Supporting information

Visible-Light Photocatalyzed Reductions of N-heterocyclic Nitroaryls to anilines utilizing ascorbic acid reductant

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General information

The general experimental procedures, specific details for representative reactions and spectroscopic information for all new compounds are presented below. All commercial chemicals were used as received. Photocatalysts were purchased from TCI Europe ($Ru(bpy)_3Cl_2*6H_2O$) and $Ir(ppy)_3$ and Sigma-Aldrich $[Ru(bpz)_3][PF_6]_2$, $((Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ and $[Ir(dtbbpy)(ppy)_2]PF_6$. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 27 °C using Varian Mercury 300 [299.95 MHz] or at 25 °C using Bruker Avance Neo 500 [499.83 MHz] and Bruker Avance Neo 400 [400.15 MHz] spectrometers. ^1H and $^{13}C\{^1H\}$ spectra were referenced to the residual solvent signals (in $CDCl_3$ 7.26 and 77.2 ppm, respectively; in DMSO-d_6 2.50 and 39.5 ppm, respectively). No special notation was used for equivalent carbons. Fluorescence spectra were measured with Horiba Jobin Yvon Fluromax-4 spectrofluorometer using standard 10 mm fluorescence cuvettes. IR spectra were measured with FTIR Bruker Alpha spectrometer. GC measurements were done on Bruker Scion 436-GC with flame ionization detector with biphenyl as internal standard. High resolution mass spectra were obtained with Bruker ESI microTOF$_{LC}$ instrument in positive ionisation mode. Supelco silica gel TLC-cards with fluorescent indicator (254 nm) were used for TLC chromatography and R_f-value determinations. The melting points were determined in capillary tubes with Büchi 510 melting point apparatus and are reported uncorrected. All photoreductive nitro transformations were performed in 10 mL Schlenk-tubes (ca. 110 x 10 mm) under an argon atmosphere. The distance from the light source was 5 cm. The 5 x 3W blue (455 nm) LEDs were positioned in a vertical row along the Schlenk-tube.

Optimization studies

2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (varying equiv) and respective photocatalyst (varying equiv) were weighted in a Schlenk-tube equipped with stirrer bar. The tube was evacuated and back filled with Argon three times. Solvent (10 mL) degassed by bubbling with argon for 15 minutes was added and the tube was placed under a blue light irradiation (455 nm) on a magnetic stirrer plate for 1 hour at room temperature. Next, 1 mL aliquot of the reaction mixture was quenched by Et_3N (2 equiv) and the crude was filtrated trough plug of SiO_2 and was washed with DCM:EtOAc (1:1). The filtrate was concentrated and 0.5 mL of biphenyl (0.02 M in EtOAc) was added as internal standart. The sample was diluted to 5 mL with EtOAc and 1 mL of it was filtrated trough 0.2 µm Phenex™ PVDF syringe filter and transfered to GC vial. The yields and convertions were determined as average of two runs by calibrated GC-FID analisys with biphenyl as internal standart.

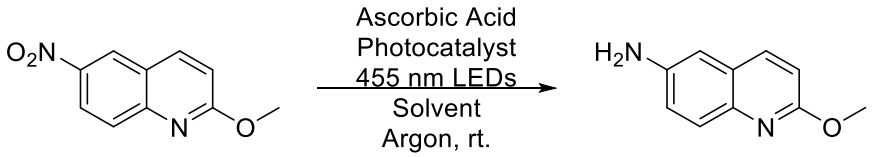


Table S1. Optimization of Photocatalyst. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and respective photocatalyst, concentration 0.02M, 10 mL MeOH/H_2O (4:1). nd – not detected

Entry	Variation: Photocatalyst	GC left SM %	GC conversion %	GC yield %
S1	**$Ru(bpy)_3Cl_2*6H_2O$ 1 mol %**	**nd**	**100**	**82.9**
S2	$[Ru(bpz)_3][PF_6]_2$ 1 mol %	94.2	5.8	3.5
S3	$(Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ 1 mol %	43	57	27.7
S4	$[Ir(dtbbpy)(ppy)_2]PF_6$ 1 mol %	83.6	16.4	16.3
S5	$Ir(ppy)_3$ 1 mol %	88.7	11.3	3.9

Table S2. Optimization of Photocatalyst loading. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (varying equiv), concentration 0.02M, 10 mL MeOH/H_2O (4:1). nd – not detected

Entry	Variation: Photocatalyst loading	GC left SM %	GC conversion %	GC yield %
S1	cat. 0.5 mol %	nd	100	51.5
S2	**cat. 1 mol %**	**nd**	**100**	**82.9**
S3	cat. 2 mol %	nd	100	82.9
S4	cat. 5 mol %	nd	100	80.9

Table S3. Optimization of reaction concentration. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol), concentration varying, needed amount MeOH/H_2O (4:1). nd – not detected

Entry	Variation: Concentration	GC left SM %	GC conversion %	GC yield %
S1	0.01 M (20 mL)	nd	100	60.6
S2	0.013 M (15 mL)	nd	100	74.2
S3	**0.02 M (10 mL)**	**nd**	**100**	**82.9**
S4	0.027 M (7.5 mL)	nd	100	50
S5	0.04 M (5 mL)	nd	100	33.3
S6	0.2 M (1 mL)	57.5	42.5	25.1

Table S4. Optimization of Ascorbic acid loading. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (varying equiv) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol), concentration 0.02M, 10 mL MeOH/H_2O (4:1). nd – not detected

Entry	Variation: Ascorbic acid loading	GC left SM %	GC conversion %	GC yield %
S1	2 equiv Ascorbic acid	9.4	90.6	18.1
S2	3 equiv Ascorbic acid	nd	100	79.2
S3	**4 equiv Ascorbic acid**	**nd**	**100**	**82.9**
S4	5 equiv Ascorbic acid	nd	100	80.8
S5	6 equiv Ascorbic acid	nd	100	80.7

Table S5. Optimization of solvent. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol), concentration 0.02 M, 10 mL varying solvent. nd – not detected

Entry	Variation: Solvent	GC left SM %	GC conversion %	GC yield %
S1	MeOH:H_2O (10:1)	nd	100	41.4
S2	MeOH:H_2O (8:1)	nd	100	53.2
S3	MeOH:H_2O (6:1)	nd	100	61.8
S4	**MeOH:H_2O (4:1)**	**nd**	**100**	**82.9**
S5	MeOH:H_2O (2:1)	nd	100	70.6
S6	MeOH:H_2O (1:1)	nd	100	68.7
S7	EtOH:H_2O (10:1)	12.3	87.7	10.8
S8	EtOH:H_2O (8:1)	nd	100	13.7
S9	EtOH:H_2O (6:1)	nd	100	16.6
S10	EtOH:H_2O (4:1)	nd	100	42.2
S11	EtOH:H_2O (2:1)	nd	100	55.9
S12	EtOH:H_2O (1:1)	nd	100	80.9
S13	EtOH:H_2O (1:2)	6.2	93.8	68.5

S14	EtOH:H_2O (1:3)	6.3	93.7	78.3
S15	MeCN:H_2O (1:1)	39.5	60.5	23.5
S16	THF:H_2O (1:1)	11.4	88.6	14.3
S17	EtOH	79.6	20.4	9
S18	MeOH	nd	100	28.5
S19	MeCN	93.3	6.7	nd
S20	THF	95.1	4.9	nd
S21	*i*-PrOH	94.5	5.5	nd
S22	DMSO	90	10	5.9
S23	DMF	10	90	11.2
S24	H_2O (due to unsolubility of the SM there is error in the sample preparation.)	83	17	nd

Table S6. Optimization of time. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol), concentration 0.02 M, 10 mL MeOH/H_2O (4:1). nd – not detected

Entry	Variation: time	GC left SM %	GC conversion %	GC yield %
S1	10 min	56.4	43.6	18.6
S2	20 min	22.7	77.3	33.5
S3	30 min	nd	100	35.7
S4	**60 min**	**nd**	**100**	**82.9**
S5	90 min	nd	100	73
S6	120 min	nd	100	72.6

Table S7. Optimization of others. Conditions: 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol), concentration 0.02 M, 10 mL MeOH/H_2O (4:1). nd – not detected

Entry	Variation: Miscellaneous	GC left SM %	GC conversion %	GC yield %
S1	not degassed (Air)	27.1	72.9	27.8
S2	aditive of 10% (volume) AcOH	15.9	84.1	66
S3	aditive of 10% (volume) HFIP	nd	100	57.9
S4	same as *Green Chem.*, **2014**, *16*, 1082-1086, 24 hours	89.7	11.3	nd
S5	3 equiv Ascorbic acid + 2 equiv Methansulfonic acid	71.1	28.9	nd
S6	Quercetine instead of Asc. Acid	95.9	4.1	nd
S7	Na-ascorbate instead of Asc. Acid	61.3	38.7	nd
S8	only Ascorbic acid	95.8	4.2	nd
S9	only catalyst	96.1	3.9	nd
S10	only light	95.8	4.2	nd
S11	catalyst and light	96.8	3.2	nd
S12	Ascorbic acid and light	82.4	17.6	nd
S13	Ascorbic acid and catalyst	97.2	2.8	nd

Fluorescence quenching studies

The fluorescence quenching studies were performed in degassed MeOH/H_2O (4:1) solvent mixture under Argon. The concentration of the photocatalyst ($Ru(bpy)_3Cl_2*6H_2O$) was set to 10 μM, the excitation wavelength was set at 455 nm and the emission range was set between 500 – 800 nm. The quenchers (ascorbic acid, sodium ascorbate, nitrobenzene – **4**, 2-methyl-8-nitroquinoline – **1k** and the complexes of 2-methyl-8-nitroquinoline – **1k** and lactic acid and ascorbic acid) with concentration of 0.2 M (1 μl = 10 equiv) were added to the photocatalyst solution in steps of 10, 100, 500, 1000 and 2500 equiv. The quenching was monitored in the range from 10 equiv ($2*10^{-7}$ M) to 10000 equiv ($2.8*10^{-4}$ M) of the corresponding quencher. The Stern-Volmer plots were prepared by analyzing emission intensity at 602 nm of the titration curve (Figure S1-S6).

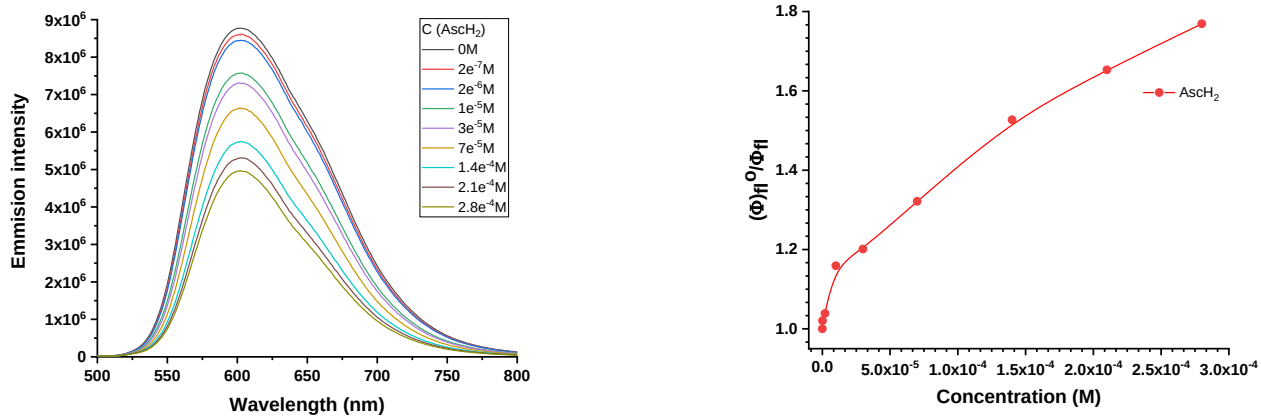


Figure S1. Fluorescence titration of [Ru] with ascorbic acid from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

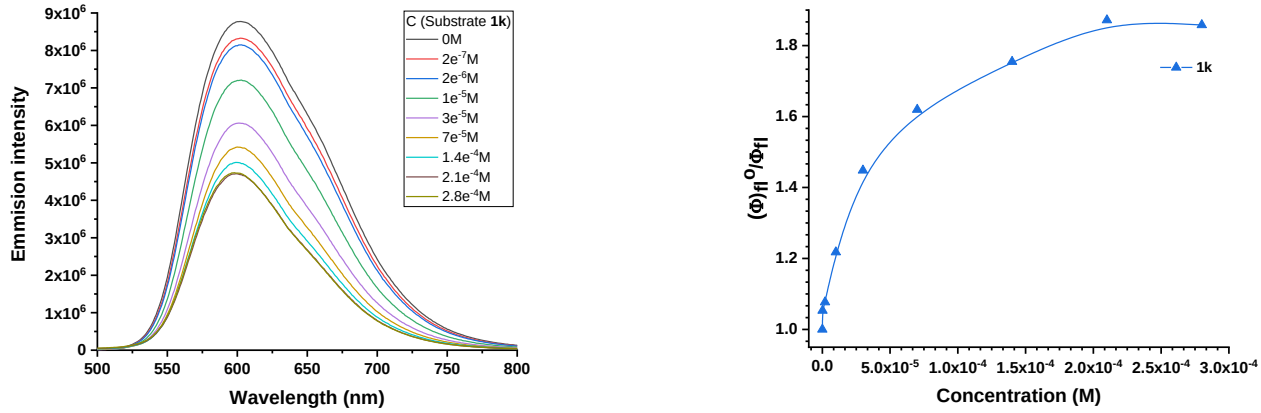


Figure S2. Fluorescence titration of [Ru] with 2-methyl-8-nitroquinoline - **1k** from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

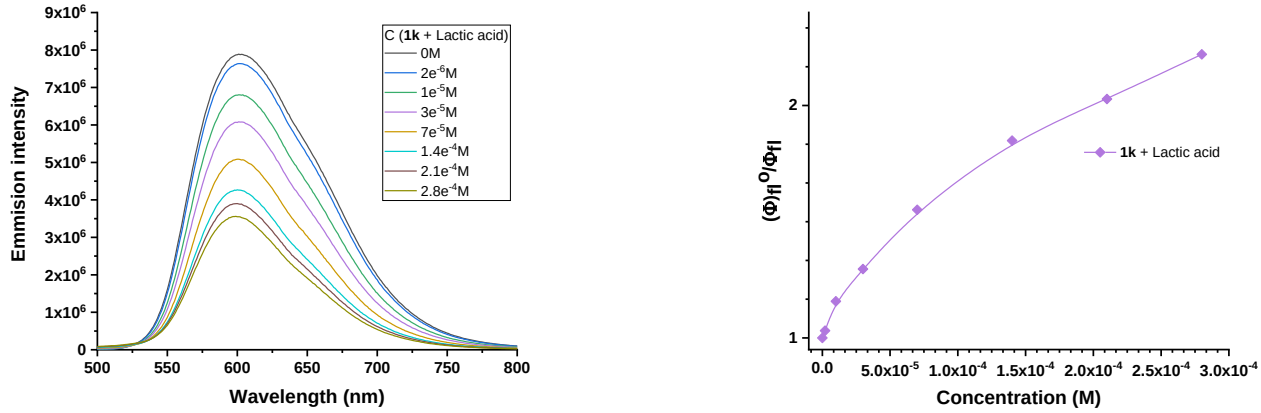


Figure S3. Fluorescence titration of [Ru] with 2-Methyl-8-nitroquinoline - **1k** complex with lactic acid from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

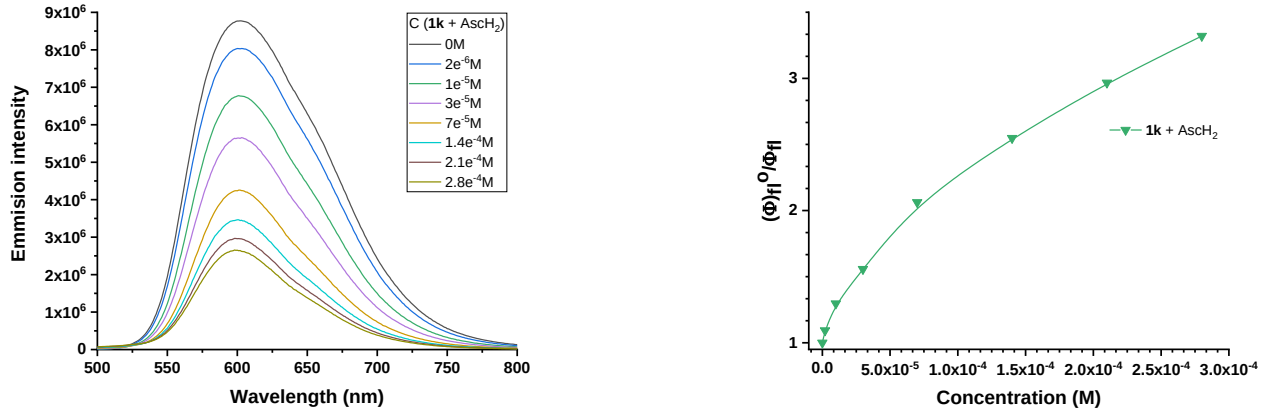


Figure S4. Fluorescence titration of [Ru] with 2-Methyl-8-nitroquinoline - **1k** complex with ascorbic acid from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

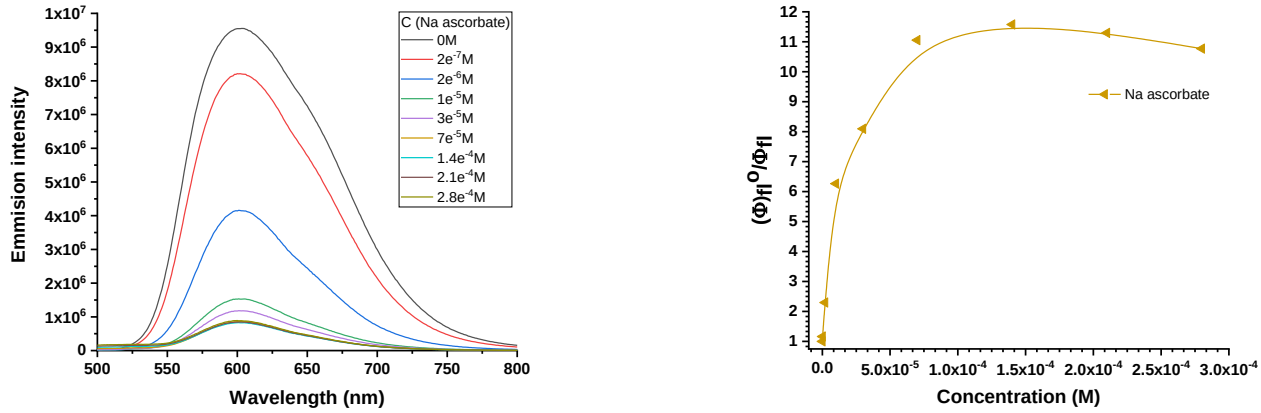


Figure S5. Fluorescence titration of [Ru] with sodium ascorbate from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

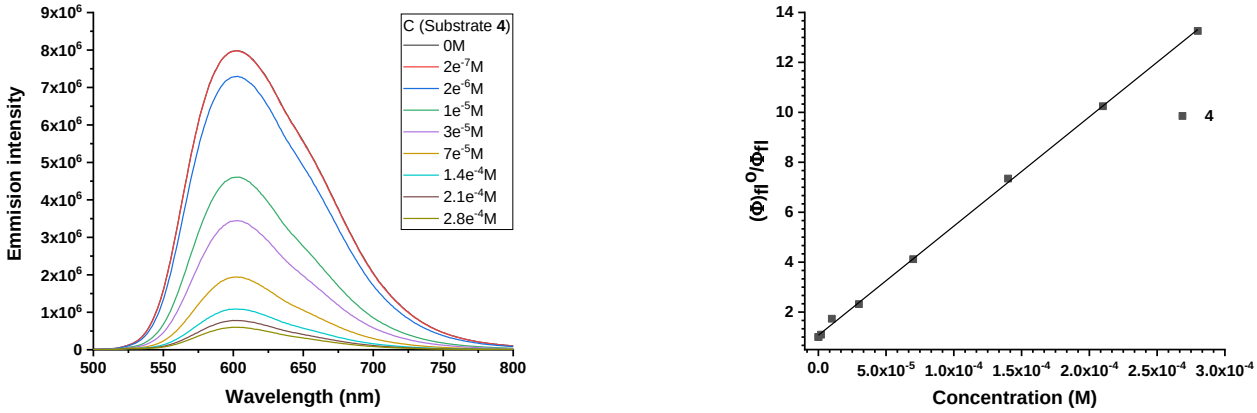


Figure S6. Fluorescence titration of [Ru] with nitrobenzene **4** from 0-10000 equiv (left). Stern-Volmer plot from 602 nm (right).

The quenching ability of the ascorbic acid, sodium ascorbate, nitrobenzene – **4**, 2-methyl-8-nitroquinoline – **1k**, and 1:1 mixtures of **1k** with either lactic acid (pK_a 3.86) or ascorbic acid (pK_a 4.12) were compared (Figure S1-S6). Sodium ascorbate was determined to be the most competent quencher compared to the others, although no amine formation was observed in the reaction with sodium ascorbate (Table S7, entry S7). The **1k**:$AscH_2$ complex was determined to be a better quencher than the respective components, and the lactic acid complex of **1k**. This implies that the concentration of the **1k**:$AscH_2$ complex has a direct connectivity to the photocatalyst fluorescence quenching at the reaction related concentration. Nitrobenzene – **4** appears to be a potent quencher, which is consistent with computed energetics for electron transfer (Table S9).

Distinctively, several Stern-Volmer plots show downward curvature (Figure S7-left), which can be associated with partial inaccessibility of quencher to the fluorophore.[1] To evaluate this phenomenon further, modified Stern-Volmer plots were made to identify the linear accessible fraction (f_a, Figure S7-right). The y-intercepts give reciprocal of the accessible quencher ($1/f_a$). Possible reasons for this behavior could be e.g. limited solubility and/or ionic character of quencher.[1]

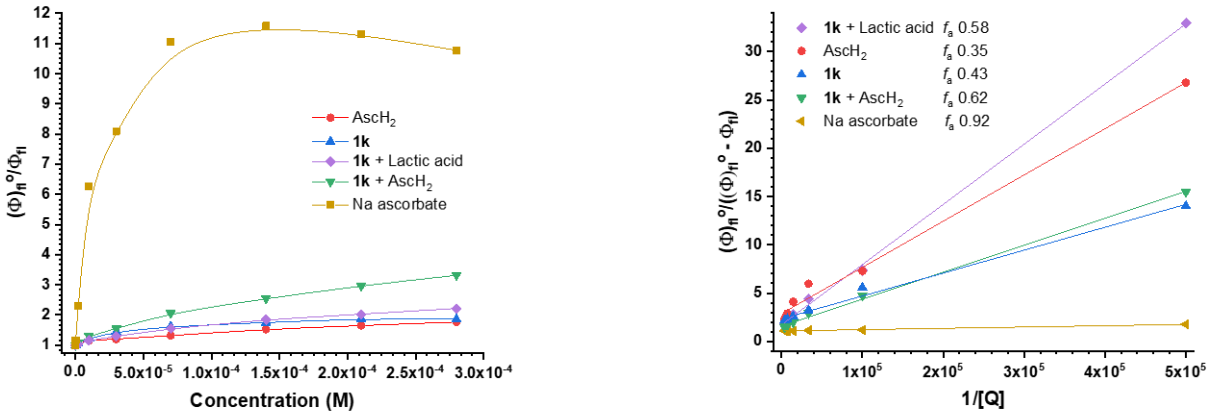


Figure S7. Combined Stern-Volmer plot for all the quenchers (left). Modified combined Stern-Volmer plot for all the quenchers (right).

The results from the Stern-Volmer quenching studies led us to investigate further the possibility of **1k** + $AscH_2$ to participate in PCET-type reaction. Qiu and Knowles[2] recently have developed a method to extract simultaneously hydrogen-bonding equilibrium constants and the rate constants for PCET processes from Stern-Volmer quenching experiments. The authors have noted that non-linearity in the modified Stern-Volmer plot can be

indicative of PCET-type reaction. Following their reasoning we performed analogues Stern-Volmer titrations. The concentration of the photocatalyst and one of the quencers are kept constant, whereas the Δc of other quencher component should cover a vast concentration range. The modified Stern-Volmer titrations were performed in degassed MeOH/H_2O (4:1) solvent mixture under Argon. The concentration of the photocatalyst ($Ru(bpy)_3Cl_2*6H_2O$) was set to 10 μM, concentration of nitrobenzene – **4** or 2-Methyl-8-nitroquinoline – **1k** was set to 10 mM, and the concentration of ascorbic acid was varied from 1 equiv (0.01 M) to 40 equiv (0.4 M) according to the loading of **4** or **1k** (Figure S8-S9).

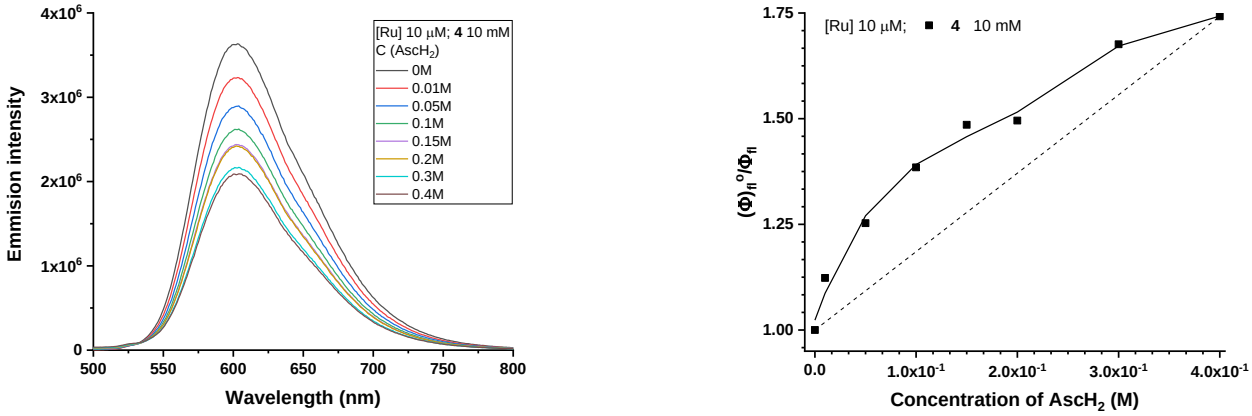


Figure S8. Fluorescence titration of [Ru] – 10 μM, nitrobenzene **4** – 10 mM with ascorbic acid from 0-40 equiv (left). Modified Stern-Volmer plot from 602 nm (right).

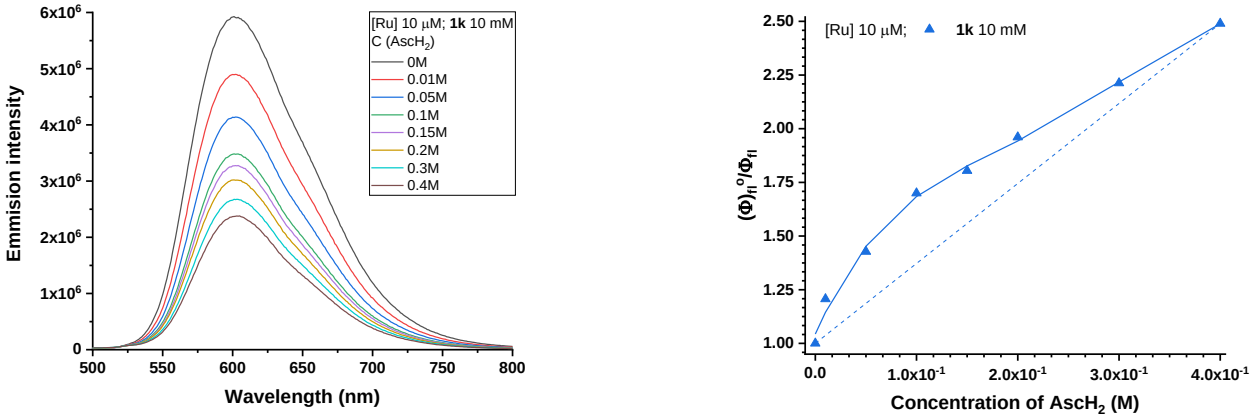


Figure S9. Fluorescence titration of [Ru] – 10 μM, 2-Methyl-8-nitroquinoline - **1k** – 10 mM with ascorbic acid from 0-40 equiv (left). Modified Stern-Volmer plot from 602 nm (right).

Mechanistic studies

NMR experiments

4-methoxy-8-nitroquinoline – **1c** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol) were weighted in a Schlenk-tube equipped with a stirrer bar. The tube was evacuated and back filled with Argon three times. A 10 mL of degassed by bubbling with argon for 15 minutes CD_3OD/D_2O (4:1) solvent mixture was added and the tube was placed under a blue light irradiation (455 nm) on a magnetic stirrer plate for 2 h at room temperature.

NMR monitoring of the reaction progress: sample was prepared by taking an aliquot of 0.5 mL of the above mentioned reaction mixture every 15 minutes in the course of 2 h. To each taken sample was added 0.1 mL of DMSO solution (0.1 M in CD_3OD) as internal standard. The ^1H NMR spectra were acquired on Bruker Avance Neo 500 [499.82 MHz] with D1 time of 25 s (Figure S10-S12-left).

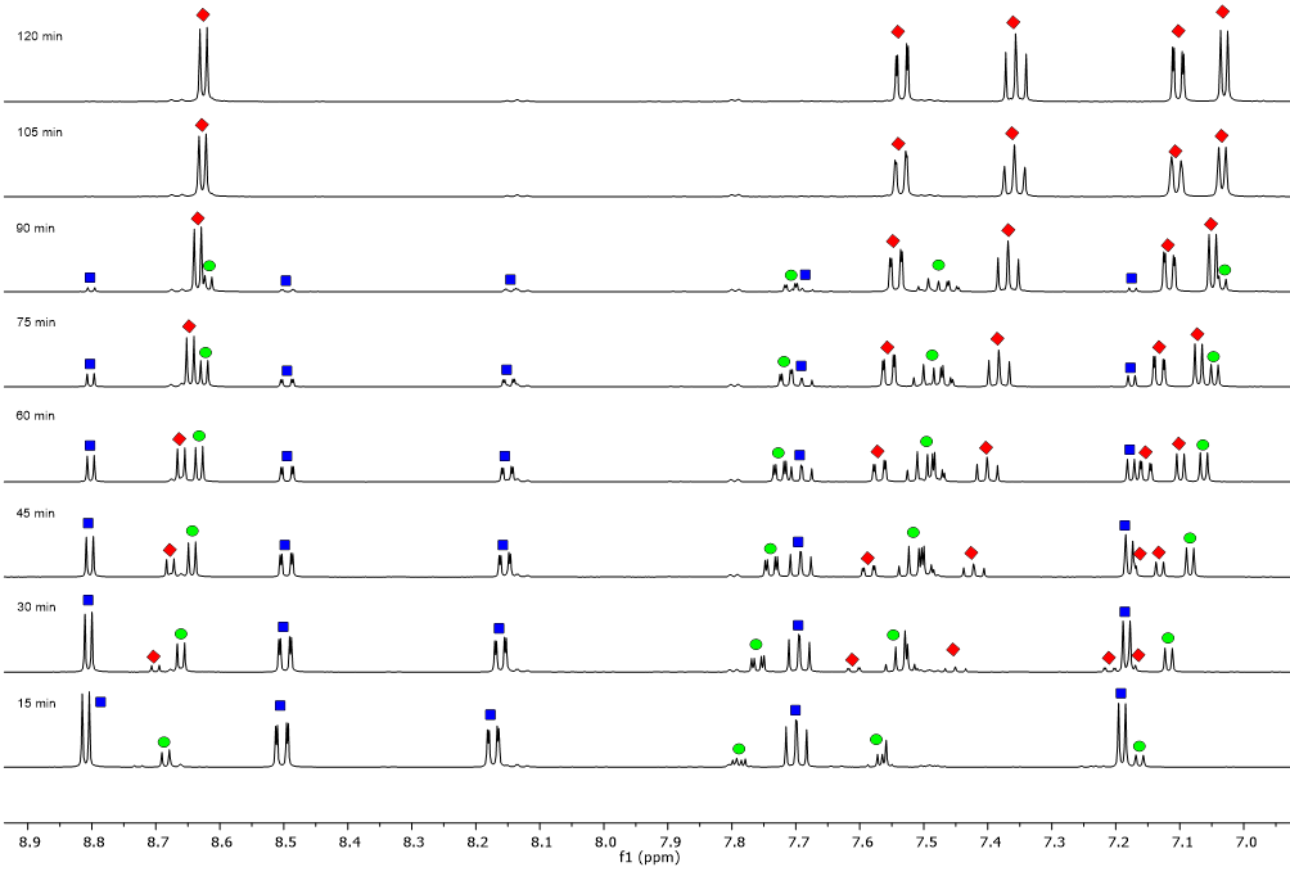


Figure S10. NMR monitoring of the reaction progress in CD_3OD/D_2O (4:1) (aromatic region). Blue Square - 4-methoxy-8-nitroquinoline – **1c**, Green Circle – N-(4-methoxyquinolin-8-yl)hydroxylamine – **1c`**, Red Diamond - 4-methoxyquinolin-8-amine – **2c**.

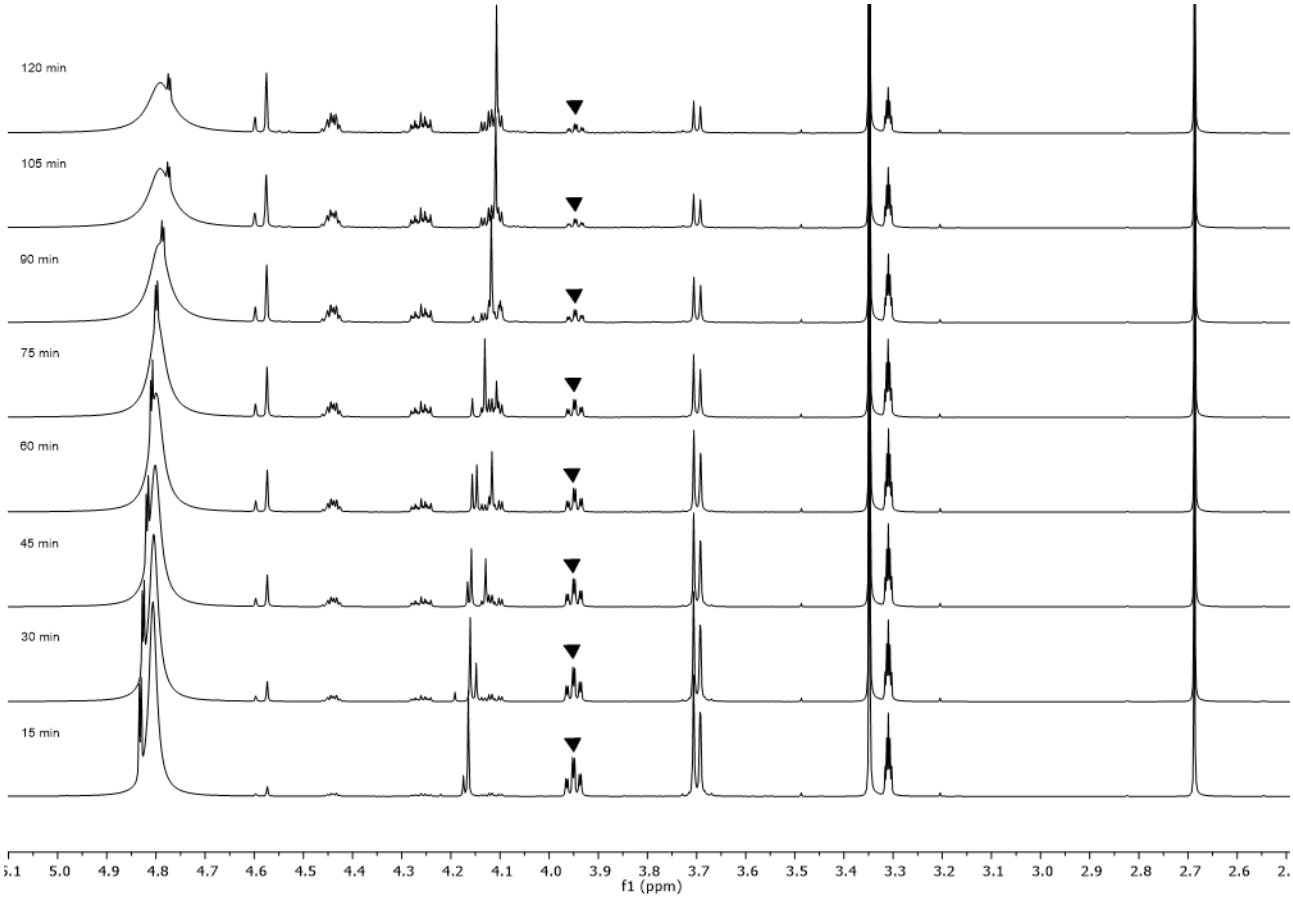


Figure S11. NMR monitoring of the reaction progress in CD_3OD/D_2O (4:1) (aliphatic region). Black triangle – ascorbic acid.

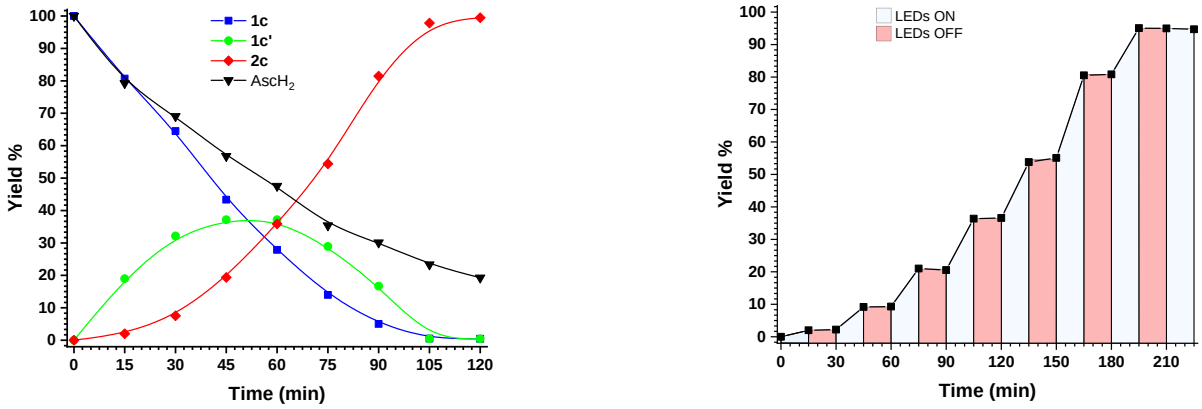


Figure S12. NMR monitoring of the reaction conversion in CD_3OD/D_2O (4:1). Blue Square - 4-methoxy-8-nitroquinoline – **1c**, Green Circle – N-(4-methoxyquinolin-8-yl)hydroxylamine – **1c`**, Red Diamond - 4-methoxyquinolin-8-amine – **2c**, Black triangle – Ascorbic acid (left). NMR monitoring of the product conversion **1c** to **2c** in CD_3OD/D_2O (4:1) upon switch ON/OFF cycles (right).

NMR monitoring of the reaction progress START/STOP experiment: sample of an aliquot of 0.45 mL were taken from the above-mentioned reaction mixture between 15–minute intervals (when the light was off and then when the light was on) during 4 h period. To each sample 0.1 mL of DMSO (0.1 M, CD_3OD) solution was added as an internal standard. The ^1H NMR spectra were measured on Bruker Avance Neo 500 [499.82 MHz] with D1 time of

25 s (Figure S12-right). This experiment shows the importance of light for the progress of reaction, but does not conclusively rule out possibility of radical chain reactions.[3]

High-resolution mass spectra of the Intermediate: sample was prepared by taking an aliquot of 0.5 mL from a reaction performed as described for NMR monitoring experiments in MeOH/H_2O (4:1) solvent mixture at the 45 min from the beginning of the reaction (Figure S13).

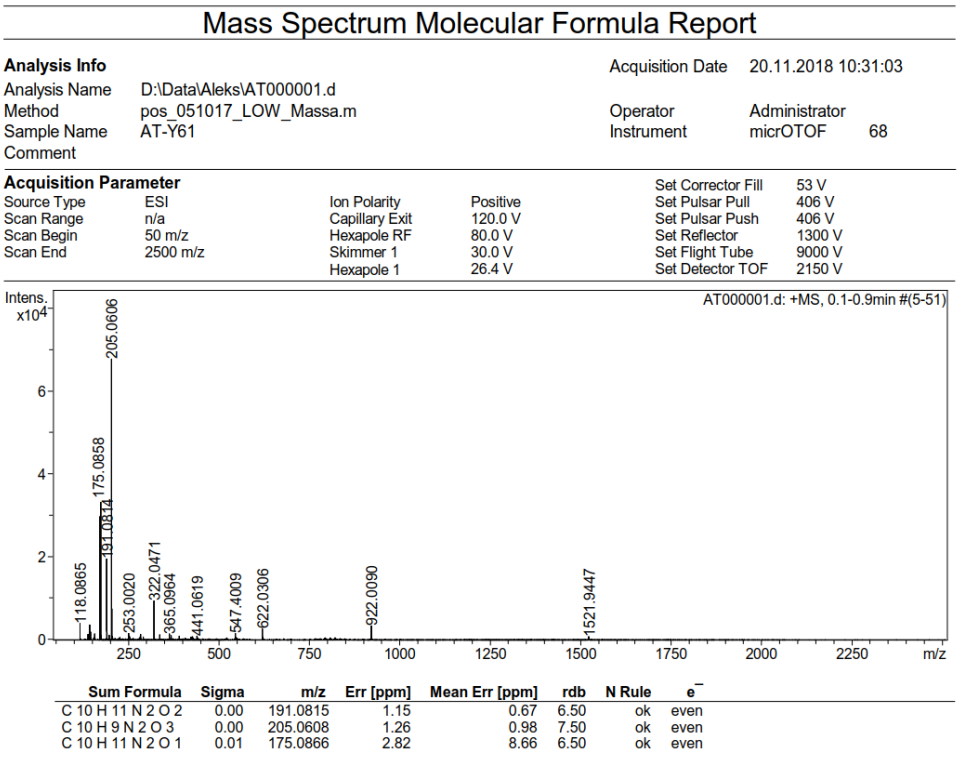


Figure S13. HRMS recorded from reaction mixture at the 45 min from the beginning of the reaction.

N-(4-methoxyquinolin-8-yl)hydroxylamine – **1c`**: Calculated for $C_{10}H_{11}N_2O_2$ 191.0815 (M+H); found 191.0814

4-methoxy-8-nitroquinoline – **1c**: Calculated for $C_{10}H_9N_2O_3$ 205.0608 (M+H); found 205.0606

4-methoxyquinolin-8-amine – **2c**: Calculated for $C_{10}H_{11}N_2O_1$ 175.0866 (M+H); found 175.0858

Substrate scope – schematic representation

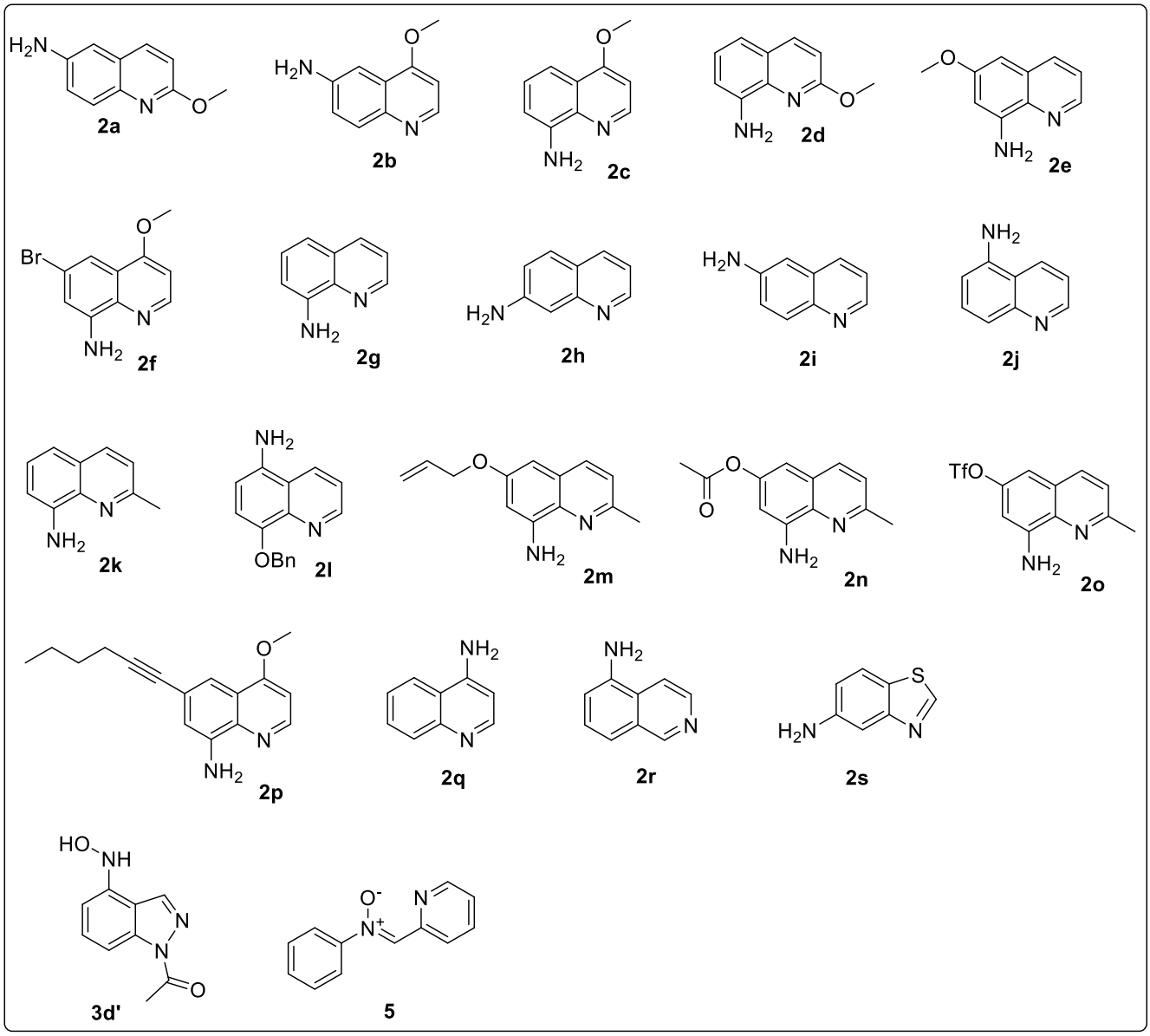
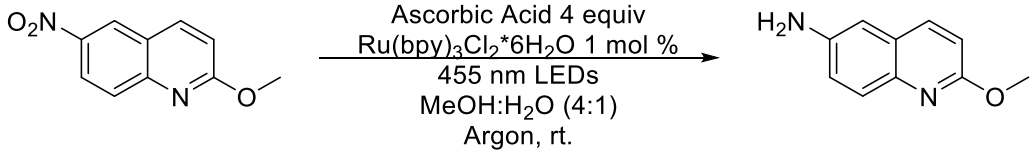


Figure S14. Substrate scope.

General procedures

General procedure for photocatalytic nitro reduction to amine:

The corresponding nitro compound (1 equiv), ascorbic acid (4 equiv) and $Ru(bpy)_3Cl_2*6H_2O$ (1 mol %) were weighted in a Schlenk-tube equipped with a stirrer bar. The tube was evacuated and back filled with Argon three times. A 10 mL of degassed (three freeze-pump-thaw cycles) MeOH/H_2O (4:1) solvent mixture was added and the tube was placed under a blue light irradiation (455 nm) on a magnetic stirrer plate for a reaction period at room temperature. The reaction was monitored with TLC and after completion, the reaction mixture was quenched by Et_3N (2 equiv). The crude was absorbed on SiO_2 and purified with SiO_2 flash chromatography.

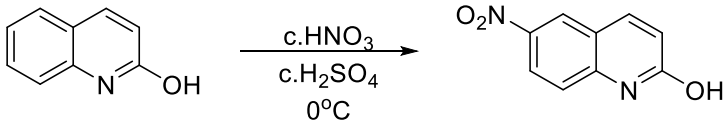


Scheme S1. Representative example for the nitro reduction according to the general procedure.

General procedure for nitration:

Method A – using hydroxyquinoline

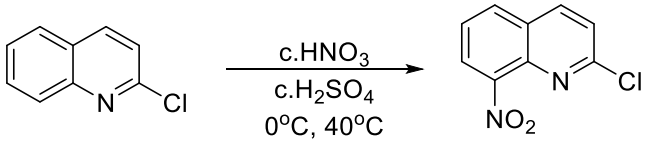
A round-bottom flask equipped with a stirrer bar was charged with the corresponding hydroxyquinoline (1 equiv) and 5 mL conc. H_2SO_4 acid. The reaction mixture was cooled down to 0 °C and conc. HNO_3 acid (3.5 equiv) was added dropwise. The reaction mixture was stirred for 1 hour at 0 °C on a magnetic stirrer plate and was quenched with ice/water mixture. The formed solids were filtrated off and were washed with plenty of water. The crude was dried and used without further purification.



Scheme S2. Representative example for the nitration according **Method A**.

Method B – using chloroquinoline

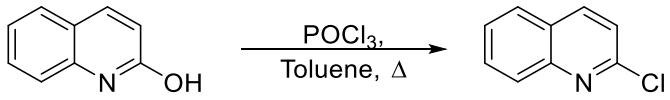
A round-bottom flask equipped with a stirrer bar was charged with the corresponding chloroquinoline (1 equiv) and 5 mL conc. H_2SO_4 acid. The reaction mixture was cooled down to 0 °C and conc. HNO_3 acid (3.5 equiv) was added dropwise. The reaction mixture was stirred for 5 minutes at 0 °C and further for 30 minutes at 40 °C on a magnetic stirrer plate. The crude was quenched with ice/water mixture. The reaction mixture was extracted with EtOAc and the organic layer was washed with sat. $NaHCO_3$, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography.



Scheme S3. Representative example for the nitration according **Method B**.

General procedure for chlorination of hydroxyquinolines:

A round-bottom flask equipped with a stirrer bar was charged with the corresponding hydroxyquinoline (1 equiv) suspended in 50 mL of dry Toluene. Phosphorous oxychloride (10 equiv) was added to the suspension and the reaction mixture was refluxed under argon for 20 hours on a magnetic stirrer plate. After completion of the reaction, the mixture was carefully quenched with water (NB! exothermic reaction) and basified with aqueous NH_4OH. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography.

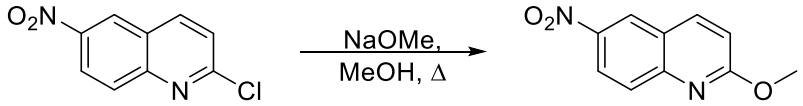


Scheme S4. Representative example for the chlorination of hydroxyquinolines according to the general procedure.

General procedure for the preparation of ethers:

Method A – Methyl ether

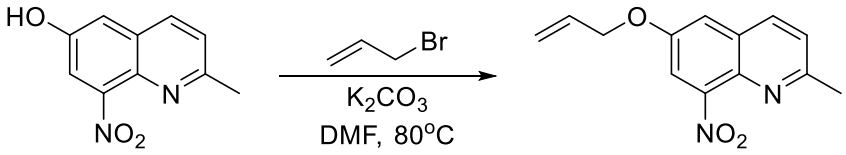
A round-bottom flask equipped with a stirrer bar was charged with the corresponding chloroquinoline (1 equiv) suspended in 20 mL of MeOH. 5 M solution of sodium methoxide (1.2 equiv) was added to the suspension and the reaction mixture was refluxed under Argon for 2 hours on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography.



Scheme S5. Representative example for the preparation of methyl ethers according to the general procedure.

Method B – Allyl and Benzyl ethers

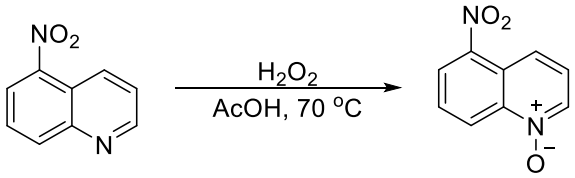
A round-bottom flask equipped with a stirrer bar was charged with the corresponding hydroxyquinoline (1 equiv) and potassium carbonate (2 equiv) suspended in 10 mL/mmol of DMF. Corresponding allyl bromide (1.2 equiv) or benzyl bromide (1.5 equiv) was added to the suspension and the reaction mixture was kept at 80 °C under Argon for 24 hours on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography.



Scheme S6. Representative example for the preparation of allyl/benzyl ethers according to the general procedure.

General procedure for the preparation of quinoline *N*-oxides:

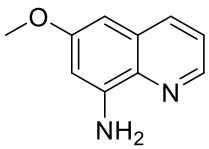
A round-bottom flask equipped with a stirrer bar was charged with the corresponding quinoline (1 equiv) dissolved in 5 mL of AcOH. Hydrogen peroxide 33% assay (1.5 equiv) was added to the solution and the reaction mixture was stirred at 70 °C for a reaction period on a magnetic stirrer plate. After completion of the reaction, the reaction mixture was extracted with EtOAc, organic layer was washed with sat. $NaHCO_3$ and was dried over Na_2SO_4 followed by evaporation to dryness. The crude was purified by SiO_2 flash chromatography.



Scheme S7. Representative example for the preparation of quinoline *N*-oxides according to the general procedure.

Synthesis of target compounds

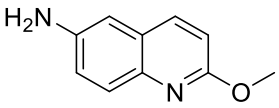
4 mmol scale synthesis of 6-methoxyquinolin-8-amine– 2e.



6-methoxy-8-nitroquinoline (0.817 g, 4 mmol), ascorbic acid (2.818 g, 16 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.015 g, 0.02 mmol) were weighted in a Schlenk-tube equipped with stirrer bar. The tube was evacuated and back filled with Argon three times. A 200 mL of degassed (three freeze-pump-thaw cycles) $MeOH/H_2O$ (4:1) solvent mixture was added and the tube was placed under a blue light irradiation (455 nm) on a magnetic stirrer plate for 24 h at room temperature. The reaction was monitored with TLC and after completion, the reaction mixture was quenched by sat. $NaHCO_3$, extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography using DCM:EtOAc (20:1) as eluent. Yield 73% (0.509 g, 2.92 mmol).

Substrate scope

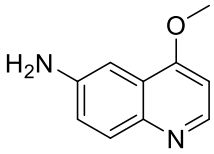
Synthesis of 2-methoxyquinolin-6-amine – 2a.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 2-methoxy-6-nitroquinoline – **1a** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 1 h. Yield 81.8% (0.0285 g, 0.16 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:0→20:1) as eluent.[4]

Characterization data: brownish solid; R_f = 0.24 (DCM:EtOAc (20:1)); **mp.** 99-100 °C; **^{1}H NMR** (300 MHz; DMSO-d_6) δ_h 7.85 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.84 – 6.74 (m, 2H), 5.22 (s, 2H), 3.88 (s, 3H); **^{13}C NMR** (75 MHz; DMSO-d_6) δ_c 159.7, 145.9, 139.5, 137.7, 127.9, 126.8, 121.6, 113.0, 107.4, 53.3; **FTIR**(cm^{-1}) 3463(w), 3348(w), 3206(w), 3011(w), 2989(w), 2946(w), 2849(w). **HRMS** calcd for $C_{10}H_{11}N_2O$ 175.0866 (M+H), found 175.0871.

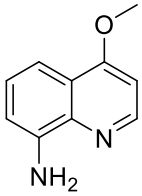
Synthesis of 4-methoxyquinolin-6-amine – 2b.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 4-methoxy-6-nitroquinoline – **1b** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $1^{1/2}$ h. Yield 96.8% (0.0337 g, 0.19 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (2:1→1:2) as eluent.[5]

Characterization data: brownish solid; R_f = 0.17 (EtOAc); **mp.** 156-157 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.33 (d, *J* = 5.1 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.79 (d, *J* = 5.1 Hz, 1H), 5.53 (s, 2H), 3.96 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 159.5, 146.6, 145.9, 142.5, 129.3, 122.3, 121.1, 100.4, 99.3, 55.6; **FTIR**(cm^{-1}) 3405(w), 3324(w), 3200(w), 3001(w), 2966(w), 2936(w), 2842(w). **HRMS** calcd for $C_{10}H_{11}N_2O$ 175.0866 (M+H), found 175.0869.

Synthesis of 4-methoxyquinolin-8-amine – 2c.

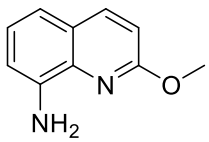


The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 4-methoxy-8-nitroquinoline – **1c** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 2 h. Yield 89.7% (0.0312 g, 0.18 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc

(20:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[6]

Characterization data: white-yellowish solid; R_f = 0.18 (DCM:EtOAc (10:1)); **mp.** 106-107 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.56 (d, *J* = 5.1 Hz, 1H), 7.22 (s, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 6.83 (dd, *J* = 5.2, 3.7 Hz, 1H), 5.84 (s, 2H), 3.98 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 161.5, 147.9, 145.0, 138.2, 126.5, 121.1, 109.1, 107.1, 100.9, 55.9; **FTIR**(cm^{-1}) 3433(w), 3296(w), 3168(w).

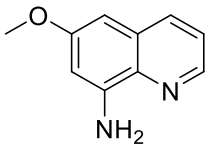
Synthesis of 2-methoxyquinolin-8-amine – 2d.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 2-methoxy-8-nitroquinoline – **1d** (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $3^{1/2}$ h. Yield 40.3% (0.0140 g, 0.08 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[7]

Characterization data: white-yellowish solid; R_f = 0.37 (DCM); **mp.** 75-76 °C; **^{1}H NMR** (300 MHz; DMSO-d_6) δ_h 8.06 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.07 (m, 1H), 7.00 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.62 (s, 2H), 3.99 (s, 3H); **^{13}C NMR** (75 MHz; DMSO-d_6) δ_c 159.9, 143.5, 139.4, 134.4, 124.9, 124.7, 114.0, 112.3, 109.9, 52.9; **FTIR**(cm^{-1}) 3463(w), 3368(w), 3011(w), 2979(w), 2936(w).

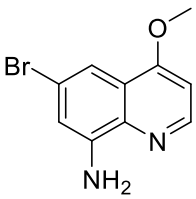
Synthesis of 6-methoxyquinolin-8-amine– 2e.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 6-methoxy-8-nitroquinoline (0.0408 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 5 h. Yield 86.2% (0.0300 g, 0.17 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[8]

Characterization data: yellowish oil; R_f = 0.27 (DCM:EtOAc (20:1)); **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.53 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.1 Hz, 1H), 6.52 – 6.46 (m, 2H), 5.92 (s, 2H), 3.79 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 158.6, 146.3, 144.4, 134.7, 134.5, 129.6, 121.8, 99.5, 92.9, 54.9; **FTIR**(cm^{-1}) 3469(w), 3363(w), 3000(w), 2957(w) 2936 (w) 2833(w).

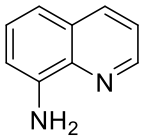
Synthesis of 6-bromo-4-methoxyquinolin-8-amine – 2f.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 6-bromo-4-methoxy-8-nitroquinoline – **1f** (0.0566 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $2^{1/2}$ h. Yield 98.3% (0.0497 g, 0.196 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent.

Characterization data: white solid; R_f = 0.22 (DCM:EtOAc (20:1)); **mp.** 123-124 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.58 (d, *J* = 5.1 Hz, 1H), 7.28 (d, *J* = 2.2 Hz, 1H), 7.01 (d, *J* = 5.1 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.19 (s, 2H), 4.00 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 160.6, 148.4, 147.0, 136.9, 122.1, 120.1, 111.0, 108.5, 102.1, 56.1; **FTIR**(cm^{-1}) 3487(w), 3420(w), 3383(w), 3322(w), 1504(s), 821(s); **HRMS** calcd for $C_{10}H_{10}BrN_2O$ 252.9971 (M+H), found 252.9959.

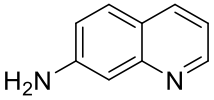
Synthesis of quinolin-8-amine – 2g.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 8-nitroquinoline (0.0348 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 4 h. Yield 74.5% (0.0215 g, 0.15 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[9]

Characterization data: yellowish solid; R_f = 0.33 (DCM:EtOAc (20:1)); **mp.** 64-65 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.72 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.90 (s, 2H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 146.9, 145.2, 137.4, 135.8, 128.5, 127.6, 121.4, 113.6, 108.6; **FTIR**(cm^{-1}) 3450(w), 3349(w).

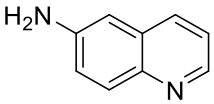
Synthesis of quinolin-7-amine – 2h.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 7-nitroquinoline (0.0348 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $4^{1/2}$ h. Yield 98.8% (0.0285 g, 0.197 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (2:1→1:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[10]

Characterization data: yellow solid; R_f = 0.19 (EtOAc); **mp.** 90-91 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.58 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.07 (dd, *J* = 8.0, 4.3 Hz, 1H), 6.99 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 5.74 (s, 2H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 150.1, 150.0, 150.0, 135.2, 128.5, 120.5, 118.7, 116.5, 106.3; **FTIR**(cm^{-1}) 3428(w), 3308(w), 3165(w).

Synthesis of quinolin-6-amine – 2i.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine.

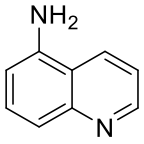
Starting from 6-nitroquinoline (0.0348 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 3 h. Yield 69.3% (0.0200 g, 0.14 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→5:1) as eluent.

Starting from 6-nitroquinoline 1-oxide – **1i** (0.0380 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 5 h. Yield 34.7% (0.0070 g, 0.05 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→5:1) as eluent.

The characterization data of the obtained compound are in agreement with the literature values.[8b]

Characterization data: yellowish solid; R_f = 0.22 (DCM:EtOAc (1:1)); **mp.** 112-113 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.46 (d, *J* = 4.1 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.26 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 – 7.12 (m, 1H), 6.80 – 6.76 (m, 1H), 5.58 (s, 2H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 147.0, 145.0, 142.0, 132.8, 129.8, 129.6, 121.6, 121.2, 104.7; **FTIR**(cm^{-1}) 3399(w), 3308(w), 3180(w).

Synthesis of quinolin-5-amine – 2j.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine.

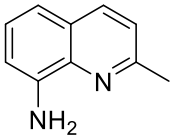
Starting from 5-nitroquinoline (0.0348 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $3^{1/2}$ h. Yield 76.4% (0.0220 g, 0.15 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→10:1) as eluent.

Starting from 5-nitroquinoline 1-oxide – **1j** (0.0380 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 5 h. Yield 34.7% (0.0100 g, 0.07 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→10:1) as eluent.

The characterization data of the obtained compound are in agreement with the literature values.[8b]

Characterization data: yellow solid; R_f = 0.29 (DCM:EtOAc (1:1)); **mp.** 106-107 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.76 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 5.96 (s, 2H); **^{13}C NMR** (126MHz; DMSO-d_6) δ_c 149.8, 148.9, 145.3, 130.8, 130.2, 118.7, 117.5, 116.0, 107.3; **FTIR**(cm^{-1}) 3327(w), 3189(w).

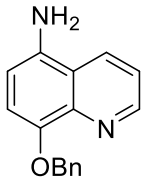
Synthesis of 2-methylquinolin-8-amine – 2k.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 2-methyl-8-nitroquinoline (0.0376 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $3^{1/2}$ h. Yield 90.0% (0.0284 g, 0.18 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[11]

Characterization data: yellow solid; R_f = 0.47 (DCM:EtOAc (20:1)); **mp.** 51-52 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.06 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.78 (s, 2H), 2.64 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 155.1, 144.4, 136.7, 136.0, 126.6, 126.5, 122.0, 113.6, 108.8, 24.8; **FTIR**(cm^{-1}) 3465(w), 3379(w), 3339(w), 3046(w), 2914(w).

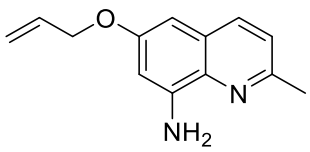
Synthesis of 8-(benzyloxy)quinolin-5-amine – 2l.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 8-(benzyloxy)-5-nitroquinoline – **1l** (0.0561 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 6 h. Yield 15.8% (0.0079 g, 0.03 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→10:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[12]

Characterization data: dark yellow solid; R_f = 0.35 (DCM:EtOAc (1:1)); **mp.** 179-180 °C; **^{1}H NMR** (400 MHz; DMSO-d_6) δ_h 8.80 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.47 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.28 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 5.46 (s, 2H), 5.17 (s, 2H); **^{13}C NMR** (101 MHz; DMSO-d_6) δ_c 148.6, 145.2, 140.7, 139.0, 138.0, 131.1, 128.3, 127.7, 127.6, 119.4, 119.0, 113.7, 107.1, 71.1; **FTIR**(cm^{-1}) 3419(w), 3304(w), 3204(w), 1089(s), 699(s).

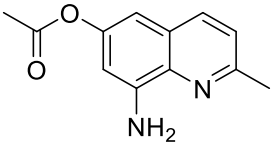
Synthesis of 6-(allyloxy)-2-methylquinolin-8-amine – 2m.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 6-(allyloxy)-2-methyl-8-nitroquinoline – **1m** (0.0489 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 4 h. Yield 82.6% (0.0354 g, 0.17 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (5:1) as eluent.

Characterization data: colorless oil; R_f = 0.47 (DCM:EtOAc (20:1)); **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 7.92 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.47 (d, *J* = 2.7 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.2 Hz, 1H), 5.82 (s, 2H), 5.42 (dq, *J* = 17.3, 1.8 Hz, 1H), 5.26 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.57 (dt, *J* = 5.3, 1.6 Hz, 2H), 2.58 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 156.7, 152.5, 145.6, 135.0, 133.9, 133.7, 127.4, 122.4, 117.2, 99.9, 94.0, 68.0, 24.5; **FTIR**(cm^{-1}) 3473(w), 3372(w), 2916(w), 2860(w), 1591(s), 1168(s), 831(s); **HRMS** calcd for $C_{13}H_{15}N_2O$ 215.1179 (M+H), found 215.1185.

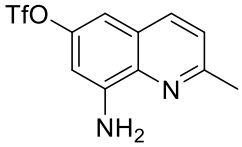
Synthesis of 8-amino-2-methylquinolin-6-yl acetate – 2n.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 2-methyl-8-nitroquinolin-6-yl acetate – **1n** (0.0492 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 3 h. Yield 90.9% (0.0392 g, 0.18 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent.

Characterization data: off-white solid; R_f = 0.33 (DCM:EtOAc (20:1)); **mp.** 102-103 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.04 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.73 (s, 1H), 6.55 (s, 1H), 6.02 (s, 2H), 2.63 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 169.2, 154.9, 148.8, 145.8, 135.8, 134.9, 126.7, 122.7, 104.2, 103.3, 24.7, 20.9; **FTIR**(cm^{-1}) 3492(w), 3377(w), 1746(s), 1210(s), 846(s); **HRMS** calcd for $C_{12}H_{13}N_2O_2$ 217.0972 (M+H), found 217.0982.

Synthesis of 8-amino-2-methylquinolin-6-yl trifluoromethanesulfonate – 2o.

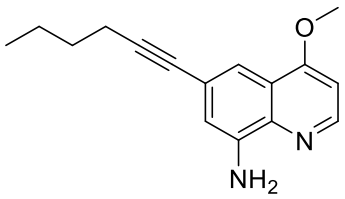


The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 2-methyl-8-nitroquinolin-6-yl trifluoromethanesulfonate – **1o** (0.0672 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was $7^{1/2}$ h. Yield 96.4% (0.0591 g, 0.19 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent.

Characterization data: yellow solid; R_f = 0.22 (*n*-hexane:EtOAc (5:1)); **mp.** 60-61 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.19 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.40 (s, 2H), 2.65 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 156.7, 147.4, 147.3, 136.5, 135.6, 126.5, 123.8, **122.1, 119.5, 117.0, 114.4** (q, *J* = 320.8 Hz), 103.6, 100.3, 24.8; **^{19}F NMR** (470 MHz; DMSO-d_6) δ_f -72.99; **FTIR**(cm^{-1}) 3453(w), 3342(w), 3318(w), 1204(s), 1133(s), 596(s); **HRMS** calcd for $C_{11}H_{10}F_3N_2O_3S$ 307.0359 (M+H), found 307.0348.

Synthesis of 6-(hex-1-yn-1-yl)-4-methoxyquinolin-8-amine – 2p.

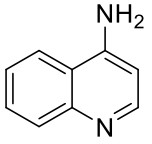
The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 6-(hex-1-yn-1-yl)-4-methoxy-8-nitroquinoline – **1p** (0.0569 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 23 h. Yield 78.9% (0.0401 g, 0.16 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent.



Characterization data: orange solid; R_f = 0.30 (DCM:EtOAc (10:1)); **mp.** 64-65 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.55 (d, *J* = 5.1 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 5.93 (s, 2H), 3.99 (s, 3H), 2.43 (t, *J* = 6.9 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.50 – 1.40 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 161.0, 148.5, 145.2, 137.6, 121.1, 120.9, 110.9, 110.3, 101.6, 89.7, 81.5, 56.0, 30.3, 21.4, 18.3, 13.5; **FTIR**(cm^{-1}) 3469(w), 3352(w), 2957(w), 2932(w), 1504(s), 1053(s), 821(s); **HRMS** calcd for $C_{16}H_{19}N_2O$ 255.1492 (M+H), found 255.1481.

Synthesis of Quinolin-4-amine – 2q.

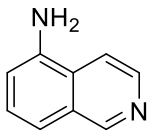
The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 4-nitroquinoline 1-oxide (0.0380 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 3 h. Yield 57.7% (0.0166 g, 0.12 mmol). Purification: Flash chromatography (SiO_2) using $CHCl_3$:MeOH:NH_4OH (5:1:0.1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[8b]



Characterization data: off-white solid; R_f = 0.15 (Acetone); **mp.** 143-144 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 8.31 (d, *J* = 5.2 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.75 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.59 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.39 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 6.82 (s, 2H), 6.55 (d, *J* = 5.2 Hz, 1H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 151.6, 150.1, 148.5, 128.9, 128.6, 123.5, 122.3, 118.5, 102.2; **FTIR**(cm^{-1}) 3393(w), 3331(w), 3208(w), 3055(w).

Synthesis of isoquinolin-5-amine – 2r.

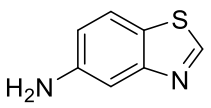
The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 5-nitroisoquinoline (0.0348 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 5 h. Yield 33.8% (0.0097 g, 0.07 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (20:1→5:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[8b]



Characterization data: yellowish solid; R_f = 0.18 (DCM:EtOAc (1:1)); **mp.** 125-126 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 9.09 (s, 1H), 8.35 (d, *J* = 5.9 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.86 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.96 (s, 2H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 152.1, 144.0, 140.8, 129.3, 128.2, 124.7, 115.4, 114.2, 110.6; **FTIR**(cm^{-1}) 3429(w), 3318(w), 3174(w).

Synthesis of benzo[*d*]thiazol-5-amine – 2s.

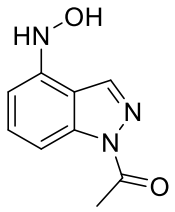
The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 5-nitrobenzo[d]thiazole (0.0360 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 2 h. Yield 53.2% (0.0160 g, 0.11 mmol). Purification: Flash chromatography (SiO_2) using



DCM:EtOAc (10:1→2:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[13]

Characterization data: yellow solid; R_f = 0.33 (DCM:EtOAc (1:1)); **mp.** 72-73 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 9.16 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.2 Hz, 1H), 5.29 (s, 2H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 155.3, 154.8, 147.9, 122.0, 120.3, 115.1, 105.8; **FTIR**(cm^{-1}) 3413(w), 3295(w), 3196(w), 3058(w).

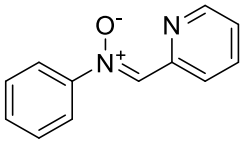
Synthesis of 1-(4-(hydroxyamino)-1H-indazol-1-yl)ethan-1-one – 3d'.



The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from 1-(4-nitro-1H-indazol-1-yl)ethan-1-one – **3d** (0.0410 g, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 7 h. Yield 78.7% (0.0301 g, 0.16 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent.

Characterization data: orange solid; R_f = 0.20 (DCM:EtOAc (10:1)); **mp.** 219-220 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 9.21 (d, *J* = 1.5 Hz, 1H), 8.82 (d, *J* = 1.7 Hz, 1H), 8.39 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 2.68 (s, 3H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 170.7, 145.7, 139.5, 138.7, 130.7, 113.5, 105.4, 104.8, 22.9; **FTIR**(cm^{-1}) 3338(w), 3260(w), 3211(w), 2790(br. w), 1695(m), 1343(s); **HRMS** calcd for $C_9H_{10}N_3O_2$ 192.0768 (M+H), found 192.0774.

Synthesis of *N*-phenyl-1-(pyridin-2-yl)methanimine oxide - 5.



Step 1 ***N*-phenylhydroxylamine**: The title compound was synthesized following the general procedure for photocatalytic nitro reduction to amine. Starting from nitrobenzene (0.0205 ml, 0.2 mmol), ascorbic acid (0.1409 g, 0.8 mmol) and $Ru(bpy)_3Cl_2*6H_2O$ (0.0015 g, 0.002 mmol). Reaction time was 1 h. The reaction was monitored with TLC and after completion, the light source was switched off.

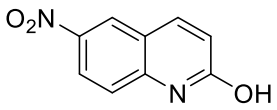
Step 2: To the reaction mixture from Step 1 was added picolinaldehyde (0.0209 ml, 0.22 mmol). Thereafter, the reaction mixture was kept at room temperature in dark for 20 h. The crude was purified by SiO_2 flash chromatography. Yield 54.2% (0.0215 g, 0.11 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (3:1→2:1) as eluent.

The characterization data of the obtained compound are in agreement with the literature values.[14]

Characterization data: white-yellowish solid; R_f = 0.40 (DCM:EtOAc (1:1)); **mp.** 66-67 °C; **^{1}H NMR** (500 MHz; DMSO-d_6) δ_h 9.22 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 4.7 Hz, 1H), 8.46 (s, 1H), 7.97 (q, *J* = 7.1, 6.3 Hz, 3H), 7.59 – 7.54 (m, 3H), 7.48 (t, *J* = 6.2 Hz, 1H); **^{13}C NMR** (126 MHz; DMSO-d_6) δ_c 150.0, 149.6, 148.2, 137.0, 134.4, 130.4, 129.2, 124.8, 123.0, 121.6; **FTIR**(cm^{-1}) 3108(w), 3053(w), 1072(m), 764(s), 681(s), 512(s).

Starting materials

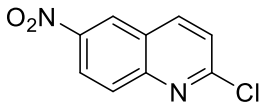
Synthesis of 6-nitroquinolin-2-ol – S1.



The title compound was synthesized following the general procedure for nitration Method A. Starting from 2-hydroxyquinoline (0.726 g, 5 mmol) and c.HNO_3 acid (0.729 mL, 17.5 mmol). Reaction time was 1 h. Yield 84% (0.799 g, 4.20 mmol). The crude was used without further purification. The characterization data of the obtained compound are in agreement with the literature values.[15]

Characterization data: yellowish solid; R_f = 0.29 (DCM:EtOAc (1:1)); **mp.** 279-280 °C; **^{1}H NMR** (300 MHz; DMSO-d_6) δ_h 12.24 (s, 1H), 8.65 (d, *J* = 2.6 Hz, 1H), 8.29 (dd, *J* = 9.1, 2.6 Hz, 1H), 8.09 (d, *J* = 9.6 Hz, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 6.64 (d, *J* = 9.6 Hz, 1H); **^{13}C NMR** (75 MHz; DMSO-d_6) δ_c 162.6, 144.0, 142.1, 140.8, 125.7, 125.0, 124.5, 119.2, 116.7; **FTIR**(cm^{-1}) 3084(w), 2984(w),2883(w), 2819(w), 2773(w), 2733(w).

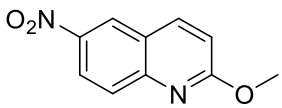
Synthesis of 2-chloro-6-nitroquinoline – S2.



The title compound was synthesized following the general procedure for chlorination of hydroxyquinolines. Starting from 6-nitroquinolin-2-ol – **S1** (0.773 g, 4.1 mmol) and $POCl_3$ (3.710 mL, 41 mmol). Reaction time was 20 h. Yield 91% (0.778 g, 3.73 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[14a,16]

Characterization data: white-yellowish solid; R_f = 0.57 (DCM); **mp.** 225-226 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 8.80 (d, *J* = 2.5 Hz, 1H), 8.52 (dd, *J* = 9.2, 2.5 Hz, 1H), 8.31 (d, *J* = 8.7 Hz, 1H), 8.17 (d, *J* = 9.2 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 154.7, 150.0, 145.9, 140.4, 130.6, 125.9, 124.7, 124.4, 124.3; **FTIR**(cm^{-1}) 3087(w), 2989(w), 825(s).

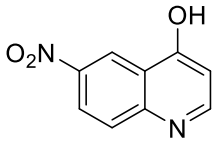
Synthesis of 2-methoxy-6-nitroquinoline – 1a.



The title compound was synthesized following the general procedure for preparation of ethers Method A. Starting from 2-chloro-6-nitroquinoline – **S2** (0.772 g, 3.7 mmol) and 5M solution of NaOMe (0.888 mL, 4.44 mmol). Reaction time was 2 h. Yield 99% (0.748 g, 3.66 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[17]

Characterization data: white-yellowish solid; R_f = 0.49 (*n*-hexane:EtOAc (5:1)); **mp.** 179-180 °C; **^{1}H NMR** (300 MHz; $CDCl_3$) δ_h 8.66 (dd, *J* = 2.6, 0.4 Hz, 1H), 8.39 (dd, *J* = 9.2, 2.6 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.91 (dt, *J* = 9.2, 0.6 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 4.11 (s, 3H); **^{13}C NMR** (75 MHz; $CDCl_3$) δ_c 165.0, 150.1, 144.0, 139.9, 128.7, 124.3, 124.0, 123.5, 115.6, 54.2; **FTIR**(cm^{-1}) 3091(w), 3035(w), 2947(w),1281(m).

Synthesis of 6-nitroquinolin-4-ol – S3.

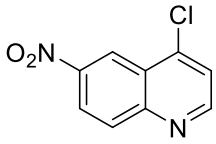


The title compound was synthesized following the general procedure for nitration Method A. Starting from 4-hydroxyquinoline (0.726 g, 5 mmol) and c.HNO_3 acid (0.729 mL, 17.5 mmol). Reaction time was 1 h. Yield 28% (0.266 g, 1.40 mmol). Purification: Flash chromatography (SiO_2) using Acetone as eluent. The characterization data of the obtained compound are in agreement with the literature values.[14a,18]

Characterization data: yellow solid; R_f = 0.22 (DCM:EtOAc (20:1)); **mp.** 325-326 °C; **^{1}H NMR** (400 MHz; DMSO-d_6) δ_h 12.25 (s, 1H), 8.81 (d, *J* = 2.7 Hz, 1H), 8.39 (dd, *J* = 9.1, 2.7 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 6.17 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (101 MHz; DMSO-d_6) δ_c 176.4, 143.8, 142.5, 140.7, 125.8, 124.7, 121.6, 120.2, 110.3; **FTIR**(cm^{-1}) 2854(w), 2769(w).

Synthesis of 4-chloro-6-nitroquinoline – S4.

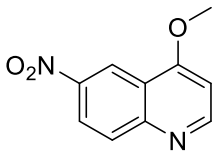
The title compound was synthesized following the general procedure for chlorination of hydroxyquinolines. Starting from 6-nitroquinolin-4-ol – **S3** (0.618 g, 3.25 mmol) and $POCl_3$ (2.941 mL, 32.5 mmol). Reaction time was 20 h. Yield 42% (0.285 g, 1.37 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[14a,19]



Characterization data: white-yellowish solid; R_f = 0.22 (DCM); **mp.** 142-143 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 9.19 (d, *J* = 2.5 Hz, 1H), 8.96 (d, *J* = 4.7 Hz, 1H), 8.53 (dd, *J* = 9.2, 2.5 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 4.7 Hz, 1H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 153.4, 151.1, 146.4, 144.7, 132.1, 126.1, 124.0, 123.0, 121.5; **FTIR**(cm^{-1}) 3083(w), 3048(w), 1342(s), 856(s).

Synthesis of 4-methoxy-6-nitroquinoline – 1b.

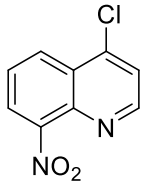
The title compound was synthesized following the general procedure for preparation of ethers Method A. Starting from 4-chloro-6-nitroquinoline – **S4** (0.250 g, 1.2 mmol) and 5M solution of NaOMe (0.288 mL, 1.44 mmol). Reaction time was 2 h. Yield 94% (0.230 g, 1.13 mmol). Purification: Flash chromatography (SiO_2) using DCM:EtOAc (10:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[20]



Characterization data: yellowish solid; R_f = 0.14 (DCM:EtOAc (20:1)); **mp.** 177-178 °C; **^{1}H NMR** (300 MHz; $CDCl_3$) δ_h 9.12 (d, *J* = 2.6 Hz, 1H), 8.89 (d, *J* = 5.3 Hz, 1H), 8.42 (dd, *J* = 9.2, 2.6 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 6.85 (d, *J* = 5.3 Hz, 1H), 4.11 (s, 3H); **^{13}C NMR** (75 MHz; $CDCl_3$) δ_c 163.8, 155.1, 151.5, 145.1, 130.9, 123.5, 120.7, 119.8, 101.8, 56.4; **FTIR**(cm^{-1}) 3098(w), 3053(w), 2968(w), 2910(w), 2842(w), 1340(s) 1299(s).

Synthesis of 4-chloro-8-nitroquinoline – S5.

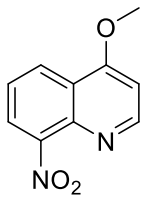
The title compound was synthesized following the general procedure for nitration Method B. Starting from 4-chloroquinoline (0.818 g, 5 mmol) and c.HNO_3 acid (0.729 mL, 17.5 mmol). Reaction time was 30 min. Yield 62% (0.647 g, 3.10 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (5:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[18]



Characterization data: white-yellowish solid; R_f = 0.48 (DCM); **mp.** 125-126 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 8.93 (d, *J* = 4.7 Hz, 1H), 8.48 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.66 (d, *J* = 4.7 Hz, 1H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 152.1, 148.8, 143.3, 140.6, 128.3, 127.5, 126.5, 124.5, 123.1; **FTIR**(cm^{-1}) 3070(w), 3046(w), 3026(w), 1354(s), 748(s).

Synthesis of 4-methoxy-8-nitroquinoline – 1c.

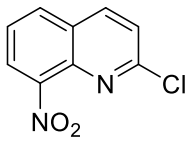
The title compound was synthesized following the general procedure for preparation of ethers Method A. Starting from 4-chloro-8-nitroquinoline – **S5** (0.209 g, 1.0 mmol) and 5M solution of NaOMe (0.240 mL, 1.2 mmol). Reaction time was 2 h. Yield 99% (0.202 g, 0.99 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (1:2) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[19]



Characterization data: white-yellowish solid; R_f = 0.15 (DCM); **mp.** 178-179 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 8.90 (d, *J* = 5.2 Hz, 1H), 8.42 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.01 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.88 (d, *J* = 5.2 Hz, 1H), 4.10 (s, 3H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 162.3, 153.9, 148.2, 140.7, 126.4, 124.3, 124.2, 122.8, 101.7, 56.3; **FTIR**(cm^{-1}) 3034(w), 2968(w), 2932(w), 1505(s), 757(s).

Synthesis of 2-chloro-8-nitroquinoline – S6.

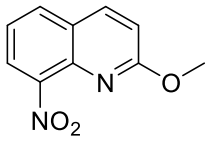
The title compound was synthesized following the general procedure for nitration Method B. Starting from 2-chloroquinoline (0.818 g, 5 mmol) and c.HNO_3 acid (0.729 mL, 17.5 mmol). Reaction time was 30 min. Yield 53% (0.553 g, 2.65 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (5:1→0:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[6b]



Characterization data: white-yellowish solid; R_f = 0.23 (*n*-hexane:EtOAc (3:1)); **mp.** 147-148 °C; **^{1}H NMR** (300 MHz; $CDCl_3$) δ_h 8.20 (d, *J* = 8.7 Hz, 1H), 8.15 – 7.99 (m, 2H), 7.71 – 7.57 (m, 1H), 7.53 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$) δ_c 153.2, 146.8, 138.7, 138.4, 131.5, 127.3, 125.5, 124.6, 124.3; **FTIR**(cm^{-1}) 1525(s), 1115(m), 759(s).

Synthesis of 2-methoxy-8-nitroquinoline – 1d.

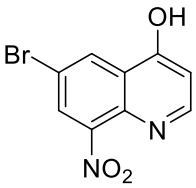
The title compound was synthesized following the general procedure for preparation of ethers Method A. Starting from 2-chloro-8-nitroquinoline – **S6** (0.209 g, 1.0 mmol) and 5M solution of NaOMe (0.240 mL, 1.2 mmol). Reaction time was 2 h. Yield 98% (0.200 g, 0.98 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[6]



Characterization data: white-yellowish solid; R_f = 0.37 (*n*-hexane:EtOAc (5:1)); **mp.** 125-126 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 8.04 (d, *J* = 8.9 Hz, 1H), 7.96 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 4.07 (s, 3H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 163.9, 146.7, 138.6, 138.3, 131.6, 126.3, 124.1, 122.7, 115.2, 54.2; **FTIR**(cm^{-1}) 2989(w), 2949(w), 1276(s).

Synthesis of 6-bromo-8-nitroquinolin-4-ol – S7.

Step 1: Preparation of intermediate. A round-bottom flask equipped with a stirrer bar was charged with Meldrum's acid (12.972 g, 90.00 mmol) and trimethyl orthoformate (171.161 mL, 1500.00 mmol). The reaction mixture was refluxed for 4 h on a magnetic stirrer plate after which 4-bromo-2-nitroaniline (13.021 g, 60.00 mmol) was added and the refluxing was continued for 20 h. After completion of the reaction, the excess of trimethyl orthoformate was evaporated and the solids were suspended in Et_2O. The solids were then filtrated off and washed with Et_2O.

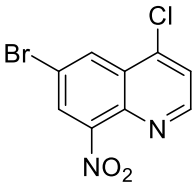


Step 2: Cyclization. A round-bottom flask equipped with a stirrer bar was charged with the crude intermediate (6.000 g, 16.17 mmol), which was dissolved in PhOPh (2 mL/mmol) and refluxed for 4 h in a heating mantle on magnetic stirrer plate. After completion, the reaction mixture was cooled down and diluted with Et_2O. The precipitated solids were then filtrated off and washed with Et_2O. Yield 55% (2.392 g, 8.89 mmol). The characterization data of the obtained compound are in agreement with the literature values.[21]

Characterization data: brown solid; R_f = 0.31 (DCM:EtOAC (1:1)); **mp.** 253-254 °C; **^{1}H NMR** (400 MHz; DMSO-d_6) δ_h 11.89 (s, 1H), 8.72 (s, 1H), 8.60 – 8.54 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR** (101 MHz; DMSO-d_6) δ_c 174.5, 141.4, 137.5, 135.2, 133.0, 132.0, 129.0, 113.5, 110.7; **FTIR**(cm^{-1}) 3183(w), 3076(w), 1475(s), 1280(s), 1177(s).

Synthesis of 6-bromo-4-chloro-8-nitroquinoline – S8.

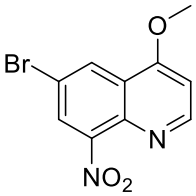
The title compound was synthesized following the general procedure for chlorination of hydroxyquinolines. Starting from 6-bromo-8-nitroquinolin-4-ol – **S7** (1.345 g, 5.00 mmol) and $POCl_3$ (4.662 mL, 50.00 mmol). Reaction time was 22 h. Yield 28% (0.403 g, 1.40 mmol). Purification: Flash chromatography (SiO_2) using DCM as eluent. The characterization data of the obtained compound are in agreement with the literature values.[20]



Characterization data: orange solid; R_f = 0.54 (DCM); **mp.** 176-177°C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.92 (d, *J* = 4.7 Hz, 1H), 8.61 (d, *J* = 2.1 Hz, 1H), 8.15 (d, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 4.7 Hz, 1H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 152.3, 149.0, 142.1, 139.4, 130.4, 128.6, 127.9, 123.8, 120.0; **FTIR**(cm^{-1}) 3063(w), 3035(w), 3002(w), 1528(s), 1339(s), 872(s), 723(s).

Synthesis of 6-bromo-4-methoxy-8-nitroquinoline – 1f.

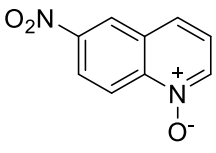
The title compound was synthesized following the general procedure for preparation of ethers Method A. Starting from 6-bromo-4-chloro-8-nitroquinoline – **S8** (0.359 g, 1.25 mmol) and 5M solution of NaOMe (0.300 mL, 1.5 mmol). Reaction time was 1 h. Yield 91% (0.322 g, 1.14 mmol). Purification: Flash chromatography (SiO_2) using DCM→DCM:EtOAc (20:1) as eluent.



Characterization data: white-yellowish solid; R_f = 0.22 (DCM); **mp.** 138-139 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.87 (d, *J* = 5.2 Hz, 1H), 8.56 (d, *J* = 2.2 Hz, 1H), 8.08 (d, *J* = 2.3 Hz, 1H), 6.88 (d, *J* = 5.2 Hz, 1H), 4.09 (s, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 161.4, 154.1, 148.5, 139.4, 128.8, 127.5, 123.8, 117.3, 102.4, 56.5; **FTIR**(cm^{-1}) 3079(w), 2985(w), 2949(w), 1344(s), 1303(s), 1020(s), 840(s); **HRMS** calcd for $C_{10}H_8BrN_2O_3$ 282.9713 (M+H), found 282.9706.

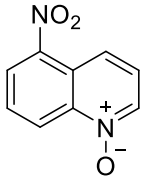
Synthesis of 6-nitroquinoline 1-oxide – 1i.

The title compound was synthesized following the general procedure for preparation of quinoline *N*-oxides. Starting from 6-nitroquinoline (0.522 g, 3.0 mmol) and H_2O_2 33% assay (0.463 g, 4.5 mmol). Reaction time was 4 h. Yield 28% (0.161 g, 0.85 mmol). Purification: Flash chromatography (SiO_2) using EtOAC→Acetone as eluent. The characterization data of the obtained compound are in agreement with the literature values.[14a,22]



Characterization data: yellow solid; R_f = 0.40 (DCM:MeOH (20:1)); **mp.** 216-217 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 9.15 (d, *J* = 2.4 Hz, 1H), 8.77 (dd, *J* = 6.1, 1.0 Hz, 1H), 8.71 (dt, *J* = 9.6, 0.7 Hz, 1H), 8.48 (dd, *J* = 9.5, 2.5 Hz, 1H), 8.28 – 8.20 (m, 1H), 7.66 (dd, *J* = 8.5, 6.1 Hz, 1H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 146.7, 142.7, 138.0, 129.9, 126.6, 125.5, 124.1, 123.4, 121.4; **FTIR**(cm^{-1}) 3114(w), 3055(w), 1347(m), 796(s), 753(s).

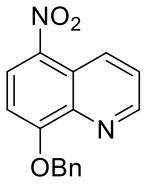
Synthesis of 5-nitroquinoline 1-oxide – 1j.



The title compound was synthesized following the general procedure for preparation of quinoline *N*-oxides. Starting from 5-nitroquinoline (0.522 g, 3.0 mmol) and H_2O_2 33% assay (0.463 g, 4.5 mmol). Reaction time was 3 h. Yield 49% (0.280 g, 1.47 mmol). Purification: Flash chromatography (SiO_2) using DCM:MeOH (40:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[21,23]

Characterization data: yellow solid; R_f = 0.19 (EtOAc); **mp.** 159-160 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.94 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 6.1 Hz, 1H), 8.54 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 9.0 Hz, 1H), 7.98 (t, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 9.1, 6.1 Hz, 1H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 146.0, 141.6, 136.2, 129.0, 126.7, 125.4, 124.9, 123.1, 119.8; **FTIR**(cm^{-1}) 3097(w), 3079(w), 1509(s), 1339(s), 1261(s), 772(s).

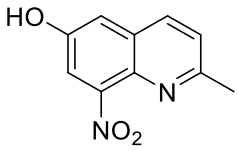
Synthesis of 8-(benzyloxy)-5-nitroquinoline – 1l.



The title compound was synthesized following the general procedure for preparation of ethers Method B. Starting from 5-nitroquinolin-8-ol (0.951 g, 5.0 mmol), K_2CO_3 (1.382 g, 10.0 mmol) and benzyl bromide (0.891 mL, 7.5 mmol). Reaction time was 24 h. Yield 53% (0.743 g, 2.65 mmol). Purification: Flash chromatography (SiO_2) using DCM→DCM:EtOAc (20:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[11]

Characterization data: dark yellow solid; R_f = 0.20 (DCM); **mp.** 108-109 °C; **^{1}H NMR** (500 MHz; $CDCl_3$) δ_h 9.22 (dd, *J* = 8.9, 1.6 Hz, 1H), 9.07 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 7.70 (dd, *J* = 8.9, 4.2 Hz, 1H), 7.51 (ddt, *J* = 7.4, 1.3, 0.7 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.38 – 7.30 (m, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 5.55 (s, 2H); **^{13}C NMR** (126 MHz; $CDCl_3$) δ_c 159.9, 150.4, 139.8, 137.9, 135.5, 132.7, 129.1, 128.6, 127.4, 127.3, 124.7, 123.3, 107.4, 71.6; **FTIR**(cm^{-1}) 3092(w), 3059(w), 3030(w), 1291(s), 741(s), 723(s), 692(s).

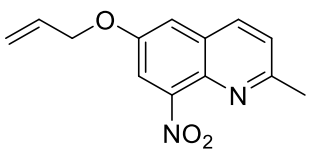
Synthesis of 2-methyl-8-nitroquinolin-6-ol – S9.



A round-bottom flask equipped with a stirrer bar was charged with 4-Amino-3-nitrophenol (4.624 g, 30.00 mmol) suspended in a mixture of 35 mL of conc. HCl and 15 g *o*.H_3PO_4. The suspension was warmed up to 80 °C. Crotonaldehyde (2.734 mL, 33.00 mmol) was added to the suspension dropwise during $2^{1/2}$ h. After the complete addition of the Crotonaldehyde the reaction mixture was kept at 95 °C for 3 h on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The reaction mixture was extracted with EtOAc. The organics were discarded and the aqueous layer was neutralize with $NaHCO_3$ and re extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography. Yield 40% (2.450 g, 12.00 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (4:1→1:1) as eluent. The characterization data of the obtained compound are in agreement with the literature values.[24]

Characterization data: dark orange solid; R_f = 0.31 (DCM:EtOAc (20:1)); **mp.** >330 °C; **^{1}H NMR** (400 MHz; DMSO-d_6) δ_h 10.60 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 2.6 Hz, 1H), 2.58 (s, 3H); **^{13}C NMR** (101 MHz; DMSO-d_6) δ_c 1157.9, 153.6, 148.1, 134.8, 132.9, 128.1, 124.0, 114.8, 112.3, 24.8; **FTIR**(cm^{-1}) 3600(w), 3000(br. w), 1528(s), 871(s), 780(s).

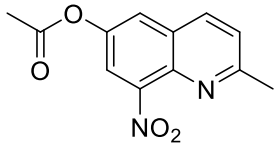
Synthesis of 6-(allyloxy)-2-methyl-8-nitroquinoline – 1m.



The title compound was synthesized following the general procedure for preparation of ethers Method B. Starting from 2-methyl-8-nitroquinolin-6-ol – **S9** (0.408 g, 2.0 mmol), K_2CO_3 (0.553 g, 4.0 mmol) and allyl bromide (0.203 mL, 2.4 mmol). Reaction time was 24 h. Yield 57% (0.279 g, 1.14 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (4:1) as eluent.

Characterization data: white-yellowish solid; R_f = 0.5 (DCM); **mp.** 114-115 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 7.97 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 2.7 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.2 Hz, 1H), 5.47 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.36 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.67 (dt, *J* = 5.2, 1.5 Hz, 2H), 2.71 (s, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 159.5, 154.5, 148.6, 135.1, 134.9, 132.2, 128.3, 124.1, 118.7, 116.1, 110.8, 69.8, 25.6; **FTIR**(cm^{-1}) 1538(s), 1245(s), 783(s); **HRMS** calcd for $C_{13}H_{13}N_2O_3$ 245.0921 (M+H), found 245.0930.

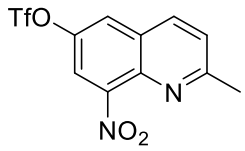
Synthesis of 2-methyl-8-nitroquinolin-6-yl acetate – 1n.



A round-bottom flask equipped with a stirrer bar was charged with 2-methyl-8-nitroquinolin-6-ol – **S9** (0.408 g, 2.0 mmol) suspended in 20 mL of DCM. Pyridine (0.322 mL, 4.0 mmol) was added to the suspension and the reaction mixture was cooled down to 0 °C. Acetic anhydride (0.284 mL, 3.0 mmol) dissolved in 5 mL of DCM was added to the cooled reaction mixture dropwise during 10 min. After the complete addition of the Acetic anhydride the reaction mixture was kept at room temperature under Argon for 24 h on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The reaction mixture was extracted with DCM, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography. Yield 72% (0.354 g, 1.44 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (4:1→2:1) as eluent.

Characterization data: yellowish solid; R_f = 0.43 (DCM); **mp.** 159-160 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.06 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 2.76 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 168.9, 162.0, 148.2, 146.0, 137.3, 135.7, 127.6, 124.4, 122.4, 119.1, 25.8, 21.2; **FTIR**(cm^{-1}) 1752(m), 1533(s), 1192(s), 918(s), 782(s); **HRMS** calcd for $C_{12}H_{11}N_2O_4$ 247.0713 (M+H), found 247.0705.

Synthesis of 2-methyl-8-nitroquinolin-6-yl trifluoromethanesulfonate – 1o.

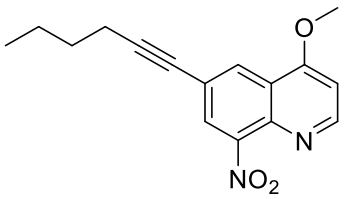


A round-bottom flask equipped with a stirrer bar was charged with 2-methyl-8-nitroquinolin-6-ol – **S9** (1.021 g, 5.0 mmol) suspended in 50 mL of DCM. Pyridine (0.805 mL, 10.0 mmol) was added to the suspension and the reaction mixture was cooled down to 0 °C. Trifluoromethanesulfonic anhydride (1.230 mL, 7.5 mmol) dissolved in 10 mL of DCM was added to the cooled reaction mixture dropwise during 10 min. After the complete addition of the trifluoromethanesulfonic anhydride the reaction mixture was kept at room temperature under Argon for 24 h on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The reaction mixture was extracted with DCM, dried over Na_2SO_4 and evaporated to dryness. The crude was purified by SiO_2 flash chromatography. Yield 51% (0.857 g, 2.55 mmol). Purification: Flash chromatography (SiO_2) using *n*-hexane:EtOAc (4:1) as eluent.

Characterization data: yellow solid; R_f = 0.22 (*n*-hexane:EtOAc (5:1)); **mp.** 111-112 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.16 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 2.7 Hz, 1H), 7.86 (d, *J* = 2.7 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 2.80 (s, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 163.9, 148.8, 144.2, 138.2, 135.9, 127.7, 125.4, 122.9, 117.5, **123.6, 120.4, 117.2, 114.0**

(q, *J* = 321.1 Hz), 26.0; **^{19}F NMR** (376 MHz; $CDCl_3$) δ_f -72.37;**FTIR**(cm^{-1}) 3081(w), 1209(m), 1137(m), 610(s); **HRMS** calcd for $C_{11}H_8F_3N_2O_5S$ 337.0101 (M+H), found 337.0089.

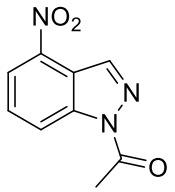
Synthesis of 6-(hex-1-yn-1-yl)-4-methoxy-8-nitroquinoline – 1p.



A Schlenk-tube equipped with a stirrer bar was charged with 6-bromo-4-methoxy-8-nitroquinoline – **1f** (0.198 g, 0.70 mmol), Bis(triphenylphosphine)palladium(II) dichloride (0.025 g, 0.035 mmol) and Copper(I) iodide (0.007 g, 0.035 mmol). The tube was evacuated and back filled with Argon three times. A 10 mL of degassed solvent mixture THF/Et_3N (1:1) was added to the Schlenk-tube followed by degassed 1-Hexyne (0.121 mL, 1.05 mmol). The reaction mixture was refluxed under Argon for $2^{1/2}$ h on a magnetic stirrer plate. After completion of the reaction, the mixture was evaporated to dryness. The crude was purified by SiO_2 flash chromatography. Yield 92% (0.183 g, 0.64 mmol). Purification: Flash chromatography (SiO_2) using DCM→DCM:EtOAc (40:1) as eluent.

Characterization data: white-brownish solid; R_f = 0.23 (DCM); **mp.** 90-91 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.84 (d, *J* = 5.3 Hz, 1H), 8.40 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 5.3 Hz, 1H), 4.08 (s, 3H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.67 – 1.58 (m, 2H), 1.55 – 1.45 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 161.7, 153.7, 147.8, 139.5, 128.7, 127.0, 122.5, 120.7, 101.9, 93.8, 78.7, 56.2, 30.5, 22.0, 19.1, 13.6; **FTIR**(cm^{-1}) 2953(w), 2932(w), 2871(w), 2227(w), 1526(s), 1345(s), 1302(s), 1018(s), 749(s); **HRMS** calcd for $C_{16}H_{17}N_2O_3$ 285.1234 (M+H), found 285.1224.

Synthesis of 1-(4-nitro-1H-indazol-1-yl)ethan-1-one – 3d.



A round-bottom flask equipped with a stirrer bar was charged with 4-nitro-1H-indazole (0.489 g, 3.0 mmol) then acetic anhydride 10 mL was added and the reaction mixture was refluxed for 2 h on a magnetic stirrer plate. After completion of the reaction, the mixture was quenched with water. The formed solids were filtrated off and were washed with plenty of water. The solids were dissolved in EtOAc and were extracted between EtOAc and saturated solution of $NaHCO_3$, dried over Na_2SO_4 and evaporated to dryness. Yield 94% (0.579 g, 2.82 mmol). The characterization data of the obtained compound are in agreement with the literature values.[25]

Characterization data: light-orange solid; R_f = 0.44 (*n*-hexane:EtOAc (5:1)); **mp.** 140-141 °C; **^{1}H NMR** (400 MHz; $CDCl_3$) δ_h 8.85 (dt, *J* = 8.4, 0.8 Hz, 1H), 8.80 (d, *J* = 0.8 Hz, 1H), 8.29 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 2.85 (s, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$) δ_c 171.4, 140.5, 140.5, 138.2, 129.2, 122.3, 121.1, 119.9, 23.3; **FTIR**(cm^{-1}) 1723(s), 1333(s), 1180(s), 939(s), 741(s).

Computational details

All computations were performed using TURBOMOLE 7.3 program package.[26] Structures were optimized using the PBE0-D3[27,28] dispersion corrected hybrid density functional with triple-ζ basis sets, def2-TZVP.[29] Final energies were computed using PW6B95-D3[30] density functional and def2-TZVPD basis sets.[31] In structure optimizations, solvent effects were accounted for using the COSMO[32] solvation model for methanol (ε = 32.7), being the main component of the solvent. The solvation free energies for final energies were then calculated using the COSMO-RS[33] solvation model for 1:4 (v/v) mixture of water and methanol. These were performed using the COSMOthermX19 program package with parameter file BP_TZVPD_FINE_19.ctd based on BP86[34]/def2-TZVPD computational level. Standard state Gibbs free energies were computed according to protocol described elsewhere:[35,36] $G_{soln} = E_{gas}(SCF) + c.p. + G_{solv}$, where $E_{gas}(SCF)$ is the gas-phase energy at PW6B95-D3/def2-TZVPD level, c.p. is the chemical potential, and G_{solv} is the solvation free energy to solvent mixture. Internal Gibbs free energy (c.p.) was calculated by quasi-RRHO approximation proposed by Grimme.[35] All thermodynamic functions were calculated in 298.15 K and no scaling factor was used for harmonic vibrational frequencies.

pK_a and pK_{aH} values were calculated as $pK_{a(H)} = -\Delta G_{soln} / RTln(10) + pK_{ref} \approx -\Delta G_{soln} / 1.3642 + pK_{ref}$, where pK_{ref} = 4.76 of acetic acid was used for neutral acids, and pK_{ref} = 6.95 of imidazolinium cation was used for cationic acids. The effect of using 1:4 H_2O:MeOH solvent mixture instead of pure water on $pK_{a(H)}$ is approximated to be small and systematic:[37] acidity of neutral acids decreases and cationic acids increases.

Redox potentials are calculated against SCE in methanol[38] using $E° = -\Delta G_{soln} / nF - E°_{ref} \approx -\Delta G_{soln} / 23.061 - E°_{ref}$, where *n* is the number of transferred electron, F is the Faraday's constant, and $E°_{ref}$ = 4.597 V.

Substrate comparison

For understanding the operative reaction mechanism, we studied selected substrates with three different reactivities (Figure S15):

1) Different derivatives of 8-nitro-quinolines (**1c**, **1d**, and **1g**) were considered as reactive substrates
2) Pyrazole **3a**, quinoxazole **3b**, and 5-nitro-8-hydroxylquinoline **3c** represent three unreactive ones
3) Nitrobenzene **4**, and 1-acetyl-4-nitroindazole **3d**, were selected as substrates that yield exclusively hydroxyl amine

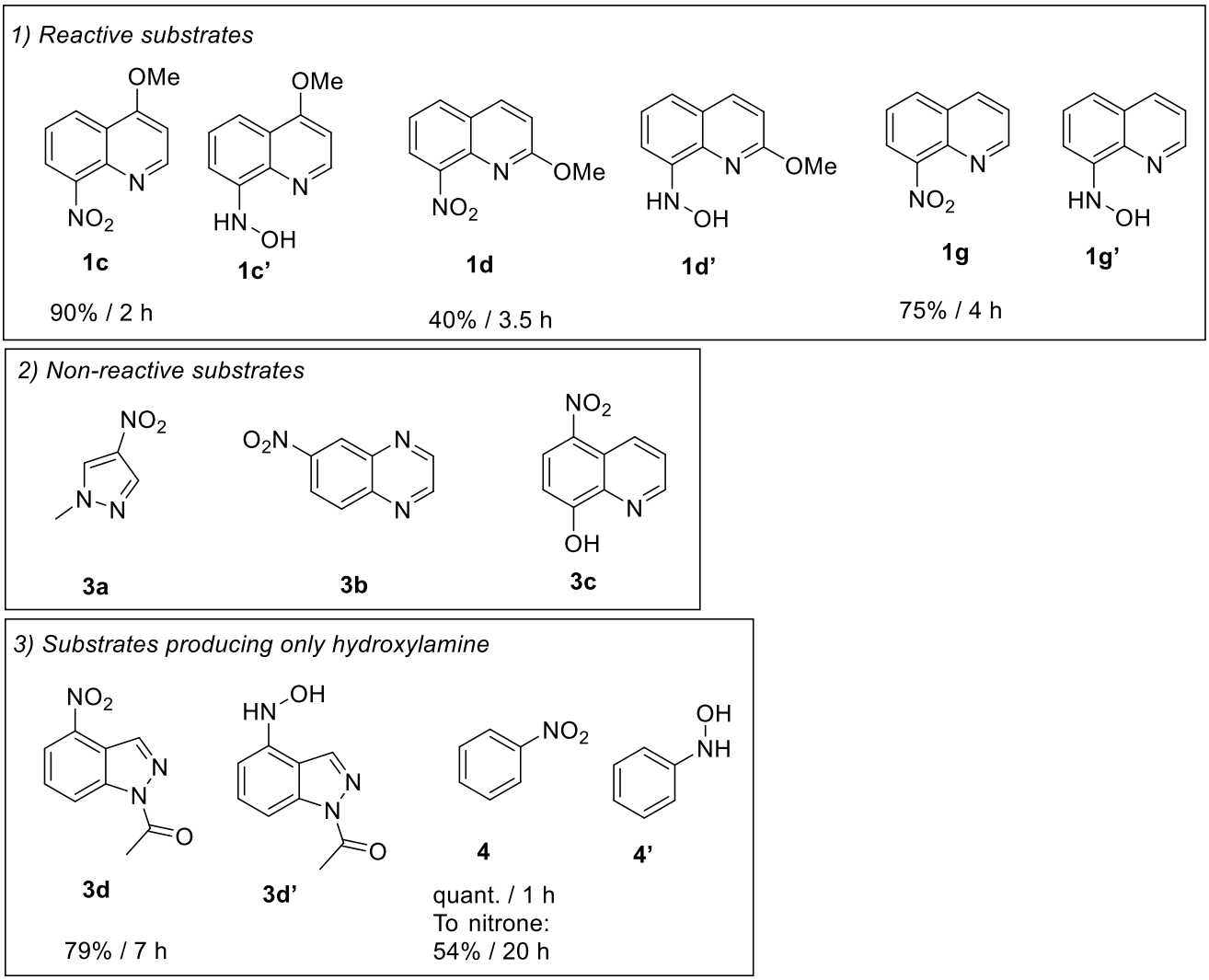


Figure S15. List of substrates and corresponding hydroxylamines used for comparison: top row - working substrates; middle row - no reaction; bottom row - hydroxylamine as the product.

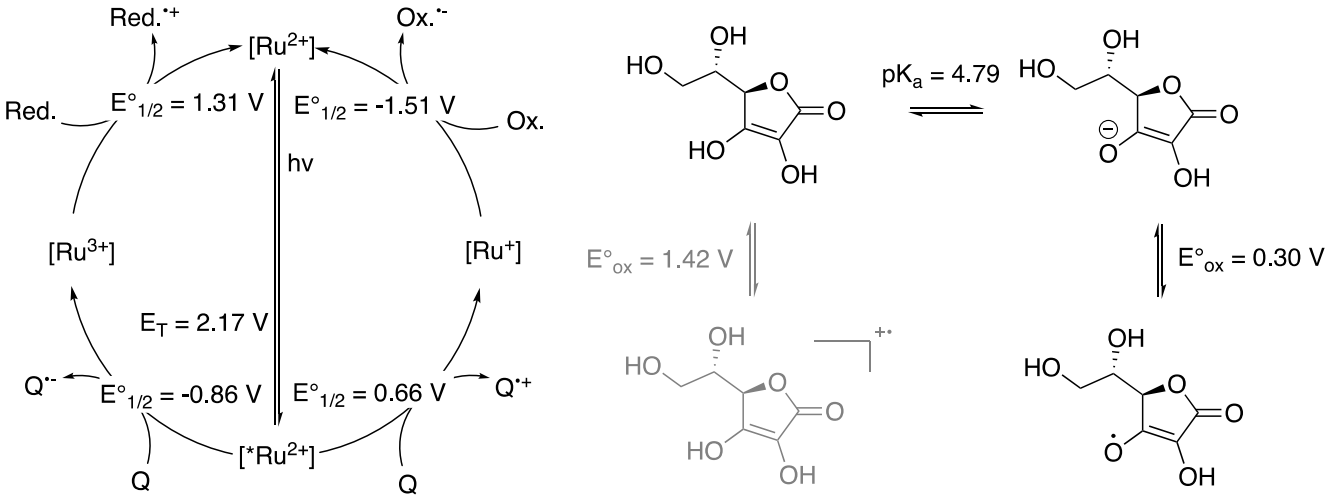
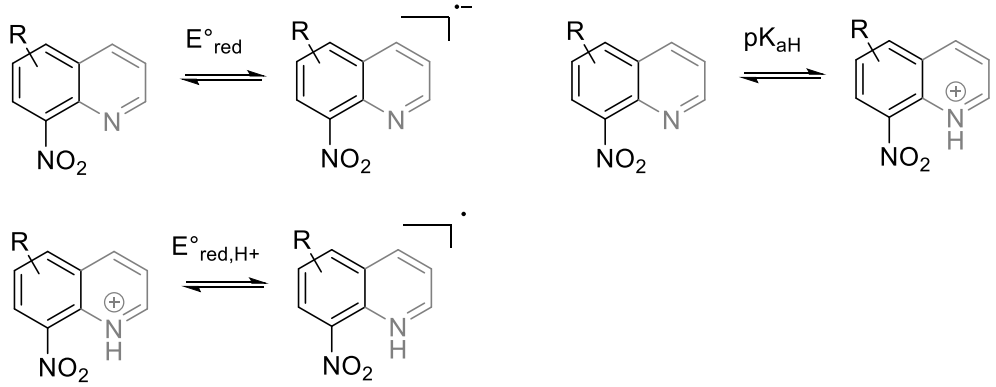


Figure S16. Computational redox-potentials for $Ru(bpy)_3^{2+}$ ($[Ru^{2+}]$) and $AscH_2$ against SCE in methanol, and pK_a-values for $AscH_2$ in methanol:water 4:1 (v/v) referenced to acetic acid.

Table S8. Oxidation potentials, (V, SCE) and Gibbs free energies (kcal/mol) for ascorbic acid

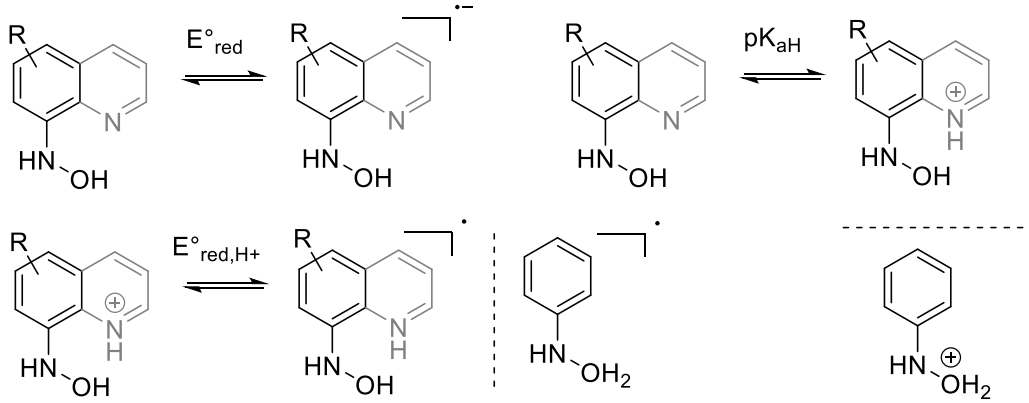
Entry	$\mathbf{E°_{ox}}$(SCE)	$\mathbf{\Delta G_{ox}}$(*Ru^{2+})	$\mathbf{\Delta G_{ox}}$(Ru^{3+})
1	1.42	17.5	2.5
2	0.30	-8.3	-23.3

Table S9. Reduction potentials, (V, SCE), pK_{aH}-values, and Gibbs free energies (kcal/mol) for selected nitro-quinolines



Entry	Substrate	E°_{red} (SCE)	ΔG_{red} ($*Ru^{2+}$)	ΔG_{red} (Ru^{+})	$E^{\circ}_{red,H+}$ (SCE)	$\Delta G_{red,H+}$ ($*Ru^{2+}$)	$\Delta G_{red,H+}$ (Ru^{+})	pK_{aH}	ΔG ($AscH_2$)
1	**1c**	-0.95	2.1	-12.91	-0.42	-10.1	-25.1	4.30	0.7
2	**1d**	-1.05	4.4	-10.61	-0.48	-8.8	-23.8	0.75	5.5
3	**1g**	-1.00	3.2	-11.76	-0.31	-12.7	-27.7	0.60	5.7
4	**3a**	-1.04	4.2	-10.84	-0.79	-1.6	-16.6	-6.51	15.4
5	**3b**	-0.73	-3.0	-17.99	0.03	-20.5	-35.5	-4.92	13.2
6	**3c**	-0.99	3.0	-11.99	-0.49	-8.5	-23.5	0.21	6.2
7	**3d**	-0.93	1.6	-13.38	-0.82	-0.9	-15.9	-6.51	15.4
8	**4**	-0.92	1.4	-13.61	-	-	-	-	-

Table S10. Reduction potentials, (V, SCE), pK_{aH}-values, and Gibbs free energies (kcal/mol) for selected hydroxylamine-quinolines

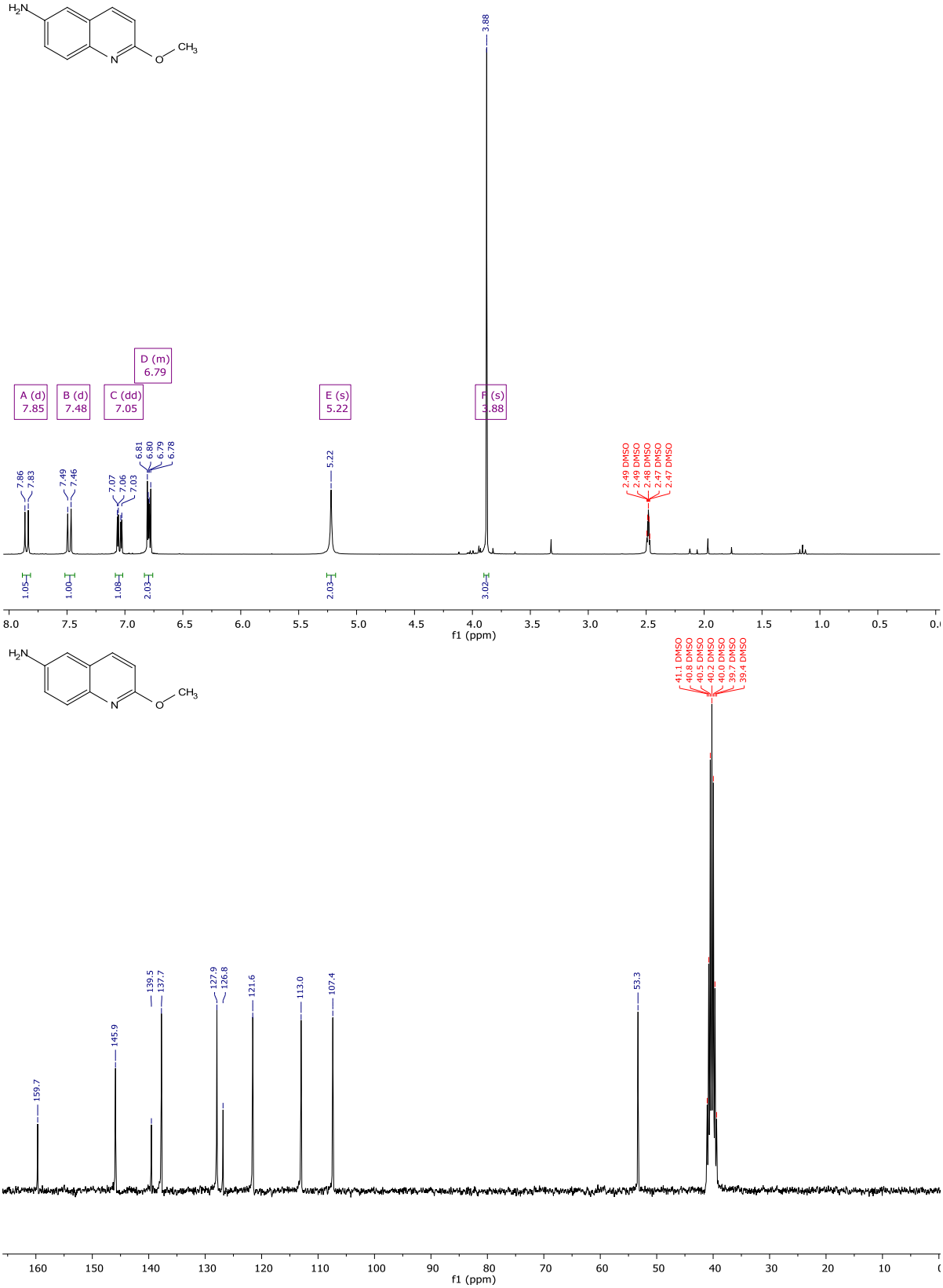


Entry	Substrate	E°_{red} (SCE)	ΔG_{red} (*Ru^{2+})	ΔG_{red} (Ru^{+})	$E^{\circ}_{red,H+}$ (SCE)	$\Delta G_{red,H+}$ (*Ru^{2+})	$\Delta G_{red,H+}$ (Ru^{+})	pK_{aH}	ΔG ($AscH_2$)
1	**1c'**	-2.28	32.7	17.8	-1.40	12.5	-2.5	5.34	-0.8
2	**1d'**	-2.14	29.5	14.5	-1.26	9.2	-5.8	3.05	2.4
3	**1g'**	-2.07	27.9	12.9	-1.07	4.8	-10.1	3.34	2.0
4	**3d'**	-2.21	31.1	16.1	-1.20	7.8	-7.1	-2.60	10.1
5	**4'**[a]	-3.41	58.8	43.8	-0.15	-16.4	-31.4	-1.76	8.9

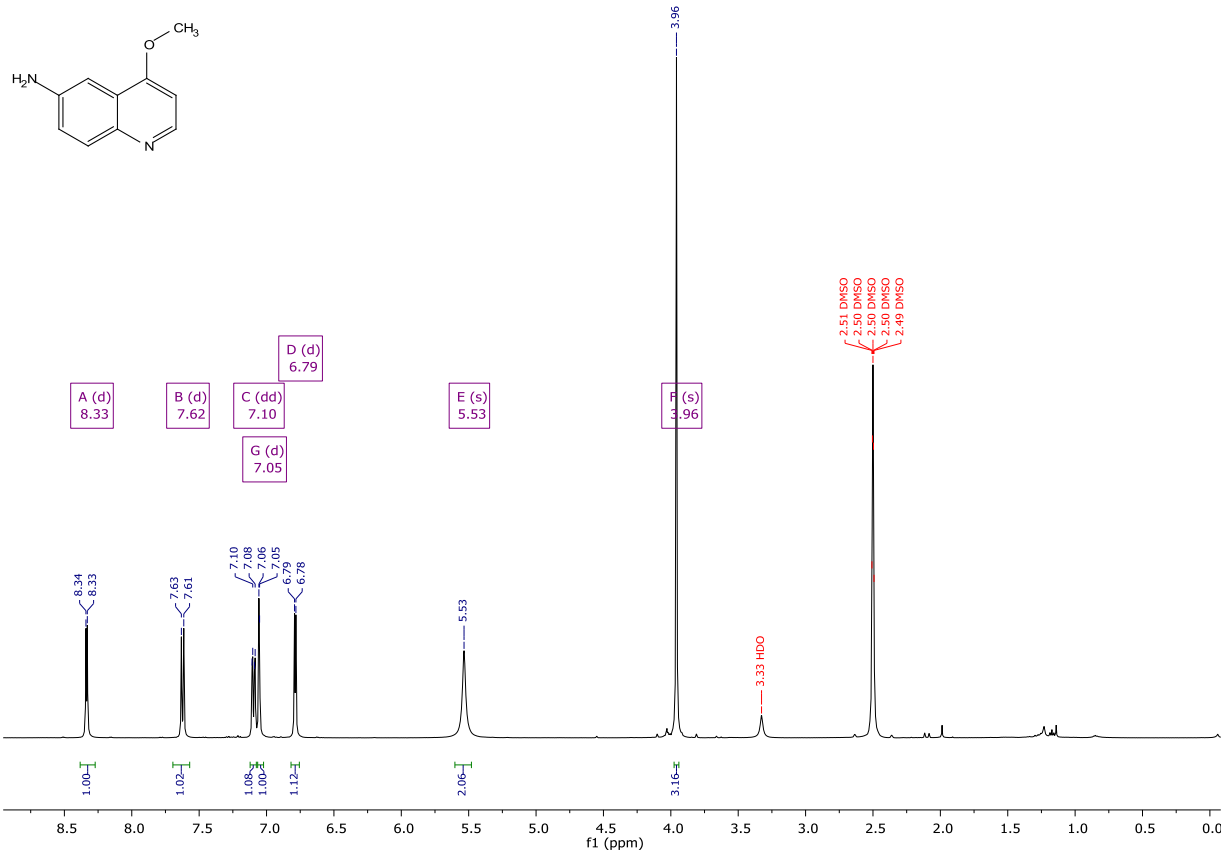
[a]Protonation of **4'** at oxygen in hydroxylamine.

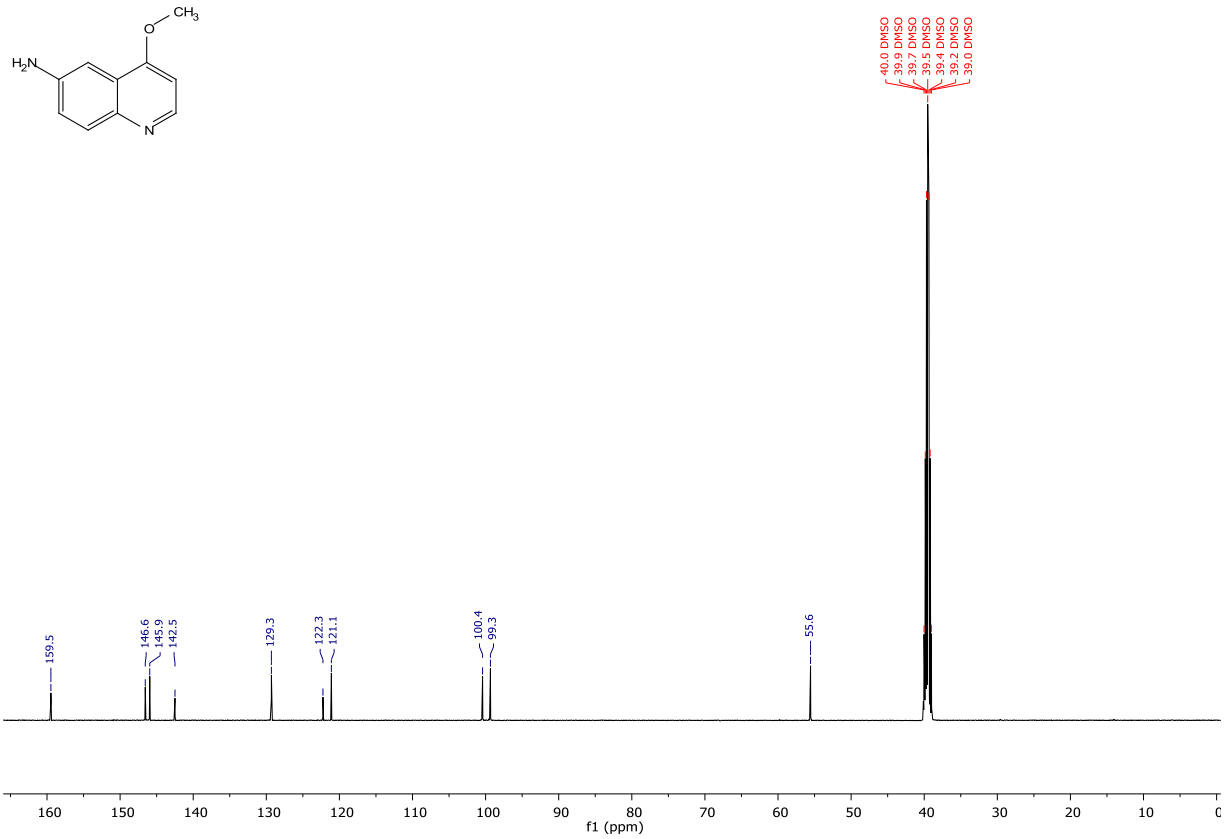
Copy of spectral data

^{1}H and $^{13}C\{1H\}$ spectra of 2-methoxyquinolin-6-amine – **2a** in DMSO-d_6.

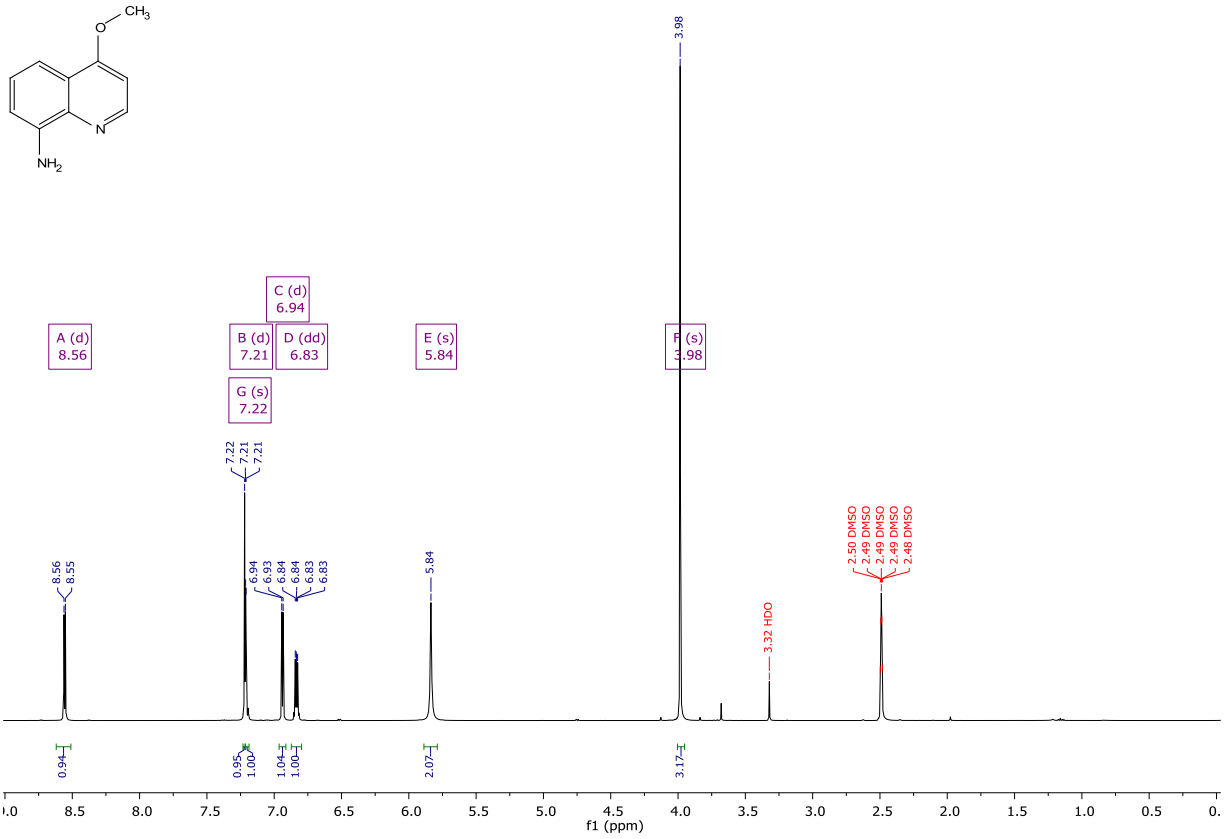


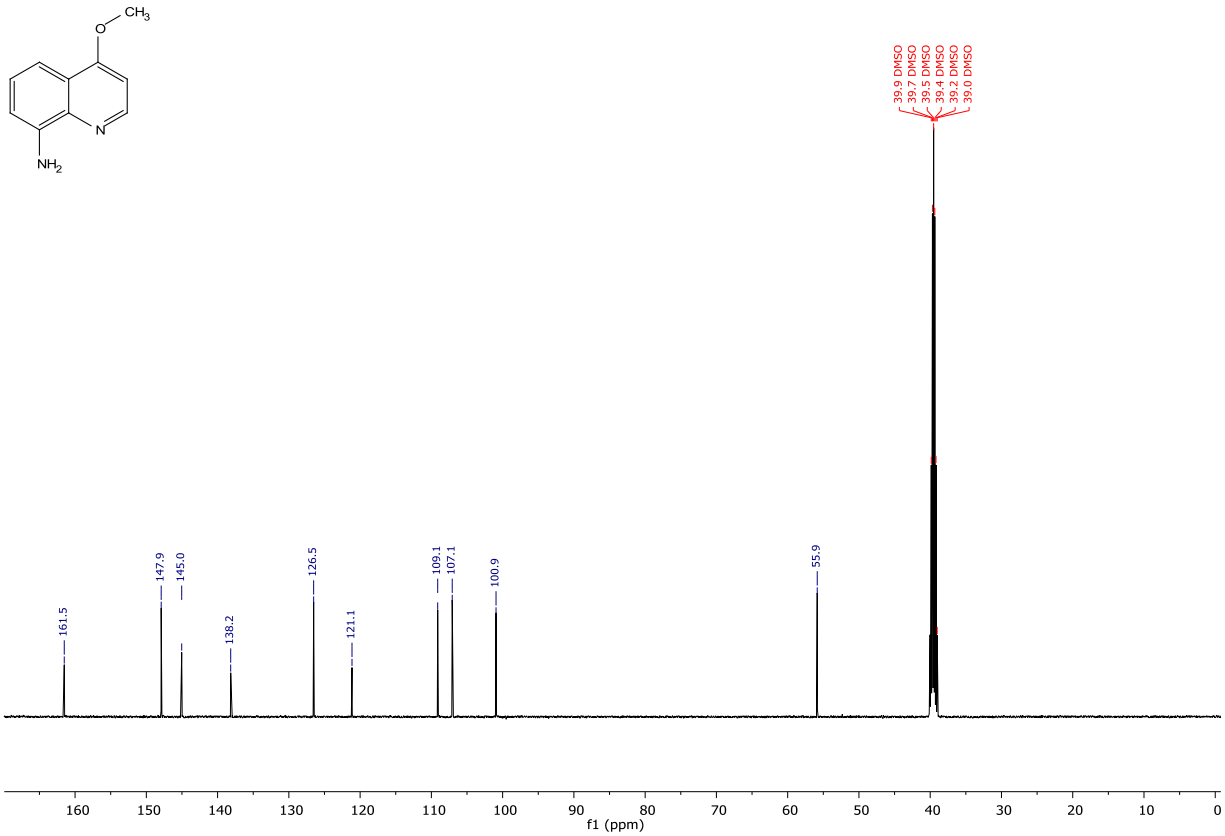
^{1}H and ^{13}C{1H} spectra of 4-methoxyquinolin-6-amine – **2b** in DMSO-d_6.



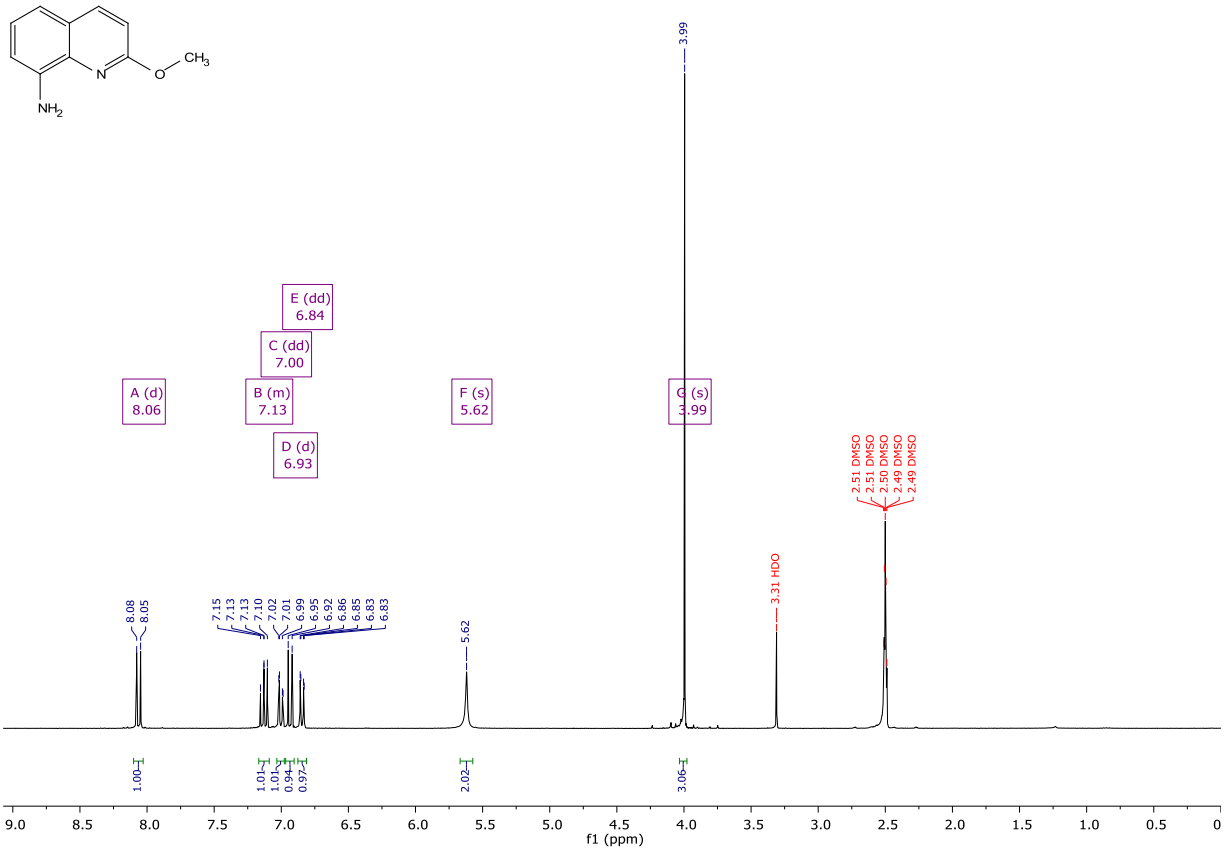


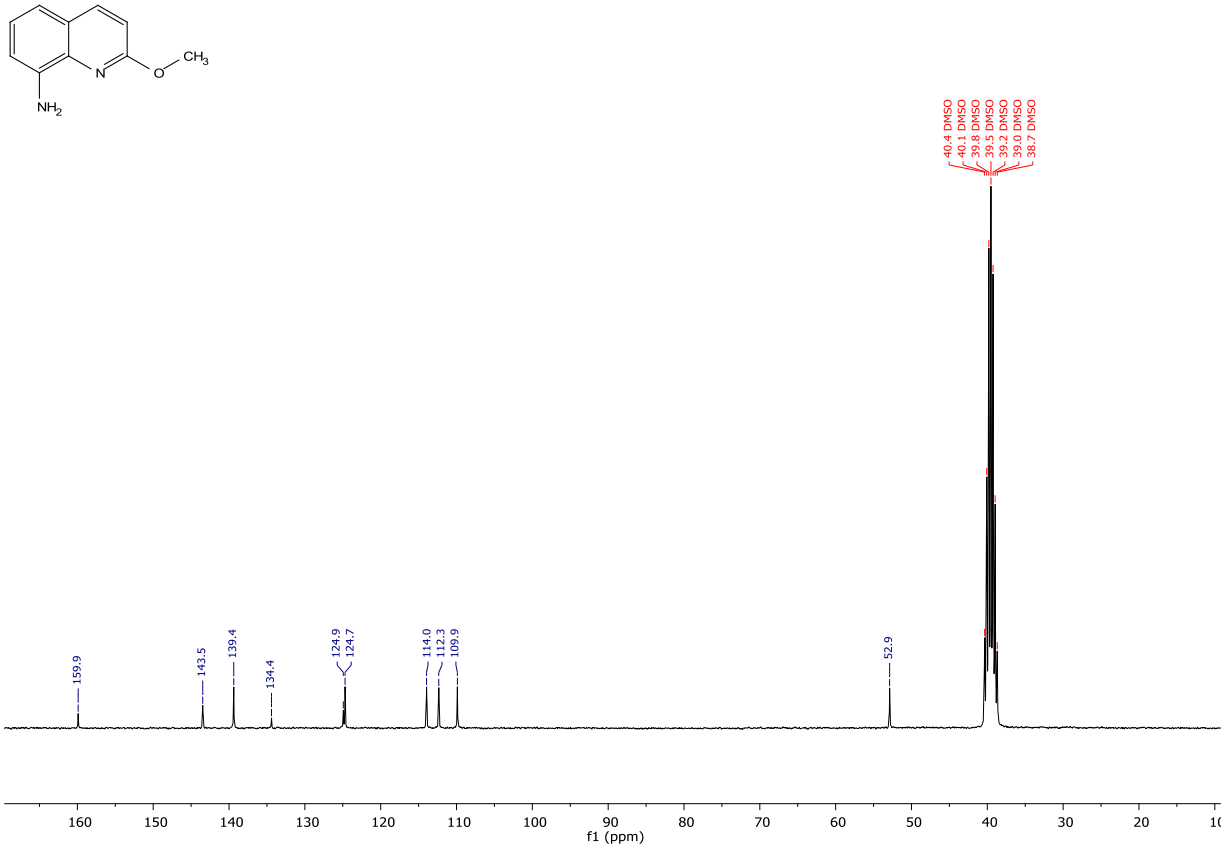
^{1}H and ^{13}C{1H} spectra of 4-methoxyquinolin-8-amine – **2c** in DMSO-*d*$_6$.



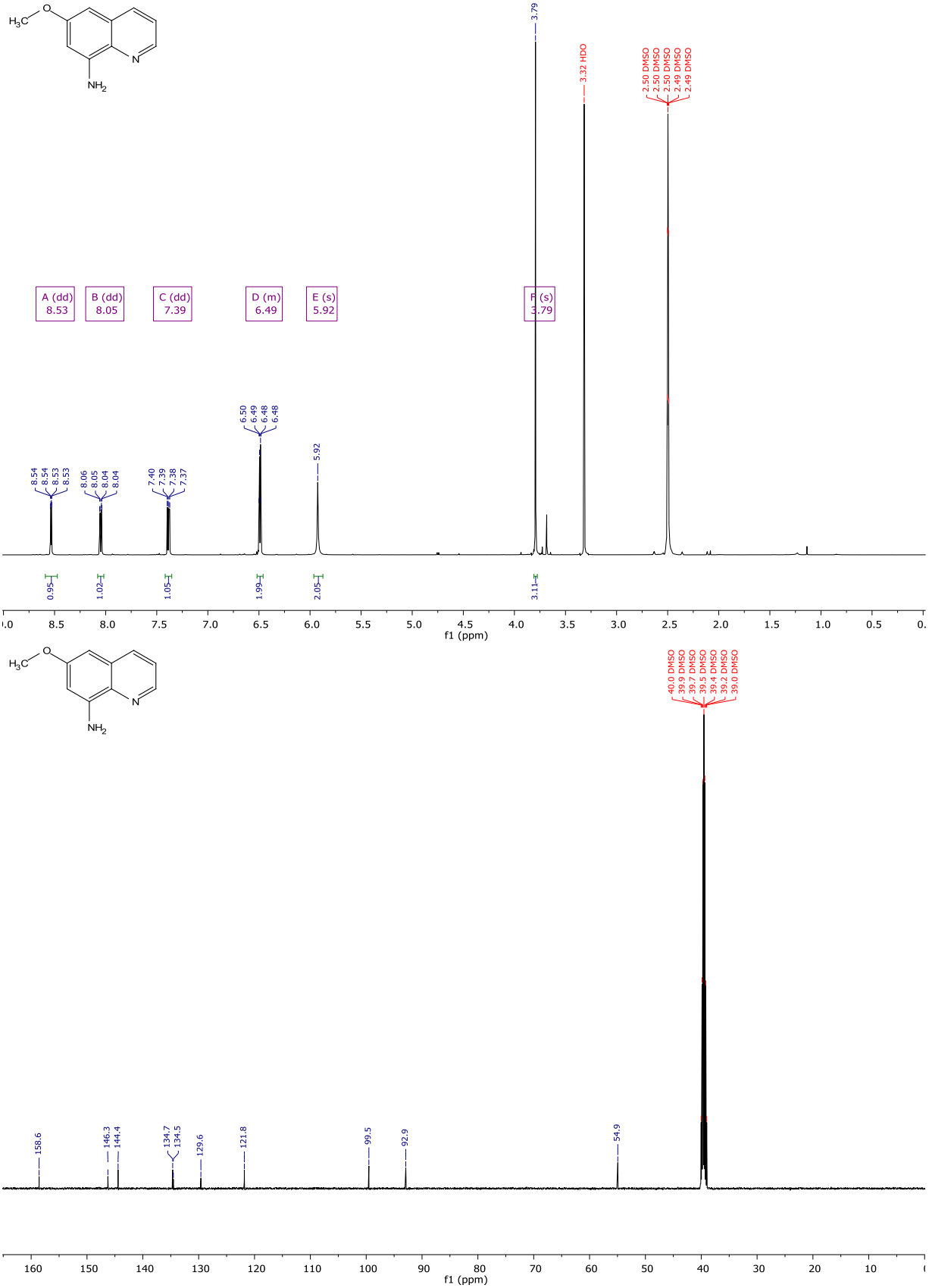


^{1}H and ^{13}C{1H} spectra of 2-methoxyquinolin-8-amine – **2d** in DMSO-d_6.



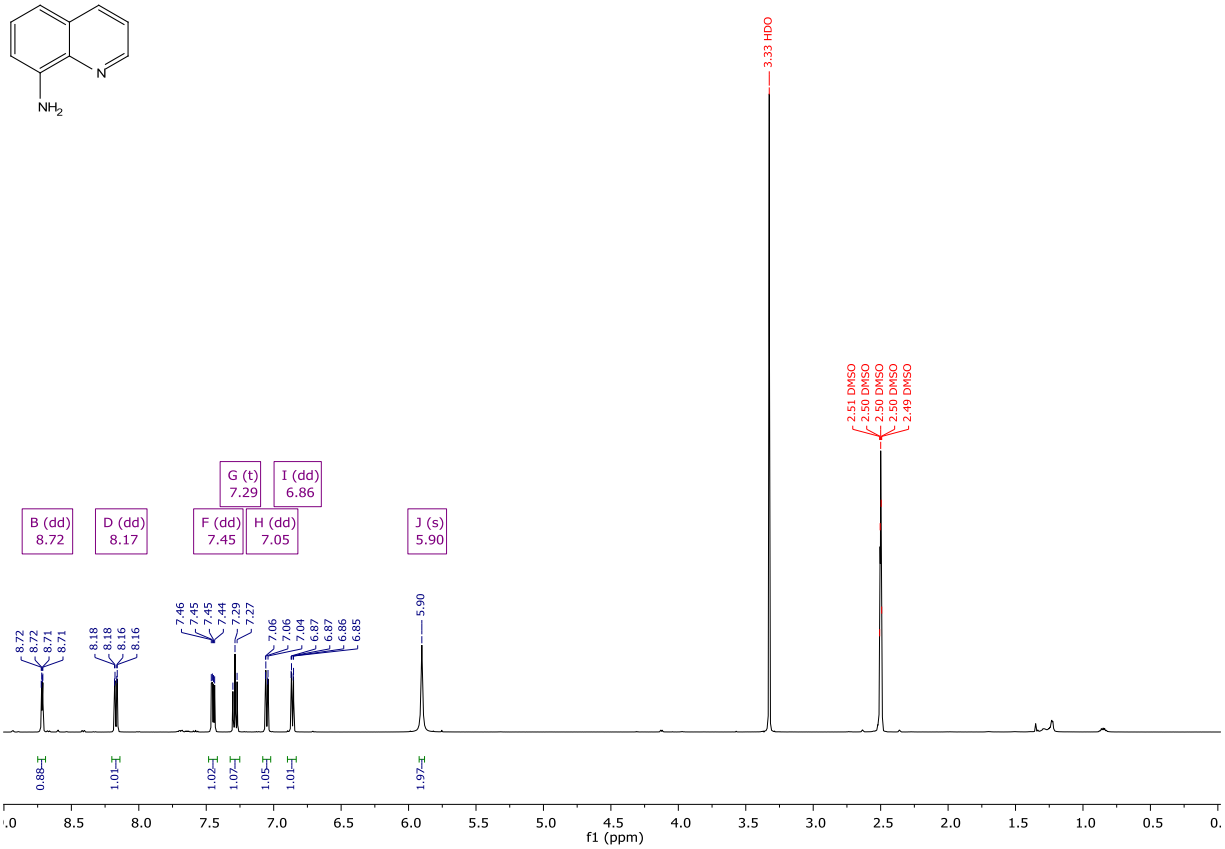


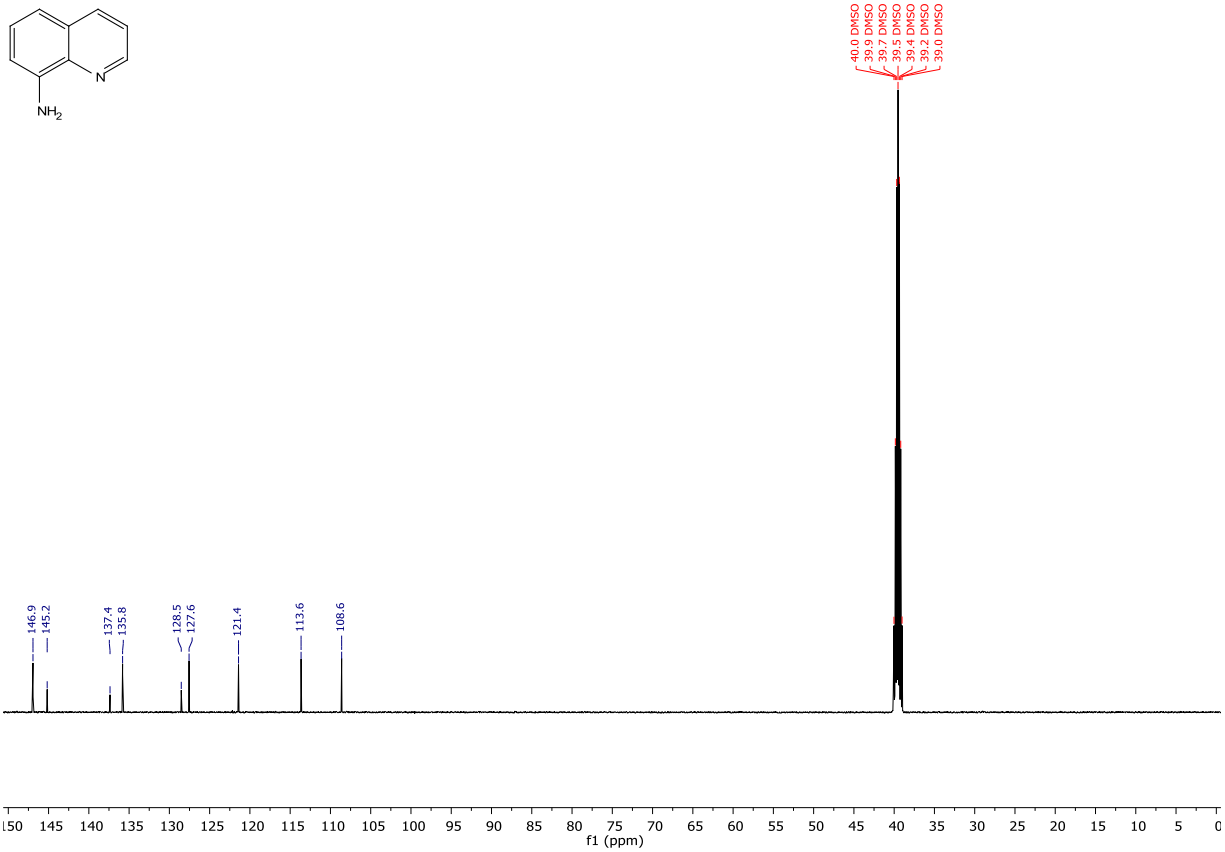
^{1}H and ^{13}C{1H} spectra of 6-methoxyquinolin-8-amine – **2e** in DMSO-d_6.



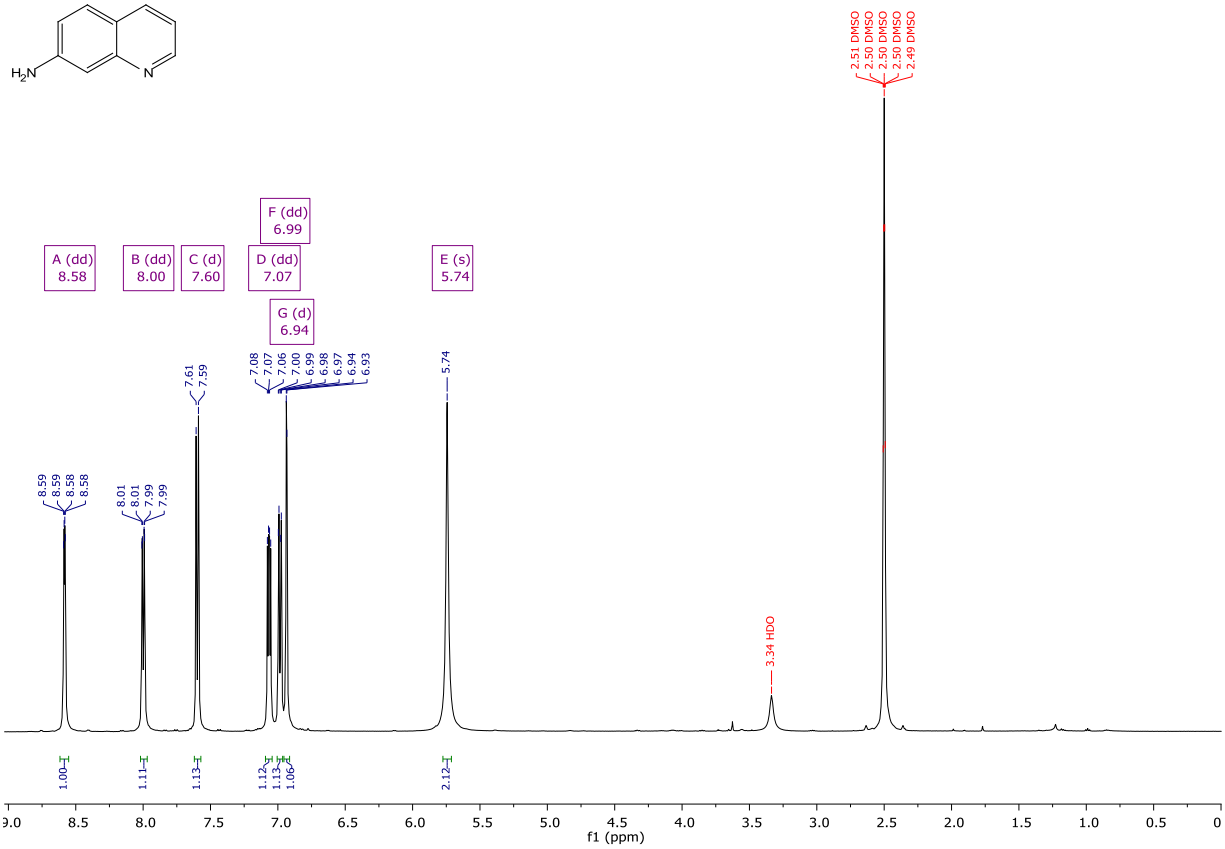
^{1}H and ^{13}C{1H} spectra of 6-bromo-4-methoxyquinolin-8-amine – **2f** in DMSO-d_6.

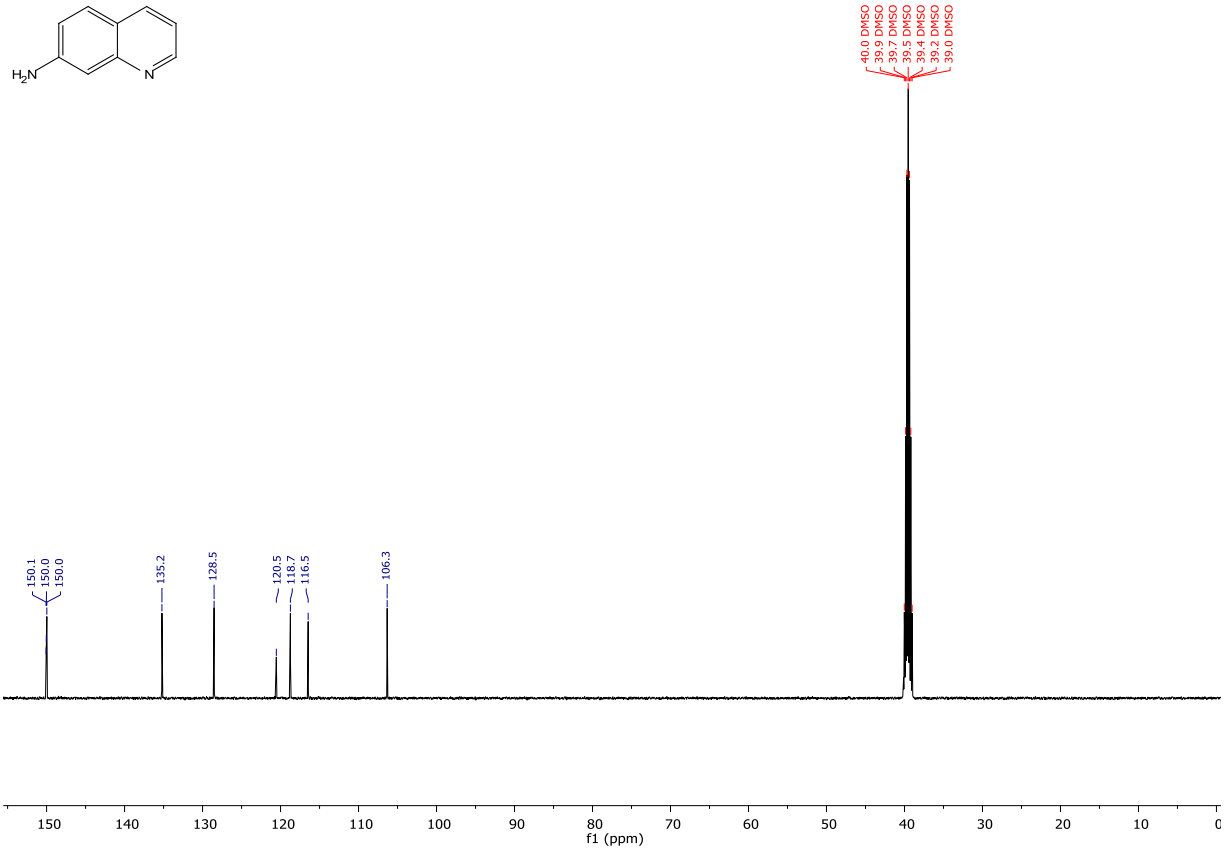
^{1}H and ^{13}C{1H} spectra of quinolin-8-amine – **2g** in DMSO-*d*$_6$.



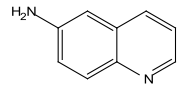


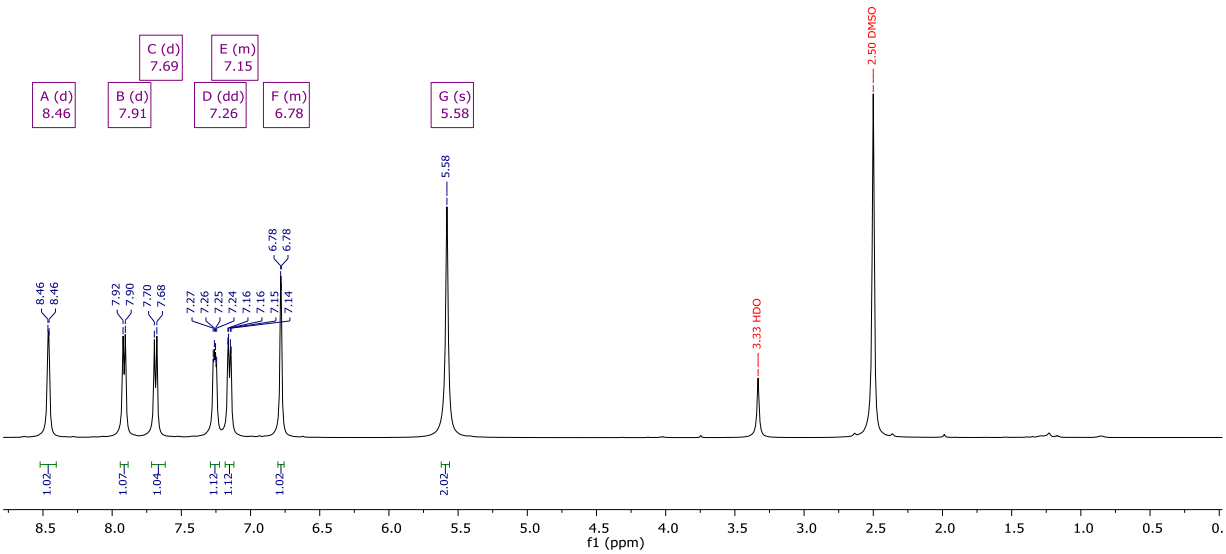
^{1}H and ^{13}C{1H} spectra of quinolin-7-amine – **2h** in DMSO-d_6.

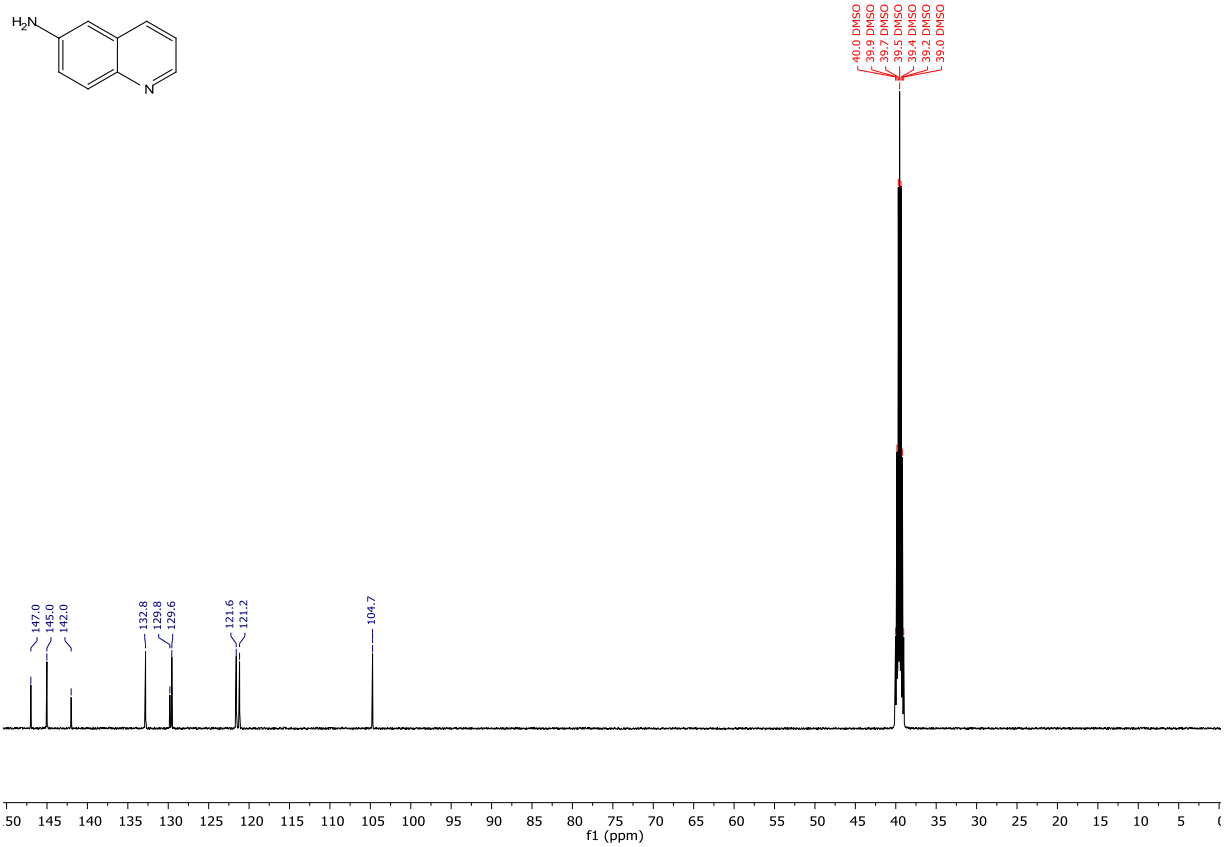




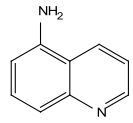
^{1}H and ^{13}C{1H} spectra of quinolin-6-amine – **2i** in DMSO-d_6.

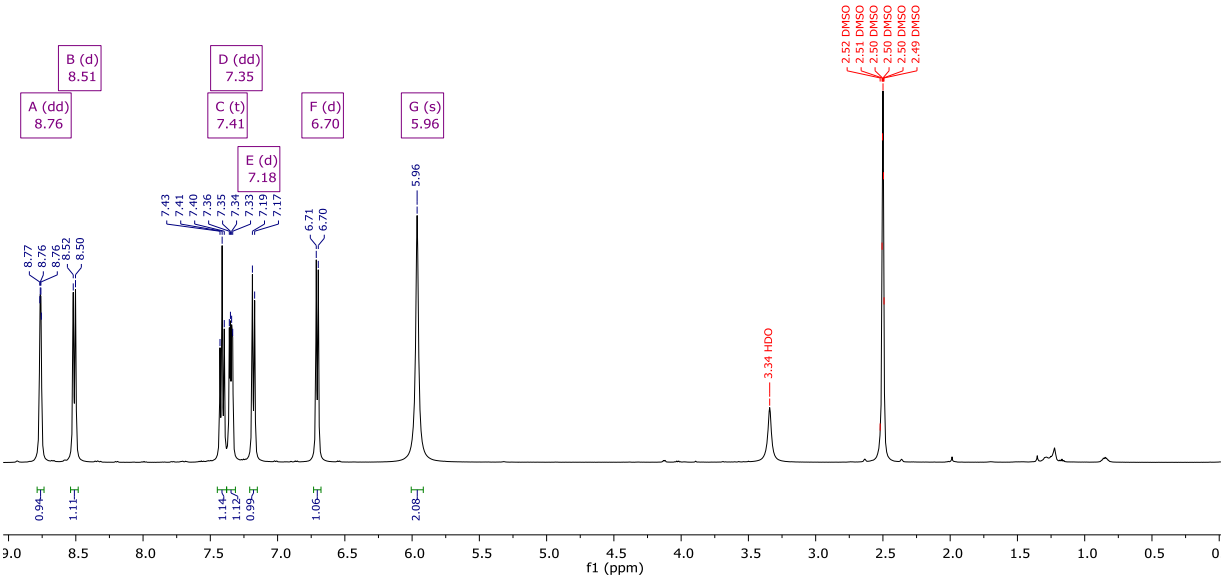


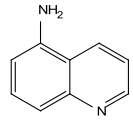




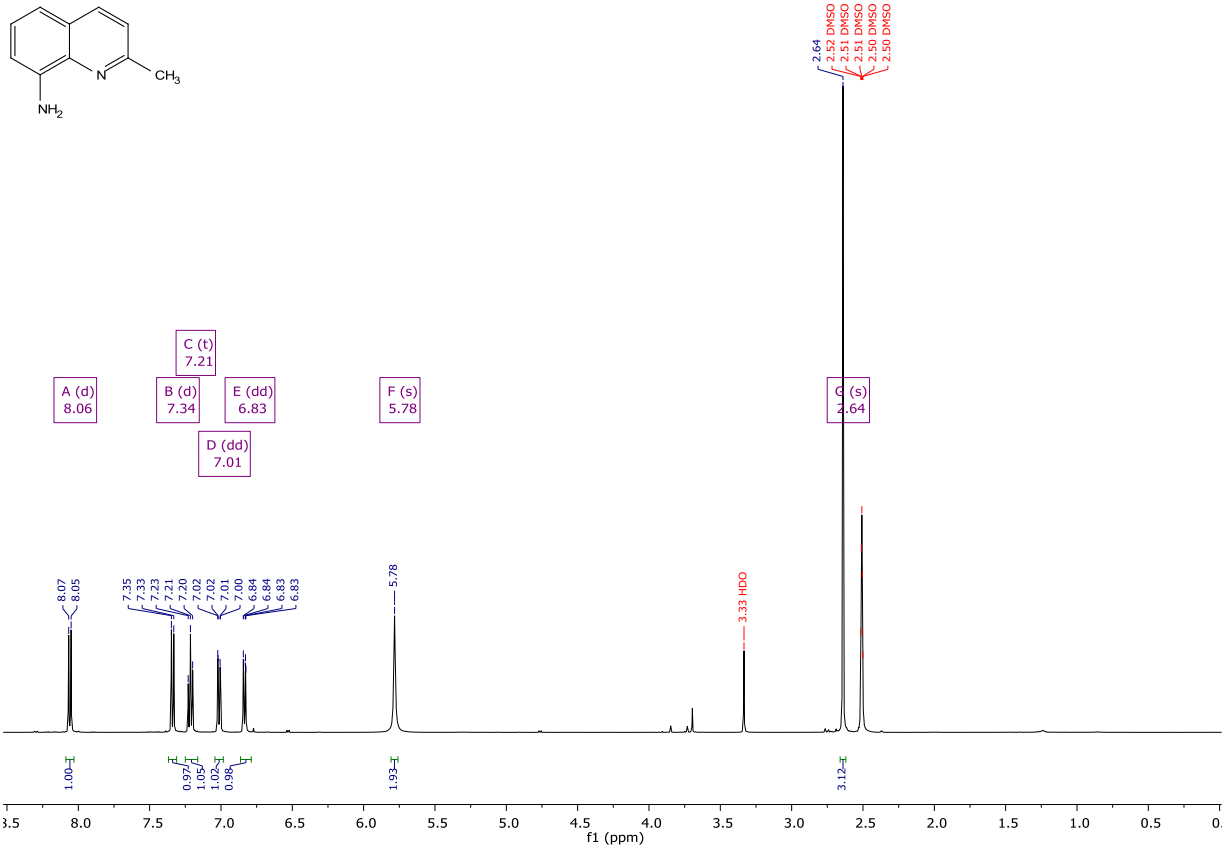
^{1}H and ^{13}C{1H} spectra of quinolin-5-amine – **2j** in DMSO-d_6.

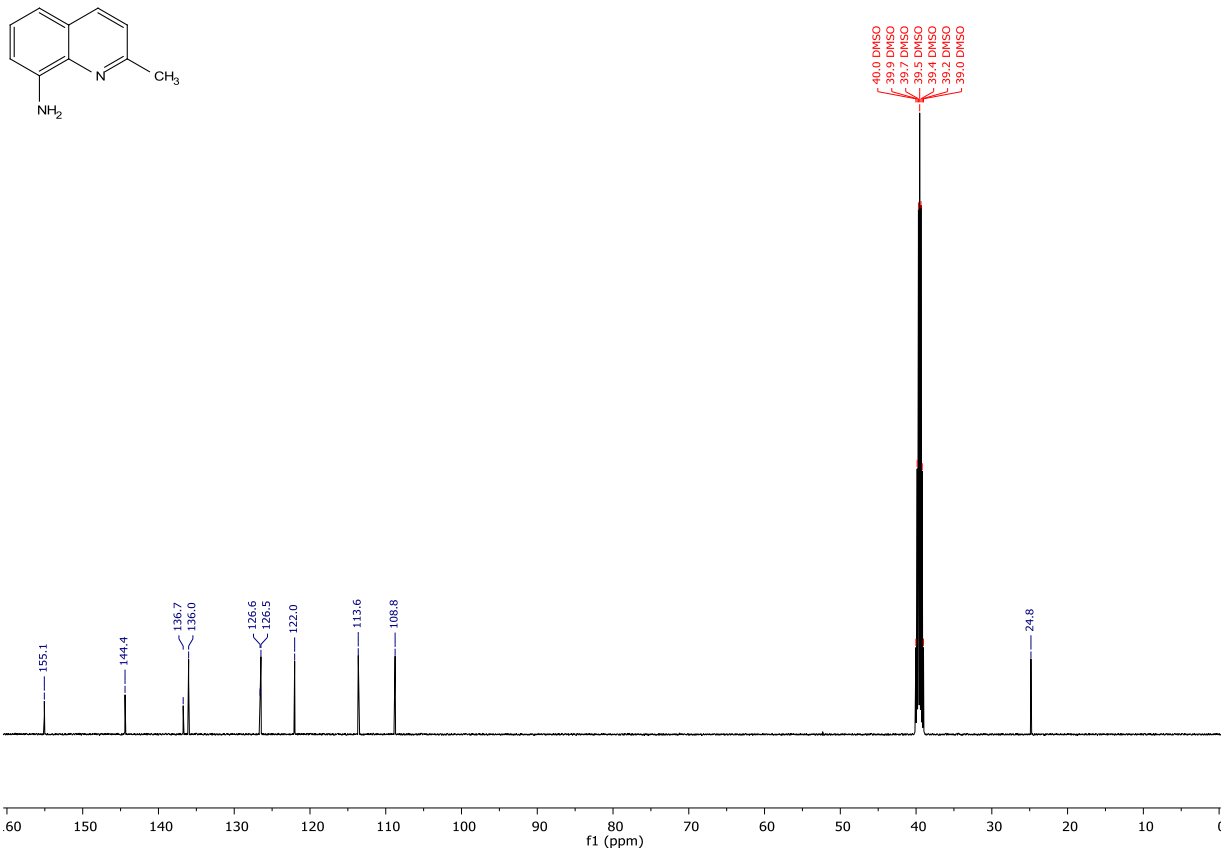




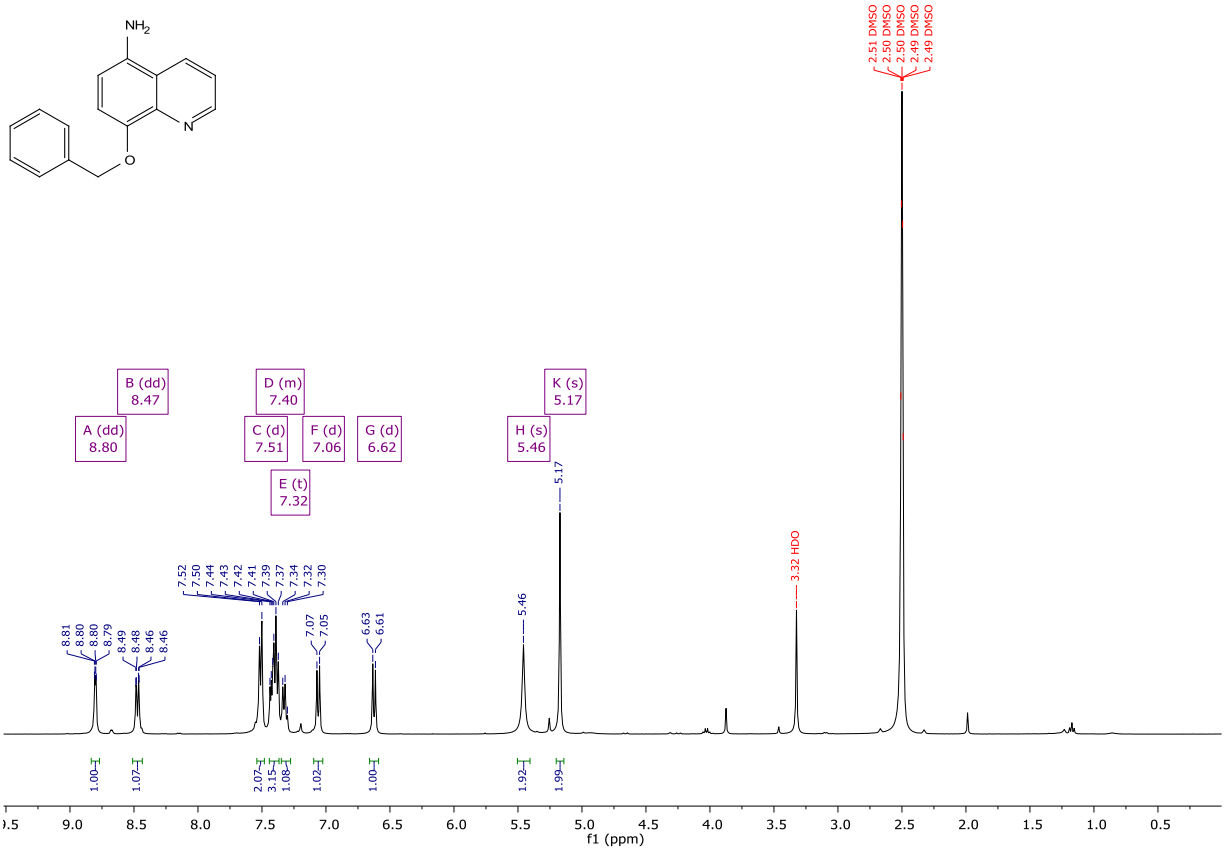


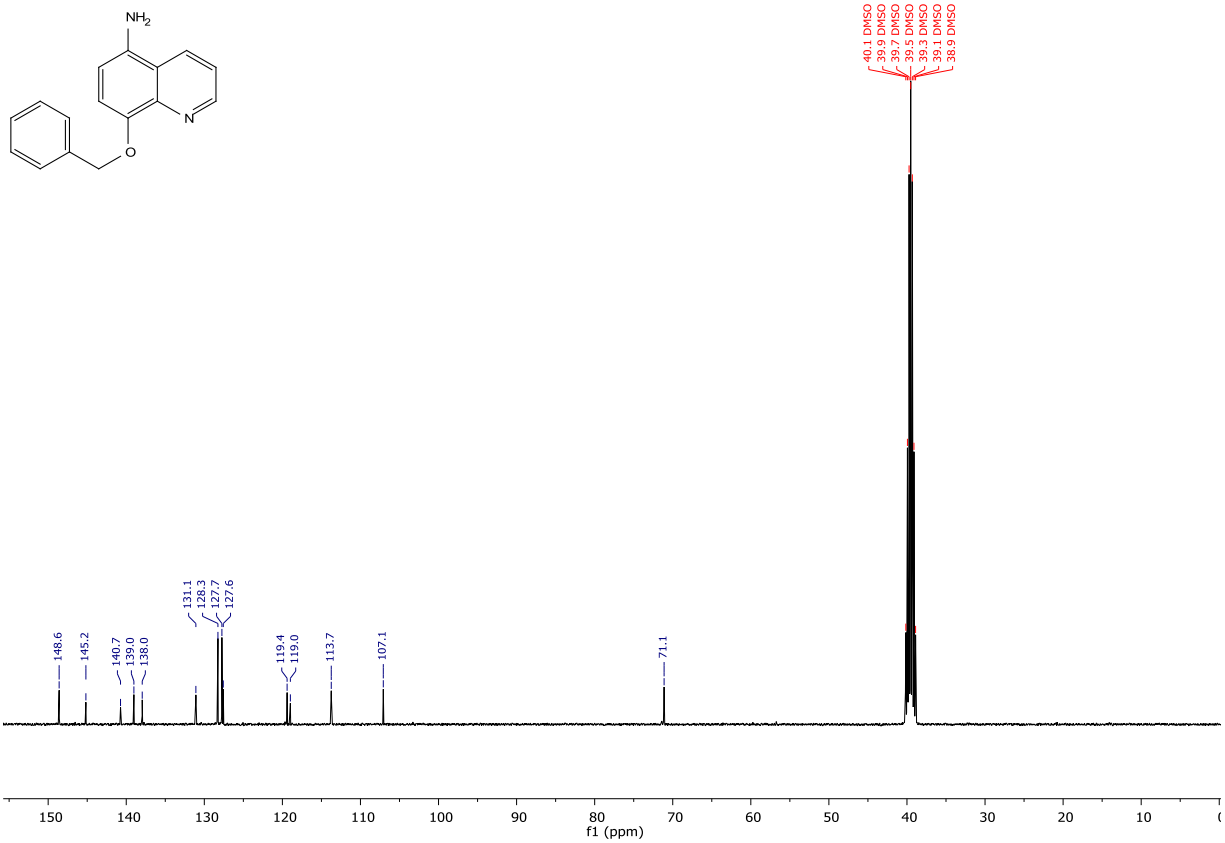
^{1}H and ^{13}C{1H} spectra of 2-methylquinolin-8-amine – **2k** in DMSO-d_6.



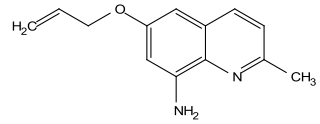


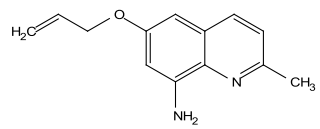
^{1}H and ^{13}C{1H} spectra of 8-(benzyloxy)quinolin-5-amine – **2l** in DMSO-*d*$_6$.



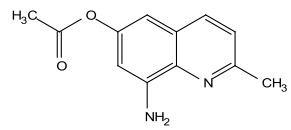


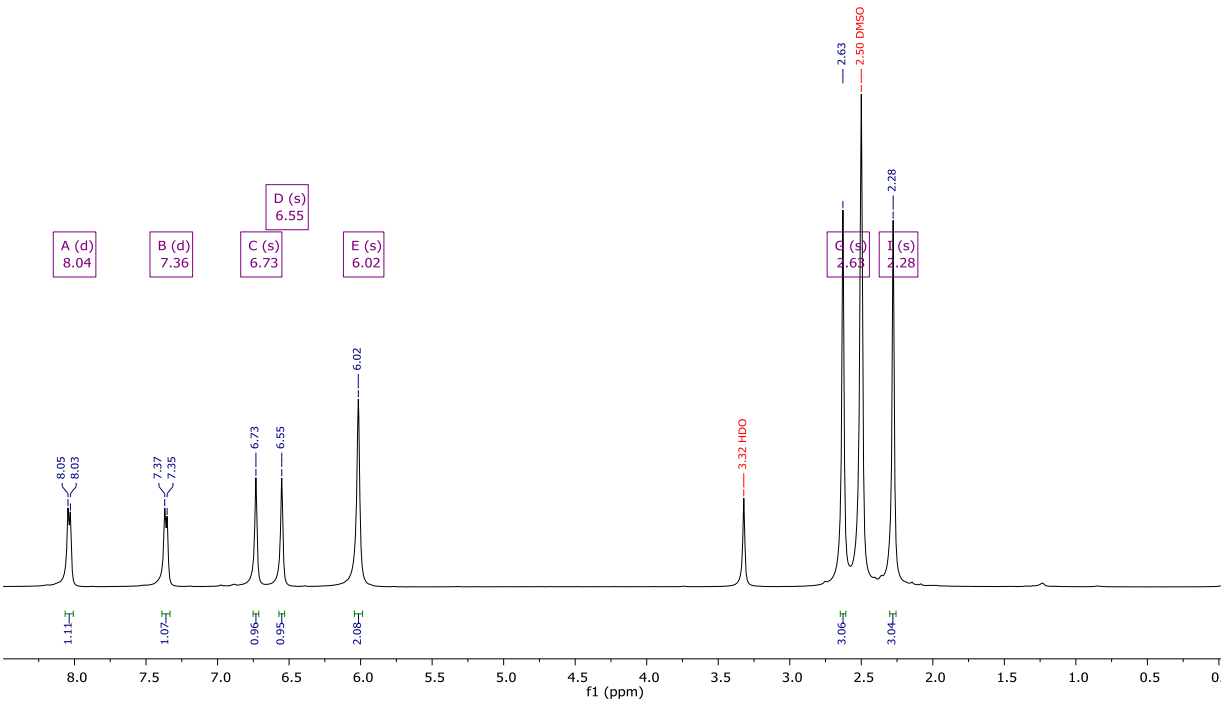
^{1}H and ^{13}C{1H} spectra of 6-(allyloxy)-2-methylquinolin-8-amine – **2m** in DMSO-*d*$_6$.

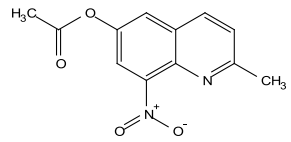




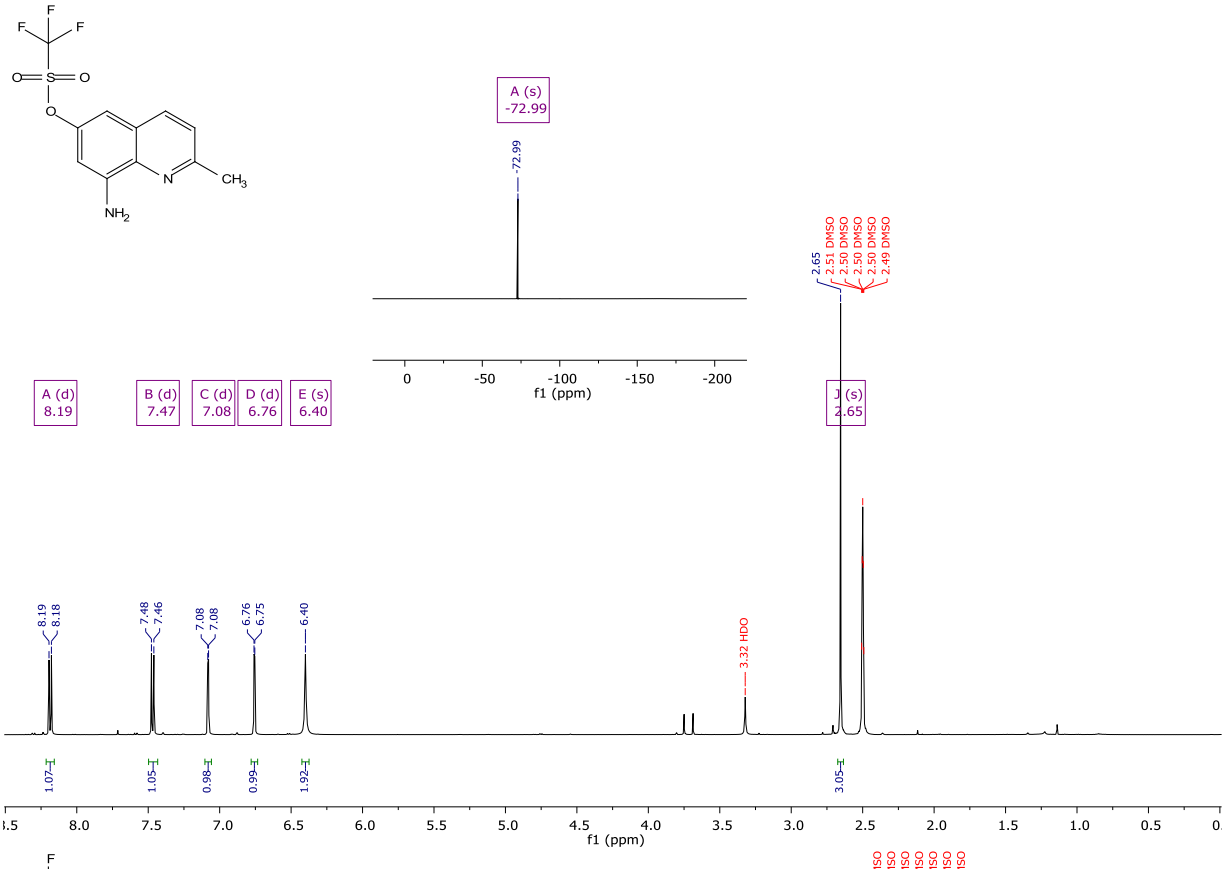
^{1}H and ^{13}C{1H} spectra of 8-amino-2-methylquinolin-6-yl acetate – **2n** in DMSO-d_6.

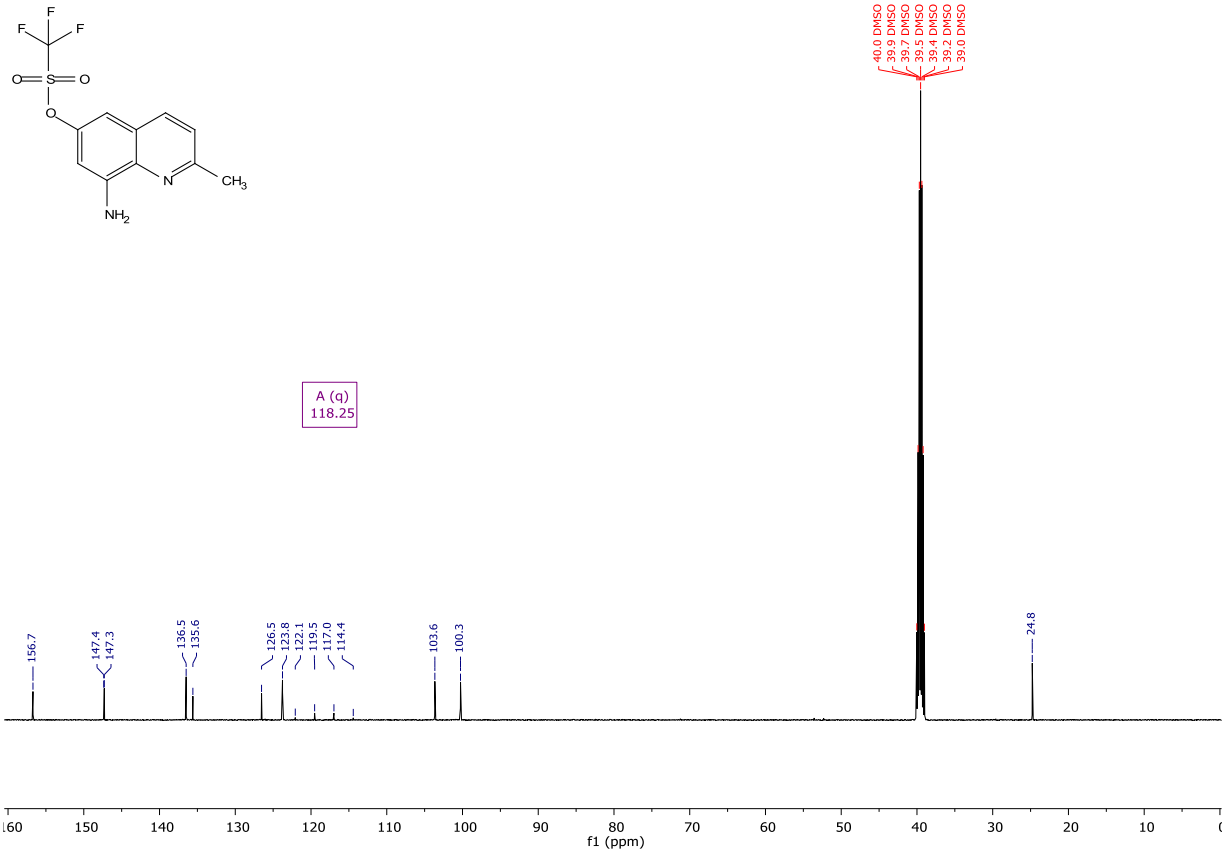




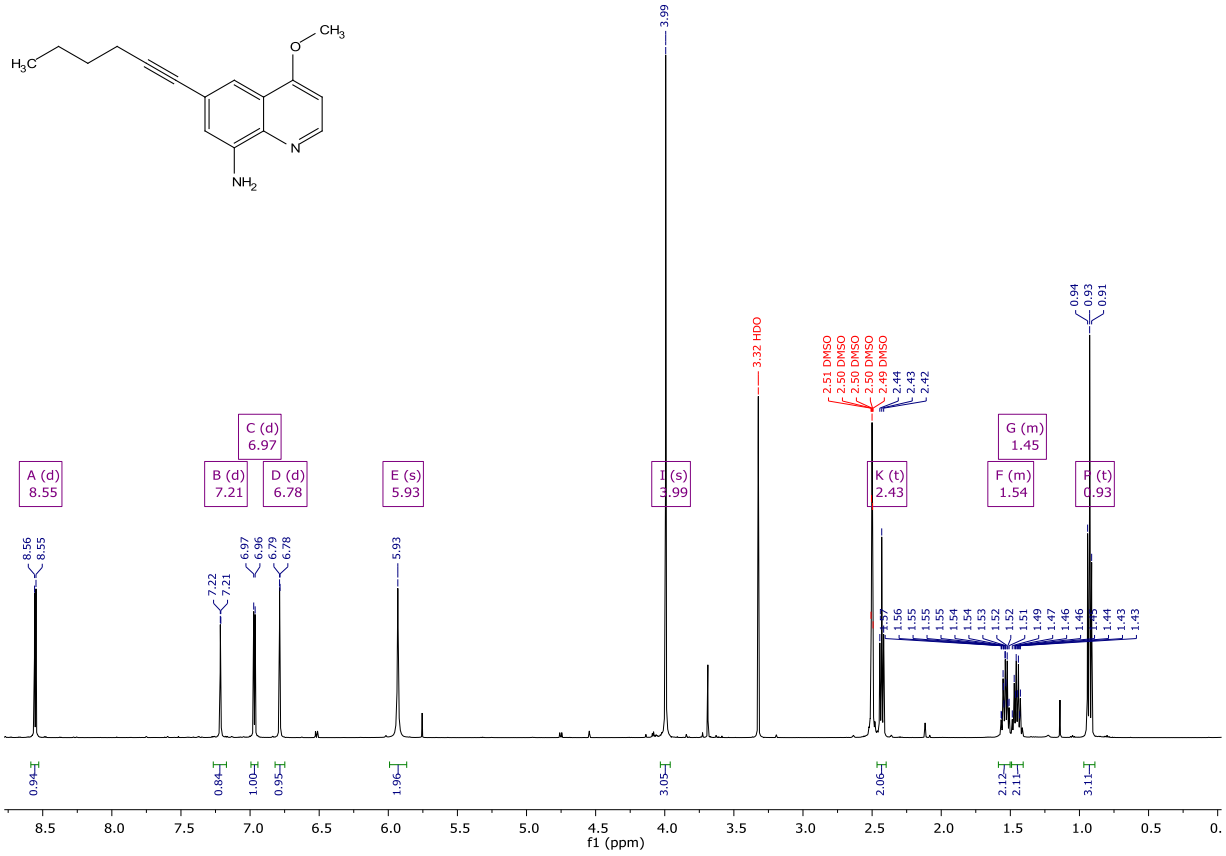


^{1}H, ^{19}F (inset) and ^{13}C{1H} spectra of 8-amino-2-methylquinolin-6-yl trifluoromethanesulfonate – **2o** in DMSO-d_6.

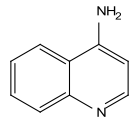


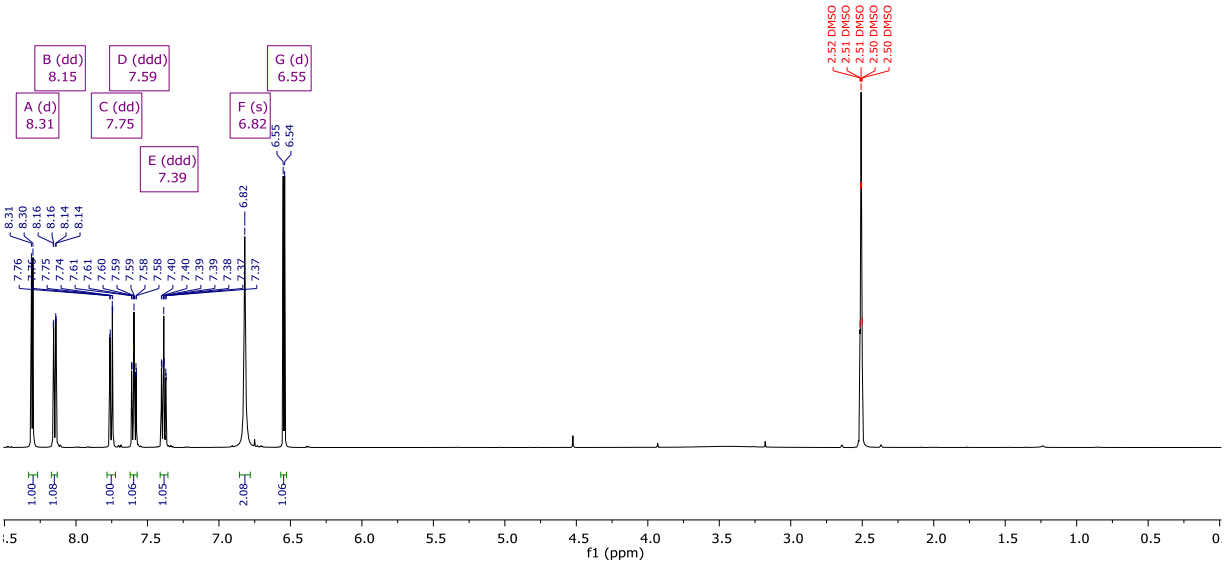


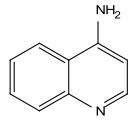
^{1}H and ^{13}C{1H} spectra of 6-(hex-1-yn-1-yl)-4-methoxyquinolin-8-amine – **2p** in DMSO-*d*$_6$.



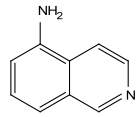
^{1}H and ^{13}C{1H} spectra of Quinolin-4-amine – **2q** in DMSO-d_6.

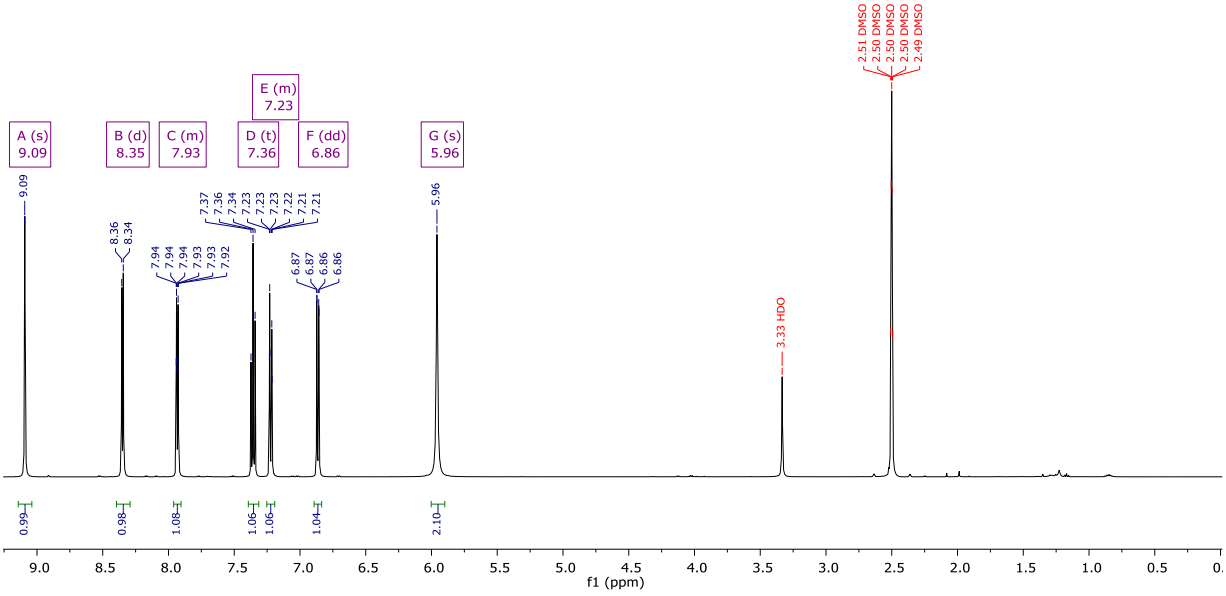


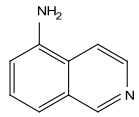




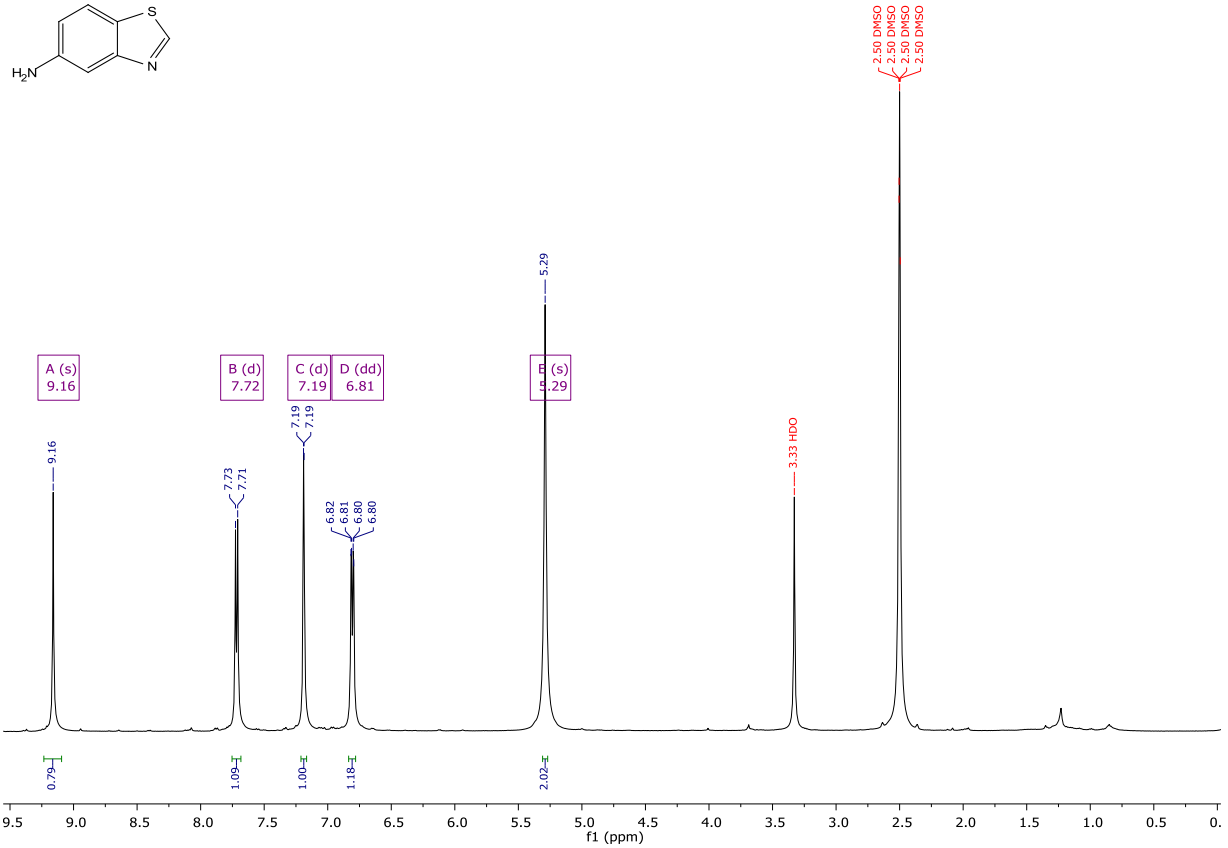
^{1}H and ^{13}C{1H} spectra of isoquinolin-5-amine – **2r** in DMSO-d_6.

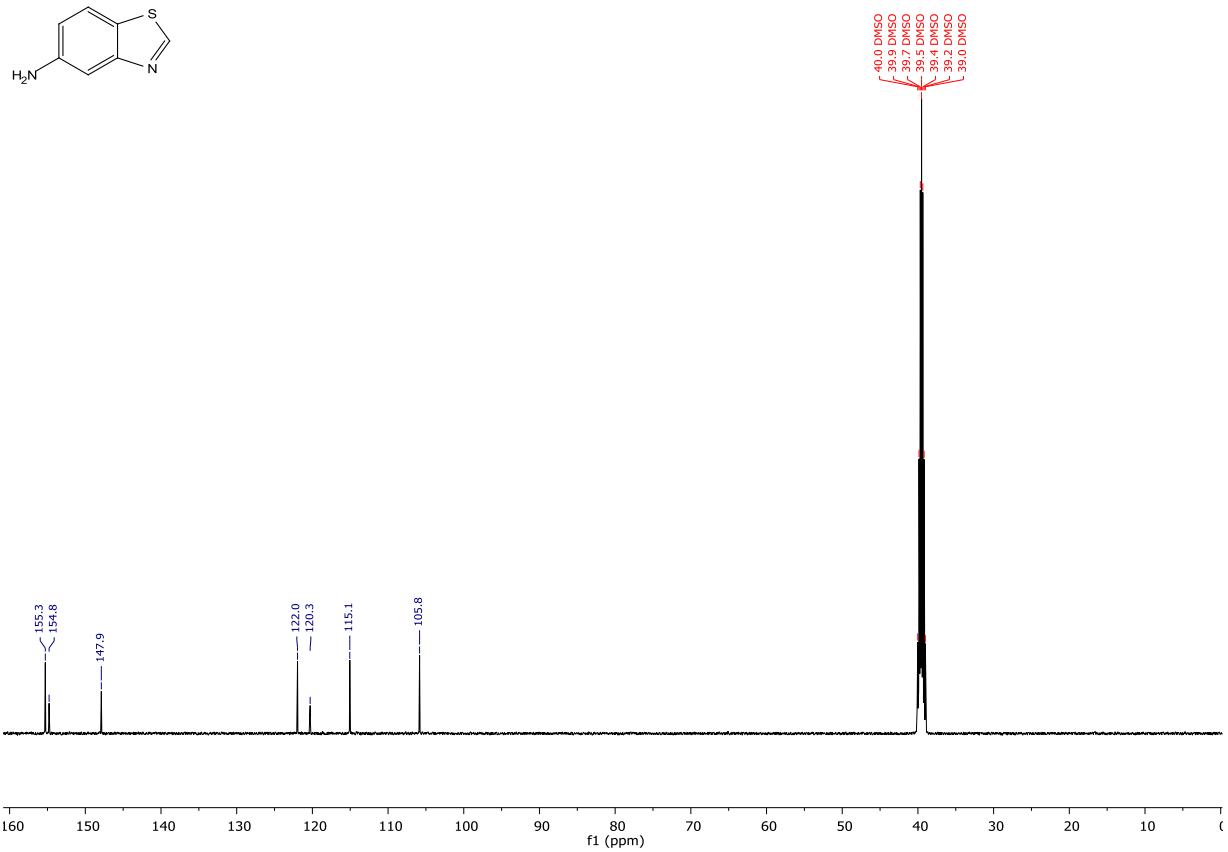




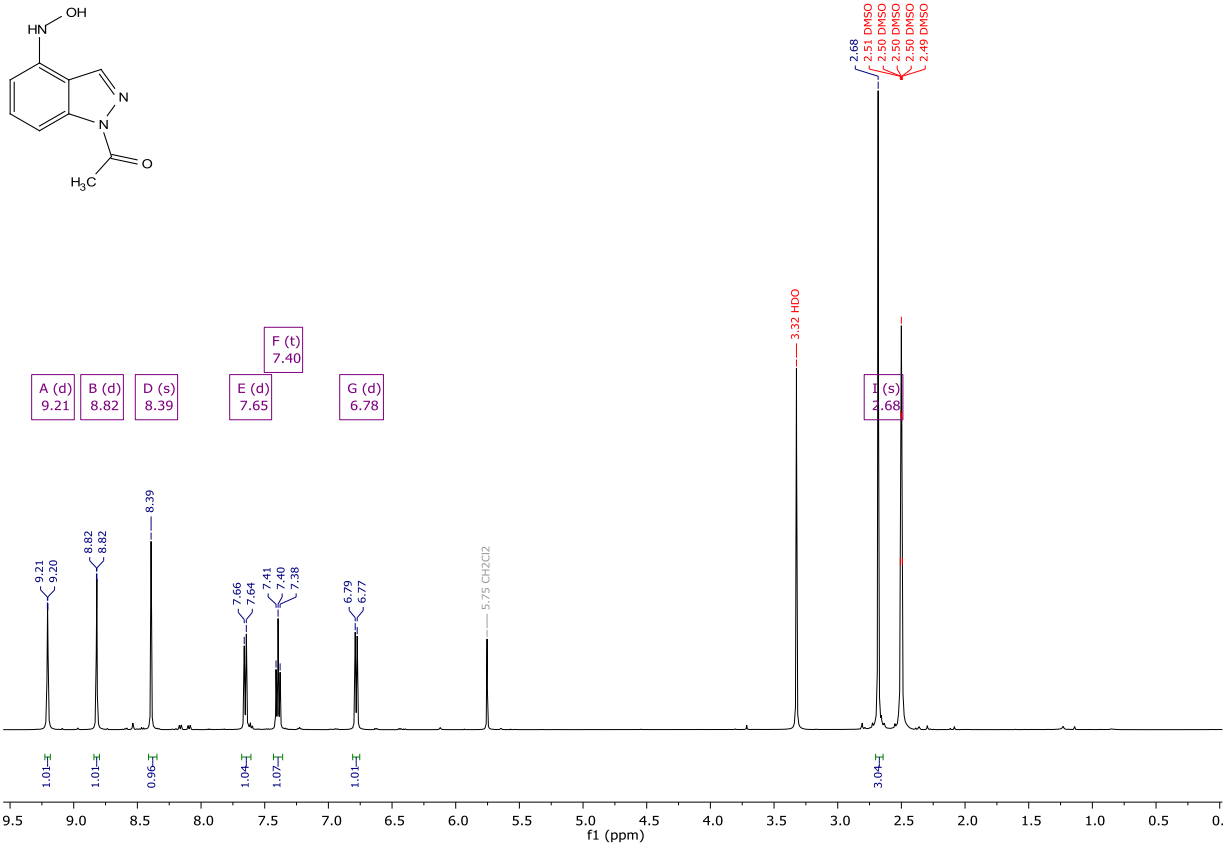


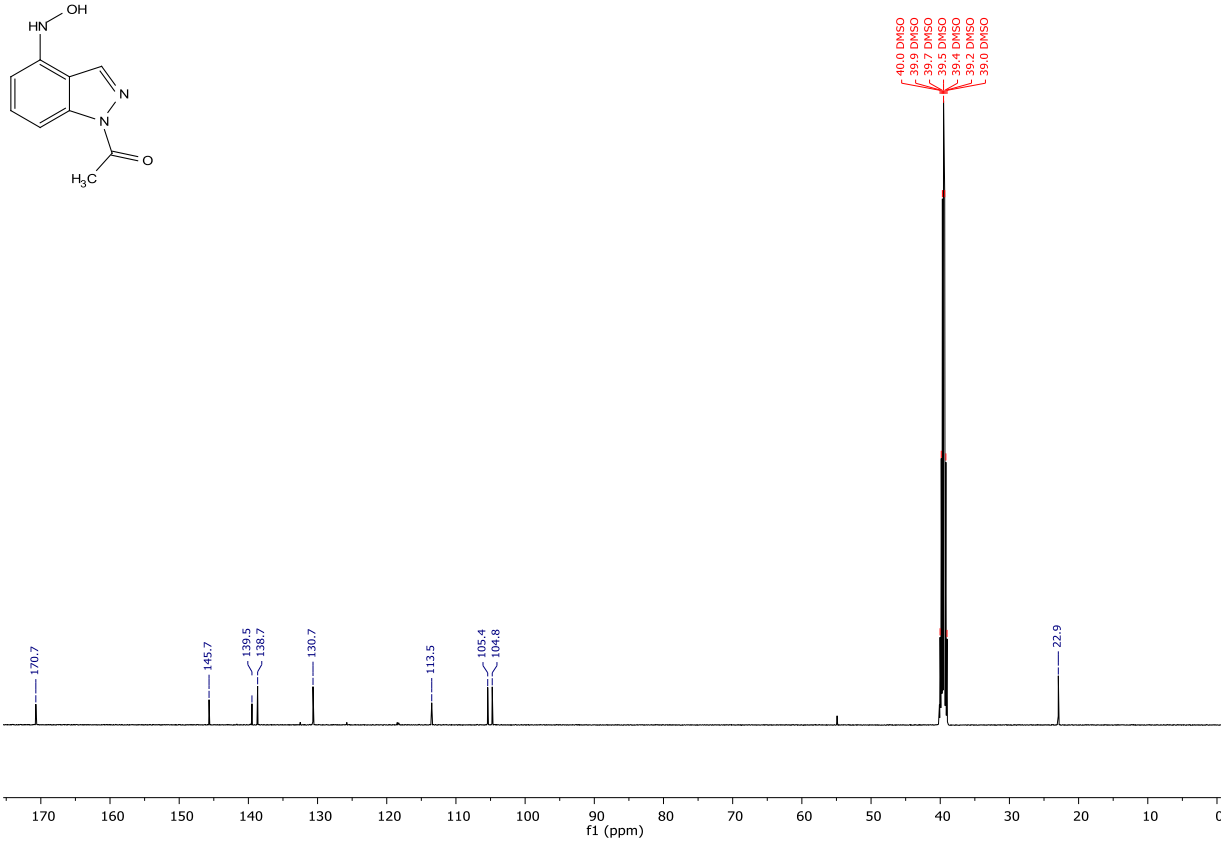
^{1}H and ^{13}C{1H} spectra of benzo[*d*]thiazol-5-amine – **2s** in DMSO-d_6.



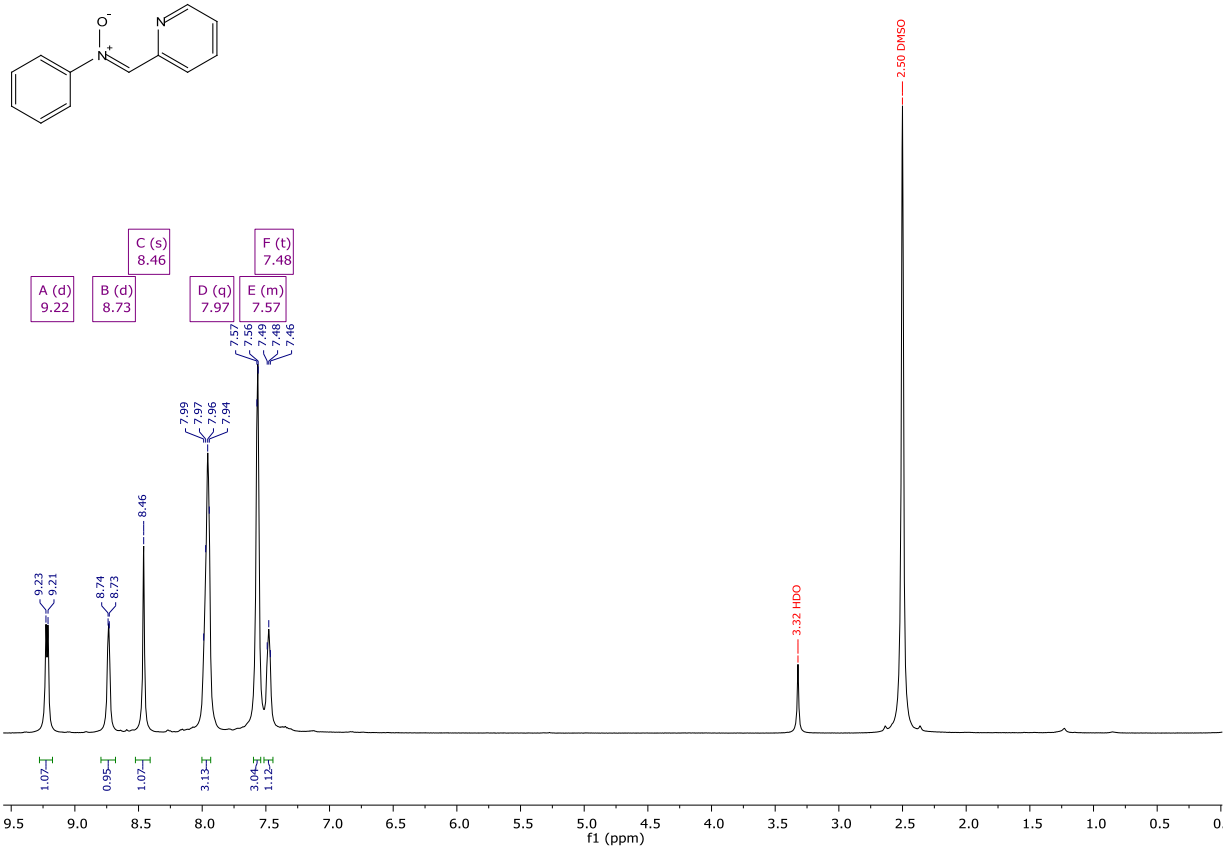


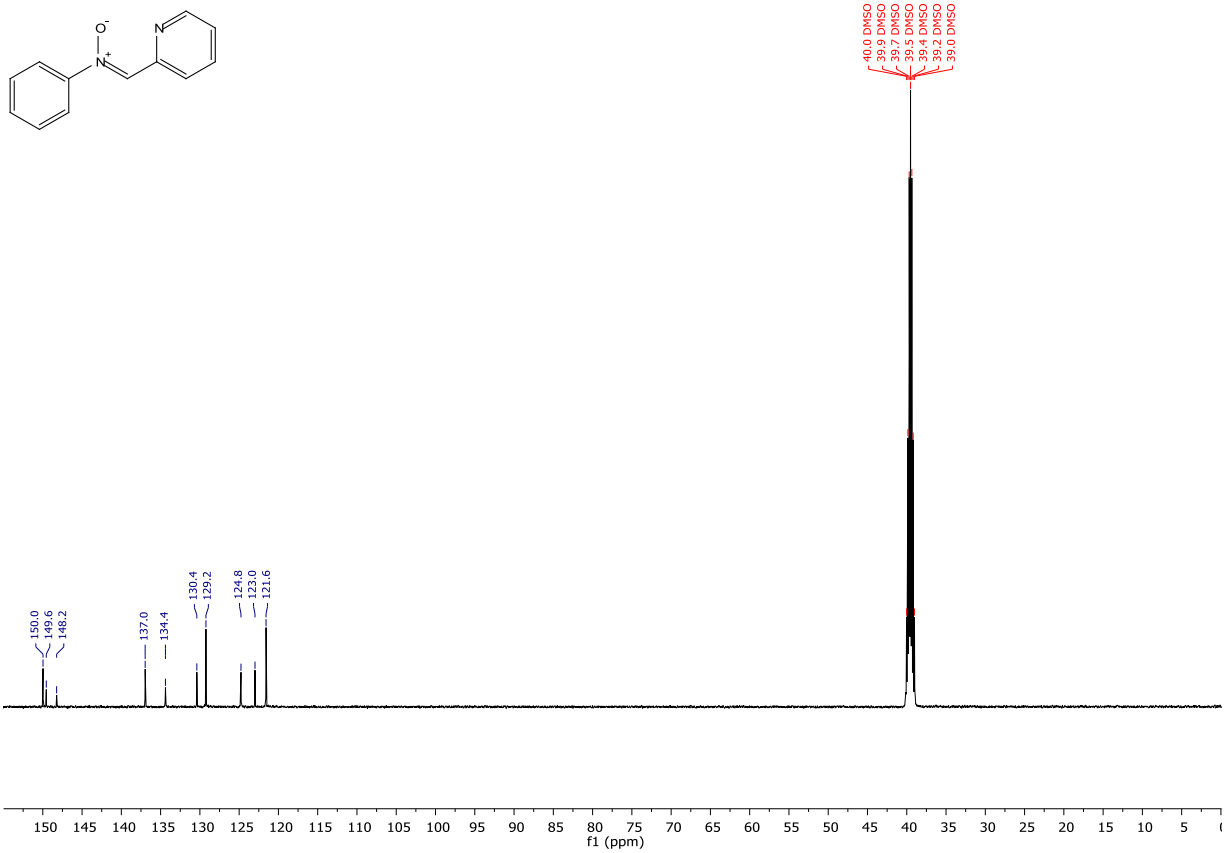
^{1}H and ^{13}C{1H} spectra of 1-(4-(hydroxyamino)-1H-indazol-1-yl)ethan-1-one – **3d`** in DMSO-*d*$_6$.



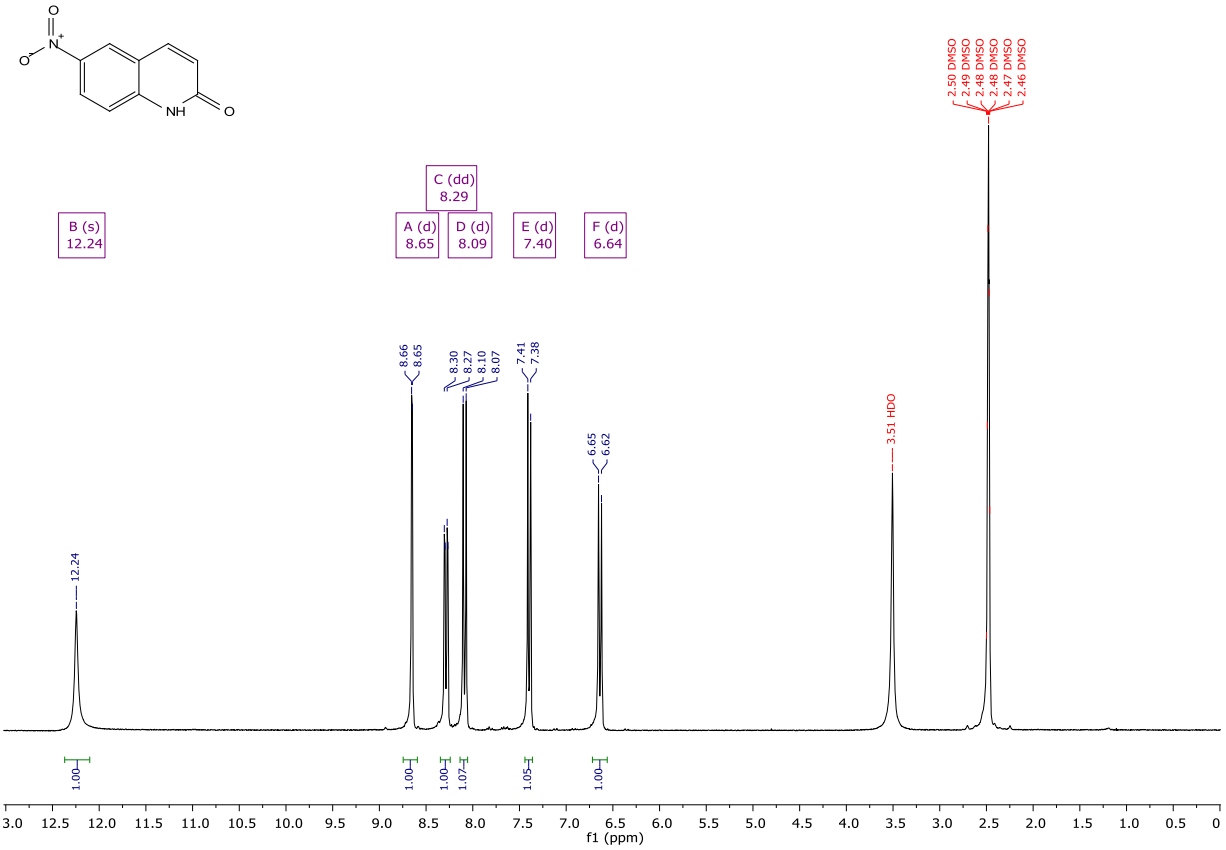


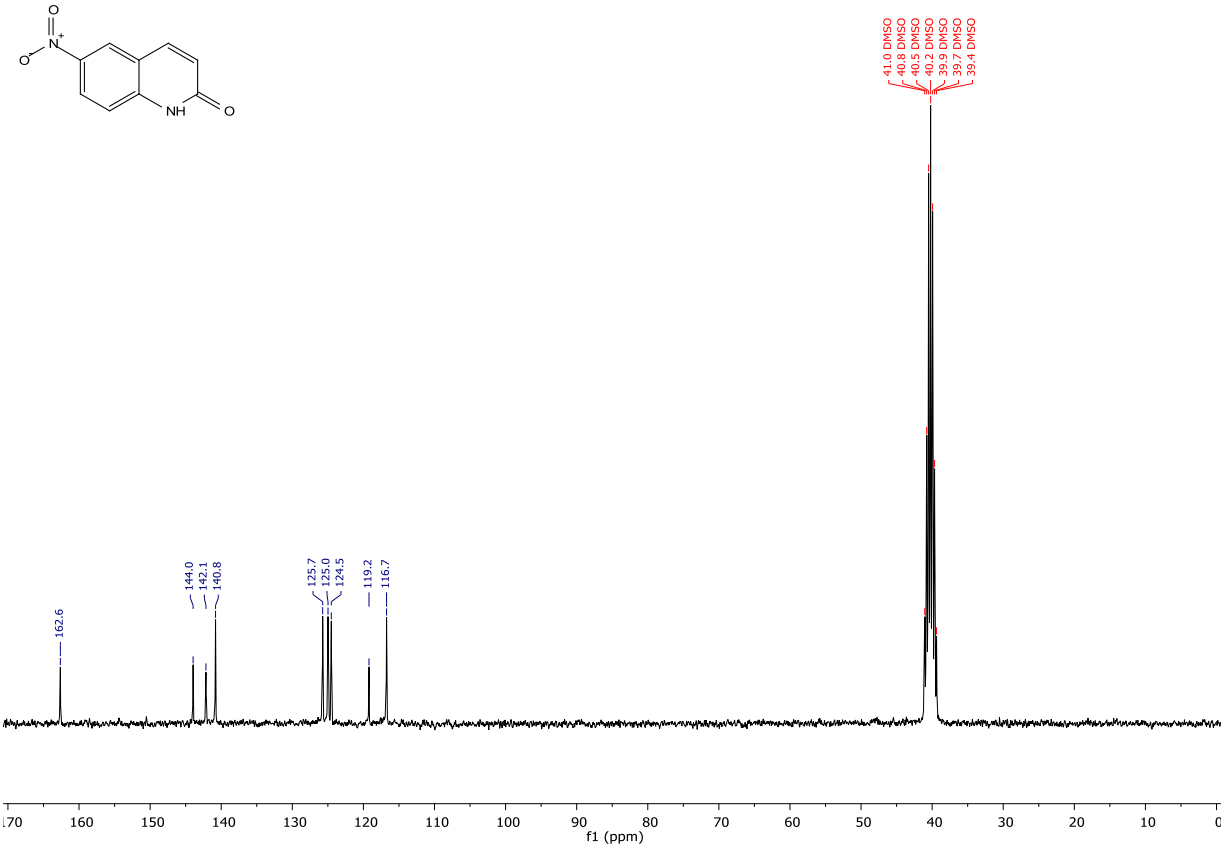
^{1}H and ^{13}C{1H} spectra of *N*-phenyl-1-(pyridin-2-yl)methanimine oxide – **5** in DMSO-d_6.



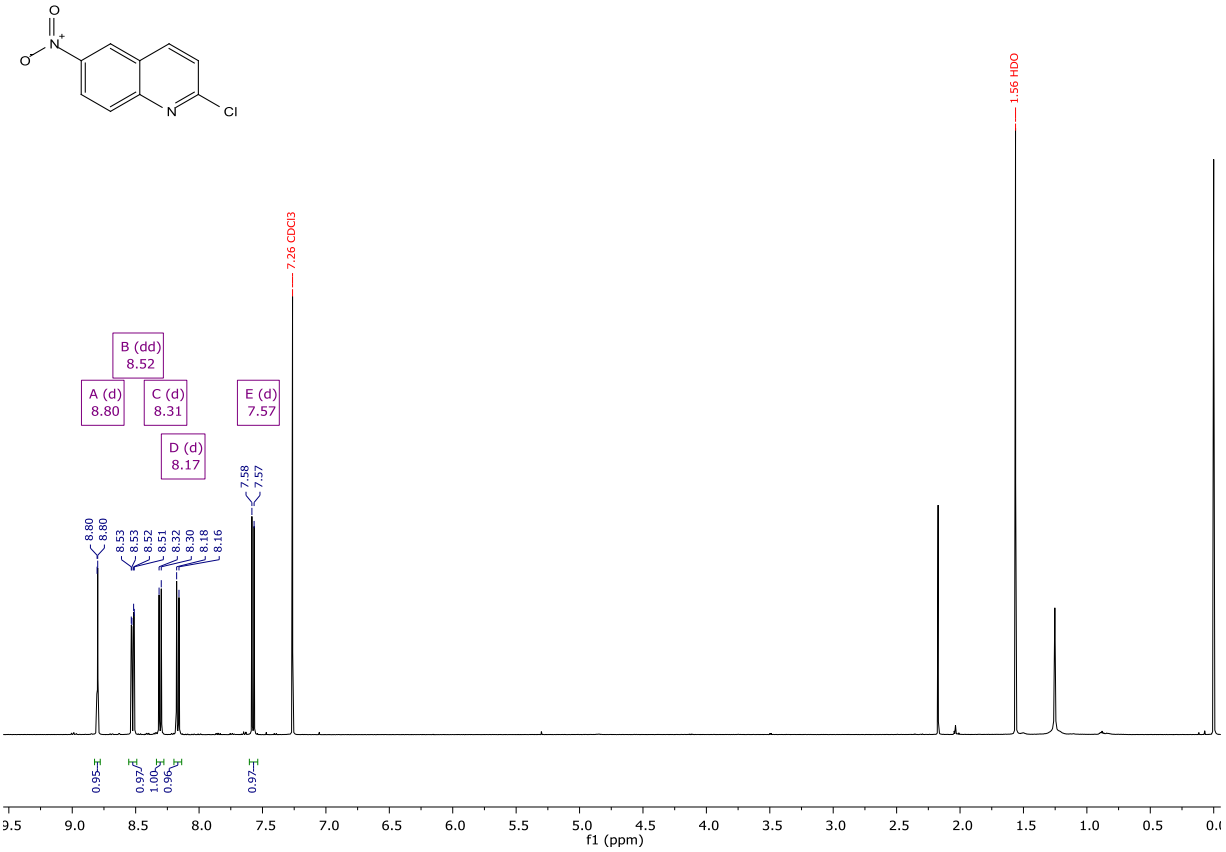


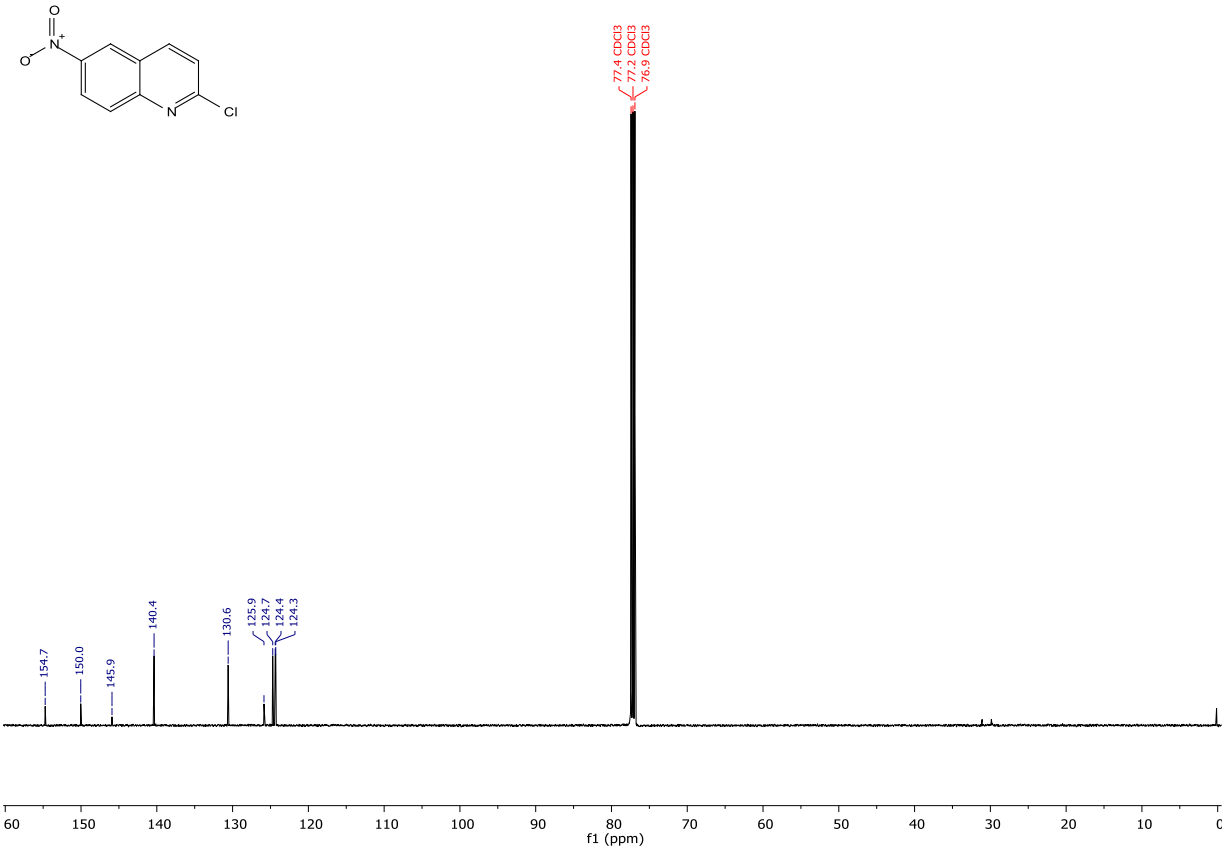
^{1}H and ^{13}C{1H} spectra of 6-nitroquinolin-2-ol – **S1** in DMSO-d_6.



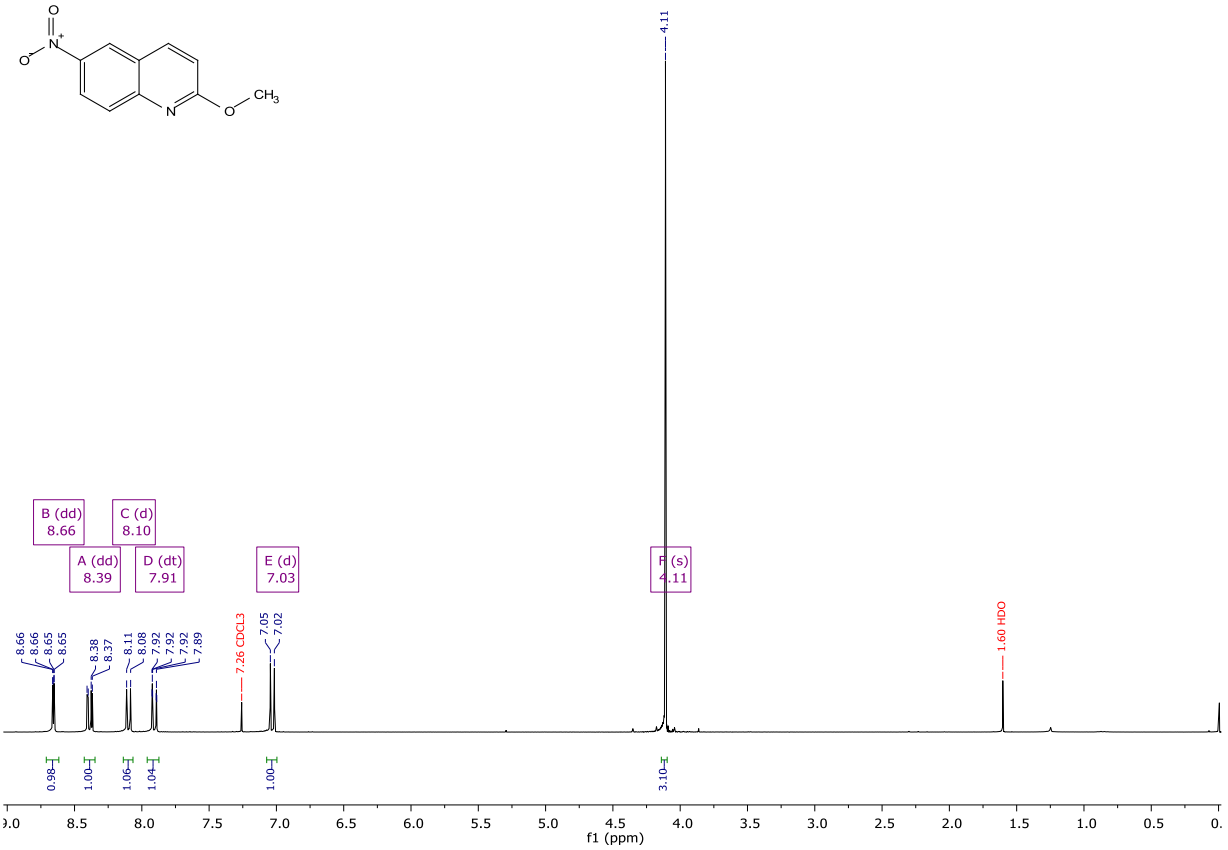


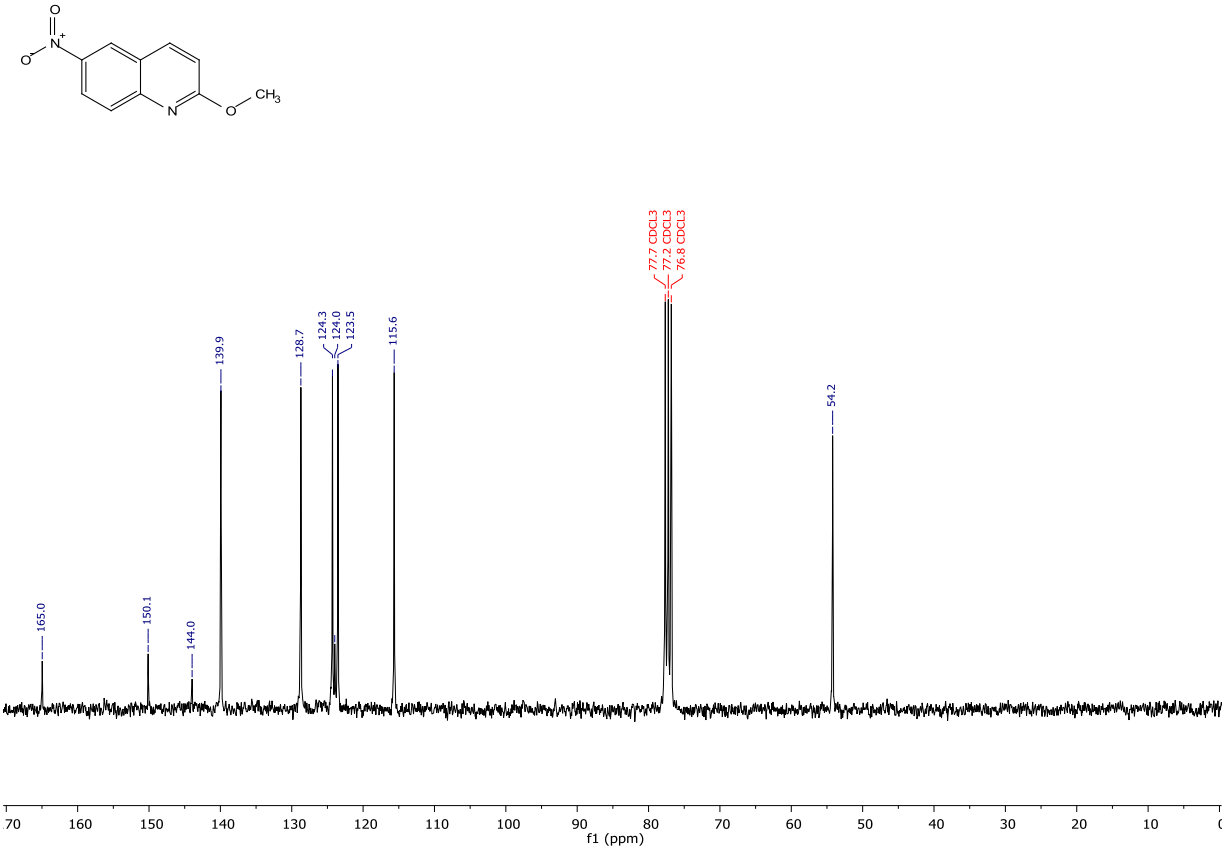
^{1}H and $^{13}C\{1H\}$ spectra of 2-chloro-6-nitroquinoline – **S2** in CDCl3.



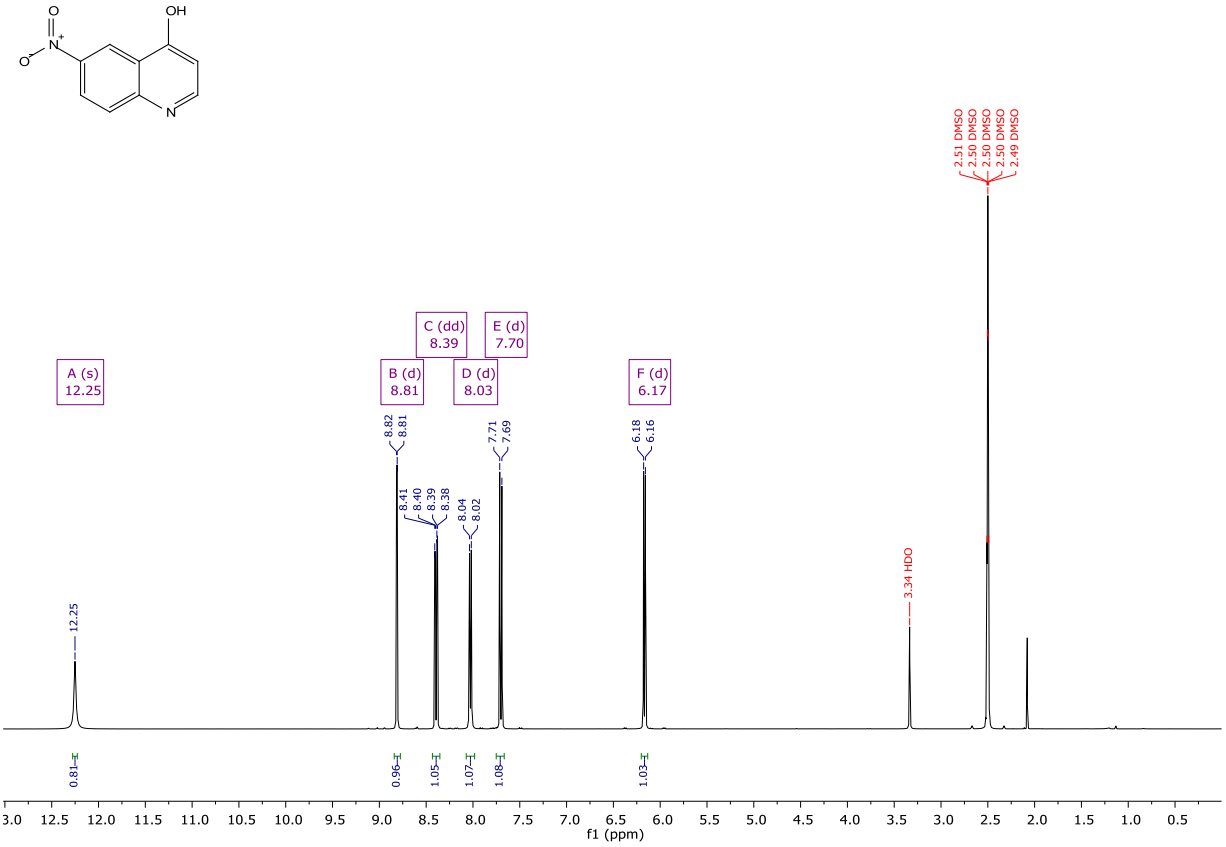


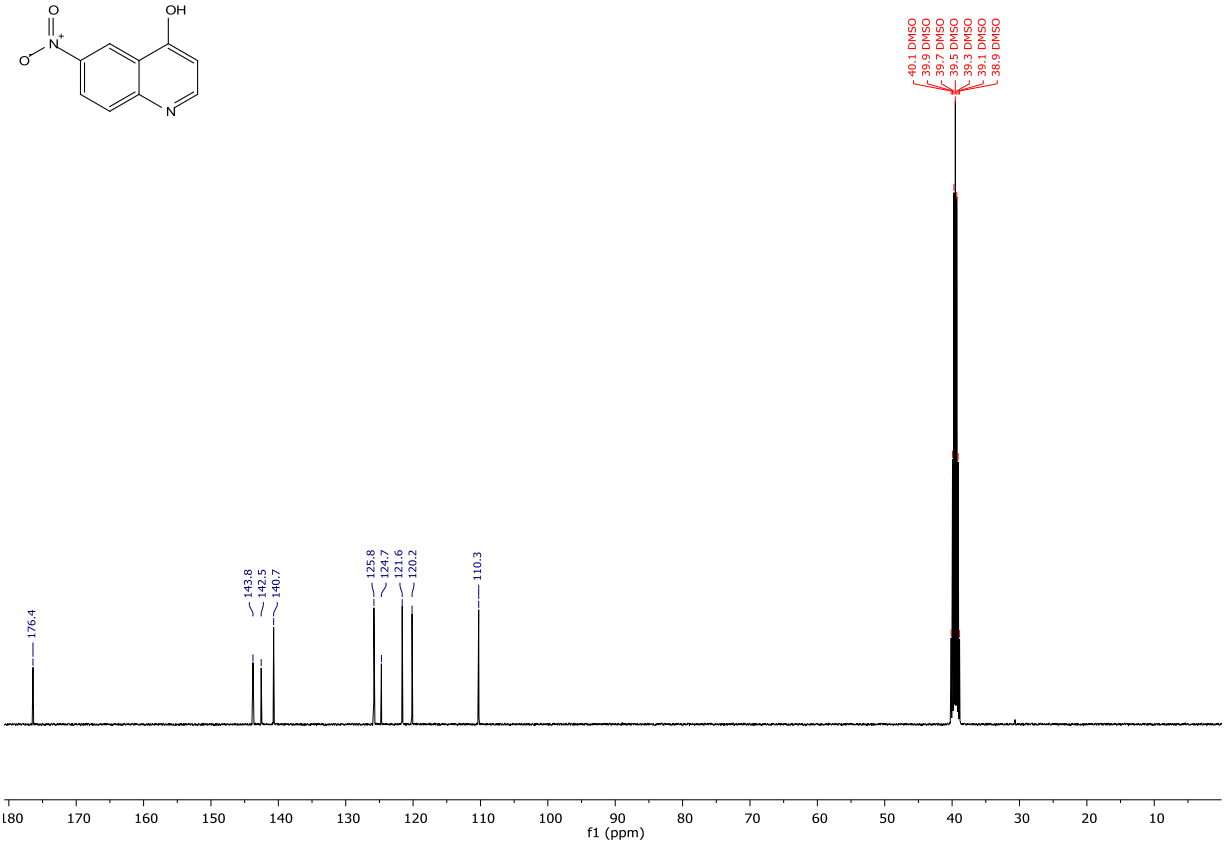
^{1}H and ^{13}C{1H} spectra of 2-methoxy-6-nitroquinoline – **1a** in CDCl3.



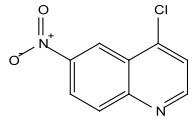


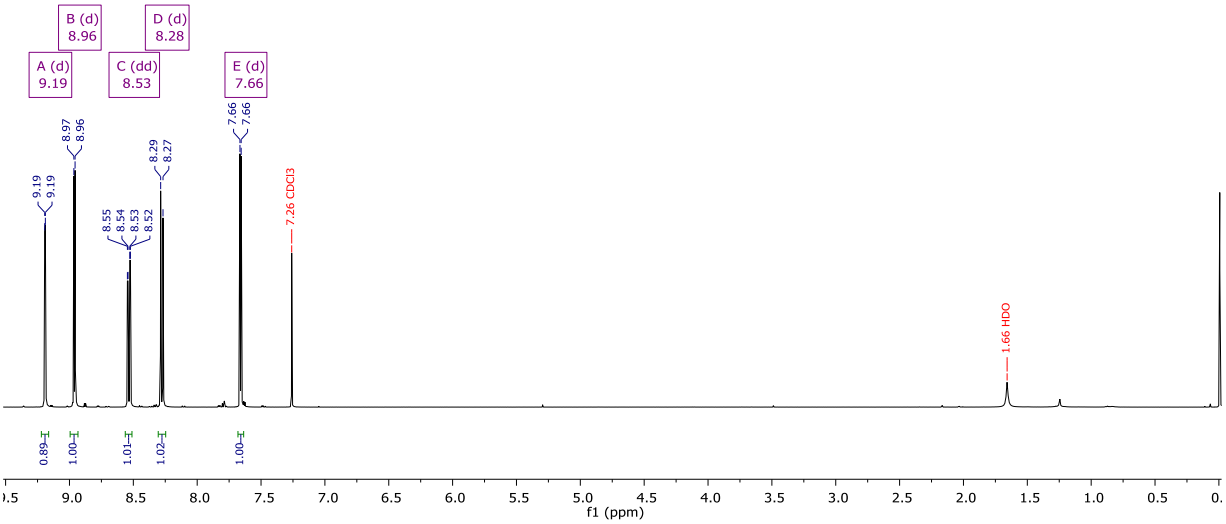
^{1}H and ^{13}C{1H} spectra of **6-nitroquinolin-4-ol** – **S3** in DMSO-d_6.

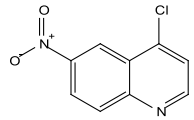




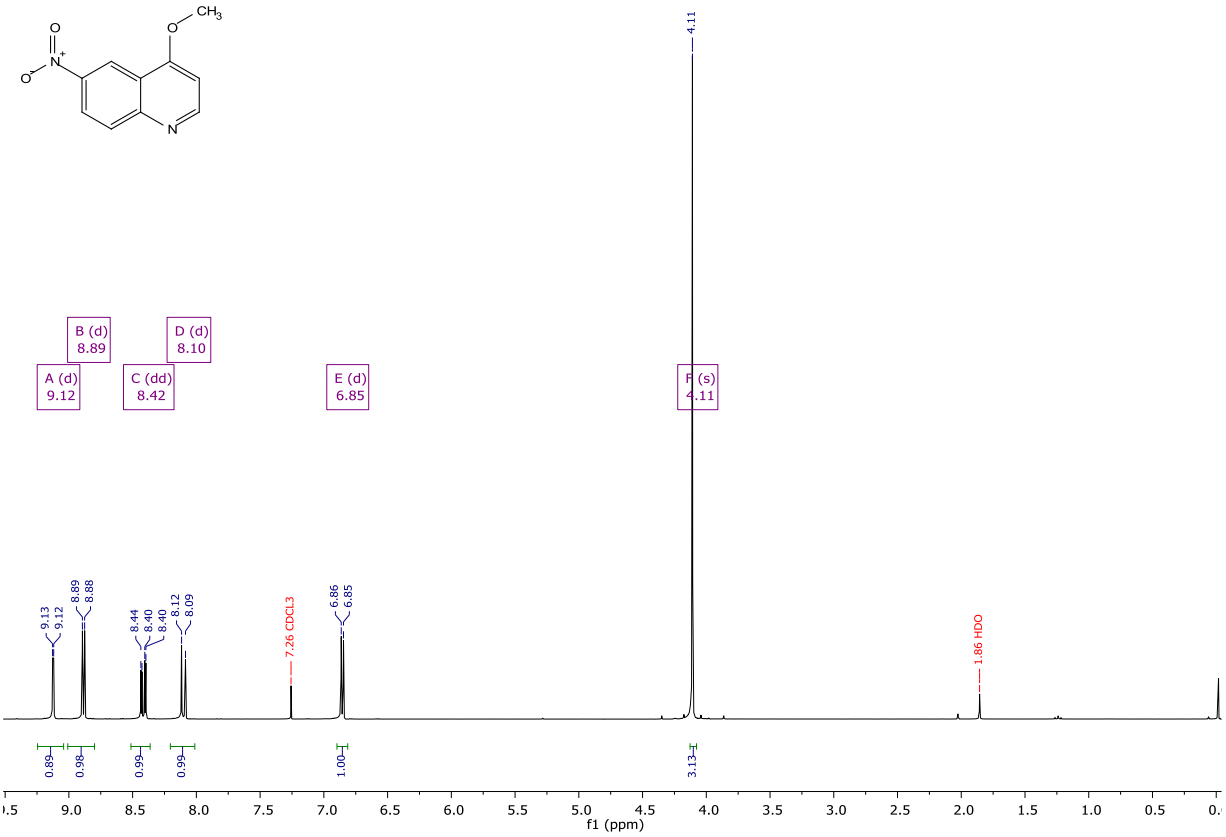
^{1}H and ^{13}C{1H} spectra of 4-chloro-6-nitroquinoline – **S4** in CDCl3.

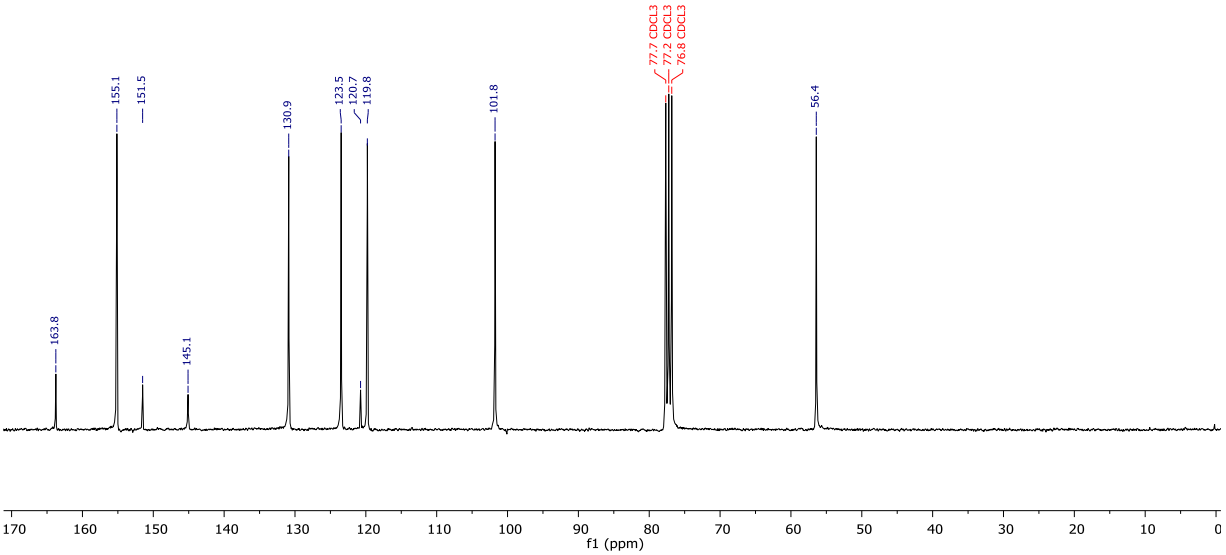




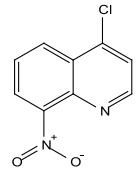


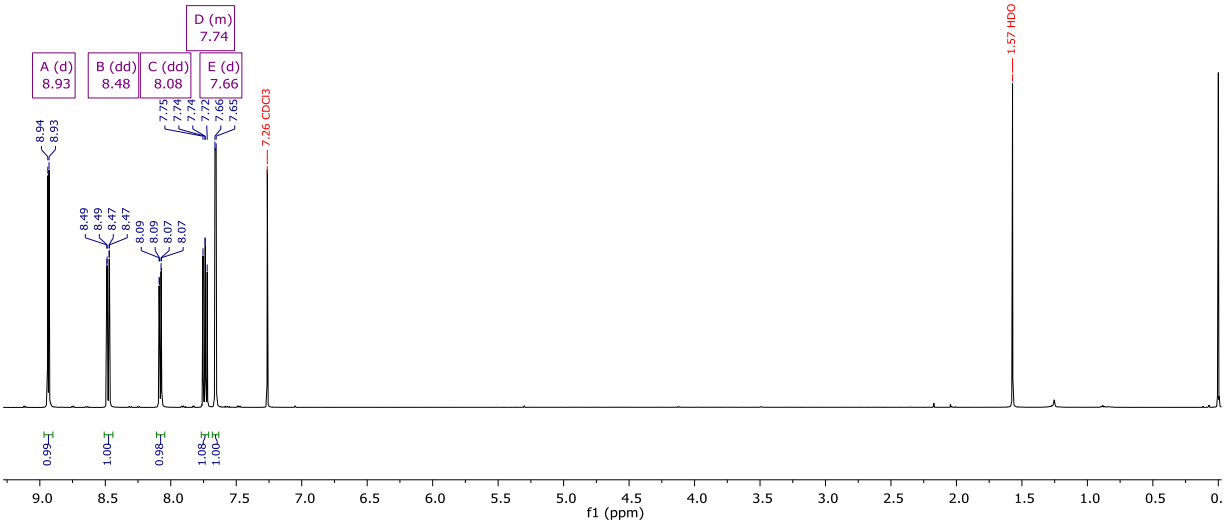
^{1}H and ^{13}C{1H} spectra of 4-methoxy-6-nitroquinoline – **1b** in CDCl3.

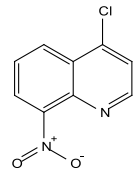




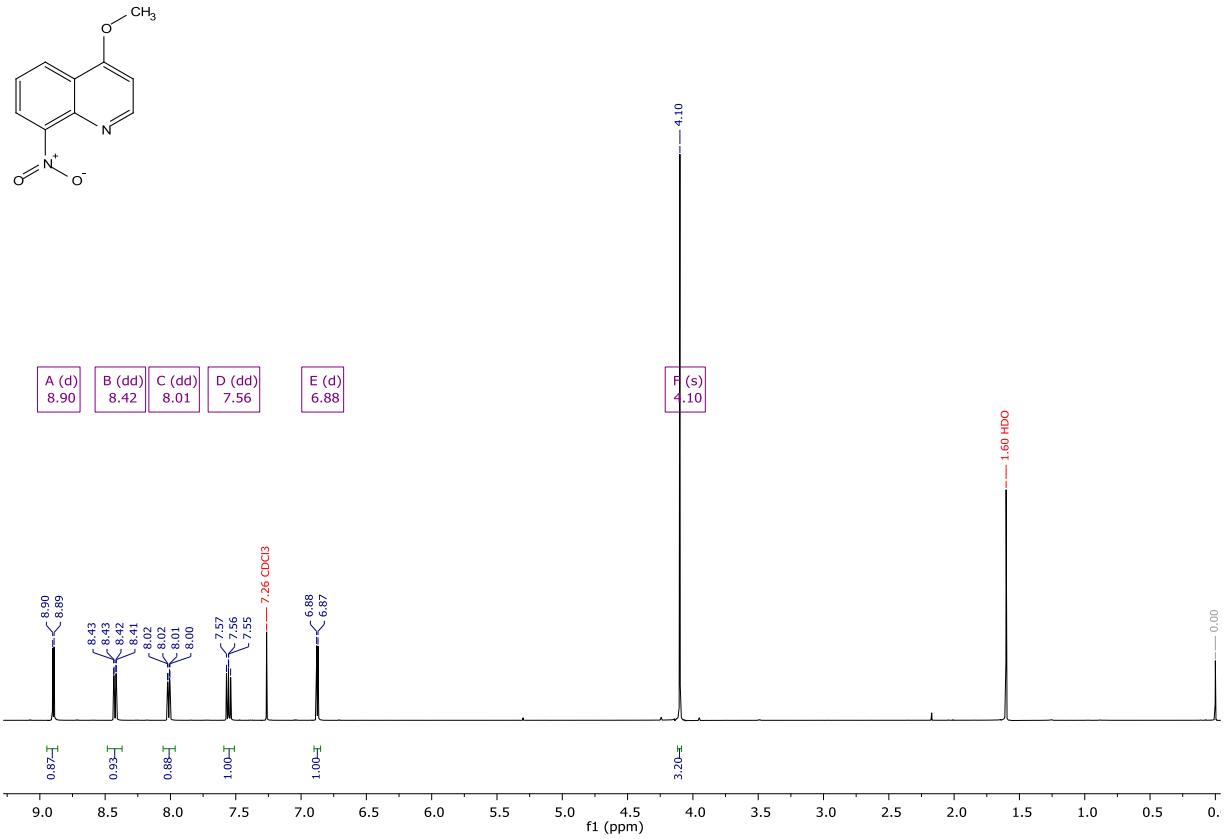
^{1}H and $^{13}C\{1H\}$ spectra of 4-chloro-8-nitroquinoline – **S5** in CDCl3.

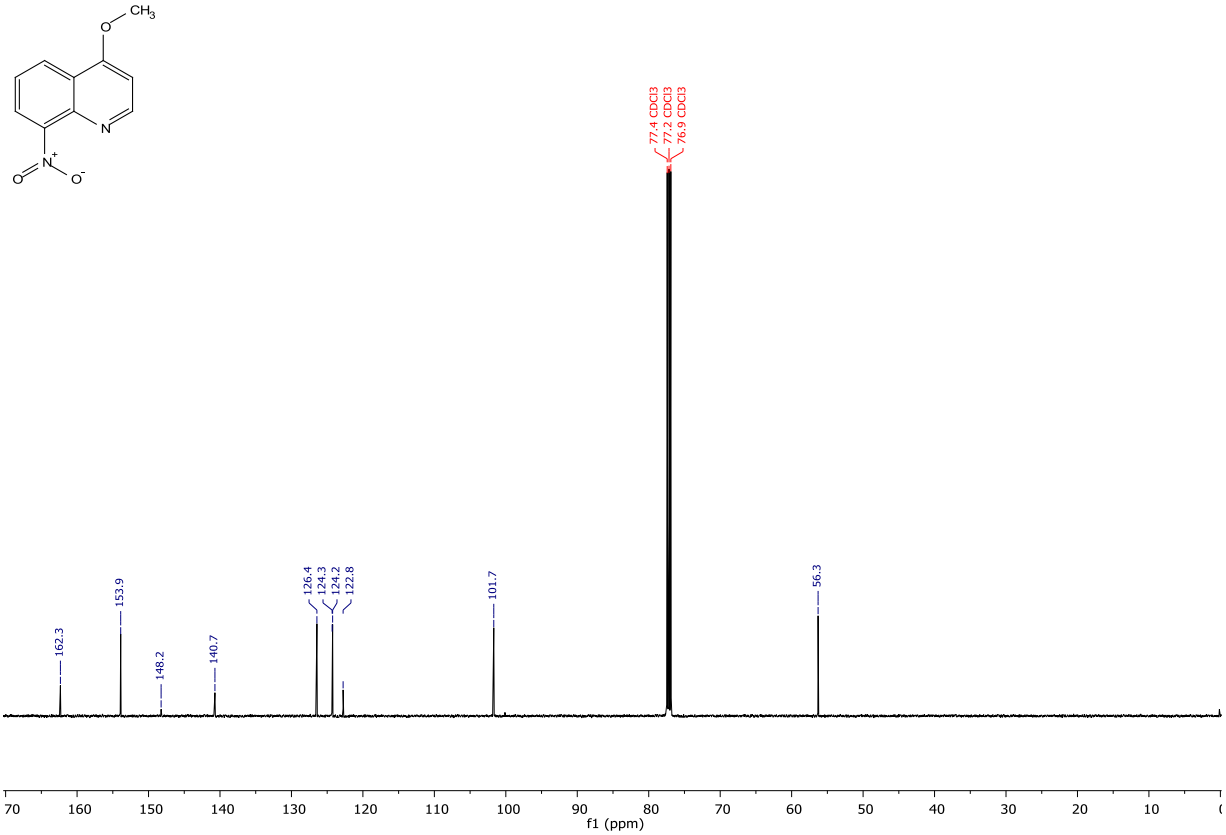




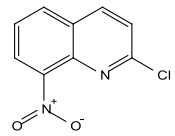


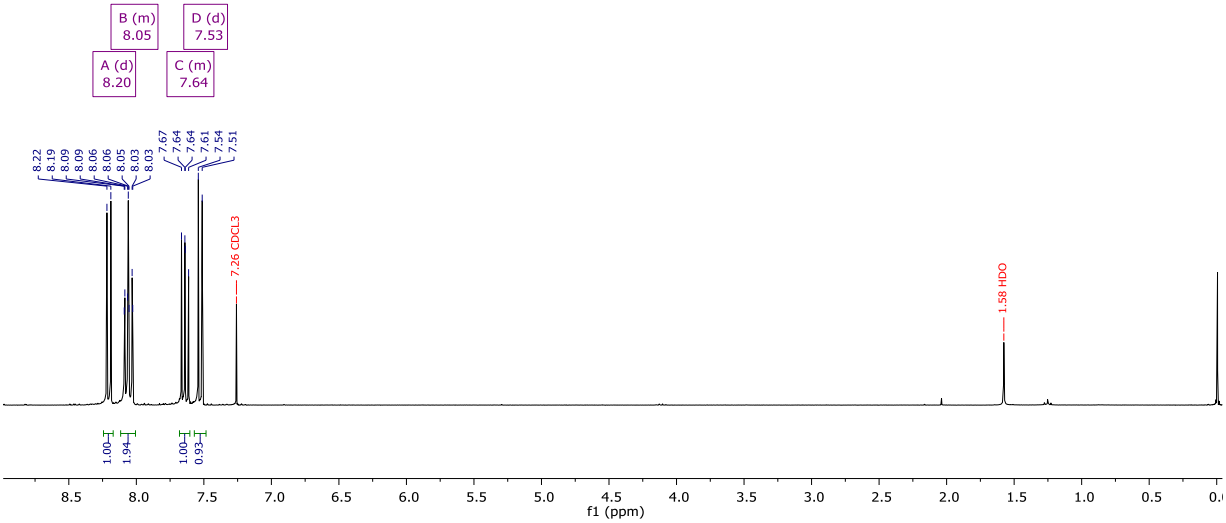
^{1}H and $^{13}C\{1H\}$ spectra of 4-methoxy-8-nitroquinoline – **1c** in CDCl3.

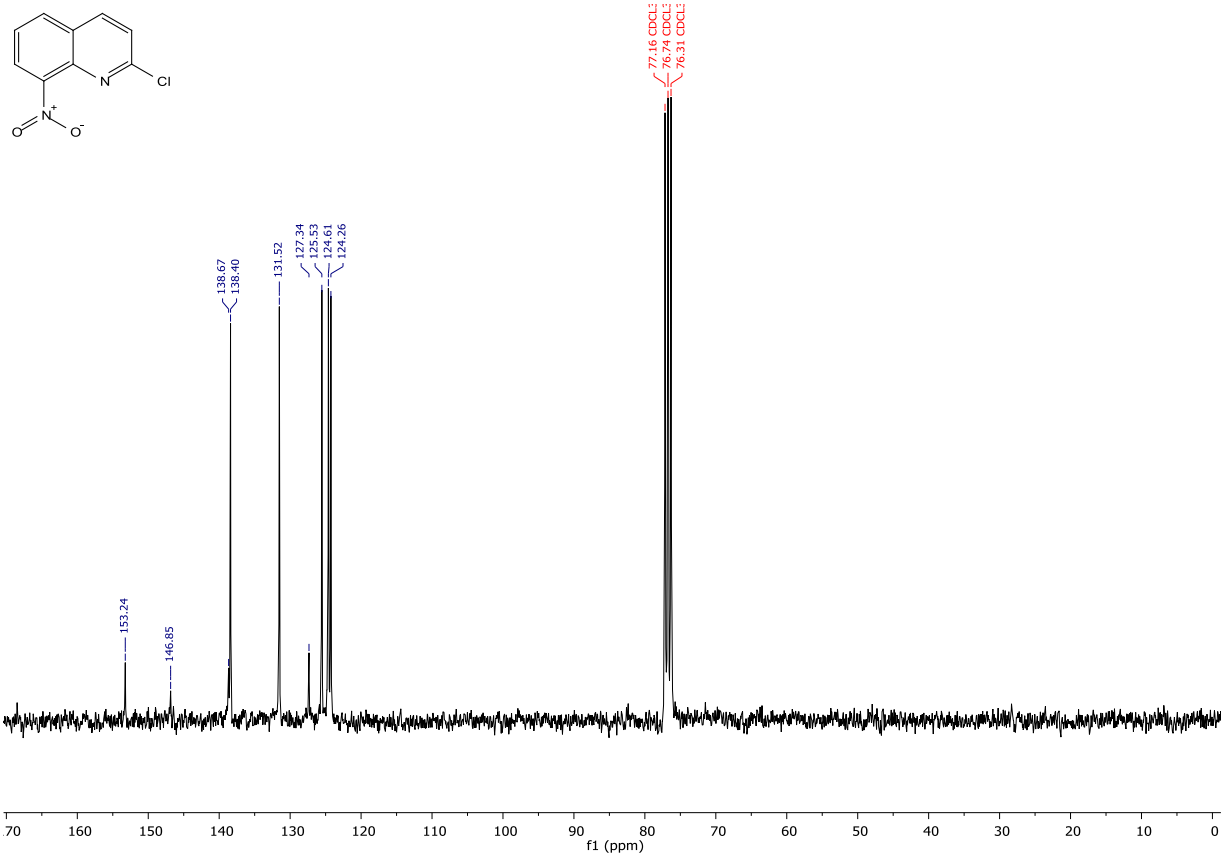




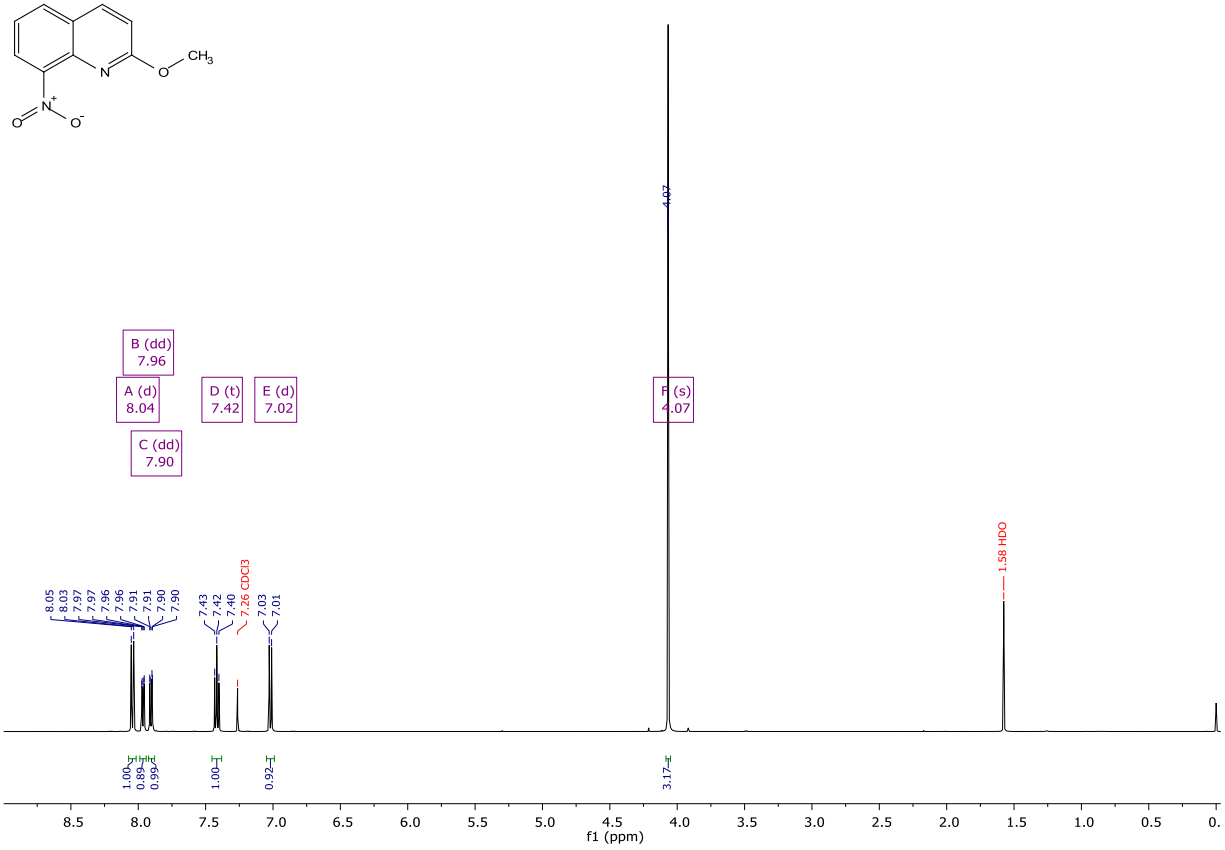
^{1}H and $^{13}C\{1H\}$ spectra of 2-chloro-8-nitroquinoline – **S6** in CDCl3.

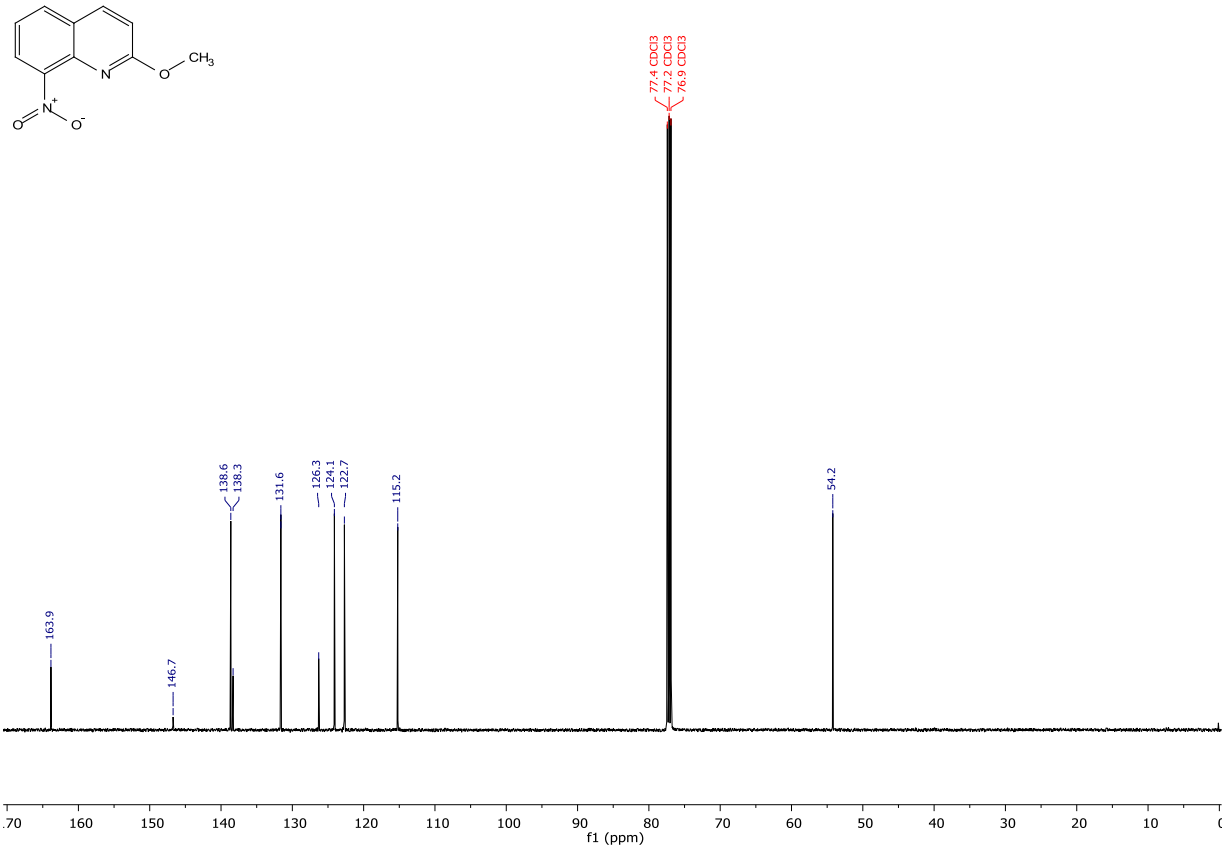




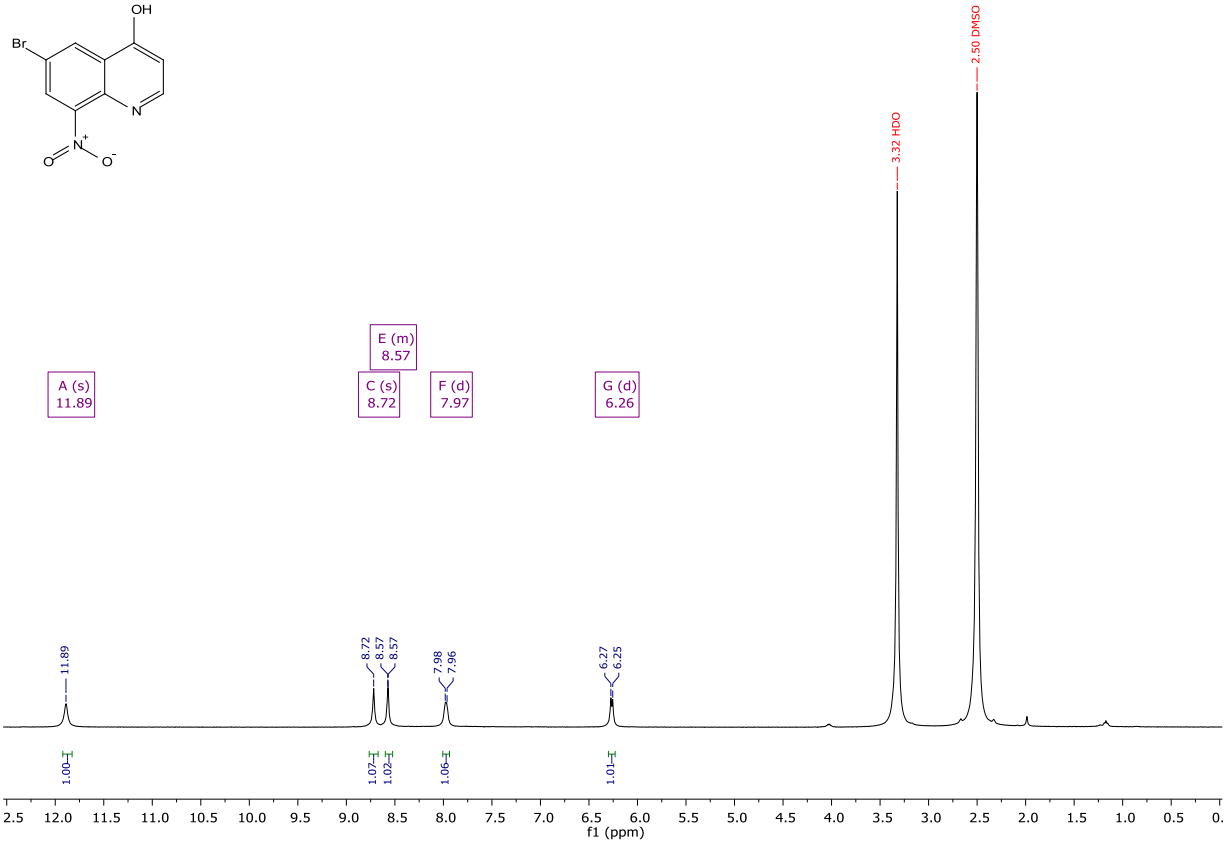


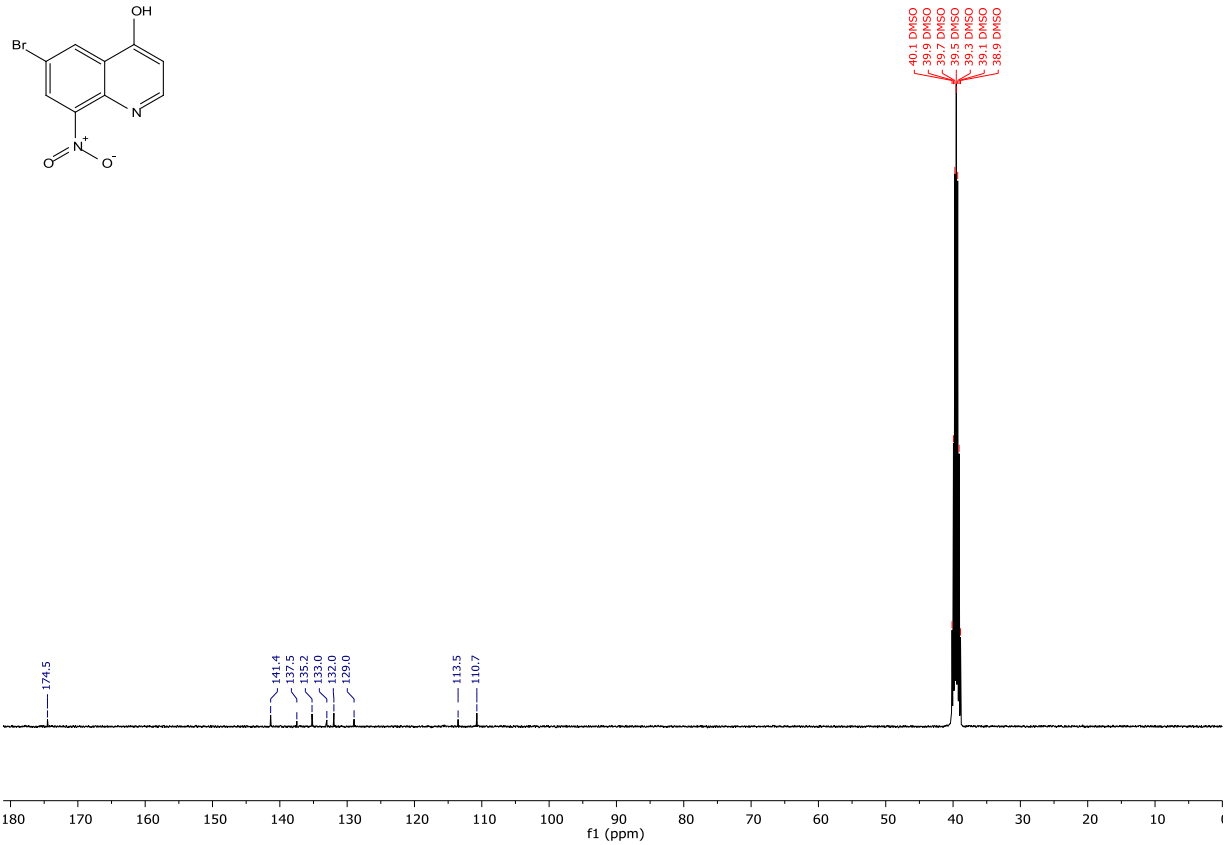
^{1}H and $^{13}C\{1H\}$ spectra of 2-methoxy-8-nitroquinoline – **1d** in CDCl3.



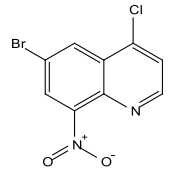


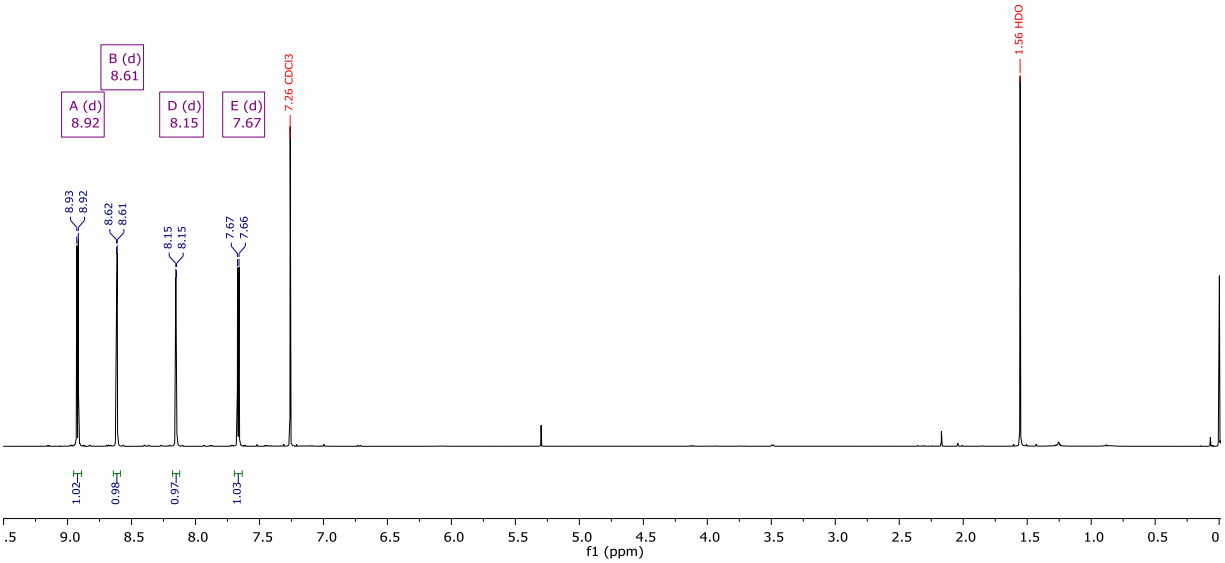
^{1}H and ^{13}C{1H} spectra of 6-bromo-8-nitroquinolin-4-ol – **S7** in DMSO-d_6.

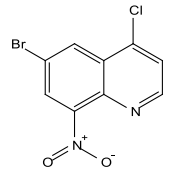




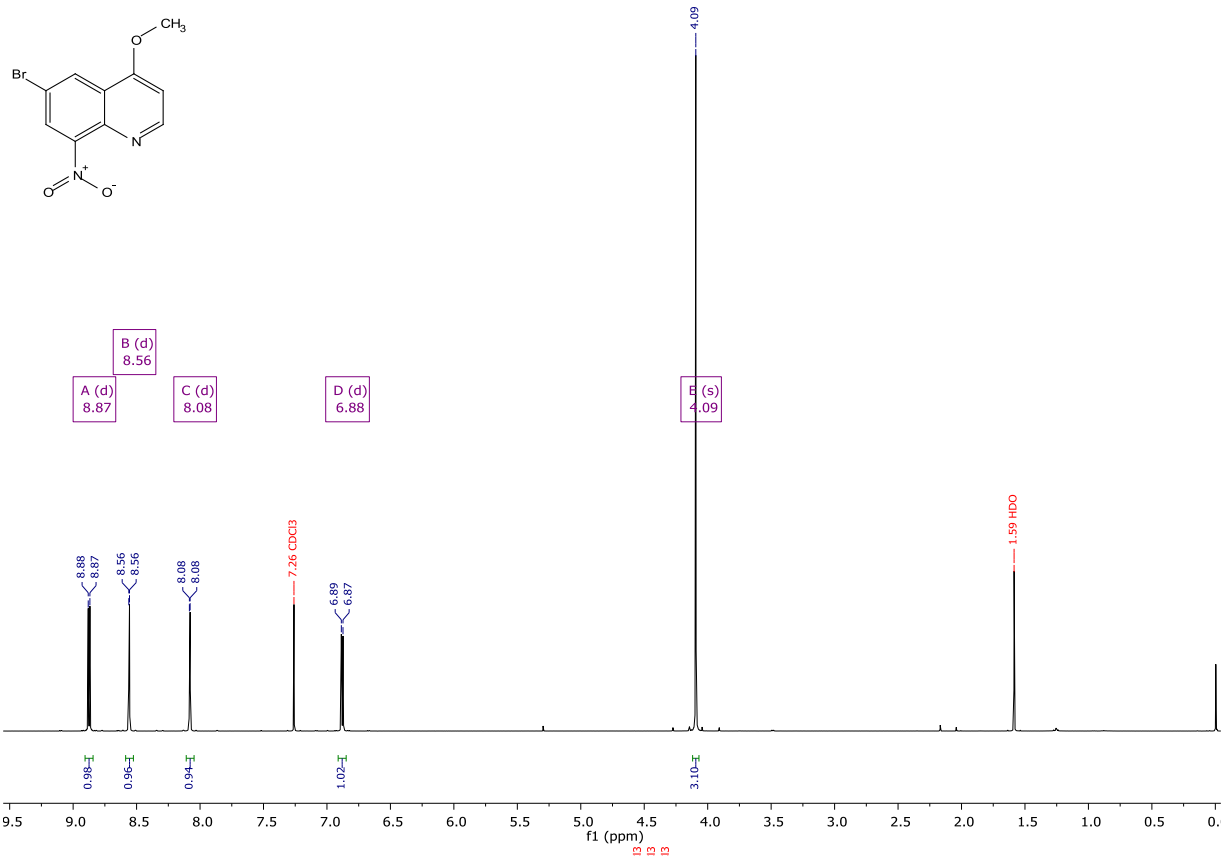
^{1}H and $^{13}C\{1H\}$ spectra of 6-bromo-4-chloro-8-nitroquinoline – **S8** in $CDCl_3$.

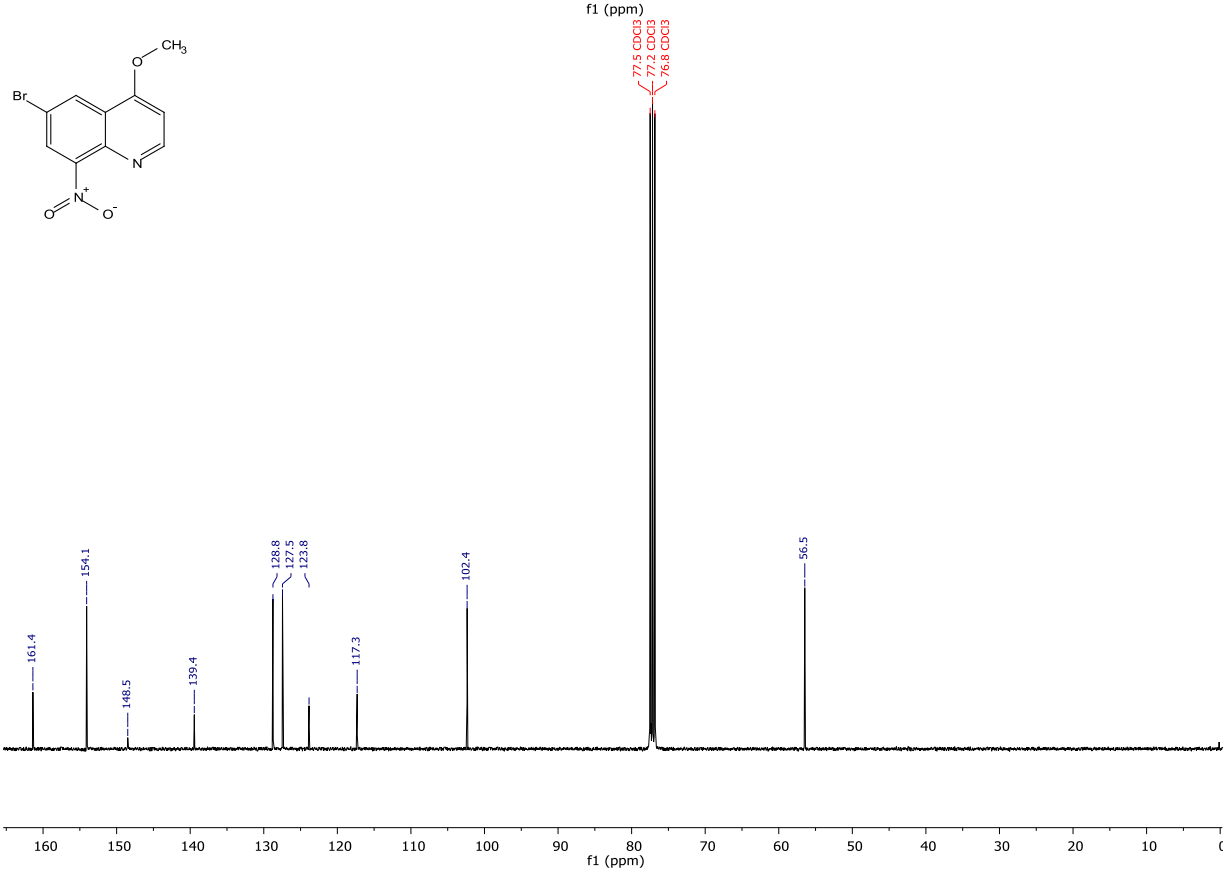




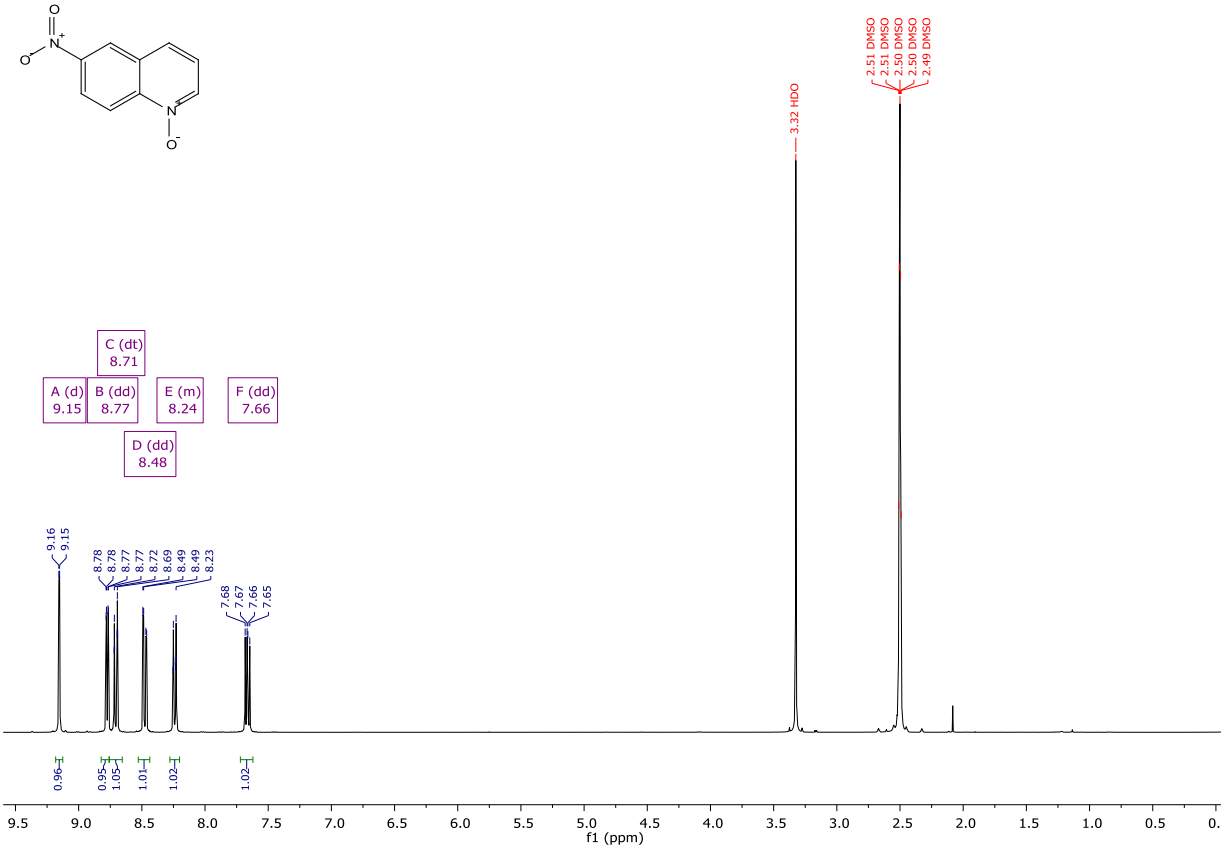


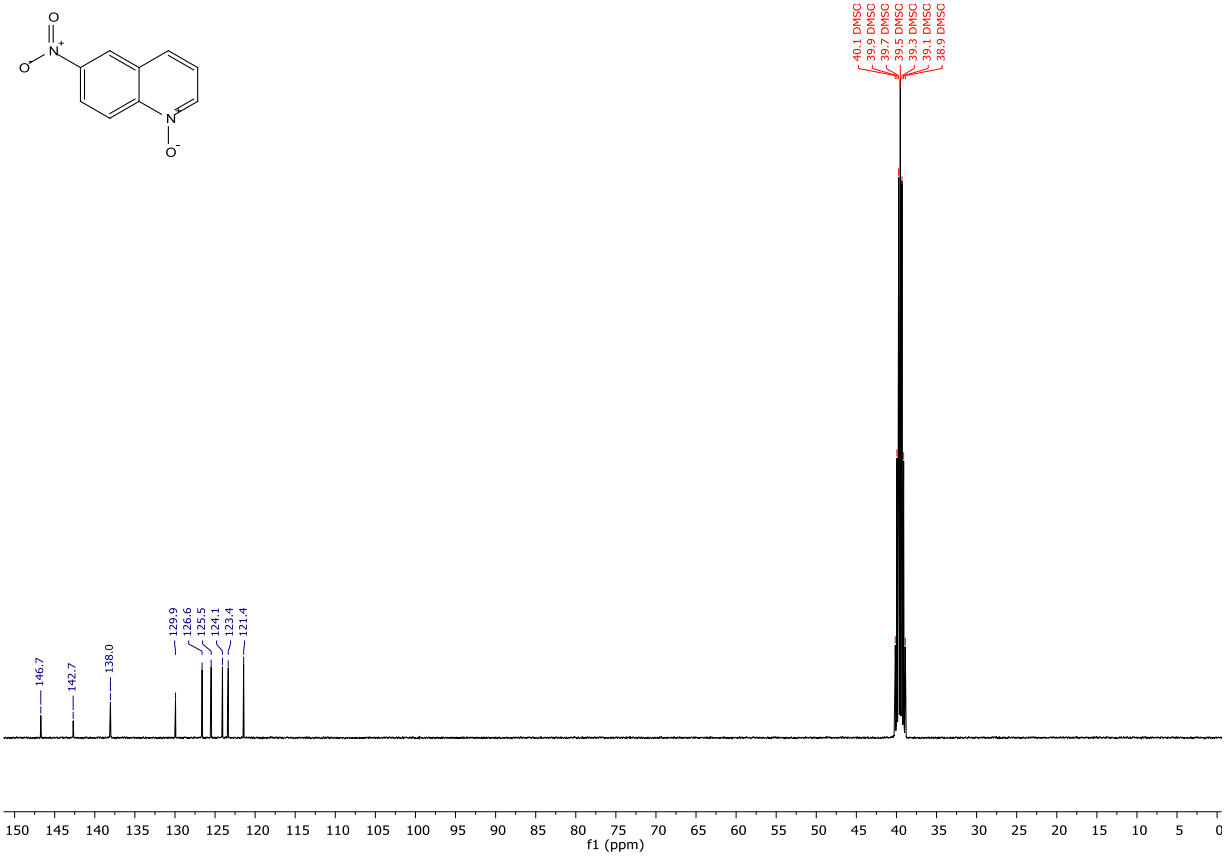
^{1}H and $^{13}C\{1H\}$ spectra of 6-bromo-4-methoxy-8-nitroquinoline – **1f** in $CDCl_3$.



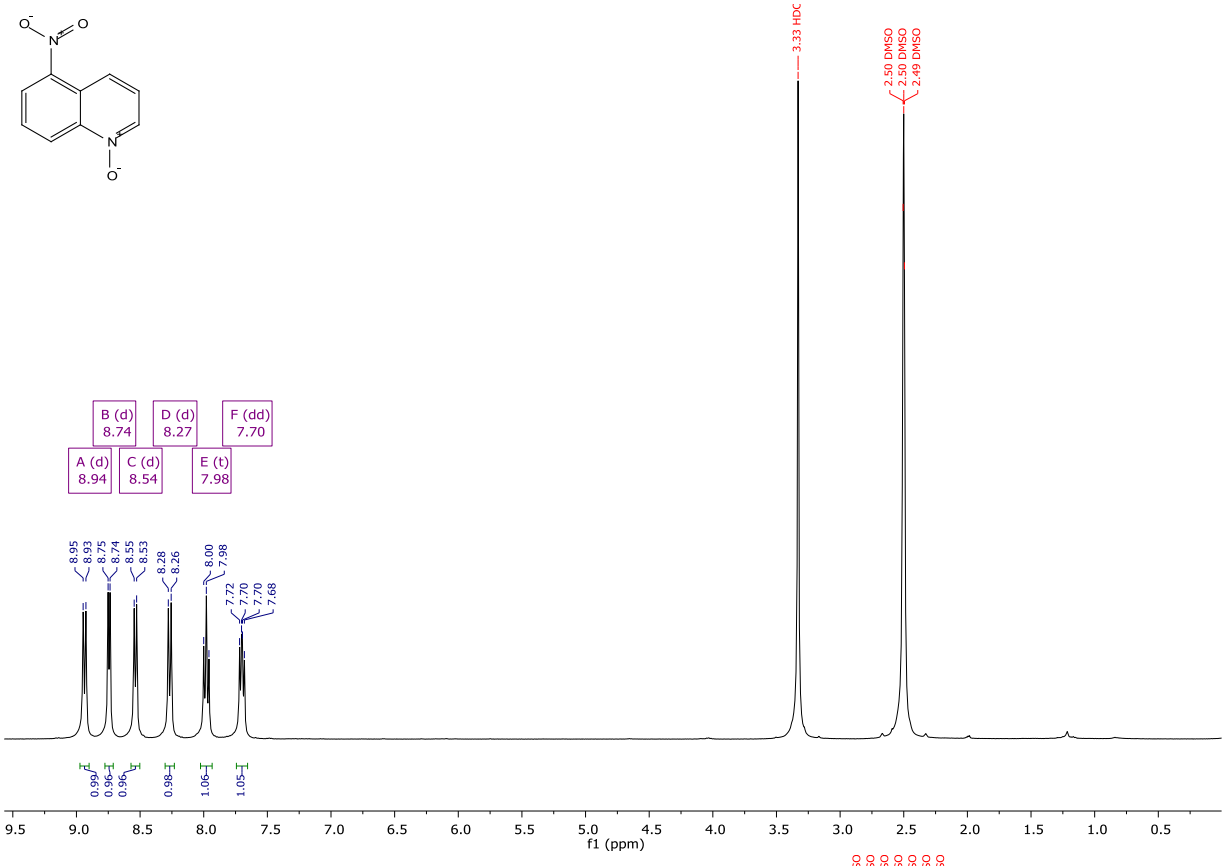


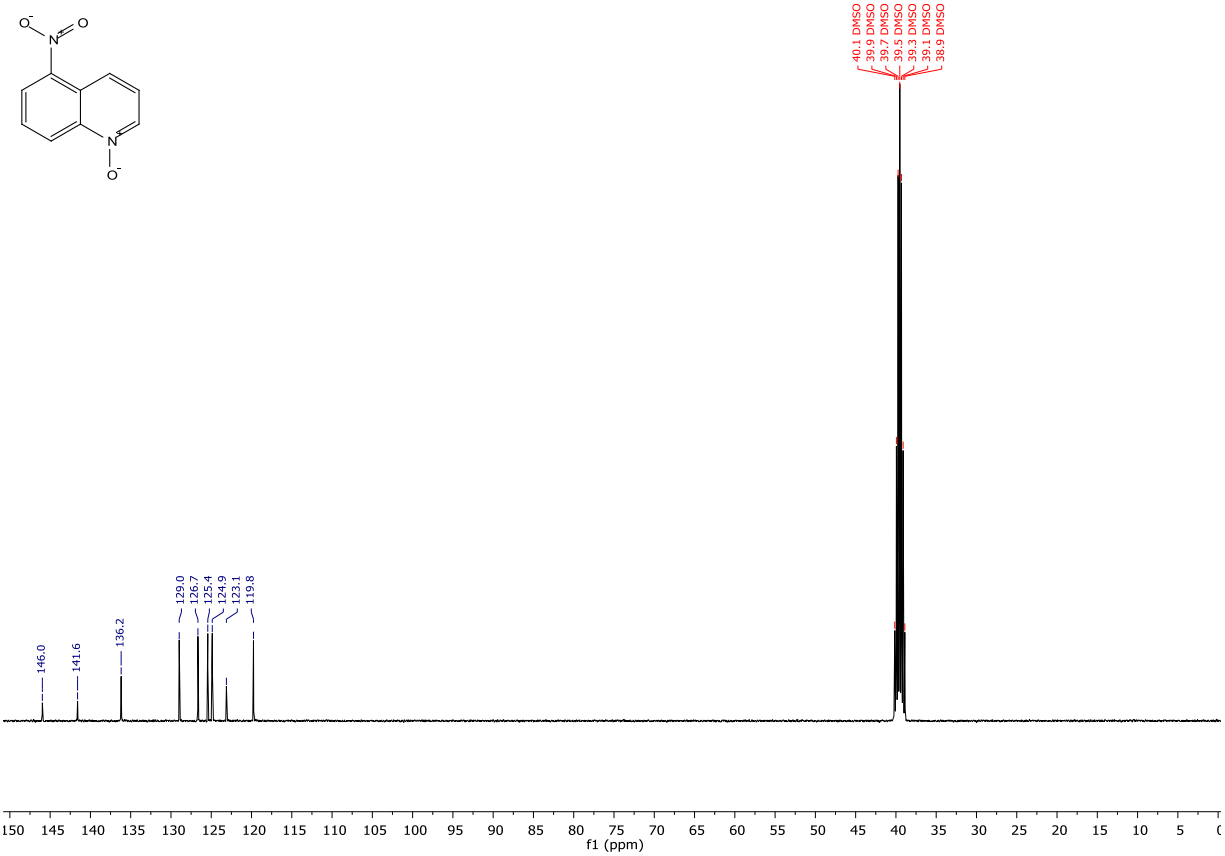
^{1}H and ^{13}C{1H} spectra of 6-nitroquinoline 1-oxide – **1i** in DMSO-d_6.



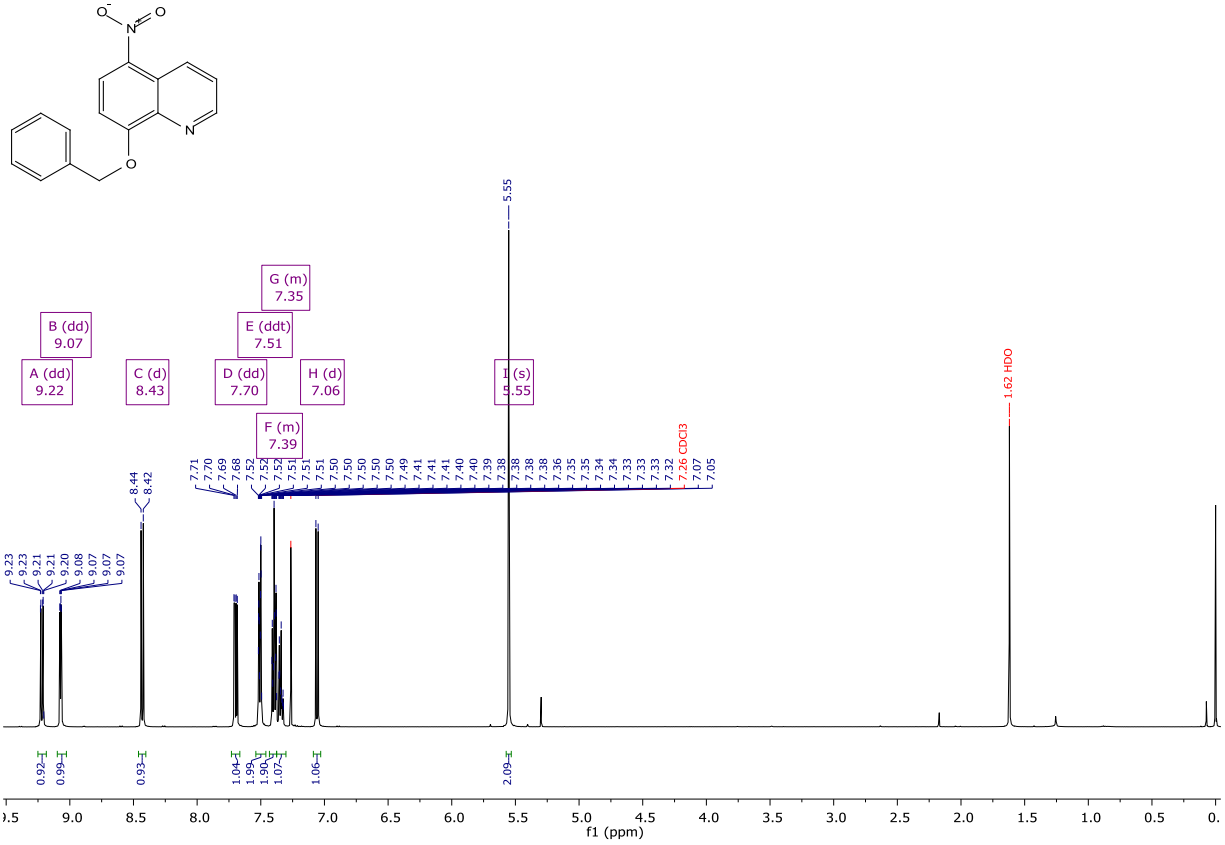


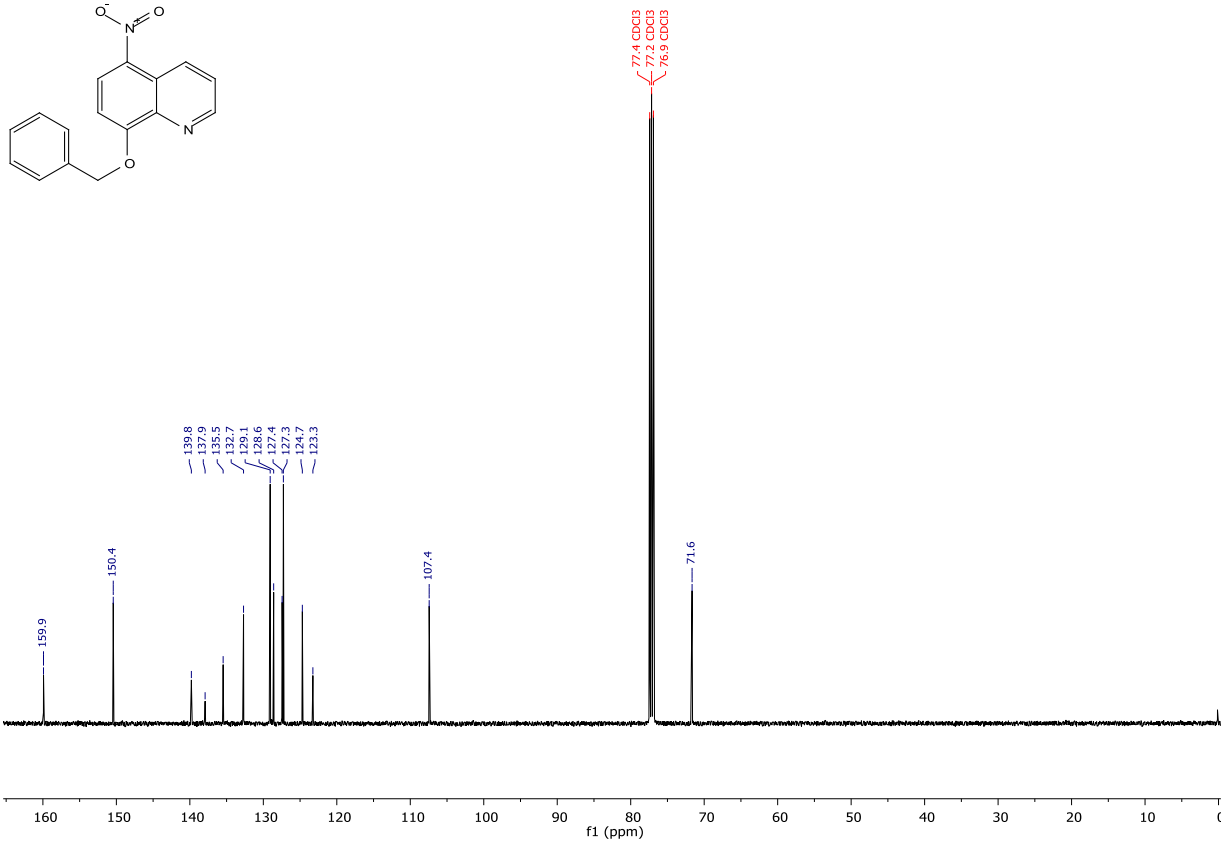
^{1}H and ^{13}C{1H} spectra of 5-nitroquinoline 1-oxide – **1j** in DMSO-d_6.



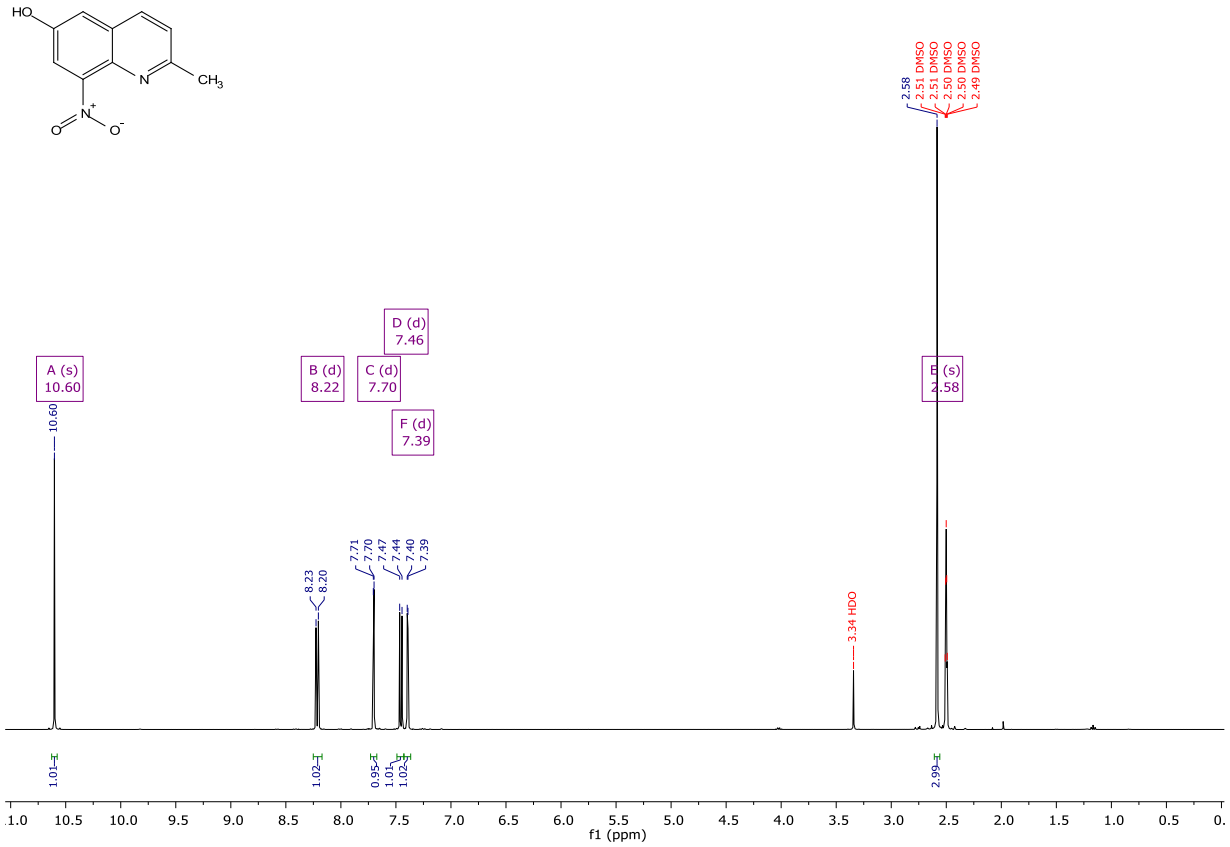


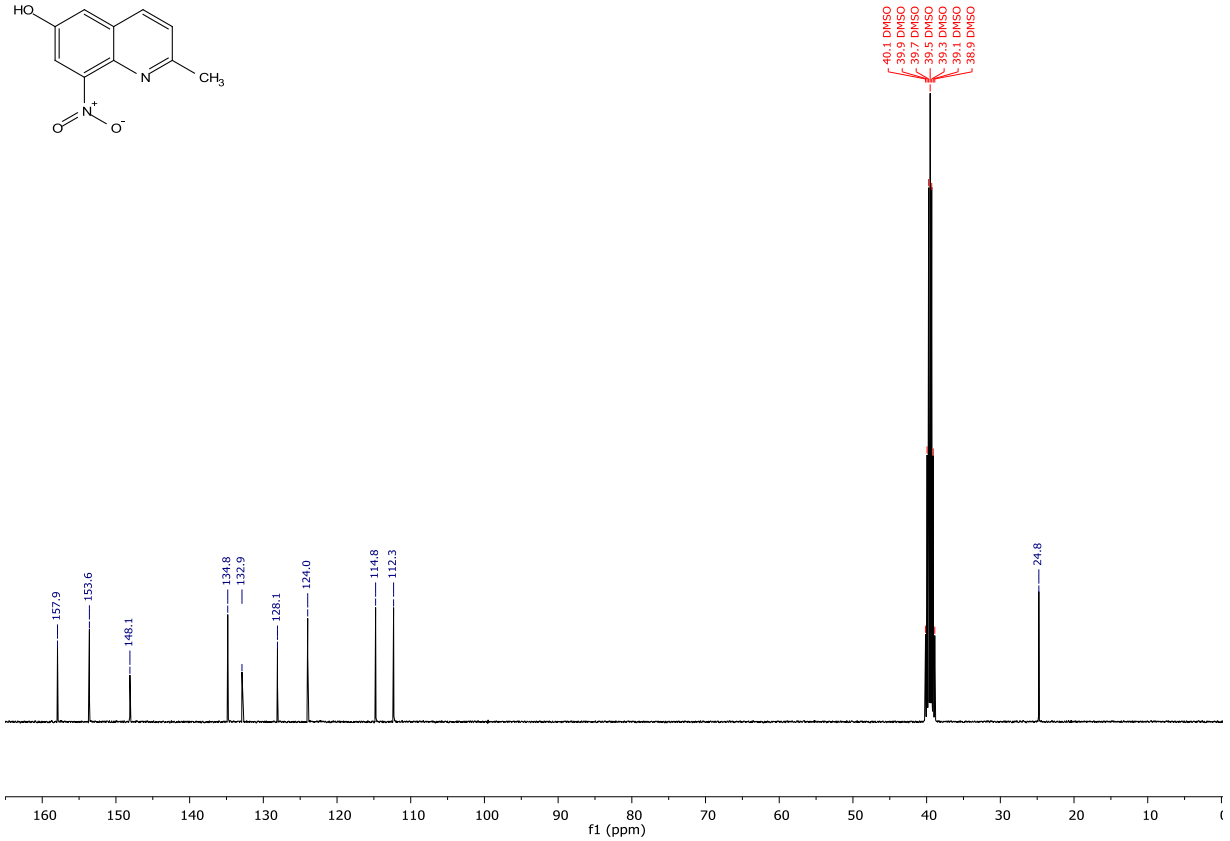
^{1}H and $^{13}C\{1H\}$ spectra of 8-(benzyloxy)-5-nitroquinoline – **1l** in $CDCl_3$.



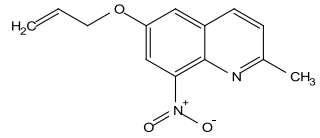


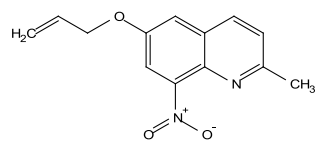
^{1}H and ^{13}C{1H} spectra of 2-methyl-8-nitroquinolin-6-ol – **S9** in DMSO-d_6.



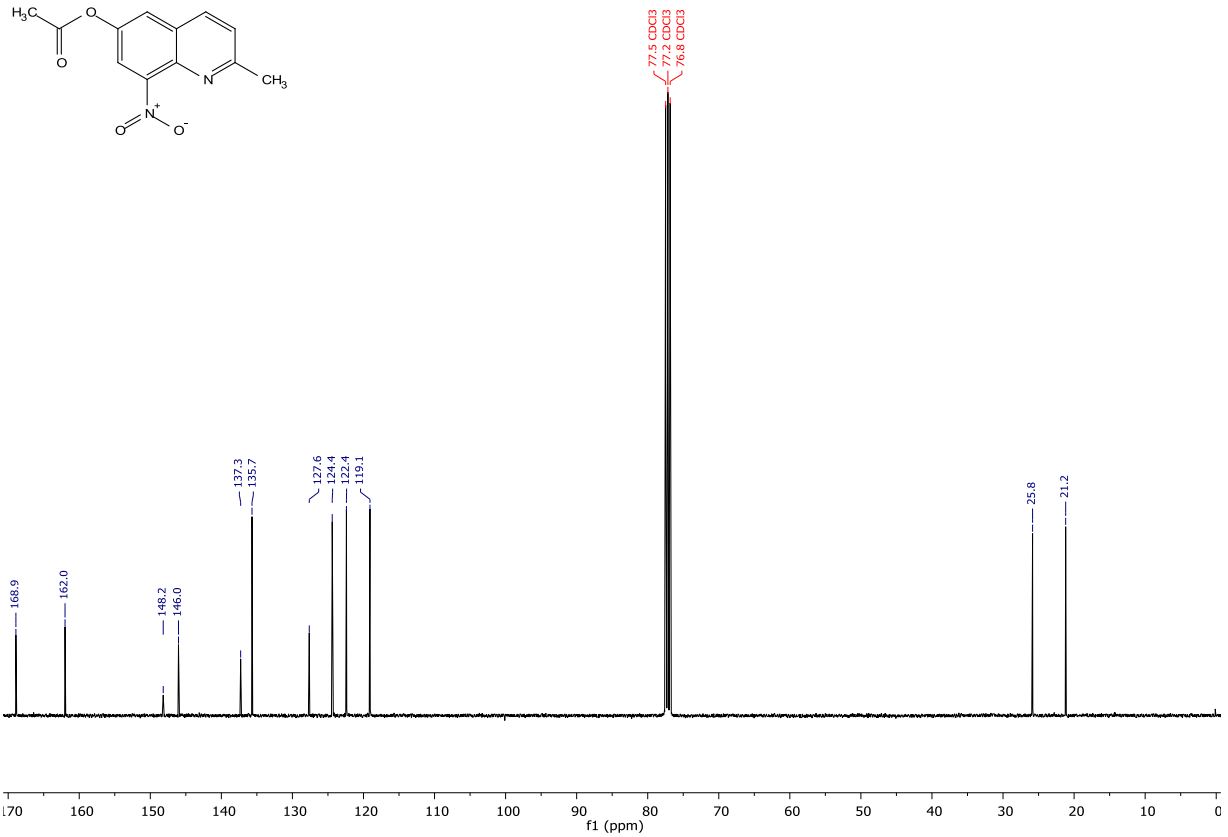


^{1}H and $^{13}C\{1H\}$ spectra of 6-(allyloxy)-2-methyl-8-nitroquinoline – **1m** in $CDCl_3$.

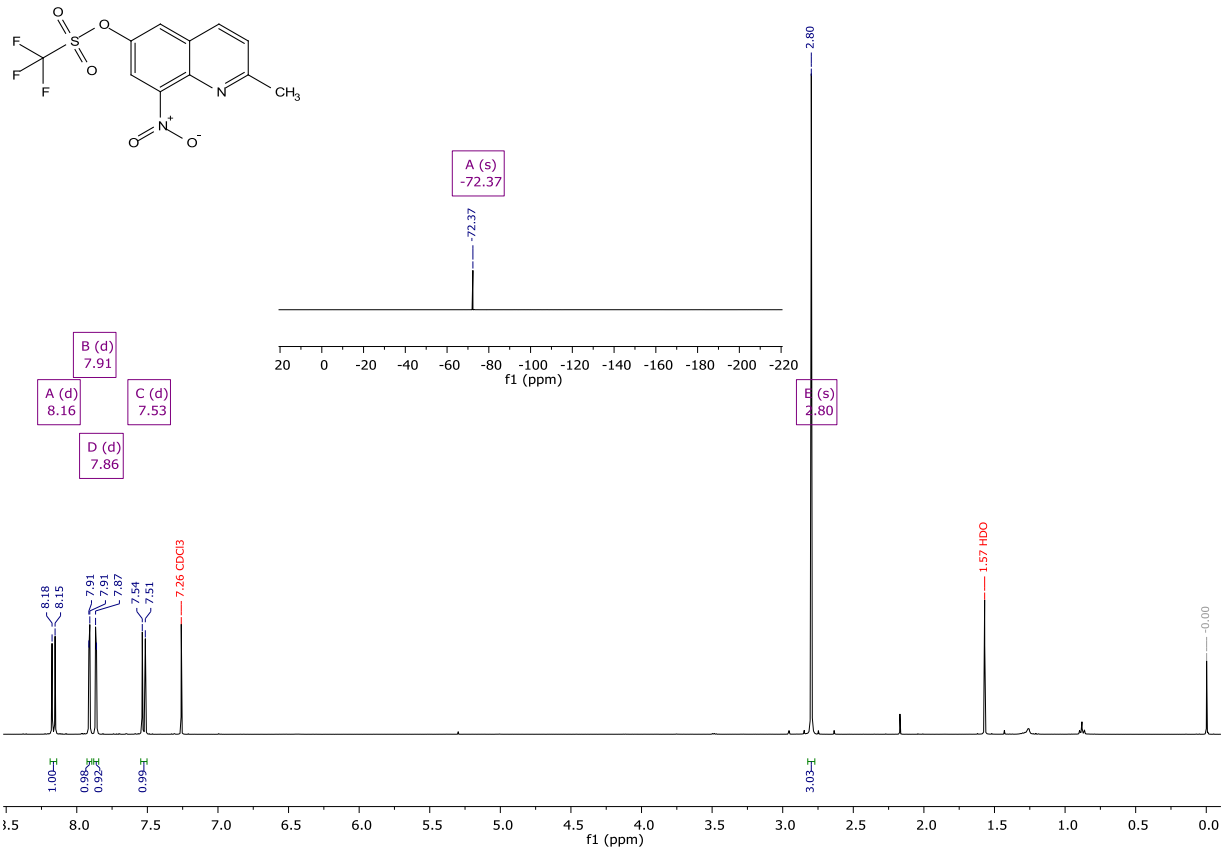


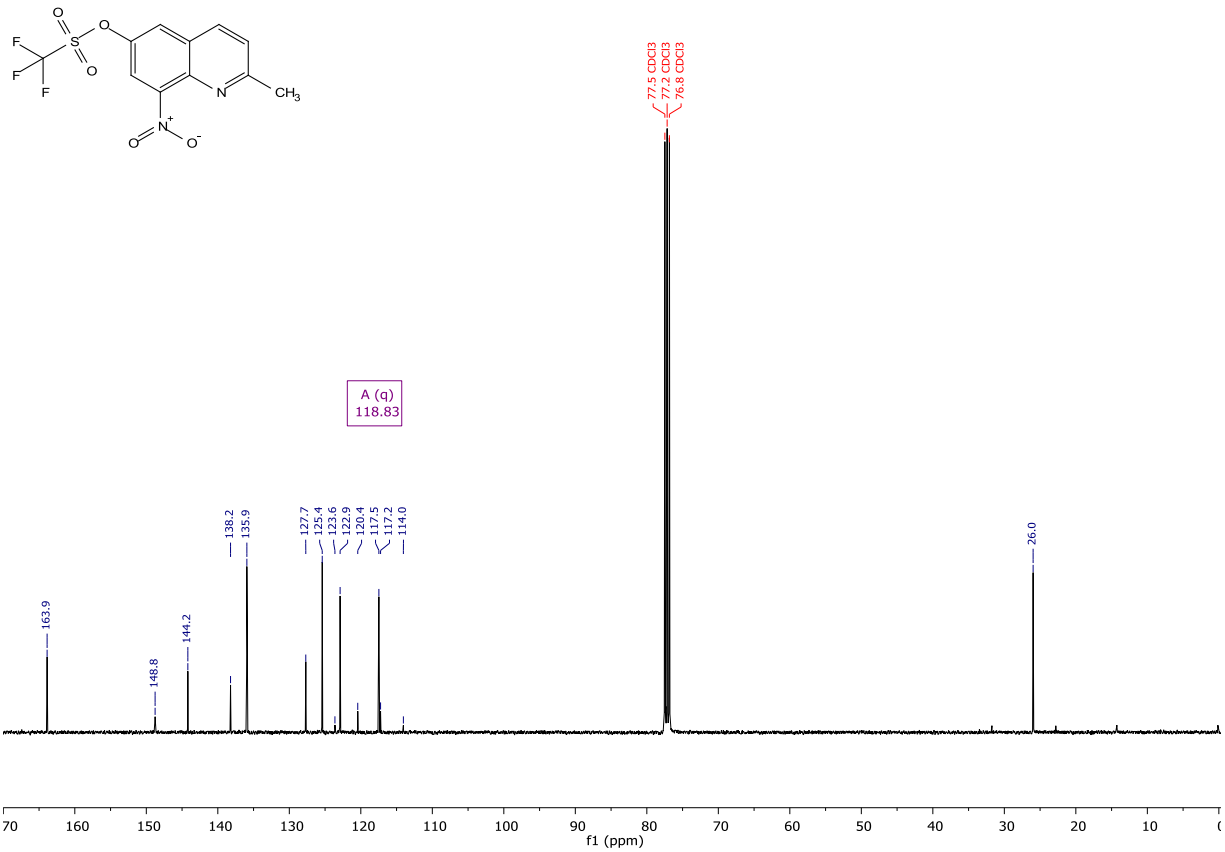


^{1}H and $^{13}C\{1H\}$ spectra of 2-methyl-8-nitroquinolin-6-yl acetate – **1n** in $CDCl_3$.

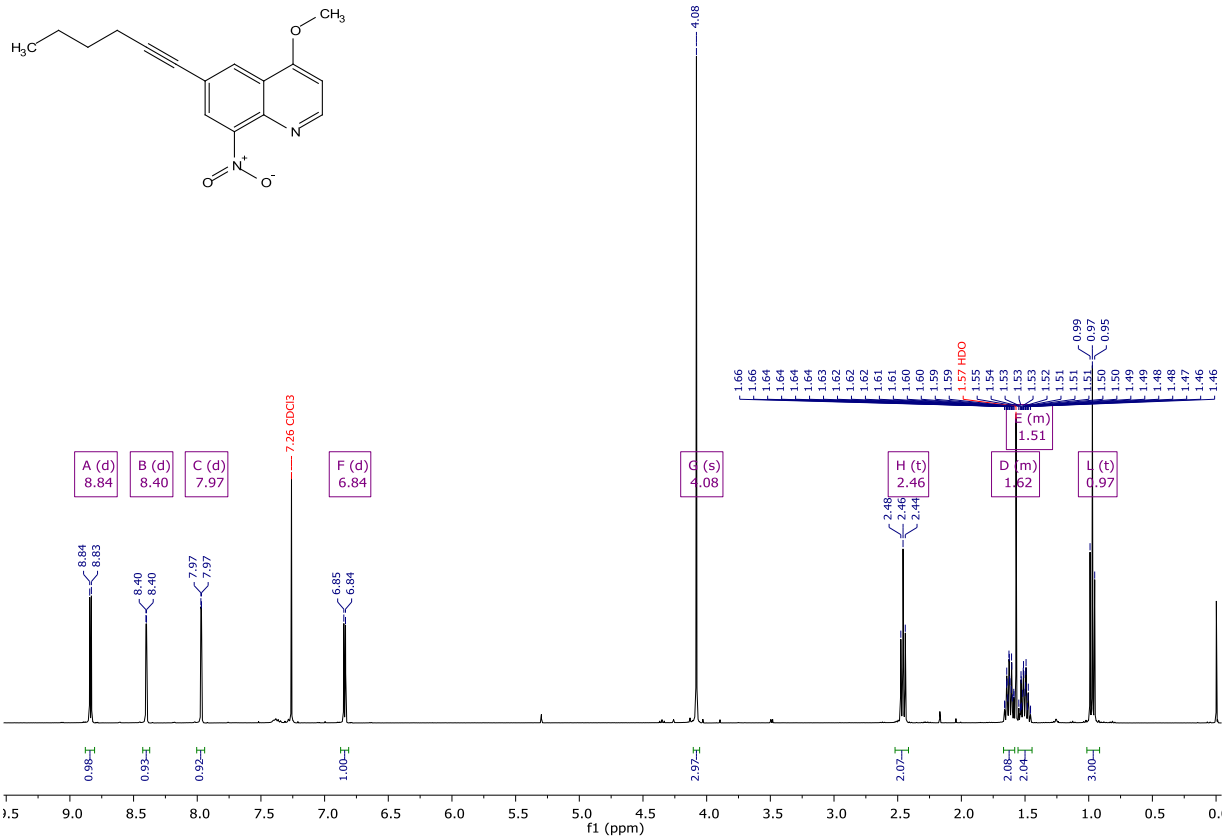


^{1}H, ^{19}F (inset) and ^{13}C{1H} spectra of 2-methyl-8-nitroquinolin-6-yl trifluoromethanesulfonate – **1o** in $CDCl_3$.

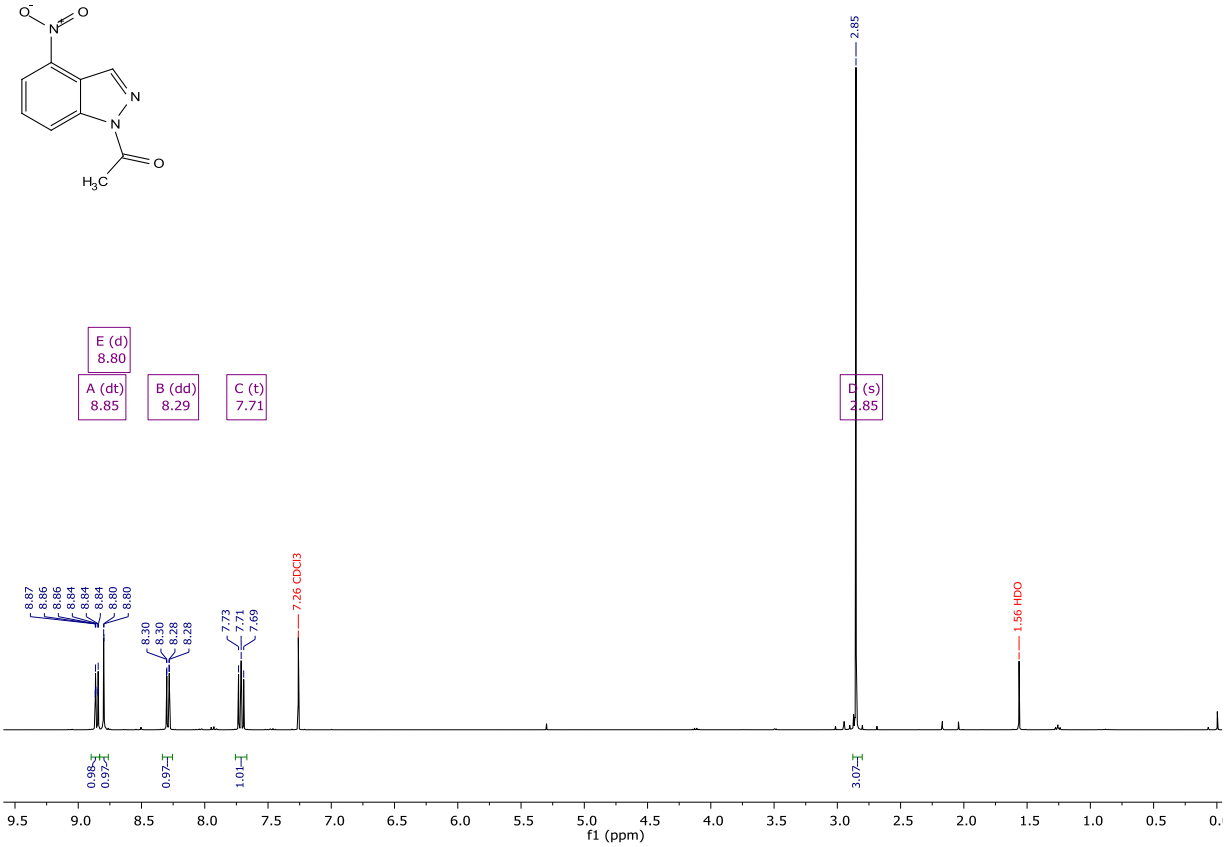


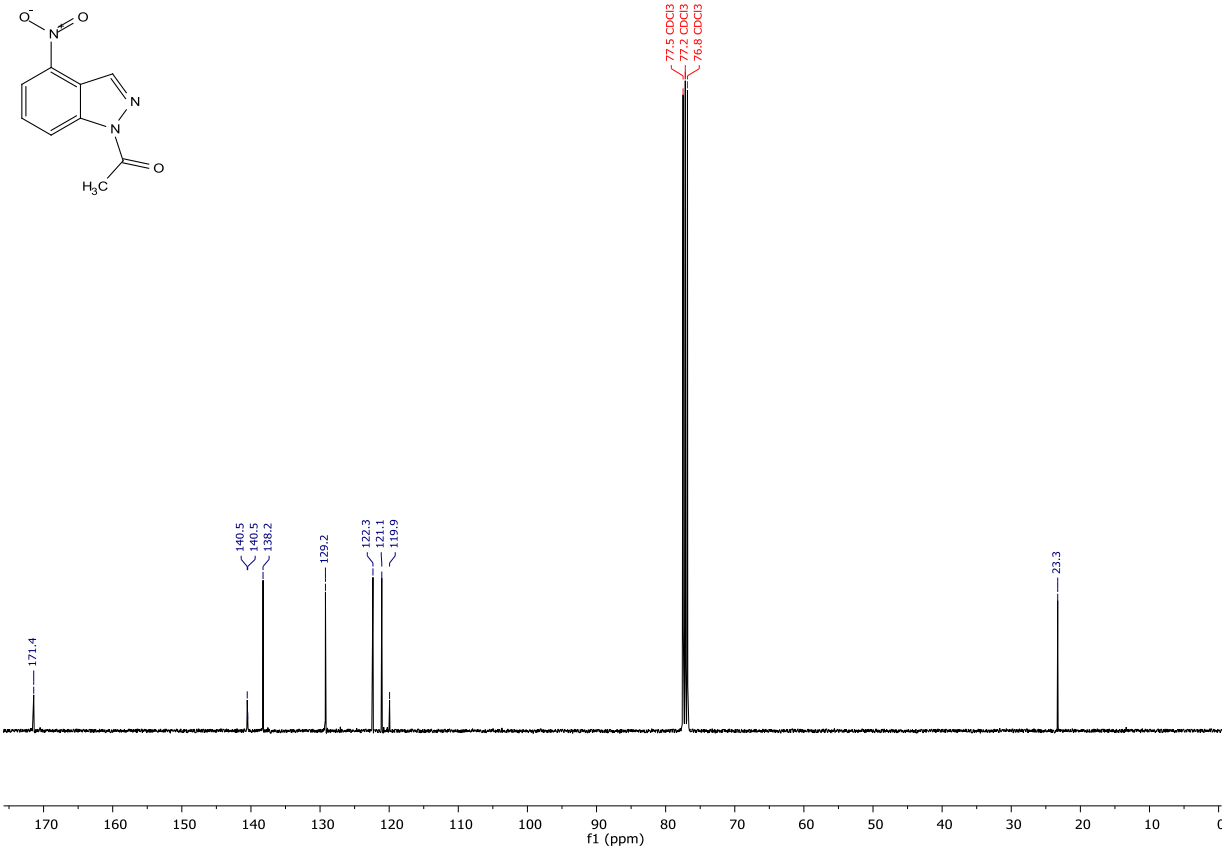


^{1}H and $^{13}C\{1H\}$ spectra of 6-(hex-1-yn-1-yl)-4-methoxy-8-nitroquinoline – **1p** in $CDCl_3$.



^{1}H and $^{13}C\{1H\}$ spectra of 1-(4-nitro-1H-indazol-1-yl)ethan-1-one – **3d** in $CDCl_3$.





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