Supporting Information

Practical copper-catalyzed chloronitration of alkenes with TMSCl and guanidine nitrate

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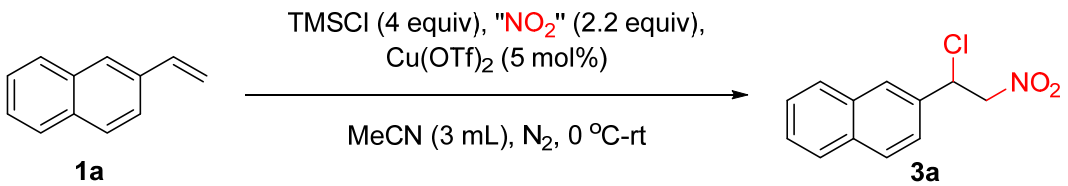
I. General Information

All manipulations were maintained under an atmosphere of nitrogen unless otherwise stated. Commercially available reagents were used without further purification. Solvents were pre-dried over activated 4 Å molecular sieves and were refluxed over sodium-benzophenone (toluene, tetrahydrofurane), phosphorus pentoxide (chlorobenzene) or calcium hydride (dichloromethane, dichloroethane, acetonitrile). Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 101 MHz NMR spectrometer. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series FT-IR spectrometer. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry. The Raman spectra at 25 °C were taken with Jobin Yvon confocal laser Raman system (SuperLabRam II), which was equipped with a He–Ne laser at 632.8 nm with a power of approximately 5 mW. **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1h**, **1i**, **1j**, **1k**, **1r** **1s**, **1ab**, **1ac**, **1ad**, **4a**,**12a**, **12b**, **12c**, **12d** was commercially available; **1t**[1], **1u**[1], **1v**[1], **1w**[1], **1x**[1], **1y**[1], **1z**[1], **1ae**[2], **1af**[2], **4b**[3], **4c**[3], **4d**[3], **4e**[3], **4f**[3], **4h**[4] was prepared according to published procedures.

CAUTION: nitration reagents, intermediates, or side products such polynitrated compounds might been potentially explosive. Although under the conditions and scale described here we did not encounter any problems, appropriate precautions should be taken when handling these compounds in general. All nitration reactions and subsequent workups were performed behind a blast shield.

II. Optimization of Reaction Conditions

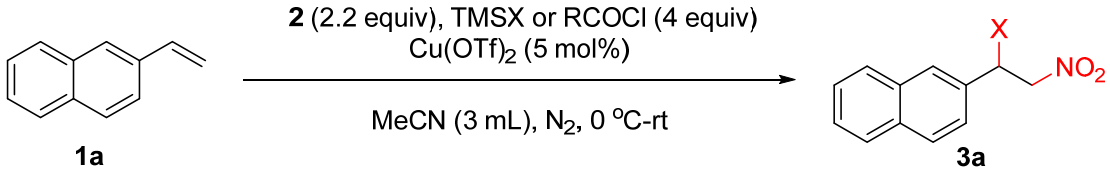
Table S1. Optimization of the Reaction Conditions ("NO_2" source) for the Synthesis of Product 3a[a]



Entry	"NO_2"	Time (h)	Yield[b] (%)
1	$AgNO_3$	2	80
2	$LiNO_3$	23	86
3	$NaNO_3$	8	78
4	**2**	12	92
5	Me_4NO_3	72	trace
6	$^{n}Bu_4NO_3$	72	trace
7	$NaNO_2$	14	30
8	$AgNO_2$	3	12
9[c]	$Cu(NO_3)_2{\cdot}3H_2O$[d]	1	93

[a] Reaction condition: **1a** (0.50 mmol), TMSCl (4 equiv), "NO_2" (2.2 equiv), $Cu(OTf)_2$ (5 mol%), MeCN (3 mL), N_2. [b] The yield was determined with ^1H NMR by adding 1,2- dichloroethane as an internal standard. [c] $Cu(OTf)_2$ (5 mol%) was not added in this reaction. [d] 0.75 equivalent amount of $Cu(NO_3)_2{\cdot}3H_2O$ was used.

Table S2. Optimization of the Reaction Conditions (TMSX or RCOCl) for the Synthesis of Product 3a[a]

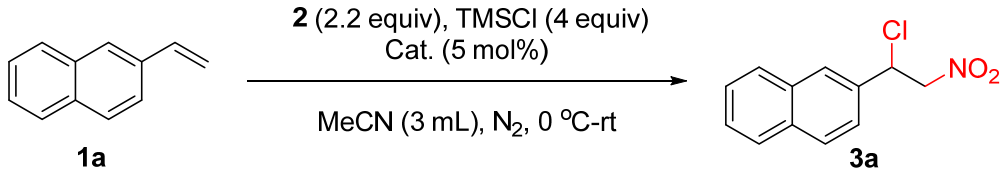


1a **3a**

Entry	TMSX or RCOCl	Time (h)	Yield[b] (%)
1	TMSBr	72	n.d.
2	TMSOTf	72	n.d.
3	TMSCN	72	trace
4	$TMSCF_3$	72	trace
5	$TMSN_3$	72	complex
6	AcCl	24	80
7	PivCl	72	15
8	PhOCOCl	72	trace
9	MeOCOCl	72	15

[a] Reaction condition: **1a** (0.50 mmol), TMSX or RCOCl (4 equiv), **2** (2.2 equiv), $Cu(OTf)_2$ (5 mol%), MeCN (3 mL), N_2. [b] The yield was determined with ^1H NMR by adding 1,2- dichloroethane as an internal standard. n.d.: no detected

Table S3. Optimization of the Reaction Conditions (Cat.) for the Synthesis of Product 3a[a]

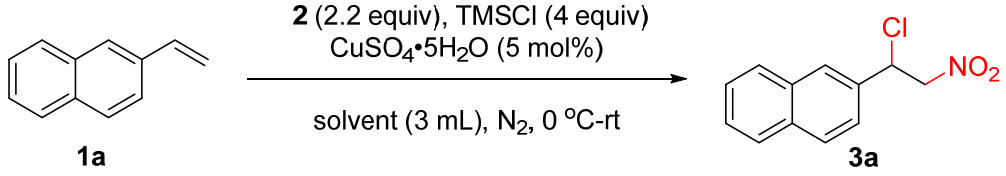


1a **3a**

Entry	Cat.	Time (h)	Yield[b] (%)
1	CuCl	6	91
2	$CuCl_2$	18	91
3	$Cu(NO_3)_2$	18	93
4	$CuSO_4•5H_2O$	16	93
5	Cu	21	90
6	Cu_2O	6	80
7	CuO	15	93
8	$FeCl_2$	72	trace
9	$MnCl_2$	72	trace
10	$Zn(OAc)_2$	72	trace
11	$Co(OAc)_2•4H_2O$	72	trace
12	$Mg(OTf)_2$	72	trace

[a] Reaction condition: **1a** (0.50 mmol), TMSCl (4 equiv), **2** (2.2 equiv), Cat. (5 mol%), MeCN (3 mL), N_2. [b] The yield was determined with ^1H NMR by adding 1,2-dichloroethane as an internal standard.

Table S4. Optimization of the Reaction Conditions (solvent) for the Synthesis of Product 3a[a]



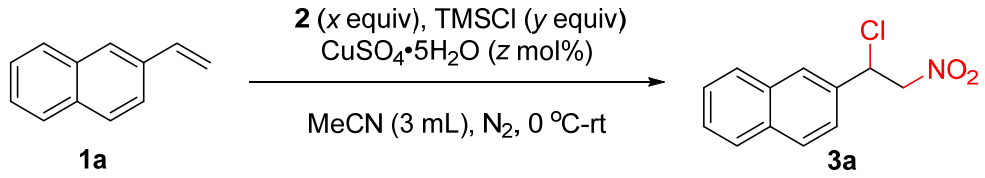
1a **3a**

Entry	solvent	Time (h)	Yield[b] (%)

1	DCM	72	trace
2	DCE	72	trace
3	THF	72	trace
4	Toluene	72	trace
5	EtOH	72	trace
6	AcOH	72	trace
7	DMF	72	trace
8	DMSO	72	trace

[a] Reaction condition: **1a** (0.50 mmol), TMSCl (4 equiv), **2** (2.2 equiv), $CuSO_4•5H_2O$ (5 mol%), solvent (3 mL), N_2. [b] The yield was determined with ^1H NMR by adding 1,2- dichloroethane as an internal standard.

Table S5. Optimization of the Reaction Conditions (reactant amounts) for the Synthesis of Product 3a[a]

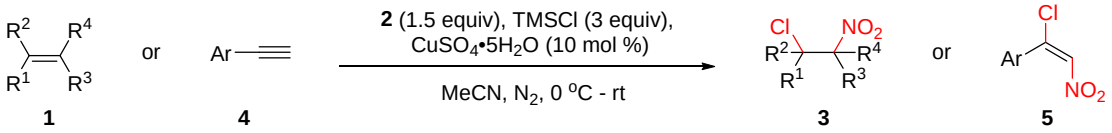


Entry	*x*	*y*	*z*	Time (h)	Yield[b] (%)
1	2.2	0	5	72	n.d.
2	2.2	2	5	120	64
3	2.2	4	5	16	93
4	2.2	6	5	18	75
5	2.0	4	5	19	91
6	1.5	4	5	19	90
7	1.2	4	5	20	83
8	2.2	4	1	72	91
9	2.2	4	0	72	n.d.
10	2.2	4	10	8	99
11	1.5	3	10	9	99
12[c]	1.5	3	10	12	95

[a] Reaction condition: **1a** (0.50 mmol), TMSCl (*x* equiv), **2** (*y* equiv), $CuSO_4•5H_2O$ (*z*

mol%), solvent (3 mL), N_2. [b] The yield was determined with ^1H NMR by adding 1,2-dichloroethane as an internal standard. [c] **1a** (5 mmol), TMSCl (3 equiv), **2** (1.5 equiv), $CuSO_4•5H_2O$ (10 mol%), solvent (10 mL), N_2.

III. Chloronitration



General Procedure (A) for Chloronitration of Alkenes

To a 50 mL dry flask were added alkene (5.0 mmol), **2** (915 mg, 7.5 mmol), TMSCl(1.65 mL, 15 mmol), $CuSO_4•5H_2O$ (125 mg, 0.50 mmol) and MeCN (10 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃, and then warmed to room temperature as monitoring by TLC. Upon completion, the reaction mixture was filtered. The filtrate was concentrated and purified by short column chromatography (about 5 cm high) via silica gel to give the desired product.

General Procedure (B) for Chloronitration of Alkenes

To a 50 mL dry flask were added alkene (10 mmol), **2** (1.83 g, 15 mmol), TMSCl(3.3 mL, 30 mmol), $CuSO_4•5H_2O$ (250 mg, 1.0 mmol) and MeCN (25 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃, and then warmed to room temperature as monitoring by TLC. Upon completion, the reaction mixture was filtered. The filtrate was concentrated and purified by short column chromatography (about 5 cm high) via silica gel to give the desired product.

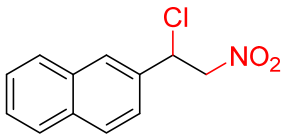
General Procedure (C) for Chloronitration of Alkenes

To a 10 mL dry flask were added alkene (0.50 mmol), **2** (91.5 mg, 0.75 mmol), TMSCl(165 μL, 1.5 mmol), $CuSO_4•5H_2O$ (12.5 mg, 0.05 mmol) and MeCN (3 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃ then warmed to room temperature as monitoring by TLC. Upon completion, the reaction mixture was concentrated and purified by short column chromatography (about 5 cm high) via

silica gel to give the desired product.

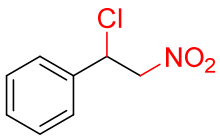
General Procedure (D) for Chloronitration of Alkynes

To a 10 mL dry flask were added alkyne (0.50 mmol), **2** (91.5 mg, 0.75 mmol), TMSCl(165 μL, 1.5 mmol), $CuSO_4$•$5H_2O$ (12.5 mg, 0.05 mmol) and MeCN (3 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃ then warmed to room temperature as monitoring by TLC. Upon completion, the reaction mixture was concentrated and purified by column chromatography via silica gel to give the desired product.



3a

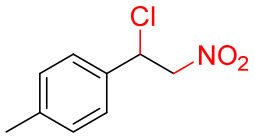
2-(1-chloro-2-nitroethyl)naphthalene (3a); It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.: 109.5-111.9 ℃); 92% yield (1.081 g, 4.6 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.86 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.58 – 7.50 (m, 3H), 5.74 (dd, *J* = 9.0, 5.7 Hz, 1H), 5.01 (dd, *J* = 13.5, 9.0 Hz, 1H), 4.89 (dd, *J* = 13.5, 5.7 Hz, 1H); **^{13}C[5] NMR (101 MHz, Chloroform-*d*)** δ 133.8, 133.1, 129.6, 128.3, 128.0, 127.4, 127.2, 127.1, 124.0, 80.9, 57.3; **IR *v* (neat, cm^{-1}):** 3010, 2985, 1632, 1275, 1260, 706; **HRMS (ESI, m/z):** calcd for $C_{12}H_{11}ClNO_2^+$ $[M+H]^+$: 236.0473; found: 236.0462.



3b

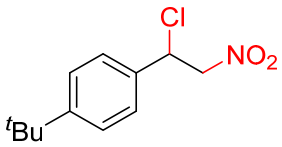
(1-chloro-2-nitroethyl)benzene (3b)[6]; It was prepared according to general procedure (**B**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h;

petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 95% yield (1.762 g, 9.5 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.45 – 7.39 (m, 5H), 5.57 (dd, J = 9.2, 5.5 Hz, 1H), 4.91 (dd, J = 13.5, 9.2 Hz, 1H), 4.78 (dd, J = 13.4, 5.5 Hz, 1H).



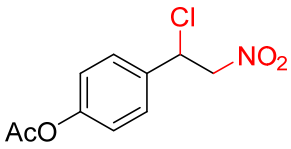
3c

1-(1-chloro-2-nitroethyl)-4-methylbenzene (3c); It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.: 63.6-64.5 ℃); 85% yield (848 mg, 4.2 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.53 (dd, *J* = 9.1, 5.7 Hz, 1H), 4.90 (dd, *J* = 13.4, 9.1 Hz, 1H), 4.77 (dd, *J* = 13.4, 5.7 Hz, 1H), 2.37 (s, 3H); **^{13}C^5 NMR (101 MHz, Chloroform-*d*)** δ 140.1, 133.1, 130.1, 127.2, 81.0, 57.0, 21.3; **IR *v* (neat, cm^{-1}):** 3005, 2918, 1557, 1374, 1275, 1260, 816, 750; **HRMS (ESI, m/z):** calcd for $C_9H_{11}ClNO_2^+$ $[M+H]^+$: 200.0473; found: 200.0455.



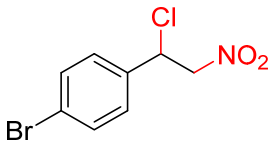
3d

1-(*tert*-butyl)-4-(1-chloro-2-nitroethyl)benzene (3d); It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 22 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 89% yield (1.076 g, 4.5 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.55 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.90 (dd, *J* = 13.5, 9.2 Hz, 1H), 4.77 (dd, *J* = 13.5, 5.5 Hz, 1H), 1.32 (s, 9H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 153.2, 132.9, 127.0, 126.4, 81.0, 56.9, 34.9, 31.3; **IR *v* (neat, cm^{-1}):** 2965, 1559, 1519, 1376, 1274, 1109, 969, 837, 745, 682, 563; **HRMS (ESI, m/z):** calcd for $C_{12}H_{17}ClNO_2^+$ $[M+H]^+$: 242.0943; found: 242.0971.



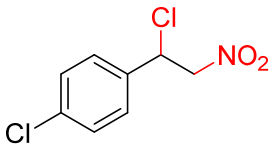
3e

4-(1-chloro-2-nitroethyl)phenyl acetate (3e); It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 15 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.2 (PE/EA=20 : 1, UV); white solid (m.p.: 85.8-89.2 ℃); 89% yield (1.080 g, 4.4 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.57 (dd, *J* = 9.1, 5.5 Hz, 1H), 4.89 (dd, *J* = 13.5, 9.1 Hz, 1H), 4.76 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.31 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 169.2, 151.7, 133.4, 128.6, 122.6, 80.9, 56.3, 21.2; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1632, 1507, 1275, 1206, 896, 748; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}ClNO_4^+$ $[M+H]^+$: 244.0371; found: 244.0355.



3f

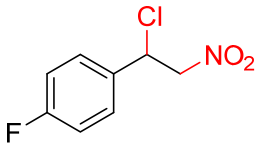
1-bromo-4-(1-chloro-2-nitroethyl)benzene (3f)[7]; It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 10 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.: 74.3-75.7 ℃); 96% yield (1.263 g, 4.8 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.52 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.89 (dd, *J* = 13.5, 8.7 Hz, 1H), 4.76 (dd, *J* = 13.5, 6.0 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 135.0, 132.6, 129.0, 124.1, 80.6, 56.1; **IR *v* (neat, cm^{-1}):** 3005, 2984, 1601, 1558, 1372, 1274, 1160, 831, 751; **HRMS (ESI, m/z):** calcd for $C_8H_8BrClNO_2^+$ $[M+H]^+$: 263.9422; found: 263.9421.



3g

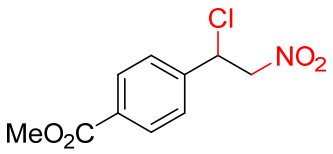
1-chloro-4-(1-chloro-2-nitroethyl)benzene (3g); It was prepared according to

general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.: 70.0-70.4 ℃); 90% yield (993 mg, 4.5 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.39 (d, *J*=8.9 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 5.53 (dd, *J* = 8.7, 6.0 Hz, 1H), 4.89 (dd, *J* = 13.5, 8.7 Hz, 1H), 4.76 (dd, *J* = 13.5, 6.0 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 135.9, 134.5, 129.6, 128.7, 80.7, 56.1; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1556, 1493, 1376, 1275, 1260, 897, 748; **HRMS (ESI, m/z):** calcd for $C_8H_8Cl_2NO_2^+$ $[M+H]^+$: 219.9927; found: 219.9826.



3h

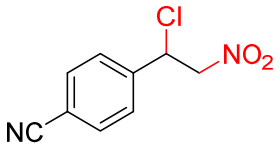
1-(1-chloro-2-nitroethyl)-4-fluorobenzene (3h); It was prepared according to general procedure **(A)**, reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.: 63.2-64.0 ℃); 95% yield (1.932 g, 9.5 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.39 (m, 2H), 7.15 – 7.06 (m, 2H), 5.55 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.90 (dd, *J* = 13.4, 8.7 Hz, 1H), 4.77 (dd, *J* = 13.4, 6.0 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 163.4 (d, *J* = 250.1 Hz), 131.9 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 8.6 Hz), 116.5 (d, *J* = 22.0 Hz), 80.8, 56.1; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ 96.38; **IR *v* (neat, cm^{-1}):** 3005, 2984, 1602, 1557, 1374, 1274, 1260, 1160, 835, 749, 521; **HRMS (ESI, m/z):** calcd for $C_8H_8ClFNO_2^+$ $[M+H]^+$: 204.0222; found: 204.0217.



3i

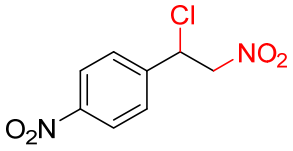
methyl 4-(1-chloro-2-nitroethyl)benzoate (3i); It was prepared according to general procedure (**B**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 15 h ; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.2 (PE/EA=20 : 1, UV); white solid (m.p.: 60.3-60.9 ℃); 83% yield (2.013 g, 8.3 mmol); **^{1}H NMR (400 MHz,**

Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.60 (dd, *J* = 8.8, 5.9 Hz, 1H), 4.92 (dd, *J* = 13.5, 8.8 Hz, 1H), 4.80 (dd, *J* = 13.5, 5.9 Hz, 1H), 3.94 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 166.2, 140.6, 131.7, 130.7, 127.5, 80.6, 56.2, 52.5; **IR *v* (neat, cm^{-1}):** 2955, 2922, 1634, 1560, 1376, 1276, 1110, 968, 749, 706; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}ClNO_4^+$ $[M+H]^+$: 244.0371; found: 244.0269.



3j

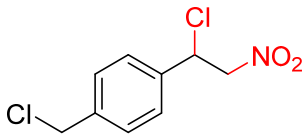
4-(1-chloro-2-nitroethyl)benzonitrile (3j); It was prepared according to general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 5 h ; petroleum ether/ethyl acetate = 10 : 1; **TLC:** R_f = 0.1 (PE/EA=9 : 1, UV); white solid (m.p.: 62.3-63.4 ℃); 81% yield (858 mg, 4.1 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.73 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 5.58 (dd, J = 8.5, 6.3 Hz, 1H), 4.92 (dd, J = 13.6, 8.5 Hz, 1H), 4.79 (dd, J = 13.6, 6.3 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 140.9, 133.2, 128.3, 117.9, 113.9, 80.2, 55.6; **IR *v* (neat, cm^{-1}):** 3005, 2918, 2227, 1639, 1549, 1275, 1260, 750, 749; **HRMS (ESI, m/z):** calcd for $C_9H_8ClN_2O_2^+$ $[M+H]^+$: 211.0269; found: 211.0273.



3k

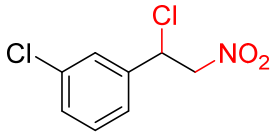
1-(1-chloro-2-nitroethyl)-4-nitrobenzene (3k); It was prepared according to general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 4 h; petroleum ether/ethyl acetate = 10 : 1; TLC: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 83.4-84.7 ℃); 89% yield (1.026 g, 4.4 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 5.64 (dd, *J* = 8.3, 6.4 Hz, 1H), 4.95 (dd, *J* = 13.6, 8.3 Hz, 1H), 4.83 (dd, *J* = 13.6, 6.4 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 142.7, 129.9, 128.6, 124.6, 80.2, 55.2; **IR *v* (neat, cm^{-1}):** 2985, 1555, 1520, 1347, 1260, 913, 749, 704; **HRMS (ESI, m/z):** calcd for

$C_8H_8ClN_2O_4^+$ $[M+H]^+$: 231.0167; found: 231.0165.



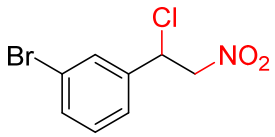
3l

1-(1-chloro-2-nitroethyl)-4-(chloromethyl)benzene (3l); It was prepared according to general procedure (**A**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.3 (PE/EA=20 : 1, UV); green yellow oil; 98% yield (1.147 g, 4.9 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.46-7.42 (m, 4H), 5.56 (dd, *J* = 8.9, 5.8 Hz, 1H), 4.90 (dd, *J* = 13.5, 9.0 Hz, 1H), 4.77 (dd, *J* = 13.5, 5.8 Hz, 1H), 4.58 (s, 2H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 139.3, 136.1, 129.6, 127.8, 80.8, 56.4, 45.4; **IR *v* (neat, cm^{-1}):** 3006, 2987, 1634, 1556, 1375, 1275, 1216, 968, 749, 680; **HRMS (ESI, m/z):** calcd for $C_9H_{10}Cl_2NO_2^+$ $[M+H]^+$: 233.0083; found: 233.0075.



3m

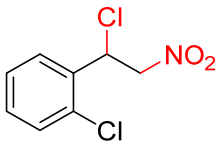
1-chloro-3-(1-chloro-2-nitroethyl)benzene (3m); It was prepared according to general procedure **(B)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 15 h;; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 93% yield (2.046 g, 9.3 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.31 (dt, *J* = 6.7, 2.0 Hz, 1H), 5.52 (dd, *J* = 8.8, 5.9 Hz, 1H), 4.89 (dd, *J* = 13.5, 8.8 Hz, 1H), 4.77 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 137.9, 135.4, 130.7, 130.2, 127.6, 125.5, 80.6, 56.0; **IR *v* (neat, cm^{-1}):** 3006, 1635, 1474, 1275, 1190, 1082, 876, 751, 702; **HRMS (ESI, m/z):** calcd for $C_8H_8Cl_2NO_2^+$ $[M+H]^+$: 219.9927; found: 220.0017.



3n

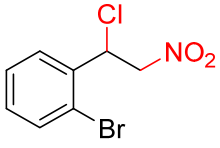
1-bromo-3-(1-chloro-2-nitroethyl)benzene (3n); It was prepared according to

general procedure **(B)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 20 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 95% yield (1.256 g, 4.7 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (t, *J* = 1.9 Hz, 1H), 7.56-7.50 (m, 1H), 7.37 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 5.51 (dd, *J* = 8.8, 5.8 Hz, 1H), 4.88 (dd, *J* = 13.5, 8.8 Hz, 1H), 4.77 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 138.1, 133.1, 130.9, 130.5, 126.0, 123.3, 80.6, 55.9; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1556, 1473, 1260, 897, 750, 706; **HRMS (ESI, m/z):** calcd for $C_8H_8BrClNO_2^+$ $[M+H]^+$: 263.9422; found: 263.9323.



3o

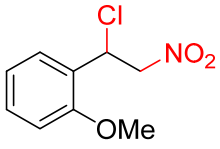
1-chloro-2-(1-chloro-2-nitroethyl)benzene (3o); It was prepared according to general procedure **(B)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 14 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 92% yield (2.015 g, 9.2 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.61 (dd, J = 7.3, 2.2 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.32 (m, 2H), 6.10 (dd, J = 8.7, 5.5 Hz, 1H), 4.88 – 4.84 (m, 1H), 4.84 – 4.78 (m, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 133.3, 132.9, 130.9, 130.4, 128.9, 128.0, 79.7, 53.7; **IR *v* (neat, cm^{-1}):** 3005, 1556, 1474,1374, 1260, 897, 749, 704; **HRMS (ESI, m/z):** calcd for $C_8H_8Cl_2NO_2^+$ $[M+H]^+$: 219.9927; found: 219.9815.



3p

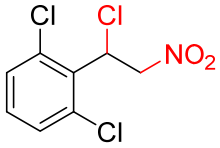
1-bromo-2-(1-chloro-2-nitroethyl)benzene (3p); It was prepared according to general procedure **(B)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 14 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 85% yield (2.248 g, 8.5 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.7 Hz 1H), 6.09 (dd, *J*

= 9.4, 4.7 Hz, 1H), 4.85 (dd, *J* = 13.7, 4.7 Hz, 1H), 4.78 (dd, *J* = 13.7, 9.4 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 134.9, 133.6, 131.2, 129.1, 128.6, 123.0, 79.8, 56.2; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1632, 1556, 1469, 1260, 897, 764, 704; **HRMS (ESI, m/z):** calcd for $C_8H_8BrClNO_2^+$ $[M+H]^+$: 263.9422; found: 263.9501.



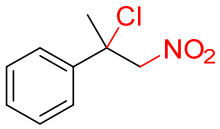
3q

1-(1-chloro-2-nitroethyl)-2-methoxybenzene (3q); It was prepared according to general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 22 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.2 (PE/EA=20 : 1, UV); green yellow oil; 72% yield (776 mg, 3.6 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.48 (d, J = 7.3 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.00 (dd, J = 8.8, 5.3 Hz, 1H), 4.94 – 4.76 (m, 2H), 3.90 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 156.4, 131.0, 128.7, 123.8, 121.2, 111.2, 80.1, 55.8, 52.8; **IR *v* (neat, cm^{-1}):** 3006, 2969, 2841, 1588, 1376, 1275, 1123, 971, 748; **HRMS (ESI, m/z):** calcd for $C_9H_{11}ClNO_3^+$ $[M+H]^+$: 216.0422; found: 216.0389.



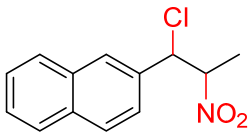
3r

1,3-dichloro-2-(1-chloro-2-nitroethyl)benzene (3r); It was prepared according to general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 16 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.2 (PE/EA=20 : 1, UV); green yellow oil; 72% yield (916 mg, 3.6 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 6.56 (dd, *J* = 8.5, 5.3 Hz, 1H), 5.44 (dd, *J* = 14.1, 8.8 Hz, 1H), 5.08 (dd, *J* = 14.2, 5.2 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 135.9, 131.3, 130.8, 129.4, 129.2, 77.8, 51.6; **IR *v* (neat, cm^{-1}):** 3012, 2990, 1556, 1437, 1280, 766, 738, 716; **HRMS (ESI, m/z):** calcd for $C_8H_7Cl_3NO_2^+$ $[M+H]^+$: 253.9537; found: 253.9485.



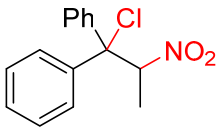
3s

(2-chloro-1-nitropropan-2-yl)benzene (3s); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 11 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow oil; 88% yield (88 mg, 0.44 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 – 7.53 (m, 2H), 7.45 – 7.36 (m, 3H), 4.93 (d, *J* = 3.0 Hz, 2H), 2.23 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 140.2, 129.1, 128.9, 126.3, 86.1, 67.1, 29.2; **IR *v* (neat, cm^{-1}):** 2919, 1587, 1446, 1372, 1061, 696, 652, 611; **HRMS (ESI, m/z):** calcd for $C_9H_{11}ClNO_2^+$ [M+H]$^+$: 200.0473; found: 200.0471.



3t

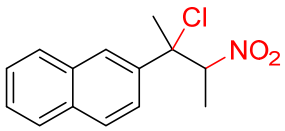
2-(1-chloro-2-nitropropyl)naphthalene (3t); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 14 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); white solid (m.p.:69-70 ℃); 82% yield (dr = 1 : 0.52, 102 mg, 0.41 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*, major)** δ 7.87 – 7.84 (m, 3H), 7.84 (d, *J* = 2.6 Hz, 1H), 7.55 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.54 – 7.51 (m, 2H), 5.55 (d, *J* = 7.7 Hz, 1H), 5.05 (p, *J* = 6.6 Hz, 1H), 1.80 (d, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*, major)** δ 133.8, 133.6, 133.6, 129.2, 128.4, 127.9, 127.5, 127.2, 127.0, 124.2, 87.6 , 63.1, 16.0; **IR *v* (neat, cm^{-1}):** 2920, 1647, 1554, 1450, 1358, 1275, 1260, 820, 749, 662, 477; **HRMS (ESI, m/z):** calcd for $C_{13}H_{13}ClNO_2^+$ [M+H]$^+$: 250.0630; found: 250.0628.



3u

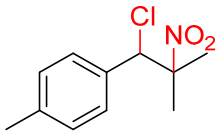
(1-chloro-2-nitropropane-1,1-diyl)dibenzene (3u); It was prepared according to

general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 30 h; petroleum ether/ethyl acetate = 20 : 1; **TLC:** R_f = 0.3 (PE/EA=20 : 1, UV); white solid (m.p.:100.3-101.1 ℃); 64% yield (879 mg, 3.2 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.46 (m, 4H), 7.40 – 7.27 (m, 6H), 5.79 (q, *J* = 6.6 Hz, 1H), 1.81 (d, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 141.24, 141.21, 128.6, 128.5, 128.4, 128.0, 127.6, 89.4, 77.3, 17.4; **IR *v* (neat, cm^{-1}):** 3005, 2990, 1557, 1446, 1275, 1260, 1043, 911, 749, 699; **HRMS (ESI, m/z):** calcd for $C_{15}H_{15}ClNO_2^+$ $[M+H]^+$: 276.0786; found: 276.0779.



3v

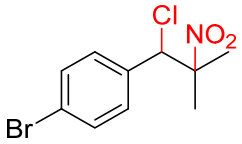
2-(2-chloro-3-nitrobutan-2-yl)naphthalene (3v); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 9 h; petroleum ether/ethyl acetate = 40 : 1; **TLC:** R_f = 0.6 (PE/EA=20 : 1, UV); white solid (m.p.:95.1-97.2 ℃); 74% yield (98 mg, 0.37 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 2.1 Hz, 1H), 7.91 – 7.80 (m, 3H), 7.66 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.58 – 7.47 (m, 2H), 5.27 (q, *J* = 6.7 Hz, 1H), 2.26 (s, 3H), 1.71 (d, *J* = 6.7 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 137.8, 133.0, 132.8, 128.69, 128.67, 127.6, 127.2, 126.9, 126.1, 124.0, 91.5, 71.7, 27.2, 15.4; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1553, 1456, 1275, 1260, 897, 816, 764; **HRMS (ESI, m/z):** calcd for $C_{14}H_{15}ClNO_2^+$ $[M+H]^+$: 264.0786; found: 264.0758.



3w

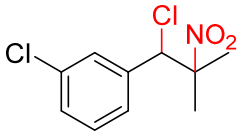
1-(1-chloro-2-methyl-2-nitropropyl)-4-methylbenzene (3w); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100 : 1; **TLC:** R_f = 0.3 (PE/EA=50 : 1, UV); green yellow oil; 77% yield (88 mg, 0.39 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 2.36

(s, 3H), 1.74 (s, 3H), 1.48 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 139.5, 132.5, 129.2, 128.9, 92.4, 67.0, 24.9, 21.3, 20.5; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1546, 1464, 1344, 1275, 768, 742, 520; **HRMS (ESI, m/z):** calcd for $C_{11}H_{15}ClNO_2^+$ $[M+H]^+$: 228.0786; found: 228.0789.



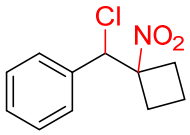
3x

1-bromo-4-(1-chloro-2-methyl-2-nitropropyl)benzene (3x)[8]; It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 11 h; petroleum ether/ethyl acetate = 100 : 1; **TLC:** R_f = 0.1 (PE, UV); white solid (m.p.: 43.1-46.7 ℃); 91% yield (133 mg, 0.45 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (dt, *J* = 8.4 Hz, 2H), 5.55 (s, 1H), 1.73 (s, 3H), 1.49 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 134.5, 131.8, 130.6, 123.7, 92.0, 66.2, 24.5, 20.9; **IR *v* (neat, cm^{-1}):** 3004, 2983, 1548, 1459, 1278, 1253, 746, 695; **HRMS (ESI, m/z):** calcd for $C_{10}H_{12}BrClNO_2^+$ $[M+H]^+$: 291.9735; found: 291.9729.



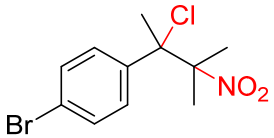
3y

1-chloro-3-(1-chloro-2-methyl-2-nitropropyl)benzene (3y); It was prepared according to general procedure (**C**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 73% yield (91 mg, 0.37 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 (d, *J* = 1.9 Hz, 1H), 7.36 (dt, *J* = 7.5, 1.9 Hz, 1H), 7.34 – 7.27 (m, 2H), 5.56 (s, 1H), 1.75 (s, 3H), 1.51 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)** δ 137.5, 134.7, 129.8, 129.7, 129.1, 127.2, 92.1, 66.0, 24.6, 20.9; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1547, 1469, 1345, 1275, 1260, 897, 768, 742; **HRMS (ESI, m/z):** calcd for $C_{10}H_{12}Cl_2NO_2^+$ $[M+H]^+$: 248.0240; found: 248.0227.



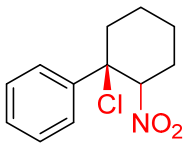
3z

(chloro(1-nitrocyclobutyl)methyl)benzene (3z); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 50 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); colorless oil; 89% yield (100 mg, 0.44 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 3H), 5.55 (s, 1H), 3.01 – 2.91 (m, 1H), 2.80 – 2.69 (m, 1H), 2.68 – 2.52 (m, 2H), 1.84-1.76 (m, 1H), 1.36 – 1.24 (m, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 135.3, 129.6, 128.8, 128.4, 92.8, 64.1, 30.7, 28.7, 13.3; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1478, 1457, 1275, 1260, 897, 751, 696; **HRMS (ESI, m/z):** calcd for $C_{10}H_{13}ClNO_2^+$ $[M+H]^+$: 226.0630; found: 226.0638.



3aa

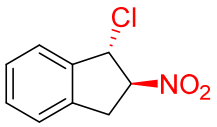
1-bromo-4-(2-chloro-3-methyl-3-nitrobutan-2-yl)benzene (3aa); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 13 h; petroleum ether/ethyl acetate = 200 : 1; **TLC:** R_f = 0.4 (PE/EA=100 : 1, UV); colorless oil; 50% yield (77 mg, 0.25 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 2.16 (s, 3H), 1.75 (s, 3H), 1.64 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 139.1, 131.1, 129.9, 123.1, 94.9, 74.9, 28.3, 23.6, 23.5; **IR *v* (neat, cm^{-1}):** 3014, 2997, 1537, 1488, 1380, 1348, 1282, 1260, 774, 745; **HRMS (ESI, m/z):** calcd for $C_{11}H_{14}BrClNO_2^+$ $[M+H]^+$: 305.9891; found: 305.9794.



3ab

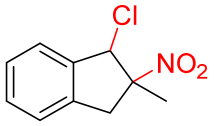
((1*R*)-1-chloro-2-nitrocyclohexyl)benzene (3ab)[6]; It was prepared according to

general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 9 h; petroleum ether/ethyl acetate = 40 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); light yellow solid; 93% yield (111 mg, 0.47 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.58 – 7.54 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 5.41 (dt, *J* = 4.6, 2.0 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.66 – 2.53 (m, 1H), 2.42 (d, *J* = 14.4 Hz, 1H), 2.31 – 2.22 (m, 1H), 2.05 – 1.91 (m, 2H), 1.78 – 1.62 (m, 2H).



3ac

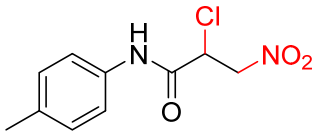
(1S,2S)-1-chloro-2-nitro-2,3-dihydro-1H-indene (3ac); It was prepared according to general procedure **(A)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 20 h; petroleum ether/ethyl acetate = 40 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); green yellow oil; 84% yield (831 mg, 4.2 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.49 – 7.44 (m, 1H), 7.39 – 7.34 (m, 2H), 7.28 (d, *J* = 3.8 Hz, 1H), 5.93 (d, *J* = 4.4 Hz, 1H), 5.34 (ddd, *J* = 8.0, 5.4, 4.4 Hz, 1H), 3.74 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.60 (dd, *J* = 16.7, 5.4 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 138.9, 137.7, 130.3, 128.7, 125.5, 124.9, 92.5, 62.5, 36.4; **IR *v* (neat, cm^{-1}):** 3091, 2918, 1551, 1496, 1369, 1215, 913, 819, 602; **HRMS (ESI, m/z):** calcd for $C_9H_9ClNO_2^+$ $[M+H]^+$: 198.0317; found: 198.0309.



3ad

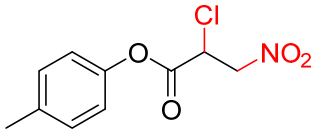
1-chloro-2-methyl-2-nitro-2,3-dihydro-1H-indene (3ad); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 14 h; petroleum ether/ethyl acetate = 50 : 1; **TLC:** R_f = 0.6 (PE/EA=20 : 1, UV); yellow oil; 77% yield (dr = 1 : 0.3, 82 mg, 0.39 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*, major)** δ 7.44 – 7.41 (m, 1H), 7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 6.04 (s, 1H), 3.87 (d, *J* = 16.4 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 1.88 (s, 3H); **^{13}C{^{1}H} NMR (101**

MHz, Chloroform-*d*, major) δ 139.4, 137.8, 129.9, 128.4, 125.3, 124.8, 97.6, 66.5, 42.9, 22.4; **IR *v* (neat, cm^{-1}):** 3108, 2920, 1646, 1546, 1382, 1269, 842, 749, 602; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}ClNO_2^+$ $[M+H]^+$: 212.0473; found: 212.0477.



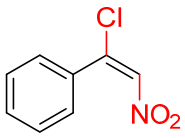
3ae

2-chloro-3-nitro-N-(p-tolyl)propanamide (3ae); It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20: 1 to 5 : 1; **TLC:** R_f = 0.2 (PE/EA=5 : 1, UV); yellow solid (m.p.:95.5-101.5 ℃); 57% yield (69 mg, 0.28 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.24 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.13 (dd, *J* = 14.2, 4.0 Hz, 1H), 5.05 (dd, *J* = 6.7, 4.0 Hz, 1H), 4.97 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 162.7, 135.8, 133.8, 129.9, 120.6, 77.1, 54.1, 21.1; **IR *v* (neat, cm^{-1}):** 3005, 2920, 1679, 1559, 1374, 1275, 1260, 816, 746; **HRMS (ESI, m/z):** calcd for $C_{10}H_{12}ClN_2O_3^+$ $[M+H]^+$: 243.0531; found: 243.0522.



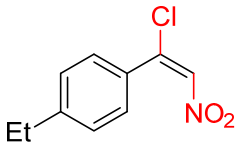
3af

***p*-tolyl-2-chloro-3-nitropropanoate (3af);** It was prepared according to general procedure **(C)**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 20: 1; **TLC:** R_f = 0.3 (PE/EA=10 : 1, UV); light pink solid (m.p.:67.1-68.4 ℃); 65% yield (79 mg, 0.32 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.14 – 5.04 (m, 2H), 4.93-4.86 (m, 1H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 165.4, 148.0, 136.8, 130.3, 120.7, 75.6, 49.8, 21.1; **IR *v* (neat, cm^{-1}):** 3005, 2989, 1766, 1564, 1375, 1275, 1260, 749; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}ClNO_4^+$ $[M+H]^+$: 244.0371; found: 243.0363.



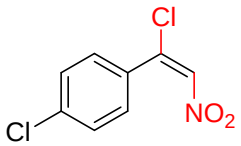
5a

(*E*)-(1-chloro-2-nitrovinyl)benzene (5a)[9]; It was prepared according to procedure (**D**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100: 1; **TLC:** R_f = 0.3 (PE/EA=50 : 1, UV); yellow solid; 54% yield (50 mg, 0.27 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.49 – 7.46 (m, 2H), 7.46 – 7.41 (m, 4H).



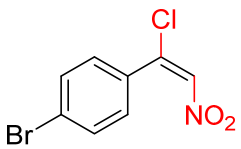
5b

(*E*)-1-(1-chloro-2-nitrovinyl)-4-ethylbenzene (5b)[9]; It was prepared according to procedure (**D**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100: 1; **TLC:** R_f = 0.3 (PE/EA=50 : 1, UV); yellow solid; 56% yield (59 mg, 0.28 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).



5c

(*E*)-1-chloro-4-(1-chloro-2-nitrovinyl)benzene (5c)[9]; It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100: 1; **TLC:** R_f = 0.3 (PE/EA=50 : 1, UV); yellow solid; 37% yield (40 mg, 0.18 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.47 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H).

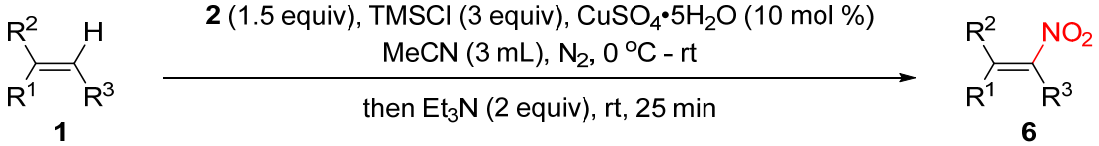


5d

(*E*)-1-bromo-4-(1-chloro-2-nitrovinyl)benzene (5d)[9]; It was prepared according to procedure (**D**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100: 1; **TLC:** R_f = 0.3 (PE/EA=50 : 1, UV); yellow solid; 53% yield (70 mg, 0.27 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H).

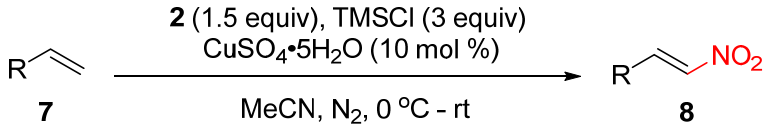
IV. The Synthesis of Nitroalkenes

General Procedure (E) for Nitroalkenes



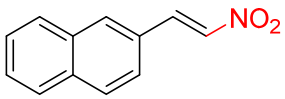
To a 10 mL dry flask were added alkene (0.50 mmol), **2** (91.5 mg, 0.75 mmol), TMSCl (165 μL, 1.5 mmol), $CuSO_4$•$5H_2O$ (12.5 mg, 0.05 mmol) and MeCN (3 mL) at 0 ℃ under N_2 atmosphere. The mixture was stirred for 2 h at 0 ℃ first and then warmed to room temperature as monitoring by TLC. Upon completion, Et_3N (100 μL, 1.0 mmol) was added to the mixture and stirred for 25 min at room temperature. After that, the reaction mixture was concentrated and purified by column chromatography on silica gel to give the desired product.

General Procedure (F) for Nitroalkenes



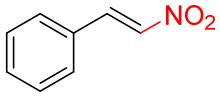
To a 10 mL dry flask were added alkene (0.50 mmol), **2** (91.5 mg, 0.75 mmol), TMSCl (165 μL, 1.5 mmol), $CuSO_4$•$5H_2O$ (12.5 mg, 0.05 mmol) and MeCN (3 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃ first and then warmed to room temperature as monitoring by TLC. Upon completion, the reaction

mixture was concentrated and purified by column chromatography on silica gel to give the desired product.



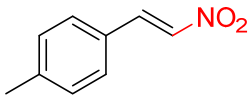
6a

(*E*)-2-(2-nitrovinyl)naphthalene (6a)[10]; It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethyl acetate = 20: 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 99% yield (99 mg, 0.50 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.17 (d, *J* = 13.6 Hz, 1H), 8.03 (s, 1H), 7.97 – 7.82 (m, 3H), 7.71 (d, *J* = 13.6 Hz, 1H), 7.65 – 7.50 (m, 3H).



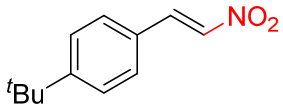
6b

(*E*)-(2-nitrovinyl)benzene (6b)[11]; It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 87% yield(66 mg, 0.44 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.53 – 7.42 (m, 3H).



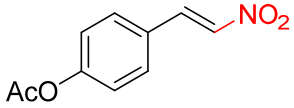
6c

(*E*)-1-methyl-4-(2-nitrovinyl)benzene (6c)[10]; It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 84% yield(63 mg, 0.42 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 13.7 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H).



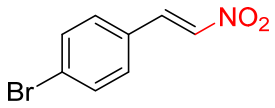
6d

(*E*)-1-(tert-butyl)-4-(2-nitrovinyl)benzene (6d)[11]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 85% yield(87 mg, 0.42 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 13.6 Hz, 1H), 7.58 (d, *J* = 13.6 Hz, 1H), 7.51-7.46 (m, 4H), 1.34 (s, 9H).



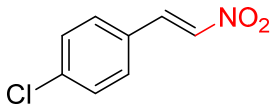
6e

(*E*)-4-(2-nitrovinyl)phenyl acetate (6e)[11]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.6 (PE/EA=10 : 1, UV); yellow solid; 94% yield(97 mg, 0.47 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.20 (dt, *J* = 8.4, 2H), 2.33 (s, 3H).



6f

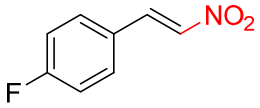
(E)-1-bromo-4-(2-nitrovinyl)benzene (6f)[11]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 98% yield(112 mg, 0.49 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 13.7 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H).



6g

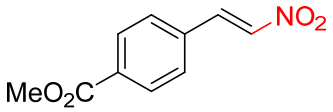
(*E*)-1-chloro-4-(2-nitrovinyl)benzene (6g)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 89% yield(82 mg, 0.47 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d,

J = 13.7 Hz, 1H), 7.56 (d, *J* = 13.7 Hz, 1H), 7.49 (dt, *J* = 8.4 Hz, 2H), 7.44 (dt, *J* = 8.4, 2H).



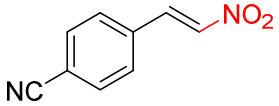
6h

(*E*)-1-fluoro-4-(2-nitrovinyl)benzene (6h)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 79% yield(66 mg, 0.40 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 13.7 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.15 (t, *J* = 8.4 Hz, 2H).



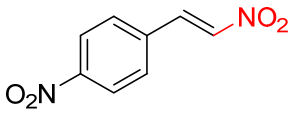
6i

methyl (*E*)-4-(2-nitrovinyl)benzoate (6i)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 8.5 h; petroleum ether/ethylacetate = 10 : 1; **TLC:** R_f = 0.4 (PE/EA=10 : 1, UV); yellow solid; 82% yield(85 mg, 0.41 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 13.7 Hz, 1H), 7.67 – 7.59 (m, 3H), 3.95 (s, 3H).



6j

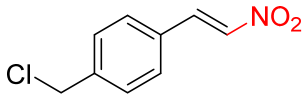
(*E*)-4-(2-nitrovinyl)benzonitrile (6j)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 6.5 h; petroleum ether/ethylacetate = 10 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 87% yield(76 mg, 0.44 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 13.7 Hz, 1H).



6k

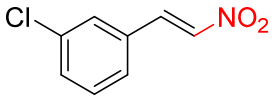
(*E*)-1-nitro-4-(2-nitrovinyl)benzene (6k)[12]**;** It was prepared according to general

procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 6.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 72% yield(70 mg, 0.36 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 13.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 13.8 Hz, 1H).



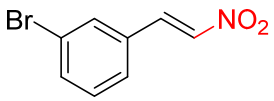
6l

(*E*)-1-(chloromethyl)-4-(2-nitrovinyl)benzene (6l)[13]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); pale yellow solid; 99% yield(98 mg, 0.50 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 4.61 (s, 2H).



6m

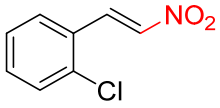
(*E*)-1-chloro-3-(2-nitrovinyl)benzene (6m)[14]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); pale yellow solid; 84% yield(77 mg, 0.42 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 13.7 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.50 – 7.37 (m, 3H).



6n

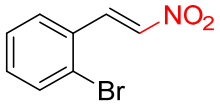
(*E*)-1-bromo-3-(2-nitrovinyl)benzene (6n)[11]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 90% yield(103 mg, 0.45 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 13.7 Hz, 1H), 7.69 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 13.7 Hz, 1H),

7.48 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H).



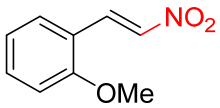
6o

(*E*)-1-chloro-2-(2-nitrovinyl)benzene (6o)[13]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 92% yield(84 mg, 0.46 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.41 (d, *J* = 13.7 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.38 – 7.31 (m, 1H).



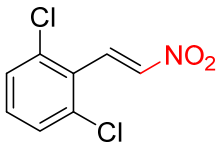
6p

(*E*)-1-bromo-2-(2-nitrovinyl)benzene (6p)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 90% yield(103 mg, 0.45 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.40 (d, *J* = 13.6 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.54 (d, *J* = 13.6 Hz, 1H), 7.41 – 7.31 (m, 2H).



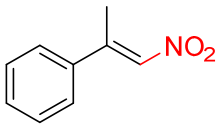
6q

(*E*)-1-methoxy-2-(2-nitrovinyl)benzene (6q)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 70% yield(63 mg, 0.35 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.15 (d, *J* = 13.6 Hz, 1H), 7.88 (d, *J* = 13.6 Hz, 1H), 7.46 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H).



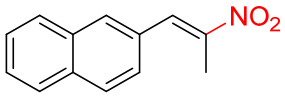
6r

(*E*)-1,3-dichloro-2-(2-nitrovinyl)benzene (6r)[15]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.3 (PE/EA=20 : 1, UV); yellow solid; 74% yield(81 mg, 0.37 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.26 (d, *J* = 14.0 Hz, 1H), 7.85 (d, *J* = 14.0 Hz, 1H), 7.49 – 7.36 (m, 2H), 7.31 (dd, *J* = 8.8, 7.4 Hz, 1H).



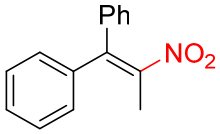
6s

(*E*)-(1-nitroprop-1-en-2-yl)benzene (6s)[10]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.3 (PE/EA=20 : 1, UV); yellow solid; 88% yield(72 mg, 0.44 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (s, 5H), 7.31 (s, 1H), 2.65 (s, 3H).



6t

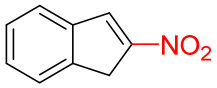
(*E*)-2-(2-nitroprop-1-en-1-yl)naphthalene (6t)[16]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.5 (PE/EA=20 : 1, UV); yellow solid; 83% yield(88 mg, 0.41 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.26 (s, 1H), 7.99 – 7.83 (m, 4H), 7.64 – 7.44 (m, 3H), 2.55 (s, 3H).



6u

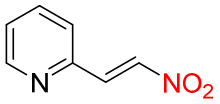
(2-nitroprop-1-ene-1,1-diyl)dibenzene (6u); It was prepared according to general

procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.3 (PE/EA=20 : 1, UV); yellow solid (m.p.:61.4-64.1 ℃); 67% yield(80 mg, 0.33 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.33 (m, 3H), 7.34 – 7.28 (m, 3H), 7.23 – 7.18 (m, 2H), 7.18 – 7.12 (m, 2H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 146.5, 140.0, 138.4, 138.3, 129.5, 128.9, 128.71, 128.70, 128.67, 128.3, 18.3; **IR *v* (neat, cm^{-1}):** 3005, 2989, 2277, 1632, 1560, 1503, 1333, 1275, 966, 897, 745, 481; **HRMS (ESI, m/z):** calcd for $C_{15}H_{14}ClNO_2^+$ $[M+H]^+$: 240.1019; found: 240.0989.



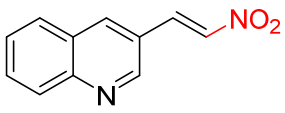
6ac

2-nitro-1H-indene (6ac)[17]**;** It was prepared according to general procedure (**E**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12.5 h; petroleum ether/ethylacetate = 20 : 1; **TLC:** R_f = 0.4 (PE/EA=20 : 1, UV); yellow solid; 80% yield(64 mg, 0.40 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 – 7.89 (m, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.48 (td, *J* = 7.4, 1.3 Hz, 1H), 7.45 – 7.38 (m, 1H), 3.99 (d, *J* = 2.0 Hz, 2H).



8a

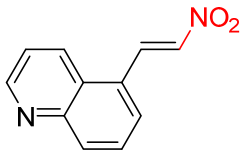
(*E*)-2-(2-nitrovinyl)pyridine (8a)[13]**;** It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 10: 1; **TLC:** R_f = 0.1 (PE/EA=10 : 1, UV); yellow solid; 79% yield (59 mg, 0.39 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.75 – 8.63 (m, 1H), 8.02 (d, *J* = 13.2 Hz, 1H), 7.92 (d, *J* = 13.2 Hz, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 7.7, 4.8 Hz, 1H).



8b

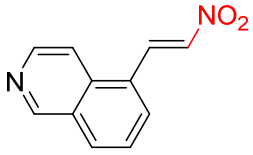
(*E*)-3-(2-nitrovinyl)quinoline (8b); It was prepared according to procedure (**F**);

reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 10: 1; **TLC:** R_f = 0.1 (PE/EA=10 : 1, UV); yellow solid (m.p.:109.7-111.4 ℃); 74% yield (74 mg, 0.37 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.07 (d, *J* = 2.3 Hz, 1H), 8.34 (d, *J* = 2.3 Hz, 1H), 8.23 – 8.10 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.79 (d, *J* = 13.8 Hz, 1H), 7.65 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 149.4, 148.9, 138.2, 137.6, 135.9, 131.9, 129.8, 128.7, 128.2, 127.5, 123.4; **IR *v* (neat, cm^{-1}):** 3361, 3188, 2849, 1646, 1511, 1345, 972, 847, 715, 477; **HRMS (ESI, m/z):** calcd for $C_{11}H_9N_2O_2^+$ $[M+H]^+$: 201.0659; found: 201.0663.



8c

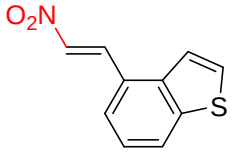
(*E*)-5-(2-nitrovinyl)quinoline (8c); It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 10: 1; **TLC:** R_f = 0.1 (PE/EA=10 : 1, UV); yellow solid (m.p.:75.8-80.1 ℃); 42% yield (42 mg, 0.21 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.03 (d, *J* = 4.2 Hz, 1H), 8.76 (d, *J* = 13.4 Hz, 1H), 8.50 (d, *J* = 8.6 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 13.4 Hz, 1H), 7.58 (dd, *J* = 8.6, 4.2 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 151.3, 148.6, 139.4, 134.6, 134.0, 131.5, 129.2, 127.5, 127.1, 126.8, 122.4; **IR *v* (neat, cm^{-1}):** 3005, 2240, 1630, 1489, 1347, 1275, 961, 794, 749; **HRMS (ESI, m/z):** calcd for $C_{11}H_9N_2O_2^+$ $[M+H]^+$: 201.0659; found: 201.0648.



8d

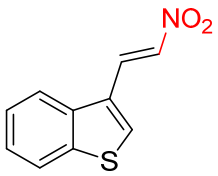
(*E*)-5-(2-nitrovinyl)isoquinoline (8d); It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 10: 1; **TLC:** R_f = 0.1 (PE/EA=10 : 1, UV); yellow solid (m.p.:189.4-190.2 ℃); 62% yield (62 mg, 0.31 mmol); **^{1}H NMR (400 MHz,**

Chloroform-*d*) δ 9.34 (s, 1H), 8.77 – 8.66 (m, 2H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 6.0 Hz, 1H), 7.73 – 7.65 (m, 2H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 153.6, 144.9, 139.4, 134.5, 134.3, 132.1, 130.3, 127.1, 126.4, 116.0; **IR *v* (neat, cm^{-1}):** 3005, 2989, 2319, 1654, 1514, 1275, 1260, 897, 724; **HRMS (ESI, m/z):** calcd for $C_{11}H_9N_2O_2^+$ $[M+H]^+$: 201.0659; found: 201.0618.



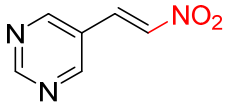
8e

(*E*)-4-(2-nitrovinyl)benzo[*b*]thiophene (8e); It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100 : 1; **TLC:** R_f = 0.2 (PE/EA=50 : 1, UV); yellow solid (m.p.:89.2-91.3 ℃); 51% yield (52 mg, 0.52 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.53 (d, *J* = 13.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.66 – 7.61 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 141.3, 139.3, 137.9, 136.7, 129.6, 126.4, 125.1, 124.5, 124.3, 121.2; **IR *v* (neat, cm^{-1}):** 3005, 2998, 2700, 2314, 1633, 1504, 1462, 1336, 1260, 898, 788; **HRMS (ESI, m/z):** calcd for $C_{10}H_8NO_2S^+$ $[M+H]^+$: 206.0270; found: 206.0233.



8f

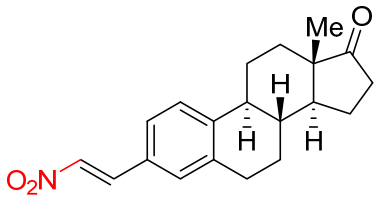
(*E*)-3-(2-nitrovinyl)benzo[*b*]thiophene (8f)[10]**;** It was prepared according to procedure (**F**); reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 100: 1; **TLC:** R_f = 0.1 (PE/EA=50 : 1, UV); yellow solid; 50% yield (51 mg, 0.25 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.31 (d, *J* = 13.7 Hz, 1H), 8.03 – 7.89 (m, 3H), 7.77 (d, *J* = 13.7 Hz, 1H), 7.58 – 7.45 (m, 2H).



8g

(*E*)-5-(2-nitrovinyl)pyrimidine (8g); It was prepared according to procedure (**F**);

reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 5: 1; **TLC:** R_f = 0.1 (PE/EA=5 : 1, UV); yellow solid; 47% yield (36 mg, 0.24 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.30 (s, 1H), 8.94 (s, 2H), 7.96 (d, *J* = 13.9 Hz, 1H), 7.67 (d, *J* = 13.9 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 160.6, 156.5, 139.6, 131.9, 124.8; **IR *v* (neat, cm^{-1}):** 3015, 2708, 2065, 1639, 1528, 1418, 1275, 958, 696; **HRMS (ESI, m/z):** calcd for $C_6H_6N_3O_2^+$ $[M+H]^+$: 152.0455; found: 152.0413.



8h

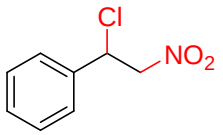
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((*E*)-2-nitrovinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (8h); It was prepared according to procedure (**F**), $LiNO_3$ (52 mg, 0.75 mmol) was instead of **2**; reaction temperature: 0 ℃ (2 h) then rt; reaction time: 12 h; petroleum ether/ethyl acetate = 5: 1; **TLC:** R_f = 0.1 (PE/EA=5 : 1, UV); pale yellow solid (m.p.:210.3-212.8 ℃); 77% yield (125 mg, 0.38 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 13.7 Hz, 1H), 7.56 (d, *J* = 13.7 Hz, 1H), 7.35 (q, *J* = 9.2, 8.8 Hz, 2H), 7.28 (s, 1H), 2.98 – 2.93 (m, 2H), 2.58 – 2.48 (m, 1H), 2.42 (s, 1H), 2.39 – 2.27 (m, 1H), 2.23 – 2.11 (m, 1H), 2.10 – 2.02 (m, 2H), 2.02 – 1.94 (m, 1H), 1.67 – 1.59 (m, 3H), 1.55 (d, *J* = 2.8 Hz, 1H), 1.52 – 1.44 (m, 2H), 0.94 – 0.92 (m, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 220.6, 145.0, 139.3, 138.0, 136.6, 130.1, 127.7, 126.7, 126.6, 50.6, 48.0, 44.8, 37.9, 35.9, 31.6, 29.3, 26.3, 25.7, 21.7, 13.9; **IR *v* (neat, cm^{-1}):** 2921, 2270, 1736, 1634, 1509, 1340, 1275, 969, 820, 749; **HRMS (ESI, m/z):** calcd for $C_{20}H_{24}NO_3^+$ $[M+H]^+$: 326.1751; found: 326.1738.

V. 100 mmol Scale of Chloronitration of Alkenes

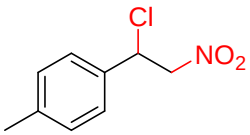
To a 250 mL dry flask were added alkene (**1b**, **1c** or **1l**; 100 mmol), **2** (18.3 g, 150

mmol), TMSCl (33 mL, 300 mmol), $CuSO_4$•$5H_2O$ (2.5 g, 10 mmol) and MeCN (100 mL) at 0 ℃ under N_2 atmosphere. The solution was stirred for 2 h at 0 ℃ first and then warmed to room temperature as monitoring by TLC. Upon completion, the reaction mixture was filtered. The filtrate was concentrated and purified by column chromatography via silica gel to give the desired product **3b** (17.21 g, 92.73 mmol, 92%); **3c** (14.70 g, 73.65 mmol, 74%); **3l** (21.86 g, 93.38 mmol, 93%).

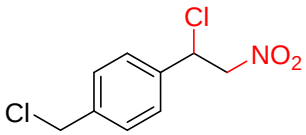
100 mmol Scale:



3b, **17.21 g** (92%)



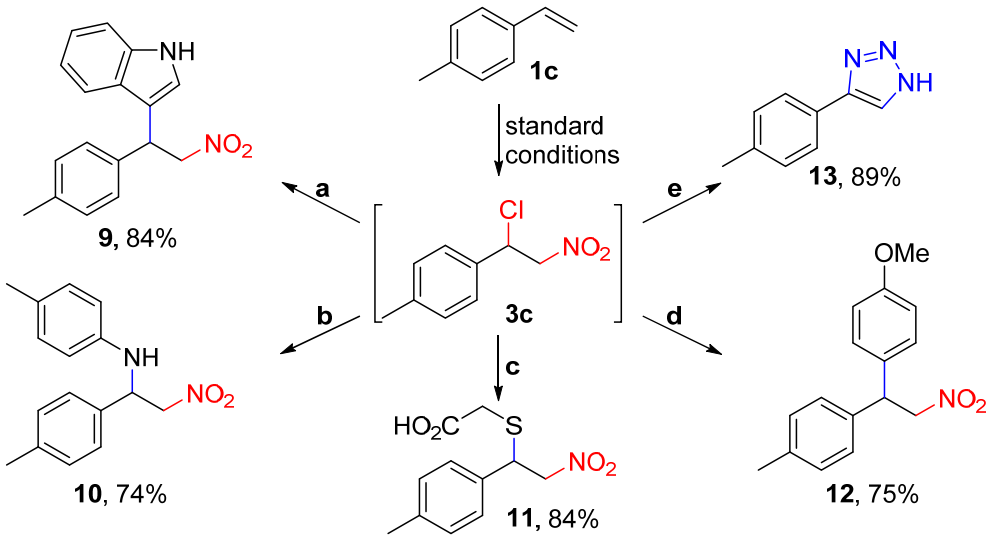
3c, **14.70 g** (74%)



3l, **21.86 g** (93%)

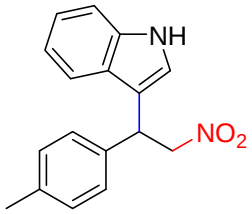
VI. Sequential Further Transformations

Sequential Further Transformations:



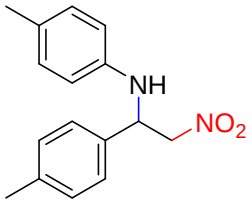
Reaction conditions: **a)** 1*H*-indole (2 equiv), $Sc(OTf)_3$ (2.5 mol %), H_2O, rt. **b)** 4-methylaniline (1.5 equiv), Na_2CO_3 (2 equiv), MeCN, rt. **c)** 2-mercaptoacetic acid (1.5 equiv), MeONa (3 equiv), MeOH, reflux. **d)** (4-methoxyphenyl)-magnesium bromide (2 equiv), THF, 50 °C. **e)** NaN_3 (4 equiv), DMF, rt. ***Note***: Reported yields represent total isolated yields for two steps.

The reaction of **1c** with **2** was carried out according to general procedure (**C**). Upon completion, the mixture was filtered and then removed the solvent via vacum to afford crude **3c**. **3c** was used directly to next step without further purification.



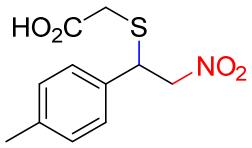
9

3-(2-nitro-1-(p-tolyl)ethyl)-1*H*-indole (9)[18]**;** 1*H*-indole (117 mg, 1.0 mmol), $Sc(OTf)_3$ (6.1 mg, 0.0125 mmol) and H_2O (1 mL) was added to crude **3c**, and stirred at room temperature for 36 h, monitored by TLC. Upon completion, extracted with ethyl acetate (3 mL) three times. Combined the organic layers, dried over with Na_2SO_4, concentrated the organic phase, and then purified by column chromatography on silica gel to give the desired product **9**; **TLC:** R_f= 0.1 (PE/EA=20 : 1, UV); brown oil; 84% yield (113 mg, 0.40 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.07 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.08 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 5.16 (t, *J* = 8.0 Hz, 1H), 5.05 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.92 (dd, *J* = 12.3, 8.4 Hz, 1H), 2.31 (s, 3H).



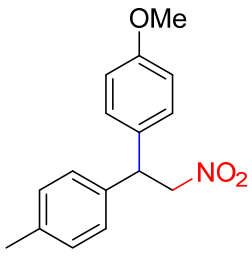
10

4-methyl-*N*-(2-nitro-1-(p-tolyl)ethyl)aniline (10)[19]**;** While **1c** was completed, the mixture was filtered, then 4-methylaniline (81 mg, 0.75 mmol) and Na_2CO_3 (106 mg, 1.0 mmol) was added to the mixture, and stirred at room temperature for 10 h, monitored by TLC. Upon completion, concentrated and purified by column chromatography on silica gel to give the desired product **10**; **TLC:** R_f = 0.2 (PE/EA=20 : 1, UV); brown oil; 74% yield (100 mg, 0.37 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 5.10 (t, *J* = 6.7 Hz, 1H), 4.71 – 4.65 (m, 2H), 4.22 (s, 1H), 2.33 (s, 3H), 2.21 (s, 3H).



11

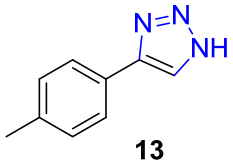
2-((2-nitro-1-(*p*-tolyl)ethyl)thio)acetic acid (11); 2-mercaptoacetic acid (69 mg, 0.75 mmol) was added to MeONa (30 w.t.% in MeOH, 260 μL, 1.5 mmol) in 3 mL MeOH and stirred at room temperature for 10 min, crude **3c** was added to the mixture. Then the mixture was warmed to 85 ℃ for 10 h, monitored by TLC. Upon completion, the reaction mixture was poured into crush ice, neutrailized with 2*N* HCl (3 mL), exctraced with DCM (10 mL) three times. Combined the organic layers, dried over with Na_2SO_4, concentrated the organic phase, and then purified by column chromatography on silica gel to give the desired product **11**; **TLC:** R_f = 0.1 (PE/EA=3 : 1, UV); gray solid (m.p.:87.4-88.7 ℃); 84% yield (107 mg, 0.42 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.70 (brs, 1H), 7.26 – 7.22 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.90 – 4.74 (m, 3H), 3.18 (d, *J* = 15.5 Hz, 1H), 3.08 (d, *J* = 15.5 Hz, 1H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 175.9, 139.0, 132.7, 130.0, 128.0, 78.7, 32.5, 21.3; **IR *v* (neat, cm^{-1}):** 3443, 2989, 2706, 2318, 1636, 1556, 1462, 1376, 1260, 1192, 897, 753, 706; **HRMS (ESI, m/z):** calcd for $C_{11}H_{14}NO_4S^+$ $[M+H]^+$: 256.0638; found: 256.0607.



12

1-methoxy-4-(2-nitro-1-(p-tolyl)ethyl)benzene (12); (4-methoxyphenyl)-magnesium bromide (1.0 M in THF, 1 mL, 1.0 mmol) and THF (3 mL) was added to crude **3c** under N_2 atmosphere at 0 ℃, and stirred at room temperature for 24 h, monitored by TLC. Upon completion, the mixture was quenched with saturated NH_4Cl (5 mL), extracted with EA (5 mL) three times. Combined the organic layers, dried over with Na_2SO_4, concentrated the organic phase, and then purified by column chromatography

on silica gel to give the desired product **12**; **TLC:** R_f = 0.1 (PE/EA=20 : 1, UV); yellow oil; 75% yield (102 mg, 0.38 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.21 – 7.01 (m, 6H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.93 (d, *J* = 9.0 Hz, 2H), 4.83 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H), 2.31 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)** δ 159.0, 137.3, 136.6, 131.6, 129.8, 128.8, 127.5, 114.5, 79.7, 55.4, 48.0, 21.2; **IR *v* (neat, cm^{-1}):** 3005, 2985, 1609, 1552, 1464, 1375, 1275, 1031, 913, 803, 749, 572; **HRMS (ESI, m/z):** calcd for $C_{16}H_{18}NO_3^+$ $[M+H]^+$: 272.1281; found: 272.1248.

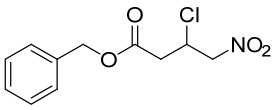


13

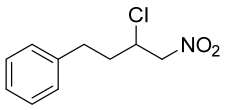
4-(*p*-tolyl)-1*H*-1,2,3-triazole (13)[20]**;** NaN_3 (130 mg, 2.0 mmol) and DMF (5 mL) was added to crude **3c**, and stirred at room temperature for 8 h, monitored by TLC. Upon completion, The mixture was diluted by saturated $NaHCO_3$ (15 mL), extracted with Et_2O(10 mL) three times. Combined the organic layers, dried over with Na_2SO_4, concentrated the organic phase, and then purified by column chromatography on silica gel to give the desired product **13**; **TLC:** R_f = 0.3 (PE/EA=5 : 1, UV); white solid; 89% yield (71 mg, 0.47 mmol); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz,, 2H), 2.40 (s, 3H).

VII. Substrate Limitation

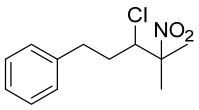
Impure products:



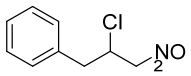
3ag, 17%



3ah, 34%



3ai, 39%



3aj, 38%

Impure products was detected by NMR:

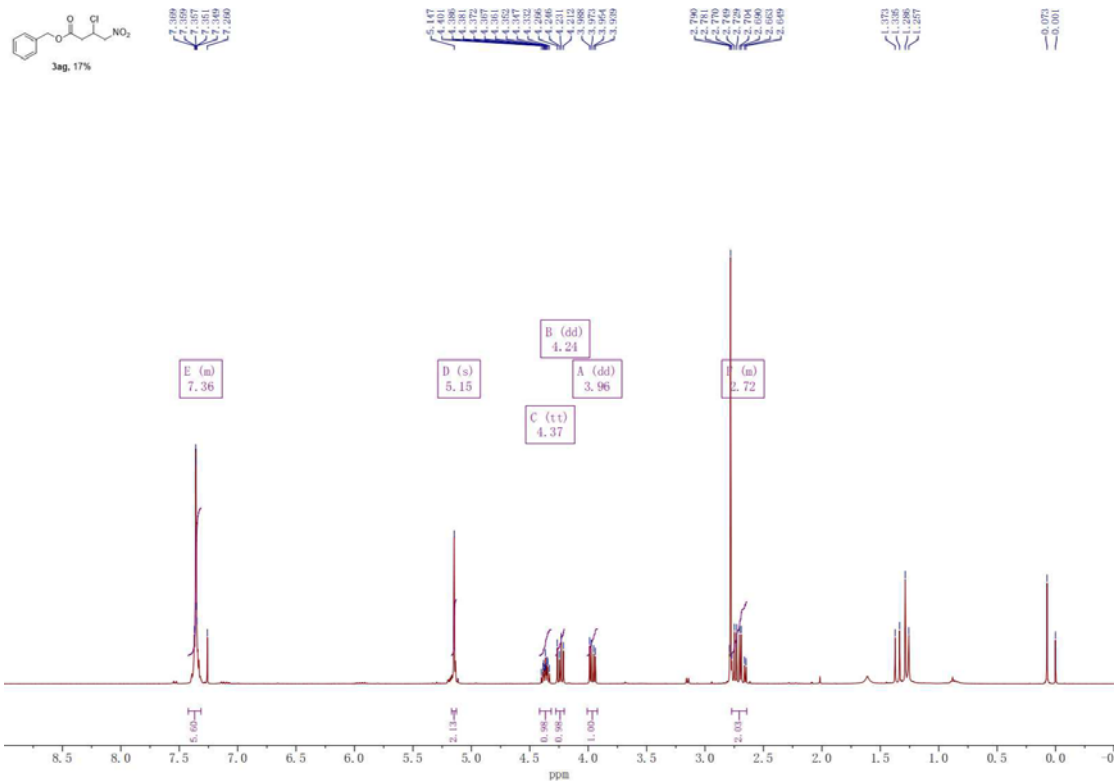


Figure S1. ^{1}H NMR spectra of **3ag** in $CDCl_3$

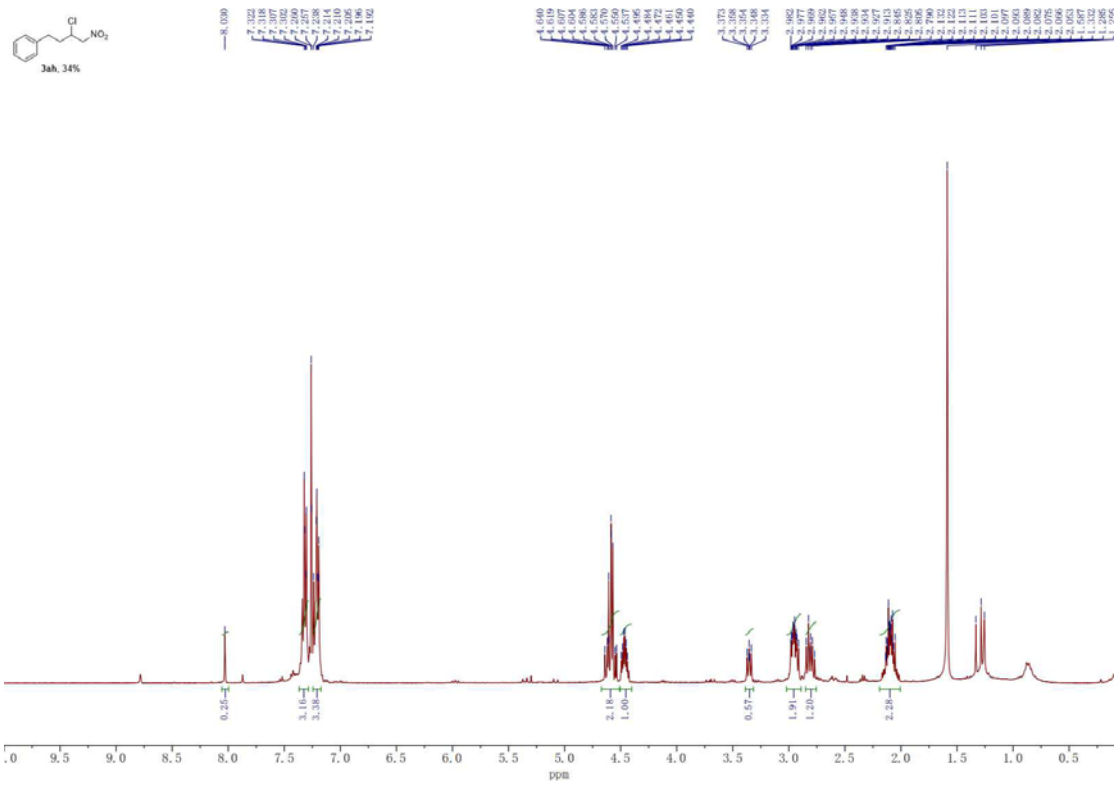


Figure S2. ^{1}H NMR spectra of **3ah** in $CDCl_3$

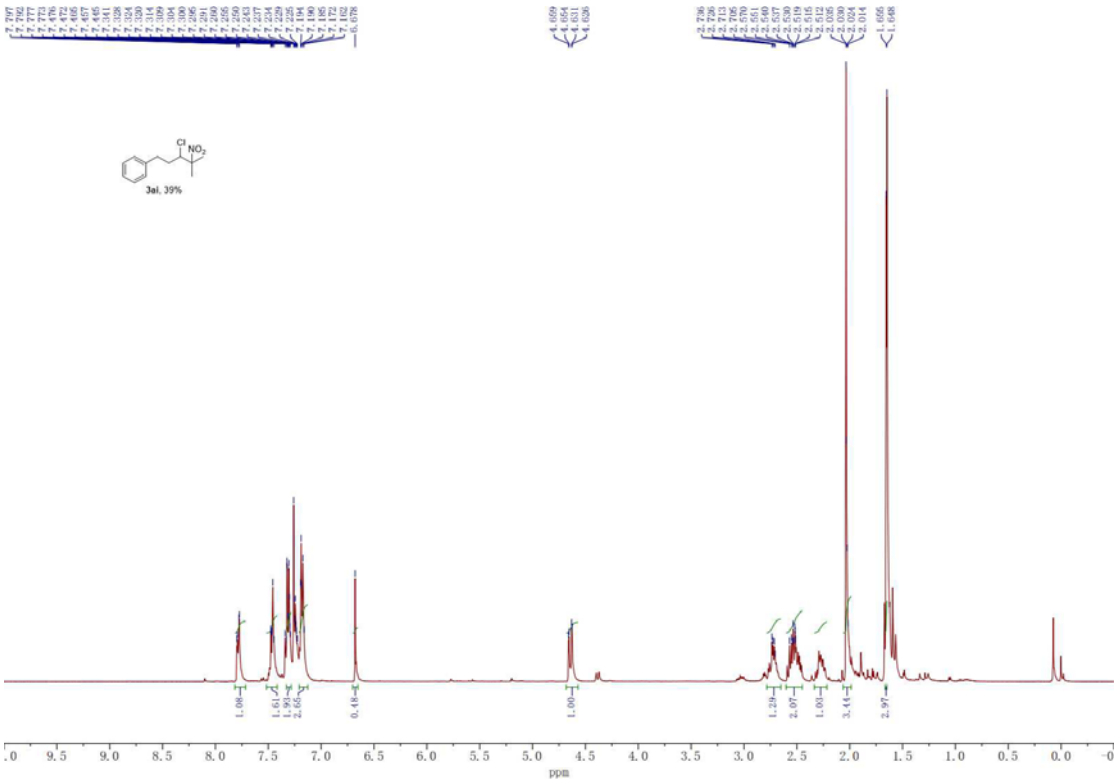


Figure S3. ^{1}H NMR spectra of **3ai** in $CDCl_3$

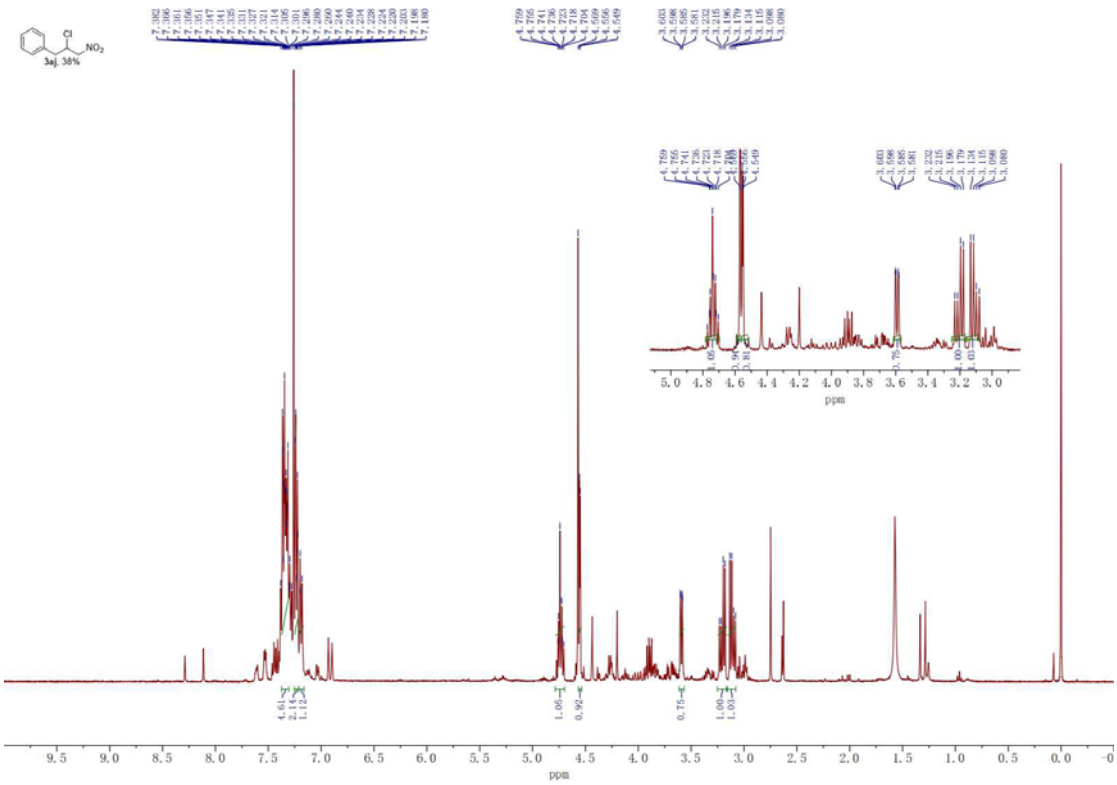
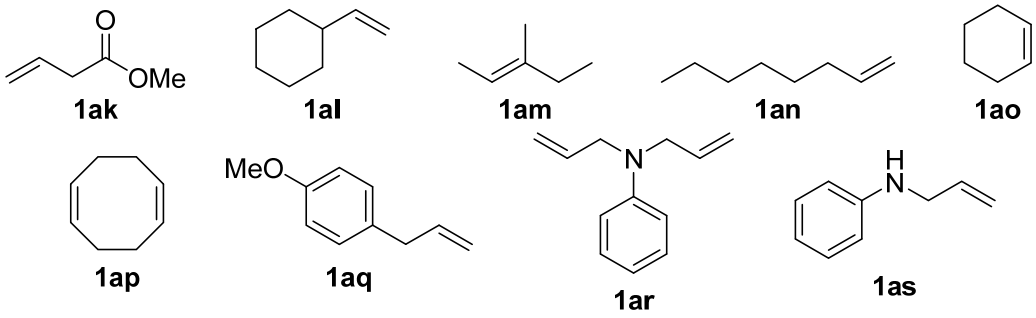
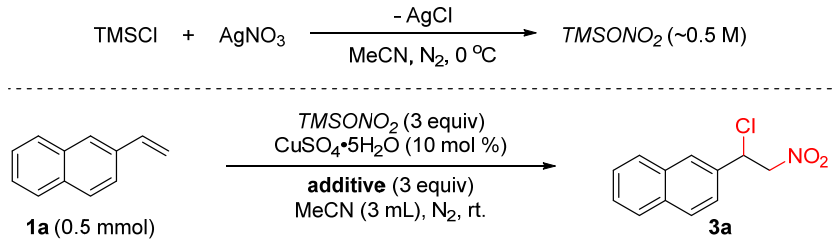


Figure S4. ^{1}H NMR spectra of **3aj** in $CDCl_3$

Decomposed subtrates:



VIII. Control Experiments



additive:	No	TMSCl	LiCl	TMSCN	CsF	TBAF[b]
results:	trace	**3a**, 83%[a]	**3a**, 81%[a]	N.R.[c]	N.R.[c]	N.R.[c]

[a] The yield was determined with ^{1}H NMR by adding 1,2-dichloroethane as an internal standard. [b] **TBAF** = Tetrabutylammonium fluoride. [c] The reaction did not work and only starting marterials were detected by ^{1}H NMR.

First step: To a 50 mL dry flask equipped with a stir bar was added $AgNO_3$ (1.019 g, 6.0 mmol), MeCN (10 mL) and TMSCl (543 mg, 5.0 mmol) at 0 ℃ under N_2 atmosphere. The mixture was stirred for 1 h at 0 ℃ to obtain *TMSONO*$_2$ (~0.5 M in MeCN).

Second step: To a 10 mL dry flask equipped with a stir bar was added **1a** (77 mg, 0.50 mmol), additive (1.5 mmol; TMSCl, LiCl, TMSCN, CsF, TBAF or without additive) and $CuSO_4$•$5H_2O$ (12.5 mg, 0.05 mmol) under N_2 atmosphere, *TMSONO*$_2$ (1.5 mmol, 3 mL) was added via syringe. The mixture was stirred at room temperature and monitered by TLC. Upon completion, the reaction mixture was concentrated and fast column chromatography via silica gel, eluted with DCM (60 mL) to give the crude product. The crude product was dissolved with $CDCl_3$, 1,2-dichloroethane (49.5 mg, 0.50 mmol) was added to the solution as an internal standard. Then the sample was detected and analyzed via ^{1}H NMR.

IX. Raman Spectra

The Raman spectra at 25 °C were taken with a Jobin Yvon confocal laser Raman system (SuperLabRam II), which was equipped with a He–Ne laser at 632.8 nm with a power of approximately 5 mW.

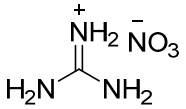
Raman Analysis

I. MeCN (3 mL)

II. MeCN (3 mL) + $AgNO_3$ (1 mmol)

III. MeCN (3 mL) + **2** (1 mmol)

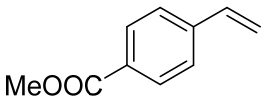
IV. MeCN (3 mL) + TMSCl (1 mmol)



2

V. MeCN (3 mL) + $AgNO_3$ (1.2 mmol) + TMSCl (1 mmol)

VI. MeCN (3 mL) + **1i** (0.5 mmol)



1i

VII. MeCN (3 mL) + **2** (0.75 mmol) + TMSCl (1.5 mmol) + **1i** (0.5 mmol) + $CuSO_4 \cdot 5H_2O$ (0.05 mmol)

Under N_2 atmosphere, to seven 10 mL dry flasks equipped with a stir bar was separately added MeCN (3 mL) (No.**I**); MeCN (3 mL) and $AgNO_3$ (167 mg, 1 mmol) (No.**II**); MeCN (3 mL) and **2** (122 mg, 1 mmol) (No.**III**); MeCN (3 mL) and TMSCl (108.6 mg, 1 mmol) (No.**IV**); MeCN (3 mL), $AgNO_3$ (204 mg, 1.2 mmol) and TMSCl (108.6 mg, 1 mmol) (No.**V**); MeCN (3 mL) and **1i** (81 mg, 0.5 mmol) (No.**VI**); MeCN (3 mL), **2** (91.5 mg, 0.75 mmol), TMSCl (163 mg, 1.5 mmol), **1i** (81 mg, 0.5 mmol) and $CuSO_4 \cdot 5H_2O$ (12.5 mg, 0.05 mmol) (No.**VII**). All of the reactions were stirred at 0 °C for 2 h. Then the samples were taken from each flask and were separately detected by Raman.

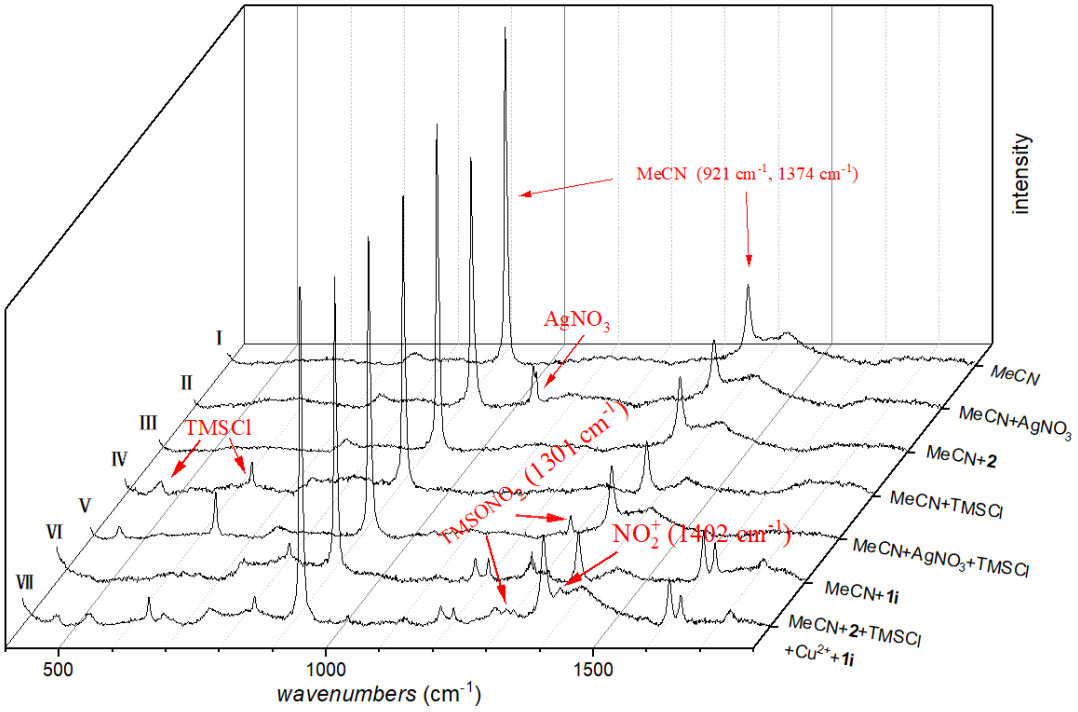


Figure S5. Raman spectra for **I-VII**

Discussion of Figure S5: As shown in Figure S5, the peaks at 921 and 1374 cm^{-1} can be assigned to the Raman signals of MeCN.[5] In No.**V**, the reaction of TMSCl with $AgNO_3$ could generate $TMSONO_2$ in situ.[21] By comparing the signal of $AcONO_2$ (1309 cm^{-1}),[22] it is reasonable that the new band at 1301 cm^{-1} in the spectrum of No. **V** possibly belongs to $TMSONO_2$. The band at 1301 cm^{-1} also appears in the spectrum of No. VII, suggesting that $TMSONO_2$ is probably the intermediate of the reaction. Note that a weak band of NO_2^+ (1402 cm^{-1})[22-24] was also observed (Figure S1. No.**VII**), which indicated that NO_2^+ was formed during the reaction and NO_2^+ may be the active species for this reaction.

X. NMR Monitoring Experiments

To over dried NMR tube was added **2** (18.3 mg, 0.15 mmol), $CuSO_4$•$5H_2O$ (2.5 mg, 0.01 mmol), styrene derivative (0.10 mmol; *p*-Me, *p*-H, *p*-AcO, *p*-CN or *p*-NO_2), TMSCl (32.6 mg, 0.3 mmol), DCE (9.9 mg, 0.10 mmol, as an internal standard) and

CD_3CN (0.5 mL) under N_2 atmosphere. And then this tube was placed ice bath for 1 h firstly and then was allowed to warm to room temperature. The sample was detected by ^1H NMR per 15 min or 30 min. The concentration of product **3** was measured by monitoring the appearance of product **3** signals on ^1H NMR, which was normalized against the internal standard peak (DCE). The data shown in Figure S6 indicated that the substrates bearing electron-withdrawing groups (NO_2, CN, OAc) reacted more rapidly than the styrene with electron-donating group (Me).

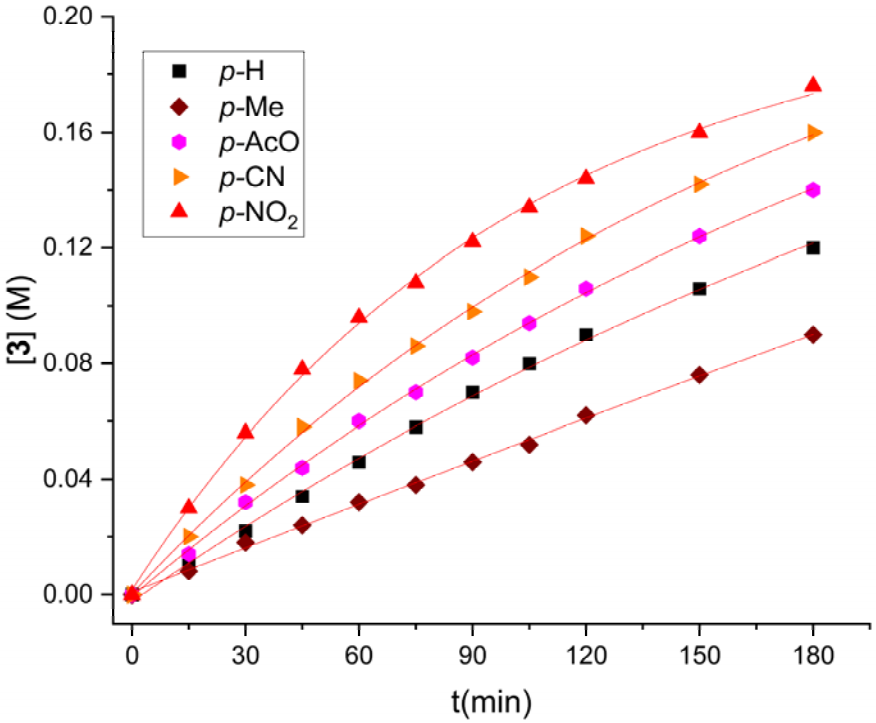


Figure S6. Relative rate comparison determined by ^1H NMR

In addition, during the reaction, we detected the generation of TMSOTMS by ^1H NMR (Figure S7), which demonstrated that TMSOTMS was a by-product of this reaction.

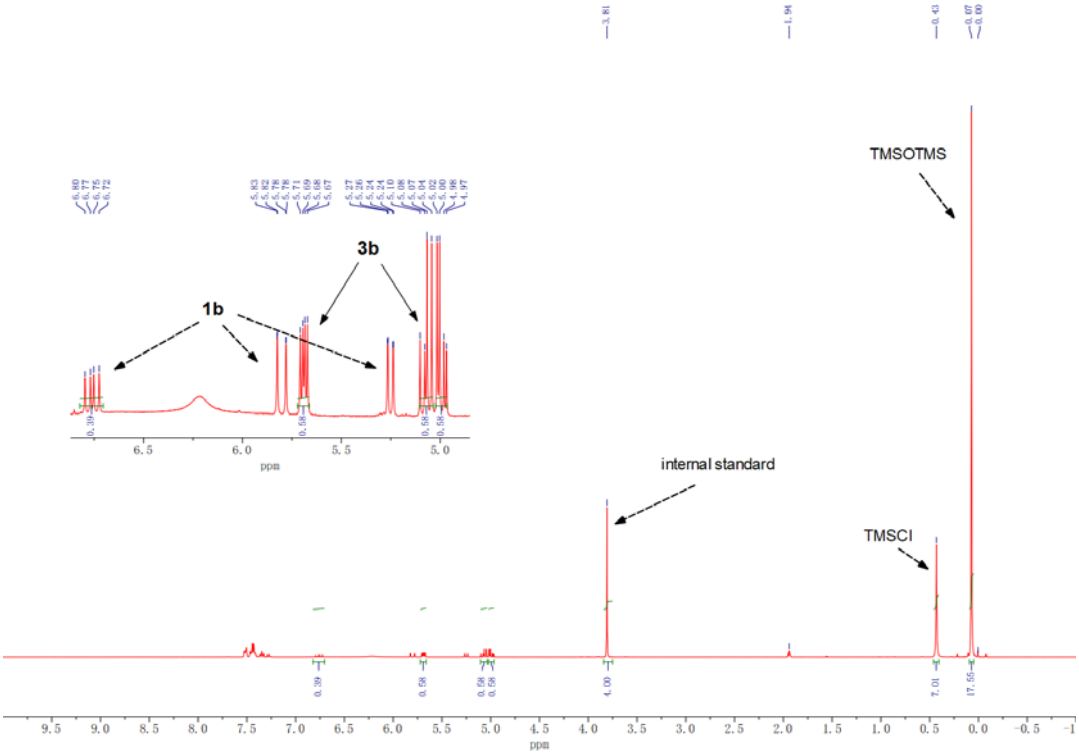


Figure S7. ^{1}H NMR spectra of **3b** in CD_3CN at 180 min by adding 1,2-dichloroethane as an internal standard

XI. ^{1}H-^{1}H NOE spectrum of 3ac

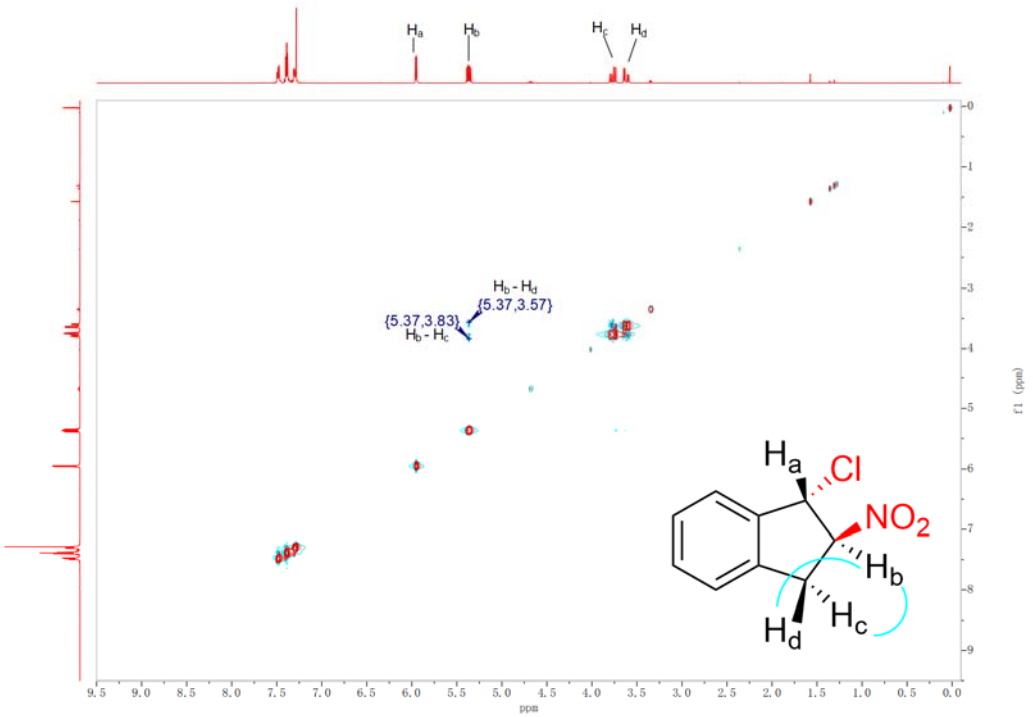
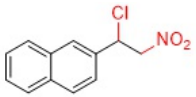


Figure S8. ^{1}H-^{1}H NOE spectrum of **3ac** in $CDCl_3$ at 25 ℃, recorded at 400 MHz

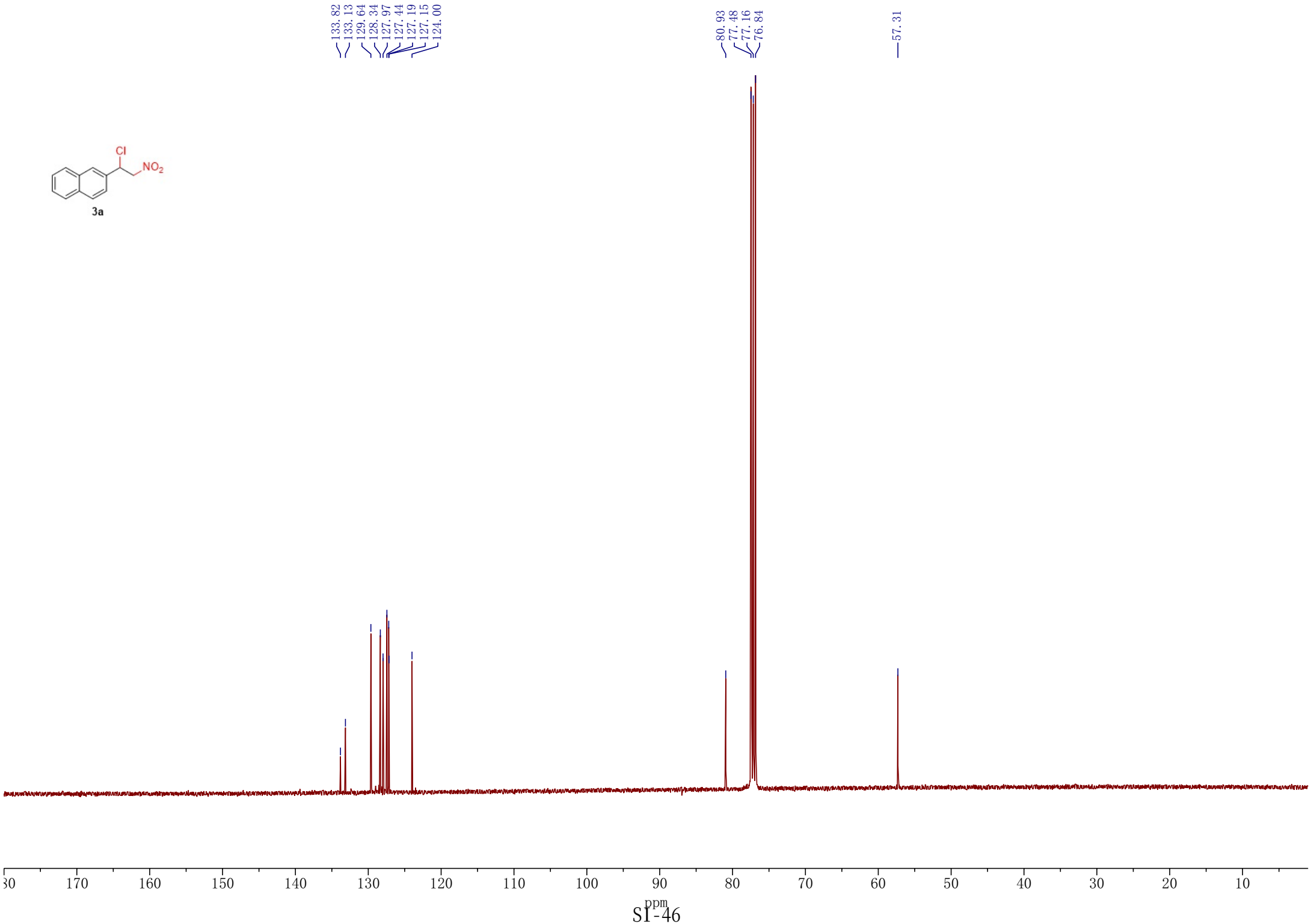
XII. References

1. Zhou, S.; Song, T.; Chen, H.; Liu, Z.; Shen, H.; Li, C., *Org. Lett.* **2017,** *19*, 698-701.
2. Xiao, Q.; He, Q.; Li, J.; Wang, J., *Org. Lett.* **2015,** *17*, 6090-6093.
3. Molander, G. A.; Brown, A. R., *J. Org. Chem.* **2006,** *71*, 9681-9686.
4. Duan, Y.; Lin, J.-H.; Xiao, J.-C.; Gu, Y.-C., *Org. Lett.* **2016,** *18*, 2471-2474.
5. Dou, Z.; Wang, Y.; Fang, W.; Sun, C.; Men, Z., *Journal of Molecular Liquids* **2020,** *312*, 113392.
6. Taniguchi, T.; Fujii, T.; Ishibashi, H., *J. Org. Chem.* **2010,** *75*, 8126-8132.
7. Canestrari, D.; Lancianesi, S.; Badiola, E.; Strinna, C.; Ibrahim, H.; Adamo, M. F. A., *Org. Lett.* **2017,** *19*, 918-921.
8. Fukunaga, K.; Okamoto, A.; Kimura, M., *Chem. Soc. Jap.* **1983**, 542-550.
9. Gao, M.; Xu, B., *Org. Lett.* **2016,** *18*, 4746-4749.
10. Maity, S.; Manna, S.; Rana, S.; Naveen, T.; Mallick, A.; Maiti, D., *J. Am. Chem. Soc.* **2013,** *135*, 3355-3358.
11. Ambala, S.; Singh, R.; Singh, M.; Cham, P. S.; Gupta, R.; Munagala, G.; Yempalla, K. R.; Vishwakarma, R. A.; Singh, P. P., *RSC Adv.* **2019,** *9*, 30428-30431.
12. Roshandel, S.; Gurung, L.; Mathew, T.; Prakash, G. K. S., *Tetra. Lett.* **2017,** *58*, 2842-2845.
13. Maity, S.; Naveen, T.; Sharma, U.; Maiti, D., *Org. Lett.* **2013,** *15*, 3384-3387.
14. Zhang, K.; Jelier, B.; Passera, A.; Jeschke, G.; Katayev, D., *Chem.* **2019,** *25*, 12929-12939.
15. Yu, S.-W.; Zhao, S.-H.; Chen, H.; Xu, X.-Y.; Yuan, W.-C.; Zhang, X.-M., *ChemistrySelect* **2018,** *3*, 4827-4830.
16. Vidal-Albalat, A.; Swiderek, K.; Izquierdo, J.; Rodriguez, S.; Moliner, V.; Gonzalez, F. V., *Chem. Commun.* **2016,** *52*, 10060-3.
17. Hwu, J. R.; Chen, K.-L.; Ananthan, S.; Patel, H. V., *Organometallics* **1996,** *15*, 499-505.
18. Chiu, C.-C.; Chiu, H.-T.; Lee, D.-S.; Lu, T.-J., *RSC Adv.* **2018,** *8*, 26407-26415.
19. Yang, L.; Xia, C.; Huang, H., *Chin. J. Catal.* **2011,** *32*, 1573-1576.
20. Sharma, P.; Kumar, N.; Senwar, K.; Forero-Doria, O.; Nachtigall, F.; Santos, L.; Shankaraiah, N., *J. Braz. Chem. Soc.* **2017,** *28,* 589-597.
21. Prakash, G. K. S.; Panja, C.; Mathew, T.; Surampudi, V.; Petasis, N. A.; Olah, G. A., *Org. Lett.* **2004,** *6*, 2205-2207.
22. Zelenov, V. P.; Bukalov, S. S.; Subbotin, A. N., *Mendeleev Commun.* **2017,** *27*, 355-356.
23. Harrar, J. E.; Rigdon, L. P.; Rice, S. F., *J. Raman Spectrosc.* **1997,** *28*, 891-899.
24. Lippold, M.; Patzig-Klein, S.; Kroke, E., *Z. Naturforsch.* **2011,** *66*, 155-163.

XIII. NMR Spectra of New Compounds (^{1}H NMR, ^{13}C NMR, ^{19}F NMR)



3a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76.84
57.31
Cl
NO2
3a
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150
140
130
120
110
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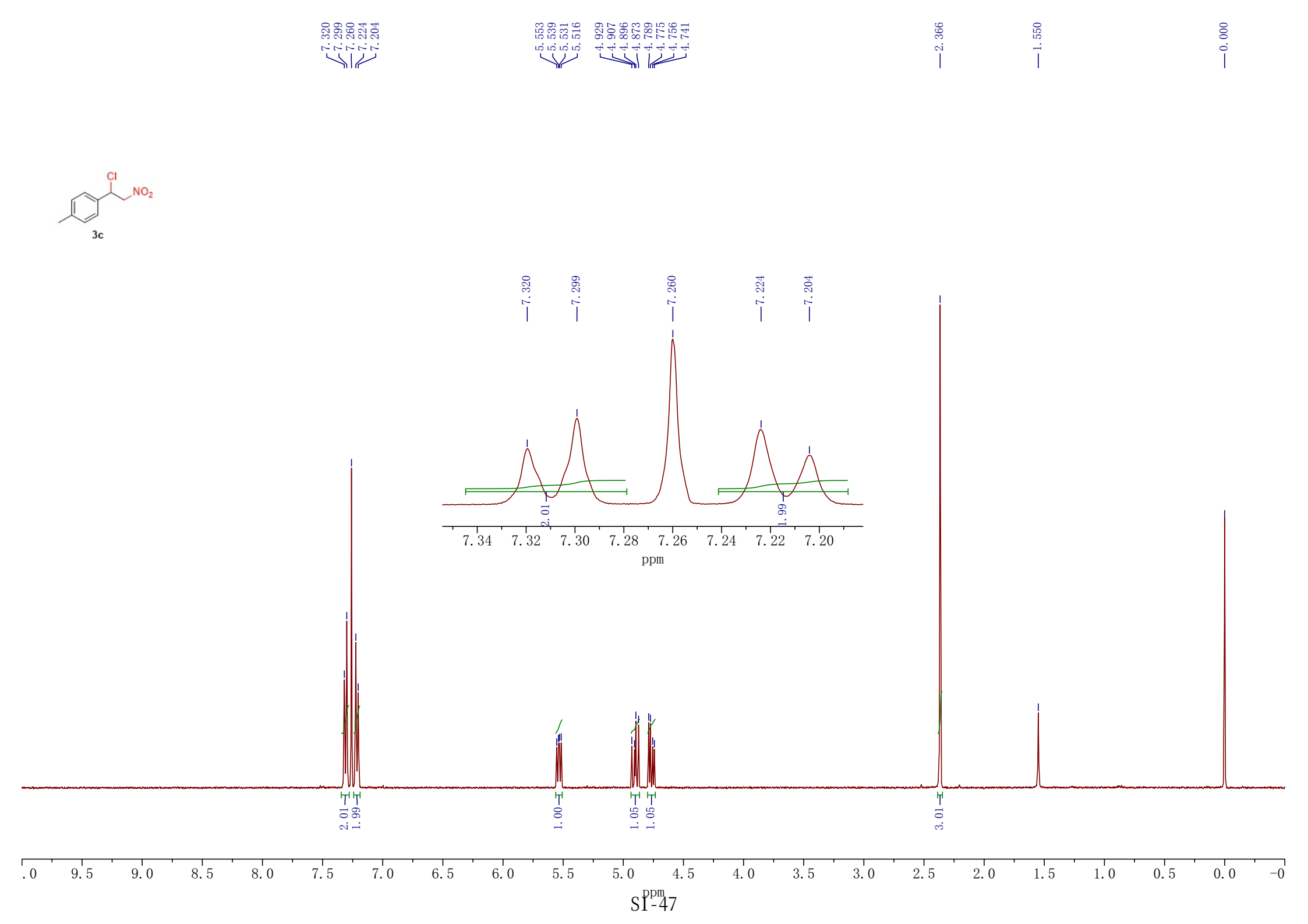
90
80
70
60
50
40
30
20
10
ppm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4.789
4.775
4.756
4.741
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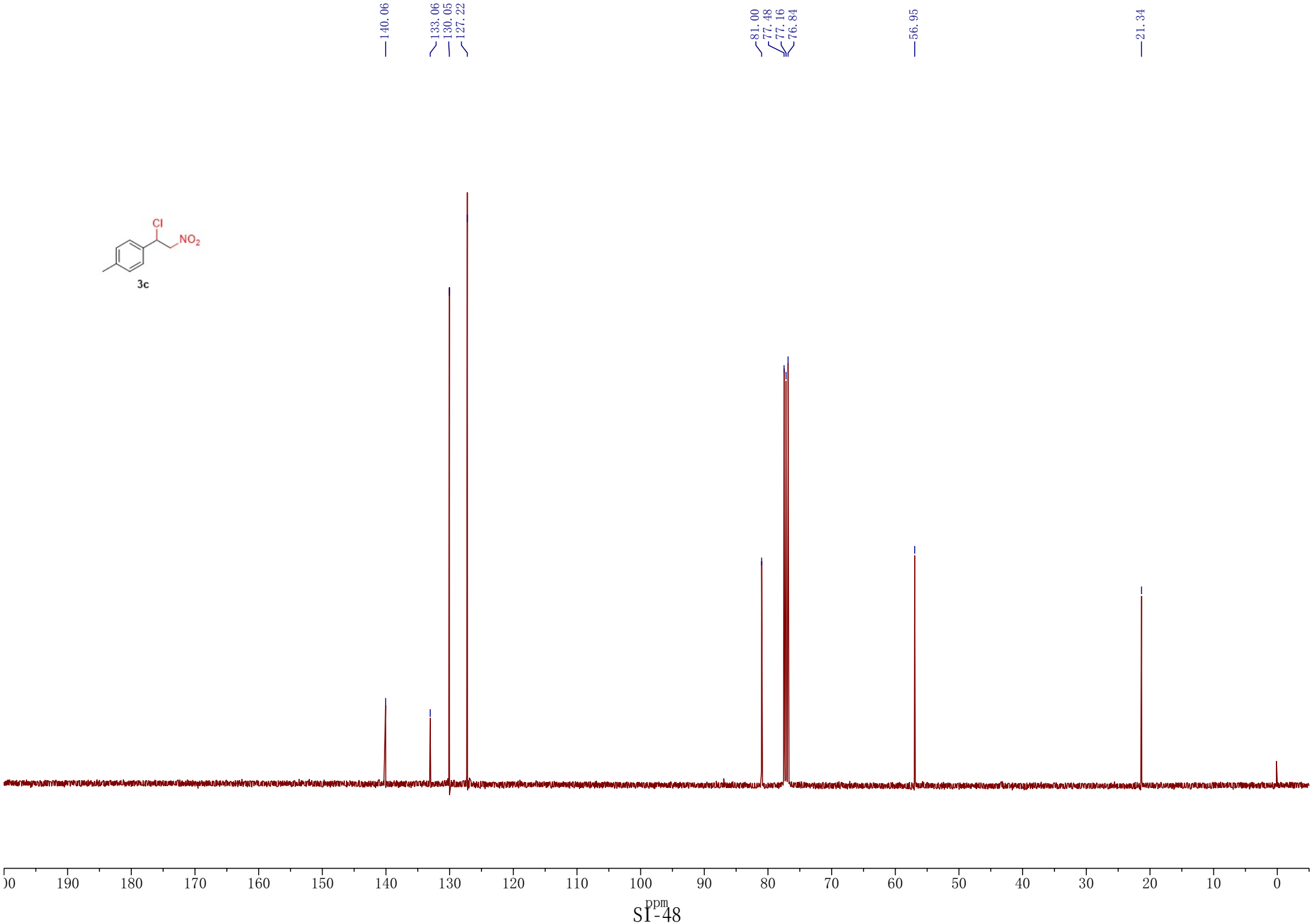
3.01
ppm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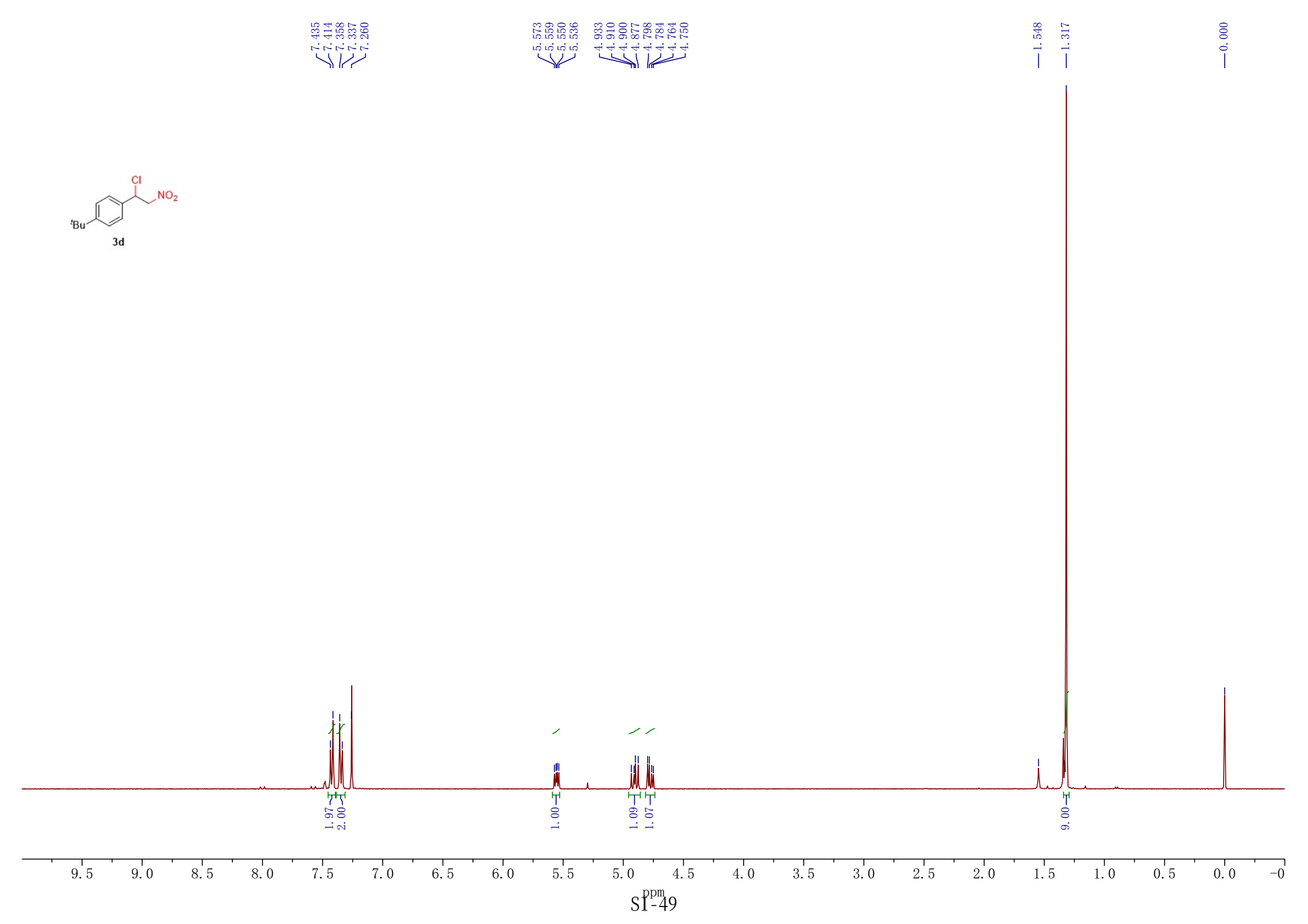
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4.798
4.784
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tBu
3d
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1.00
1.09
1.07
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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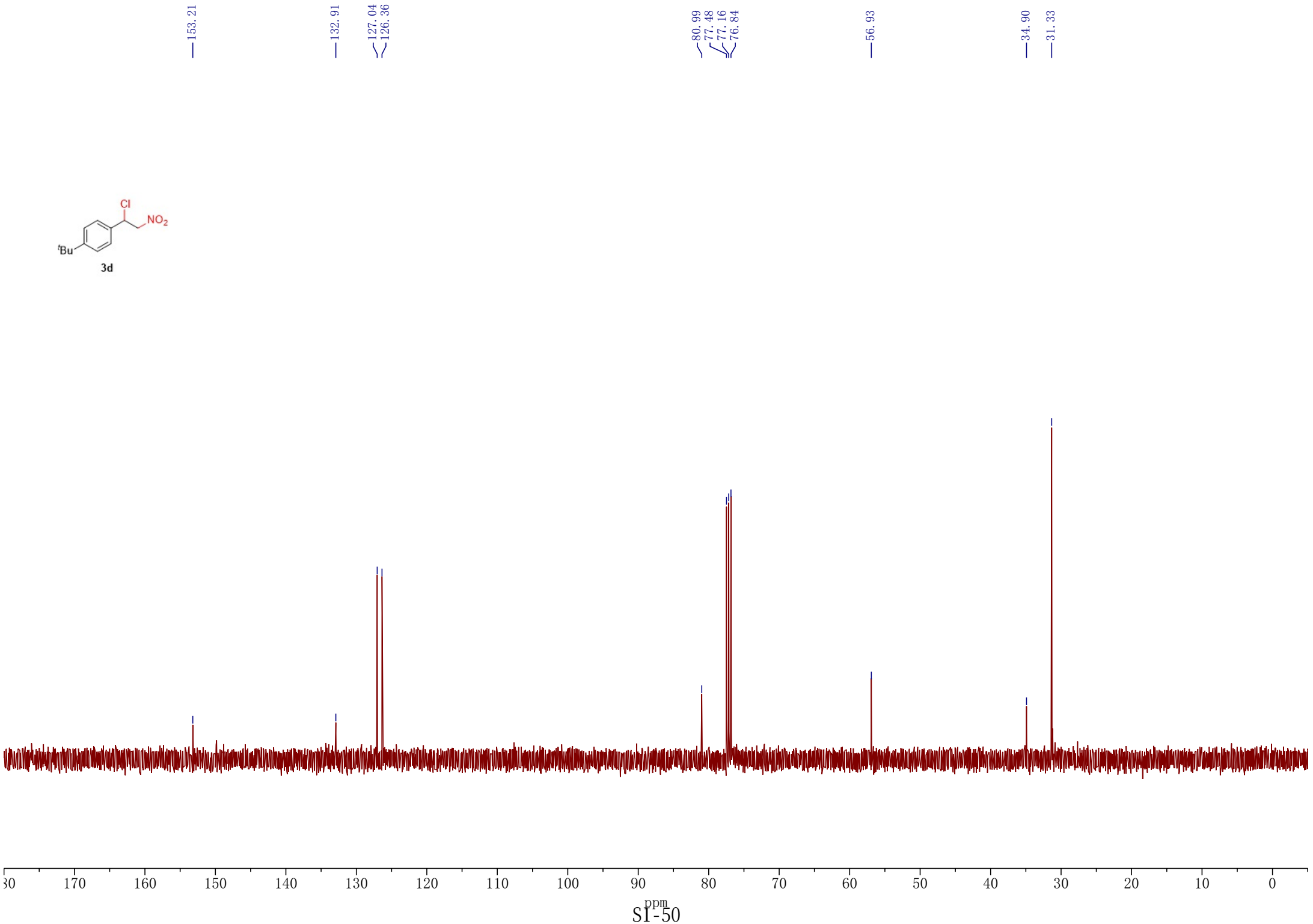
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77.16
76.84
56.93
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31.33
Cl
NO2
tBu
3d
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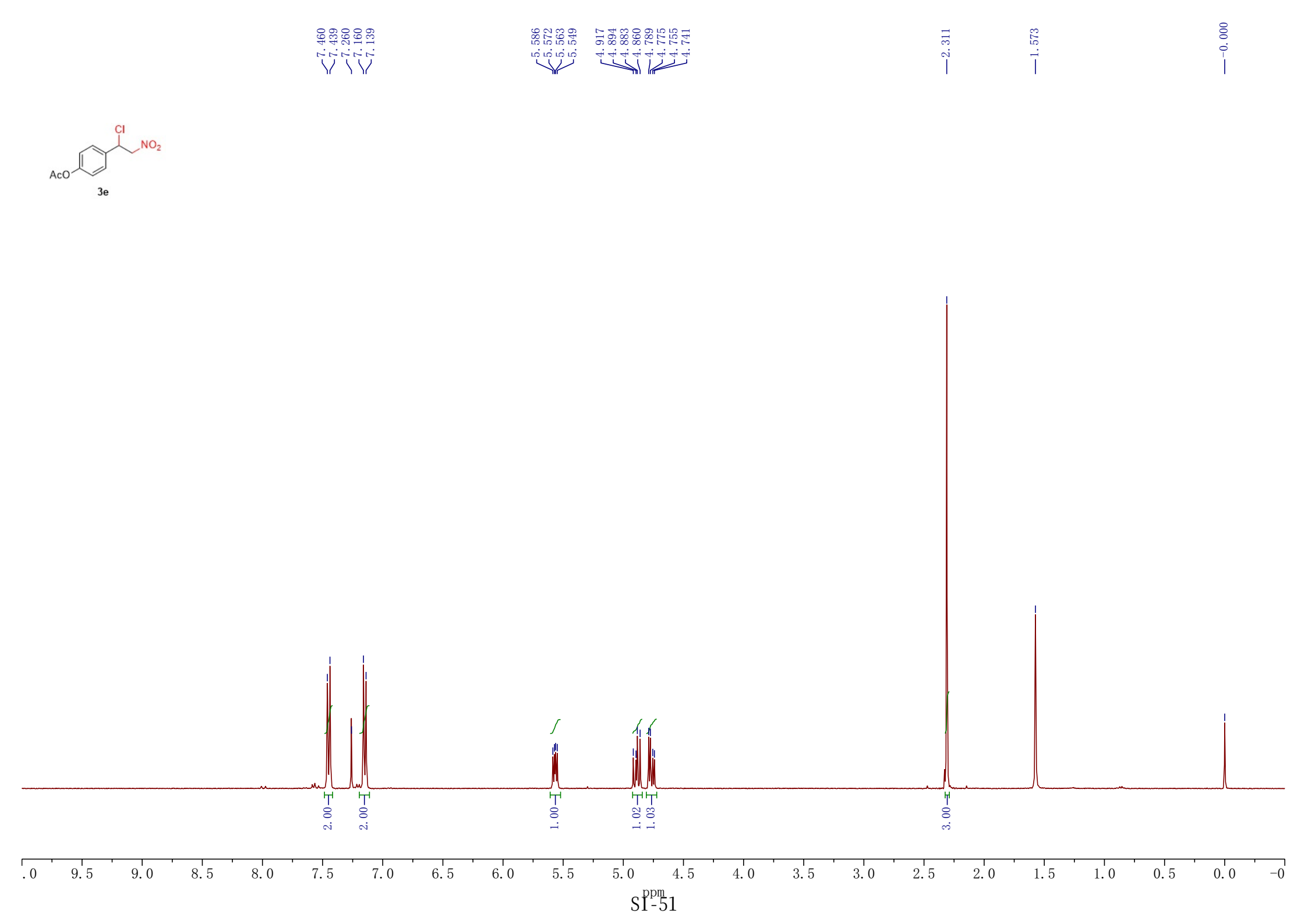
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.860
4.789
4.775
4.755
4.741
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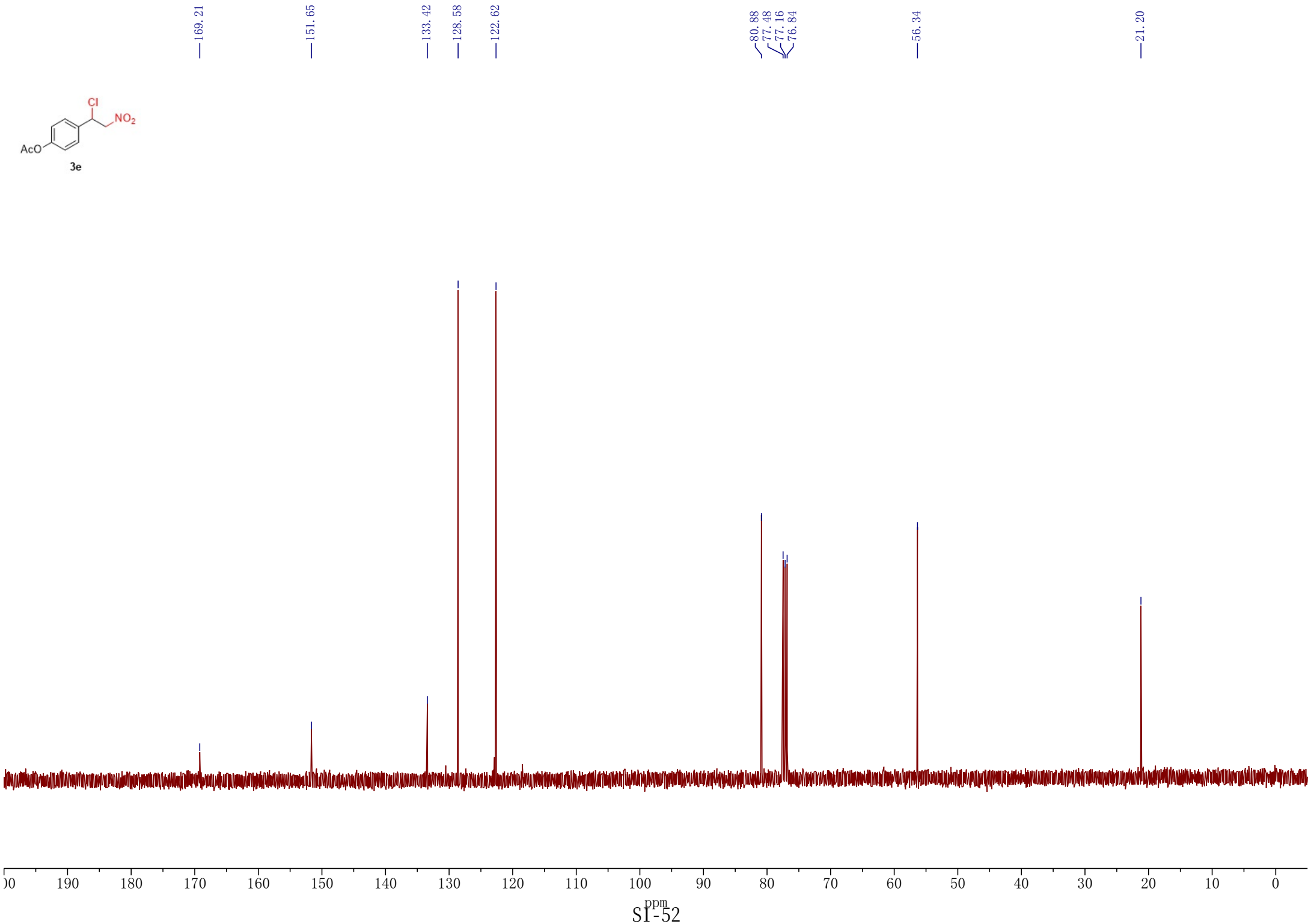
1.02
1.03
3.00
ppm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AcO
3e
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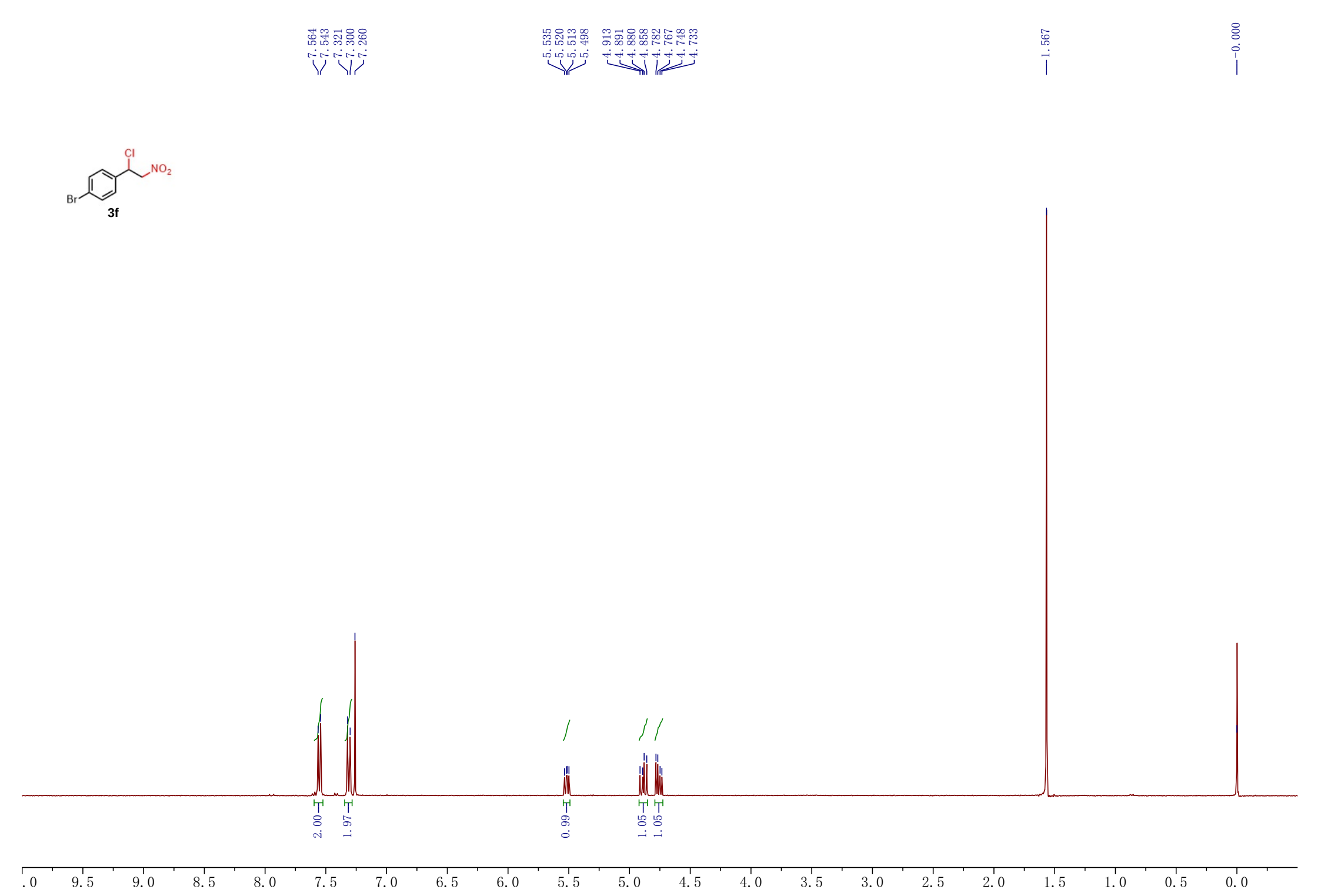
20
10
0
ppm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4.782
4.767
4.748
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Br
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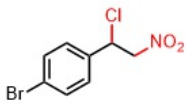
1.05
ppm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Br

3f

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77.16
76.84
56.10
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180
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160
150
140
130
120
110
100
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70
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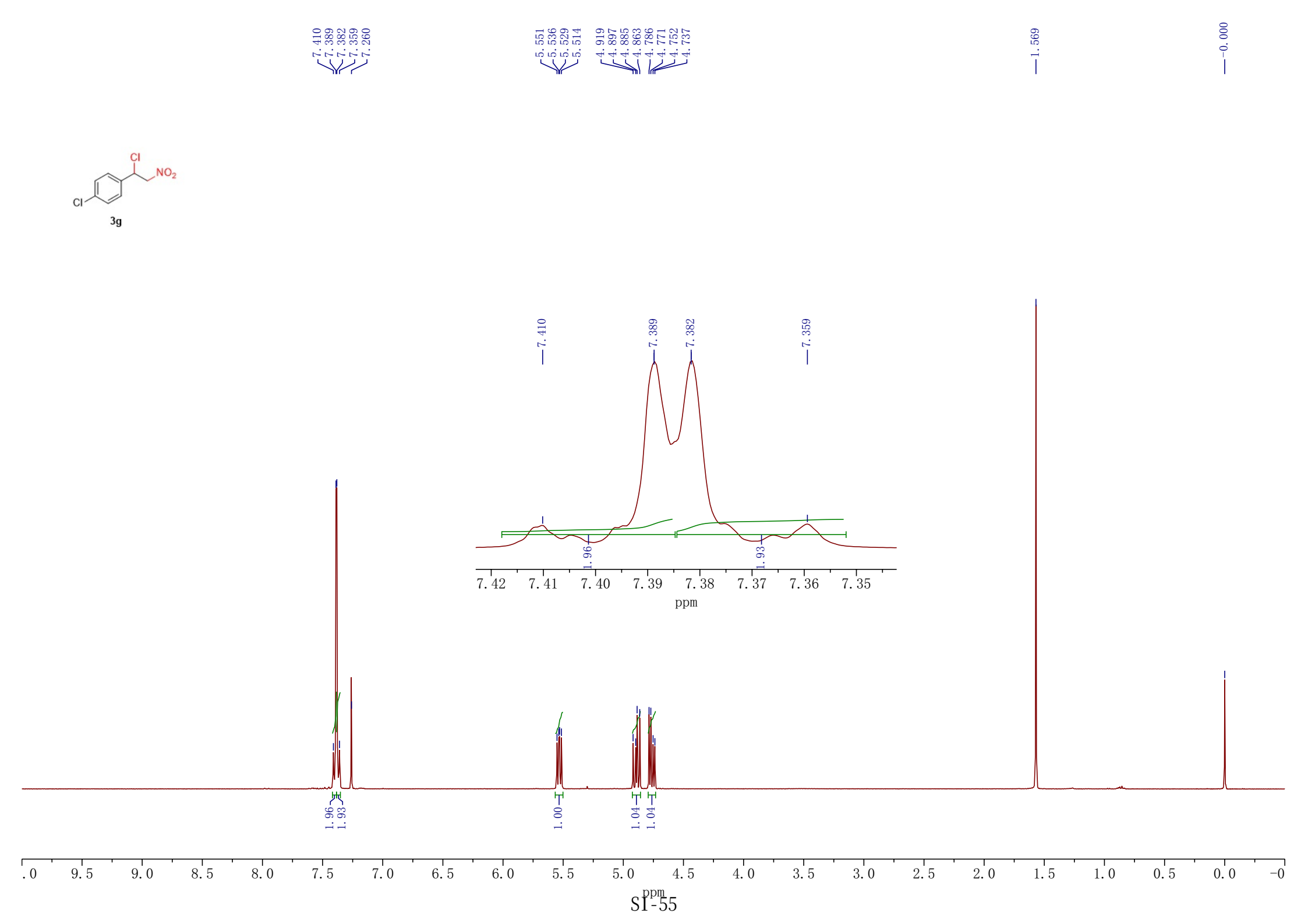
40
30
20
10
ppm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4.863
4.786
4.771
4.752
4.737
1.569
0.000
Cl
NO2
Cl
3g
1.96
1.93
1.00
1.04
1.04
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7.38
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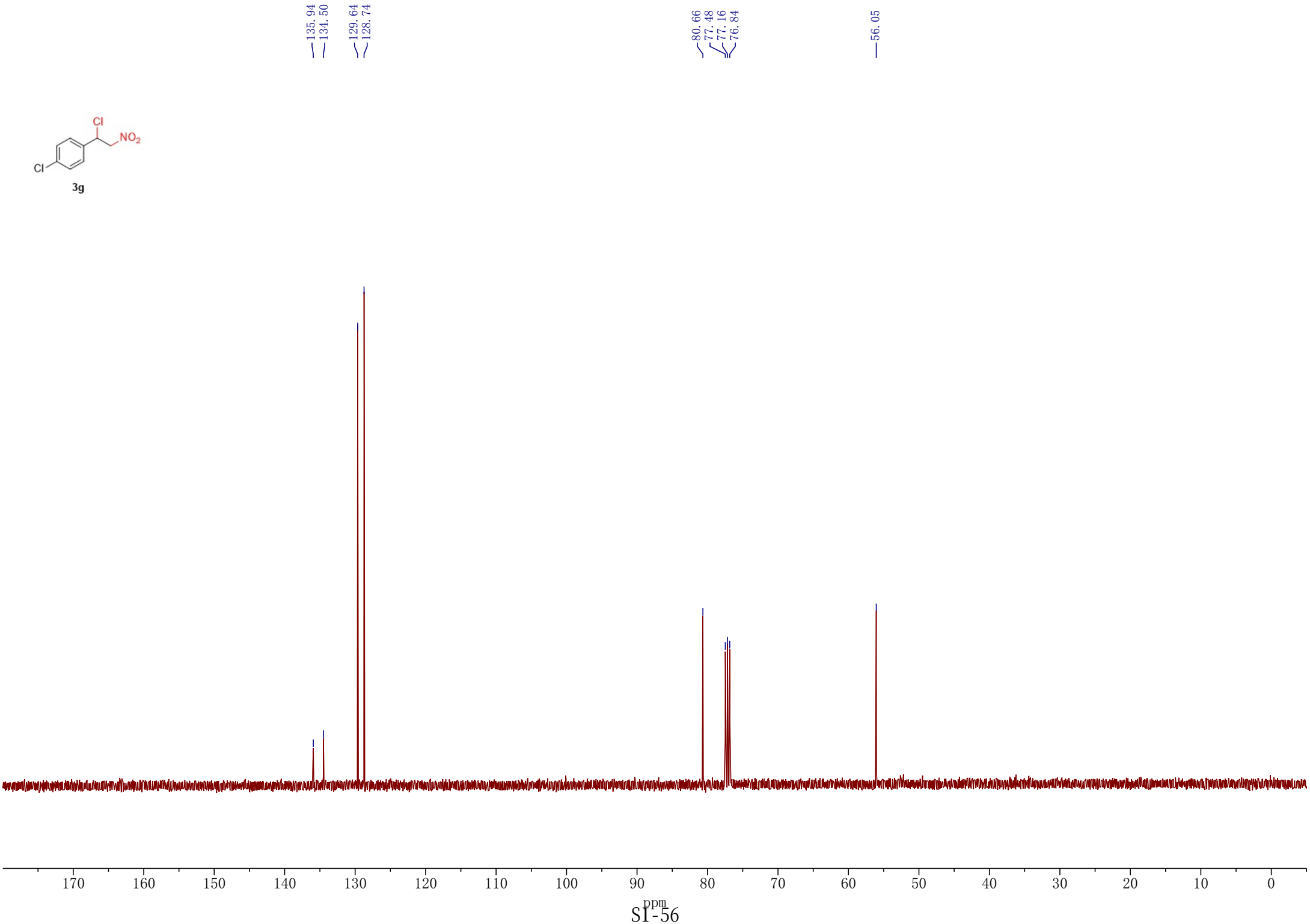
7.36
7.35
ppm
ppm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Cl
3g
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140
130
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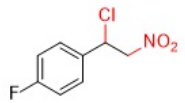
60
50
40
30
20
10
0
ppm


Cl
NO2
F

3h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7.405
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7.128
7.122
7.111
7.106
7.101
7.090
7.085
7.077

5.568
5.553
5.546
5.531

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4.871
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4.774
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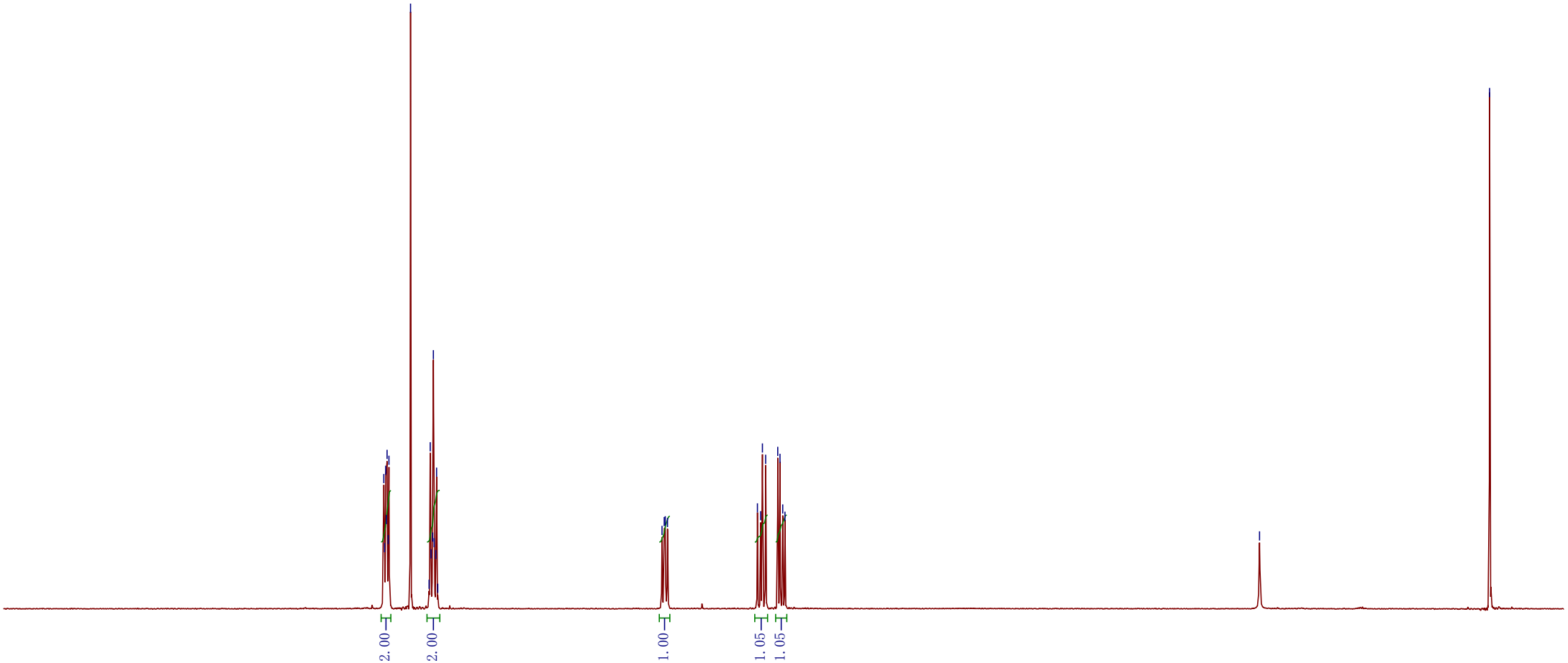
4.741


1.548

0.000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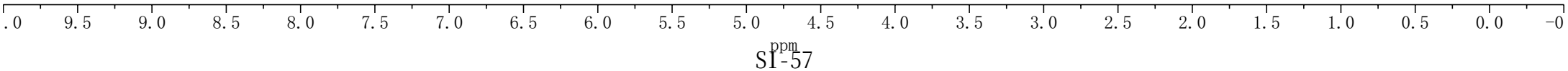
1.00
1.05
1.05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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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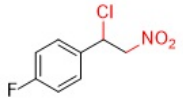
1.5
1.0
0.5
0.0
-0
ppm



3h

164.66
162.17
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129.37
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80.87
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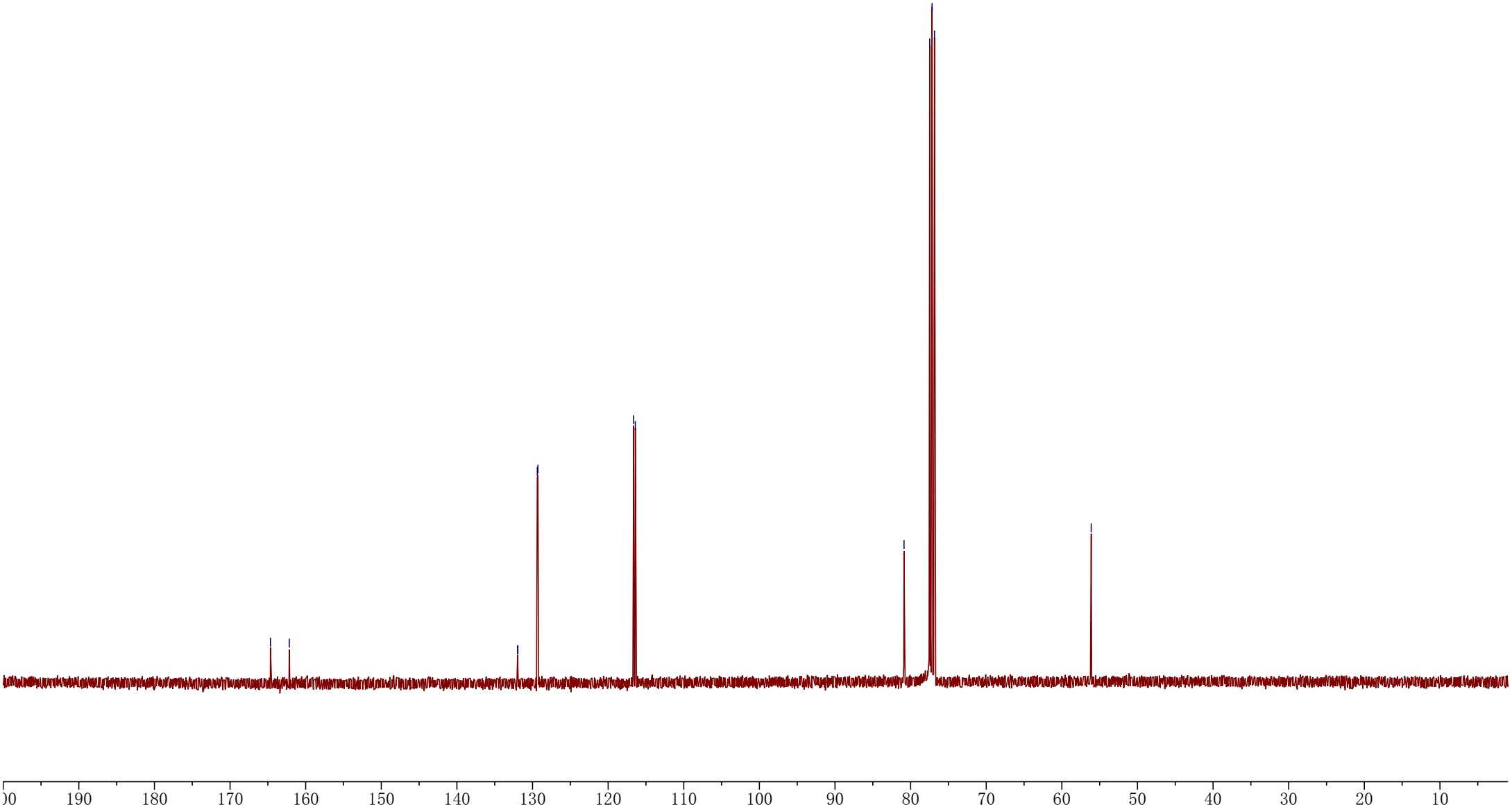
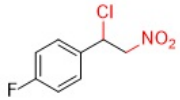
77.16
76.84
56.12




Cl
NO2
F

3h

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300
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260
240
220
200
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140
120
100
80
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40
20
0
-20
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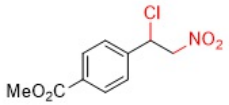
-60
-80
-10
ppm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MeO2C

3i

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4.947
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4.913
4.891
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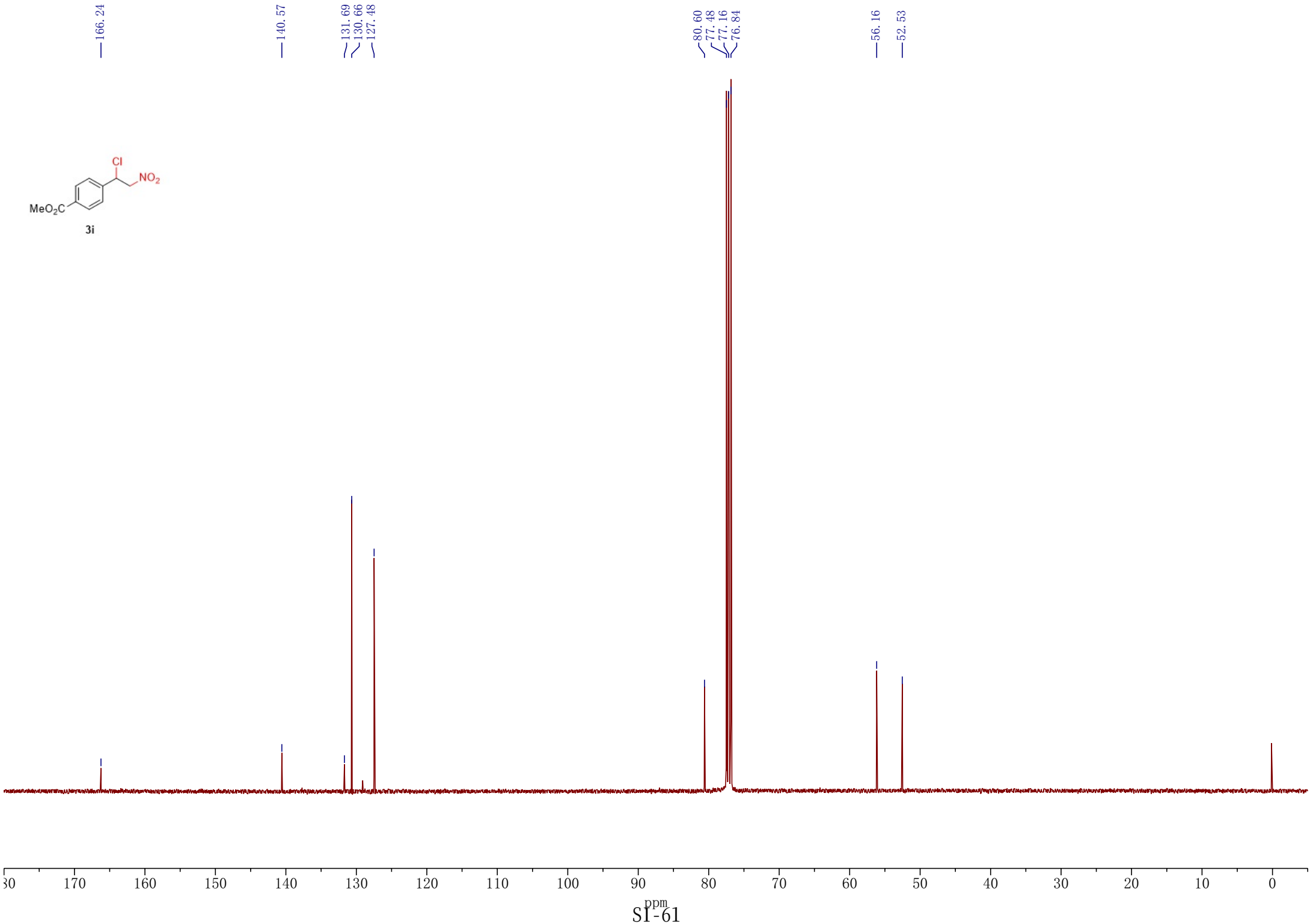
3.06
ppm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MeO2C
3i
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140
130
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60
50
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30
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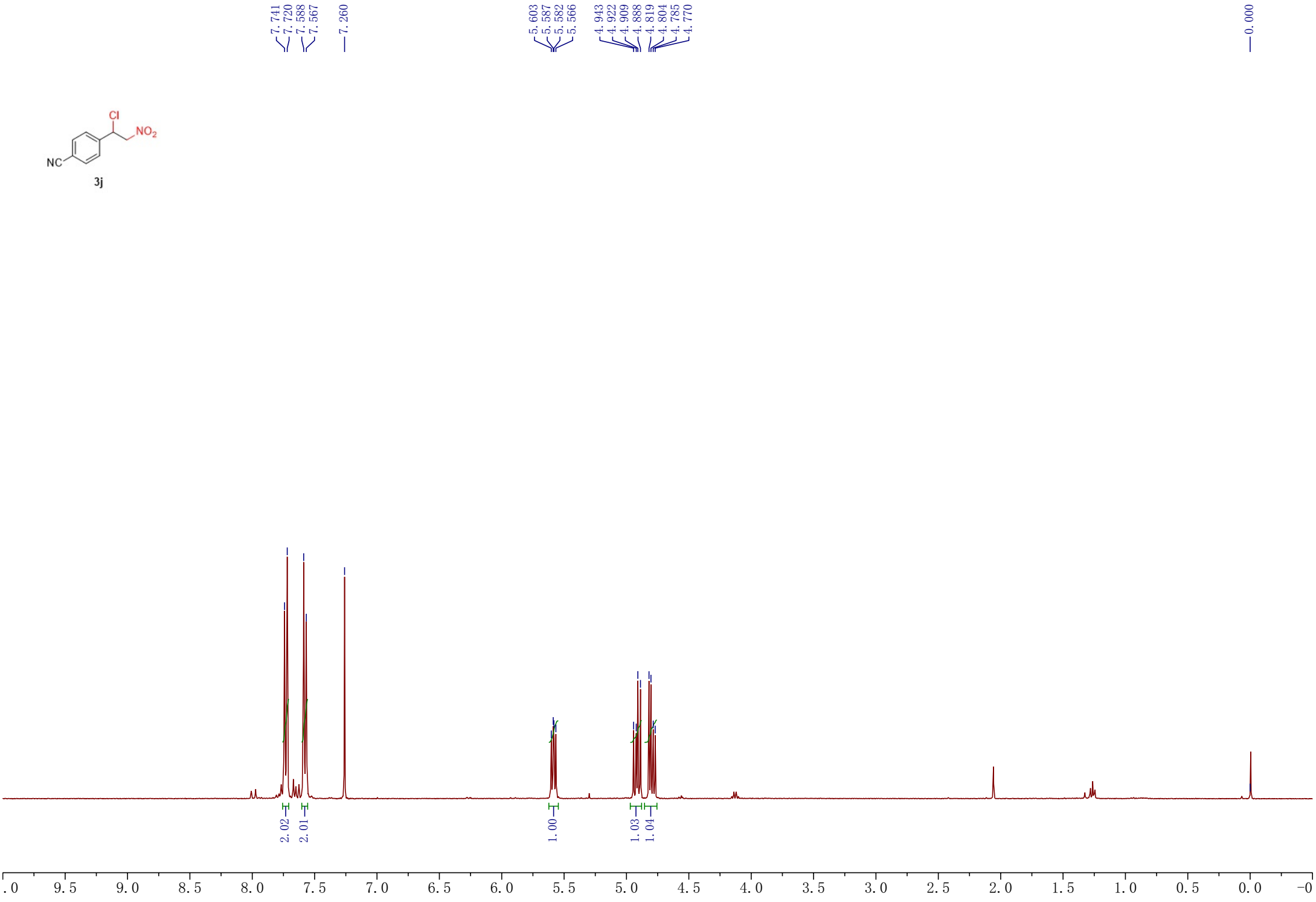
10
0
ppm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1.03
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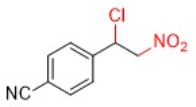
ppm



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77.16
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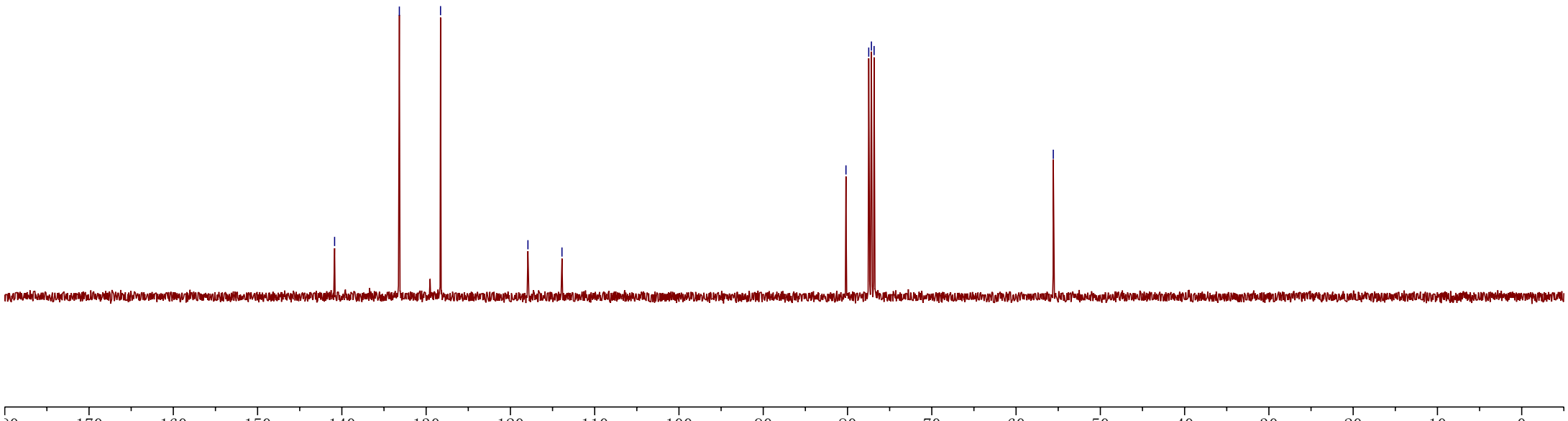
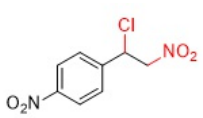
55.58

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NO2
O2N

3k

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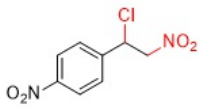
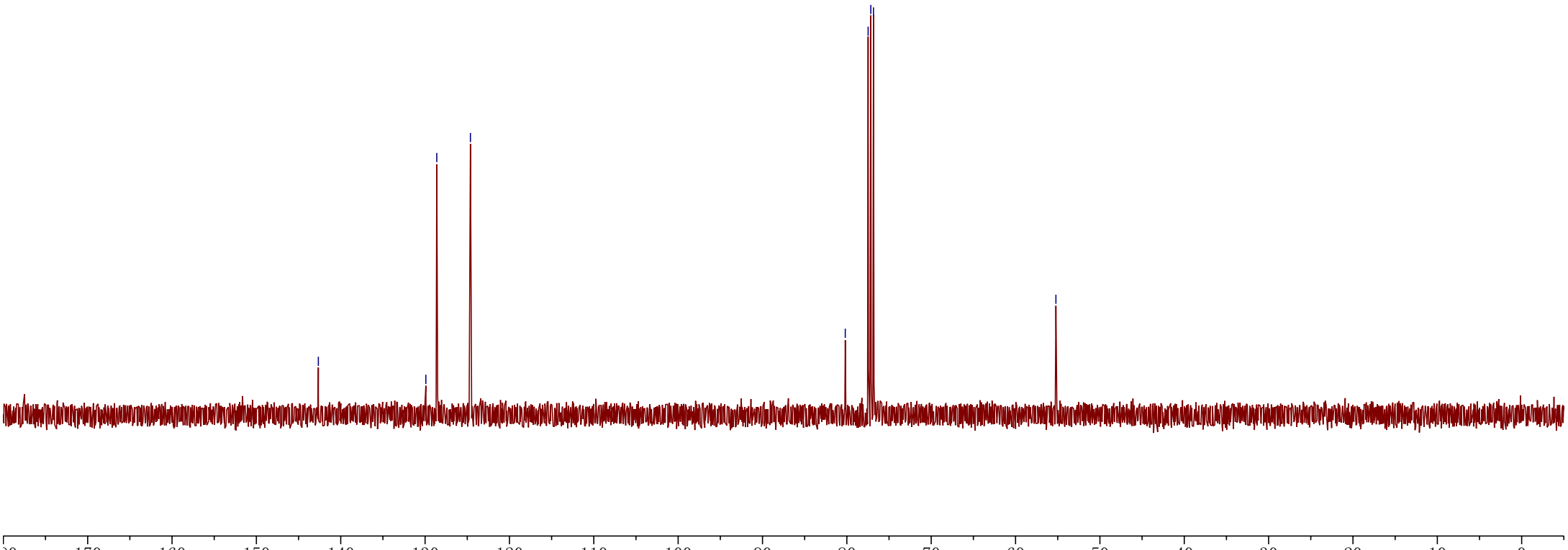
4.955
4.942
4.921
4.852
4.836
4.818
4.802
1.587
0.000
2.02
2.04
1.00
1.05
1.05
ppm



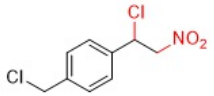
3k

142.66
129.91
128.62
124.63
80.19
77.48
77.16
76.84
55.22



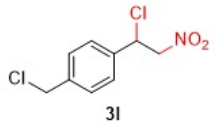
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Cl
NO2
Cl

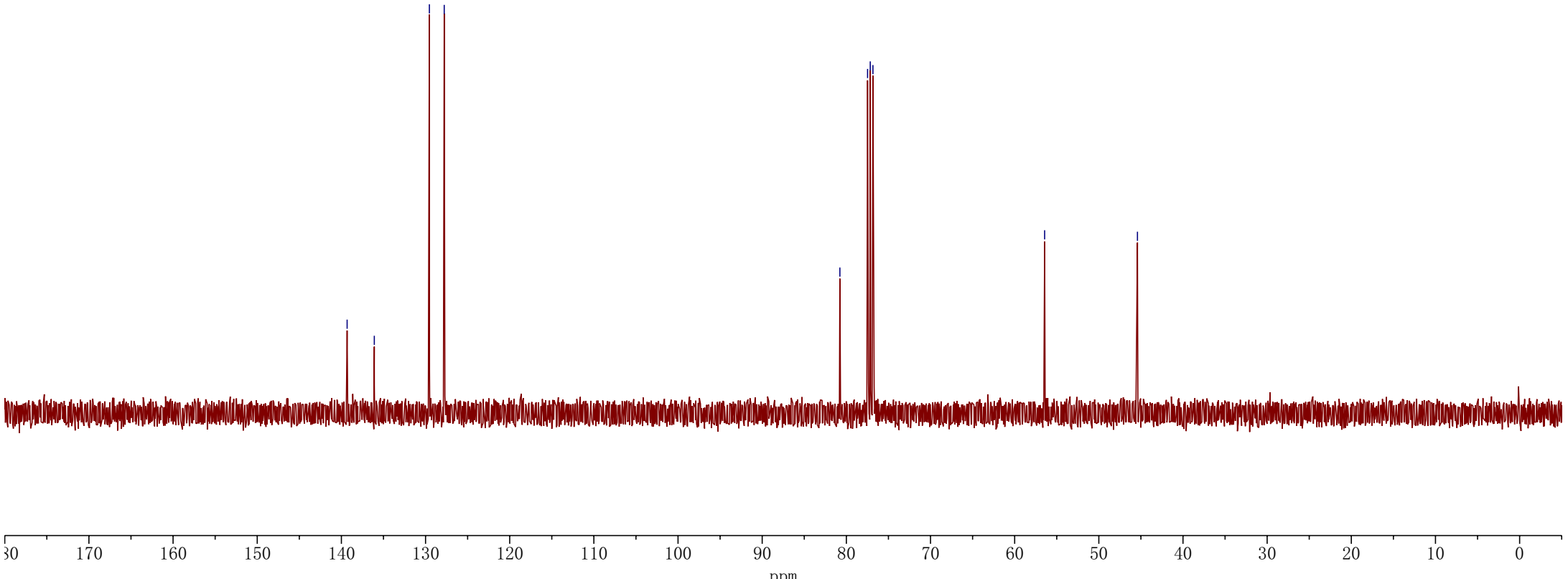
3l

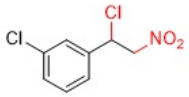
7.460
7.437
7.416
7.260
5.581
5.566
5.558
5.544
4.929
4.907
4.895
4.873
4.798
4.784
4.765
4.750
4.583
0.000
4.00
1.00
1.04
1.05
2.02
ppm
7.460
7.437
7.416
4.00
7.49
7.47
7.45
7.43
7.41
7.39
7.37
ppm



3l

139.32
136.09
129.55
127.78
80.77
77.48
77.16
76.84
56.44
45.41





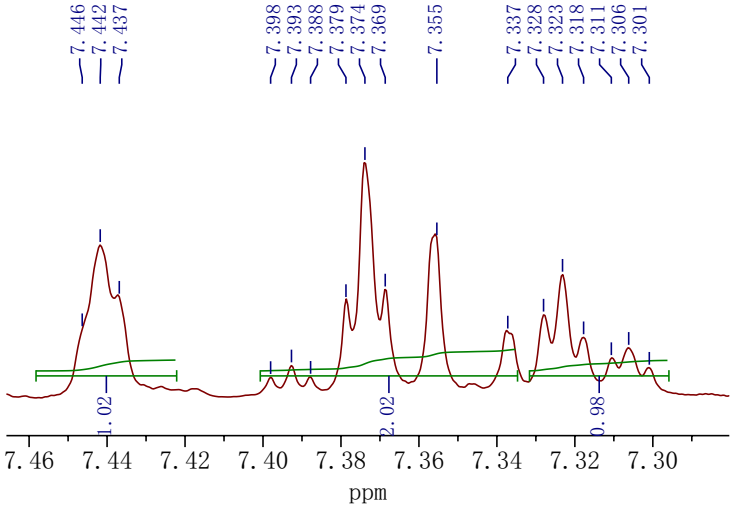
3m

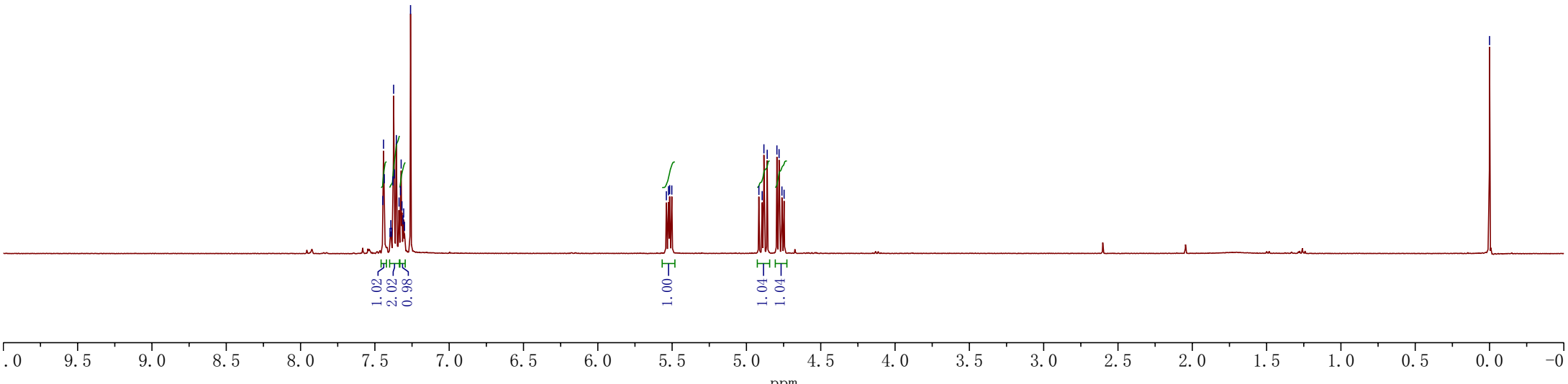
7.446 7.442 7.437 7.398 7.393 7.388 7.379 7.374 7.369 7.355 7.337 7.328 7.323 7.318 7.311 7.306 7.301 7.260

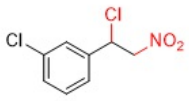
5.539 5.524 5.517 5.502

4.916 4.894 4.882 4.860 4.795 4.780 4.761 4.747

0.000





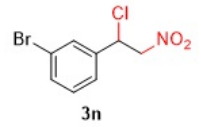


3m

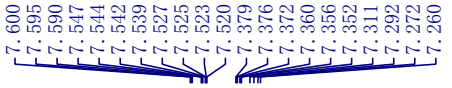
137.87
135.35
130.70
130.16
127.64
125.53
80.64
77.48
77.16
76.84
55.98

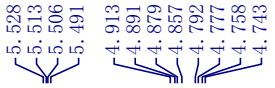
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Cl
Br
NO2

3n

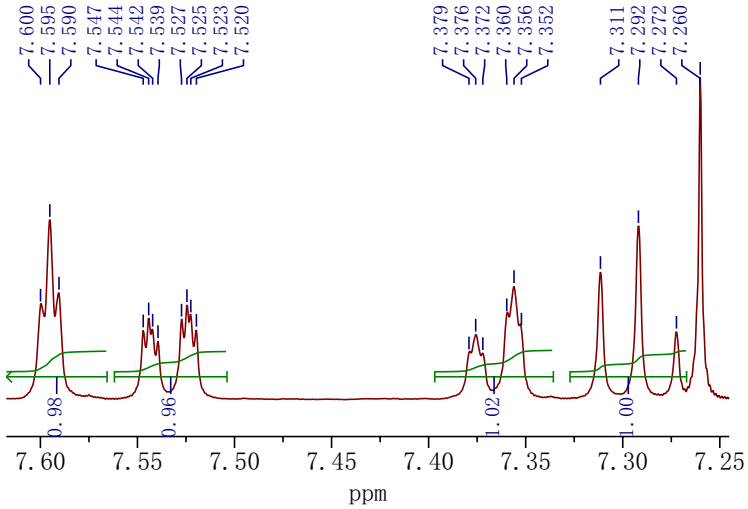

7.600
7.595
7.590
7.547
7.544
7.542
7.539
7.527
7.525
7.523
7.520
7.379
7.376
7.372
7.360
7.356
7.352
7.311
7.292
7.272
7.260

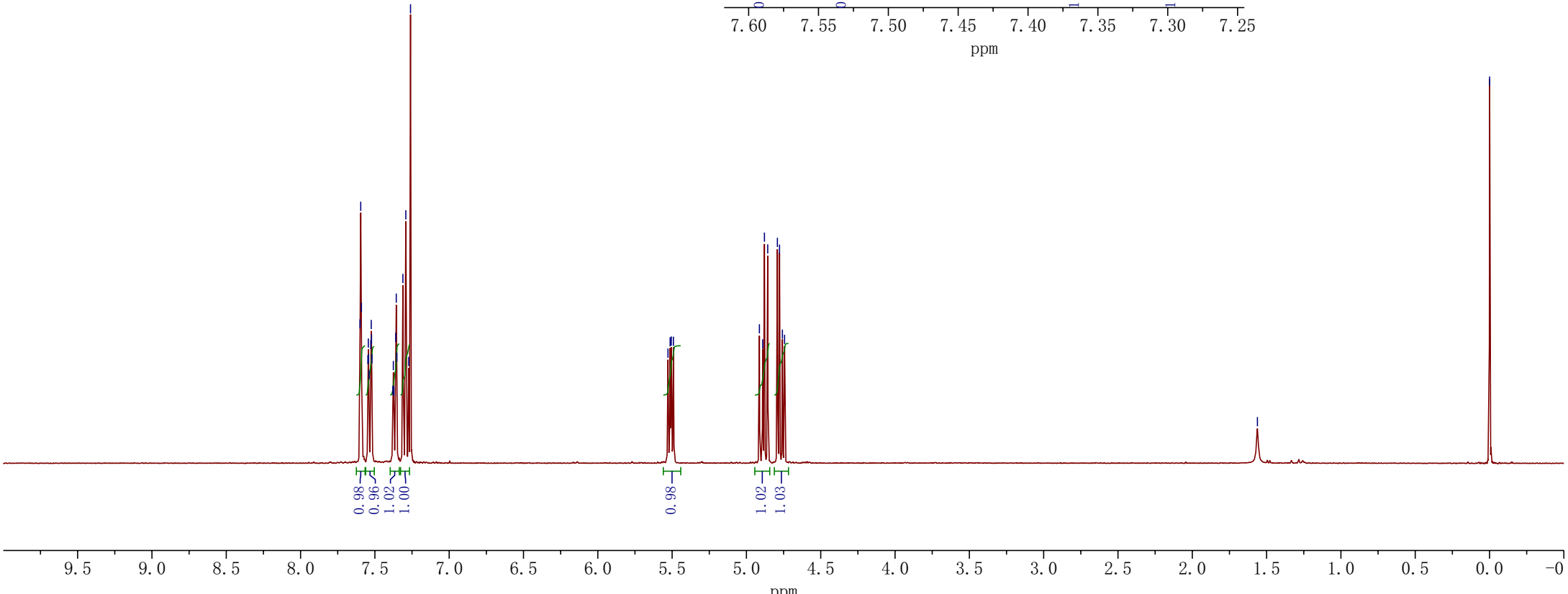

5.528
5.513
5.506
5.491

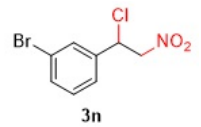
4.913
4.891
4.879
4.857
4.792
4.777
4.758
4.743

1.562

0.000

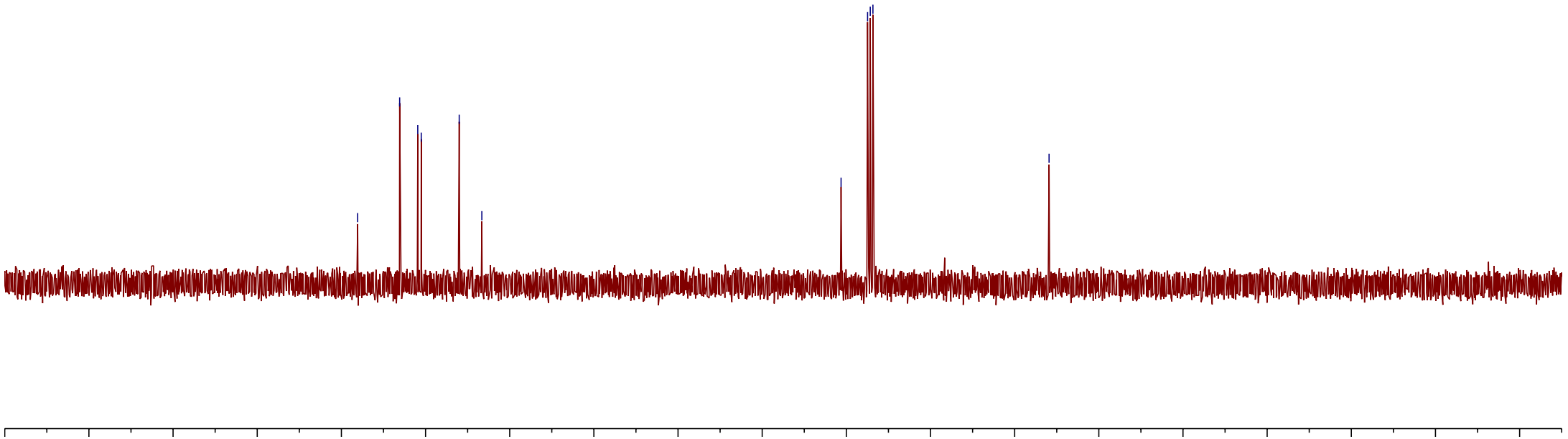

7.600
7.595
7.590
7.547
7.544
7.542
7.539
7.527
7.525
7.523
7.520
7.379
7.376
7.372
7.360
7.356
7.352
7.311
7.292
7.272
7.260
0.98
0.96
1.02
1.00
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
ppm


0.98
0.96
1.02
1.00
0.98
1.02
1.03
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
-0
ppm



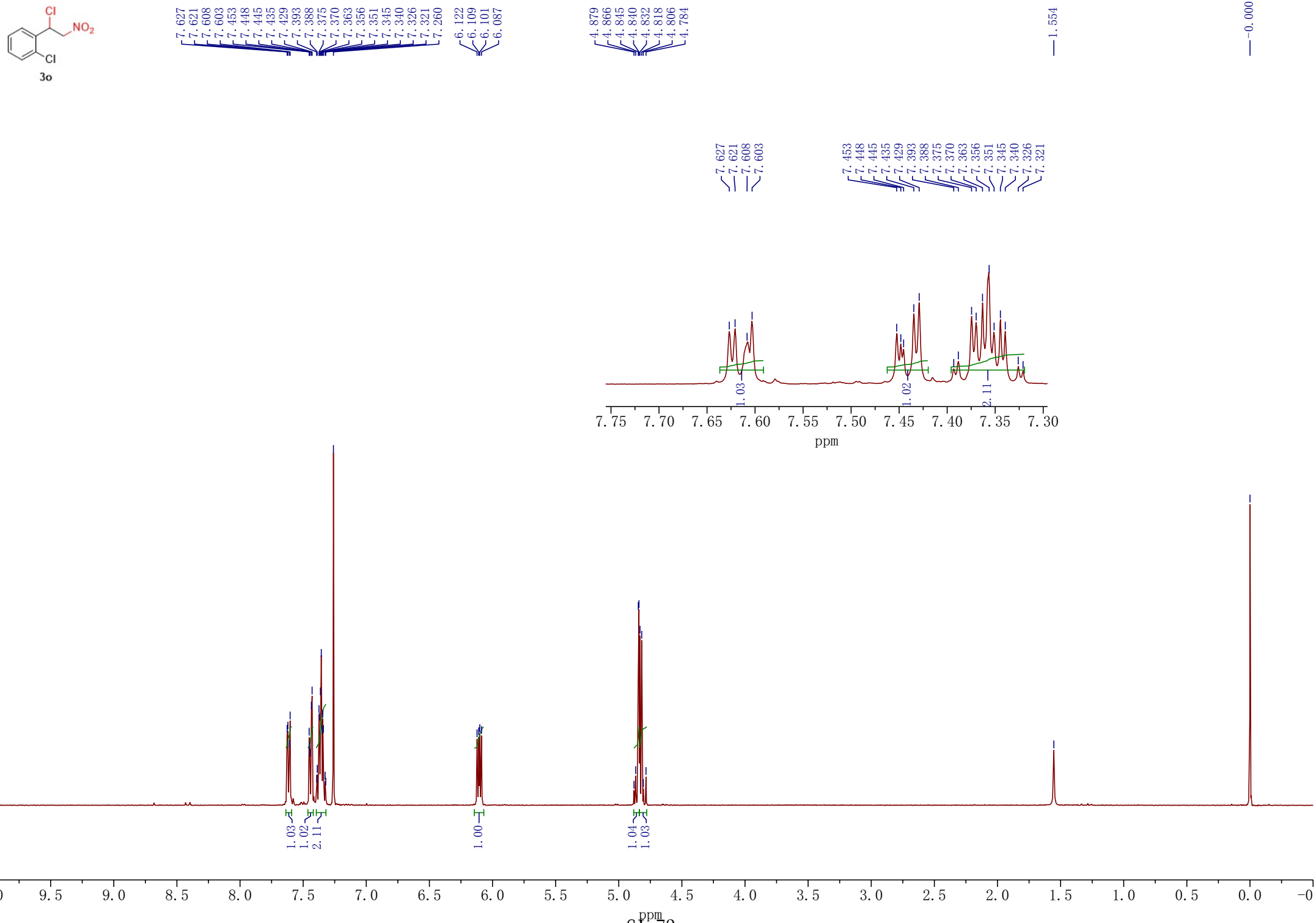
3n

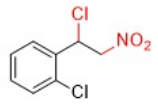
138.07
133.08
130.92
130.51
126.00
123.31
80.63
77.48
77.16
76.84
55.91



30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Cl
NO2
Cl
3o
7.627
7.621
7.608
7.603
7.453
7.448
7.445
7.435
7.429
7.393
7.388
7.375
7.370
7.363
7.356
7.351
7.345
7.340
7.326
7.321
7.260
6.122
6.109
6.101
6.087
4.879
4.866
4.845
4.840
4.832
4.818
4.806
4.784
1.554
0.000
1.03
1.02
2.11
1.00
1.04
1.03
ppm



3o

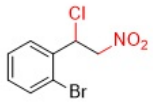
133.25
132.90
130.92
130.35
128.89
127.96

79.70
77.48
77.16
76.84

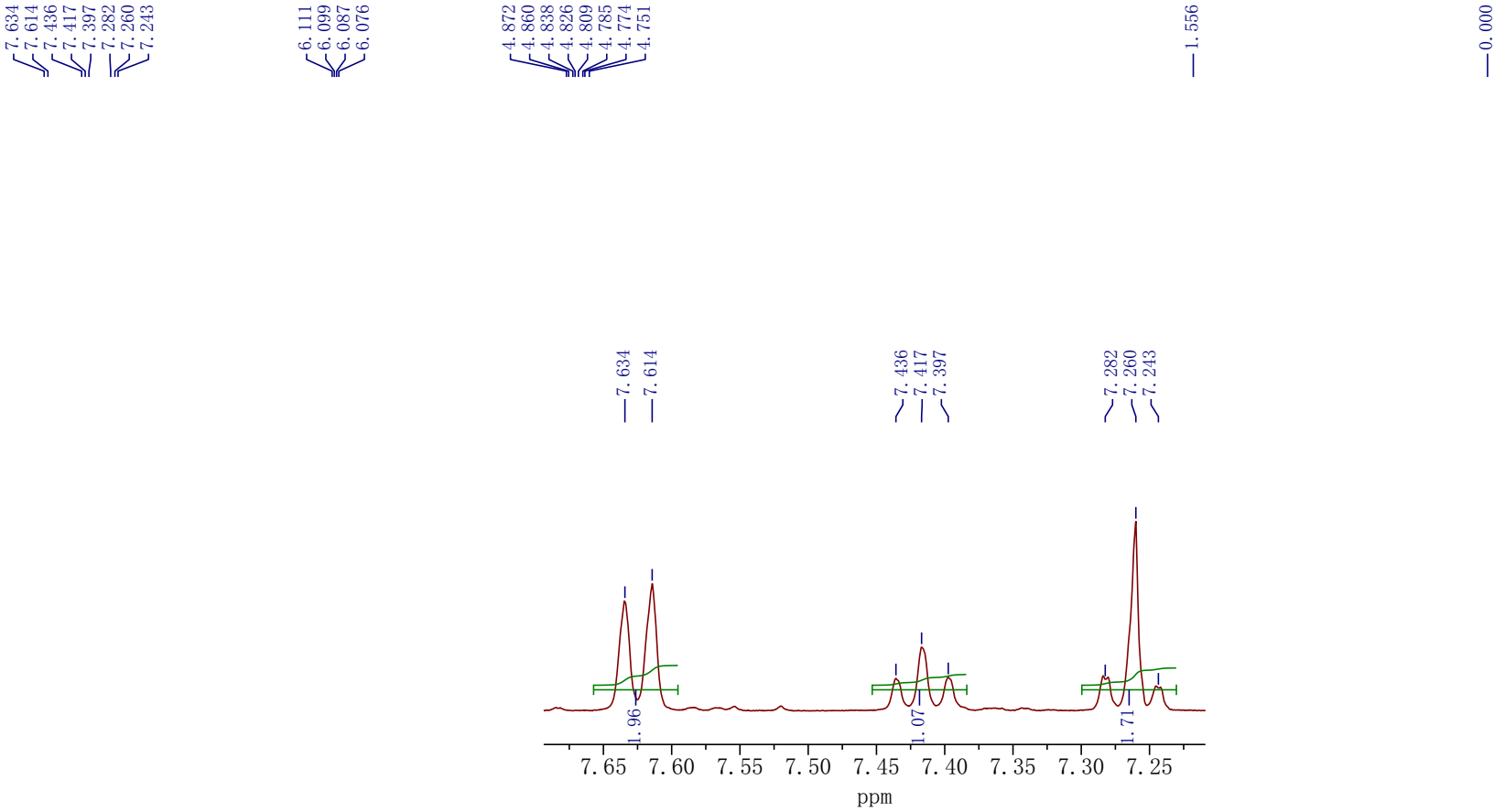
53.68

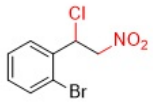
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Cl
NO2
Br

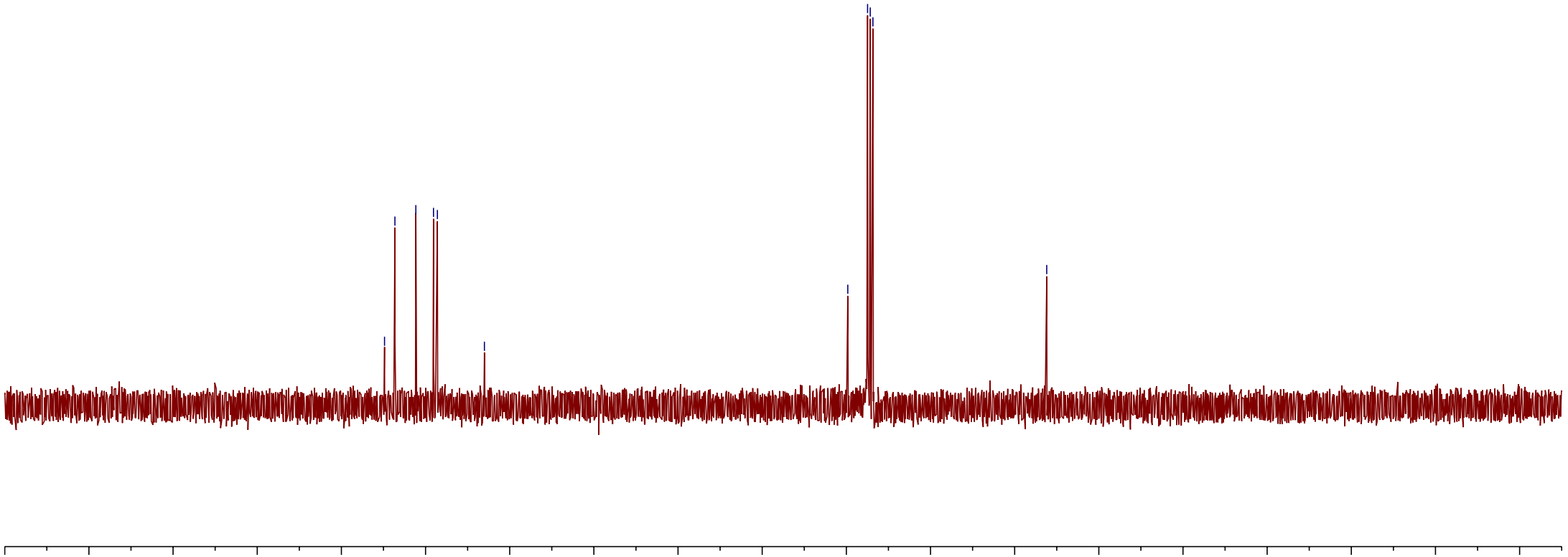
3p


7.634
7.614
7.436
7.417
7.397
7.282
7.260
7.243
6.111
6.099
6.087
6.076
4.872
4.860
4.838
4.826
4.809
4.785
4.774
4.751
1.556
0.000
1.96
1.07
1.71
1.00
1.03
1.03
ppm



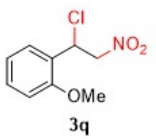
3p

134.87
133.64
131.15
129.06
128.59
123.01
79.83
77.48
77.16
76.84
56.19



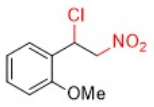
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Cl
NO2
OMe

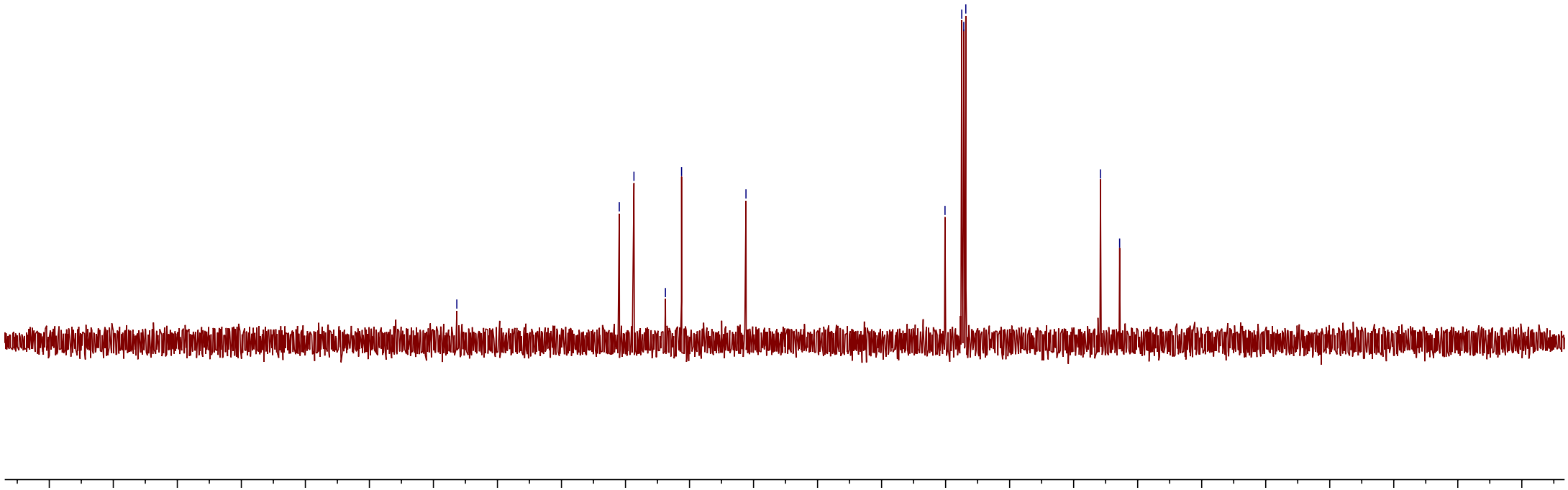
3q

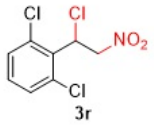
7.485
7.467
7.387
7.367
7.348
7.260
7.036
7.017
6.998
6.941
6.920
6.017
6.004
5.995
5.982
4.900
4.866
4.851
4.844
4.838
4.817
4.813
3.905
0.000
1.00
1.00
1.03
0.97
0.87
1.95
3.06
ppm



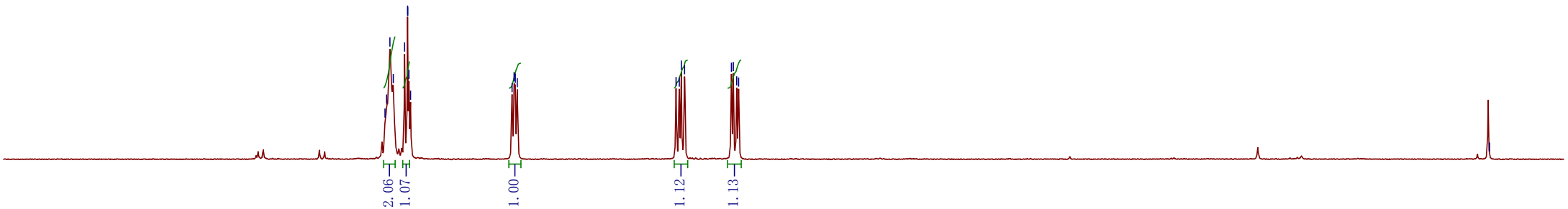
3q

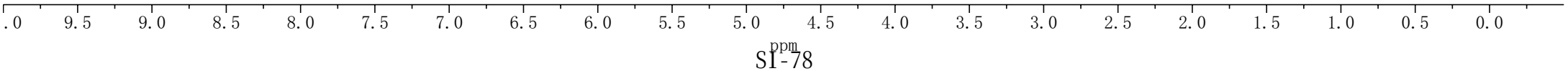
156.35
130.97
128.68
123.76
121.24
111.18
80.09
77.48
77.16
76.84
55.82
52.82

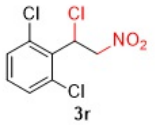




7.432
7.421
7.399
7.376
7.300
7.280
7.279
7.271
7.260
6.577
6.563
6.555
6.542
5.474
5.452
5.438
5.416
5.101
5.088
5.066
5.053
0.000

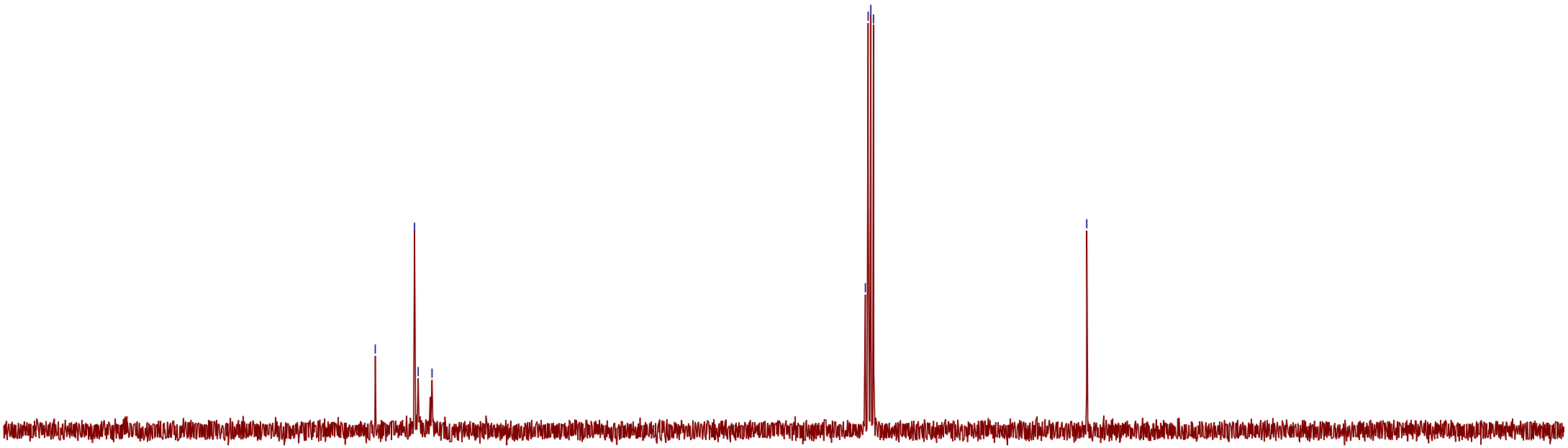






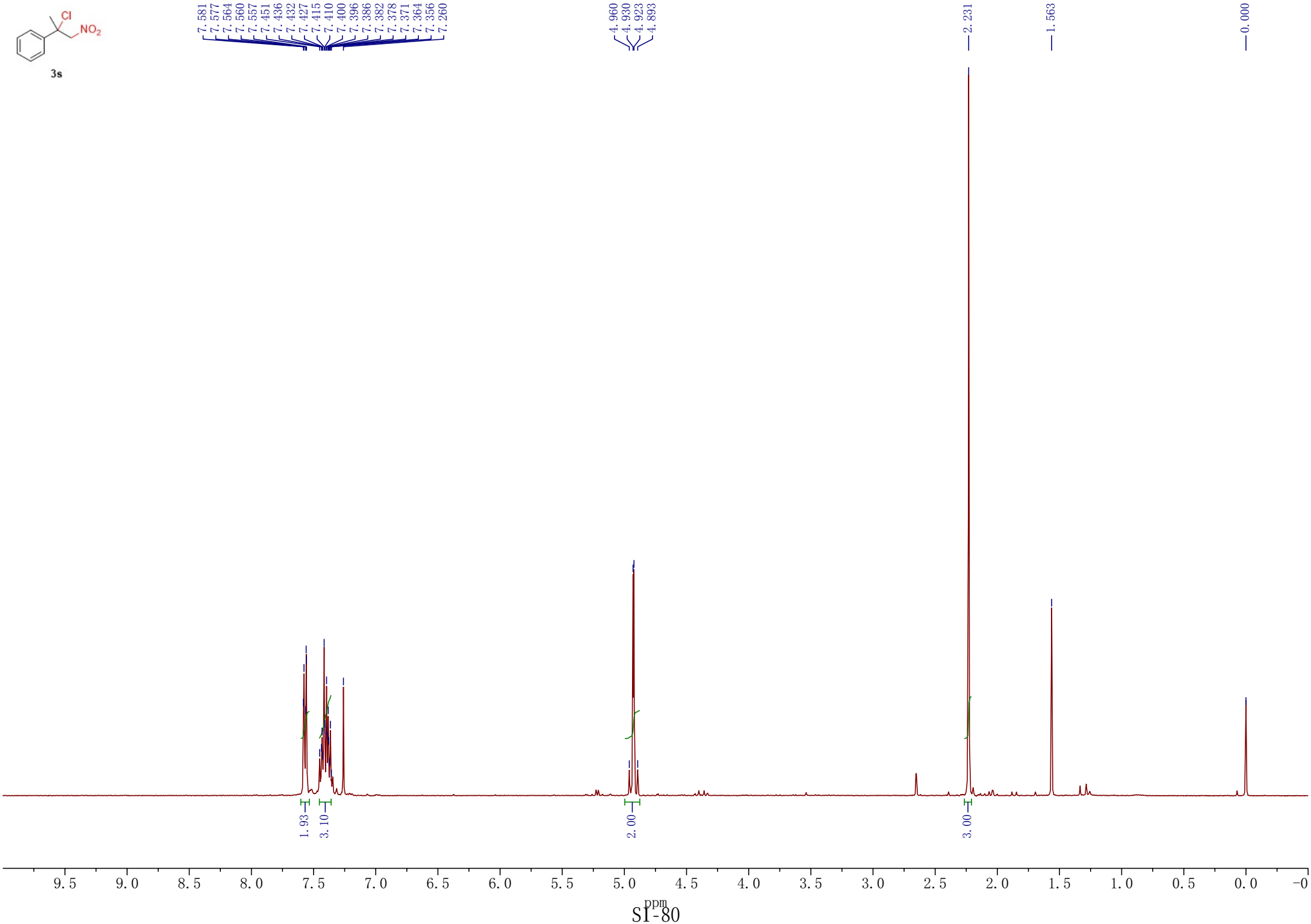
3r

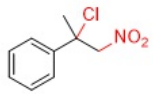
135.91
131.25
130.82
129.18
77.81
77.48
77.16
76.84
51.56



30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

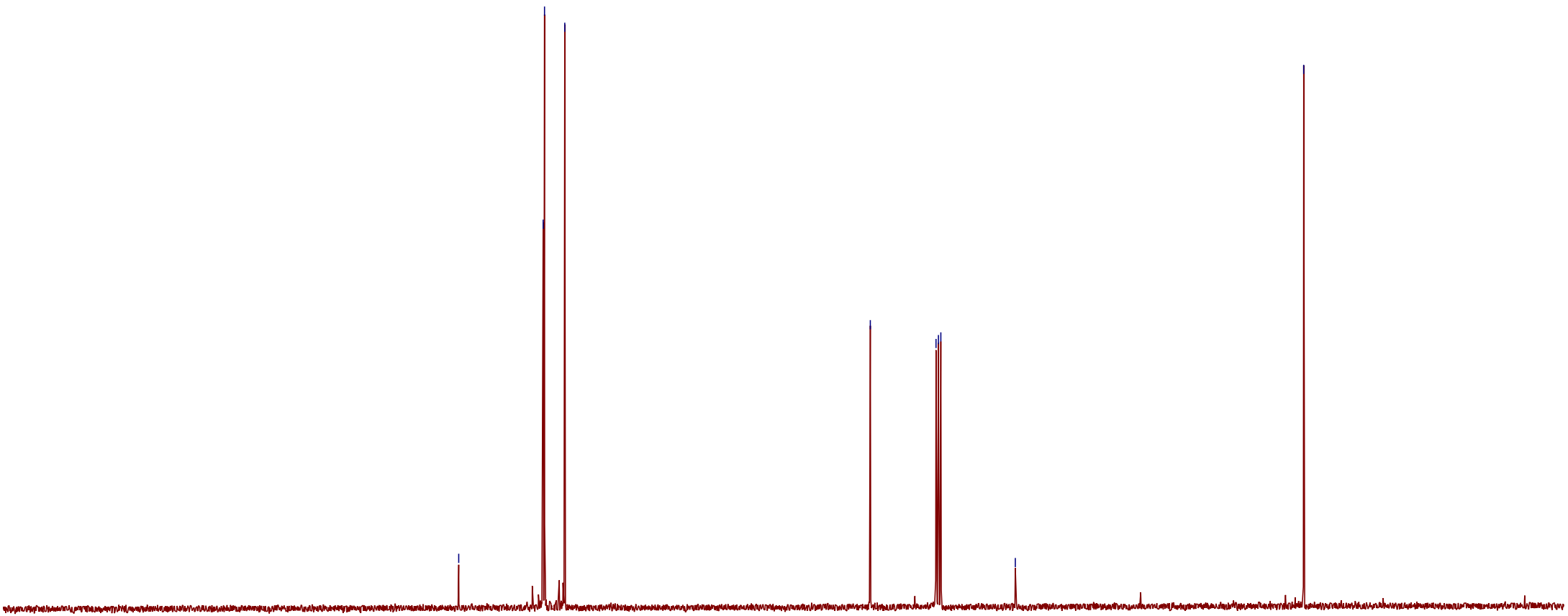
ppm

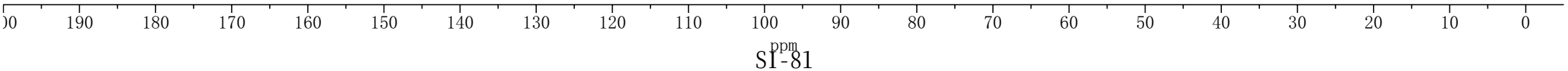

Cl
NO2
3s
7.581
7.577
7.564
7.560
7.557
7.451
7.436
7.432
7.427
7.415
7.410
7.400
7.396
7.386
7.382
7.378
7.371
7.364
7.356
7.260
4.960
4.930
4.923
4.893
2.231
1.563
0.000
1.93
3.10
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

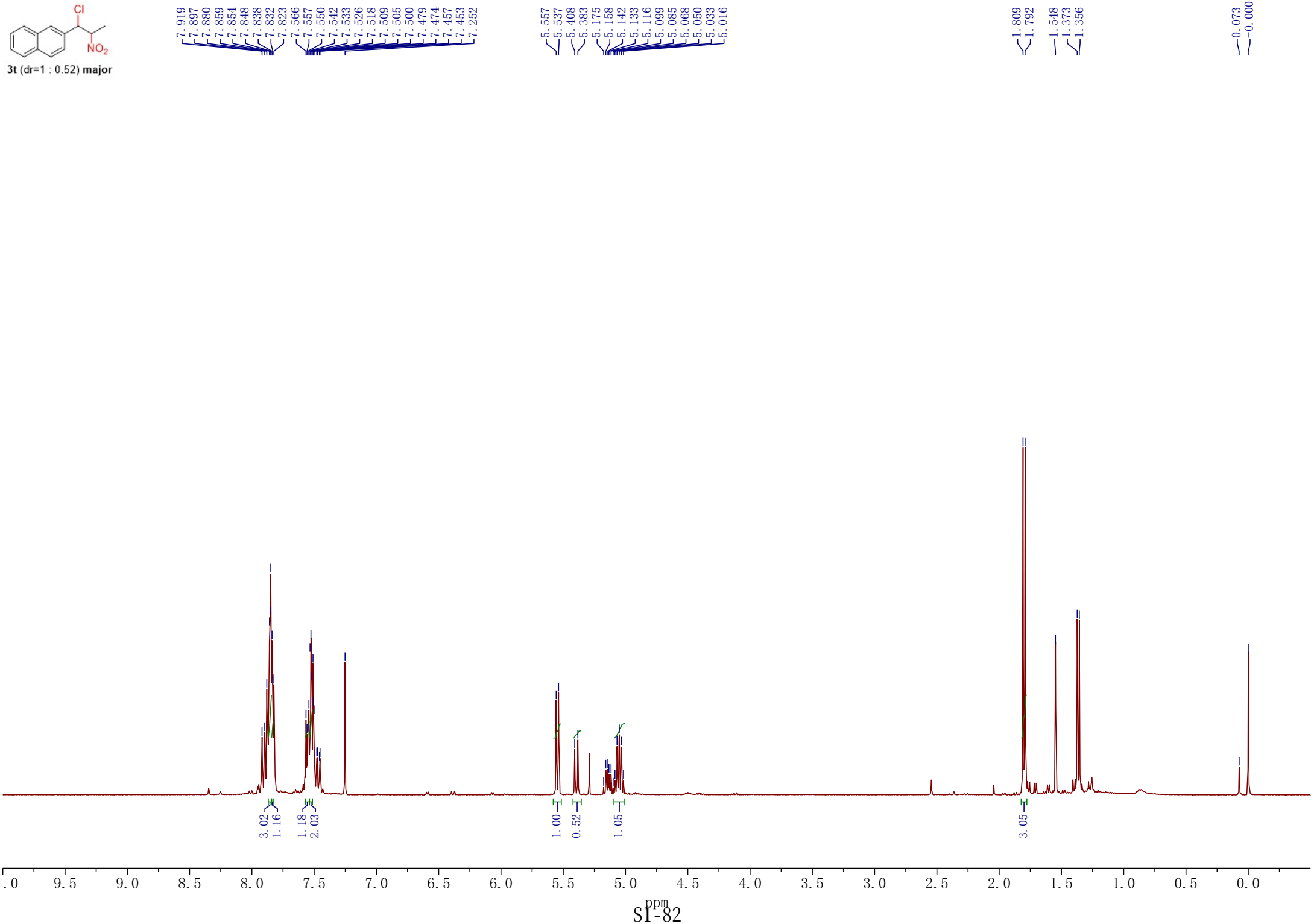


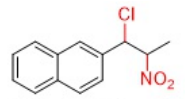
3s

140.18
129.08
128.90
126.25
86.11
77.48
77.16
76.84
67.06
29.17



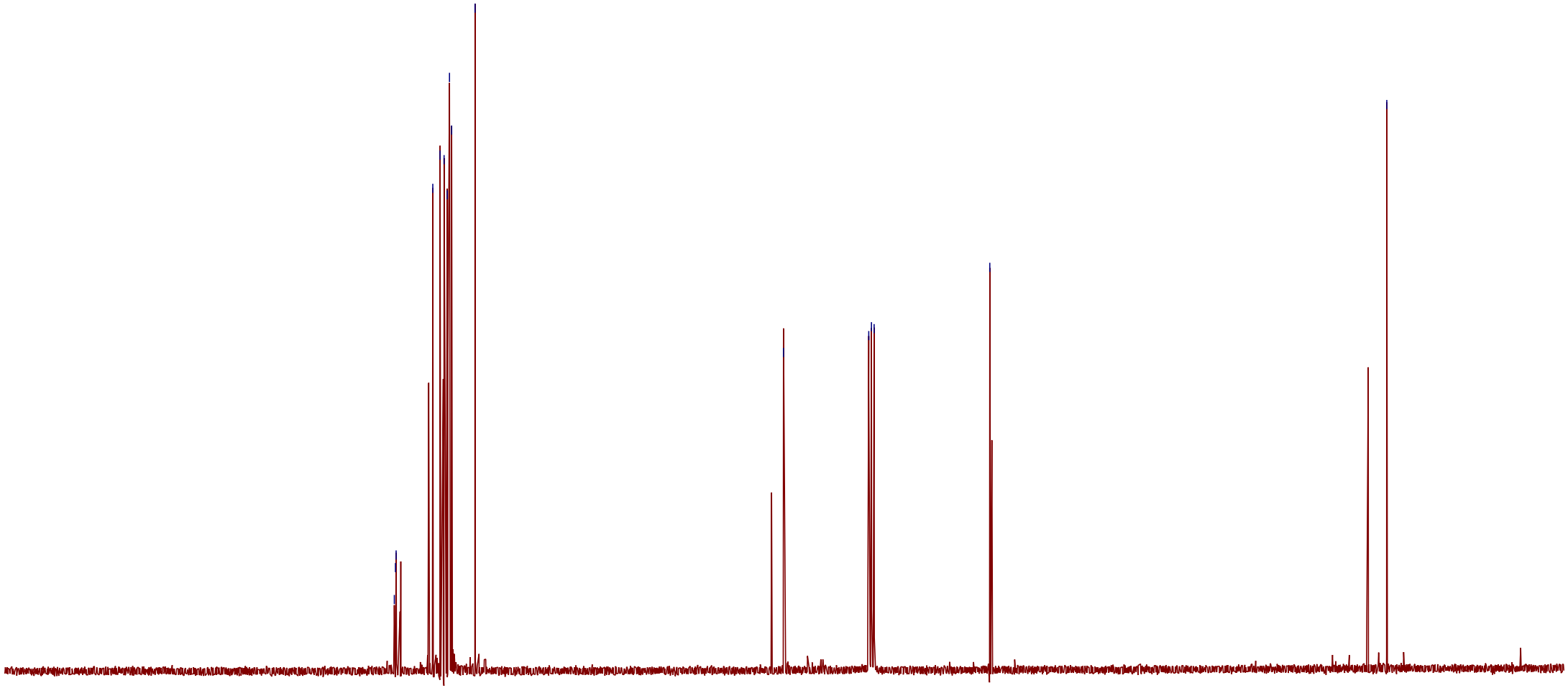



Cl
NO2
3t (dr=1 : 0.52) major
7.919
7.897
7.880
7.859
7.854
7.848
7.838
7.832
7.823
7.566
7.557
7.550
7.542
7.533
7.526
7.518
7.509
7.505
7.500
7.479
7.474
7.457
7.453
7.252
5.557
5.537
5.408
5.383
5.175
5.158
5.142
5.133
5.116
5.099
5.085
5.068
5.050
5.033
5.016
1.809
1.792
1.548
1.373
1.356
0.073
0.000
3.02
1.16
1.18
2.03
1.00
0.52
1.05
3.05
ppm



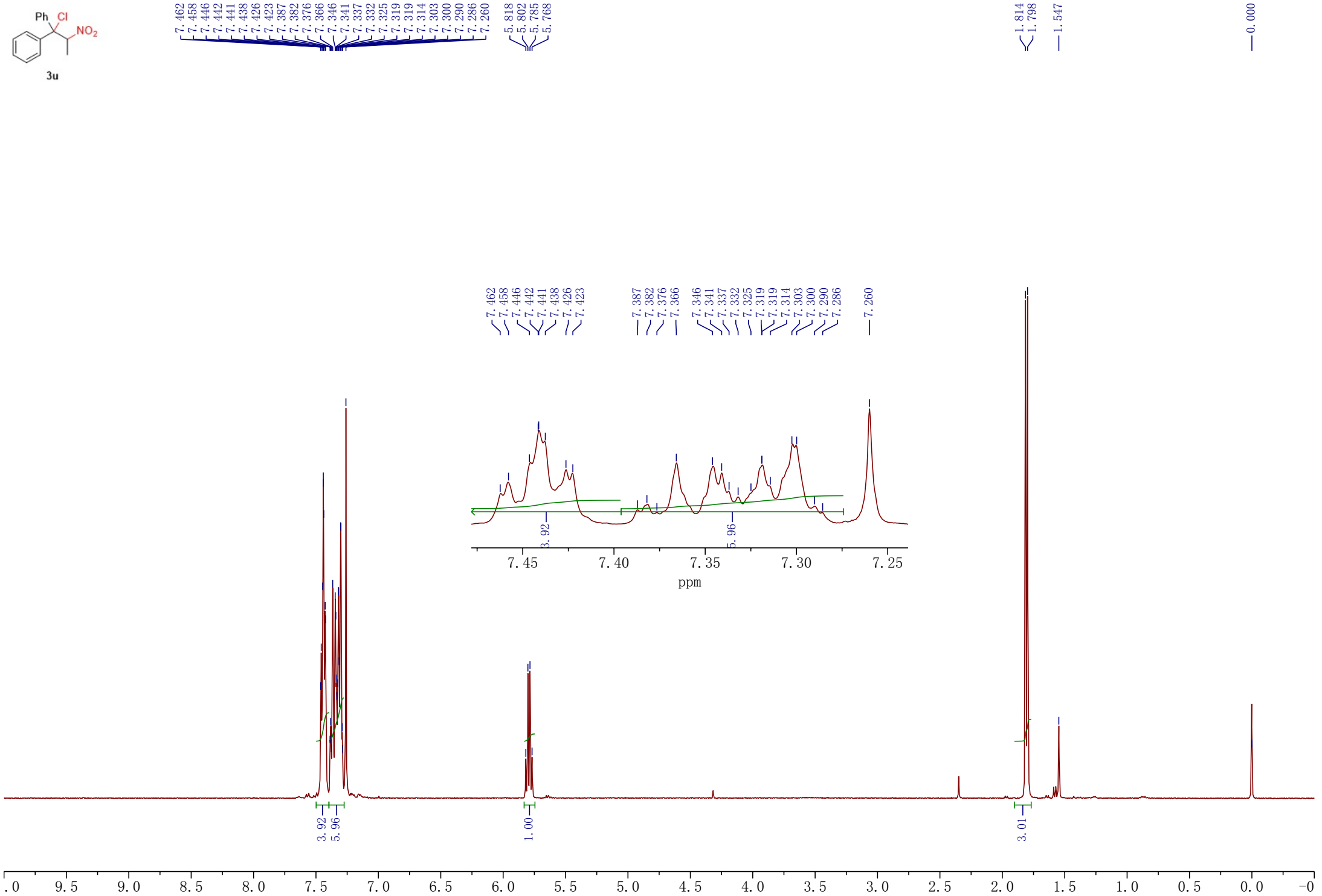
3t (dr=1 : 0.52) **major**

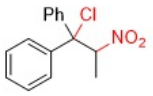
133.77
133.64
133.56
129.21
128.35
127.87
127.50
127.23
126.97
124.20
87.60
77.48
77.16
76.84
63.12
16.01



30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Ph
Cl
NO2
3u
7.462
7.458
7.446
7.442
7.441
7.438
7.426
7.423
7.387
7.382
7.376
7.366
7.346
7.341
7.337
7.332
7.325
7.319
7.319
7.314
7.303
7.300
7.290
7.286
7.260
5.818
5.802
5.785
5.768
1.814
1.798
1.547
0.000
3.92
5.96
1.00
3.01
7.45
7.40
7.35
7.30
7.25
ppm



3u

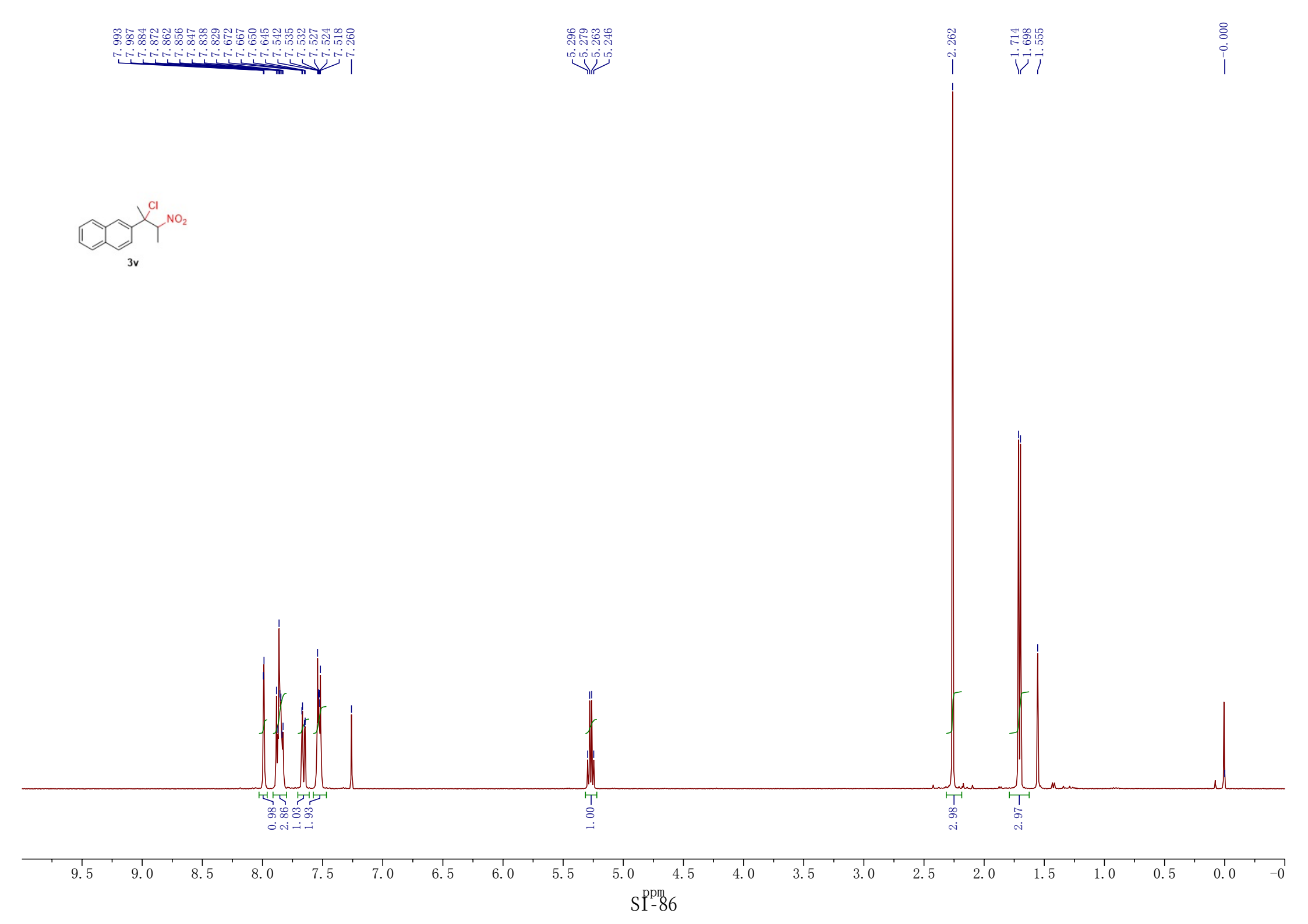
141.24
141.21
128.57
128.52
128.39
127.96
127.61
89.41
77.48
77.27
77.16
76.84
17.35

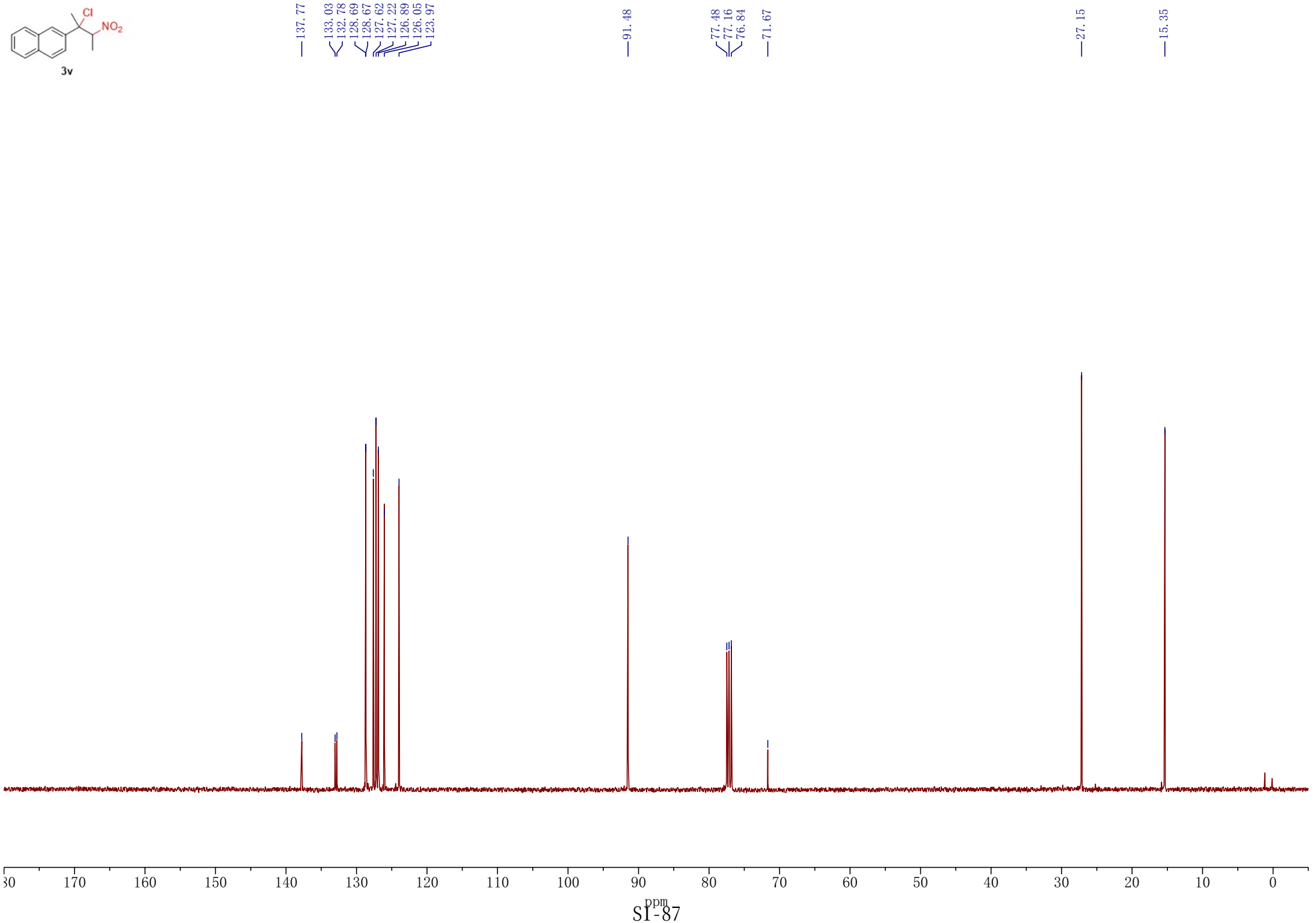
141.35 141.25 141.15 141.05 ppm

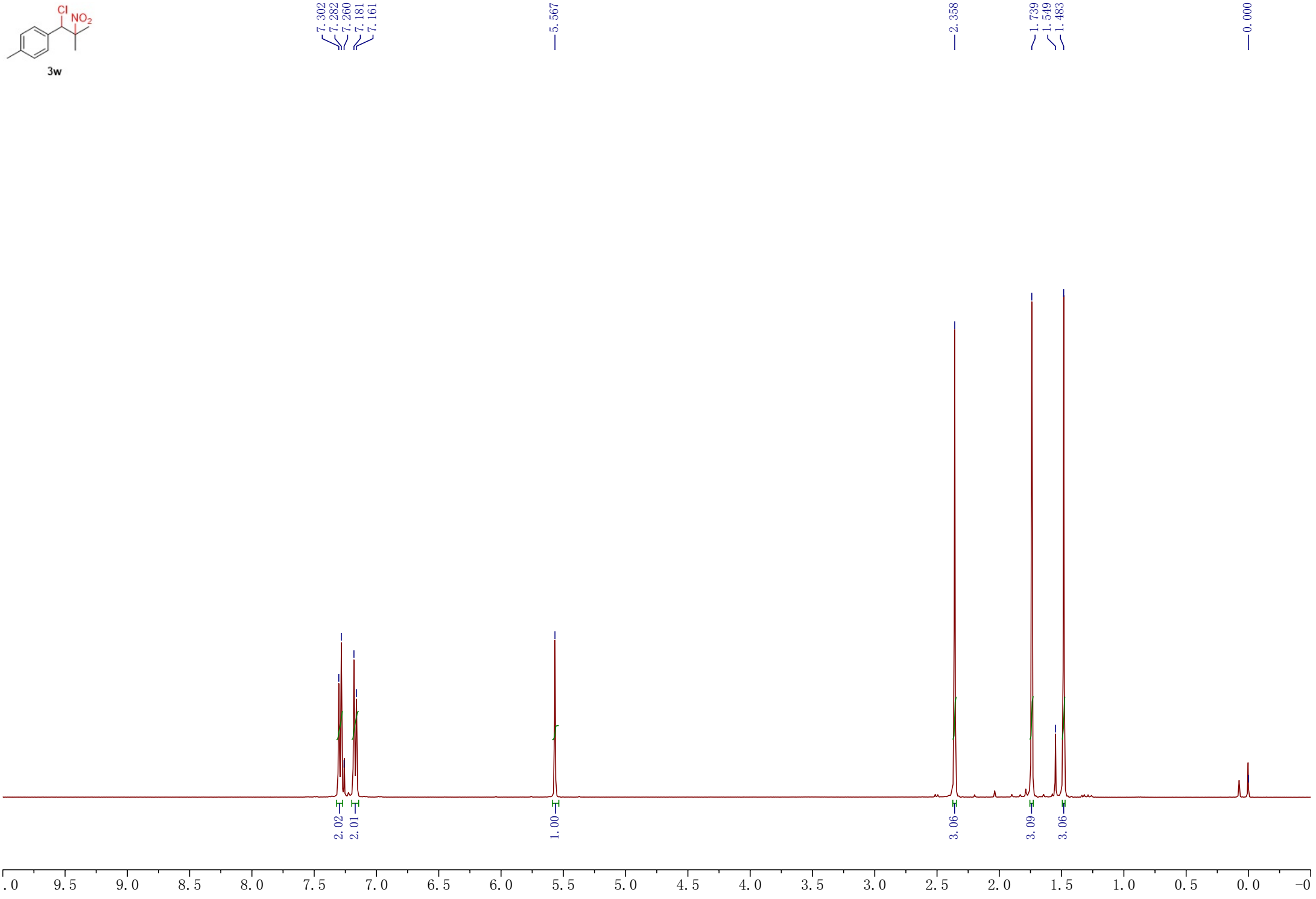
128.7 128.5 128.3 128.1 127.9 127.7 127.5 ppm

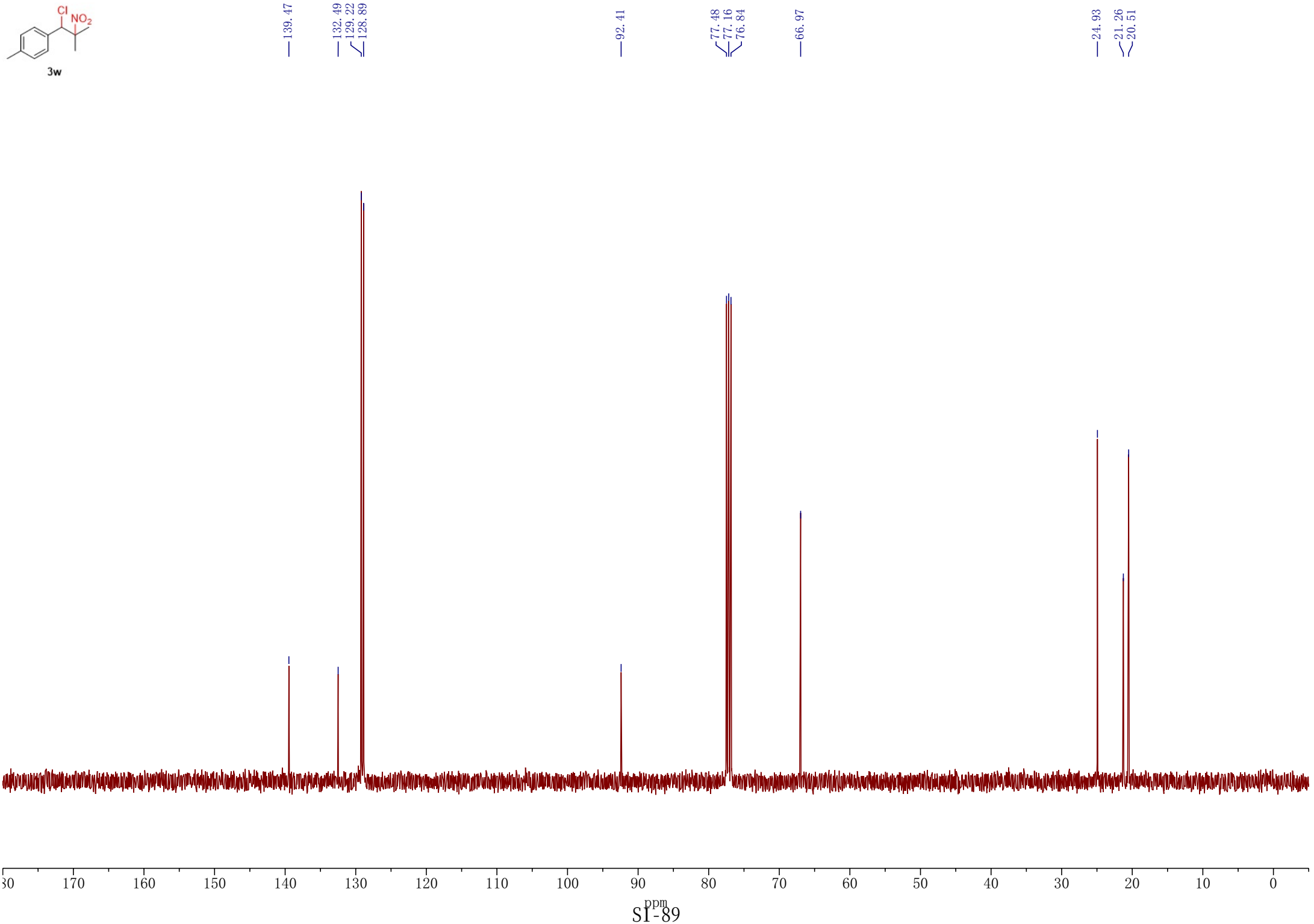
77.8 77.6 77.4 77.2 77.0 76.8 76.6 76.4 ppm

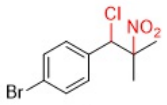
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.993
7.987
7.884
7.872
7.862
7.856
7.847
7.838
7.829
7.672
7.667
7.650
7.645
7.542
7.535
7.532
7.527
7.524
7.518
7.260
5.296
5.279
5.263
5.246
2.262
1.714
1.698
1.555
0.000
Cl
NO2
3v
0.98
2.86
1.03
1.93
1.00
2.98
2.97
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
ppm


Cl
NO2
3v
137.77
133.03
132.78
128.69
128.67
127.62
127.22
126.89
126.05
123.97
91.48
77.48
77.16
76.84
71.67
27.15
15.35
ppm

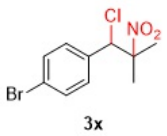

Cl
NO2
3w
7.302
7.282
7.260
7.181
7.161
5.567
2.358
1.739
1.549
1.483
0.000
2.02
2.01
1.00
3.06
3.09
3.06
ppm


Cl
NO2
3w
139.47
132.49
129.22
128.89
92.41
77.48
77.16
76.84
66.97
24.93
21.26
20.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Cl
NO2
Br

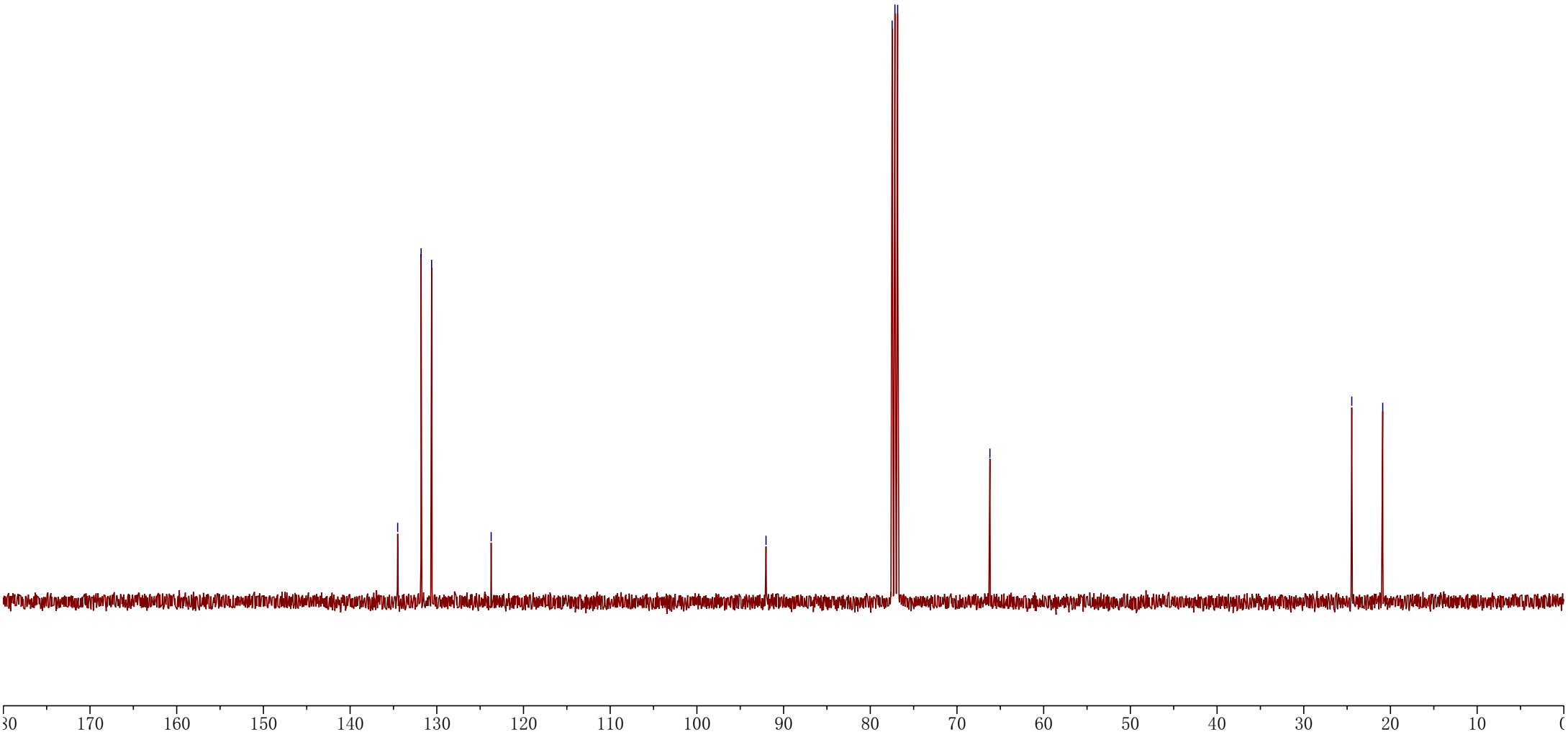
3x

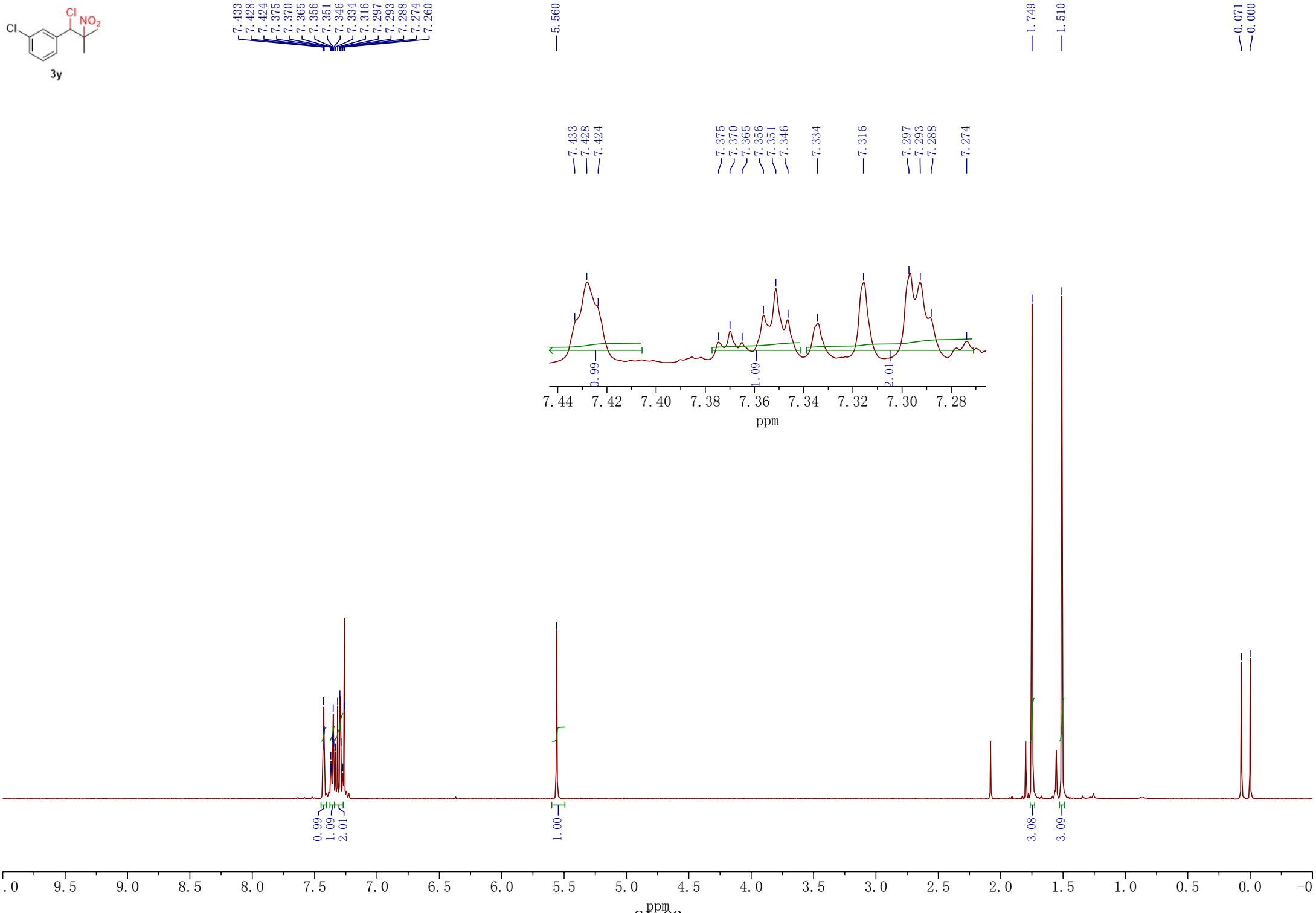
7.523
7.502
7.298
7.277
7.260
5.550
1.732
1.560
1.492
0.001
7.523
7.502
7.298
7.277
1.93
1.95
7.50
7.45
7.40
7.35
7.30
ppm
1.93
1.95
1.00
3.10
3.06
ppm

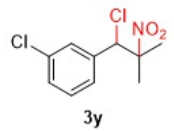


3x

134.51
131.81
130.60
123.73
92.03
77.48
77.16
76.84
66.20
24.46
20.89




Cl
NO2
3y
7.433
7.428
7.424
7.375
7.370
7.365
7.356
7.351
7.346
7.334
7.316
7.297
7.293
7.288
7.274
7.260
5.560
1.749
1.510
0.071
0.000
0.99
1.09
2.01
1.00
3.08
3.09
ppm

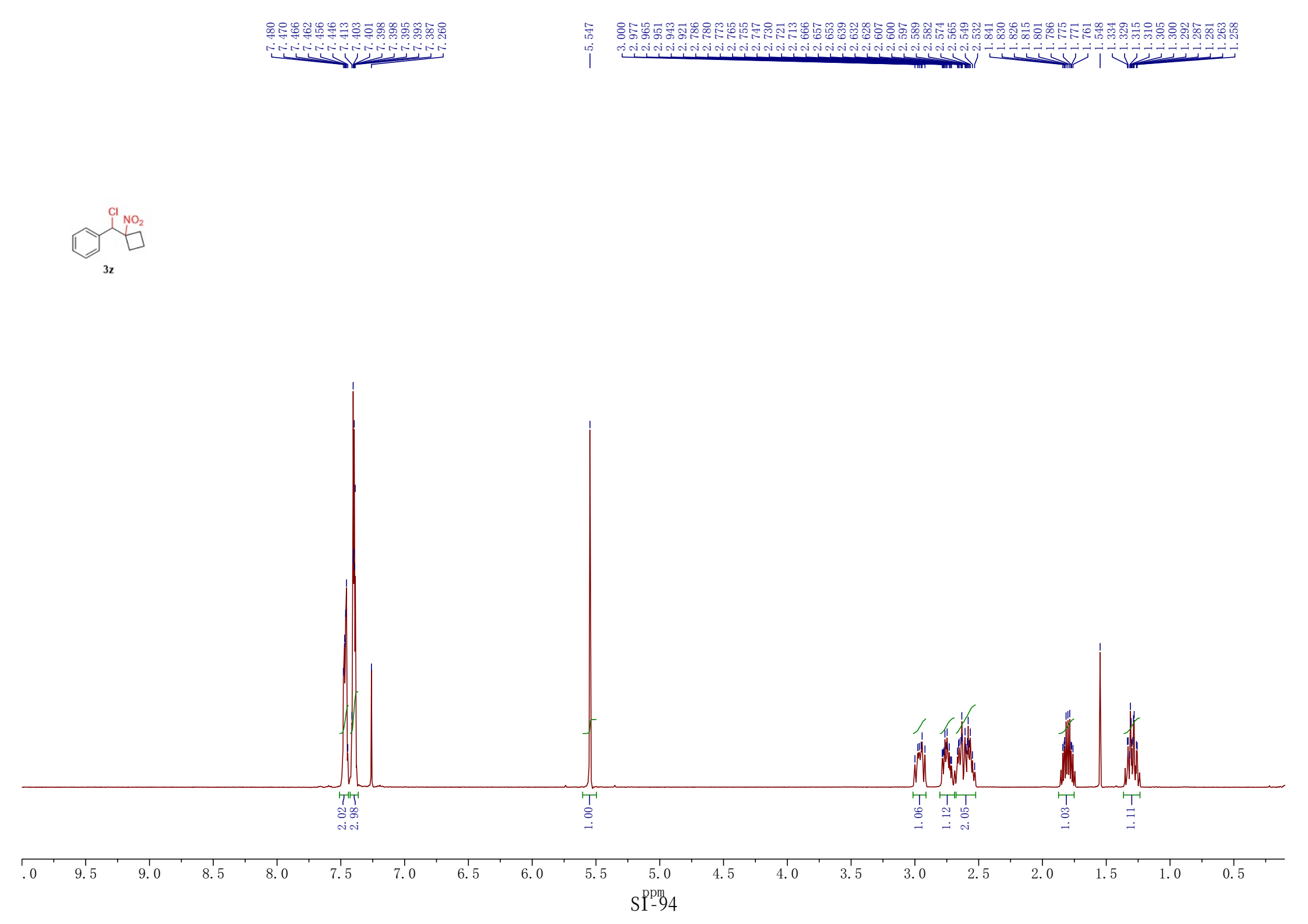


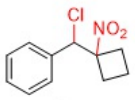
3y

137.45
134.65
129.84
129.72
129.14
127.24
92.05
77.48
77.16
76.84
66.03
24.62
20.86

30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

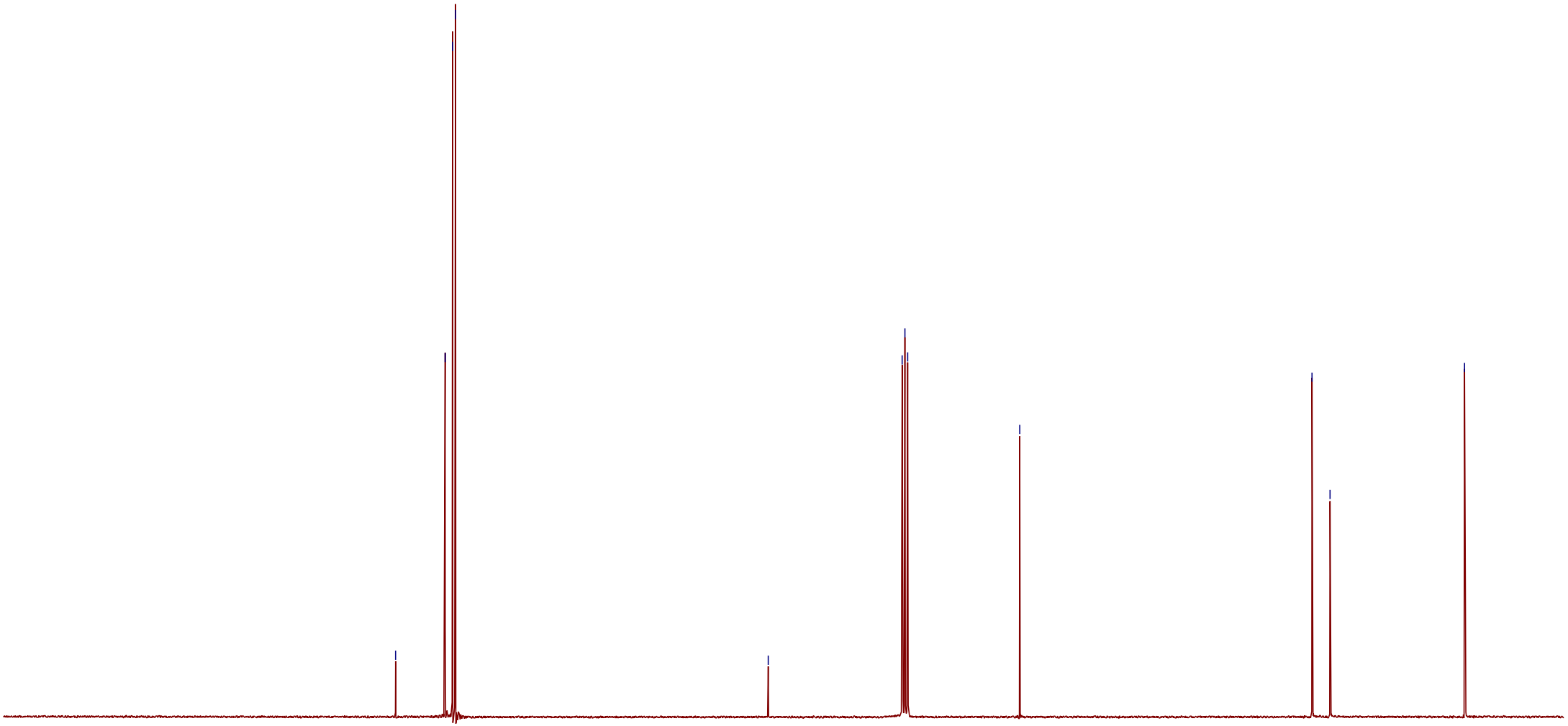
ppm


7.480
7.470
7.466
7.462
7.456
7.446
7.413
7.403
7.401
7.398
7.398
7.395
7.393
7.387
7.260
5.547
3.000
2.977
2.965
2.951
2.943
2.921
2.786
2.780
2.773
2.765
2.755
2.747
2.730
2.721
2.713
2.666
2.657
2.653
2.639
2.632
2.628
2.607
2.600
2.597
2.589
2.582
2.574
2.565
2.549
2.532
1.841
1.830
1.826
1.815
1.801
1.786
1.775
1.771
1.761
1.548
1.334
1.329
1.315
1.310
1.305
1.300
1.292
1.287
1.281
1.263
1.258
Cl
NO2
3z
2.02
2.98
1.00
1.06
1.12
2.05
1.03
1.11
.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
ppm



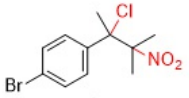
3z

135.26
129.60
128.76
128.42
92.75
77.48
77.16
76.84
64.06
30.73
28.67
13.33



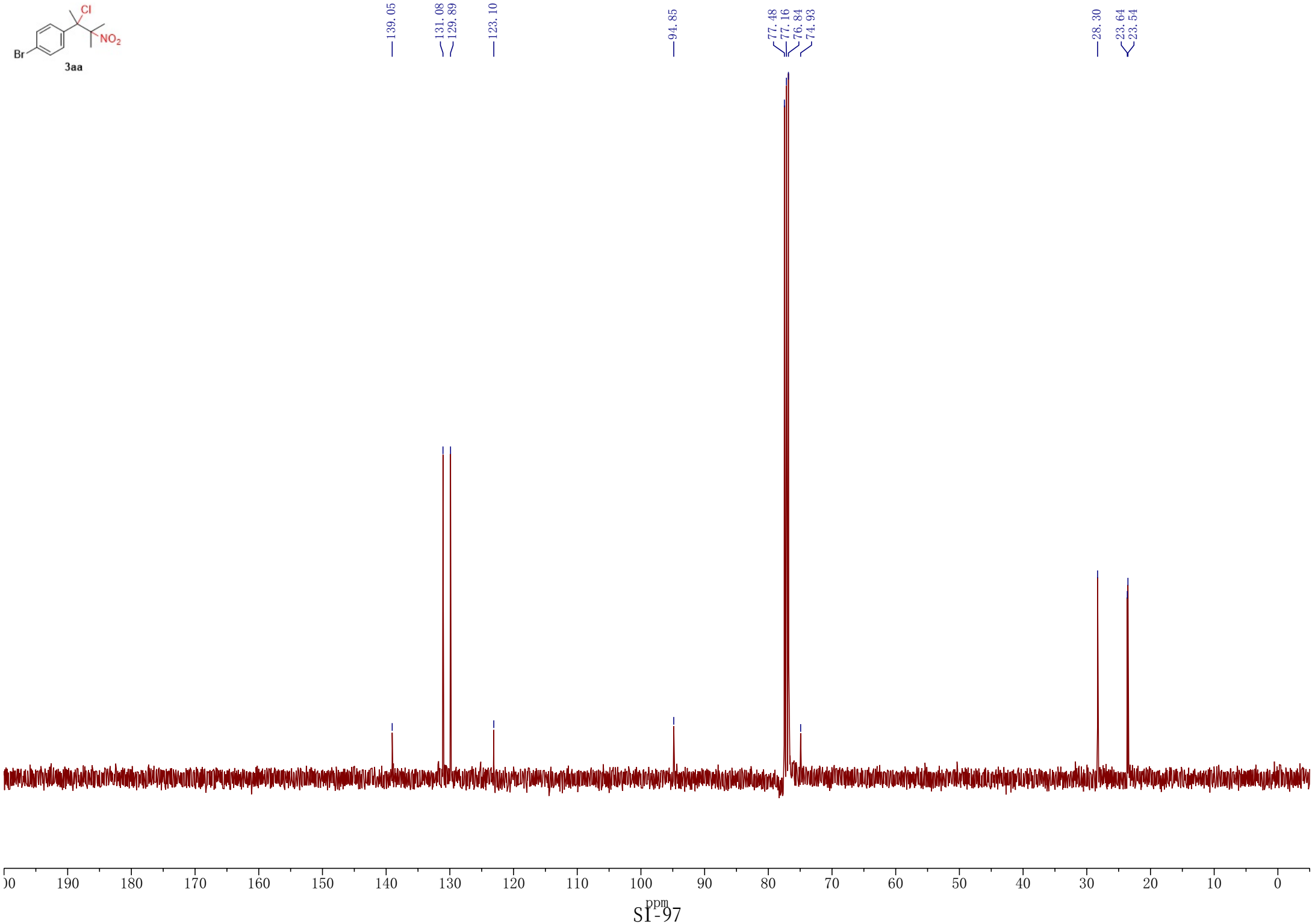
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

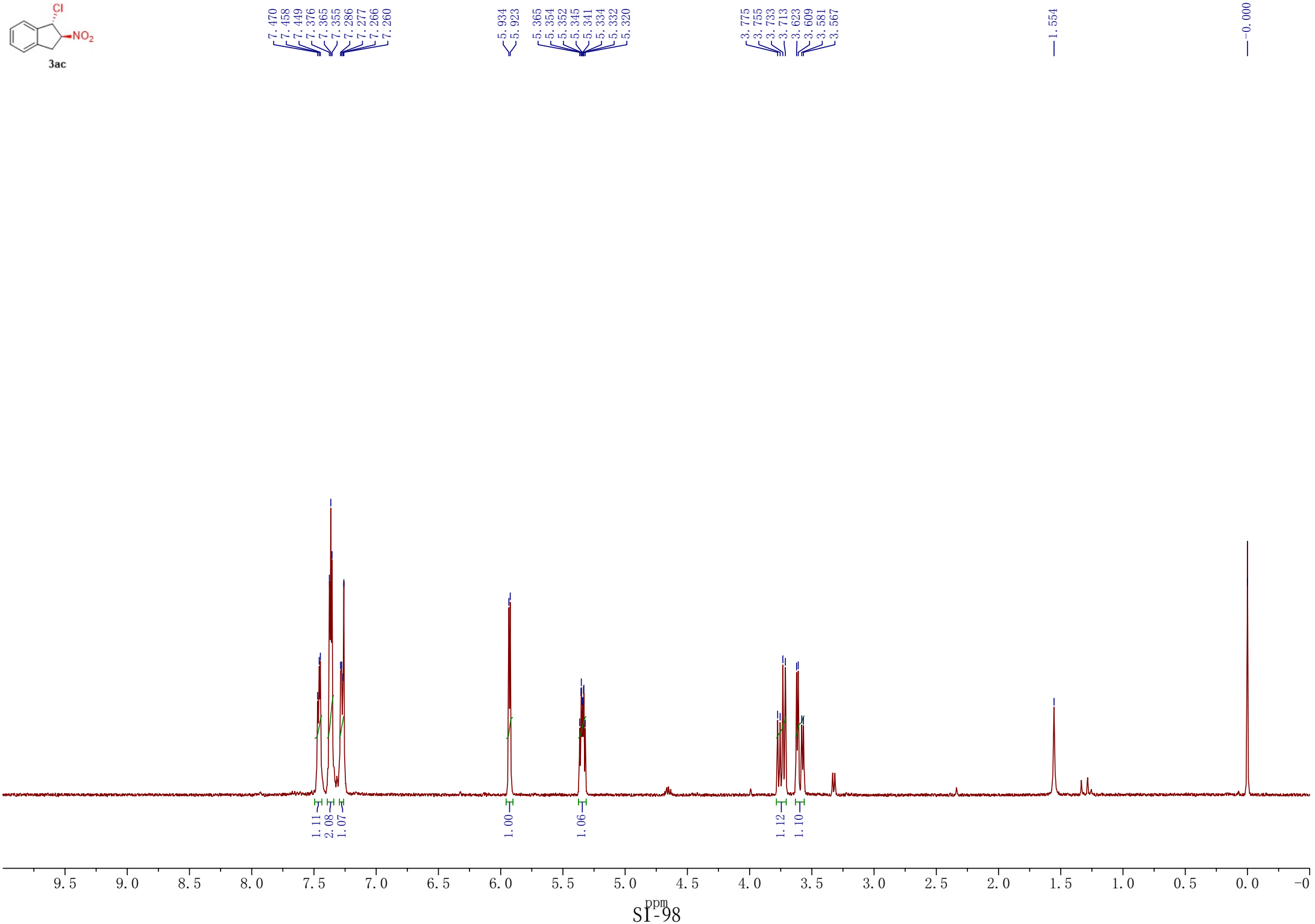
ppm

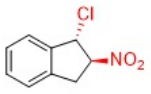

Cl
NO2
Br

3aa

7.488
7.466
7.396
7.374
7.260
2.160
1.753
1.642
1.566
0.003
2.00
1.95
2.93
3.10
2.97
.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
ppm

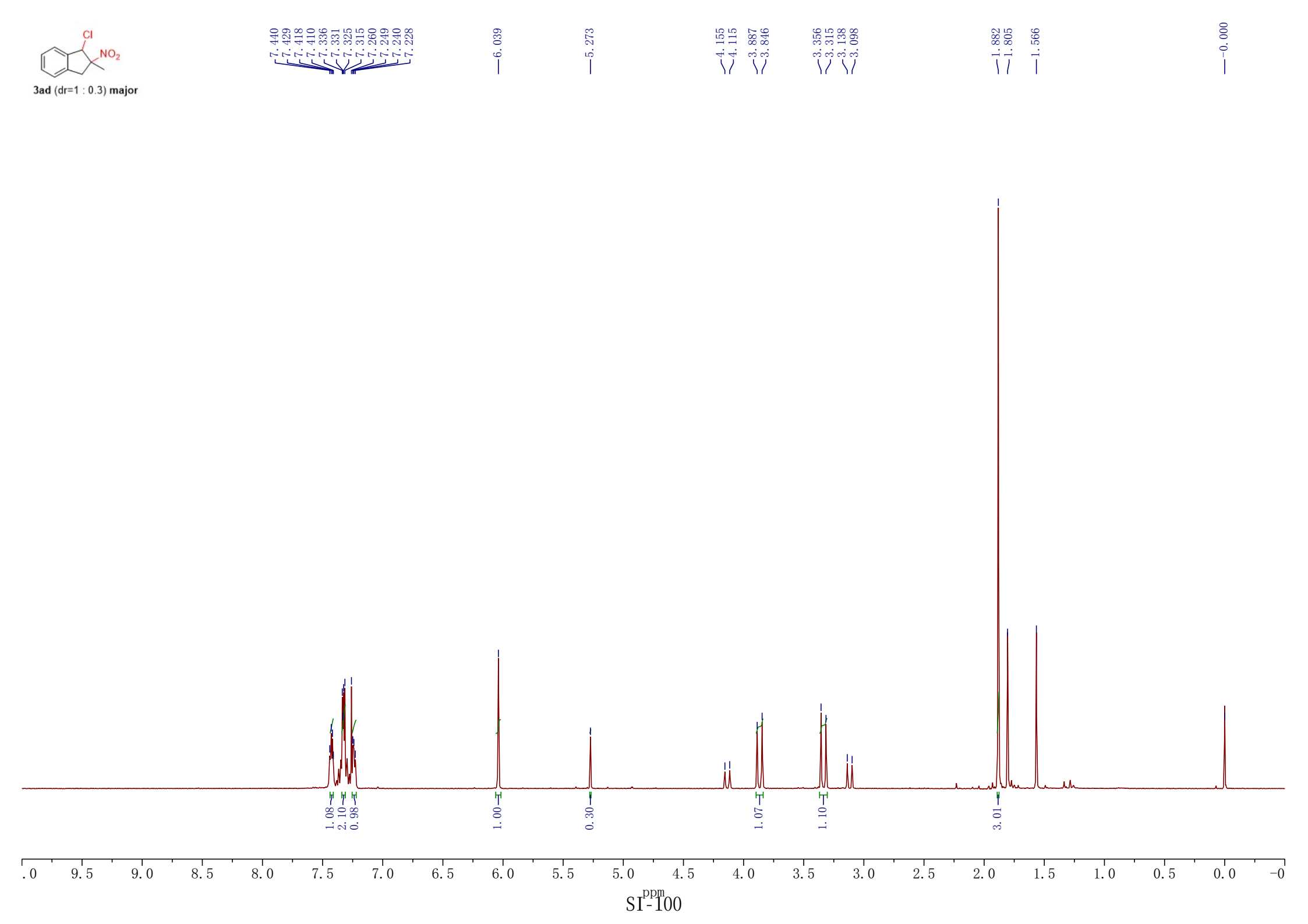

Cl
NO2
Br
3aa
139.05
131.08
129.89
123.10
94.85
77.48
77.16
76.84
74.93
28.30
23.64
23.54
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

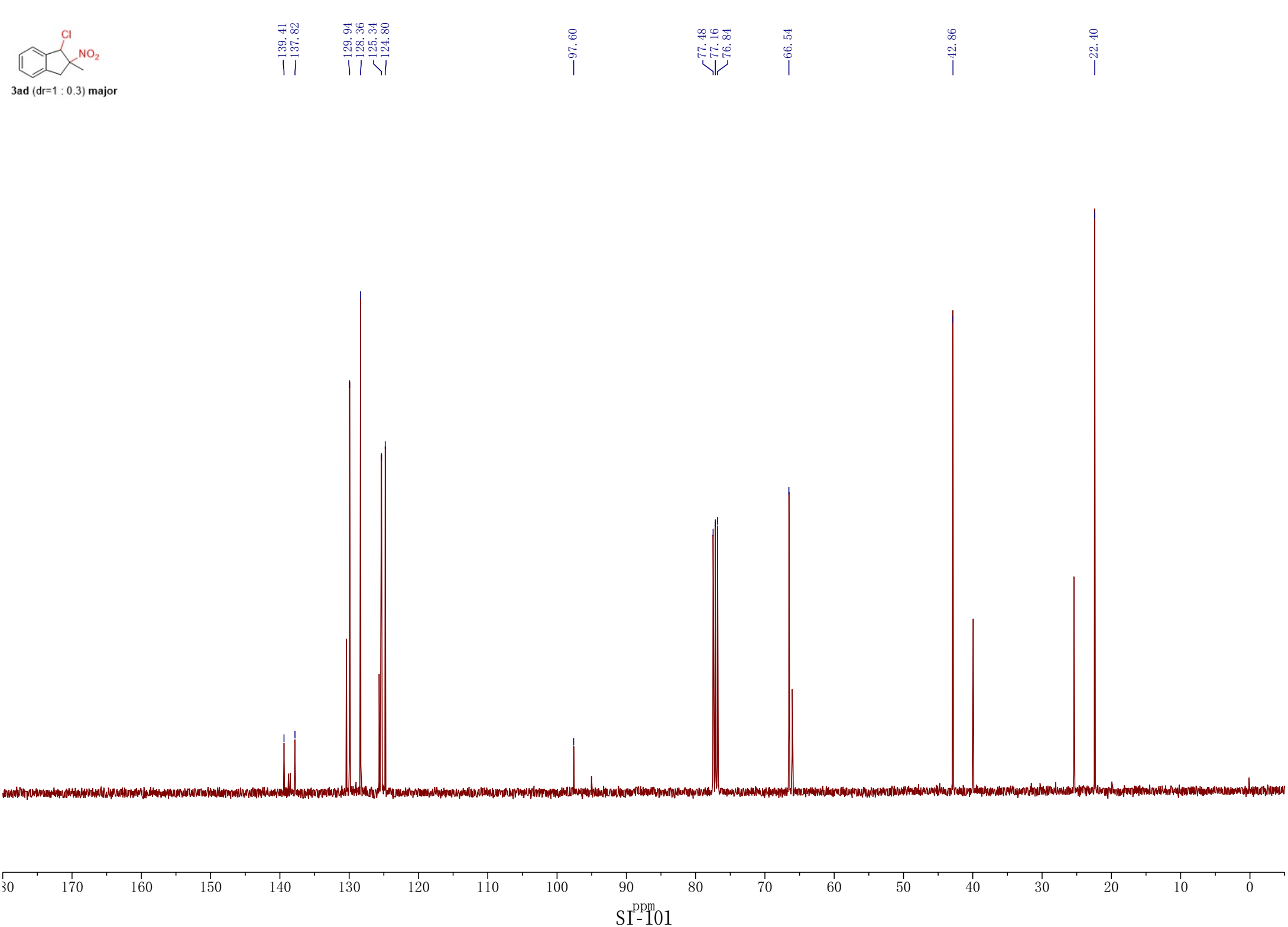

Cl
NO2
3ac
7.470
7.458
7.449
7.376
7.365
7.355
7.286
7.277
7.266
7.260
5.934
5.923
5.365
5.354
5.352
5.345
5.341
5.334
5.332
5.320
3.775
3.755
3.733
3.713
3.623
3.609
3.581
3.567
1.554
0.000
1.11
2.08
1.07
1.00
1.06
1.12
1.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

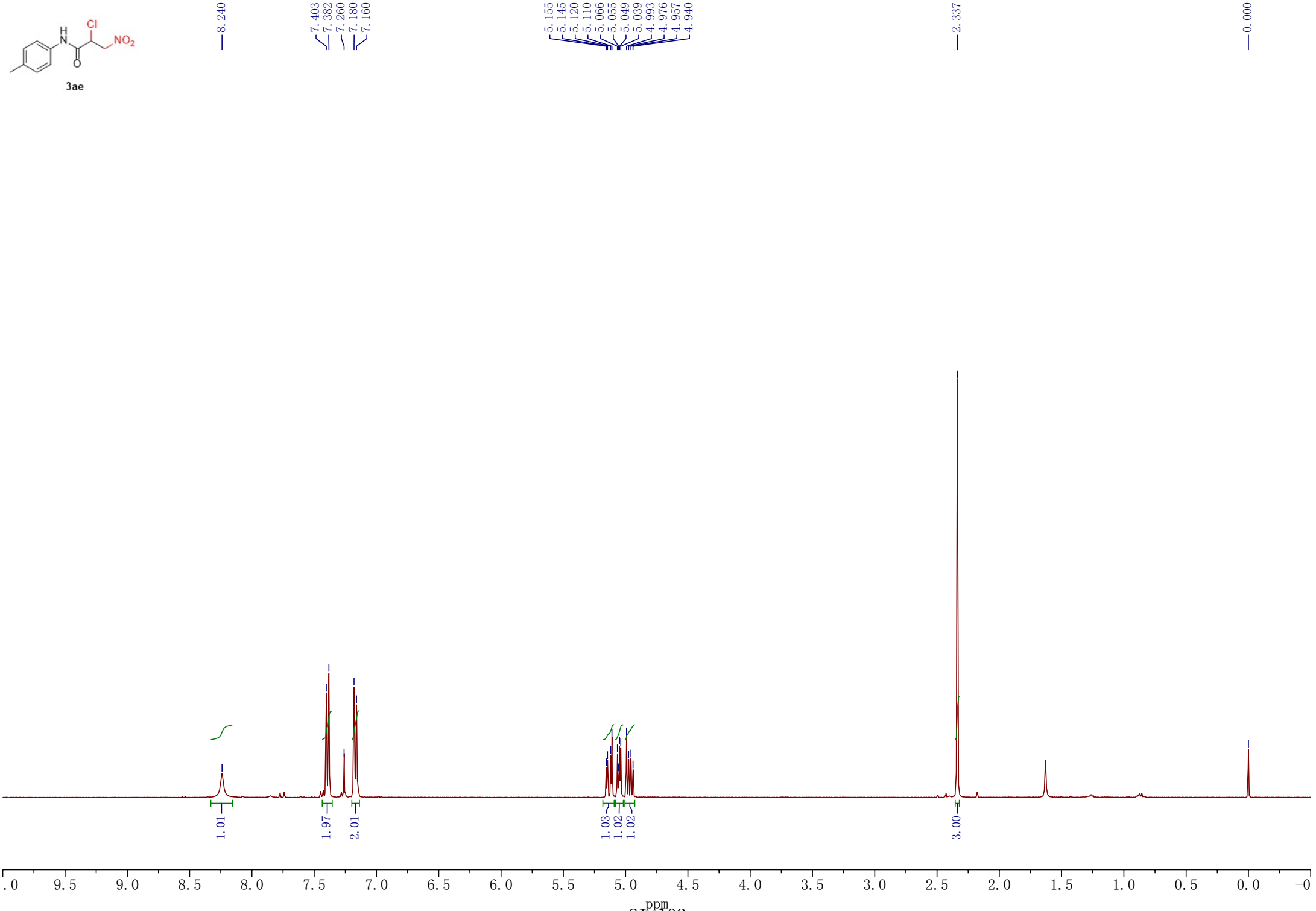

Cl
NO2

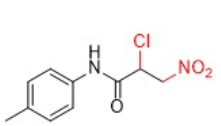
3ac

138.86
137.71
130.27
128.71
125.46
124.88
92.52
77.48
77.16
76.84
62.51
36.42
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm


Cl
NO2
3ad (dr=1 : 0.3) major
7.440
7.429
7.418
7.410
7.336
7.331
7.325
7.315
7.260
7.249
7.240
7.228
6.039
5.273
4.155
4.115
3.887
3.846
3.356
3.315
3.138
3.098
1.882
1.805
1.566
0.000
1.08
2.10
0.98
1.00
0.30
1.07
1.10
3.01
.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
-0
ppm

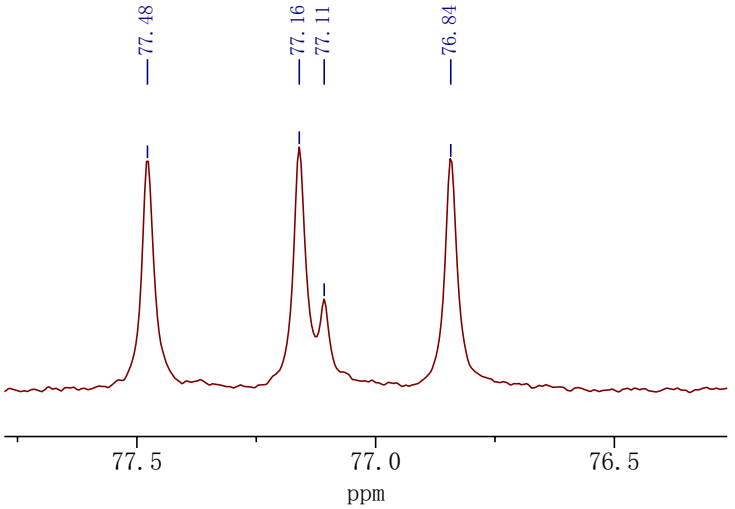

Cl
NO2
3ad (dr=1 : 0.3) major
139.41
137.82
129.94
128.36
125.34
124.80
97.60
77.48
77.16
76.84
66.54
42.86
22.40
ppm

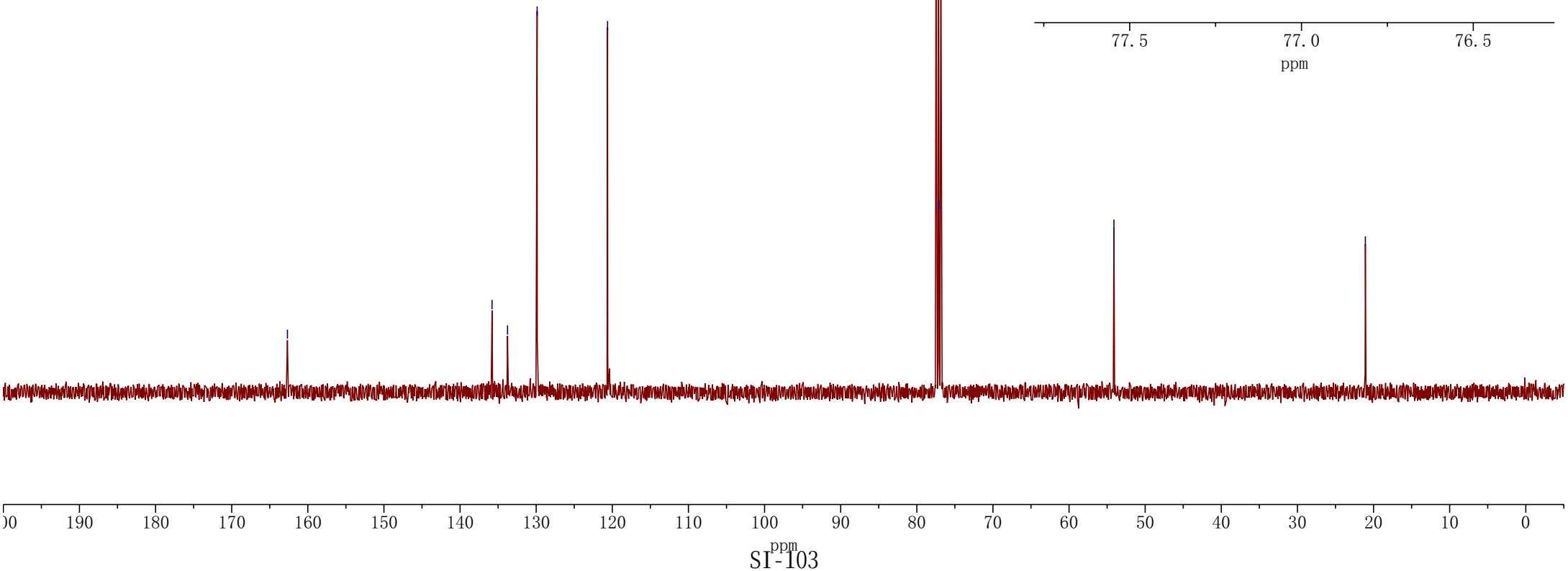

3ae
8.240
7.403
7.382
7.260
7.180
7.160
5.155
5.145
5.120
5.110
5.066
5.055
5.049
5.039
4.993
4.976
4.957
4.940
2.337
0.000
1.01
1.97
2.01
1.03
1.02
1.02
3.00
ppm

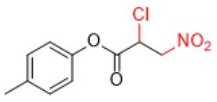


3ae

162.68
135.80
133.76
129.88
120.62
77.48
77.16
77.11
76.84
54.10
21.07

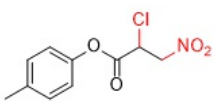





Cl
NO2
O
O

3af

7.260
7.220
7.200
7.036
7.016
5.122
5.104
5.082
5.078
5.060
4.927
4.905
4.882
4.860
2.362
0.000
2.00
1.99
2.01
1.10
3.02
ppm

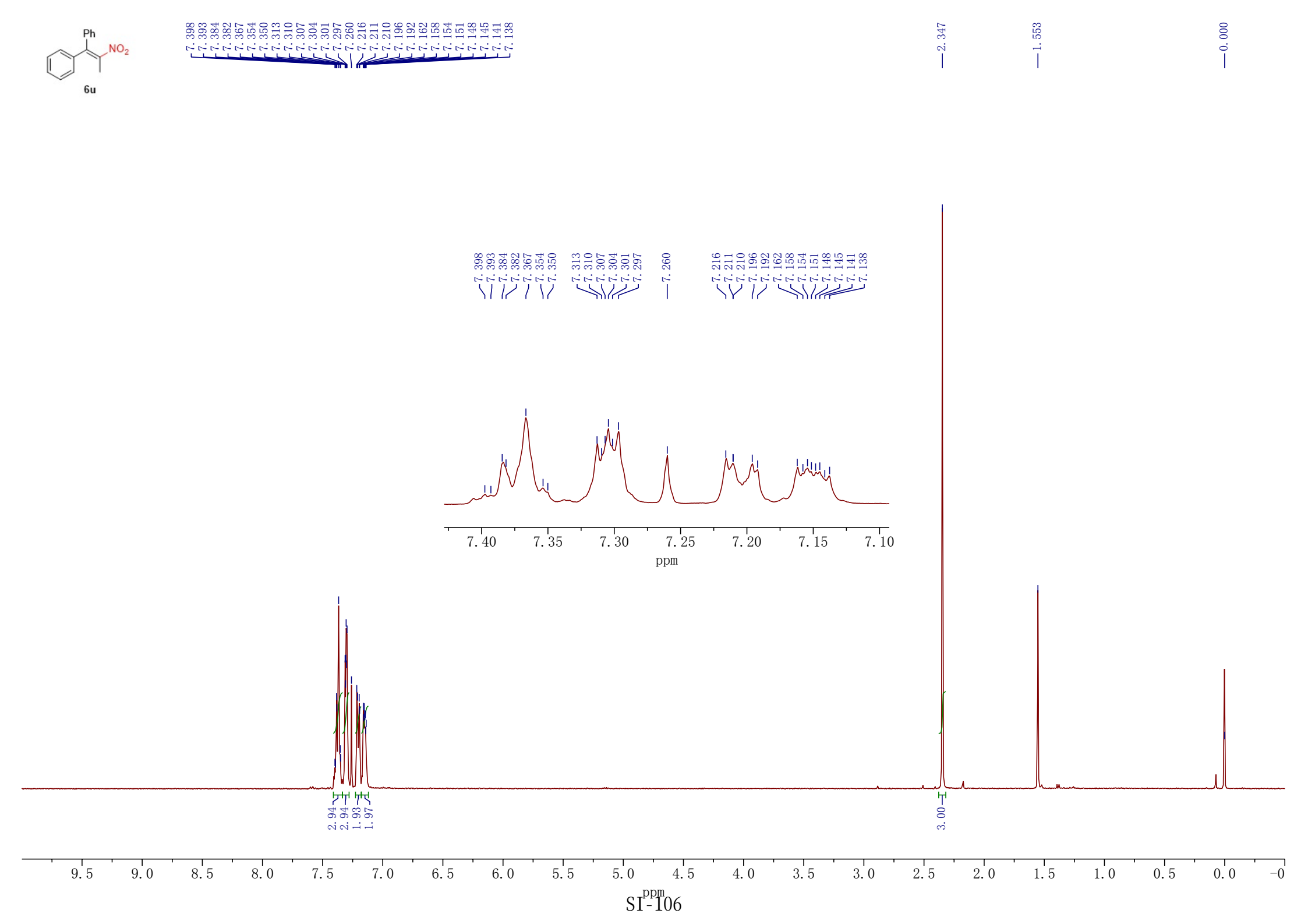


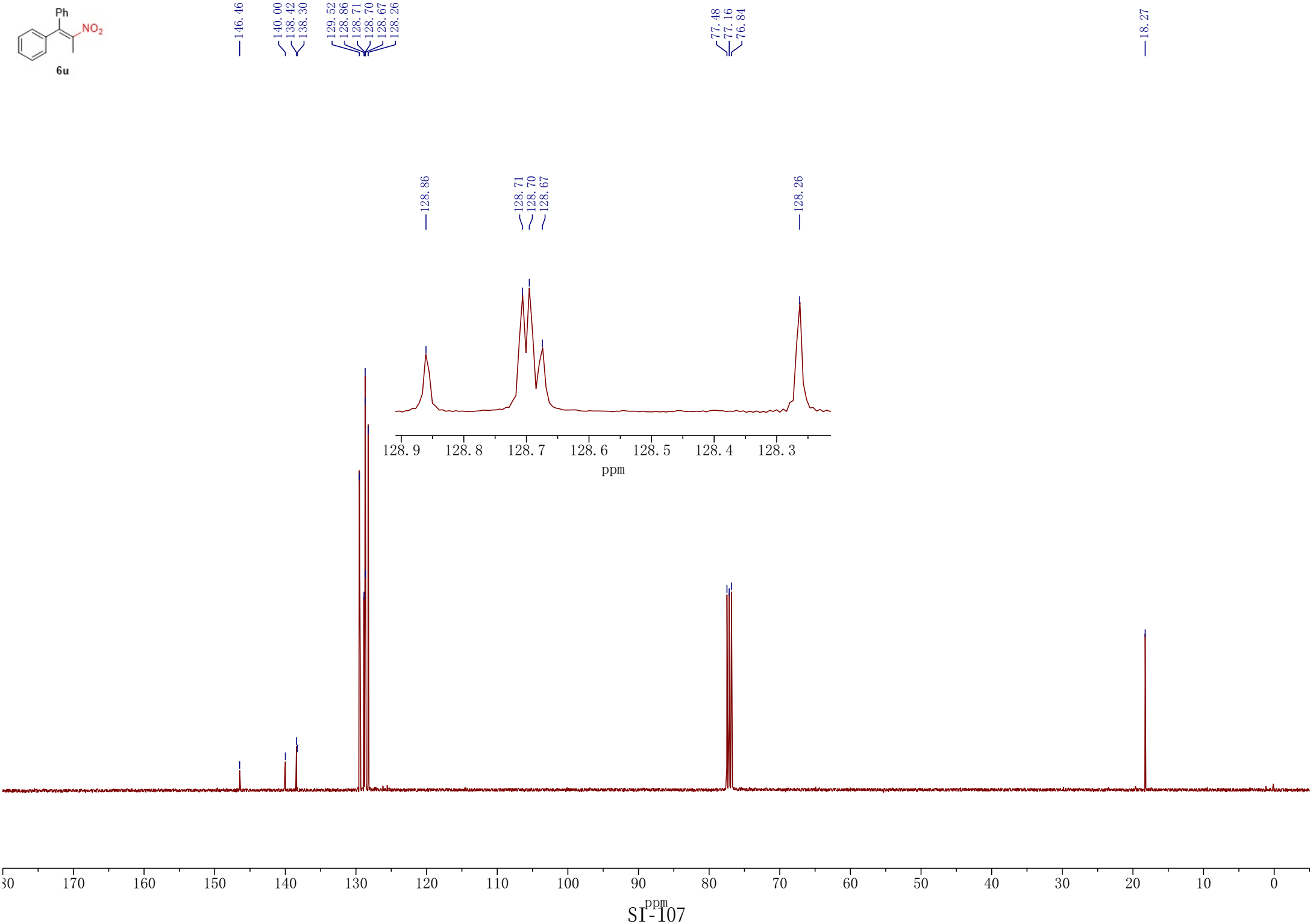
3af

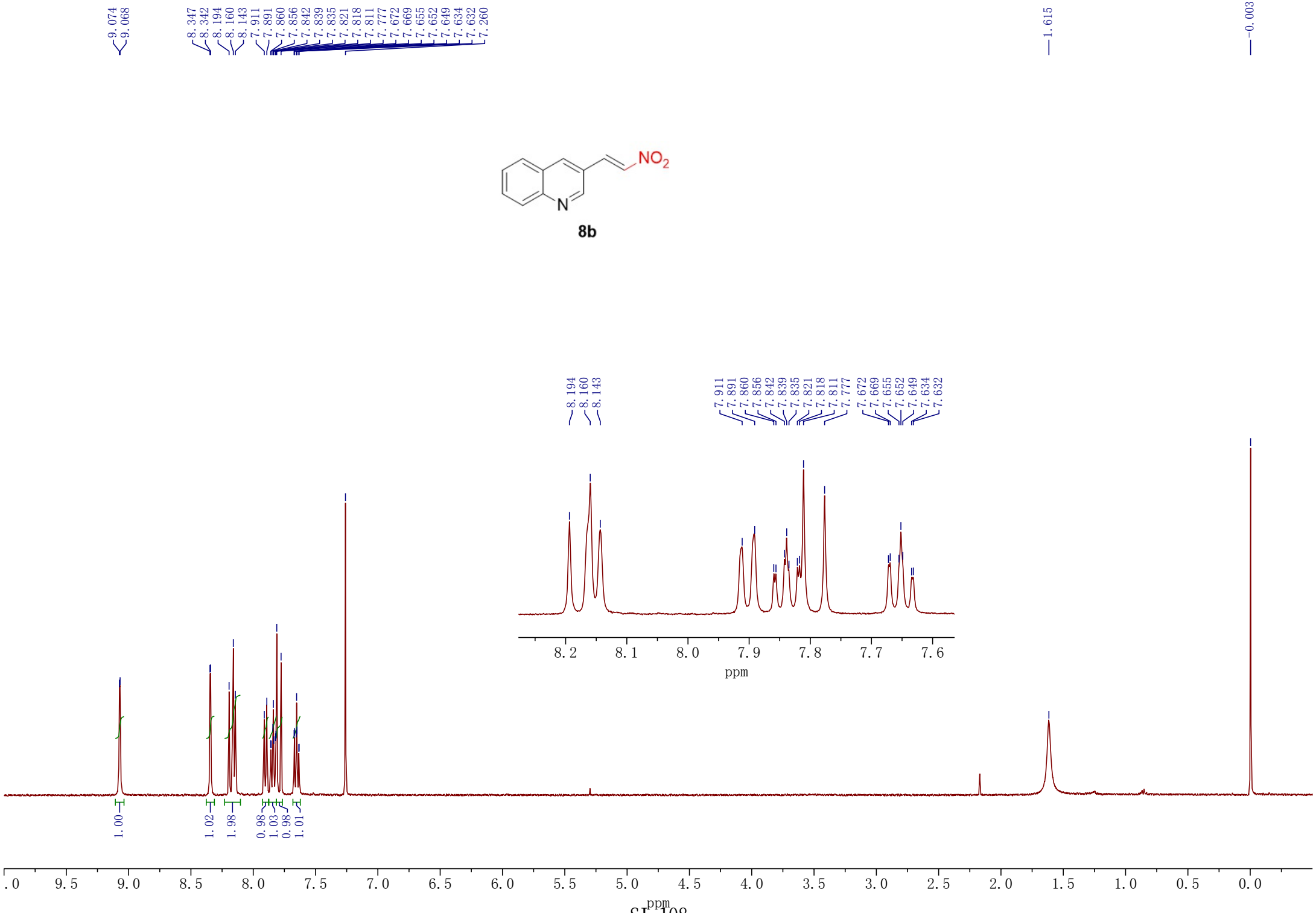
165.41
148.01
136.77
130.34
120.66
77.48
77.16
76.84
75.55
49.78
21.05

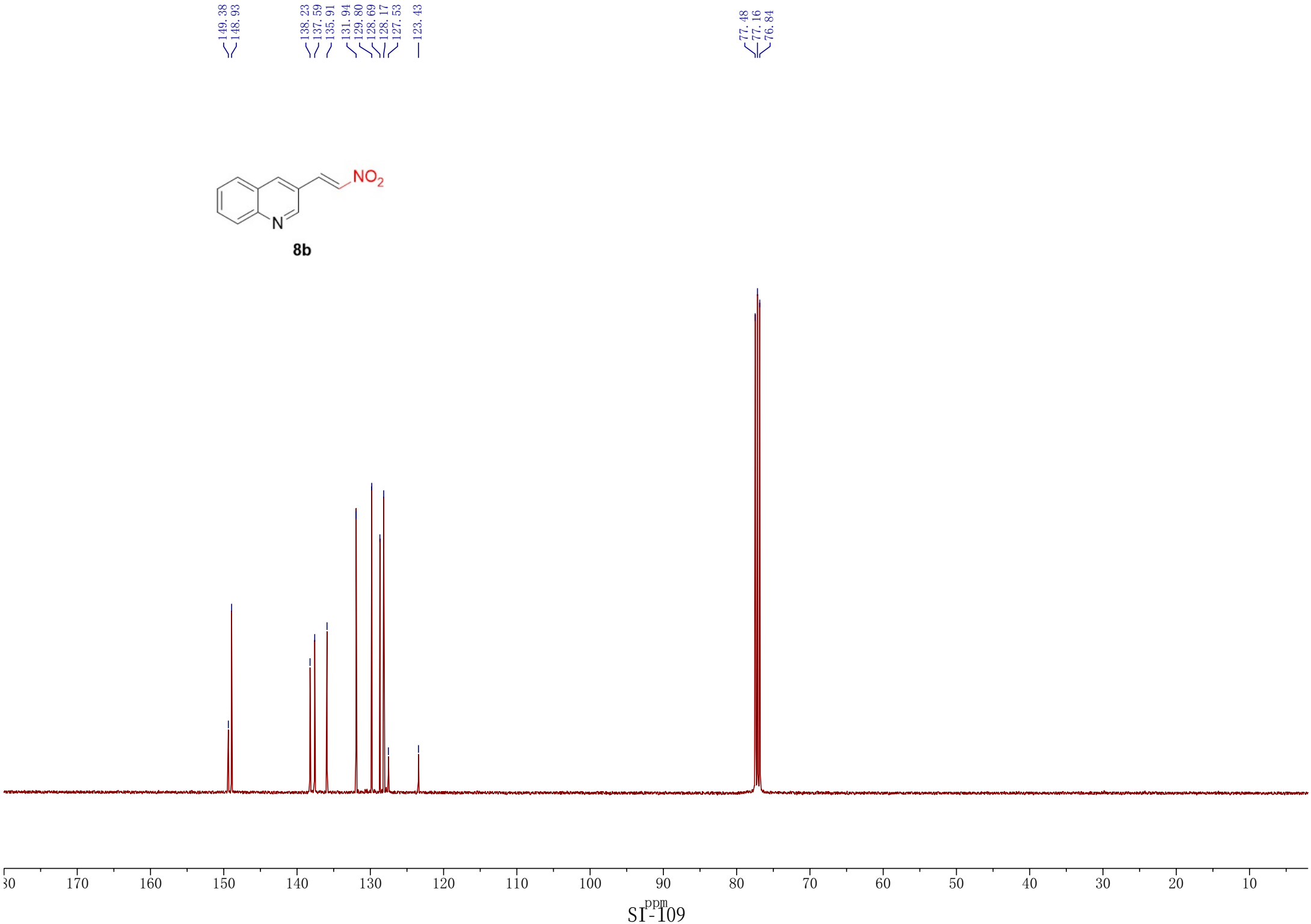
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

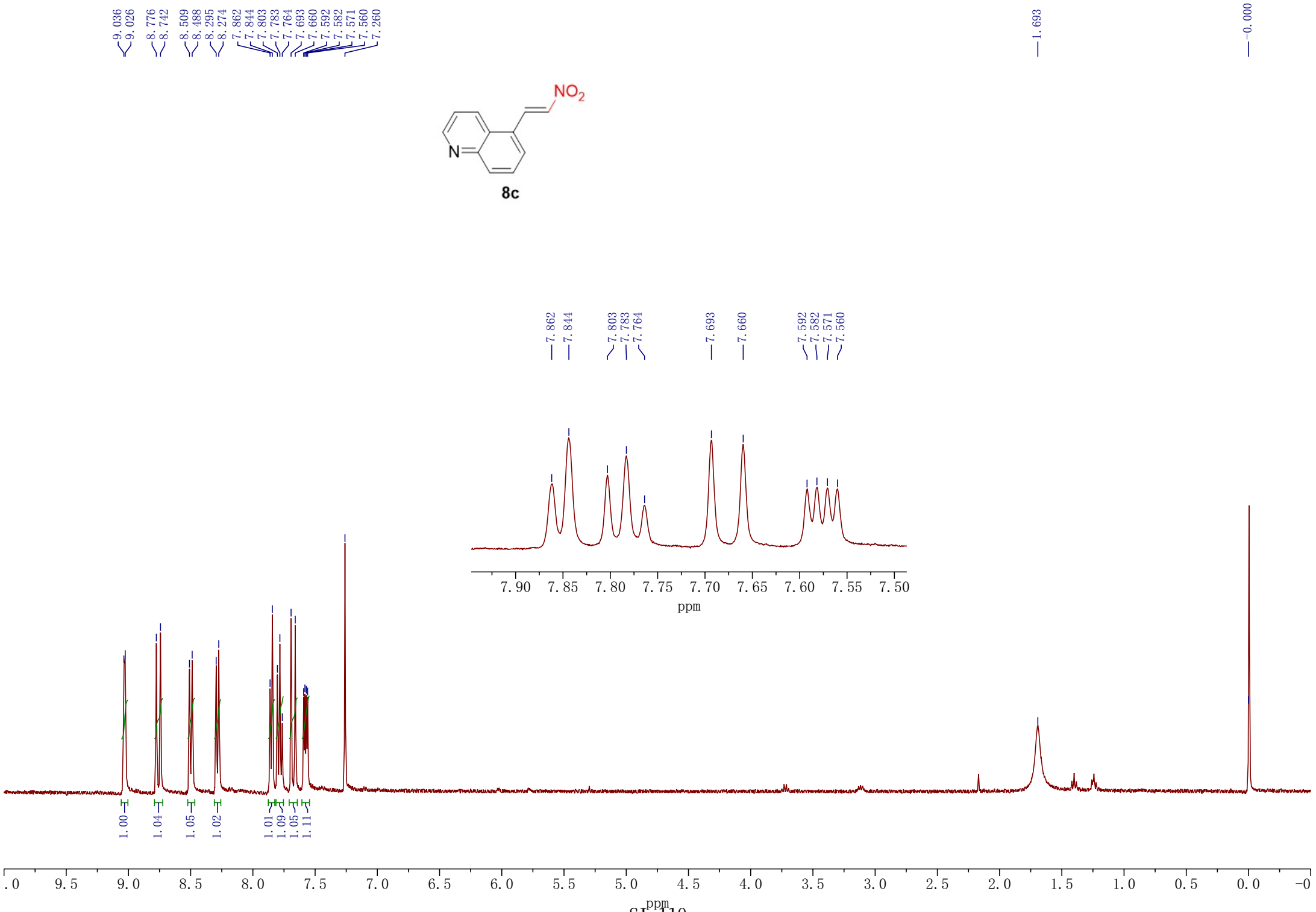
ppm

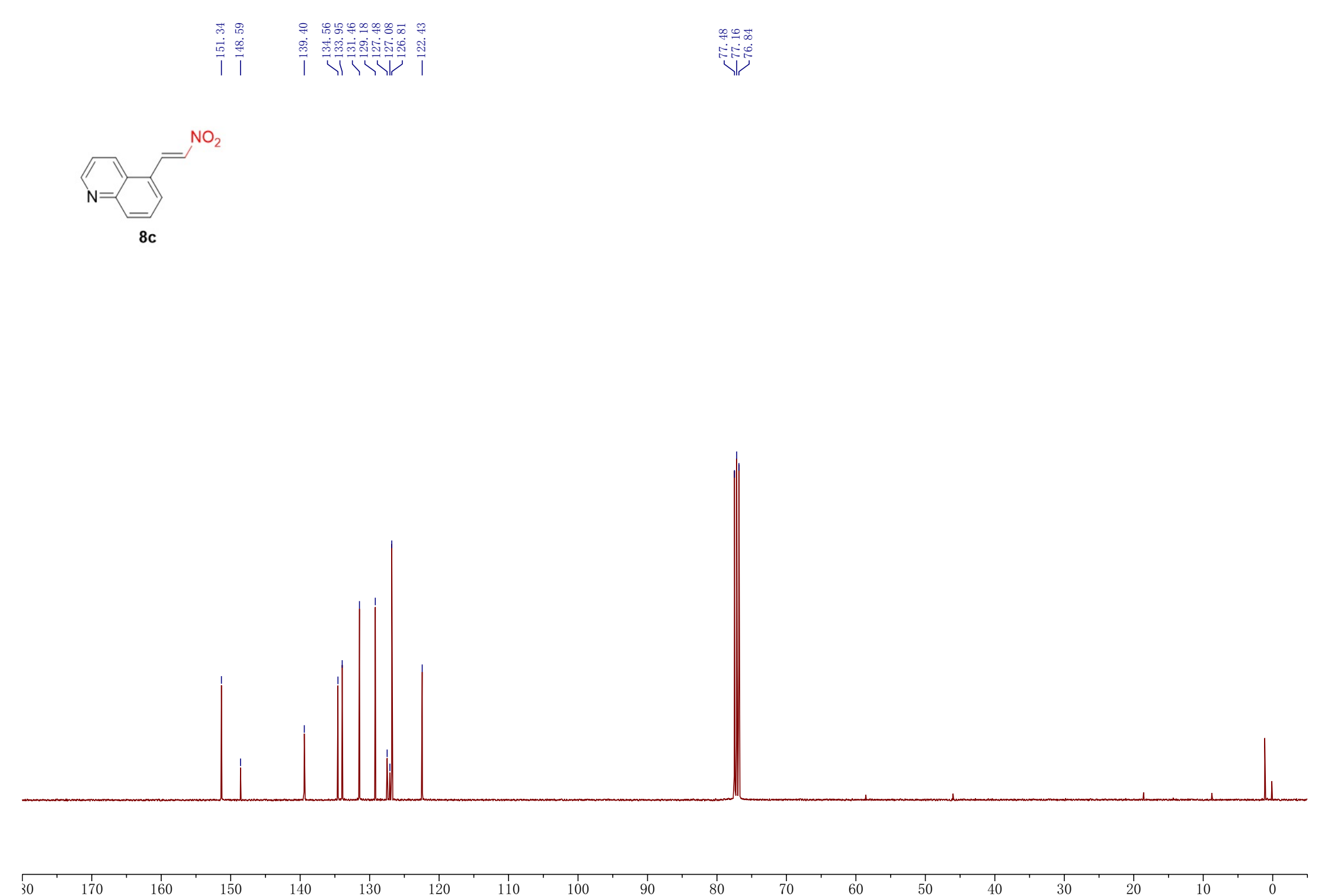

Ph
NO2
6u
7.398
7.393
7.384
7.382
7.367
7.354
7.350
7.313
7.310
7.307
7.304
7.301
7.297
7.260
7.216
7.211
7.210
7.196
7.192
7.162
7.158
7.154
7.151
7.148
7.145
7.141
7.138
2.347
1.553
0.000
7.40
7.35
7.30
7.25
7.20
7.15
7.10
ppm
2.94
2.94
1.93
1.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm


Ph
NO2
6u
146.46
140.00
138.42
138.30
129.52
128.86
128.71
128.70
128.67
128.26
77.48
77.16
76.84
18.27
128.86
128.71
128.70
128.67
128.26
128.9
128.8
128.7
128.6
128.5
128.4
128.3
ppm
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.074
9.068
8.347
8.342
8.194
8.160
8.143
7.911
7.891
7.860
7.856
7.842
7.839
7.835
7.821
7.818
7.811
7.777
7.672
7.669
7.655
7.652
7.649
7.634
7.632
7.260
1.615
0.003
NO2
N
8b
1.00
1.02
1.98
0.98
1.03
0.98
1.01
ppm


149.38
148.93
138.23
137.59
135.91
131.94
129.80
128.69
128.17
127.53
123.43
77.48
77.16
76.84
NO2
N
8b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.036
9.026
8.776
8.742
8.509
8.488
8.295
8.274
7.862
7.844
7.803
7.783
7.764
7.693
7.660
7.592
7.582
7.571
7.560
7.260
1.693
0.000
NO2
N
8c
7.862
7.844
7.803
7.783
7.764
7.693
7.660
7.592
7.582
7.571
7.560
7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50
ppm
1.00
1.04
1.05
1.02
1.01
1.09
1.05
1.11
.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 -0
ppm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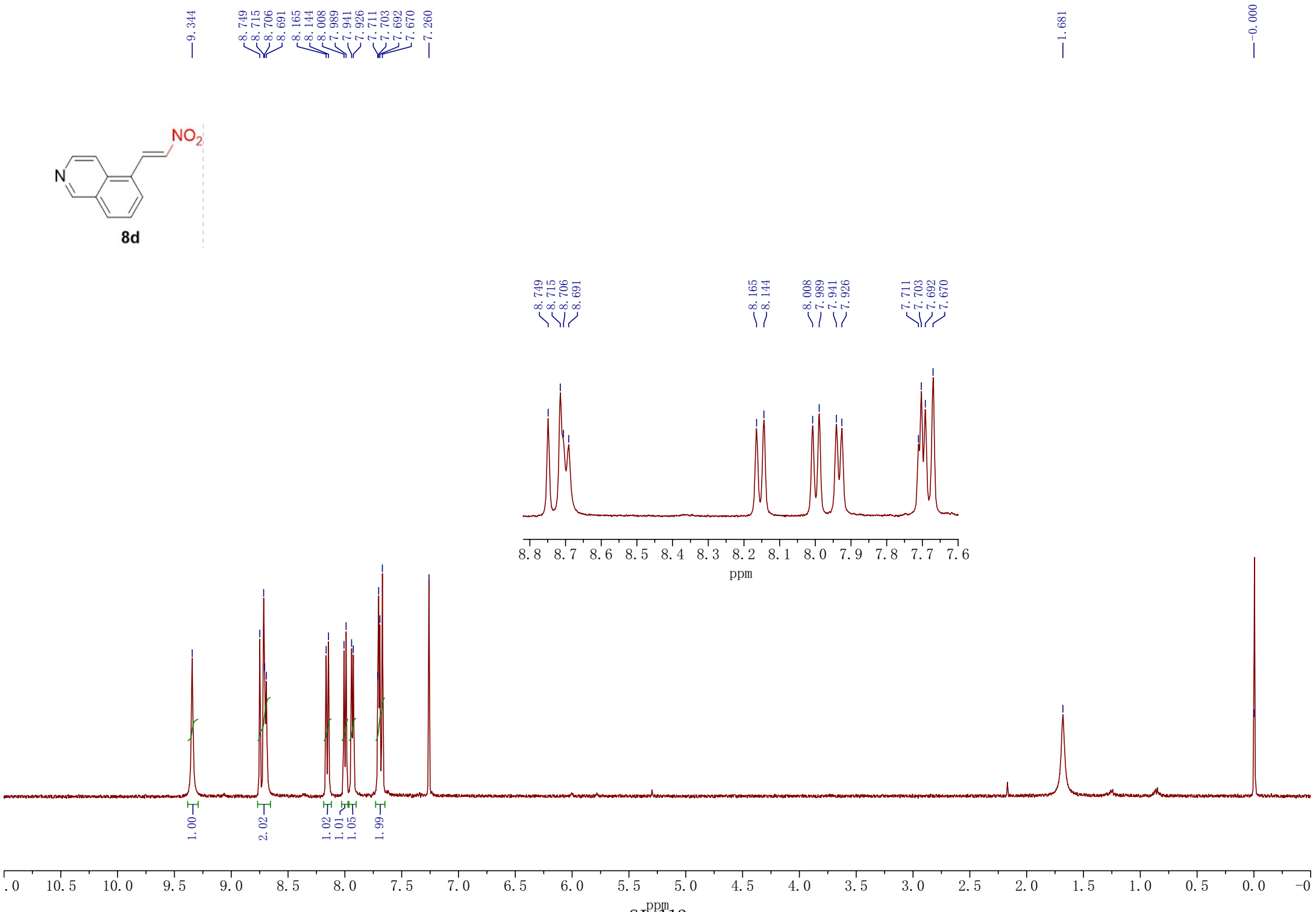
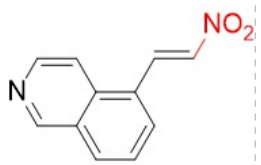
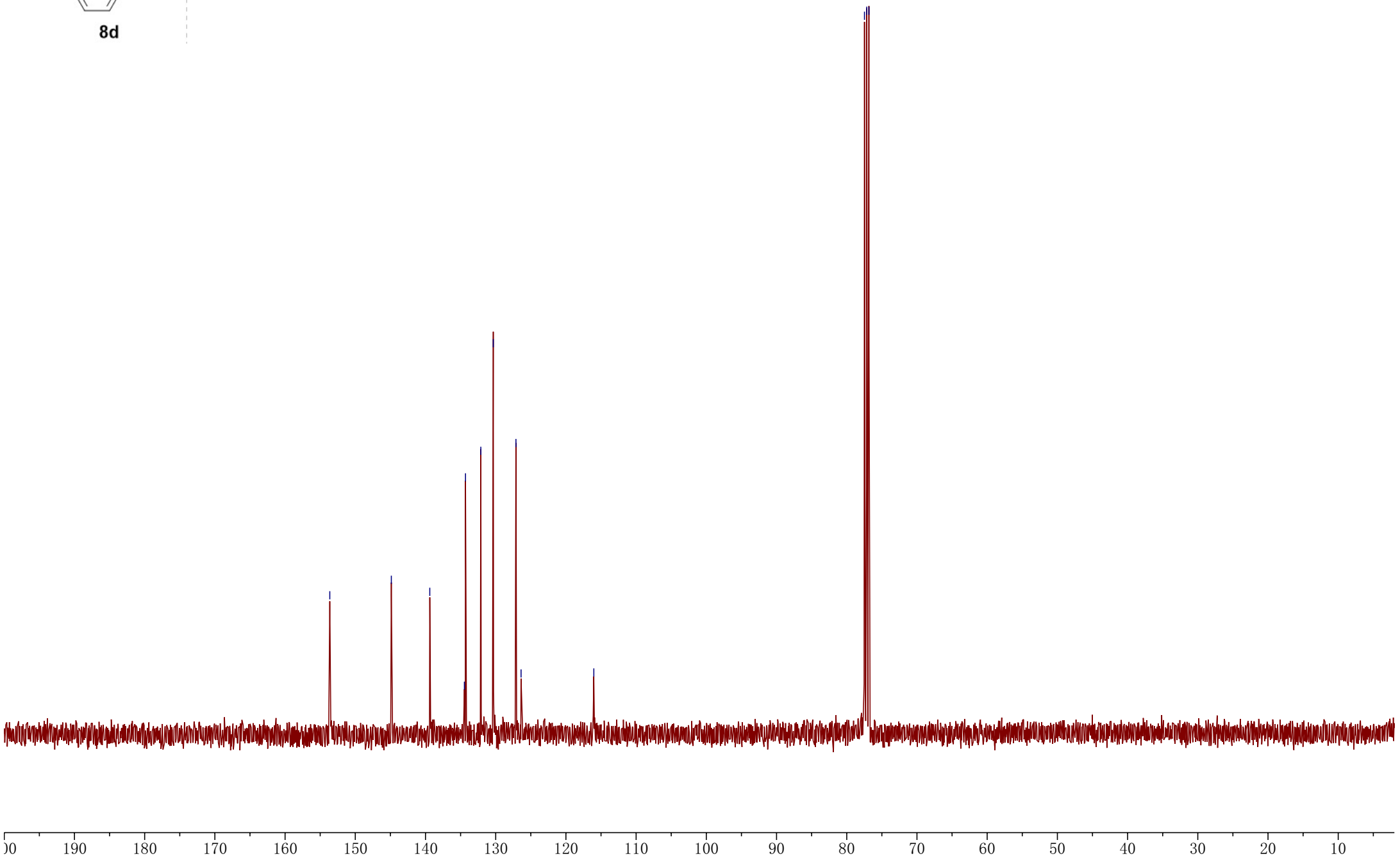
148.59
139.40
134.56
133.95
131.46
129.18
127.48
127.08
126.81
122.43
77.48
77.16
76.84
NO2
N
8c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

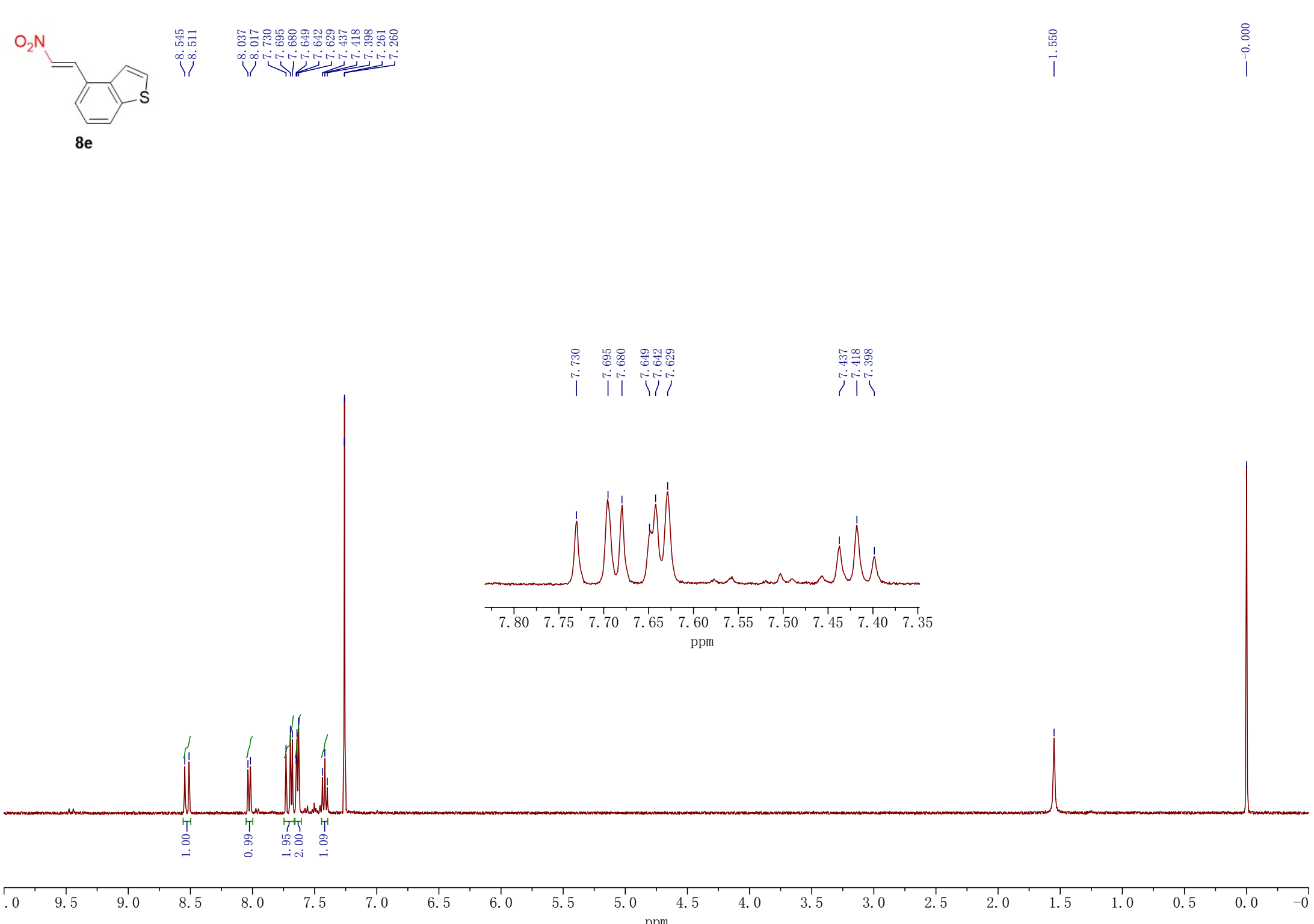

9.344
8.749
8.715
8.706
8.691
8.165
8.144
8.008
7.989
7.941
7.926
7.711
7.703
7.692
7.670
7.260
1.681
0.000
NO2
N
8d
1.00
2.02
1.02
1.01
1.05
1.99
ppm
SI-112

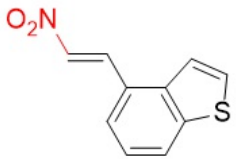


8d

153.63
144.87
139.39
134.46
134.30
132.12
130.34
127.12
126.39
116.03
77.48
77.16
76.84

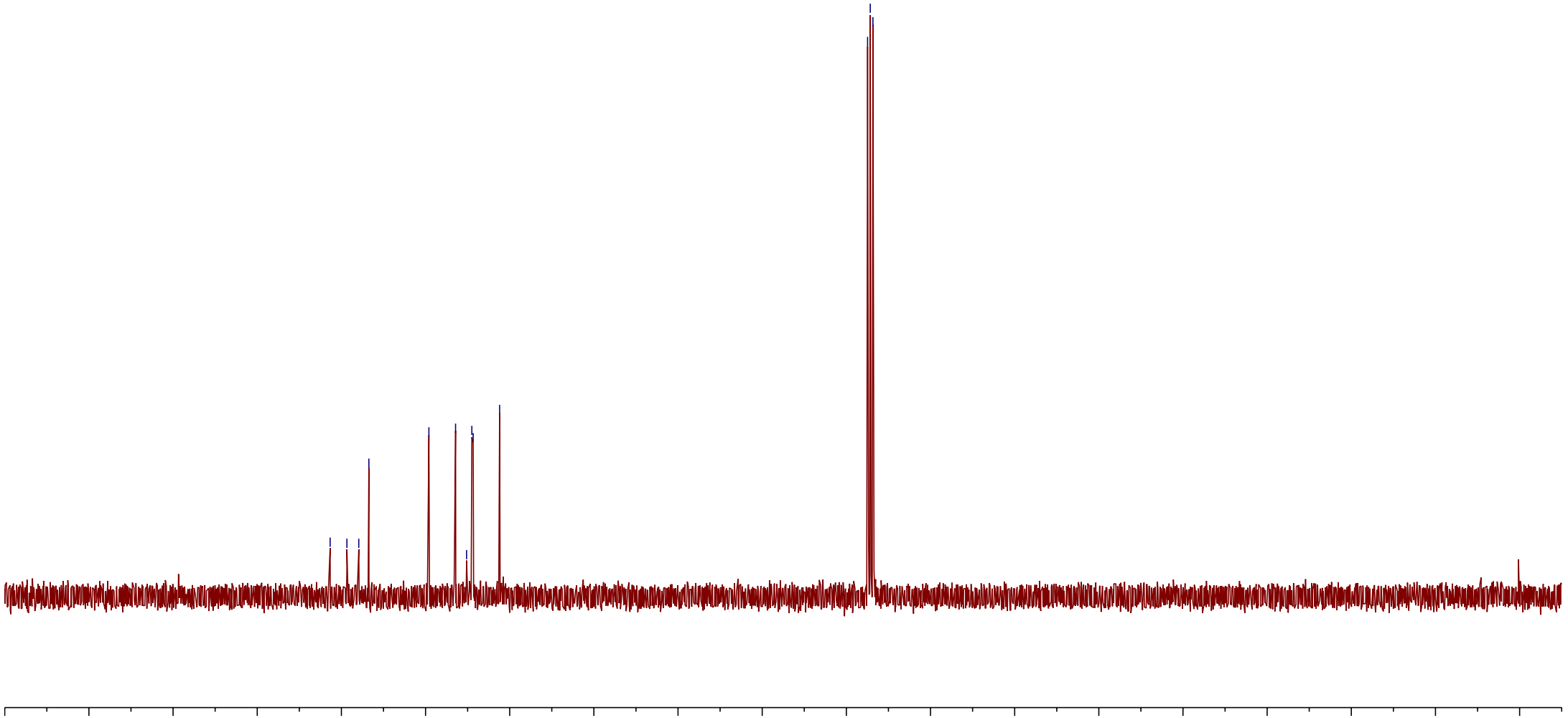


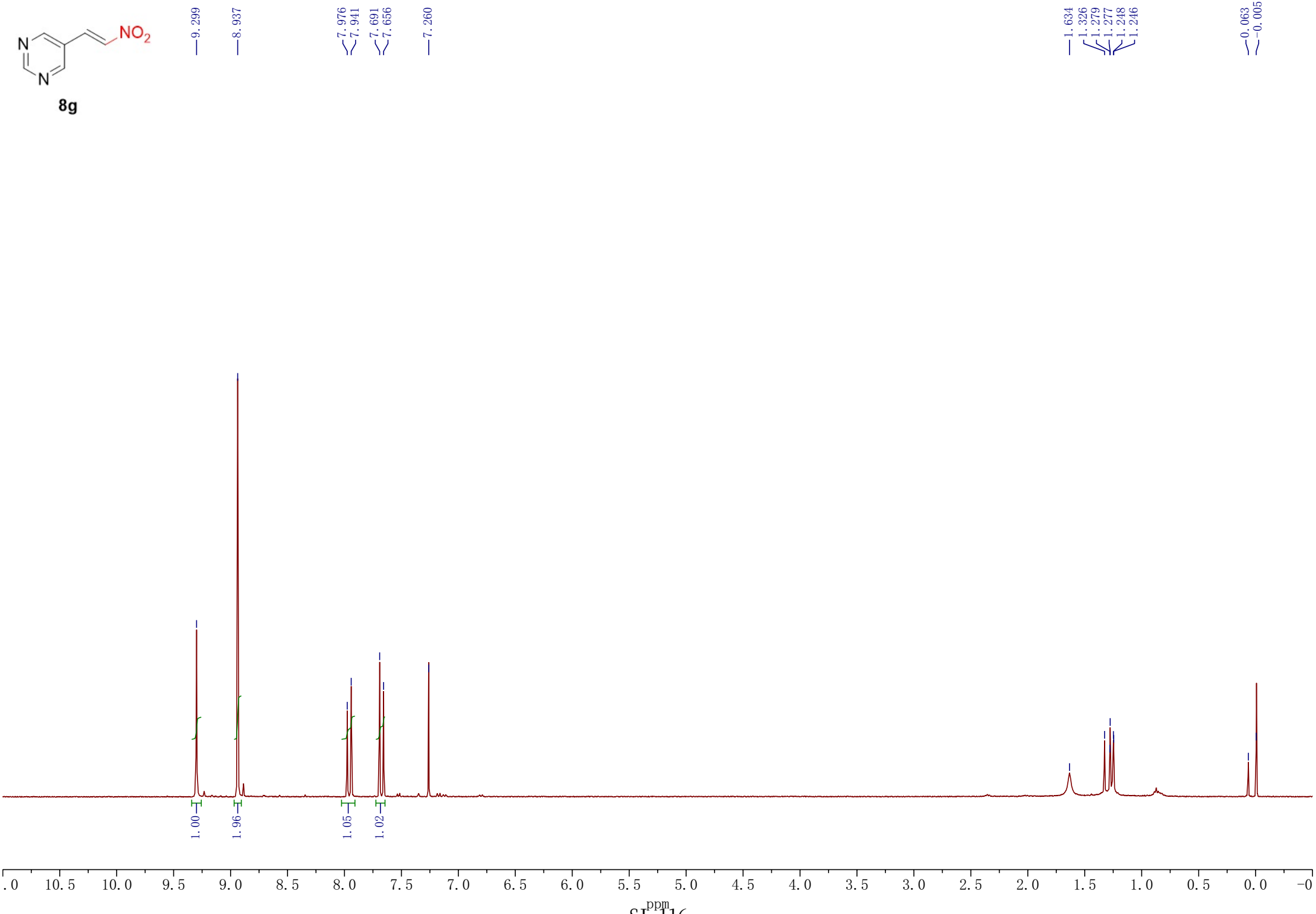

O2N
S
8e
8.545
8.511
8.037
8.017
7.730
7.695
7.680
7.649
7.642
7.629
7.437
7.418
7.398
7.261
7.260
1.550
0.000
1.00
0.99
1.95
2.00
1.09
ppm

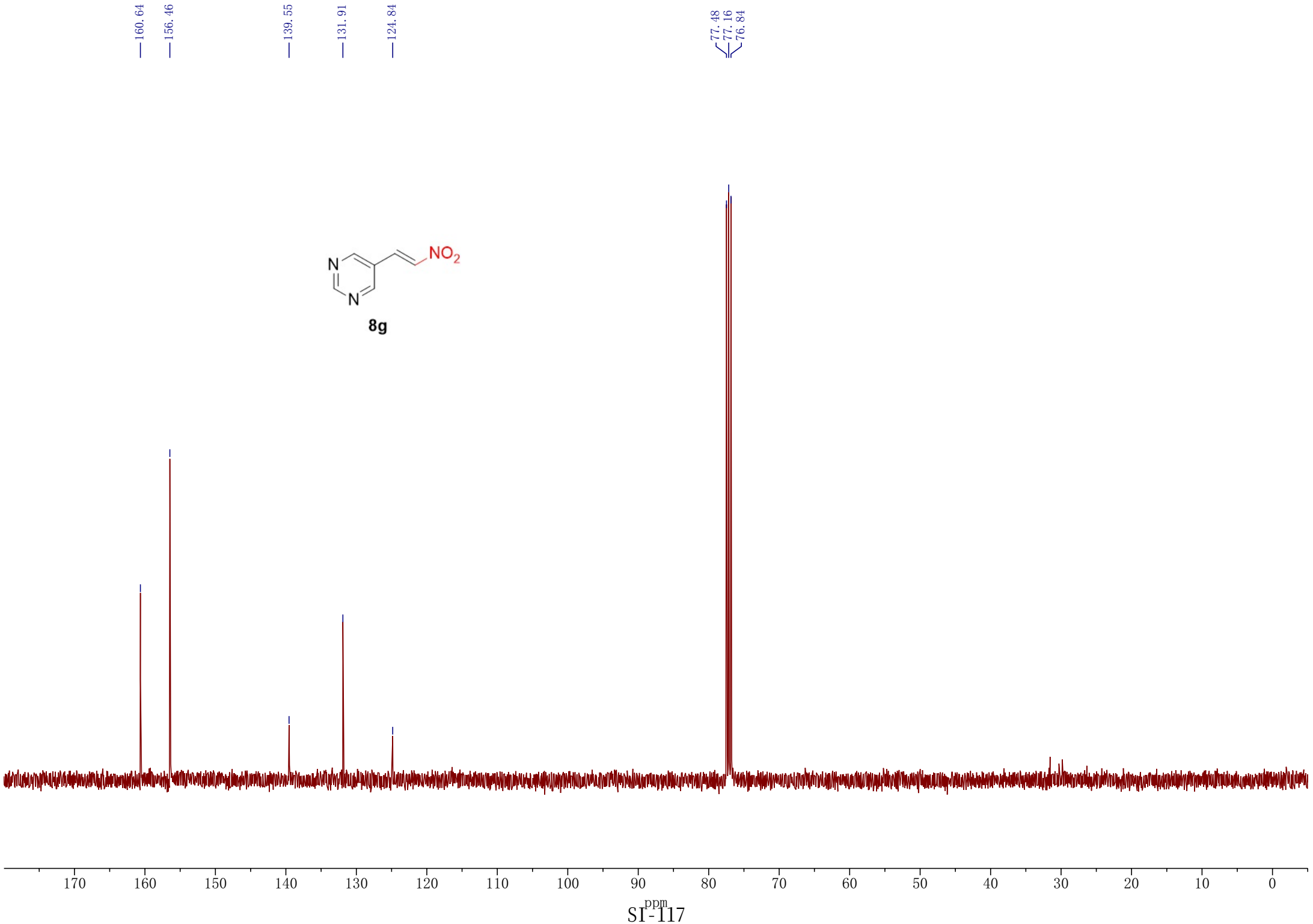


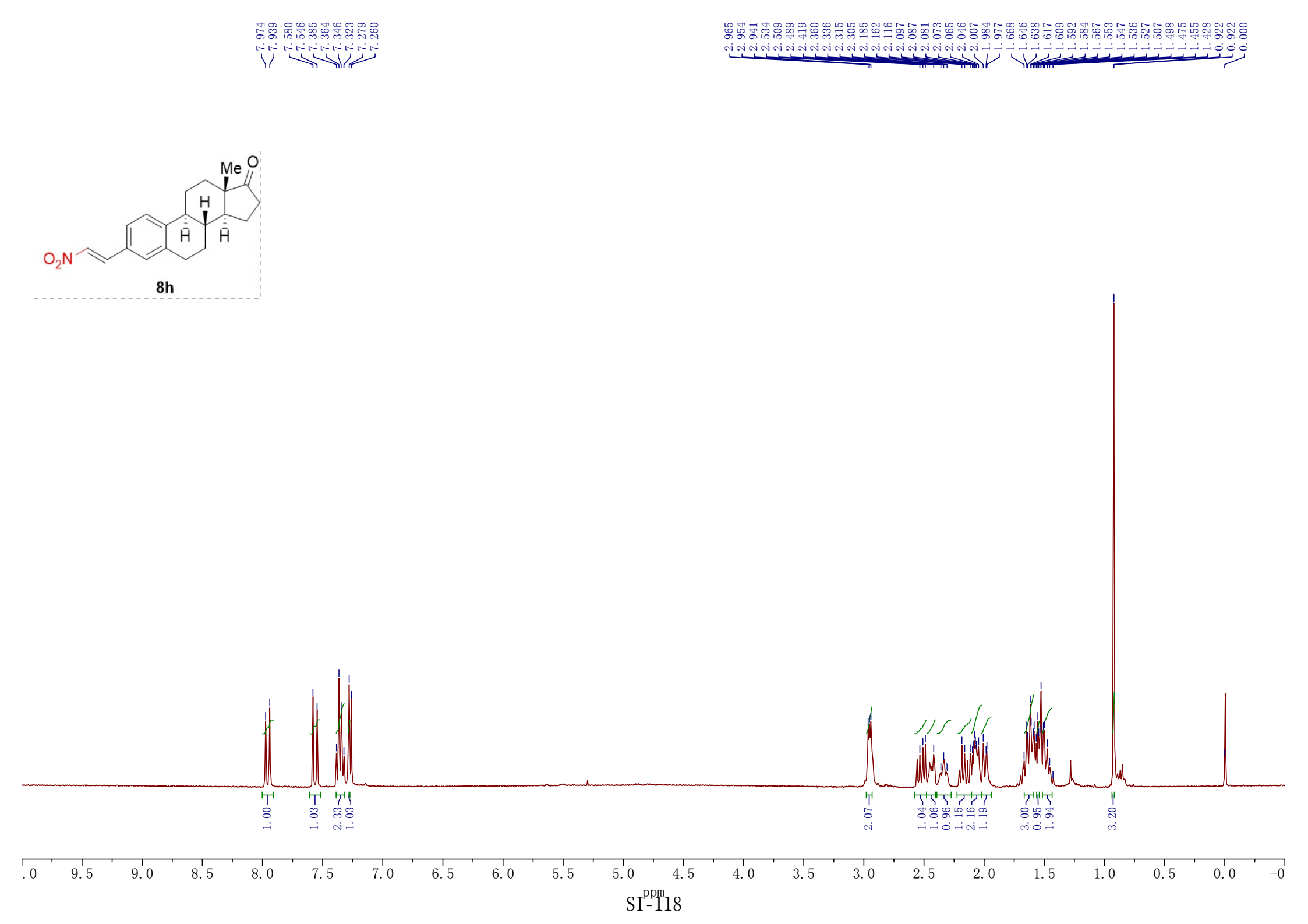
8e

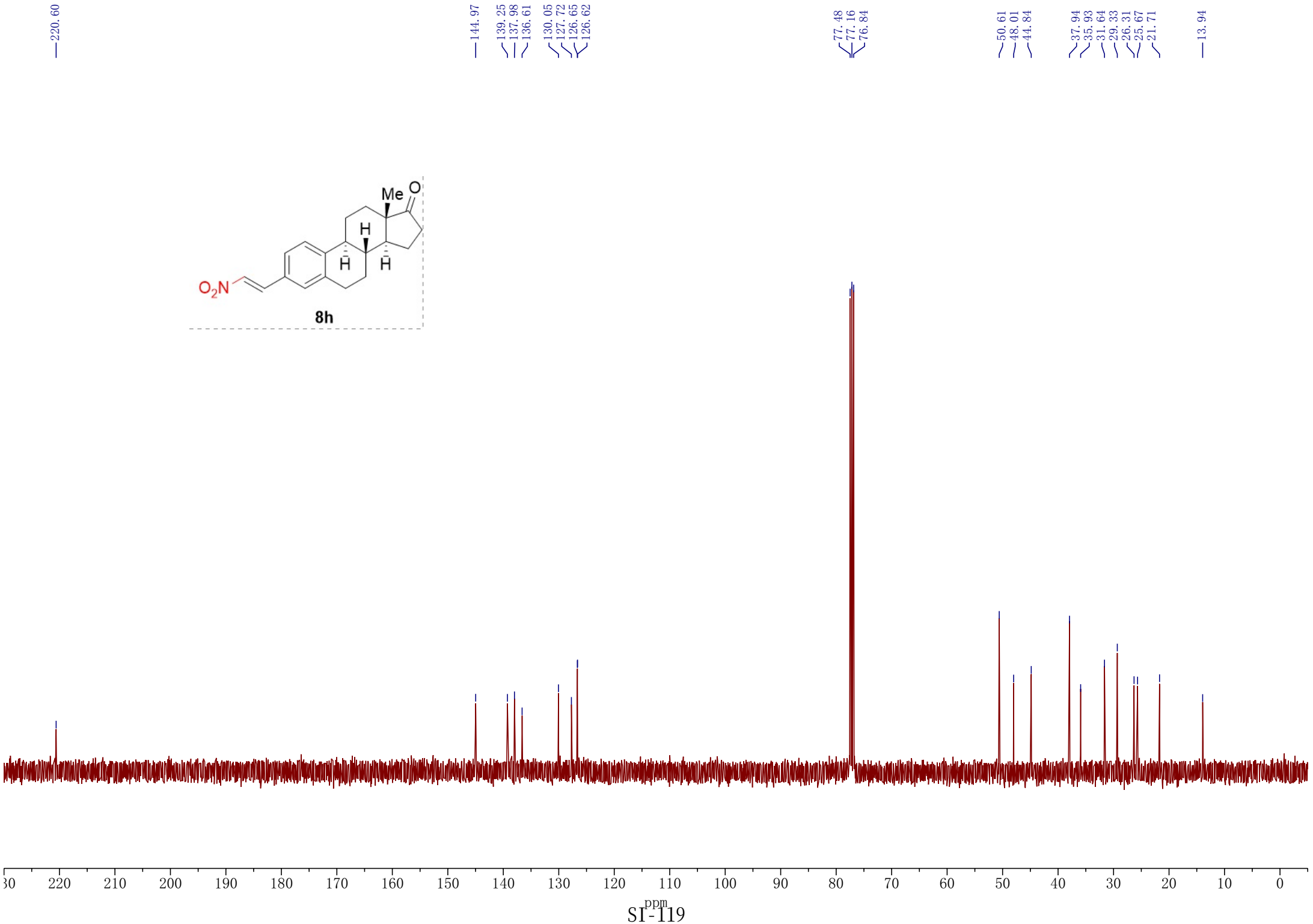
141.34
139.34
137.93
136.73
129.60
126.43
125.12
124.50
124.34
121.20
77.48
77.16
76.84

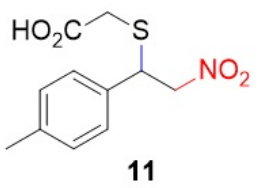



8g
9.299
8.937
7.976
7.941
7.691
7.656
7.260
1.634
1.326
1.279
1.277
1.248
1.246
0.063
-0.005
1.00
1.96
1.05
1.02
ppm


160.64
156.46
139.55
131.91
124.84
77.48
77.16
76.84
N
N
NO2
8g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

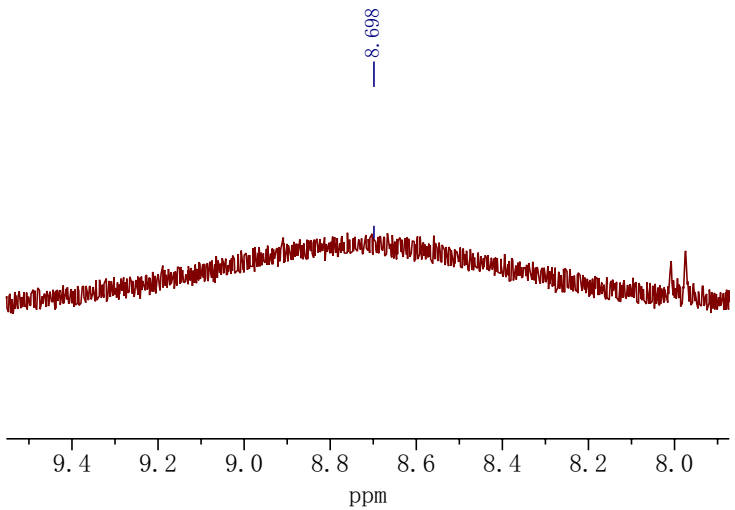

7.974
7.939
7.580
7.546
7.385
7.364
7.346
7.323
7.279
7.260
2.965
2.954
2.941
2.534
2.509
2.489
2.419
2.360
2.336
2.315
2.305
2.185
2.162
2.116
2.097
2.087
2.081
2.073
2.065
2.046
2.007
1.984
1.977
1.668
1.646
1.638
1.617
1.609
1.592
1.584
1.567
1.553
1.547
1.536
1.527
1.507
1.498
1.475
1.455
1.428
0.922
0.922
0.000
Me
O
H
H
H
O2N
8h
1.00
1.03
2.33
1.03
2.07
1.04
1.06
0.96
1.15
2.16
1.19
3.00
0.95
1.94
3.20
.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
-0
ppm

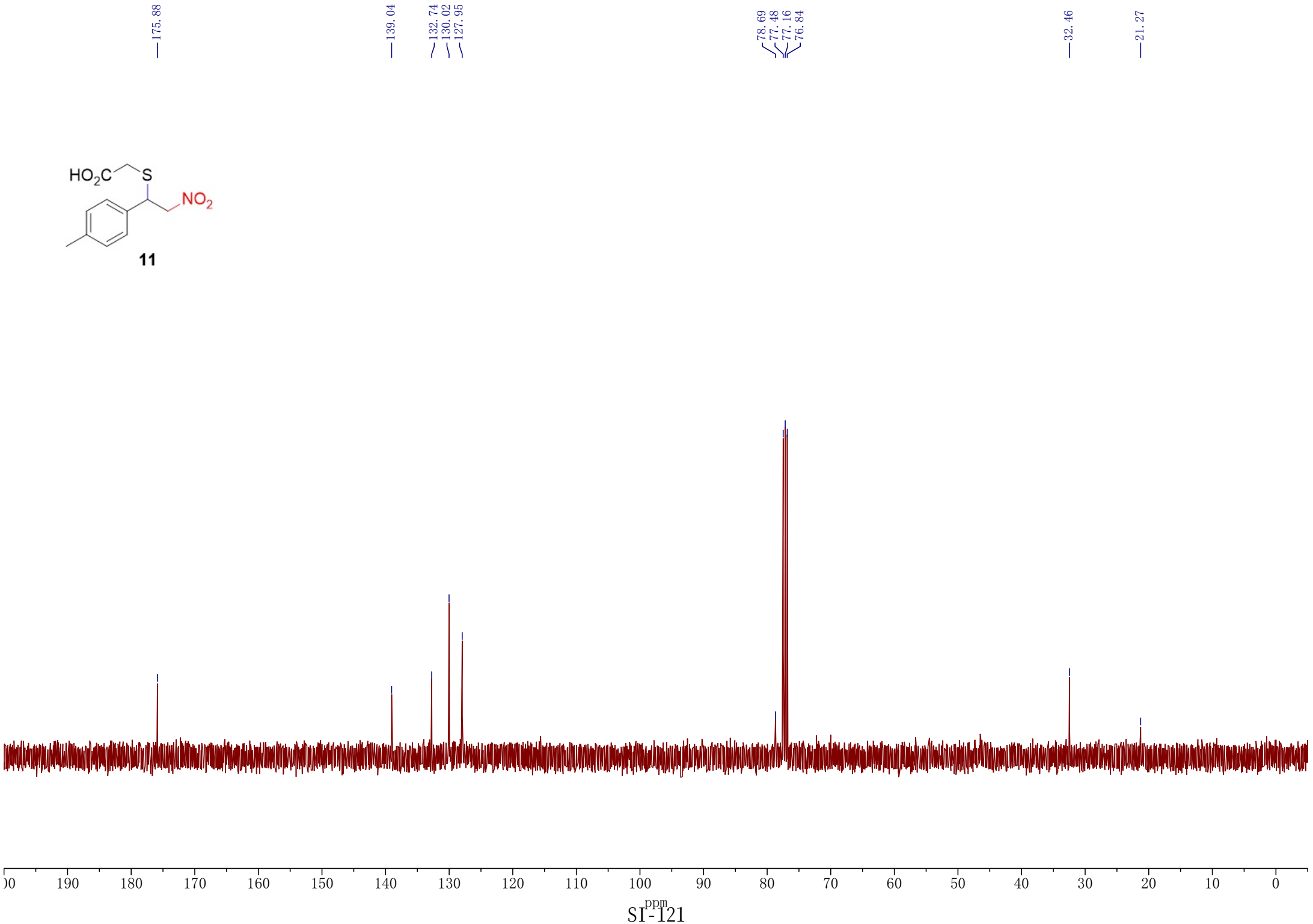

220.60
144.97
139.25
137.98
136.61
130.05
127.72
126.65
126.62
77.48
77.16
76.84
50.61
48.01
44.84
37.94
35.93
31.64
29.33
26.31
25.67
21.71
13.94
Me
O
H
H
H
O2N
8h
ppm



11

8.698
7.260
7.256
7.236
7.189
7.169
4.852
4.825
4.821
4.816
4.794
3.199
3.160
3.097
3.058
2.341
0.000

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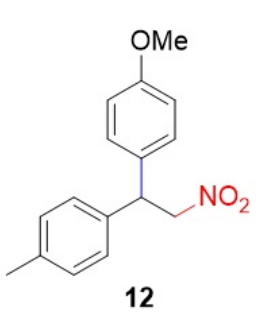
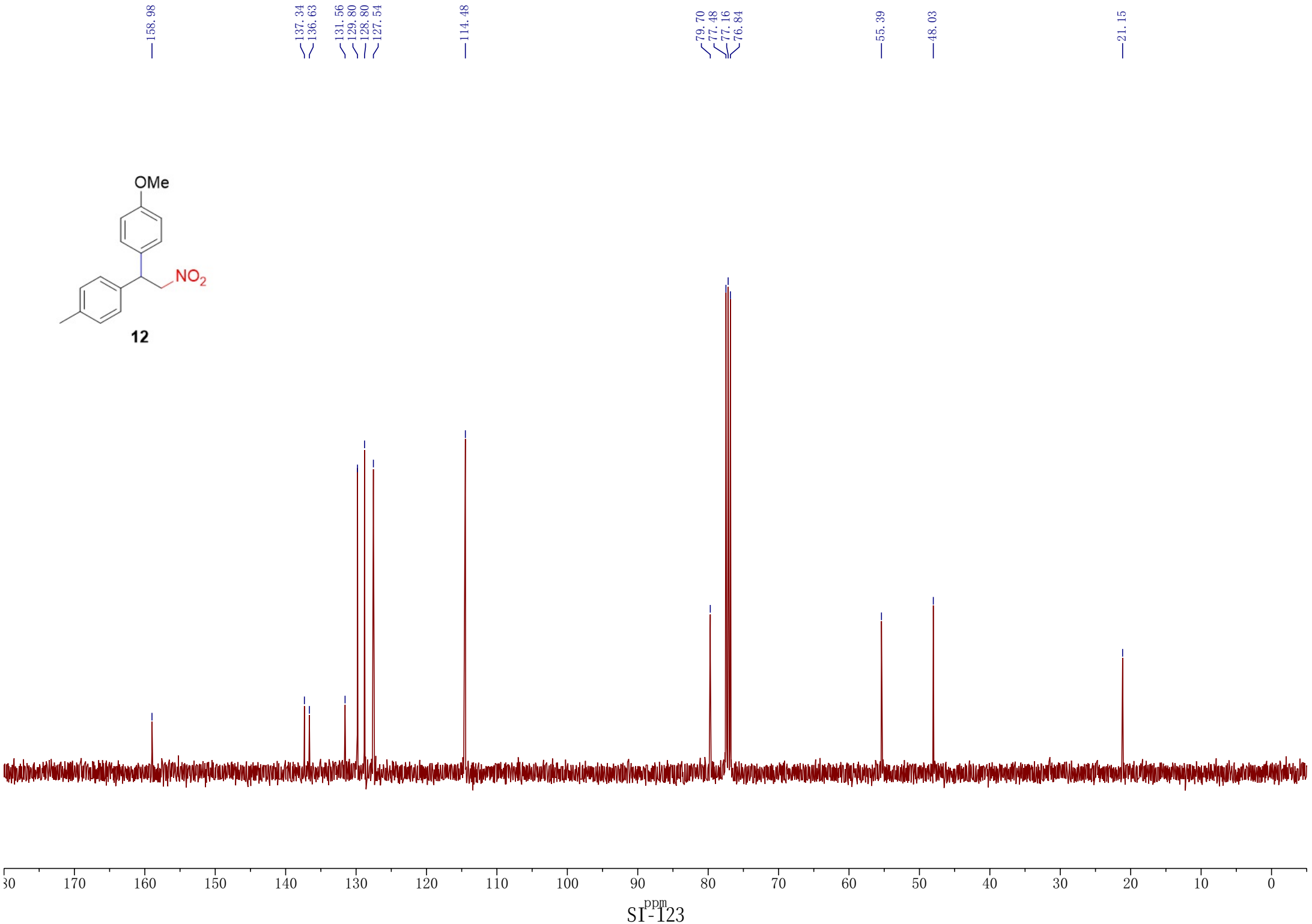
139.04
132.74
130.02
127.95
78.69
77.48
77.16
76.84
32.46
21.27
HO2C
S
NO2
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
NO2

12

7.260
7.159
7.138
7.122
7.100
6.861
6.840
4.942
4.938
4.920
4.841
4.821
3.775
2.313
0.000
7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
ppm
6.01
2.09
2.05
1.00
2.99
3.12
ppm


158.98
137.34
136.63
131.56
129.80
128.80
127.54
114.48
79.70
77.48
77.16
76.84
55.39
48.03
21.15
OMe
NO2
12
ppm