Supporting Information

Direct Access to Quinazolines Enabled by Transient Directing Groups

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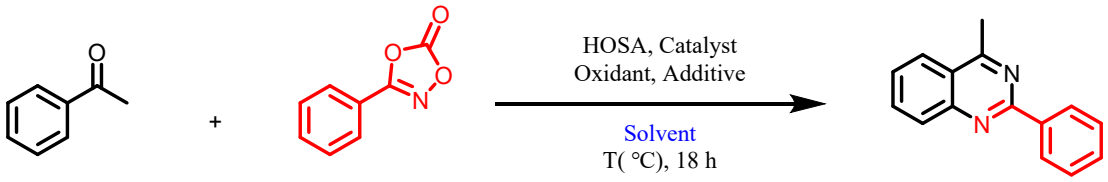
1. General information

Unless otherwise specified, all reagents are obtained from commercial sources and can be used without further purification. Chromatographic purification of products was performed by flash column chromatography on silica gel (200−300 meshes). Thin-layer chromatography (TLC) was carried out on silica plates (TLC Silica GF254). The compounds were visualized by projecting UV light onto the developed plates. The experiments were conducted in a 10 mL of sealed tube or a 100 mL of round bottom flask for gram-scale synthesis.NMR spectra were mostly recorded for ^{1}H NMR at 400 MHz and for ^{13}C NMR at 101 MHz. $CDCl_3$ and DMSO-D_6 were used as solvents. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm; DMSO-D_6: ^{1}H NMR: δ 2.50 ppm, ^{13}C NMR: δ 39.52 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J) are reported in Hertz (Hz). HRMS was performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI).

2. Experimental Section

2.1. Optimization of reaction conditions

Table S1 Optimization of solvent[a]

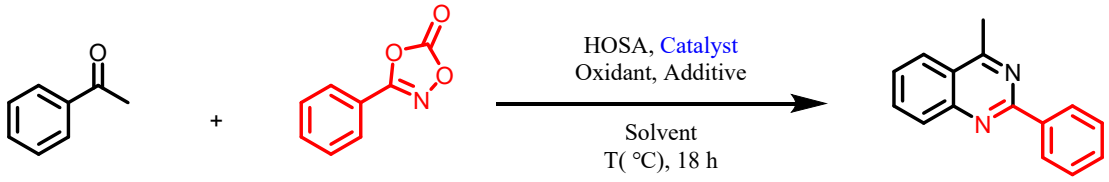


1a **2a** **3a**

Entry	Solvent	Catalyst	Additive	Oxidant	T(°C)	Yield (%)[b]
1	THF	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	47
2	MeOH	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	n.d.
3	DCM	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	n.d.
4	MeCN	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	n.d.
5	DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	41
6	TFE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	n.d.
7	MeOH:THF:DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	22
8	MeOH:DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	n.d.
9	THF:DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	76

[a]The reaction was conducted with **1a** (0.5 mmol, 1.0 equiv.) , **2a** (0.75 mmol,1.5 equiv.) , HOSA(1.0 mmol, 1.0 equiv.) , Catalyst (5.0 mol %) , Oxidant (1.0 mmol, 2.0 equiv.) and Additive (1.5 mmol , 3.0 equiv.) in the solvent (5.0mL).[b] Isolated yield based on **1a**.

Table S2 Optimization of catalyst[a]

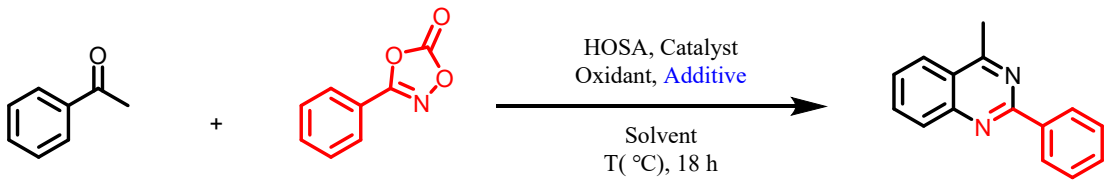


1a **2a** **3a**

Entry	Solvent	Catalyst	Additive	Oxidant	T(ºC)	Yield (%)[b]
1	THF:DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	$AgCO_3$	100	72
2	THF:DCE	$[Cp^*IrCl_2]_2$	$AcONa{\cdot}3H_2O$	$AgCO_3$	100	n.d.
3	THF:DCE	$[Cp^*RuCl_2]_2$	$AcONa{\cdot}3H_2O$	$AgCO_3$	100	n.d.
4	THF:DCE	Cp^*CoCOI_2	$AcONa{\cdot}3H_2O$	$AgCO_3$	100	n.d.

[a]The reaction was conducted with **1a** (0.5 mmol ,1.0 equiv.), **2a** (0.75 mmol ,1.5equiv.) , HOSA(0.75 mmol, 1.5 equiv.), Catalyst(5.0 mol %), Oxidant (1.0 mmol,2.0 equiv.) and Additive (1.5 mmol,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S3 Optimization of additive[a]

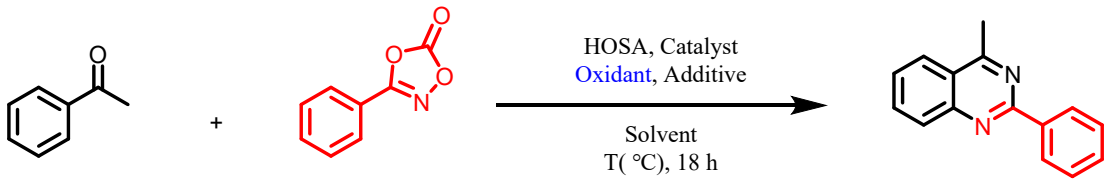


1a **2a** **3a**

Entry	Solvent	Catalyst	Additive	Oxidant	T(ºC)	Yield (%)[b]
1	THF:DCE	$[Cp^*RhCl_2]_2$	$AcONa{\cdot}3H_2O$	Ag_2CO_3	100	72
2	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	100	83
3	THF:DCE	$[Cp^*RhCl_2]_2$	AcOAg	Ag_2CO_3	100	45
4	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Cu$	Ag_2CO_3	100	58

[a]The reaction was conducted with **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol ,1.5equiv.) , HOSA(0.75 mmol, 1.5 equiv.) , Catalyst(5.0 mol %) , Oxidant (1.0 mmol,2.0 equiv.) and Additive(1.5 mmol,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S4 Optimization of oxidant[a]

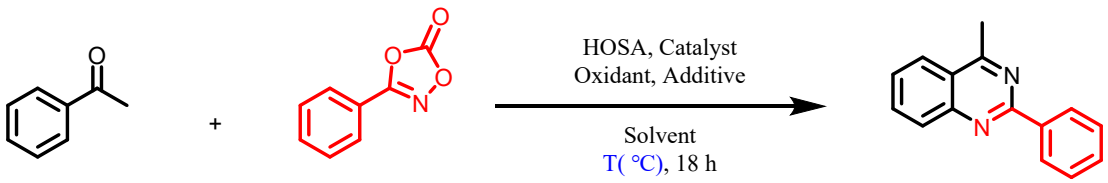


1a **2a** **3a**

Entry	Solvent	Catalyst	Additive	Oxidant	T(°C)	Yield (%)[b]
1	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	100	72
2	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2O	100	n.d.
3	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	$AgSbF_6$	100	58

[a]The reaction was conducted with **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol ,1.5equiv.) , HOSA(0.75 mmol , 1.5 equiv.) ,Catalyst(5.0 mol %) , Oxidant (1.0 mmol ,2.0 equiv.) and Additive(1.5 mmol ,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S5 Optimization of temperature(°C)[a]

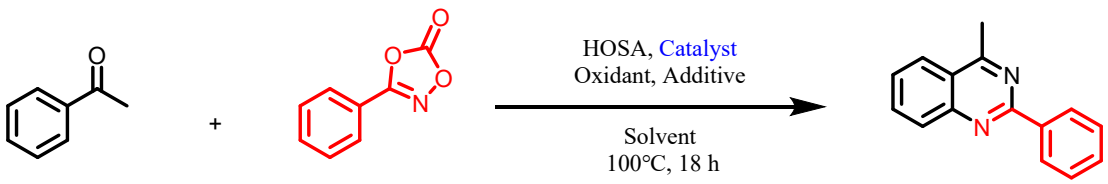


1a **2a** **3a**

Entry	Solvent	Catalyst	Additive	Oxidant	T(°C)	Yield (%)[b]
1	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	60	10<
2	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	70	23
3	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	80	58
4	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	90	74
5	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	100	93
6	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	110	87
7	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	120	89
8	THF:DCE	$[Cp^*RhCl_2]_2$	$(AcO)_2Co$	Ag_2CO_3	130	72

[a]The reaction was conducted with **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol,1.5equiv.), Catalyst(5.0 mol %), Oxidant (1.0 mmol,2.0 equiv.) and Additive (1.5 mmol,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S6 Optimization of the equivalent of catalyst[a]



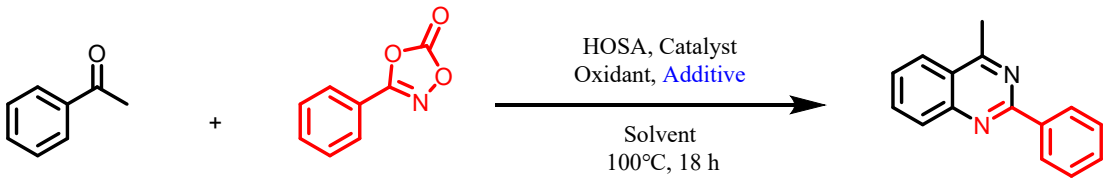
1a **2a** **3a**

Entry	Equivalent of catalyst[c]	Yields (%)[b]
1	/	n.d.
2	1.0 mol% (0.01 equiv)	43
3	5.0 mol% (0.05 equiv)	86

4	10.0 mol% (0.10 equiv)	91
5	20.0 mol% (0.20 equiv)	89

[a] Reaction conditions: **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol,1.5equiv.), HOSA(0.75 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ **(**Additions were made according to the stoichiometric equivalents listed in Table s6)[c], Ag_2CO_3 (1.0 mmol,2.0 equiv.) and $(AcO)_2Co$ (1.5 mmol,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S7 Optimization of the equivalent of additive[a]

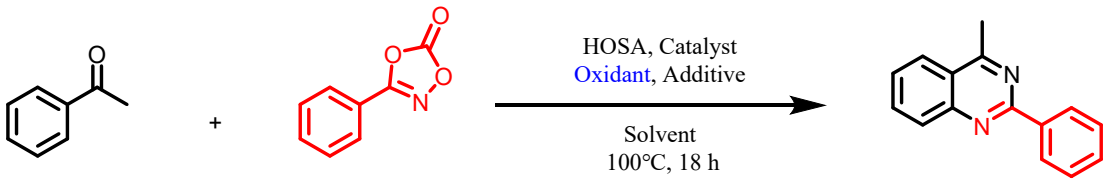


1a **2a** **3a**

Entry	Equivalent of additive[c]	Yields (%)[b]
1	/	n.d.
2	0.5 equiv	21
3	1.0 equiv	53
4	2.0 equiv	84
5	3.0 equiv	50

[a] Reaction conditions: **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol,1.5equiv.), HOSA(0.75 mmol, 1.5 equiv.) $[Cp^*RhCl_2]_2$ (5.0 mol %), Ag_2CO_3 (1.0 mmol,2.0 equiv.) and $(AcO)_2Co$ (Additions were made according to the stoichiometric equivalents listed in Table s7)[c] in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

Table S8 Optimization of the equivalent of oxidant[a]



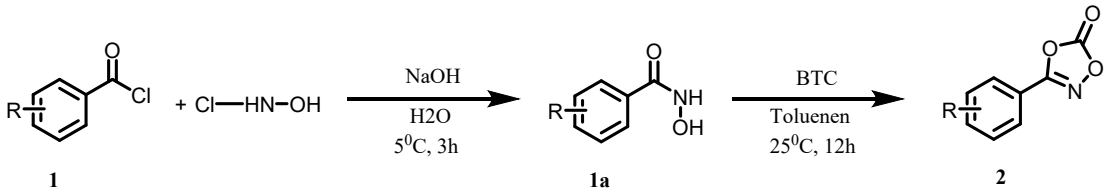
1a **2a** **3a**

Entry	Equivalent of additive[c]	Yields (%)[b]
1	/	n.d.
2	1.0 equiv	30
3	2.0 equiv	84
4	2.5 equiv	88
5	3.0 equiv	93

[a] Reaction conditions: **1a** (0.5 mmol,1.0 equiv.), **2a** (0.75 mmol,1.5equiv.), HOSA(0.75 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$(5.0 mol %), Ag_2CO_3 **(**Additions were made according to the stoichiometric equivalents listed in Table s8)[c] and $(AcO)_2Co$ (1.5 mmol,3.0 equiv.) in the THF:DCE=1:1 (5.0mL).[b] Isolated yield based on **1a**.

2.2. Synthesis and characterization of products 2 and 3

2.2.1 Preparation of 3-phenyl-1,4,2-dioxazol-5-one(2) products[1]

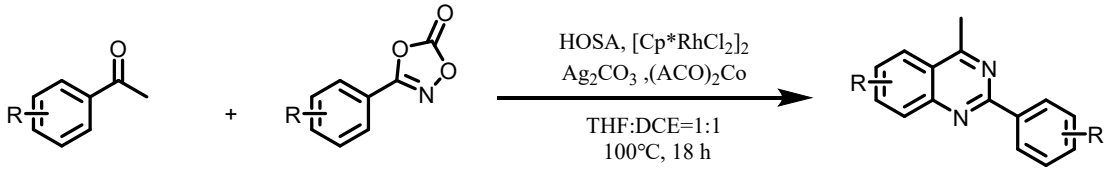


1 **1a** **2**

To a 250 mL three-neck flask, hydroxylamine hydrochloride (0.1 mol, 1.0 equiv), sodium hydroxide (0.32 mol, 3.2 equiv), and water (60ml) were added. The mixture was stirred under a dry and inert nitrogen atmosphere, then cooled to 5 °C. Benzoyl chloride (0.1 mol, 1.0 equiv) was added dropwise at this temperature. After complete addition, the reaction mixture was maintained at 5 °C for 3 hours. A pale yellow clear solution was obtained, which was used directly as the crude reaction solution for the next step.

The BTC (0.033 mol,0.033equiv) was dissolved in toluene (90 mL) and maintained at 25 °C. The crude reaction solution from the first step was added dropwise to the triphosgene solution under stirring. The reaction mixture was stirred at 25 °C for 12 hours. Upon completion, the mixture was cooled to 2 °C, and an aqueous solution of $KHCO_3$ (5%) was added to adjust the pH to 7. The biphasic mixture was washed with water and separated. The organic layer was treated with *n*-heptane (40ml), resulting in the precipitation of a white solid. The product was collected by filtration and dried to afford 15 g of white needle-like crystals of **3-phenyl-1,4,2-dioxazol-5-one (2)**.

2.2.2 Preparation of 4-methyl-2-phenylquinazoline(3) products (Method A)



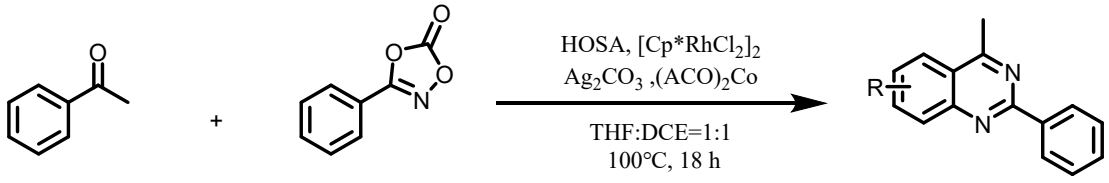
1 **2** **3**

A reaction tube (10 mL) with magnetic stir bar was charged with compound **1** (0.5 mmol, 1.0 equiv), HOSA (1.0 mmol, 2.0 equiv) and 5 mL mixed solvent (THF:DCE=1:1). Then the mixture

was stirred at room temperature for 3h. TLC (PET: EtOAc= 4:1) showed that the complete consumption of compound **1**. Then compound **2** (0.75 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.025mmol, 5 mol%), Ag_2CO_3 (1.5mmol, 3.0 equiv) and $(AcO)_2Co$ (1.0 mmol, 2.0 equiv) was added, The reaction system was stirred at 100 °C for 18h.

After cooling to room temperature, TLC (PET: EtOAc= 10:1) showed that the reaction was complete. Then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford product **3**.

2.3 Synthesis of 3a on 5.0 mmol scale

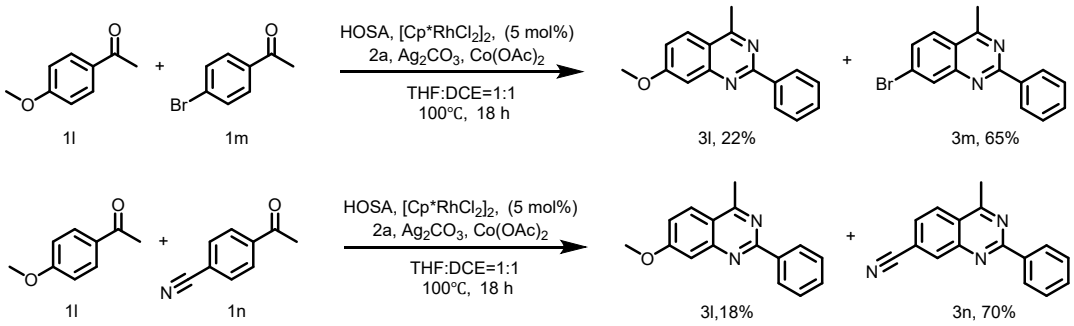


1a **2a** **3a**

A 100 mL oven-dried Schlenk tube with magnetic stir bar was charged with compound **1a** (0.60 g, 5.0 mmol, 1.0 equiv), HOSA (0.848g, 7.5 mmol, 1.5equiv) and 25 mL mixed solvent (THF:DCE= 1:1). Then the mixture was stirred at room temperature for 3h. TLC (PET: EtOAc= 4:1) showed that the complete consumption of compound **1a**. Then compound **2a** (1.23 g, 7.5 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.15 g 0.25mmol, 5 mol%), Ag_2CO_3 (4.14 g, 15.0mmol, 3.0 equiv) and $Co(AcO)_2$ (1.73g, 10.0 mmol, 2.0 equiv) was added, The reaction system was stirred at 80 °C for 24h.

After cooling to room temperature, TLC (PET: EtOAc= 10:1) showed that the reaction was complete. Then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford product **3a** as white solids (902.1 mg) in 82 % yield.

2.4 Competitive Experiment



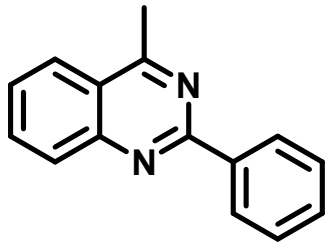
A reaction tube (10 mL) equipped with a magnetic stir bar was charged with compound 1l (75.09 mg, 0.5 mmol, 1.0 equiv), compound 1m (99.52 mg, 0.5 mmol, 1.0 equiv), HOSA (169.64 mg, 1.5 mmol, 3.0 equiv), and 5 mL of a mixed solvent (THF:DCE = 1:1). The resulting mixture was stirred at room temperature for 3 h. TLC analysis (PET:EtOAc = 4:1) indicated complete consumption of the starting materials.

Subsequently, compound 2a (83 mg, 0.5 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (62.0 mg, 0.05 mmol, 10 mol%), Ag_2CO_3(827.25 mg, 3.0 mmol, 6.0 equiv), and $Co(AcO)_2$ (354.04 mg, 2.0 mmol, 4.0 equiv) were added to the reaction mixture. The sealed tube was then stirred in an oil bath at 100^0C for 18 h.

After cooling to room temperature, TLC analysis (PET:EtOAc = 10:1) showed completion of the reaction. The solvent was removed under reduced pressure, and the crude residue was purified by silica gel column chromatography to afford products **3l** (22% yield) and **3m** (65% yield)**.**

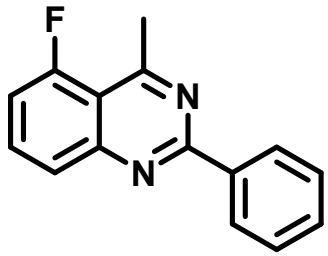
Similarly, a competitive reaction between compound 1l (75.09 mg, 0.5 mmol, 1.0 equiv) and compound 1n (72.58 mg, 0.5 mmol, 1.0 equiv) was carried out under identical conditions. After the same work-up and purification procedures, the corresponding products **3l** (18% yield) and **3n** (70% yield) were obtained.

3. Experimental data for described substances



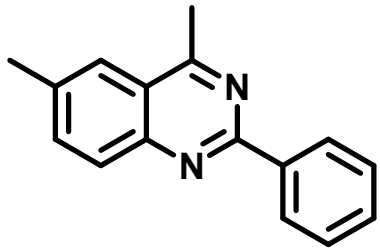
4-methyl-2-phenylquinazoline (3a)[2]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (92.4 mg) in 84 % yield according to the Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 2H), 8.09 (t, *J* = 8.5 Hz, 2H), 7.92 – 7.79 (m, 1H), 7.67 – 7.40 (m, 4H), 3.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.33, 160.27, 150.46, 138.35, 133.60, 130.44, 129.31, 128.62, 128.59, 126.94, 125.06, 123.08, 77.28, 22.11. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073, found 221.1075.



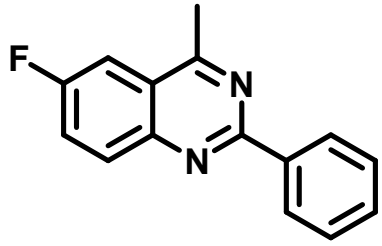
fluoro-4-methyl-2-phenylquinazoline(3c)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (79.8 mg) in 67% yield according to the Method A.^{1}H NMR (400 MHz, DMSO) δ 8.56 (ddd, *J* = 5.8, 3.3, 1.3 Hz, 2H), 7.96 (td, *J* = 8.2, 5.9 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.49 (dd, *J* = 11.6, 7.8 Hz, 1H), 3.06 (dd, *J* = 6.0, 1.2 Hz, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.24, 169.18, 161.48, 159.04, 147.41, 137.80, 132.05, 131.96, 131.22, 129.20, 128.48, 124.97, 124.71, 123.68, 123.59, 110.31, 110.09, 22.56. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FN_2$ $[M+H]^+$ 239.0979, found 239.0980.



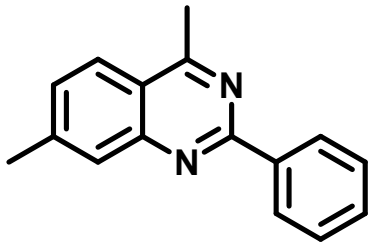
4,6-dimethyl-2-phenylquinazoline (3d)[4]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (101.9 mg) in 87 % yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.54 (d, *J* = 6.3 Hz, 2H), 8.06 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 6.7 Hz, 3H), 2.96 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.43, 158.62, 148.61, 138.17, 137.72, 136.77, 130.96, 129.13, 128.75, 128.41, 124.99, 122.99, 22.40, 21.83. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2$ $[M+H]^+$ 235.1230, found 235.1232.



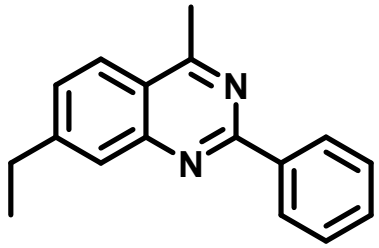
5-fluoro-4-methyl-2-phenylquinazoline(3e)[6]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (94.0 mg) in 81% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.60 – 8.53 (m, 2H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.72 – 7.64 (m, 1H), 7.57 (d, *J* = 5.7 Hz, 3H), 3.01 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.61, 159.41, 158.53, 155.98, 140.48, 140.36, 137.66, 131.52, 129.26, 128.70, 127.75, 127.68, 124.45, 122.42, 122.38, 118.88, 118.70, 22.84. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FN_2$ $[M+H]^+$ 239.0979, found 239.0982.



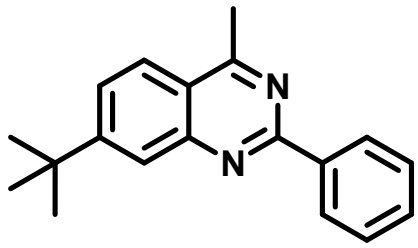
4,7-dimethyl-2-phenylquinazoline (3f)[3]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (97.2 mg) in 82 % yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.66 – 8.47 (m, 2H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.82 (s, 1H), 7.55 (q, *J* = 5.2 Hz, 4H), 2.96 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.68, 159.39, 150.42, 145.32, 138.19, 131.06, 129.96, 129.13, 128.50, 127.84, 126.03, 121.25, 31.66, 30.34, 22.29, 22.09. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2$ $[M+H]^+$ 235.1230, found 235.1234.



7-ethyl-4-methyl-2-phenylquinazoline(3g)

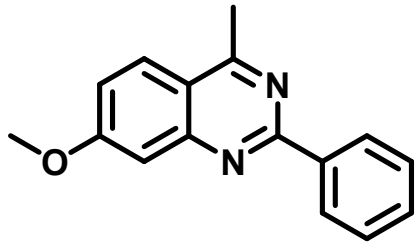
The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (100.5 mg) in 81% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.56 (dd, *J* = 5.9, 2.1 Hz, 2H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.83 (s, 1H), 7.61 – 7.52 (m, 4H), 2.97 (s, 3H), 2.87 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (101 MHz, DMSO) δ 168.66, 159.36, 151.23, 150.48, 138.18, 131.05, 129.12, 128.95, 128.49, 126.50, 126.16, 121.44, 28.97, 22.29, 15.48. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386, found 249.1387.



7-(tert-butyl)-4-methyl-2-phenylquinazoline(3h)

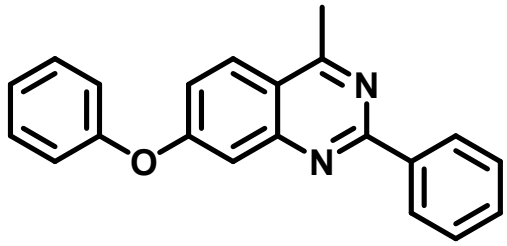
The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (120.2 mg) in 87 % yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.57

(d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.91 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 5.9 Hz, 3H), 2.97 (s, 3H), 1.42 (s, 9H).^{13}C NMR (101 MHz, DMSO) δ 168.71, 159.38, 151.28, 150.52, 138.20, 131.07, 129.14, 128.99, 128.51, 126.54, 126.21, 121.48, 29.00, 22.32, 15.52. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}N_2$ $[M+H]^+$ 277.1699, found 277.1706.



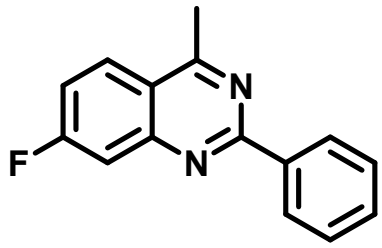
7-methoxy-4-methyl-2-phenylquinazoline(3i)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (116.3 mg) in 93% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.60 – 8.50 (m, 2H), 8.18 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 5.6 Hz, 3H), 7.38 (s, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 3.99 (s, 3H), 2.92 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 167.91, 164.13, 159.87, 152.71, 138.23, 131.07, 129.10, 128.51, 127.84, 120.32, 118.36, 107.13, 56.39, 22.23. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179, found 251.1183.



4-methyl-7-phenoxy-2-phenylquinazoline(3j)

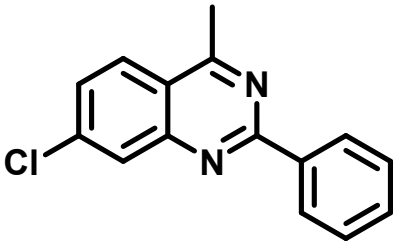
The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (146.7 mg) in 94% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.50 (t, *J* = 4.1 Hz, 2H), 8.32 (d, *J* = 9.2 Hz, 1H), 7.59 – 7.49 (m, 5H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.13 (s, 1H), 2.95 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 168.54, 162.73, 160.07, 155.01, 152.05, 137.91, 131.23, 131.07, 129.10, 128.91, 128.59, 125.92, 121.18, 120.44, 119.34, 111.85, 22.35. HRMS (ESI) *m/z* calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1335, found 313.1336.



8-fluoro-4-methyl-2-phenylquinazoline(3k)[5]

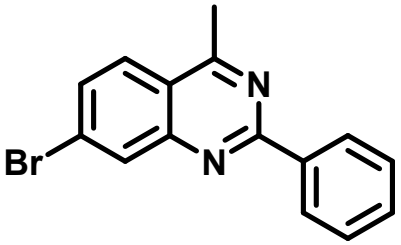
The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (96.4 mg) in 79% yield according to the Method A.^{1}H NMR (400 MHz, DMSO) δ 8.55 (dd, *J* = 4.9, 2.9 Hz, 2H), 8.40 (dd, *J* = 10.0, 5.4 Hz, 1H), 7.77 (d, *J* = 10.1 Hz, 1H), 7.62 (t, *J* = 8.9 Hz, 1H), 7.59 – 7.54 (m, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.36, 166.94, 164.43, 160.37, 152.07,

151.93, 137.69, 131.47, 129.89, 129.78, 129.20, 128.70, 120.57, 118.07, 117.82, 112.63, 112.43, 22.56. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FN_2$ $[M+H]^+$ 239.0979, found 239.0984.



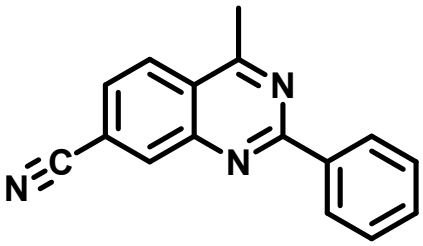
6-chloro-4-methyl-2-phenylquinazoline(3l)[7]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (115.6 mg) in 91% yield according to the Method A.^{1}H NMR (400 MHz, DMSO) δ 8.58 – 8.50 (m, 2H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.05 (s, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.55 (s, 3H), 2.96 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.69, 160.36, 150.87, 139.35, 137.60, 131.53, 129.21, 128.71, 128.60, 128.43, 127.64, 121.69, 22.46. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}ClN_2$ $[M+H]^+$ 255.0684, found 255.0682.



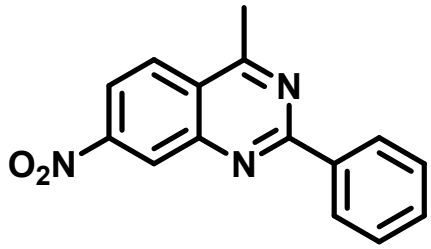
7-bromo-4-methyl-2-phenylquinazoline(3m)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (126.7 mg) in 85% yield according to the Method A.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.0 Hz, 2H), 8.26 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 6.8 Hz, 3H), 2.99 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.45, 161.07, 151.30, 137.84, 131.64, 130.83, 130.47, 128.71, 128.66, 128.20, 126.40, 121.69, 22.08. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}BrN_2$ $[M+H]^+$ 299.0178, found 299.0180.



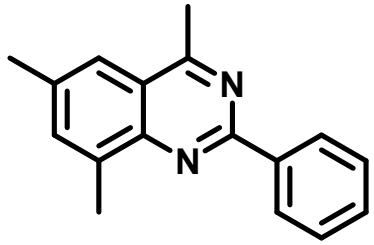
5-methyl-2-phenylquinazoline-7-carbonitrile(3n)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (102.94 mg) in 84% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.61 – 8.52 (m, 3H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.54 (m, 3H), 3.03 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 170.54, 160.62, 149.28, 137.29, 134.76, 131.81, 129.32, 128.80, 128.73, 128.30, 124.74, 118.41, 116.97, 22.60. HRMS (ESI) *m/z* calcd for $C_{16}H_{12}N_3$ $[M+H]^+$ 246.1026, found 246.1031.



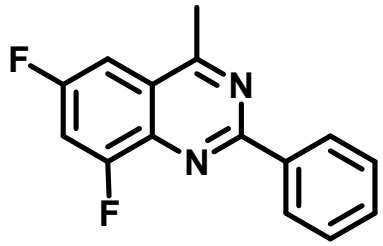
4-methyl-7-nitro-2-phenylquinazoline (3o)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (115.3 mg) in 87% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.73 (s, 1H), 8.62 – 8.52 (m, 3H), 8.36 (d, *J* = 9.0 Hz, 1H), 7.64 – 7.54 (m, 3H), 3.06 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 170.63, 161.07, 151.23, 149.80, 137.14, 131.94, 129.35, 129.10, 128.88, 125.71, 124.42, 121.00, 22.80. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}N_3O_2$ $[M+H]^+$ 266.0924, found 266.0925.



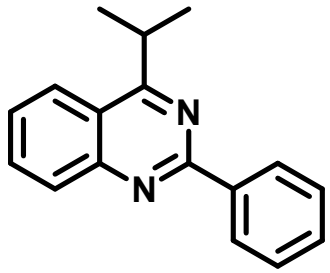
4,6,8-trimethyl-2-phenylquinazoline (3p)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (106.7 mg) in 86% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.57 (d, *J* = 8.4 Hz, 2H), 7.87 (s, 1H), 7.68 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 3H), 3.33 (s, 3H), 2.94 (s, 3H), 2.74 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 168.37, 157.61, 147.58, 138.45, 137.01, 136.57, 136.46, 130.85, 129.12, 128.39, 122.91, 122.60, 22.56, 21.87, 17.34. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386, found 249.1391.



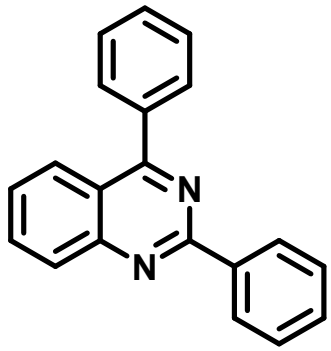
6,8-difluoro-4-methyl-2-phenylquinazoline(3q)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (103.7 mg) in 81% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.54 (dt, *J* = 4.8, 2.3 Hz, 2H), 8.06 – 7.95 (m, 2H), 7.62 – 7.52 (m, 3H), 2.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 195.63, 143.36, 135.12, 130.49, 130.24, 129.74, 129.59, 128.59, 21.66. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}F_2N_2$ $[M+H]^+$ 257.0885, found 257.0892.



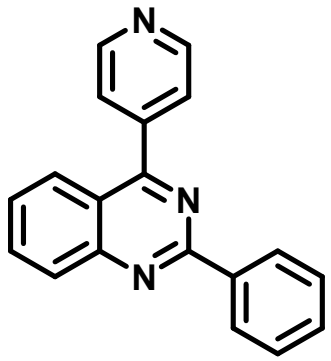
4-isopropyl-2-phenylquinazoline(3r)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (88.0 mg) in 71% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.60 (d, *J* = 7.8 Hz, 2H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.57 (d, *J* = 7.1 Hz, 3H), 4.09 (p, *J* = 6.7 Hz, 1H), 1.44 (d, *J* = 6.7 Hz, 6H).^{13}C NMR (101 MHz, DMSO) δ 176.26, 159.28, 150.71, 138.31, 134.61, 131.21, 129.40, 129.21, 128.57, 127.99, 125.36, 121.67, 30.96, 22.29. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386, found 249.1388



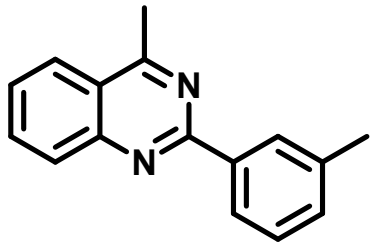
2,4-diphenylquinazoline(3s)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (111.4 mg) in 79% yield according to the Method A.^{1}H NMR (400 MHz, DMSO) δ 8.65 – 8.58 (m, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.05 (t, *J* = 7.7 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.58 (d, *J* = 5.4 Hz, 3H).^{13}C NMR (101 MHz, DMSO) δ 168.57, 159.52, 151.70, 137.98, 137.46, 134.97, 131.36, 130.67, 130.52, 129.25, 129.18, 128.66, 128.49, 127.38, 121.58. HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_2$ $[M+H]^+$ 283.1230, found 283.1235.



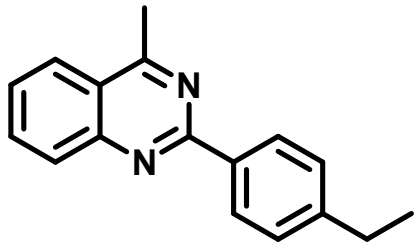
2-phenyl-4-(pyridin-4-yl)quinazoline (3t)

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (100.5 mg) in 71% yield according to the Method A. ^{1}H NMR (400 MHz, DMSO) δ 8.81 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 2H), 8.04 (t, *J* = 8.2 Hz, 3H), 7.70 (dq, *J* = 22.9, 7.7 Hz, 6H), 7.49 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 153.69, 152.54, 151.29, 127.93, 127.83, 125.07, 125.04, 123.18, 123.11, 121.06, 115.63, 115.44. HRMS (ESI) *m/z* calcd for $C_{19}H_{14}N_3$ $[M+H]^+$ 284.1182, found 284.1186.



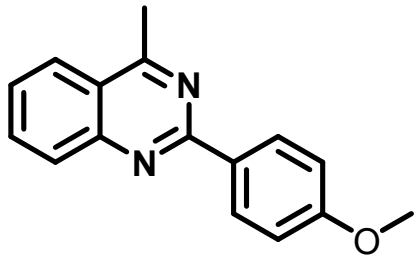
2-methyl-2-(m-tolyl)quinazoline(3u)[6]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (100.7 mg) in 86 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.41 – 8.34 (m, 2H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.06 – 7.94 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 2.99 (s, 3H), 2.44 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.24, 159.38, 150.09, 138.28, 138.01, 134.76, 131.82, 131.21, 129.07, 129.03, 128.96, 127.88, 126.33, 125.84, 123.04, 22.39, 21.67. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2$ $[M+H]^+$ 235.1230, found 235.1233.



3-(4-ethylphenyl)-4-methylquinazoline(3v)

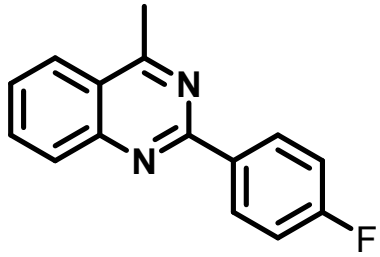
The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (101.7 mg) in 82 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.48 (d, *J* = 6.2 Hz, 2H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.04 – 7.93 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 6.2 Hz, 2H), 2.99 (s, 3H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.30 – 1.18 (t, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.20, 159.40, 150.13, 147.14, 135.65, 134.74, 128.91, 128.66, 128.59, 127.74, 126.34, 122.98, 28.61, 22.42, 15.88. HRMS (ESI) *m/z* calcd for $C_{17}H_{16}N_2$ $[M+H]^+$ 249.1386, found 249.1390.



2-(4-methoxyphenyl)-4-methylquinazoline(3w)[6]

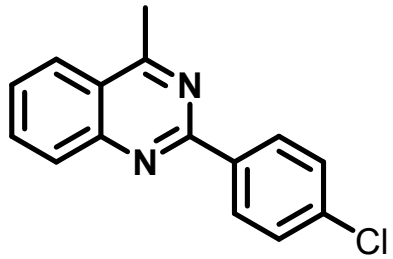
The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as white solids (115 mg) in 92 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.51 (d, *J* = 6.9 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.70 – 7.62 (m,

1H), 7.10 (d, *J* = 6.9 Hz, 2H), 3.85 (s, 3H), 2.97 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.06, 161.95, 159.20, 150.18, 134.67, 130.55, 130.25, 128.77, 127.42, 126.31, 122.75, 114.51, 55.84, 22.40. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179, found 251.1182.



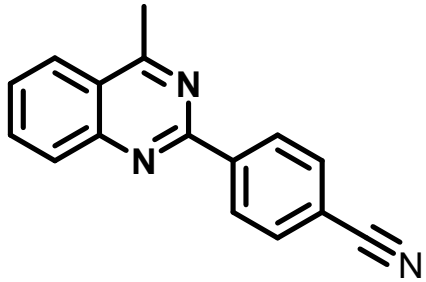
2-(4-fluorophenyl)-4-methylquinazoline(3x)[6]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (96.4 mg) in 81 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.40 (d, *J* = 7.8 Hz, 1H), 8.28 (dd, *J* = 18.9, 9.5 Hz, 2H), 8.08 – 7.97 (m, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.61 (q, *J* = 7.1 Hz, 1H), 7.39 (t, *J* = 8.5 Hz, 1H), 3.00 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.65, 164.29, 161.88, 158.04, 149.94, 140.72, 140.64, 134.99, 131.31, 131.23, 129.05, 128.35, 126.42, 124.58, 124.56, 123.24, 118.10, 117.89, 114.92, 114.69, 22.41. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FN_2$ $[M+H]^+$ 239.0979, found 239.0982.



4-(4-chlorophenyl)-4-methylquinazoline(3y)[8]

The title compound was obtained by column chromatography (PET: EtOAc = 40:1) as white solids (100.4 mg) in 79 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.58 – 8.47 (m, 2H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.13 – 7.97 (m, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 6.2 Hz, 2H), 3.02 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 135.07, 131.24, 130.95, 129.08, 128.43, 128.04, 127.09, 126.47, 22.43. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}ClN_2$ $[M+H]^+$ 255.0684, found 255.0688.

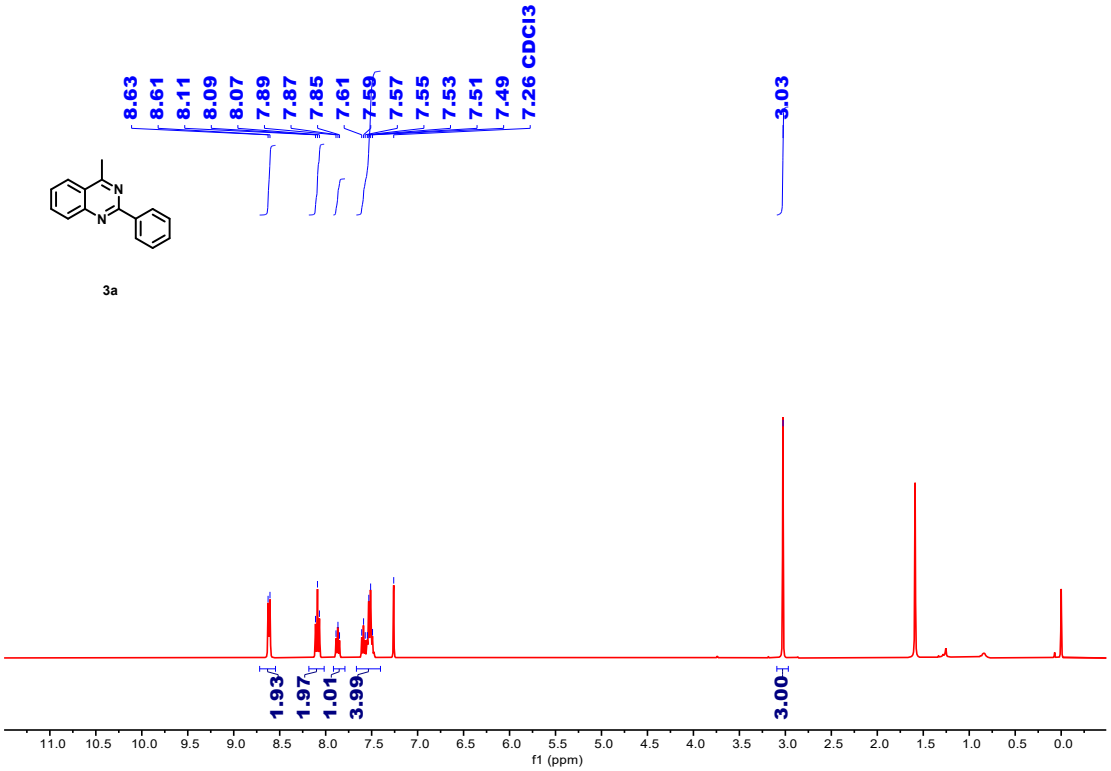


(4-methylquinazolin-2-yl)benzonitrile(3z)[9]

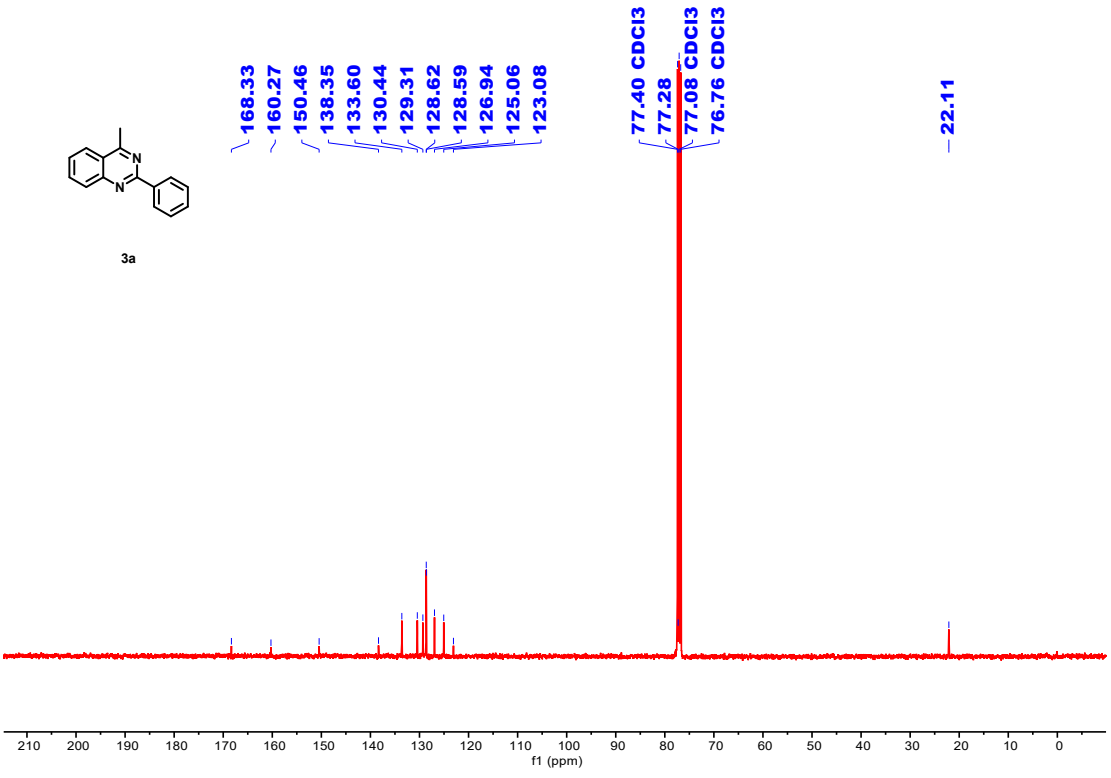
The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as white solids (99.2 mg) in 81 % yield according to the Method.A. ^{1}H NMR (400 MHz, DMSO) δ 8.71 (d, *J* = 6.4 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.12 – 8.00 (m, 4H), 7.78 (t, *J* = 7.5 Hz, 1H), 3.03 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 169.93, 157.68, 149.91, 142.22, 135.19, 133.26, 129.18, 129.13, 128.81, 126.52, 123.33, 119.27, 113.33, 22.46. HRMS (ESI) *m/z* calcd for $C_{16}H_{12}N_3$ $[M+H]^+$ 246.1026, found 246.1028.

4. NMR Spectra

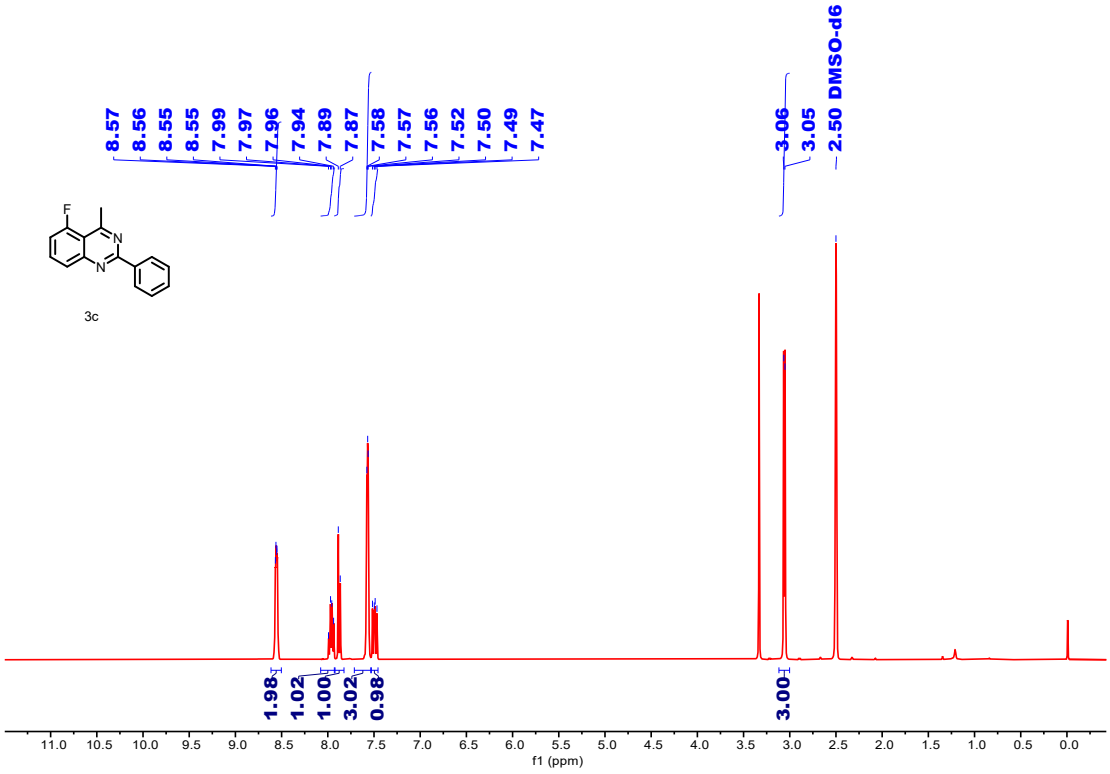
^{1}H NMR spectrum of 3a ($CDCl_3$,400 MHz)



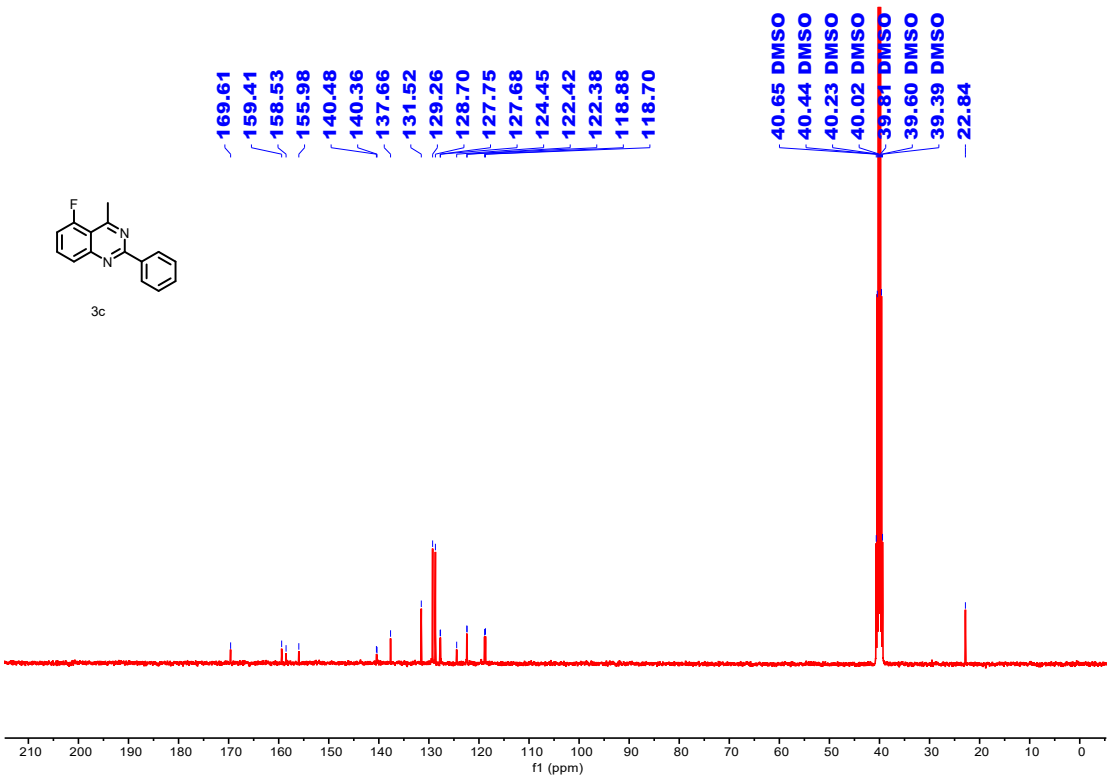
^{13}C NMR spectrum of 3a ($CDCl_3$,101MHz)



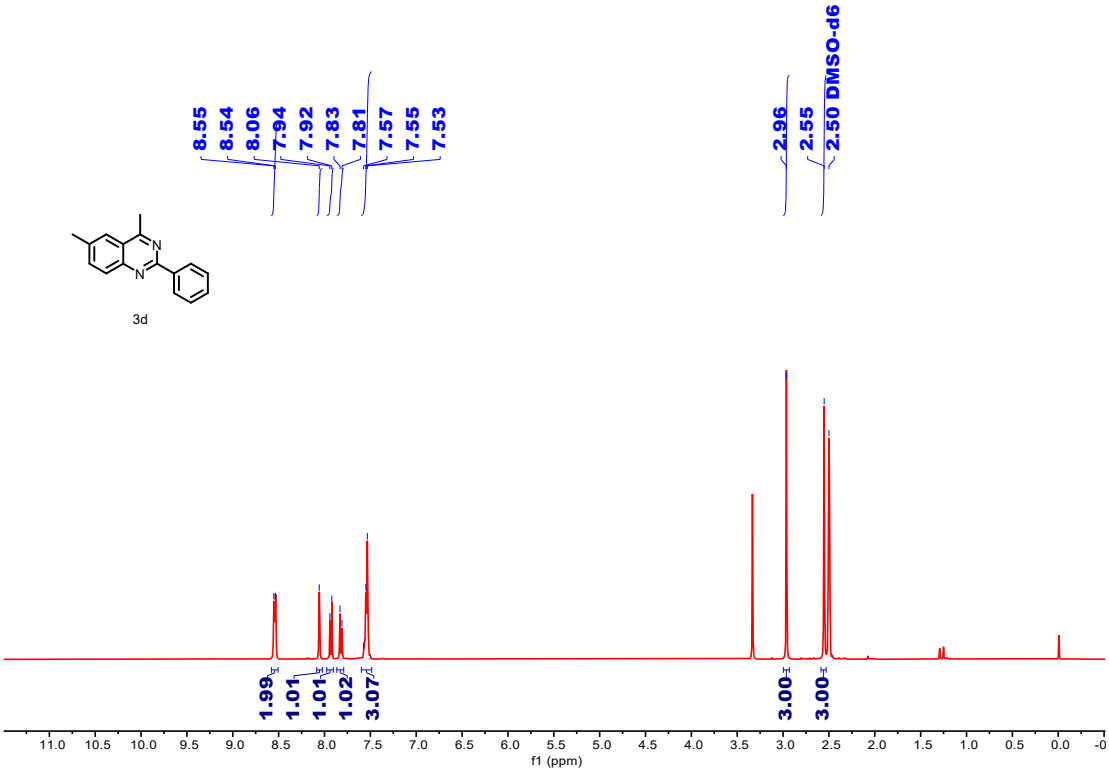
^{1}H NMR spectrum of 3c (DMSO-d6,400 MHz)



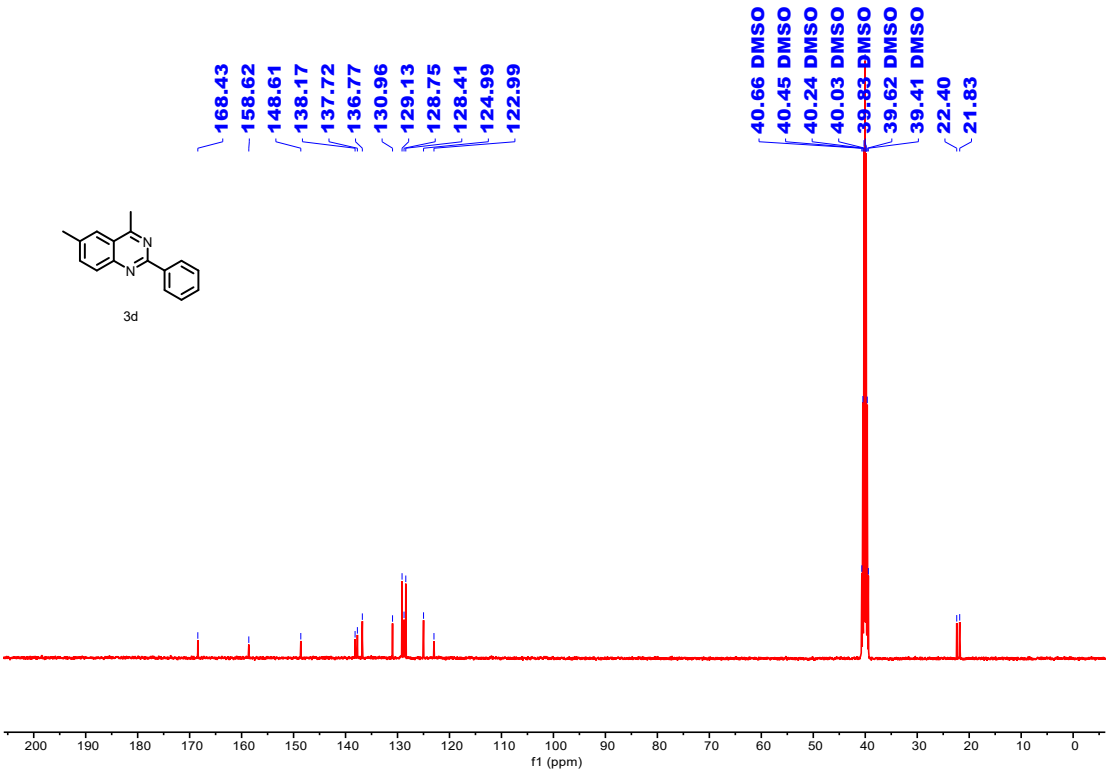
^{13}C NMR spectrum of 3c (DMSO-d6,101MHz)



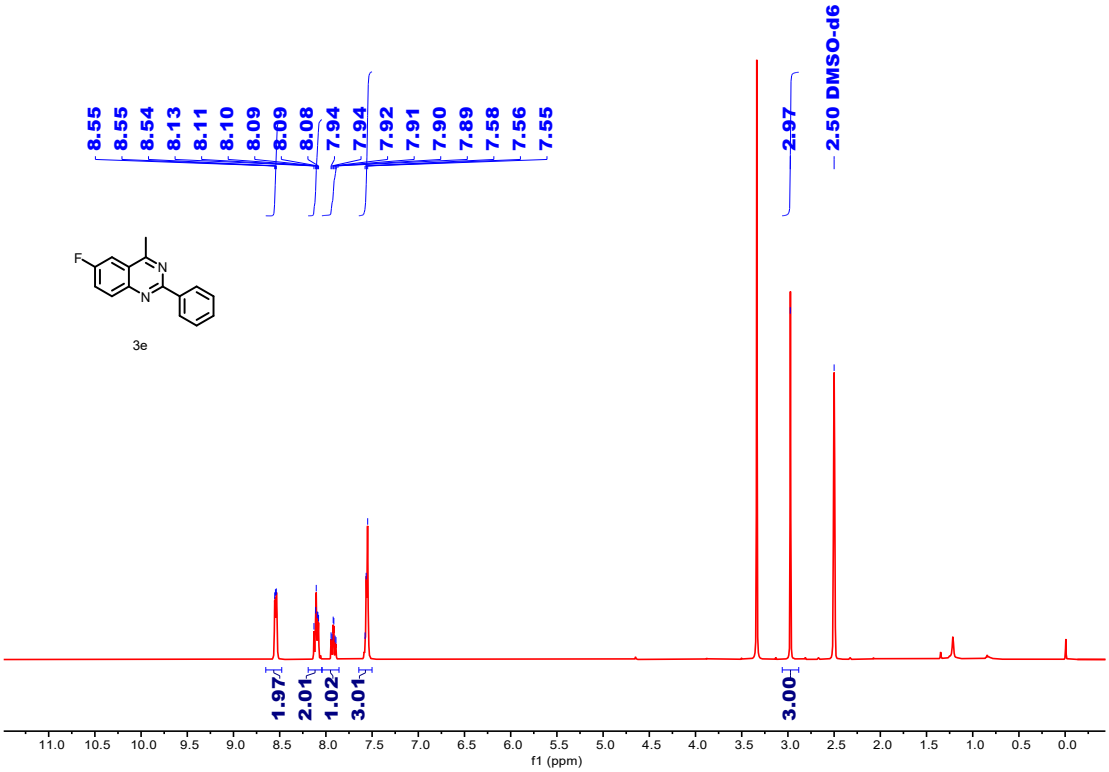
^{1}H NMR spectrum of 3d (DMSO-d6,400 MHz)



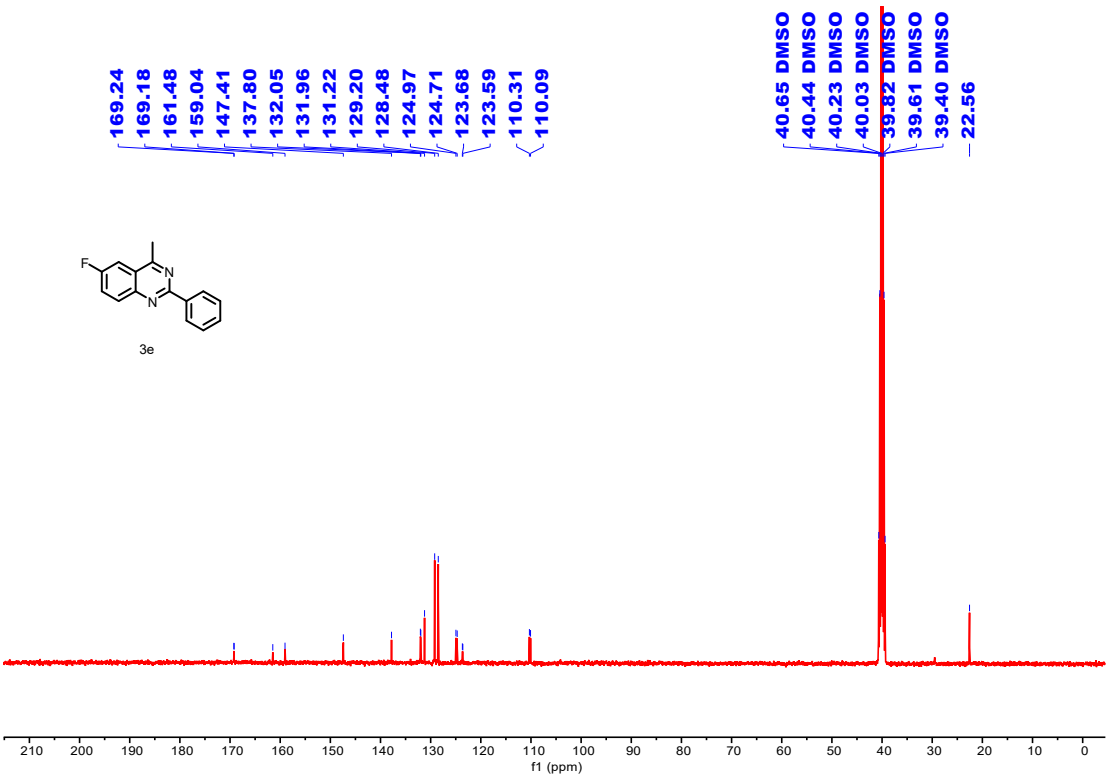
^{13}C NMR spectrum of 3d (DMSO-d6,101MHz)



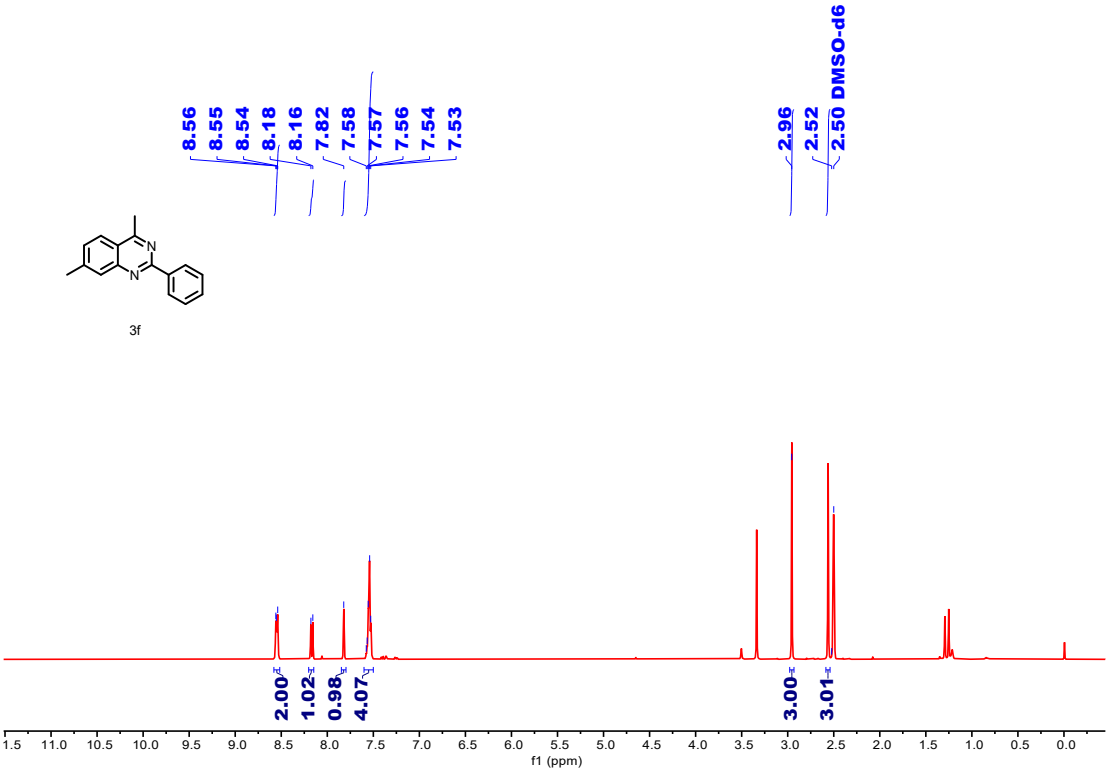
^{1}H NMR spectrum of 3e (DMSO-d6,400 MHz)



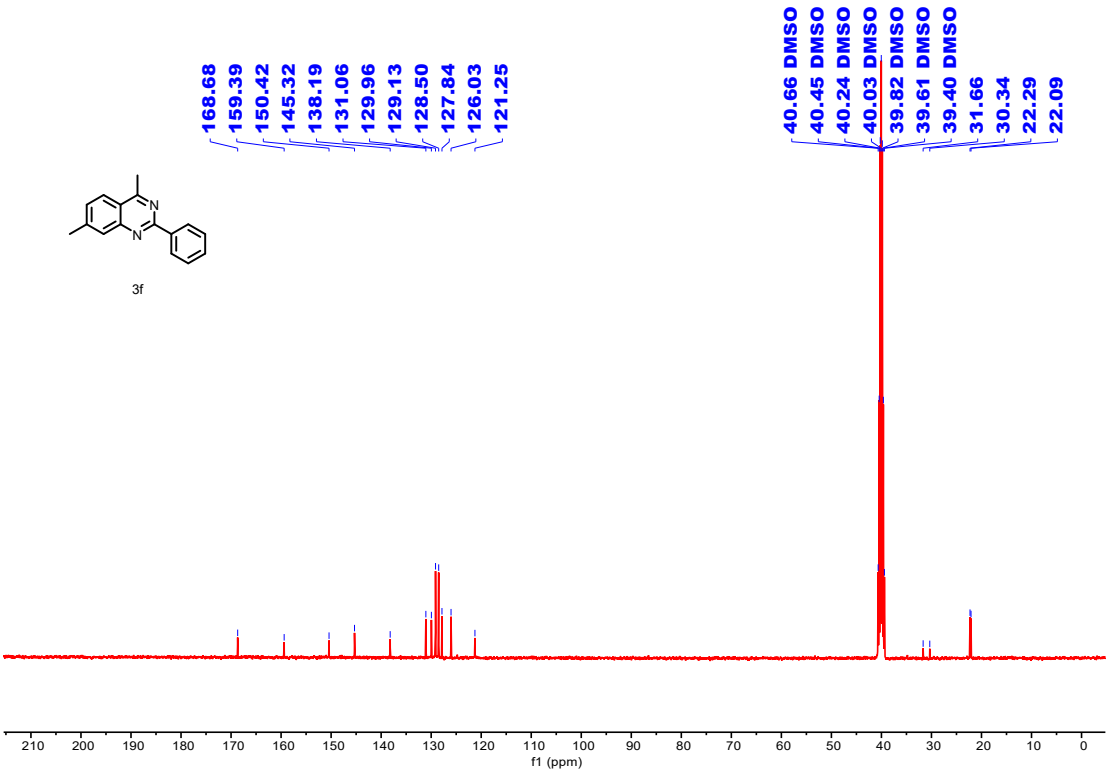
^{13}C NMR spectrum of 3e (DMSO-d6,101MHz)



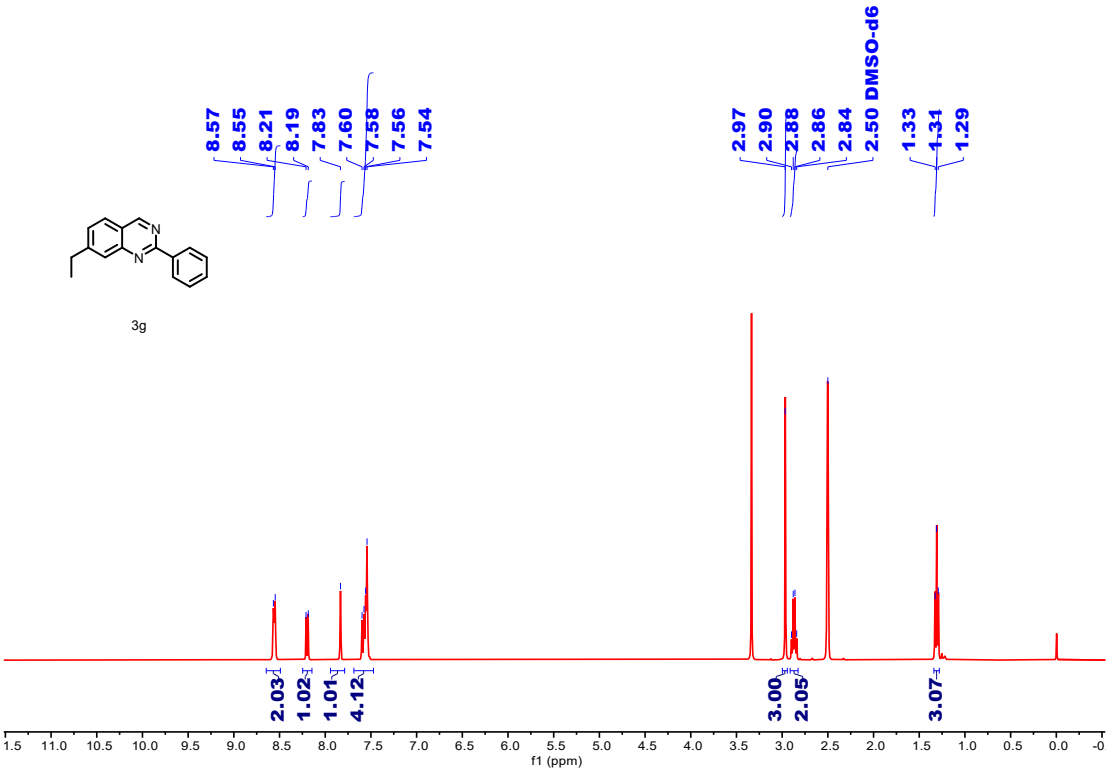
^{1}H NMR spectrum of 3f (DMSO-d6,400 MHz)



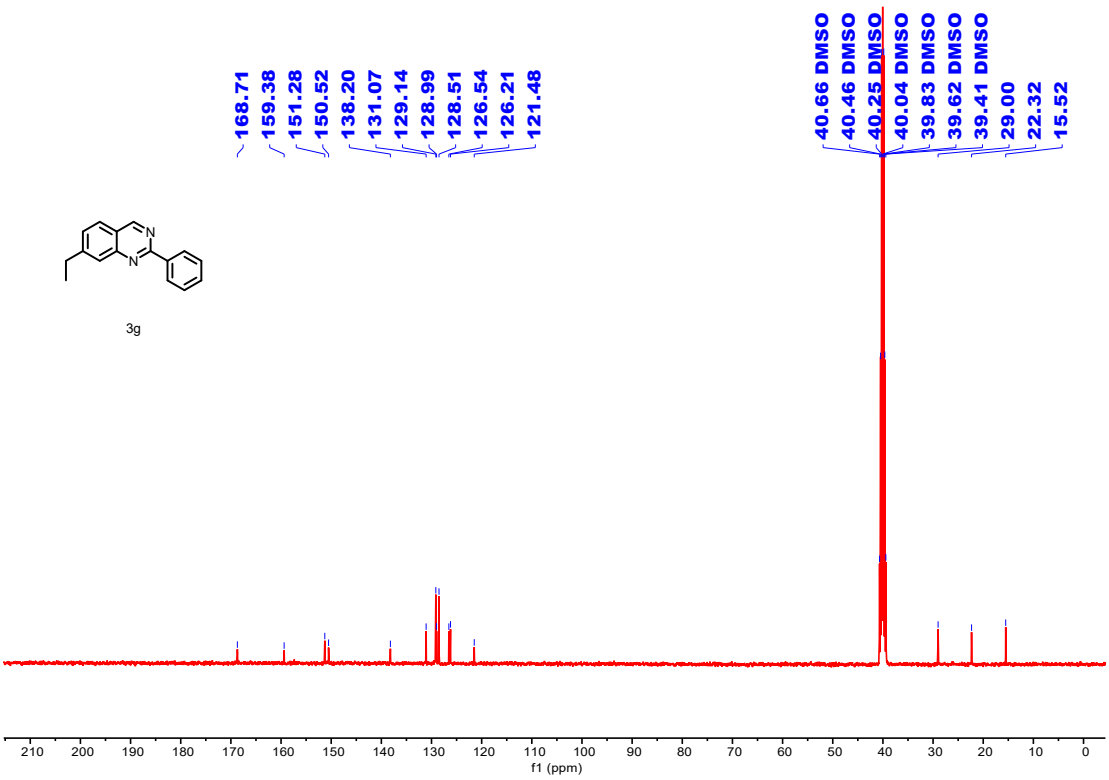
^{13}C NMR spectrum of 3f (DMSO-d6,101MHz)



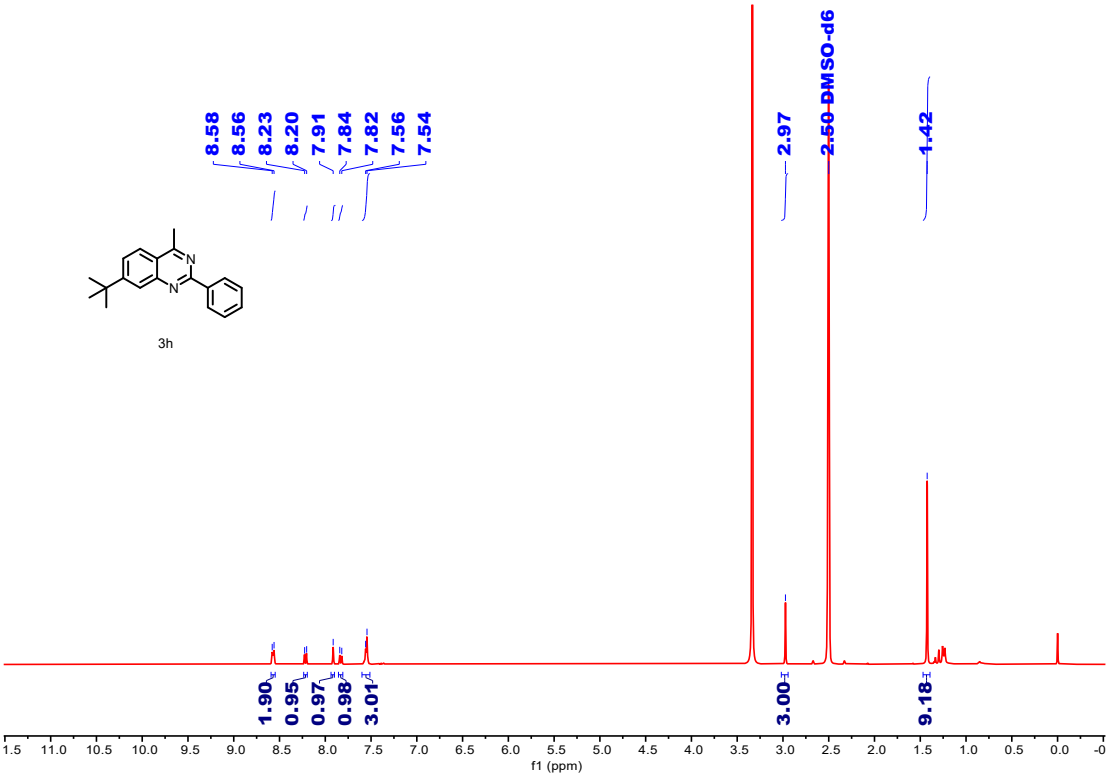
^{1}H NMR spectrum of 3g (DMSO-d6,400 MHz)



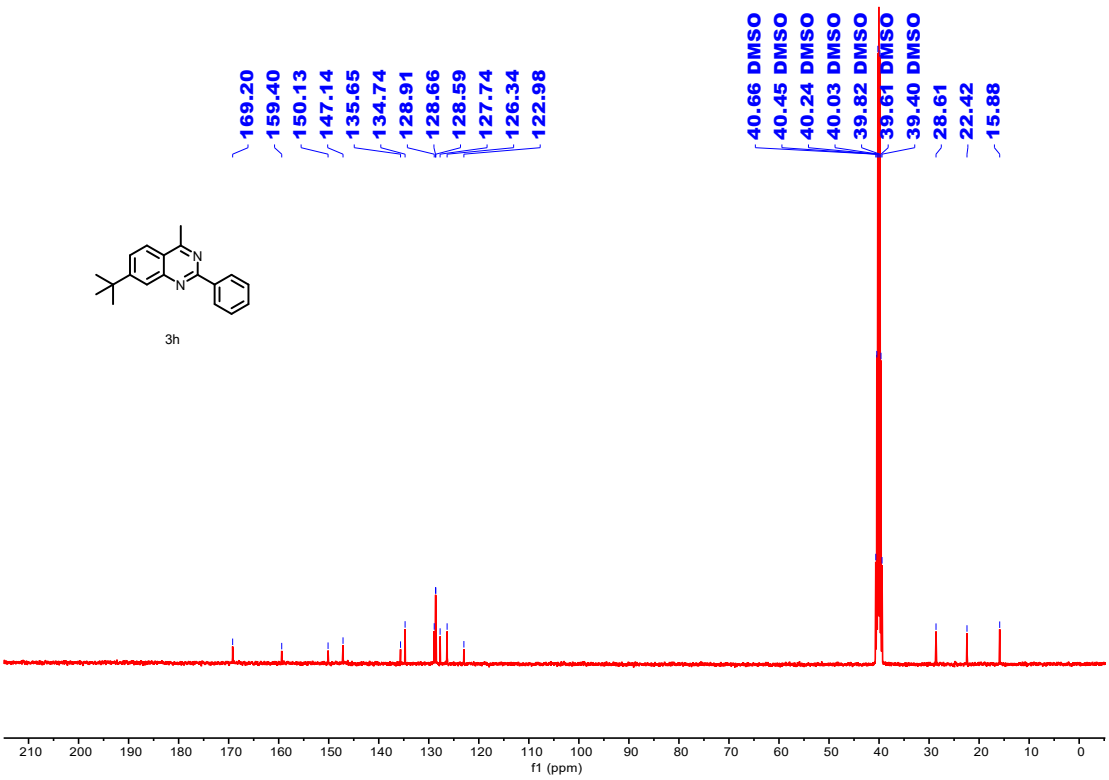
^{13}C NMR spectrum of 3g (DMSO-d6,101MHz)



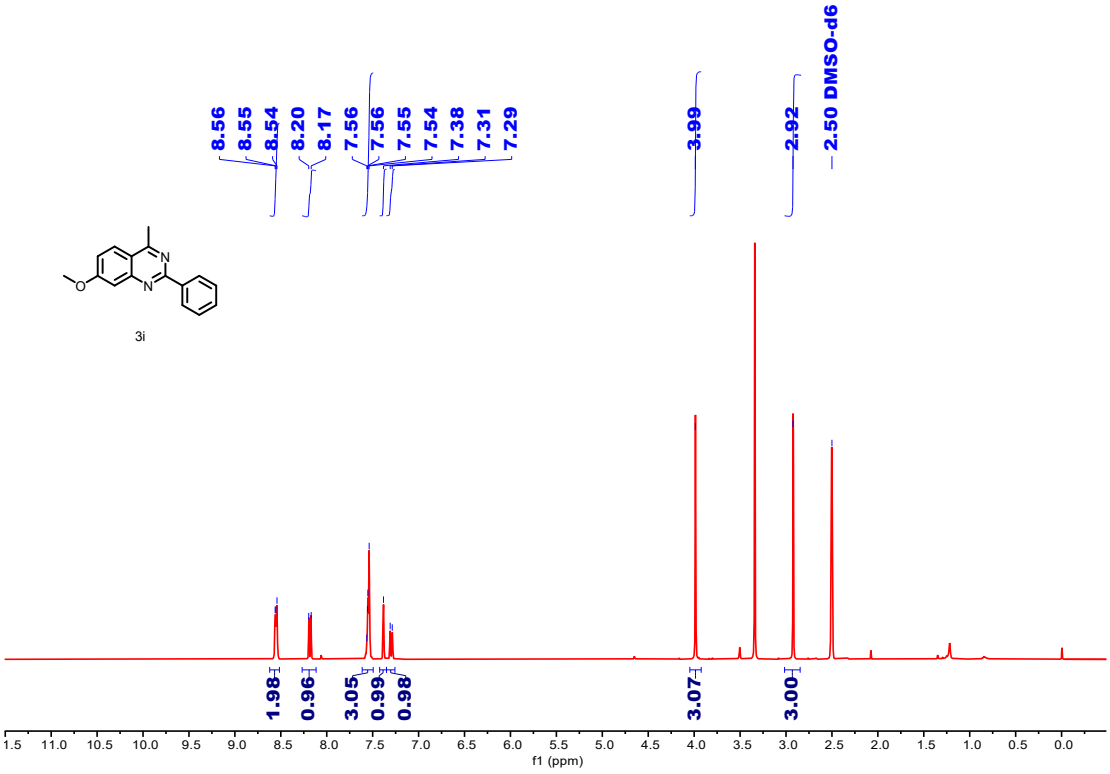
^{1}H NMR spectrum of 3h (DMSO-d6,400 MHz)



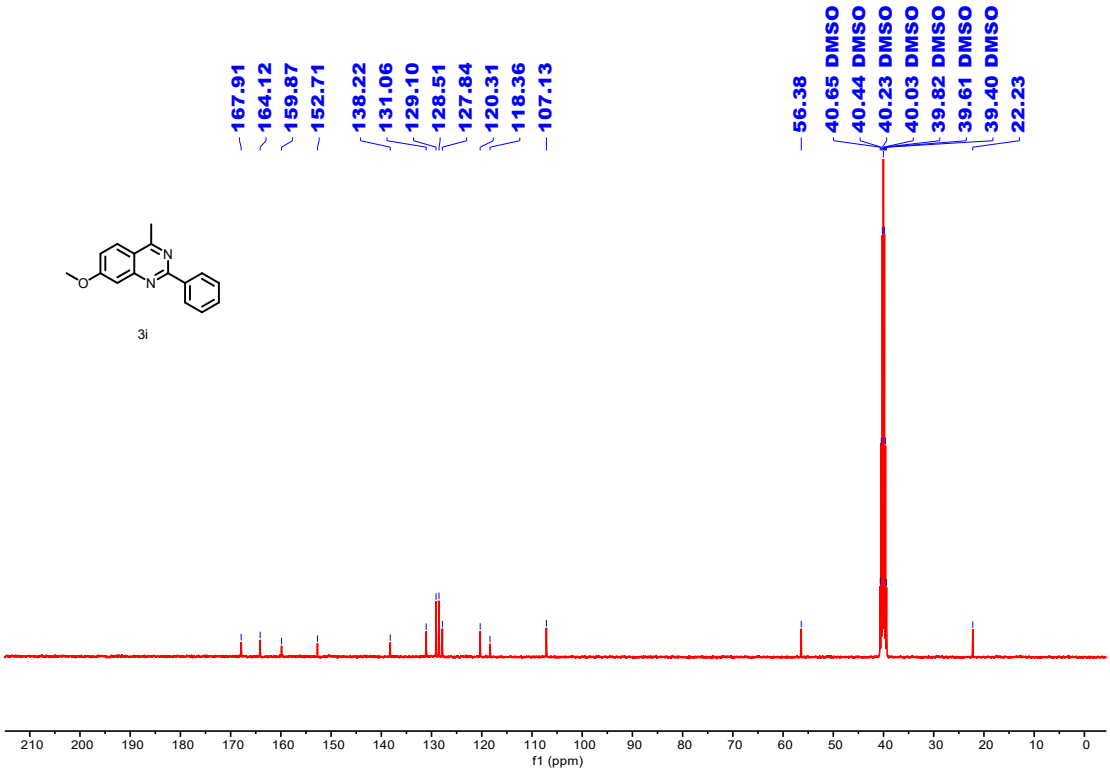
^{13}C NMR spectrum of 3h (DMSO-d6,101MHz)



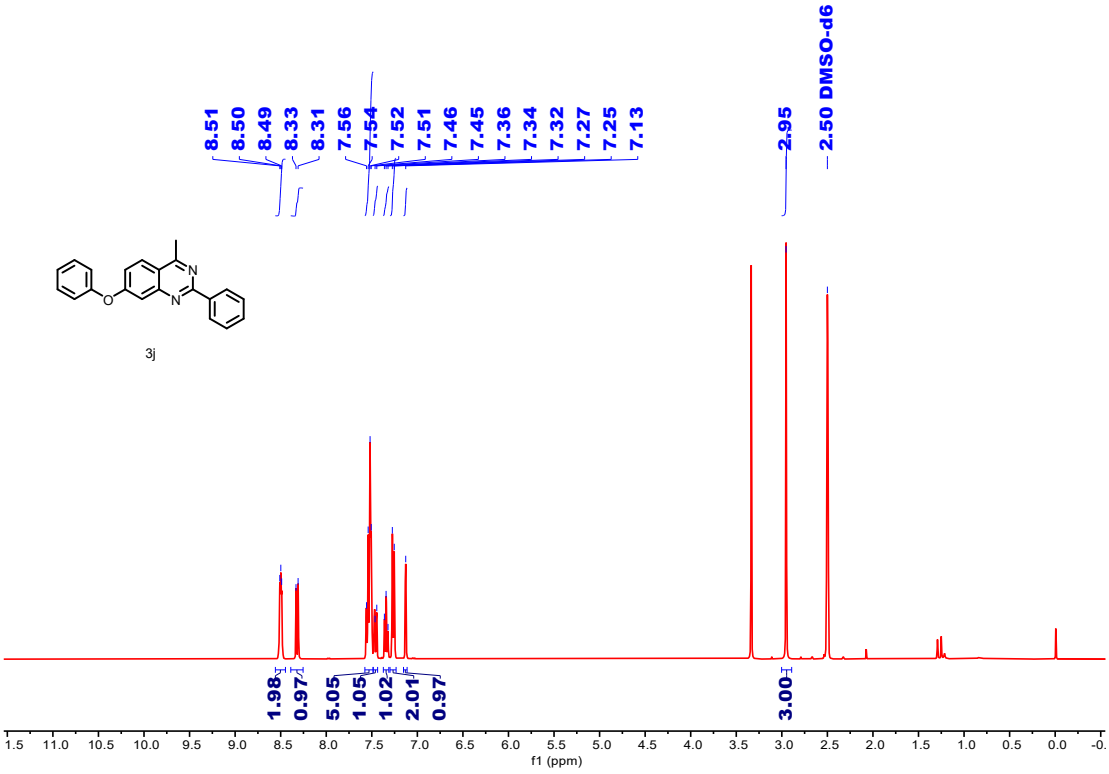
^{1}H NMR spectrum of 3i ($CDCl_3$,400 MHz)



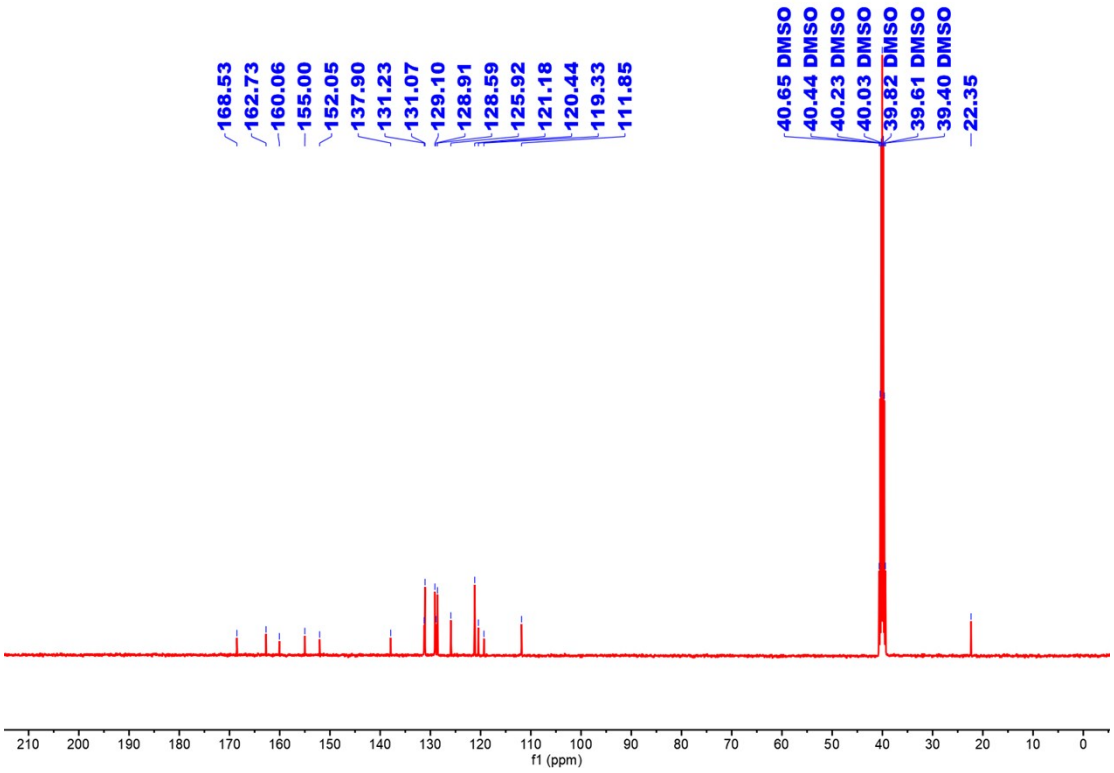
^{13}C NMR spectrum of 3i ($CDCl_3$,101MHz)



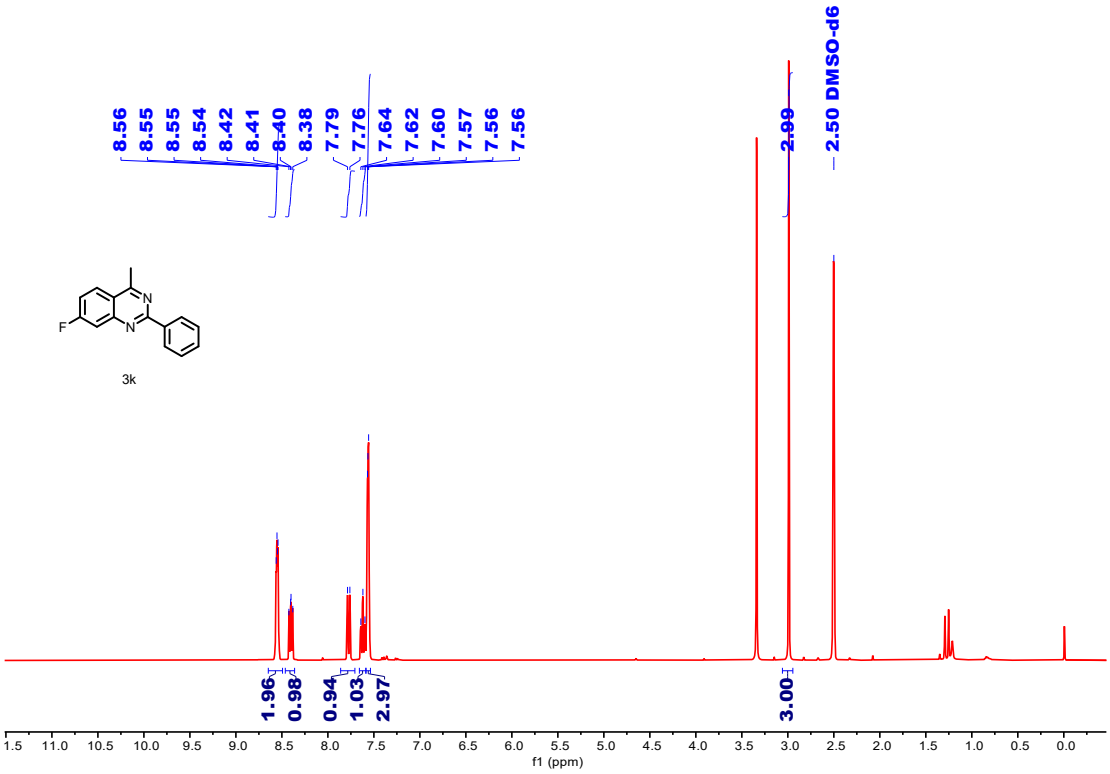
^{1}H NMR spectrum of 3j (DMSO-d6,400 MHz)



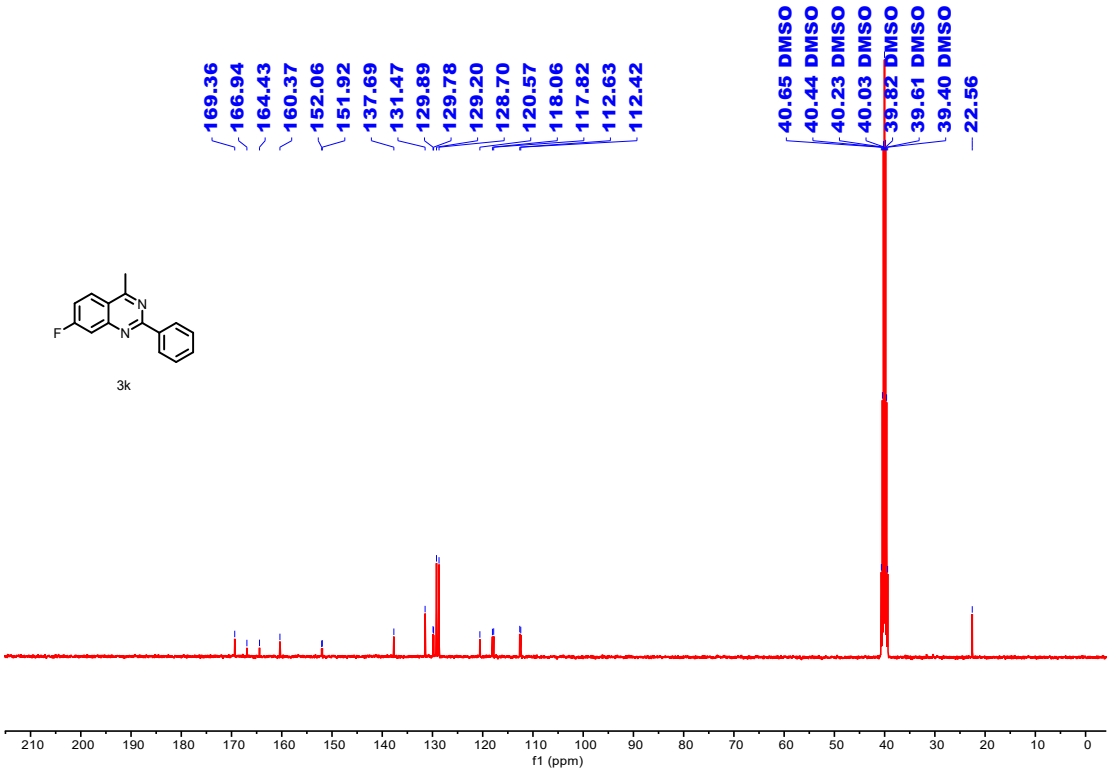
^{13}C NMR spectrum of 3j (DMSO-d6,101MHz)



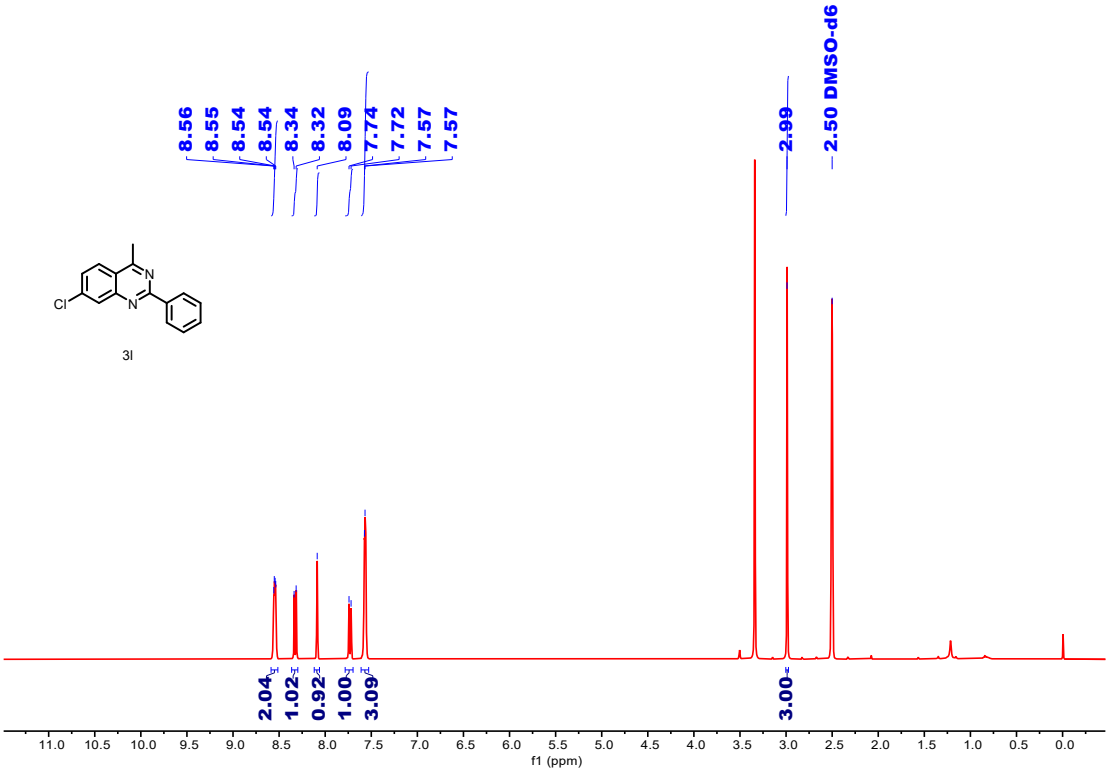
^{1}H NMR spectrum of 3k (DMSO-d6,400 MHz)



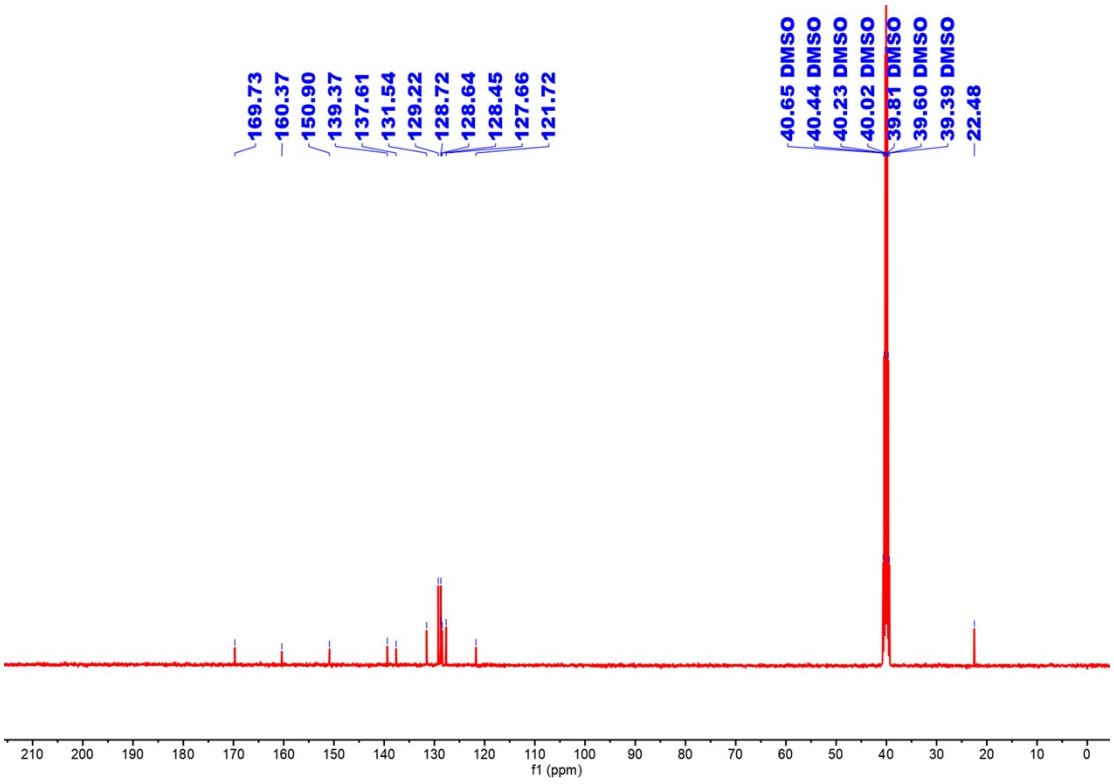
^{13}C NMR spectrum of 3k (DMSO-d6,101MHz)



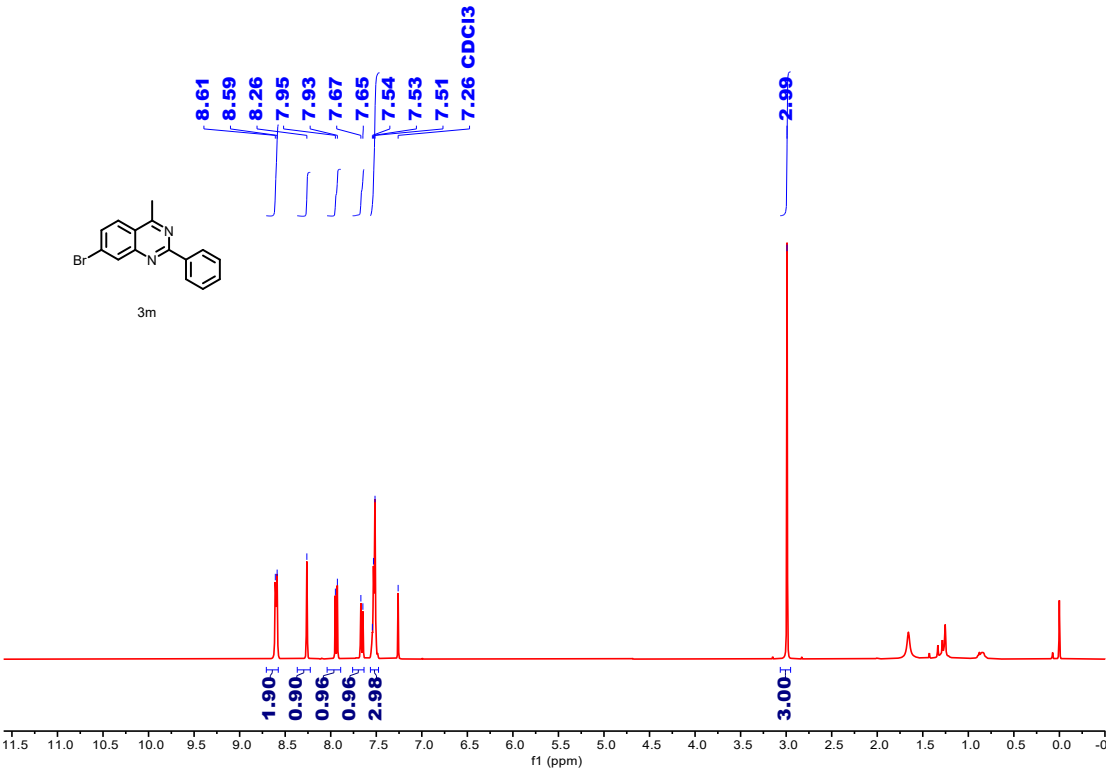
^{1}H NMR spectrum of 3l (DMSO-d6,400 MHz)



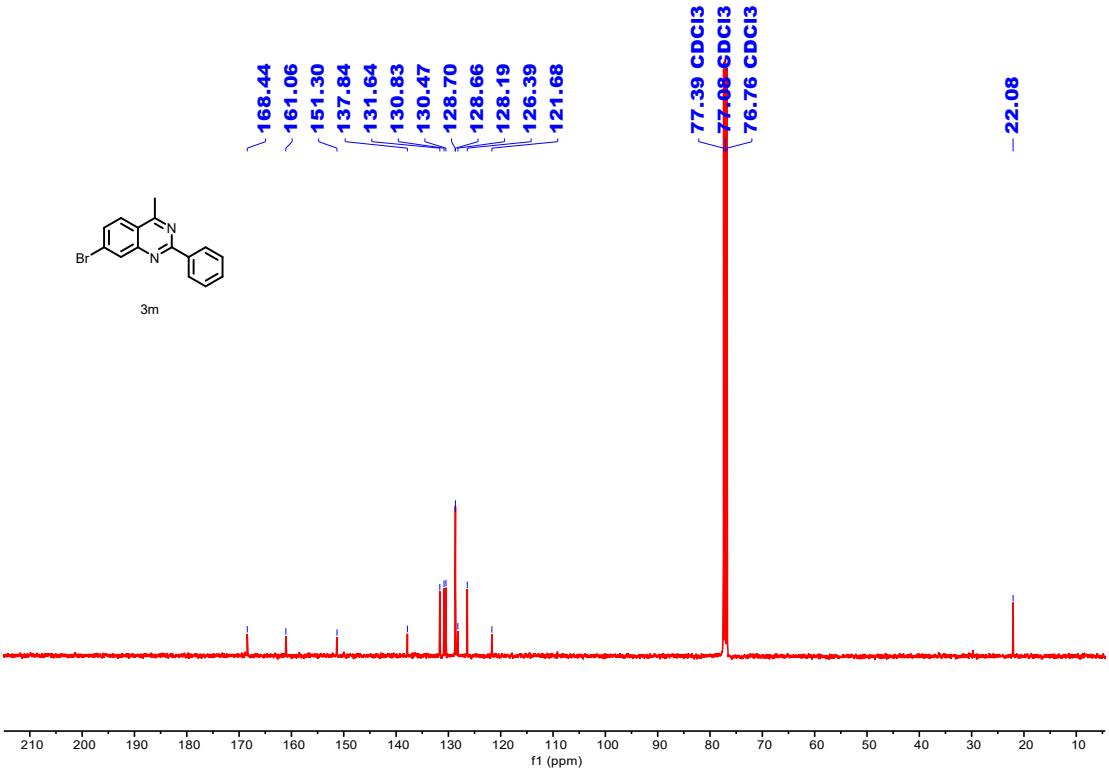
^{13}C NMR spectrum of 3l (DMSO-d6,101MHz)



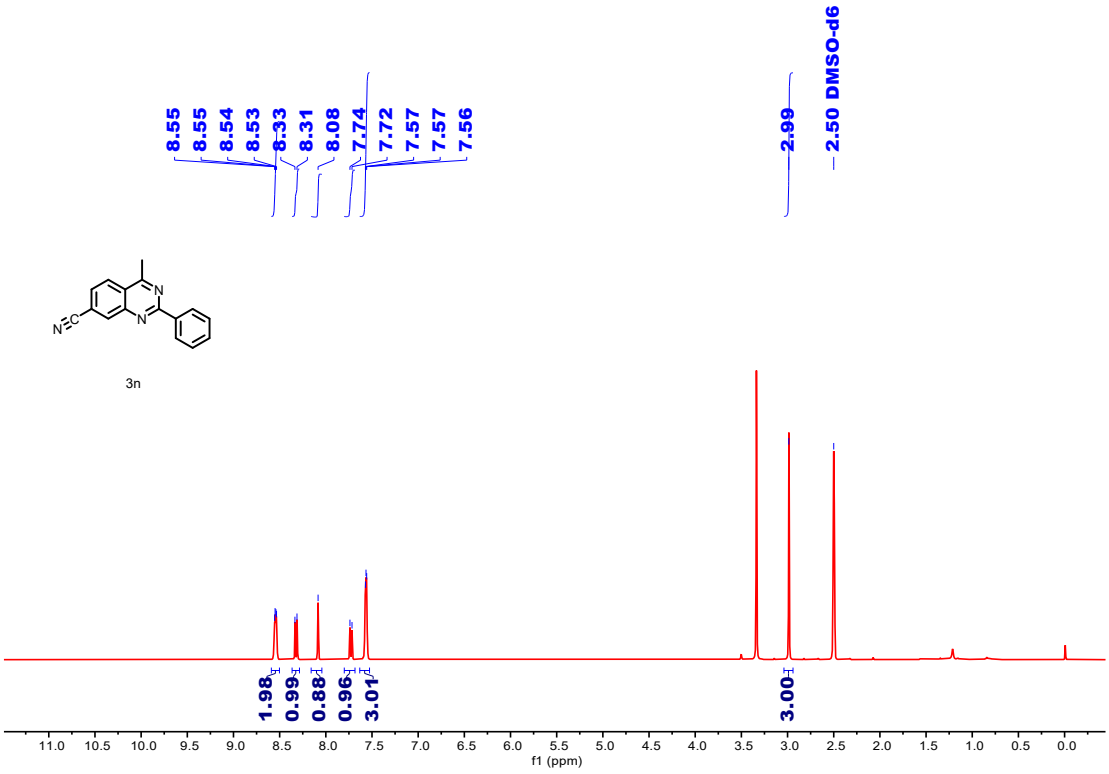
^{1}H NMR spectrum of 3m ($CDCl_3$,400 MHz)



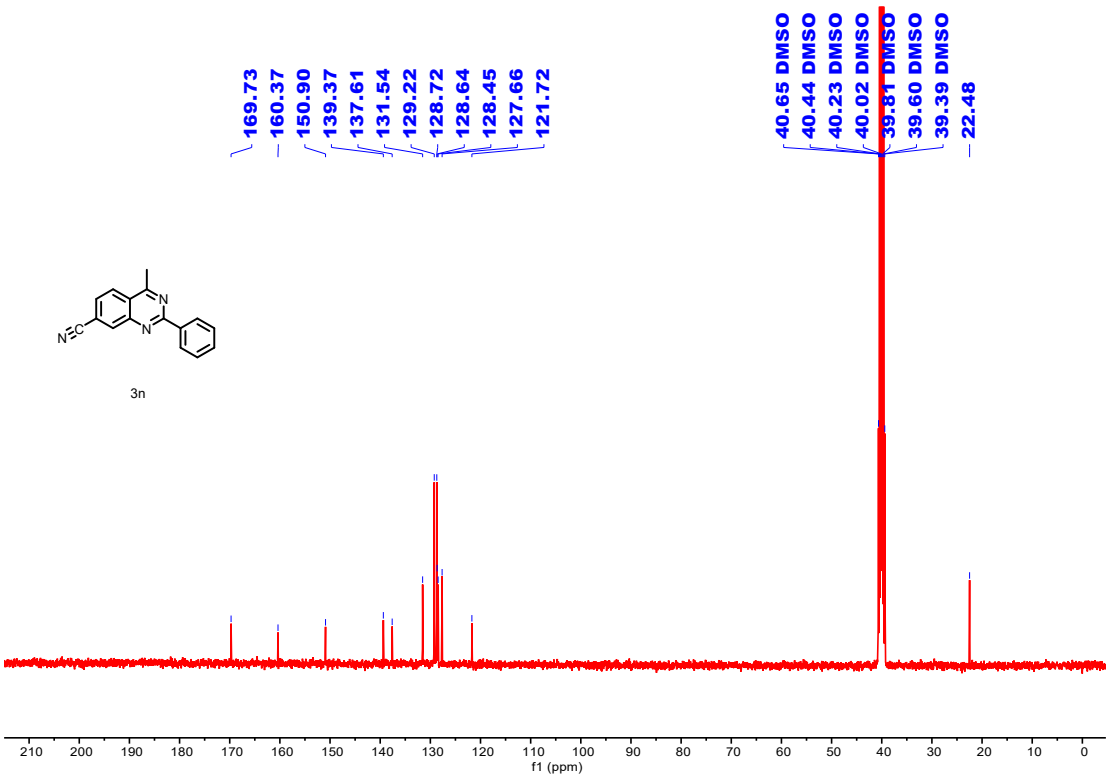
^{13}C NMR spectrum of 3m ($CDCl_3$,101MHz)



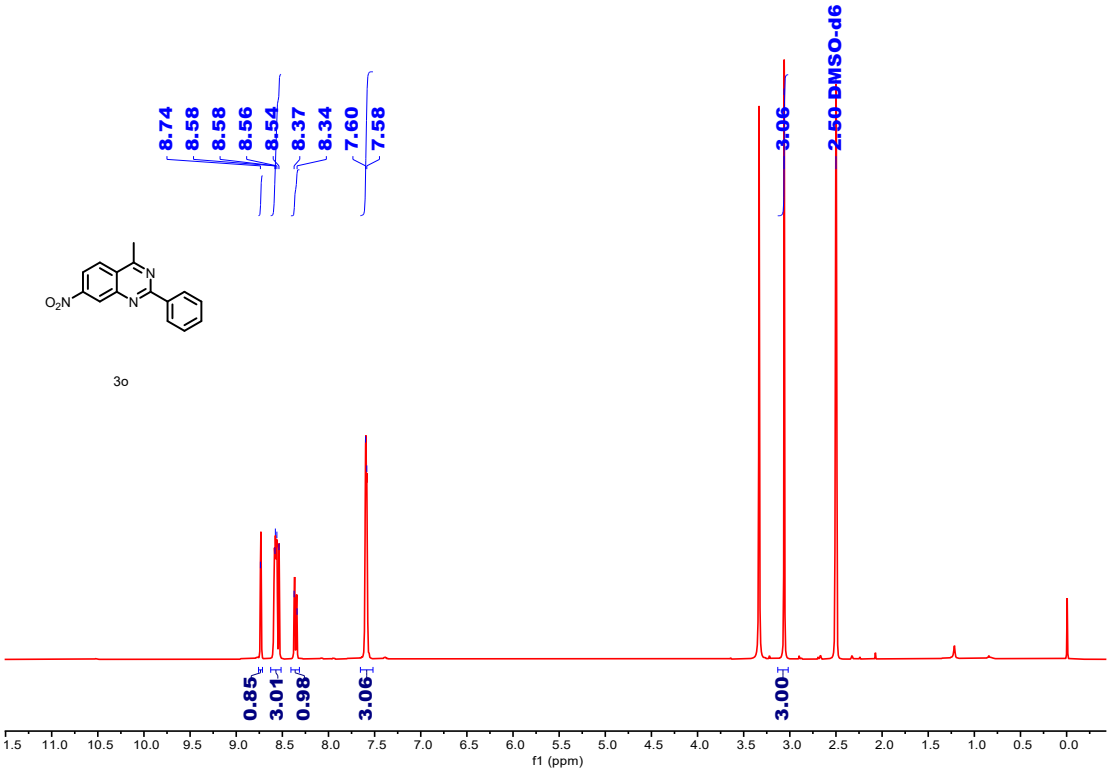
^{1}H NMR spectrum of 3n (DMSO-d6,400 MHz)



^{13}C NMR spectrum of 3n (DMSO-d6,101MHz)

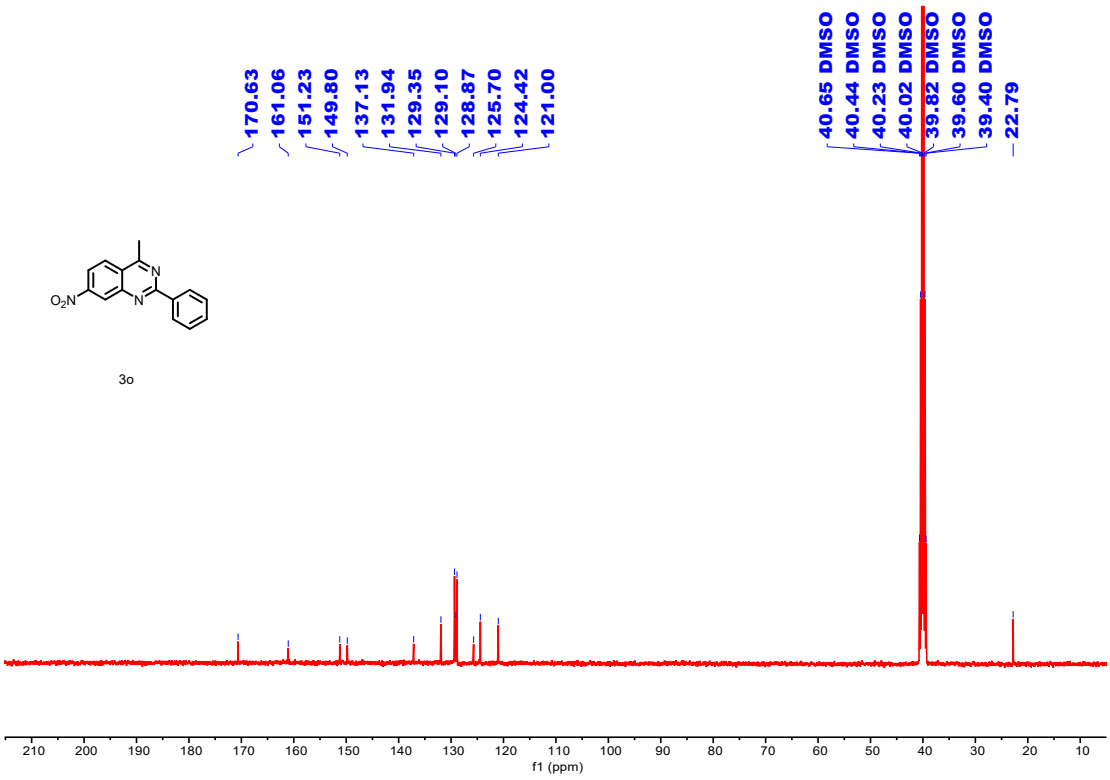


^{1}H NMR spectrum of 3o (DMSO-d6,400 MHz)



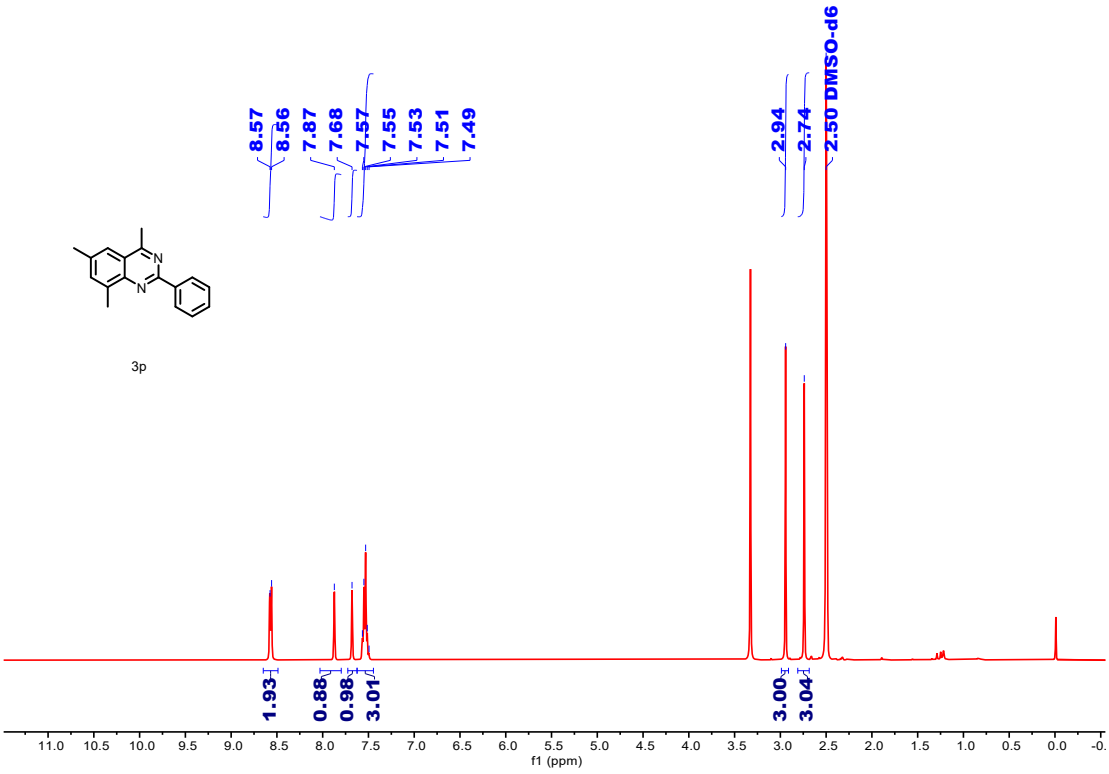
3o

^{13}C NMR spectrum of 3o (DMSO-d6,101MHz)

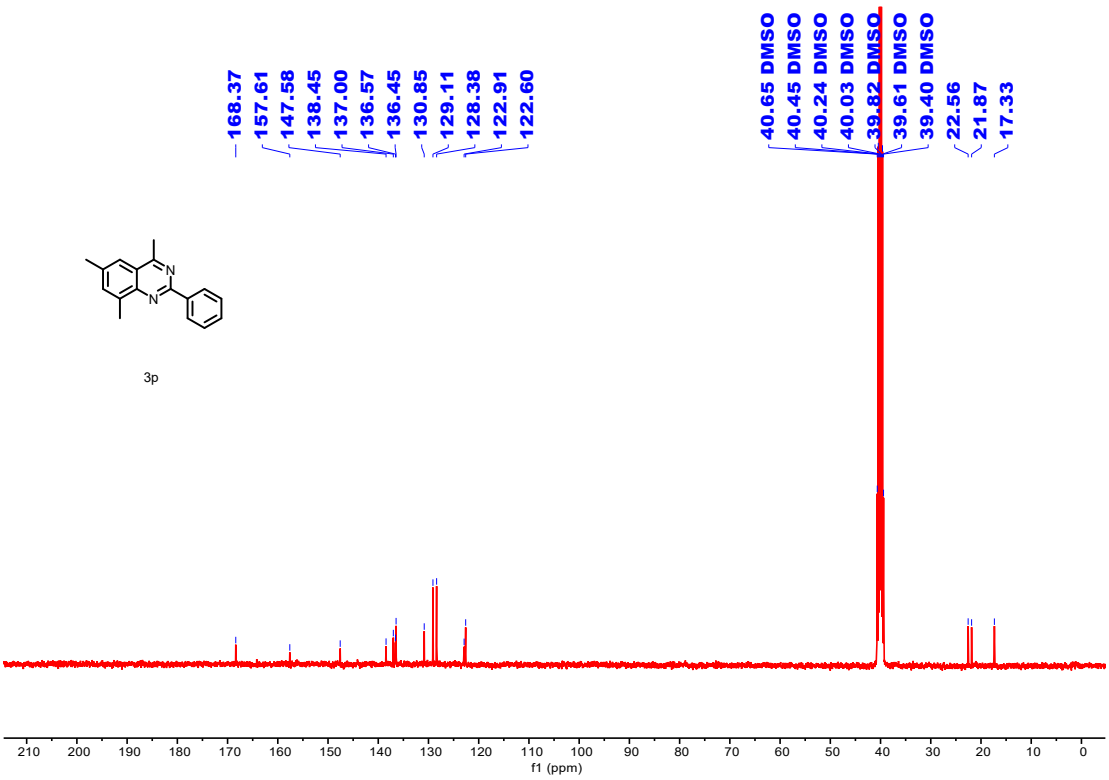


3o

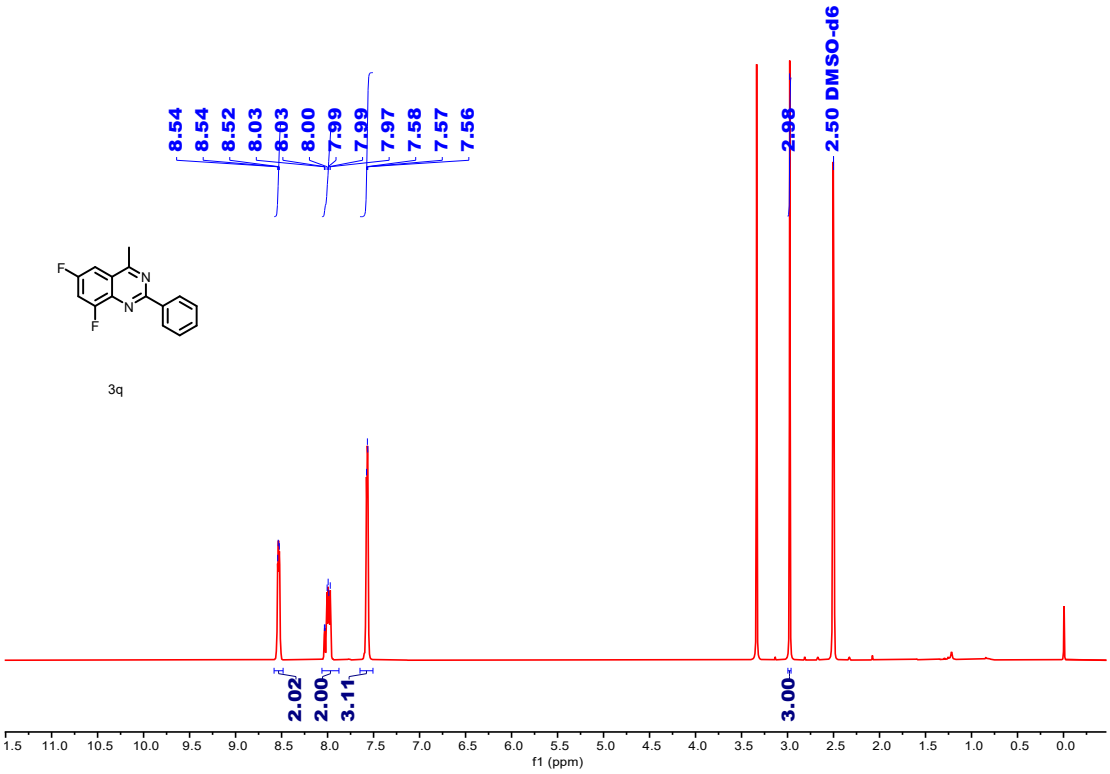
^{1}H NMR spectrum of 3p (DMSO-d6,400 MHz)



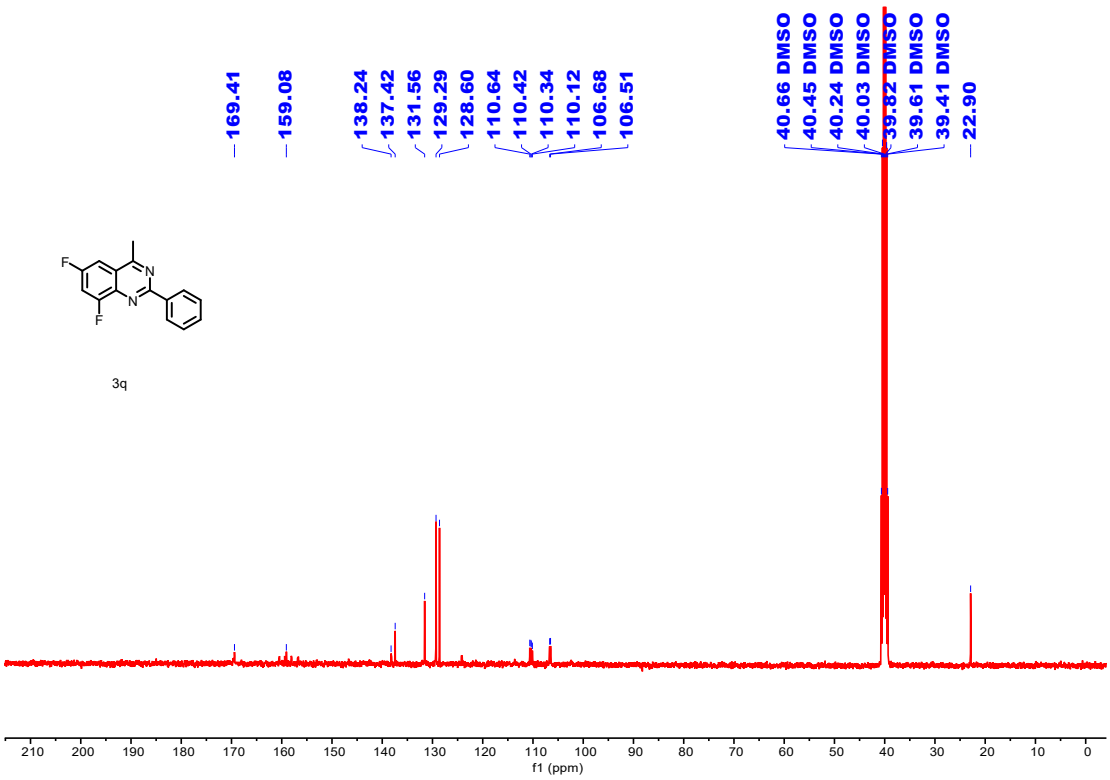
^{13}C NMR spectrum of 3p (DMSO-d6,101MHz)



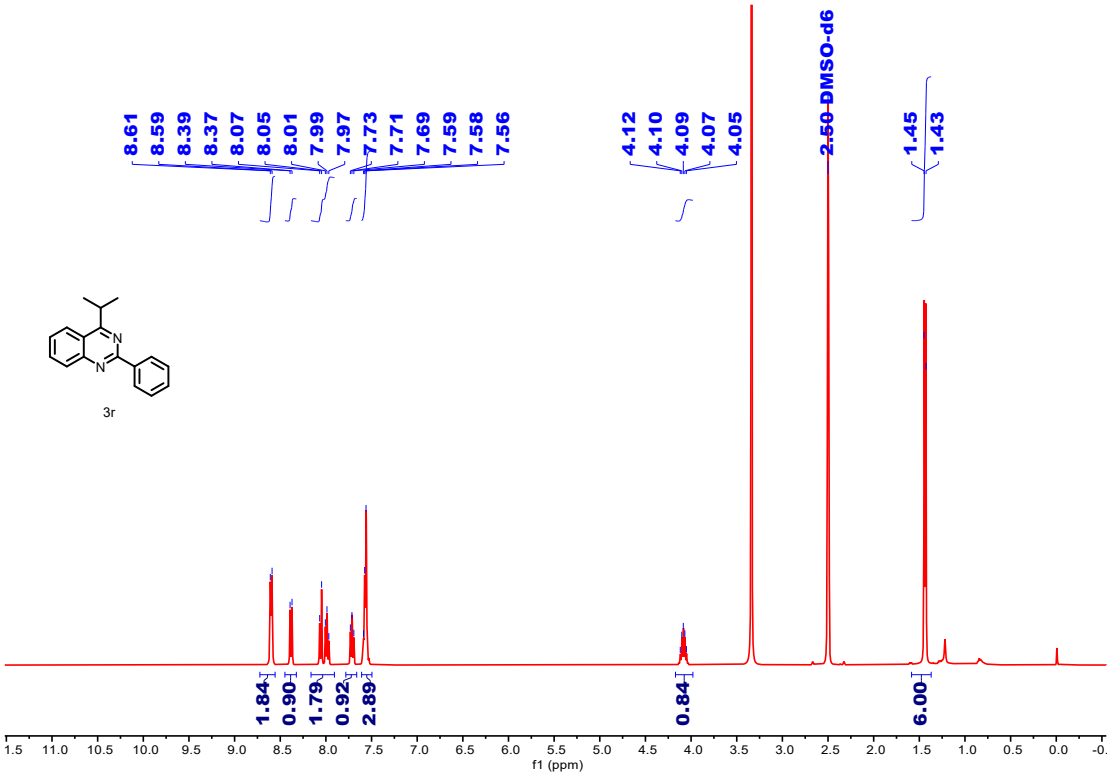
、**^{1}H NMR spectrum of 3q** (DMSO-d6,400 MHz)



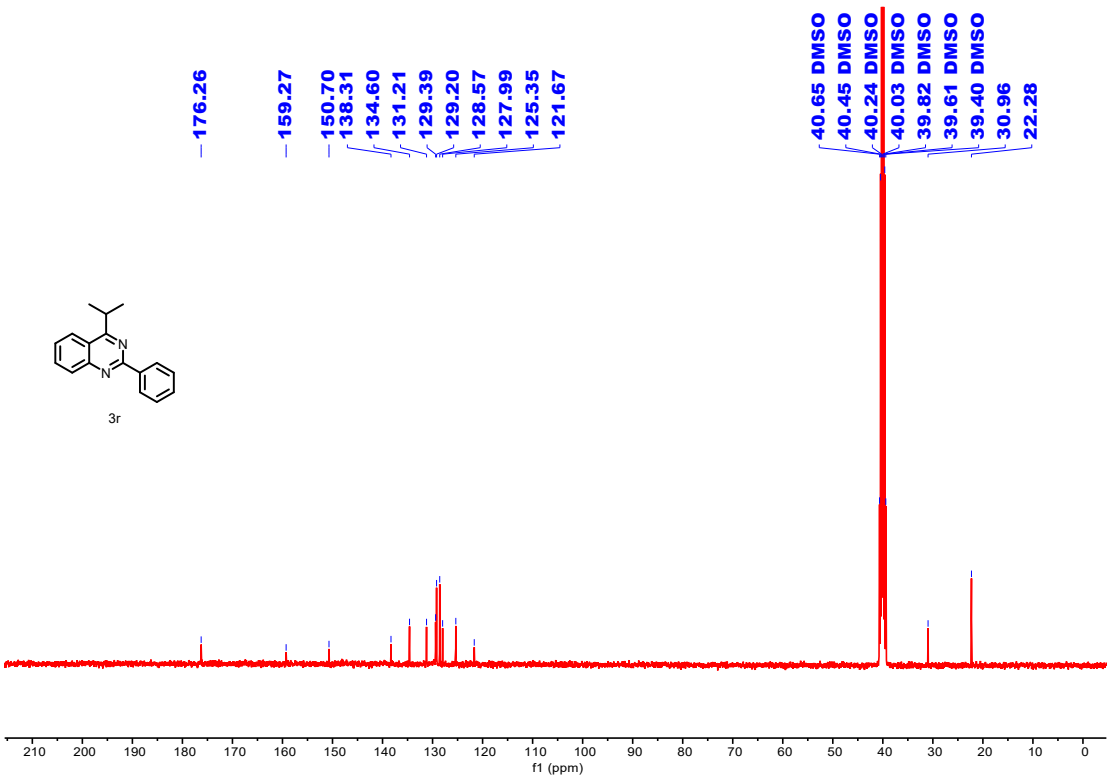
^{13}C NMR spectrum of 3q (DMSO-d6,101MHz)



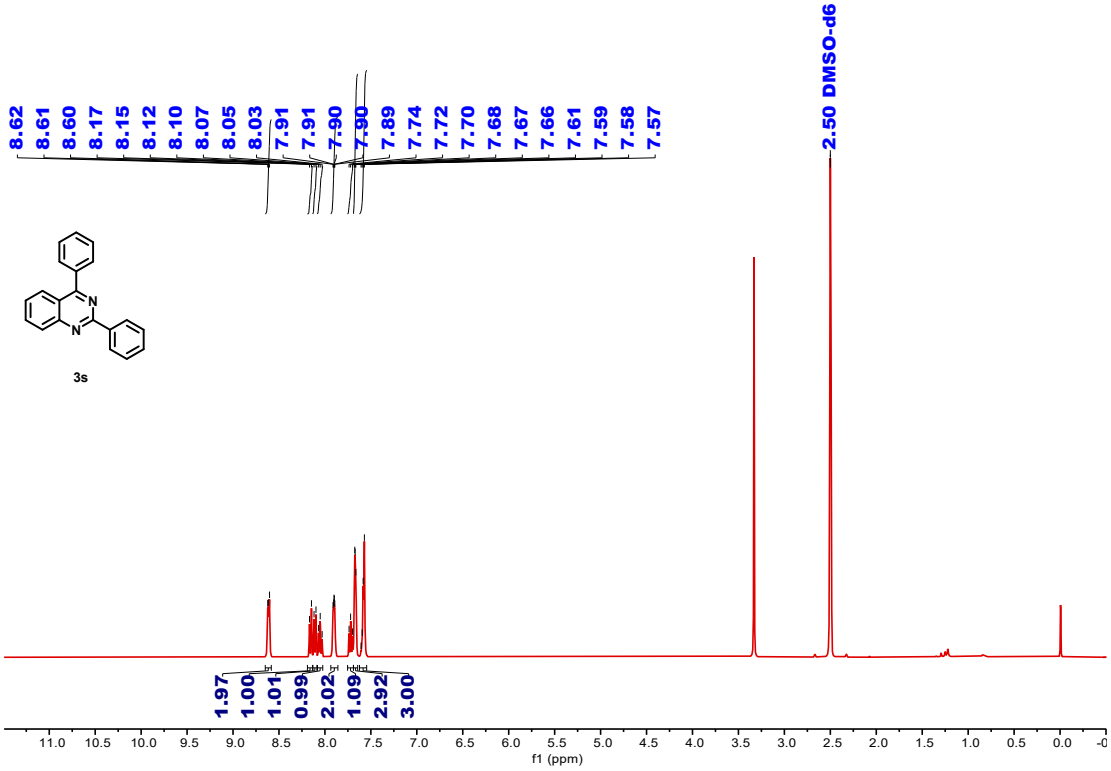
^{1}H NMR spectrum of 3r (DMSO-d6,400 MHz)



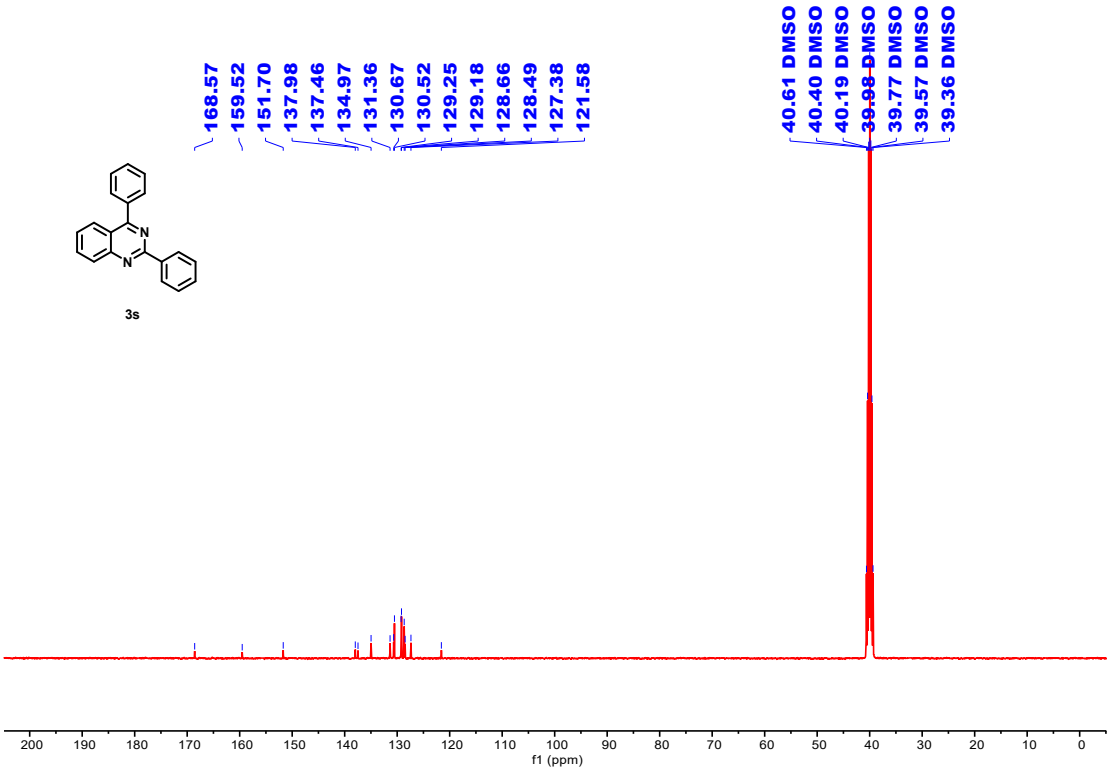
^{13}C NMR spectrum of 3r (DMSO-d6,101MHz)



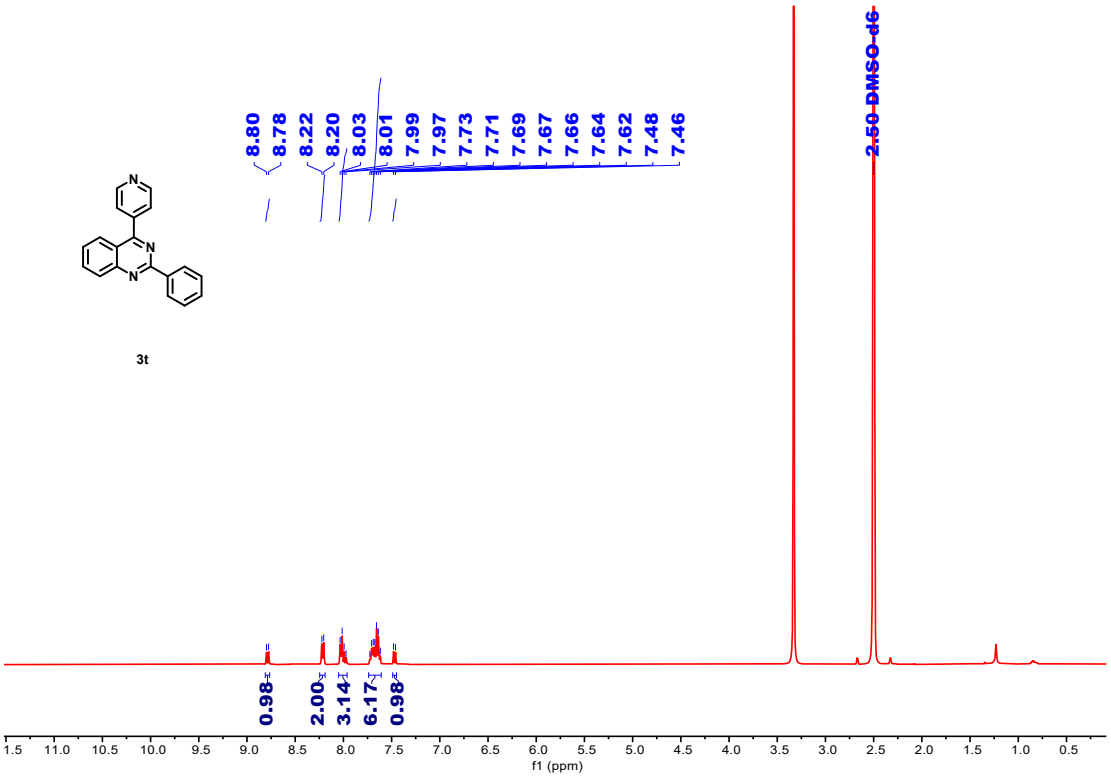
^{1}H NMR spectrum of 3s (DMSO-d6,400 MHz)



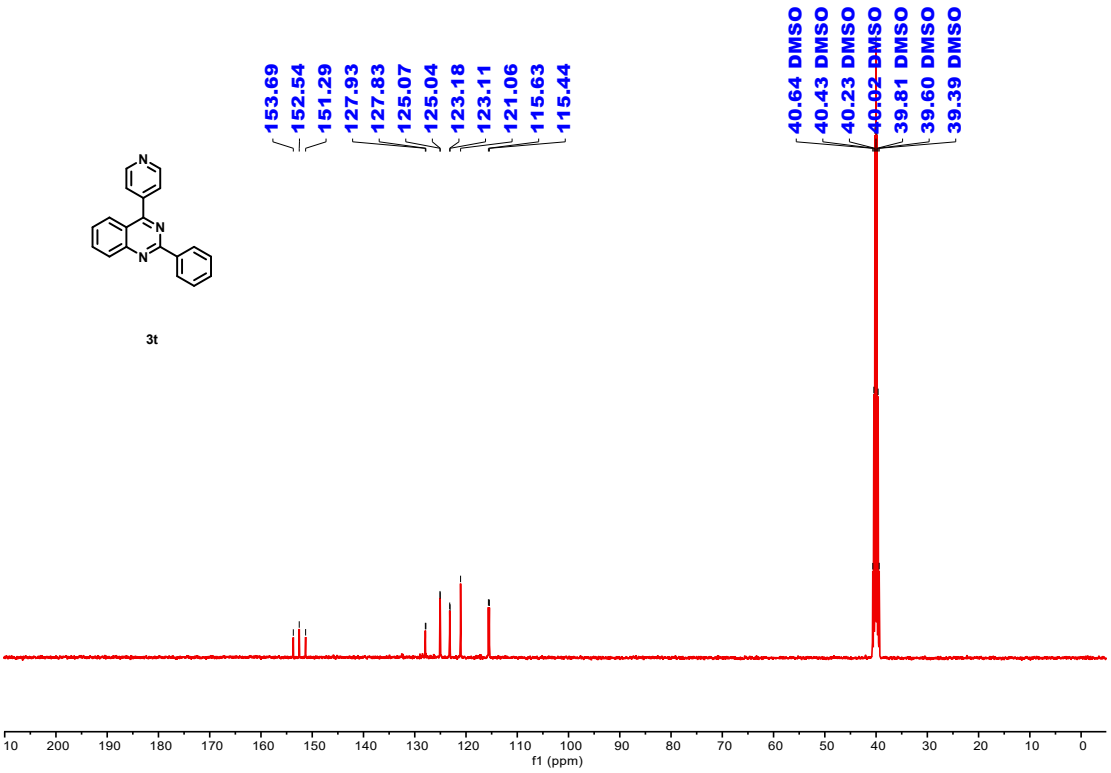
^{13}C NMR spectrum of 3s (DMSO-d6,101MHz)



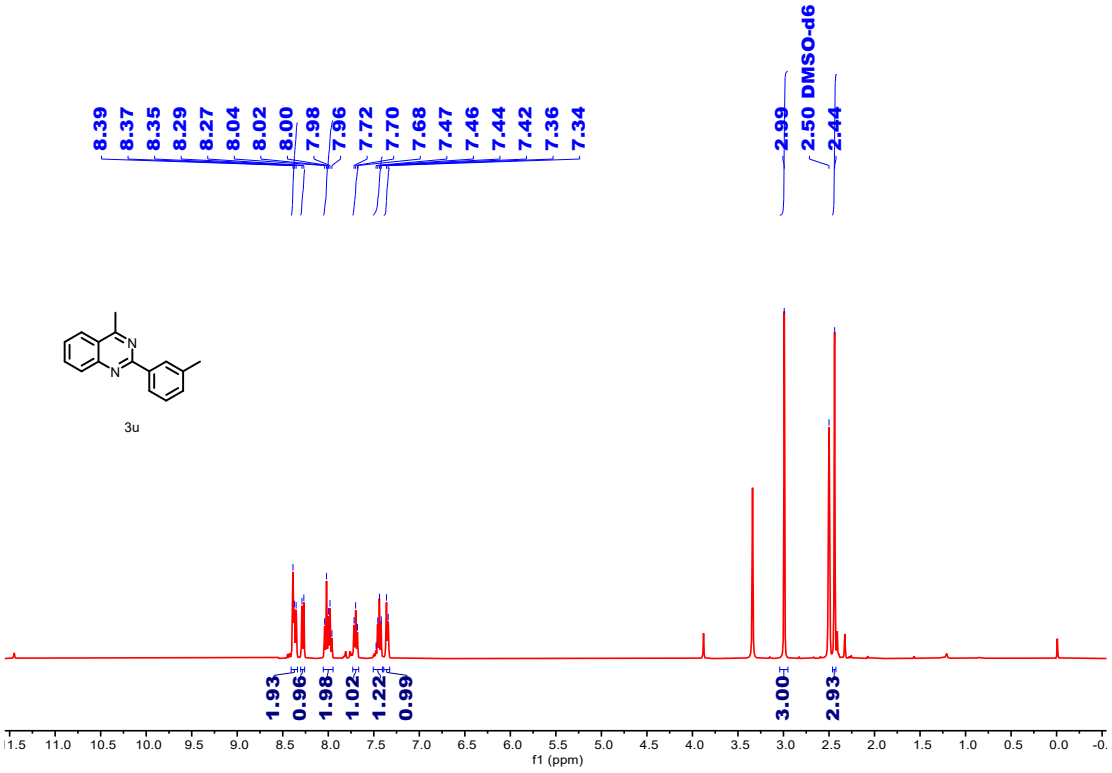
^{1}H NMR spectrum of 3t (DMSO-d6,400 MHz)



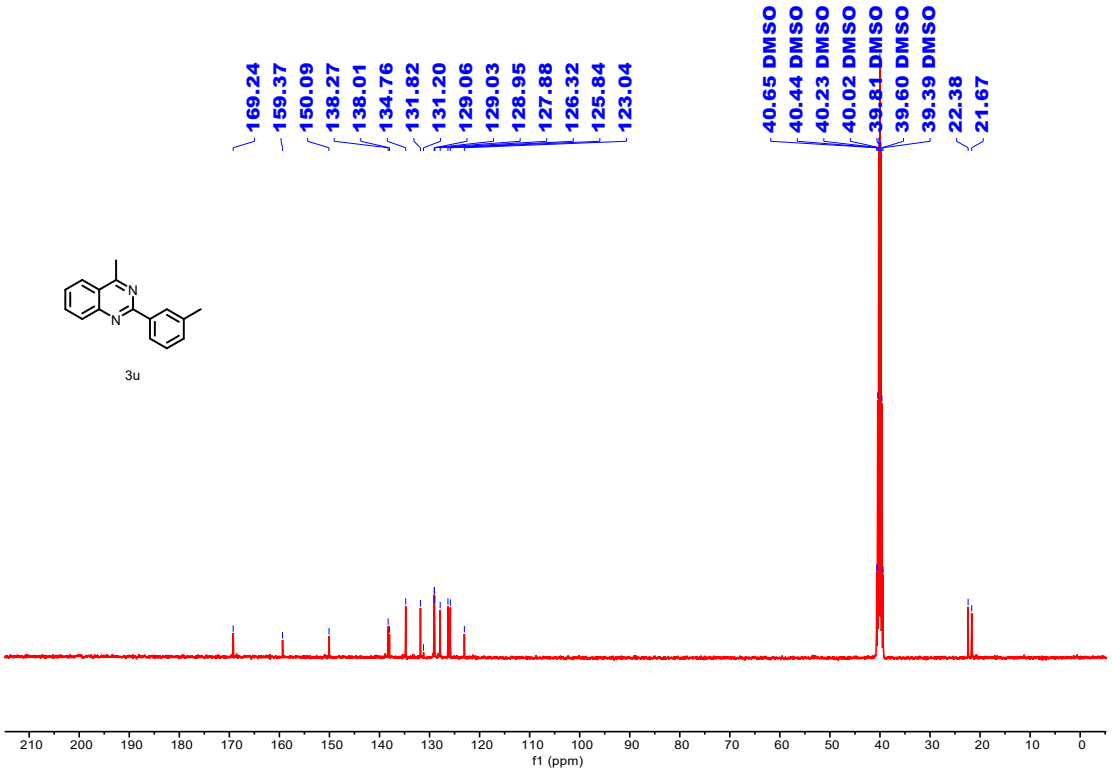
^{13}C NMR spectrum of 3t (DMSO-d6,101MHz)



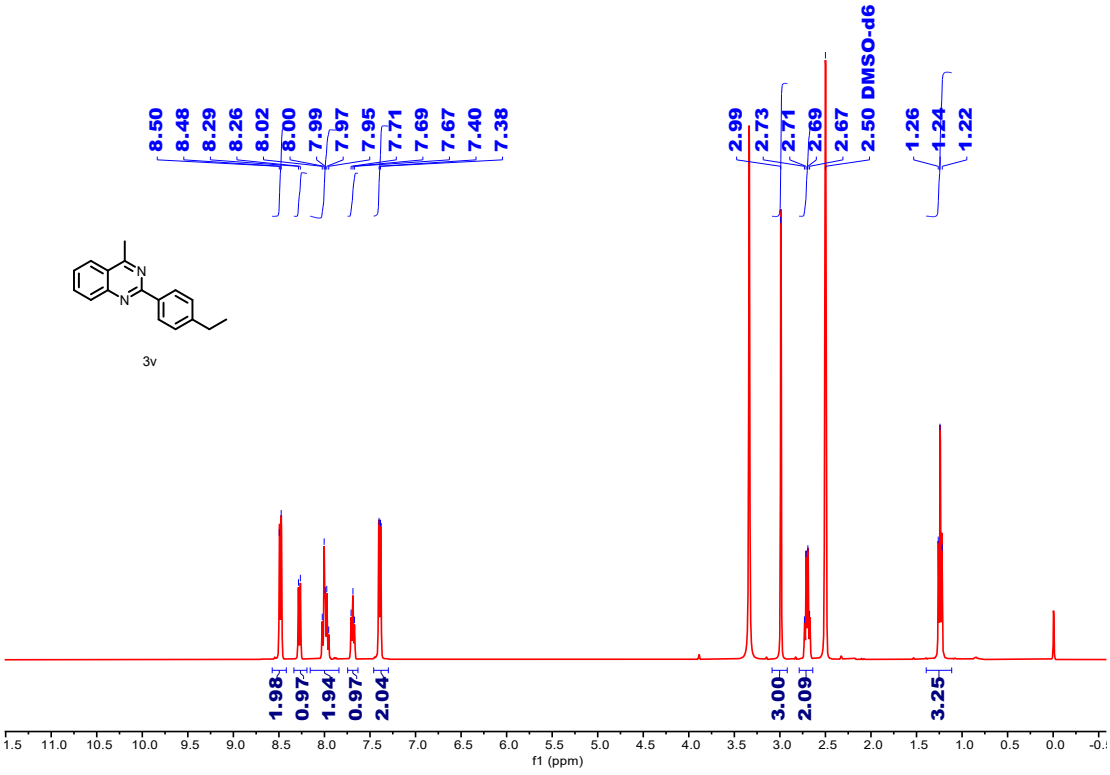
^{1}H NMR spectrum of 3u (DMSO-d6,400 MHz)



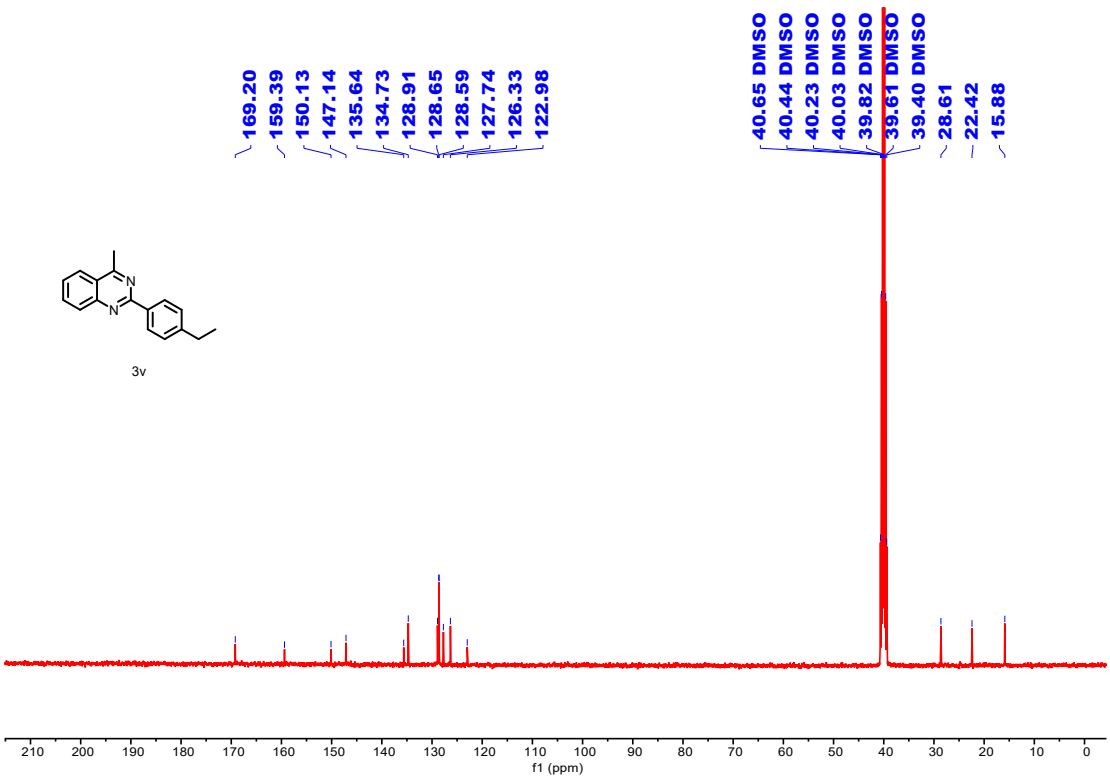
^{13}C NMR spectrum of 3u (DMSO-d6,101MHz)



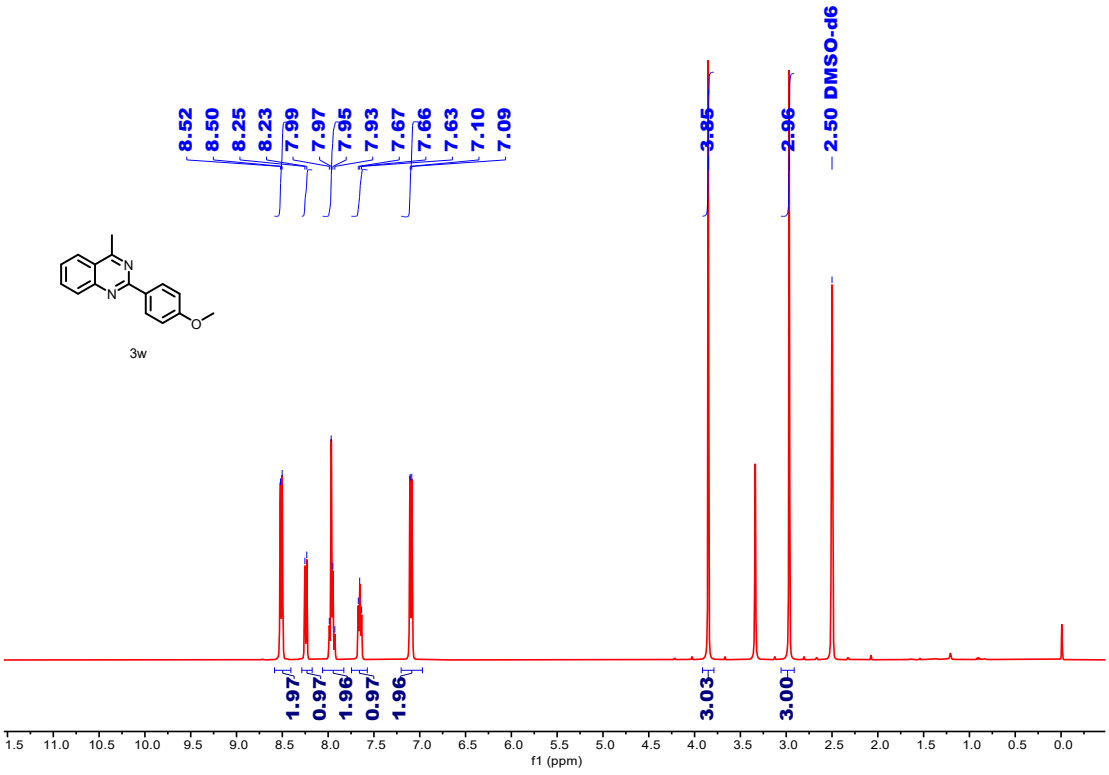
^{1}H NMR spectrum of 3v (DMSO-d6,400 MHz)



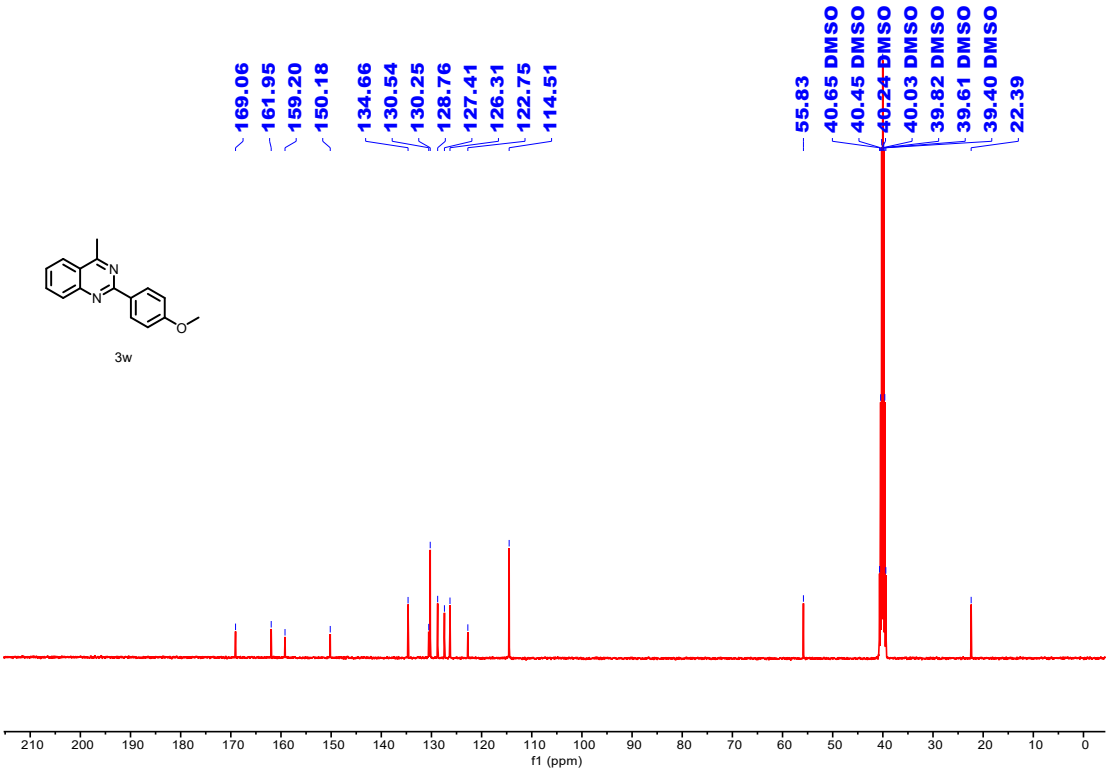
^{13}C NMR spectrum of 3v (DMSO-d6,101MHz)



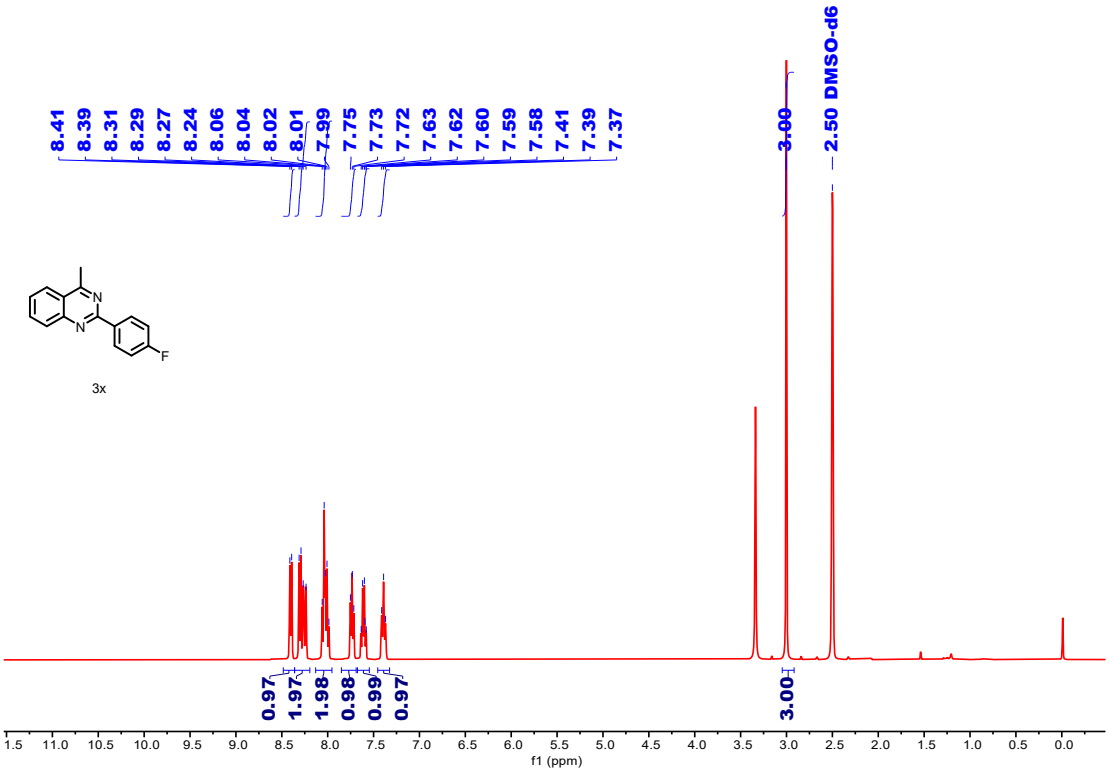
^{1}H NMR spectrum of 3w (DMSO-d6,400 MHz)



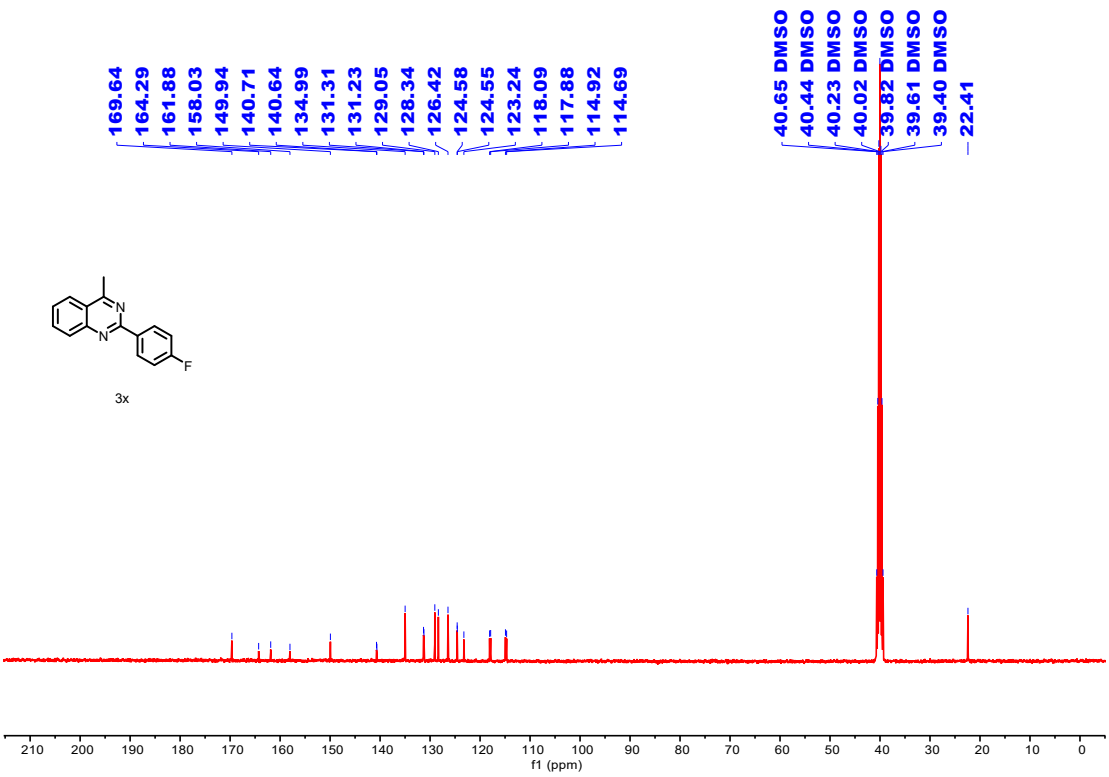
^{13}C NMR spectrum of 3w (DMSO-d6,101MHz)



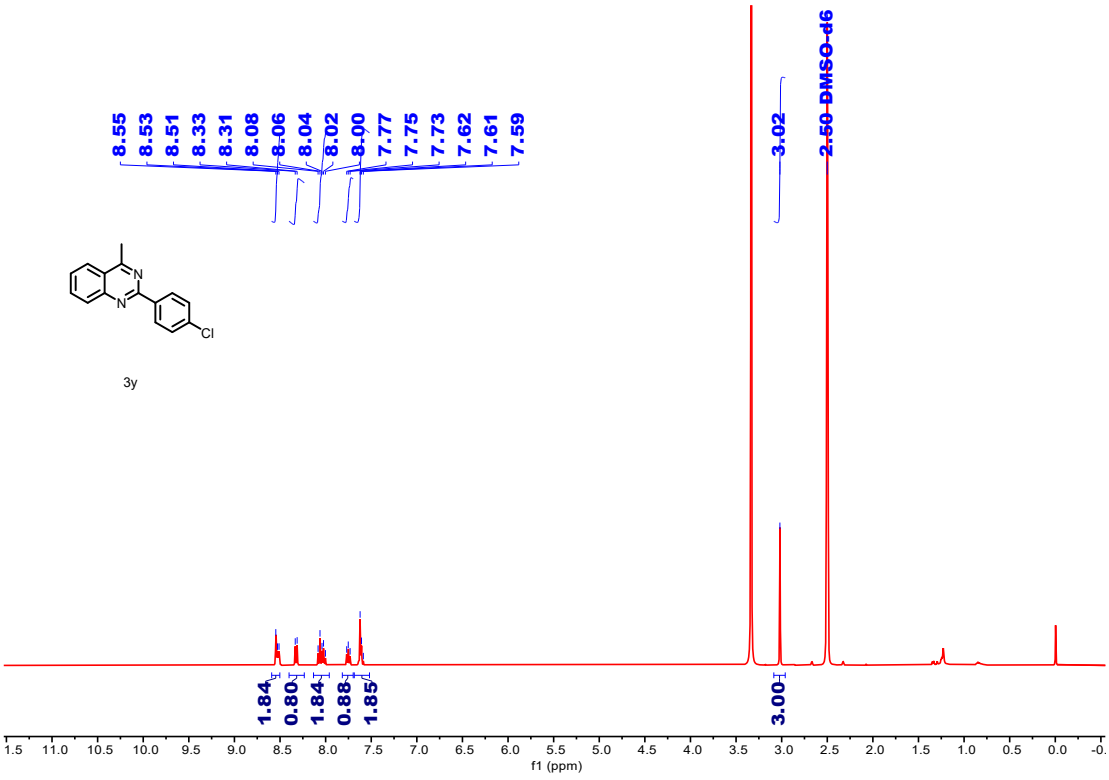
^{1}H NMR spectrum of 3x (DMSO-d6,400 MHz)



^{13}C NMR spectrum of 4g (DMSO-d6,101MHz)

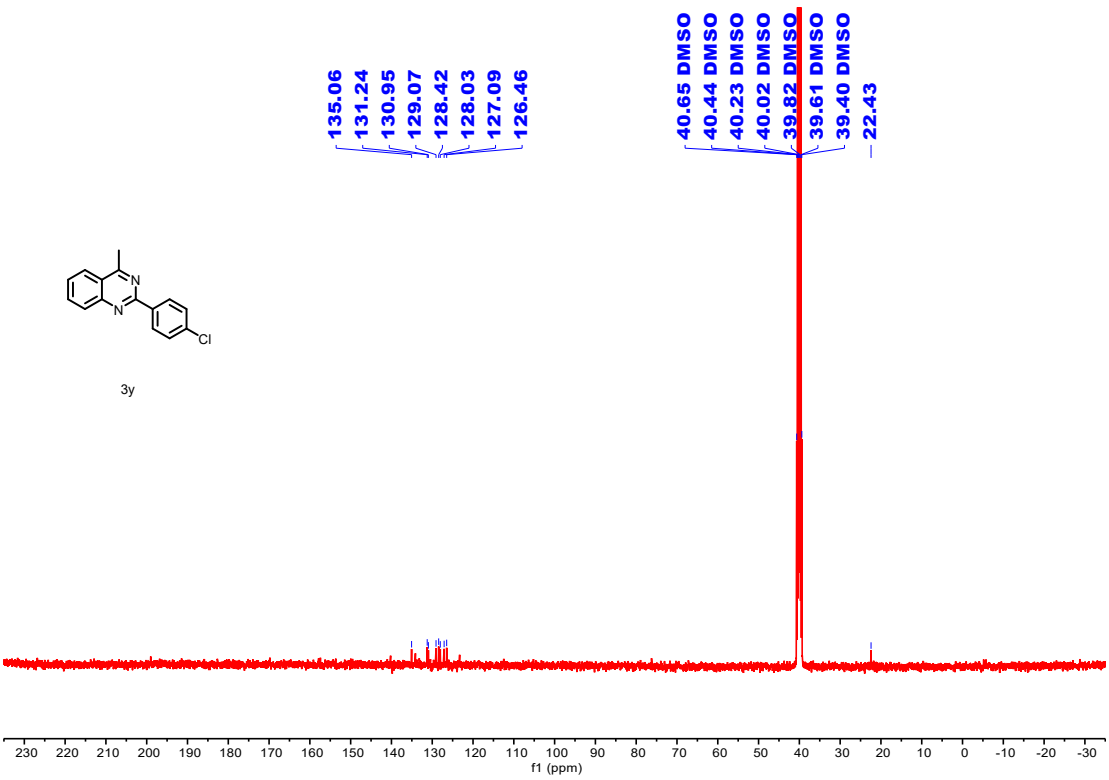


^{1}H NMR spectrum of 3y (DMSO-d6,400 MHz)



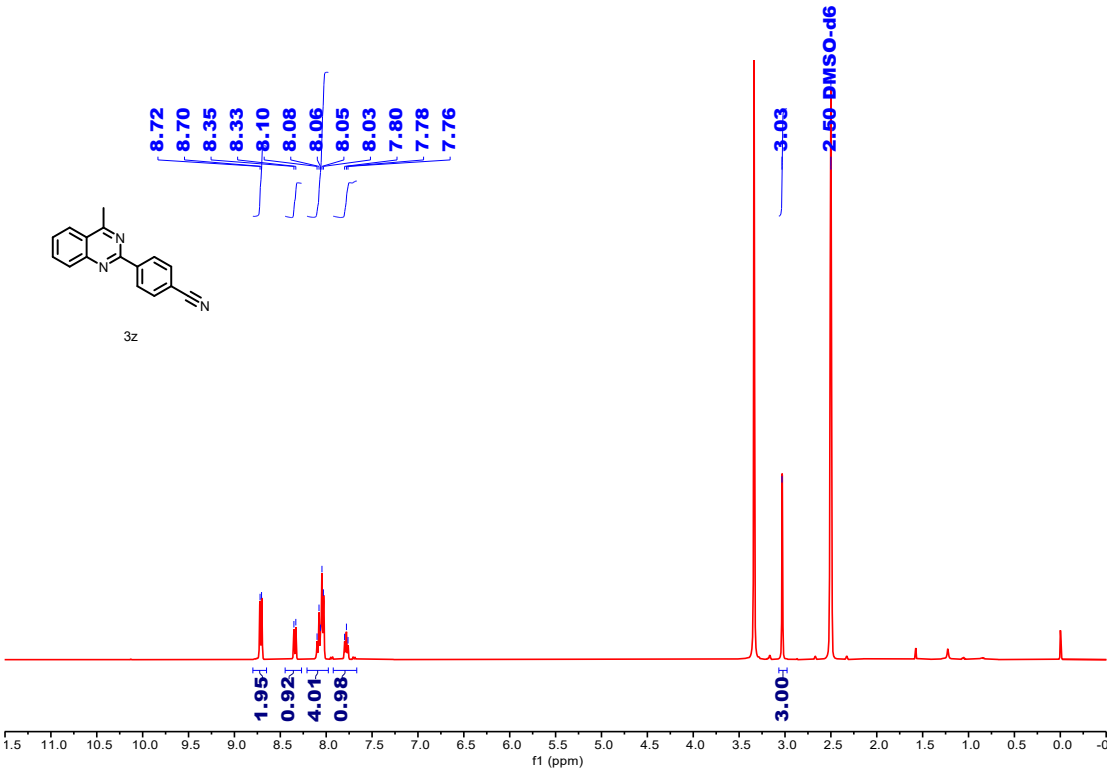
3y

^{13}C NMR spectrum of 4h (DMSO-d6,101MHz)

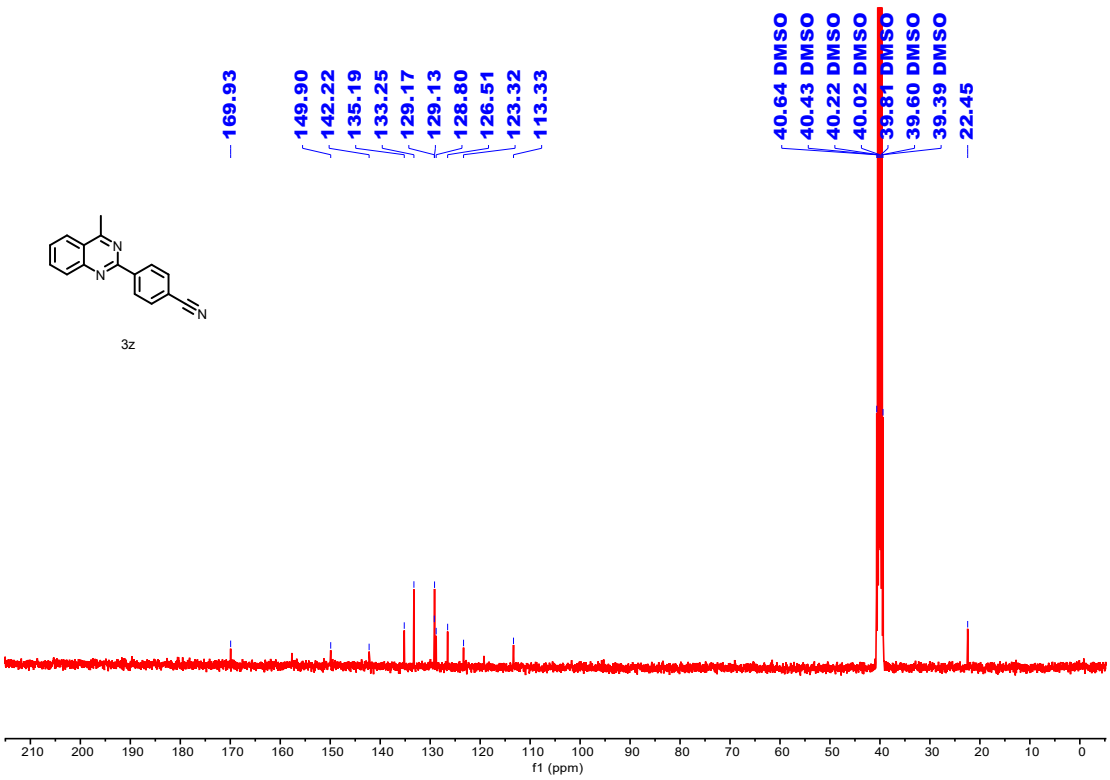


3y

^{1}H NMR spectrum of 3z (DMSO-d6,400 MHz)



^{13}C NMR spectrum of 3z (DMSO-d6,101MHz)



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