
TEMPO-catalyzed Aerobic Oxygenation and Nitrogenation of Olefins via C=C Double Bond Cleavage

(Supporting Information)

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General remarks

All manipulations were conducted with schlenk tubes. ^1H -NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with CDCl_3 (tetramethylsilane, $\delta = 0$ ppm). ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). High Resolution Mass spectra were recorded using a Fourier Transform Ion Cyclotron Resonance Mass spectrometer (APEX IV, Bruker). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The starting materials **10** to **17** and **23** were prepared according to previously reported literatures 1a and 1b.

Screening of different reaction conditions:

Table S1 Optimization of catalysts for oxidative nitrogenation of 1*H*-indene **3.^a**

entry	catalyst (mol%)	yield (%) ^b
1	TEMPO (10)	55
2	TEMPO (15)	82
3	TEMPO (50)	22
4	TEMPO (100)	<10
5	NHPI (20)	0
6	AIBN (20)	0
7	BPO (20)	0
8	4-Hydroxy-TEMPO (20)	70
9	4-Oxo-TEMPO (15)	<10
10	4-Hydroxy-TEMPO Benzoate (15)	33

^a Reaction conditions: 1*H*-indene **3** (0.3 mmol), TMSN₃ (0.45 mmol), catalyst in MeCN (2.0 mL) at 80 °C under oxygen (1 atm). ^b Isolated yields.

Table S2 Optimization of solvents for oxidative nitrogenation of 1*H*-indene **3.^a**

entry	solvent (°C)	yield (%) ^b
1	MeCN (50)	74
2	DCE (80)	46
3	PhMe (80)	trace
4	DMSO (80)	trace
5	THF (80)	trace
6	EtOH (80)	trace
7	DMF (80)	0

^a Reaction conditions: 1*H*-indene **3** (0.3 mmol), TMSN₃ (0.45 mmol), catalyst in solvent (2.0 mL) under oxygen (1 atm). ^b Isolated yields.

Scheme S1 Optimization of other conditions for oxidative nitration of 1H-indene 3.

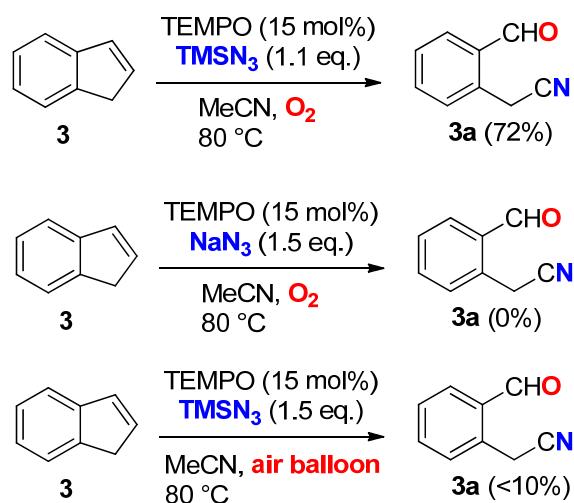


Table S3 Optimization of additives for oxidative nitration of cyclooctene 7.^a

entry	additive	yield (%) ^b	TEMPO (15 mol%)	additive (10 mol%)	TMSN ₃ (1.5 eq.)	MeCN, O ₂ , 80 °C	NC	~~~~~	CHO	7a
			7	7	7	7	7	7	7	7a
1	--	trace								
2	MnCl ₂	0								
3	MnBr ₂	0								
4	In(OAc) ₃	trace								
5	CAN	0								
6	PIDA	60								
7	HIO ₄	0								
8	NaIO ₄	0								
9	TBAI	trace								
10	I ₂	20								
11	Oxone®	33								
12	TBHP	51								
13 ^c	PIDA	13								

^a Reaction conditions: cyclooctene 7 (0.3 mmol), TMSN₃ (0.45 mmol), TEMPO (0.045 mmol) and additive (0.03 mmol) in MeCN (2.0 mL) at 80 °C under oxygen (1 atm). ^b Isolated yields. ^c Without TEMPO.

Table S4 Optimization of additives for 2-ethyl-1*H*-indene 22.^a

entry	additive	yield (%) ^b
1	—	52
2	TBHP	90
3	PIDA	64
4	Ce(SO ₄) ₂	37
5	Oxone®	42
6	MnCl ₂	23
7	MnBr ₂	33

^a Reaction conditions: cyclooctene **22** (0.3 mmol), TMSN₃ (0.45 mmol), TEMPO (0.045 mmol) and additive (0.03 mmol) in MeCN (2.0 mL) at 80 °C under oxygen (1 atm). ^b Isolated yields.

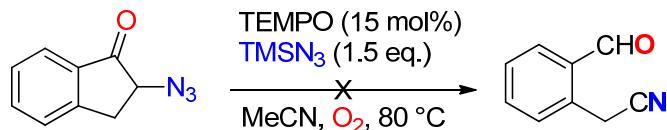
Table S5 Larger scale (10 mmol) reaction of 1*H*-indene **3.**

entry	volume of MeCN (mL)	time (h)	yield (%) ^b	recovery of 3 (%)
1	60	72	44	10
2	120	48	76	9

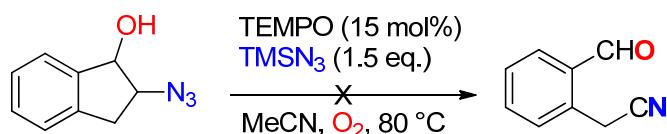
To conduct the oxidative nitration of 1*H*-indene on a synthetic larger scale, in a 250 mL three-necked flask charged with reflux condenser and oxygen balloon, 1*H*-indene (**3**) (10 mmol, 1.16 g), TMSN₃ (15 mmol, 1.73 g, 2.0 mL) and TEMPO (1.5 mmol, 234.0 mg) were stirred in 120 mL MeCN at 80 °C for 48 h. The resulting mixture was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford 1.10 g (76%) of **3a** with 9% of **3** recovery.

Further mechanism studies:

Control experiments.



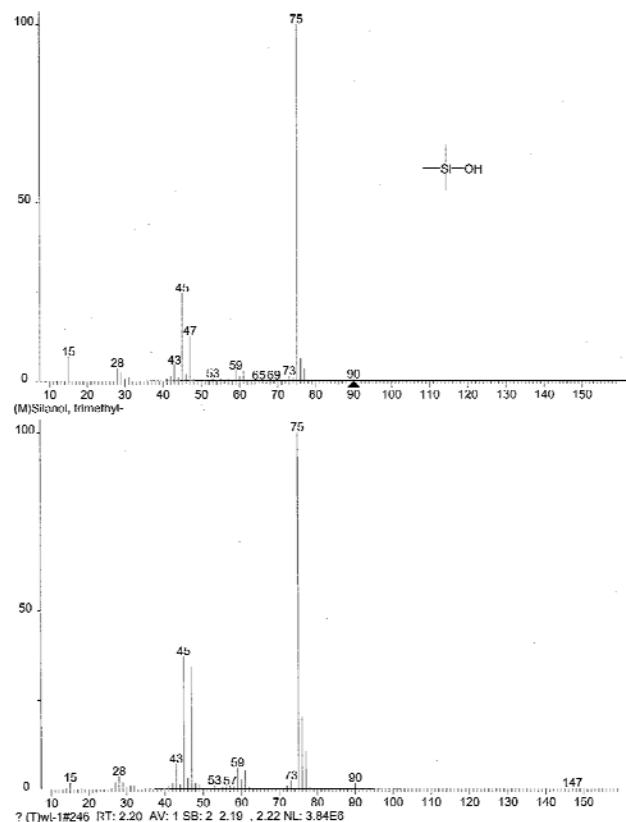
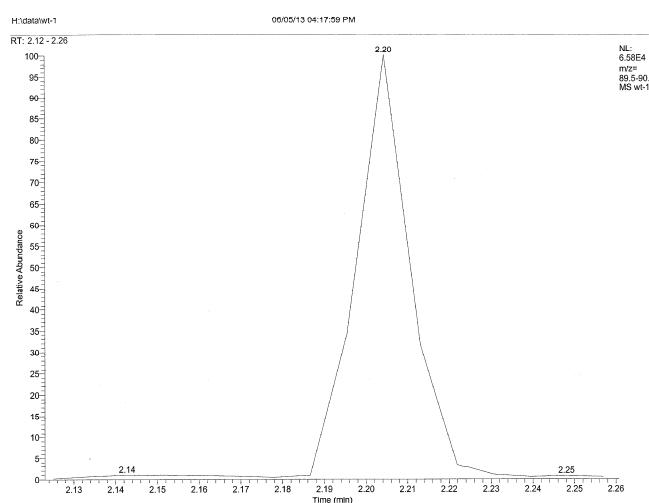
Some predicted intermediates have been investigated. 2-Azido-2,3-dihydro-1*H*-inden-1-one (α -azido ketone) can not give product. Therefore the split mechanism seems unlikely. The existing carbonyl as an electron withdrawing group is unfavorable for the nitrile formation. This result indicates oxo nitriles and α -azido ketones are obtained from different intermediates.



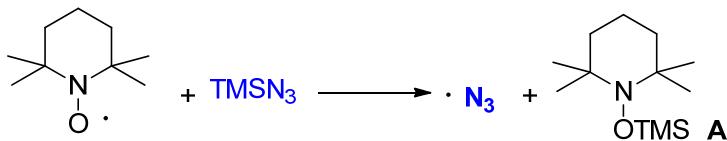
It is reported that β -hydroxy azides can produce oxo nitriles via radical fragmentations.² 2-Azido-2,3-dihydro-1*H*-inden-1-ol (β -hydroxy azides) was conducted but no desired product can be isolated from the reaction mixture.

The detection of TMSOH by GC-MS.

The Si-containing species in the reaction mixture was identified as TMSOH by GS-MS.

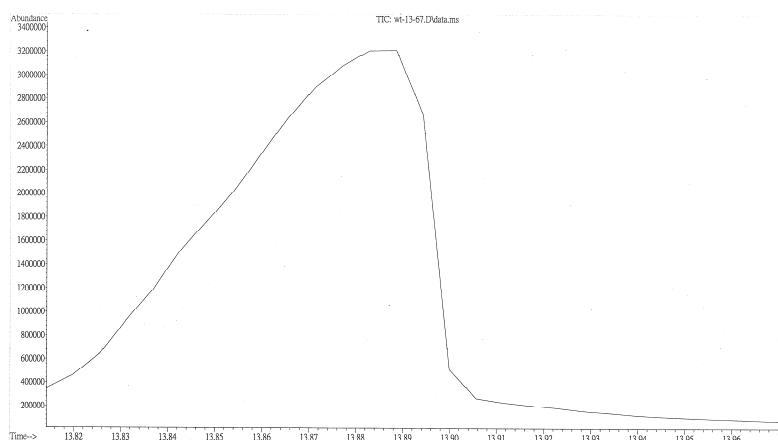


The detection of TMEPO-TMS by GC-MS.

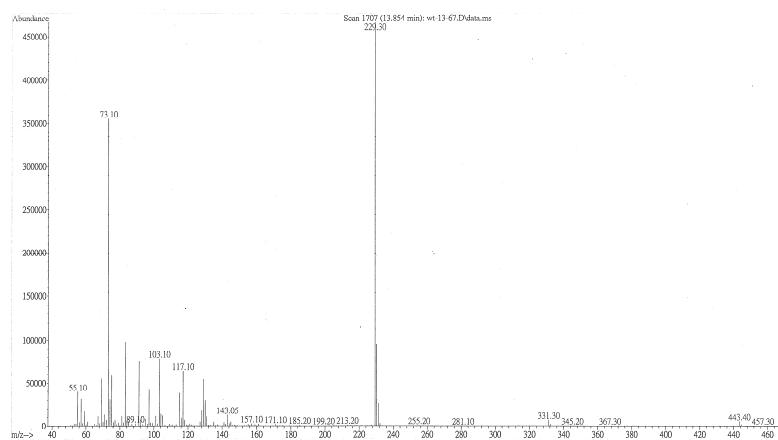


The species **A** was identified as TEMPO-TMS by GC-MS.

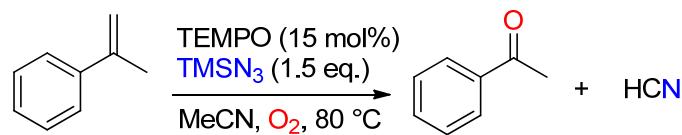
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Operator :wt
Acquired : 29 Sep 2012 10:48 using AcqMethod WT.M
Instrument : GCMSD
Sample Name: wt-13-67
Misc Info :
Vial Number: 8



File :C:\msdchem\1\data\wt-13-67.D
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Acquired : 29 Sep 2012 10:48 using AcqMethod WT.M
Instrument : GCMSD
Sample Name: wt-13-67
Misc Info :
Vial Number: 8

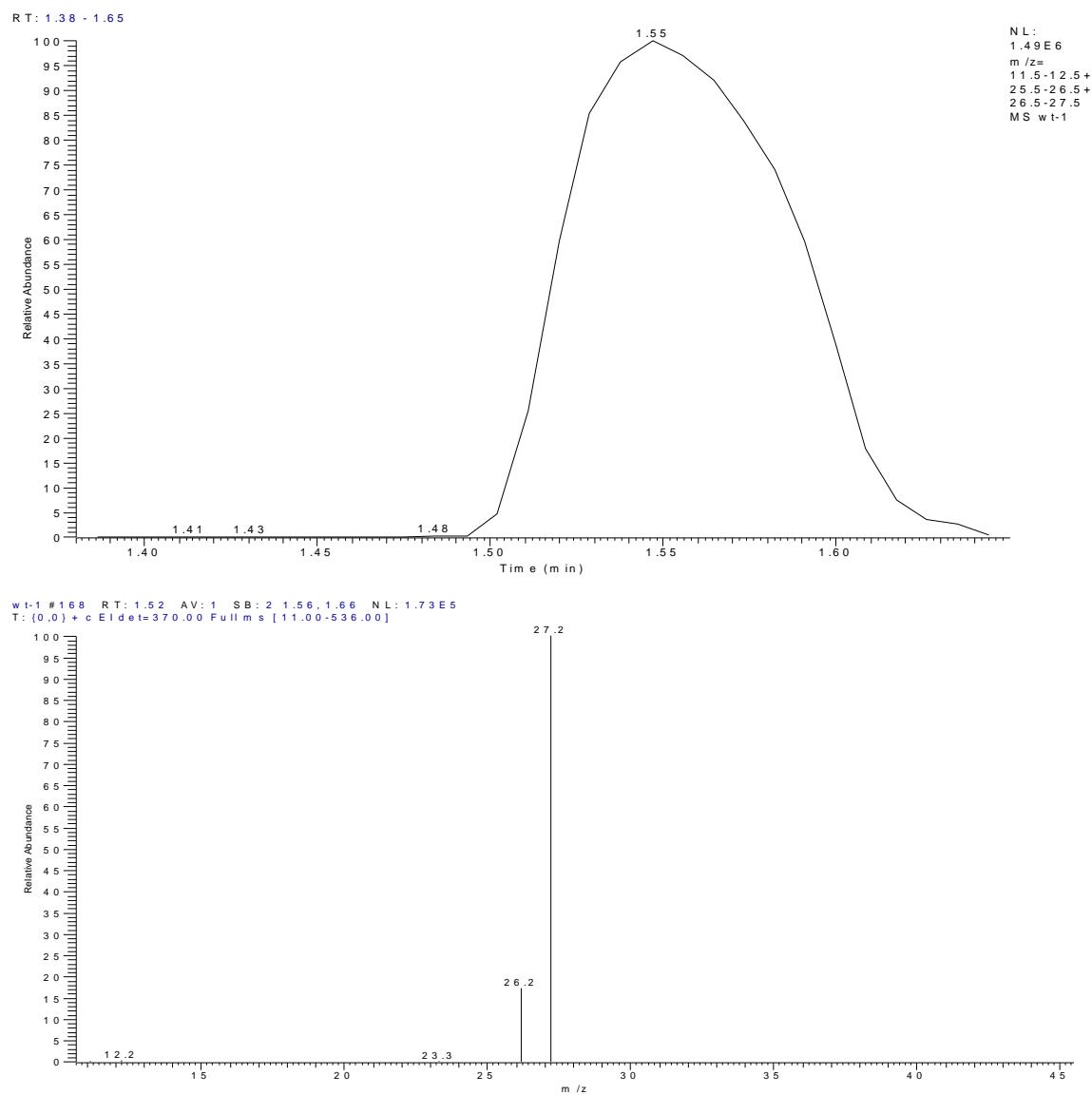


The detection of one-carbon byproduct by GC-MS.



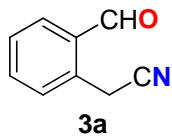
To investigate the one-carbon byproduct resulting from the reaction of terminal alkenes, α -methyl styrene was carried out under standard conditions. After the completion of the reaction, HCN was detected in the solvent by GC-MS.

CAUTION! *HCN is highly toxic and volatile! Although we did not experience any dangers during this work, safety precautions must be taken, especially in the case of scaling up reaction. The reaction should be carried out in the hood. Gloves and respirators are necessary to work up the reaction.*



Experimental procedure and characterization data

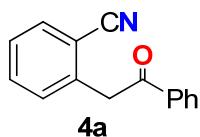
1) 2-(2-Formylphenyl)acetonitrile (**3a**)



Typical procedure:

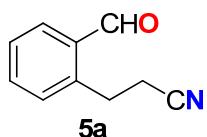
The reaction of 1*H*-indene (**3**) (0.3 mmol, 35 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) were stirred in 2 mL MeCN at 80 °C under oxygen for 24 h. The resulting mixture was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford 36 mg (82%) of **3a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 10.09 (s, 1H), 7.86 (d, *J* = 6.4 Hz, 1H), 7.66-7.61 (m, 3H), 4.28 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 193.2, 136.1, 134.3, 133.0, 131.1, 130.2, 128.8, 117.3, 22.0 ppm; IR (neat): ν = 2249, 1696, 1601, 1579, 1457, 1250, 1203, 755, 660 cm⁻¹; HRMS (ESI) Calcd for C₉H₇NNaO [M+Na]⁺: 168.04199; Found: 168.04164.

2) 2-(2-Oxo-2-phenylethyl)benzonitrile (**4a**)



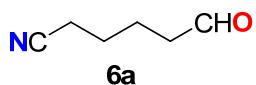
The reaction of 2-phenyl-1*H*-indene (**4**) (0.3 mmol, 58 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 33 mg (50%) of **4a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 8.05-8.03 (m, 2H), 7.68-7.66 (m, 1H), 7.60-7.53 (m, 2H), 7.51-7.47 (m, 2H), 7.39-7.36 (m, 2H), 4.54 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 195.3, 138.4, 136.2, 133.5, 132.68, 132.66, 130.9, 128.7, 128.3, 127.5, 117.8, 113.5, 43.5 ppm; IR (neat): ν = 2225, 1689, 1597, 1449, 1332, 1221, 992, 758, 690 cm⁻¹; HRMS (ESI) Calcd for C₁₅H₁₂NO [M+H]⁺: 222.09134; Found: 222.09119.

3) 3-(2-Formylphenyl)propanenitrile (**5a**)³



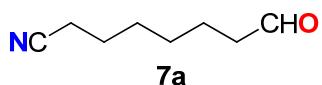
The reaction of 1,2-dihydronaphthalene (**5**) (0.3 mmol, 39 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 18 mg (38%) of **5a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 10.09 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 193.6, 139.6, 136.0, 134.1, 133.7, 131.9, 128.1, 119.1, 29.4, 18.4 ppm; IR (neat): ν = 2246, 1693, 1600, 1576, 1197, 759 cm⁻¹.

4) 6-Oxohexanenitrile (6a)⁴



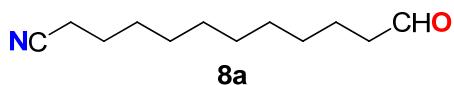
The reaction of cyclohexene (**6**) (0.3 mmol, 25 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL), TEMPO (0.045 mmol, 7.0 mg) and iodosobenzene diacetate (PIDA, 0.03 mmol, 9.7 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 10 mg (30%) of **6a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 9.79 (s, 1H), 2.54 (t, J = 6.6 Hz, 2H), 2.39 (t, J = 6.8 Hz, 2H), 1.82-1.77 (m, 2H), 1.74-1.69 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 201.0, 119.2, 42.8, 24.8, 21.0, 17.1 ppm; IR (neat): ν = 2248, 1717, 1458, 1423, 1241, 1206, 914, 745 cm⁻¹.

5) 8-Oxoctanenitrile (7a)



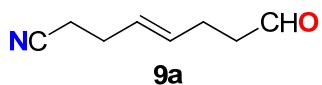
The reaction of (*Z*)-cyclooctene (**7**) (0.3 mmol, 33 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL), TEMPO (0.045 mmol, 7.0 mg) and PIDA (0.03 mmol, 9.7 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 25 mg (60%) of **7a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 9.78 (t, J = 1.4 Hz, 1H), 2.48-2.44 (m, 2H), 2.36 (t, J = 7.0 Hz, 2H), 1.69-1.62 (m, 4H), 1.51-1.45 (m, 2H), 1.41-1.35 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 202.3, 119.6, 43.6, 28.4, 28.2, 25.1, 21.6, 17.0 ppm; IR (neat): ν = 2246, 1722, 1683, 1462, 1426, 1260, 749 cm⁻¹; Anal. Calcd for C₈H₁₃NO: C, 69.03; H, 9.41; N, 10.06; O, 11.49; Found: C, 69.10; H, 9.35; N, 9.88; O, 11.67.

6) 12-Oxododecanenitrile (8a)



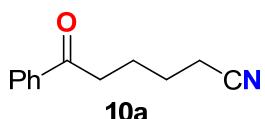
The reaction of cyclododecene (**8**) (0.3 mmol, 33 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL), TEMPO (0.045 mmol, 7.0 mg) and PIDA (0.03 mmol, 9.7 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 25 mg (43%) of **8a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 9.78 (s, 1H), 2.46-2.42 (m, 2H), 2.35 (t, J = 7.0 Hz, 2H), 1.68-1.62 (m, 4H), 1.47-1.44 (m, 2H), 1.31-0.89 (m, 10H); ¹³C NMR (CDCl₃, 100 MHz): δ = 202.9, 119.8, 43.8, 29.20, 29.18, 29.1, 29.0, 28.7, 28.6, 25.3, 22.0, 17.0 ppm; IR (neat): ν = 2245, 1681, 1451, 1245, 692 cm⁻¹; HRMS (ESI) Calcd for C₁₂H₂₁NNaO [M+Na]⁺: 218.15154; Found: 218.15137.

7) 8-Oxoct-4-enenitrile (9a)



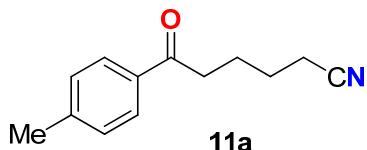
The reaction of (*1Z,5Z*)-cycloocta-1,5-diene (**9**) (0.3 mmol, 32 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L), TEMPO (0.045 mmol, 7.0 mg) and tert-butyl hydroperoxide (TBHP, 0.03 mmol, 5.5 M in decane) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 14 mg (34%) of **9a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 9.79 (t, *J* = 1.0 Hz, 1H), 5.57-5.50 (m, 1H), 5.45-5.41 (m, 1H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.45-2.37 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ = 201.4, 131.1, 126.5, 119.3, 43.4, 23.2, 19.9, 17.4 ppm; IR (neat): ν = 2245, 1720, 1644, 1458, 1260, 1020, 800, 748 cm⁻¹; HRMS (ESI) Calcd for C₈H₁₁NNaO [M+Na]⁺: 160.07329; Found: 160.07304.

8) 6-Oxo-6-phenylhexanenitrile (**10a**)⁵



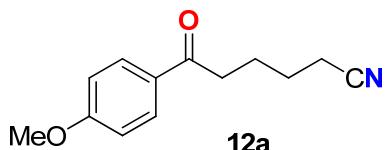
The reaction of 2,3,4,5-tetrahydro-1,1'-biphenyl (**10**) (0.3 mmol, 48 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 50 mg (90%) of **10a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 6.4 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 6.4 Hz, 2H), 2.39 (t, *J* = 6.4 Hz, 2H), 1.90-1.89 (m, 2H), 1.76 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 197.0, 134.6, 131.2, 126.6, 125.9, 117.4, 35.3, 23.0, 21.0, 15.3 ppm; IR (neat): ν = 2100, 1736, 1673, 1465, 1376, 1244, 1034 cm⁻¹.

9) 6-Oxo-6-(*p*-tolyl)hexanenitrile (**11a**)



The reaction of 4'-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (**11**) (0.3 mmol, 52 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 49 mg (82%) of **11a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.41-2.38 (m, 5H), 1.92-1.86 (m, 2H), 1.79-1.74 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 198.7, 144.0, 134.2, 129.3, 128.1, 119.4, 37.2, 25.0, 23.2, 21.6, 17.1 ppm; IR (neat): ν = 2246, 1681, 1660, 1605, 1278, 704 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₆NO [M+H]⁺: 202.12264; Found: 202.12269.

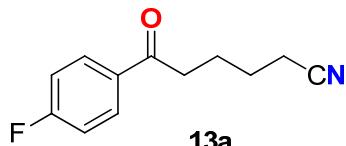
10) 6-(4-Methoxyphenyl)-6-oxohexanenitrile (**12a**)



The reaction of 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (**12**) (0.3 mmol, 56 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL

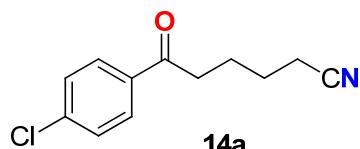
MeCN at 80 °C under oxygen for 36 h afforded 34 mg (52%) of **12a** as solid: ¹H NMR (CDCl_3 , 400 MHz): δ = 7.93 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.98 (t, J = 6.8 Hz, 2H), 2.40 (t, J = 7.0 Hz, 2H), 1.91-1.87 (m, 2H), 1.78-1.74 (m, 2H); ¹³C NMR (CDCl_3 , 100 MHz): δ = 197.6, 163.5, 130.2, 129.8, 119.5, 113.8, 55.4, 36.9, 25.0, 23.2, 17.1 ppm; IR (neat): ν = 2247, 1676, 1601, 1512, 1255, 1173, 1032, 835 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_2$ [$\text{M}+\text{Na}]^+$: 240.09950; Found: 240.09898.

11) 6-(4-Fluorophenyl)-6-oxohexanenitrile (**13a**)



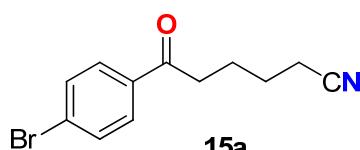
The reaction of 4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (**13**) (0.3 mmol, 53 mg), TMSN_3 (0.45 mmol, 52 mg, 60 μL) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 51 mg (83%) of **13a** as solid: ¹H NMR (CDCl_3 , 400 MHz): δ = 8.00-7.96 (m, 2H), 7.14 (t, J = 8.6 Hz, 2H), 3.02 (t, J = 7.0 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.91-1.88 (m, 2H), 1.80-1.74 (m, 2H); ¹³C NMR (CDCl_3 , 100 MHz): δ = 197.3, 165.6 (d, J = 253 Hz), 132.9 (d, J = 3.6 Hz), 130.4 (d, J = 9.1 Hz), 119.3, 115.6 (d, J = 22.9 Hz), 37.1, 24.8, 22.8, 17.0 ppm; IR (neat): ν = 2246, 1682, 1596, 1226, 839, 810 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{13}\text{FNO}$ [$\text{M}+\text{H}]^+$: 206.09757; Found: 206.09786.

12) 6-(4-Chlorophenyl)-6-oxohexanenitrile (**14a**)



The reaction of 4'-chloro-2,3,4,5-tetrahydro-1,1'-biphenyl (**14**) (0.3 mmol, 58 mg), TMSN_3 (0.45 mmol, 52 mg, 60 μL) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 63 mg (95%) of **14a** as oil: ¹H NMR (CDCl_3 , 400 MHz): δ = 7.88 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 3.01 (t, J = 7.0 Hz, 2H), 2.41 (t, J = 7.0 Hz, 2H), 1.94-1.87 (m, 2H), 1.80-1.73 (m, 2H); ¹³C NMR (CDCl_3 , 100 MHz): δ = 197.7, 139.5, 134.9, 129.3, 128.9, 119.4, 37.2, 24.8, 22.9, 17.0 ppm; IR (neat): ν = 2247, 1686, 1658, 1590, 1278, 1092, 705 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{13}\text{ClNO}$ [$\text{M}+\text{H}]^+$: 222.06802; Found: 222.06821.

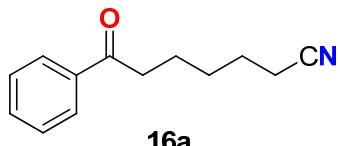
13) 6-(4-Bromophenyl)-6-oxohexanenitrile (**15a**)



The reaction of 4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl (**15**) (0.3 mmol, 71 mg),

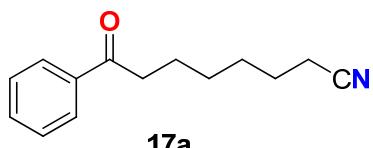
TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 44 mg (56%) of **15a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.81 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.92-1.88 (m, 2H), 1.78-1.74 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 197.9, 138.0, 135.4, 132.0, 129.5, 119.4, 37.3, 24.9, 22.9, 17.2 ppm; IR (neat): ν = 2246, 1684, 1583, 1396, 1222, 1069, 1004, 974 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₁₈NO [M+H]⁺: 266.01750; Found: 266.01797.

14) 7-Oxo-7-phenylheptanenitrile (**16a**)



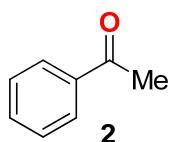
The reaction of 1-phenylcyclohept-1-ene (**16**) (0.3 mmol, 52 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 55 mg (91%) of **16a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.83-1.69 (m, 4H), 1.59-1.53 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 199.5, 136.6, 132.8, 128.4, 127.7, 119.4, 37.8, 28.0, 25.0, 22.9, 16.8 ppm; IR (neat): ν = 2244, 1684, 1449, 746, 690 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₆NO [M+H]⁺: 202.12264; Found: 202.12247.

15) 8-Oxo-8-phenyloctanenitrile (**17a**)



The reaction of 1-phenylcyclooct-1-ene (**17**) (0.3 mmol, 56 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 45 mg (70%) of **17a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.78-1.64 (m, 4H), 1.53-1.40 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 199.3, 136.1, 132.2, 127.8, 127.2, 119.0, 37.4, 27.7, 27.6, 24.4, 23.0, 16.3 ppm; IR (neat): ν = 2245, 1683, 1596, 1450, 746, 691 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₁₈NO [M+H]⁺: 216.13829; Found: 216.13806.

16) Acetophenone (**2**)⁶



The reaction of α -methylstyrene (**1**) (0.3 mmol, 35 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for

24 h afforded 32 mg (85%) of **2** as liquid: ^1H NMR (CDCl_3 , 400 MHz): δ = 7.96 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 198.0, 137.0, 133.0, 128.5, 128.2, 26.5 ppm; IR (neat): ν = 1693, 1448, 1276, 1262, 758 cm^{-1} .

17) 4-Methoxybenzaldehyde (18)⁶



18

The reaction of 1-methoxy-4-vinylbenzene (0.3 mmol, 40 mg), TMSN_3 (0.45 mmol, 52 mg, 60 μL), TEMPO (0.045 mmol, 7.0 mg) and PIDA (0.03 mmol, 9.7 mg) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 27 mg (66%) of **18** as liquid: ^1H NMR (CDCl_3 , 400 MHz): δ = 9.89 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 190.7, 164.5, 131.9, 129.8, 114.2, 55.4 ppm; IR (neat): ν = 1685, 1600, 1578, 1511, 1261, 1161, 1026, 833 cm^{-1} .

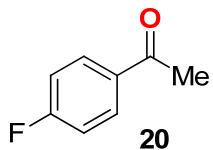
18) 4-(*tert*-Butyl)benzaldehyde (19)⁷



19

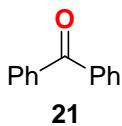
The reaction of 1-(*tert*-butyl)-4-vinylbenzene (0.3 mmol, 48 mg), TMSN_3 (0.45 mmol, 52 mg, 60 μL) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 35 mg (72%) of **19** as liquid: ^1H NMR (CDCl_3 , 400 MHz): δ = 9.98 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 192.0, 158.4, 134.1, 129.7, 126.0, 35.3, 31.0 ppm; IR (neat): ν = 1698, 1607, 1275, 1220, 1176, 830, 702 cm^{-1} .

19) 1-(4-Fluorophenyl)ethanone (20)⁸



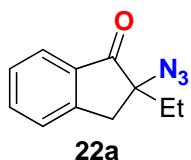
The reaction of 1-fluoro-4-(prop-1-en-2-yl)benzene (0.3 mmol, 41 mg), TMSN_3 (0.45 mmol, 52 mg, 60 μL) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 36 h afforded 31 mg (76%) of **20** as liquid: ^1H NMR (CDCl_3 , 400 MHz): δ = 8.00-7.97 (m, 2H), 7.13 (t, J = 8.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 196.2, 165.4 (d, J = 254 Hz), 133.2 (d, J = 3.1 Hz), 130.6 (d, J = 9.9 Hz), 115.3 (d, J = 22 Hz), 26.2 ppm; IR (neat): ν = 1718, 1686, 1600, 1509, 1266, 1232, 837 cm^{-1} .

20) Benzophenone (21)⁶



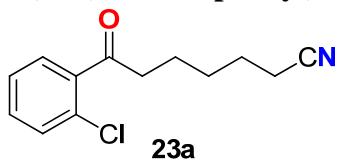
The reaction of ethene-1,1-diylbenzene (0.3 mmol, 54 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 50 mg (92%) of **21** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 7.79 (d, *J* = 7.2 Hz, 4H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 196.6, 137.4, 132.3, 129.9, 128.1 ppm; IR (neat): ν = 1658, 1598, 1578, 1447, 1317, 1278, 941, 700, 638 cm⁻¹.

21) 2-Azido-2-ethyl-2,3-dihydro-1*H*-inden-1-one (22a)



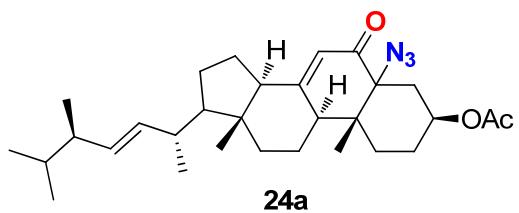
The reaction of 2-ethyl-1*H*-indene (**22**) (0.3 mmol, 43 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL), TEMPO (0.045 mmol, 7.0 mg) and TBHP (0.03 mmol, 5.5 M in decane) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 54 mg (90%) of **22a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 7.79 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.44-7.40 (m, 2H), 3.20 (d, *J* = 17.2 Hz, 1H), 3.00 (d, *J* = 17.6 Hz, 1H), 2.08-2.03 (m, 1H), 1.87-1.82 (m, 1H), 1.00 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 202.6, 150.7, 135.4, 133.7, 127.6, 125.9, 124.3, 68.3, 37.2, 26.8, 7.8 ppm; IR (neat): ν = 2100, 1719, 1609, 1465, 1272, 1247, 740 cm⁻¹; HRMS (ESI) Calcd for C₁₁H₁₁N₃NaO [M+Na]⁺: 224.07943; Found: 224.07916.

22) 7-(2-Chlorophenyl)-7-oxoheptanenitrile (23a)



The reaction of 1-(2-chlorophenyl)cyclohept-1-ene (**23**) (0.3 mmol, 62 mg), TMSN₃ (0.45 mmol, 52 mg, 60 µL) and TEMPO (0.06 mmol, 9.4 mg) in 2 mL MeCN at 95 °C under oxygen for 120 h afforded 61 mg (86%) of **23a** as oil: ¹H NMR (CDCl₃, 400 MHz): δ = 7.45-7.36 (m, 3H), 7.34-7.30 (m, 1H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.78-1.67 (m, 4H), 1.57-1.51 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 202.9, 139.3, 131.5, 130.6, 130.4, 128.5, 126.8, 119.4, 42.3, 27.9, 25.1, 23.0, 16.8 ppm; IR (neat): ν = 2246, 1698, 1590, 1465, 1432, 913, 748 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₄ClNNaO [M+Na]⁺: 258.06561; Found: 258.06484.

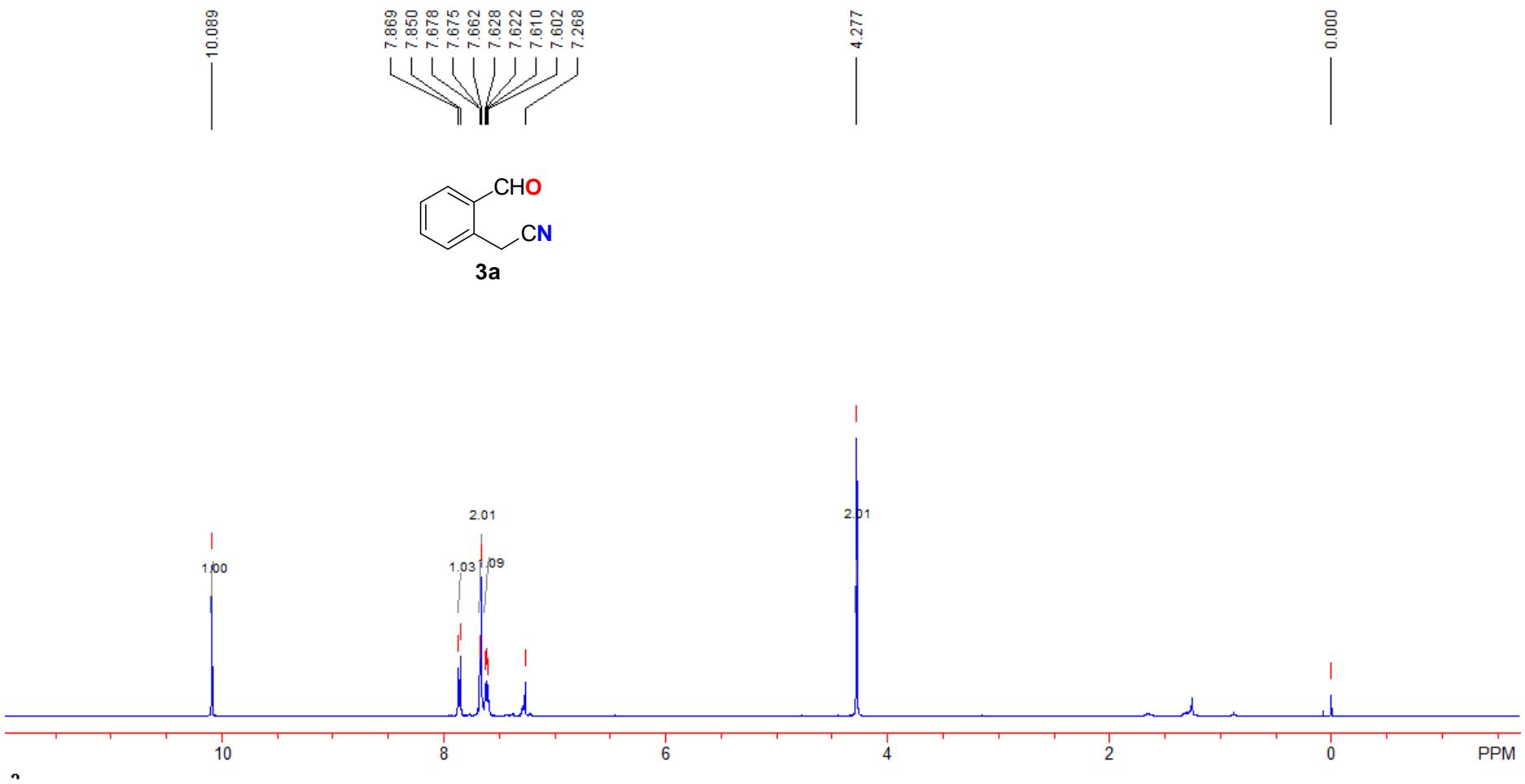
23) (3*S*,9*S*,10*R*,13*R*,14*R*)-5-Azido-17-((2*R*,5*R*,*E*)-5,6-dimethylhept-3-en-2-yl)-10,13-dimethyl-6-oxo-2,3,4,5,6,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclophanta[*a*]phenanthren-3-yl acetate (24a)

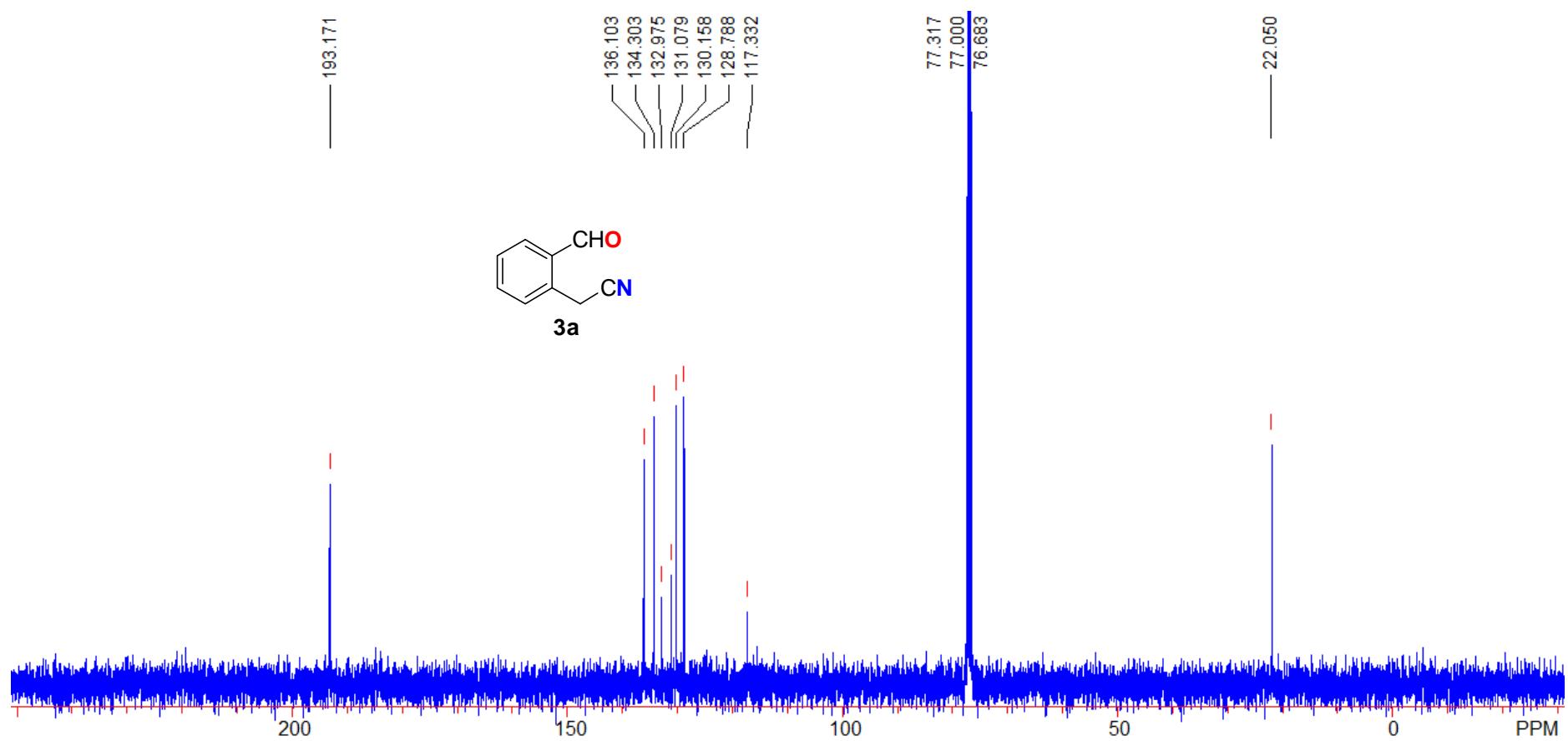


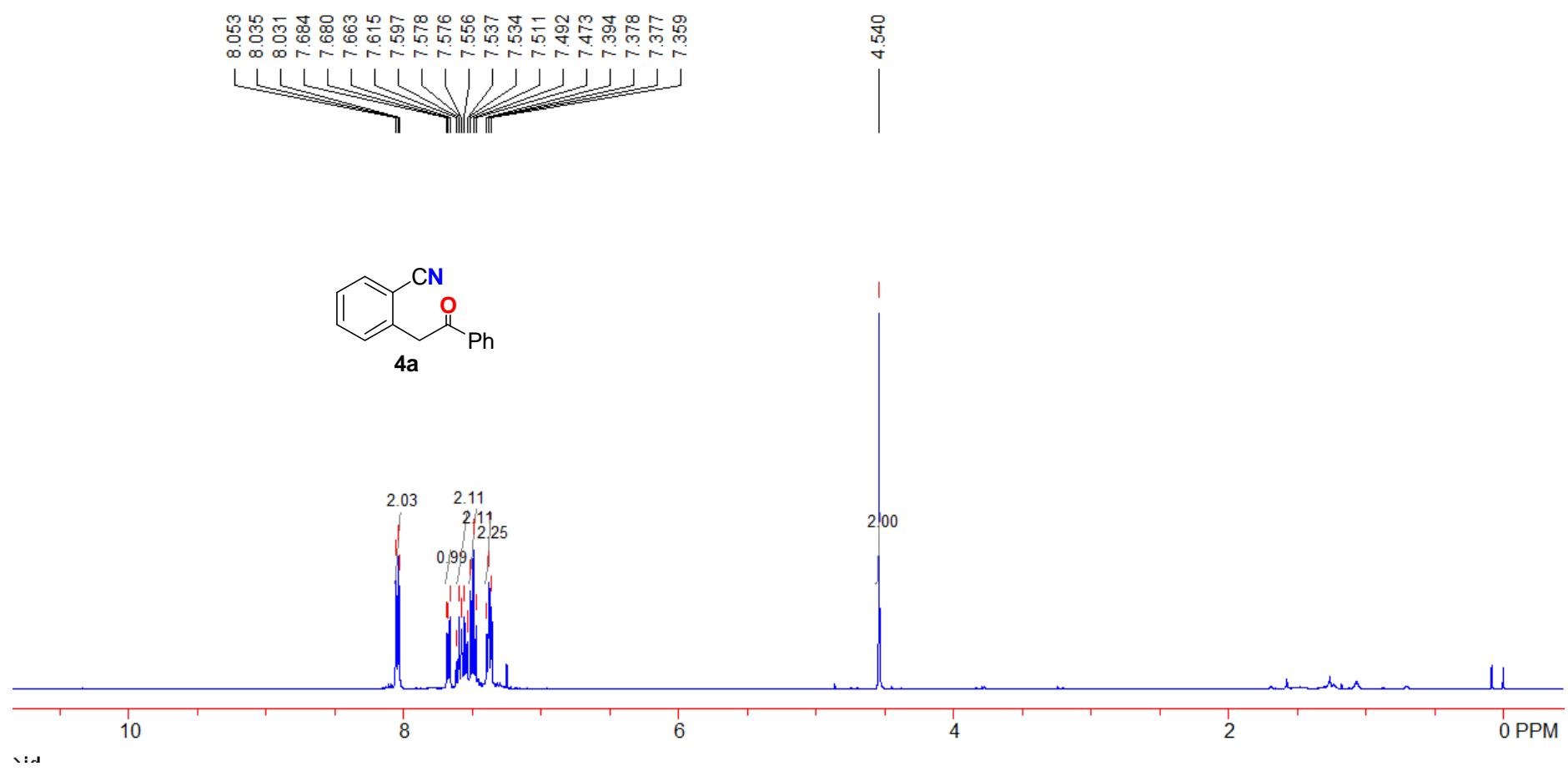
The reaction of ergosterol acetate (**24**) (0.3 mmol, 131 mg), TMSN₃ (0.45 mmol, 52 mg, 60 μ L) and TEMPO (0.045 mmol, 7.0 mg) in 2 mL MeCN at 80 °C under oxygen for 24 h afforded 95 mg (64%) of **24a** as solid: ¹H NMR (CDCl₃, 400 MHz): δ = 5.71 (m, 1H), 5.25-5.15 (m, 2H), 5.05-4.99 (m, 1H), 2.51-1.25 (comp, 20H), 2.06 (s, 3H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.00 (s, 3H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 6.8 Hz, 6H), 0.60 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 192.9, 170.3, 166.1, 134.8, 132.4, 119.7, 71.4, 69.6, 55.9, 55.6, 44.6, 44.0, 42.7, 40.2, 39.8, 38.5, 32.9, 30.2, 28.7, 27.7, 26.0, 22.3, 21.8, 21.2, 21.0, 19.8, 19.5, 17.5, 15.8, 12.6 ppm; IR (neat): ν = 2096, 1732, 1669, 1458, 1368, 1242, 739 cm⁻¹; HRMS (ESI) Calcd for C₃₀H₄₅N₃NaO₃ [M+Na]⁺: 518.33531; Found: 518.33700.

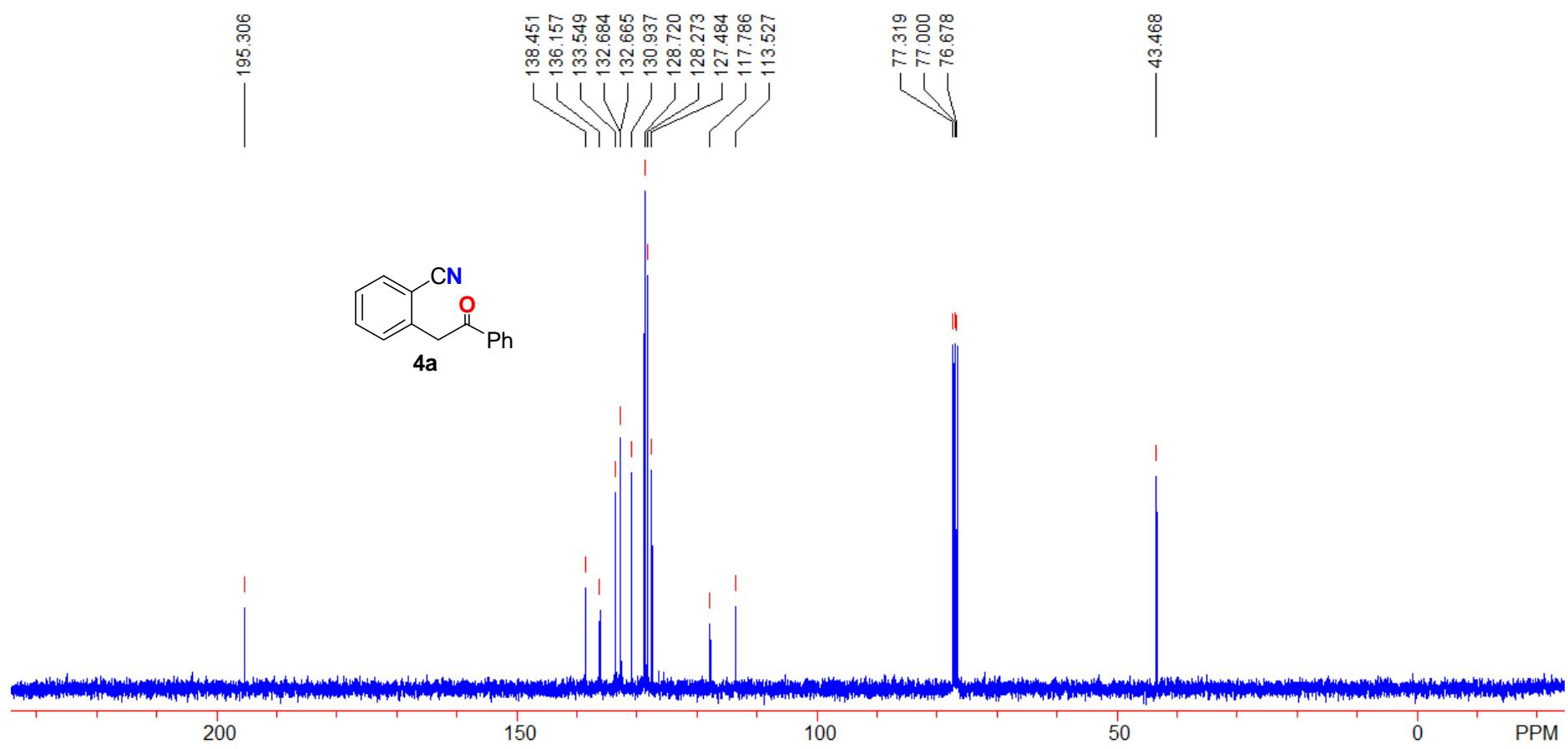
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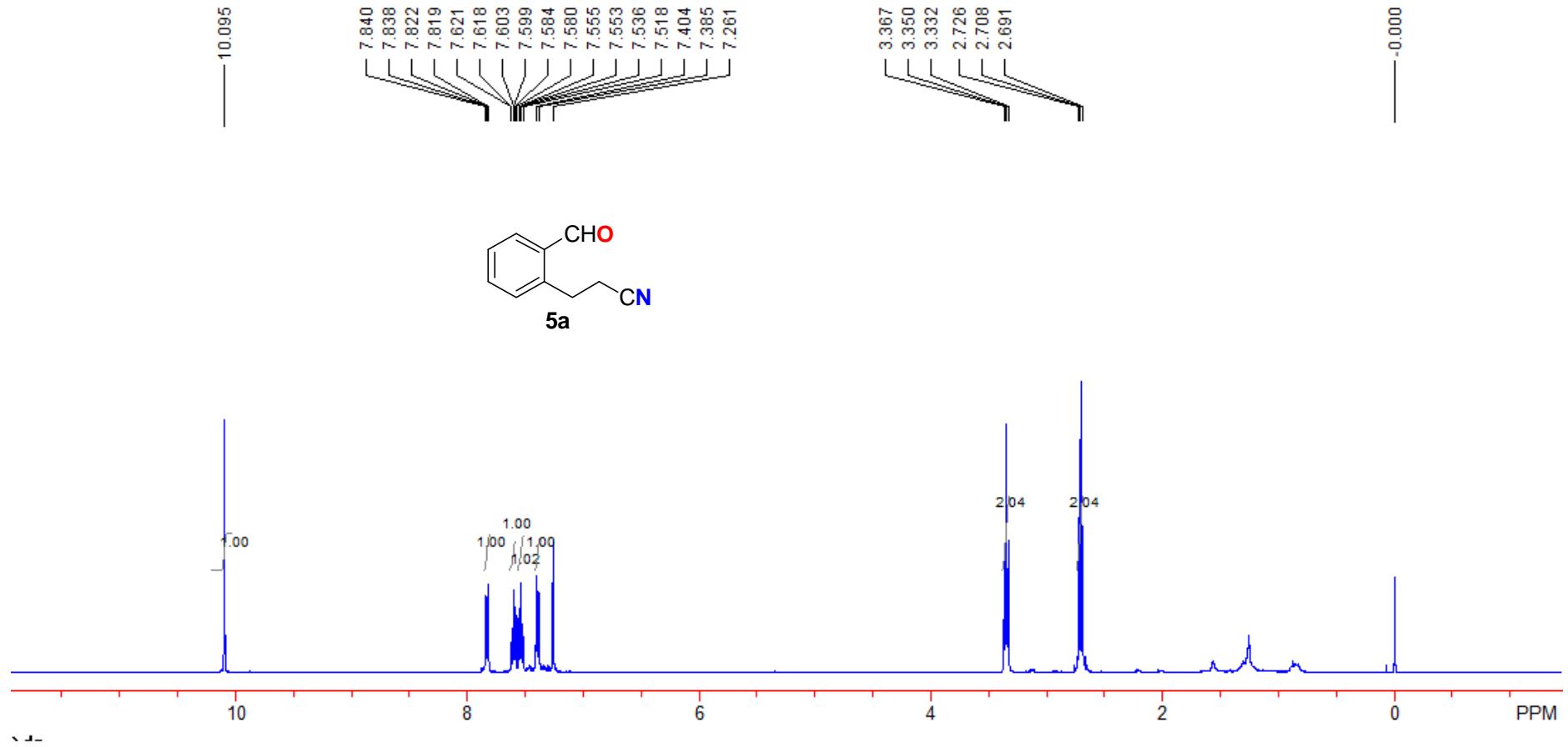
1. (a) Yanagisawa, A.; Nezu, T.; Mohri, S. *Org. Lett.* **2009**, *11*, 5286. (b) Costa, B. R.; George, C.; Li, G; He, X. *J. Org. Chem.* **1994**, *59*, 482.
2. Hernández, R.; León, E. I.; Moreno, P.; Suárez, E. *J. Org. Chem.* **1997**, *62*, 8974.
3. Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429.
4. Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. *Org. Lett.* **2001**, *3*, 735.
5. Streuff, J.; Feurer, M.; Bichovski, P.; Frey, G.; Gellrich U. *Angew. Chem. Int. Ed.* **2012**, *51*, 8661.
6. Wang, A.; Jiang, H. *J. Org. Chem.* **2010**, *75*, 2321.
7. Hamasaki, K.; Kuwada, H.; Tokunaga, M. *Tetrahedron Lett.* **2012**, *53*, 811.
8. Tang, P.; Ritter, T. *Tetrahedron* **2011**, *67*, 4449.

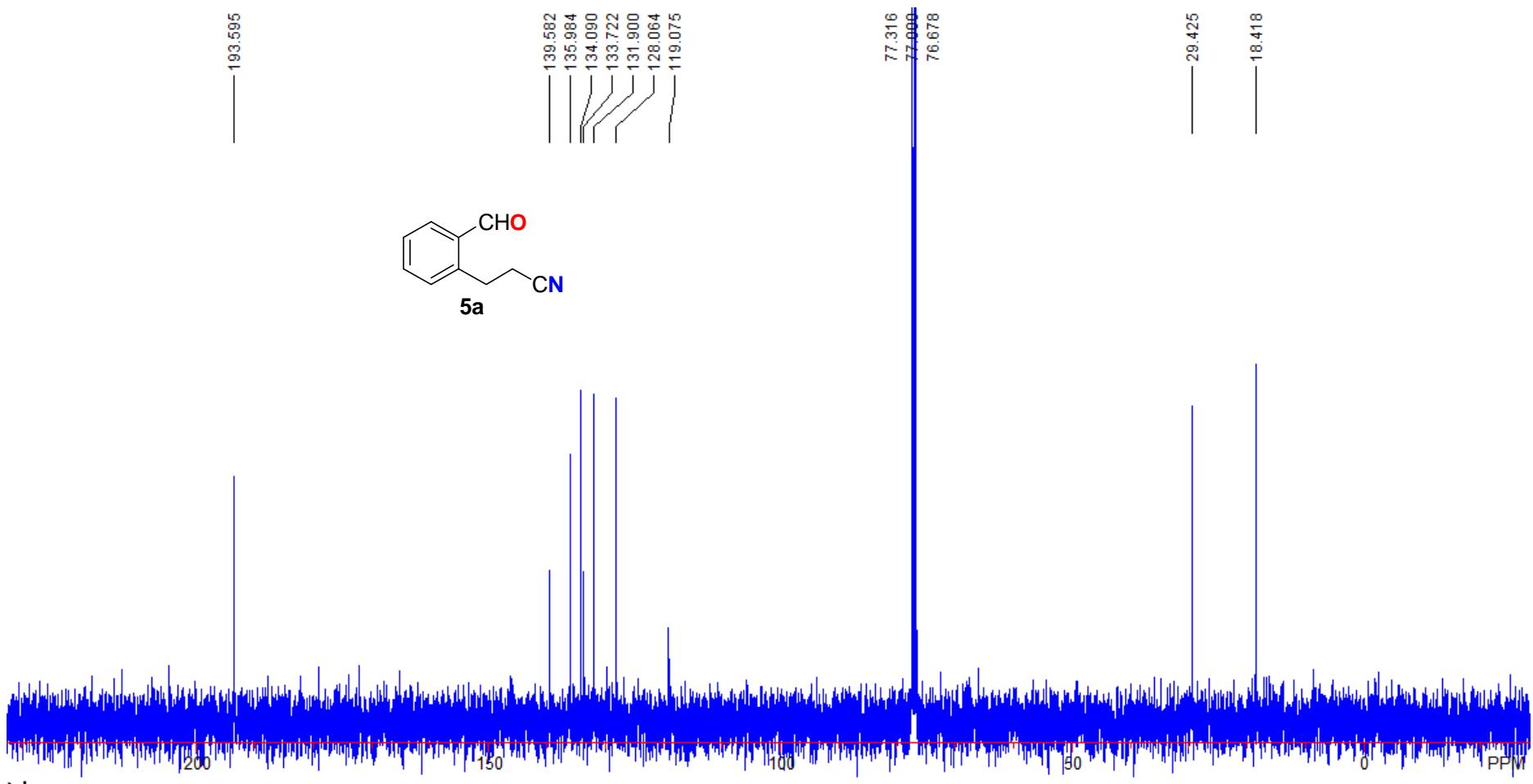


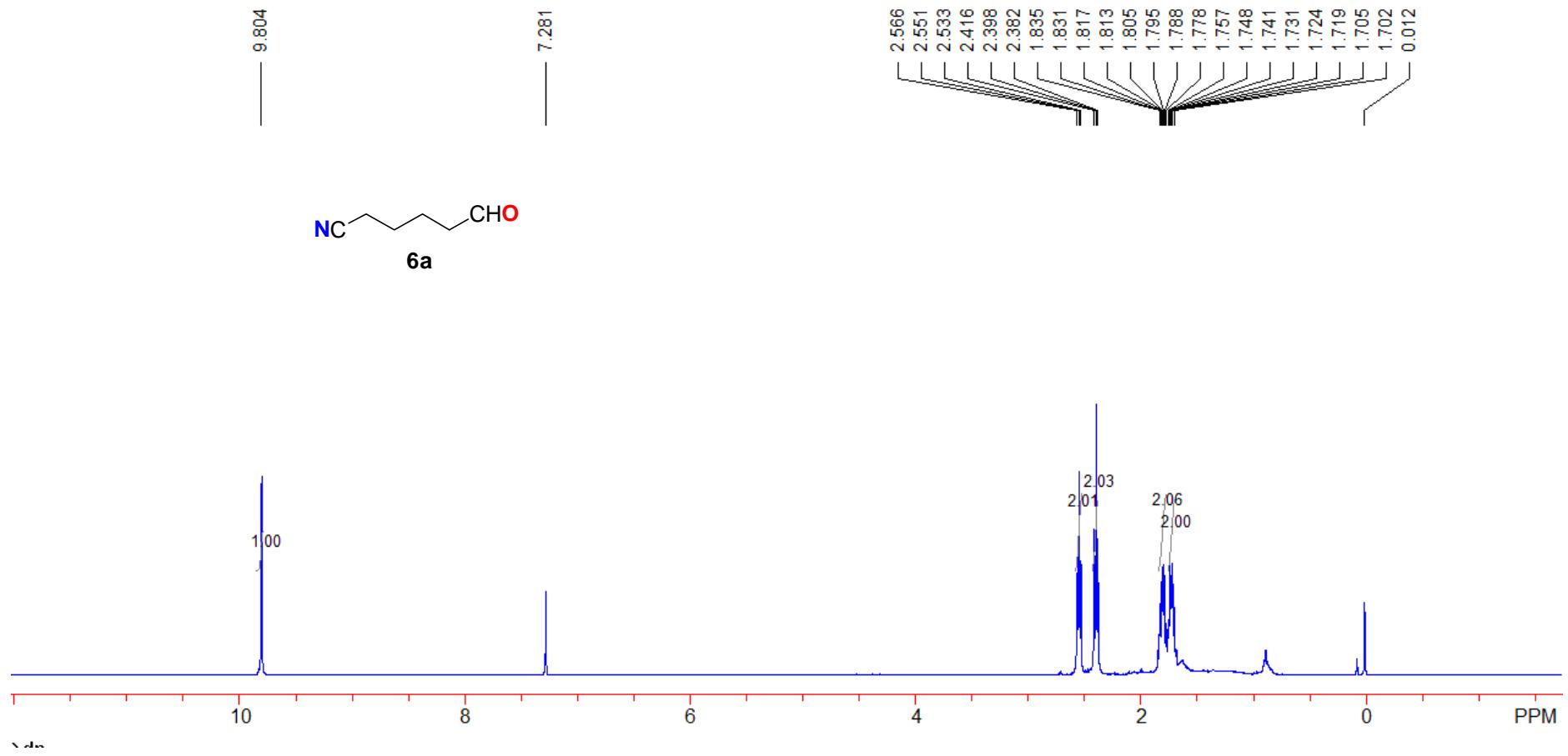


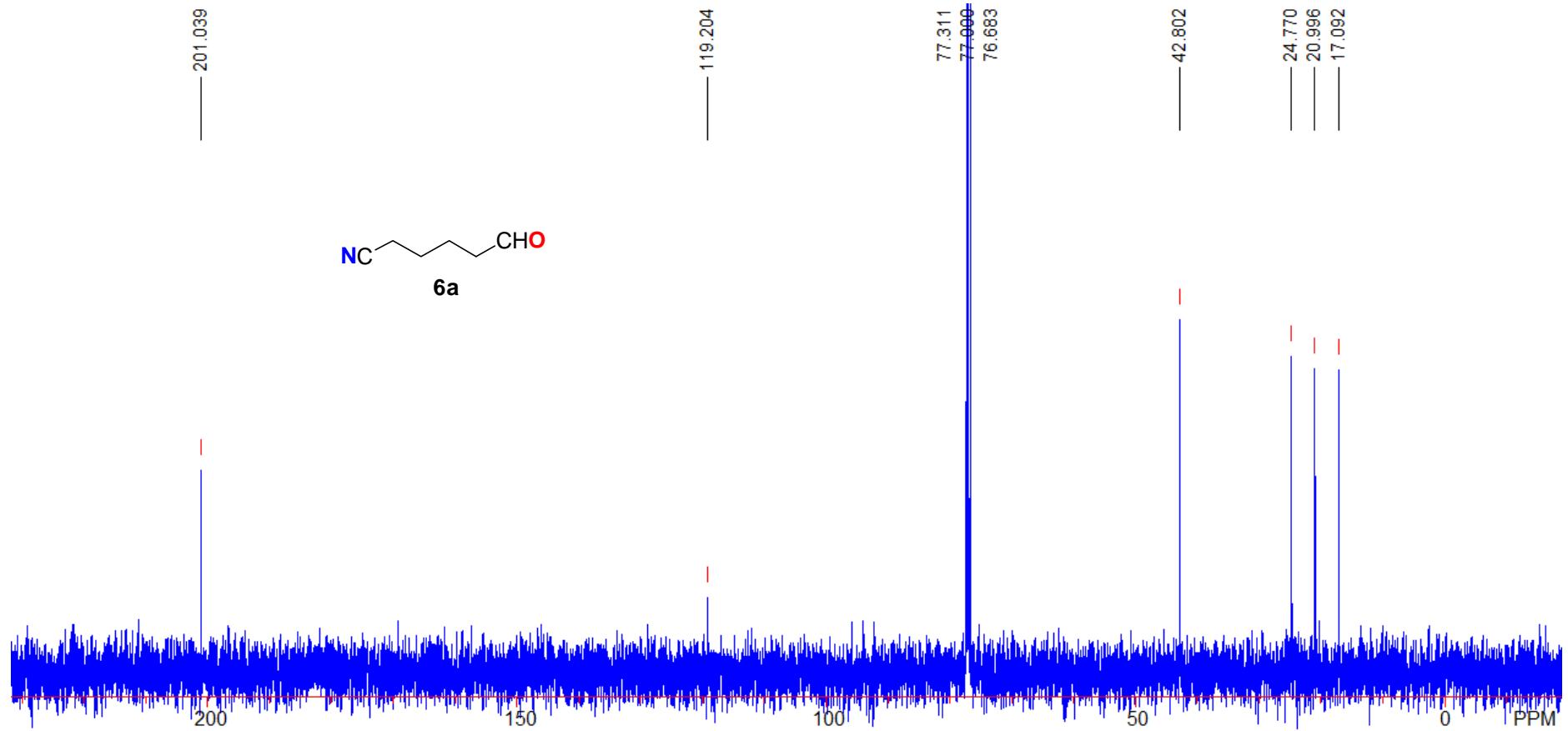


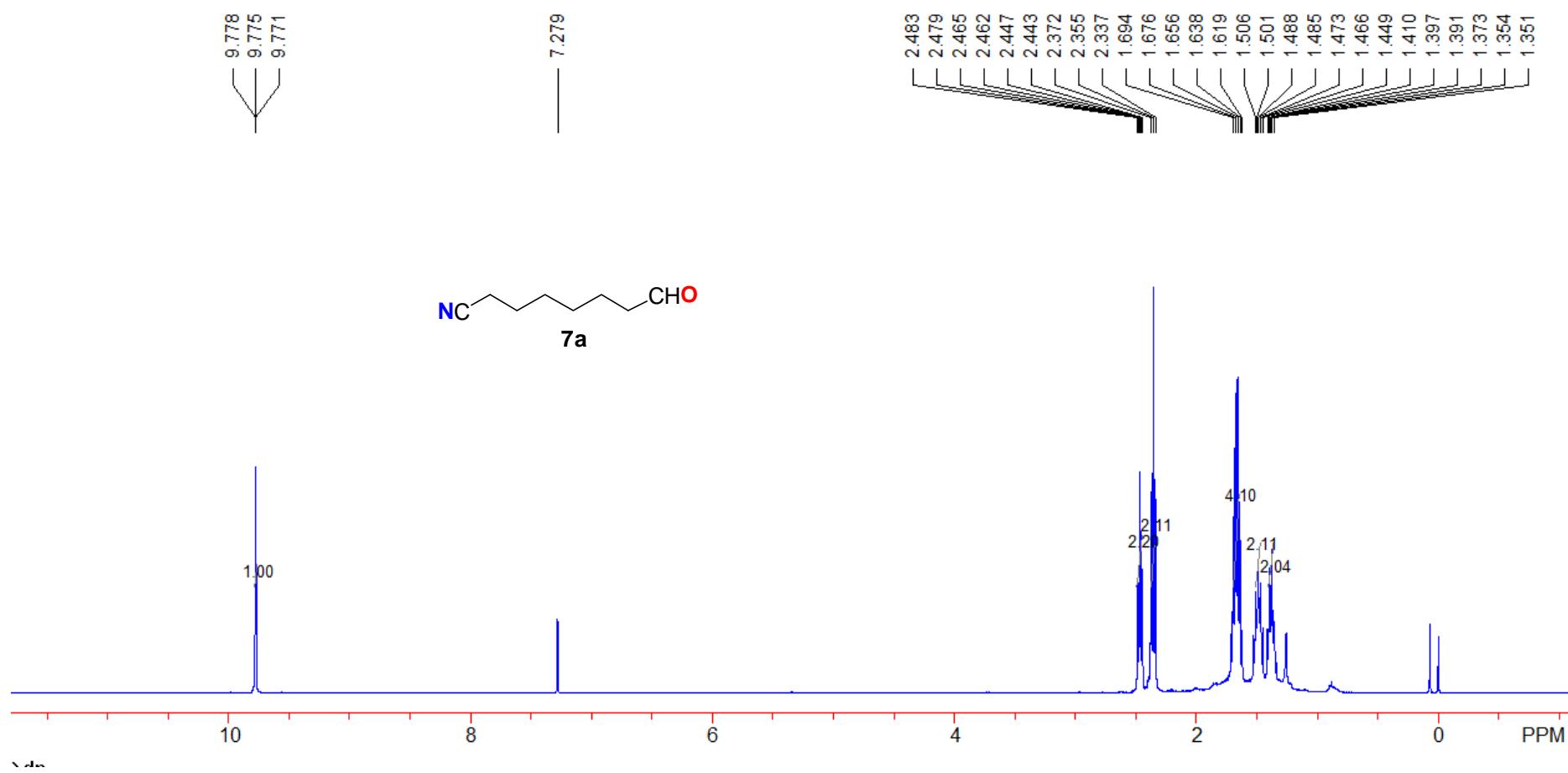


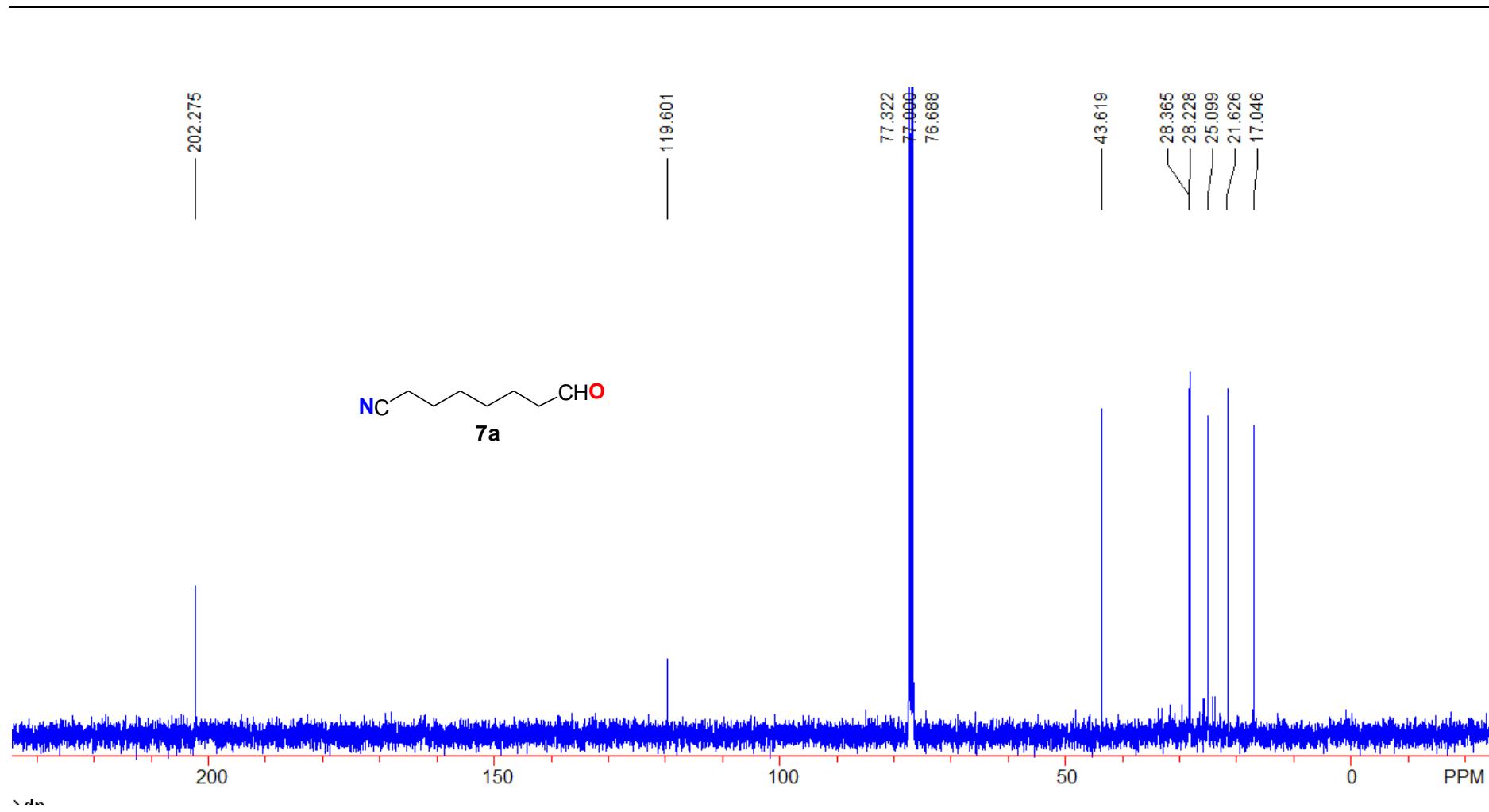


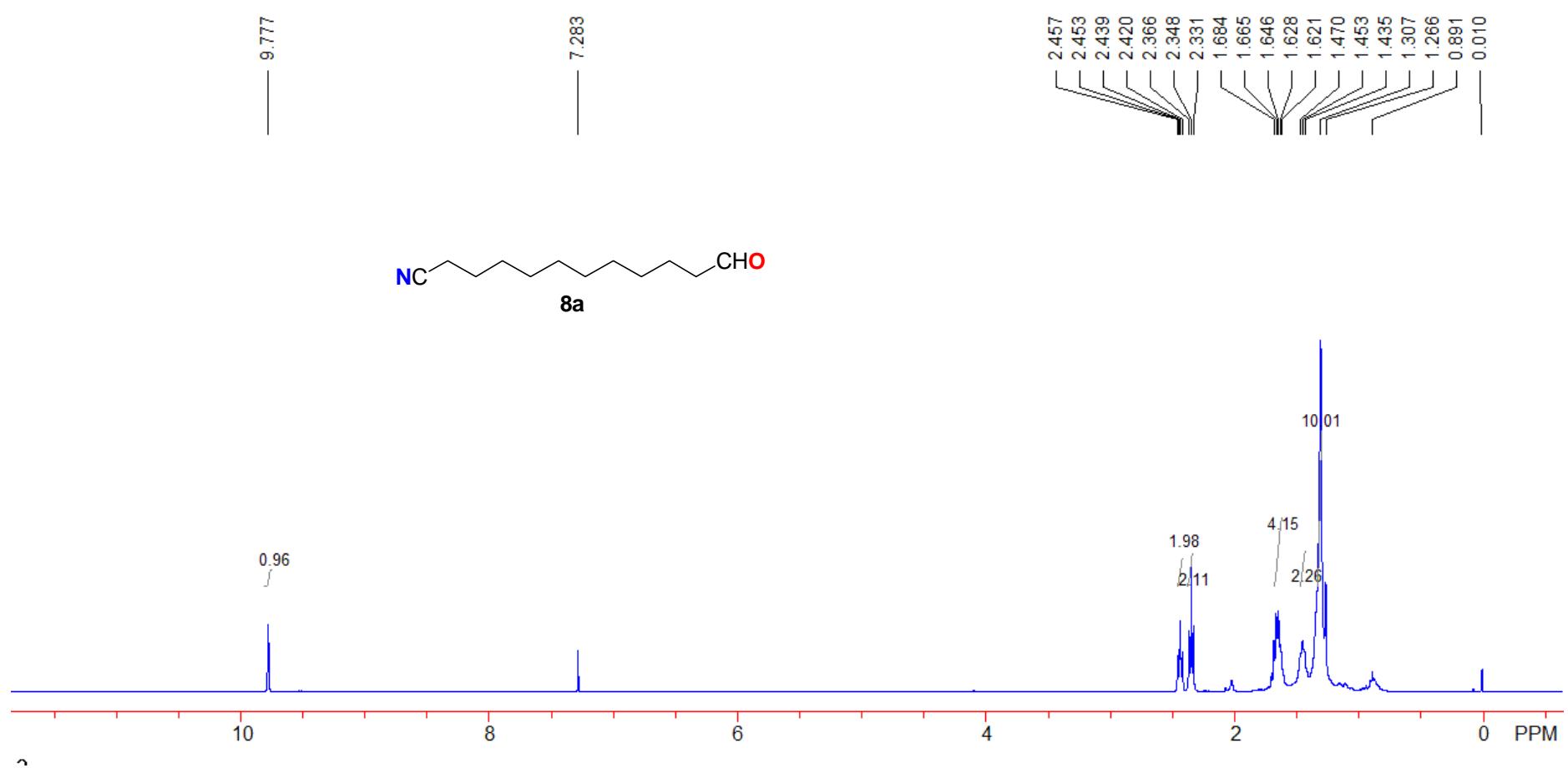


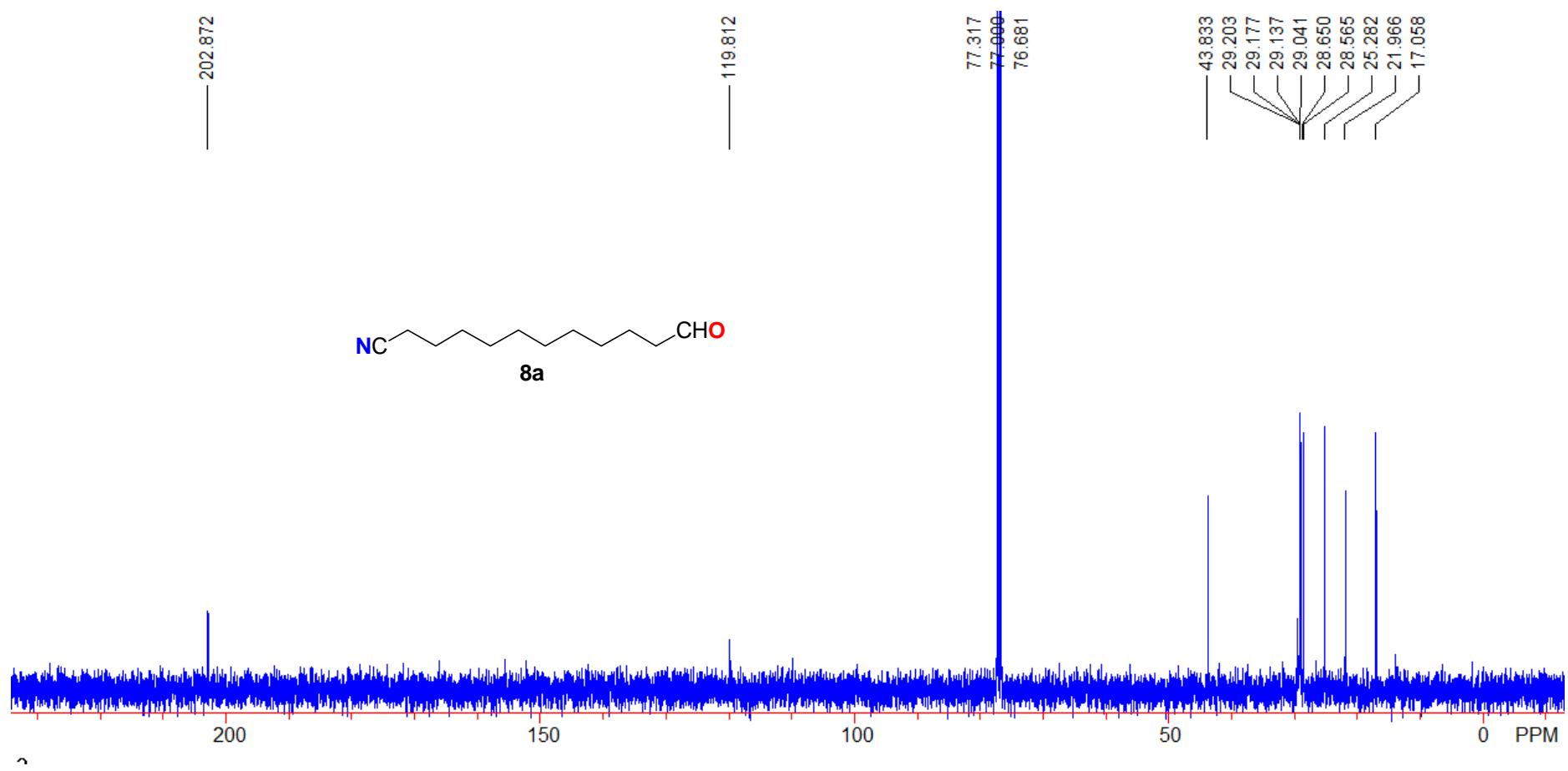


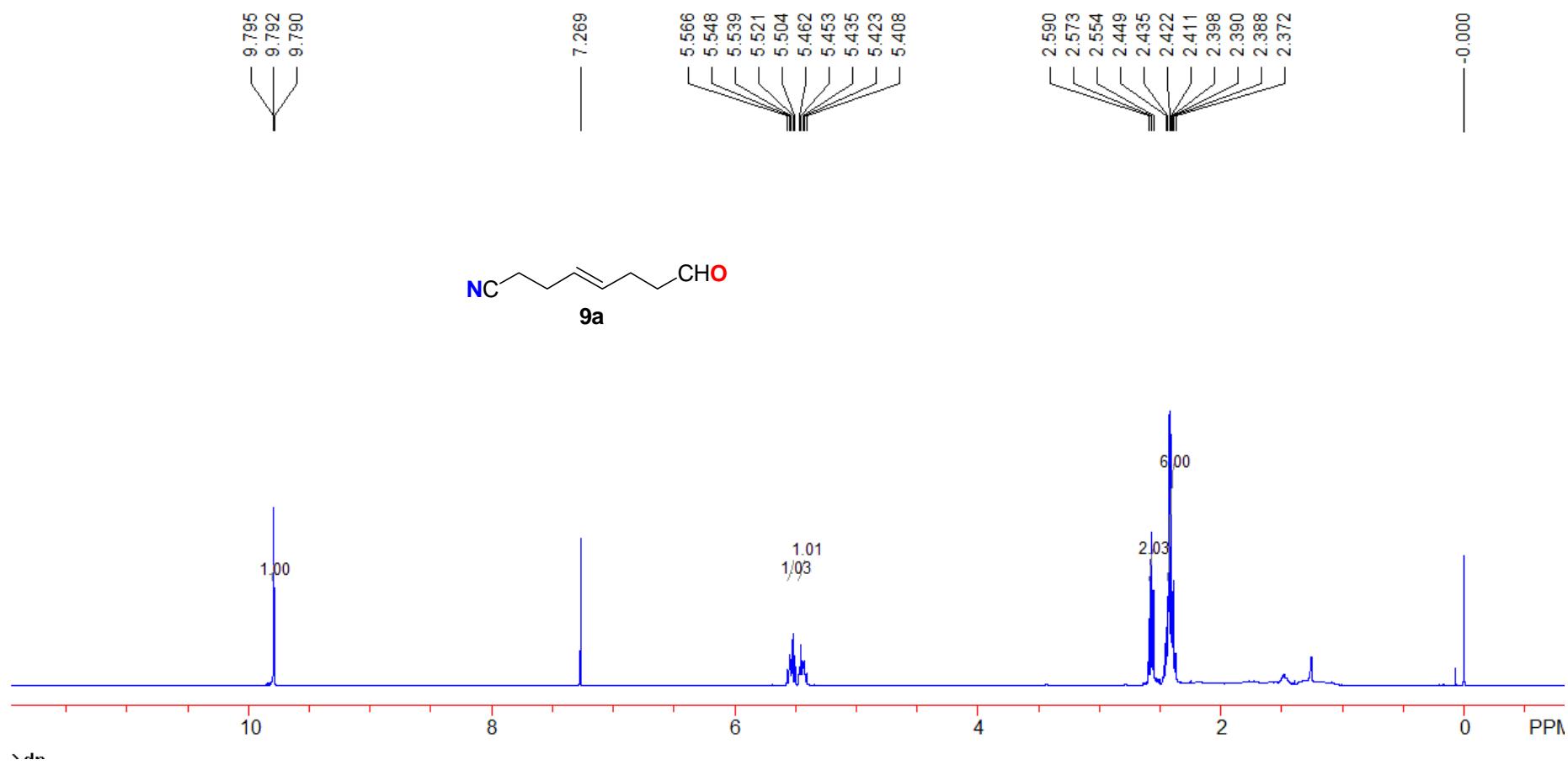


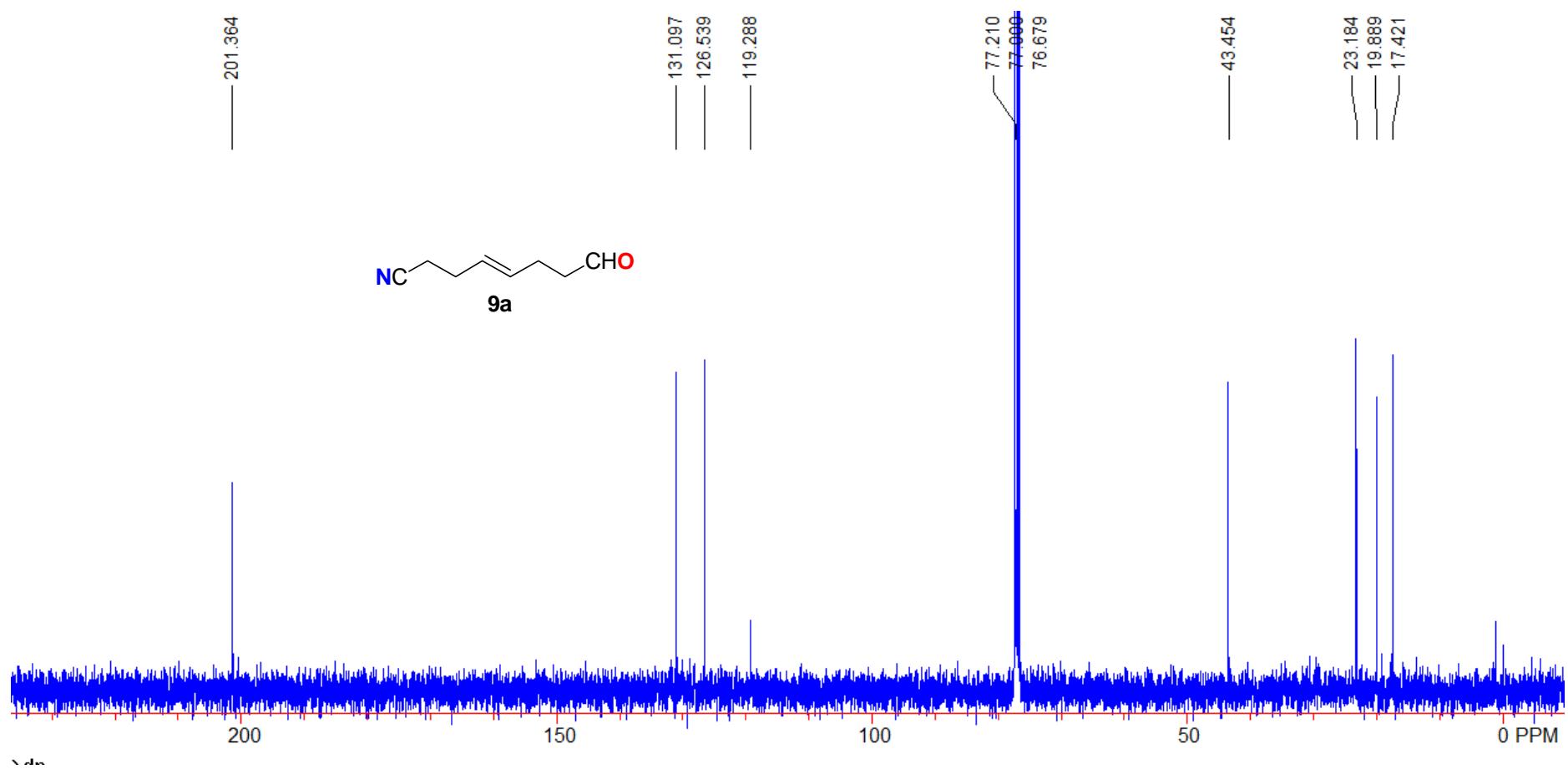


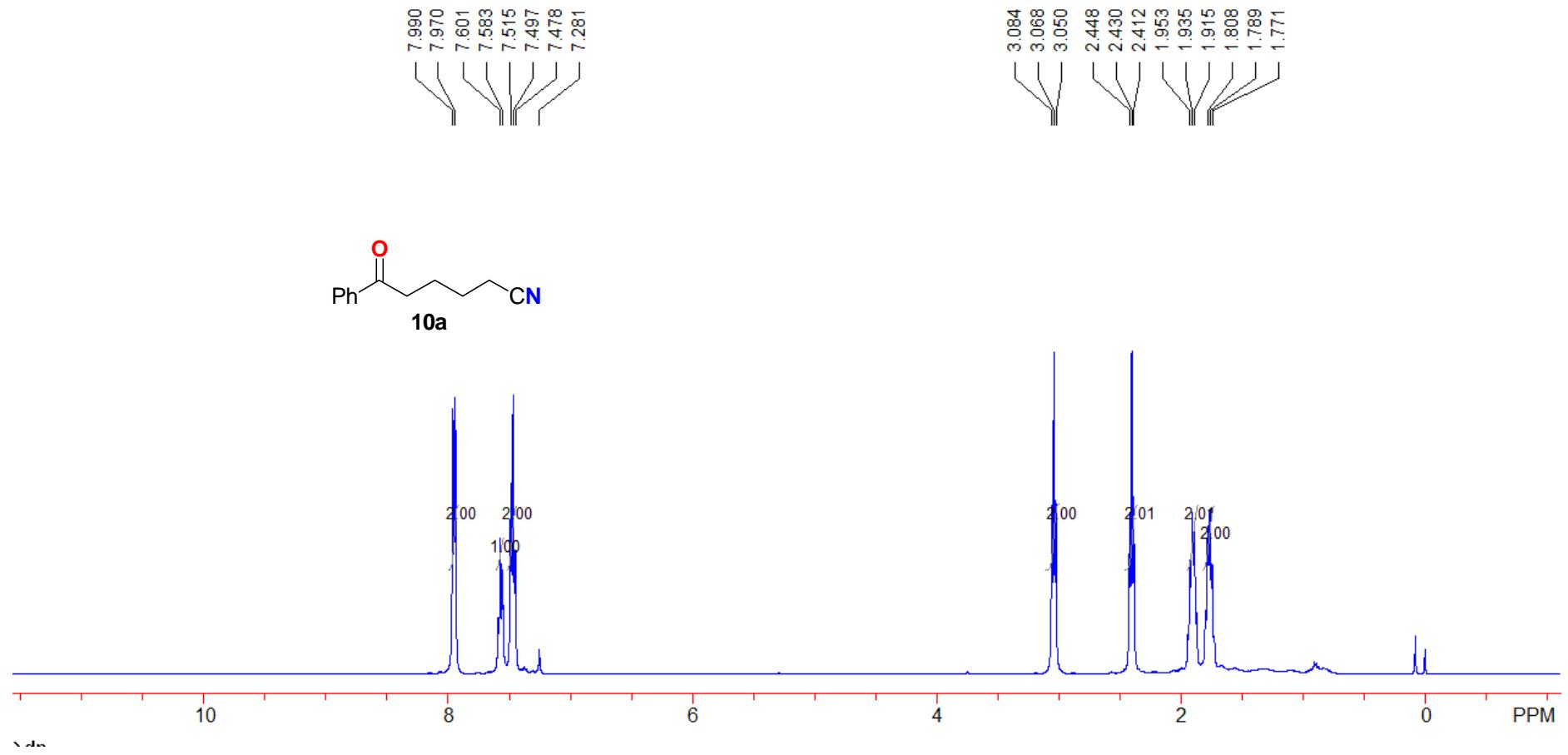


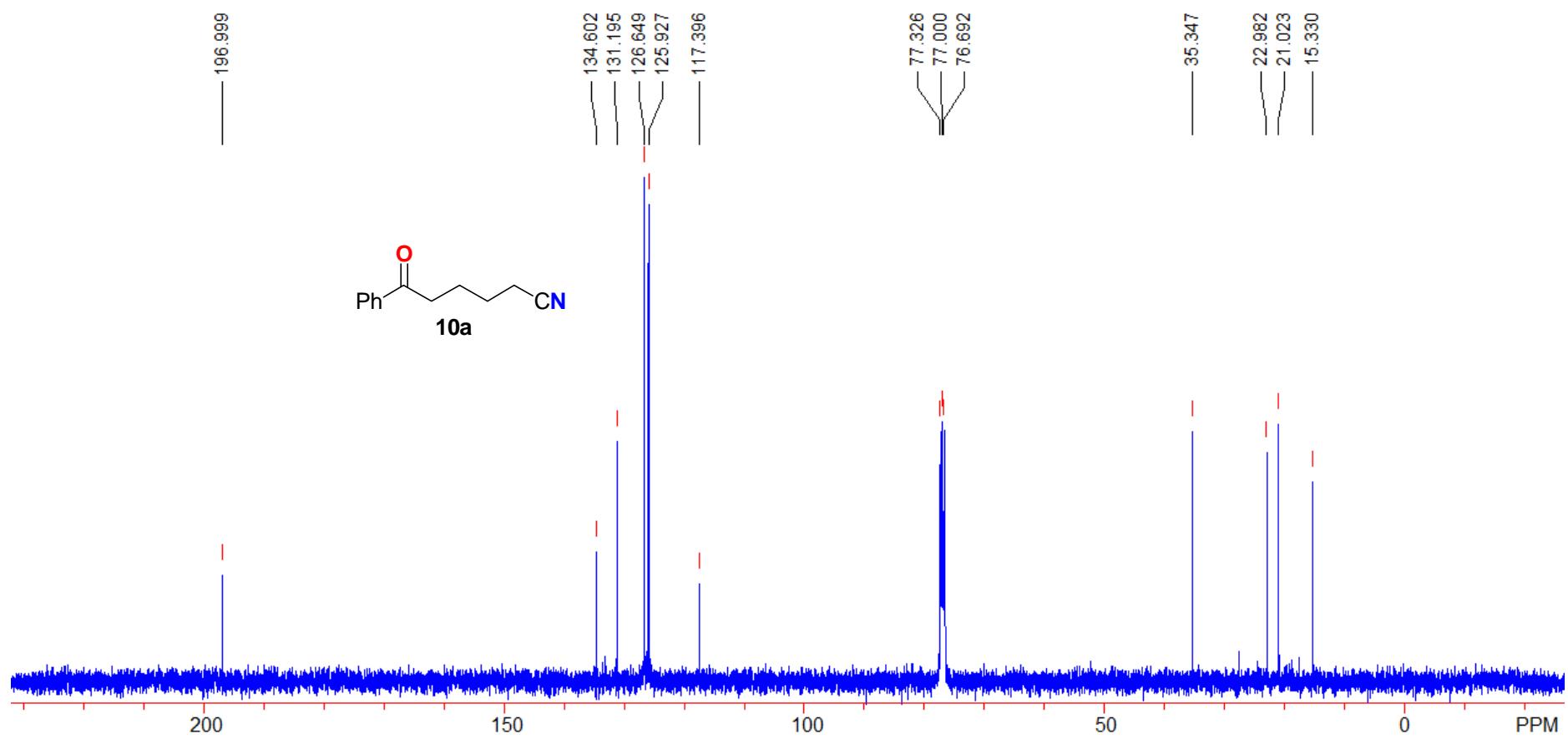


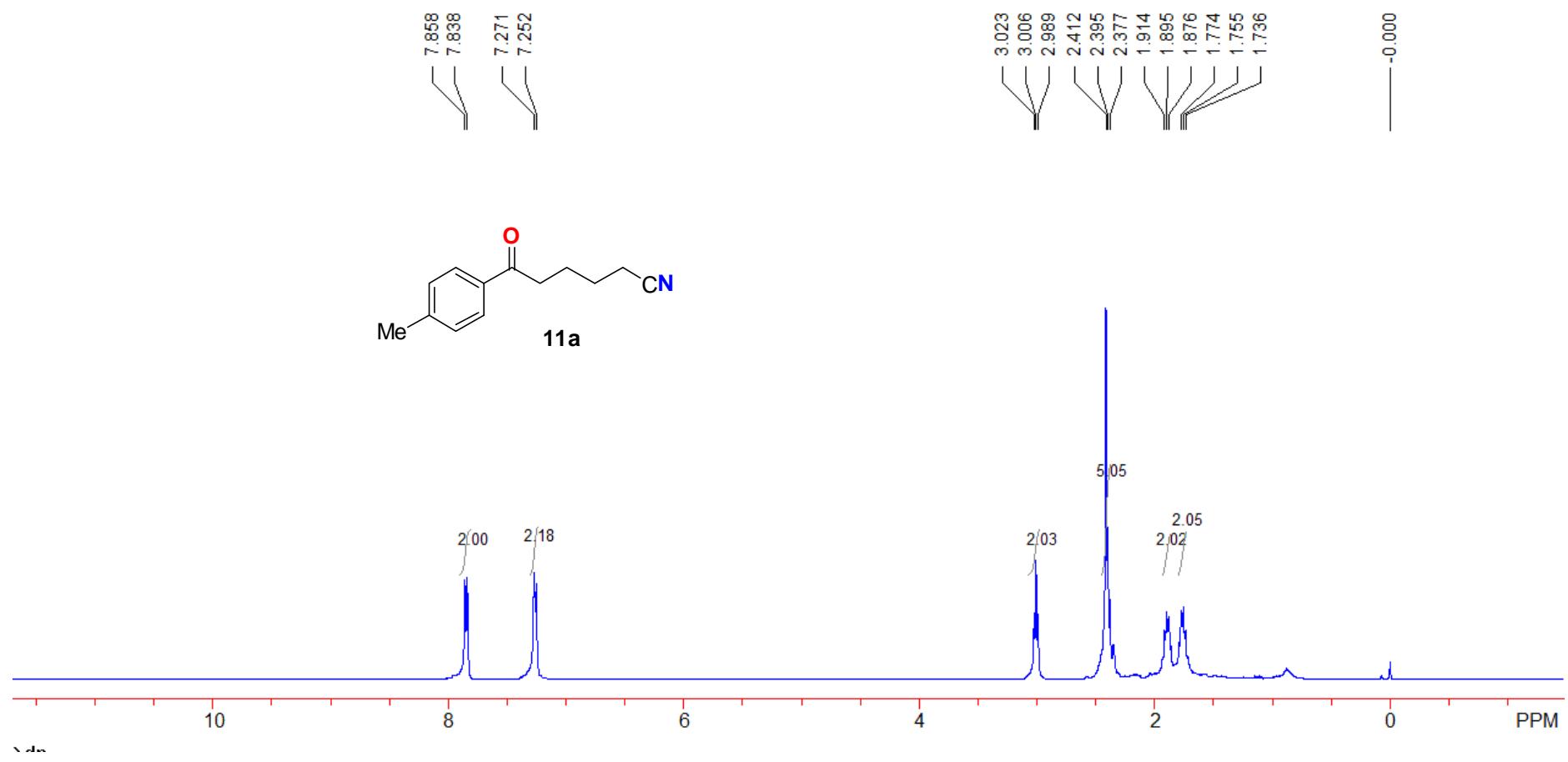


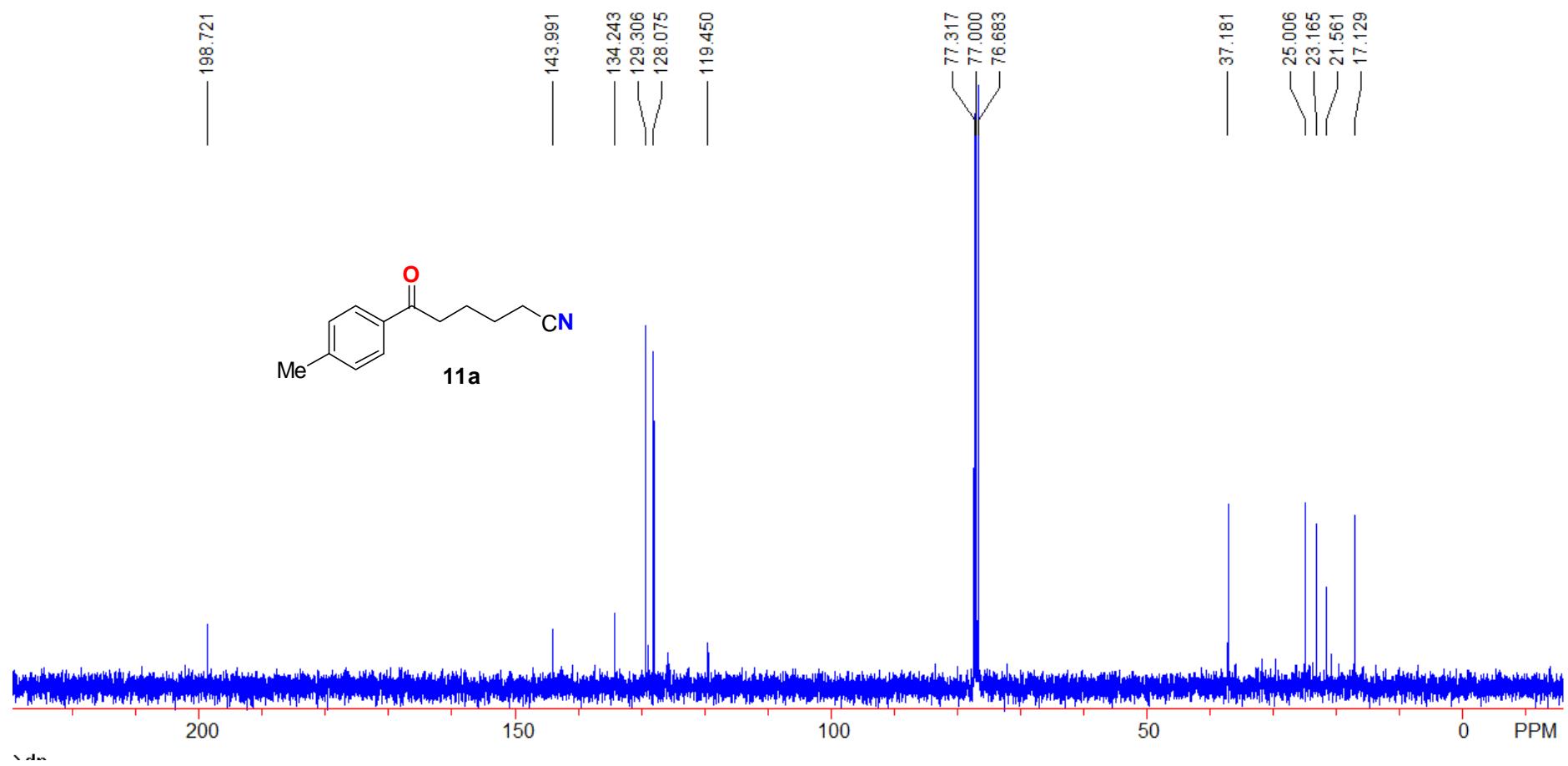


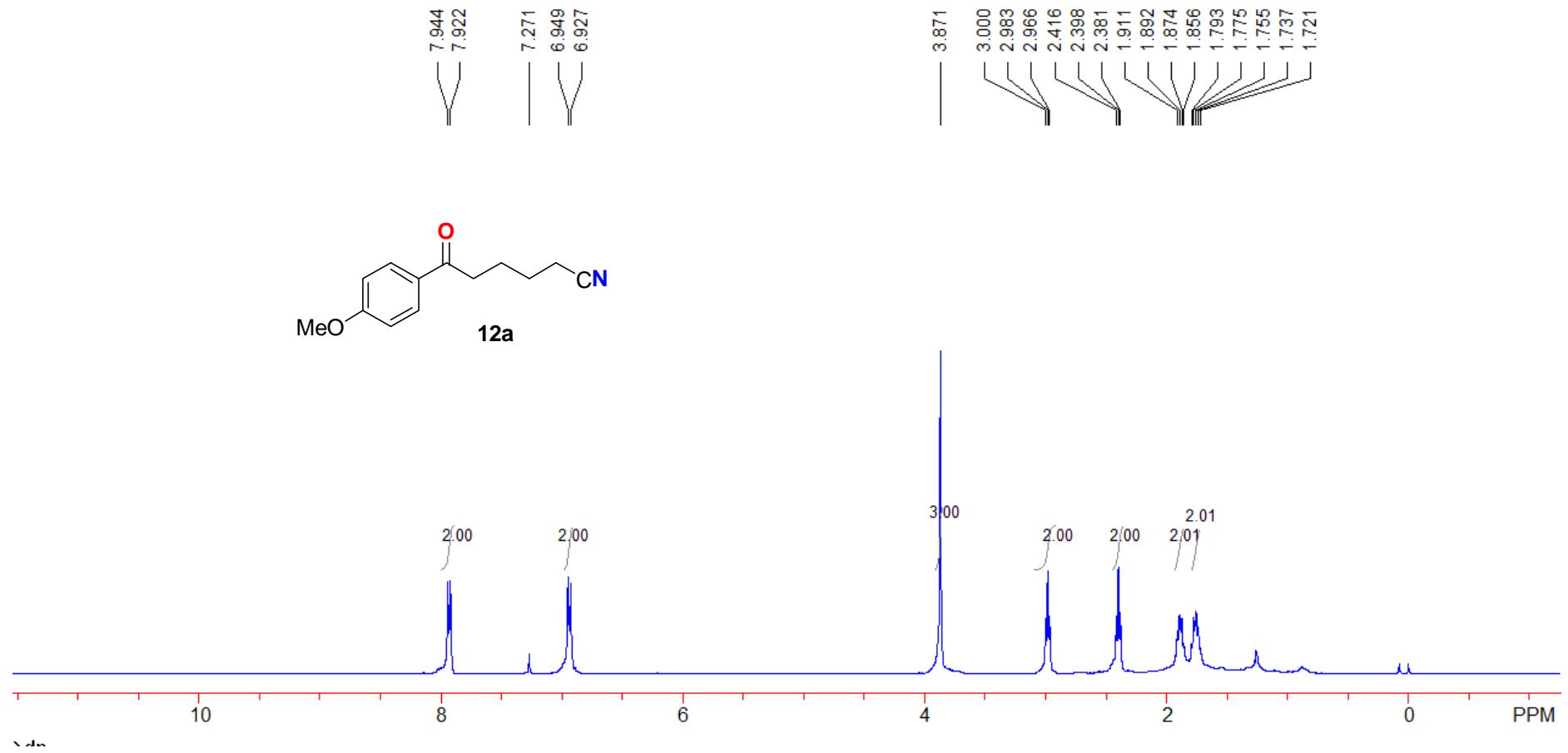


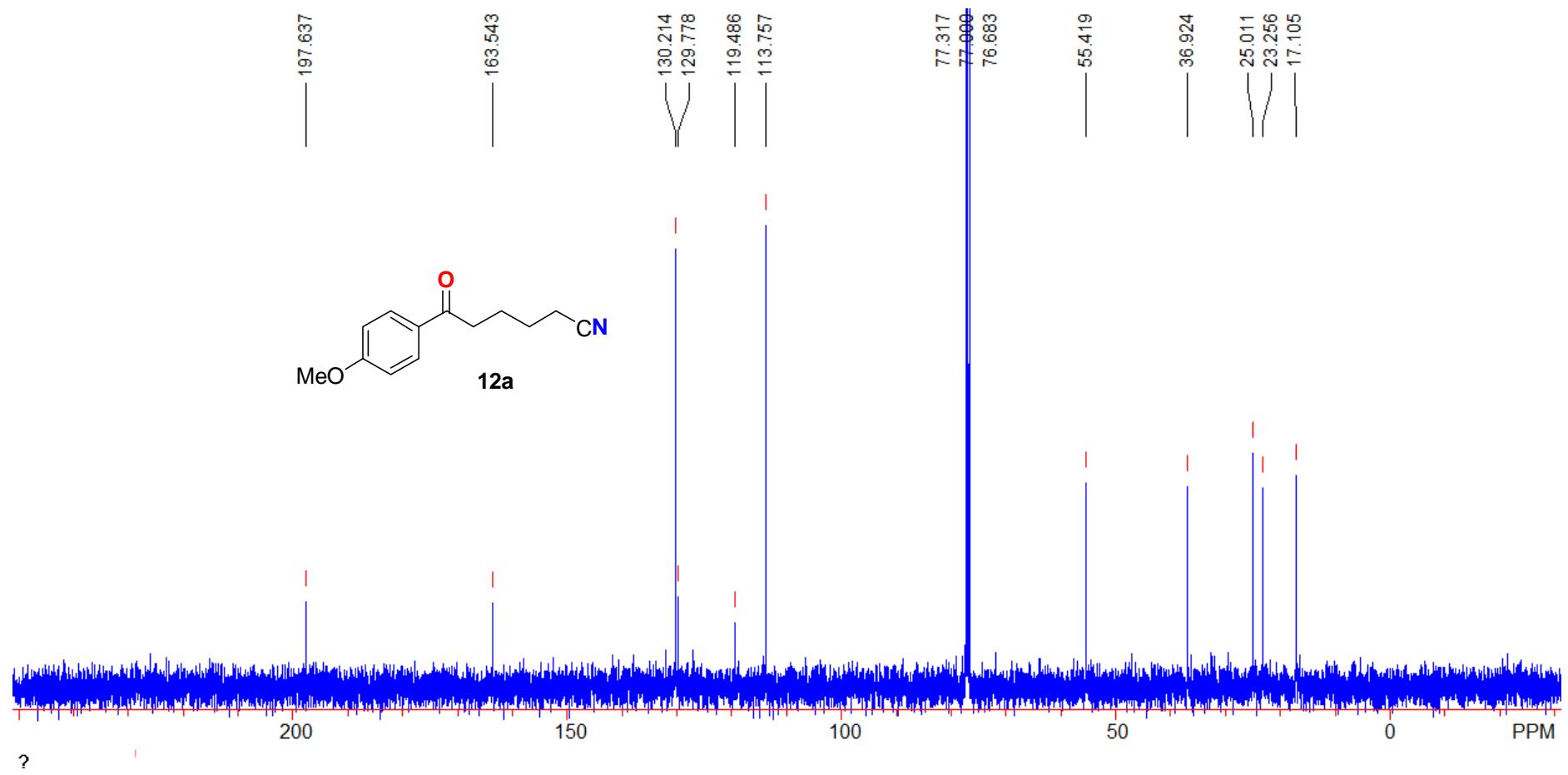




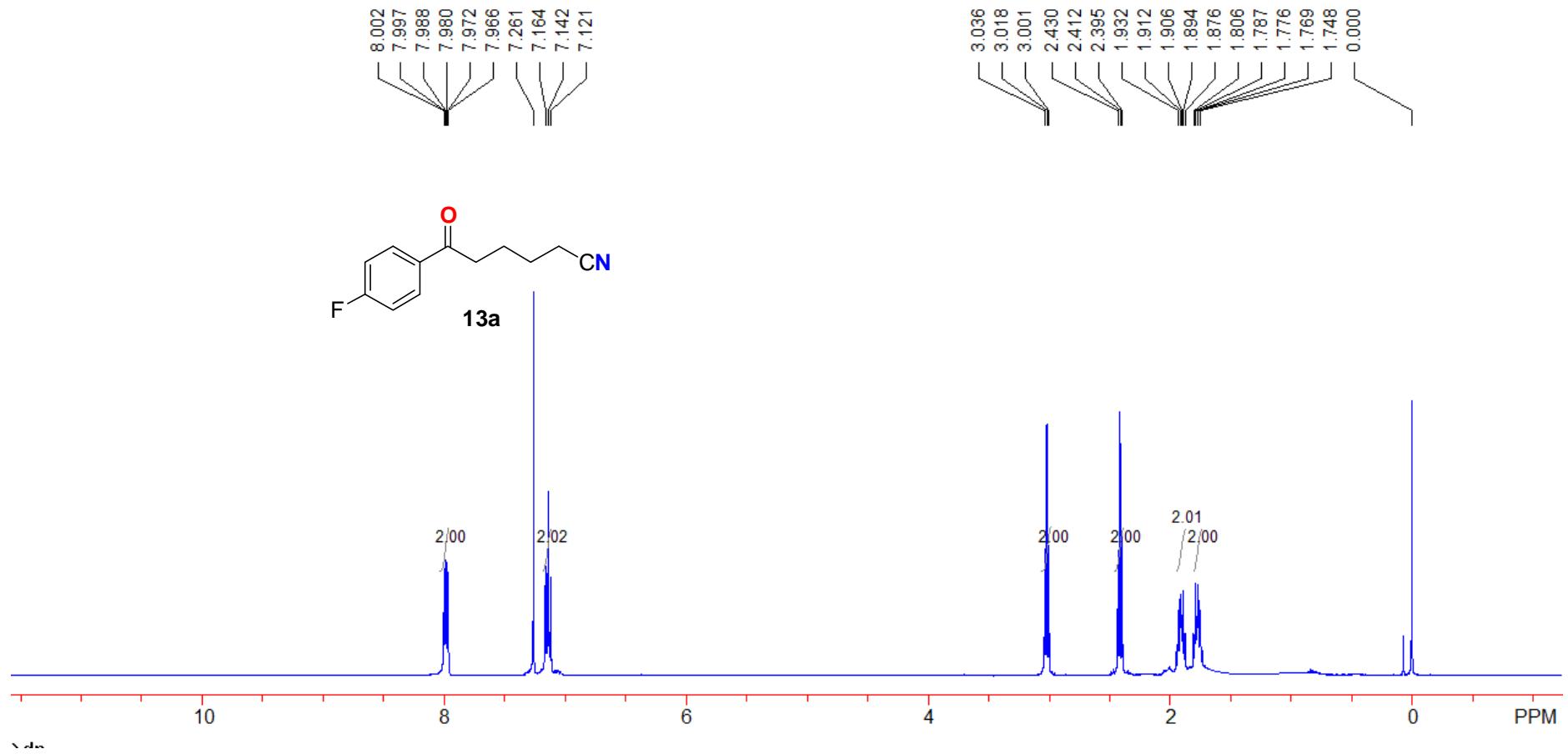


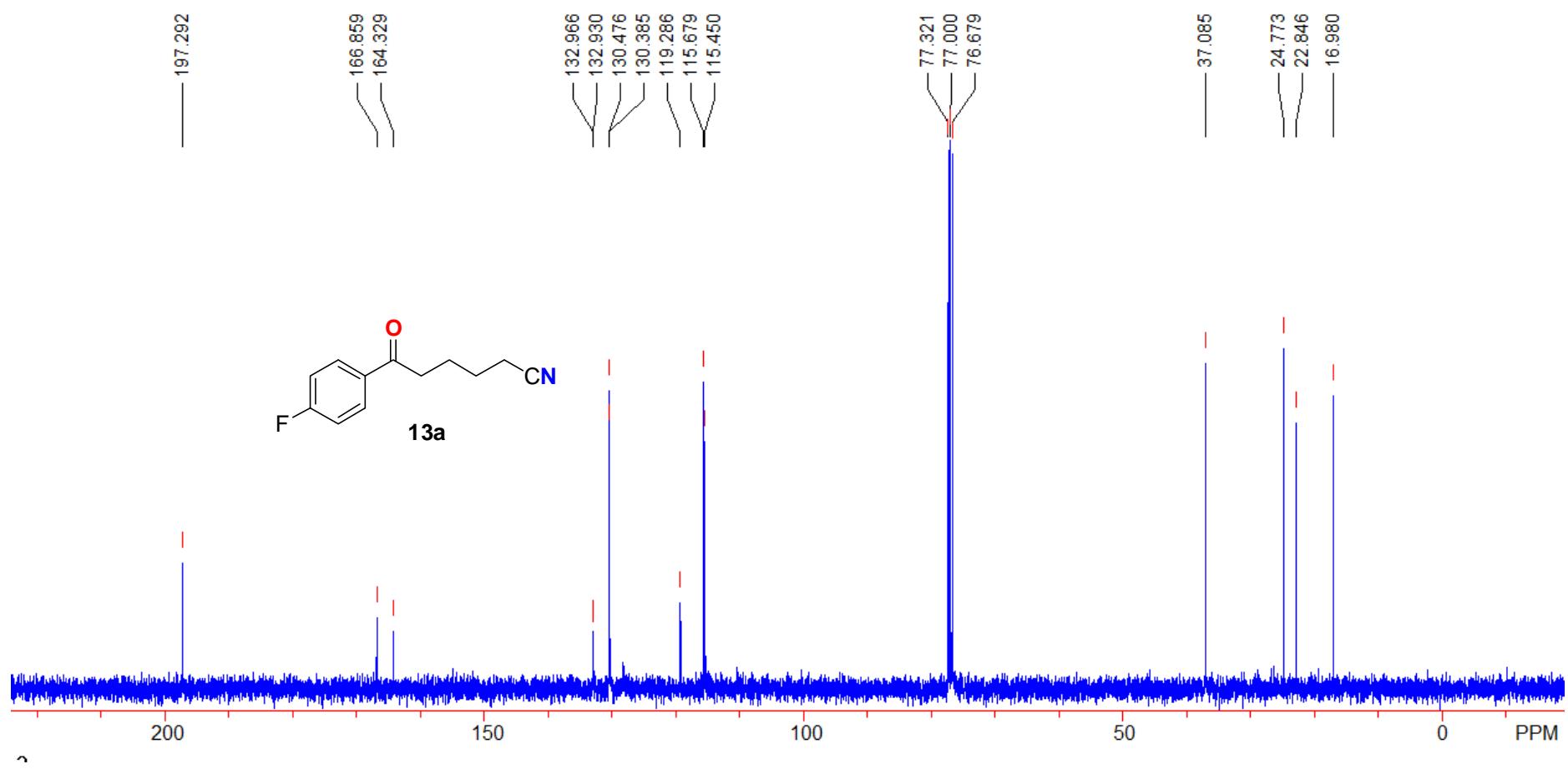


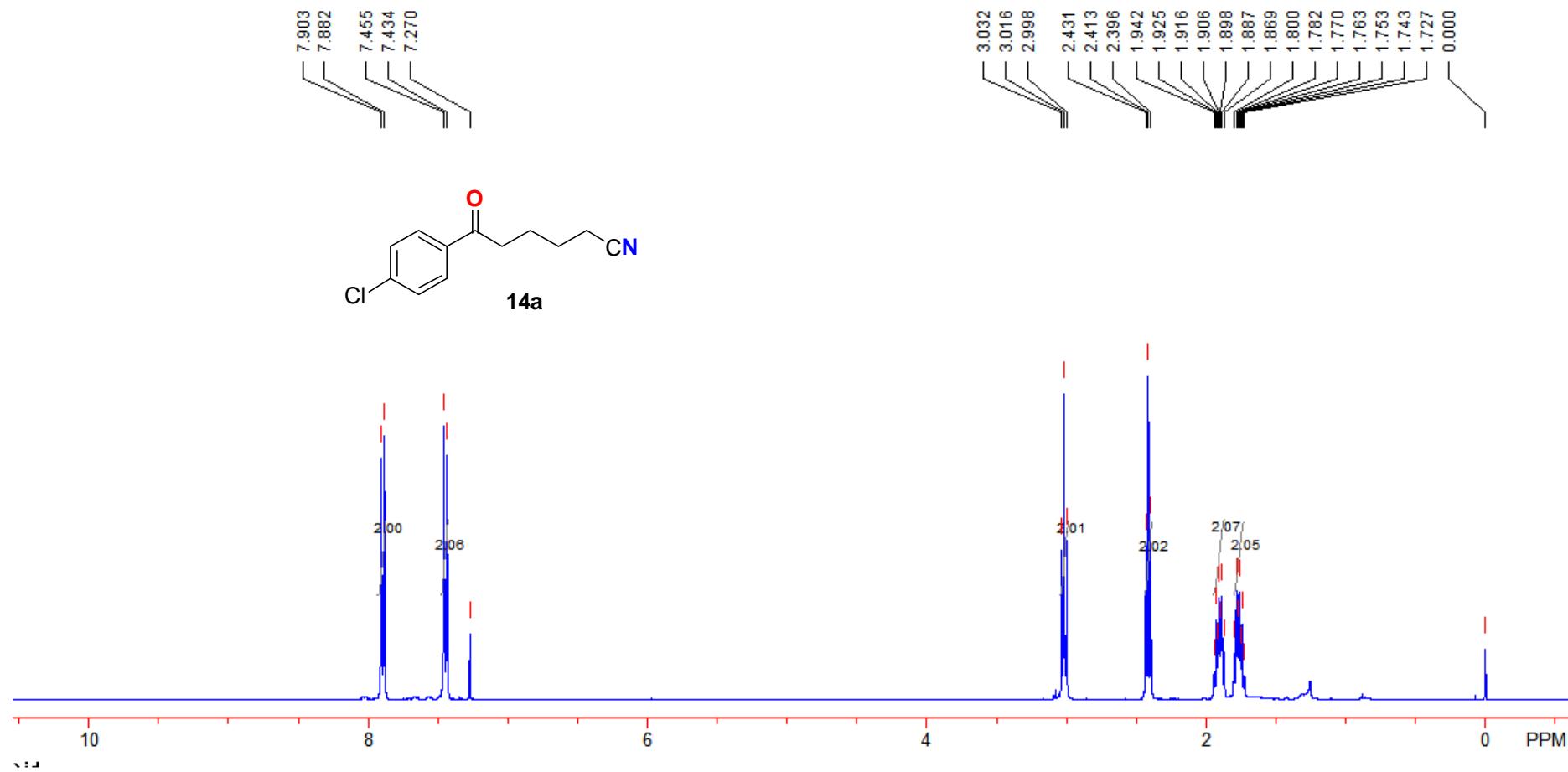


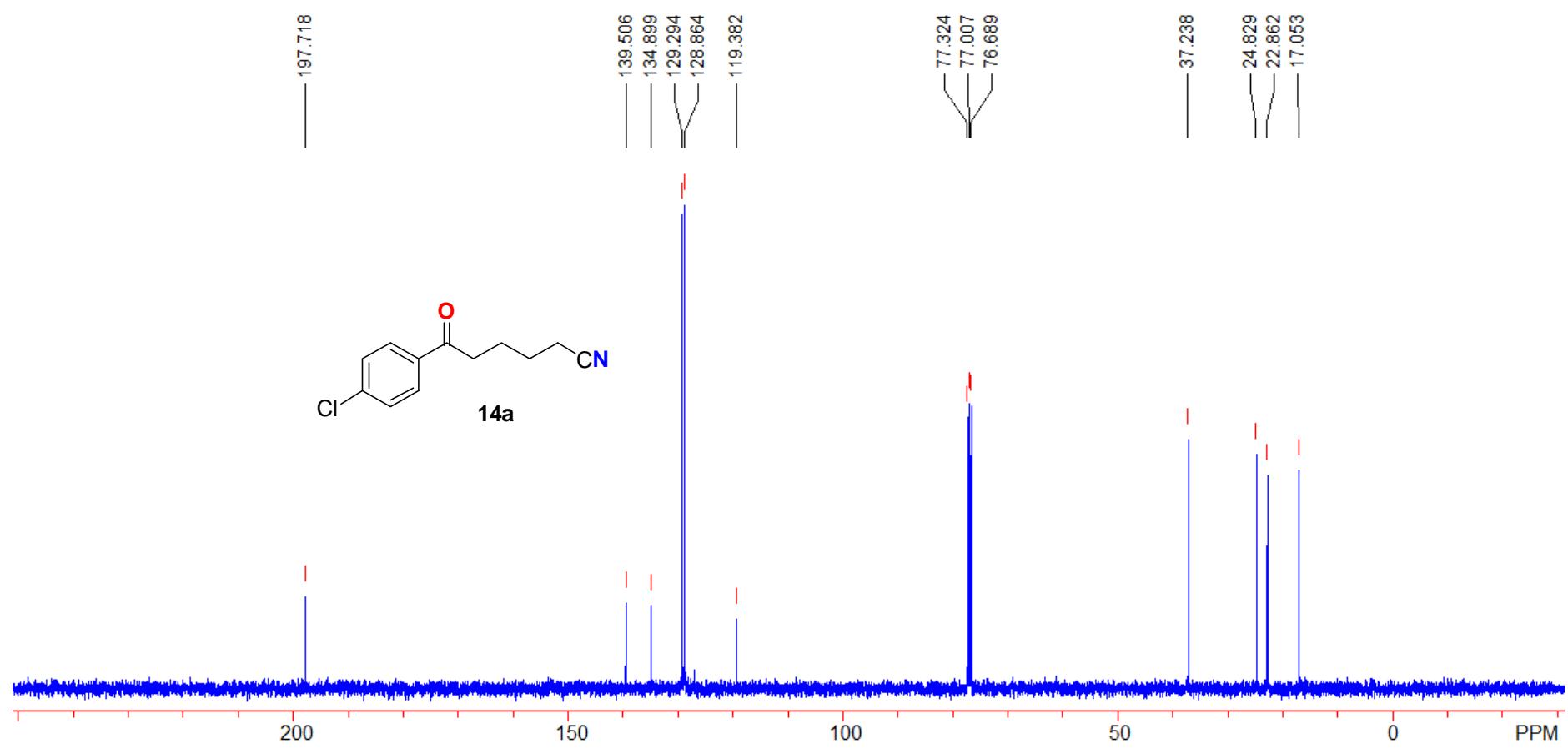


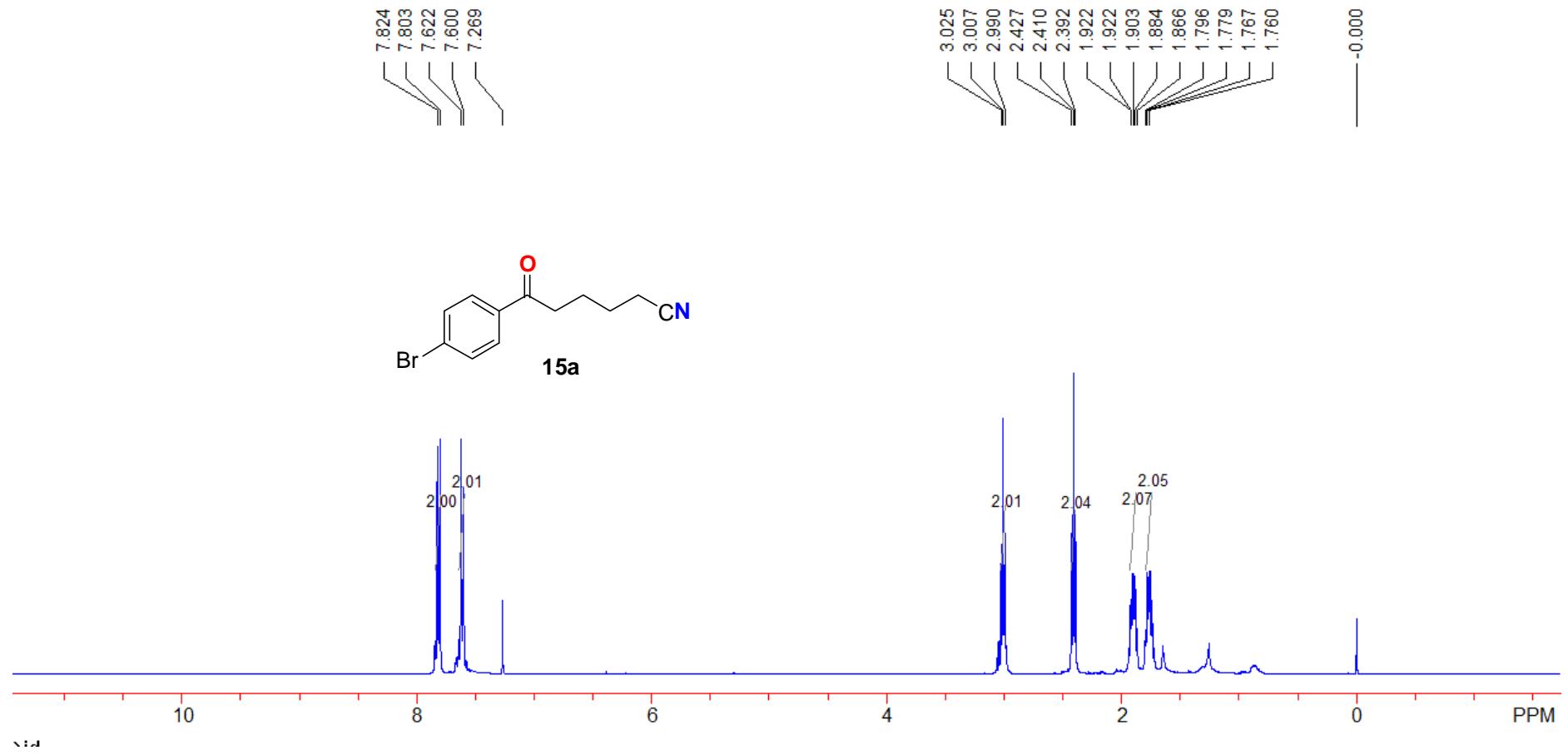
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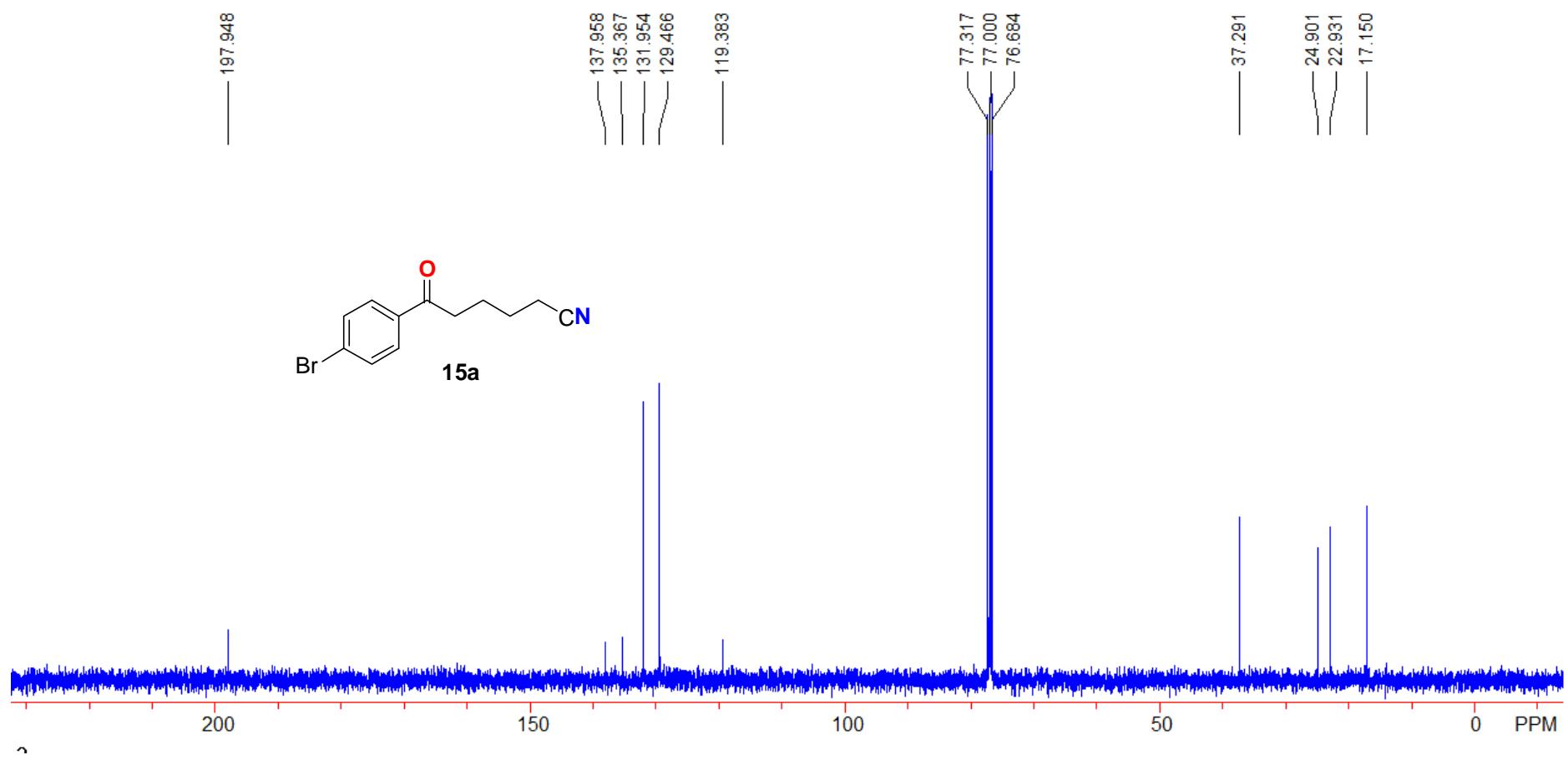


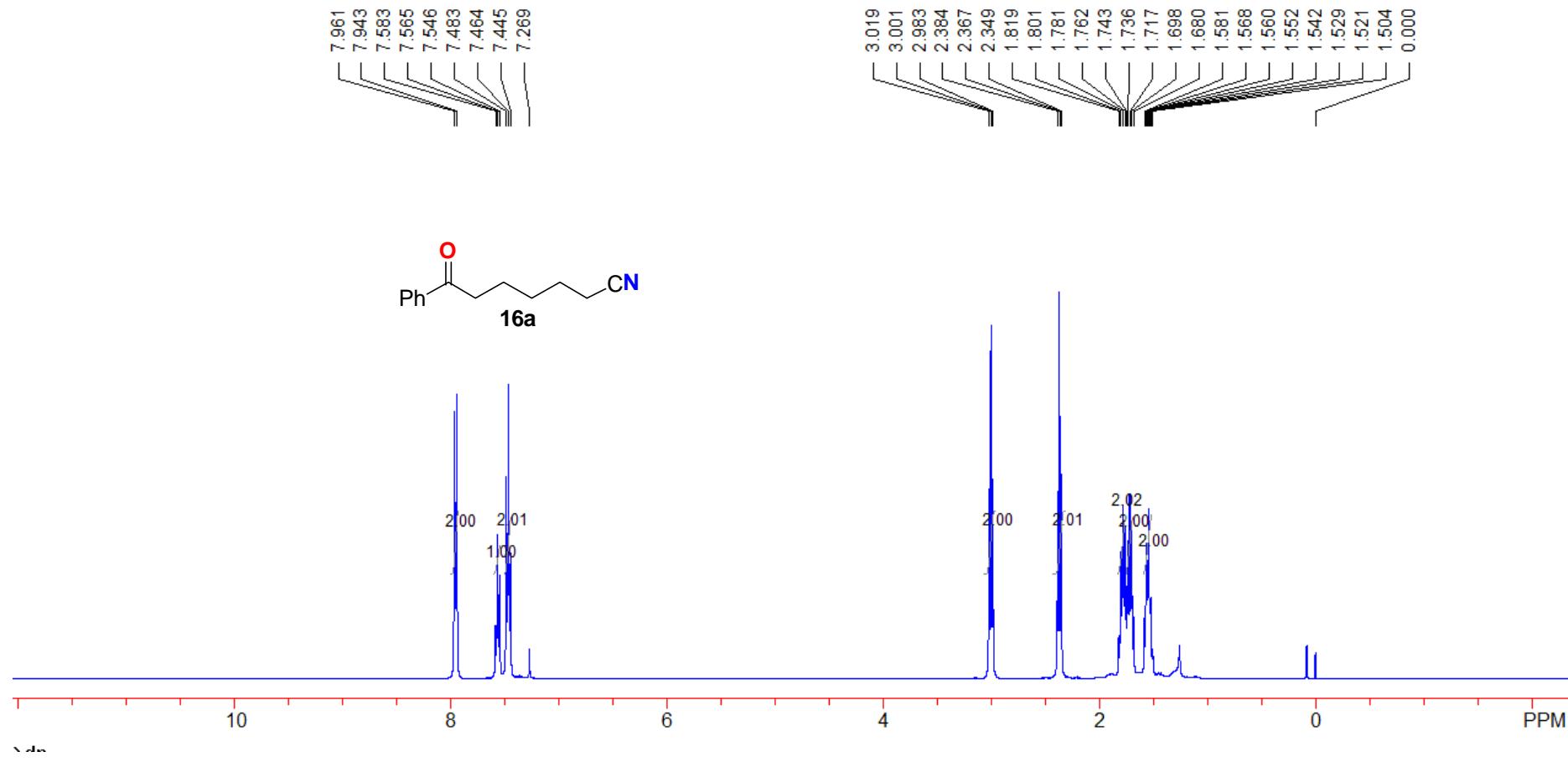


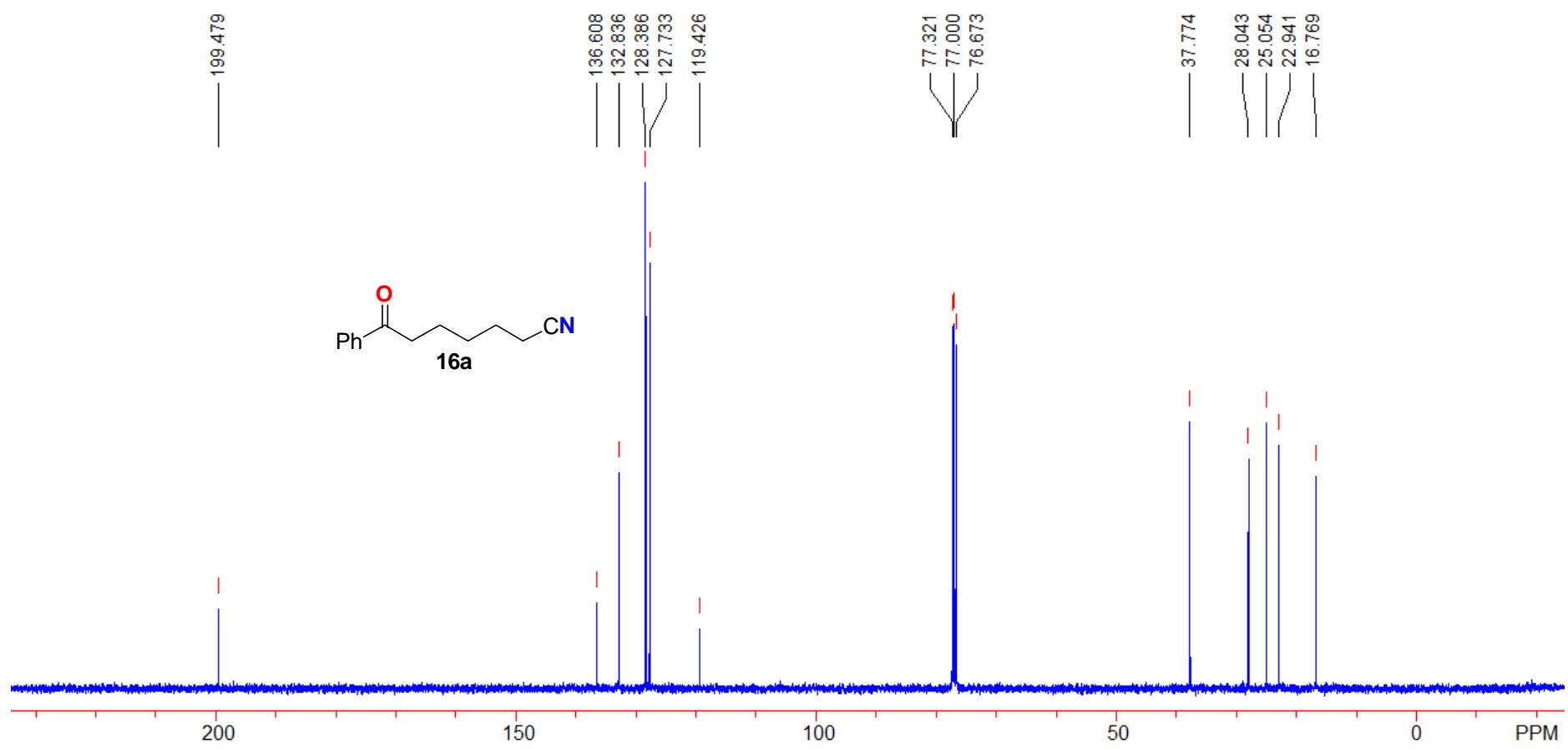


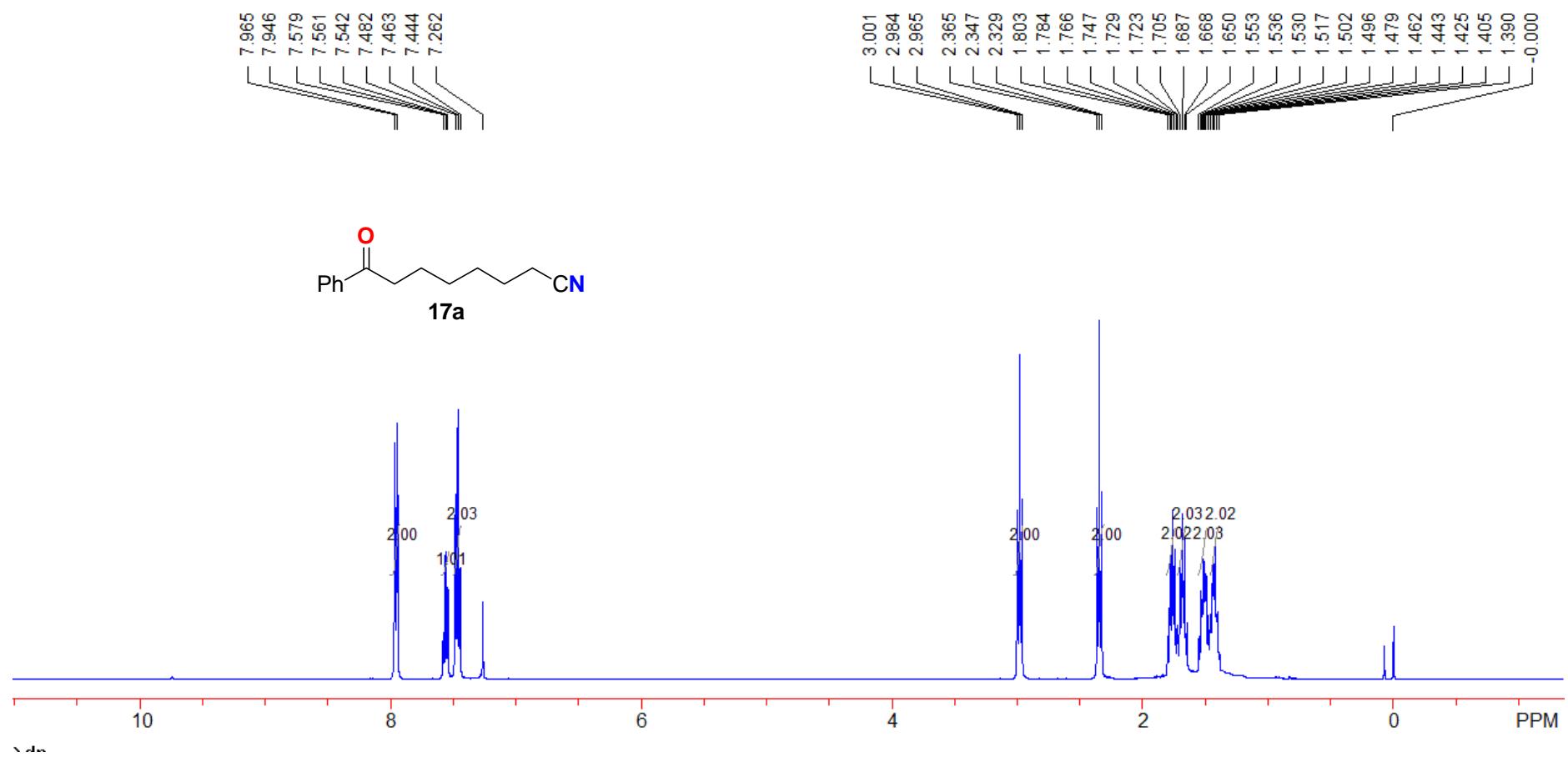


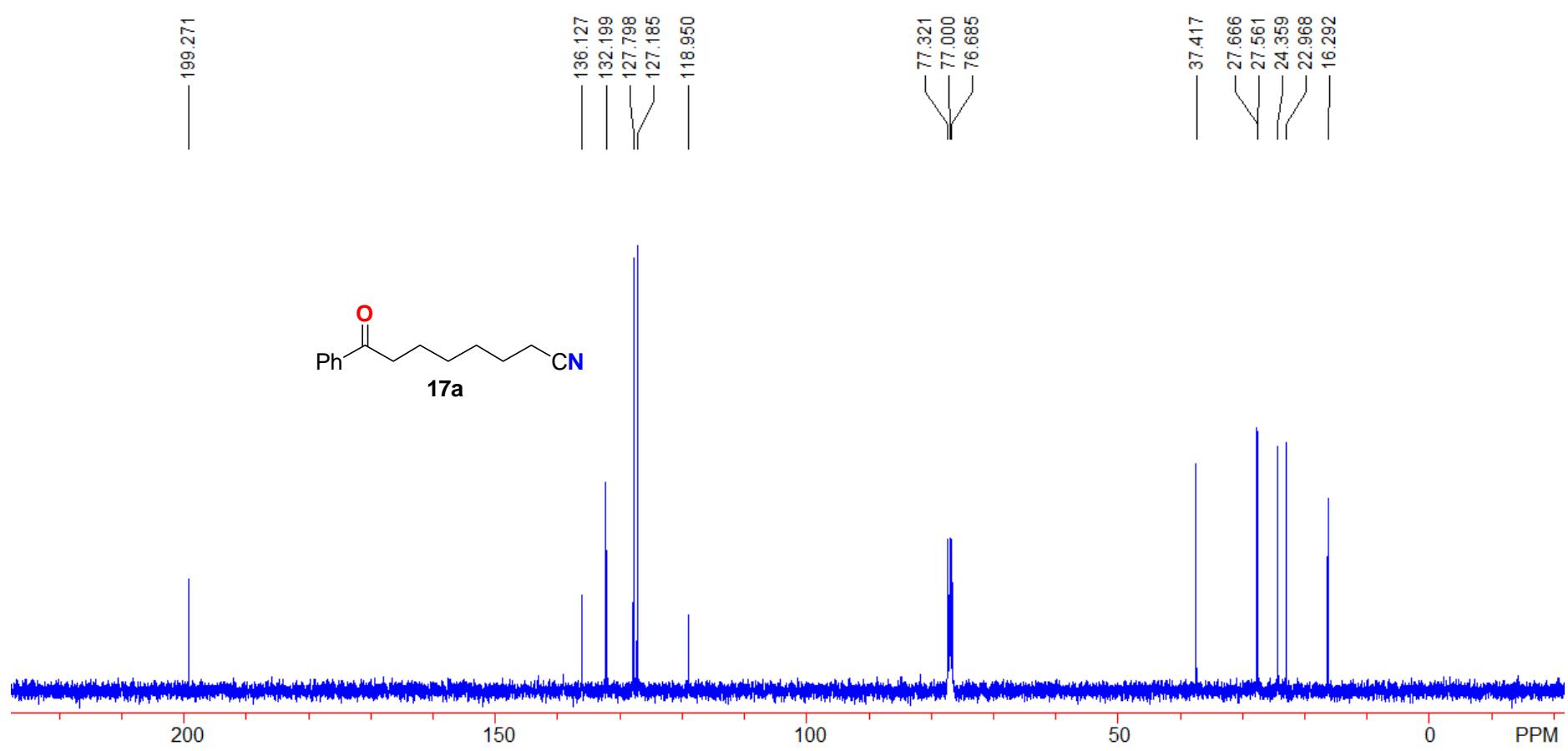


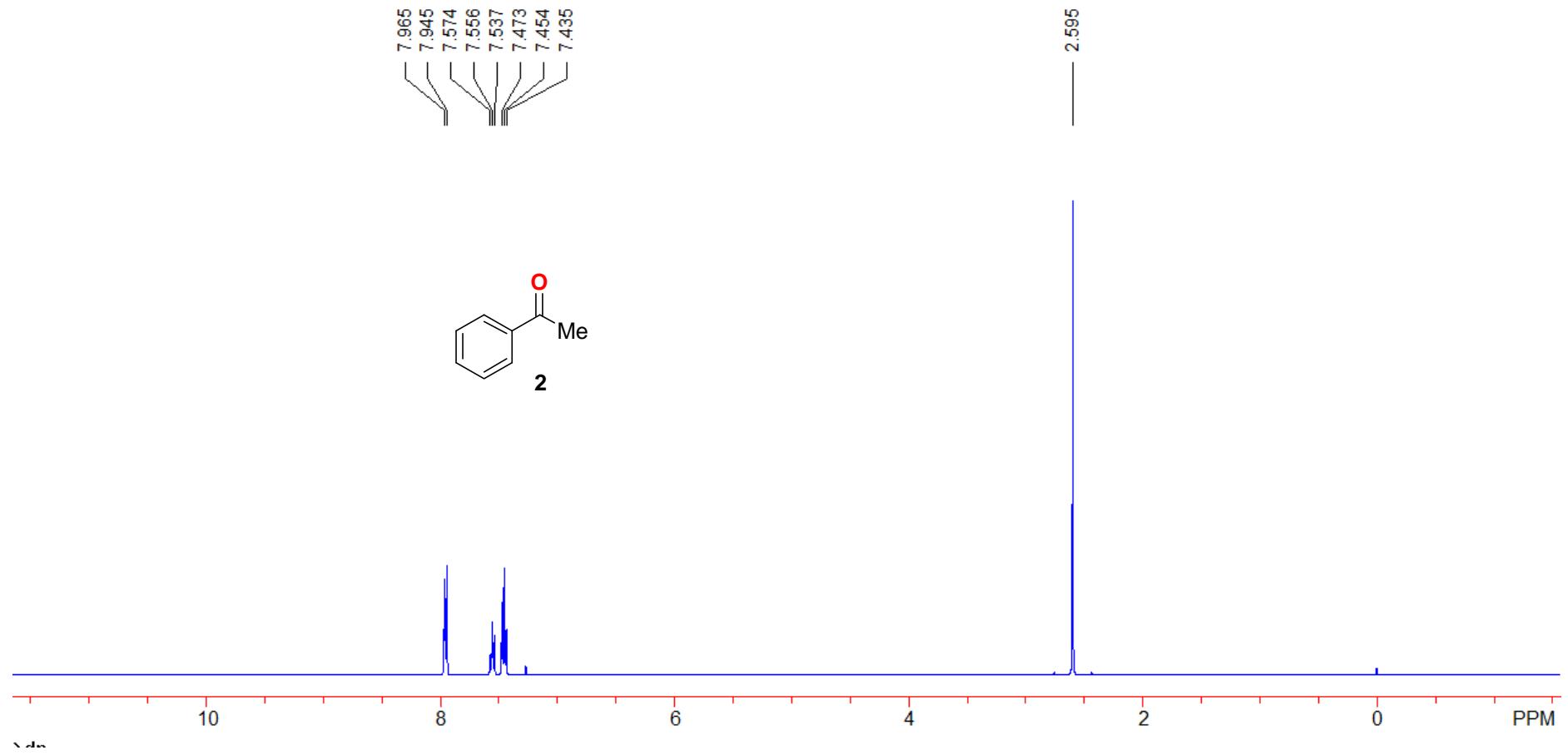


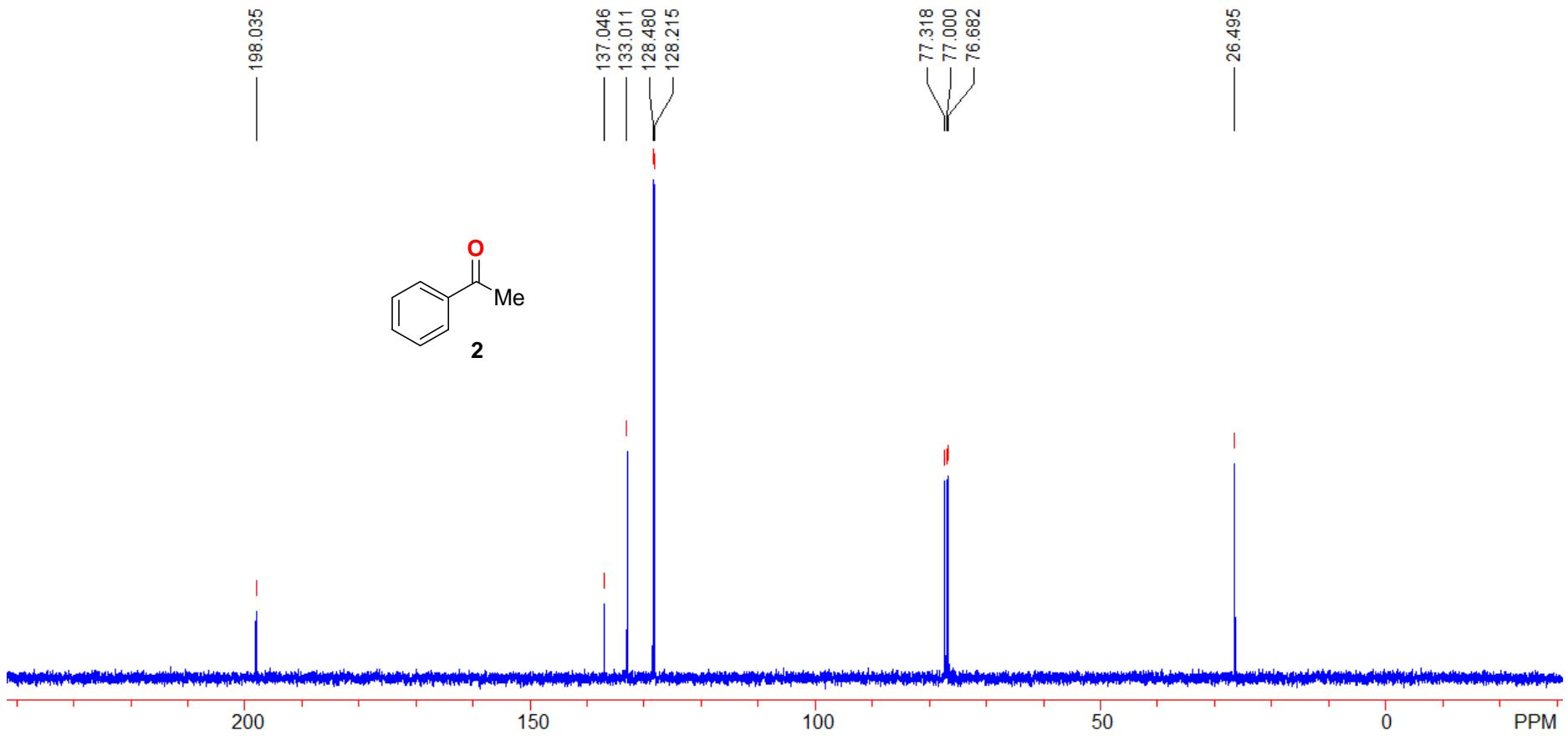


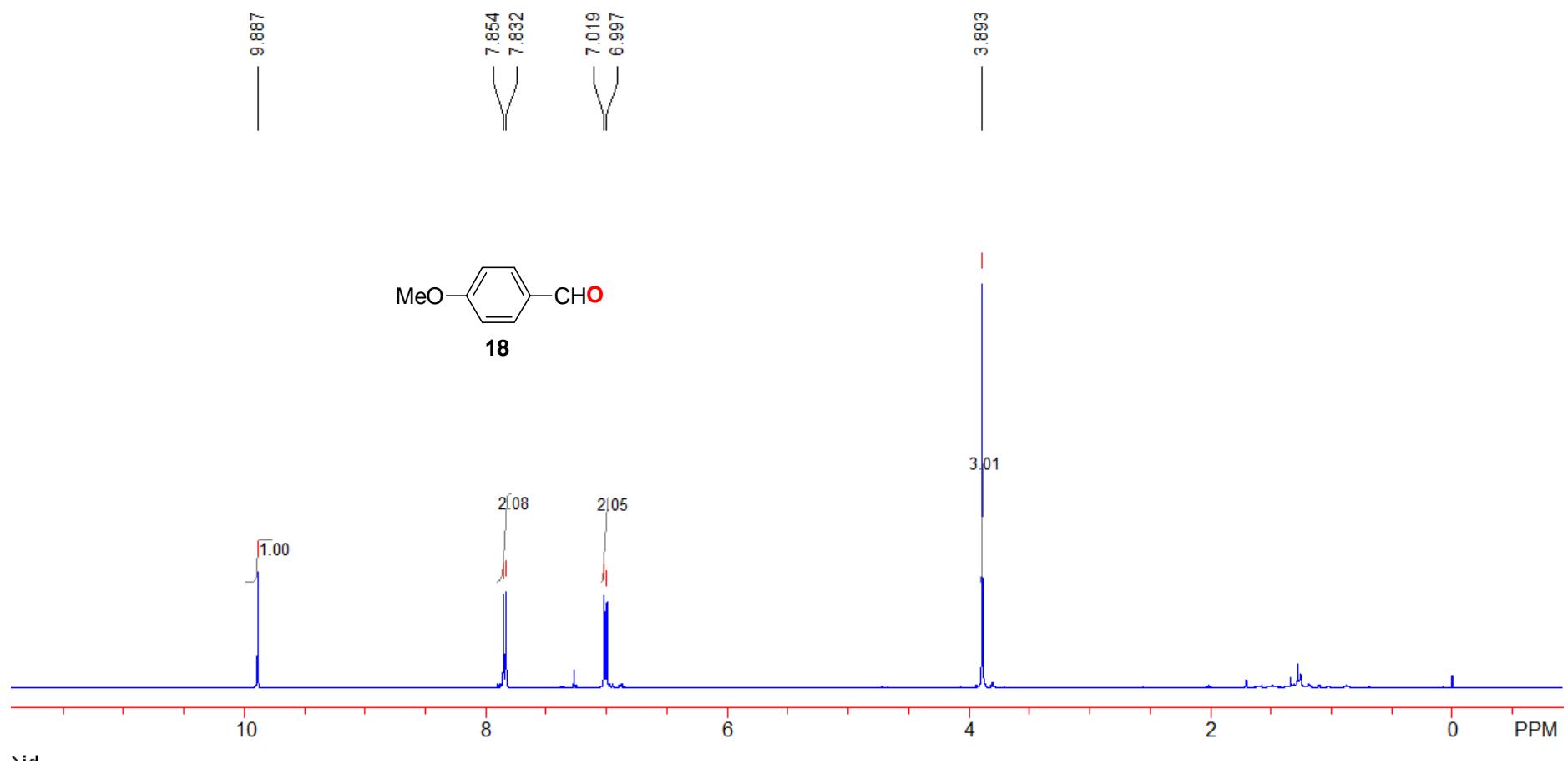


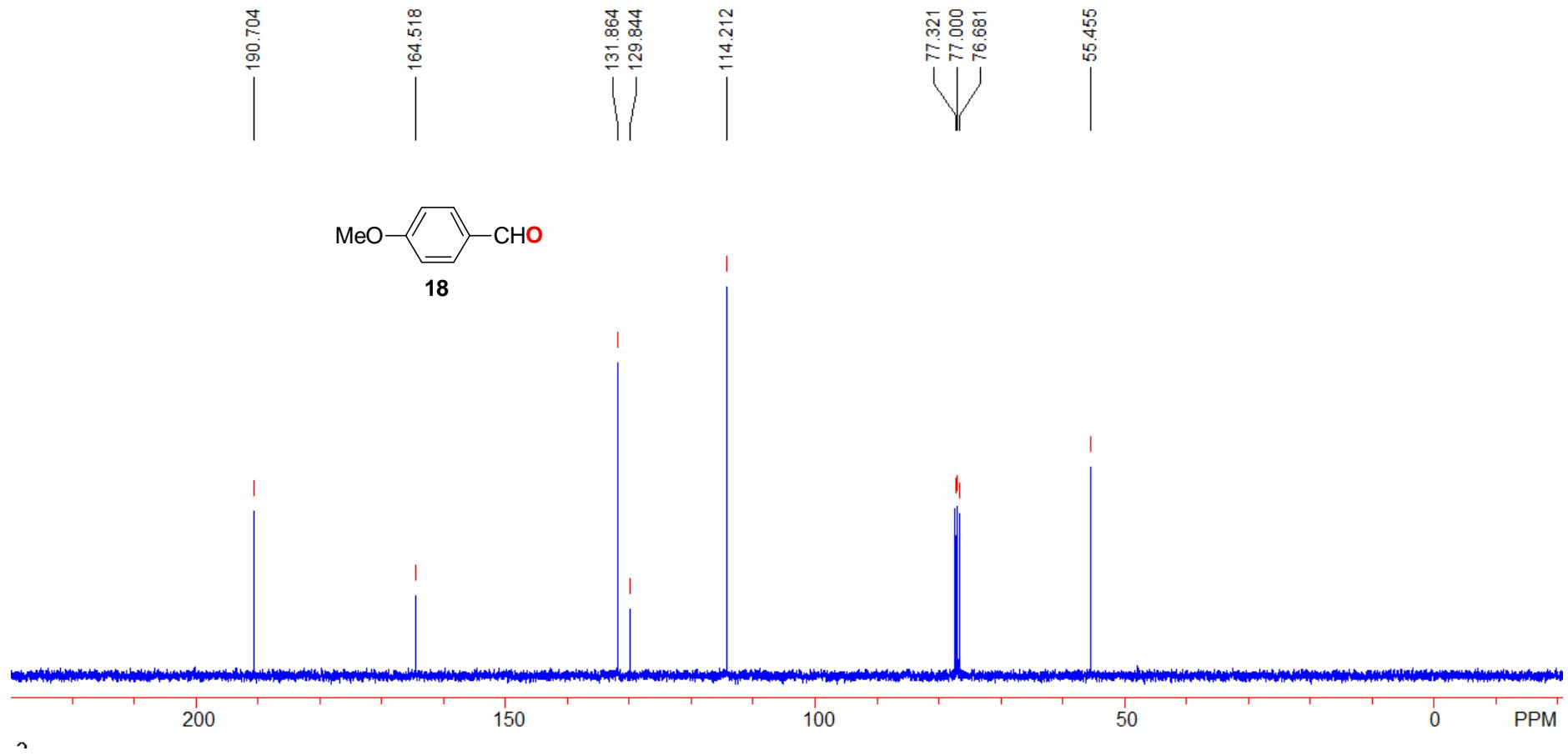


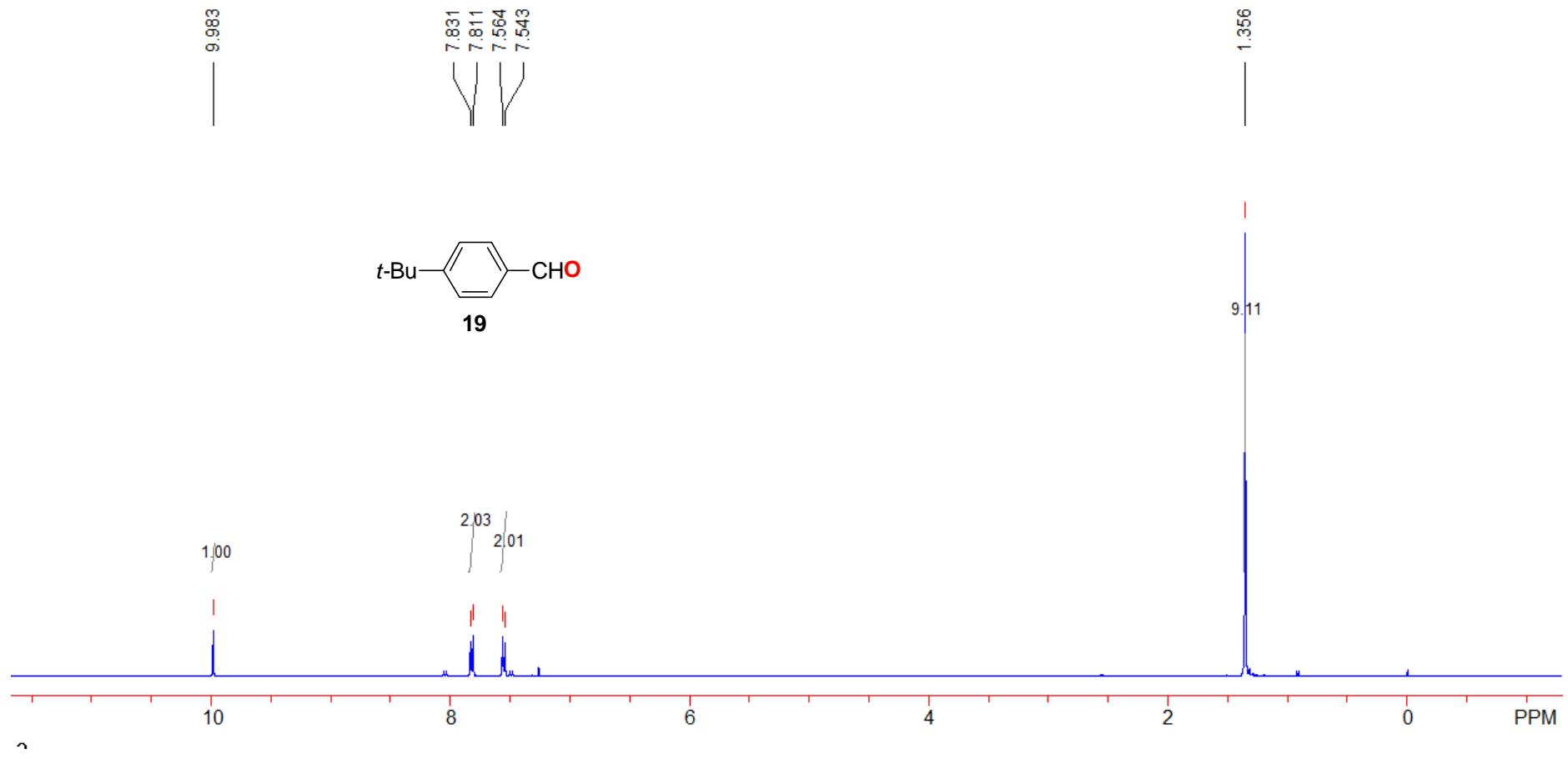


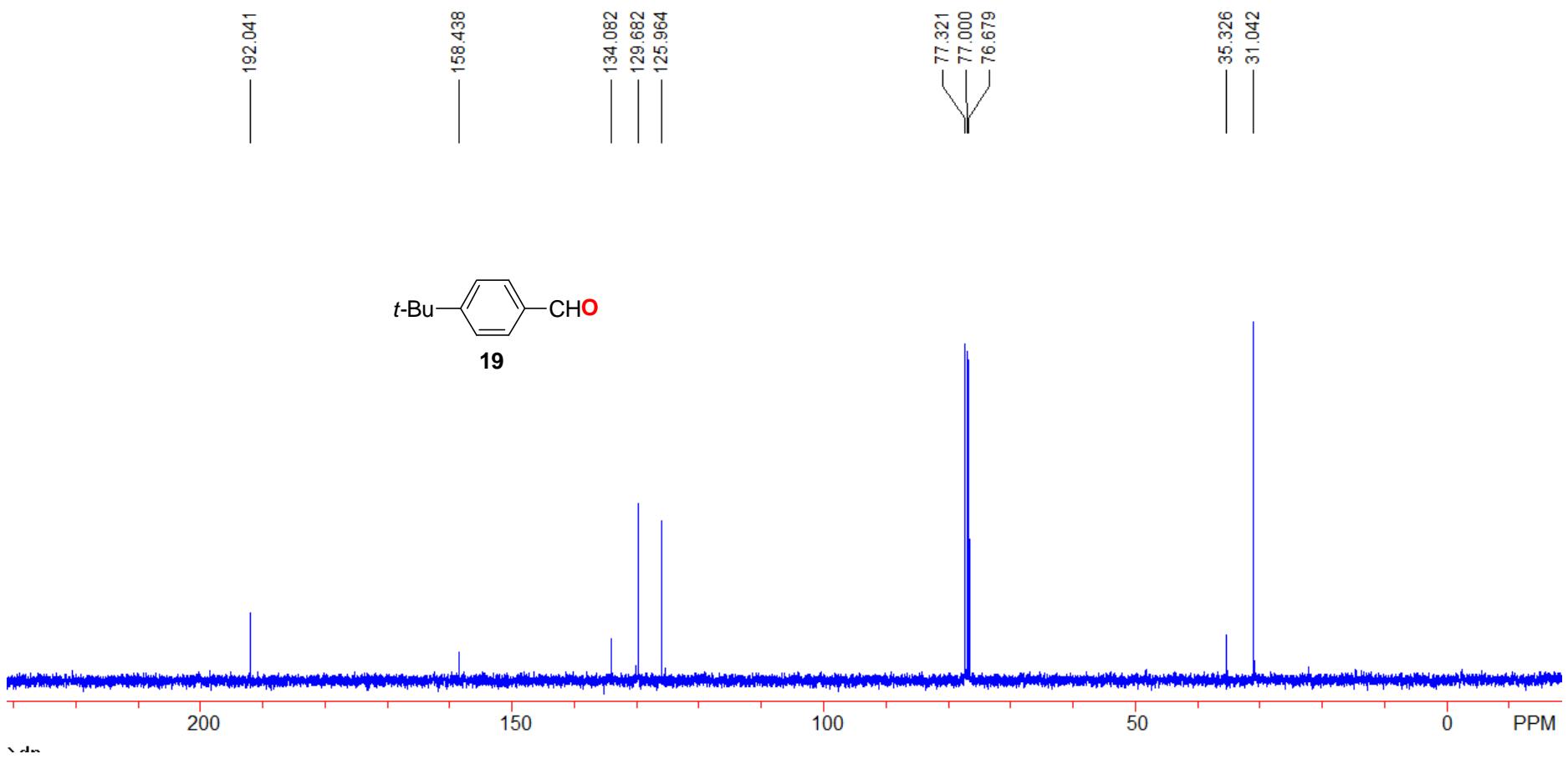


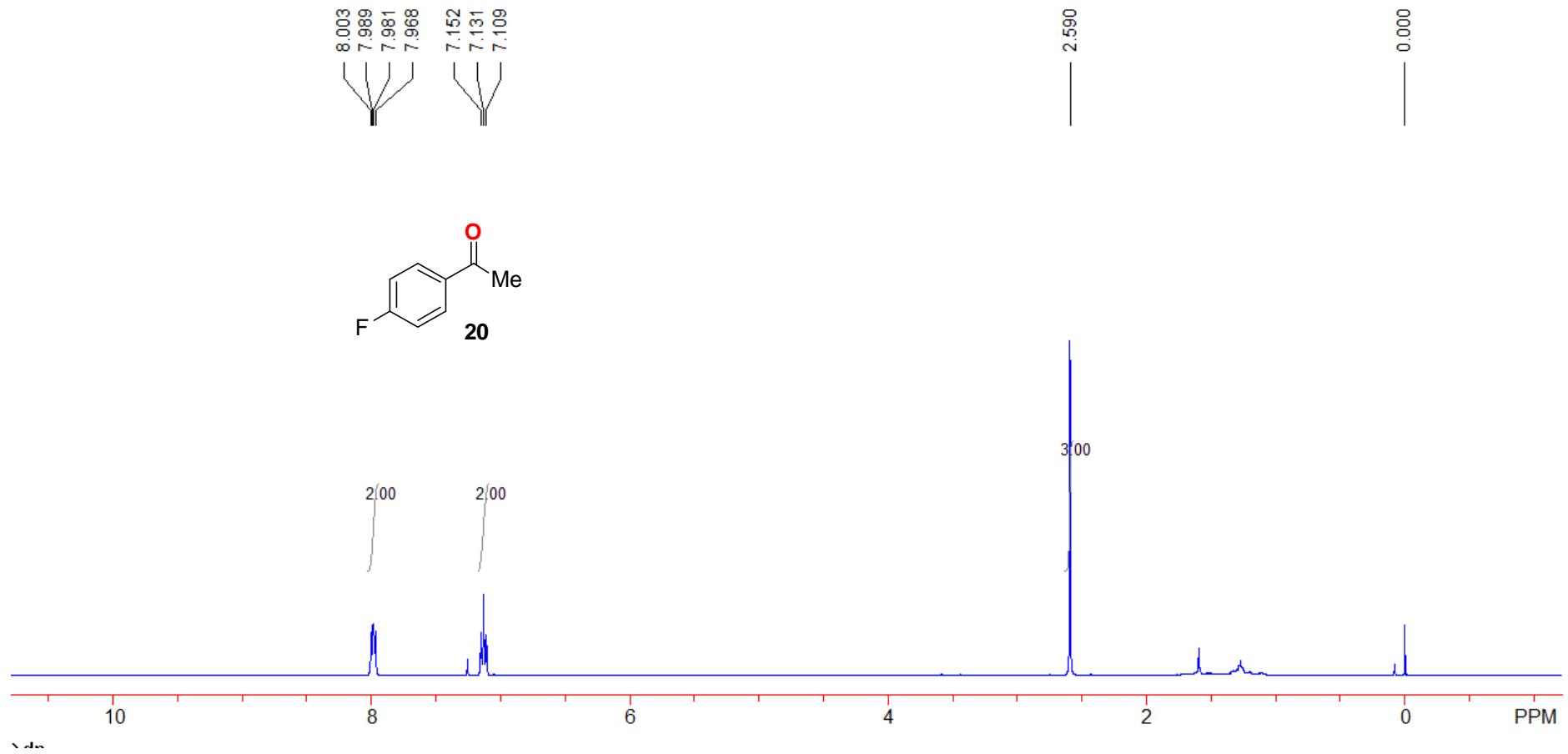


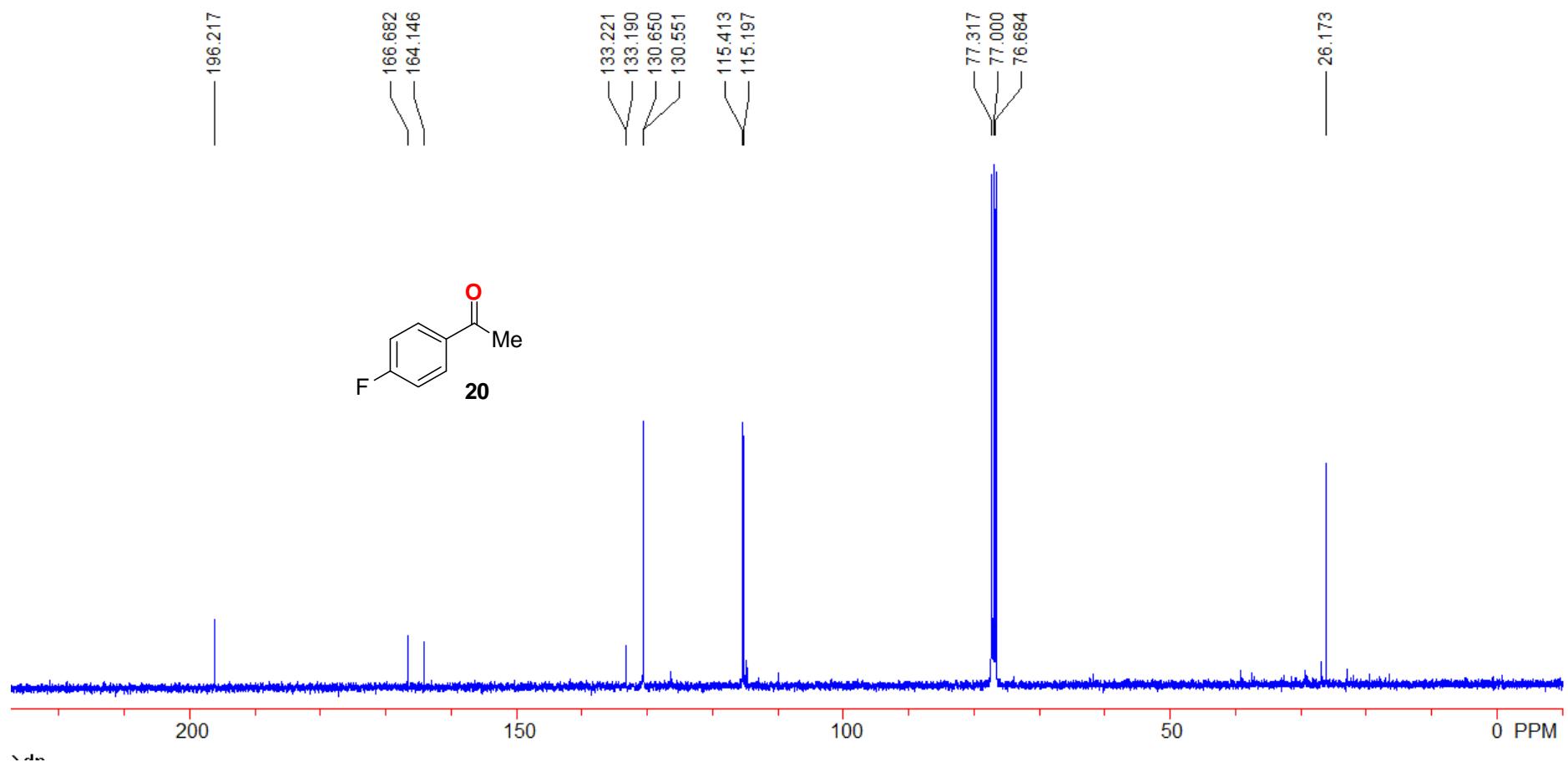


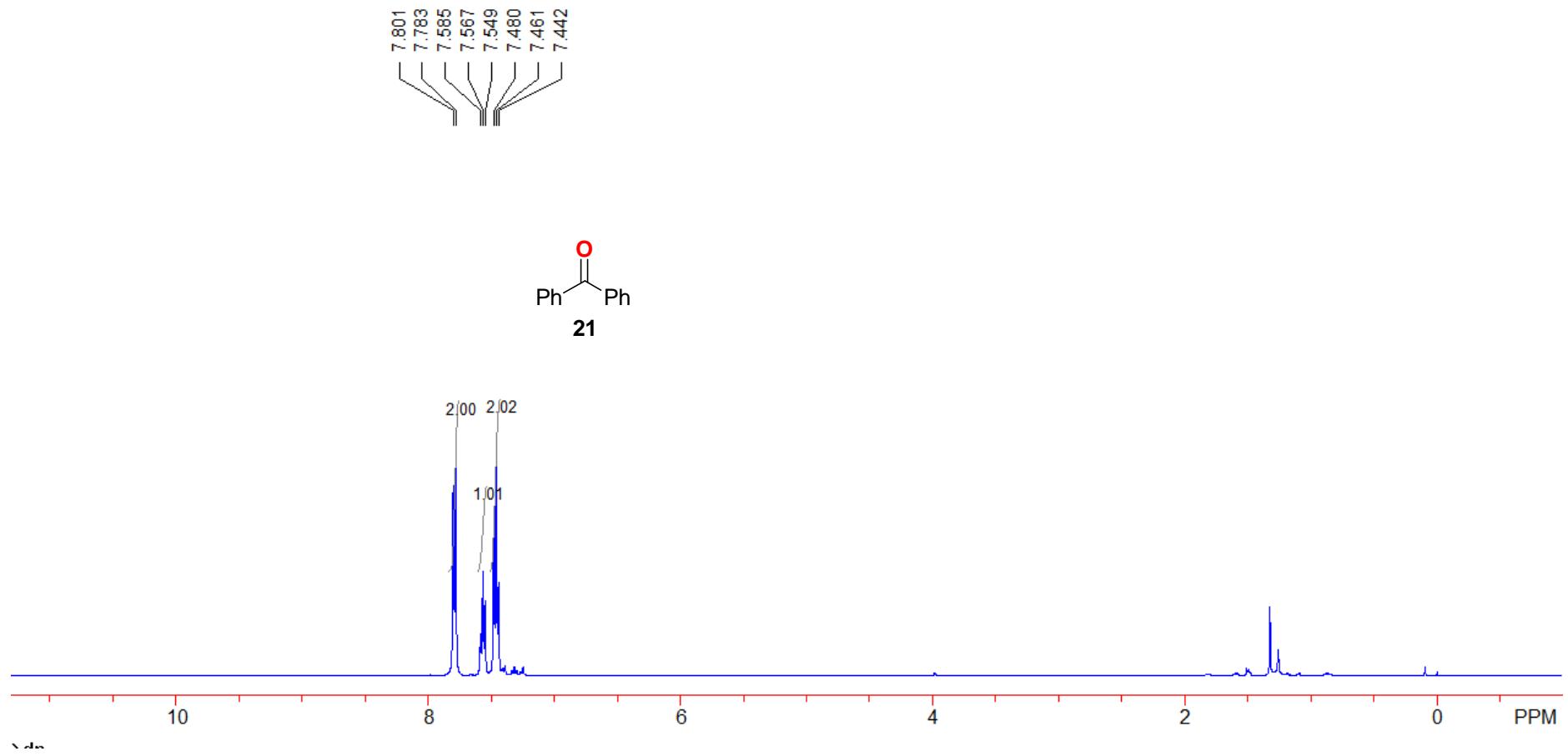


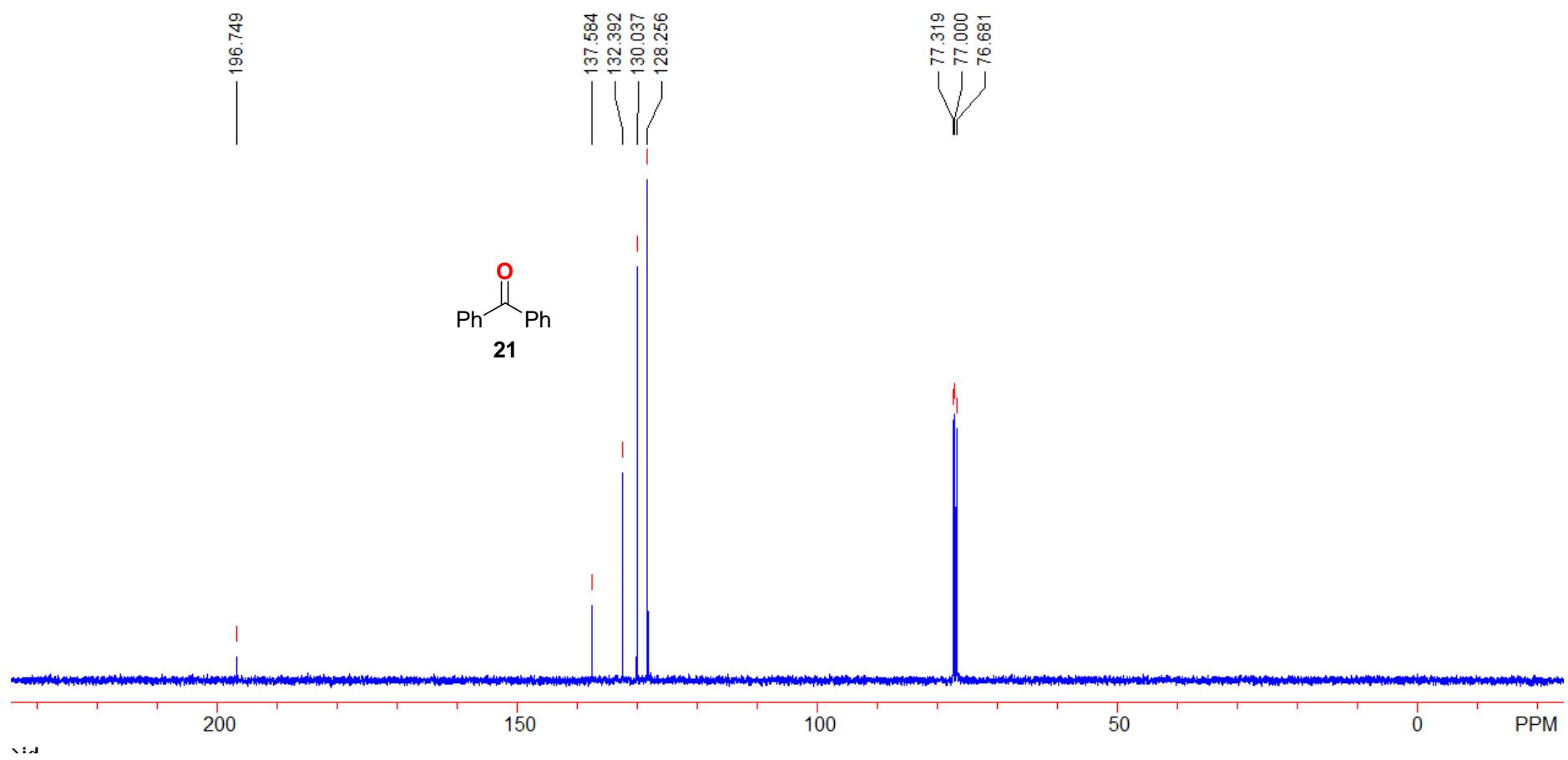


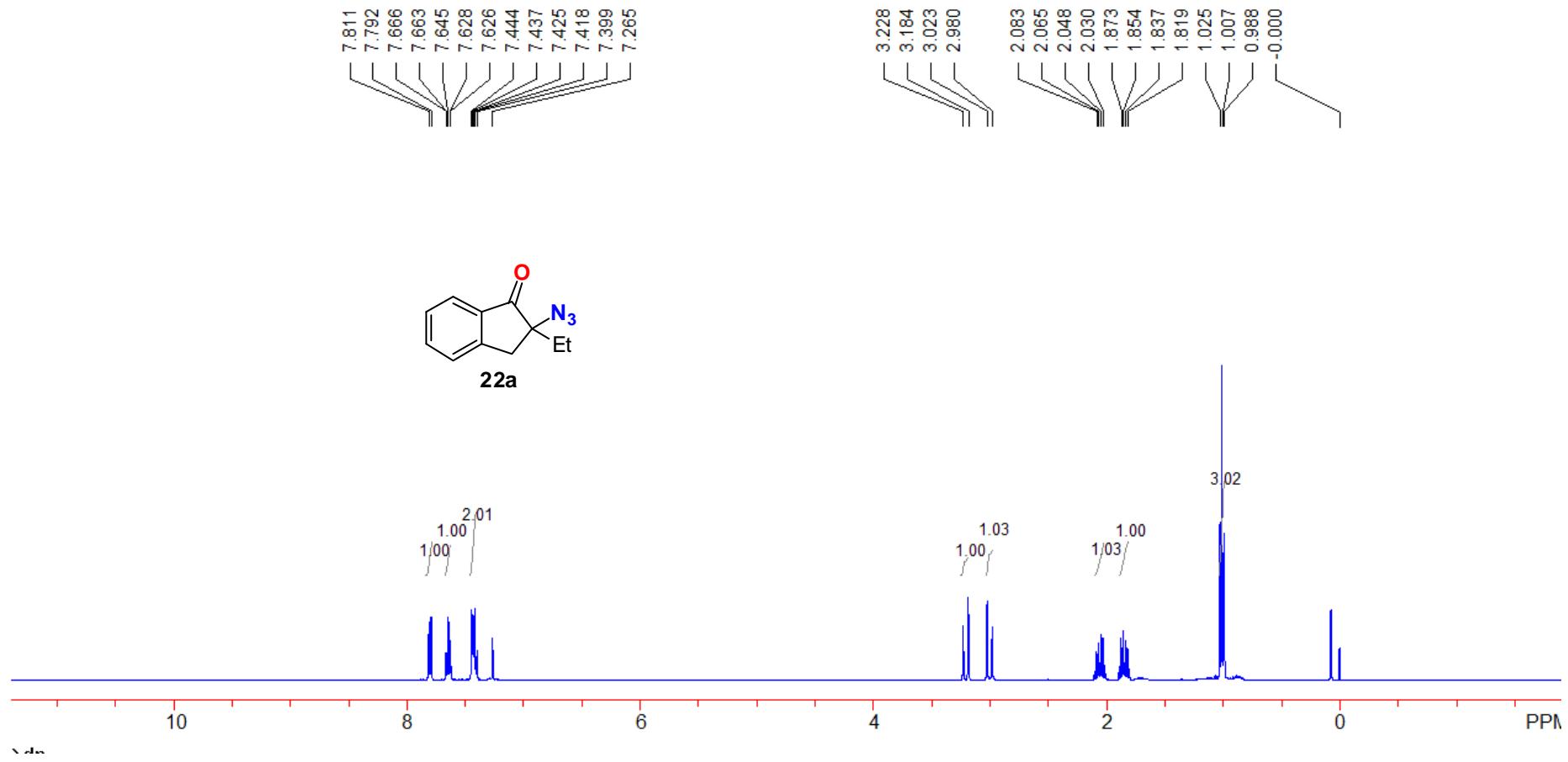


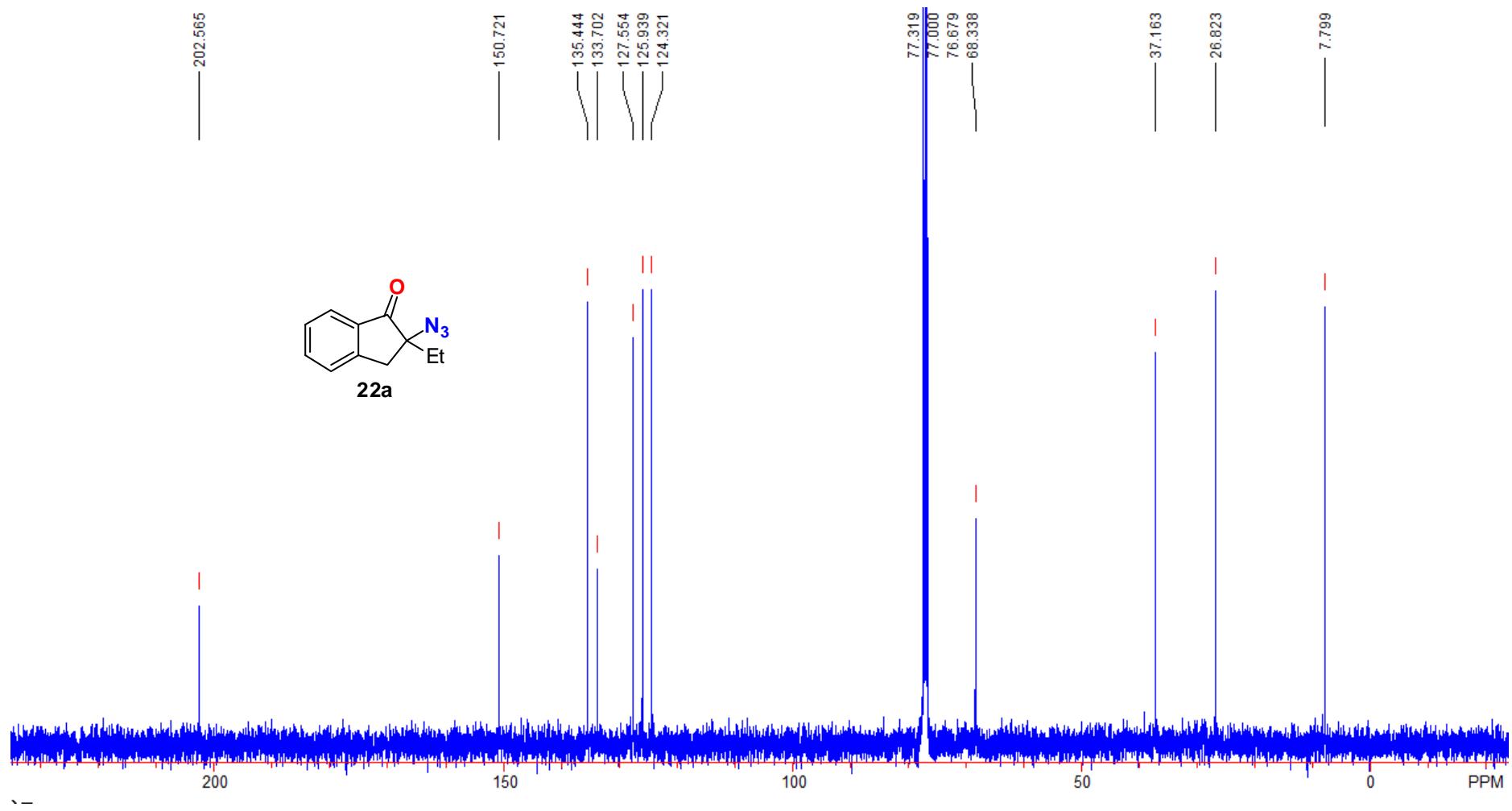


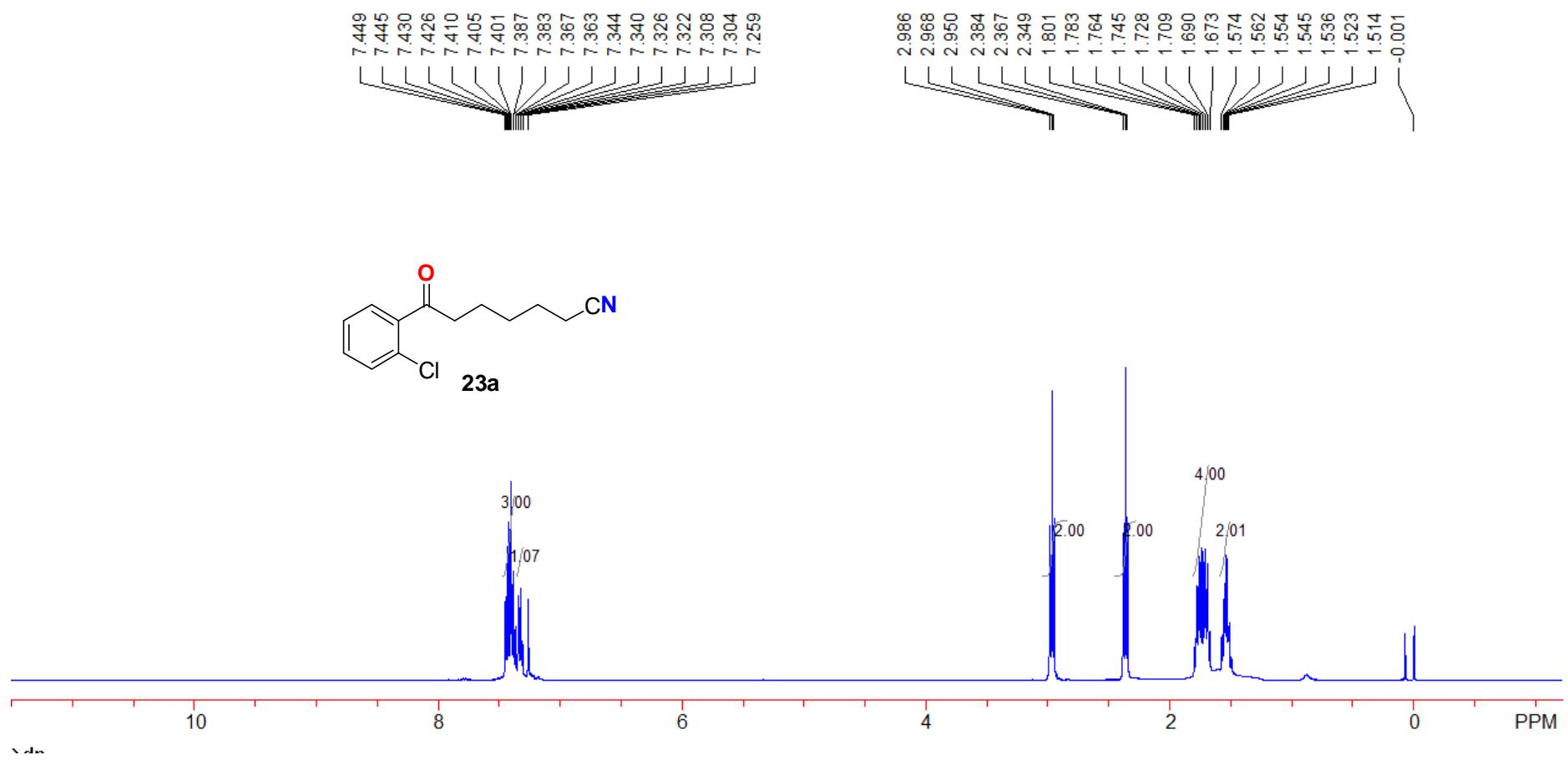


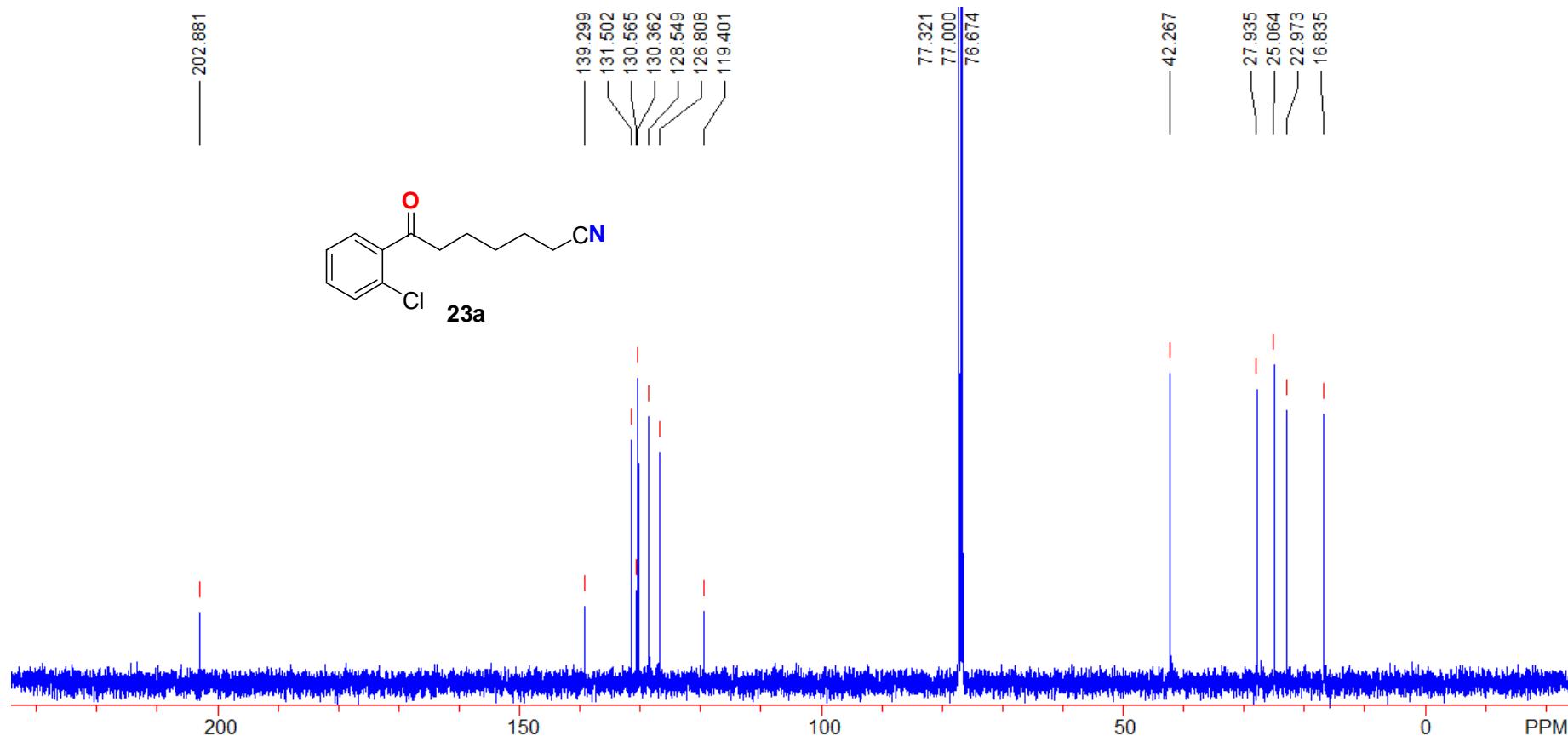


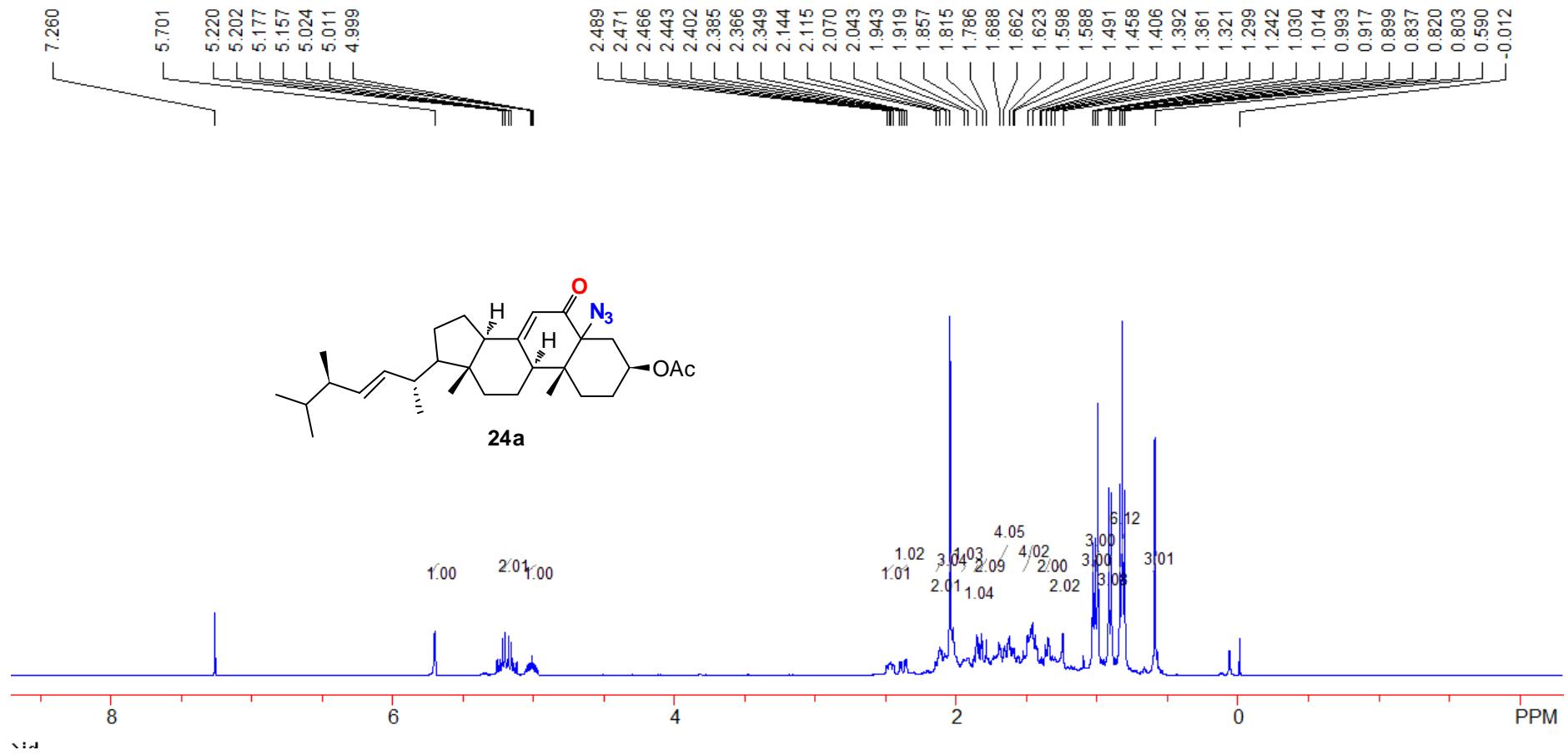


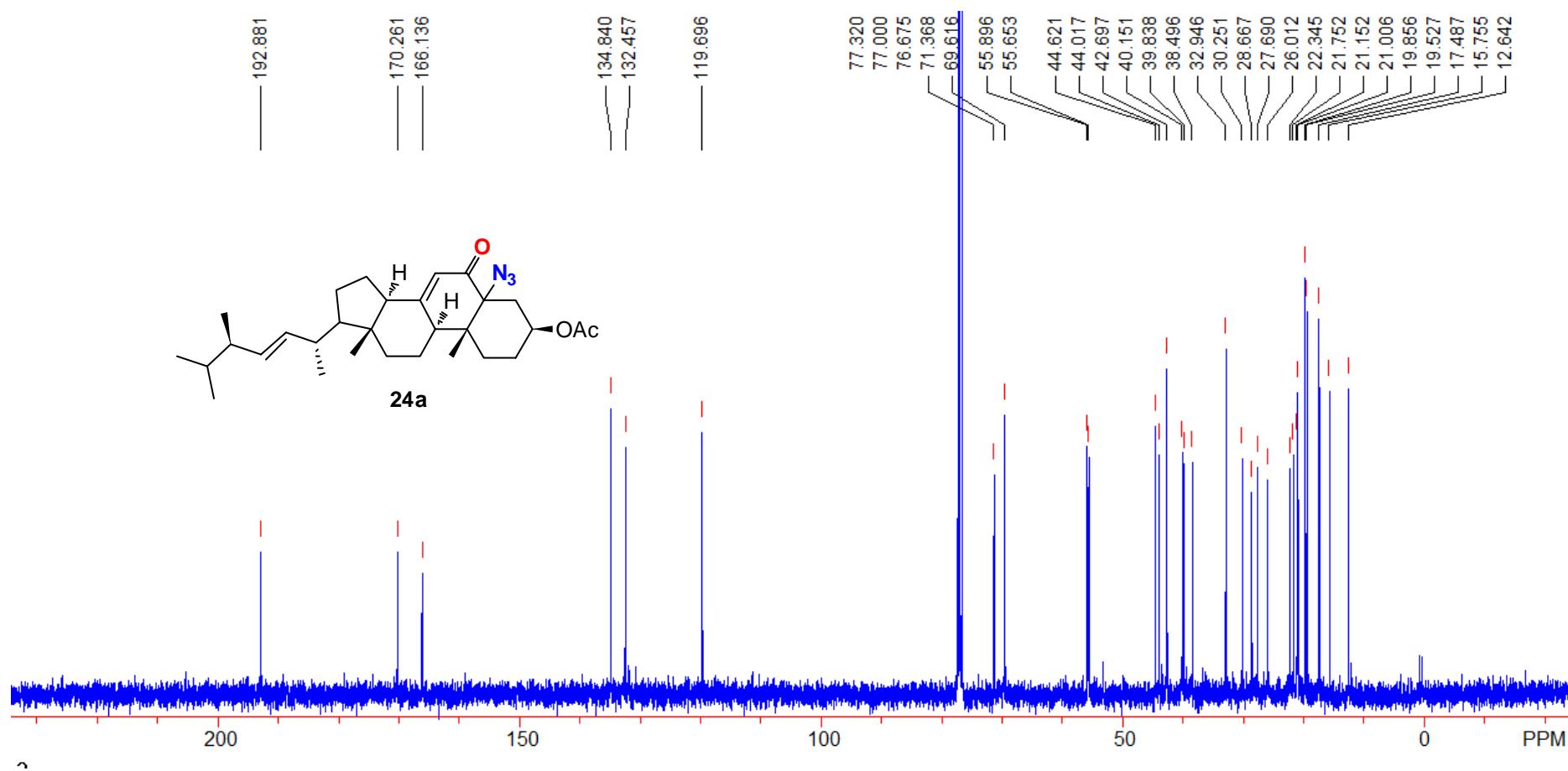




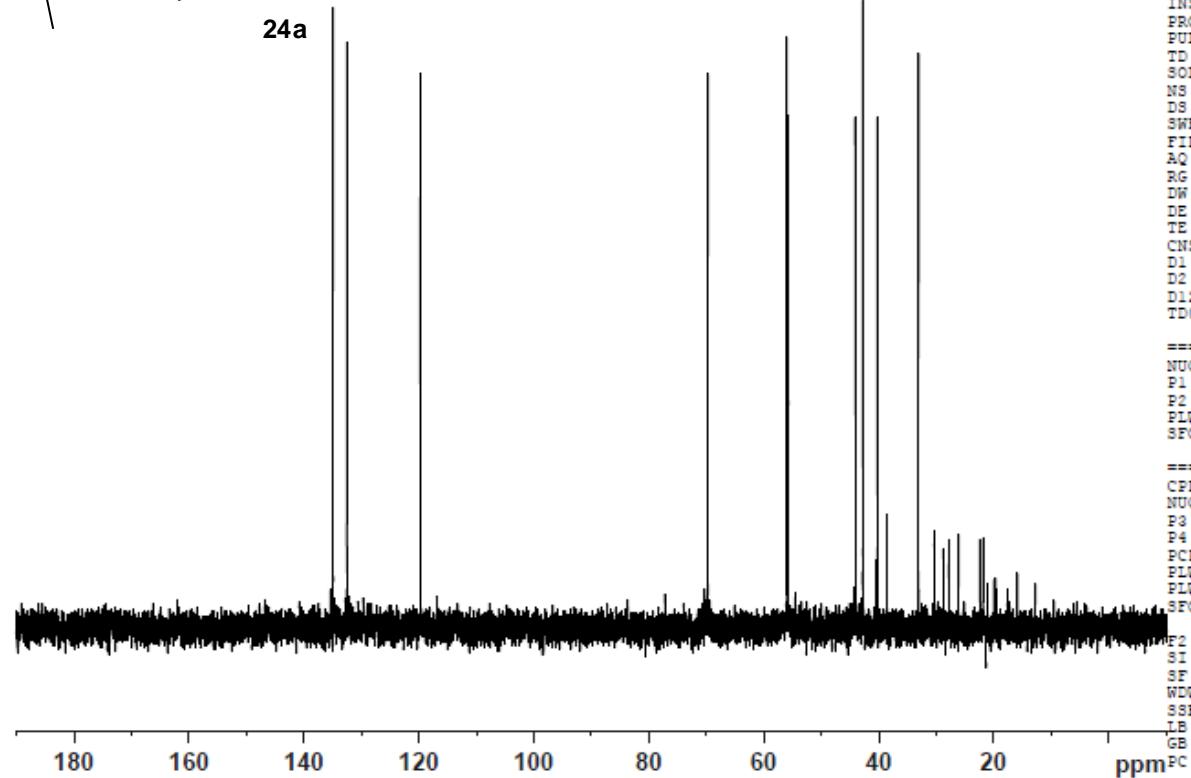
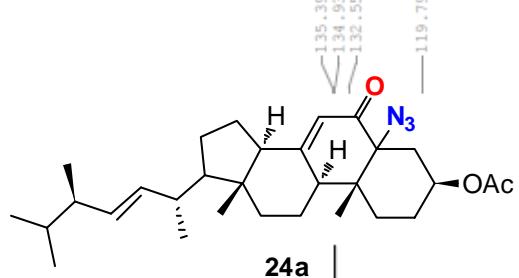








DEPT90 CDC13 (D:\data\jiaoning} jiaoning 30



Current Data Parameters
NAME WT-13-125-2
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121126
Time 10.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG dept90
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 205.82
DW 20.800 usec
DE 6.50 usec
TE 294.4 K
CNSST2 145.0000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
P2 18.00 usec
PLW1 60.95399857 W
SF01 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG[2 waltz16
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PCPD2 60.00 usec
PLW2 11.93999858 W
PLW12 0.65007001 W
SF02 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127680 MHz
WDW EM
SSB 0 1.00 Hz
LB 0 1.40
GB 0

DEPT135 CDC13 (D:\data\jiaoning} jiaoning 30



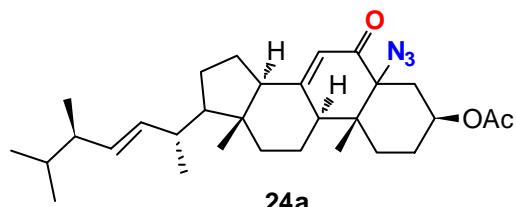
Current Data Parameters
NAME WT-13-125-2
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121126
Time_ 10.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptsp135
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 20161.291 Hz
FIDRES 0.007637 Hz
AQ 1.6252928 sec
RG 205.82
DW 24.800 usec
DE 6.50 usec
TE 294.5 K
CNUST2 145.0000000
D1 2.0000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
P13 2000.00 usec
PLW0 0 W
PLW1 60.95399857 W
SF01 100.6218241 MHz
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFF55 0 Hz
SPFW5 7.54260008 W

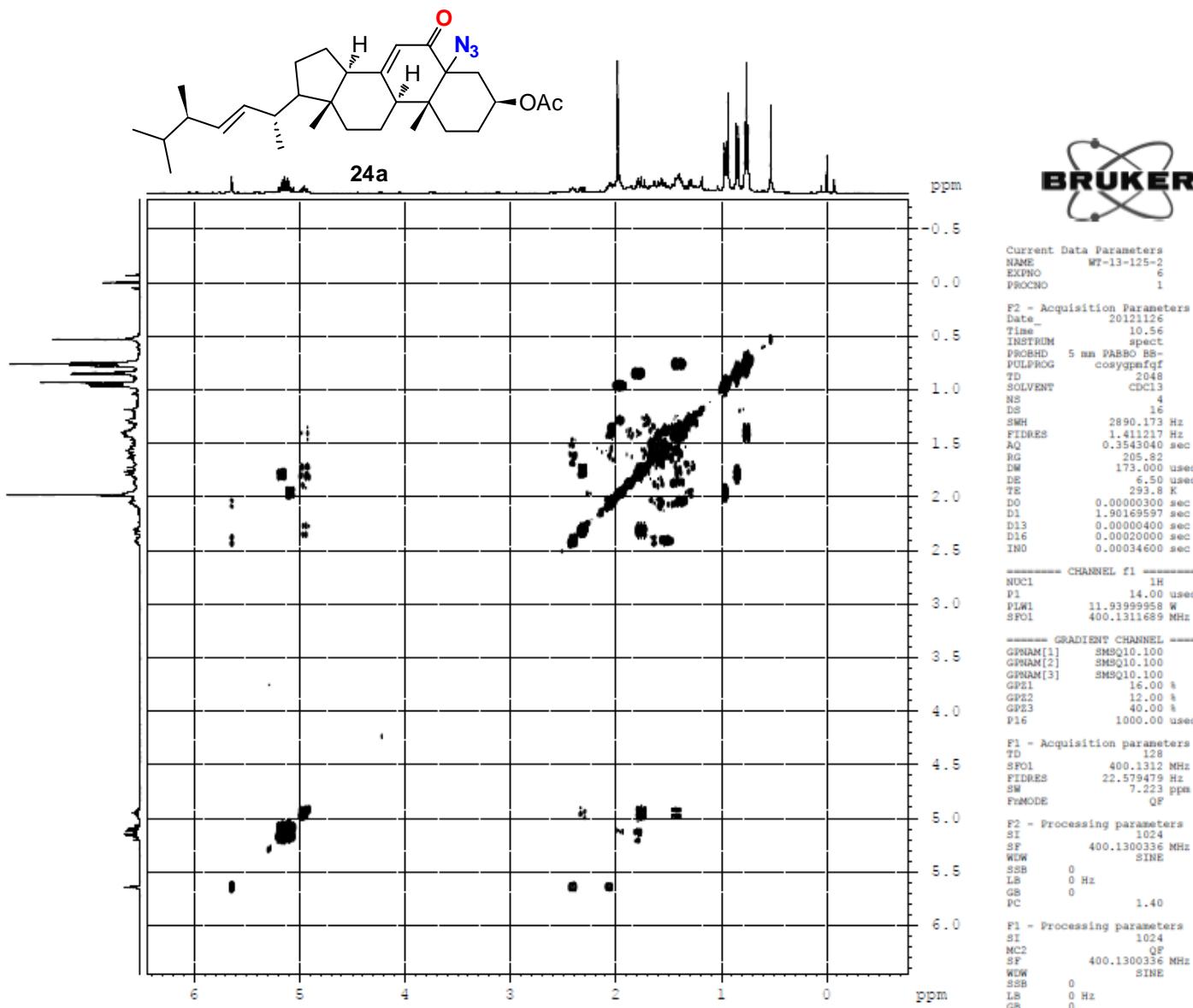
===== CHANNEL f2 =====
CPDPFG(2 waltz16
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PCPD2 60.00 usec
PLW2 11.99999958 W
PLW12 0.65007001 W
SF02 400.1316005 MHz

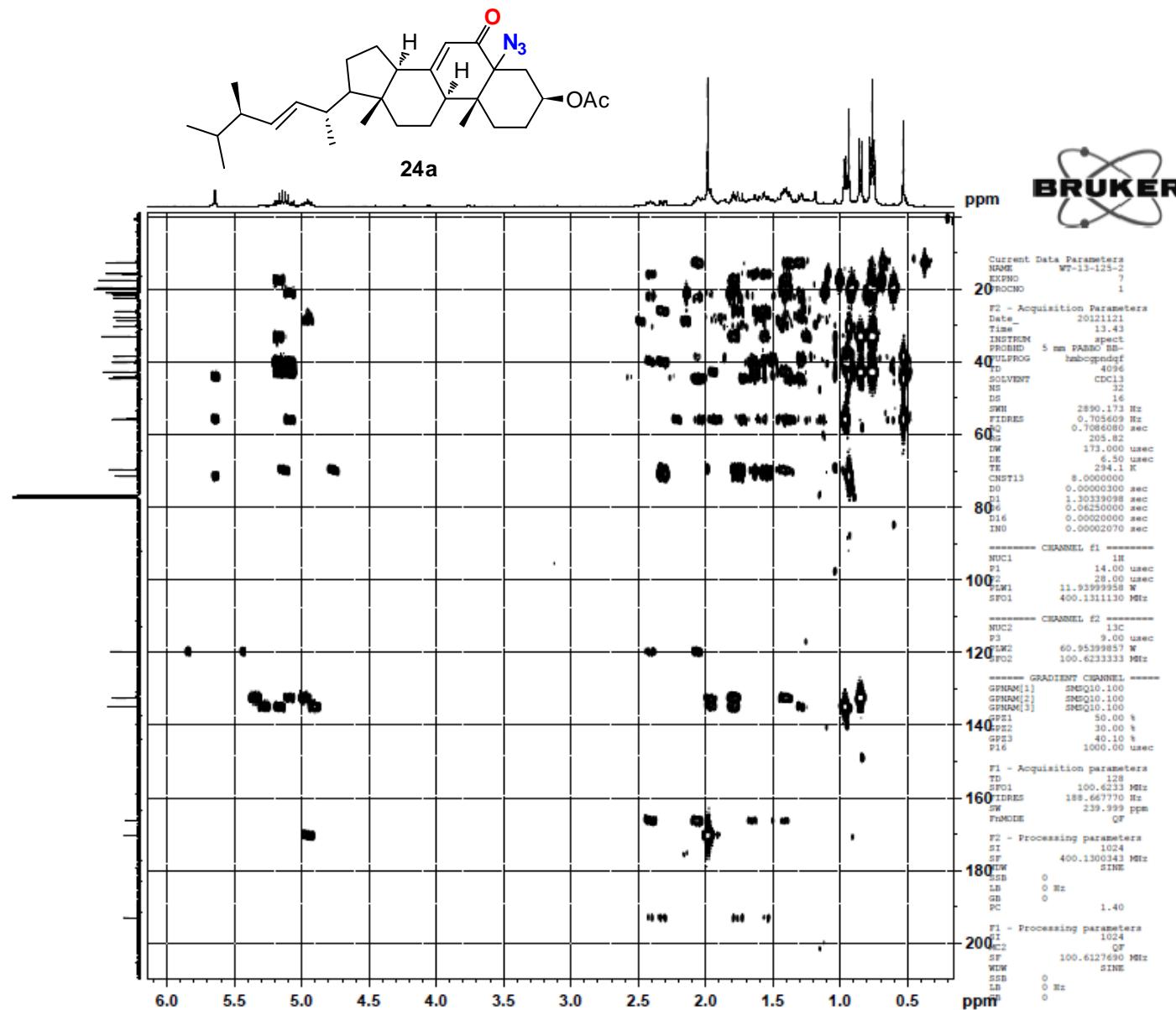
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0 1.00 Hz
LB 0 1.40
GB PC

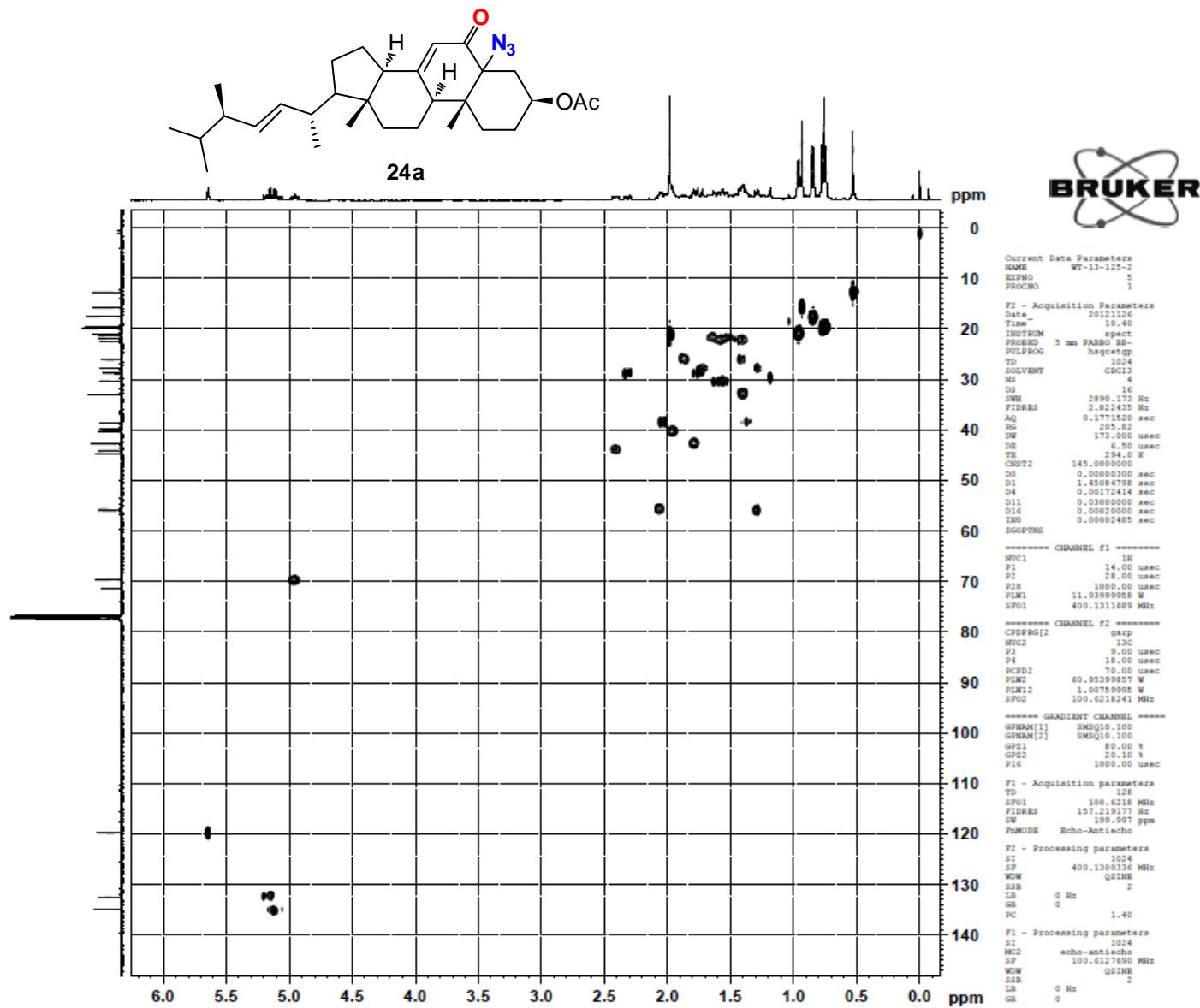


24a

180 160 140 120 100 80 60 40 20 ppm







HRMS analysis of ¹⁸O-10a

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name 12121055_20121225_000008.d
Sample wt-14-92
Comment ESI Positive

Acquisition Date 12/25/2012 4:06:39 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

