Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Iridium-catalysed highly chemoselective and efficient reduction of nitroalkenes to nitroalkanes in water

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1. General Information

All the chemicals were used directly as commercially received. Column chromatography was performed on silica gel (200–300 mesh) from Anhui Liangchen silicon source material Co., Ltd, and petroleum ether (PE, b.p. 60–90 °C) and ethyl acetate (EA, commercially received) were used as eluents. Reactions were monitored by thin-layer chromatography on silica gel from Anhui Liangchen silicon source material Co., Ltd. The plates were visualized under UV light. Melting points were obtained on a melting point apparatus and were uncorrected. The specific rotation analysis was measured by Anton Paar MCP200 Pa polarimeter. Chiral HPLC data were measured using the Agilent Technologies (1260 Infinity). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) were reported in part(s) per million (ppm). The high-resolution mass analyses were performed under ESI ionization using an Agilent LC/MSD TOF mass spectrometer. The GC-MS analyses were performed on a Thermo scientific tandem equipment.

The catalysts were synthesized according to Li's and co-workers' publications[1] and our previous publications[2]. The catalyst solution was prepared according to our previous publication.[2a]

All the nitroalkenes are known products. Their synthetic methods are identical with the listed references.

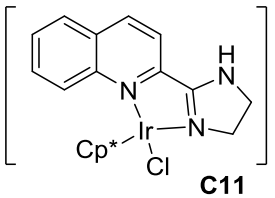
2. Preparation of new Catalyst and Nitroalkenes

2.1. The synthesis of Catalyst **11** and (*S,S*)-**C19** and (*R,R*)-**C20**

To the solution of quinoline-2-carbaldehyde (2.1 mmol) in dichloromethane (20 mL) was dropwise added ethylenediamine (0.16 mL, 2.3 mmol). The mixture was stirred for 1 h, and then was cooled to 0 °C. *N*-Bromosuccinimide (410 mg, 2.3 mmol) was added portion-wise (three times, interval 10 min)) and the mixture was stirred overnight. The reaction mixture washed with 5% KOH solution (20 mL) and then saturated $Na_2S_2O_3$ solution (20 mL). Drying with Na_2SO_4 and removal of the dichloromethane under vacuum directly gave desired 2-(4,5-dihydro-1H-imidazol-2-yl)quinoline crude products in quantitative yield. The product was directly used in next step without further purification.

To a solution of ligand (207 mg, 1.05 mmol) in 20 mL of DCM was added the powder of $[Cp^*IrCl_2]_2$ (0.5 mmol, 399 mg). The resultant red solution was stirred overnight. DCM was removed under

reduced pressure, and the resultant red solid was dissolved in minimum amount of DCM. Then a large amount of EtOAc slowly was added to precipitate an bright yellow powder as desired product, which was isolated by reduced-pressure filtration and further dried under vacuum at room temperature.



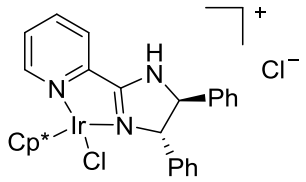
C11

Yellow powder. M.p. > 300 °C. Yield：585 mg, 96%. ^{1}H NMR (400 MHz, D_2O) δ 8.49 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 4.44 – 4.26 (t, *J* = 11.2 Hz, 1H), 4.10 – 4.02 (t, *J* = 10.2 Hz, 2H), 3.92 (t, *J* = 11.2 Hz, 1H), 1.51 (s, 15H). ^{13}C NMR (101 MHz, D_2O) δ 169.89, 146.89, 145.41, 141.72, 133.02, 130.34, 130.30, 129.47, 129.18, 119.58, 89.17, 52.29, 45.68, 8.54. HRMS (ESI): *m/z* calcd for $[M]^+$ $C_{22}H_{26}ClIrN_3^+$: 560.1439; found: 560.1446.

To the solution of 2-pyridinecarboxaldehyde (5 mmol, 535 mg) in dichloromethane (40 mL) was dropwise added (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (1.072 g, 5.05 mmol). The mixture was stirred for 0.5 h, and then was cooled to 0 °C. *N*-Bromosuccinimide (900 mg, 5.05 mmol) was added portion-wise (three times, interval 10 min)) and the mixture was stirred overnight. The reaction mixture was washed with 5% NaOH solution (20 mL) and then saturated $Na_2S_2O_3$ solution (20 mL). Drying with Na_2SO_4 and subsequent removal of the dichloromethane under vacuum gave desired crude 2-((4*R*,5*R*)-4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)pyridine (1.42 g, 95%). The crude products was recrystallized from PE/EA to give pure products as white solid (1.12g, 75%).

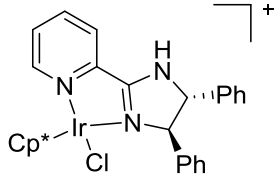
The 2-((4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)pyridine was synthesized according to the same procedure described above. The yield of crude product is 1.44 g (96%), and the yield of recrystallized pure product is 1.21 g (81%).

To a solution of the $[Cp^*IrCl_2]_2$ (0.2 mmol, 797 mg) in 10 mL of DCM was added the solution of chiral ligand (0.42 mmol, 135 mg) in 5 mL of DCM. The resultant red solution was stirred overnight. DCM was then removed under reduced pressure, and the resultant orange solid was dissolved in minimum amount of DCM. Then a large amount of EtOAc was slowly added to precipitate an orange solid, which was isolated by reduced-pressure filtration and further dried under vacuum at room temperature.



(*S,S*)-**C19**

(*S,S*)-C19: Yellow solid, 220 mg, 79%. mp>300 °C, $[\alpha]_D^{20}$ = + 215 (*c* = 0.32, CH_3Cl). **Because of the chirality of the Ir center, two inseparable isomers were obtained (*dr* = 2:1)**. **Isomer 1**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.49 (s, 1H), 9.72 (d, *J* = 7.6 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.10 (t, *J* = 7.6 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.54 – 7.15 (m, 10H), 5.29 (d, *J* = 11.4 Hz, 1H), 5.10 (d, *J* = 11.4 Hz, 1H), 1.45 (s, 15H). **Isomer 2**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.45 (s, 0.5H), 9.64 (d, *J* = 7.6 Hz, 0.5H), 8.84 (d, *J* = 5.6 Hz, 0.5H), 8.10 (t, *J* = 7.6 Hz, 0.5H), 7.72 (m, 0.5H), 7.50 – 7.19 (m, 5H), 5.09 (d, *J* = 7.6 Hz, 0.5H), 4.92 (d, *J* = 7.6 Hz, 0.5H), 1.42 (s, 7.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.56, 168.96, 150.85, 147.13, 141.86, 140.91, 140.36, 140.36, 140.11, 140.11, 139.29, 138.57, 129.62, 129.21, 129.03, 128.82, 128.60, 128.45, 128.26, 127.70, 126.94, 126.64, 88.11, 87.61, 79.29, 79.02, 72.28, 72.14, 9.05. HRMS (ESI): m/z calcd for $C_{30}H_{32}ClIrN_3^+$ [M-Cl$^-$]$^+$: 662.1909, found: 662.1907.

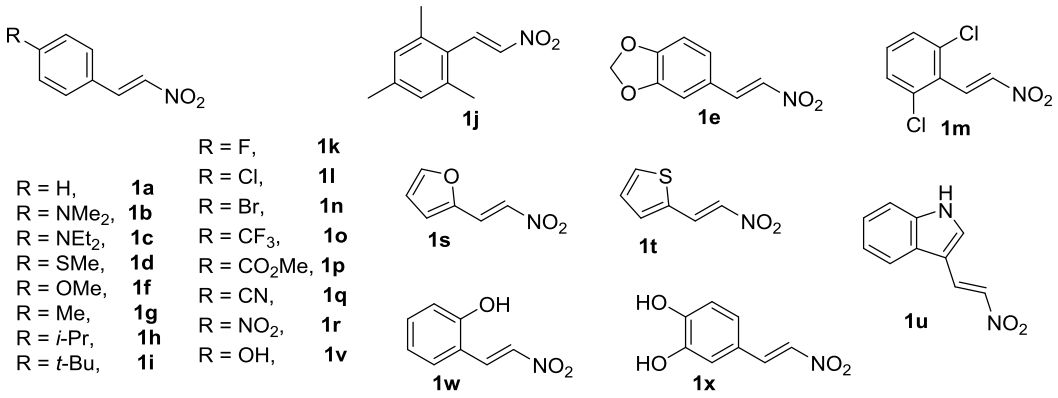


(*R,R*)-**C20**

(*R,R*)-C20: Yellow solid, 200 mg, 72%. mp>300 °C, $[\alpha]_D^{20}$ = -165 (*c* = 0.32, CH_3Cl). **Because of the chirality of the Ir center, two inseparable isomers were obtained (*dr* = 2:1)**. **Isomer 1**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.48 (s, 1H), 9.72 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 5.2 Hz, 1H), 8.11 (t, *J* = 7.2 Hz, 1H), 7.72 (t, *J* = 6.8 Hz, 1H), 7.51 – 7.18 (m, 10H), 5.30 (d, *J* = 11.2 Hz, 1H), 5.11 (d, *J* = 11.2 Hz, 1H), 1.45 (s, 15H). **Isomer 2**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.43 (s, 0.5H), 9.64 (d, *J* = 7.6 Hz, 0.5H), 8.82 (d, *J* = 5.2 Hz, 0.5H), 8.10 (q, *J* = 7.2 Hz, .0.5H), 7.72 (t, *J* = 6.8 Hz, 0.5H), 7.54 – 7.17 (m, 5H), 5.09 (m, 0.5H), 4.92 (d, *J* = 7.6 Hz, 0.5H), 1.42 (s, 7.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47, 168.87, 150.87, 150.79, 147.97, 147.01, 141.76, 140.84, 140.26, 140.01, 139.21, 138.48, 129.57, 129.17, 128.95, 128.74, 128.51, 128.37, 128.18, 126.86, 126.56, 88.05, 87.55, 79.21, 78.94, 72.20, 72.05, 9.14, 8.98.HRMS (ESI): m/z calcd for $C_{30}H_{32}ClIrN_3^+$ [M-Cl$^-$]$^+$: 662.1909, found: 662.1913.

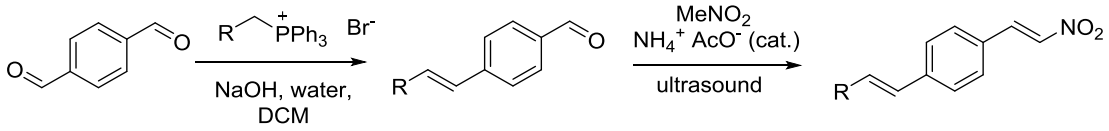
2.2. Synthesis of β-disubstituted nitroalkenes **1a-1z**.

Table S1. Synthesis of nitroalkanes **1a-1x** directly according to previously published methods



Compound	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k	1l	1m
Reference	3a	3c	3c	3a	3b	3a	3a	3b	3a	3a	3a	3a	3d
Compound	1n	1o	1p	1q	1r	1s	1t	1u	1v	1w	1x	1y	1z
Reference	3a	3a	3a	3a	3a	3d	3c	3f	3f	3e	3g	3h,i	3h,i

Nitroalkenes **1y** and **1z** were prepared by a modified version of reported procedure.[3h,i]

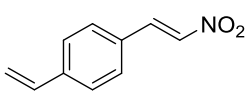


Scheme S1. Preparation of nitroalkenes **1y** and **1z.**

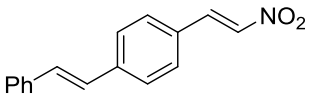
A 50%(*w*/*w*) aqueous solution of NaOH (2 mL) at 0 °C was added dropwise to the mixture of terephthalaldehyde (402 mg, 3 mmol) and methyltriphenylphosphonium bromide (1.07 g, 3 mmol) or benzyltriphenylphosphonium bromide (1.3 g, 3 mmol) in 40 mL of DCM. After 30 min, the reaction mixture was warmed to room temperature and stirred for 4 h. Then, the reaction mixture was washed by water and extracted with DCM. **T**he organic solvent was dried by Na_2SO_4 and evaporated under reduced pressure to give crude aldehyde products. The crude products were purified by column chromatography (PE/EA, 15:1 to 20:1, *v/v*) to give 4-vinylbenzaldehyde (231 mg, 58%) or 4-styrylbenzaldehyde (205 mg, 33%).

A mixture of 4-vinylbenzaldehyde (198 mg, 1.5 mmol) or 4-styrylbenzaldehyde (193 mg, 0.93 mmol) and nitromethane (4.5 mL) was introduced into a 25 mL round-bottom flask; a catalytic amount of ammonium acetate (24 mg, 0.3 mmol) was added and the flask was placed inside an ultrasound apparatus preheated at 60 °C. After 4 h, the mixture was cooled to room temperature and the nitromethane was evaporated under reduced pressure to give crude products. The crude

product was purified by column chromatography (PE/EA, 30:1, *v/v*) to give desired nitroalkenes **1y** and **1z**.



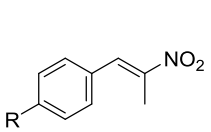
(E)-1-(2-nitrovinyl)-4-vinylbenzene (**1y**): CAS No.1268834-87-2 Isolate yield: 73 mg, 28 %; yellow solid, m.p.: 75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.58 (d, *J* = 13.6 Hz, 1H), 7.53 – 7.43 (m, 4H), 6.73 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.33, 138.59, 136.70, 135.68, 129.45, 129.30, 127.06, 116.64. HRMS (ESI): m/z calcd for $C_{10}H_{10}NO_2^+$ $[M+H]^+$: 176.0706 found: 176.0714.



1-((E)-2-nitrovinyl)-4-((E)-styryl)benzene (1z): CAS No. 179822-15-2, yield: 70 mg, 30%. yellow solid, m.p.: 137 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ8.01 (d, *J* = 14.0 Hz, 1H), δ7.63 (d, *J* = 14.0 Hz, 1H),7.64 – 7.51 (m, 6H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.11 (d, *J* = 16.4 Hz, 1H). HRMS (ESI): m/z calcd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$: 252.1019 found: 252.1023.

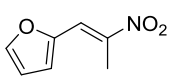
2.3. The Synthesis of α, β-disubstituted nitroalkenes **3a-3q**.

Table S2. Synthesis of nitroalkenes **3a-3q** directly according to published methods

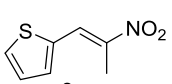


R = H, **3a**
R = NMe, **3b**
R = SMe, **3c**
R = OMe, **3d**
R = Me, **3e**
R = *i*-Pr, **3f**
R = F, **3g**

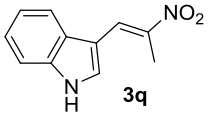
R = Cl, **3h**
R = Br, **3i**
R = CF_3, **3j**
R = CO_2Me, **3k**
R = CN, **3l**
R = SO_2Me, **3m**
R = NO_2, **3n**



3o



3p

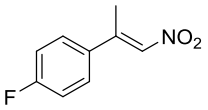


3q

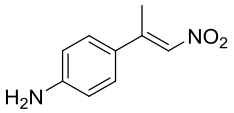
Compound	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**
Reference	4a	4a	4a	4a	4b	4a	4c	4a	4a
Compound	**3j**	**3k**	**3l**	**3m**	**3n**	**3o**	**3p**	**3q**	
Reference	4a	4a	4a	4a	4a	3f	3f	3f	

2.4 The Synthesis of β,β-disubstituted nitroalkenes.

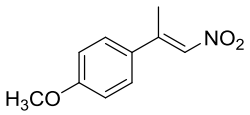
Table S3. Synthesis of nitroalkenes **7a-7d** directly synthesized according to published methods



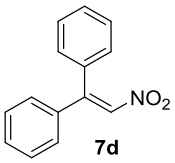
7a



7b



7c



7d

Compound	**7a**	**7b**	**7c**	**7d**
Reference	5a	5a	5a	5a

3. Optimization of reaction conditions

3.1. Optimization of catalysts in entries 1-18, Table 1.

A 10-mL reaction tube was charged with (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1 mL of catalyst solution (0.00005 mol/L for *S/C* = 5000, ***C1***-***C18***) in deionized water. The mixture was stirred for 2 minutes at 80 °C, and then formic acid (76 μL, 2.0 mmol, 8 equiv) was added. After stirring for 1 h, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 15 of the Electronic Supplementary Information.

3.2. Optimization of catalyst type in entries 19-21, Table 1.

A 10-mL reaction tube was charged with (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1 mL of catalyst solution (0.000025 mol/L, ***C3***-***C5***) in deionized water. The mixture was stirred for 2 minutes at 80 °C, and then formic acid (76 μL, 2.0 mmol, 8 equiv) was added. After stirring for 1 h, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 15 of the Electronic Supplementary Information.

3.3. Optimization of catalyst amount in entries 19, 22, 23, Table 1.

A 10-mL reaction tube was charged with (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (0.000025 mol/L for *S/C* = 10000; 0.0000125 mol/L for *S/C* = 20000; 0.00000625

mol/L for *S/C* = 40000) in deionized water. The mixture was stirred for 2 minutes at 80 °C, and then formic acid (76 μL, 2.0 mmol, 8 equiv) was added. After stirring for 1 h, the reaction mixture was cooled to room temperature, The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 15 of the Electronic Supplementary Information.

3.4. Optimization of HCOOH amount in entries 24-26, Table 1.

A 10-mL reaction tube was charged with (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (0.000025 mol/L for *S/C* = 10000) in deionized water. The mixture was stirred for 2 minutes at 80 °C, and then formic acid (10 μL, 0.25 mmol, 1 equiv; 19 μL, 0.5 mmol, 2 equiv; 38 μL, 1 mmol, 4 equiv) was added. After stirring for 1 h, the reaction mixture was cooled to room temperature, The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 15 of the Electronic Supplementary Information.

3.5 Optimization of reaction conditions in entries 1-5, Table 5.

A 10-mL reaction tube was charged with (2-nitroprop-1-en-1-yl)benzene (**3a**, 41 mg, 0.25 mmol), HCOONa·2H$_2$O (26 mg, 0.25 mmol, 1 equiv; 52 mg, 0.5 mmol, 2 equiv), 1 mL of ***C3*** catalyst solution (0.000025 mol/L for *S/C* = 10000; 0.0000125 mol/L for *S/C* = 20000; 0.00000625 mol/L for *S/C* = 40000) in deionized water. The mixture was stirred at 80 °C. After stirring for 1 h, the reaction mixture was cooled to room temperature, The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 18 of the Electronic Supplementary Information.

4. Procedure for studies on TOF against reaction time in Table 2

To five 10-mL reaction tubes were individually added (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (*S/C* = 20000, 0.0000125 mol/L) in deionized water. The mixture was

heated for 2 minutes at 80 °C, and then formic acid (76 μL, 2 mmol, 8 equiv) was added in one portion. The five tubes were stirred for 5 min, 20 min, 30 min, 60 min, and 75 min, respectively. After the indicated time, the reaction mixture was quickly diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 16 of the Electronic Supplementary Information.

5. Procedure for studies on correlation between initial pH values and catalyst efficiencies in Table 3

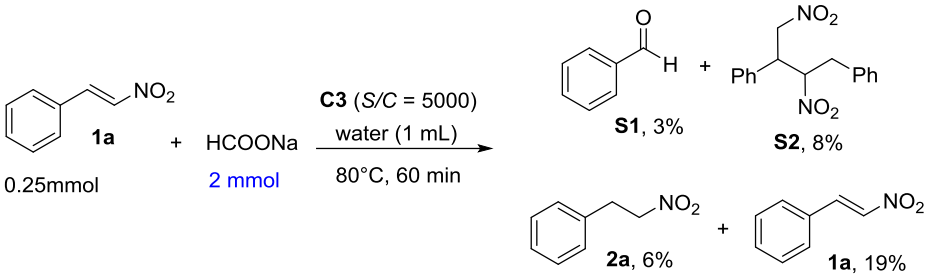
A 10-mL reaction tube was charged with (2-nitrovinyl)benzene (**1a**, 37 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (9.3 mg, 0.05 mmol), HCOONa·2H_2O (*x* mmol)，formic acid (*y* mmol), the mixture was stirred at 80 °C. Then 1 mL of ***C3*** catalyst solution (0.00005 mol/L) in deionized water was added, and was immersed in a preheated 80 °C heating mantle. After stirring for 1 h, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR yield determination. The ^{1}H NMR spectra were provided in Section 17 of the Electronic Supplementary Information.

Table S4. pH values correlating to molar ratios of HCO_2H and HCO_2Na

pH of reaction media		1.58	3.02	3.52	4.02	7.14
HCO_2H:HCO_2Na molar ratio		8/0	6/2	3/3	2/6	0/8
HCOOH	μL	76	57	29	19	0
	x mmol	2	1.5	0.75	0.5	0
HCOONa	mg	0	52	78	156	208
	y mmol	0	0.5	0.75	1.5	2
Yield (%)		99	99	99	99	6

Analysis of by-products of the reduction at pH = 7.14.

For the ^{1}H NMR data and spectrum of the dimeric product, see ref 5b. In addition, a solid was also obtained, which did not dissolve in any organic solvent and water.



Scheme S2. Reduction of **1a** under basic conditions

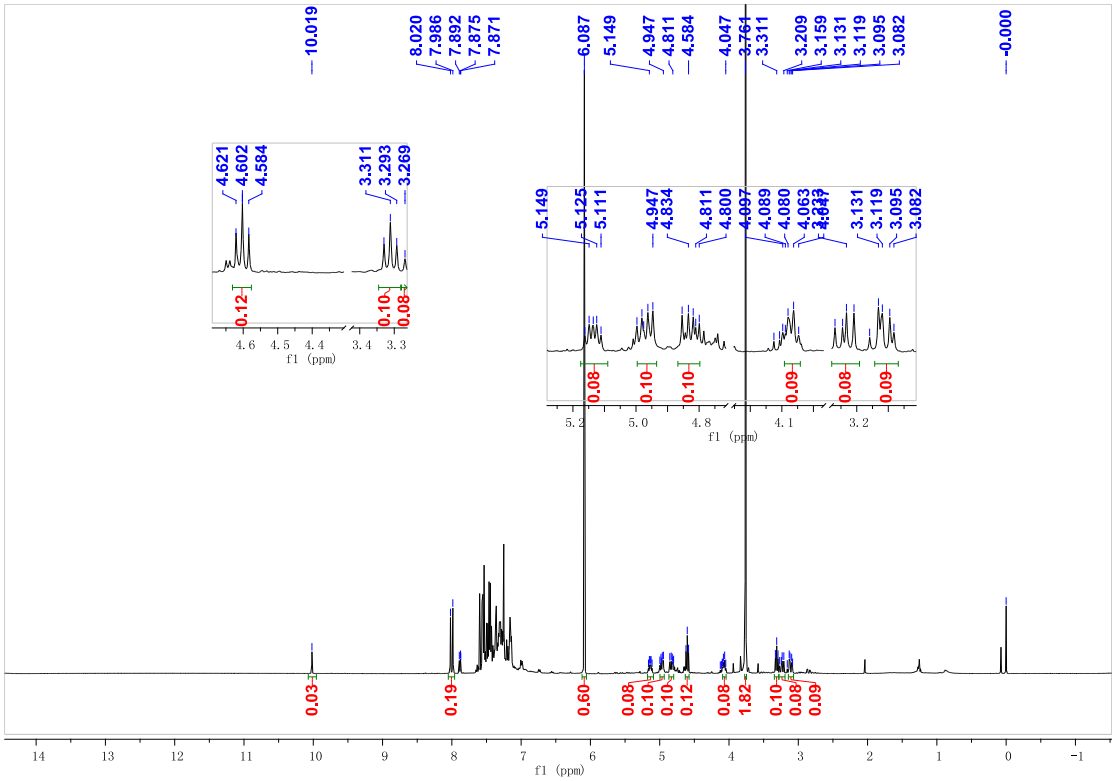
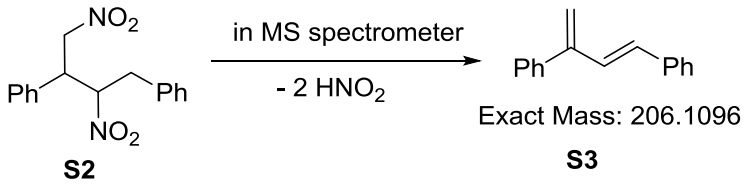


Figure S1. ^{1}H NMR of the crude reaction mixture for reduction of **1a** under basic conditions

The dimeric product was also observed by GC-MS. For detail, see the following.



Scheme S3. Elimination of nitric acids from **S2** to form **S3** in GC-MS

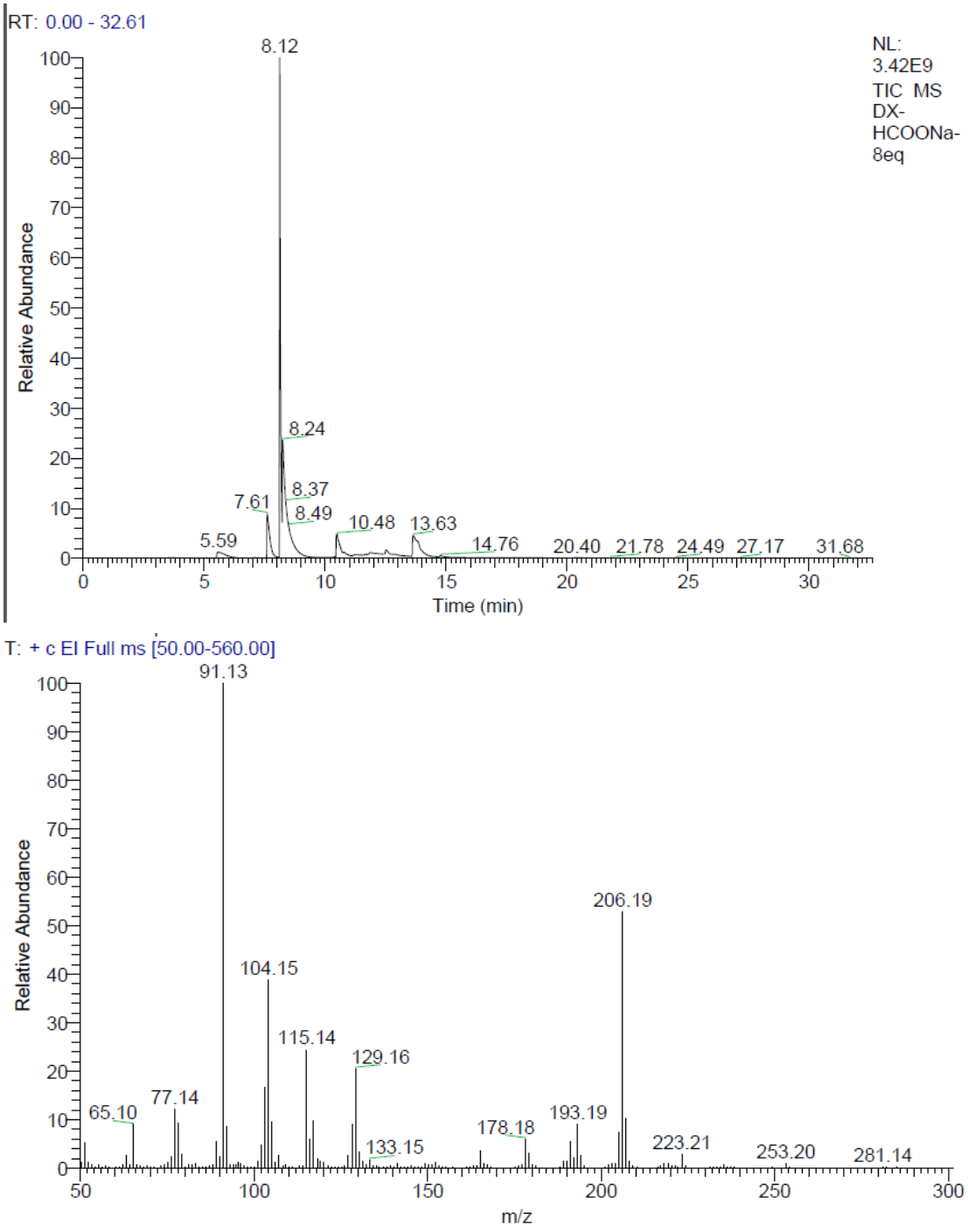


Figure S2. GC-MS spectra of for analysis of **S2** and **S3**

6. General procedure for the reduction of β-monosubstituted nitroalkenes:

A 10-mL reaction tube was charged with (2-nitrovinyl)arene **1** (0.25 mmol), 1 mL of ***C3*** catalyst solution (0.000025 mol/L for *S/C* = 10000; 0.00005 mol/L for *S/C* = 5000) in deionized water. The mixture was stirred for 2 minutes at 80 °C. If the 2-nitrovinylarene was not melted, 0.5 mL of EtOH was added, and then formic acid (38 µL, 1 mmol, 4 equiv) was added. The mixture was monitored by TLC

analysis. Once nitroalkene was completely consumed, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was dried by Na_2SO_4 and evaporated under reduced pressure to give desired products, which were demonstrated pure by ^1H NMR spectra. The ^1H and ^{13}C NMR spectra were provided in Section 14 of the Electronic Supplementary Information.

7. General procedure for the reduction of α,β-disubstituted nitroalkenes:

A 10-mL reaction tube was charged with (2-nitroprop-1-en-1-yl)arene **3** (0.25 mmol), HCOONa·2 H_2O (52 mg , 0.5 mmol, 2 equiv), 1 mL of ***C3*** catalyst solution (0.000025 mol/L for *S/C* = 10000; 0.00005 mol/L for *S/C* = 5000) in deionized water, then 0.4 mL of EtOH was added. The mixture was stirred at 80 °C, and was monitored by TLC analysis. Once nitroalkene was completely consumed, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic phase was dried by Na_2SO_4 and evaporated under reduced pressure to give desired products, which were demonstrated pure by ^1H NMR spectra. The ^1H and ^{13}C NMR spectra were provided in Section 14 of the Electronic Supplementary Information.

8. General procedure for Hydrogenation of β,β-disubstituted nitroalkenes:

A 10-mL reaction tube was charged with β,β-disubstituted nitroalkenes **7** (0.25 mmol), 1 mL of ***C3*** catalyst solution (0.00005 mol/L for *S/C* = 5000) in deionized water, and 0.4 mL of EtOH. The mixture was stirred for 2 minutes at 80 °C. Then formic acid (38 μL, 1 mmol, 4 equiv) was added. The mixture was monitored by TLC analysis. Once nitroalkene was completely consumed, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was dried by Na_2SO_4 and evaporated under reduced pressure to give desired products, which were demonstrated pure by ^1H NMR spectra. The ^1H and ^{13}C NMR spectra were provided in Section 14 of the Electronic Supplementary Information.

9. Gram-scale Reactions.

9.1. Gram-scale reduction of (2-nitrovinyl)benzene (**1a**):

To a 250-mL flask was sequentially added (2-nitrovinyl)benzene **(1a**, 11.92 g, 80 mmol), ***C3*** catalyst (4.6 mg, 0.008 mmol, *S/C* = 10000), and tap water (160 mL). The flask was equipped with a reflux condenser, and then immersed in a preheated 80 °C oil-bath for 5 min, followed by slow addition of

formic acid (15 g, 320 mmol) during 10 min. The resultant reaction mixture was stirred for 1 h, and TLC indicated the full conversion of substrate. After cooling to room temperature, the product (**2a**) appeared from the solution as an oil. The mixture was diluted with water (150 mL) and extracted with ethyl acetate (50 mL × 2). The organic solvent was dried by Na_2SO_4 and then evaporated under reduced pressure to afford desired product as brownish oil in 99% yield (11.91 g). The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

9.2. An improved gram-scale reduction of (2-nitrovinyl)benzene (**1a**):

To a 250-mL flask was sequentially added (2-nitrovinyl)benzene **(1a**, 11.92 g, 80 mmol), ***C3*** catalyst (4.6 mg, 0.008 mmol, *S/C* = 10000), and tap water (80 mL). The flask was equipped with a reflux condenser, and then immersed in a preheated 80 °C oil-bath for 5 min, followed by slow addition of formic acid (15 g, 320 mmol) during 10 min. The resultant reaction mixture was stirred for 1 h, and TLC indicated the full conversion of substrate. After cooling to room temperature, the product (**2a**) appeared from the solution as an oil. The mixture was extracted with ethyl acetate (20 mL × 2). The water phase (ca 80 mL, referred to as **CS-1**), which was actually the catalyst solution, was kept for use in next reactions. Without drying with desiccant, the organic solvent was directly distilled under atmospheric pressure to recover EA (29 mL, 72.5%). Then the residue was evaporated under reduced pressure to afford desired product as brownish oil in 98% yield (11.85 g) with >99% conversion. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

9.3. Gram-scale reduction of (2-nitrovinyl)benzene (**1a**) with waste catalyst solution **CS-1**:

To a 50-mL flask was sequentially added (2-nitrovinyl)benzene **(1a**, 2.98g, 20 mmol), 20 mL of recovered ***C3*** catalyst solution (**CS-1**) obtained from Section 9.2. The flask was equipped with a reflux condenser, and then immersed in a preheated 80 °C oil-bath for 5 min, followed by slow addition of formic acid (3.75 g, 80 mmol). The resultant reaction mixture was stirred for 1 h, and TLC indicated the full conversion of substrate. After cooling to room temperature, the mixture was extracted with **recovered ethyl acetate** (5 mL × 2). The water phase containing ***C3*** catalyst (ca 20 mL, referred to as **CS-2**) was kept for use in the next reaction. The organic solvent evaporated under reduced pressure to afford desired product as brownish oil in 98% yield (2.97 g). The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

Further use of 20 mL of the recovered **CS-2** catalyst solution to reduce **1a** following the same procedure only gave 33% ^{1}H NMR conversion of **1a.** The rest was starting material **1a**.

9.4. Gram-scale reduction of (2-nitropropyl)benzene (**3a**):

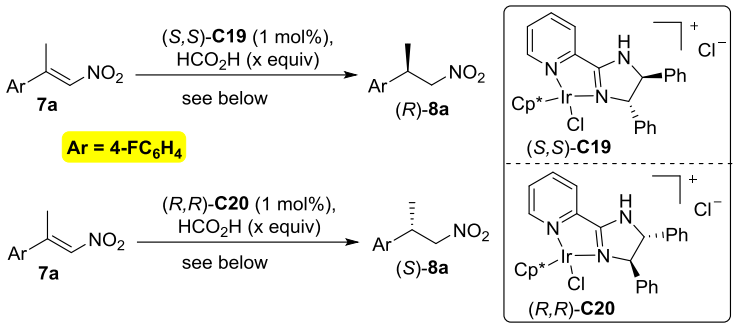
To a 250-mL flask was sequentially added (2-nitroprop-1-en-1-yl)benzene (**3a**, 13.05 g, 80 mmol), HCOONa·2H_2O (16.5 g, 160 mmol), ***C3*** catalyst (4.6 mg, 0.008 mmol, *S/C* = 10000), and tap water (160 mL). Then 2 mL of EtOH was used to wash down the substrate on the flask wall. The flask was equipped with a reflux condenser, and then immersed in a preheated 80 °C oil-bath The resultant reaction mixture was stirred for 1 h, and TLC indicated the full conversion of substrate. After cooling to room temperature, the product (**4a**) appeared from the solution as an oil. The mixture was diluted with water (150 mL) and extracted with ethyl acetate (50 mL × 2). The organic solvent was dried by Na_2SO_4 and then evaporated under reduced pressure to afford desired product as brownish oil in 98% yield (12.9 g). The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

10. Attempts on asymmetric reduction of nitroalkene 7a with (*S,S*)-C19 and (*R,R*)-C20

General procedure:

A 10-mL reaction tube was charged with (*E*)-1-fluoro-4-(1-nitroprop-1-en-2-yl)benzene (22.6 mg, 0.125 mmol), chiral catalyst (*S,S*)-**C19** or (*R,R*)-**C20** (0.9 mg, 0.00125 mmol), 0.5 mL of deionized water and 0.5 mL of the co-solvent. The mixture was stirred for 2 minutes at 80 °C. Then formic acid (47.5 μL, 1.25 mmol, 10 equiv) was added. The mixture was monitored by TLC analysis. After stirring for a certain time, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was dried by Na_2SO_4 and evaporated under reduced pressure. The residue was submitted to column chromatography to afford desired nitroalkane product.

Table S5. Asymmetric Hydrogenation of β,β-disubstituted nitroalkenes (see section 20 for the HPLC spectra)



entry	catalyst	solvent	time (h)	temp. (°C)	yield (%)[a]	ee (%)	$[\alpha]^{D}_{20}$
1	**C3**	EtOH/H_2O (0.2 ml/0.5 ml)	2	80	96	0	
2	*(S,S)-**C19***	EtOH/H_2O (0.5 ml/0.5 ml)	2.5	80	70	38	
3	*(S,S)-**C19***	MeOH/H_2O (0.5 ml/0.5 ml)	24	r.t.	74	42	
4	*(S,S)-**C19***	MeOH/H_2O (0.5 ml/0.5 ml)	1.5	80	61	46	+16.5
5	*(S,S)-**C19***	*i*-PrOH/H_2O (0.5 ml/0.5 ml)	3	80	65	43	
6	(*R,R*)-**C20**	MeOH/H_2O (0.5 ml/0.5 ml)	1.5	80	74	-46	-22
7	*(S,S)-**C19***	CH_3CN/H_2O (0.5 ml/0.5 ml)	1.5	80	0	-	

[a]isolated yield by column chromatography.

11. Other procedures.

11.1. Reduction of (2-nitroprop-1-en-1-yl)benzene under acidic conditions in Scheme 2.

A 10-mL reaction tube was charged with (2-nitroprop-1-en-1-yl)benzene (**3a**, 41 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (*S/C* = 5000, 0.00005 mol/L) in deionized water. The mixture was stirred for 2 minutes at 80 °C, and then formic acid (38 µL, 1 mmol, 4 equiv) was added in one portion. After stirring for 60 min, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR to determine the distribution of nitroalkane, oxime, and ketone. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

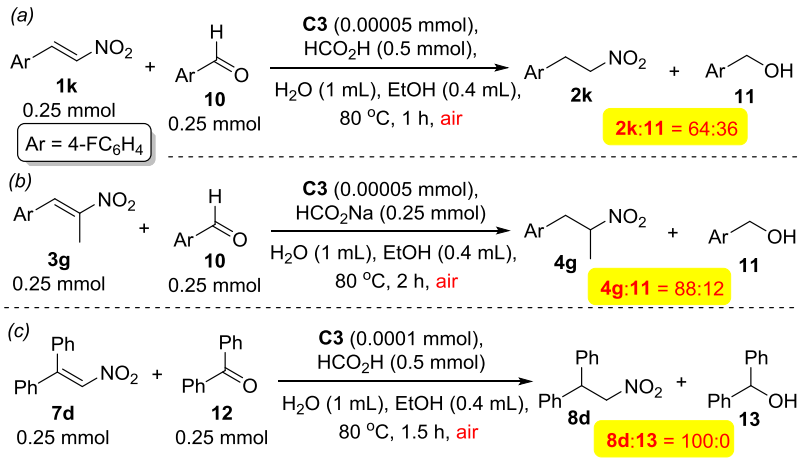
11.2. Reduction of (2-nitroprop-1-en-1-yl)benzene under acidic conditions in Scheme 3.

Two 10-mL reaction tubes were individually charged with

1-(1-nitroprop-1-en-2-yl)-4-(trifluoromethyl)benzene (**7b**, 58 mg, 0.25 mmol), $HCOONa{\cdot}2H_2O$ (52 mg, 0.5 mmol, 2 equiv). Then 1 mL of ***C3*** catalyst solution (*S/C* = 5000, 0.00005 mol/L) and 1 mL of water were added to the two tubes, respectively. After stirring at 80 °C for 1 h, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR to determine the ratios of **7b** and its isomer **9b**, or nitroalkane **8b** and **9b**. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

11.3. Procedure for comparison of reactivities between nitroalkenes, aldehydes, and ketones in Scheme 4.

In our previous work, aldehydes and ketones were also susceptible to reductions under similar conditions. Thus, their reactivity was compared with that of nitroalkenes (Scheme 4). Equimolar β-monosubstituted nitroalkene **1k** and aldehyde **9** were exposed to the same conditions, and the two desired products **2k** and **10** were formed in 64:36 ratio (Scheme 4a). Similar treatment of equimolar α,β-disubstituted nitroalkene **3g** and **9** gave **4g** and **10** in 75:25 ratio (Scheme 4b), while the treatment of equimolar β,β-disubstituted nitroalkene **7d** and ketone **11** only delivered nitroalkane **8d** (Scheme 4c). These results suggest that nitroalkenes are more reactive than their corresponding aldehyde or ketone precursors.



Scheme S4. Comparison of reactivity between nitroalkenes, aldehydes, and ketones.

Scheme S4. (a):

A 10-mL reaction tube was charged with 1-fluoro-4-(2-nitrovinyl)benzene (**1k,** 42 mg, 0.25 mmol), 4-fluorobenzaldehyde(**10**, 31 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (*S/C* = 5000 for each compound, 0.00005 mol/L) in deionized water, and 0.4 mL of EtOH. The mixture was stirred for 2 minutes at 80 °C, then formic acid (19 μL, 0.5 mmol) was added in one portion. After stirring for 1 h, the reaction mixture was cooled to room temperature. The mixture was diluted with water (2 mL) and extracted with ethyl acetate (2 mL × 3). The organic solvent was evaporated under reduced pressure. The crude residue was submitted to ^{1}H NMR to determine the ratio of two reduction products. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

Scheme S4. (b):

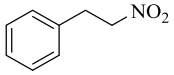
A 10-mL reaction tube was charged with 1-fluoro-4-(2-nitroprop-1-en-1-yl)benzene (**3g**, 45 mg, 0.25 mmol), 4-fluorobenzaldehyde(**10**, 31 mg, 0.25 mmol), HCOONa·2H$_2$O (26 mg , 0.25 mmol), 1 mL of ***C3*** catalyst solution (0.00005 mol/L) in deionized water, and 0.4 mL EtOH. The mixture was stirred at 80 °C for 2 h. Similar workup as above gave the ratio of two reduction products. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

Scheme S4. (c):

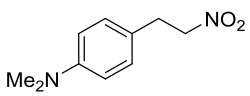
A 10-mL reaction tube was charged with (2-nitroethene-1,1-diyl)dibenzene (**7d**, 56 mg, 0.25 mmol), benzophenone (**12**, 46 mg, 0.25 mmol), 1 mL of ***C3*** catalyst solution (0.0001 mol/L) in deionized water and 0.4 mL EtOH. Then formic acid (10 μL, 0.25 mmol) was added. The mixture was stirred at 80 °C for 1.5 h. Similar workup as above gave the ratio of two reduction products. The ^{1}H NMR spectra were provided in Section 19 of the Electronic Supplementary Information.

12. Characterization data of products

12.1. Characterization data for the nitroalkanes **2a-2x**.

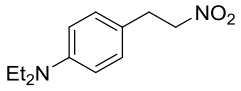


(2-Nitroethyl)benzene (2a) [6a]: CAS No. 6125-24-2; Isolate yield: 38 mg, 99%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.31 (m, 2H), 7.30-7.26 (m, 1H), 7.24-7.18 (m, 2H), 4.61 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 128.9, 128.5, 127.4, 76.2, 33.4.

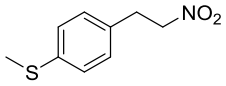


***N,N*-Dimethyl-4-(2-nitroethyl)aniline (2b) [4a]:** CAS No. 23630-92-4; Isolate

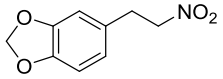
yield: 48 mg, 96%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.4Hz, 2H), 4.55 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.84, 129.21, 123.03, 112.84, 76.76, 40.51, 32.69.



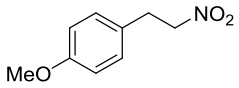
***N,N*-Diethyl-4-(2-nitroethyl)aniline (2c):** CAS No. 1824264-08-5; Isolate yield: 52 mg, 94%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8Hz, 2H), 4.54 (t, *J* = 7.6 Hz, 2H), 3.33 (q, *J* = 7.2 Hz, 4H), 3.21 (t, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.03, 129.44, 121.74, 112.03, 76.85, 44.30, 32.70, 12.50.



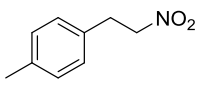
Methyl(4-(2-nitroethyl)phenyl)sulfane (2d) [3c]**:** CAS No. 951386-14-4; Isolate yield: 52 mg, 94%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.58 (t, *J* = 7.2 Hz, 2H), 3.27 (t, *J* = 7.2 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.71, 132.32, 129.00, 127.05, 76.17, 32.86, 15.79.



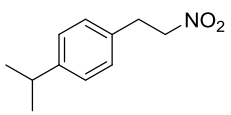
5-(2-Nitroethyl)benzo[d][1,3]dioxole (2e) [6a]**:** CAS No. 21473-47-2; Isolate yield: 45 mg, 93%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.75 (d, *J* = 8.0 Hz, 2H), 6.70-6.62 (m, 2H), 5.94 (s, 2H), 4.56 (t, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.00, 146.89, 129.18, 121.68, 108.86, 108.60, 101.10, 76.49, 33.18.



1-Methoxy-4-(2-nitroethyl)benzene (2f) [3c]**:** CAS No. 31236-71-2; Isolate yield: 42 mg, 92%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.57 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.26 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.85, 129.57, 127.54, 114.29, 76.54, 55.22, 32.65.

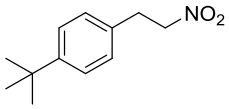


1-Methyl-4-(2-nitroethyl)benzene (2g) [7]**:** CAS No.72538-33-1; Isolate yield: 45 mg, 93%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18-7.05 (m, 4H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.06, 132.50, 129.58, 128.39, 76.39, 33.04, 21.00.

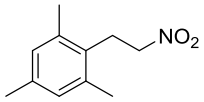


1-Isopropyl-4-(2-nitroethyl)benzene (2h): CAS No. 1268141-27-0; Isolate

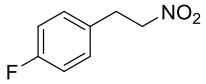
yield: 45 mg, 93%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.60 (t, *J* = 7.6 Hz, 2H), 3.30 (t, *J* = 7.6Hz, 2H), 3.03 – 2.72 (h, *J* = 6.8 Hz 1H), 1.25 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.05, 132.86, 128.47, 126.96, 76.31, 33.72, 33.03, 23.91.



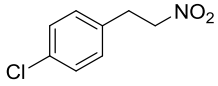
1-(Tert-butyl)-4-(2-nitroethyl)benzene (2i): CAS No. 1267108-03-1; Isolate yield: 45 mg, 93%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.60 (t, *J* = 7.6 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.35, 132.50, 128.22, 125.83, 76.27, 34.47, 32.92, 31.28.



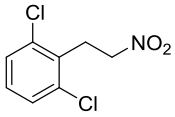
1,3,5-Trimethyl-2-(2-nitroethyl)benzene (2j): CAS No. 99985-88-3; Isolate yield: 48 mg, 99%; white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (s, 2H), 4.46–4.37 (m, 2H), 3.43– 3.34 (m, 2H), 2.34 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.88, 136.48, 129.35, 128.71, 73.56, 27.67, 20.77, 19.54.



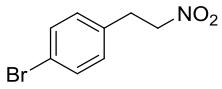
1-Fluoro-4-(2-nitroethyl)benzene (2k) [8]**:** CAS No. 947177-23-3; Isolate yield: 39 mg, 92%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21-7.13 (m, 2H), 7.05-6.97 (m, 2H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.08 (d, *J* = 246.0 Hz), 131.34 (d, *J* = 3.3 Hz), 130.12 (d, *J* = 8.1 Hz), 115.82 (d, *J* = 21.5 Hz), 76.24, 32.56.



1-Chloro-4-(2-nitroethyl)benzene (2l) [7]**:** CAS No. 60947-43-5; Isolate yield: 45 mg, 97%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.09, 133.28, 129.87, 129.03, 75.91, 32.60.

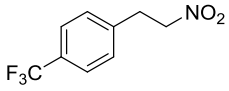


1,3-Dichloro-2-(2-nitroethyl)benzene (2m) [10]**:** CAS No. 953810-72-5; Isolate yield: 51 mg, 94%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.60 – 4.53 (m, 2H), 3.77 – 3.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.77, 131.37, 129.32, 128.51, 71.99, 29.03.

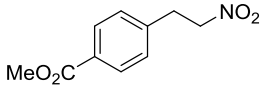


1-Bromo-4-(2-nitroethyl)benzene (2n) [7]**:** CAS No. 137521-07-4; Isolate yield: 52 mg, 90%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.27 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz,

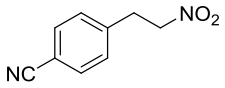
$CDCl_3$) δ 134.59, 132.06, 130.25, 121.42, 75.86, 32.73.



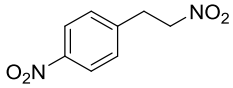
1-(2-Nitroethyl)-4-(trifluoromethyl)benzene (2o) [6a]**:** CAS No. 1312540-60-5; Isolate yield: 46 mg, 85%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 7.2 Hz, 2H), 3.38 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.70, 129.85 (q, *J* = 32.6 Hz), 128.96, 127.05, 125.90 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 273.0 Hz), 75.61, 32.98.



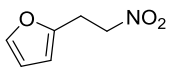
Methyl-4-(2-nitroethyl)benzoate (2p) [11]**:** CAS No. 745059-98-7; Isolate yield: 46 mg, 88%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 7.2Hz, 2H), 3.90 (s,3H), 3.37 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 140.79, 130.18, 129.40, 128.58, 75.60, 52.12, 33.17.



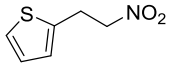
4-(2-Nitroethyl)benzonitrile (2q) [7]**:** CAS No. 126158-10-9; Isolate yield: 45 mg, 99%; white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.65 (t, *J* = 7.2 Hz, 2H), 3.38 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.10, 132.69, 129.39, 118.38, 111.57, 75.25, 33.11.



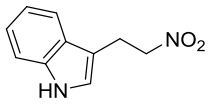
1-Nitro-4-(2-nitroethyl)benzene (2r) [6a]**:** CAS No. 21473-45-0; Isolate yield: 46 mg, 94%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21-7.13 (m, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.29, 160.84, 131.35, 131.32, 130.15, 130.07, 115.91, 115.70, 76.23, 32.56.



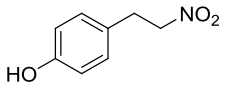
2-(2-Nitroethyl)furan (2s) [8]**:** CAS No. 5462-90-8; Isolate yield: 36 mg, 99%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 2.0 Hz, 1H), 6.30 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 4.64 (t, *J* = 7.2 Hz, 2H), 3.36 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.28, 142.22, 110.48, 107.38, 73.32, 26.02.



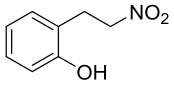
2-(2-Nitroethyl)thiophene (2t) [8]**:** CAS No. 30807-46-6; Isolate yield: 38 mg, 97%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.89 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.63 (t, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.31, 127.22, 126.23, 124.83, 75.96, 27.46.



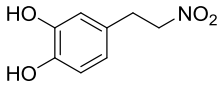
3-(2-Nitroethyl)-1H-indole(2u) [12]**:** CAS No. 31731-23-4; Isolate yield: 45 mg, 97%; red solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 4.67 (t, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.19, 126.62, 122.51, 119.88, 118.10, 111.40, 110.03, 75.69, O23.61.



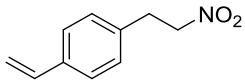
4-(2-Nitroethyl)phenol (2v) [11]**:** CAS No. 37567-58-1; Isolate yield: 38 mg, 92%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 5.42 (s, 1H), 4.57 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.78, 129.77, 127.64, 115.75, 76.59, 32.60.



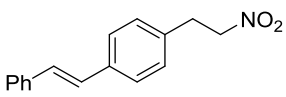
2-(2-Nitroethyl)phenol (2w) [8]**:** CAS No. 96853-36-0; Isolate yield: 39 mg, 94%; yellow liquid;^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18-7.09 (m, 2H), 6.88 (t, *J* = 7.6Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 2H), 3.33 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.65, 131.06, 128.81, 122.15, 121.16, 115.37, 74.65, 28.80.



4-(2-Nitroethyl)benzene-1,2-diol (2x): CAS No. 146897-58-7; Isolate yield: 38 mg, 83%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.35 (s, 2H), 4.55 (t, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.85, 142.77, 128.59, 121.08, 115.76, 115.66, 76.53, 32.84.



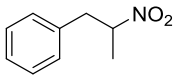
1-(2-nitroethyl)-4-vinylbenzene (2y): CAS No. 55032-27-4. Isolate yield: 41 mg, 93%; colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 4.60 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.75, 136.14, 135.10, 135.08, 128.69, 126.67, 114.06, 76.09, 33.06. HRMS (ESI): m/z calcd for $C_{10}H_{11}$ [M-NO_2]: 131.0861 found: 131.0868.



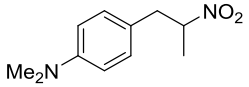
1-(2-Nitroethyl)-4-styrylbenzene (2z): Isolate yield: 24 mg, 80%; white

solid, m.p. 132 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 2H), 4.61 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.14, 136.61, 134.89, 129.00, 128.90, 128.69, 127.93, 127.73, 127.00, 126.51, 76.14, 33.16. HRMS (ESI): m/z calcd for $C_{16}H_{15}$ [M-NO_2]: 207.1174 found: 207.1176.

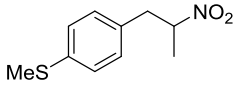
12.2. Characterization data for the nitroalkanes **4a** - **4q**.



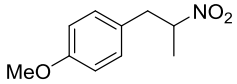
(2-Nitropropyl)benzene (4a) [10]**:** CAS No. 17322-34-8; Isolate yield: 41 mg, 99%; yellow liquid ; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 3H), 7.19 – 7.12 (m, 2H), 4.77 (h, *J* = 6.8 Hz, 1H), 3.32 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.00 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.46, 128.92, 128.76, 127.35, 84.38, 41.10, 18.75.



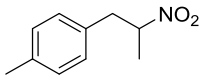
***N,N*-Dimethyl-4-(2-nitropropyl)aniline (4b)** [4a]**:** CAS No. 321132-09-6; Isolate yield: 49 mg, 94%; yellow liquid ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.72 (h, *J* = 6.8 Hz, 1H), 3.23 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.92 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.93 (s, 6H), 1.52 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.81, 129.62, 123.00, 112.70, 84.75, 40.46, 40.42, 18.51.



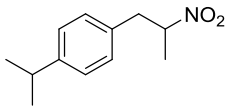
Methyl(4-(2-nitropropyl)phenyl)sulfane (4c) [13]**:** CAS No. 1434488-75-1; Isolate yield: 46 mg, 85%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.81 – 4.68 (h, *J* = 6.8 Hz, 1H), 3.26 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.97 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.46 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.65, 132.15, 129.39, 126.86, 84.32, 40.56, 18.73, 15.72.



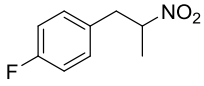
1-Methoxy-4-(2-nitropropyl)benzene (4d) [9]**:** CAS No. 29865-49-4; Isolate yield: 44 mg, 88%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 4.79 – 4.66 (h, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 3.25 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.96 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82, 129.95, 127.42, 114.13, 84.61, 55.16, 40.33, 18.62.



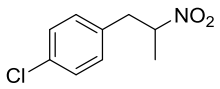
1-Methyl-4-(2-nitropropyl)benzene (4e) [9]**:** CAS No. 29865-50-7; Isolate yield: 46 mg, 99%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.74 (h, *J* = 6.8 Hz, 1H), 3.27 (dd, *J* = 14.0, 77.2 Hz, 1H), 2.96 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.31 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.98, 132.39, 129.43, 128.79, 84.49, 40.76, 20.97, 18.67.



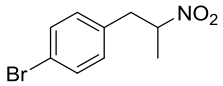
1-Isopropyl-4-(2-nitropropyl)benzene (4f) : CAS No. 872286-74-3: Isolate yield: 49 mg, 95%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.77 (h, *J* = 6.8 Hz, 1H), 3.31 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.98 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.89 (hept, *J* = 6.8 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.99, 132.75, 128.89, 126.82, 84.47, 40.77, 33.70, 23.91, 18.79.



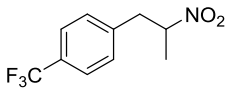
1-Fluoro-4-(2-nitropropyl)benzene (4g) [9]**:** CAS No. 29865-52-9; Isolate yield: 41 mg, 90%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.09 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.75 (h, *J* = 6.8 Hz, 1H), 3.27 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.99 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07 (d, *J* = 246.1 Hz), 131.18 (d, *J* = 3.3 Hz), 130.48 (d, *J* = 8.1 Hz), 115.67 (d, *J* = 21.5 Hz), 84.41, 40.24, 18.74.



1-Chloro-4-(2-nitropropyl)benzene (4h) [9]**:** CAS No. 29865-54-1; Isolate yield: 41 mg, 84%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.75 (h, *J* = 6.8 Hz, 1H), 3.27 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.99 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.90, 133.35, 130.27, 128.95, 84.17, 40.35, 18.79.

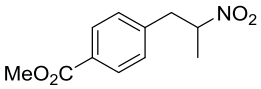


1-Bromo-4-(2-nitropropyl)benzene (4i) [9]**:** CAS No. 124941-10-2; Isolate yield: 52 mg, 86%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.74 (h, *J* = 6.8 Hz, 1H), 3.26 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.97 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.55 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.41, 131.93, 130.63, 121.45, 84.09, 40.43, 18.82.

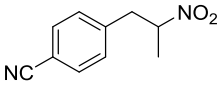


1-(2-Nitropropyl)-4-(trifluoromethyl)benzene (4j) : CAS No. 29865-58-5;

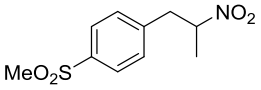
Isolate yield: 56 mg, 96%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.80 (h, *J* = 6.8 Hz, 1H), 3.36 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.08 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.58 (q, *J* = 1.4 Hz), 129.79 (q, *J* = 32.7 Hz), 129.36, 125.77 (q, *J* = 3.8 Hz), 124.01(q, *J* = 272.0 Hz), 83.99, 40.69, 18.94.



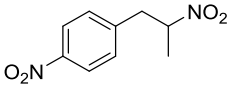
Methyl-4-(2-nitropropyl)benzoate (4k): Isolate yield: 54 mg, 97%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.79 (h, *J* = 6.8 Hz, 1H), 3.89 (s, 3H), 3.35 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.06 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 140.61, 130.02, 129.34, 128.96, 83.90, 52.06, 40.84, 18.85. HRMS (ESI): m/z calcd for $C_{11}H_{14}NO_4^+$ $[M+H]^+$: 224.0917 found: 224.0915.



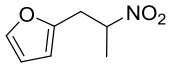
4-(2-Nitropropyl)benzonitrile (4l) [14]**:** CAS No. 115170-82-6; Isolate yield: 44 mg, 93%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.85 – 4.74 (m, 1H), 3.35 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.09 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.85, 132.52, 129.72, 118.38, 111.48, 83.68, 40.77, 18.99.



1-(Methylsulfonyl)-4-(2-nitropropyl)benzene (4m): Isolate yield: 61 mg, 99%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.87 – 4.76 (m, 1H), 3.39 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.12 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.04 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 139.73, 129.95, 127.88, 83.75, 44.41, 40.59, 19.09. HRMS (ESI): m/z calcd for $C_{10}H_{14}NO_4S^+$ $[M+H]^+$: 244.0638 found: 244.0634.

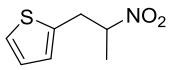


1-Nitro-4-(2-nitropropyl)benzene (4n) [9]**:** CAS No. 29865-60-9; Isolate yield: 52 mg, 91%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.91 – 4.80 (m, 1H), 3.43 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.17 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.30, 142.91, 129.86, 123.94, 83.68, 40.48, 19.03.

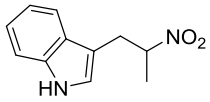


2-(2-Nitropropyl)furan (4o) [9]**:** CAS No. 181211-54-1; Isolate yield: 37 mg, 96%;

pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 1.6, 0.8 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.13 (dd, *J* = 3.2, 0.4 Hz, 1H), 4.84 (h, *J* = 6.8 Hz, 1H), 3.36 (dd, *J* = 15.2, 7.2 Hz, 1H), 3.08 (dd, *J* = 15.2, 6.8 Hz, 1H), 1.57 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.31, 142.28, 110.45, 108.01, 81.78, 33.42, 18.81.

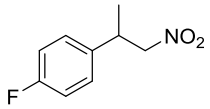


2-(2-Nitropropyl)thiophene (4p) [9]**:** CAS No. 122861-44-3; Isolate yield: 40 mg, 94%; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.86 (dt, *J* = 3.6, 1.2 Hz, 1H), 4.78 (h, *J* = 6.8 Hz, 1H), 3.54 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.25 (dd, *J* = 15.2, 6.4 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.96, 127.19, 126.77, 124.98, 84.20, 34.96, 18.77.

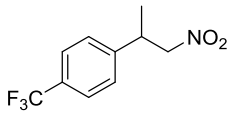


3-(2-Nitropropyl)-1H-indole (4q) [15]**:** CAS No. 4771-72-6; Isolate yield: 48 mg, 94%; tawny liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 4.90 (h, *J* = 6.8 Hz, 1H), 3.50 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.21 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.11, 126.91, 122.97, 122.35, 119.79, 118.21, 111.37, 109.86, 83.80, 31.20, 18.94.

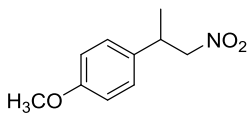
12.3. Characterization data for the nitroalkanes **8a - 8d**.



1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a) [5a]**:** CAS No. 1532525-80-6. Isolate yield: 44 mg, 96%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 4.55 – 4.43 (m, 2H), 3.63 (h, *J* = 7.2 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.04(d, *J* = 246 Hz), 136.53(d, *J* = 2.7 Hz), 128.44(d, *J* = 8.0 Hz), 115.84(d, *J* = 21.5 Hz), 81.81, 37.96, 18.83.

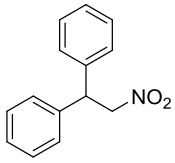


1-(1-Nitropropan-2-yl)-4-(trifluoromethyl)benzene (8b) [5a]**:** CAS No. 1402166-99-7. Isolate yield: 55 mg, 94%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.61 – 4.49 (m, 2H), 3.72 (h, *J* = 7.2 Hz, 1H), 1.40 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.90, 129.95(q, *J* = 32.5 Hz), 127.35, 125.95(q, *J* = 3.8 Hz), 125.43(q, *J* = 272.9 Hz), 81.19, 38.41, 18.67.



1-Methoxy-4-(1-nitropropan-2-yl)benzene (8c) [5a]**:** CAS No. 70360-85-9;

Isolate yield: 48mg, 98%; pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.54 – 4.41 (m, 2H), 3.79 (s, 3H), 3.59 (h, *J* = 7.2 Hz, 1H), 1.35 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 132.78, 127.85, 114.24, 82.04, 55.19, 37.87, 18.74.



(2-Nitroethene-1,1-diyl)dibenzene (8d) [16]**:** CAS No. 5582-87-6. Isolate yield: 57 mg, 99%; yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 4H), 7.28 – 7.19 (m, 6H), 4.99 – 4.95 (m, 2H), 4.90 (dd, *J* = 9.2, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.16, 128.99, 127.62, 127.55, 79.20, 48.92.

13. Reference

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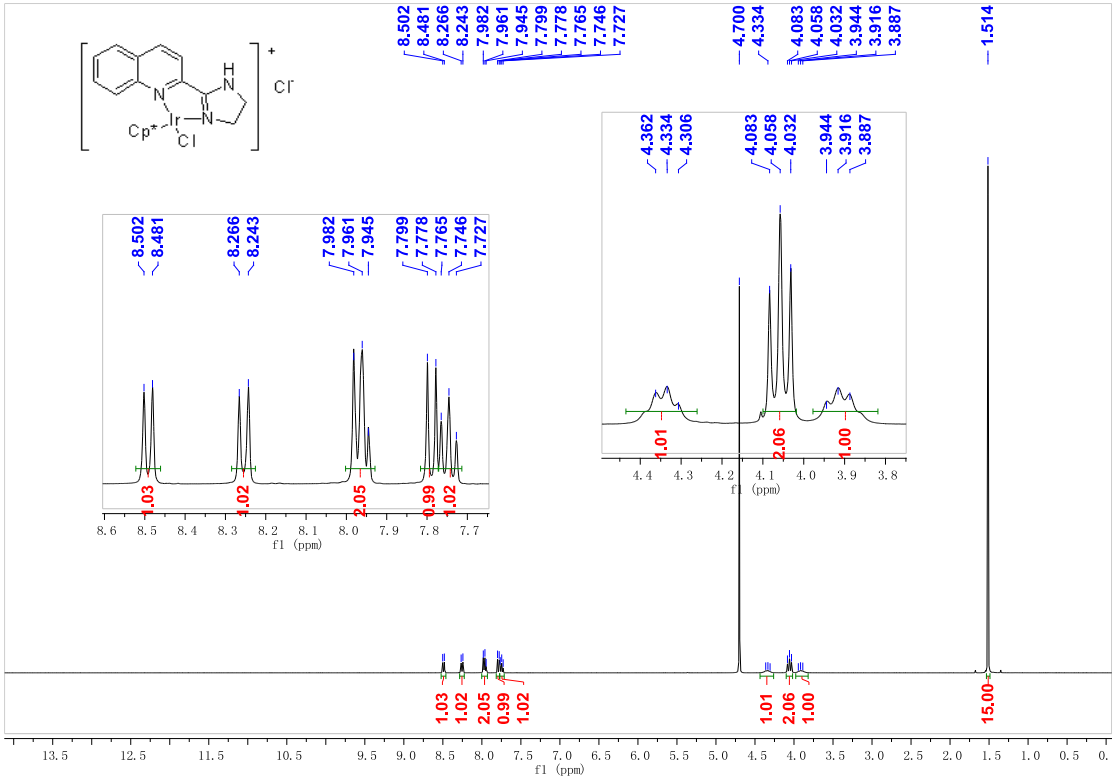
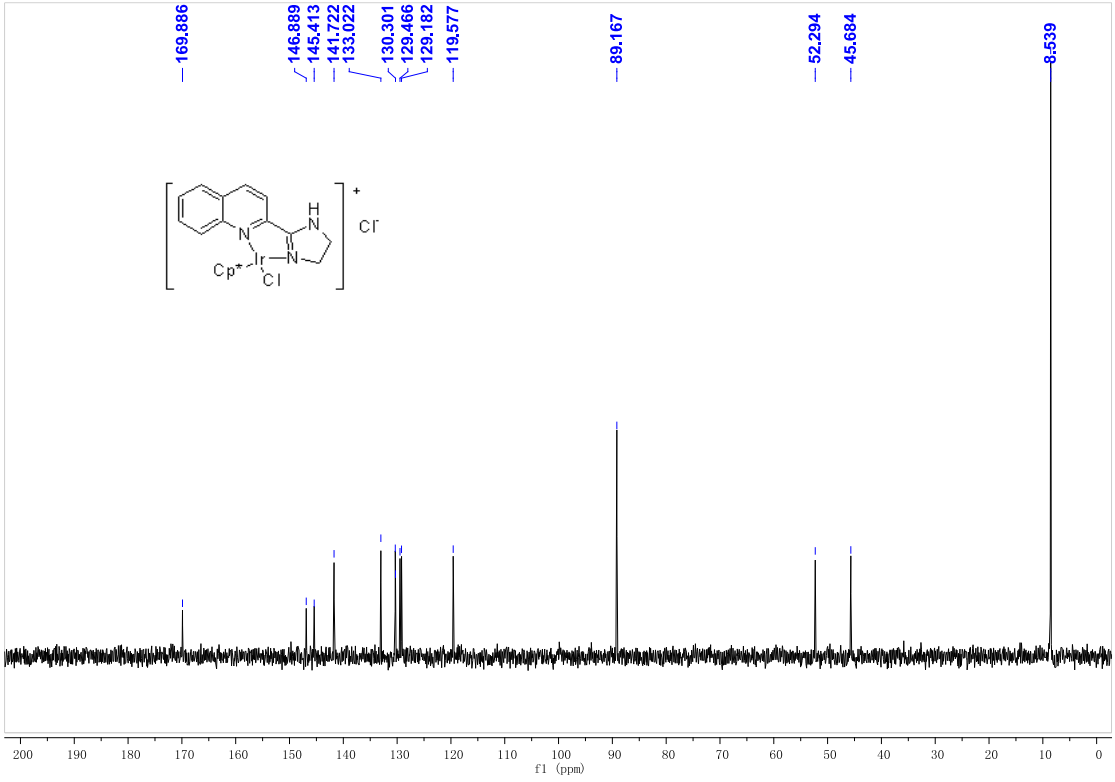
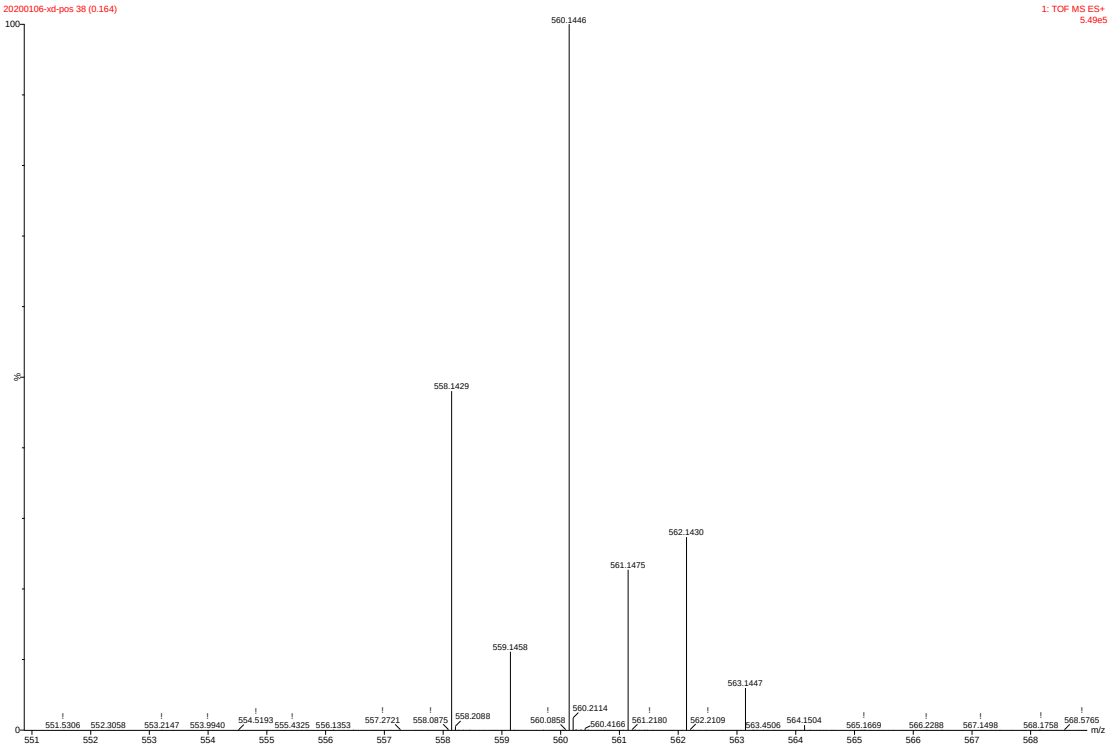
14. Copies of ^{1}H and ^{13}C NMR and HRMS spectra of pure catalyst and products

Catalyst C11:



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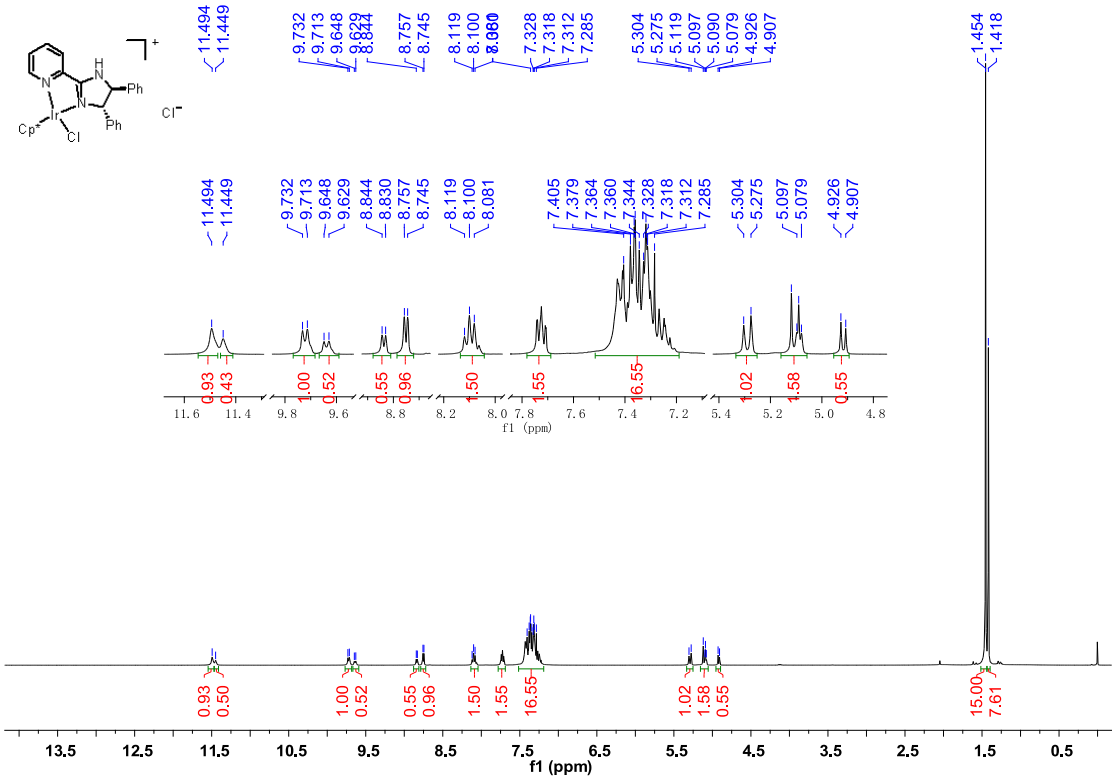
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4.926
4.907
1.454
1.418
0.93
0.50
1.00
0.52
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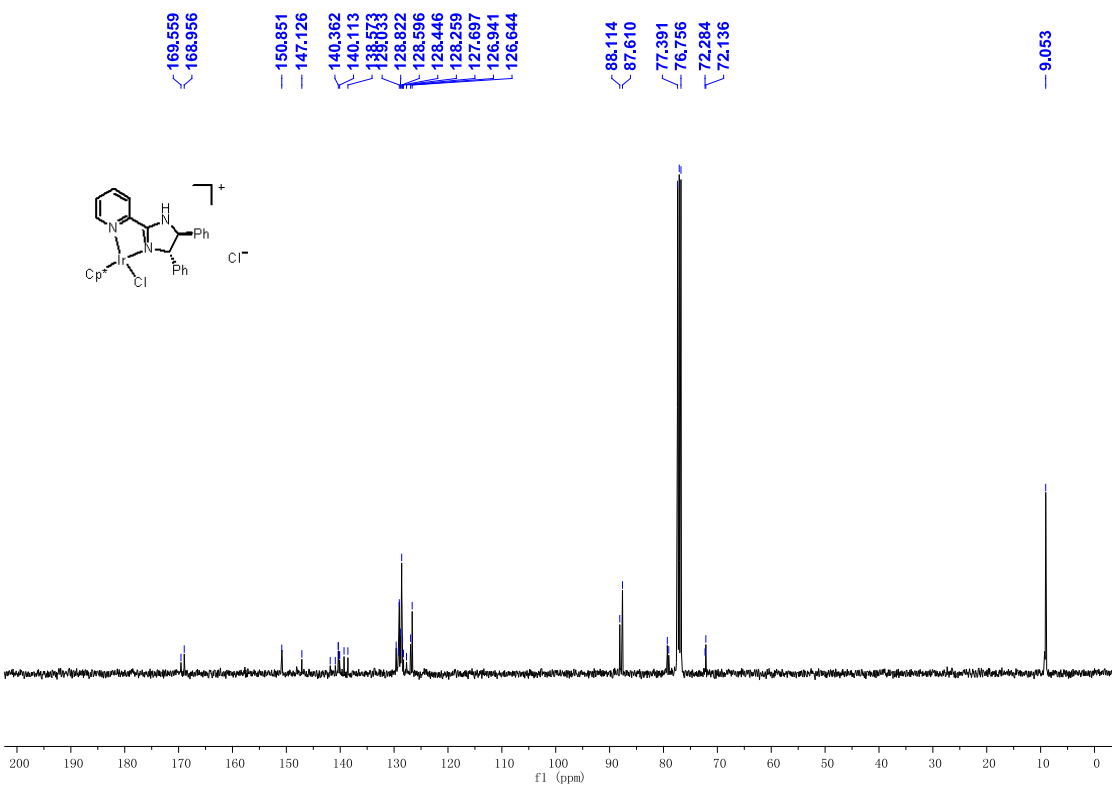
f1 (ppm)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87.610
77.391
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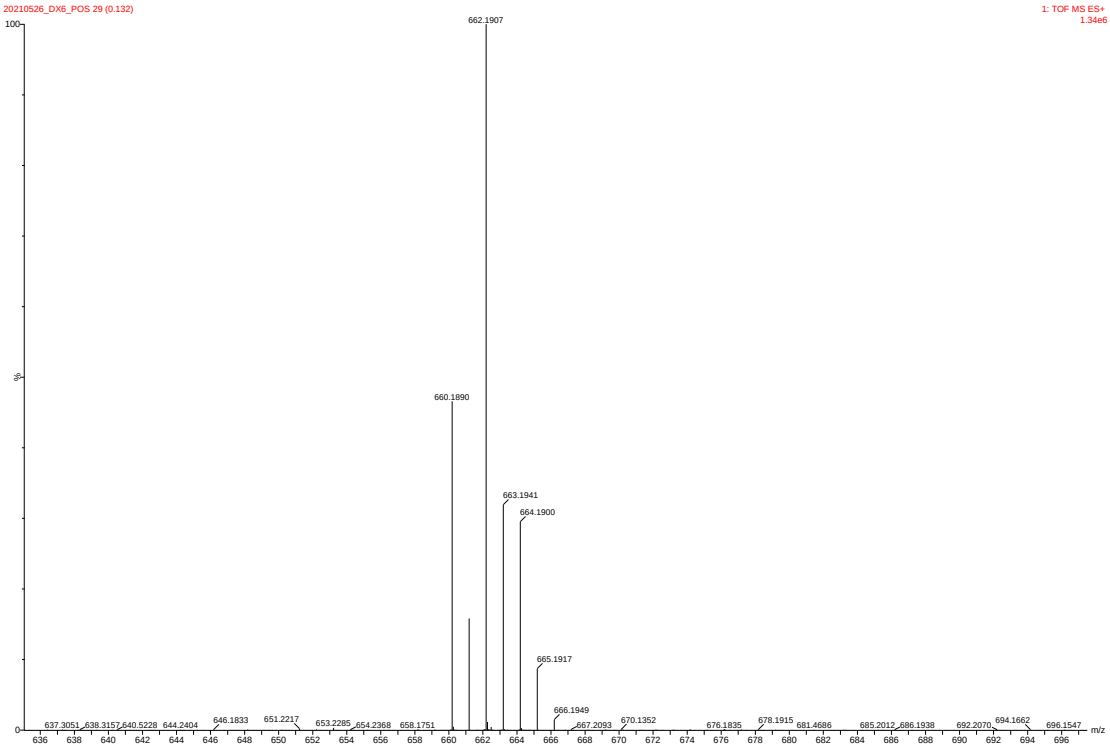
f1 (ppm)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685.2012
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694.1662
696.1547
m/z
636
638
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642
644
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650
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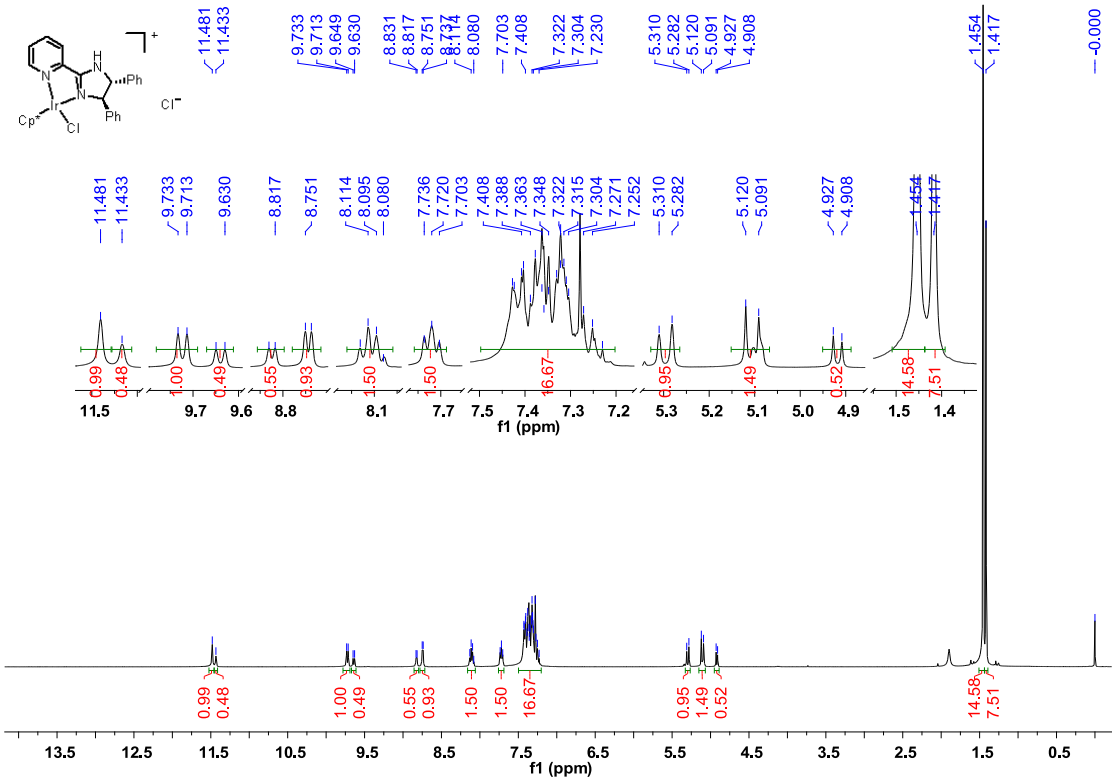
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5.282
5.120
5.091
4.927
4.908
1.454
1.417
-0.000
Ph
Ph
Cp*
Ir
Cl
Cl⁻
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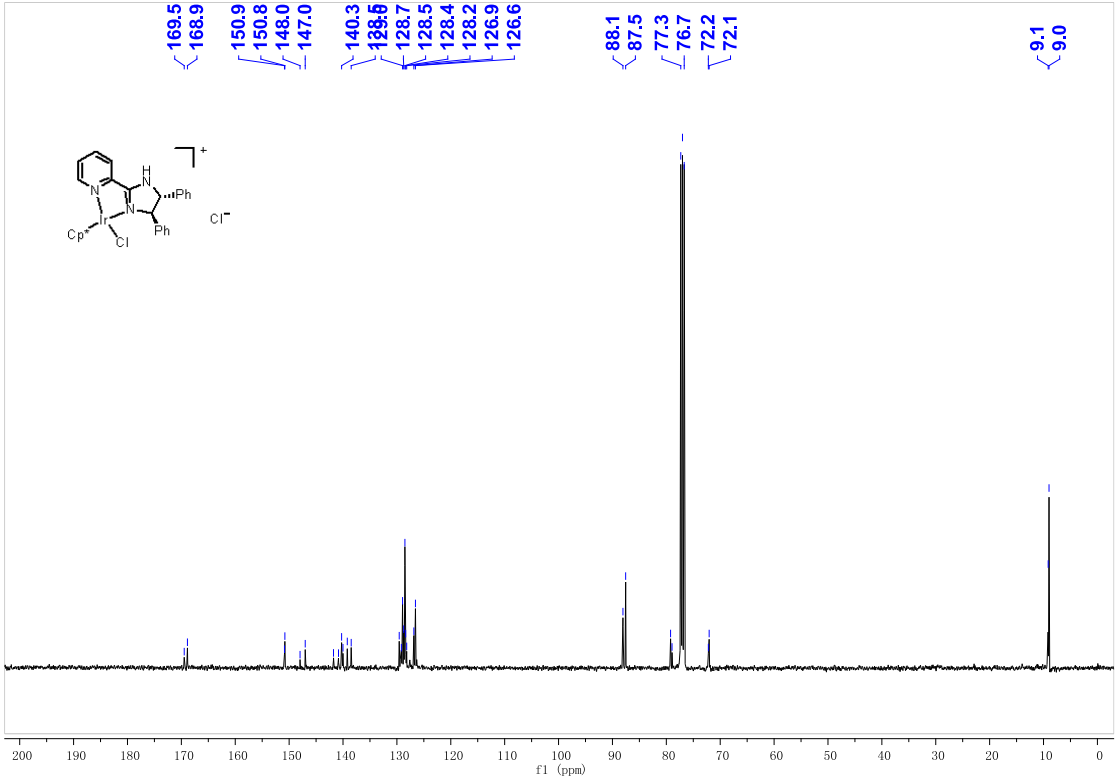
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87.5
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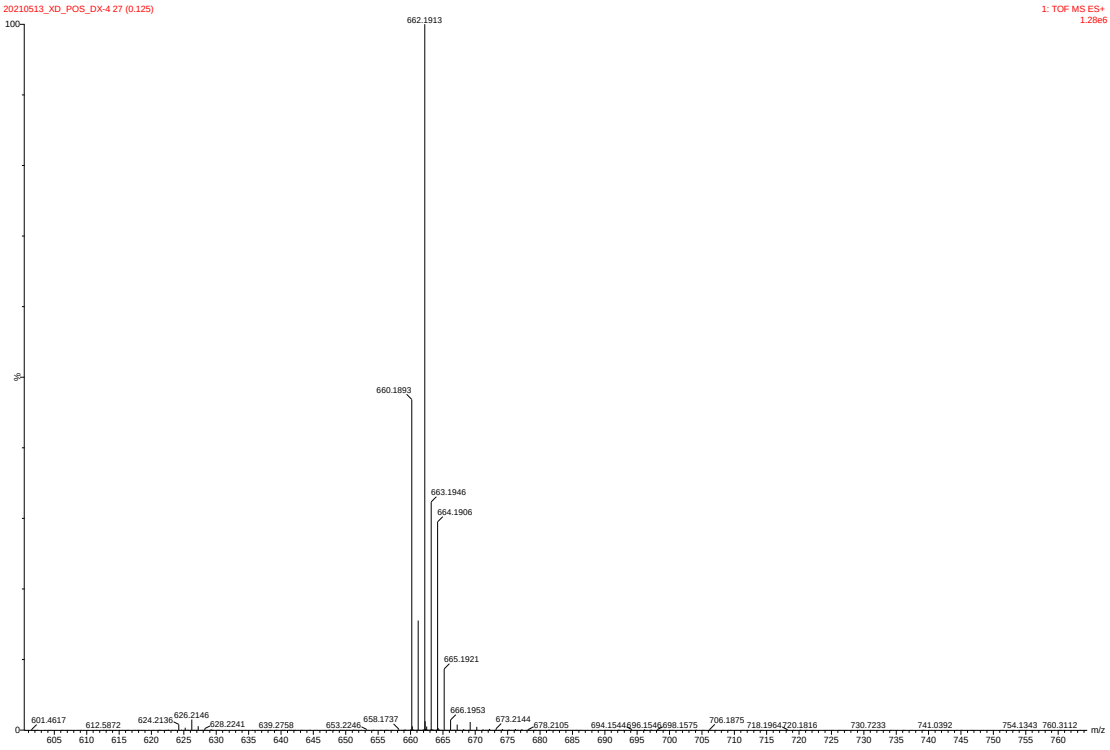
Ph
Cp*
Ir
Cl
Cl⁻
f1 (ppm)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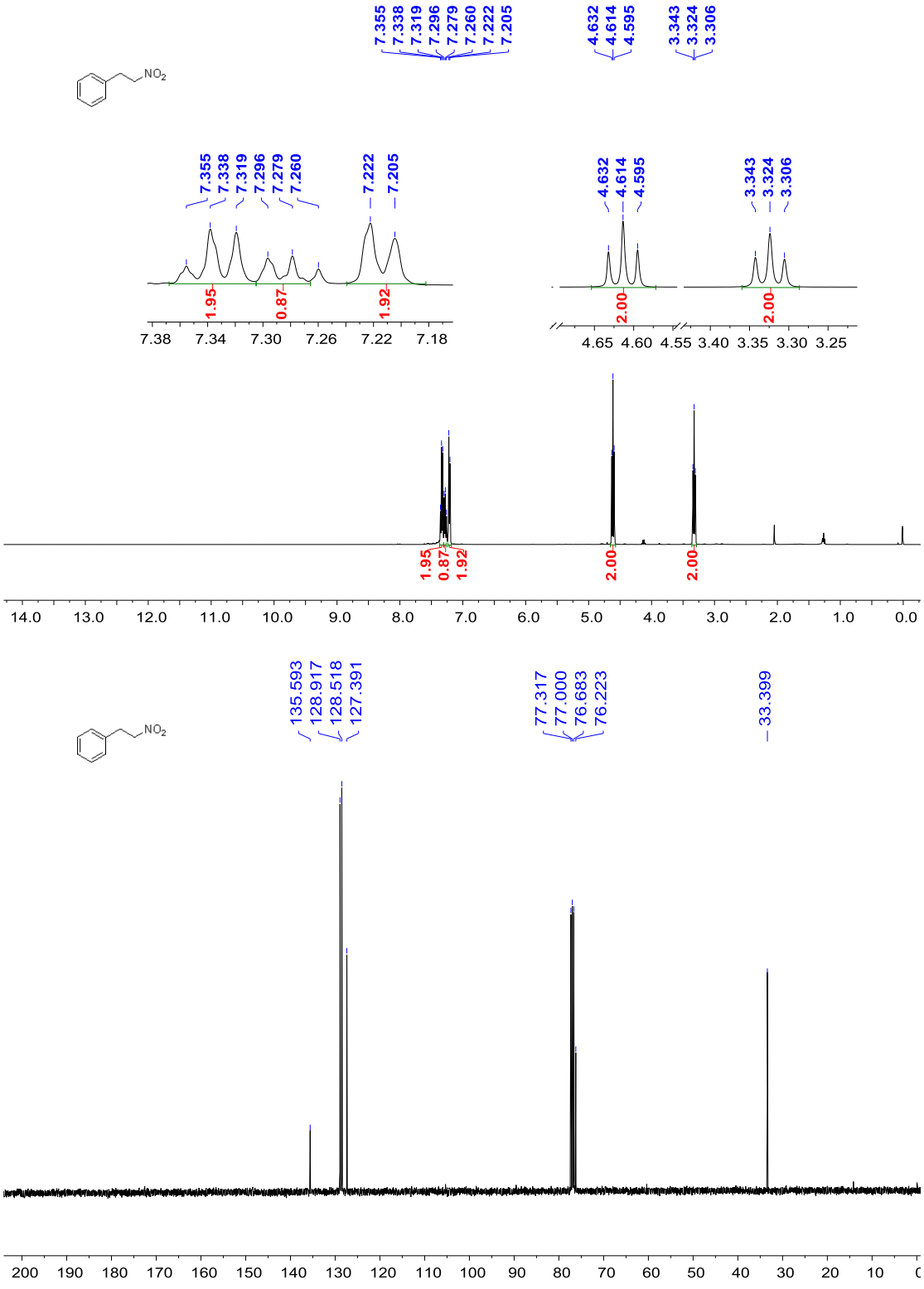
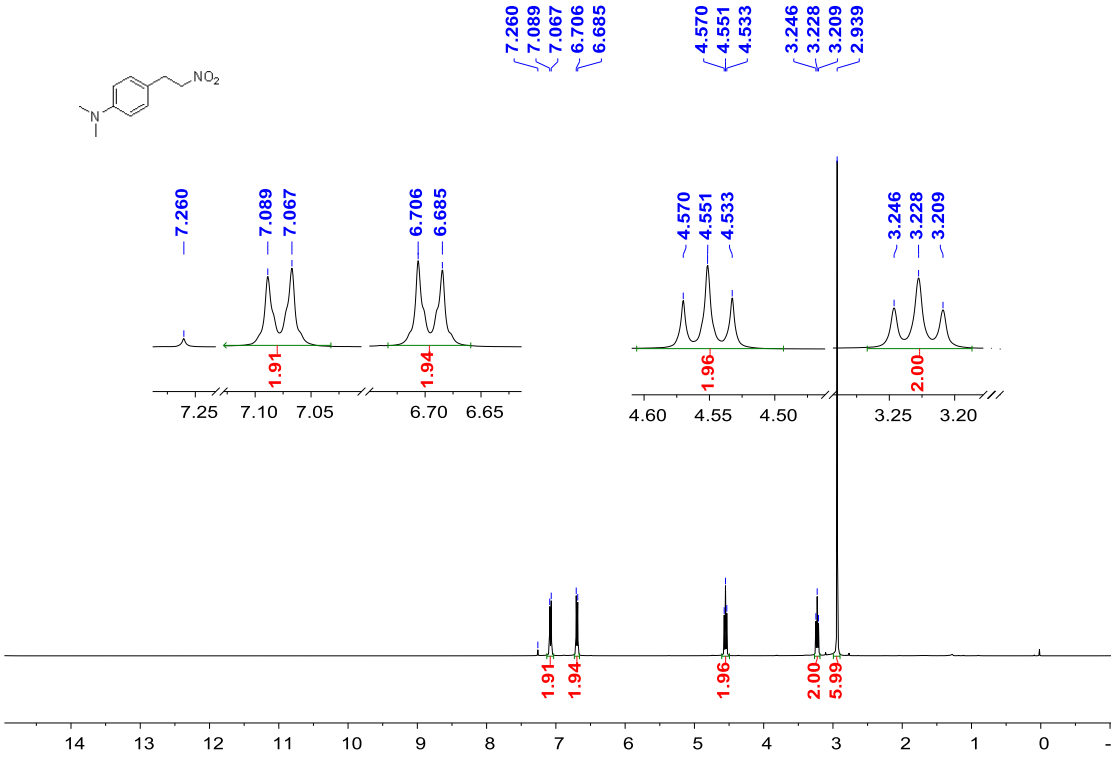
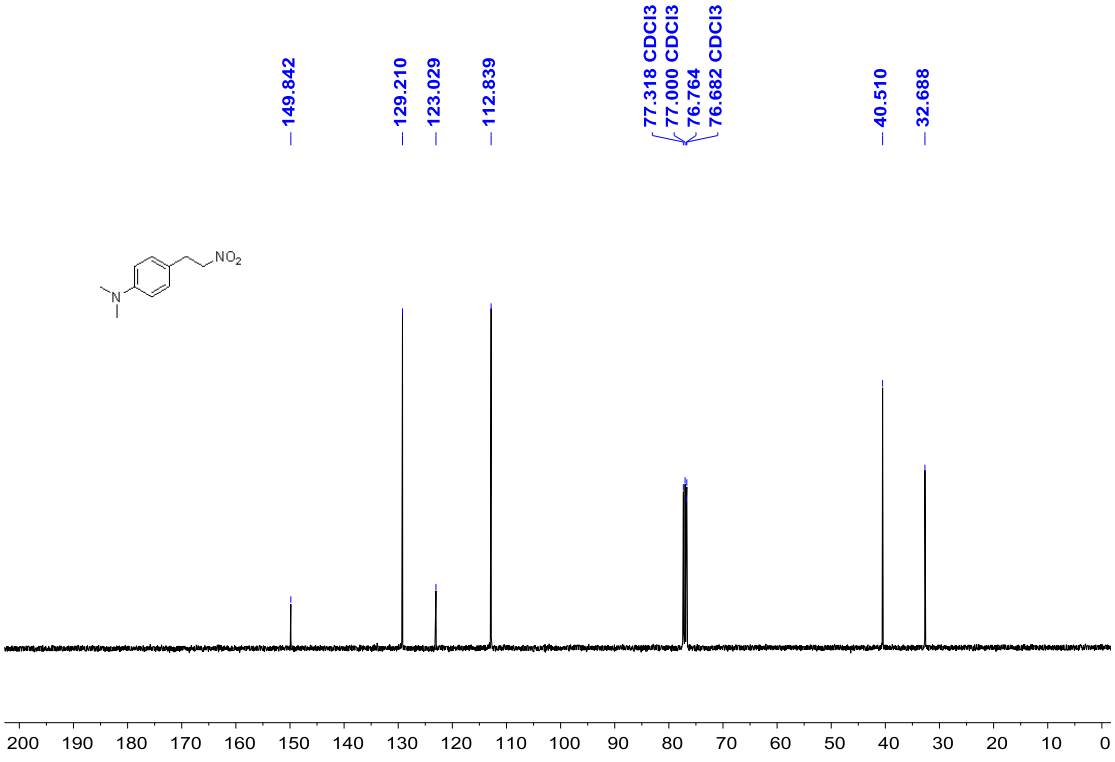
730.7233
741.0392
754.1343
760.3112
m/z
605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760

(2-Nitroethyl)benzene (2a):

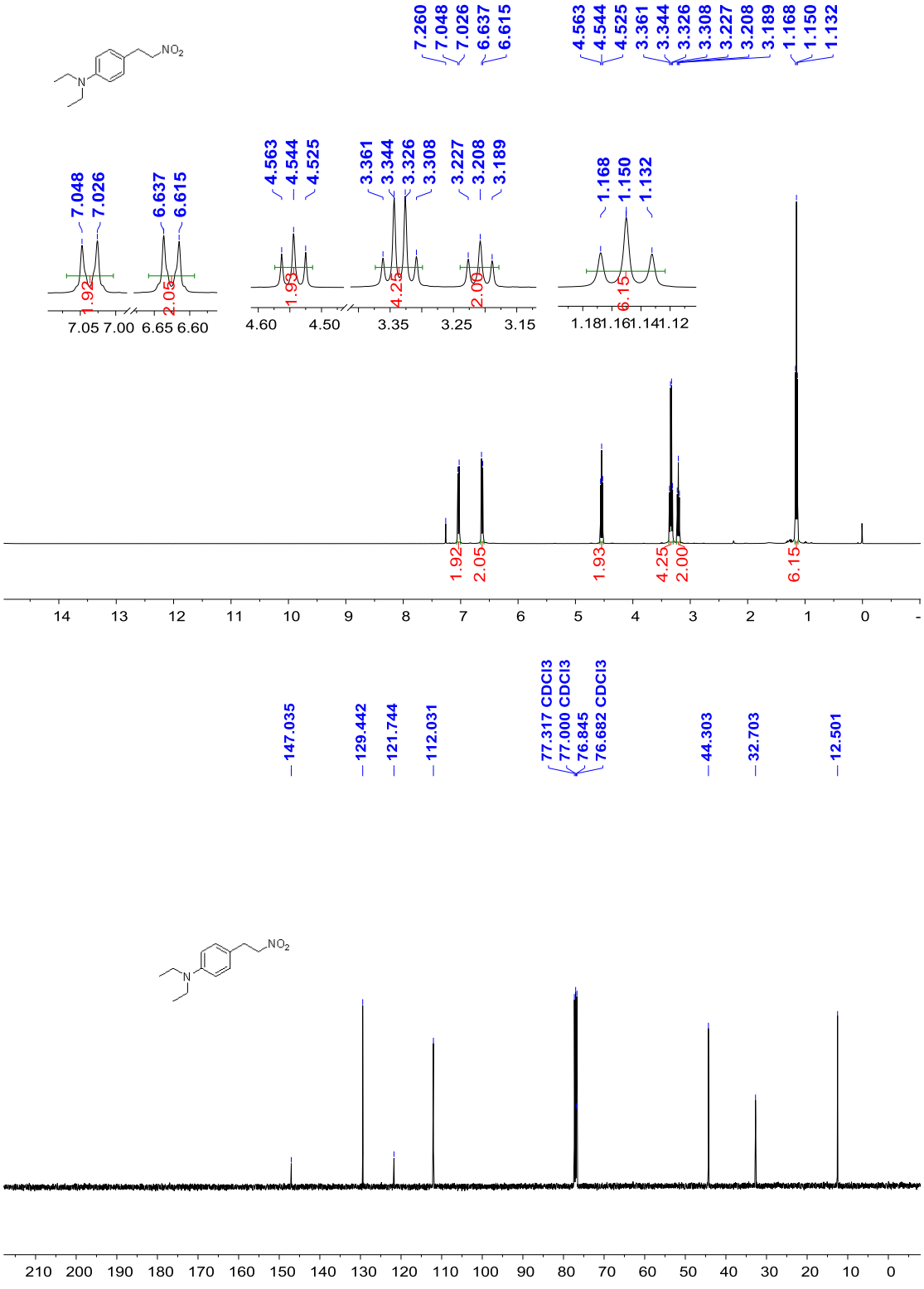


***N, N*-Dimethyl-4-(2-nitroethyl)aniline (2b):**

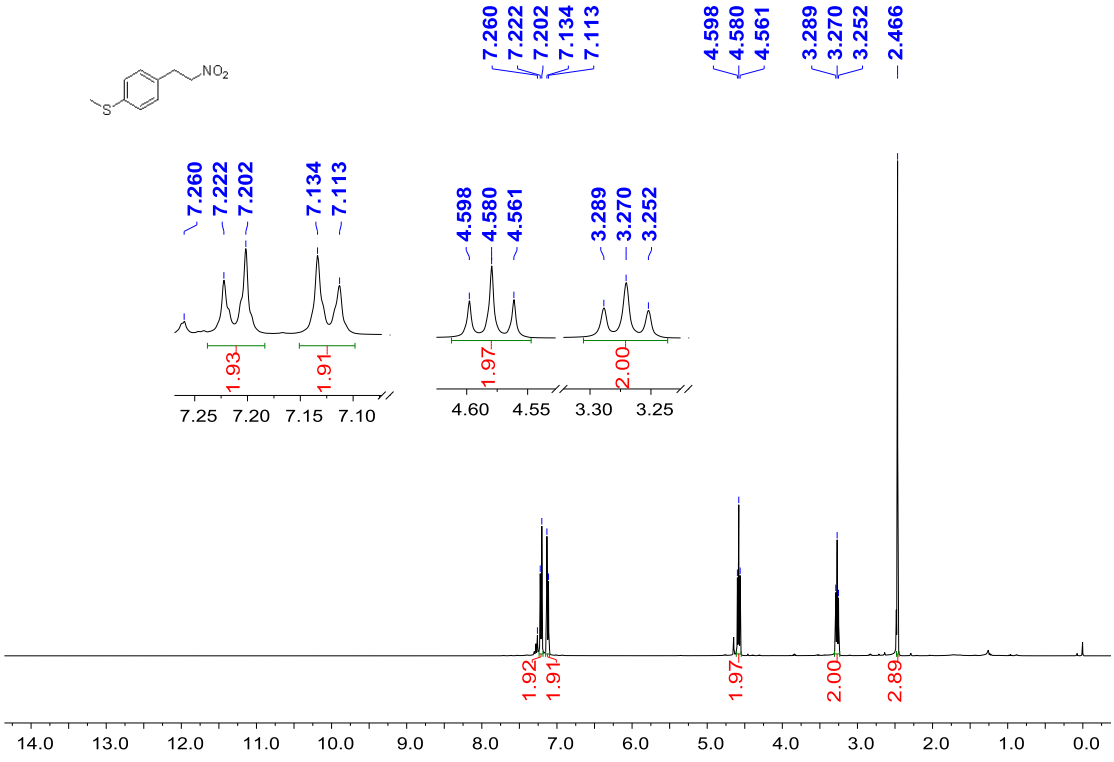


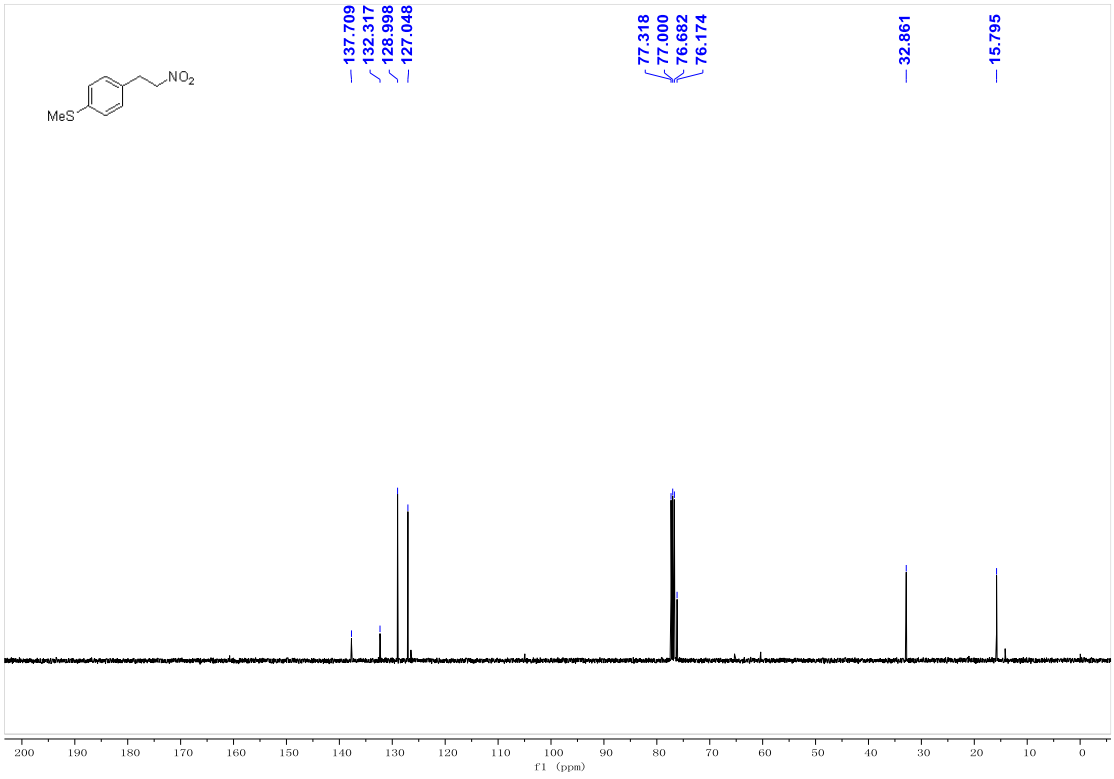


***N, N*-Diethyl-4-(2-nitroethyl)aniline (2c):**

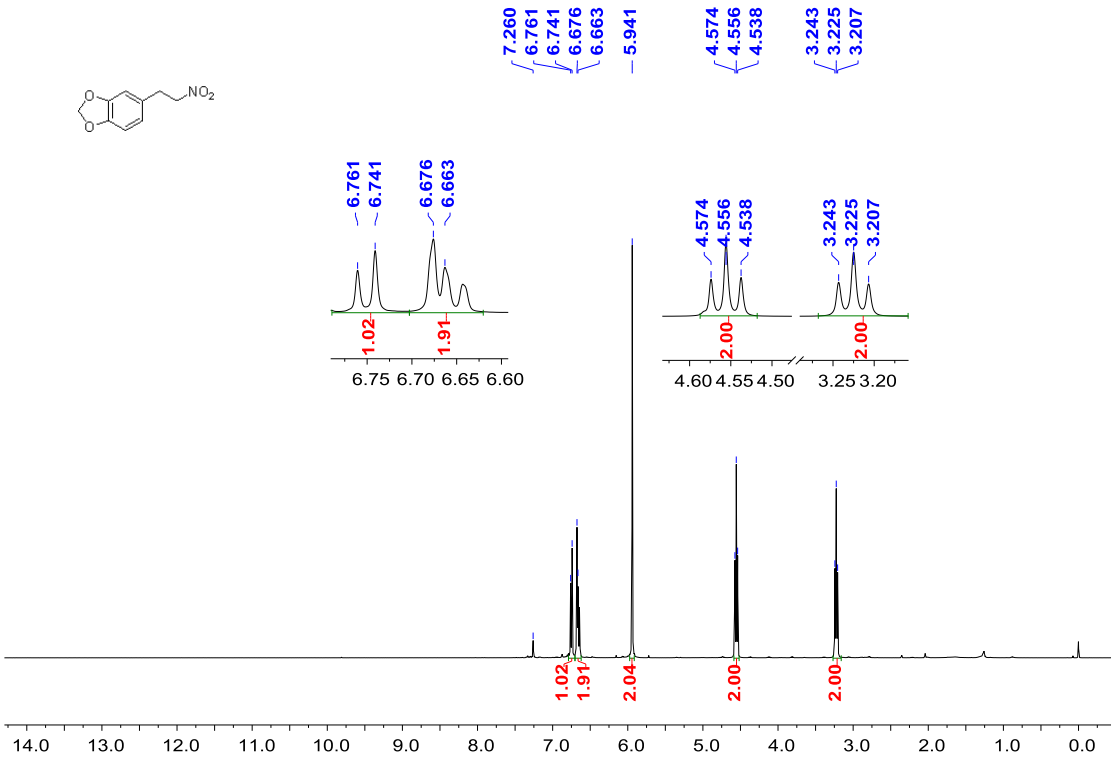


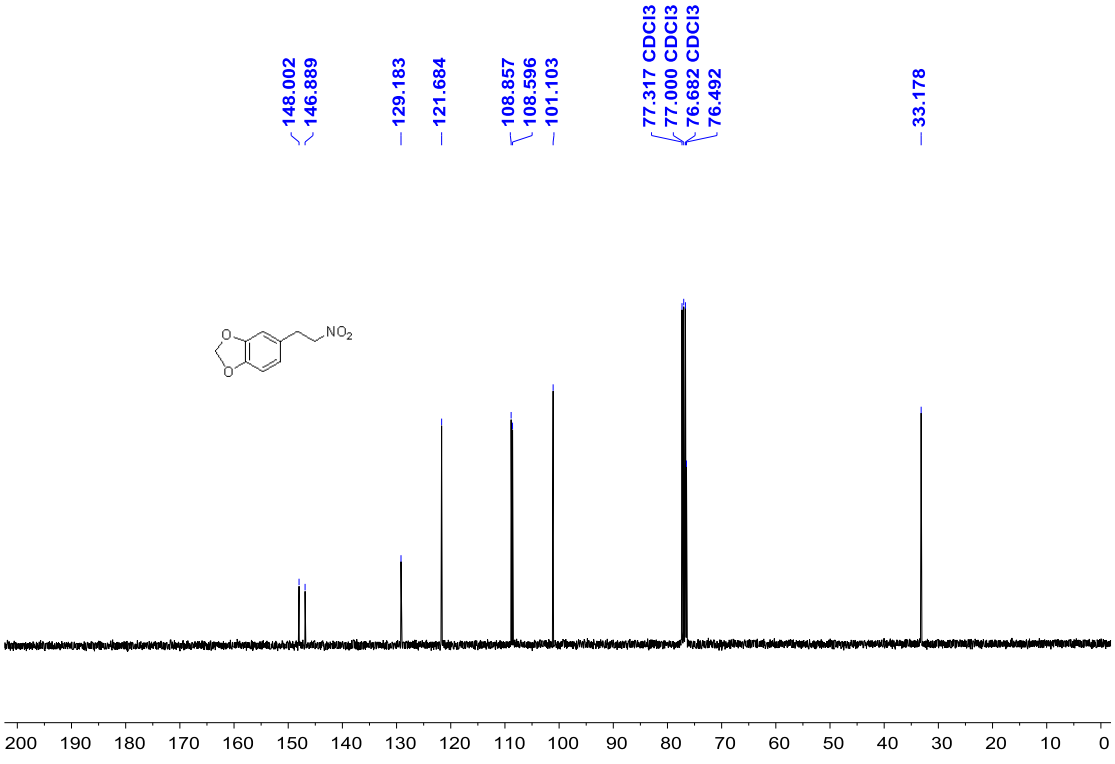
Methyl(4-(2-nitroethyl)phenyl)sulfane (2d):



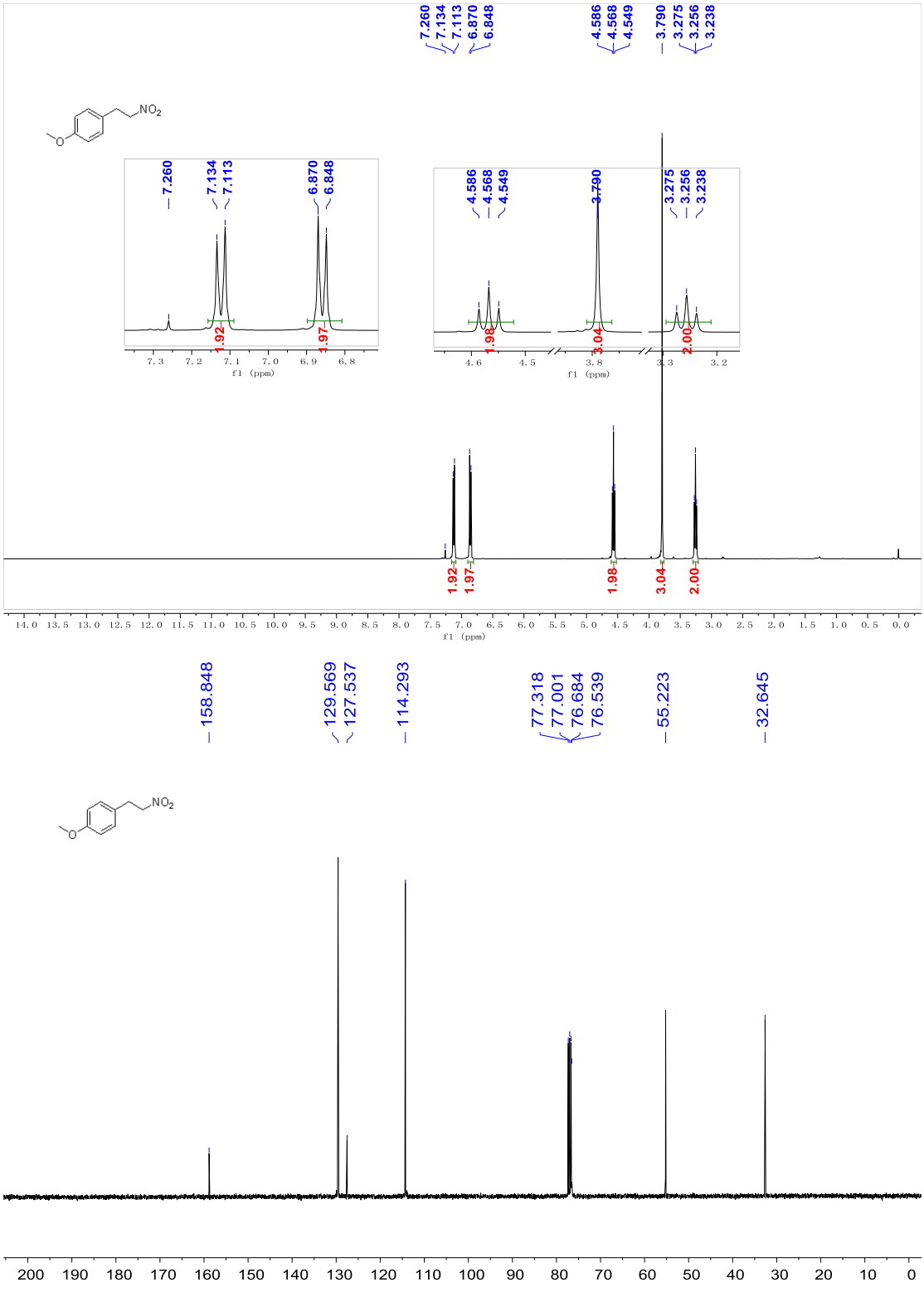


5-(2-Nitroethyl)benzo[d][1,3]dioxole (2e):

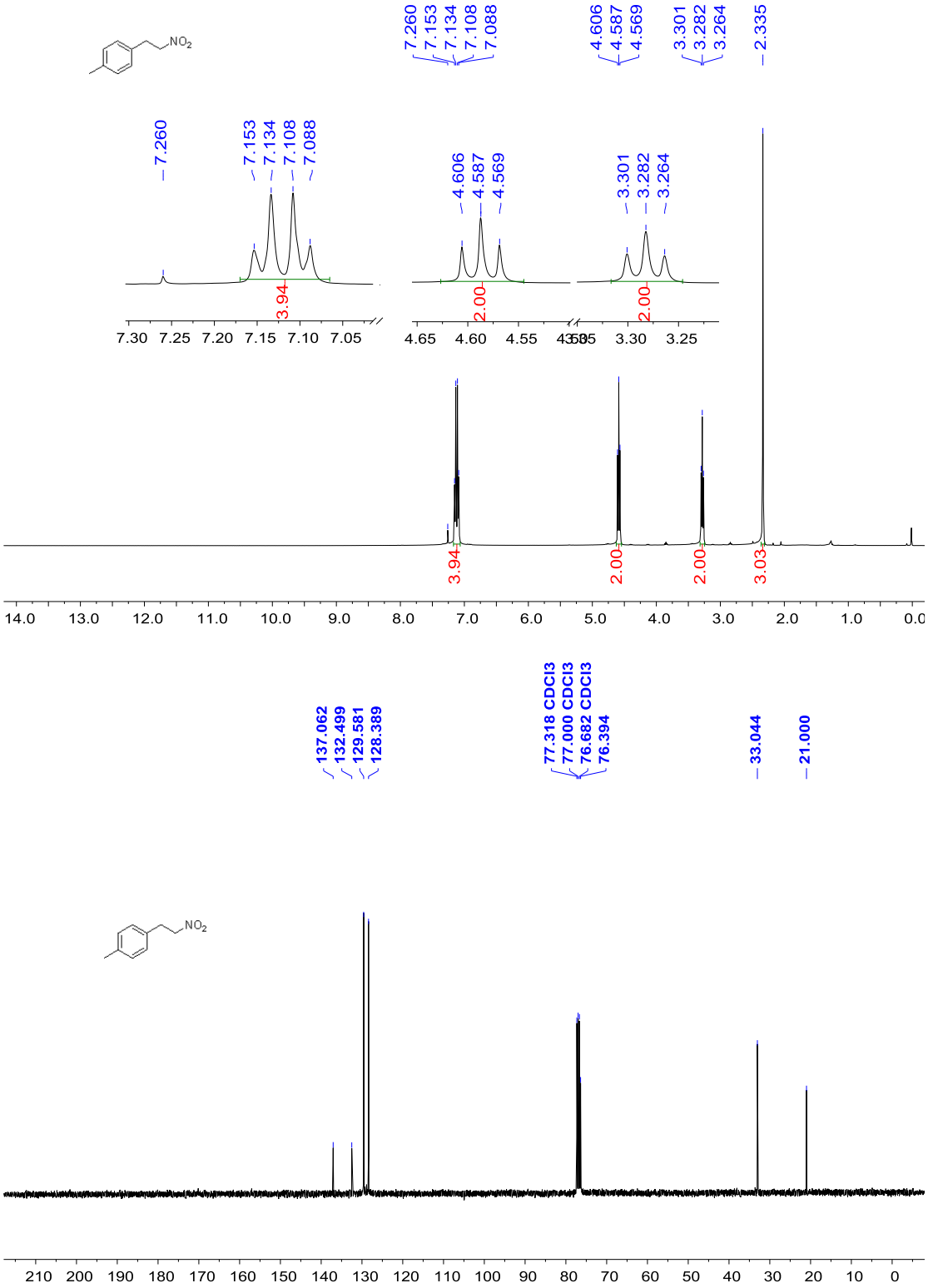




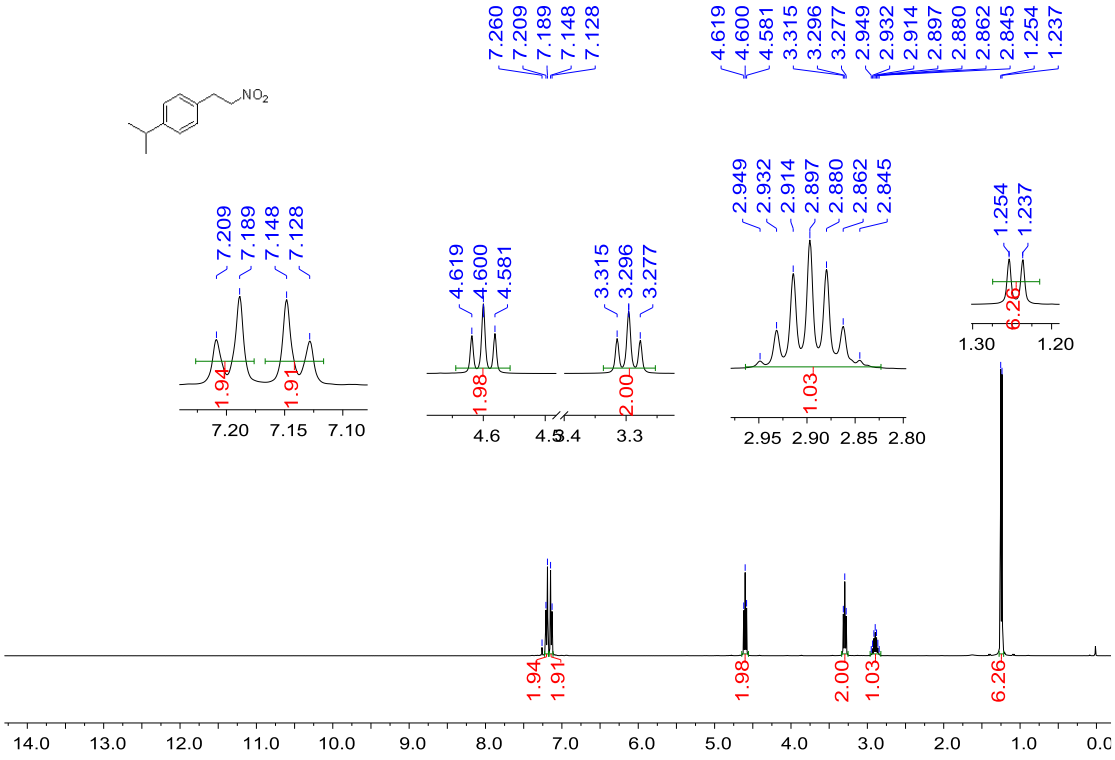
1-Methoxy-4-(2-nitroethyl)benzene (2f):

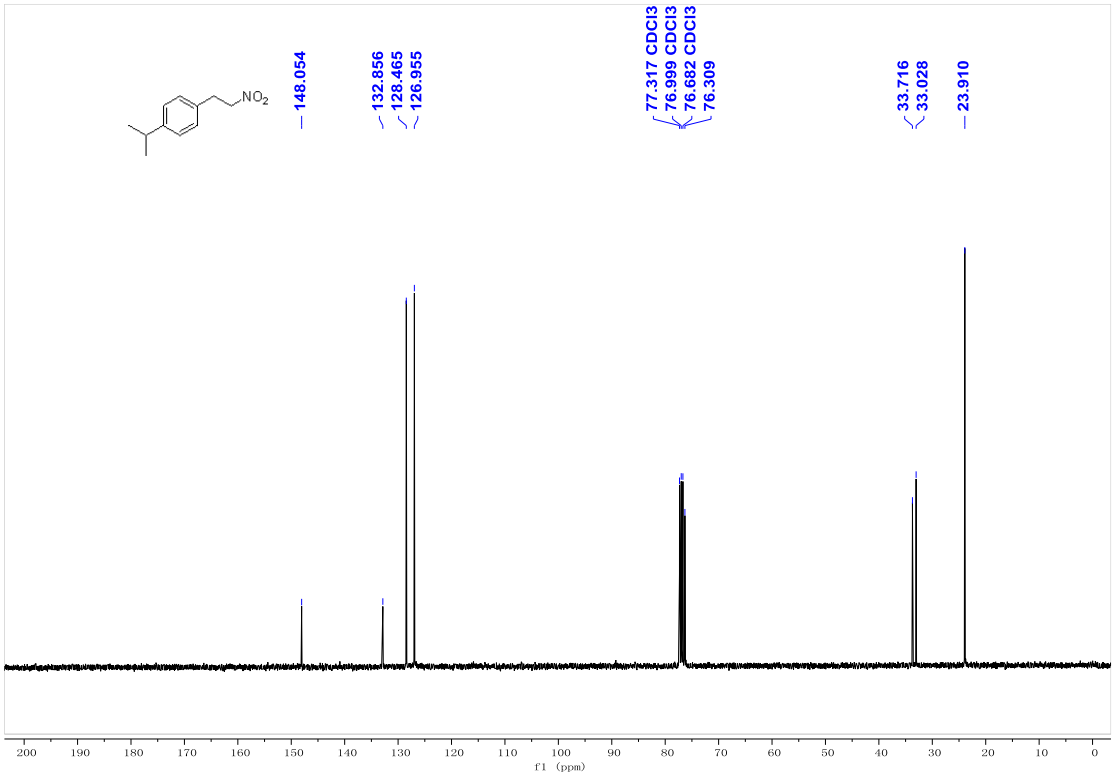


1-Methyl-4-(2-nitroethyl)benzene (2g):

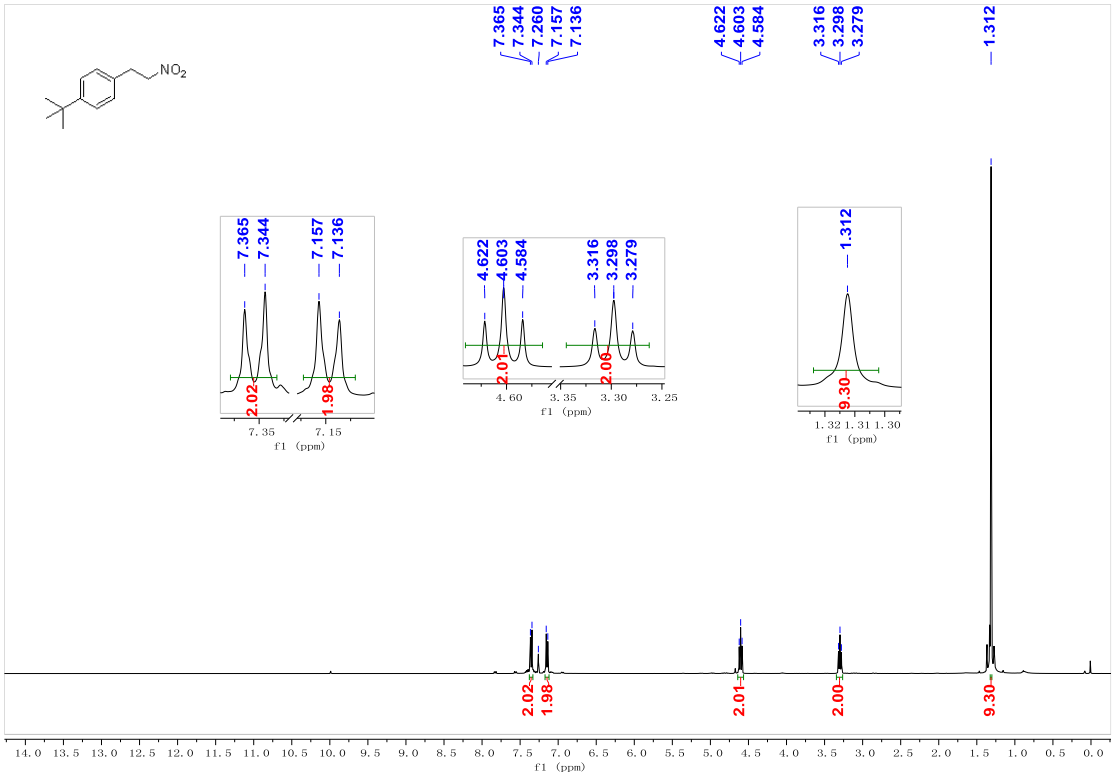


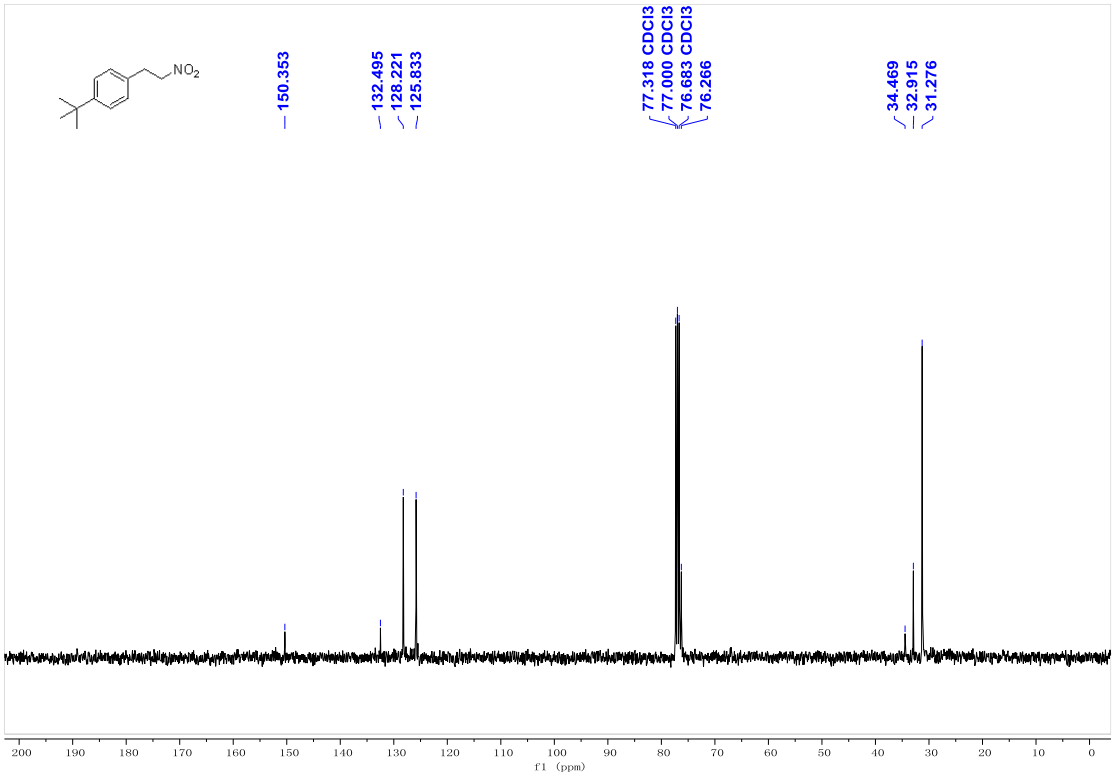
1-Isopropyl-4-(2-nitroethyl)benzene (2h):



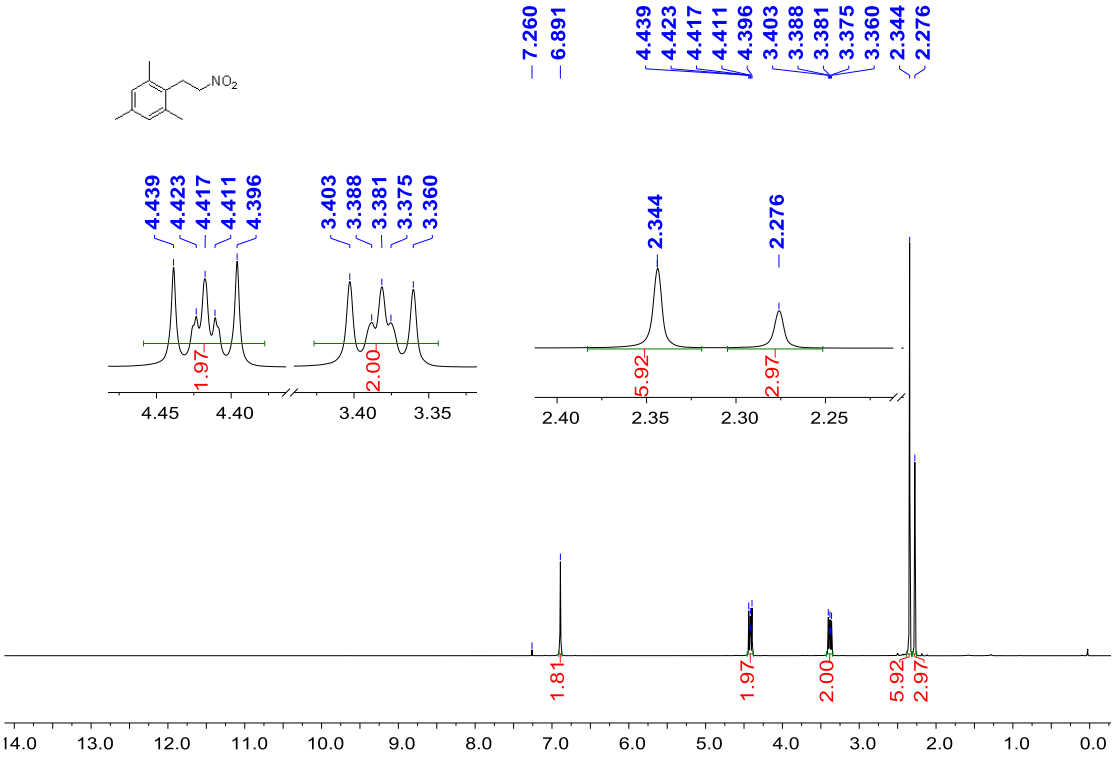


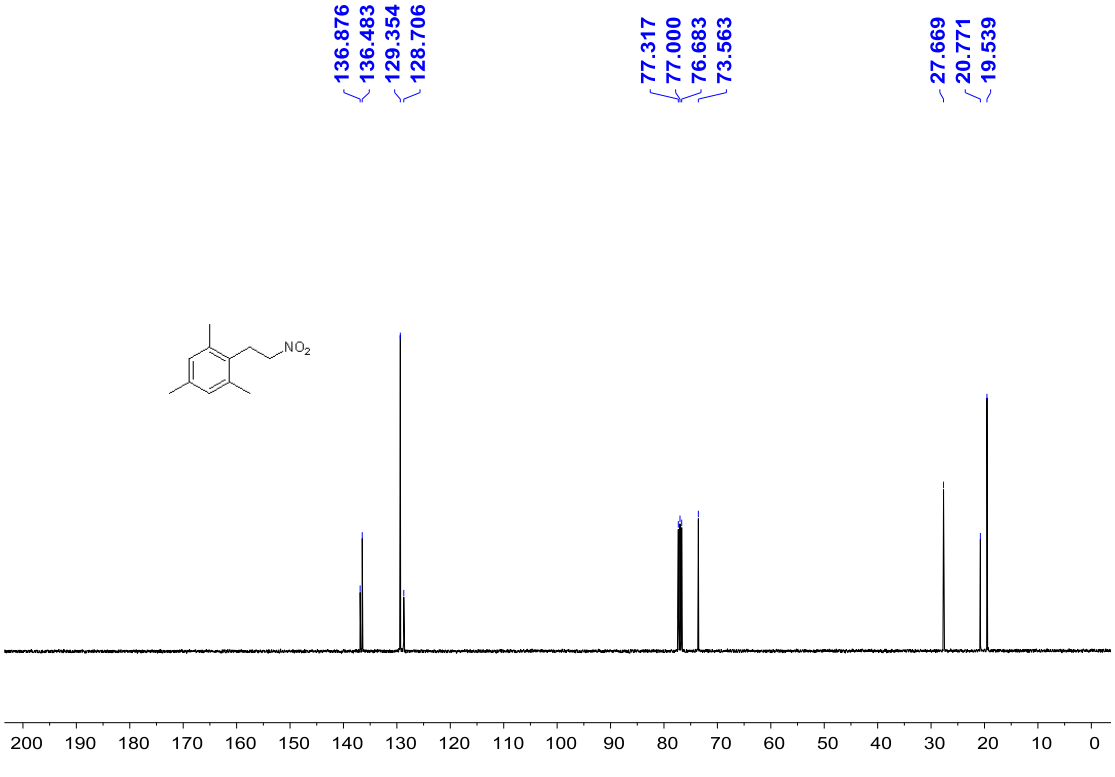
1-(Tert-butyl)-4-(2-nitroethyl)benzene (2i):



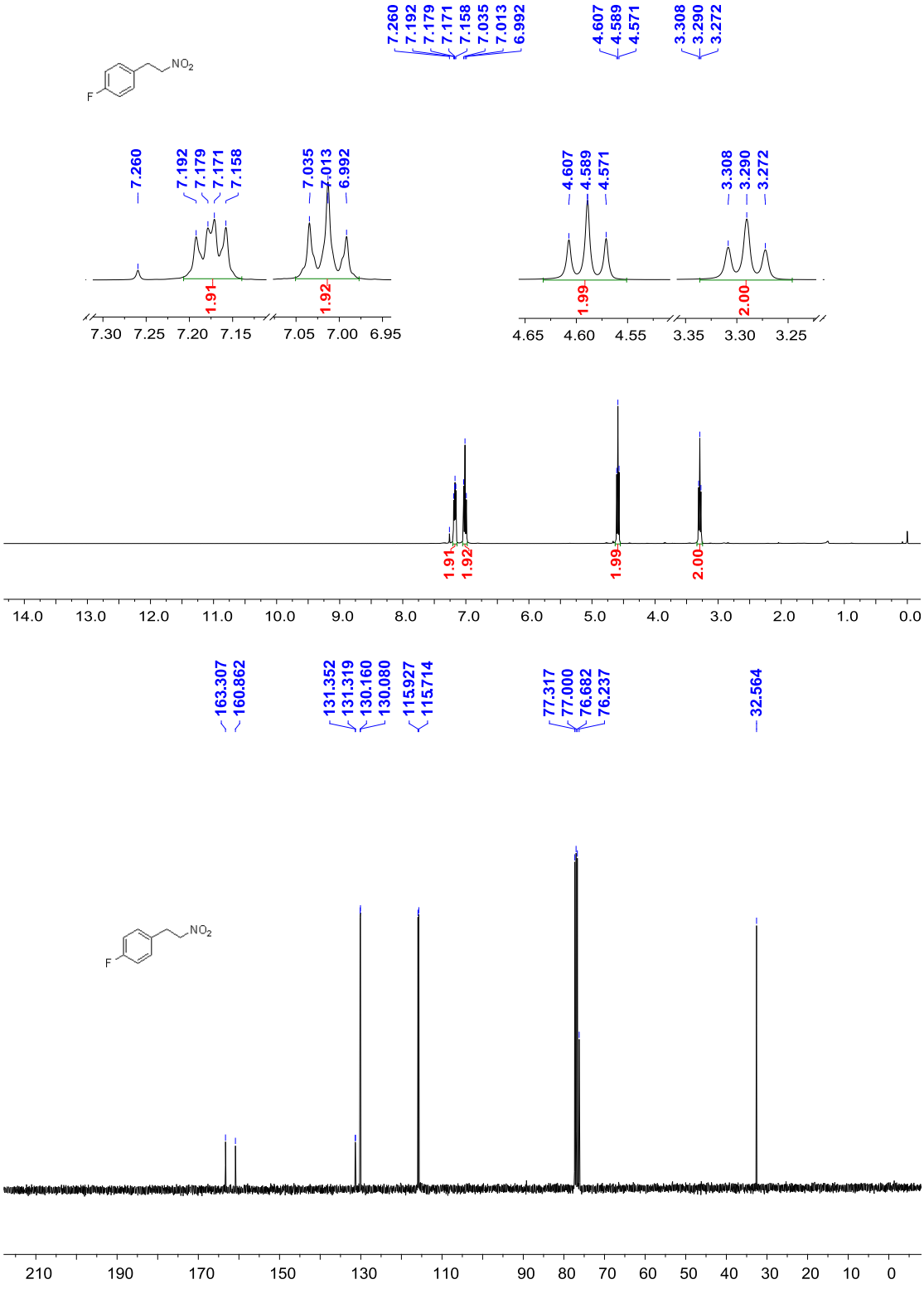


1,3,5-Trimethyl-2-(2-nitroethyl)benzene (2j):

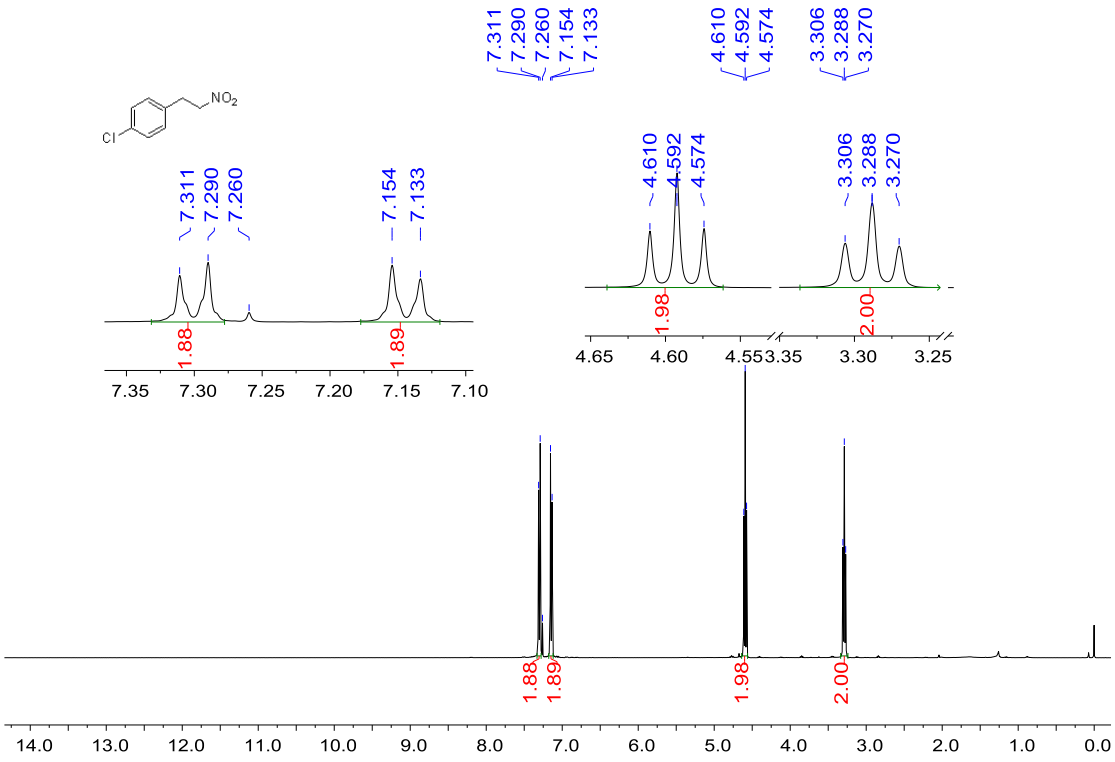


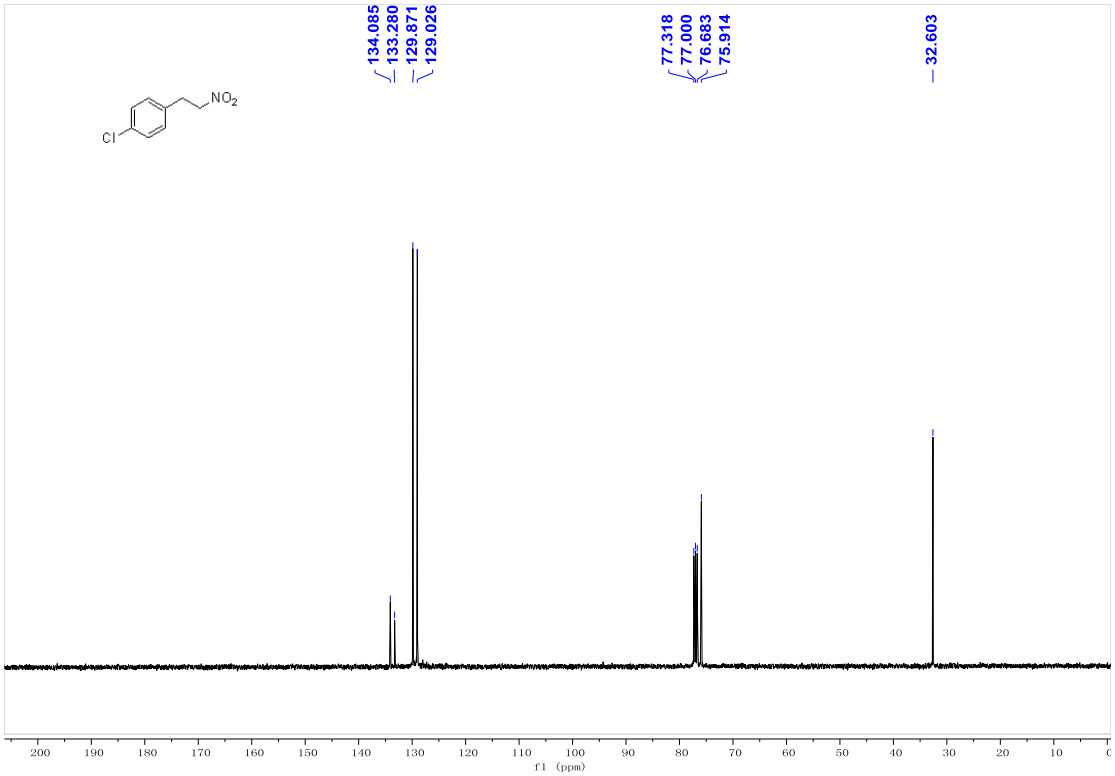


1-Fluoro-4-(2-nitroethyl)benzene (2k):

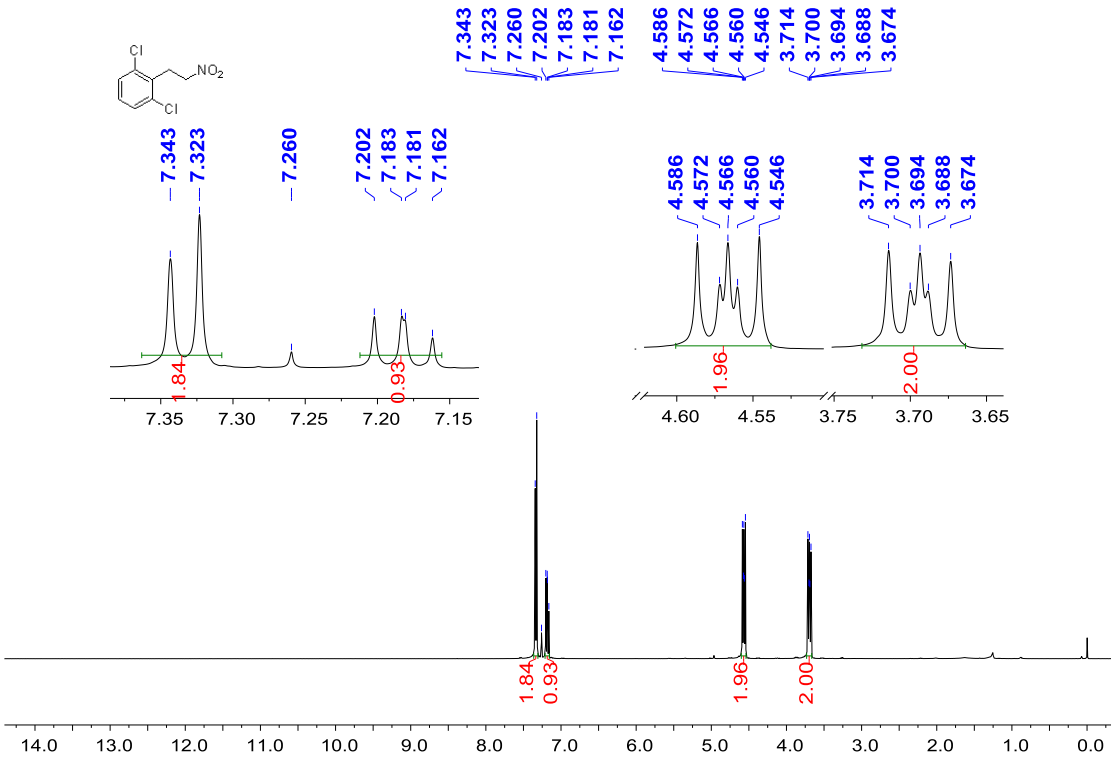


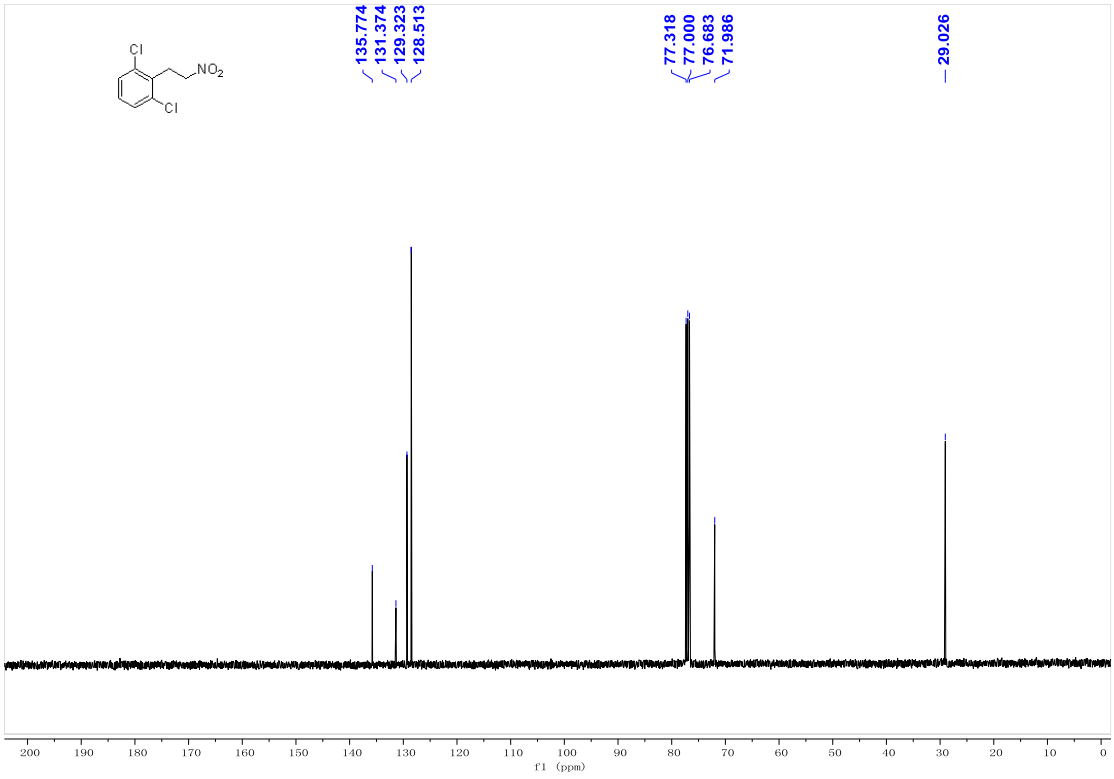
1-Chloro-4-(2-nitroethyl)benzene (2l):



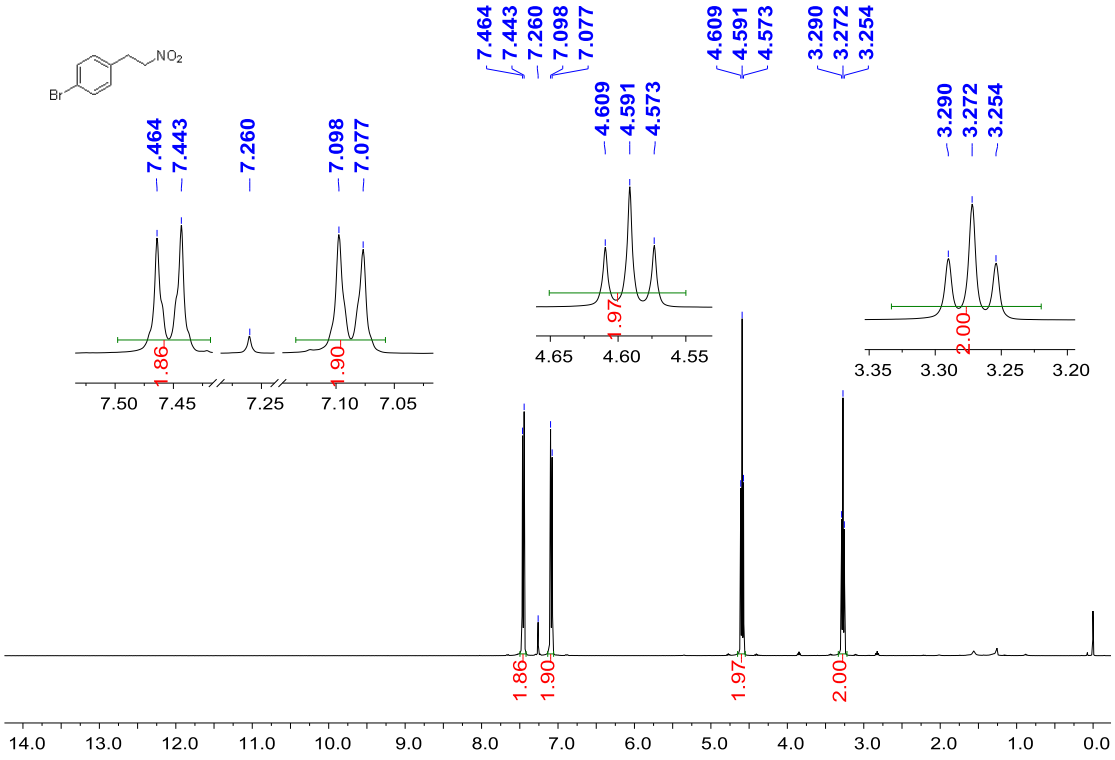


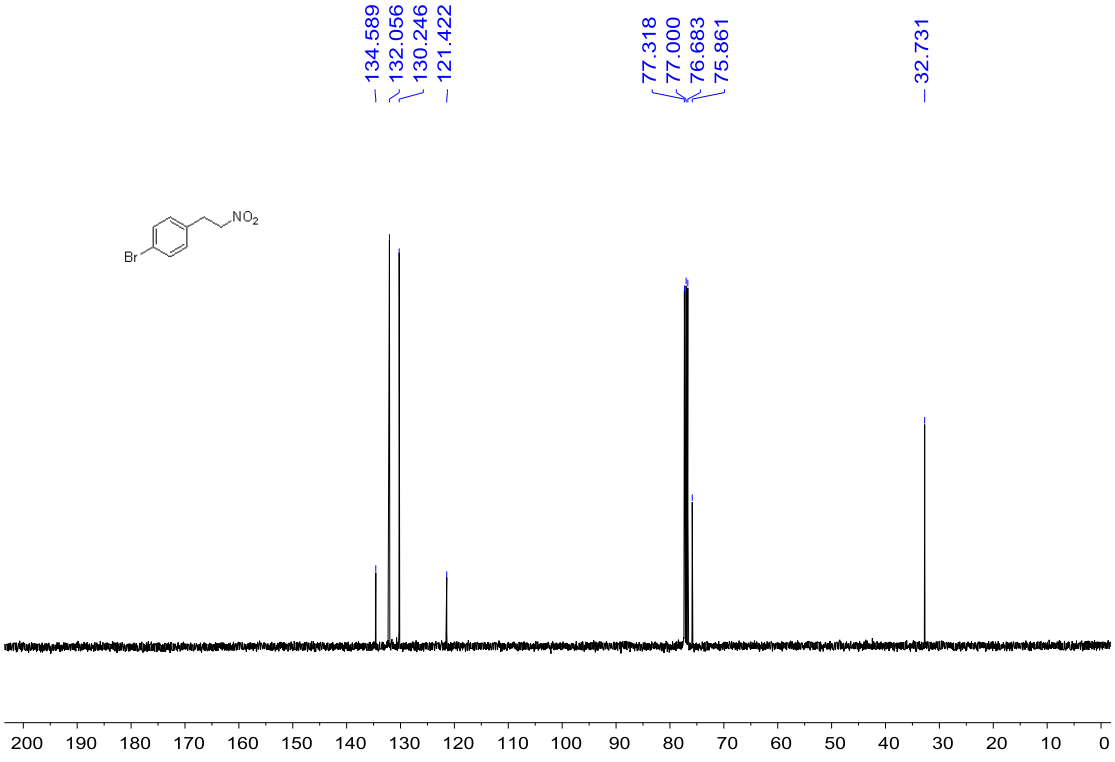
1,3-Dichloro-2-(2-nitroethyl)benzene (2m):



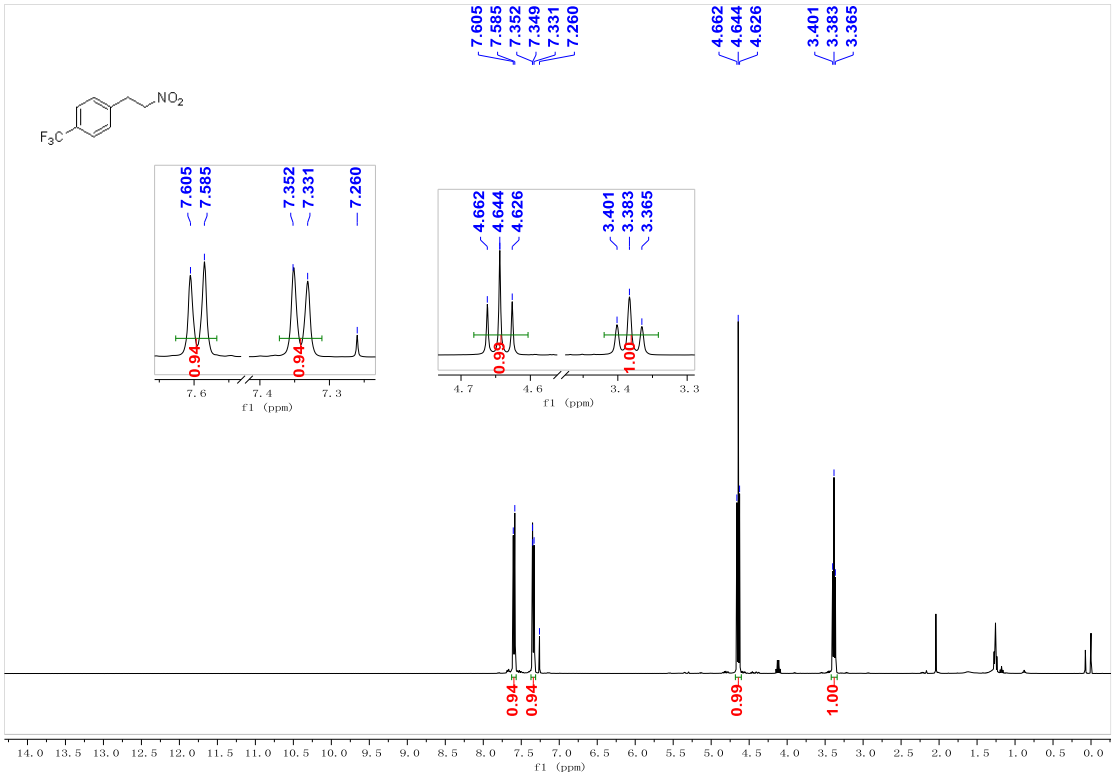


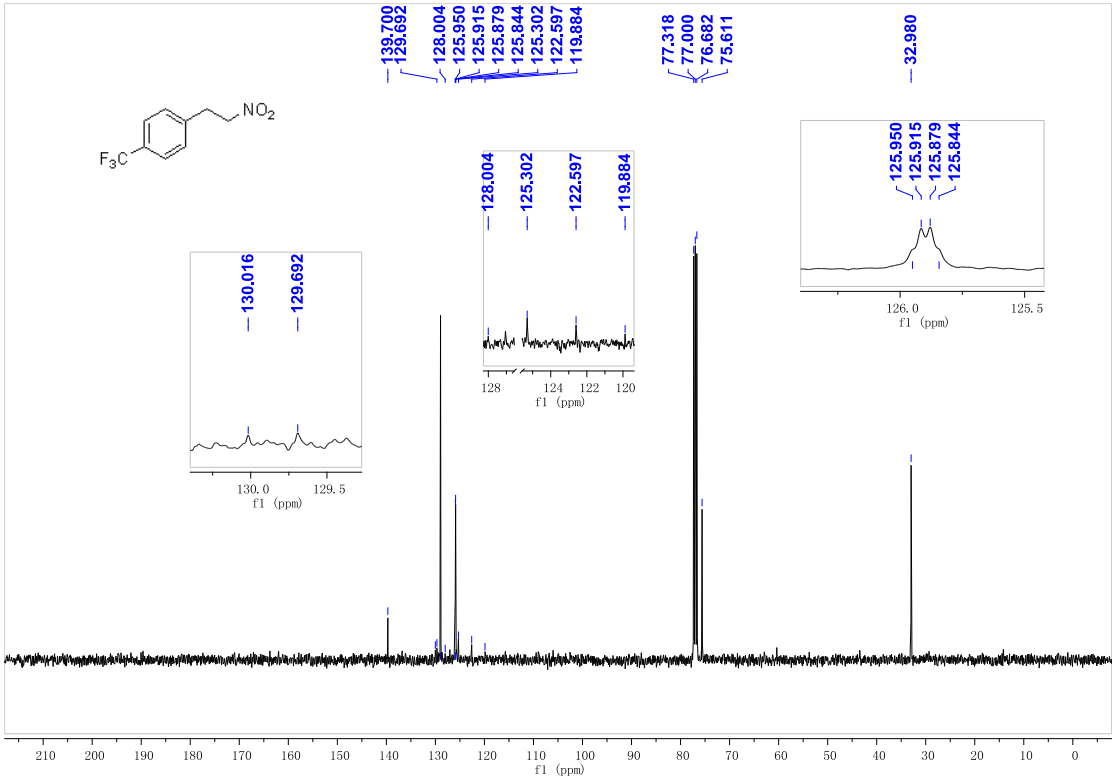
1-Bromo-4-(2-nitroethyl)benzene (2n):



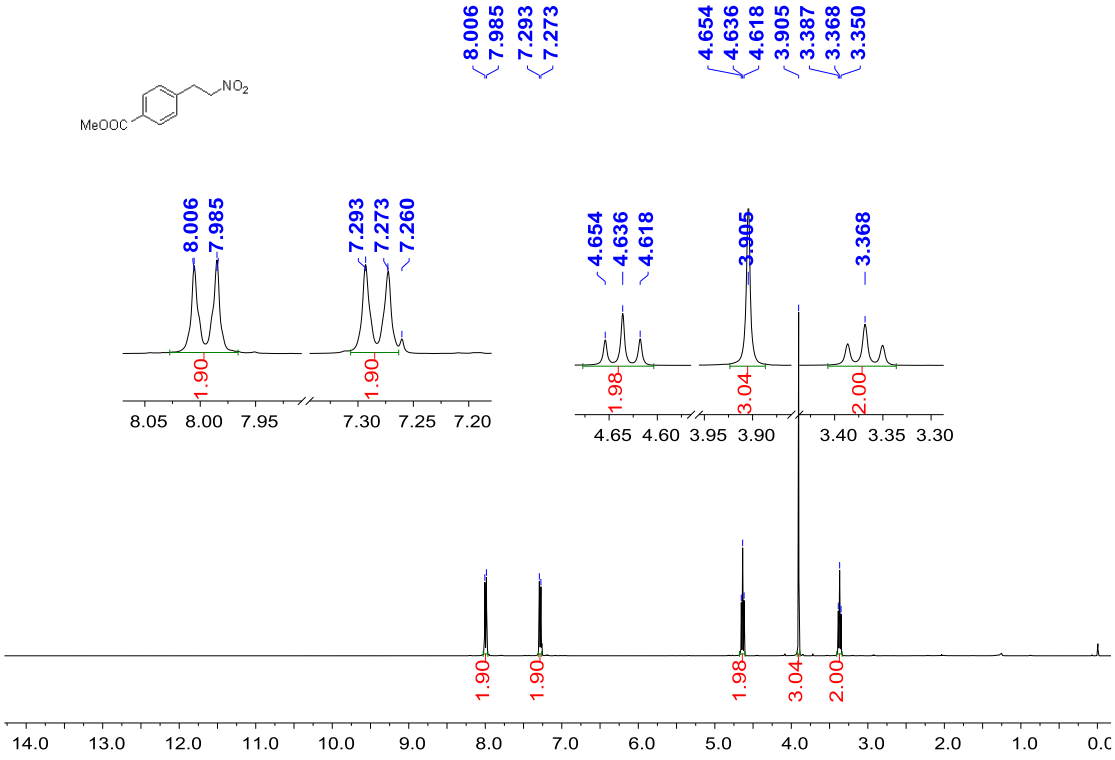


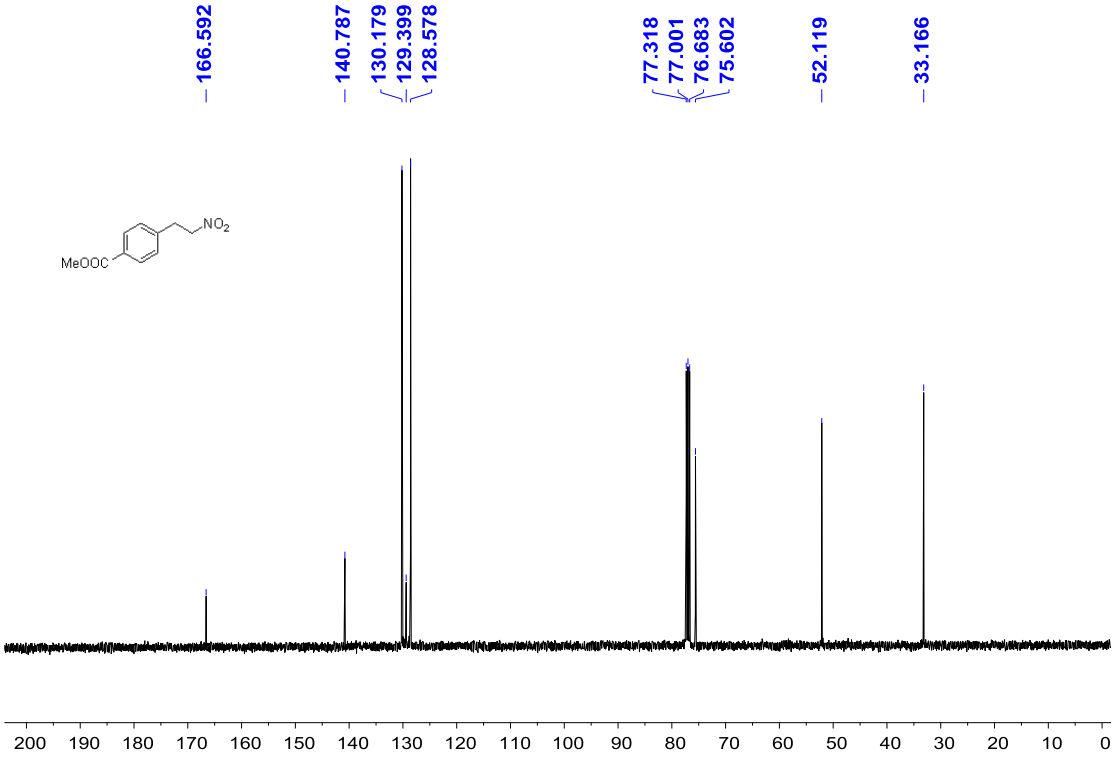
1-(2-Nitroethyl)-4-(trifluoromethyl)benzene (2o):



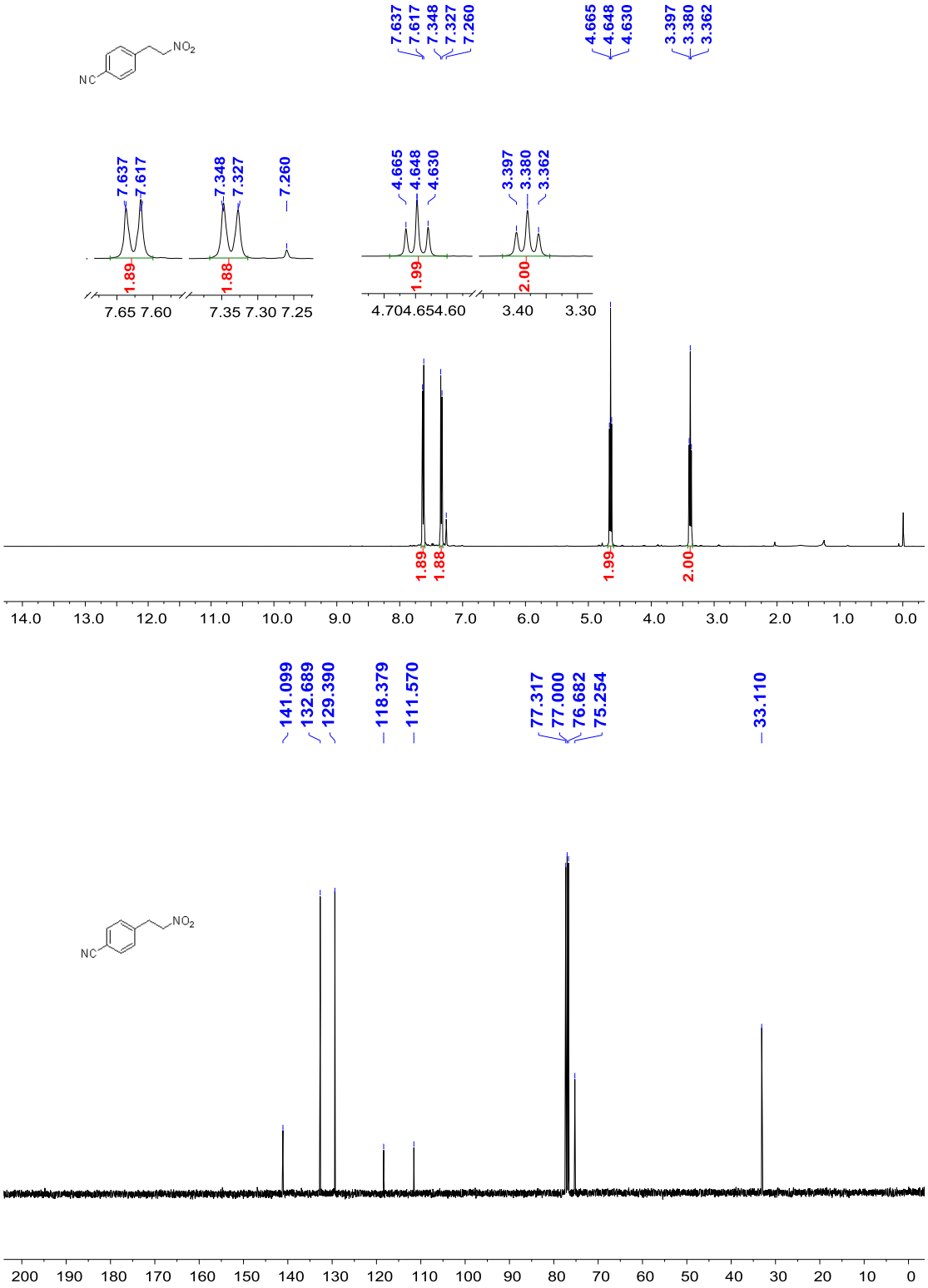


Methyl 4-(2-nitroethyl)benzoate (2p):

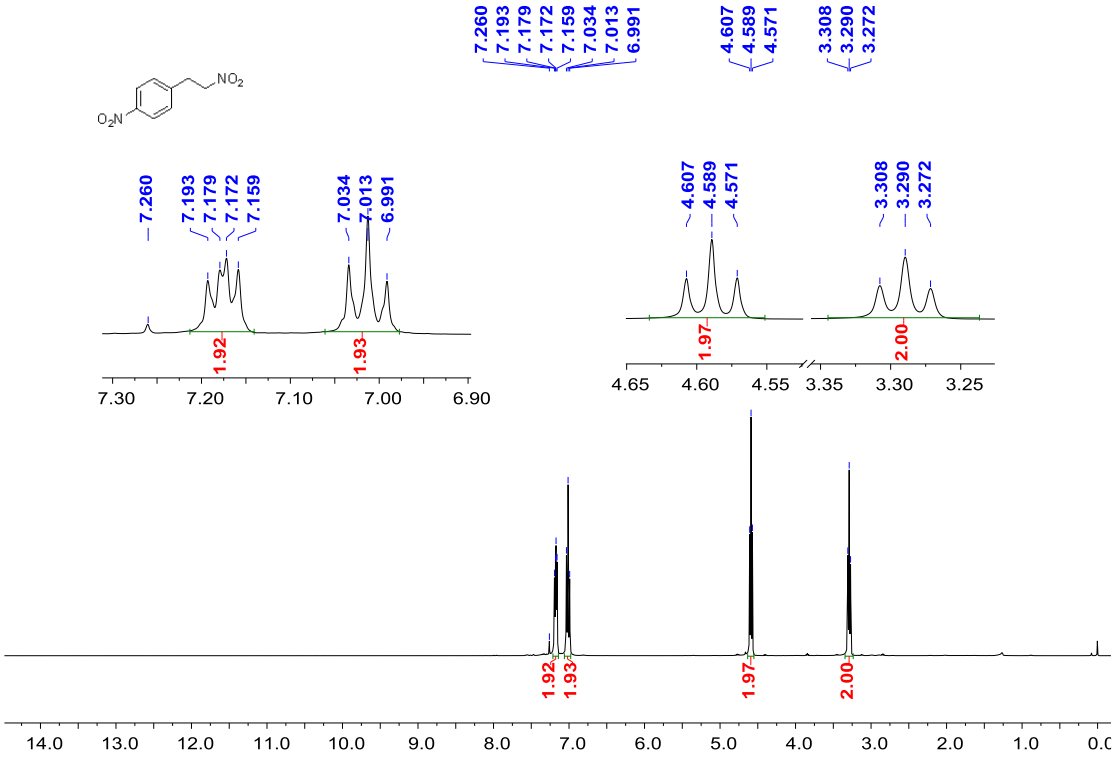


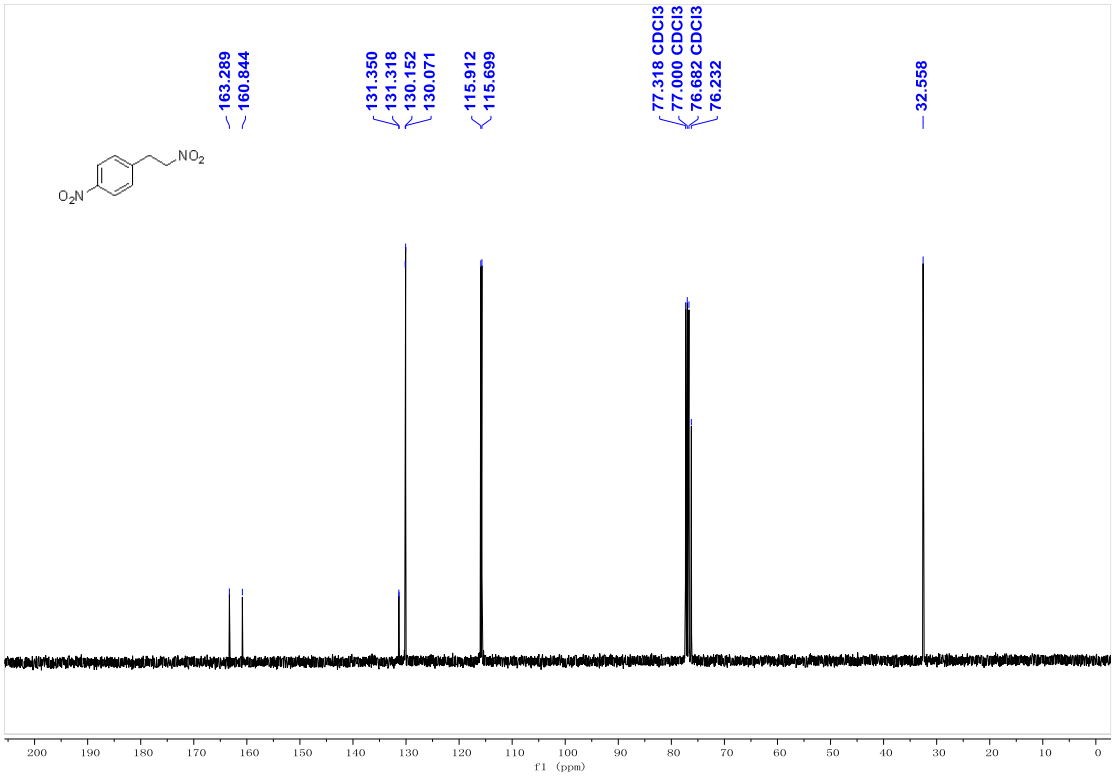


4-(2-Nitroethyl)benzonitrile (2q):

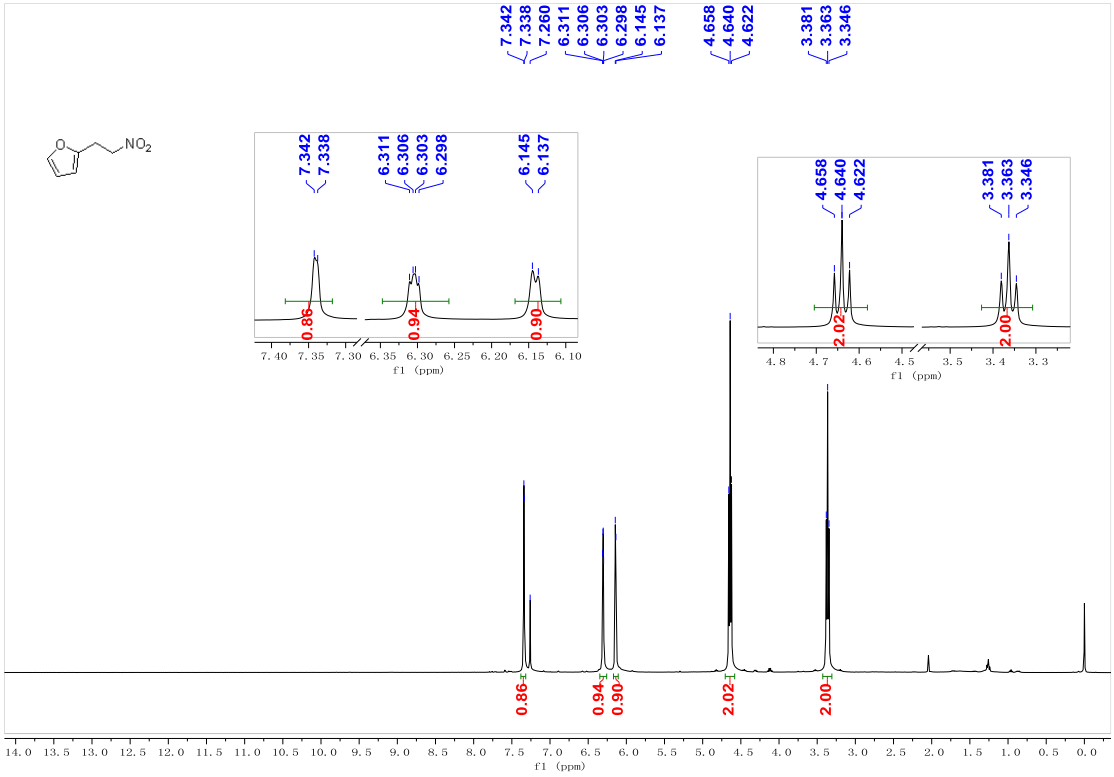


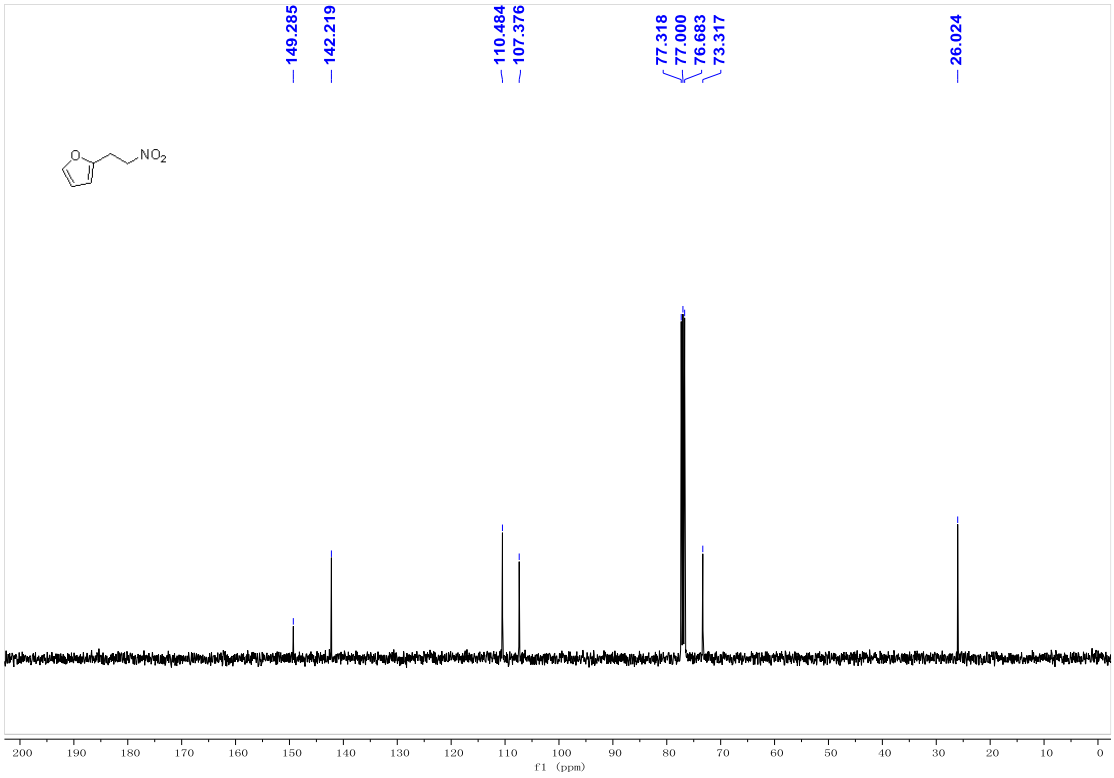
1-Nitro-4-(2-nitroethyl)benzene (2r):



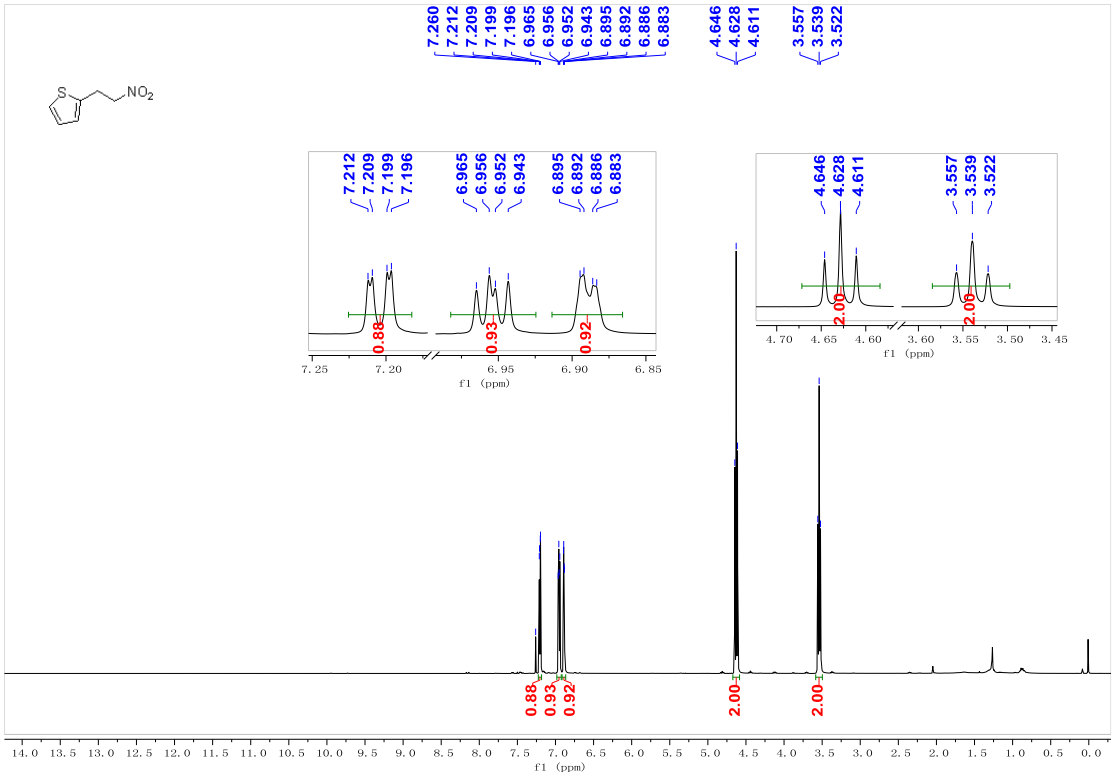


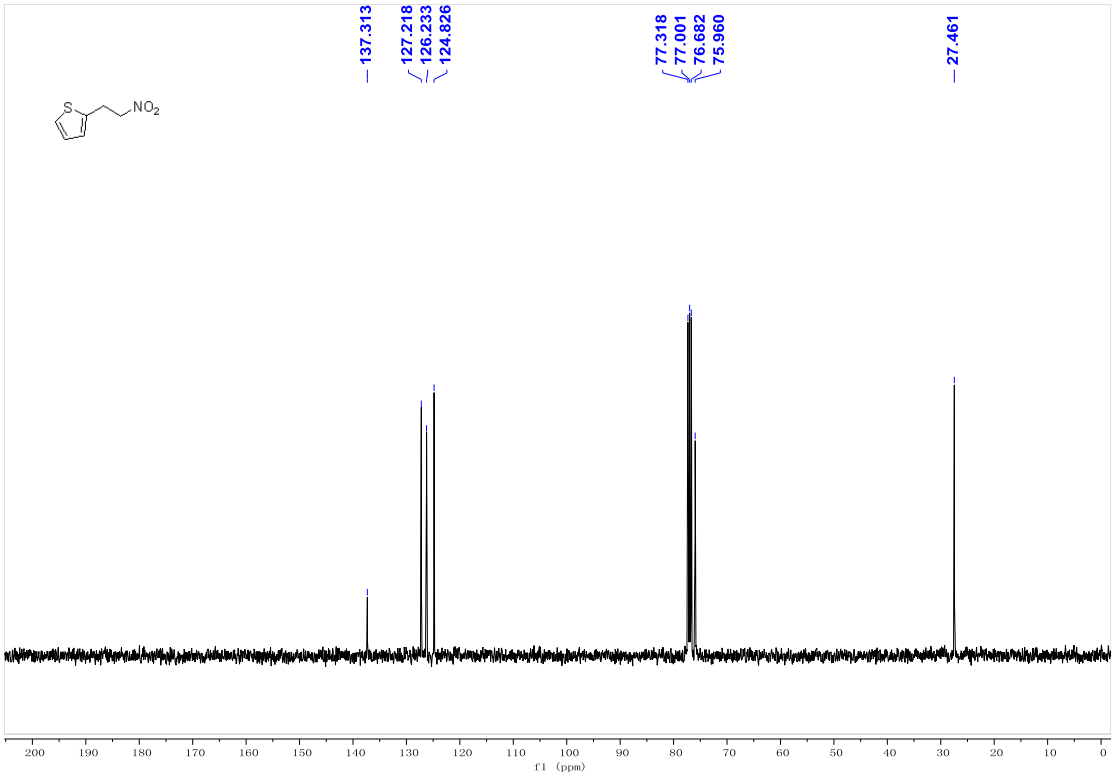
2-(2-Nitroethyl)furan (2s):



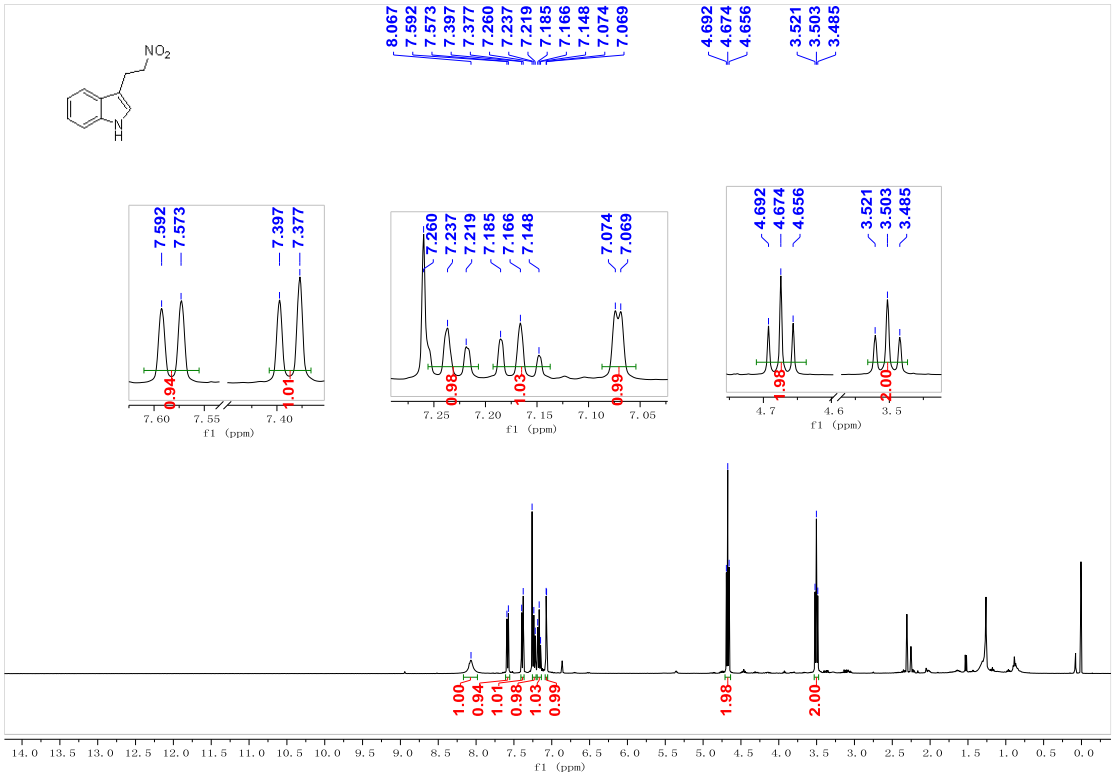


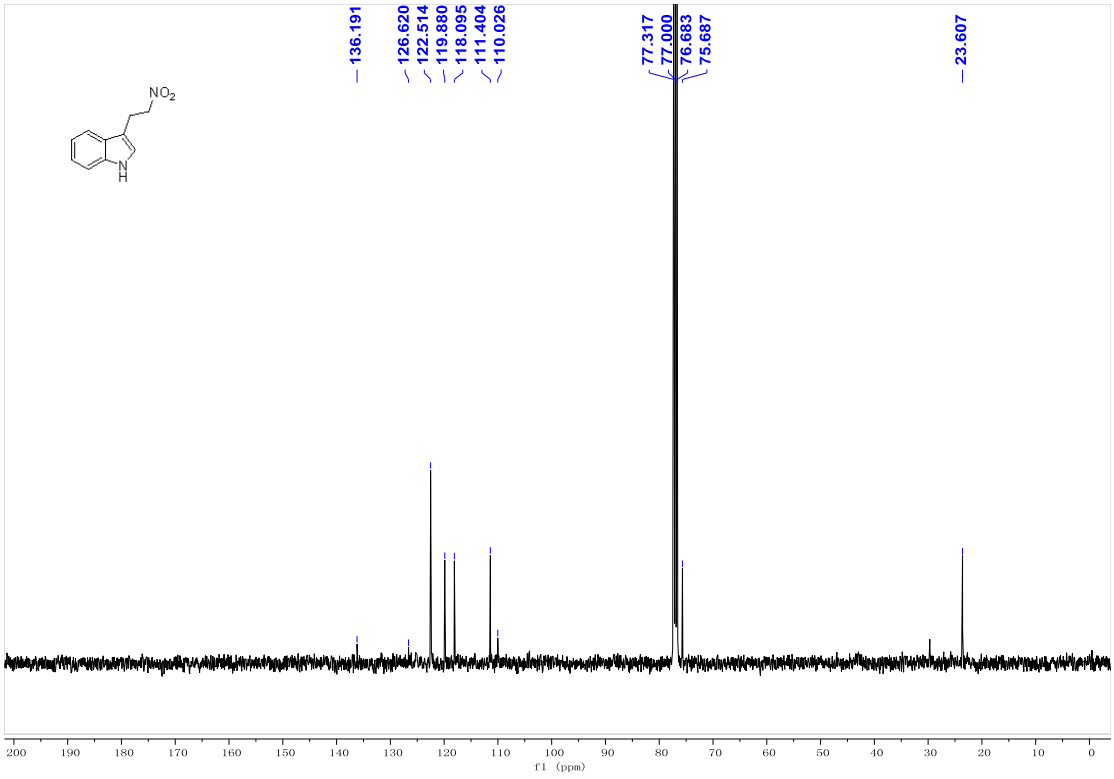
2-(2-Nitroethyl)thiophene (2t):



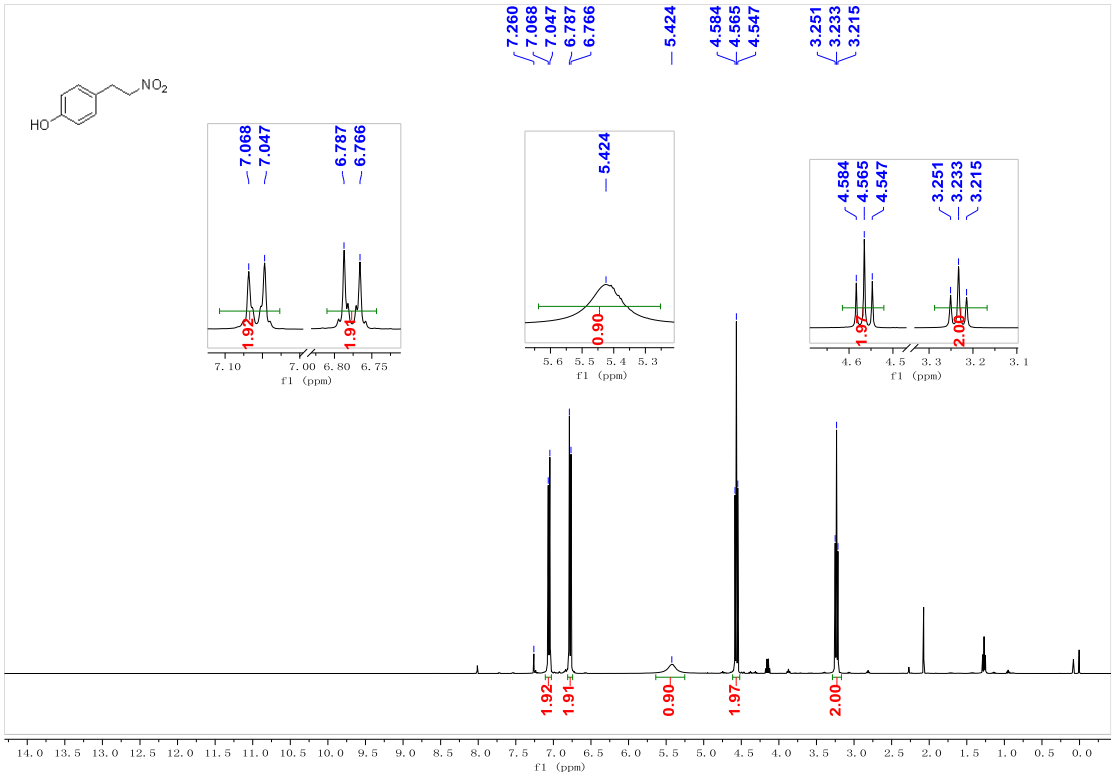


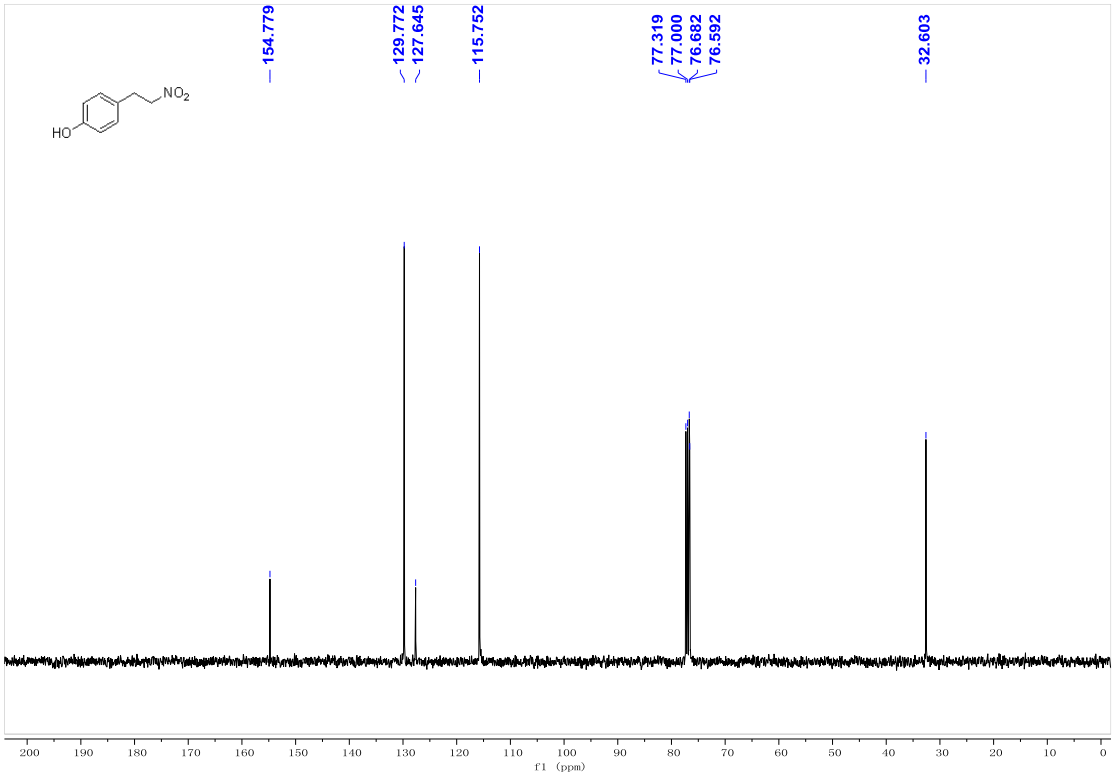
3-(2-Nitroethyl)-1H-indole (2u):



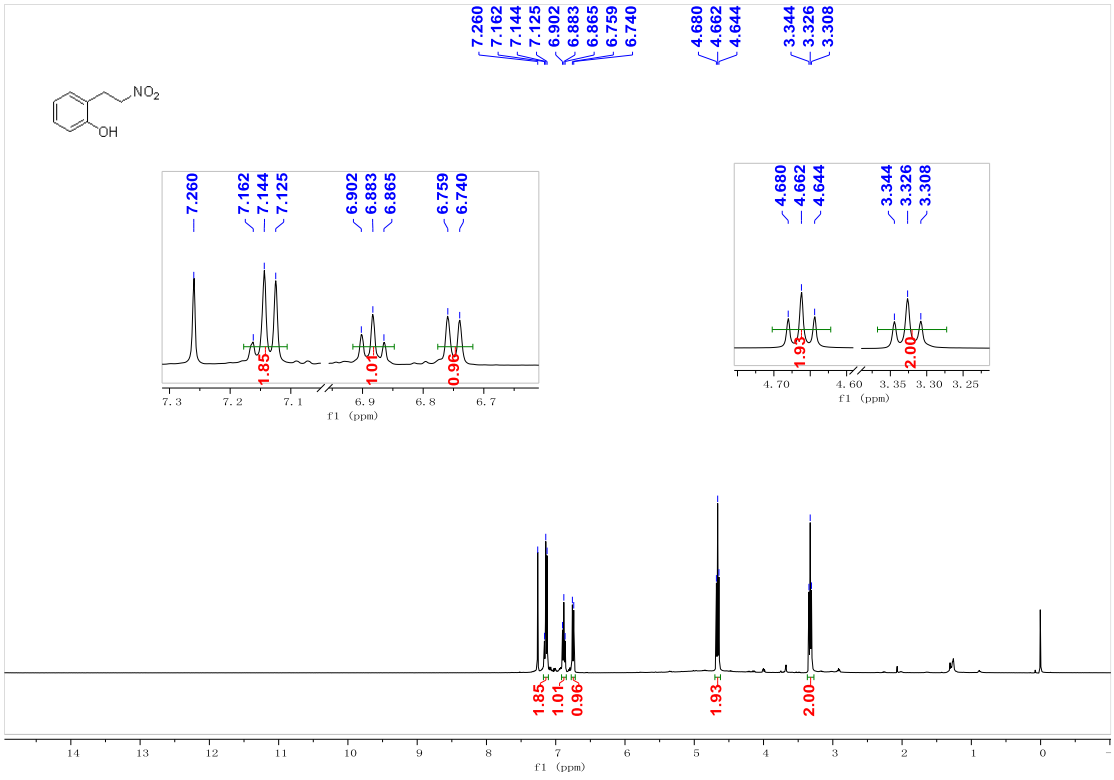


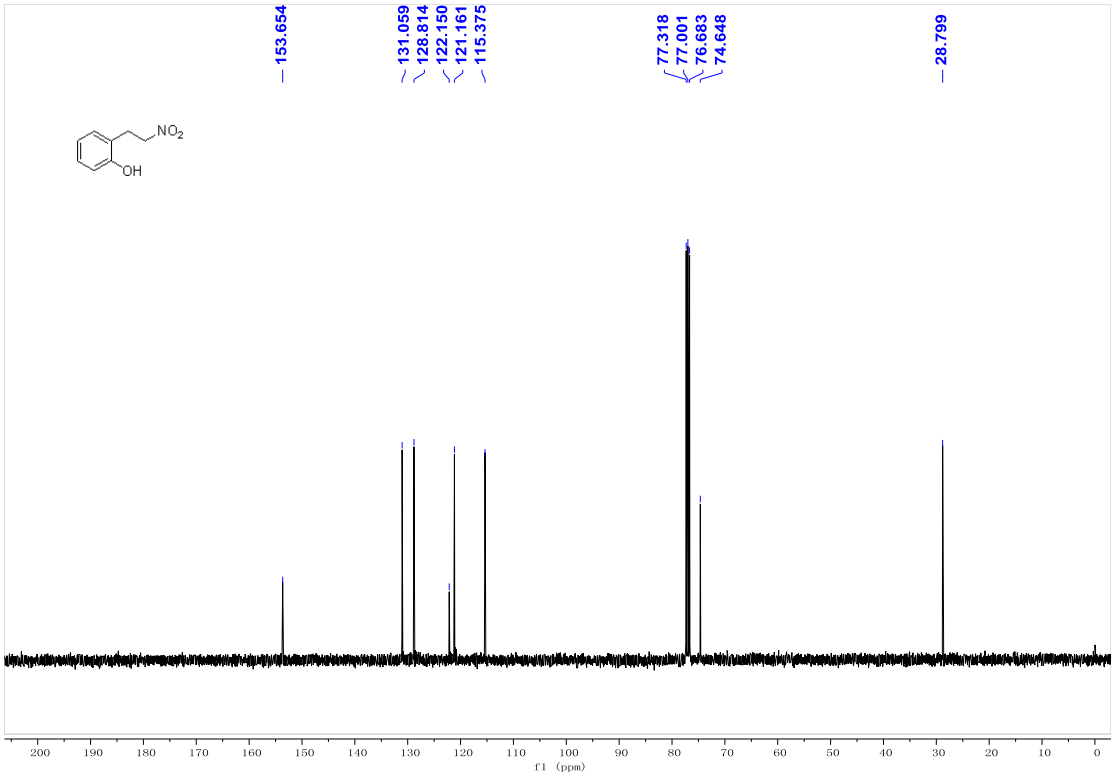
4-(2-Nitroethyl)phenol (2v):



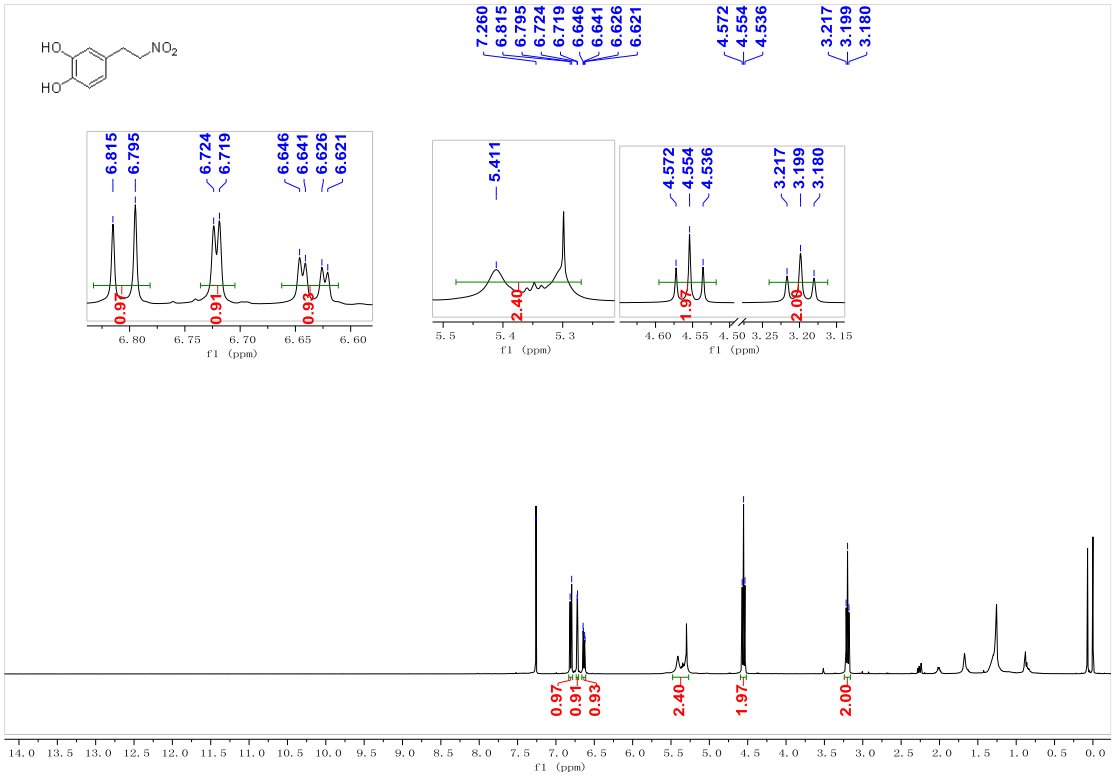


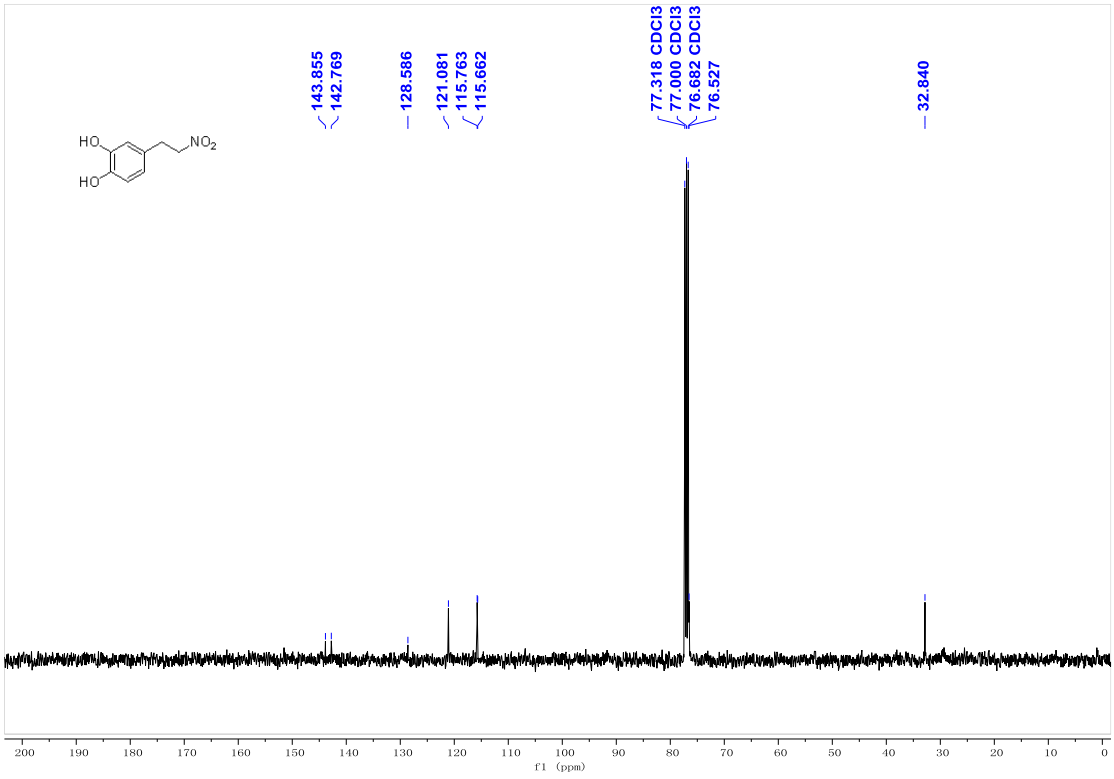
2-(2-Nitroethyl)phenol (2w):



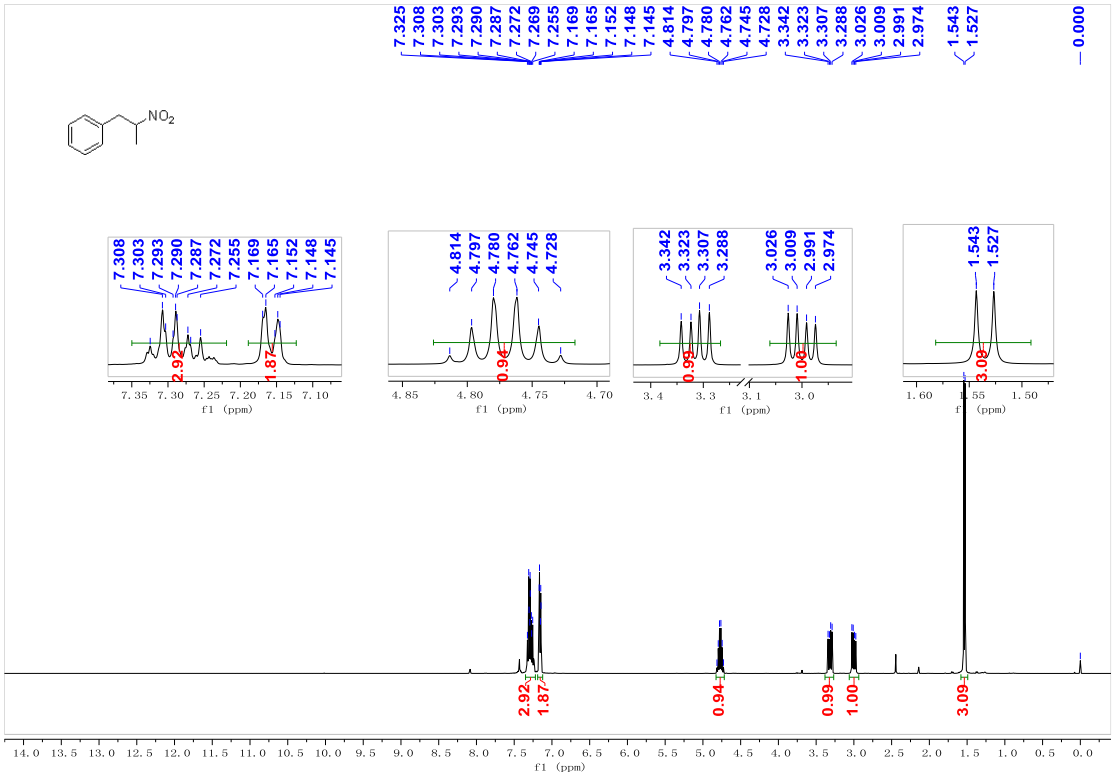


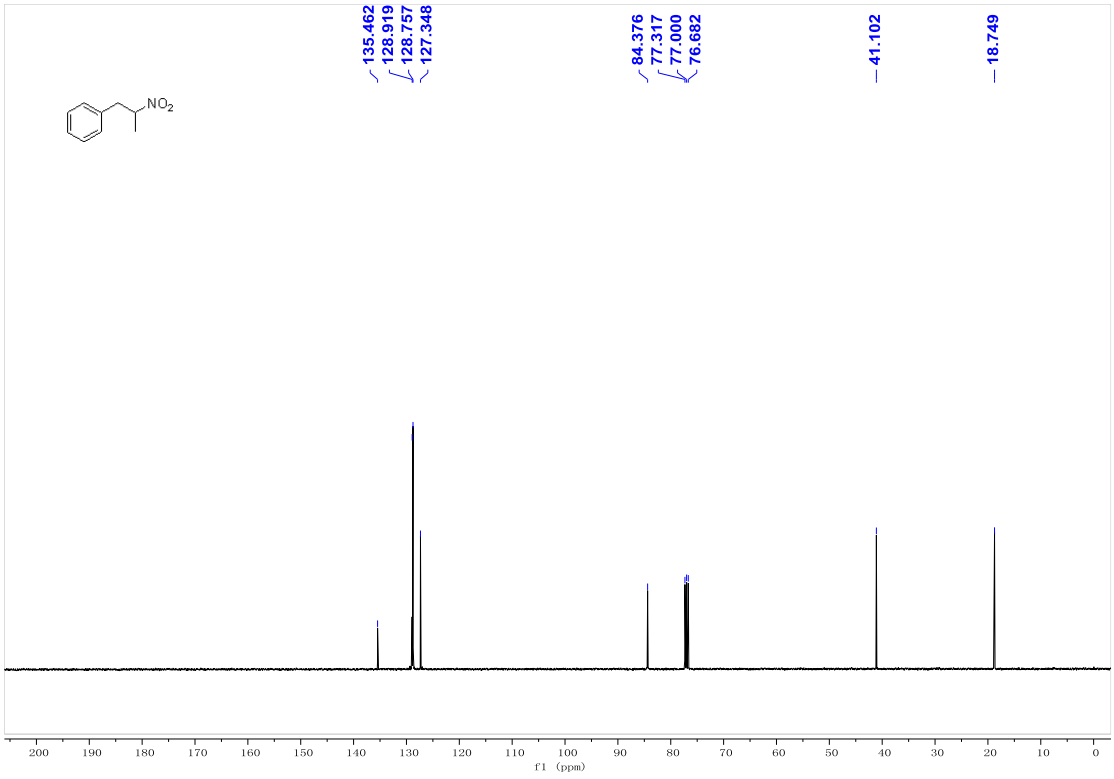
4-(2-Nitroethyl)benzene-1,2-diol (2x):



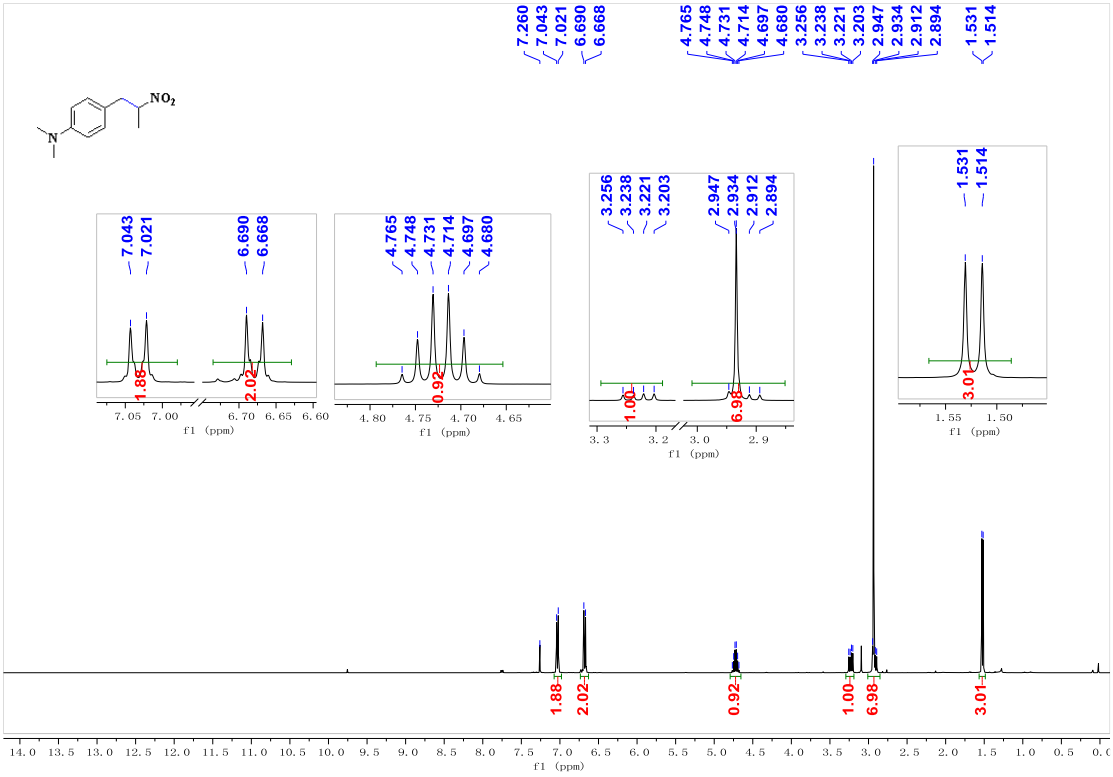


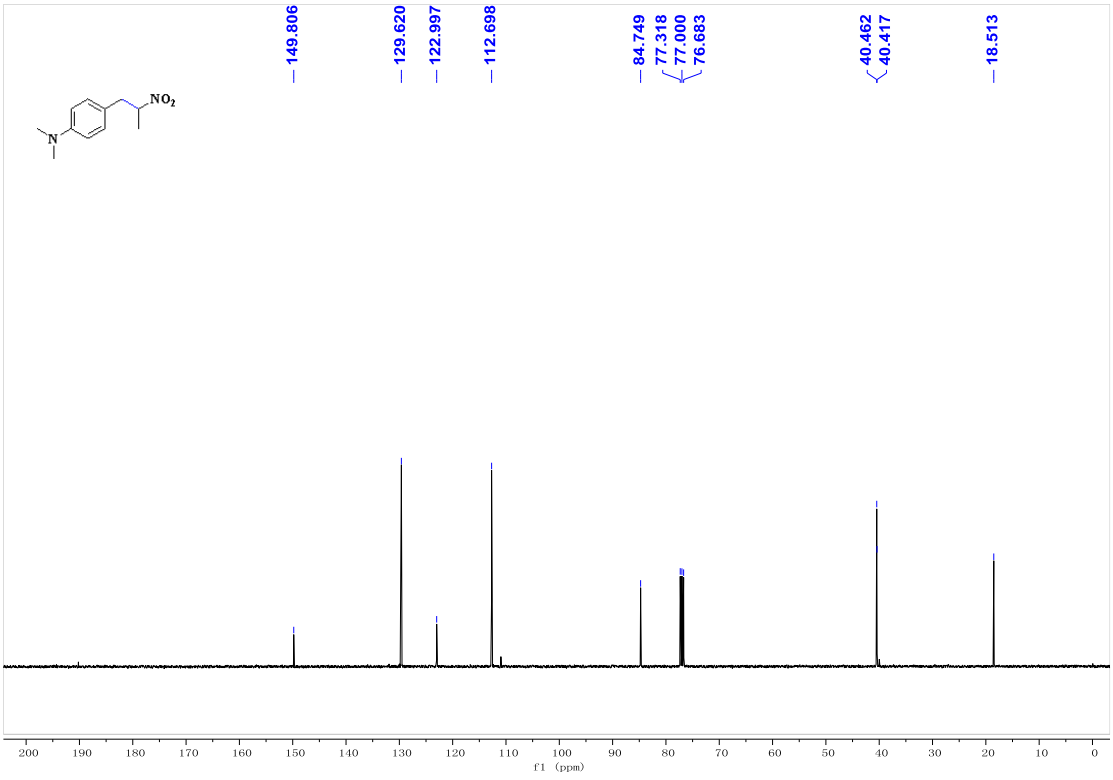
(2-Nitropropyl)benzene(4a):



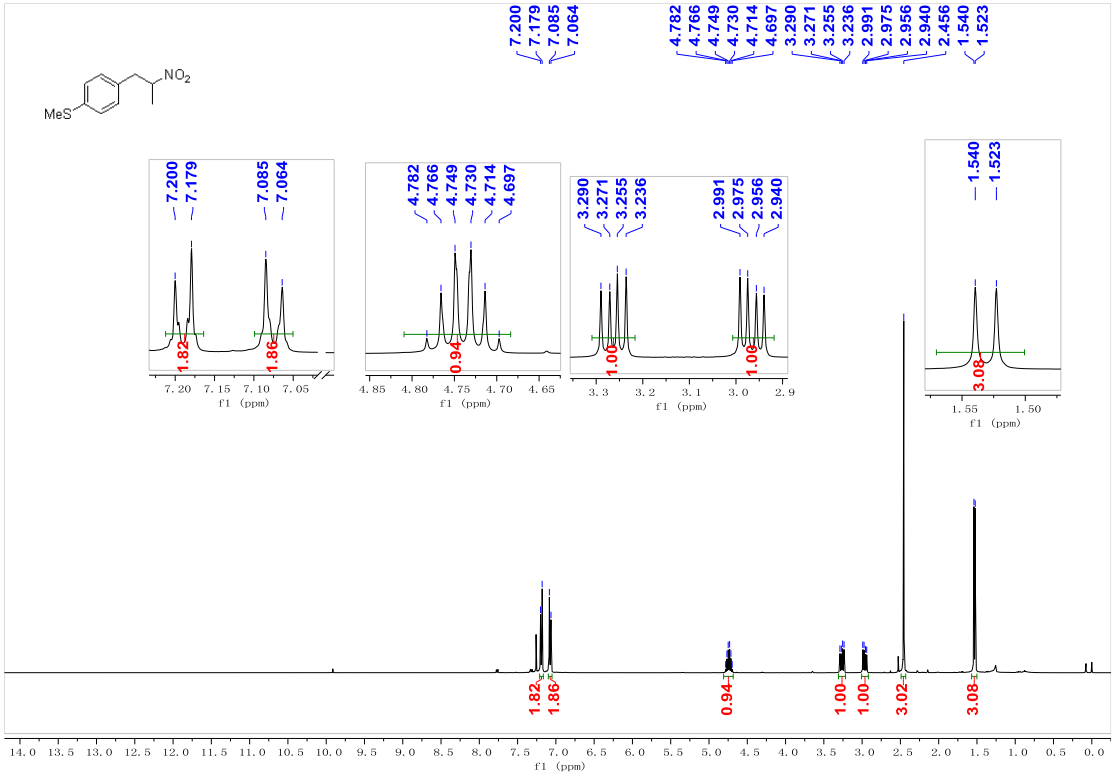


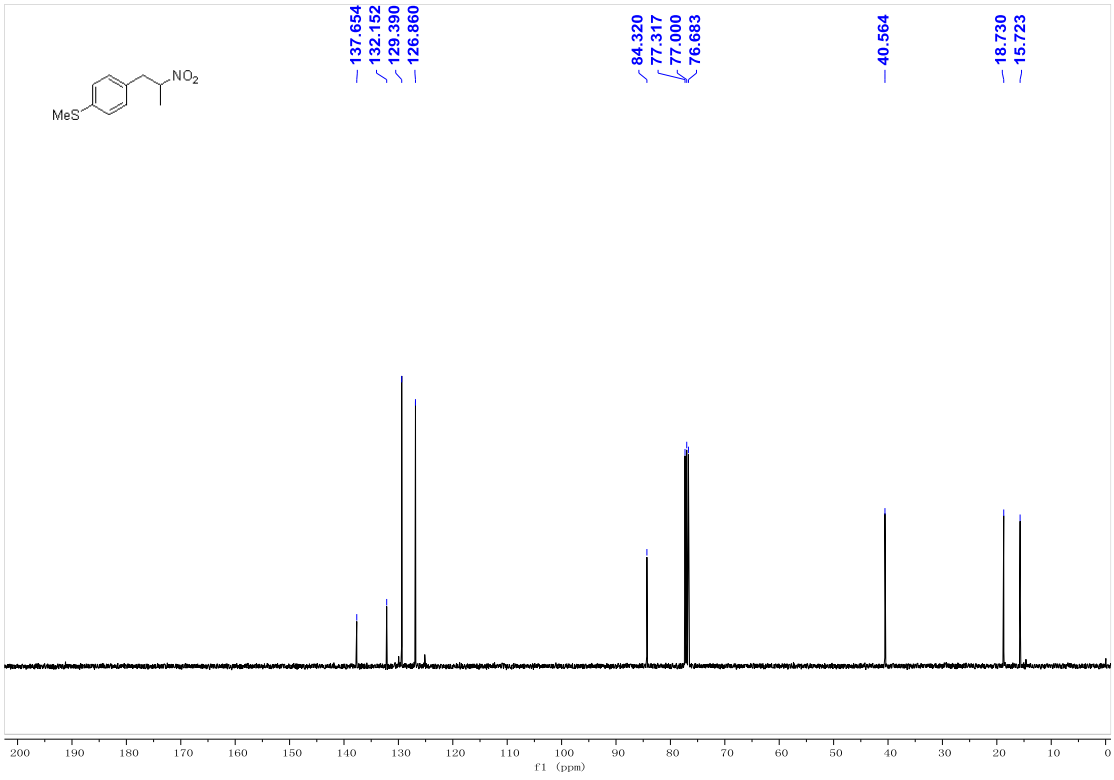
N,N-Dimethyl-4-(2-nitropropyl)aniline(4b):



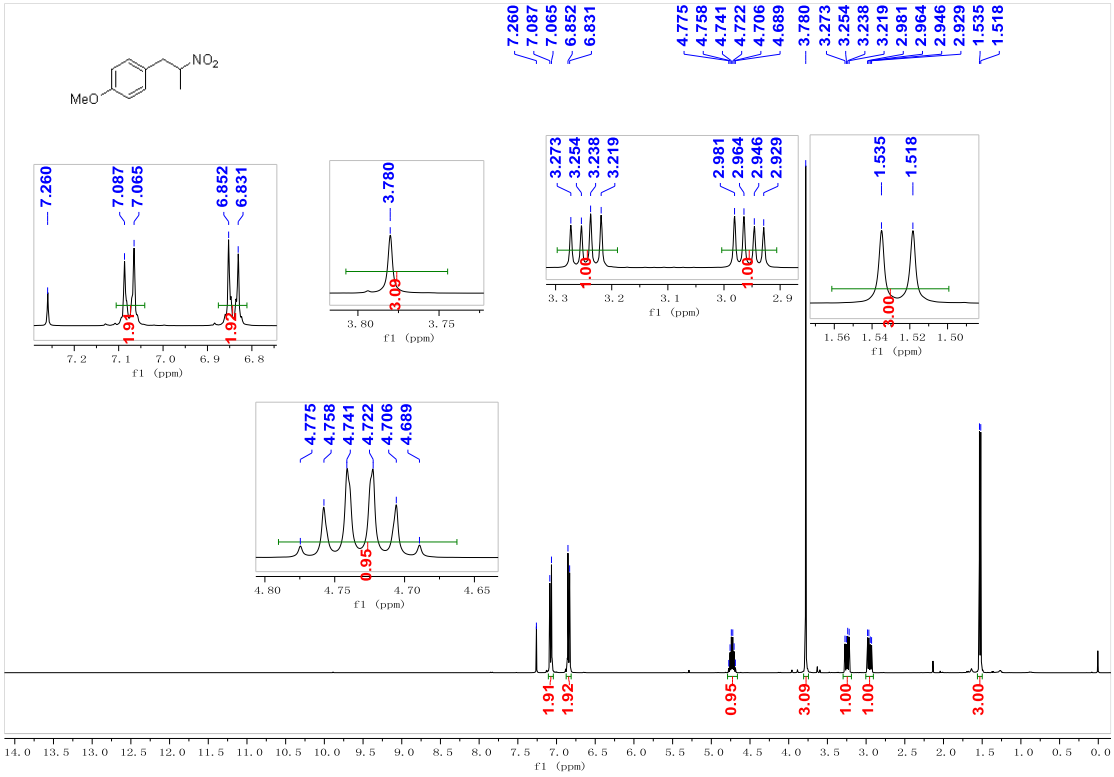


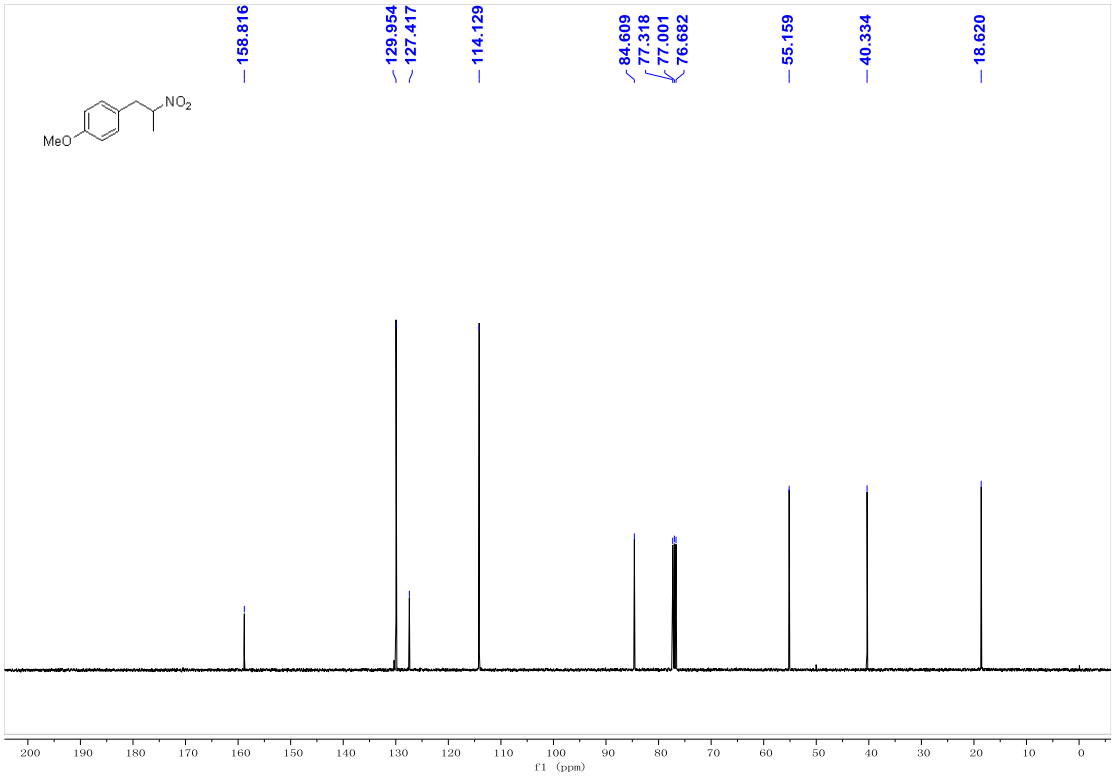
Methyl(4-(2-nitropropyl)phenyl)sulfane(4c):



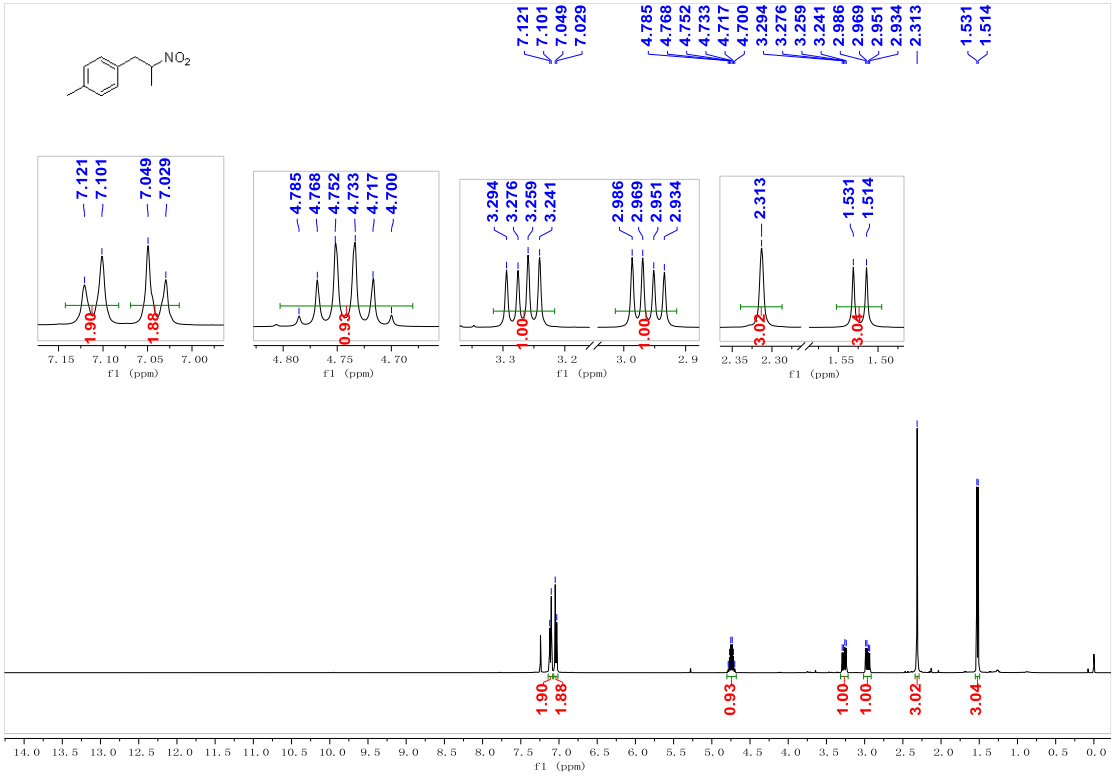


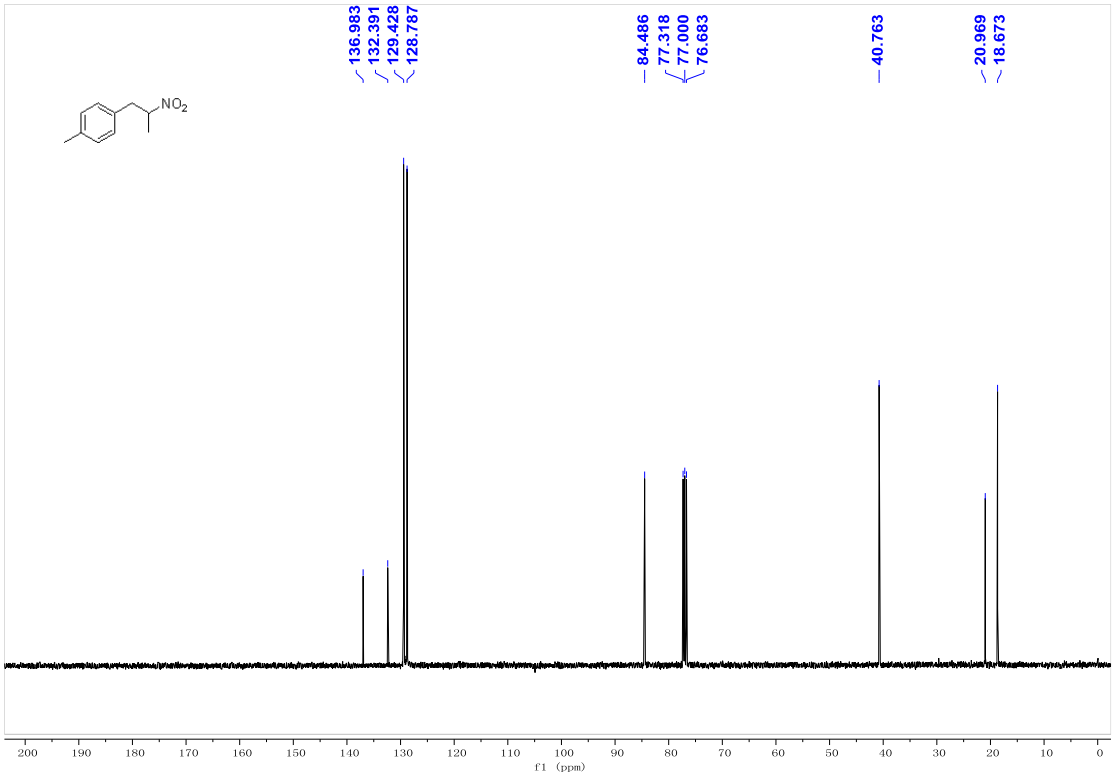
1-Methoxy-4-(2-nitropropyl)benzene(4d):



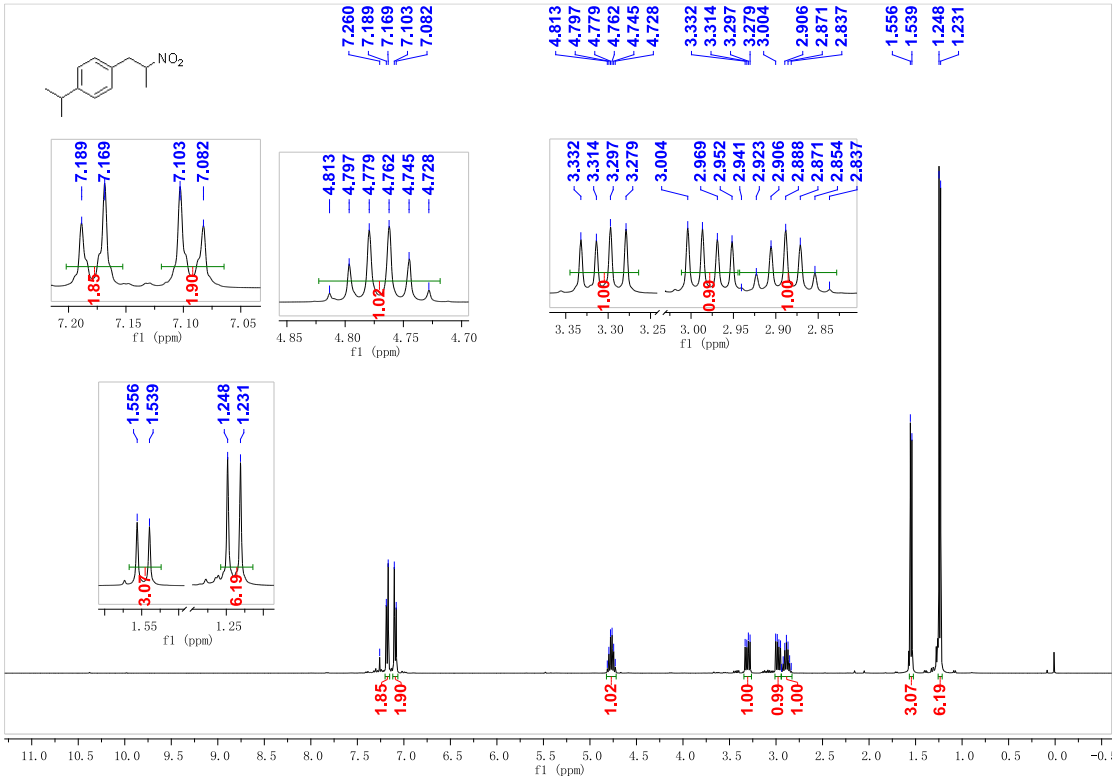


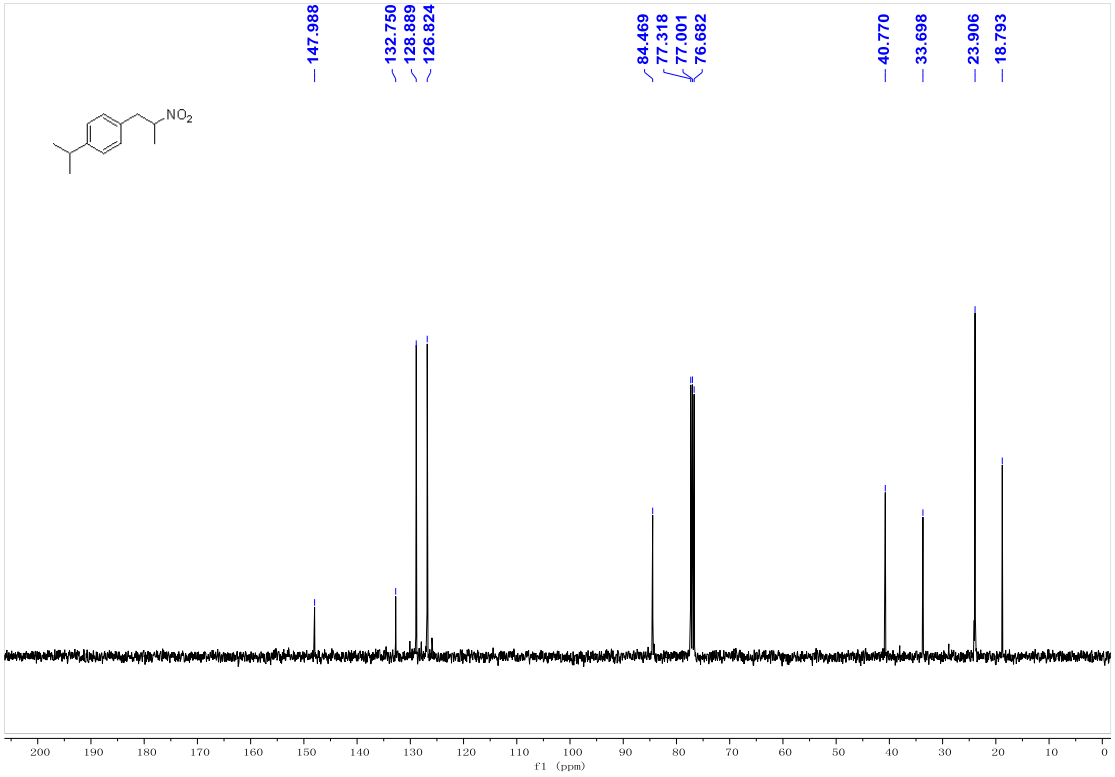
1-Methyl-4-(2-nitropropyl)benzene(4e):



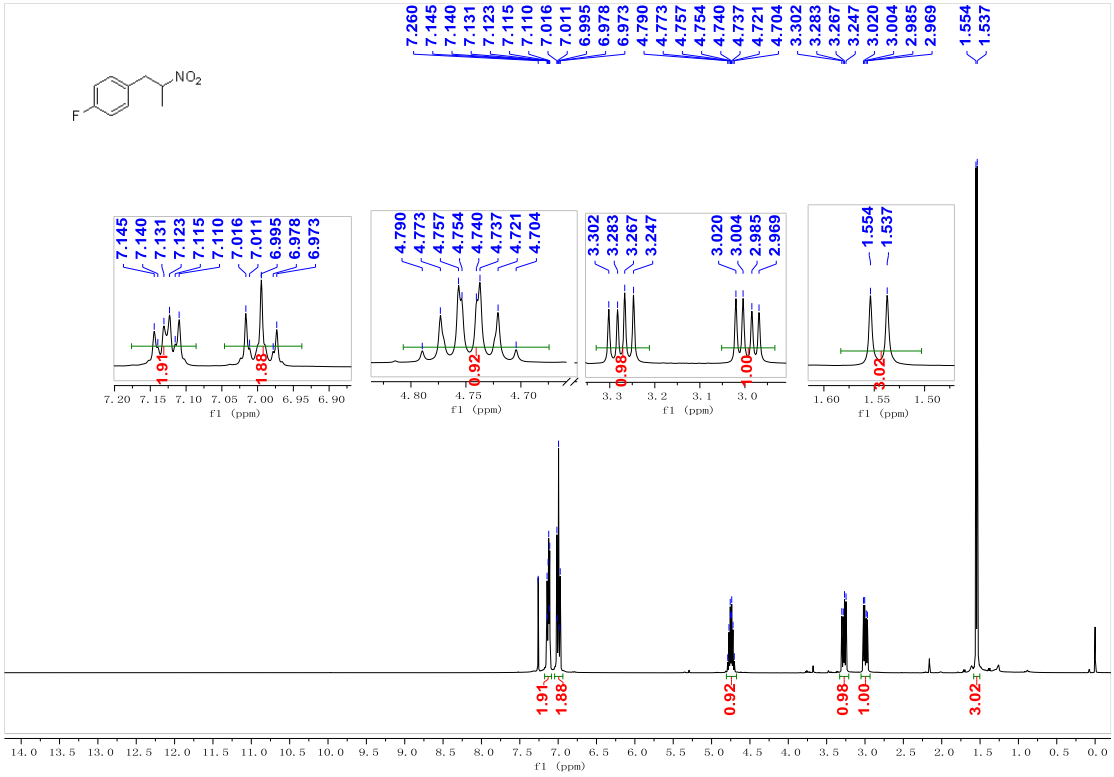


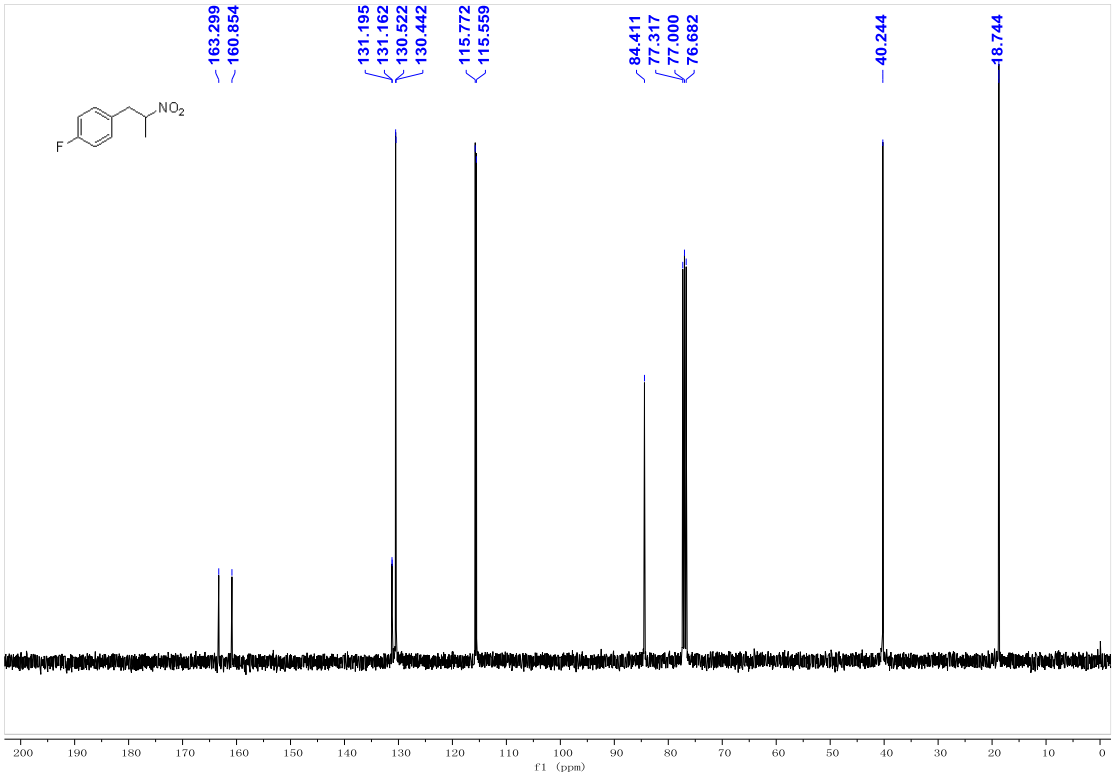
1-Isopropyl-4-(2-nitropropyl)benzene(4f):



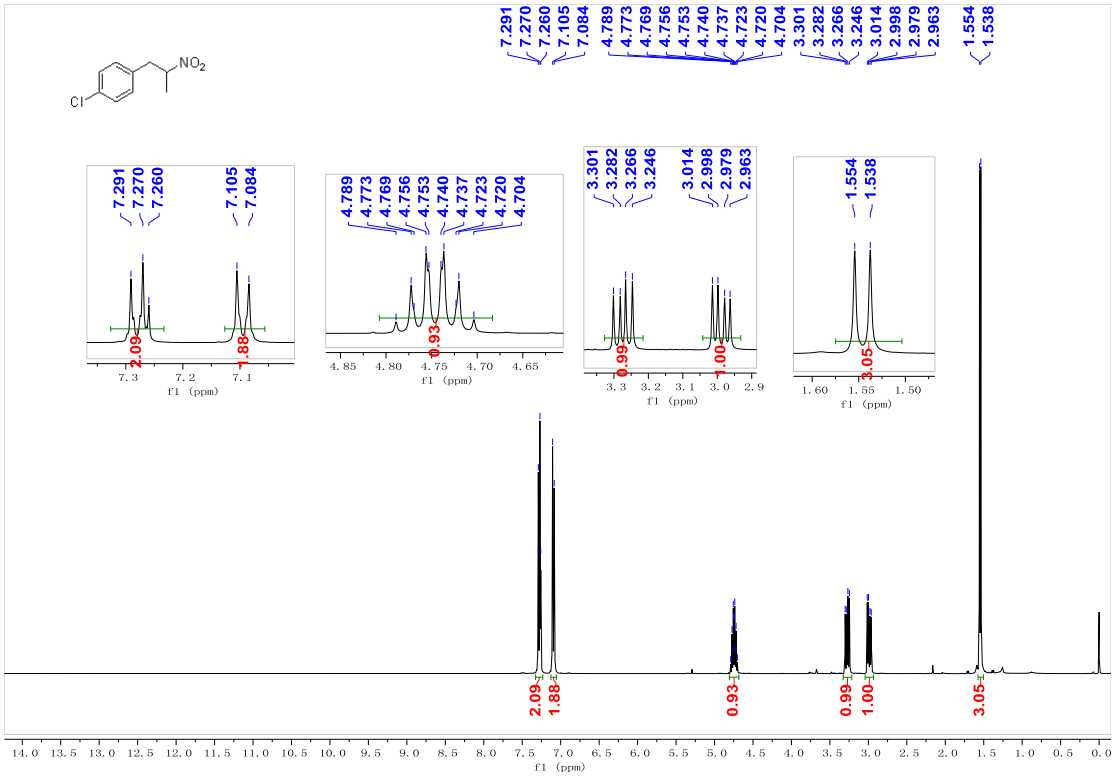


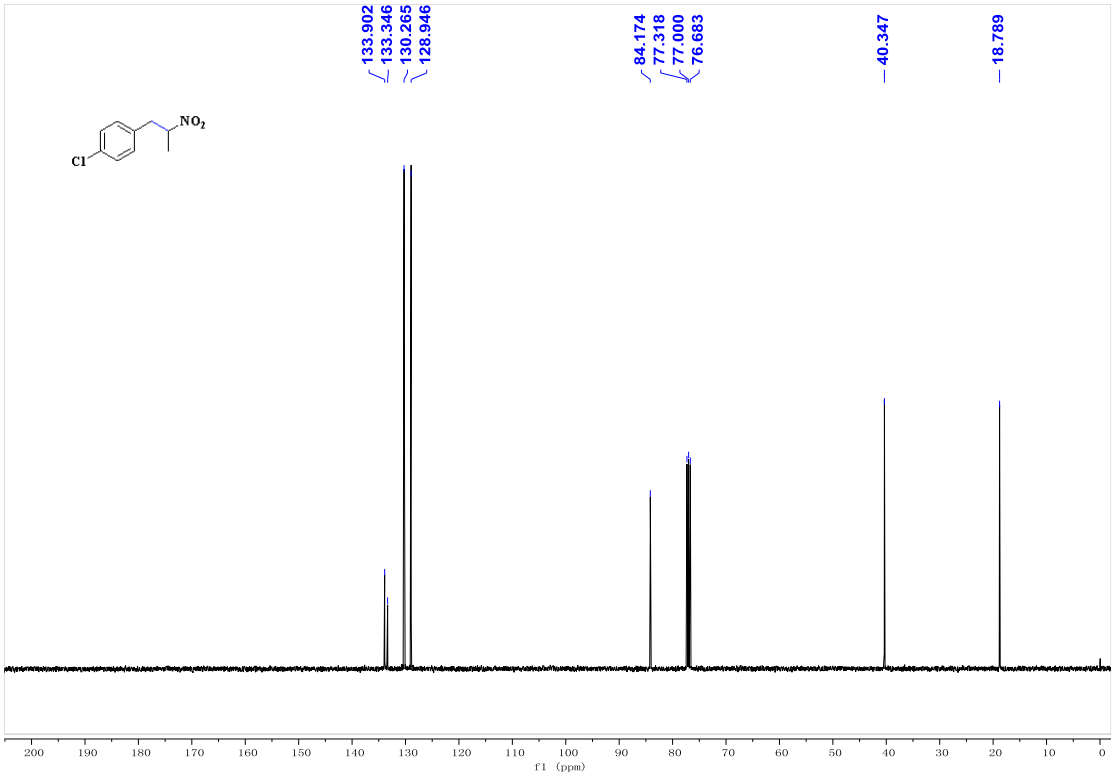
1-Fluoro-4-(2-nitropropyl)benzene(4g):



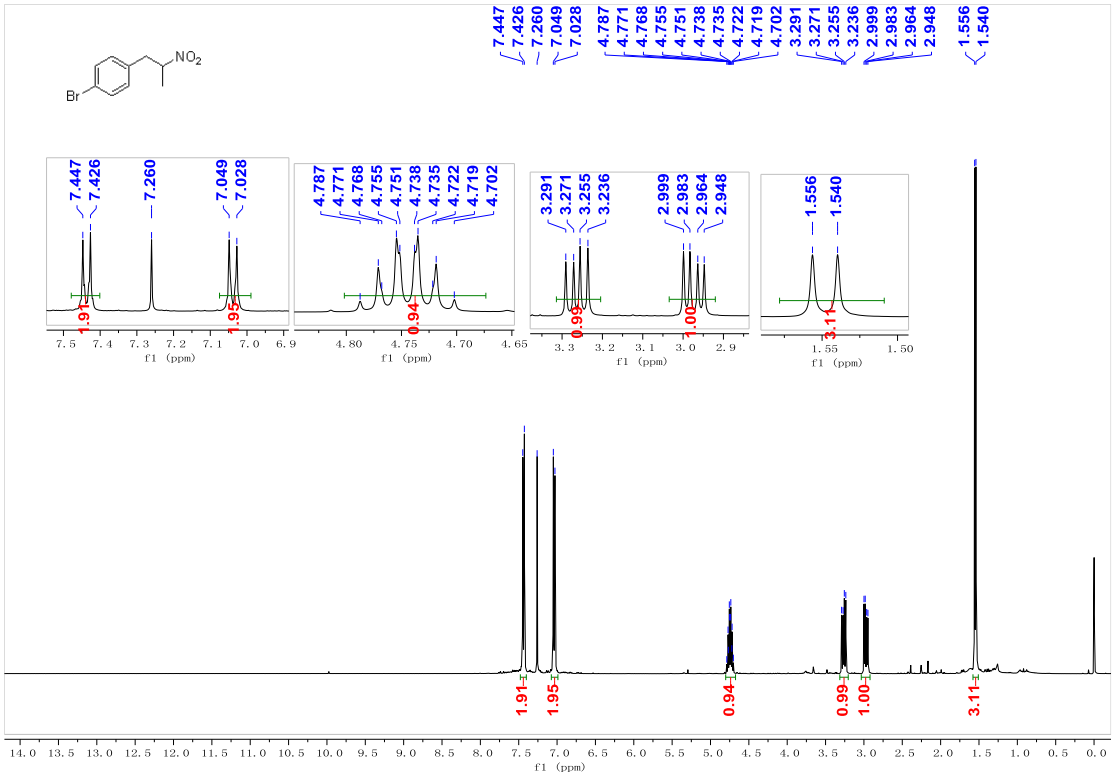


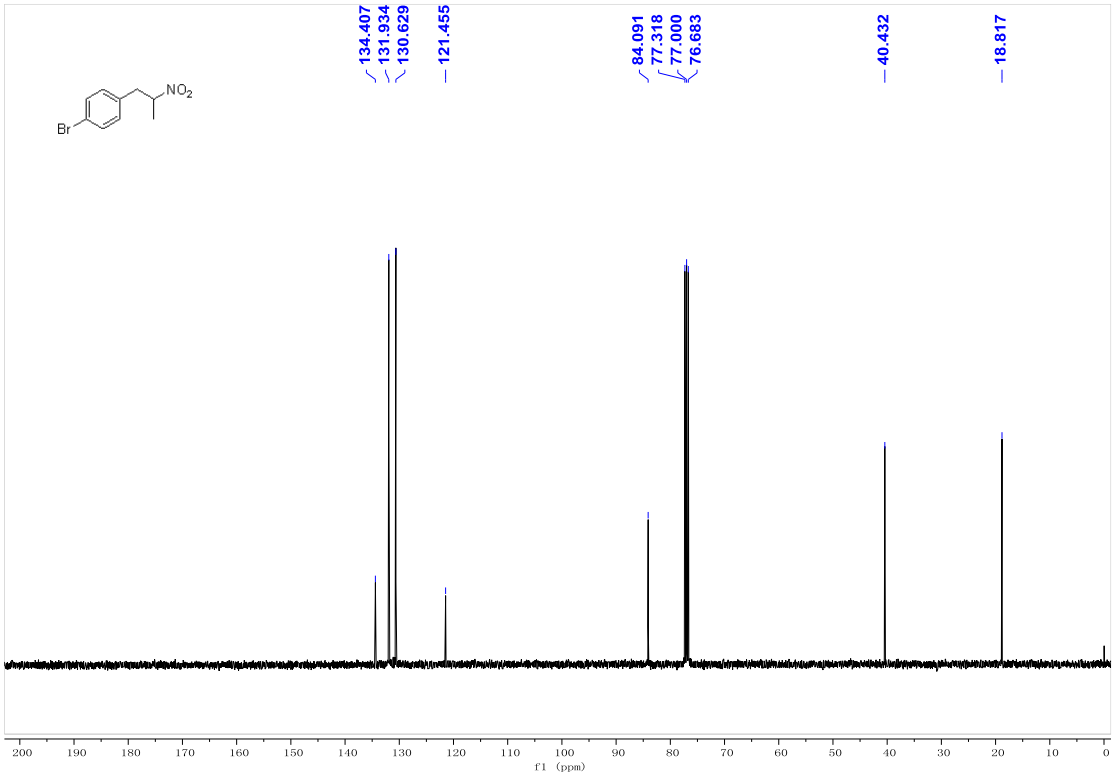
1-Chloro-4-(2-nitropropyl)benzene(4h):



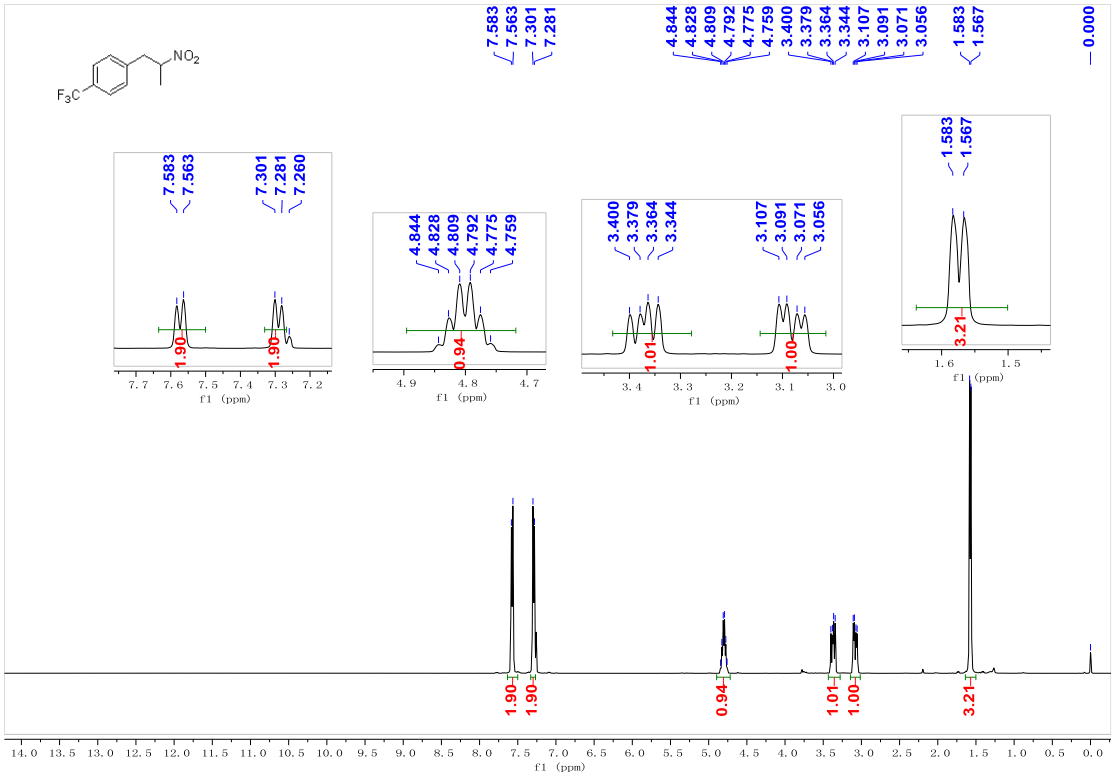


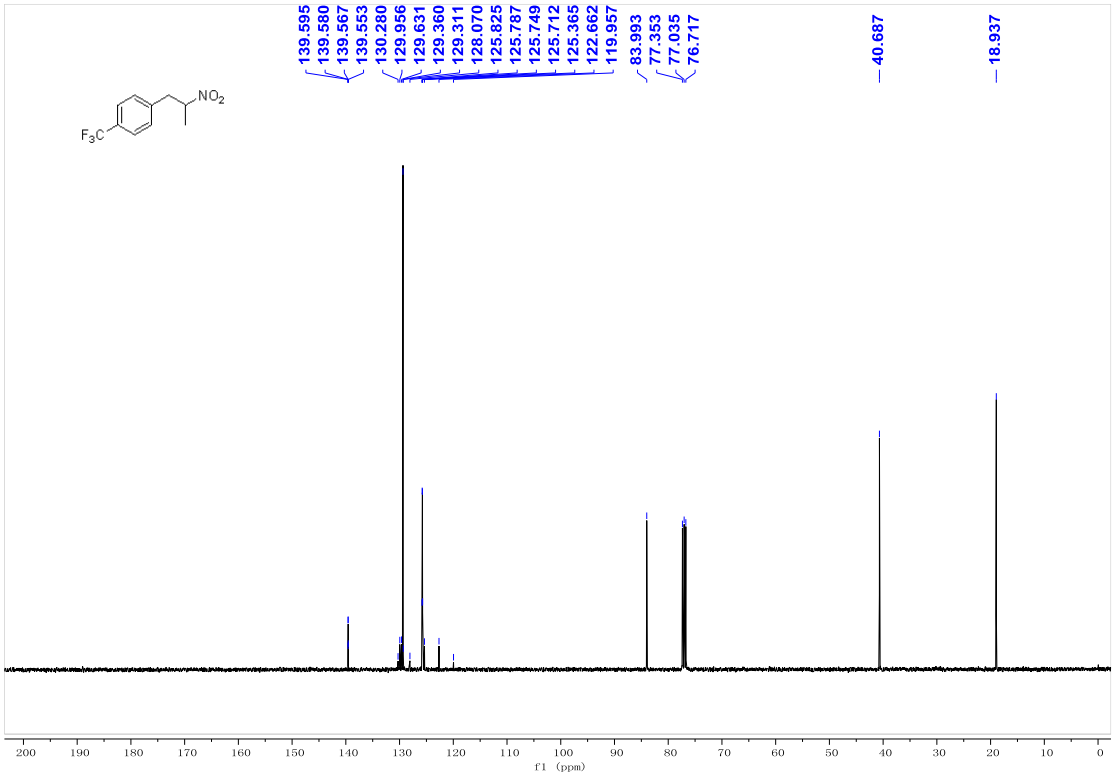
1-Bromo-4-(2-nitropropyl)benzene(4i):



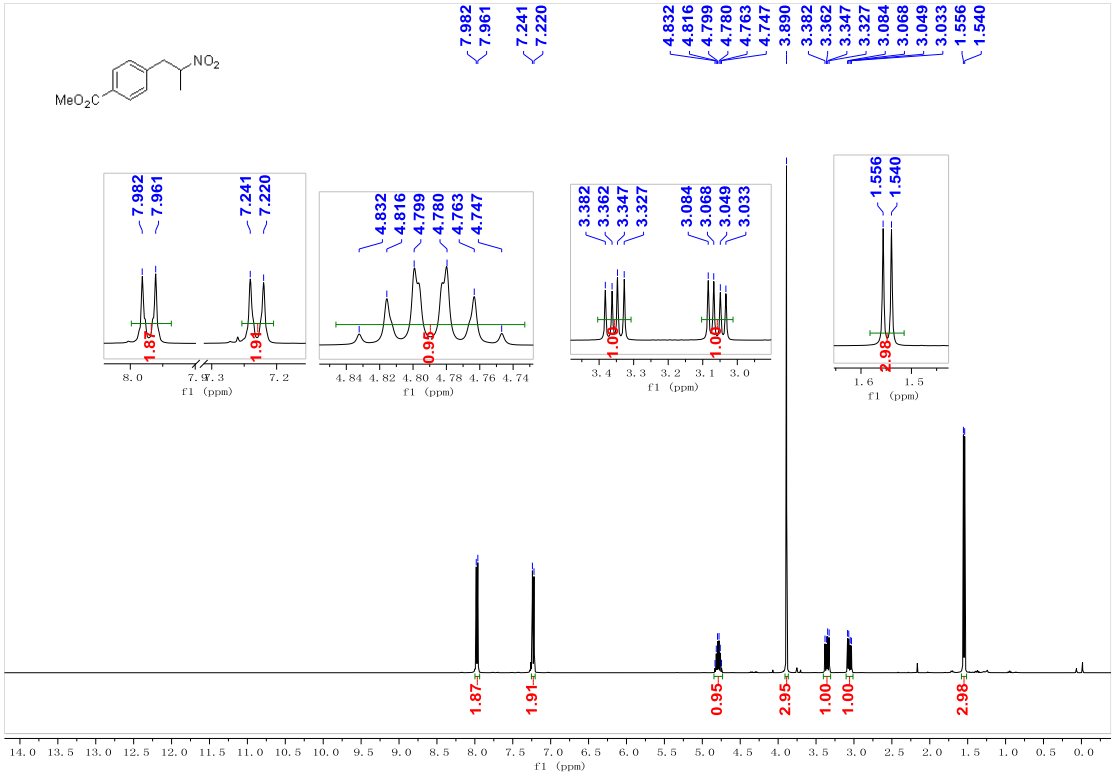


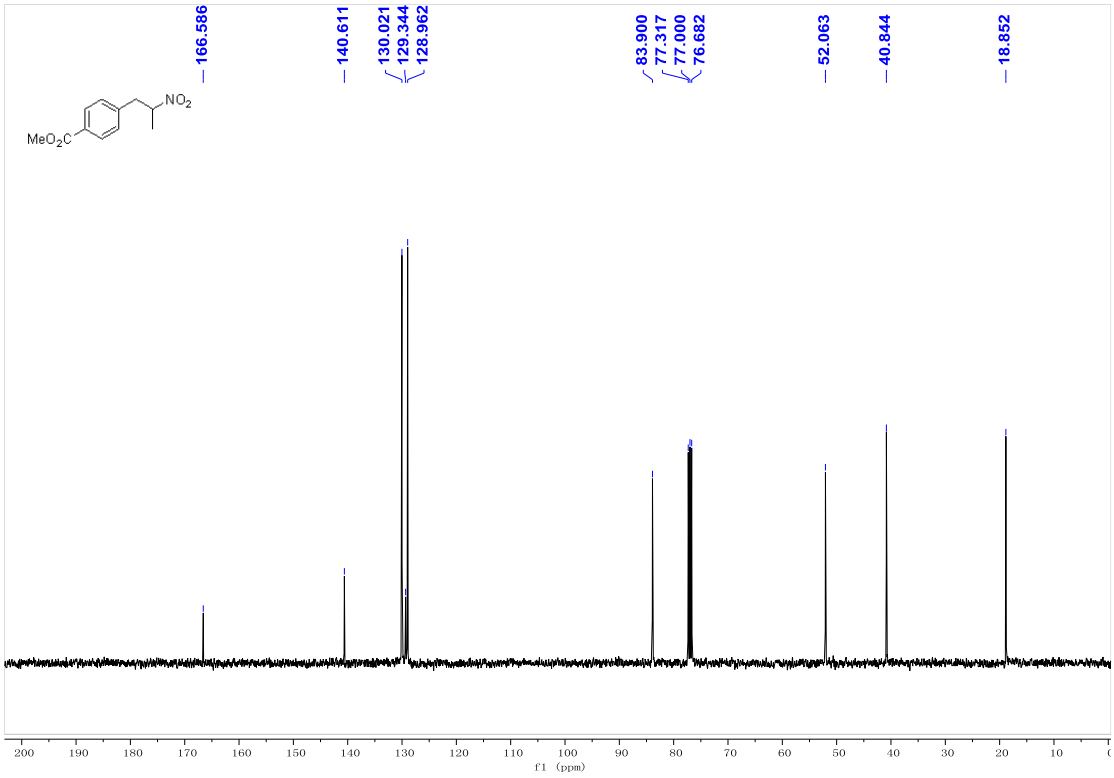
1-(2-Nitropropyl)-4-(trifluoromethyl)benzene(4j):

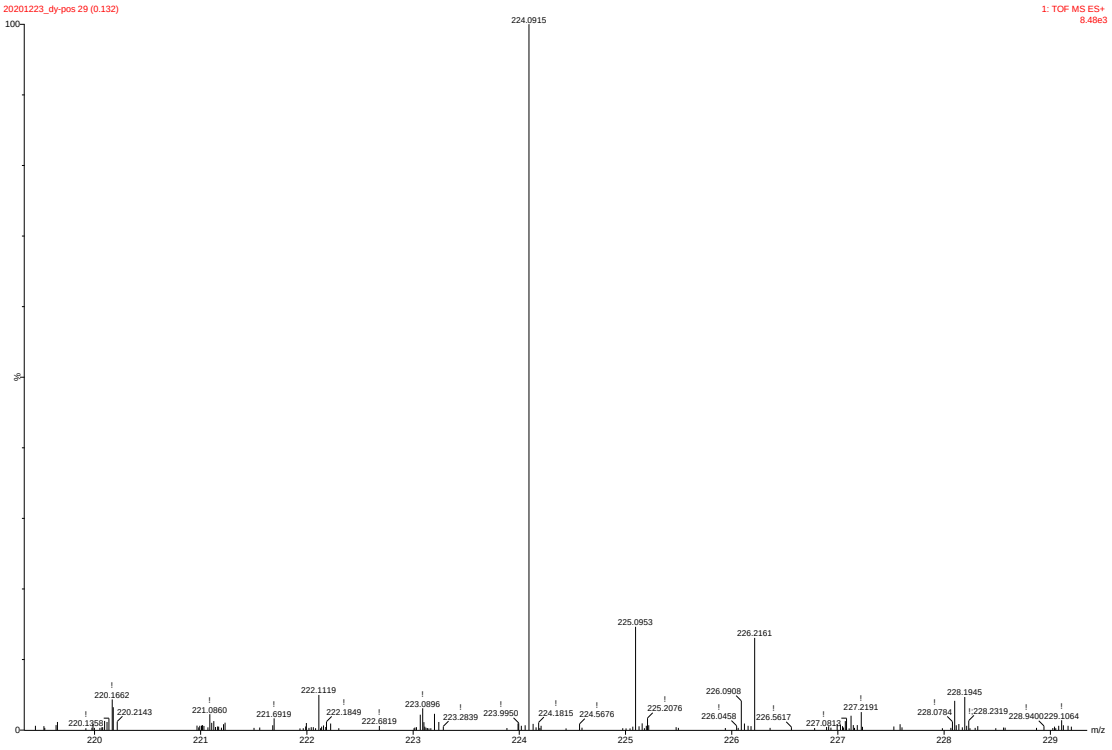




Methyl-4-(2-nitropropyl)benzoate(4k):



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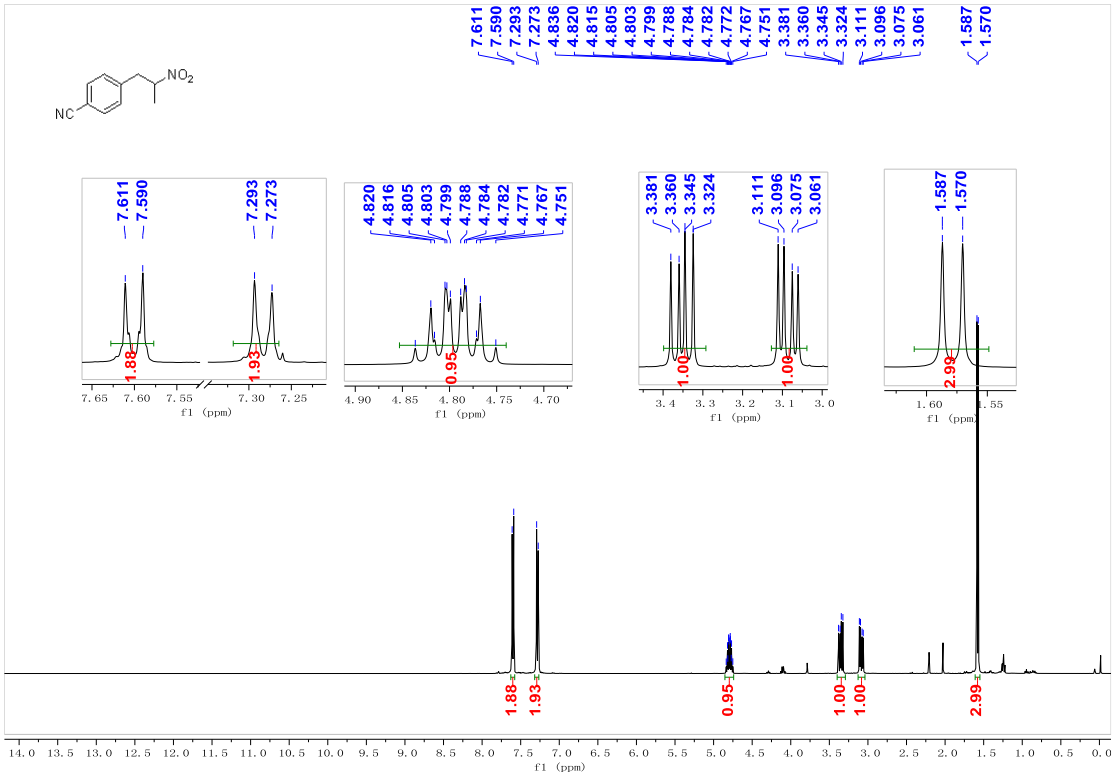
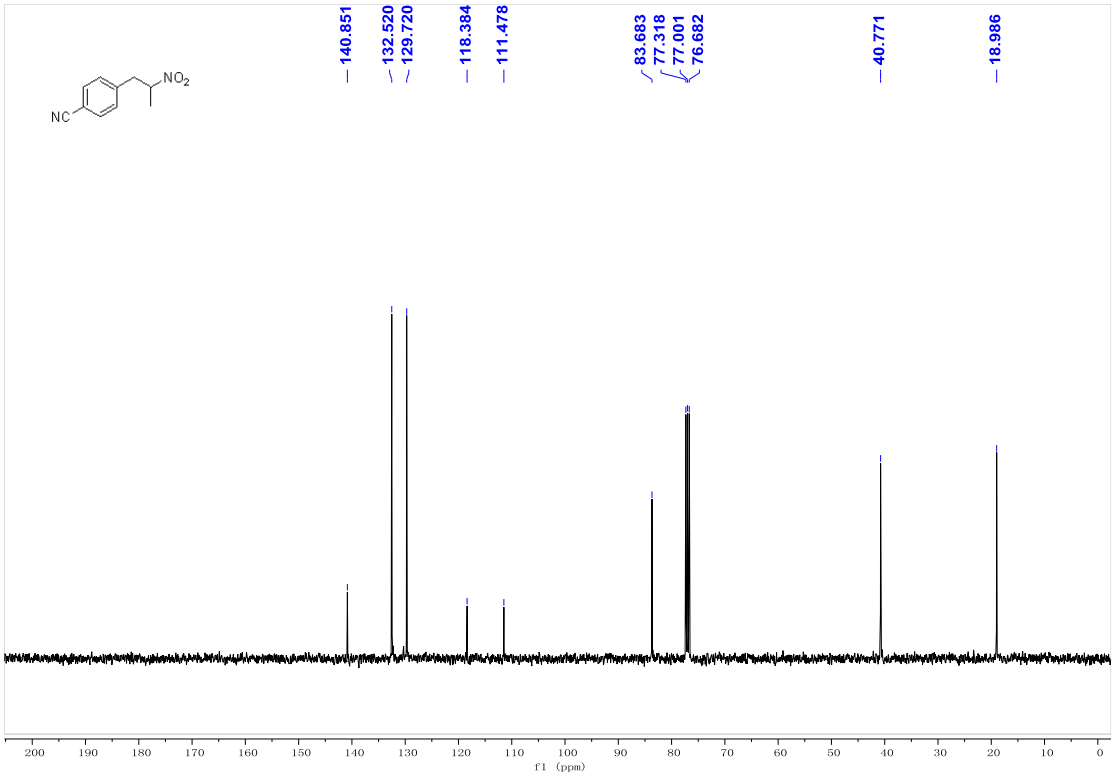
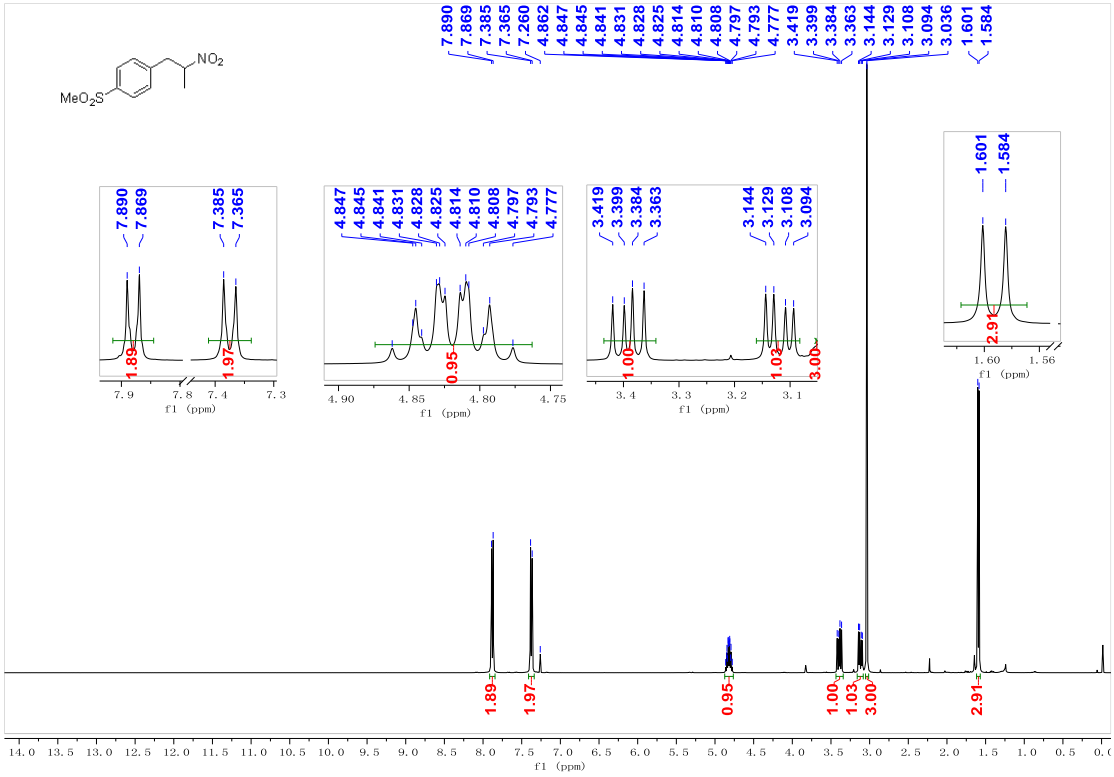
228.0784
228.2319
228.9400
229.1064
222.6819
m/z
220
221
222
223
224
225
226
227
228
229

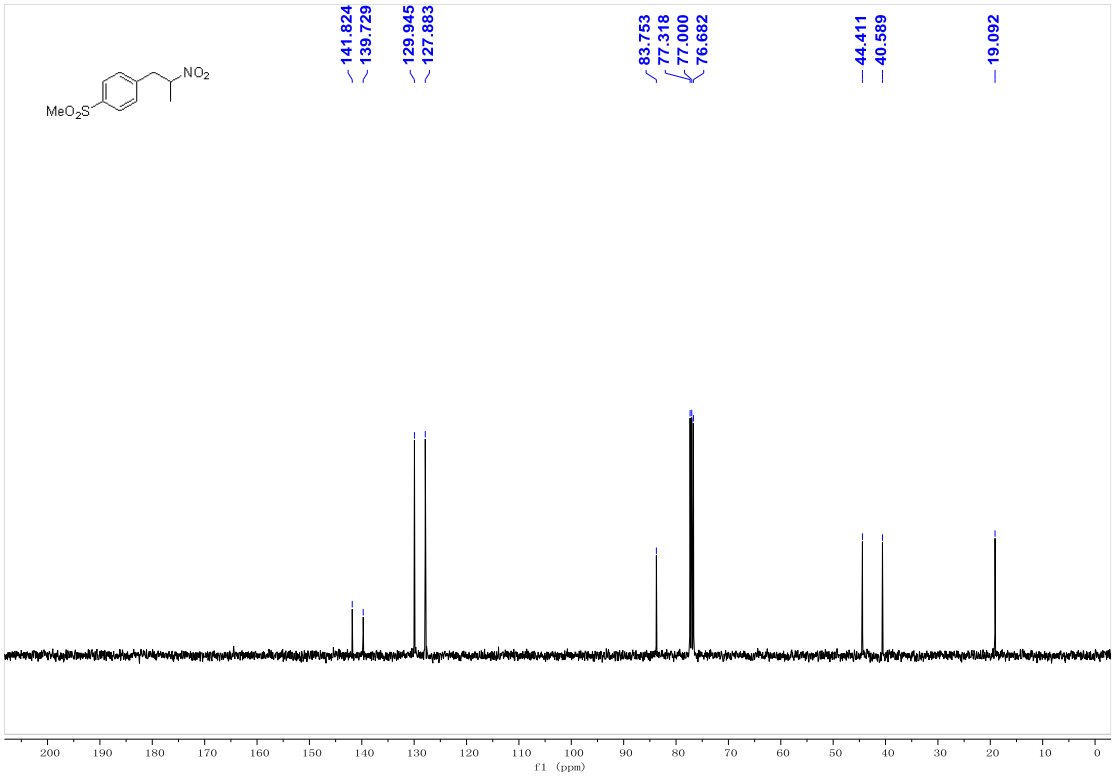
4-(2-Nitropropyl)benzonitrile(4l):

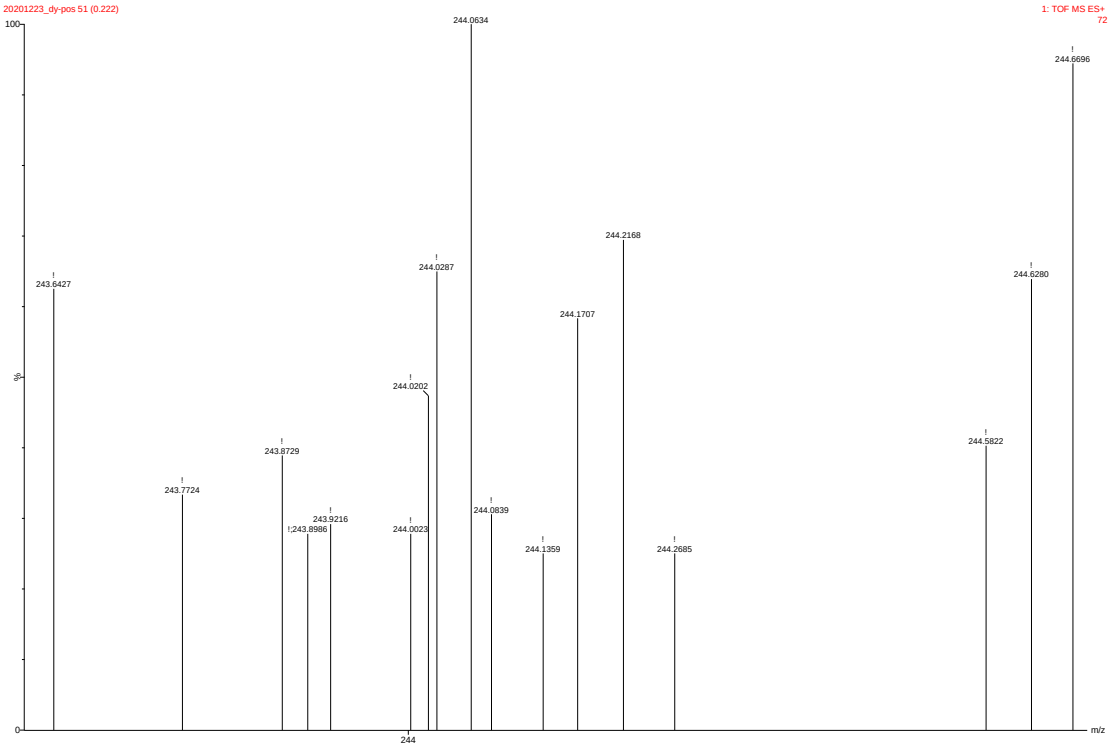




1-(Methylsulfonyl)-4-(2-nitropropyl)benzene(4m):



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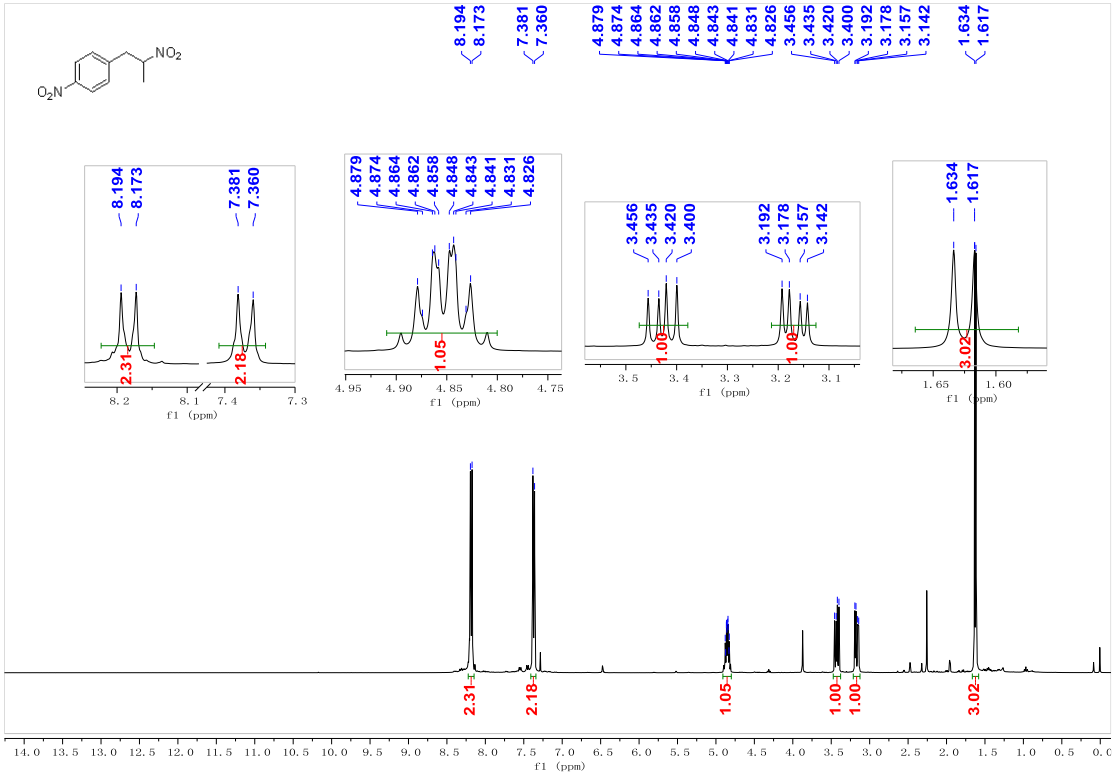
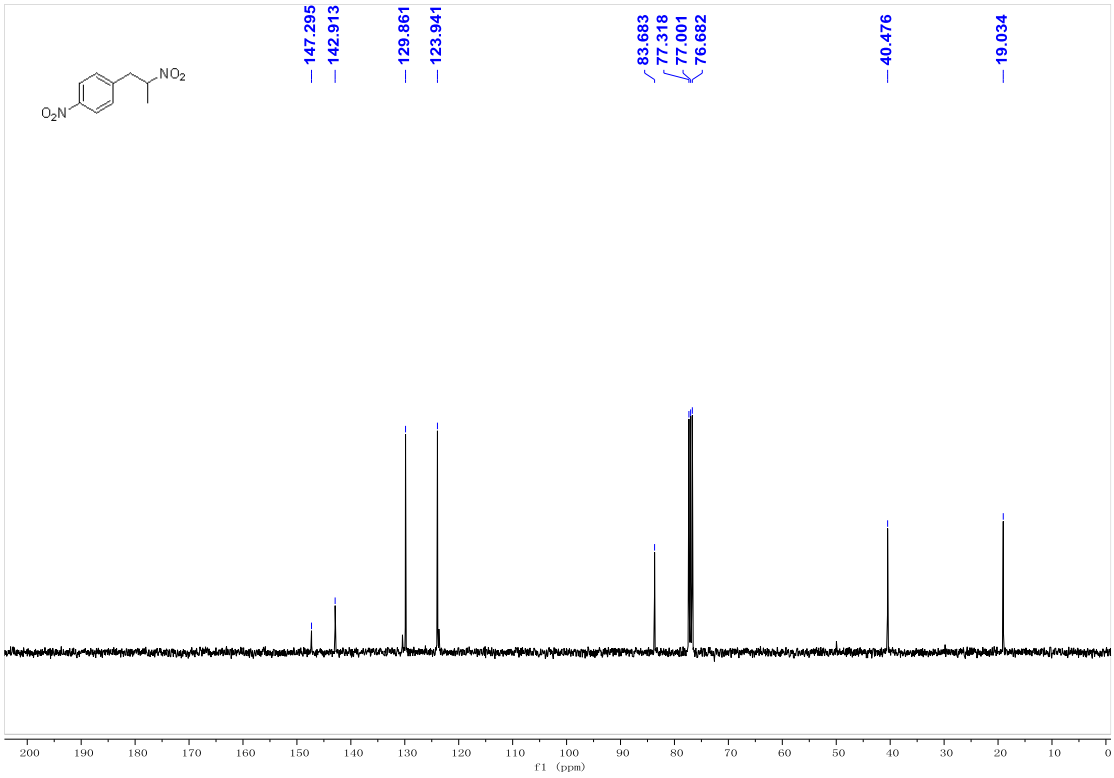
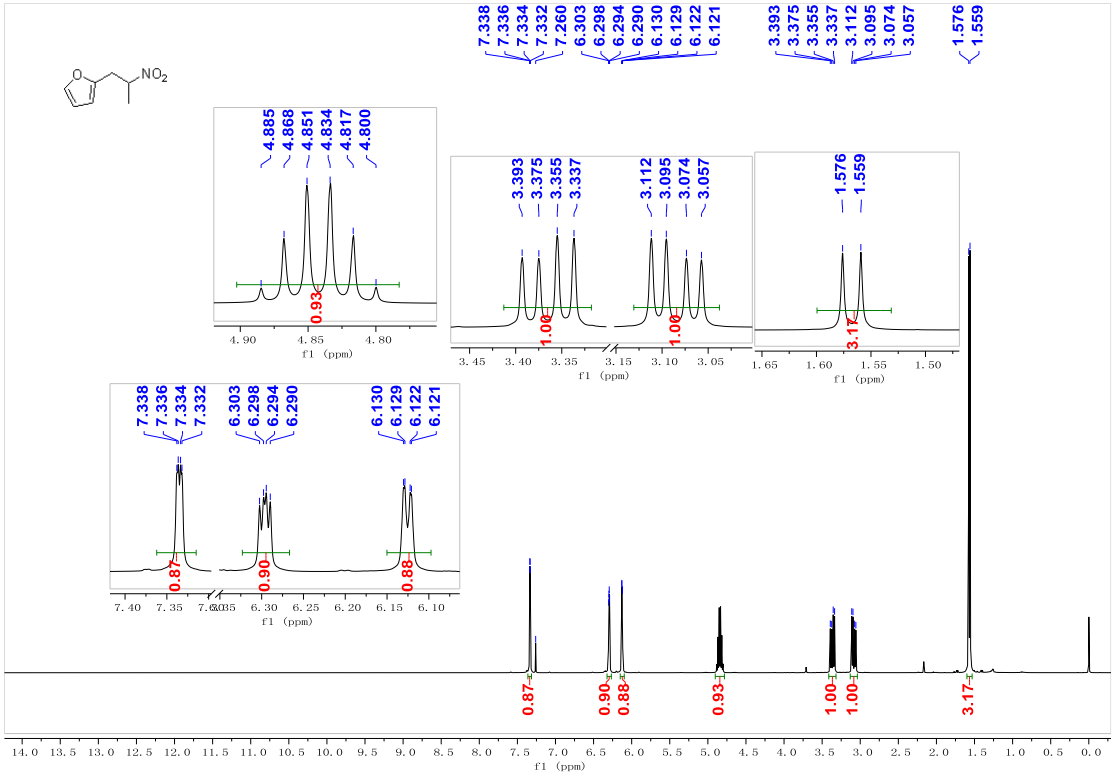
244.2685
244
m/z

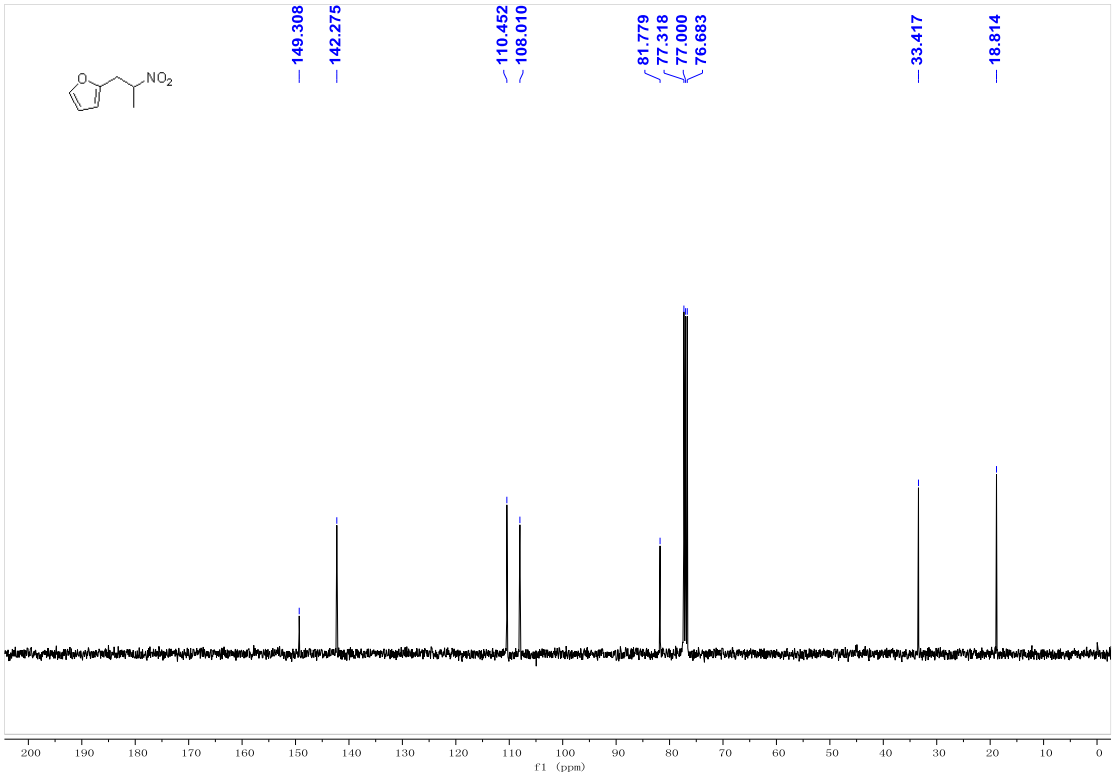
1-Nitro-4-(2-nitropropyl)benzene(4n):



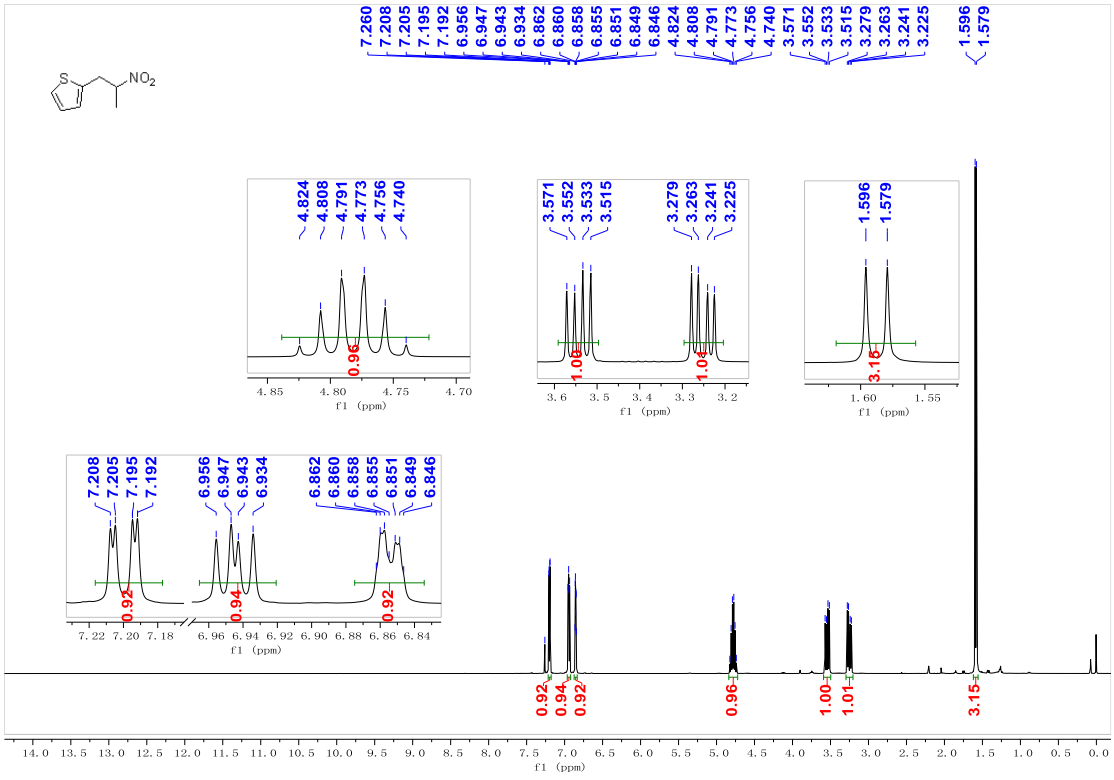


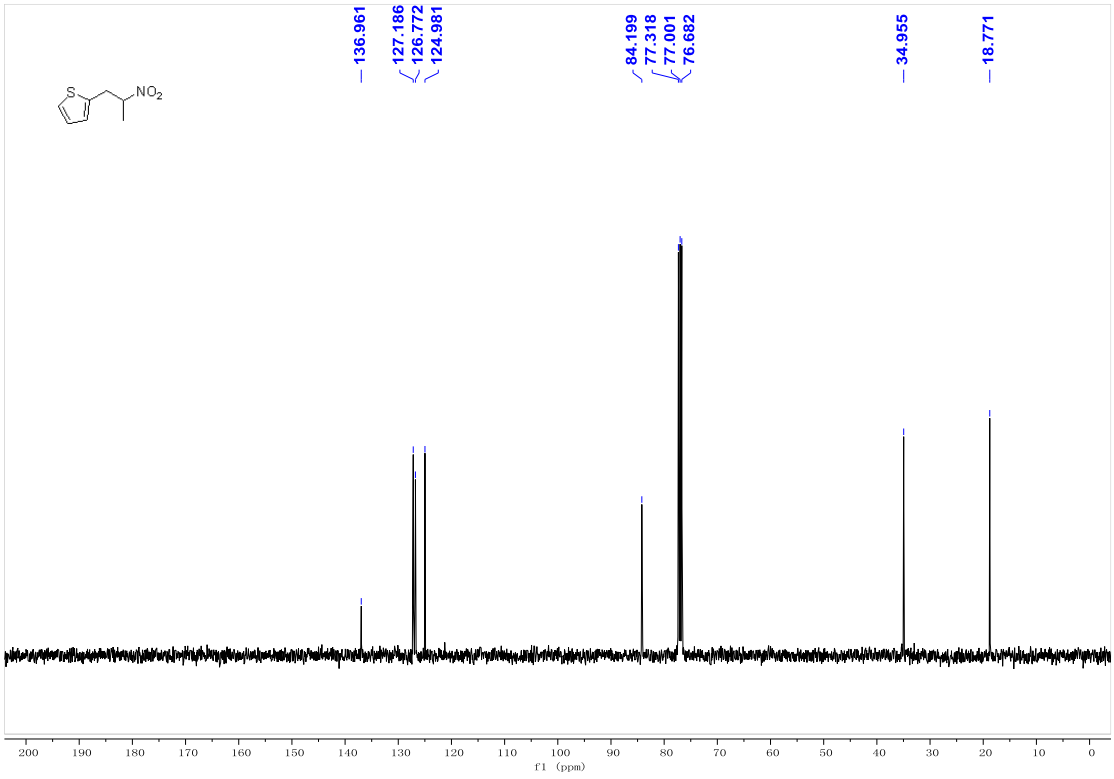
2-(2-Nitropropyl)furan(4o):



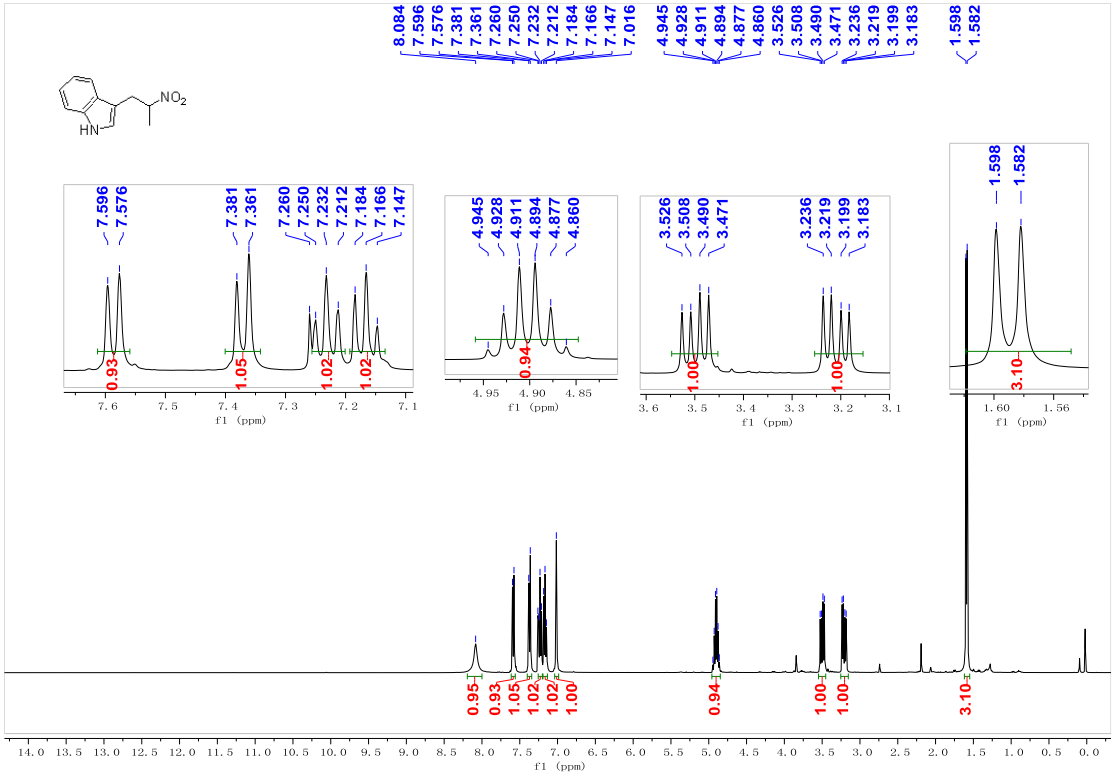


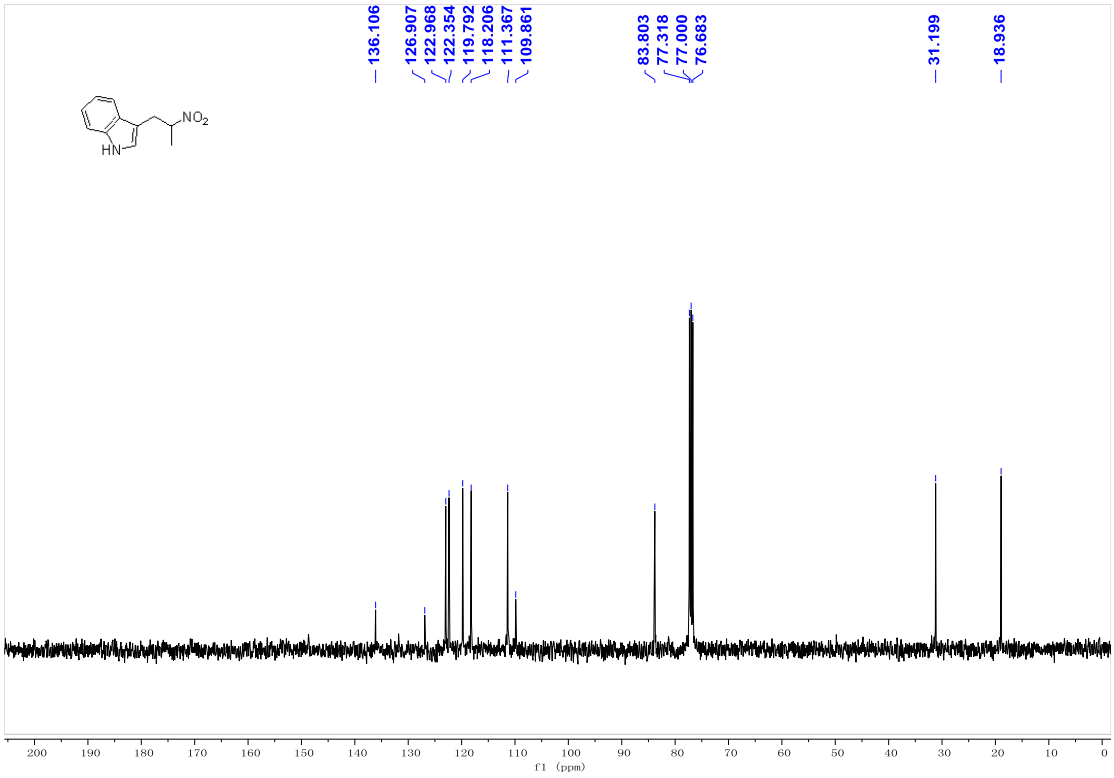
2-(2-Nitropropyl)thiophene(4p):



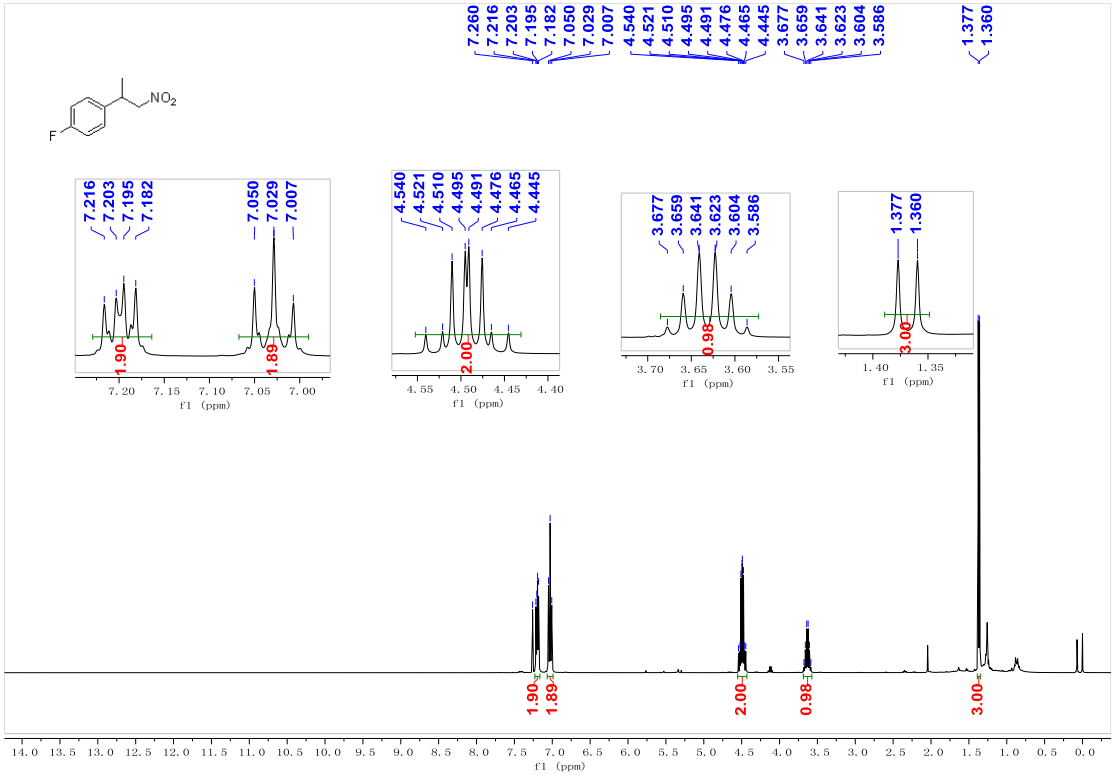


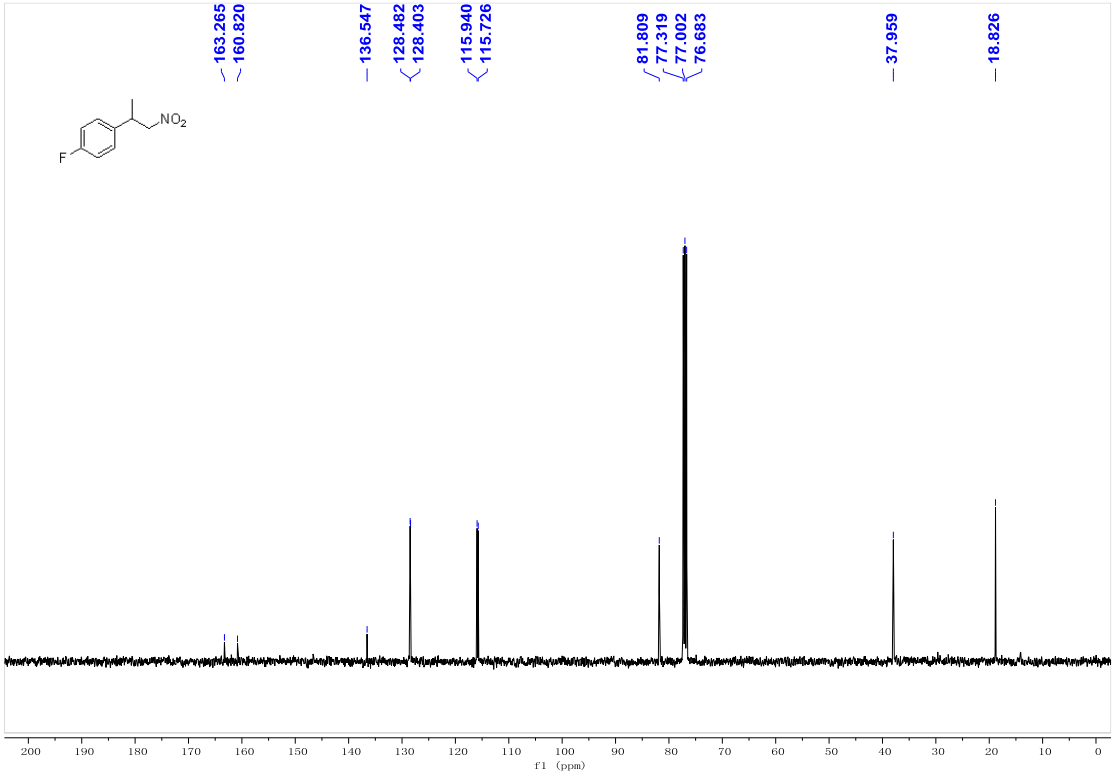
3-(2-Nitropropyl)-1H-indole(4q):



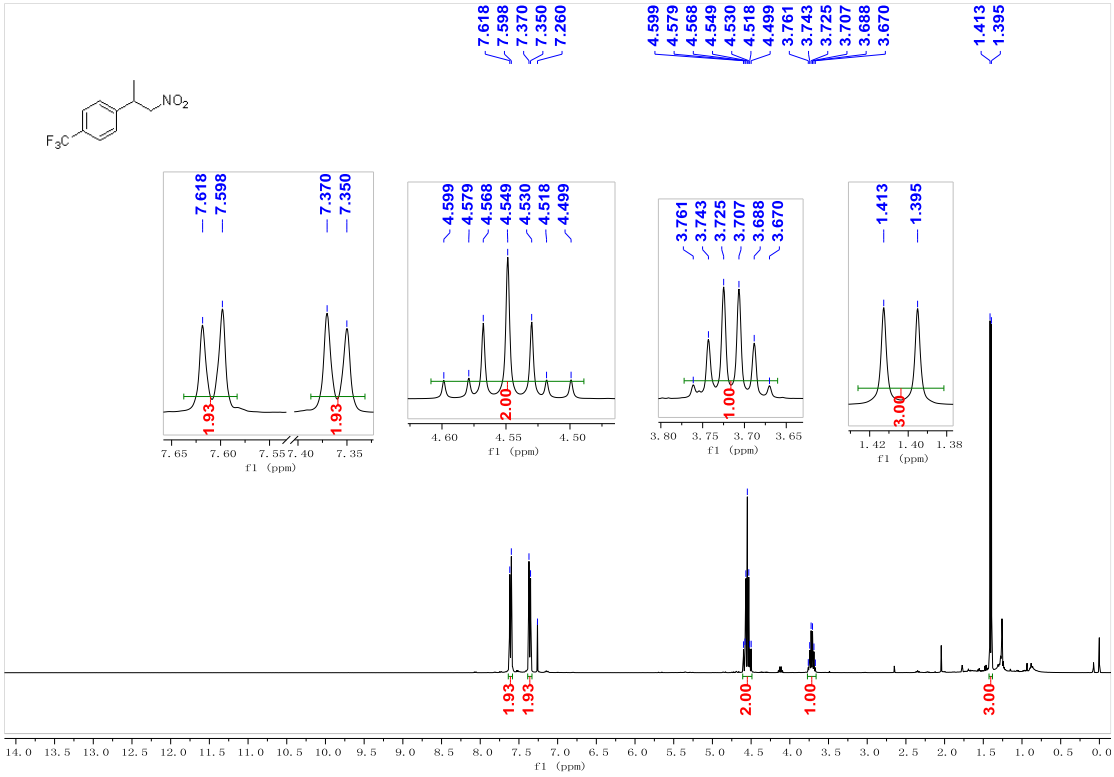


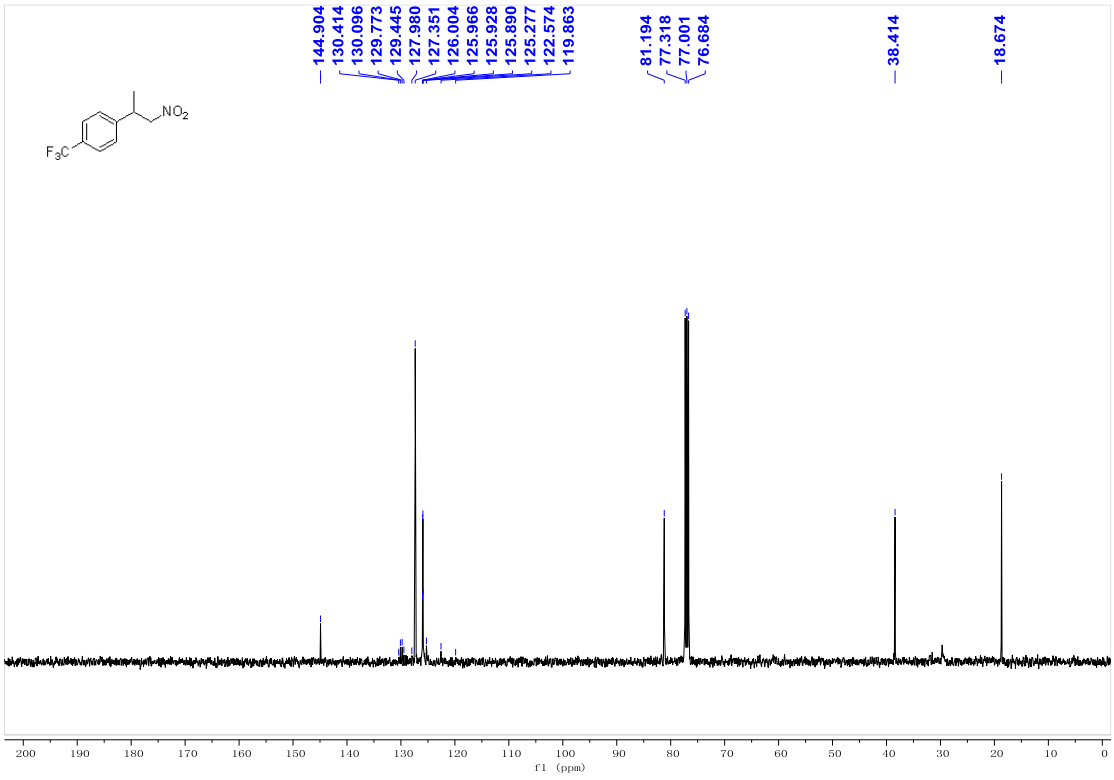
1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a):



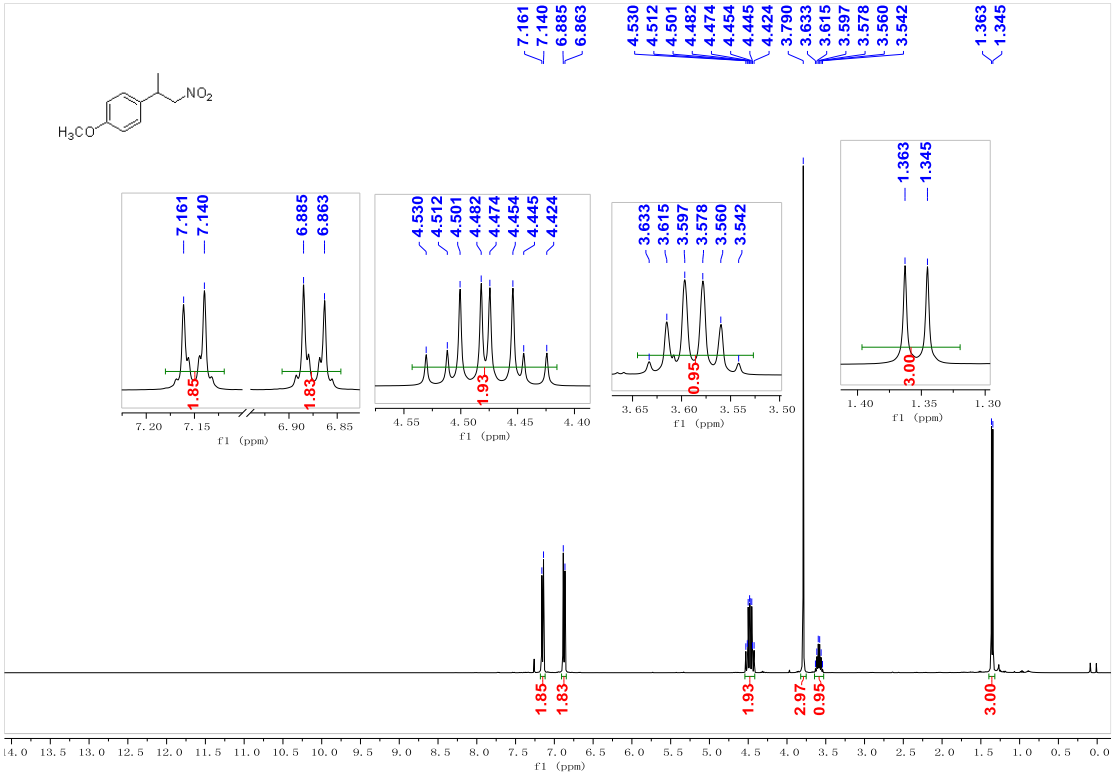


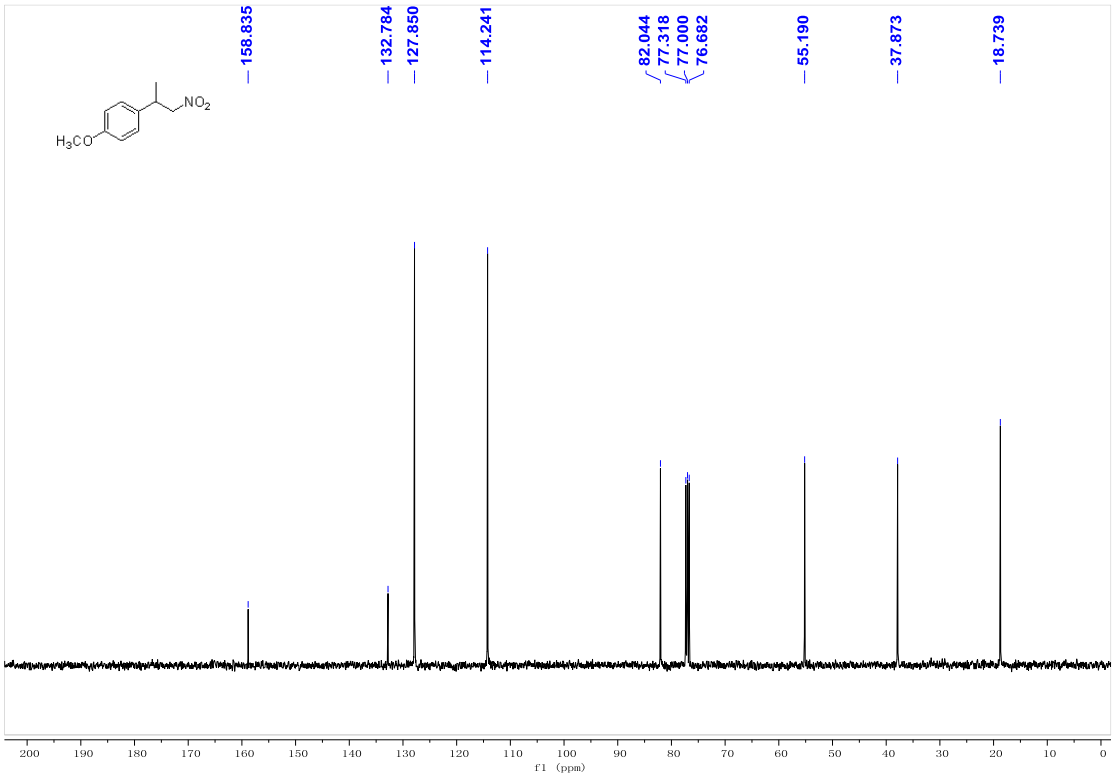
1-(1-Nitropropan-2-yl)-4-(trifluoromethyl)benzene (8b):



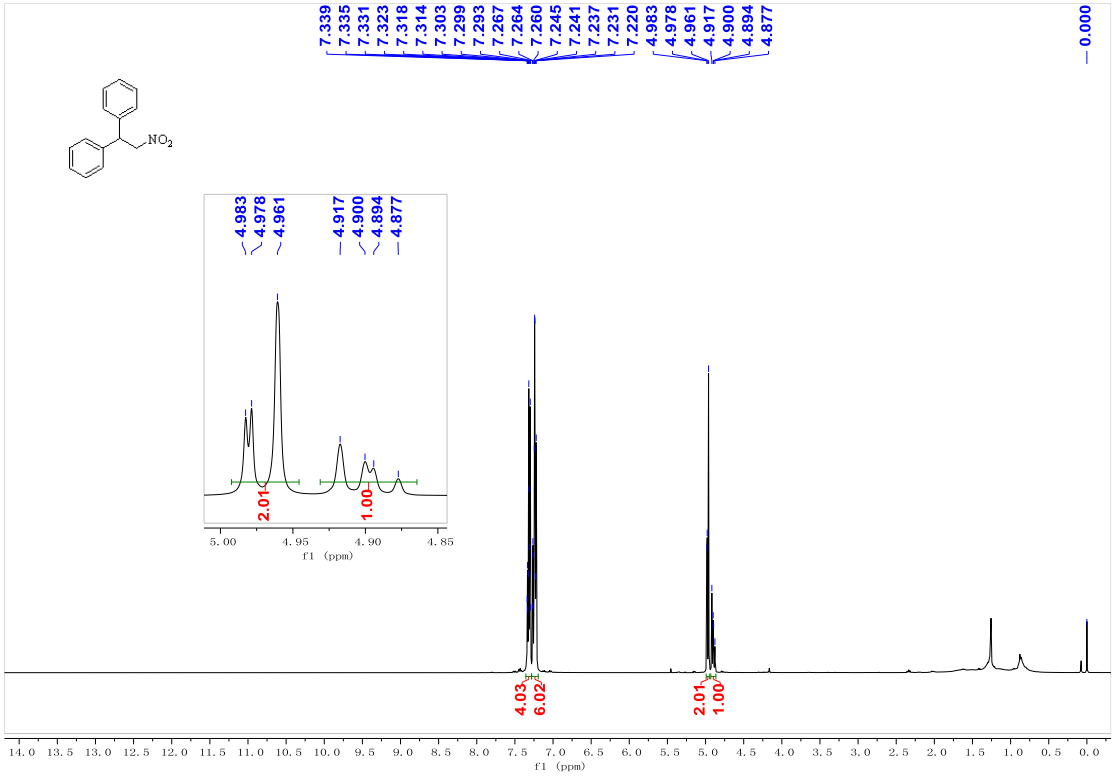


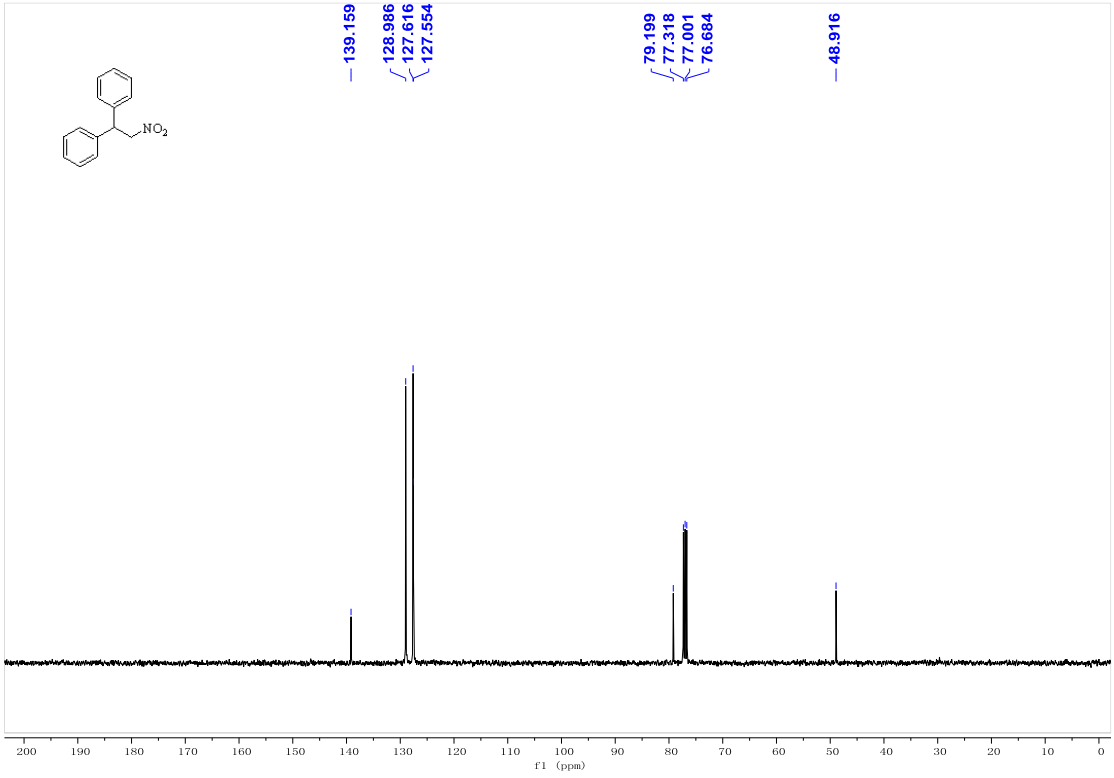
1-Methoxy-4-(1-nitropropan-2-yl)benzene (8c):





(2-Nitroethene-1,1-diyl)dibenzene (8d):





15. ^{1}H NMR spectra of crude reaction mixtures in optimization (Table 1)

Table 1, entry 1.

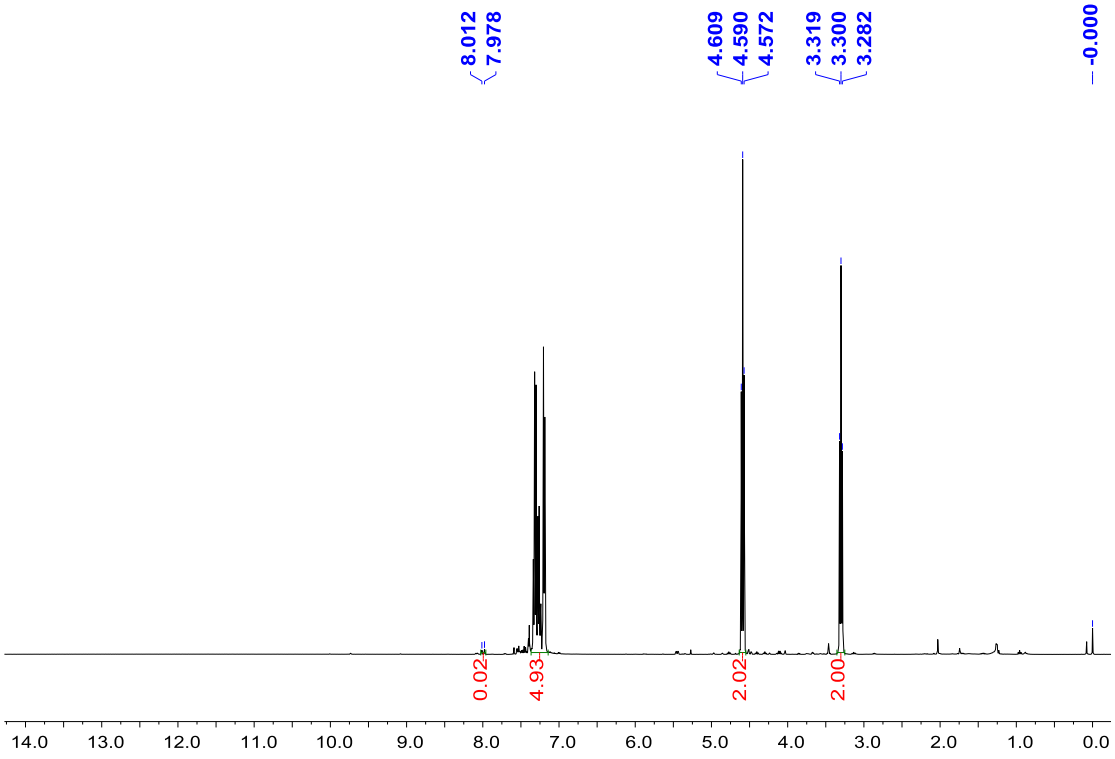
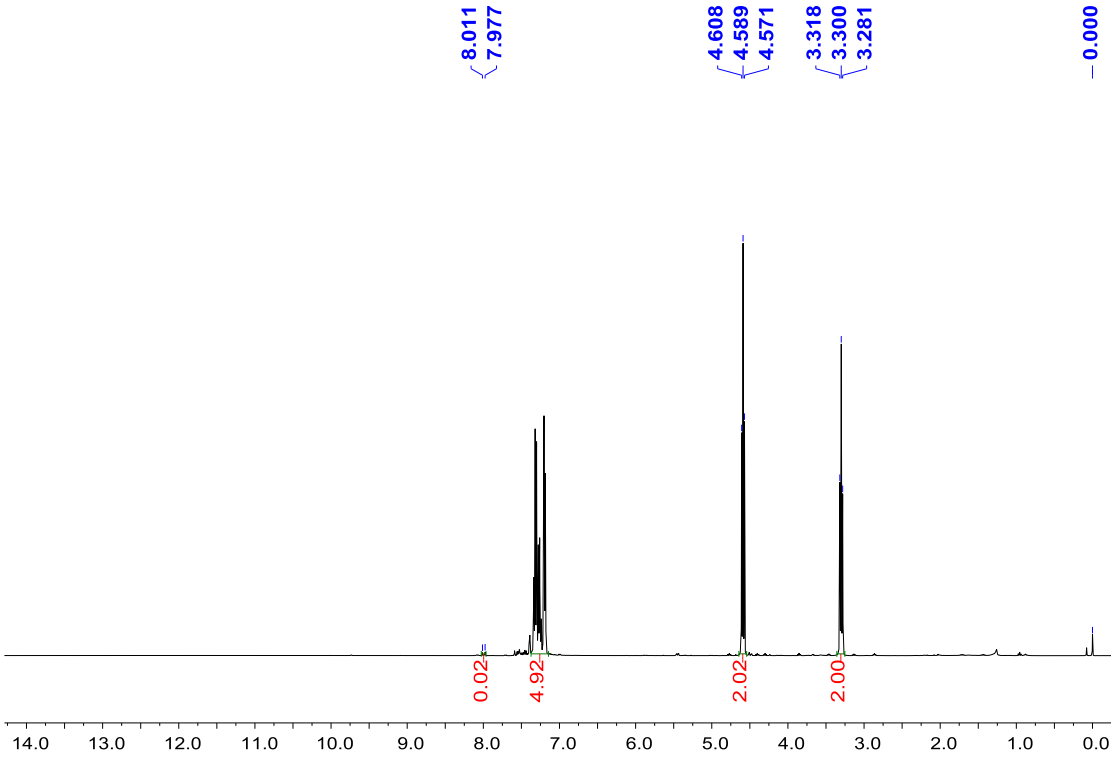


Table 1, entry 2.



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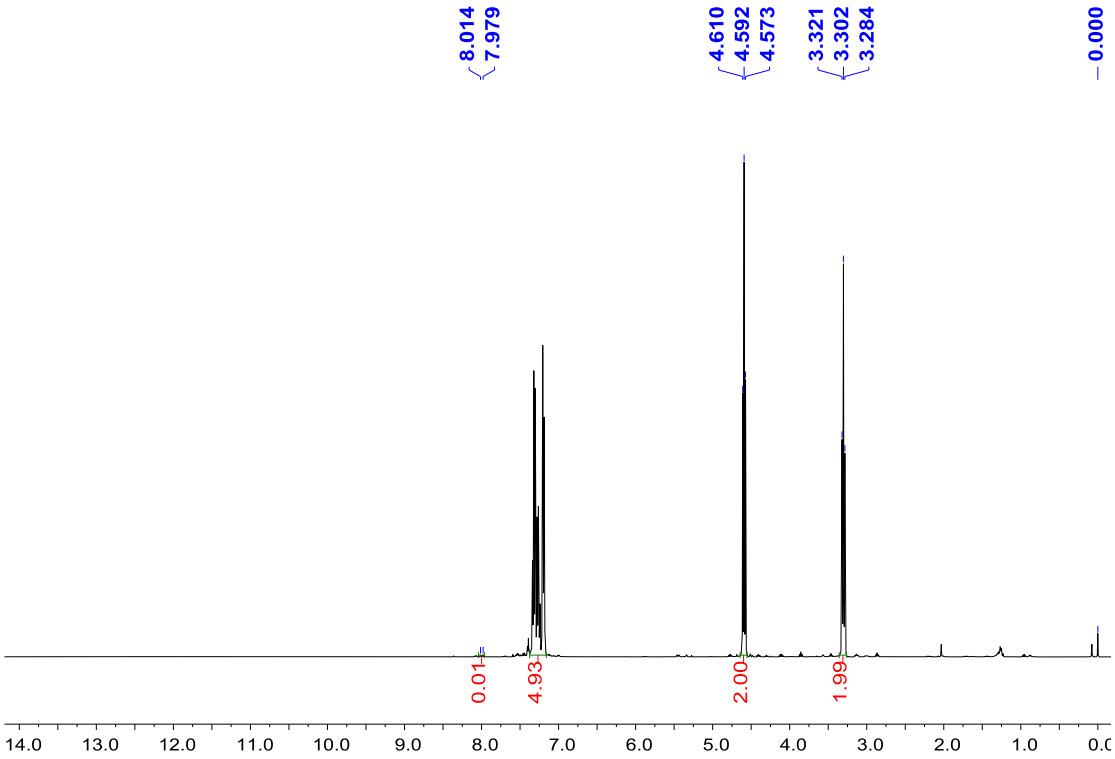
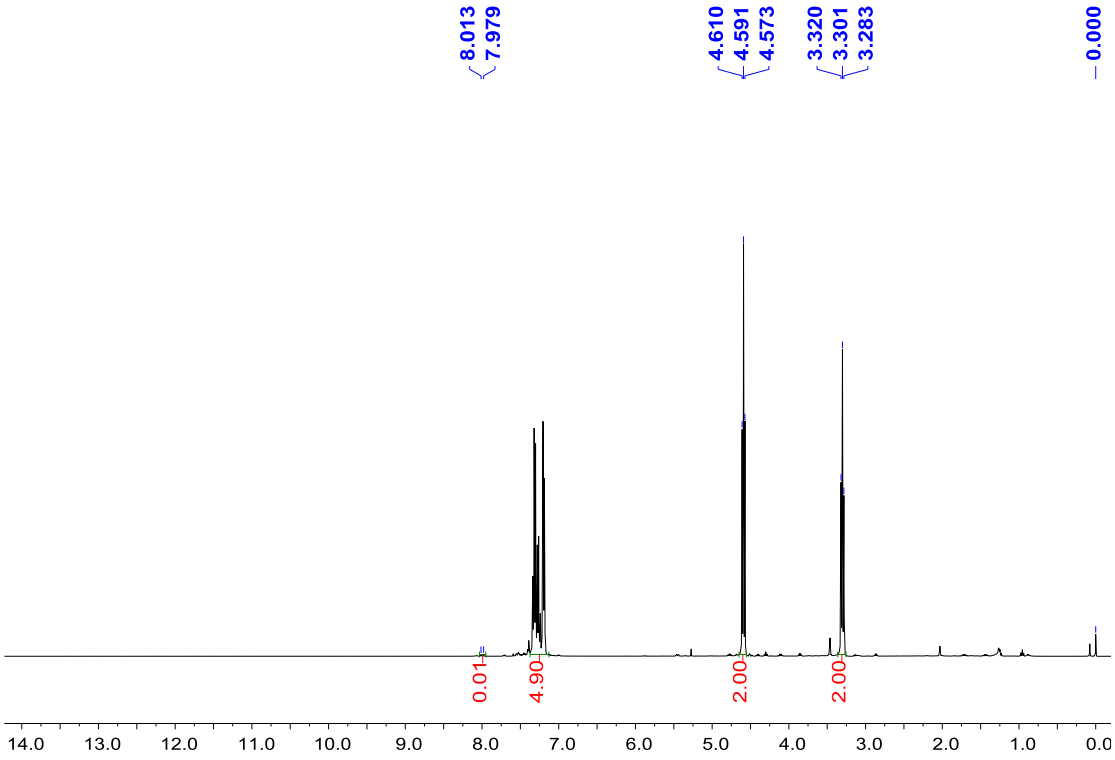


Table 1, entry 4.



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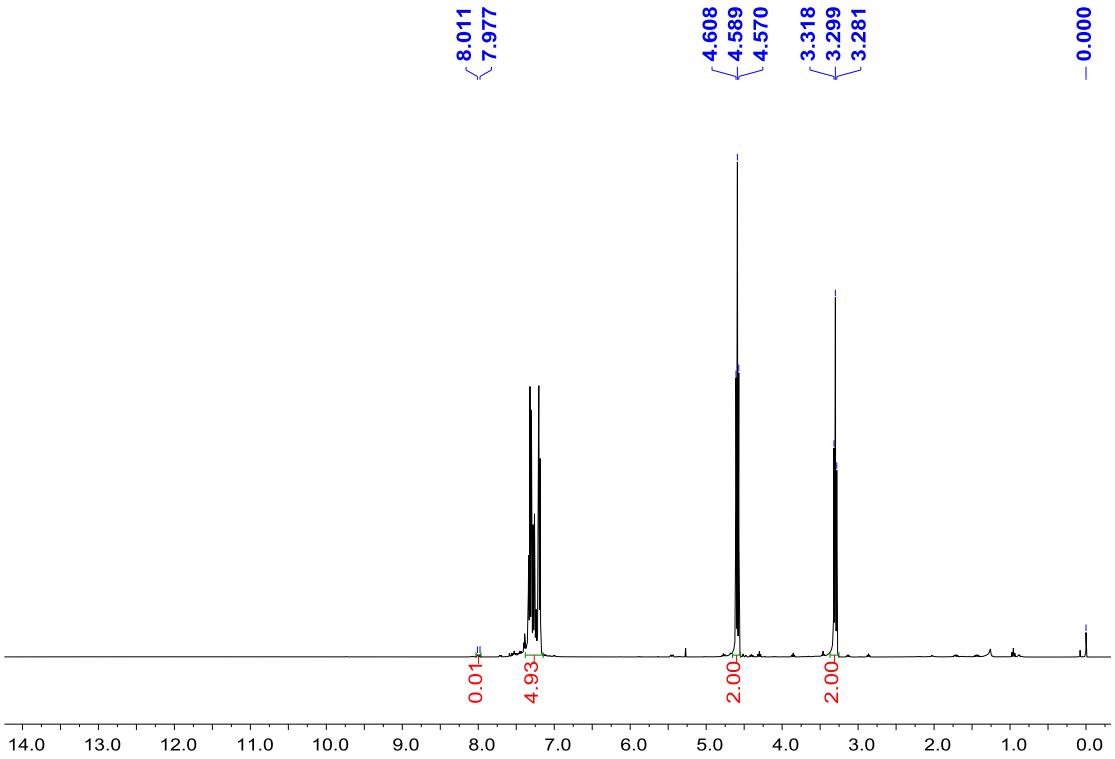

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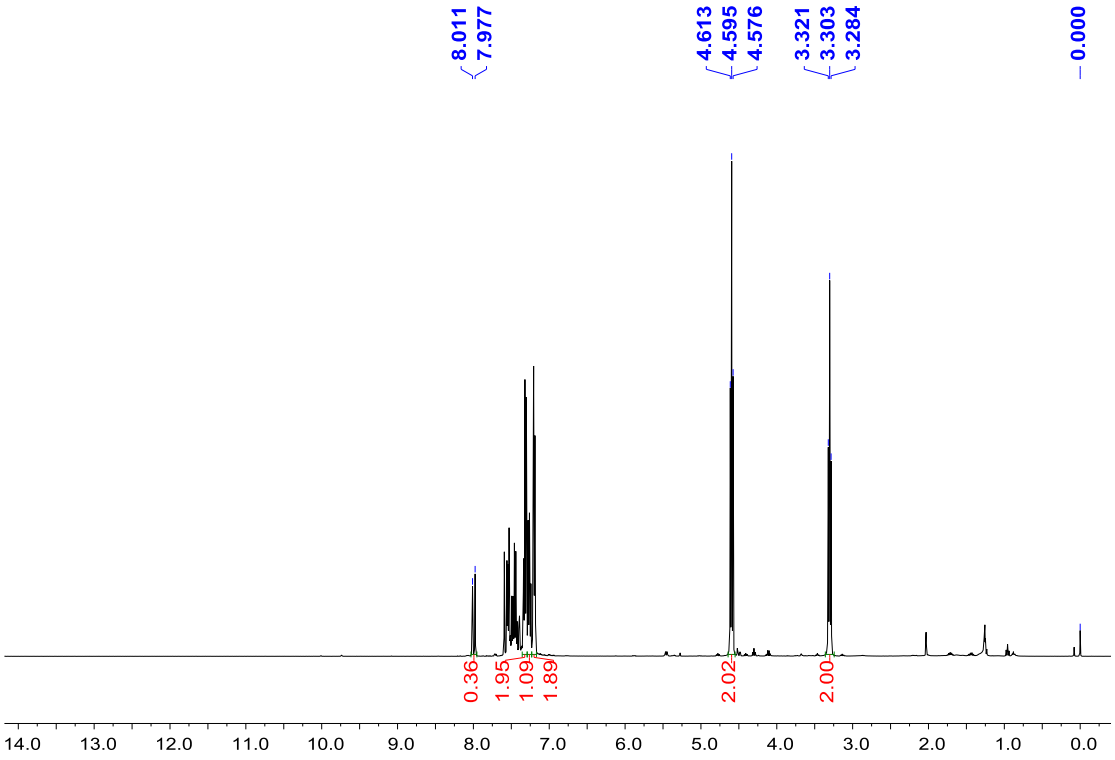

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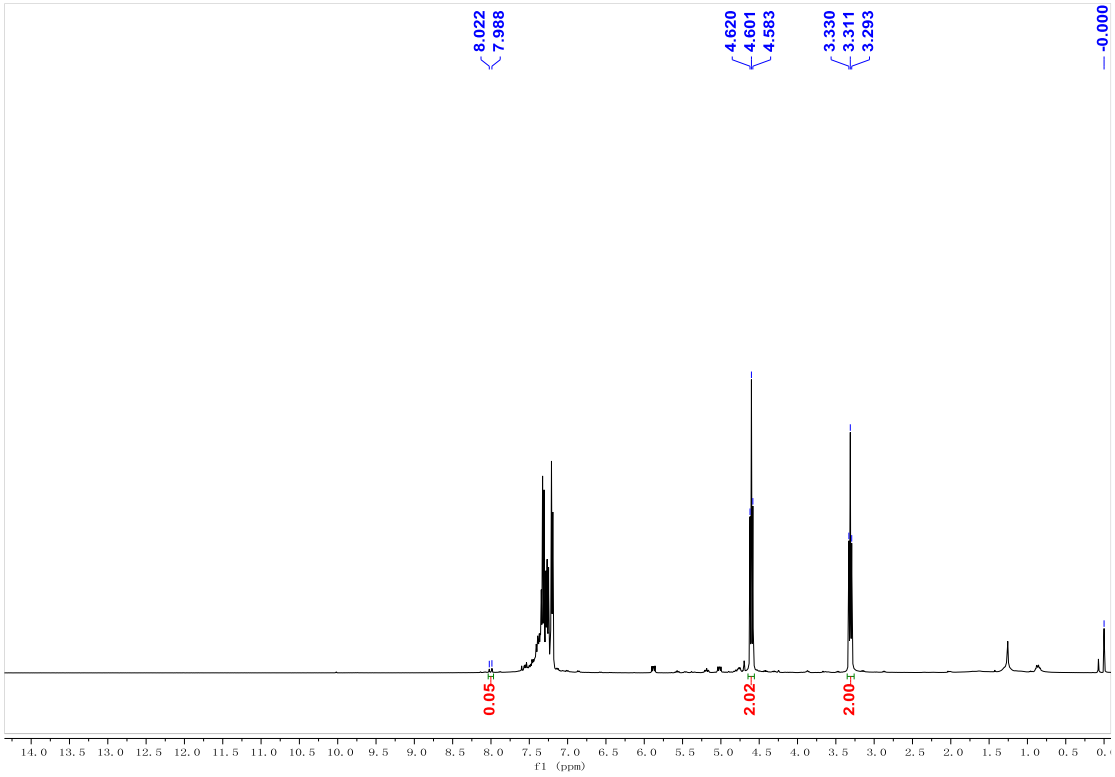

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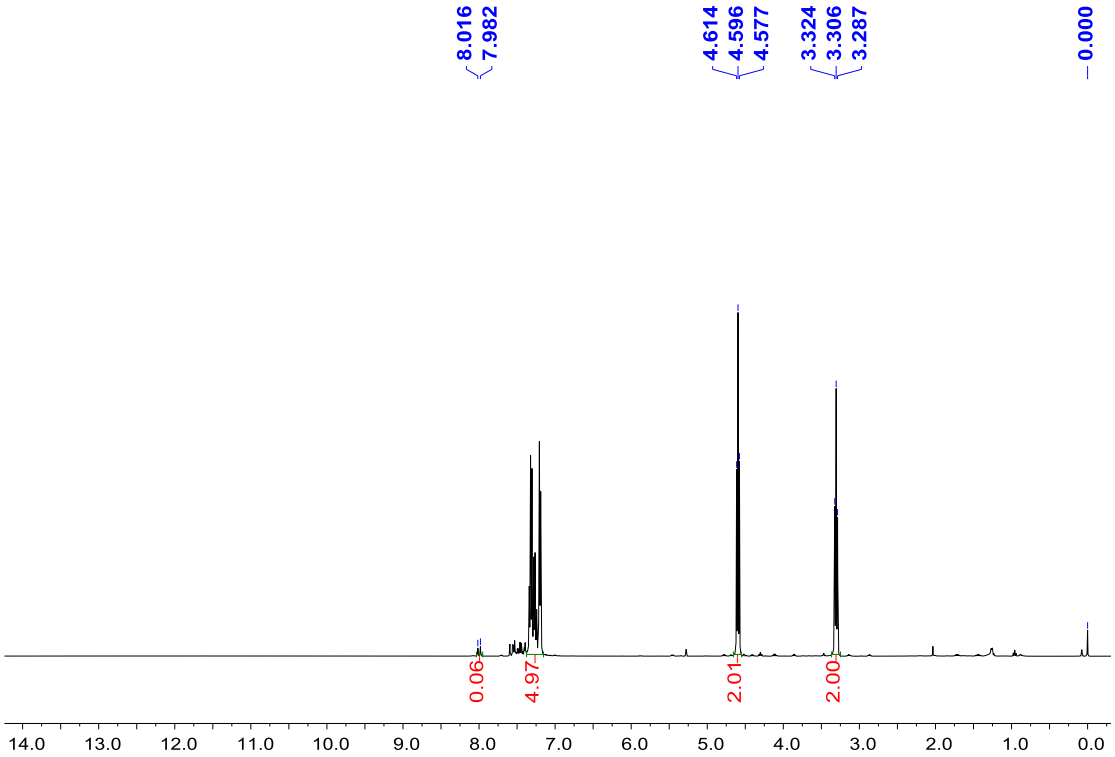
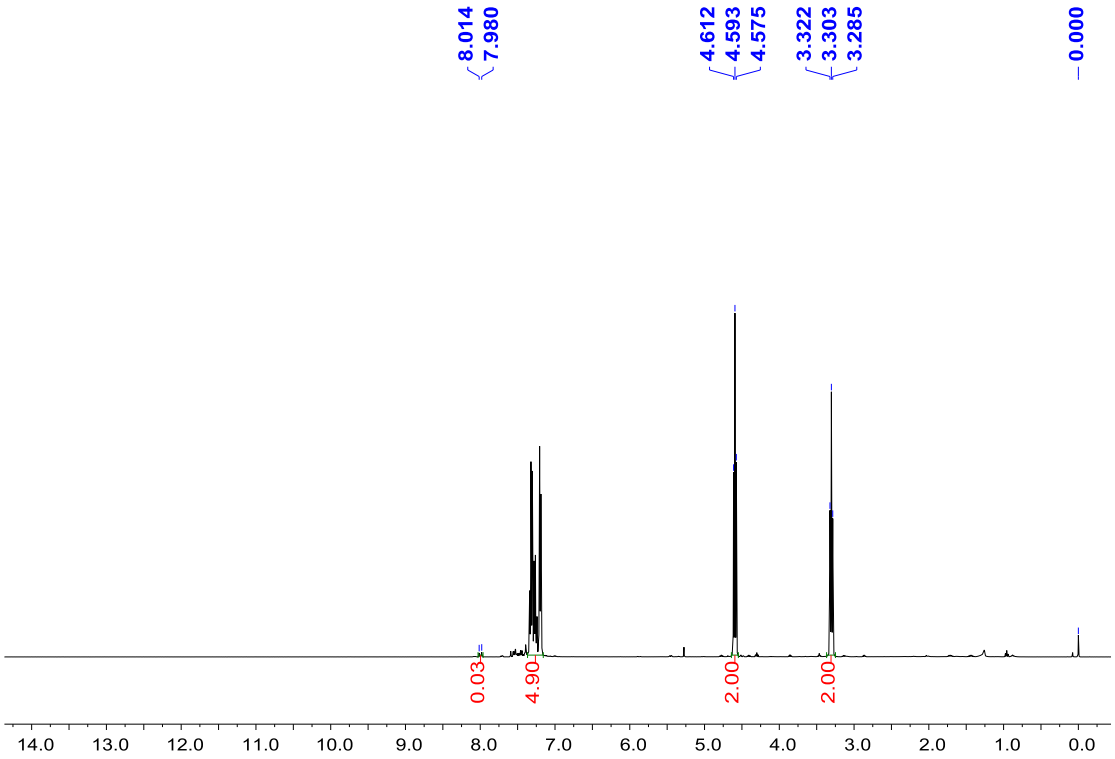


Table 1, entry 9.



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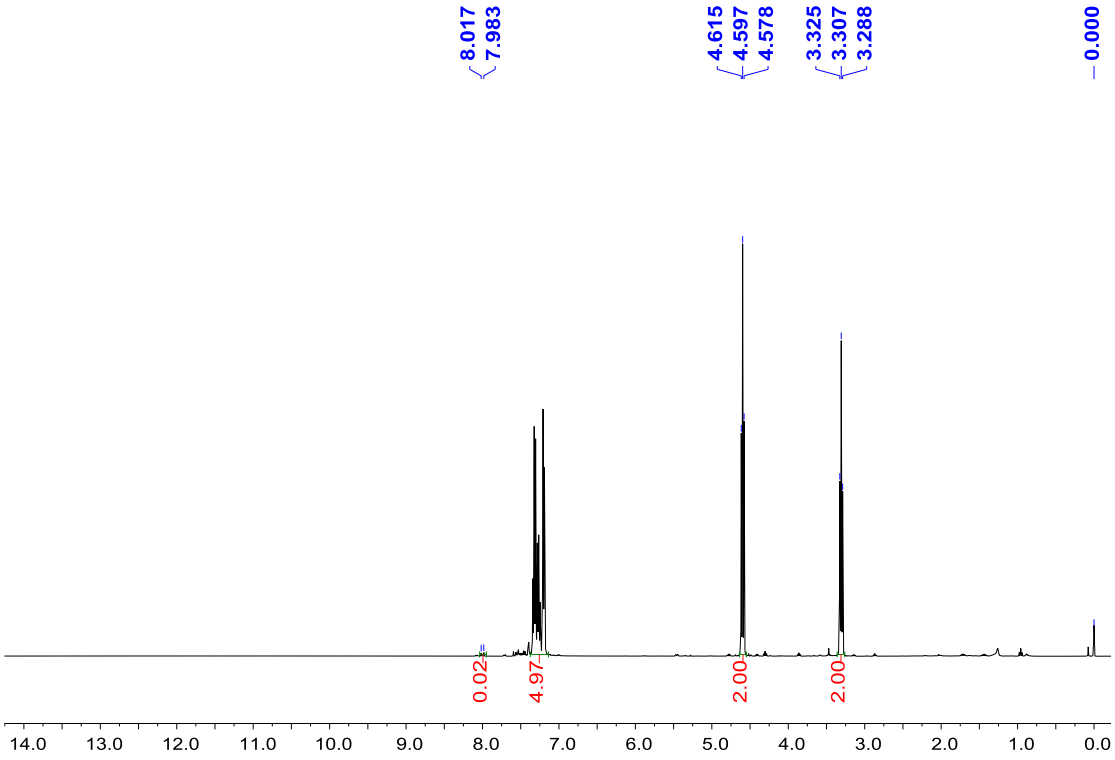

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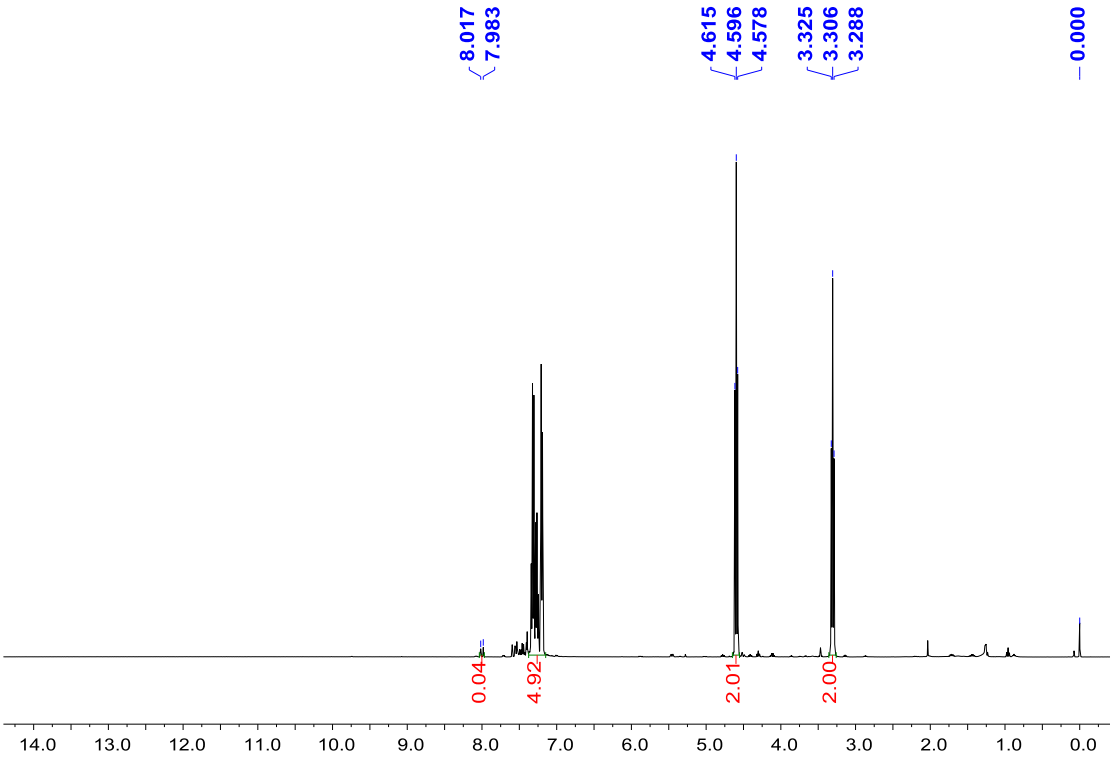

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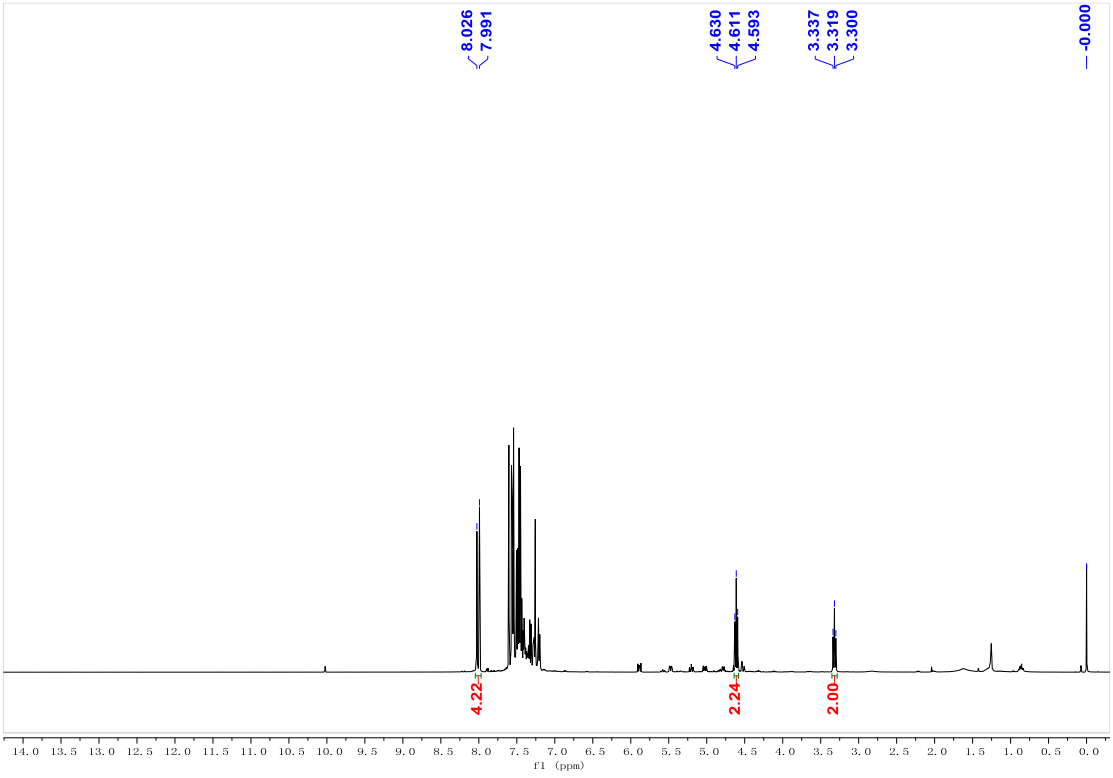


Table 1, entry 13.

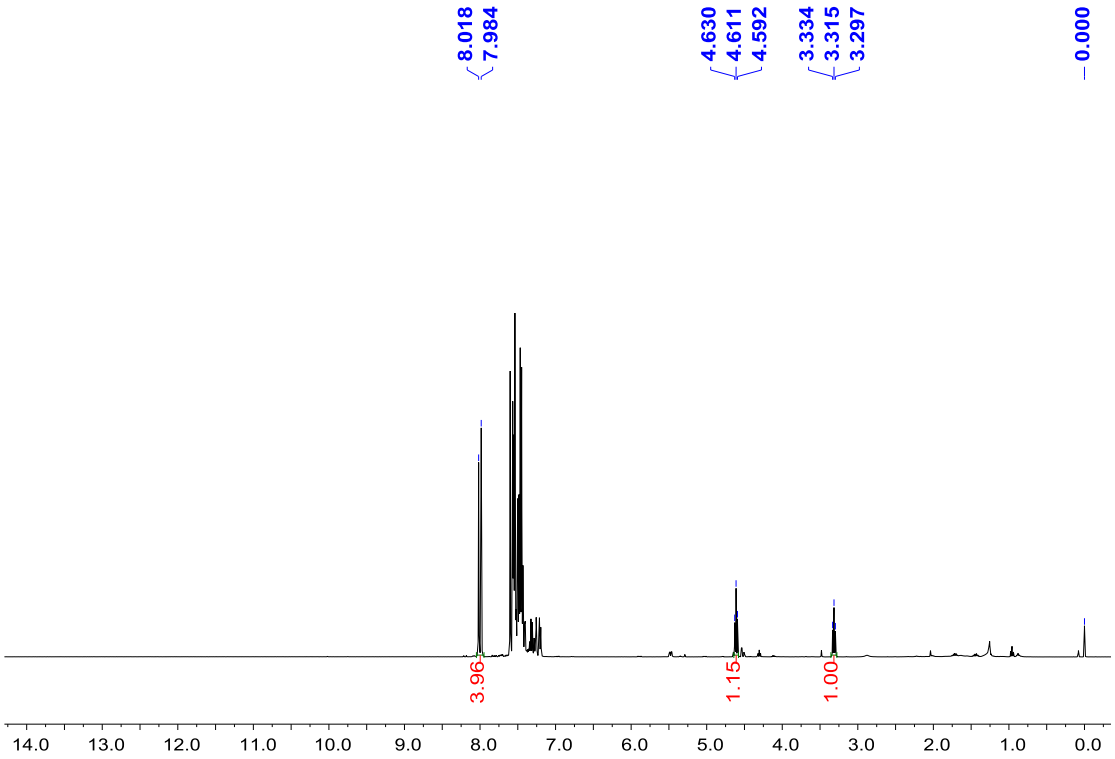


Table 1, entry 14.

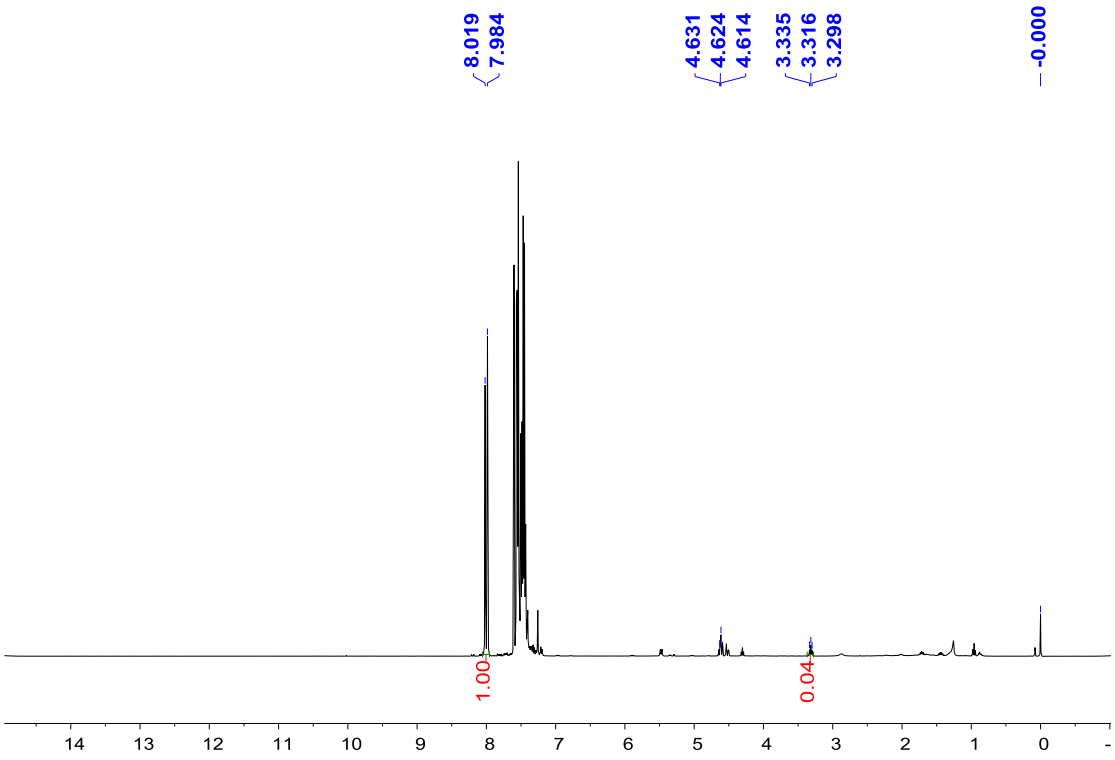


Table 1, entry 15.

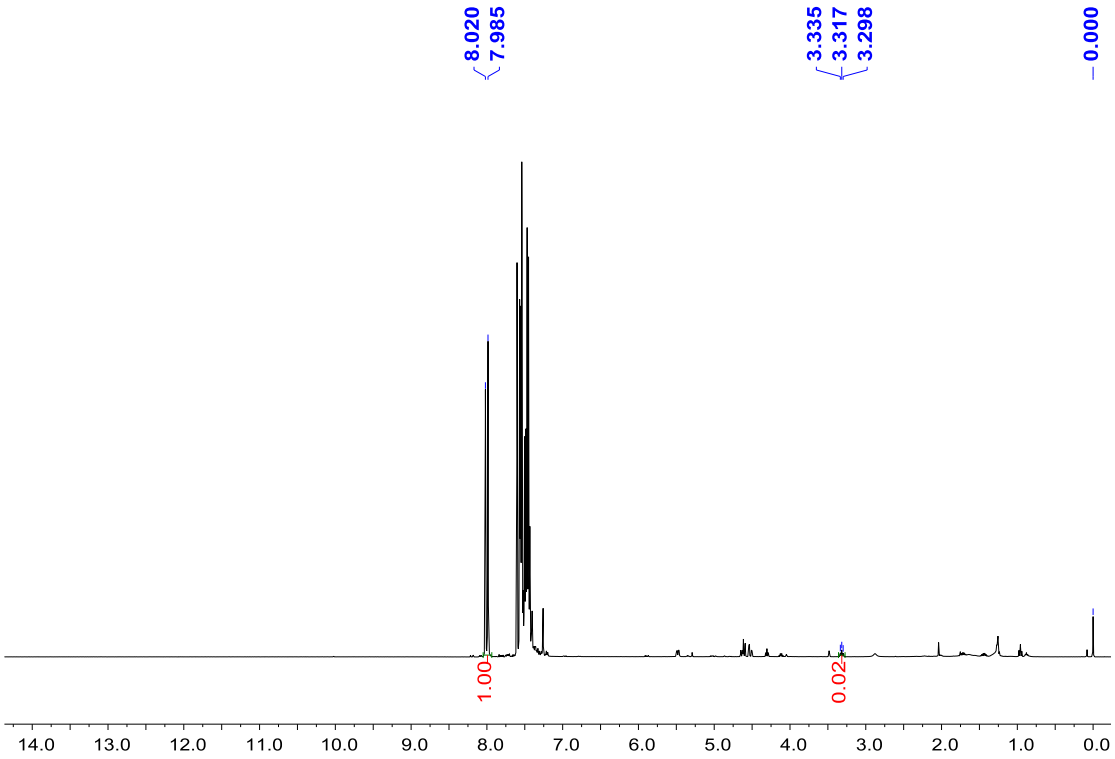


Table 1, entry 16.

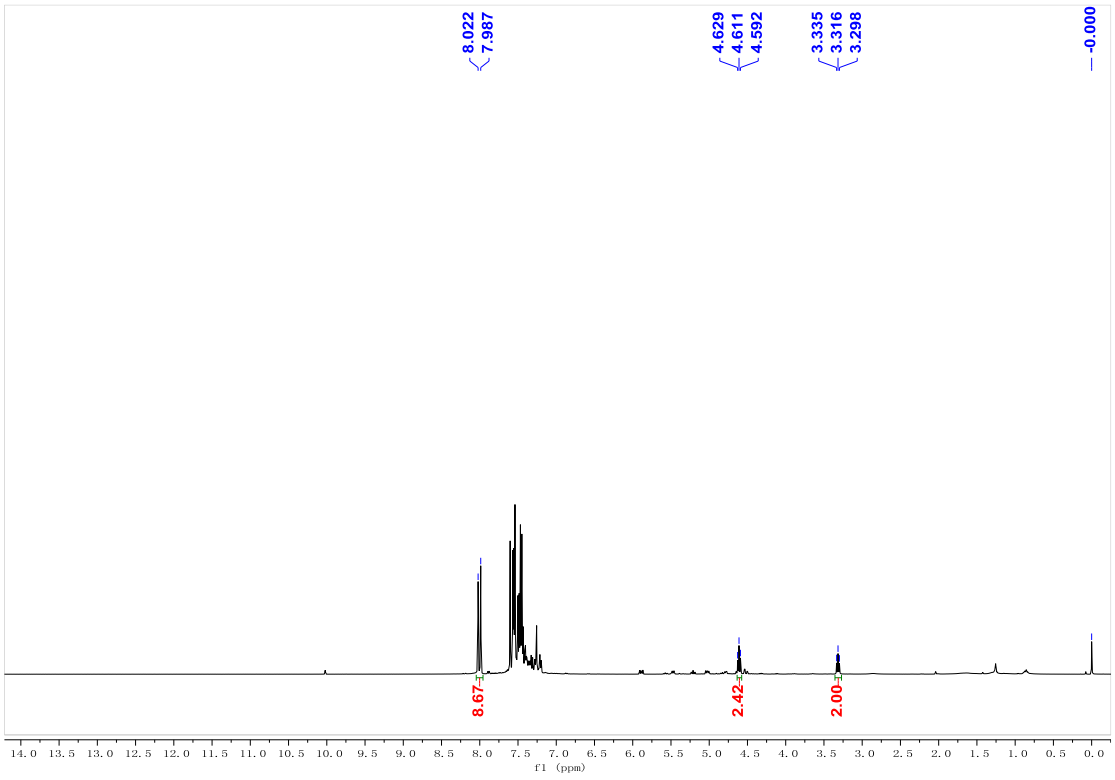


Table 1, entry 17.

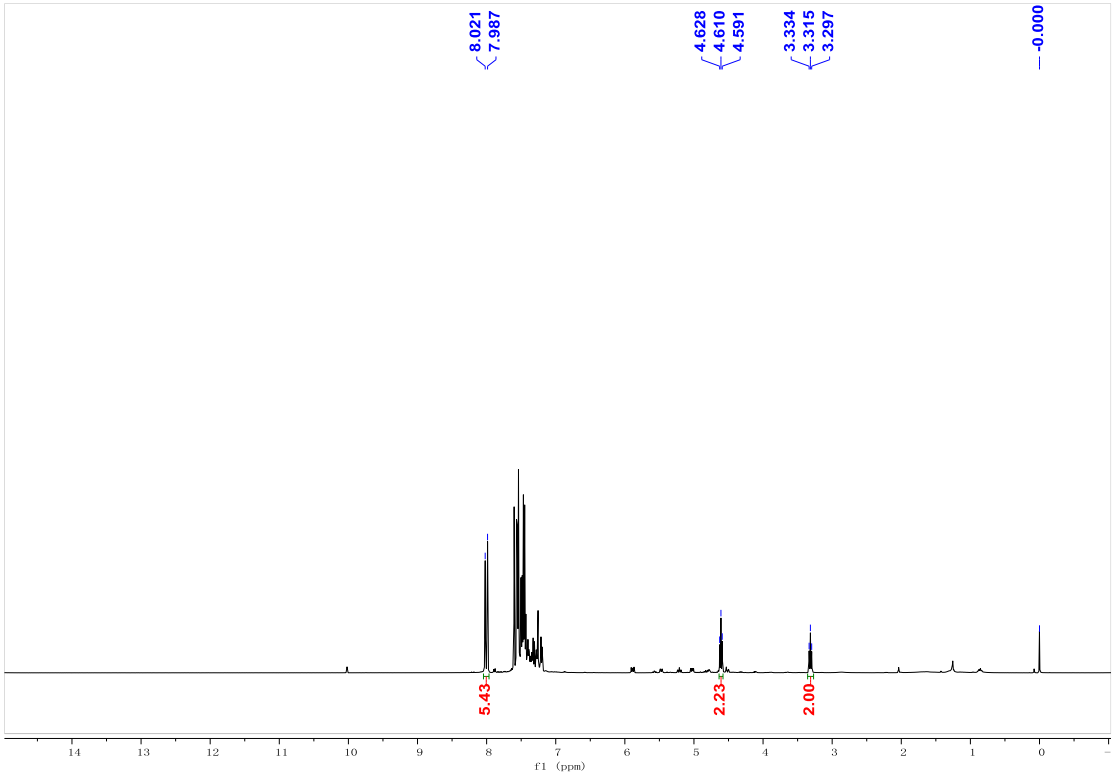


Table 1, entry 18.

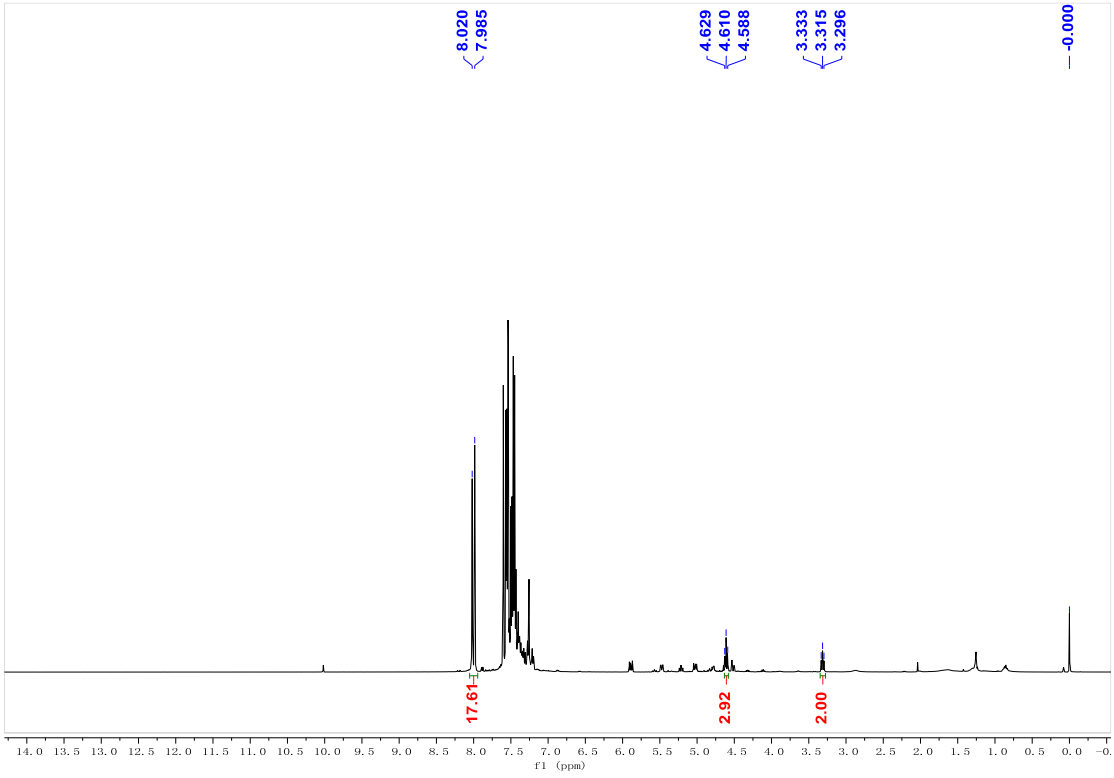


Table 1, entry 19.

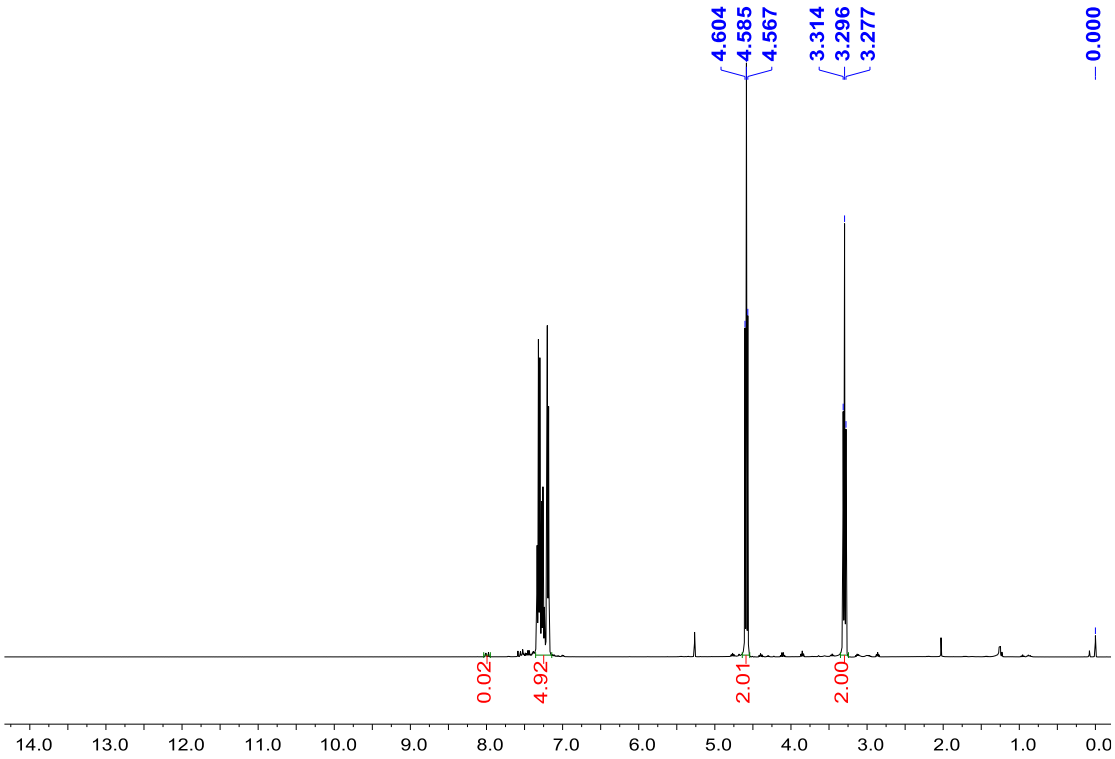


Table 1, entry 20.

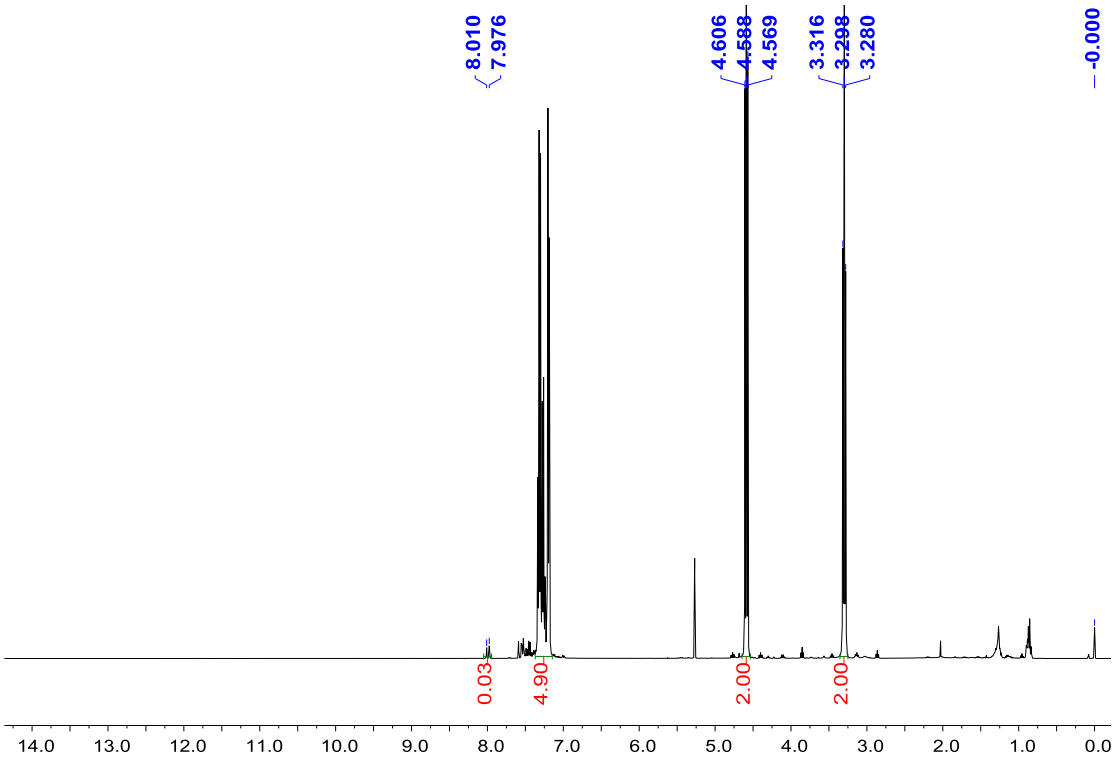


Table 1, entry 21.

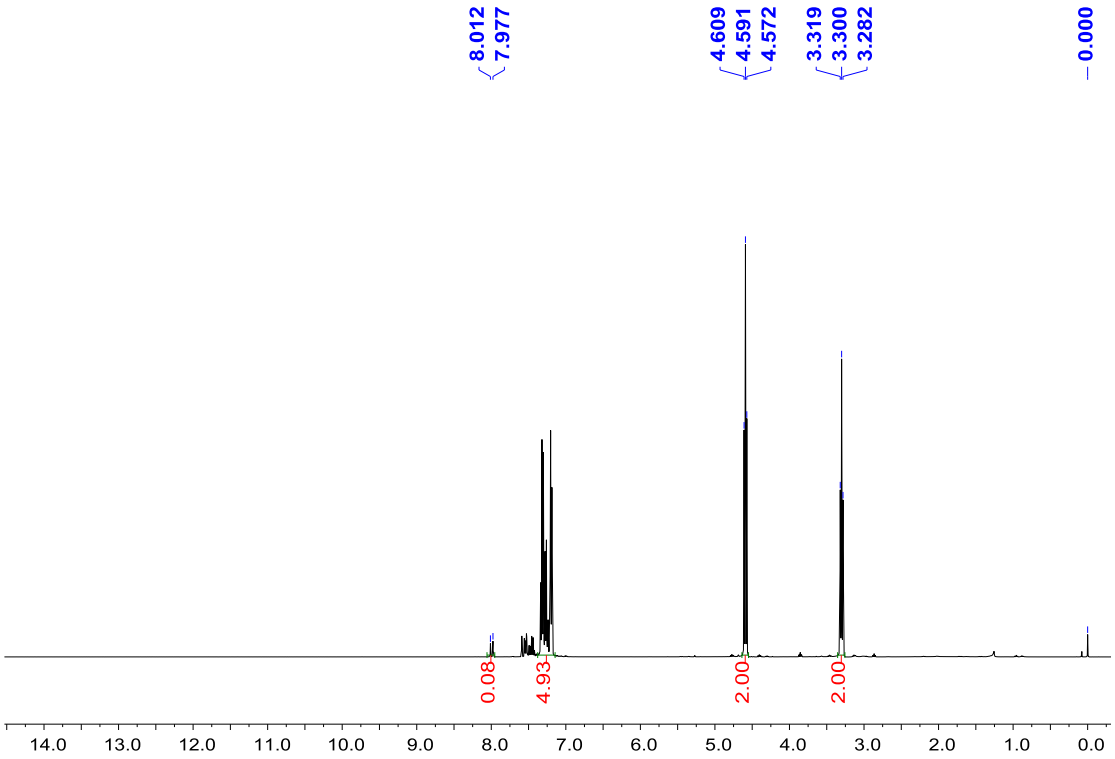


Table 1, entry 22.

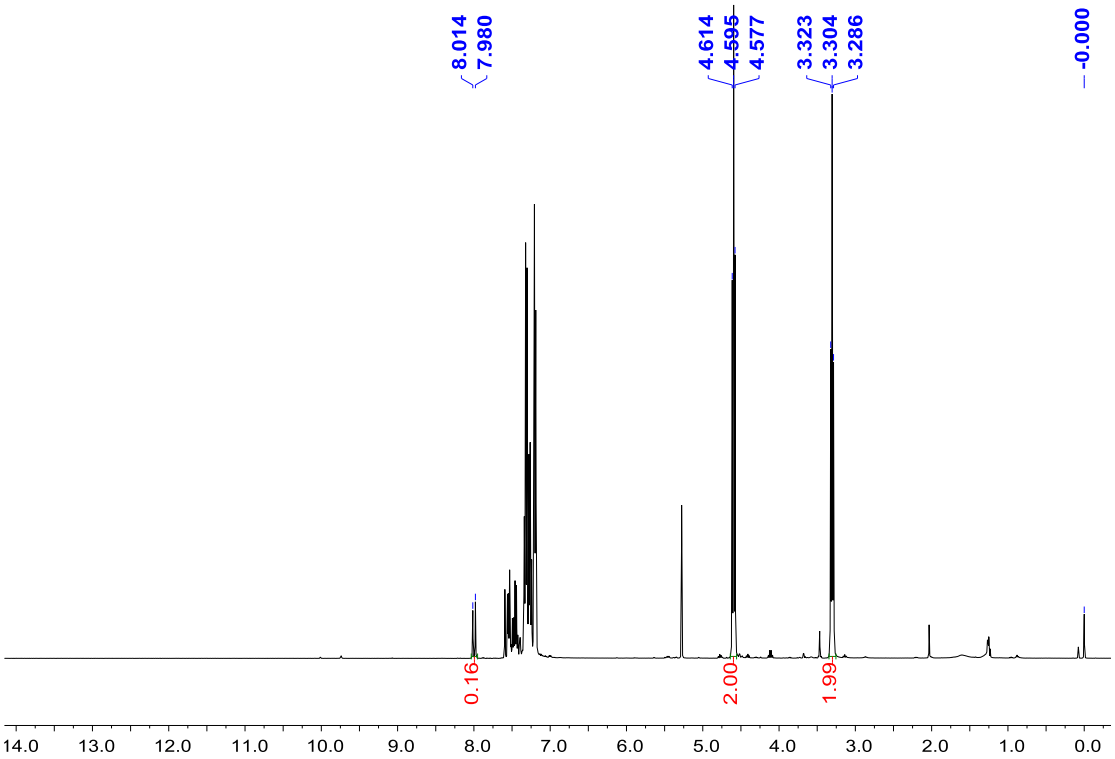


Table 1, entry 23.

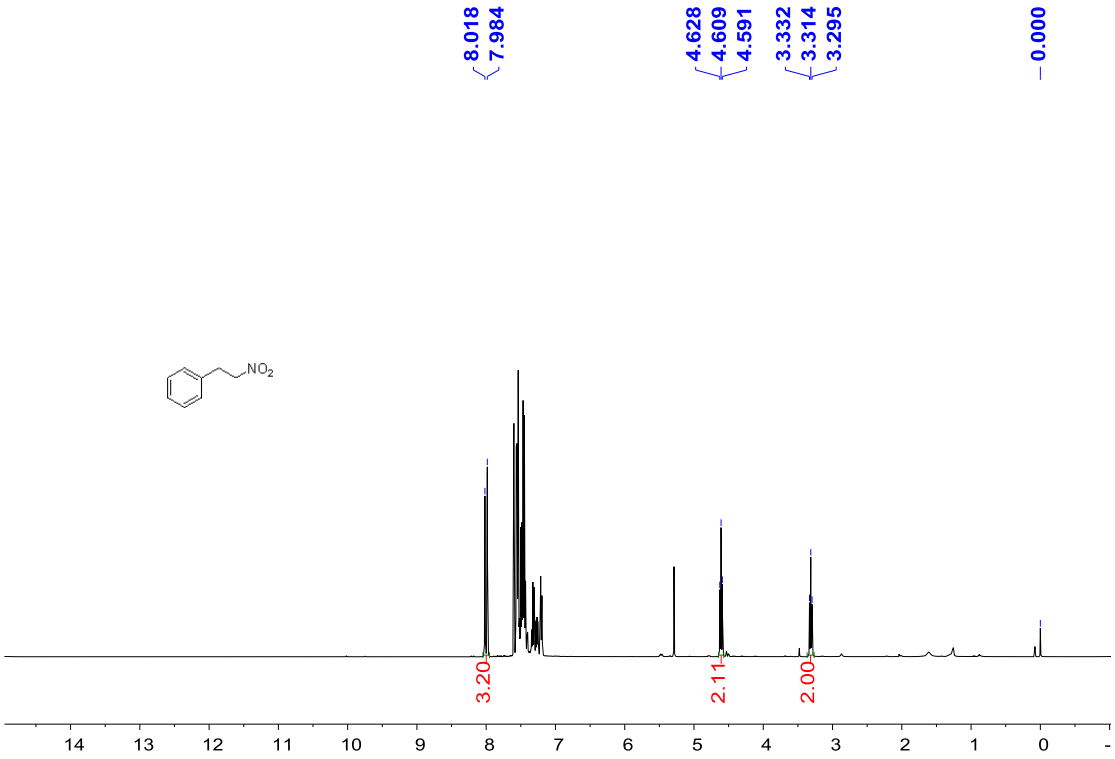


Table 1, entry 24.

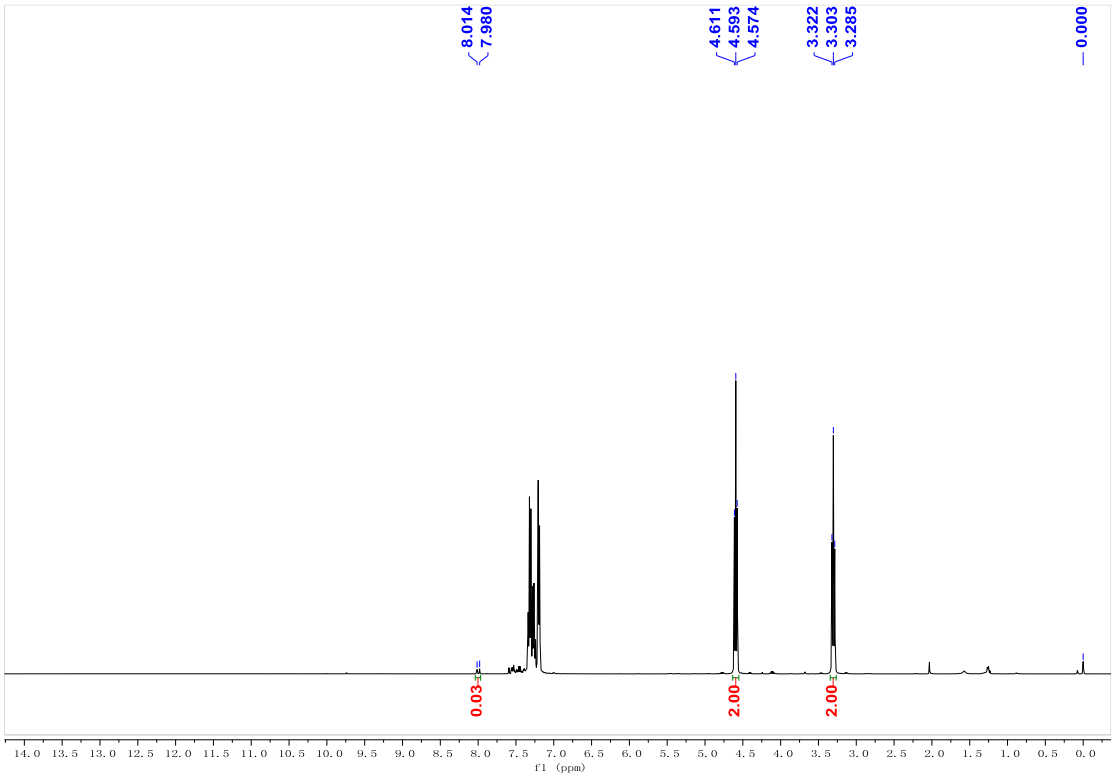


Table 1, entry 25.

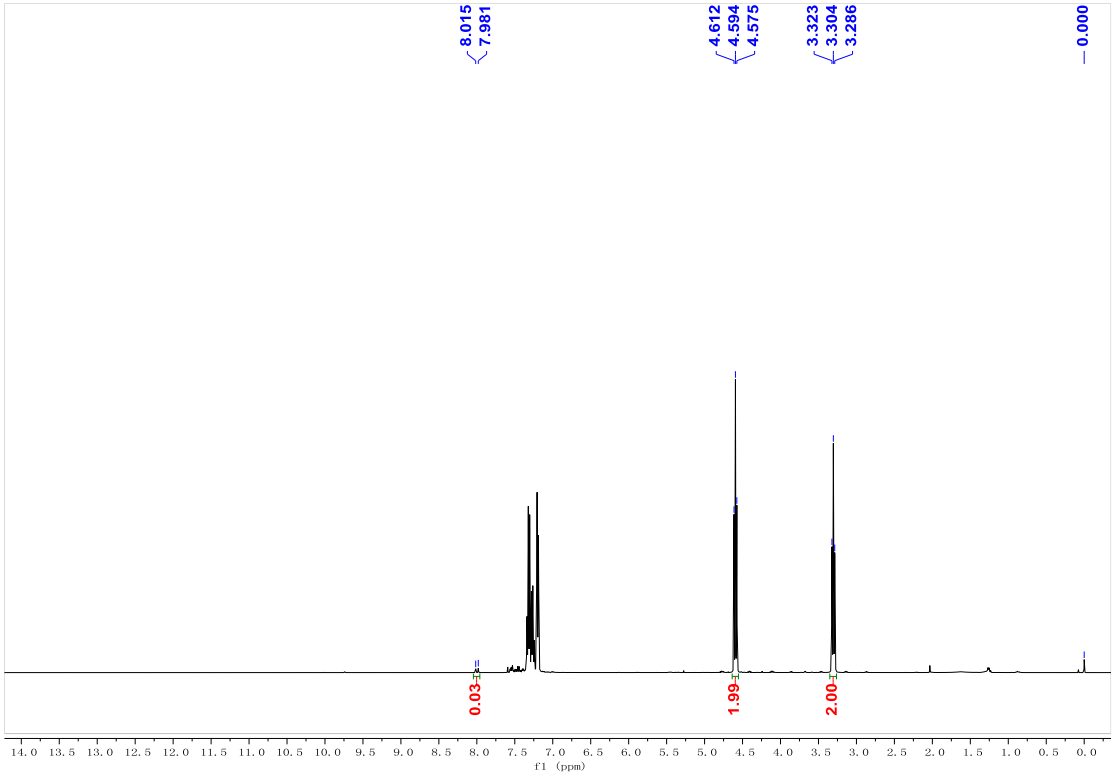
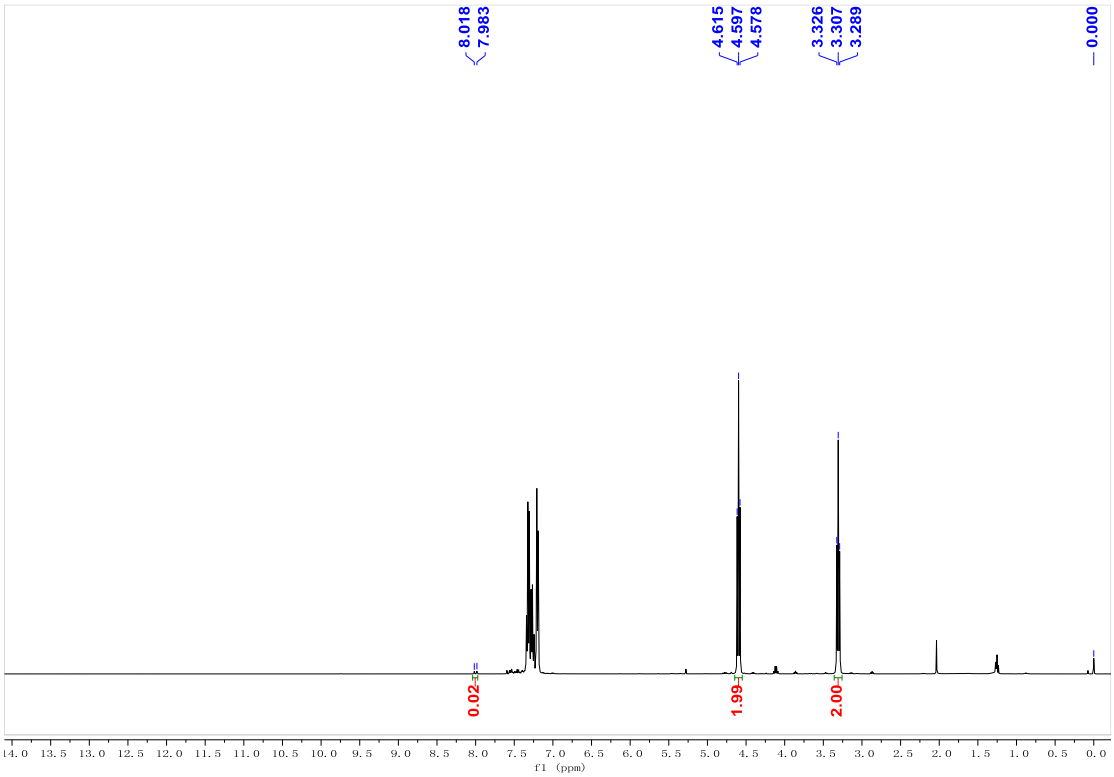
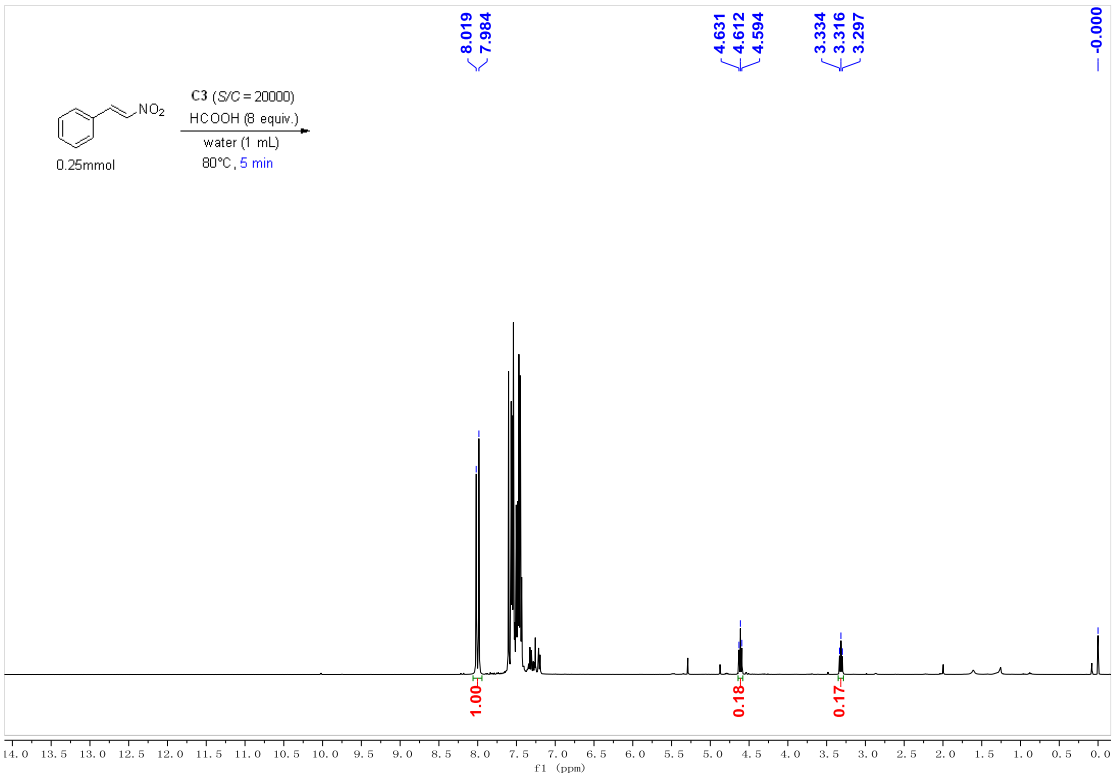
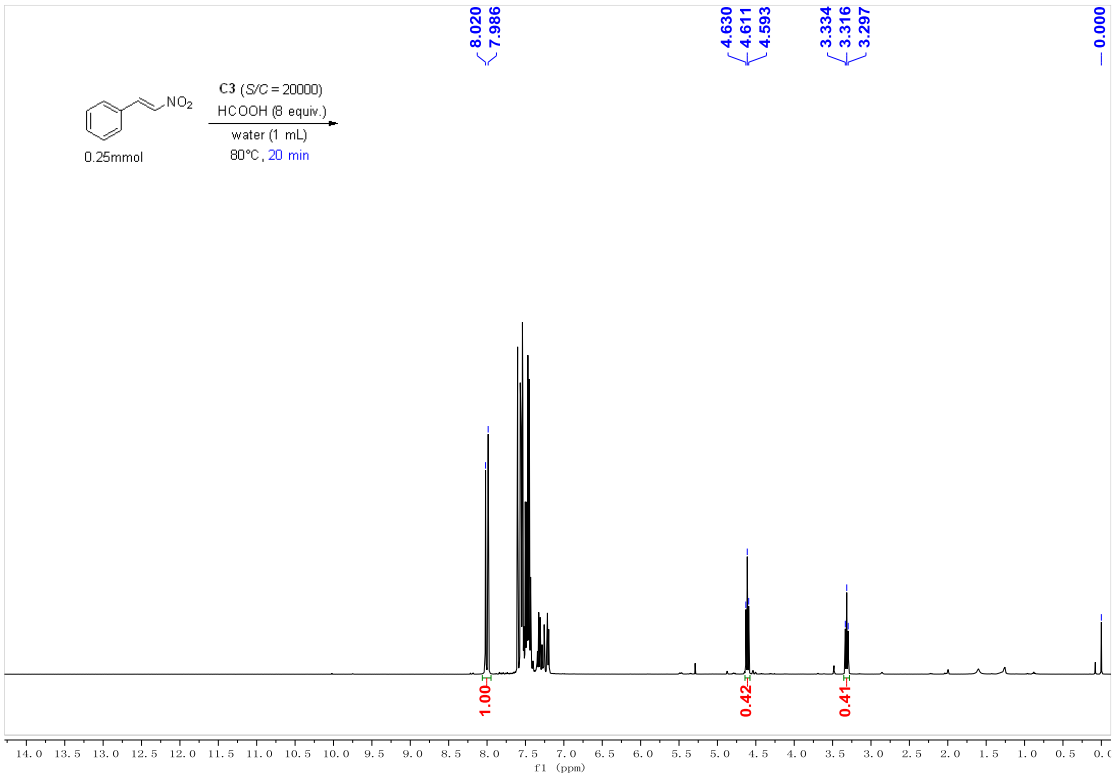


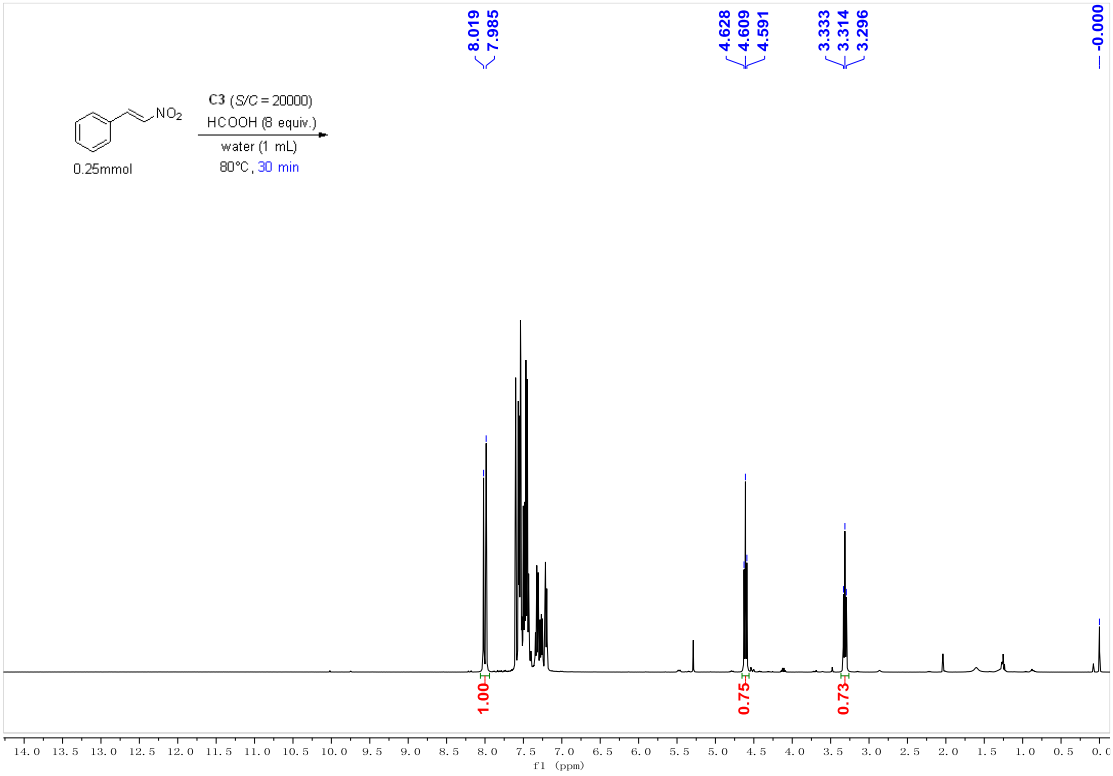
Table 1, entry 26.

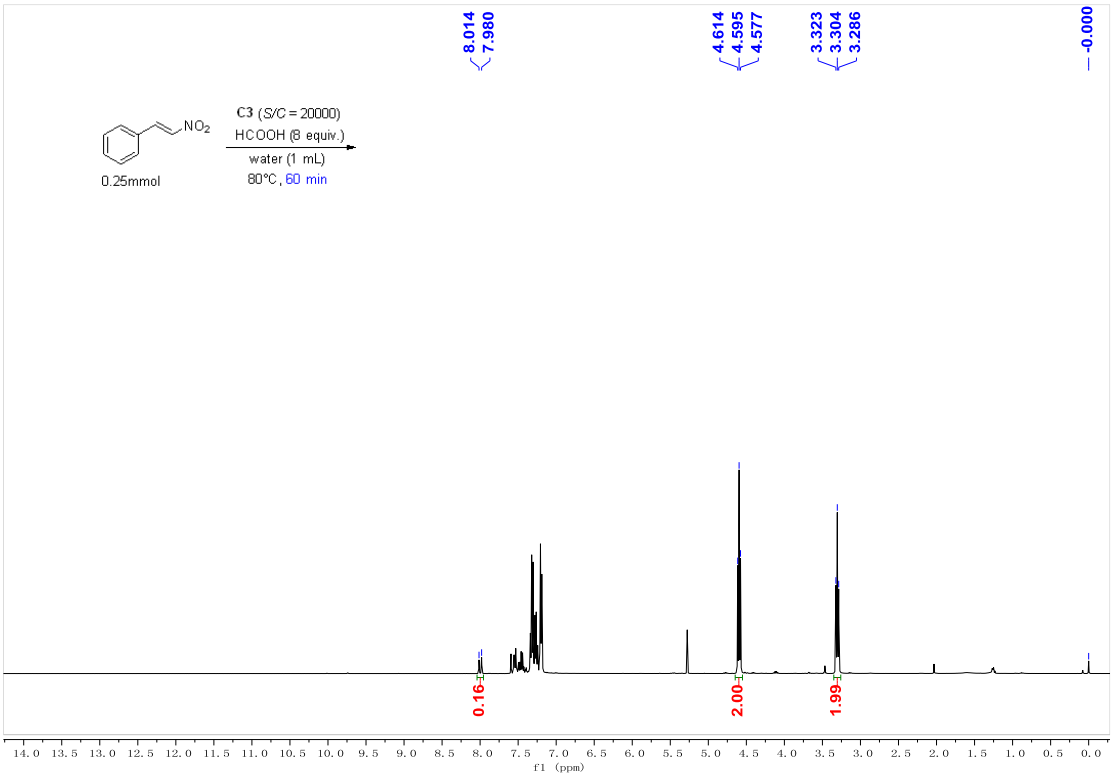


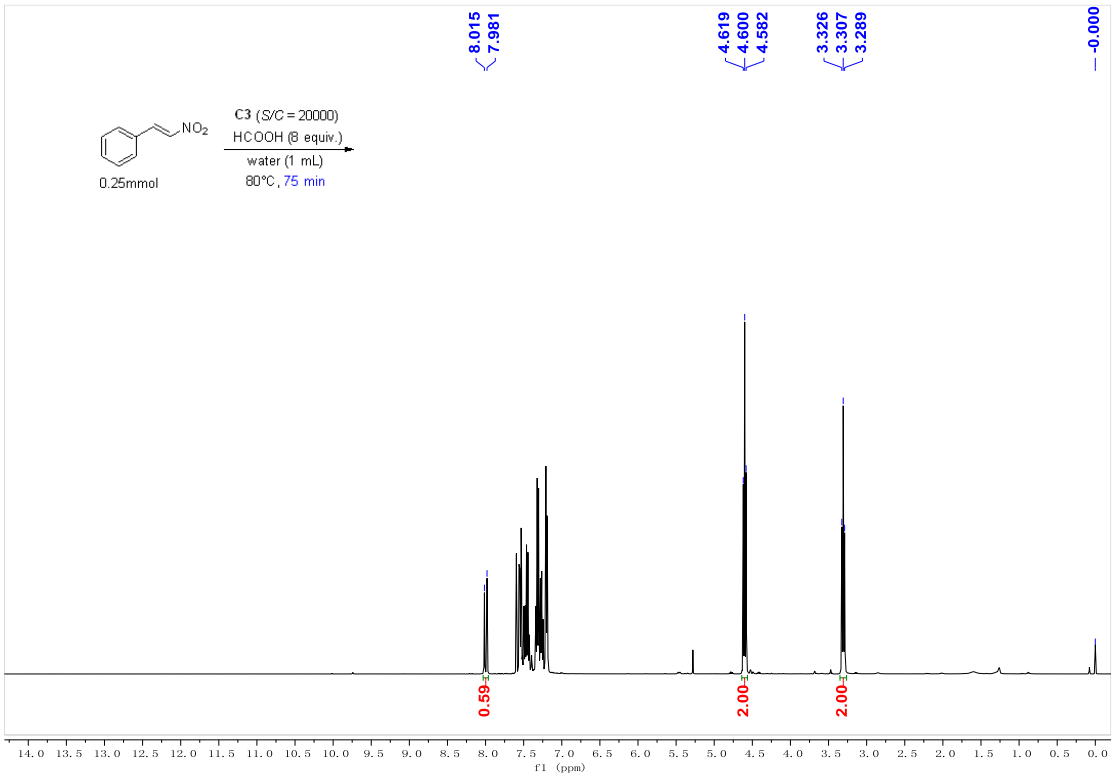
16. ^{1}H NMR spectra of crude reaction mixtures in Table 2.



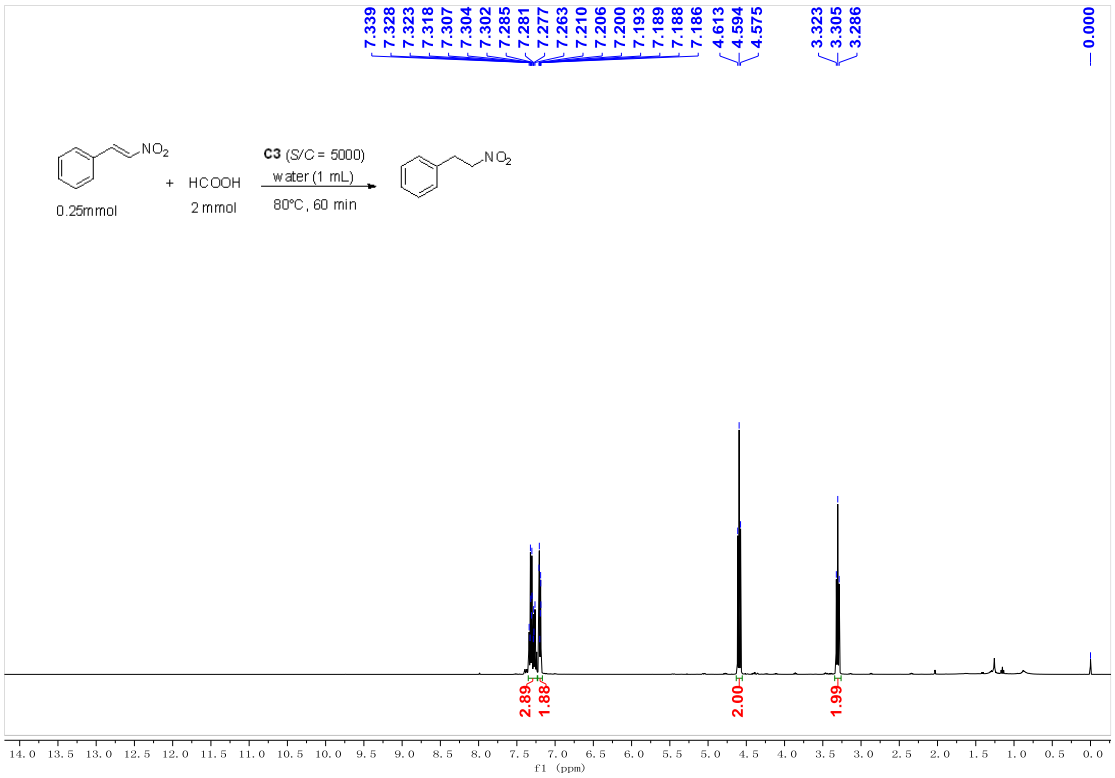


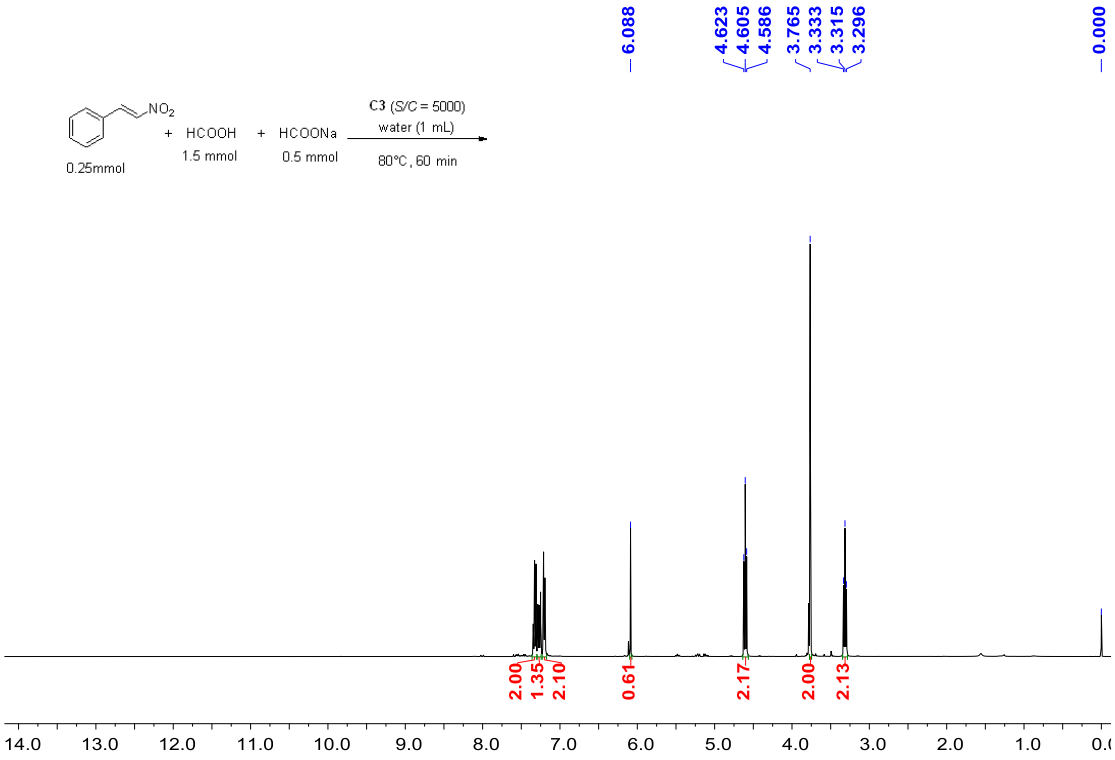

8.019
7.985
4.628
4.609
4.591
3.333
3.314
3.296
-0.000
NO2
0.25mmol
C3 (S/C = 20000)
HCOOH (8 equiv.)
water (1 mL)
80°C, 30 min
1.00
0.75
0.73
f1 (ppm)

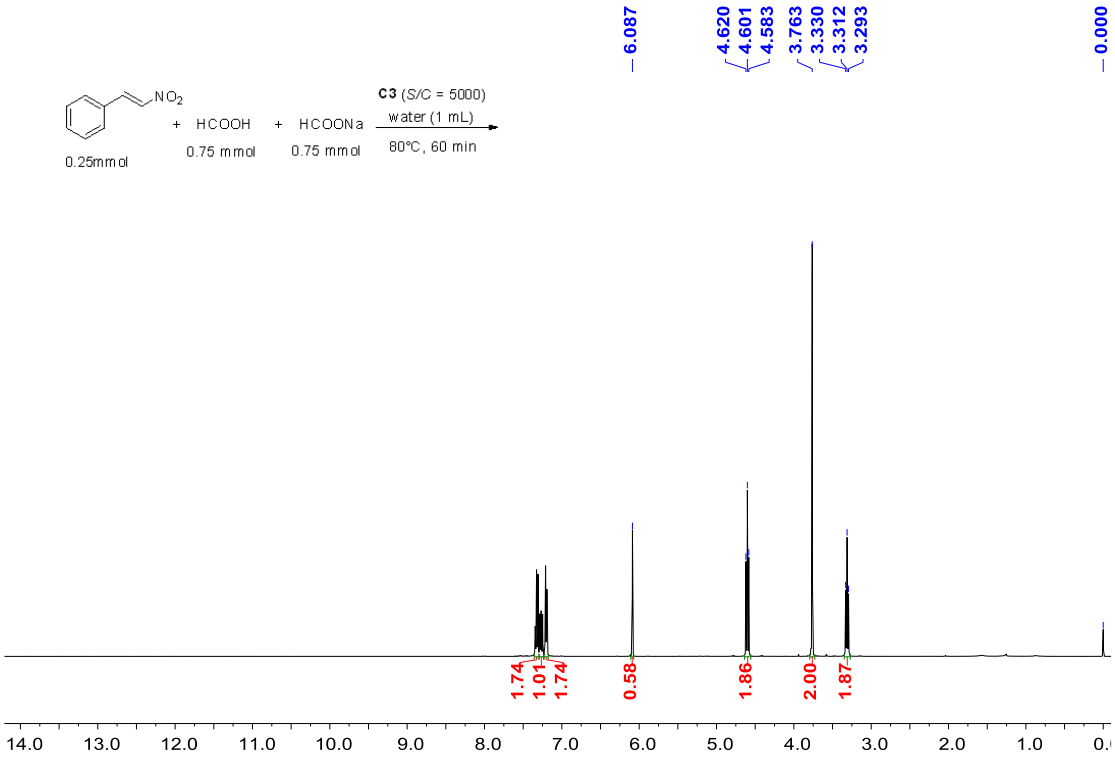

8.014
7.980
4.614
4.595
4.577
3.323
3.304
3.286
-0.000
NO2
0.25mmol
C3 (S/C = 20000)
HCOOH (8 equiv.)
water (1 mL)
80°C, 60 min
0.16
2.00
1.99
f1 (ppm)

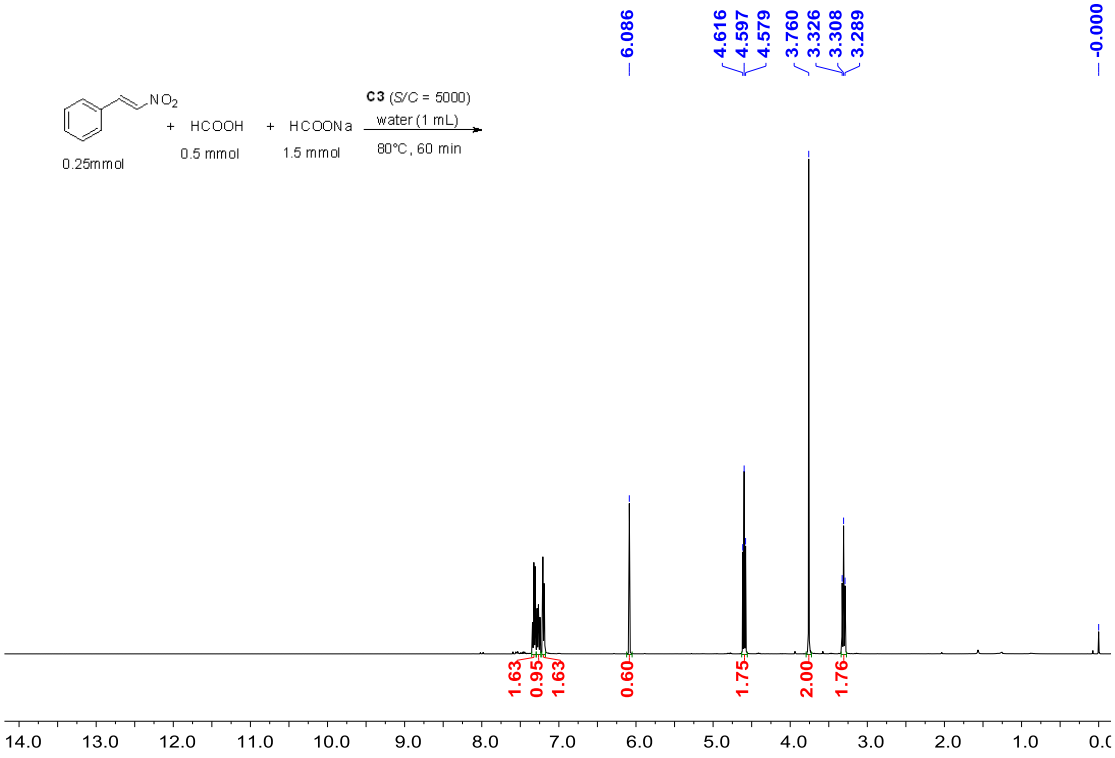

8.015
7.981
4.619
4.600
4.582
3.326
3.307
3.289
-0.000
NO2
C3 (S/C = 20000)
HCOOH (8 equiv.)
water (1 mL)
80°C, 75 min
0.25mmol
0.59
2.00
2.00
f1 (ppm)

17. ^{1}H NMR spectra of crude reaction mixtures in Table 3.






6.087
4.620
4.601
4.583
3.763
3.330
3.312
3.293
0.000
NO2
+ HCOOH
0.75 mmol
+ HCOONa
0.75 mmol
C3 (S/C = 5000)
water (1 mL)
80°C, 60 min
0.25mmol
1.74
1.01
1.74
0.58
1.86
2.00
1.87
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


6.086
4.616
4.597
4.579
3.760
3.326
3.308
3.289
-0.000
NO2
+ HCOOH
0.5 mmol
+ HCOONa
1.5 mmol
C3 (S/C = 5000)
water (1 mL)
80°C, 60 min
0.25mmol
1.63
0.95
1.63
0.60
1.75
2.00
1.76
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

18. ^{1}H NMR spectra of crude reaction mixtures in **Table 5.**

Table 5. entry 1.

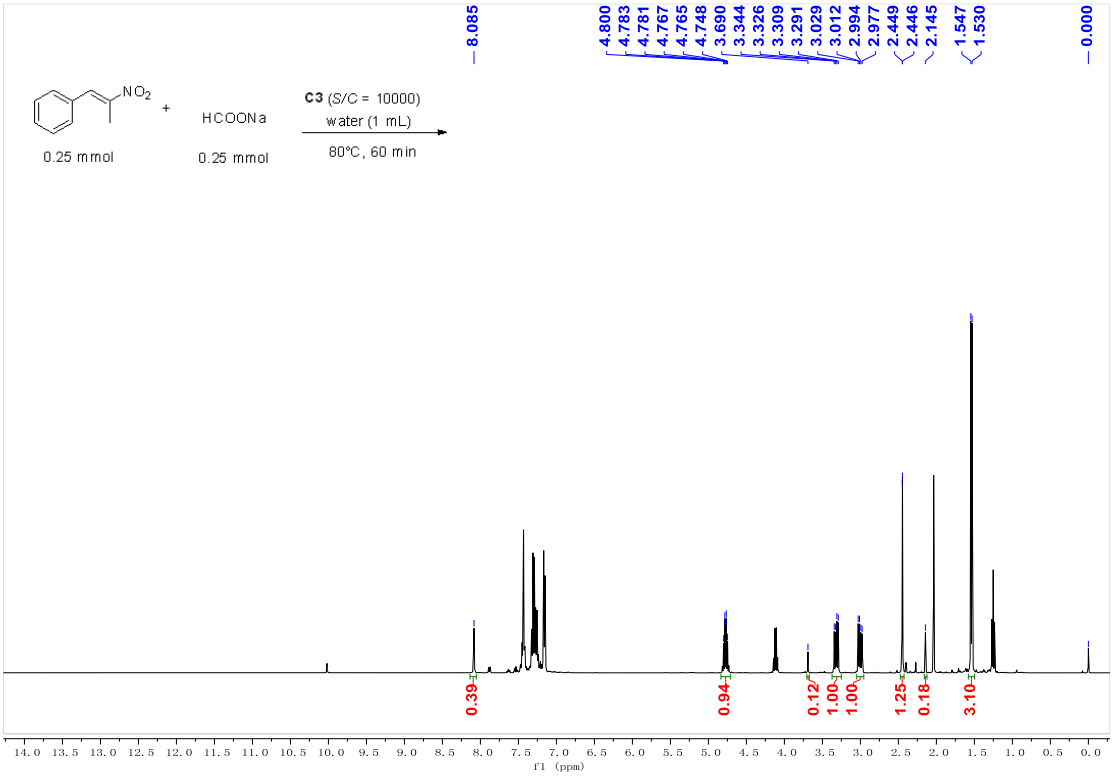


Table 5. entry 2.

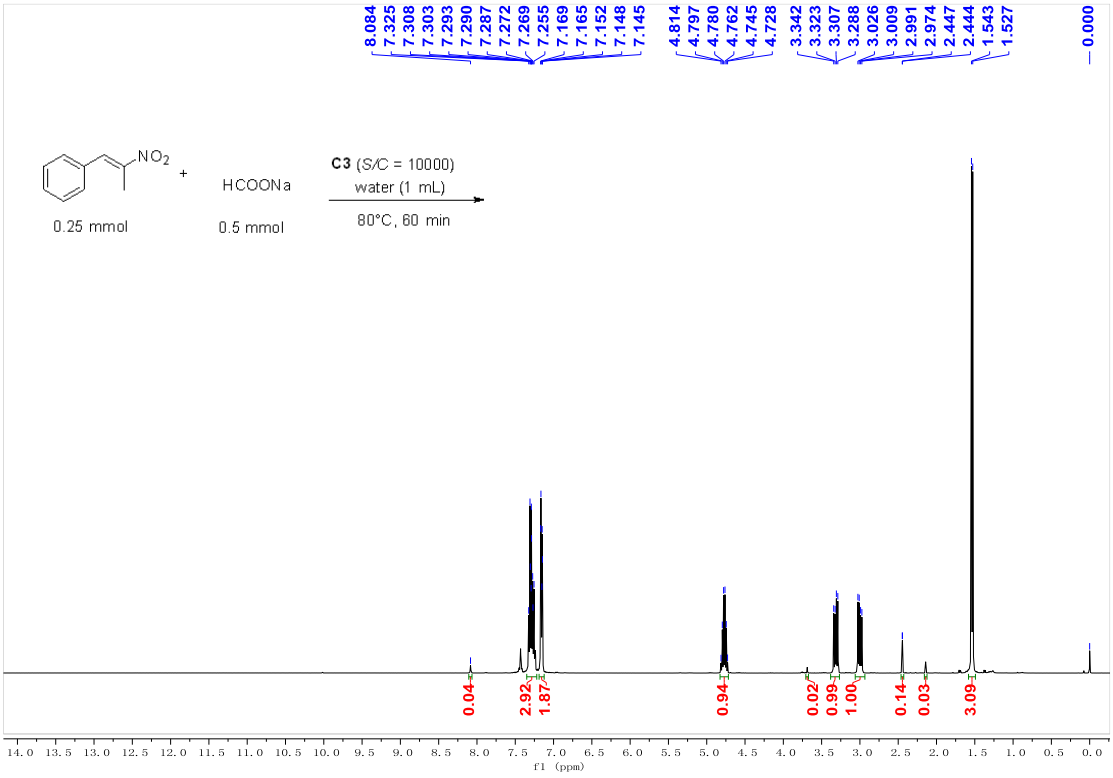


Table 5. entry 3.

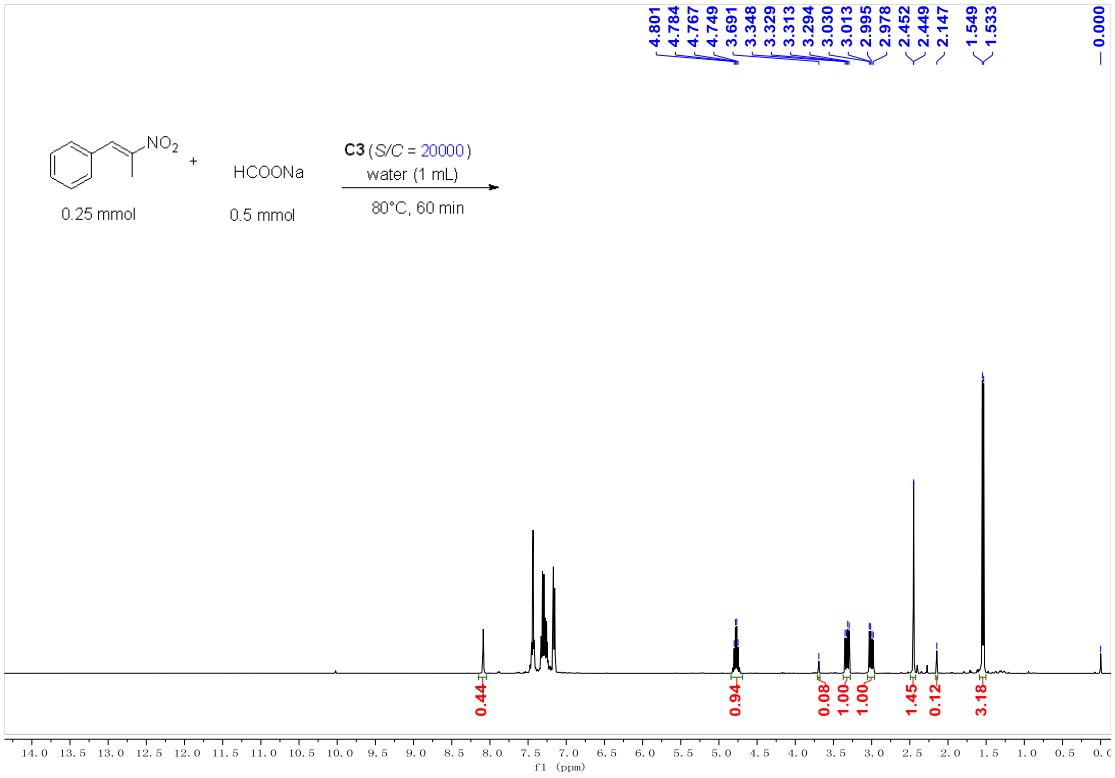


Table 5. entry 4.

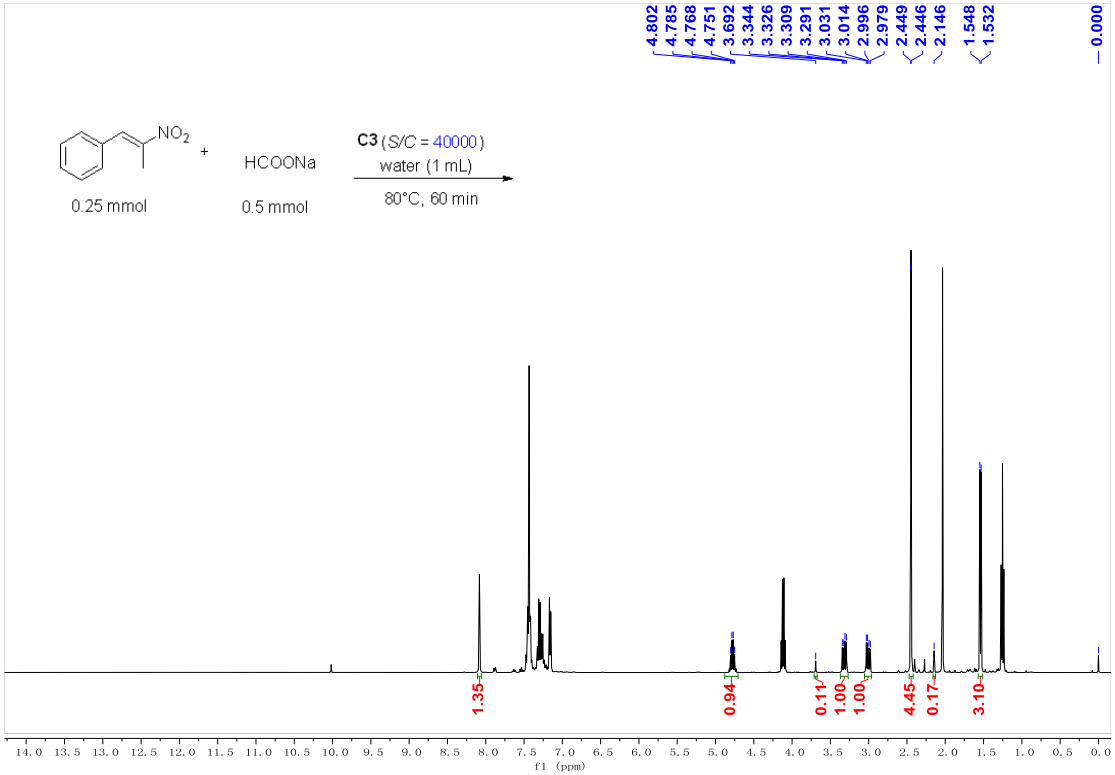
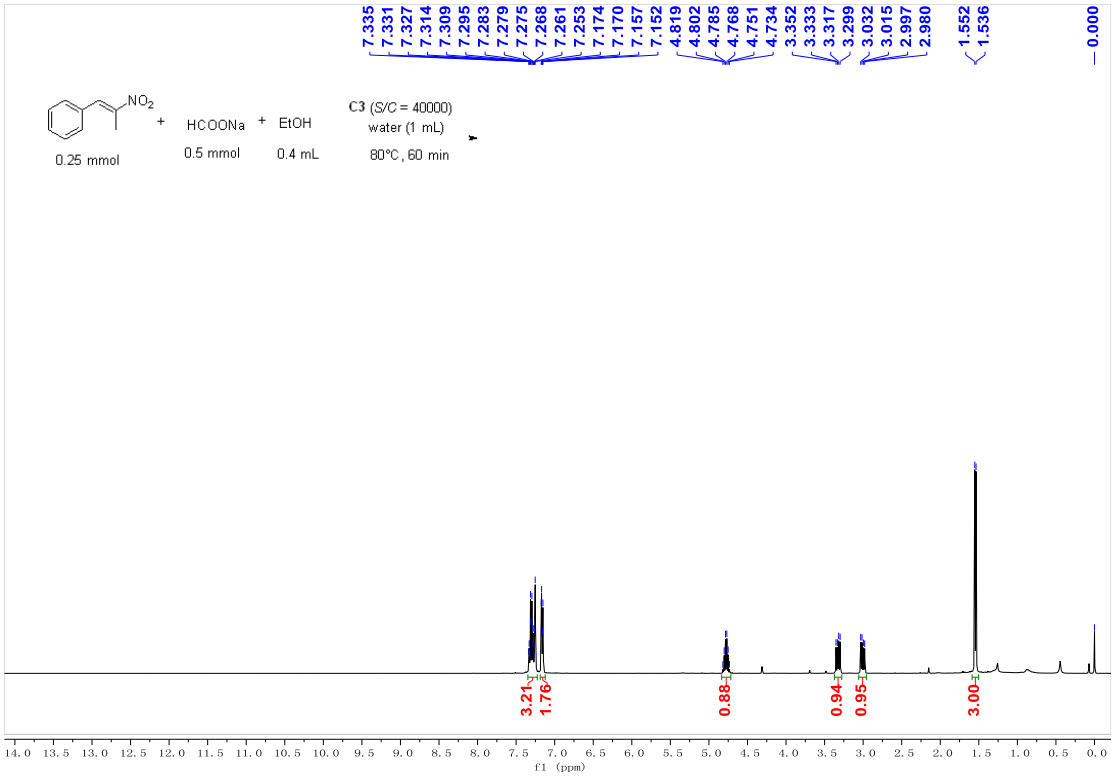
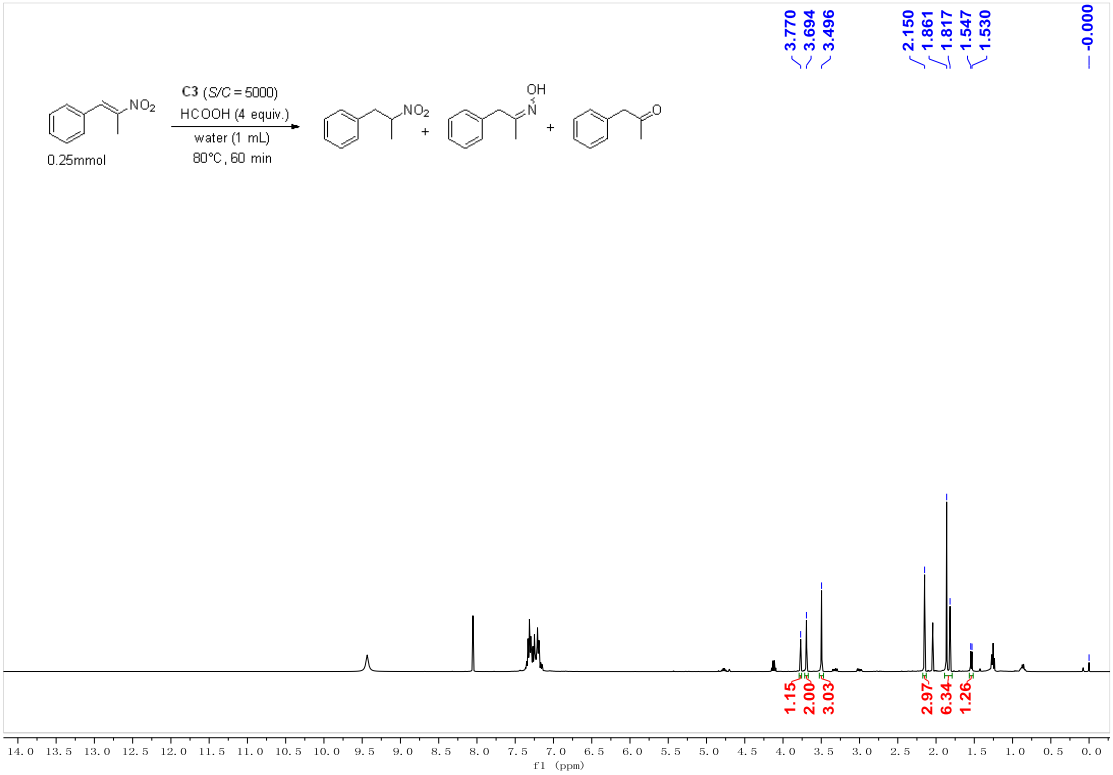


Table 5. entry 5.

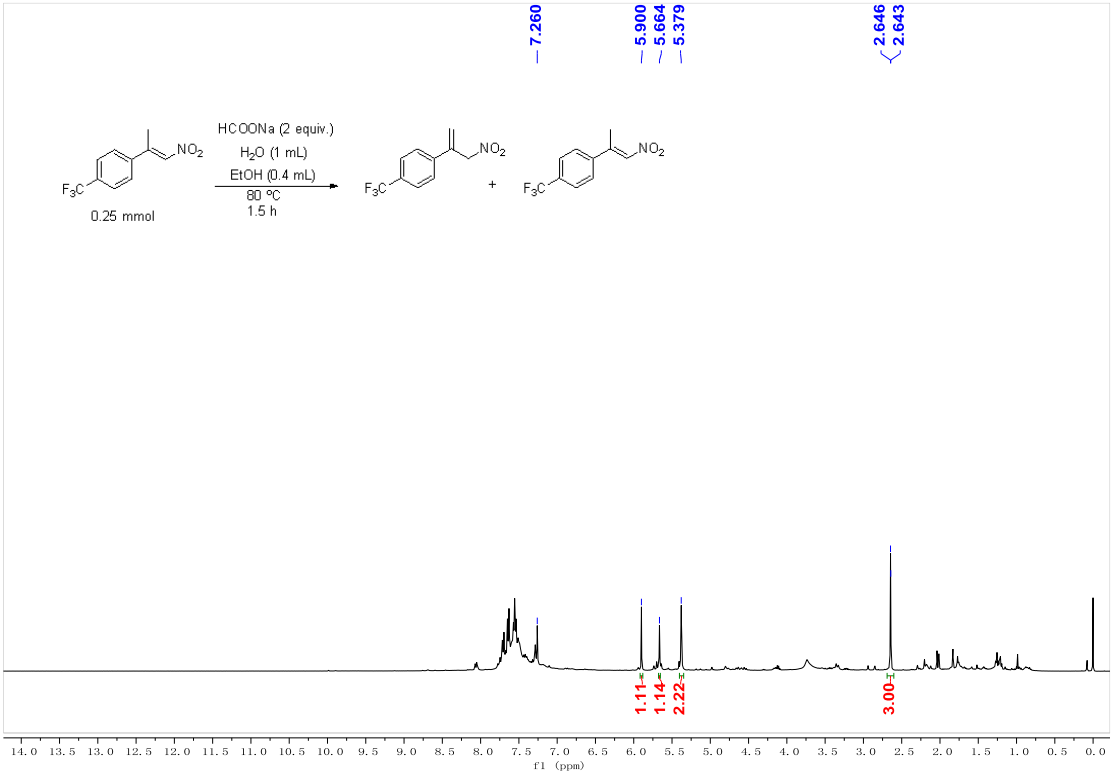


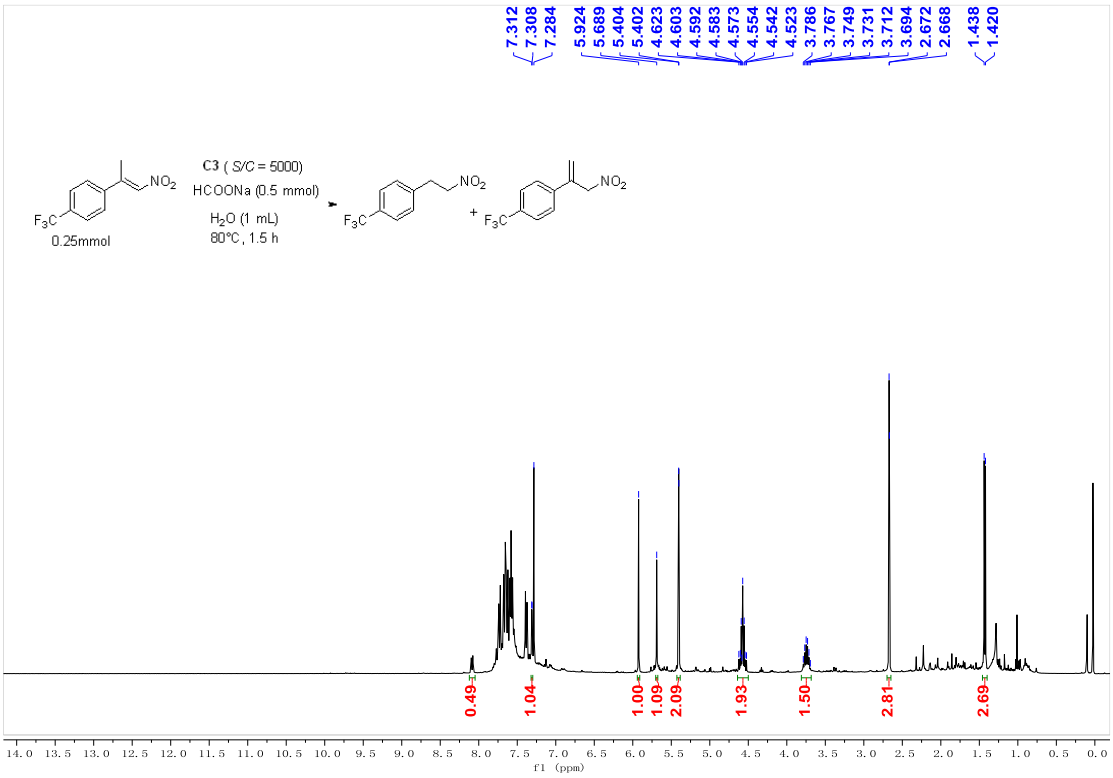
19. Other ^{1}H NMR spectra

19.1. ^{1}H NMR spectra of crude reaction mixture in Scheme 2.

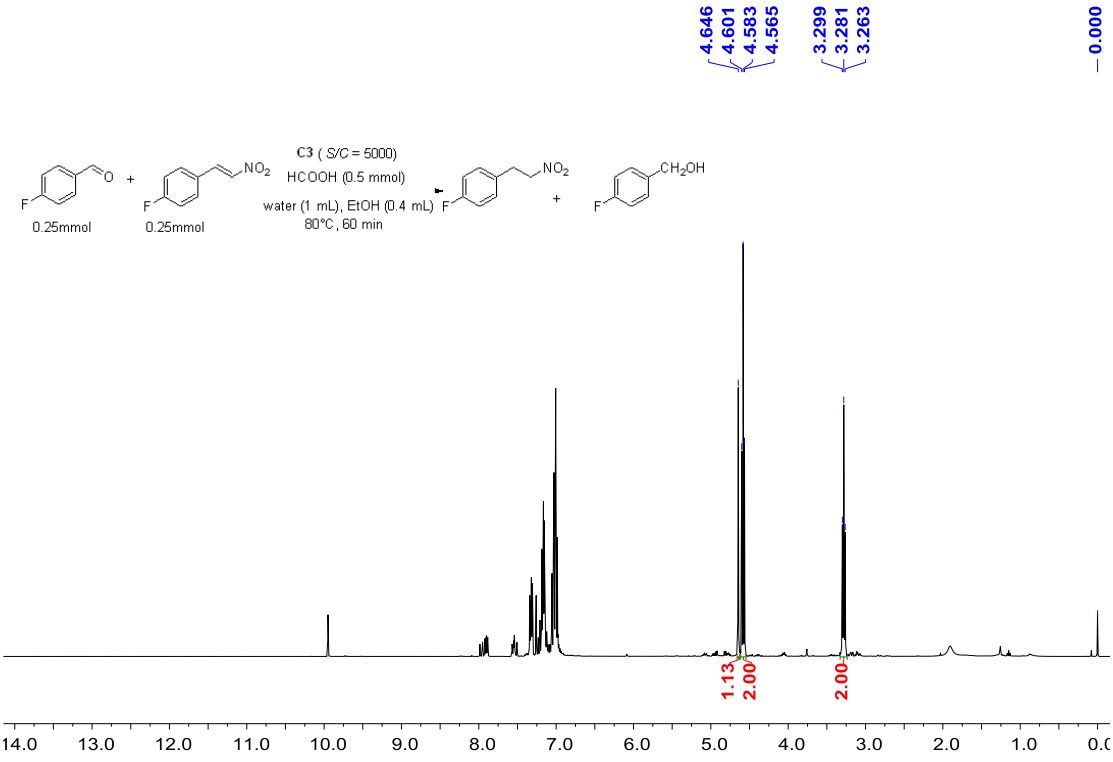


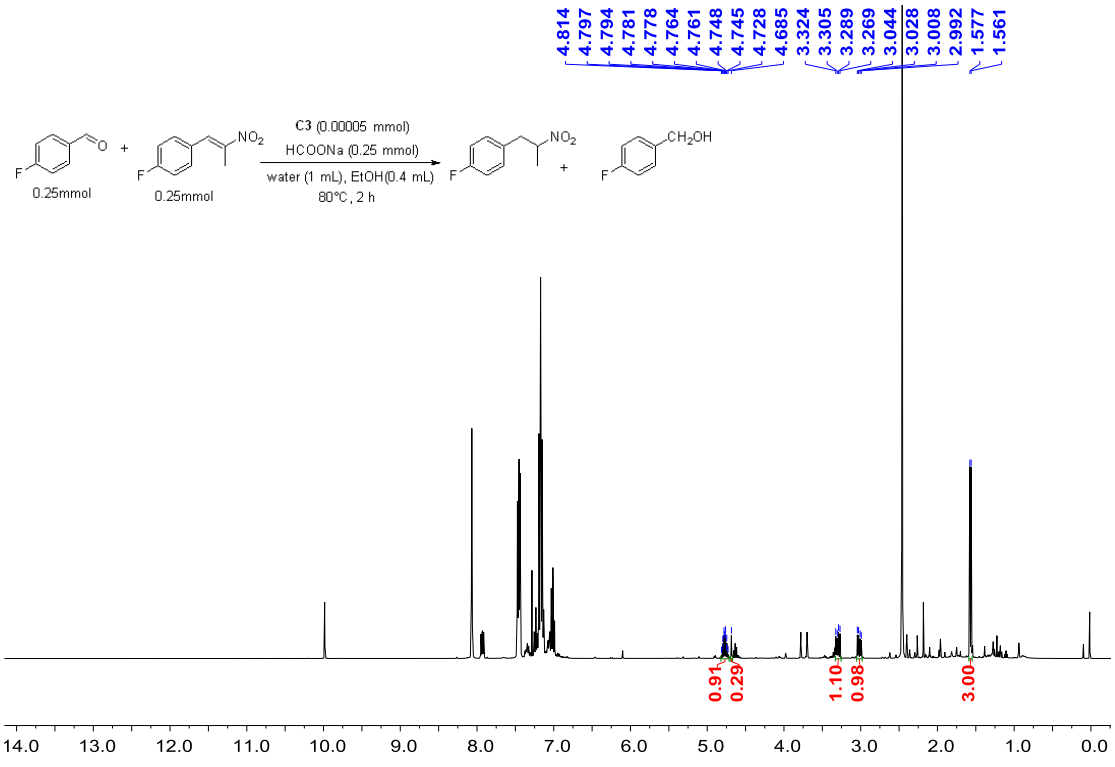
19.2. ^{1}H NMR spectra of crude reaction mixtures in Scheme 3.

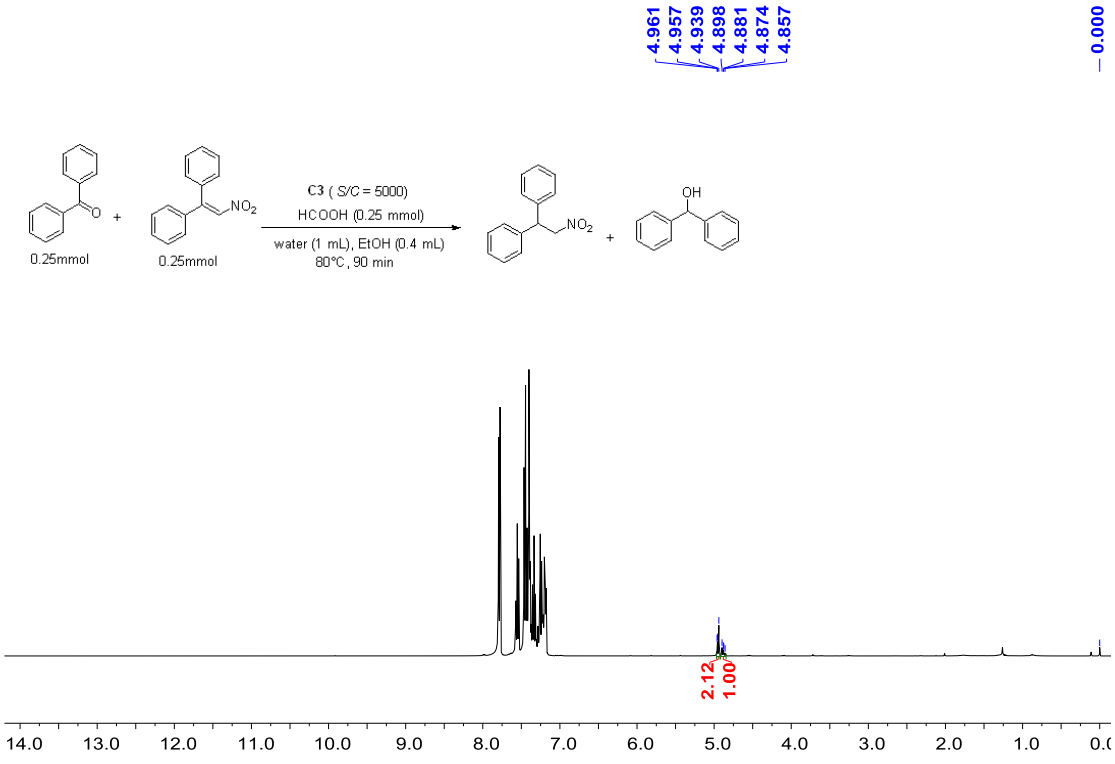




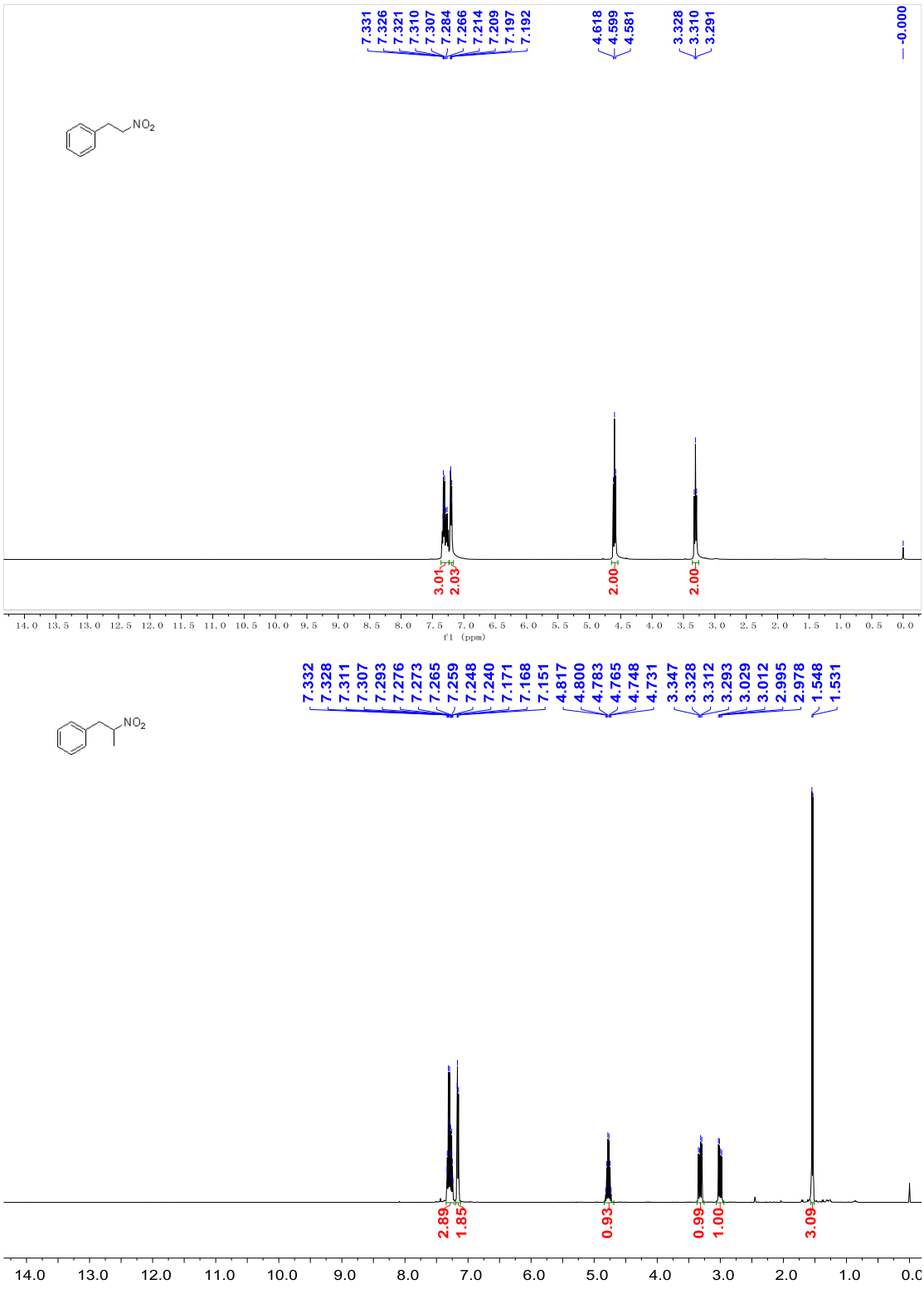
19.3. ^{1}H NMR spectra of crude reaction mixtures in Scheme S4.



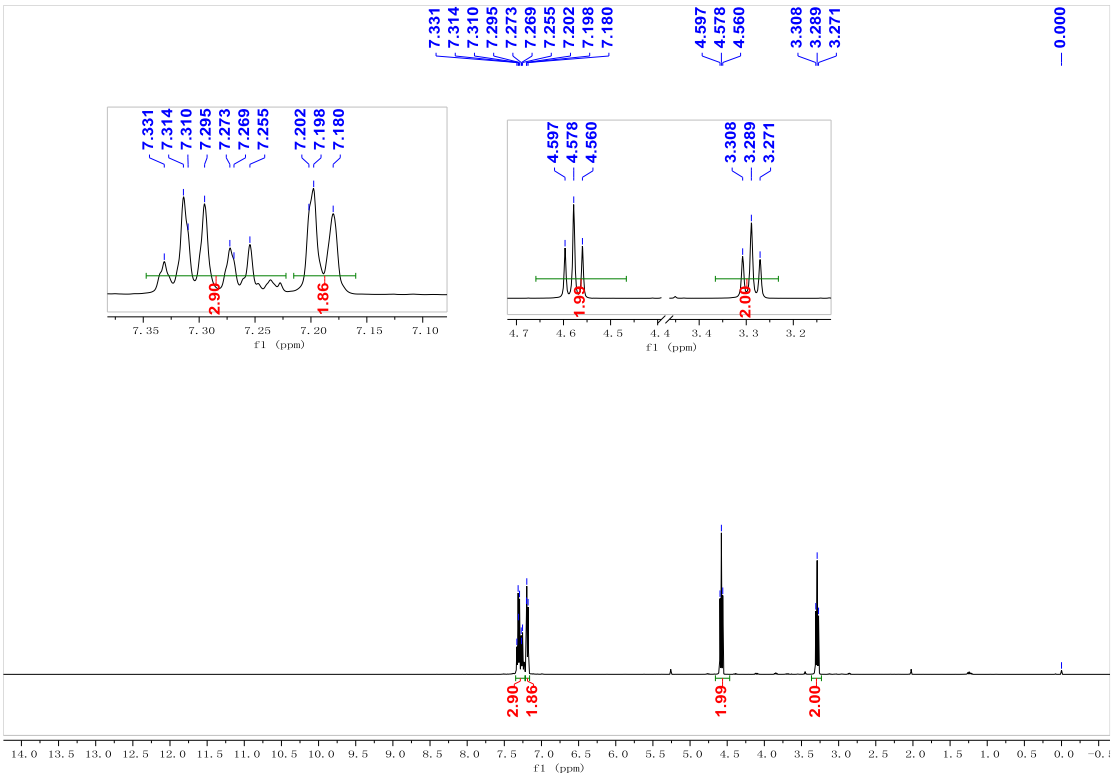

4.814
4.797
4.794
4.781
4.778
4.764
4.761
4.748
4.745
4.728
4.685
3.324
3.305
3.289
3.269
3.044
3.028
3.008
2.992
1.577
1.561
C3 (0.00005 mmol)
HCOONa (0.25 mmol)
water (1 mL), EtOH(0.4 mL)
80°C, 2 h
0.25mmol
0.25mmol
0.91
0.29
1.10
0.98
3.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


4.961
4.957
4.939
4.898
4.881
4.874
4.857
0.000
C3 (S/C = 5000)
HCOOH (0.25 mmol)
water (1 mL), EtOH (0.4 mL)
80°C, 90 min
0.25mmol
0.25mmol
2.12
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

19.4 ^{1}H NMR spectra of pure **3a** and **4a** in gram-scale reduction

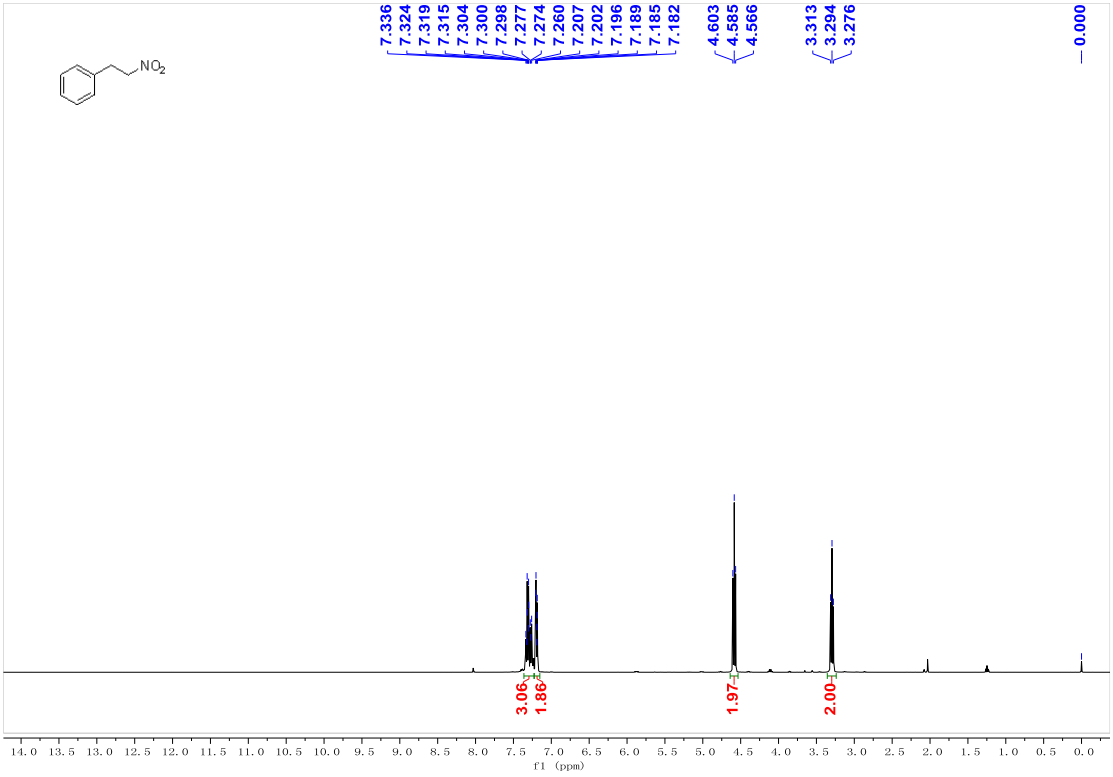


19.5 ^{1}H NMR spectra of pure **3a** in modified gram-scale reduction

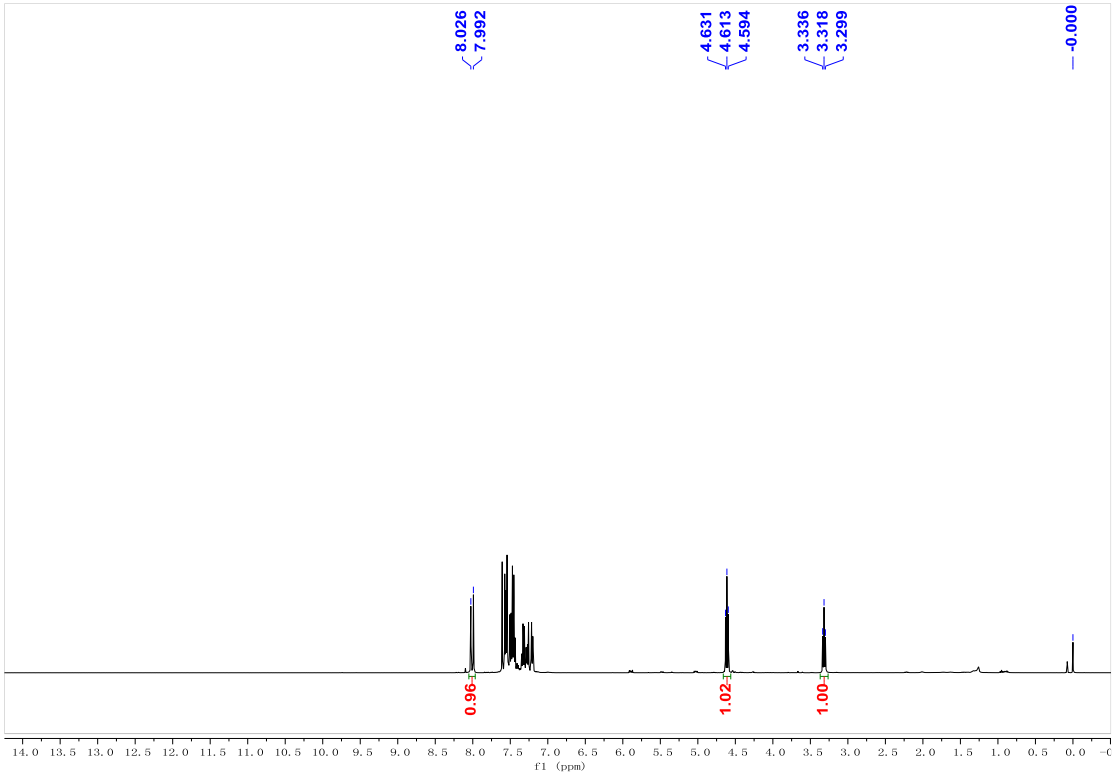


19.6 ^{1}H NMR spectra of crude reaction mixture for reduction of **1a** using recovered catalyst solution.

First reuse

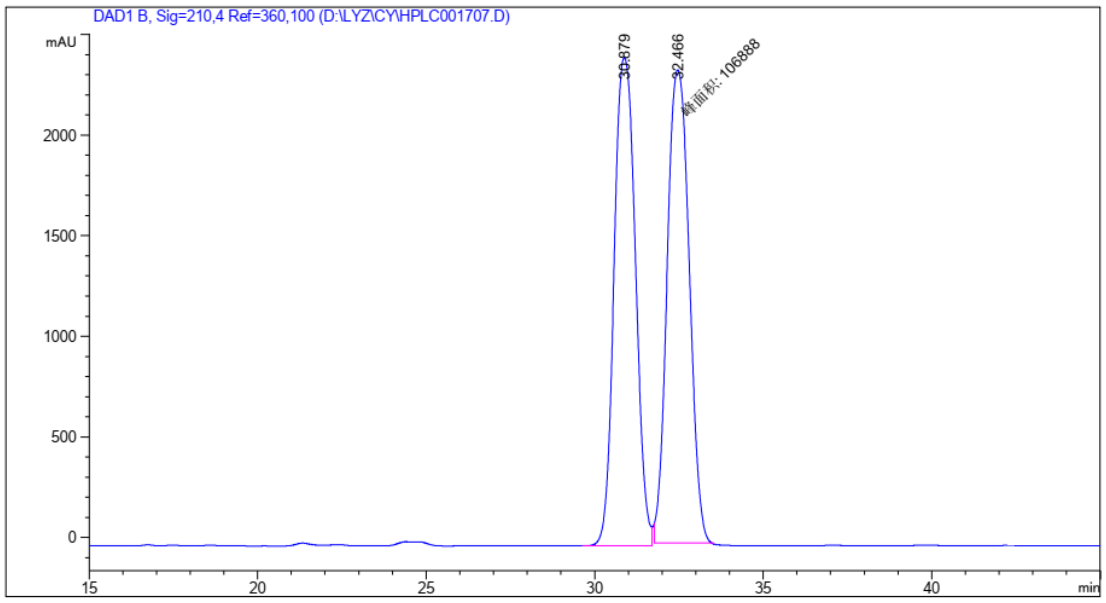


Second reuse



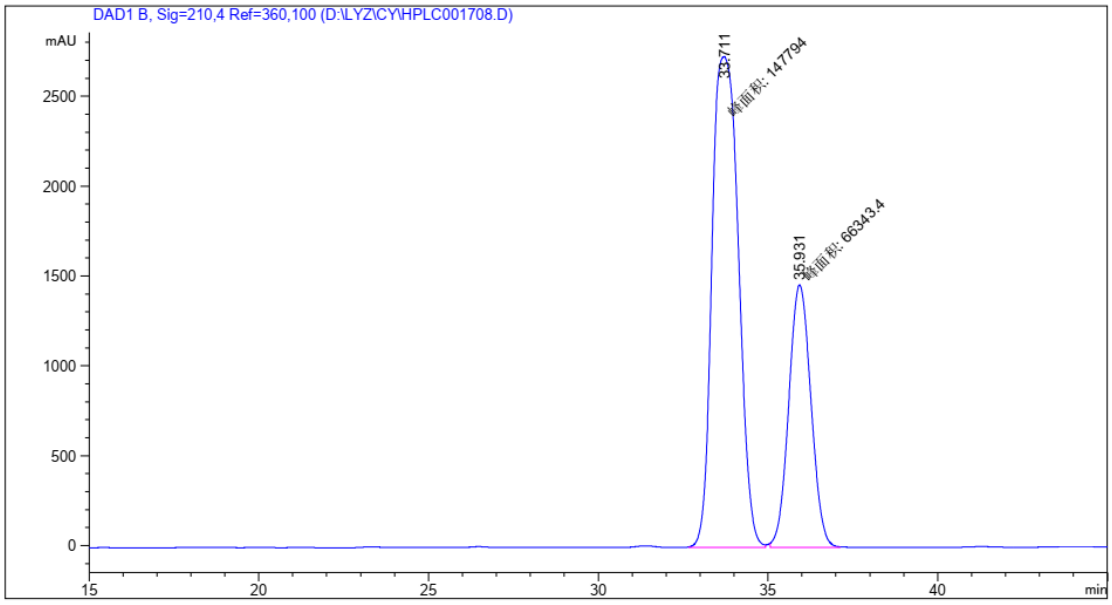
20. Chiral HPLC spectra for asymmetric catalysis in Table S5.

Entry 1: **1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was 0 %, t_R = 30.88 min, t_R= 32.47 min (Chiralcel AD-H, λ = 210 nm, hexane/^{i}PrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



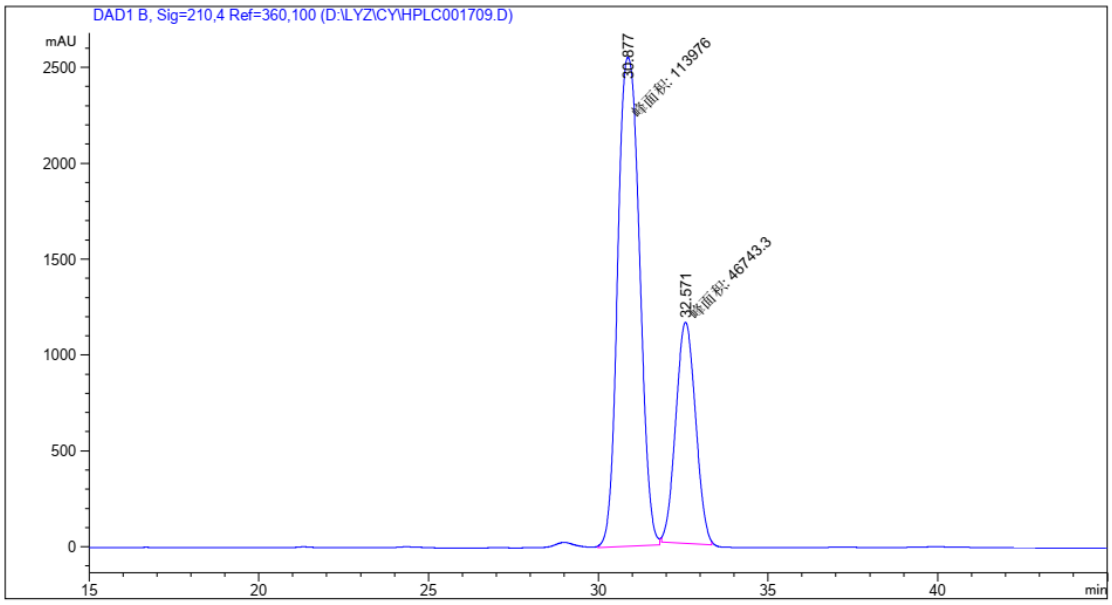
Peak	Ret. Time	Type	Width	Area	Height	Area
1	30.879	BV	0.7029	1.06622e5	2425.37061	49.9378
2	32.466	MM	0.7577	1.06888e5	2351.14941	50.0622

Entry 2: **(*R*)-1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was 38 %, t_R (major) = 33.71 min, t_R (minor) = 35.73 min (Chiralcel AD-H, λ = 210 nm, hexane/iPrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



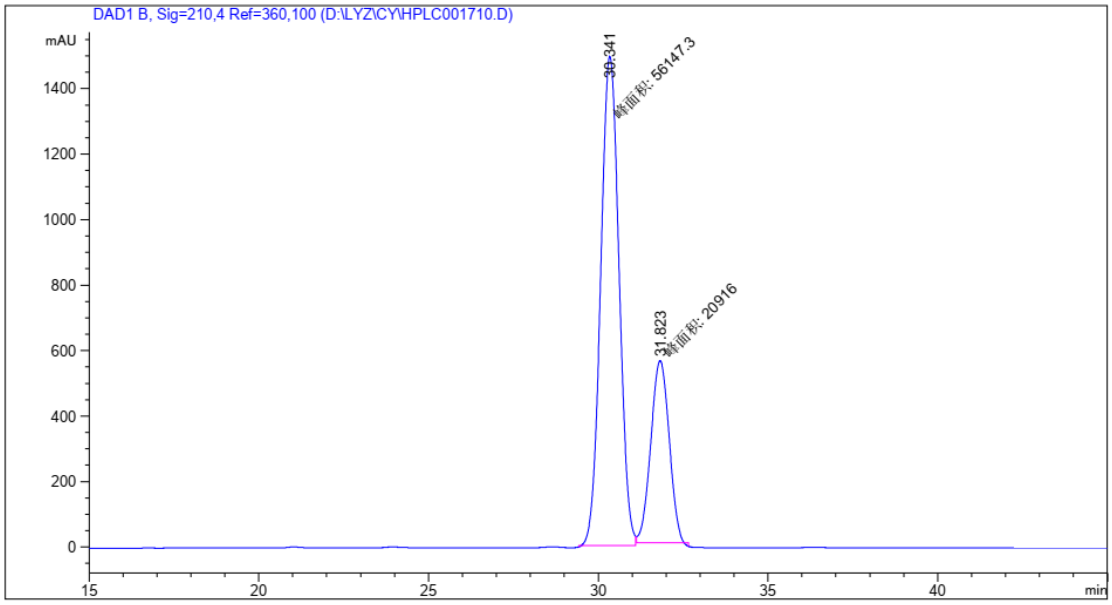
Peak	Ret. Time	Type	Width	Area	Height	Area
1	33.711	MM	0.9023	1.47794e5	2730.08325	69.0183
2	35.931	MM	0.7569	6.63434e4	1460.86438	30.9817

Entry 3: **(*R*)-1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was 42 %, t_R (major) = 30.87 min, t_R (minor) = 32.57 min (Chiralcel AD-H, λ = 210 nm, hexane/iPrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



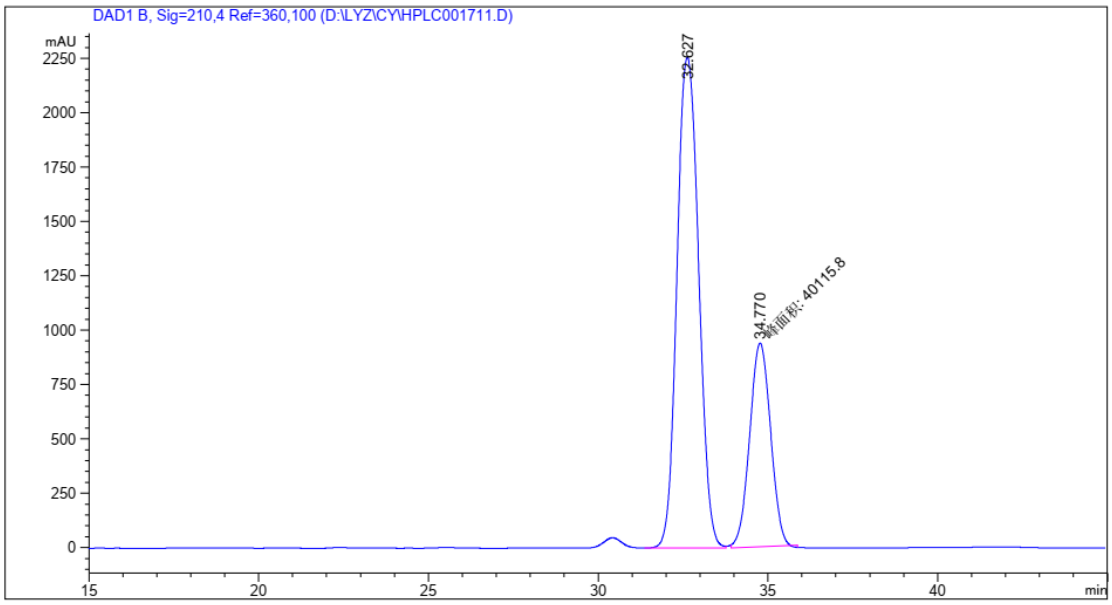
Peak	Ret. Time	Type	Width	Area	Height	Area
1	30.877	MM	0.7448	1.13976e5	2550.42456	70.9162
2	32.571	MM	0.6754	4.67433e4	1153.41724	29.0838

Entry 4: ***(R)*-1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was 46 %, $[\alpha]^{D}_{20}$ = +16.5 (c = 0.2, CH_3Cl). t_R (major) = 30.34 min, t_R (minor) = 31.82 min (Chiralcel AD-H, λ = 210 nm, hexane/iPrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



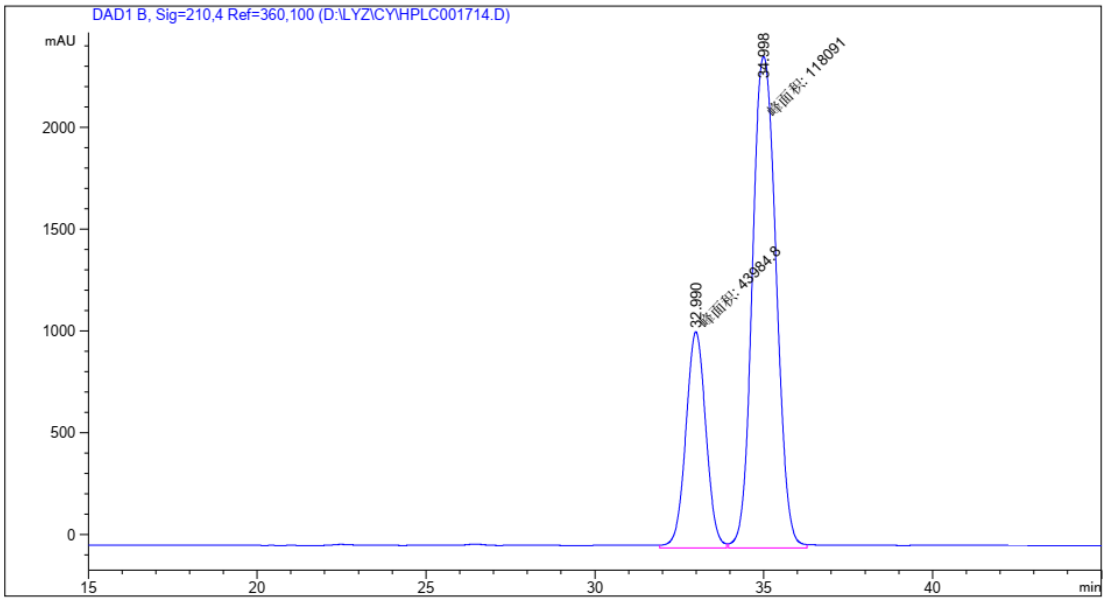
Peak	Ret. Time	Type	Width	Area	Height	Area
1	30.341	MM	0.6263	5.61473e4	1494.07190	72.8586
2	31.823	MM	0.6264	2.09160e4	556.52228	27.1414

Entry 5: **(*R*)-1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was 43 %, t_R (major) = 32.62 min, t_R (minor) = 33.77 min (Chiralcel AD-H, λ = 210 nm, hexane/iPrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



Peak	Ret. Time	Type	Width	Area	Height	Area
1	32.627	BV	0.7075	1.00032e5	2255.13257	71.3761
2	34.770	MM	0.7136	4.01158e4	936.92133	28.6239

Entry 6 **(*S*)-1-Fluoro-4-(1-nitropropan-2-yl)benzene (8a)**. The ee value was - 46 %, $[\alpha]^{D}_{20}$ = -22 (c = 0.2, CH_3Cl). t_R (minor) = 32.99 min, t_R (major) = 35.00 min (Chiralcel AD-H, λ = 210 nm, hexane/iPrOH= 99:1, flow rate = 0.4 mL/min, t 24 °C).



Peak	Ret. Time	Type	Width	Area	Height	Area
1	32.990	MM	0.6899	4.39848e4	1062.54089	27.1384
2	34.998	MM	0.8153	1.18091e5	2413.93677	72.8616