Electronic Supporting Information

The development of carbene-stabilized N–O radical coupling strategy in metal-free regioselective C–H azidation of quinoline N–oxides

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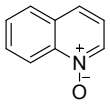
General Information:

All reagents purchased from commercial sources were used as received. Quinoline derivative 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 39.6 ppm for ^{13}C in DMSO–d_6). The HRMS spectra were recorded on a Bruker MicroTOF QII spectrometer. EPR spectra were recorded on a Bruker A-300 spectrometer.

Experimental Procedure and Data of the Quinoline N–Oxides

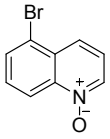
Under vigorous magnetic stirring, 3-chloroperbenzoic acid (*m*CPBA) (381 mg, 2.2 mmol) in CH_2Cl_2 (5 mL) was dropped into solution of quinoline derivatives (2 mmol) in CH_2Cl_2 (5 mL) at 25 ºC for 2 h. Then saturated $NaHCO_3$ aqueous solution was added to the mixture to neutralize residual *m*CPBA. The resulting mixture was extracted with CH_2Cl_2. The organic phase were combined and washed with brine. 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 as eluent).

Following the above procedure, the following quinoline N–oxides were prepared:



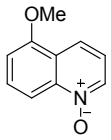
1a

Quinoline N–oxide: ^{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, 130.5 (2 C), 128.7, 128.1, 126.1, 120.9, 119.7.



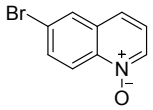
1b

5-Bromoquinoline N–oxide: ^{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.



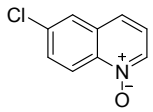
1c

5-Methoxyquinoline N–oxide: ^{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.



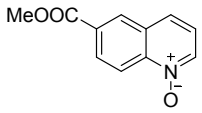
1d

6-Bromoquinoline N–oxide: ^{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.



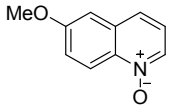
1e

6-Chloroquinoline N–oxide: ^{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.



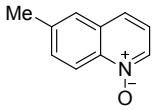
1f

6-(Methoxycarbonyl)quinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 9.1 Hz, 1 H), 8.64 (d, J = 5.9 Hz, 1 H), 8.59 (d, J = 1.4 Hz, 1 H), 8.30 (dd, J = 9.1, 1.6 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.37 (dd, J = 8.3, 6.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 143.1, 137.5, 131.0, 130.5, 130.1, 130.0, 127.4, 121.9, 120.4, 52.8.



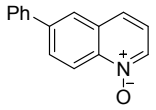
1g

6-Methoxyquinoline N–oxide: ^{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.



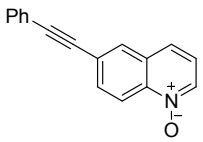
1h

6-Methylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.9 Hz, 1 H), 8.44 (d, *J* = 5.9 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.59 (s, 1 H), 7.55 (dd, *J* = 8.9, 1.6 Hz, 1 H), 7.22 (dd, *J* = 8.4, 6.0 Hz, 1 H); 2.51 (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.



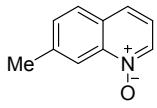
1i

6-Phenylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.9 Hz, 1 H), 8.50 (d, *J* = 6.0 Hz, 1 H), 8.02–7.91 (m, 2 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.70–7.62 (m, 2 H), 7.52–7.45 (m, 2 H), 7.43–7.37 (m, 1 H), 7.30–7.26 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.6, 139.0, 135.3, 130.7, 129.9, 128.9, 128.2, 127.3, 125.9, 125.5, 121.2, 120.2.



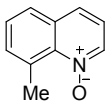
1j

6-(Phenylethynyl)quinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 9.0 Hz, 1 H), 8.50 (d, *J* = 5.9 Hz, 1 H), 8.00 (d, *J* = 1.1 Hz, 1 H), 7.82 (dd, *J* = 9.0, 1.5 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.57–7.55 (m, 2 H), 7.42–7.34 (m, 3 H), 7.32–7.21 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 135.9, 132.9, 131.6, 130.8, 130.2, 128.8, 128.4, 125.4, 124.1, 122.3, 121.6, 119.9, 92.1, 87.8.



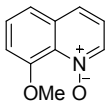
1k

7-Methylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55–8.52 (m, 2 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.45 (dt, *J* = 8.9, 2.7 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.



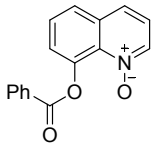
1l

8-Methylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 6.0, 0.6 Hz, 1 H), 7.56 (td, *J* = 7.8, 4.5 Hz, 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.



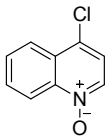
1m

8-Methoxyquinoline N–oxide: ^{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.



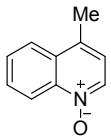
1n

8-(Benzoyloxy)quinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 6.1 Hz, 1 H), 8.28 (d, *J* = 7.3 Hz, 2 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.61 (q, *J* = 7.9 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.45–7.39 (m, 1 H), 7.27–7.21 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 143.4, 137.9, 135.1, 133.3, 133.2, 130.5, 129.9, 128.5, 128.4, 126.7, 125.6, 124.2, 121.4.



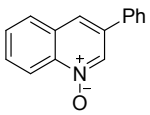
1o

4-Chloroquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81–8.74 (m, 1 H), 8.44 (d, *J* = 6.6 Hz, 1 H), 8.22 (dd, *J* = 8.3, 0.9 Hz, 1 H), 7.84 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1 H), 7.76 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.38 (d, *J* = 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.1, 131.2, 129.9, 129.7, 128.1, 125.2, 121.0, 120.4.



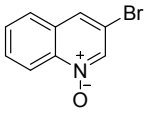
1p

4-Methylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.6, 3.4 Hz, 1 H), 8.44 – 8.32 (m, 1 H), 7.91 (dd, *J* = 7.9, 4.1 Hz, 1 H), 7.77–7.57 (m, 2 H), 7.06 (d, *J* = 4.8 Hz, 1 H), 2.61 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 134.8, 134.4, 129.9, 129.7, 128.4, 124.6, 121.3, 120.2, 18.2.



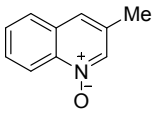
1q

3-Phenylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 1.4 Hz, 1 H), 8.74 (d, *J* = 8.7 Hz, 1 H), 7.91 (d, *J* = 8.9 Hz, 2 H), 7.74 (ddd, *J* = 8.5, 7.0, 1.2 Hz, 1 H), 7.70–7.61 (m, 3 H), 7.55–7.48 (m, 2 H), 7.48–7.43 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 135.9, 135.0, 134.9, 130.3, 130.1, 129.3, 129.1, 128.9, 128.3, 127.0, 123.4, 119.7.



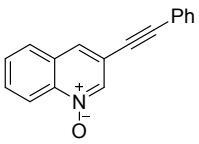
1r

3-Bromoquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 8.0, 5.2 Hz, 2 H), 7.79 (s, 1 H), 7.73–7.61 (m, 2 H), 7.60–7.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 136.8, 130.3, 129.9, 129.6, 127.5, 127.1, 119.5, 114.1.



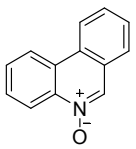
1s

3-Methylquinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.7 Hz, 1 H), 8.41 (s, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.67 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 1 H), 7.63–7.55 (m, 1 H), 7.52 (s, 1 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.0, 131.2, 130.2, 129.4, 128.7, 127.4, 125.6, 119.5, 18.7.



1t

3-(Phenylethynyl)quinoline N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.7 Hz, 1 H), 8.63 (d, *J* = 1.3 Hz, 1 H), 7.89 (s, 1 H), 7.88–7.84 (m, 1 H), 7.77 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1 H), 7.67 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.43–7.38 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 137.0, 131.9, 130.8, 129.9, 129.4, 129.3, 128.6, 128.3, 128.1, 121.9, 119.9, 117.9, 93.3, 84.3.



1u

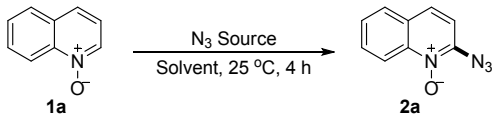
Phenanthridine N–oxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95–8.91 (m, 1 H), 8.90 (s, 1 H), 8.61–8.55 (m, 1 H), 8.50 (d, *J* = 8.2 Hz, 1 H), 7.88–7.71 (m, 4 H), 7.68–7.63 (m, 1 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 139.3, 134.6, 129.6, 129.5, 129.3, 128.8, 126.7, 126.63, 126.57, 126.1, 122.7, 122.1, 120.7.

General Procedure for the 2-Azidequinoline N–Oxides under Varied Conditions

To a 15 mL tubes with a stir bar was added quinoline N–oxides **1a** (44 mg, 0.3 mmol), azide source. Solvent (3 mL) was added, followed by the oxidant. The mixture was stirred at 25 ºC for 4 h, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford the desired product **2a**.

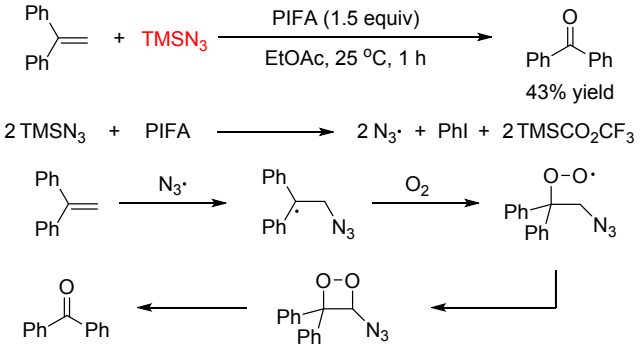
Table S1. C2-azidation of quinoline N–oxides under varied conditions[a]



Entry	N_3 Source [equiv]	Oxidant [equiv]	Solvent	Yield [%]
1	NaN_3 (3)	PIFA (1.8)	MeCN	43
2	$TMSN_3$ (3)	PIFA (1.8)	MeCN	71
3	$TMSN_3$ (3)	PIDA (1.8)	MeCN	34
4	$TMSN_3$ (3)	PIFA (1.8)	Toluene	73
5	$TMSN_3$ (3)	PIFA (1.8)	DCE	79
6	$TMSN_3$ (3)	PIFA (1.8)	DCM	86
7	$TMSN_3$ (3)	PIFA (1.8)	EtOAc	86
8	$TMSN_3$ (2.5)	PIFA (1.5)	EtOAc	90
9	$TMSN_3$ (1.5)	PIFA (1.5)	EtOAc	75
10	$TMSN_3$ (2.5)		EtOAc	N. R.
11[b]	$TMSN_3$ (2.5)	PIFA (1.5)	EtOAc	90

[a] All reactions were carried out on a 0.3 mmol scale in 3 mL of solvent in 15 mL pressure tubes at ambient temperature for 4 h. Isolated yield. N. R. = no reaction. [b] 10 min instead of 4 h.

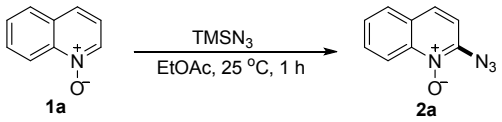
Control experiment



Scheme S1. The generation of benzophenone from 1, 1-diphenylethylene with azide radical.

To a 15 mL tube with a stir bar was added 1, 1-diphenylethylene (54 mg, 0.3 mmol), $TMSN_3$ (86 mg, 0.75 mmol). EtOAc (3 mL) was added, followed by PIFA (194 mg, 0.45 mmol). The mixture was stirred at 25 ºC for 1 h, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford benzophenone (23 mg, 43% yield).

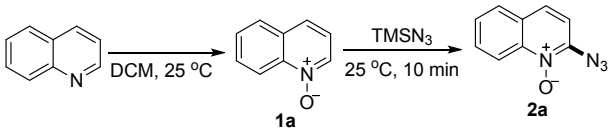
Experimental Procedure for the Scale up Experiment in 10 mmol



Scheme S2. Gram-scale synthesis of **2a**.

To a 250 mL flask with a stir bar was added quinoline N–oxides **1a** (1.45 g, 10 mmol), $TMSN_3$ (2.87 g, 25 mmol) and EtOAc (100 mL). Then PIFA (6.45 g, 15 mmol) was added slowly in batches of 3 mmol in 10 min intervals. The mixture was still stirred at 25 ºC for additional 10 min, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford the desired product **2a** (1.49 g, 80% yield).

Experimental Procedure for One-pot Synthesis of 2-Azidequinoline N–Oxide

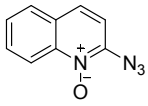


Scheme S3. One-pot synthesis of **2a** from quinoline.

To a 15 mL tube with a stir bar was added quinoline (39 mg, 0.3 mmol) and CH_2Cl_2 (3 mL), followed by 3-chlorobenzoperoxoic acid (57 mg, 0.33 mmol). The mixture was stirred at 25 ºC for 1 h. Then $TMSN_3$ (86 mg, 0.75 mmol) and PIFA (194 mg, 0.45 mmol) was added. The mixture was stirred at 25 ºC for 10 min, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford the desired product **2a** (39 mg, 70% yield).

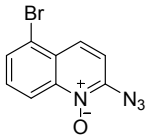
Experimental Procedures and Data of the Quinoline N–Oxides

To a 15 mL tube with a stir bar was added quinoline N–oxide **1** (0.3 mmol), azidotrimethylsilane (86 mg, 0.75 mmol). EtOAc (3 mL) was added, followed by iodobenzene bis(trifluoroacetate) (194 mg, 0.45 mmol). The mixture was stirred at 25 ºC for 10 min, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford the desired product **2**.



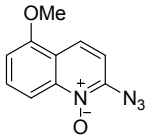
2a

2-Azidoquinoline N–oxide: 50 mg of **2a** was obtained from **1a** (44 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.6 Hz, 1 H), 7.79–7.73 (m, 2 H), 7.63 (d, *J* = 8.9 Hz, 1 H), 7.58–7.54 (m, 1 H), 6.92 (d, *J* = 8.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.7, 131.0, 128.1, 127.5, 127.2, 126.9, 118.1, 114.7; HRMS (ESI) Calcd for $C_9H_7N_4O$ [M+H$^+$] 187.0614, Found 187.0610.



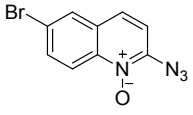
2b

2-Azido-5-bromoquinoline N–oxide: 49 mg of **2b** was obtained from **1b** (67 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.8 Hz, 1 H), 7.98 (d, *J* = 9.3 Hz, 1 H), 7.82 (d, *J* = 7.6 Hz, 1 H), 7.61–7.55 (m, 1 H), 7.02 (d, *J* = 9.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.3, 131.4, 131.1, 126.6, 126.2, 122.5, 118.0, 115.5; HRMS (ESI) Calcd for $C_9H_5BrN_4NaO$ [M+Na$^+$] 286.9539, Found 286.9532.



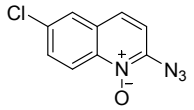
2c

2-Azido-5-methoxyquinoline N–oxide: 40 mg of **2c** was obtained from **1c** (53 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1 H), 8.04 (d, *J* = 9.2 Hz, 1 H), 7.66 (t, *J* = 8.4 Hz, 1 H), 6.92–6.87 (m, 2 H), 4.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 141.7, 141.5, 131.6, 122.7, 119.2, 113.2, 109.9, 105.9, 56.0; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 239.0539, Found 235.0533.



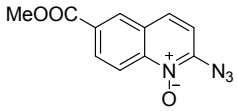
2d

2-Azido-6-bromoquinoline N–oxide: 64 mg of **2d** was obtained from **1d** (67 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.2 Hz, 1 H), 7.96 (d, *J* = 2.0 Hz, 1 H), 7.83 (dd, *J* = 9.2, 2.0 Hz, 1 H), 7.55 (d, *J* = 9.0 Hz, 1 H), 6.97 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.7, 134.3, 130.1, 128.0, 126.1, 121.7, 120.0, 116.0; HRMS (ESI) Calcd for $C_9H_5N_4NaO$ [M+Na$^+$] 286.9539, Found 286.9533.



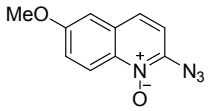
2e

2-Azido-6-chloroquinoline N–oxide: 48 mg of **2e** was obtained from **1e** (54 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.2 Hz, 1 H), 7.79 (d, *J* = 2.1 Hz, 1 H), 7.70 (dd, *J* = 9.2, 2.2 Hz, 1 H), 7.55 (d, *J* = 9.0 Hz, 1 H), 6.98 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.4, 133.7, 131.6, 127.6, 126.8, 126.1, 112.0, 116.0; HRMS (ESI) Calcd for $C_9H_5ClN_4NaO$ [M+Na$^+$] 243.0068, Found 243.0044.



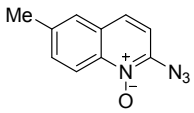
2f

2-Azido-6-(methoxycarbonyl)quinoline N–oxide: 61 mg of **2f** was obtained from **1f** (61 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 9.1 Hz, 1 H), 8.54 (d, *J* = 1.7 Hz, 1 H), 8.35 (dd, *J* = 9.1, 1.8 Hz, 1 H), 7.74 (d, *J* = 9.0 Hz, 1 H), 7.02 (d, *J* = 9.0 Hz, 1 H), 4.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.7, 142.4, 130.8, 130.8, 129.2, 128.5, 126.2, 118.5, 115.6, 52.6; HRMS (ESI) Calcd for $C_{11}H_8N_4NaO_3$ [M+Na$^+$] 267.0489, Found 267.0478.



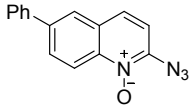
2g

2-Azido-6-methoxyquinoline N–oxide: 40 mg of **2g** was obtained from **1g** (53 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 9.5 Hz, 1 H), 7.54 (d, *J* = 9.0 Hz, 1 H), 7.38 (dd, *J* = 9.5, 2.7 Hz, 1 H), 7.07 (d, *J* = 2.6 Hz, 1 H), 6.91 (d, *J* = 9.0 Hz, 1 H), 3.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.1, 136.6, 128.2, 126.4, 122.7, 119.9, 115.3, 106.6, 55.7; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO_2$ [M+Na$^+$] 239.0539, Found 239.0538.



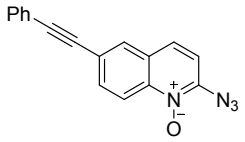
2h

2-Azido-6-methylquinoline N–oxide: 42 mg of **2h** was obtained from **1h** (48 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.8 Hz, 1 H), 7.59–7.54 (m, 3 H), 6.90 (d, *J* = 9.0 Hz, 1 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.5, 137.7, 133.1, 127.2, 127.0, 126.8, 118.0, 114.7, 21.2; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 223.0590, Found 223.0581.



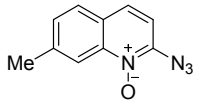
2i

2-Azido-6-phenylquinoline N–oxide: 70 mg of **2i** was obtained from **1i** (66 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 9.0 Hz, 1 H), 8.01 (dd, *J* = 9.0, 1.9 Hz, 1 H), 7.96 (d, *J* = 1.8 Hz, 1 H), 7.72–7.65 (m, 3 H), 7.53–7.47 (m, 2 H), 7.46–7.39 (m, 1 H), 6.97 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.5, 140.2, 139.2, 130.6, 129.1, 128.2, 127.34, 127.32, 127.2, 125.7, 118.8, 115.1; HRMS (ESI) Calcd for $C_{15}H_{11}N_4O$ [M+Na$^+$] 263.0927, Found 263.0920.



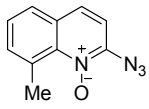
2j

2-Azido-6-(phenylethynyl)quinoline N–oxide: 57 mg of **2j** was obtained from **1j** (74 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.0 Hz, 1 H), 7.96 (d, *J* = 1.3 Hz, 1 H), 7.86 (dd, *J* = 9.0, 1.6 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.58–7.55 (m, 2 H), 7.39–7.37 (m, 3 H), 6.96 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.1, 133.8, 131.7, 131.0, 128.9, 128.5, 126.8, 126.7, 122.9, 122.5, 118.4, 115.5, 91.9, 87.8; HRMS (ESI) Calcd for $C_{17}H_{11}N_4O$ [M+H$^+$] 287.0927, Found 287.0917.



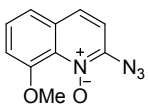
2k

2-Azido-7-methylquinoline N–oxide: 42 mg of **2k** was obtained from **1k** (48 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 7.67 (d, *J* = 8.3 Hz, 1 H), 7.59 (d, *J* = 8.9 Hz, 1 H), 7.38 (d, *J* = 8.3 Hz, 1 H), 6.86 (d, *J* = 8.9 Hz, 1 H), 2.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.9, 140.8, 129.5, 127.8, 127.4, 124.9, 117.3, 113.6, 22.1; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 223.0590, Found 223.0585.



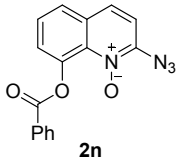
2l

2-Azido-8-methylquinoline N–oxide: 40 mg of **2l** was obtained from **1l** (48 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2 H), 7.43–7.41 (m, 1 H), 7.38–7.34 (m, 1 H), 6.88 (d, *J* = 8.9 Hz, 1 H), 3.13 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.5, 134.3, 131.9, 128.7, 128.1, 127.1, 126.9, 114.4, 24.5; HRMS (ESI) Calcd for $C_{10}H_9N_4O$ [M+H$^+$] 201.0771, Found 201.0770.



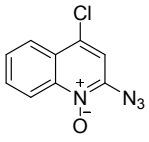
2m

2-Azido-8-methoxyquinoline N–oxide: 52 mg of **2m** was obtained from **1m** (53 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 6.89 (d, *J* = 9.0 Hz, 1 H), 4.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 142.5, 132.8, 129.8, 127.6, 127.5, 120.6, 114.9, 111.8, 56.8; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 223.0590, Found 223.0594.



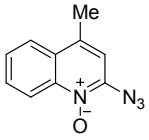
2n

2-Azido-8-(benzoyloxy)quinoline N–oxide: 37 mg of **2n** was obtained from **1n** (80 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.26 (m, 2 H), 7.72–7.70 (m, 1 H), 7.66–7.61 (m, 2 H), 7.57–7.51 (m, 3 H), 7.44–7.41 (m, 1 H), 6.95 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 142.7, 142.0, 134.5, 133.4, 130.5, 129.8, 129.5, 128.5, 127.3, 126.8, 126.7, 125.1, 115.1; HRMS (ESI) Calcd for $C_{16}H_{10}N_4NaO_3$ [M+Na$^+$] 329.0645, Found 329.0641.



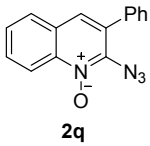
2o

2-Azido-4-chloroquinoline N–oxide: 35 mg of **2o** was obtained from **1o** (54 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.7 Hz, 1 H), 8.14 (dd, *J* = 8.4, 0.8 Hz, 1 H), 7.85–7.81 (m, 1 H), 7.69–7.65 (m, 1 H), 7.06 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.7, 131.9, 131.7, 128.2, 125.2, 124.7, 118.6, 114.5; HRMS (ESI) Calcd for $C_9H_5N_4NaOCl$ [M+Na$^+$] 243.0044, Found 243.0038.



2p

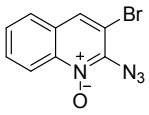
2-Azido-4-methylquinoline N–oxide: 41 mg of **2p** was obtained from **1p** (48 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.7 Hz, 1 H), 7.91 (d, *J* = 8.3 Hz, 1 H), 7.80–7.76 (m, 1 H), 7.63–7.59 (m, 1 H), 6.80 (s, 1 H), 2.62 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 140.1, 138.5, 131.3, 127.4, 126.5, 124.7, 118.4, 114.8, 18.4; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 223.0590, Found 223.0595.



2q

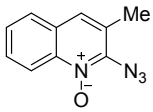
2-Azido-3-phenylquinoline N–oxide: 77 mg of **2q** was obtained from **1q** (66 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.7 Hz, 1 H), 7.86–7.75 (m, 2 H), 7.67 (s, 1 H), 7.64–7.58 (m, 1 H), 7.56–7.44 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.8, 135.5, 130.9, 129.3,

129.1, 128.8, 128.5, 128.1, 127.8, 127.8, 126.0, 118.2; HRMS (ESI) Calcd for $C_{15}H_{10}N_4NaO$ [M+Na$^+$] 285.0747, Found 285.0749.



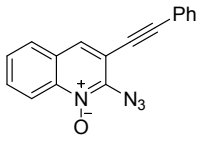
2r

2-Azido-3-bromoquinoline N–oxide: 65 mg of **2r** was obtained from **1r** (67 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.7 Hz, 1 H), 7.94 (s, 1 H), 7.81–7.70 (m, 2 H), 7.63–7.56 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 140.0, 131.2, 130.0, 128.3, 127.2, 126.0, 118.4, 107.7; HRMS (ESI) Calcd for $C_9H_5BrN_4ONa$ [M+Na$^+$] 286.9539, Found 286.9536.



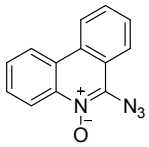
2s

2-Azido-3-methylquinoline N–oxide: 49 mg of **2s** was obtained from **1s** (48 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 1 H), 7.72–7.67 (m, 2 H), 7.56–7.51 (m, 1 H), 7.48 (s, 1 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.2, 129.8, 127.4, 127.2, 126.9, 126.0, 124.8, 117.9, 17.9; HRMS (ESI) Calcd for $C_{10}H_8N_4NaO$ [M+Na$^+$] 223.0590, Found 223.0594.



2t

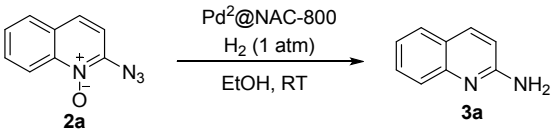
2-Azido-3-(phenylethynyl)quinoline N–oxide: 69 mg of **2t** was obtained from **1t** (74 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 9.1 Hz, 1 H), 7.82 (s, 1 H), 7.75–7.71 (m, 2 H), 7.63–7.54 (m, 3 H), 7.41–7.36 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.1, 131.8, 131.4, 130.1, 129.2, 128.5, 128.4, 127.9, 125.7, 121.9, 118.1, 111.2, 96.4, 82.6; HRMS (ESI) Calcd for $C_{17}H_{11}N_4O$ [M+H$^+$] 287.0927, Found 287.0916.



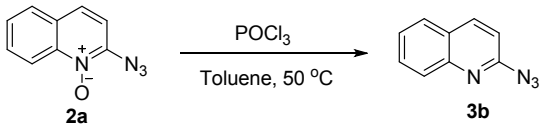
2u

6-Azidophenanthridine N–oxide: 60 mg of **2u** was obtained from **1u** (59 mg, 0.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1 H), 8.43 (d, *J* = 7.9 Hz, 1 H), 8.40 (d, *J* = 8.2 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.79–7.74 (m, 1 H), 7.73–7.66 (m, 2 H), 7.65–7.59 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.8, 129.9, 129.9, 128.7, 128.0, 127.1, 124.3, 123.4, 122.5, 122.0, 120.9, 118.9; HRMS (ESI) Calcd for $C_{13}H_9N_4O$ [M+H$^+$] 237.0771, Found 237.0773.

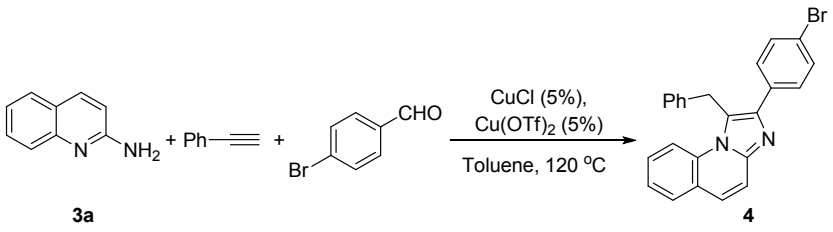
The Functionalization of 2-Azidoquinoline N–Oxide



To a 15 mL tube with a stir bar was added 2-azidoquinoline N–oxide **2a** (56 mg, 0.3 mmol), Pd^2@NAC-800 (80 mg, 0.015 mmol). EtOH (3 mL) was added, and purged with hydrogen (1 atm). The mixture was stirred at 25 ºC for 24 h, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to afford the desired product **3a** (37 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.83 (m, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.62 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.56 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1 H), 7.29–7.23 (m, 1 H), 6.71 (dd, *J* = 8.8, 5.7 Hz, 1 H), 4.88 (s broad, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 147.7, 138.1, 129.7, 127.5, 126.0, 123.6, 122.7, 111.7.



To a 15 mL tube with a stir bar was added 2-azidoquinoline N–oxide **2a** (56 mg, 0.3 mmol) and toluene (3 mL), followed by $POCl_3$ (69 mg, 0.45 mmol). The mixture was stirred at 50 ºC for 4 h, and 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 (PE/EA) to afford the desired product **3b** (37 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1 H), 7.96 (t, *J* = 9.0 Hz, 2 H), 7.86 (t, *J* = 8.8 Hz, 2 H), 7.71 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 133.3, 131.2, 130.8, 128.9, 128.0, 123.8, 116.8, 112.6; HRMS (ESI) Calcd for $C_9H_7N_2$ [M+H$^+$–N_2] 143.0609, Found 143.0604.



To a 15 mL tube with a stir bar was added quinolin-2-amine **3a** (43 mg, 0.3 mmol), ethynylbenzene (34 mg, 0.33 mmol), 4-bromobenzaldehyde (61 mg, 0.33 mmol) and toluene (3 mL), followed by CuCl (2 mg, 5 mol% mmol) and $Cu(OTf)_2$ (5 mg, 5 mol% mmol). The mixture was stirred at 120 ºC for 12 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 (PE/EA) to afford the desired product **4** (80 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 1 H), 7.73 (dd, *J* = 7.4, 1.9 Hz, 1 H), 7.60 (d, *J* = 9.3 Hz, 1 H), 7.56–7.45 (m, 5 H), 7.35–7.21 (m, 7 H), 4.75 (s, 2 H); ^{13}C NMR (100 MHz,

CDCl3) δ 144.5, 143.7, 138.0, 134.1, 133.4, 131.6, 129.9, 129.3, 129.2, 128.2, 127.9, 127.0, 126.7, 124.6, 124.4, 121.8, 121.7, 117.4, 116.4, 33.0; HRMS (ESI) calcd for $C_{24}H_{18}BrN_2$ [M+H$^+$] 413.0648, found 413.0653.

EPR Experiments

Procedure for EPR Investigation of 1a, $TMSN_3$ and PIFA in EtOAc.

Quinoline N–oxide **1a** (44 mg, 0.3 mmol) and $TMSN_3$ (86 mg, 0.75 mmol) were dissolved in 3 mL EtOAc, followed by PIFA (194 mg, 0.45 mmol). Then 20 uL of this solution was taken out into a small tube and analyzed by EPR at room temperature (Figure S1).

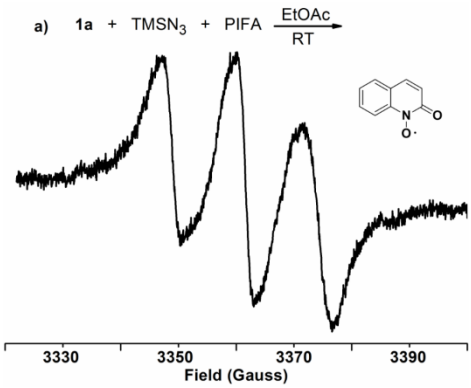


Figure S1. EPR spectra from the reaction between **1a**, $TMSN_3$ and PIFA in EtOAc at room temperature.

Procedure for EPR Investigation of 1a and PIFA in EtOAc.

Quinoline N–oxide **1a** (43.5 mg, 0.3 mmol) was dissolved in 3 mL EtOAc, followed by PIFA (194 mg, 0.45 mmol). Then 20 uL of this solution was taken out into a small tube and analyzed by EPR at room temperature (Figure S2).

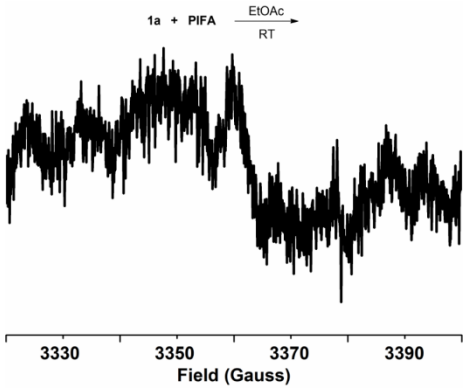


Figure S2. EPR spectra of **1a** and PIFA in EtOAc at room temperature.

Procedure for EPR Investigation of $TMSN_3$ and PIFA in EtOAc.

$TMSN_3$ (86 mg, 0.75 mmol) was dissolved in 3 mL EtOAc, followed by PIFA (194 mg, 0.45 mmol). Then 20 uL of this solution was taken out into a small tube and analyzed by EPR at room temperature (Figure S3).

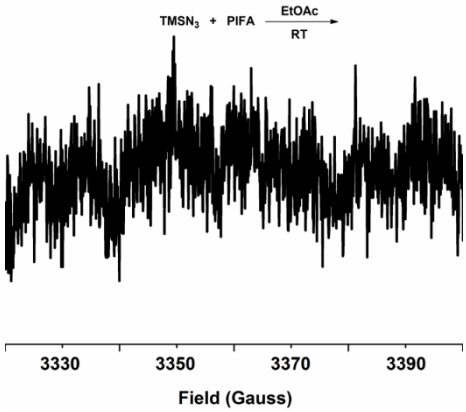


Figure S3. EPR spectra of $TMSN_3$ and PIFA in EtOAc at room temperature.

Procedure for EPR Investigation of 1a, $TMSN_3$, PIFA and MNP in EtOAc.

Quinoline N–oxide **1a** (43.5 mg, 0.3 mmol), $TMSN_3$ (86 mg, 0.75 mmol) and MNP (10 mg, 0.06 mmol) were dissolved in 3 mL EtOAc, followed by PIFA (194 mg, 0.45 mmol). Then 20 uL of this solution was taken out into a small tube and analyzed by EPR at room temperature (Figure S4–6).

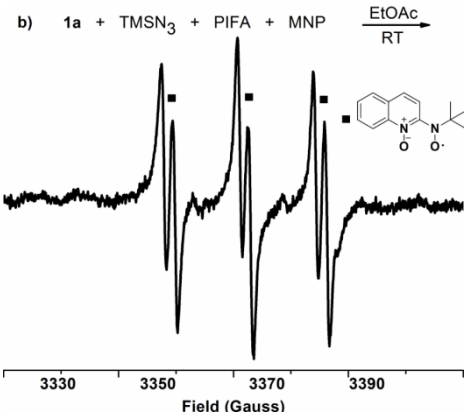


Figure S4. EPR spectra of **1a**, $TMSN_3$, PIFA and MNP in EtOAc at room temperature.

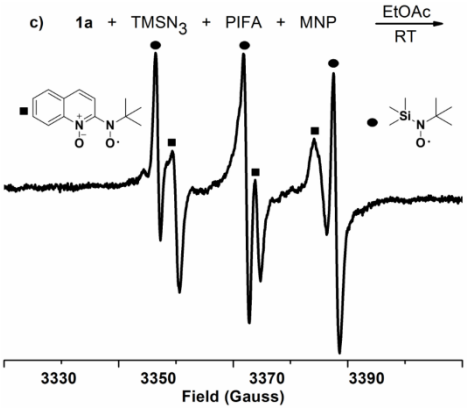


Figure S5. Ten minutes later, EPR spectra of **1a**, $TMSN_3$, PIFA and MNP in EtOAc at room temperature.

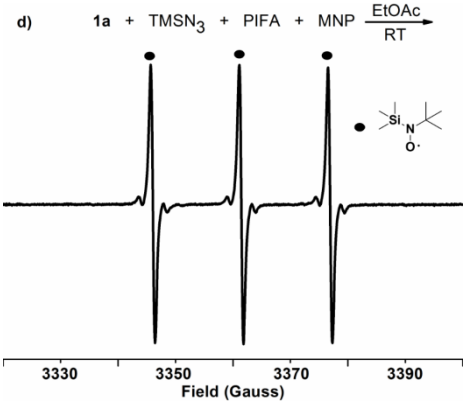


Figure S6. Four hour later, EPR spectra of **1a**, $TMSN_3$, PIFA and MNP in EtOAc at room temperature.

Procedure for EPR Investigation of $TMSN_3$, PIFA and MNP in EtOAc.

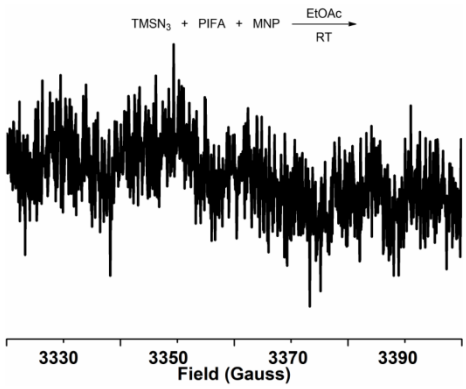
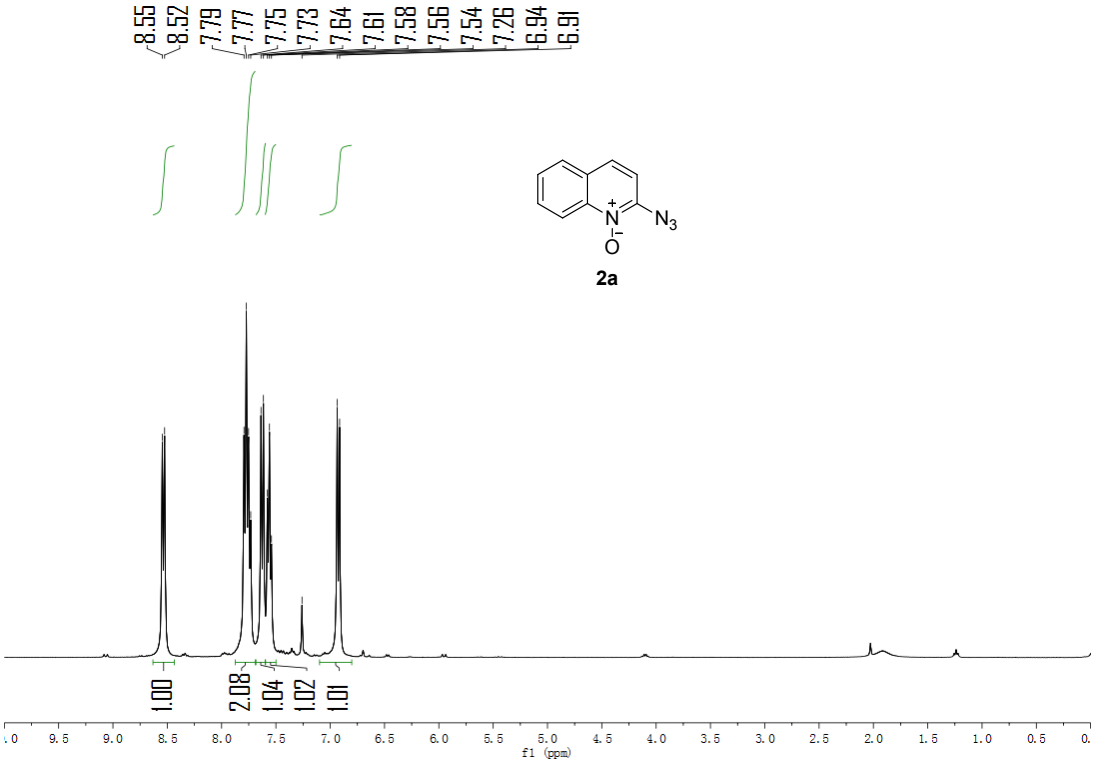
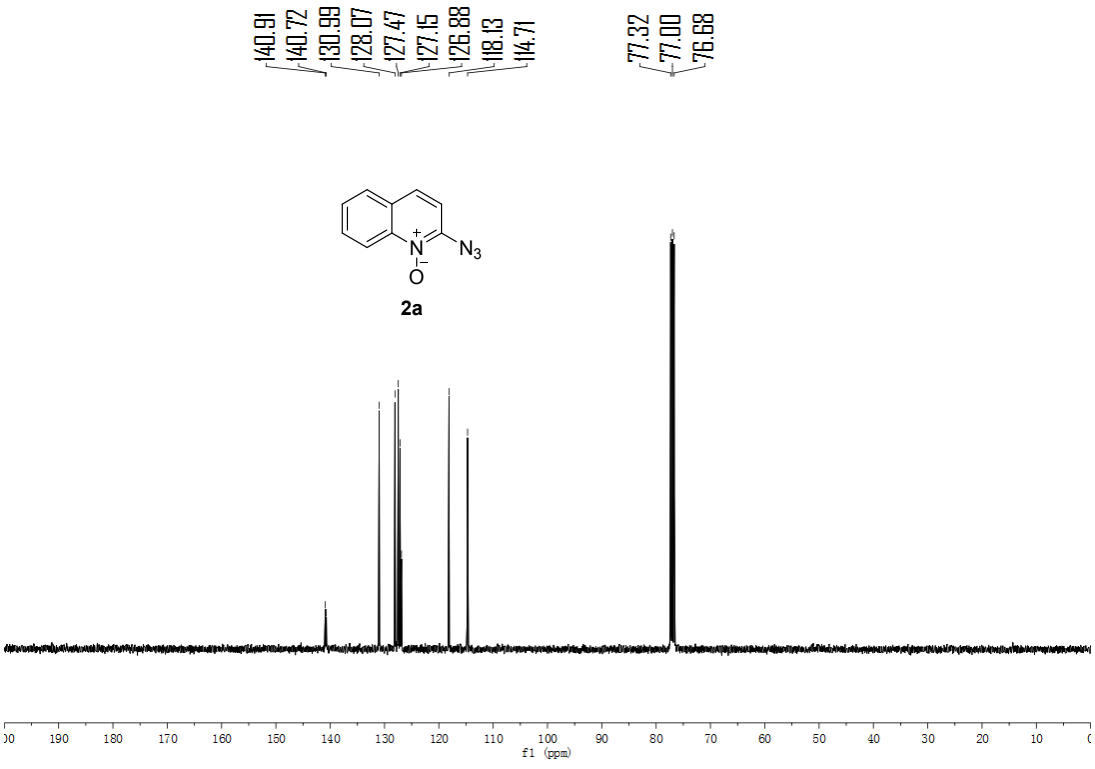
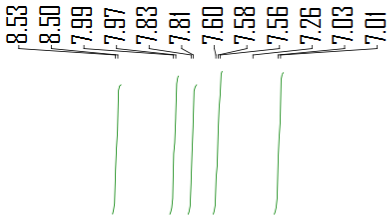


Figure S6. EPR spectra of $TMSN_3$, PIFA and MNP in EtOAc at room temperature.

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



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7.58
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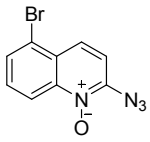
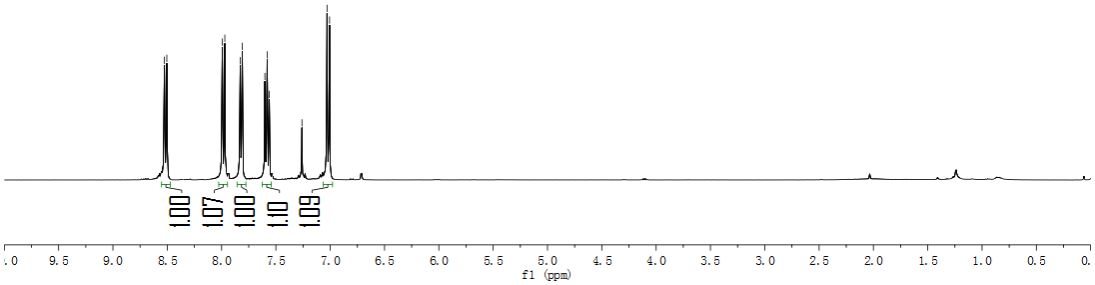
7.26
7.03
7.01


Br
N3
O

2b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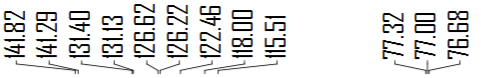
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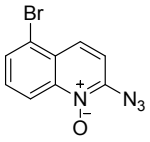
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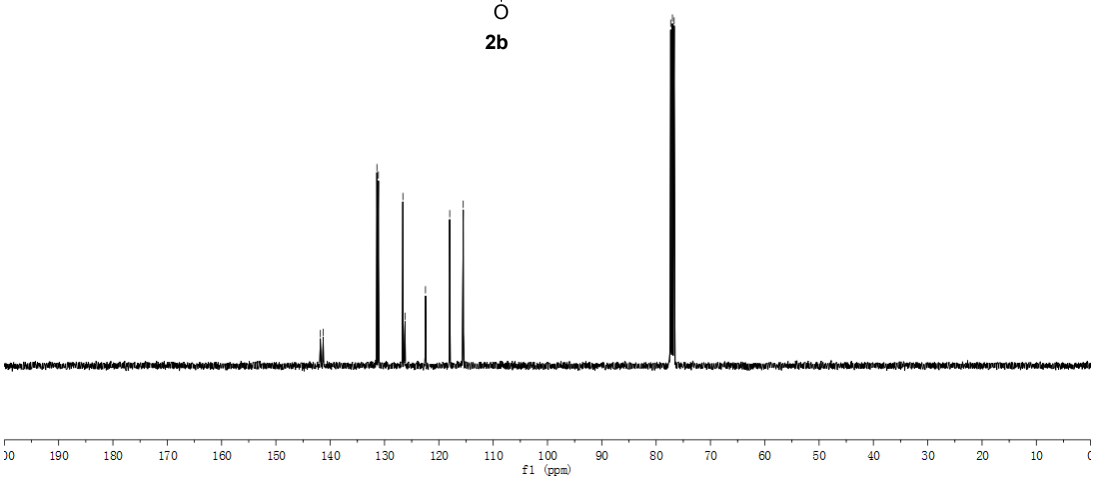
N3
O

2b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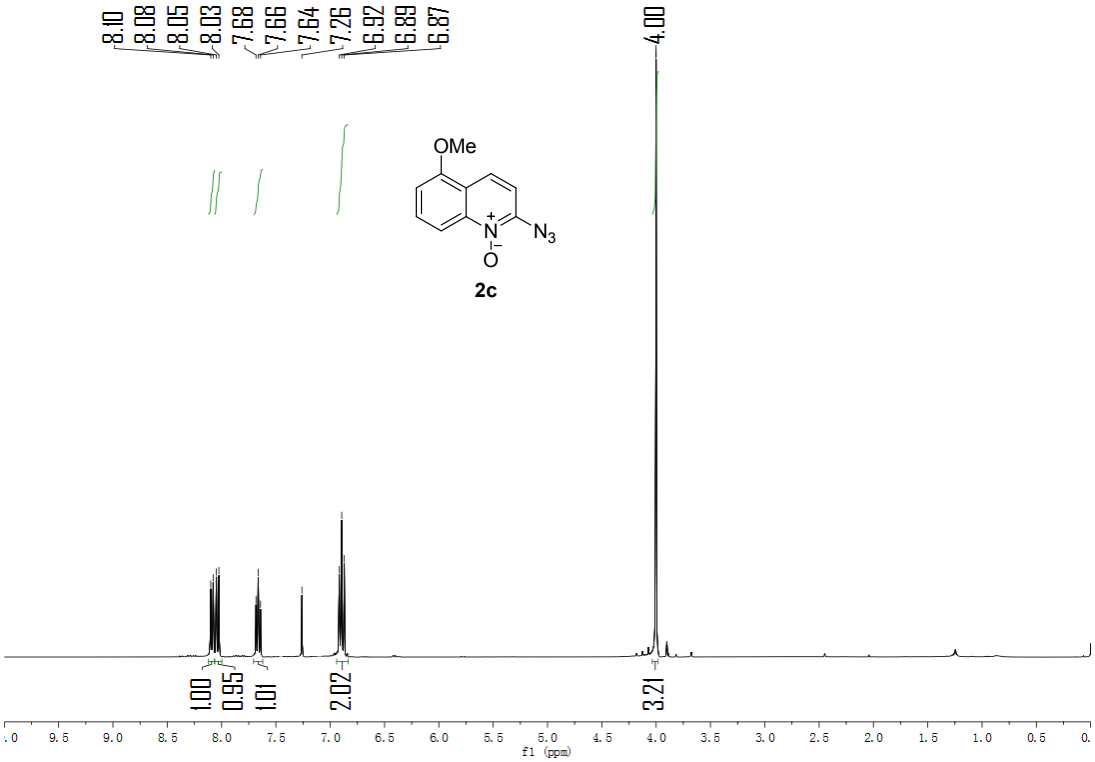
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2c
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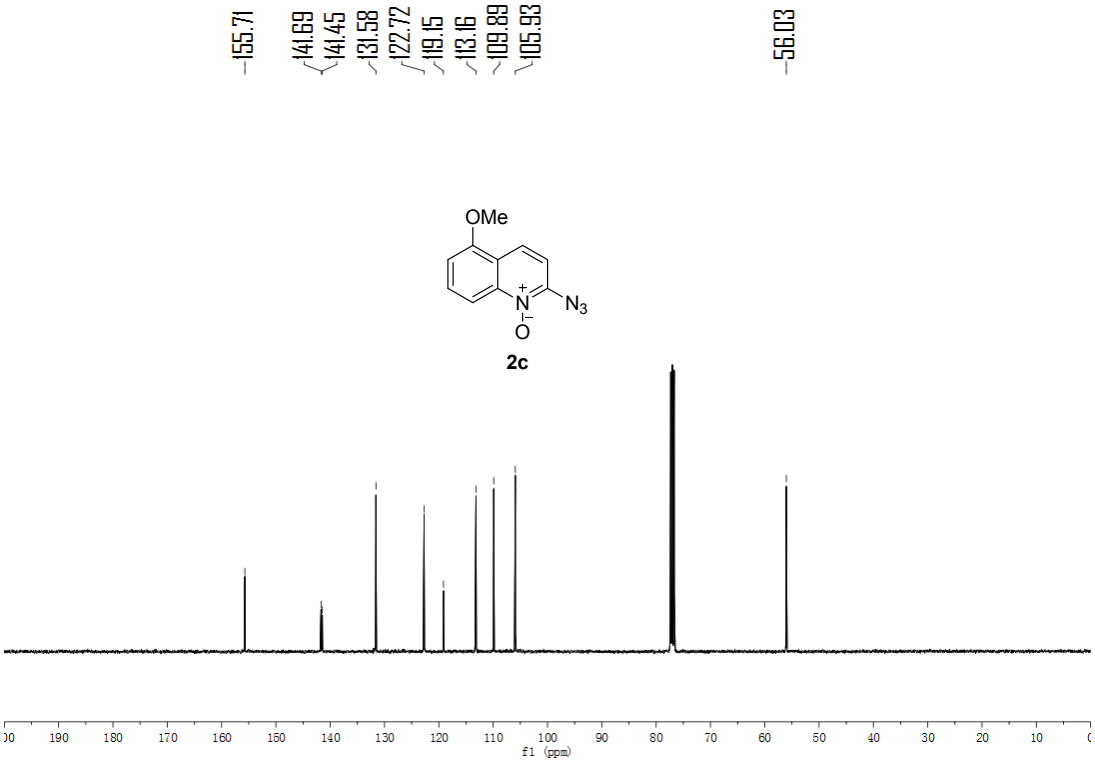
f1 (ppm)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OMe
N3
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7.82
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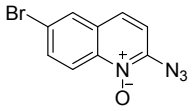
6.96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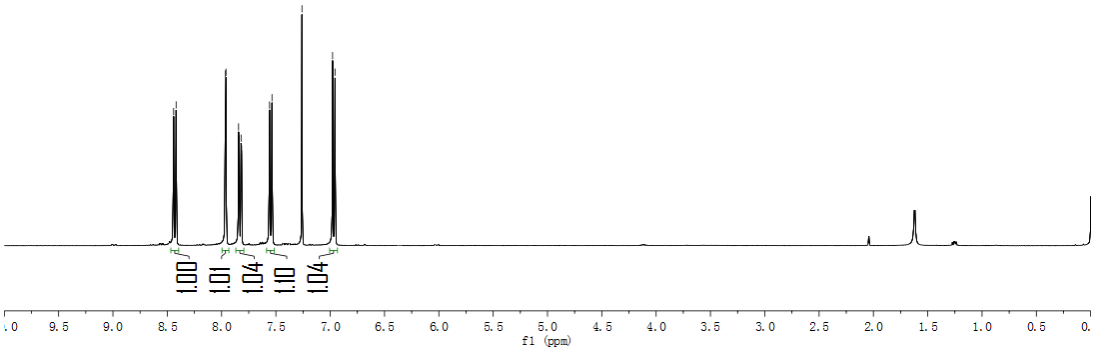
2d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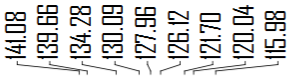
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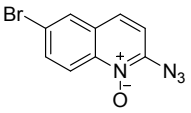
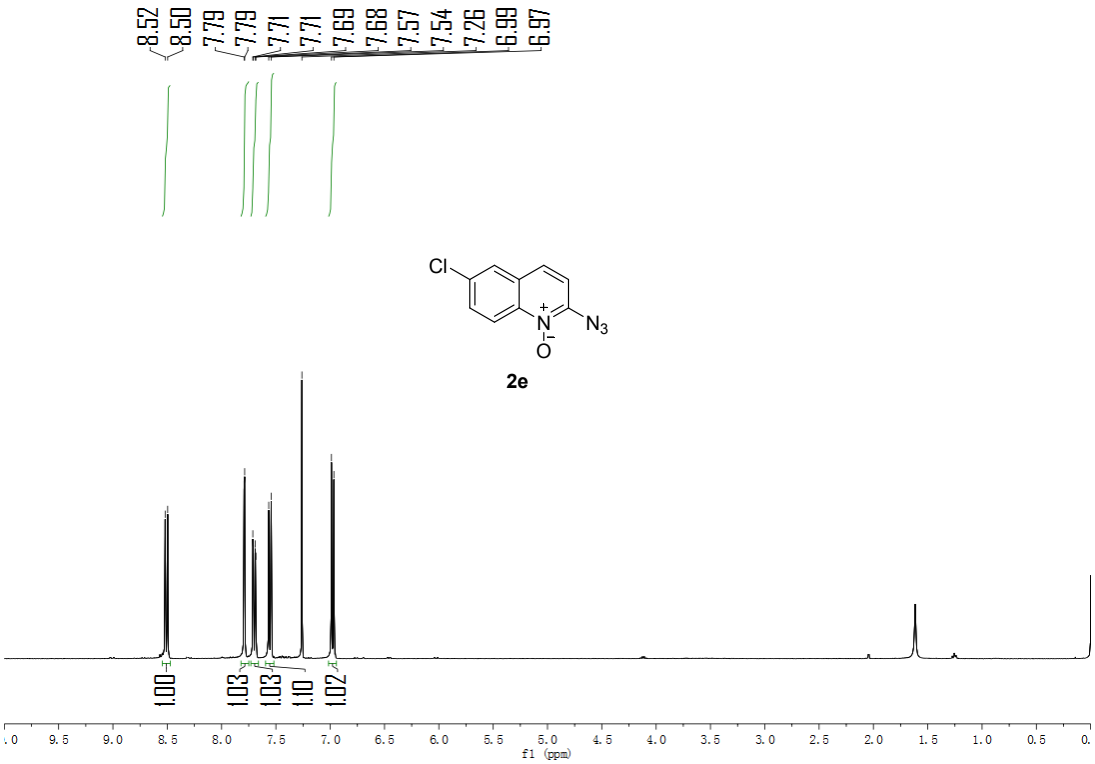

Br
N
O
N3

2d

f1 (ppm)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O
N3
2e
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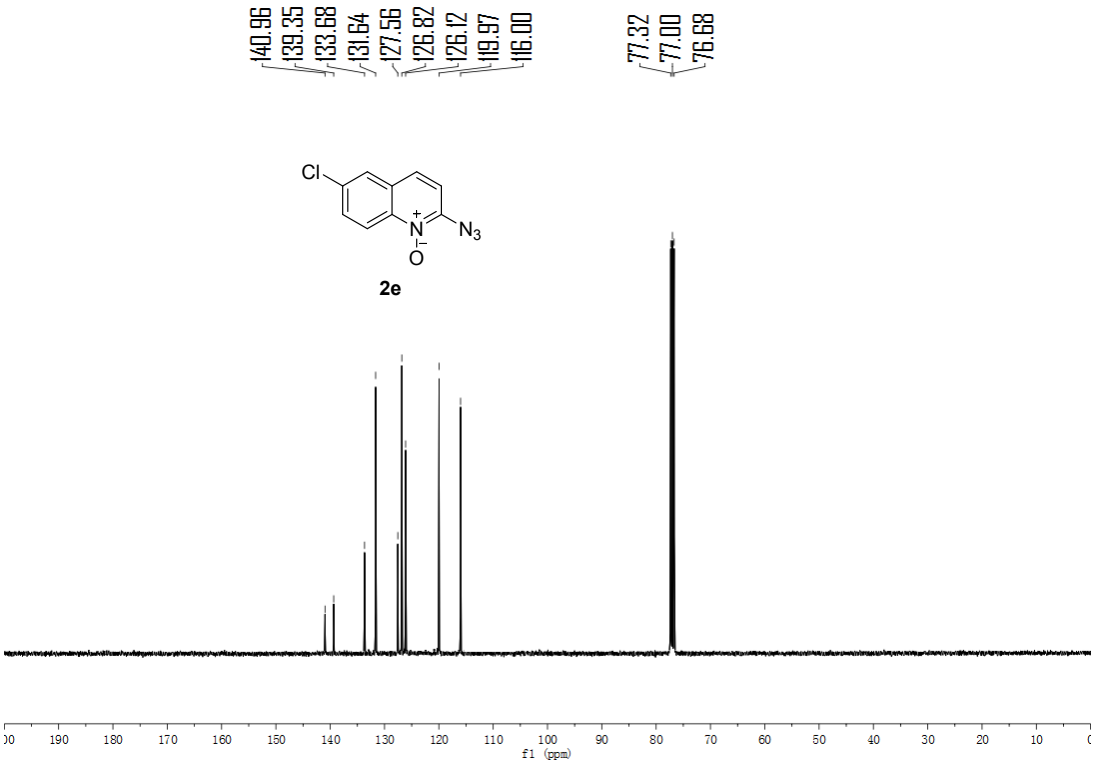
1.02
f1 (ppm)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Cl
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O
N3
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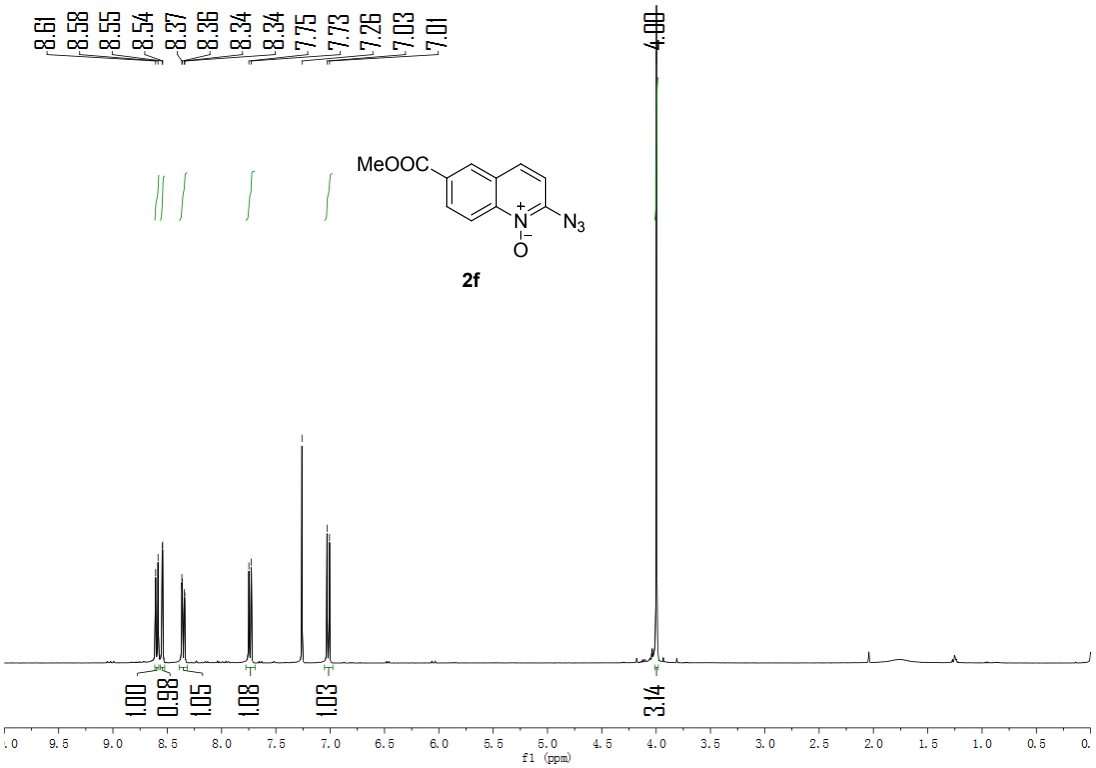
f1 (ppm)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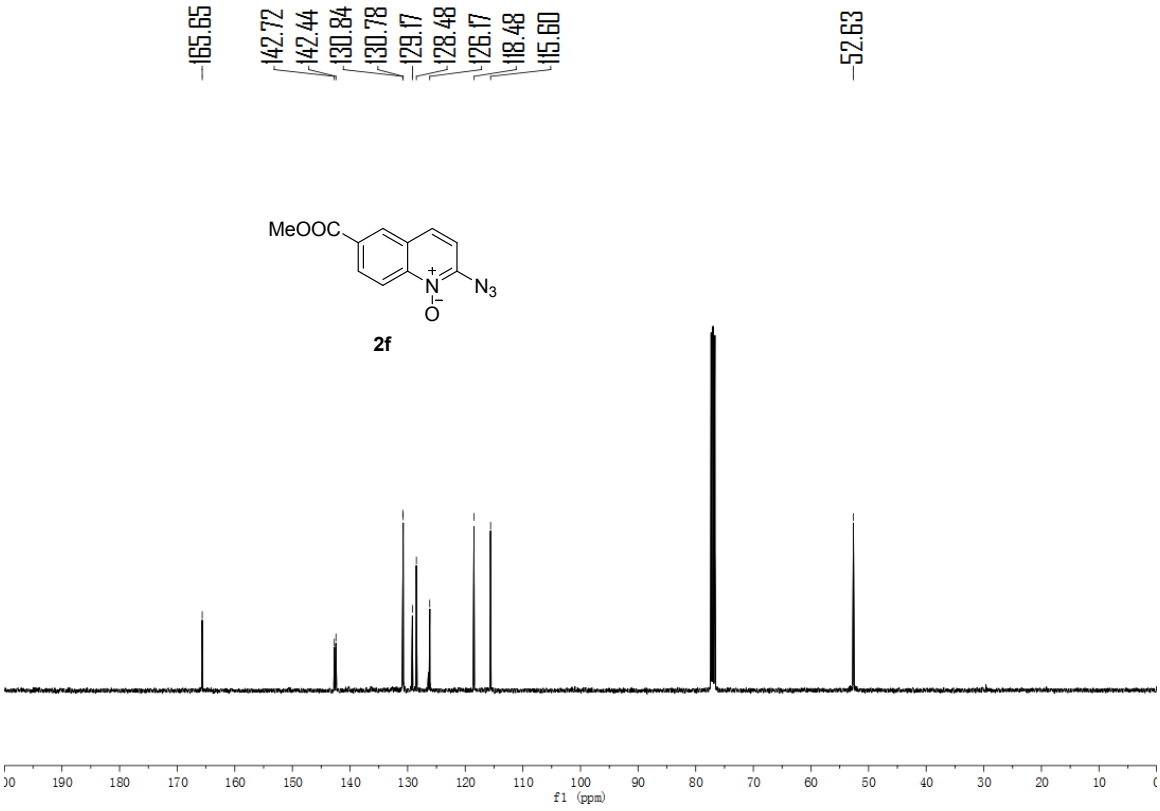
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MeOOC
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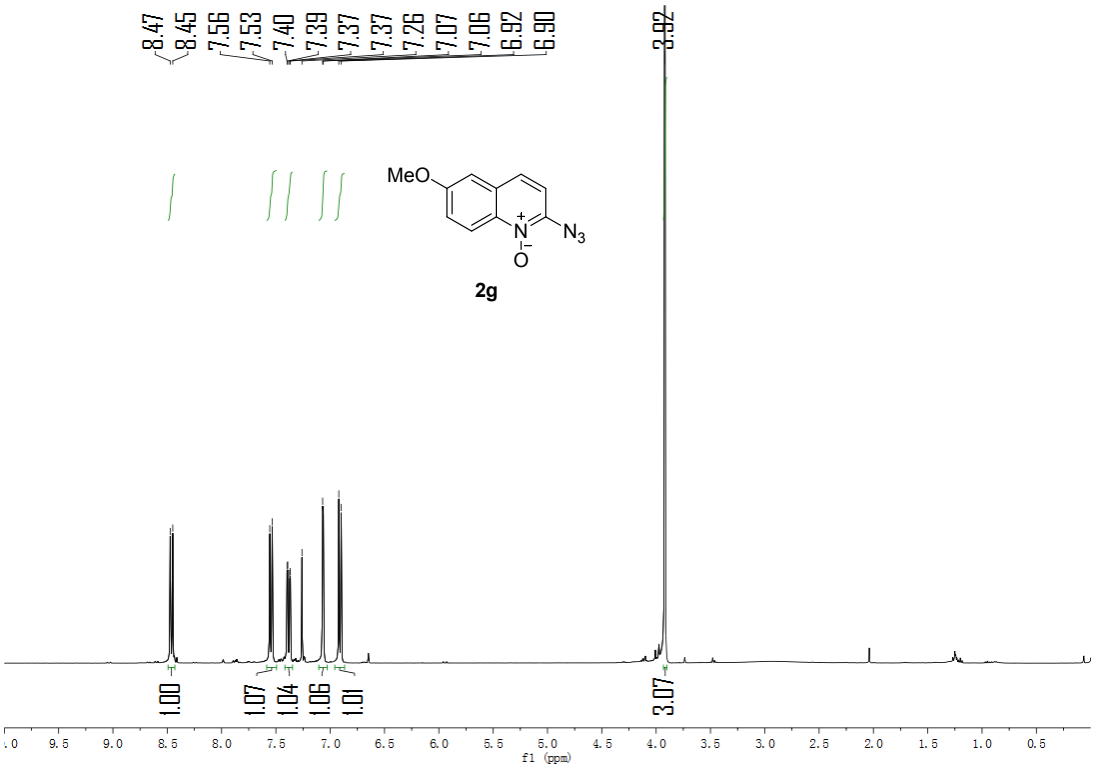
f1 (ppm)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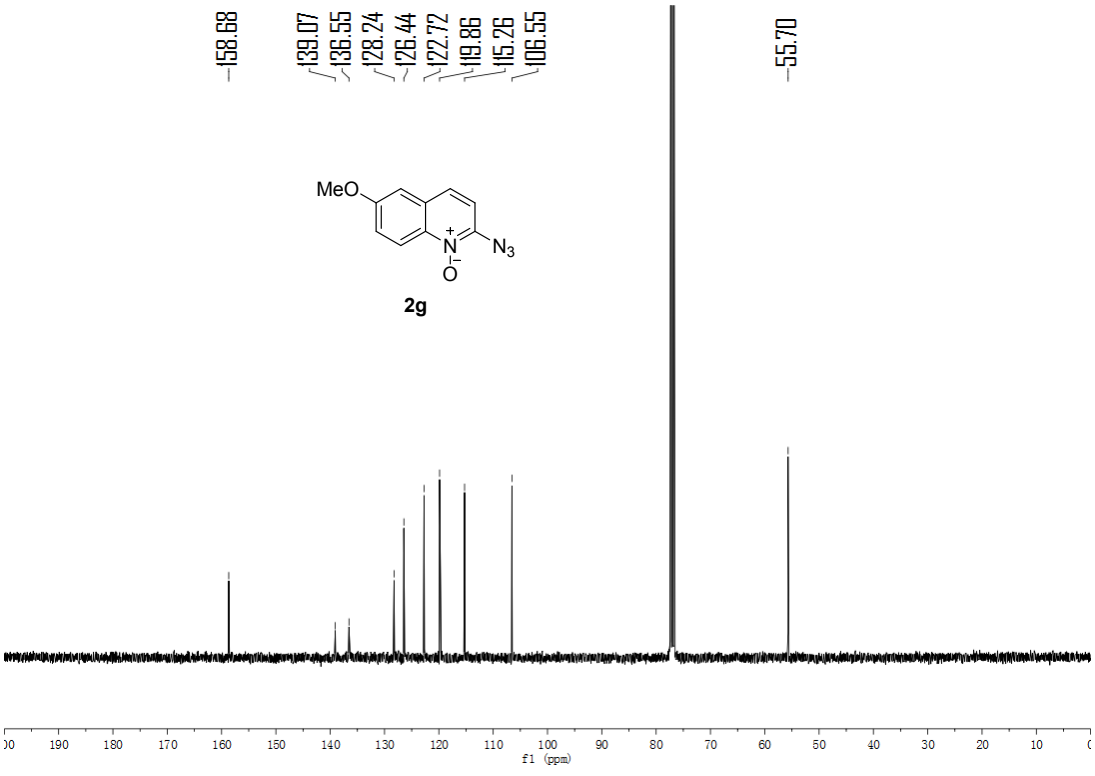
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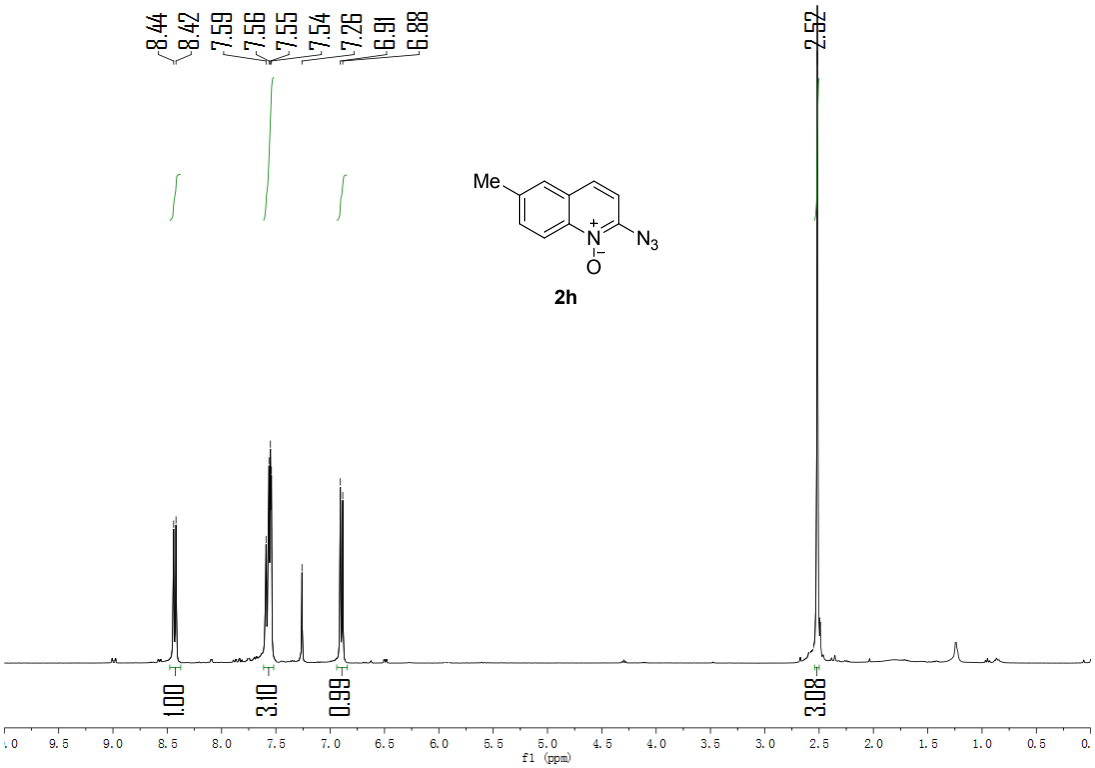
f1 (ppm)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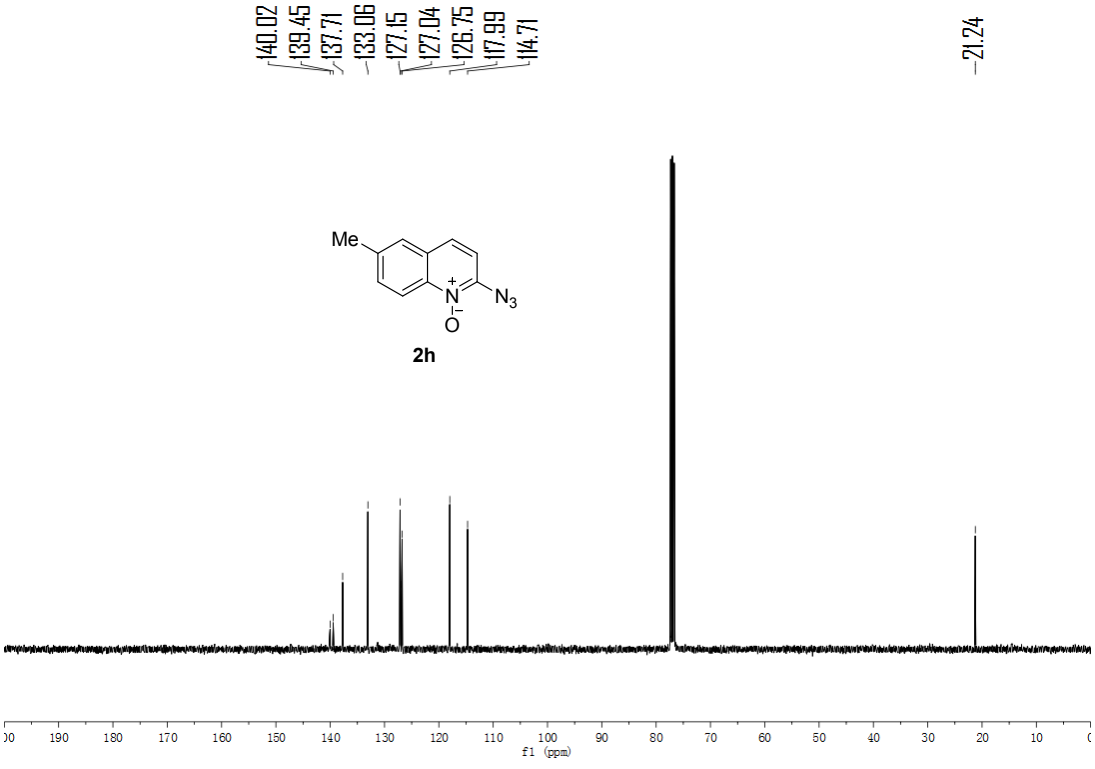
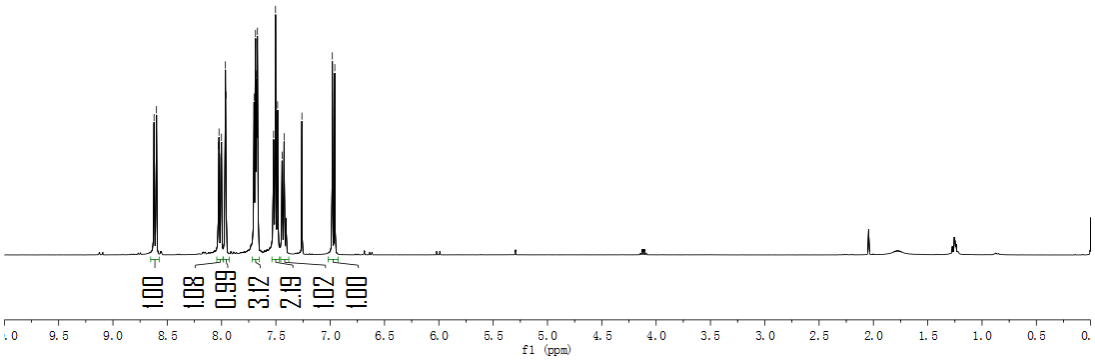
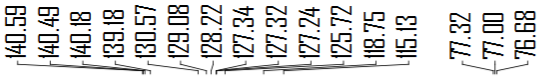
N
O
N3
2h
1.00
3.10
0.99
3.08
f1 (ppm)

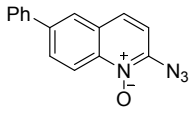

140.02
139.45
137.71
133.06
127.15
127.04
126.75
117.99
114.71
21.24
Me
N
O
N3
2h
f1 (ppm)


8.62
8.60
8.03
8.02
8.01
8.00
7.96
7.96
7.70
7.69
7.69
7.68
7.67
7.52
7.50
7.50
7.48
7.44
7.42
7.26
6.98
6.96
Ph
N3
O

2i

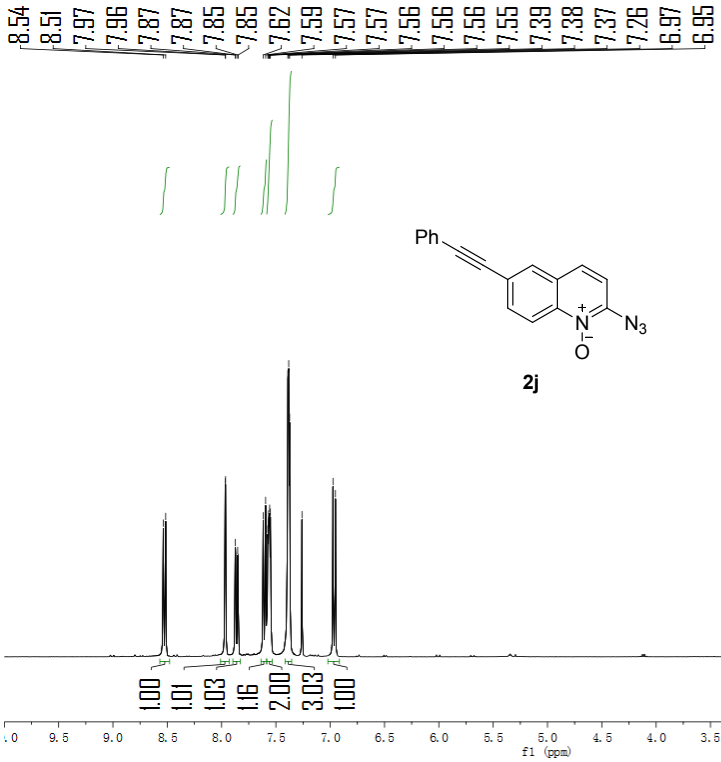

1.00
1.08
0.99
3.12
2.19
1.02
1.00
f1 (ppm)

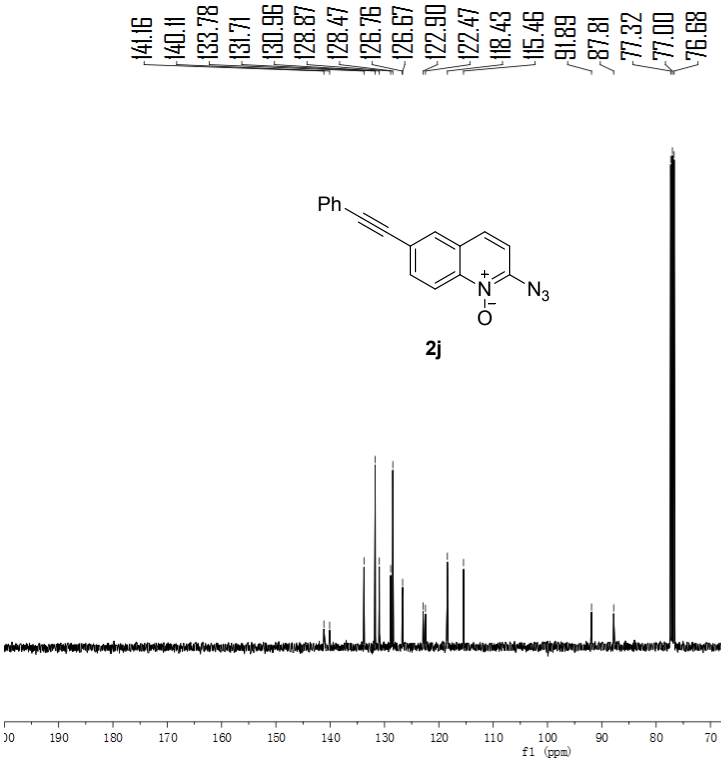

140.59
140.49
140.18
139.18
130.57
129.08
128.22
127.34
127.32
127.24
125.72
118.75
115.13
77.32
77.00
76.68

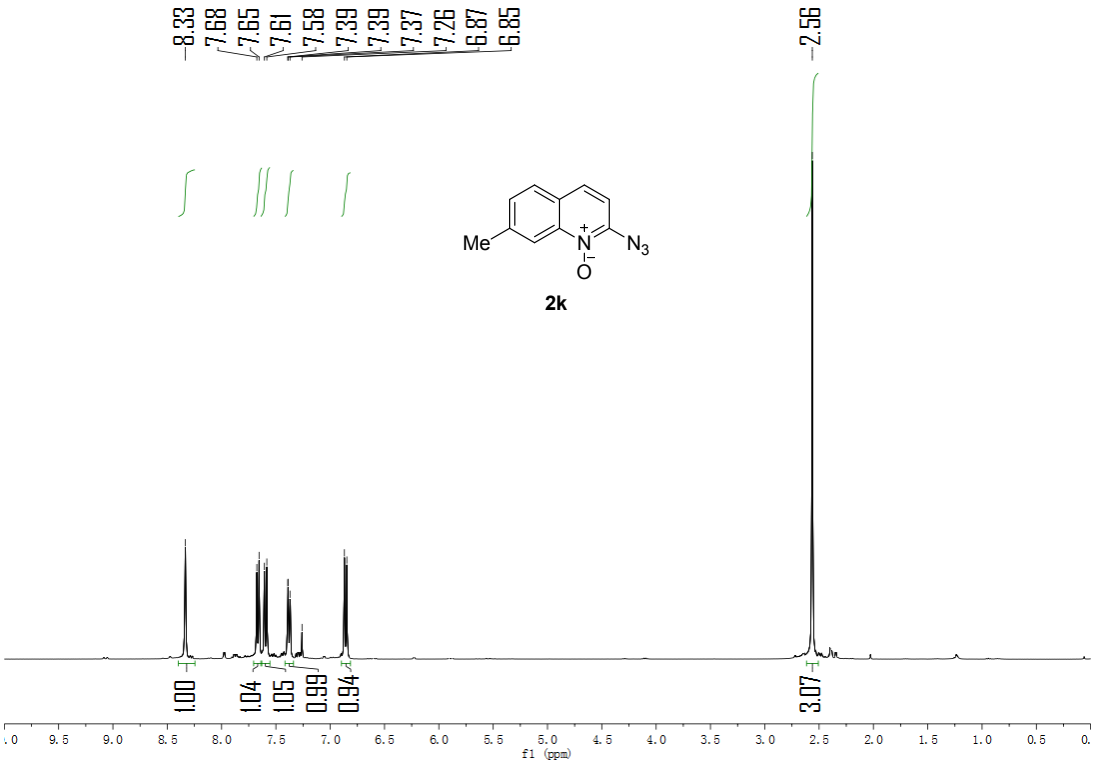

Ph
N3
O

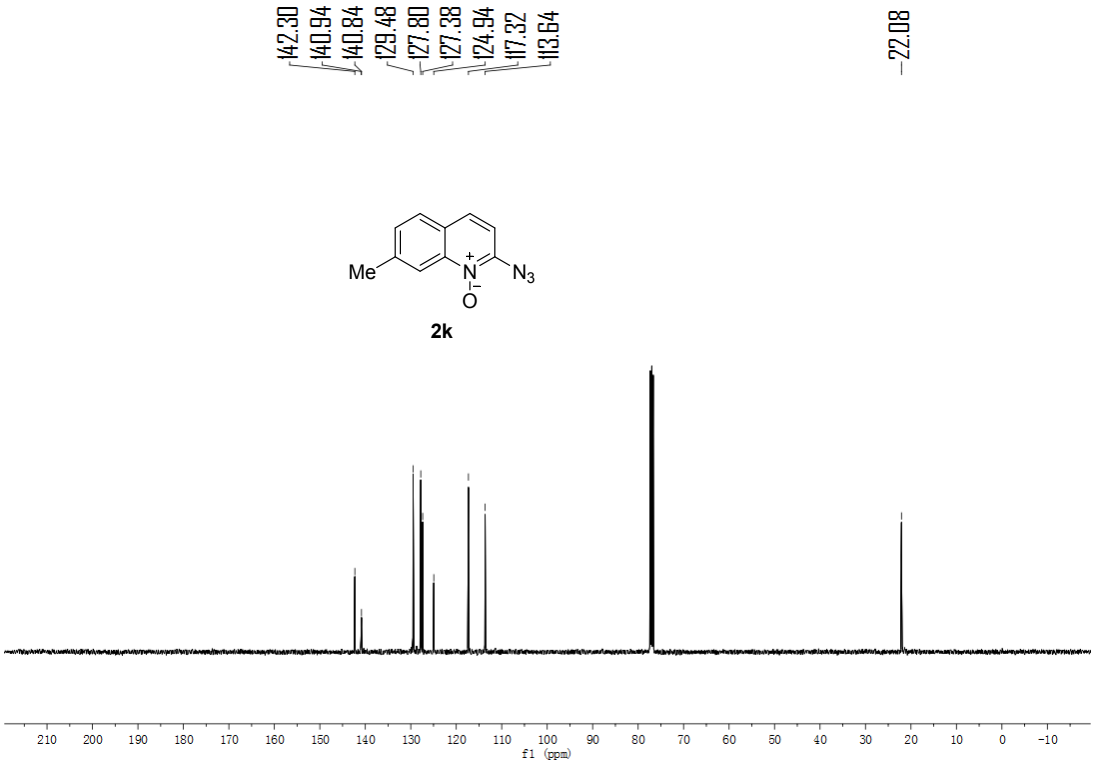
2i

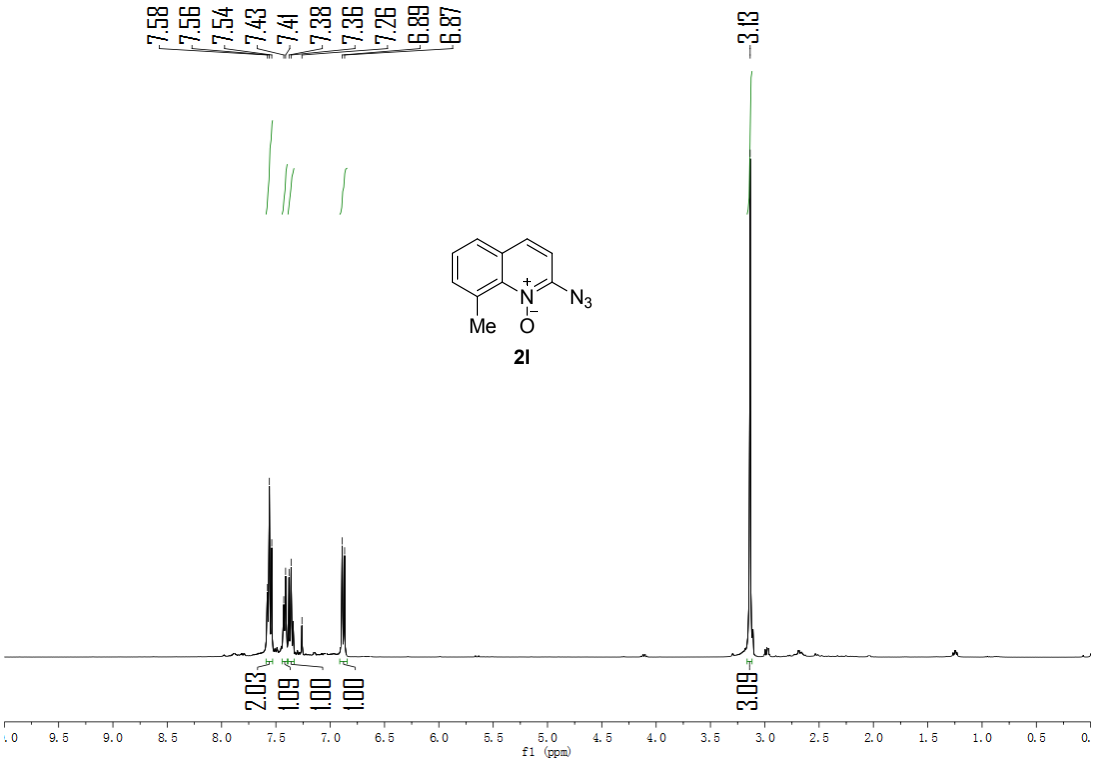
f1 (ppm)

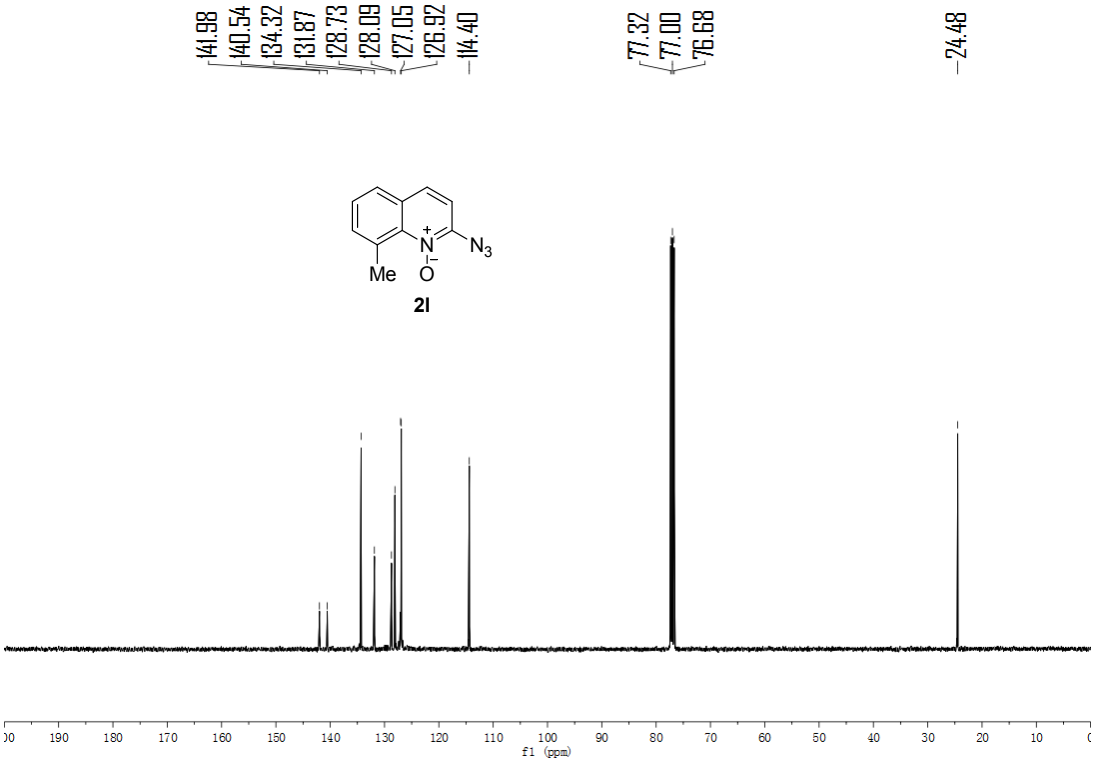

8.54
8.51
7.97
7.96
7.87
7.87
7.85
7.85
7.62
7.59
7.57
7.57
7.56
7.56
7.56
7.55
7.39
7.38
7.37
7.26
6.97
6.95
Ph
N3
O
2j
1.00
1.01
1.03
1.16
2.00
3.03
1.00
f1 (ppm)

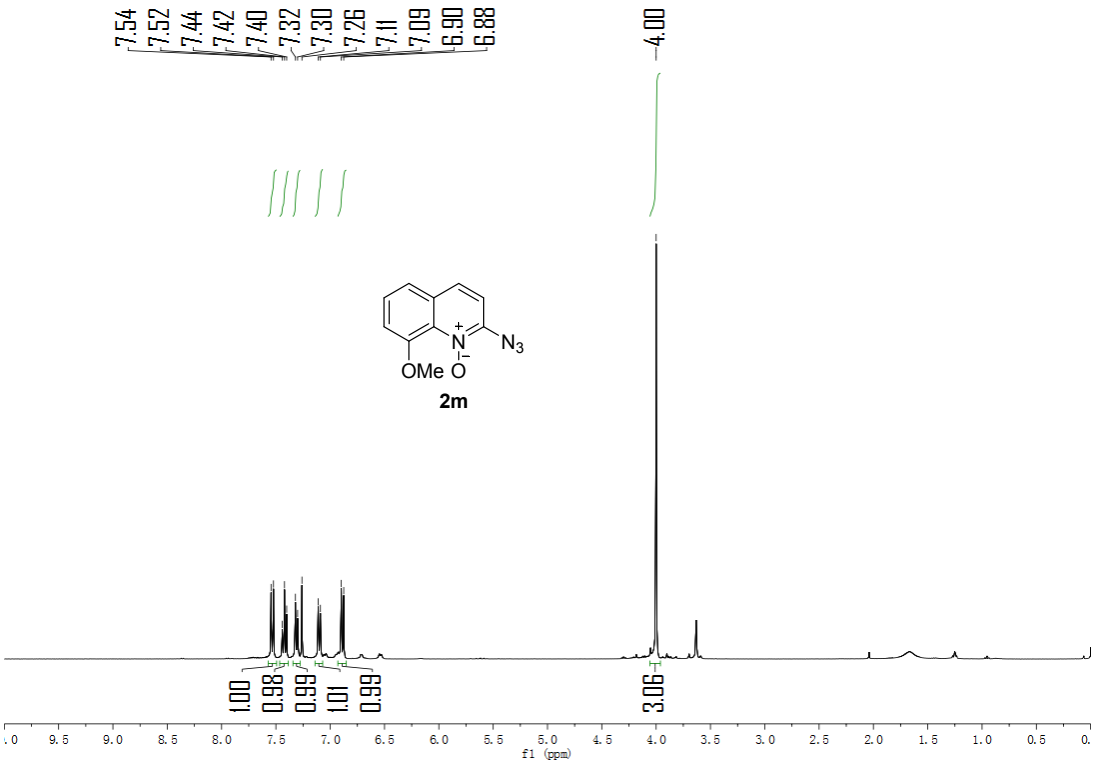

144.16
140.11
133.78
131.71
130.96
128.87
128.47
126.76
126.67
122.90
122.47
118.43
115.46
91.89
87.81
77.32
77.00
76.68
Ph
N3
O
2j
f1 (ppm)

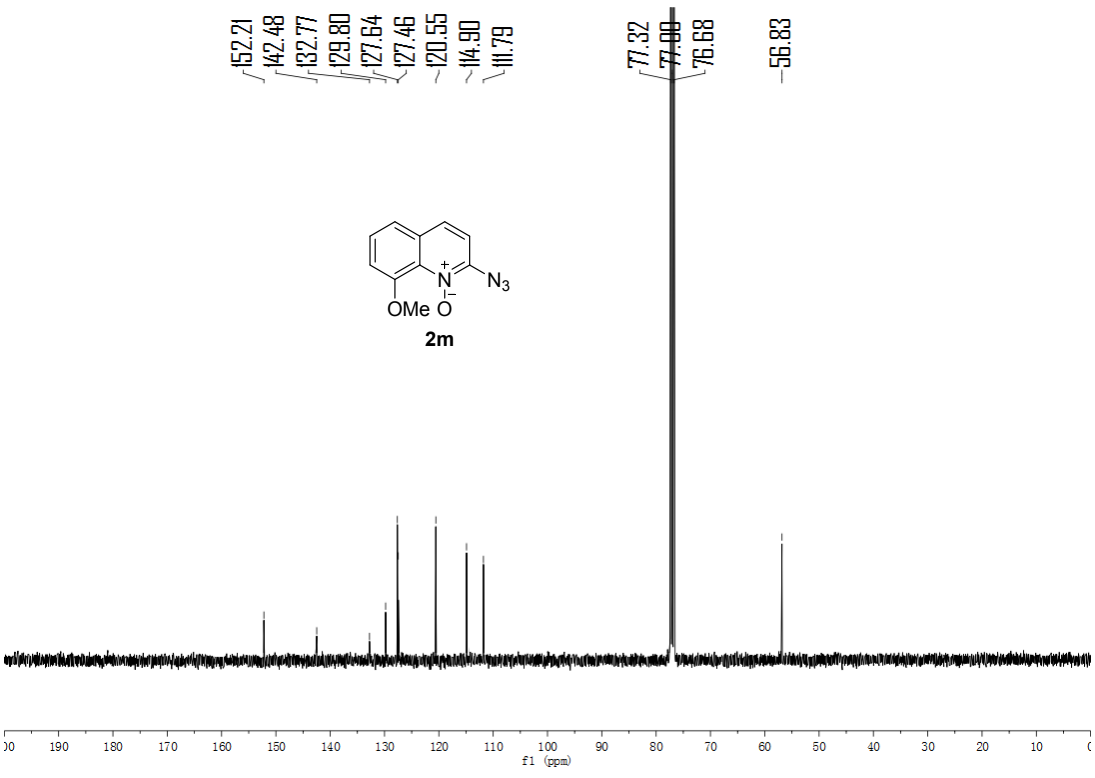

8.33
7.68
7.65
7.61
7.58
7.39
7.39
7.37
7.26
6.87
6.85
2.56
Me
N
O
N3
2k
1.00
1.04
1.05
0.99
0.94
3.07
f1 (ppm)

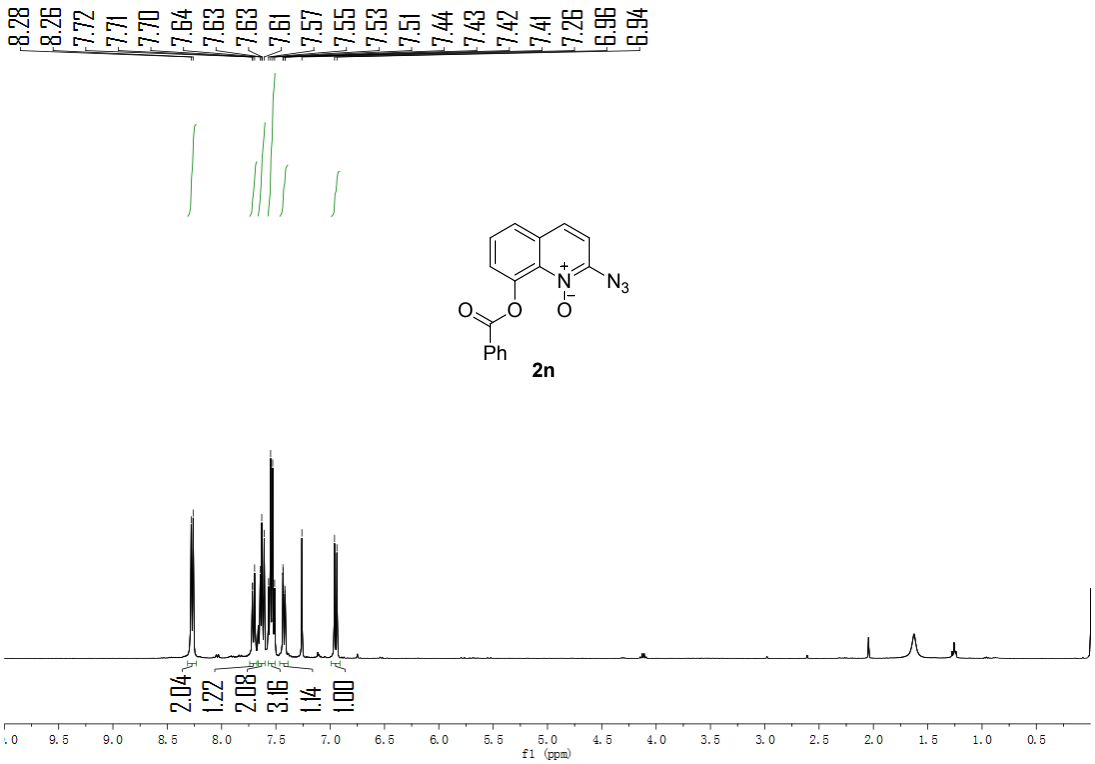

142.30
140.94
140.84
129.48
127.80
127.38
124.94
117.32
113.64
22.08
Me
N
O
N3
2k
f1 (ppm)


7.58
7.56
7.54
7.43
7.41
7.38
7.36
7.26
6.89
6.87
3.13
Me
O
N3
2l
2.03
1.09
1.00
1.00
3.09
f1 (ppm)

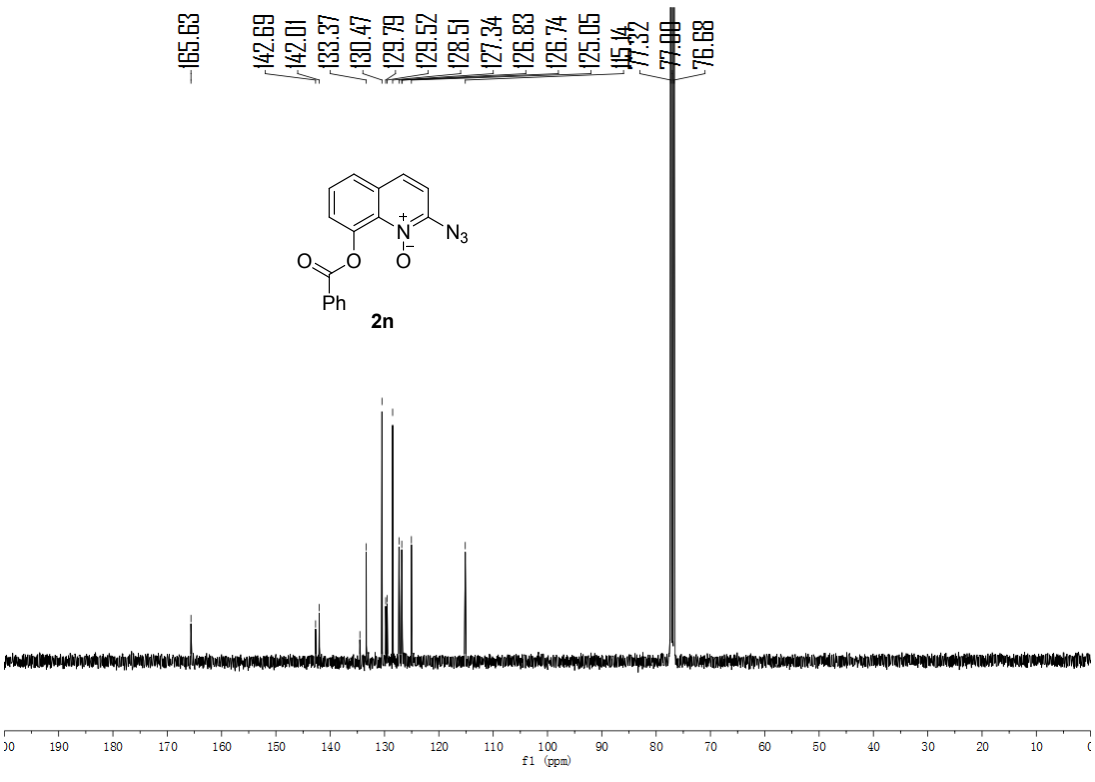

141.98
140.54
134.32
131.87
128.73
128.09
127.05
126.92
114.40
77.32
77.00
76.68
24.48
Me
O
N3
2l
f1 (ppm)


7.54
7.52
7.44
7.42
7.40
7.32
7.30
7.26
7.11
7.09
6.90
6.88
4.00
N3
OMe O
2m
1.00
0.98
0.99
1.01
0.99
3.06
f1 (ppm)

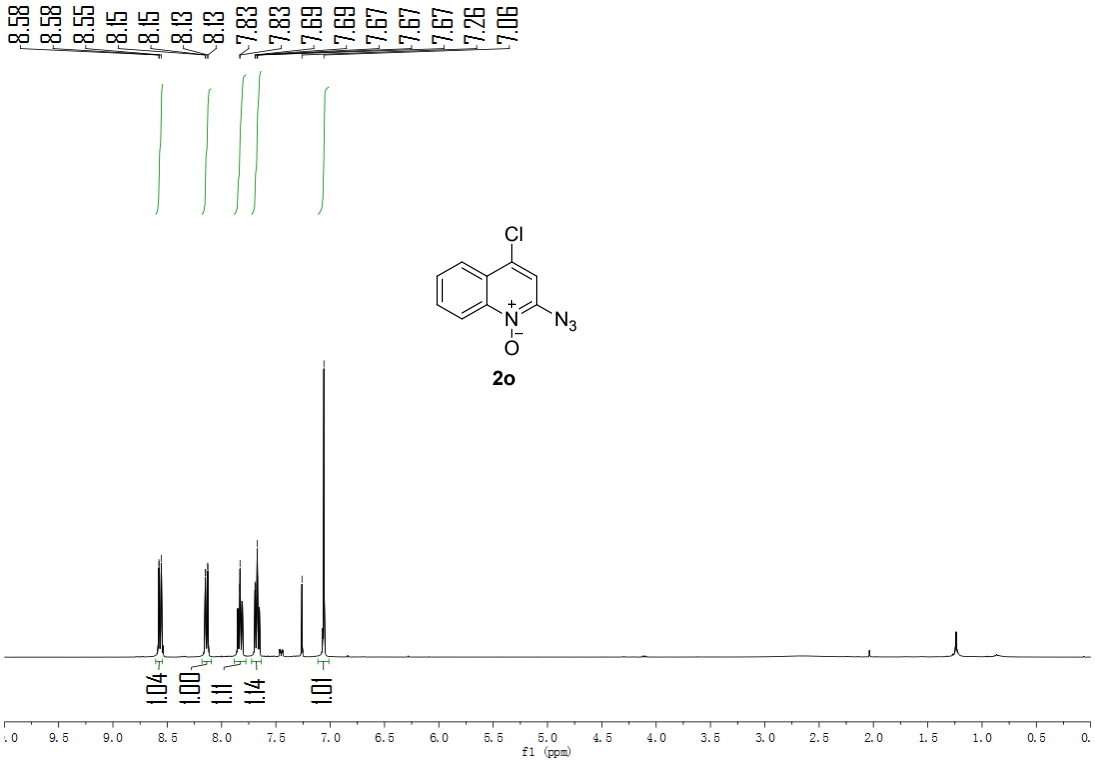

152.21
142.48
132.77
129.80
127.64
127.46
120.55
114.90
111.79
77.32
77.00
76.68
56.83
N3
OMe O
2m
f1 (ppm)

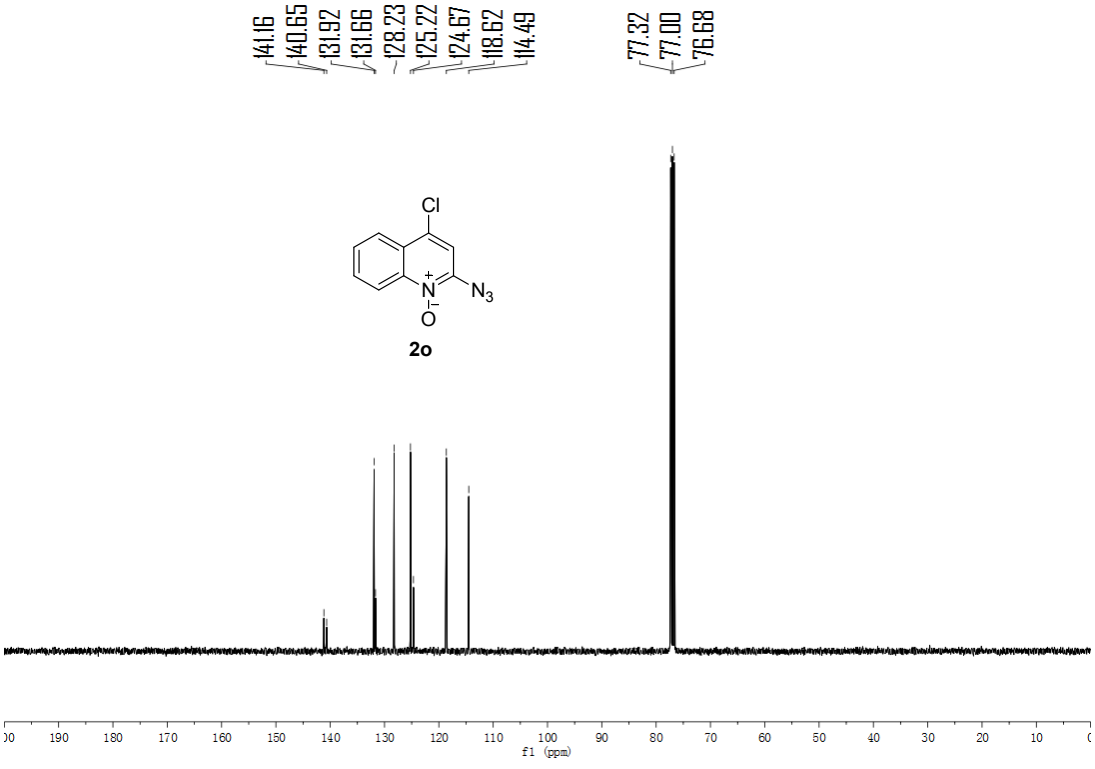

8.28
8.26
7.72
7.71
7.70
7.64
7.63
7.63
7.61
7.57
7.55
7.53
7.51
7.44
7.43
7.42
7.41
7.26
6.96
6.94
N3
O
O
Ph
2.04
1.22
2.08
3.16
1.14
1.00
f1 (ppm)

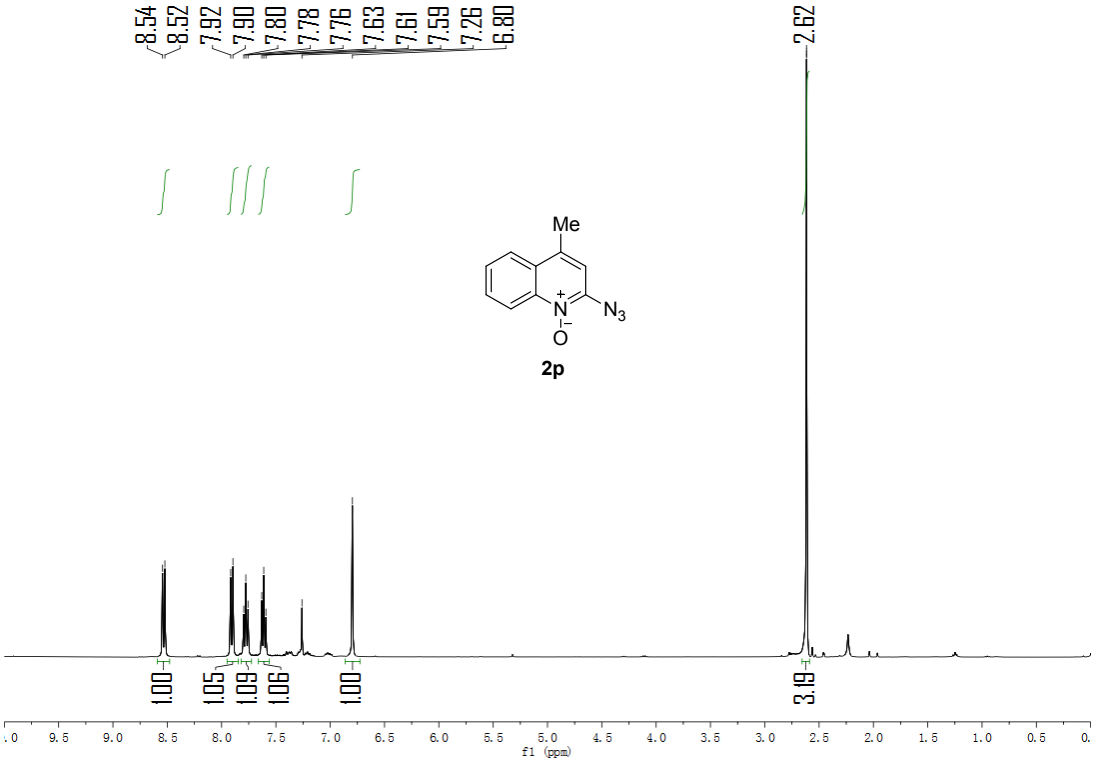
2n

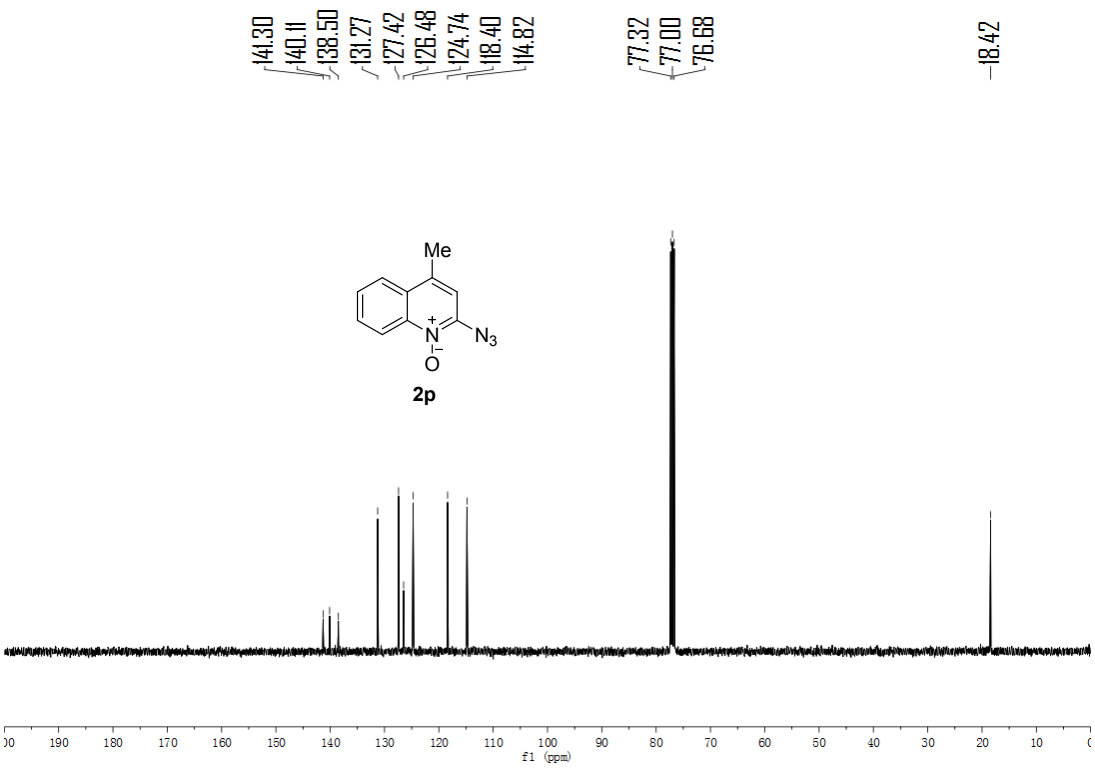

165.63
142.69
142.01
133.37
130.47
129.79
129.52
128.51
127.34
126.83
126.74
125.05
115.46
77.32
77.00
76.68
N3
O
O
Ph
f1 (ppm)

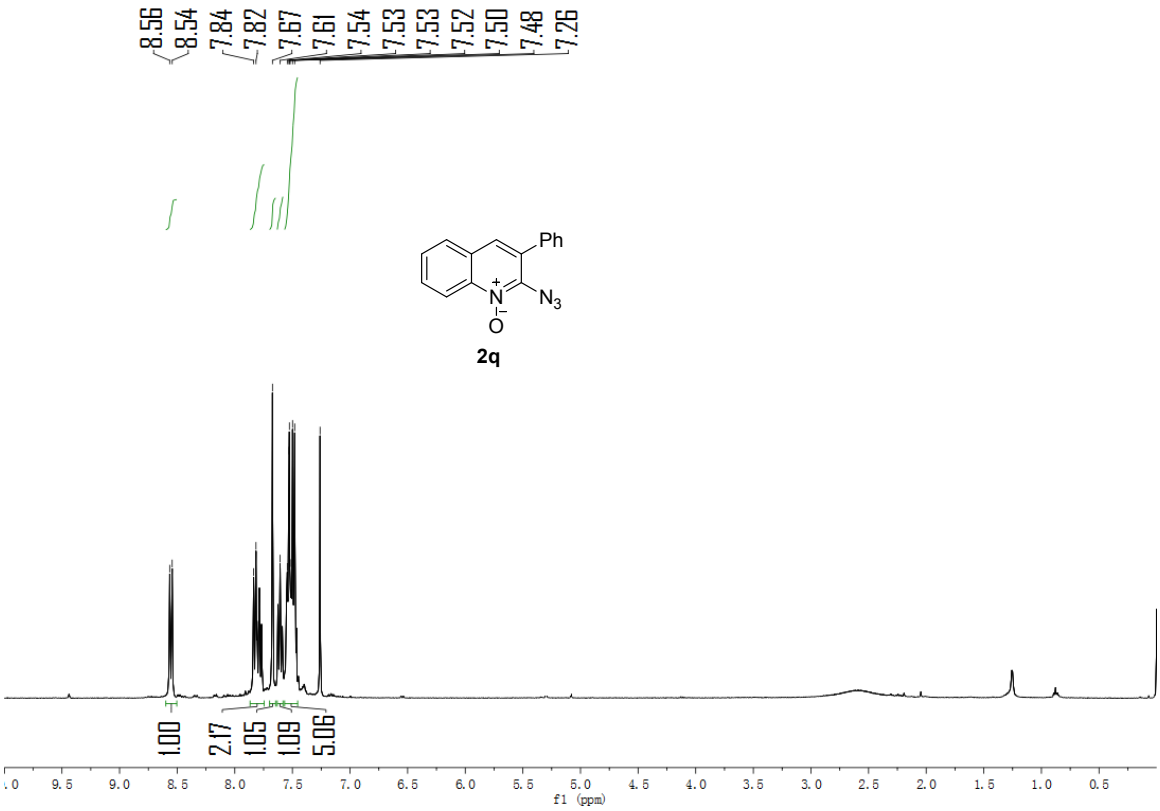
2n

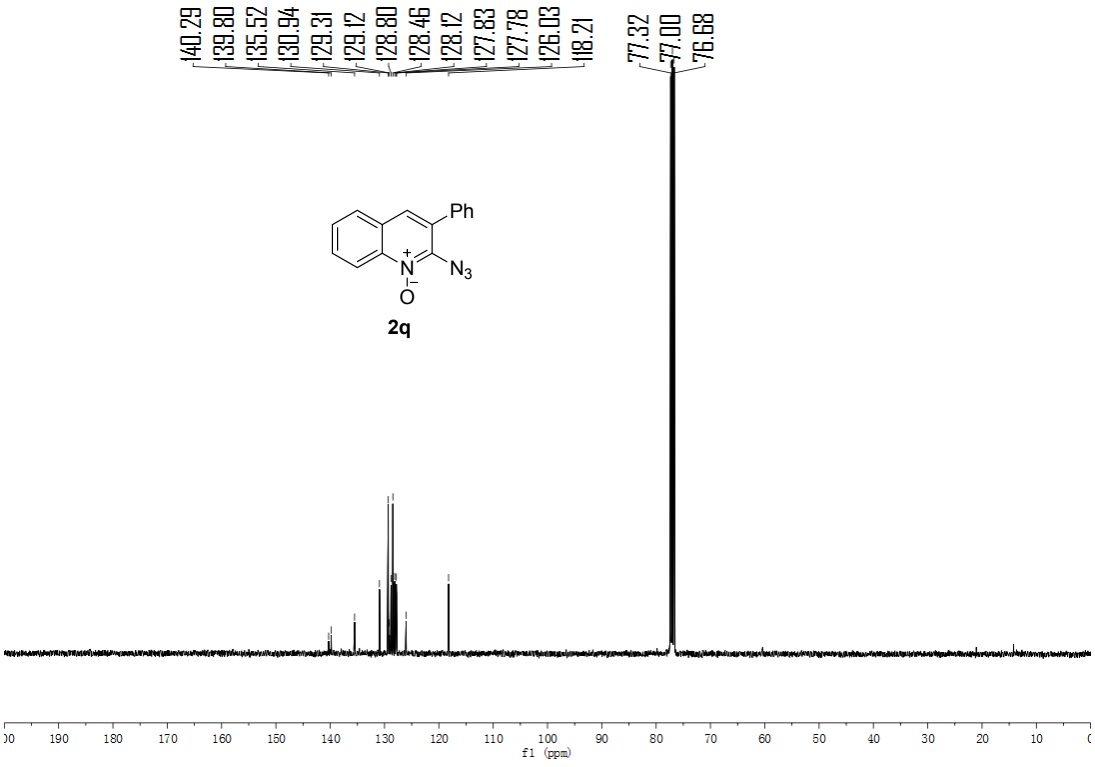

8.58
8.58
8.55
8.15
8.15
8.13
8.13
7.83
7.83
7.69
7.69
7.67
7.67
7.67
7.26
7.06
Cl
N3
O
2o
1.04
1.00
1.11
1.14
1.01
f1 (ppm)

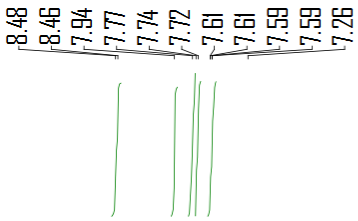

141.16
140.65
131.92
131.66
128.23
125.22
124.67
118.62
114.49
77.32
77.00
76.68
Cl
N3
O
2o
f1 (ppm)

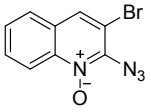

8.54
8.52
7.92
7.90
7.80
7.78
7.76
7.63
7.61
7.59
7.26
6.80
2.62
Me
N3
2p
1.00
1.05
1.09
1.06
1.00
3.19
f1 (ppm)


141.30
140.11
138.50
131.27
127.42
126.48
124.74
118.40
114.82
77.32
77.00
76.68
18.42
Me
N3
2p
f1 (ppm)

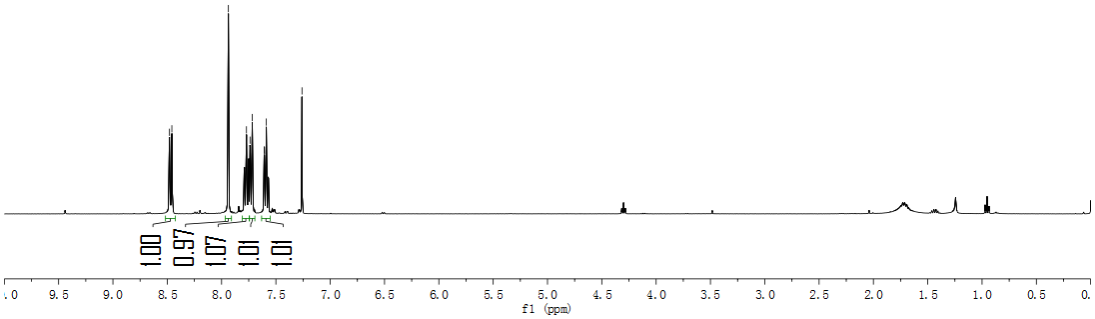

8.56
8.54
7.84
7.82
7.67
7.61
7.54
7.53
7.53
7.52
7.50
7.48
7.26
Ph
N3
2q
1.00
2.17
1.05
1.09
5.06
f1 (ppm)

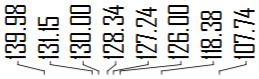

140.29
139.80
135.52
130.94
129.31
129.12
128.80
128.46
128.12
127.83
127.78
126.03
118.21
77.32
77.00
76.68
Ph
N3
2q
f1 (ppm)


8.48
8.46
7.94
7.77
7.74
7.72
7.61
7.61
7.59
7.59
7.26

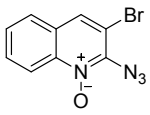

Br
N3
+
N
O
−

2r


1.00
0.97
1.07
1.01
1.01
f1 (ppm)

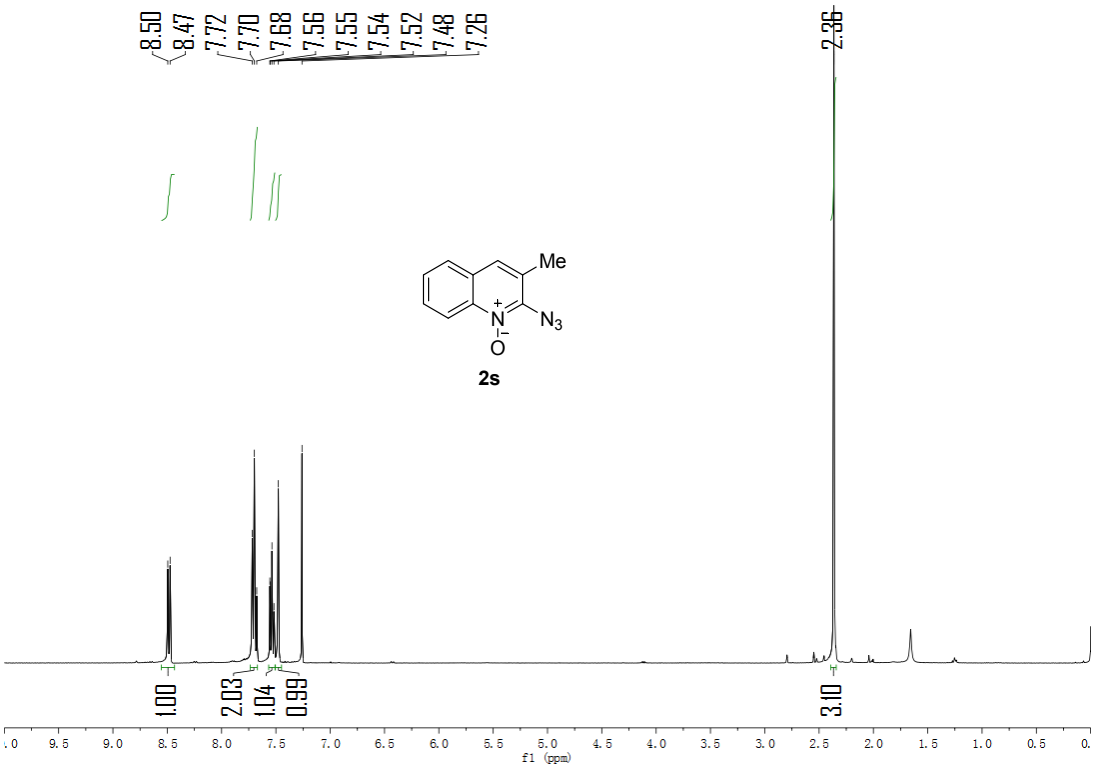

139.98
131.15
130.00
128.34
127.24
126.00
118.38
107.74

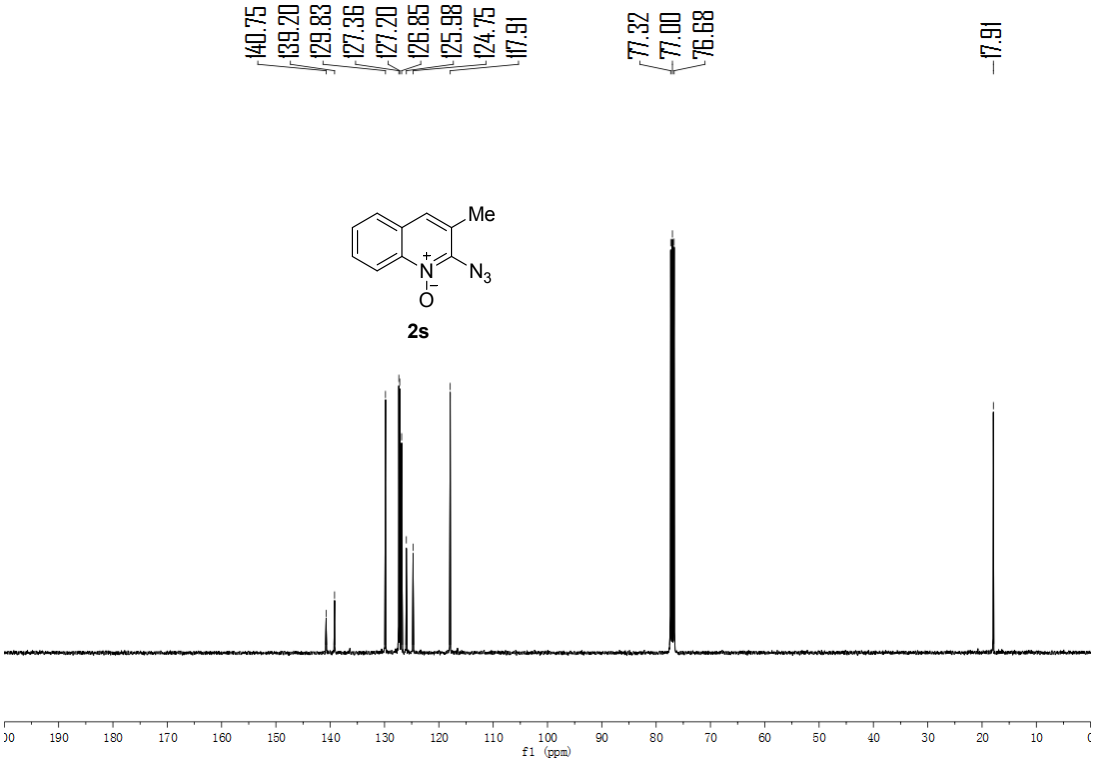

77.32
77.00
76.68

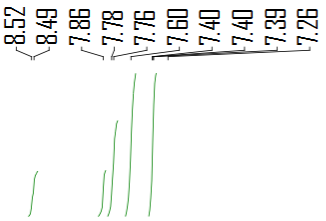

Br
N3
+
N
O
−

2r

f1 (ppm)


8.50
8.47
7.72
7.70
7.68
7.56
7.55
7.54
7.52
7.48
7.26
2.36
Me
N3
2s
1.00
2.03
1.04
0.99
3.10
f1 (ppm)


140.75
139.20
129.83
127.36
127.20
126.85
125.98
124.75
117.91
77.32
77.00
76.68
17.91
Me
N3
2s
f1 (ppm)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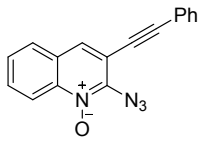
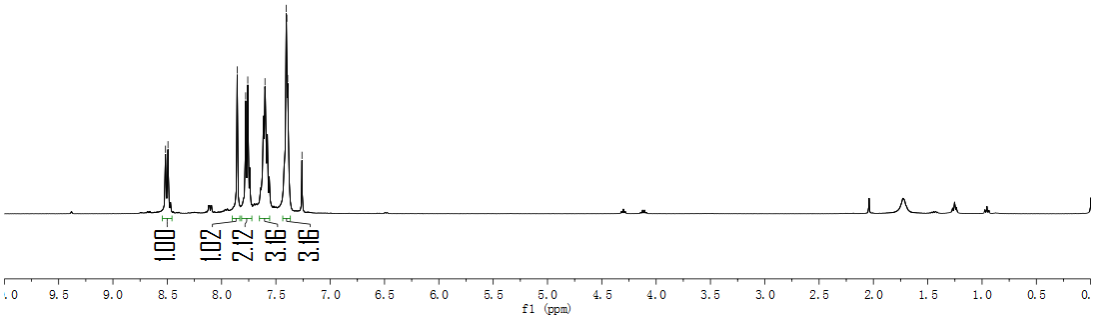
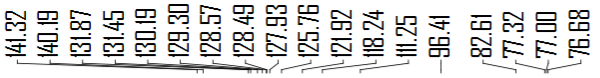
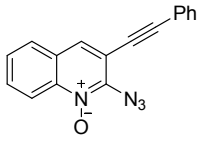
7.86
7.78
7.76
7.60
7.40
7.40
7.39
7.26


Ph
N3
O

2t

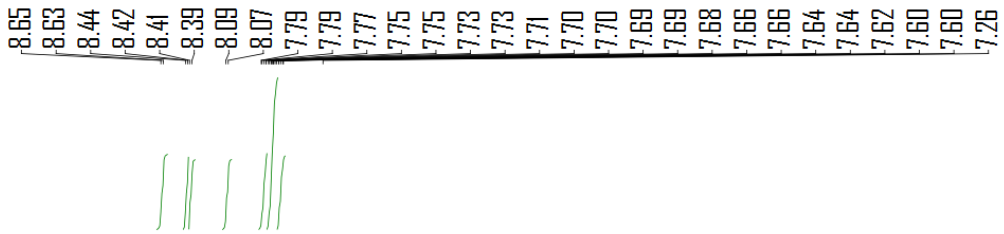

1.00
1.02
2.12
3.16
3.16
f1 (ppm)


141.32
140.19
131.87
131.45
130.19
129.30
128.57
128.49
127.93
125.76
121.92
118.24
111.25
96.41
82.61
77.32
77.00
76.68


Ph
N3
O

2t

f1 (ppm)


8.65
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8.41
8.39
8.09
8.07
7.79
7.79
7.77
7.75
7.75
7.73
7.73
7.71
7.70
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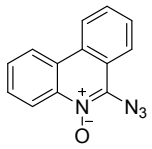
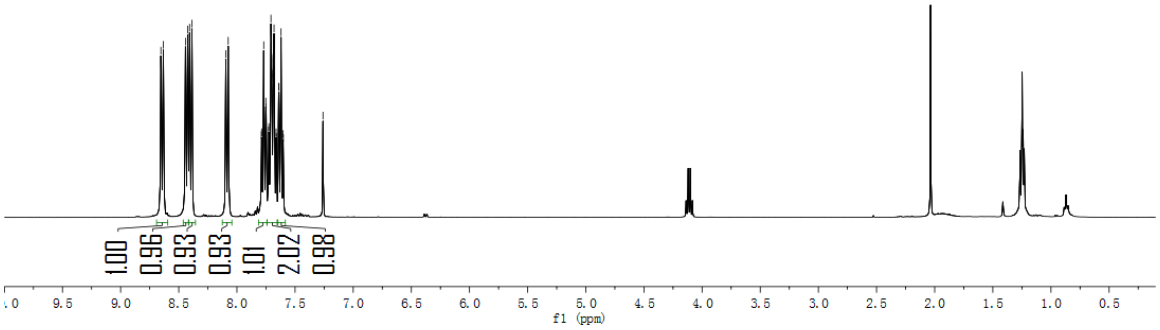
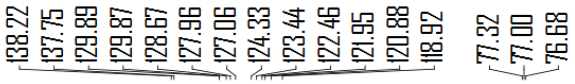
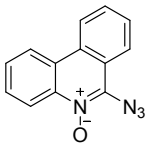
7.64
7.62
7.60
7.60
7.26


N3
O

2u

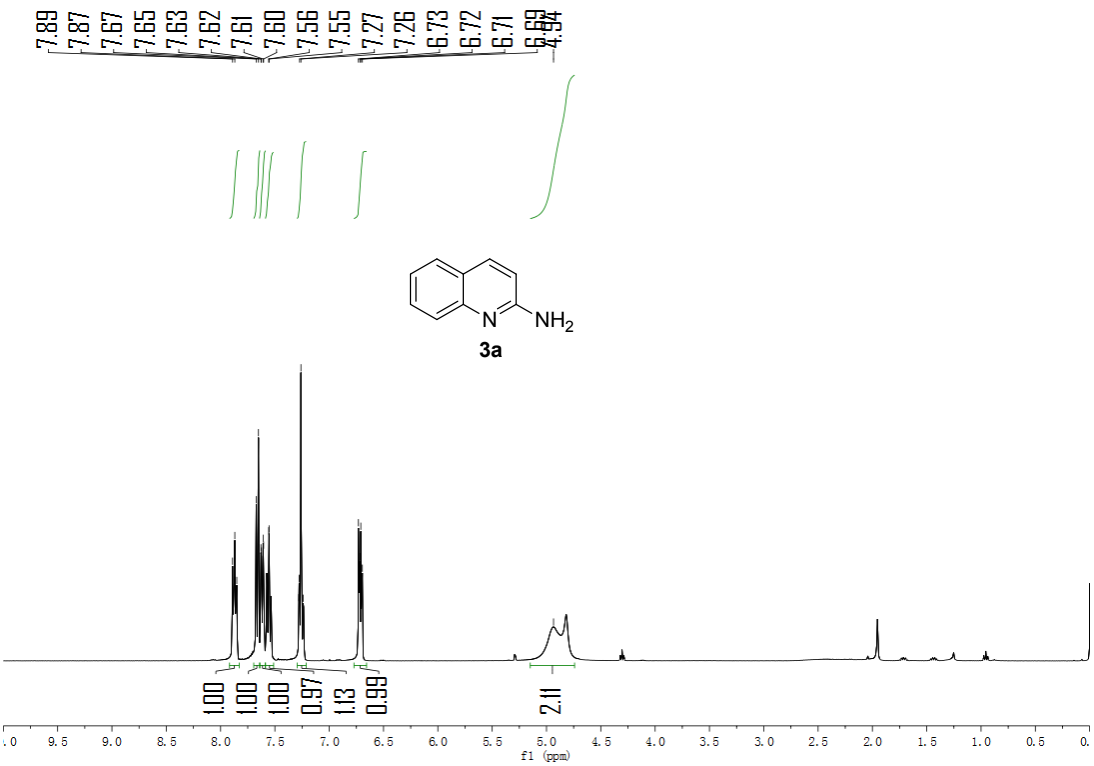

1.00
0.96
0.93
0.93
1.01
2.02
0.98
f1 (ppm)

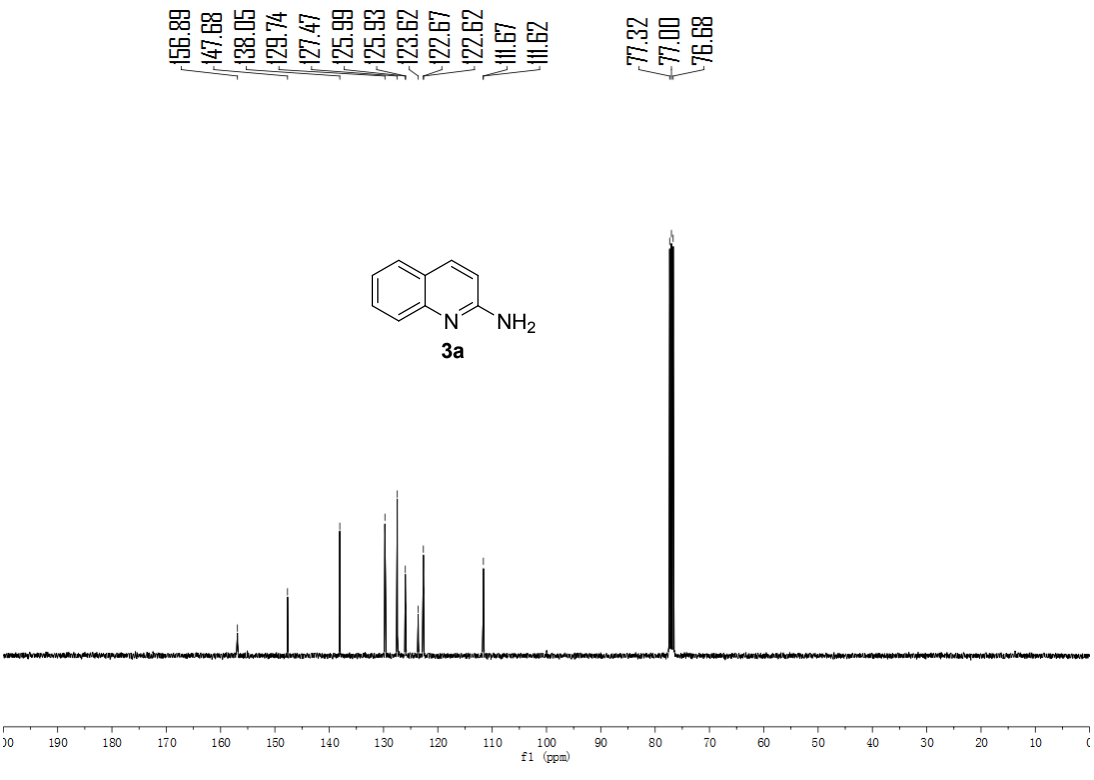

138.22
137.75
129.89
129.87
128.67
127.96
127.06
124.33
123.44
122.46
121.95
120.88
118.92
77.32
77.00
76.68

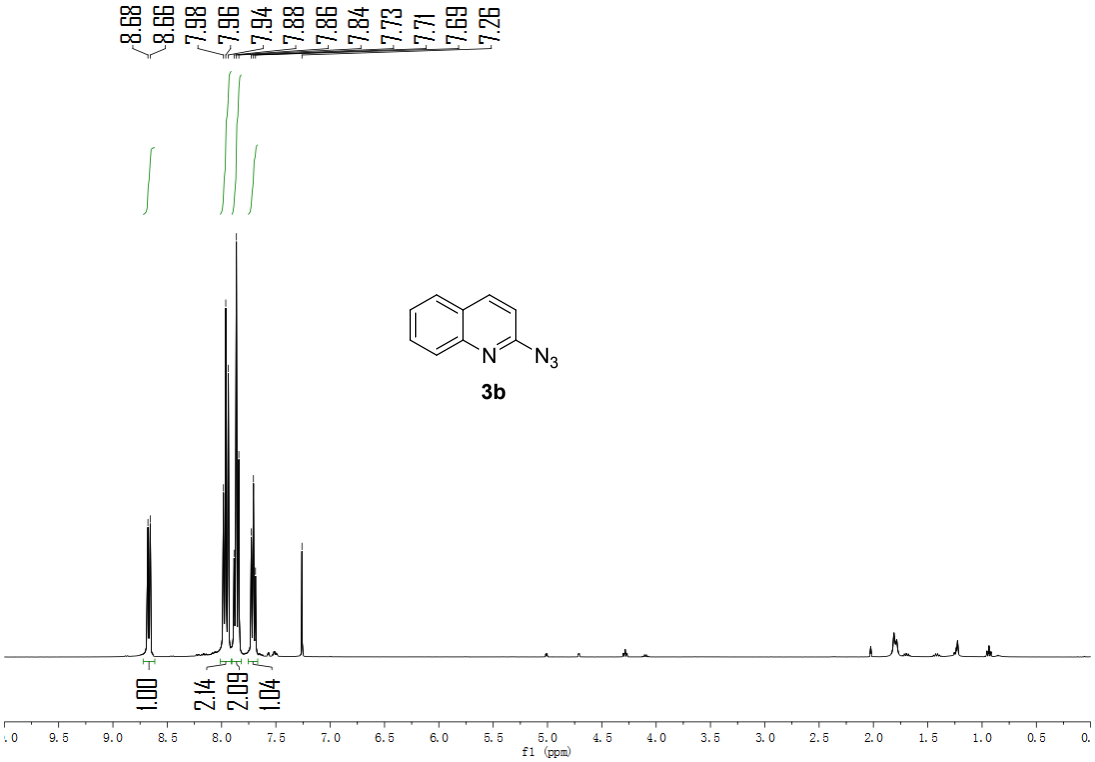

N3
O

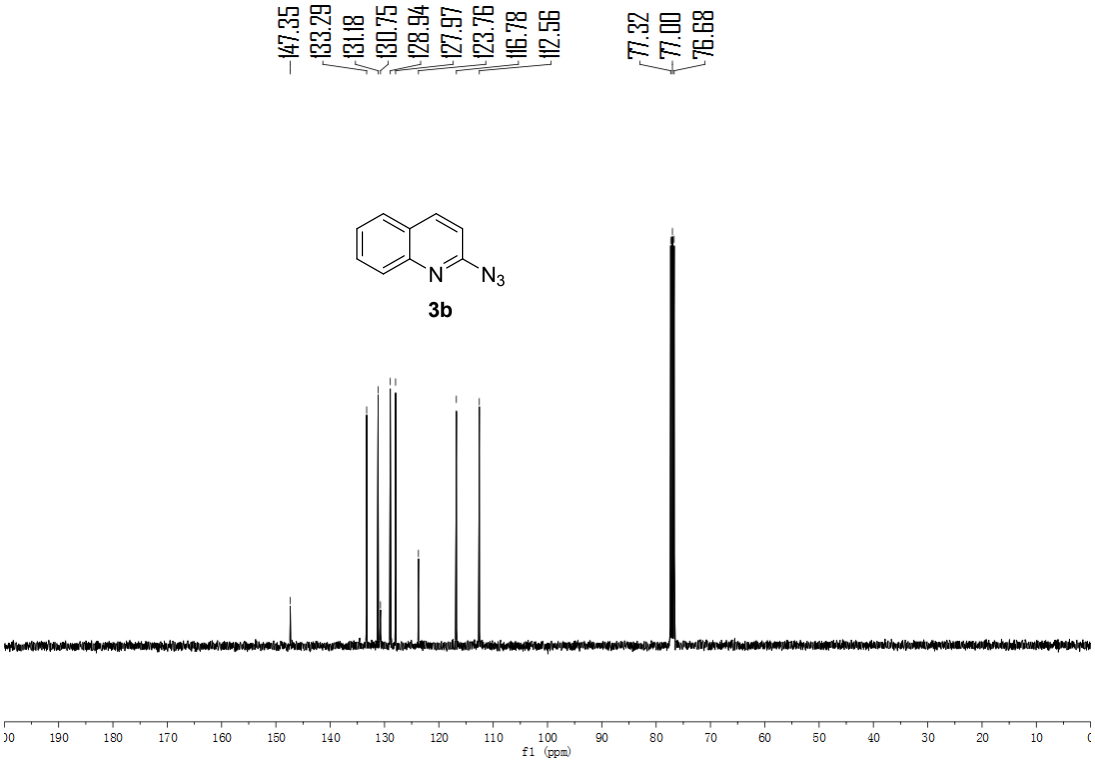
2u

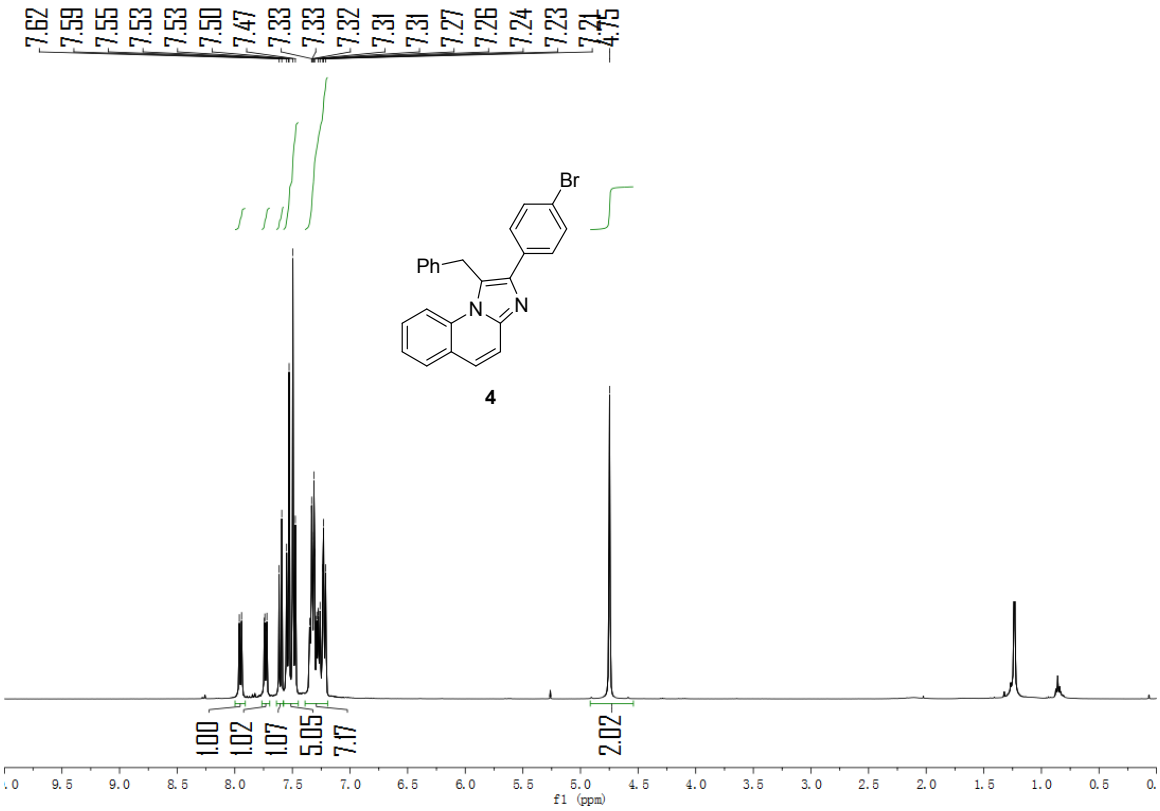
f1 (ppm)

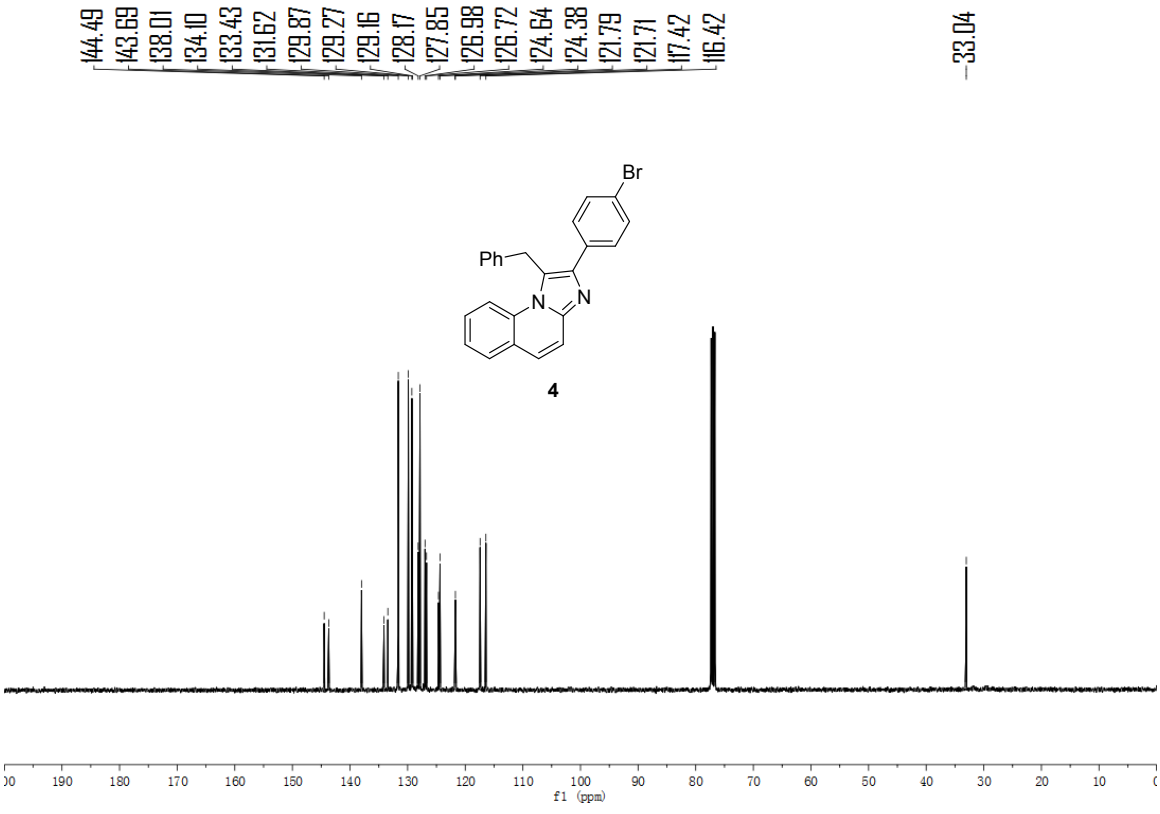

7.89
7.87
7.67
7.65
7.63
7.62
7.61
7.60
7.56
7.55
7.27
7.26
6.73
6.72
6.71
6.69
4.94
N
NH2
3a
1.00
1.00
1.00
0.97
1.13
0.99
2.11
f1 (ppm)


156.89
147.68
138.05
129.74
127.47
125.99
125.93
123.62
122.67
122.62
111.67
111.62
77.32
77.00
76.68
N
NH2
3a
f1 (ppm)


8.68
8.66
7.98
7.96
7.94
7.88
7.86
7.84
7.73
7.71
7.69
7.26
N
N3
3b
1.00
2.14
2.09
1.04
f1 (ppm)


147.35
133.29
131.18
130.75
128.94
127.97
123.76
116.78
112.56
77.32
77.00
76.68
N
N3
3b
f1 (ppm)


7.62
7.59
7.55
7.53
7.53
7.50
7.47
7.33
7.33
7.32
7.31
7.31
7.27
7.26
7.24
7.23
7.21
4.75
Br
Ph
N
N
4
1.00
1.02
1.07
5.05
7.17
2.02
f1 (ppm)


144.49
143.69
138.01
134.10
133.43
131.62
129.87
129.27
129.16
128.17
127.85
126.98
126.72
124.64
124.38
121.79
121.71
117.42
116.42
33.04
Br
Ph
N
N
4
f1 (ppm)