Rh-Catalyzed [4 + 2] Benzannulation Enabling the Construction of Quinazoline-2,4-diones from Uracil and Ynamides

Yuan-Jie Meng,[a] Yang Li,[a] Wen-Rong Wu,[a] Xin-Xing Liu,[a] Xiang Liu,*[b] Pengju Feng,*[a] Shang-Shi Zhang*[a]

[a]*Center for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China.*

[b]*School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China.*

E-mail: zhangshangshi@gdpu.edu.cn.

E-mail: fengpengju@gdpu.edu.cn.

E-mail: liux96@gdpu.edu.cn.

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, MeCN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra HRMS-ESI (TOF) was recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1 and 2

The substrates of 6-Methyluracil-5-carbaldehyde derivatives **1** were prepared according to the previous procedure.[1] The substrates of ynamides **2** were prepared according to the previous procedure.[2] All the characteristic data are consistent with the data reported before.

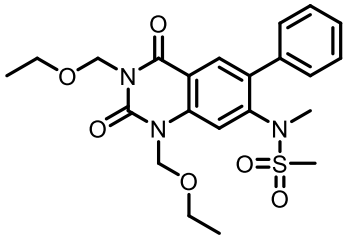
3. General procedure and characterization of products

(a) General procedure A

In an oven-dried Schlenk tube, a mixture of the 6-Methyluracil-5-carbaldehyde derivatives **1** (0.1 mmol, 1.0 equiv), ynamides **2** (0.2 mmol, 2.0 equiv), [Cp*Rh($MeCN_3$)(SbF_6)$_2$ (5.0 mol%), CsOPiv (0.1 mmol, 1.0 equiv) and Toluene (0.5 mL, 0.2 M) was stirred at 80 °C in the oil bath for 8.0 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3** or **4**.

(b) Characterization of products

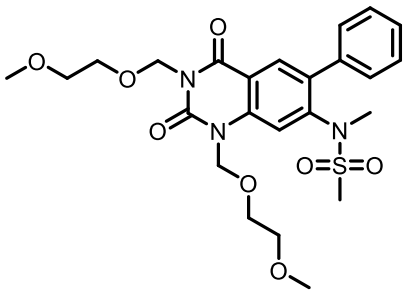
***N*-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (3a)**



Following the above procedure A, the product **3a** was obtained in 72% yield (66.5 mg, 0.142 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.52 (s, 1H), 7.49 – 7.37 (m, 5H), 5.64 (s, 2H), 5.58 (s, 2H), 3.71 (qd, *J* = 7.0, 2.0 Hz, 4H), 3.14 (s, 3H), 2.58 (s, 3H), 1.23 (td, *J* = 7.0, 3.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.24, 151.31, 145.84, 139.64, 137.77, 137.40, 131.67, 129.14, 128.60, 128.12, 115.44, 115.18, 73.95, 71.18, 65.98, 64.79, 38.91, 38.72, 15.23, 15.02. ESI-MS: calculate $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290; Found 317.1289. ESI-MS: calculated $C_{22}H_{28}N_3O_6S$ $[M+H]^+$ 462.1699; Found 462.1698.

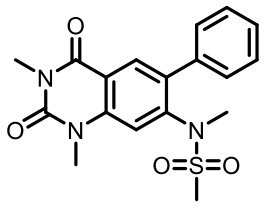
***N*-(1,3-bis((2-methoxyethoxy)methyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (3b)**

Following the above procedure A, the product **3b** was obtained in 58% yield (60.4 mg, 0.116 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f



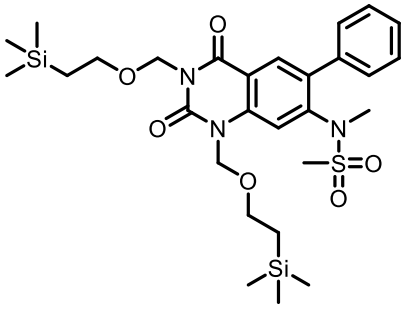
(Petroleum ether/EtOAc 1:3): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.51 (s, 1H), 7.47 – 7.37 (m, 5H), 5.67 (s, 2H), 5.62 (s, 2H), 4.00 – 3.74 (m, 4H), 3.53 (q, J = 4.9 Hz, 4H), 3.34 (s, 3H), 3.32 (s, 3H), 3.14 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.23, 151.38, 145.92, 139.59, 137.77, 137.58, 131.63, 129.15, 128.59, 128.11, 115.46, 115.19, 74.29, 71.74, 71.42, 69.87, 68.35, 59.06, 38.86, 38.74. ESI-MS: calculated $C_{24}H_{31}N_3O_8SNa$ $[M+Na]^+$ 544.1730; Found 544.1733.

_N_-(1,3-dimethyl-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3c)



Following the above procedure A, the product **3c** was obtained in 54% yield (40.2 mg, 0.108 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.48 – 7.36 (m, 5H), 7.25 (s, 1H), 3.64 (s, 3H), 3.50 (s, 3H), 3.17 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.25, 151.10, 145.51, 140.39, 137.97, 136.57, 131.57, 129.20, 128.60, 128.12, 115.05, 114.39, 39.09, 38.96, 31.08, 28.68. ESI-MS: calculated $C_{18}H_{20}N_3O_4S$ $[M+H]^+$ 374.1175; Found 374.1179.

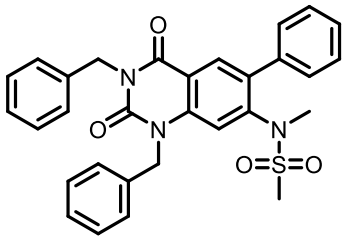
_N_-(2,4-dioxo-6-phenyl-1,3-bis((2-(trimethylsilyl)ethoxy)methyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3d)



Following the above procedure A, the product **3d** was obtained in 54% yield (65.4 mg, 0.108 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). R_f (Petroleum ether/EtOAc 4:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.49 (s, 1H), 7.47 – 7.37 (m, 5H), 5.62 (s, 2H), 5.55 (s, 2H), 3.72 (td, J = 9.1, 7.8 Hz, 4H), 3.13 (s, 3H), 2.57 (s, 3H), 1.03 – 0.79 (m, 4H), -0.00 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.29, 151.35, 145.85, 139.79, 137.90, 137.36, 131.77, 129.26, 128.69,

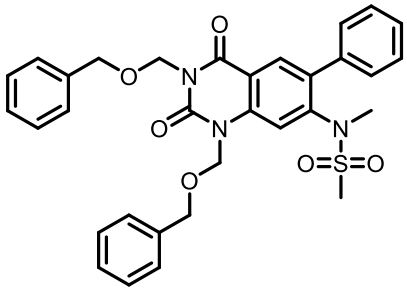
128.19, 115.48, 115.28, 73.75, 70.86, 67.74, 67.02, 39.07, 38.76, 18.29, 18.04, -1.20, -1.28. ESI-MS: calculated $C_{28}H_{43}N_3O_6SSi_2Na$ $[M+Na]^+$ 628.2309; Found 628.2307.

_N_-(1,3-dibenzyl-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3e)



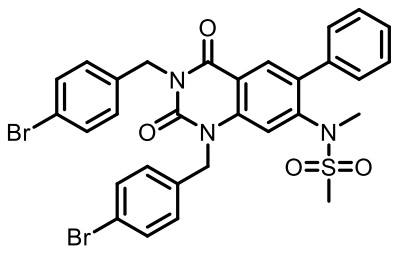
Following the above procedure A, the product **3e** was obtained in 36% yield (37.4 mg, 0.072 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.52 (d, J = 7.0 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.37 – 7.32 (m, 5H), 7.31 (d, J = 4.8 Hz, 2H), 7.28 (t, J = 3.5 Hz, 3H), 7.13 (s, 1H), 5.41 (s, 2H), 5.35 (s, 2H), 2.92 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01, 151.35, 145.34, 139.61, 137.70, 136.74, 136.64, 135.37, 131.89, 129.20, 129.08, 128.89, 128.56, 128.05, 127.98, 127.77, 126.65, 126.40, 115.35, 114.90, 47.67, 45.27, 38.56, 38.47. ESI-MS: calculated $C_{30}H_{28}N_3O_4S$ $[M+H]^+$ 526.1801; Found 526.1801.

_N_-(1,3-bis((benzyloxy)methyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3f)



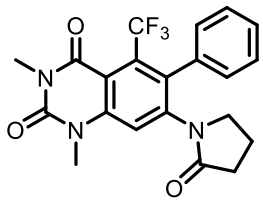
Following the above procedure A, the product **3f** was obtained in 48% yield (55.8 mg, 0.096 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.50 (s, 1H), 7.48 – 7.36 (m, 8H), 7.34 – 7.27 (m, 7H), 5.71 (s, 2H), 5.63 (s, 2H), 4.73 (s, 2H), 4.70 (s, 2H), 3.13 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.16, 151.25, 145.83, 139.46, 137.75, 137.47, 137.01, 131.67, 129.21, 129.16, 128.63, 128.46, 128.36, 128.16, 128.10, 127.90, 127.79, 127.77, 115.51, 115.10, 73.84, 72.30, 71.41, 70.98, 38.97, 38.72. ESI-MS: calculated $C_{32}H_{31}N_3O_6SNa$ $[M+Na]^+$ 608.1831; Found 608.1835.

_N_-(1-(3-bromobenzyl)-3-(4-bromobenzyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3g)



Following the above procedure A, the product **3g** was obtained in 50% yield (66.6 mg, 0.100 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.34 (m, 5H), 7.33 – 7.27 (m, 4H), 7.26 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.28 (s, 2H), 5.20 (s, 2H), 2.89 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.96, 151.16, 145.57, 139.36, 137.49, 136.91, 135.48, 134.25, 132.22, 131.87, 131.60, 130.68, 128.97, 128.57, 128.47, 128.14, 121.88, 121.81, 115.08, 114.85, 46.98, 44.63, 38.57, 38.51. ESI-MS: calculated $C_{30}H_{26}Br_2N_3O_4S$ $[M+H]^+$ 682.0011; Found 682.0012.

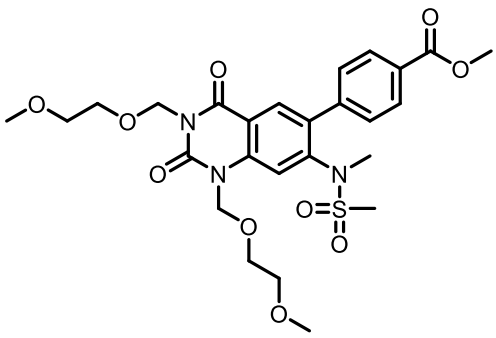
1,3-dimethyl-7-(2-oxopyrrolidin-1-yl)-6-phenyl-5-(trifluoromethyl)quinazoline-2,4(1*H*,3*H*)-dione (3h)



Following the above procedure A, the product **3h** was obtained in 25% yield (20.9 mg, 0.050 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 3H), 7.38 (s, 1H), 7.28 – 7.24 (m, 2H), 3.63 (s, 3H), 3.49 (s, 3H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 1.74 (p, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.93, 159.31, 150.56, 144.01, 141.65, 136.29 (d, *J* = 2.7 Hz), 135.77, 131.03 (d, *J* = 31.8 Hz), 128.79 (d, *J* = 1.9 Hz), 128.45, 128.20, 122.82 (d, *J* = 277.6 Hz), 118.15, 114.07, 49.91, 31.63, 30.75, 29.23, 19.20. ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.31. ESI-MS: calculated $C_{21}H_{19}F_3N_3O_3$ $[M+H]^+$ 418.1379; Found 418.1382.

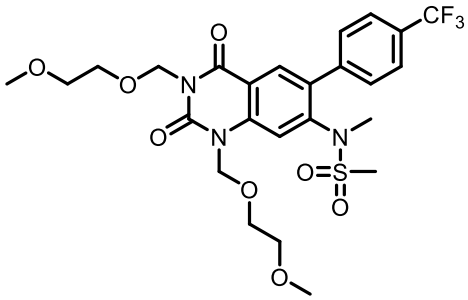
Methyl 4-(1,3-bis((2-methoxyethoxy)methyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (3i)

Following the above procedure A, the product **3i** was obtained in 56% yield (64.9 mg, 0.112 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f



(Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.15 – 8.07 (m, 2H), 7.51 (d, *J* = 2.8 Hz, 2H), 7.49 (s, 1H), 5.68 (s, 2H), 5.61 (s, 2H), 3.93 (s, 3H), 3.85 – 3.75 (m, 4H), 3.54 – 3.50 (m, 4H), 3.32 (s, 3H), 3.32 (s, 3H), 3.13 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.70, 161.11, 151.29, 145.72, 142.34, 140.00, 136.60, 131.54, 129.80, 129.67, 129.24, 115.28, 115.23, 74.27, 71.79, 71.73, 71.38, 69.92, 68.35, 59.06, 59.04, 52.34, 38.72, 38.55. ESI-MS: calculated $C_{26}H_{33}N_3O_{10}SNa$ $[M+Na]^+$ 602.1784; Found 602.1785.

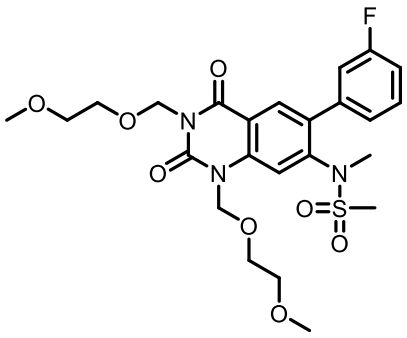
_N_-(1,3-bis((2-methoxyethoxy)methyl)-2,4-dioxo-6-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3j)



Following the above procedure A, the product **3j** was obtained in 48% yield (56.6 mg, 0.096 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.53 (s, 1H), 5.68 (s, 2H), 5.62 (s, 2H), 3.90 – 3.74 (m, 4H), 3.58 – 3.49 (m, 4H), 3.33 (s, 6H), 3.12 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.04, 151.27, 145.69, 141.28, 140.07, 136.26, 131.69, 130.16 (d, *J* = 32.7 Hz), 129.57, 125.51 (dd, *J* = 7.3, 3.5 Hz), 124.02 (d, *J* = 272.1 Hz), 115.37, 115.05, 74.28, 71.81, 71.73, 71.36, 69.94, 68.34, 59.06, 59.03, 38.71, 38.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49. ESI-MS: calculated $C_{25}H_{30}F_3N_3O_8SNa$ $[M+Na]^+$ 612.1603; Found 612.1606.

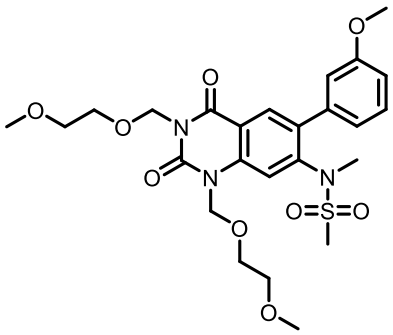
_N_-(6-(3-fluorophenyl)-1,3-bis((2-methoxyethoxy)methyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3k)

Following the above procedure A, the product **3k** was obtained in 60% yield (64.7 mg, 0.120 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f



(Petroleum ether/EtOAc 1:3): 0.20.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.51 (s, 1H), 7.45 – 7.37 (m, 1H), 7.24 – 7.19 (m, 1H), 7.17 – 7.05 (m, 2H), 5.67 (s, 2H), 5.61 (s, 2H), 3.96 – 3.74 (m, 4H), 3.58 – 3.49 (m, 4H), 3.32 (s, 3H), 3.32 (s, 3H), 3.13 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.58 (d, *J* = 247.1 Hz), 161.11, 151.31, 145.73, 139.88, 139.74 (d, *J* = 7.9 Hz), 136.33 (d, *J* = 2.2 Hz), 131.61, 130.18 (d, *J* = 8.4 Hz), 125.00 (d, *J* = 3.0 Hz), 116.22 (d, *J* = 22.1 Hz), 115.32, 115.26, 115.07 (d, *J* = 20.9 Hz), 74.26, 71.77, 71.73, 71.38, 69.90, 68.35, 59.06, 59.05, 38.73, 38.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.39. ESI-MS: calculated $C_{24}H_{30}FN_3O_8SNa$ $[M+Na]^+$ 562.1635; Found 562.1636.

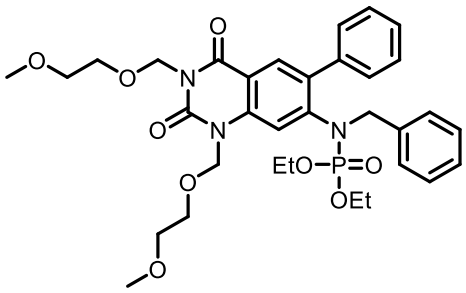
_N_-(1,3-bis((2-methoxyethoxy)methyl)-6-(4-methoxyphenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3l)



Following the above procedure A, the product **3l** was obtained in 54% yield (59.0 mg, 0.108 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.51 (s, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.90 (m, 3H), 5.68 (s, 2H), 5.62 (s, 2H), 3.84 (s, 3H), 3.84 – 3.79 (m, 4H), 3.59 – 3.46 (m, 4H), 3.34 (s, 3H), 3.33 (s, 3H), 3.10 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.23, 159.60, 151.37, 145.82, 139.56, 138.92, 137.29, 131.66, 129.61, 121.41, 115.50, 115.14, 114.62, 113.85, 74.28, 71.75, 71.73, 71.40, 69.86, 68.32, 59.06, 55.41, 53.50, 39.10, 38.65. ESI-MS: calculated $C_{25}H_{33}N_3O_9SNa$ $[M+Na]^+$ 574.1835; Found 574.1838.

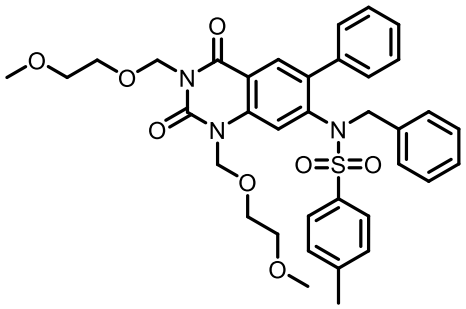
diethyl benzyl(1,3-bis((2-methoxyethoxy)methyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)phosphoramidate (3m)

Following the above procedure A, the product **3m** was obtained in 67% yield (87.9 mg, 0.134 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f



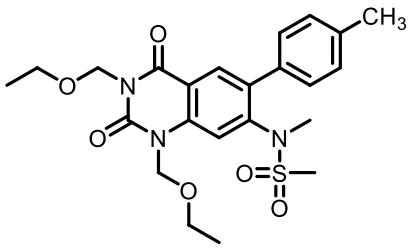
(Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.48 – 7.41 (m, 3H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.28 (s, 1H), 7.19 – 7.08 (m, 3H), 6.95 (d, *J* = 4.2 Hz, 2H), 5.57 (s, 2H), 5.47 (s, 2H), 4.16 – 4.03 (m, 4H), 4.00 (t, *J* = 7.3 Hz, 2H), 3.83 – 3.75 (m, 2H), 3.72 – 3.67 (m, 2H), 3.52 – 3.48 (m, 2H), 3.46 – 3.42 (m, 2H), 3.30 (s, 3H), 3.27 (s, 3H), 1.29 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.51, 151.57, 146.15, 138.88, 138.14, 136.67, 136.24, 131.63, 129.15, 129.11, 128.43, 128.17, 127.80, 127.62, 116.92, 113.63, 74.23, 71.75, 71.59, 71.43, 69.80, 68.20, 63.26, 63.20, 59.01, 58.99, 53.21, 16.26, 16.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.47. ESI-MS: calculated $C_{33}H_{43}N_3O_9P$ $[M+H]^+$ 656.2737; Found 656.2740.

_N_-benzyl-_N_-(1,3-bis((2-methoxyethoxy)methyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-4-methylbenzenesulfonamide (3n)



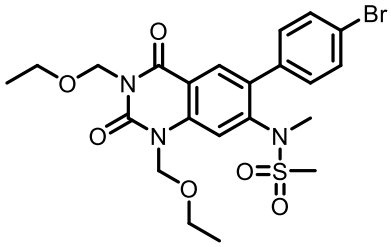
Following the above procedure A, the product **3n** was obtained in 30% yield (39.4 mg, 0.060 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.30 (m, 5H), 7.19 (s, 1H), 7.17 – 7.11 (m, 3H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.70 (d, *J* = 6.8 Hz, 2H), 5.59 (s, 2H), 5.43 (s, 2H), 4.32 (s, 2H), 3.87 – 3.78 (m, 2H), 3.77 – 3.72 (m, 2H), 3.57 – 3.47 (m, 4H), 3.33 (s, 3H), 3.30 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.28, 151.39, 144.19, 143.38, 138.65, 138.47, 137.37, 136.81, 134.40, 131.71, 129.91, 129.31, 129.24, 128.33, 128.25, 128.18, 128.00, 127.81, 116.48, 114.97, 73.92, 71.78, 71.69, 71.51, 69.90, 68.32, 59.05, 54.54, 21.69. ESI-MS: calculated $C_{36}H_{39}N_3O_8SNa$ $[M+Na]^+$ 696.2356; Found 696.2360.

_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(p-tolyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3o)



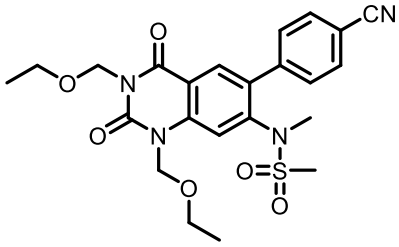
Following the above procedure A, the product **3o** was obtained in 26% yield (25.0 mg, 0.052 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.51 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 5.64 (s, 2H), 5.58 (s, 2H), 3.71 (qd, *J* = 7.0, 1.2 Hz, 4H), 3.14 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H), 1.23 (td, *J* = 7.0, 2.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.27, 151.32, 145.83, 139.43, 137.98, 137.39, 134.76, 131.71, 129.31, 128.96, 115.43, 115.17, 73.95, 71.18, 65.98, 64.78, 38.98, 38.70, 21.28, 15.23, 15.02. ESI-MS: calculated $C_{23}H_{29}N_3O_6SNa$ $[M+Na]^+$ 498.1675; Found 498.1677.

_N_-(6-(4-bromophenyl)-1,3-bis(ethoxymethyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3p)



Following the above procedure A, the product **3p** was obtained in 31% yield (33.1 mg, 0.062 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 2H), 5.57 (s, 2H), 3.69 (q, *J* = 7.0 Hz, 4H), 3.11 (s, 3H), 2.76 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11, 151.22, 145.60, 139.83, 136.52, 136.24, 131.80, 131.60, 130.76, 122.50, 115.30, 115.16, 73.98, 71.22, 66.04, 64.83, 38.75, 38.68, 15.23, 15.02. ESI-MS: calculated $C_{22}H_{26}BrN_3O_6SNa$ $[M+Na]^+$ 562.0623; Found 562.0624.

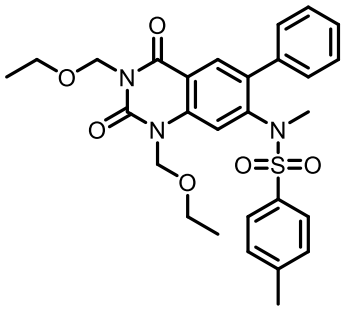
_N_-(6-(4-cyanophenyl)-1,3-bis(ethoxymethyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (3q)



Following the above procedure A, the product **3q** was obtained in 40% yield (40.0 mg, 0.080 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.76 (d, *J* = 8.4

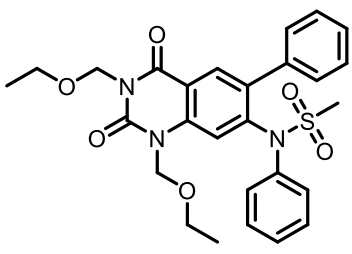
Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.50 (s, 1H), 5.64 (s, 2H), 5.56 (s, 2H), 3.69 (q, *J* = 7.1 Hz, 4H), 3.13 (s, 3H), 2.82 (s, 3H), 1.21 (td, *J* = 7.0, 0.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.94, 151.14, 145.49, 142.35, 140.34, 135.72, 132.34, 131.67, 129.95, 118.55, 115.46, 114.86, 111.94, 74.01, 71.27, 66.10, 64.90, 38.76, 38.12, 15.22, 15.02. ESI-MS: calculated $C_{23}H_{26}N_4O_6SNa$ $[M+Na]^+$ 509.1471; Found 509.1465.

_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_,4-dimethylbenzenesulfonamide (3r)



Following the above procedure A, the product **3r** was obtained in 21% yield (23.0 mg, 0.042 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 1.9 Hz, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 5.56 (s, 2H), 5.45 (s, 2H), 3.69 (q, *J* = 7.0 Hz, 2H), 3.64 (q, *J* = 7.0 Hz, 2H), 2.92 (s, 3H), 2.45 (s, 3H), 1.21 (td, *J* = 7.1, 6.3, 1.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.29, 151.33, 145.99, 144.00, 139.22, 137.45, 137.41, 135.74, 131.79, 129.82, 129.08, 128.51, 127.92, 127.90, 114.98, 114.60, 73.72, 71.16, 65.99, 64.71, 38.72, 21.65, 15.24, 15.03. ESI-MS: calculated $C_{28}H_{31}N_3O_6SNa$ $[M+Na]^+$ 560.1831; Found 560.1835.

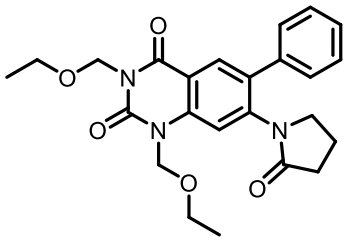
_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-phenylmethanesulfonamide (3s)



Following the above procedure A, the product **3s** was obtained in 55% yield (57.9 mg, 0.110 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.75 (s, 1H), 7.35 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 1H), 7.16 (q, *J* = 5.0 Hz, 3H), 6.94 (dd, *J* = 7.8, 2.0 Hz, 2H), 5.69 (s, 2H), 5.57 (s, 2H), 3.90 – 3.59 (m, 4H), 2.93 (s, 3H), 1.23 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.32, 151.41, 145.08, 140.02, 139.51, 137.91, 137.43, 132.05, 129.47,

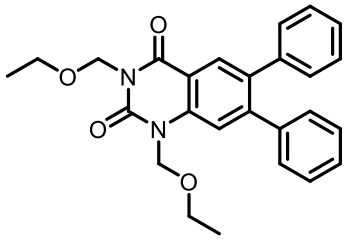
129.23, 128.37, 128.12, 127.11, 126.43, 116.67, 115.19, 74.17, 71.26, 66.09, 64.72, 40.25, 15.33, 15.14. ESI-MS: calculated $C_{27}H_{29}N_3O_6SNa$ $[M+Na]^+$ 546.1675; Found 546.1676.

1,3-bis(ethoxymethyl)-7-(2-oxopyrrolidin-1-yl)-6-phenylquinazoline-2,4(1*H*,3*H*)-dione (3t)



Following the above procedure A, the product **3t** was obtained in 83% yield (72.7 mg, 0.166 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.43 (s, 1H), 7.39 (dd, *J* = 8.2, 3.0 Hz, 2H), 7.36 – 7.30 (m, 3H), 5.61 (s, 2H), 5.55 (s, 2H), 3.67 (dq, *J* = 9.7, 7.0 Hz, 4H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 8.0 Hz, 2H), 1.89 (q, *J* = 7.4 Hz, 2H), 1.20 (dt, *J* = 10.1, 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.64, 161.39, 151.40, 143.02, 139.54, 137.39, 135.07, 131.42, 128.79, 128.20, 128.17, 115.16, 114.71, 73.87, 71.14, 65.89, 64.93, 49.72, 31.15, 19.03, 15.24, 15.01. ESI-MS: calculated $C_{24}H_{27}N_3O_5Na$ 460.1848; Found 460.1850.

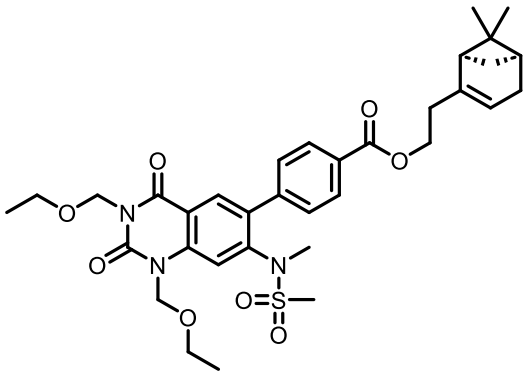
1,3-bis(ethoxymethyl)-6,7-diphenylquinazoline-2,4(1*H*,3*H*)-dione (3u)



Following the above procedure A, the product **3u** was obtained in 13% yield (11.4 mg, 0.026 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). R_f (Petroleum ether/EtOAc 8:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.50 (s, 1H), 7.29 – 7.25 (m, 3H), 7.24 – 7.21 (m, 3H), 7.18 – 7.15 (m, 2H), 7.12 (t, *J* = 4.0 Hz, 2H), 5.67 (s, 2H), 5.61 (s, 2H), 3.87 – 3.63 (m, 4H), 1.23 (td, *J* = 7.1, 2.7 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.86, 151.61, 148.06, 140.03, 139.48, 138.78, 136.75, 130.74, 129.77, 129.65, 128.20, 128.10, 127.70, 127.02, 116.96, 114.60, 73.72, 71.14, 65.92, 64.78, 15.24, 15.05. ESI-MS: calculated $C_{26}H_{27}N_2O_4$ $[M+H]^+$ 431.1971; Found 431.1970.

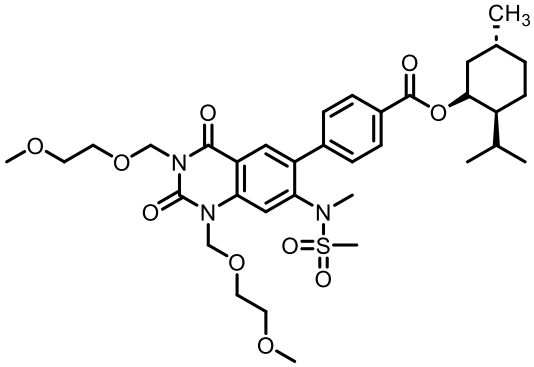
2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-(1,3-bis(ethoxymethyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4a)

Following the above procedure A, the product **4a** was obtained in 62% yield (81.1 mg, 0.124 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f



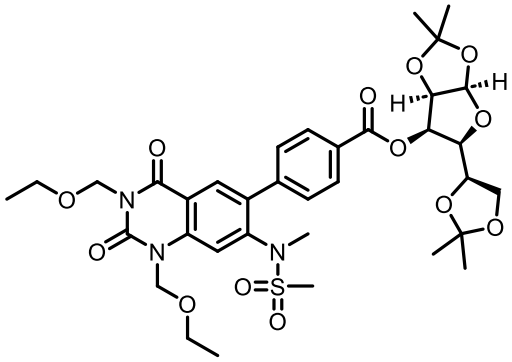
(Petroleum ether/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 1H), 7.51 (d, *J* = 6.5 Hz, 2H), 5.64 (s, 2H), 5.57 (s, 2H), 5.38 (s, 1H), 4.36 (td, *J* = 6.9, 2.5 Hz, 2H), 3.70 (qd, *J* = 7.0, 1.4 Hz, 4H), 3.13 (s, 3H), 2.67 (s, 3H), 2.48 – 2.43 (m, 2H), 2.39 (dt, *J* = 8.5, 5.6 Hz, 1H), 2.32 – 2.19 (m, 2H), 2.12 (dt, *J* = 10.6, 4.9 Hz, 2H), 1.28 (s, 3H), 1.22 (td, *J* = 7.0, 2.5 Hz, 6H), 1.18 (d, *J* = 8.6 Hz, 1H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.16, 161.12, 151.23, 145.65, 144.13, 142.24, 142.20, 140.04, 136.44, 131.61, 130.00, 129.80, 129.20, 119.06, 115.27, 73.98, 71.23, 66.05, 64.85, 63.57, 45.69, 40.68, 38.74, 38.05, 36.03, 31.72, 31.40, 29.44, 26.28, 21.20, 15.23, 15.03. ESI-MS: calculated $C_{34}H_{44}N_3O_8S$ $[M+H]^+$ 654.2849; Found 654.2852.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(1,3-bis((2-methoxyethoxy)methyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4b)



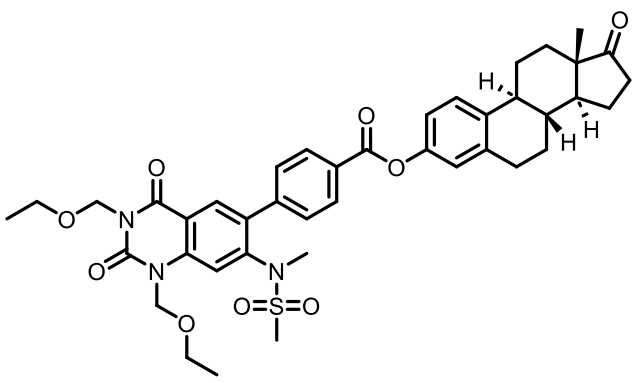
Following the above procedure A, the product **4b** was obtained in 56% yield (78.8 mg, 0.112 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 3.6 Hz, 2H), 7.50 (s, 1H), 5.68 (s, 2H), 5.62 (s, 2H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1H), 3.99 – 3.75 (m, 4H), 3.53 (dt, *J* = 6.6, 2.6 Hz, 4H), 3.33 (s, 3H), 3.33 (s, 3H), 3.13 (s, 3H), 2.73 (s, 3H), 2.20 – 2.11 (m, 1H), 2.06 – 1.92 (m, 1H), 1.74 (d, *J* = 13.0 Hz, 2H), 1.57 (td, *J* = 10.8, 9.9, 2.9 Hz, 2H), 1.18 – 1.04 (m, 2H), 0.94 (d, *J* = 1.3 Hz, 3H), 0.93 (d, *J* = 1.7 Hz, 3H), 0.91 – 0.85 (m, 1H), 0.81 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 161.07, 151.29, 145.72, 142.08, 139.96, 136.66, 131.63, 130.46, 129.77, 129.14, 115.33, 115.22, 75.16, 74.29, 71.81, 71.76, 71.41, 69.93, 68.35, 59.03, 59.01, 47.27, 40.99, 38.74, 34.31, 31.48, 29.70, 26.48, 23.61, 22.06, 20.82, 16.51. ESI-MS: calculated $C_{35}H_{50}N_3O_{10}S$ $[M+H]^+$ 704.3217; Found 704.3217.

(3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(1,3-bis(ethoxymethyl)-7-(N-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4c)



Following the above procedure A, the product **4c** was obtained in 36% yield (53.8 mg, 0.072 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.16 – 8.01 (m, 2H), 7.61 – 7.54 (m, 2H), 7.52 (s, 1H), 5.88 (d, *J* = 4.1 Hz, 1H), 5.64 (s, 2H), 5.57 (s, 2H), 5.34 (t, *J* = 6.0 Hz, 1H), 4.95 (dd, *J* = 5.7, 4.1 Hz, 1H), 4.78 (dt, *J* = 9.0, 6.8 Hz, 1H), 4.30 – 4.09 (m, 2H), 3.73 – 3.68 (m, 4H), 3.67 – 3.62 (m, 1H), 3.14 (s, 3H), 2.76 (s, 3H), 1.54 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.22 (td, *J* = 7.1, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.13, 161.03, 151.19, 145.55, 143.09, 140.15, 136.22, 131.74, 129.99, 129.51, 128.48, 115.38, 115.02, 114.92, 109.62, 105.11, 81.17, 79.06, 75.13, 74.00, 72.52, 71.24, 66.44, 66.07, 64.88, 38.80, 38.35, 27.00, 26.93, 26.73, 25.36, 15.23, 15.03. ESI-MS: calculated $C_{35}H_{46}N_3O_{13}S$ $[M+H]^+$ 748.2751; Found 748.2747.

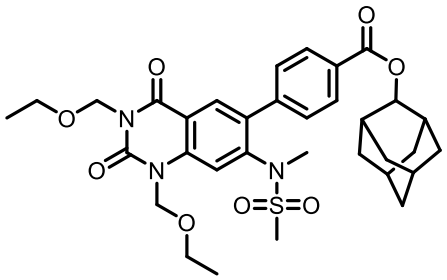
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(1,3-bis(ethoxymethyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4d)



Following the above procedure A, the product **4d** was obtained in 31% yield (47.0 mg, 0.062 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 2H), 8.27 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.35 (d, *J* = 8.4 Hz,

1H), 7.07 – 6.92 (m, 2H), 5.65 (s, 2H), 5.58 (s, 2H), 3.71 (q, *J* = 7.0 Hz, 4H), 3.15 (s, 3H), 2.96 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.77 (s, 3H), 2.52 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.33 (t, *J* = 8.8 Hz, 1H), 2.20 – 2.07 (m, 2H), 2.00 (dd, *J* = 16.8, 6.0 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.55 (d, *J* = 13.1 Hz, 2H), 1.49 (d, *J* = 13.6 Hz, 2H), 1.23 (td, *J* = 7.0, 1.7 Hz, 6H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.10, 161.10, 151.21, 148.74, 145.63, 142.94, 140.12, 138.20, 137.60, 136.36, 131.68, 130.40, 129.39, 129.18, 126.59, 121.71, 118.85, 115.34, 115.15, 74.00, 71.25, 66.07, 64.87, 50.42, 48.00, 44.20, 38.78, 38.56, 38.00, 35.91, 31.55, 29.48, 26.37, 25.79, 21.63, 15.24, 15.04, 13.87. ESI-MS: calculated $C_{35}H_{45}N_3O_{13}SNa$ $[M+Na]^+$ 780.2930; Found 780.2921.

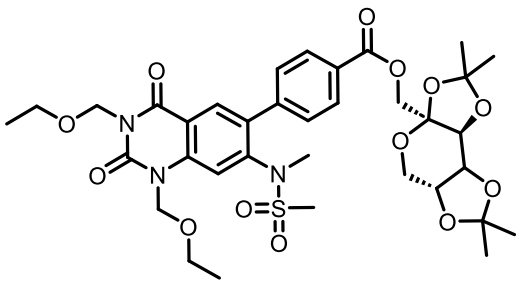
(1*r*,3*r*)-adamantan-2-yl 4-(1,3-bis(ethoxymethyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4e)



Following the above procedure A, the product **4e** was obtained in 25% yield (32.0 mg, 0.050 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.18 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.52 (d, *J* = 3.4 Hz, 2H), 5.64 (s, 2H), 5.57 (s, 2H), 5.22 (d, *J* = 3.3 Hz, 1H), 3.70 (q, *J* = 7.0 Hz, 4H), 3.13 (s, 3H), 2.72 (s, 3H), 2.20 (s, 1H), 2.18 – 2.14 (m, 2H), 1.96 – 1.91 (m, 2H), 1.86 (d, *J* = 12.8 Hz, 1H), 1.79 (d, *J* = 2.9 Hz, 2H), 1.67 (d, *J* = 3.3 Hz, 1H), 1.63 (d, *J* = 13.1 Hz, 4H), 1.22 (td, *J* = 7.1, 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44, 161.12, 151.23, 145.64, 142.10, 140.01, 136.52, 131.68, 130.70, 129.82, 129.18, 115.30, 115.22, 77.84, 73.98, 71.24, 66.05, 64.85, 38.76, 37.37, 36.36, 32.03, 27.30, 27.00, 15.24, 15.03. ESI-MS: calculated $C_{33}H_{42}N_3O_8S$ $[M+H]^+$ 640.2693; Found 640.2693.

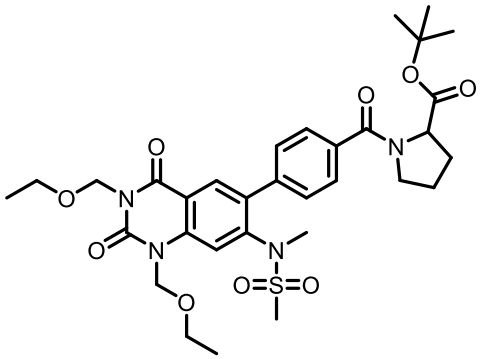
((3a*S*,5a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-(1,3-bis(ethoxymethyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoate (4f)

Following the above procedure A, the product **4f** was obtained in 30% yield (44.9 mg, 0.060 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). R_f



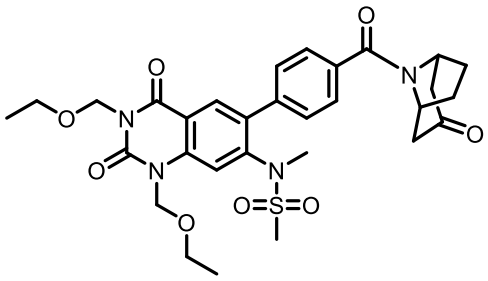
(Petroleum ether/EtOAc 1:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 2H), 7.53 (s, 1H), 7.51 (d, *J* = 3.6 Hz, 2H), 5.64 (s, 2H), 5.57 (s, 2H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.47 (d, *J* = 2.6 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.27 (d, *J* = 9.6 Hz, 1H), 3.97 (dd, *J* = 13.1, 1.9 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H), 3.70 (q, *J* = 7.0 Hz, 4H), 3.11 (s, 3H), 2.68 (s, 3H), 1.56 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.22 (td, *J* = 7.0, 2.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.56, 161.11, 151.21, 145.64, 142.55, 140.09, 136.30, 131.60, 130.01, 129.46, 129.28, 115.27, 115.24, 109.20, 108.92, 101.62, 73.99, 71.23, 70.77, 70.58, 70.06, 66.06, 65.61, 64.86, 61.37, 38.70, 26.55, 25.92, 25.55, 24.02, 15.23, 15.02. ESI-MS: calculated $C_{35}H_{45}N_3O_{13}SNa$ $[M+Na]^+$ 770.2571; Found 770.2570.

tert-butyl (4-(1,3-bis(ethoxymethyl)-7-(*N*-methylmethylsulfonamido)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)benzoyl)prolinate (4g)



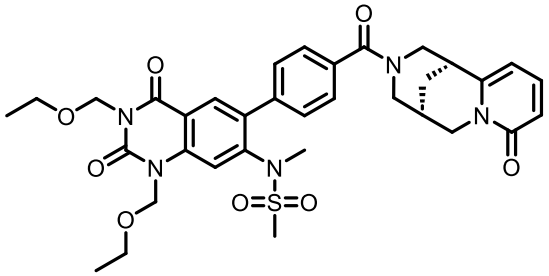
Following the above procedure A, the product **4g** was obtained in 92% yield (115.7 mg, 0.184 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.47 (dd, *J* = 12.0, 8.0 Hz, 2H), 5.63 (s, 2H), 5.57 (s, 2H), 4.57 (dd, *J* = 8.2, 5.5 Hz, 1H), 3.70 (q, *J* = 7.0 Hz, 4H), 3.09 (s, 3H), 2.72 (s, 3H), 2.38 – 2.17 (m, 2H), 2.11 – 2.01 (m, 2H), 2.00 – 1.84 (m, 2H), 1.51 (s, 9H), 1.22 (td, *J* = 7.0, 2.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.38, 168.91, 161.15, 151.24, 145.71, 139.87, 139.49, 136.49, 136.07, 131.67, 129.03, 127.84, 127.61, 127.13, 115.34, 115.23, 81.47, 73.97, 71.21, 66.02, 64.82, 60.07, 50.10, 38.91, 38.72, 29.45, 28.05, 25.48, 15.23, 15.02. ESI-MS: calculated $C_{32}H_{42}N_4O_9SNa$ $[M+Na]^+$ 681.2570; Found 681.2572.

_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(4-((1*R*,5*S*)-3-oxo-8-azabicyclo[3.2.1]octane-8-carbonyl)phenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (4h)



Following the above procedure A, the product **4h** was obtained in 73% yield (89.5 mg, 0.146 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.20. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.61 (s, 1H), 7.54 (t, J = 4.2 Hz, 2H), 5.66 (s, 2H), 5.40 (s, 2H), 3.61 (dt, J = 13.2, 6.9 Hz, 4H), 3.38 (s, 1H), 3.26 (s, 1H), 3.16 (s, 3H), 2.92 (s, 3H), 2.85 – 2.66 (m, 2H), 2.41 – 2.19 (m, 2H), 2.08 (d, J = 12.8 Hz, 2H), 1.66 (d, J = 8.3 Hz, 2H), 1.11 (dt, J = 13.6, 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.28, 168.32, 161.06, 151.21, 145.67, 140.07, 139.99, 136.30, 135.07, 131.74, 129.74, 129.45, 127.68, 127.52, 115.33, 115.11, 74.00, 71.23, 66.03, 64.85, 42.71, 41.48, 38.74, 38.67, 32.87, 15.21, 15.00. ESI-MS: calculated $C_{30}H_{37}N_4O_8S$ $[M+H]^+$ 613.2332; Found 613.2336.

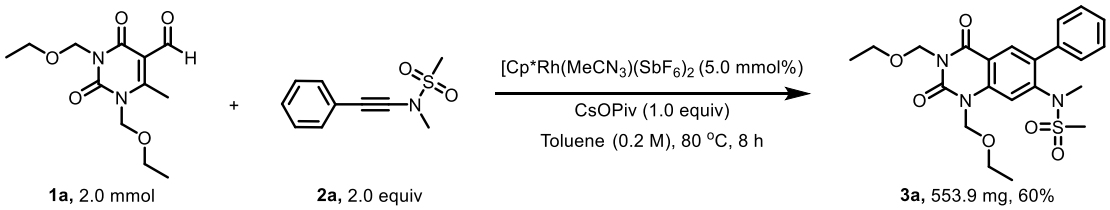
_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(4-((1_S_,5_R_)-8-oxo-1,3,4,5,6,8-hexahydro-2_H_-1,5-methanopyrido[1,2-_a_][1,5]diazocine-3-carbonyl)phenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (4i)



Following the above procedure A, the product **4i** was obtained in 42% yield (56.9 mg, 0.084 mmol, 8.0 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:3 v/v). R_f (Petroleum ether/EtOAc 1:3): 0.10. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.57 (s, 1H), 7.51 – 7.28 (m, 4H), 6.80 (dd, J = 50.2, 23.3 Hz, 2H), 6.31 (d, J = 9.2 Hz, 1H), 5.64 (s, 2H), 5.39 (s, 2H), 3.97 (d, J = 6.6 Hz, 1H), 3.72 (d, J = 35.5 Hz, 2H), 3.59 (dd, J = 12.1, 7.0 Hz, 4H), 3.22 (s, 2H), 3.11 (s, 3H), 3.02 (d, J = 29.5 Hz, 2H), 2.92 (s, 3H), 2.10 – 1.86 (m, 2H), 1.10 (p, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.24, 162.64, 161.13, 151.23, 149.98, 146.00, 140.05, 139.54, 139.13, 136.45, 135.98, 130.30, 129.16, 126.66, 126.61, 116.55, 115.77, 115.10, 105.44, 73.47, 71.12, 65.14, 64.02, 49.06, 41.94, 41.25, 37.96, 32.91, 29.45, 27.47, 25.66, 15.53, 15.32. ESI-MS: calculated $C_{34}H_{40}N_5O_8S$ $[M+H]^+$ 678.2598; Found 678.2601.

4. Scale-up experiment and synthetic applications

(a) Scale-up experiment:

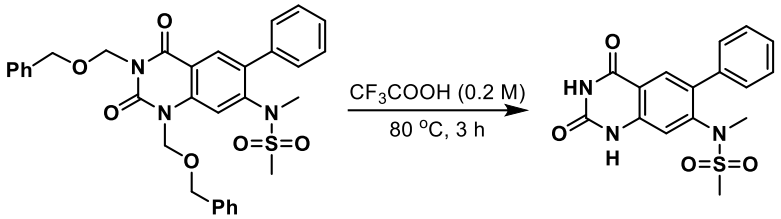


1a, 2.0 mmol **2a,** 2.0 equiv **3a,** 553.9 mg, 60%

In an oven-dried Schlenk tube, a mixture of the 6-Methyluracil-5-carbaldehyde derivatives **1a** (2.0 mmol, 1.0 equiv), *N*-methyl-*N*-(phenylethynyl)methanesulfonamide **2a** (4.0 mmol, 2.0 equiv), [Cp*Rh(MeCN$_3$)(SbF$_6$)$_2$ (5.0 mol%), CsOPiv (2.0 mmol, 1.0 equiv) and Toluene (10.0 mL, 0.2 M) was stirred at 80 °C in the oil bath for 8 h. The reaction mixture was then diluted with DCM (50.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3a** (553.9 mg, 60 %) as a yellow oil.

(b) Products transformation:

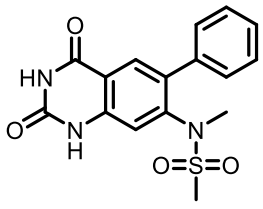
1.Procedure for the synthesis of product 5[3]



3f, 0.1 mmol **5,** 83%

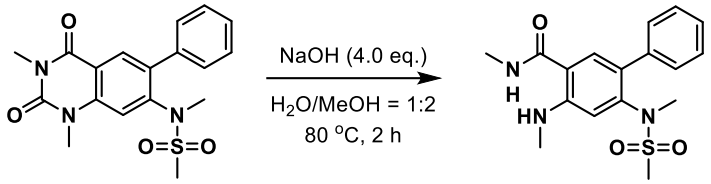
3f (58.6 mg, 0.1 mmol, 1.0 equiv) was dissolved in CF_3CO_2H (3.0 mL, 0.02 M). After being stirred at 80 °C for 3 h, the reaction mixture was concentrated in vacuo. The reaction mixture was then diluted with DCM (20.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 4:1) to give **5** (28.7 mg, 83%) as a white solid.

***N*-(2,4-dioxo-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (5)**



^{1}H NMR (400 MHz, DMSO-d_6) δ 11.42 (s, 1H), 11.22 (s, 1H), 7.79 (s, 1H), 7.53 – 7.34 (m, 5H), 7.31 (s, 1H), 2.98 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.60, 150.64, 145.67, 141.22, 138.49, 135.72, 129.46, 129.38, 128.80, 127.98, 115.20, 114.30, 38.57, 38.52. ESI-MS: calculated $C_{16}H_{16}N_3O_4S$ $[M+H]^+$ 346.0862; Found 346.0860.

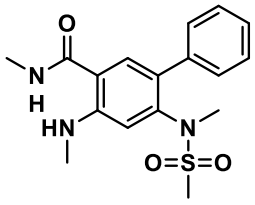
2. Procedure for the synthesis of product 6[4]



3c, 0.1 mmol **6,** 85%

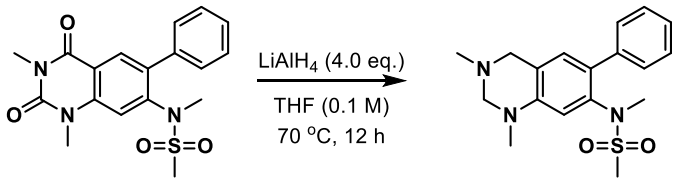
To a solution of **3c** (37.3 mg, 0.1 mmol, 1.0 equiv) in MeOH/H_2O (2:1, 2.0 mL, 0.05 M) was added NaOH (16.0 mg, 0.4 mmol, 4.0 equiv) at 25 °C. After being stirred at 80 °C for 2 h, the reaction mixture was concentrated in vacuo. The product was extracted with EtOAc (three times), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Acetone : *n*-Hexane = 2:1) to give **6** (29.5 mg, 85%) as a white solid.

***N*-methyl-4-(methylamino)-6-(*N*-methylmethylsulfonamido)-[1,1'-biphenyl]-3-carboxamide (6)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42 – 7.30 (m, 5H), 7.2 9 (s, 1H), 6.62 (s, 1H), 6.11 (s, 1H), 3.12 (s, 3H), 2.91 (d, *J* = 4.8 H z, 3H), 2.88 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 16 9.65, 150.58, 143.08, 139.38, 130.11, 129.27, 128.34, 127.82, 127.07, 115.61, 110.39, 38.79, 38.66, 29.81, 26.53. ESI-MS: calculated $C_{17}H_{22}N_3O_3S$ $[M+H]^+$ 348.13 82; Found 348.1386.

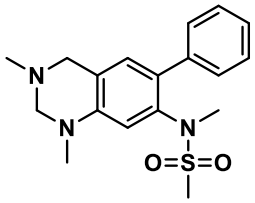
3. Procedure for the synthesis of product 7[4]



3c, 0.1 mmol **7,** 56%

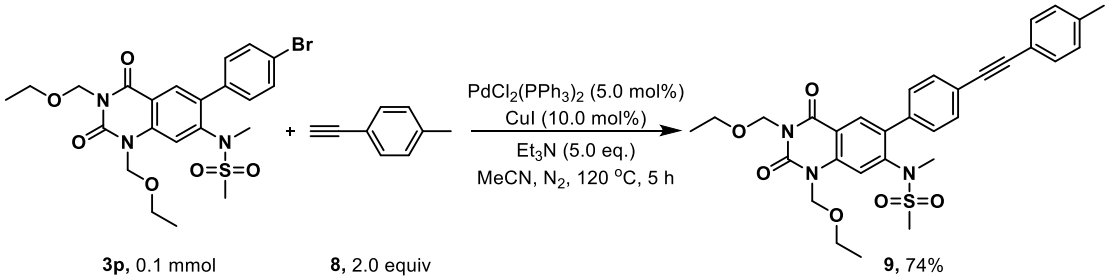
To a dry Schlenk tube containing compound **3c** (37.3 mg, 0.1 mmol, 1.0 equiv) in THF (1.0 mL, 0.1 M) was added $LiAlH_4$ (15.2 mg, 0.40 mmol, 4.0 equiv) at 0 °C. The resulting mixture was allowed for stir 12 h at 70 °C (pre-heated oil bath was used). Then to the solution two drops of saturated NH_4Cl solution was added and was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (70:30) to afford **6** (19.3 mg, 56%) as a white oil.

***N*-(1,3-dimethyl-6-phenyl-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (7)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 6.90 (s, 1H), 6.60 (s, 1H), 3.96 (s, 2H), 3.84 (s, 2H), 3.15 (s, 3H), 2.91 (s, 3H), 2.52 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.16, 139.92, 138.28, 130.03, 129.32, 129.19, 128.19, 126.79, 120.31, 110.68, 72.54, 55.25, 41.61, 39.16, 38.63, 36.61. ESI-MS: calculated $C_{18}H_{24}N_3O_2S$ $[M+H]^+$ 346.1589; Found 346.1593.

4. Procedure for the synthesis of product 9[5].

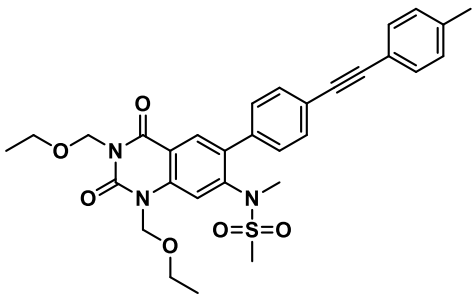


3p, 0.1 mmol **8,** 2.0 equiv **9,** 74%

To a solution of **3p** (53.9 mg, 0.1 mmol, 1.0 equiv) in CH_3CN (0.4 mL, 0.2 M) and NEt_3 (1.0 mL, 0.1 M) were added $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 10 mol%), CuI (1.0 mg, 0.005 mmol, 5 mol%), and 1-ethynyl-4-methylbenzene **8** (23.0 mg 0.2mmol, 2.0 equiv) under N_2. After being stirred at 120 °C for 5 h, the reaction mixture was concentrated in vacuo. The residue was purified

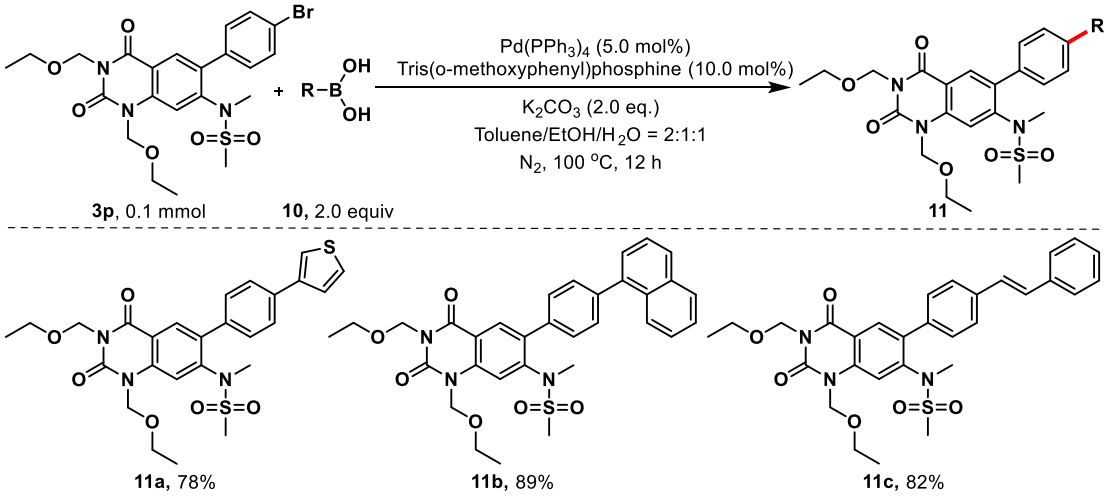
by column chromatography on silica gel (Petroleum ether/EtOAc = 1/1, v/v) to give **9** (42.6 mg, 74%) as a yellow oil.

_N_-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(4-(p-tolylethynyl)phenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-_N_-methylmethanesulfonamide (9)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.51 (s, 1H), 7.47 – 7.37 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.64 (s, 2H), 5.58 (s, 2H), 3.70 (q, *J* = 7.0 Hz, 4H), 3.13 (s, 3H), 2.69 (s, 3H), 2.38 (s, 3H), 1.23 (td, *J* = 7.1, 2.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.16, 151.25, 145.74, 139.79, 138.71, 137.35, 136.70, 131.77, 131.72, 131.56, 129.20, 129.13, 123.42, 119.91, 115.39, 115.26, 90.86, 88.18, 73.98, 71.21, 66.00, 64.81, 39.00, 38.69, 21.56, 15.22, 15.01. ESI-MS: calculated $C_{31}H_{33}N_3O_6SNa$ $[M+Na]^+$ 598.1988; Found 598.1983.

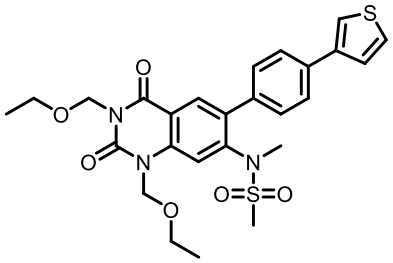
5. Procedure for the synthesis of product 11[6].



To a solution of **3p** (53.9 mg, 0.1 mmol, 1.0 equiv) in toluene (1.0 mL) was added phenylboronic acid **10** (0.2 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (5.8 mg, 0.05 mmol, 5.0 mol%), tris(o-methoxyphenyl)phosphine (3.6 mg, 0.01 mmol, 10.0 mol%), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.). Absolute EtOH (0.5 mL) and H_2O (0.5 mL) was then added to the reaction mixture. The resulting mixture was degassed with N_2 and then heated to 100 °C (oil bath) for 12 h. After cooling to room temperature, the organic layer was separated and the sodium chloride aqueous solution fraction was extracted with EtOAc. The organic fractions were dried over Na_2SO_4. Removal of the solvents in

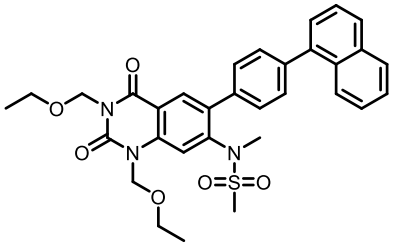
vacuo gave a crude mixture that was purified by column chromatography (n-hexane/EtOAc = 2/1-1/1, v/v) to afford the product **11** as a yellow oil.

***N*-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(4-(thiophen-3-yl)phenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (11a)**



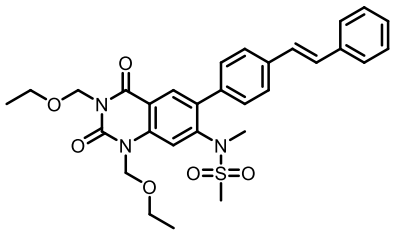
Following the above procedure, the product **11a** was obtained in 78% yield (42.4 mg, 8 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 - 1:1 v/v). R_f (Petroleum ether/EtOAc 2:1): 0.2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.71 (s, 1H), 7.69 (s, 1H), 7.52 (d, *J* = 3.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 3.1 Hz, 2H), 5.64 (s, 2H), 5.58 (s, 2H), 3.71 (q, *J* = 7.0 Hz, 4H), 3.15 (s, 3H), 2.69 (s, 3H), 1.23 (td, *J* = 7.1, 3.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21, 151.28, 145.81, 141.41, 139.62, 136.93, 136.38, 135.51, 131.66, 129.59, 126.57, 126.50, 126.14, 120.80, 115.37, 115.26, 73.98, 71.20, 65.99, 64.80, 39.03, 38.70, 15.23, 15.01. ESI-MS: calculated $C_{26}H_{29}N_3O_6S_2Na$ $[M+Na]^+$ 566.1395; Found 566.1398.

***N*-(1,3-bis(ethoxymethyl)-6-(4-(naphthalen-1-yl)phenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (11b)**



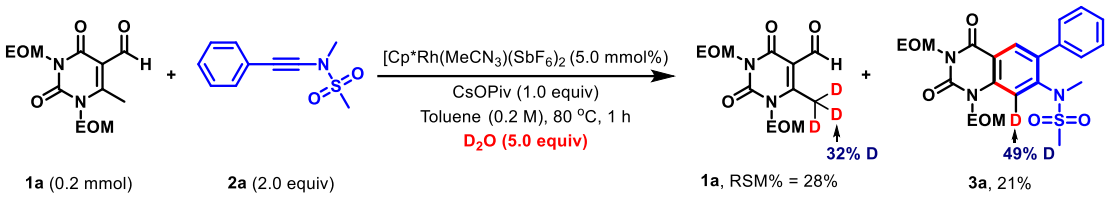
Following the above procedure, the product **11b** was obtained in 89% yield (52.3 mg, 12 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 - 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.91 (q, *J* = 8.2, 7.6 Hz, 3H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.58 (s, 1H), 7.57 – 7.53 (m, 3H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 6.7 Hz, 2H), 5.66 (s, 2H), 5.60 (s, 2H), 3.73 (qd, *J* = 7.1, 2.3 Hz, 4H), 3.23 (s, 3H), 2.74 (s, 3H), 1.34 – 1.15 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.22, 151.32, 145.89, 140.66, 139.71, 139.36, 137.08, 136.70, 133.86, 131.82, 131.43, 130.30, 129.09, 128.45, 128.02, 127.10, 126.29, 125.92, 125.67, 125.41, 115.44, 115.32, 74.00, 71.22, 66.01, 64.83, 38.98, 38.84, 15.24, 15.03. ESI-MS: calculated $C_{32}H_{34}N_3O_6S$ $[M+H]^+$ 588.2168; Found 588.2163.

(*E*)-*N*-(1,3-bis(ethoxymethyl)-2,4-dioxo-6-(4-styrylphenyl)-1,2,3,4-tetrahydroquinazolin-7-yl)-*N*-methylmethanesulfonamide (11c)



Following the above procedure, the product **11c** was obtained in 82% yield (46.2 mg, 8 h) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 - 1:1 v/v). R_f (Petroleum ether/EtOAc 1:1): 0.2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.3 Hz, 1H), 5.64 (s, 2H), 5.58 (s, 2H), 3.71 (q, *J* = 7.0 Hz, 4H), 3.15 (s, 3H), 2.69 (s, 3H), 1.23 (td, *J* = 7.0, 3.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21, 151.28, 145.80, 139.60, 137.16, 137.07, 136.96, 136.79, 131.62, 129.60, 129.45, 128.77, 127.92, 127.80, 126.67, 126.62, 115.39, 115.25, 73.98, 71.20, 65.99, 64.80, 39.04, 38.69, 15.23, 15.01. ESI-MS: calculated $C_{30}H_{33}N_3O_6SNa$ $[M+Na]^+$ 586.1988; Found 586.1981.

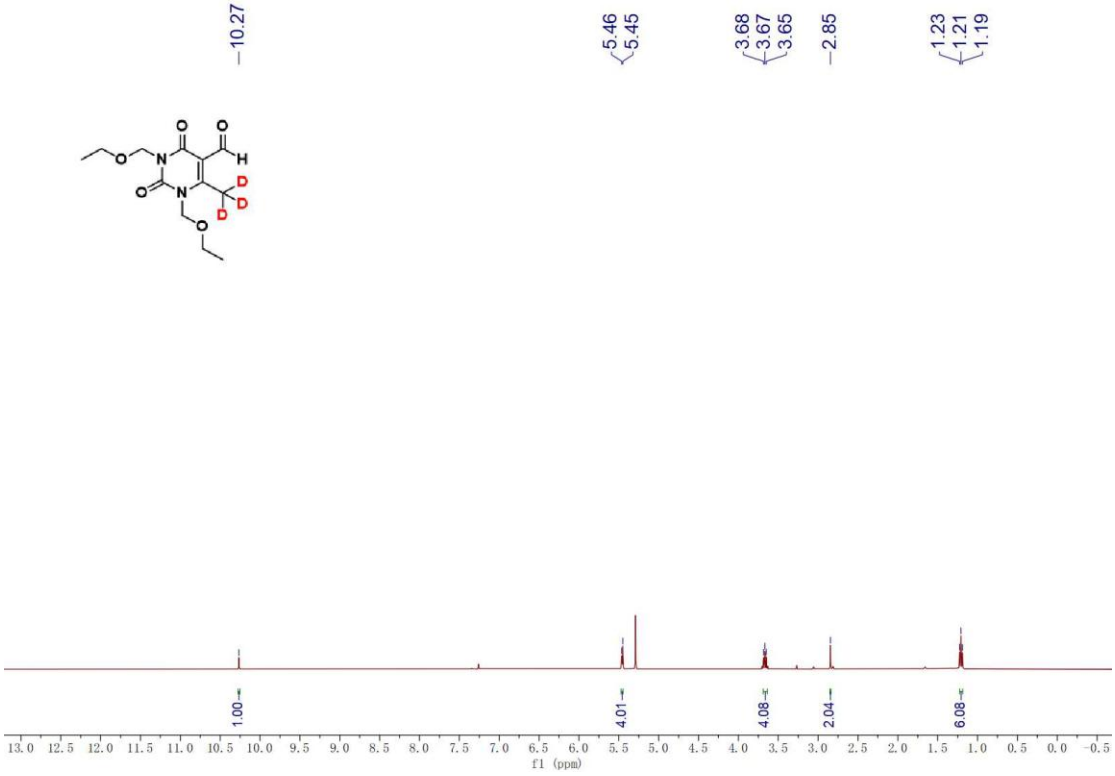
5. Mechanistic studies



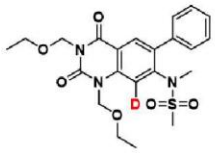
1a (0.2 mmol) **2a** (2.0 equiv) **1a**, RSM% = 28% **3a**, 21%

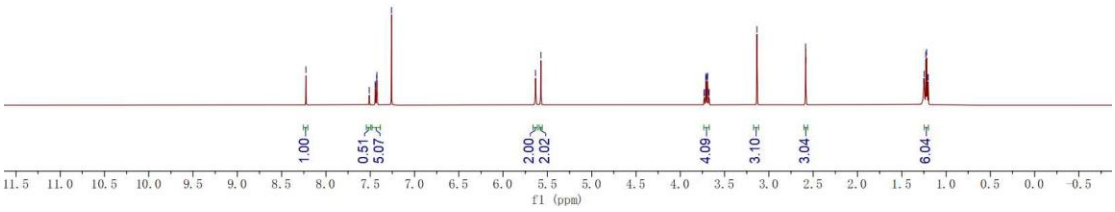
In an oven-dried Schlenk tube, a mixture of the 6-Methyluracil-5-carbaldehyde derivatives **1a** (0.2 mmol, 1.0 equiv), *N*-methyl-*N*-(phenylethynyl)methanesulfonamide **2a** (0.4 mmol, 2.0 equiv), [Cp*Rh(MeCN$_3$)(SbF$_6$)$_2$ (5.0 mol%), D$_2$O (5.0 equiv), CsOPiv (0.2 mmol, 1.0 equiv) and Toluene (1.0 mL, 0.2 M) was stirred at 80 °C in the oil bath for 1.0 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H$_2$O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na$_2$SO$_4$. The product was purified by flash column chromatography on silica with an appropriate solvent to afford the starting material **1a** (16.2 mg, RSM% = 28%). Afford the pure product **3a** (19.4 mg, 21%) as a yellow oil.

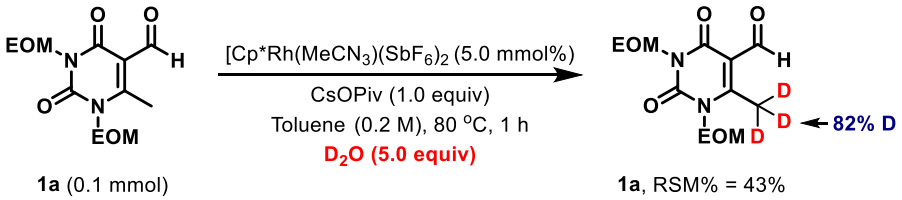
^{1}H NMR (400 MHz, CDCl$_3$) Spectra of **1a**



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3a**



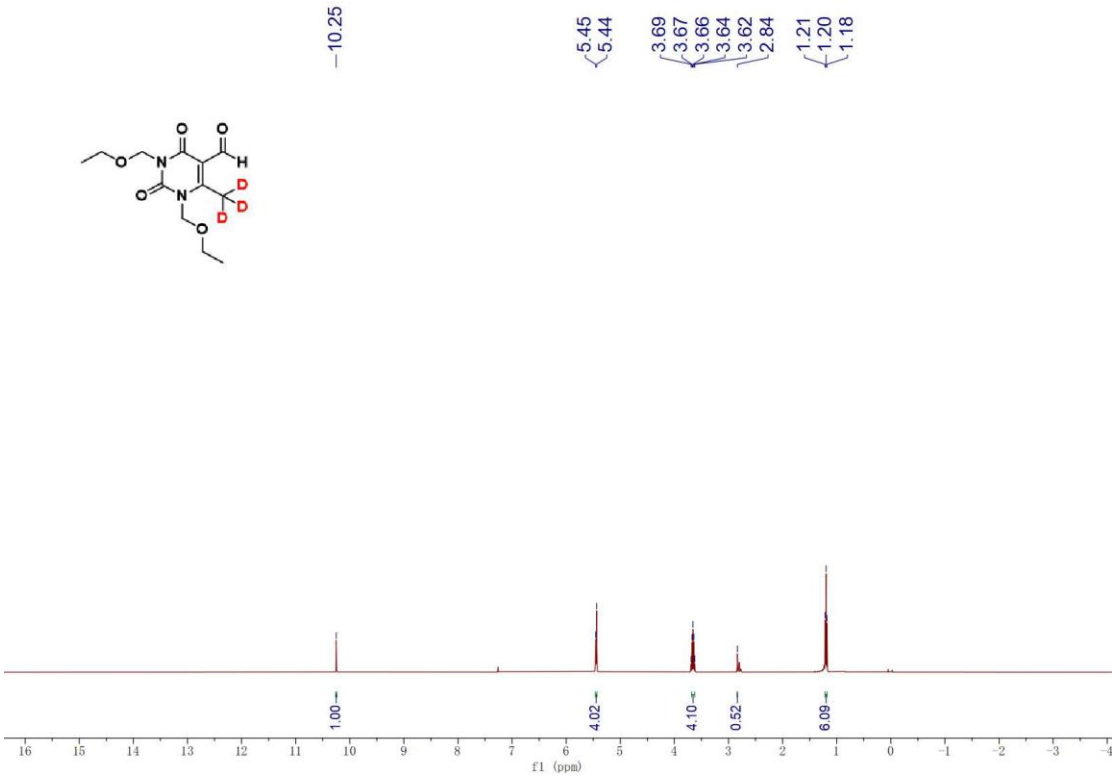




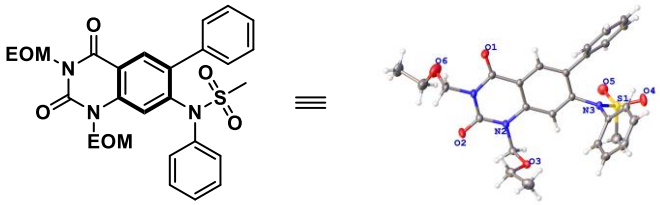
1a (0.1 mmol) **1a**, RSM% = 43%

In an oven-dried Schlenk tube, a mixture of the 6-Methyluracil-5-carbaldehyde derivatives **1a** (0.1 mmol, 1.0 equiv), [Cp*Rh(MeCN$_3$)(SbF$_6$)$_2$ (5.0 mol%), D_2O (5.0 equiv), CsOPiv (0.1 mmol, 1.0 equiv) and Toluene (0.5 mL, 0.2 M) was stirred at 80 °C in the oil bath for 1.0 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The product was purified by flash column chromatography on silica with an appropriate solvent to afford the starting material **1a** (11.5 mg, RSM% = 43%).

^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **1a**



6. Single-Crystal X-ray of 3s



3s **CCDC：2527078**

The crystal structure of **3s** by X-ray analysis.

X-ray-quality crystal was obtained by slow diffusion of petroleum ether into a dilute dichloromethane mixture solution of **3s** at room temperature under air. Thermal ellipsoids drawn at the 50% probability level. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at 200.00(10) K during data collection.

Table 1 Crystal data and structure refinement for 3s.

Identification code	**3s**
Empirical formula	$C_{27}H_{29}N_3O_6S$
Formula weight	523.59
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.34920(10)
b/Å	10.29990(10)
c/Å	17.91330(10)
α/°	90
β/°	104.5770(10)
γ/°	90
Volume/Å^3	2562.28(4)
Z	4

ρ_{calc}g/cm^3	1.357
μ/mm^{-1}	1.524
F(000)	1104.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.99 to 145.706
Index ranges	-17 ≤ h ≤ 13, -12 ≤ k ≤ 11, -21 ≤ l ≤ 22
Reflections collected	19963
Independent reflections	4949 [R_{int} = 0.0149, R_{sigma} = 0.0099]
Data/restraints/parameters	4949/41/365
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0414, wR_2 = 0.1002
Largest diff. peak/hole / e Å^{-3}	0.52/-0.46

Crystal structure determination of 3s

Crystal Data for $C_{27}H_{29}N_3O_6S$ (*M* =523.59 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.34920(10) Å, *b* = 10.29990(10) Å, *c* = 17.91330(10) Å, *β* = 104.5770(10)°, *V* = 2562.28(4) Å^3, *Z* = 4, *T* = 150.00(10) K, μ(Cu Kα) = 1.524 mm^{-1}, *Dcalc* = 1.357 g/cm^3, 19963 reflections measured (9.99° ≤ 2Θ ≤ 145.706°), 4949 unique (R_{int} = 0.0149, R_{sigma} = 0.0099) which were used in all calculations. The final R_1 was 0.0408 (I > 2σ(I)) and wR_2 was 0.1002 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3s. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2675.7(3)	-201.4(4)	1985.6(2)	25.04(11)
O1	2591.7(9)	5780.4(13)	4376.7(7)	38.1(3)
O2	4733.0(9)	6948.2(11)	3010.8(8)	34.6(3)
O3	3651.9(8)	4854.6(10)	1328.7(6)	25.8(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3s. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	2031.9(9)	-1269.5(11)	1752.6(8)	37.2(3)
O5	3314.1(9)	-189.8(12)	2740.7(7)	35.2(3)
O6	4414.0(13)	7456(2)	4845.9(10)	71.1(5)
N1	3641.8(10)	6381.5(13)	3681.1(8)	25.6(3)
N2	3926.0(9)	5050.1(12)	2687.0(7)	21.9(3)
N3	2033.7(9)	1120.4(12)	1925.4(7)	20.7(3)
C1	2734.0(11)	4393.5(15)	3356.3(8)	22.0(3)
C2	2958.5(11)	5543.9(16)	3849.6(9)	25.4(3)
C3	4136.2(11)	6174.4(15)	3112.3(9)	24.2(3)
C4	3240.5(10)	4154.3(14)	2799.1(8)	20.1(3)
C5	3036.2(10)	3027.2(14)	2354.1(8)	20.6(3)
C6	2320.8(10)	2191.7(14)	2452.4(8)	19.7(3)
C7	1794.5(10)	2427.3(15)	3004.9(8)	21.3(3)
C8	2020.1(11)	3536.9(15)	3450.3(8)	23.6(3)
C9	4360.0(11)	4870.5(15)	2027.2(9)	24.3(3)
C10	3239.5(13)	6104.7(17)	1096.6(11)	33.9(4)
C11	2430.2(15)	5924(2)	389.4(12)	44.9(5)
C12	1015.0(11)	1547.8(15)	3111.5(8)	22.3(3)
C13	80.2(11)	2013.7(16)	3004.7(9)	26.0(3)
C14	-649.0(13)	1205.6(18)	3116.5(10)	32.7(4)
C15	-445.8(14)	-58.1(18)	3351.6(11)	37.1(4)
C16	485.3(15)	-528.5(17)	3474.2(10)	36.1(4)
C17	1213.6(13)	263.0(16)	3348.4(9)	27.9(3)
C18	1273.1(11)	1392.3(14)	1239.0(8)	20.6(3)
C19	370.9(11)	849.7(16)	1156.4(9)	25.4(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3s. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	-357.1(12)	1151.6(17)	507.0(10)	31.1(4)
C21	-184.4(13)	1994.9(17)	-45.6(10)	33.0(4)
C22	716.3(13)	2544.9(17)	46.5(9)	33.0(4)
C23	1452.8(12)	2239.1(16)	686.6(9)	27.8(3)
C24	3356.7(14)	-60.0(19)	1297.5(11)	38.3(4)
C25	3829.3(17)	7595(2)	4131.5(12)	44.1(5)
C26	5430(3)	7671(4)	4866.2(19)	57.5(11)
C27	5863(2)	8411(4)	5589.4(19)	49.3(9)
C28	5921(11)	7933(16)	5204(11)	103(4)
C29	5218(8)	6767(14)	4942(8)	92(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	23.5(2)	18.77(19)	31.9(2)	-2.05(14)	5.19(15)	1.96(14)
O1	45.5(7)	38.8(7)	37.2(7)	-17.7(6)	23.7(6)	-16.3(6)
O2	36.9(6)	24.6(6)	48.2(7)	-10.6(5)	21.4(6)	-12.8(5)
O3	31.4(6)	20.6(5)	27.3(6)	-0.5(4)	11.0(5)	1.4(4)
O4	34.2(6)	17.7(6)	58.1(8)	-5.4(5)	8.3(6)	-1.6(5)
O5	30.7(6)	35.4(7)	35.2(7)	2.7(5)	0.3(5)	8.8(5)
O6	65.6(10)	92.1(14)	52.4(9)	-30.3(9)	8.7(7)	-28.1(9)
N1	29.1(7)	20.8(6)	28.4(7)	-7.3(5)	10.3(5)	-6.1(5)
N2	21.5(6)	19.2(6)	26.5(6)	-3.8(5)	9.0(5)	-3.5(5)
N3	22.6(6)	17.0(6)	20.7(6)	-2.7(5)	2.3(5)	-0.1(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	22.7(7)	21.5(7)	21.5(7)	-2.9(6)	4.8(6)	-2.8(6)
C2	25.6(8)	25.7(8)	25.5(8)	-5.2(6)	7.4(6)	-4.4(6)
C3	22.8(7)	20.5(7)	29.6(8)	-2.9(6)	7.2(6)	-1.8(6)
C4	18.2(7)	20.1(7)	21.3(7)	0.4(6)	3.5(5)	-1.0(5)
C5	20.6(7)	20.4(7)	20.8(7)	-1.3(6)	5.2(5)	0.0(6)
C6	21.4(7)	16.8(7)	19.1(7)	-0.9(5)	1.9(5)	0.2(5)
C7	22.1(7)	21.1(7)	19.8(7)	0.5(6)	3.5(5)	-2.7(6)
C8	25.8(7)	24.9(8)	21.2(7)	-2.9(6)	8.0(6)	-3.4(6)
C9	22.5(7)	22.5(8)	31.0(8)	-2.8(6)	12.7(6)	-0.9(6)
C10	40.7(10)	24.9(8)	39.4(9)	5.2(7)	16.4(8)	7.1(7)
C11	42.8(11)	47.3(12)	44.3(11)	12.5(9)	10.0(9)	8.6(9)
C12	27.8(8)	22.5(7)	17.0(7)	-2.3(6)	6.4(6)	-6.8(6)
C13	29.3(8)	24.6(8)	24.7(7)	-2.9(6)	7.6(6)	-5.1(6)
C14	29.1(8)	38.2(10)	33.0(9)	-8.3(7)	11.7(7)	-10.5(7)
C15	45.0(10)	35.8(10)	36.0(9)	-8.5(8)	20.6(8)	-21.2(8)
C16	58.4(12)	22.6(8)	30.8(9)	0.8(7)	17.4(8)	-10.1(8)
C17	35.6(9)	25.1(8)	23.2(8)	0.9(6)	8.2(6)	-2.0(7)
C18	23.5(7)	18.4(7)	18.7(7)	-4.1(5)	3.0(6)	1.6(6)
C19	25.9(8)	23.5(8)	26.6(8)	-4.5(6)	6.2(6)	-0.5(6)
C20	24.4(8)	33.9(9)	32.5(8)	-8.9(7)	2.4(6)	2.2(7)
C21	35.8(9)	33.8(9)	24.6(8)	-5.4(7)	-1.4(7)	11.1(7)
C22	46.6(10)	29.3(9)	21.7(8)	1.9(6)	6.0(7)	3.4(8)
C23	32.6(8)	25.9(8)	24.6(8)	-1.3(6)	6.6(6)	-2.6(7)
C24	35.5(9)	39.0(10)	45.0(10)	-10.0(8)	18.9(8)	3.2(8)
C25	60.6(12)	32.4(10)	45.9(10)	-20.6(8)	25.5(9)	-20.1(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	67.0(17)	64(2)	42.3(17)	-19.8(15)	15.1(15)	-25.9(17)
C27	42.4(16)	53.5(19)	39.1(17)	-10.6(14)	-13.8(12)	-6.5(14)
C28	92(6)	96(5)	117(8)	40(5)	19(6)	-13(5)
C29	92(2)	93(2)	93(2)	-0.2(10)	25.8(11)	-1.3(10)

Table 4 Bond Lengths for 3s.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O4	1.4296(12)	C1	C8	1.394(2)
S1	O5	1.4301(13)	C4	C5	1.397(2)
S1	N3	1.6321(13)	C5	C6	1.384(2)
S1	C24	1.7611(18)	C6	C7	1.409(2)
O1	C2	1.216(2)	C7	C8	1.385(2)
O2	C3	1.2166(19)	C7	C12	1.488(2)
O3	C9	1.3995(19)	C10	C11	1.499(3)
O3	C10	1.434(2)	C12	C13	1.392(2)
O6	C25	1.350(3)	C12	C17	1.397(2)
O6	C26	1.467(4)	C13	C14	1.390(2)
O6	C29	1.328(11)	C14	C15	1.376(3)
N1	C2	1.395(2)	C15	C16	1.386(3)
N1	C3	1.397(2)	C16	C17	1.388(2)
N1	C25	1.475(2)	C18	C19	1.384(2)
N2	C3	1.3772(19)	C18	C23	1.391(2)
N2	C4	1.3994(19)	C19	C20	1.389(2)
N2	C9	1.4797(19)	C20	C21	1.385(3)

Table 4 Bond Lengths for 3s.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N3	C6	1.4431(18)	C21	C22	1.382(3)
N3	C18	1.4512(18)	C22	C23	1.386(2)
C1	C2	1.465(2)	C26	C27	1.497(4)
C1	C4	1.397(2)	C28	C29	1.563(14)

Table 5 Bond Angles for 3s.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	S1	O5	119.71(8)	C6	C5	C4	119.99(13)
O4	S1	N3	108.07(7)	C5	C6	N3	119.40(13)
O4	S1	C24	106.91(9)	C5	C6	C7	121.87(13)
O5	S1	N3	105.78(7)	C7	C6	N3	118.42(13)
O5	S1	C24	108.97(9)	C6	C7	C12	122.56(13)
N3	S1	C24	106.75(8)	C8	C7	C6	117.25(13)
C9	O3	C10	113.72(12)	C8	C7	C12	120.18(13)
C25	O6	C26	112.6(2)	C7	C8	C1	121.69(14)
C29	O6	C25	119.5(6)	O3	C9	N2	111.03(12)
C2	N1	C3	125.25(13)	O3	C10	C11	107.97(15)
C2	N1	C25	116.55(14)	C13	C12	C7	120.13(14)
C3	N1	C25	118.18(14)	C13	C12	C17	118.96(14)
C3	N2	C4	122.62(13)	C17	C12	C7	120.87(14)
C3	N2	C9	117.99(12)	C14	C13	C12	120.53(16)
C4	N2	C9	118.98(12)	C15	C14	C13	120.07(17)
C6	N3	S1	122.08(10)	C14	C15	C16	120.04(16)
C6	N3	C18	115.89(11)	C15	C16	C17	120.28(17)

Table 5 Bond Angles for 3s.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	N3	S1	120.56(10)	C16	C17	C12	120.09(16)
C4	C1	C2	119.92(14)	C19	C18	N3	119.77(13)
C8	C1	C2	119.74(14)	C19	C18	C23	120.88(14)
C8	C1	C4	120.34(14)	C23	C18	N3	119.30(13)
O1	C2	N1	120.62(14)	C18	C19	C20	119.03(15)
O1	C2	C1	123.93(15)	C21	C20	C19	120.45(16)
N1	C2	C1	115.44(13)	C22	C21	C20	120.11(15)
O2	C3	N1	120.99(14)	C21	C22	C23	120.06(16)
O2	C3	N2	122.18(14)	C22	C23	C18	119.46(15)
N2	C3	N1	116.82(13)	O6	C25	N1	114.41(19)
C1	C4	N2	119.82(13)	O6	C26	C27	107.0(3)
C5	C4	N2	121.35(13)	O6	C29	C28	95.9(10)
C5	C4	C1	118.83(13)				

Table 6 Torsion Angles for 3s.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N3	C6	C5	77.63(16)	C6	C7	C12	C17	62.8(2)
S1	N3	C6	C7	-108.62(14)	C7	C12	C13	C14	-178.83(14)
S1	N3	C18	C19	83.48(16)	C7	C12	C17	C16	177.46(14)
S1	N3	C18	C23	-99.08(15)	C8	C1	C2	O1	4.0(3)
O4	S1	N3	C6	146.51(12)	C8	C1	C2	N1	-176.31(14)
O4	S1	N3	C18	-47.85(13)	C8	C1	C4	N2	177.20(14)
O5	S1	N3	C6	17.17(13)	C8	C1	C4	C5	-1.7(2)
O5	S1	N3	C18	-177.18(11)	C8	C7	C12	C13	59.4(2)

Table 6 Torsion Angles for 3s.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C4	C5	C6	-176.80(13)	C8	C7	C12	C17	-118.04(17)
N3	C6	C7	C8	-173.51(13)	C9	O3	C10	C11	-174.31(13)
N3	C6	C7	C12	5.6(2)	C9	N2	C3	O2	-7.4(2)
N3	C18	C19	C20	178.04(13)	C9	N2	C3	N1	173.64(13)
N3	C18	C23	C22	-177.22(14)	C9	N2	C4	C1	-171.89(13)
C1	C4	C5	C6	2.1(2)	C9	N2	C4	C5	7.0(2)
C2	N1	C3	O2	-178.89(15)	C10	O3	C9	N2	72.92(16)
C2	N1	C3	N2	0.0(2)	C12	C7	C8	C1	-178.85(14)
C2	N1	C25	O6	79.2(2)	C12	C13	C14	C15	1.5(2)
C2	C1	C4	N2	-3.3(2)	C13	C12	C17	C16	0.0(2)
C2	C1	C4	C5	177.80(14)	C13	C14	C15	C16	-0.3(3)
C2	C1	C8	C7	-178.99(14)	C14	C15	C16	C17	-1.1(3)
C3	N1	C2	O1	177.08(16)	C15	C16	C17	C12	1.2(3)
C3	N1	C2	C1	-2.6(2)	C17	C12	C13	C14	-1.3(2)
C3	N1	C25	O6	-102.3(2)	C18	N3	C6	C5	-88.64(16)
C3	N2	C4	C1	0.6(2)	C18	N3	C6	C7	85.11(16)
C3	N2	C4	C5	179.42(14)	C18	C19	C20	C21	-0.7(2)
C3	N2	C9	O3	-114.72(14)	C19	C18	C23	C22	0.2(2)
C4	N2	C3	O2	-179.96(15)	C19	C20	C21	C22	-0.1(3)
C4	N2	C3	N1	1.1(2)	C20	C21	C22	C23	0.9(3)
C4	N2	C9	O3	58.09(17)	C21	C22	C23	C18	-1.0(2)
C4	C1	C2	O1	-175.49(16)	C23	C18	C19	C20	0.6(2)
C4	C1	C2	N1	4.2(2)	C24	S1	N3	C6	-98.80(13)
C4	C1	C8	C7	0.5(2)	C24	S1	N3	C18	66.85(13)
C4	C5	C6	N3	172.24(13)	C25	O6	C26	C27	140.2(3)
C4	C5	C6	C7	-1.3(2)	C25	O6	C29	C28	114.1(8)

Table 6 Torsion Angles for 3s.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	C6	C7	C8	0.1(2)	C25	N1	C2	O1	-4.6(2)
C5	C6	C7	C12	179.23(14)	C25	N1	C2	C1	175.67(16)
C6	N3	C18	C19	-110.02(15)	C25	N1	C3	O2	2.8(2)
C6	N3	C18	C23	67.41(18)	C25	N1	C3	N2	-178.24(16)
C6	C7	C8	C1	0.3(2)	C26	O6	C25	N1	91.8(3)
C6	C7	C12	C13	-119.69(16)	C29	O6	C25	N1	45.9(8)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3s.

Atom	*x*	*y*	*z*	U(eq)
H5	3388.14	2834.1	1984	25
H8	1679.63	3719.07	3829.52	28
H9A	4819	5585.17	2019.96	29
H9B	4722.19	4042.84	2089.21	29
H10A	3732.54	6691.71	982.98	41
H10B	2994.74	6494.66	1515.44	41
H11A	2666.41	5457.48	-3.36	67
H11B	2181.13	6774.06	187.79	67
H11C	1914.15	5421.13	521.43	67
H13	-60.84	2890.87	2854.06	31
H14	-1288.11	1525.99	3030.63	39
H15	-944.22	-608.07	3429.89	45
H16	625.61	-1396.52	3645.07	43
H17	1848.02	-69.46	3423.4	33
H19	250.94	278.93	1538.32	30

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3s.

Atom	*x*	*y*	*z*	U(eq)
H20	-977.6	777.27	441.31	37
H21	-685.78	2195.65	-488.55	40
H22	830.48	3133.03	-329.3	40
H23	2075.25	2604.81	747.51	33
H24A	3771.38	707.83	1413.06	57
H24B	2921.81	27.77	781.96	57
H24C	3755.78	-836.91	1314.7	57
H25A	4090(17)	8240(20)	3821(14)	54(7)
H25B	3141(17)	7890(20)	4221(13)	52(6)
H26A	5487.41	8173.54	4408.7	69
H26B	5765.59	6830.53	4867.95	69
H27A	5560.81	9269.04	5561.68	74
H27B	6556.6	8513.95	5645.57	74
H27C	5756.15	7936	6034.3	74
H28A	5681.53	8693.37	4884.74	155
H28B	6561.76	7701.42	5146.74	155
H28C	5961.24	8135.29	5746.19	155
H29A	5286.76	6367.26	4456.58	110
H29B	5280.1	6096.08	5347.57	110

Table 8 Atomic Occupancy for 3s.

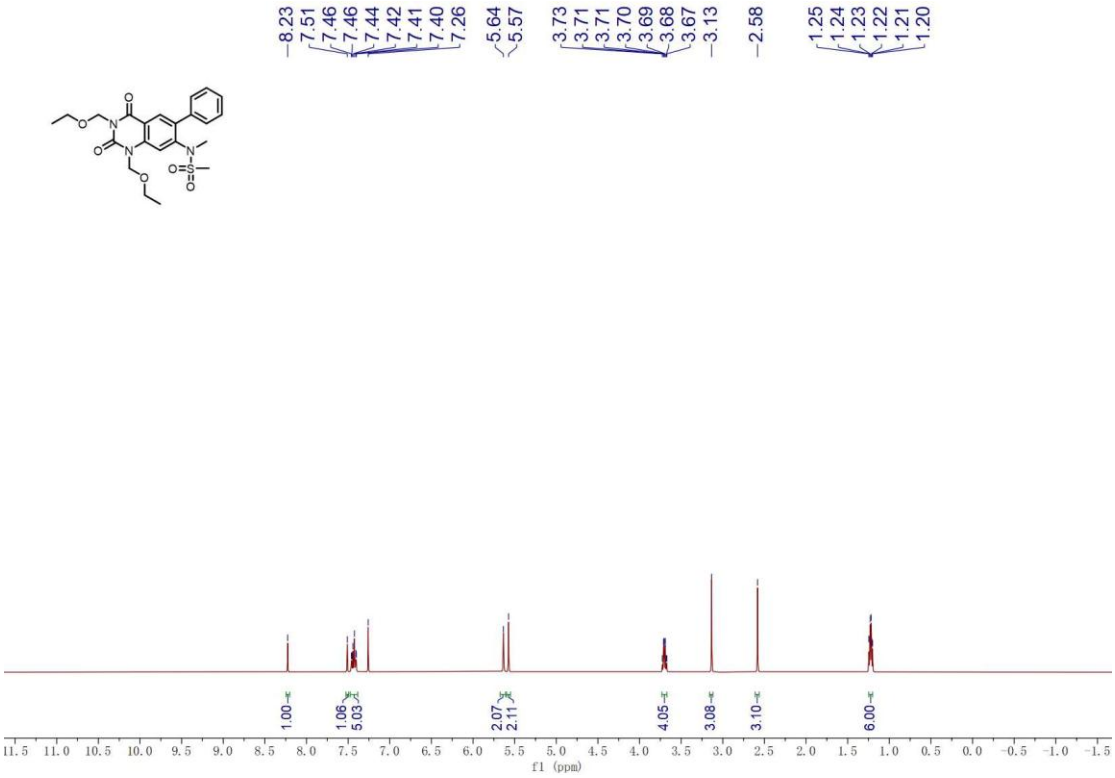
Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C26	0.711(7)	H26A	0.711(7)	H26B	0.711(7)
C27	0.711(7)	H27A	0.711(7)	H27B	0.711(7)

Table 8 Atomic Occupancy for 3s.

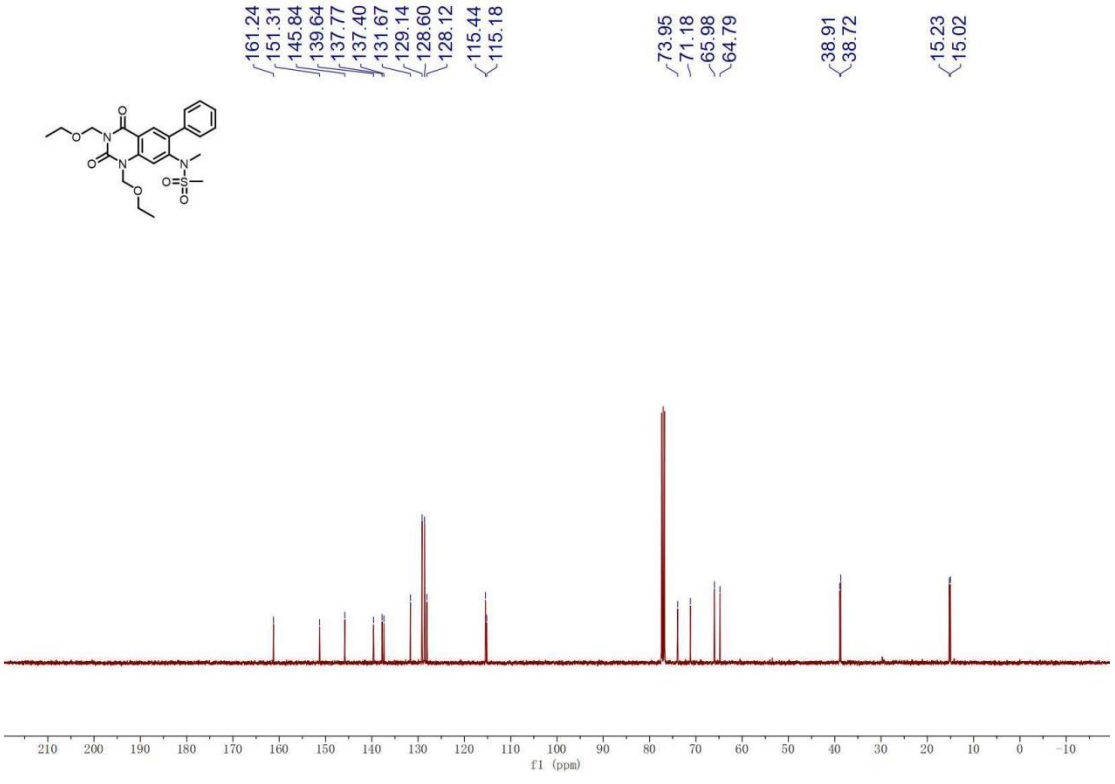
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H27C	0.711(7)	C28	0.289(7)	H28A	0.289(7)
H28B	0.289(7)	H28C	0.289(7)	C29	0.289(7)
H29A	0.289(7)	H29B	0.289(7)		

7. NMR Spectra for New Compounds

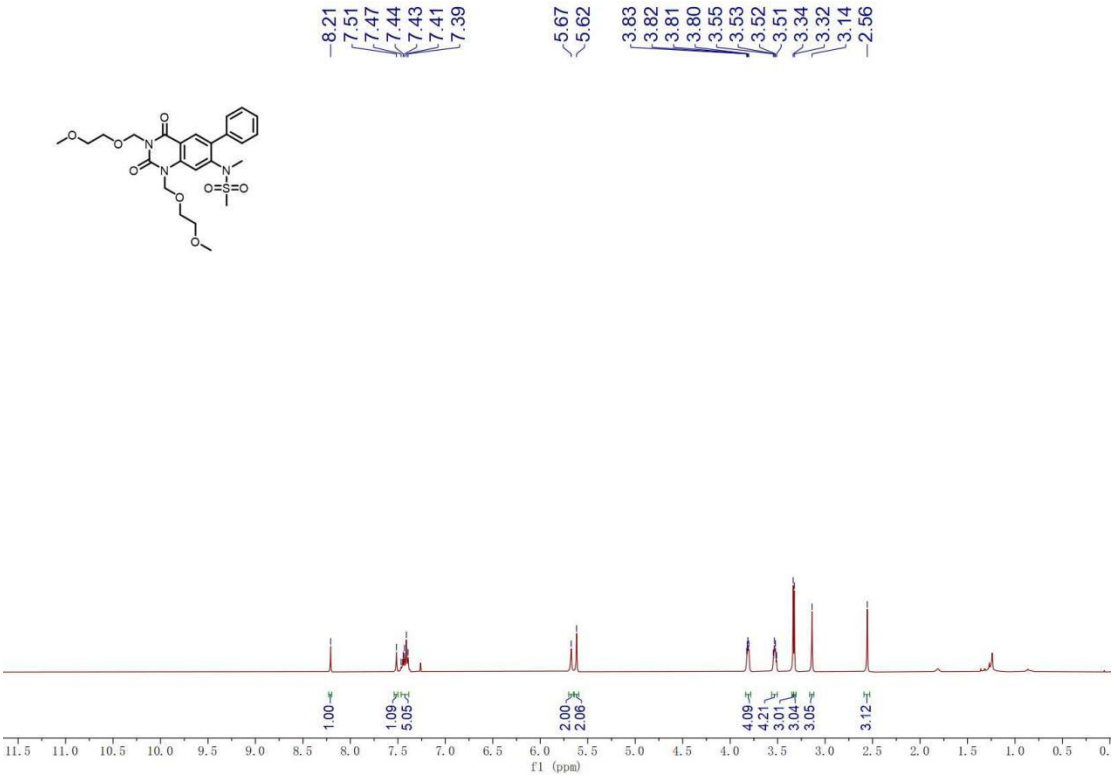
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3a**



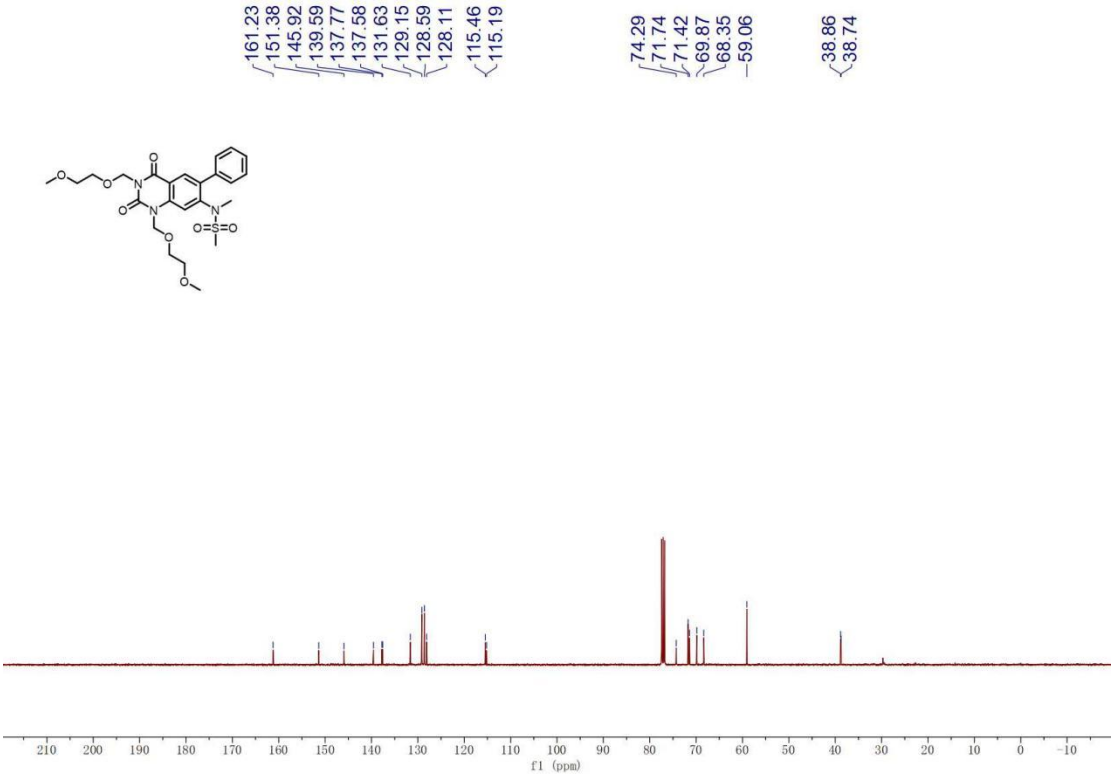
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3a**



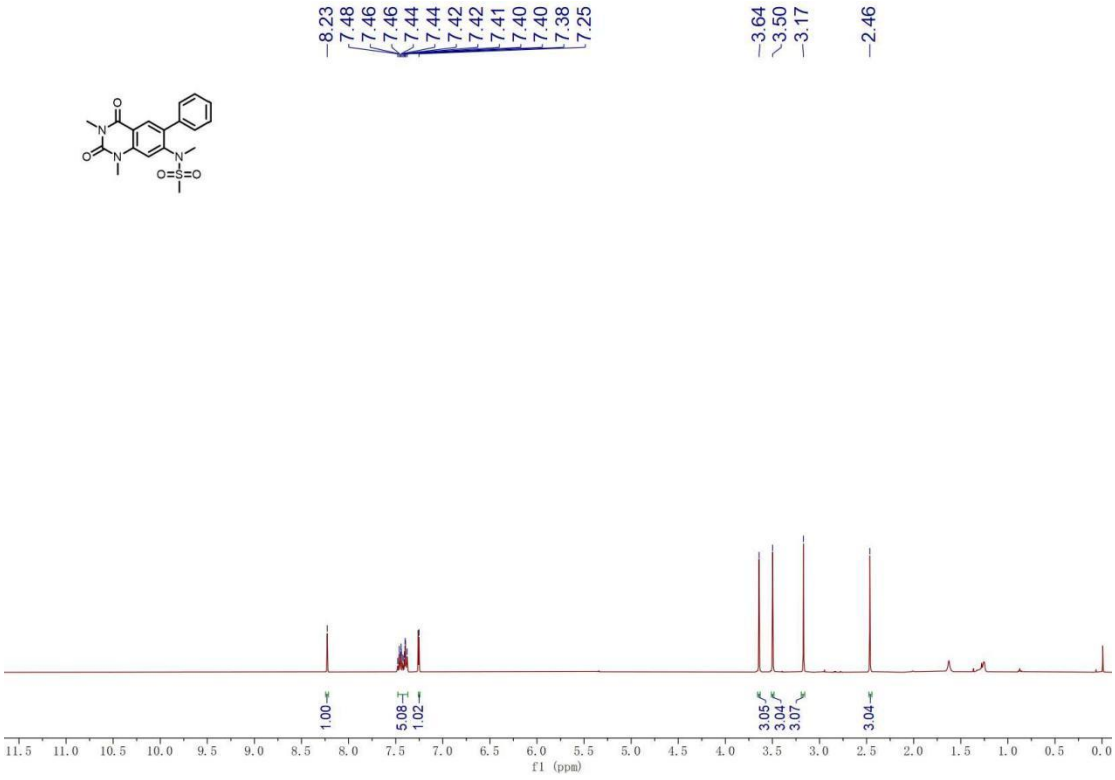
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3b**



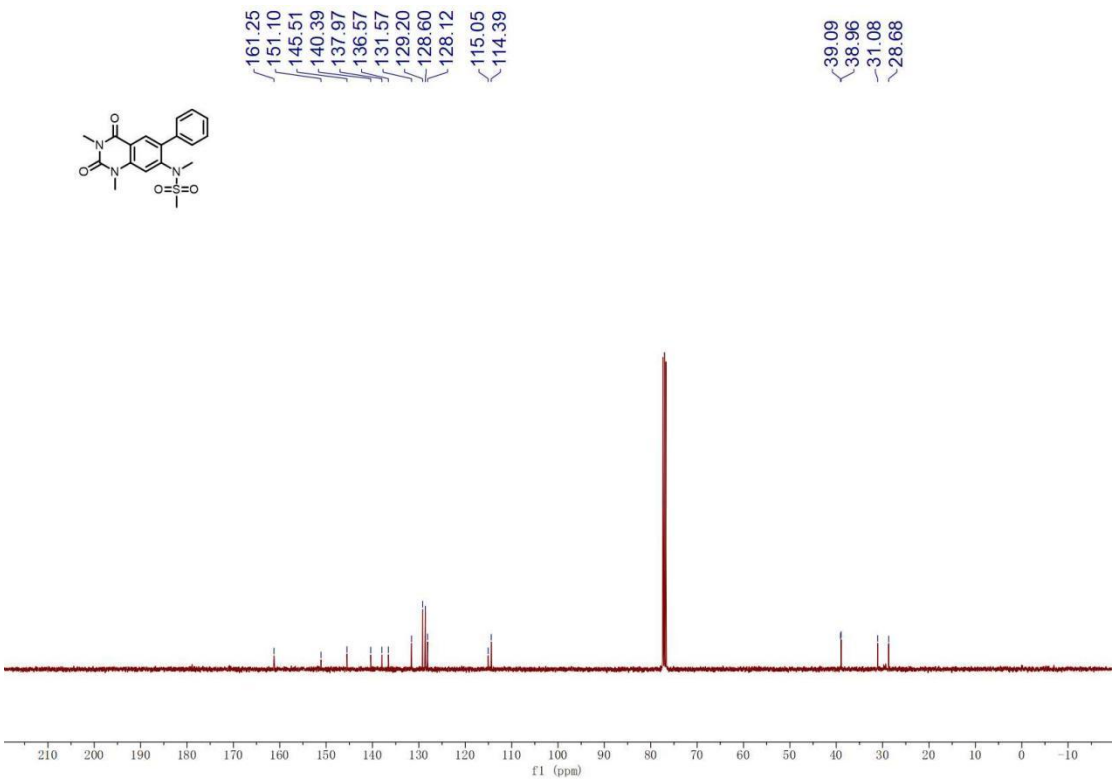
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3b**



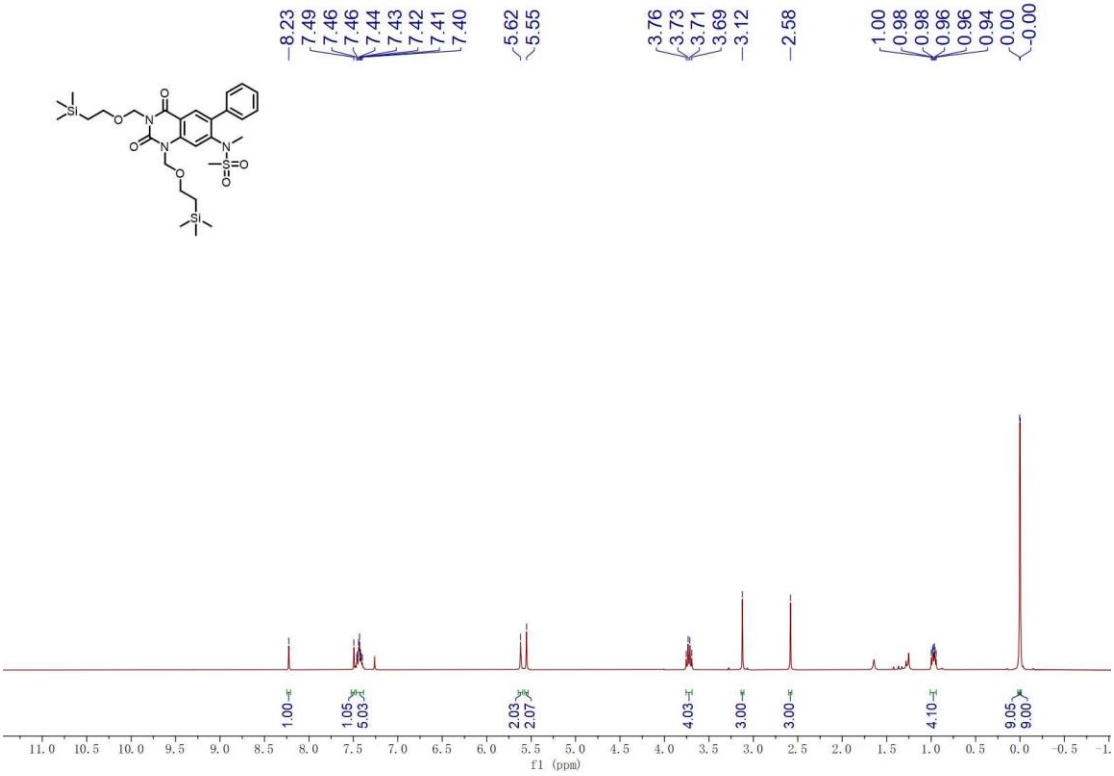
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3c**



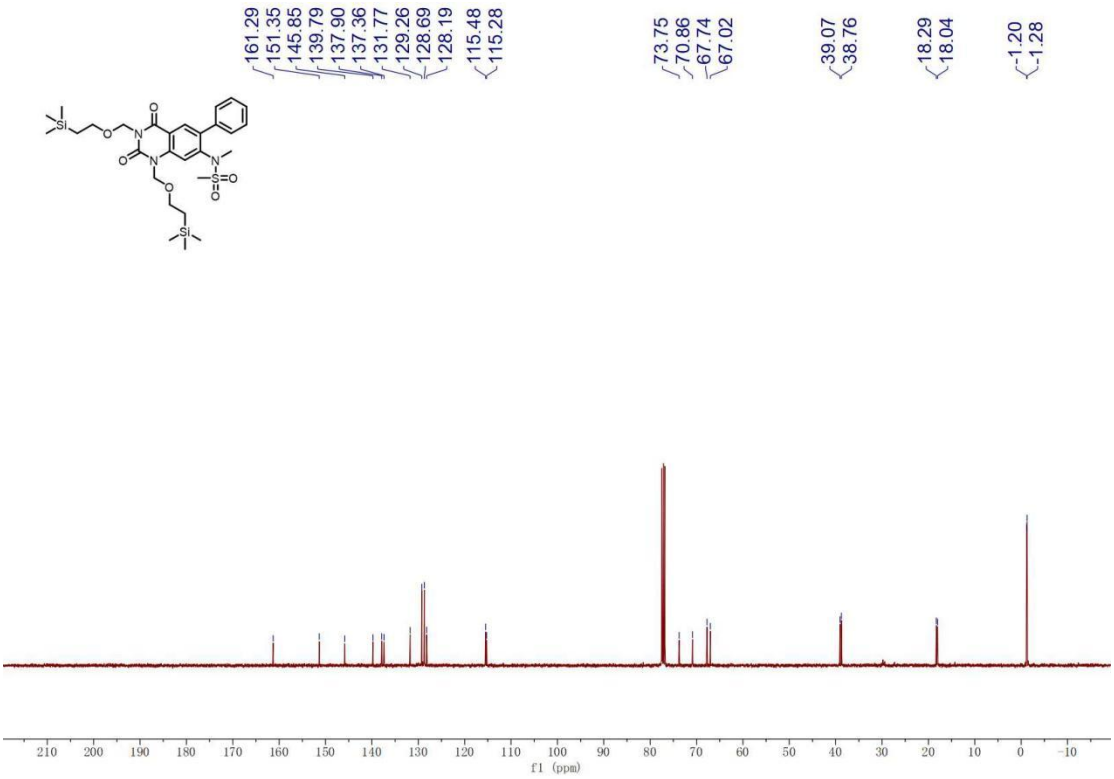
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3c**



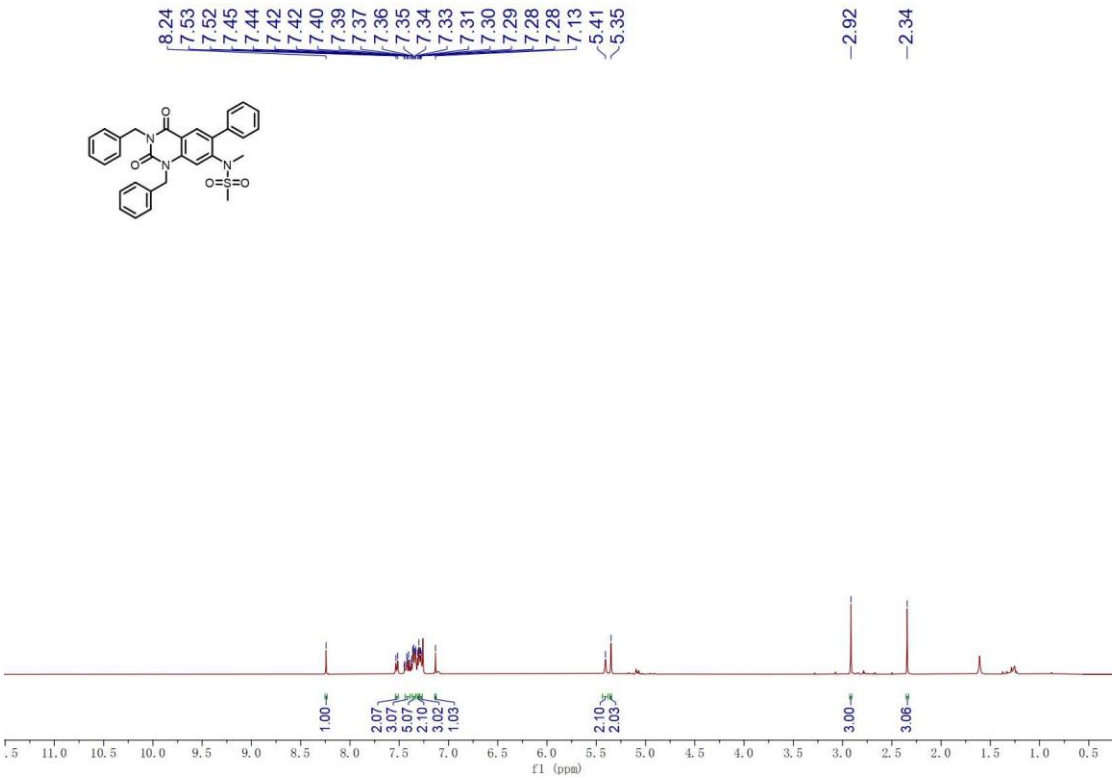
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3d**



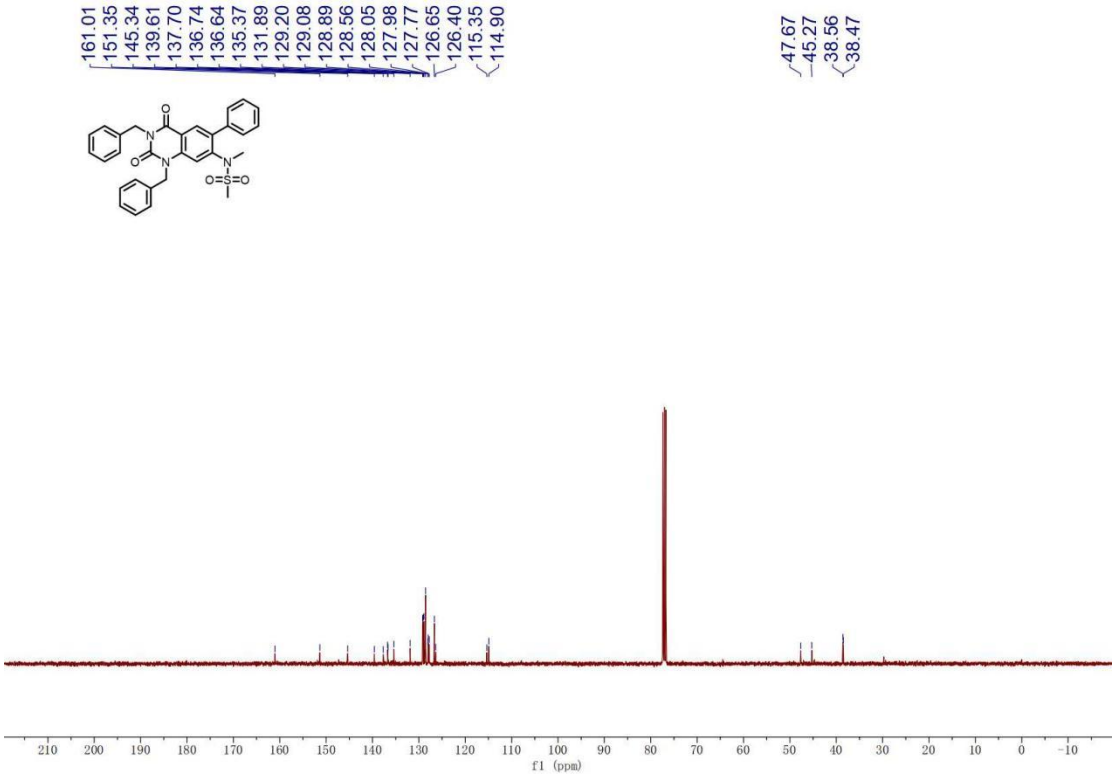
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3d**



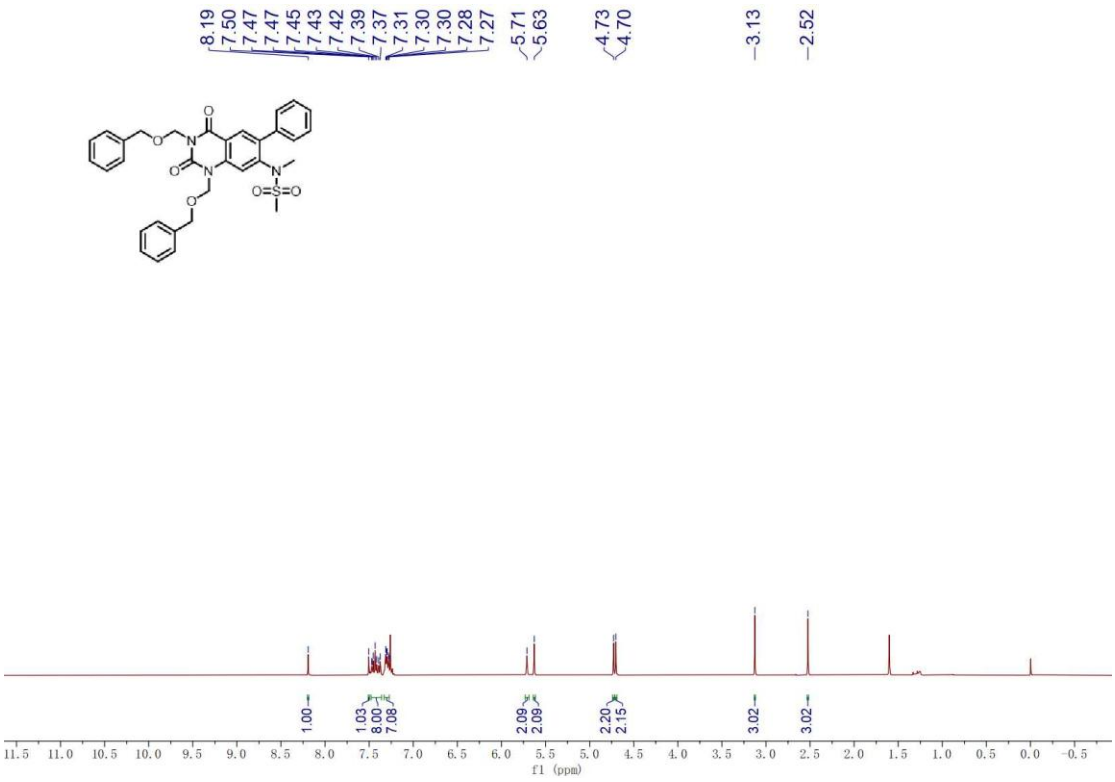
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3e**



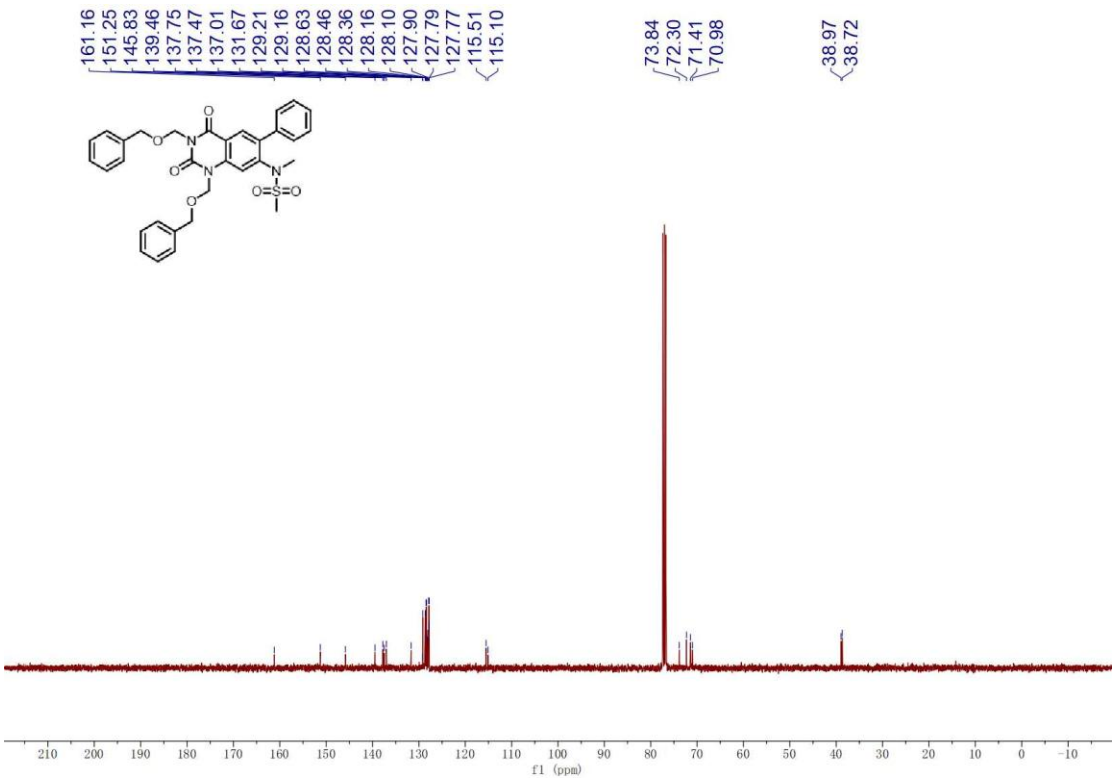
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3e**



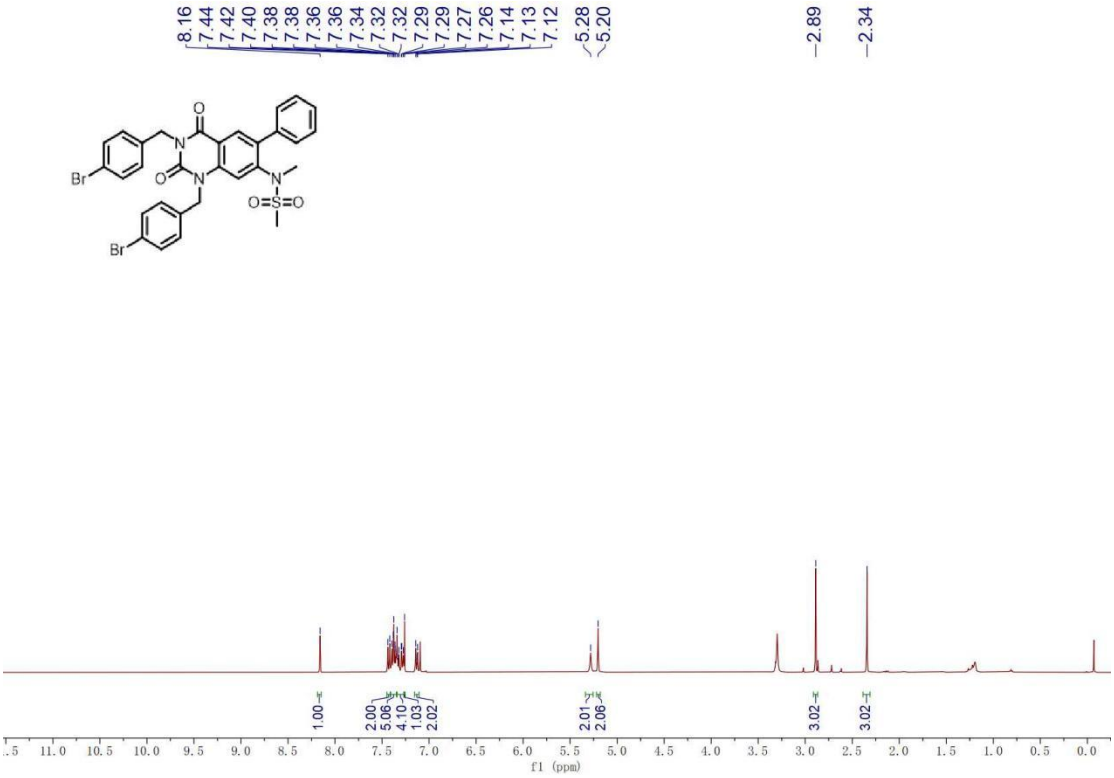
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3f**



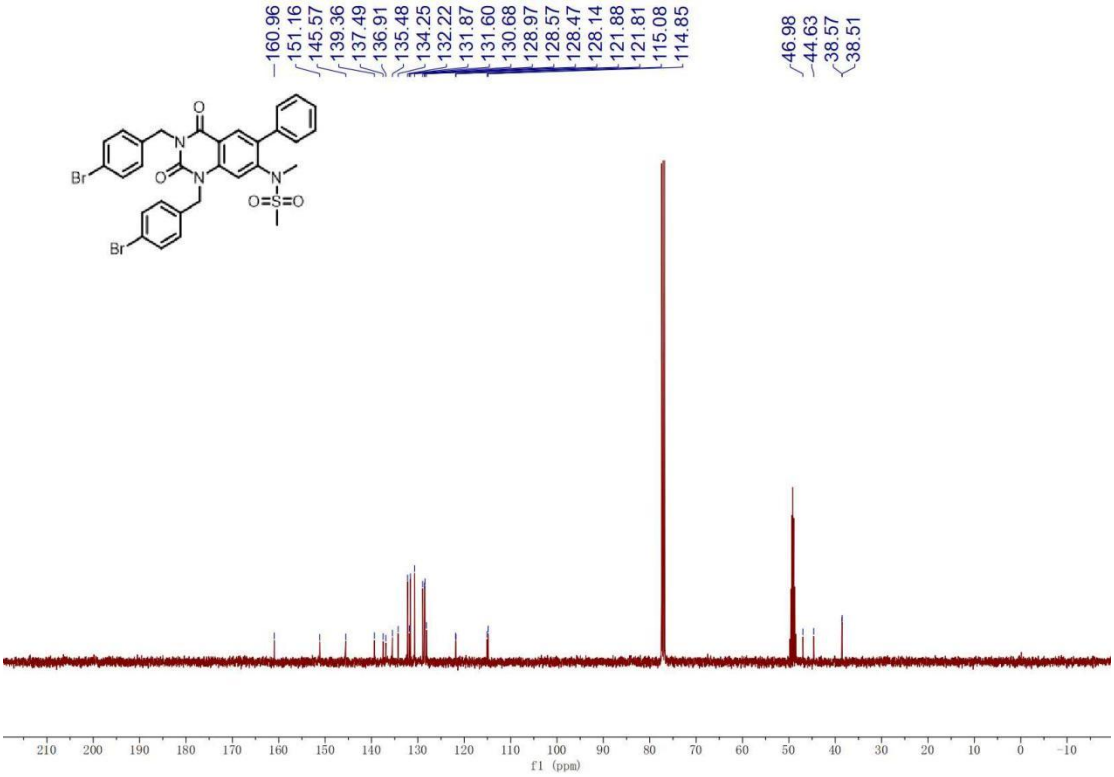
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3f**



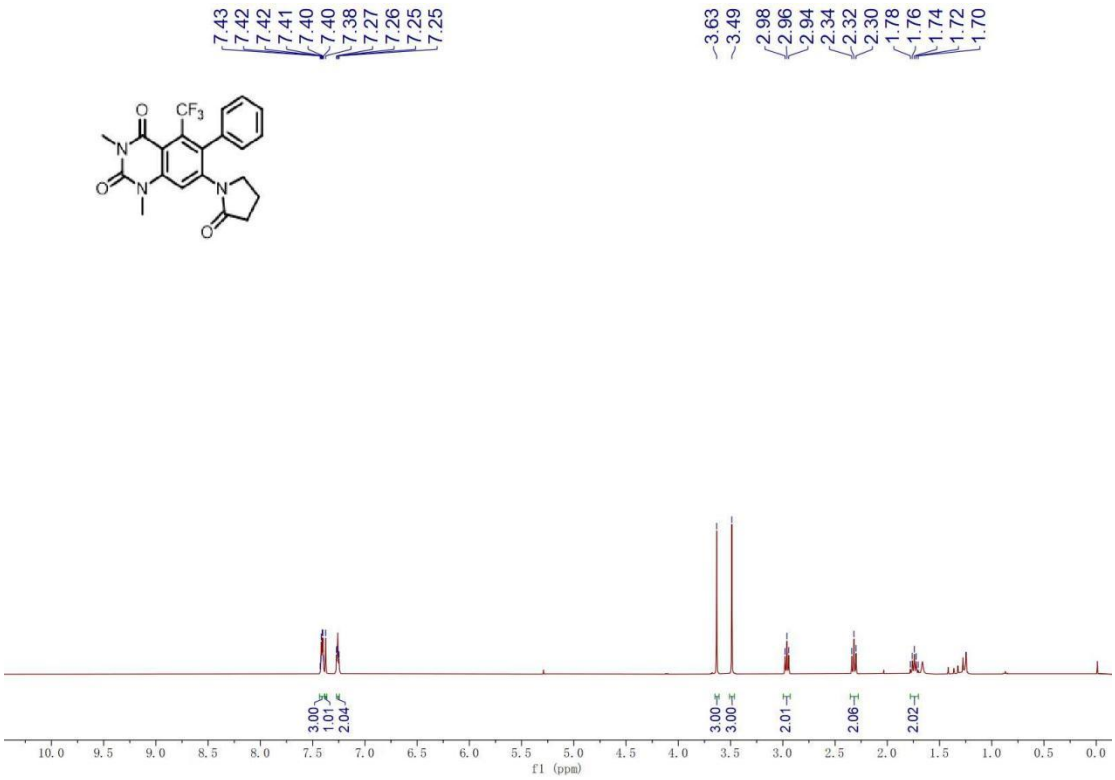
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3g**



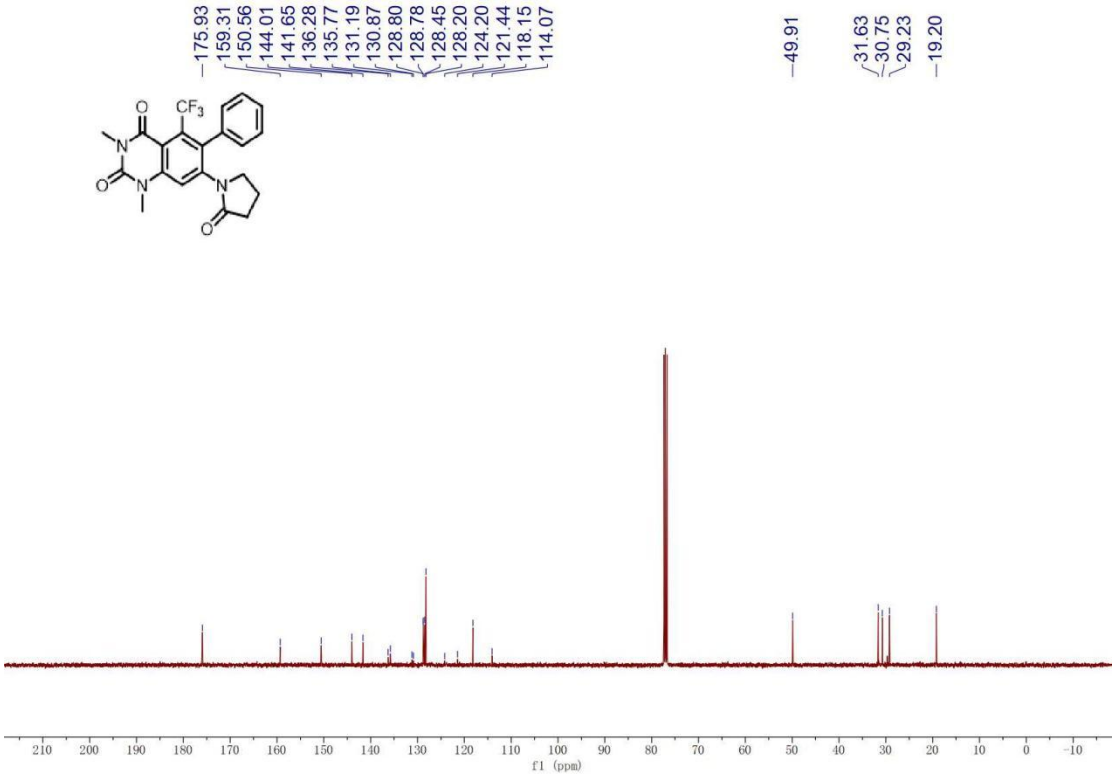
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3g**



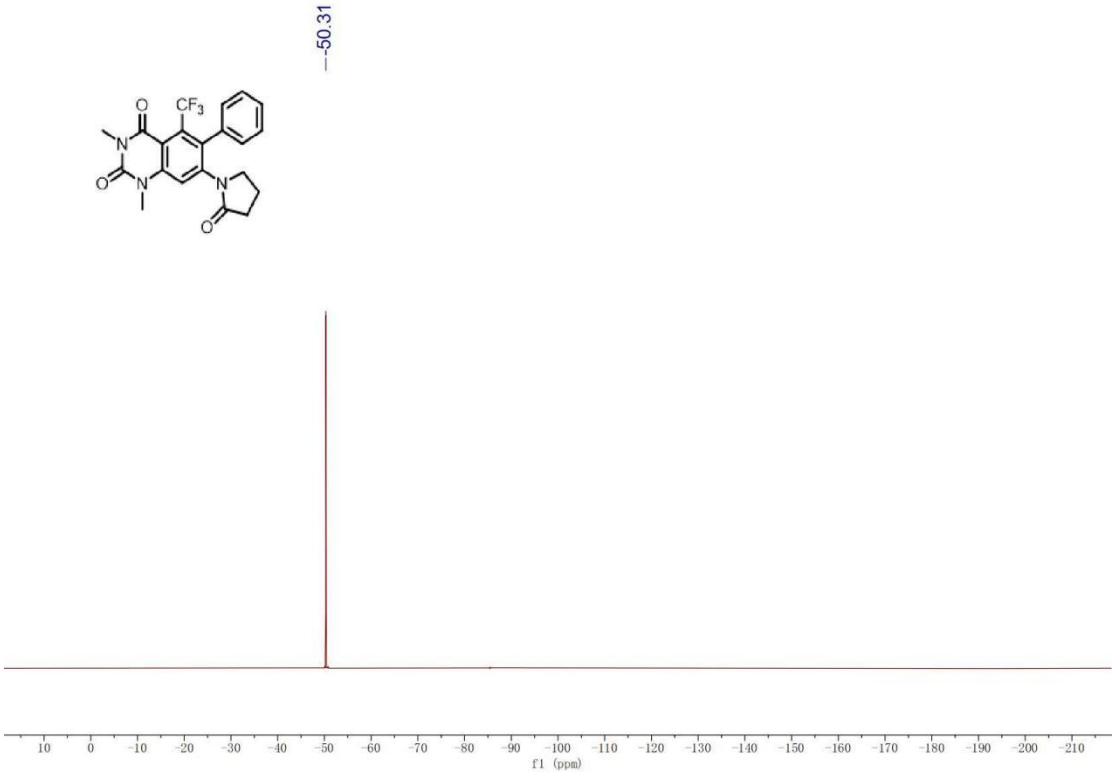
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3h**



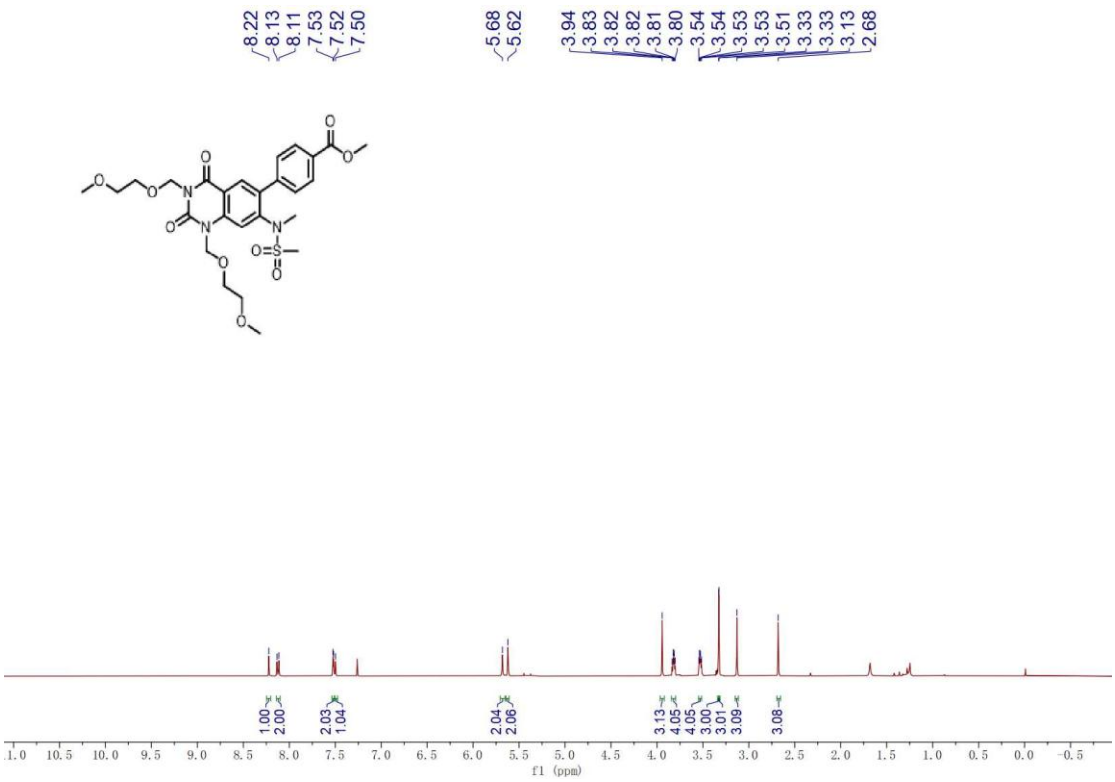
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3h**



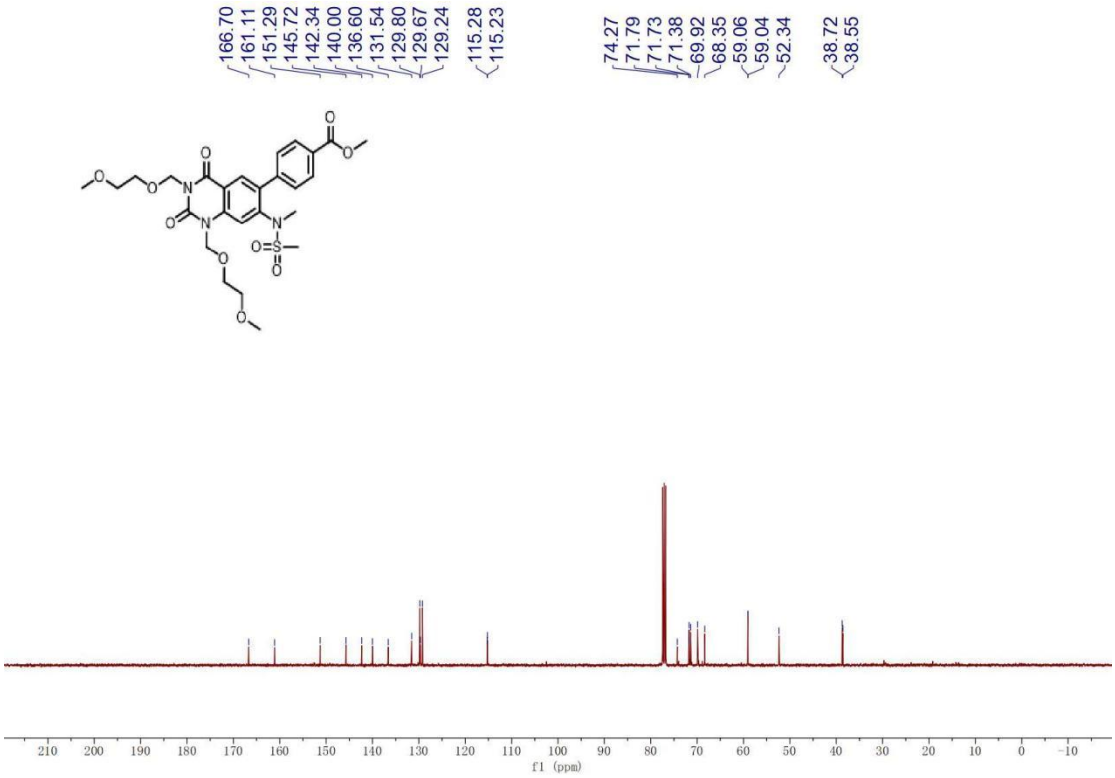
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **3h**



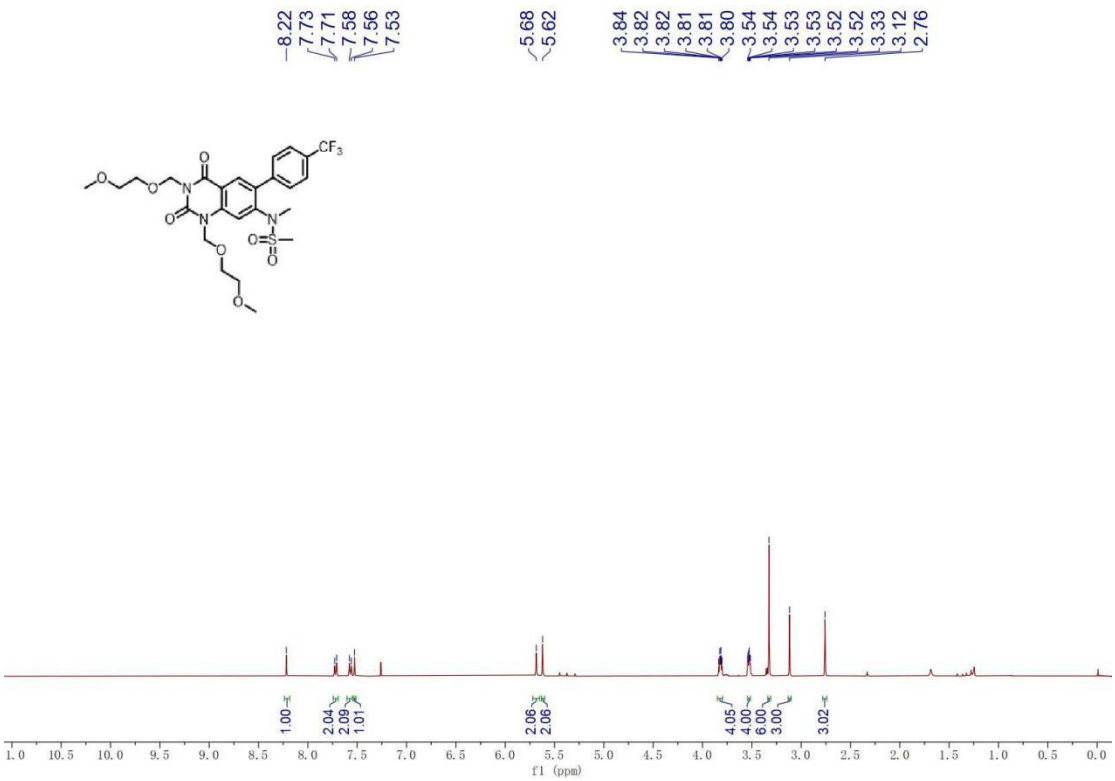
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3i**



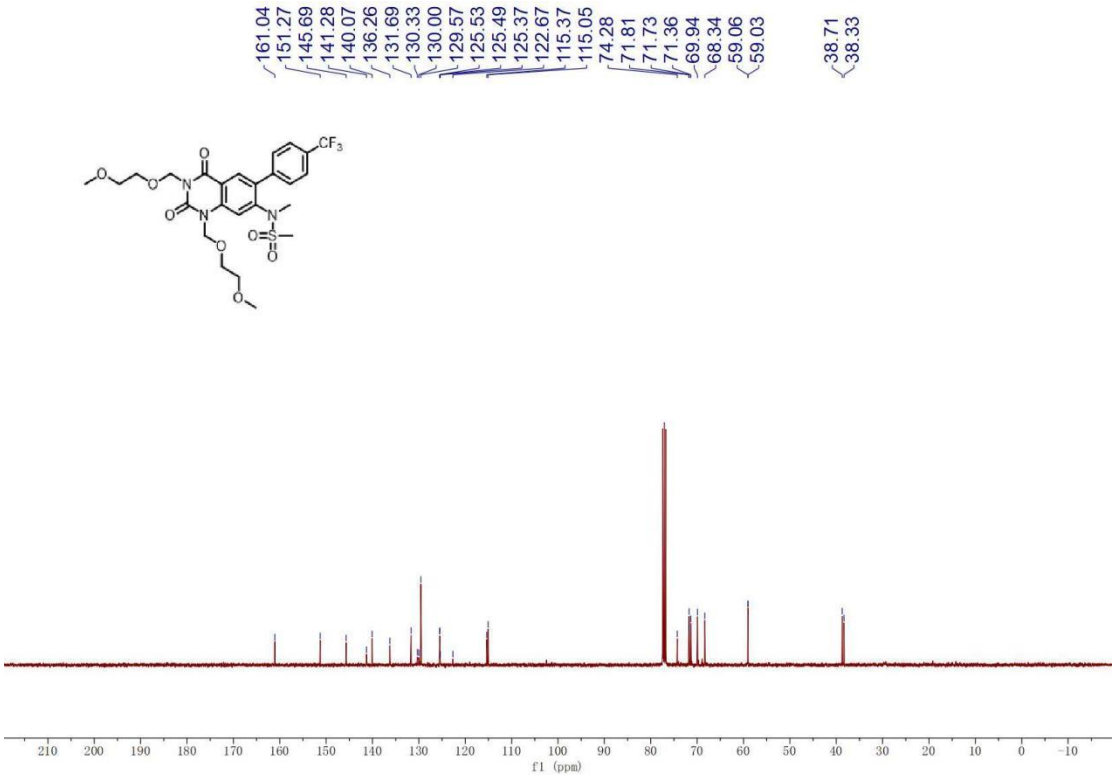
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3i**



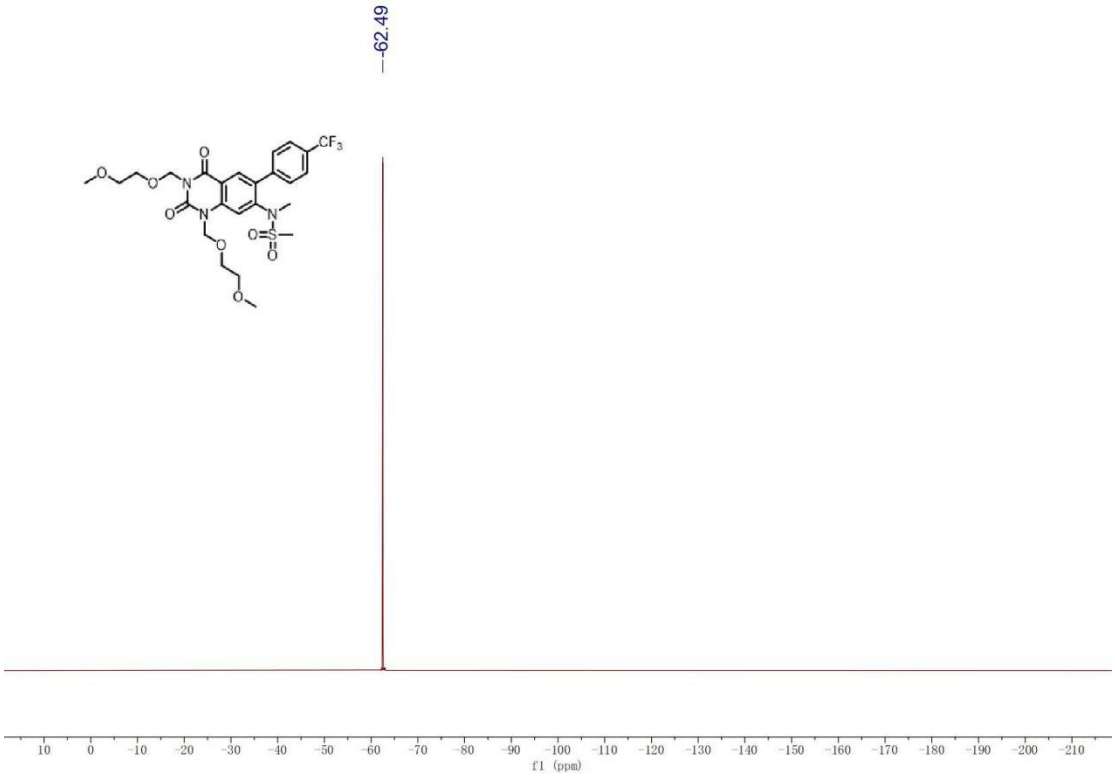
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3j**



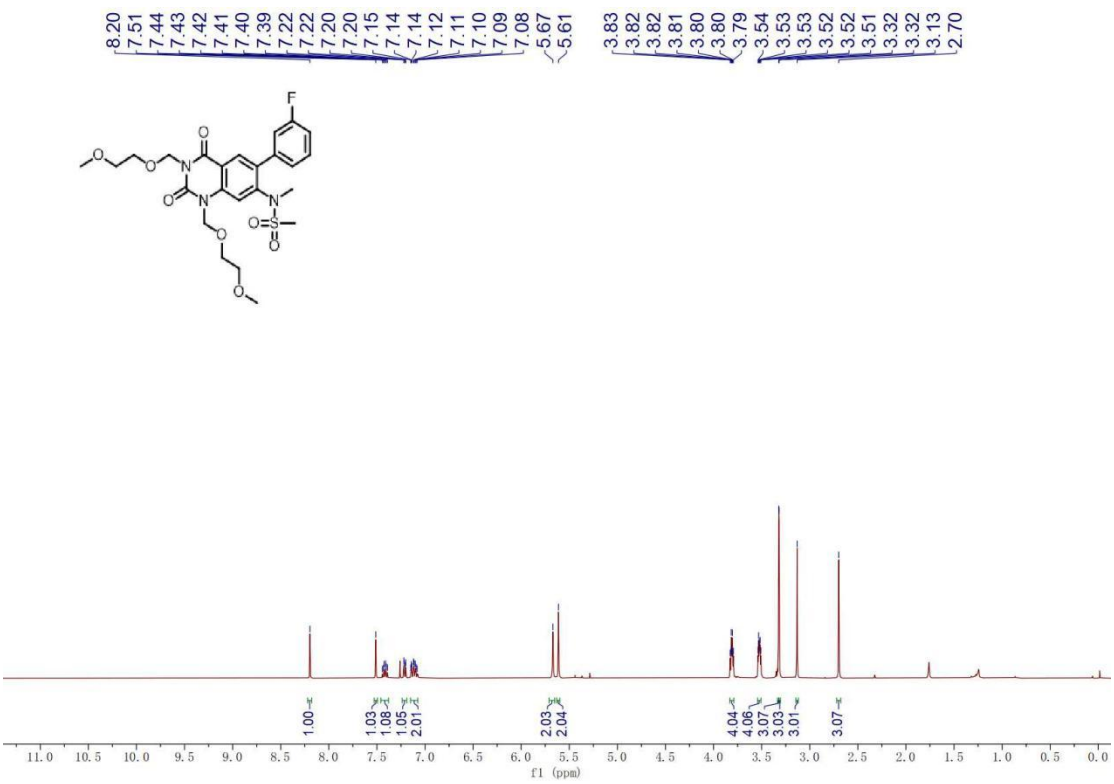
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3j**



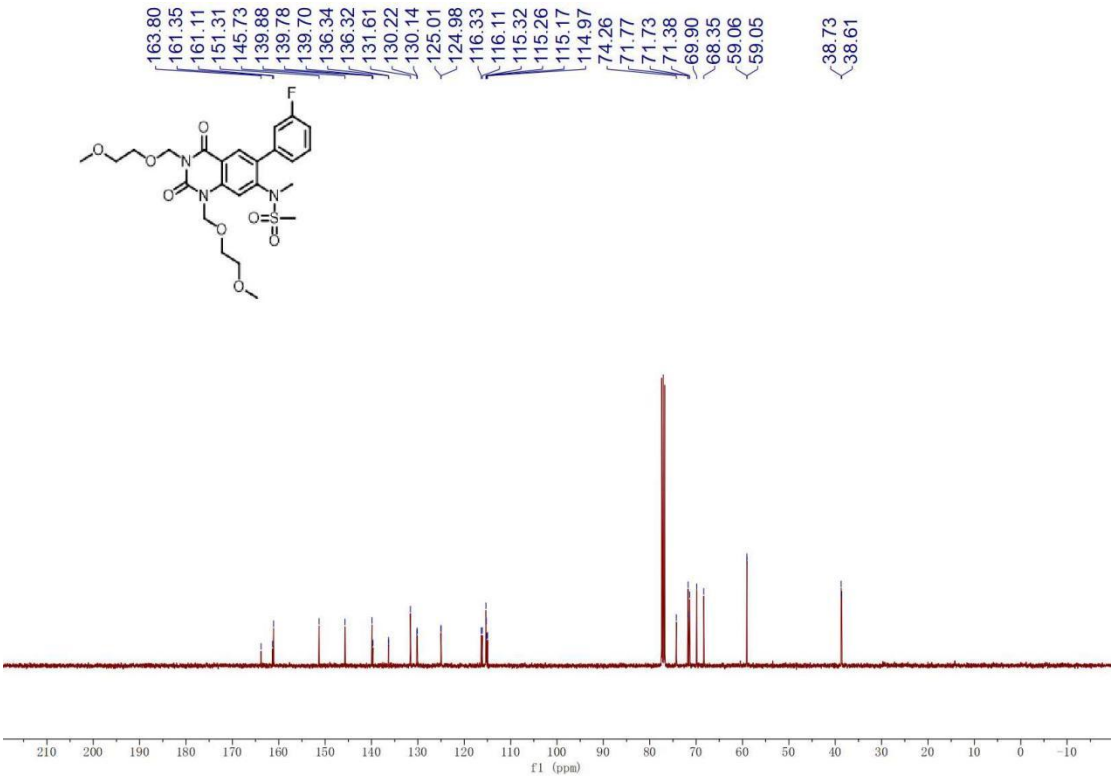
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **3j**



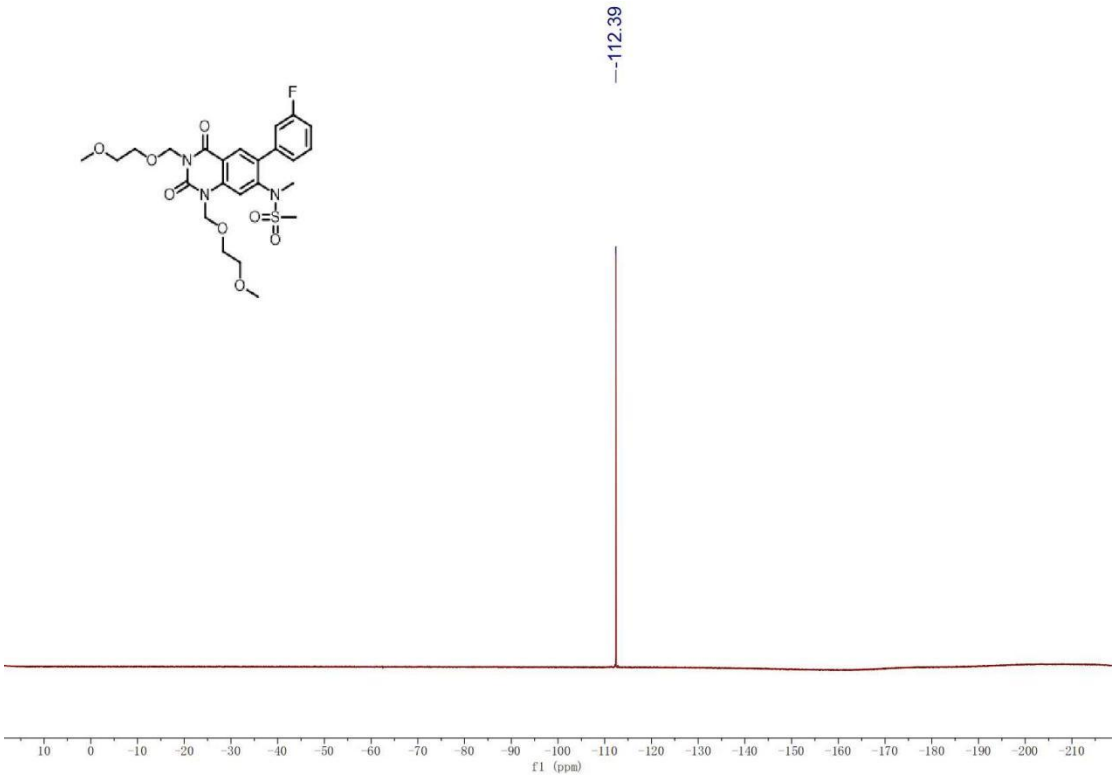
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3k**



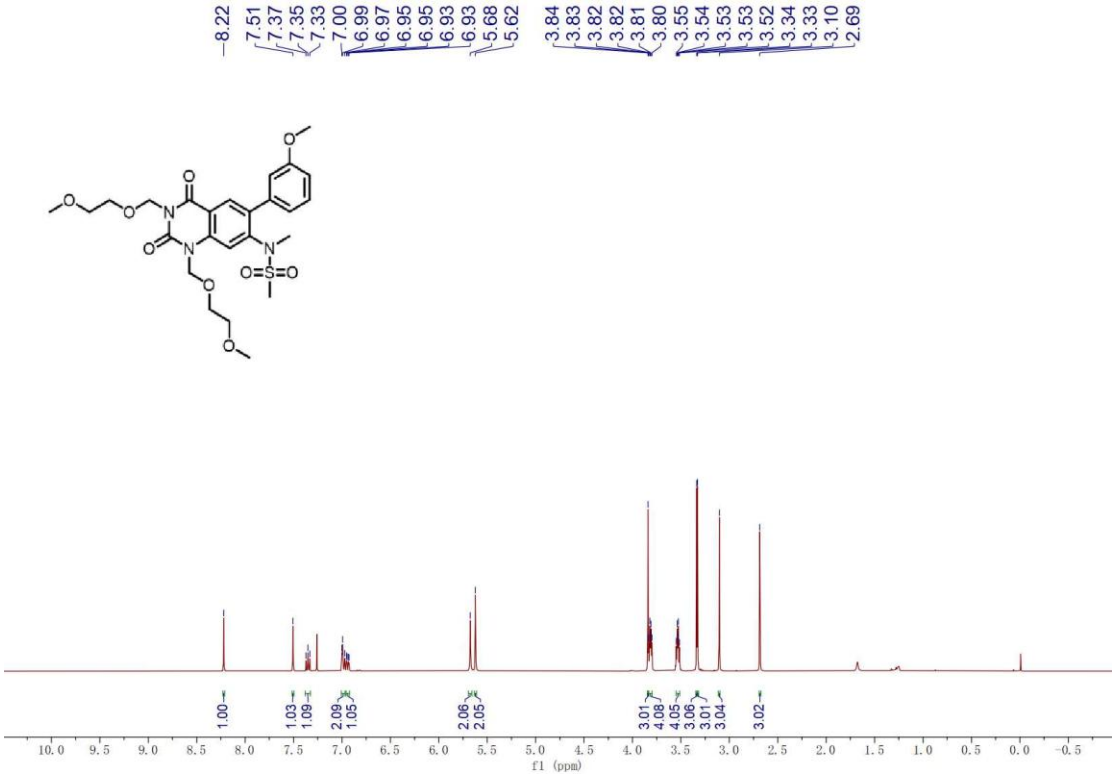
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3k**



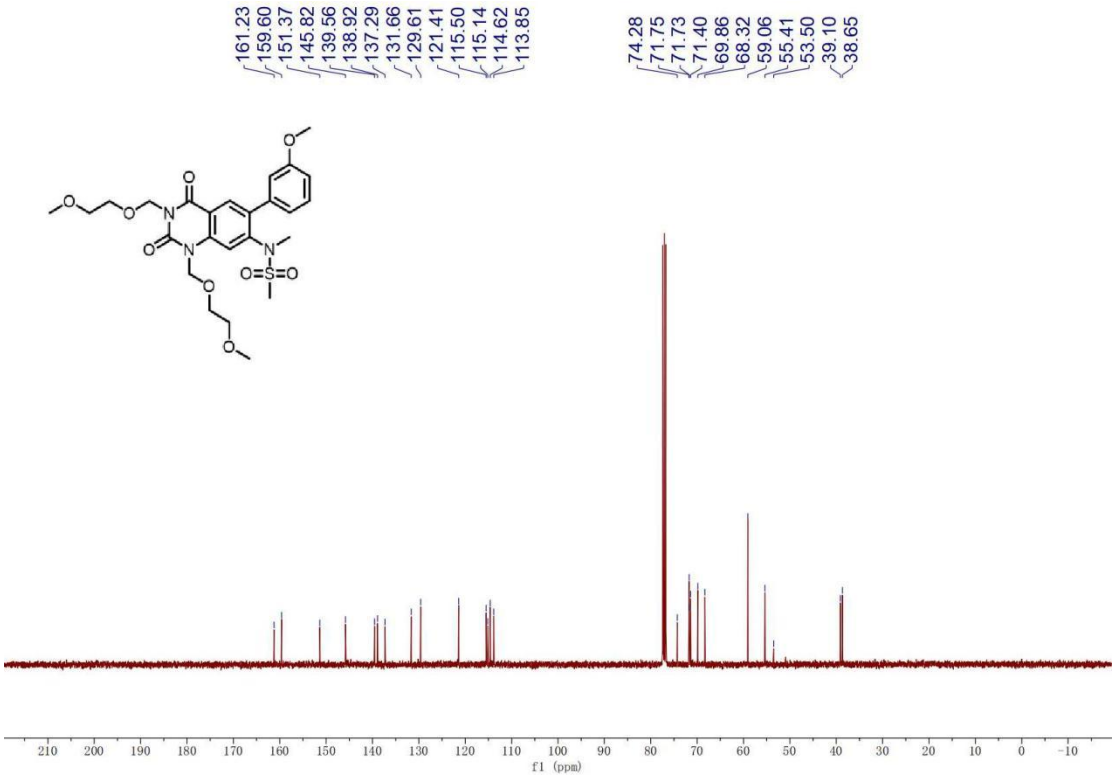
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **3k**



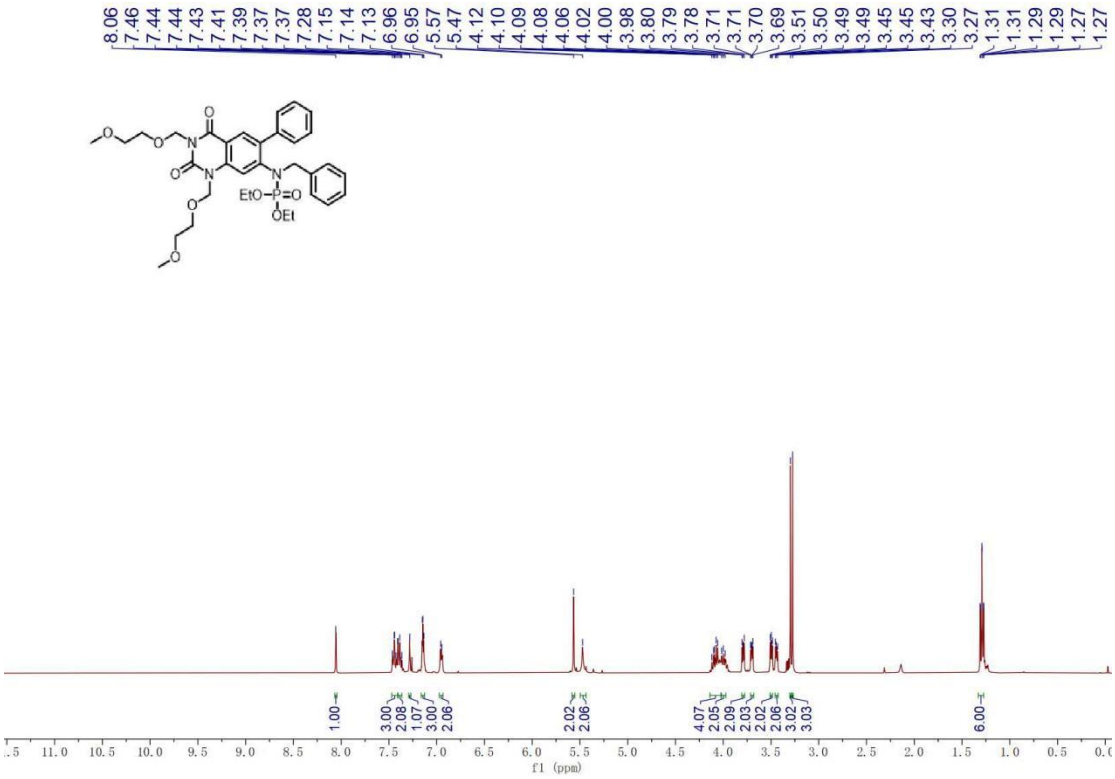
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3l**



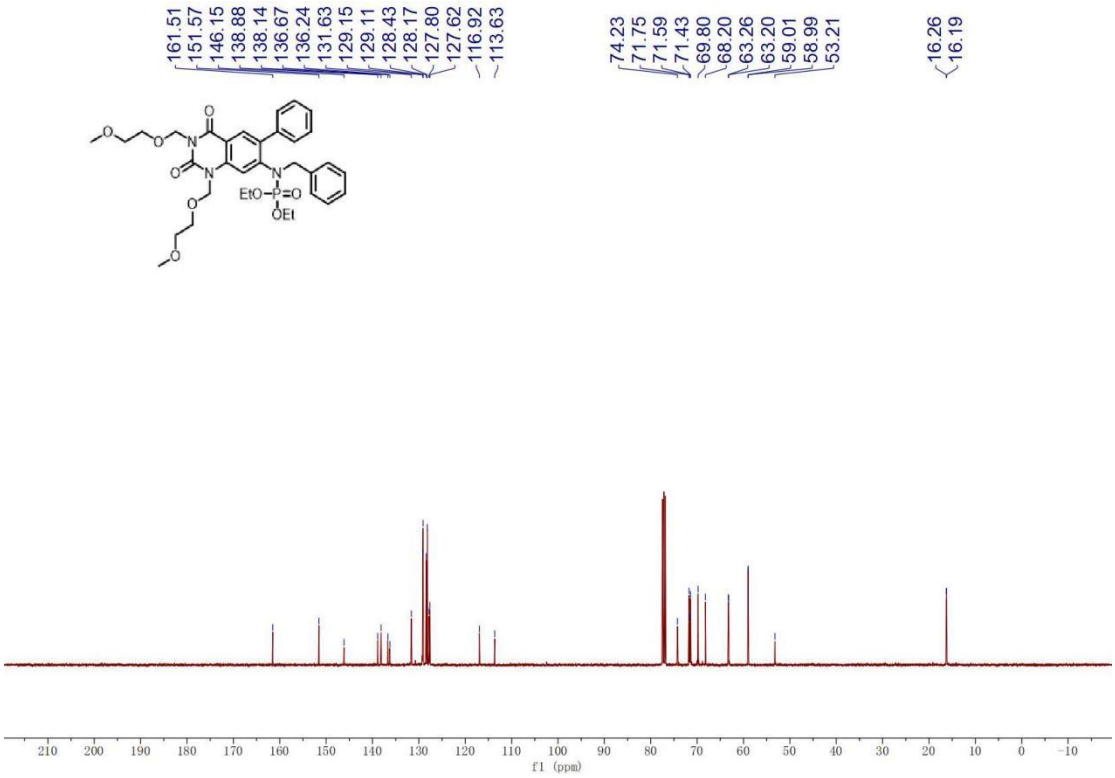
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3l**



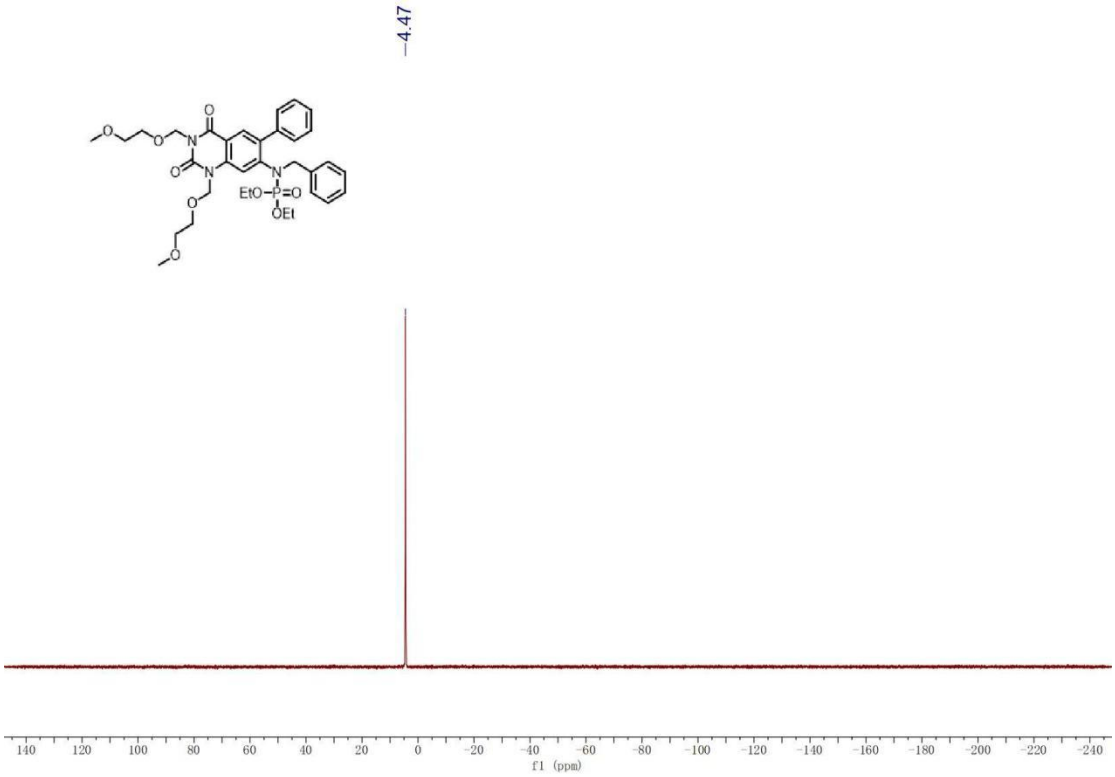
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3m**



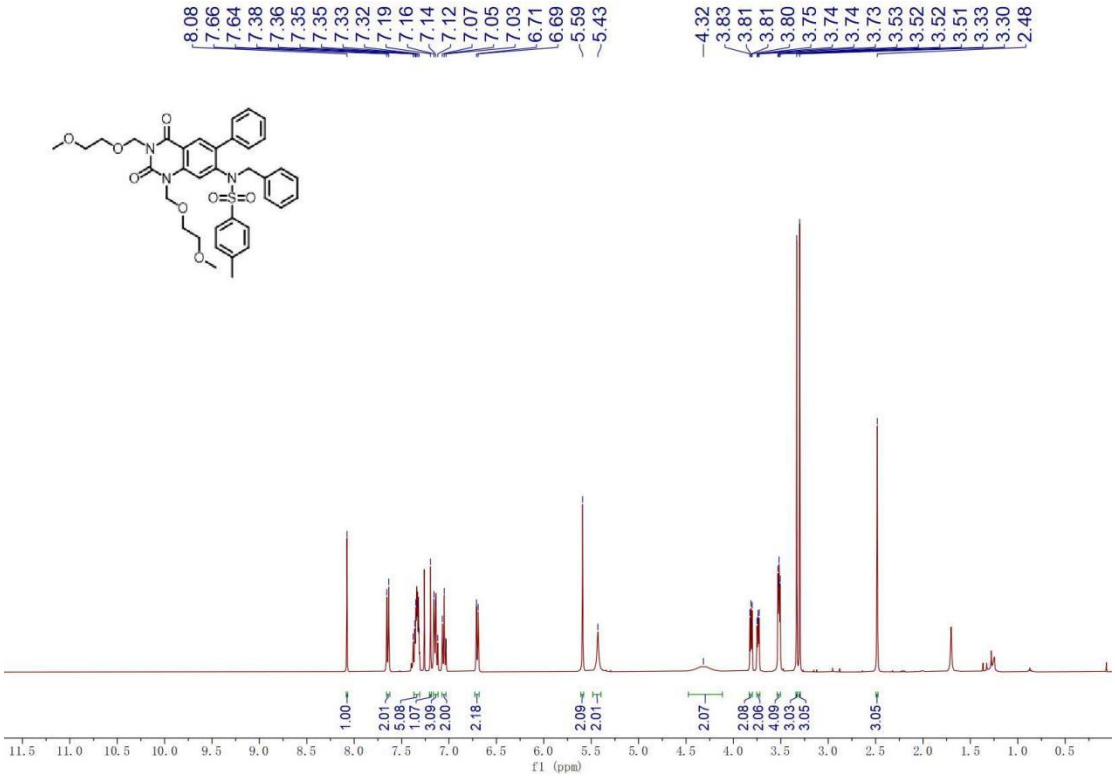
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3m**



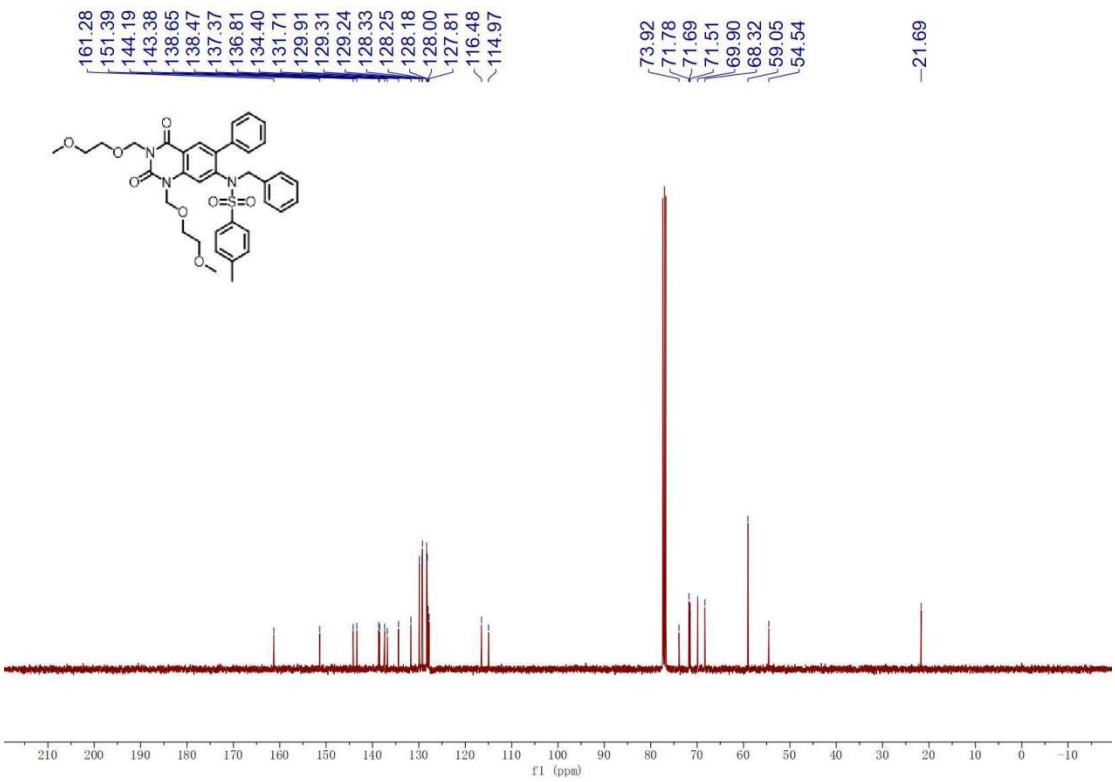
^{31}P NMR (162 MHz, $CDCl_3$) Spectra of **3m**



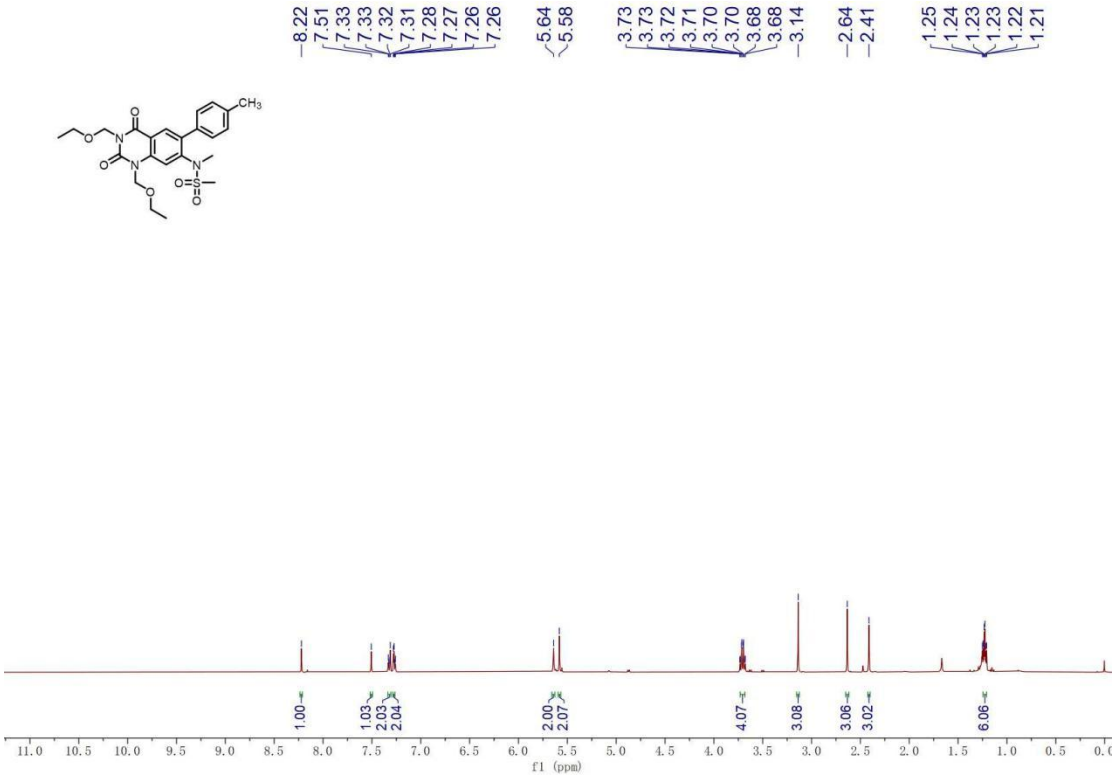
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3n**



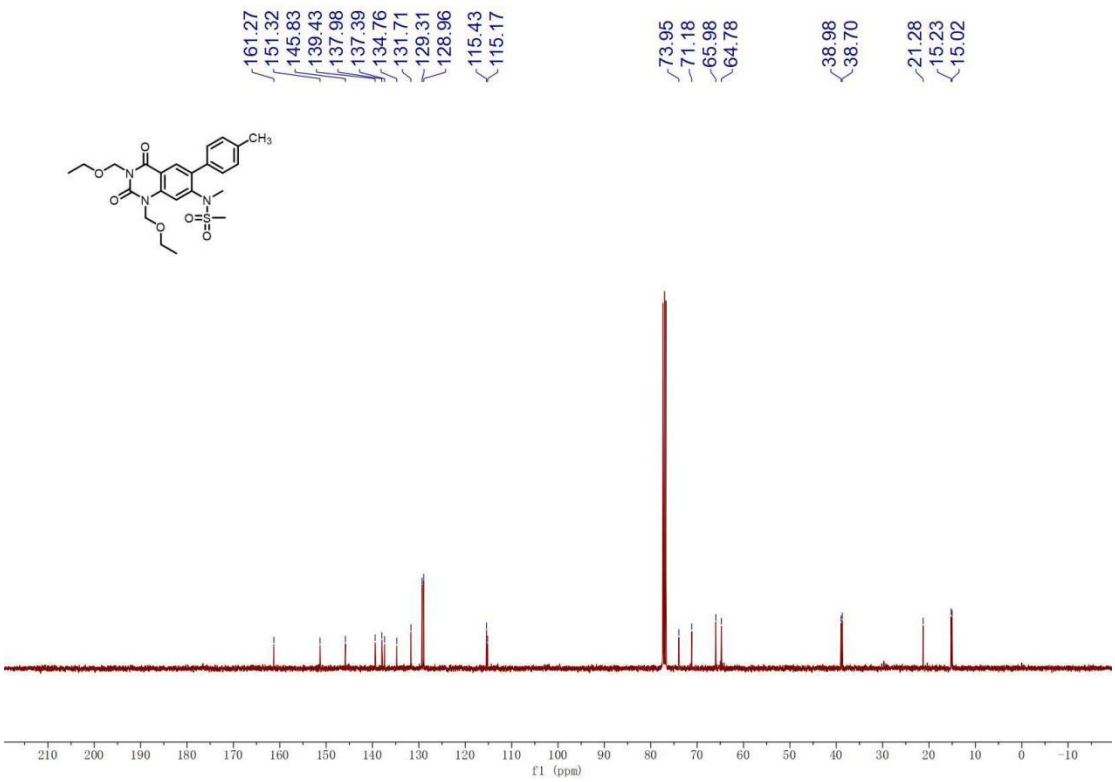
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3n**



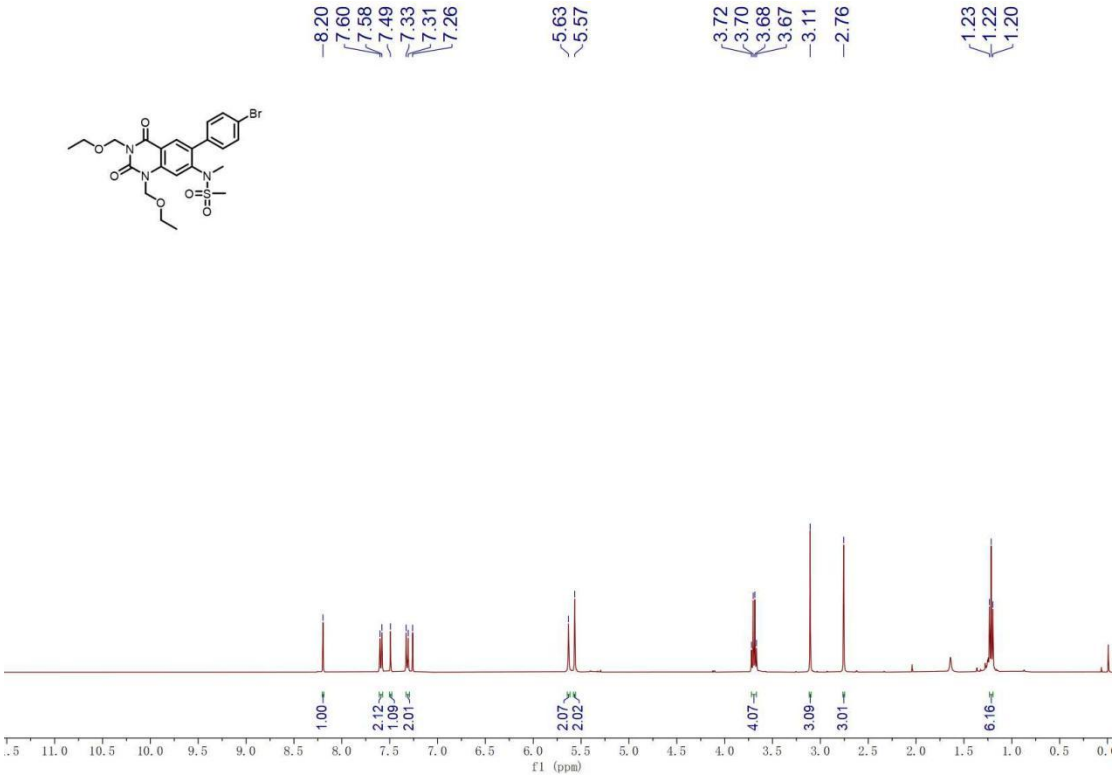
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3o**



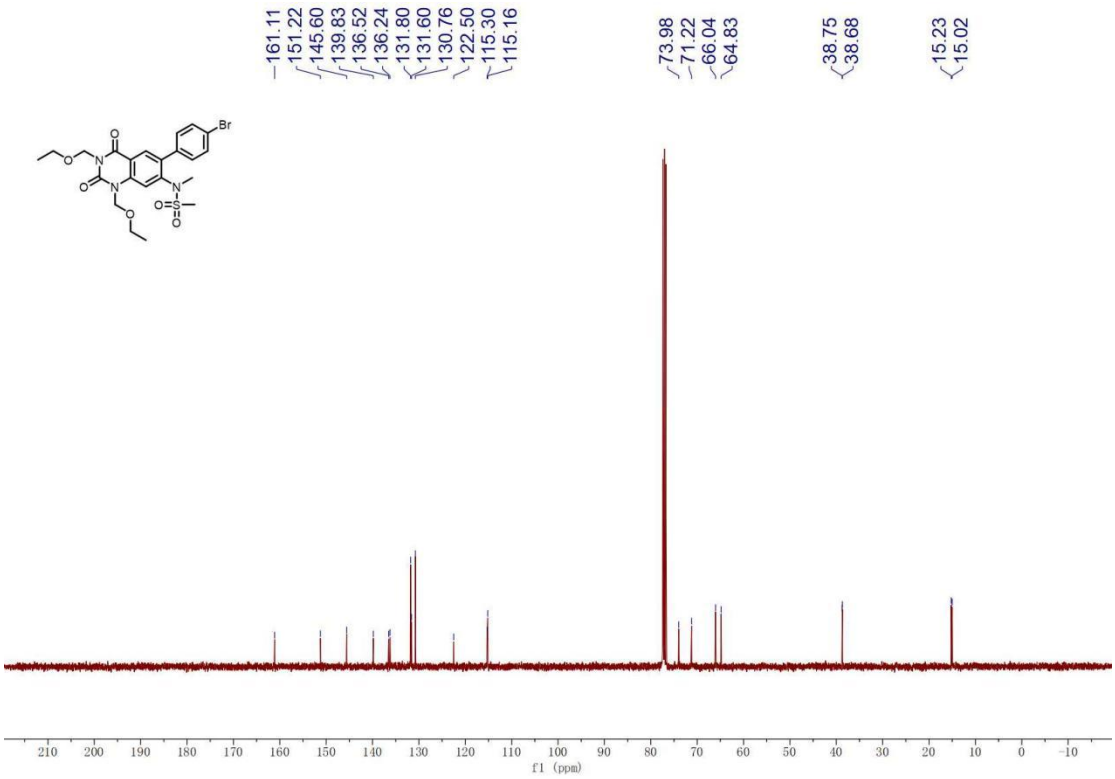
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3o**



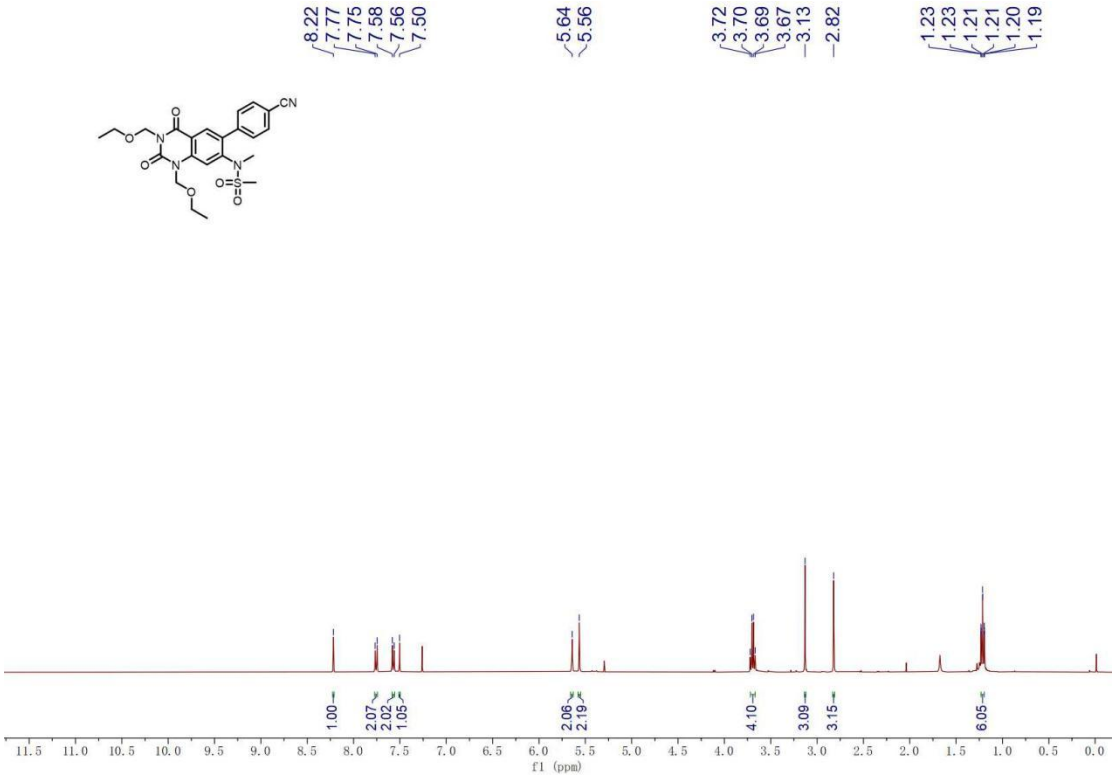
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3p**



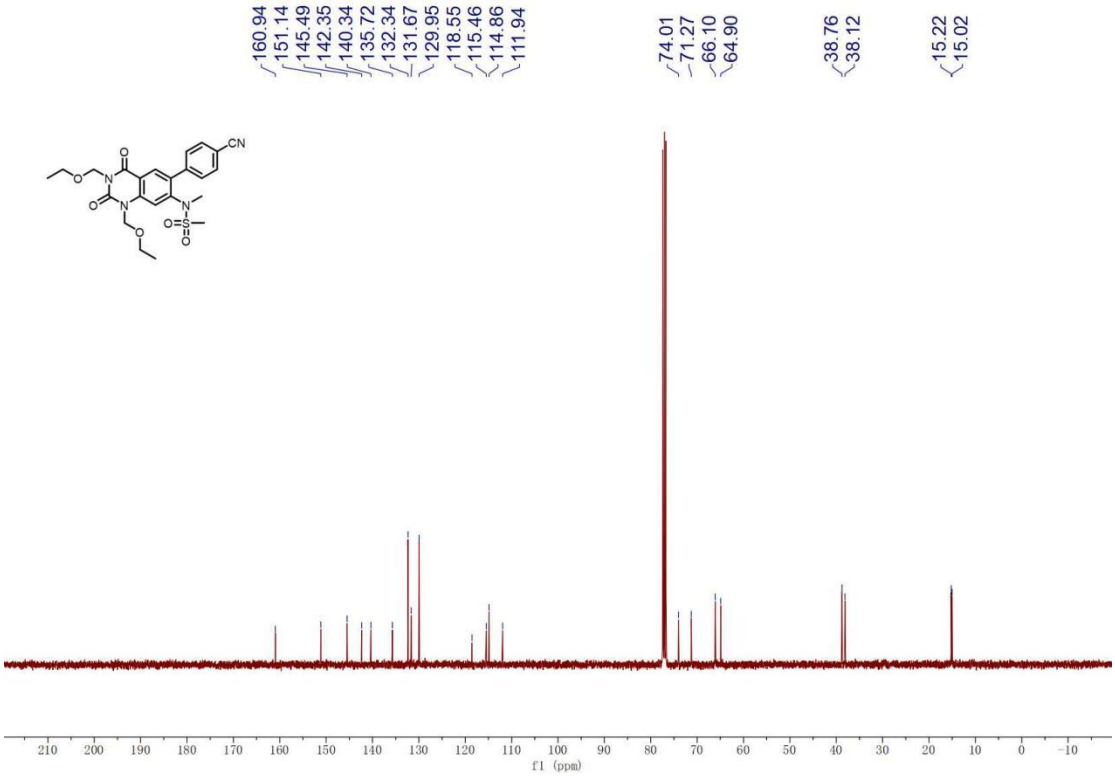
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3p**



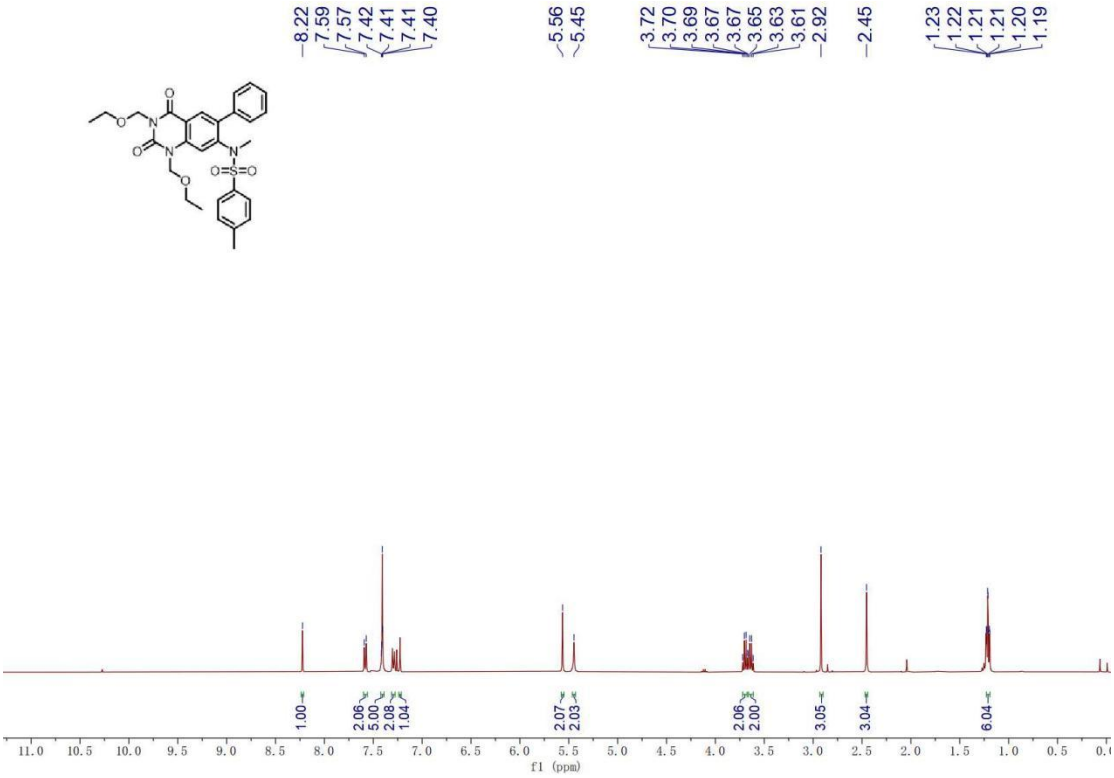
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3q**



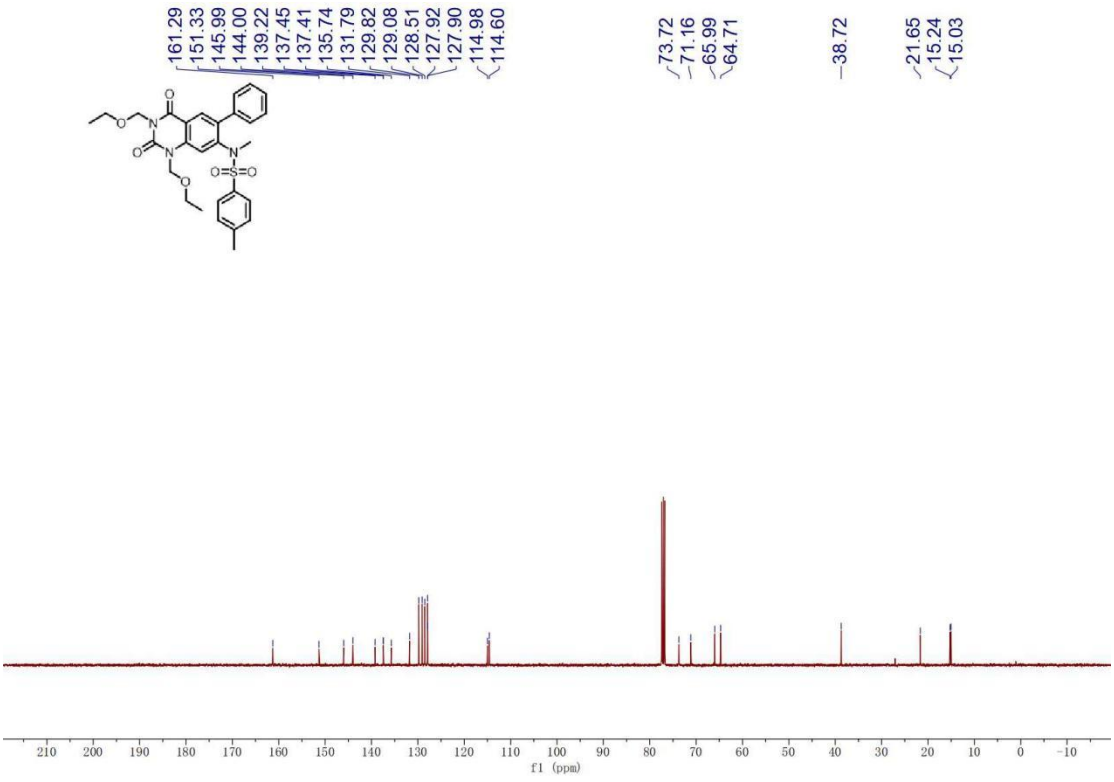
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3q**



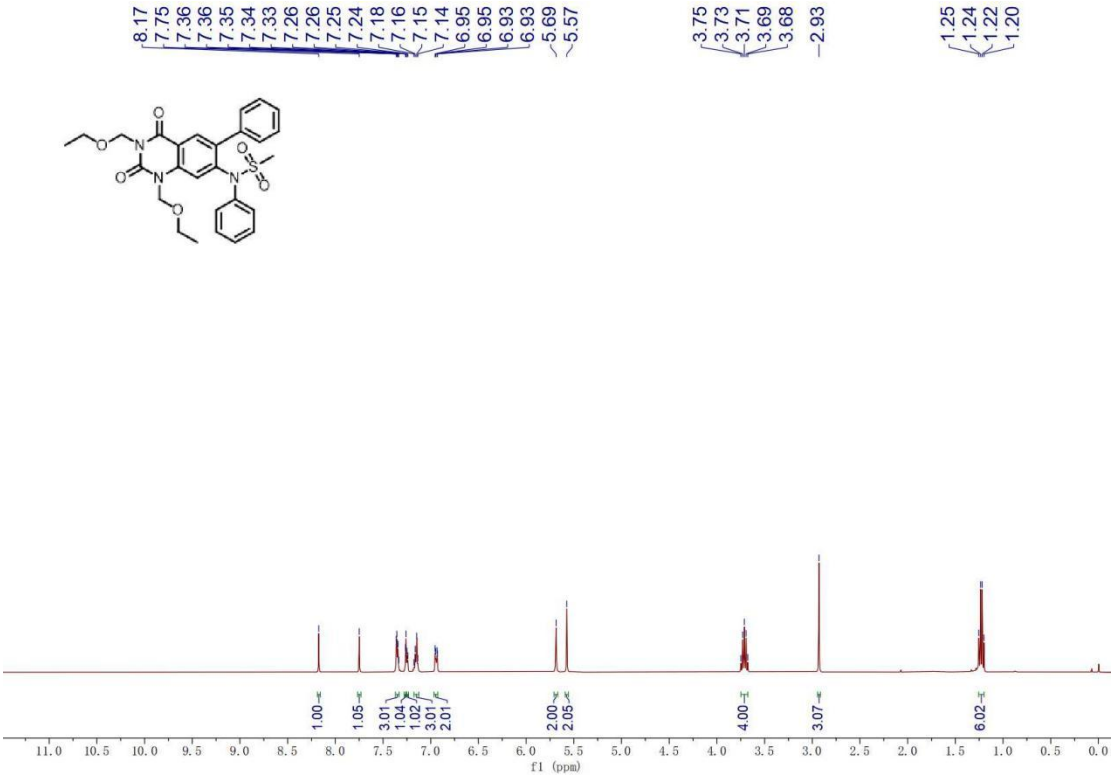
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3r**



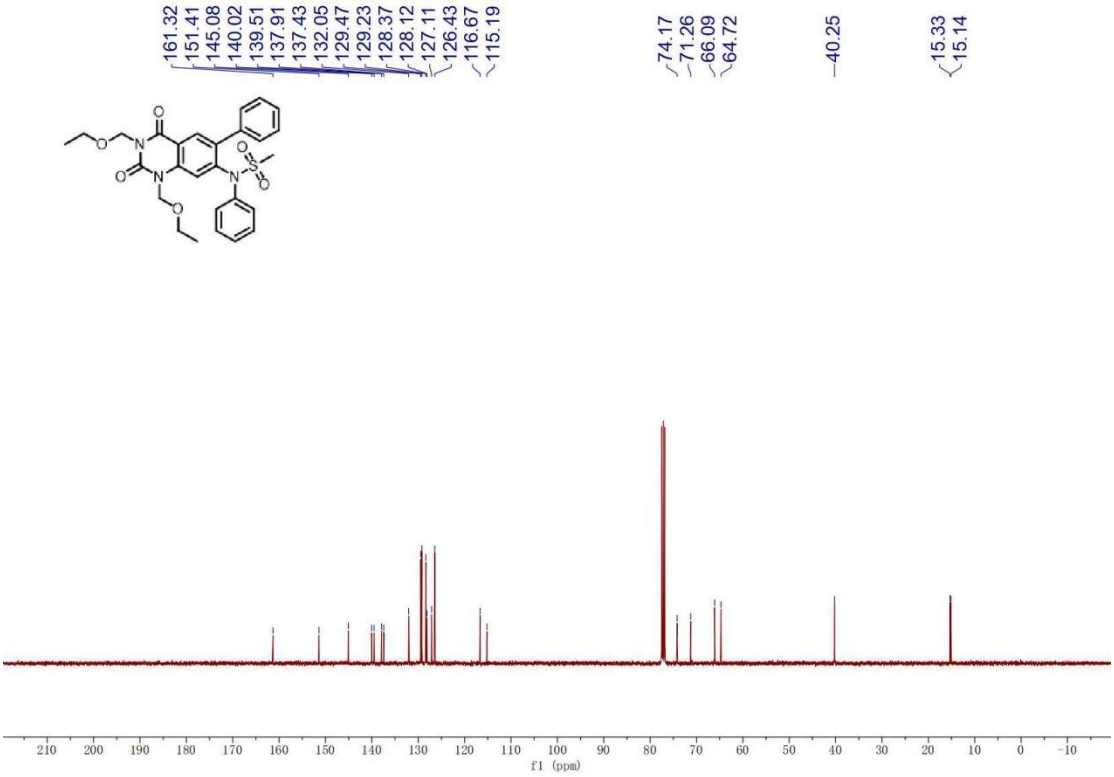
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3r**



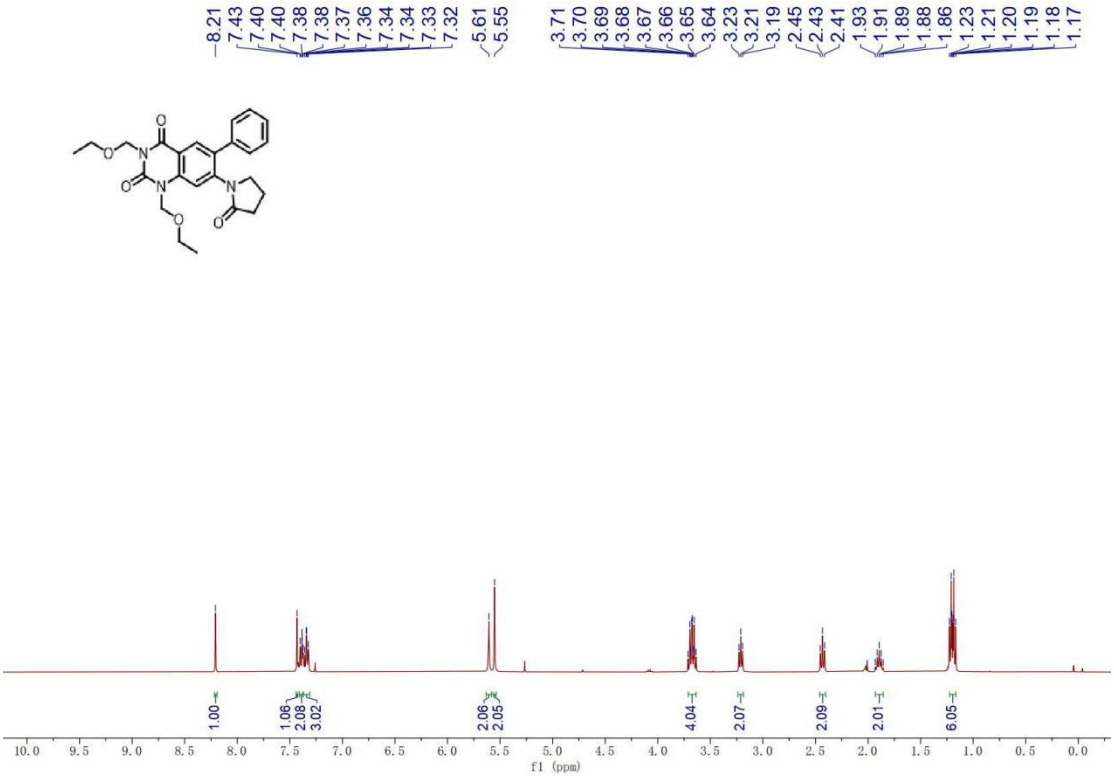
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3s**



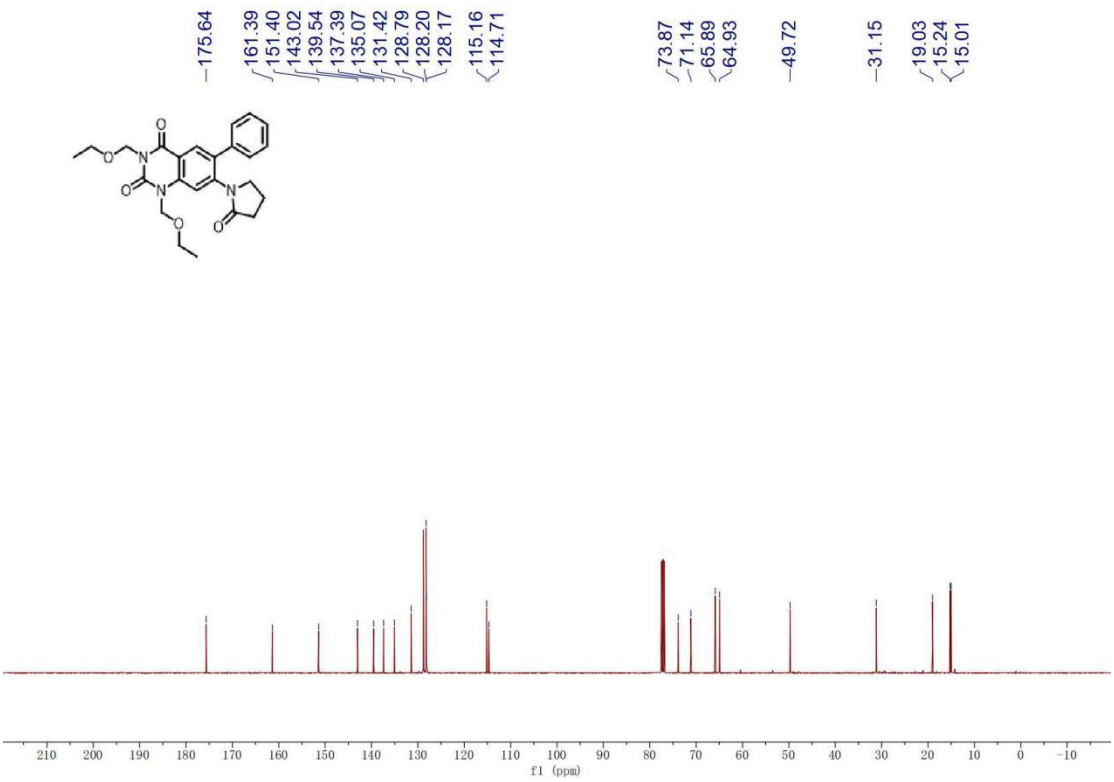
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3s**



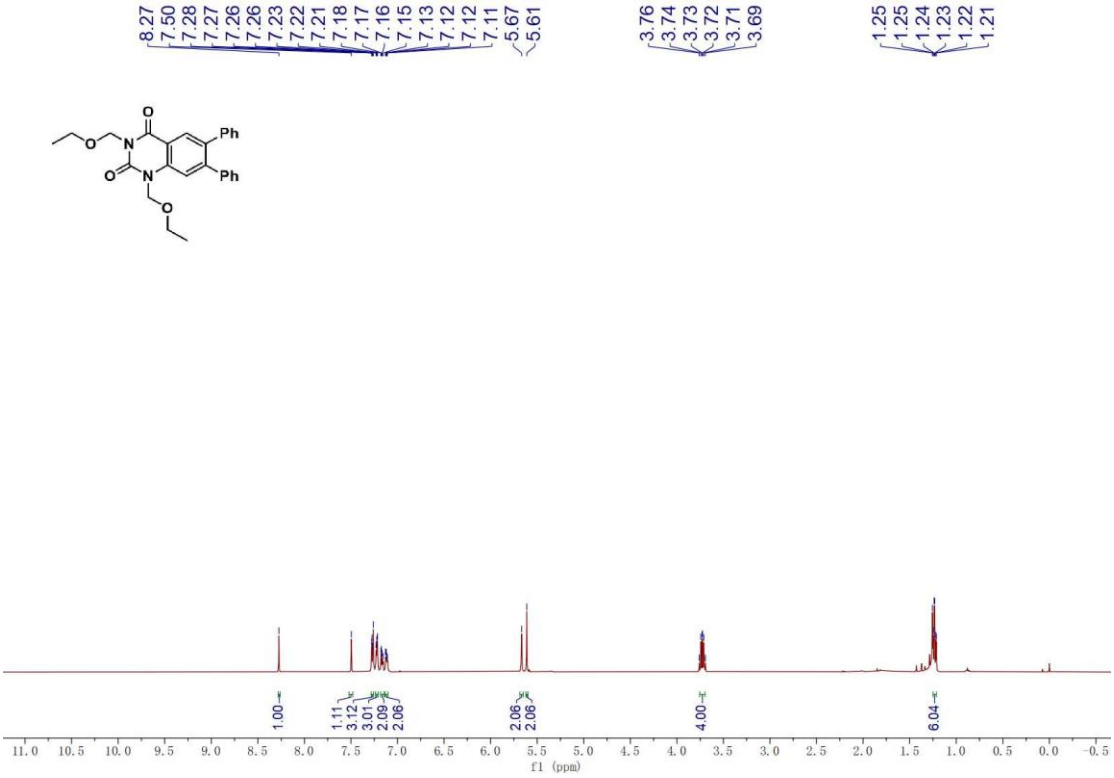
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3t**



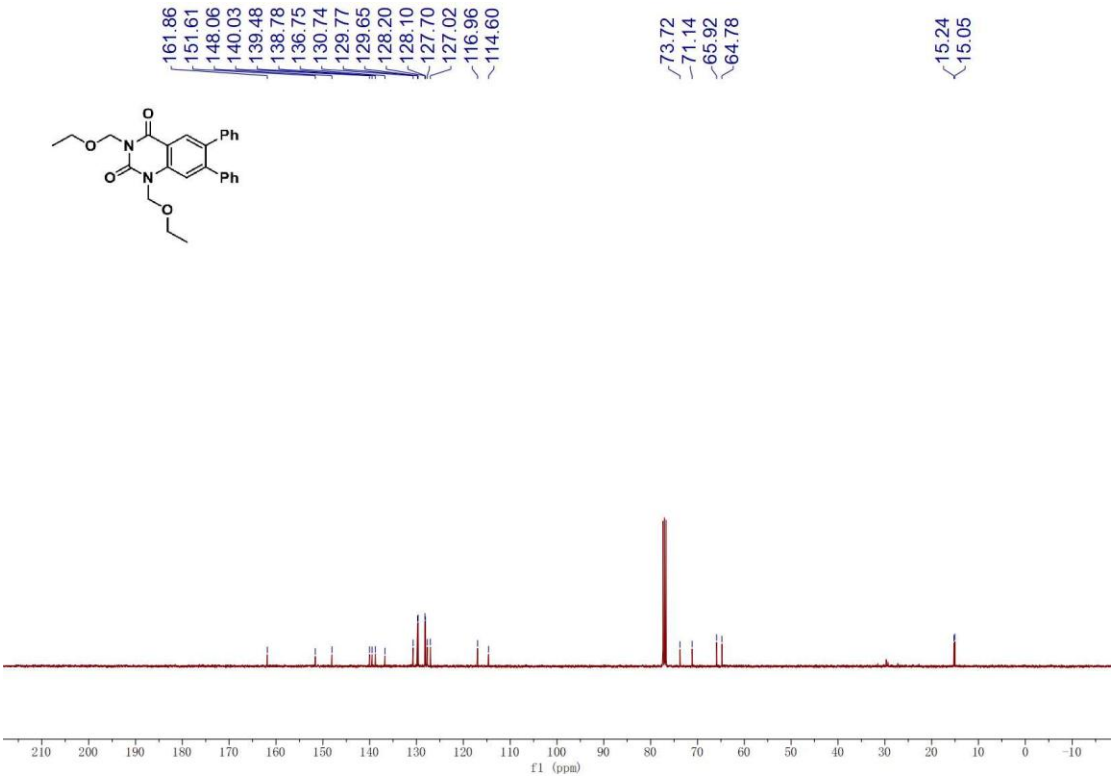
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3t**



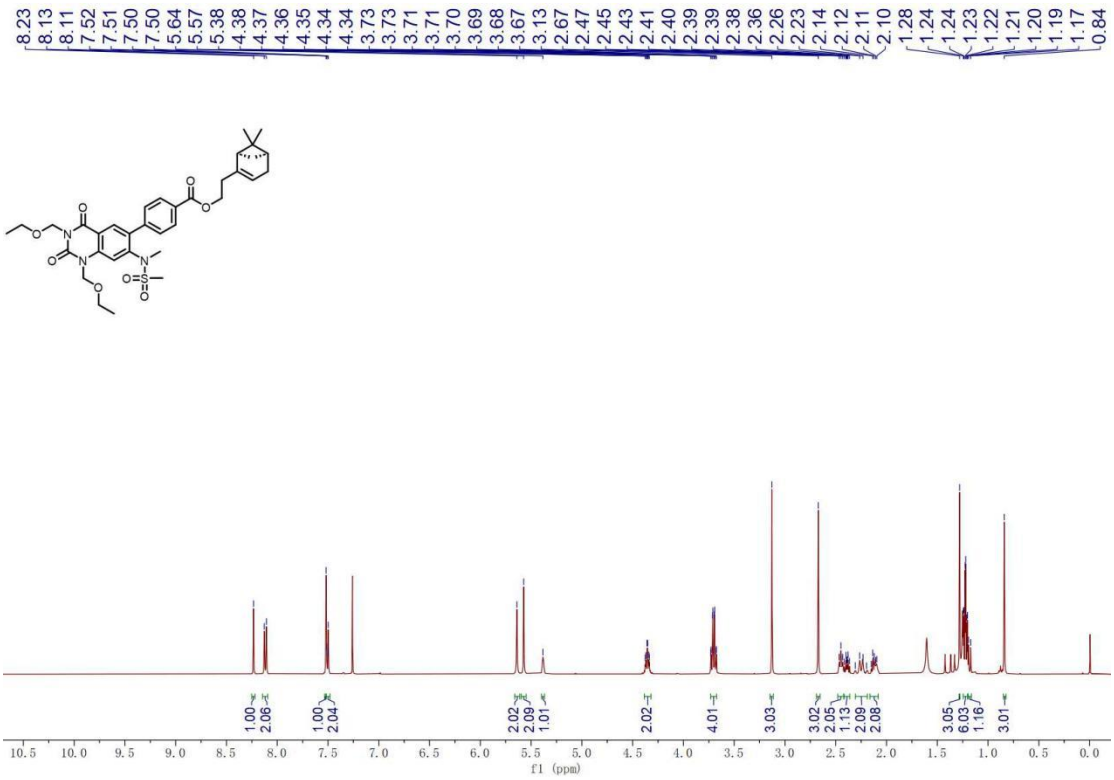
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3u**



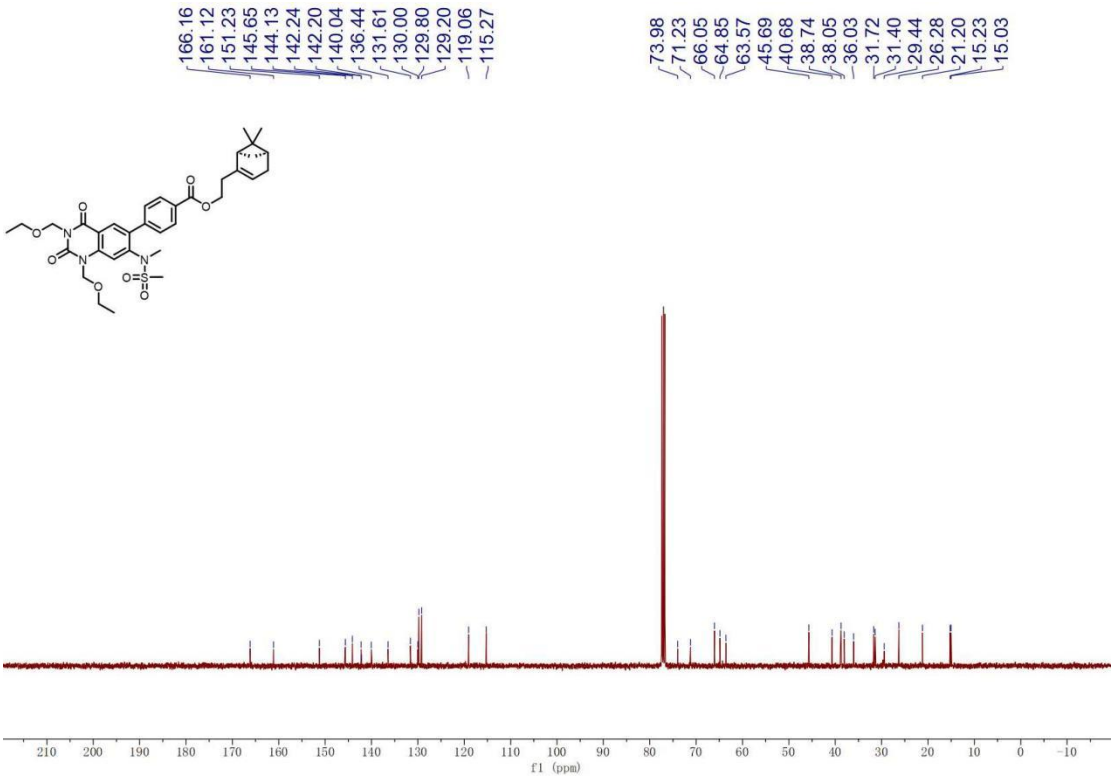
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3u**



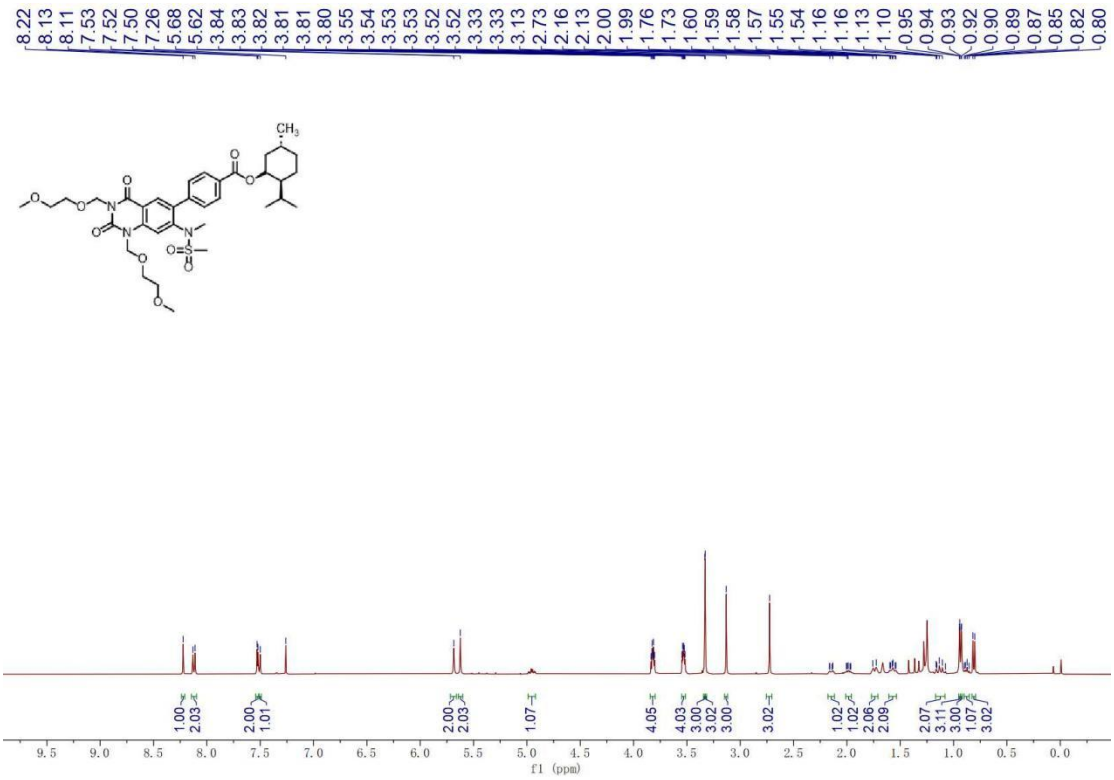
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4a**



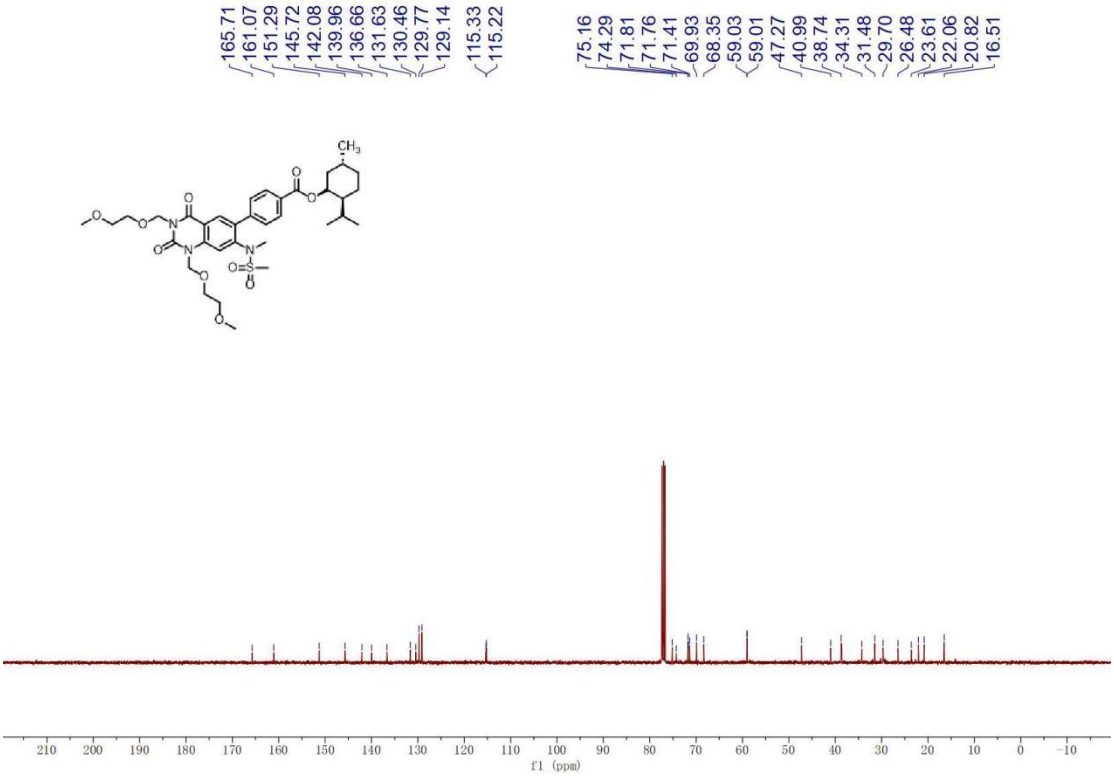
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4a**



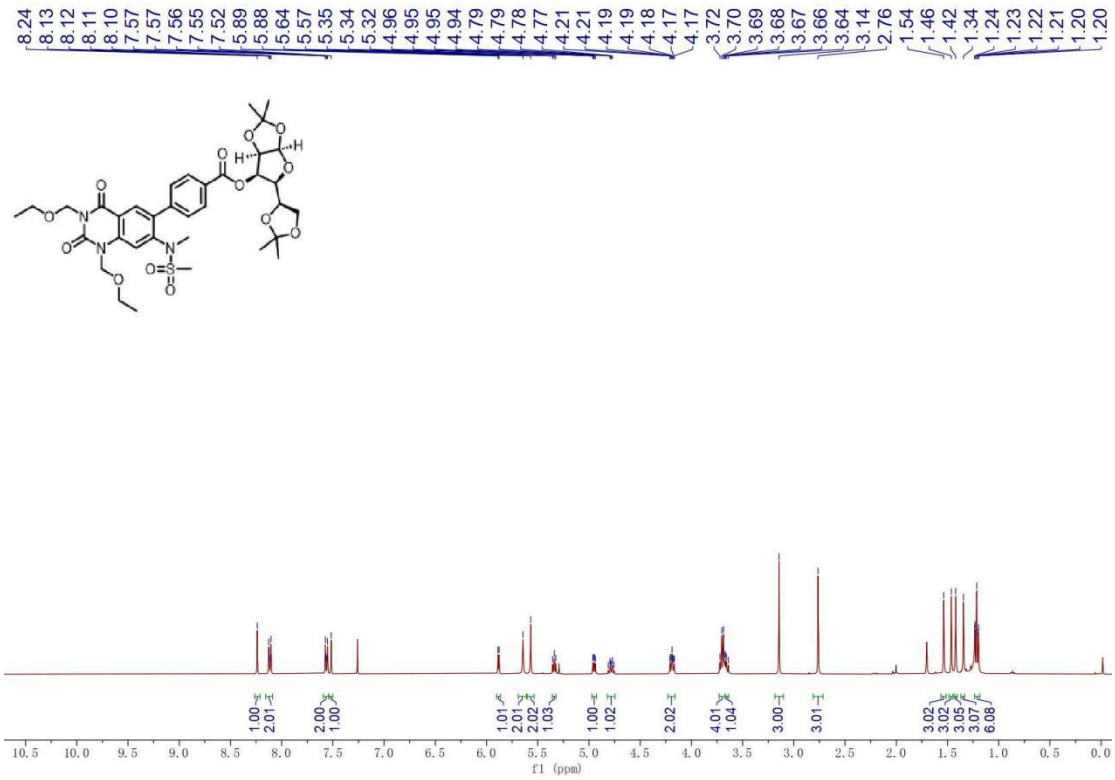
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4b**



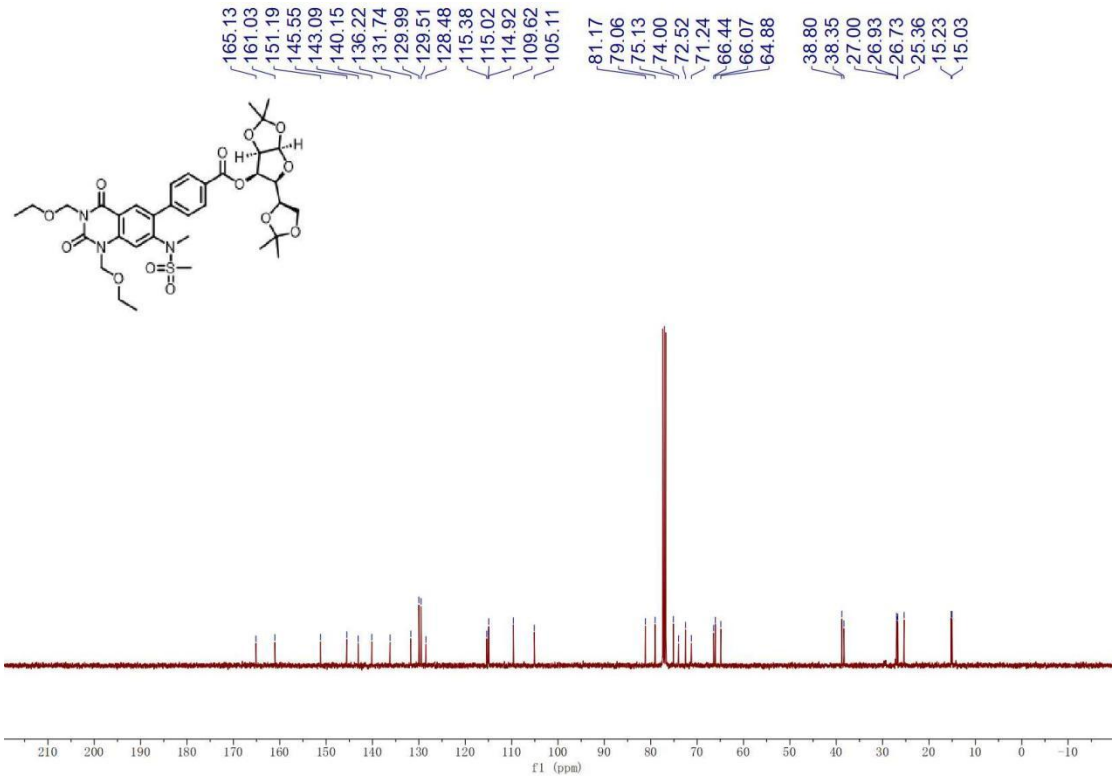
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4b**



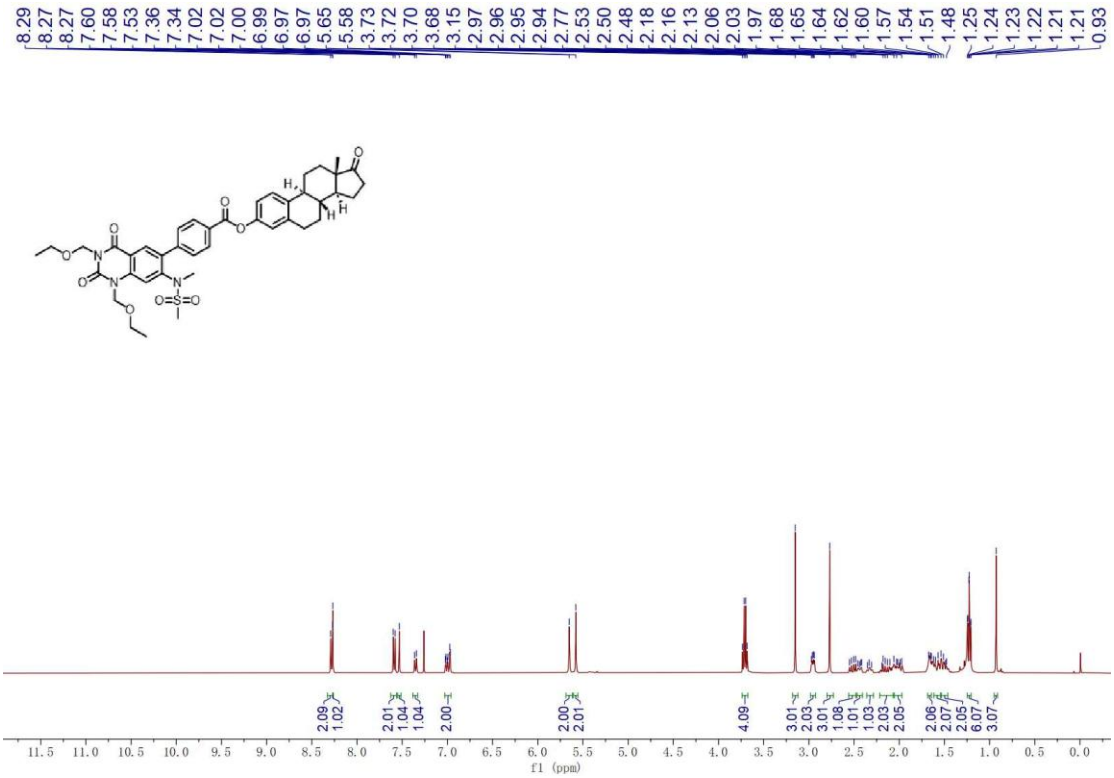
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4c**



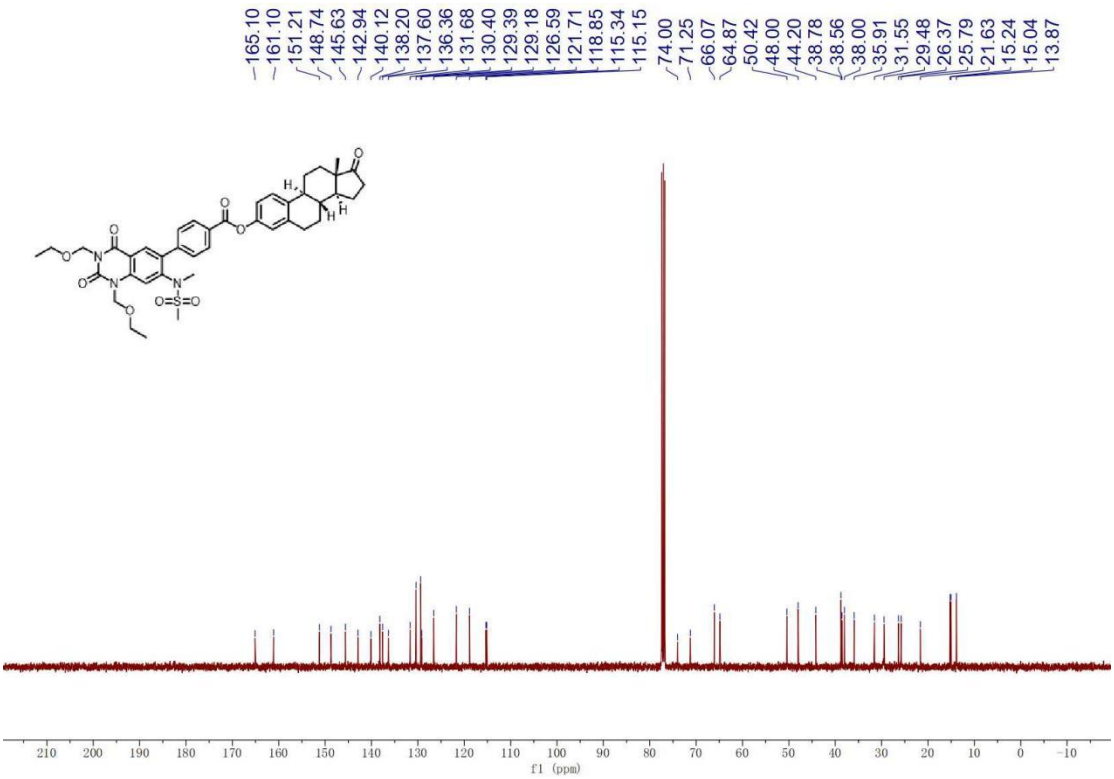
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4c**



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4d**



^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4d**



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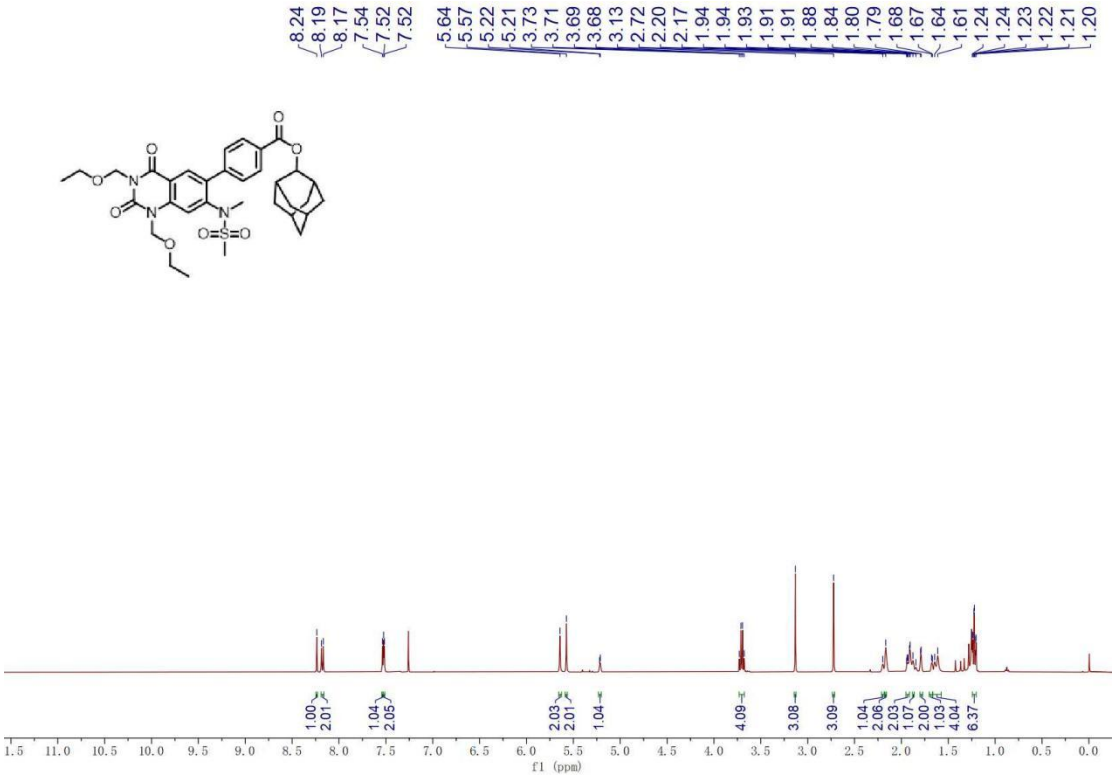

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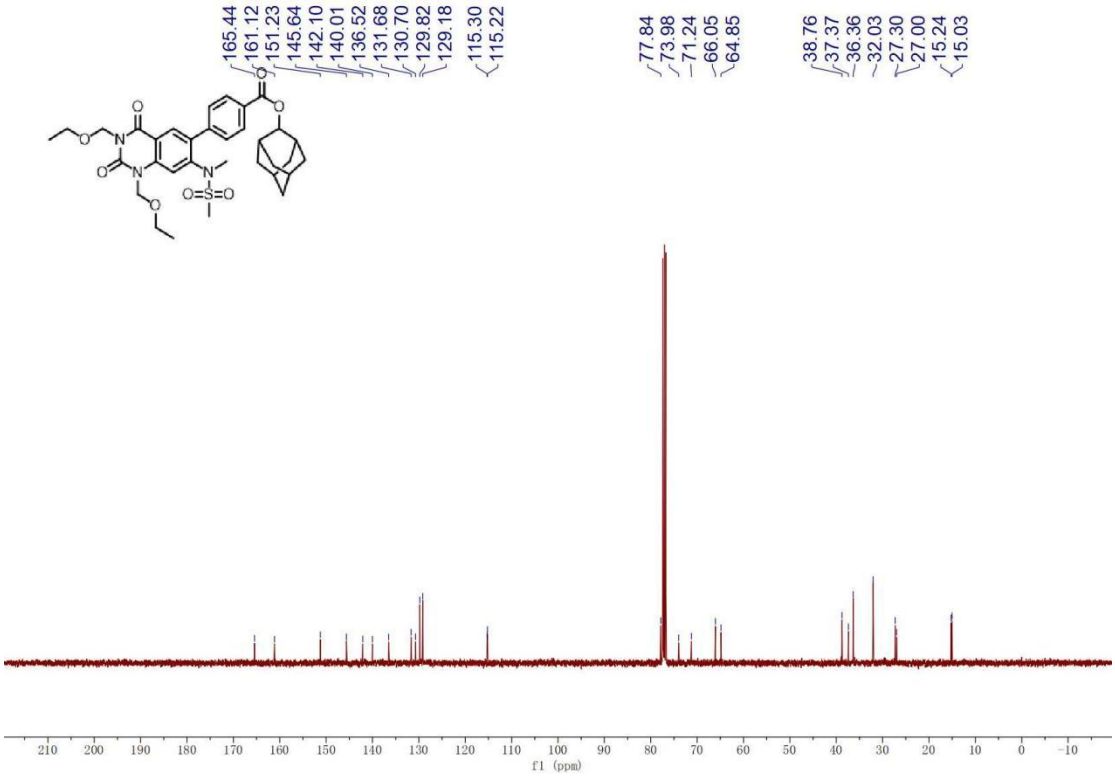
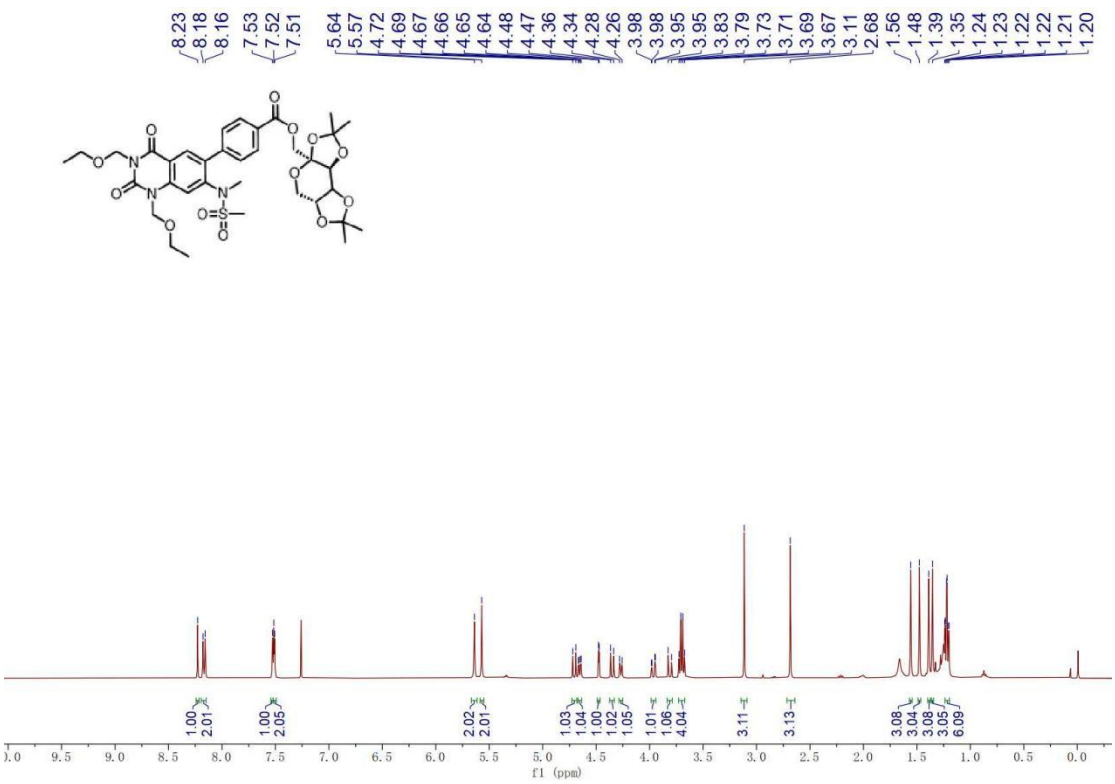
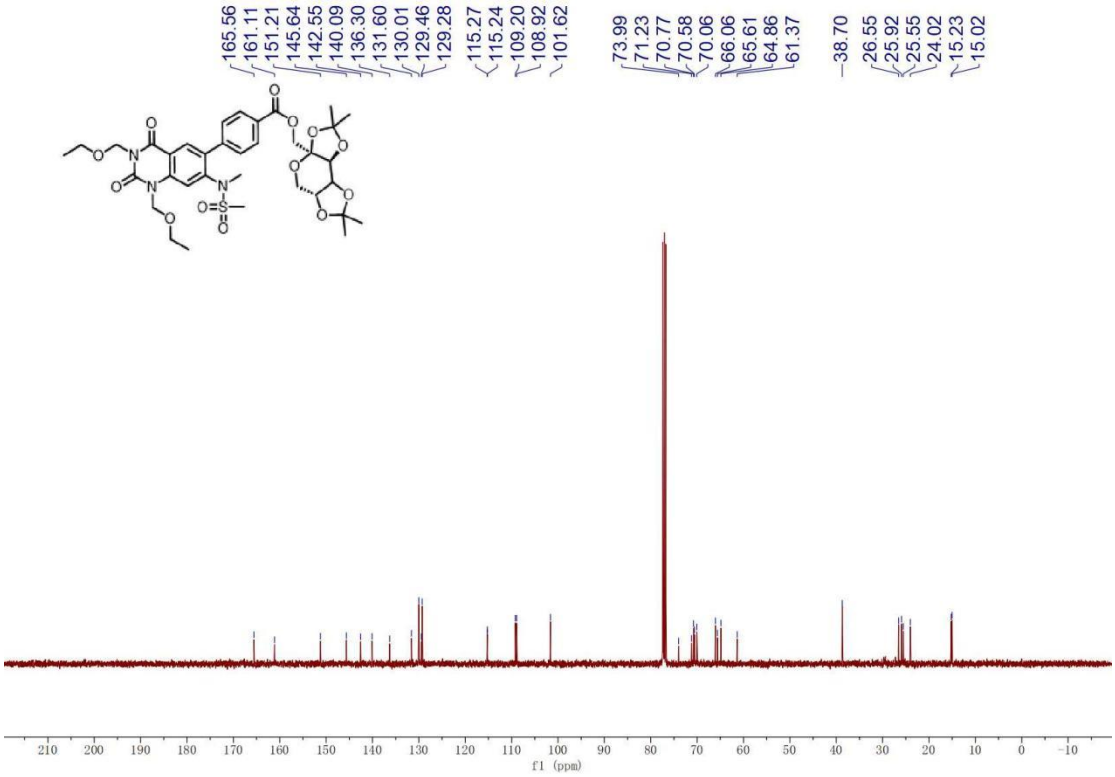


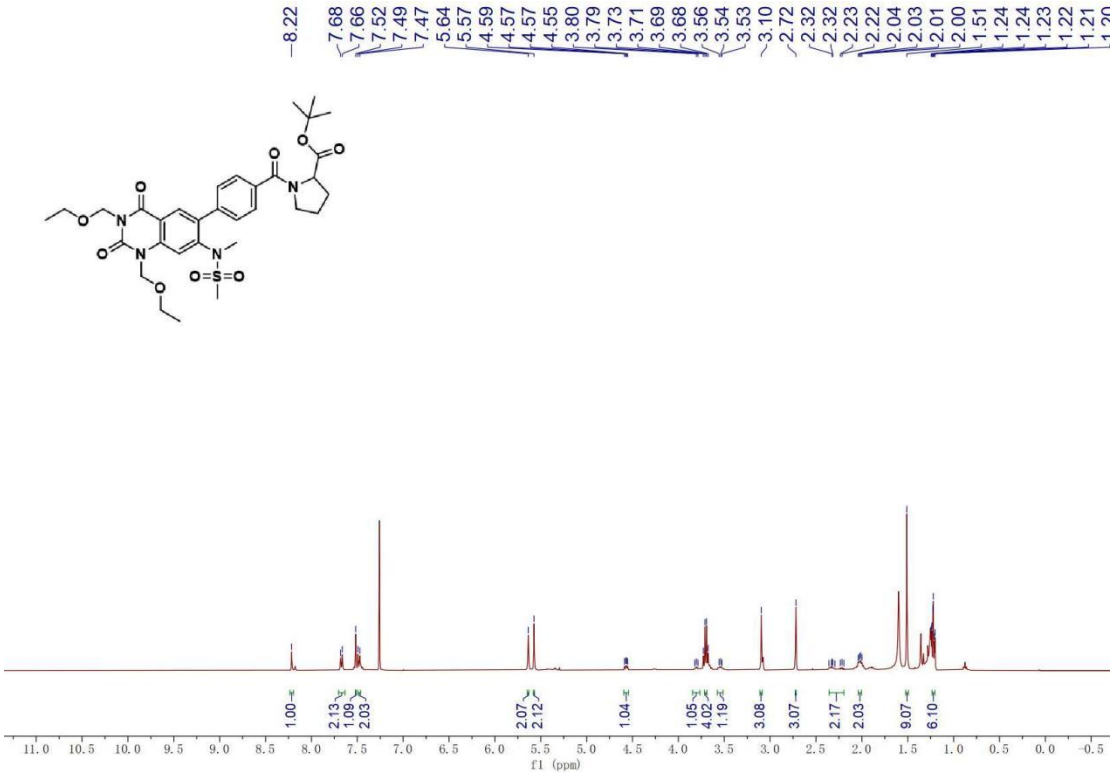
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4f**



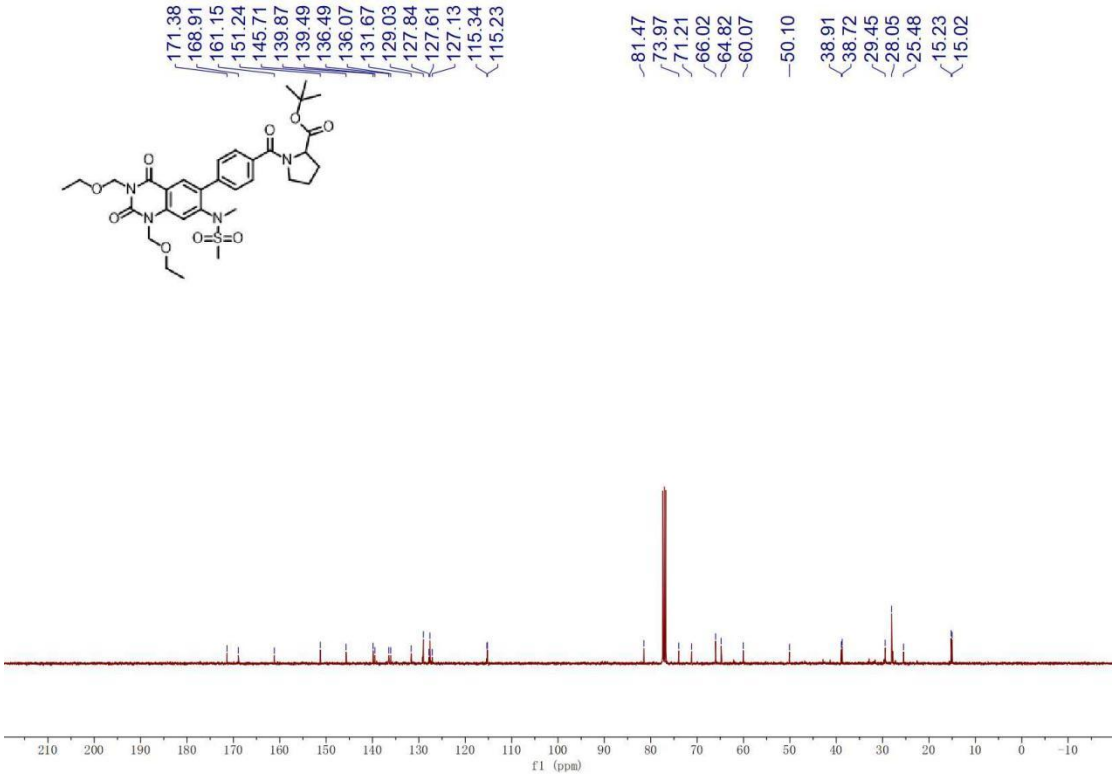
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4f**



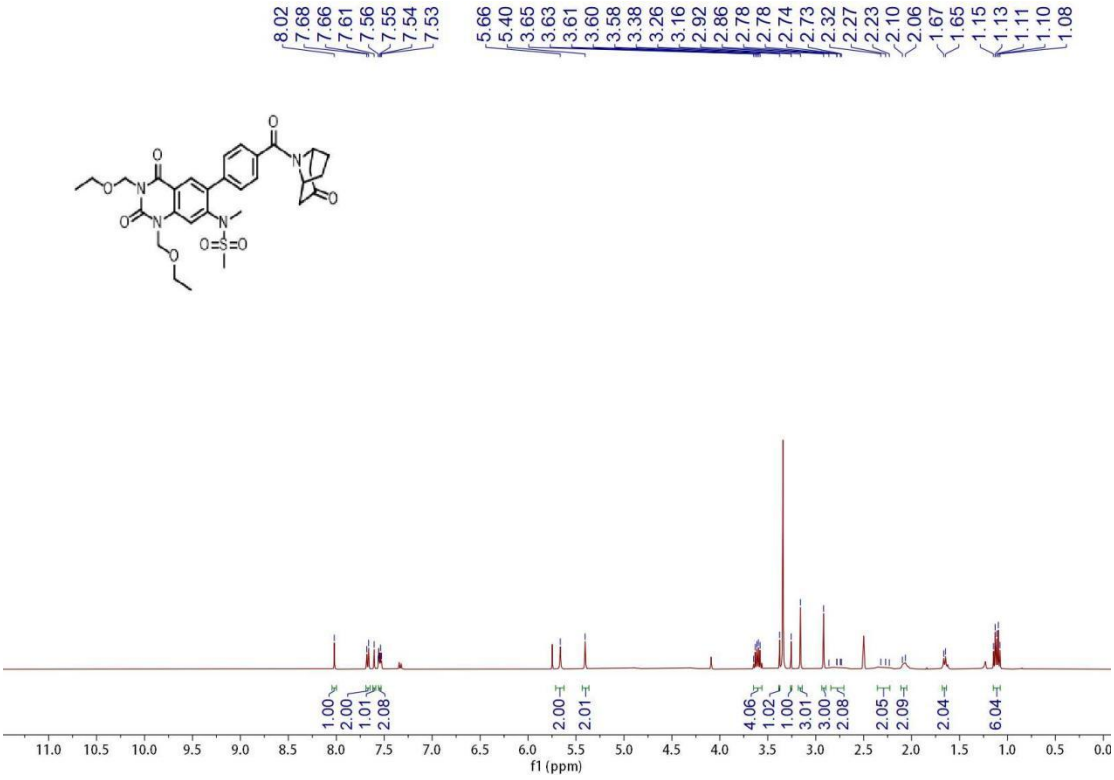
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4g**



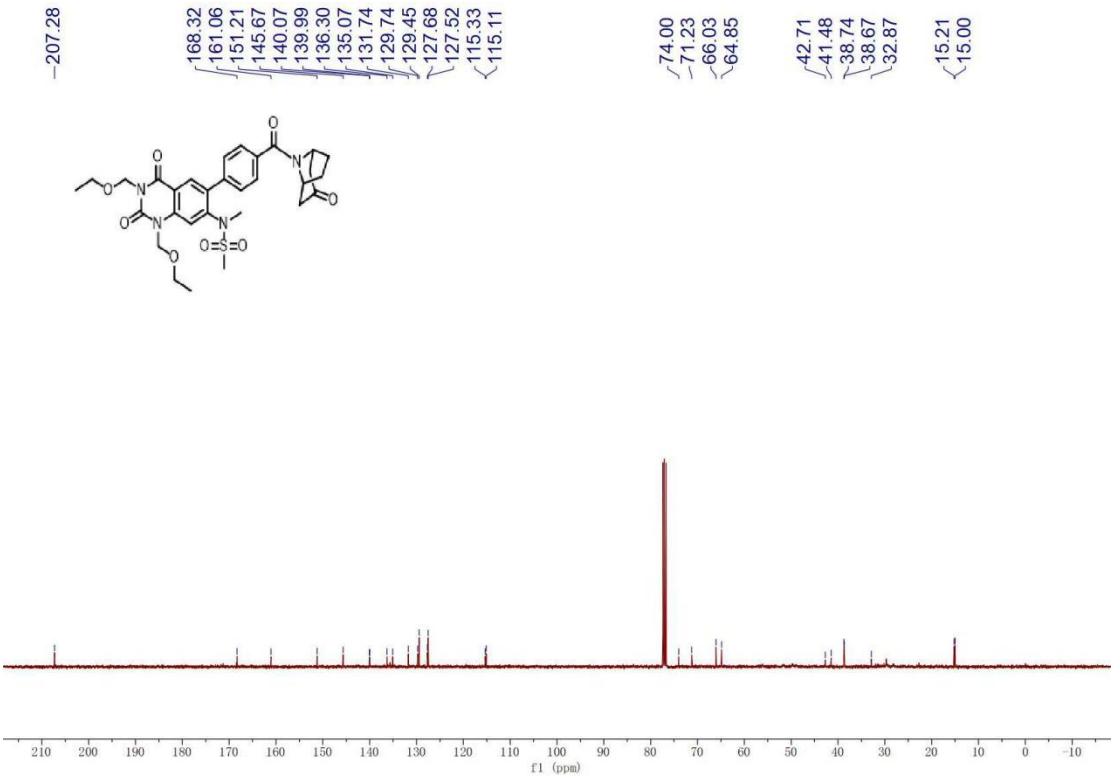
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4g**



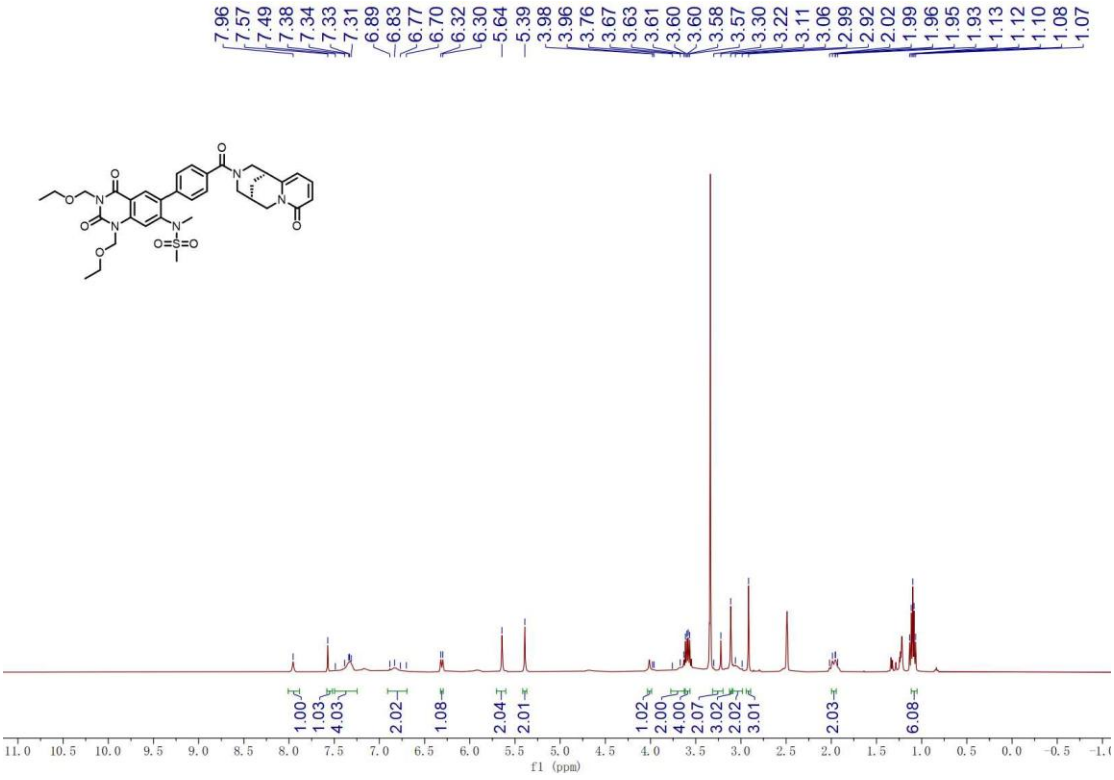
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **4h**



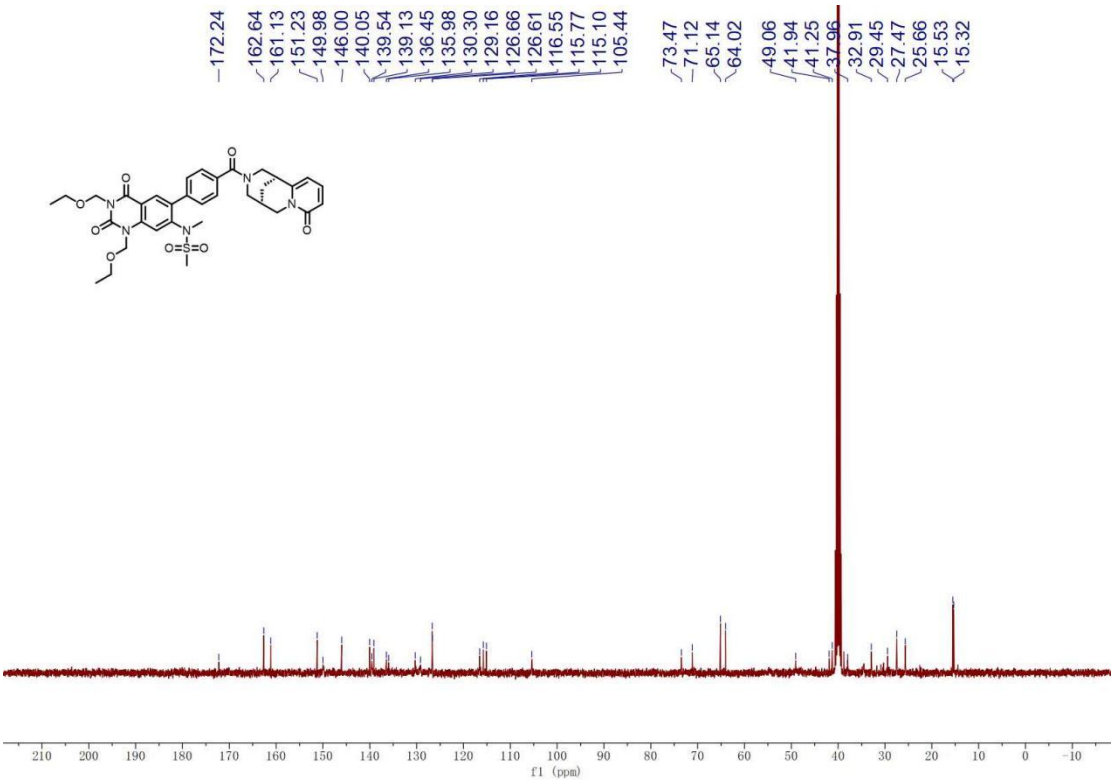
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **4h**



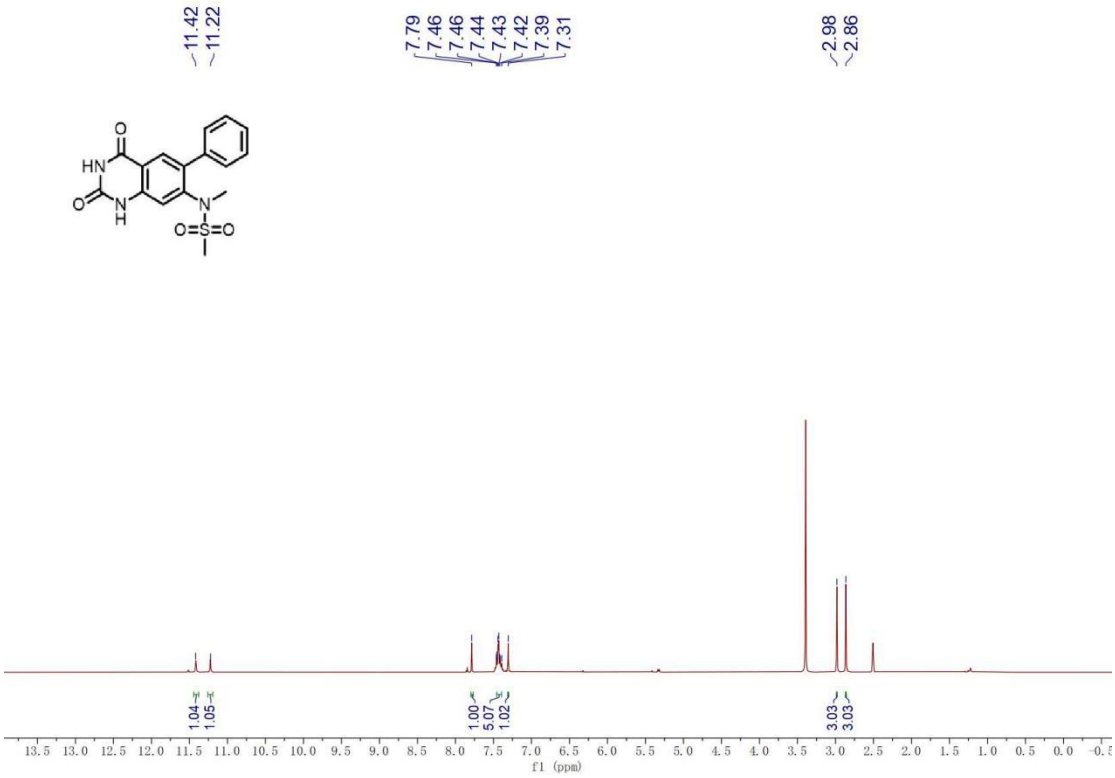
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **4i**



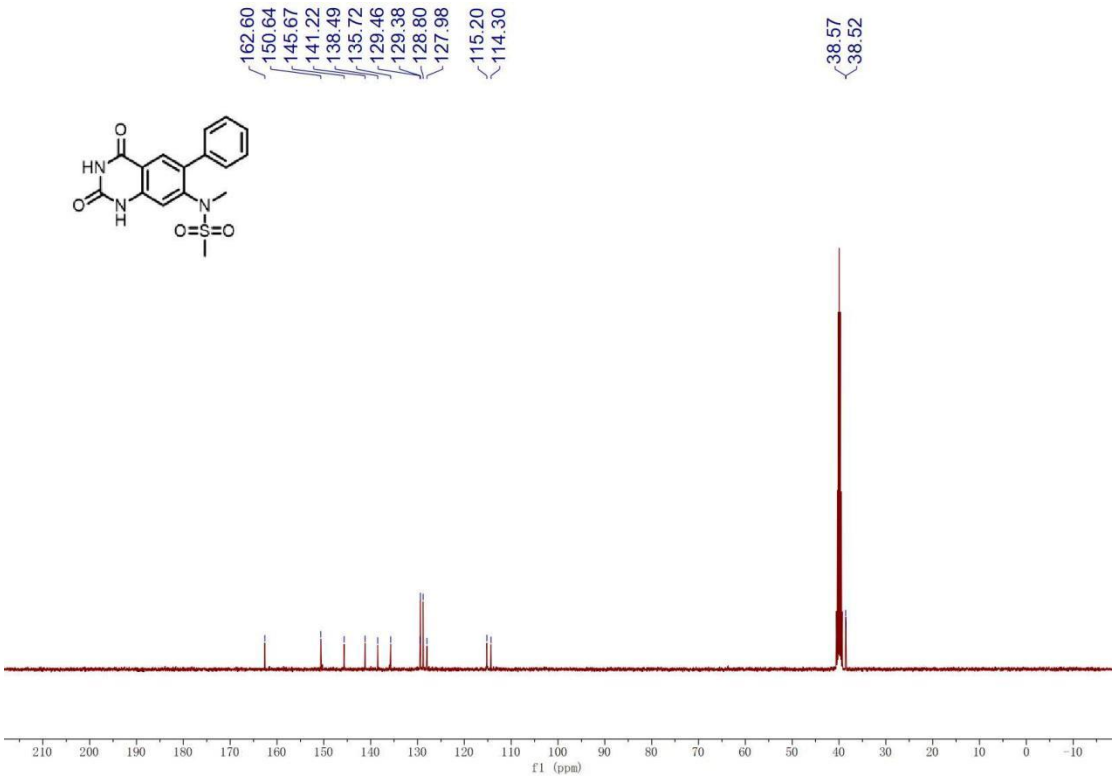
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **4i**



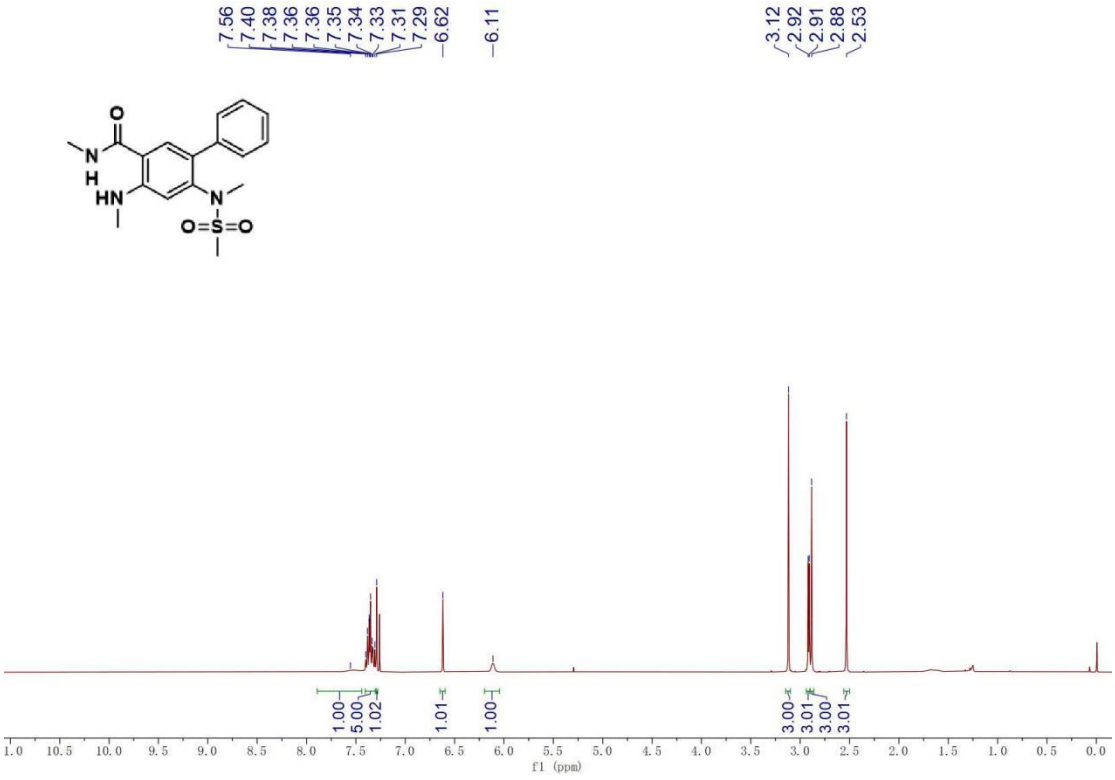
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **5**



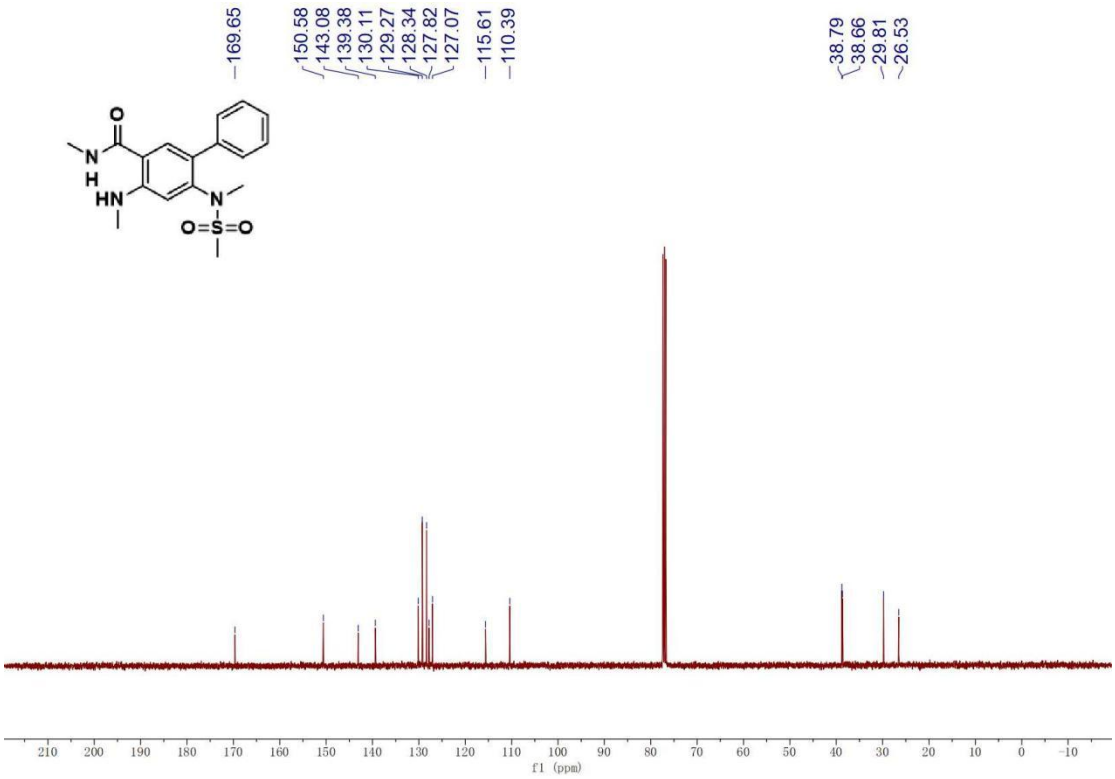
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **5**



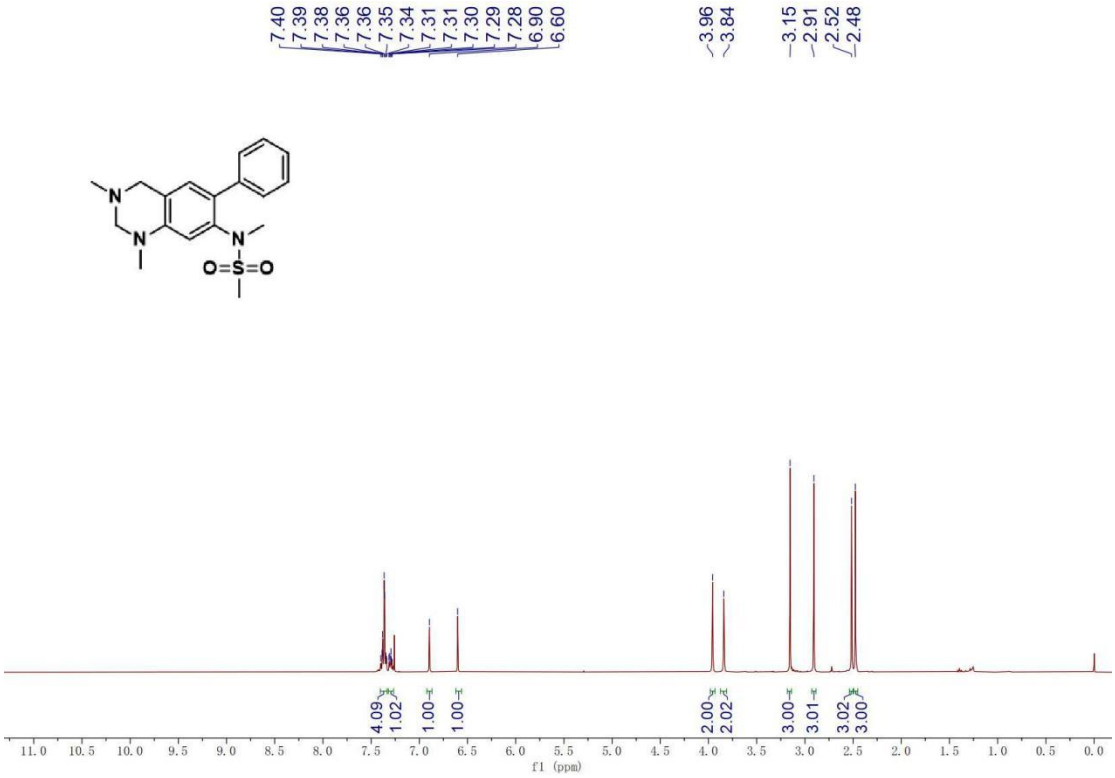
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **6**



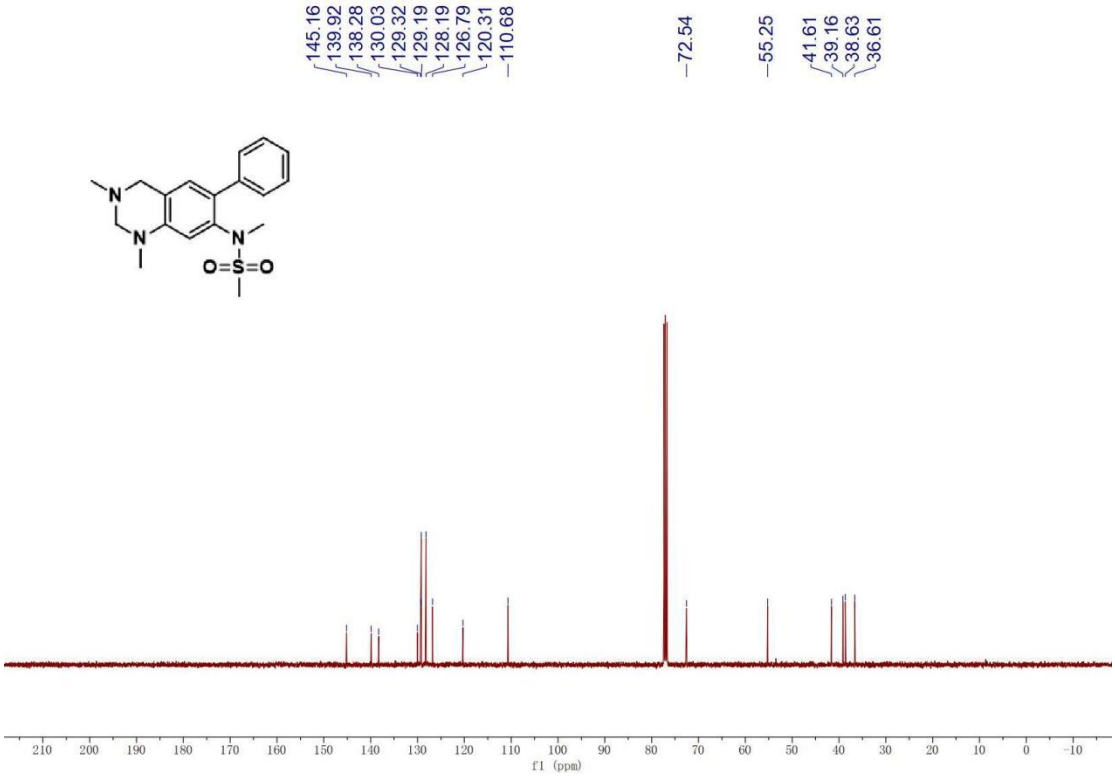
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **6**



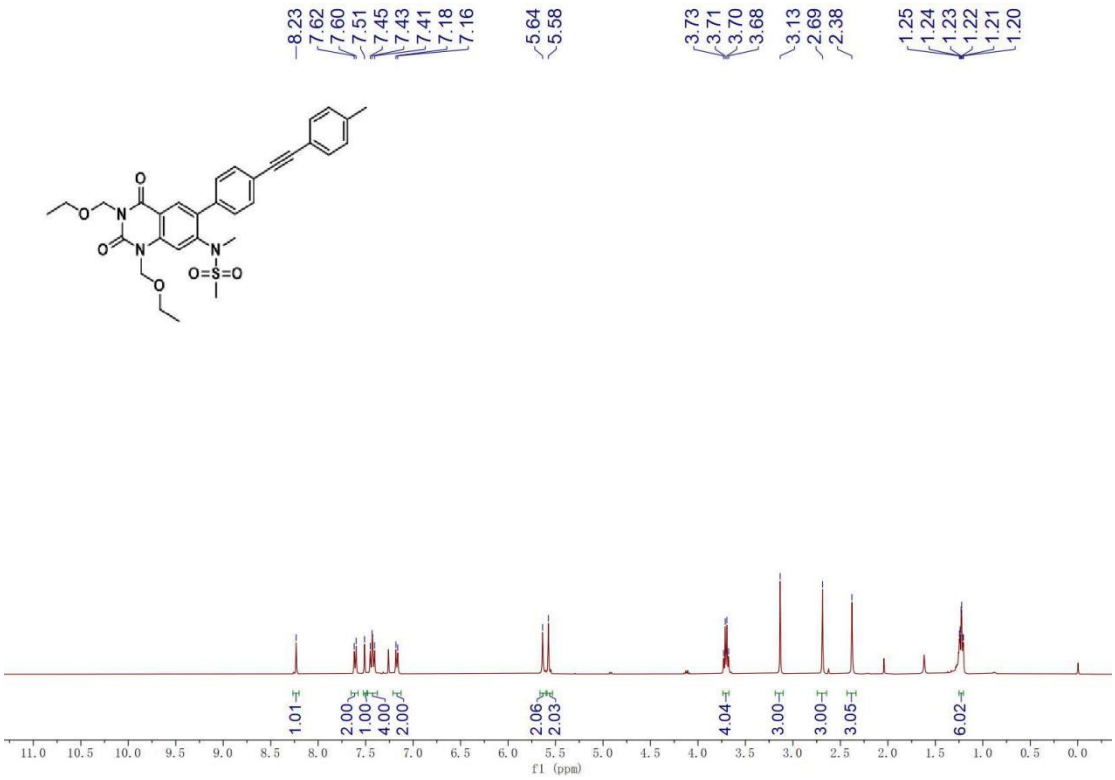
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **7**



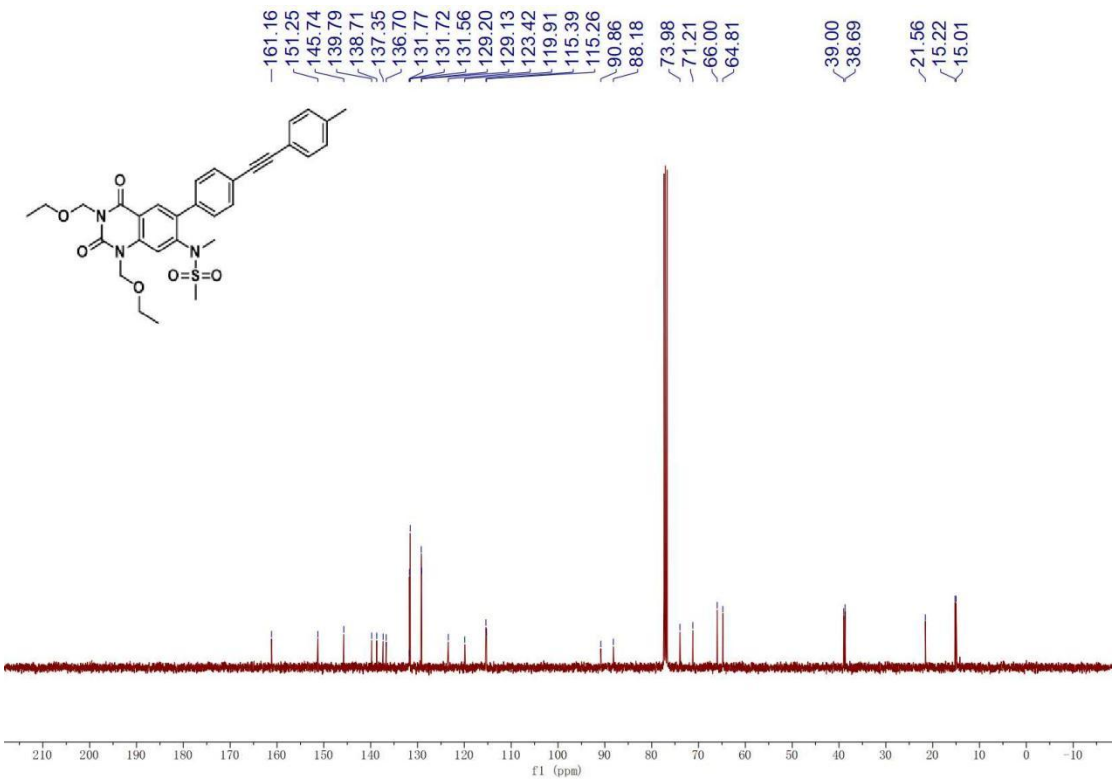
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **7**



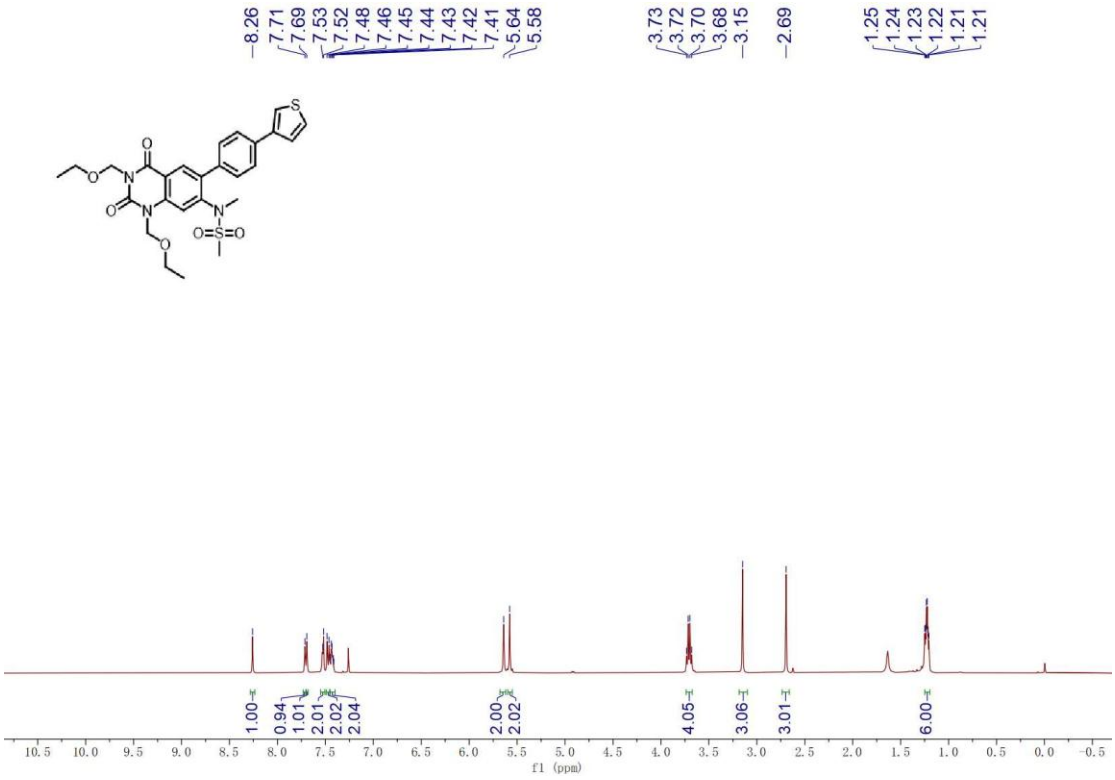
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **9**



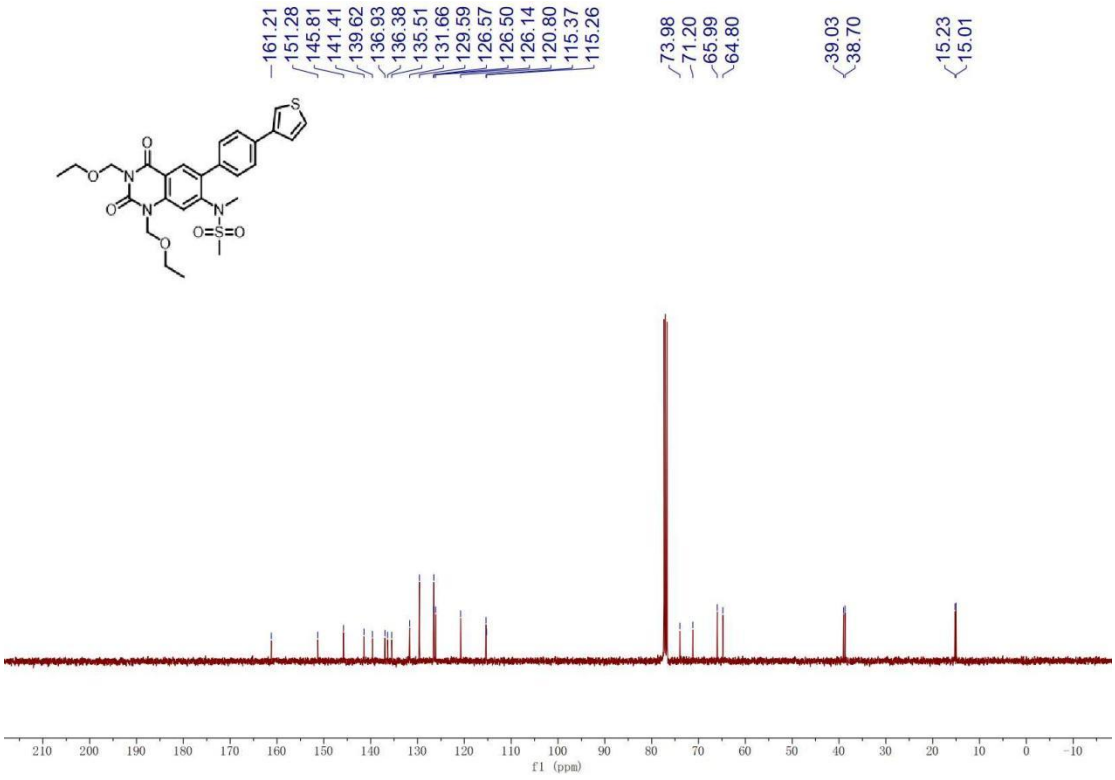
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **9**



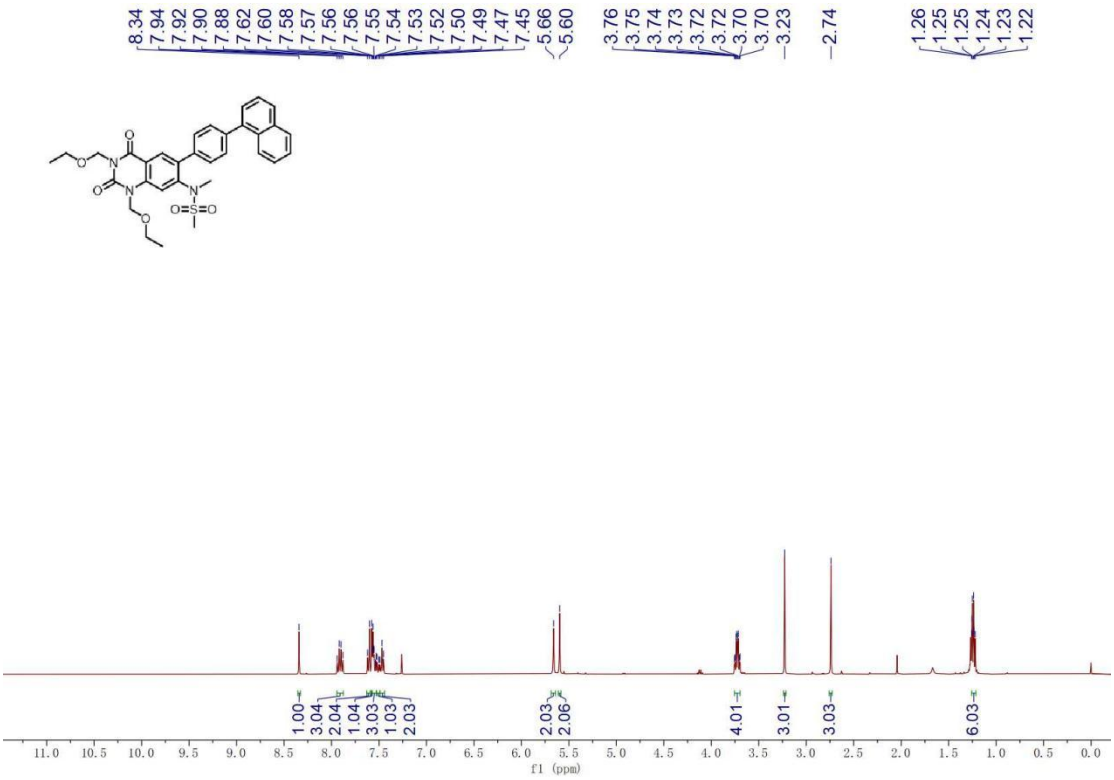
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **11a**



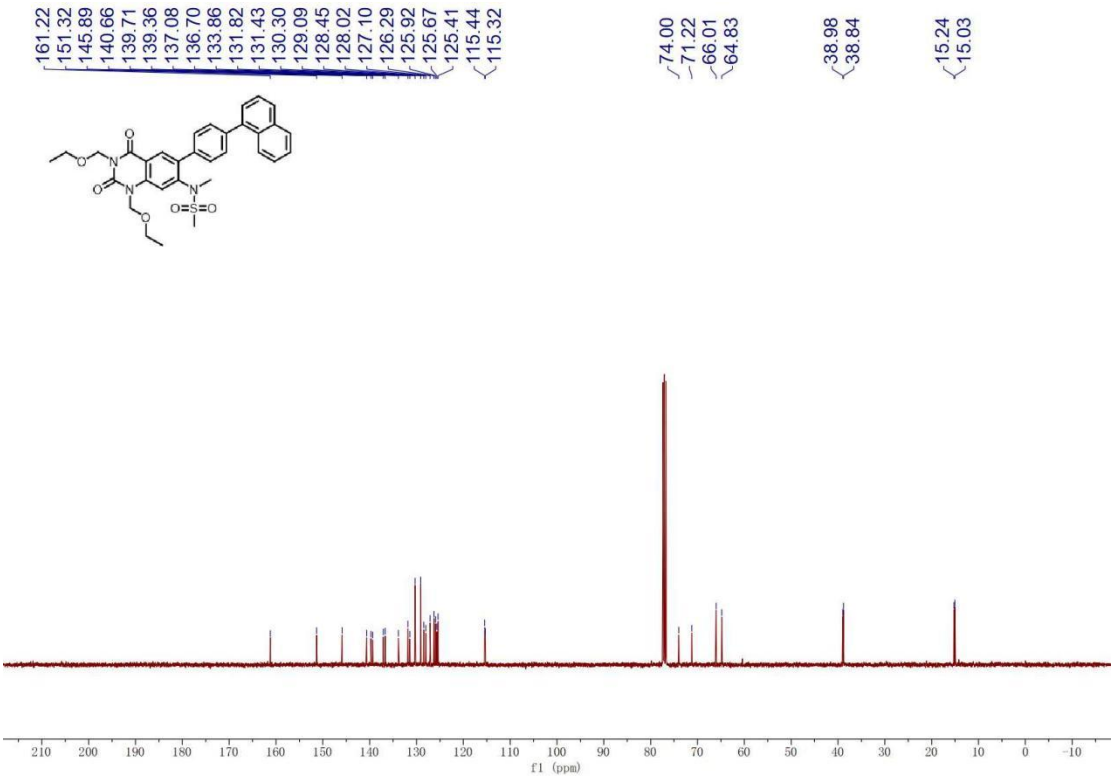
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **11a**



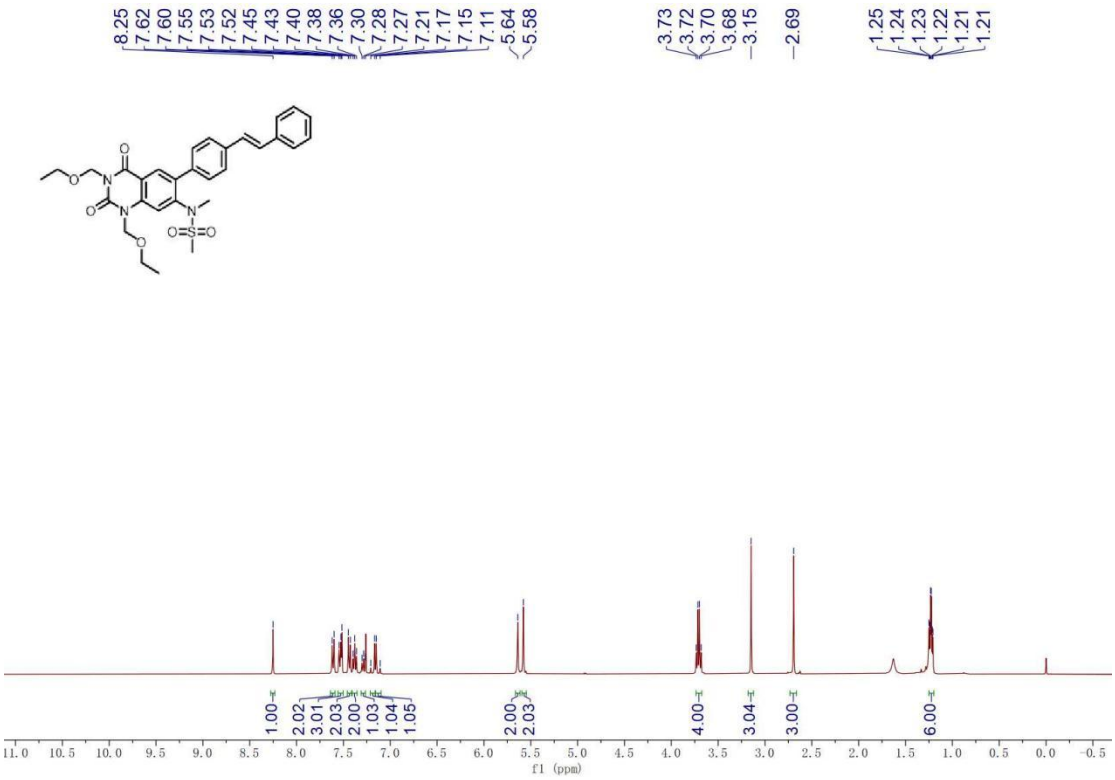
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **11b**



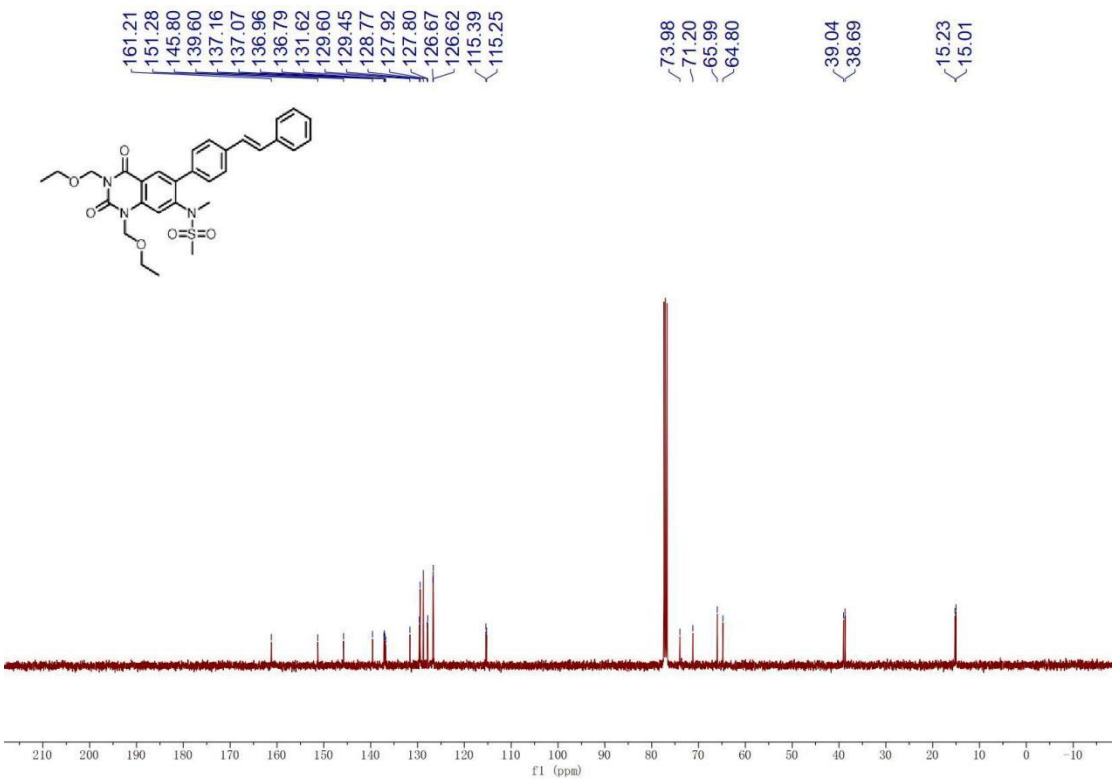
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **11b**



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **11c**



^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **11c**



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