# Electronic Supplementary Information

## Metal-free regioselective C-3 nitration of quinoline *N*-oxides with *tert*-butyl nitrite

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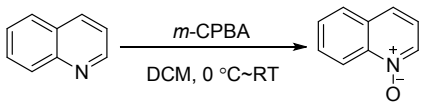
**Electronic Supplementary Information Contents:**

## General Information:

All reagents purchased from commercial sources were used as received. Quinoline derivatives were purchased from Adamas-beta. The silica gel for column chromatography was supplied as 300–400 meshes. The $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for $^{1}H$ and 77.0 ppm for $^{13}C$ in $CDCl_3$, 2.50 ppm for $^{1}H$ and 39.5 ppm for $^{13}C$ in $d_6$-DMSO). The HRMS spectra were recorded on a Bruker MicroTOF QII spectrometer.

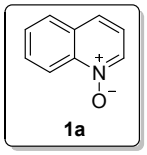
## General Procedure for Quinoline *N*-Oxide Derivatives:




**1a**

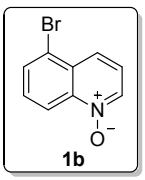
Under vigorous magnetic stirring, 3-chloroperbenzoic acid (*m*-CPBA) (345 mg, 2 mmol) in $CH_2Cl_2$ (10 mL) was dropped into solution of quinoline derivatives (2 mmol) in $CH_2Cl_2$ (10 mL) cooled to 0 °C. After the completion of this course, the reaction mixture was allowed up to room temperature and stirred overnight. An aqueous solution of saturated $NaHCO_3$ was added to the mixture to neutralize residual *m*-CPBA. The resulting mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The organic phase were combined and washed with saturated NaCl solution (3 × 5 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered and evaporated under reduced pressure to give crude products, which were purified by column chromatography (silica gel 300–400 mesh, EA: MeOH (8:1) as eluent). The products were identified by $^{1}H$ NMR and $^{13}C$ NMR spectra and compared to the previous literatures.
Following the above procedure, the following Quinoline *N*-Oxide Derivatives were prepared:

## Characterization Data of the Quinoline *N*-Oxide Derivatives:



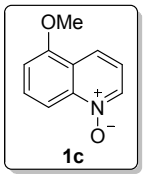

**1a**

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.72 (d, $J$ = 8.8 Hz, 1 H), 8.52 (dd, $J$ = 6.0, 0.6 Hz, 1 H), 7.85 (d, $J$ = 8.1 Hz, 1 H), 7.79–7.70 (m, 2 H), 7.67–7.60 (m, 1 H), 7.28 (dd, $J$ = 8.5, 6.2 Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 141.5, 135.6, 130.46, 130.45, 128.7, 128.1, 126.1, 120.9, 119.7.



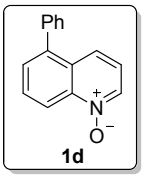

**1b**

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.72 (d, $J$ = 8.9 Hz, 1 H), 8.53 (d, $J$ = 6.0 Hz, 1 H), 8.06 (d, $J$ = 8.8 Hz, 1 H), 7.89 (dd, $J$ = 7.5, 0.9 Hz, 1 H), 7.57 (dd, $J$ = 8.8, 7.6 Hz, 1 H), 7.37 (dd, $J$ = 8.8, 6.1 Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 142.6, 135.8, 132.7, 130.3, 129.9, 125.1, 122.3, 121.7, 119.7.

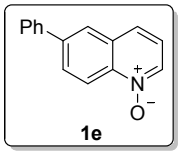



**1c**

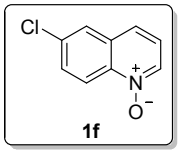
$^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 8.58 (d, $J$ = 6.0 Hz, 1 H), 8.07 (d, $J$ = 8.8 Hz, 1 H), 8.01 (d, $J$ = 8.6 Hz, 1 H), 7.72 (t, $J$ = 8.3 Hz, 1 H), 7.42 (dd, $J$ = 8.6, 6.1 Hz, 1 H), 7.19 (d, $J$ = 7.8 Hz, 1 H), 4.00 (s, 3 H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 155.3, 141.8, 135.7, 130.6, 122.6, 120.9, 119.0, 110.6, 107.3, 56.4.



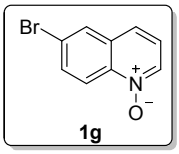

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.8 Hz, 1 H), 8.55 (dd, *J* = 6.0, 0.8 Hz, 1 H), 7.83–7.75 (m, 2 H), 7.59 (dd, *J* = 7.1, 1.1 Hz, 1 H), 7.54–7.41 (m, 5 H), 7.23 (dd, *J* = 8.8, 6.0 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.1, 138.6, 135.3, 129.9, 129.8, 129.5, 129.2, 128.6, 128.1, 124.5, 120.6, 119.1.



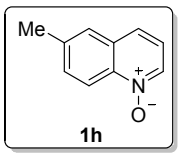

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.8 Hz, 1 H), 8.53 (d, *J* = 5.7 Hz, 1 H), 8.05–7.98 (m, 2 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.72–7.65 (m, 2 H), 7.52–7.48 (m, 2 H), 7.45–7.41 (m, 1 H), 7.31 (dd, *J* = 8.4, 6.1 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.8, 139.2, 135.5, 130.8, 130.1, 129.1, 128.3, 127.4, 126.2, 125.6, 121.3, 120.3.



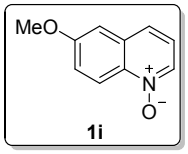

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.3 Hz, 1 H), 8.45 (d, *J* = 6.0 Hz, 1 H), 7.79 (d, *J* = 2.1 Hz, 1 H), 7.64–7.57 (m, 2 H), 7.28 (dd, *J* = 8.4, 6.2 Hz, 1 H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.9, 135.5, 134.9, 131.1, 130.9, 126.6, 124.5, 122.1, 121.5.



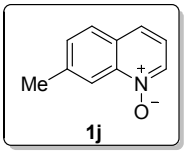

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 9.3 Hz, 1 H), 8.47 (d, *J* = 5.6 Hz, 1 H), 7.97 (d, *J* = 2.0 Hz, 1 H), 7.75 (dd, *J* = 9.3, 2.0 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.27 (dd, *J* = 8.5, 6.1 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.2, 135.7, 133.6, 131.4, 130.0, 124.5, 123.1, 122.1, 121.6.



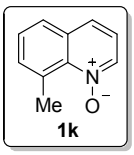

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.9 Hz, 1 H), 8.44 (d, *J* = 5.9 Hz, 1 H), 7.66–7.58 (m, 2 H), 7.55 (dd, *J* = 8.9, 1.6 Hz, 1 H), 7.22 (dd, *J* = 8.4, 6.0 Hz, 1 H), 2.48 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.0, 134.9, 132.5, 130.6, 126.9, 125.4, 120.9, 119.5, 21.4.



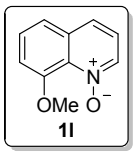

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 9.5 Hz, 1 H), 8.34 (dd, *J* = 6.0, 0.7 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 1 H), 7.32 (dd, *J* = 9.5, 2.7 Hz, 1 H), 7.19 (dd, *J* = 8.5, 6.0 Hz, 1 H), 7.05 (d, *J* = 2.7 Hz, 1 H), 3.88 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.1, 133.7, 131.9, 124.8, 122.6, 121.4, 121.3, 105.6, 55.6.




$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.55–8.52 (m, 2 H), 7.75–7.70 (m, 2 H), 7.45 (dd, *J* = 8.3, 1.4 Hz, 1 H), 7.22 (dd, *J* = 8.4, 6.1 Hz, 1 H), 2.57 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.3, 135.9, 130.9, 128.6, 127.8, 126.4, 119.9, 118.6, 22.0.

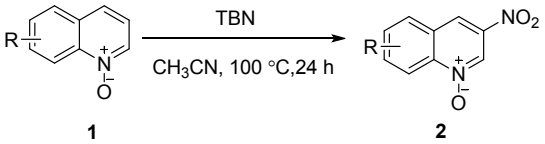



$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 6.0, 0.6 Hz, 1 H), 7.57–7.54 (m, 2 H), 7.38–7.30 (m, 2 H), 7.10 (dd, *J* = 8.4, 6.1 Hz, 1 H), 3.12 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.1, 133.4, 133.2, 132.3, 127.9, 126.7, 126.2, 120.5, 24.7.



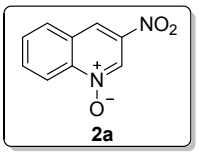

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 6.1, 1.0 Hz, 1 H), 7.62–7.56 (m, 1 H), 7.47-7.43 (m, 1 H), 7.35 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.17 (dd, *J* = 8.4, 6.1 Hz, 1 H), 7.08–7.00 (m, 1 H), 4.00 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 138.0, 134.2, 133.6, 128.6, 125.5, 121.2, 120.5, 110.9, 57.0.

## General Procedure for 3-Nitroquinoline *N*-Oxide Derivatives:

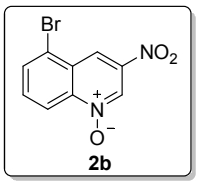



To a 15 mL sealed tube with a stir bar was added 0.3 mmol of quinoline *N*-Oxide **1**, 3 mL of $CH_3CN$ and TBN (1.05 mmol, 3.5 equiv.), then the reaction mixture was stirred at 100 ºC for 24 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **2**.

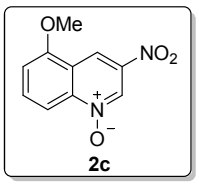
## Characterization Data of the 3-Nitroquinoline *N*-Oxide Derivatives Products:



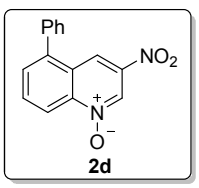

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 1.9 Hz, 1 H), 8.78 (d, *J* = 8.8 Hz, 1 H), 8.60 (d, *J* = 1.3 Hz, 1 H), 8.11 (d, *J* = 8.1 Hz, 1 H), 7.98 (ddd, *J* = 8.6, 7.0, 1.3 Hz, 1 H), 7.89–7.78 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.9, 133.9, 130.8, 130.6, 129.9, 127.6, 120.8, 120.3; HRMS (ESI) Calcd for $C_9H_7N_2O_3$ [M+H] 191.0451, Found 191.0448.[1]



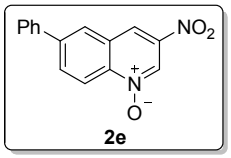

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 1.9 Hz, 1 H), 8.93 (d, *J* = 0.9 Hz, 1 H), 8.77 (d, *J* = 8.8 Hz, 1 H), 8.09 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.80 (dd, *J* = 8.8, 7.6 Hz, 1 H);$^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.5, 134.7, 133.7, 130.2, 127.8, 125.0, 120.2, 120.0; HRMS (ESI) Calcd for $C_9H_5BrN_2NaO_3$ [M+Na] 290.9383, Found 290.9376.[new compound]



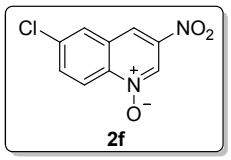

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.21 (m, 1 H), 8.69 (m, 1 H), 8.15–7.97 (m, 2 H), 7.42 (d, *J* = 7.7 Hz, 1 H), 4.09 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 157.2, 143.9, 141.2, 135.0, 130.1, 119.3, 115.1, 110.7, 109.6, 56.9; HRMS (ESI) Calcd for $C_{10}H_9N_2O_4$ [M+H] 221.0557, Found 221.0553. [new compound]



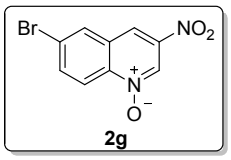

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.36 (d, *J* = 1.8 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.47 (s, 1 H), 7.22 (dd, *J* = 8.7, 7.4 Hz, 1 H), 6.99 (d, *J* = 7.1 Hz, 1 H), 6.77 – 6.65 (m, 5 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 143.8, 143.2, 142.0, 137.1, 133.6, 131.3, 130.0, 129. 5, 129.0, 128.8, 125.6, 118.7, 118.6; HRMS (ESI) Calcd for $C_{15}H_{10}N_2O_3Na$ [M+Na] 289.0584, Found 289.0583. [new compound]



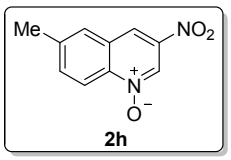

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.32 (d, $J$ = 1.9 Hz, 1 H), 8.12 (d, $J$ = 1.6 Hz, 1 H), 7.87 (d, $J$ = 1.9 Hz, 1 H), 7.76 (d, $J$ = 9.1 Hz, 1 H), 7.51 (dd, $J$ = 9.1, 2.0 Hz, 1 H), 7.03–6.96 (m, 2 H), 6.74-6.70 (m, 2 H), 6.64 (t, $J$ = 7.3 Hz, 1 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 142.4, 142.3, 141.9, 137.6, 132.9, 129.6, 129.3, 128.9, 128.5, 128.1, 127.3, 121.5, 119.9; HRMS (ESI) Calcd for $C_{15}H_{10}N_2O_3Na$ [M+Na] 289.0584, Found 289.0578. [new compound]



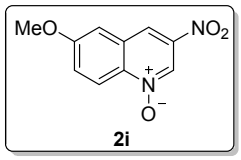

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, $J$ = 1.8 Hz, 1 H), 8.73 (d, $J$ = 9.3 Hz, 1 H), 8.49 (s, 1 H), 8.08 (d, $J$ = 2.1 Hz, 1 H), 7.89 (dd, $J$ = 9.3, 2.2 Hz, 1 H); $^{13}$C NMR (100 MHz, DMSO) δ 143.0, 141.8, 135.2, 134.0, 130.1, 129.8, 128.7, 121.5, 120.4; HRMS (ESI) Calcd for $C_9H_5ClN_2NaO_3$ [M+Na] 246.9880, Found 246.9881. [new compound]



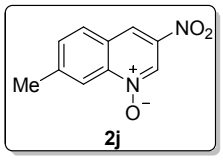

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.22 (d, $J$ = 1.6 Hz, 1 H), 8.91 (s, 1 H), 8.72 (d, $J$ = 1.7 Hz, 1 H), 8.47 (d, $J$ = 9.2 Hz, 1 H), 8.16 (dd, $J$ = 9.2, 1.9 Hz, 1 H); $^{13}$C NMR (100 MHz, DMSO) δ 142.9, 142.0, 136.7, 133.0, 130.2, 129.1, 123.9, 121.4, 120.3; HRMS (ESI) Calcd for $C_9H_5BrN_2NaO_3$ [M+Na] 290.9383, Found 290.9376. [new compound]



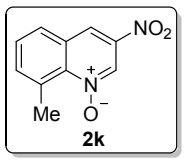

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, $J$ = 1.9 Hz, 1 H), 8.66 (d, $J$ = 8.9 Hz, 1 H), 8.51 (d, $J$ = 1.4 Hz, 1 H), 7.85 (s, 1 H), 7.79 (dd, $J$ = 8.9, 1.7 Hz, 1 H), 2.61 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.4, 142.0, 141.6, 136.1, 129.4, 129.3, 127.8, 120.4, 120.0, 21.5; HRMS (ESI) Calcd for $C_{10}H_9N_2O_3$ [M+H] 205.0612, Found 205.0608. [new compound]



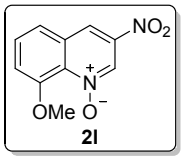

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.05 (d, $J$ = 2.0 Hz, 1 H), 8.83 (d, $J$ = 1.7 Hz, 1 H), 8.50 (d, $J$ = 9.5 Hz, 1 H), 7.88 (d, $J$ = 2.7 Hz, 1 H), 7.67 (dd, $J$ = 9.5, 2.8 Hz, 1 H), 3.95 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO) δ 160.1, 142.6, 138.5, 129.4, 127.8, 125.5, 120.8, 120.2, 109.6, 56.1; HRMS (ESI) Calcd for $C_{10}H_8N_2NaO_4$ [M+Na] 243.0376, Found 243.0365. [new compound]




$^1$H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, $J$ = 1.9 Hz, 1 H), 8.66 (d, $J$ = 8.9 Hz, 1 H), 8.51 (d, $J$ = 1.4 Hz, 1 H), 7.85 (s, 1 H), 7.79 (dd, $J$ = 8.9, 1.7 Hz, 1 H), 2.61 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.4, 142.0, 141.6, 136.1, 129.4, 129.3, 127.8, 120.4, 120.0, 21.5; HRMS (ESI) Calcd for $C_{10}H_9N_2O_3$ [M+H] 205.0608, Found 205.0602. [new compound]

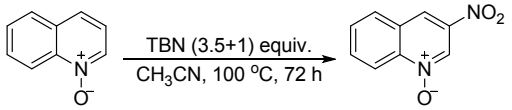



$^1$H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, $J$ = 1.8 Hz, 1 H), 8.45 (d, $J$ = 1.8 Hz, 1 H), 7.92–7.83 (m, 1 H), 7.61 (dd, $J$ = 7.9, 5.4 Hz, 2 H), 3.17 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.3, 136.9, 134.5, 131.0, 130.0, 129.7, 129.2, 121.0, 24.4; HRMS (ESI) Calcd for $C_{10}H_9N_2O_3$ [M+H] 205.0608, Found 205.0606. [new compound]



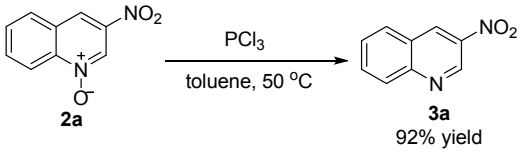

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 2.5 Hz, 1 H), 8.98 (d, *J* = 2.5 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.59 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.29–7.26 (m, 1 H), 4.13 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.5, 142.6, 141.6, 141.5, 132.0, 129.3, 127.3, 121.1, 111.4, 56.3; HRMS (ESI) Calcd for $C_{10}H_9N_2O_4$ [M+H] 221.0557, Found 221.0550. [new compound]

## Gram Scale Synthesis of 3-Nitroquinoline *N*-Oxide 2a:

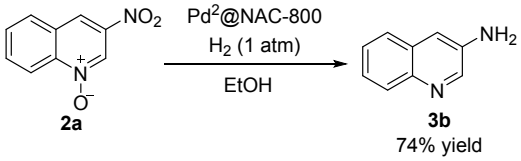



To a reaction kettle with a stir bar was added quinoline *N*-Oxide **1a** (10 mmol, 1.45 g), 30 mL of $CH_3CN$ and TBN (35 mmol, 3.5 equiv.). The reaction mixture was stirred at 100 ºC for 48 h, the quinoline *N*-Oxide **1a** did not react completely by TLC. Then additional TBN (10 mmol, 1 equiv.) was added to the reaction solution. The reaction mixture was stirred at 100 ºC for another 24 h until the starting material **1a** disappear, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **2a** (1.36g, 72% yield).

## General Procedure for Transformations of 3-Nitroquinoline *N*-Oxide



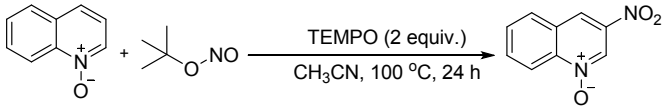

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3-nitroquinoline *N*-oxide **2a**, 3 mL of toluene, $PCl_3$ (0.6 mmol, 2 equiv.). The reaction mixture was stirred at 50 ºC for 2 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **3a**[2] (48 mg, 92% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.6 Hz, 1 H), 9.05 (d, *J* = 2.4 Hz, 1 H), 8.24 (d, *J* = 8.2 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.95 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1 H), 7.74 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.1, 144.0, 140.9, 133.4, 132.3, 129.8, 129.8, 128.8, 126.0; HRMS (ESI) Calcd for $C_9H_7N_2O_2$ [M+H] 175.0510, Found 175.0502.




To a 25 mL Schlenk tubes with a stir bar was added 0.3 mmol of 3-nitroquinoline *N*-oxide **2a**, 3 mL of EtOH, Pd@NAC-800 (80 mg). Then the tube was sealed and pressurized with 1.0 atm $H_2$ gas after it was vacuumed and flushed with $H_2$ three times. The reaction mixture was stirred at room temperature for 12 h, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **3b**[3] (32 mg, 74% yield). $^1$H NMR (400 MHz, $CDCl_3$) d 8.50 (d, *J* = 2.7

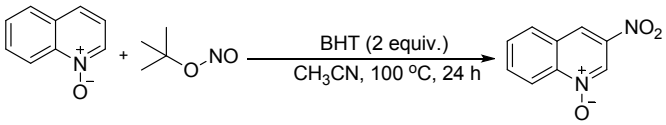
Hz, 1 H), 8.00–7.93 (m, 1 H), 7.59–7.56 (m, 1 H), 7.46–7.39 (m, 2 H), 7.21 (d, $J$ = 2.9 Hz, 1 H), 3.95 (s, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.7, 139.7, 129.1, 129.0, 126.9, 125.8, 125.6, 114.9; HRMS (ESI) Calcd for $C_9H_8N_2$ [M+H] 145.0768, Found 145.0760.

## General Procedure for Radical Trapping Experiments:



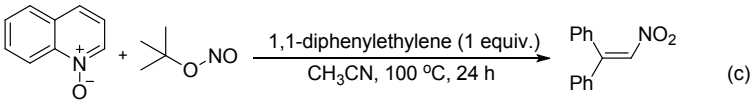

**1a** **2a**, N.D.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of quinoline *N*-Oxide **1a**, 3 mL of $CH_3CN$, TBN (1.05 mmol, 3.5 equiv.) and TEMPO (0.6 mmol, 2 equiv.). The reaction mixture was stirred at 100 ºC for 24 h. And the desired **2a** was not detected by GC-MS.




**1a** **2a**, N.D.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of quinoline *N*-Oxide **1a**, 3 mL of $CH_3CN$, TBN (1.05 mmol, 3.5 equiv.) and BHT (0.6 mmol, 2 equiv.). The reaction mixture was stirred at 100 ºC for 24 h. And the desired **2a** was not detected by GC-MS.




**1a** **4**, 55% yield

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of quinoline *N*-Oxide **1a**, 3 mL of $CH_3CN$, TBN (1.05 mmol, 3.5 equiv.) and 1,1-diphenylethylene (0.3 mmol, 1 equiv.). The reaction mixture was stirred at 100 ºC for 24 h, cooled to room temperature, and the desired **2a** was not detected by GC-MS. To our delight, we detected the nitroolefin **4**.[4] The reaction solution was poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford compound **4** in 55% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.95 (s, 1 H), 7.50–7.42 (m, 6 H), 7.36–7.32 (m, 2 H), 7.24–7.19 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.5, 137.0, 135.5, 134.4, 130.9, 129.3, 128.9, 128.84, 128.76, 128.5; HRMS (ESI) Calcd for $C_{14}H_{11}NnaO_2$ [M+Na] 243.0671, Found 243.0682.

## Reference:

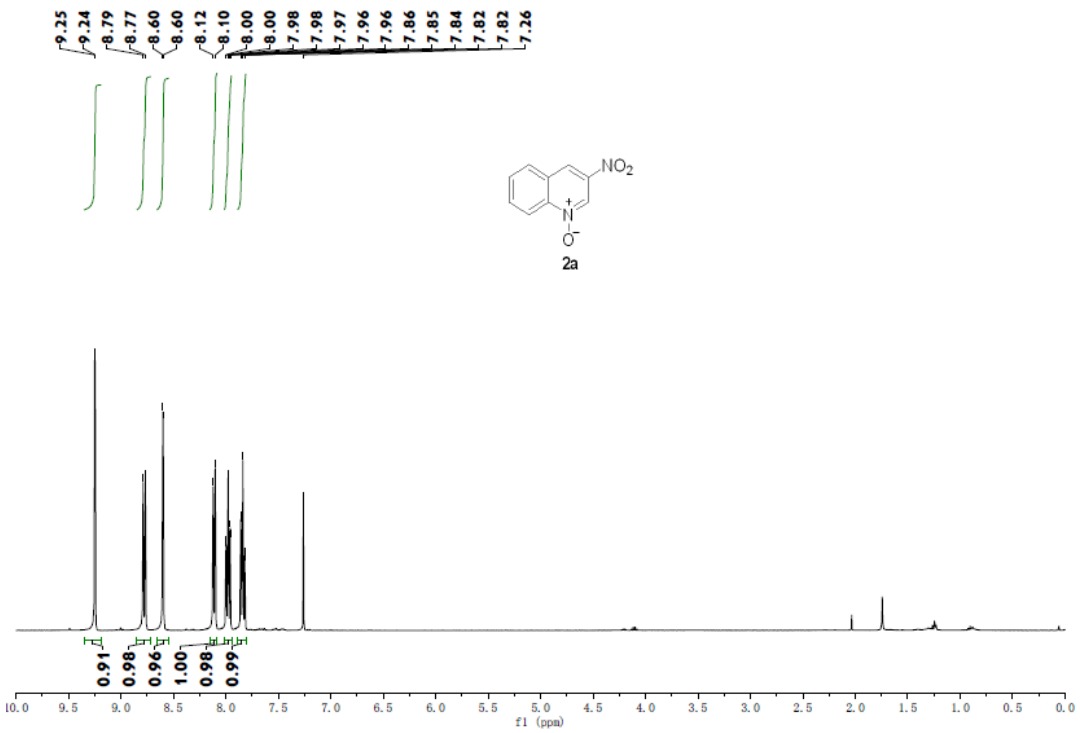
[1] K. S. Sharma, S. Kumari and R. P. Singh, *Synthesis*., 1981, 316.

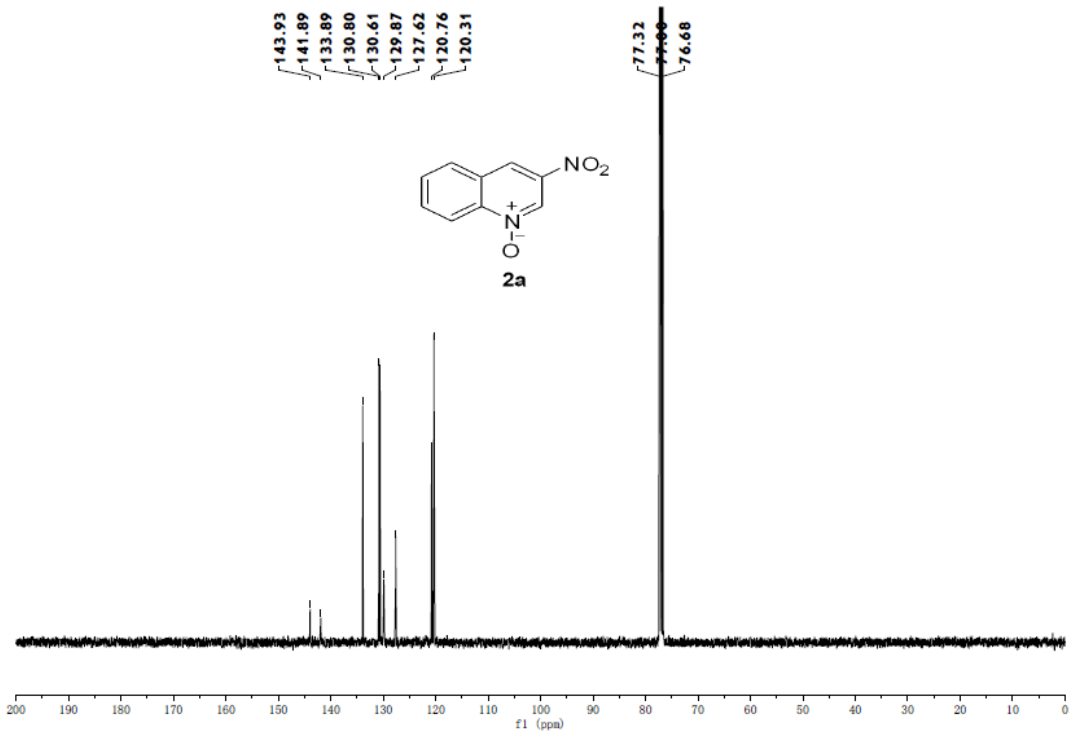
[2] H. Nakagawa, T. Higuchi, K. Kikuchi, Y. Urano and T. Naano, *Chem. Pharm. Bull*., 1998, **46**, 1656.

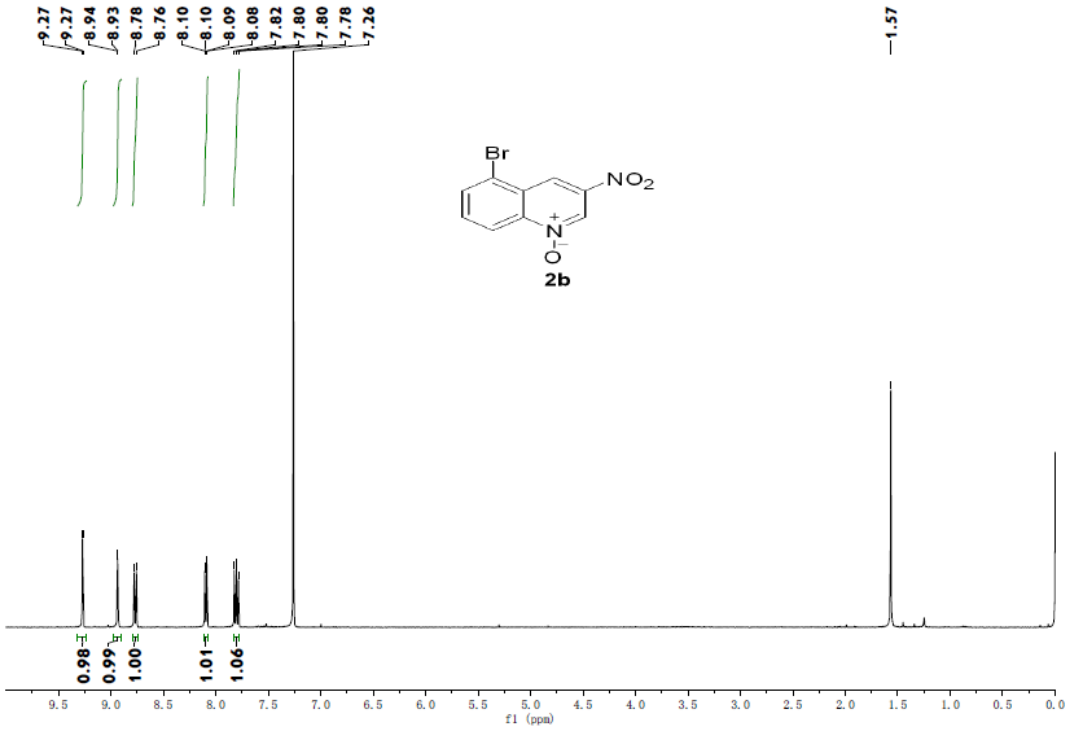
[3] S. Fantasia, J. Windisch and M. Scalone., *Adv. Synth. Catal*., 2013, **355**, 627.

[4] S. Maity, S. Manna, S. Rana, N. Togati, A. Mallick and D. Maiti, *J. Am. Chem. Soc*., 2013, **135**, 3355.

Copies of $^{1}H$ and $^{13}C$ NMR Spectra of the Products

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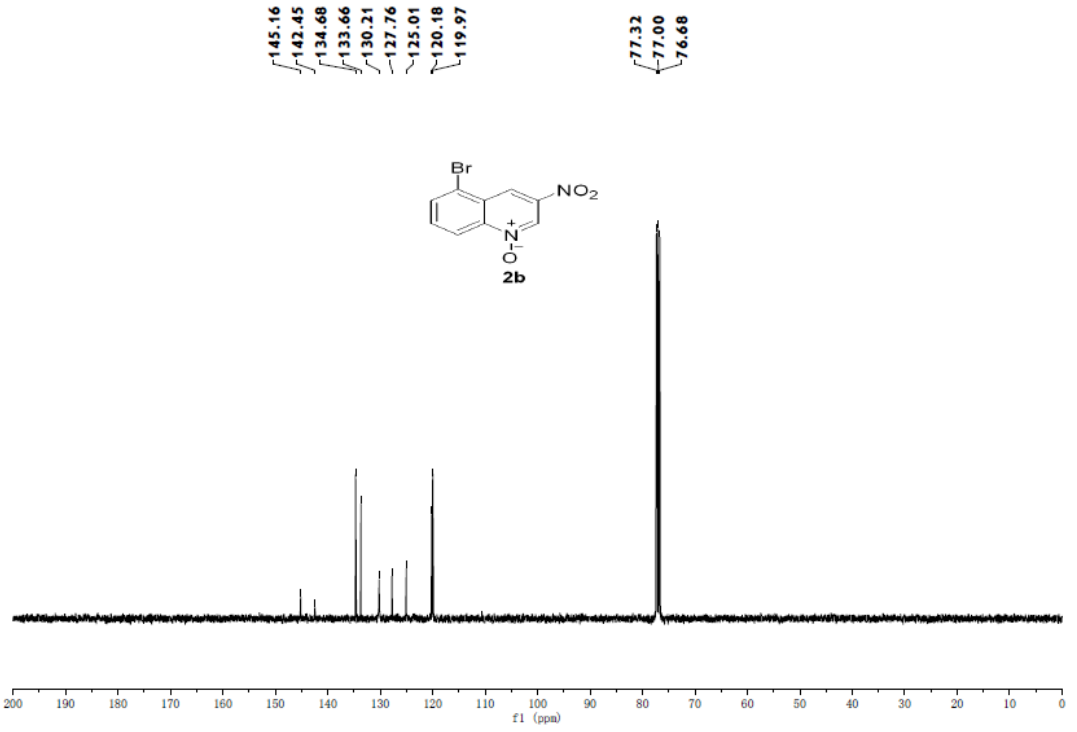
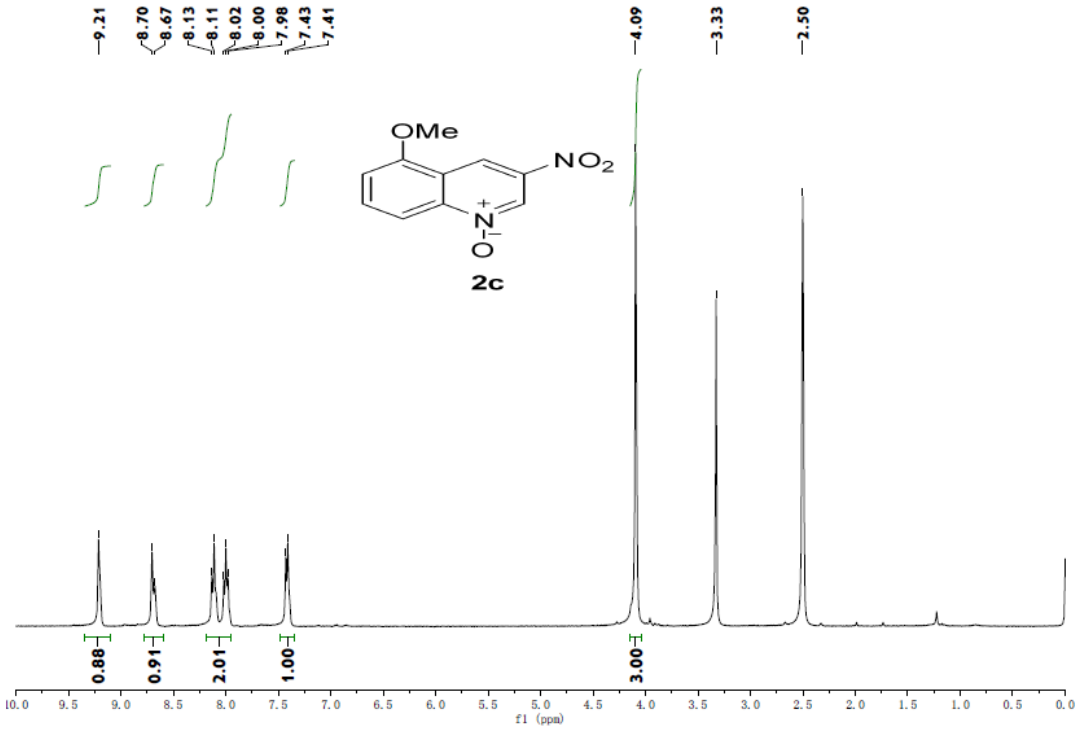
9.27
8.94
8.93
8.78
8.76
8.10
8.10
8.09
8.08
7.82
7.80
7.80
7.78
7.26
1.57
Br
NO2
N+
O−
2b
0.98
0.99
1.00
1.01
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.16
142.45
134.68
133.66
130.21
127.76
125.01
120.18
119.97
77.32
77.00
76.68
Br
NO2
N+
O−
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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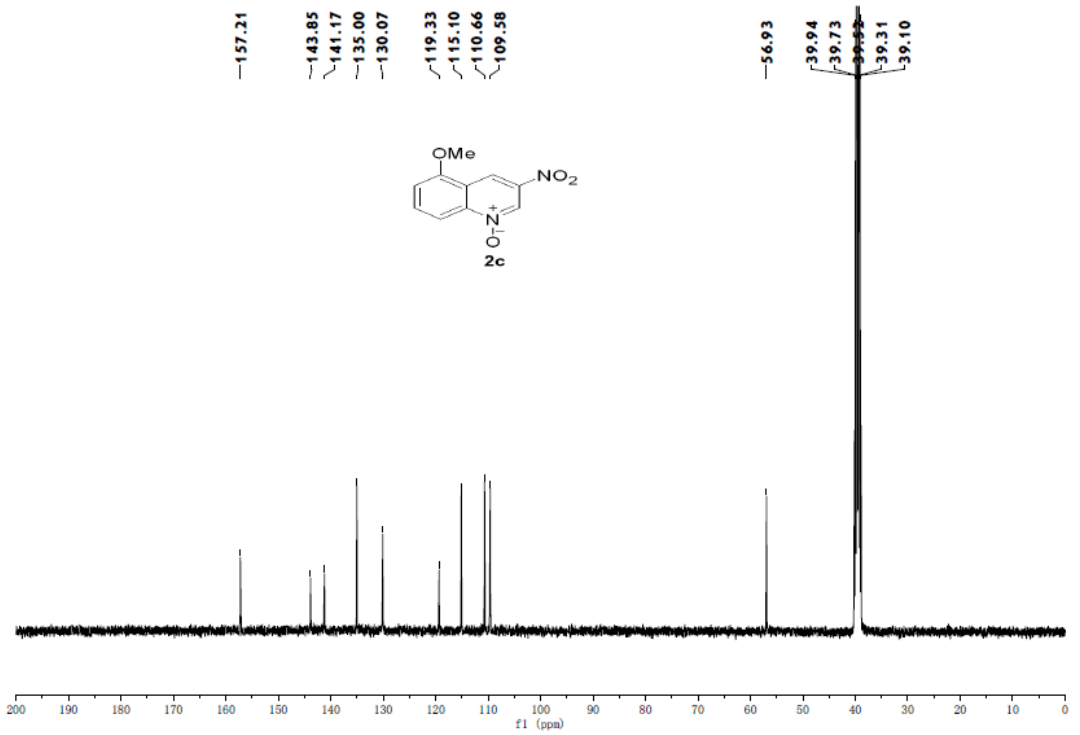
8.70
8.67
8.13
8.11
8.02
8.00
7.98
7.43
7.41
4.09
3.33
2.50
OMe
NO2
2c
0.88
0.91
2.01
1.00
3.00
f1 (ppm)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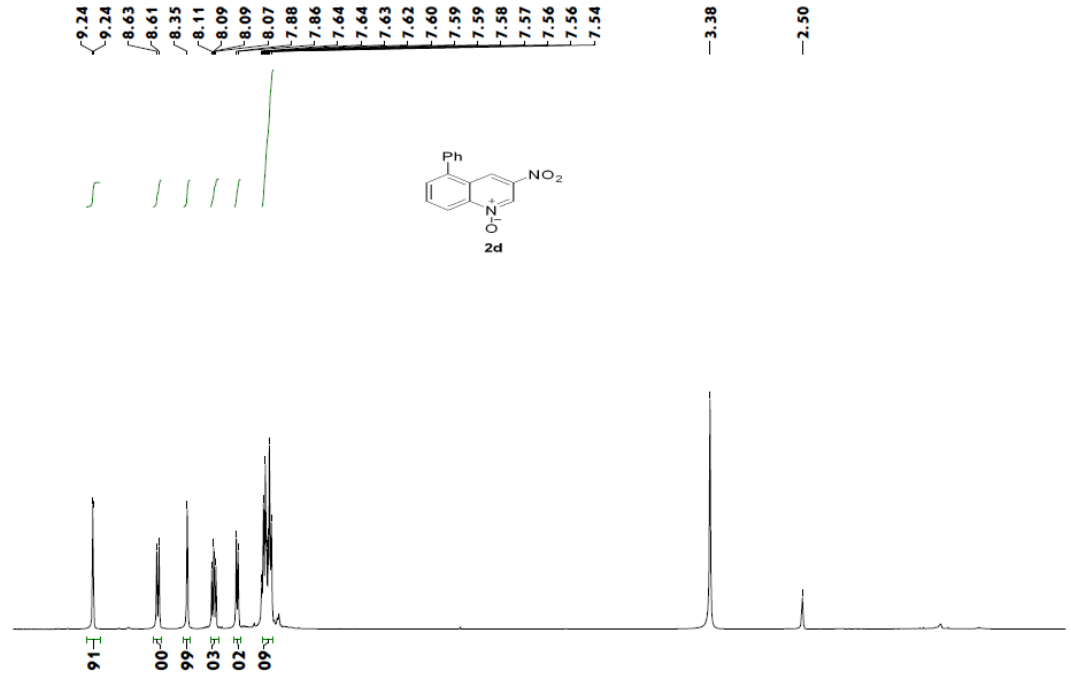
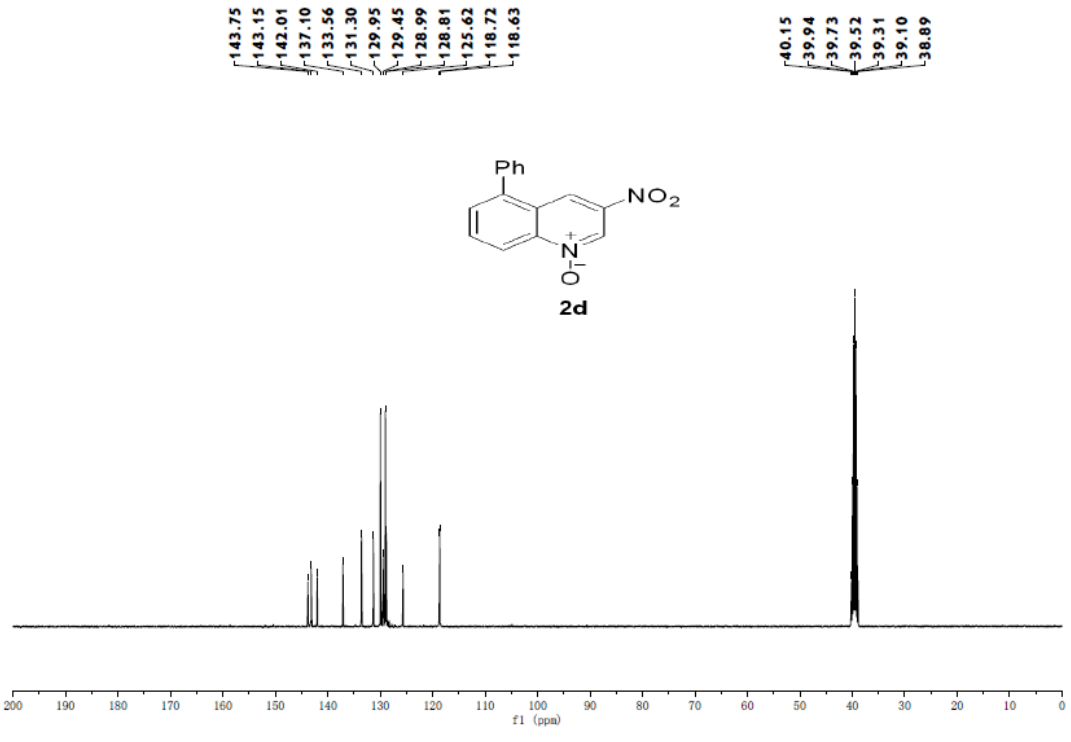
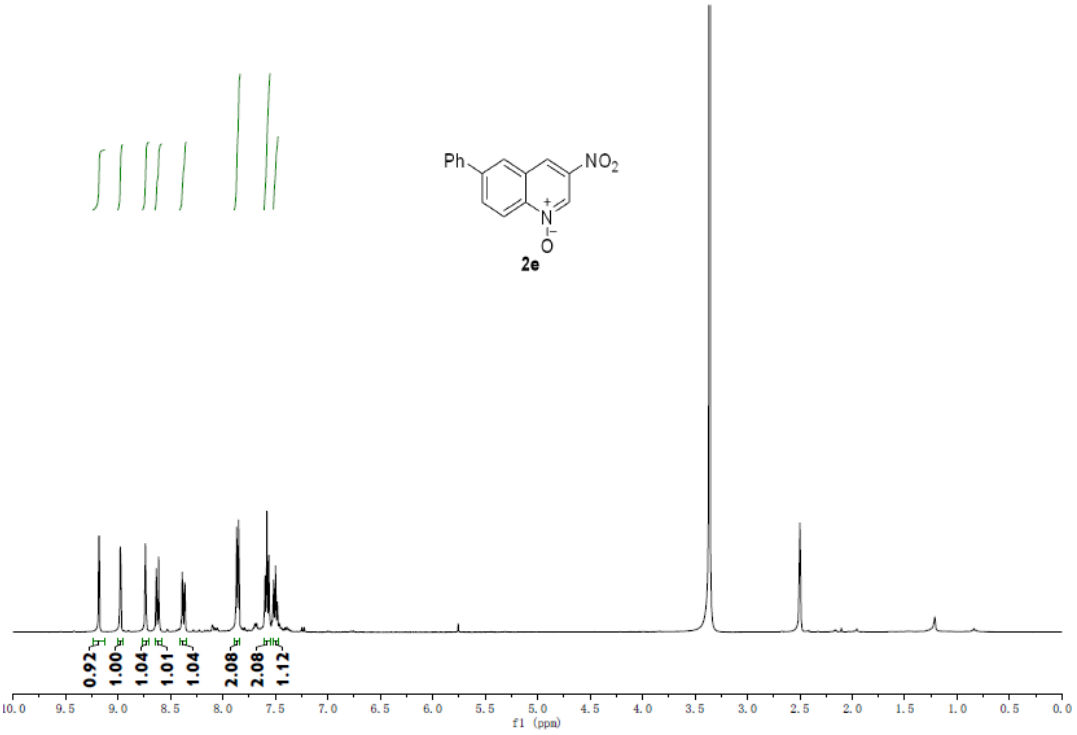
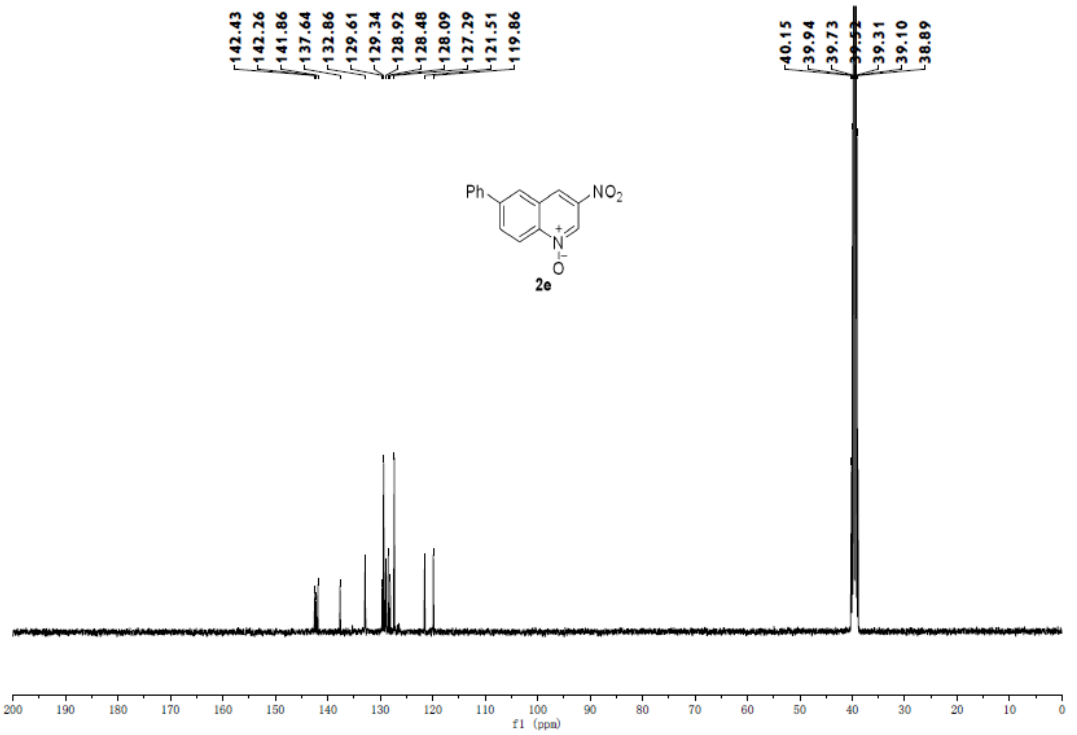
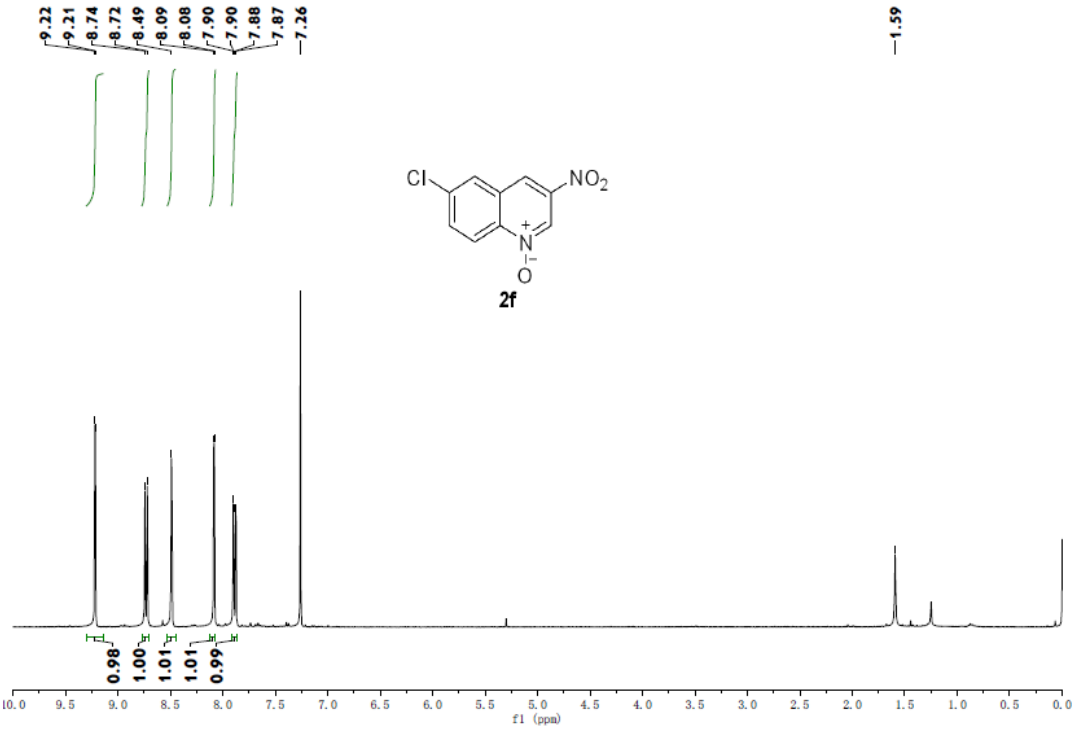
143.85
141.17
135.00
130.07
119.33
115.10
110.66
109.58
56.93
39.94
39.73
39.31
39.10
OMe
NO2
2c
f1 (ppm)


9.24
9.24
8.63
8.61
8.35
8.11
8.09
8.09
8.07
7.88
7.86
7.64
7.64
7.63
7.62
7.60
7.59
7.59
7.58
7.57
7.56
7.56
7.54
3.38
2.50
Ph
NO2
N
O
2d
1.91
2.00
0.99
1.03
1.02
5.09


143.75
143.15
142.01
137.10
133.56
131.30
129.95
129.45
128.99
128.81
125.62
118.72
118.63
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Ph
NO2
N
O
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
NO2
N+
O−
2e
0.92
1.00
1.04
1.01
1.04
2.08
2.08
1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.43
142.26
141.86
137.64
132.86
129.61
129.34
128.92
128.48
128.09
127.29
121.51
119.86
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Ph
NO2
N+
O−
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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9.21
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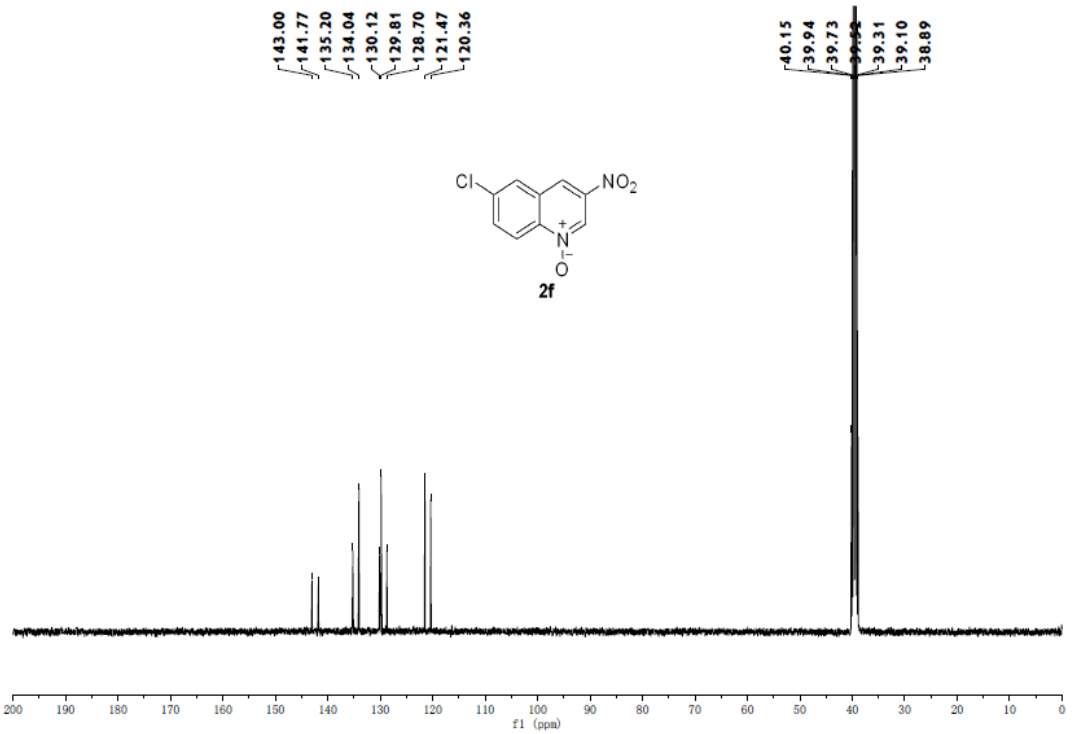
8.49
8.09
8.08
7.90
7.90
7.88
7.87
7.26
1.59
Cl
NO2
N
O
2f
0.98
1.00
1.01
1.01
0.99
f1 (ppm)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141.77
135.20
134.04
130.12
129.81
128.70
121.47
120.36
40.15
39.94
39.73
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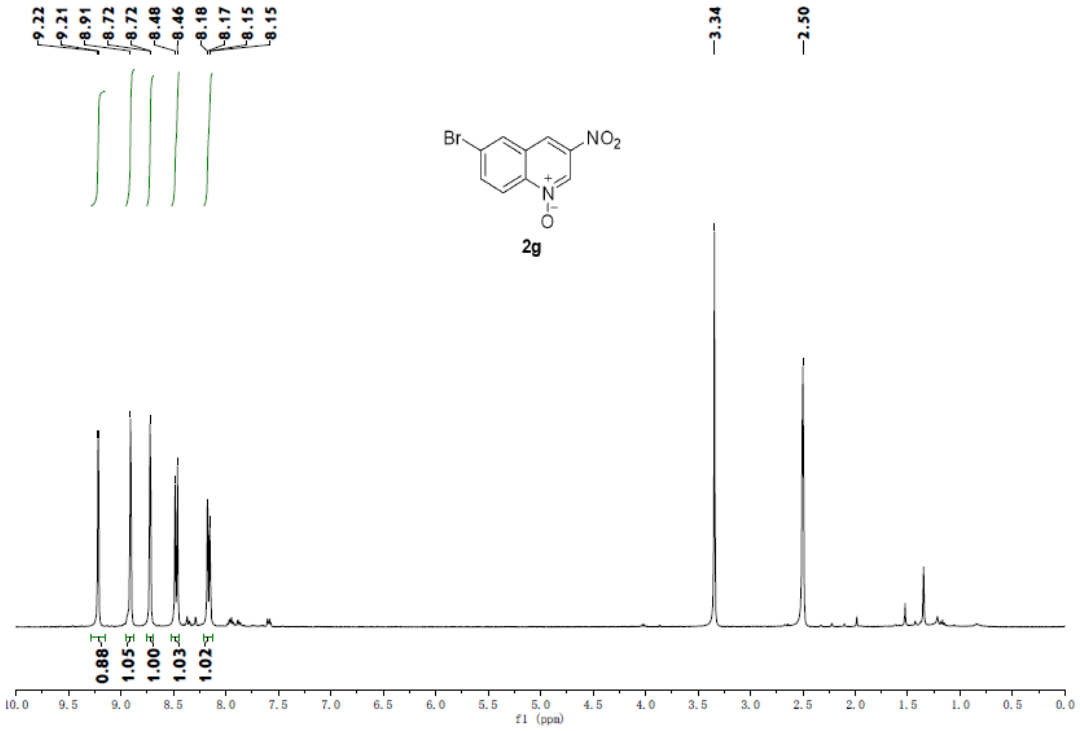
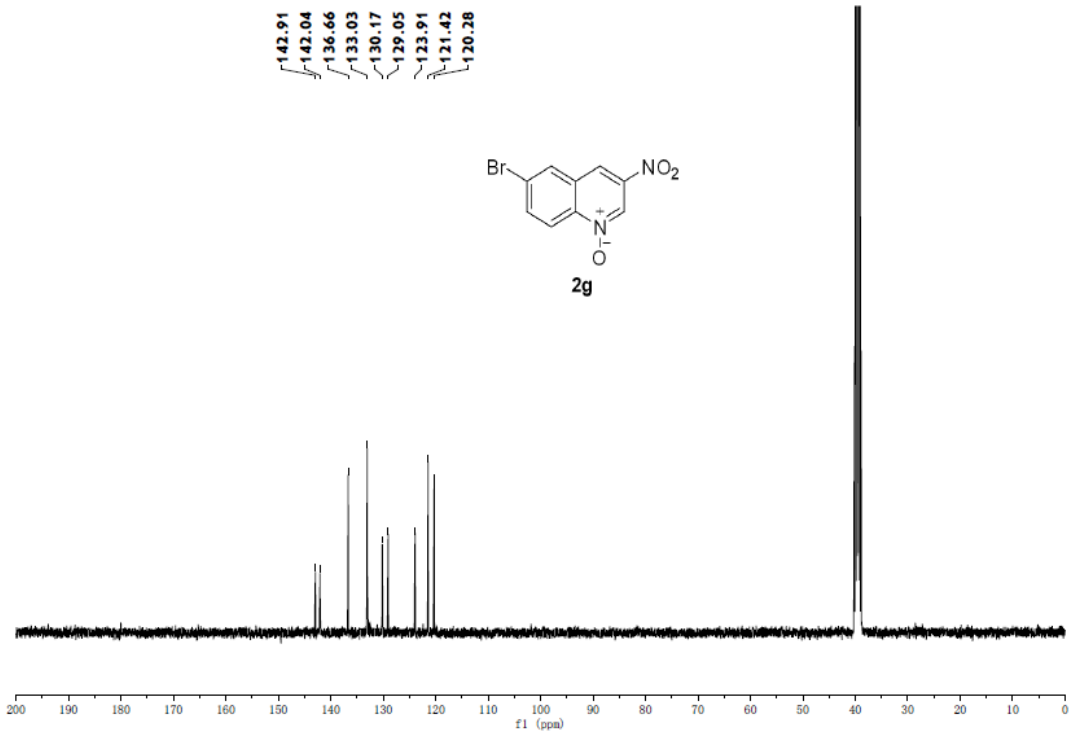
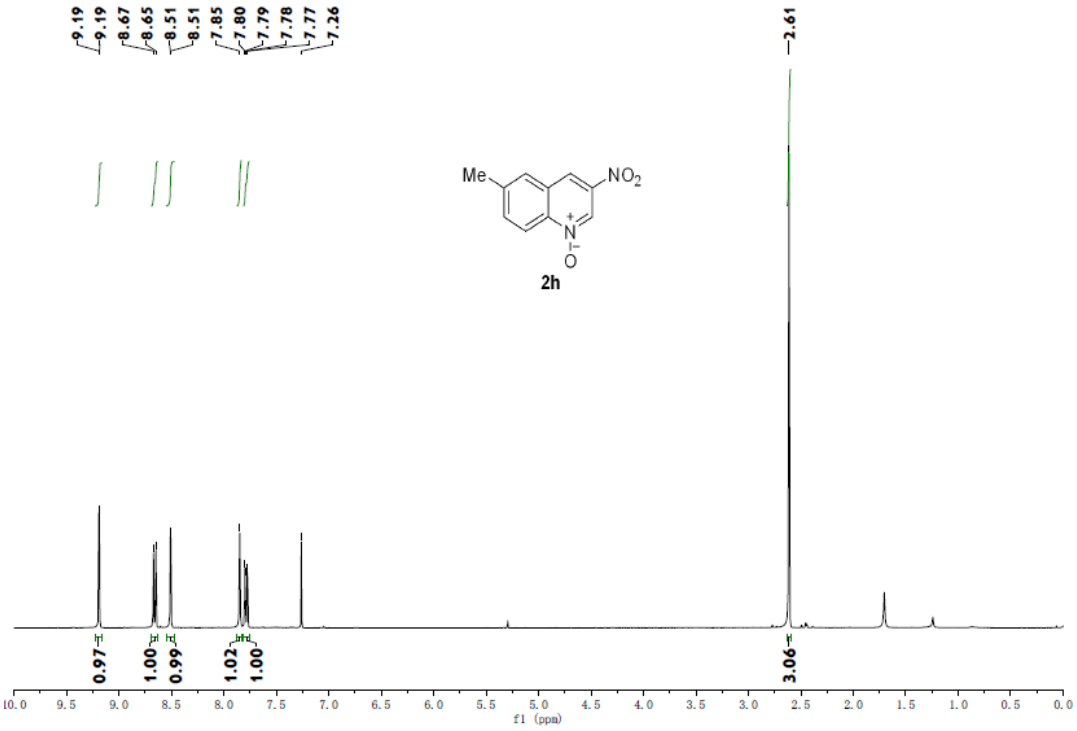
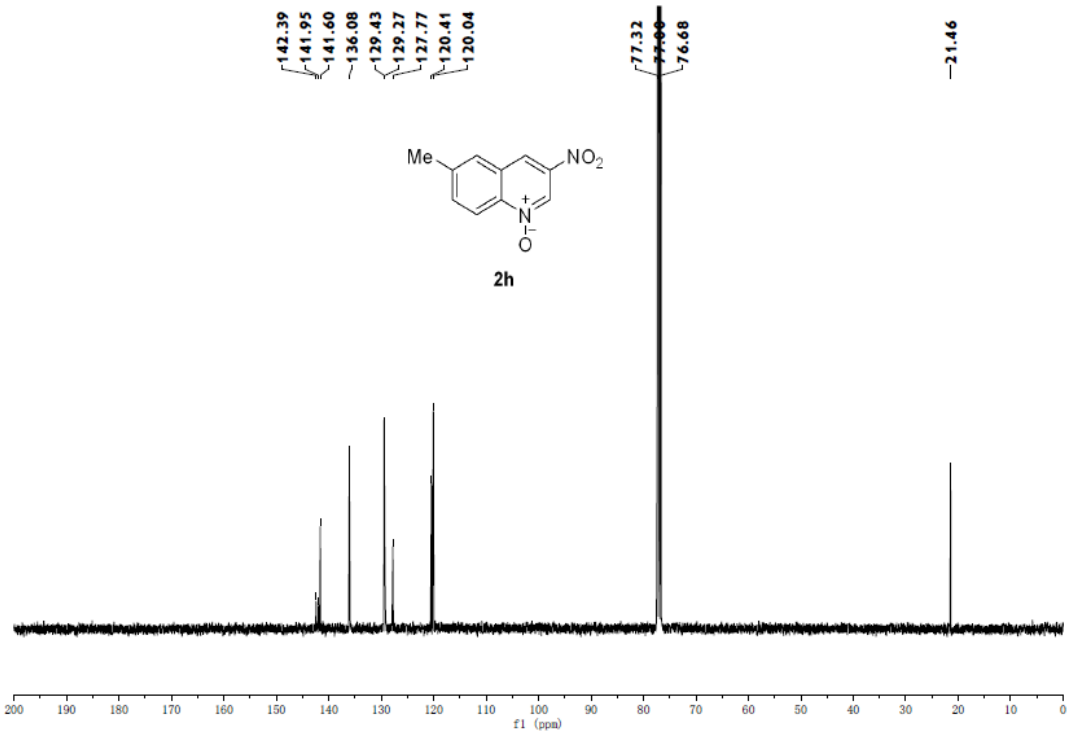
38.89
Cl
NO2
N
O
2f
f1 (ppm)


9.22
9.21
8.91
8.72
8.72
8.48
8.46
8.18
8.17
8.15
8.15
3.34
2.50
Br
NO2
N
O
2g
0.88
1.05
1.00
1.03
1.02
f1 (ppm)


142.91
142.04
136.66
133.03
130.17
129.05
123.91
121.42
120.28
Br
NO2
N
O
2g
f1 (ppm)


9.19
9.19
8.67
8.65
8.51
8.51
7.85
7.80
7.79
7.78
7.77
7.26
2.61
Me
NO2
N+
O−
2h
0.97
1.00
0.99
1.02
1.00
3.06
f1 (ppm)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136.08
129.43
129.27
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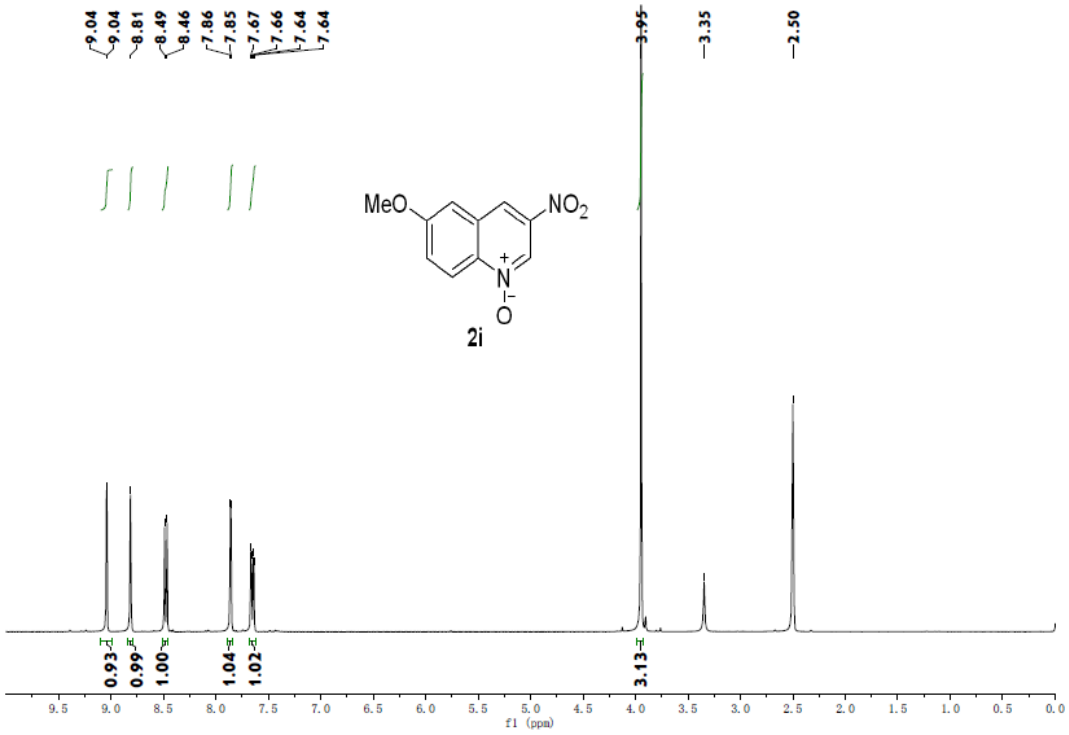
120.04
77.32
76.68
21.46
Me
NO2
N+
O−
2h
f1 (ppm)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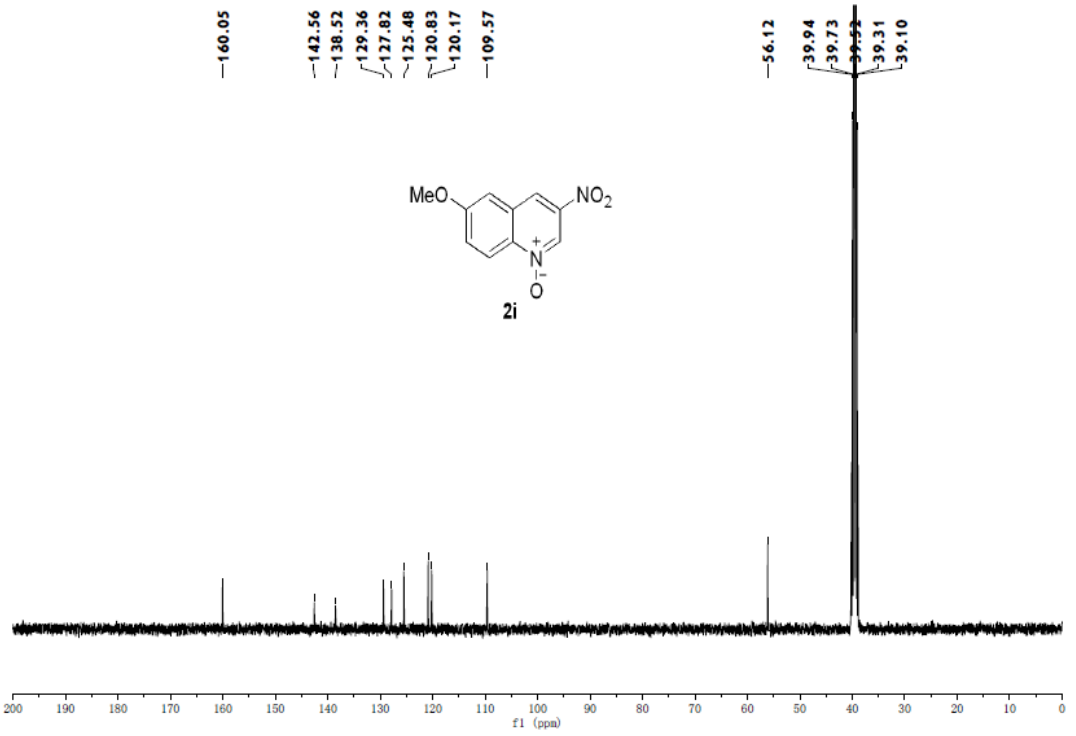
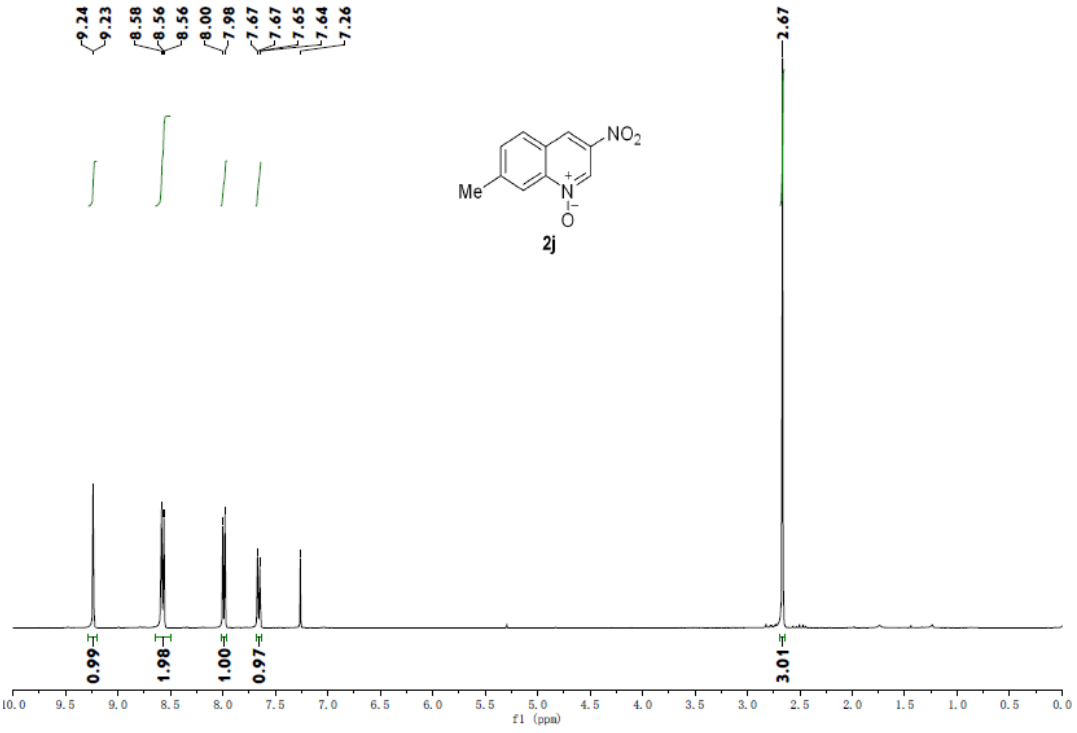
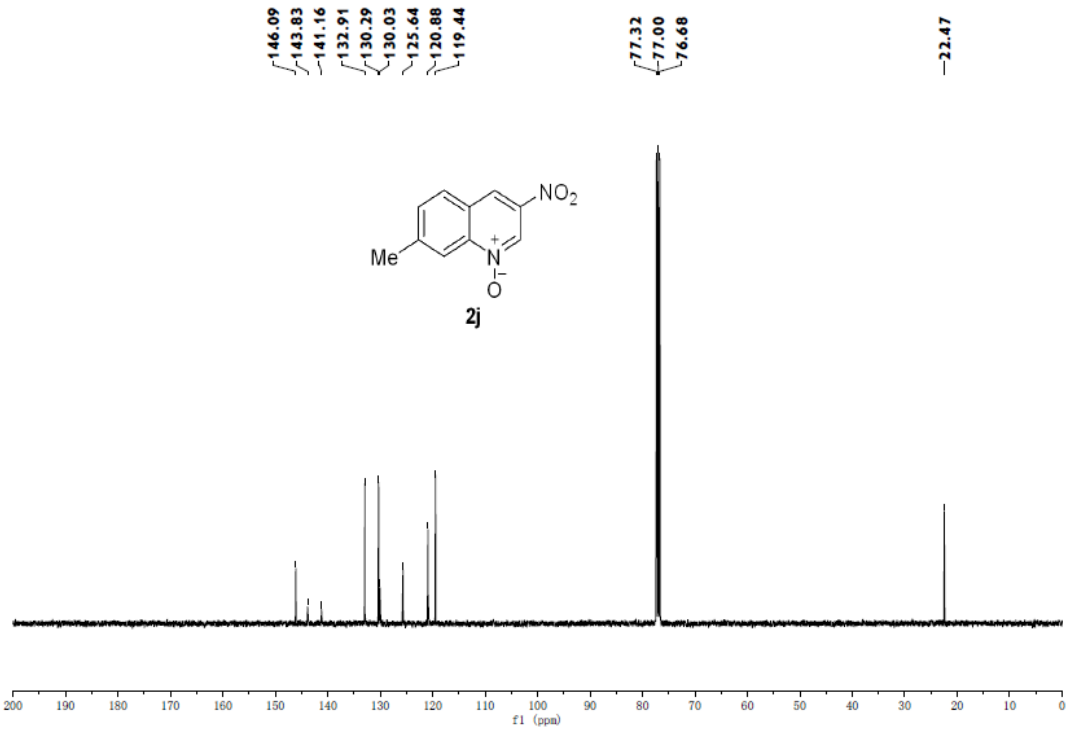
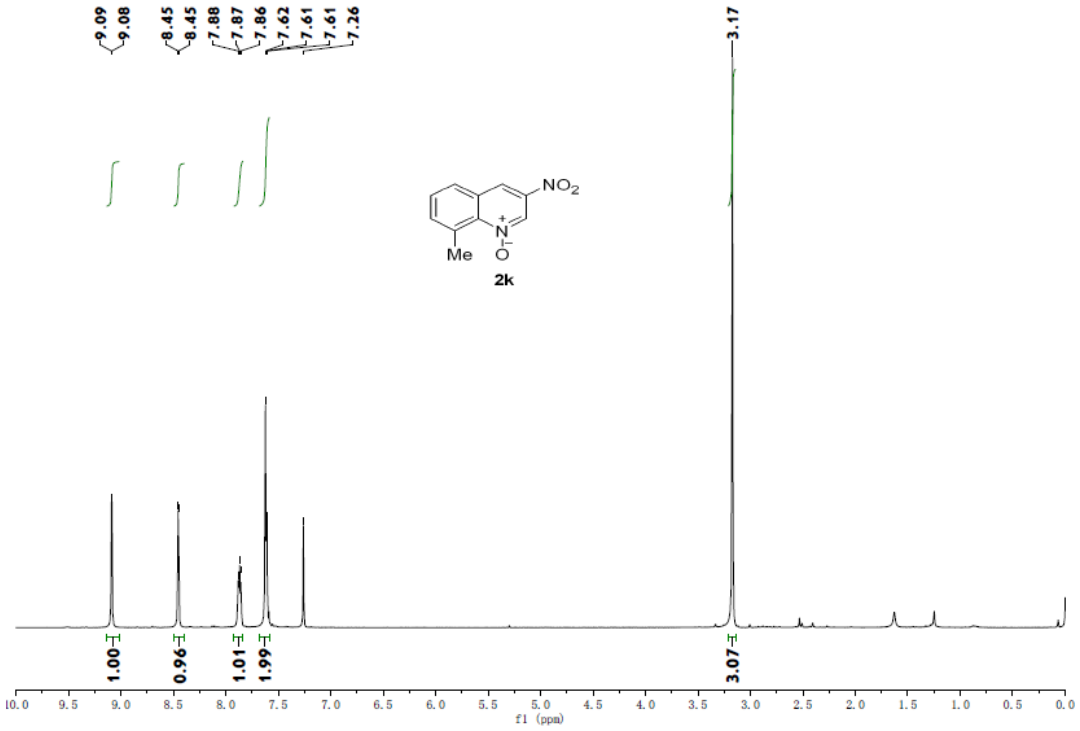
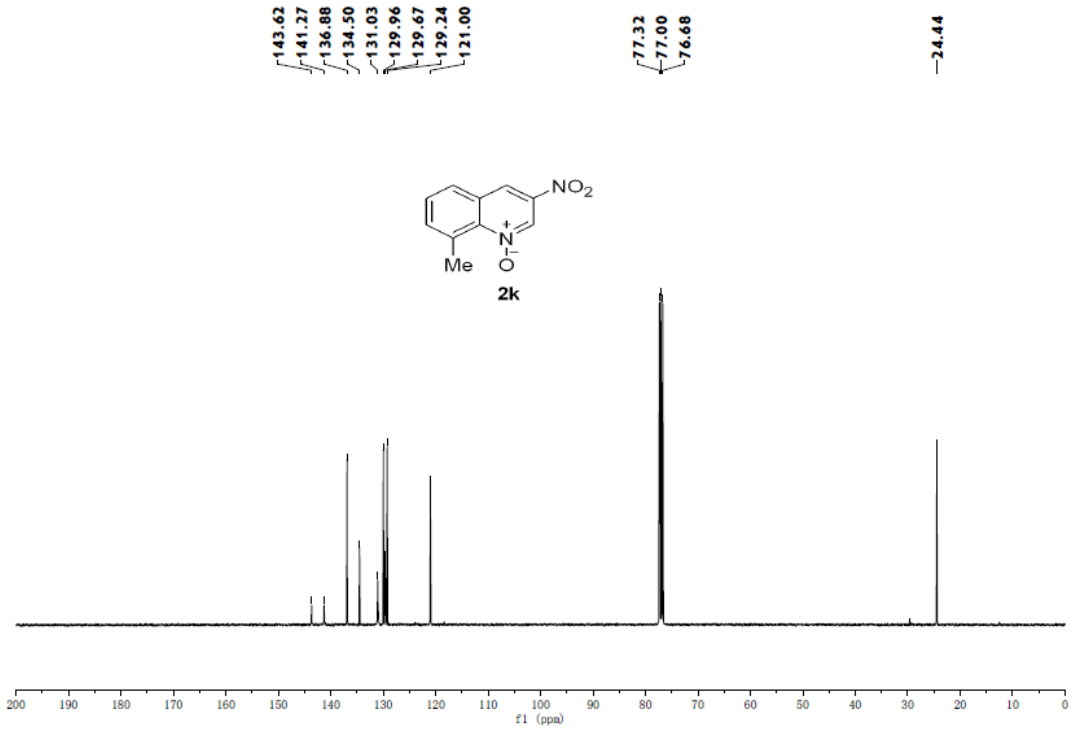
8.49
8.46
7.86
7.85
7.67
7.66
7.64
7.64
3.95
3.35
2.50
MeO
NO2
N+
O−
2i
0.93
0.99
1.00
1.04
1.02
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

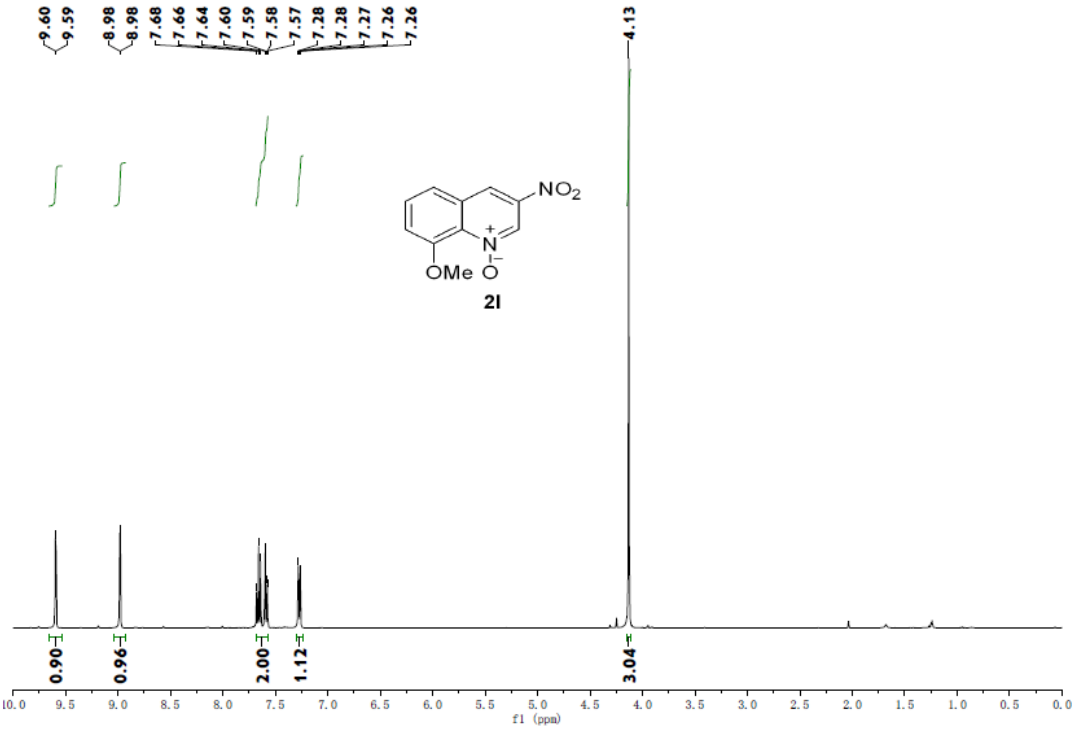

160.05
142.56
138.52
129.36
127.82
125.48
120.83
120.17
109.57
56.12
39.94
39.73
39.52
39.31
39.10
MeO
NO2
N+
O−
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

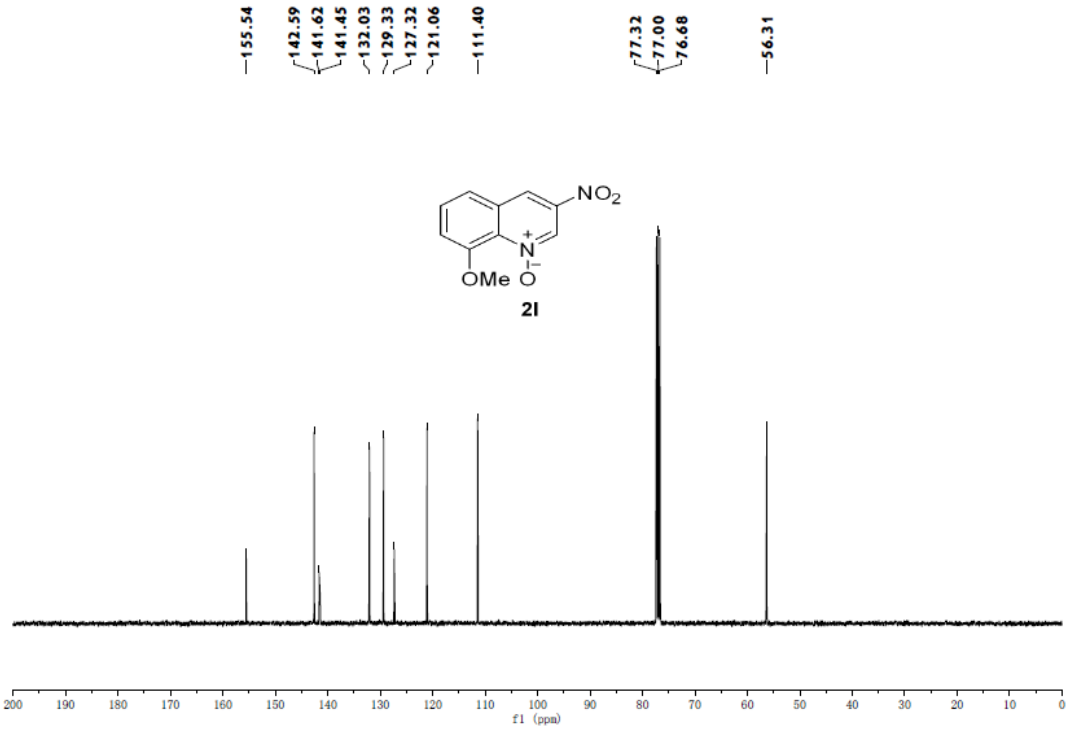

9.24
9.23
8.58
8.56
8.56
8.00
7.98
7.67
7.67
7.65
7.64
7.26
2.67
NO2
Me
N
O
2j
0.99
1.98
1.00
0.97
3.01
f1 (ppm)

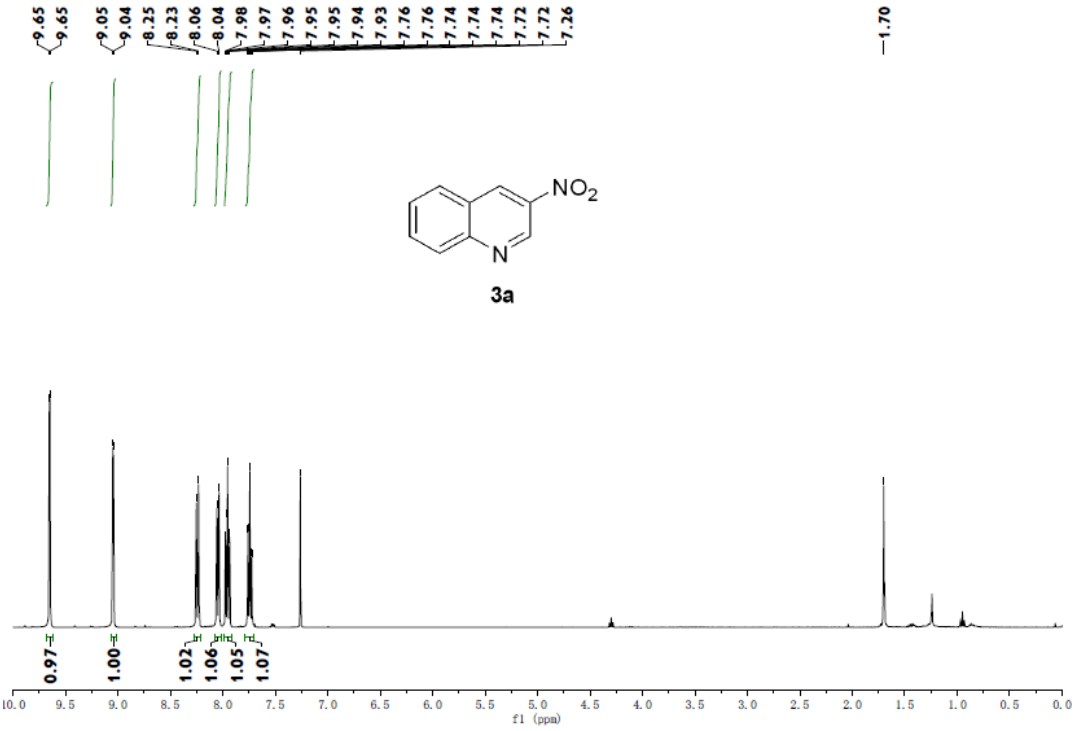

146.09
143.83
141.16
132.91
130.29
130.03
125.64
120.88
119.44
77.32
77.00
76.68
22.47
NO2
Me
N
O
2j
f1 (ppm)

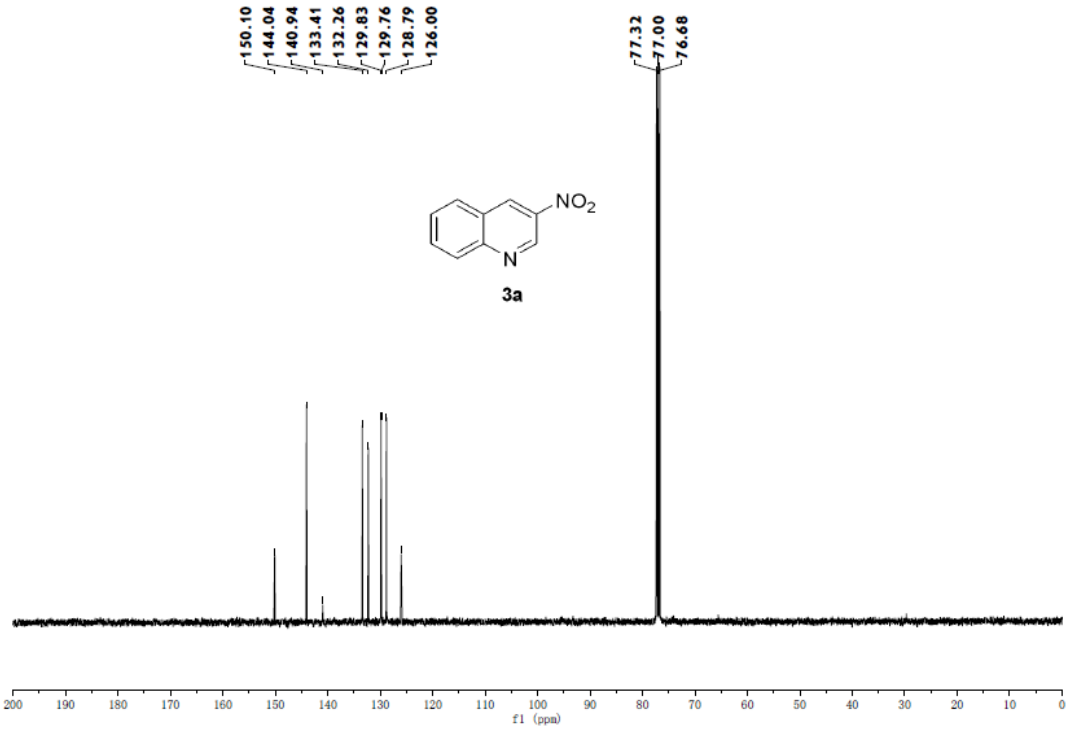

9.09
9.08
8.45
8.45
7.88
7.87
7.86
7.62
7.61
7.61
7.26
3.17
NO2
Me
2k
1.00
0.96
1.01
1.99
3.07
f1 (ppm)

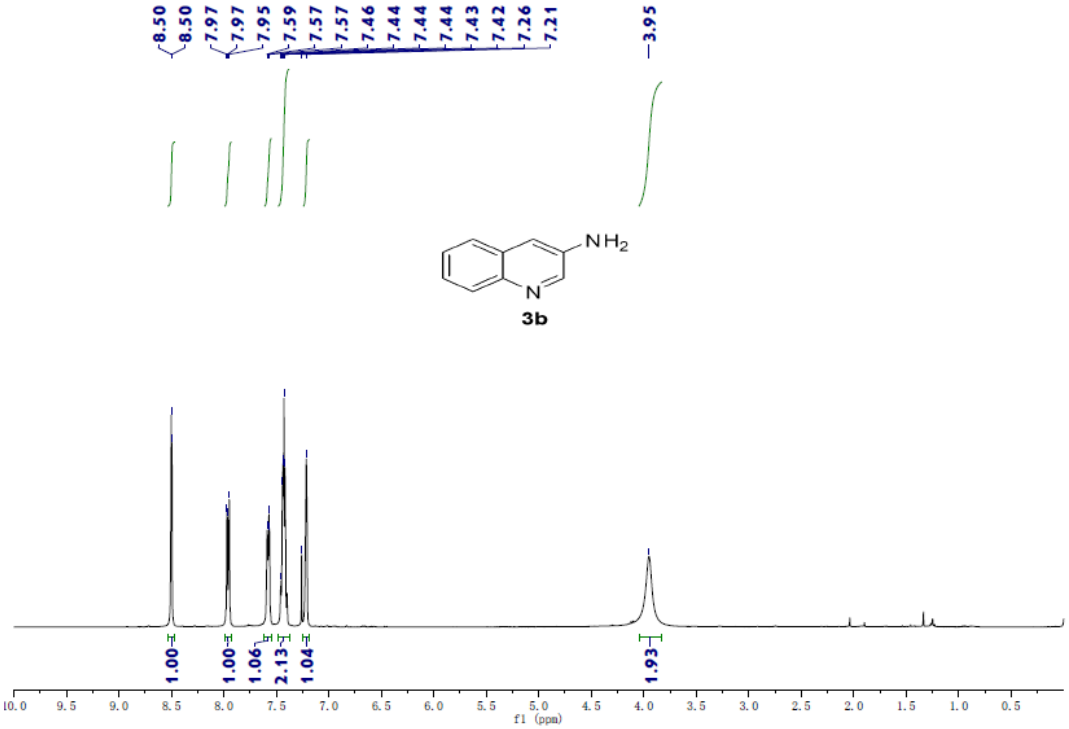

143.62
141.27
136.88
134.50
131.03
129.96
129.67
129.24
121.00
77.32
77.00
76.68
24.44
NO2
Me
2k
f1 (ppm)

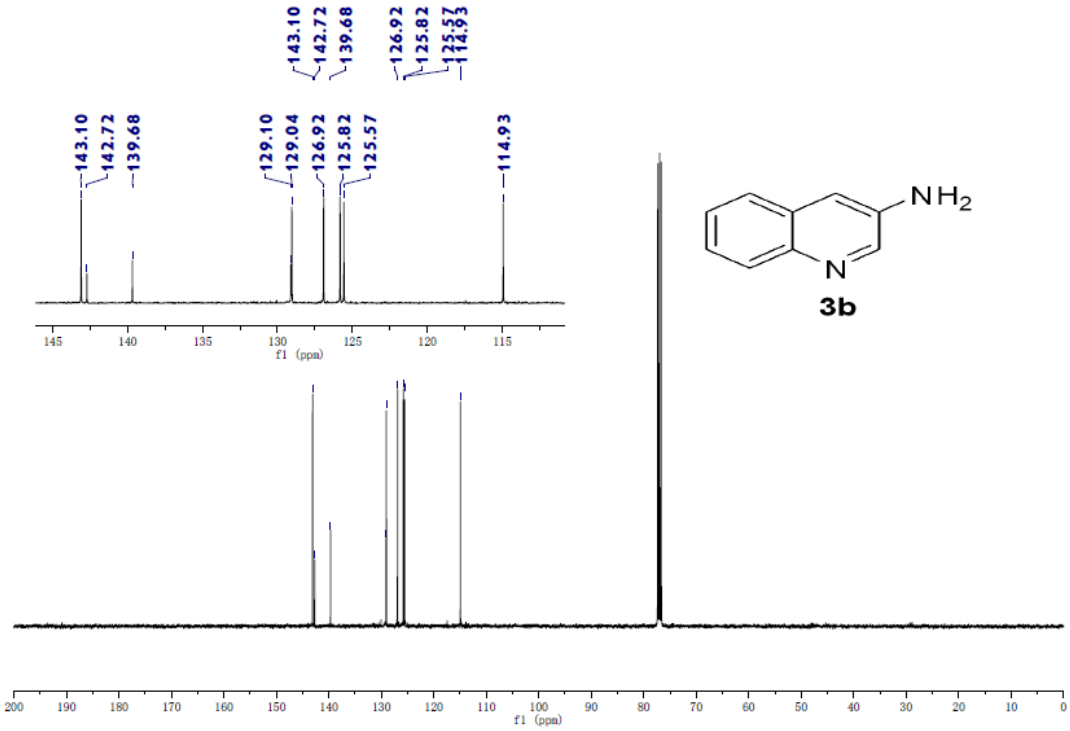

9.60
9.59
8.98
8.98
7.68
7.66
7.64
7.60
7.59
7.58
7.57
7.28
7.28
7.27
7.26
7.26
4.13
NO2
N+
O−
OMe
2l
0.90
0.96
2.00
1.12
3.04
f1 (ppm)

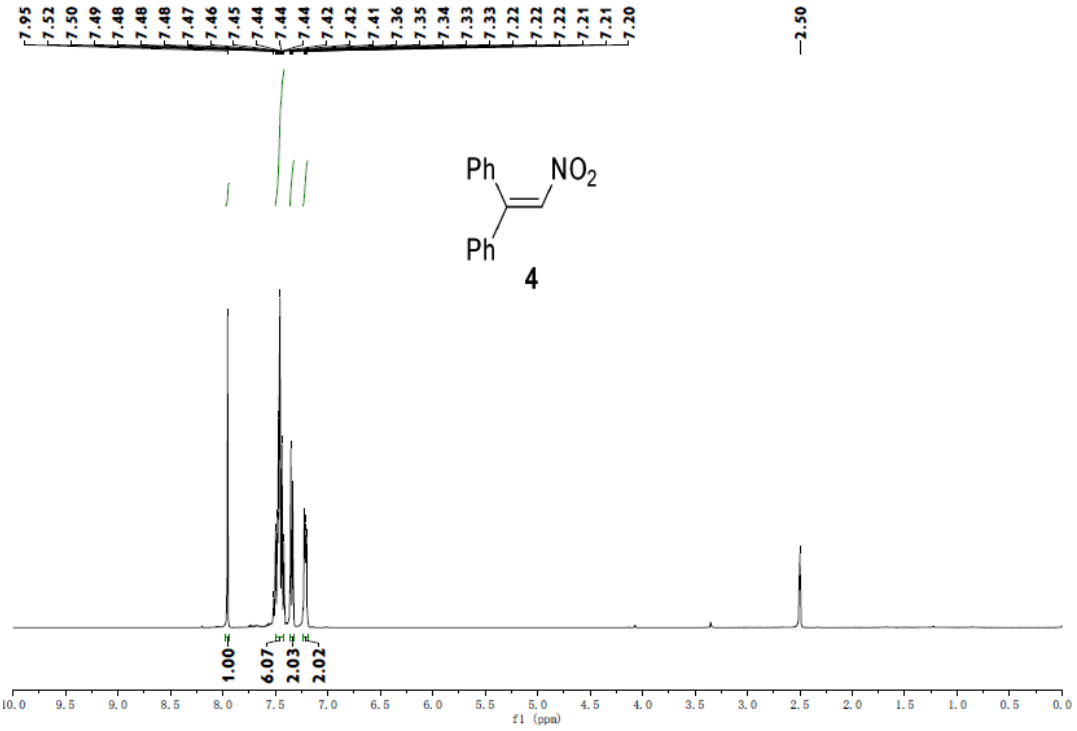

155.54
142.59
141.62
141.45
132.03
129.33
127.32
121.06
111.40
77.32
77.00
76.68
56.31
NO2
N+
O−
OMe
2l
f1 (ppm)

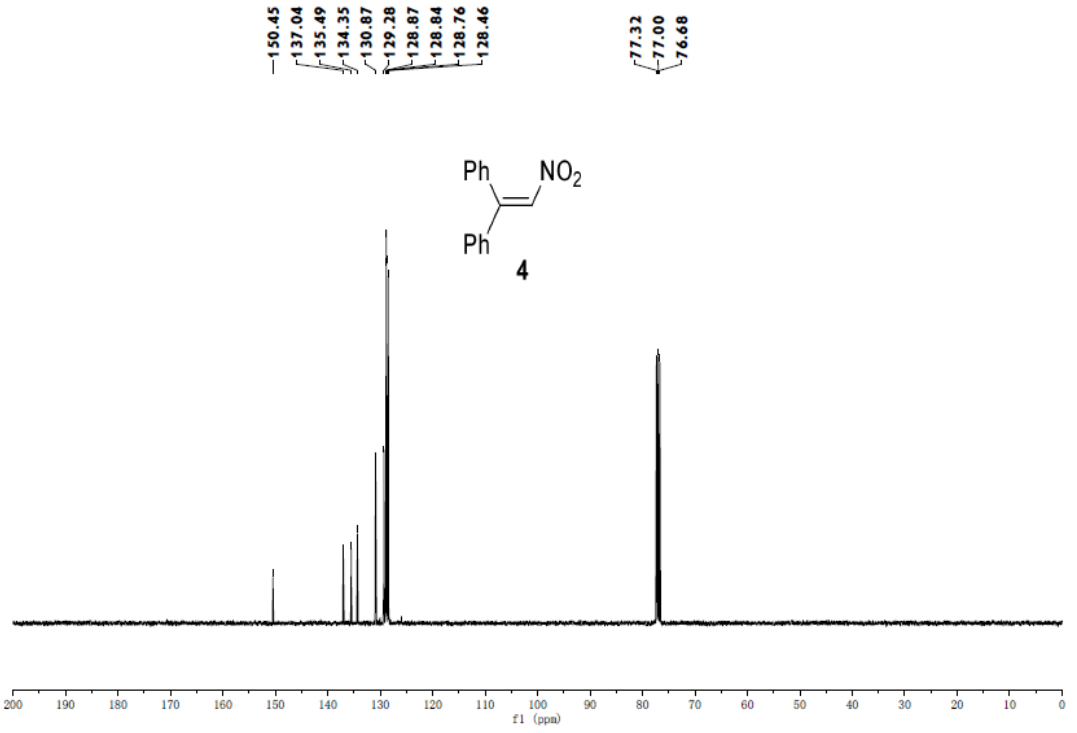

9.65
9.65
9.05
9.04
8.25
8.23
8.06
8.04
7.98
7.97
7.96
7.95
7.95
7.94
7.93
7.76
7.76
7.74
7.74
7.74
7.72
7.72
7.26
1.70
NO2
N
3a
0.97
1.00
1.02
1.06
1.05
1.07
f1 (ppm)


150.10
144.04
140.94
133.41
132.26
129.83
129.76
128.79
126.00
77.32
77.00
76.68
NO2
N
3a
f1 (ppm)


8.50
8.50
7.97
7.97
7.95
7.59
7.57
7.57
7.46
7.44
7.44
7.44
7.43
7.42
7.26
7.21
3.95
NH2
N
3b
1.00
1.00
1.06
2.13
1.04
1.93
f1 (ppm)


143.10
142.72
139.68
129.10
129.04
126.92
125.82
125.57
114.93
NH2
N
3b
f1 (ppm)


7.95
7.52
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.44
7.42
7.42
7.41
7.36
7.35
7.34
7.33
7.33
7.22
7.22
7.22
7.21
7.21
7.20
2.50
Ph
NO2
Ph
4
1.00
6.07
2.03
2.02
f1 (ppm)


150.45
137.04
135.49
134.35
130.87
129.28
128.87
128.84
128.76
128.46
77.32
77.00
76.68
Ph
NO2
Ph
4
f1 (ppm)