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Iridium-Catalysed Direct Sulfamidation of Quinazolinones

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General Information

All manipulations were conducted under air atmosphere. Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400MHz, ^{13}C 100MHz), using DMSO-d_6 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (DMSO-d_6: ^{1}H d 2.50, ^{13}C d 39.5). High-resolution mass spectra (HRMS) were obtained on Q-TOF spectrometer using Agilent 6450 spectrometer. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254).

General Catalytic Procedure

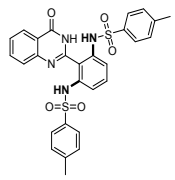
To a 20 mL flask were added **1** (0.20 mmol), **2** (0.60 mmol), Ir (0.002 mmol), Ag (0.008 mmol), CF_3COOH (0.80 mmol) followed by addition of DCE (2.0 mL). The mixture was stirred at 80 ^{o}C for 2.5 h. The reaction was monitored by TLC. The reaction was then quenched with H_2O (10 mL), extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with saturated sodium bicarbonate solution, dried over sodium sulfate, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1 to 1:1) to afford the desired products **3**.

Procedure for the synthesis of product 3a on a 1 mmol scale

To a flask were added **1a** (222.2 mg, 1.0 mmol), **2a** (591.6 mg, 3.0 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.01 mmol), $AgSb_6$ (14.0 mg, 0.04 mmol), CF_3COOH (456.0 mg, 4.0 mmol), followed by addition of DCE (10.0 mL). The reaction mixture was stirred at 80 ^{o}C for 2.5 h and monitored by TLC. The reaction was then quenched with H_2O (10 mL), extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with saturated sodium bicarbonate solution, dried over sodium sulfate, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to afford the desired product **3a** (330.0 mg, 59% yield).

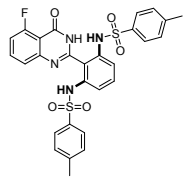
Characterization of the Products

N,N'-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3a)



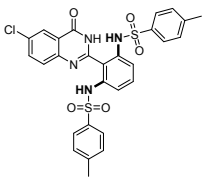
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 96% (108 mg): mp 275 - 276 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 9.80 (s, 2H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 4H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.6, 149.4, 148.1, 143.2, 136.4, 136.2, 134.0, 130.8, 129.5, 127.0, 126.7, 126.5, 125.5, 121.9, 121.7, 120.8, 21.0; HRMS (ESI) *m/z* calcd for $C_{28}H_{24}N_4O_5S_2$ $[M + H]^+$ 561.1261, found 561.1264.

N,N'-(2-(5-fluoro-4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3b)



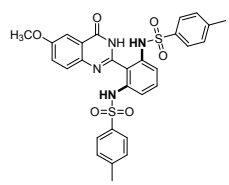
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 86% (99 mg): mp 287 - 288 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 9.70 (s, 2H), 7.77 (td, *J* = 8.2, 5.6 Hz, 1H), 7.39 (t, *J* = 8.3 Hz, 5H), 7.31 – 7.18 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 4H), 6.98 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 159.2, 159.0 (d, *J* = 2.6 Hz), 150.5, 150.3, 143.3, 136.6, 136.2, 134.5 (d, *J* = 10.1 Hz), 130.9, 129.5, 126.5, 121.8 (d, *J* = 273.8 Hz), 121.3, 112.9 (d, *J* = 20.7 Hz), 111.3, 21.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.1; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}FN_4O_5S_2$ $[M + H]^+$ 579.1167, found 579.1164.

N,N'-(2-(6-chloro-4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3c)



Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 78% (93 mg): mp 295 - 296 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.06 (s, 1H), 9.69 (s, 2H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.84 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 149.7, 147.1, 143.2, 136.6, 136.2, 134.0, 130.9, 130.8, 129.5, 129.4, 126.5, 124.5, 123.2, 121.8, 120.7, 21.0; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}ClN_4O_5S_2$ $[M + H]^+$ 595.0871, found 595.0873.

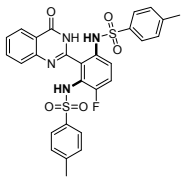
N,N'-(2-(6-methoxy-4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3d)



Eluent: petroleum ether/ethyl acetate (1:1). White solid. Yield: 92% (108 mg): mp 261 - 262 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 9.78 (s, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 2.9 Hz, 1H), 7.44 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 4H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.3, 161.3, 158.0, 147.1, 143.2, 142.5, 136.3, 136.2, 130.7, 129.5, 128.7, 126.4, 123.2, 122.6, 121.4, 105.8, 55.8, 21.0; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}N_4O_6S_2$ [M

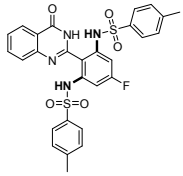
+ H]$^+$ 591.1367, found 591.1369.

***N,N′*-(4-fluoro-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3e)**



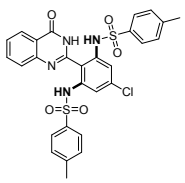
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 65% (75 mg): mp 227 - 228 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.65 (s, 1H), 9.65 (s, 1H), 9.53 (s, 1H), 8.01 (ddd, *J* = 18.5, 7.9, 1.2 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.68 – 7.38 (m, 3H), 7.36 – 7.25 (m, 1H), 7.25 – 7.17 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.85 (dd, *J* = 18.4, 8.0 Hz, 2H), 2.19 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.0, 157.9, 155.5, 148.4, 147.8, 143.3, 142.8, 137.4, 135.0 (d, *J* = 222.0 Hz), 131.84 (d, *J* = 3.1 Hz), 129.5, 129.3 (d, *J* = 18.1 Hz), 129.0, 127.2, 126.9, 126.6 (d, *J* = 8.6 Hz), 126.3, 125.9, 125.4, 123.3 (d, *J* = 16.2 Hz), 121.5, 118.0 (d, *J* = 22.2 Hz), 21.0, 20.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -119.6; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}FN_4O_5S_2$ [M + H]$^+$ 579.1167, found 579.1170.

***N,N′*-(5-fluoro-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3f)**



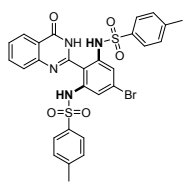
Eluent: petroleum ether/ethyl acetate (2:1). White solid. Yield: 94% (109 mg): mp 240 - 241 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.80 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.66 – 7.36 (m, 6H), 7.18 (d, *J* = 8.1 Hz, 4H), 6.77 (d, *J* = 10.5 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.3, 167.0, 163.2, 161.4 (d, *J* = 127.4 Hz), 148.4, 143.6, 138.6, 136.4, 133.9, 130.1 (d, *J* = 286.1 Hz), 129.7, 127.0, 126.6, 125.6, 122.3, 104.7, 21.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -106.2; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}FN_4O_5S_2$ [M + H]$^+$ 579.1167, found 579.1165.

***N,N′*-(5-chloro-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3g)**



Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 60% (71 mg): mp>300 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 17.6, 7.6 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 4H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.03 (s, 1H), 6.96 (t, *J* = 7.7 Hz, 4H), 6.76 (s, 2H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 148.0, 143.5, 142.0, 141.5, 136.8, 135.1, 134.9, 134.2, 129.9, 129.8, 129.4, 126.8, 126.7, 126.6, 125.7, 21.1; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}ClN_4O_5S_2$ [M + H]$^+$ 595.0871, found 595.0872.

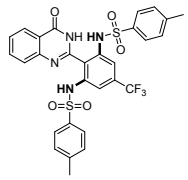
***N,N′*-(5-bromo-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3h)**



Eluent: petroleum ether/ethyl acetate (2:1). Brown solid. Yield: 87% (111 mg): mp>300 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.61 – 7.49 (m, 2H), 7.49 – 7.38 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 4H), 7.12 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 148.3, 143.6, 136.3, 133.9, 129.8, 129.7, 127.4, 127.1, 126.7, 126.5, 125.5, 124.2, 122.7, 122.3, 121.1, 21.0; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}BrN_4O_5S_2$ [M + H]$^+$ 639.0366,

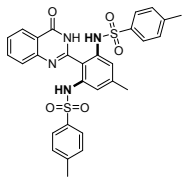
found 639.0363.

***N,N′*-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)-5-(trifluoromethyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3i)**



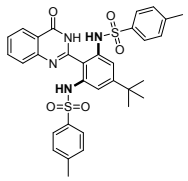
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 96% (121mg): mp>300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.81 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 (t, *J* = 7.0 Hz, 4H), 7.23 (s, 2H), 7.19 (d, *J* = 8.0 Hz, 4H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 148.5, 147.8, 143.7, 137.9, 136.3, 133.9, 130.4 (d, *J* = 32.5 Hz), 129.7, 129.3, 129.3 (d, *J* = 122.6 Hz), 127.3, 126.8, 126.6, 125.6, 123.6 (dd, *J* = 287.1, 112.0 Hz), 114.1, 21.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.4; HRMS (ESI) *m/z* calcd for $C_{29}H_{23}F_3N_4O_5S_2$ $[M + H]^+$ 629.1135, found 629.1134.

***N,N′*-(5-methyl-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3j)**



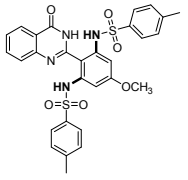
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 70% (80 mg): mp 242 - 243 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 9.79 (s, 2H), 8.13 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.87 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.68 – 7.54 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 6.89 (s, 2H), 2.27 (s, 6H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 149.6, 147.9, 143.2, 140.8, 136.3, 135.9, 134.1, 129.5, 126.9, 126.7, 126.4, 125.5, 122.4, 121.6, 119.5, 21.0, 21.0; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}N_4O_5S_2$ $[M + H]^+$ 575.1417, found 575.1415.

***N,N′*-(5-(tert-butyl)-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3k)**



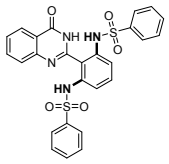
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 91% (112 mg): mp>300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 9.78 (d, *J* = 19.0 Hz, 2H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.84 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.36 (d, *J* = 8.3 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 6.84 (s, 2H), 2.25 (s, 6H), 0.97 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 153.3, 149.8, 148.0, 143.3, 141.8, 136.0, 134.1, 129.4, 129.3, 126.9, 126.7, 125.6, 121.6, 120.0, 119.0, 34.3, 30.2, 20.9; HRMS (ESI) *m/z* calcd for $C_{32}H_{32}N_4O_5S_2$ $[M + H]^+$ 617.1887, found 617.1889.

***N,N′*-(5-methoxy-2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3l)**



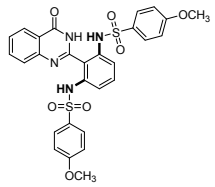
Eluent: petroleum ether/ethyl acetate (1:1). White solid. Yield: 90% (106 mg): mp 265 - 266 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.00 (s, 2H), 8.10 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.89 – 7.76 (m, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.12 (d, *J* = 8.1 Hz, 4H), 6.51 (s, 2H), 3.55 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.6, 160.1, 149.7, 148.0, 143.4 137.6, 136.1, 134.1, 129.6, 126.7, 126.6, 126.6, 125.6, 121.6, 113.4, 105.9, 55.3, 21.0; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}N_4O_6S_2$ $[M + H]^+$ 591.1367, found 591.1365.

***N,N′*-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)dibenzenesulfonamide (3m)**



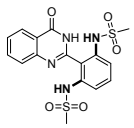
Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 83% (88 mg): mp 254 - 255 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (s, 1H), 9.93 (s, 2H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.44 (m, 7H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.20 (t, *J* = 8.2 Hz, 1H), 6.94 (dd, *J* = 8.2, 3.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 149.4, 148.3, 139.4, 136.3, 133.9, 132.9, 130.7, 129.1, 127.1, 126.7, 126.5, 125.6, 122.0, 121.6, 120.0; HRMS (ESI) *m/z* calcd for $C_{26}H_{20}N_4O_5S_2$ $[M + H]^+$ 533.0948, found 533.0949.

***N,N′*-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)bis(4-methoxybenzenesulfonamide) (3n)**



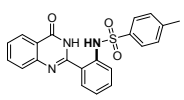
Eluent: petroleum ether/ethyl acetate (1:1). White solid. Yield: 89% (105 mg): mp>300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.84 (s, 1H), 9.74 (s, 2H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.42 (d, *J* = 8.9 Hz, 4H), 7.25 (t, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.78 (m, 4H), 3.73 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.1, 162.4, 161.6, 149.5, 148.1, 136.3, 134.0, 130.8, 128.7, 127.0, 126.7, 125.6, 121.8, 121.5, 120.6, 114.2, 55.5; HRMS (ESI) *m/z* calcd for $C_{28}H_{24}N_4O_7S_2$ $[M + H]^+$ 593.1159, found 593.1157.

***N,N′*-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)-1,3-phenylene)dimethanesulfonamide (3o)**



Eluent: petroleum ether/ethyl acetate (20:1). White solid. Yield: 80% (65 mg): mp 198 - 199 °C . ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.08 (s, 1H), 9.34 (s, 2H), 8.14 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.78 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.45 (dd, *J* = 8.9, 7.5 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.98 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.3, 149.4, 148.9, 136.8, 133.8, 130.6, 128.5, 127.0, 126.5, 125.6, 122.7, 122.1, 120.0; HRMS (ESI) *m/z* calcd for $C_{16}H_{16}N_4O_5S_2$ $[M + H]^+$ 409.0635, found 409.0634.

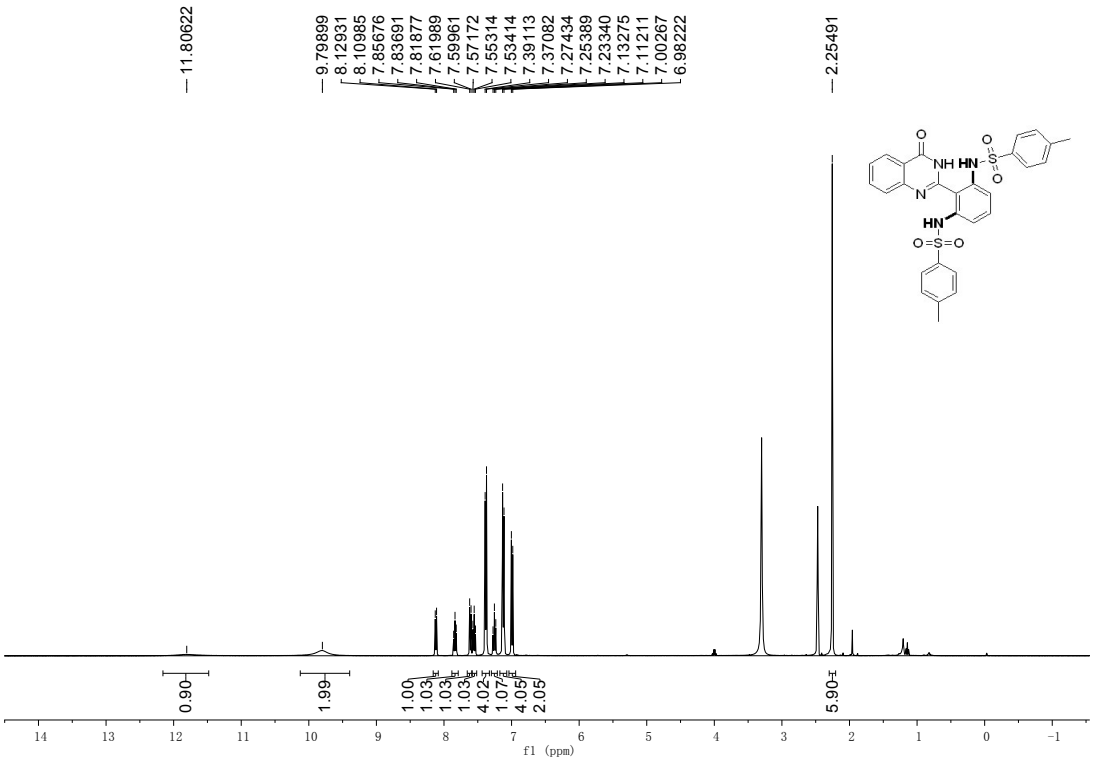
4-Methyl-*N*-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)phenyl)benzenesulfonamide (4a)

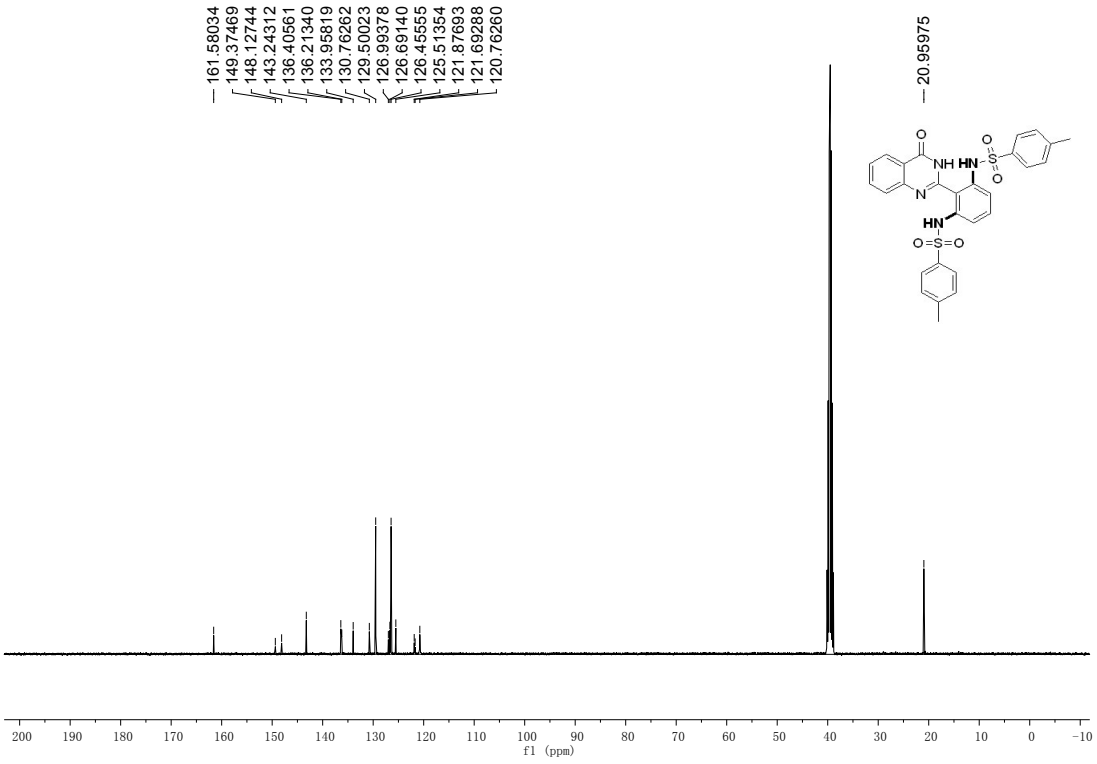


Eluent: petroleum ether/ethyl acetate (4:1). White solid. Yield: 43% (34 mg): mp 178 - 188 °C . ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.30 (s, 1H), 11.67 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 13.2, 3.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.19 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 152.3, 146.8, 143.6, 136.8, 135.6, 134.9, 132.0, 129.6, 129.6, 128.6, 127.2, 126.5, 125.8, 124.5, 122.4, 122.1, 120.9, 20.9; HRMS (ESI) *m/z* calcd for $C_{21}H_{17}N_3O_3S$ $[M + H]^+$ 392.1063, found 392.1067.

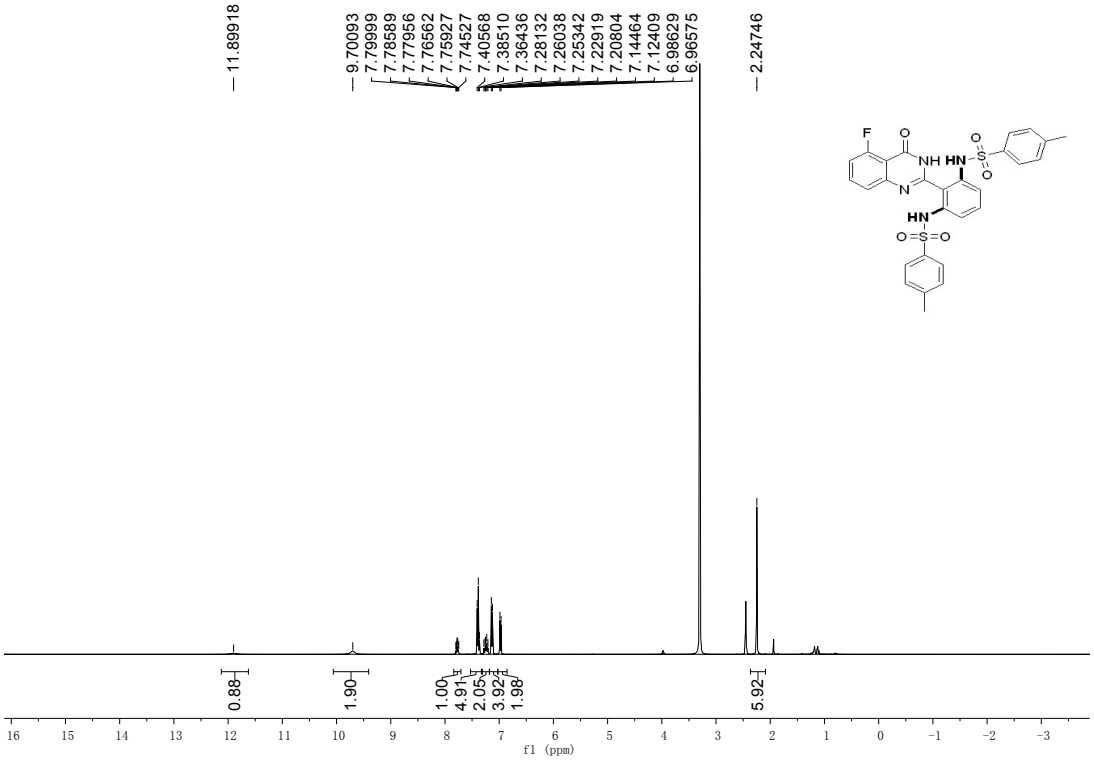
^{1}H and ^{13}C NMR Spectra

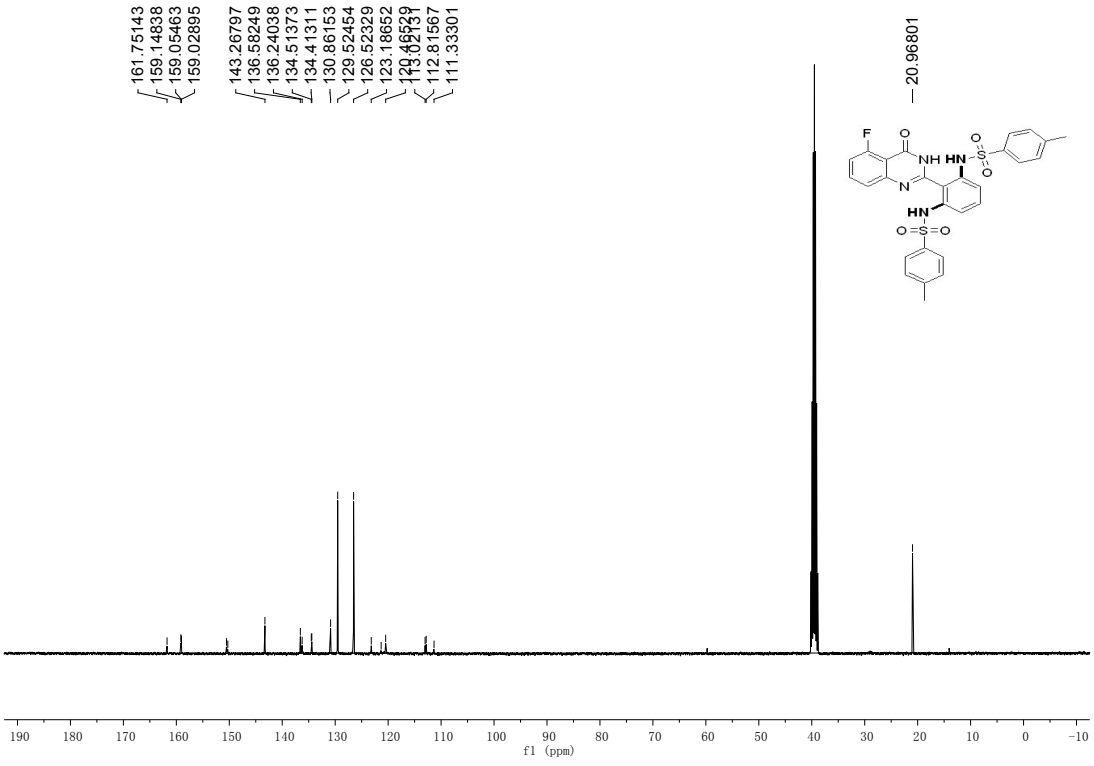
The ^{1}H and ^{13}C NMR spectra of **3a**



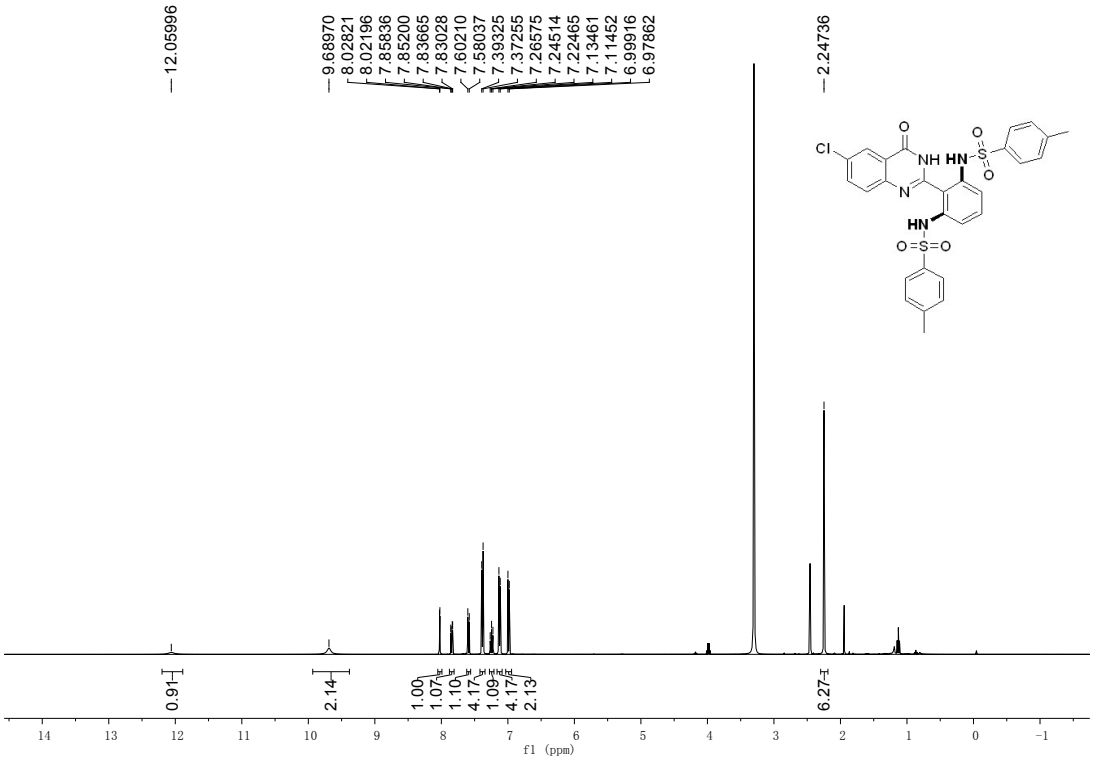


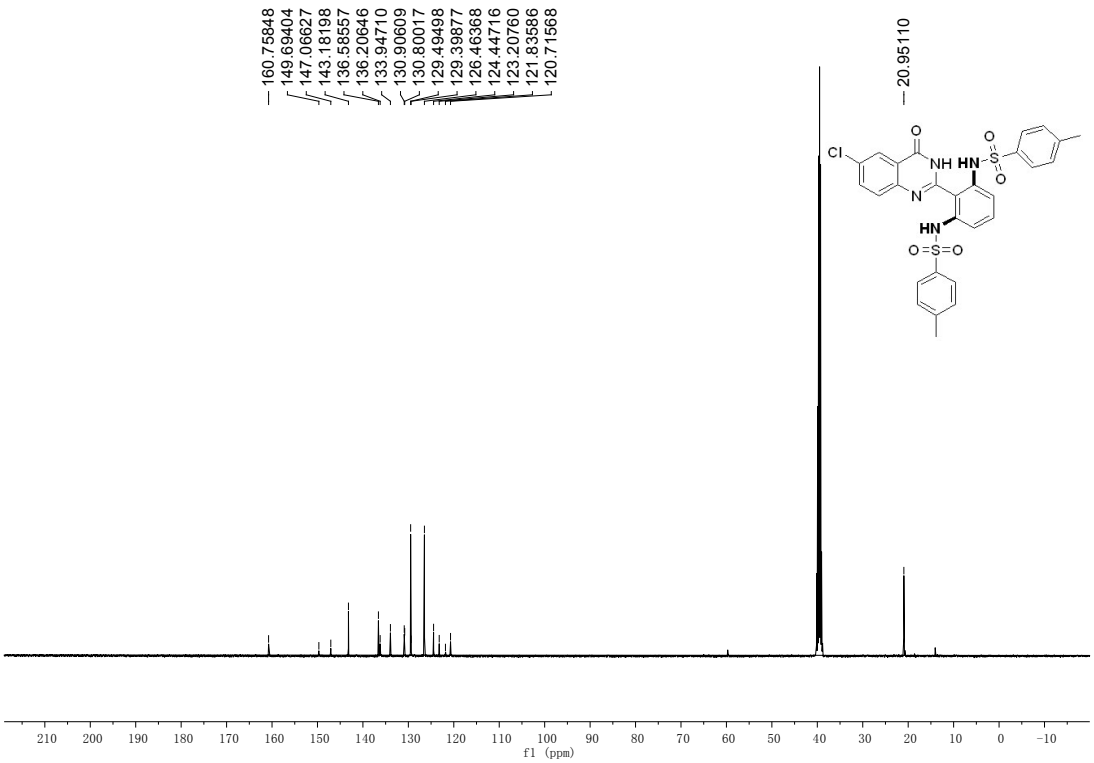
The ^{1}H and ^{13}C NMR spectra of **3b**



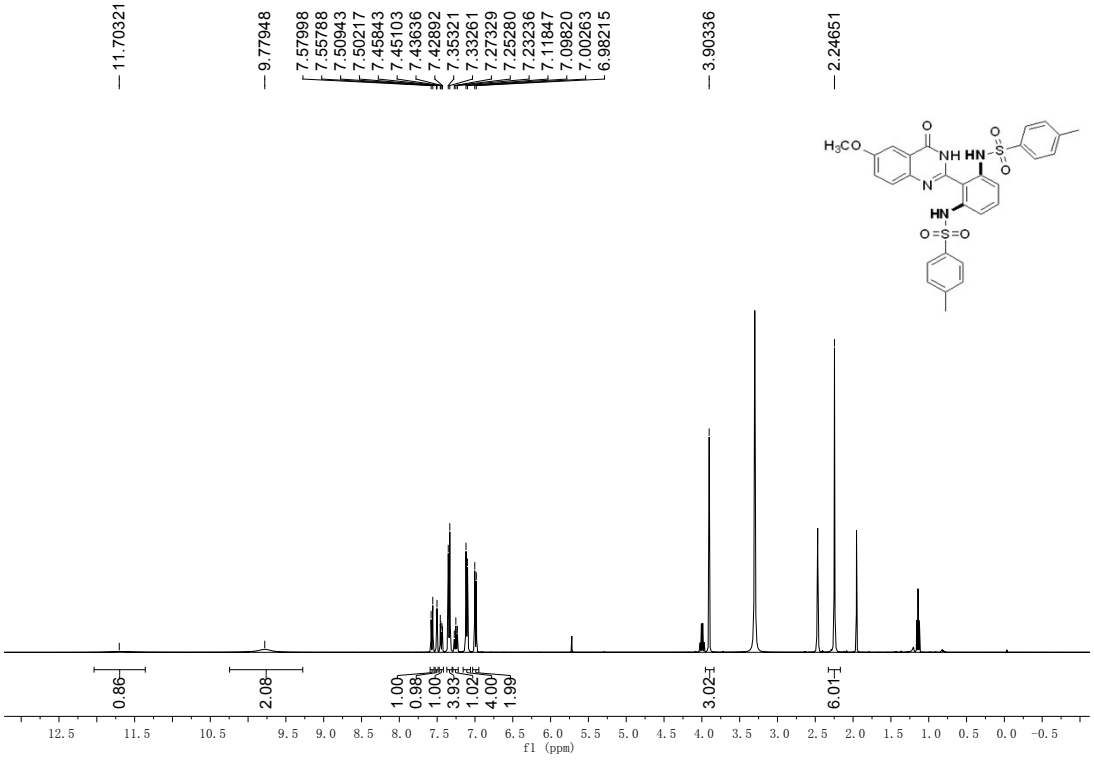


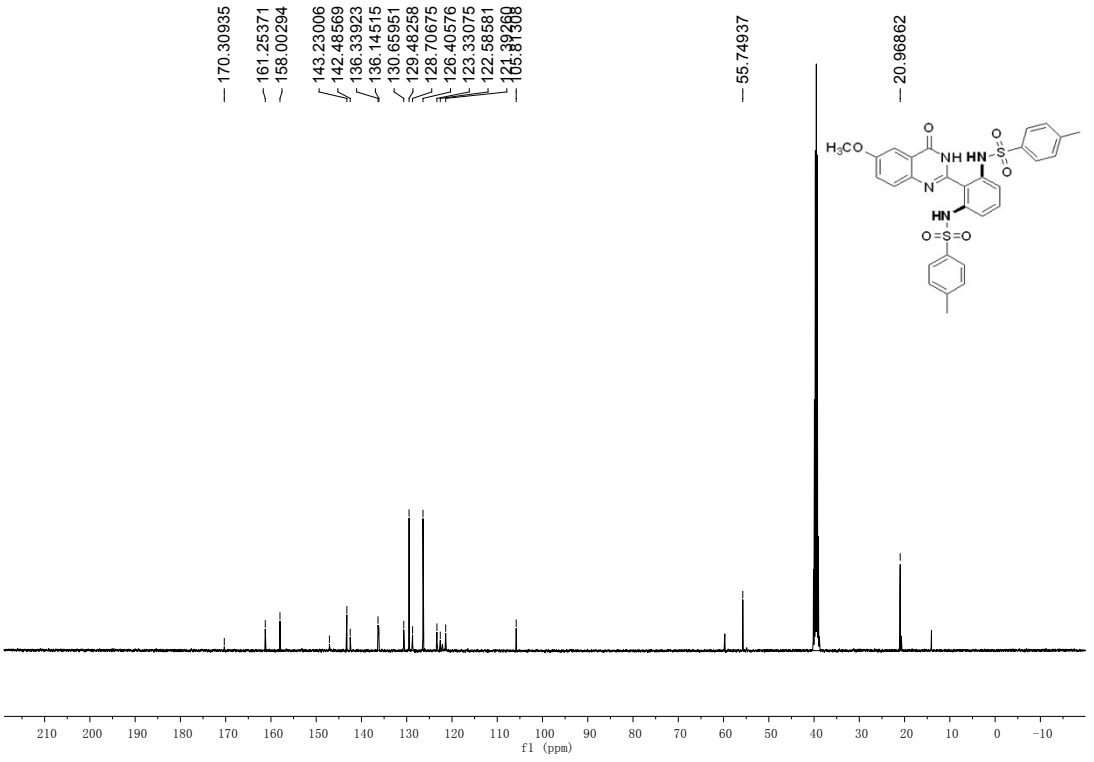
The ^{1}H and ^{13}C NMR spectra of **3c**



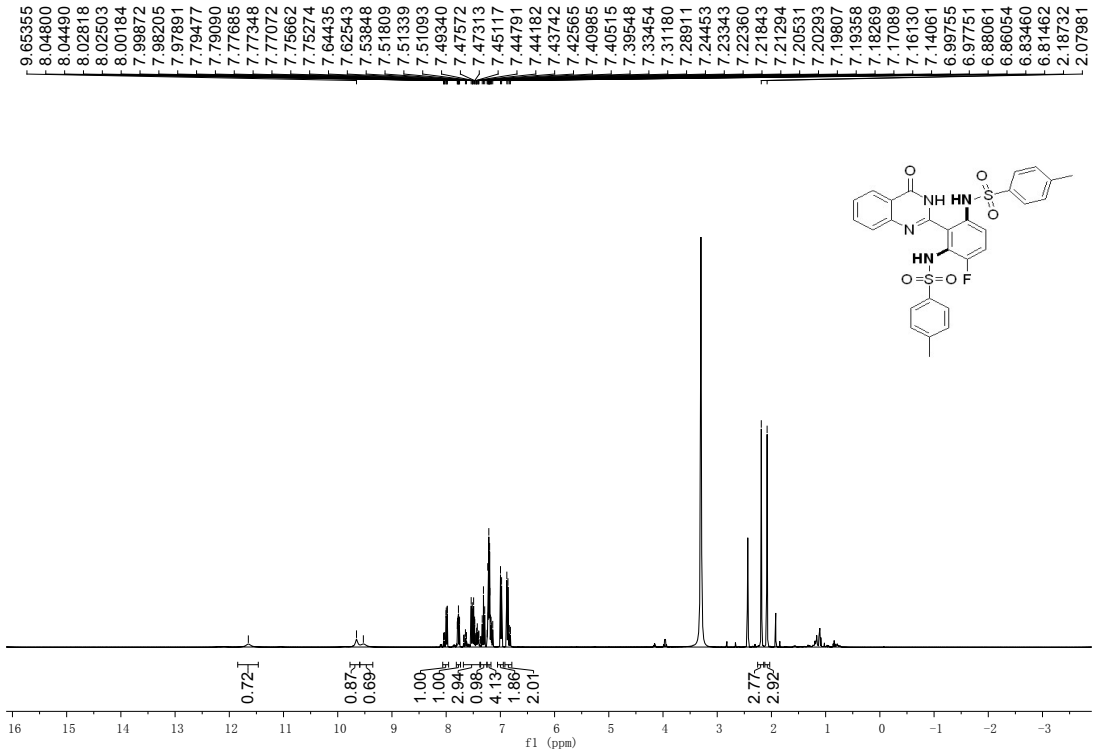


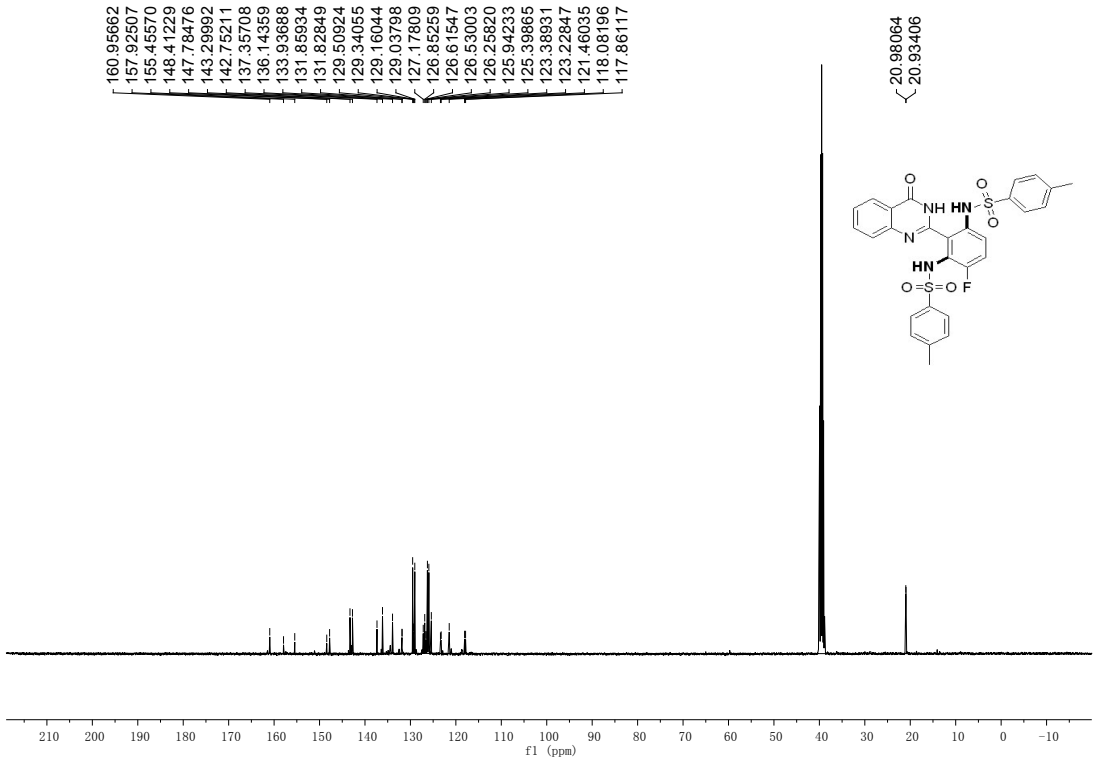
The ^{1}H and ^{13}C NMR spectra of **3d**



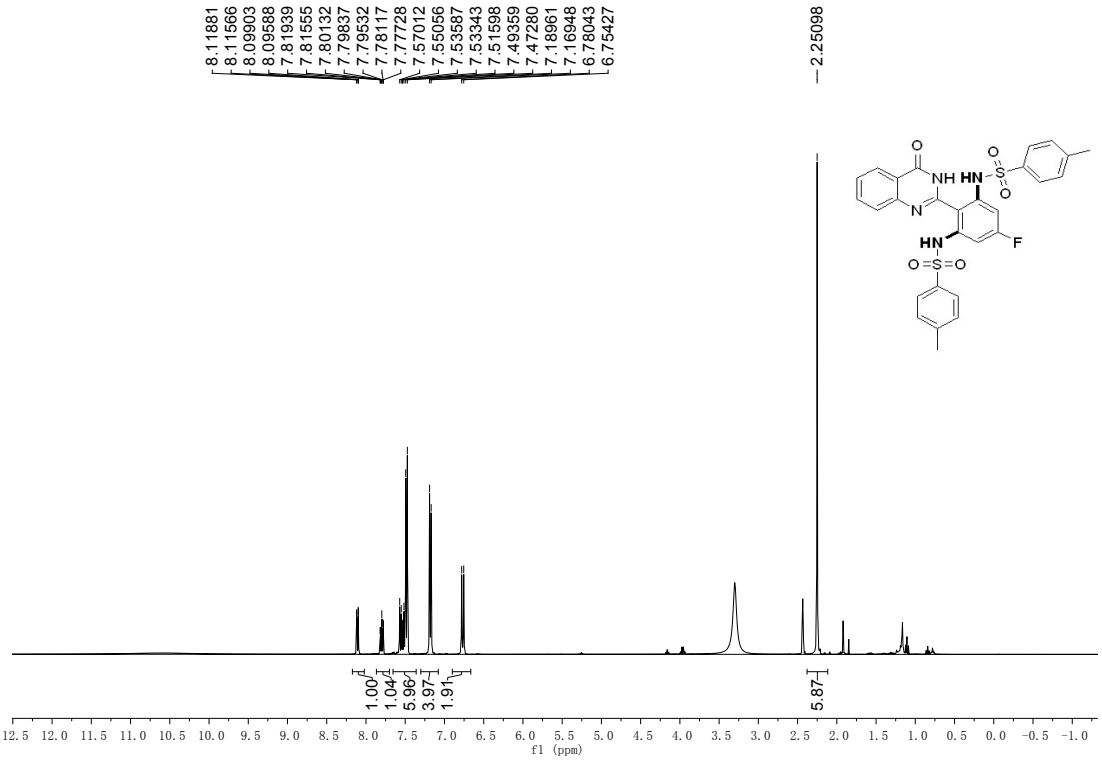


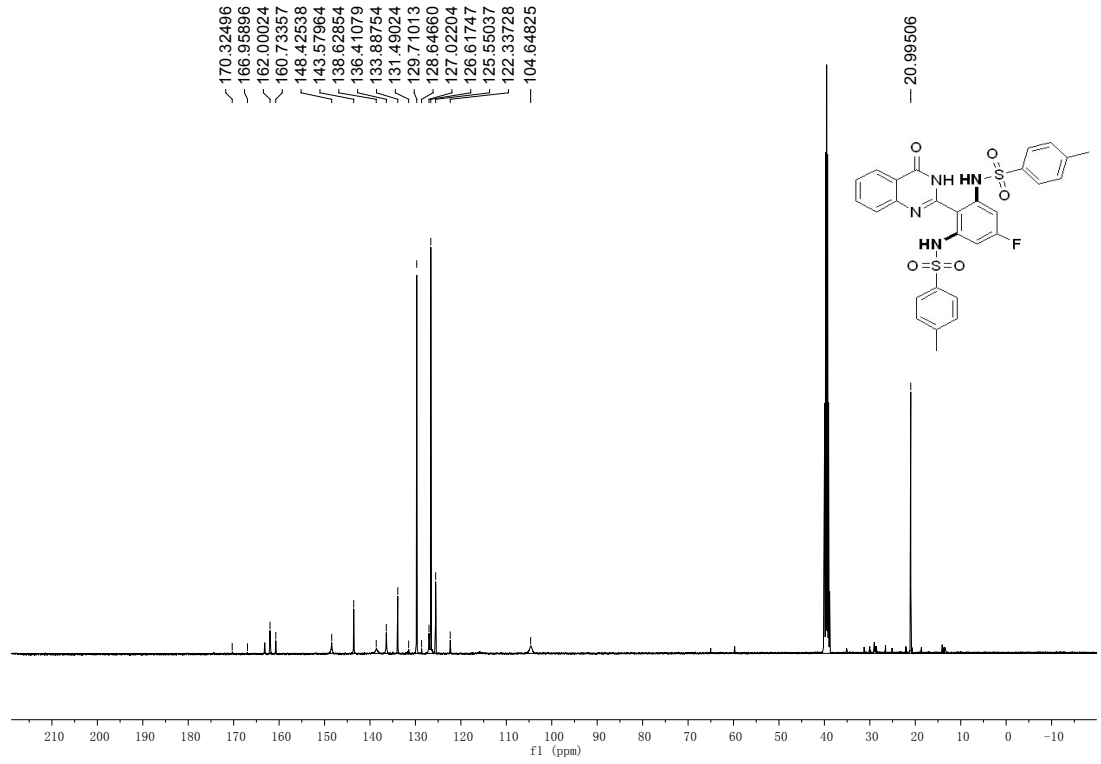
The ^{1}H and ^{13}C NMR spectra of **3e**



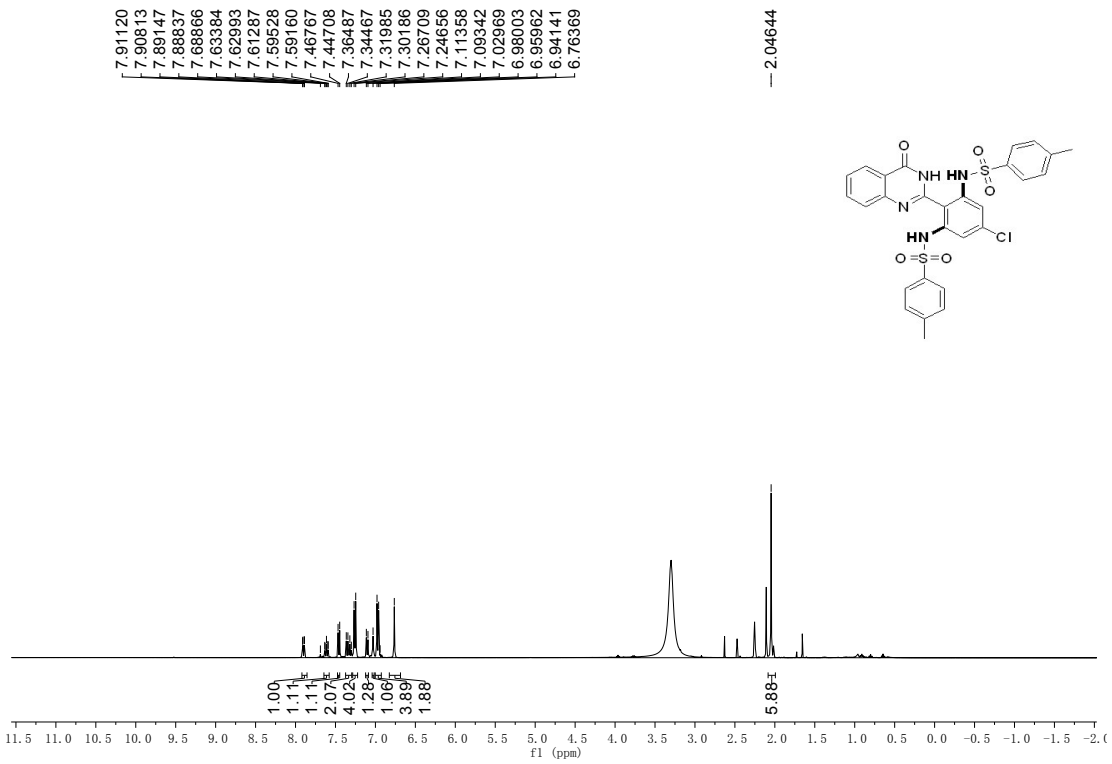


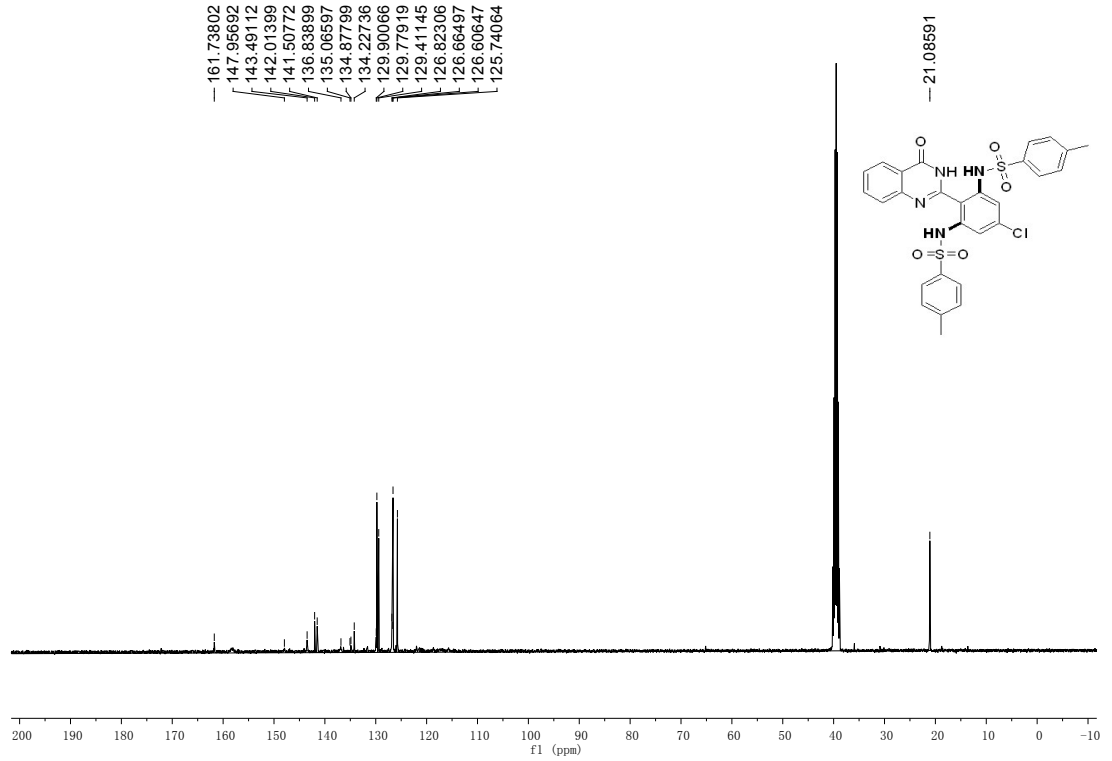
The ^{1}H and ^{13}C NMR spectra of **3f**



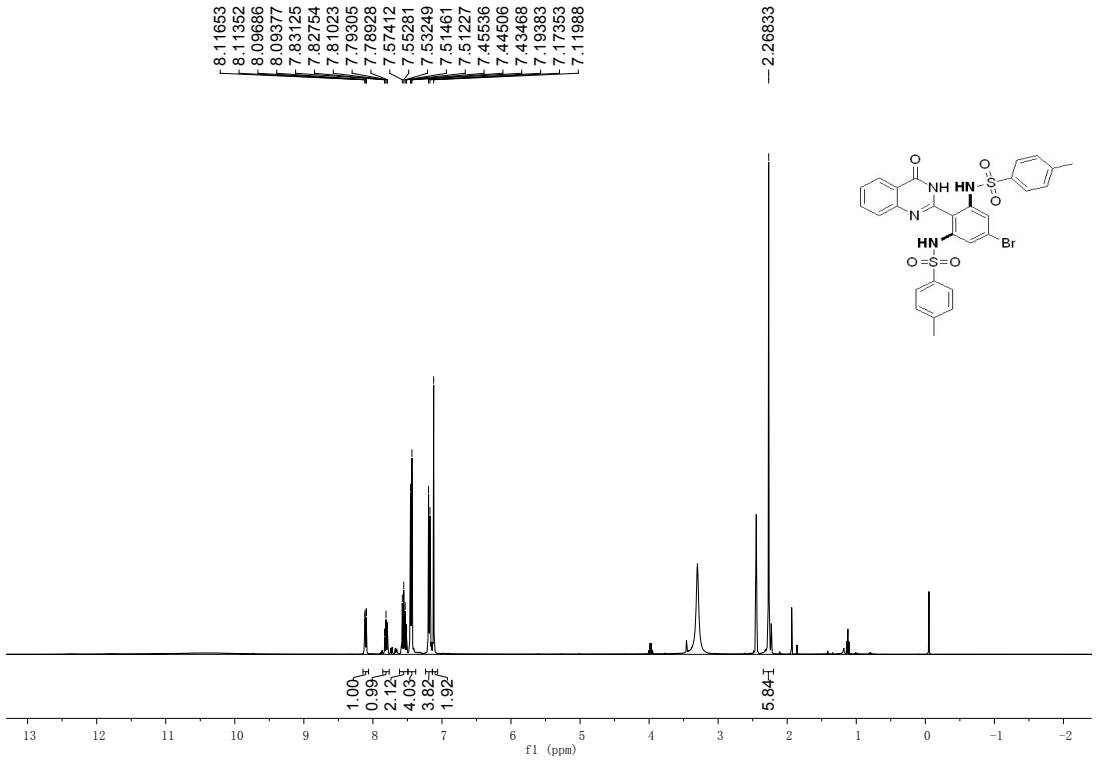


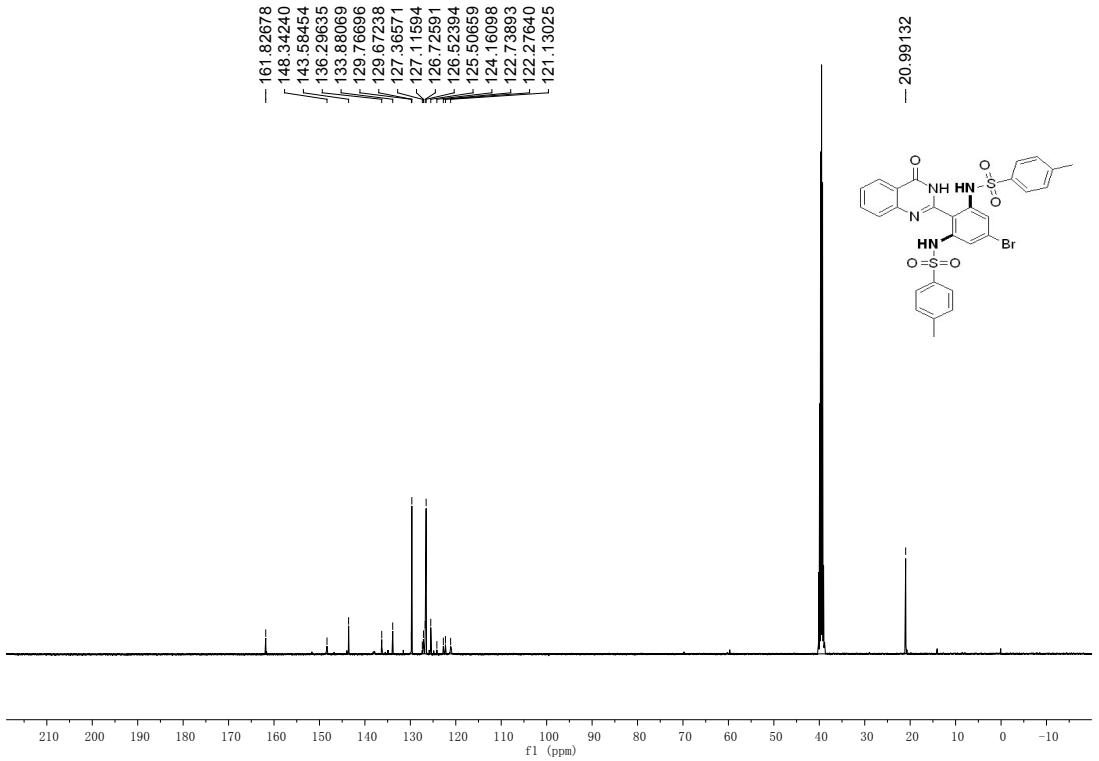
The ^{1}H and ^{13}C NMR spectra of **3g**



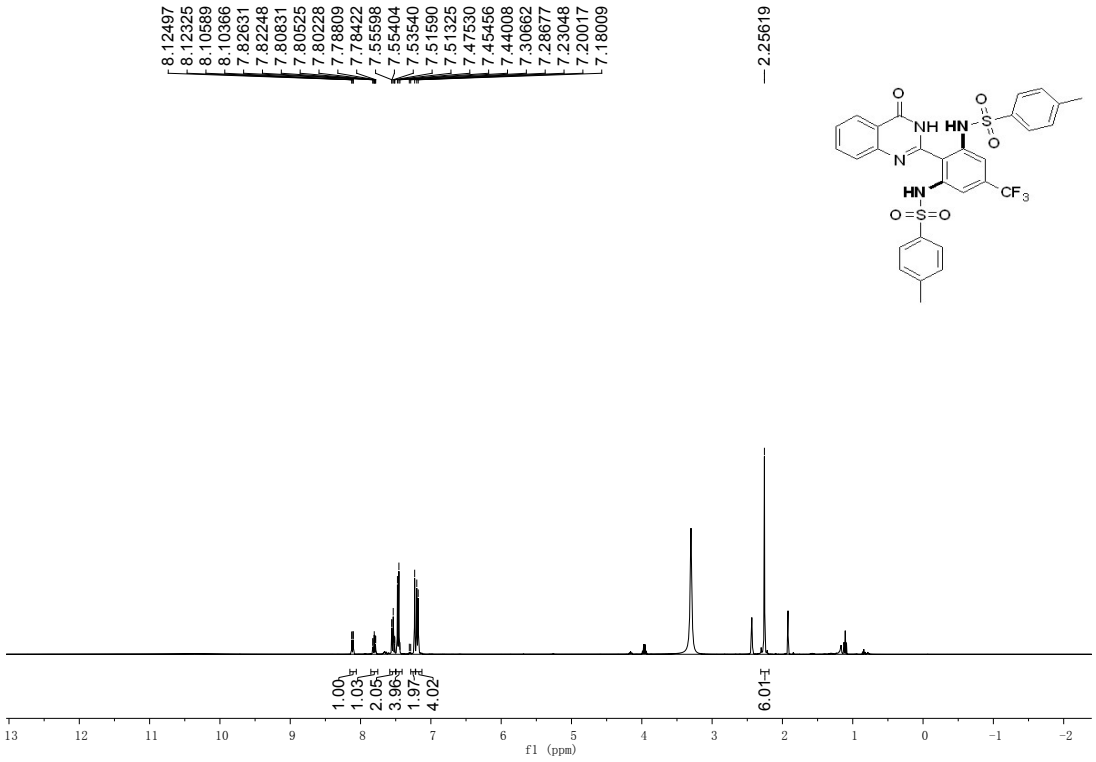


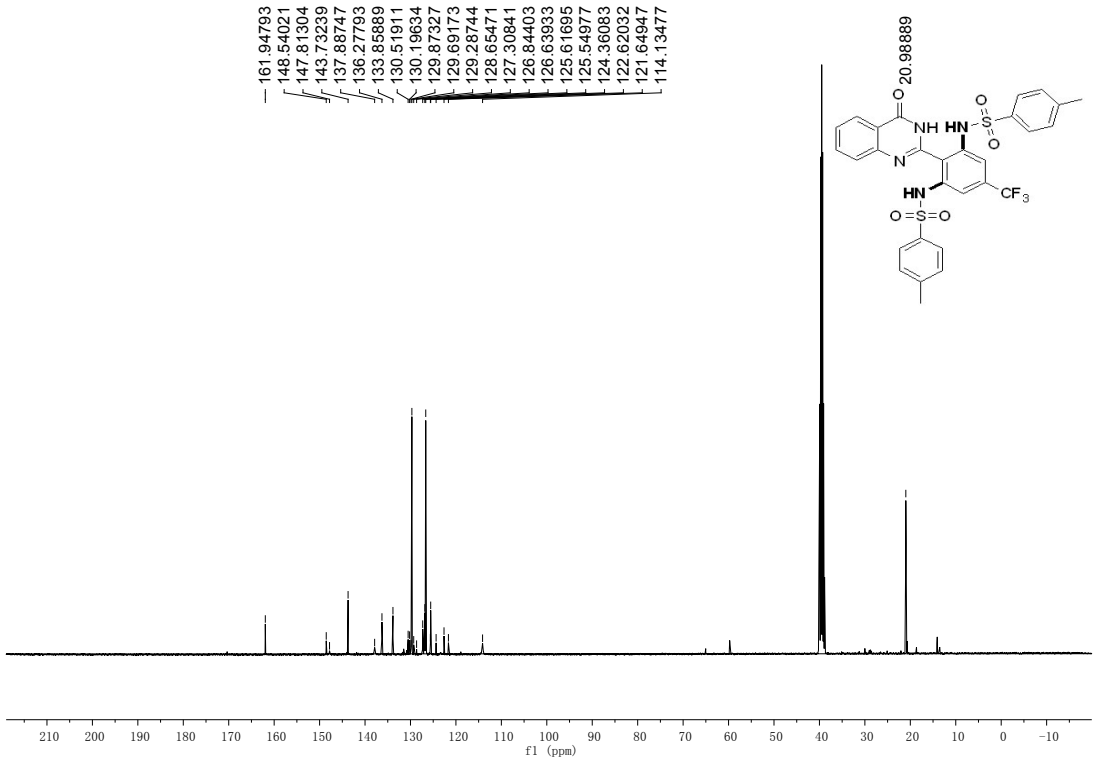
The ^{1}H and ^{13}C NMR spectra of **3h**



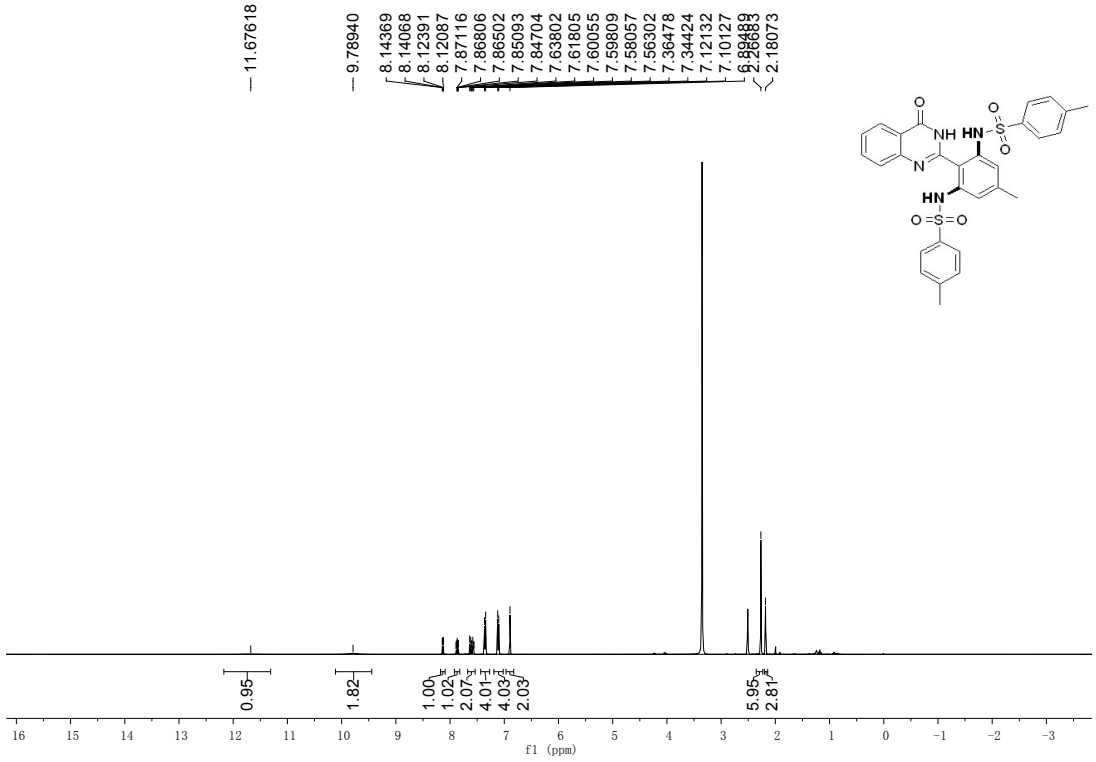


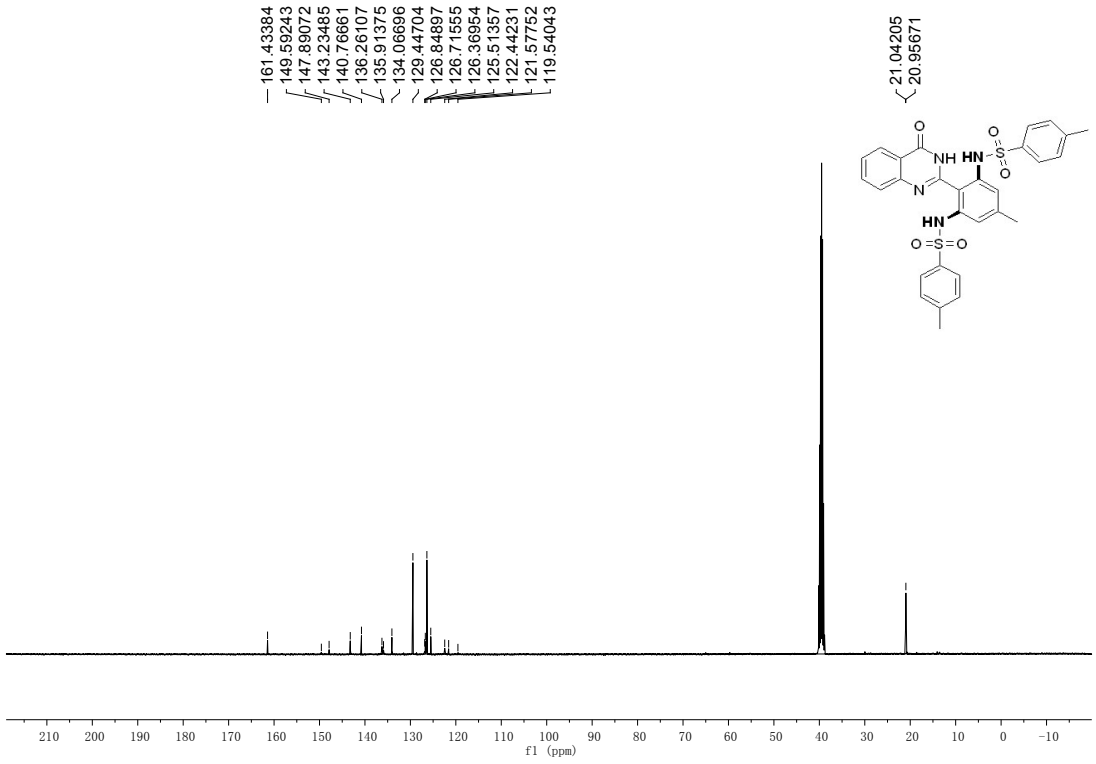
The ^{1}H and ^{13}C NMR spectra of **3i**



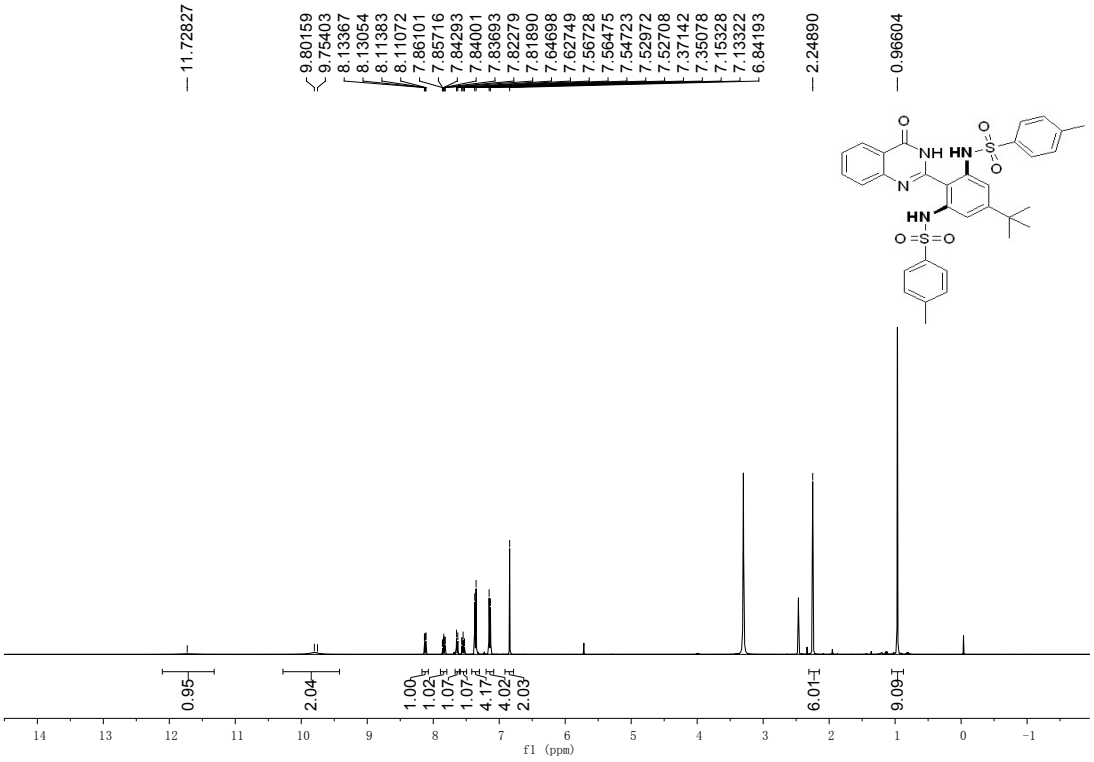


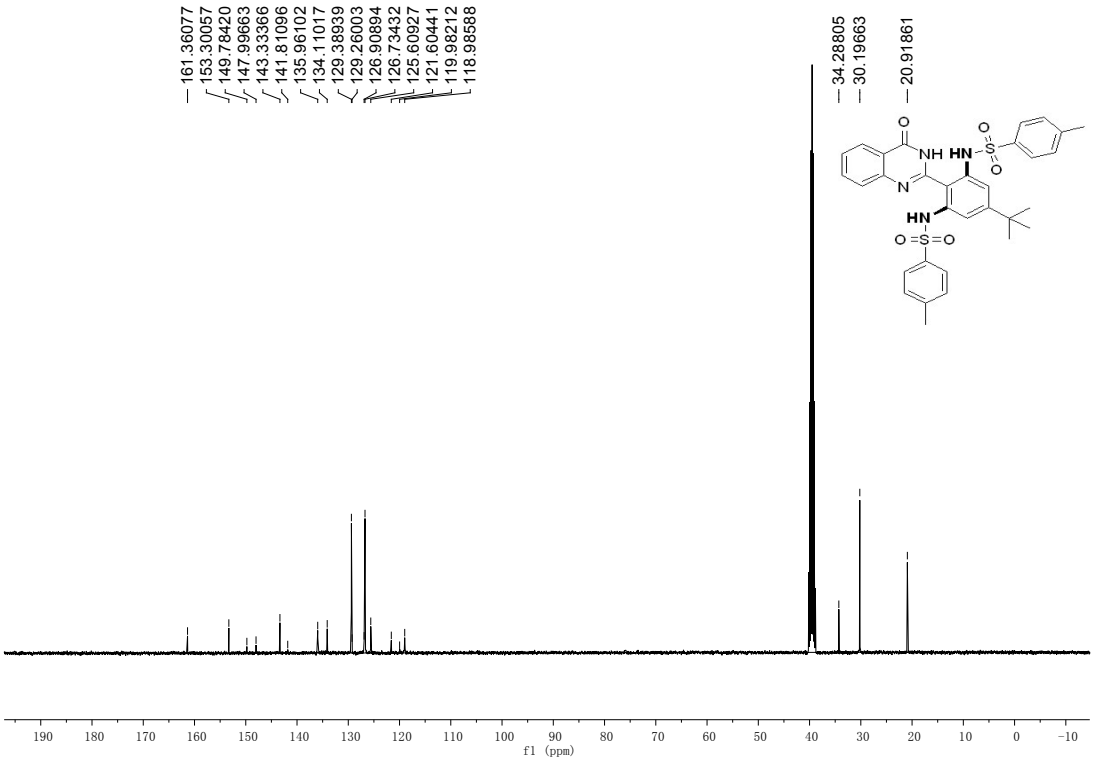
The ^{1}H and ^{13}C NMR spectra of **3j**



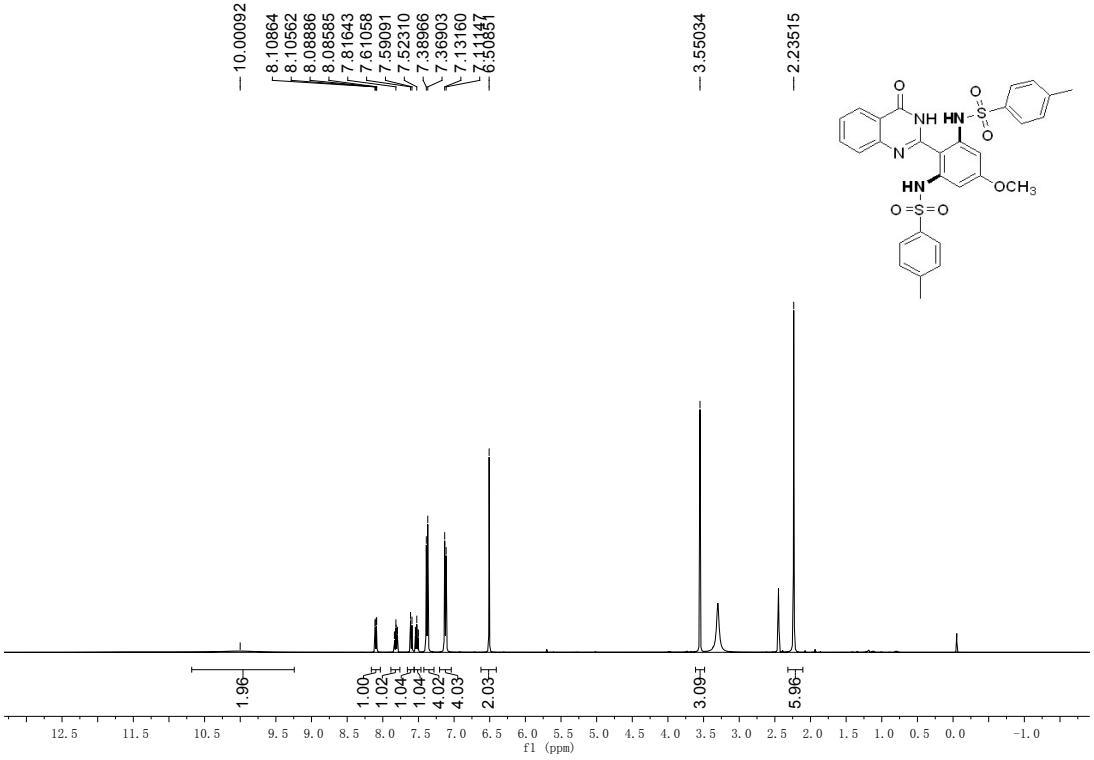


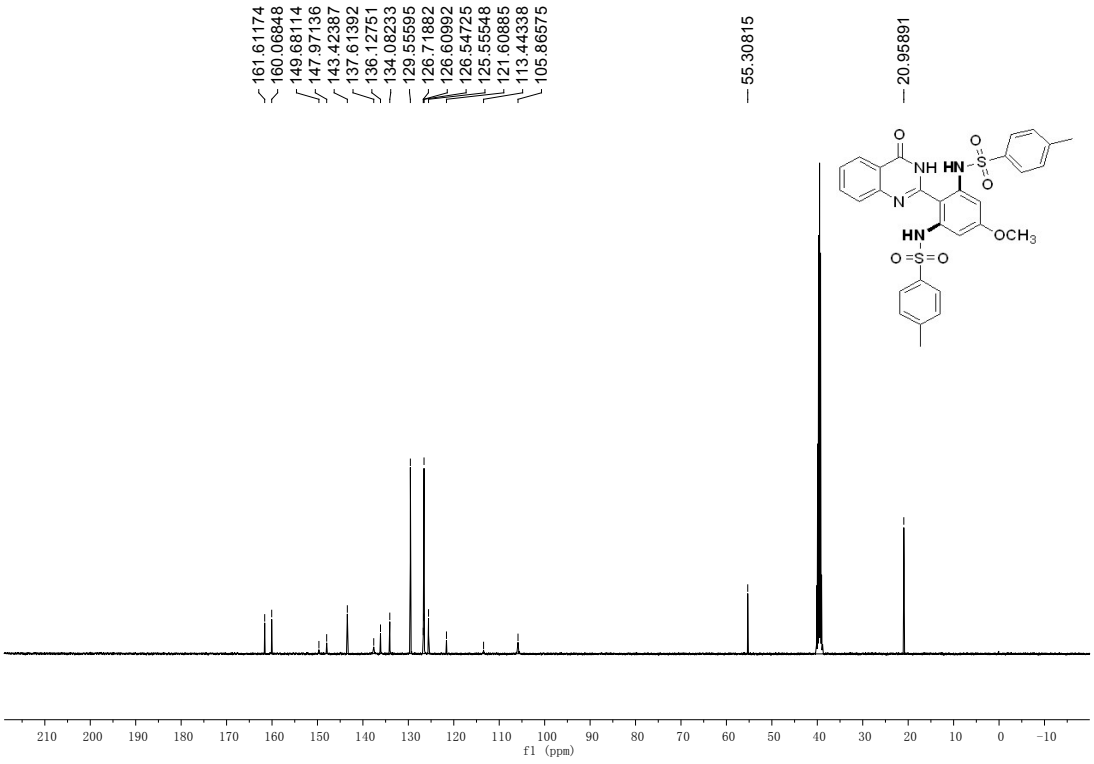
The ^{1}H and ^{13}C NMR spectra of **3k**



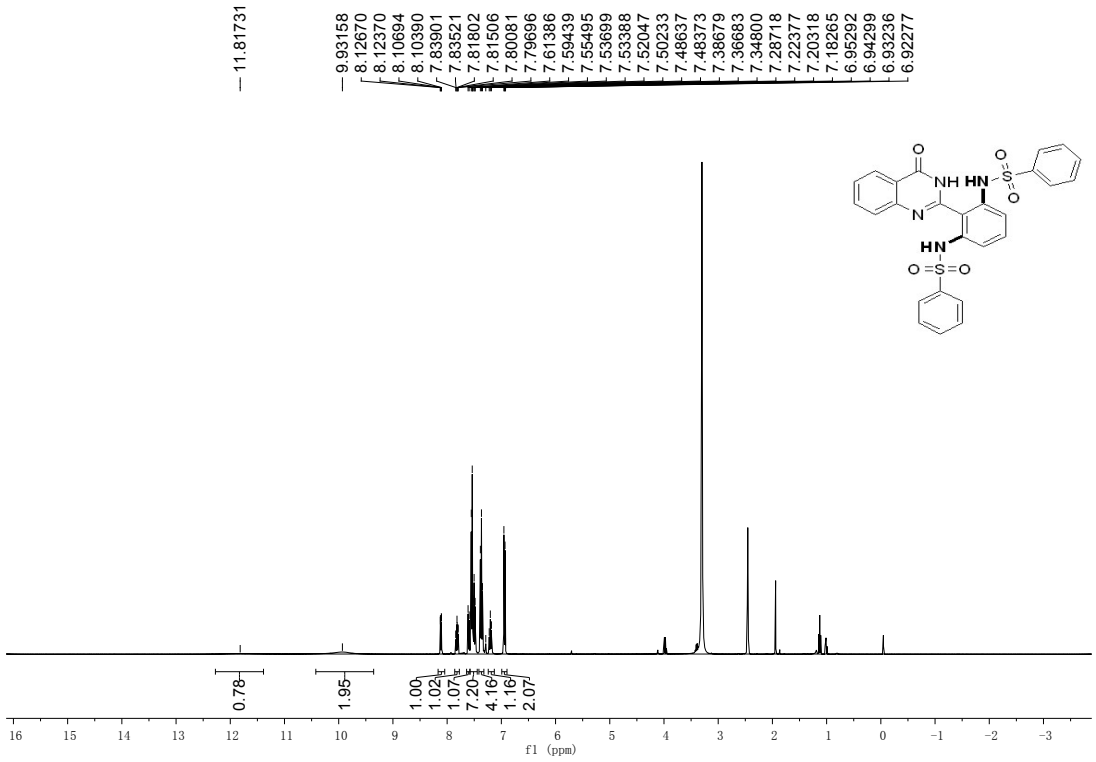


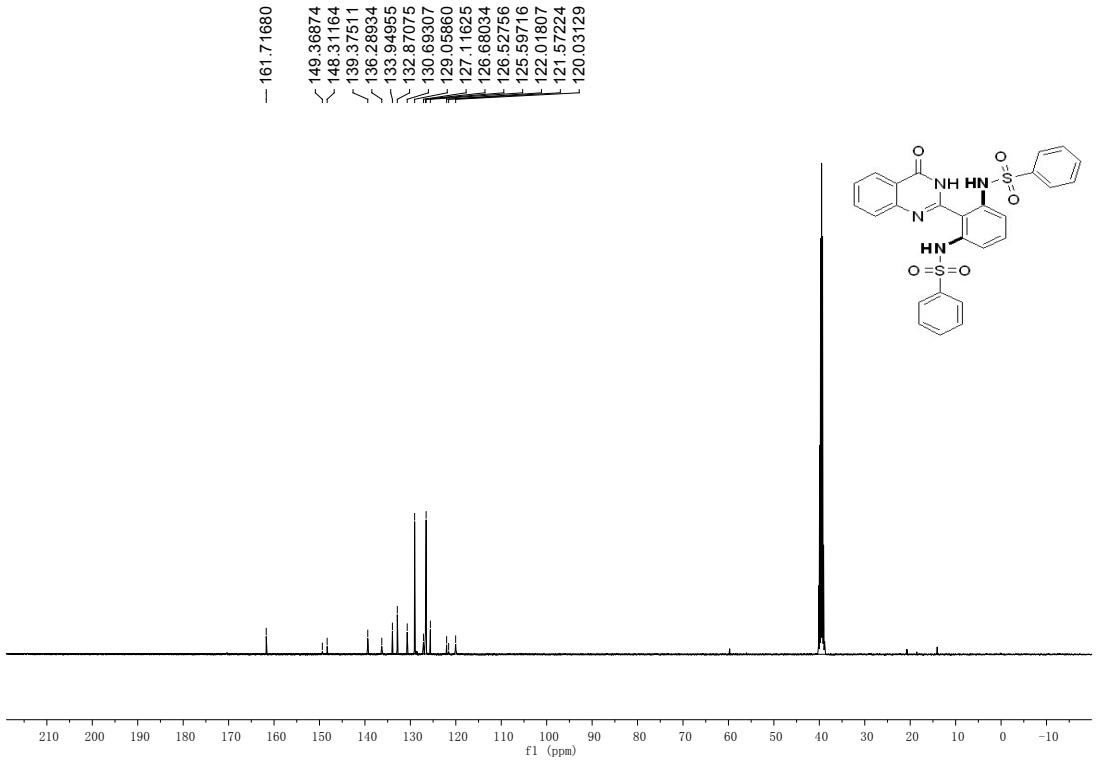
The ^{1}H and ^{13}C NMR spectra of **3l**



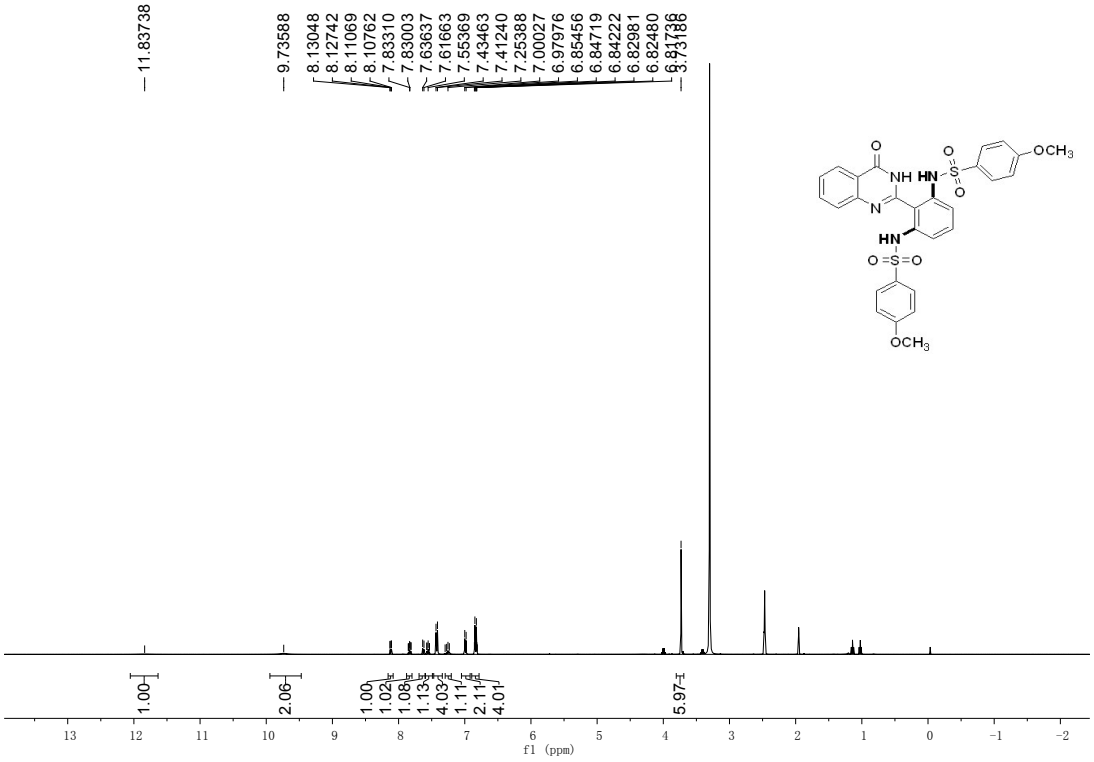


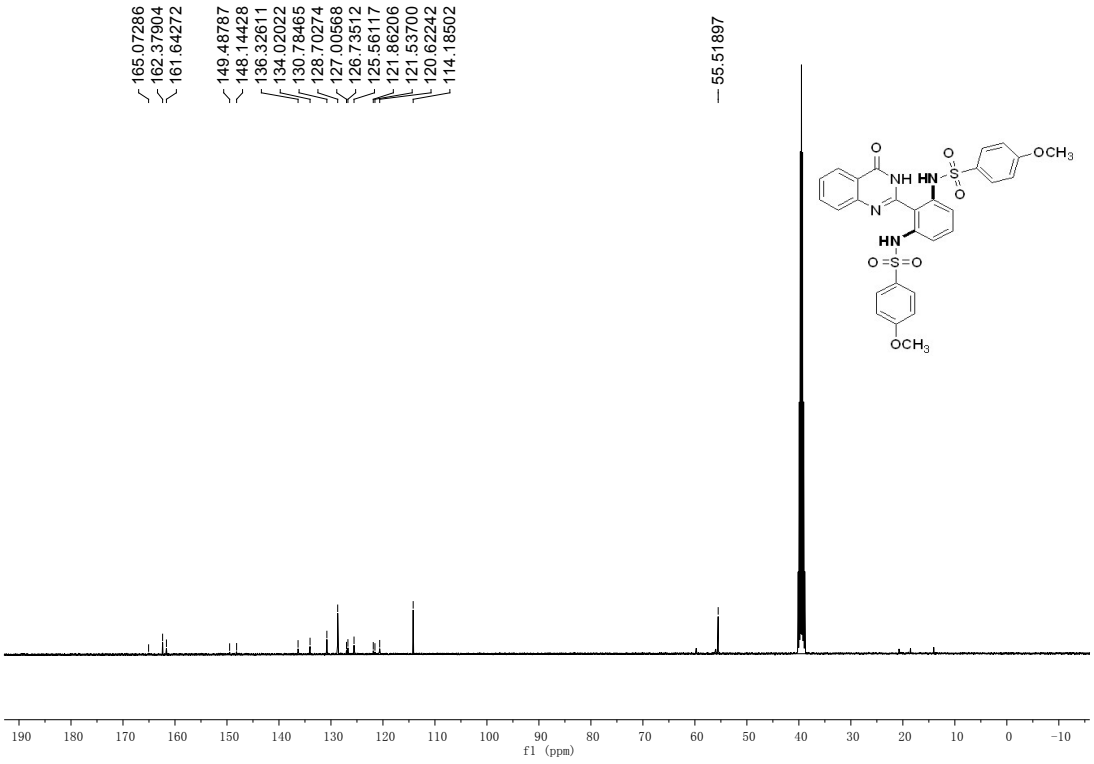
The ^{1}H and ^{13}C NMR spectra of **3m**



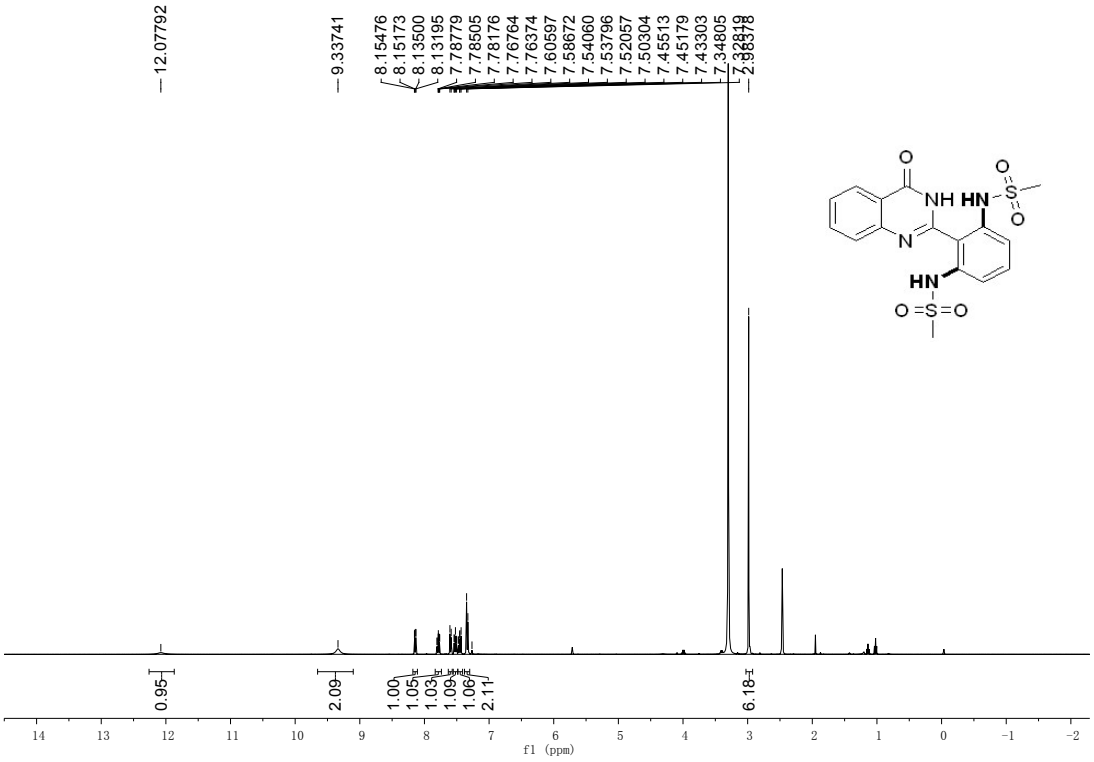


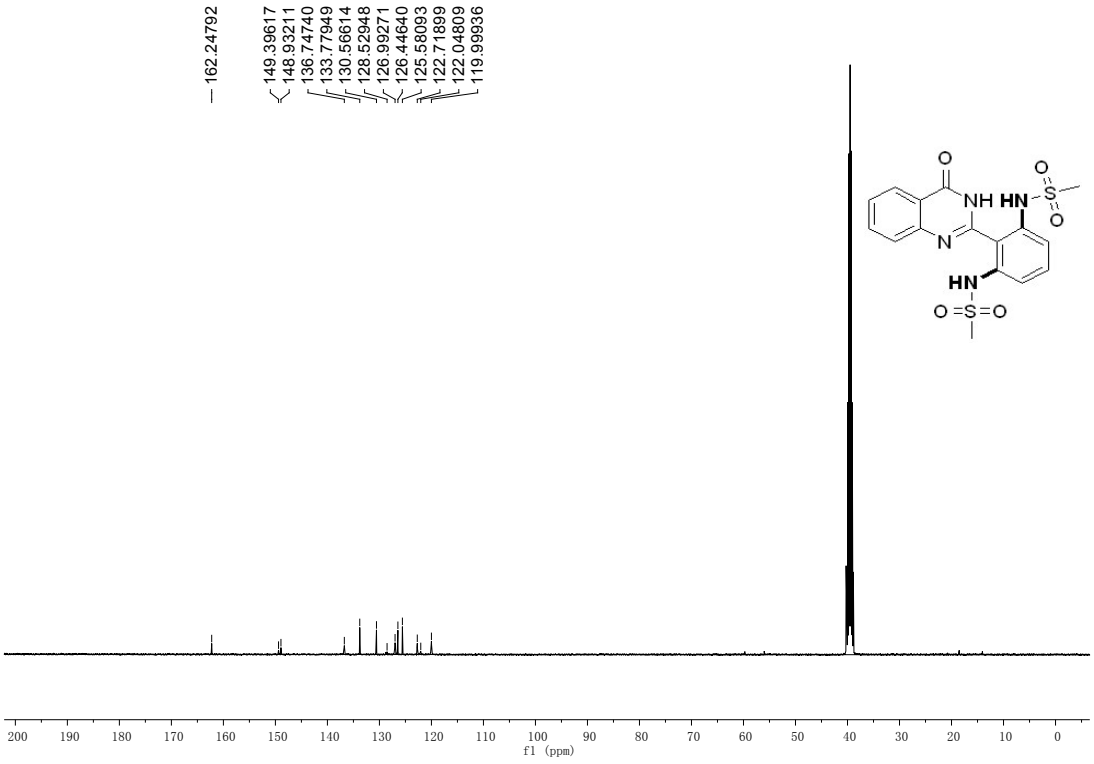
The ^{1}H and ^{13}C NMR spectra of **3n**



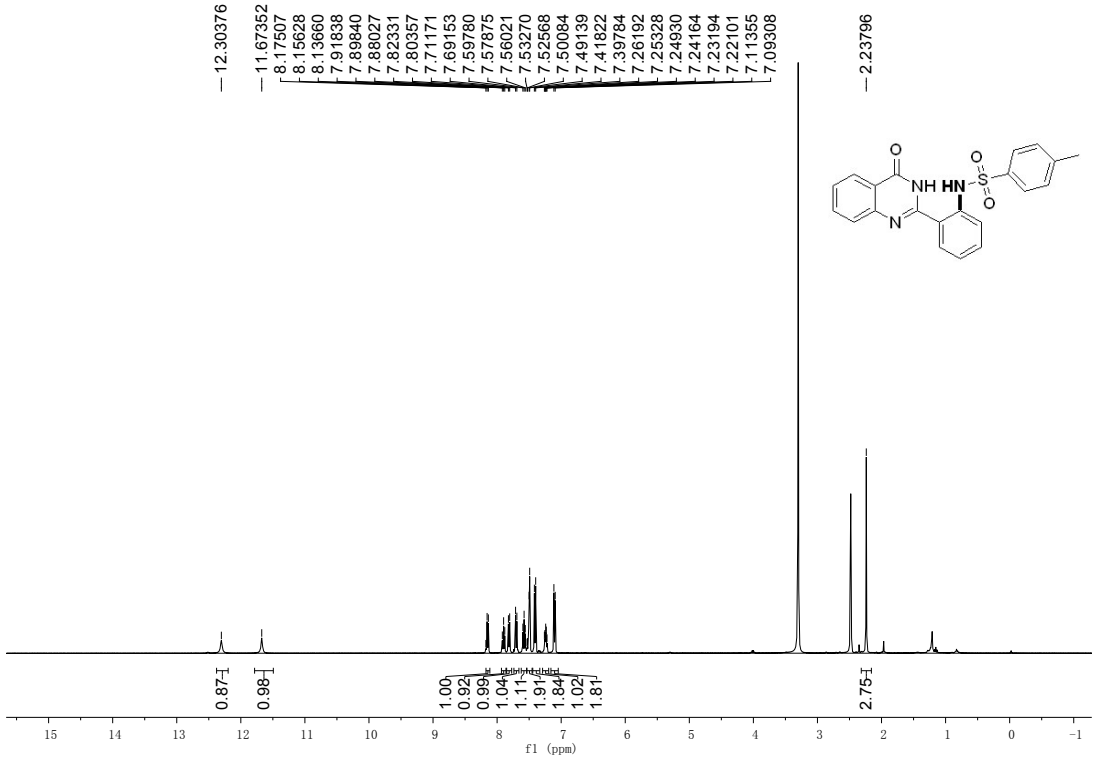


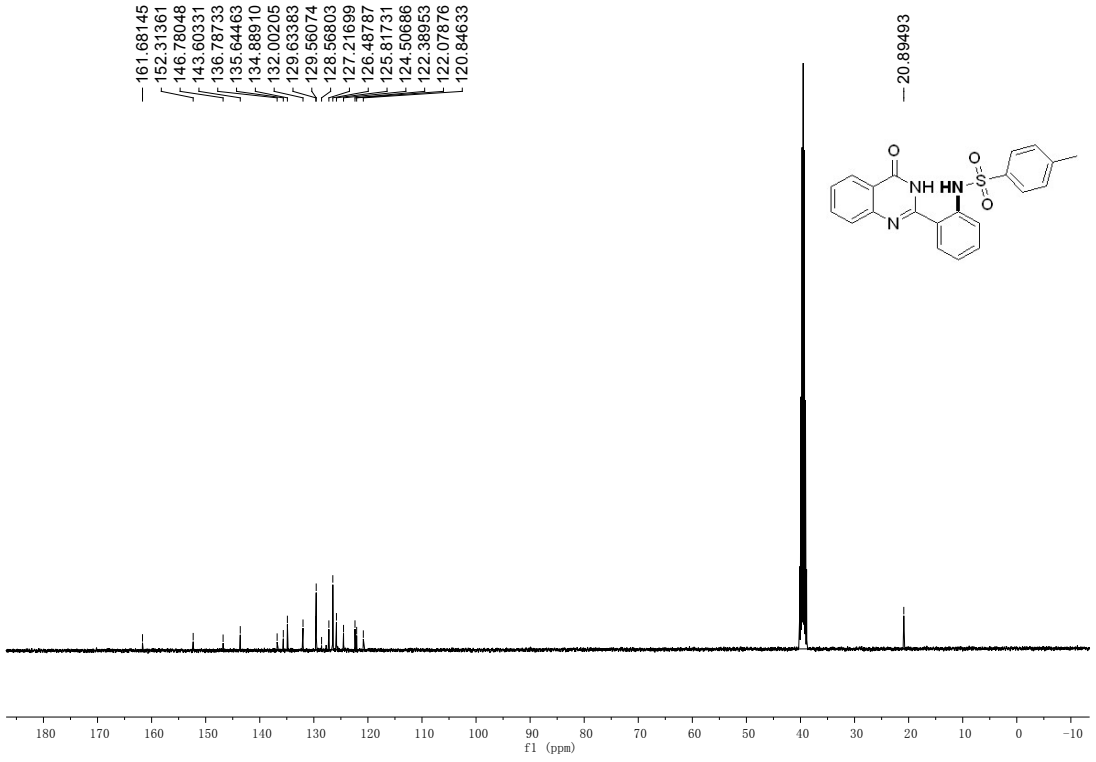
The ^{1}H and ^{13}C NMR spectra of **3o**





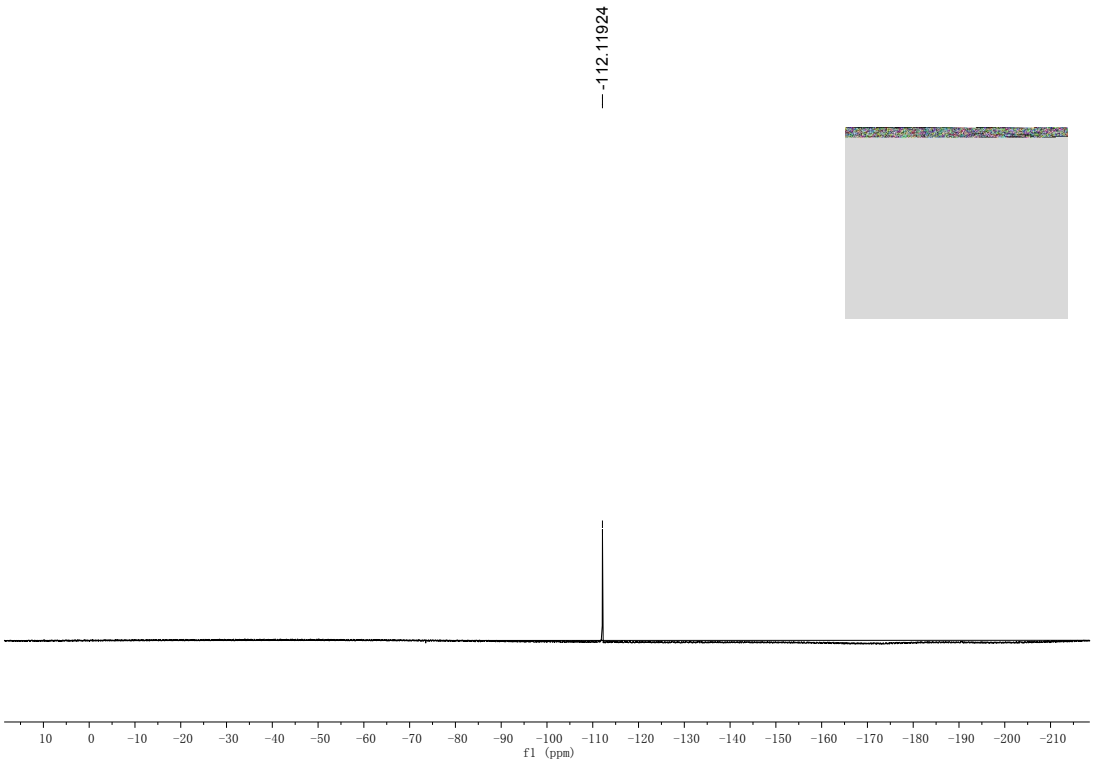
The ^{1}H and ^{13}C NMR spectra of **4a**



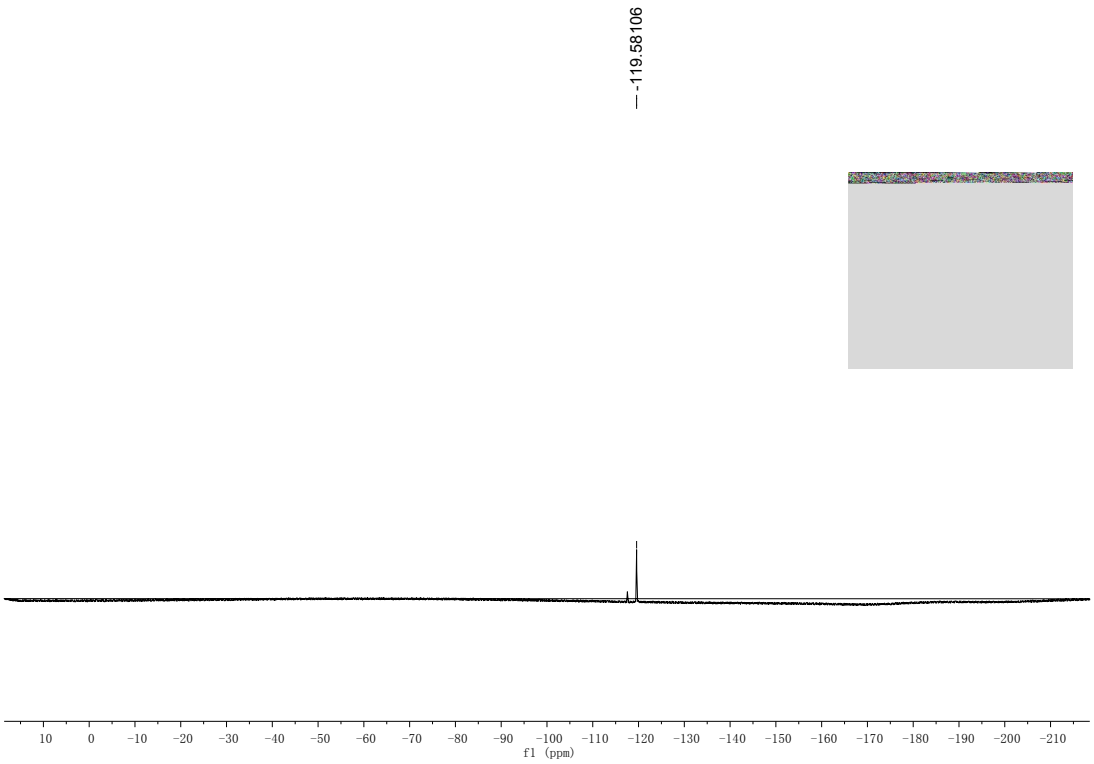


^{19}F NMR Spectra

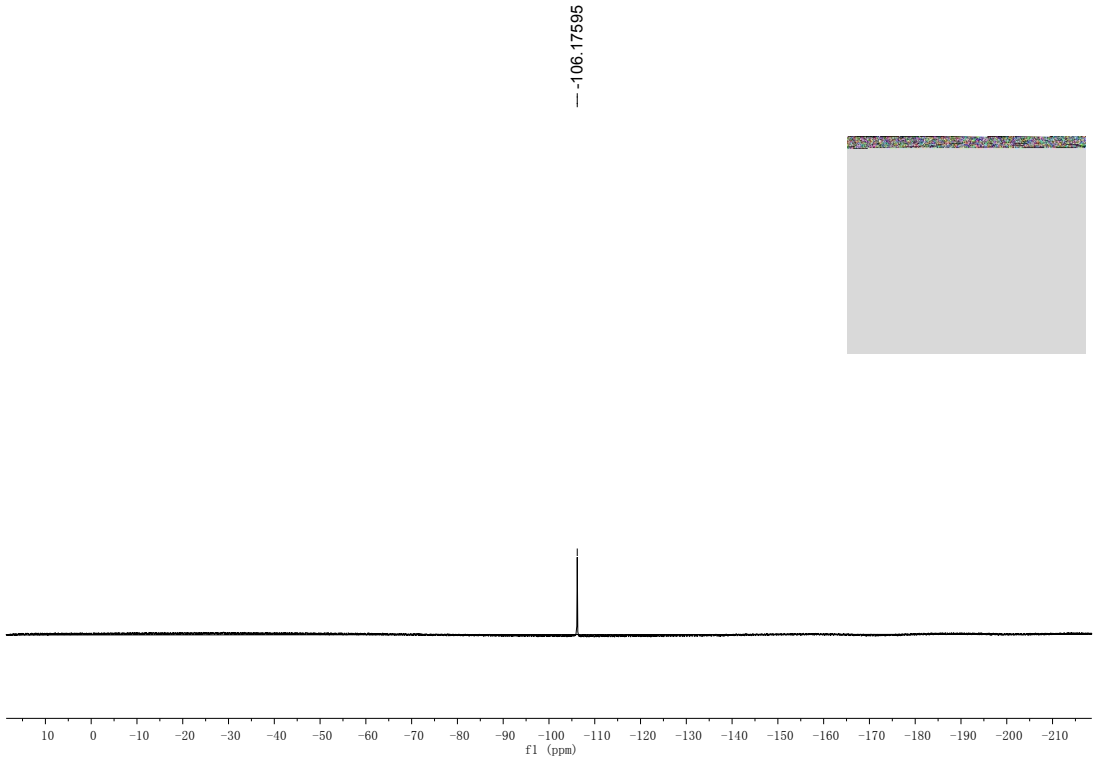
The ^{19}F NMR spectrum of **3b**



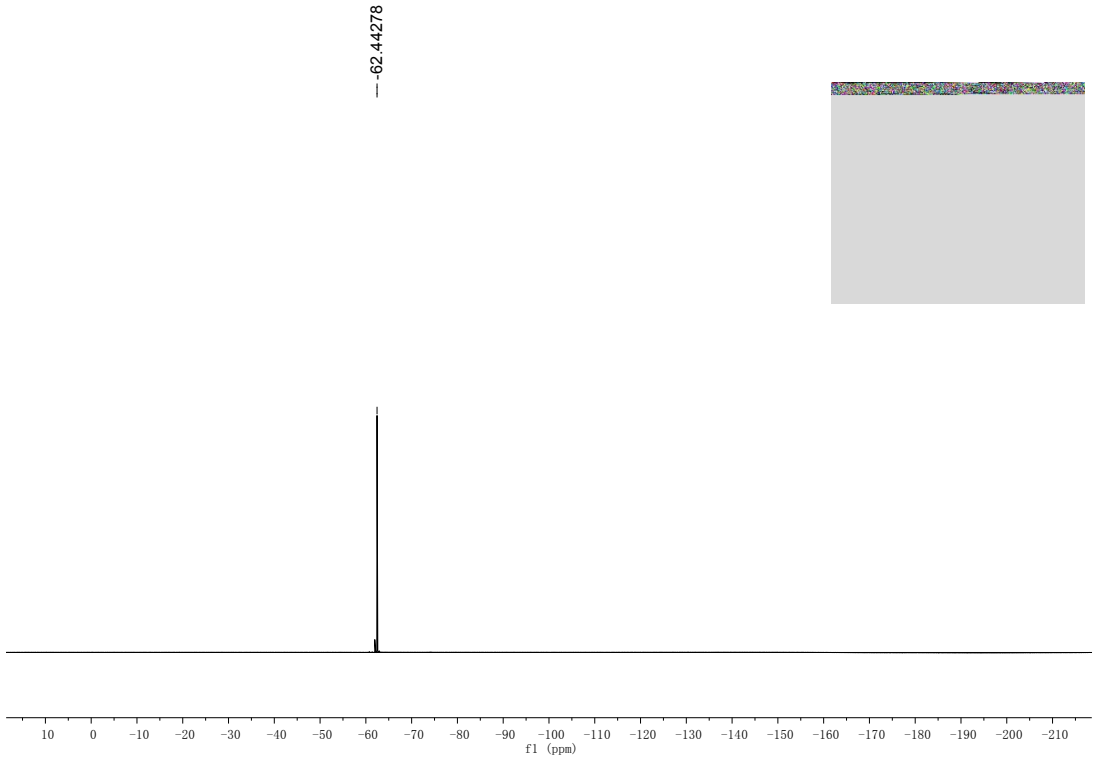
The ^{19}F NMR spectrum of **3e**



The ^{19}F NMR spectrum of **3f**



The ^{19}F NMR spectrum of **3i**



The HRMS of 3a and 4a

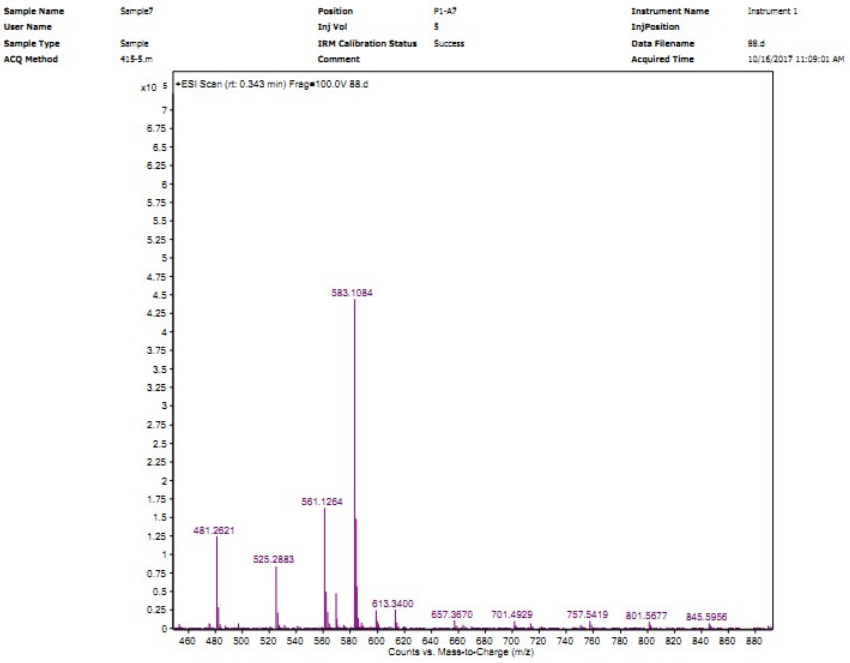


Figure S1. **3a** HRMS (ESI) *m/z* calcd for $C_{28}H_{24}N_4O_5S_2$ $[M + H]^+$ 561.1261, found 561.1264.

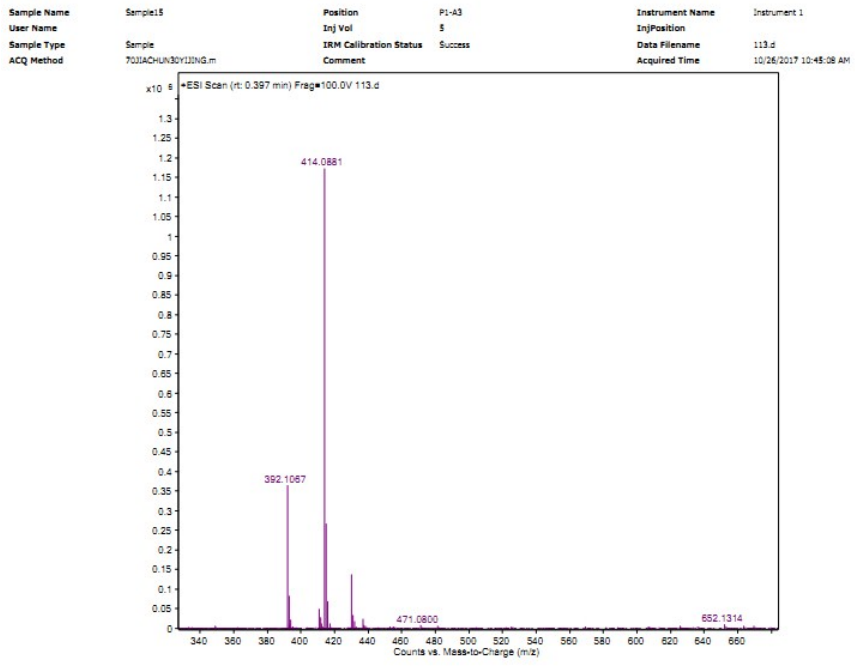


Figure S2. **4a** HRMS (ESI) *m/z* calcd for $C_{21}H_{17}N_3O_3S$ $[M + H]^+$ 392.1063, found 392.1067.