Supporting Information

Visible Light Mediated direct C8-H Arylation of Quinolines and C2-H Arylation of Quinolin-N-oxides and Pyridines under Organic Photocatalysis

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1.1 General Information

Commercial reagents and solvents were purchased from Merck, Thermo fischer, TCI, Spectrochem, Avra chemicals, and they were directly used without any further purification. Organic solutions were concentrated under reduced pressure using Buchi rotary evaporator and chiller. Flash column chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed on Merck (Darmstadt, Germany) TLC Aluminium plates precoated with silica gel 60 F_{254} of size (20 x 20 cm). ^{1}H and ^{13}C NMR were recorded on Bruker 300 MHz (75 MHz) and 400 MHz (100 MHz) instruments, ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm). ^{13}C NMR chemical shifts are reported in ppm relative to chloroform (77.16 ppm) (chemical shifts were internally referenced to TMS). Coupling constants are reported in Hz. Data for ^{1}H NMR is written following the pattern: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplets, br = broad signal), coupling constants (*J* Hz). Data for ^{13}C NMR are reported in terms of chemical shifts only. Melting points were recorded on DBK- Programmable Melting point Apparatus. ESMS were recorded on LC/triple quadrupole mass spectrometer by electrospray ionisation. High resolution mass spectra (HRMS) were acquired on LC/QTOF (quadrupole time of flight) mass spectrometer with electrospray ionisation source.

2. Experimental Procedures

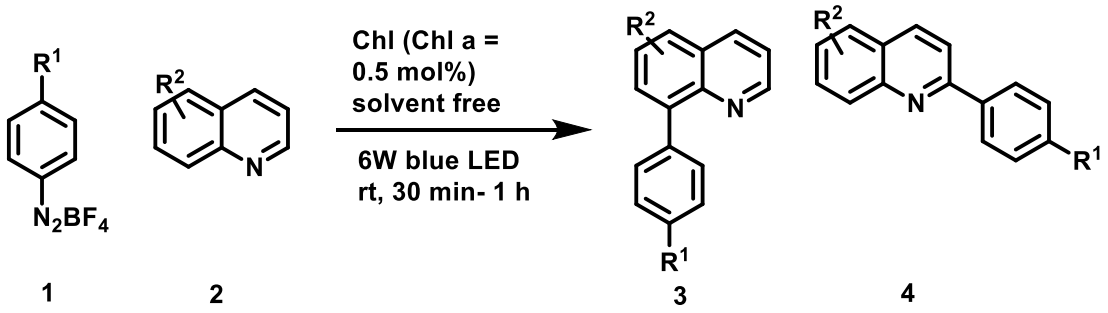
2.1. Method for estimation of Chlorophyll a

The natural pigment chlorophyll we used was purchased from Tokyo Chemical Industry (TCI, Product No. C0780, EC No. 215-800-7, Lot. BF4IC-SB). This is a mixture of chlorophyll, lactose, and dry gum Arabic (according to the product description). The mass percentage of chlorophyll a content in this reagent was determined and found to be 0.51% (mass percentage) by measuring the absorbance of chlorophyll at 663 nm and 645 nm in 90% acetone solution following the Wellburn estimation method.

It was observed that different Lot. of the commercially available chlorophyll contained different concentrations of chlorophyll a,[1] so we had estimated the chlorophyll-a concentration of a particular bottle before installing reactions with it.

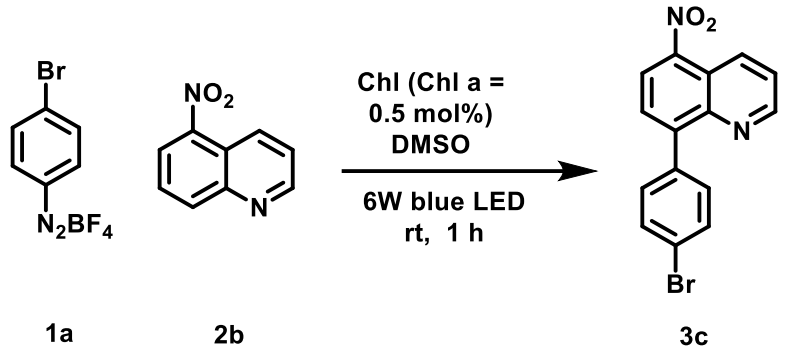
2.2. General Procedure for Arylation of quinoline derivatives

2.2.1. General Procedure for synthesis of 3 (A)



Quinoline (**2**) (30 equiv., 6.0 mmol) and chlorophyll (Chl a = 0.5 mol%) was added to a glass vial (30 mL) and the reaction mixture was stirred under the irradiation of 3W blue LED (approximately 2 cm away from the light source) under aerobic condition. Thereafter, phenyl diazonium salt (**1**) (1 equiv., 0.2 mmol) was added to the reaction media in a portion-wise manner for 30 minutes to 1 hour. In the case of solid analogues of quinoline (**2**), at first, substrate **2** was dissolved in 0.5-0.7 mL of DMSO and stirred for half an hour, afterward, the PC (Chl, 0.5 mol%) was added followed by portion-wise addition of phenyl diazonium salts **1**. The reaction mixture was stirred for 30 minutes to 1 hour under the irradiation of a 6 W blue LED. After completion of the reaction, the reaction mixture was diluted with brine solution, then extracted with (3 x 50 mL) EtOAc. Thereafter, the combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give desired products **3** using hexane/ EtOAc as the eluent, and the unreacted quinoline was recovered.

Gram Scale Experiment



1a 2b 3c

5-nitroquinoline (**2b**) (29 g, 166.51 mmol), at first was dissolved in 10 mL of DMSO and stirred for half an hour, afterward, the PC (Chl, 0.5 mol%) was added followed by portion-wise addition of 4-bromobenzene diazonium tetrafluoroborate salt (**1a**) (1.58 g, 5.83 mmol). The reaction mixture was stirred for 1 hour under the irradiation of a 6 W blue LED. The desired product 8-(4-bromophenyl)-5-nitroquinoline (**3c)** was obtained in 79% yield (1.51 g)

As, arene diazonium tetrafluoroborate salts possess an easily accessible reduction potential, and the commonly employed organic dyes such as eosin Y, rose bengal, rhodamine B, methylene blue bear compatible excited state oxidation potentials,[2] capable to initiate SET and generate aryl radical. Henceforth, to check the effectiveness of these dyes under our protocol, reactions were installed (Table TS1) that afforded the desired product in good to moderate yields with C8/ C2 ratios of 3:1 to 4:1, comparable to that of the chlorophyll-catalyzed reaction. Also, the reaction was performed under different conditions, Table TS1 reports all these reactions performed.

Table TS1:

Entry	Conditions	Yield (%)[b] (3a:4a)
1	2a (15 equiv.), DMSO, K_3PO_4 (1.5 equiv.), 16 h	14 (1:1)
2	2a (15 equiv.), H_2O, K_3PO_4 (1.5 equiv.), 16 h	7 (1:1)
3	2a (15 equiv.), DMSO, Et_3N (1.5 equiv.), 16 h	Trace
4	2a (15 equiv.), DMSO, DABCO (1.5 equiv.), 16 h	Trace
5	2a (15 equiv.), DMSO, NaN_3 (1.5 equiv.), 16 h	Trace
6	2a (15 equiv.), DMSO, no light, 48 h	16 (2:1)
7	2a (15 equiv.), DMSO, no photocatalyst, 48 h	45 (3:1)
8	2a (30 equiv.), no light, 30 min	Trace
9	2a (30 equiv.), no photocatalyst, 30 min	Trace
10	2a (30 equiv.), Eosin Y, 1 h, 6W blue LED	57 (4:1)
11	2a (30 equiv.), Rose bengal, 1 h, 6W blue LED	55 (4:1)

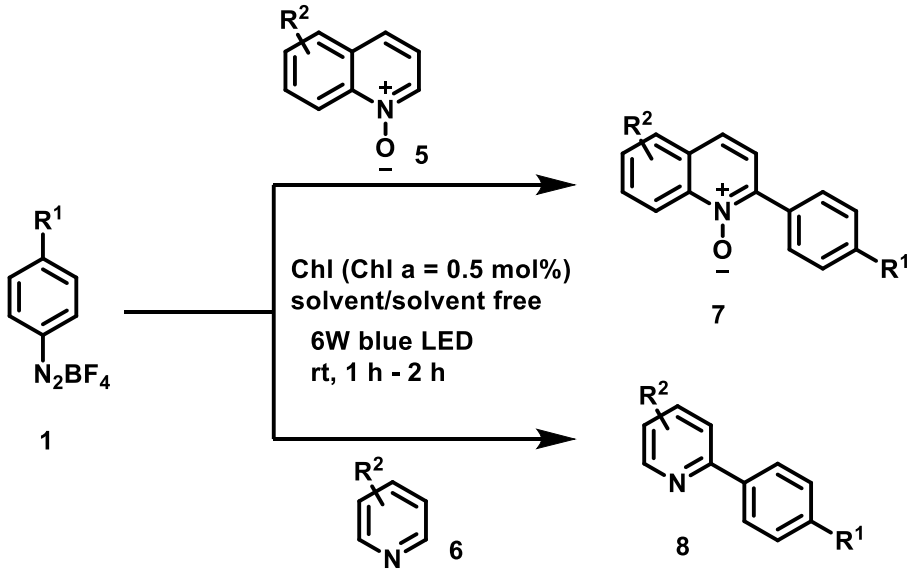
12	2a (30 equiv.), Rhodamine B, 1 h, 6W green LED	60 (3:1)
13	2a (30 equiv.), Methylene blue, 1 h, 6 W white LED	62 (3:1)

[a]**Reaction conditions:** 0.20 mmol **1a**, solvent free or solvent 0.5-0.7 mL, open atmosphere, 25 ºC. [b]NMR yield based on **1a**, by using dibromomethane as the internal standard.

2.2.2. General Procedure for synthesis of 7, 8 (B)

In a 30 mL glass vial, quinoline-N-oxide **5** (3 equiv., 0.6 mmol) was dissolved in DMSO (0.5-0.7 mL) and stirred for 30 minutes, afterward, the PC (Chl, 0.5 mol%), phenyl diazonium salts **1** were added to the reaction media. The resulting mixture was stirred for one hour to one and half hours under the irradiation of a 6 W blue LED. After completion of the reaction, the reaction mixture was diluted with brine solution, then extracted with (3 x 50 mL) EtOAc. Thereafter, the combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to give desired products **7** using hexane/ EtOAc as the eluent.

In the case of pyridines **6** (15 equiv., 3.0 mmol), a similar reaction procedure; as described for quinolines (**2**) was followed, which afforded the C2-arylated pyridines **8** via column chromatography.



2.2.3. General Procedure for Synthesis of quinoline-N-oxides 5

Quinoline N-oxides **5** were synthesized according to the reported methods.[3] Quinoline **2** (1 equiv.) and *m*-chloroperoxybenzoic acid (1.2 equiv.) were dissolved in reagent grade dichloromethane (DCM) (0.5M) and the reaction mixture was allowed to stir at room temperature for 24 hours, which precipitated a white solid (*m*-chlorobenzoic acid). The solvent was then evaporated under reduced pressure and the crude reaction mixture was purified by column chromatography to afford the corresponding *N*-oxides **5**.

3. Mechanistic Investigation

3.1. Stern-Volmer Fluorescence quenching experiments with 2a (Quinoline) and 1a (4-Bromobenzene tetrafluoroborate salt) as quenchers respectively

To explore the mechanism of the visible light mediated direct arylation of quinoline derivatives, Stern-Volmer fluorescence quenching experiments were carried out. The experiments were performed on the FlexStation 3 Multi-Mode Microplate Reader. As discussed in our earlier reports,[4] a 672 nm fluorescence was launched by chlorophyll (PC) on excitation at 433 nm. The fluorescence quenching experiments were conducted by adding 200 μL solution of chlorophyll (Chl a conc. = 1μM) in DMSO, to the individual well of Corning 96 well cell plate, then 1mM solution of quencher in DMSO was added into the well by 10μL successively, and the emission spectrum of the sample was recorded. At first 1mM solution of 4-bromobenzene tetrafluoroborate salt (**1a**) in DMSO was used as the quencher. The solution was excited at λ = 433 nm (excitation maxima of Chl a) and the emission intensity at λ = 672 nm (670 nm) (emission maxima of Chl a) was observed, a significant decrease in emission intensity occurred on subsequent addition of quencher **1a** (Figure 1). The induced fit plot depicted that the emission intensity of **PC** decreases linearly with the gradual addition of **1a** (Figure 2). Thereafter we conducted another Stern-Volmer fluorescence quenching experiment with a 1mM solution of quinoline (**2a**) as the quencher to investigate its effect on the fluorescence intensity of chlorophyll. Following the same procedure as in the case of quencher **1a**, the solution was excited at λ = 433 nm and emission

intensity at λ = 672 nm was recorded (Figure 3) and there was no significant decrease in emission intensity of chlorophyll. The induced fit plot showed that the emission intensity of **PC** remained unchanged even with the gradual addition of **2a** (Figure 4). As per the observations, the probability of an electron transfer between chlorophyll and quencher **1a** could be envisioned, at the same time electron transfer between PC and quinoline **2a** could be negated. Furthermore, the reduction potential of arene diazonium salts is reported to be 0.0 V vs SCE (0.244 V vs SHE),[5] that is higher than $E_{1/2ox}$ (Chl) = -0.53 V vs SHE, and the fluorescence quenching experiments indicated that **1a** could acquire a single electron from PC under visible light irradiation.

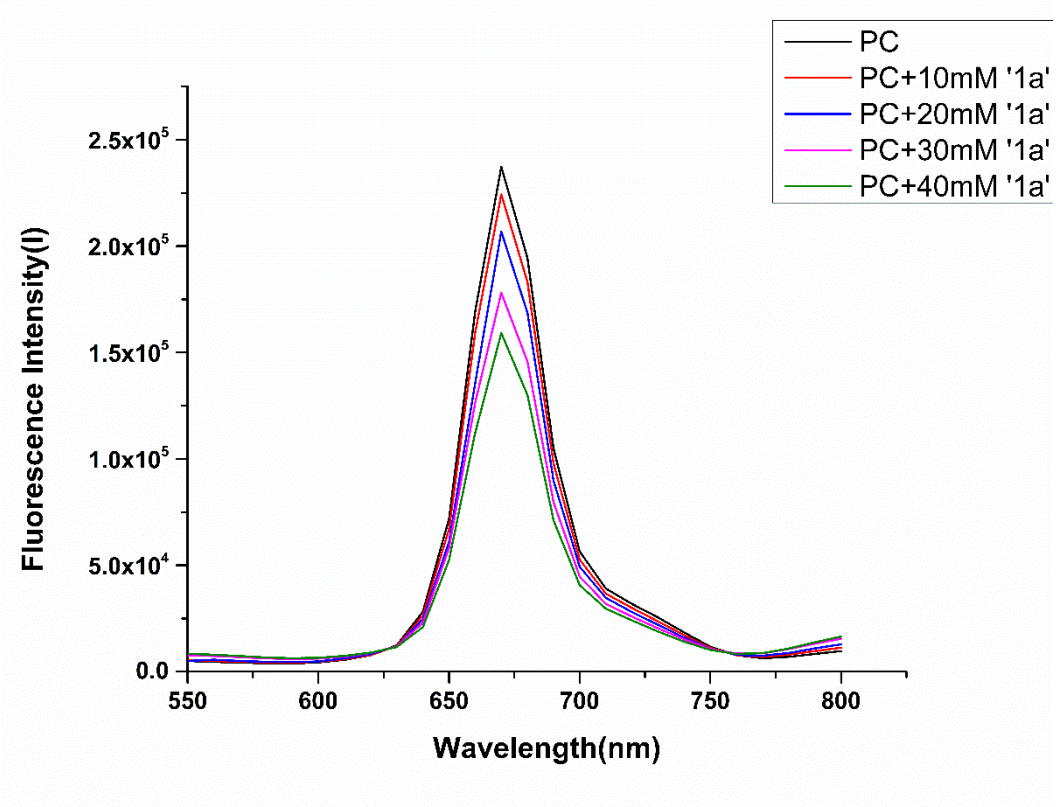


Figure 1. The fluorescence emission spectra of chlorophyll with different concentrations of added quencher (**1a**) excited at 433 nm.

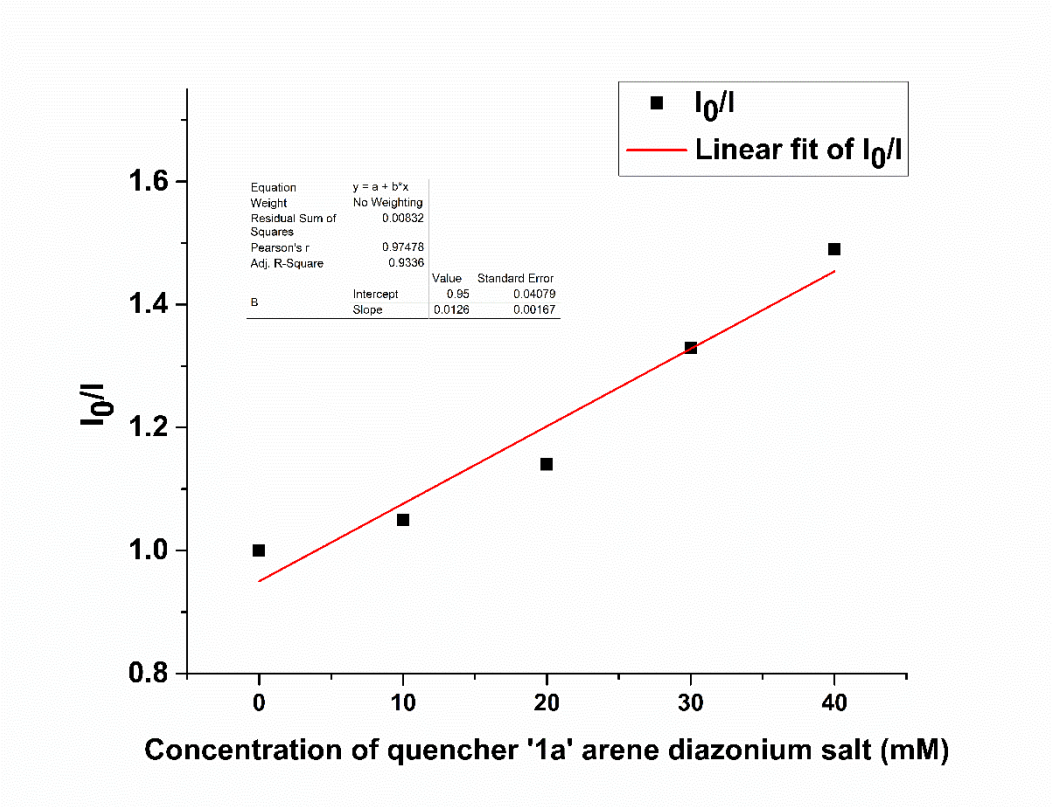


Figure 2. Chl (**PC**) emission quenching by **1a**. Linear quenching was observed.

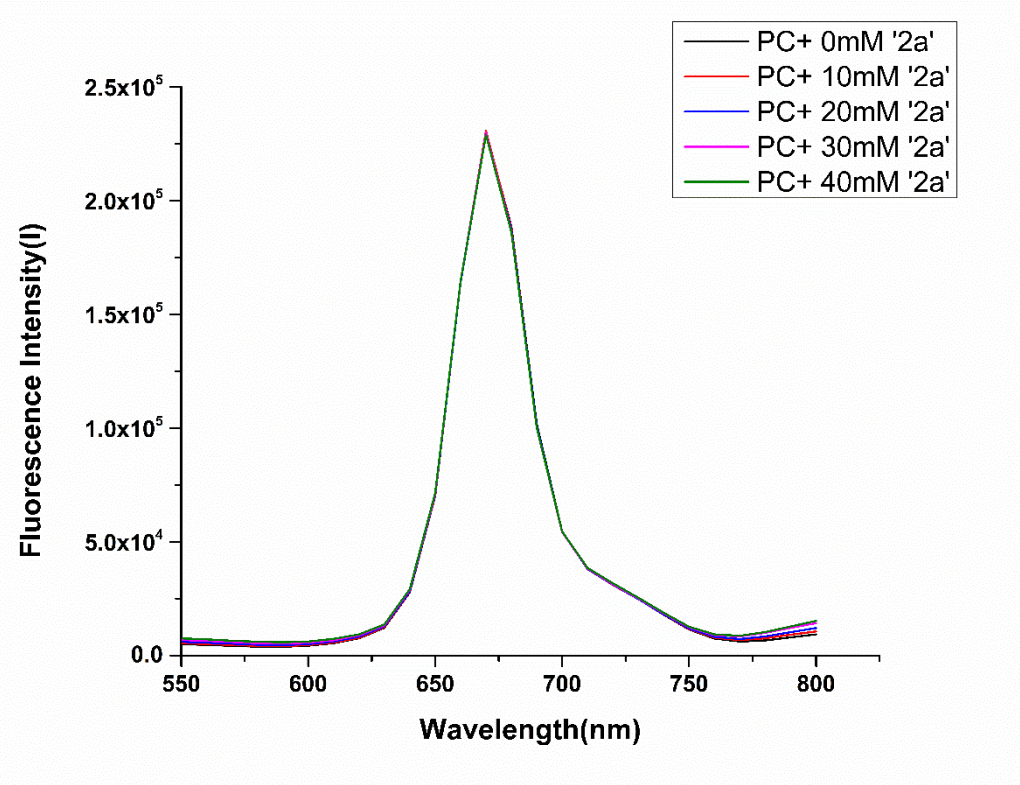


Figure 3. The fluorescence emission spectra of chlorophyll with different concentrations of added quencher (**2a**) excited at 433 nm.

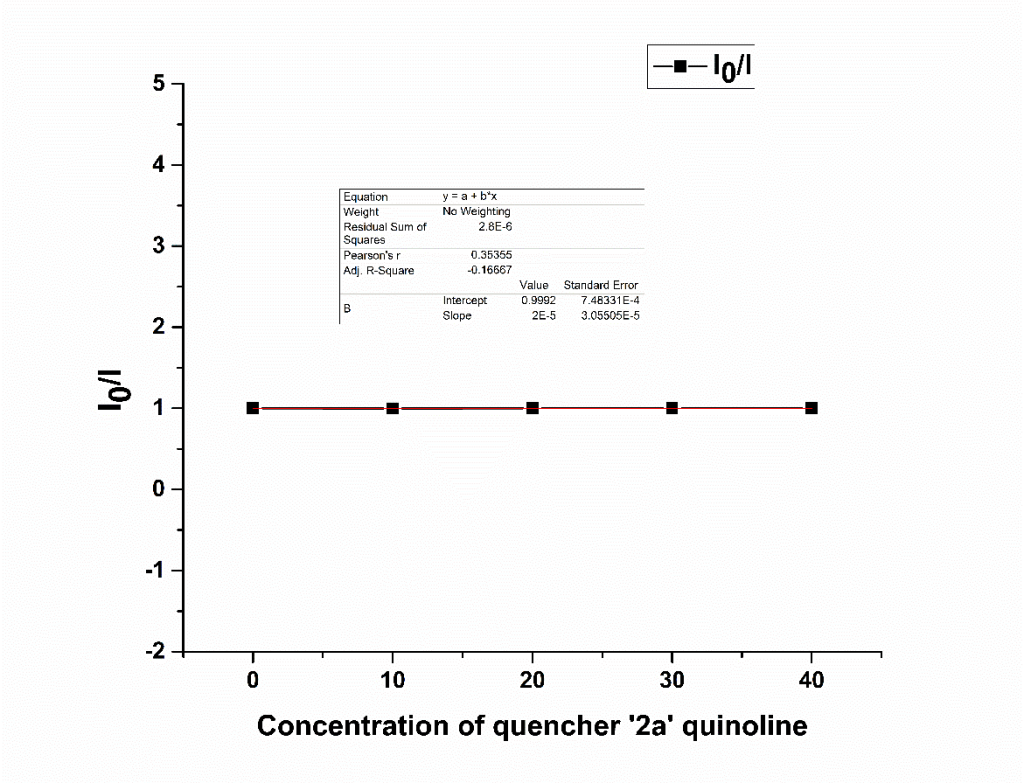
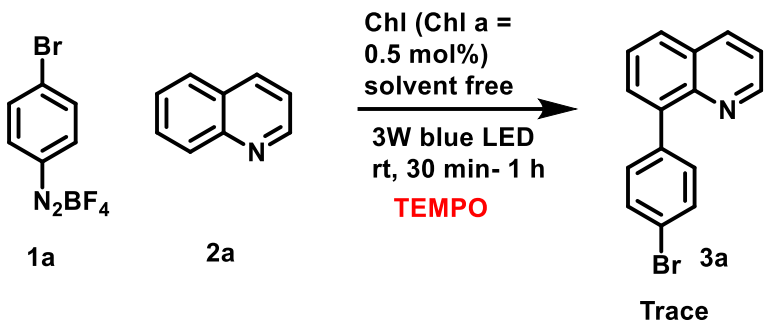
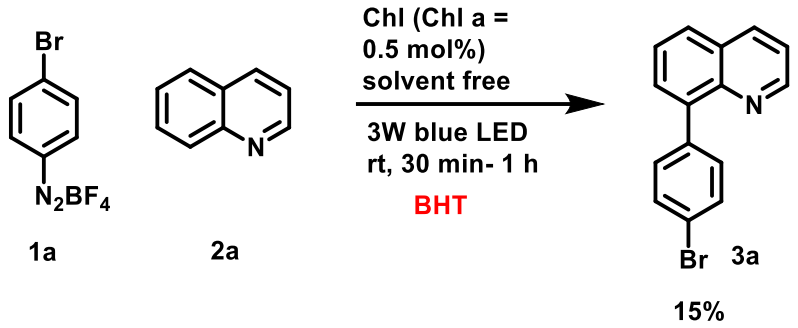


Figure 4. Chl (**PC**) emission quenching by **2a**. There was no significant quenching.

3.2. Control Experiments (by using Radical scavengers)

To gain further insight into the mechanism of the photocatalytic direct arylation reaction, some control experiments were performed using 4-bromobenzene tetrafluoroborate salt (**1a**) and quinoline (**2a**) as the model substrates (Scheme 1). When TEMPO (2,2,6,6-tetramethylpiperidinooxy) or BHT (2,6-di-tert-butyl-4-methylphenol) (radical scavengers) (0.6 mmol, 3 equiv.) was added to the reaction system comprising of **1a** and **2a**, the yield of **3a** decreased, which suggested for the involvement of a radical intermediate.





Scheme 1. Radical scavenger experiments. Yields were determined by ^{1}H NMR using dibromomethane as the internal standard.

3.3. Electron-donor acceptor (EDA) complex formation Investigation

To find out whether chlorophyll could combine with either 4-bromobenzene tetrafluoroborate salt (**1a**) or quinoline (**2a**) to form the electron donor-acceptor (EDA) complexes, UV-visible experiments were performed on LABINDIA UV 3092 Spectrophotometer with a quartz cuvette of 1.0 cm path length. UV-Vis spectra of crude chlorophyll (**PC**) and **1a, 2a** in DMSO are shown in Figure 5, Figure 6, and Figure 7 respectively.

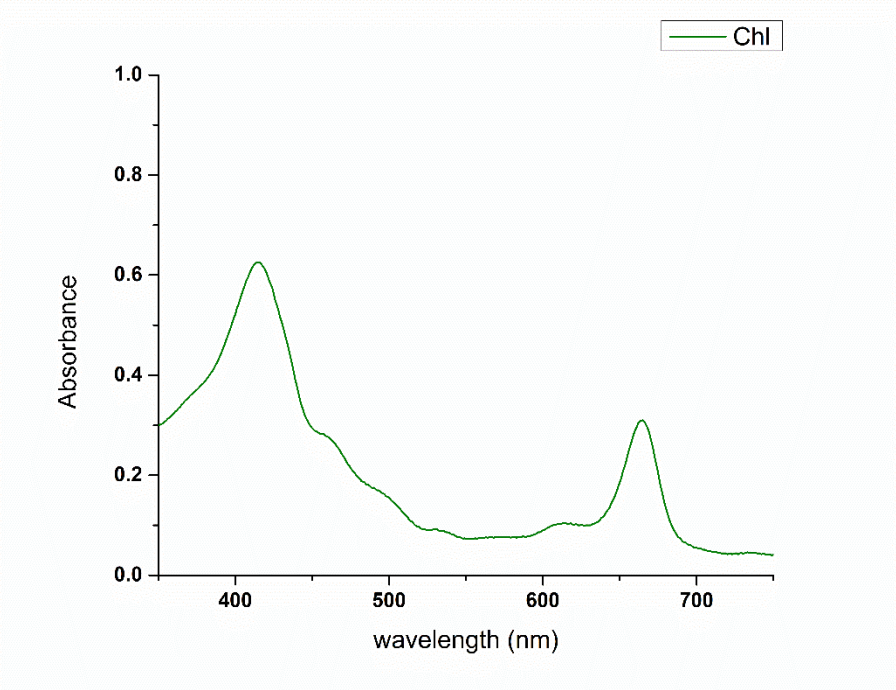


Figure 5. UV-visible spectrum of **PC** (10^{-6} M in DMSO)

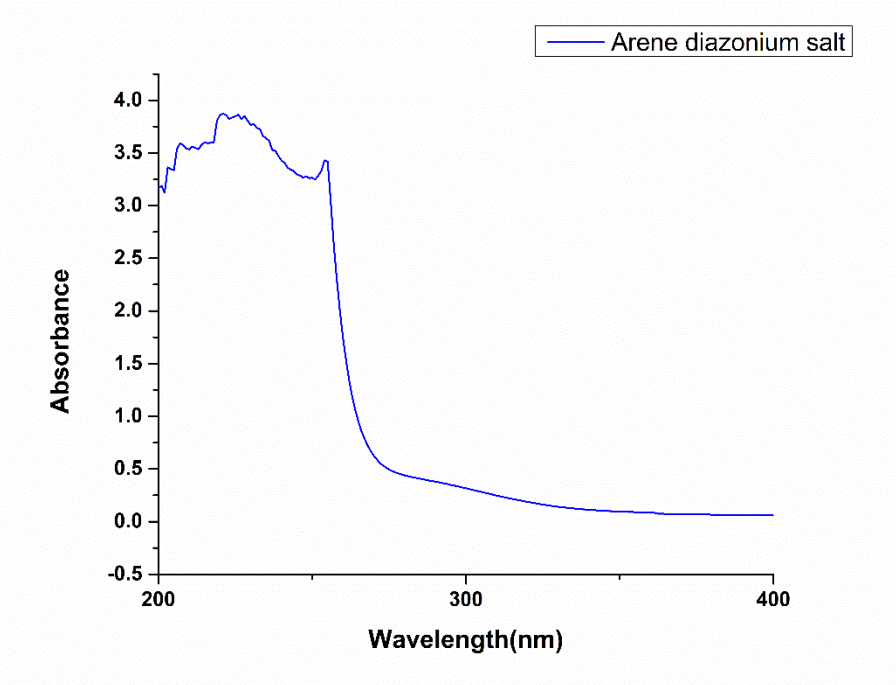


Figure 6. UV-visible spectrum of **1a** (10^{-2} M in DMSO)

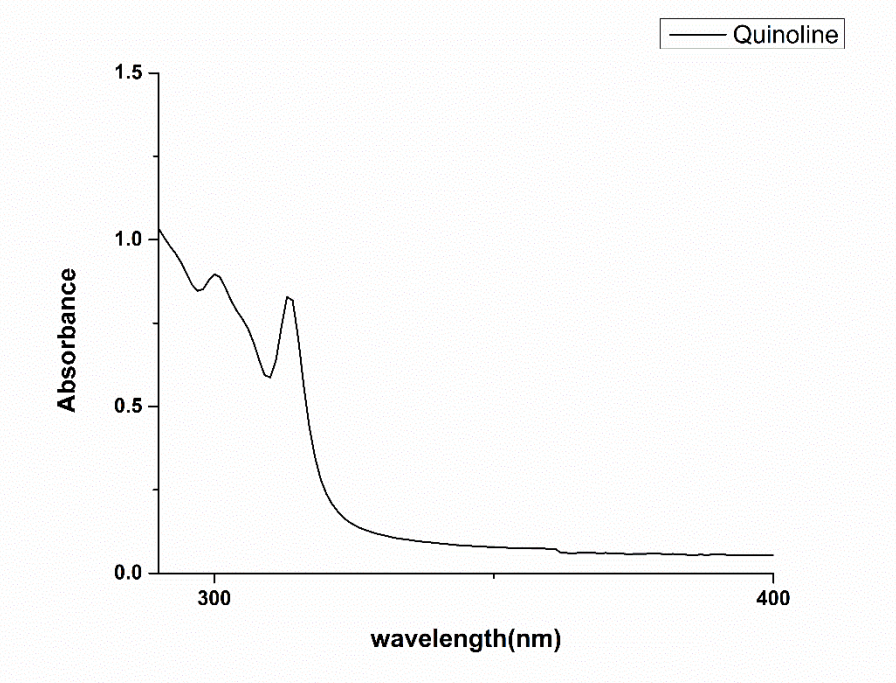


Figure 7. UV-visible spectrum of **2a** (10^{-2} M in DMSO)

At first, a solution of **1a** (10^{-2} M in DMSO) was added to the 10^{-6} M (Chl a= 10^{-6} M in DMSO) solution of **PC** and the UV-Vis spectra were recorded. As could be observed from Figure 8, there was no red shift band, which ruled out the formation of any EDA complex between **PC** and substrate **1a**. However, a new absorbance (blue shift) band was observed, most probably due to the generation of $Chl^{\bullet+}$, which provided evidence for photoinduced SET as the mechanism for aryl radical generation. Thereafter, the solution of quinoline **2a** (10^{-2} M in DMSO) was added to the 10^{-6} M (Chl a= 10^{-6} M in DMSO) solution of **PC**, and we recorded the UV-Vis spectra (Figure 9), there was no bathochromic shift, which indicated non-involvement of quinoline-Chl EDA complex formation. However, it was observed that the solubility of chlorophyll increased in organic solvent in presence of substrate **2a**.

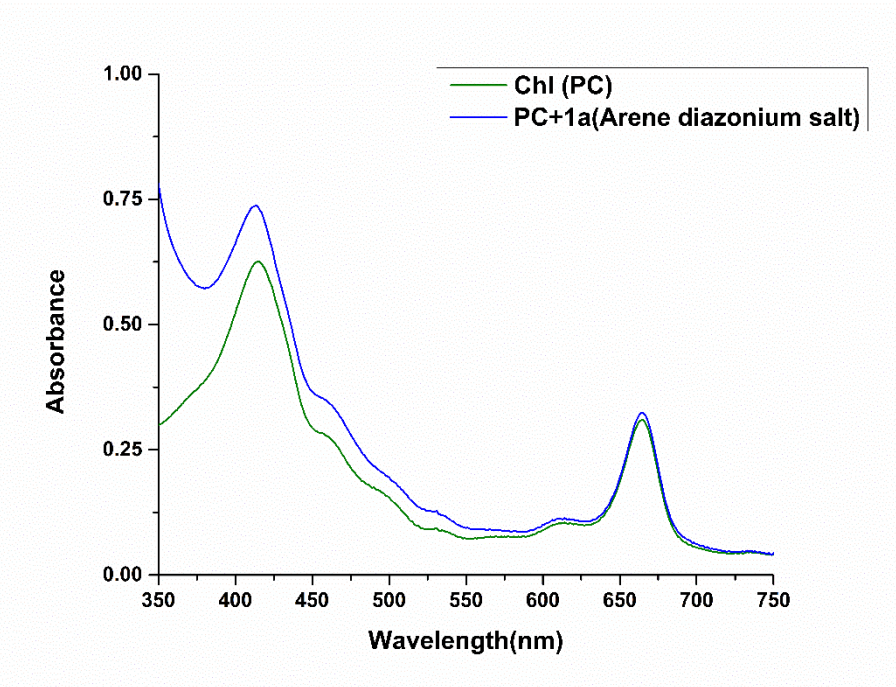


Figure 8. UV-visible spectra of PC (10^{-6} M in DMSO) on the addition of **1a**. No red-shift band was observed

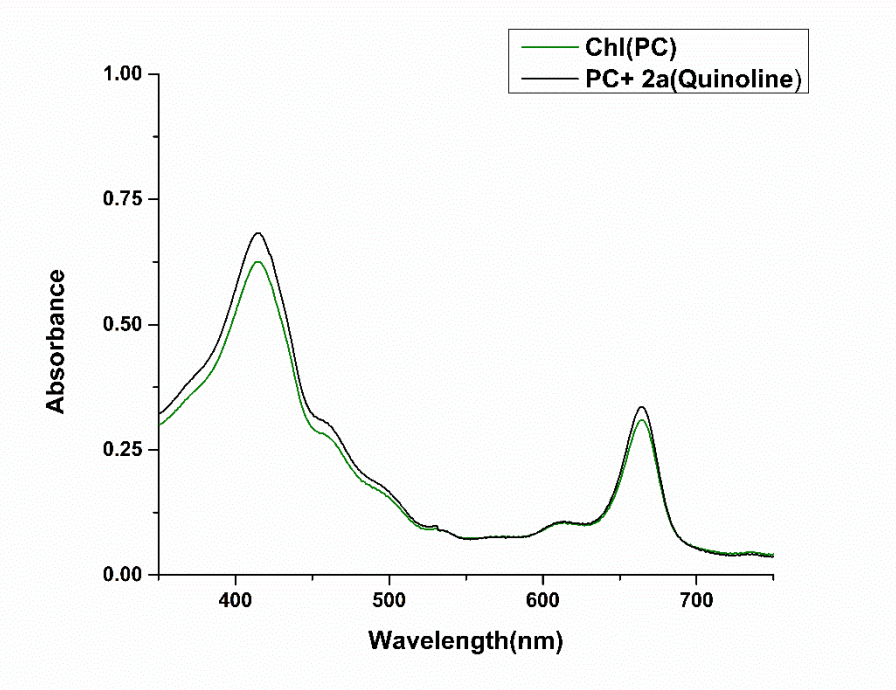


Figure 9. UV-visible spectra of PC (10^{-6} M in DMSO) on the addition of **2a**. No red-shift band was observed

3.4. Electron-Spin Resonance Studies

Next, we attempted to find out the types of radicals formed under different conditions by electron paramagnetic resonance (EPR) in presence of DMPO (5,5-dimethyl-1-pyrroline N-oxide) as a spin trapping agent. Electron spin resonance (ESR) spectra were recorded on a JEOL JES FA200 (X-band). The reactions were performed in a glass vial (30 mL) under different conditions, then smaller fractions of the samples were transferred to the capillaries, and ESR spectra were recorded (Figure 10). At first, the mixture of chlorophyll (containing Chl a; 0.5 mol%), DMPO (0.14 mM) in DMSO was irradiated with 6W blue LED for 5 minutes at room temperature, then the ESR spectrum was recorded (Figure 11). From the spectrum, we could ascertain that only chlorophyll could not produce radicals under irradiation of visible light. When the mixture of quinoline **2a** (1.35mM), chlorophyll (Chl a; 0.5 mol%), DMPO (0.14 mM) in DMSO was irradiated with 6W blue LED for 5 minutes at room temperature and ESR spectrum was recorded, no signal was observed (Figure 11), thus nullifying the involvement of electron transfer in between PC and **2a** (in line with fluorescence quenching experiments). Next, a mixture of 4-bromobenzene tetrafluoroborate salt **1a** (0.09 mM), chlorophyll (Chl a; 0.5 mol%), DMPO (0.14 mM) in DMSO was irradiated with 6W blue LED at room temperature for 5 minutes, and ESR spectrum showed a new poorly resolved quartet signal with g = 2.0003 (Figure 12). From the observation and

earlier literature report, it was envisaged that the signal corresponds to aryldiazenyl radical-DMPO adduct (ArN=N-DMPO) which could be observed for several hours,[6] aryldiazenyl radical might have been formed as an intermediate, upon single electron transfer from Chl to the substrate **1a**. The radical spin-DMPO adduct was expected to exhibit a quartet of triplets, however in our case, we ended up with a broadened quartet signal, we believe that each set of triplet signals gets merged into broad singlets. Thereafter, mixture of 4-bromobenzene tetrafluoroborate salt **1a** (0.09 mM), quinoline **2a** (1.35 Mm), chlorophyll (Chl a; 0.5 mol%), DMPO (0.14 mM) in DMSO was irradiated with 6W blue LED for 5 minutes, and ESR spectrum showed a new triplet signal with g = 2.0003, $a_N = a_H = 1.35$ mT which indicated the formation of aryl radical (C-centered)-DMPO adduct[7] (Figure 13). Henceforth, based on the observed ESR spectra along with the earlier literature reports,[6-7] it could be ascribed that the aryl radicals were the major arylating agent under this visible light photocatalytic arylation process, intermediacy of other radical species *viz*. N-centered aryldiazenyl radical (Ar-N=N•) had also been predicted.

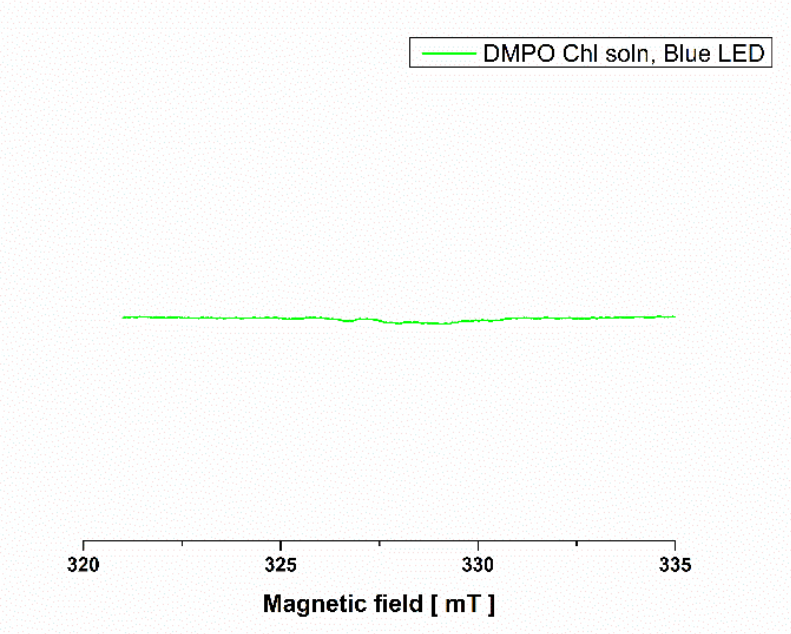


Figure 10. ESR spectrum of mixture of DMPO, Chl in DMSO irradiated with 6W blue LED for 5 minutes.

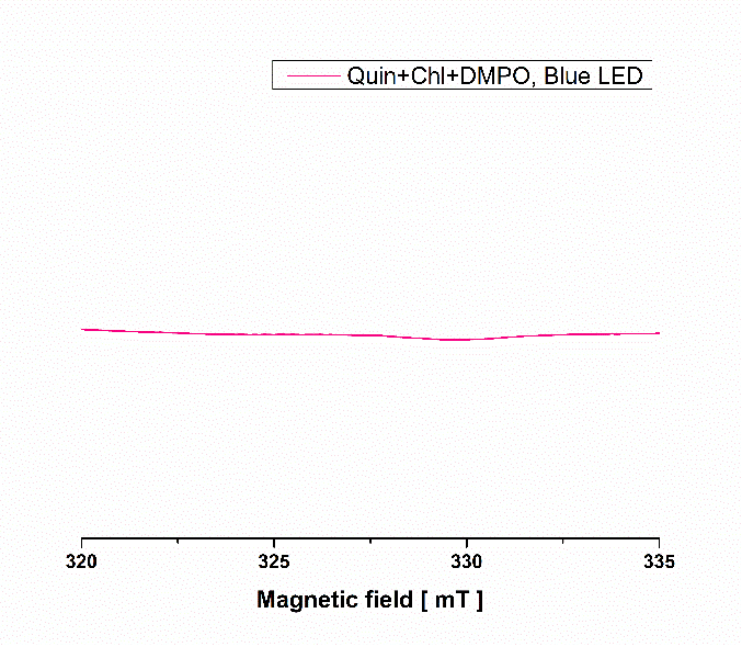


Figure 11. ESR spectrum of mixture of DMPO, Chl, **2a** in DMSO irradiated with 6W blue LED for 5 minutes.

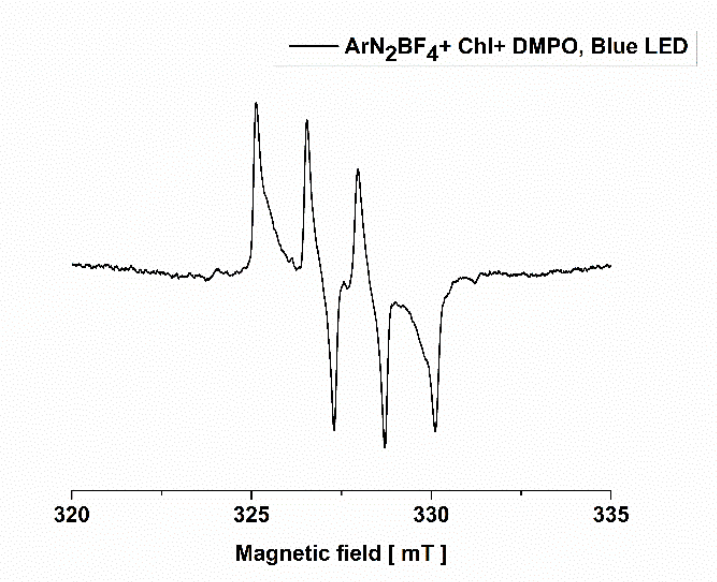


Figure 12. ESR spectrum of mixture of DMPO, Chl, **1a** in DMSO irradiated with 6W blue LED for 5 minutes.

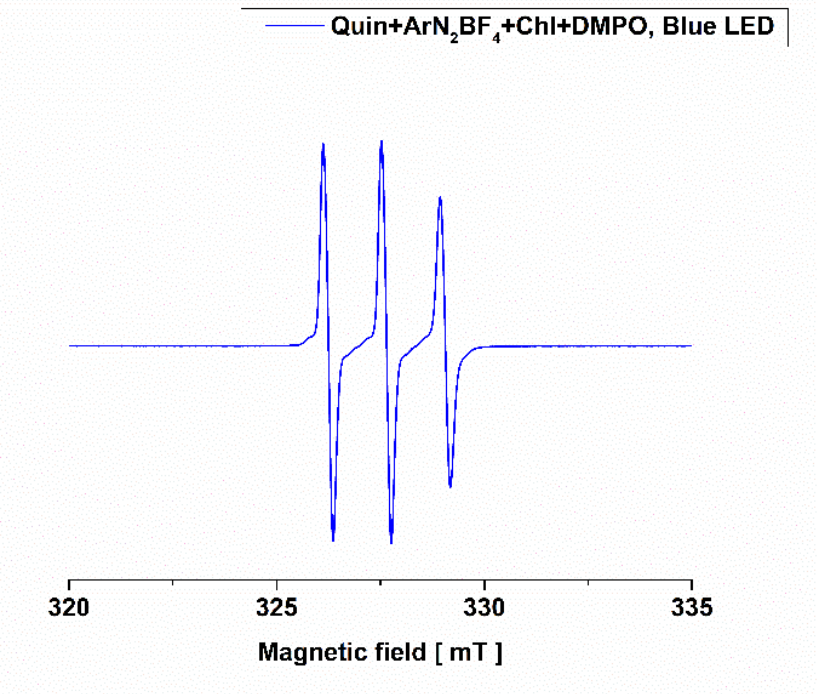


Figure 13. ESR spectrum of mixture of DMPO, Chl, **1a**, **2a** in DMSO irradiated with 6W blue LED for 5 minutes. **ESR conditions**: Frequency = 9.17 GHz, Power = 0.998 mW, Modulation width = 2.0 mT, Centre field = 390.317 mT, Amplitude = 2.000 x 1 (modulation frequency 100 kHz), Sweep width = 4 x 100 mT, Sweep time = 30 sec, Time constant = 0.03, Temperature = 25 ^{o}C.

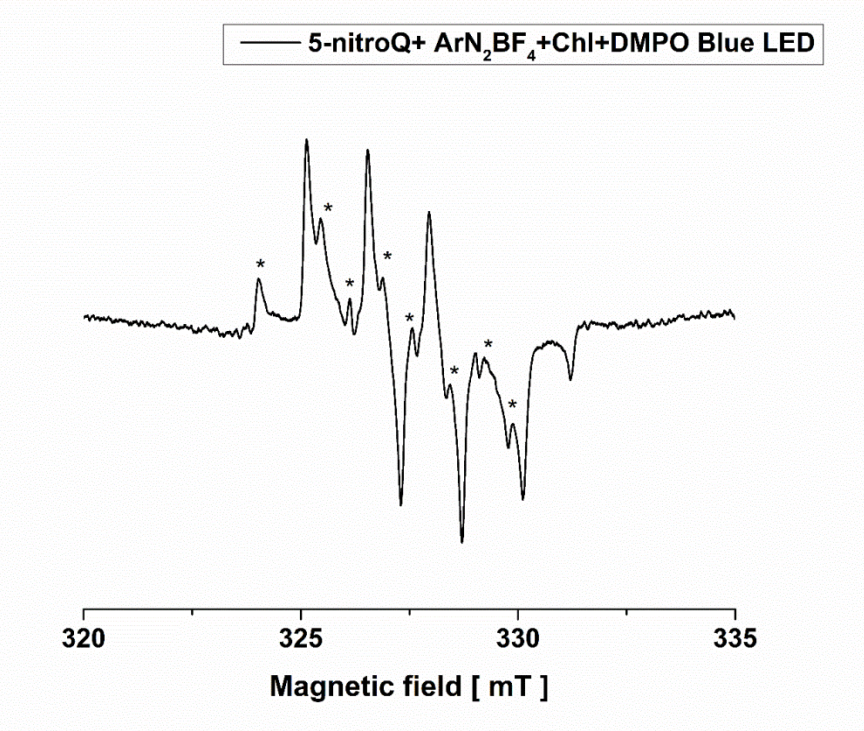
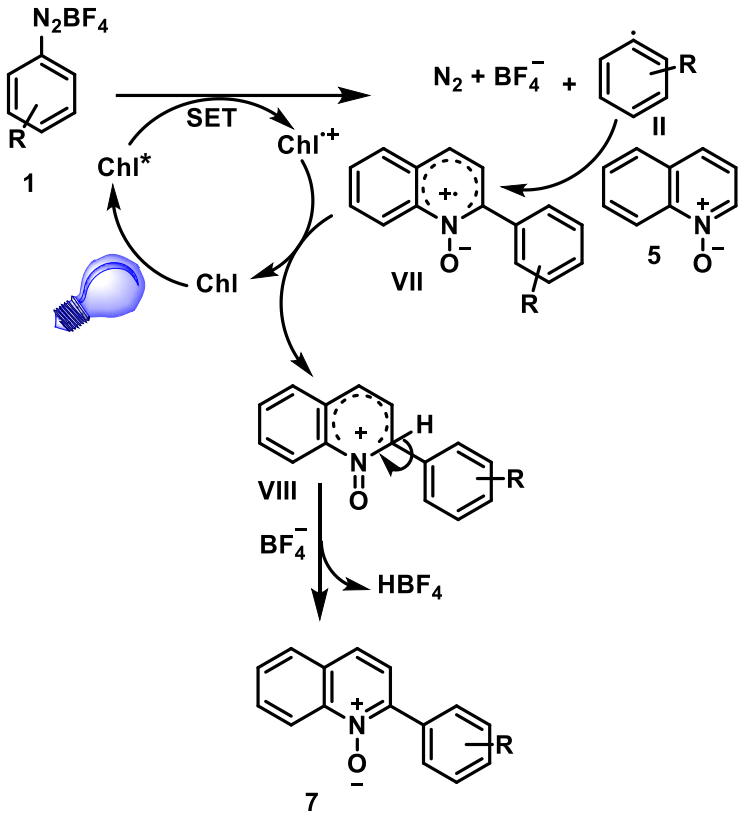


Figure 14. ESR spectrum of mixture of DMPO, 5-nitroquinoline (**2c**), **1a**, Chl in DMSO irradiated with 6W blue LED. **ESR conditions**: Frequency = 9.17 GHz, Power = 0.998 mW, Modulation width = 2.0 mT, Centre field = 390.317 mT, Amplitude = 2.000 x 1 (modulation frequency 100 kHz), Sweep width = 4 x 100 mT, Sweep time = 30 sec, Time constant = 0.03, Temperature = 25 ^{o}C

Apart from this, a mixture of 4-bromobenzene tetrafluoroborate salt **1a** (0.09 mM), 5-nitroquinoline **2c** (1.35 mM), chlorophyll (Chl a; 0.5 mol%), DMPO (0.14 mM) in DMSO was irradiated with 6W blue LED for 5 minutes, and the recorded ESR spectrum displayed a new complex spectrum (g = 2.0003) which suggested the simultaneous presence of two or more type of radicals (Figure 14). We envisage that the ESR spectra correspond to a mixture of N-centered and C-centered aryl radicals-DMPO adducts present in reaction media.

4. Plausible Mechanism



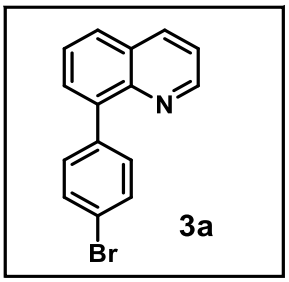
Scheme 2. Plausible reaction mechanism for direct arylation of quinoline N-oxides **6**

Similar to quinolines **2**, in the case of quinoline-N-oxides **5,** and pyridines **6** in situ generated aryl radical led to the formation of C2-arylated quinoline-N-oxides **7** and C2-arylated pyridines **8** respectively. It is well known that quinoline is transformed into its N-oxide analogues to impart selectivity and higher reactivity at the C2 position.[8] Based on the literature reports and our observations the tentative mechanism for the C2-arylation of quinoline-N-oxides is proposed as shown in Scheme 2. Following the same methodology as in scheme 2 of the main article, at first aryl radical **II** is generated via SET. Thereafter, the aryl radical **II** attacks selectively at the C2 position of quinoline-N-oxides **5** (or pyridine **6**) to generate intermediate **VII**, which undergoes another SET reaction to furnish intermediate **VIII**, with the regeneration of ground state Chl. Lastly, intermediate **VIII** deprotonates to afford the final products **7** (or **8**).

5. Characterization data of Compounds 3(4), 7, 8

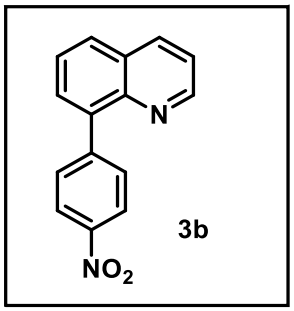
5.1. Characterization data of C8-Aryl Quinolines 3

Compound 3a: 8-(4-bromophenyl)quinoline[9]



3a was prepared according to the general procedure (**A)** using quinoline **2a** (710 μL, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 2% EtOAc/Hexane afforded **3a** (24 mg, 43%, based on **1a**) as a light brown semi-solid compound. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.51. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.63 – 7.56 (m, 5H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 145.9, 139.7, 138.5, 136.5, 132.4 (2C), 131.3 (2C), 130.2, 128.9, 128.0, 126.4, 121.9, 121.3. **HRMS** (ESI^+): Calcd for $C_{15}H_{11}BrN$, $[M+H]^+$ m/z 284.0069. Found 284.0067.

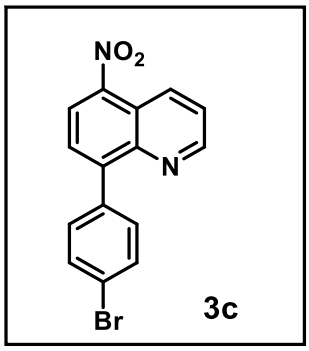
Compound 3b: 8-(4-nitrophenyl)quinoline



3b was prepared according to the general procedure (**A)** using quinoline **2a** (710 μL, 6.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 2% EtOAc/Hexane afforded **25b** (27 mg, 54%, based on **1b**) as a yellow solid. $\mathbf{R_f}$

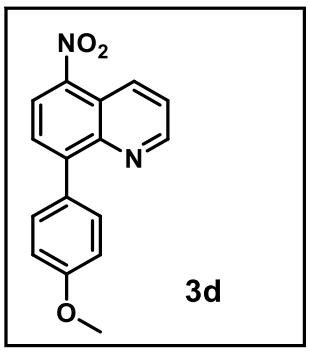
(EtOAc:Hexane = 1:9) = 0.53. **M.P.** 168-170 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.36 – 8.33 (m, 2H), 8.25 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.92 (dd, *J* = 6.9, 1.3 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.76 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.65 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.7, 147.2, 146.5, 145.7, 138.6, 136.6, 131.6 (2C), 130.5, 129.1, 128.9, 126.4, 123.3 (2C), 121.6. **HRMS (ESI$^+$)**: Calcd for $C_{15}H_{11}N_2O_2$, $[M+H]^+$ m/z 251.0815. Found 251.0821.

Compound 3c: 8-(4-bromophenyl)-5-nitroquinoline



3c was prepared according to the general procedure (**A)** using quinoline **2b** (1 g, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 2% EtOAc/Hexane afforded **3c** (58 mg, 89%, based on **1a**) as a yellow solid. **R_f** (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 147-149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.08 (dd, *J* = 8.8, 1.7 Hz, 1H), 9.05 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.65 (m, 3H), 7.57 – 7.54 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 146.7, 145.8, 145.0, 136.9, 132.4 (2C), 132.2, 131.5 (2C), 128.2, 124.4, 123.9, 123.3, 121.9. **HRMS (ESI$^+$)**: Calcd for $C_{15}H_{10}BrN_2O_2$, $[M+H]^+$ m/z 328.9920. Found 328.9924.

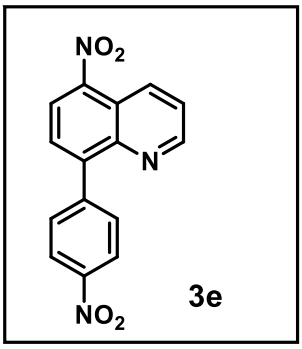
Compound 3d: 8-(4-methoxyphenyl)-5-nitroquinoline



3d was prepared according to the general procedure (**A)** using quinoline **2b** (1 g, 6.0 mmol), 4-methoxybenzenediazonium tetrafluoroborate salt **1c** (45 mg, 0.20 mmol) and chlorophyll

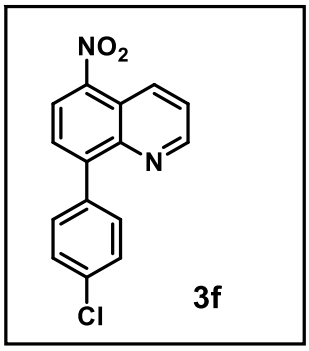
(0.5 mol%). The crude reaction mixture was purified by column chromatography using 2% EtOAc/Hexane afforded **3d** (48 mg, 86%, based on **1c**) as a dark green solid. **R_f** (EtOAc:Hexane = 1:9) = 0.53. **M.P.** 158-161 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 8.8, 1.7 Hz, 1H), 9.05 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.3, 151.1, 147.8, 146.0, 144.3, 132.3 (2C), 132.2, 130.5, 128.0, 124.7, 123.7, 122.1, 114.0 (2C), 55.6. **HRMS (ESI$^+$)**: Calcd for $C_{16}H_{13}N_2O_3$, $[M+H]^+$ m/z 281.0921. Found 281.0924.

Compound 3e: 5-nitro-8-(4-nitrophenyl)quinoline



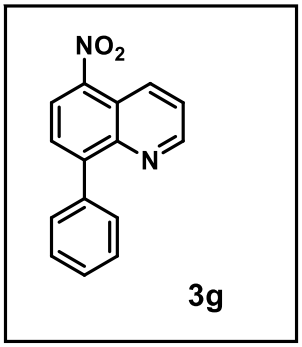
3e was prepared according to the general procedure (**A)** using quinoline **2b** (1 g, 6.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 5% EtOAc/Hexane afforded **3e** (52 mg, 88%, based on **1b**) as off-white solid. **R_f** (EtOAc:Hexane = 1:8) = 0.53. **M.P.** 189-191 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.07 (dd, *J* = 8.8, 1.7 Hz, 1H), 9.04 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.39 – 8.36 (m, 2H), 7.86 – 7.83 (m, 3H), 7.71 (dd, *J* = 8.8, 4.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 147.9, 145.7, 145.3, 144.6, 132.3, 131.7, 128.5, 124.1, 124.16, 123.4, 121.9. **ESMS (ESI$^+$)**: Calcd for $C_{15}H_{10}N_3O_4$, $[M+H]^+$ m/z 296.3. Found 296.4.

Compound 3f: 8-(4-chlorophenyl)-5-nitroquinoline



3f was prepared according to the general procedure (**A)** using quinoline **2b** (1 g, 6.0 mmol), 4-chlorobenzenediazonium tetrafluoroborate salt **1d** (45 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3f** (43 mg, 75%, based on **1d**) as a pale yellow solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.47. **M.P.** 153-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.08 (dd, *J* = 8.8, 1.6 Hz, 1H), 9.04 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 146.7, 145.8, 144.9, 136.4, 135.0, 132.2, 132.1 (2C), 128.5 (2C), 128.2, 124.4, 123.8, 121.9. HRMS (ESI^+): Calcd for $C_{15}H_{10}ClN_2O_2$, $[M+H]^+$ m/z 285.0425. Found 285.0426.

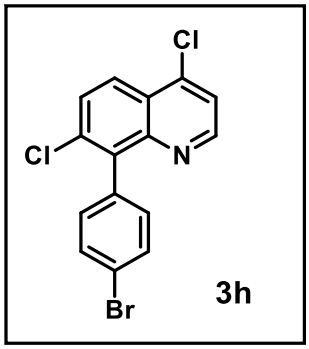
Compound 3g: 5-nitro-8-phenylquinoline



3g was prepared according to the general procedure (**A)** using quinoline **2b** (1 g, 6.0 mmol), benzenediazonium tetrafluoroborate salt **1e** (43 mg, 0.22 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 2% EtOAc/Hexane afforded **3g** (40 mg, 73%, based on **1e**) as an off-white solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 144-146 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.08 (dd, *J* = 8.8, 1.7 Hz, 1H), 9.05 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.65 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.50-7.46 (m,

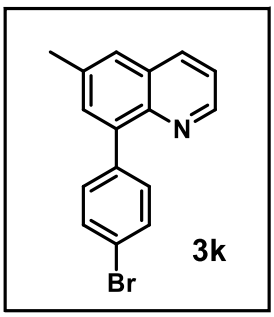
1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 148.1, 146.0, 144.7, 138.1, 132.14, 130.8, 128.7, 128.4, 128.3, 124.4, 123.7, 121.9. **HRMS (ESI$^+$)**: Calcd for $C_{15}H_{11}N_2O_2$, $[M+H]^+$ m/z 251.0815. Found 251.0810.

Compound 3h: 8-(4-bromophenyl)-4,7-dichloroquinoline



3h was prepared according to the general procedure (**A)** using quinoline **2c** (1.2 g, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3h** (13 mg, 19%, based on **1a**) as an off-white solid. **R_f** (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 155-157 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H), 8.24 (d, *J* = 9.1 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 4.7 Hz, 1H), 7.27 – 7.25 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.7, 142.9, 138.4, 135.7, 132.3 (2C), 132.0, 131.4 (2C), 129.3, 128.4, 125.6, 125.0, 122.4, 121.4. **HRMS (ESI$^+$):** Calcd for $C_{15}H_9NBrCl_2$, $[M+H]^+$ m/z 353.9269. Found 353.9275.

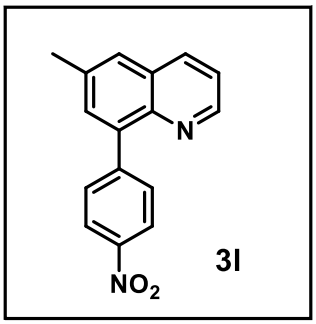
Compound 3k: 8-(4-bromophenyl)-6-methylquinoline



3k was prepared according to the general procedure (**A)** using quinoline **2d** (805 μL, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3k** (17 mg, 29%, based on **1a**) as a brown solid. **R_f**

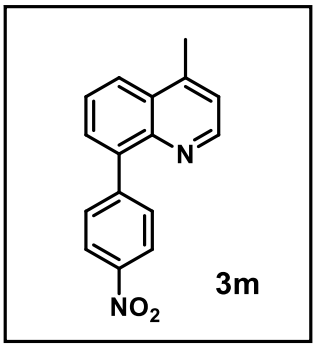
(EtOAc:Hexane = 1:9) = 0.51. **M.P.** 91-94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.42 – 8.25 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.95 – 7.82 (m, 2H), 7.68 (s, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.61 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.6, 144.6, 139.4, 138.6, 136.1, 135.7, 132.5, 132.3 (2C), 131.2 (2C), 129.0, 126.9, 121.8, 121.3, 21.7. **HRMS (ESI^+)**: Calcd for $C_{16}H_{13}NBr$, $[M+H]^+$ m/z 298.0226. Found 298.0226.

Compound 3l: 6-methyl-8-(4-nitrophenyl)quinoline



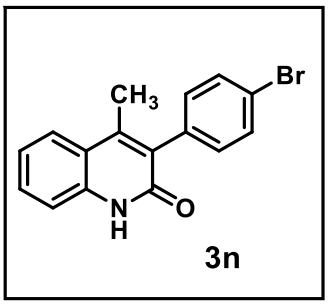
3l was prepared according to the general procedure (**A)** using quinoline **2d** (805 μL, 6.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3l** (23 mg, 45%, based on **1b**) as a pale yellow solid. **R_f** (EtOAc:Hexane = 1:9) = 0.49. **M.P.** 173-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.35 – 8.33 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.67 (s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.9, 147.2, 146.6, 144.3, 138.3, 136.2, 135.9, 132.8, 131.6 (2C), 129.0, 127.9, 123.2 (2C), 121.6, 21.7. **HRMS (ESI^+)**: Calcd for $C_{16}H_{13}N_2O_2$, $[M+H]^+$ m/z 265.0972. Found 265.0979.

Compound 3m: 4-methyl-8-(4-nitrophenyl)quinoline



3m was prepared according to the general procedure (**A)** using quinoline **2e** (805 μL, 6.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3m** (19 mg, 36%, based on **1b**) as a white solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.49. **M.P.** 82-84 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.3 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 2H), 8.11 (b d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 4.2 Hz, 1H), 2.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.4, 147.1, 147.1, 145.5, 144.7, 139.1, 131.7 (2C), 130.2, 128.9, 126.1, 125.1, 123.2 (2C), 122.4, 19.2. **HRMS (ESI$^+$)**: Calcd for $C_{16}H_{13}N_2O_2$, $[M+H]^+$ m/z 265.0972. Found 265.0977.

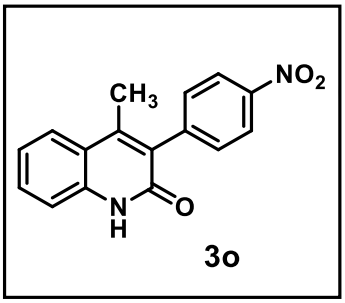
Compound 3n: 3-(4-bromophenyl)-4-methylquinolin-2(1H)-one



3n was prepared according to the general procedure (**A)** using quinoline **2f** (954 mg, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 45% EtOAc/Hexane afforded **3n** (37 mg, 59%, based on **1a**) as an off-white solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:1) = 0.50. **M.P.** 271-272 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.47 (br, s, 1H), 7.82 – 7.70 (m, 1H), 7.63 – 7.58 (m, 2H), 7.51 – 7.45 (m, 1H), 7.27-7.20 (m, 5H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 145.3, 137.4, 134.9, 132.2 (2C), 131.6 (2C),

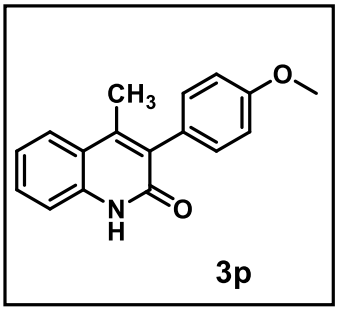
131.1, 130.5, 125.1, 122.7, 122.0, 120.9, 116.3, 17.0. **HRMS (ESI$^+$)**: Calcd for $C_{16}H_{13}NBrO$, $[M+H]^+$ m/z 314.0175. Found 314.0182.

Compound 3o: 4-methyl-3-(4-nitrophenyl)quinolin-2(1H)-one



3o was prepared according to the general procedure (**A)** using quinoline **2f** (954 mg, 6.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 50% EtOAc/Hexane afforded **3o** (35 mg, 63%, based on **1b**) as pale-yellow solid. **R$_f$** (EtOAc:Hexane = 1:1) = 0.50. **M.P.** 287-289 °C. **^{1}H NMR** (400 MHz, $CDCl_3$+CD_3OD) δ 8.18 (d, *J* = 8.76, 2H), 7.66 (d, *J* = 8.29, 1H), 7.42 (m, 1H), 7.37 (m, 2H), 7.19 (m, 2H), 2.23 (s, 3H**) ^{13}C NMR** (100 MHz, $CDCl_3$+CD_3OD) δ 161.7, 147.1, 145.9, 143.1, 137.4, 131.4 (2C), 130.8, 129.9, 125.1, 123.3 (2C), 122.8, 120.4, 115.8, 16.7 **HRMS (ESI$^+$)**: Calcd for $C_{16}H_{13}N_2O_3$, $[M+H]^+$ m/z 281.0921. Found 281.0924.

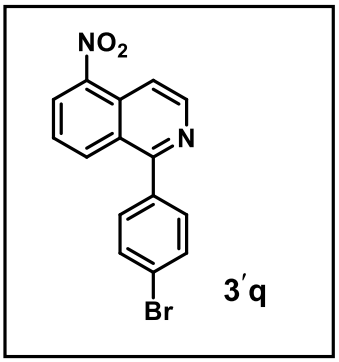
Compound 3p: 3-(4-methoxyphenyl)-4-methylquinolin-2(1H)-one



3p was prepared according to the general procedure (**A)** using quinoline **2f** (954 mg, 6.0 mmol), 4-methoxybenzenediazonium tetrafluoroborate salt **1c** (45 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 50% EtOAc/Hexane afforded **3l** (24 mg, 45%, based on **1c**) as an off-white solid. **R$_f$** (EtOAc:Hexane = 1:1) = 0.50. **M.P.** 243-245 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.99 (s,

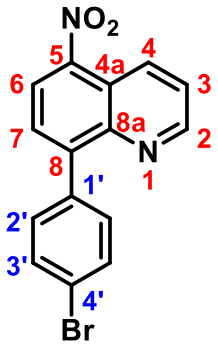
1H), 7.73 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.28-7.20 (m, 4H), 7.03 – 7.00 (m, 2H), 3.87 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 159.1, 144.9, 137.2, 131.9, 131.5 (2C), 130.0, 128.1, 125.0, 122.5, 121.1, 115.9, 113.8 (2C), 55.3, 17.0. **HRMS (ESI$^+$)**: Calcd for $C_{17}H_{16}NO_2$, $[M+H]^+$ m/z 266.1176. Found 266.1174.

Compound 3´q: 1-(4-bromophenyl)-5-nitroisoquinoline



3´q was prepared according to the general procedure (**A)** using 5-nitroisoquinoline **2´g** (954 mg, 6.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 3% EtOAc/Hexane afforded **3´q** (23 mg, 35%, based on **1a**) as a brown solid. **R$_f$** (EtOAc:Hexane = 1:9) = 0.45. **M.P.** 171-173 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 6.2 Hz, 1H), 8.52 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.45 (dd, *J* = 6.2, 0.9 Hz, 1H), 8.38 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.67 – 7.63 (m, 1H), 7.56 – 7.53 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 145.5, 137.7, 134.3, 131.9 (2C), 131.7, 129.8, 129.4, 128.1, 127.3, 125.8, 124.0, 115.1. **HRMS (ESI$^+$)**: Calcd for $C_{15}H_{10}BrN_2O_2$, $[M+H]^+$ m/z 328.9920. Found 328.9930.

5.1A. 2D-NMR data analysis of Compound 3c; 8-(4-bromophenyl)-5-nitroquinoline

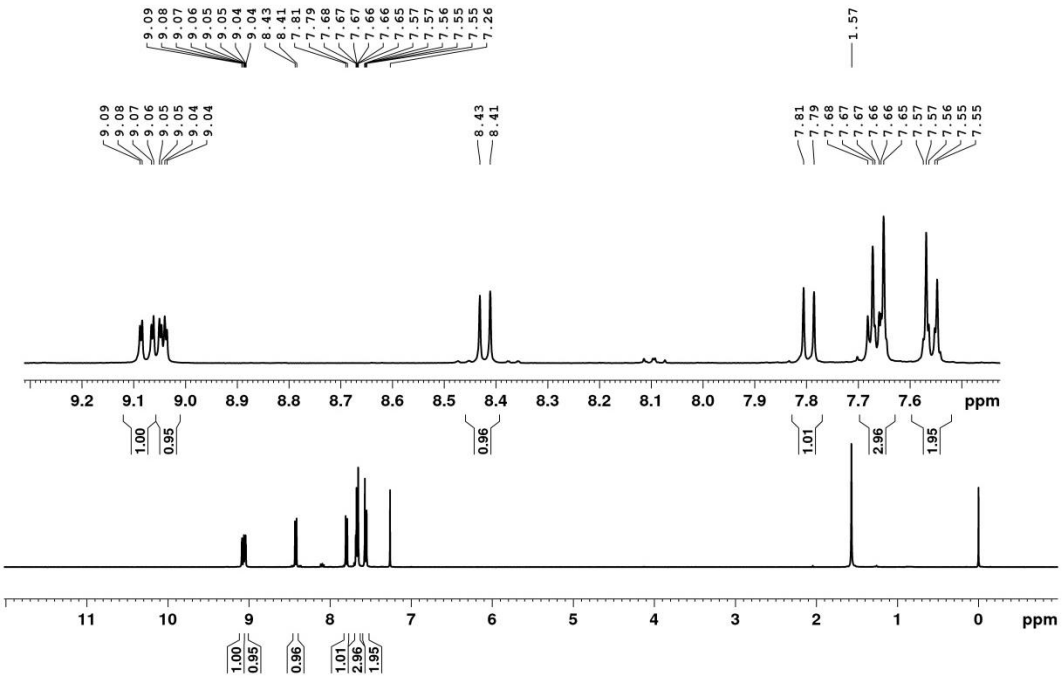


8-(4-bromophenyl)-5-nitroquinoline

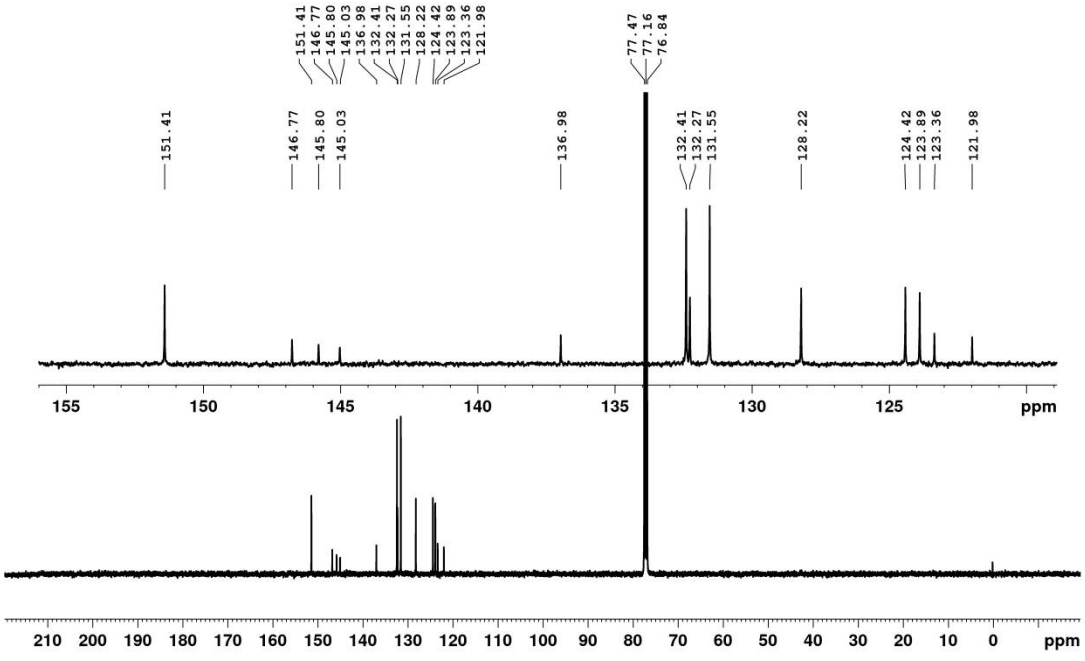
Table 4: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data for compound 3c in $CDCl_3$

Position	**^{1}H (δ), *J* (Hz)**	**^{13}C (δ) mult.***
1	-	-
2	9.05 (1H, *dd*, *J* = 4.1, 1.7)	151.4 (CH)
3	7.68-7.65 (1H, *m*, *overlapped*)	123.9 (CH)
4	9.08 (1H, *dd*, *J* = 8.8, 1.7)	132.2 (CH)
4a	-	121.9 (C)
5	-	145.8 (C)
6	8.42 (1H, *d*, *J* = 8.0)	124.4 (CH)
7	7.80 (1H, *d*, *J* = 8.0)	128.2 (CH)
8	-	146.7 (C)
8a	-	145.0 (C)
1'	-	136.9 (C)
2', 3'	7.68-7.65 (2H, *m*, *overlapped*)	131.5 (2CH)
	7.57-7.54 (2H, *m*)	132.4 (2CH)
4'	-	123.3 (C)

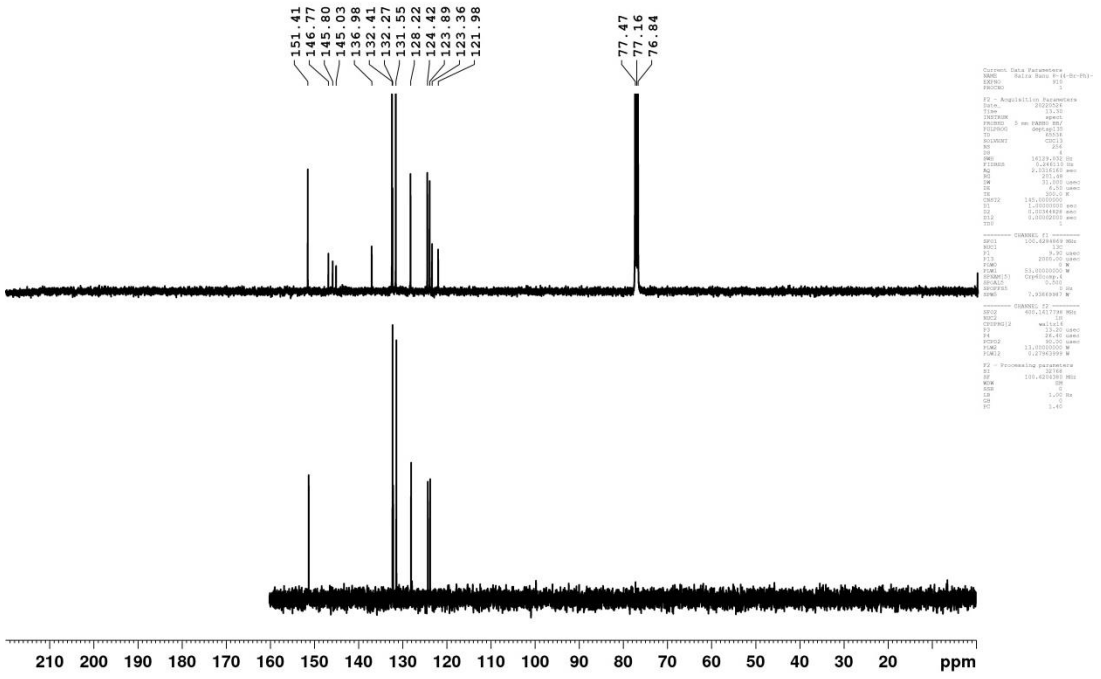
*Assigned based on DEPT 135° and HSQC spectrums



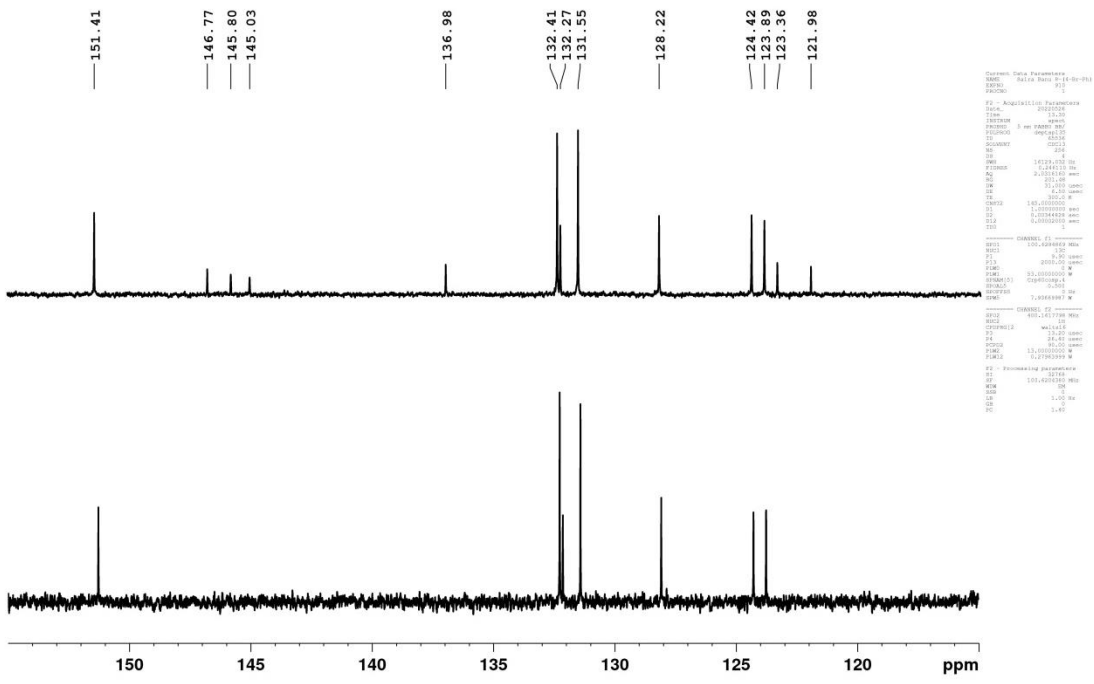
^{1}H NMR spectrum (400 MHz) of **3c** in $CDCl_3$



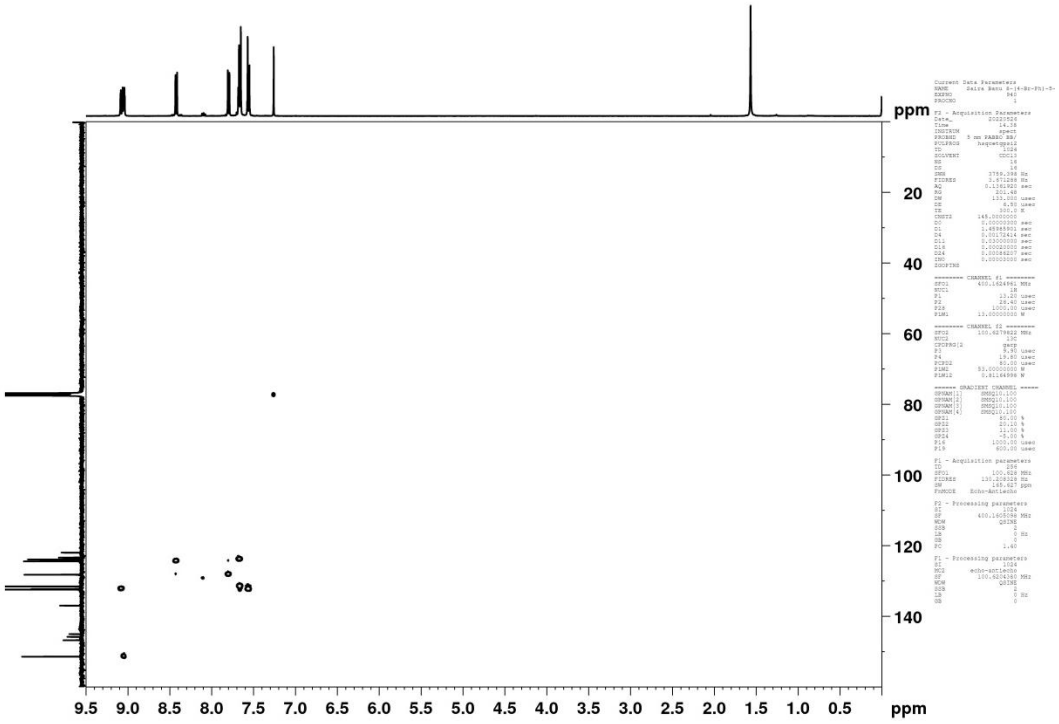
^{13}C NMR spectrum (100 MHz) of **3c** in $CDCl_3$



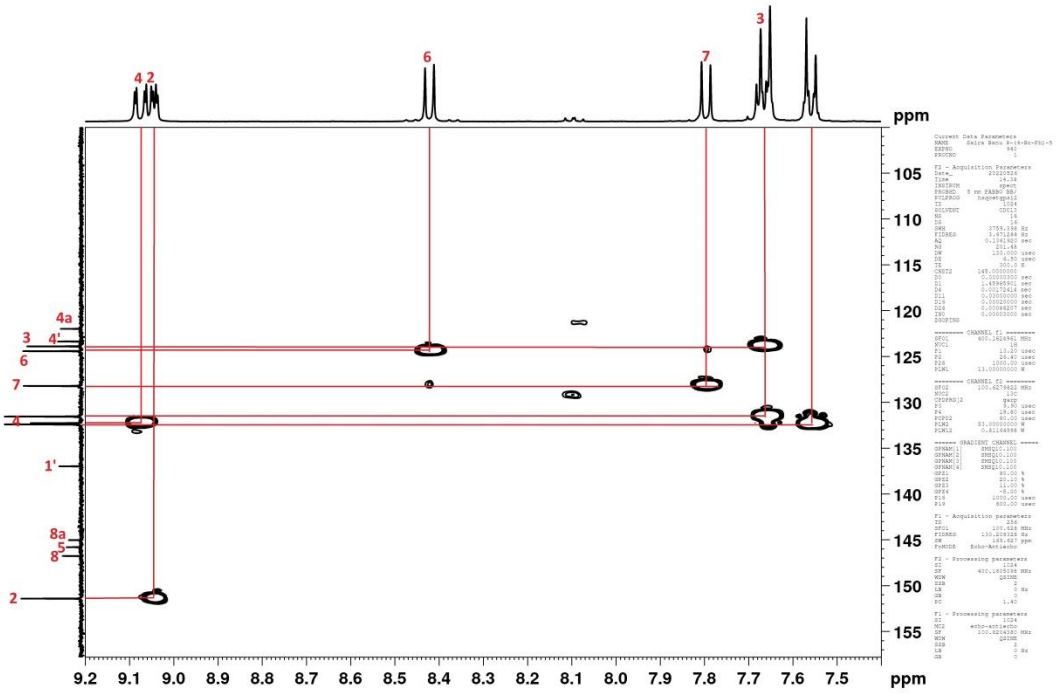
^{13}C and DEPT 135° (100 MHz) of **3c** in $CDCl_3$



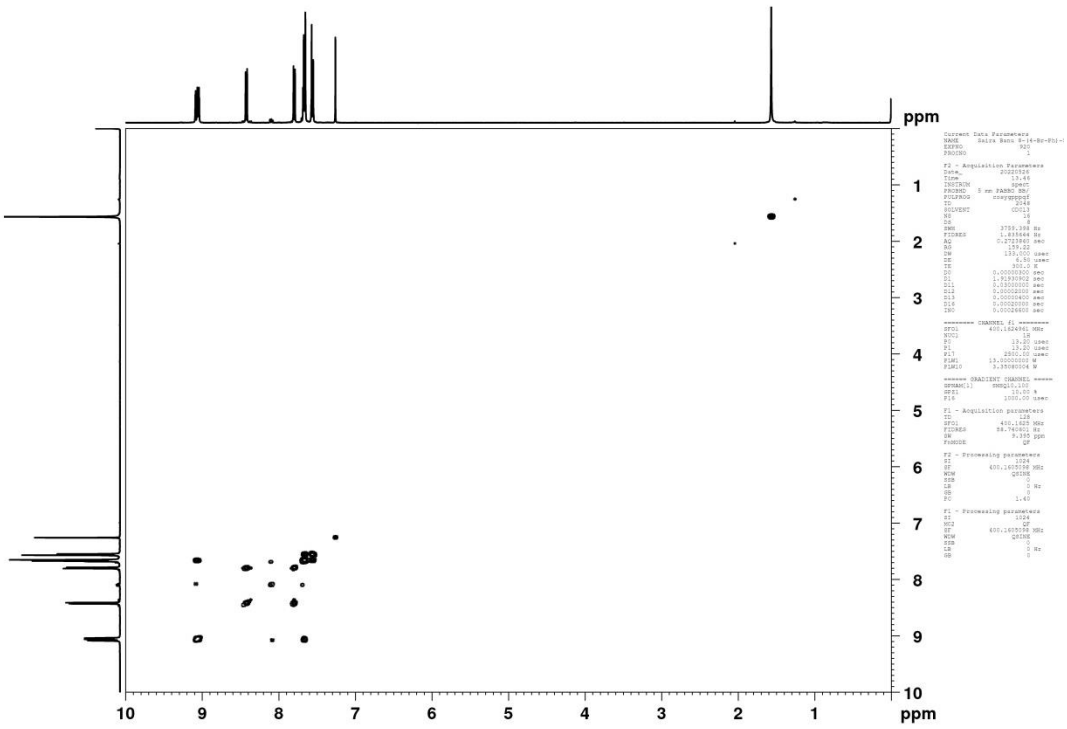
Expansion of ^{13}C and DEPT 135° (100 MHz) of **3c** in $CDCl_3$



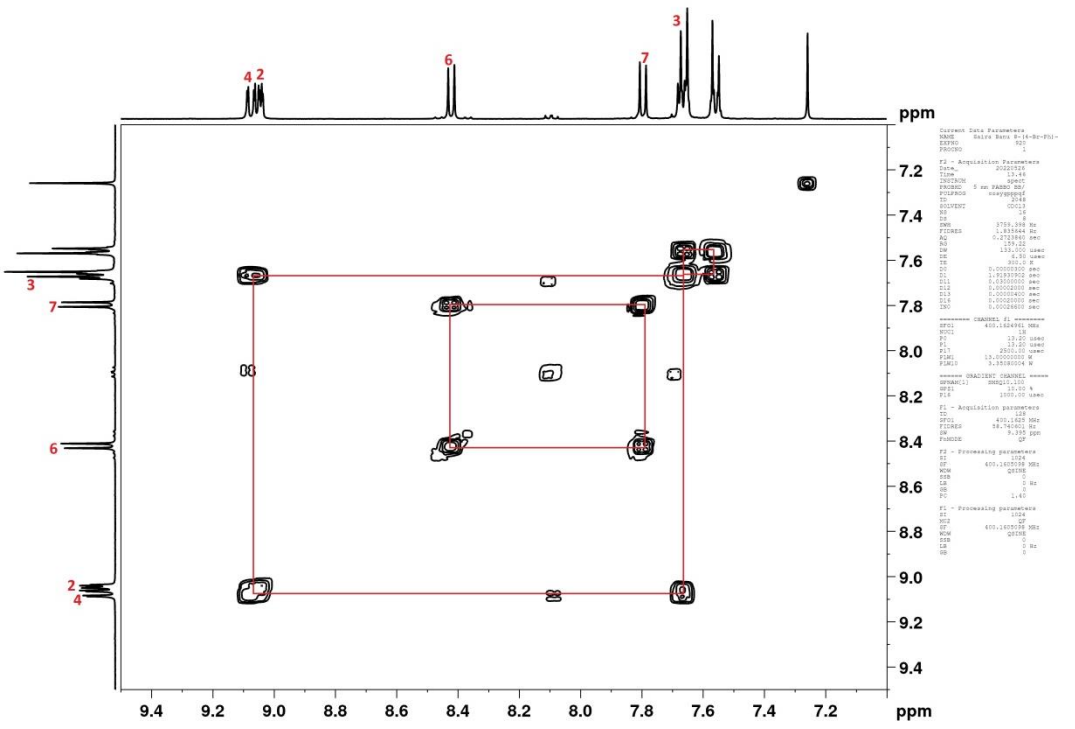
HSQC spectrum (400 MHz) of **3c** in $CDCl_3$



Expansion of HSQC spectrum (400 MHz) of **3c** in $CDCl_3$



^{1}H-^{1}H COSY spectrum (400 MHz) of **3c** in $CDCl_3$



Expansion of ^{1}H-^{1}H COSY spectrum (400 MHz) of **3c** in $CDCl_3$

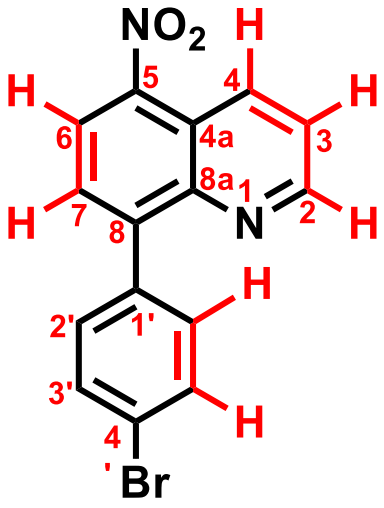
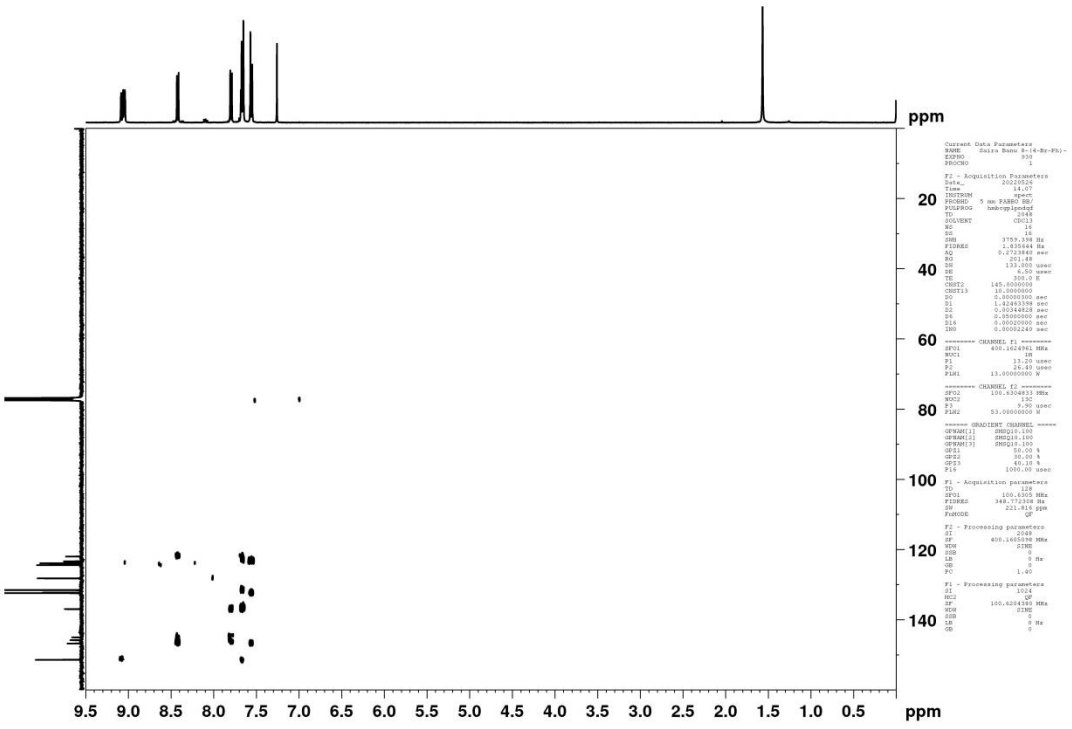
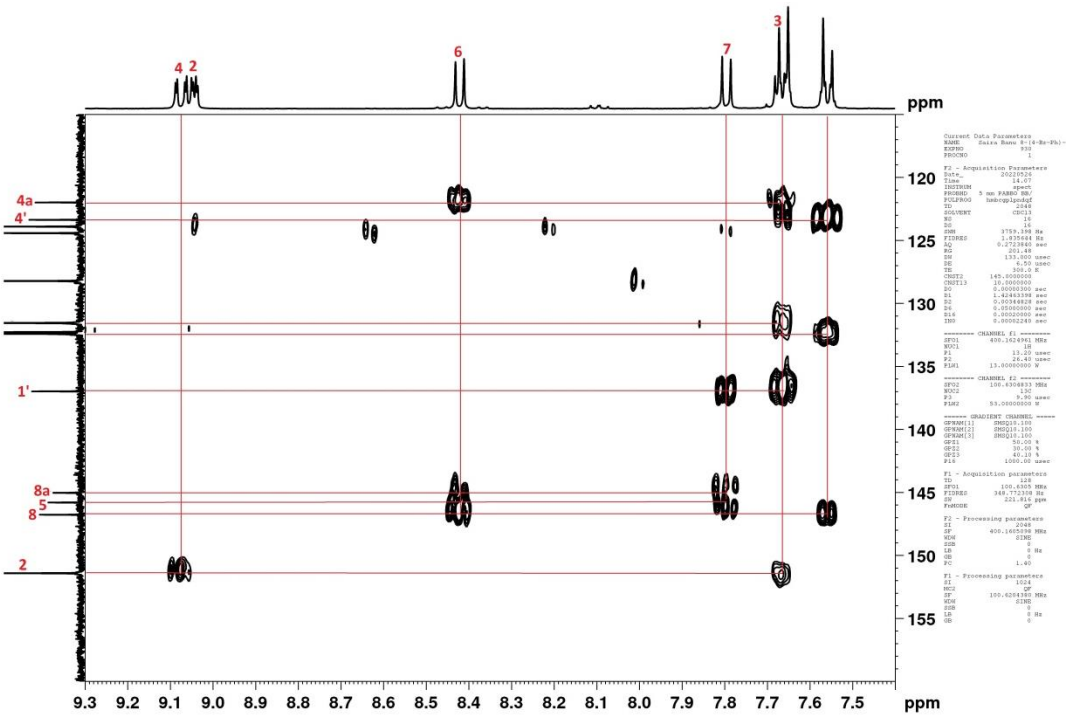


Figure 16: Selected ^{1}H-^{1}H COSY correlations (———)



HMBC spectrum (400 MHz) of **3c** in $CDCl_3$



Expansion of HMBC spectrum (400 MHz) of **3c** in $CDCl_3$

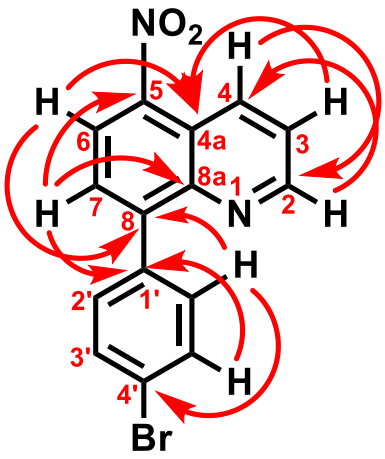
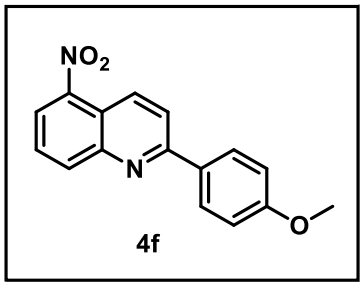


Figure 17: Selected HMBC ( ) Correlation

5.1.1. Representative Compound for C2-arylated quinolines 4 with ^{1}H, ^{13}C data and spectra

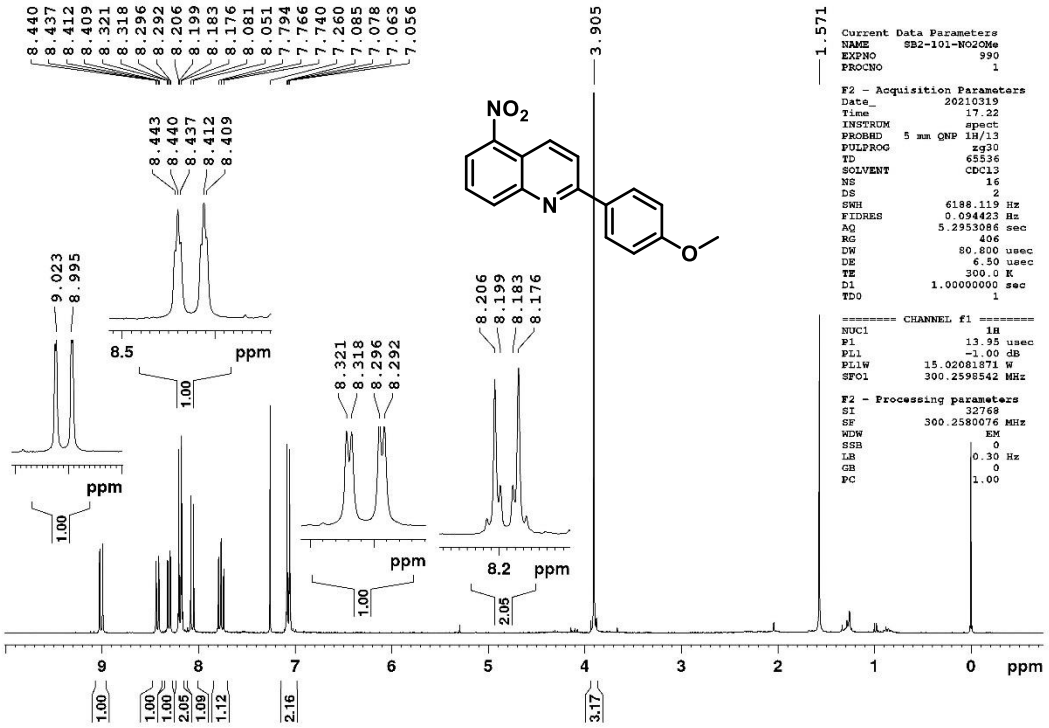
Compound 4d: 2-(4-methoxyphenyl)-5-nitroquinoline



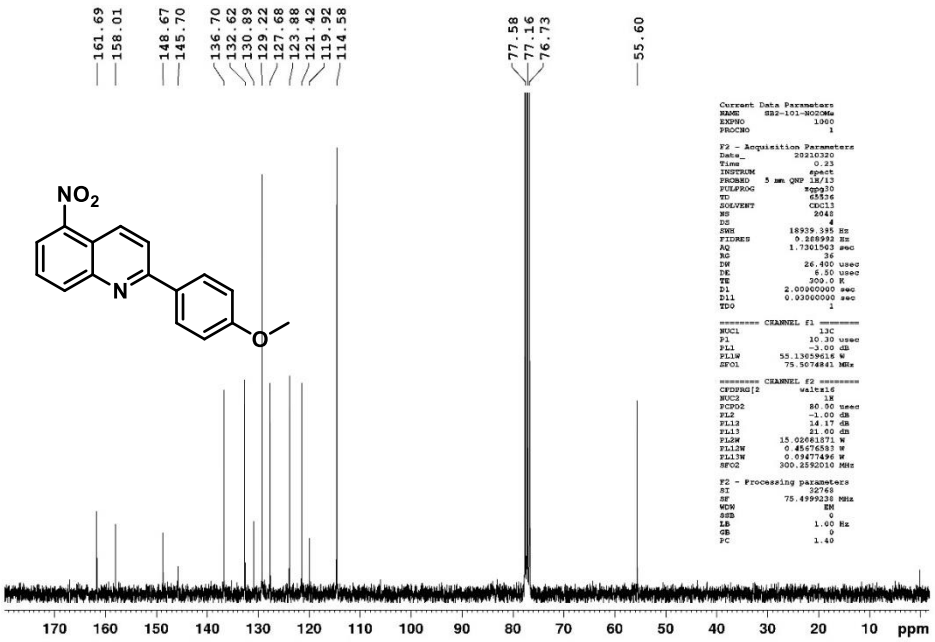
2% EtOAc/Hexane afforded **4d** (6 mg, 11%, based on **1c**) as a yellow needle-like crystalline solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.55. **M.P.** 146 -148 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (d, *J* = 9.2 Hz, 1H), 8.42 (dt, *J* = 8.4, 0.9 Hz, 1H), 8.30 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.20 – 8.17 (m, 2H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.76 (t, *J* = 8.3, 7.8 Hz, 1H), 7.13 – 7.04 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 158.0, 148.6, 145.7, 136.7, 132.6, 130.8, 129.2, 127.6, 123.8, 121.4, 119.9, 114.5, 55.6. **HRMS (ESI^+)**: Calcd for $C_{16}H_{13}N_2O_3$, $[M+H]^+$ m/z 281.0921. Found 281.0923.



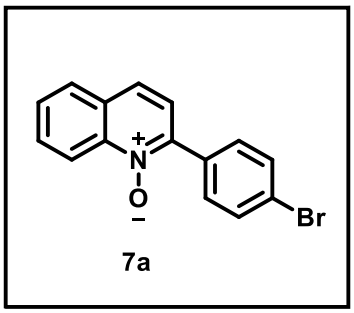
^{1}H NMR spectrum of **4d** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4d** (75 MHz, $CDCl_3$)

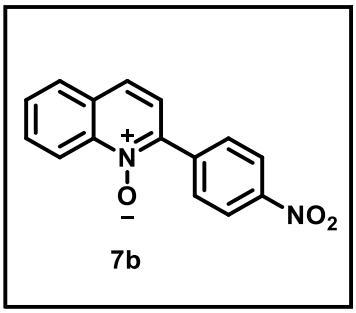
5.2. Characterization data of C2-Aryl Quinoline-N-Oxides 7

Compound 7a: 2-(4-bromophenyl)quinoline 1-oxide



7a was prepared according to the general procedure (**B)** using quinoline 1-oxide **5a** (87 mg, 0.6 mmol), 4-bromobenzene diazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 25% EtOAc/Hexane afforded **7a** (39 mg, 65%, based on **1a**) as a pale brown solid. **R_f** (EtOAc:Hexane = 1:2) = 0.45. **M.P.** 175-179 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.7 Hz, 1H), 7.89-7.86 (m, 3H), 7.81-7.75 (m, 2H), 7.67-7.63 (m, 3H), 7.48 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.1, 142.4, 132.4, 131.7 (2C), 131.3 (2C), 130.8, 129.8, 128.7, 128.1, 125.5, 124.1, 122.9, 120.3. **HRMS (ESI$^+$):** Calcd for $C_{15}H_{11}BrNO$, $[M+H]^+$ m/z 300.0019. Found 300.0021.

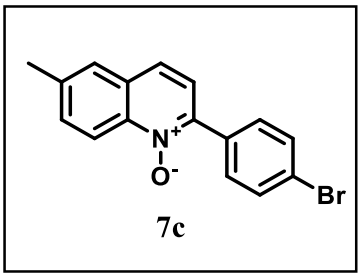
Compound 7b: 2-(4-nitrophenyl)quinoline 1-oxide



7b was prepared according to the general procedure (**B)** using quinoline 1-oxide **5a** (87 mg, 0.6 mmol), 4-nitrobenzene diazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 30% EtOAc/Hexane afforded **7b** (35 mg, 67%, based on **1b**) as a yellow solid. **R_f** (EtOAc:Hexane = 1:2) = 0.50. **M.P.** 222-225 ℃. **^{1}H NMR** (400 MHz, $DMSO_6$) δ 8.64 (d, *J* = 8.8 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.05

(d, *J* = 8.6 Hz, 1H), 7.90-7.86 (m, 1H), 7.81-7.71 (m, 2H). **^{13}C NMR** (100 MHz, $DMSO_6$) δ 147.4, 141.9, 141.4, 139.6, 131.0, 130.9, 129.8, 129.2, 128.7, 125.1, 123.3, 123.1, 119.3. **HRMS (ESI$^+$)**: Calcd for $C_{15}H_{11}N_2O_3$, $[M+H]^+$ m/z 267.0764. Found 267.0777.

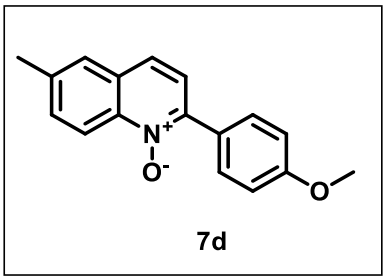
Compound 7c: 2-(4-bromophenyl)-6-methylquinoline 1-oxide



7c

7c was prepared according to the general procedure (**B)** using 6-methyl quinoline 1-oxide **5b** (96 mg, 0.6 mmol), 4-bromobenzene diazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 30% EtOAc/Hexane afforded **7c** (33 mg, 53%, based on **1a**) as a red solid. **R_f** (EtOAc:Hexane = 1:2) = 0.50. **M.P.** 140-143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.68-7.59 (m, 5H), 7.42 (d, *J* = 8.6 Hz, 1H), 2.55 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.4, 140.9, 139.05, 133.05, 132.5, 131.6 (2C), 131.3 (2C), 129.9, 127.1, 125.1, 123.8, 122.9, 120.1, 21.5. **HRMS (ESI$^+$)**: Calcd for $C_{16}H_{13}BrNO$, $[M+H]^+$ m/z 314.0175. Found 314.0173

Compound 7d: 2-(4-methoxyphenyl)-6-methylquinoline 1-oxide



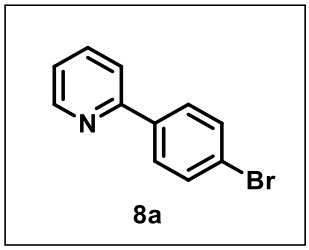
7d

7d was prepared according to the general procedure (**B)** using 6-methylquinoline 1-oxide **5b** (96 mg, 0.6 mmol), 4-methoxybenzenediazonium tetrafluoroborate salt **1c** (45 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 30% EtOAc/Hexane afforded **7d** (22 mg, 41%, based on **1c**) as a pale brown solid. **R_f** (EtOAc:Hexane = 1:2) = 0.45. **M.P.** 143-146 °C. **^{1}H NMR** (300 MHz,

$CDCl_3$) δ 8.72 (d, *J* = 9.3 Hz, 1H), 8.02-7.98 (m, 2H), 7.64-7.56 (m,3H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.04-7.01 (m, 2H), 3.87 (s, 3H), 2.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.5, 144.1, 140.9, 138.4, 132.7, 131.3 (2C), 129.5, 126.9, 125.9, 124.9, 123.1, 120.1, 113.7 (2C), 55.4, 21.4. **HRMS (ESI$^+$)**: Calcd for $C_{17}H_{16}NO_2$, $[M+H]^+$ m/z 266.1176. Found 266.1173.

5.3. Characterization data of C2-Aryl Pyridines 8

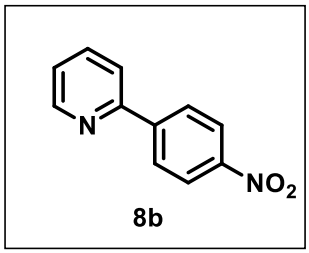
Compound 8a: 2-(4-bromophenyl)pyridine[10]



8a

8a was prepared according to the general procedure (**A)** using pyridine **6a** (242 μL, 3.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 5% EtOAc/Hexane afforded **8a** (24 mg, 51%, based on **1a**) as a brown solid. **R$_f$** (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 63-65 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 4.8, 1.6, 0.9 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.78 – 7.67 (m, 2H), 7.61 – 7.57 (m, 2H), 7.26 – 7.22 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.3, 149.8, 138.3, 137.0, 132.0 (2C), 128.6 (2C), 123.6, 122.5, 120.4. **HRMS (ESI$^+$):** Calcd for $C_{11}H_9BrN$, $[M+H]^+$ m/z 233.9913. Found 233.9912.

Compound 8b: 2-(4-nitrophenyl)pyridine

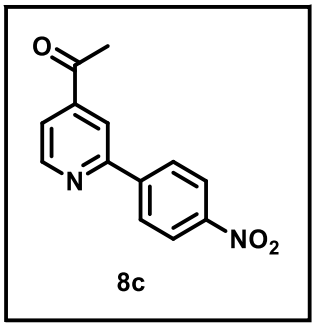


8b

8b was prepared according to the general procedure (**A)** using pyridine **6a** (242 μL, 3.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 5% EtOAc/Hexane afforded **8b** (21 mg, 53%, based on **1b**) as a white solid. **R$_f$**

(EtOAc:Hexane = 1:9) = 0.50. **M.P.** 127-129 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 – 8.74 (m, 1H), 8.34 – 8.31 (m, 2H), 8.19 – 8.17 (m, 2H), 7.83 – 7.81 (m, 2H), 7.33 (ddd, *J* = 6.7, 4.8, 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 150.2, 148.2, 145.3, 137.2, 127.7 (2C), 124.1 (2C), 123.6, 121.3. **HRMS (ESI$^+$):** Calcd for $C_{11}H_9N_2O_2$, $[M+H]^+$ m/z 201.0659. Found 201.0656.

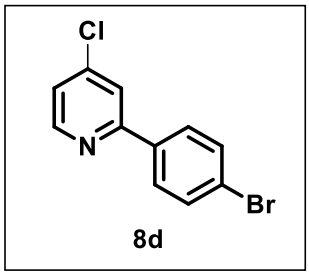
Compound 8c: 1-(2-(4-nitrophenyl)pyridin-4-yl)ethan-1-one



8c

8c was prepared according to the general procedure (**A)** using 1-(pyridin-4-yl)ethan-1-one **6b** (333 μL, 3.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 6% EtOAc/Hexane afforded **8c** (27.5 mg, 57%, based on **1b**) as an off-white solid. **R_f** (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 151-153 ℃. **^{1}H NMR (**500 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 5.0, 0.7 Hz, 1H), 8.35 – 8.33 (m, 2H), 8.25 – 8.23 (m, 3H), 7.75 (dd, *J* = 5.0, 1.5 Hz, 1H), 2.70 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.0, 156.3, 151.4, 148.6, 144.5, 144.2, 128.0 (2C), 124.2 (2C), 121.3, 18.6, 26.9. **HRMS (ESI$^+$):** Calcd for $C_{13}H_{11}N_2O_3$, $[M+H]^+$ m/z 243.0764. Found 243.0771.

Compound 8d: 2-(4-bromophenyl)-4-chloropyridine[11]

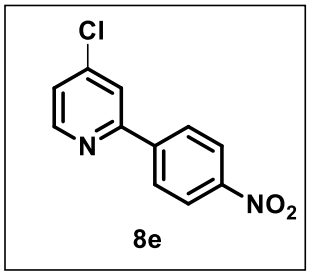


8d

8d was prepared according to the general procedure (**A)** using 4-chloropyridine hydrochloride **6c** (450 mg, 3.0 mmol), 4-bromobenzenediazonium tetrafluoroborate salt **1a** (54 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by

column chromatography using 5% EtOAc/Hexane afforded **8d** (31 mg, 58%, based on **1a**) as brown semi-solid compound. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.55. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.3 Hz, 1H), 7.97 – 7.81 (m, 2H), 7.61 – 7.46 (m, 2H), 7.25 – 7.24 (m, 1H). **HRMS (ESI$^+$):** Calcd for $C_{11}H_8BrClNO$, $[M+H]^+$ m/z 267.9523. Found 267.9523.

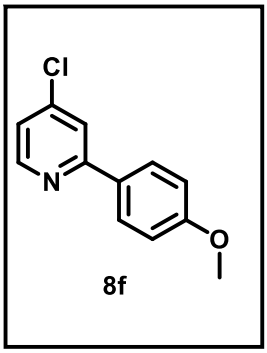
Compound 8e: 4-chloro-2-(4-nitrophenyl)pyridine



8e

8e was prepared according to the general procedure (**A)** using 4-chloropyridine hydrochloride **6c** (450 mg, 3.0 mmol), 4-nitrobenzenediazonium tetrafluoroborate salt **1b** (48 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 5% EtOAc/Hexane afforded **8e** (30 mg, 64%, based on **1b**) as a yellow solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.50. **M.P.** 137-139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.3 Hz, 1H), 8.35 – 8.32 (m, 2H), 8.18 – 8.15 (m, 2H), 7.82 – 7.81 (m, 1H), 7.36 (dd, *J* = 5.3, 1.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 151.0, 148.7, 145.4, 144.0, 128.0 (2C), 124.2 (2C), 123.8, 121.7. **HRMS (ESI$^+$):** Calcd for $C_{11}H_8ClN_2O_2$, $[M+H]^+$ m/z 235.0269. Found 235.0266.

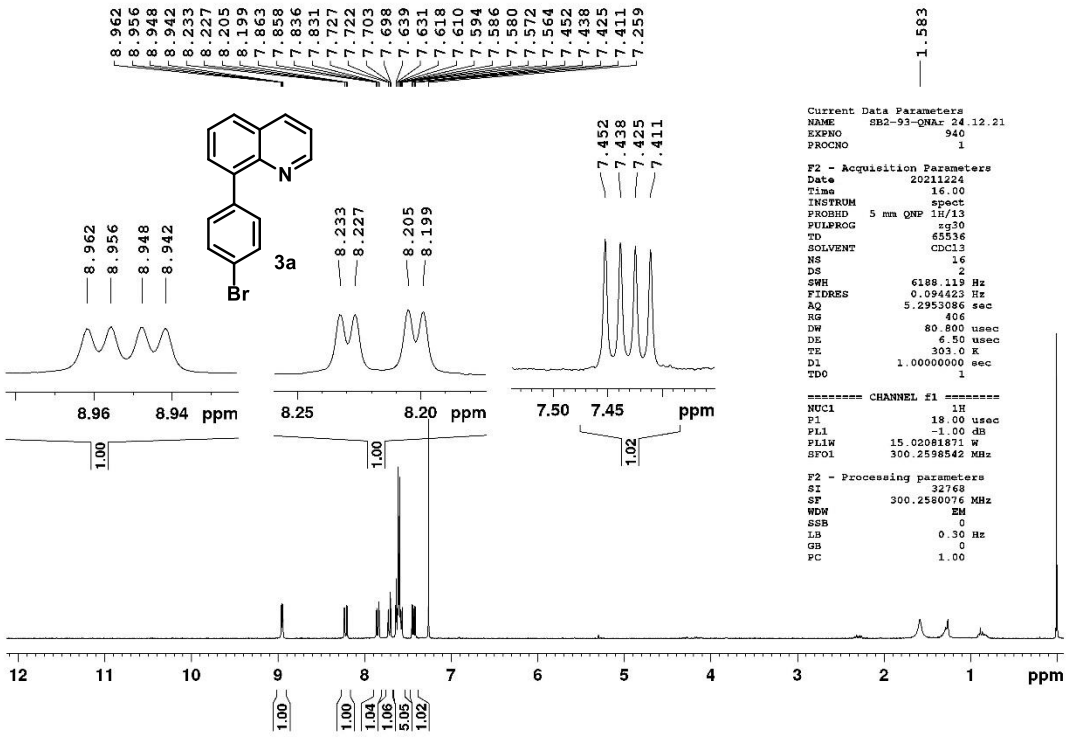
Copound 8f: 4-chloro-2-(4-methoxyphenyl)pyridine[11]



8f

8f was prepared according to the general procedure (**A)** using 4-chloropyridine hydrochloride **6c** (450 mg, 3.0 mmol), 4-methoxybenzenediazonium tetrafluoroborate salt **1c** (45 mg, 0.20 mmol) and chlorophyll (0.5 mol%). The crude reaction mixture was purified by column chromatography using 6% EtOAc/Hexane afforded **8f** (25 mg, 57%, based on **1c**) as a yellow solid. $\mathbf{R_f}$ (EtOAc:Hexane = 1:9) = 0.45. **M.P.** 98-100 ℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.3 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.18 (dd, *J* = 5.3, 1.9 Hz, 1H), 7.01 – 6.95 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.1, 158.8, 150.5, 144.8, 130.7, 128.5 (2C), 121.7, 120.2, 114.3 (2C), 55.5. **HRMS (ESI$^+$):** Calcd for $C_{11}H_8ClN_2O_2$, $[M+H]^+$ m/z 220.0524. Found 220.0523.

6. NMR Spectral data of Compounds 3, 7, 8



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PROCNO 1

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DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 406
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DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1

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F2 - Processing parameters
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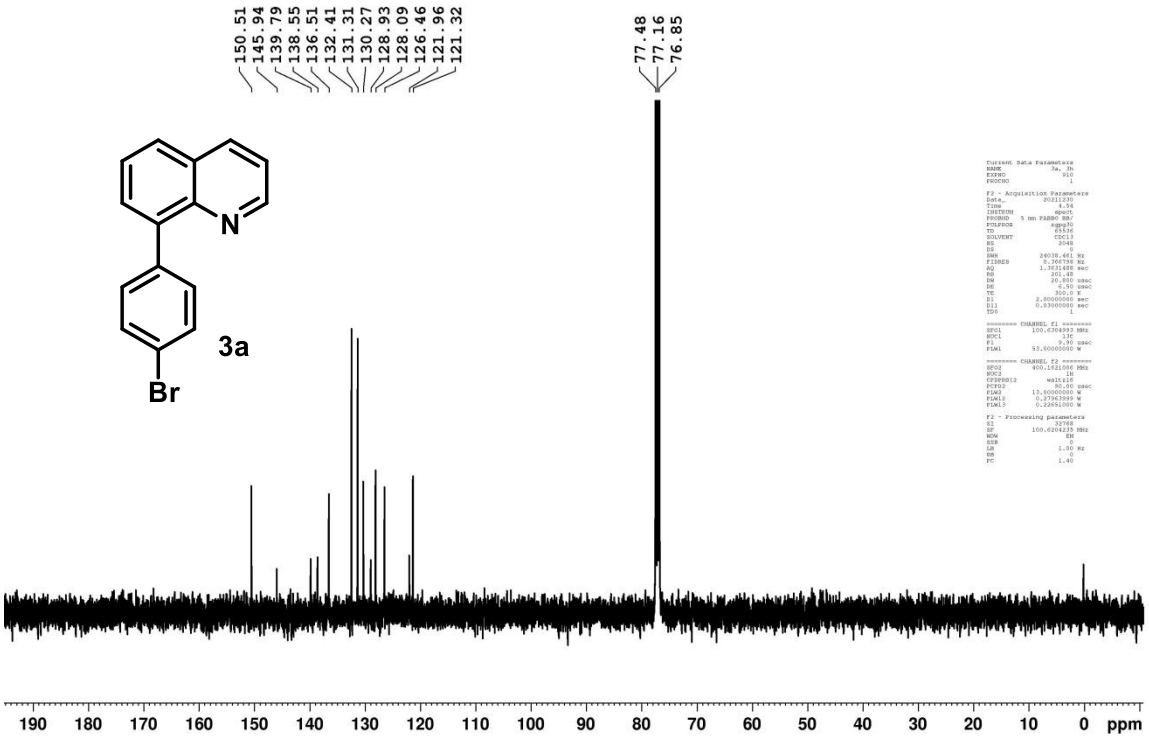
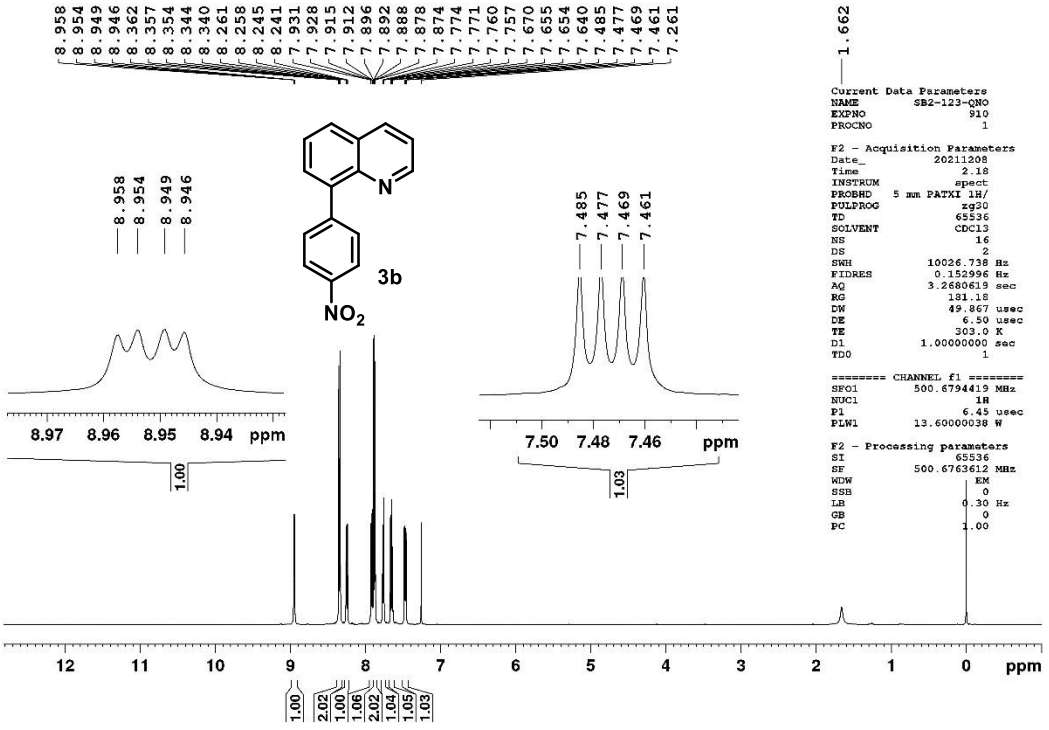
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





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EXPNO 910
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 181.18
DW 49.867 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1

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NUC1 1H
P1 6.45 usec
PLW1 13.60000038 W

F2 - Processing parameters
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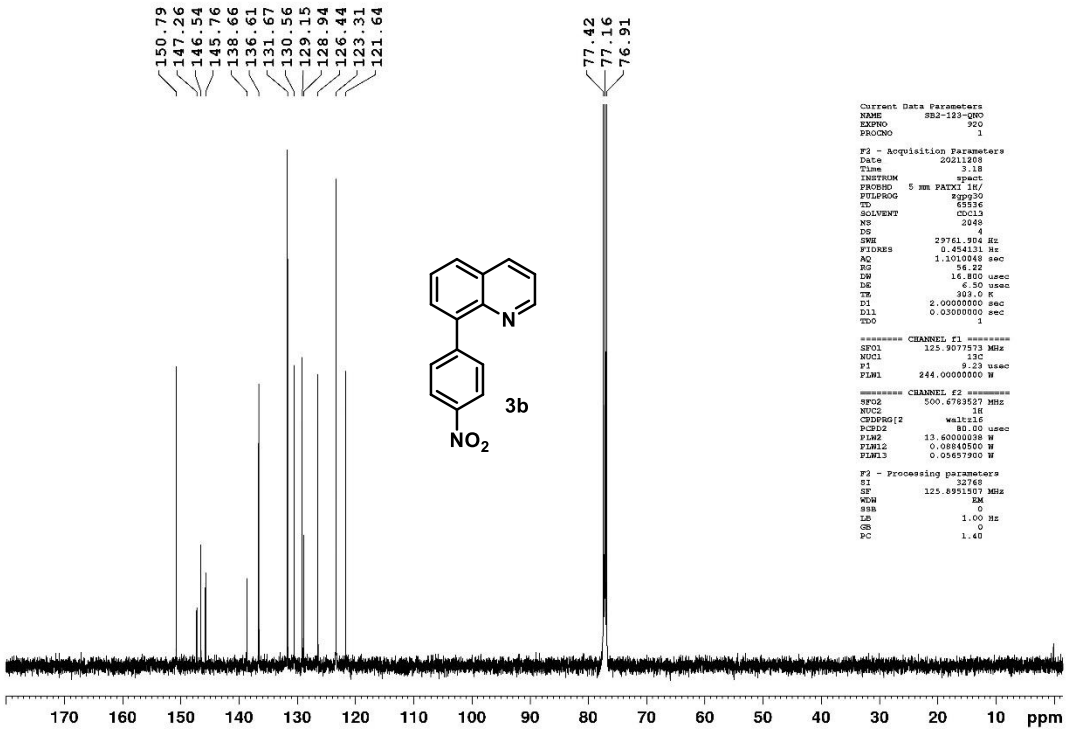
LB 0.30 Hz
GB 0
PC 1.00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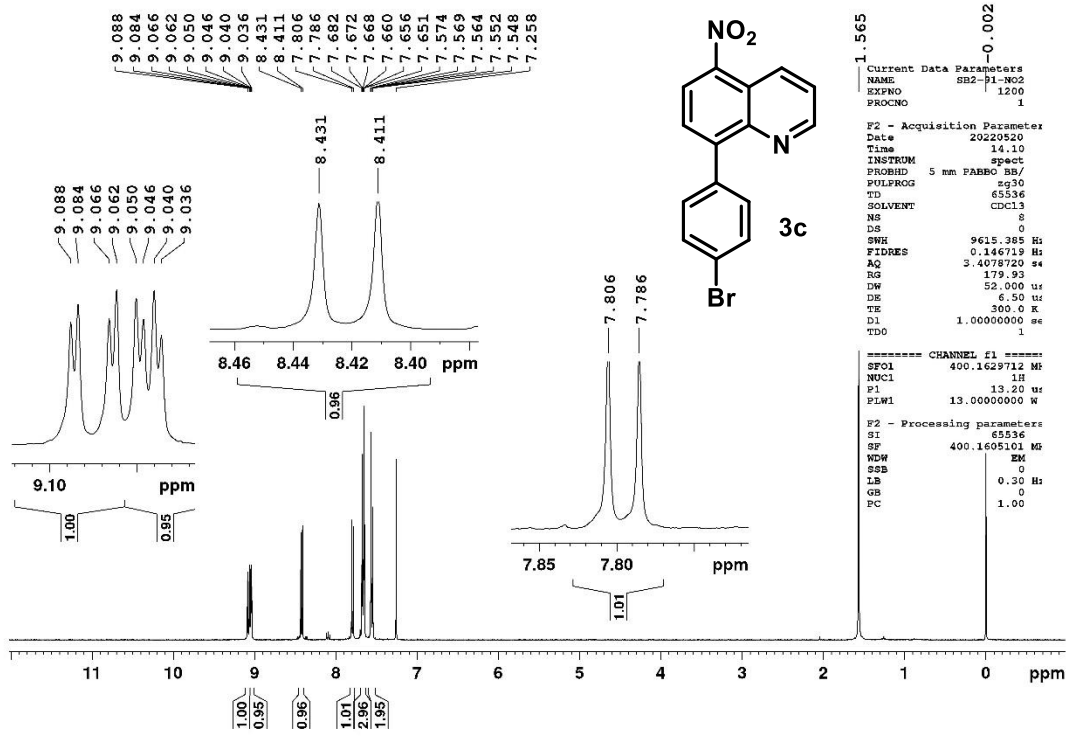
146.54
145.76
138.66
136.61
131.67
130.56
129.15
128.94
126.44
123.31
121.64
77.42
77.16
76.91
N
NO2
3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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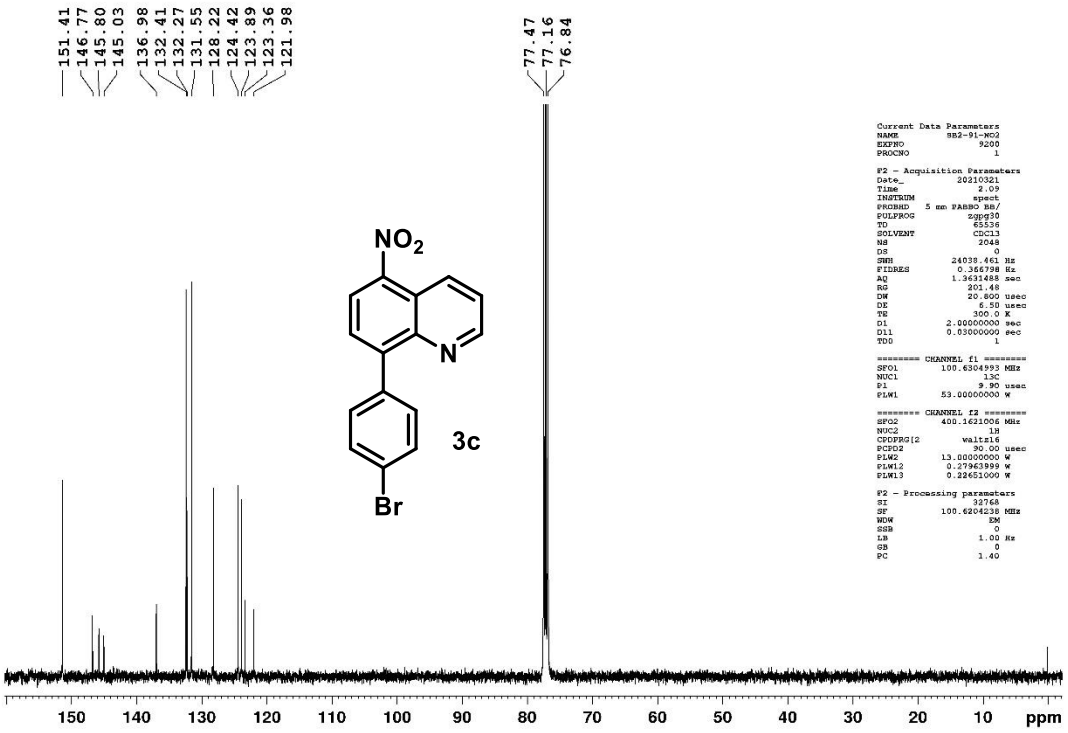
9.066
9.062
9.050
9.046
9.040
9.036
8.431
8.411
7.806
7.786
7.682
7.672
7.668
7.660
7.656
7.651
7.574
7.569
7.564
7.552
7.548
7.258
NO2
N
Br
3c
8.46 8.44 8.42 8.40 ppm
9.10 ppm
7.85 7.80 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm


151.41
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145.80
145.03
136.98
132.41
132.27
131.55
128.22
124.42
123.89
123.36
121.98
77.47
77.16
76.84
NO2
N
Br
3c
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PROCNO 1
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Time 2.09
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PULPROG zgpg30
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SWH 24038.461 Hz
FIDRES 0.366798 Hz
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RG 201.48
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DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 9.90 usec
PLW1 53.00000000 W
======== CHANNEL f2 ========
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.27963989 W
PLW13 0.22651000 W
F2 - Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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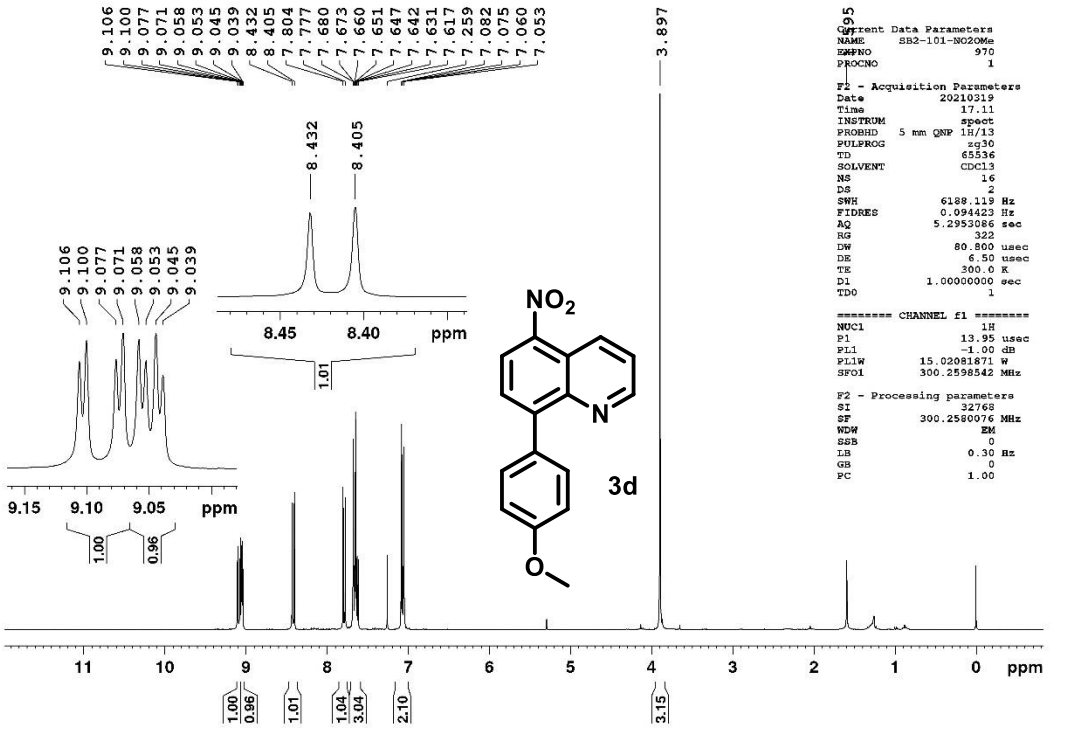
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9.058
9.053
9.045
9.039
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8.405
7.804
7.777
7.680
7.673
7.660
7.651
7.647
7.642
7.631
7.617
7.259
7.082
7.075
7.060
7.053
3.897
8.45 8.40 ppm
1.01
9.15 9.10 9.05 ppm
1.00
0.96
NO2
N
O
3d
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.96
1.01
1.04
3.04
2.10
3.15
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EXPNO 970
PROCNO 1
F2 - Acquisition Parameters
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Time 17.11
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 322
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DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
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PL1 -1.00 dB
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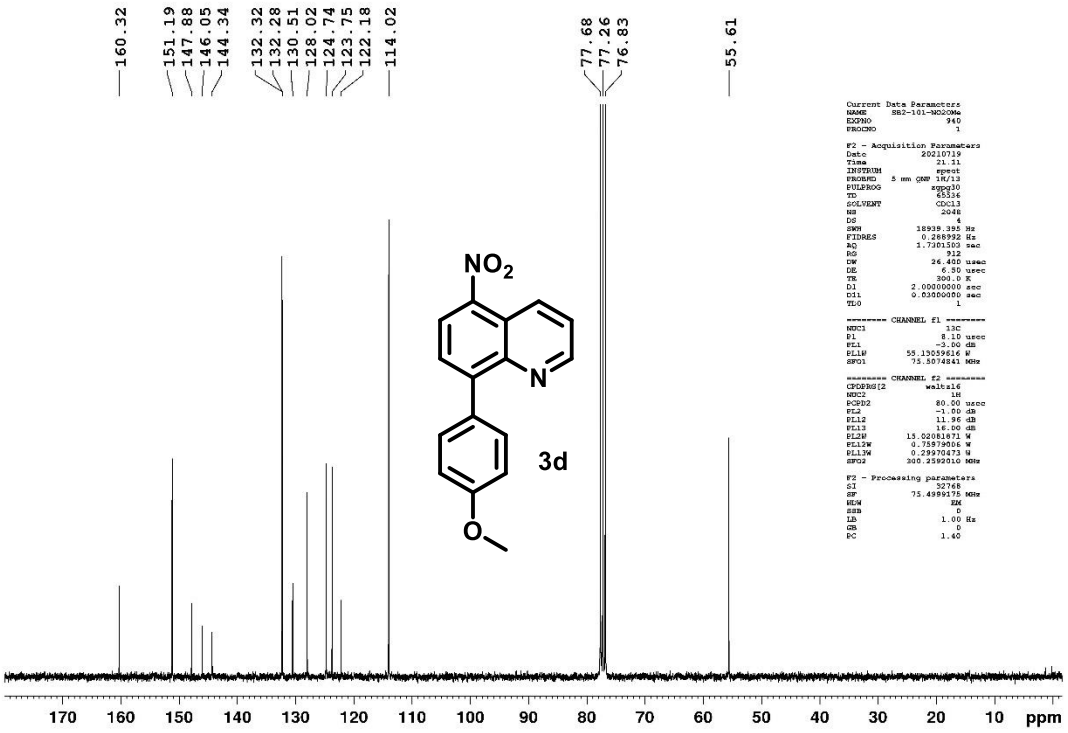
F2 - Processing parameters
SI 32768
SF 300.2580076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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130.51
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123.75
122.18
114.02
77.68
77.26
76.83
55.61
NO2
N
O
3d
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EXPNO 940
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210719
Time 21.11
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 18939.395 Hz
FIDRES 0.288992 Hz
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RG 912
DW 26.400 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 -3.00 dB
PLW1 55.13059616 W
SFO1 75.5074841 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 11.96 dB
PL13 16.00 dB
PL2W 15.02081871 W
PL12W 0.75979006 W
PL13W 0.29970473 W
SFO2 300.2592010 MHz
F2 - Processing parameters
SI 32768
SF 75.4998175 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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150
140
130
120
110
100
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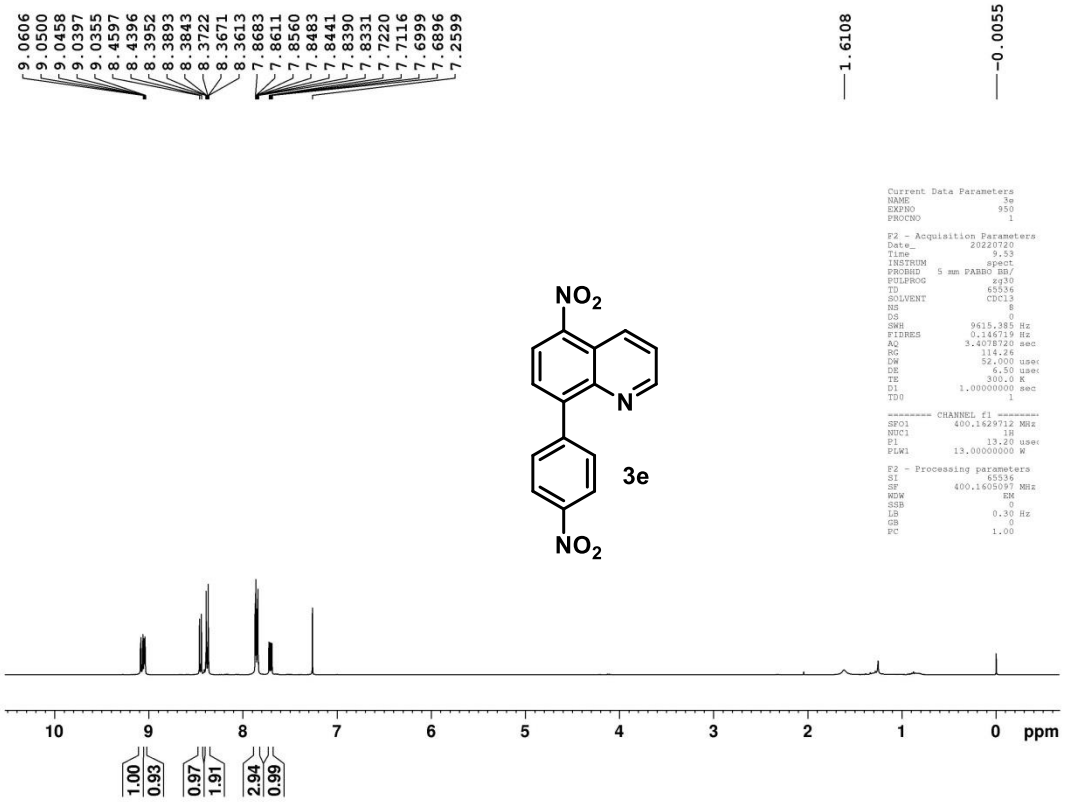
80
70
60
50
40
30
20
10
ppm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8.3671
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7.8683
7.8611
7.8560
7.8483
7.8441
7.8390
7.8331
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NO2
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NO2
3e
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NAME 3e
EXPNO 950
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220720
Time 9.53
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
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FIDRES 0.146719 Hz
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DE 6.50 usec
TE 300.0 K
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TD0 1
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NUC1 1H
P1 13.20 usec
PLW1 13.00000000 W
F2 - Processing parameters
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SF 400.1605097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
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4
3
2
1
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ppm
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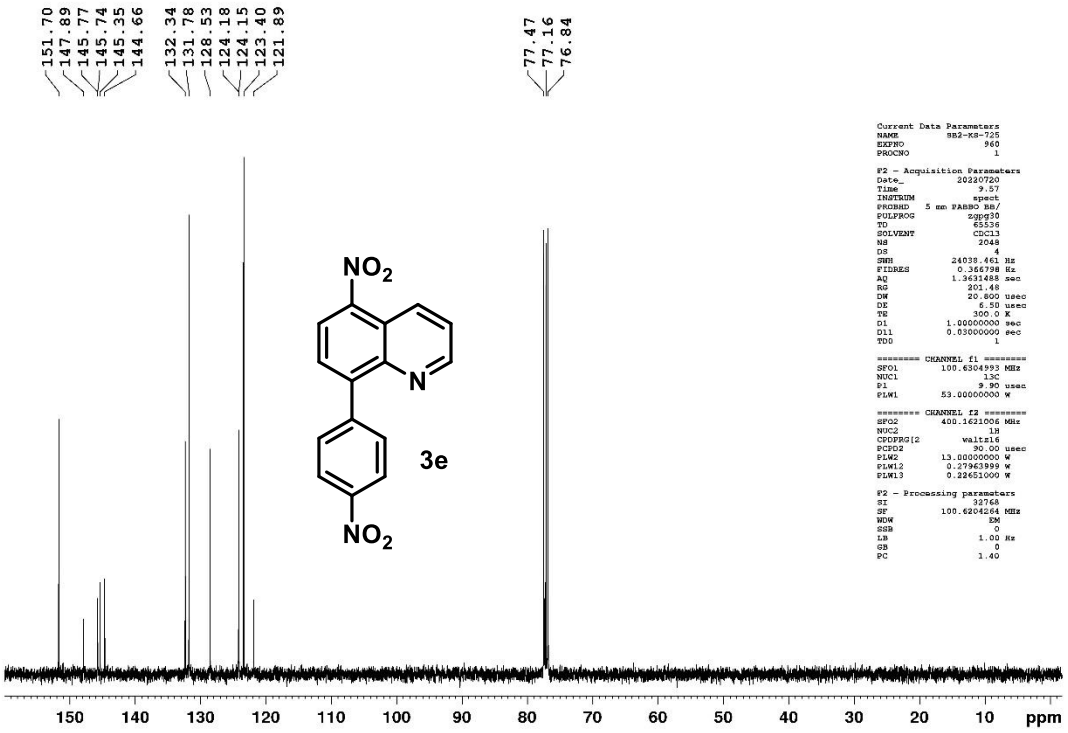
0.99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76.84
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NO2
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150
140
130
120
110
100
90
80
70
60
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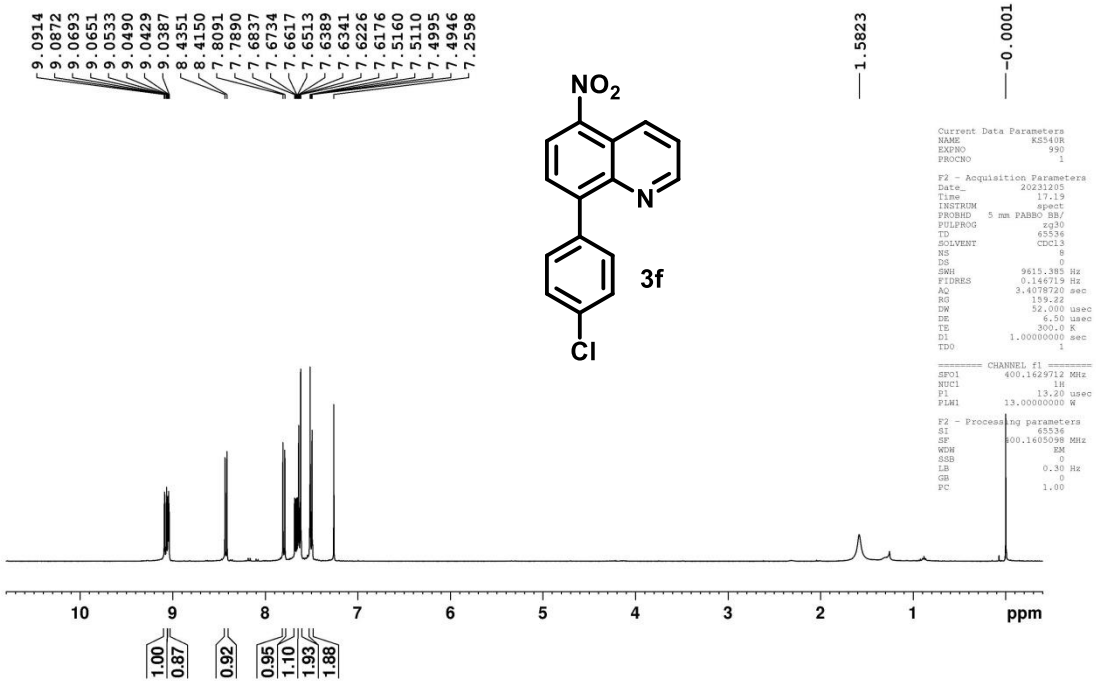
40
30
20
10
ppm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7.6837
7.6734
7.6617
7.6513
7.6389
7.6341
7.6226
7.6176
7.5160
7.5110
7.4995
7.4946
7.2598
1.5823
0.0001
NO2
N
3f
Cl
10
9
8
7
6
5
4
3
2
1
ppm
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0.92
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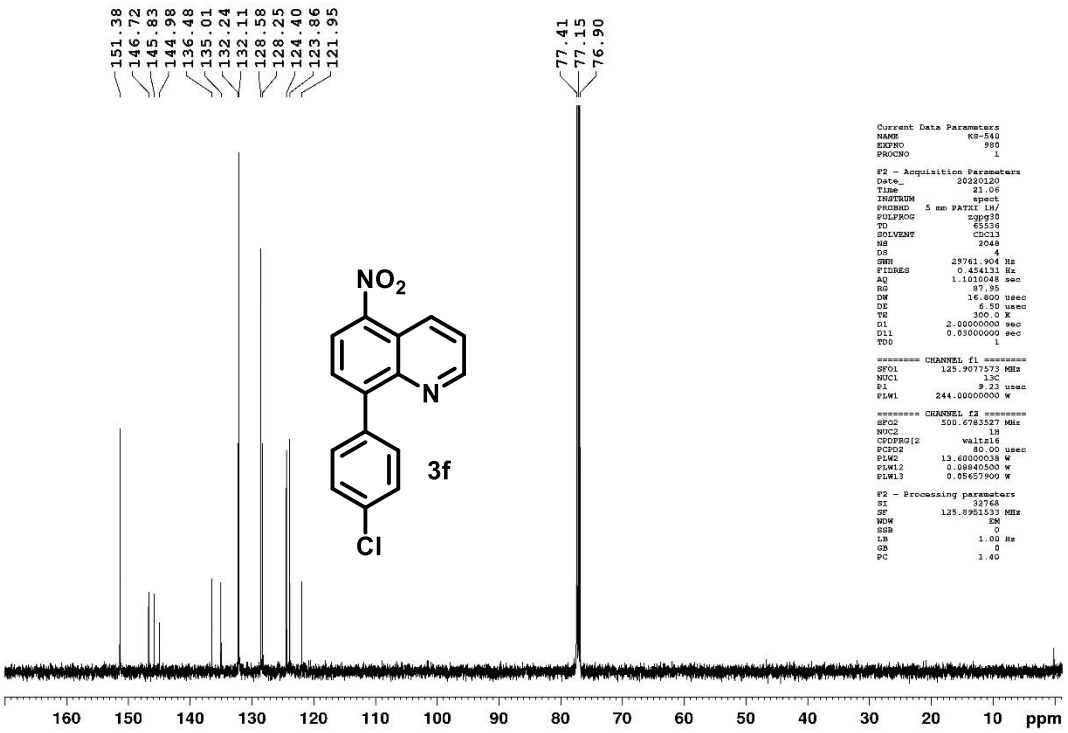
1.10
1.93
1.88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136.48
135.01
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128.25
124.40
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77.15
76.90
NO2
N
Cl
3f
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EXPNO 980
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220120
Time 21.06
INSTRUM spect
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PULPROG zgpg30
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DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 87.95
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DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W
======== CHANNEL f2 ========
SFO2 500.6783527 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.08840500 W
PLW13 0.05657900 W
F2 - Processing parameters
SI 32768
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WDW EM
SSB 0
LB 1.00 Hz
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150
140
130
120
110
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80
70
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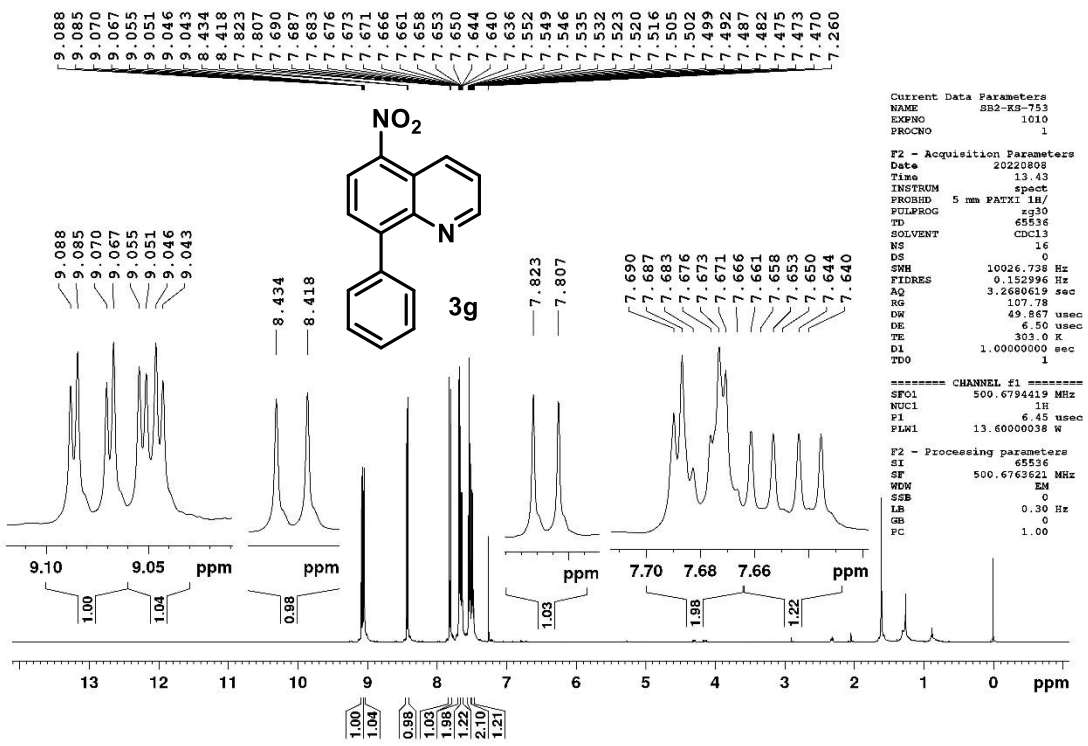
40
30
20
10
ppm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NO2
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3g
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EXPNO 1010
PROCNO 1
F2 - Acquisition Parameters
Date 20220808
Time 13.43
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 107.78
DW 49.867 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
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PLW1 13.60000038 W
F2 - Processing parameters
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SF 500.6763621 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
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8.43 8.42 ppm
7.82 7.81 ppm
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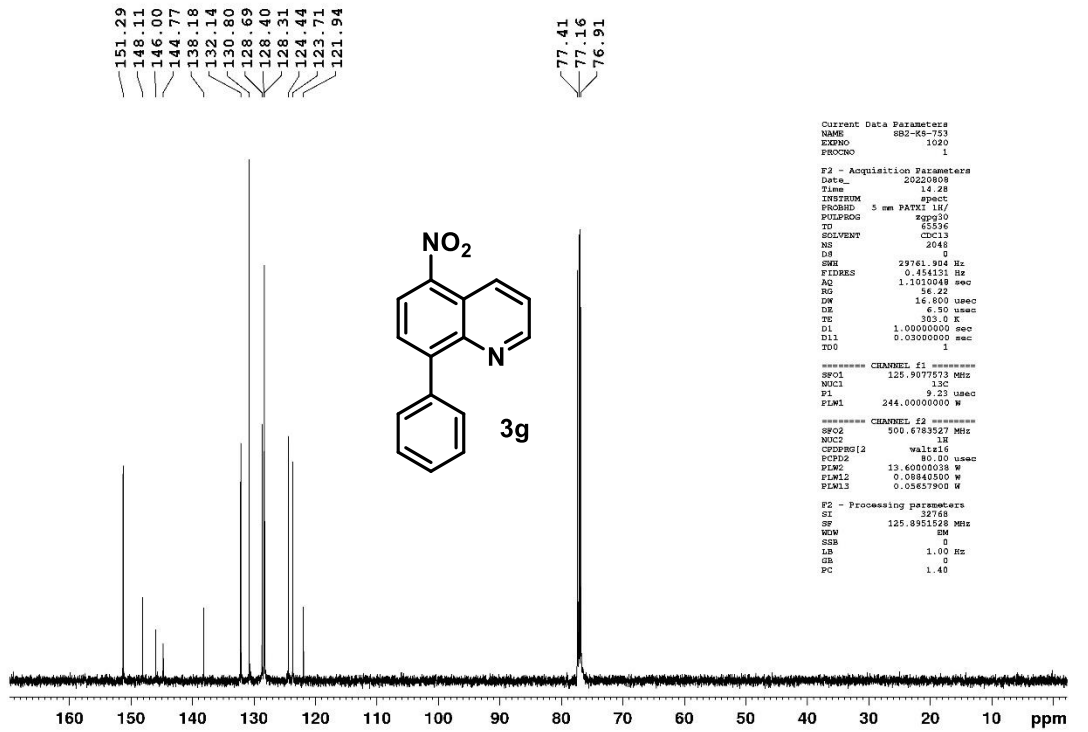
1.00 1.04 0.98 1.03 1.98 1.22 2.10 1.21
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm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NO2
N
3g
Current Data Parameters
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EXPNO 1020
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220808
Time 14.28
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PULPROG zgpg30
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SOLVENT CDCl3
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DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 56.22
DW 16.800 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
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SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W
======== CHANNEL f2 ========
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NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.08840500 W
PLW13 0.05657908 W
F2 - Processing parameters
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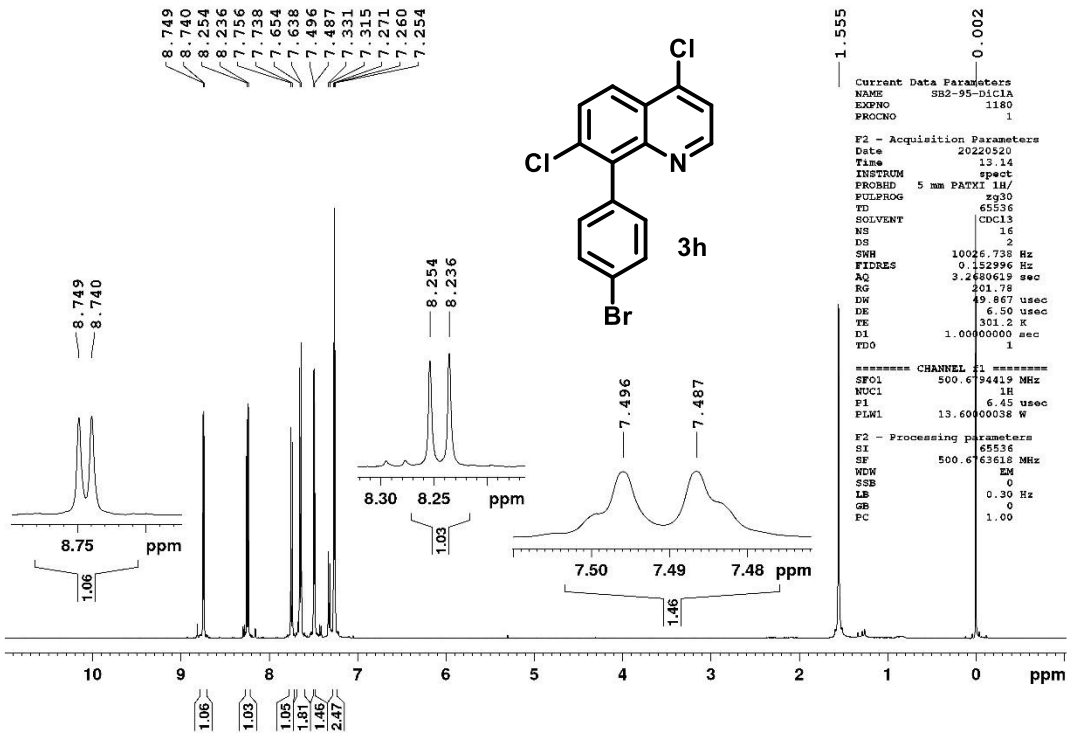
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7.638
7.496
7.487
7.331
7.315
7.271
7.260
7.254
1.555
0.002
Cl
Cl
N
Br
3h
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EXPNO 1180
PROCNO 1
F2 - Acquisition Parameters
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Time 13.14
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PULPROG zg30
TD 65536
SOLVENT CDCl3
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DS 2
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 201.78
DW 49.867 usec
DE 6.50 usec
TE 301.2 K
D1 1.00000000 sec
TD0 1
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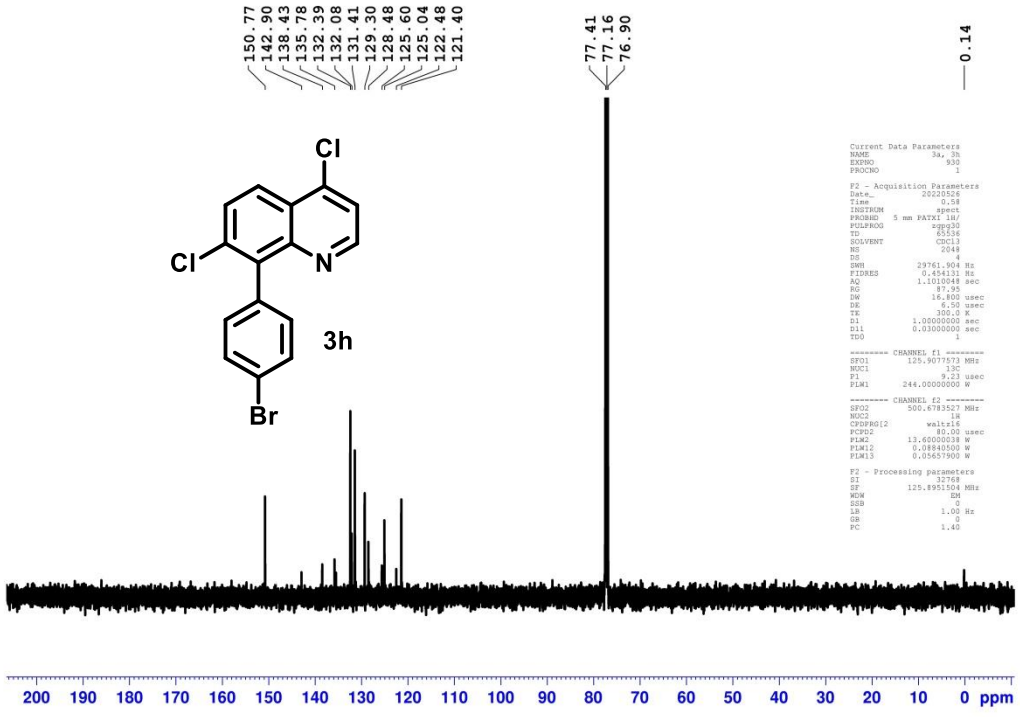
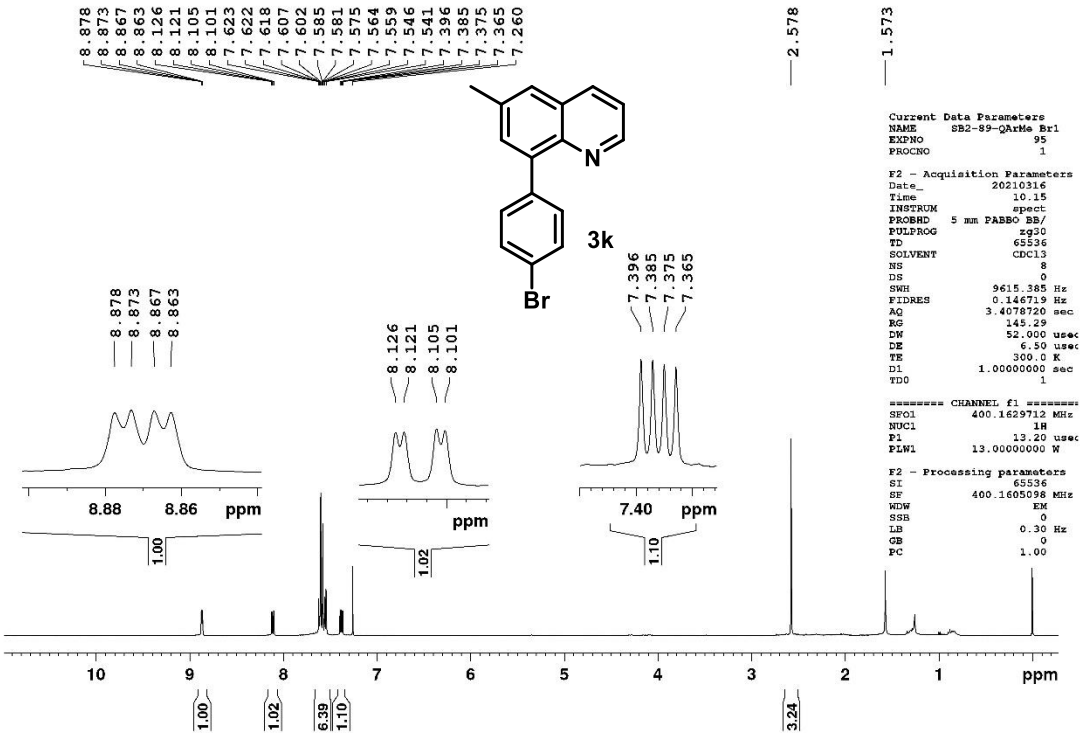
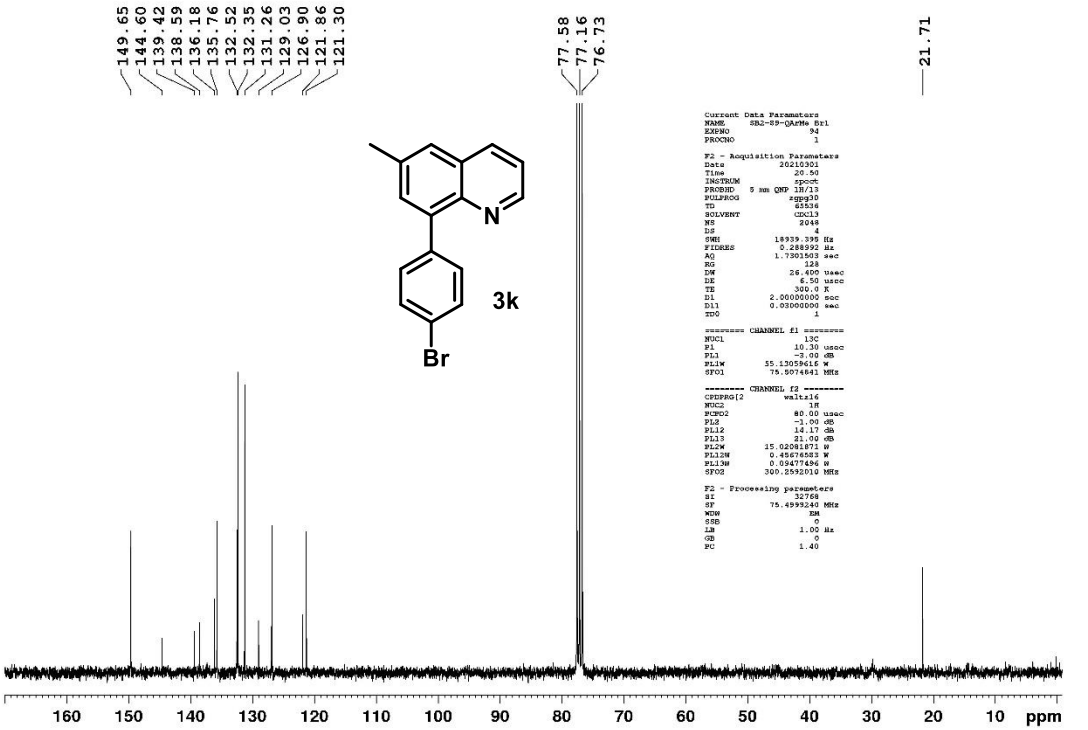
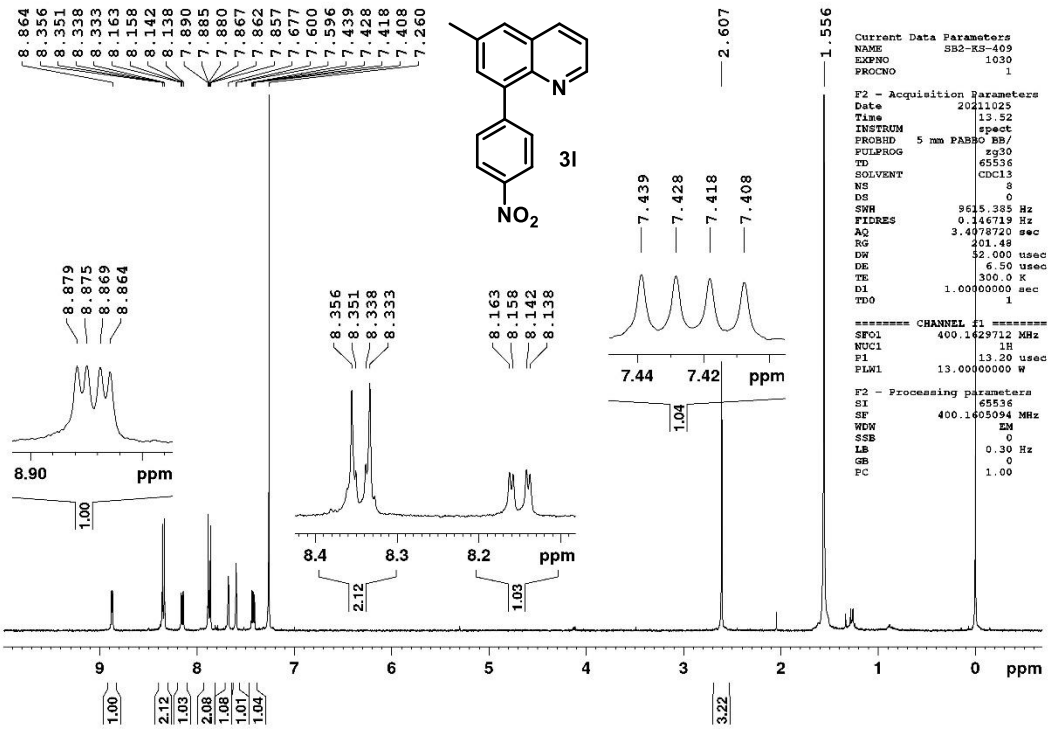
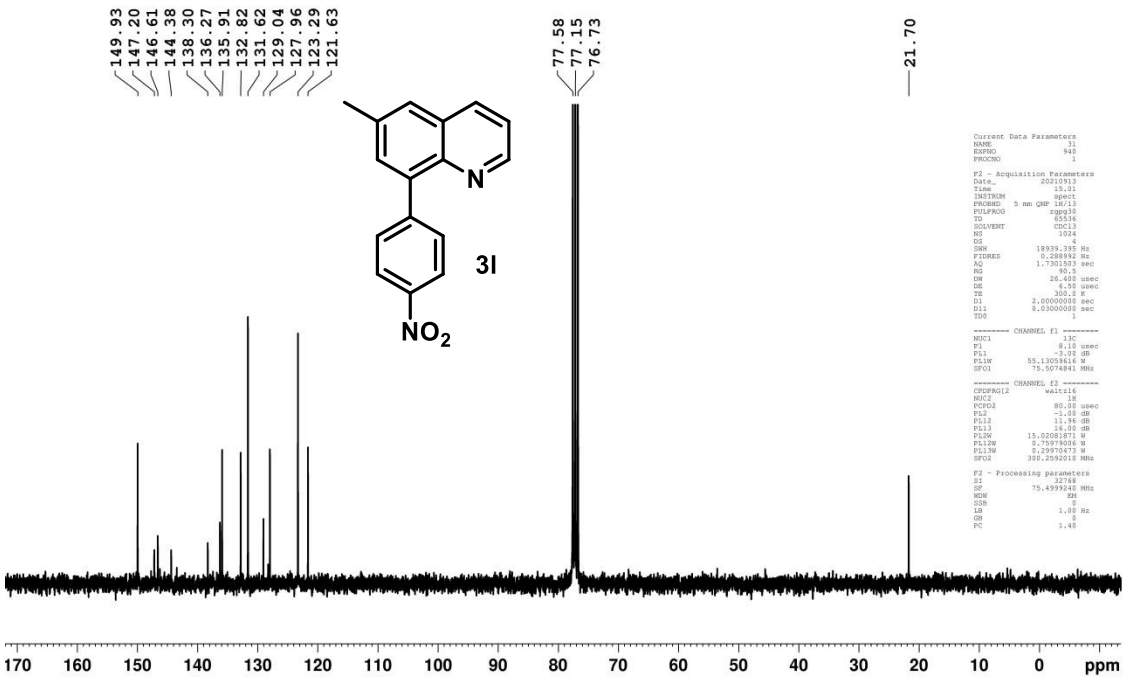
NUC1 1H
P1 6.45 usec
PLW1 13.60000038 W
F2 - Processing parameters
SI 65536
SF 500.6763618 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.749
8.740
8.75 ppm
1.06
8.254
8.236
8.30 8.25 ppm
1.03
7.496
7.487
7.50 7.49 7.48 ppm
1.46
10 9 8 7 6 5 4 3 2 1 0 ppm
1.06 1.03 1.05 1.81 1.46 2.47

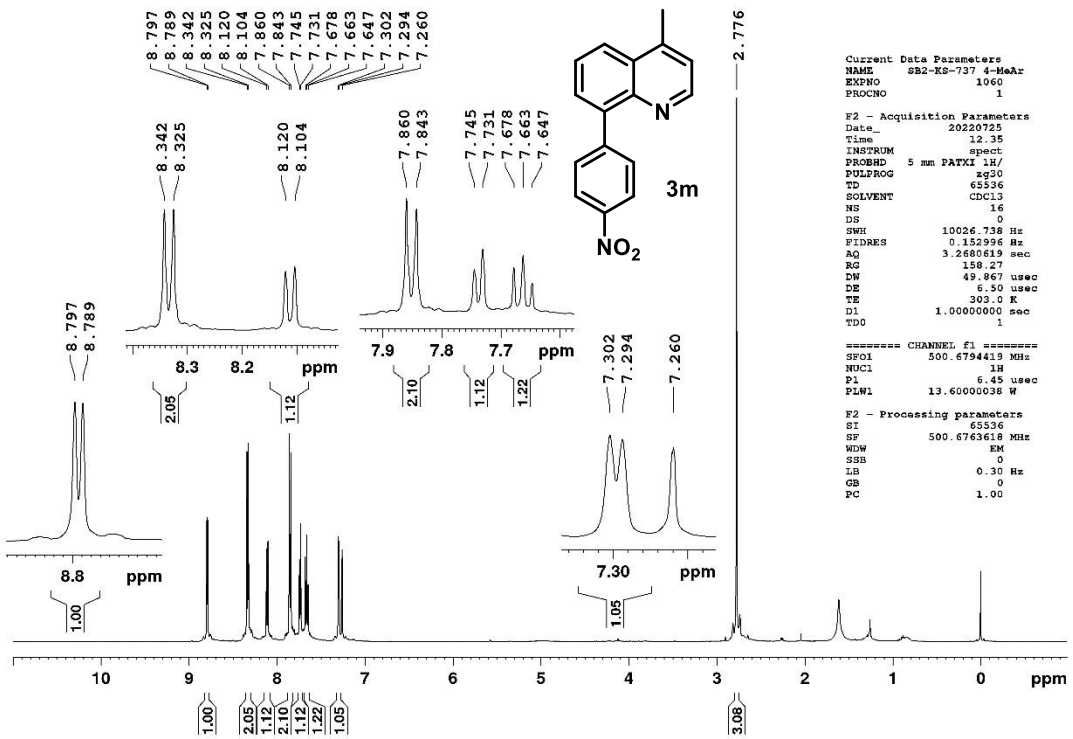

150.77
142.90
138.43
135.78
132.39
132.08
131.41
129.30
128.48
125.60
125.04
122.48
121.40
77.41
77.16
76.90
0.14
Cl
Cl
N
Br
3h
Current Data Parameters
NAME 3a, 3h
EXPNO 930
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220526
Time 0.58
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 87.95
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W
======== CHANNEL f2 ========
SFO2 500.6783527 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.08840500 W
PLW13 0.05657900 W
F2 - Processing parameters
SI 32768
SF 125.8951504 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.878
8.873
8.867
8.863
8.126
8.121
8.105
8.101
7.623
7.622
7.618
7.607
7.602
7.585
7.581
7.575
7.564
7.559
7.546
7.541
7.396
7.385
7.375
7.365
7.260
2.578
1.573
3k
Br
8.88
8.86
ppm
7.40
ppm
1.00
1.02
1.10
6.39
3.24


149.65
144.60
139.42
138.59
136.18
135.76
132.52
132.35
131.26
129.03
126.90
121.86
121.30
77.58
77.16
76.73
21.71
3k
Br
ppm


8.864
8.356
8.351
8.338
8.333
8.163
8.158
8.142
8.138
7.890
7.885
7.880
7.867
7.862
7.857
7.677
7.600
7.596
7.439
7.428
7.418
7.408
7.260
2.607
1.556
3l
NO2
8.879
8.875
8.869
8.864
8.90 ppm
1.00
8.356
8.351
8.338
8.333
8.163
8.158
8.142
8.138
8.4
8.3
8.2 ppm
2.12
1.03
7.439
7.428
7.418
7.408
7.44
7.42 ppm
1.04
9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.12
1.03
2.08
1.08
1.01
1.04
3.22
Current Data Parameters
NAME SB2-KS-409
EXPNO 1030
PROCNO 1
F2 - Acquisition Parameters
Date 20211025
Time 13.52
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 201.49
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1629712 MHz
NUC1 1H
P1 13.20 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1605094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


149.93
147.20
146.61
144.38
138.30
136.27
135.91
132.82
131.62
129.04
127.96
123.29
121.63
77.58
77.15
76.73
21.70
3l
NO2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

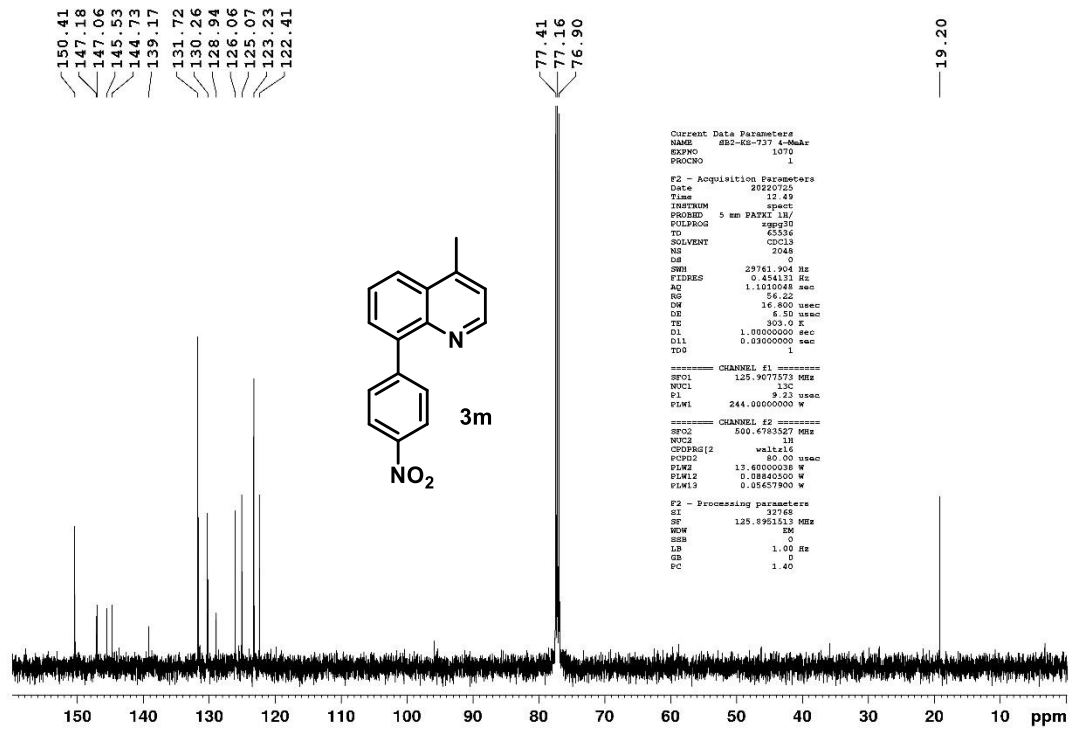


Current Data Parameters
NAME SB2-KS-737 4-MeAr
EXPNO 1060
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220725
Time 12.35
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 158.27
DW 49.867 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.6794419 MHz
NUC1 1H
P1 6.45 usec
PLW1 13.60000038 W

F2 - Processing parameters
SI 65536
SF 500.6763618 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



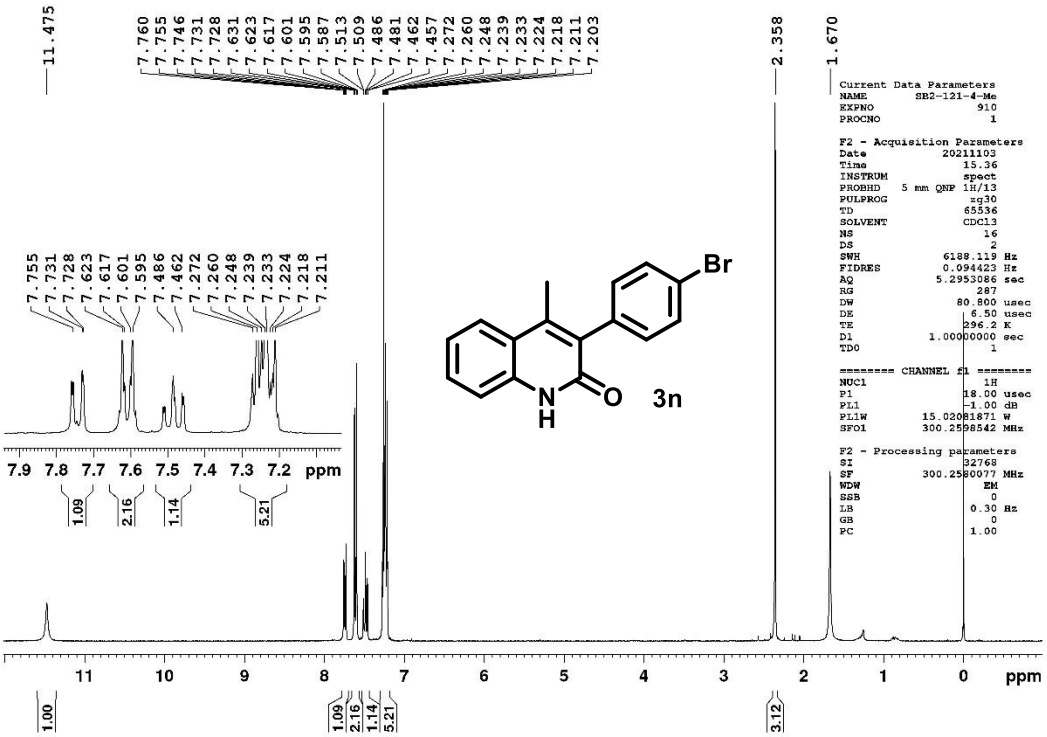
Current Data Parameters
NAME SB2-KS-737 4-MeAr
EXPNO 1070
PROCNO 1

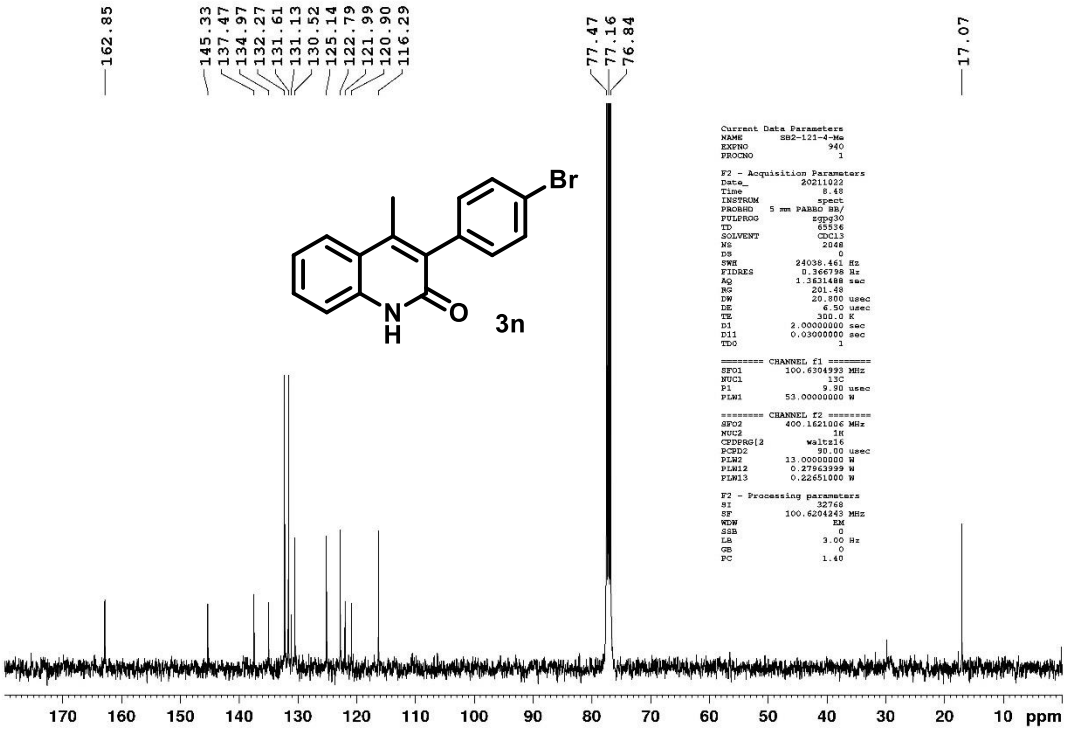
F2 - Acquisition Parameters
Date_ 20220725
Time 12.49
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 56.22
DW 16.800 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

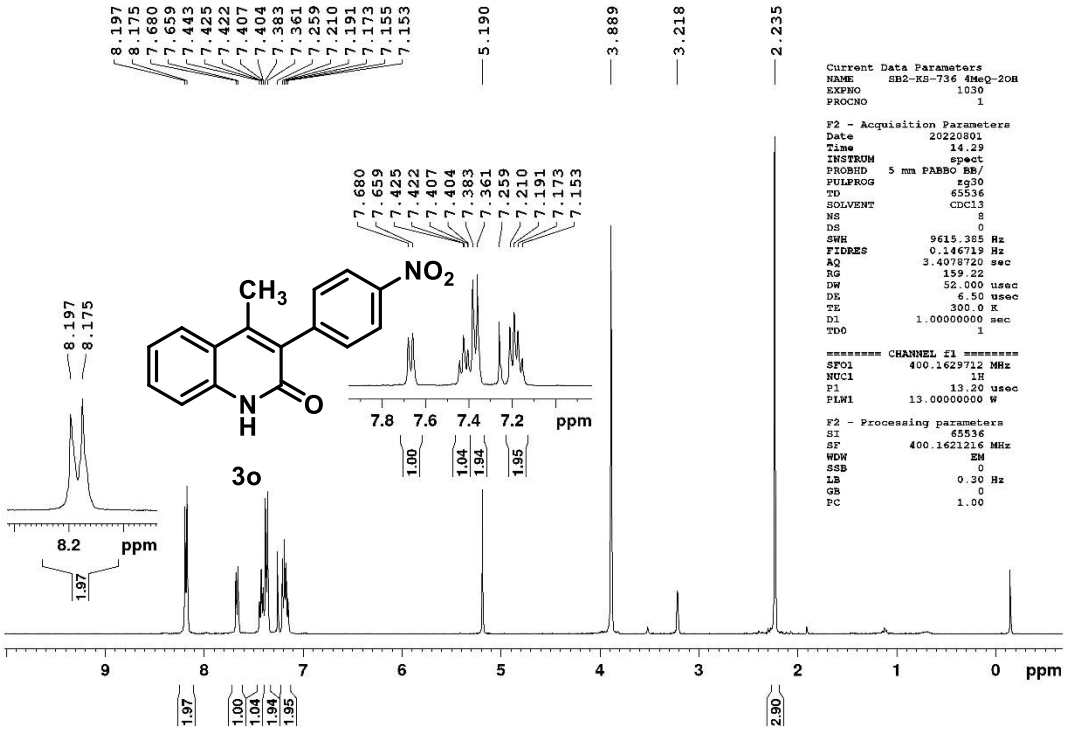
======== CHANNEL f1 ========
SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W

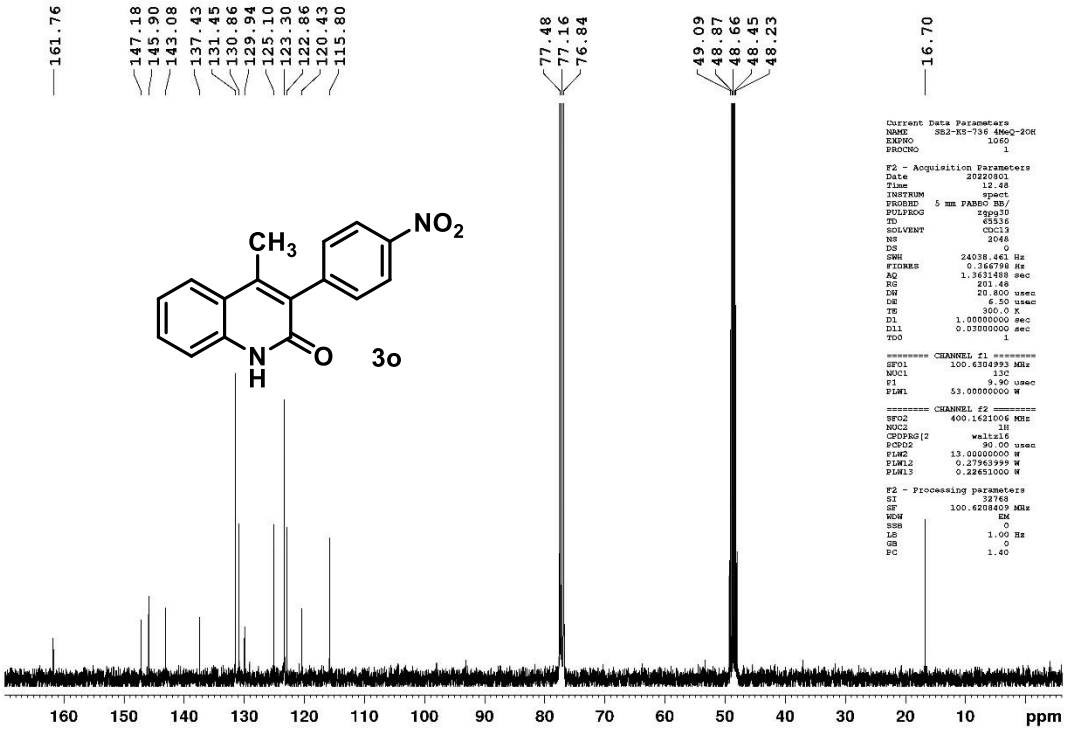
======== CHANNEL f2 ========
SFO2 500.6793527 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.88840500 W
PLW13 0.05657900 W

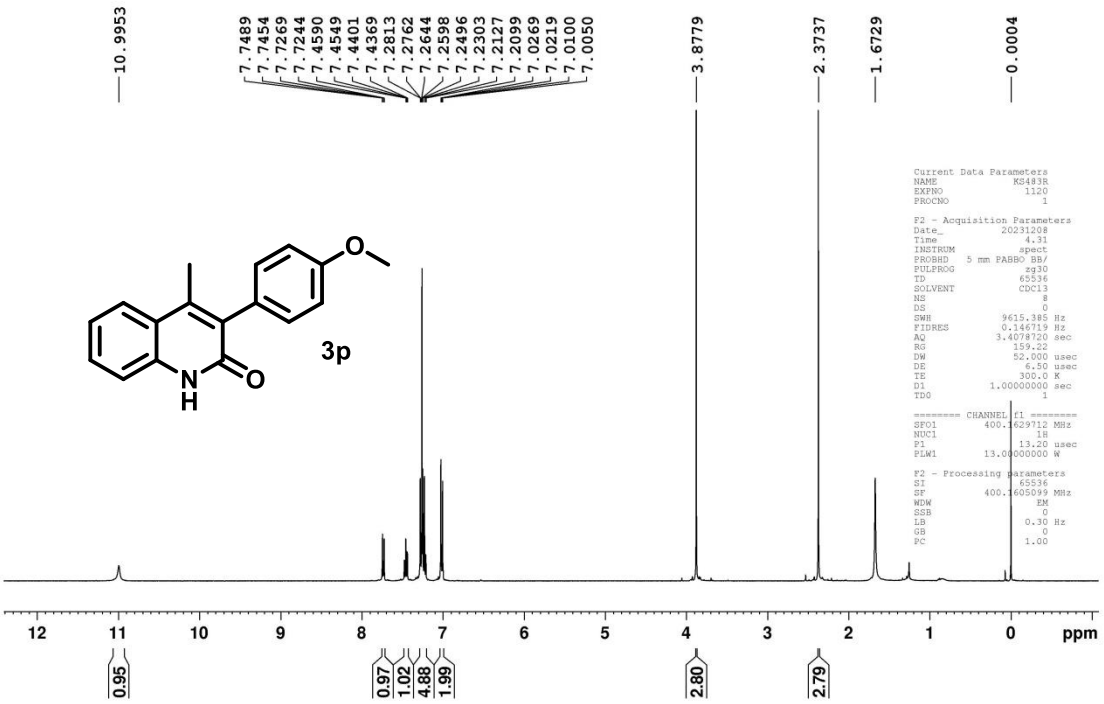
F2 - Processing parameters
SI 32768
SF 125.8951513 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


11.475
7.760
7.755
7.746
7.731
7.728
7.631
7.623
7.617
7.601
7.595
7.587
7.513
7.509
7.486
7.481
7.462
7.457
7.272
7.260
7.248
7.239
7.233
7.224
7.218
7.211
7.203
2.358
1.670
Br
N
H
O
3n
Current Data Parameters
NAME SB2-121-4-Me
EXPNO 910
PROCNO 1
F2 - Acquisition Parameters
Date 20211103
Time 15.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 287
DW 80.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.00 usec
PL1 -1.00 dB
PL1W 15.02081871 W
SFO1 300.2598542 MHz
F2 - Processing parameters
SI 32768
SF 300.2580077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
1.09
2.16
1.14
5.21
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.09
2.16
1.14
5.21
3.12


162.85
145.33
137.47
134.97
132.27
131.61
131.13
130.52
125.14
122.79
121.99
120.90
116.29
77.47
77.16
76.84
17.07
Br
N
H
O
3n
Current Data Parameters
NAME SB2-121-4-Me
EXPNO 940
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211022
Time 8.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6304993 MHz
NUC1 13C
P1 9.90 usec
PLW1 53.00000000 W
======== CHANNEL f2 ========
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.27963999 W
PLW13 0.22651000 W
F2 - Processing parameters
SI 32768
SF 100.6204243 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.197
8.175
7.680
7.659
7.443
7.425
7.422
7.407
7.404
7.383
7.361
7.259
7.210
7.191
7.173
7.155
7.153
5.190
3.889
3.218
2.235
Current Data Parameters
NAME SB2-KS-736 4MeO-2OH
EXPNO 1030
PROCNO 1
F2 - Acquisition Parameters
Date 20220801
Time 14.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4078720 sec
RG 159.22
DW 52.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1629712 MHz
NUC1 1H
P1 13.20 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1621216 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CH3
NO2
N
H
O
3o
8.2 ppm
1.97
7.8 7.6 7.4 7.2 ppm
1.00 1.04 1.94 1.95
9 8 7 6 5 4 3 2 1 0 ppm
1.97 1.00 1.04 1.94 1.95 2.90


161.76
147.18
145.90
143.08
137.43
131.45
130.86
129.94
125.10
123.30
122.86
120.43
115.80
77.48
77.16
76.84
49.09
48.87
48.66
48.45
48.23
16.70
Current Data Parameters
NAME SB2-KS-736 4MeO-2OH
EXPNO 1060
PROCNO 1
F2 - Acquisition Parameters
Date 20220801
Time 12.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6304993 MHz
NUC1 13C
P1 9.90 usec
PLW1 53.00000000 W
======== CHANNEL f2 ========
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.27963999 W
PLW13 0.22651000 W
F2 - Processing parameters
SI 32768
SF 100.6208409 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CH3
NO2
N
H
O
3o
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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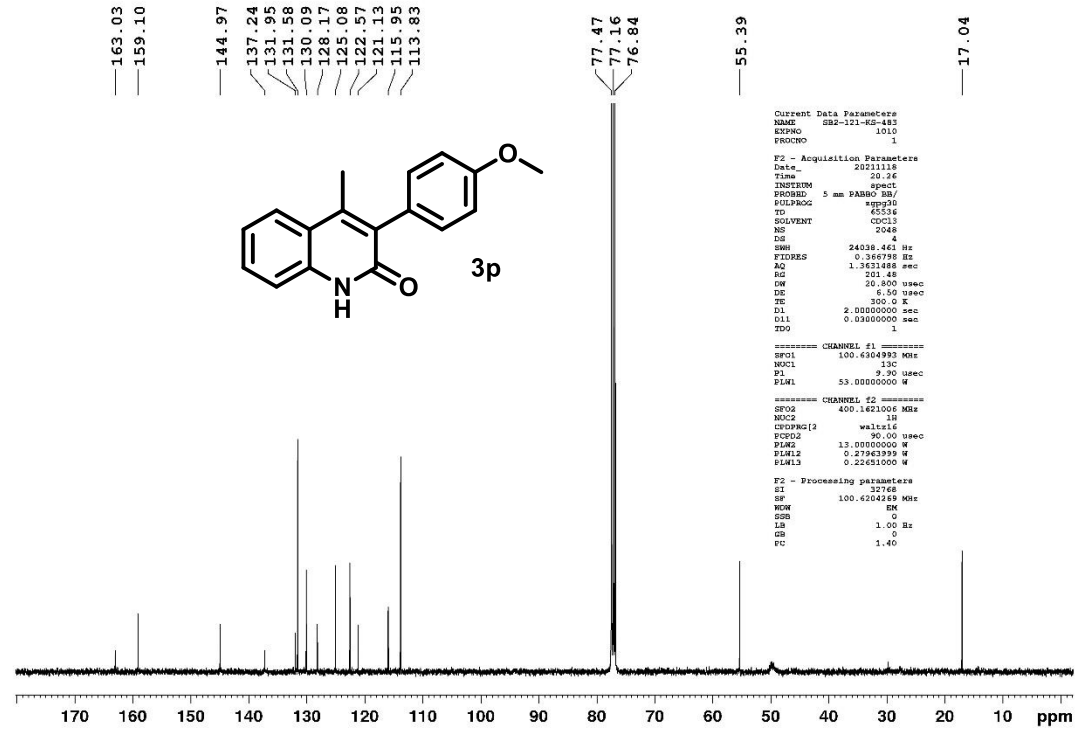
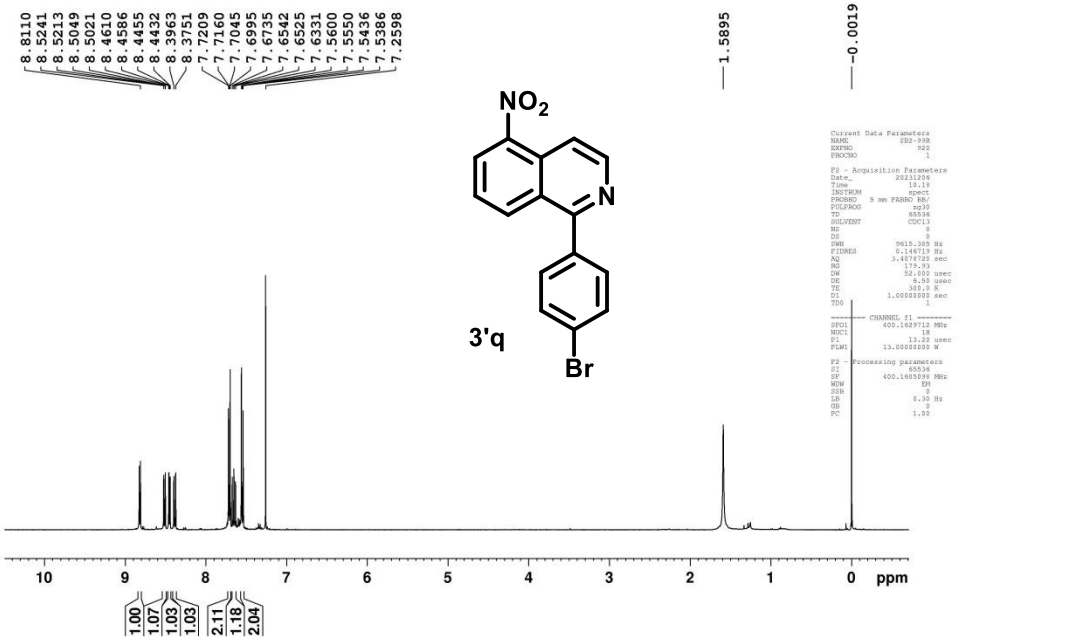
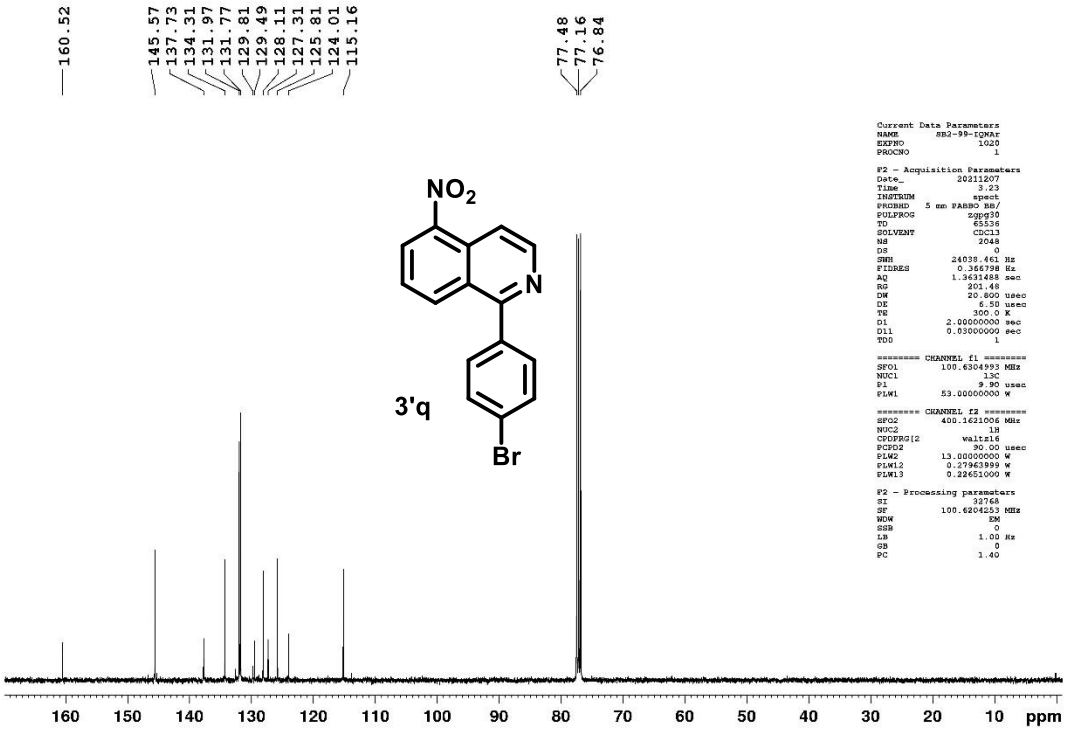
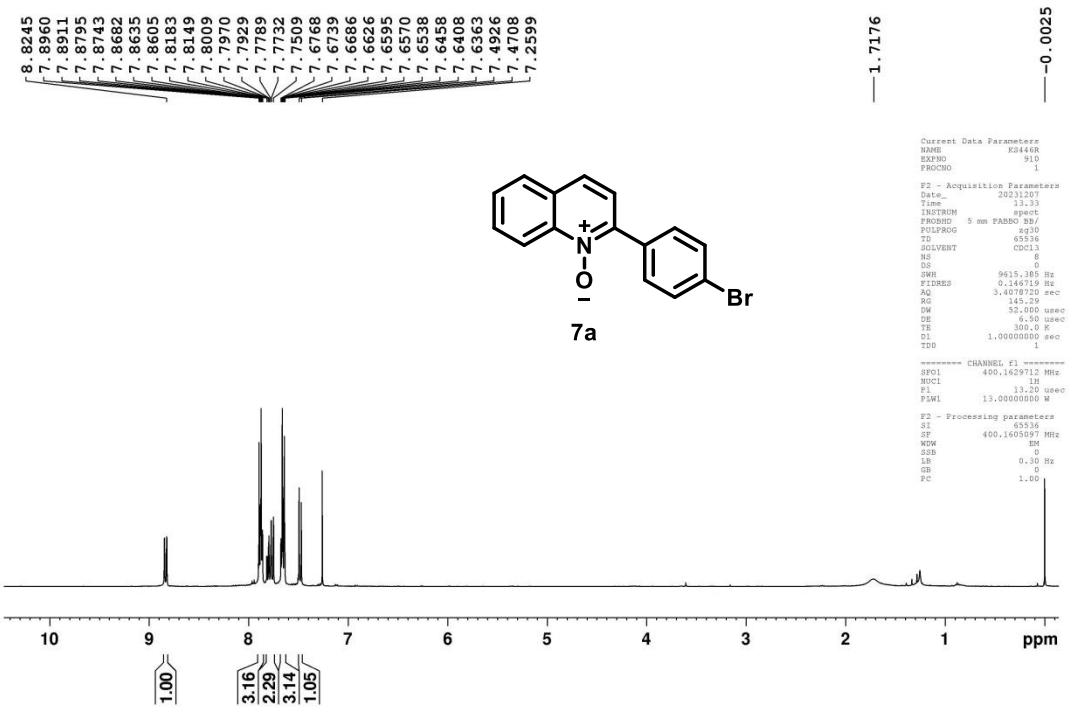
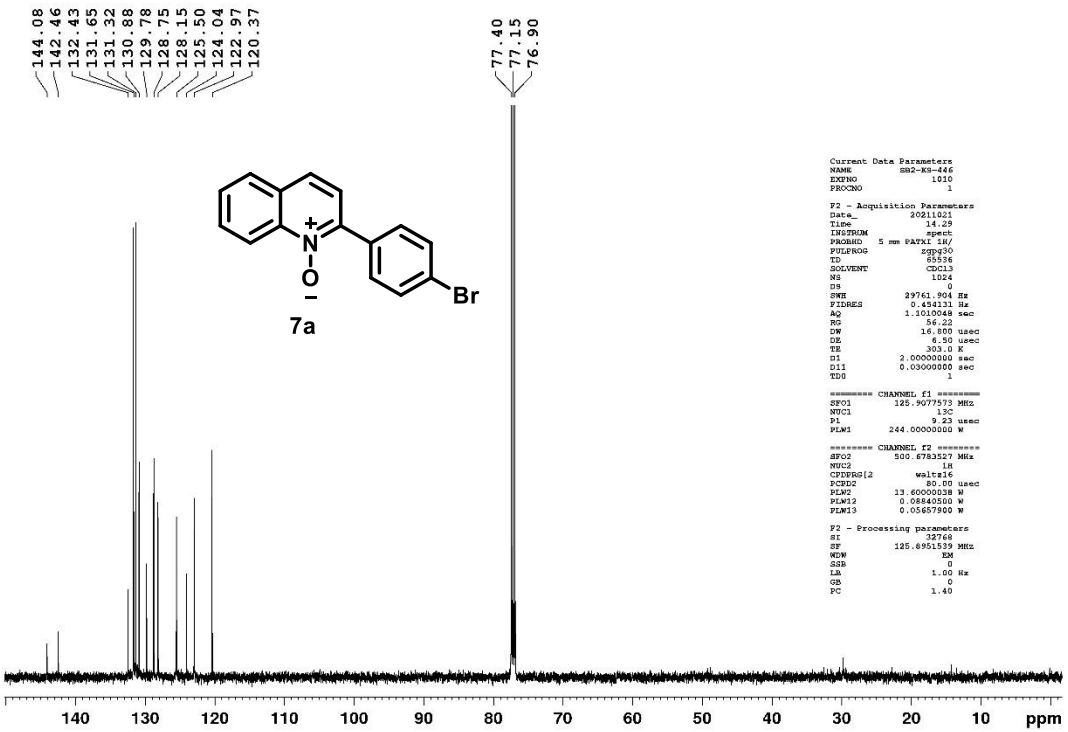
7.7489
7.7454
7.7269
7.7244
7.4590
7.4549
7.4401
7.4369
7.2813
7.2762
7.2644
7.2598
7.2496
7.2303
7.2127
7.2099
7.0269
7.0219
7.0100
7.0050
3.8779
2.3737
1.6729
0.0004
3p
0.95
0.97
1.02
4.88
1.99
2.80
2.79
ppm

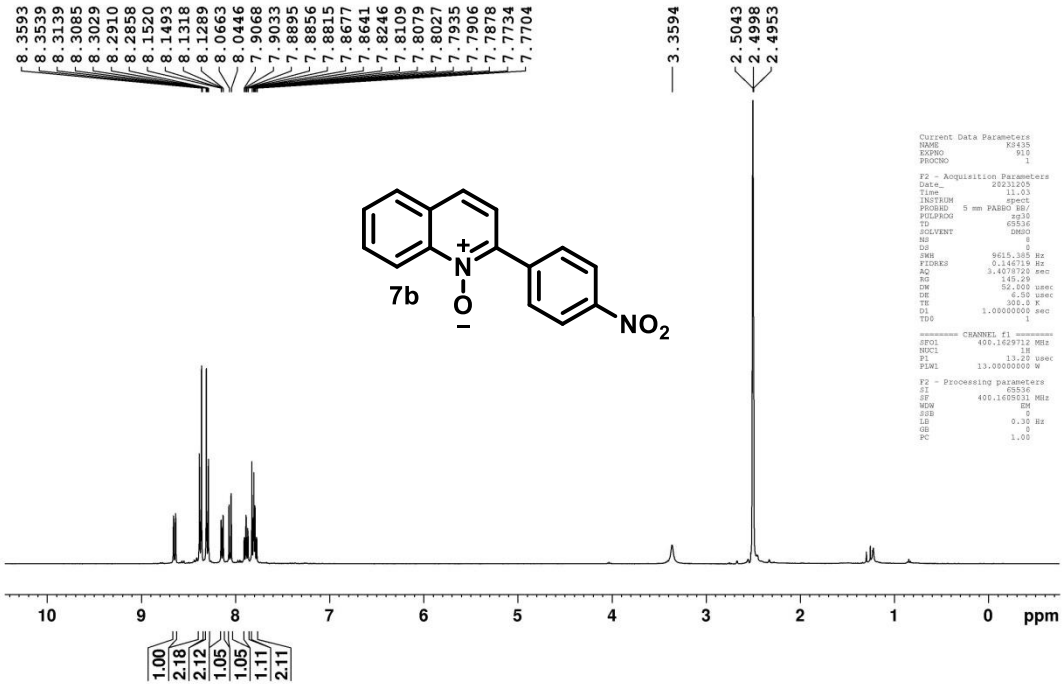

163.03
159.10
144.97
137.24
131.95
131.58
130.09
128.17
125.08
122.57
121.13
115.95
113.83
77.47
77.16
76.84
55.39
17.04
3p
ppm

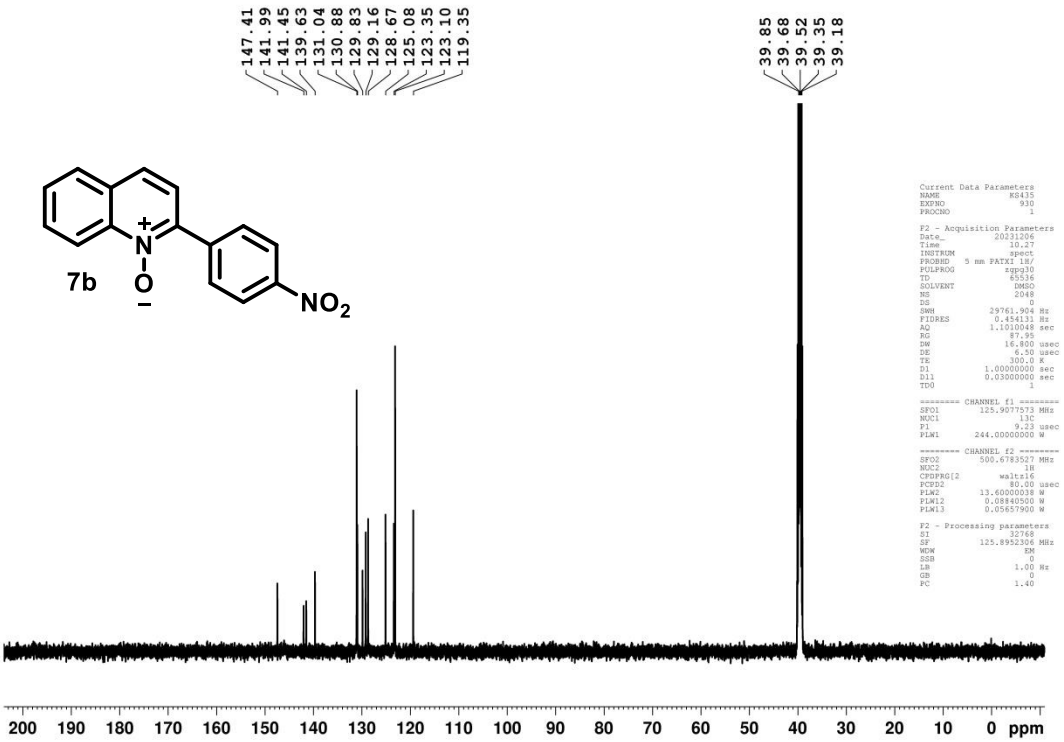

8.8110
8.5241
8.5213
8.5049
8.5021
8.4610
8.4586
8.4455
8.4432
8.3963
8.3751
7.7209
7.7160
7.7045
7.6995
7.6735
7.6542
7.6525
7.6331
7.5600
7.5550
7.5436
7.5386
7.2598
1.5895
0.0019
NO2
N
Br
3'q
1.00
1.07
1.03
1.03
2.11
1.18
2.04
10
9
8
7
6
5
4
3
2
1
0
ppm

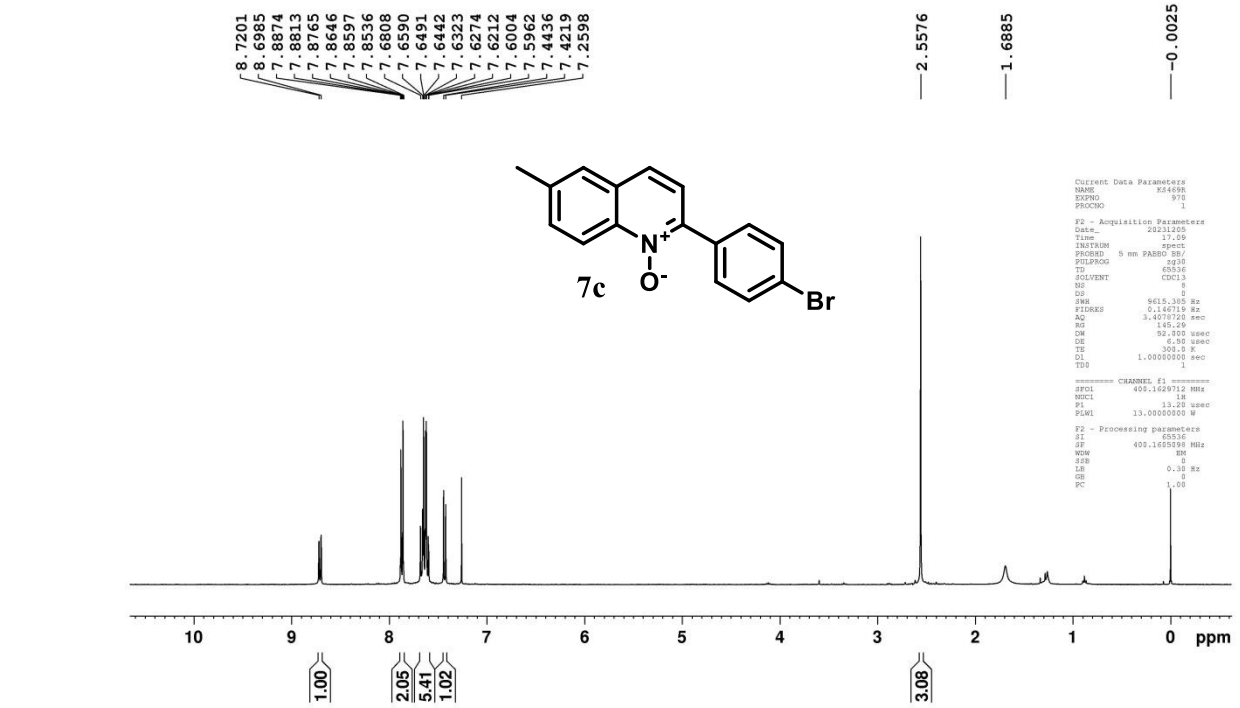

160.52
145.57
137.73
134.31
131.97
131.77
129.81
129.49
128.11
127.31
125.81
124.01
115.16
77.48
77.16
76.84
NO2
N
Br
3'q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.8245
7.8960
7.8911
7.8795
7.8743
7.8682
7.8635
7.8605
7.8183
7.8149
7.8009
7.7970
7.7929
7.7789
7.7732
7.7509
7.6768
7.6739
7.6686
7.6626
7.6595
7.6570
7.6538
7.6458
7.6408
7.6363
7.4926
7.4708
7.2599
1.7176
0.0025
Br
7a
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.16
2.29
3.14
1.05


144.08
142.46
132.43
131.65
131.32
130.88
129.78
128.75
128.15
125.50
124.04
122.97
120.37
77.40
77.15
76.90
Br
7a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.3593
8.3539
8.3139
8.3085
8.3029
8.2910
8.2858
8.1520
8.1493
8.1318
8.1289
8.0663
8.0446
7.9068
7.9033
7.8895
7.8856
7.8815
7.8677
7.8641
7.8246
7.8109
7.8079
7.8027
7.7935
7.7906
7.7878
7.7734
7.7704
3.3594
2.5043
2.4998
2.4953
7b
NO2
1.00
2.18
2.12
1.05
1.05
1.11
2.11
10
9
8
7
6
5
4
3
2
1
0
ppm


147.41
141.99
141.45
139.63
131.04
130.88
129.83
129.16
128.67
125.08
123.35
123.10
119.35
39.85
39.68
39.52
39.35
39.18
7b
NO2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.8765
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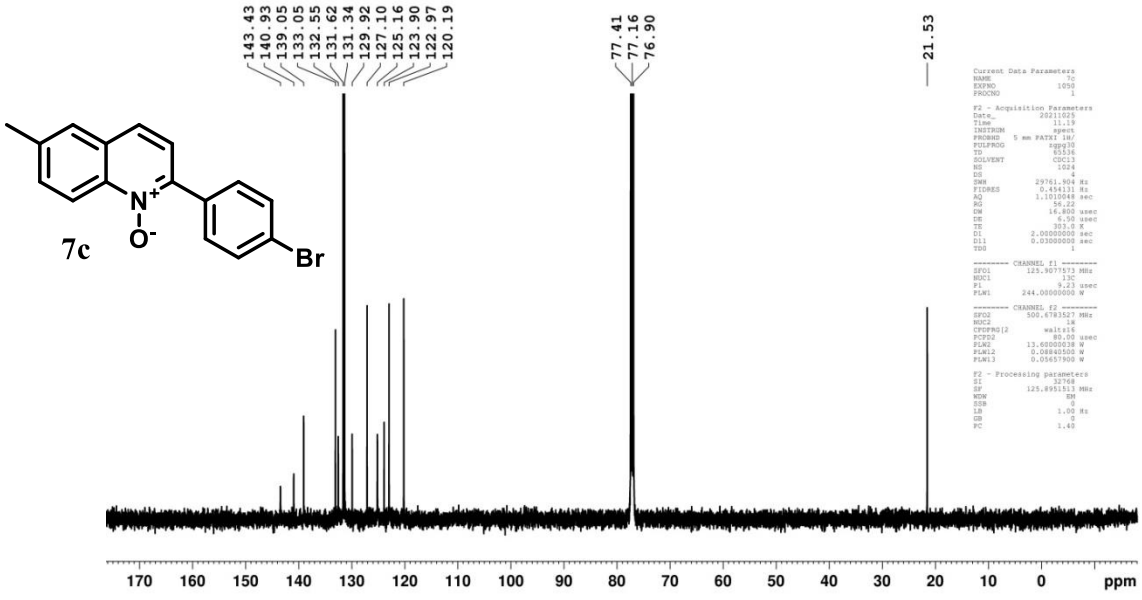
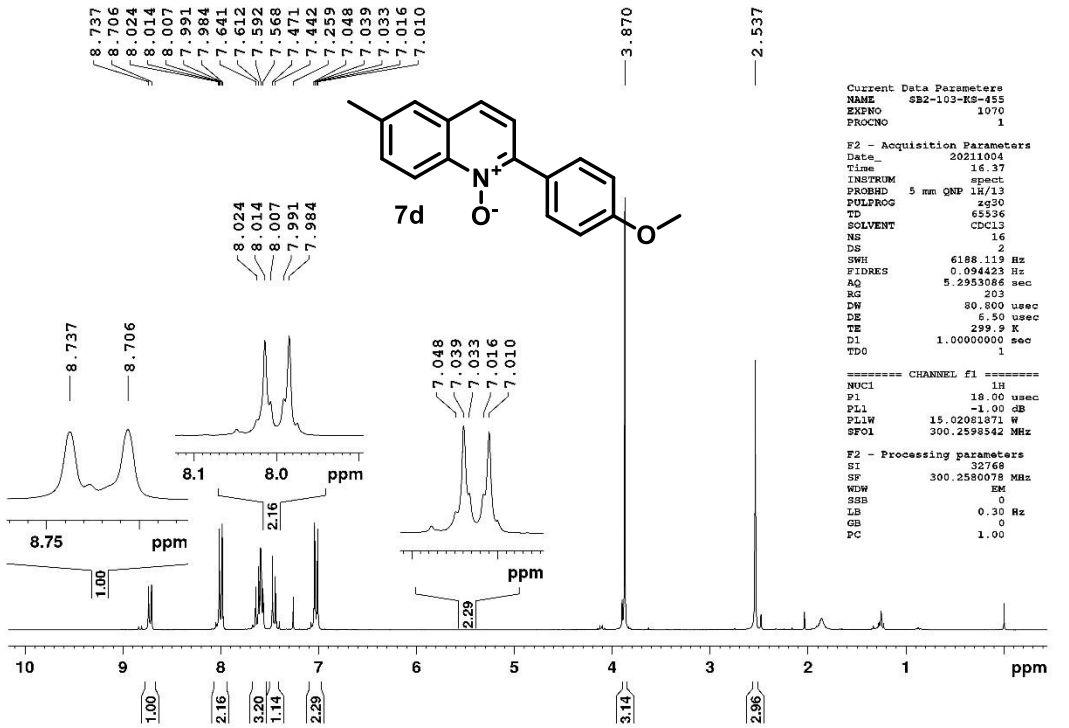
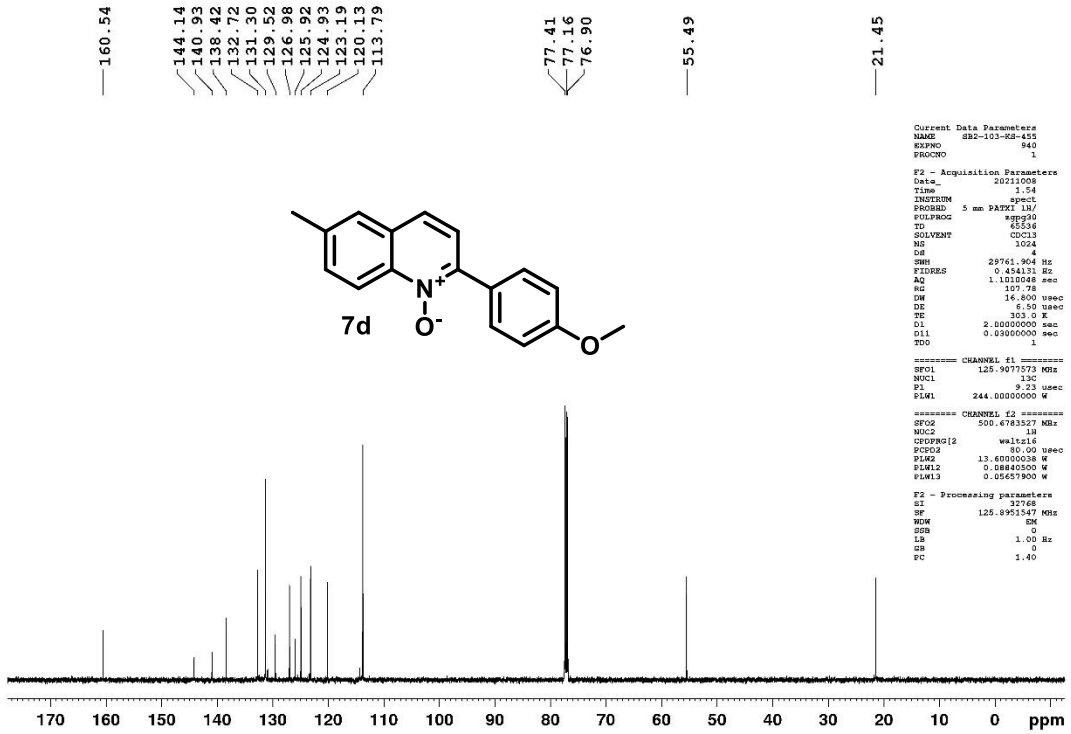
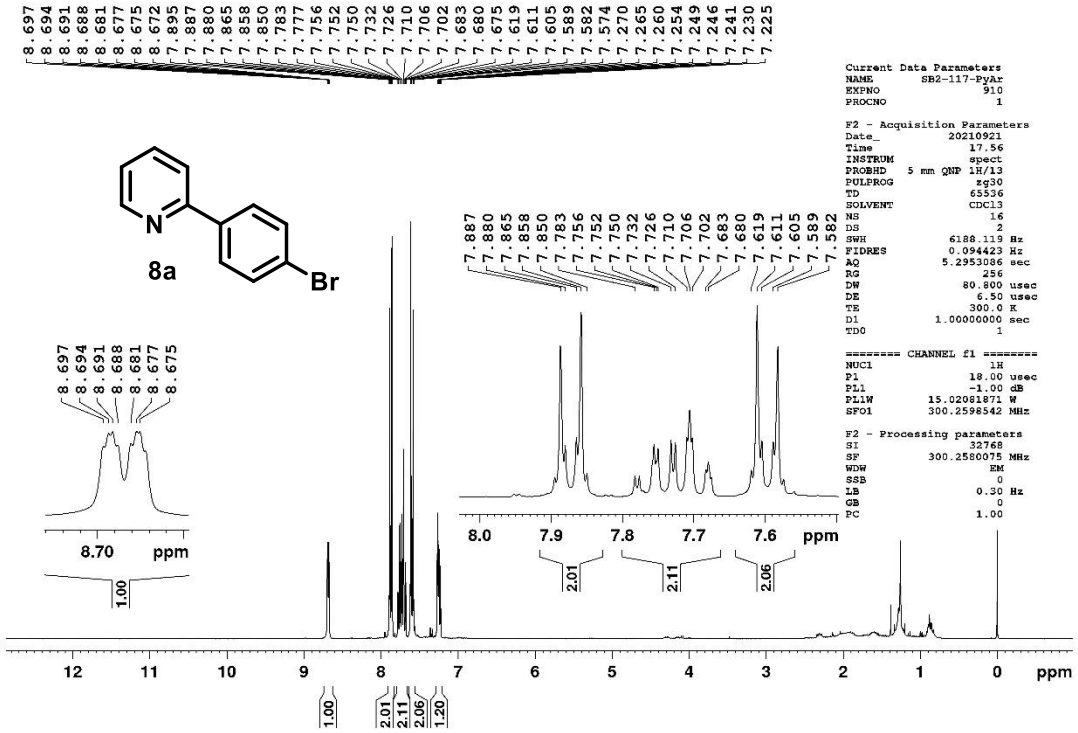
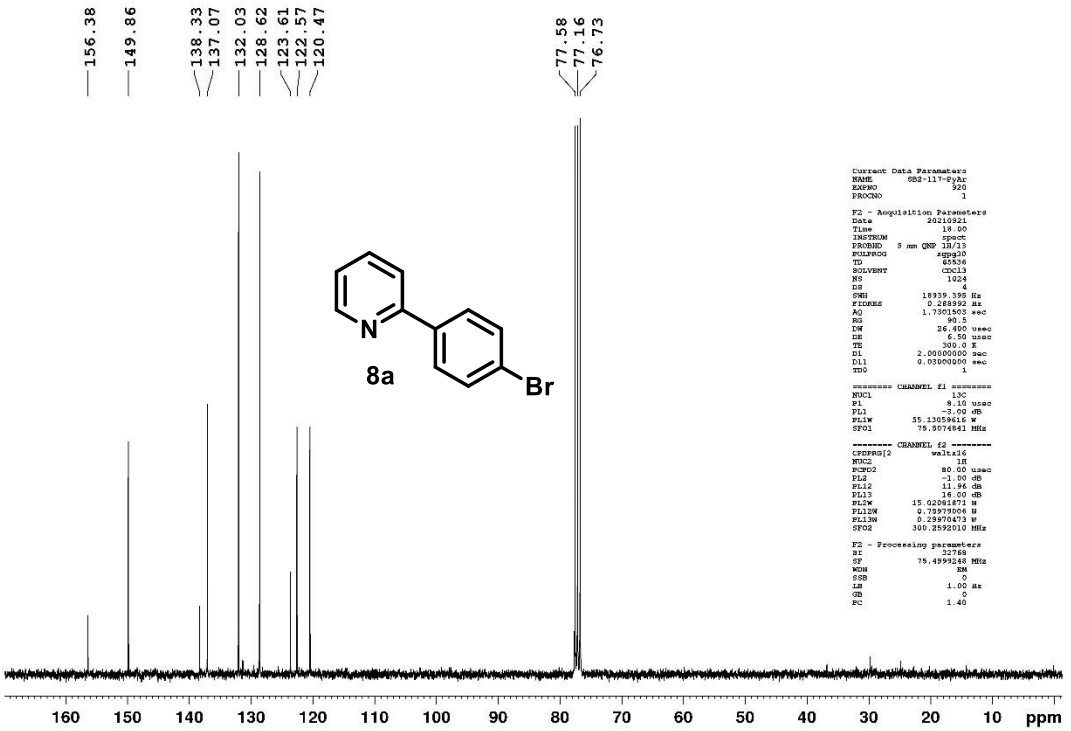
7.8597
7.8536
7.6808
7.6590
7.6491
7.6442
7.6323
7.6274
7.6212
7.6004
7.5962
7.4436
7.4219
7.2598
2.5576
1.6885
-0.0025
7c
Br
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.05
5.41
1.02
3.08

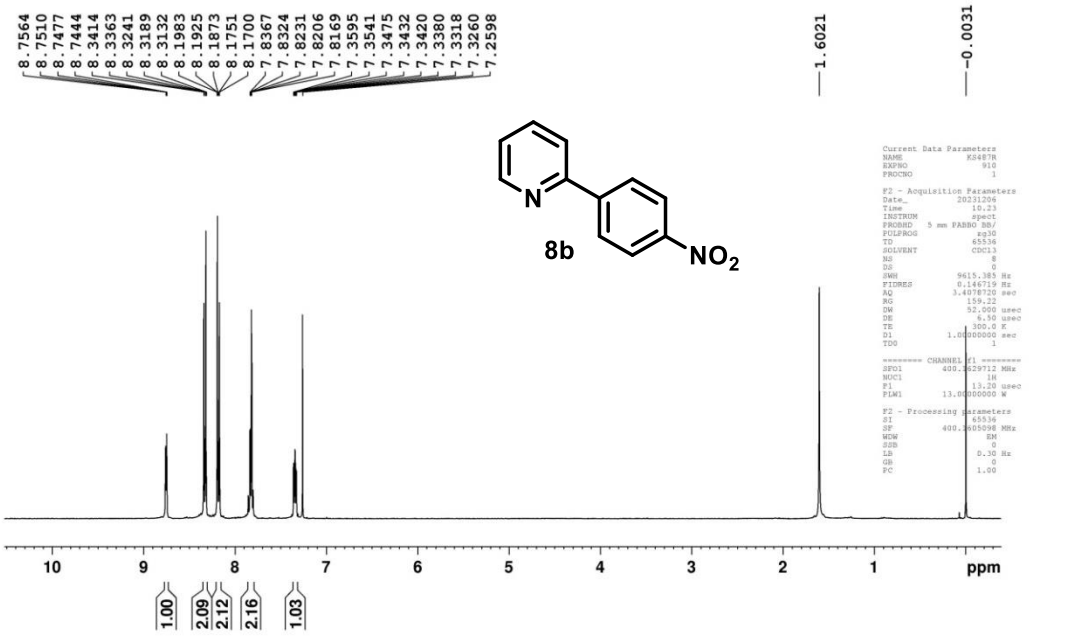

143.43
140.93
139.05
133.05
132.55
131.62
131.34
129.92
127.10
125.16
123.90
122.97
120.19
77.41
77.16
76.90
21.53
7c
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.737
8.706
8.024
8.014
8.007
7.991
7.984
7.641
7.612
7.592
7.568
7.471
7.442
7.259
7.048
7.039
7.033
7.016
7.010
3.870
2.537
7d
Current Data Parameters
NAME SB2-103-KS-455
EXPNO 1070
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211004
Time 16.37
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.00 usec
PL1 -1.00 dB
PL1W 15.02081871 W
SFO1 300.2598542 MHz
F2 - Processing parameters
SI 32768
SF 300.2580078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.75
ppm
8.1
8.0
ppm
ppm
1.00
2.16
2.29
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.16
3.20
1.14
2.29
3.14
2.96


160.54
144.14
140.93
138.42
132.72
131.30
129.52
126.98
125.92
124.93
123.19
120.13
113.79
77.41
77.16
76.90
55.49
21.45
7d
Current Data Parameters
NAME SB2-103-KS-455
EXPNO 940
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211008
Time 1.54
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 107.78
DW 16.800 usec
DE 6.50 usec
TE 303.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PL1 244.00000000 W
======== CHANNEL f2 ========
SFO2 500.6783527 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PL2 13.60000038 W
PL12 0.08840500 W
PL13 0.05657900 W
F2 - Processing parameters
SI 32768
SF 125.8951547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8a
Br
Current Data Parameters
NAME SB2-117-PyAr
EXPNO 910
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210921
Time 17.56
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 256
DW 80.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.00 usec
PL1 -1.00 dB
PL1W 15.02081871 W
SFO1 300.2598542 MHz
F2 - Processing parameters
SI 32768
SF 300.2580075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.70 ppm
8.0 7.9 7.8 7.7 7.6 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm


8a
Br
Current Data Parameters
NAME SB2-117-PyAr
EXPNO 920
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210921
Time 18.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18939.395 Hz
FIDRES 0.288992 Hz
AQ 1.7301503 sec
RG 90.5
DW 26.400 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 -3.00 dB
PL1W 55.13059616 W
SFO1 75.5074841 MHz
-------- CHANNEL f2 --------
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 11.96 dB
PL13 16.00 dB
PL1W 15.02081871 W
PL12W 0.75979006 W
PL13W 0.29970473 W
SFO2 300.2592010 MHz
F2 - Processing parameters
SI 32768
SF 75.4992248 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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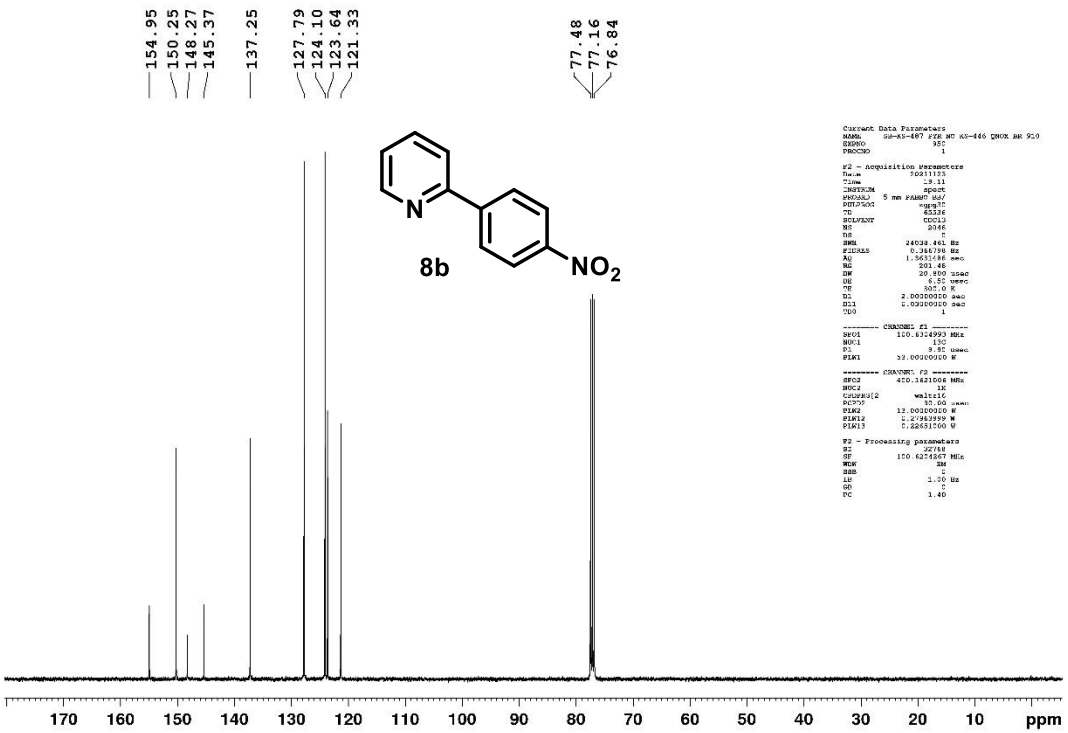
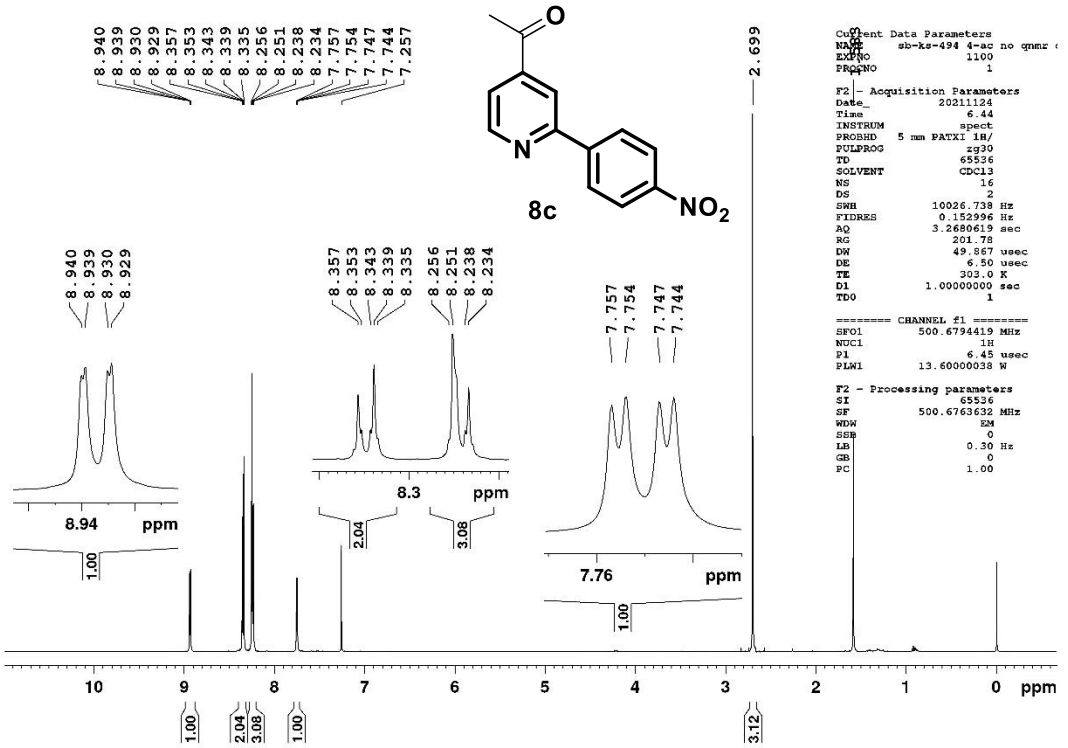
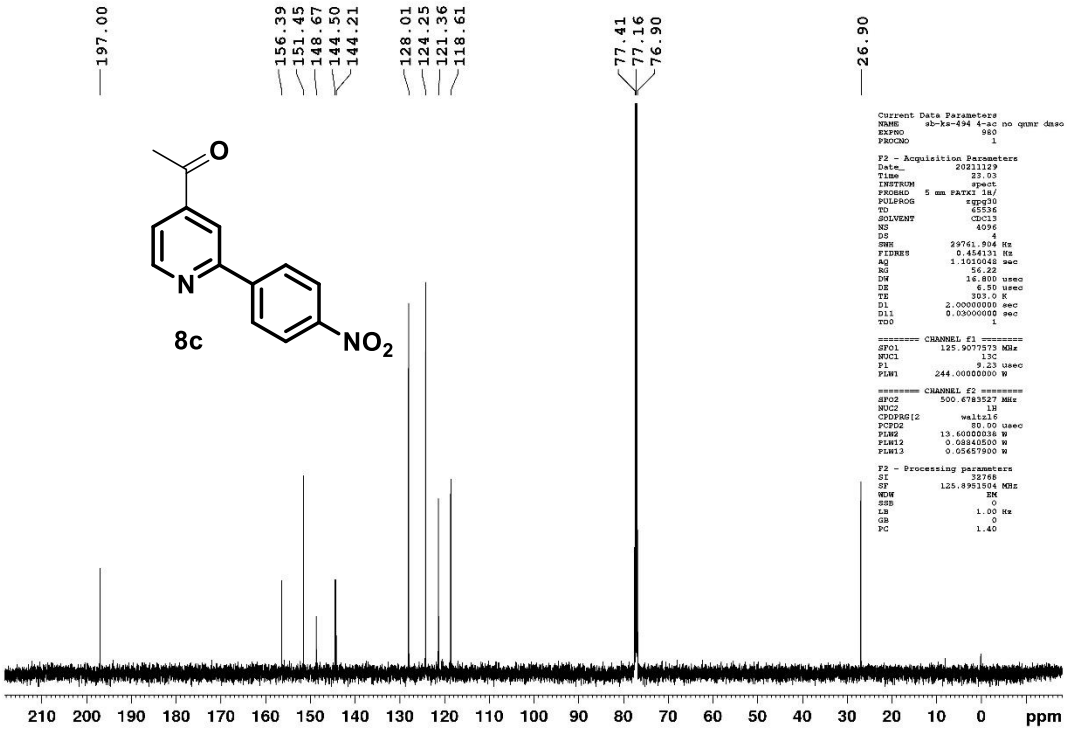
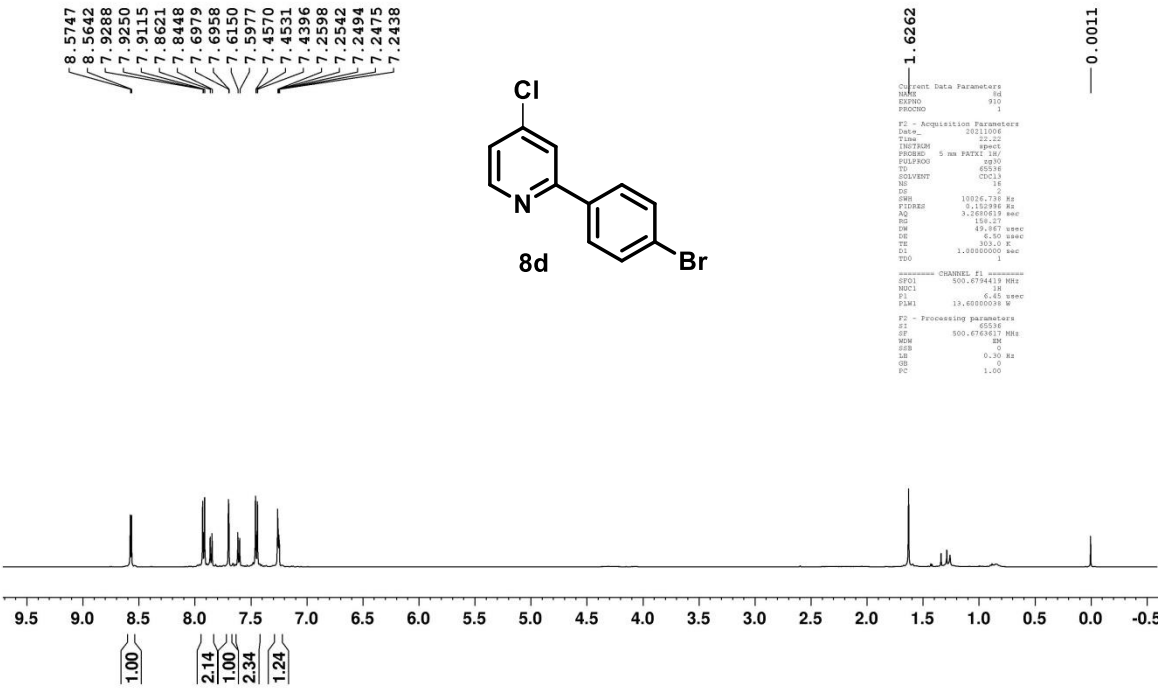
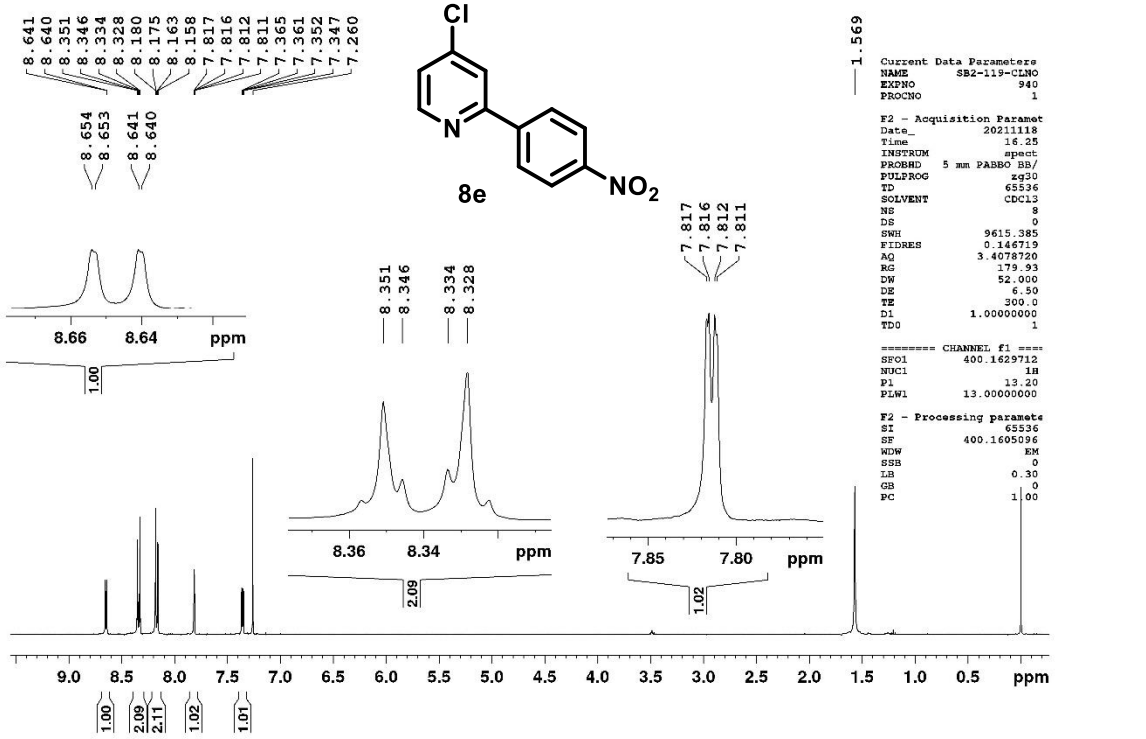
8.7510
8.7477
8.7444
8.3414
8.3363
8.3241
8.3189
8.3132
8.1983
8.1925
8.1873
8.1751
8.1700
7.8367
7.8324
7.8231
7.8206
7.8169
7.3595
7.3541
7.3475
7.3432
7.3420
7.3380
7.3318
7.3260
7.2598
1.6021
0.0031
8b
NO2
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.09
2.12
2.16
1.03

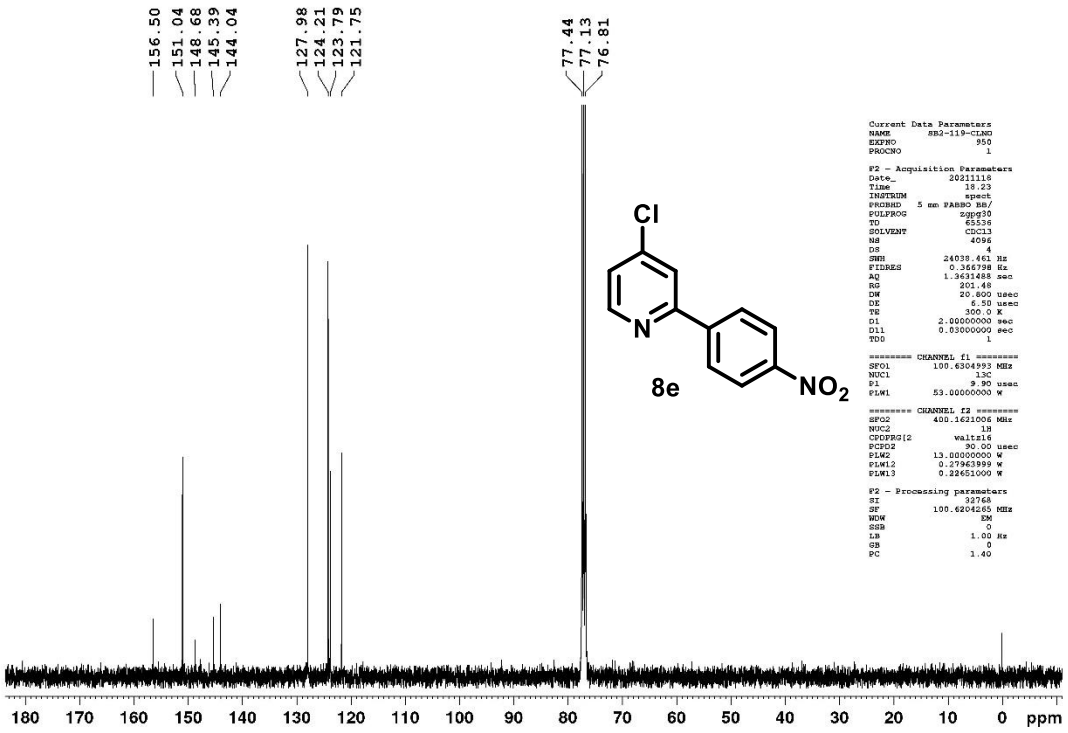

154.95
150.25
148.27
145.37
137.25
127.79
124.10
123.64
121.33
77.48
77.16
76.84
8b
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

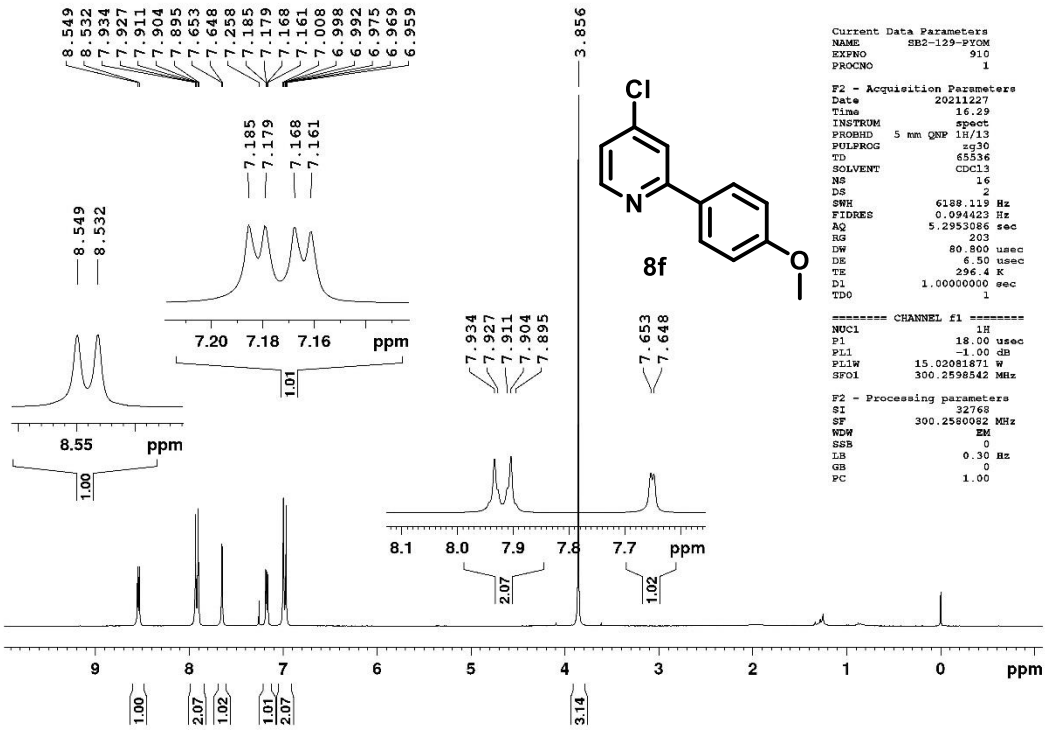

8.940
8.939
8.930
8.929
8.357
8.353
8.343
8.339
8.335
8.256
8.251
8.238
8.234
7.757
7.754
7.747
7.744
7.257
2.699
8c
NO2
8.94 ppm
8.3 ppm
7.76 ppm
1.00
2.04
3.08
3.12
10 9 8 7 6 5 4 3 2 1 0 ppm

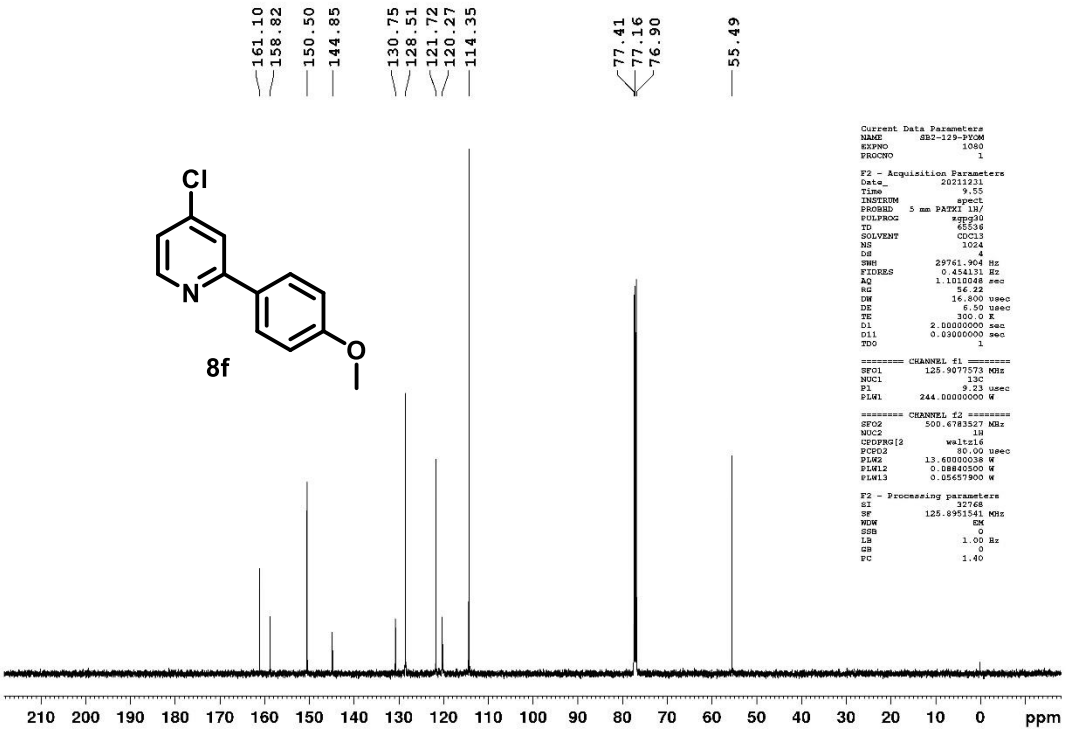

197.00
156.39
151.45
148.67
144.50
144.21
128.01
124.25
121.36
118.61
77.41
77.16
76.90
26.90
8c
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.5747
8.5642
7.9288
7.9250
7.9115
7.8621
7.8448
7.6979
7.6958
7.6150
7.5977
7.4570
7.4531
7.4396
7.2598
7.2542
7.2494
7.2475
7.2438
Cl
N
Br
8d
1.6262
0.0011
1.00
2.14
1.00
2.34
1.24


8.641
8.640
8.351
8.346
8.334
8.328
8.180
8.175
8.163
8.158
7.817
7.816
7.812
7.811
7.365
7.361
7.352
7.347
7.260
Cl
N
NO2
8e
1.569
8.654
8.653
8.641
8.640
8.66
8.64
ppm
1.00
8.351
8.346
8.334
8.328
8.36
8.34
ppm
2.09
7.817
7.816
7.812
7.811
7.85
7.80
ppm
1.02
1.00
2.09
2.11
1.02
1.01


156.50
151.04
148.68
145.39
144.04
127.98
124.21
123.79
121.75
77.44
77.13
76.81
Cl
N
NO2
8e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Current Data Parameters
NAME SB2-119-CLNO
EXPNO 950
PROCNO 1
F2 - Acquisition Parameters
Date_ 20211118
Time 18.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 201.48
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6304993 MHz
NUC1 13C
P1 9.90 usec
PLW1 53.00000000 W
======== CHANNEL f2 ========
SFO2 400.1621006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.27963989 W
PLW13 0.22651000 W
F2 - Processing parameters
SI 32768
SF 100.6204265 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


8.549
8.532
7.934
7.927
7.911
7.904
7.895
7.653
7.648
7.258
7.185
7.179
7.168
7.161
7.008
6.998
6.992
6.975
6.969
6.959
3.856
Cl
N
O
8f
7.20 7.18 7.16 ppm
1.01
8.55 ppm
1.00
8.1 8.0 7.9 7.8 7.7 ppm
2.07
1.02
9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.07
1.02
1.01
2.07
3.14
Current Data Parameters
NAME SB2-129-PYOM
EXPNO 910
PROCNO 1
F2 - Acquisition Parameters
Date 20211227
Time 16.29
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.00 usec
PL1 -1.00 dB
PL1W 15.02081871 W
SFO1 300.2598542 MHz
F2 - Processing parameters
SI 32768
SF 300.2580082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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