Micelle-Enabled Sustainable Palladium Catalysis for Convenient sp^2-sp^3 Coupling of Nitroalkanes with Aryl Bromides in Water Under Mild Conditions

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Supporting Information

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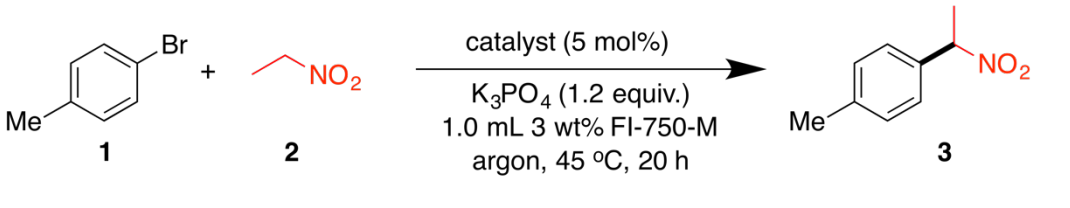
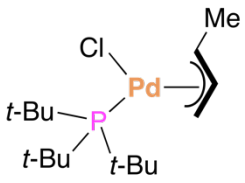
1. General Experimental Details

All manipulations were carried out under air unless otherwise noted. TLC plates (UV 254 indicator, glass backed, thickness 200 mm) and silica gel (standard grade, 230 – 400 mesh) were purchased from Merck. Diethyl ether, THF, ethyl acetate, methylene chloride, and hexanes were purchased from Fisher Scientific. Methyl *tert*-butyl ether and isopropyl acetate were purchased from Sigma-Aldrich. N*i*Pr_2Et, and NEt_3were distilled and stored under argon. K_3PO_4 and K_2CO_3 were purchased from Fisher Scientific and used as such without any further purification. Ligands were either purchased from Sigma-Aldrich or gifted by Johnson Matthey. Palladium acetate was purchased from Strem Chemicals and used as such without further purification. Allyl palladium complexes were received as a gift from Johnson-Matthey. Pure NMR solvents were purchased from Cambridge Isotopes Laboratories. Toluene was purchased from Fisher Chemicals and used as such without further purification. Nitroalkanes were purchased from Sigma-Aldrich. The coupling reactions were performed in 4 mL close-cap microwave vials under argon atmosphere. Microwave vials were purchased from VWR International and Biotage. Reaction vials were also recycled and reused. Bulk aqueous solution of surfactant Faisal-750-M (FI-750-M) was prepared with HPLC grade water and thoroughly purged with argon before use. Melting points were determined using a MEL-TEMP II melting point apparatus with samples in Kimble Kimex 51 capillaries (1.5-1.8 x 90 mm). Unless otherwise mentioned, all NMR spectra were recorded at 23 °C on Varian Unity INOVA (400, 500 and 700 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks. HRMS spectra were obtained on a Thermo Electron MAT 95XP mass spectrometer using either electron ionization (EI) or chemical ionization (CI).

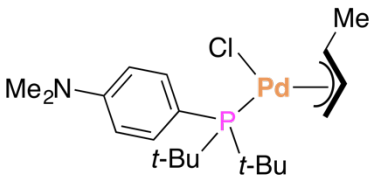
2. Reaction Optimization

2a. Catalyst Screening

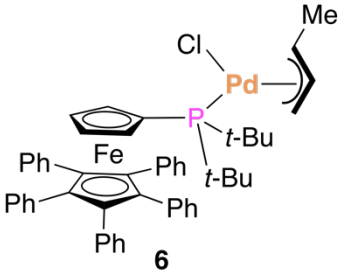




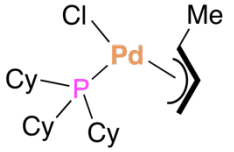
4
[P(*t*-Bu)$_3$Pd(crotyl)Cl]



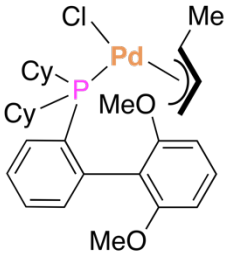
5
[AmPhosPd(crotyl)Cl]



6
[QPhosPd(crotyl)Cl]



7
[(Cy)$_3$PPd(crotyl)Cl]



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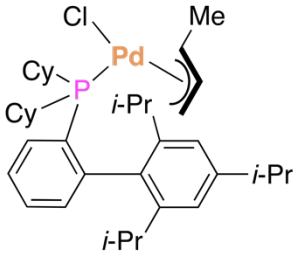
SPhosPd(crotyl)Cl



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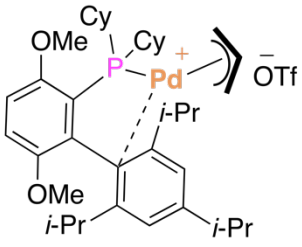
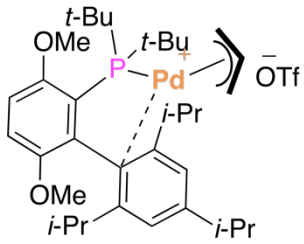
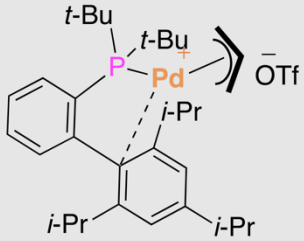
XPhosPd(crotyl)Cl



10
BrettPhosPd(allyl)]OTf



11
t-BuBrettPhosPd(allyl)]OTf



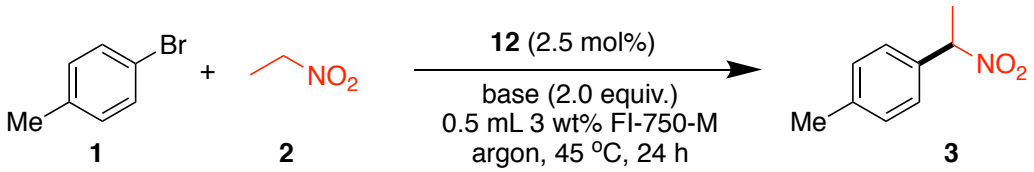
12
t-BuXPhosPd(allyl)]OTf

entry	catalyst	**3** (%)*
1	none	0
2	**4**	8
3	**5**	0
4	**6**	4
5	**7**	0
6	**8**	traces
7	**9**	8
8	**10**	19
9	**11**	74
10	**12**	99

*conversions based on GCMS

Conditions: **1** (0.25 mmol, 43 mg), **2** (2.5mmol, 180 µL), [Pd] catalyst (5 mol%), K_3PO_4 (0.3 mmol, 65 mg), 1.0 mL 3 wt% FI-750-M, 45 °C, 20 h, argon atmosphere.

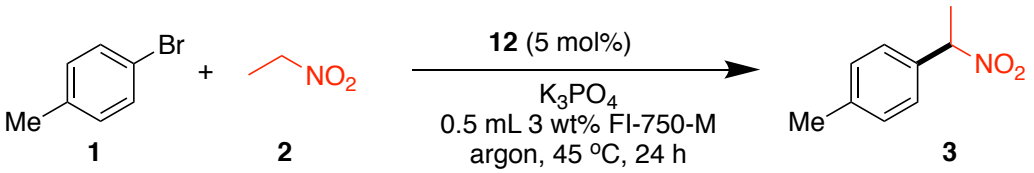
2b. Base Screening



entry	base	**3** (%)*
1	*i*-PrNEt$_2$	68
2	NEt$_3$	60
3	K$_2$CO$_3$	81
4	KOH	51
5	K$_3$PO$_4$	100

Conditions: **1** (0.25 mmol, 43 mg), **2** (2.5 mmol, 180 µL), **12** (9 mg, 5 mol%), base (0.5 mmol, 2.0 equiv.), 0.5 mL 3 wt% FI-750-M, 45 °C, 24 h, argon atmosphere. *Conversions based on GCMS.

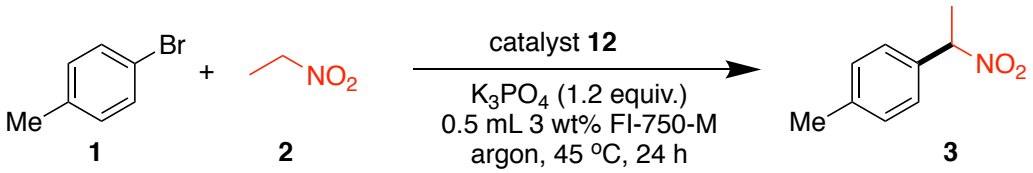
2c. Equivalents of Base



entry	K_3PO_4(equiv.)	**3** (%)*
1	3	100
2	2	100
3	1.5	100
4	1.2	100
5	1.0	92
6	none	0

Conditions: **1** (0.25 mmol, 43 mg), **2** (2.5 mmol, 180 µL), **12** (9 mg, 5 mol%), K_3PO_4, 0.5 mL 3 wt% FI-750-M, 45 °C, 24 h, argon atmosphere. *Conversions based on GCMS.

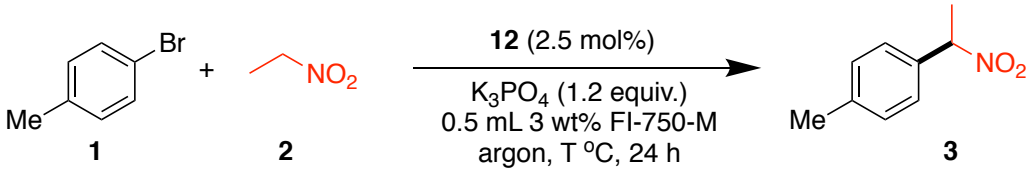
2d. Catalyst Loading



entry	**12** (mol%)	**3** (%)*
1	10	100
2	5	100
3	4	100
4	3	100
5	2.5	100
6	2	95

Conditions: **1** (0.25 mmol, 43 mg), **2** (2.5 mmol, 180 µL), **12**, K_3PO_4 (65 mg, 0.3 mmol), 0.5 mL 3 wt % FI-750-M, 45 °C, 24 h, argon atmosphere. *Conversions based on GCMS.

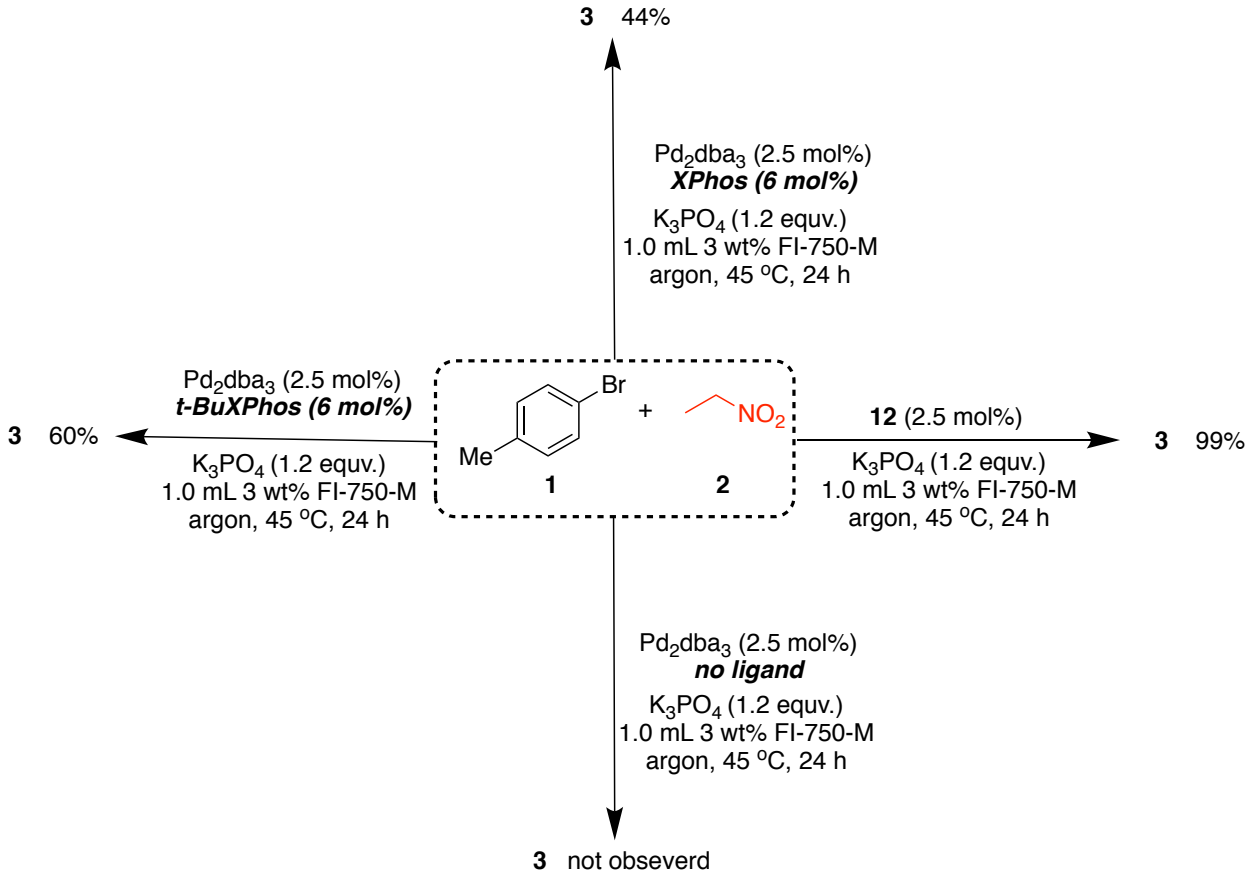
2e. Reaction Temperature



entry	Temperature (°C)	**1**(%)*
1	rt	traces
2	**45**	**99**
3	55	99
4	65	99

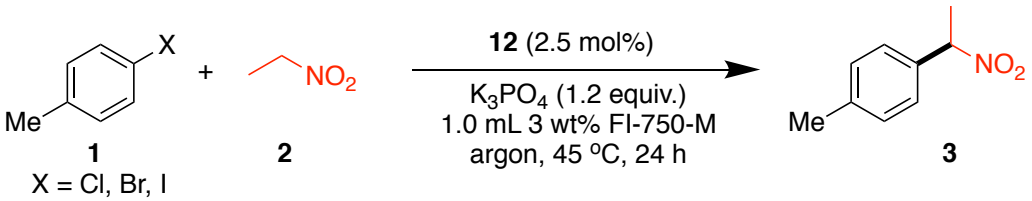
Conditions: **1** (0.25 mmol, 43 mg), **2** (2.5 mmol, 180 µL), **12** (4.5 mg, 2.5mol%), K_3PO_4 (65 mg, 0.3 mmol), 0.5 mL 3 wt% FI-750-M, 24 h, argon atmosphere. *Conversions based on GCMS.

2f. Role of Ligand and Nature of Catalyst



Reaction scale: **1** (0.5 mmol) and **2** (5 mmol, 10 equiv.). Conversions based on GCMS. Ligand and Pd_2dba_3 were pre-complexed in dry toluene before exposed to reaction conditions.

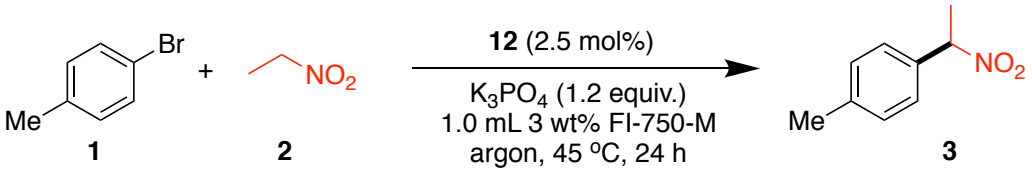
2g. Nature of Aryl Halide



entry	X	**3** (%)*
1	I	traces
2	Br	99
3	Cl	50†
4	F	NR

Conditions: **1** (0.5 mmol), **2** (2.5 mmol, 180 µL), **12** (9 mg, 2.5 mol%), K_3PO_4 (128 mg, 0.6mmol), 1.0 mL 3 wt% FI-750-M, 45 °C, 24 h, argon atmosphere. *Conversions based on GCMS. †Reaction temperature 65 °C.

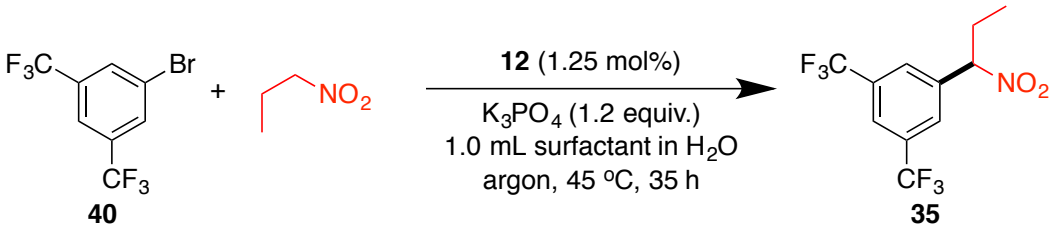
2h. Stoichiometry of Coupling Partners



entry	**2** (equiv.)	**3** (%)*
1	20	100
2	10	100
3	5	100
4	2	85

Conditions: **1** (0.5 mmol), **2**, **12** (9 mg, 5 mol%), K_3PO_4 (128 mg, 0.6mmol), 1.0 mL 3 wt % FI-750-M, 45 °C, 24 h, argon atmosphere. *Conversions based on GCMS.

2i. Role of Surfactant



entry	3 wt% surfactant in H_2O	**35** (%)*
1	no surfactant/on water	13
2	FI-750-M	84
3	TPGS-750-M	28
5	PTS	22

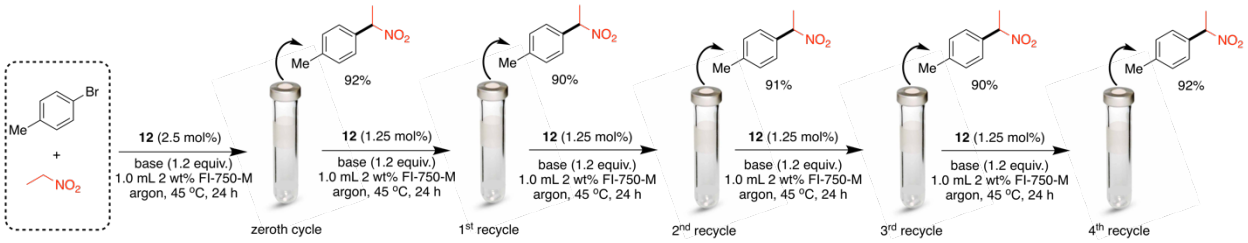
Conditions: **40** (0.5 mmol), nitropropane (2.5mmol), **12** (1.25 mol%), K_3PO_4 (0.6mmol), 1.0 mL surfactant solution, 45 °C, 35 h, argon atmosphere. *Conversions based on GCMS.

3. Optimal General Procedure for Catalytic Reactions

In a 4 mL reaction vial containing a PTFE-coated magnetic stir bar, allyl(2-di-*tert*-butylphosphino-2′,4′,6′-triisopropyl-1,1'-biphenyl)palladium(II) triflate (**12**, 9.0 mg, 5 mol%), nitroalkane (2.5 – 5.0 mmol, 5 – 10 equiv.), tribasic potassium phosphate (128 mg, 0.6 mmol, 1.2 equiv.), and aryl/heteroaryl bromide (0.5 mmol) were sequentially added. The reaction vial was closed with a rubber septum and subsequently evacuated and back-filled with argon. A 1 mL volume of 3 wt% aqueous FI-750-M was added to the reaction mixture. The septum was wrapped with PTFE tape and black electrical tape. The reaction vessel was allowed to stir at 45 °C in an oil bath.

After complete consumption of starting material, as monitored by GCMS or TLC, 1 mL EtOAc or *i*-PrOAc or MTBE was added to the reaction mixture, which was then gently stirred for 2 min. The organic layer was separated via centrifuge. This extraction was repeated. The combined extracts were dried over anhydrous sodium sulfate and volatiles were evaporated under reduced pressure to obtain crude product, which was further purified by flash chromatography over silica gel using EtOAc/hexanes or Et_2O/hexanes as eluent.

4. E Factor and Recycle Study



$$\text{E Factor} = \frac{\text{waste (in mg) in each cycle}}{\text{product (in mg) in each cycle}}$$

$$= \frac{410 + 389 + 400 + 403 + 390 \text{ (in mg)}}{76 + 74 + 75 + 74 + 76 \text{ (in mg)}}$$

$$= \frac{1992 \text{ mg}}{375 \text{ mg}} = \mathbf{5.3}$$

$$\text{E factor (involving solvent for column chromatography)} = \frac{67.41 + 0.39 + 0.40 + 0.40 + 0.40 \text{ (in grams)}}{0.76 + 0.74 + 0.75 + 0.74 + 0.76 \text{ (in grams)}} = 18.4$$

(solvent was recycled after zeroth cycle)

i) Initial reaction: In a 4 mL reaction vial containing a PTFE coated magnetic stir bar, allyl(2-di-*tert*-butylphosphino-2′,4′,6′-triisopropyl-1,1'-biphenyl)palladium(II) triflate **12** (9.0 mg, 2.5mol%), nitroethane (357 µL, 5.0 mmol), tribasic potassium phosphate (128 mg, 0.6 mmol, 1.2 equiv.), and 4-bromotoluene (86 mg, 0.5 mmol) were sequentially added. Reaction vial was closed with a rubber septum. Reaction vial was evacuated and back-filled with argon. A 1 mL volume of 3 wt% aqueous FI-750-M solution was added to the reaction mixture. Septum was sealed with Teflon tape and black electrical tape. Reaction vessel was wrapped with aluminum foil and allowed to stir for 24 h at 45 °C.

After complete consumption of starting material, as monitored by GCMS, 0.3 mL MTBE was added to the reaction mixture, which was then gently stirred for 2 min. Stirring was stopped and the organic layer was carefully taken out by Pasteur pipette or syringe. Another extraction was likewise performed using an additional 0.2 mL MTBE. The combined extracts were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as an orange oil. The crude product was purified by flash chromatography over silica gel using 5% Et_2OAc/hexanes as eluent. Solvent used in the chromatography was collected and reused in each cycle. Pure product was obtained as a pale colorless oil, R_f = 0.45 (1:9, EtOAc/hexanes), yield 76 mg, 92%.

ii) 1st recycle: *To the aqueous system obtained from above, catalyst **12** (4.5 mg, 1.25 mol%) was*

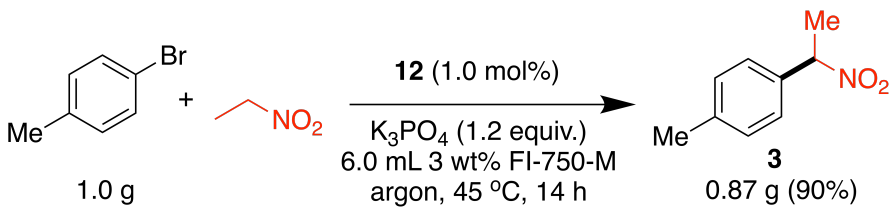
added under Ar. The resulting mixture was stirred for 5 min at ambient temperature before use for next cycle.

In a 4 mL microwave reaction vial containing the above surfactant suspension, recycled catalyst, and a PTFE coated magnetic stir bar, allyl(2-di-*tert*-butylphosphino-2′,4′,6′-triisopropyl-1,1'-biphenyl)palladium(II) triflate **12** (4.5 mg, 1.25 mol%), nitroethane (357 µL, 5.0 mmol), tribasic potassium phosphate (128 mg, 0.6 mmol, 1.2 equiv.), and 4-bromotoluene (86 mg, 0.5 mmol) were sequentially added. Reaction vial was closed with a rubber septum. Reaction vial was evacuated and back-filled with argon. Septum was sealed with Teflon tape and black electrical tape. Reaction mixture was wrapped with aluminum foil and allowed to stir for 24 h at 45 ^{o}C.

After complete consumption of starting material, as monitored by GCMS, 0.3 mL MTBE was added to the reaction mixture, which was then gently stirred for 2 min. Stirring was stopped and the organic layer was carefully taken out by Pasteur pipette or syringe. A similar extraction procedure was repeated using an additional 0.2 mL MTBE. The combined extracts were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as orange oil. Crude product was purified by flash chromatography over silica gel using 5% Et_2OAc/hexanes as eluent. Pure product was obtained as oil, R_f = 0.45 (1:9, EtOAc/hexanes. Pure product was obtained as oil, yield 74 mg, 90%.

iii) 2nd, 3rd, and 4th recycle: For the 2nd, 3rd, and 4th recycles, similar procedures were used as described above. Yields of 75 mg (91%), 74 mg (90%), and 76 mg (92%) for the 2nd, 3rd and 4th recycles were obtained.

5. Gram-Scale Reaction

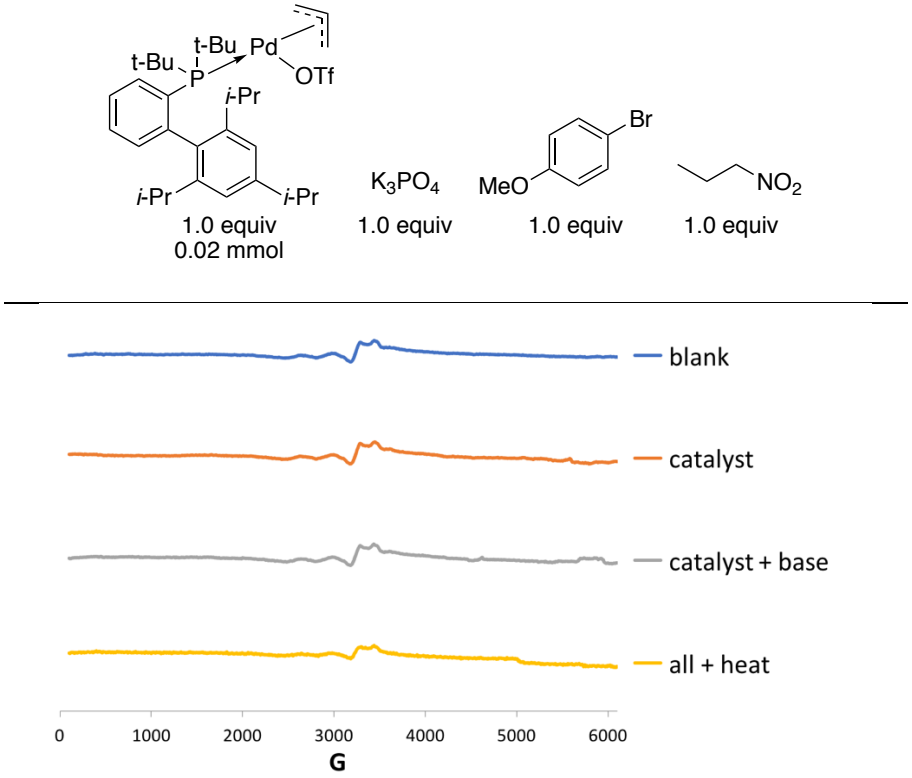


In a 20 mL round-bottom flask containing a PTFE-coated magnetic stir bar, allyl(2-di-*tert*-butylphosphino-2′,4′,6′-triisopropyl-1,1'-biphenyl)palladium(II) triflate (**12**, 42 mg, 1.0 mol%), nitroethane (2.1 mL, 29.2 mmol), tribasic potassium phosphate (1.5 g, 7.0 mmol, 1.2 equiv.), and 4-bromotoluene (1.0 g, 5.85mmol, 1.0 equiv.) were sequentially added. The reaction flask was closed with a rubber septum and was evacuated and back-filled with argon. A 6.0 mL volume of aqueous 3 wt% FI-750-M was added to the reaction mixture (the surfactant solution was purged with argon immediately prior to use). The septum was wrapped with PTFE tape and black electrical tape and the reaction flask was covered with aluminum foil and allowed to stir for 14 h at 45 ^{o}C. After complete consumption of starting material, as monitored by GCMS, 10 mL EtOAc was added to the reaction mixture, which was then gently stirred for 2 min. Stirring was stopped and the organic layer was carefully taken out by Pasteur pipette or syringe. A similar extraction procedure was repeated using an additional 5 mL EtOAc. The combined extracts were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as an orange oil. Crude product was purified by flash chromatography over silica gel using 5% Et_2OAc/hexanes as eluent. Pure product was obtained as oil, R_f = 0.45 (1:9, EtOAc/hexanes), yield 0.87 g, 90%.

6. EPR Experiment

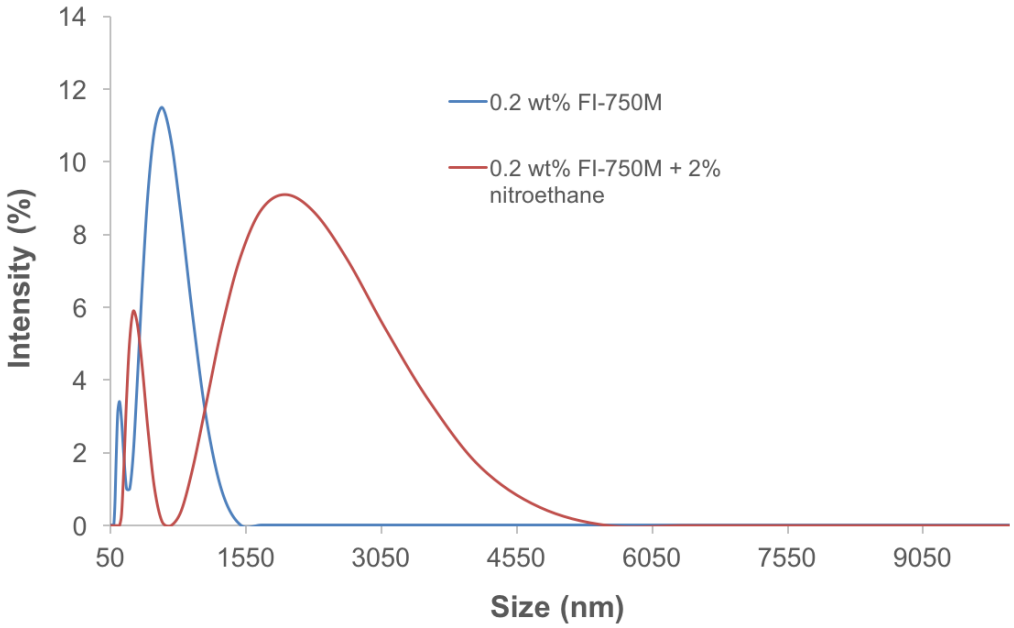
EPR spectra were recorded on a Bruker EMX spectrometer. Typical parameters were 9.8590 GHz operation frequency, 3100.00 G center field, 6000.00 G sweep width, 10.0 dB attenuator setting, 1.00 x 10^5 receiver gain, 100.00 kHz modulation frequency, 4.00 G modulation amplitude, 327.68 msec time constant, and 81.92 msec conversion time for one scan with a resolution of 4096.

All EPR samples were prepared with dry 1,4-dioxane and argon atmosphere, and all components were equimolar at 0.02 mmol. The following samples were analyzed: (1) a blank with an empty EPR tube; (2) catalyst **12**; (3) **12** + K_3PO_4; (4) a mixture of **12** + K_3PO_4 + *p*-bromoanisole + 1-nitropropane briefly heated with a heat gun and then placed in oil bath at 45 °C for 10 minutes. Other than those weakly present in the blank, no signals were observed. The lower signal intensity of the experiment with all components and heating is attributable to the use of 20.0 dB as the attenuator setting in that case.

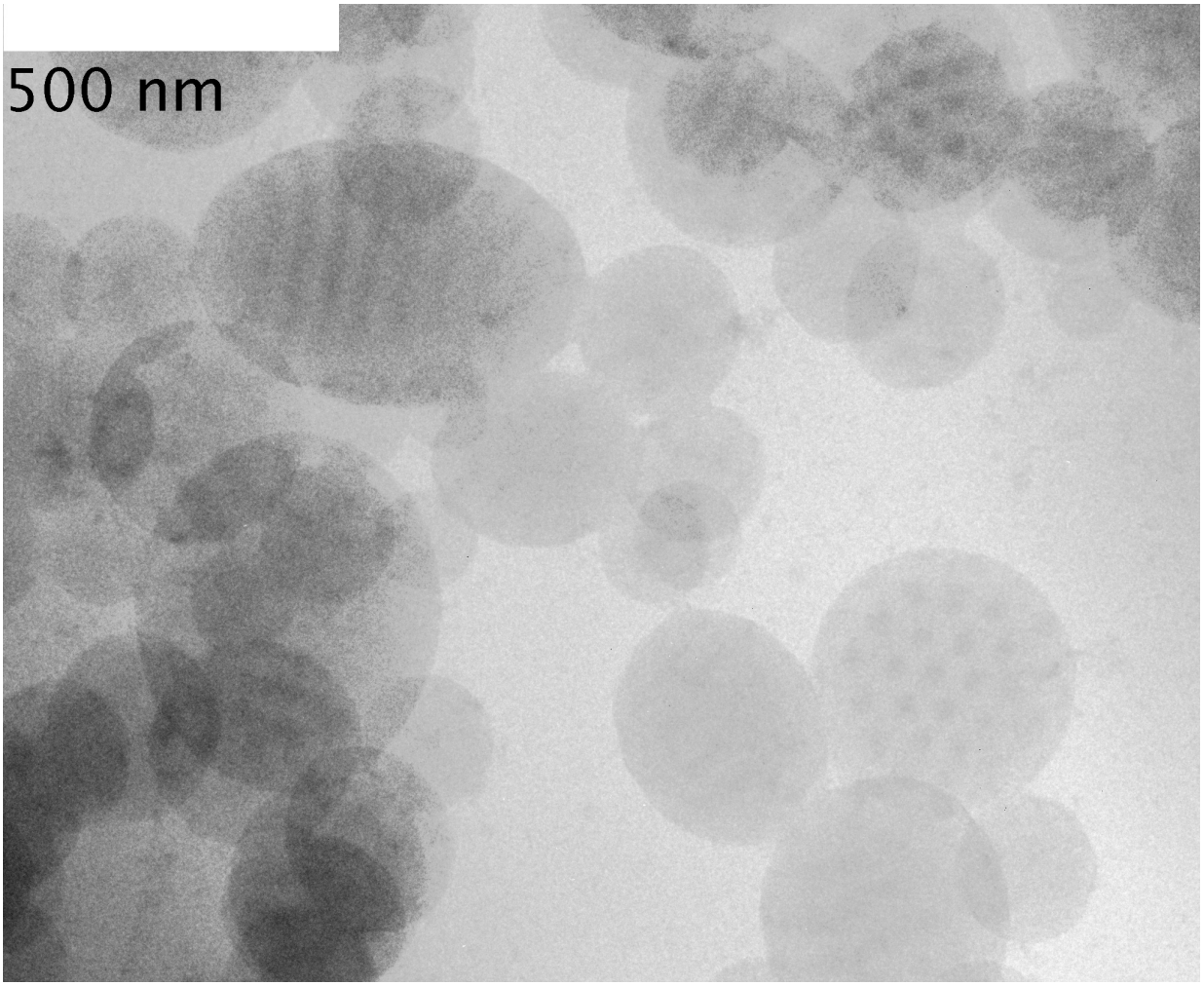


7. Particle Size Analysis

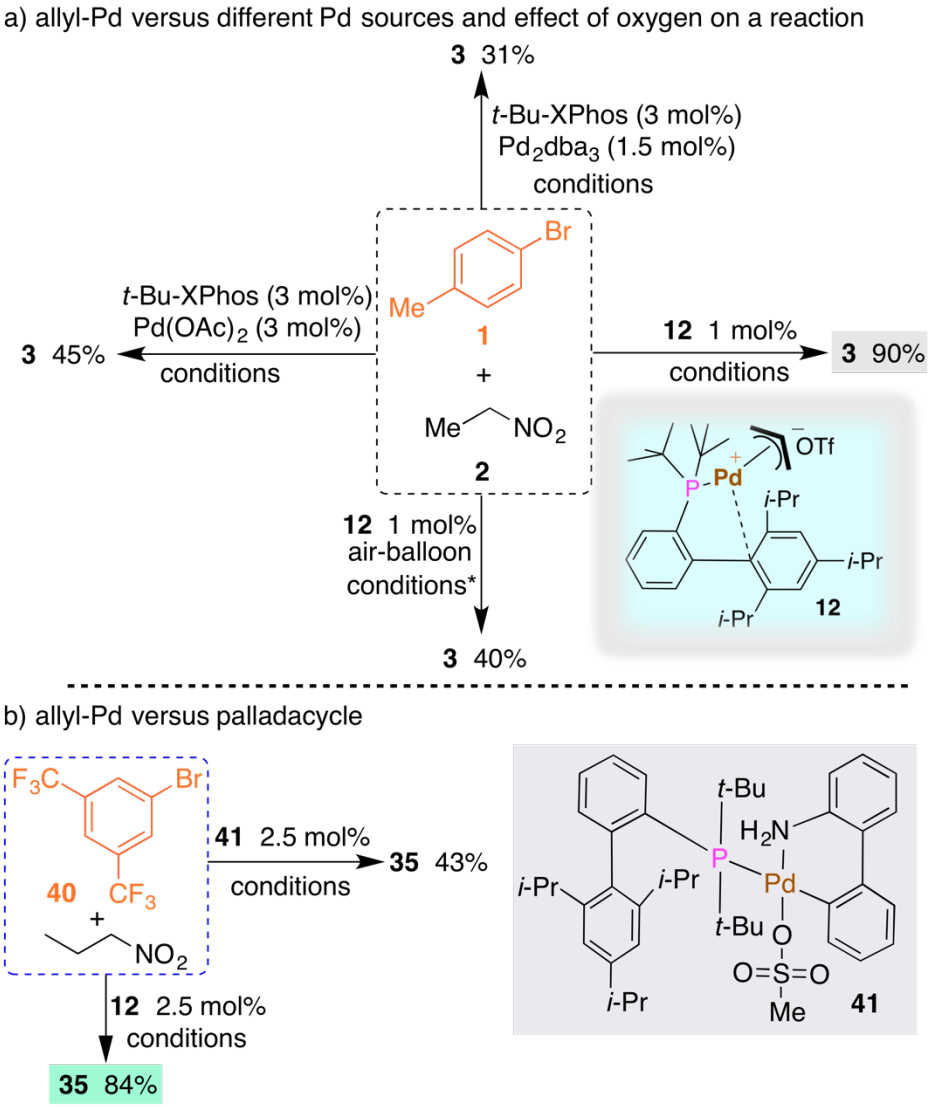
a) **Dynamic light scattering experiment:** Particle size measurements were acquired with a Zetasizer Nano ZS90 from Malvern Instruments Ltd. A 0.2 wt% aqueous solution of FI-750-M was analyzed for particle size distribution. In a separate experiment, 2% (w/v) of nitroethane was dissolved in 0.2 wt% aqueous solution of FI-750-M. After mixing for 5 minutes, resulting solution was immediately analyzed for particle size determination.



b) Cryo-TEM: Cryo-TEM analysis was performed in the Facility of High Resolution Microscopy, California Nanoscience Institute, University of California, Santa Barbara. A 2 wt% aqueous solution of FI-750-M was directly analyzed for high resolution images to determine the particle size and morphology.



8. Control Experiments



Conditions: unless otherwise noted, Ar—Br (0.5 mmol), nitroethane/nitropropane (2.5 mmol), catalyst as shown in scheme, K_3PO_4 (0.6 mmol, 1.2 equiv.), 1.0 mL 3 wt% FI-750-M, argon atmosphere, 45 °C. *Air balloon instead argon atmosphere.

a)

i) **Using *t*-BuXPhos and Pd_2dba_3 combination**: In an oven dried 4.0 mL microwave reaction vial, *t*-BuXPhos (6.4 mg, 3 mol%) and Pd_2dba_3 (6.9 mg, 1.5 mol%) were added. 1 mL dry toluene was added to the reaction mixture. Under completely inert atmosphere, mixture was stirred for 15 minutes at 50 °C. Reaction mixture was allowed to cool to room temperature and toluene was removed under reduced pressure to obtain yellow solid.

Under positive pressure of argon, 4-bromoanisole (63 µL, 0.5 mmol), nitroethane (178 µL, 2.5 mmol), and tribasic potassium phosphate (128 mg, 0.6 mmol) were sequentially added. Reaction vial was closed with a rubber septum. A freshly purged 3 wt% aqueous solution of FI-750-M (1 mL) was added to the reaction mixture. Reaction mixture was stirred at 45 ^{o}C for 24 h.

After 24 h, reaction mixture was allowed to cool at rt. Reaction mixture was extracted with 1x3 mL EtOAc. Combined organic layers were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as yellow oil. Crude product was analyzed for percentage conversion to product by GCMS using mesitylene as an internal standard. 31% product was detected along with remaining unreacted 4-bromoanisole.

ii) ***t*-BuXPhos and $Pd(OAc)_2$ combination in catalysis**: In an oven dried 4.0 mL microwave reaction vial, *t*-BuXPhos (6.4 mg, 3 mol%) and $Pd(OAc)_2$ (3.4 mg, 3 mol%) were added. 1 mL dry toluene was added to the reaction mixture. Under completely inert atmosphere, mixture was stirred for 15 minutes at 50 ^{o}C. Reaction mixture was allowed to cool to room temperature and toluene was removed under reduced pressure to obtain yellow solid.

Under positive pressure of argon, 4-bromoanisole (63 µL, 0.5 mmol), nitroethane (178 µL, 2.5 mmol), and tribasic potassium phosphate (128 mg, 0.6 mmol) were sequentially added. Reaction vial was closed with a rubber septum. A freshly purged 3 wt% aqueous solution of FI-750-M (1 mL) was added to the reaction mixture. Reaction mixture was stirred at 45 ^{o}C for 24 h.

After 24 h, reaction mixture was allowed to cool at rt. Reaction mixture was extracted with 1x3 mL EtOAc. Combined organic layers were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as yellow oil. Crude product was analyzed for percentage conversion to product by GCMS using mesitylene as an internal standard. 45% product was detected along with remaining unreacted 4-bromoanisole.

iii) **Using standard optimized conditions**: 90% isolated yield of **3** was obtained.

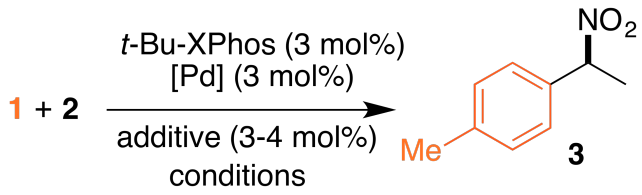
iv) **Using standard optimized conditions but under air**: 40% isolated yield of **3** was obtained.

b) Palladacycle versus pi–allyl complex 12

i) **Using *t*-BuXPhos G3 palladacycle as catalyst**: In an oven dried 4.0 mL microwave reaction vial, palladacycle **41** (10 mg, 2.5 mol%), 3,5-bis(trifluoromethyl)-5-bromobenzene (873 µL, 0.5 mmol), nitropropane (223 µL, 2.5 mmol), and tribasic potassium phosphate (128 mg, 0.6 mmol) were sequentially added. Reaction vial was closed with a rubber septum. A freshly purged 3 wt% aqueous solution of FI-750-M (1 mL) was added to the reaction mixture. Reaction mixture was stirred at 45 ^{o}C for 35 h. After 35 h, reaction mixture was allowed to cool at rt. Reaction mixture was extracted with 1x3 mL EtOAc. Combined organic layers were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as yellow oil. Crude product was purified by flash chromatography over silica gel suing ethyl acetate/hexanes as eluent (2%), yield 64 mg (43%).

ii) **Using pi-allyl palladium 12 as a catalyst**: Using exactly identical conditions but with catalyst **12**, 125 mg (84%) pure product was obtained.

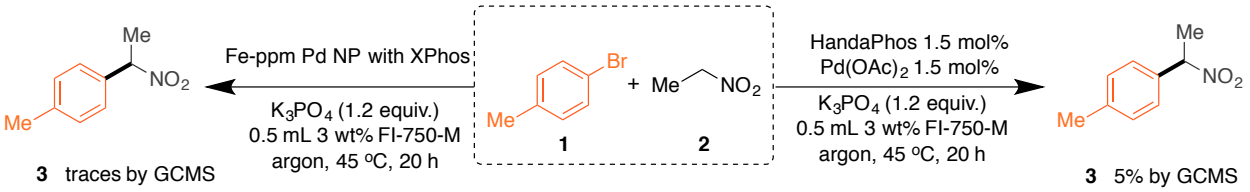
9. Further Experiments to Determine Plausible Mechanism



[Pd]	additive	**3** (%)
$Pd(OAc)_2$	AgOTf	42
$Pd(OAc)_2$	*AgOTf	42
**Pd_2dba_3	AgOTf	28
$Pd(OAc)_2$	propylene	90
$Pd(OAc)_2$	allyl bromide	89

Conditions: 1 (0.5 mmol, 85 mg), **2** (2.5 mmol, 180 µL), [Pd] (3 mol%) K_3PO_4 (0.6 mmol, 1.2 equiv.), 1.0 mL 3 wt% FI-750-M, 45 °C, 24 h, argon atmosphere. Propylene was used as a 0.1 M solution (0.2 mL, 4 mol%) in hexanes. *100 ppm AgOTf was used as a co-catalyst. **Pd_2dba_3 loading was 1.5 mol%.

10. Activity of Fe-ppm Pd Nanoparticles and Other Ligands



i) **Using Fe-ppm Pd nanoparticles:** In an oven-dried 4 mL microwave reaction vial, anhydrous $FeCl_3$ (4.0 mg, 5 mol%), XPhos (12 mg, 5 mol%), $Pd(OAc)_2$ (0.5 mg) were sequentially added. 1 mL dry THF was added to the mixture and then it was stirred for 15 minutes at rt. 0.2 M solution of MeMgBr (50 µL) was added to the reaction mixture. Reaction mixture was stirred at rt for 5 minutes. Reaction mixture was quenched with 1.0 mL 3 wt% FI-750-M (freshly purged with argon) to obtain active nanoparticles.

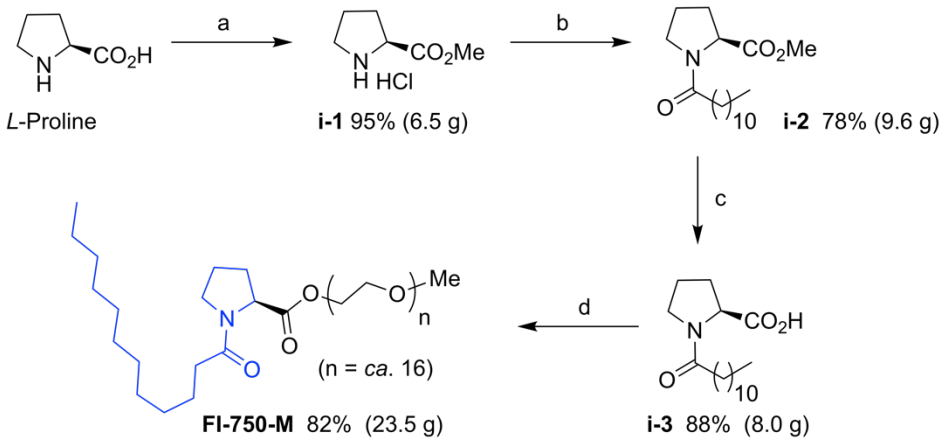
To the above nanoparticles, under inert atmosphere, 4-bromoanisole (63 µL, 0.5 mmol), nitroethane (178 µL, 2.5 mmol), and tribasic potassium phosphate (128 mg, 0.6 mmol) were sequentially added. Reaction vial was closed with a rubber septum. Freshly purged 3 wt% aqueous solution of FI-750-M (1 mL) was added to the reaction mixture. Reaction mixture was stirred at 45 °C for 24 h.

After 24 h, reaction mixture was allowed to cool at rt. Reaction mixture was extracted with 1x3 mL EtOAc. Combined organic layers were dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure to obtain crude product as yellow oil. Only traces of product were detected by GCMS and over a TLC.

ii) **Using HandaPhos-Pd:** Percentage conversion = 5% by GCMS.

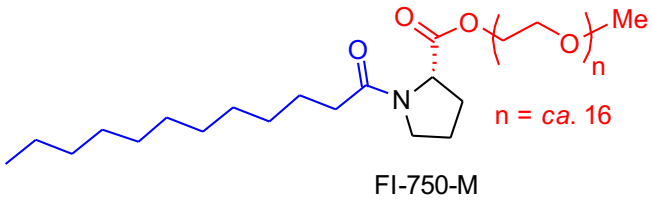
11. Synthesis of Surfactant FI-750-M

11a. General scheme for surfactant synthesis



conditions:
a) *L*-proline (5.0 g, 43.4 mmol), $SOCl_2$ (3.8 mL, 52.1 mmol), MeOH (60 mL), 0 °C - rt, 12 h;
b) lauryl chloride (13.7 mL, 59 mmol), Et_3N (15.2 mL, 118 mmol), CH_2Cl_2 (100 mL), 0 °C - rt, 12 h
c) i) $LiOH{\cdot}H_2O$ (5.2 g, 123 mmol), EtOH (25 mL)/H_2O (25 mL). 10 h; ii) 2 N HCl (100 mL)
d) *p*-tolenesulfonic acid (40 mg), mPEG-750 (40.5 g, 54 mmol), toluene (100 mL), reflux, 14 h.

11b. Faisal-750-M

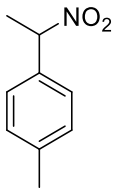


FI-750-M

Waxy solid, yield 19 g (86% overall), R_f 0.35 (9:1, EtOAc/MeOH). ^{1}H NMR (700 MHz, cdcl$_3$) δ 4.44 – 4.19 (m, 2H), 3.63 – 3.49 (mPEG), 3.47 – 3.43 (m, 1H), 3.32 (s, 3H, OMe-PEG), 2.28 – 2.19 (m, 2H), 2.13 – 1.99 (m, 2H), 1.96 – 1.84 (m, 2H), 1.59 – 1.57 (m, 2H), 1.20 – 1.18 (m, 16 H), 0.83 (t, J = 6.3 Hz, 3H); ^{13}C NMR (176 MHz, cdcl$_3$) δ 172.4, 172.1, 71.9, 70.7 – 70.4 (mPEG), 69.1, 63.9, 61.7, 59.1, 59.0, 58.7, 58.6, 47.0, 34.5, 31.9, 29.6, 20.4, 24.8, 22.7, 14.2, and 14.1 ppm. MALDI-TOFF -1060.3683.

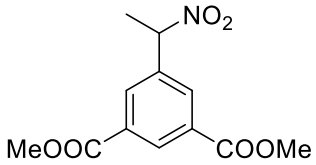
12. Analytical Data

1-methyl-4-(1-nitroethyl)benzene (3)[1]



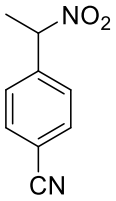
Pale oil, yield 868 mg (90%), R_f 0.45 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.59 (q, *J* = 6.9 Hz, 1H), 2.37 (s, 3H), 1.88 (d, *J* = 7.2 Hz, 3H). **IR** ν (cm^{-1}) = 2991 (w), 1613 (w), 1546 (s).

Dimethyl 5-(1-nitroethyl)isophtalate (13)



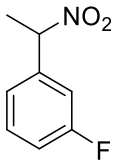
White solid, mp = 115–118°C, yield 110 mg (82%), R_f 0.41 (7:3, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.31 (s, 2H), 5.708 (q, *J* = 7.2 Hz, 1H), 3.95 (s, 6H), 1.95 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 165.5, 136.4, 132.9, 132.8, 132.0, 131.9, 131.7, 85.3 (d, *J* =5.45 Hz), 52.8, 52.7, 19.4 (d, *J* = 10.2 Hz). **IR** ν (cm^{-1}) = 3006 (w), 2958 (w), 1720 (s), 1554 (s). **HRMS** [(CI), $(C_{12}H_{13}NO_6 + H)^+$] calcd = 268.0816, found m/z 268.0811.

4-(1-nitroethyl)benzonitrile (14)[2]



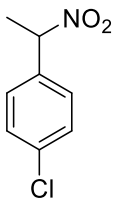
Pale oil, yield 69 mg (78%), R_f 0.4 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8Hz, 2H), 5.65 (q, *J* = 7.2 Hz, 1H), 1.90 (d, *J* =6.8 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 140.1, 132.9, 128.4, 118.0, 113.9, 85.4, 19.4. **IR** ν (cm^{-1}) = 2993 (w), 2232 (m), 1733 (m), 1549 (s).

1-fluoro-3-(1-nitroethyl)benzene (15) CAS number 29865-67-6



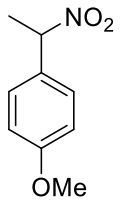
Yellow oil, yield 64 mg (75%), R_f 0.49 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8 Hz and J = 6Hz, 1H), 7.23 (d, *J* = 4 Hz, 1H), 7.19 (d, *J* = 9.2 Hz, 1H), 7.11 (td, *J* = 8.4 Hz and 2 Hz, 1H), 5.60 (q, *J* = 7.2 Hz, 1H), 1.88 (d, *J* = 7.2 Hz, 3H). **IR** ν (cm^{-1}) = 2995 (w), 1595 (m), 1548 (s).

1-chloro-4-(1-nitroethyl)benzene (16)[1]



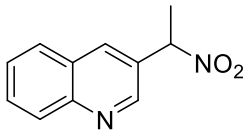
Pale oil, yield 61 mg (66 %), R_f 0.49 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 4H), 5.59 (q, *J* = 7 Hz, 1H), 1.88 (d, *J* = 6.8 Hz, 3H). **IR** ν (cm^{-1}) = 2991 (w), 1808 (w), 1547 (s).

1-methoxyn-4-(1-nitroethyl)benzene (17)[1]



Pale oil, yield 77 mg (83%), R_f 0.6 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.57 (q, *J* = 7 Hz, 1H), 3.18 (s, 3H), 1.87 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 160.7, 128.9, 127.7, 114.3, 85.8, 55.4, 19.4. **IR** ν (cm^{-1}) = 2939 (w), 2840 (m), 1611 (m), 1546 (s), 1514 (s), 1457 (m).

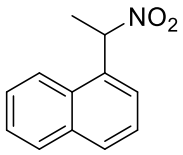
3-(1-nitroethyl)quinoline (18)



Orange solid, mp = 62–94°C, yield 66 mg (65%), R_f 0.33 (1:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 1.2 Hz, 1H), 8.25 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8Hz, 1H), 7.765 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H) , 5.82 (q, *J* = 6.8 Hz ,1H), 2.03 (d, *J* = 6.8 Hz, 3H) **^{13}C NMR** (176 MHz, $CDCl_3$) δ 149.3, 148.6, 135.2, 130.8, 129.4, 128.2, 127.6,

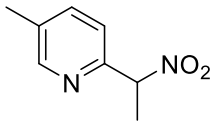
127.4, 84.0, 19.5. **IR** ν (cm^{-1}) = 3143 (w), 3063 (w), 2773 (w), 1682 (m), 1619 (w), 1569 (m), 1495 (m). **HRMS** [(CI), ($C_{11}H_{10}N_2O_2 + H)^+$] calcd = 203.0815, found m/z 203.0814.

1-(1-nitroethyl)naphthalene (19)



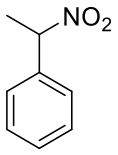
Pale yellow oil, yield 88 mg (88 %), R_f 0.39 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.92 (t, *J* = 6.3 Hz, 2H), 7.69 (d, *J* = 7 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.52 (m, 2H), 6.48 (q, *J* = 7 Hz, 1H), 2.09 (d, *J* = 7 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 133.9, 131.3, 130.5, 129.3, 127.5, 126.3, 125.4, 125.1, 122.2, 82.0, 19.5. **IR** ν (cm^{-1}) = 3054 (w), 2995 (w), 1599 (w), 1545 (s), 1512 (m), 1449 (m). HMRS [(CI), ($C_{12}H_{11}NO_2)^+$] calcd 201.0790, found m/z 201.0780.

5-methyl-2-(1-nitroethyl)pyridine (20)



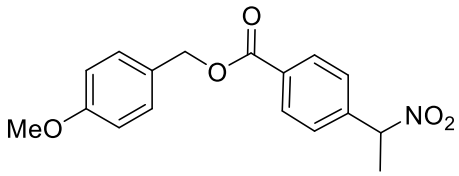
Yellow oil, yield 54 mg (65 %), R_f 0.52 (7:3, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 5.72 (q, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 1.92 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 151.7, 150.31, 137.9, 134.3, 121.9, 86.8, 18.4. **IR** ν (cm^{-1}) = 2926 (w), 1693 (m), 1632 (w), 1568 (s), 1510 (m), 1479 (m). **HRMS** [(CI), ($C_8H_{10}N_2O_2 - H)^+$] calcd = 165.0659, found m/z 165.0652.

(1-nitroethyl)benzene (21)[1]



White pale oil, yield 69 mg (91%), R_f 0.41 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 5H), 5.62 (q, *J* = 7Hz, 1H), 1.90 (d, *J* = 7 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 135.6, 129.8, 129.1, 127.5, 86.2, 19.5. **IR** ν (cm^{-1}) = 2992 (w), 1735 (m), 1546 (s), 1498 (m), 1455 (m).

4-methoxybenzyl 4-(1-nitroethyl)benzoate (22)

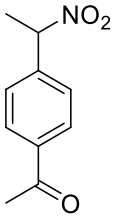


Pale solid, mp = 40–41°C, yield 68 mg (80%), R_f 0.33 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.65 (q, *J* = 7 Hz, 1H), 5.30 (s, 2H), 3.81 (s, 3H), 1.91 (d, *J* = 7 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 165.8, 159.8, 140.1, 131.7, 130.5, 130.3, 127.9, 127.5, 114.1, 85.7, 67.0, 55.43, 19.6. **IR** ν (cm^{-1}) = 2959 (w), 2838 (w), 1716 (s), 1612 (m), 1550 (s), 1514 (s). **HRMS** [(ESI), $(C_{17}H_{17}NO_5 + Na)^+$] calcd 338.1004, found m/z 338.0998.

1,3-difluoro-5-(1-nitropropyl)benzene (23)

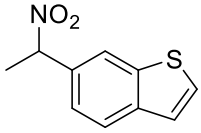
Yellow oil, yield 66 mg (70%), R_f 0.33 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 5.6 Hz, 2H), 6.87 (t, *J* = 8.8 Hz, 1H), 5.56 (q, *J* = 6.8 Hz, 1H), 1.87 (d, *J* = 6.8 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 107.75 (t, *J* = 5 Hz) **^{13}C NMR** (176 MHz, $CDCl_3$) δ 163.9 (d, *J* = 12.3 Hz), 162.5 (d, *J* =12.1 Hz), 138.7, 110.9 (q, *J* = 16.4 Hz and 4.7 Hz), 105.7 (t, *J* = 25.2 Hz), 85.1, 19.4. **IR** ν (cm^{-1}) = 3094 (w), 2941 (w), 1732 (m), 1624 (m), 1599 (s), 1552 (s), 1448 (m). **HRMS** [(CI), $(C_8H_7F_2NO_2 + H)^+$] calcd 188.0518, found m/z 188.0520.

1-(4-(1-nitroethyl)phenyl)ethan-1-one (24)



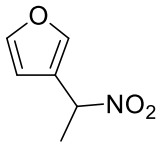
Yellow oil, yield 65 mg (67%), R_f 0.36 (7:3, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 5.66 (q, *J* = 7 Hz, 1H), 2.60 (s, 3H), 1.91 (d, *J* = 6.8 Hz, 3H) **^{13}C NMR** (176 MHz, $CDCl_3$) δ 197.4, 140.1, 138.2, 129.1, 127.8, 85.7, 26.1, 19.5; **IR** ν (cm^{-1}) = 2994 (w), 1682 (s), 1609 (m), 1542 (s), 1550 (s), 1417 (m). **HRMS** [(CI), $(C_{10}H_{11}NO_3 + H)^+$] calcd 194.0812, found m/z 194.0809.

6-(1-nitroethyl)benzo[d]thiophene (25)



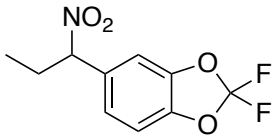
Pale orange solid, mp = 42-45 °C, yield 80 mg (77%), R_f 0.35 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 5.6 Hz, 1H), 7.46 (d, *J* = 8 Hz, 1H), 7.35 (d, *J*= 5.2 Hz, 1H), 5.74 (q, *J* = 6.8 Hz, 1H), 1.97 (d, *J* = 7.2 Hz, 3H) **^{13}C NMR** (176 MHz, $CDCl_3$) δ 140.6, 140.1, 131.6, 128.5, 124.2, 123.7, 123.5, 121.8, 86.4, 19.7; **IR** ν (cm^{-1}) = 3104 (w), 2934 (w), 1733 (w), 1599 (w), 1535 (s), 1463 (m). **HRMS** [(CI), $(C_{10}H_9NO_2S + H)^+$] calcd = 208.0427, found m/z 208.0423.

3-(1-nitroethyl)furan (26)



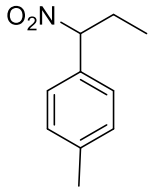
Orange oil, yield 23 mg (32%), R_f 0.42 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.43 (s, 1H), 6.53 (s, 1H), 5.56 (q, J = 6.8 Hz, 1H), 1.84 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 144.1, 141.4, 121.5, 109.1, 78.4, 19.2. **IR** ν (cm^{-1}) = 3139 (w), 2963 (w), 1549 (s), 1506 (m), 1454 (w). **HRMS** [(CI), $(C_6H_7NO_3 + H)^+$] calcd 142.0499, found m/z 142.0503.

2,2-difluoro-5-(1-nitropropyl)benzo[*d*][1,3]dioxole (27)



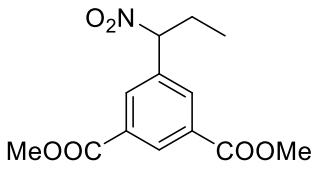
Yellow oil, yield 113 mg (92%), R_f 0.17 (9:1, hexanes/dichloromethane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.19 (d, 1H, *J* = 8.8 Hz), 7.08 (d, 1H, *J* = 8.4 Hz), 5.34 (t, 1H, *J* = 7.2 Hz), 2.56–2.41 (m, 1H), 2.16–2.02 (m, 1H), 0.99 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6 (d, *J* = 51.6 Hz), 131.8 (t, *J* = 255.2), 130.5, 124.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –49.8. **IR** ν (cm^{-1}) = 3133 (w), 3093 (w), 3062 (w), 2980 (m), 2942 (m), 2885 (m), 1551 (s). **HRMS** [(CI), $(C_{10}H_9F_2NO_4 + H)^+$] calcd 246.0572, found m/z 246.0576.

1-methyl-4-(1-nitropropyl)benzene (28)[3]



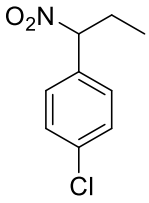
Pale oil, yield 58 mg (65 %), R_f 0.47 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 5.34 (dd, *J* = 6.5 Hz and 2.5 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.36 (s, 3H), 2.14 – 2.05 (m, 1H), 0.98 (t, *J* = 6.5 Hz, 3H); **IR** ν (cm^{-1}) = 2977 (w), 2938 (w), 2882 (w), 1614 (w), 1546 (s), 1515 (m), 1458 (m).

Dimethyl 5-(1-nitropropyl)isophtalate (29)



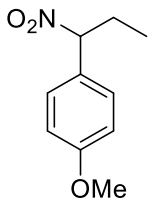
White solid, mp = 70–71 °C, yield 108 mg (77%), R_f 0.43 (7:3, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (t, *J* = 1.5 Hz, 1H), 8.32 (d, *J* = 1.5 Hz, 2H), 5.47 (dd, *J* = 6.5 Hz, and 2 Hz, 1H), 3.96 (s, 6H), 2.62 – 2.53 (m, 1H), 2.20 – 2.12 (m, 1H), 1.0 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 165.5, 135.4, 133.2, 132.0, 131.6, 92.0, 52.8, 27.4, 10.7. **IR** ν (cm^{-1}) = 2953 (w), 1718 (s), 1606 (w), 1547 (s), 1436 (m). **HRMS** [(ESI), $(C_{13}H_{15}NO_6 + Na)^+$] calcd 304.0797, found m/z 304.0792.

1-chloro-4-(1-nitropropyl)benzene (30)[3]



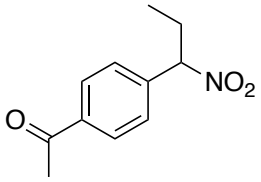
Yellow oil, yield 42 mg (83%), R_f 0.44 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 5.34 (t, *J* = 7.5 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.14 – 2.03 (m, 1H), 0.98 (t, *J* = 7.6 Hz, 3H). **IR** ν (cm^{-1}) = 2977 (w), 2939 (w), 2882 (w), 1547 (s), 1493 (m).

1-methoxy-4-(1-nitropropyl)benzene (31)



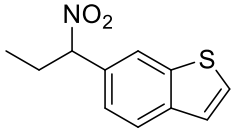
Yellow oil, yield 64 mg (65%), R_f 0.32 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 9.92 – 6.89 (m, 2H), 5.32 (dd, *J* = 7 Hz and 2 Hz, 1H), 3.81 (s, 3H), 2.53 – 2.44 (m, 1H), 2.13 – 2.04 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 160.7, 129.3, 126.7, 114.3, 92.7, 55.4, 27.3, 10.8. **IR** ν (cm^{-1}) = 2975 (w), 2939 (w), 1840 (w), 1611 (m), 1545 (s), 1514 (s), 1460 (m).

1-(4-(1-nitropropyl)phenyl)ethan-1-one (32)[4]



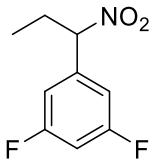
Yellow semisolid, yield 78 mg (75%), R_f 0.24 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.5 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 5.42 (dd, 1H, *J* = 8.5 and 6.5 Hz), 2.60 (s, 3H), 2.57–2.46 (m, 1H), 2.19–2.07 (m, 1H), 0.99 (t, 3H, *J* = 7.5 Hz).

6-(1-nitropropyl)benzo[d]thiophene (33)



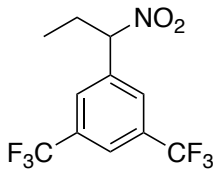
Pale yellow oil, yield 89 mg (80%), R_f 0.45 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 5.6 Hz, 1H), 5.49 (t, *J* = 7.6 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.25 – 2.14 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 140.7, 140.1, 130.6, 128.4, 124.2, 123.8, 123.7, 122.3, 93.2, 27.6, 10.8. **IR** ν (cm^{-1}) = 3105 (w), 2975 (w), 2937 (w), 2880 (w), 1734 (w), 1544 (s), 1462 (m). **HRMS** [(CI), $(C_{11}H_{11}NO_2S + H)^+$] calcd 222.0583, found m/z 222.0584.

1,3-difluoro-5-(1-nitropropyl)benzene (34)



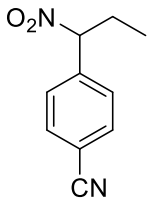
Pale yellow oil, yield 42 mg (42%), R_f 0.44 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 6 Hz, 2H), 6.87 (t, *J* = 8.8 Hz, 1H), 5.31 (t, *J* = 7.8 Hz, 1H), 2.52 – 2.41 (m, 1H), 2.14 – 2.03 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 107.83 (t, *J* = 7.2 Hz); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 163.9 (d, *J* = 12.8 Hz), 162.5 (d, *J* = 3 Hz), 137.7, 111.2 (q, *J* = 16.4 Hz and 4.75 Hz), 105.5 (d, *J* = 25 Hz), 91.9, 27.5, 10.6. **IR** (cm^{-1}) = 3096 (w), 2979 (w), 1623 (m), 1598 (s), 1552 (s), 1464 (m). **HRMS** [(CI), $(C_9H_9F_2NO_2 + H)^+$] calcd 202.0674, found m/z 202.0667.

1-(1-nitropropyl)-3,5-bis(trifluoromethyl)benzene (35)



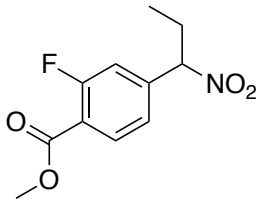
Pale yellow oil, yield 63 mg (84%), R_f 0.30 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (s, 3H), 5.49 (dd, 1H, *J* = 9.0 and 6.5 Hz), 2.64–2.52 (m, 1H), 2.20–2.10 (m, 1H), 1.04 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.7, 132.8 (q, *J* = 33.6 Hz), 128.3, 124.1, 123.0 (q, *J* = 273.0 Hz), 91.8, 27.8, 10.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –63.0. **IR** ν (cm^{-1}) = 3101 (w), 3072 (w), 2983 (m), 2945 (m), 2888 (m), 1557 (s). **HRMS** [(CI), $(C_{11}H_9F_6NO_2 - F)^+$] calcd 282.0548, found m/z 282.0541.

4-(1-nitropropyl)benzonitrile (36)



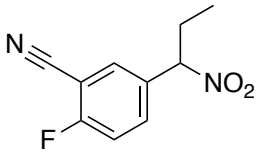
Oil, yield 31 mg (33%), R_f 0.32 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 5.40 (q, *J* = 6.5 Hz and 2.5 Hz, 1H), 2.55 – 2.49 (m, 1H), 2.14 – 2.07 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 139.1, 132.9, 128.7, 118.1, 114.0, 92.3, 27.6, 10.7. **IR** ν (cm^{-1}) = 2979 (w), 2940 (w), 2232 (m), 1734(m), 1549 (s), 1506 (m), 1460 (w). **HRMS** [(CI), $(C_{10}H_{10}N_2O_2 + H)^+$] calcd 191.0815, found m/z 191.0807.

methyl 2-fluoro-4-(1-nitropropyl)benzoate (37)



Yellow semisolid, yield 41 mg (68%), R_f 0.13 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (t, 1H, *J* = 7.6 Hz), 7.34–7.24 (m, 2H), 5.39 (t, 1H, *J* = 7.6 Hz), 3.94 (s, 3H), 2.56–2.42 (m, 1H), 2.18–2.04 (m, 1H), 1.00 (s, 3H, *J* = 6.8 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 161.9 (d, *J* = 260.5 Hz), 140.9 (d, *J* = 8.4 Hz), 123.5 (d, *J* = 3.1 Hz), 120.0 (d, *J* = 10.6 Hz), 116.5 (d, *J* = 23.5 Hz), 91.9, 52.7, 27.6, 10.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –107.6 (dd, *J* = 10.9 and 7.9 Hz). **IR** ν (cm^{-1}) = 3096 (w), 3073 (w), 3054 (w), 2977 (m), 2957 (m), 2941 (w), 2921 (m), 2885 (m), 2850 (m), 1723 (s), 1624 (m), 1551 (s). **HRMS** [(CI), $(C_{11}H_{12}FNO_4 + H)^+$] calcd 242.0823, found m/z 242.0814.

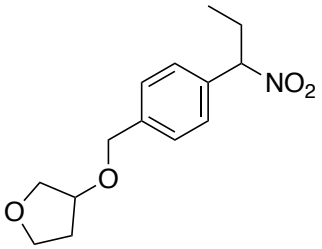
2-fluoro-5-(1-nitropropyl)benzonitrile (38)



Yellow oil, yield 27 mg (52%), R_f 0.12 (4:5, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79–7.68 (m, 2H), 7.29 (t, 1H, *J* = 8.5 Hz), 5.37 (dd, 1H, *J* = 8.0 and 7.0 Hz), 2.56–2.42 (m, 1H), 2.14–2.00 (m, 1H), 1.00 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.8 (d, *J* = 264.3 Hz), 134.8 (d, *J* = 8.6 Hz), 133.4, 131.6, 117.5 (d, *J* = 20.2 Hz), 113.1, 102.7, 91.2, 27.6, 10.6; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –104.0- –104.2 (m, 1F). **IR** ν (cm^{-1}) = 3128 (w), 3074 (w),

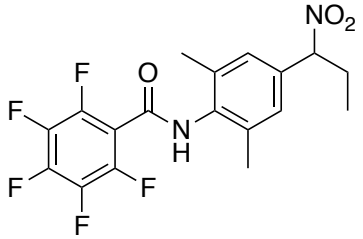
3056 (w), 2978 (m), 2923 (m), 2884 (w), 2852 (m), 2238 (m), 1551 (s). **HRMS** [(CI), $(C_{10}H_9FN_2O_2 + H)^+$] calcd 209.0721, found m/z 209.0725.

3-((4-(1-nitropropyl)benzyl)oxy)tetrahydrofuran (39)



Yellow oil, yield 54 mg (82%), R_f 0.14 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 5.36 (t, 1H, *J* = 8.4 Hz), 4.55–4.46 (m, 2H), 4.21 (s, 1H), 3.91 (q, 1H, *J* = 7.6 Hz), 3.89–3.77 (m, 3H), 2.56–2.43 (m, 1H), 2.16–1.95 (m, 3H), 0.97 (t, 3H, *J* = 7.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 133.9, 128.1, 128.0, 92.9, 79.4, 72.9, 70.5, 67.2, 32.7, 27.4, 10.7. **IR** ν (cm^{-1}) = 3060 (w), 3034 (w), 2975 (m), 2940 (m), 2868 (m), 1547 (s). **HRMS** [(CI), $(C_{14}H_{19}NO_4 - H)^+$] calcd 264.1230, found m/z 264.1224.

***N*-(2,6-dimethyl-4-(1-nitropropyl)phenyl)-2,3,4,5,6-pentafluorobenzamide (43)**



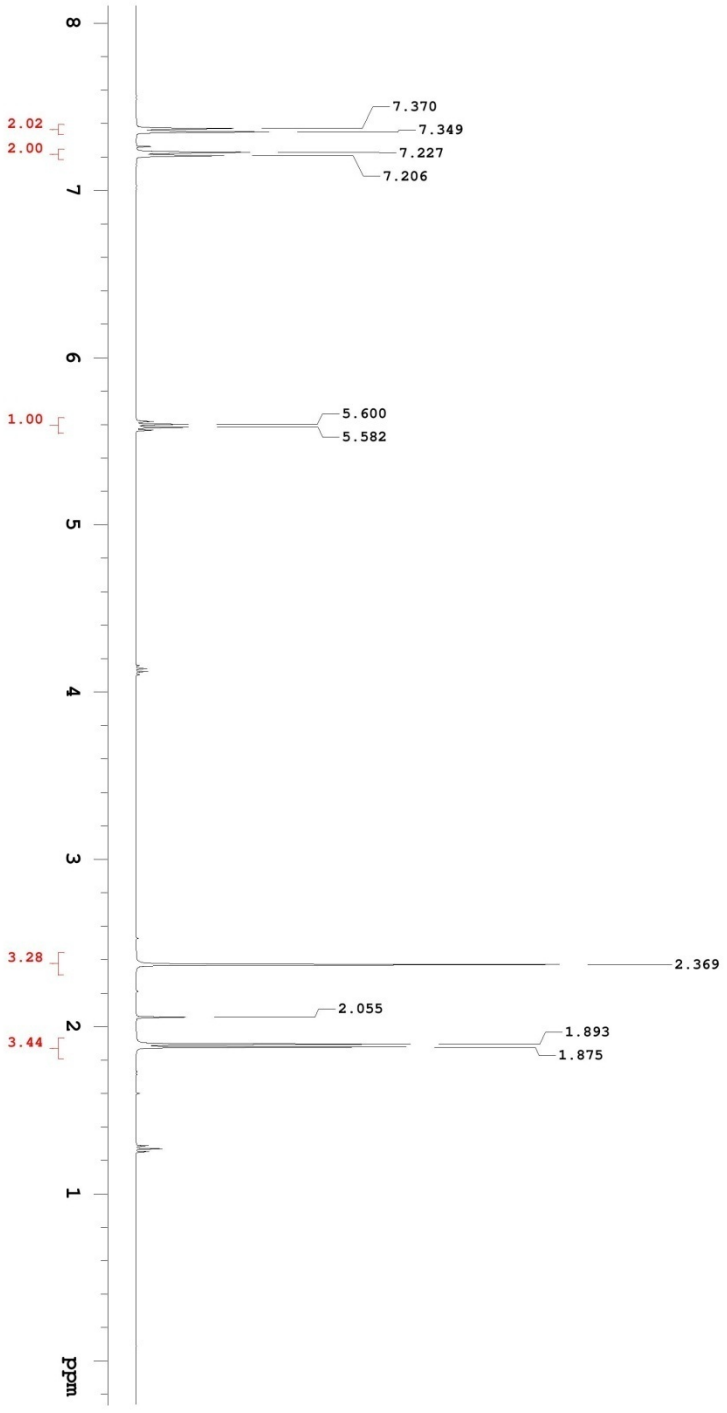
White powder, m.p. = 158–160 °C, yield 43 mg (59%), R_f 0.23 (4:1, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.18 (s, 2H), 5.31 (t, *J* = 6.8 Hz, 1H), 2.56–2.44 (m, 1

H), 2.23 (s, 6 H), 2.107–2.00 (m, 1H), 1.00 (t, J = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 144.7 (d, J = 161.7 Hz), 142.1 (d, J = 167.8 Hz), 139.1, 136.6, 134.4, 133.8, 127.8, 111.5 (t, J = 19.7 Hz), 92.8, 27.4, 18.5, 10.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –140.2 – –140.5 (m, 2F), –150.2 (t, J = 20.7 Hz, 1F), – 159.5 – –157.8 (m, 1F). **IR** ν (cm^{-1}) = 3228 (m), 3196 (s), 3138 (s), 3041 (m), 1918 (s) 2850 (s), 1662 (s). **HRMS** [(ESI), $(C_{18}H_{15}F_5N_2O_3 + H)^+$] calcd 403.1081, found m/z 403.1077.

13. References

1. A. Baruah, B. Kalita, N. C. Barua *Synlett* **2000**, 1064.
2. A. Kamimura, N. Ono *Bull. Chem. Soc. Jpn.* **1998**, *61*, 3629.
3. J. Xu, X. Li, J. Wu, W.-M. Dei *Tetrahedron* **2014**, *70*, 6384.
4. E. M. Vogl, S. L. Buchwald *J. Org. Chem.* **2002**, *67*, 106.

14. NMR Spectra


8
7
6
5
4
3
2
1
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1.00
3.28
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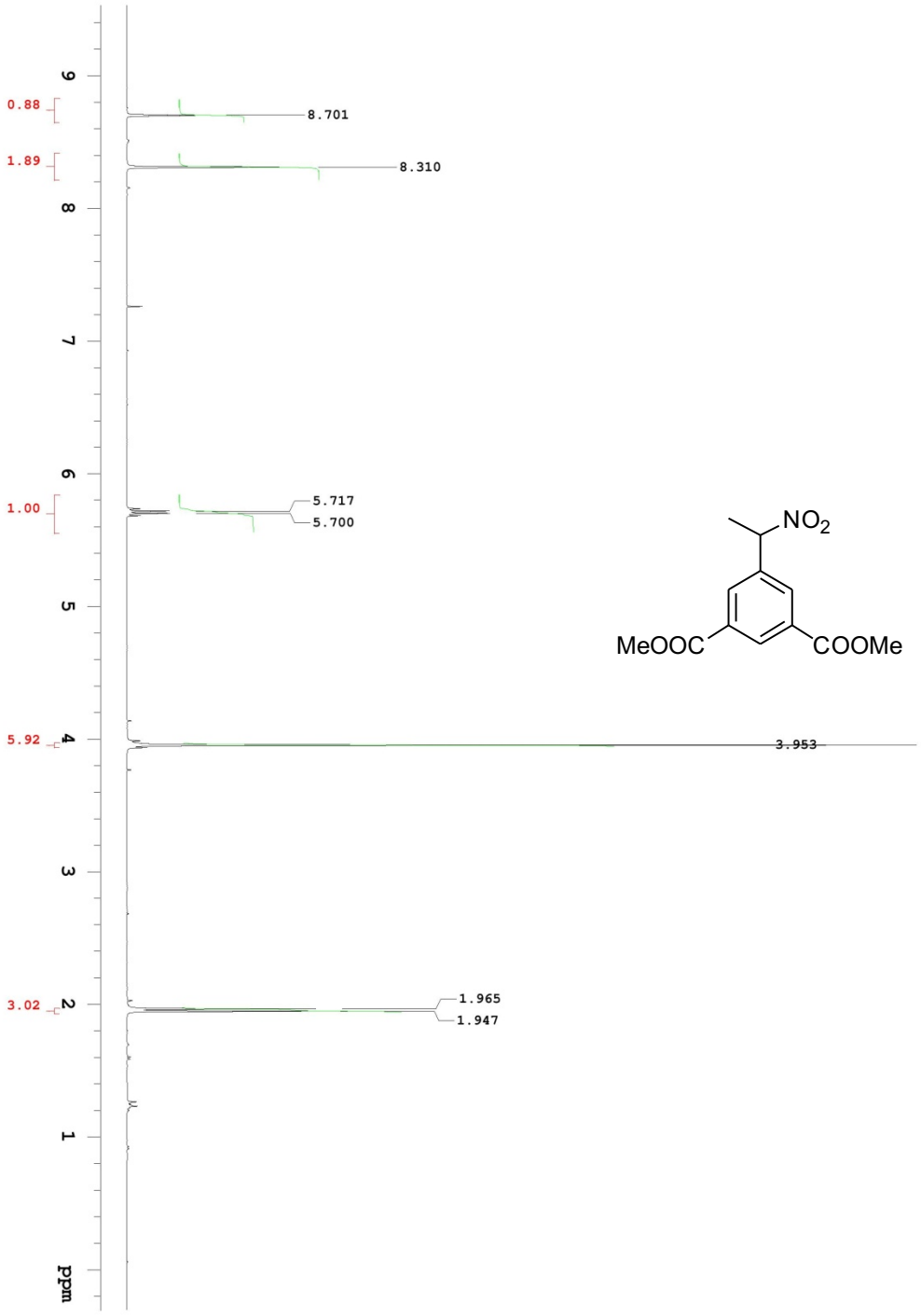
5.582
2.369
2.055
1.893
1.875
NO2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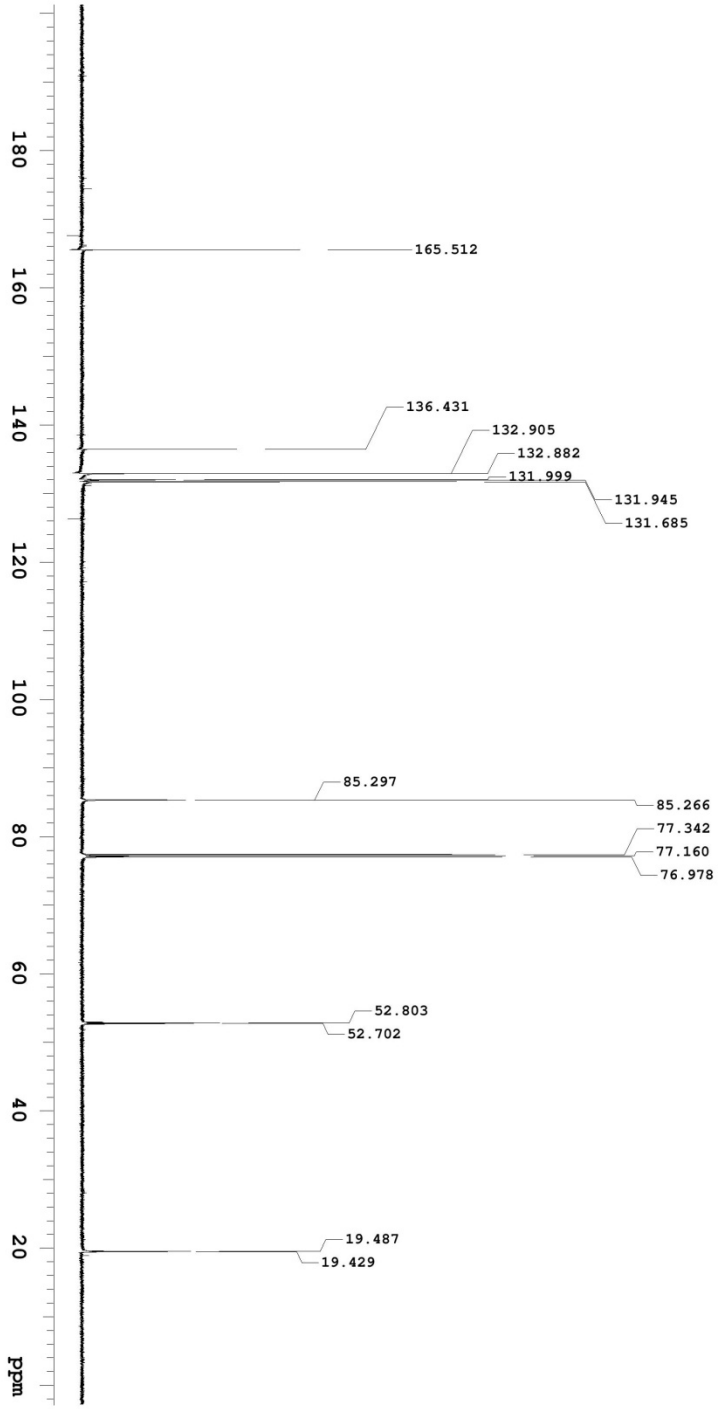
COOMe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140
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100
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40
20
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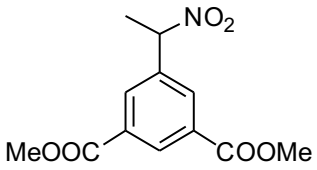
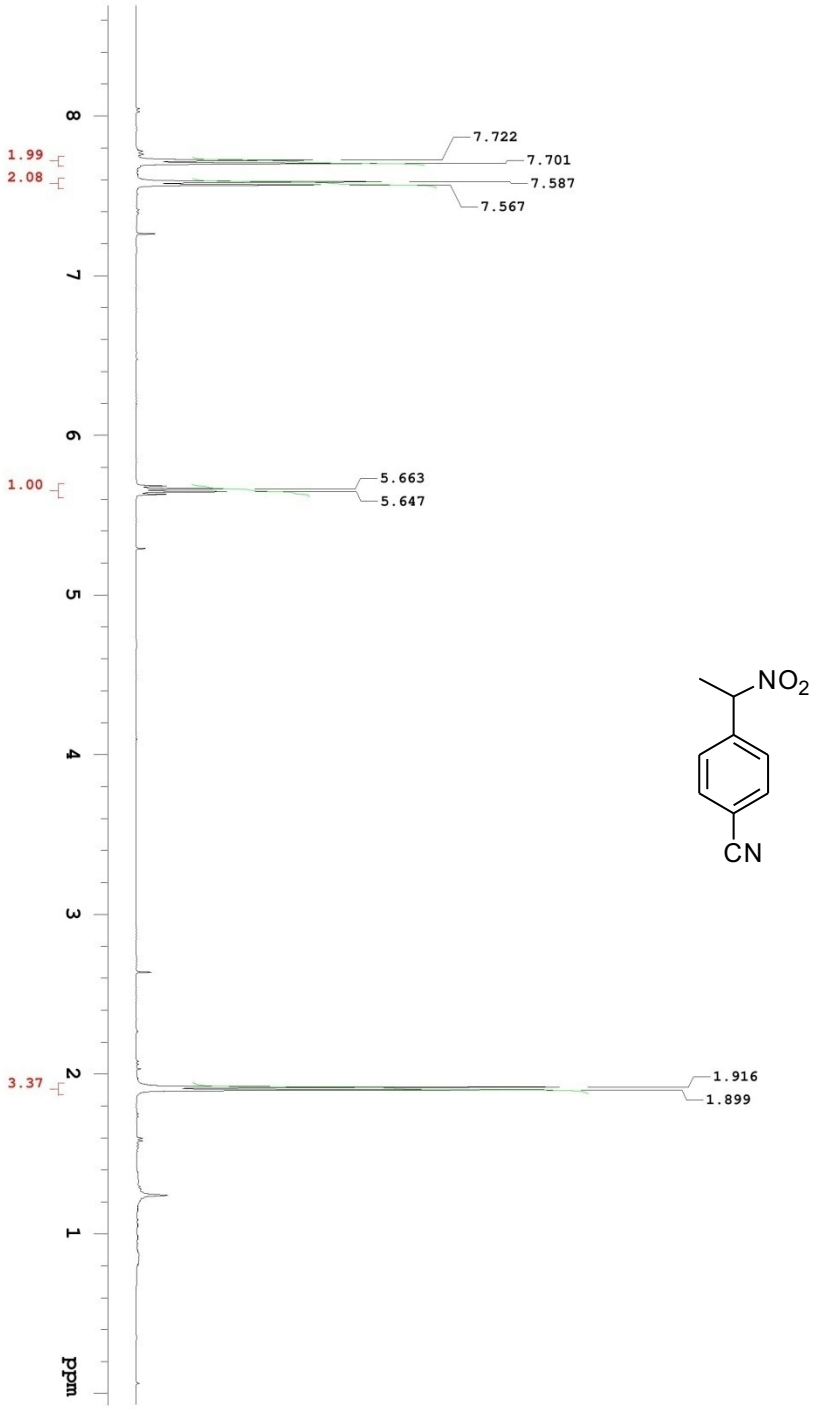
77.160
76.978
52.803
52.702
19.487
19.429


NO2
MeOOC
COOMe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7
6
5
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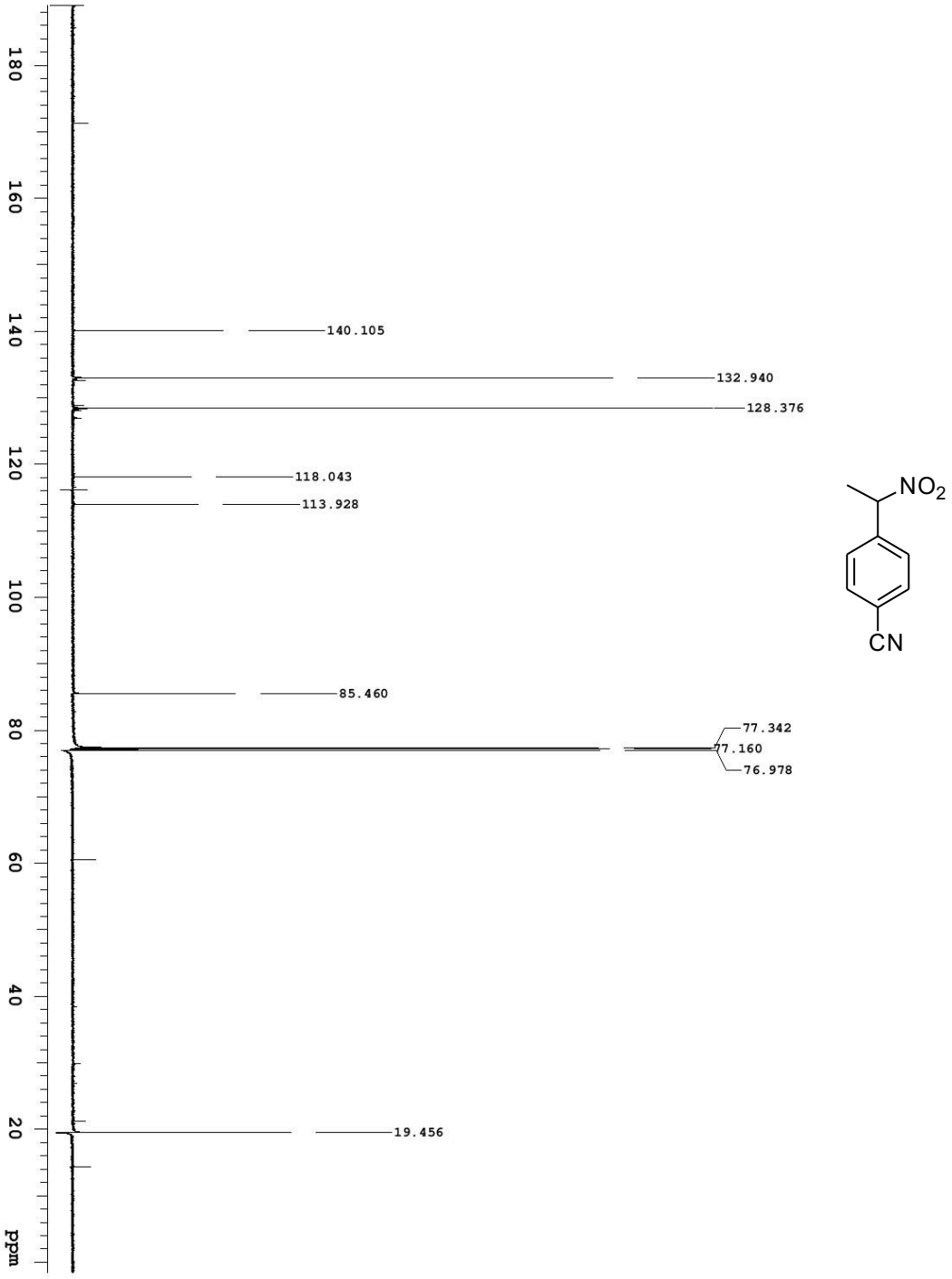
NO2
CN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77.160
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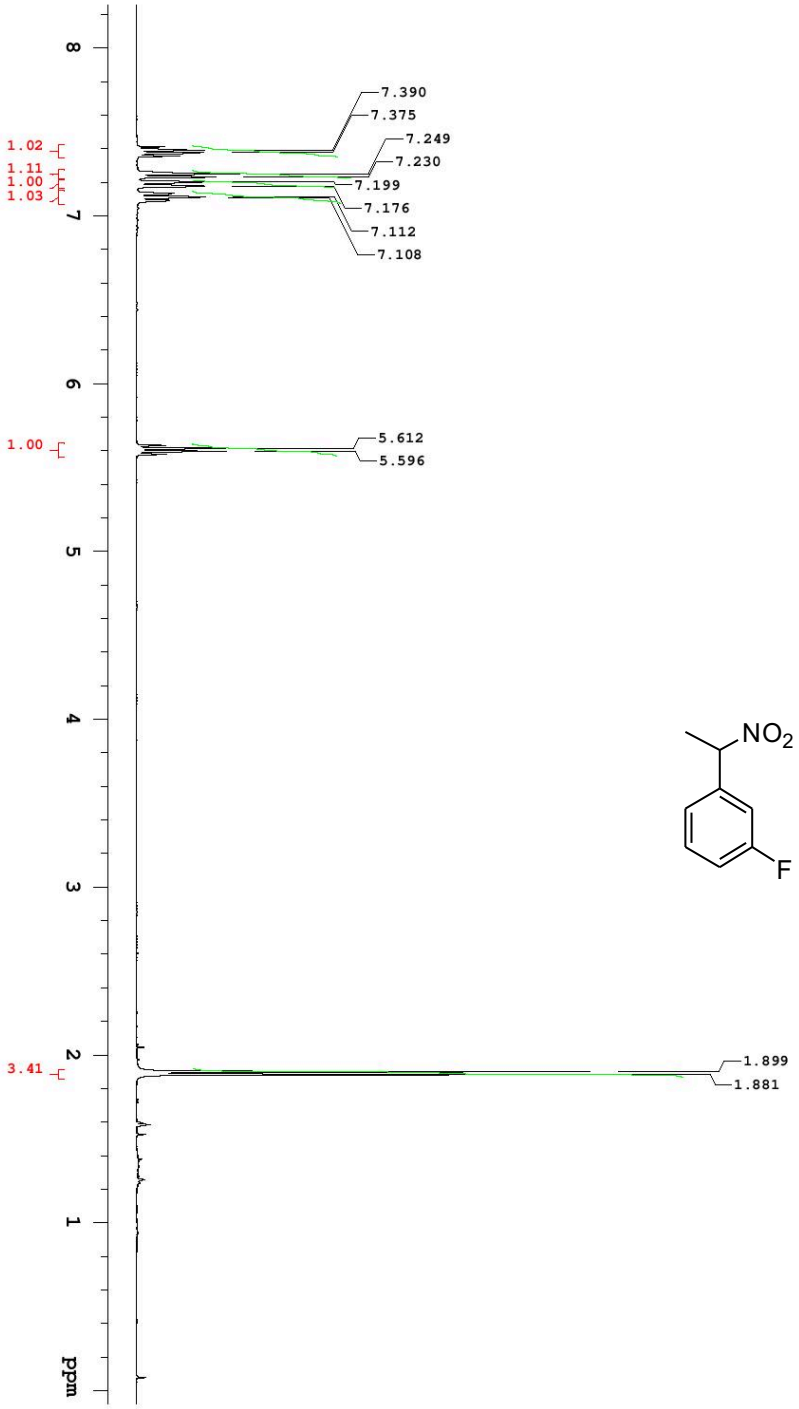
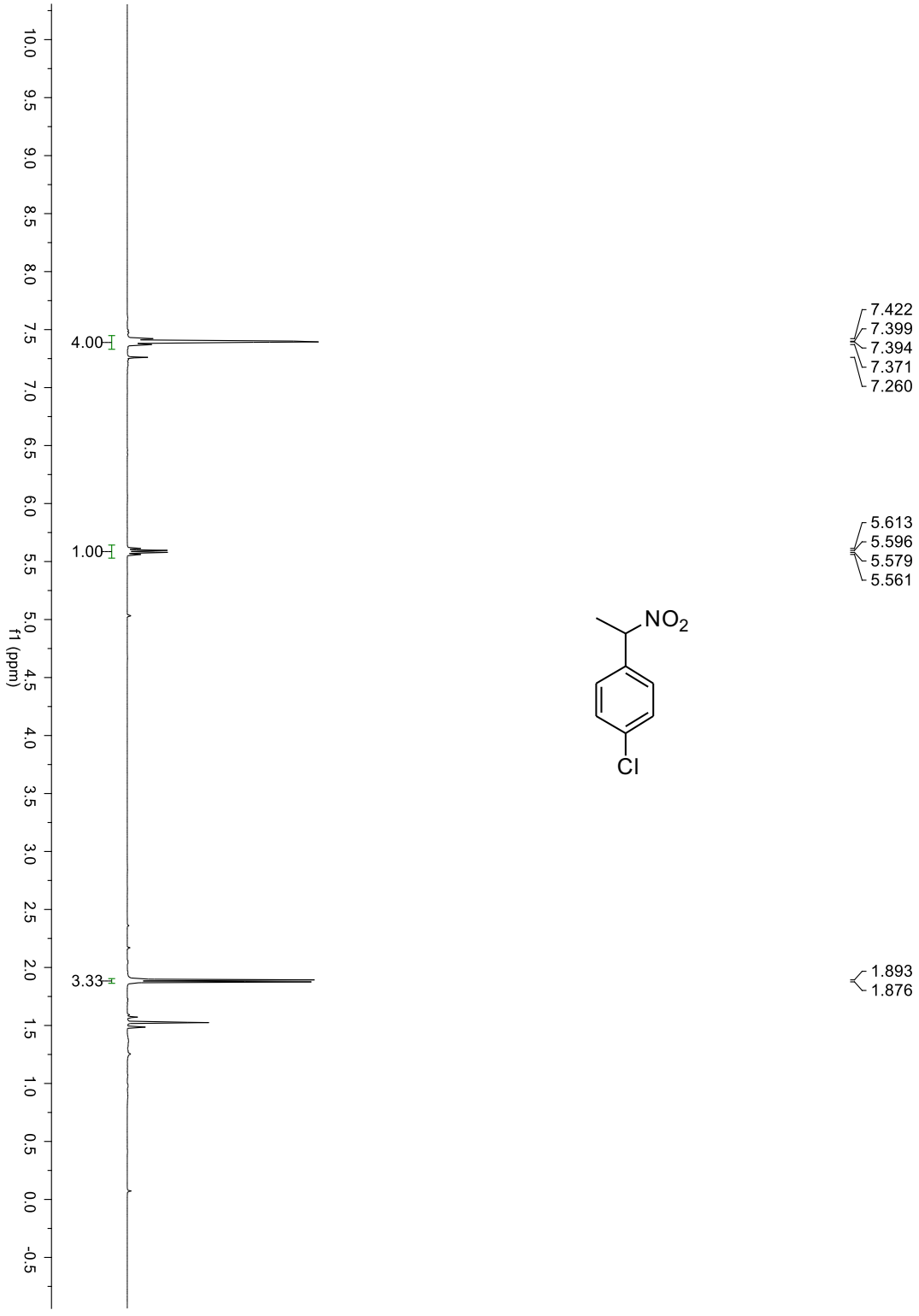
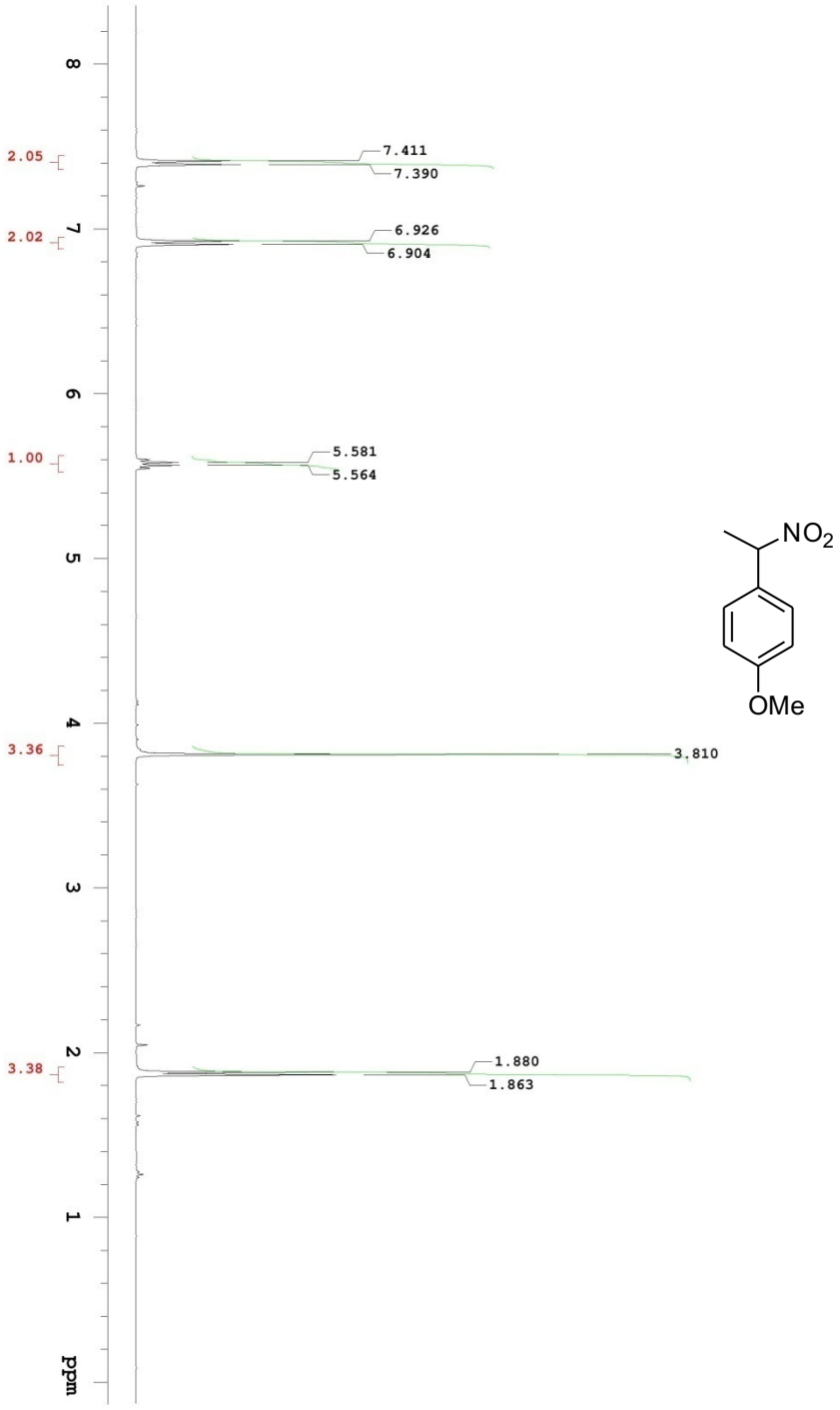
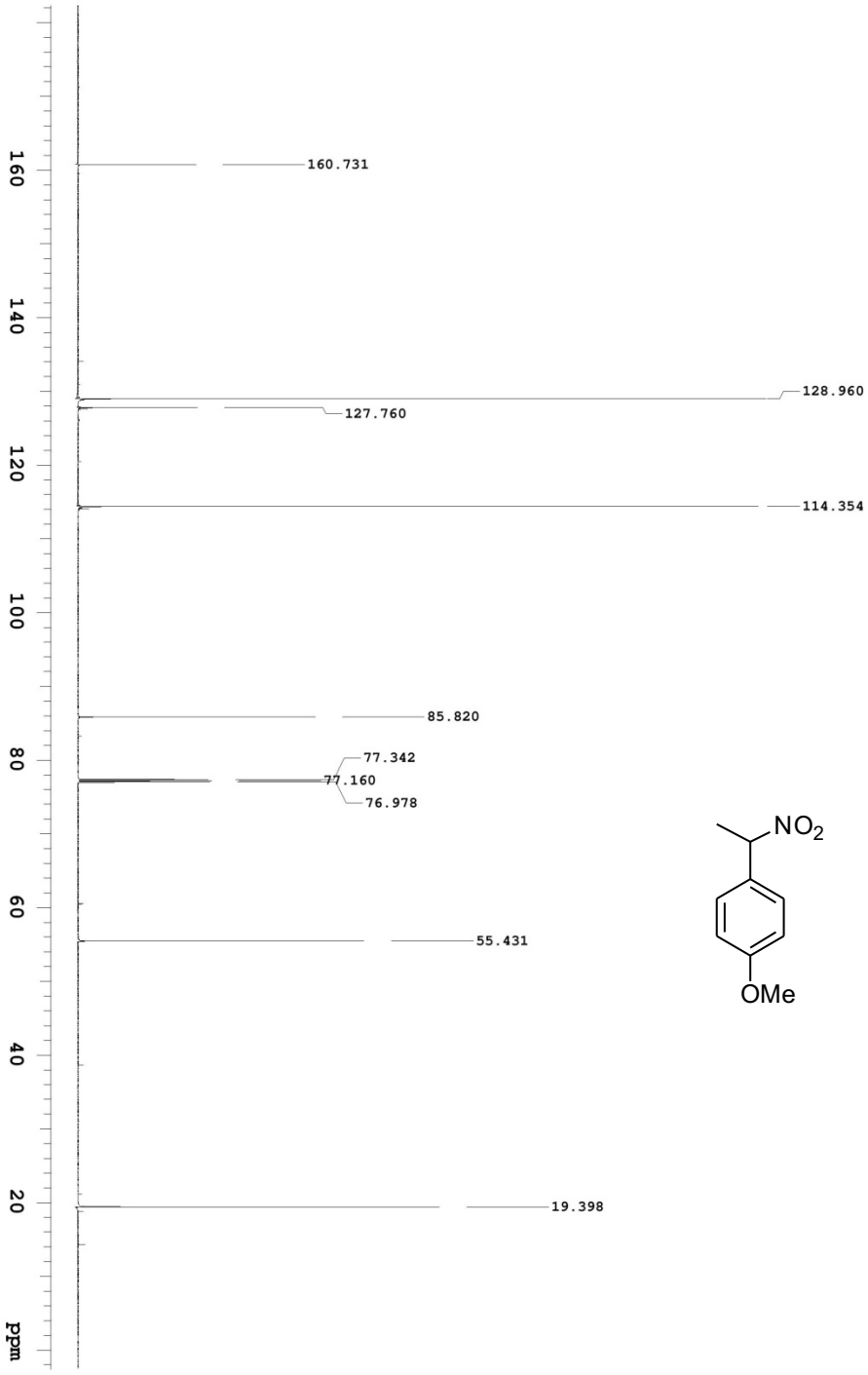
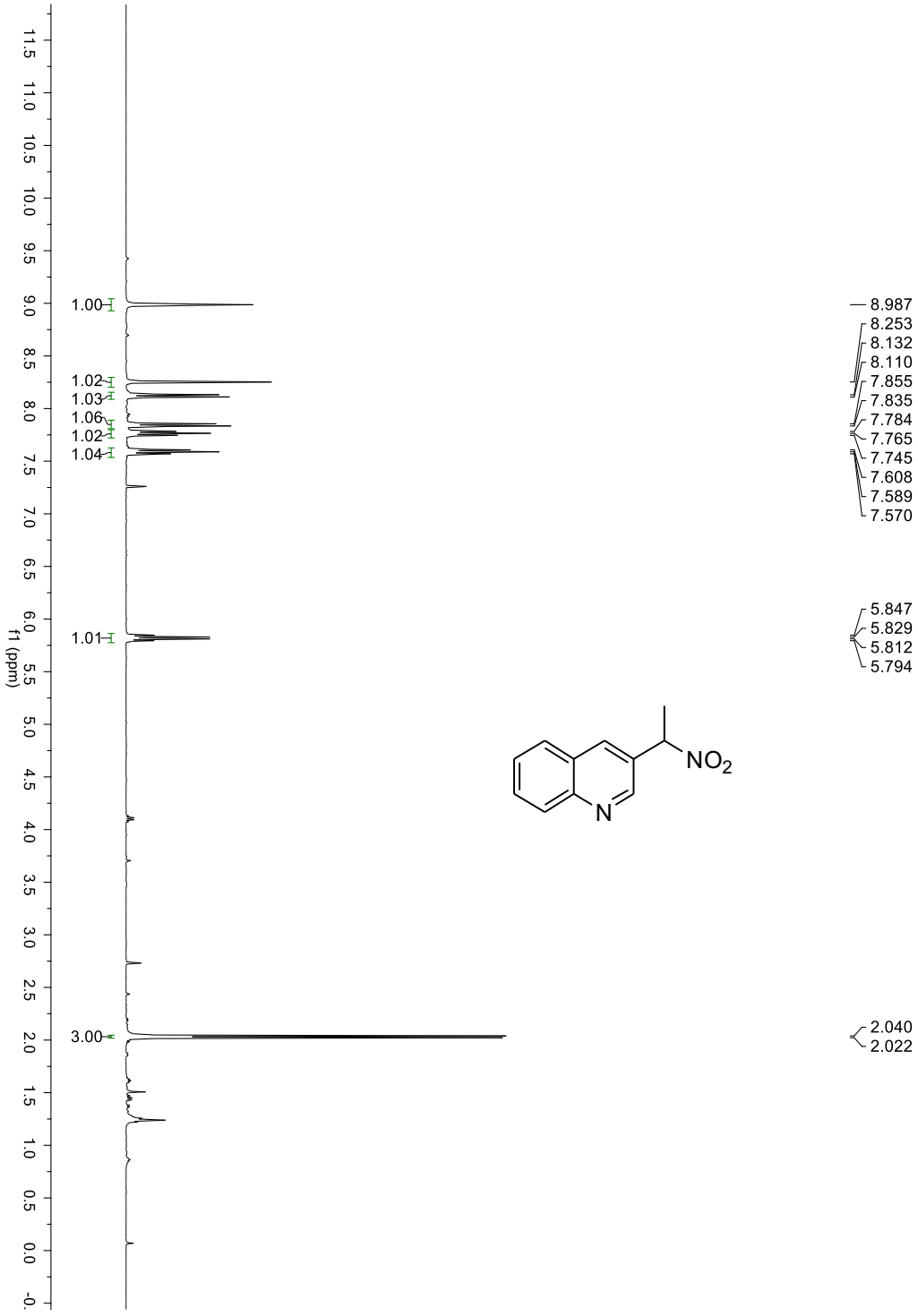
NO2
CN

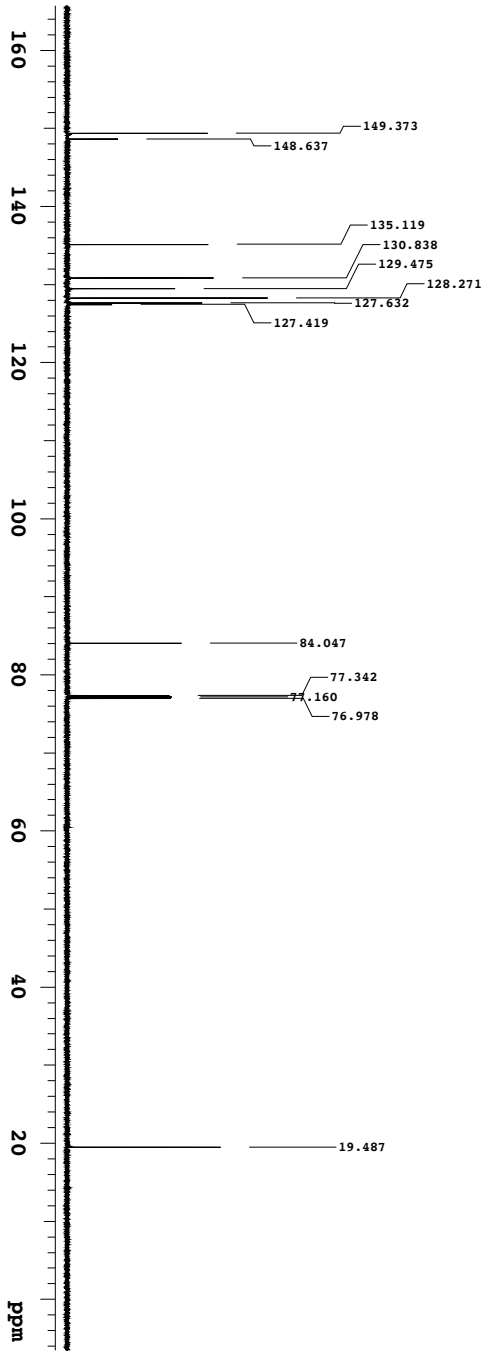

7.390
7.375
7.249
7.230
7.199
7.176
7.112
7.108
1.02
1.11
1.00
1.03
5.612
5.596
1.00
1.899
1.881
3.41
NO2
F
ppm

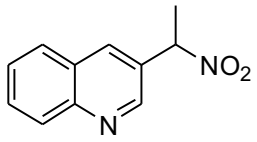

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
4.00
1.00
3.33
7.422
7.399
7.394
7.371
7.260
5.613
5.596
5.579
5.561
1.893
1.876
NO2
Cl

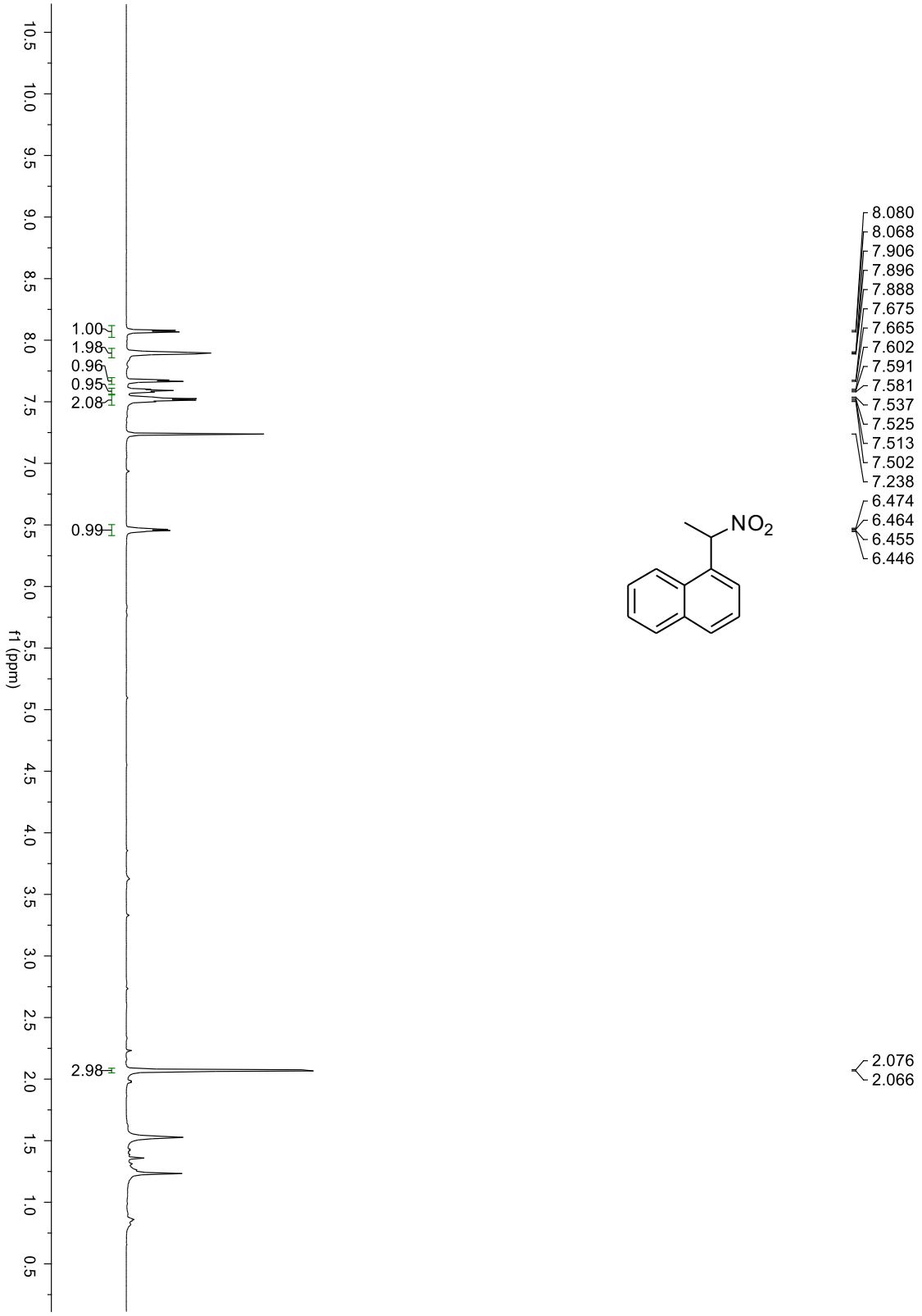

7.411
7.390
6.926
6.904
5.581
5.564
3.810
1.880
1.863
2.05
2.02
1.00
3.36
3.38
NO2
OMe
ppm

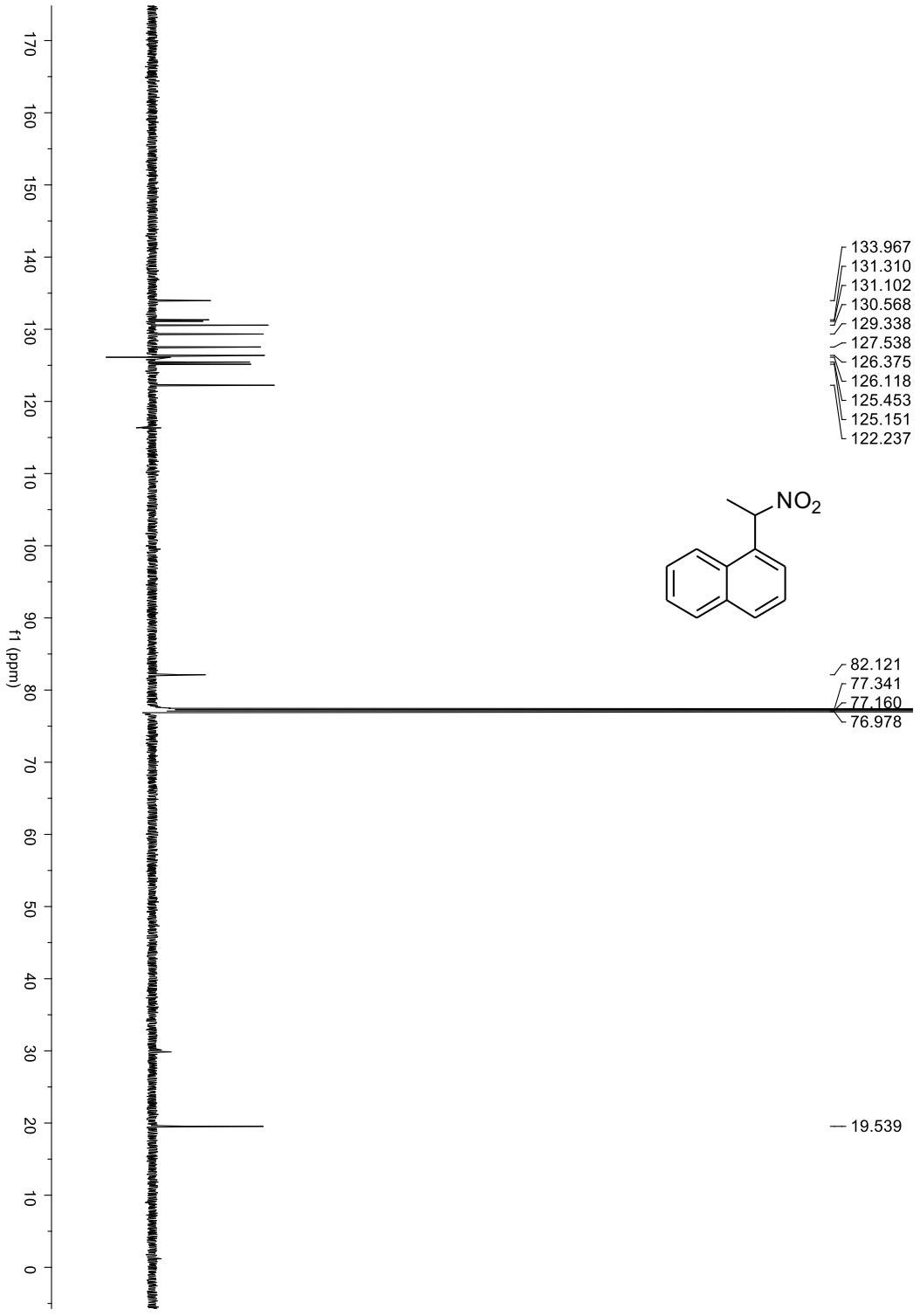

160.731
128.960
127.760
114.354
85.820
77.342
77.160
76.978
55.431
19.398
160
140
120
100
80
60
40
20
ppm
NO2
OMe

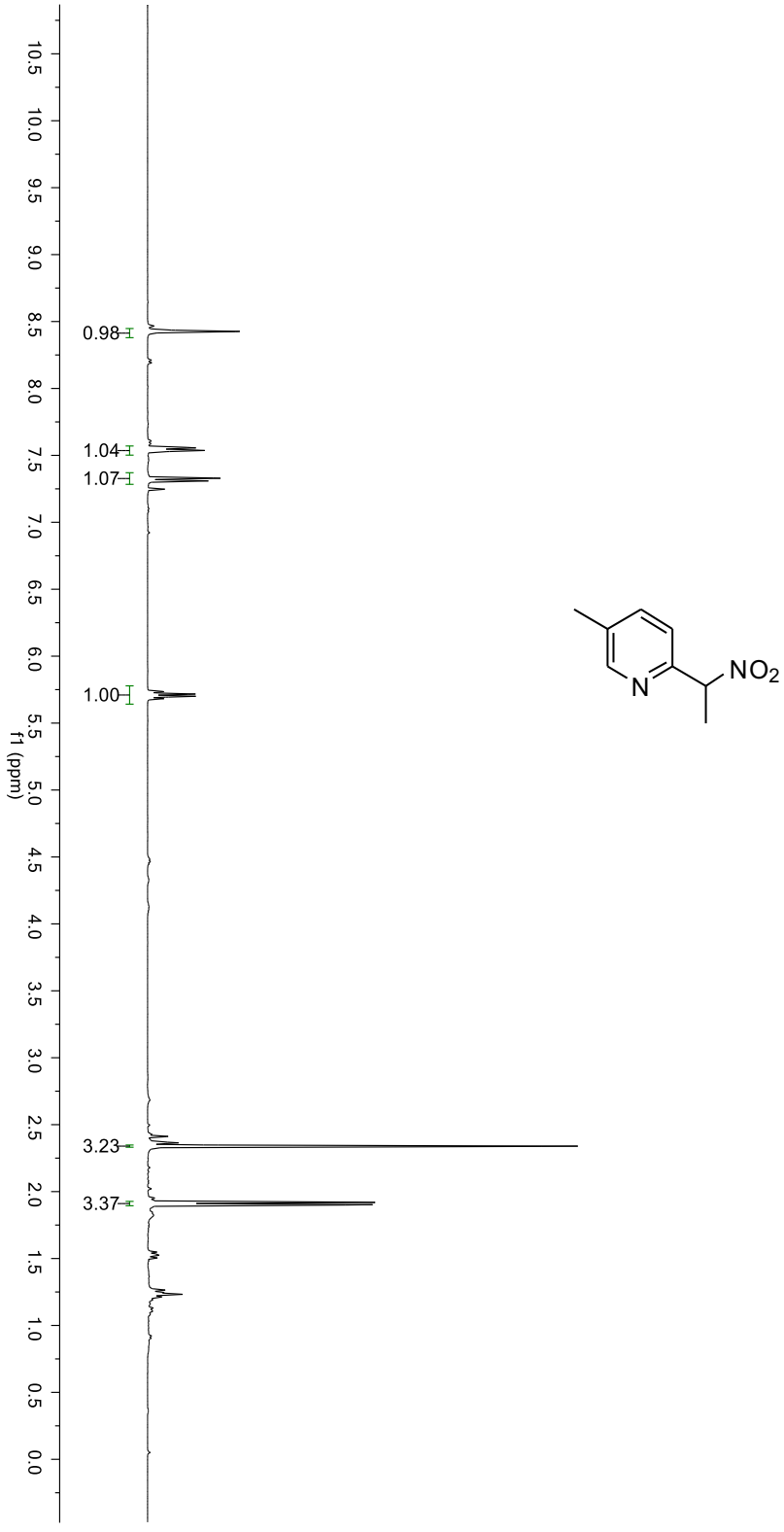

f1 (ppm)
1.00
1.02
1.03
1.06
1.02
1.04
1.01
3.00
8.987
8.253
8.132
8.110
7.855
7.835
7.784
7.765
7.745
7.608
7.589
7.570
5.847
5.829
5.812
5.794
2.040
2.022
NO2
N

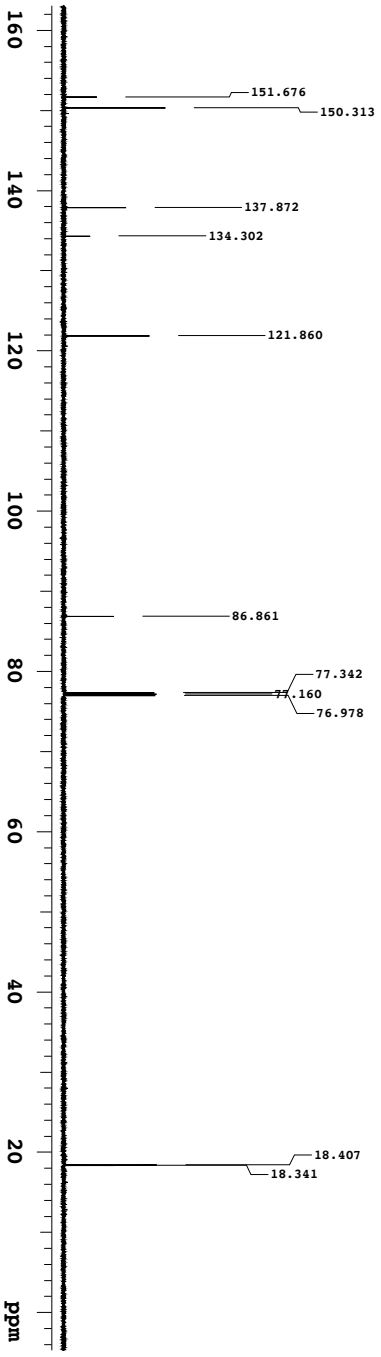

160
140
120
100
80
60
40
20
ppm
149.373
148.637
135.119
130.838
129.475
128.271
127.632
127.419
84.047
77.342
77.160
76.978
19.487

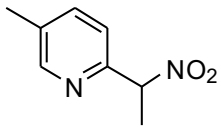

NO2
N

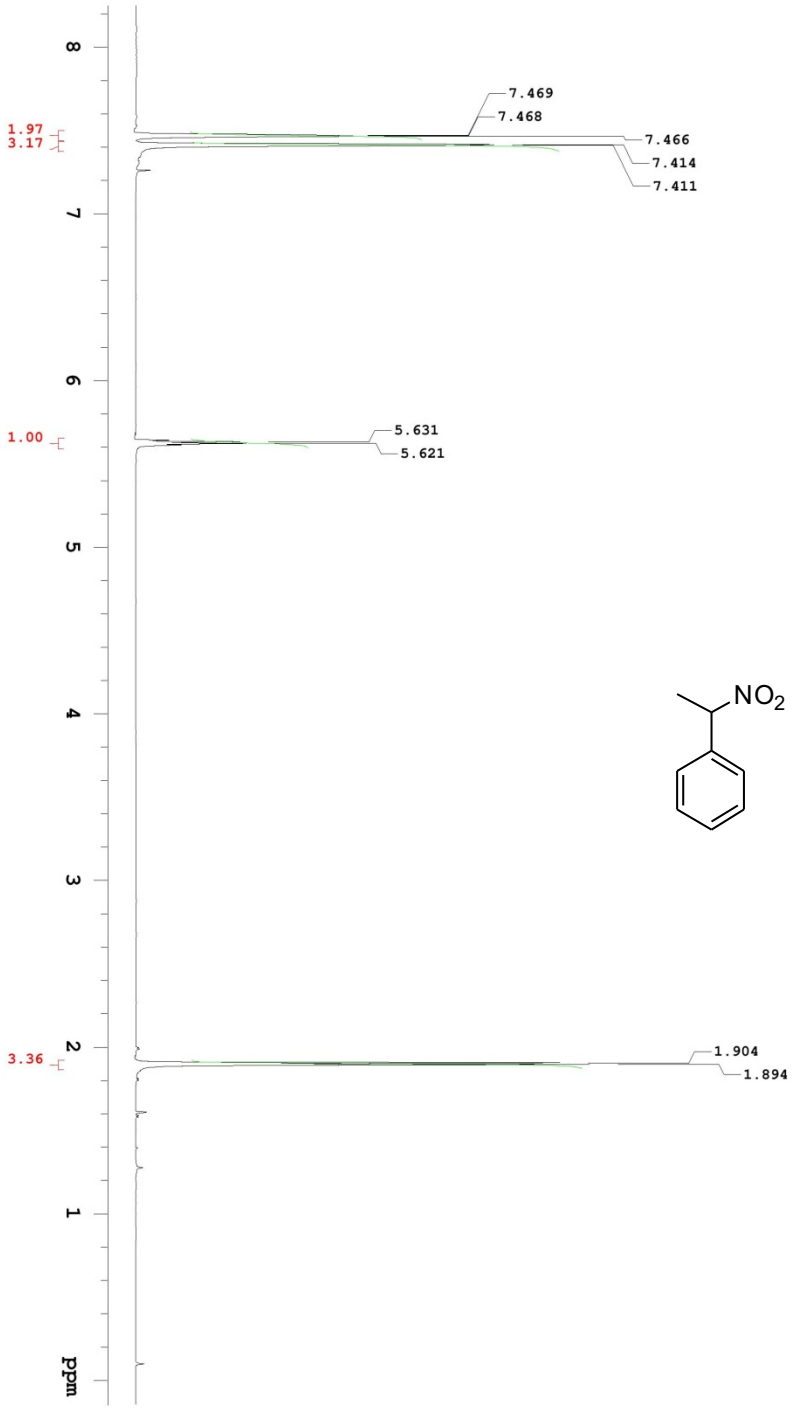

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
1.00
1.98
0.96
0.95
2.08
0.99
2.98
NO2
8.080
8.068
7.906
7.896
7.888
7.675
7.665
7.602
7.591
7.581
7.537
7.525
7.513
7.502
7.238
6.474
6.464
6.455
6.446
2.076
2.066

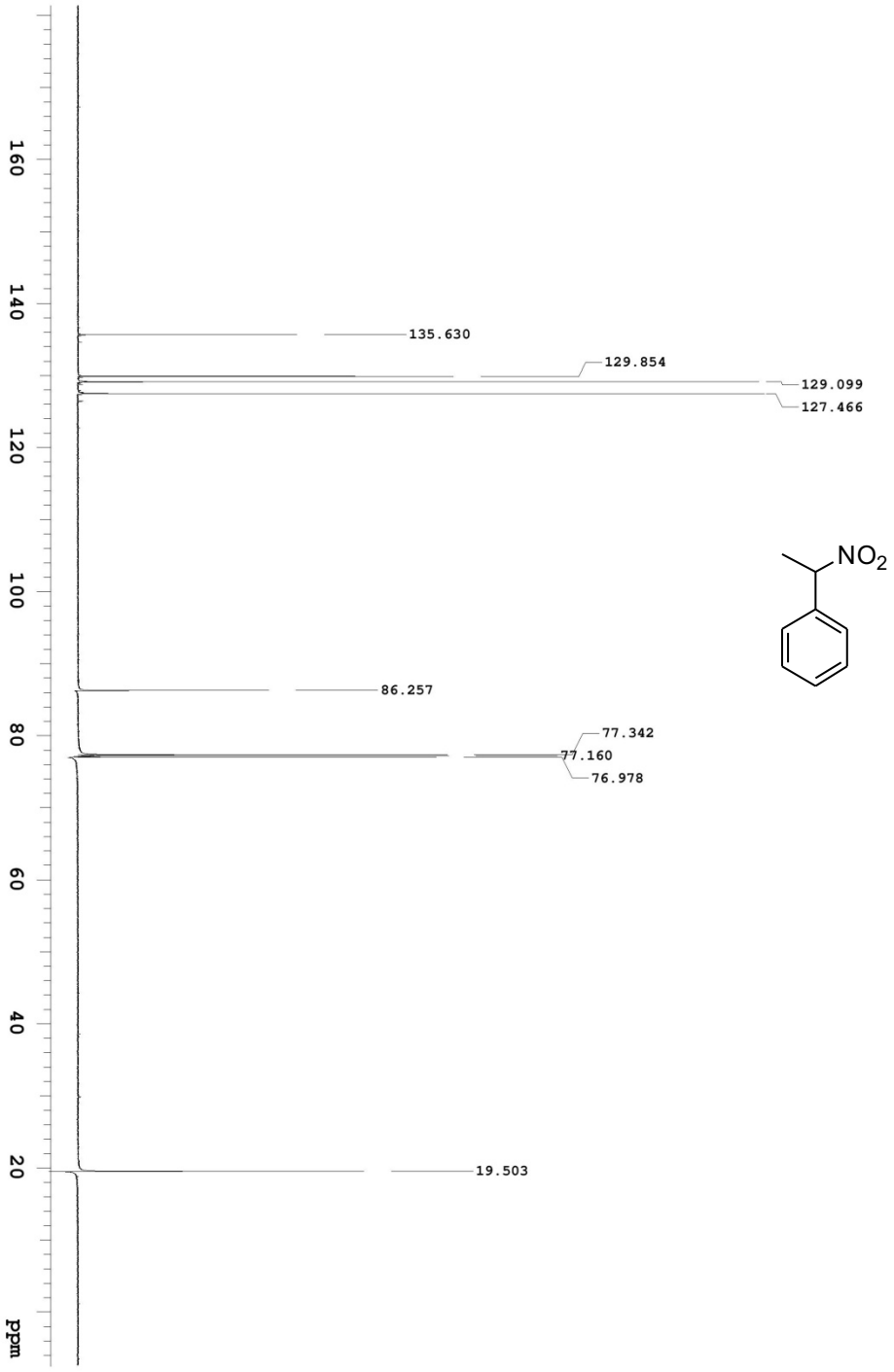

133.967
131.310
131.102
130.568
129.338
127.538
126.375
126.118
125.453
125.151
122.237
NO2
82.121
77.341
77.160
76.978
19.539
f1 (ppm)

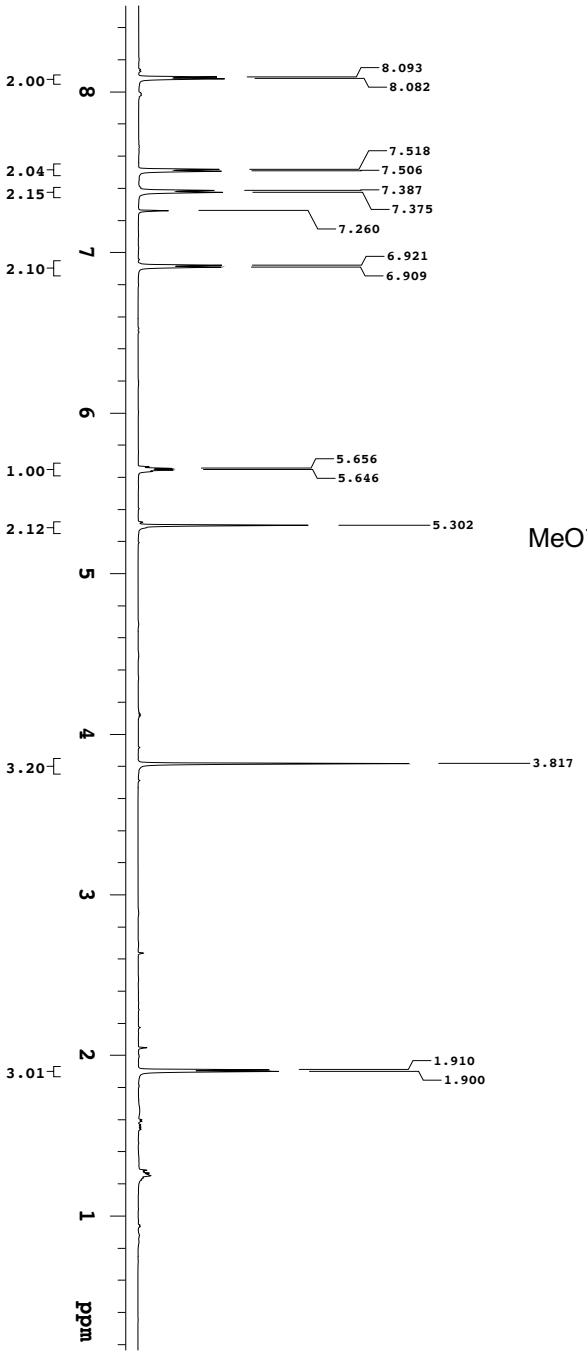

0.98
1.04
1.07
1.00
3.23
3.37
f1 (ppm)
N
NO2

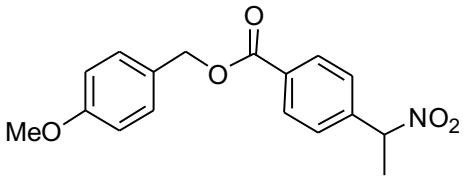

160
140
120
100
80
60
40
20
ppm
151.676
150.313
137.872
134.302
121.860
86.861
77.342
77.160
76.978
18.407
18.341

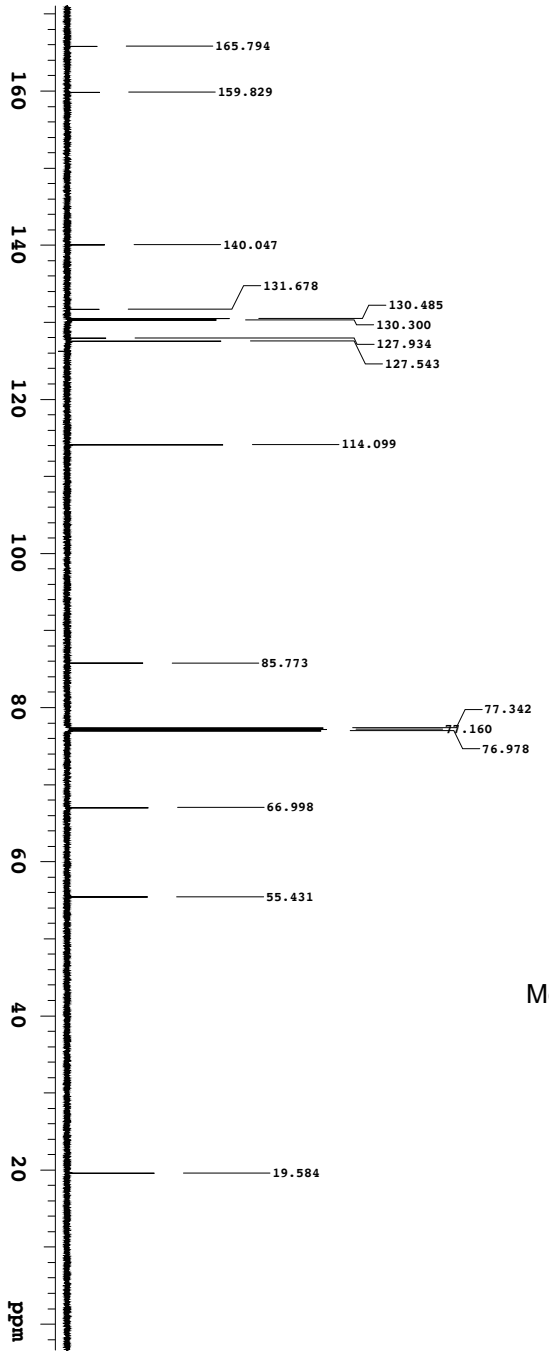

N
NO2

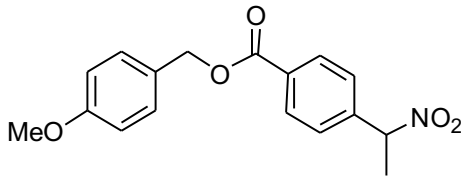

7.469
7.468
7.466
7.414
7.411
1.97
3.17
5.631
5.621
1.00
1.904
1.894
3.36
NO2
8
7
6
5
4
3
2
1
ppm

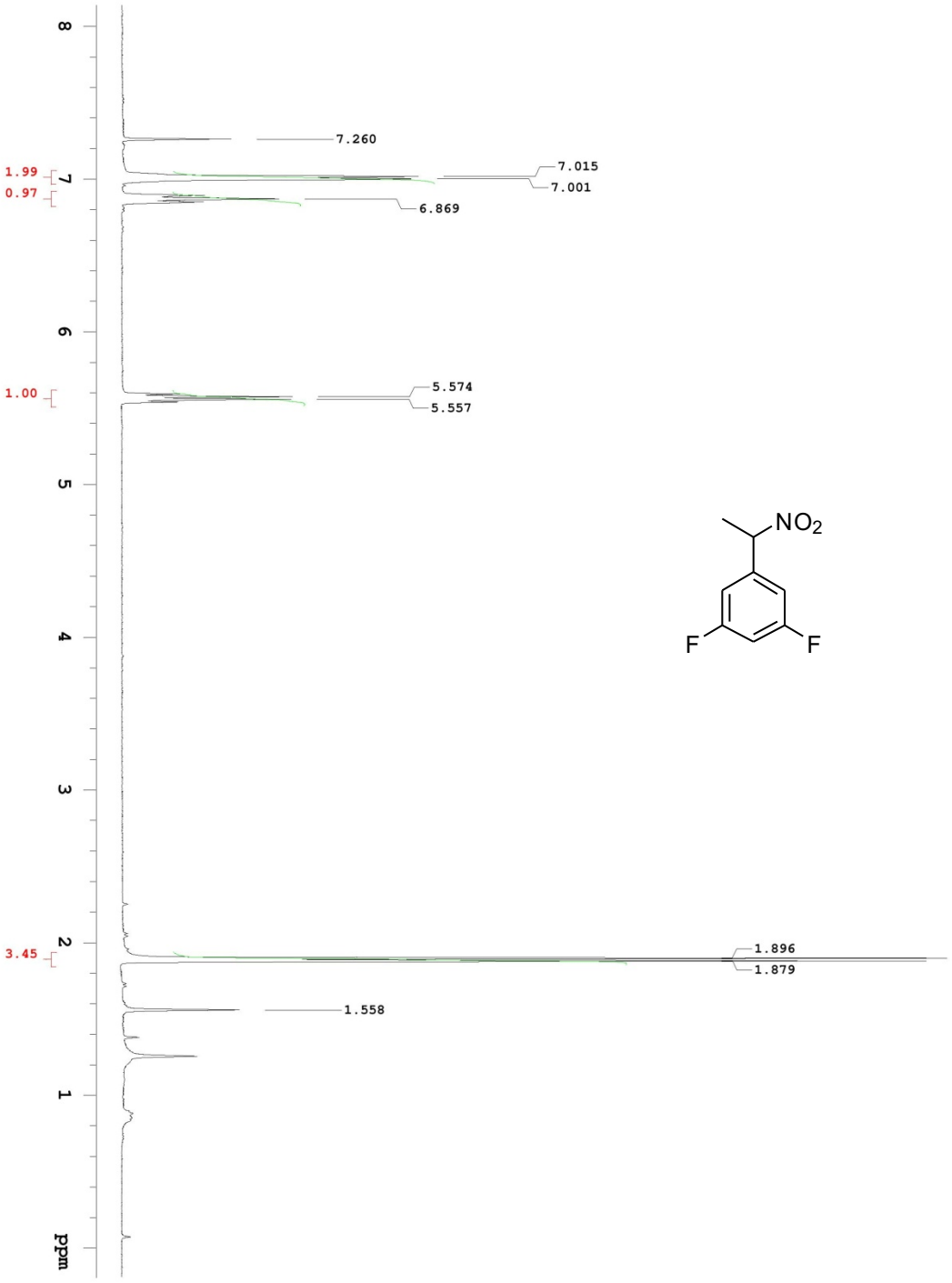

160
140
120
100
80
60
40
20
ppm
135.630
129.854
129.099
127.466
86.257
77.342
77.160
76.978
19.503
NO2

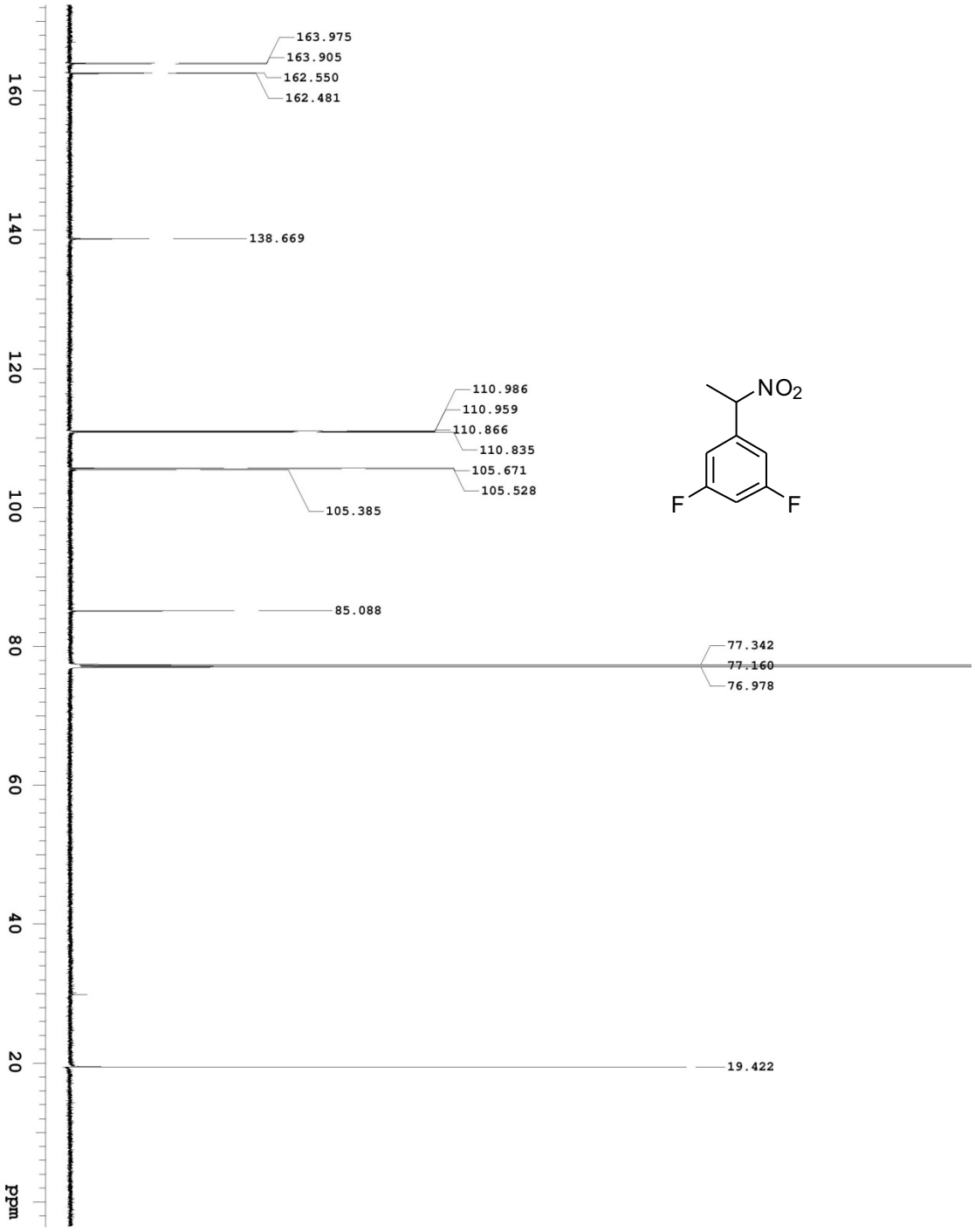

8.093
8.082
7.518
7.506
7.387
7.375
7.260
6.921
6.909
5.656
5.646
5.302
3.817
1.910
1.900
2.00
2.04
2.15
2.10
1.00
2.12
3.20
3.01
8
7
6
5
4
3
2
1
ppm

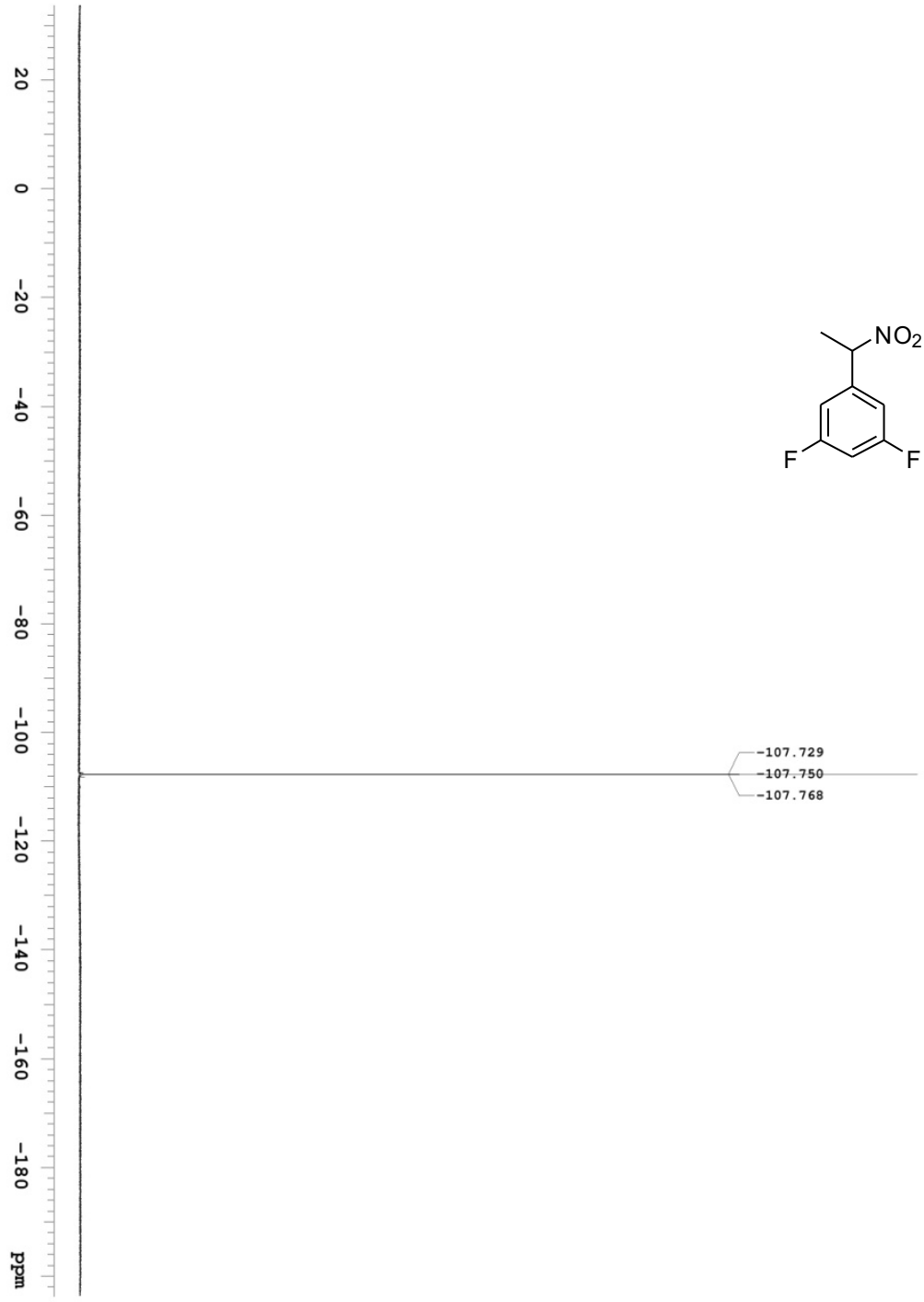

O
O
MeO
NO2

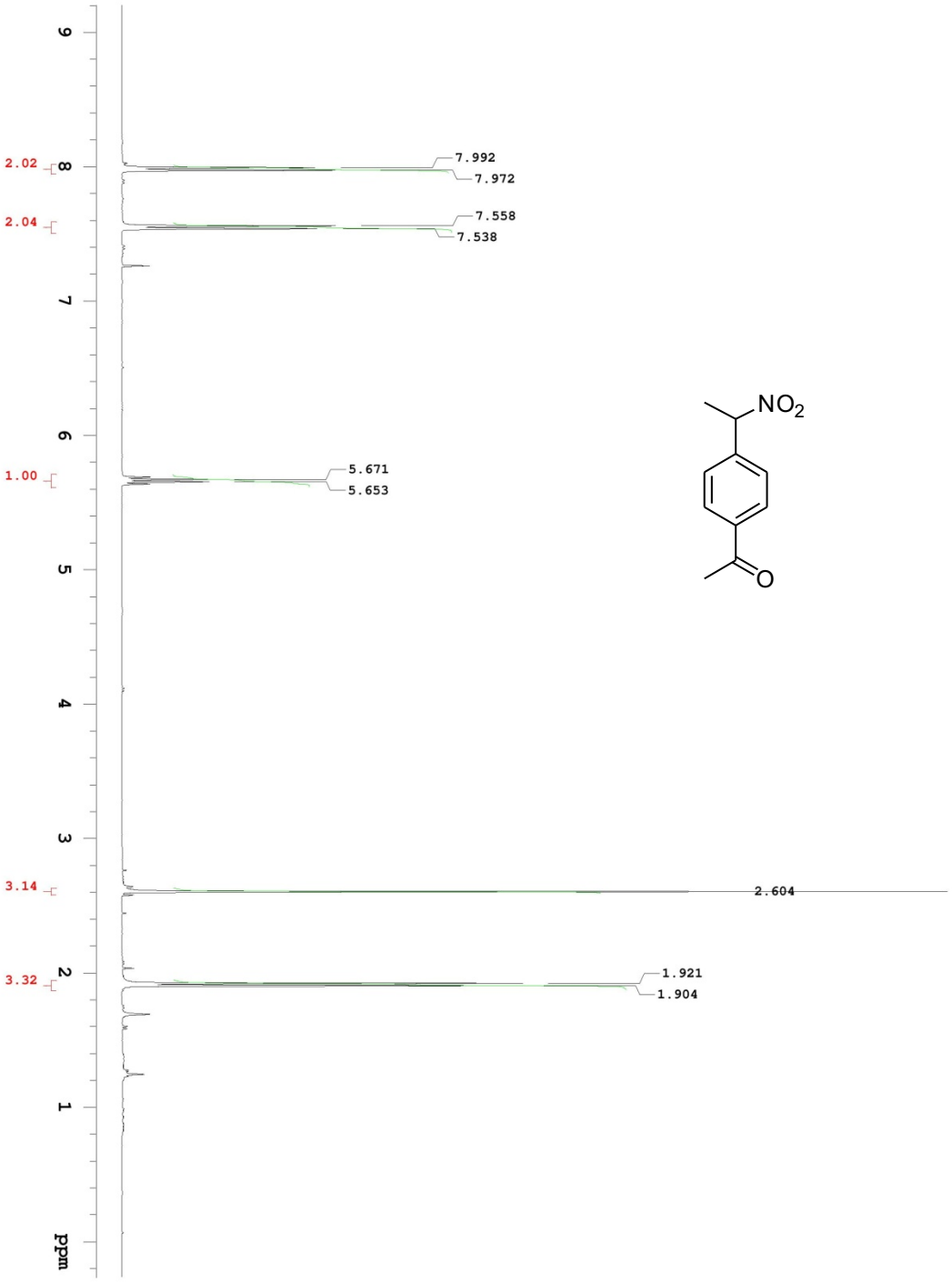

165.794
159.829
140.047
131.678
130.485
130.300
127.934
127.543
114.099
85.773
77.342
77.160
76.978
66.998
55.431
19.584
160
140
120
100
80
60
40
20
ppm

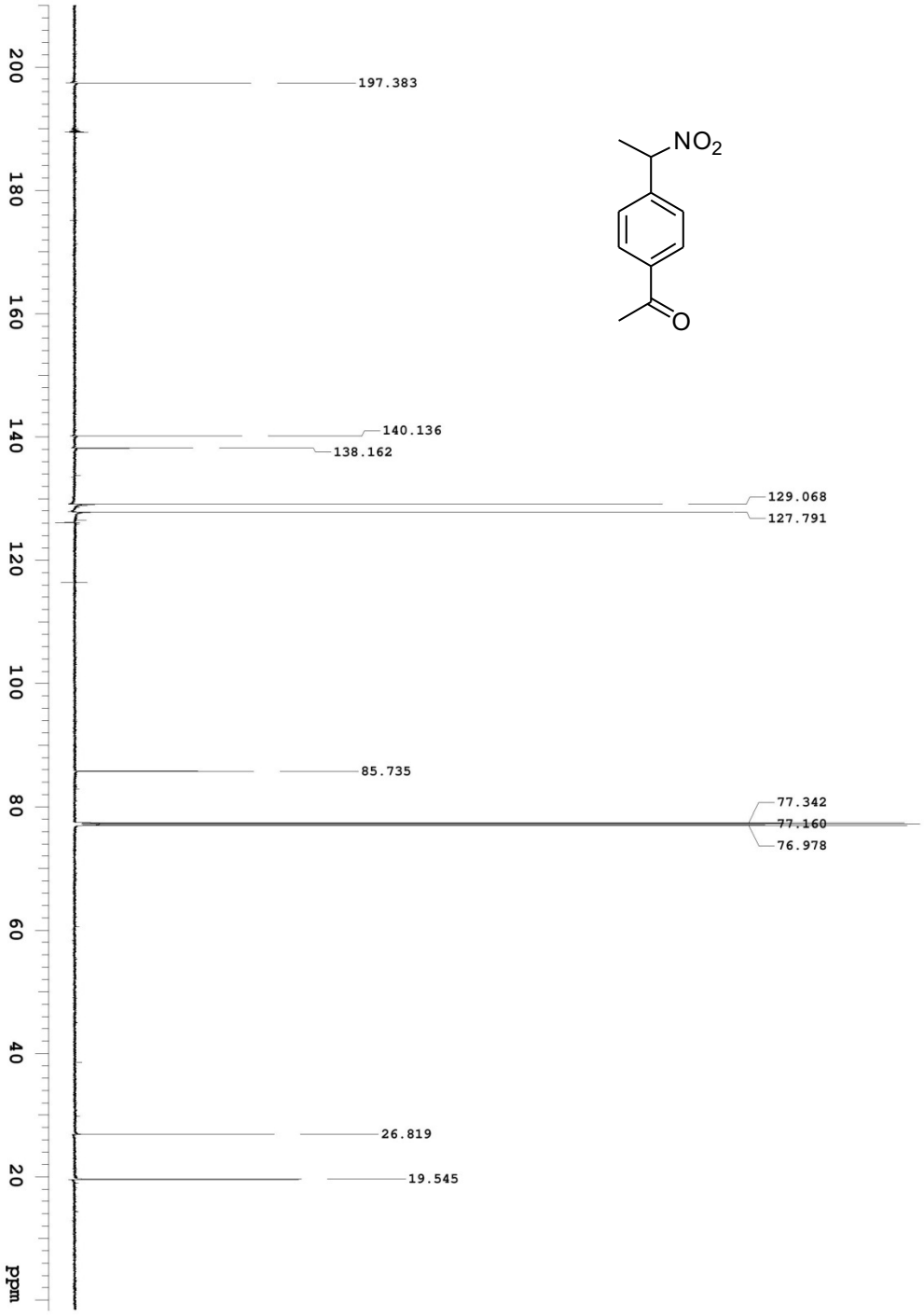

O
O
MeO
NO2

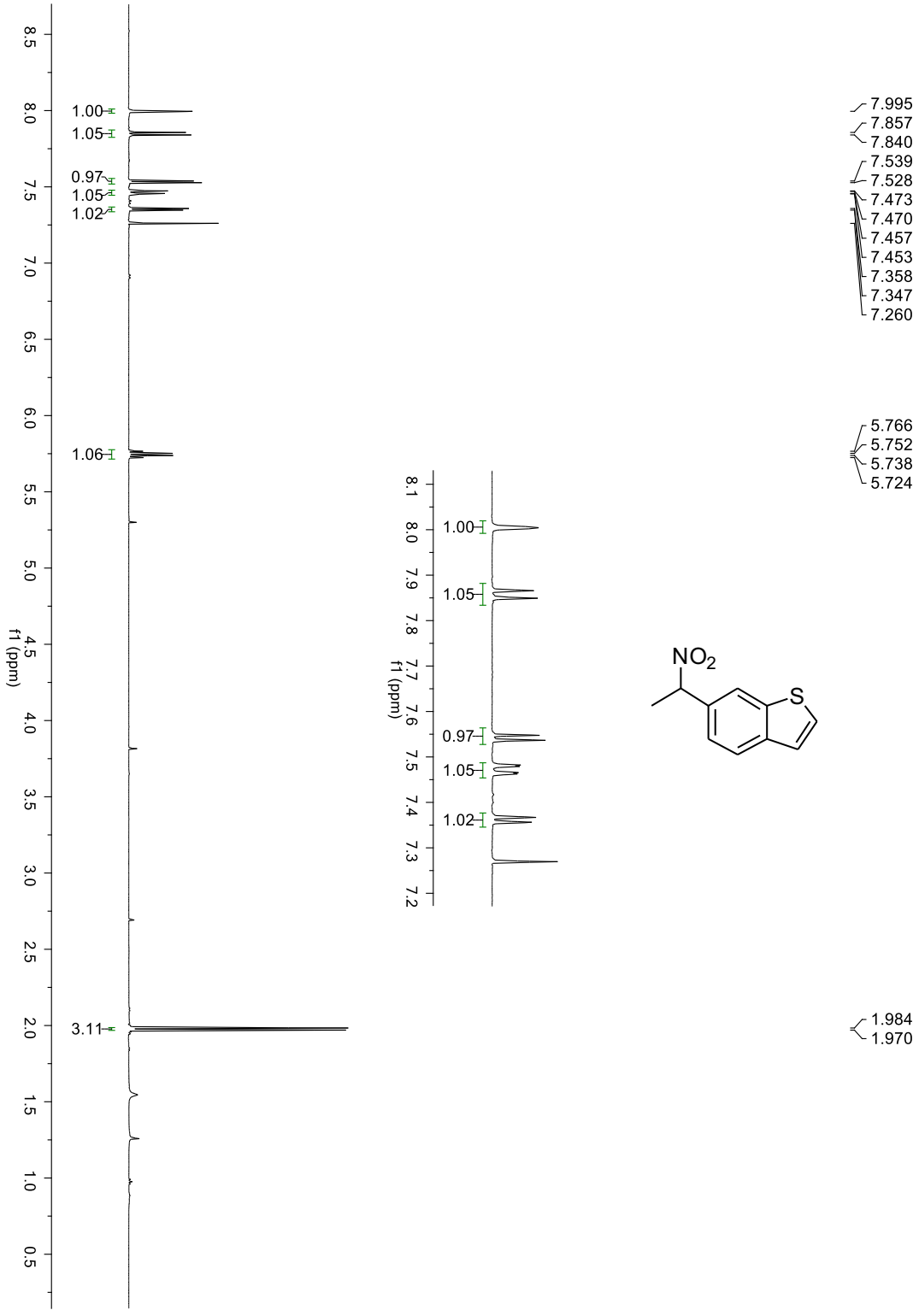

7.260
7.015
7.001
6.869
5.574
5.557
1.896
1.879
1.558
1.99
0.97
1.00
3.45
NO2
F
F
ppm

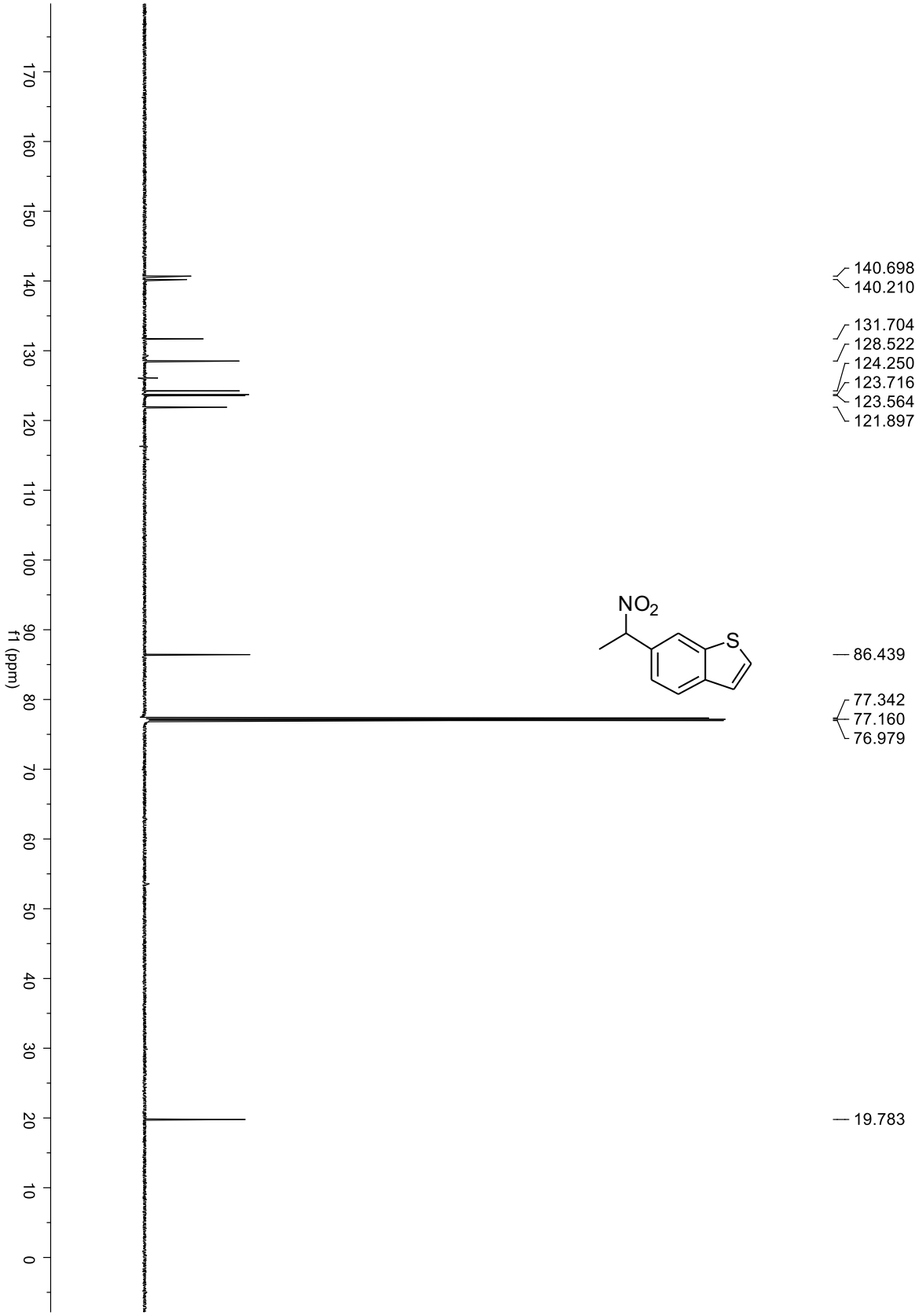

163.975
163.905
162.550
162.481
138.669
110.986
110.959
110.866
110.835
105.671
105.528
105.385
85.088
77.342
77.160
76.978
19.422
160
140
120
100
80
60
40
20
ppm
NO2
F
F

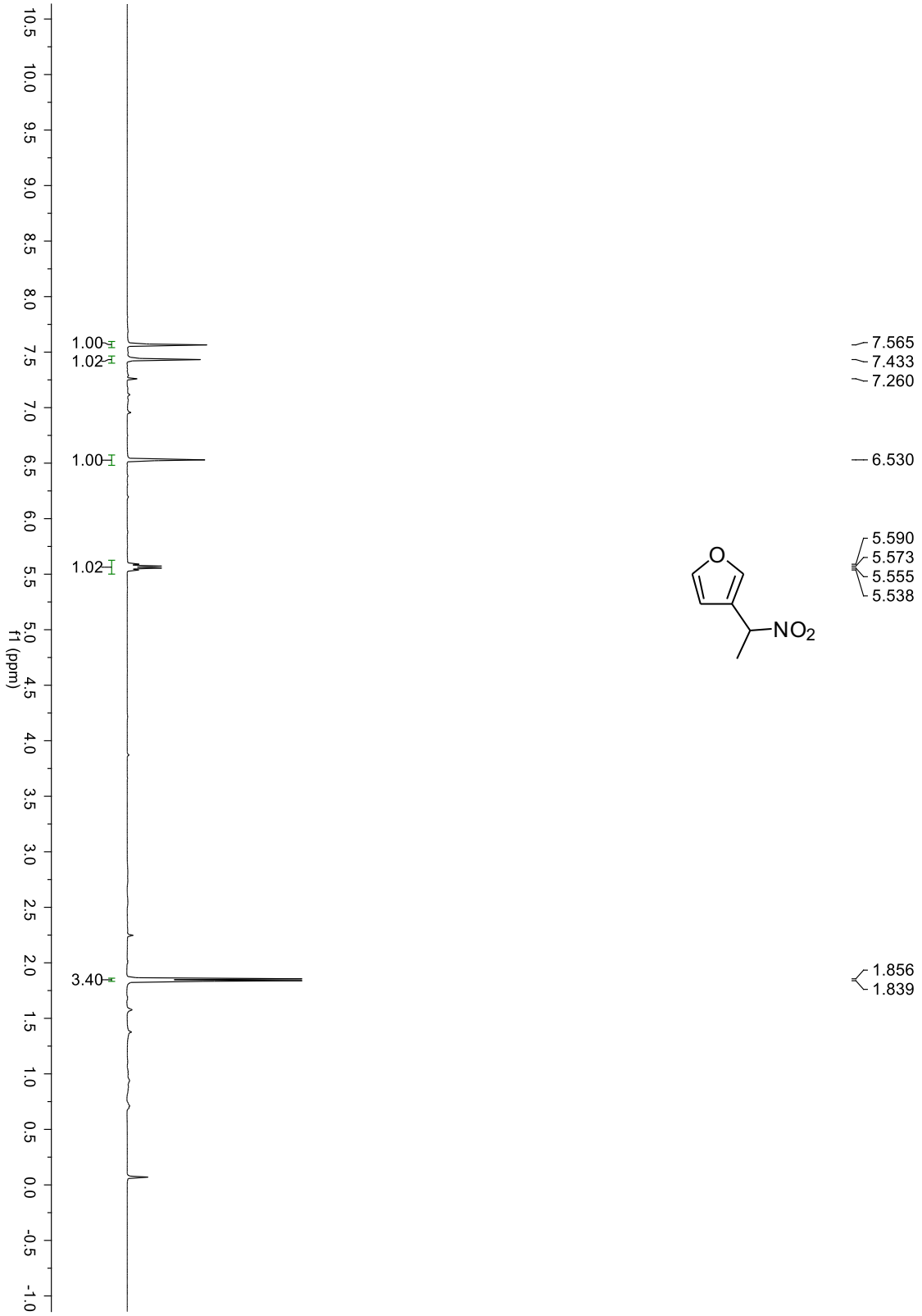

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-107.729
-107.750
-107.768
NO2
F
F

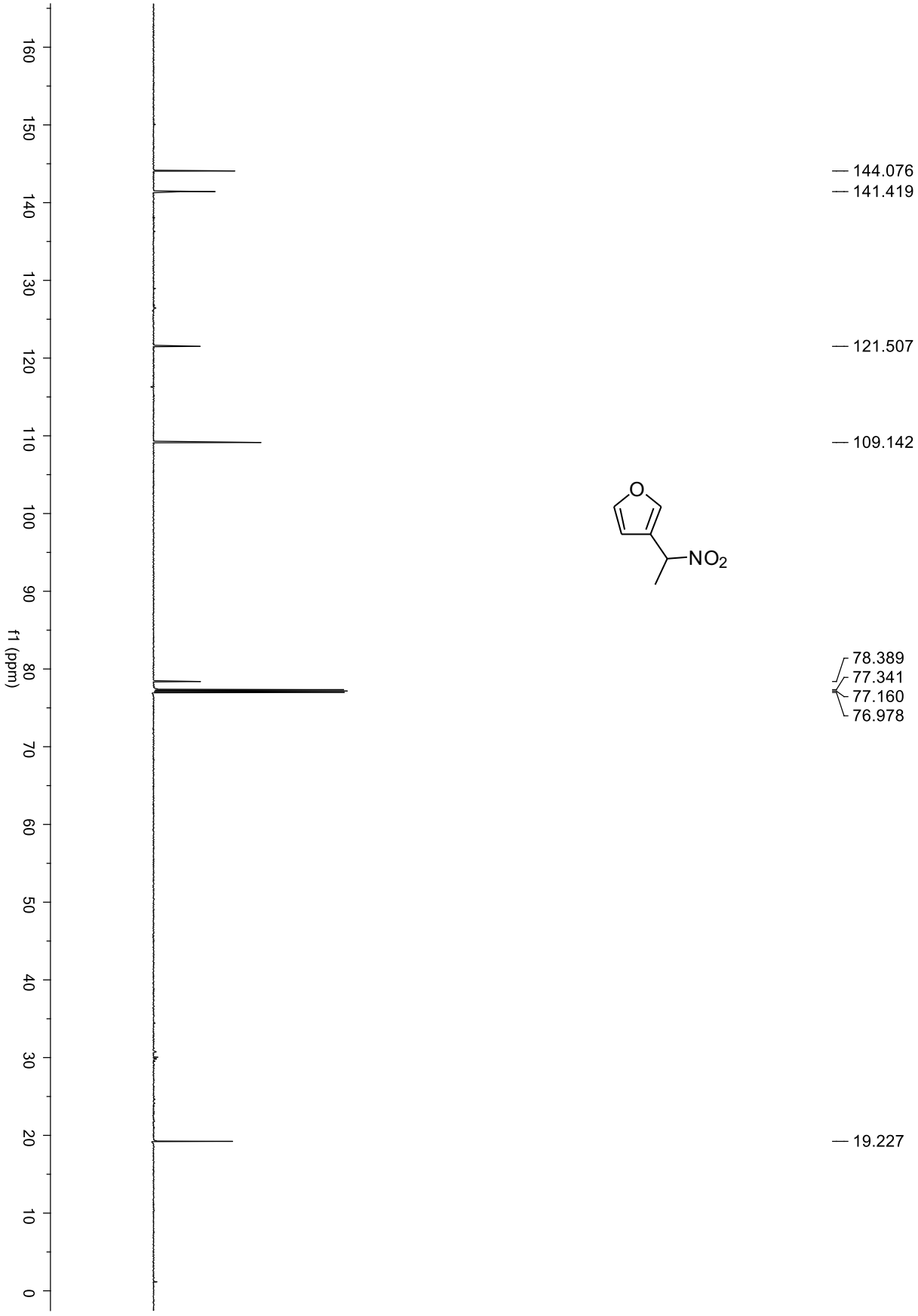

9
8
7
6
5
4
3
2
1
ppm
2.02
2.04
1.00
3.14
3.32
7.992
7.972
7.558
7.538
5.671
5.653
2.604
1.921
1.904
NO2
O

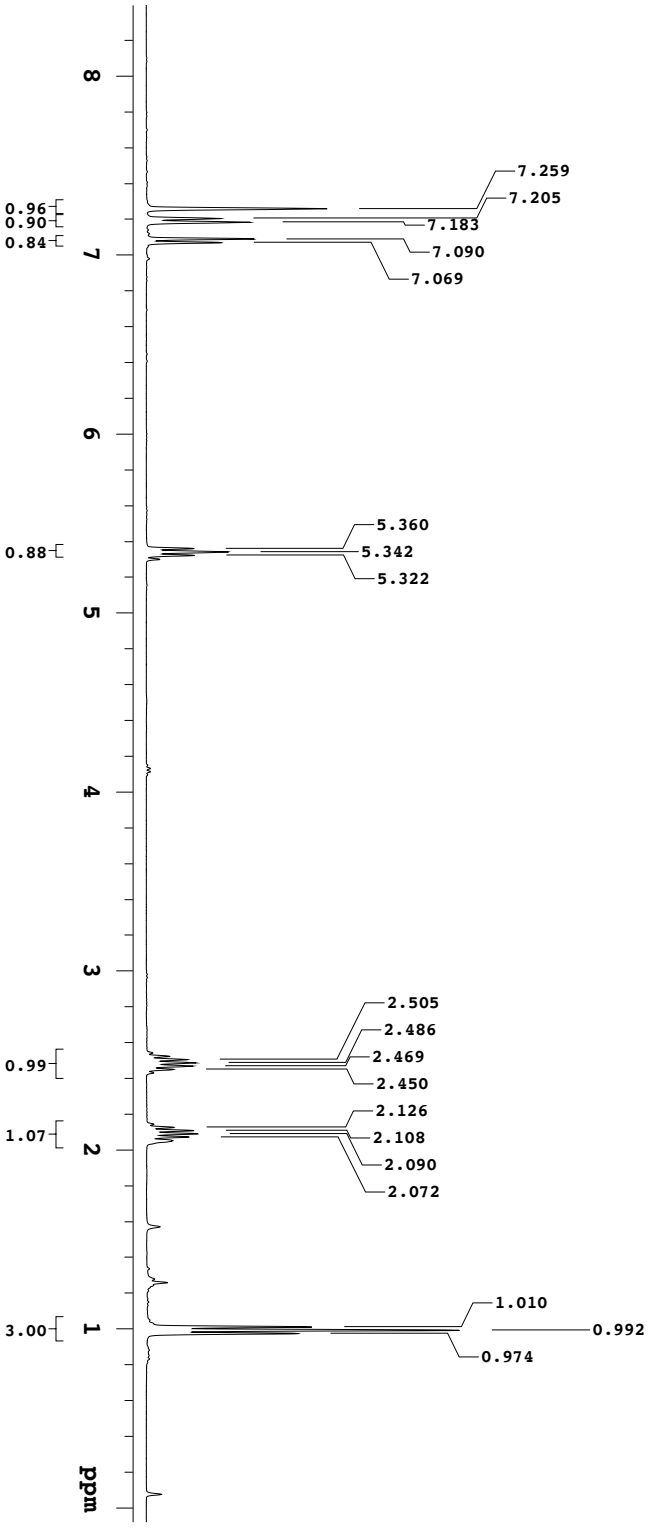

197.383
140.136
138.162
129.068
127.791
85.735
77.342
77.160
76.978
26.819
19.545
NO2
O
200
180
160
140
120
100
80
60
40
20
ppm

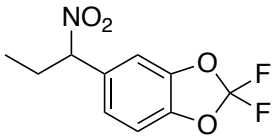

1.00
1.05
0.97
1.05
1.02
1.06
3.11
f1 (ppm)
7.995
7.857
7.840
7.539
7.528
7.473
7.470
7.457
7.453
7.358
7.347
7.260
5.766
5.752
5.738
5.724
1.984
1.970
NO2
S

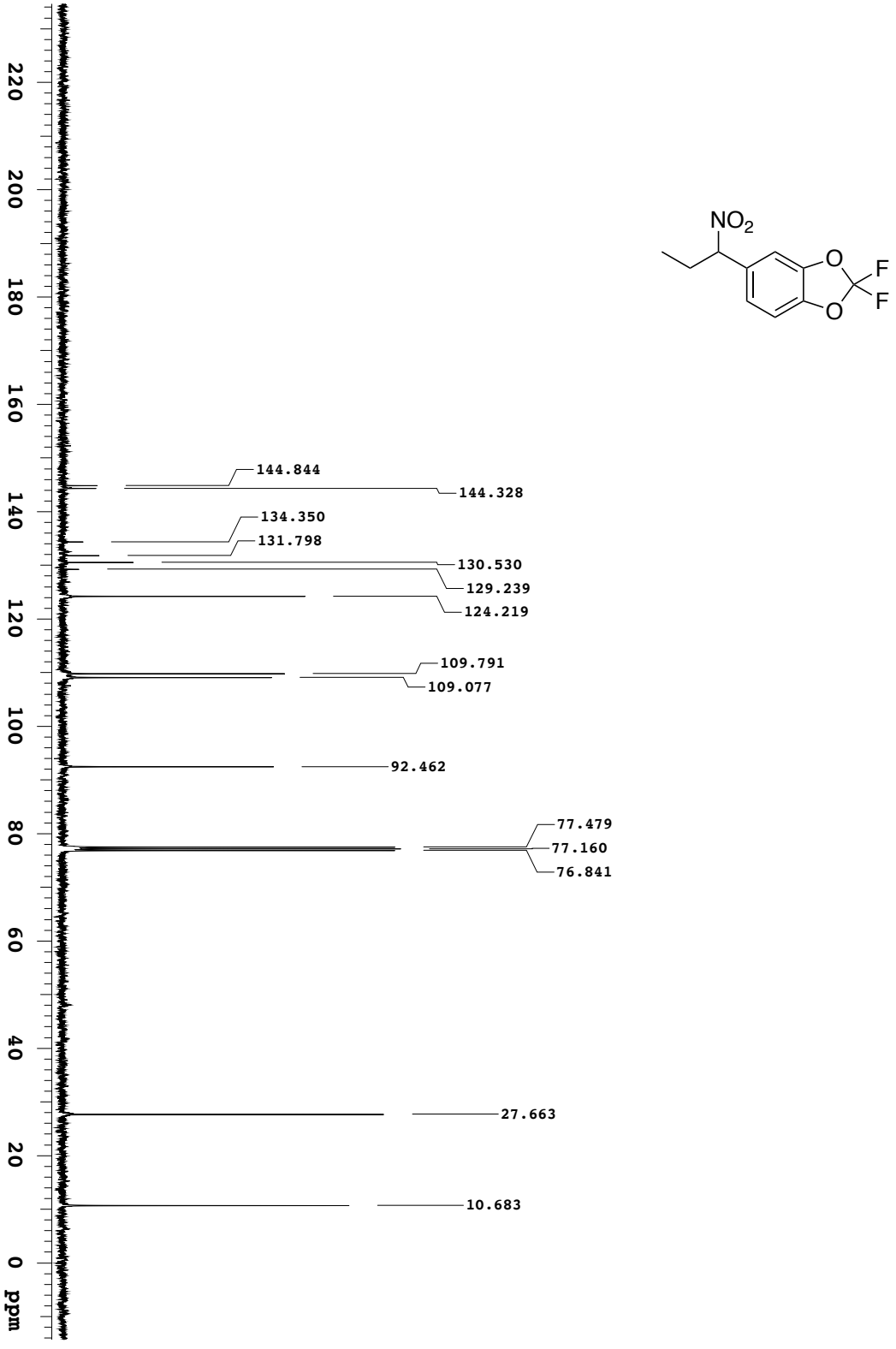

140.698
140.210
131.704
128.522
124.250
123.716
123.564
121.897
NO2
S
86.439
77.342
77.160
76.979
19.783
f1 (ppm)

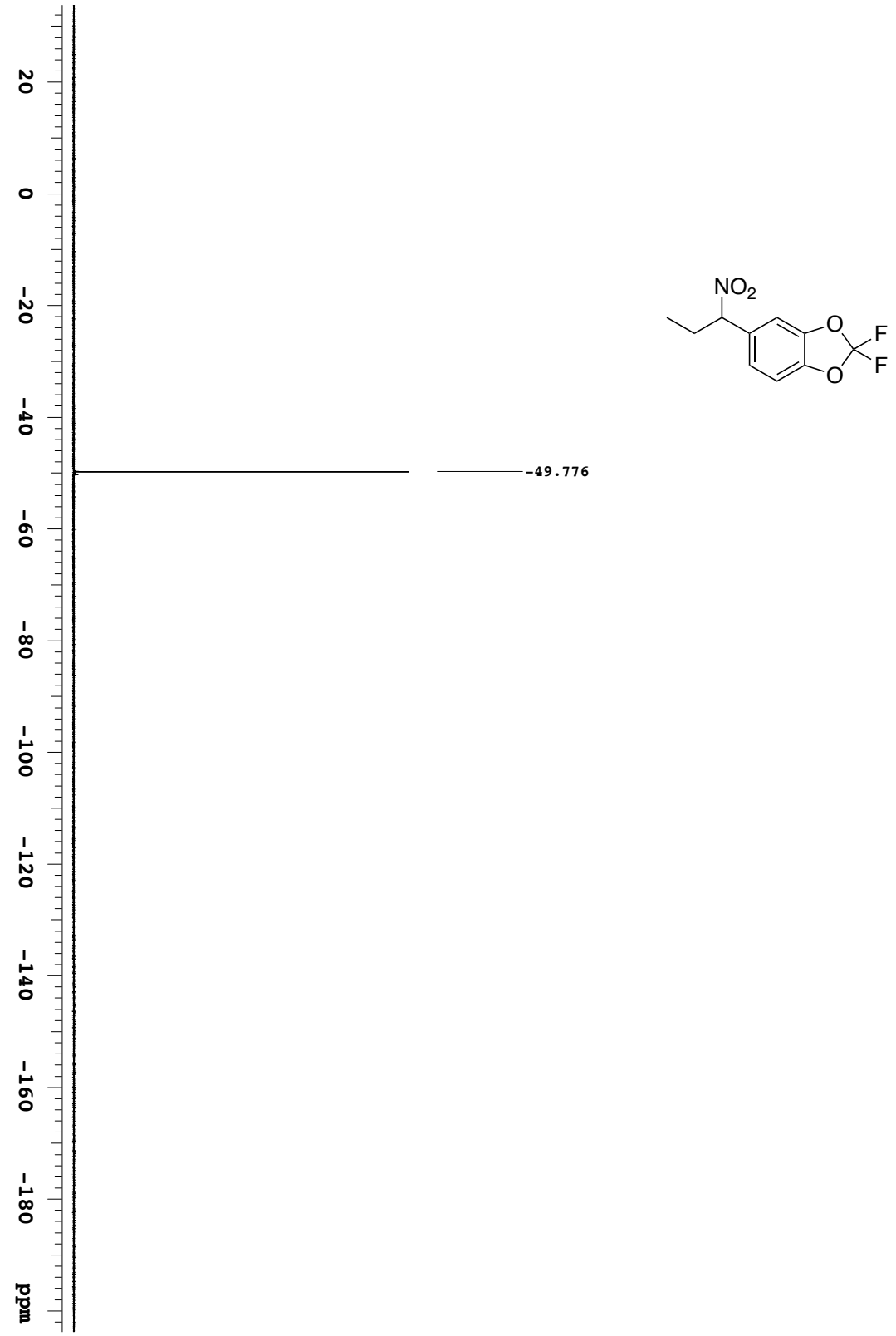

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
1.00
1.02
1.00
1.02
3.40
7.565
7.433
7.260
6.530
5.590
5.573
5.555
5.538
1.856
1.839
O
NO2

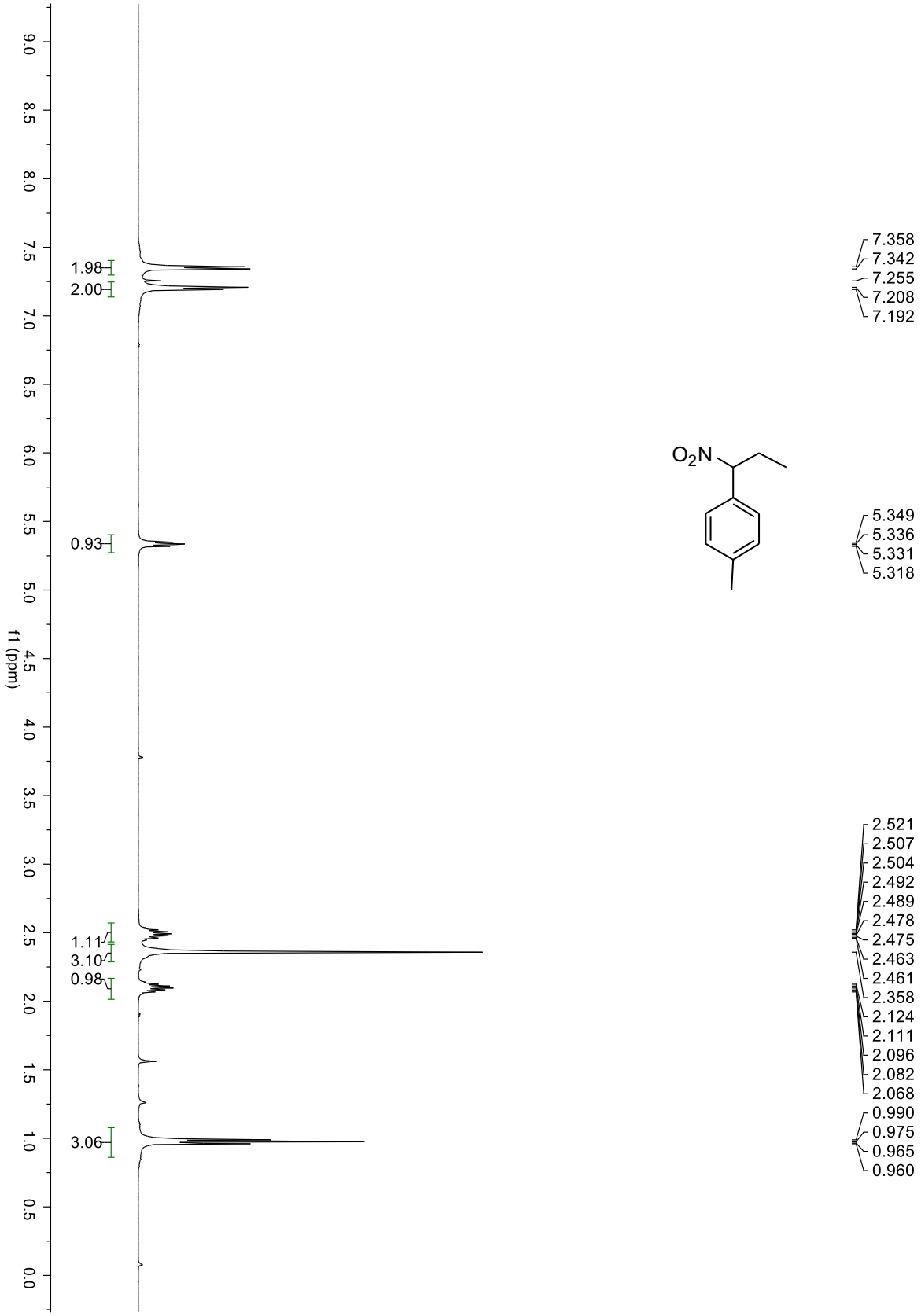

144.076
141.419
121.507
109.142
78.389
77.341
77.160
76.978
19.227
O
NO2
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

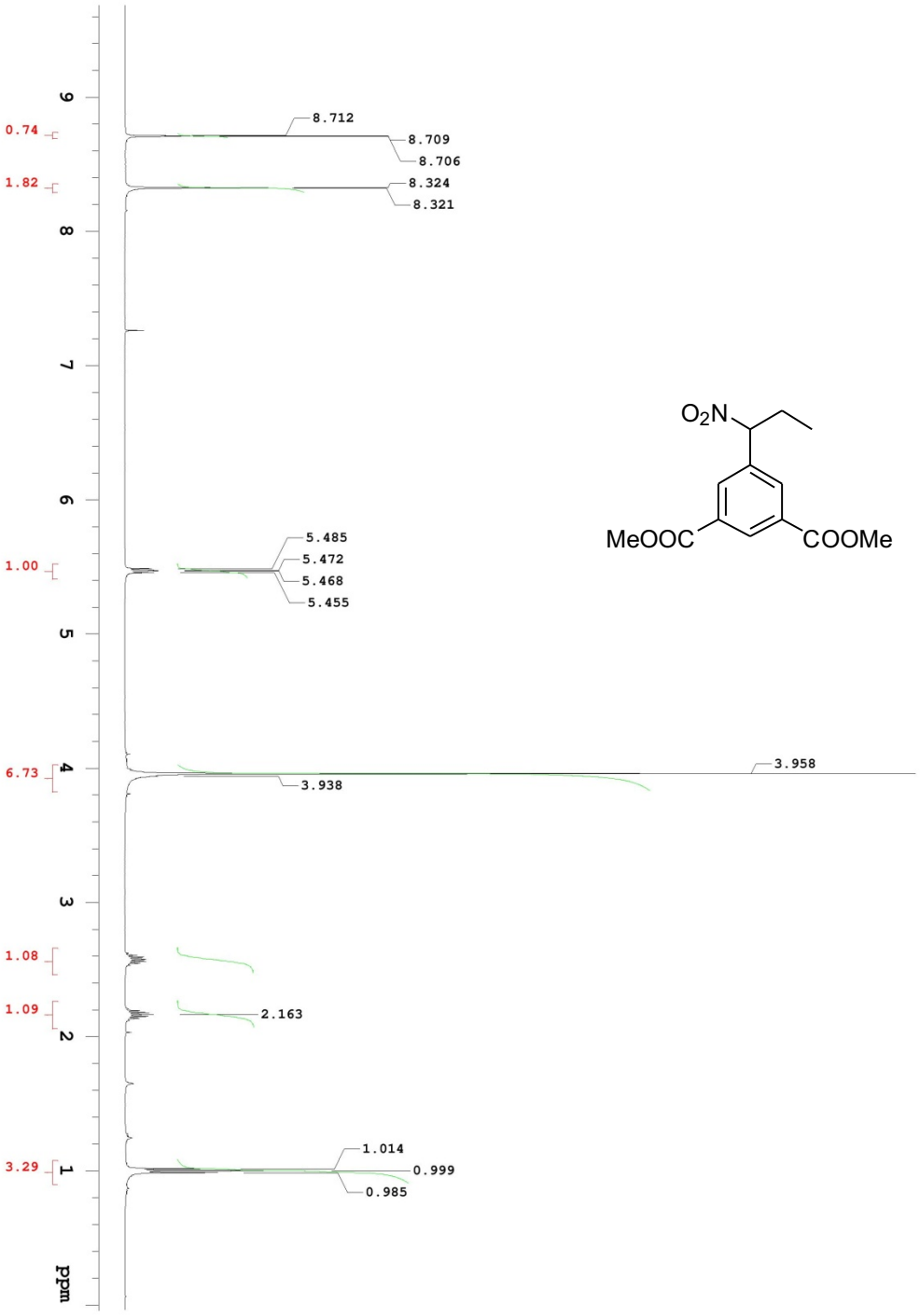

8
7
6
5
4
3
2
1
ppm
7.259
7.205
7.183
7.090
7.069
0.96
0.90
0.84
5.360
5.342
5.322
0.88
2.505
2.486
2.469
2.450
2.126
2.108
2.090
2.072
0.99
1.07
1.010
0.992
0.974
3.00

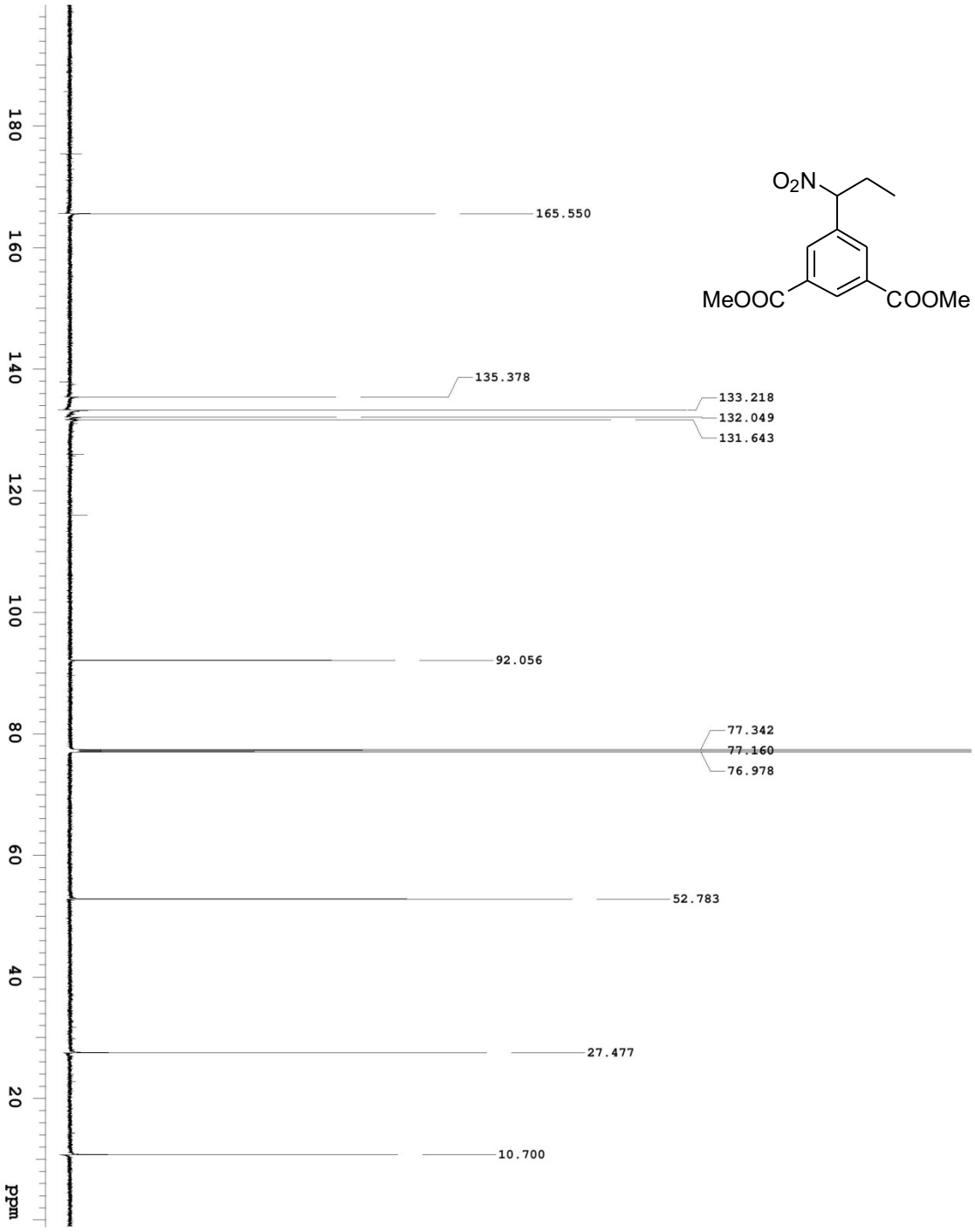

NO2
O
F
F
O

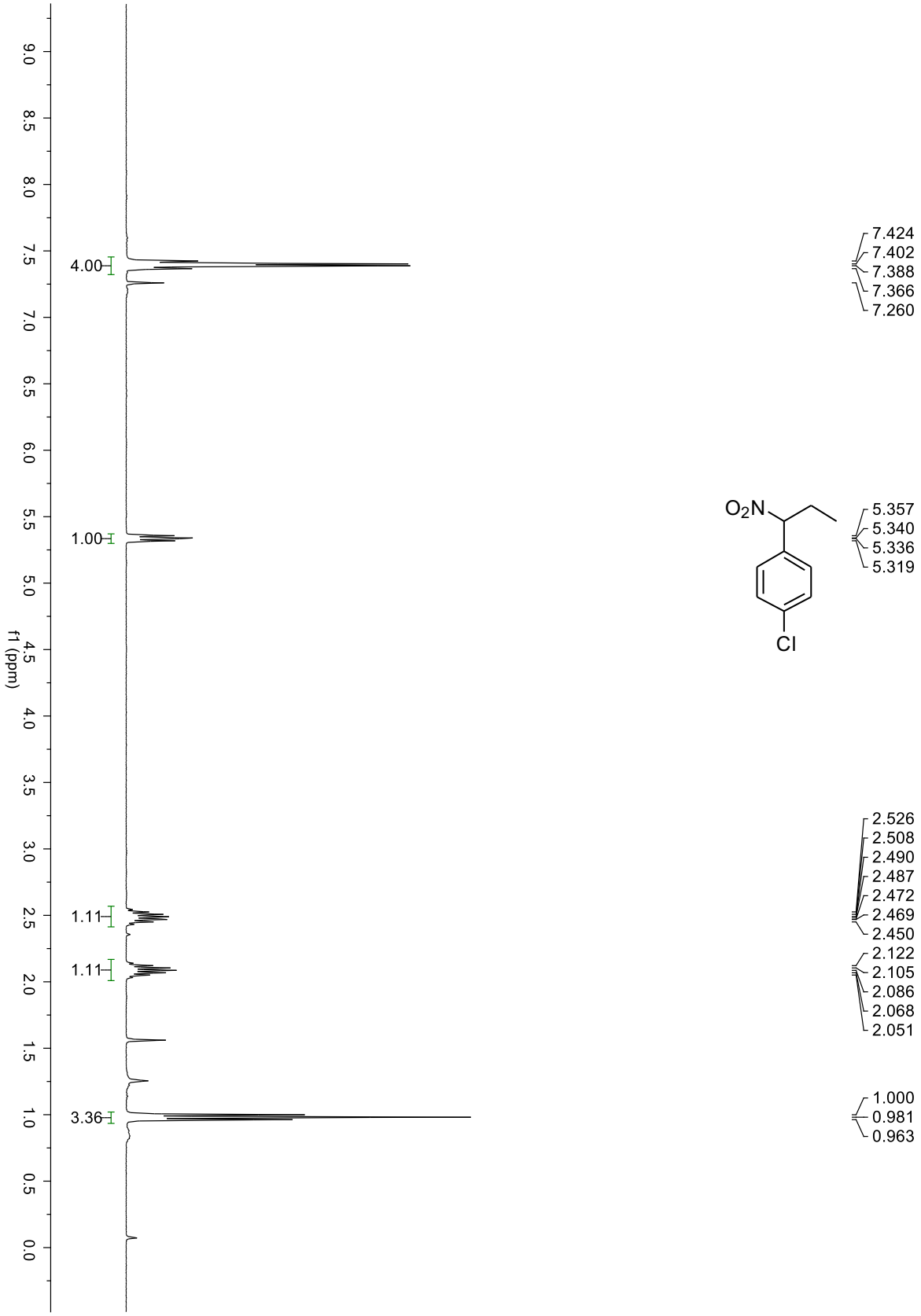

NO2
O
O
F
F
144.844
144.328
134.350
131.798
130.530
129.239
124.219
109.791
109.077
92.462
77.479
77.160
76.841
27.663
10.683
220
200
180
160
140
120
100
80
60
40
20
0 ppm

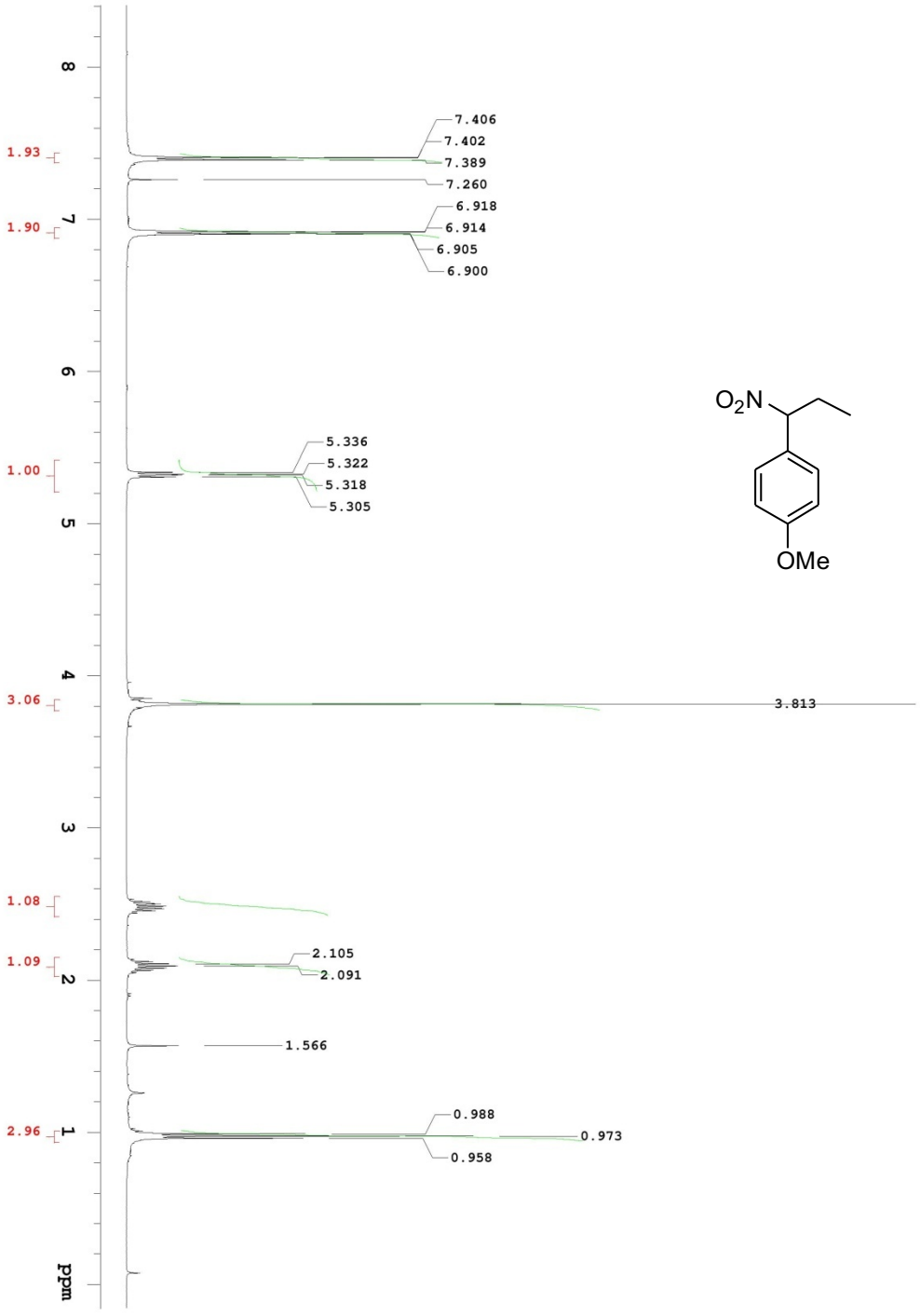

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-49.776
NO2
O
F
F
O

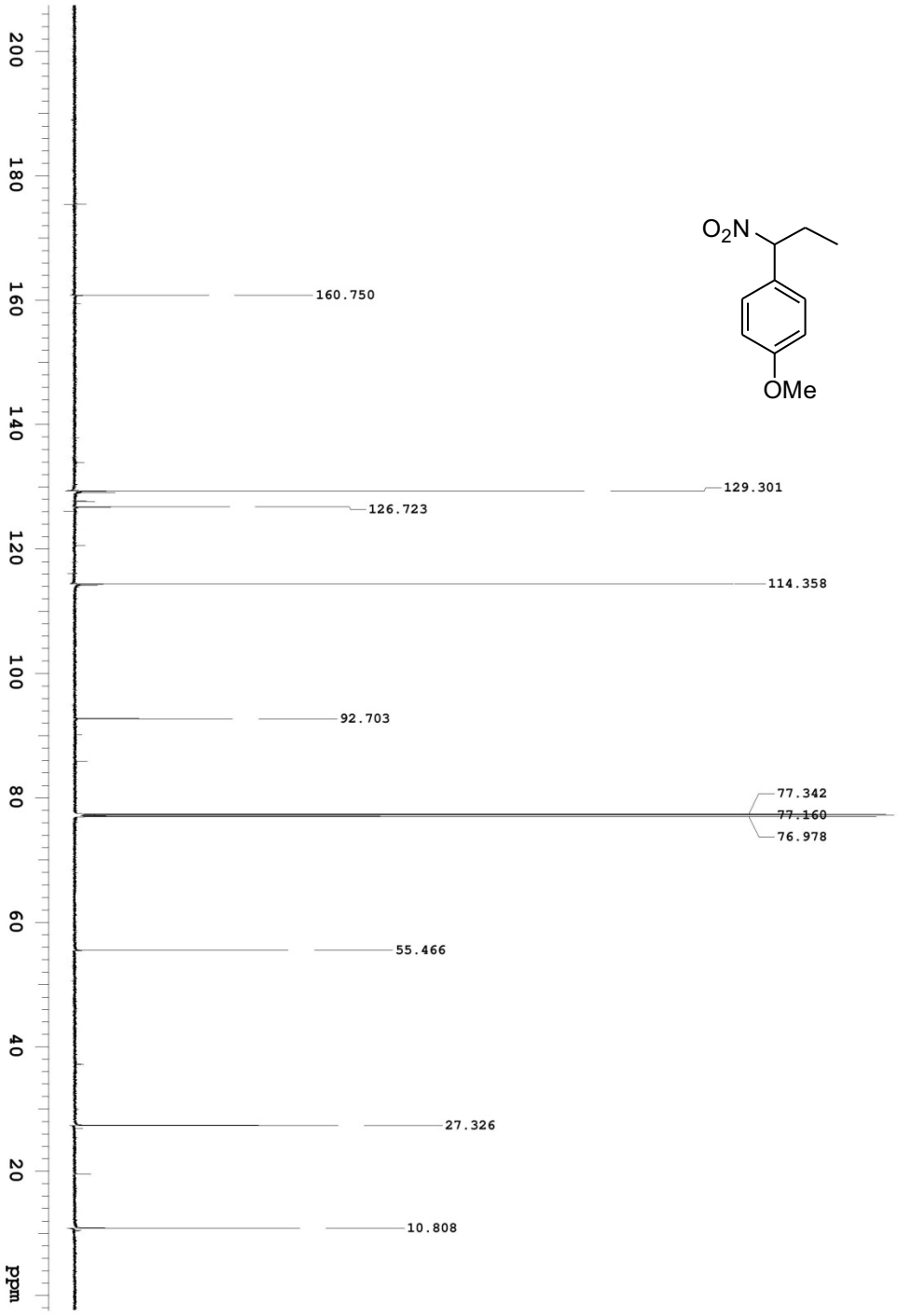

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.98
2.00
0.93
1.11
3.10
0.98
3.06
O2N
7.358
7.342
7.255
7.208
7.192
5.349
5.336
5.331
5.318
2.521
2.507
2.504
2.492
2.489
2.478
2.475
2.463
2.461
2.358
2.124
2.111
2.096
2.082
2.068
0.990
0.975
0.965
0.960

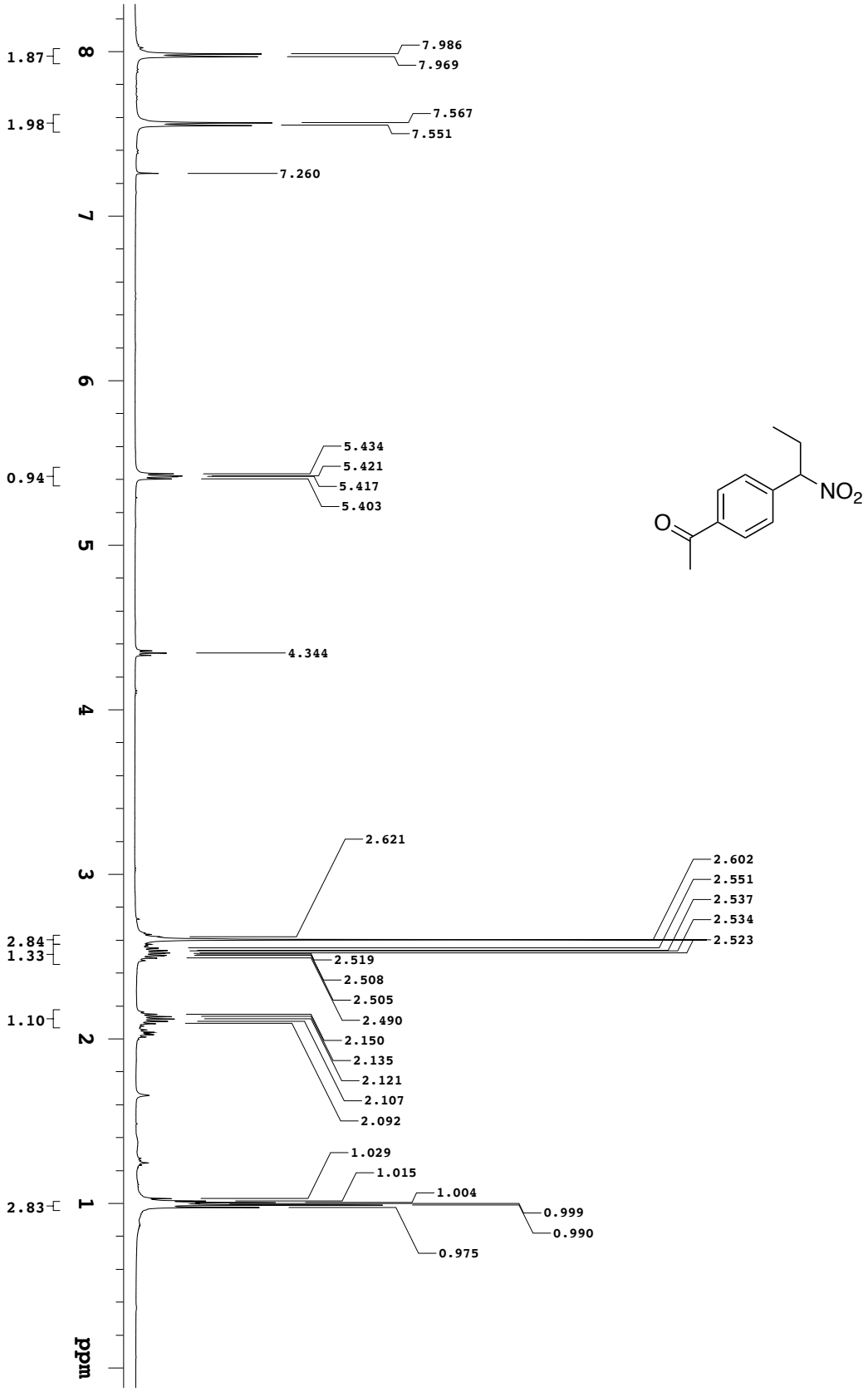

8.712
8.709
8.706
8.324
8.321
5.485
5.472
5.468
5.455
3.958
3.938
2.163
1.014
0.999
0.985
0.74
1.82
1.00
6.73
1.08
1.09
3.29
ppm
O2N
MeOOC
COOMe

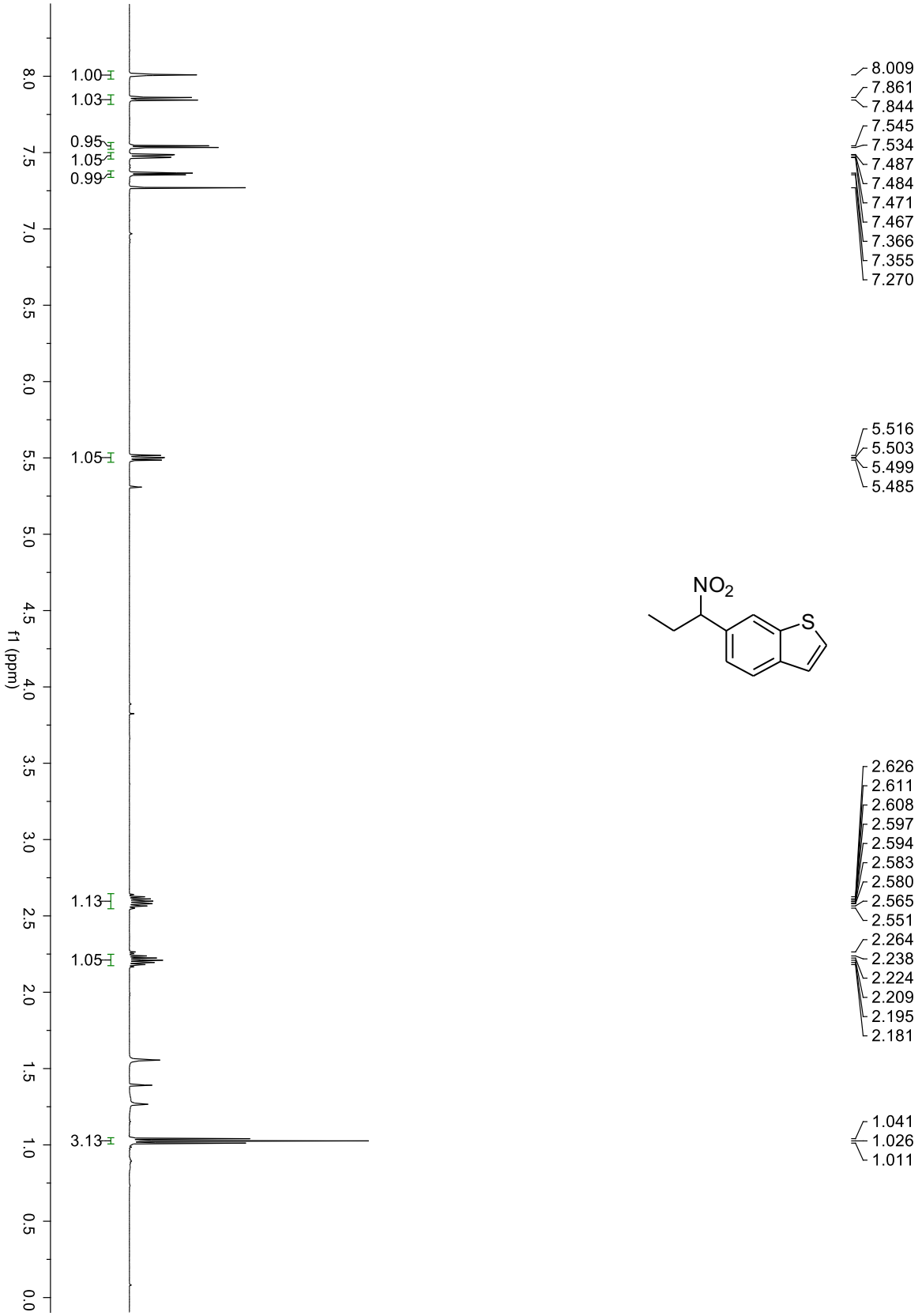

165.550
135.378
133.218
132.049
131.643
92.056
77.342
77.160
76.978
52.783
27.477
10.700
ppm
180
160
140
120
100
80
60
40
20
O2N
MeOOC
COOMe

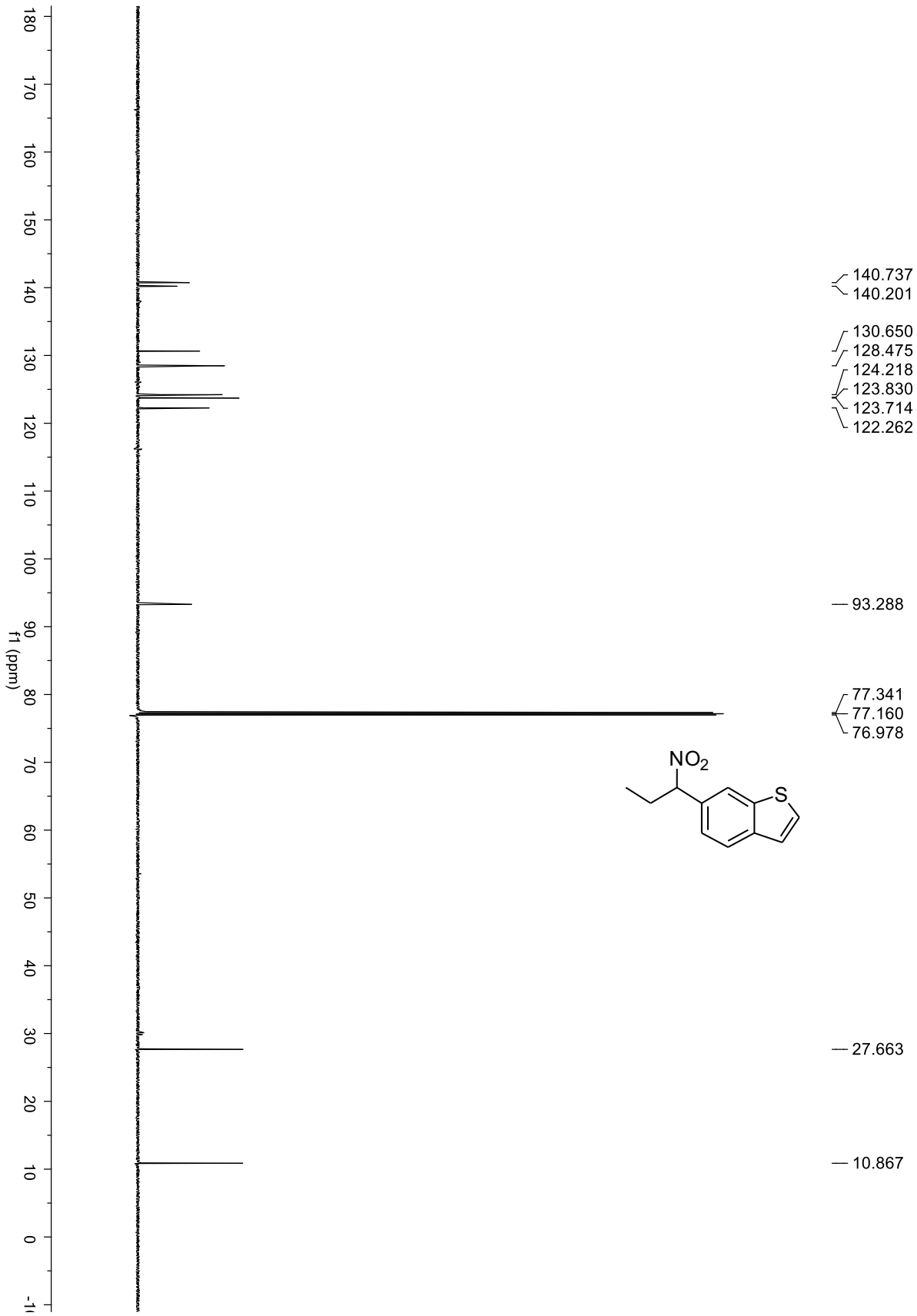

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.00
1.00
1.11
1.11
3.36
7.424
7.402
7.388
7.366
7.260
5.357
5.340
5.336
5.319
2.526
2.508
2.490
2.487
2.472
2.469
2.450
2.122
2.105
2.086
2.068
2.051
1.000
0.981
0.963
O2N
Cl

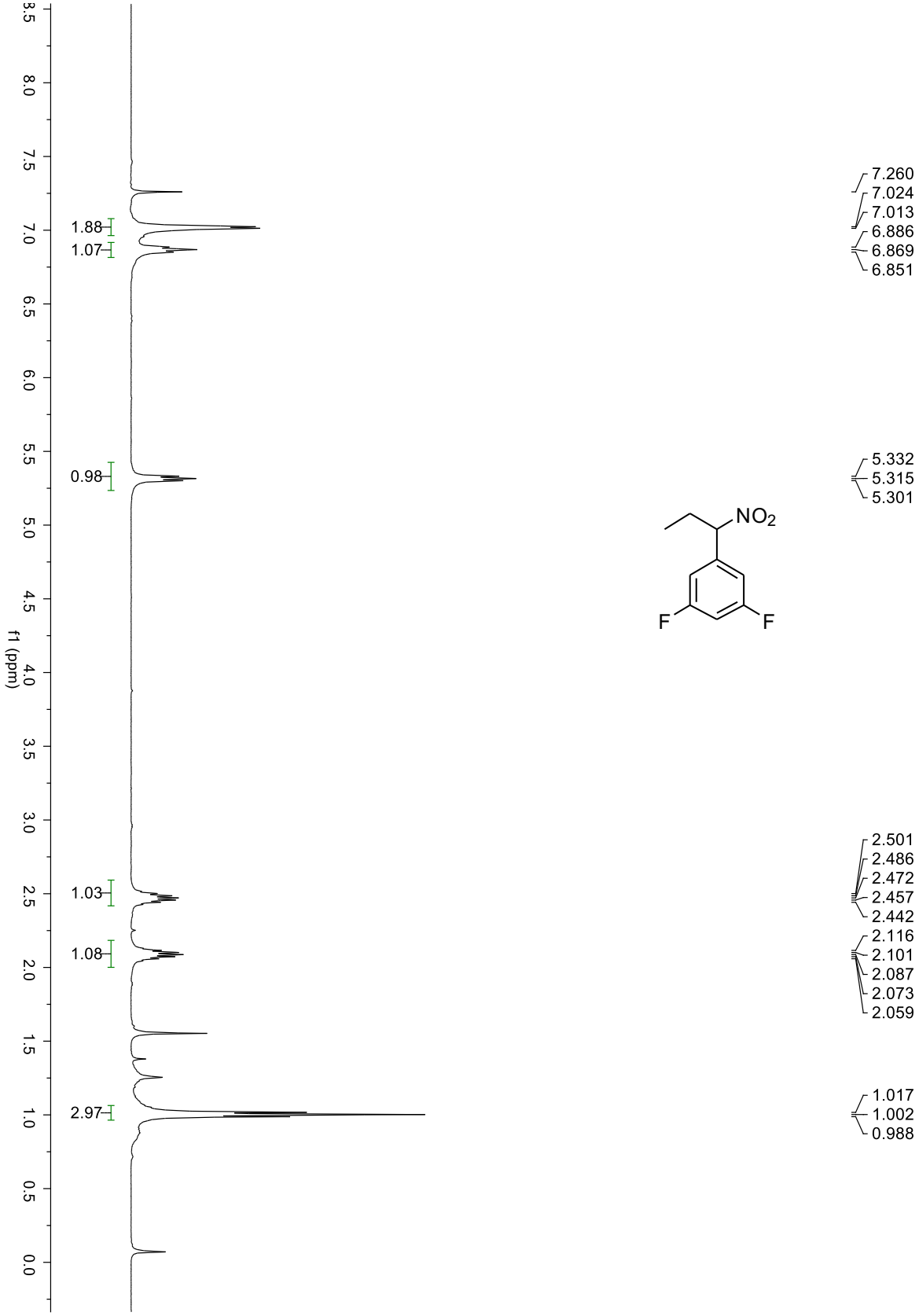

7.406
7.402
7.389
7.260
6.918
6.914
6.905
6.900
5.336
5.322
5.318
5.305
3.813
2.105
2.091
1.566
0.988
0.973
0.958
1.93
1.90
1.00
3.06
1.08
1.09
2.96
ppm
O2N
OMe

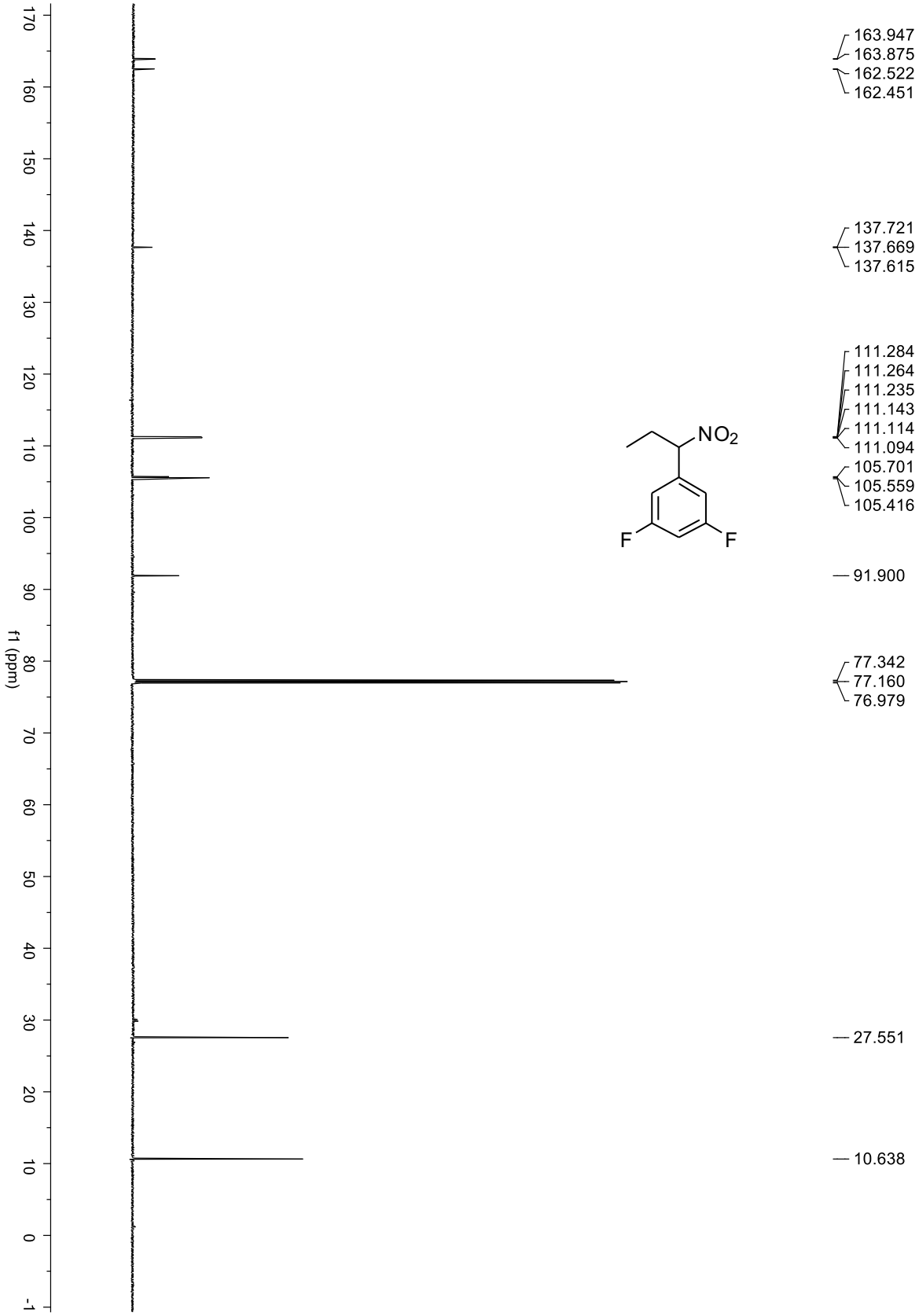

200
180
160
140
120
100
80
60
40
20
ppm
160.750
129.301
126.723
114.358
92.703
77.342
77.160
76.978
55.466
27.326
10.808
O2N
OMe

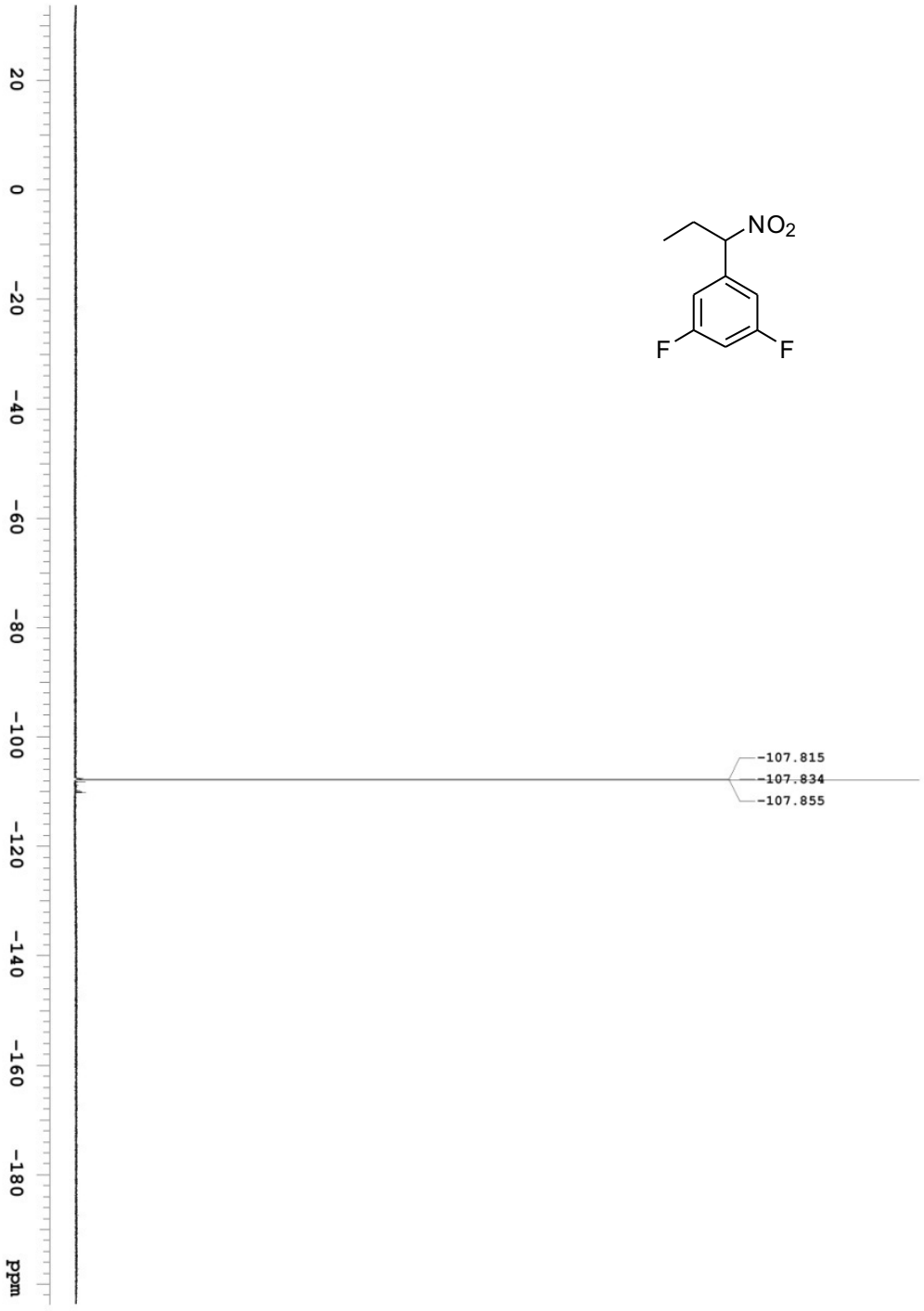

1.87
1.98
0.94
2.84
1.33
1.10
2.83
8
7
6
5
4
3
2
1
ppm
7.986
7.969
7.567
7.551
7.260
5.434
5.421
5.417
5.403
4.344
2.621
2.602
2.551
2.537
2.534
2.523
2.519
2.508
2.505
2.490
2.150
2.135
2.121
2.107
2.092
1.029
1.015
1.004
0.999
0.990
0.975
O
NO2

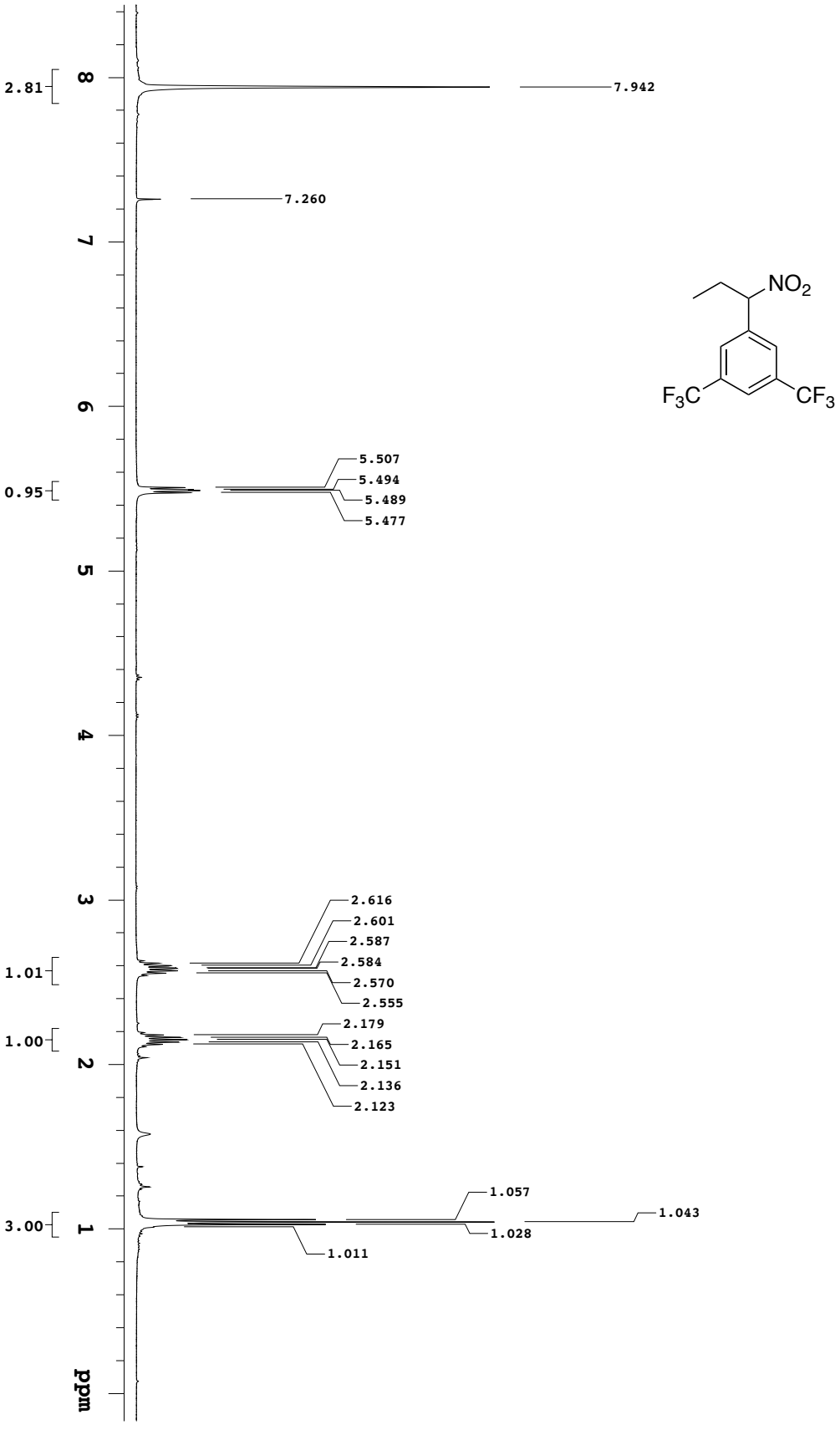

8.009
7.861
7.844
7.545
7.534
7.487
7.484
7.471
7.467
7.366
7.355
7.270
5.516
5.503
5.499
5.485
2.626
2.611
2.608
2.597
2.594
2.583
2.580
2.565
2.551
2.264
2.238
2.224
2.209
2.195
2.181
1.041
1.026
1.011
1.00
1.03
0.95
1.05
0.99
1.05
1.13
1.05
3.13
NO2
S
f1 (ppm)

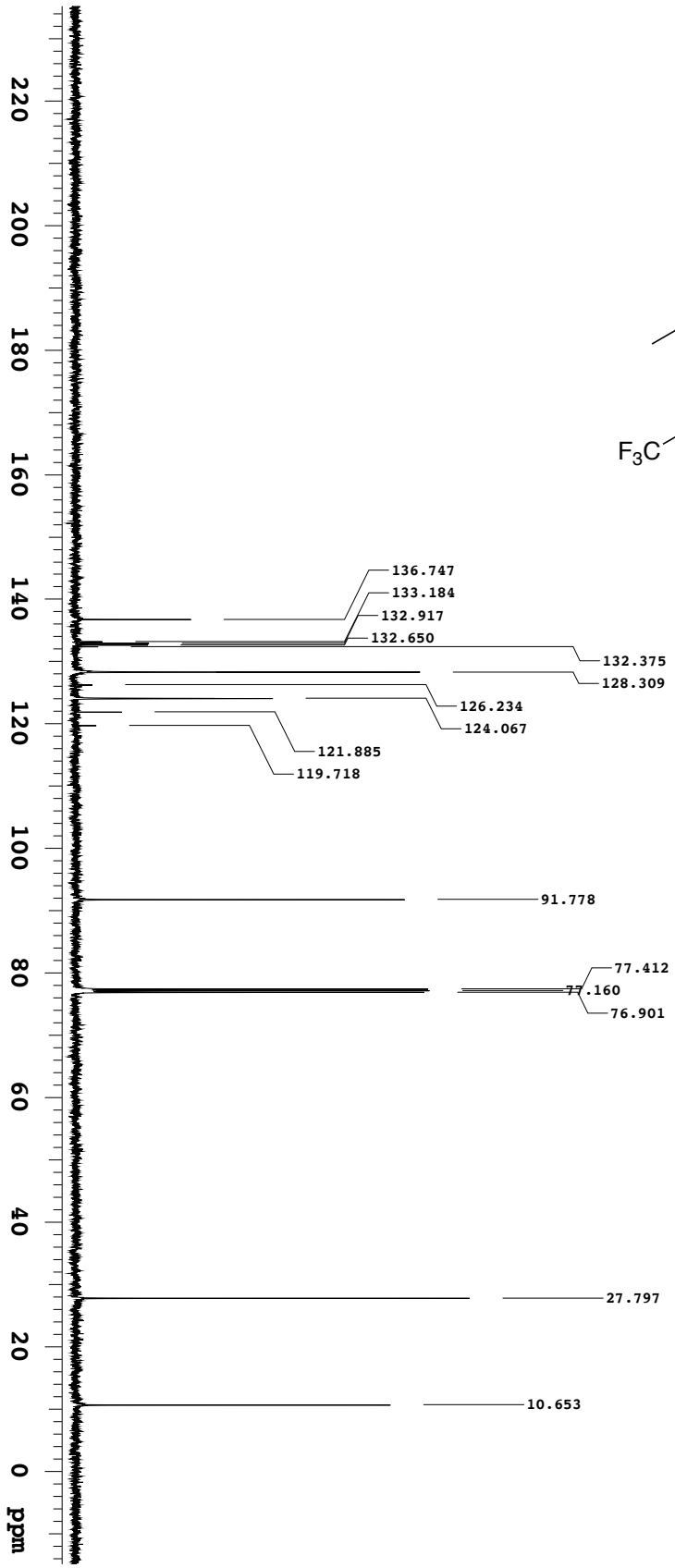

140.737
140.201
130.650
128.475
124.218
123.830
123.714
122.262
93.288
77.341
77.160
76.978
27.663
10.867
f1 (ppm)
NO2
S

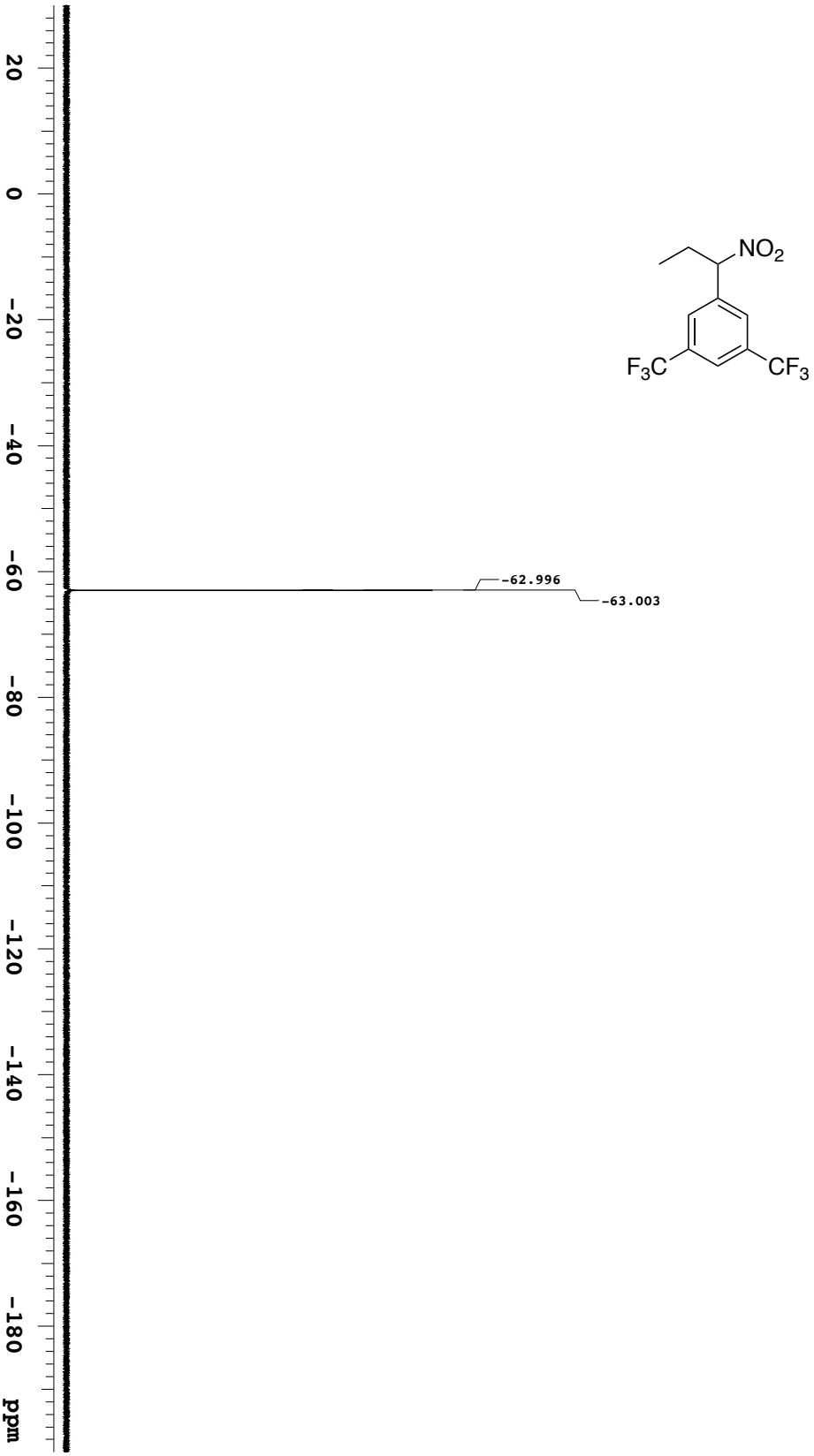

3.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.88
1.07
0.98
1.03
1.08
2.97
7.260
7.024
7.013
6.886
6.869
6.851
5.332
5.315
5.301
2.501
2.486
2.472
2.457
2.442
2.116
2.101
2.087
2.073
2.059
1.017
1.002
0.988
NO2
F
F

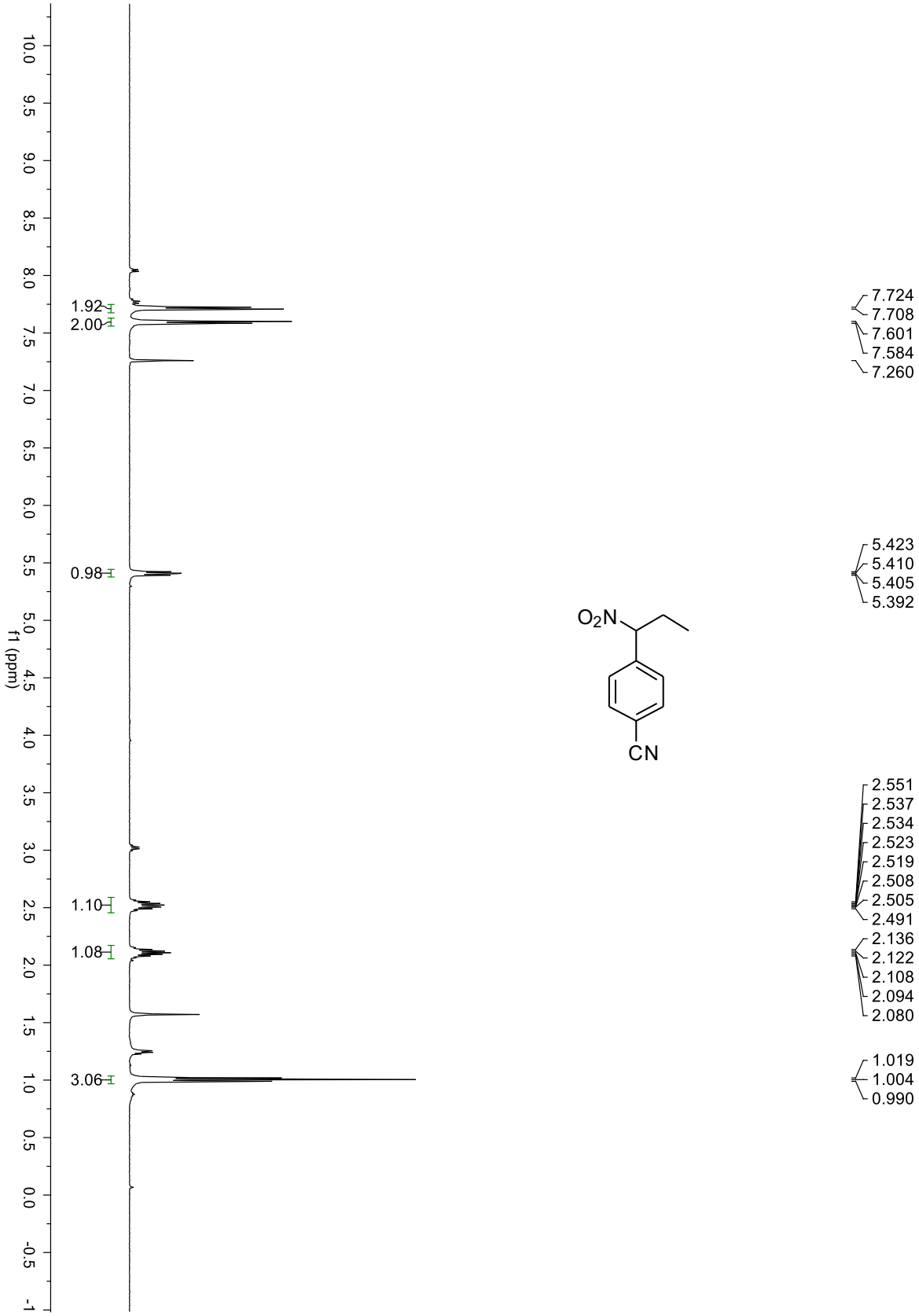

163.947
163.875
162.522
162.451
137.721
137.669
137.615
111.284
111.264
111.235
111.143
111.114
111.094
105.701
105.559
105.416
91.900
77.342
77.160
76.979
27.551
10.638
NO2
F
F
f1 (ppm)

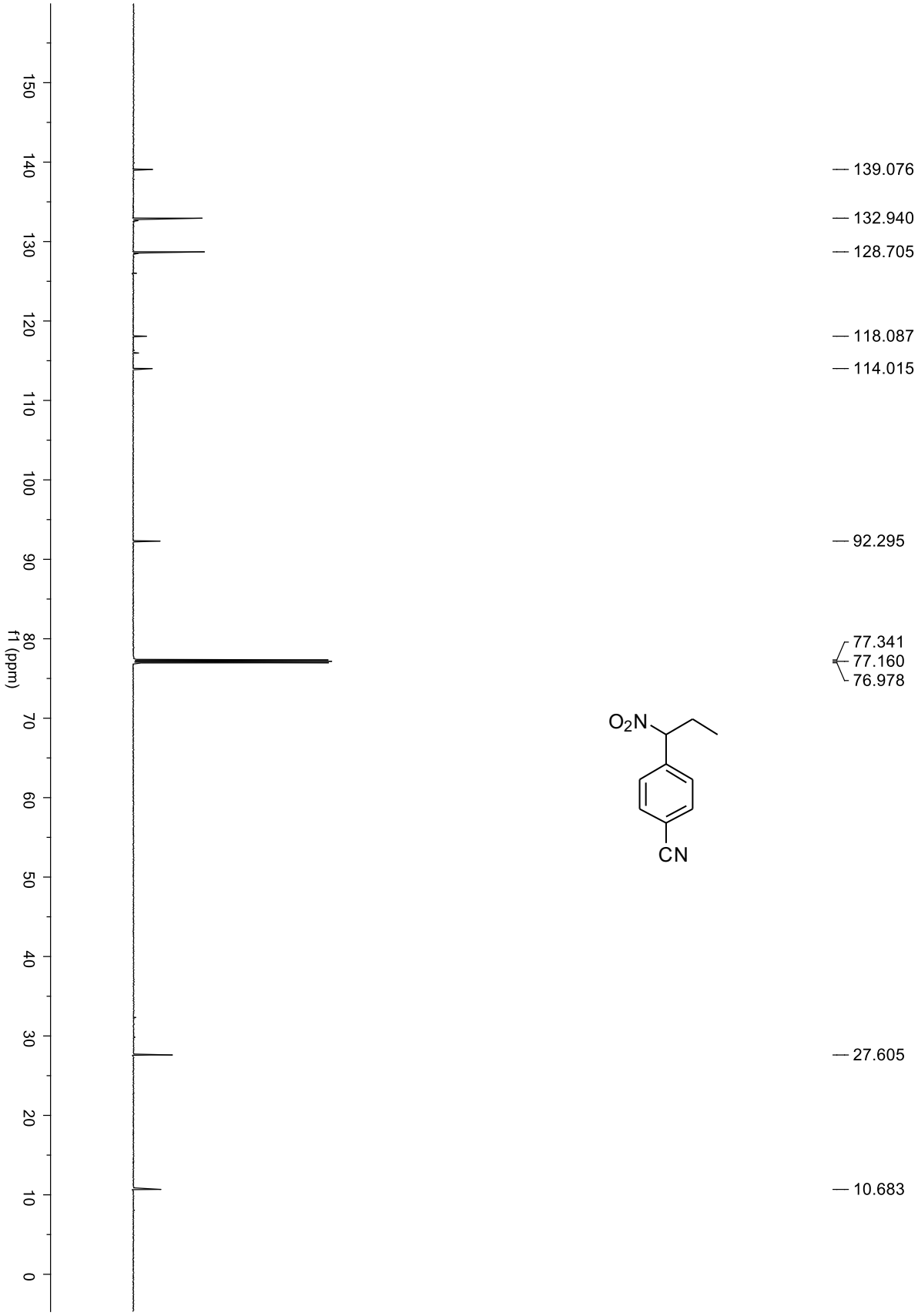

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
NO2
F
F
-107.815
-107.834
-107.855

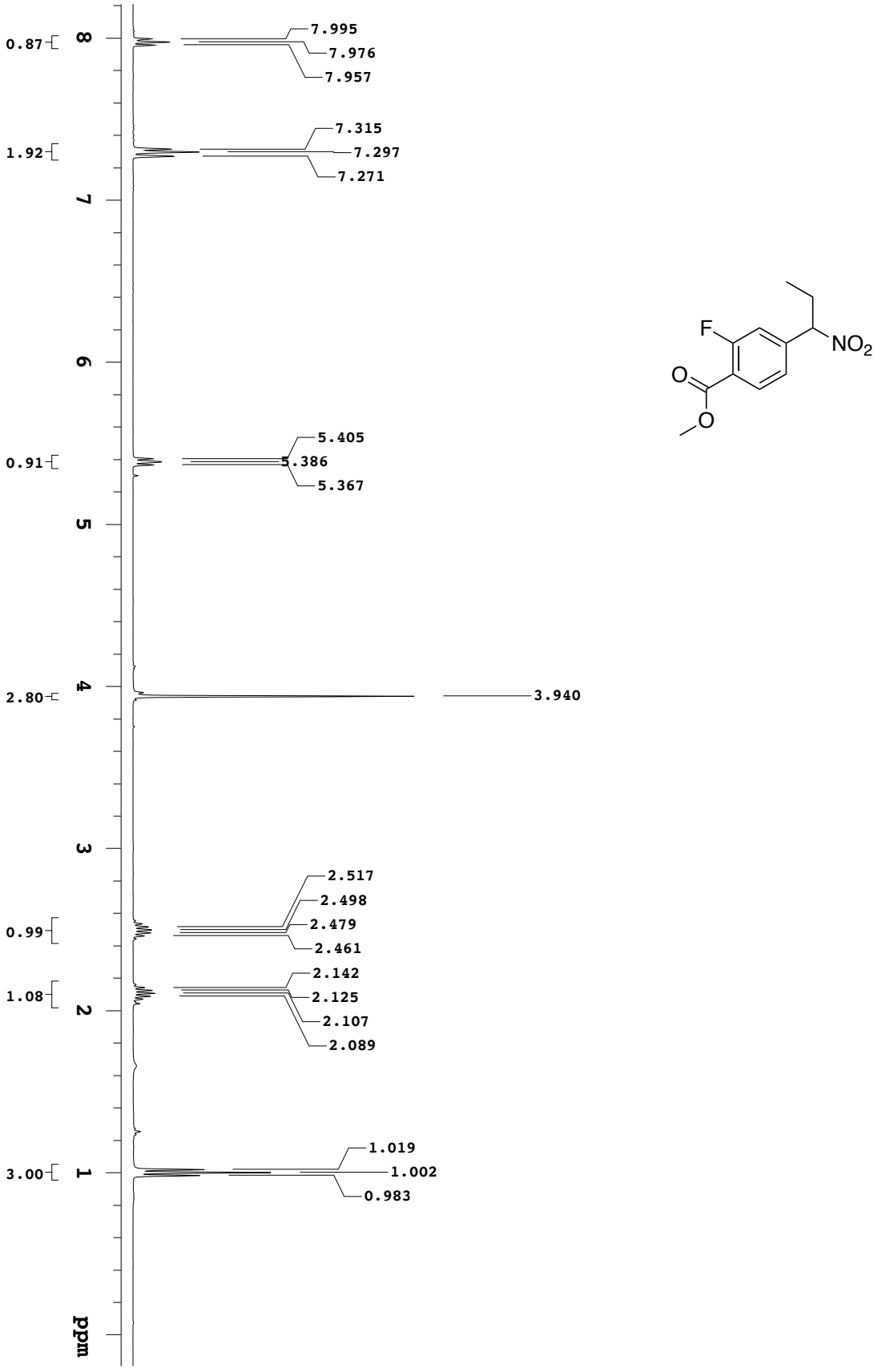

2.81
0.95
1.01
1.00
3.00
8
7
6
5
4
3
2
1
ppm
7.942
7.260
5.507
5.494
5.489
5.477
2.616
2.601
2.587
2.584
2.570
2.555
2.179
2.165
2.151
2.136
2.123
1.057
1.043
1.028
1.011
NO2
F3C
CF3

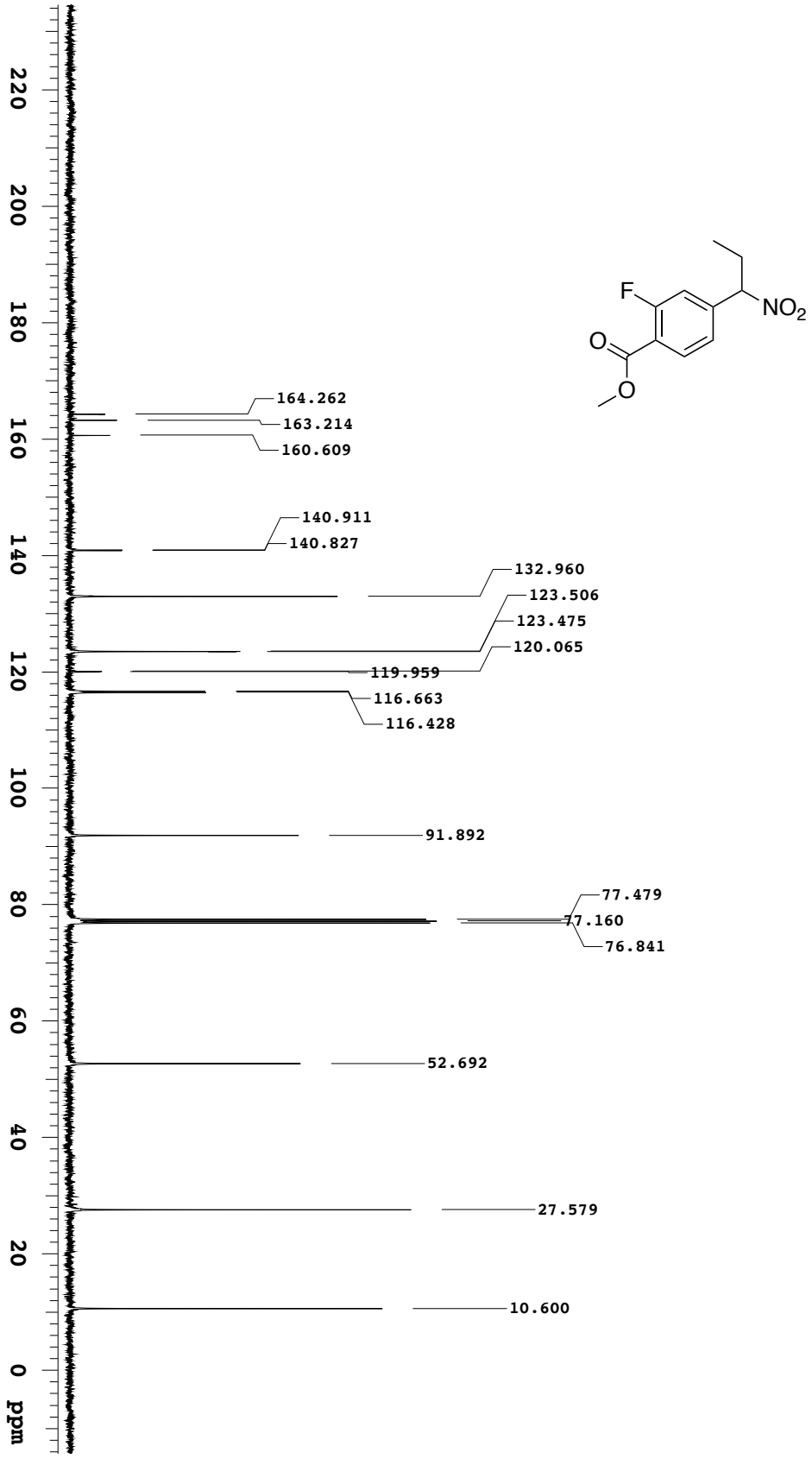

220
200
180
160
140
120
100
80
60
40
20
0
ppm
136.747
133.184
132.917
132.650
132.375
128.309
126.234
124.067
121.885
119.718
91.778
77.412
77.160
76.901
27.797
10.653
NO2
F3C
CF3

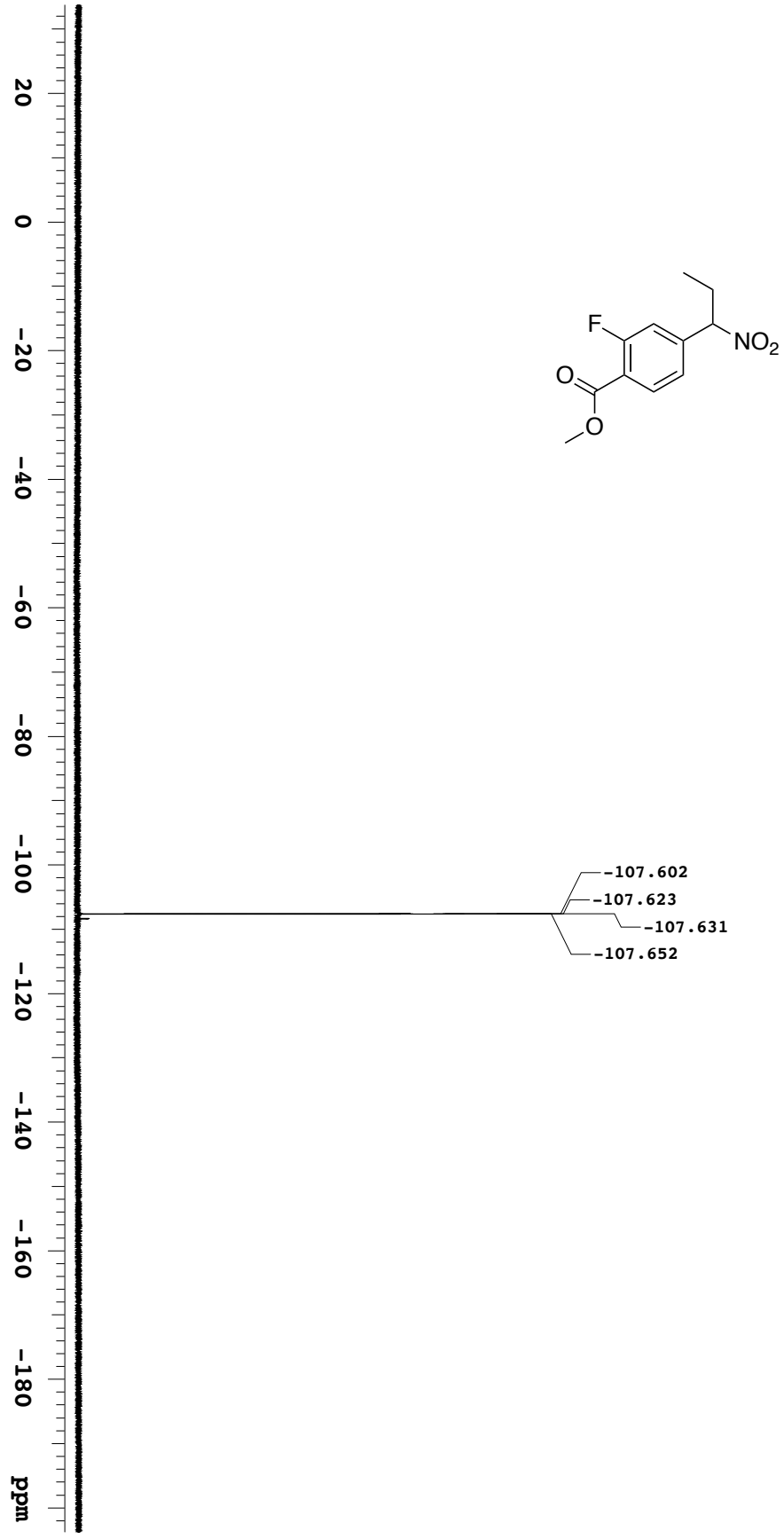

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-62.996
-63.003
NO2
F3C
CF3

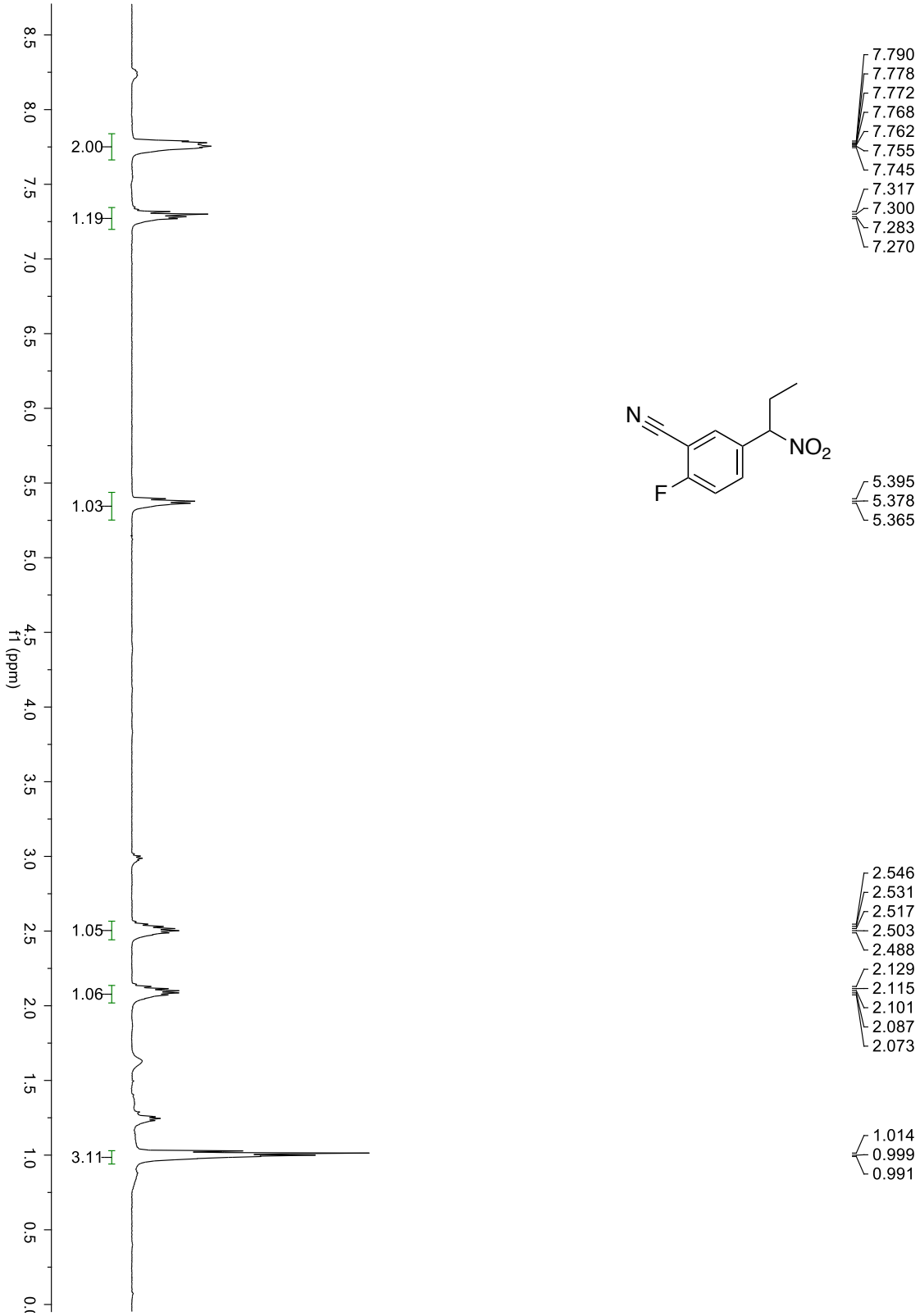

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
1.92
2.00
0.98
1.10
1.08
3.06
O2N
CN
7.724
7.708
7.601
7.584
7.260
5.423
5.410
5.405
5.392
2.551
2.537
2.534
2.523
2.519
2.508
2.505
2.491
2.136
2.122
2.108
2.094
2.080
1.019
1.004
0.990

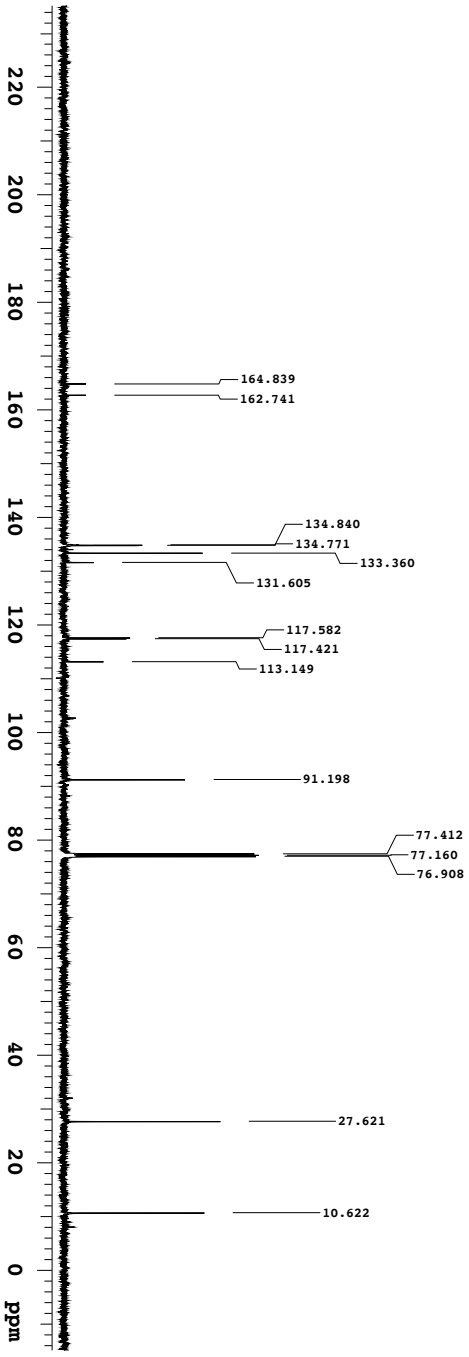

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
139.076
132.940
128.705
118.087
114.015
92.295
77.341
77.160
76.978
27.605
10.683
O2N
CN

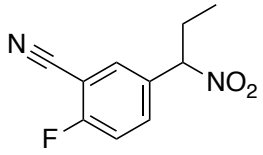

7.995
7.976
7.957
7.315
7.297
7.271
5.405
5.386
5.367
3.940
2.517
2.498
2.479
2.461
2.142
2.125
2.107
2.089
1.019
1.002
0.983
0.87
1.92
0.91
2.80
0.99
1.08
3.00
ppm
F
NO2
O
O

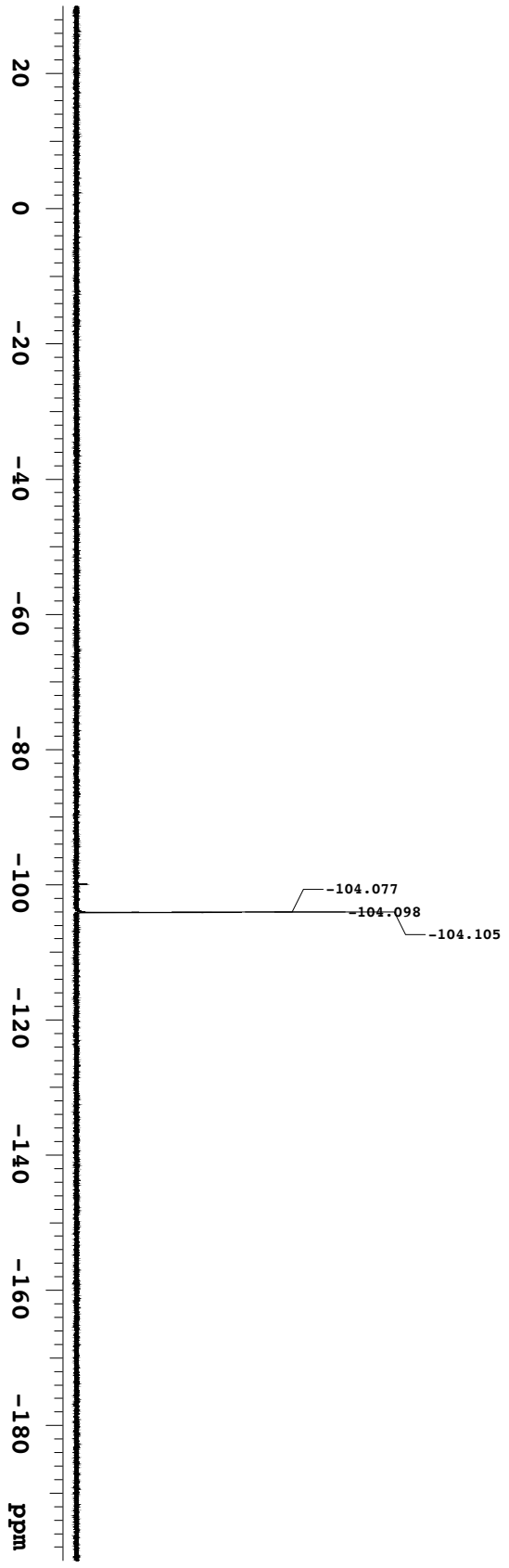

220
200
180
160
140
120
100
80
60
40
20
0
ppm
164.262
163.214
160.609
140.911
140.827
132.960
123.506
123.475
120.065
119.959
116.663
116.428
91.892
77.479
77.160
76.841
52.692
27.579
10.600
F
NO2
O
O

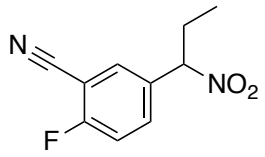

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
F
NO2
O
O
-107.602
-107.623
-107.631
-107.652

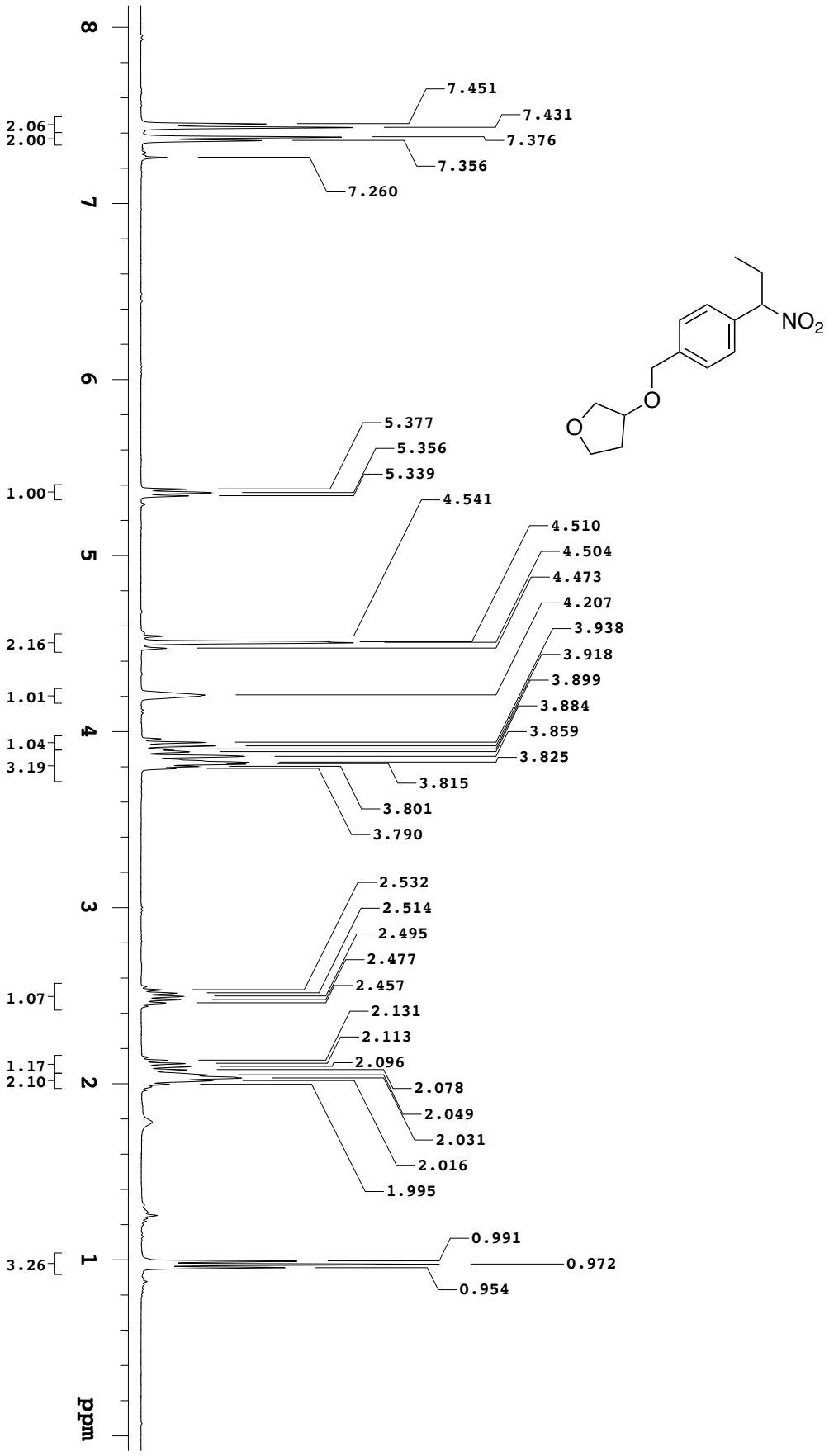

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
2.00
1.19
1.03
1.05
1.06
3.11
7.790
7.778
7.772
7.768
7.762
7.755
7.745
7.317
7.300
7.283
7.270
N
NO2
F
5.395
5.378
5.365
2.546
2.531
2.517
2.503
2.488
2.129
2.115
2.101
2.087
2.073
1.014
0.999
0.991

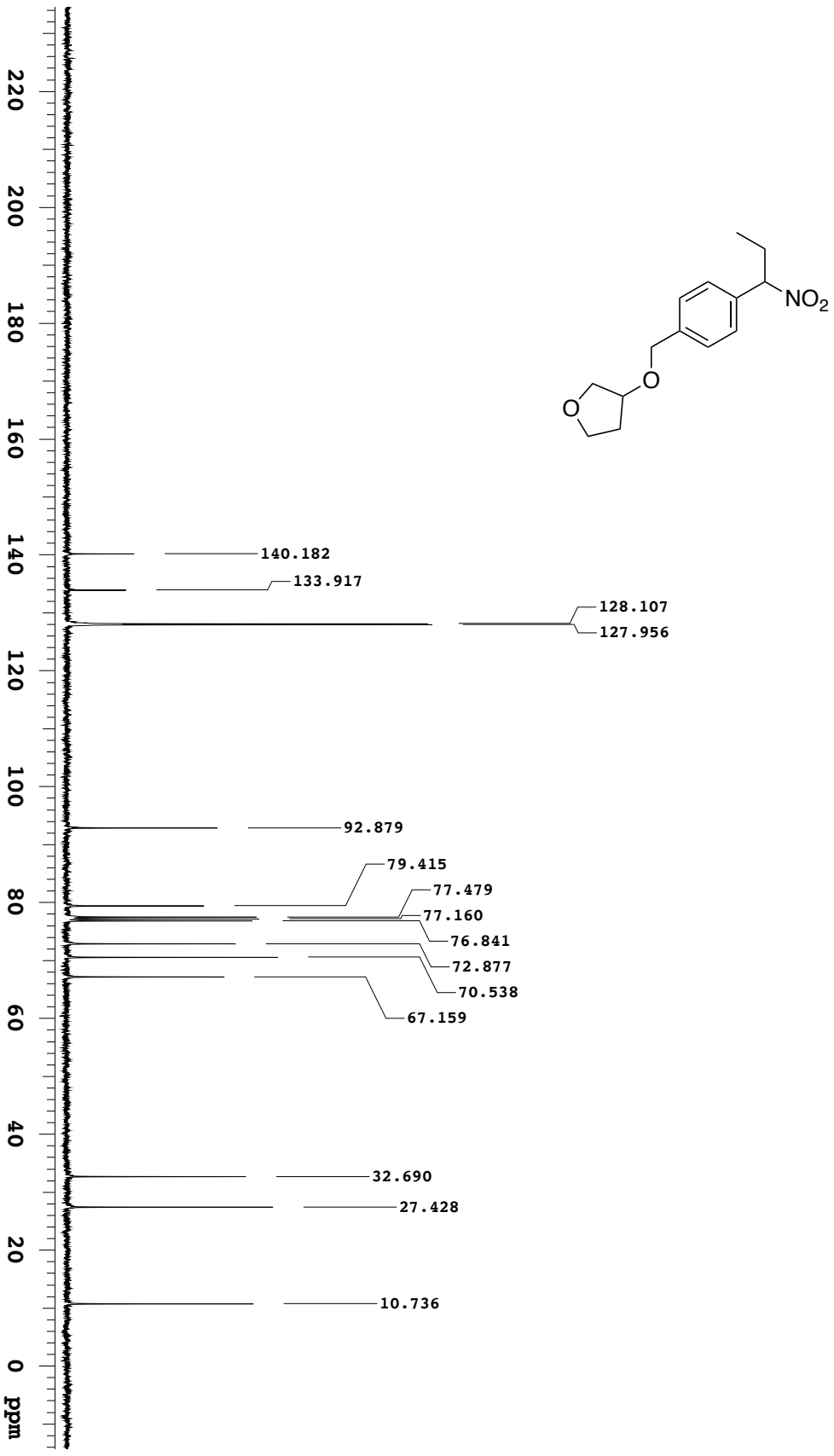

220
200
180
160
140
120
100
80
60
40
20
0
ppm
164.839
162.741
134.840
134.771
133.360
131.605
117.582
117.421
113.149
91.198
77.412
77.160
76.908
27.621
10.622

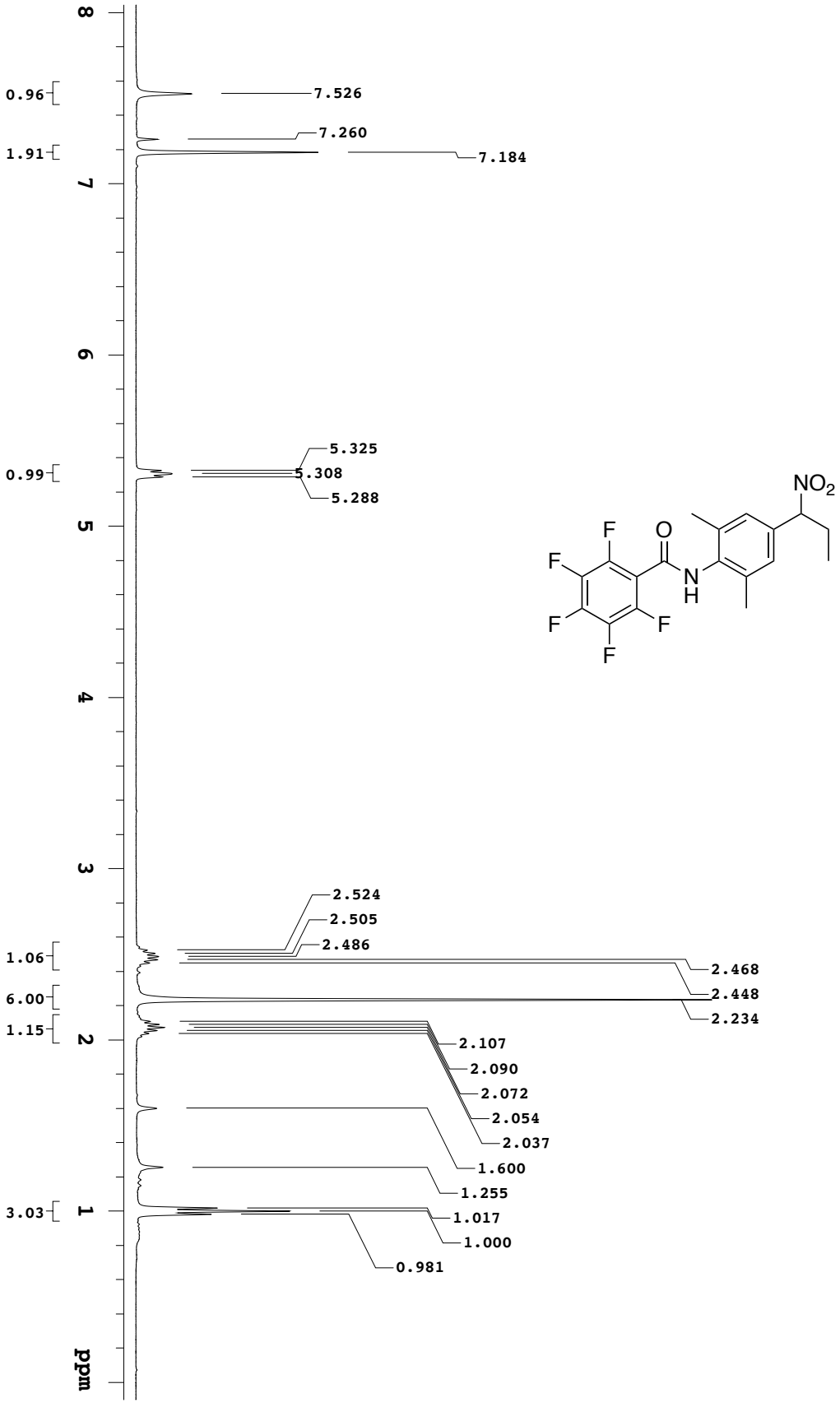

N
NO2
F

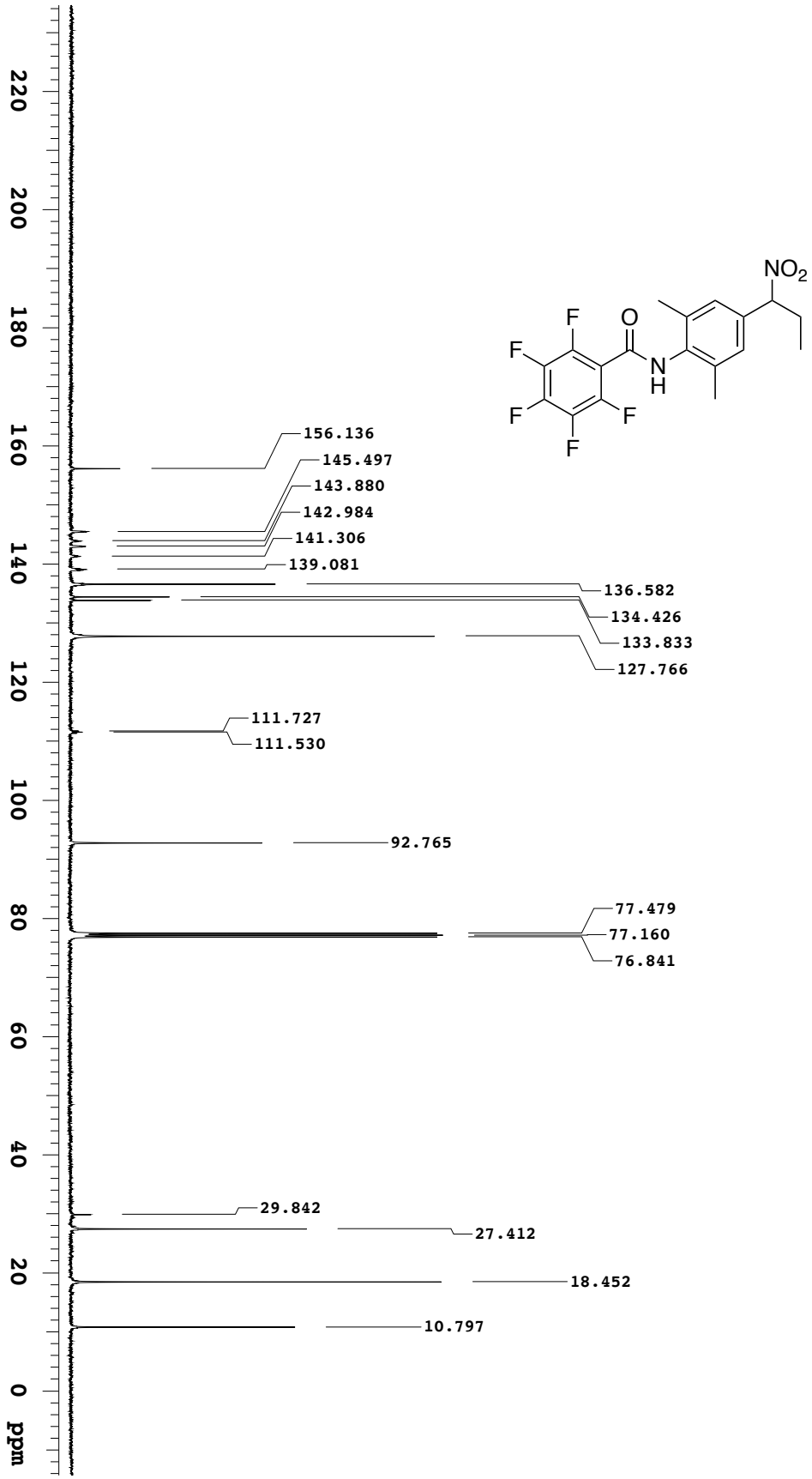

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-104.077
-104.098
-104.105

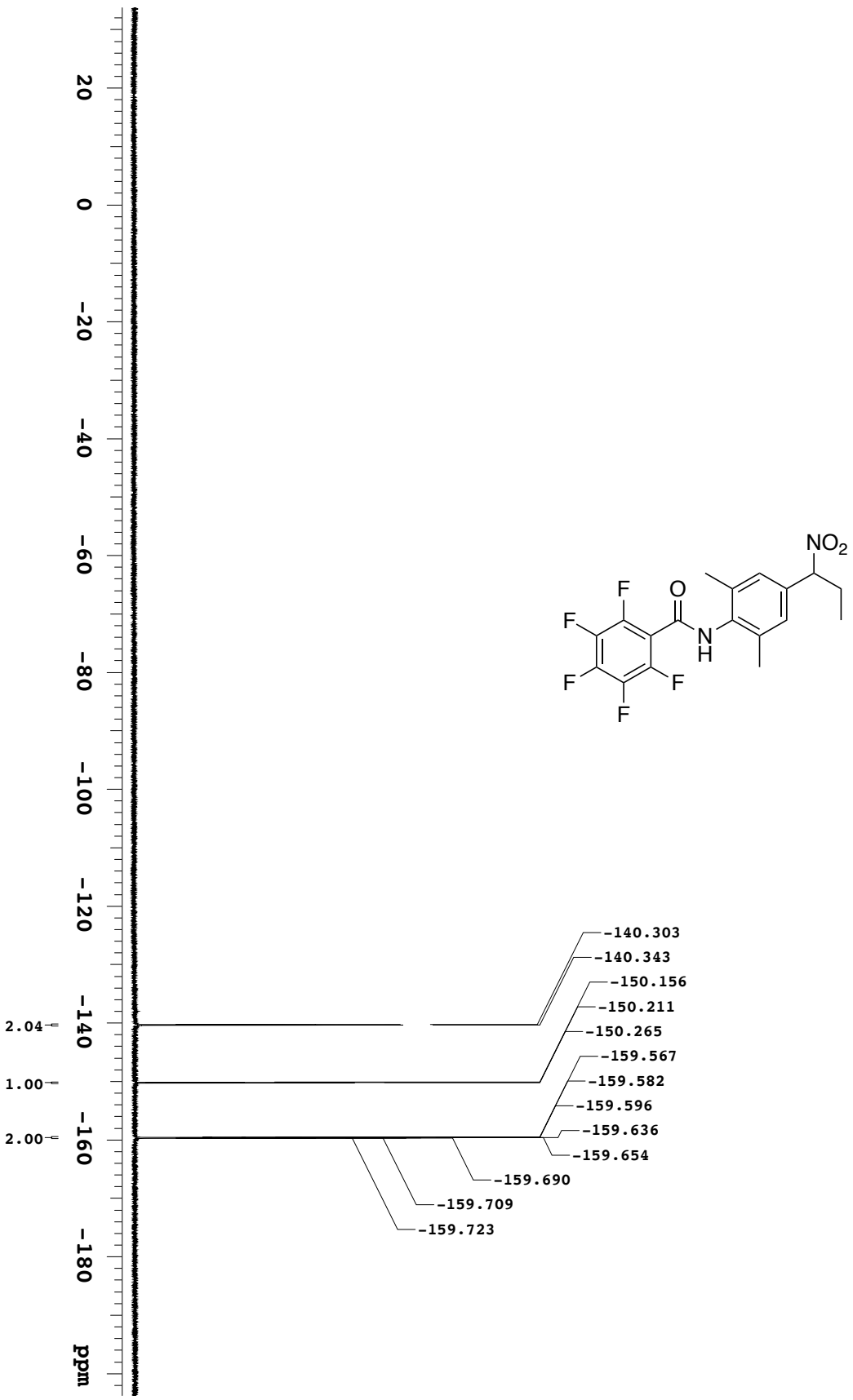

N
NO2
F

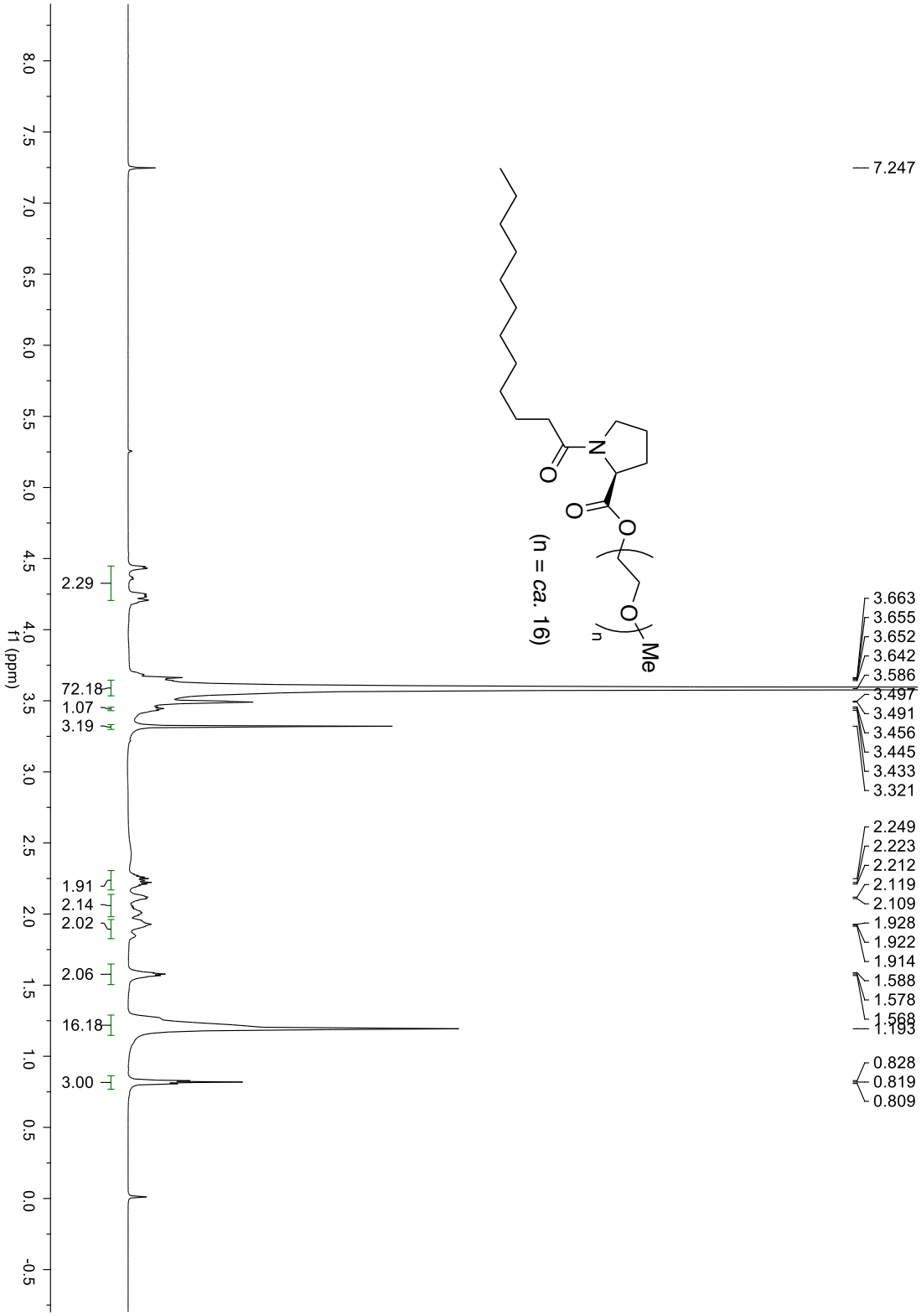

8
7
6
5
4
3
2
1
ppm
7.451
7.431
7.376
7.356
7.260
5.377
5.356
5.339
4.541
4.510
4.504
4.473
4.207
3.938
3.918
3.899
3.884
3.859
3.825
3.815
3.801
3.790
2.532
2.514
2.495
2.477
2.457
2.131
2.113
2.096
2.078
2.049
2.031
2.016
1.995
0.991
0.972
0.954
2.06
2.00
1.00
2.16
1.01
1.04
3.19
1.07
1.17
2.10
3.26
NO2
O
O

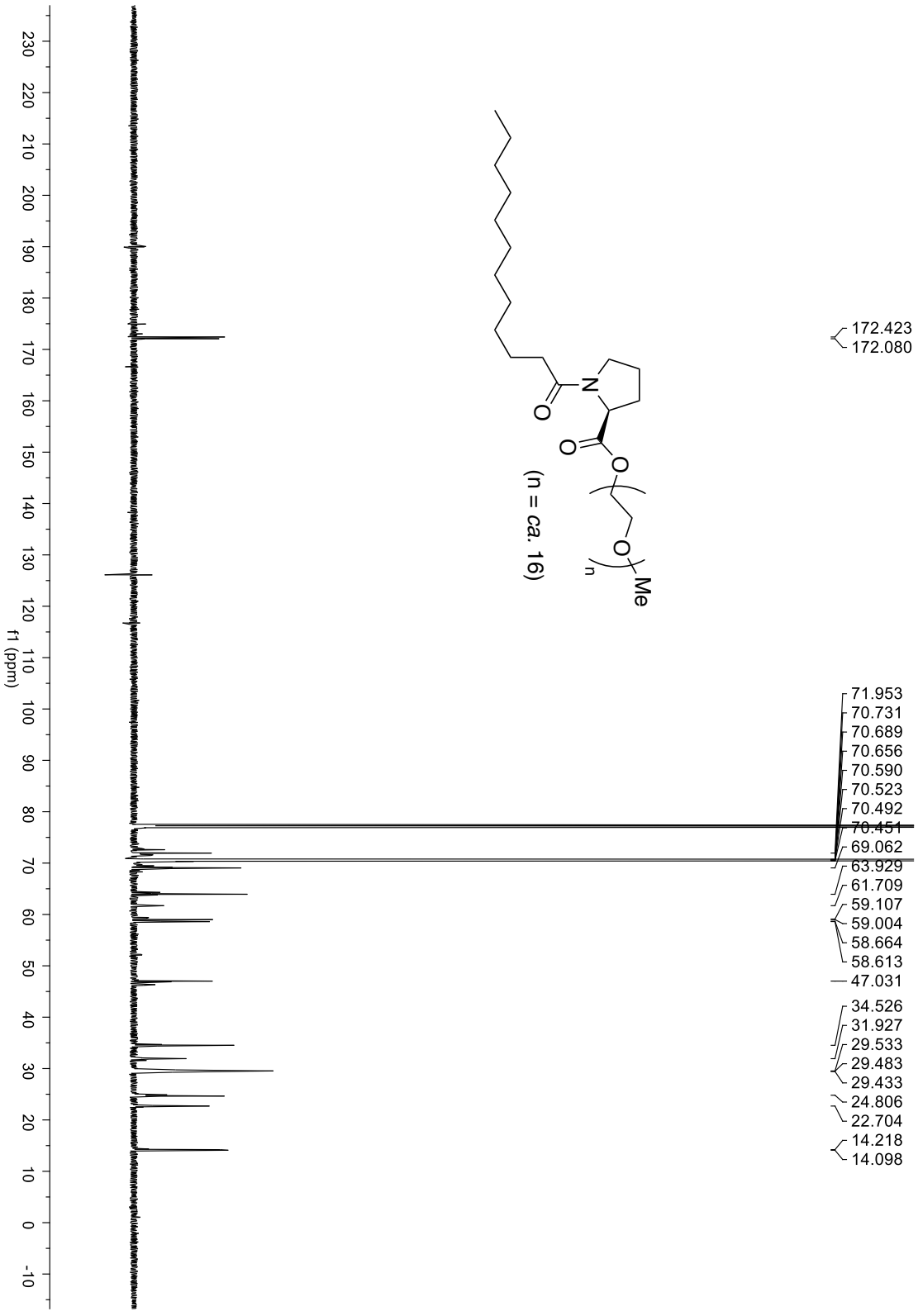

220
200
180
160
140
120
100
80
60
40
20
0
ppm
140.182
133.917
128.107
127.956
92.879
79.415
77.479
77.160
76.841
72.877
70.538
67.159
32.690
27.428
10.736
NO2
O
O


0.96
1.91
0.99
1.06
6.00
1.15
3.03
7.526
7.260
7.184
5.325
5.308
5.288
2.524
2.505
2.486
2.468
2.448
2.234
2.107
2.090
2.072
2.054
2.037
1.600
1.255
1.017
1.000
0.981
ppm
NO2
F
O
N
H


NO2
F
O
F
N
H
F
F
F
156.136
145.497
143.880
142.984
141.306
139.081
136.582
134.426
133.833
127.766
111.727
111.530
92.765
77.479
77.160
76.841
29.842
27.412
18.452
10.797
220
200
180
160
140
120
100
80
60
40
20
0
ppm


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.04
1.00
2.00
-140.303
-140.343
-150.156
-150.211
-150.265
-159.567
-159.582
-159.596
-159.636
-159.654
-159.690
-159.709
-159.723
F
O
N
H
F
F
F
F
NO2


f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
2.29
72.18
1.07
3.19
1.91
2.14
2.02
2.06
16.18
3.00
(n = ca. 16)
7.247
3.663
3.655
3.652
3.642
3.586
3.497
3.491
3.456
3.445
3.433
3.321
2.249
2.223
2.212
2.119
2.109
1.928
1.922
1.914
1.588
1.578
1.568
1.193
0.828
0.819
0.809


172.423
172.080
71.953
70.731
70.689
70.656
70.590
70.523
70.492
70.451
69.062
63.929
61.709
59.107
59.004
58.664
58.613
47.031
34.526
31.927
29.533
29.483
29.433
24.806
22.704
14.218
14.098
(n = ca. 16)
f1 (ppm)