Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Metal-Free Nitro-Carbocyclization of Activated Alkenes: Direct Approach to Oxindoles by Cascade C-N and C-C Bond Formation **

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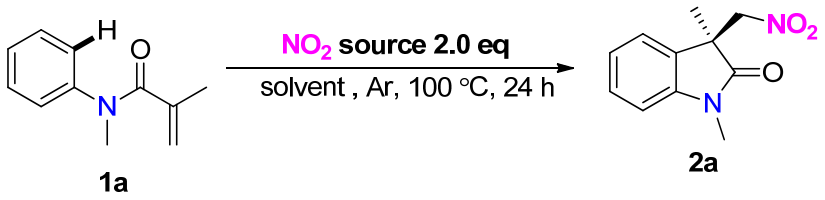
General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar and Across, solvents were from Beijing Ouhe and Beijing Chemical Works and used as received without further purification. Reactions were performed in a schlenk tube under standard conditions (specific reaction conditions are described below). Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. ^{1}H-NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were were calibrated with $CDCl_3$ (tetramethylsilane, δ = 0 ppm) and DMSO(δ = 2.54 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) and DMSO(δ = 40.45 ppm.) Mass spectra were recorded using a PE SCLEX DDSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionisation (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer.

Table S1. Screening with Different Reaction Conditions for Metal-Free C-H Nitrification of Activated Alkenes.[a]



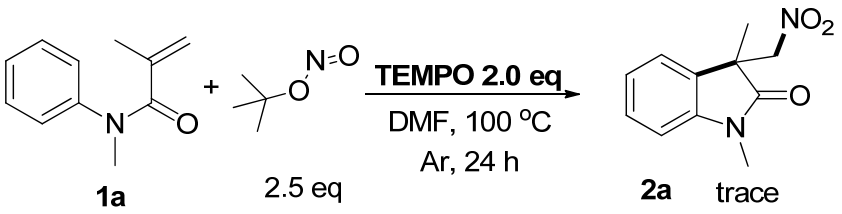
1a **2a**

Entry	NO_2 source	solvent	yield of **2a** (%)
1	$Fe(NO_3)_3 \cdot 9H_2O$	MeCN	31
2	$AgNO_3$	MeCN	12
3	$NaNO_2$	MeCN	0
4	$AgNO_2$	MeCN	38
5	*t*-BuONO	MeCN	44
6	*t*-BuONO	THF	trace
7	*t*-BuONO	$CHCl_3$	trace
8	*t*-BuONO	DCE	35
9	*t*-BuONO	DMSO	36
10	*t*-BuONO	toluene	31
11	*t*-BuONO	HOAc	31
12[b]	*t*-BuONO	DMF	31
13	*t*-BuONO	DMF	68
14[c]	***t*-BuONO**	**DMF**	**74**
15[d]	*t*-BuONO	DMF	29
16[e]	*t*-BuONO	DMF	40
17[f]	*t*-BuONO	DMF	43

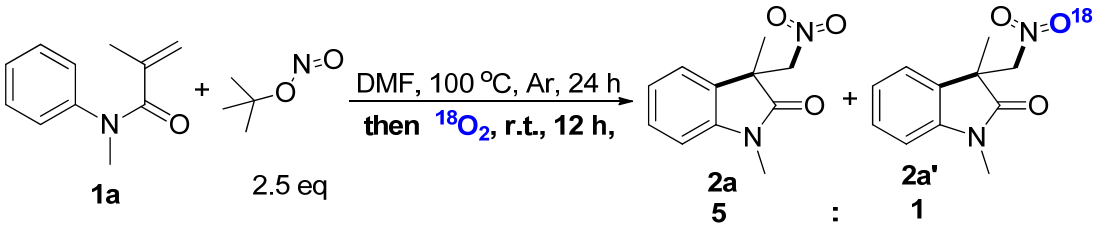
[a] [a] Reaction conditions: 1a (0.2 mmol) and *t*-BuONO (0.4 mmol) in dry DMF (2 mL) with stirring at 100 ℃ for 24 h. Isolated yield [b] 10% TEMPO was used [c] 2.5 edd of *t*-BuONO was used and was added into two portions. [d]. The reaction was carried out under air. [e]. The reaction was carried out under at .60 ℃ for 24 h [f] The reaction was carried out under at .120℃ for 24 h.

Mechanistic Studies

Eq. S1



Eq. S2



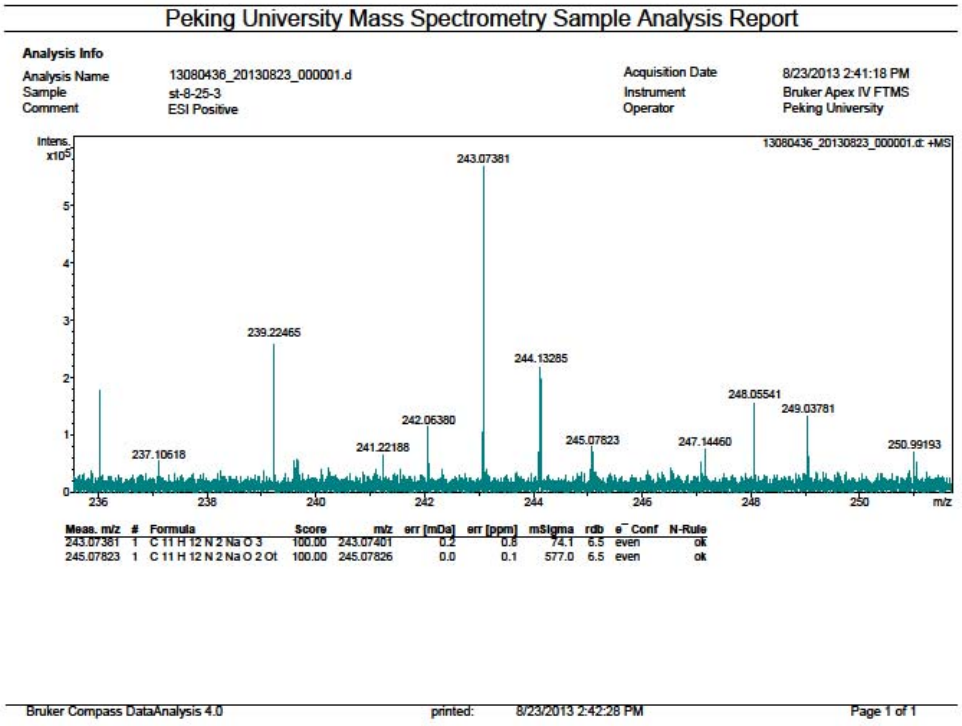
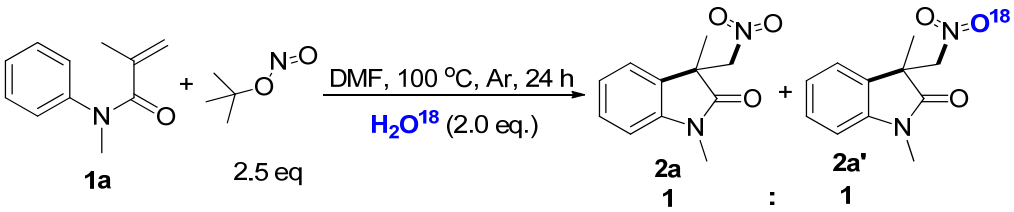


Figure S1 Standard reaction under ^{18}O

Eq. S3



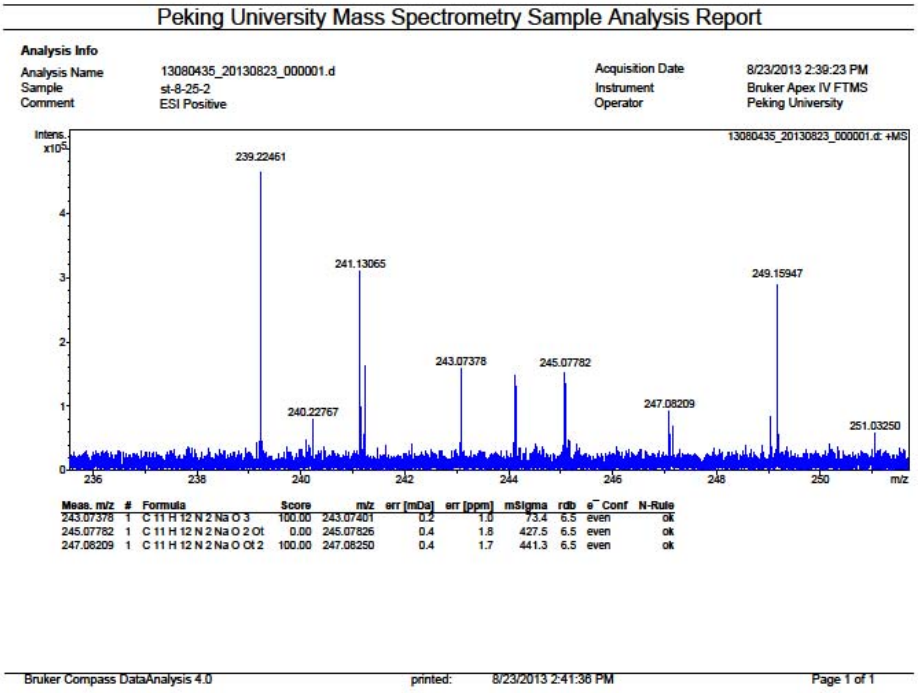
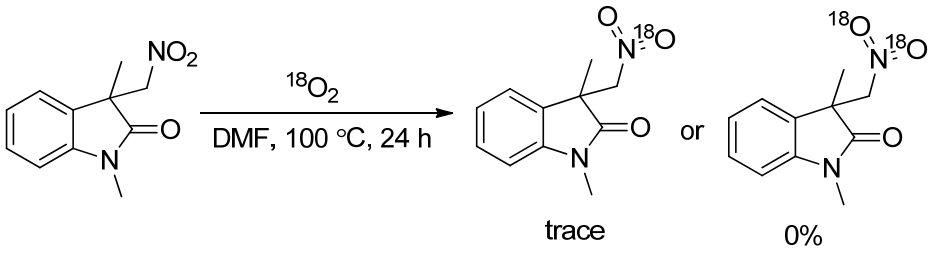


Figure S2 Standard reaction with $H_2{}^{18}O$

Eq. S4



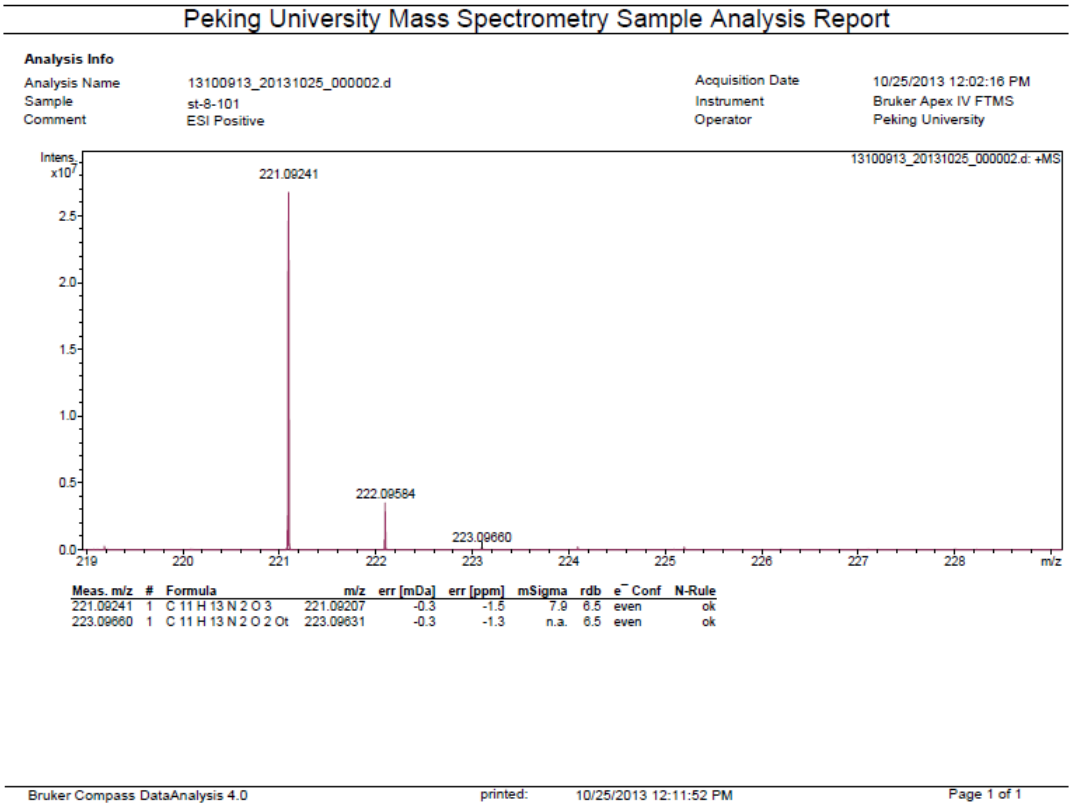
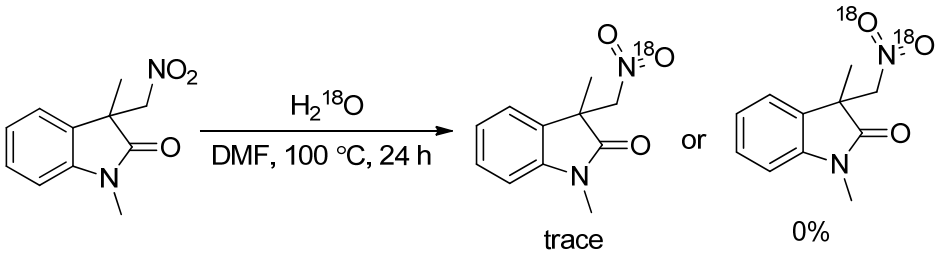


Figure S3 Labeled experiment with $^{18}O_2$

Eq. S5



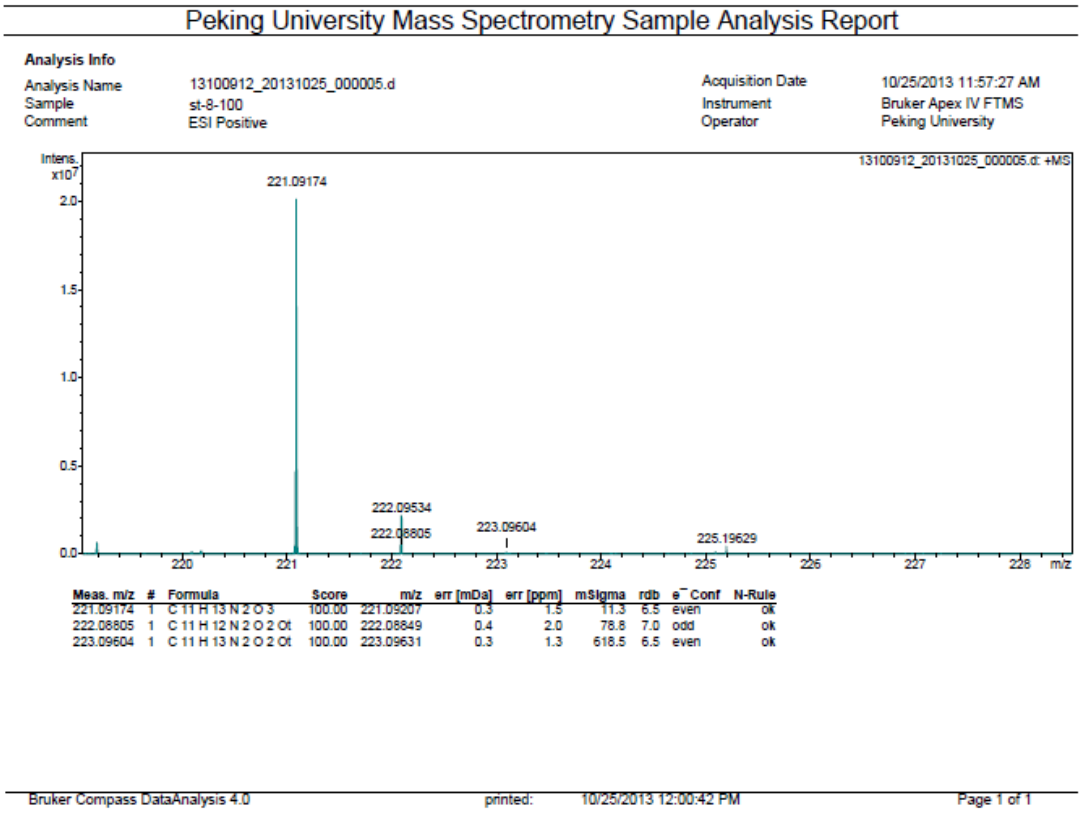
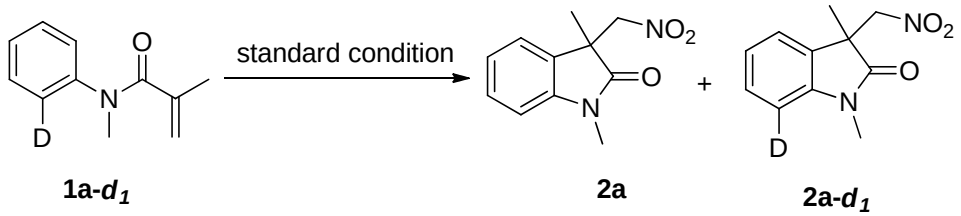


Figure S4 Labeled experiment with $H_2{}^{18}O$

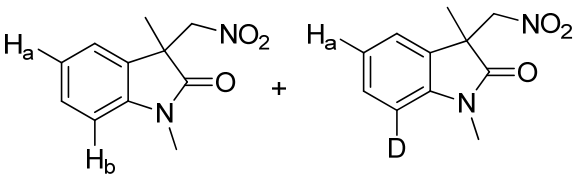
Eq. S6 **Competing kinetic isotope effect (KIE) experiment:**

a) Intramolecular KIE experiment: **1a-*d*$_1$** were synthesized deuterium substrates according the literature procedure.[S5] In a Schlenk tube, **1a-*d*$_1$** (52 mg, 0.20 mmol), *t*-BuONO (52 mg, 0.5 mmol) were added and charged with Ar three times. Then, anhydrous DMF (2 mL) were added. The mixture was allowed to stir at 100℃ for 24 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product **2a** and **2-*d*$_1$**. The products were under $_1$H-NMR analysis (Figure S3).



1a-*d*$_1$ **2a** **2a-*d*$_1$**

24.0 h, 77% yield, K_H/K_D = 1.1



2a **2a-*d*$_1$**

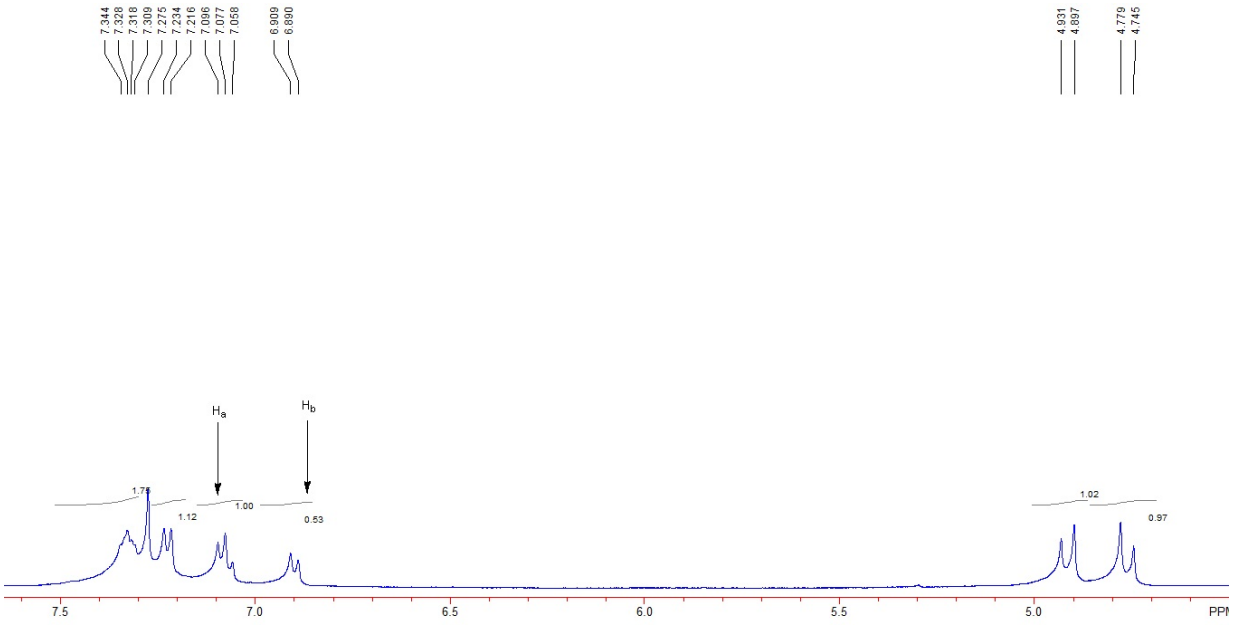
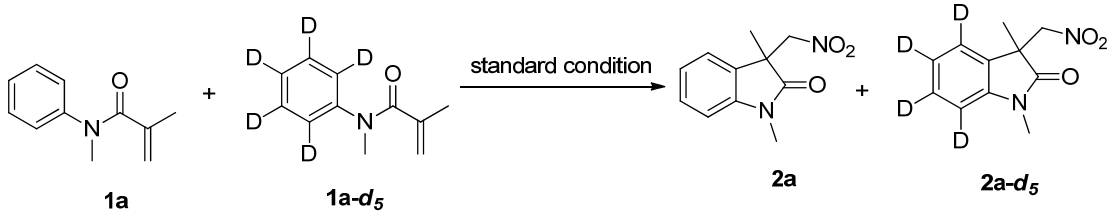
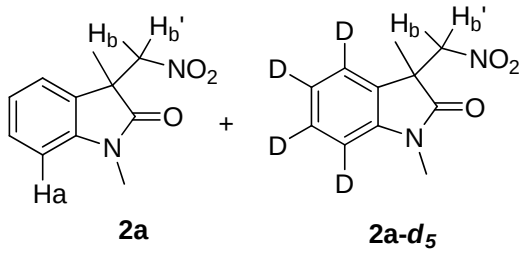


Figure S5 Intramolecular KIE experiment

b) Intermolecular KIE experiment: **1a-*d*5** were synthesized deuterium substrates according the literature procedure.[S5] In a Schlenk tube, **1a** (17.5 mg, 0.1 mmol), **1a-*d*5** (18.0 mg, 0.1 mmol), *t*-BuONO (52 mg, 0.5 mmol) were added and charged with Ar three times. Then, anhydrous DMF (2 mL) were added. The mixture was allowed to stir at 100℃ for 24 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product **2a** and **2a-*d*5**. The products were under 1H-NMR analysis (Figure S4).





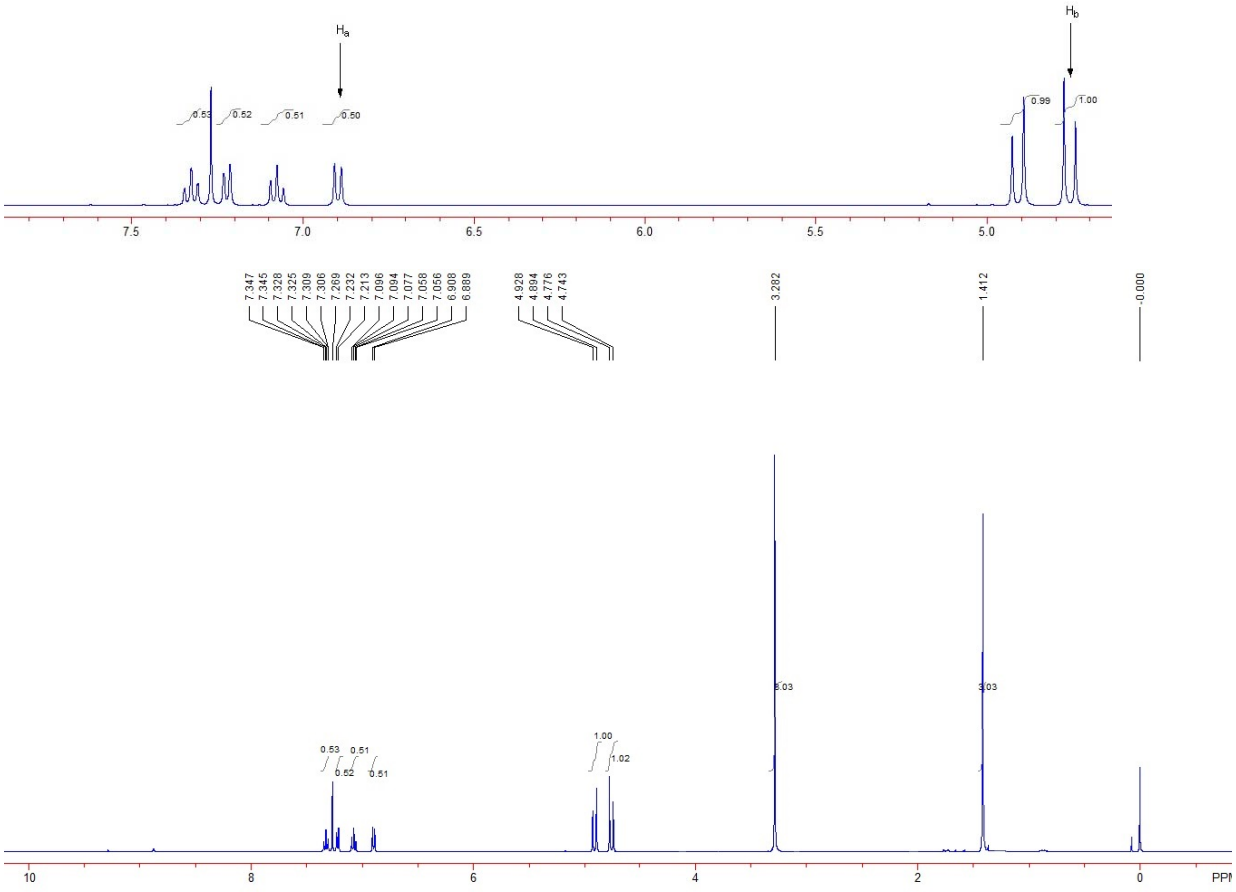
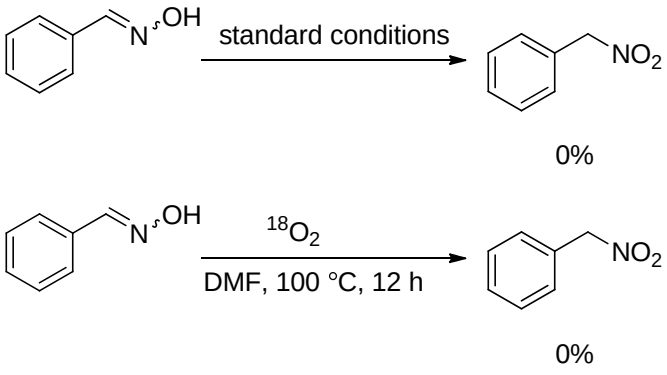


Figure S6 Intermolecular KIE experiment

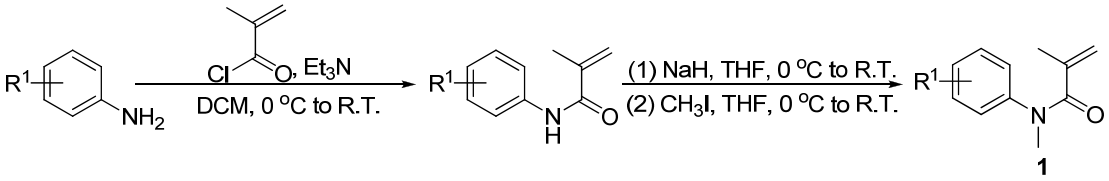
Eq S7 Test oxime as the possible intermediate



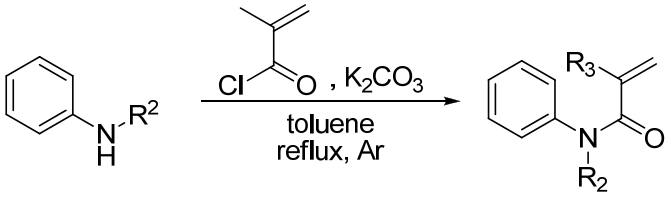
Experimental Section:

Typical Procedure for the Synthesis of Substrates

Method A: Substrate 1 was prepared according to literatures.[s2]

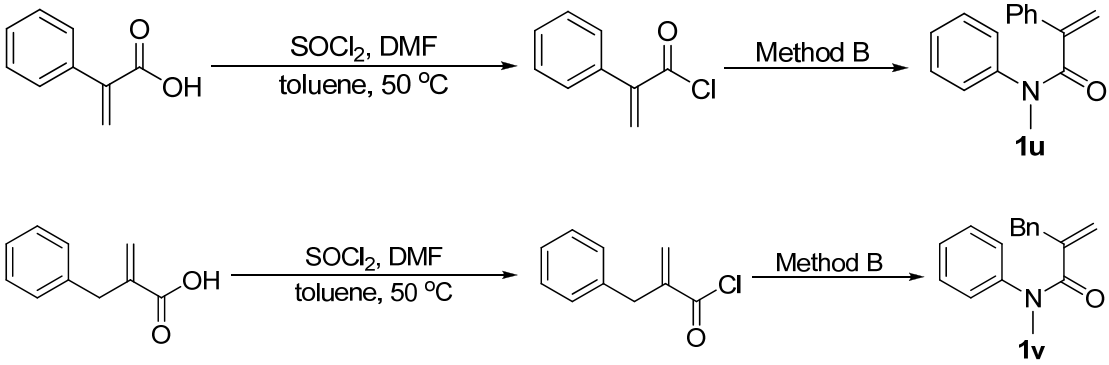


Method B: Substrate 1 was prepared according to literature.[s3]

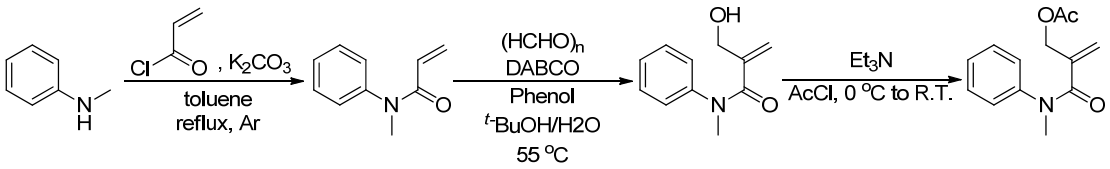


1a, 1b, 1c, 1x

Substrates 1u and 1v were prepared according to literatures.[s3, s4]



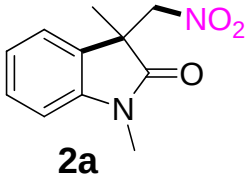
Substrate 1w was prepared according to literature.[s2]



General Procedure for the Synthesis of nitro-containing oxindoles:

1 (0.2 mmol) was added to a Schlenk tube with a magnetic bar and under Ar, then *t*-BuONO (0.3 mmol) and dry DMF (2 mL) added in, after refluxed at 100 ℃ for 12 h under Ar, another 0.2 mmol *t*-BuONO added in and refluxed at 100 ℃ for another 12 h. The reaction was stopped monitored by TLC, then H_2O 10 mL was added in, the mixture was extracted with EtOAc (5 mL*3), then dried over anhydrous magnesium, after concentrated *in vacuo* giving the resulting material, which was purified by column chromatography (petroleum etherto : ethyl acetate = 5:1) to give product 2.

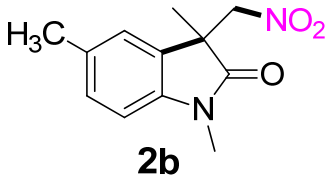
Characterization of new compounds.



2a

1) **1,3-Dimethyl-3-(nitromethyl)indolin-2-one (2a)**

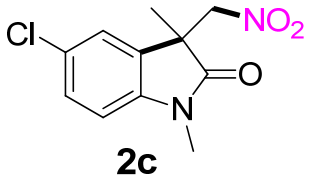
The reaction of **1a** (35.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 32.6 mg (74%) of **2a**; **2a**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.35-7.30 (m, 1H); 7.22 (d, J = 7.6 Hz, 1H); 7.10-7.06 (m, 1H); 6.90 (d, J = 8.0 Hz, 1H); 4.92 (d, J = 13.6 Hz, 1H, CH_2); 4.76 (d, J = 13.6 Hz, 1H, CH_2); 3.28 (s, 3H); 1.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 177.2; 143.5; 129.2; 129.1; 122.9; 122.4; 108.8; 79.0; 47.0; 26.6; 21.7. IR (neat): v = 2963; 1718; 1614; 1555; 1472; cm^{-1}. FTMS: calc. for $C_{11}H_{13}N_2O_3$ $(M+H)^+$, 221.09163; found, 221.09207.



2b

2) **1,3,5-Trimethyl-3-(nitromethyl)indolin-2-one (2b)**

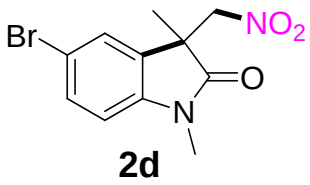
The reaction of **1b** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 31.8 mg (68%) of **2b**; **2b**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.12 (dd, J = 7.6 Hz, J = 0.4 Hz, 1H); 7.03 (s, 1H); 6.79 (d, J = 7.6 Hz, 1H); 4.91 (d, J = 13.6 Hz, 1H, CH_2); 4.74 (d, J = 13.6 Hz, 1H, CH_2); 3.26 (s, 3H); 2.33 (s, 3H); 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 177.1; 141.1; 132.5; 129.4; 129.1; 123.2; 108.5; 79.0; 47.1; 26.6; 21.7; 21.0. IR (neat): v = 2929; 1718; 1555; 1501; 1382; cm^{-1}. FTMS: calc. for $C_{12}H_{15}N_2O_3S$ $(M+H)^+$, 235.10716; found, 235.10772.



2c

3) **5-Chloro-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2c)**

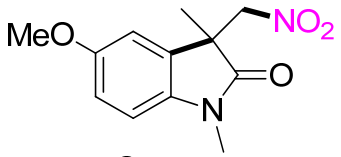
The reaction of **1c** (42.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 38.6 mg (76%) of **2c**; **2c**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.31 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H); 7.21 (d, J = 2.0 Hz, 1H); 6.83 (d, J = 8.4 Hz 1H); 4.93 (d, J = 13.8 Hz, 1H, CH_2); 4.74 (d, J = 13.8 Hz, 1H, CH_2); 3.27 (s, 3H); 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.7; 142.2; 130.8; 129.2; 128.3; 123.0; 109.8; 78.6; 47.1; 26.8; 21.6. IR (neat): v = 2962; 1720; 1612; 1556; 1492; 1363; cm^{-1}. FTMS: calc. for $C_{11}H_{12}ClN_2O_3$ $(M+H)^+$, 255.05288; found, 255.05310..



2d

4) **5-Bromo-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2d)**

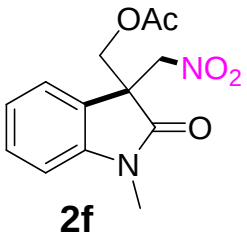
The reaction of **1d** (51.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 36.8 mg (62%) of **2d**; **2d**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.46 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H); 7.34 (d, J = 2.0 Hz, 1H); 6.85 (d, J = 8.4 Hz 1H); 4.93 (d, J = 14.0 Hz, 1H, CH_2); 4.74 (d, J = 14.0 Hz, 1H, CH_2); 3.27 (s, 3H); 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.7; 142.6; 132.1; 131.2; 125.7; 115.4; 110.3; 78.6; 47.0; 26.7; 21.7. IR (neat): ν = 2962; 1719; 1608; 1555; 1491; 1382; cm^{-1}. FTMS: calc. for $C_{11}H_{12}BrN_2O_3$ $(M+H)^+$, 299.00286; found, 299.00258.



2e

5) **5-Methoxy-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2e)**

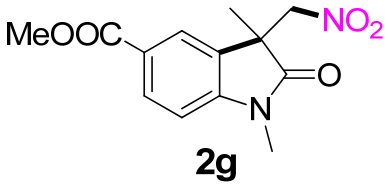
The reaction of **1e** (41.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 37.0 mg (74%) of **2e**; **2e**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 6.85 - 6.78 (m, 3H); 4.91 (d, J = 13.6 Hz, 1H, CH_2); 4.73 (d, J = 13.6 Hz, 1H, CH_2); 3.78 (s, 3H); 3.26 (s, 3H); 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 178.8; 156.2; 136.9; 130.4; 113.1; 110.2; 109.1; 78.9; 55.8; 47.4; 26.7; 21.8. IR (neat): ν = 2961; 1713; 1601; 1500; 1292; cm^{-1}. FTMS: calc. for $C_{12}H_{15}N_2O_4$ $(M+H)^+$, 251.10232; found, 251.10263.



2f

6) **1-Methyl-3-(nitromethyl)-2-oxoindolin-3-ylmethyl acetate (2f)**

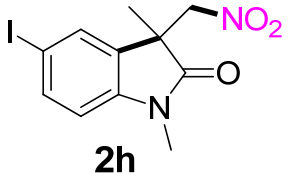
The reaction of **1f** (46.6.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 41.9 mg (75%) of **2f**; **2f**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.37 – 7.35 (m, 1H); 7.28 (d, J = 2.0 Hz, 1H); 7.08 (d, J = 8.0 Hz, 1H); 6.92 (d, J = 7.6 Hz, 1H); 5.05 (d, J = 13.6 Hz, 1H, CH_2); 4.99 (d, J = 13.6 Hz, 1H, CH_2); 4.39 (d, J = 10.2 Hz, 1H, CH_2); 4.14 (d, J = 10.2 Hz, 1H, CH_2); 3.30 (s, 3H); 2.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 173.8; 169.8; 144.1; 129.9; 126.7; 123.5; 122.9; 108.9; 75.9; 64.8; 50.7; 26.7; 20.4. IR (neat): ν = 2924; 1716; 1555; 1457; 746; cm^{-1}.



2g

7) **Methyl 1,3-dimethyl-3-(nitromethyl)-2-oxoindoline-5-carboxylate (2g)**

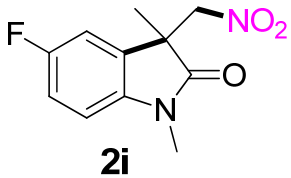
The reaction of **1g** (47.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 26.7 mg (48%) of **2g**; **2g**: yellow solid; ^{1}H NMR (d_6-DMSO, 400 MHz): 8.14 (d, J = 1.6 Hz, 1H); 7.98 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H); 7.19 (d, J = 8.4 Hz, 1H); 5.45 (d, J = 14.8 Hz, 1H, CH_2); 5.16 (d, J = 14.8 Hz, 1H, CH_2); 3.83 (s, 3H); 3.23 (s, 3H); 1.32 (s, 3H). ^{13}C NMR (d_6-DMSO, 100 MHz): 178.0; 166.5; 148.3; 131.6; 130.7; 124.2; 124.1; 109.3; 78.6; 52.4; 47.1; 27.0; 21.6. IR (neat): ν = 3422; 1652; 1553; 1026; 764; cm^{-1}.



2h

8) **5-Iodo-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2h)**

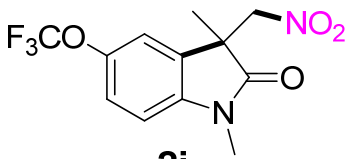
The reaction of **1h** (60.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 47.0 mg (68%) of **2h**; **2h**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.65 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H); 7.50 (d, J = 2.0 Hz, 1H); 6.69 (d, J = 8.4 Hz, 1H); 4.92 (d, J = 14.0 Hz, 1H, CH_2); (d, J = 14.0 Hz, 1H, CH_2); 3.26 (s, 3H); 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.4; 143.4; 138.1; 131.6; 131.2; 110.8; 85.2; 78.6; 46.8; 26.7; 21.7. IR (neat): ν = 2978; 1717; 1555; 1489; 1360; cm^{-1}. FTMS: calc. for $C_{11}H_{12}IN_2O_3$ $(M+H)^+$, 346.98881; found, 346.98871.



2i

9) **5-Fluoro-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2i)**

The reaction of **1i** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 38.6 mg (81%) of **2i**; **2i**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.06 – 6.98 (m, 2H), 6.85 – 6.81 (m, 1H), 4.92 (d, J = 13.8 Hz, 1H, CH_2); 4.73 (d, J = 13.8 Hz, 1H, CH_2); 3.27 (s, 3H); 1.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.8; 159.2 (d, J = 240.5 Hz); 139.5; 130.7 (d, J = 8.8 Hz); 115.5 (d, J = 22.3 Hz); 110.9 (d, J = 24.1 Hz); 109.4 (d, J = 7.5 Hz); 78.7; 47.7; 26.7; 21.6. IR (neat): ν = 2935; 1714; 1556; 1496; 1119; cm^{-1}. FTMS: calc. for $C_{11}H_{12}FN_2O_3$ $(M+H)^+$, 239.08217; found, 239.08265.

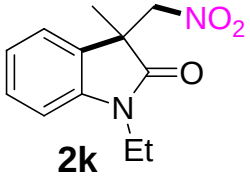


2j

10) **1, 3-Dimethyl-3-(nitromethyl)-5-(trifluoromethoxy)indolin-2-one (2j)**

The reaction of **1j** (52.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 48.6 mg (80%) of **2j**; **2j**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.22 (d, J = 1.6 Hz, 1H); 7.21 – 7.18 (m, 1H); 6.90 (d, J = 8.4 Hz, 1H); 4.93 (d, J = 13.6 Hz, 1H, CH_2); 4.76 (d, J = 14.0 Hz, 1H,

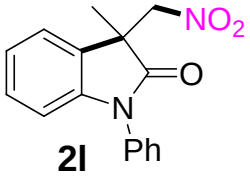
CH_2); 3.29 (s, 3H); 1.42 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): 176.9; 144.8; 142.2; 130.6; 119.4 (q, 600 Hz); 121.7; 119.2; 78.56; 47.2; 26.8; 21.6. IR (neat): ν = 2937; 1724; 1557; 1219; 1163; cm^{-1}. FTMS: calc. for $C_{12}H_{12}F_3N_2O_4$ $(M+H)^+$, 305.07379; found, 305.07437.



2k

11) **1-Ethyl-3-methyl-3-(nitromethyl)indolin-2-one (2k)**

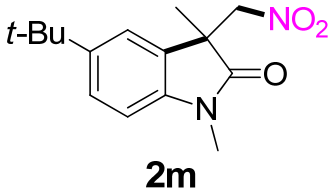
The reaction of **1k** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 25.3 mg (54%) of **2k**; **2k**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.34 – 7.29 (m, 1H); 7.22 (d, J = 7.2 Hz, 1H); 7.06 (t, J = 7.6 Hz, 1H); 6.91 (d, J = 8.0 Hz, 1H); 4.93 (d, J = 13.4 Hz, 1H, CH_2); 4.76 (d, J = 13.4 Hz, 1H, CH_2); 3.96 – 3.87 (m, 1H); 3.78 – 3.69 (m, 1H); 1.40 (s, 3H); 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.8; 142.6; 129.3; 129.1; 122.6; 122.5; 109.0; 79.0; 46.9; 35.0; 21.7; 21.2. IR (neat): ν = 2979; 1714; 1613; 1556; 1380; cm^{-1}. FTMS: calc. for $C_{12}H_{15}N_2O_3$ $(M+H)^+$, 235.10726; found, 235.10772.



2l

12) **3-Methyl-3-(nitromethyl)-1-phenylindolin-2-one (2l)**

The reaction of **1l** (47.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 31.6 mg (56%) of **2l**; **2l**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.56 – 7.53 (m, 2H); 7.47 – 7.44 (m, 3H); 7.29 – 7.22 (m, 2H); 7.12 – 7.08 (m, 1H); 6.82 (d, J = 7.6 Hz, 1H); 5.05 (d, J = 13.6 Hz, 1H, CH_2); 4.84 (d, J = 13.6 Hz, 1H, CH_2); 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.9; 143.8; 134.2; 129.7; 129.1; 128.7; 128.4; 126.7; 123.3; 122.5; 110.1; 79.2; 47.1; 21.9. IR (neat): ν = 1723; 1555; 1501; 1372; 756; cm^{-1}. FTMS: calc. for $C_{16}H_{15}N_2O_3$ $(M+H)^+$, 283.10746; found, 283.10772.

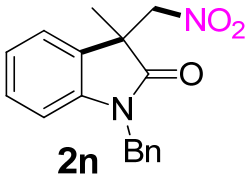


2m

13) **5-(tert-Butyl)-1, 3-dimethyl-3-(nitromethyl)indolin-2-one (2m)**

The reaction of **1m** (46.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 37.0 mg (67%) of **2m**; **2m**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.24 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H); 7.24 (d, J = 2.0 Hz, 1H); 6.82 (d, J = 8.0 Hz, 1H); 4.89 (d, J = 13.0 Hz, 1H, CH_2); 4.76 (d, J = 13.0 Hz, 1H, CH_2); 3.27 (s, 3H); 1.42 (s, 3H); 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): 177.3; 146.3; 141.0; 128.7; 125.8; 119.6; 108.2; 79.2; 47.3; 34.56; 31.5; 26.6; 21.7. IR (neat): ν = 2962; 1716; 1555; 1501; 1257; cm^{-1}. FTMS: calc. for $C_{15}H_{21}N_2O_3$ $(M+H)^+$, 277.15454; found,

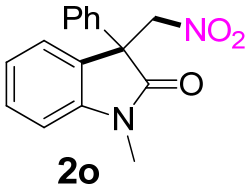
277.15467.



2n

14) **1-Benzyl-3-methyl-3-(nitromethyl)indolin-2-one (2n)**

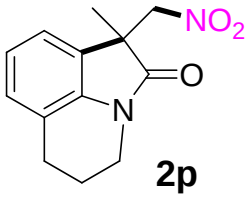
The reaction of **1n** (50.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 28.4 mg (48%) of **2n**; **2n**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.34 - 7.33 (m, 4H); 7.29 - 7.26 (m, 1H); 7.22 - 7.17 (m, 2H); 7.05 - 7.01 (m, 1H); 6.75 (d, J = 8.0 Hz, 1H); 5.05 – 4.90 (m, 3H); 4.81 (d, J = 13.6 Hz, 1H, CH_2); 1.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 177.3; 142.6; 135.4; 129.1; 129.0; 128.8; 127.7; 127.2; 122.9; 122.3; 109.9; 78.7; 47.1; 44.2; 22.4. IR (neat): ν = 2979; 1715; 1613; 1555; 1182; cm^{-1}. FTMS: calc. for $C_{17}H_{17}N_2O_3$ $(M+H)^+$, 297.12352; found, 297.12337.



2o

15) **1-Methyl-3-(nitromethyl)-3-phenylindolin-2-one (2o)**

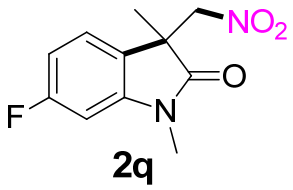
The reaction of **1o** (48.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 28.2 mg (50%) of **2o**; **2o**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.19 (d, J = 8.8 Hz, 2H); 7.59 (dd, J = 6.8 Hz, J = 1.6 Hz, 2H); 7.50 – 7.45 (m, 1H); 7.40 (dd, J = 7.2 Hz, J = 0.8 Hz, 1H); 7.25 – 7.21 (m, 2H); 7.00 (d, J = 8.0 Hz, 1H); 5.35 (d, J = 13.6 Hz, 1H, CH_2); 5.12 (d, J = 13.6 Hz, 1H, CH_2); 3.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 174.2; 147.9; 144.4; 142.1; 130.5; 128.1; 125.7; 125.0; 124.1; 123.4; 109.6; 78.8; 54.5; 27.1. IR (neat): ν = 2962; 1718; 1557; 1520; 1349; cm^{-1}. FTMS: calc. for $C_{16}H_{15}N_2O_3$ $(M+H)^+$, 283.10763; found, 283.10772.



2p

16) **1-Methyl-1-(nitromethyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]dduinolin-2(4H)-one (2p)**

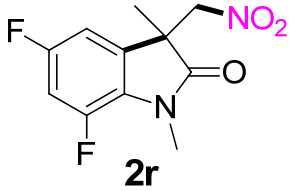
The reaction of **1p** (40.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 37.9 mg (77%) of **2p**; **2p**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.08 - 7.05 (m, 2H); 6.98 – 6.94 (m, 1H); 4.89 (d, J = 13.2 Hz, 1H, CH_2); 4.75 (d, J = 13.2 Hz, 1H, CH_2); 3.83 – 3.72 (m, 2H); 2.79 (t, J = 6.0 Hz, 2H); 2.07 – 2.01 (m, 2H); 1.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 175.9; 139.3; 128.0; 127.6; 122.3; 120.9; 120.3; 79.1; 48.2; 39.1; 24.4; 21.3; 21.0. IR (neat): ν = 2931; 1713; 1555; 1357; 1244; cm^{-1}. FTMS: calc. for $C_{13}H_{15}N_2O_3$ $(M+H)^+$, 247.10701; found, 247.10772.



2q

17) **6-Fluoro-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2dd)**

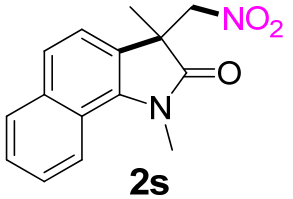
The reaction of **1q** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 24.8 mg (52%) of **2q**; **2q**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.06 - 6.98 (m, 2H); 6.83 (dd, *J* = 4.0 Hz, 1H); 4.92 (d, *J* = 13.8 Hz, 1H, CH_2); 4.74 (d, *J* = 13.8 Hz, 1H, CH_2); 3.27 (s, 3H); 1.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.8; 159.2 (d, *J* = 240.5 Hz); 139.5; 130.7 (d, *J* = 8.8 Hz); 115.5 (d, *J* = 22.3 Hz); 110.9 (d, *J* = 24.1 Hz); 109.4 (d, *J* = 7.5 Hz); 78.7; 47.7; 26.7; 21.6. FTMS: calc. for $C_{11}H_{12}FN_2O_3$ $(M+H)^+$, 239.08210; found, 239.08245.



2r

18) **5,7-Difluoro-1,3-dimethyl-3-(nitromethyl)indolin-2-one (2r)**

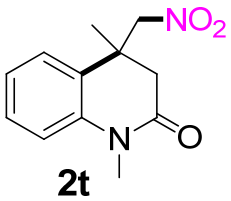
The reaction of **1r** (42.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 15.9 mg (31%) of **2r**; **2r**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.53 – 6.47 (m, 2H); 4.96 (d, *J* = 13.6 Hz, 1H, CH_2); 4.92 (d, *J* = 14.0 Hz, 1H, CH_2); 3.26 (s, 3H); 1.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.9; 164.0 (dd, *J* = 252.0 Hz, *J* = 17.3 Hz); 158.7 (dd, *J* = 247.0 Hz, *J* = 11.5 Hz); 146.4 (t, *J* = 15.6 Hz); 98.1 (t, *J* = 26.2 Hz); 94.2 (dd, *J* = 27.5 Hz, *J* = 4.1 Hz); 46.4; 27.1; 20.1. IR (neat): ν = 2961; 1730; 1637; 1557; 744; cm^{-1}. FTMS: calc. for $C_{11}H_{11}F_2N_2O_3$ $(M+H)^+$, 257.07259; found, 257.07323.



2s

19) **1,3-Dimethyl-3-(nitromethyl)-1H-benzo[g]indol-2(3H)-one (2s)**

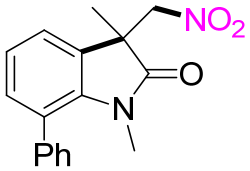
The reaction of **1s** (45.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 22.7 mg (42%) of **2s**; **2s**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.76 (dd, *J* = 8.4 Hz, *J* = 0.4 Hz, 1H); 7.56 – 7.46 (m, 3H); 7.40 (dd, *J* = 7.2 Hz, *J* = 0.8 Hz, 1H); 7.05 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H); 5.69 (d, *J* = 14.6 Hz, 1H, CH_2); 4.99 (d, *J* = 14.6 Hz, 1H, CH_2); 3.61 (s, 3H); 1.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6; 136.1; 133.9; 133.6; 127.2; 126.8; 123.0; 121.2; 120.0; 119.2; 109.3; 81.5; 46.7; 30.1; 29.9. IR (neat): ν = 2961; 1758; 1661; 1553; 1244; cm^{-1}. FTMS: calc. for $C_{15}H_{15}N_2O_3$ $(M+H)^+$, 271.10724; found, 271.10772.



2t

20) **1,4-Dimethyl-4-(nitromethyl)-3,4-dihydrodduinolin-2(1H)-one (2t)**

The reaction of **1t** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 23.9 mg (51%) of **2t**; **2t**: yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.43 – 7.35 (m, 2H); 7.14 (d, J = 7.6 Hz, 1H); 7.08 (d, J = 8.0 Hz, 1H); 4.50 (d, J = 11.2 Hz, 1H); 4.45 (d, J = 11.0 Hz, 1H); 3.42 (s, 3H); 2.88 (d, J = 16.4 Hz, 1H, CH_2); 2.70 – 2.67 (m, 1H); 1.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 167.5; 129.2; 125.2; 124.9; 123.7; 115.5; 114.1; 81.8; 41.8; 37.2; 29.3; 23.2. IR (neat): ν = 2926; 1672; 1549; 1371; 756; cm^{-1}. FTMS: calc. for $C_{12}H_{15}N_2O_3$ $(M+H)^+$, 235.10694; found, 235.10772.



2u

21) **1,3-Dimethyl-3-(nitromethyl)-7-phenylindolin-2-one (2u)**

The reaction of **1u** (38.0 mg, 0.2 mmol), *t*-BuONO (52.0 mg, 0.5 mmol) in DMF (2 mL) afforded 24.8 mg (44%) of **2u**; **2u**: yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.44 – 7.36 (m, 5H); 7.21 (d, J = 7.2 Hz, 1H); 7.15 (d, J = 8.0 Hz, 1H); 7.08 (t, J = 8.0 Hz, 1H,); 4.96 (d, J = 13.6 Hz, 1H, CH_2); 4.79 (d, J = 13.6 Hz, 1H, CH_2); 2.79 (s, 3H); 1.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 178.3; 140.5; 138.5; 132.2; 130.1; 128.9; 127.9; 127.8; 126.2; 122.2; 121.3; 79.3; 46.4; 30.6; 22.1. IR (neat): ν = 2924; 1716; 1555; 1457; 746; cm^{-1}. FTMS: calc. for $C_{17}H_{17}N_2O_3$ $(M+H)^+$, 297.12337; found, 297.12337.

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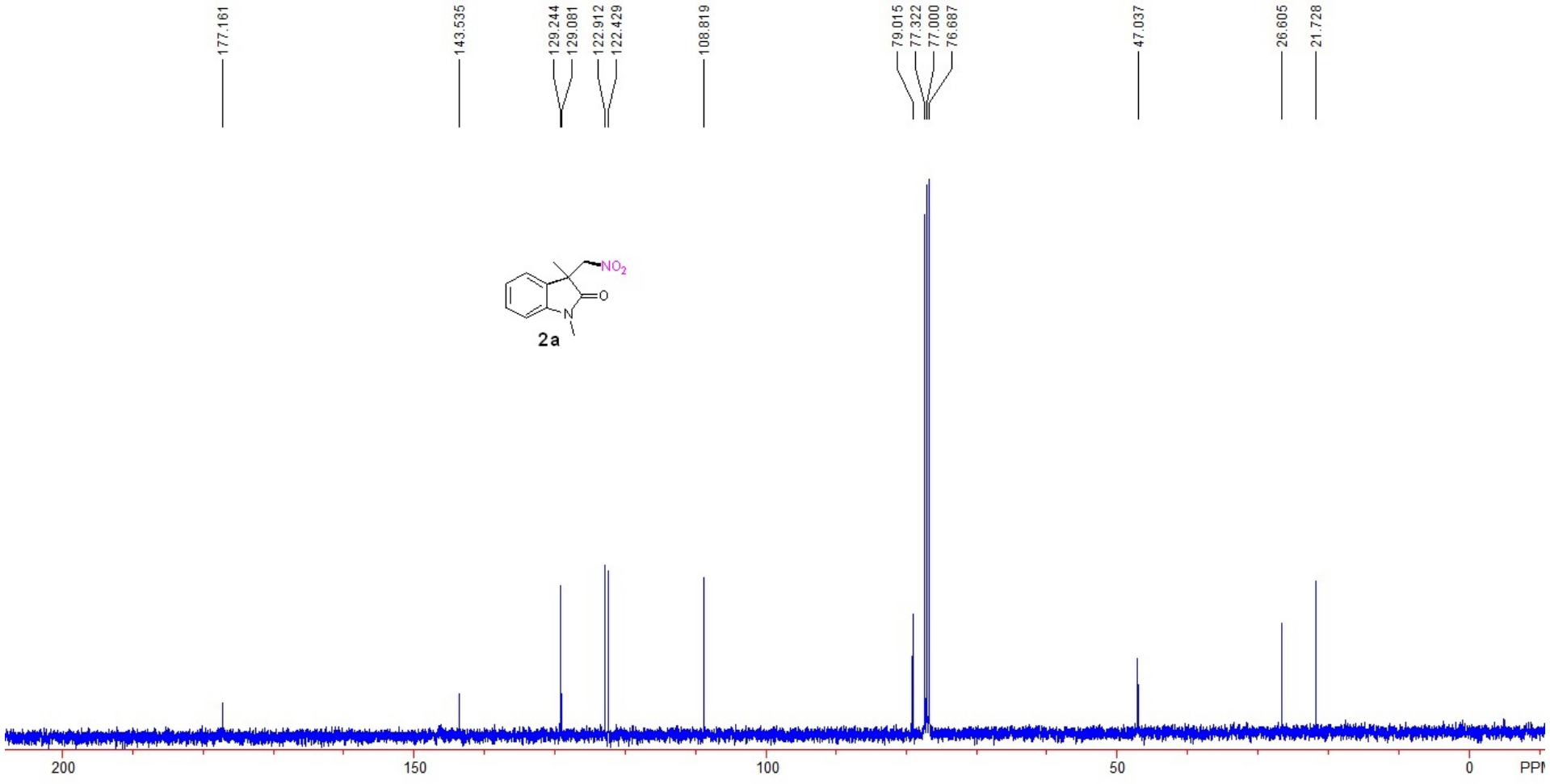
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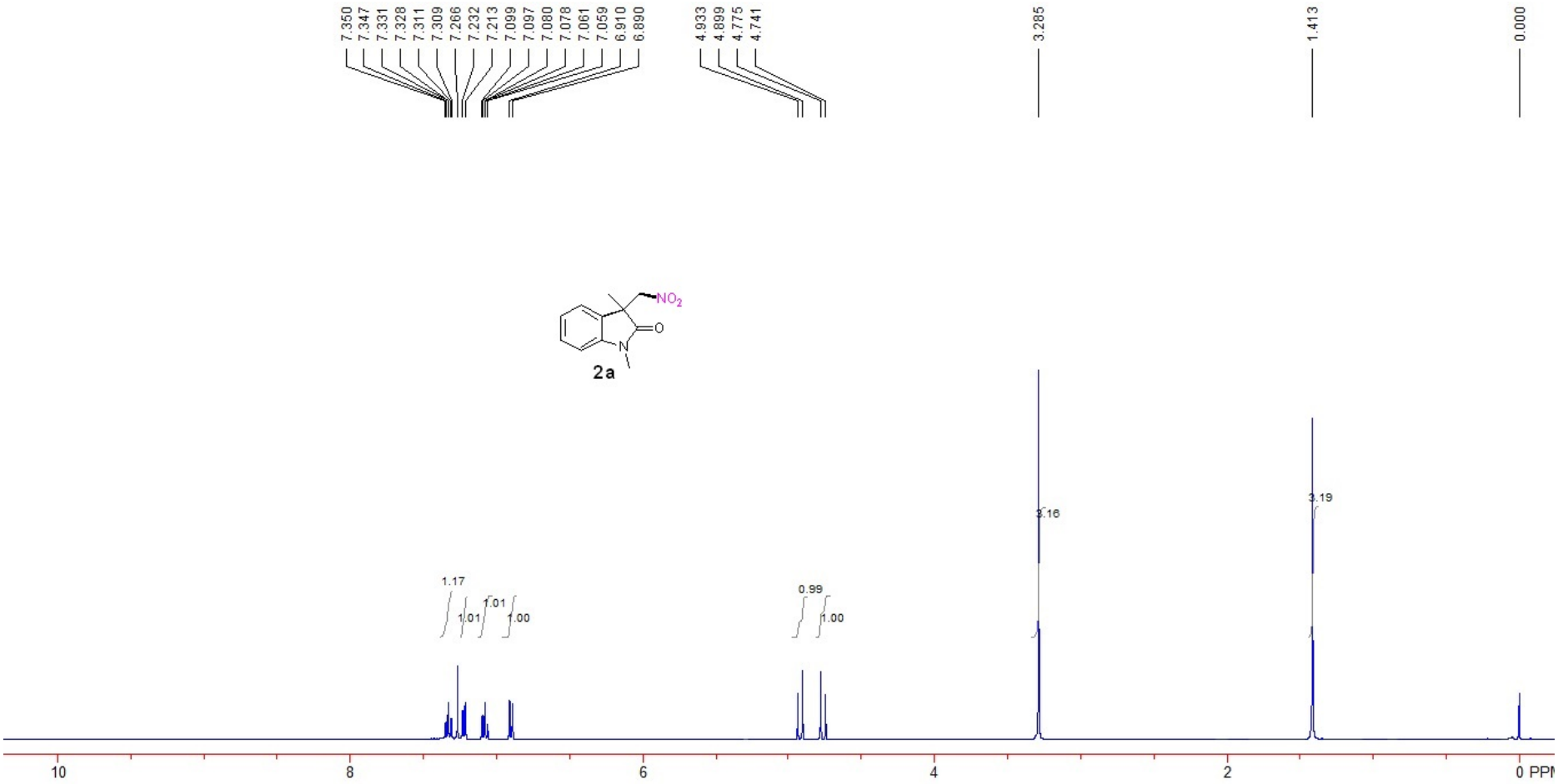

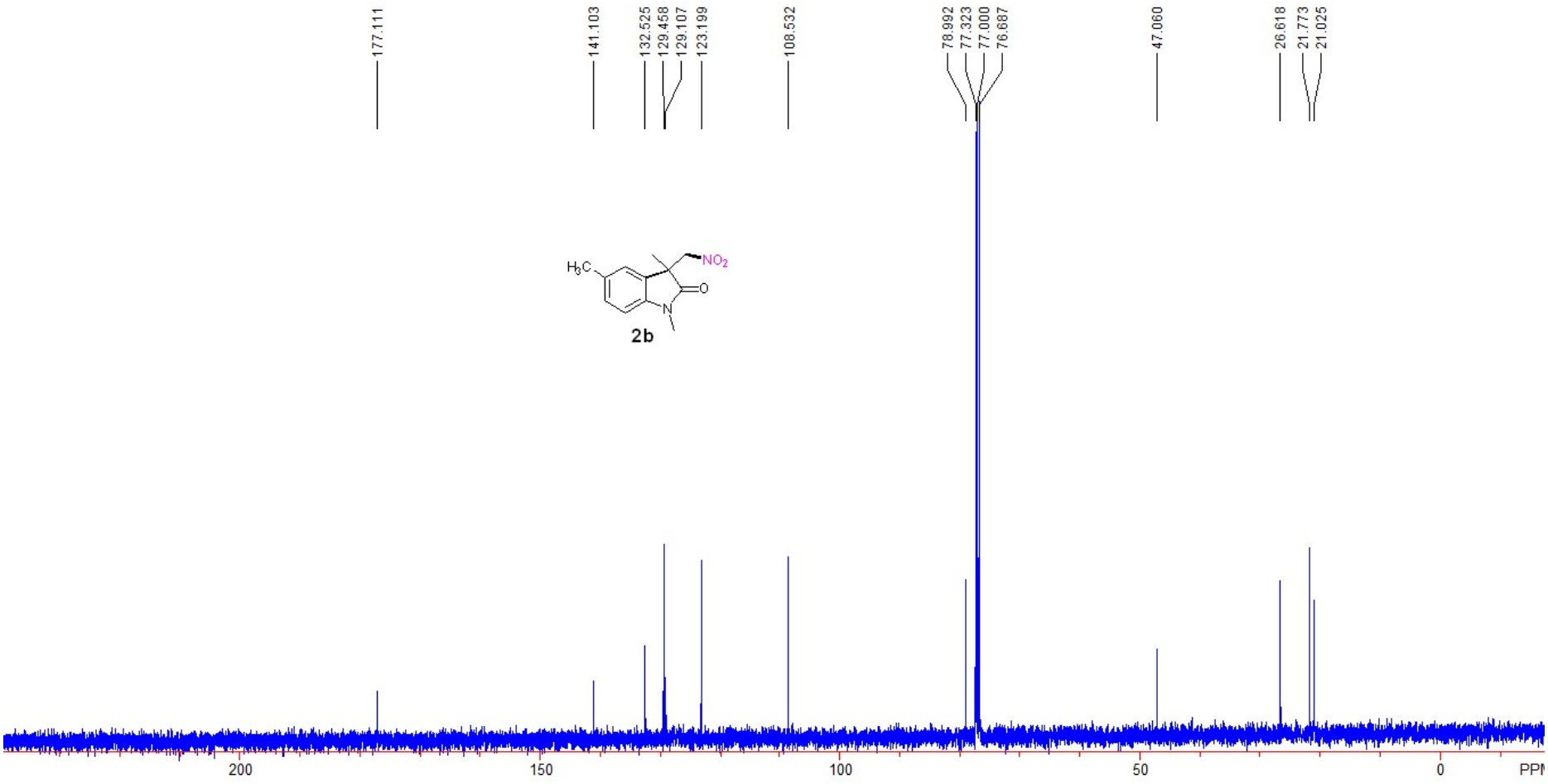

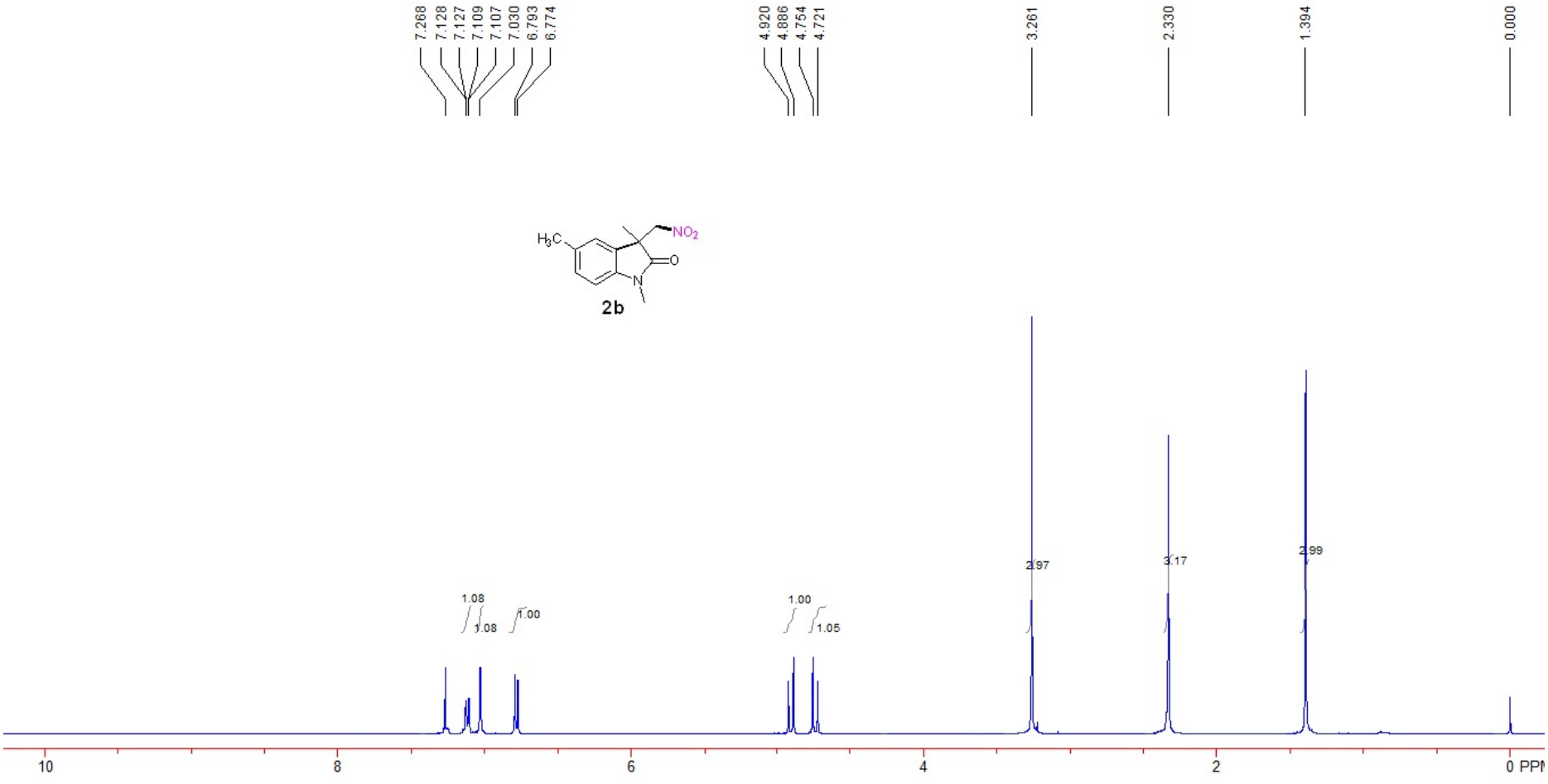

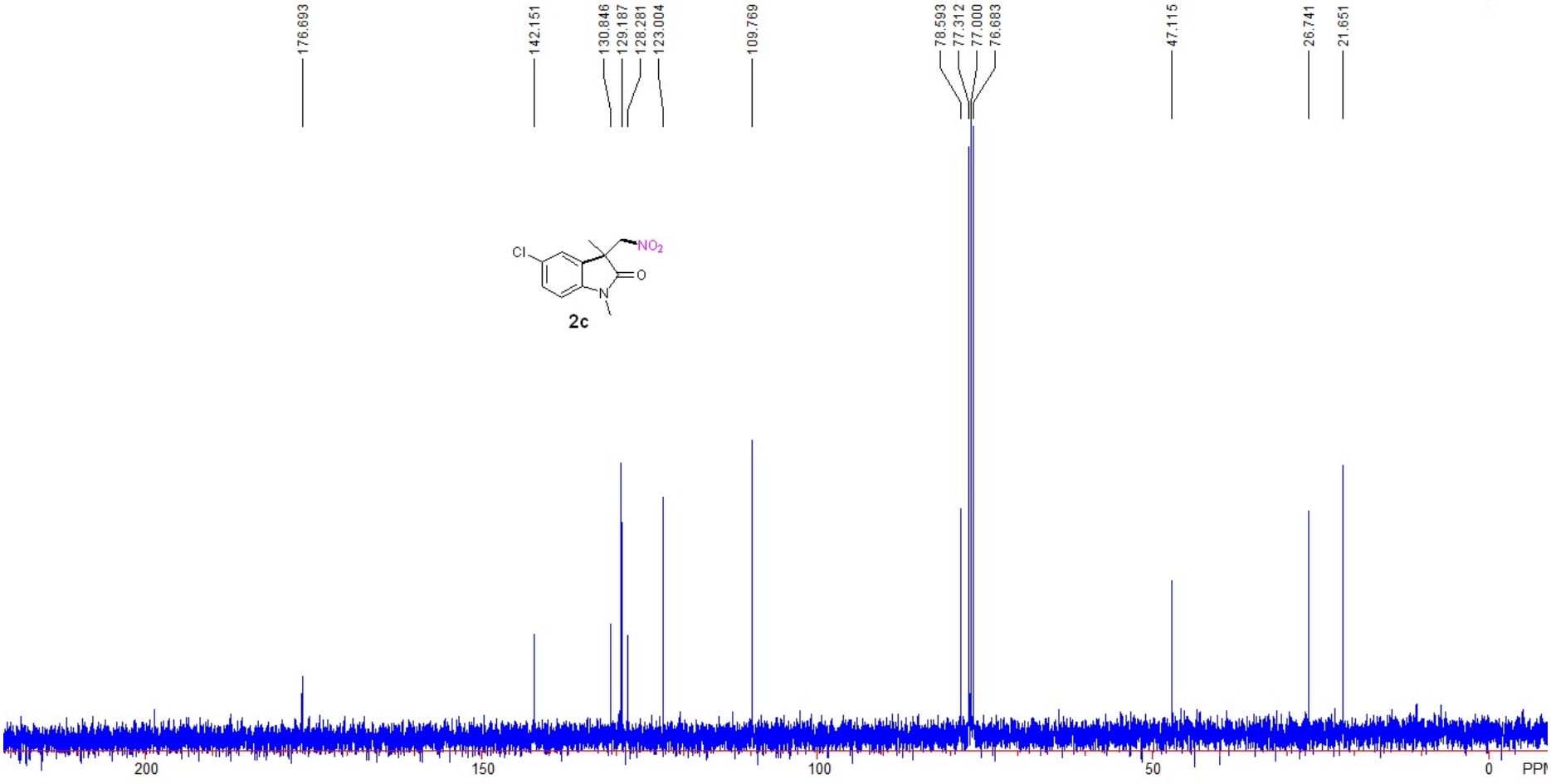

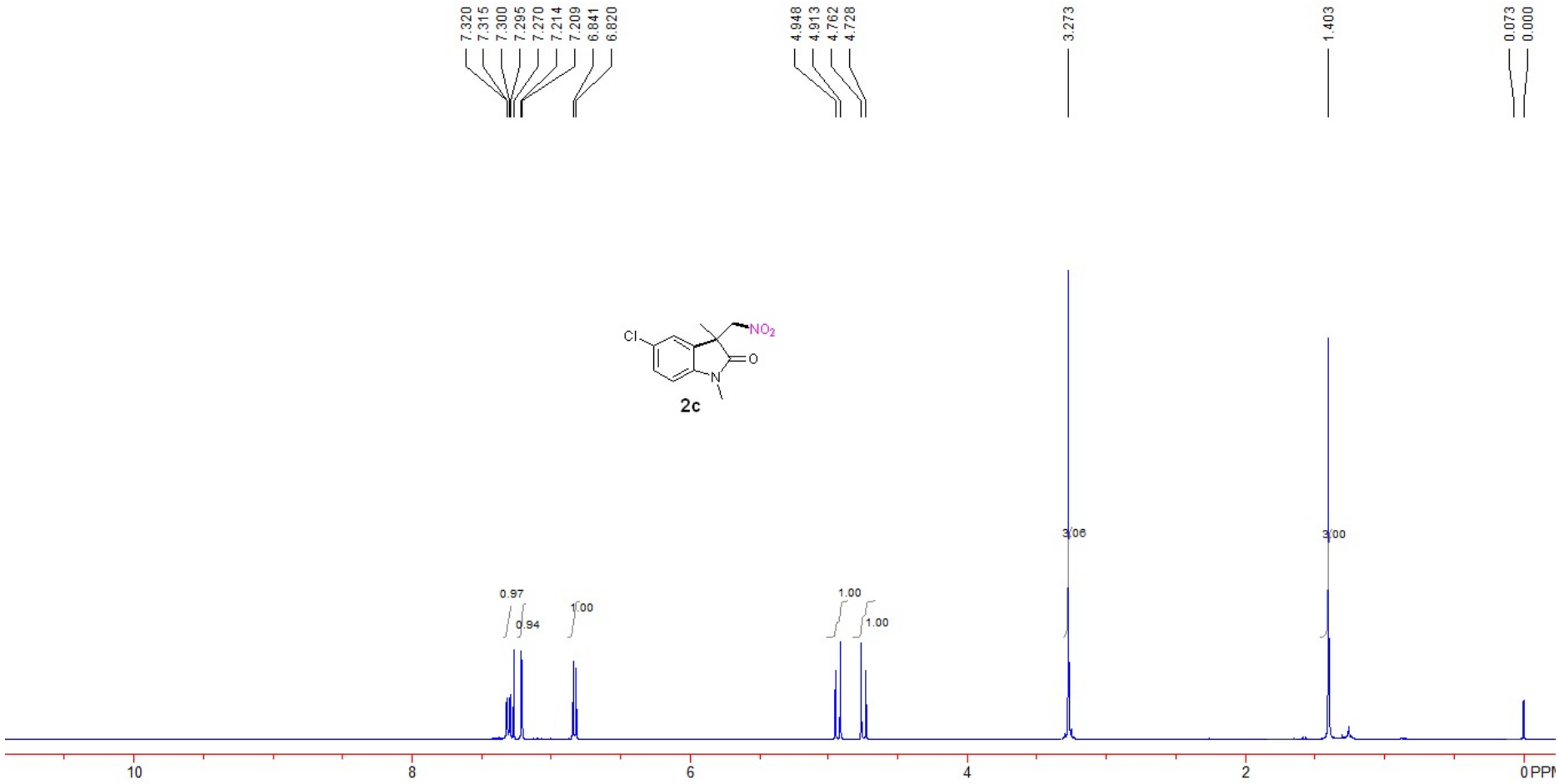

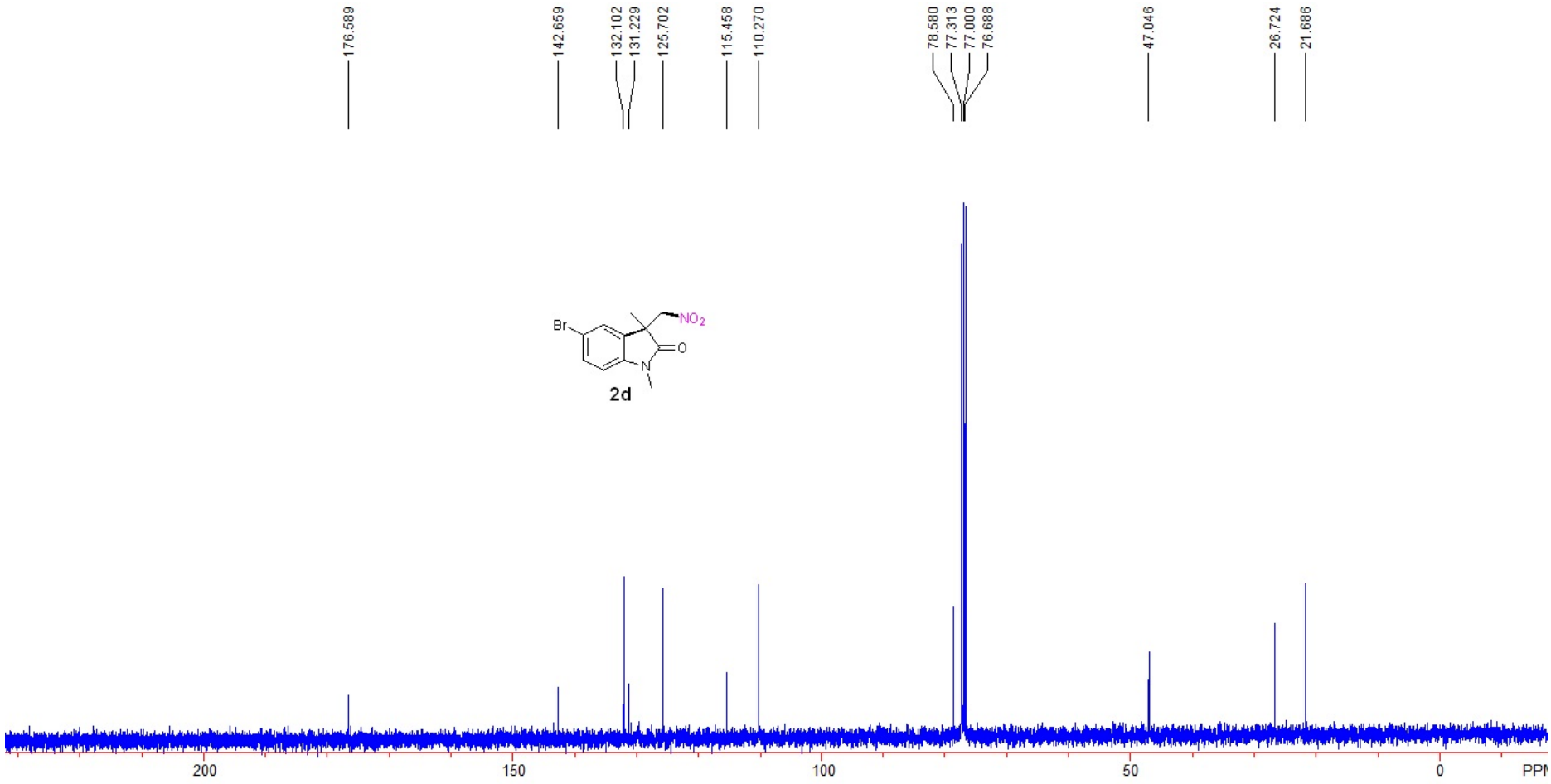

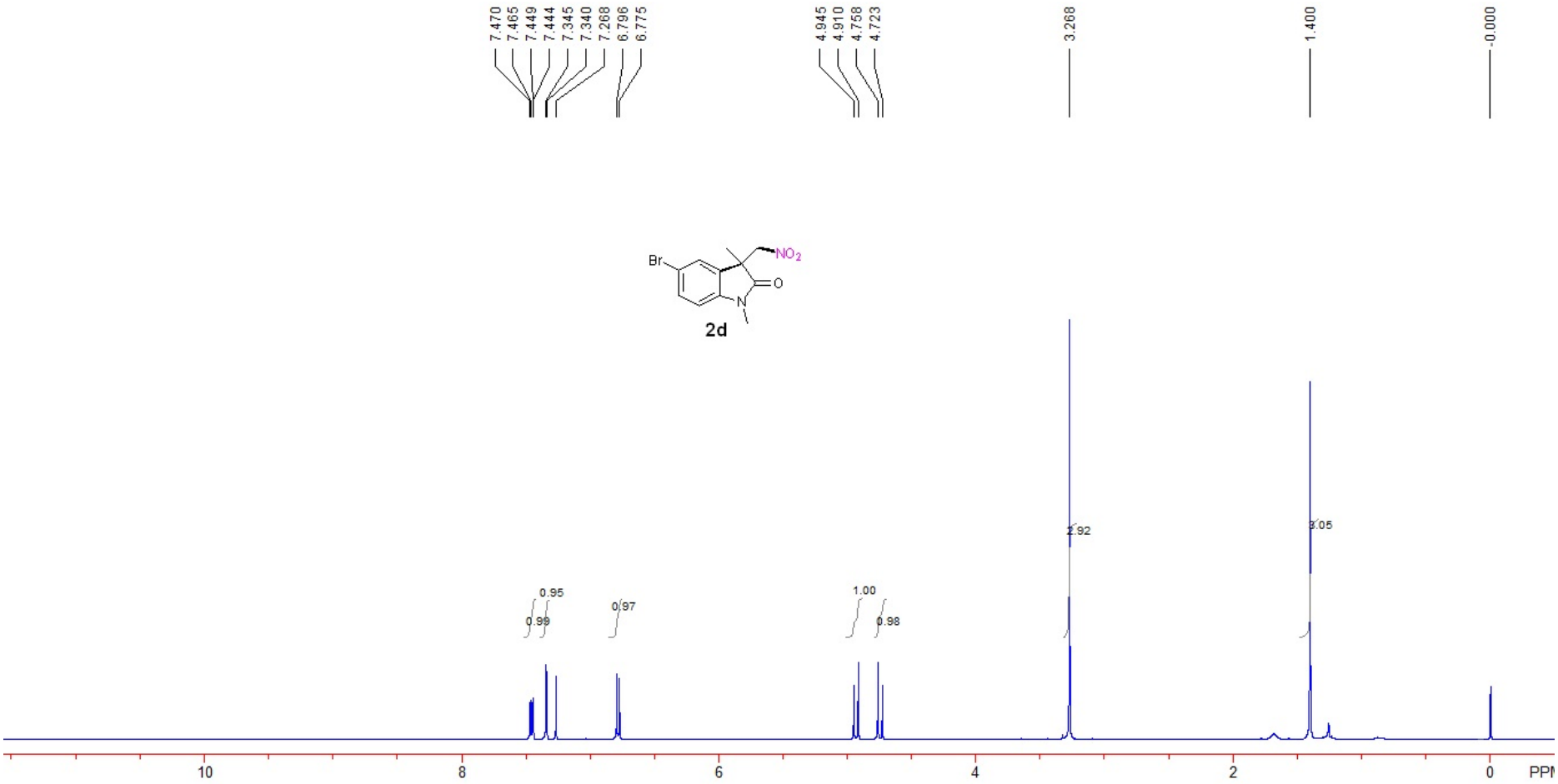

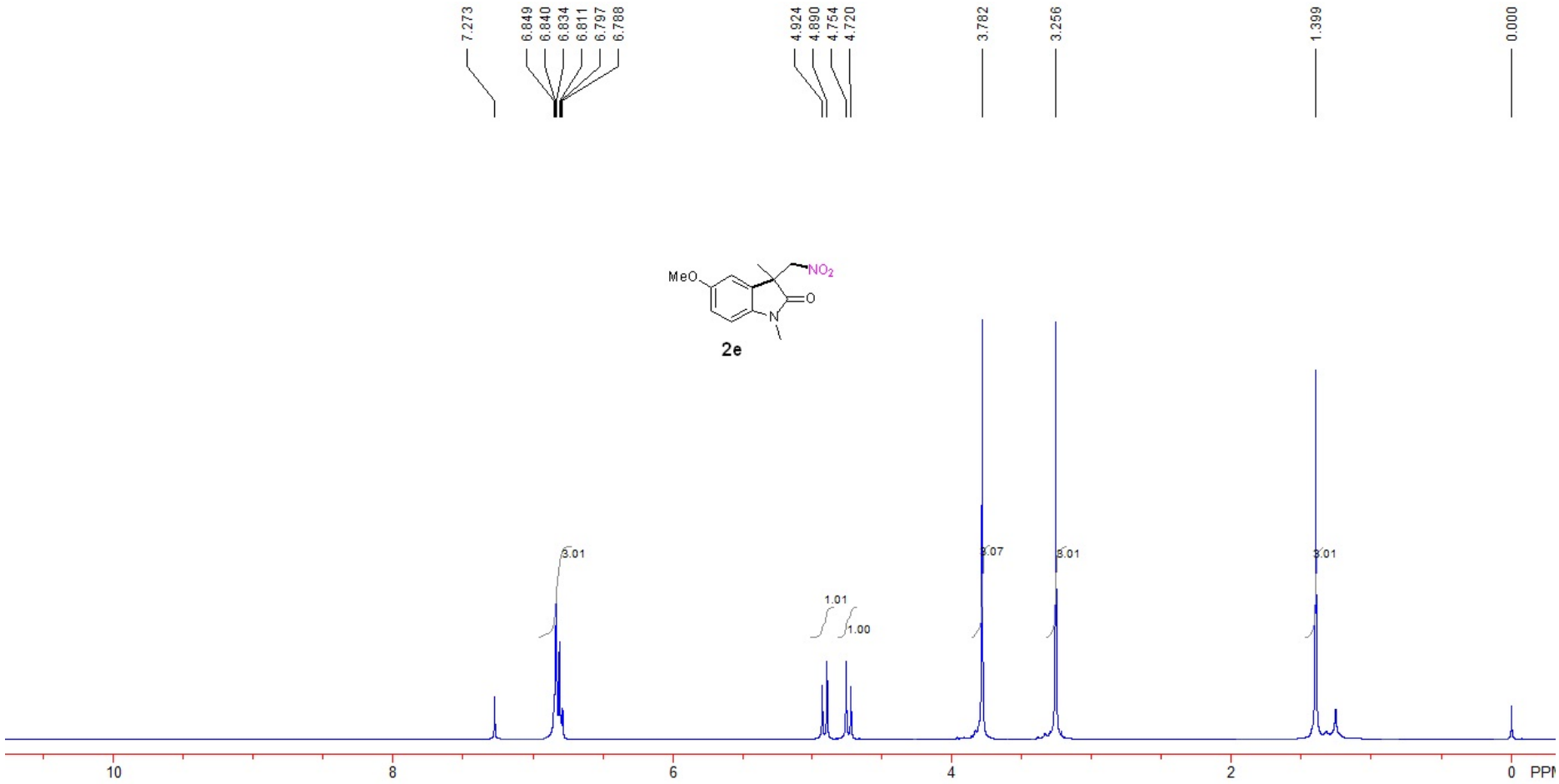

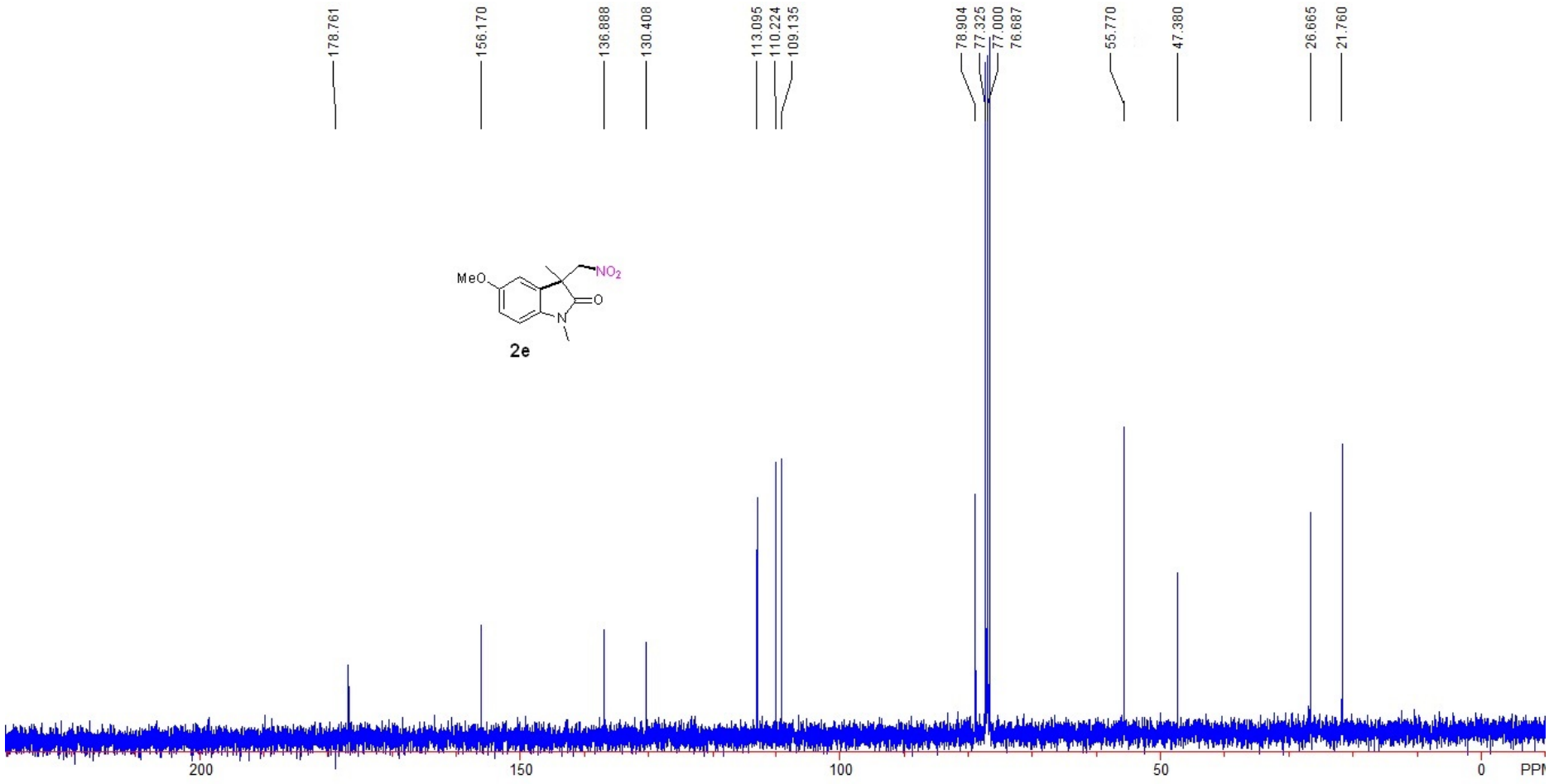

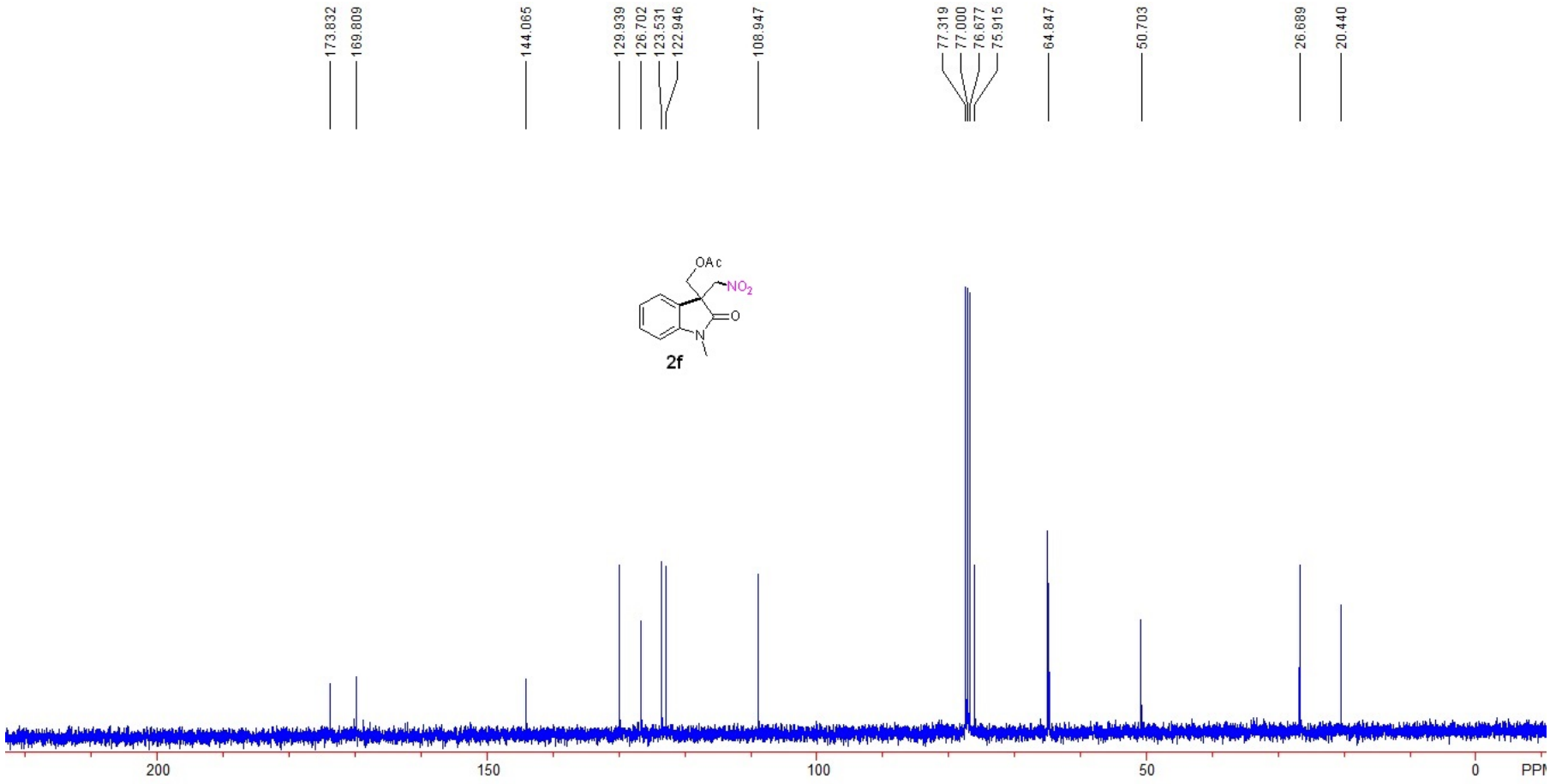

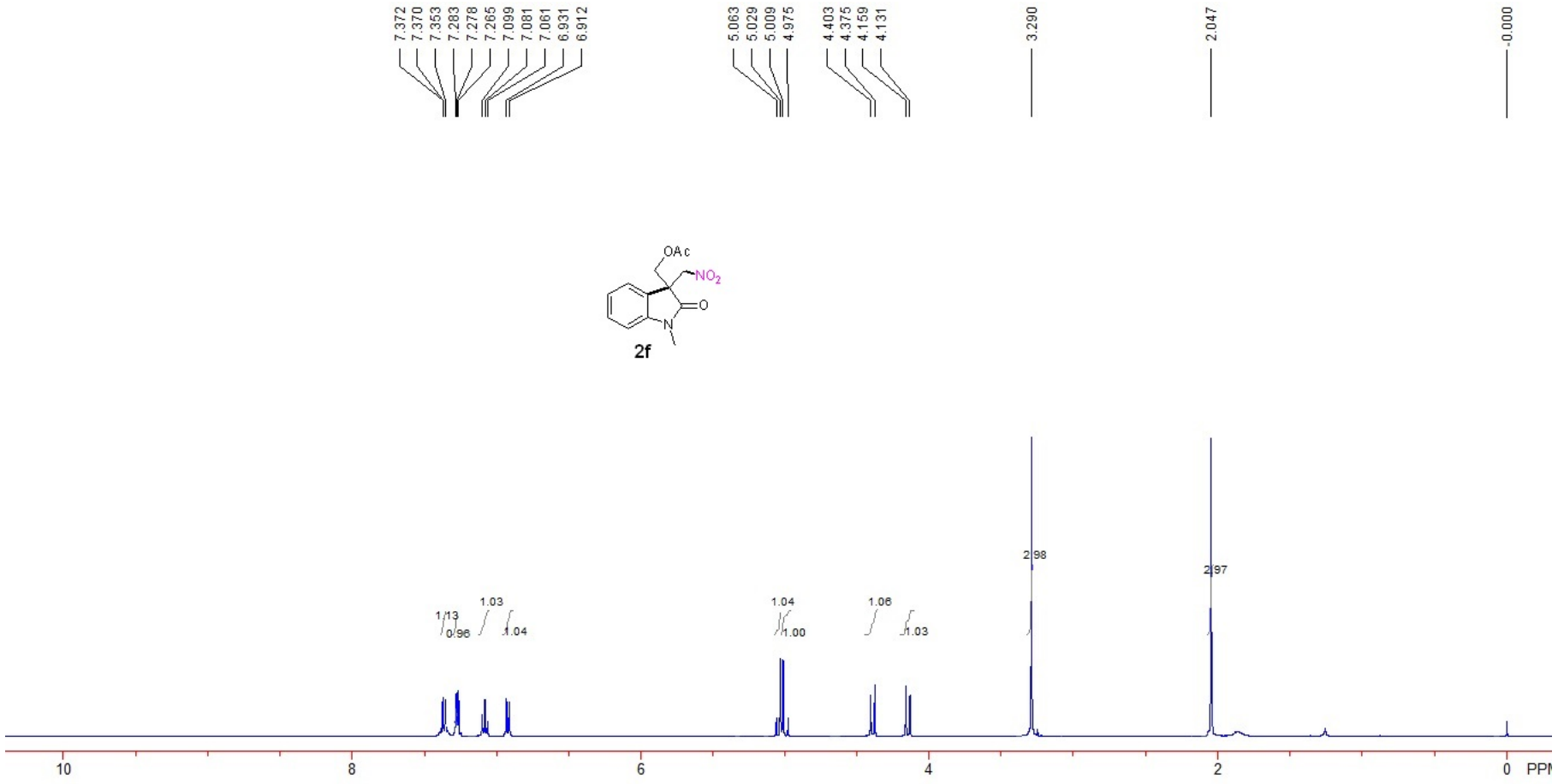

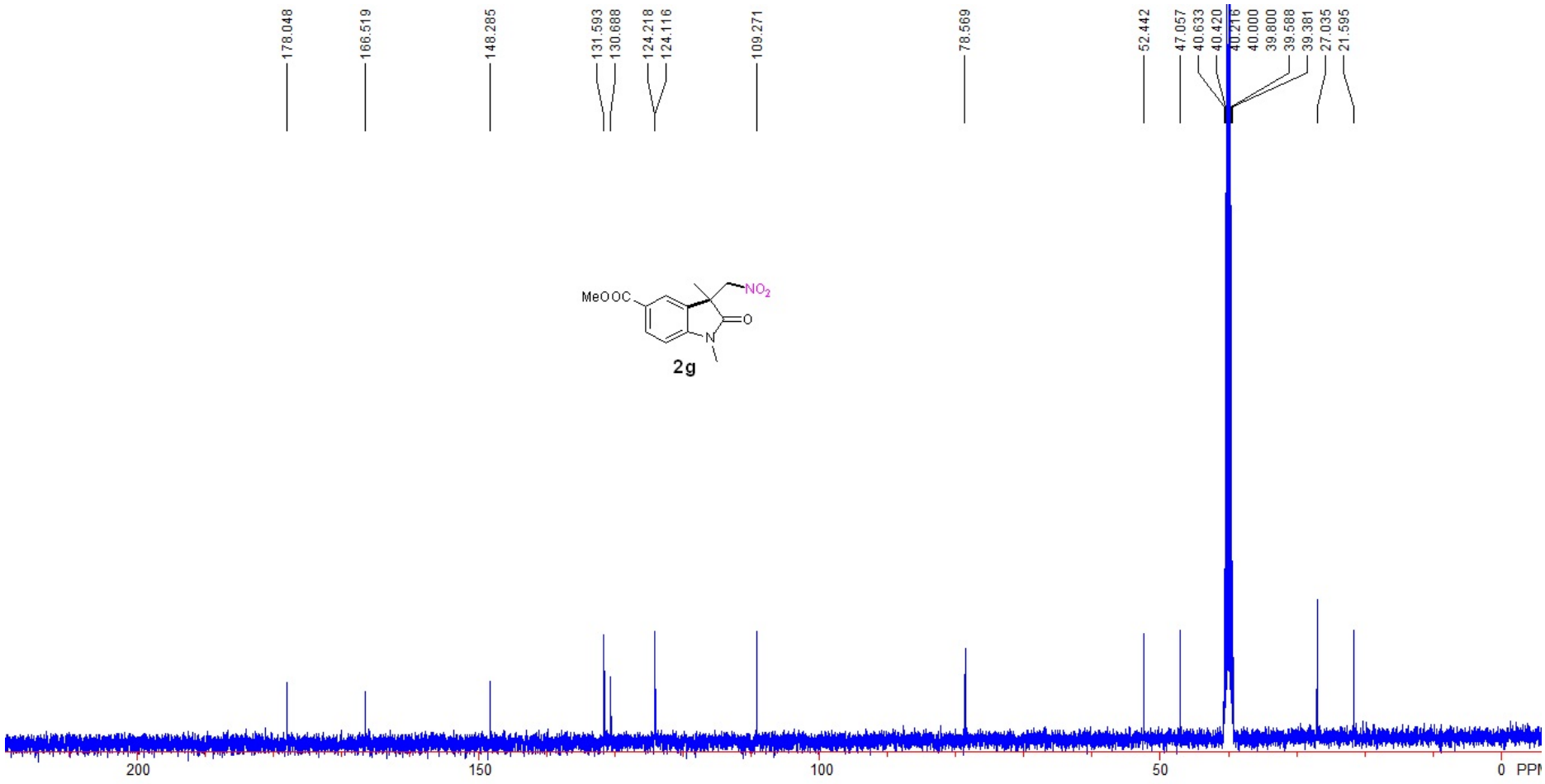

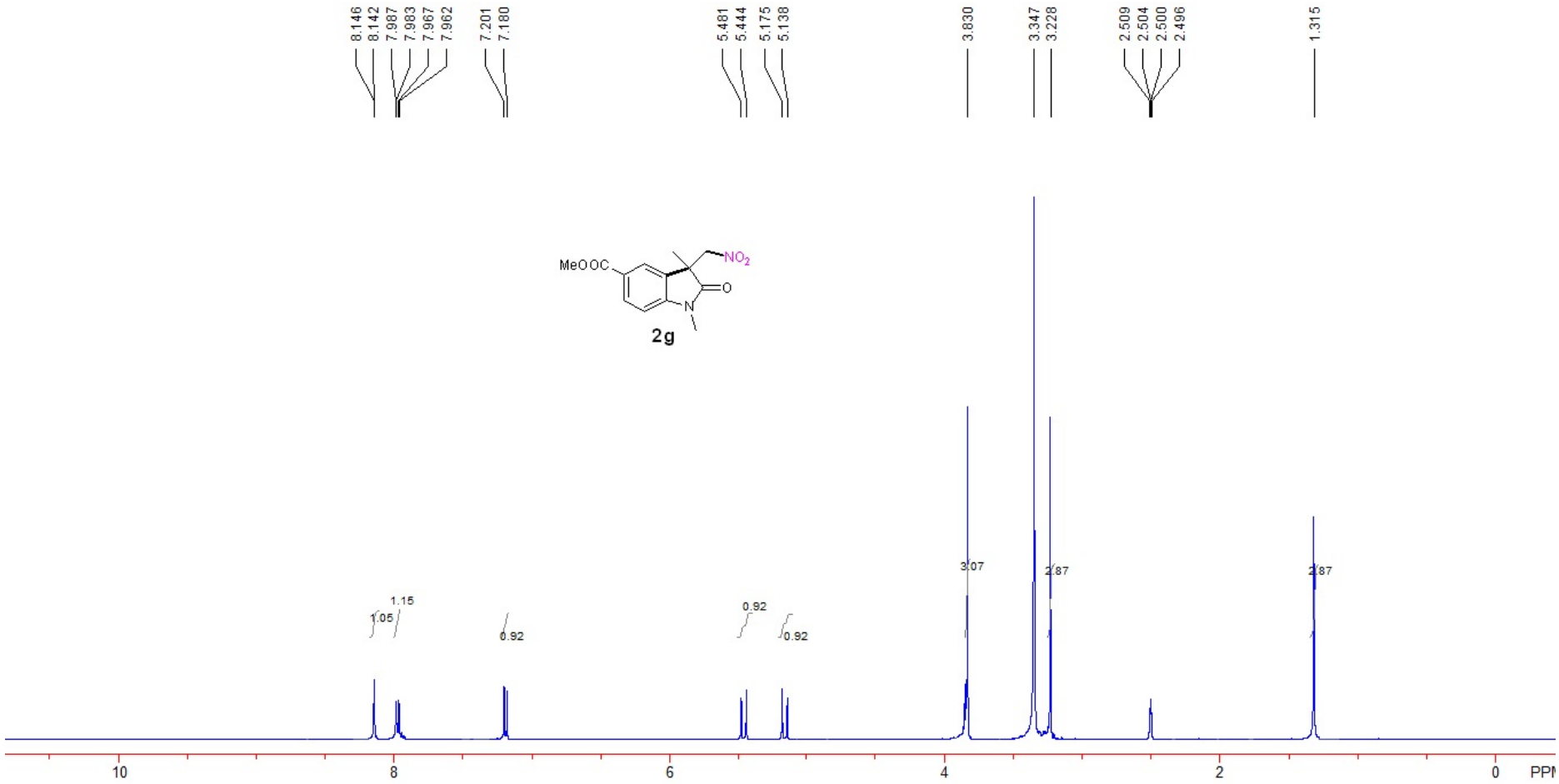

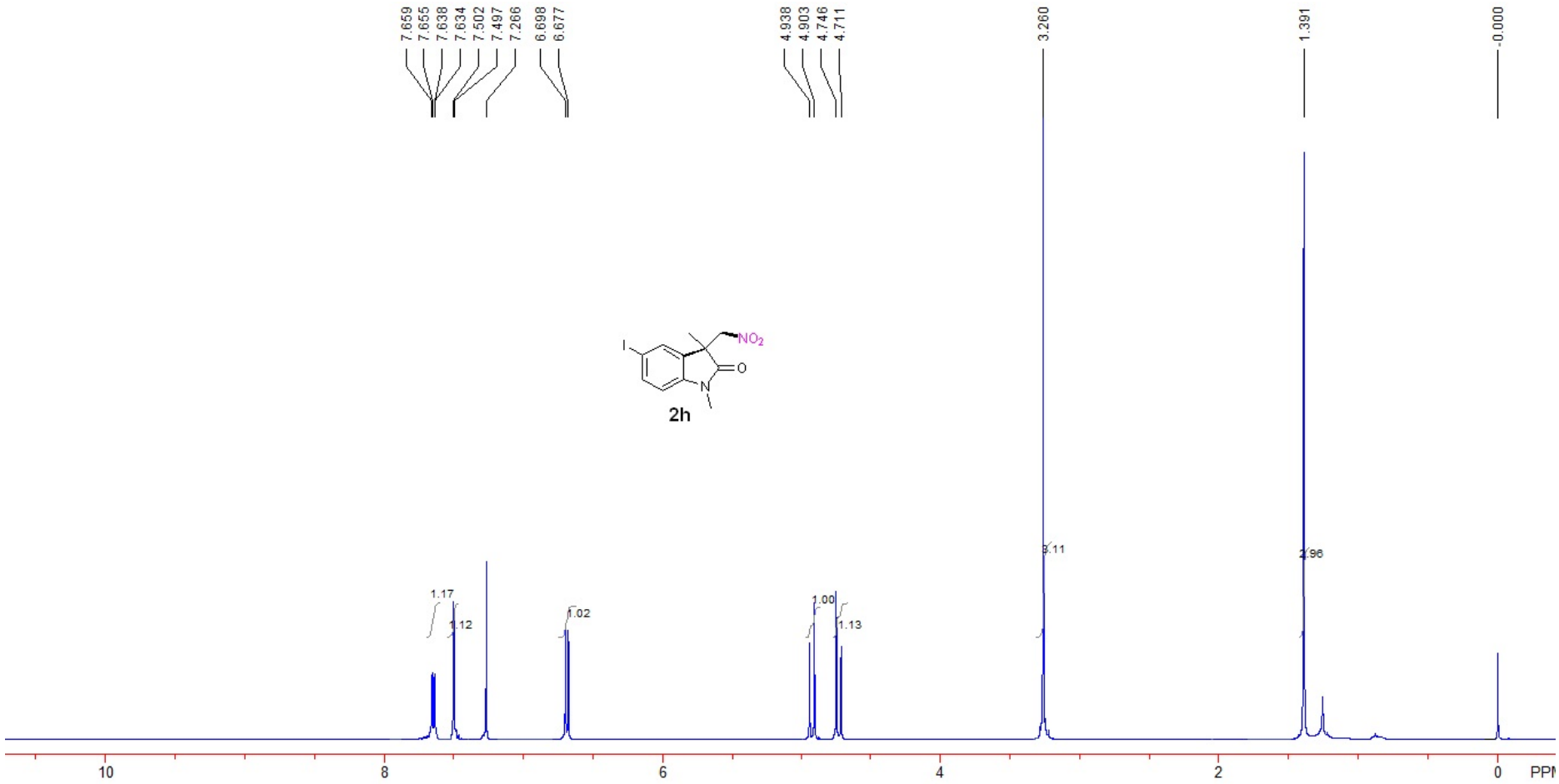

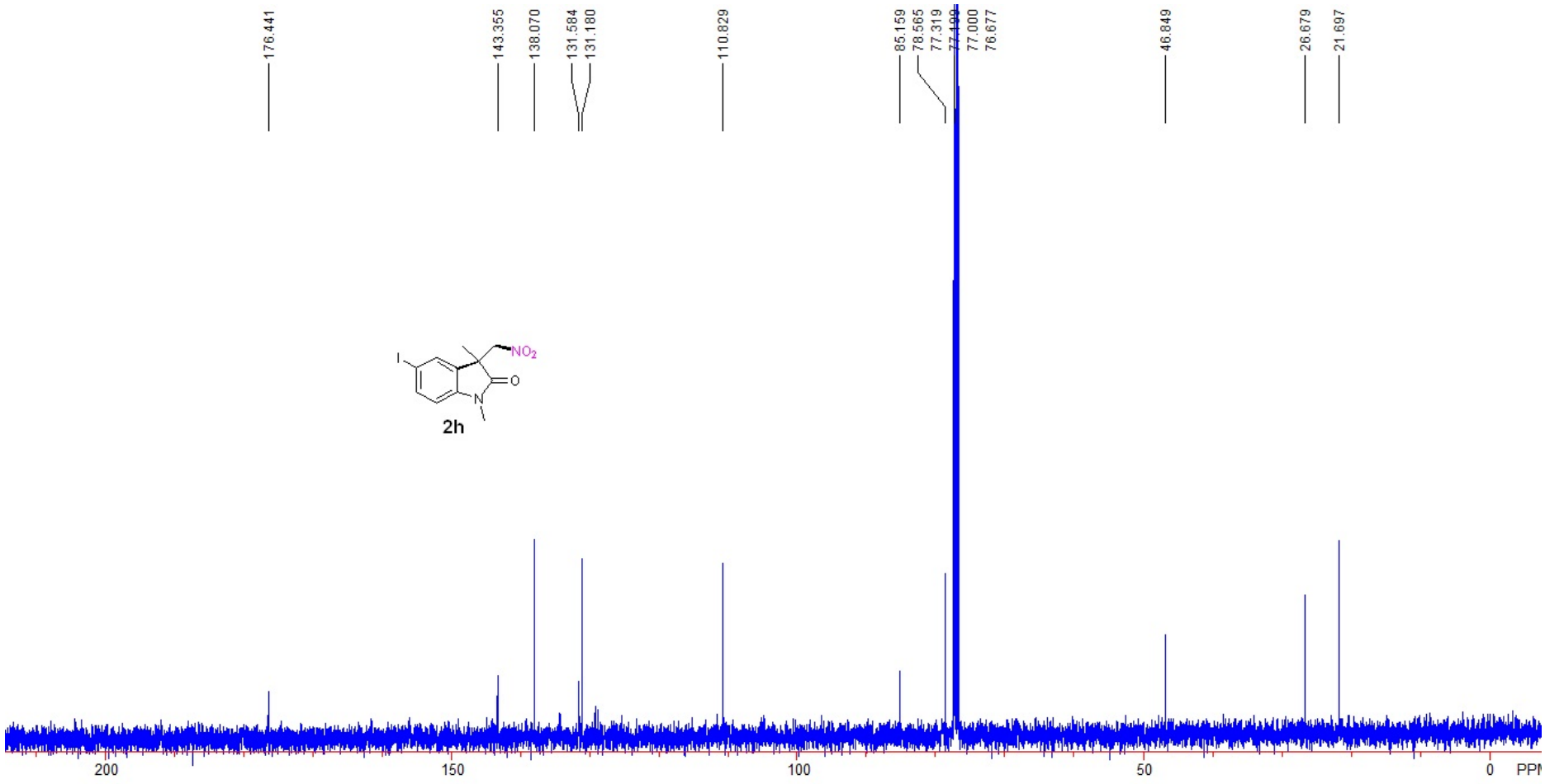

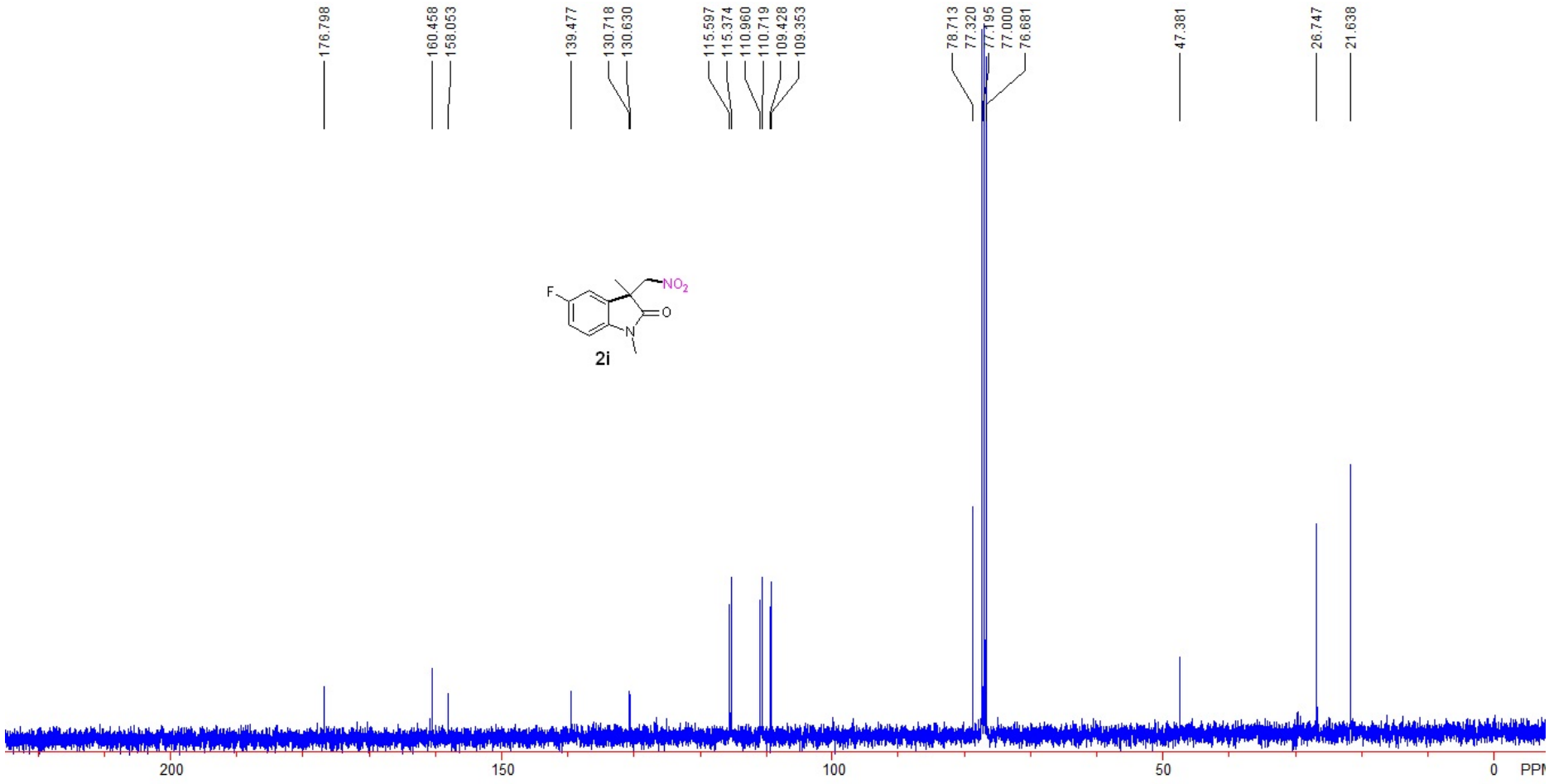

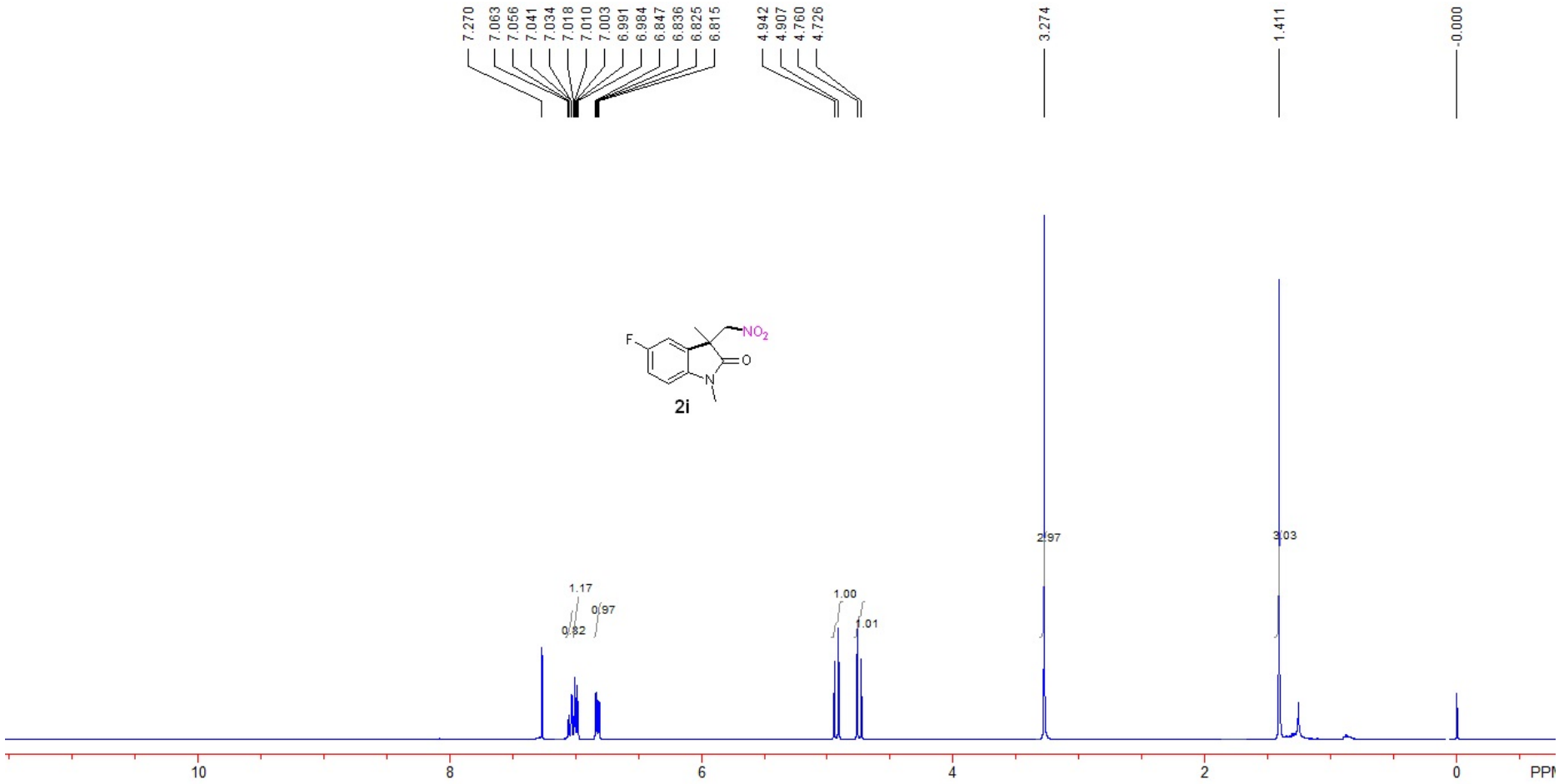

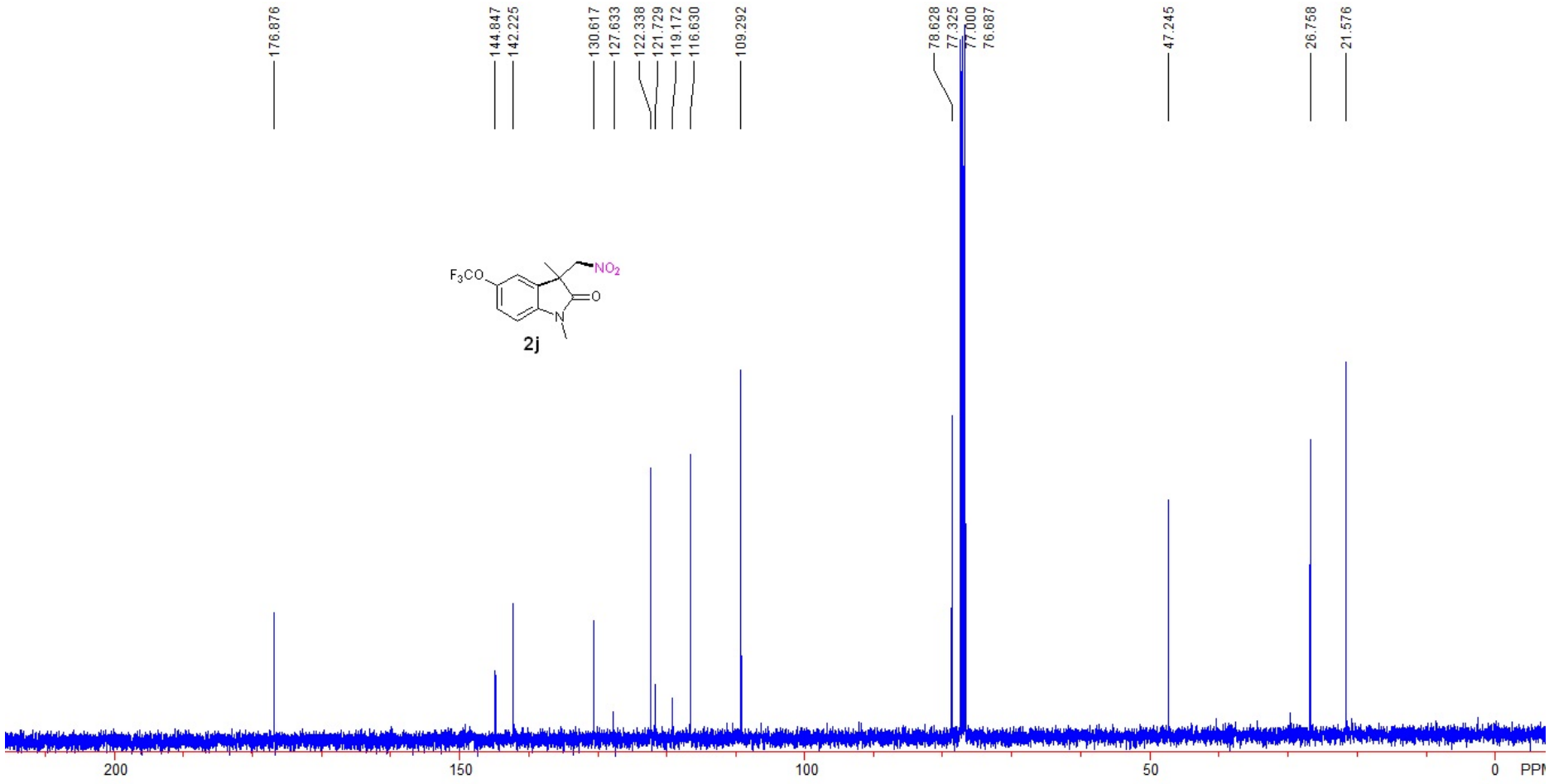

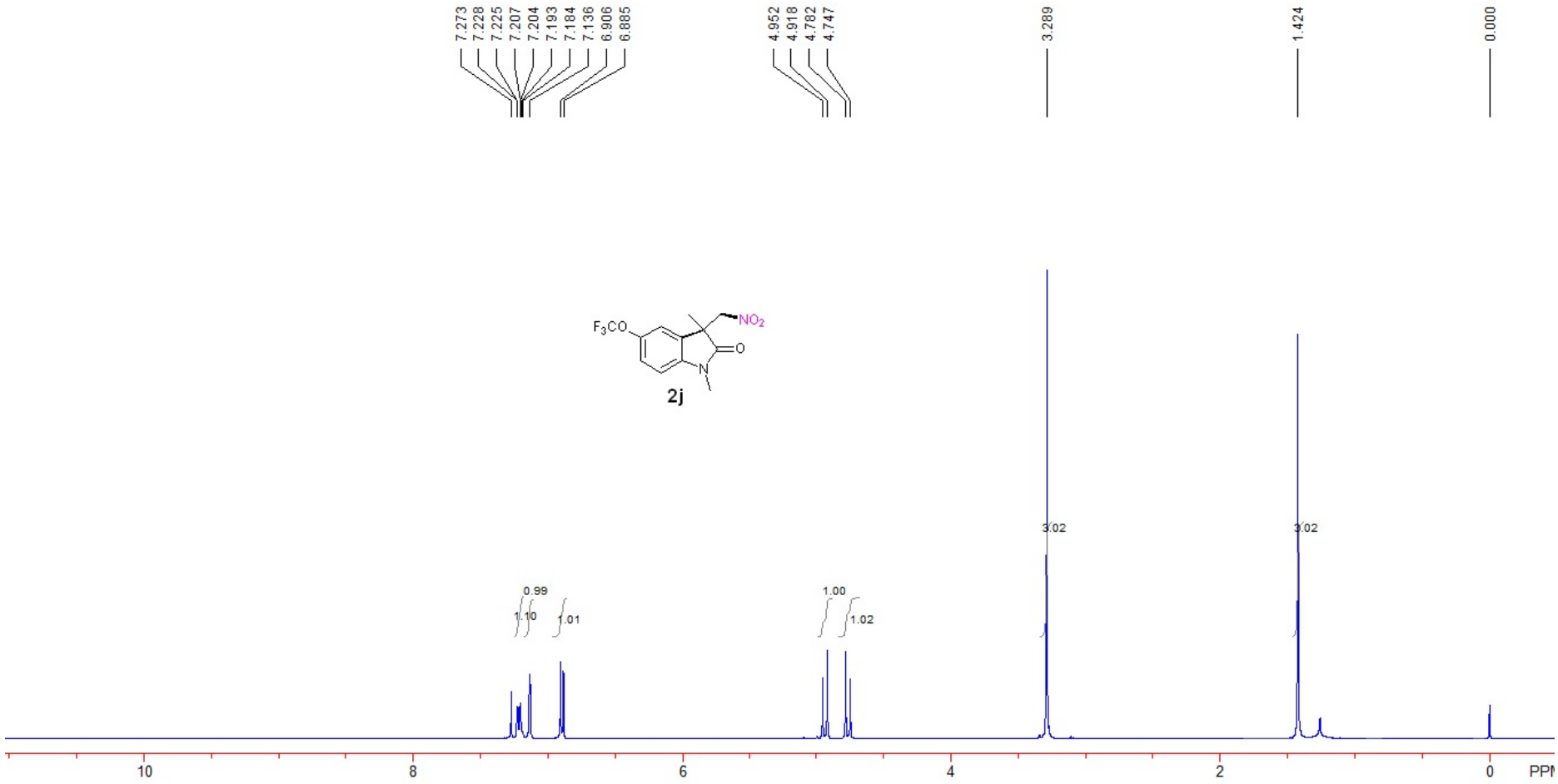

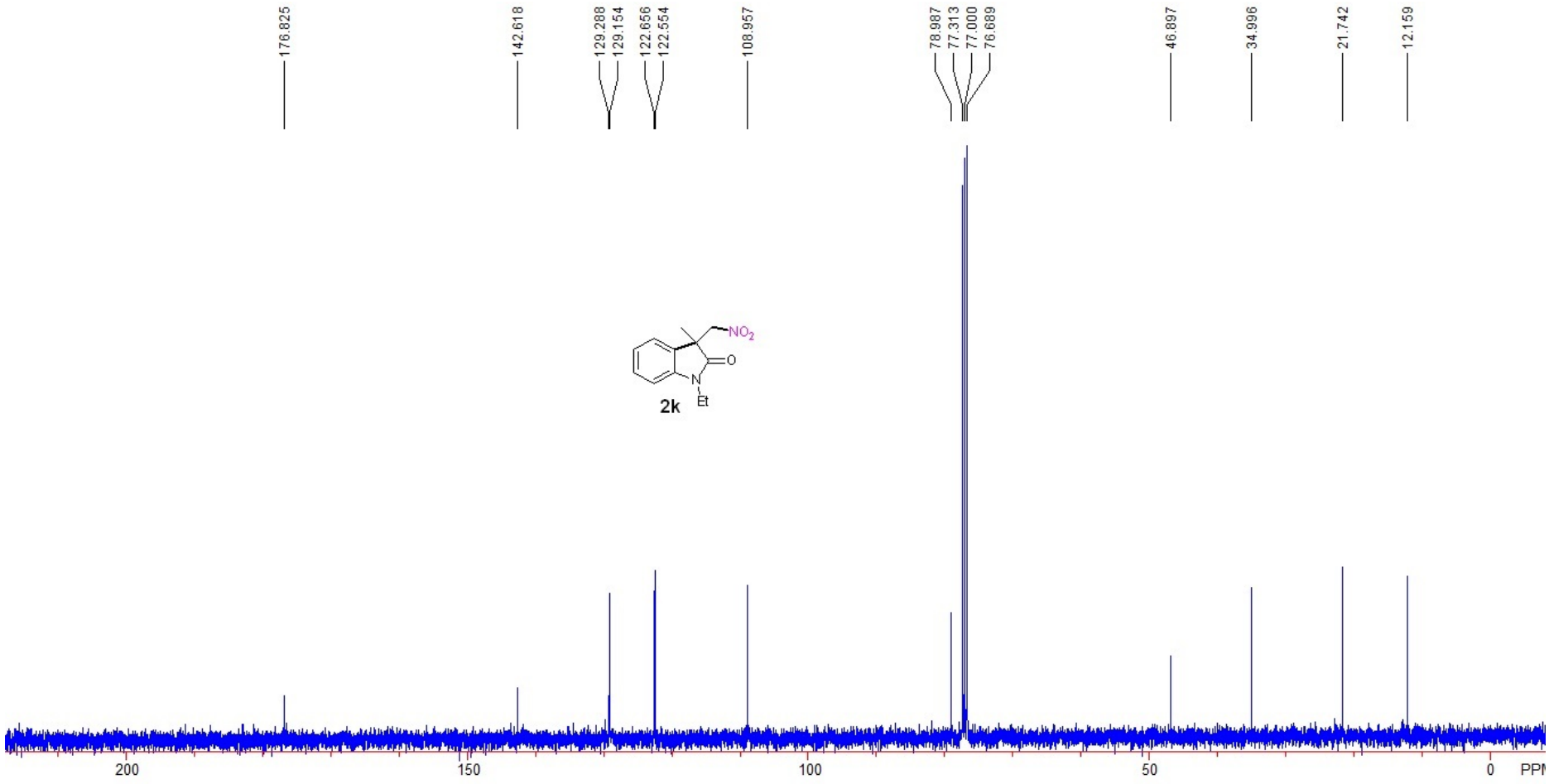
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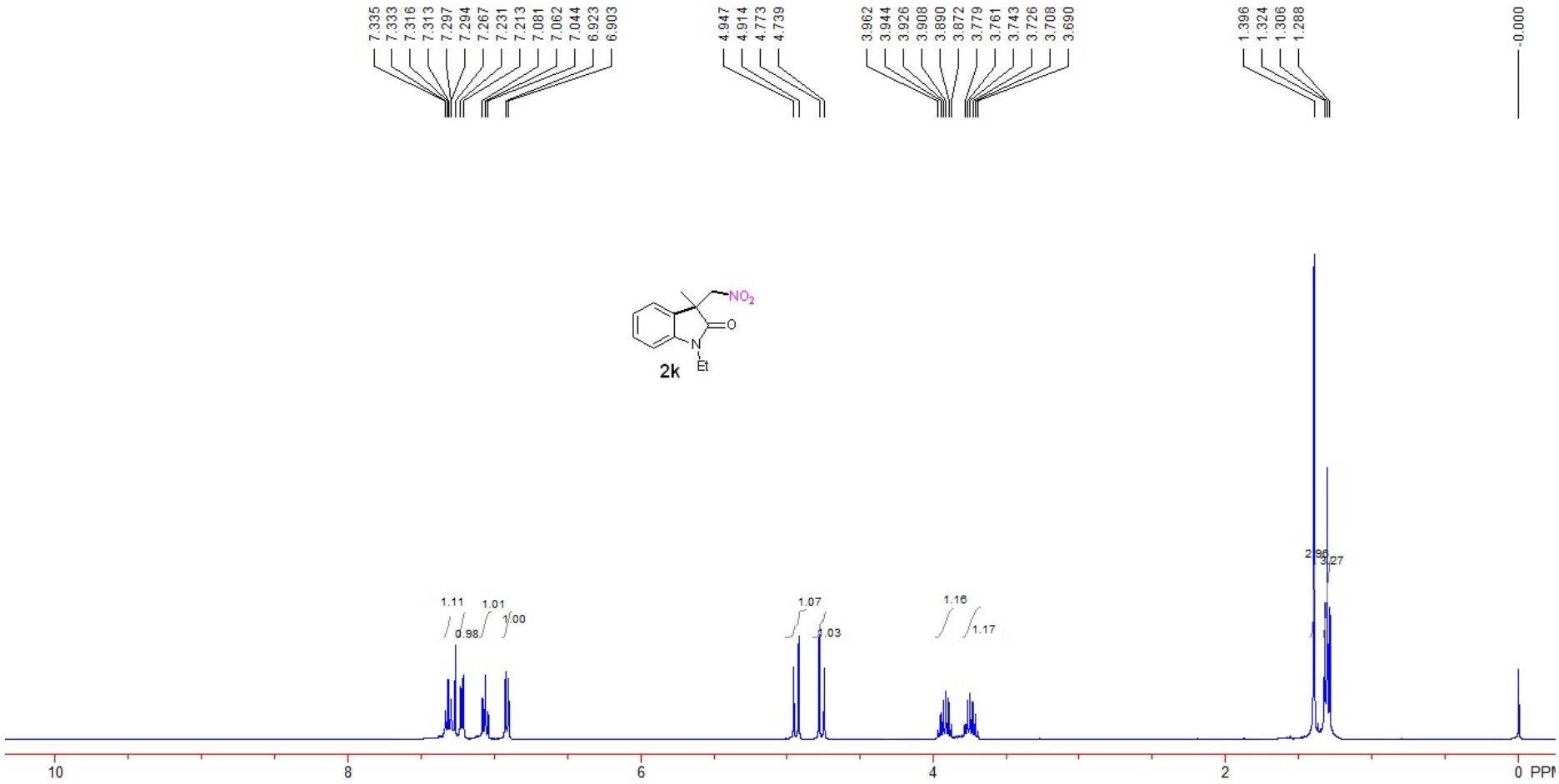

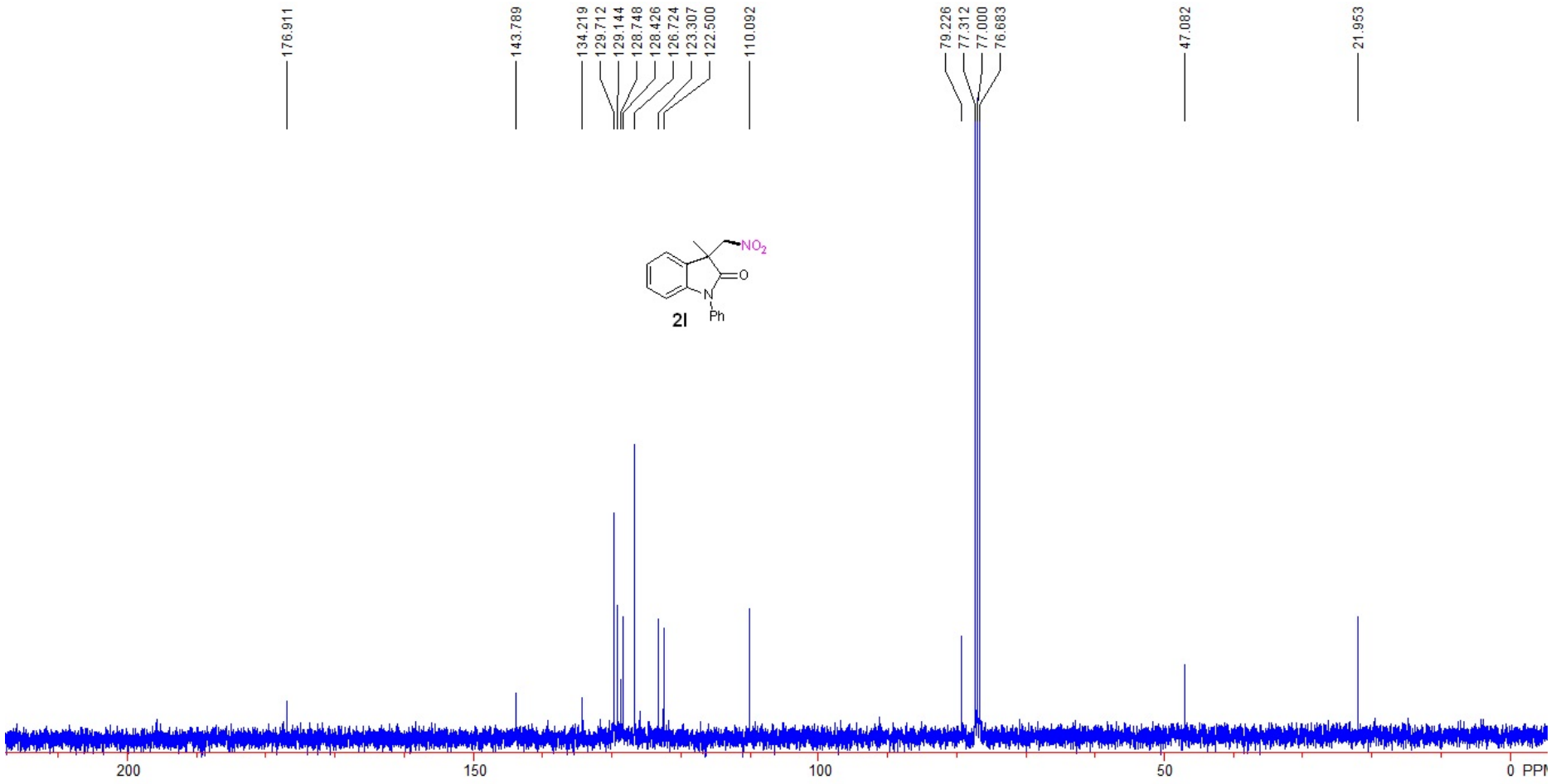

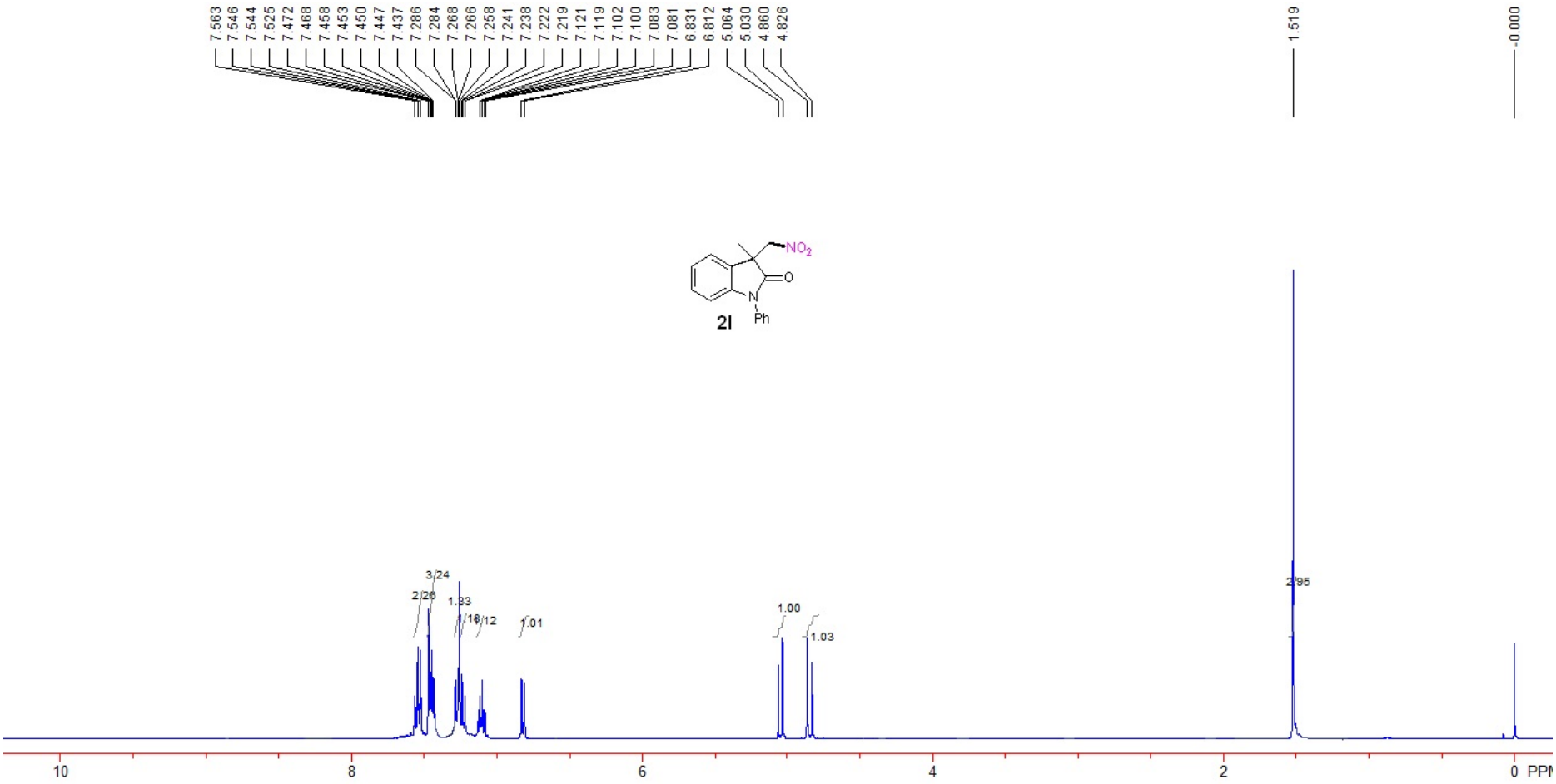

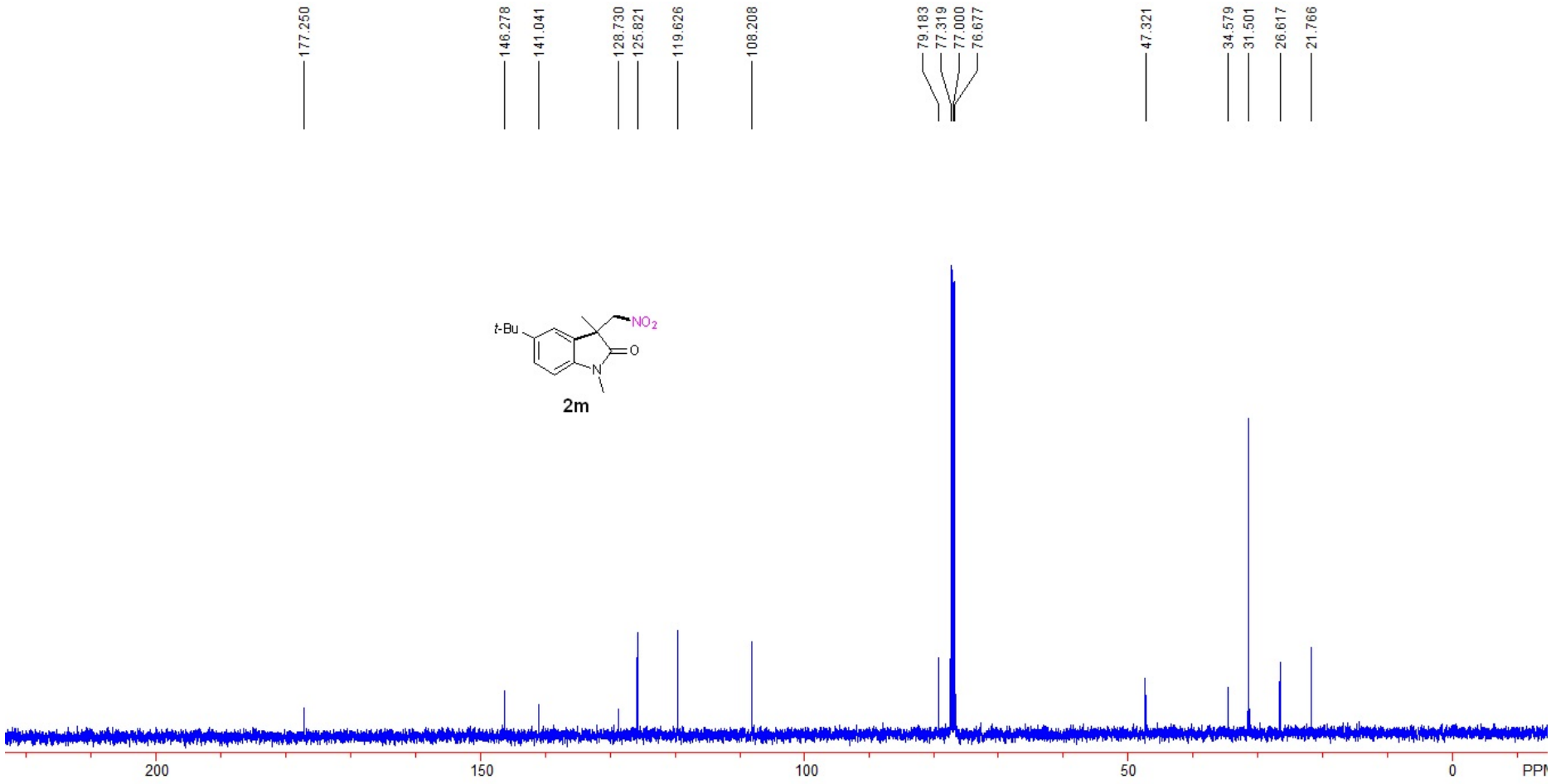

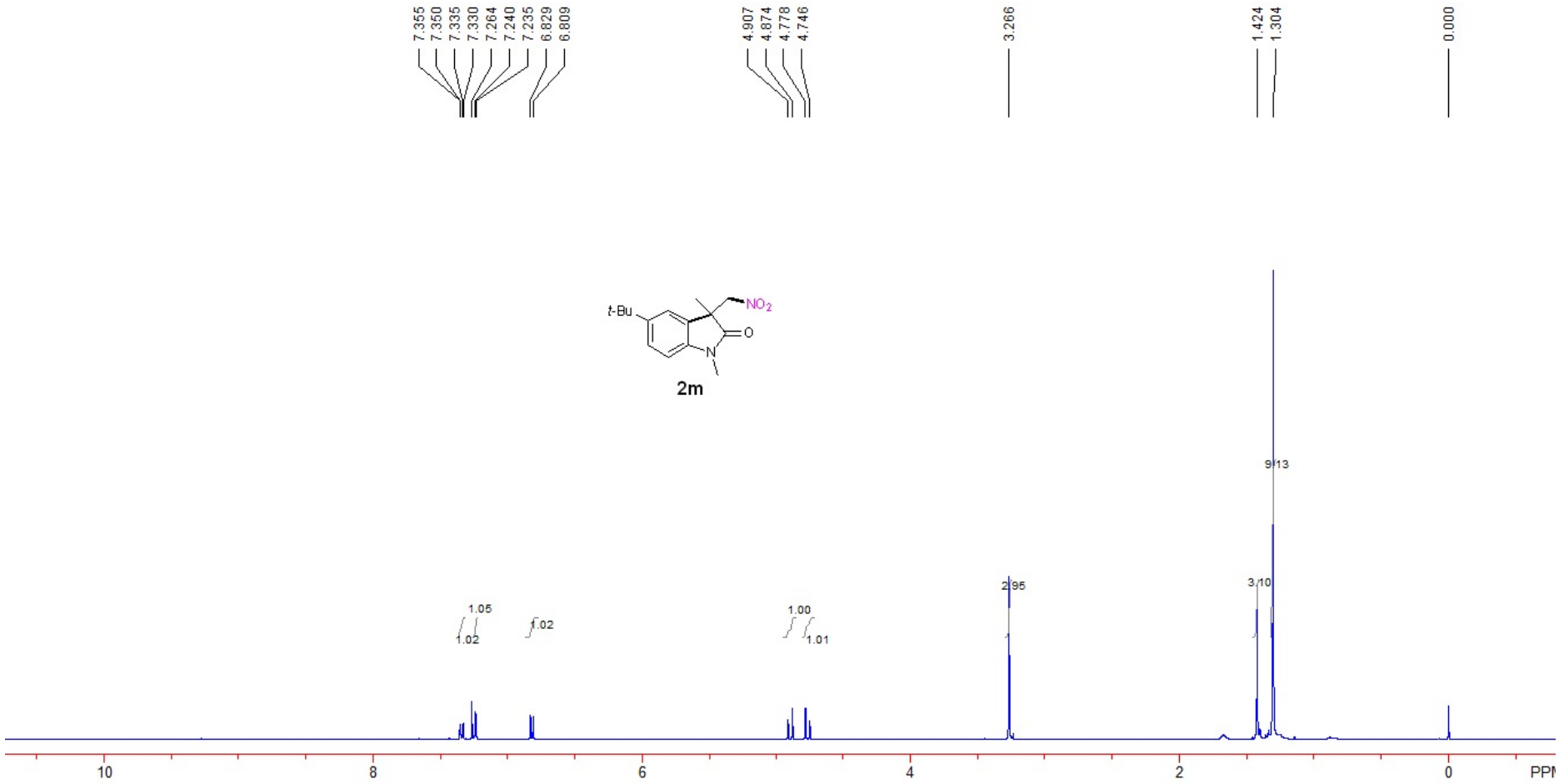

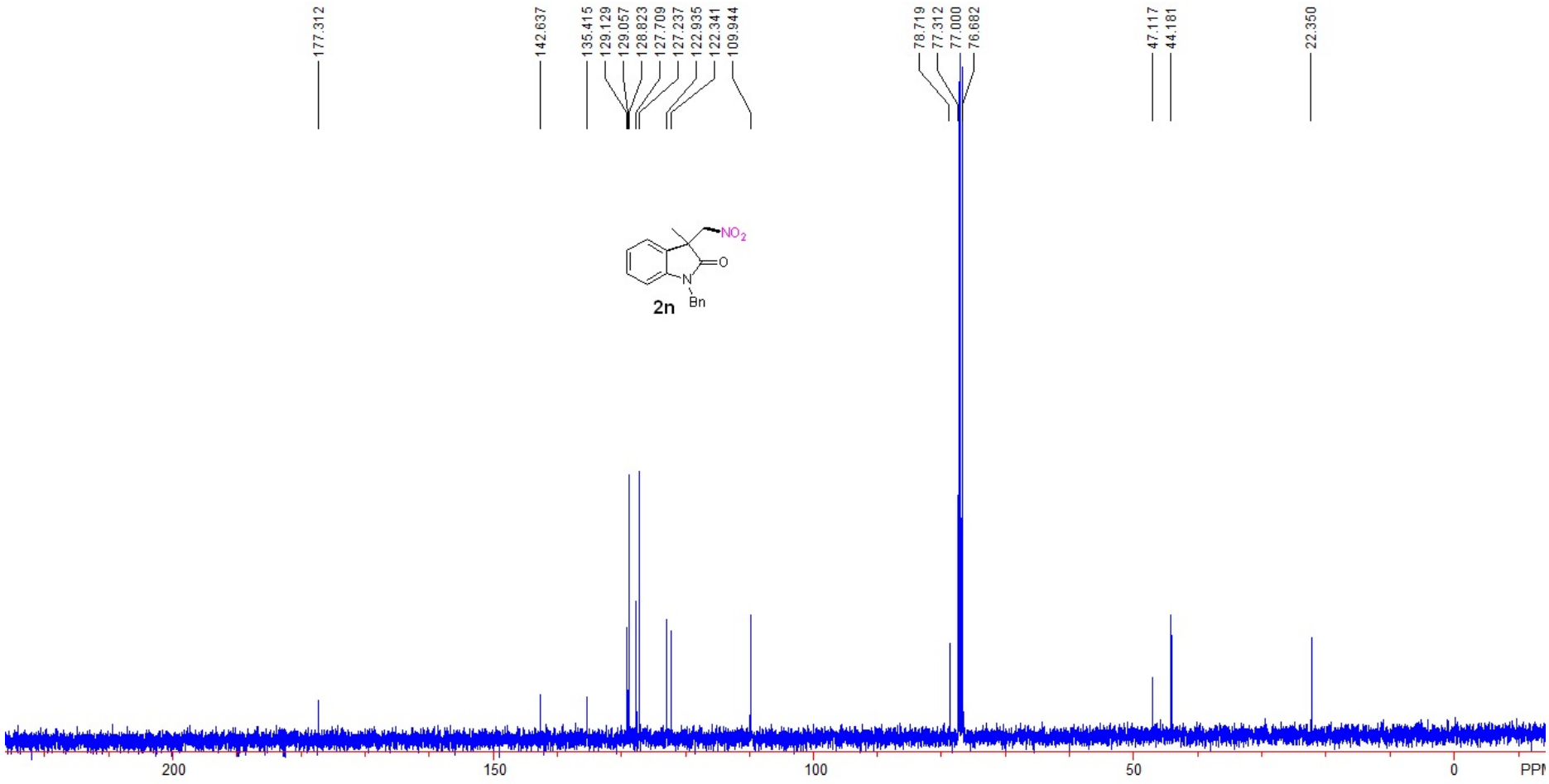
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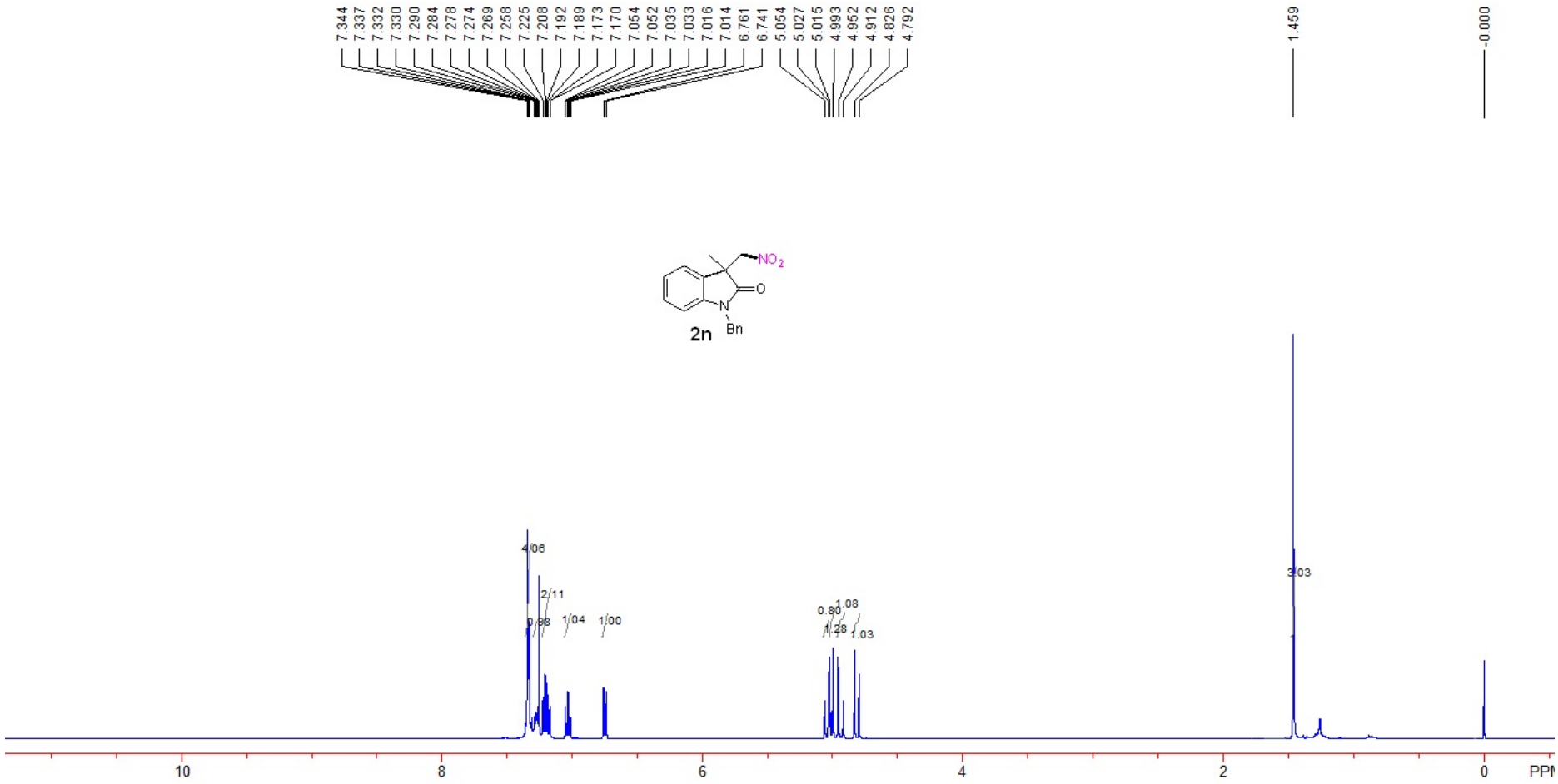

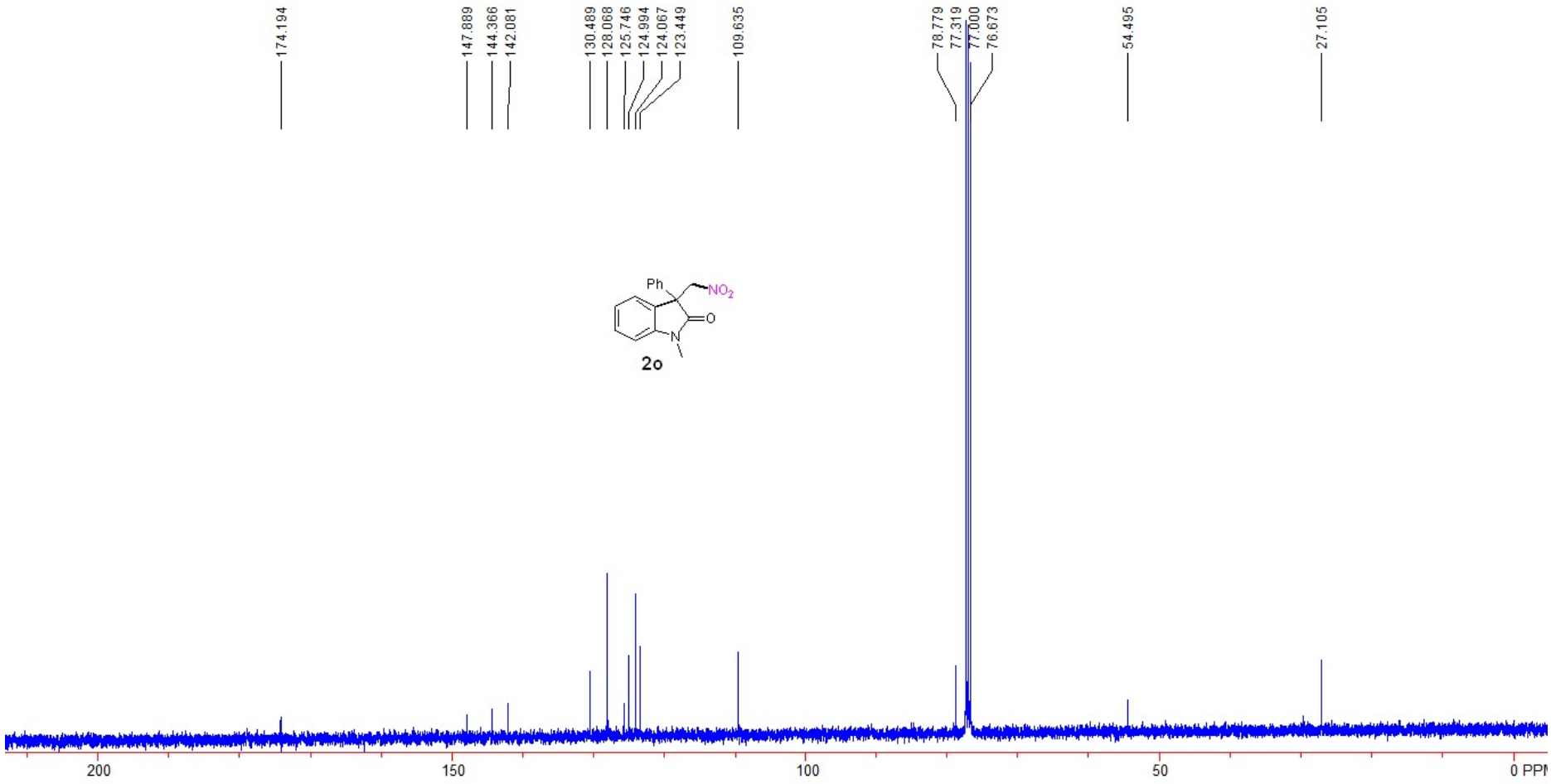

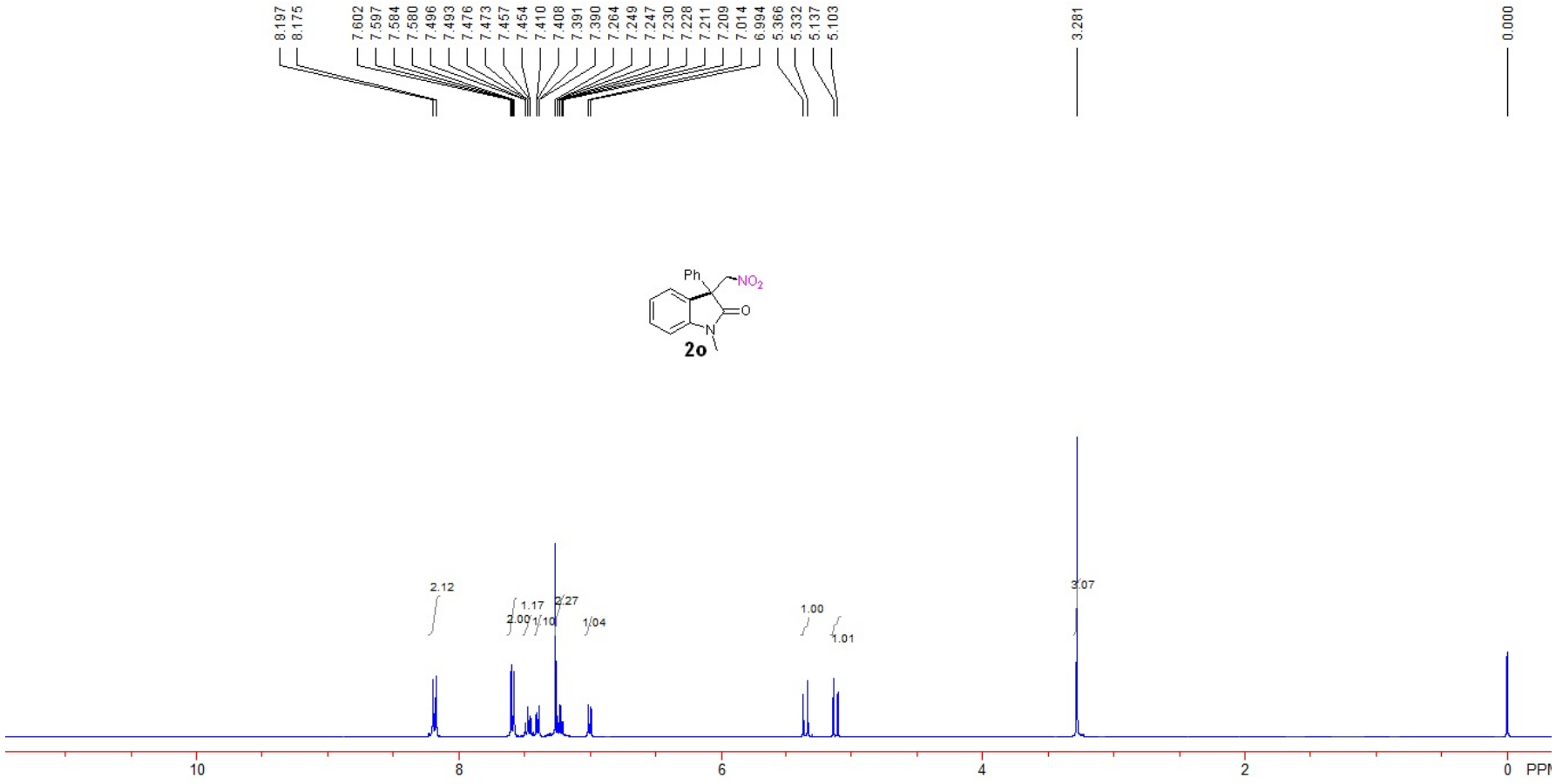

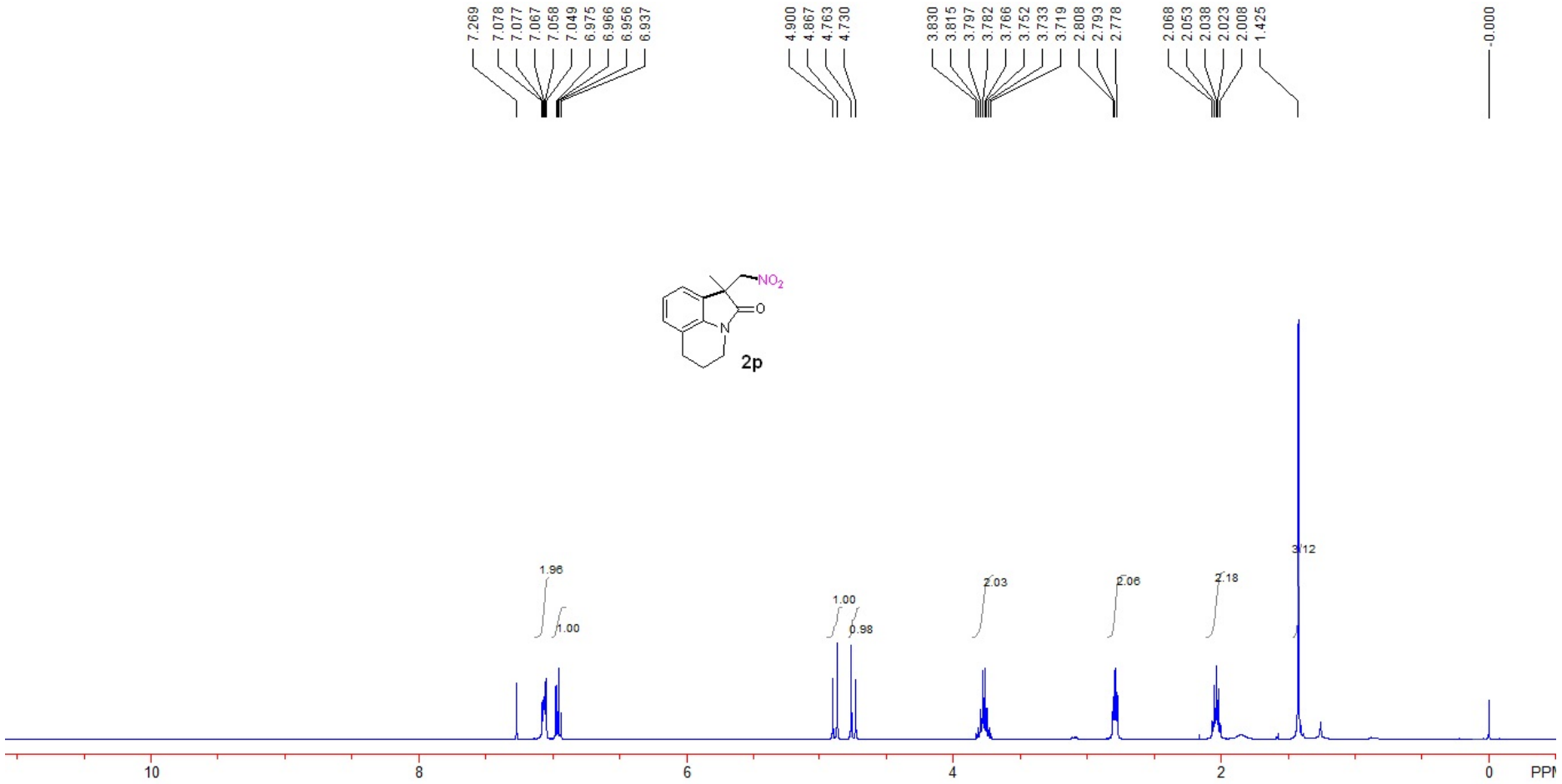

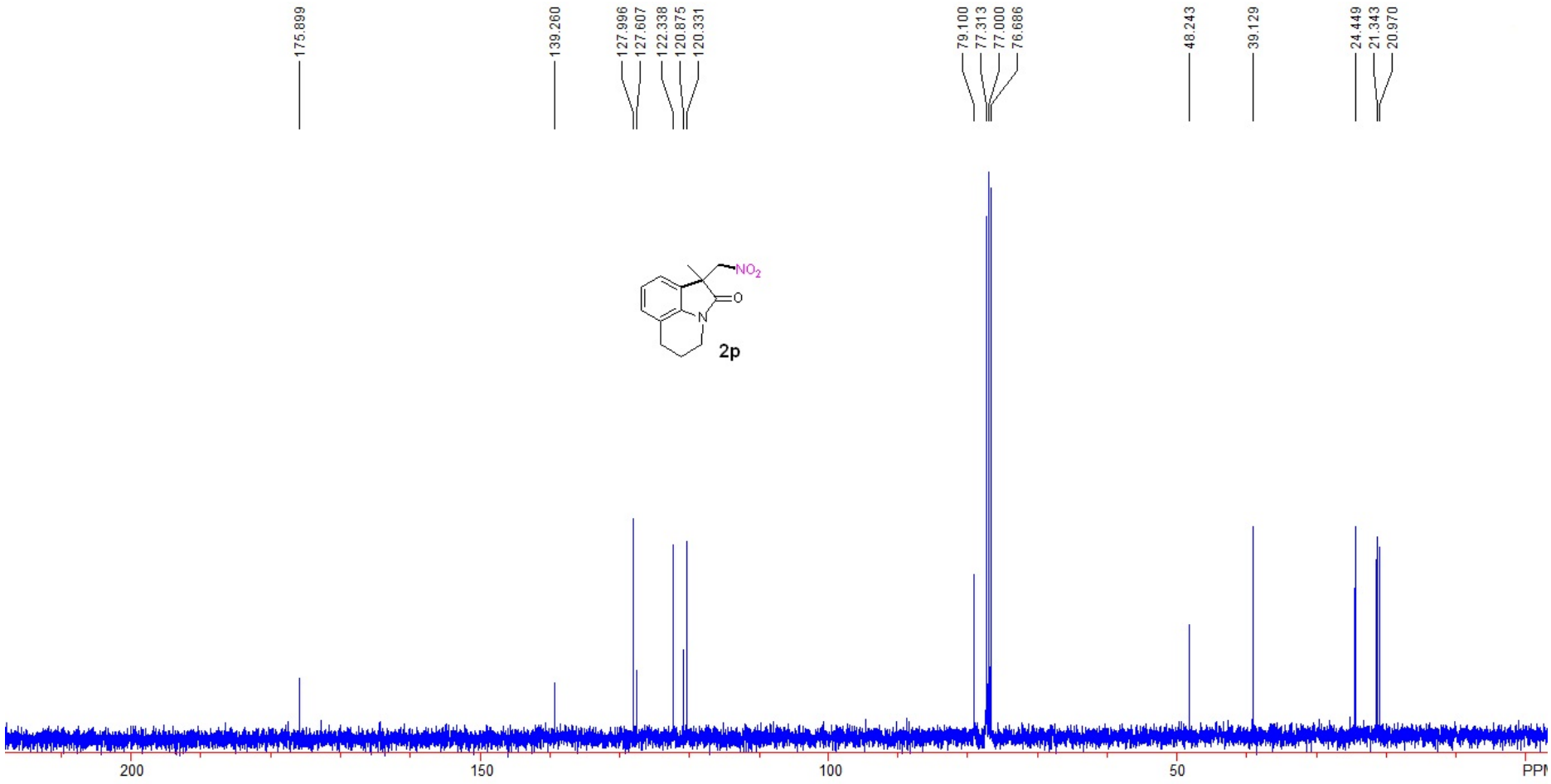

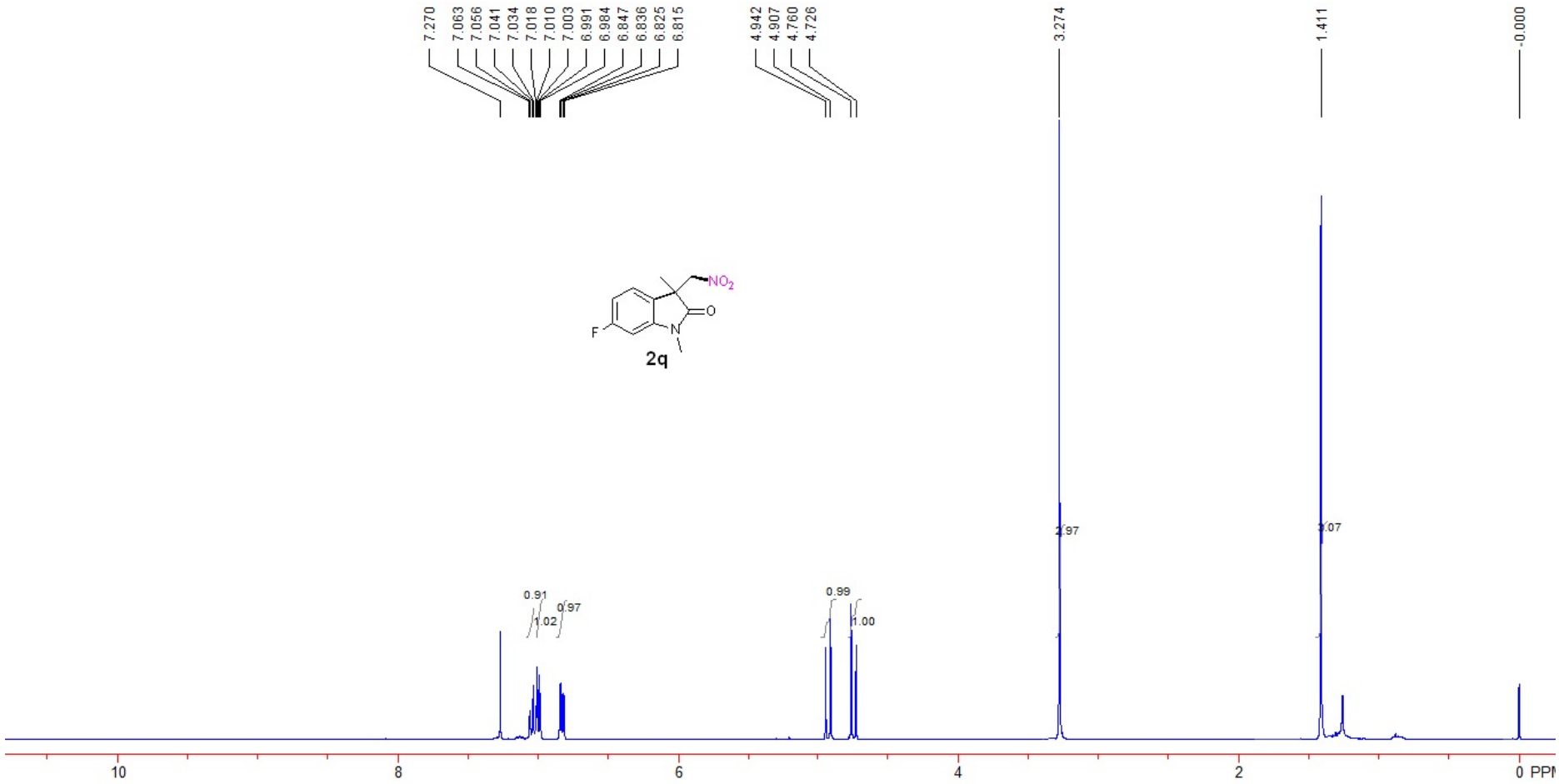

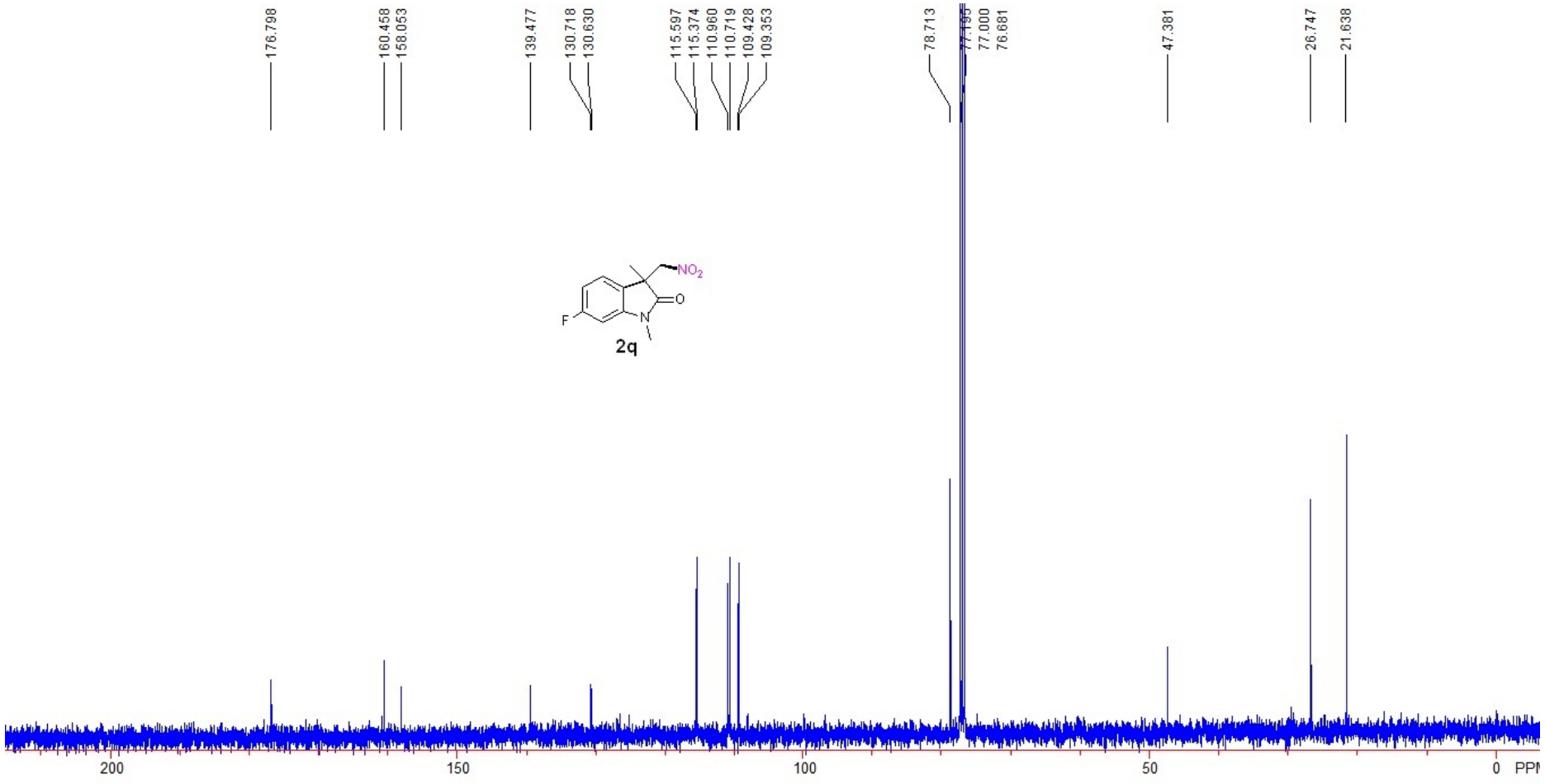

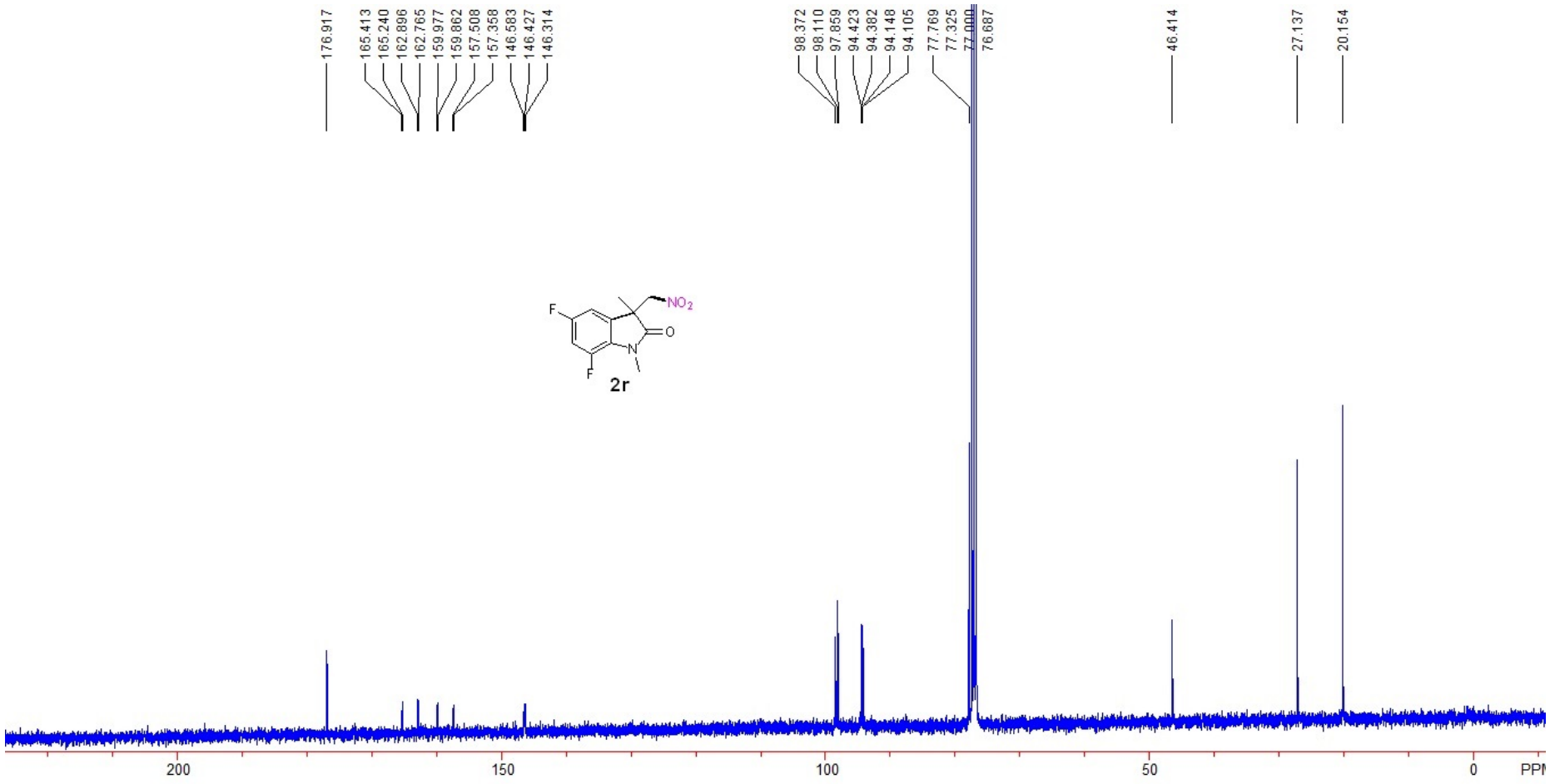

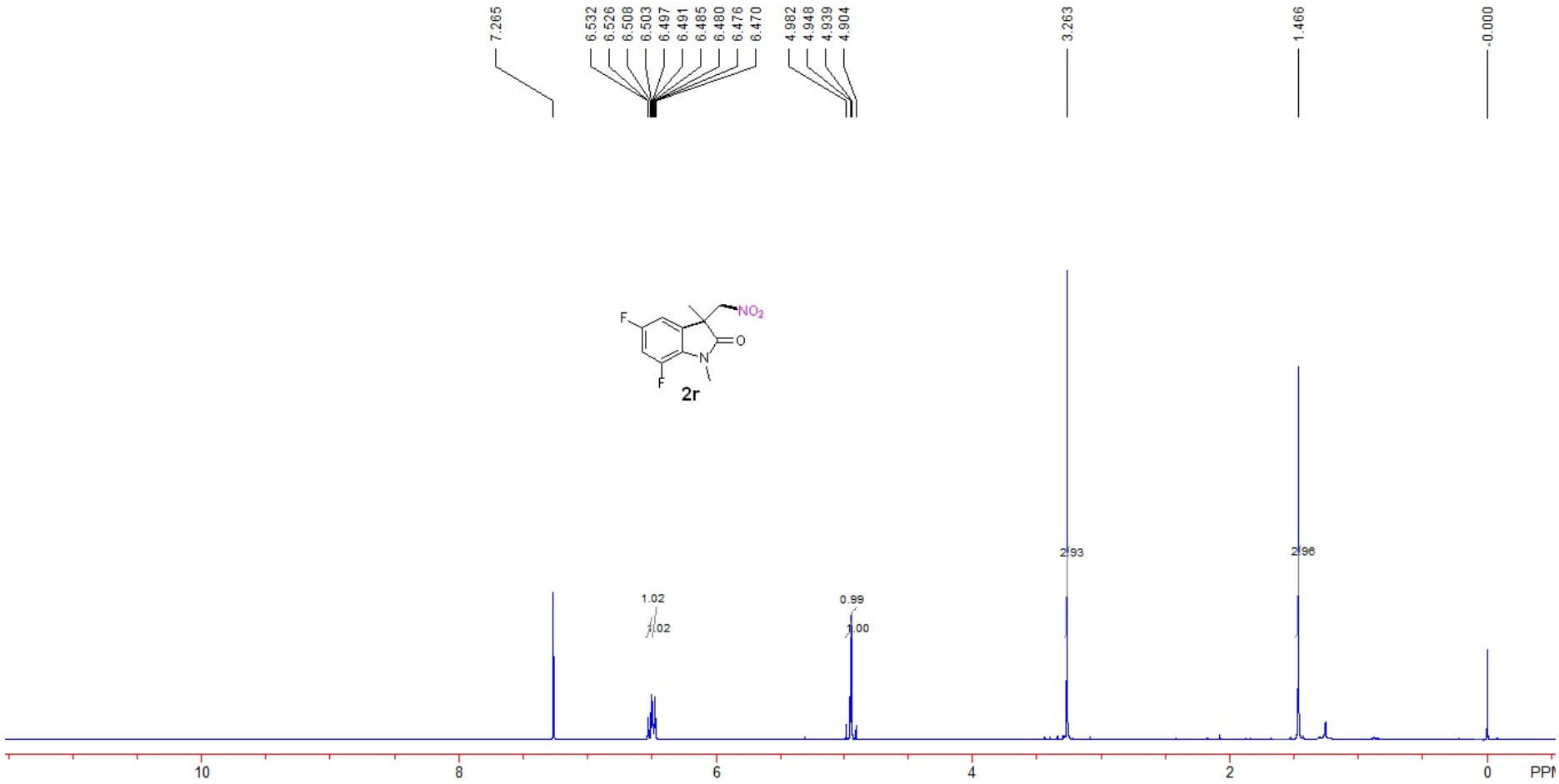

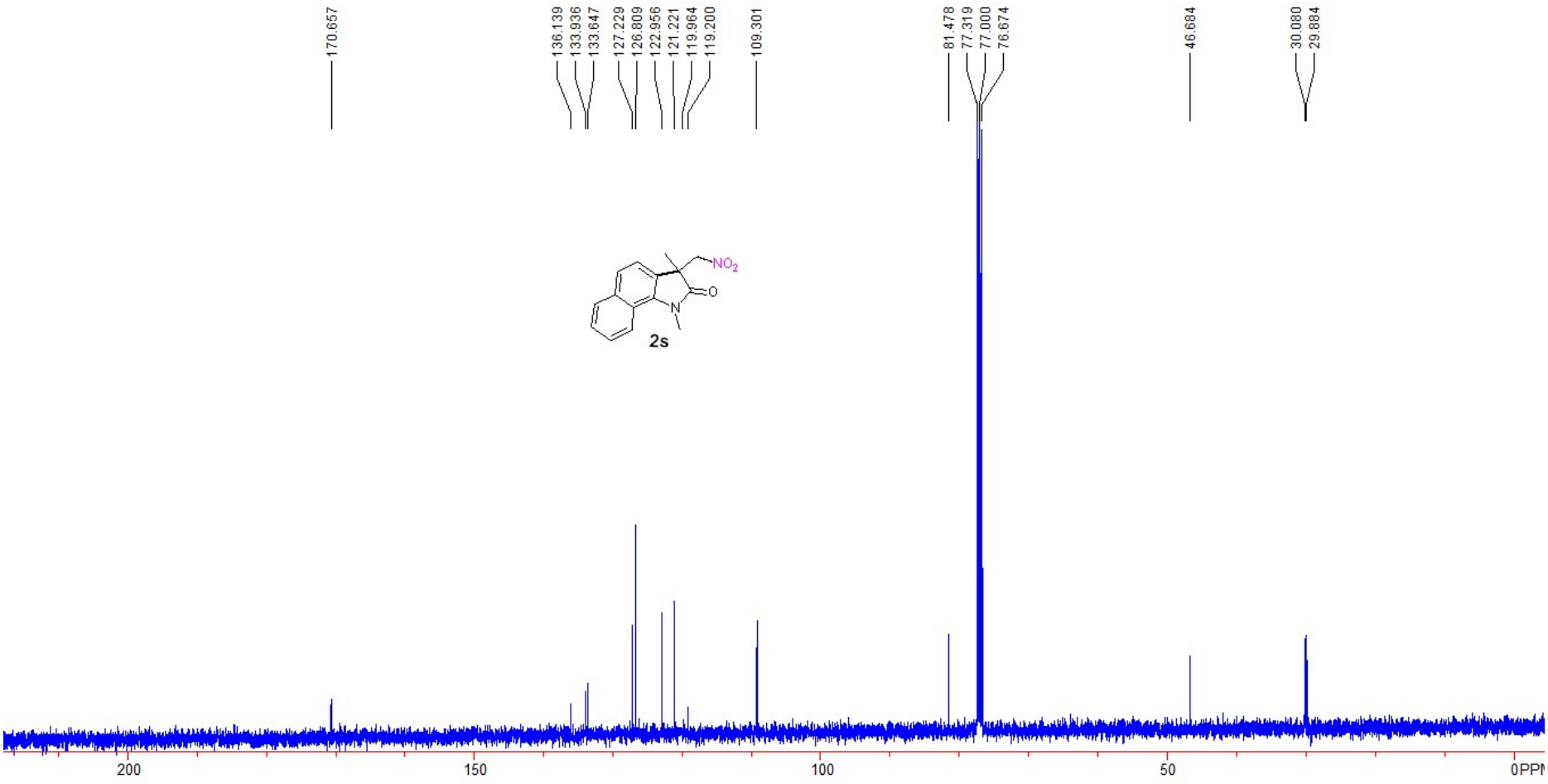
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