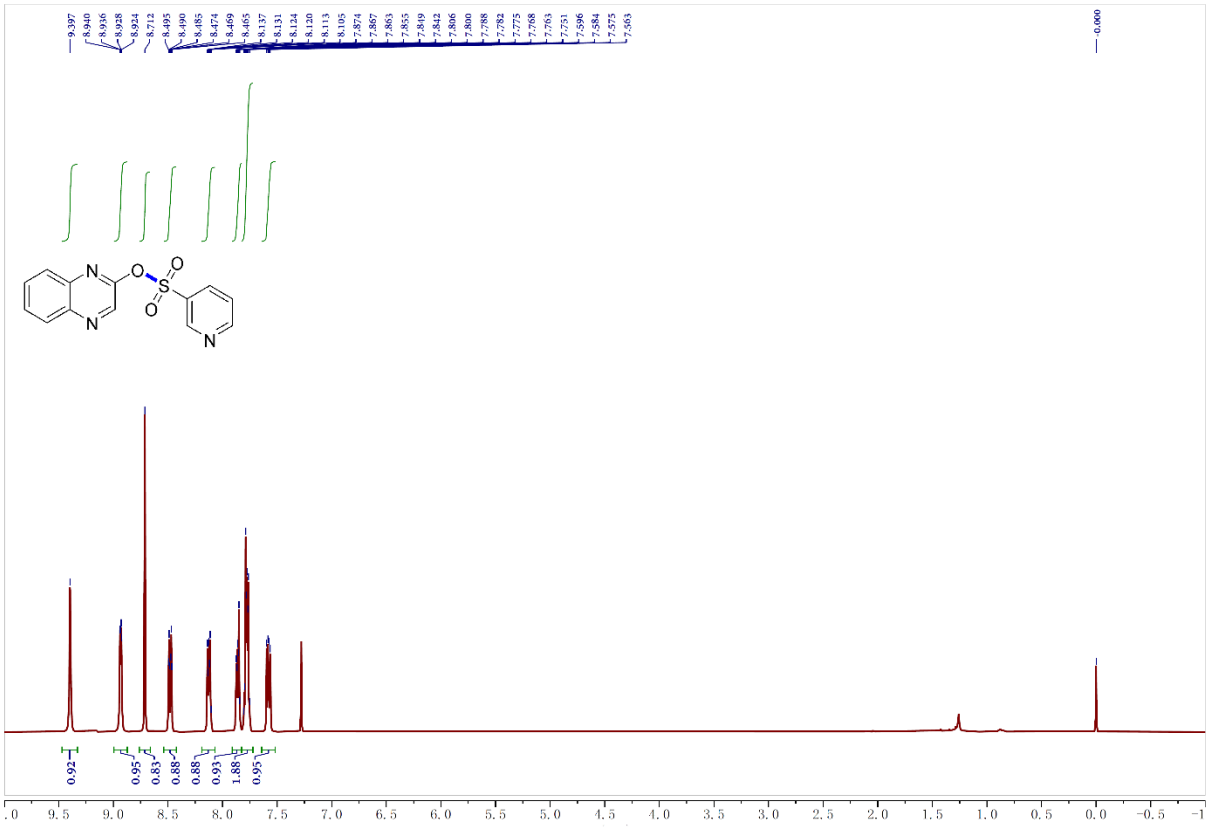
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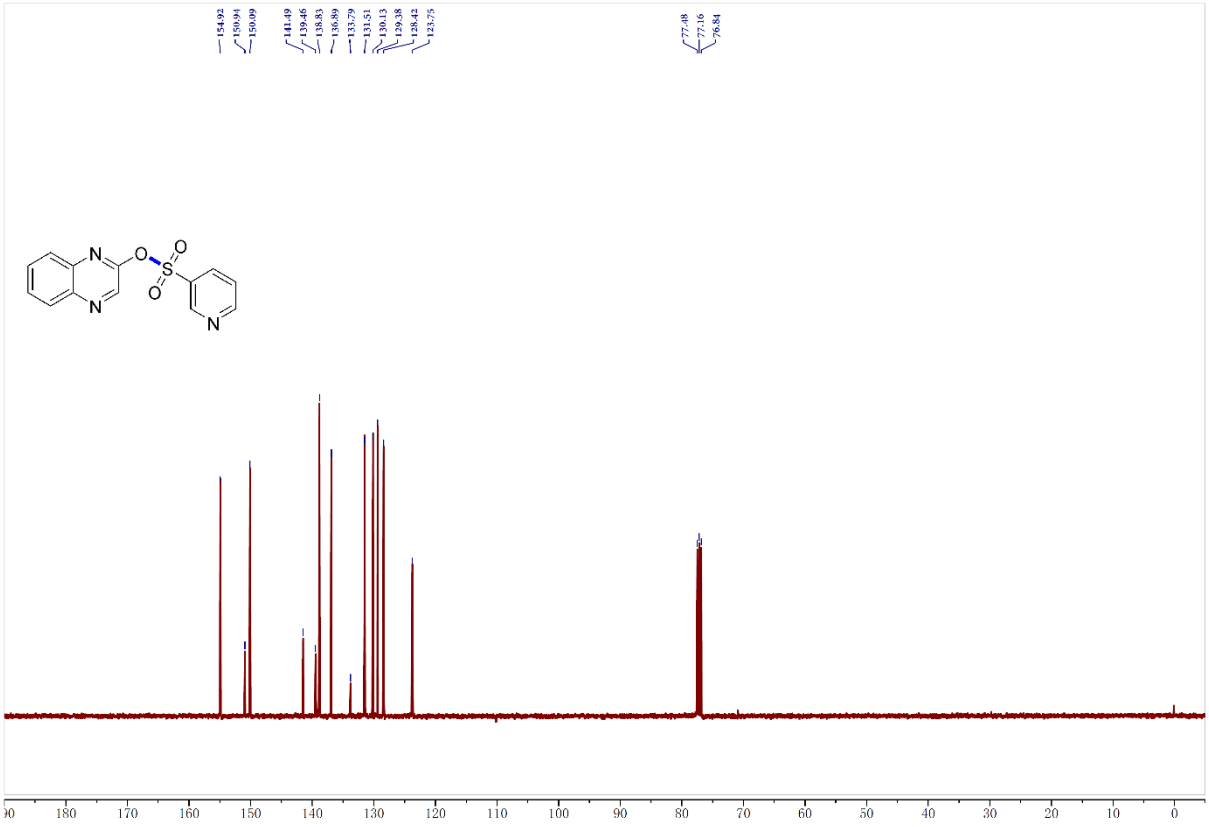
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O
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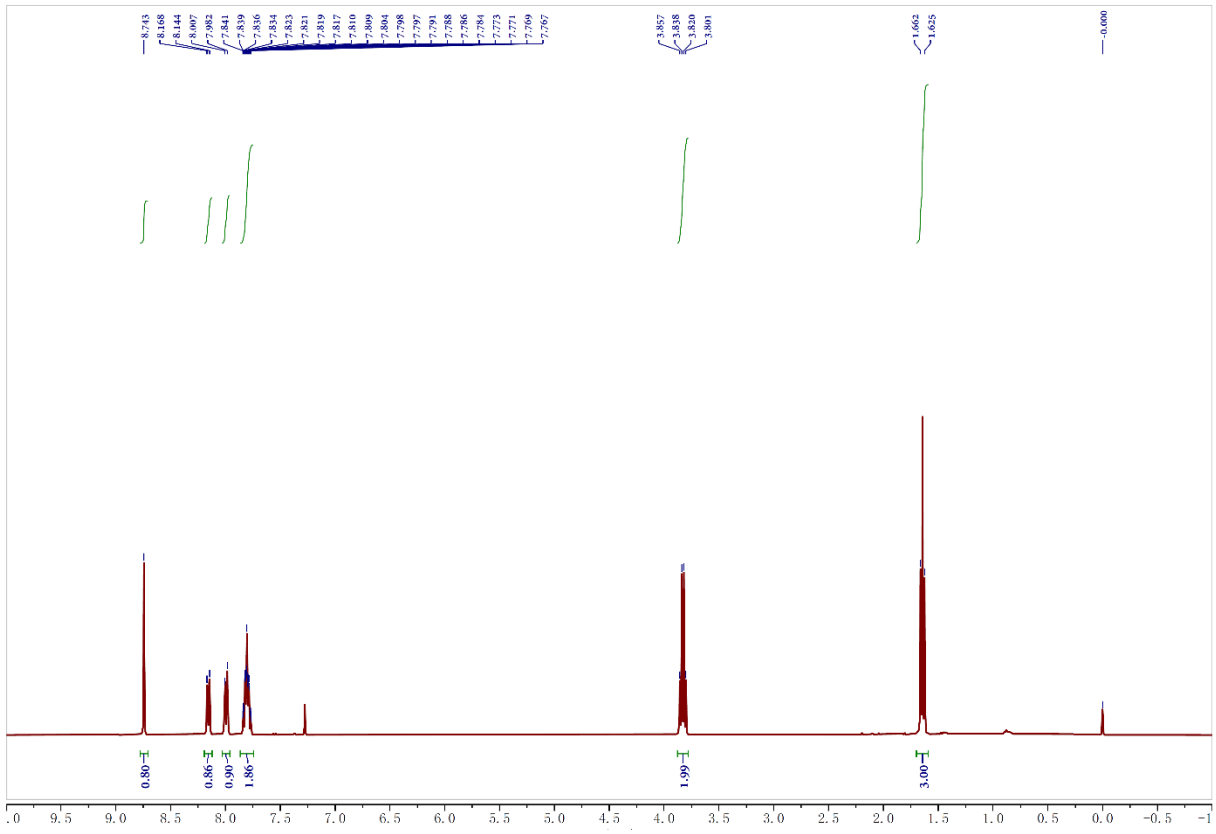
N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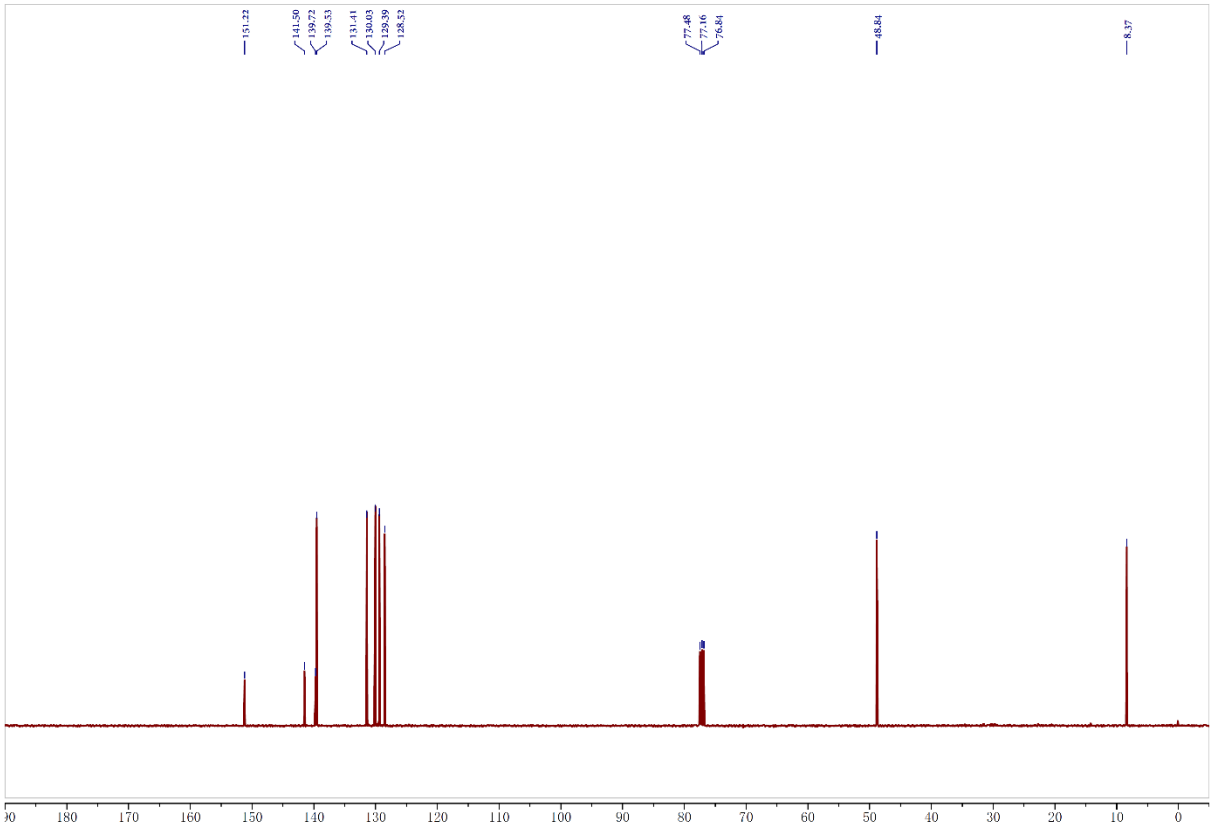
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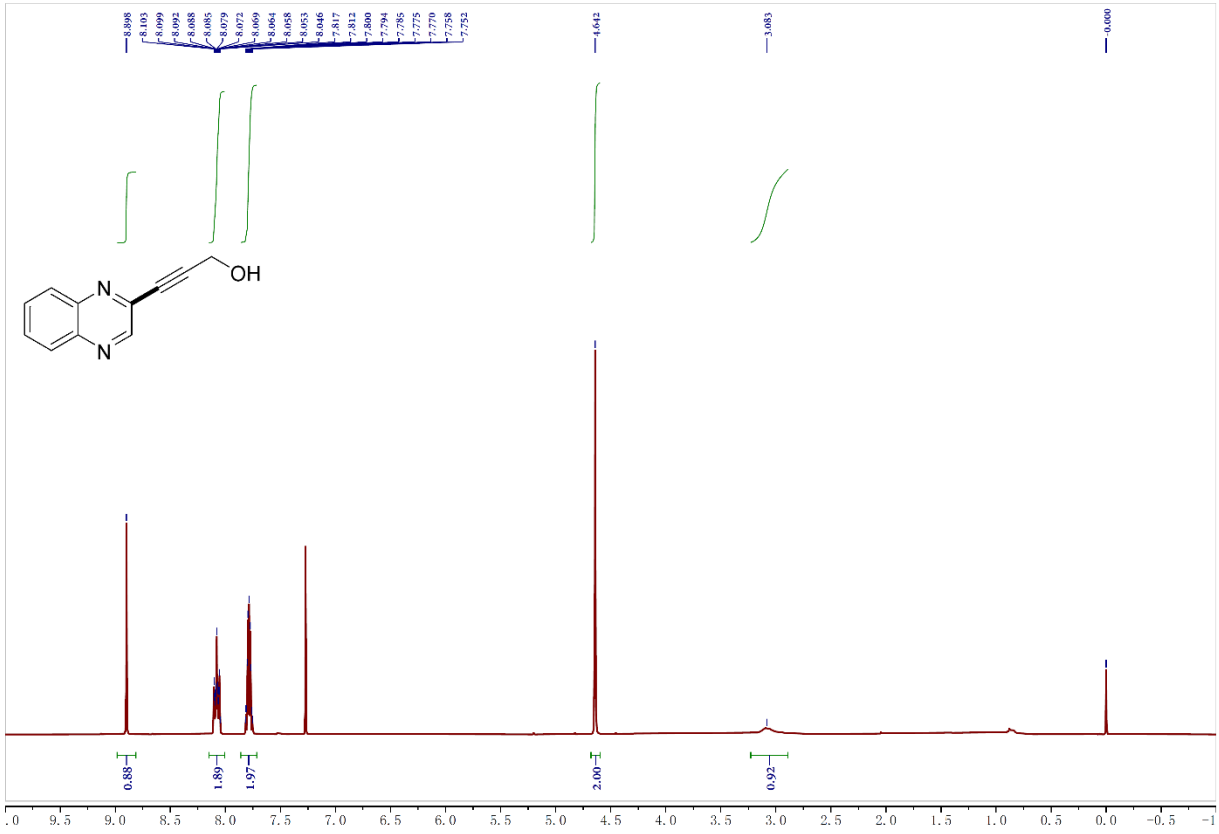
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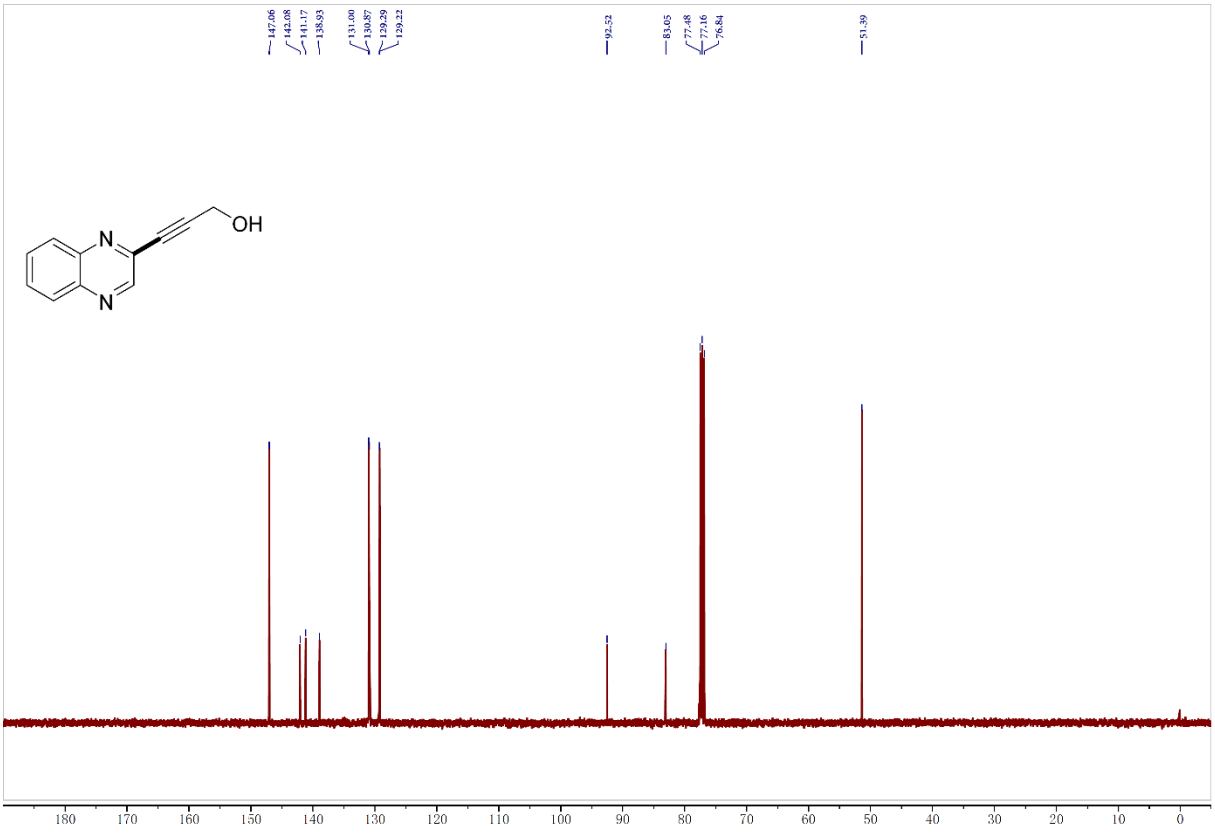
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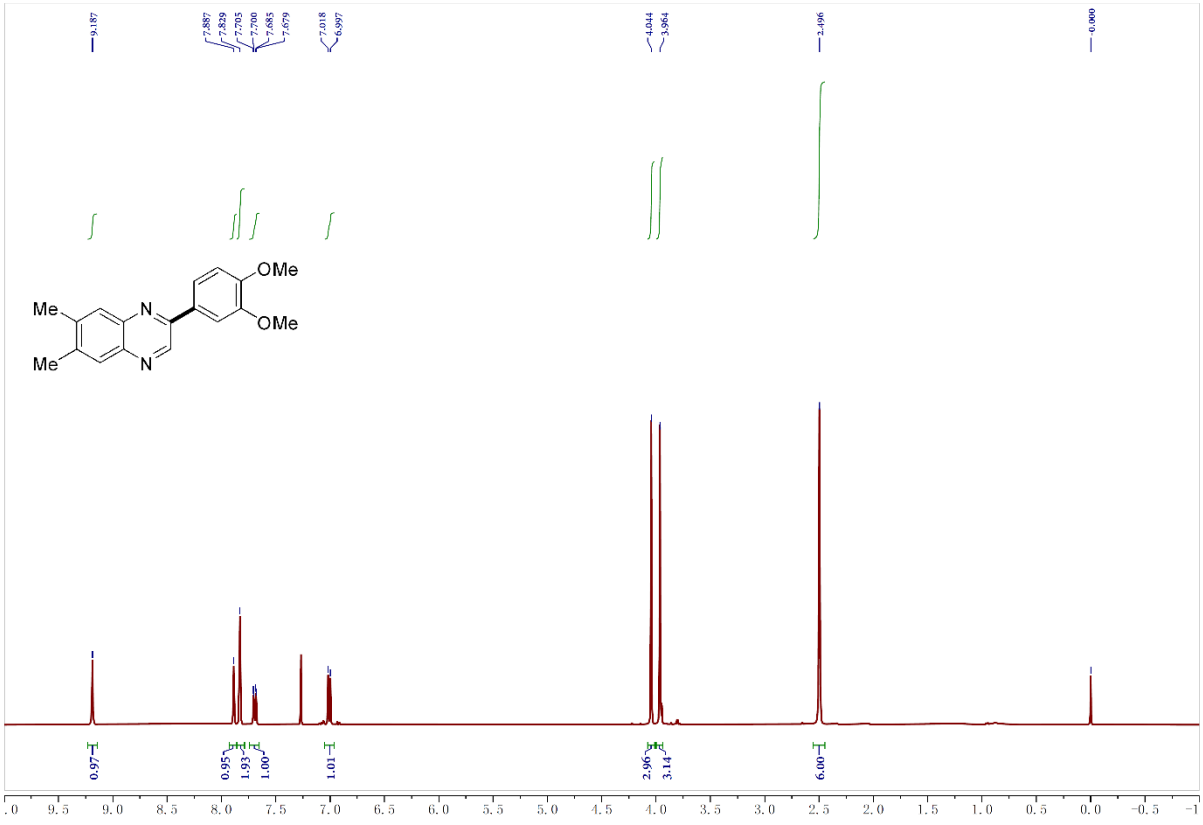
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1.00
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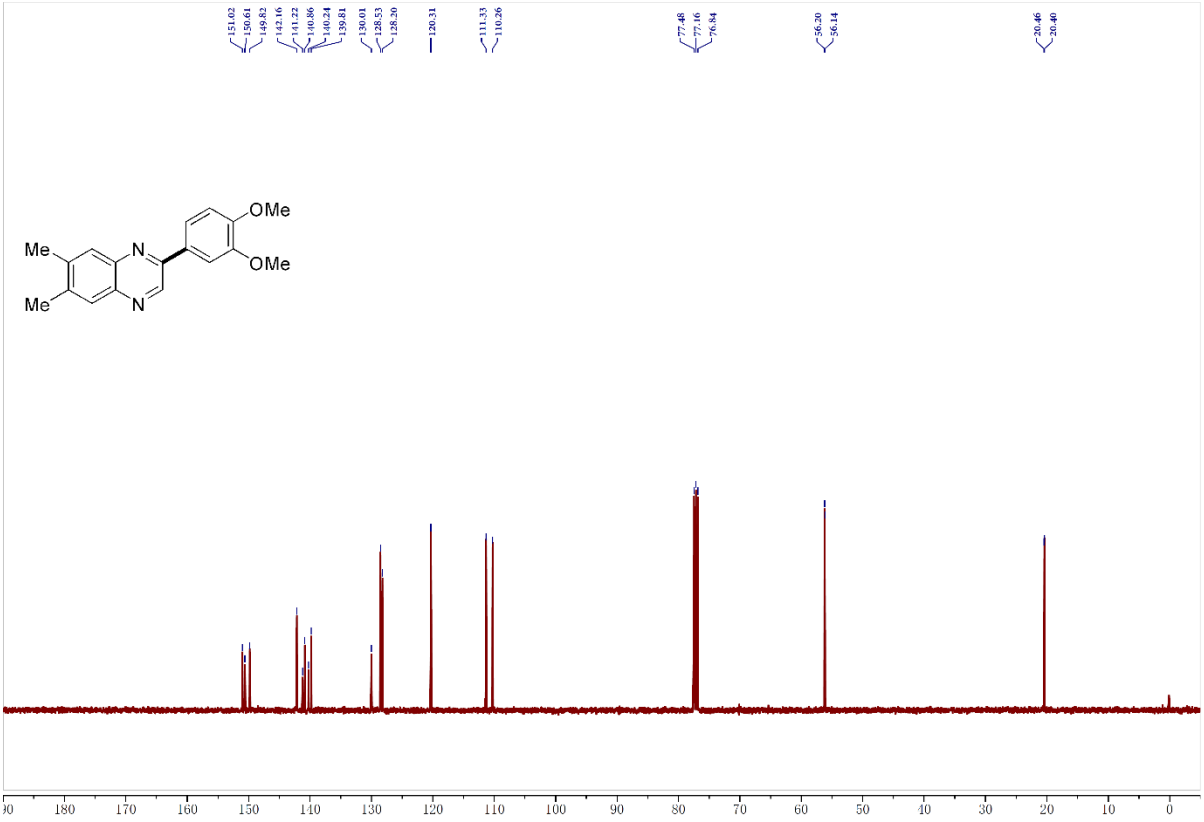
6.00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56.14
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20.40
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OMe
Me
Me
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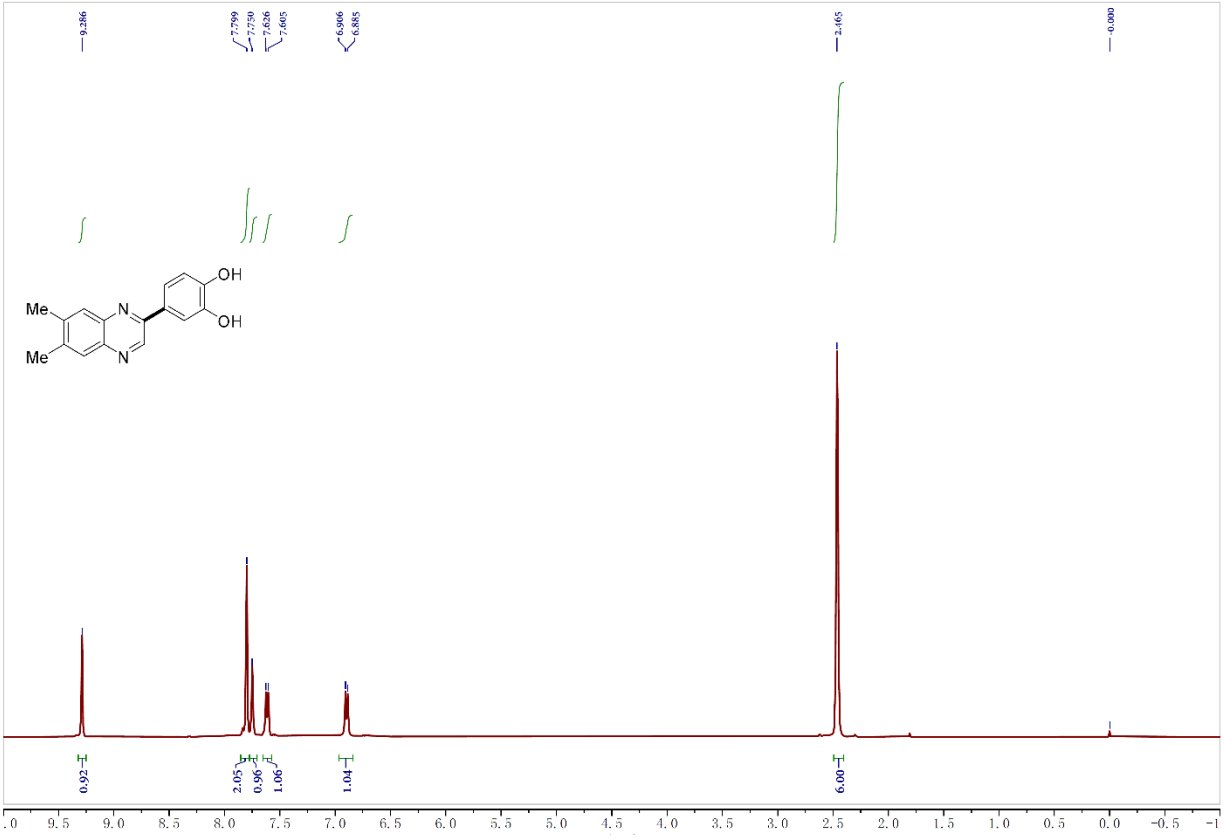
N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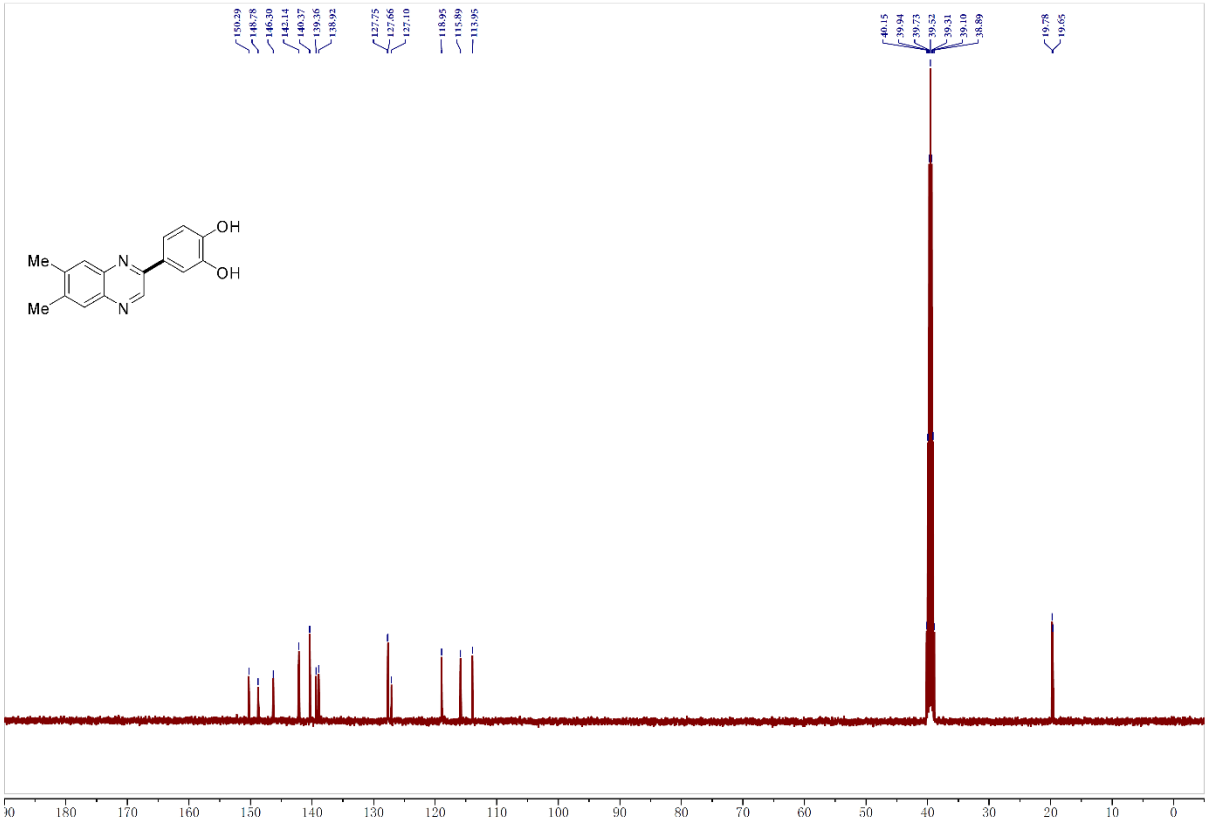
6.00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113.95
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39.10
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19.65
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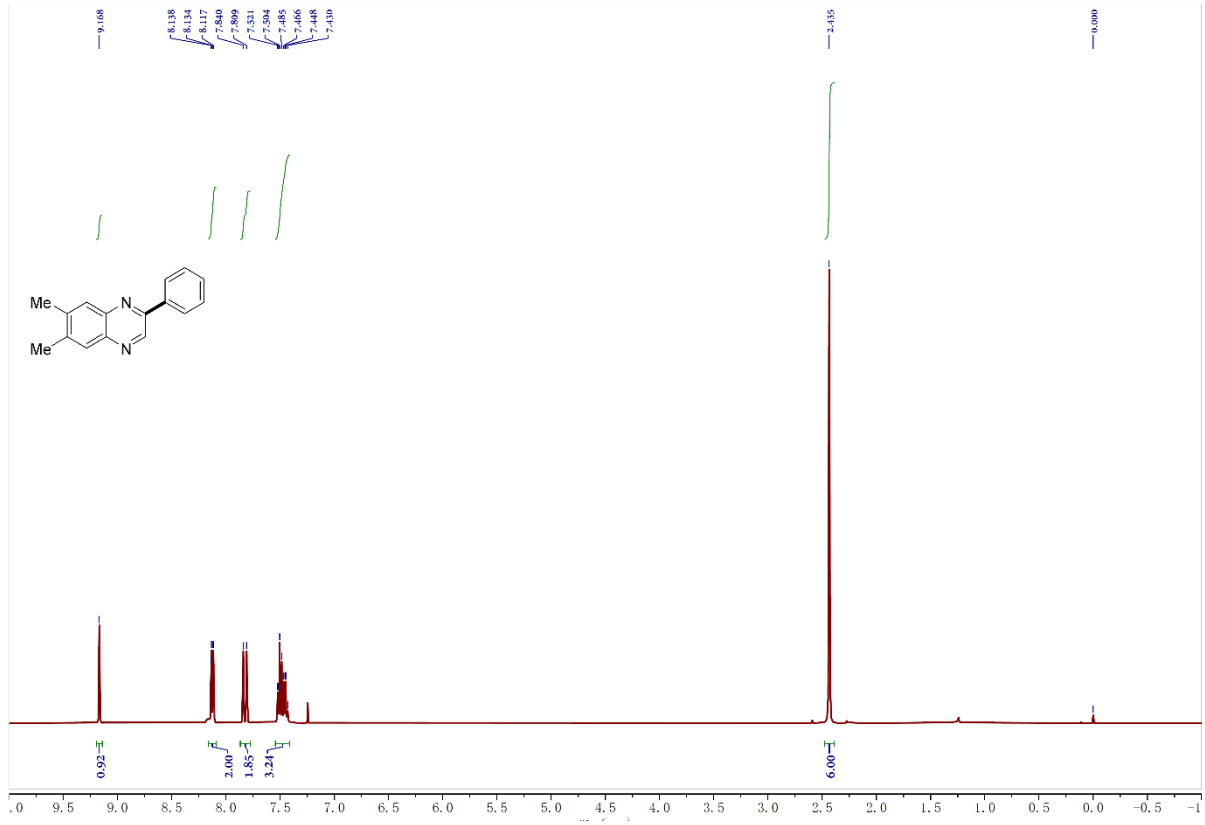
Me
Me
N
N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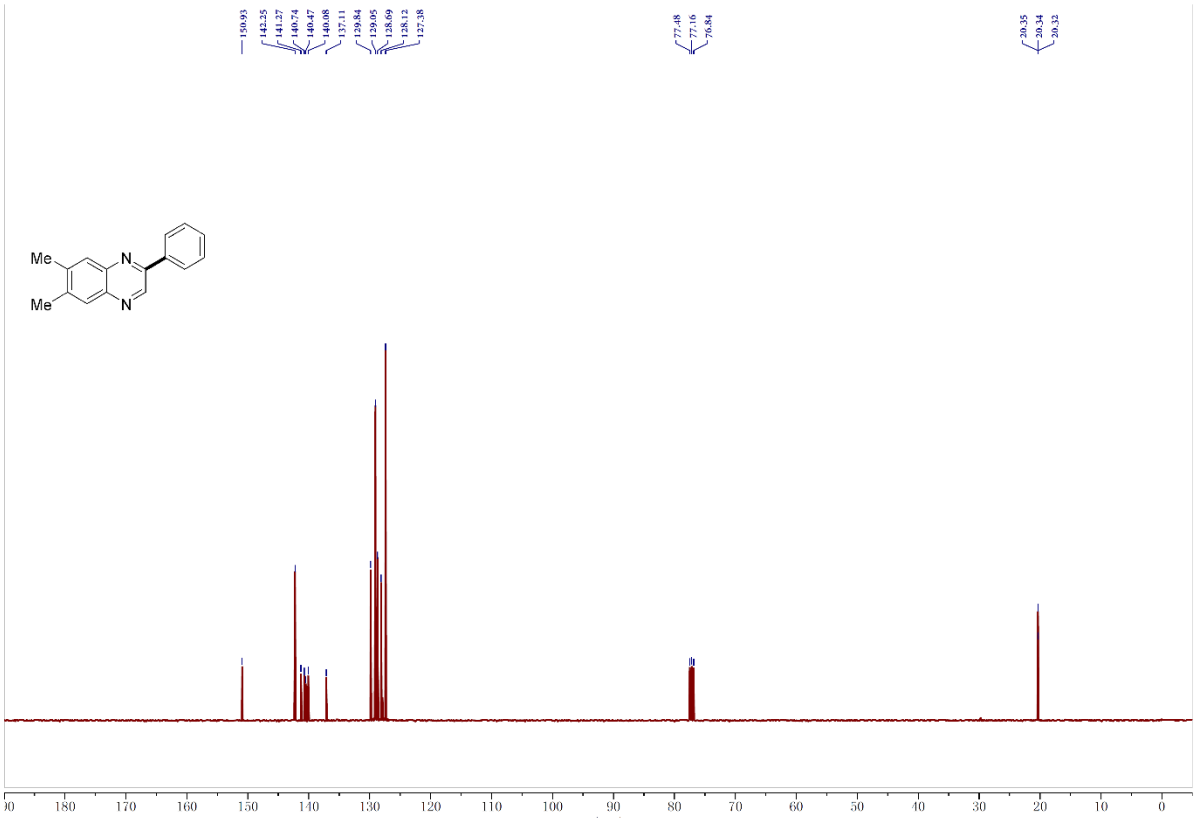
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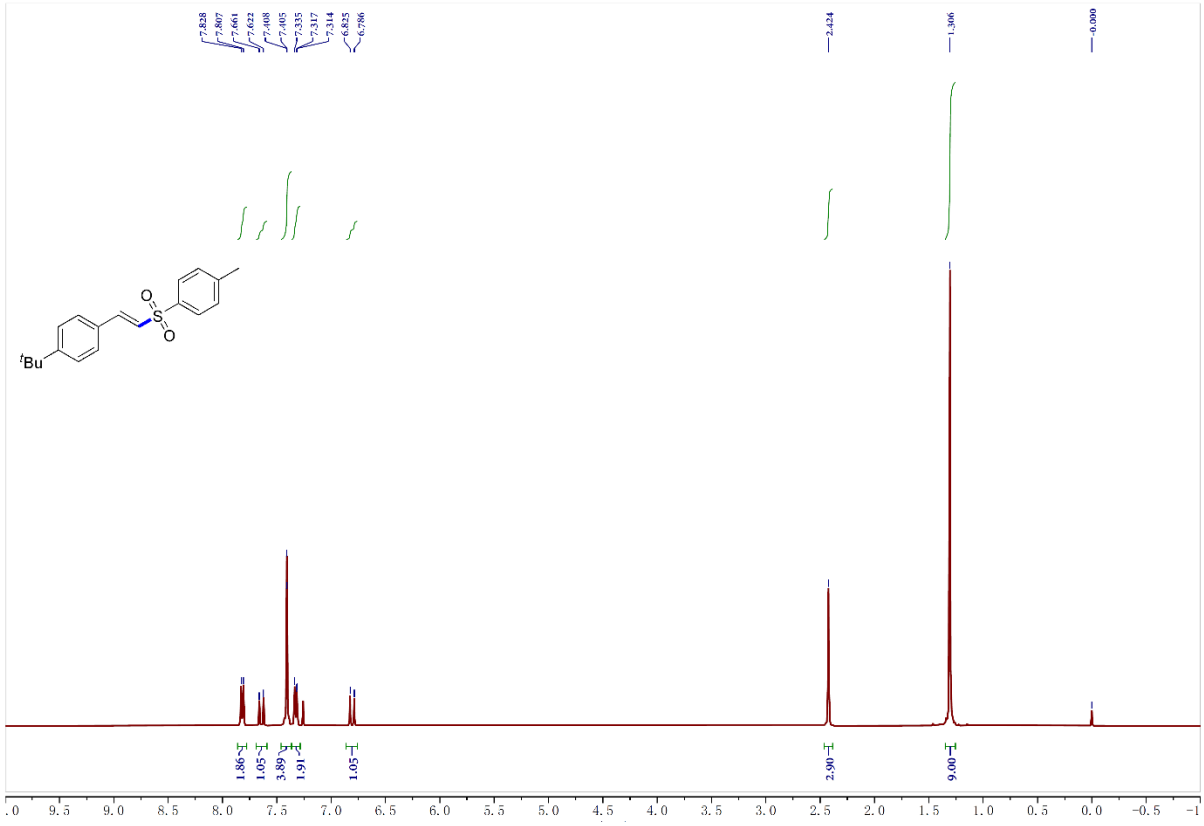
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7.314
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S
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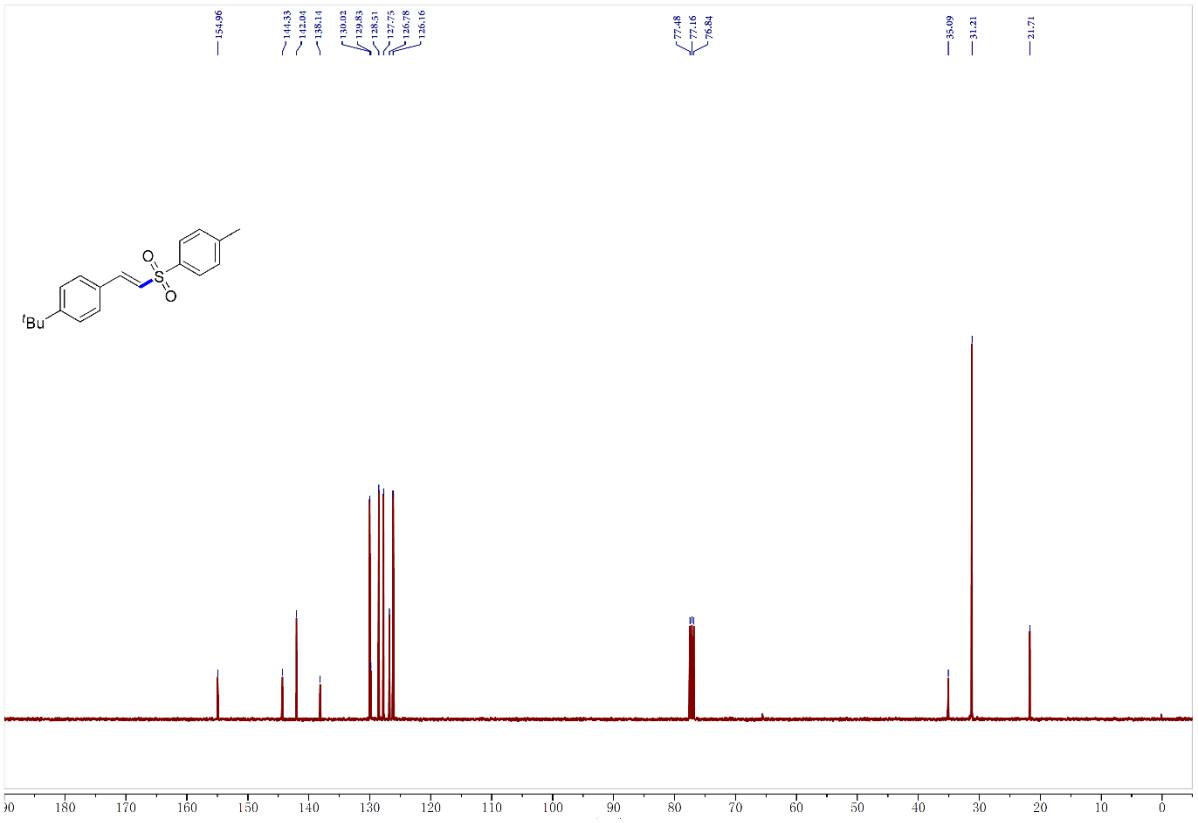
1.05
2.90
9.00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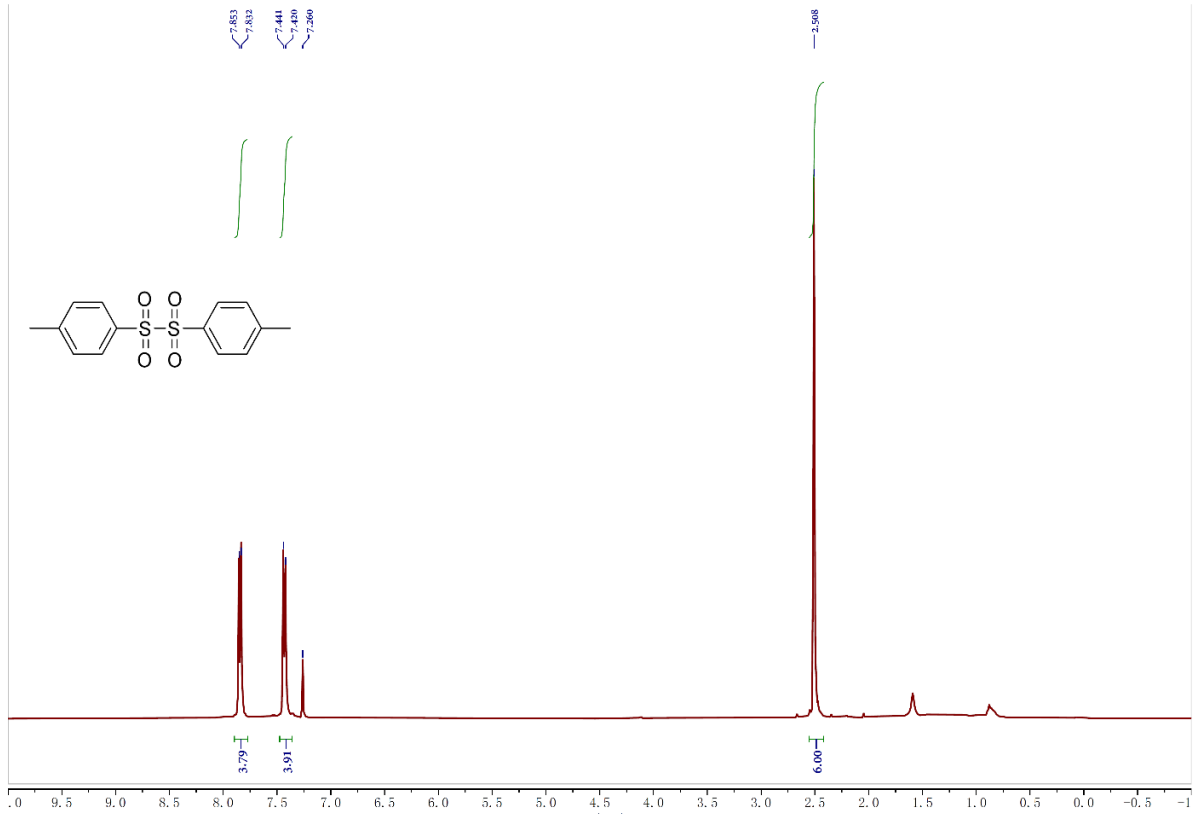
tBu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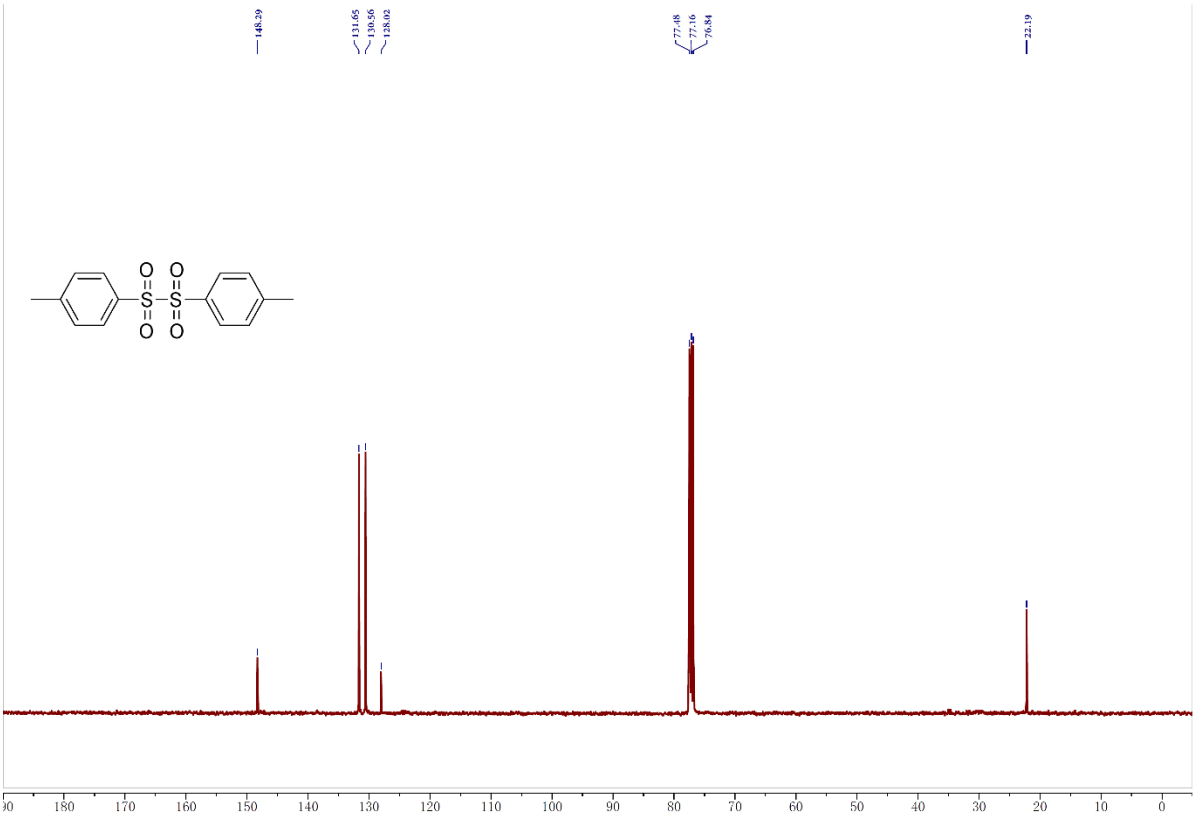
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